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A General Enamine Mediated Alkylation of α-Substituted Aldehydes.

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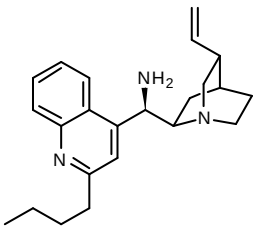
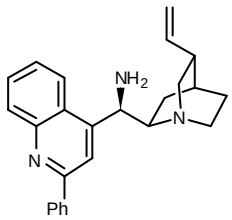
General Methods. ^{1}H NMR spectra were recorded on Varian Gemini 200 and Varian Mercury 400 spectrometers. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuterochloroform: δ= 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = duplet, t = triplet, q = quartet, bs = broad singlet, m = multiplet), coupling constants (Hz). ^{13}C NMR spectra were recorded on Varian Gemini 200 and Varian Mercury 400 spectrometers. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuterochloroform: δ= 77.0 ppm). Chromatographic purification was done with 240-400 mesh silica gel. Determination of enantiomeric ratio was performed on Agilent Technologies 1200 instrument equipped with a variable wave-length UV detector, using a Daicel Chiralpak columns (0.46 cm I.D. x 25 cm) and HPLC grade isopropanol and *n*-hexane were used as the eluting solvents. Optical rotations were determined in a 1 mL cell with a path length of 10 mm (Na_D line), specific rotation was expressed as deg $cm^3g^{-1}dm^{-1}$ and concentration as gcm^{-3}. Melting points were determined with Bibby Stuart Scientific Melting Point Apparatus SMP 3 and are not corrected. Materials: All reactions were carried out under inert gas and under anhydrous conditions. Anhydrous solvents were supplied by Aldrich in Sureseal® bottles and used avoiding purification.

Aldehydes **1a** and **1j** are commercially available. Aldehydes **1b-f** and **1i** were prepared according to reported methodologies.[1] The analytical data for **1b**, **1c**, **1f**, **1h**,[1] **1d**,[2] **1e**,[3] **1i**,[4] were consistent with the literature. **1g** was prepared according to literature.[5]

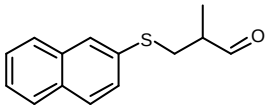
Preparation of *Cinchona* catalysts: catalyst **I-III** and **VI-VII**, were prepared according to the literature procedure.[6] **IV** and **V** were prepared using Hintermann procedure[7] followed by Connon method.[6] The analytical data for **I**,[8] **II**[6], **III**,[9] **VI**,[10] **VII**,[11] and were consistent with the literature.



IV (45%); The desired product was isolated by flash column chromatography (CH_2Cl_2/CH_3OH/NH_4OH = 95/5/1) as sticky solid; $[\alpha]_D^{20}$ +79.6 (*c* 1.3 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ= 0.96 (t, *J* = 7.3 Hz, 3H), 1.40-1.49 (m, 3H), 1.53-1.60 (m, 3H), 1.76-1.84 (m, 3H), 2.12 (bs, 3H), 2.27 (q, *J* = 7.9 Hz, 1H), 2.90-3.08 (m, 7H), 4.74 (m, 1H), 5.05 (dt, *J* = 1.4 Hz, *J* = 8.3 Hz, 1H), 5.09 (m, 1H), 5.86 (ddd, *J* = 7.0 Hz, *J* = 10.9 Hz, *J* = 17.4 Hz, 1H), 7.47 (bs, 1H), 7.51 (ddd, *J* = 1.4 Hz, *J* = 7.0 Hz, *J* = 8.2 Hz, 1H), 7.67 (ddd, *J* = 1.3 Hz, *J* = 6.9 Hz, *J* = 8.2 Hz, 1H), 8.07 (dd, *J* = 1.1 Hz, *J* = 8.3 Hz, 1H), 8.27 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ= 13.9, 22.7, 25.0, 26.6, 27.6, 32.2, 39.1, 39.6, 47.4, 49.5, 114.5, 119.7, 123.0, 125.4, 125.2, 128.1, 129.7, 140.5, 148.3, 148.7, 162.9; HMRS found M^+, 349.25151; $C_{23}H_{31}N_3$ requires: 349.25180.



V (51%); The desired product was isolated by flash column chromatography ($CH_2Cl_2/CH_3OH/NH_4OH$ = 95/5/1) as white solid; mp 54 °C (from MeOH); $[\alpha]_D^{20}$ +129.6 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ= 0.94-1.02 (m, 1H), 1.16-1.21 (m, 2H), 1.53-1.60 (m, 2H), 2.23-2.30 (m, 3H), 2.94-3.11 (m, 5H), 4.83 (d, *J* = 8.1 Hz, 1H), 5.08 (dt, *J* = 1.6 Hz, *J* = 10.6 Hz, 1H), 5.10-5.12 (m, 1H), 5.88 (ddd, *J* = 6.8 HZ, *J* = 10.6 Hz, *J* = 17.2 Hz, 1H), 7.44-7.49 (m, 1H), 7.52-7.59 (m, 3H), 7.73 (ddd, *J* = 1.2 HZ, *J* = 6.9 Hz, *J* = 8.4 Hz, 1H), 8.11 (bs, 1H), 8.19-8.23 (m, 3H), 8.32 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ= 24.9, 25.3, 26.6, 27.6, 39.6, 47.4, 49.4, 50.4, 114.5, 117.5, 123.0, 126.0, 126.7, 127.5, 128.7, 129.1, 129.2, 130.6, 139.6, 140.5, 148.6, 149.5, 157.1; HMRS found M^+, 369.22019; $C_{25}H_{27}N_3$ requires: 369.22050.



Preparation of aldehyde 1l: Following the procedure of Vedejes et al.[12] A mixture of 2-naphthalenethiol (3.6 mmol, 581 mg) and methacrolein (3.6 mmol, 300 µL) was refluxed with triethylamine (0.5 mL) for 3h. Solvent was removed under reduce pressure. Flash chromatography (cyclohexane/ethyl acetate, 95/5) of the residue give **1l** (571 mg, 69%) as sticky solid; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ= 1.29 (d, *J* = 7.3 Hz, 3H), 2.7 (m, 1H), 3.00 (dd, *J* = 6.8 Hz, *J* = 13.2 Hz, 1H), 3.00 (dd, *J* = 6.4 Hz, *J* = 13.2 Hz, 1H), 7.42-7.50 (m, 3H), 7.73-7.79 (m, 4H), 9.71 (d, *J* = 1.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ= 13.5, 34.5, 45.8, 125.9, 126.6, 127.1, 127.7, 128.0, 128.7, 132.0, 132.9, 133.7, 202.8; HMRS found M^+, 230.07610; $C_{14}H_{14}OS$ requires: 230.07654.

Screening test

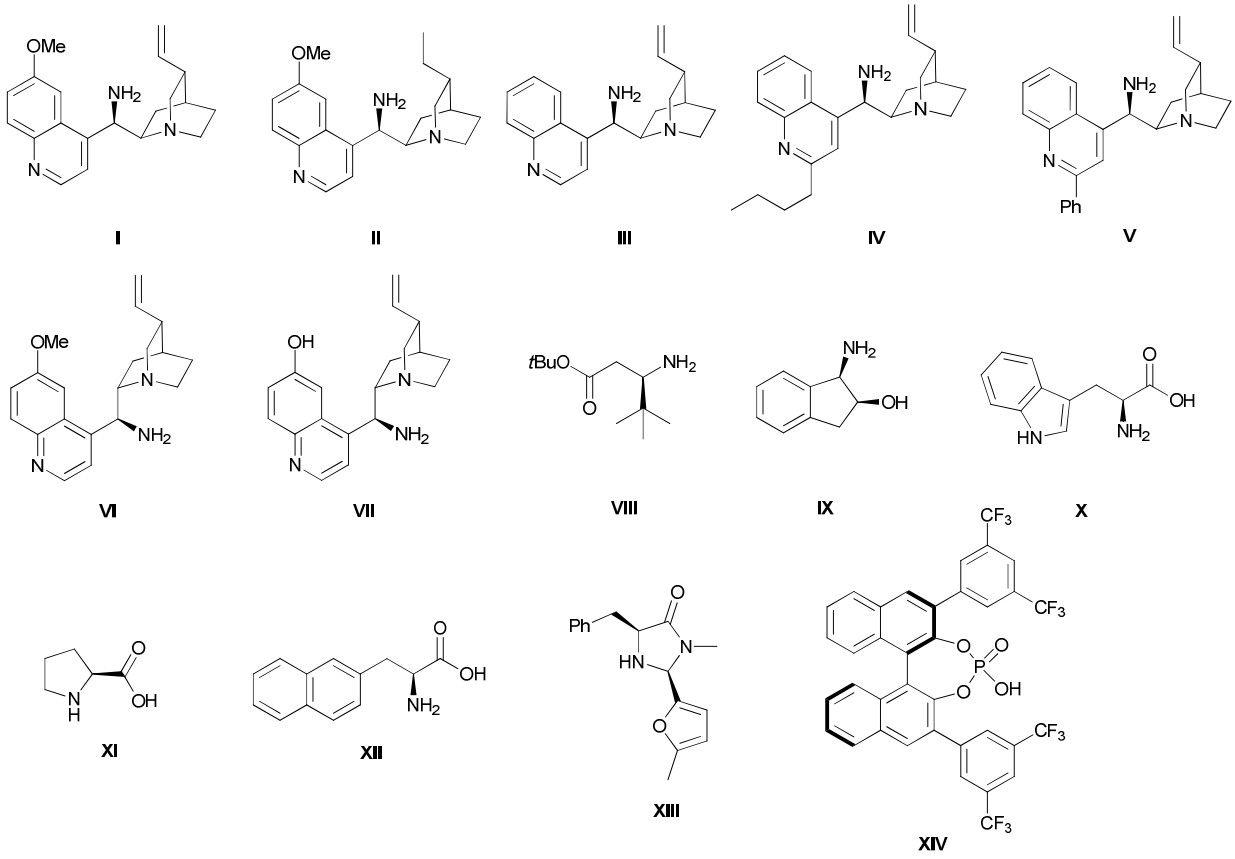


Table S1. Catalyst effect[a]

Entry	Catalyst	Acid (mol%)	Solvent	er
1	**I**	(-)-CSA (40)	CH_3CN/H_2O 1/1	92:8
2	**II**	(-)-CSA (40)	CH_3CN/H_2O 1/1	89.5:10.5
3	**III**	(-)-CSA (40)	CH_3CN/H_2O 1/1	90.5:9.5
4	**IV**	(-)-CSA (40)	CH_3CN/H_2O 1/1	90:10
5	**V**	(-)-CSA (40)	CH_3CN/H_2O 1/1	84.5:15.5
6	**VI**	(-)-CSA (40)	CH_3CN/H_2O 1/1	11:89
7	**VII**	(+)-CSA (40)	CH_3CN/H_2O 1/1	21.5:78.5
8	**VIII**	(+)-CSA (20)	CH_3CN/H_2O 1/1	50:50
9	**IX**	(+)-CSA (20)	CH_3CN/H_2O 1/1	57:43
10	**X**	PNBA[b] (20)	CH_3CN	57:43
11	**X**	PNBA[b] (20)	CH_3CN/H_2O 1/1	47:53
12	**X**	-	CH_3CN/H_2O 1/1	44:56
13	**XI**	-	CH_3CN/H_2O 1/1	47:53
14	**XI**	-	CH_3CN	50:50
15	**XII**	(-)-CSA (20)	CH_3CN/H_2O 1/1	48.5:51.5
16	-	(-)-CSA (20)	CH_3CN/H_2O 1/1	50:50
17	**XIII**	(-)-CSA (20)	CH_3CN/H_2O 1/1	60:40

[a] The reactions were performed at 0°C with 1 equiv. of **2**, 3 equiv. of aldehyde **1a** in the presence of 20 mol% of catalysts **I-XIII**, with 2 equiv. of NaH_2PO_4 and 20 mol% o 40% mol of acid as a co-catalyst in 500 μL of solvent at 0°C. The reactions were run until completion, as determined by TLC (16–24 h). [b] *p*-nitrobenzoic acid.

Table S2. Base effect[a]

Entry	Catalyst	Solvent	Base	er
1	**I**	CH_2Cl_2	Imidazole	50:50
2	**VI**	CH_3CN/H_2O 1/1	Na_2HPO_4	59:41
3	**VI**	CH_3CN/H_2O 1/1	$NaHCO_3$	55.5:44.5

[a] The reactions were performed at 0°C with 1 equiv. of **2**, 3 equiv. of aldehyde **1a** in the presence of 20 mol% of catalysts **I-VI**, with 2 equiv. of base and 40% mol of (-)-CSA as a co-catalyst in 500 μL of solvent. The reactions were run until completion, as determined by TLC (16–24 h).

Table S3. Solvent effect[a]

Entry	Catalyst	Solvent	er
1	**I**	CH_2Cl_2	31.5:68.5
2	**VI**	Toluene/CH_3CN 5/1	46.5:53.5
3	**VI**	Hexane/CH_3CN 5/1	50:50
4	**I**	CH_3CN	83:17
5	**I**	H_2O	72.5:27.5
6	**I**	CH_3CN/H_2O 1/1	92:8
7	**I**	CH_3CN/H_2O 9/1	92:8
8	**I**	CH_3CN/H_2O 1/9	89:11
9	**I**	[Bmim]OTf	28.5:71.5
10	**I**	C_2H_5CN/H_2O 1/1	86.5:13.5
11	**I**	CH_3CN/D_2O 1/1	90:10
12	**I**	Dioxane/H_2O 1/1	81.5:18.5
13	**I**	THF/H_2O 1/1	78.5:21.5
14	**I**	DME/H_2O 1/1	73.5:26.5
15	**I**	TBME/H_2O 1/1	84:16
16	**I**	Toluene/H_2O 1/1	71:29
17	**I**	DMF/H_2O 1/1	89:11
18	**I**	DMSO	54:46
19	**I**	DMSO/H_2O 1/1	82.5:17.5

[a] The reactions were performed at 0°C with 1 equiv. of **2**, 3 equiv. of aldehyde **1a** in the presence of 20 mol% of catalysts **I-VI**, with 2 equiv. of NaH_2PO_4 and 40% mol of (-)-CSA as a co-catalyst in 500 μL of solvent. The reactions were run until completion, as determined by TLC (16–24 h).

