Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Catalytic Asymmetric *exo*-Selective [6+3] Cycloaddition of Iminoesters with Fulvenes

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General Information

Unless otherwise noted, all commercially available compounds were used as provided without further purifications. Dry solvents (THF, toluene, 1,4-dioxane) were used as commercially available; CH_2Cl_2 was purified by the Solvent Purification System *M-BRAUN Glovebox Technology SPS-800*. Solvents for chromatography were technical grade.

Analytical thin-layer chromatography (TLC) was performed on *Merck silica gel aluminium plates* with F-254 indicator. Compounds were visualized by irradiation with UV light or potassium permanganate staining. Column chromatography was performed using *silica gel Merck 60* (particle size 0.040-0.063 mm). Solvent mixtures are understood as volume/volume.

^{1}H-NMR and ^{13}C-NMR were recorded on *Bruker DRX400* (400 MHz) and *INOVA500* (500 MHz) using $CDCl_3$. Data are reported in the following order: chemical shift (δ) values are reported in ppm with the solvent resonance as internal standard ($CDCl_3$: δ = 7.26 ppm for ^{1}H, δ = 77.16 ppm for ^{13}C); multiplicities are indicated br s (broadened singlet), s (singlet), d (doublet), t (triplet), q (quartet) m (multiplet); coupling constants (*J*) are given in Hertz (Hz).

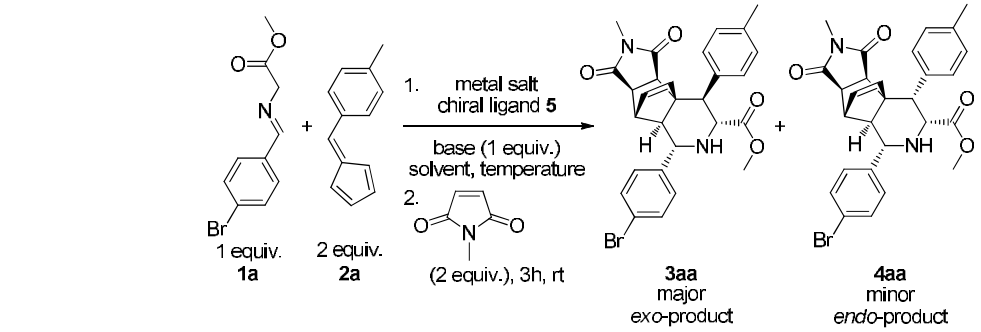
High resolution mass spectra were recorded on a *LTQ Orbitrap* mass spectrometer coupled to an *Acceka HPLC*-System (HPLC column: *Hypersyl GOLD*, 50 mm x 1 mm, particle size 1.9 µm, ionization method: electron spray ionization).

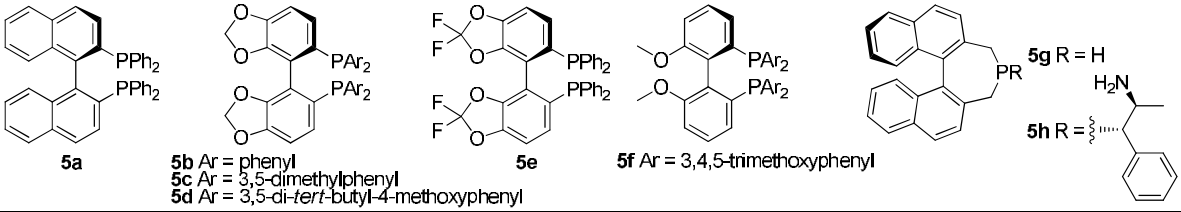
Fourier transform infrared spectroscopy (FT-IR) spectra were obtained with a *Bruker Tensor 27* spectrometer (ATR, neat) and are reported in terms of frequency of absorption (cm^{-1}). Optical rotations were measured in a *Schmidt + Haensch Polartronic HH8* polarimeter.

The enantiomeric excesses were determined by HPLC analysis using a chiral stationary phase column (column A: CHIRALCEL IC, eluent: (CH_2Cl_2/EtOH = 100/2) / *iso*-hexane; column B: CHIRALCEL IA, eluent: (CH_2Cl_2/EtOH = 100/2) / *iso*-hexane; 4.6 mm x 250 mm, particle size 5 µm). The chiral HPLC methods were calibrated with the corresponding racemic mixtures. The ratio of regioisomers and diastereomers was determined by ^{1}H-NMR analysis via integration of characteristic signals of methyl esters. Chemical yields refer to pure isolated substances. Yields and enantiomeric excesses, diastereoselectivity and regioselectivity are given in the tables.

The chemicals and solvents were purchased from the companies Sigma-Aldrich, Acros Organic, ABCR and Alfa Aesar. *R*-(-)-5,5'-Bis(diphenylphosphino)-2,2,2',2'-tetrafluoro-4-4'-bi-1,3-benzodioxole (purity: 97%) was purchased from ABCR and tetrakis(acetonitrile)copper(I) tetrafluoroborate (purity: 97%) was purchased from Sigma-Aldrich.

Table 1. Screen of reaction conditions.[a]





Entry	Catalyst	5	Solvent	Base	T [°C]	t [h]	d.r.[b]	Yield [%][c]	ee [%][d]
1	$Cu(CH_3CN)_4PF_6$	**5a**	toluene	Et_3N	0	4	75:25	58	71
2	$Cu(CH_3CN)_4PF_6$	**5b**	toluene	Et_3N	0	20	75:25	37	84
3	$Cu(CH_3CN)_4PF_6$	**5c**	toluene	Et_3N	0	2.5	60:40	37	88
4	$Cu(CH_3CN)_4PF_6$	**5d**	toluene	Et_3N	0	5.5	55:45	28	93
5	$Cu(CH_3CN)_4PF_6$	**5e**	toluene	Et_3N	0	1	80:20	66	87
6	$Cu(CH_3CN)_4PF_6$	**5f**	toluene	Et_3N	0	4	55:45	23	96
7	$Cu(CH_3CN)_4PF_6$	**5g**	toluene	Et_3N	0	20	n.d.	n.d.	n.d.
8	$Cu(CH_3CN)_4PF_6$	**5h**	toluene	Et_3N	0	20	n.d.	n.d.	n.d.
9	$Cu(CH_3CN)_4BF_4$	**5e**	toluene	Et_3N	0	1	82:18	75	86
10	CuOTf*toluene	**5e**	toluene	Et_3N	0	1	75:25	67	86
11	CuCN	**5e**	toluene	Et_3N	0	24	n.d.	n.d.	n.d.
12	$CuOTf_2$	**5e**	toluene	Et_3N	0	3	76:24	61	85
13	AgOAc	**5e**	toluene	Et_3N	0	2.5	50:50	40	68
14	AgTFA	**5e**	toluene	Et_3N	0	1.5	60:40	48	41
15	AgOTf	**5e**	toluene	Et_3N	0	1	50:50	50	48
16	$AgSbF_6$	**5e**	toluene	Et_3N	0	5	60:40	43	49
17	$Cu(CH_3CN)_4BF_4$	**5e**	THF	Et_3N	0	1	82;18	75	88
18	$Cu(CH_3CN)_4BF_4$	**5e**	DCM	Et_3N	0	3	60:40	34	85
19	$Cu(CH_3CN)_4BF_4$	**5e**	$CHCl_3$	Et_3N	0	3	75:25	31	80
20	$Cu(CH_3CN)_4BF_4$	**5e**	MeCN	Et_3N	0	5	50:50	31	87
21	$Cu(CH_3CN)_4BF_4$	**5e**	Et_2O	Et_3N	0	2	75:25	68	88
22	$Cu(CH_3CN)_4BF_4$	**5e**	MeOH	Et_3N	0	0.5	83:17	80	91
23	$Cu(CH_3CN)_4BF_4$	**5e**	EtOH	Et_3N	0	0.5	83:17	78	91
24	$Cu(CH_3CN)_4BF_4$	**5e**	nBuOH	Et_3N	0	0.5	81:19	75	88
25	$Cu(CH_3CN)_4BF_4$	**5e**	MeOH	DIPEA	0	0.5	82:18	78	90
26	$Cu(CH_3CN)_4BF_4$	**5e**	MeOH	Pyridine	0	8	n.d.	traces	n.d.
27	$Cu(CH_3CN)_4BF_4$	**5e**	MeOH	DBU	0	8	n.d.	traces	n.d.
28[e]	$Cu(CH_3CN)_4BF_4$	**5e**	MeOH	Et_3N	0	0.25	83:17	81	91
29[f]	$Cu(CH_3CN)_4BF_4$	**5e**	MeOH	Et_3N	0	0.25	82:18	79	91
30[g]	$Cu(CH_3CN)_4BF_4$	**5e**	MeOH	Et_3N	0	0.75	75:25	60	91
31[h]	$Cu(CH_3CN)_4BF_4$	**5e**	MeOH	Et_3N	0	3	67:33	50	89
32	$Cu(CH_3CN)_4BF_4$	**5e**	MeOH	Et_3N	-20	2	82:18	80	93
33	$Cu(CH_3CN)_4BF_4$	**5e**	MeOH	Et_3N	-40	6	84:16	77	96
34	$Cu(CH_3CN)_4BF_4$	**5e**	MeOH	Et_3N	-80	24	n.d.	traces.	n.d.
35	$Cu(CH_3CN)_4BF_4$	**5e**	toluene	Et_3N	-40	6	78:22	72	91
36	**$Cu(CH_3CN)_4BF_4$**	**5e**	**THF**	**Et_3N**	**-40**	**6**	**85:15**	**76**	**95**

[a] Reaction conditions: chiral ligand **5** (5 mol%), metal precursor (5 mol%), Et_3N (1 equiv.), glycine ester imine **1a** (1 equiv., 0.10 mmol) and derivative of fulvene **2a** (2.0 equiv.) in solvent (0.1M) at the given temperature; then *N*-methylmaleimide (2 equiv.) at ambient temperature. [b] Determined by ^1H NMR spectroscopy. [c] Isolated yields of the pure major diastereomer **3aa** after chromatography. [d] Determined by HPLC analysis on chiral phase. [e] Using 10 mol% of catalyst and ligand **5e**. [f] Using 7 mol% of catalyst and ligand **5e**. [g] Using 3 mol% of catalyst and ligand **5e**. [h] Using 1 mol% of catalyst and ligand **5e**. n.d. – not determined.

Determination of the absolute configuration

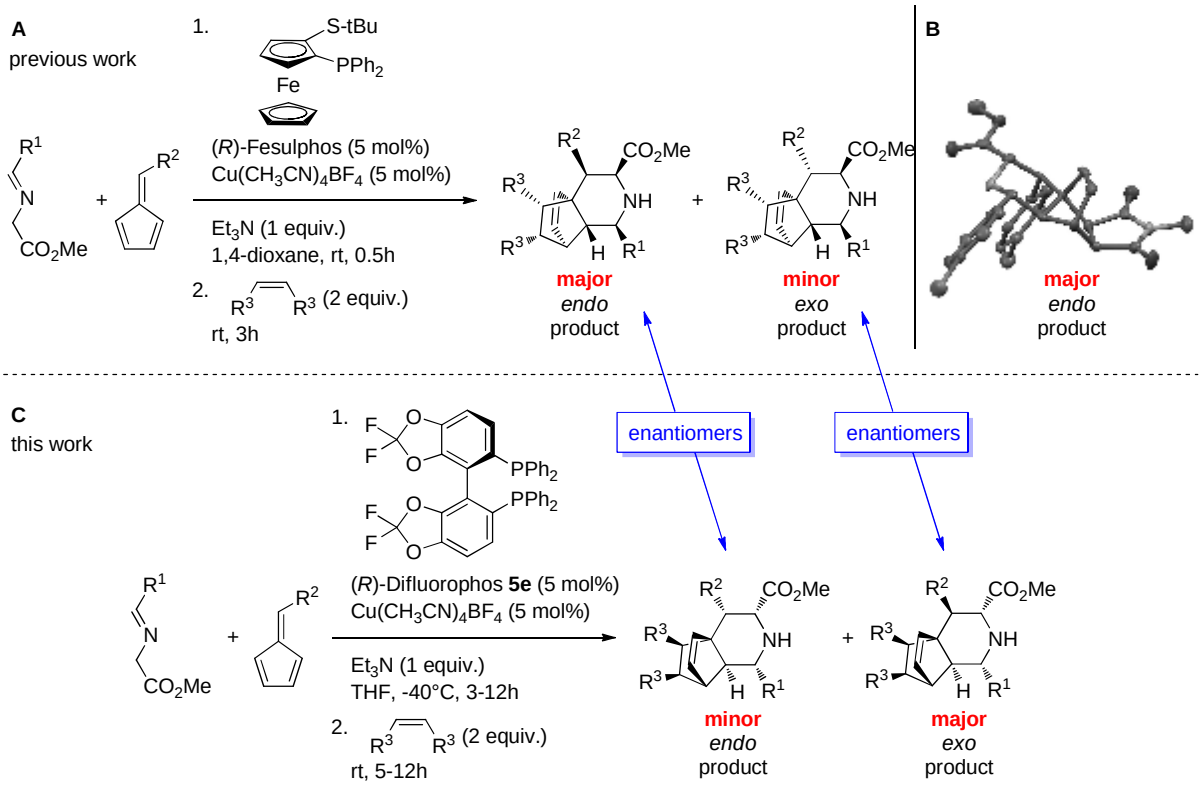
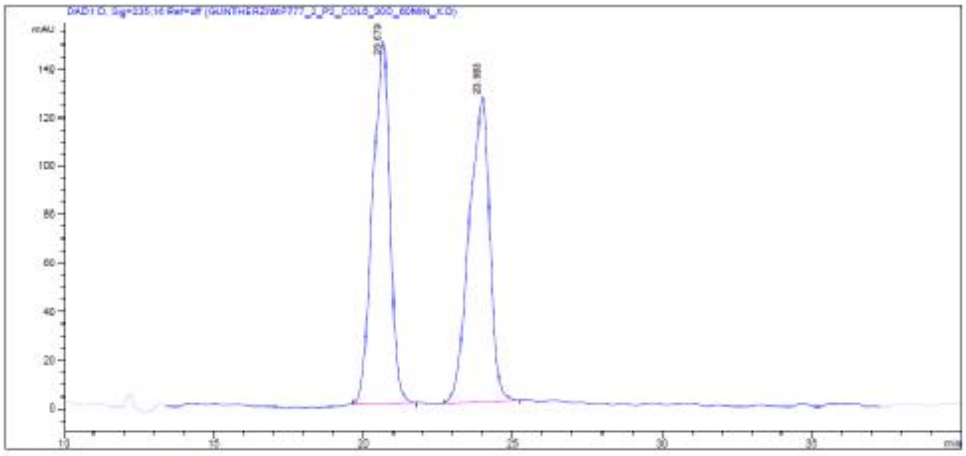


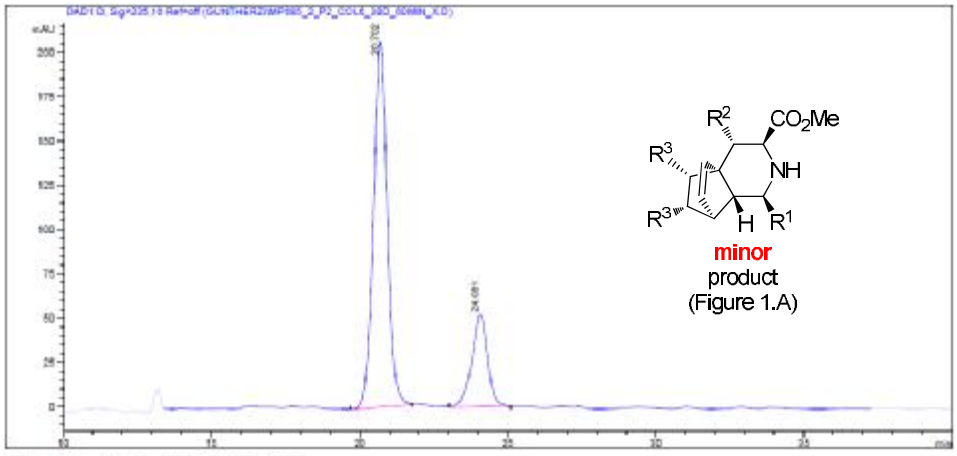
Figure 1: A. One-pot catalytic enantioselective [6+3]-cycloaddition / Diels-Alder reaction sequence using (R)-Fesulphos as chiral ligand, **B.** ORTEP plot of the major product at the 50% probability level (previous work) [1], **C**. One-pot catalytic enantioselective [6+3]-cycloaddition / Diels-Alder reaction sequence using (R)-Difluorophos as chiral ligand (this work)

In our previous work we described the enantioselective [6+3] cycloaddition of azomethine ylides with fulvenes using the copper(I)/(R)-fesulphos complex as chiral catalyst (Figure 1.A).[1] We observed the formation of two diastereomers, where the *endo*-diastereomer is the major product and exo-diastereomer is minor (Figure 1.A). The absolute configuration of the major *endo*-diastereomer was elucidated by X-ray analysis (Figure 1.B). In this work we are using the copper(I)/(R)-difluorophos complex as the chiral catalyst (Figure 1.C). These conditions led to formation of two diastereoisomers as well. In this case we obtained the *exo*-diastereomer as the major product and endo- diastereomer as the minor product, in accordance to Hong et al.[2]. The absolute configurations of those products were determined by comparison of our previous results using chiral-HPLC analysis (Figure 2). As result of the comparison with previous results, where absolute configuration of the products is known, we concluded formation of the opposite enantiomers in present work based on chiral-HPLC analysis of different products.



Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	20.679	6043.303	49.920
2	23.993	6062.653	50.080



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1	20.702	6622.632	77.345
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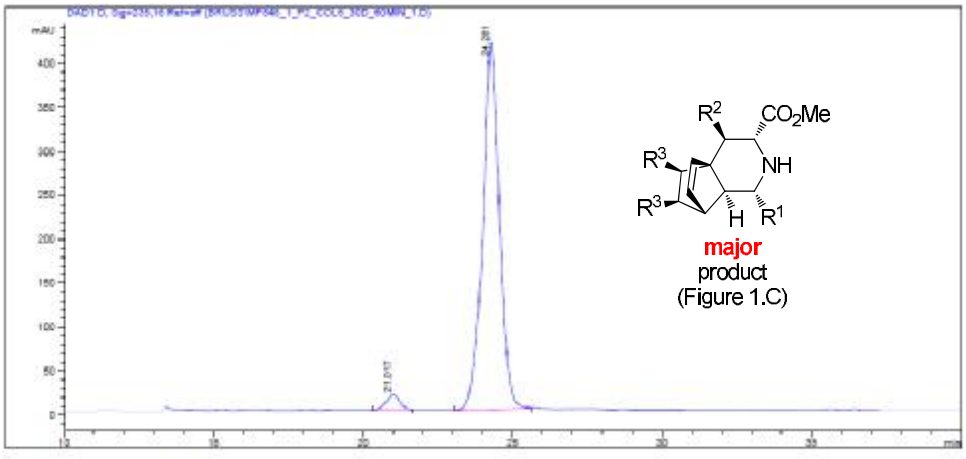


Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	21.017	880.082	3.441
2	24.281	16275.945	96.559

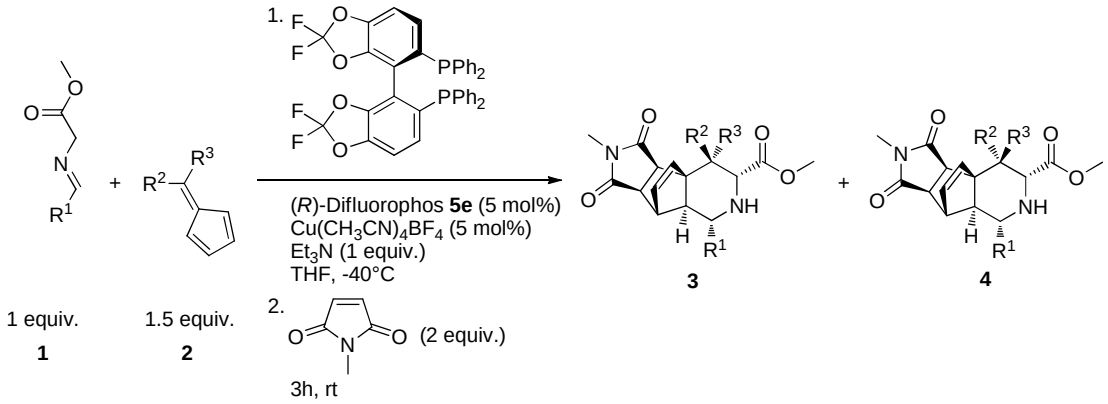
Figure 2: HPLC traces for the *exo*-product: racemate top, enantiomer of the **minor** product of the reaction shown in Figure 1A middle, enantiomer of the **major** product of the reaction shown in Figure 1C bottom:

References:

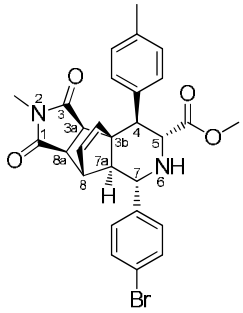
[1] M. Potowski, J.O. Bauer, C. Strohmann, A.P. Antonchick, H. Waldmann, *Angew. Chem.* **2012**, *124*, 9650-9654; *Angew. Chem. Int. Ed.* **2012**, *51*, 9512-9516.

[2] B. C. Hong, A. K. Gupta, M. F. Wu, J. H. Liao, G. H. Lee, *Org. Lett.* **2003**, *5*, 1689-1692.

General procedure

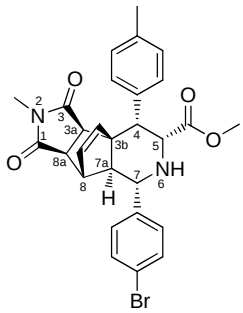


R-(-)-5,5'-Bis(diphenylphosphino)-2,2,2',2'-tetrafluoro-4-4'-bi-1,3-benzodioxole **5e** (5 mol%, 7.5 µmol) and tetrakis-(acetonitrile)copper(I) tetrafluoroborate (5 mol%, 7.5 µmol) were dissolved in THF and stirred at -40°C for 5 min. To the resulting solution α-iminoester **1** (1 equiv., 0.15 mmol), Et_3N (100 mol%, 0.15 mmol) and fulvene **2** (2 equiv., 0.30 mmol) were added and the mixture was allowed to stirr at -40°C for 3-12 h. Subsequently *N*-methylmaleimide (2 equiv., 0.20 mmol) was added and the mixture was allowed to stirr at ambient temperature for 5-12 h. The solvent was removed *in vacuo* and column chromatography on silica gel (ethyl acetate / petroleum ether (40-60°C)) yielded the pure product. Yields, enantiomeric excess, diastereoselectivity and regioselectivity are given in the tables.



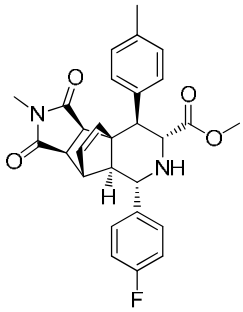
Methyl (3a*R*,3b*S*,4*R*,5*R*,7*S*,7a*S*,8*R*,8a*R*)-7-(4-bromophenyl)-2-methyl-1,3-dioxo-4-(*p*-tolyl)-2,3,3a,4,5,6,7,7a,8,8a-decahydro-1*H*-3b,8-ethenopyrrolo[3',4':3,4]cyclopenta[1,2-*c*]pyridine-5-carboxylate

3aa (major): 76% yield; amorphous white solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 7.3 Hz, 4H), 6.31 (d, *J* = 5.4 Hz, 1H), 6.07 (br s, 1H), 3.97 (m, 2H), 3.40 (s, 3H), 3.25 (m, 3H), 3.11 (br s, 1H), 2.63 (s, 3H), 2.37 (s, 3H), 1.89 ppm (br s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$)= δ = 176.32, 174.56, 171.96, 140.60, 137.05, 134.85, 133.12, 132.98, 131.95, 129.06, 128.72, 121.81, 71.01, 63.01, 61.70, 57.11, 53.54, 52.02, 51.84, 47.29, 45.93, 24.50, 21.41 ppm; FT-IR: $\tilde{\nu}$ = 2923, 1734, 1697, 1484, 1430, 1378, 1277, 1132, 1072, 1009 cm^{-1}; HRMS: calcd. for $[M+H]^+$ $C_{28}H_{28}{}^{79}BrN_2O_4$ = 535.12270, found: 535.12291; calcd. for $[M+H]^+$ $C_{28}H_{28}{}^{81}BrN_2O_4$ = 537.12065, found: 537.11986; $[a]_D^{RT}$ = -75.0 (c = 1.0 in CH_2Cl_2); HPLC conditions: CHIRALPAK IA column, (CH_2Cl_2/EtOH = 100/2) / *iso*-hexane = 30/70, flow rate = 0.5 mL min^{-1}, minor enantiomer: t_R = 21.82 min; major enantiomer: t_R = 25.204 min, 95%ee.



Methyl (3a*R*,3b*S*,4*R*,5*R*,7*R*,7a*S*,8*R*,8a*R*)-7-(4-bromophenyl)-2-methyl-1,3-dioxo-4-(*p*-tolyl)-2,3,3a,4,5,6,7,7a,8,8a-decahydro-1*H*-3b,8-ethenopyrrolo[3',4':3,4]cyclopenta[1,2-*c*]pyridine-5-carboxylate

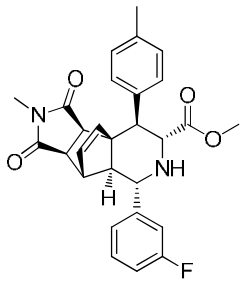
4aa (minor): 9% yield; amorphous white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (br s, 1H), 7.49 (d, *J* = 8.3 Hz, 3H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 6.13 (dd, *J* = 5.5, 2.7 Hz, 1H), 6.00 (d, *J* = 5.5 Hz, 1H), 4.13 (d, *J* = 3.5 Hz, 1H), 4.02 – 3.94 (m, 2H), 3.50 (s, 3H), 3.10 (s, 1H), 2.98 (dd, *J* = 7.5, 4.5 Hz, 1H), 2.78 (s, 3H), 2.71 (d, *J* = 7.5 Hz, 1H), 2.32 (s, 3H), 1.97 ppm (d, *J* = 9.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.04, 176.83, 172.22, 141.81, 136.75, 135.70, 133.00, 131.88, 129.38, 129.08, 128.81, 127.75, 121.57, 66.92, 61.83, 60.29, 57.54, 52.06, 47.25, 47.21, 46.13, 43.71, 24.32, 21.22 ppm; FT-IR: $\tilde{\nu}$ = 2958, 1730, 1690, 1483, 1424, 1375, 1237, 1130, 1090, 1037 cm^{-1}; HRMS: calcd. for $[M+H]^+$ $C_{28}H_{28}{}^{79}BrN_2O_4$ = 535.12270, found: 535.12284; calcd. for $[M+H]^+$ $C_{28}H_{28}{}^{81}BrN_2O_4$ = 537.12065, found: 537.12011.



Methyl (3a*R*,3b*S*,4*R*,5*R*,7*S*,7a*S*,8*R*,8a*R*)-7-(4-fluorophenyl)-2-methyl-1,3-dioxo-4-(*p*-tolyl)-2,3,3a,4,5,6,7,7a,8,8a-decahydro-1*H*-3b,8-ethenopyrrolo[3',4':3,4]cyclopenta[1,2-*c*]pyridine-5-carboxylate

3ba: 75% yield; amorphous white solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29 – 7.22 (m, 4H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.03 (t, *J* = 8.6 Hz, 2H), 6.31 (d, *J* = 5.8 Hz, 1H), 6.07 (dd, *J* = 5.6, 2.6 Hz, 1H), 3.99 (d, *J* = 5.2 Hz, 1H), 3.96 (d, *J* = 4.0 Hz, 1H), 3.40 (s, 3H), 3.30 – 3.21 (m, 3H), 3.11 (s, 1H), 2.63 (s, 3H), 2.37 (s, 3H), 1.91 ppm (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (126

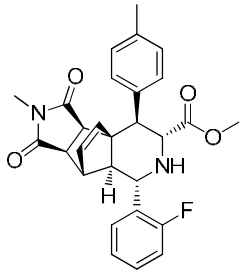
MHz, $CDCl_3$): δ = 176.43, 174.68, 172.09, 162.38 (d, *J* = 246.3 Hz), 137.02, 134.92, 133.04 (d, *J* = 19.7 Hz), 129.06, 128.54 (d, *J* = 7.8 Hz), 115.69 (d, *J* = 21.3 Hz), 71.32, 63.07, 61.70, 56.95, 52.02, 51.88, 51.56, 47.28, 45.95, 24.5, 21.44 ppm; FT-IR: $\tilde{\nu}$ = 2950, 1734, 1696, 1510, 1431, 1377, 1278, 1221, 1161, 1133, 1036 cm^{-1}; HRMS: calcd. for $[M+H]^+$ $C_{28}H_{28}FN_2O_4$ = 475.20276, found: 475.20194; $[a]_D^{RT}$ = -71.0 (c = 1.0 in CH_2Cl_2); HPLC conditions: CHIRALPAK IA column, (CH_2Cl_2/EtOH = 100/2) / *iso*-hexane = 20/80, flow rate = 0.5 mL min^{-1}, minor enantiomer: t_R = 17.89 min; major enantiomer: t_R = 21.49 min; 95%ee.



Methyl (3a*R*,3b*S*,4*R*,5*R*,7*S*,7a*S*,8*R*,8a*R*)-7-(3-fluorophenyl)-2-methyl-1,3-dioxo-4-(*p*-tolyl)-2,3,3a,4,5,6,7,7a,8,8a-decahydro-1*H*-3b,8-ethenopyrrolo[3',4':3,4]cyclopenta[1,2-*c*]pyridine-5-carboxylate

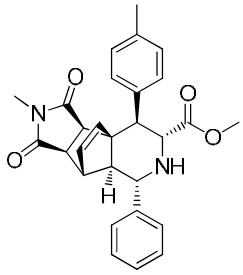
3ca: 83% yield; amorphous white solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33 – 7.27 (m, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.06 (m, 2H), 7.01 – 6.95 (m, 1H), 6.32 (d, *J* = 5.7 Hz, 1H), 6.08 (dd, *J* = 5.7, 2.9 Hz, 1H), 4.00 (m, 2H), 3.39 (s, 3H), 3.26 (m, 3H), 3.15 (t, *J* = 2.9 Hz, 1H), 2.64 (s, 3H), 2.37 (s, 3H), 1.95 ppm (br s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.35, 174.59, 171.89, 163.19 (d, *J* = 246.9 Hz), 137.10, 133.17, 132.98, 130.36 (d, *J* = 8.2 Hz), 129.13 (d, *J* = 9.1 Hz), 129.09, 122.76 (d, *J* = 3.3 Hz), 115.00 (d, *J* = 19.0 Hz), 114.03 (d, *J* = 24.4 Hz), 70.96, 62.99, 61.74, 57.33, 52.06, 51.83, 47.29, 45.97, 24.52, 21.44 ppm; FT-IR: $\tilde{\nu}$ = 2950, 1735, 1696, 1614, 1431, 1377, 1276, 1242, 1166, 1134, 1036 cm^{-1}; HRMS: calcd. for $[M+H]^+$ $C_{28}H_{28}FN_2O_4$ = 475.20276, found: 475.20203; $[a]_D^{RT}$ = -128.2 (c = 1.0 in CH_2Cl_2); HPLC conditions: CHIRALPAK IA column, (CH_2Cl_2/EtOH = 100/2)

/ *iso*-hexane = 20/80, flow rate = 0.5 mL min^{-1}, minor enantiomer: t_R = 17.57 min; major enantiomer: t_R = 22.23 min; 95%ee.



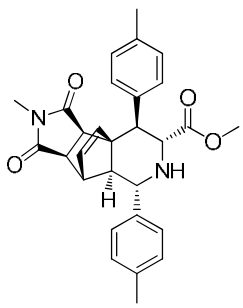
Methyl (3a*R*,3b*S*,4*R*,5*R*,7*S*,7a*S*,8*R*,8a*R*)-7-(2-fluorophenyl)-2-methyl-1,3-dioxo-4-(*p*-tolyl)-2,3,3a,4,5,6,7,7a,8,8a-decahydro-1*H*-3b,8-ethenopyrrolo[3',4':3,4]cyclopenta[1,2-*c*]pyridine-5-carboxylate

3da: 86% yield; amorphous white solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35 (t, *J* = 7.1 Hz, 1H), 7.29 – 7.23 (m, 3H), 7.18 (d, *J* = 7.5 Hz, 2H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.08 – 7.01 (m, 1H), 6.31 (d, *J* = 5.7 Hz, 1H), 6.10 (m, 1H), 4.29 (d, *J* = 10.0 Hz, 1H), 3.96 (d, *J* = 10.8 Hz, 1H), 3.41 (s, 3H), 3.24 (m, 3H), 3.11 (br s, 1H), 2.63 (s, 3H), 2.37 (s, 3H), 1.96 (d, *J* = 10.0 Hz, 1H), 1.88 ppm (br s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.46, 174.72, 172.18, 160.48 (d, *J* = 245.8 Hz), 136.99, 134.93, 133.47, 132.34, 129.34 (d, *J* = 8.5 Hz), 129.05, 128.50 (d, *J* = 13.6 Hz), 127.92 (d, *J* = 4.9 Hz), 124.72 (d, *J* = 3.1 Hz), 115.81 (d, *J* = 22.2 Hz), 70.65, 63.10, 61.68, 51.97, 51.94, 51.90, 47.17, 46.18, 24.49, 21.42 ppm; FT-IR: $\tilde{\nu}$ = 2951, 1736, 1698, 1585, 1491, 1432, 1378, 1279, 1231, 1132, 1035 cm^{-1}; HRMS: calcd. for $[M+H]^+$ $C_{28}H_{28}FN_2O_4$ = 475.20276, found: 475.20201; $[a]_D^{RT}$ = -91.9 (c = 1.0 in CH_2Cl_2); HPLC conditions: CHIRALPAK IA column, (CH_2Cl_2/EtOH = 100/2) / *iso*-hexane = 30/70, flow rate = 0.5 mL min^{-1}, minor enantiomer: t_R = 17.09 min; major enantiomer: t_R = 24.03 min; 86%ee.



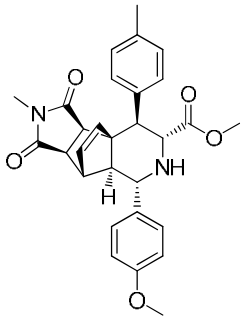
Methyl (3a*R*,3b*S*,4*R*,5*R*,7*S*,7a*S*,8*R*,8a*R*)-2-methyl-1,3-dioxo-7-phenyl-4-(*p*-tolyl)-2,3,3a,4,5,6,7,7a,8,8a-decahydro-1*H*-3b,8-ethenopyrrolo[3',4':3,4]cyclopenta[1,2-*c*] pyridine-5-carboxylate

3ea: 55% yield; amorphous white solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37 – 7.31 (m, 2H), 7.30 – 7.23 (m, 5H), 7.18 (d, *J* = 7.5 Hz, 2H), 6.32 (d, *J* = 5.5 Hz, 1H), 6.08 (br s, 1H), 3.98 (m, 2H), 3.41 (s, 3H), 3.26 (m, 3H), 3.15 (br s, 1H), 2.63 (s, 3H), 2.37 (s, 3H), 1.93 (d, *J* = 9.5 Hz, 1H), 1.81 ppm (br s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.51, 174.75, 172.21, 141.59, 136.93, 135.07, 133.15, 132.93, 129.02, 128.82, 127.94, 126.87, 71.42, 63.12, 61.72, 57.55, 51.95, 51.73, 47.30, 46.05, 24.47, 21.41 ppm; FT-IR: $\tilde{\nu}$ = 2950, 1736, 1697, 1515, 1431, 1378, 1279, 1201, 1167, 1132, 1034 cm^{-1}; HRMS: calcd. for $[M+H]^+$ $C_{28}H_{29}N_2O_4$ = 457.21218, found: 457.21152; $[a]_D^{RT}$ = -97.7 (c = 1.0 in CH_2Cl_2); HPLC conditions: CHIRALPAK IA column, (CH_2Cl_2/EtOH = 100/2) / *iso*-hexane = 30/70, flow rate = 0.5 mL min^{-1}, minor enantiomer: t_R = 17.61 min; major enantiomer: t_R = 20.91 min; 93%ee.



Methyl (3a*R*,3b*S*,4*R*,5*R*,7*S*,7a*S*,8*R*,8a*R*)-2-methyl-1,3-dioxo-4,7-di-*p*-tolyl-2,3,3a,4,5,6,7,7a,8,8a-decahydro-1*H*-3b,8-ethenopyrrolo[3',4':3,4]cyclopenta[1,2-*c*] pyridine-5-carboxylate

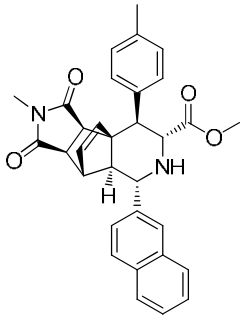
3fa: 44% yield; amorphous white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (m, 2H), 7.16 (m, 6H), 6.31 (d, *J* = 5.6 Hz, 1H), 6.06 (dd, *J* = 5.6, 2.6 Hz, 1H), 3.98 m, 2H), 3.37 (s, 3H), 3.25 (br s, 2H), 3.13 (br s, 1H), 2.63 (s, 3H), 2.37 (s, 3H), 2.33 (m, 4H), 1.99 ppm (br s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$); δ = 176.53, 174.79, 171.98, 137.79, 137.00, 133.22, 132.81, 129.84, 129.50, 129.03, 126.94, 70.94, 63.01, 61.66, 57.33, 52.05, 51.86, 47.30, 46.05, 24.52, 21.46, 21.25 ppm; FT-IR: $\tilde{\nu}$ = 2923, 1735, 1696, 1515, 1431, 1377, 1278, 1166, 1132, 1084, 1035 cm^{-1}; HRMS: calcd. for $[M+H]^+$ $C_{29}H_{31}N_2O_4$ = 471.22783, found: 471.22708; $[a]_D^{RT}$ = -95.7 (c = 1.0 in CH_2Cl_2); HPLC conditions: CHIRALPAK IA column, (CH_2Cl_2/EtOH = 100/2) / *iso*-hexane = 30/70, flow rate = 0.5 mL min^{-1}, minor enantiomer: t_R = 16.84 min; major enantiomer: t_R = 19.73 min; 90%ee.



Methyl (3a*R*,3b*S*,4*R*,5*R*,7*S*,7a*S*,8*R*,8a*R*)-7-(4-methoxyphenyl)-2-methyl-1,3-dioxo-4-(*p*-tolyl)-2,3,3a,4,5,6,7,7a,8,8a-decahydro-1*H*-3b,8-ethenopyrrolo[3',4':3,4]cyclopenta[1,2-*c*]pyridine-5-carboxylate

3ga: 25% yield; amorphous white solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26 – 7.15 (m, 6H), 6.87 (d, *J* = 7.8 Hz, 2H), 6.30 (d, *J* = 5.5 Hz, 1H), 6.06 (br s, 1H), 3.96 (m, 2H), 3.80 (s, 3H), 3.39 (s, 3H), 3.32 – 3.21 (m, 3H), 3.13 (br s, 1H), 2.63 (s, 3H), 2.37 (s, 3H), 1.96 ppm (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.54, 174.77, 172.17, 159.34, 136.96, 135.04,

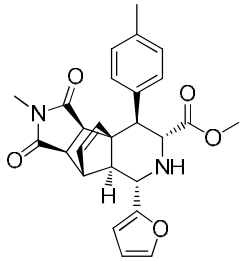
133.18, 132.87, 129.03, 128.08, 114.21, 63.14, 61.73, 56.98, 55.46, 51.98, 47.35, 46.07, 24.49, 21.43 ppm; FT-IR: $\tilde{\nu}$ = 2949, 1735, 1697, 1611, 1513, 1432, 1377, 1278, 1245, 1170, 1132, 1033 cm^{-1}; HRMS: calcd. for $[M+H]^+$ $C_{29}H_{31}N_2O_5$ = 487.22275, found: 487.22200; $[a]_D^{RT}$ = -14.2 (c = 0.5 in CH_2Cl_2); HPLC conditions: CHIRALPAK IA column, (CH_2Cl_2/EtOH = 100/2) / *iso*-hexane = 30/70, flow rate = 0.5 mL min^{-1}, minor enantiomer: t_R = 22.92 min; major enantiomer: t_R = 26.36 min; 89%ee.



Methyl (3a*R*,3b*S*,4*R*,5*R*,7*S*,7a*S*,8*R*,8a*R*)-2-methyl-7-(naphthalen-2-yl)-1,3-dioxo-4-(*p*-tolyl)-2,3,3a,4,5,6,7,7a,8,8a-decahydro-1*H*-3b,8-ethenopyrrolo[3',4':3,4]cyclopenta[1,2-*c*]pyridine-5-carboxylate

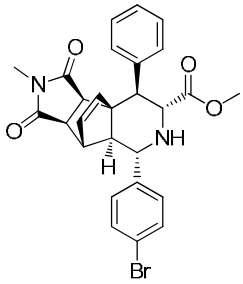
3ha: 70% yield; amorphous white solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.83 (m, *J* = 8.1 Hz, 3H), 7.77 (br s, 1H), 7.54 – 7.45 (m, 2H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.27 – 7.23 (m, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 6.32 (d, *J* = 5.4 Hz, 1H), 6.12 (br s, 1H), 4.14 (d, *J* = 9.7 Hz, 1H), 4.00 (d, *J* = 10.6 Hz, 1H), 3.42 (s, 3H), 3.35 (br s, 1H), 3.23 (m, 2H), 3.18 (br s, 1H), 2.64 (s, 3H), 2.38 (s, 3H), 2.06 ppm (br s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.45, 174.71, 172.05, 137.01, 133.52, 133.24, 133.19, 132.95, 129.06, 128.58, 127.99, 127.82, 126.48, 126.20, 125.22, 63.07, 61.78, 57.71, 52.05, 51.89, 47.33, 46.09, 24.51, 21.44 ppm; FT-IR: $\tilde{\nu}$ = 2924, 1772, 1736, 1699, 1514, 1431, 1378, 1277, 1167, 1131, 1032 cm^{-1}; HRMS: calcd. for $[M+H]^+$ $C_{32}H_{31}N_2O_4$ = 507.22783, found: 507.22711; $[a]_D^{RT}$ = -82.9 (c = 1.0 in CH_2Cl_2); HPLC

conditions: CHIRALPAK IA column, (CH_2Cl_2/EtOH = 100/2) / *iso*-hexane = 20/80, flow rate = 0.5 mL min^{-1}, minor enantiomer: t_R = 21.95 min; major enantiomer: t_R = 25.83 min; 91%ee.



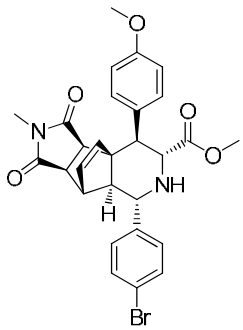
Methyl (3a*R*,3b*S*,4*R*,5*R*,7*S*,7a*S*,8*R*,8a*R*)-7-(furan-2-yl)-2-methyl-1,3-dioxo-4-(*p*-tolyl)-2,3,3a,4,5,6,7,7a,8,8a-decahydro-1*H*-3b,8-ethenopyrrolo[3',4':3,4]cyclopenta[1,2-*c*] pyridine-5-carboxylate

3ia: 60% yield; amorphous white solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35 (br s, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.32 (m, 1H), 6.29 (t, *J* = 5.4 Hz, 1H), 6.19 (d, *J* = 2.9 Hz, 1H), 6.06 m, 1H), 4.08 (d, *J* = 10.1 Hz, 1H), 3.89 (d, *J* = 11.0 Hz, 1H), 3.38 (s, 3H), 3.35 (d, *J* = 4.9 Hz, 2H), 3.28 – 3.20 (m, 1H), 3.13 (d, *J* = 11.0 Hz, 1H), 2.64 (s, 3H), 2.36 (s, 3H), 2.07 ppm (d, *J* = 10.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.45, 174.62, 172.12, 142.63, 142.20, 137.08, 134.74, 133.56, 132.32, 129.08, 110.50, 110.34, 107.11, 106.23, 68.29, 62.44, 61.48, 52.34, 51.94, 51.87, 51.09, 47.15, 46.45, 24.52, 21.43 ppm; FT-IR: $\tilde{\nu}$ = 2949, 1735, 1695, 1514, 1431, 1377, 1277, 1196, 1167, 1133, 1010 cm^{-1}; HRMS: calcd. for $[M+H]^+$ $C_{26}H_{27}N_2O_5$ = 447.19145, found: 447.19083; $[a]_D^{RT}$ = -70.6 (c = 1.0 in CH_2Cl_2); HPLC conditions: CHIRALPAK IA column, (CH_2Cl_2/EtOH = 100/2) / *iso*-hexane = 30/70, flow rate = 0.5 mL min^{-1}, minor enantiomer: t_R = 18.02 min; major enantiomer: t_R = 24.68 min; 93%ee.



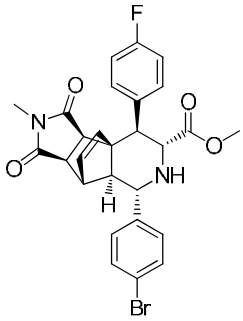
Methyl (3a*R*,3b*S*,4*R*,5*R*,7*S*,7a*S*,8*R*,8a*R*)-7-(4-bromophenyl)-2-methyl-1,3-dioxo-4-phenyl-2,3,3a,4,5,6,7,7a,8,8a-decahydro-1*H*-3b,8-ethenopyrrolo[3',4':3,4]cyclopenta[1,2-*c*]pyridine-5-carboxylate

3ab: 61% yield; amorphous white solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 7.1 Hz, 2H), 7.37 (br s, 5H), 7.17 (d, *J* = 7.1 Hz, 2H), 6.31 (d, *J* = 4.7 Hz, 1H), 6.08 (br s, 1H), 3.99 (m, 2H), 3.40 (s, 3H), 3.29 (d, *J* = 10.1 Hz, 1H), 3.23 (br s, 2H), 3.12 (br s, 1H), 2.62 (s, 3H), 1.99 (br s, 1H), 1.88 ppm (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.31, 174.50, 172.02, 140.64, 138.03, 133.23, 132.80, 131.94, 128.62, 128.33, 128.08, 127.67, 127.31, 121.75, 71.13, 62.76, 61.67, 57.02, 52.00, 51.74, 47.23, 45.91, 24.47 ppm; FT-IR: $\tilde{\nu}$ = 2948, 1734, 1697, 1486, 1431, 1377, 1278, 1242, 1202, 1131, 1039, 1009 cm^{-1}; HRMS: calcd. for $[M+H]^+$ $C_{27}H_{26}{}^{79}BrN_2O_4$ = 521.10705, found: 521.10681; calcd. for $[M+H]^+$ $C_{27}H_{26}{}^{81}BrN_2O_4$ = 523.10500, found: 523.10399; $[a]_D^{RT}$ = -63.2 (c = 1.0 in CH_2Cl_2); HPLC conditions: CHIRALPAK IC column, (CH_2Cl_2/EtOH = 100/2) / *iso*-hexane = 40/60, flow rate = 0.5 mL min^{-1}, minor enantiomer: t_R = 33.14 min; major enantiomer: t_R = 25.94 min, 96%ee.



Methyl (3a*R*,3b*S*,4*R*,5*R*,7*S*,7a*S*,8*R*,8a*R*)-7-(4-bromophenyl)-4-(4-methoxyphenyl)-2-methyl-1,3-dioxo-2,3,3a,4,5,6,7,7a,8,8a-decahydro-1*H*-3b,8-ethenopyrrolo[3',4':3,4] cyclopenta[1,2-*c*]pyridine-5-carboxylate[a]

3ac: 72% yield; amorphous white solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 7.1 Hz, 2H), 6.91 (d, *J* = 8.3 Hz, 2H), 6.29 (d, *J* = 5.4 Hz, 1H), 6.08 (br s, 1H), 3.94 (m, 2H), 3.82 (s, 3H), 3.41 (s, 3H), 3.30 – 3.18 (m, 3H), 3.12 (br s, 1H), 2.64 (s, 3H), 1.88 ppm (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.36, 174.61, 172.12, 158.98, 133.25, 132.81, 131.95, 130.00, 128.65, 121.79, 113.70, 71.20, 63.13, 61.77, 57.06, 55.20, 52.07, 51.85, 51.10, 47.30, 45.94, 24.49 ppm; FT-IR: $\tilde{\nu}$ = 2948, 1735, 1696, 1512, 1431, 1378, 1279, 1245, 1177, 1131, 1073, 1032, 1009 cm^{-1}; HRMS: calcd. for $[M+H]^+$ $C_{28}H_{28}{}^{79}BrN_2O_5$ = 551.11761, found: 551.11782; calcd. for $[M+H]^+$ $C_{28}H_{28}{}^{81}BrN_2O_5$ = 553.11556, found: 553.11492; $[a]_D^{RT}$ = -85.3 (c = 1.0 in CH_2Cl_2); HPLC conditions: CHIRALPAK IA column, (CH_2Cl_2/EtOH = 100/2) / *iso*-hexane = 30/70, flow rate = 0.5 mL min^{-1}, minor enantiomer: t_R = 21.97 min; major enantiomer: t_R = 28.38 min; 94%ee.

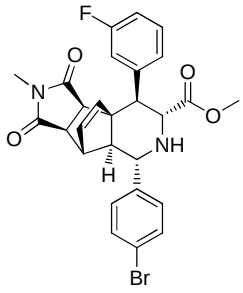


Methyl (3a*R*,3b*S*,4*R*,5*R*,7*S*,7a*S*,8*R*,8a*R*)-7-(4-bromophenyl)-4-(4-fluorophenyl)-2-methyl-1,3-dioxo-2,3,3a,4,5,6,7,7a,8,8a-decahydro-1*H*-3b,8-ethenopyrrolo[3',4':3,4]cyclopenta [1,2-*c*]pyridine-5-carboxylate

3ad: 76% yield; amorphous white solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 7.7 Hz, 2H), 7.37 – 7.29 (m, 2H), 7.17 (d, *J* = 7.7 Hz, 2H), 7.07 (t, *J* = 8.3 Hz, 2H), 6.24 (d, *J* = 5.4

[a] Z.-L. He, H.-L. Teng and C.-J. Wang, *Angew. Chem. Int. Ed.*, 2013, **52**, 2934

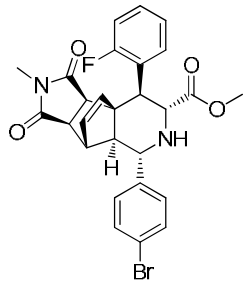
Hz, 1H), 6.10 (br s, 1H), 3.95 (d, *J* = 7.6 Hz, 2H), 3.42 (s, 3H), 3.30 (d, *J* = 10.5 Hz, 1H), 3.27 – 3.18 (m, 2H), 3.13 (br s, 1H), 2.63 (s, 3H), 1.88 ppm (d, *J* = 9.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.21, 174.59, 171.91, 162.30 (d, *J* = 246.4 Hz), 140.54, 133.85 (d, *J* = 4.8 Hz), 133.55, 132.38, 131.97, 128.62, 121.82, 115.33 (d, *J* = 21.2 Hz), 71.15, 62.86, 61.59, 57.03, 52.09, 51.77, 51.13, 47.25, 45.93, 24.47 ppm; FT-IR: $\tilde{\nu}$ = 2950, 1734, 1695, 1510, 1431, 1377, 1278, 1220, 1132, 1072, 1037, 1009 cm^{-1}; HRMS: calcd. for $[M+H]^+$ $C_{27}H_{25}{}^{79}BrFN_2O_4$ = 539.09762, found: 539.09772; calcd. for $[M+H]^+$ $C_{27}H_{25}{}^{81}BrFN_2O_4$ = 541.09558, found: 541.09476; $[a]_D^{RT}$ = -84,1 (c = 1.0 in CH_2Cl_2); HPLC conditions: CHIRALPAK IA column, (CH_2Cl_2/EtOH = 100/2) / *iso*-hexane = 30/70, flow rate = 0.5 mL min^{-1}, minor enantiomer: t_R = 23.86 min; major enantiomer: t_R = 26.41 min; 96%ee.



Methyl (3a*R*,3b*S*,4*R*,5*R*,7*S*,7a*S*,8*R*,8a*R*)-7-(4-bromophenyl)-4-(3-fluorophenyl)-2-methyl-1,3-dioxo-2,3,3a,4,5,6,7,7a,8,8a-decahydro-1*H*-3b,8-ethenopyrrolo[3',4':3,4]cyclopenta[1,2-*c*]pyridine-5-carboxylate

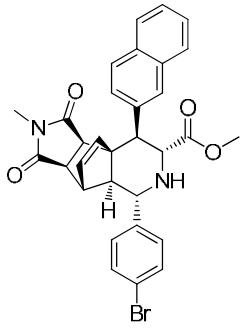
3ae: 71% yield; amorphous white solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 8.1 Hz, 2H), 7.35 (m, 1H), 7.17 (t, *J* = 8.2 Hz, 3H), 7.05 (m, 2H), 6.26 (d, *J* = 5.7 Hz, 1H), 6.09 (br s, 1H), 4.01 – 3.93 (m, 2H), 3.43 (s, 3H), 3.31 (m, 1H), 3.24 (m, 2H), 3.12 (br s, 1H), 2.63 (s, 3H), 1.89 (br s, 1H), 1.81 ppm (br s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.18, 174.43, 171.67, 162.74 (d, *J* = 245.1 Hz), 140.54 (d, *J* = 9.5 Hz), 133.57, 132.42, 131.99, 129.80 (d, *J* = 8.3 Hz), 128.69, 128.67, 121.88, 114.61 (d, *J* = 21.0 Hz), 71.02, 62.50, 61.53, 57.09, 52.17, 51.66, 51.65, 47.23, 45.89, 24.49 ppm; FT-IR: $\tilde{\nu}$ = 2951, 1735, 1694, 1589, 1432, 1378, 1276, 1242, 1197, 1134, 1073, 1009 cm^{-1}; HRMS: calcd. for $[M+H]^+$ $C_{27}H_{25}{}^{79}BrFN_2O_4$ =

539.09762, found: 539.09765; calcd. for $[M+H]^+$ $C_{27}H_{25}{}^{81}BrFN_2O_4$ = 541.09558, found: 541.09487; $[a]_D^{RT}$ = -61.7 (c = 1.0 in CH_2Cl_2); HPLC conditions: CHIRALPAK IA column, (CH_2Cl_2/EtOH = 100/2) / *iso*-hexane = 30/70, flow rate = 0.5 mL min^{-1}, minor enantiomer: t_R = 26.76 min; major enantiomer: t_R = 25.32 min; 96%ee.



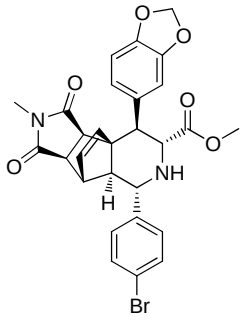
Methyl (3a*R*,3b*S*,4*S*,5*R*,7*S*,7a*S*,8*R*,8a*R*)-7-(4-bromophenyl)-4-(2-fluorophenyl)-2-methyl-1,3-dioxo-2,3,3a,4,5,6,7,7a,8,8a-decahydro-1*H*-3b,8-ethenopyrrolo[3',4':3,4]cyclopenta [1,2-*c*]pyridine-5-carboxylate

3af: 75% yield; amorphous white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 7.8 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.16 (m, 4H), 6.15 (d, *J* = 4.6 Hz, 1H), 6.06 (br s, 1H), 4.03 (d, *J* = 10.9 Hz, 1H), 3.95 (d, *J* = 9.5 Hz, 1H), 3.89 (d, *J* = 10.9 Hz, 1H), 3.47 (s, 3H), 3.43 – 3.36 (m, 1H), 3.32 – 3.20 (m, 2H), 3.12 (br s, 1H), 2.63 (s, 3H), 1.92 (d, *J* = 9.5 Hz, 1H), 1.83 ppm (br s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 176.41, 174.90, 171.58, 162.27 (d, *J* = 245.3 Hz), 140.55, 135.97, 135.21, 133.20, 132.50, 131.95, 128.86 (d, *J* = 7.7 Hz), 128.64, 128.02 (d, *J* = 3.2 Hz), 123.69 (d, *J* = 3.1 Hz), 121.80, 115.66 (d, *J* = 23.4 Hz), 70.82, 61.69, 61.14, 57.22, 52.29, 51.38, 47.67, 47.02, 45.97, 45.44, 40.86, 24.51 ppm; FT-IR: $\tilde{\nu}$ = 2950, 1736, 1697, 1488, 1432, 1378, 12765, 1230, 1131, 1099, 1009 cm^{-1}; HRMS: calcd. for $[M+H]^+$ $C_{27}H_{25}{}^{79}BrFN_2O_4$ = 539.09762, found: 539.09717; calcd. for $[M+H]^+$ $C_{27}H_{25}{}^{81}BrFN_2O_4$ = 541.09558, found: 541.09482; $[a]_D^{RT}$ = -58.4 (c = 1.0 in CH_2Cl_2); HPLC conditions: CHIRALPAK IA column, (CH_2Cl_2/EtOH = 100/2) / *iso*-hexane = 30/70, flow rate = 0.5 mL min^{-1}, minor enantiomer: t_R = 30.97 min; major enantiomer: t_R = 21.72 min; 96%ee.



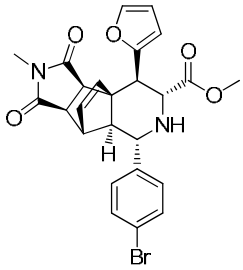
Methyl (3a*R*,3b*S*,4*R*,5*R*,7*S*,7a*S*,8*R*,8a*R*)-7-(4-bromophenyl)-2-methyl-4-(naphthalen-2-yl)-1,3-dioxo-2,3,3a,4,5,6,7,7a,8,8a-decahydro-1*H*-3b,8-ethenopyrrolo[3',4':3,4]cyclo-penta[1,2-*c*]pyridine-5-carboxylate

3ag: 85% yield; amorphous white solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.91 – 7.82 (m, 3H), 7.80 (s, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.51 – 7.44 (m, 4H), 7.20 (d, *J* = 8.3 Hz, 2H), 6.39 (d, *J* = 5.8 Hz, 1H), 6.10 (dd, *J* = 5.7, 2.7 Hz, 1H), 4.15 (d, *J* = 10.9 Hz, 1H), 4.02 (d, *J* = 9.9 Hz, 1H), 3.49 (d, *J* = 10.9 Hz, 1H), 3.31 (m, 4H), 3.27 (m, 1H), 3.18 – 3.12 (m, 1H), 2.54 (s, 3H), 1.94 ppm (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.31, 174.31, 171.94, 133.51, 133.32, 132.95, 132.79, 131.97, 128.69, 128.02, 127.99, 127.74, 126.03, 125.78, 121.81, 71.19, 62.87, 61.77, 57.14, 52.08, 51.81, 47.28, 45.91, 24.44 ppm; FT-IR: $\tilde{\nu}$ = 2951, 1734, 1696, 1485, 1431, 1378, 1276, 1131, 1074, 1036, 1009 cm^{-1}; HRMS: calcd. for $[M+H]^+$ $C_{31}H_{28}{}^{79}BrN_2O_4$ = 571.12270, found: 571.12290; calcd. for $[M+H]^+$ $C_{31}H_{28}{}^{81}BrN_2O_4$ = 573.12065, found: 573.12001; $[a]_D^{RT}$ = -115.5 (c = 1.0 in CH_2Cl_2); HPLC conditions: CHIRALPAK IA column, (CH_2Cl_2/EtOH = 100/2) / *iso*-hexane = 30/70, flow rate = 0.5 mL min^{-1}, minor enantiomer: t_R = 22.01 min; major enantiomer: t_R = 25.92 min; 94%ee.



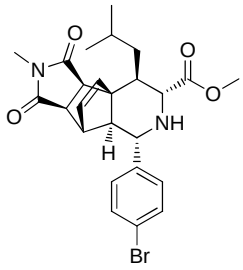
Methyl (3a*R*,3b*S*,4*R*,5*R*,7*S*,7a*S*,8*R*,8a*R*)-4-(benzo[d][1,3]dioxol-5-yl)-7-(4-bromophenyl)-2-methyl-1,3-dioxo-2,3,3a,4,5,6,7,7a,8,8a-decahydro-1*H*-3b,8-ethenopyrrolo[3',4':3,4] cyclopenta[1,2-*c*]pyridine-5-carboxylate

3ah: 80% yield; amorphous white solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 7.7 Hz, 2H), 7.16 (d, *J* = 6.6 Hz, 2H), 6.83 (m, 3H), 6.27 (d, *J* = 5.3 Hz, 1H), 6.08 (br s, 1H), 5.99 (d, *J* = 10.4 Hz, 2H), 3.92 (t, *J* = 9.9 Hz, 2H), 3.47 (s, 3H), 3.22 (m, 3H), 3.11 (br s, 1H), 2.65 (s, 3H), 1.86 (br s, 1H), 1.78 ppm (br s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.30, 174.51, 171.92, 147.62, 146.95, 133.33, 132.70, 131.95, 128.66, 121.79, 108.23, 101.09, 71.08, 62.95, 61.77, 57.05, 52.16, 51.72, 51.46, 47.26, 45.90, 24.49 ppm; FT-IR: $\tilde{\nu}$ = 2912, 1733, 1695, 1489, 1433, 1377, 1276, 1239, 1199, 1131, 1096, 1009 cm^{-1}; HRMS: calcd. for $[M+H]^+$ $C_{28}H_{26}{}^{79}BrN_2O_6$ = 565.09688, found: 565.09694; calcd. for $[M+H]^+$ $C_{28}H_{26}{}^{81}BrN_2O_6$ = 567.09483, found: 567.09423; $[a]_D^{RT}$ = -78.0 (c = 1.0 in CH_2Cl_2); HPLC conditions: CHIRALPAK IA column, (CH_2Cl_2/EtOH = 100/2) / *iso*-hexane = 30/70, flow rate = 0.5 mL min^{-1}, minor enantiomer: t_R = 27.93 min; major enantiomer: t_R = 36.31 min; 95%ee.



Methyl (3a*R*,3b*S*,4*R*,5*R*,7*S*,7a*S*,8*R*,8a*R*)-7-(4-bromophenyl)-4-(furan-2-yl)-2-methyl-1,3-dioxo-2,3,3a,4,5,6,7,7a,8,8a-decahydro-1*H*-3b,8-ethenopyrrolo[3',4':3,4]cyclopenta[1,2-*c*]pyridine-5-carboxylate

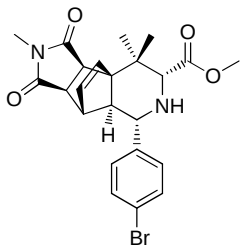
3ai: 65% yield; amorphous white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.56 (d, *J* = 5.6 Hz, 1H), 6.40 (d, *J* = 1.9 Hz, 1H), 6.26 (d, *J* = 2.9 Hz, 1H), 6.13 – 6.06 (m, 1H), 3.97 – 3.90 (m, 2H), 3.51 (s, 3H), 3.37 (d, *J* = 10.5 Hz, 1H), 3.26 (m, 1H), 3.20 – 3.09 (m, 2H), 2.71 (s, 3H), 1.86 (d, *J* = 9.4 Hz, 1H), 1.76 ppm (br s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 176.44, 174.88, 172.19, 151.87, 142.32, 140.49, 134.42, 132.94, 131.93, 128.62, 121.77, 110.23, 108.40, 70.92, 61.95, 60.51, 56.68, 52.17, 51.45, 47.13, 45.83, 45.27, 24.53 ppm; FT-IR: $\tilde{\nu}$ = 2950, 1735, 1695, 1485, 1432, 1378, 1276, 1203, 1133, 1072, 1010 cm^{-1}; HRMS: calcd. for $[M+H]^+$ $C_{25}H_{24}{}^{79}BrN_2O_5$ = 511.08631, found: 511.08616; calcd. for $[M+H]^+$ $C_{25}H_{24}{}^{81}BrN_2O_5$ = 513.08426, found: 513.08323; $[a]_D^{RT}$ = -60.9 (c = 1.0 in CH_2Cl_2); HPLC conditions: CHIRALPAK IA column, (CH_2Cl_2/EtOH = 100/2) / *iso*-hexane = 30/70, flow rate = 0.5 mL min^{-1}, minor enantiomer: t_R = 31.98 min; major enantiomer: t_R = 38.40 min; 91%ee.