Table S4. Temperature effect[a]

Entry	Catalyst	T (°C)	er
1	**I**	0	92:8
2	**I**	25	90.5:9.5
3	**VI**	0	11:89
4	**VI**	-13	11.5:88.5

[a] The reactions were performed with 1 equiv. of **2**, 3 equiv. of aldehyde **1a** in the presence of 20 mol% of catalysts **I**-**VI**, with 2 equiv. of NaH_2PO_4 and 40% mol of (-)-CSA as a co-catalyst in 500 μL of CH_3CN/H_2O 1/1. The reactions were run until completion, as determined by TLC (16–24 h).

Table S5. Acid effect[a]

Entry	Catalyst (mol%)	Acid (mol%)	er
1	**I** (20)	Benzioc acid (40)	63:37
2	**I** (20)	PNBA[b] (40)	68.5:31.5
3	**VI** (20)	*N*-Boc-*L*-His (40)	14:86
4	**VI** (20)	*N*-Boc-*D*-Phe (40)	12.5:87.5
5	**VI** (20)	*N*-Boc-*L*-Phe (40)	13.5:86.5
6	**VI** (20)	*L*-Tartaric acid (40)	39:61
7	**VI** (20)	(*R*)-Mandelic acid (40)	35:65
8	**VI** (20)	PTSA (40)	14:86
9	**VI** (20)	(+)-Canforic acid	12.5:87.5
10	**VI** (20)	**XIV** (40)	50:50
11	**VI** (20)	TfOH (40)	12:88
12	**I** (20)	(-)-CSA (40)	91:9
13	**I** (20)	(+)-CSA (40)	92:8
14	**VI** (20)	-	13:87
15	**VI** (20)	(-)-CSA (20)	15.5:84.5
16	**VI** (20)	(-)-CSA (40)	11:89
17	**VI** (20)	(-)-CSA (80)	12.5:87.5
18	**VI** (20)	(+)-CSA (40)	17.5:82.5
19	**VII** (20)	(+)-CSA (40)	21.5:78.5
20	**VII** (20)	**XIV** (40)	44:56
21	**III** (20)	HCl (40)[c]	91:9
22	**III** (20)	(-)-CSA (40)	90.5:9.5

[a] The reactions were performed at 0°C with 1 equiv. of **2**, 3 equiv. of aldehyde **1a** in the presence of 20 mol% of catalysts **I**-**IV**, with 2 equiv. of NaH_2PO_4 and different amount of acid as a co-catalyst in 500 μL of CH_3CN/H_2O 1/1. The reactions were run until completion, as determined by TLC (16–24 h). [b] *p*-nitrobenzoic acid. [c] Aqueous solution.

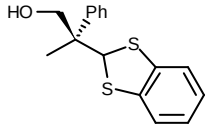
Table S6. Concentration effect[a]

Entry	Catalyst (mol%)	Acid (mol%)	Note	er
1	**I** (5)	(-)-CSA (10)	-	87:13
2	**I** (20)	(-)-CSA (40)	10 eq. di aldehyde	86:14
3	**I** (20)	(-)-CSA (40)	[Carbocation] = 0.1 M	92:8
4	**I** (20)	(-)-CSA (40)	[Carbocation] = 0.05 M	90.5:9.5
5	**I** (20)	(-)-CSA (40)	[Carbocation] = 0.2 M	91:9

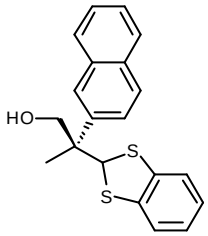
The reactions were performed at 0°C with 1 equiv. of **2**, 3 equiv. of aldehyde **1a** in the presence of catalysts **I**, with 2 equiv. of NaH_2PO_4 and and (-)-CSA as a co-catalyst in 500 μL of CH_3CN/H_2O 1/1. The reactions were run until completion, as determined by TLC (16–24 h).

Enantioselective α-alkylation of aldehydes

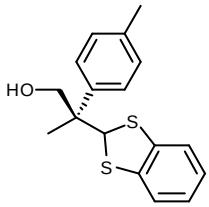
General procedure: A vial was charged with **I** (0.02 mmol, 6 mg), (-)-CSA (0.04 mmol, 9 mg), acetonitrile (0.25 mL) and water (0.25 mL). The mixture was cooled at 0°C, 1,3-benzodithiolylium tetrafluoroborate **2** (0.1 mmol, 24 mg), NaH_2PO_4 (0.2 mmol, 24 mg) and **1a** (0.3 mmol, 40 μL) were added. The mixture was stirred for 24 hours at the same temperature and a saturated solution of $NaHCO_3$ (1 mL) was added and the mixture was diluted with AcOEt (3mL). The organic layer was separated, and the aqueous layer was extracted with AcOEt (2 x 3 mL). The collected organic layers were washed with brine (5 mL), dried over Na_2SO_4 and concentrated under reduce pressure. The residue was diluted in MeOH (1 mL) and $NaBH_4$ (0.4 mmol, 15 mg) was slowly added at 0 °C. After 30 minutes, silica was added and the solvent was evaporated in vacuo. The residue was purified by flash chromatography (cyclohexane/ethyl acetate = 9/1) to give **3a**.



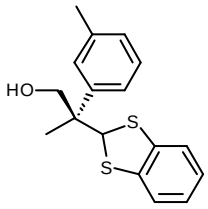
3a (26 mg, 90%); er = 92:8; The desired product was isolated by flash column chromatography (cyclohexane/ethyl acetate = 9/1) as colourless oil; The er was determined by HPLC analysis Daicel Chiralcel OD-H column: hexane/*i*-PrOH 90:10, flow rate 0.50 mL/min, 40°C, λ = 232, 254 nm: τ_{major} = 23.2 min, τ_{minor} = 25.7 min; $[\alpha]_D^{20}$ -7.1 (*c* 0.5 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ= 1.51 (s, 3H), 3.78 (d, *J* = 11.1 Hz, 1H), 4.01 (d, *J* = 11.1 Hz, 1H), 5.64 (s, 1H), 6.93-6.95 (m, 2H), 7.06-7.08 (m, 1H), 7.14-7.16 (m, 1H), 7.29 (dt, *J* = 1.4 Hz, *J* = 7.3 Hz, 1H), 7.35-7.40 (m, 2H), 7.43-7.46 (m, 2H);^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ= 16.9, 50.1, 60.6, 68.7, 121.4, 121.6, 125.1, 125.2, 127.2 (2C), 127.3, 128.6 (2C), 138.1, 141.9 (2C); HMRS found M^+, 288.06401; $C_{16}H_{16}OS_2$ requires: 288.06426.



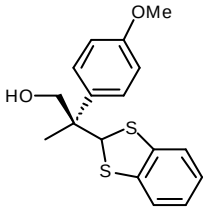
3b (28 mg, 83%); er = 93.5:6.5; The desired product was isolated by flash column chromatography (cyclohexane/ethyl acetate = 9/1) as colourless oil; The er was determined by HPLC analysis Daicel Chiralcel IA column: hexane/*i*-PrOH 90:10, flow rate 0.50 mL/min, 40°C, λ = 232, 254 nm: τ_{major} = 30.1 min, τ_{minor} = 27.9 min; $[\alpha]_D^{20}$ -104.2 (*c* 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ= 1.62 (s, 3H), 3.80 (d, *J* = 11.2 Hz, 1H), 4.11 (d, *J* = 11.2 Hz, 1H), 5.78 (s, 1H), 6.92-6.98 (m, 2H), 7.05-7.08 (m, 1H), 7.15-7.17 (m, 1H), 7.49-7.53 (m, 2H), 7.59 (dd, *J* = 2.1 Hz, *J* = 11.7 Hz, 1H), 7.82-7.89 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ= 20.0, 50.3, 60.6, 68.7, 121.5, 121.6, 124.6, 125.1, 125.3, 126.2, 126.8, 127.4, 128.2, 128.3, 132.4, 133.1, 138.0, 138.1, 139.5; HMRS found M^+, 338.07963; $C_{20}H_{18}OS_2$ requires: 338.07991.



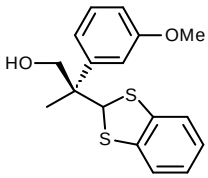
3c (27 mg, 89%); er = 90.5:9.5; The desired product was isolated by flash column chromatography (cyclohexane/ethyl acetate = 9/1) as colourless oil; The er was determined by HPLC analysis Daicel Chiralcel OD-H column: hexane/*i*-PrOH 90:10, flow rate 0.50 mL/min, 40°C, λ = 232, 254 nm: τ_{major} = 15.7 min, τ_{minor} = 17.8 min; $[\alpha]_D^{20}$ -108.7 (*c* 1.4 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ= 1.49 (s, 3H), 2.35 (s, 3H), 3.75 (d, *J* = 11.3 Hz, 1H), 3.99 (d, *J* = 11.3 Hz, 1H), 5.65 (s, 1H), 6.94-6.98 (m, 2H), 7.07-7.09 (m, 1H), 7.15-7.18 (m, 1H), 7.19-7.21 (m, 2H), 7.32-7.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ= 16.8, 20.9, 49.8, 60.8, 68.7, 121.4, 121.6, 125.1, 12.0, 129.4, 137.0, 138.1, 138.8; HMRS found M^+, 302.07969; $C_{17}H_{18}OS_2$ requires: 302.07991.



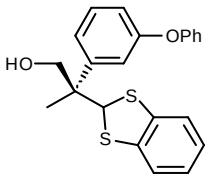
3d (26 mg, 85%); er = 92.5:7.5; The desired product was isolated by flash column chromatography (cyclohexane/ethyl acetate = 9/1) as colourless oil; The er was determined by HPLC analysis Daicel Chiralcel OD-H column: hexane/*i*-PrOH 90:10, flow rate 0.50 mL/min, 40°C, λ = 232, 254 nm: τ_{major} = 18.3 min, τ_{minor} = 15.7 min; $[\alpha]_D^{20}$ -78.7 (*c* 0.4 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ= 1.56 (s, 3H), 2.38 (s, 3H), 3.76 (dd, *J* = 6.8 Hz, *J* = 11.1 Hz, 1H), 3.99 (dd, *J* = 5.9 Hz, *J* = 11.1 Hz, 1H), 5.65 (s, 1H), 6.93-6.99 (m, 2H), 7.06-7.11 (m, 2H), 7.14-7.16 (m, 1H), 7.22-7.29 (m, 3H); ^{13}C NMR (25 MHz, $CDCl_3$, 25°C): δ= 16.9, 21.7, 50.0, 60.7, 68.8, 121.5, 121.6, 124.2, 125.1, 125.2, 127.9, 128.1, 128.5, 138.2, 141.8, 151.0; HMRS found M^+, 302.07968; $C_{17}H_{18}OS_2$ requires: 302.07991.



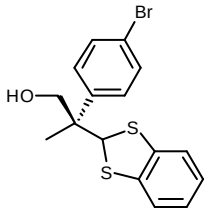
3e (28 mg, 88%); er = 85.5:14.5; The desired product was isolated by flash column chromatography (cyclohexane/ethyl acetate = 9/1) as colourless oil; The er was determined by HPLC analysis Daicel Chiralcel OD-H column: hexane/*i*-PrOH 90:10, flow rate 0.50 mL/min, 40°C, λ = 232, 254 nm: τ_{major} = 27.2 min, τ_{minor} = 29.5 min; $[\alpha]_D^{20}$ -44.8 (*c* 2.5 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ= 1.48 (s, 3H), 3.75 (d, *J* = 11.0 Hz, 1H), 3.81 (s, 3H), 3.97 (d, *J* = 11.0 Hz, 1H), 5.59 (s, 1H), 6.87-6.92 (m, 2H), 6.94-6.98 (m, 2H), 7.05-7.09 (m, 1H), 7.13-7.19 (m, 1H), 7.34-7.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ= 17.0, 49.4, 55.2, 61.0, 68.7, 113.9 (2C), 121.4, 121.6, 125.1, 125.2, 128.3 (2C), 133.6, 138.0, 138.1, 158.6; HMRS found M^+, 318.07459; $C_{17}H_{18}O_2S_2$ requires: 318.07482.



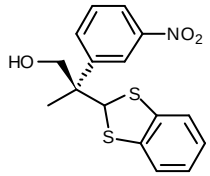
3f (28 mg, 88%); er = 91.5:8.5; The desired product was isolated by flash column chromatography (cyclohexane/ethyl acetate = 9/1) sticky solid; The er was determined by HPLC analysis Daicel Chiralcel OD-H column: hexane/*i*-PrOH 80:20, flow rate 0.50 mL/min, 40°C, λ = 232, 254 nm: τ_{major} = 23.1 min, τ_{minor} = 18.4 min; $[\alpha]_D^{20}$ -47.9 (*c* 3.7 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ= 1.46 (s, 3H), 3.72 (d, *J* = 10.6 Hz, 1H), 3.80 (s, 3H), 3.95 (d, *J* = 10.6 Hz, 1H), 5.60 (s, 1H), 6.80 (ddd, *J* = 0.8 Hz, *J* = 2.5 Hz, *J* = 8.4 Hz, 1H), 6.90-6.97 (m, 2H), 6.98-7.01 (m, 2H), 7.04-7.07 (m, 1H), 7.12-7.14 (m, 1H), 7.29 (t, *J* = 8.0 Hz, 1H)6.87-6.92 (m, 2H), 6.94-6.98 (m, 2H), 7.05-7.09 (m, 1H), 7.13-7.19 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ= 16.8, 50.2, 55.2, 60.5, 68.7, 111.8, 114.1, 119.4, 121.4, 121.6, 125.1, 125.2, 129.5, 138.1, 138.2, 143.6, 159.7; HMRS found M^+, 318.07455; $C_{17}H_{18}O_2S_2$ requires: 318.07482.