Methyl (3a*R*,3b*R*,4*R*,5*R*,7*S*,7a*S*,8*R*,8a*R*)-7-(4-bromophenyl)-4-isobutyl-2-methyl-1,3-dioxo-2,3,3a,4,5,6,7,7a,8,8a-decahydro-1*H*-3b,8-ethenopyrrolo[3',4':3,4]cyclopenta[1,2-*c*]pyridine-5-carboxylate

3aj: 47% yield; amorphous white solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 5.9 Hz, 2H), 6.05 (br s, 2H), 3.73 (m, 4H), 3.30 (d, *J* = 9.5 Hz, 1H), 3.25 (dd, *J* = 6.8, 4.5 Hz, 1H), 3.15 (d, *J* = 7.2 Hz, 1H), 3.08 (br s, 1H), 2.83 (s, 3H), 2.26 – 2.17 (m, 1H), 2.04 (br s, 1H), 1.79 (br s, 1H), 1.66 (br s, 1H), 1.46 – 1.34 (m, 2H), 1.06 (d, *J* = 6.2 Hz,

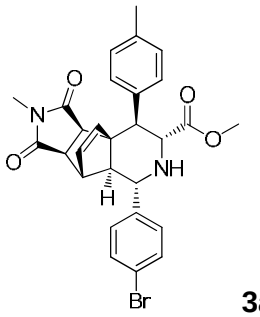
3H), 0.94 ppm (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.41, 173.56, 133.23, 132.96, 132.59, 131.90, 128.61, 121.66, 71.09, 64.62, 62.29, 56.66, 52.20, 47.40, 45.87, 42.87, 36.59, 27.57, 24.63, 23.67, 21.66 ppm; FT-IR: $\tilde{\nu}$ = 2953, 2868, 1735, 1693, 1431, 1378, 1279, 1243, 1132, 1068, 1009 cm^{-1}; HRMS: calcd. for $[M+H]^+$ $C_{25}H_{30}{}^{79}BrN_2O_4$ = 501.13835, found: 501.13825; calcd. for $[M+H]^+$ $C_{25}H_{30}{}^{81}BrN_2O_4$ = 503.13630, found: 503.13529; $[a]_D^{RT}$ = -9.9 (c = 0.5 in CH_2Cl_2); HPLC conditions: CHIRALPAK IA column, (CH_2Cl_2/EtOH = 100/2) / *iso*-hexane = 20/80, flow rate = 0.5 mL min^{-1}, minor enantiomer: t_R = 19.85 min; major enantiomer: t_R = 17.83 min; 94%ee.



Methyl (3a*R*,3b*R*,5*R*,7*S*,7a*S*,8*R*,8a*R*)-7-(4-bromophenyl)-2,4,4-trimethyl-1,3-dioxo-2,3,3a,4,5,6,7,7a,8,8a-decahydro-1*H*-3b,8-ethenopyrrolo[3',4':3,4]cyclopenta[1,2-*c*] pyridine-5-carboxylate

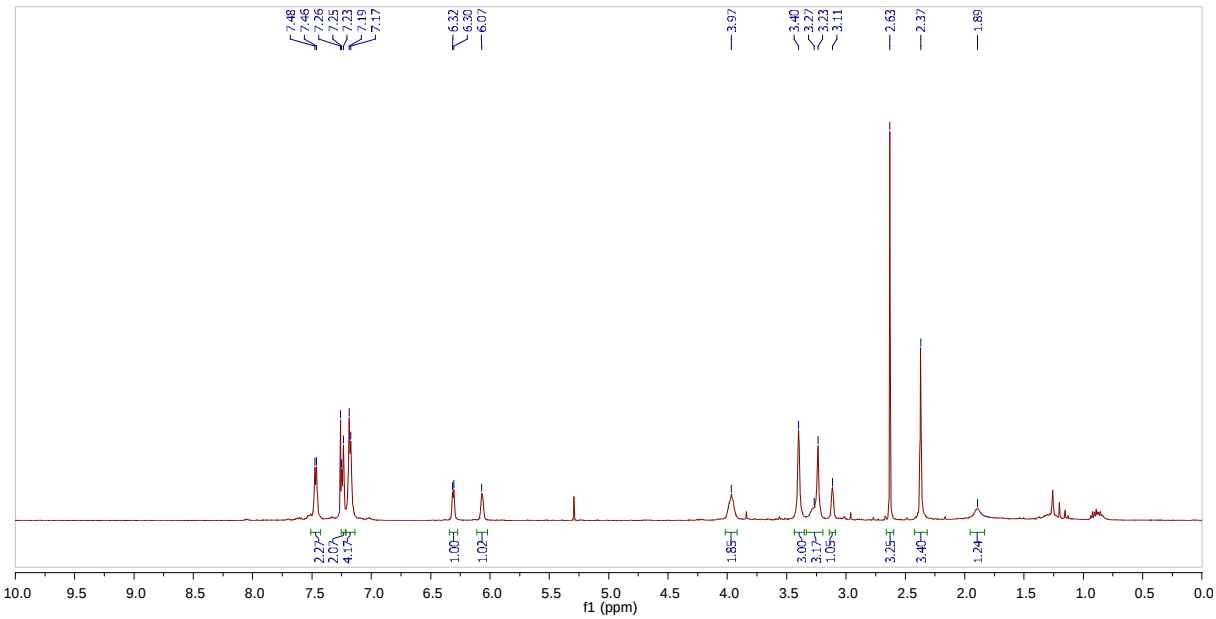
3ak: 78% yield; amorphous white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 7.7 Hz, 2H), 7.16 (d, *J* = 7.7 Hz, 2H), 6.13 (d, *J* = 5.5 Hz, 1H), 6.07 (br s, 1H), 3.78 (d, *J* = 9.5 Hz, 1H), 3.73 (s, 3H), 3.52 (br s, 1H), 3.36 (d, *J* = 7.2 Hz, 1H), 3.19 (br s, 1H), 3.05 (br s, 1H), 2.82 (s, 3H), 1.92 (d, *J* = 9.4 Hz, 1H), 1.75 (brs, 1H), 1.47 (s, 3H), 1.29 ppm (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.10, 177.06, 172.38, 133.46, 133.43, 132.11, 129.03, 121.86, 67.70, 67.15, 66.57, 57.61, 52.19, 47.76, 47.19, 46.01, 36.32, 24.91, 23.47, 19.51 ppm; FT-IR: $\tilde{\nu}$ = 2947, 1732, 1694, 1529, 1432, 1378, 1282, 1196, 1133, 1069, 1008 cm^{-1}; HRMS: calcd. for $[M+H]^+$ $C_{23}H_{26}{}^{79}BrN_2O_4$ = 473.10705, found: 473.10682; calcd. for $[M+H]^+$ $C_{23}H_{26}{}^{81}BrN_2O_4$ = 475.10500, found: 475.10385; $[a]_D^{RT}$ = -21.6 (c = 1.0 in CH_2Cl_2); HPLC

conditions: CHIRALPAK IA column, (CH_2Cl_2/EtOH = 100/2) / *iso*-hexane = 30/70, flow rate = 0.5 mL min^{-1}, minor enantiomer: t_R = 25.76 min; major enantiomer: t_R = 22.06 min; 61%ee.

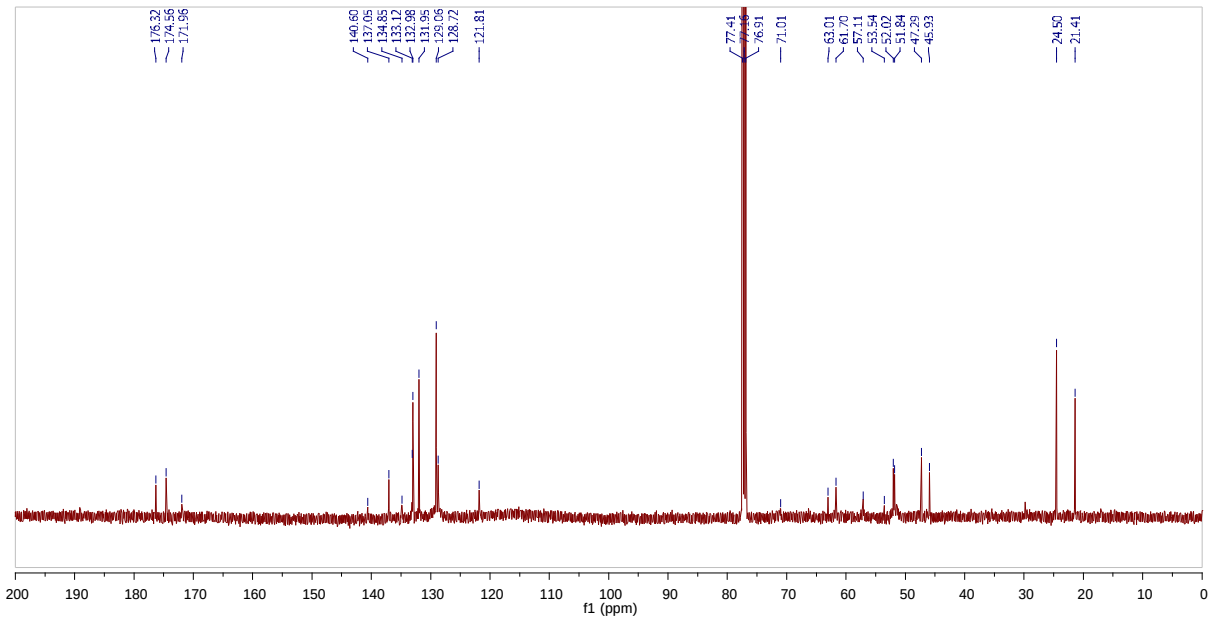


3aa

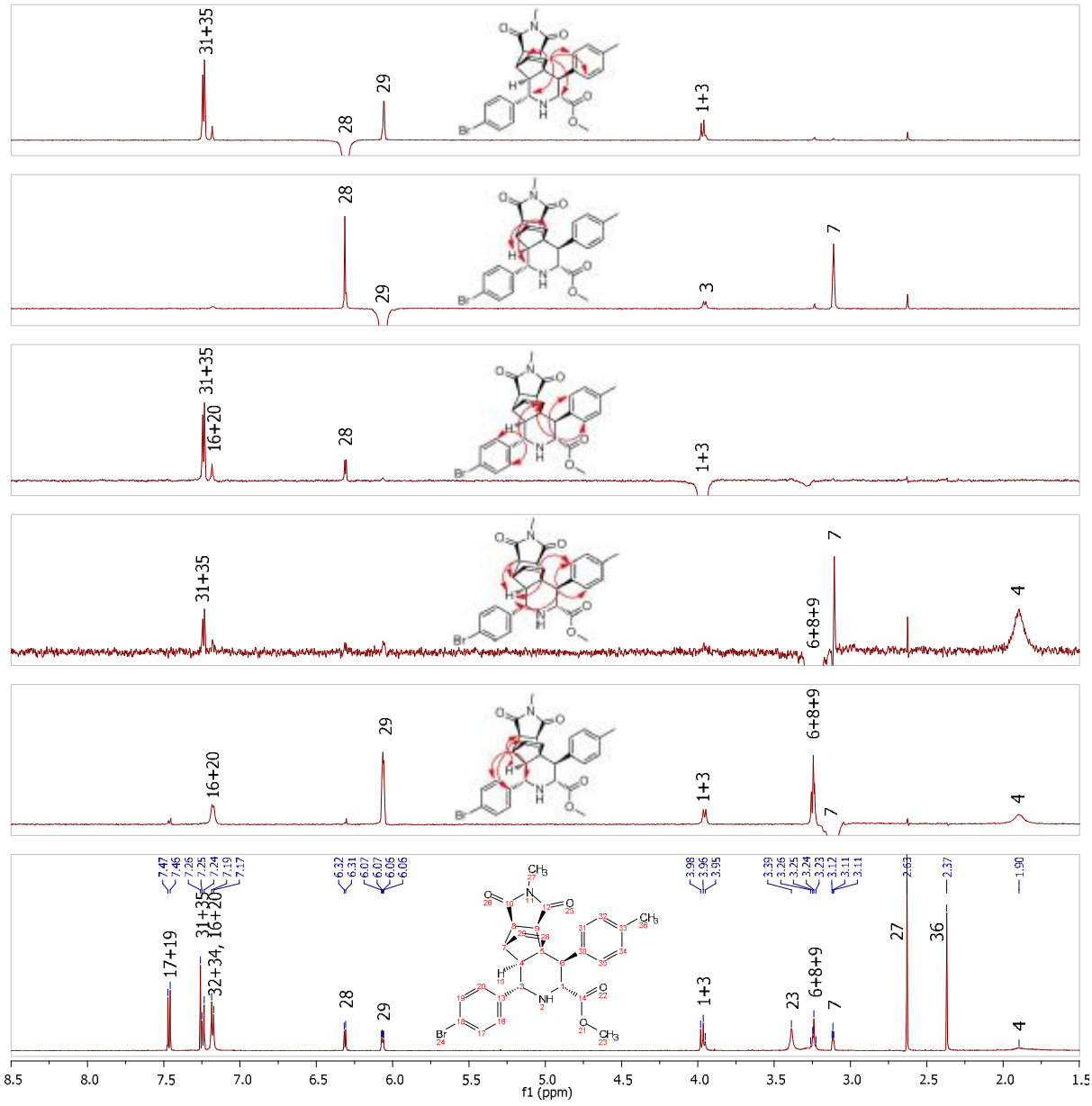
^{1}H NMR



^{13}C NMR



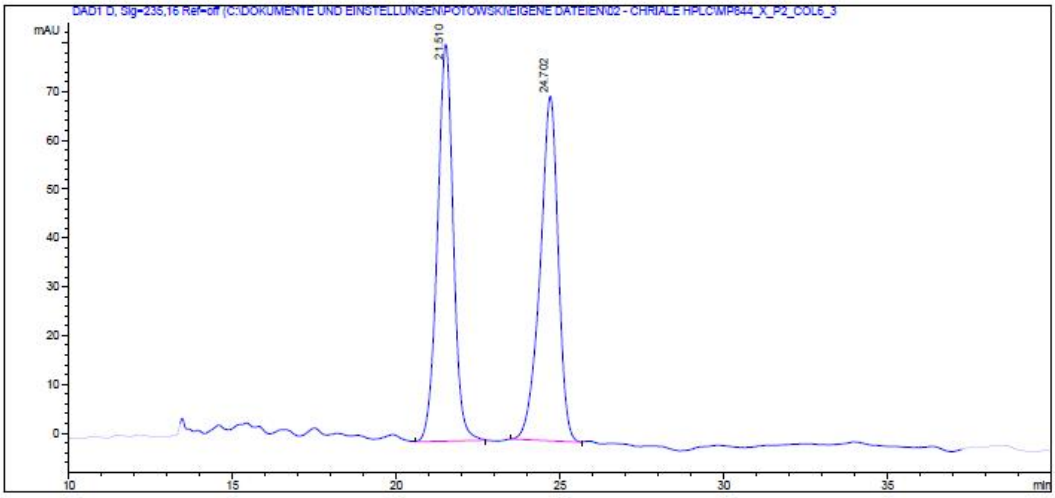
1D-NOE Experiments of compound **3aa**:



HPLC traces for **3aa**: racemat top, enantiomer bottom.

Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP844 X P2 COL6 30D 60MIN 3.D

Acq. Method :AA_6RUN_30D_60MIN.M Location : Vial 61 Inj. Vol. : 10 µl

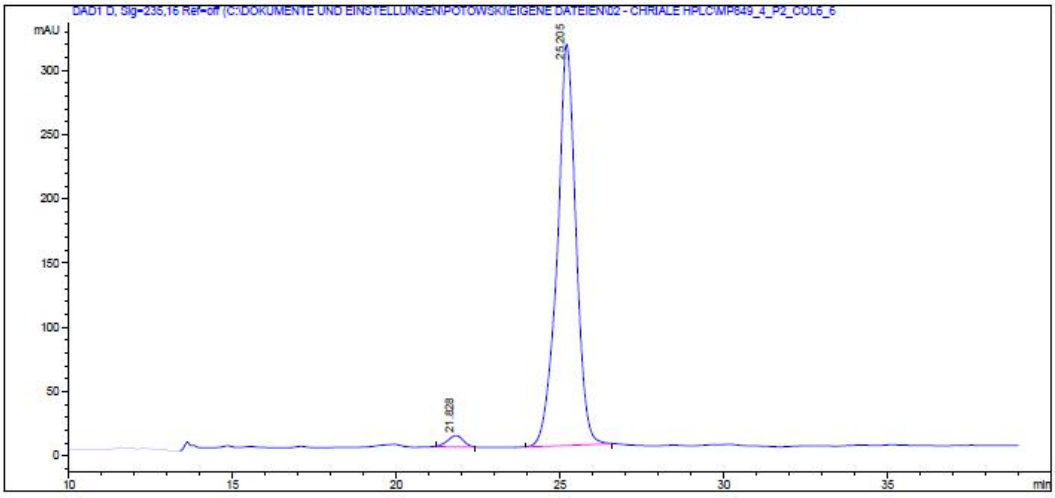


Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	21.510	2740.464	50.286
2	24.702	2709.243	49.714

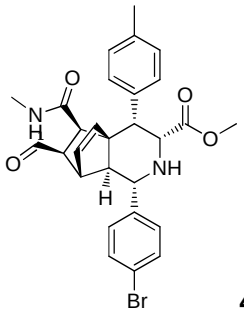
Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP849 4 P2 COL6 60MIN 1.D

Acq. Method :AA_6RUN_30D_60MIN.M Location : Vial 41 Inj. Vol. : -



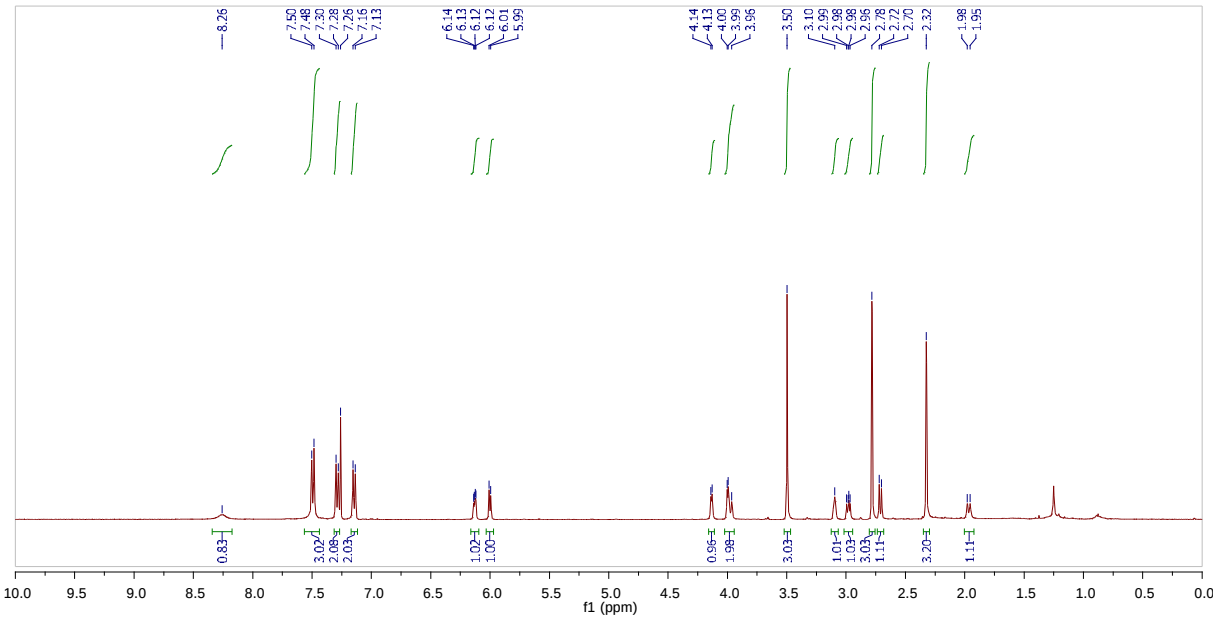
Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	21.828	297.349	2.329
2	25.205	12467.572	97.671

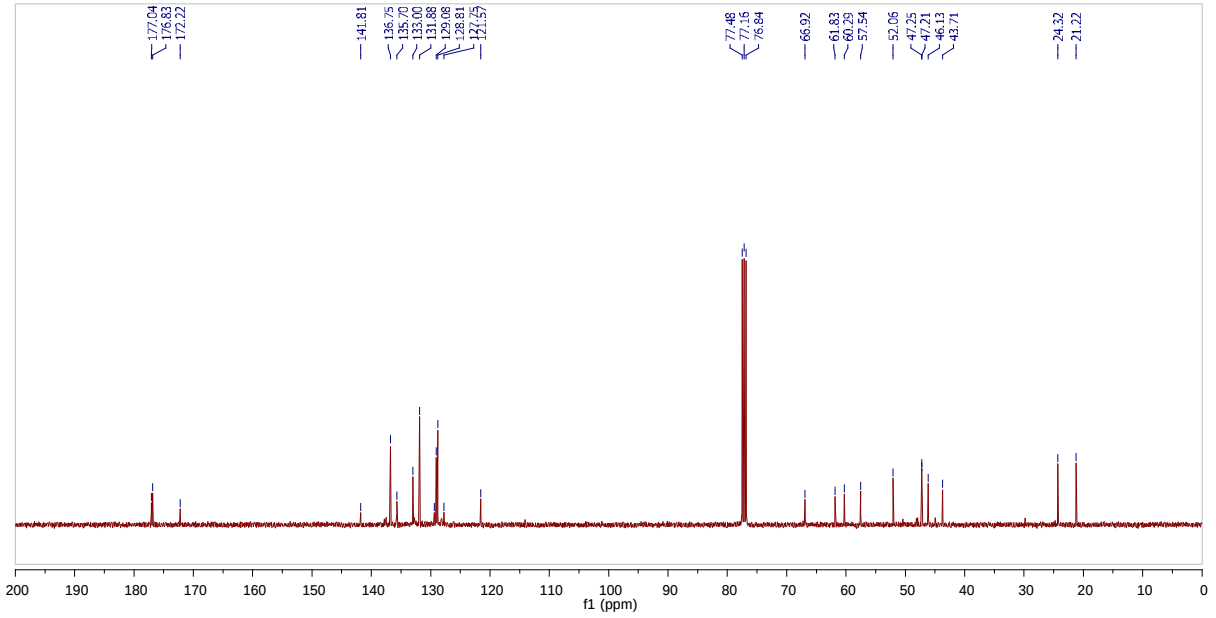


4aa

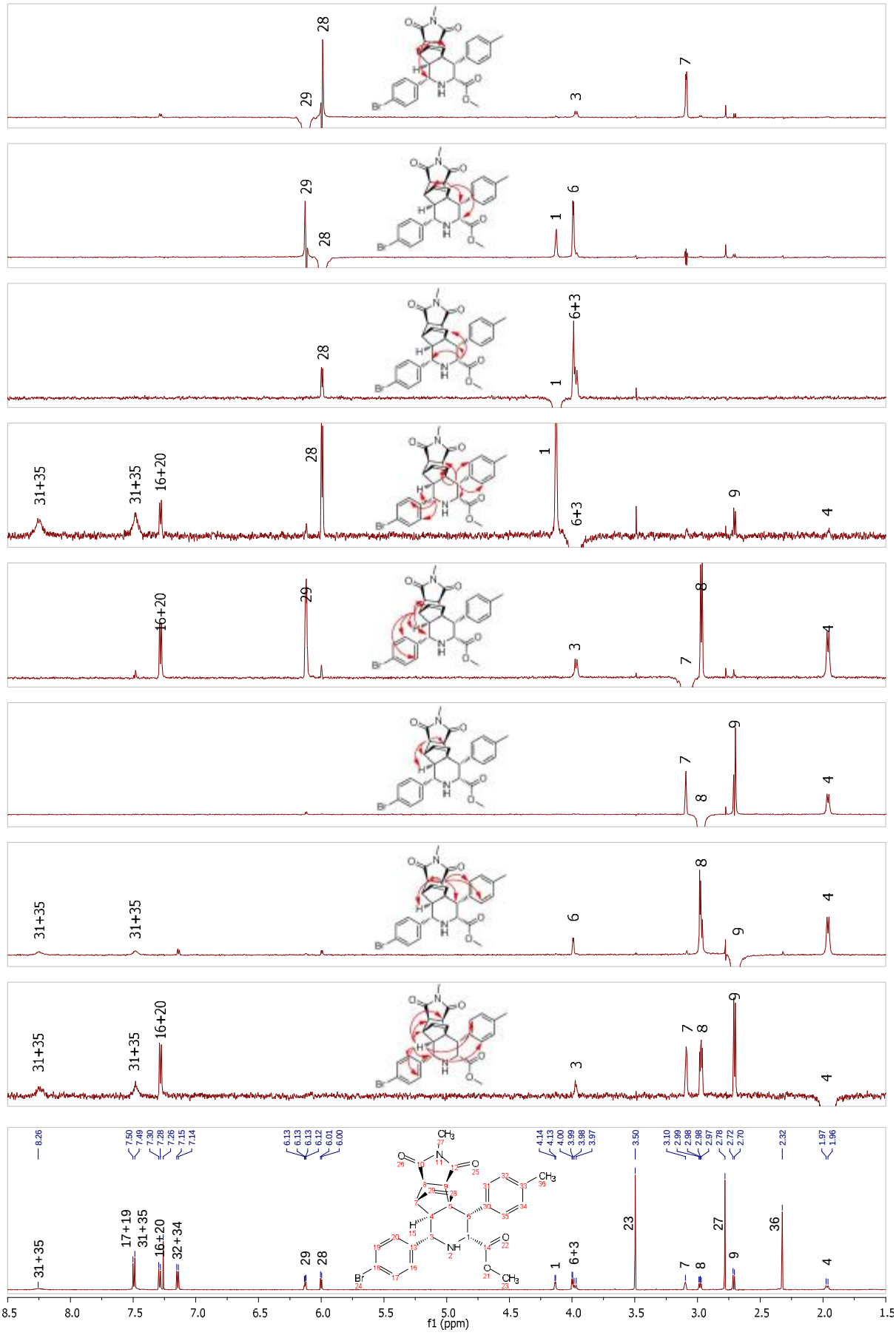
^{1}H NMR

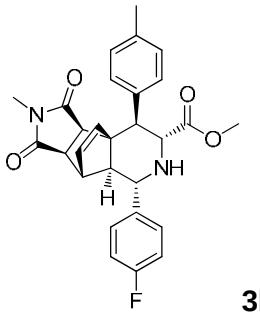


^{13}C NMR



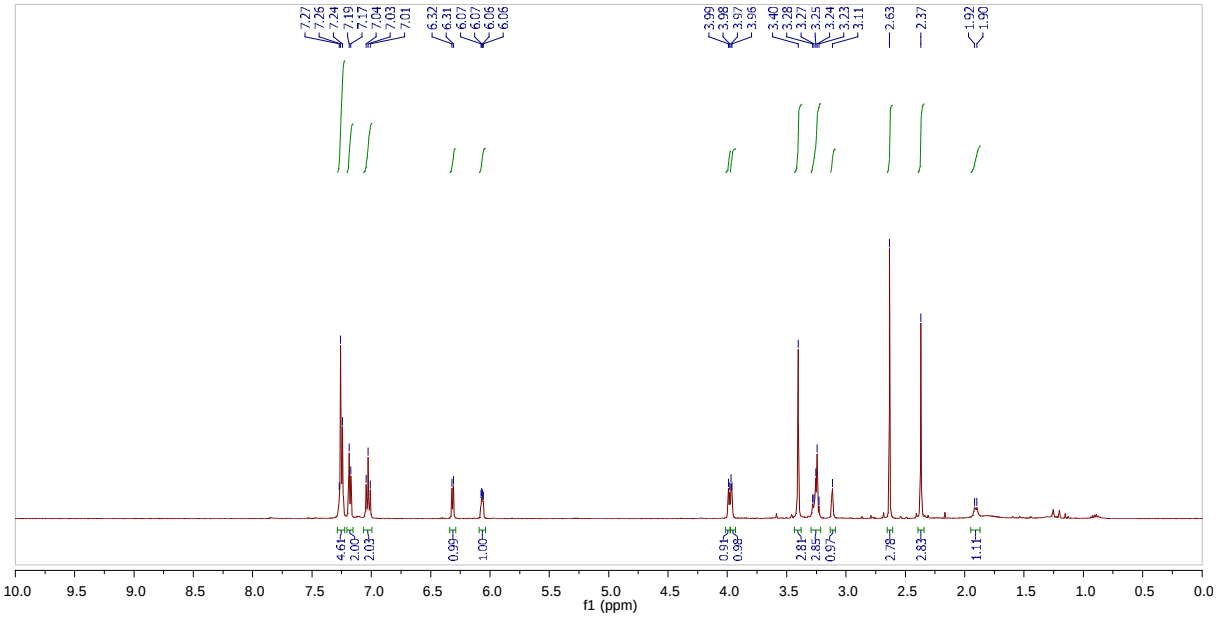
1D-NOE Experiments of compound **4aa:**



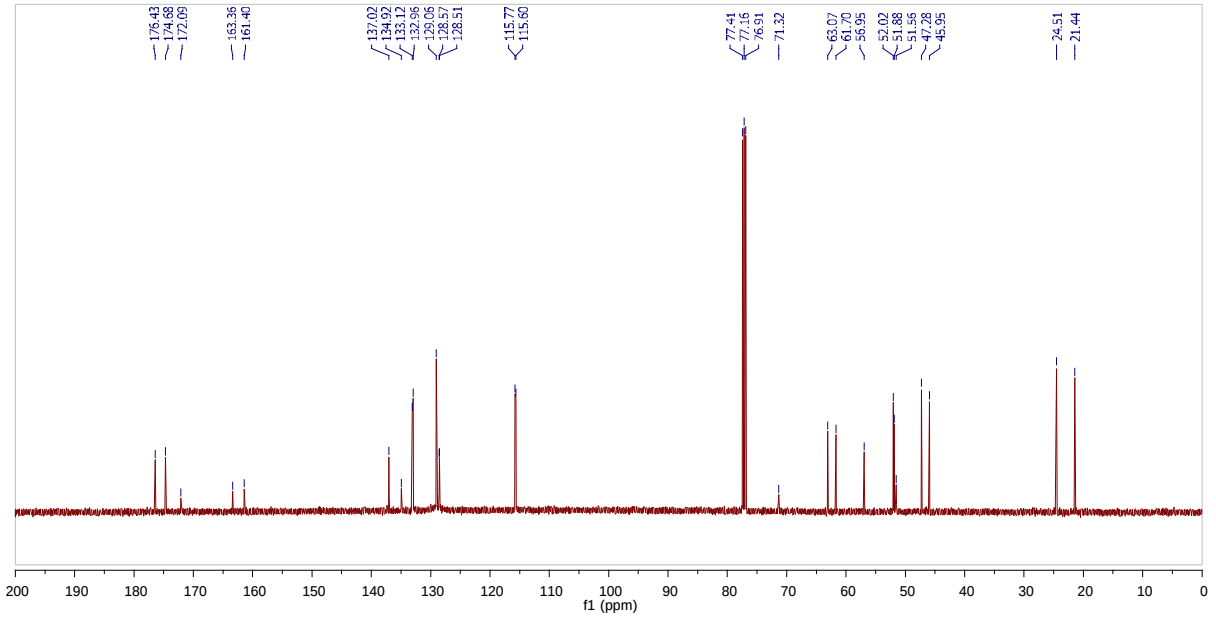


3ba

^{1}H NMR



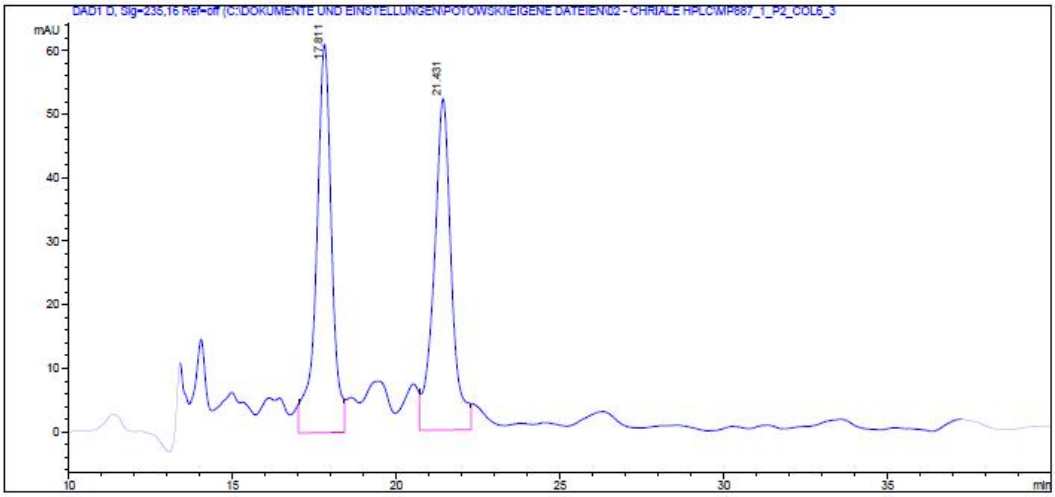
^{13}C NMR



HPLC traces for **3ba**: racemat top, enantiomer bottom.

Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP887 1 P2 COL6 30D 60MIN 1.D

Acq. Method :AA_6RUN_30D_60MIN.M Location : Vial 10 Inj. Vol. : 10 µl

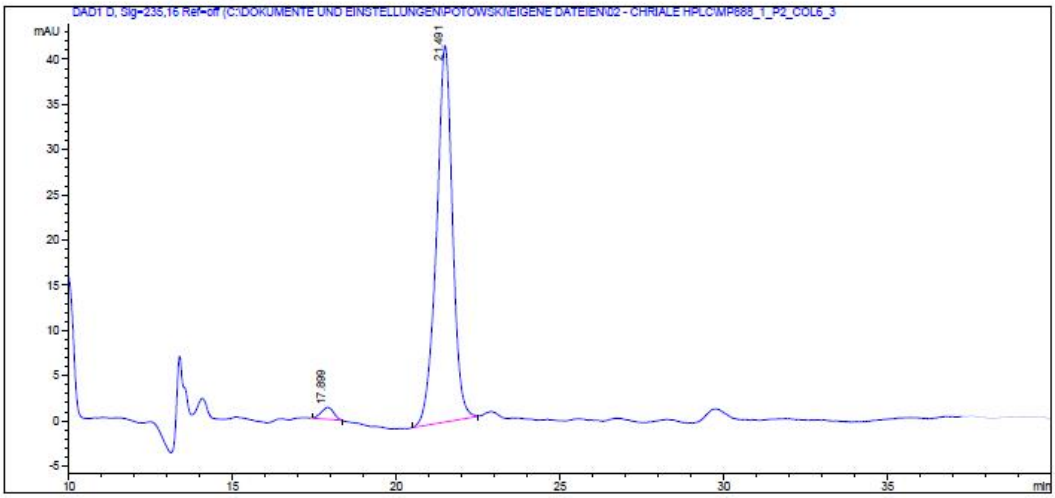


Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	17.811	1967.986	50.534
2	21.431	1926.404	49.466

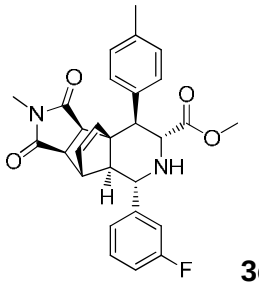
Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP888 1 P2 COL6 30D 60MIN 1.D

Acq. Method :AA_6RUN_30D_60MIN.M Location : Vial 9 Inj. Vol. : 10 µl



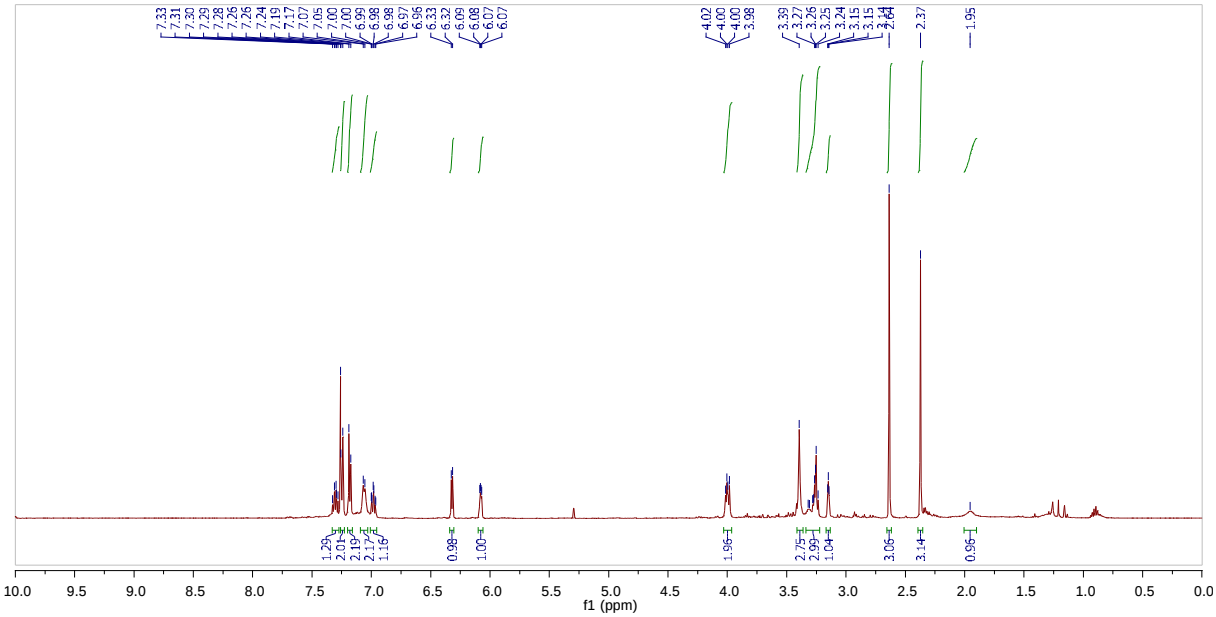
Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	17.899	34.562	2.384
2	21.491	1414.967	97.616

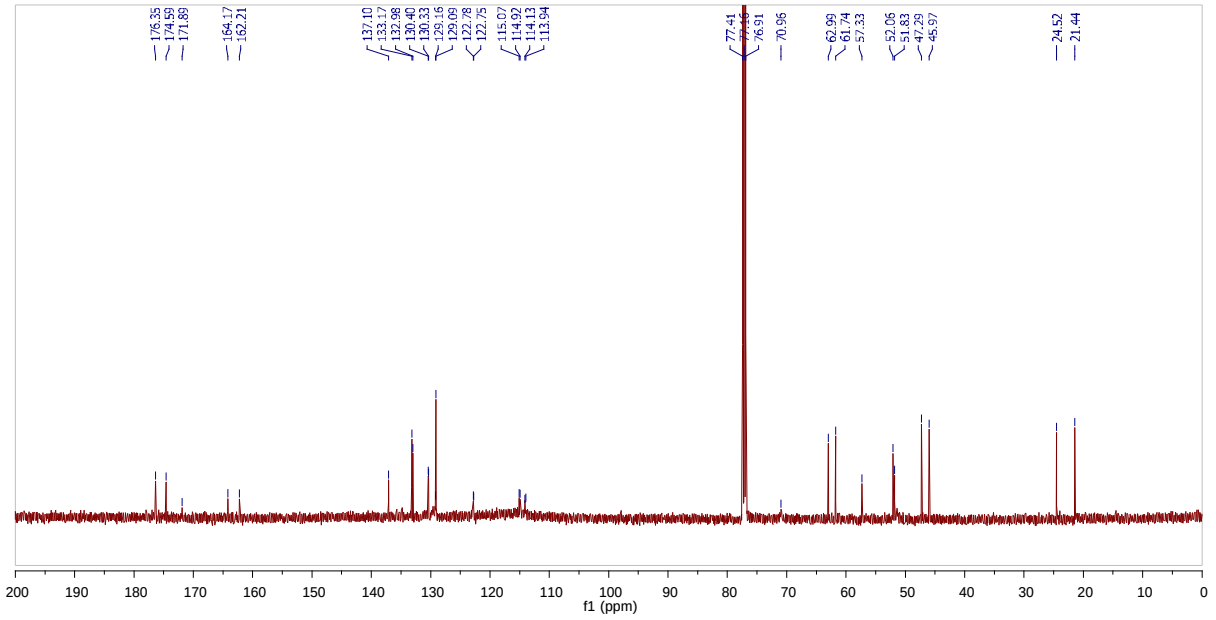


3ca

^{1}H NMR



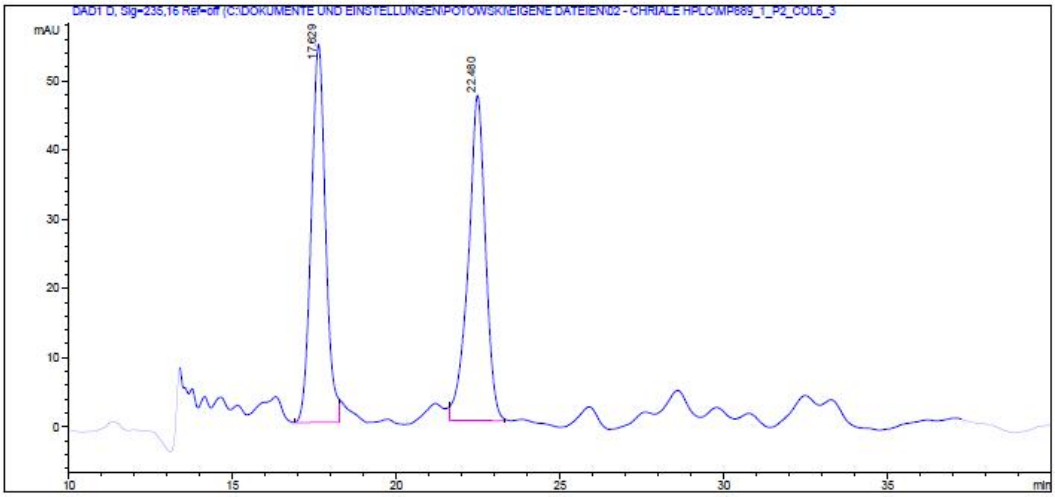
^{13}C NMR



HPLC traces for **3ca**: racemat top, enantiomer bottom.

Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP889 1 P2 COL6 30D 60MIN 1.D

Acq. Method :AA_6RUN_30D_60MIN.M Location : Vial 8 Inj. Vol. : 10 µl

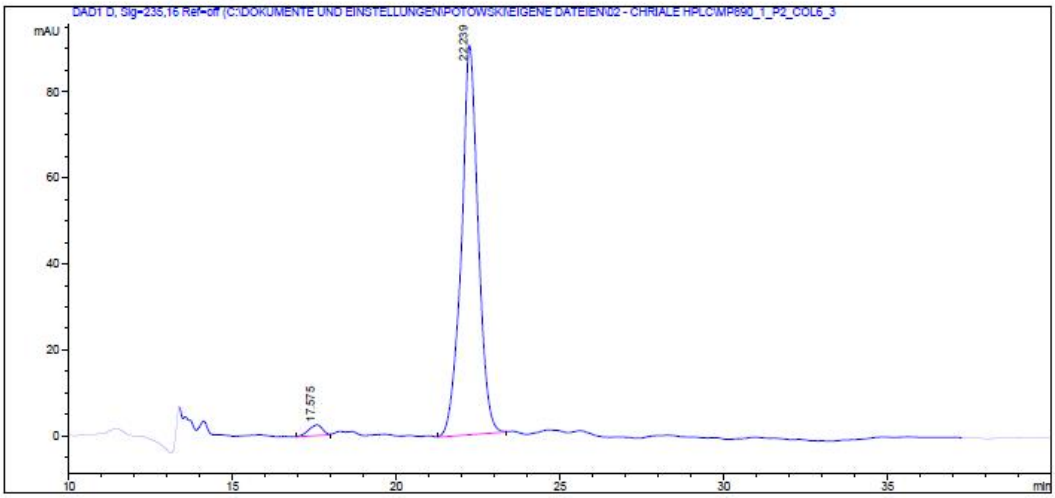


Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	17.629	1651.999	48.908
2	22.480	1725.757	51.092

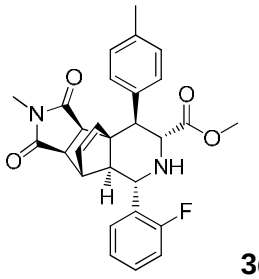
Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP890 1 P2 COL6 30D 60MIN 1.D

Acq. Method :AA_6RUN_30D_60MIN.M Location : Vial 7 Inj. Vol. : 10 µl



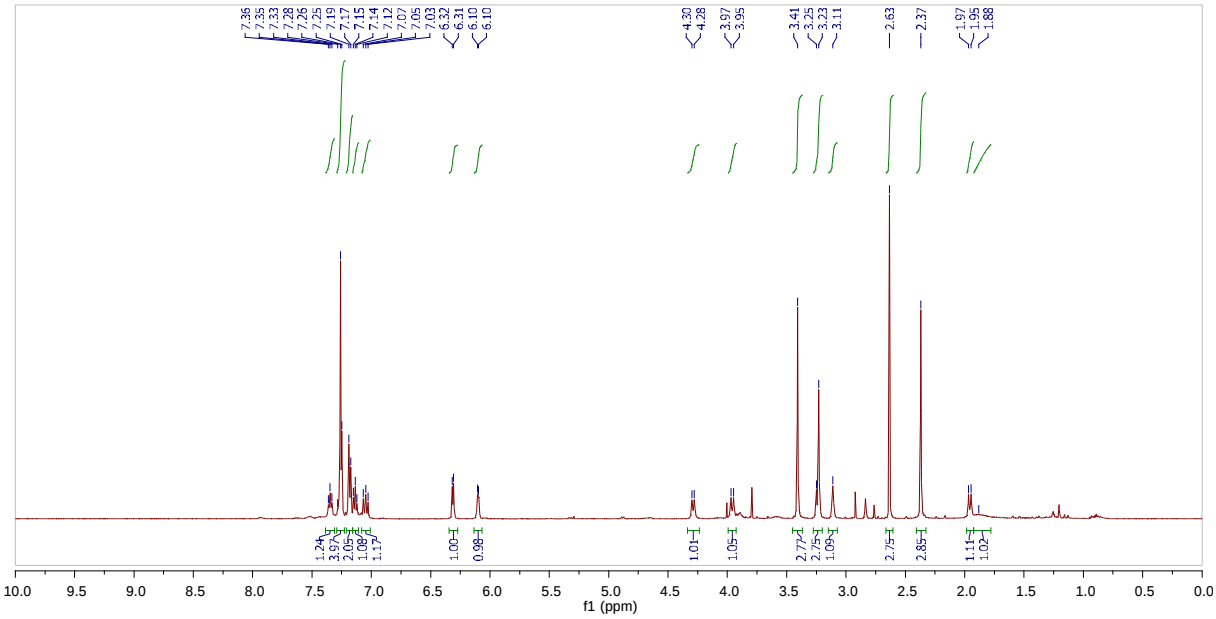
Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	17.575	73.197	2.211
2	22.239	3237.115	97.789

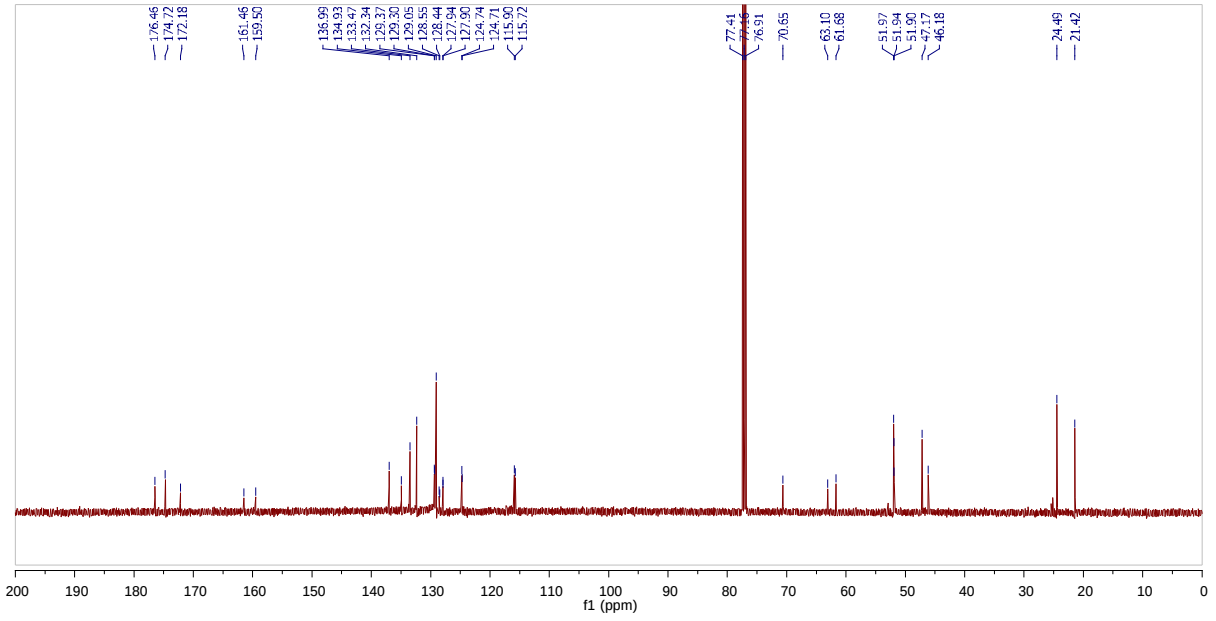


3da

^{1}H NMR



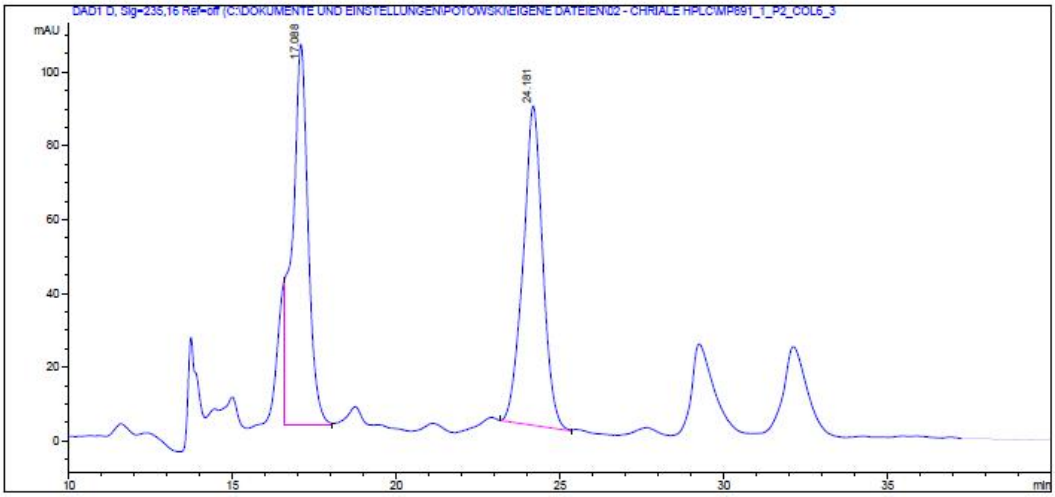
^{13}C NMR



HPLC traces for **3da**: racemat top, enantiomer bottom.

Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP891 1 P2 COL6 30D 60MIN 2.D

Acq. Method :AA_6RUN_30D_60MIN.M Location : Vial 11 Inj. Vol. : 20 µl

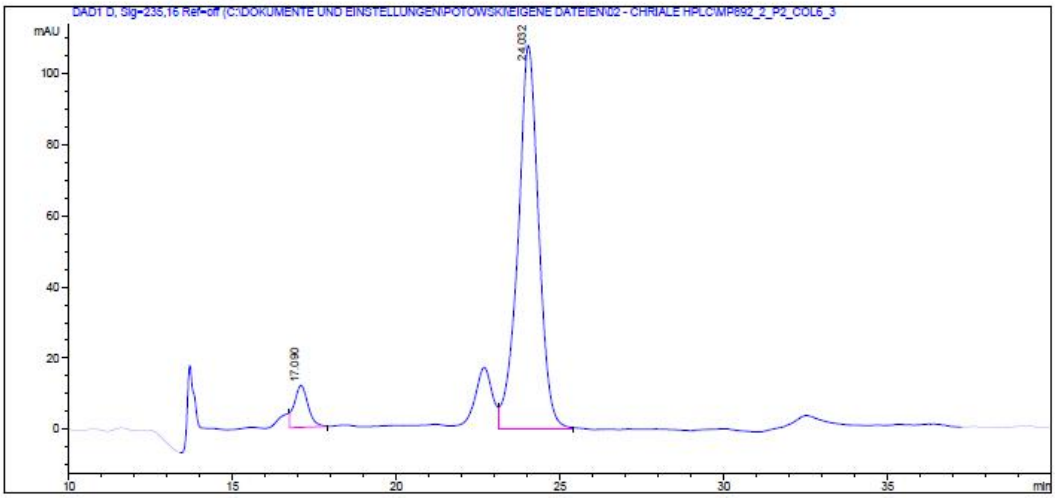


Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	17.088	3489.864	49.140
2	24.181	3612.020	50.860

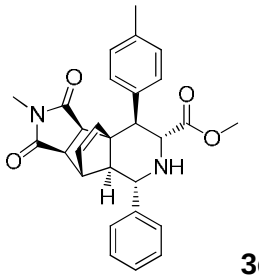
Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP892 2 P2 COL6 30D 60MIN 1.D

Acq. Method :AA_6RUN_30D_60MIN.M Location : Vial 12 Inj. Vol. : 20 µl



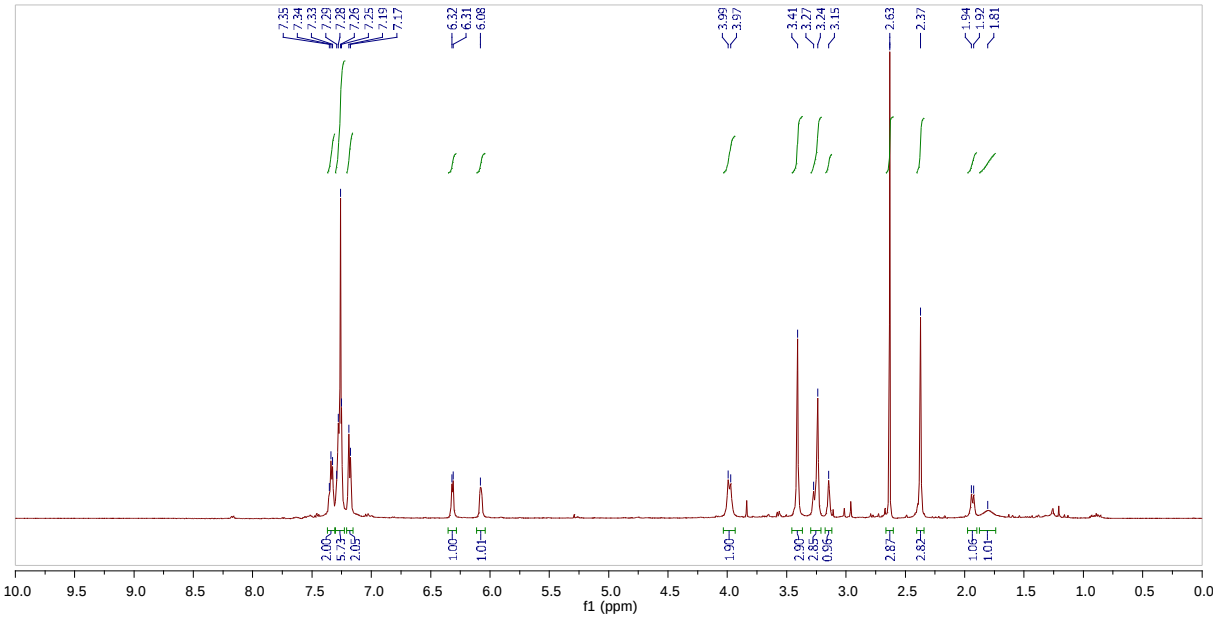
Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	17.090	345.056	6.810
2	24.032	4721.692	93.190

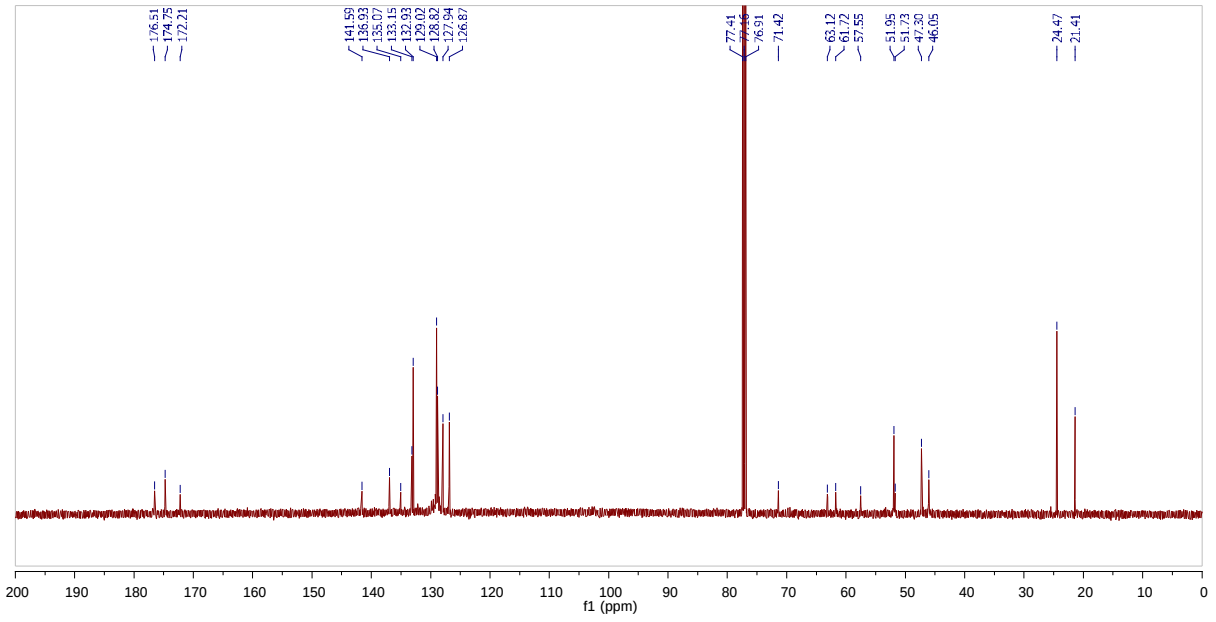


3ea

^{1}H NMR



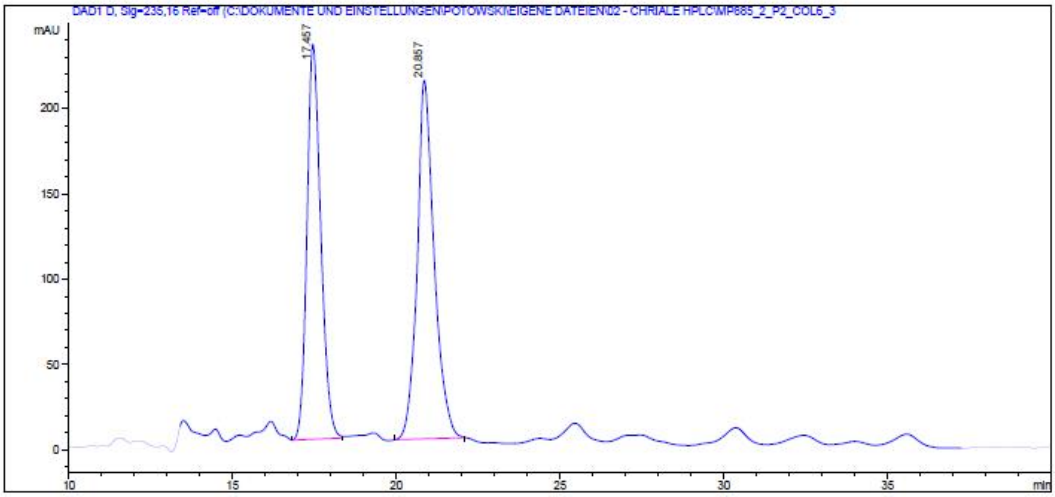
^{13}C NMR



HPLC traces for **3ea**: racemat top, enantiomer bottom.

Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP885 2 P2 COL6 30D 60MIN 2.D

Acq. Method :AA_6RUN_30D_60MIN.M Location : Vial 15 Inj. Vol. : 10 µl

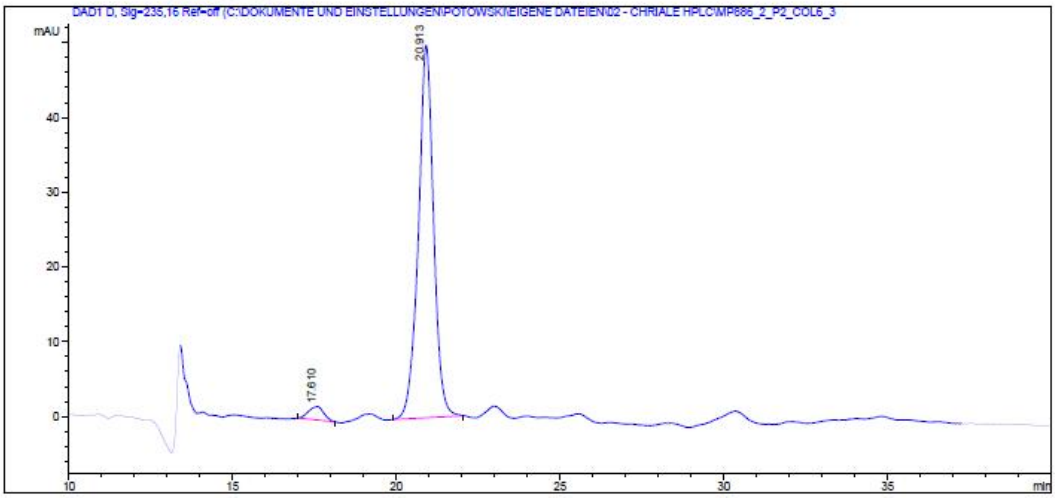


Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	17.457	6778.444	47.172
2	20.857	7591.124	52.828

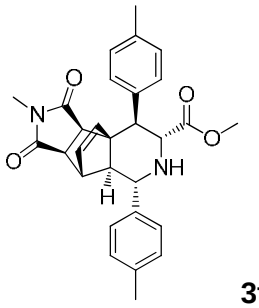
Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP886 2 P2 COL6 30D 60MIN 2.D

Acq. Method :AA_6RUN_30D_60MIN.M Location : Vial 16 Inj. Vol. : 10 µl



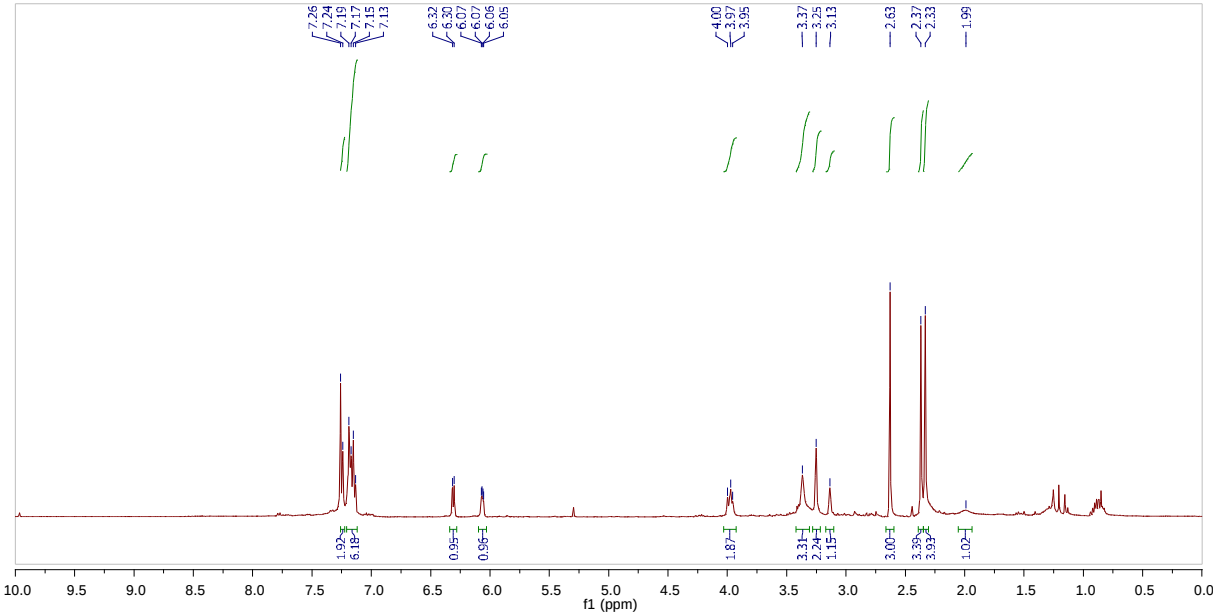
Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	17.610	57.313	3.433
2	20.913	1612.021	96.567

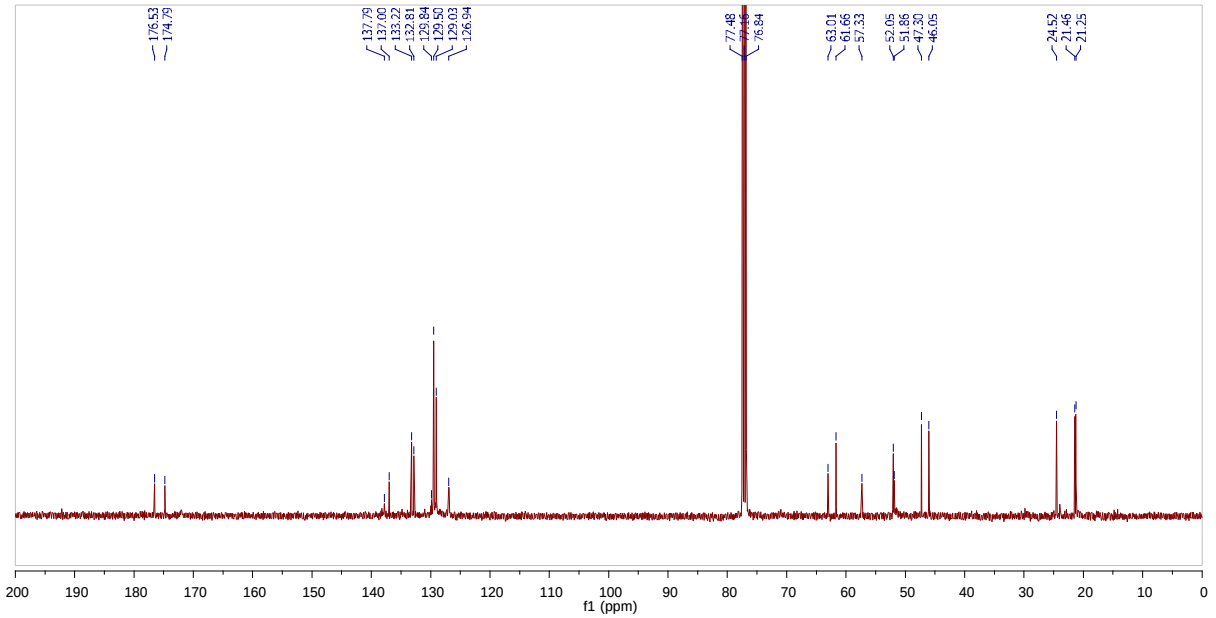


3fa

^{1}H NMR



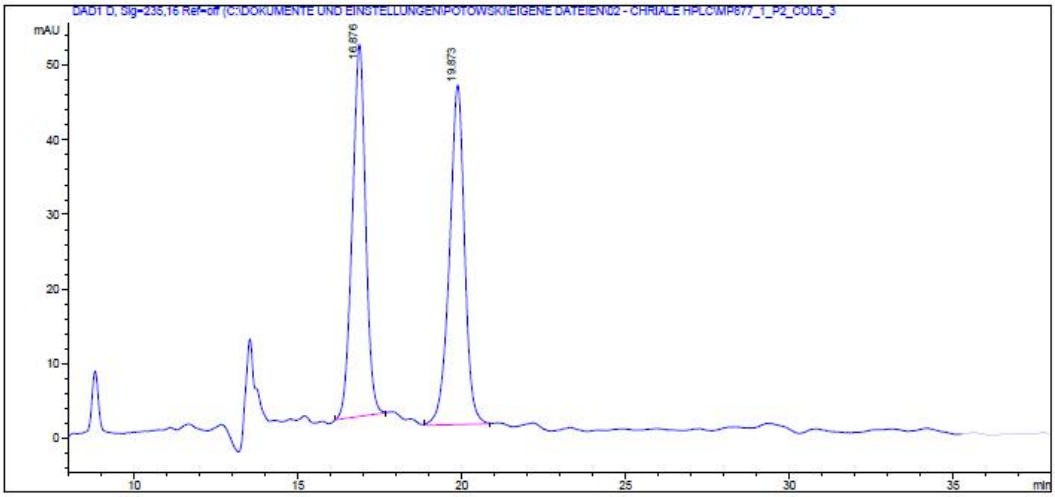
^{13}C NMR



HPLC traces for **3fa**: racemat top, enantiomer bottom.

Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP877 1 P2 COL6 30D 60MIN 2.D

Acq. Method :AA_6RUN_30D_60MIN.M Location : Vial 11 Inj. Vol. : 10 µl

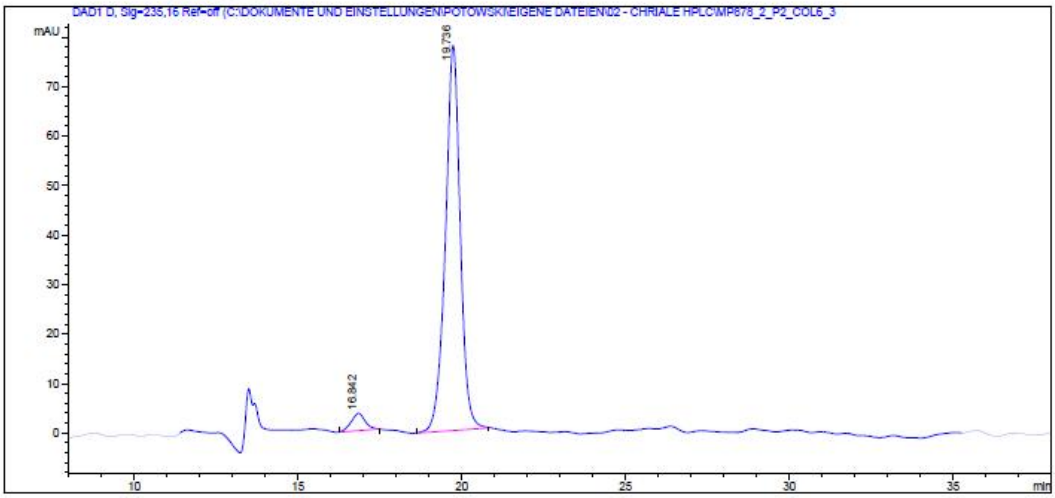


Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	16.876	1411.498	49.136
2	19.873	1461.148	50.864

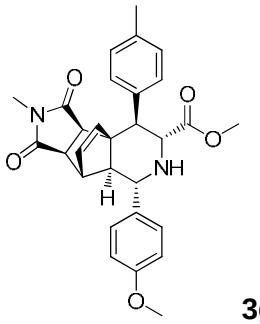
Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP878 2 P2 COL6 30D 60MIN 1.D

Acq. Method :AA_6RUN_30D_60MIN.M Location : Vial 12 Inj. Vol. : 10 µl



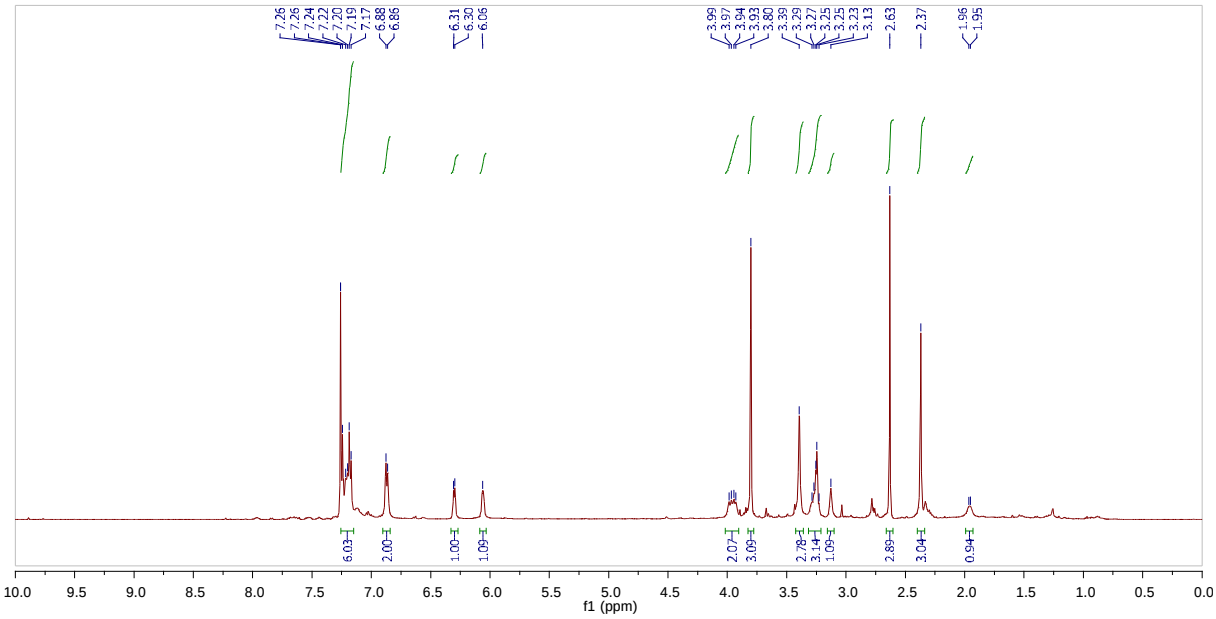
Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	16.842	102.190	3.999
2	19.736	2453.010	96.001

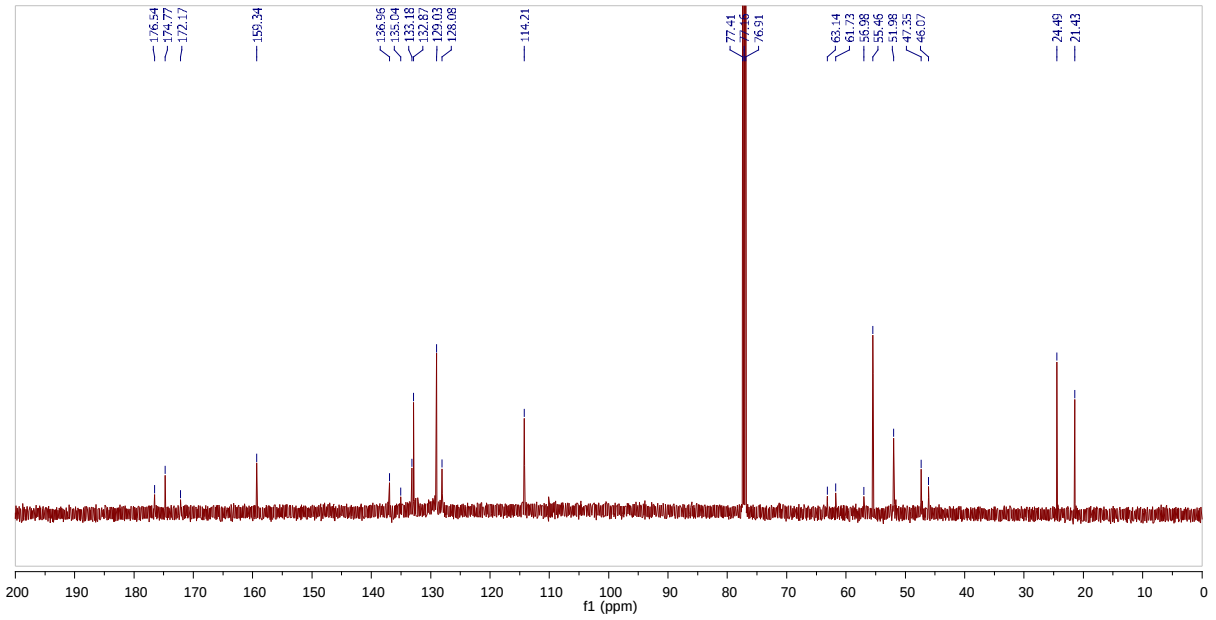


3ga

^{1}H NMR



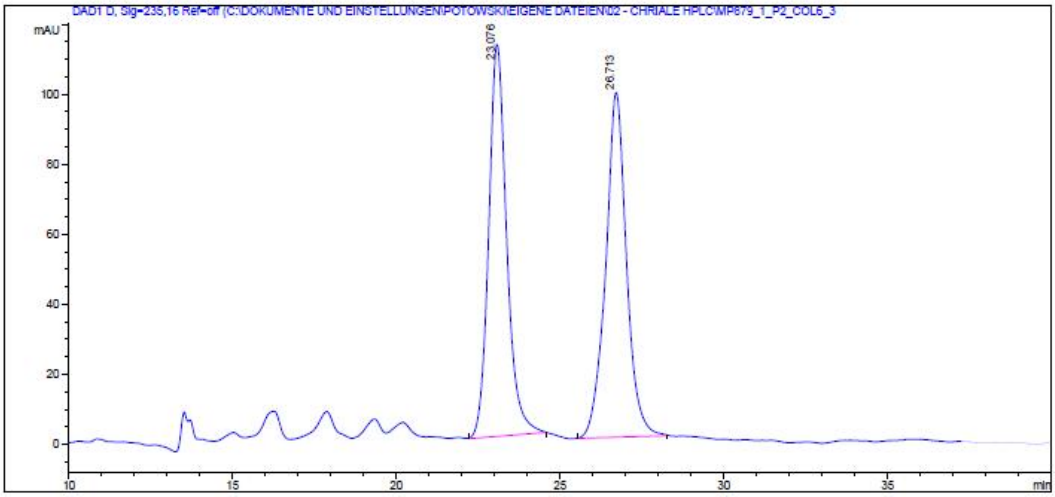
^{13}C NMR



HPLC traces for **3ga**: racemat top, enantiomer bottom.

Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP879 1 P2 COL6 30D 60MIN 2.D

Acq. Method :AA_6RUN_30D_60MIN.M Location : Vial 13 Inj. Vol. : 10 µl

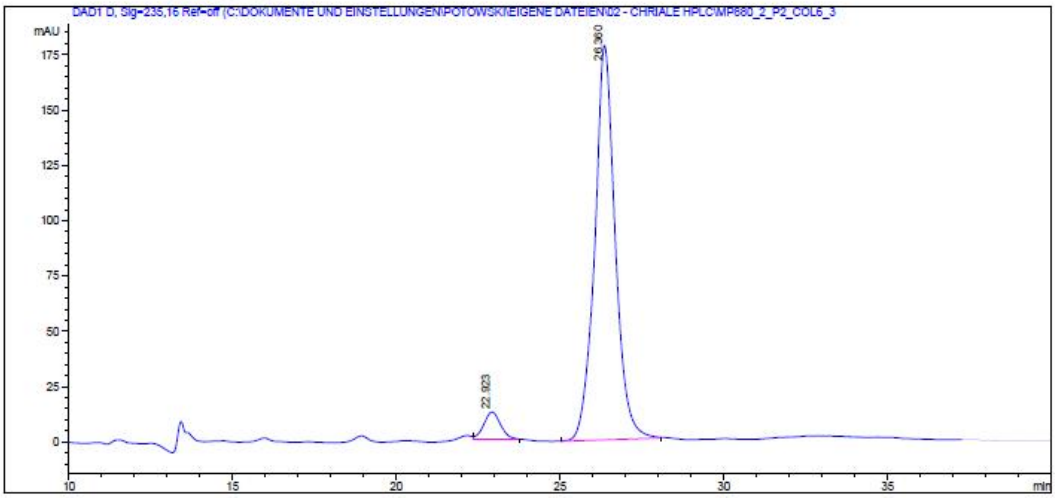


Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	23.076	4269.030	49.528
2	26.713	4350.328	50.472

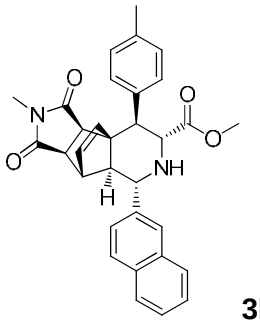
Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP880 2 P2 COL6 30D 60MIN 1.D

Acq. Method :AA_6RUN_30D_60MIN.M Location : Vial 14 Inj. Vol. : 10 µl



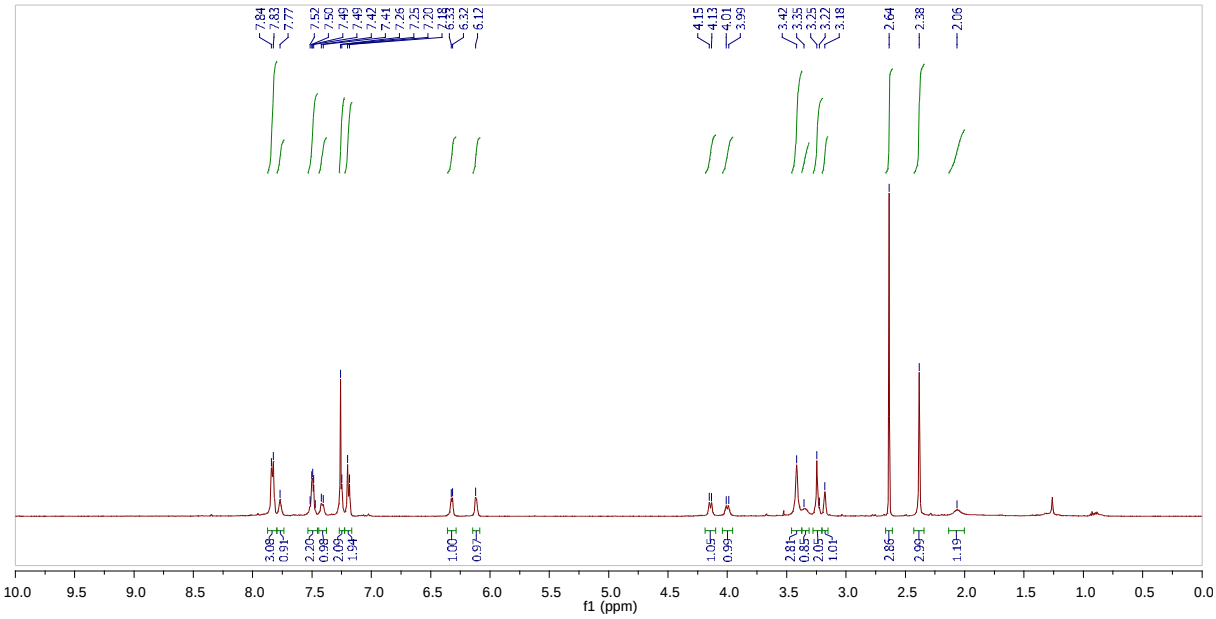
Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	22.923	442.249	5.389
2	26.360	7763.730	94.611

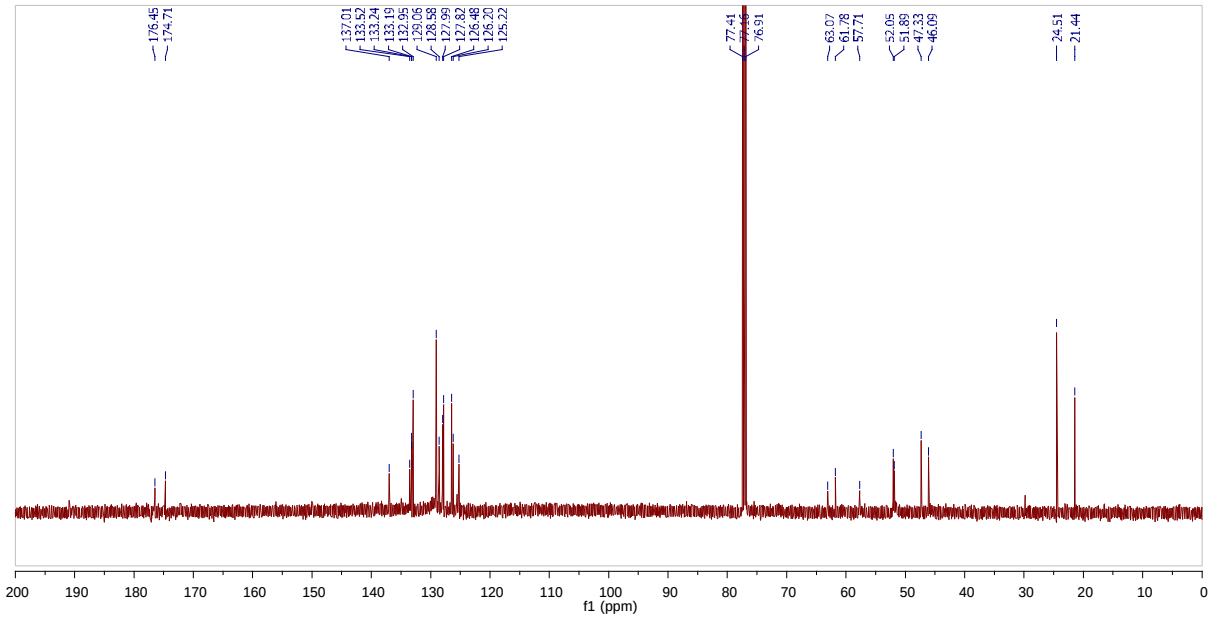


3ha

^{1}H NMR



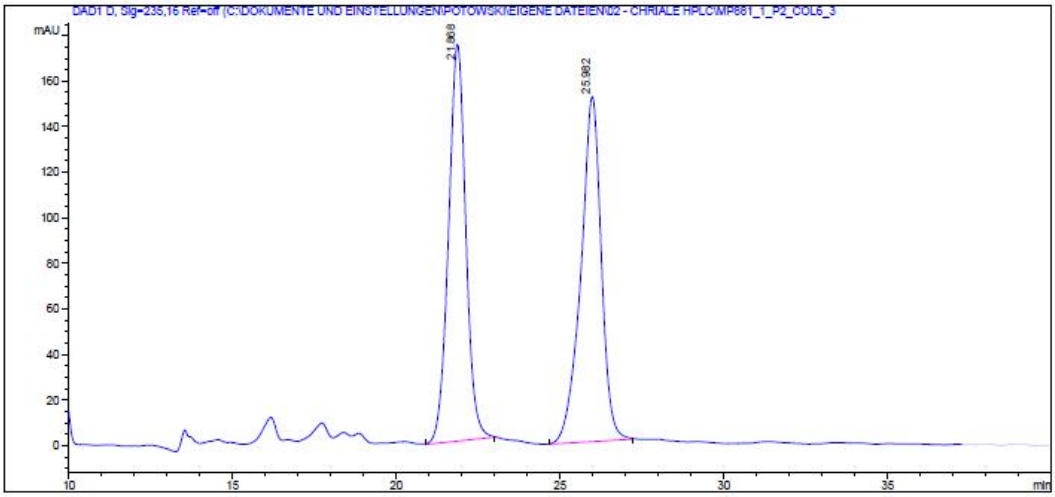
^{13}C NMR



HPLC traces for **3ha**: racemat top, enantiomer bottom.

Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP881 1 P2 COL6 30D 60MIN 3.D

Acq. Method :AA_6RUN_30D_60MIN.M Location : Vial 11 Inj. Vol. : 10 µl

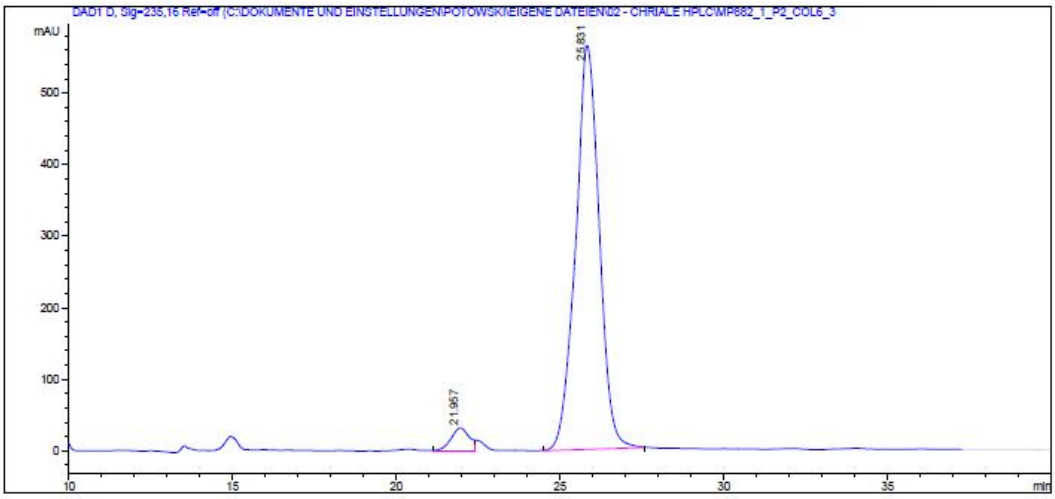


Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	21.868	6389.061	49.316
2	25.982	6566.416	50.684

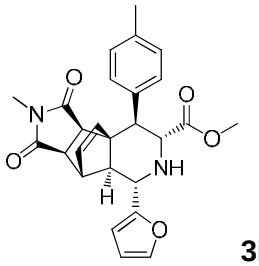
Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP882 1 P2 COL6 30D 60MIN 3.D

Acq. Method :AA_6RUN_30D_60MIN.M Location : Vial 12 Inj. Vol. : 10 µl



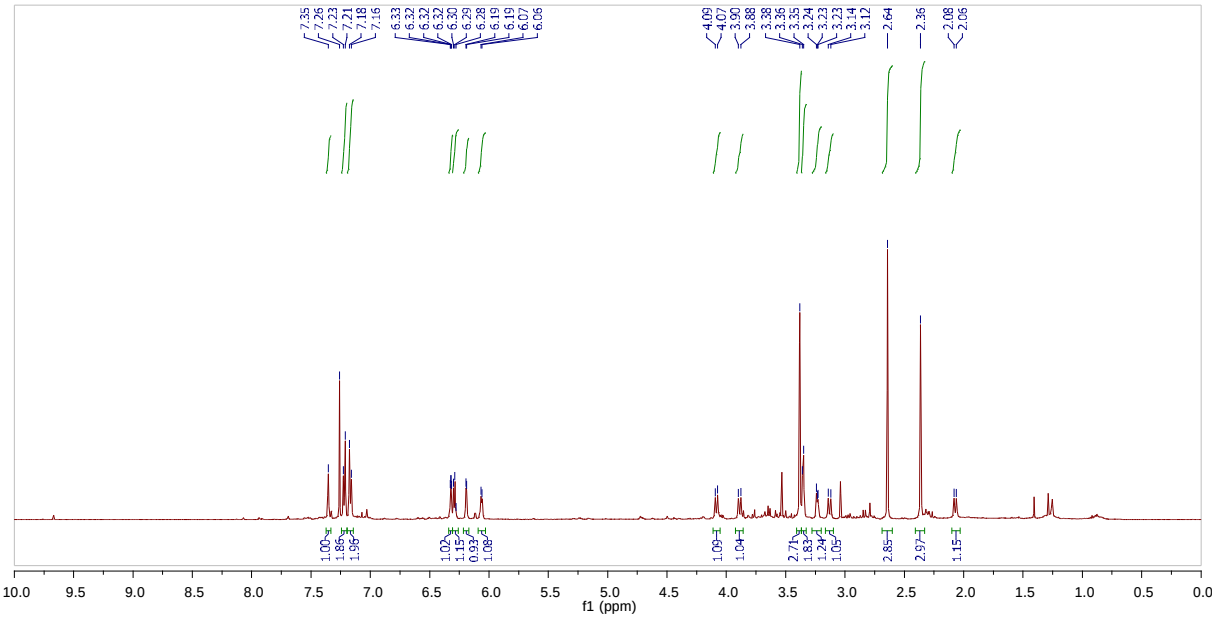
Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	21.957	1221.500	4.130
2	25.831	28357.863	95.870

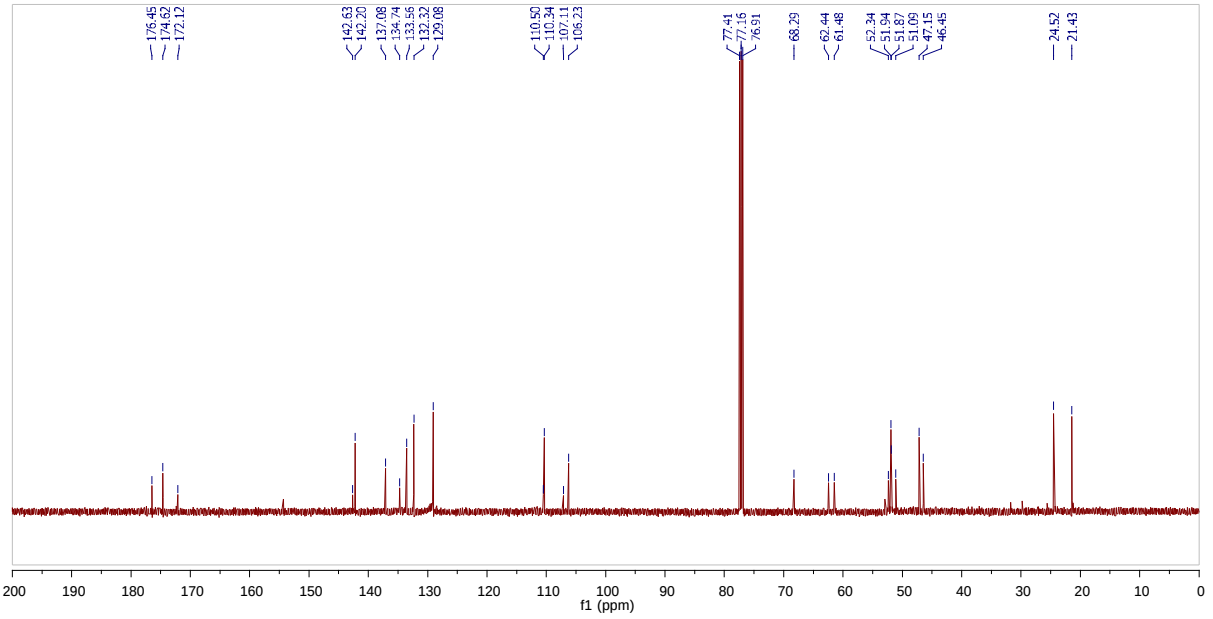


3ia

^{1}H NMR



^{13}C NMR



HPLC traces for **3ia**: racemat top, enantiomer bottom.