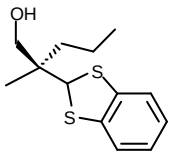
3g (20 mg, 52%); er = 90:10; desired product was isolated by flash column chromatography (cyclohexane/ethyl acetate = 9/1) as colourless oil; The er was determined by HPLC analysis Daicel Chiralcel OF column: hexane/*i*-PrOH 90:10, flow rate 0.50 mL/min, 40°C, λ = 232, 254 nm: τ_{major} = 17.7 min, τ_{minor} = 10.3 min; $[\alpha]_D^{20}$ -49.3 (*c* 0.6 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ= 1.46 (s, 3H), 1.59 (bs, 1H), 3.78 (d, *J* = 11.4 Hz, 1H), 3.99 (d, *J* = 11.4 Hz, 1H), 5.54 (s, 1H), 6.88 (ddd, *J* = 1.0 Hz, *J* = 2.4 Hz, *J* = 8.9 Hz, 1H), 6.95-6.97 (m, 2H), 6.99-7.02 (m, 2H), 7.07-7.10 (m, 1H), 7.12-7.17 (m, 3H), 7.20 (ddd, *J* = 1.0 Hz, *J* = 1.8 Hz, *J* = 7.9 Hz, 1H), 7.28-7.38 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ= 17.1, 50.1, 50.0, 60.4, 68.4, 117.4, 118.4, 118.7 (2C), 121.4 (2C), 121.6, 122.1, 123.3, 125.2, 125.3, 129.6, 129.8 (2C), 138.0, 144.0, 157.1, 157.2; HMRS found M^+, 380.09020; $C_{22}H_{20}O_2S_2$ requires: 380.09047.



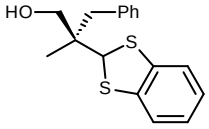
3h (31 mg, 84%); er = 86.5:13.5; The desired product was isolated by flash column chromatography (cyclohexane/ethyl acetate = 9/1) as colourless oil; The er was determined by HPLC analysis Daicel Chiralcel OD-H column: hexane/*i*-PrOH 90:10, flow rate 0.50 mL/min, 40°C, λ = 232, 254 nm: τ_{major} = 21.1 min, τ_{minor} = 19.7 min; $[\alpha]_D^{20}$ -60.2 (*c* 0.3 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ= 1.46 (s, 3H), 3.78 (d, *J* = 10.8 Hz, 1H), 4.00 (d, *J* = 10.8 Hz, 1H), 5.53 (s, 1H), 6.94-6.99 (m, 2H), 7.06-7.08 (m, 1H), 7.11-7.14 (m, 1H), 7.32-7.35 (m, 2H), 7.44-7.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ= 17.1, 49.8, 60.3, 68.2, 125.5, 121.6, 125.2, 125.3, 129.1 (2C), 131.4 (2C), 137.8, 137.9 (2C), 140.8; HMRS: no ionization was observed.



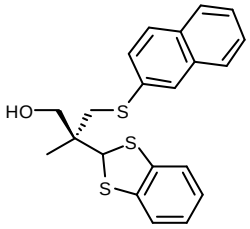
3i (25 mg, 75%); er = 84:16; The desired product was isolated by flash column chromatography (cyclohexane/ethyl acetate = 7/3) as sticky solid; The er was determined by HPLC analysis Daicel Chiralcel IA column: hexane/*i*-PrOH 90:10, flow rate 0.50 mL/min, 40°C, λ = 232, 254 nm: τ_{major} = 27.3 min, τ_{minor} = 29.1 min; $[\alpha]_D^{20}$ -46.4 (*c* 0.6 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ= 1.55 (s, 3H), 3.96 (d, *J* = 10.6 Hz, 1H), 4.09 (d, *J* = 10.6 Hz, 1H), 5.40 (s, 1H), 6.87-6.91 (m, 2H), 7.00-7.06 (m, 2H), 7.42 (t, *J* = 8.2 Hz, 1H), 7.83 (ddd, *J* = 1.0 Hz, *J* = 1.9 Hz, *J* = 8.0 Hz, 1H), 8.03 (ddd, *J* = 1.0 Hz, *J* = 1.9 Hz, *J* = 8.0 Hz, 1H), 8.4 (t, *J* = 2.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ= 18.0, 49.7, 59.9, 67.3, 121.4, 121.5, 122.1, 122.8, 125.3, 128.5, 133.8, 137.5 (2C), 143.4, 147.8; HMRS found M^+, 333.04908; $C_{16}H_{15}NO_3S_2$ requires: 333.04933.



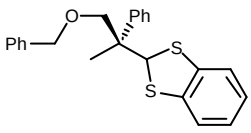
3j (19 mg, 76%); er = 72:28; The desired product was isolated by flash column chromatography (cyclohexane/ethyl acetate = 95/5) as colourless oil; The er was determined by HPLC analysis Daicel Chiralcel IC column: hexane/*i*-PrOH 98:2, flow rate 0.50 mL/min, 40°C, λ = 232, 254 nm: τ_{major} = 27.2 min., τ_{minor} = 25.5 min; $[\alpha]_D^{20}$ -28.0 (*c* 0.3 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ= 0.93 (t, *J* = 7.3 Hz, 3H), 0.94 (s, 3H), 1.27-1.39 (2H), 1.44-1.49 (m, 2H), 1.61 (bs, 1H), 3.58 (d, *J* = 11.3 Hz, 1H), 3.66 (d, *J* = 11.3 Hz, 1H), 5.26 (s, 1H), 6.97-7.01 (m, 2H), 7.16-7.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ= 14.9, 17.0, 17.8, 36.8, 41.1, 62.9, 66.4, 121.6 (2C), 125.2, 125.3, 138.1, 138.2; HMRS found M^+, 254.07971; $C_{13}H_{18}OS_2$ requires: 254.07991.



3k (24 mg, 78%); er = 73:27; The desired product was isolated by flash column chromatography (cyclohexane/ethyl acetate = 95/5) as colourless oil; The er was determined by HPLC analysis Daicel Chiralcel OJ column: hexane/*i*-PrOH 80:20, flow rate 1.00 mL/min, 40°C, λ = 232, 254 nm: τ_{major} = 10.6 min, τ_{minor} = 11.9 min; $[\alpha]_D^{20}$ -24.3 (*c* 0.5 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ= 0.91 (s, 3H), 2.80 (d, *J* = 13.3 Hz, 1H), 2.85 (d, *J* = 13.3 Hz, 1H), 3.51 (d, *J* = 11.1 Hz, 1H), 3.59 (d, *J* = 11.1 Hz, 1H), 5.20 (s, 1H), 7.00-7.02 (m, 2H), 7.20-7.25 (m, 4H), 7.27-7.32 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ= 17.4, 39.7, 45.8, 60.9, 65.4, 121.7, 125.2, 125.3 (2C), 126.5, 128.2 (2C), 130.6 (2C), 137.3, 138.2, 138.2; HMRS found M^+, 302.07913; $C_{17}H_{18}OS_2$ requires: 302.07991.



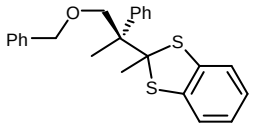
3l (30 mg, 79%); er = 66:34; The desired product was isolated by flash column chromatography (cyclohexane/ethyl acetate = 9/1) as sticky solid; The er was determined by HPLC analysis Daicel Chiralcel OJ column: hexane/*i*-PrOH 50:50, flow rate 0.5 mL/min, 40°C, λ = 232, 254 nm: τ_{major} = 29.5 min, τ_{minor} = 37.8 min; $[\alpha]_D^{20}$ -31.3 (*c* 0.5 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ= 1.06 (s, 3H), 3.28 (d, *J* = 12.6 Hz, 1H), 3.34 (d, *J* = 12.6 Hz, 1H), 3.75 (s, 2H), 5.36 (s, 1H), 7.00-7.04 (m, 2H), 7.19-7.21 (m, 2H), 7.43-7.51 (m, 3H), 7.74-7.81 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ= 17.2, 39.9, 46.8, 59.5, 65.8, 121.6, 121.7, 125.4 (2C), 125.9, 126.7, 127.1, 127.4, 127.5, 127.7, 128.6, 131.9, 133.7, 134.1, 138.1 (2C); HMRS found M^+, 384.06796; $C_{21}H_{20}OS_3$ requires: 384.06763.



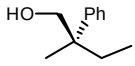
Protection of hydroxyl group: To a suspension of NaH (1.3 mmol, 52 mg of a 60% suspension in mineral oil) in anhydrous THF (3 mL) a solution of **3a** (0.65 mmol, 187 mg) in THF (1 mL) was slowly added at 0°C. After 30 minutes benzylbromide (1.0 mmol, 116 μL) was added and the mixture was stirred at room temperature for 18 hours. Water (5 mL) was slowly added and the mixture was diluted with Et_2O (3mL). The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 x 5 mL). The collected organic layers were washed with brine (5 mL), dried over Na_2SO_4 and concentrated under reduce pressure.

Flash chromatography (cyclohexane/ethyl acetate, 9/1) of the residue give **4a** (231 mg, 94%) as colourless oil. $[\alpha]_D^{20}$ -42.6 (*c* 0.5 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ= 1.45 (s, 3H), 3.61 (d, *J* = 9.2 Hz, 1H), 3.78 (d, *J* = 9.2 Hz, 1H), 4.48 (s, 2H), 5.70 (s, 1H), 6.88-6.94 (m, 2H), 7.02-7.05 (m, 1H), 7.07-7.10 (m, 1H), 7.22-7.35 (m, 8H), 7.47-7.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ= 17.5, 48.9, 60.8, 73.5, 75.8, 121.4, 121.5, 125.0, 125.1, 127.1 (2C), 127.5 (2C),

127.7 (2C), 128.1 (2C), 128.5 (2C), 138.2, 138.5, 138.6, 142.9; HMRS found M^+, 378.11092; $C_{23}H_{22}OS_2$ requires: 378.11121.



Alkylation of benzodithiol: A solution of *n*BuLi (0.033 mmol, 206 µL, 1.6 M in hexanes) was added dropwise to a solution of **4a** (0.3 mmol, 112 mg) in anhydrous in THF (2 mL) at 0°C. The mixture turns to orange colour. After 5 minutes methyl iodide (1.5 mmol, 76 µL) was added and the solution became colourless. The solution was stirred for 5 minutes and then water (1 mL) was added. The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 x 5 mL). The collected organic layers were washed with brine (5 mL), dried over Na_2SO_4 and concentrated under reduce pressure. Flash chromatography (cyclohexane/ethyl acetate = 9/1) of the residue give **5a** (107 mg, 91%) as colourless oil. $[\alpha]_D^{20}$ -15.7 (*c* 0.5 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ= 1.78 (s, 3H), 1.82 (s, 3H), 4.06 (d, *J* = 9.4 Hz, 1H), 4.26 (d, *J* = 9.4 Hz, 1H), 4.55 (d, *J* = 12.4 Hz, 1H), 4.61 (d, *J* = 12.4 Hz, 1H), 6.95-6.99 (m, 2H), 7.10-7.13 (m, 2H), 7.28-7.35 (m, 8H), 7.49-7.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ= 22.6, 29.4, 49.4, 73.4, 76.9, 122.1, 122.2, 125.0, 125.1, 127.1, 127.4, 127.5, 127.6 (3C), 128.1 (2C), 128.2 (2C), 136.8, 137.9, 138.1, 141.1; HMRS found M^+, 392.12656; $C_{24}H_{24}OS_2$ requires: 392.12686.

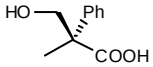


Reductive removal of benzodithiol group: To a solution of **5a** (0.08 mmol, 31 mg) in methanol (1 mL), Ni-Raney (0.450 g, slurry in water) was added and the reaction was kept under H_2 atmosphere (1 atm). After 18h the reaction mixture was filtered through a Celite pad and the organic solvent was removed under reduce pressure. The residue was diluted with AcOEt, the organic layer was separated, and the aqueous layer was extracted with AcOEt (2 x 5 mL).

The residual was dissolved in MeOH (5 mL), 10% Pd/C (10 mg) was added and the reaction was kerp under hydrogen atmosphere for 18h. The reaction mixture was filtered through a Celite pad and the organic solvent was removed under reduce pressure.

Flash chromatography (cyclohexane/ethylacetate, 8/2) of the residue give **6a** (11.3 mg, 86%) as colourless oil. All spectra data were consistent with the literature.[13] $[\alpha]_D^{20}$ -2.9 (*c* 0.5 in $CHCl_3$); lit.: $[\alpha]_D^{20}$ -3.6 (*c* 0.8 in $CHCl_3$, ee = 83%).[14]

Absolute configuration was confirmed by comparison of the chiral HPLC retention time (Daicel Chiralcel OF column: hexane/*i*-PrOH 90:10, flow rate 0.50 mL/min, 40°C, λ = 214 nm: $\tau_{major(R)}$ = 21.0 min, $\tau_{minor(S)}$ = 26.4 min;) in the literature.[13]



Oxidative removal of benzodithiol group, synthesis of (*2R*)-(+)-α-methyltropic acid: To a solution of **4a** (0.08 mmol, 30 mg) in acetonitrile (1 mL) at 0°C, 30% H_2O_2 (320 μL) was added. 40% HBr (0.16 mmol, 21 μL) was slowly added and the reaction mixture was raised at room temperature. After 4h $Na_2S_2O_5$ (1.0 g), was slowly added at 0°C and the mixture was diluited with AcOEt (5 mL). Water (0.25 mL) and $NaHCO_3$ aq. were added until pH 8.0. The organic layer was separated, and the aqueous layer was extracted with AcOEt (2 x 5 mL). HCl (0.1M) was added to the aqueous phase until pH=2 and AcOEt was added. The organic layer was separated, and the aqueous layer was extracted with AcOEt (2 x 5 mL). The collected organic layers were washed with brine (5 mL), dried over Na_2SO_4 and concentrated under reduce pressure to give a colourless oil.

The residual was dissolved in MeOH (5 mL), 10% Pd/C (10 mg) was added and the reaction was kept under hydrogen atmosphere for 18h. The reaction mixture was filtered through a Celite pad and the organic solvent was removed under reduce pressure.

Flash chromatography (cyclohexane/ethylacetate/acetic acid, 1/1/0.05) of the residue give **7a** (10.9 mg, 76%) as colourless oil. Spectroscopy data are in according with literature.[15] $[\alpha]_D^{20}$ +20.5 (*c* 0.2 in $CHCl_3$); lit.: $[\alpha]_D^{20}$ +21.3 (*c* 0.7 in $CHCl_3$).[16]

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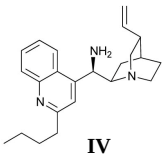
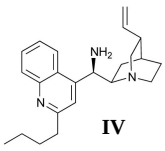
Copy of NMR spectra



IV



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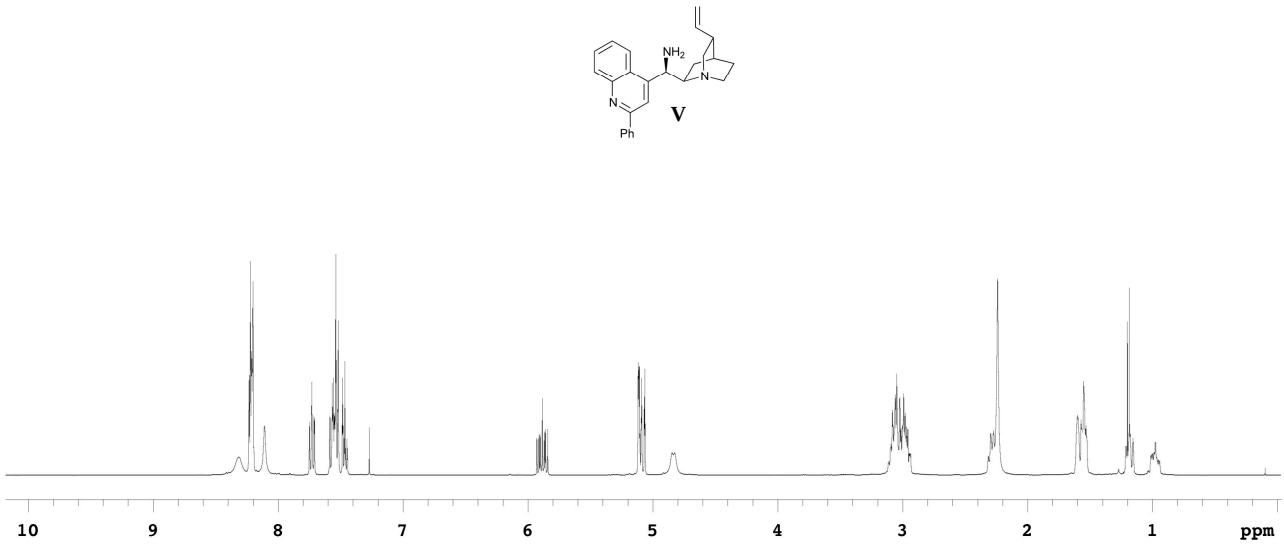
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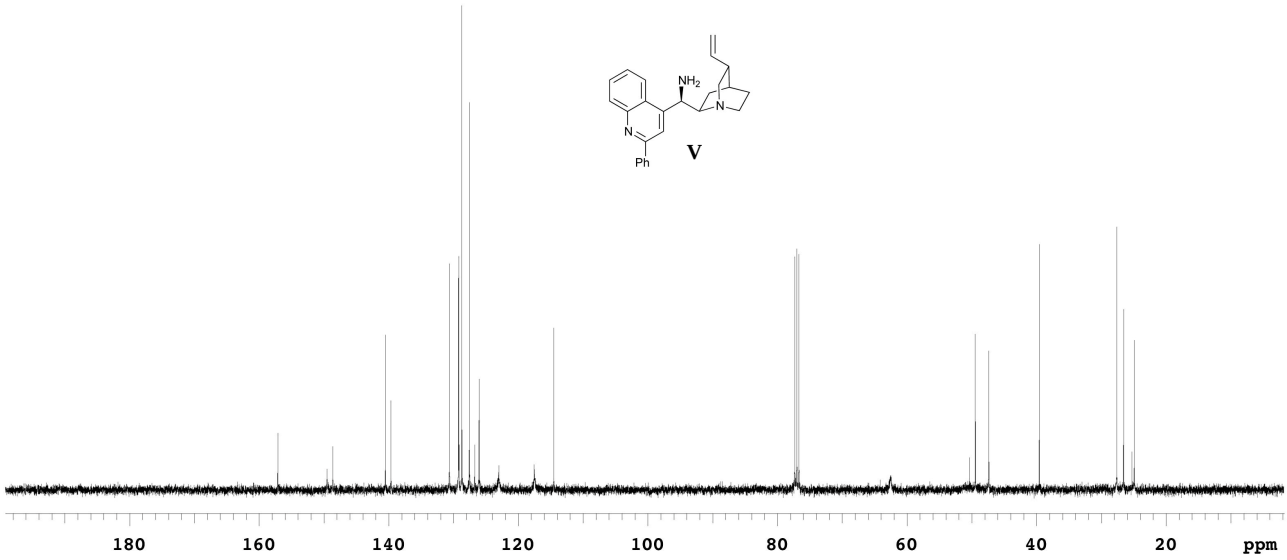
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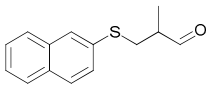

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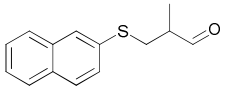

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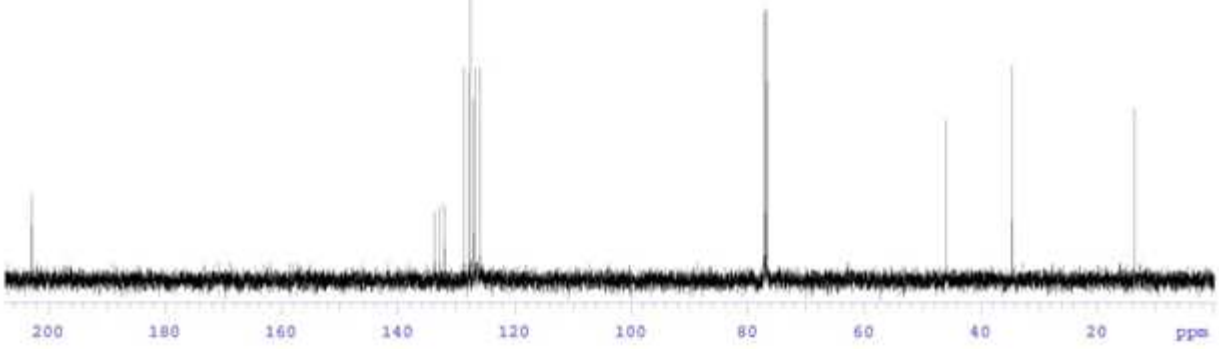