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Data file  : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP893 2 P2 COL6 30D 60MIN 2.D
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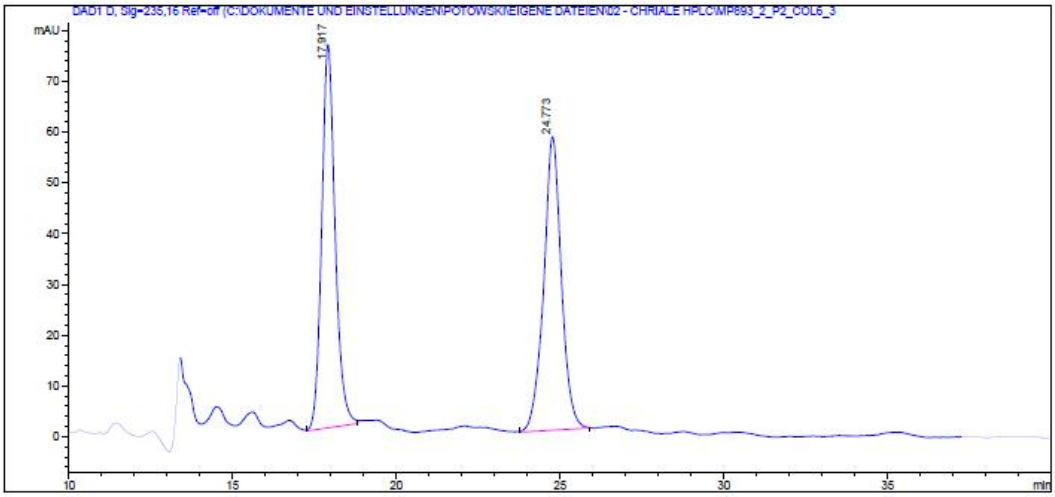
   Acq. Method     :AA_6RUN_30D_60MIN.M          Location   :     Vial 17        Inj. Vol.  :          10 µl
```




```
Signal  1: DAD1 D, Sig=235,16 Ref=off

|Peak|   RT    |    Area    | Area % |
| #  | [min]   |            |        |
|----|---------|------------|--------|
|   1|  17.917 |  2143.848  |  49.723|
|   2|  24.773 |  2167.758  |  50.277|
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```

```
Data file  : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP894 2 P2 COL6 30D 60MIN 2.D
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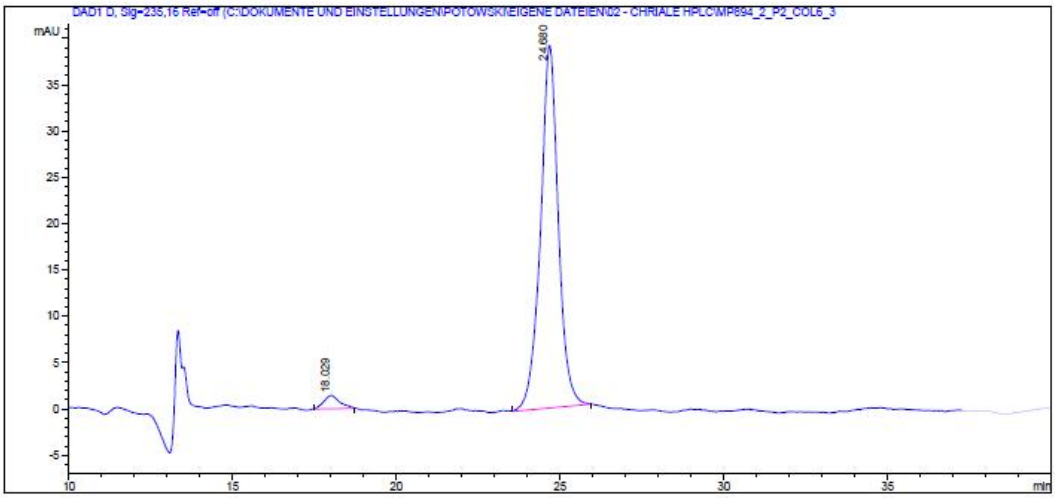
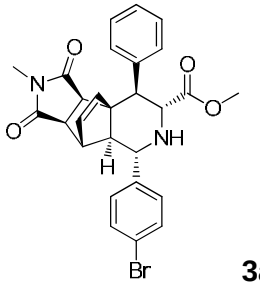
   Acq. Method     :AA_6RUN_30D_60MIN.M          Location   :     Vial 19        Inj. Vol.  :          10 µl
```



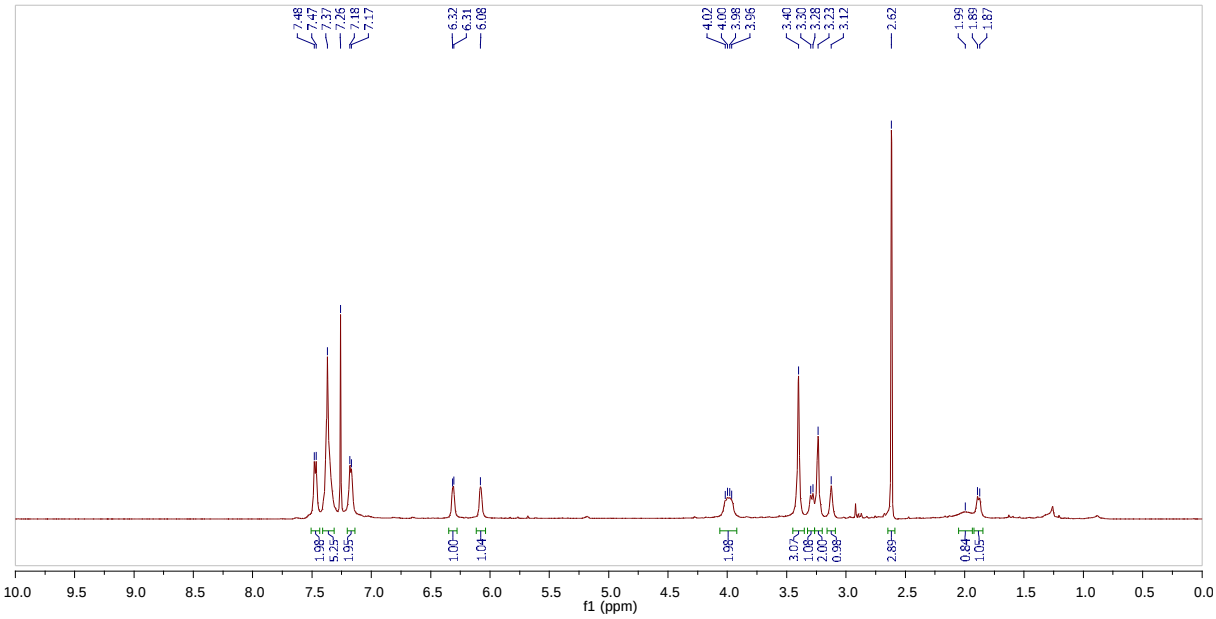

```
Signal  1: DAD1 D, Sig=235,16 Ref=off

|Peak|   RT    |    Area    | Area % |
| #  | [min]   |            |        |
|----|---------|------------|--------|
|   1|  18.029 |    48.808  |   3.190|
|   2|  24.680 |  1481.040  |  96.810|
-----------------------------------
```

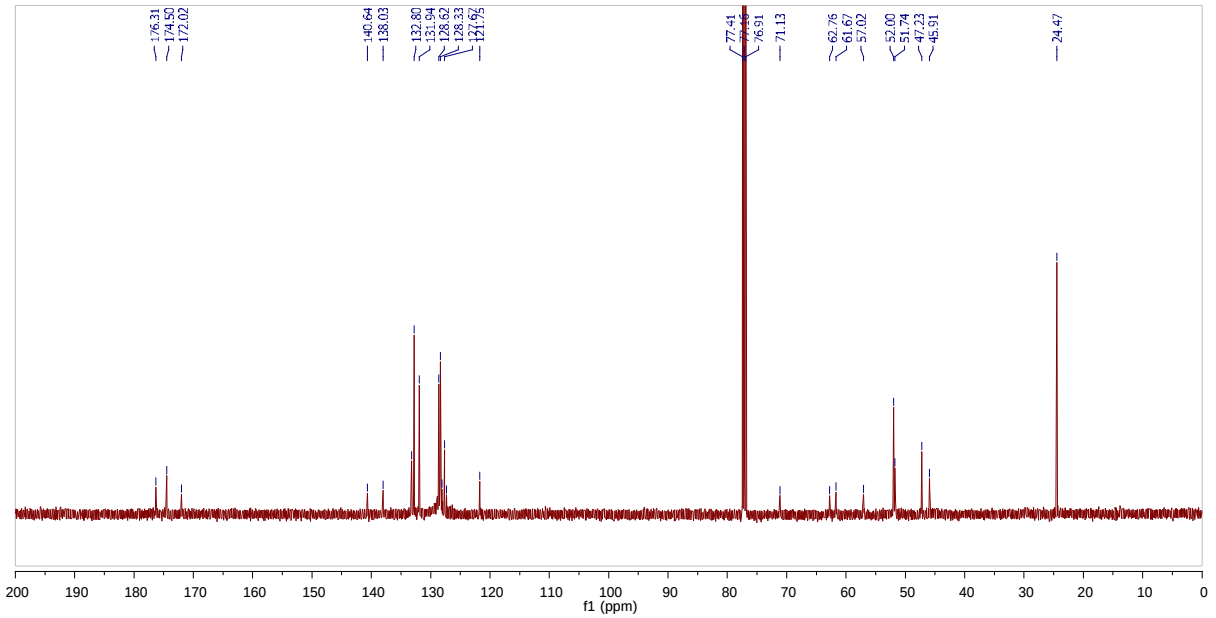


3ab

^{1}H NMR



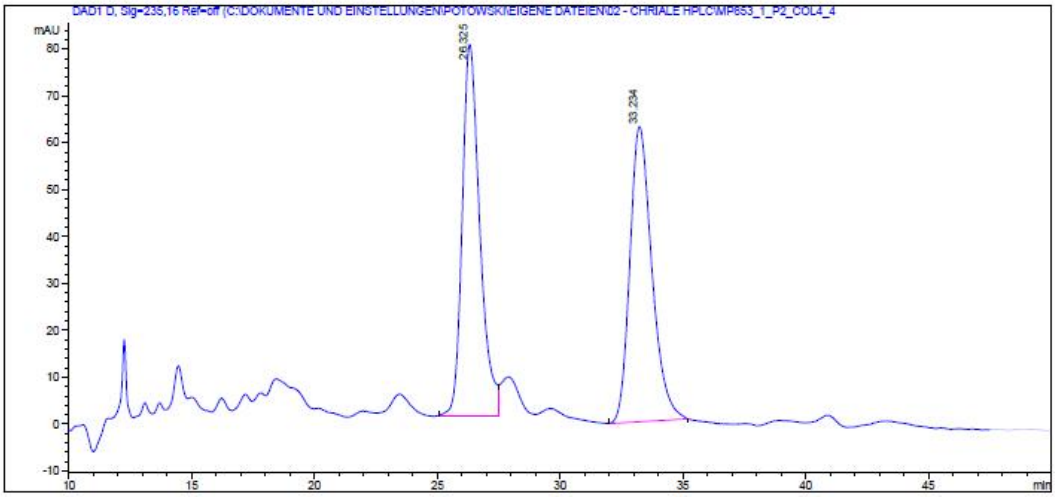
^{13}C NMR



HPLC traces for **3ab**: racemat top, enantiomer bottom.

Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP853 1 P2 COL4 40D 60MIN 1.D

Acq. Method :AA_4RUN_40D.M Location : Vial 11 Inj. Vol. : 20 µl

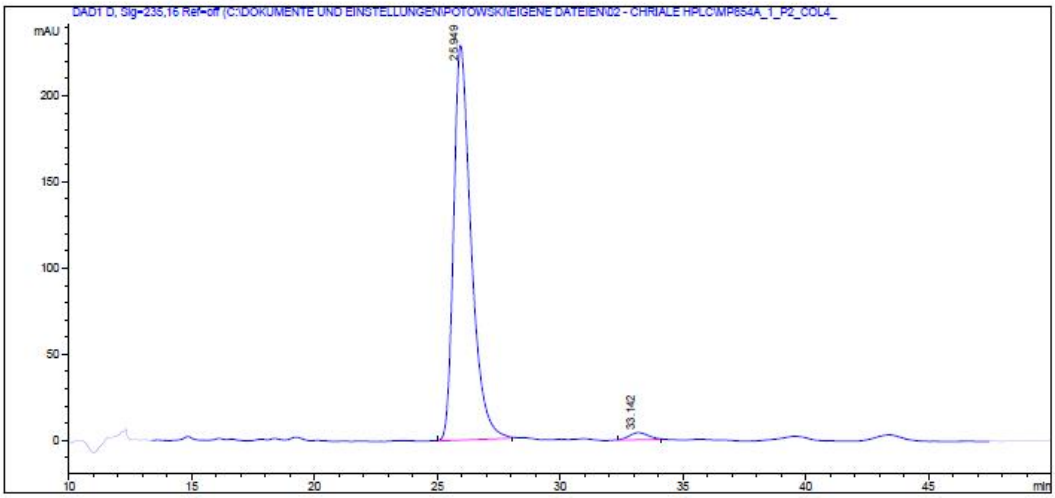


Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	26.325	3945.512	50.102
2	33.234	3929.397	49.898

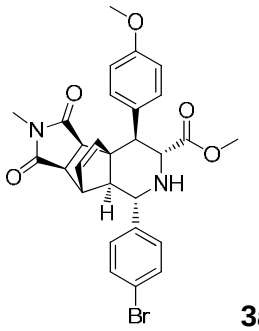
Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP854A 1 P2 COL4 40D 60MIN 1.D

Acq. Method :AA_4RUN_40D.M Location : Vial 13 Inj. Vol. : 20 µl



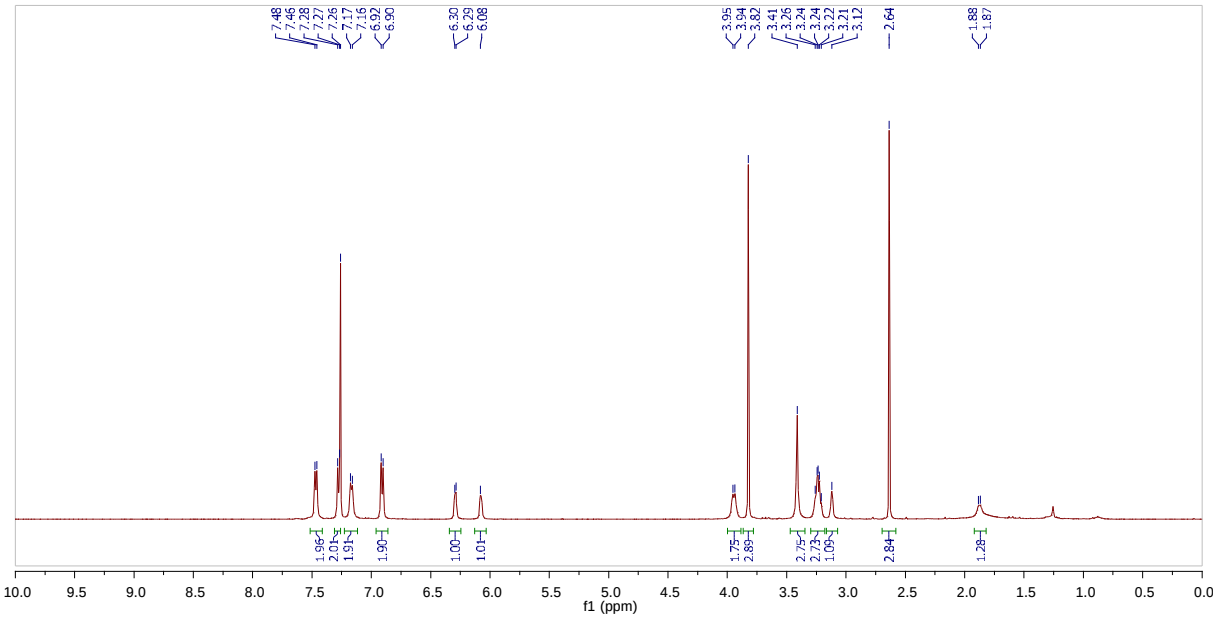
Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	25.949	11317.220	98.066
2	33.142	223.214	1.934

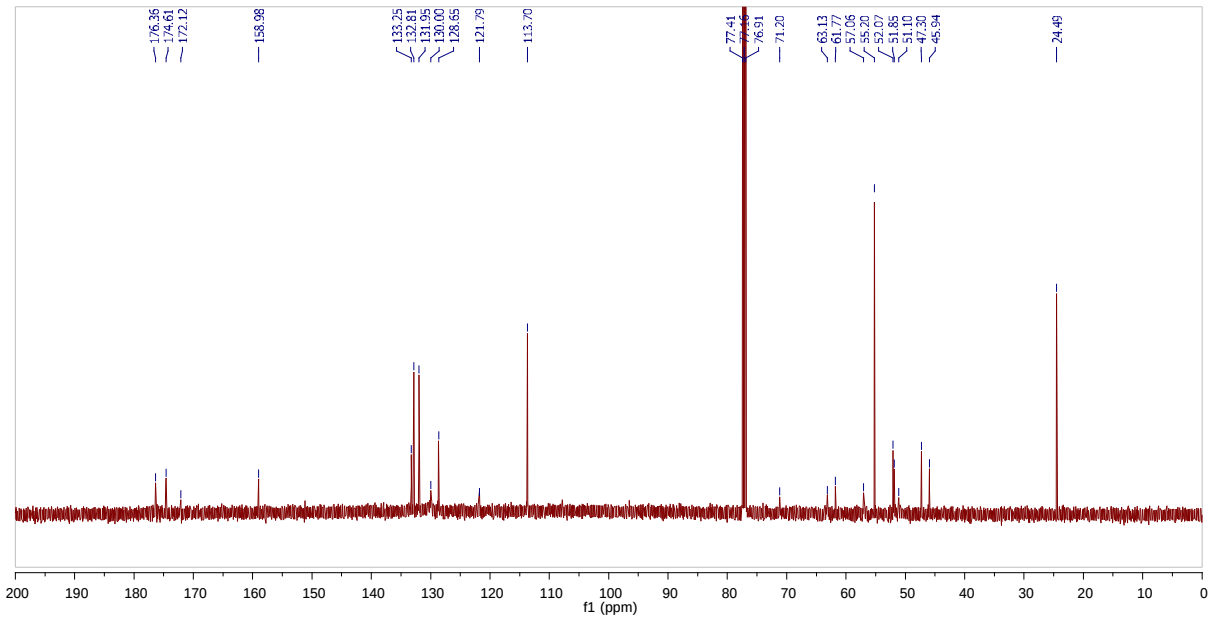


3ac

^{1}H NMR



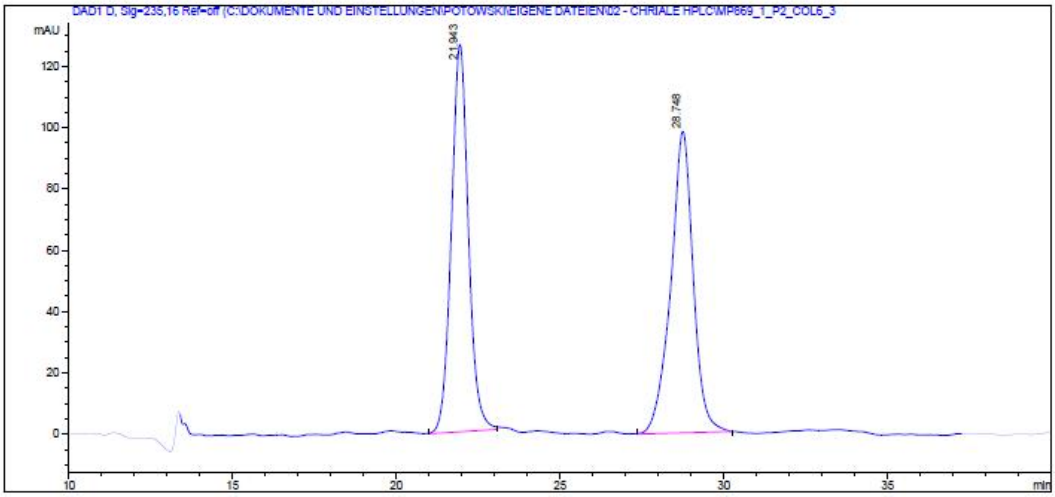
^{13}C NMR



HPLC traces for **3ac**: racemat top, enantiomer bottom.

Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP869 1 P2 COL6 30D 60MIN 1.D

Acq. Method :AA_6RUN_30D_60MIN.M Location : Vial 16 Inj. Vol. : 10 µl

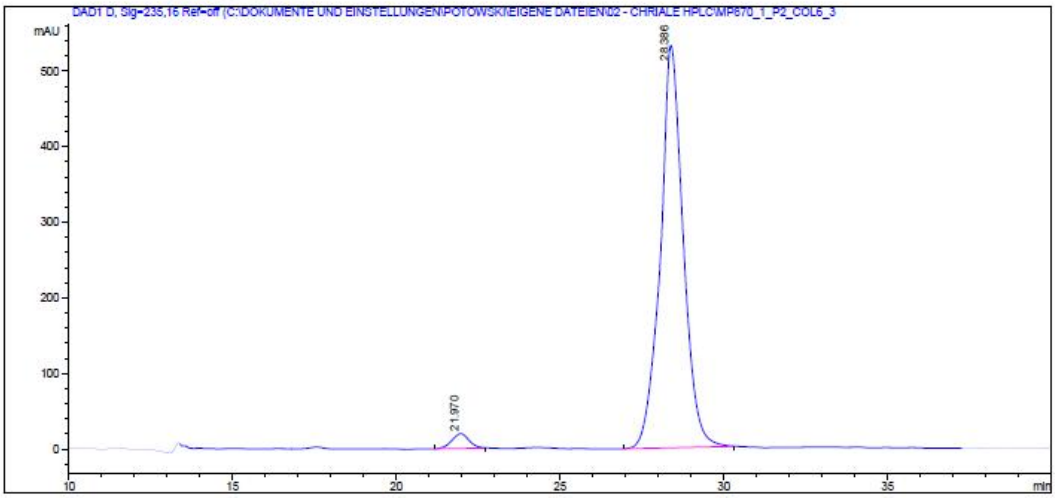


Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	21.943	4560.422	49.363
2	28.748	4678.188	50.637

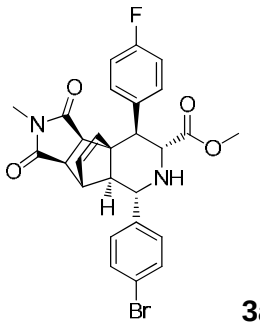
Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP870 1 P2 COL6 30D 60MIN 1.D

Acq. Method :AA_6RUN_30D_60MIN.M Location : Vial 17 Inj. Vol. : 10 µl



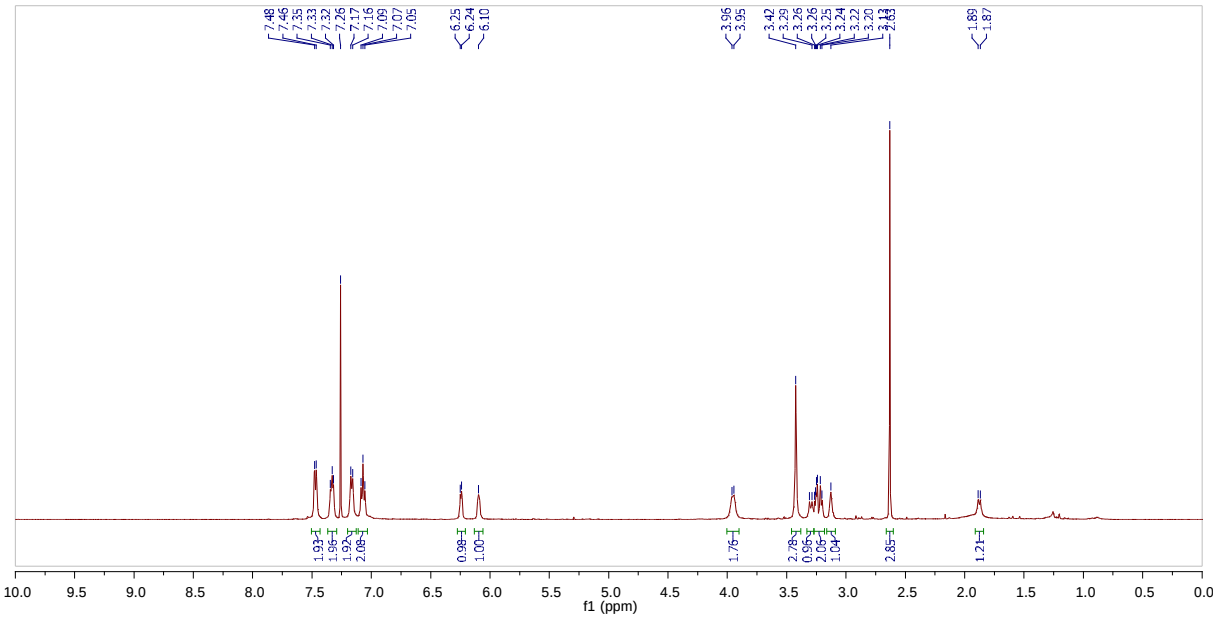
Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	21.970	714.459	2.689
2	28.386	25857.457	97.311

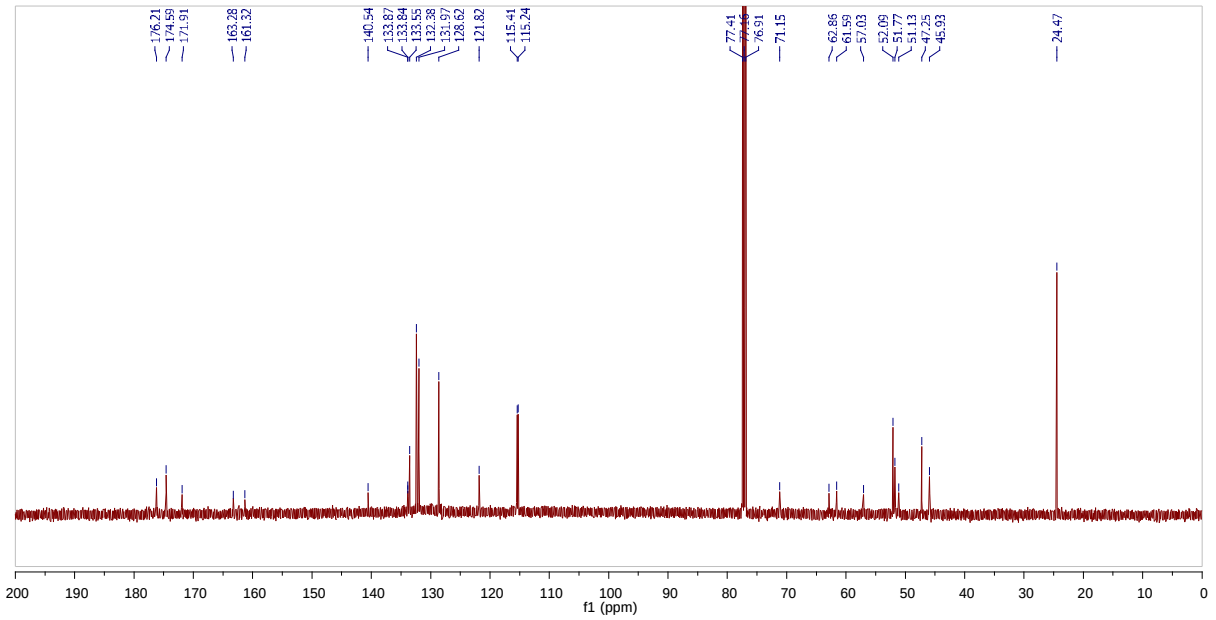


3ad

^{1}H NMR



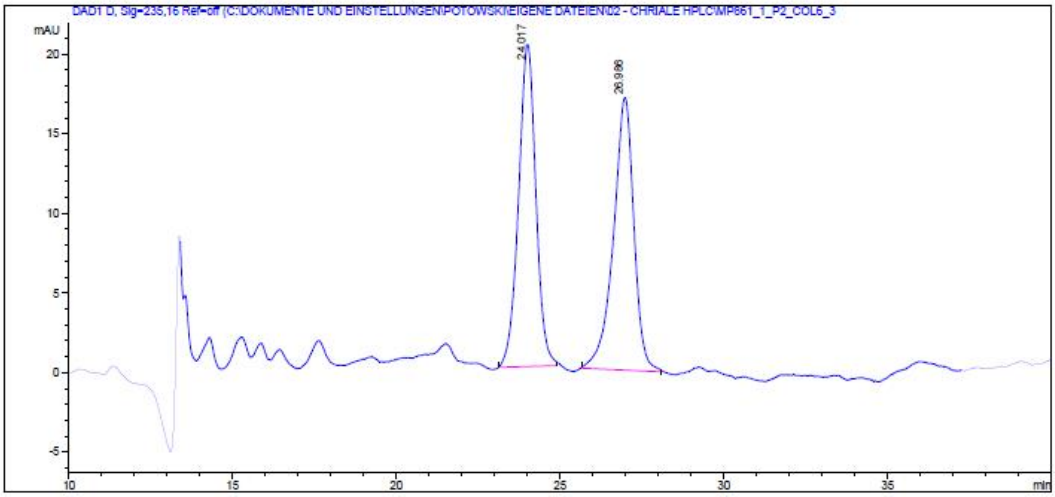
^{13}C NMR



HPLC traces for **3ad**: racemat top, enantiomer bottom.

Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP861 1 P2 COL6 30D 60MIN 1.D

Acq. Method :AA_6RUN_30D_60MIN.M Location : Vial 14 Inj. Vol. : 10 µl

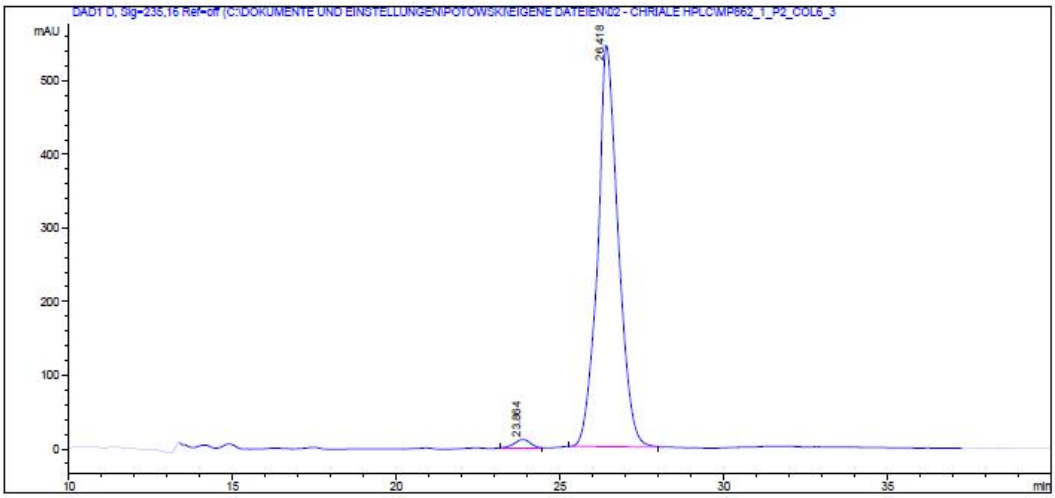


Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	24.017	744.541	49.984
2	26.986	745.011	50.016

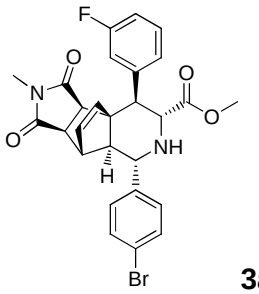
Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP862 1 P2 COL6 30D 60MIN 1.D

Acq. Method :AA_6RUN_30D_60MIN.M Location : Vial 15 Inj. Vol. : 10 µl



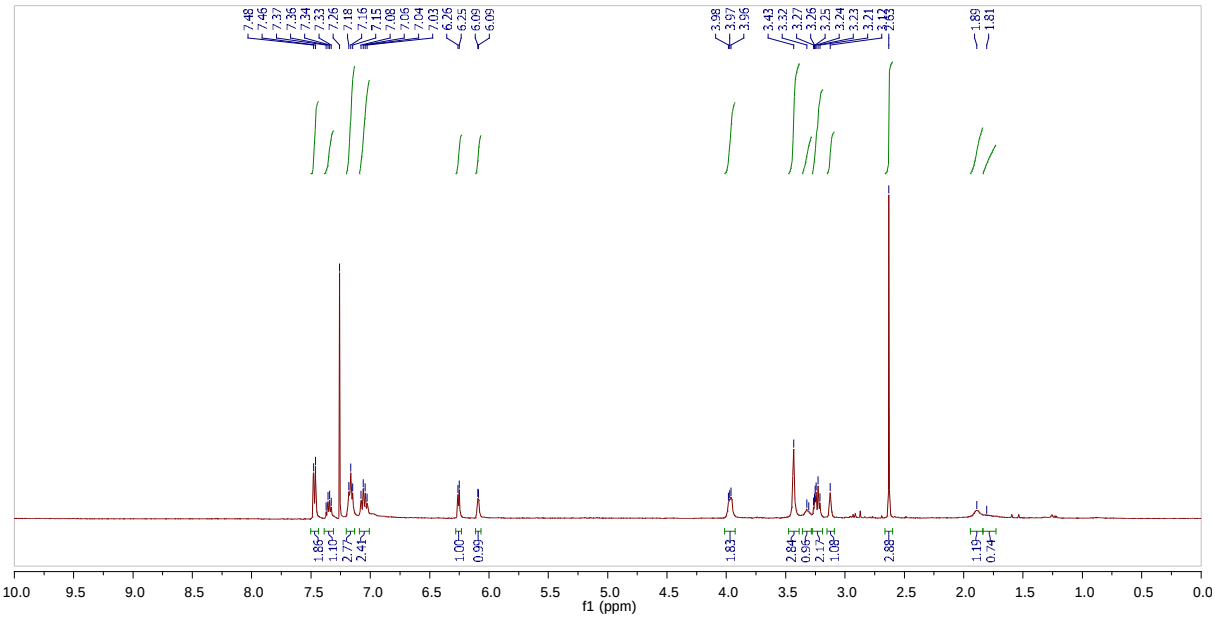
Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	23.864	412.832	1.704
2	26.418	23809.705	98.296