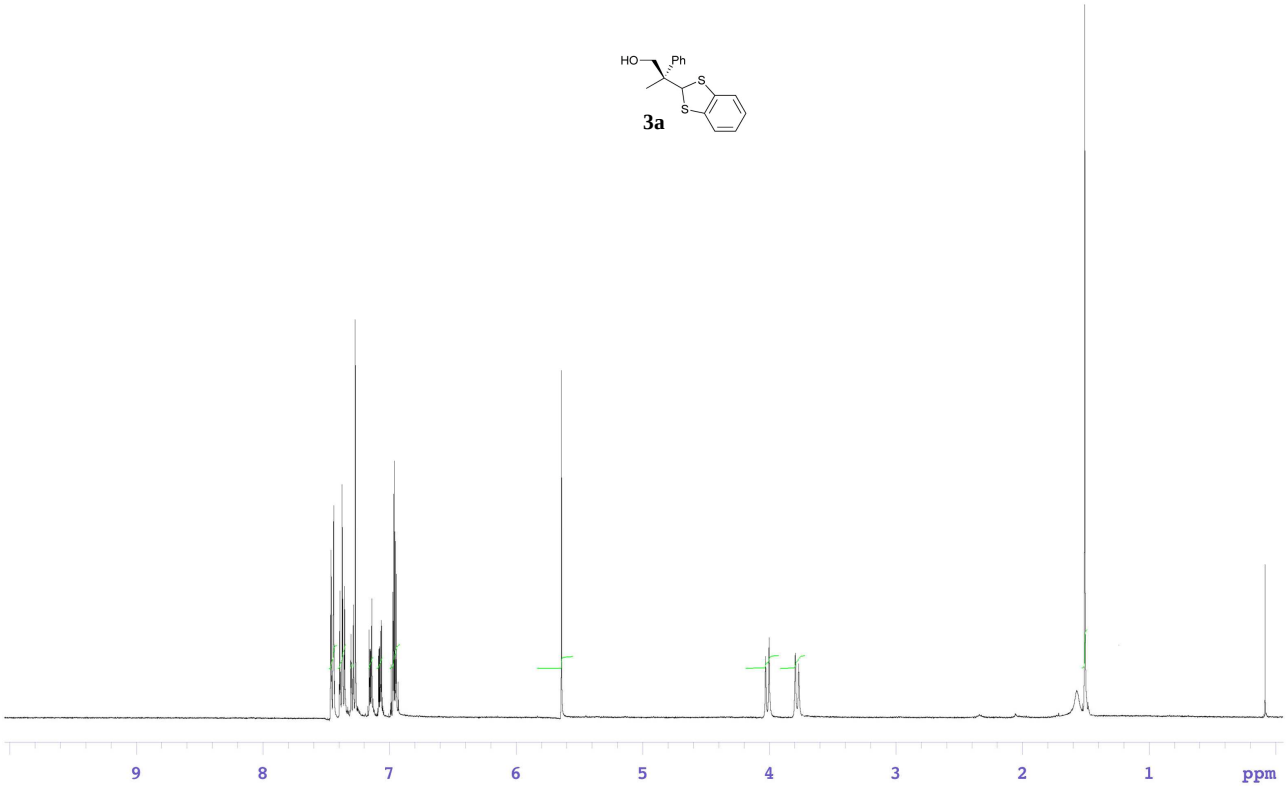
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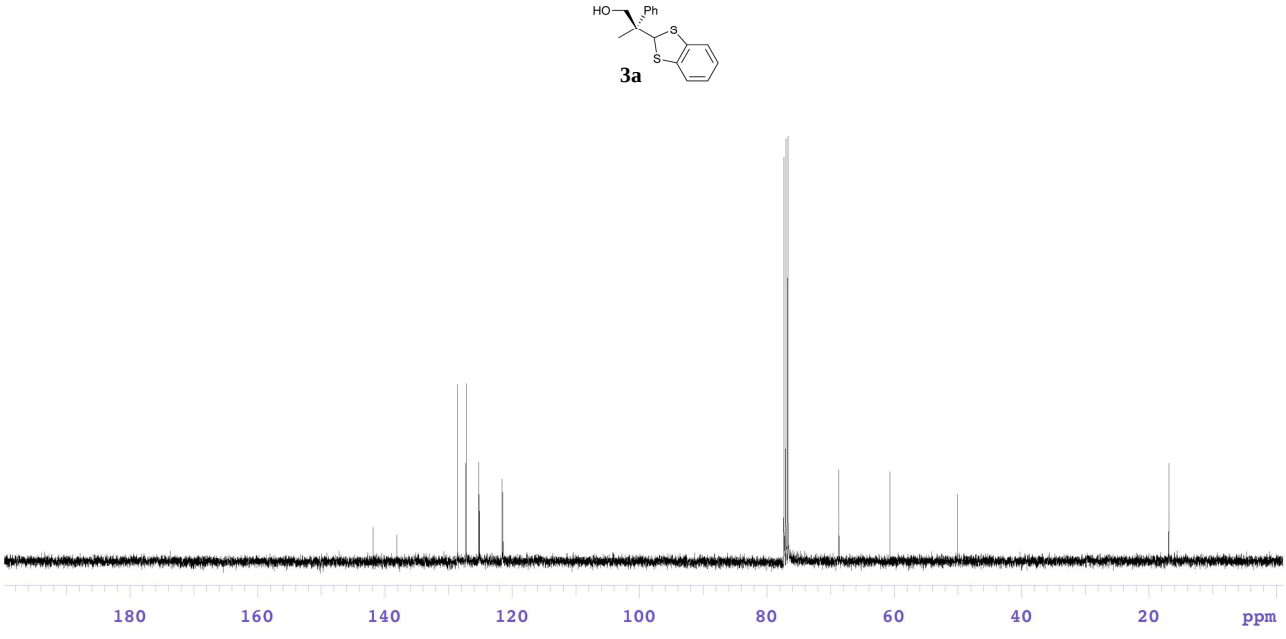
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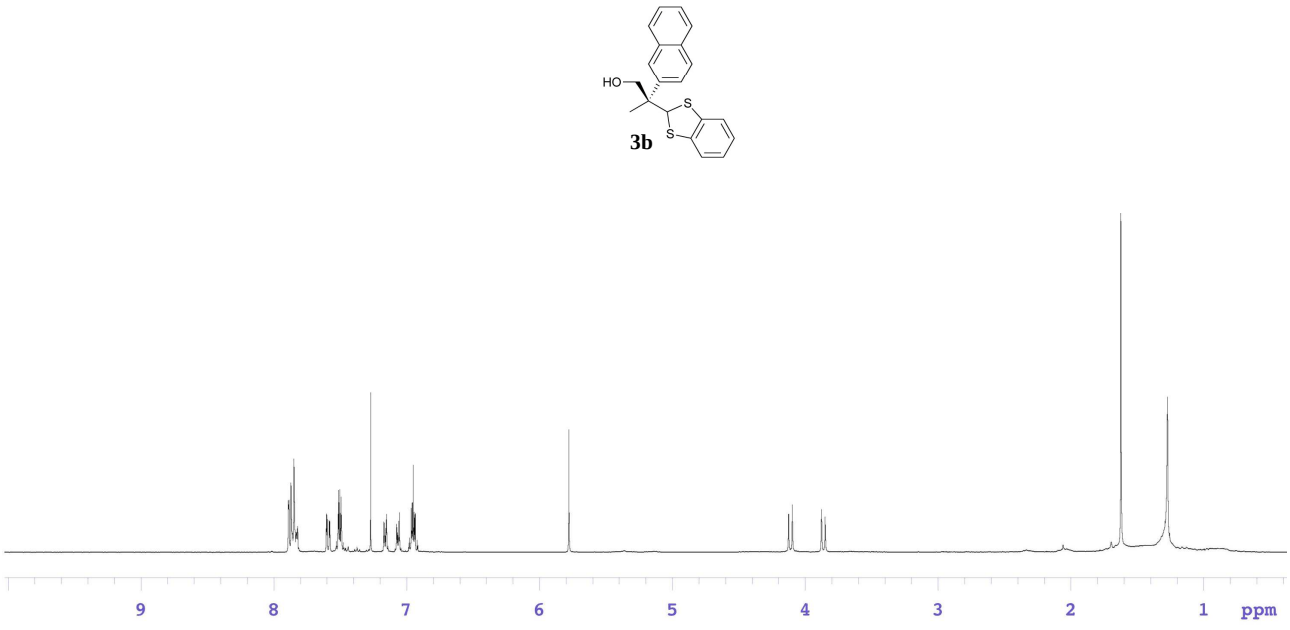
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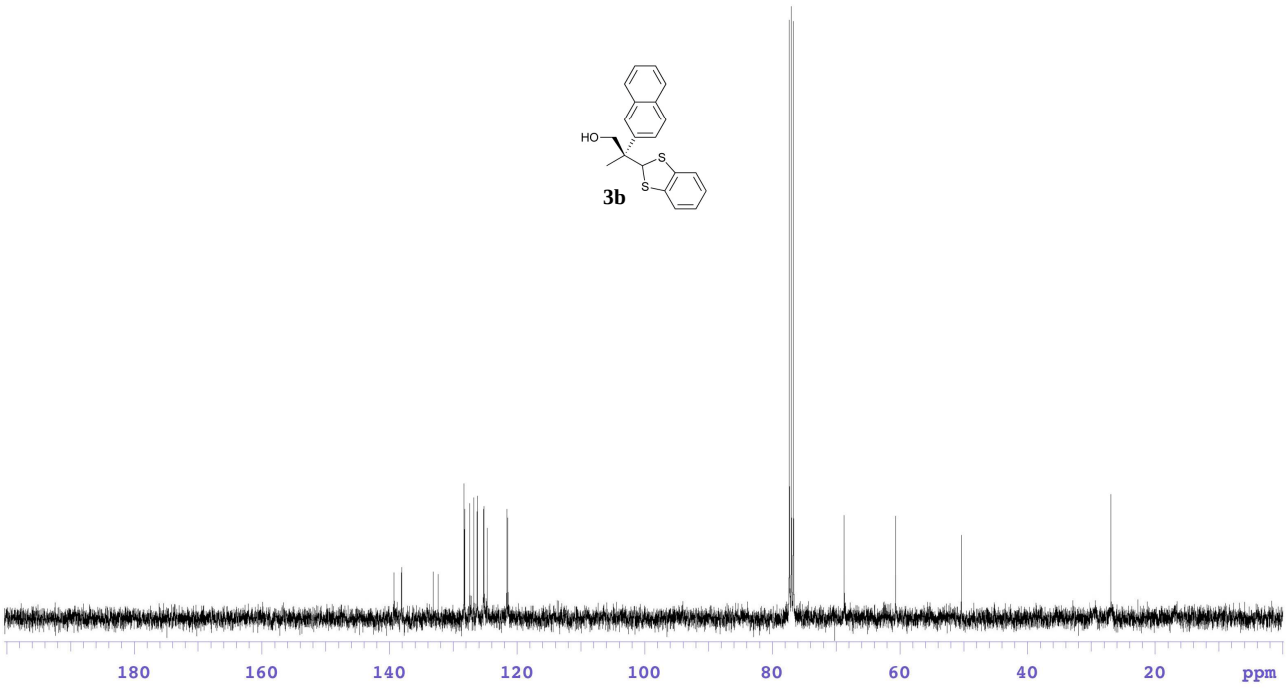
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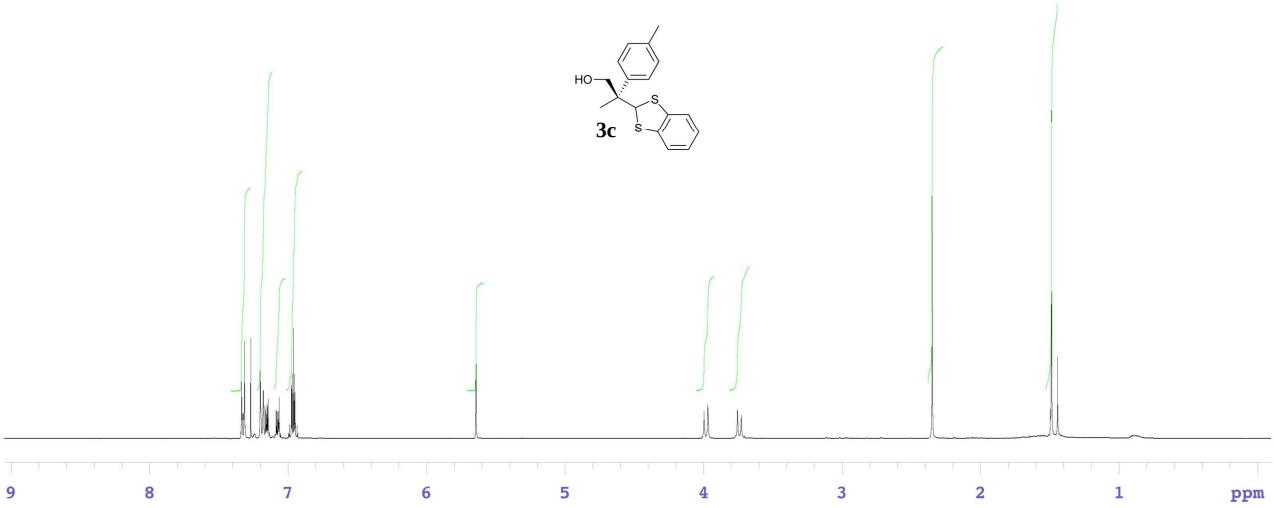
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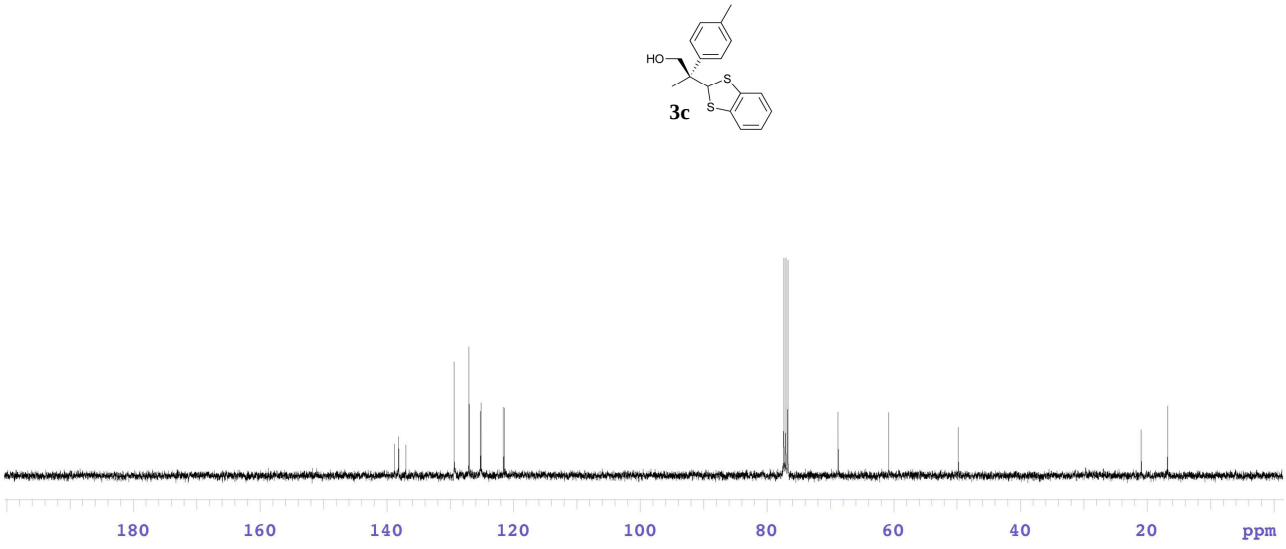
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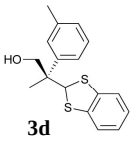

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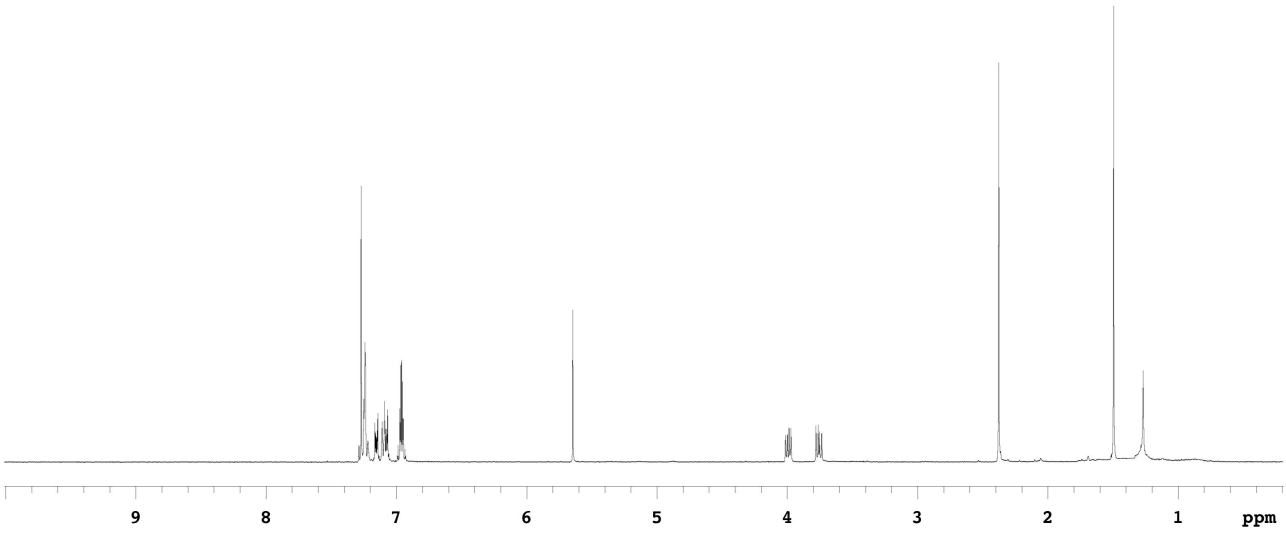