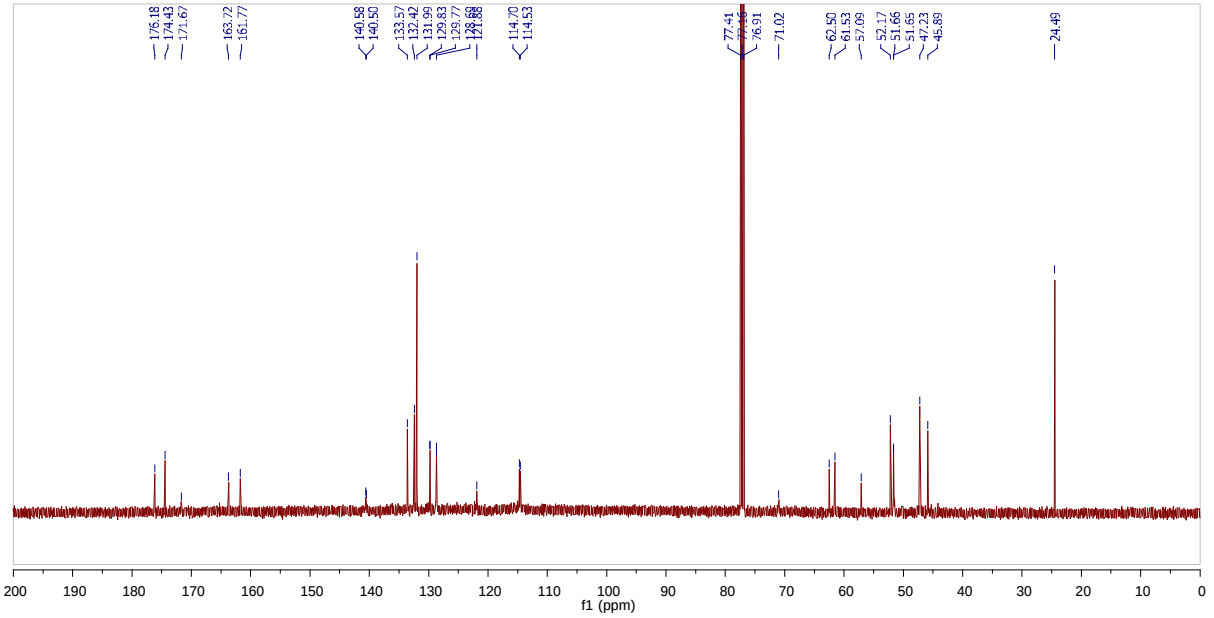


3ae

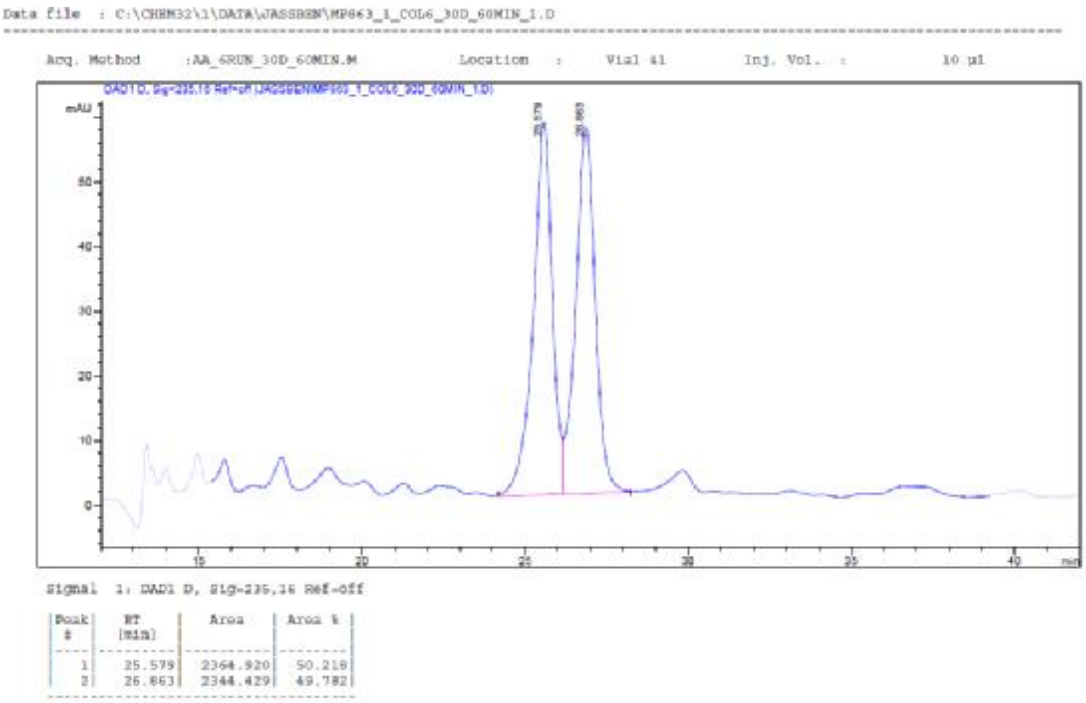
^{1}H NMR

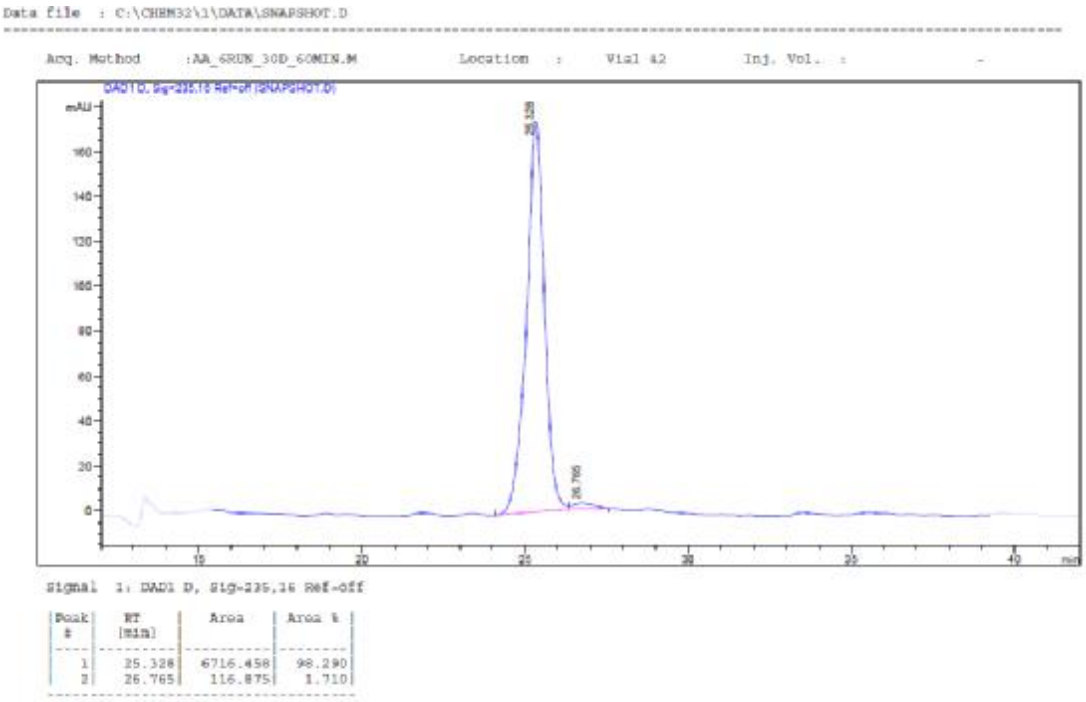


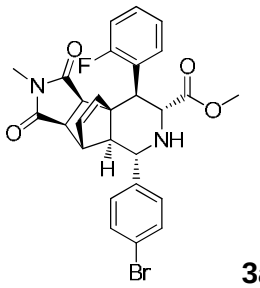
^{13}C NMR



HPLC traces for **3ae**: racemat top, enantiomer bottom.

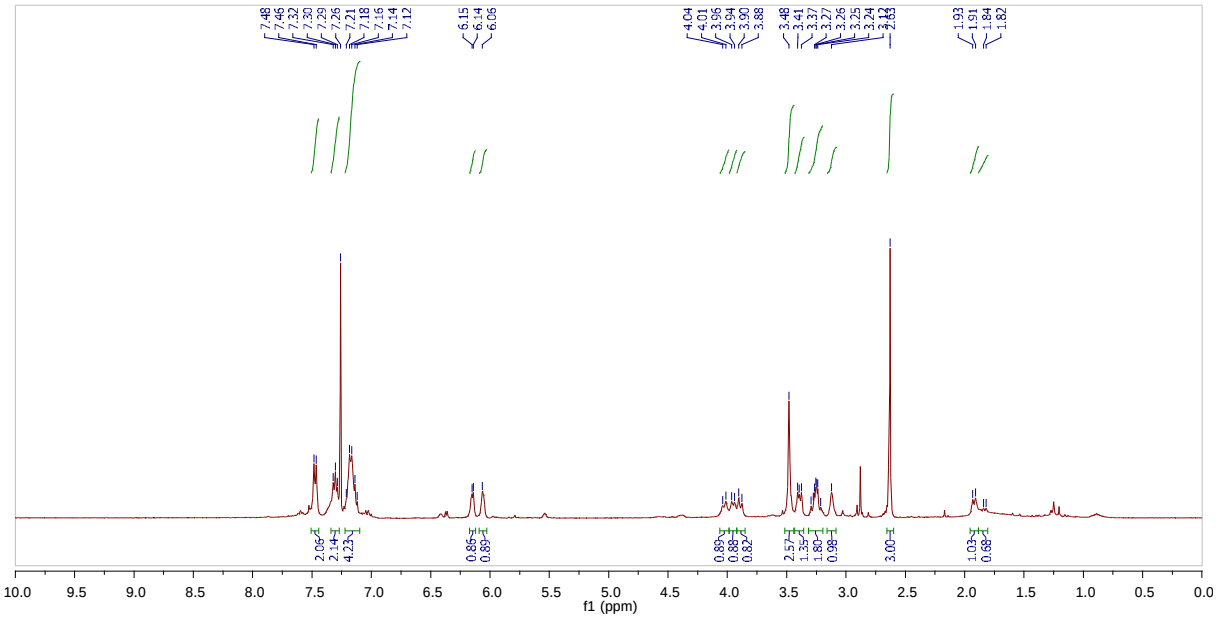




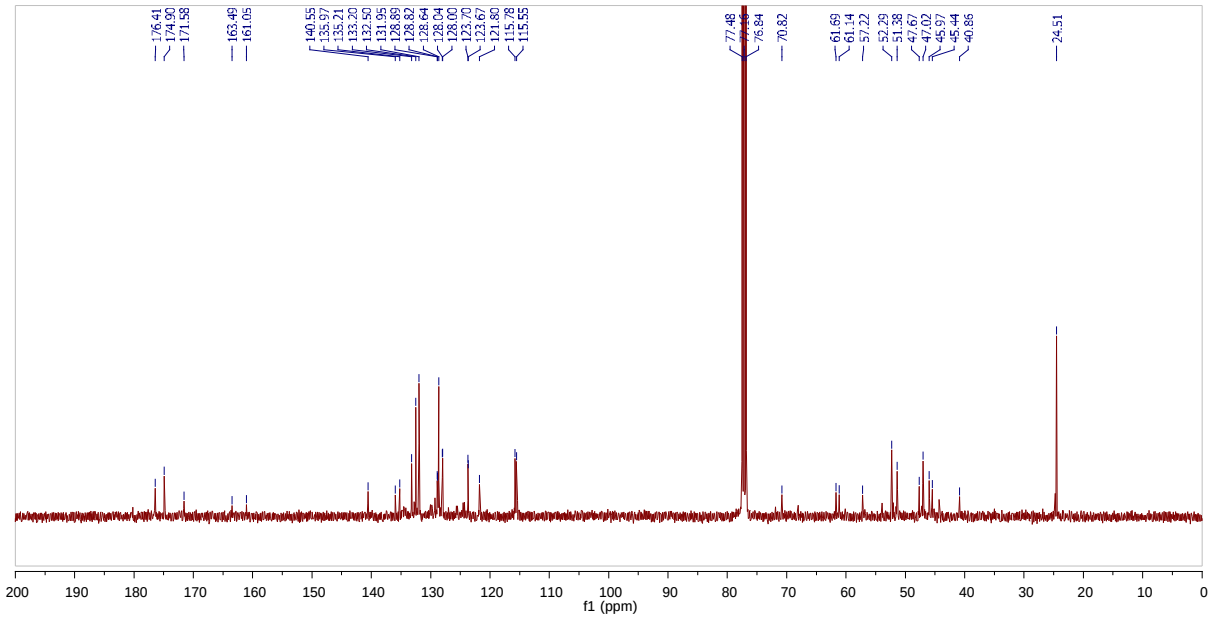


3af

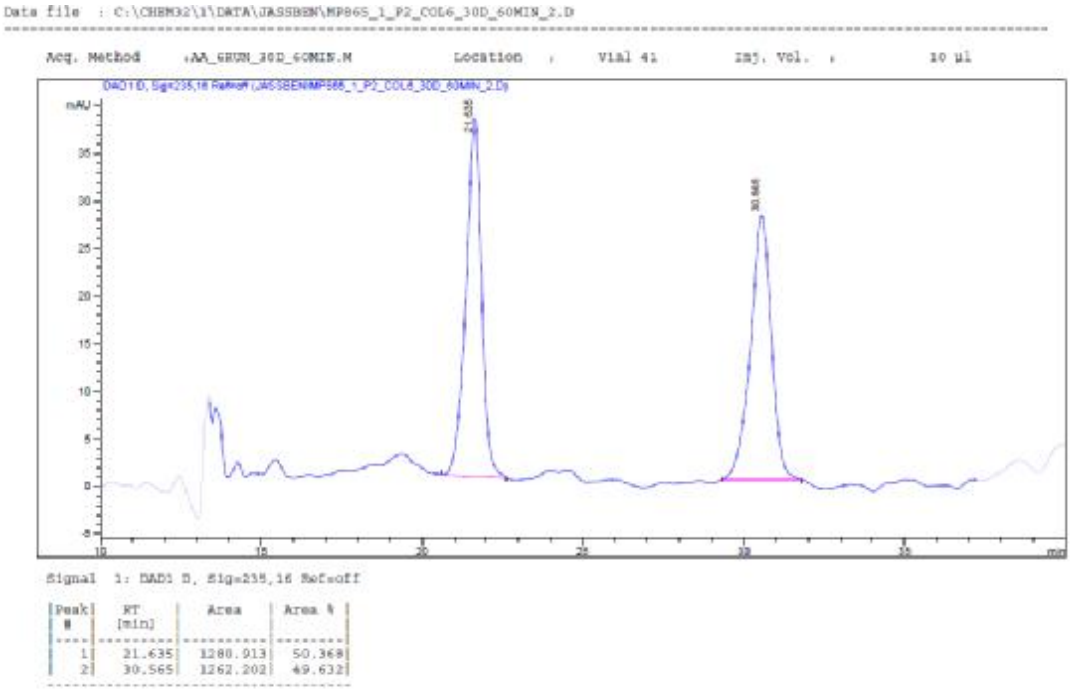
^{1}H NMR

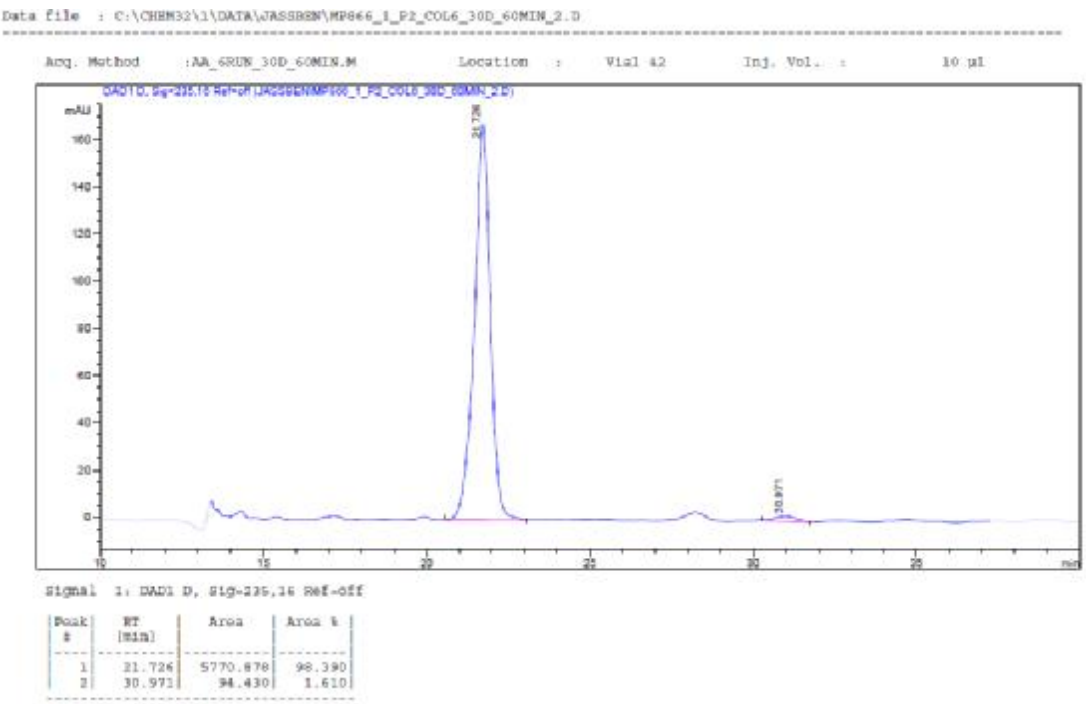


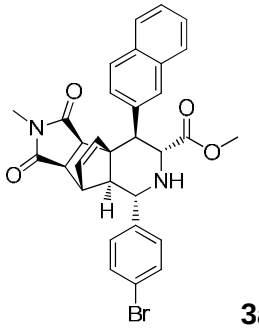
^{13}C NMR



HPLC traces for **3af**: racemat top, enantiomer bottom.

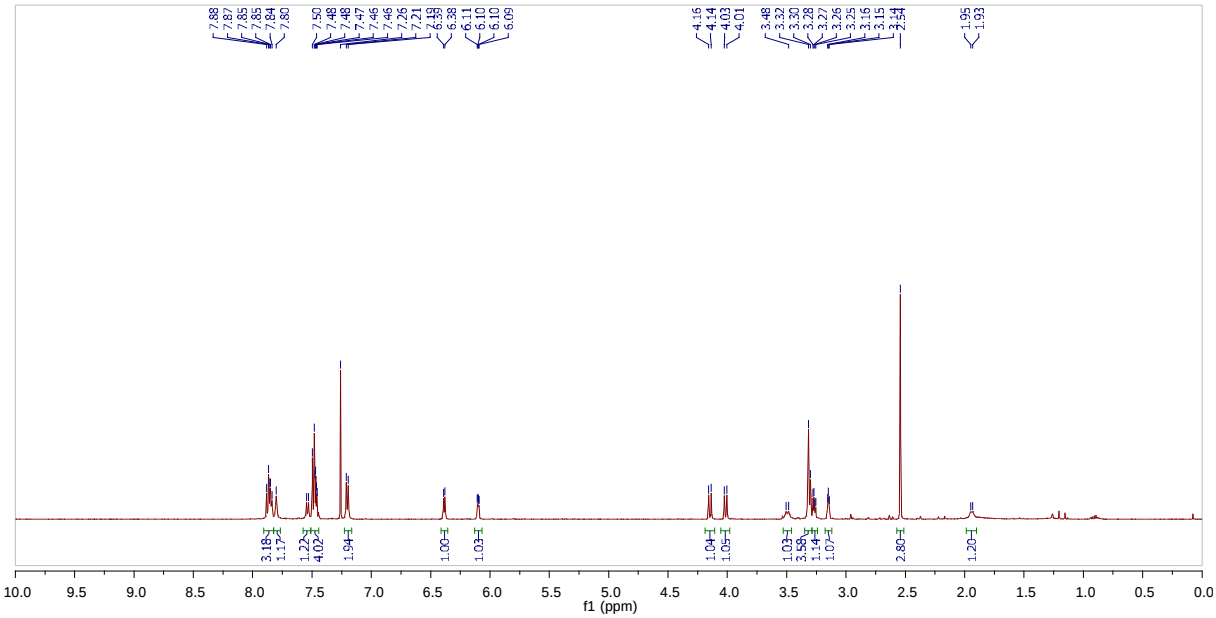




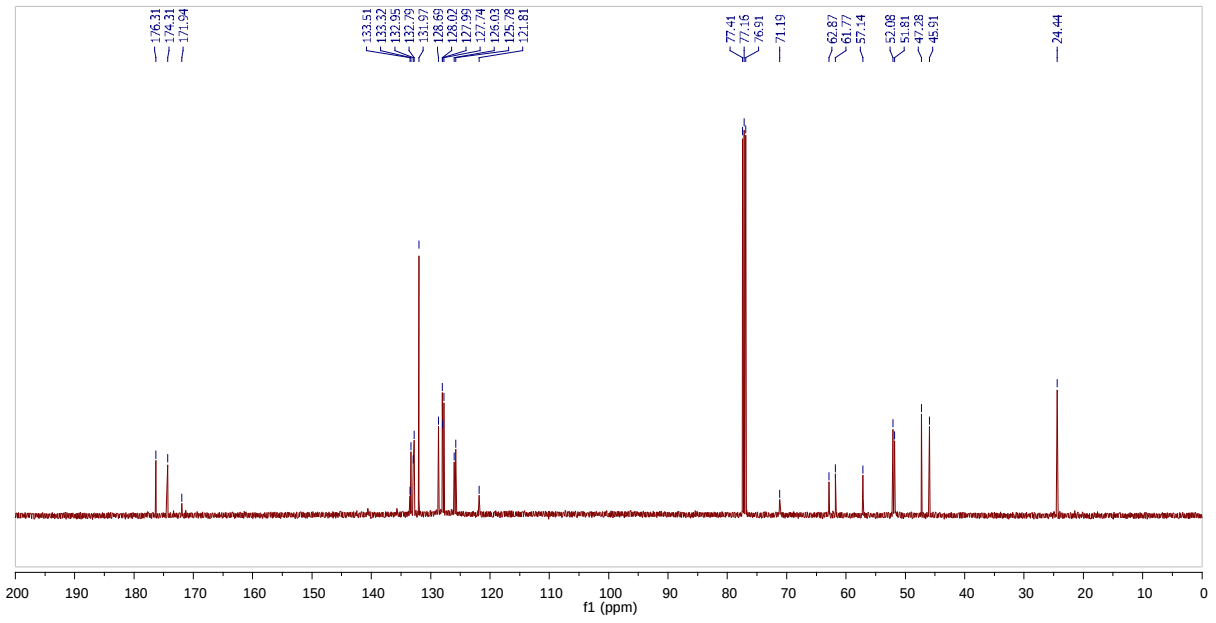


3ag

^{1}H NMR



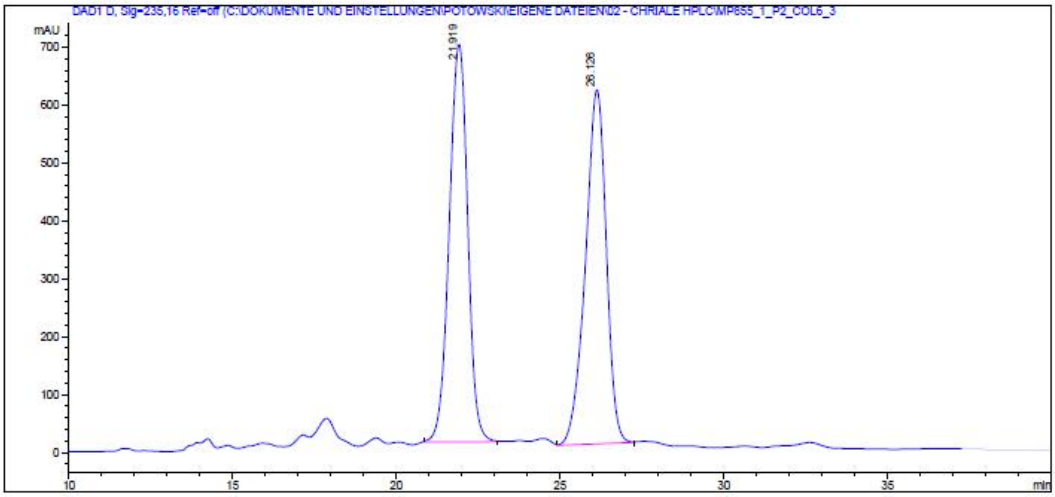
^{13}C NMR



HPLC traces for **3ag**: racemat top, enantiomer bottom.

Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP855 1 P2 COL6 30D 60MIN 1.D

Acq. Method :AA_6RUN_30D_60MIN.M Location : Vial 21 Inj. Vol. : 10 µl

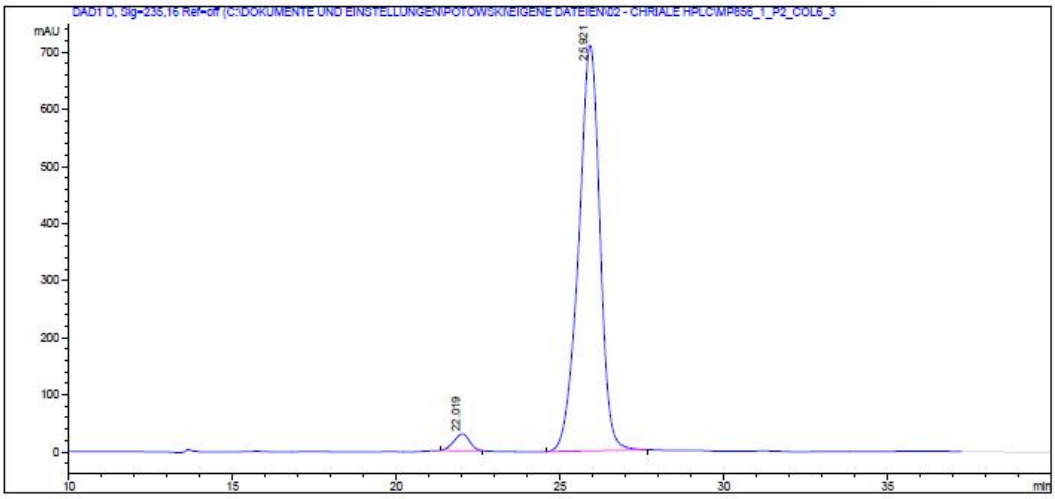


Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	21.919	26933.301	49.924
2	26.126	27014.914	50.076

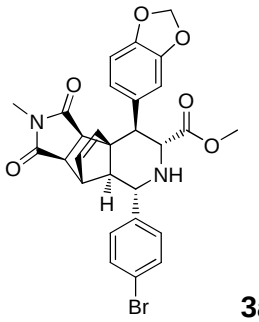
Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP856 1 P2 COL6 30D 60MIN 2.D

Acq. Method :AA_6RUN_30D_60MIN.M Location : Vial 22 Inj. Vol. : 10 µl



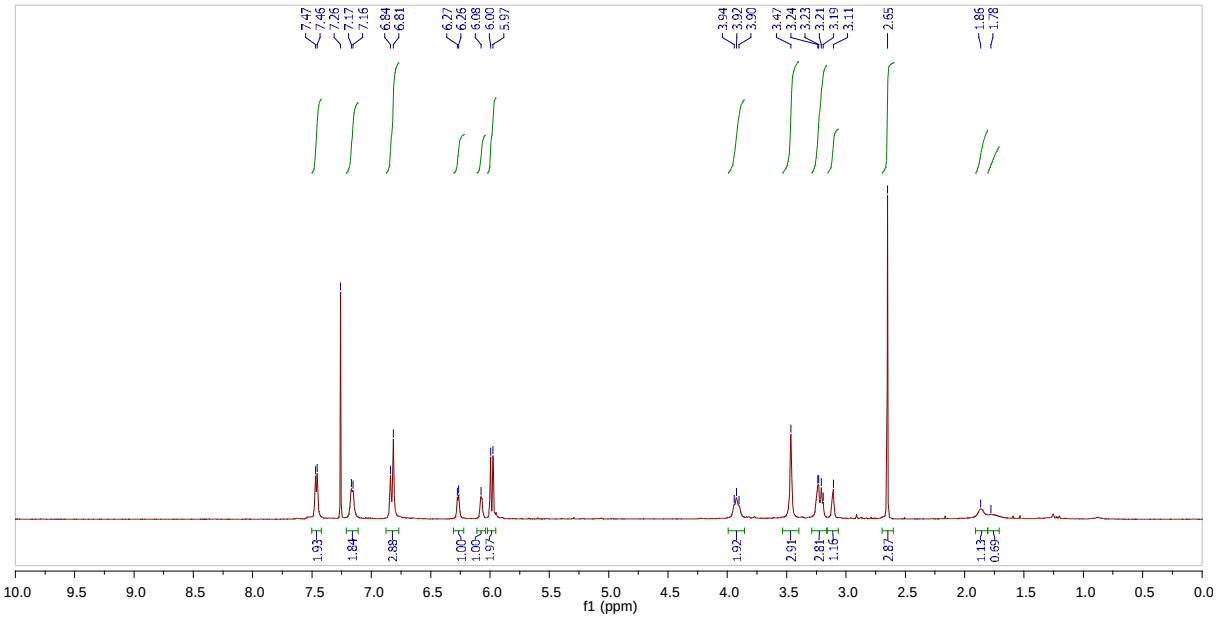
Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	22.019	986.279	2.986
2	25.921	32043.391	97.014

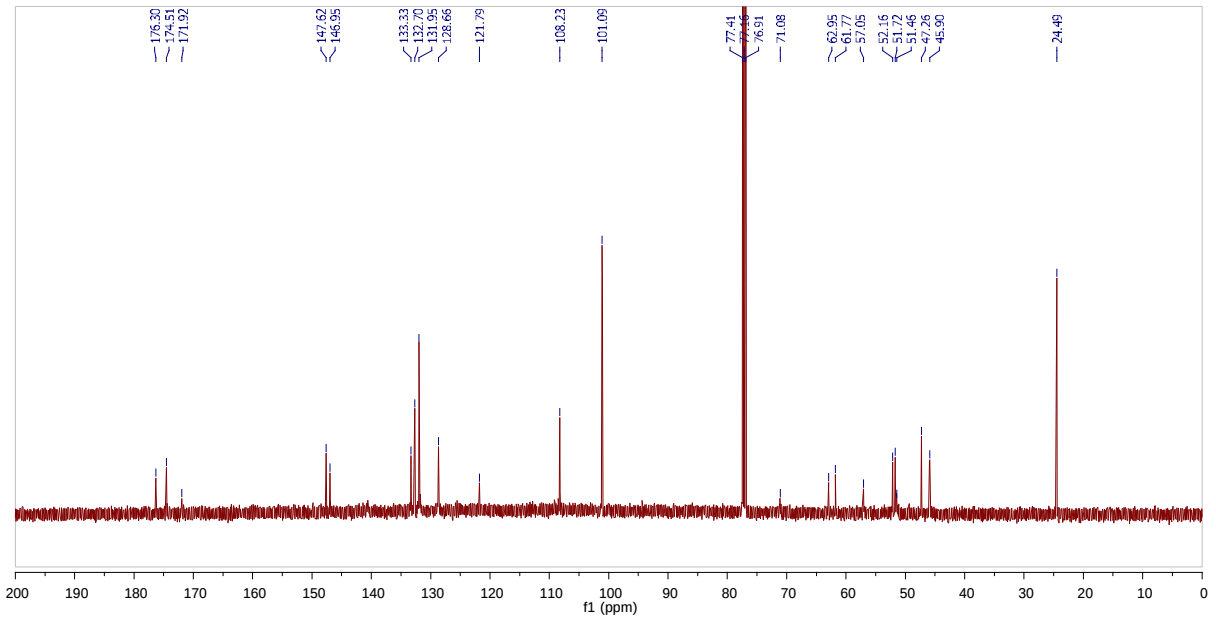


3ah

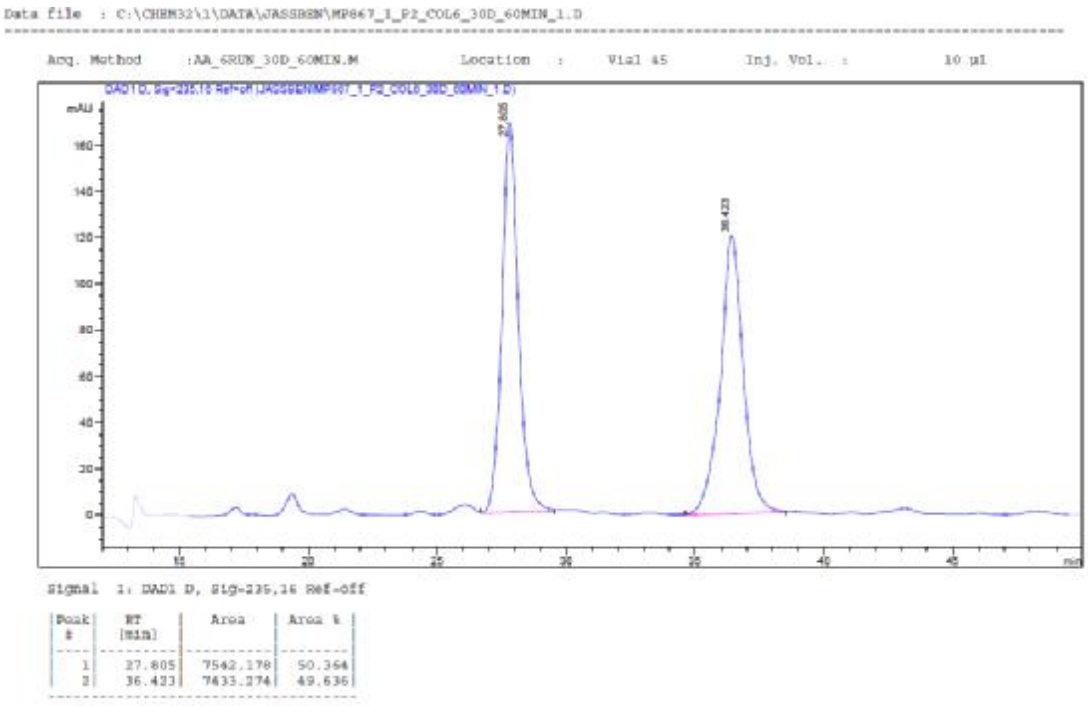
^{1}H NMR



^{13}C NMR

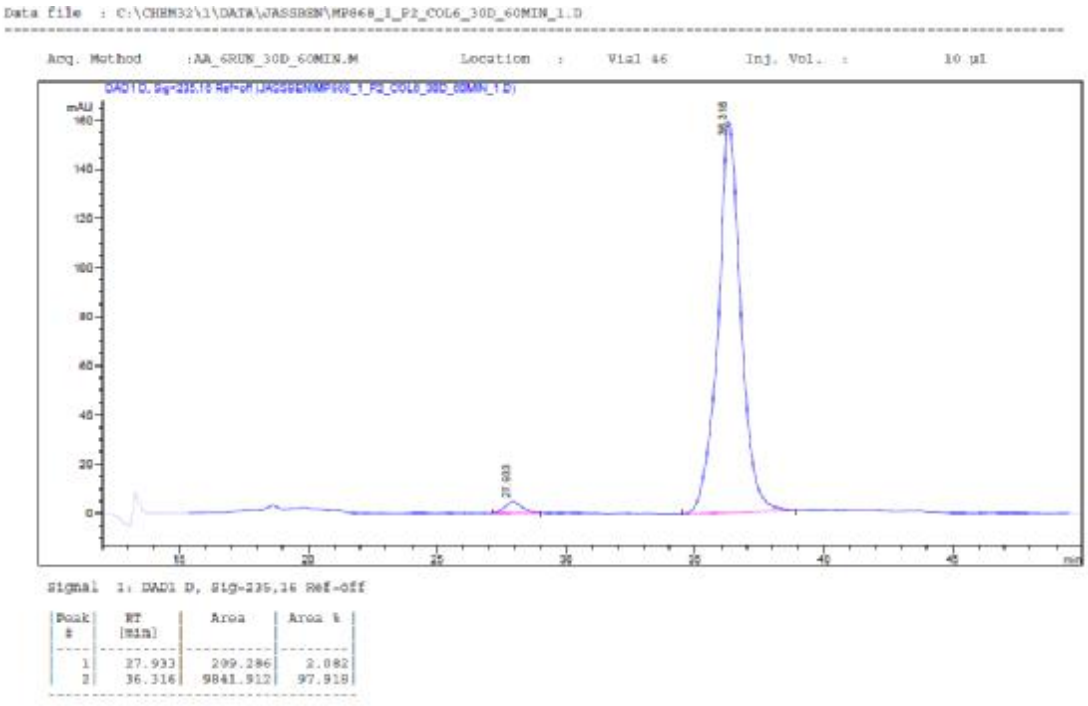


HPLC traces for **3ah**: racemat top, enantiomer bottom.



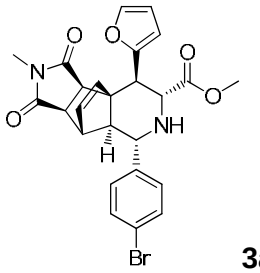
Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	27.805	7542.178	50.364
2	36.423	7433.274	49.636



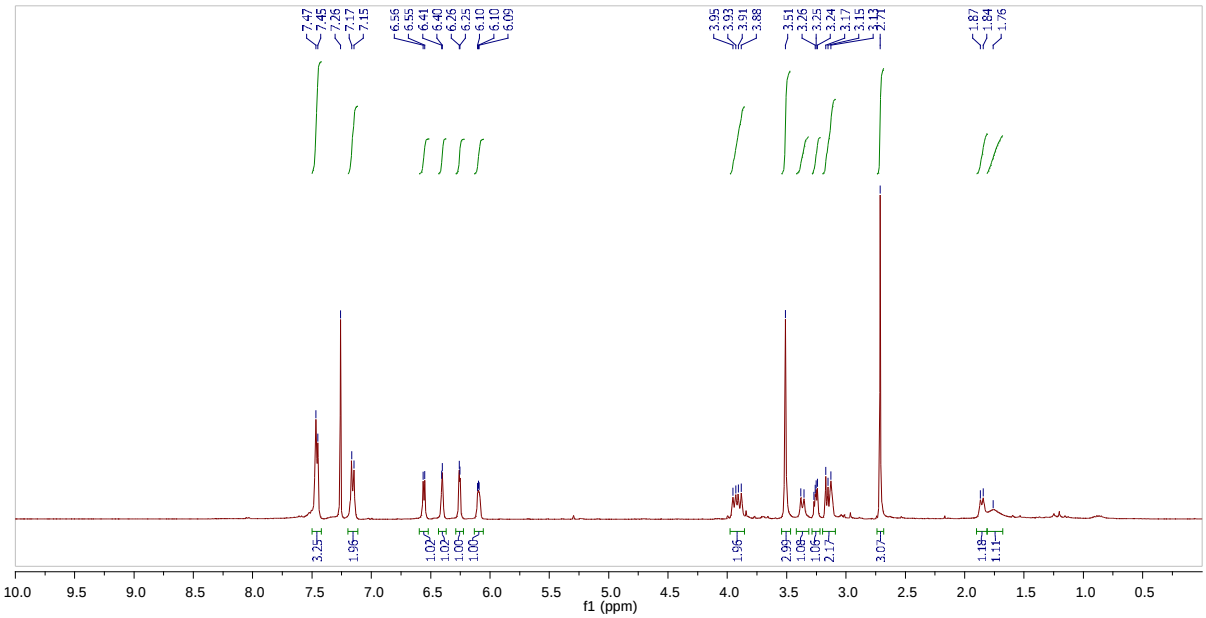
Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	27.933	209.286	2.082
2	36.316	9841.912	97.918

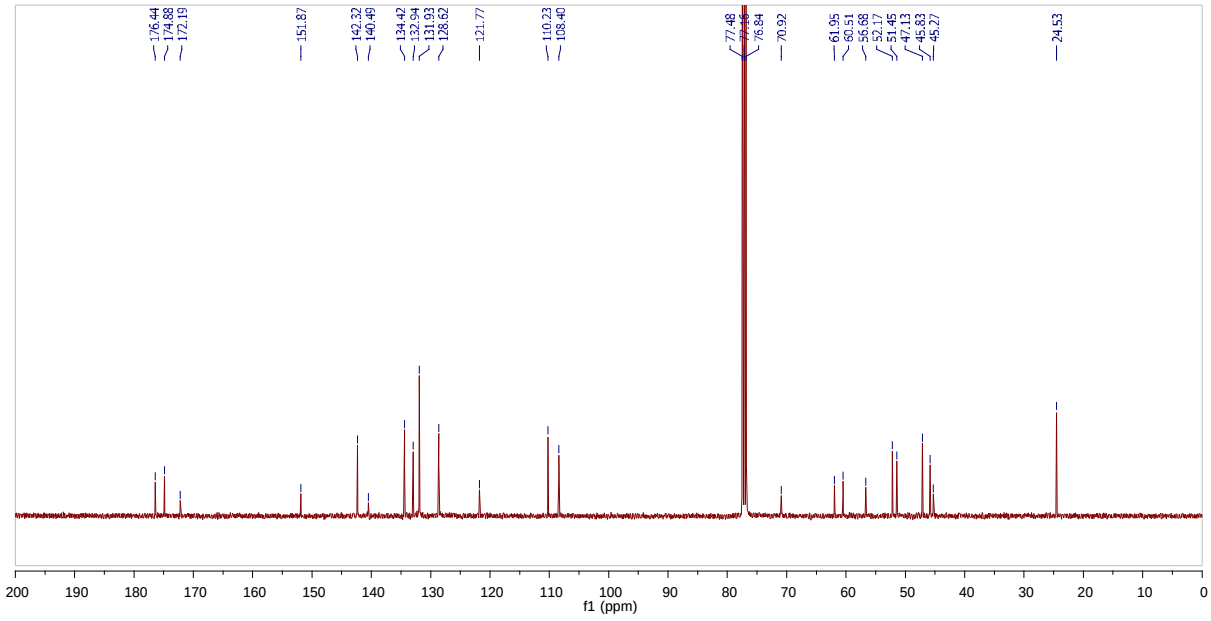


3ai

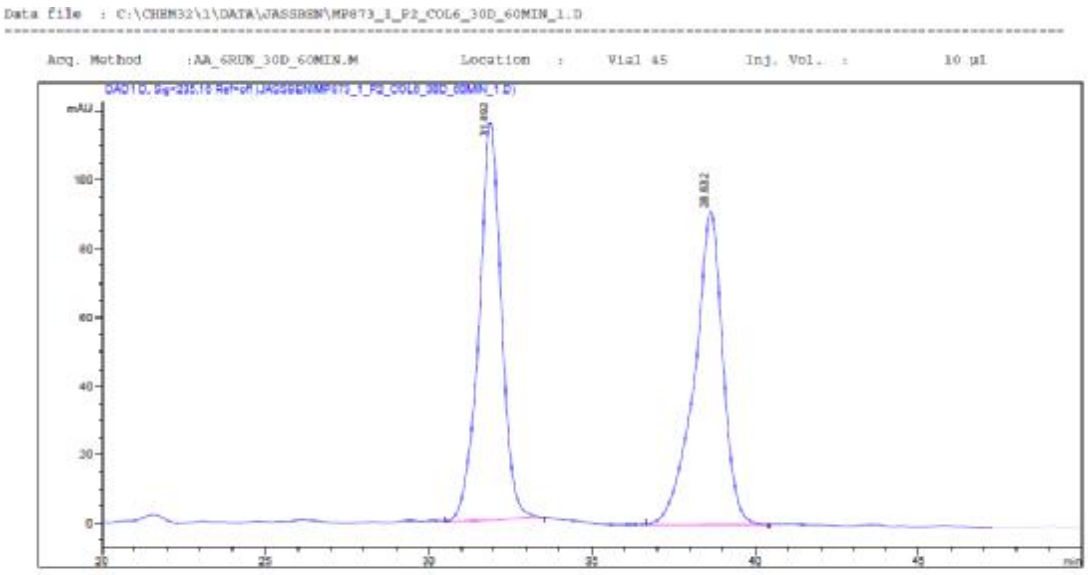
^{1}H NMR



^{13}C NMR

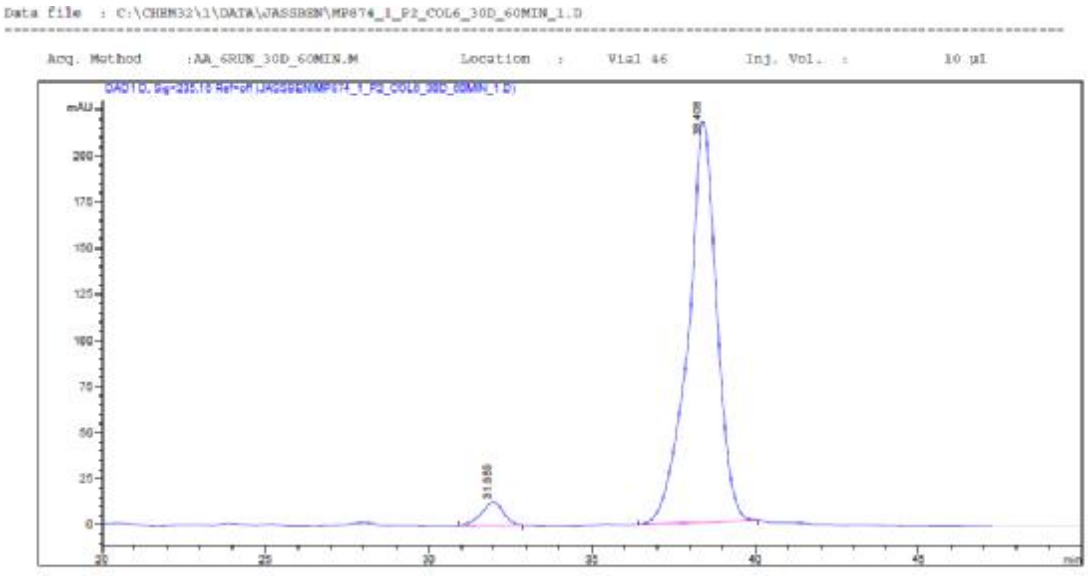


HPLC traces for **3ai**: racemat top, enantiomer bottom.



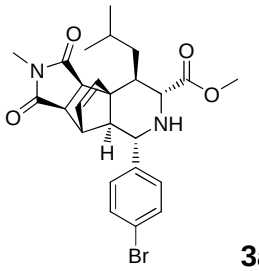
Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	31.892	5550.760	49.959
2	38.632	5559.787	50.041



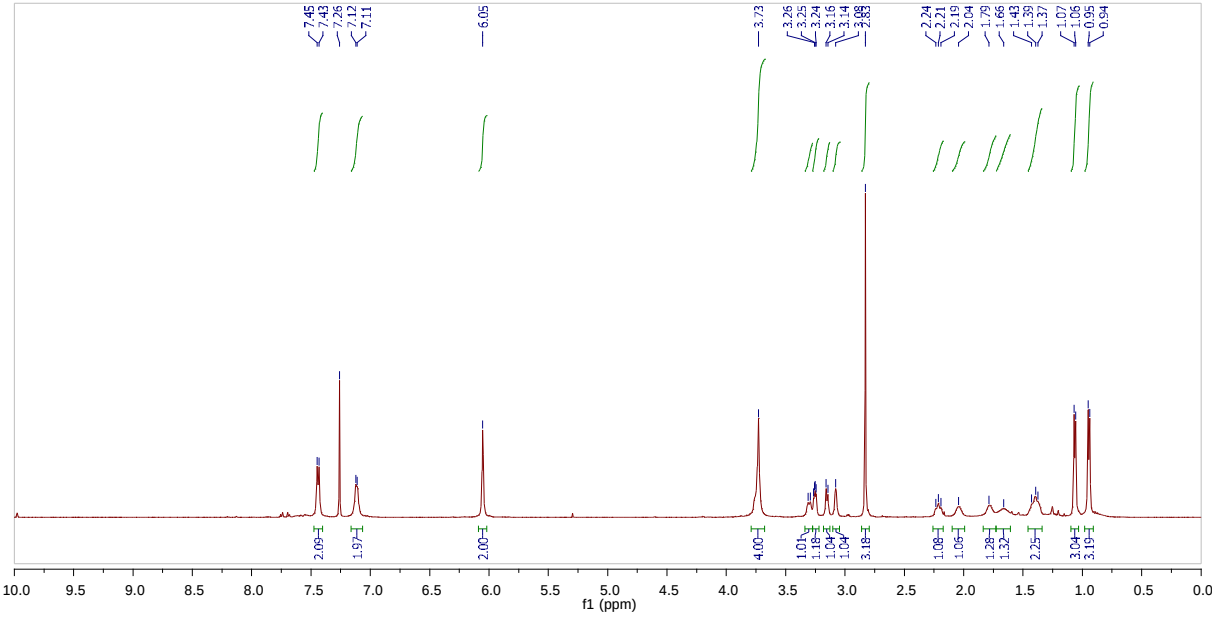
Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	31.989	575.617	4.170
2	38.408	13227.676	95.830

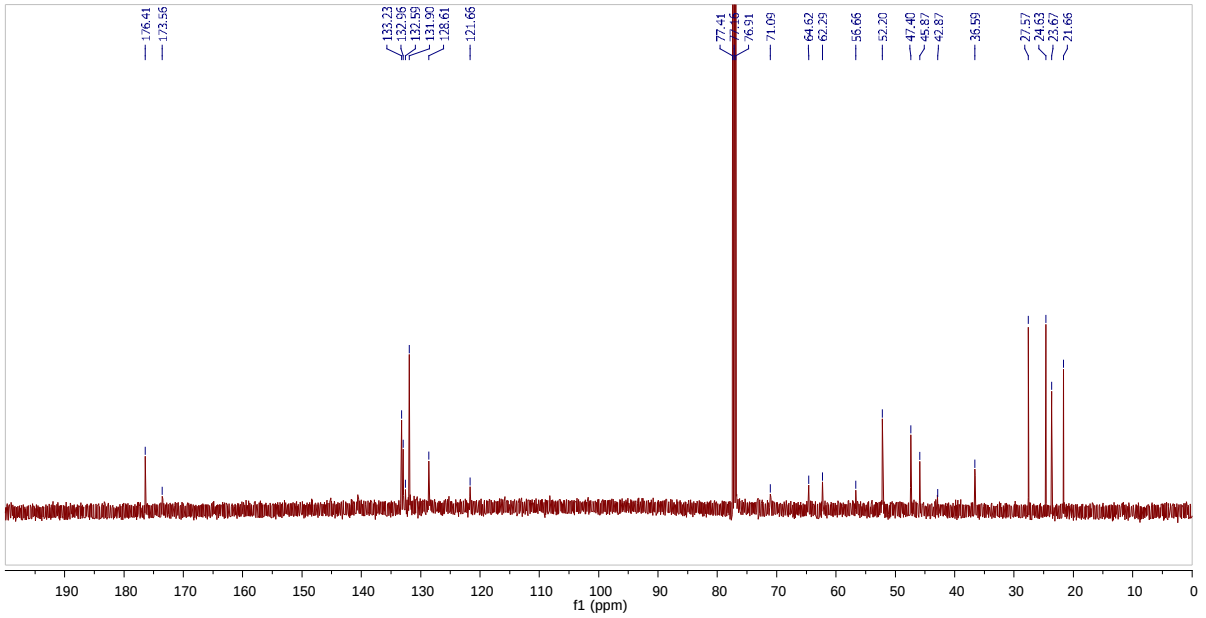


3aj

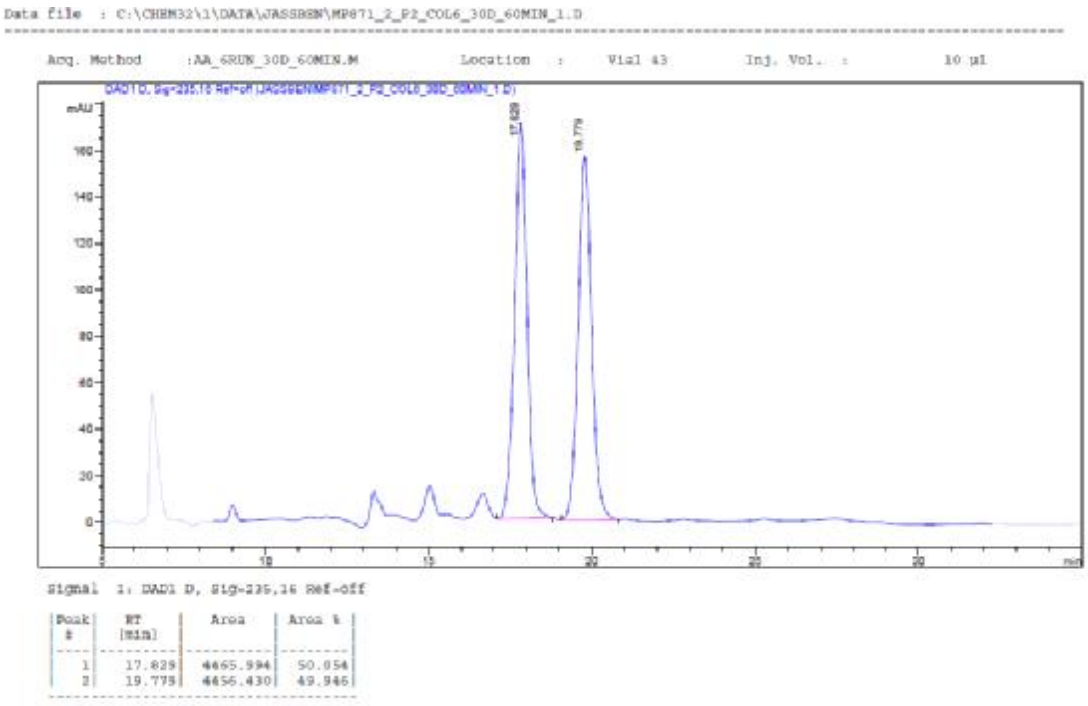
^{1}H NMR



^{13}C NMR

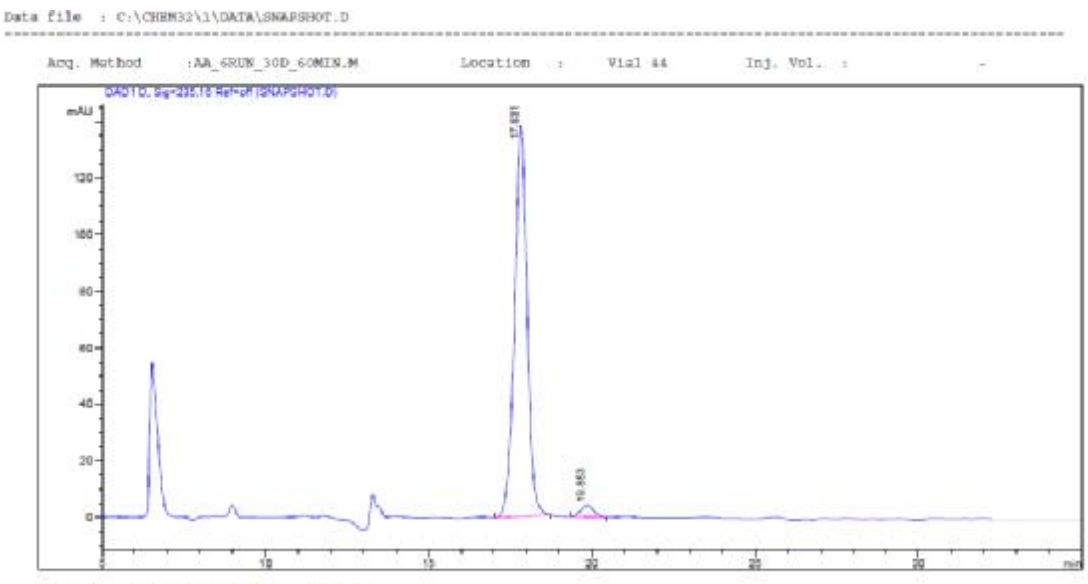


HPLC traces for **3aj**: racemat top, enantiomer bottom.



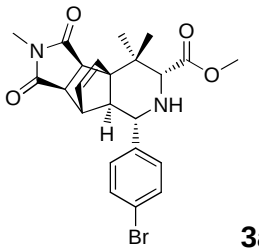
Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	17.829	4665.994	50.054
2	19.779	4656.430	49.946



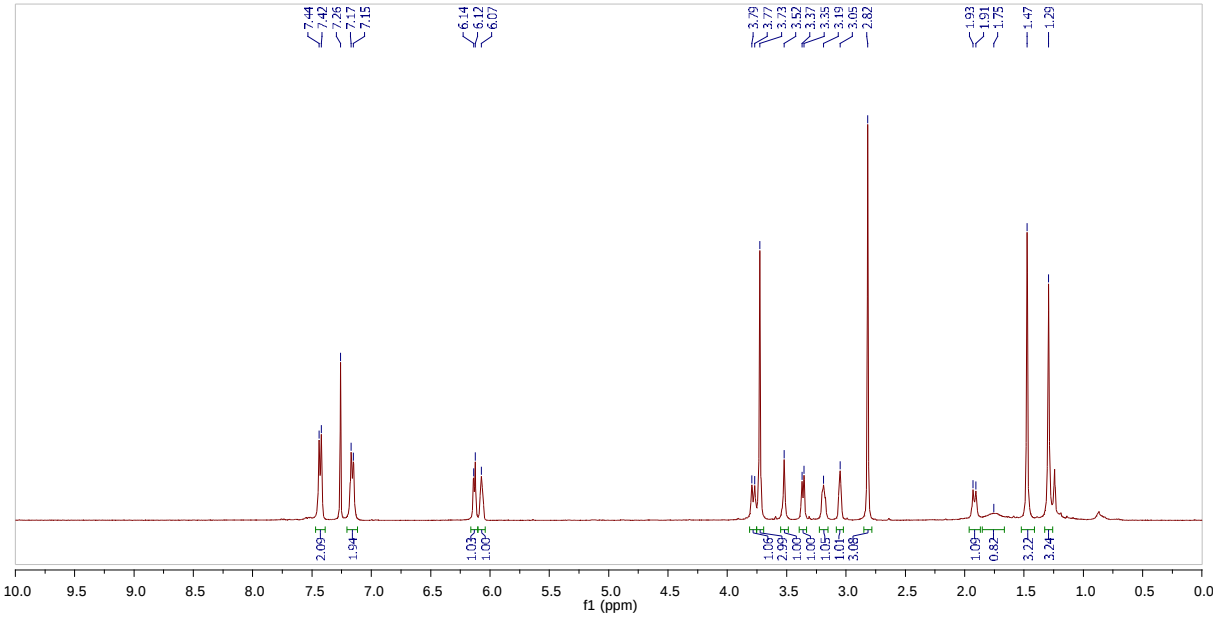
Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	17.831	3664.838	97.027
2	19.853	112.388	2.973

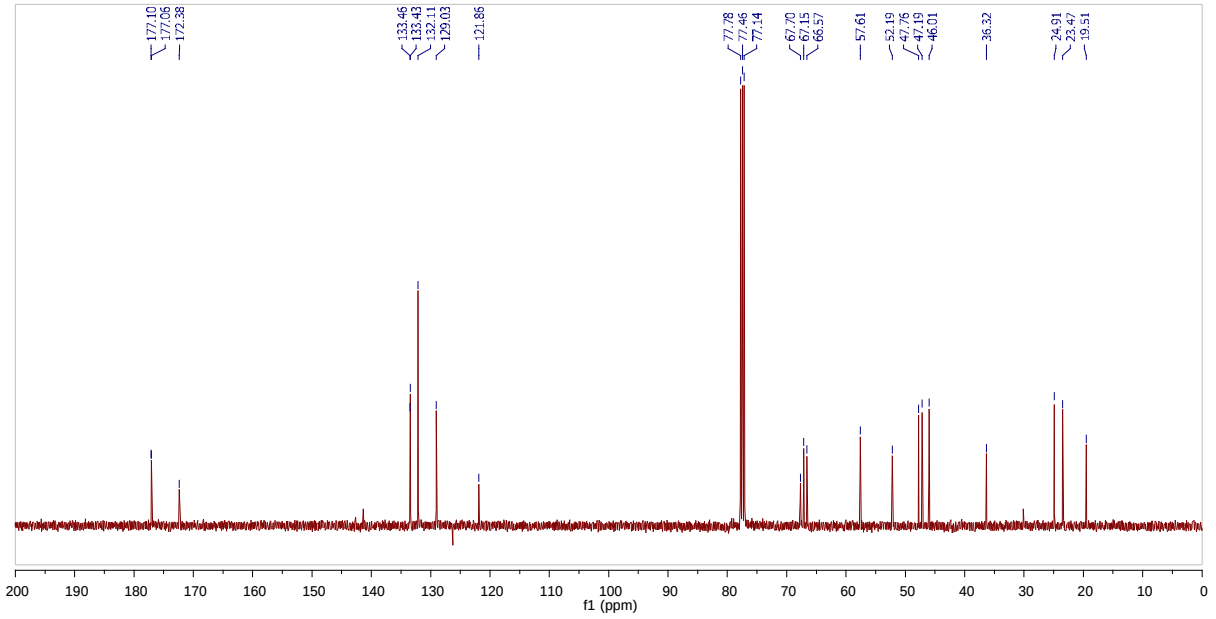


3ak

^{1}H NMR



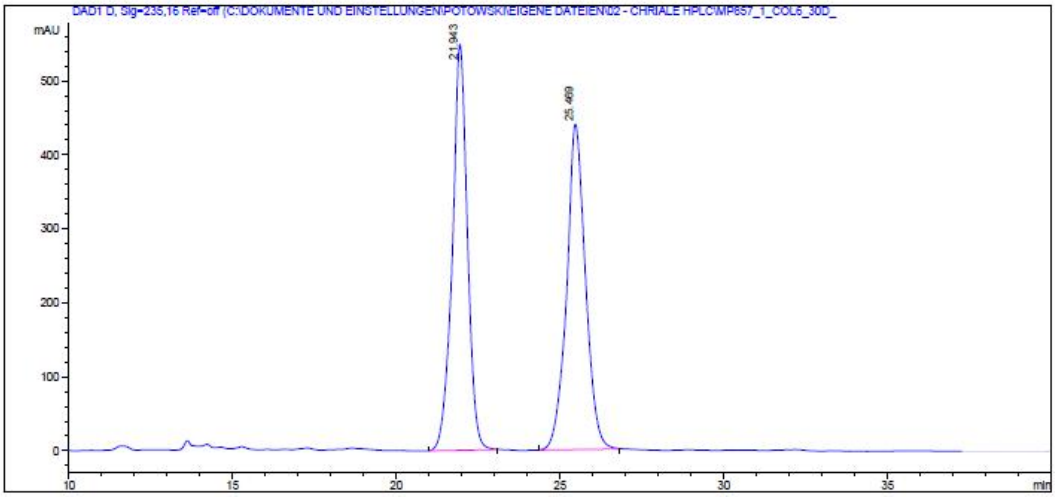
^{13}C NMR



HPLC traces for **3ak**: racemat top, enantiomer bottom.

Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP857 1 COL6 30D 60MIN 1.D

Acq. Method :AA_6RUN_30D_60MIN.M Location : Vial 23 Inj. Vol. : 10 µl

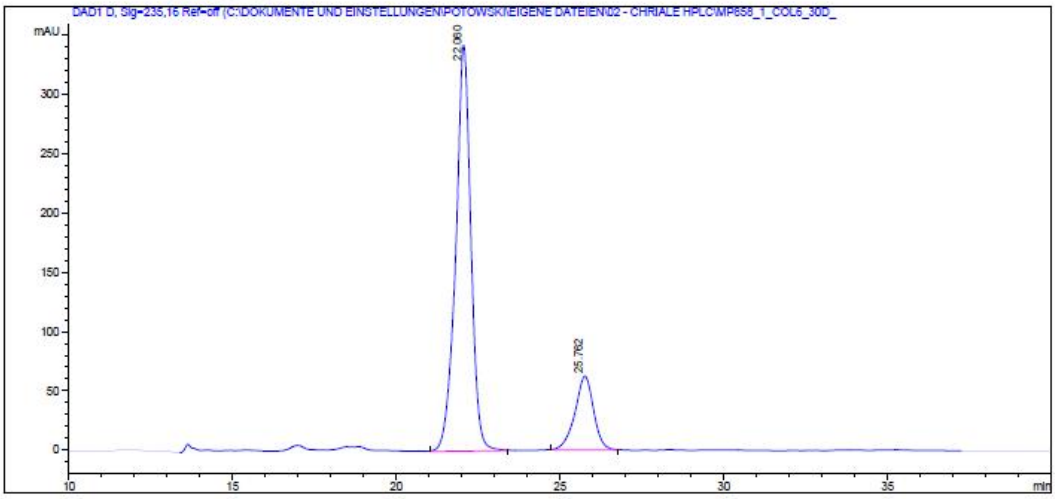


Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	21.943	17548.367	49.927
2	25.469	17599.508	50.073

Data file : C:\DOKUMENTE UND EINSTELLUNGEN\POTOWSKI\EIGENE DATEIEN\02 - CHRIALE HPLC\MP858 1 COL6 30D 60MIN 1.D

Acq. Method :AA_6RUN_30D_60MIN.M Location : Vial 24 Inj. Vol. : 10 µl



Signal 1: DAD1 D, Sig=235,16 Ref=off

Peak #	RT [min]	Area	Area %
1	22.060	11054.705	81.682
2	25.762	2479.114	18.318