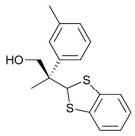

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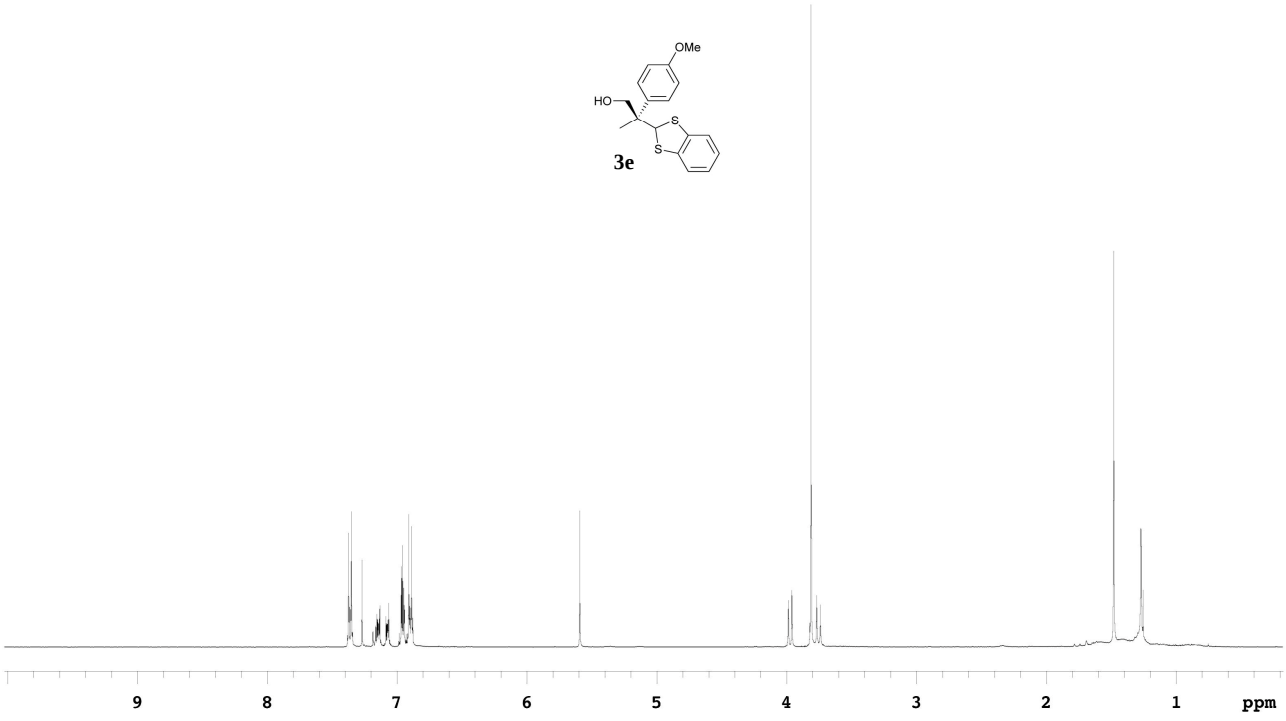

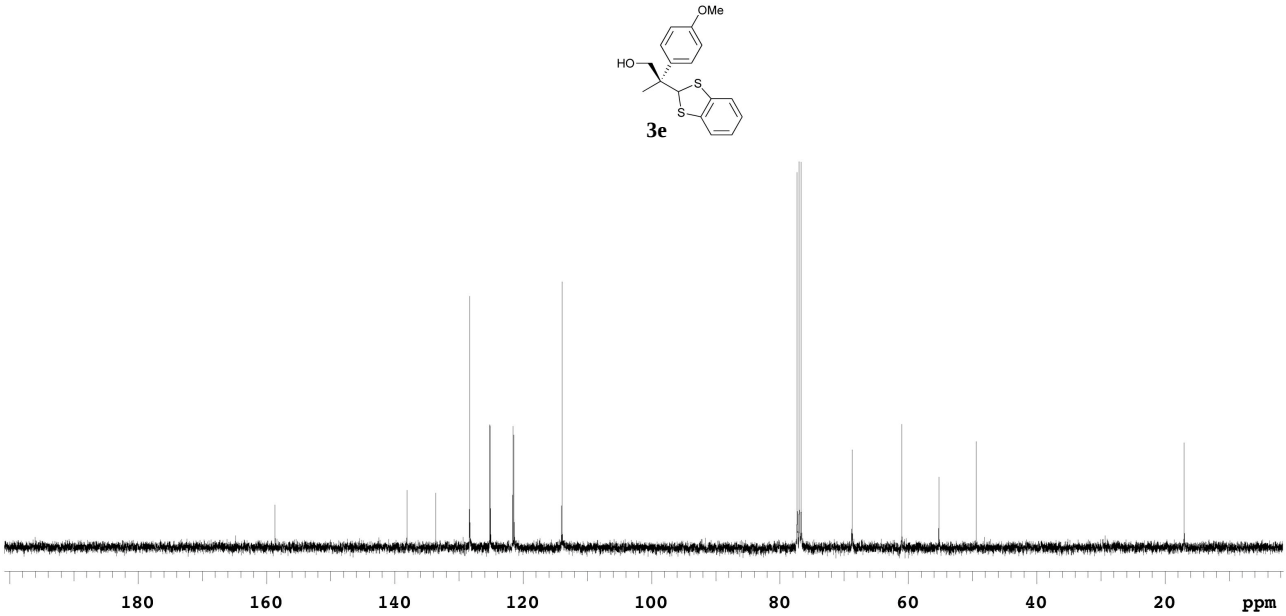

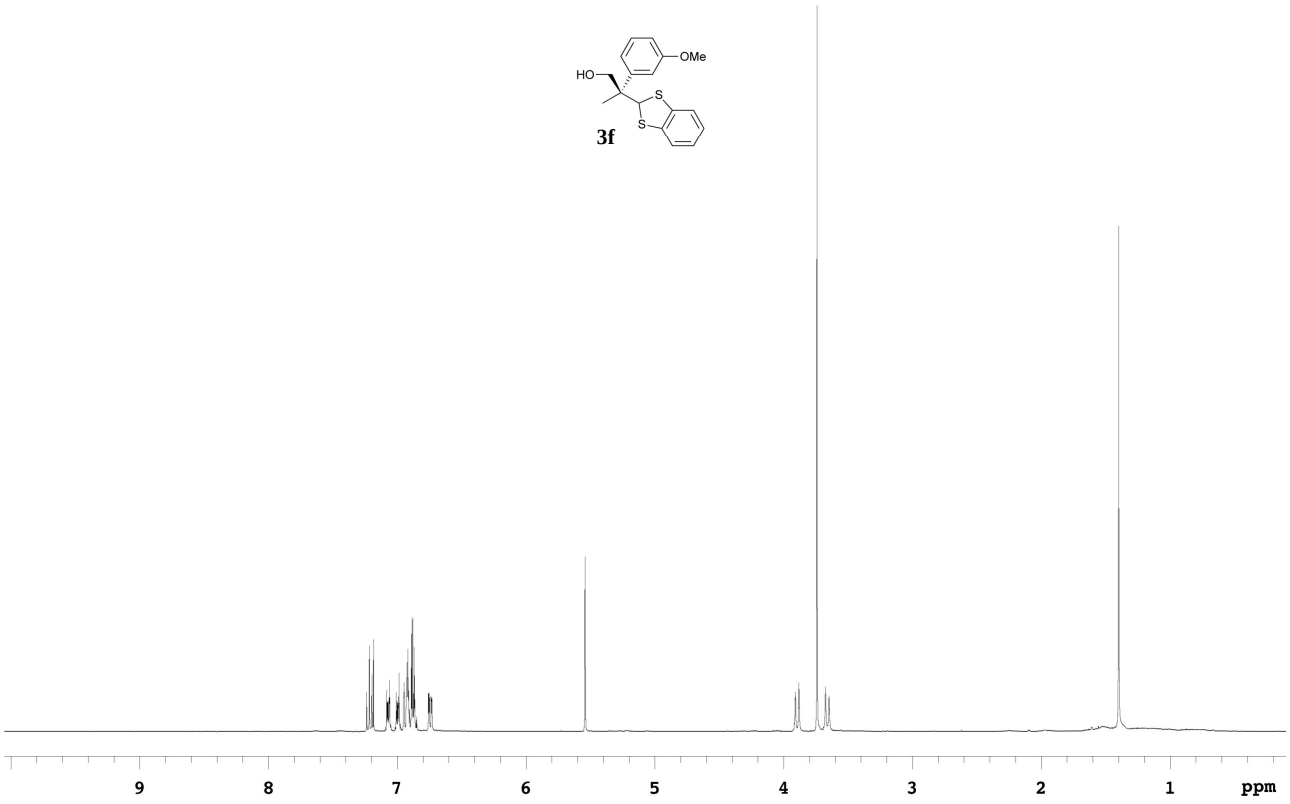
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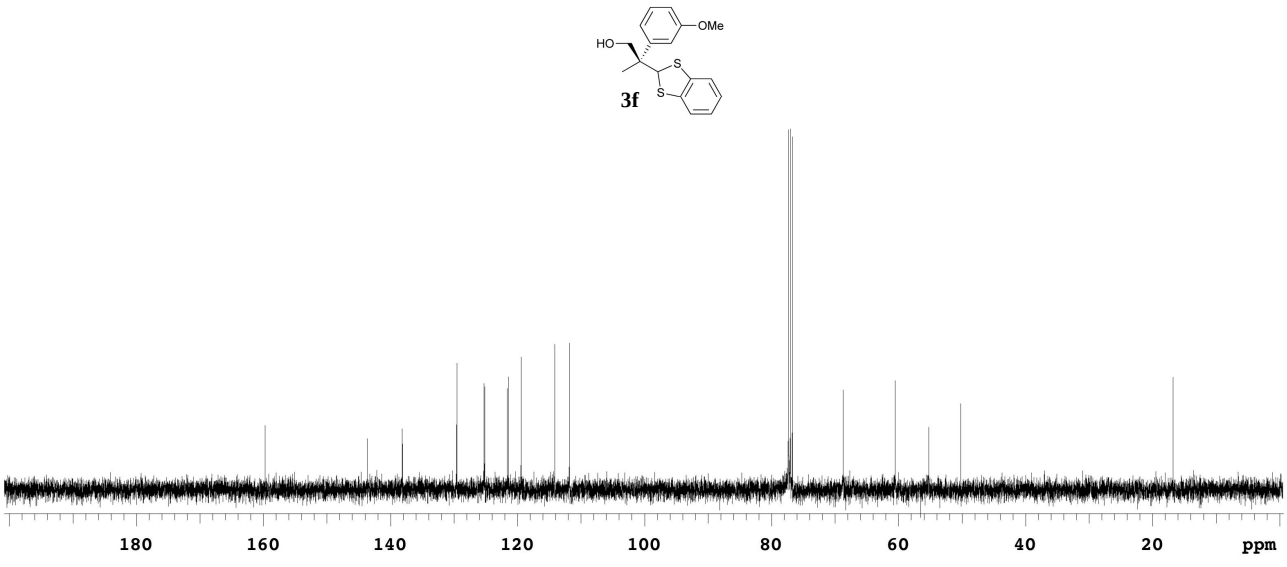
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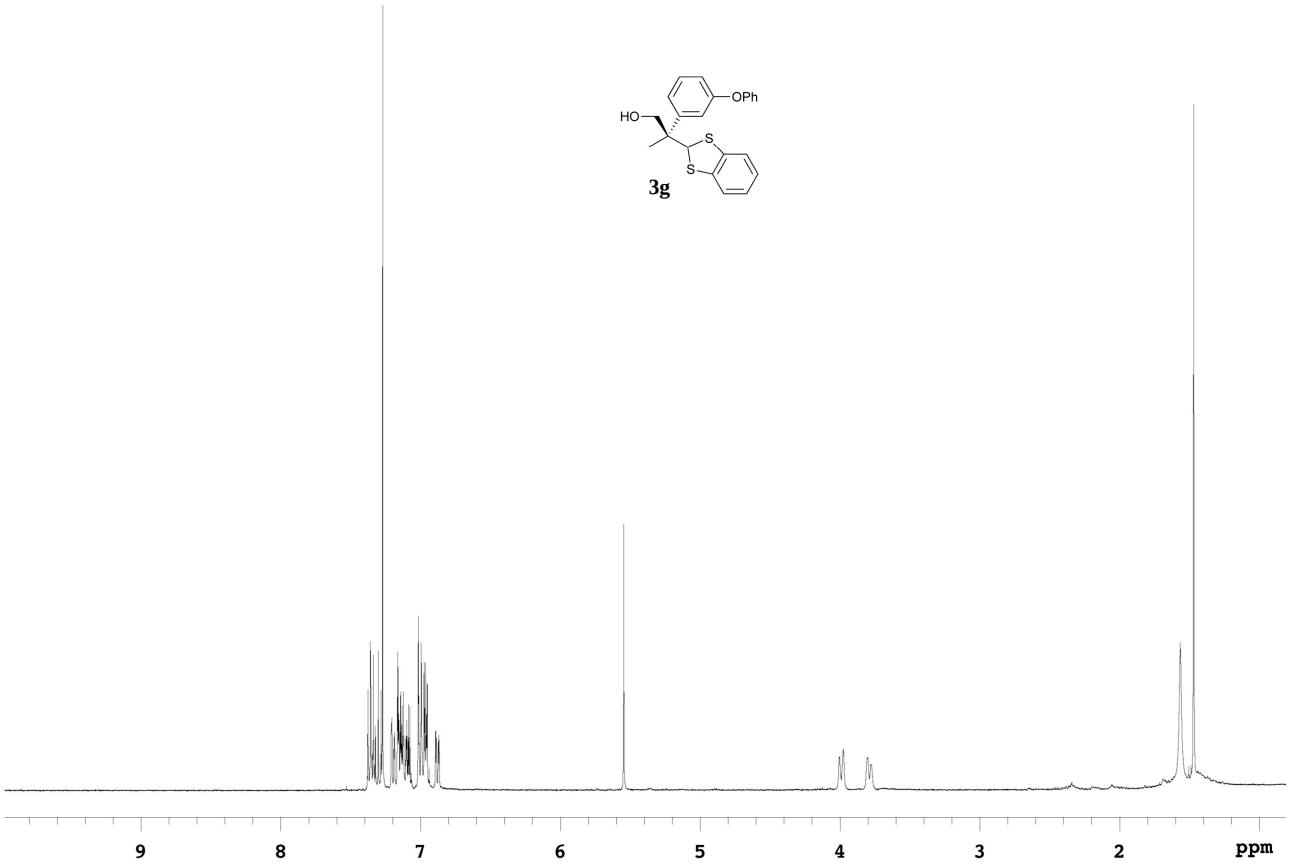
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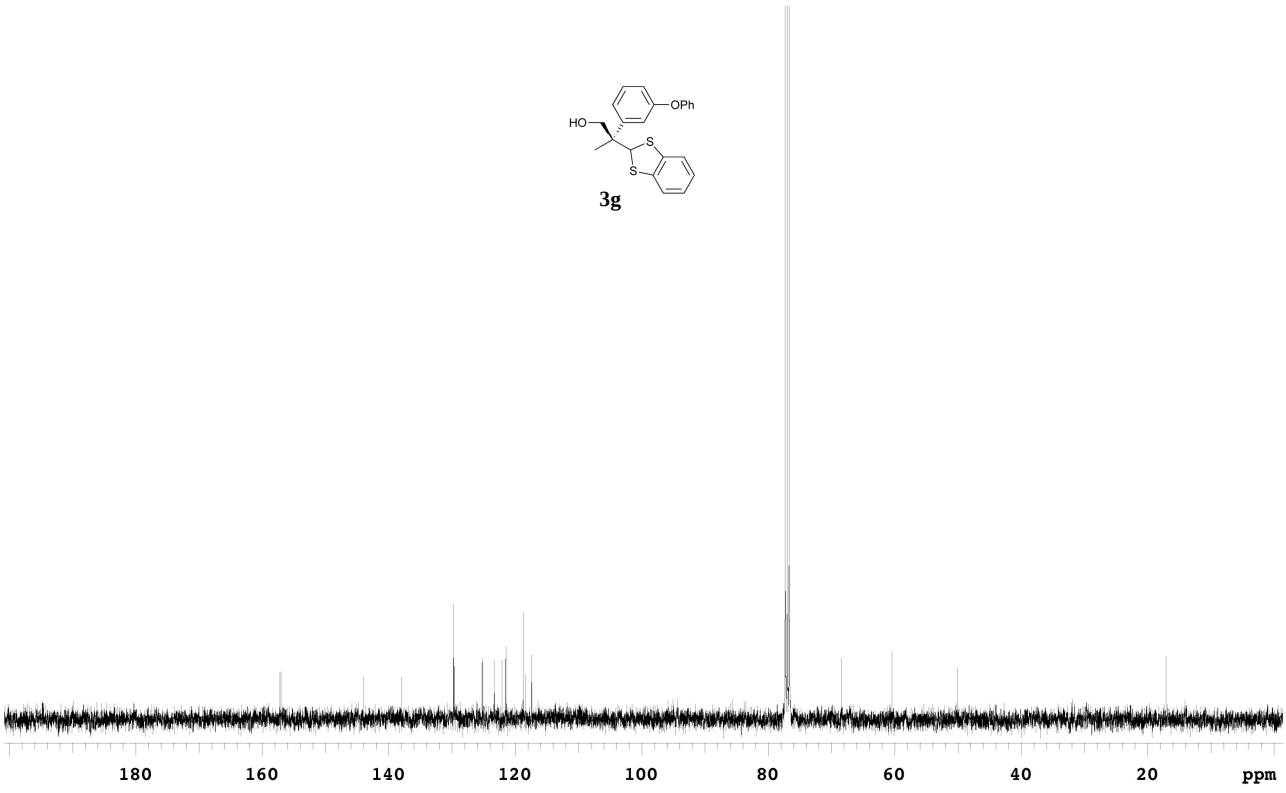
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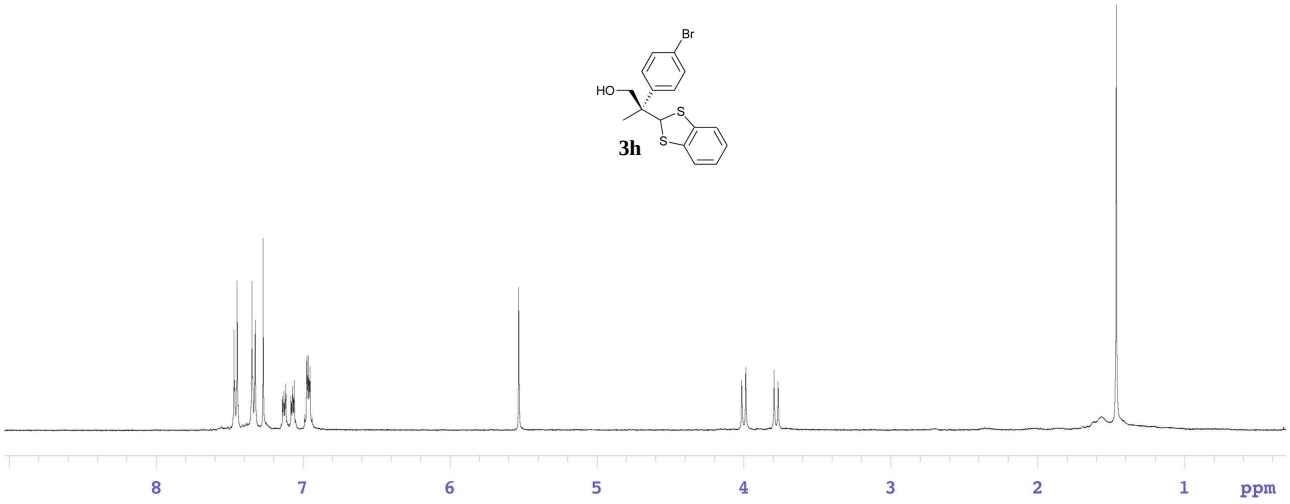
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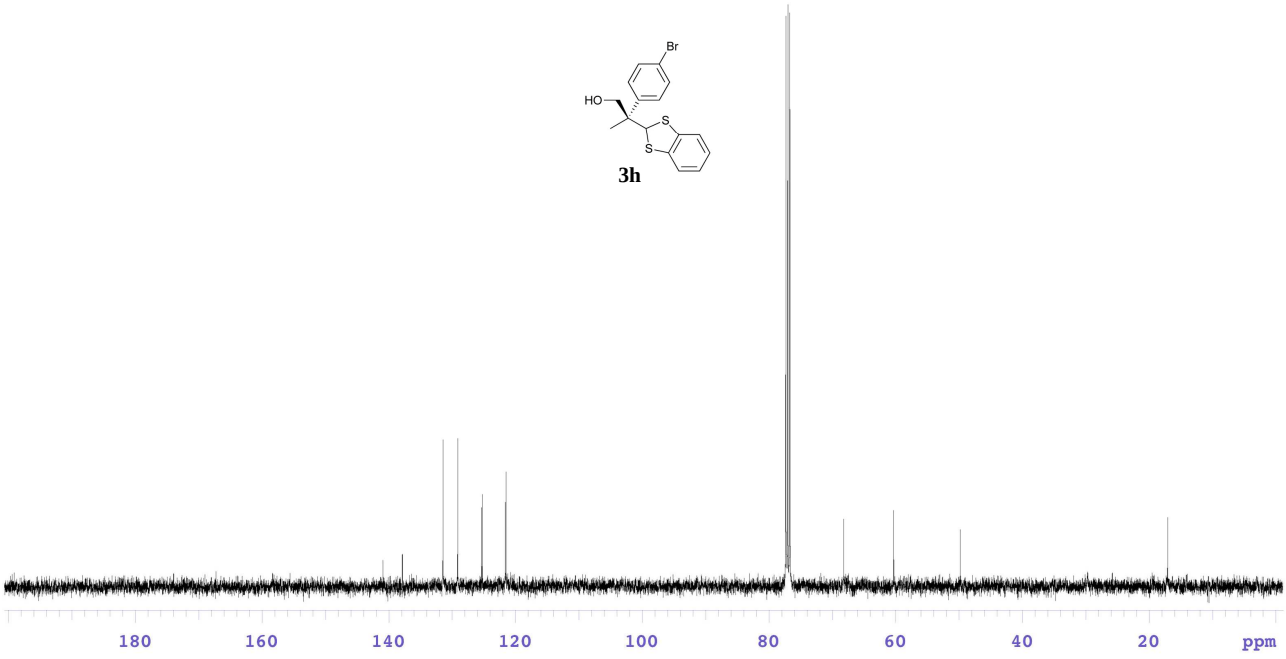
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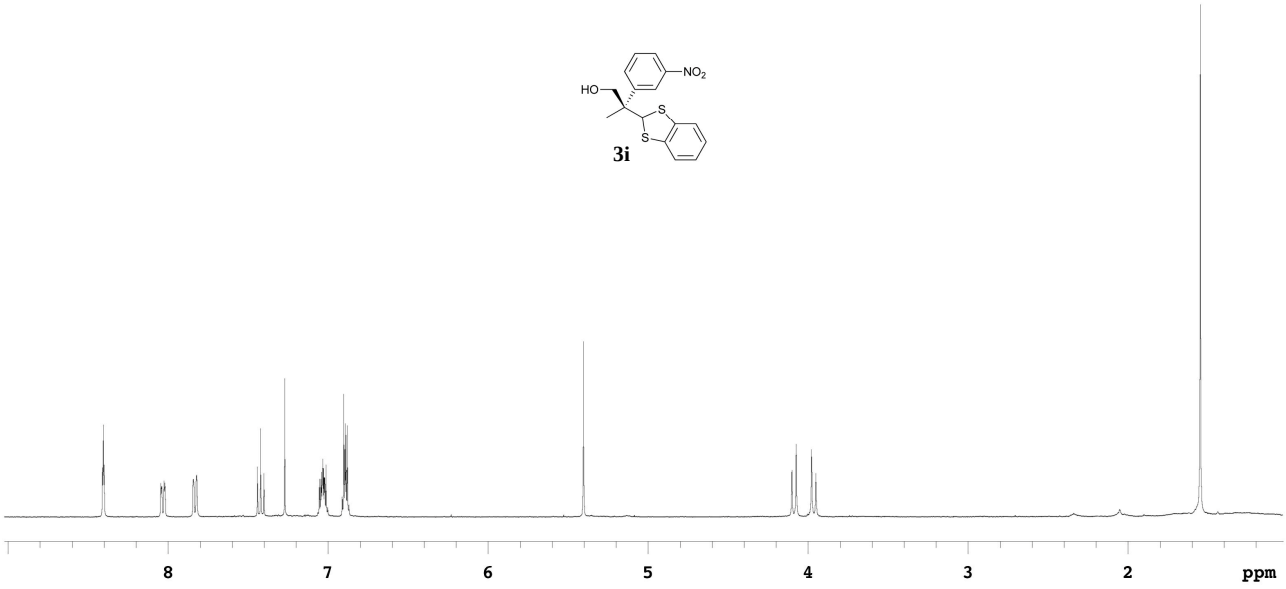
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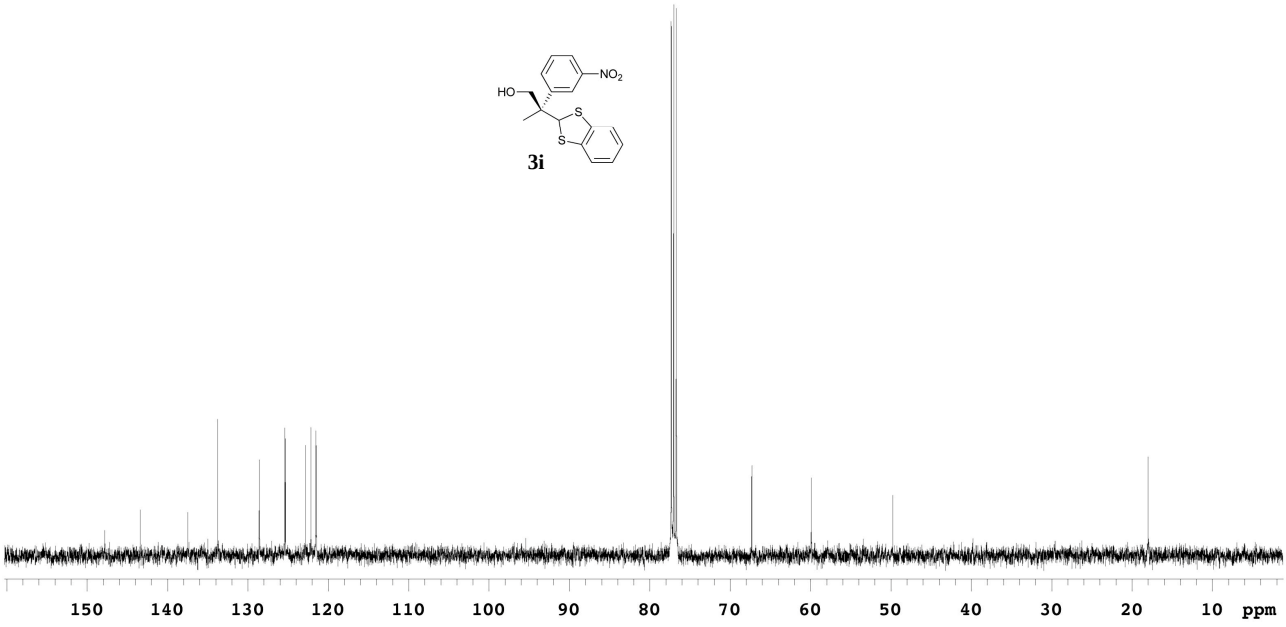
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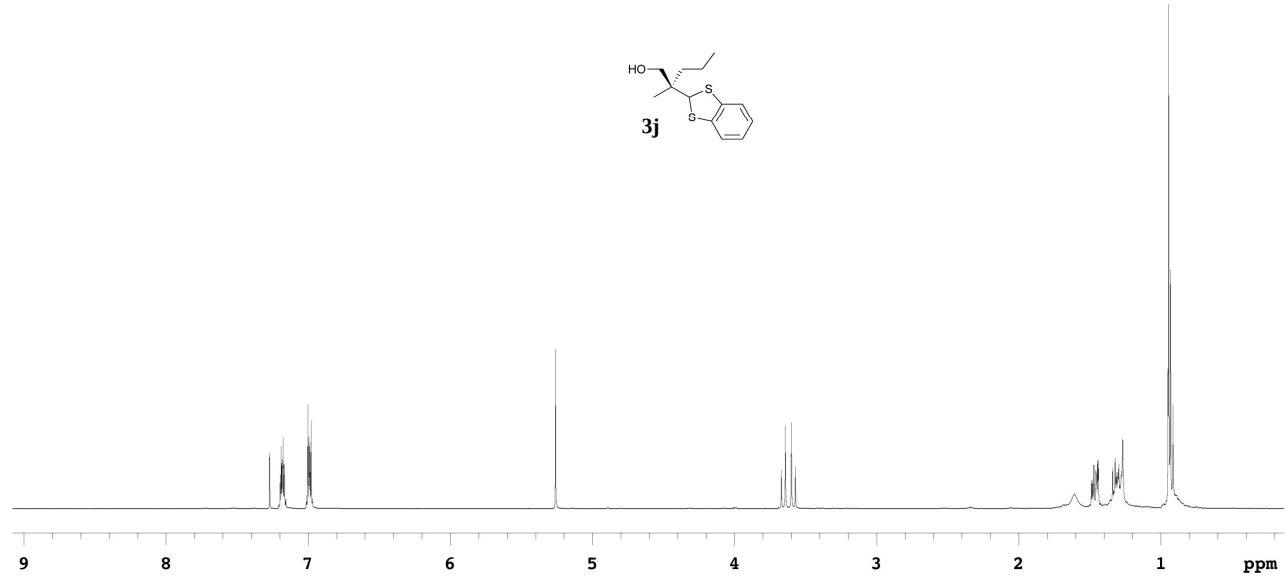
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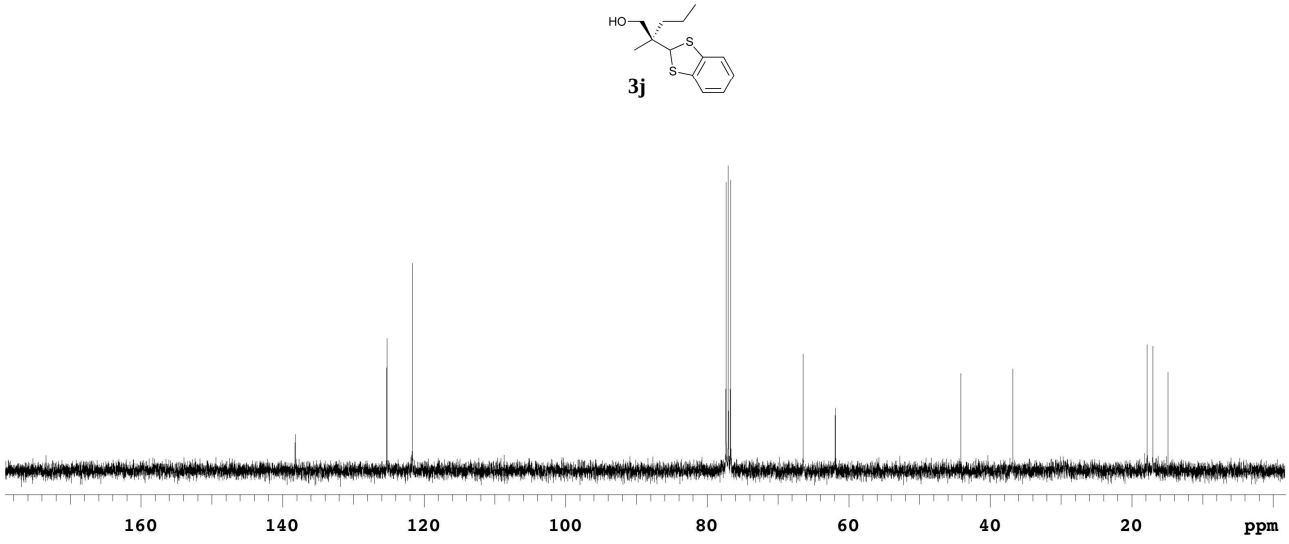
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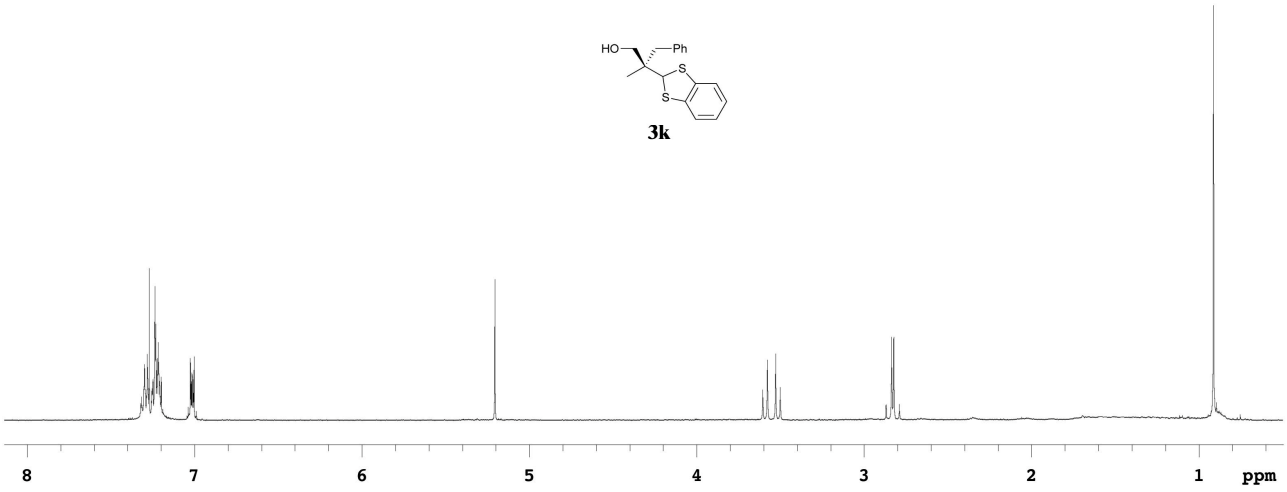
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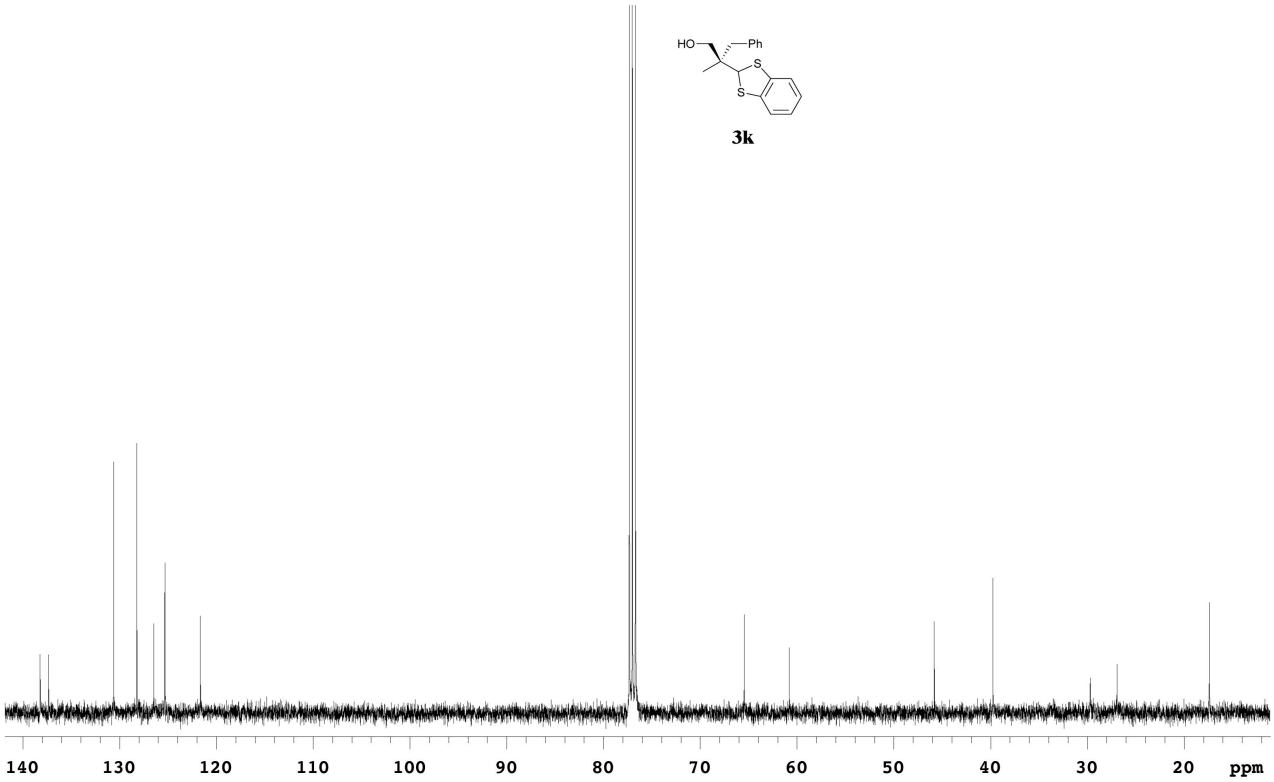
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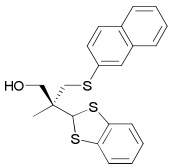

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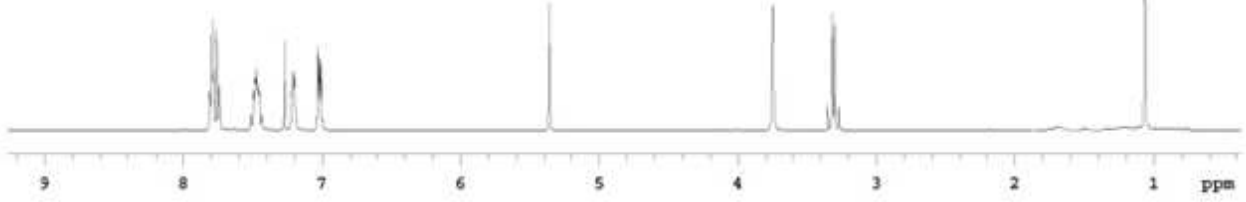

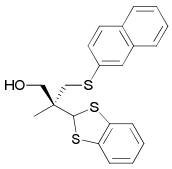

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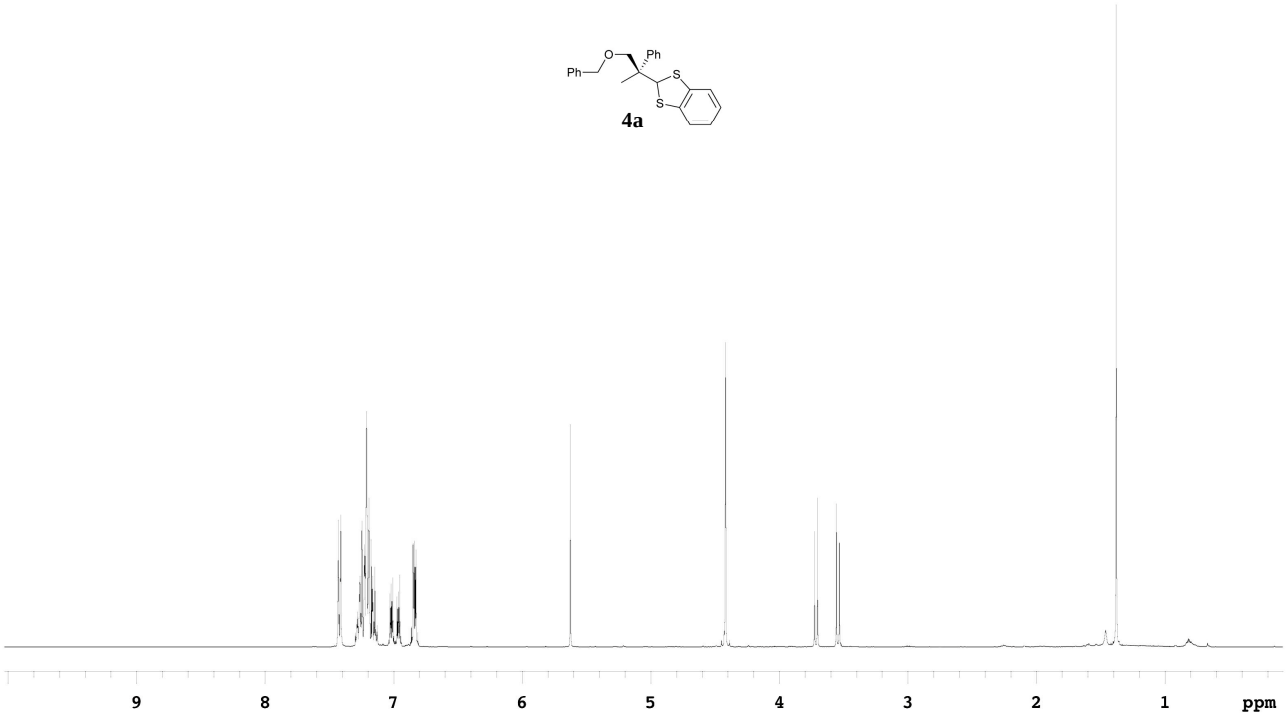
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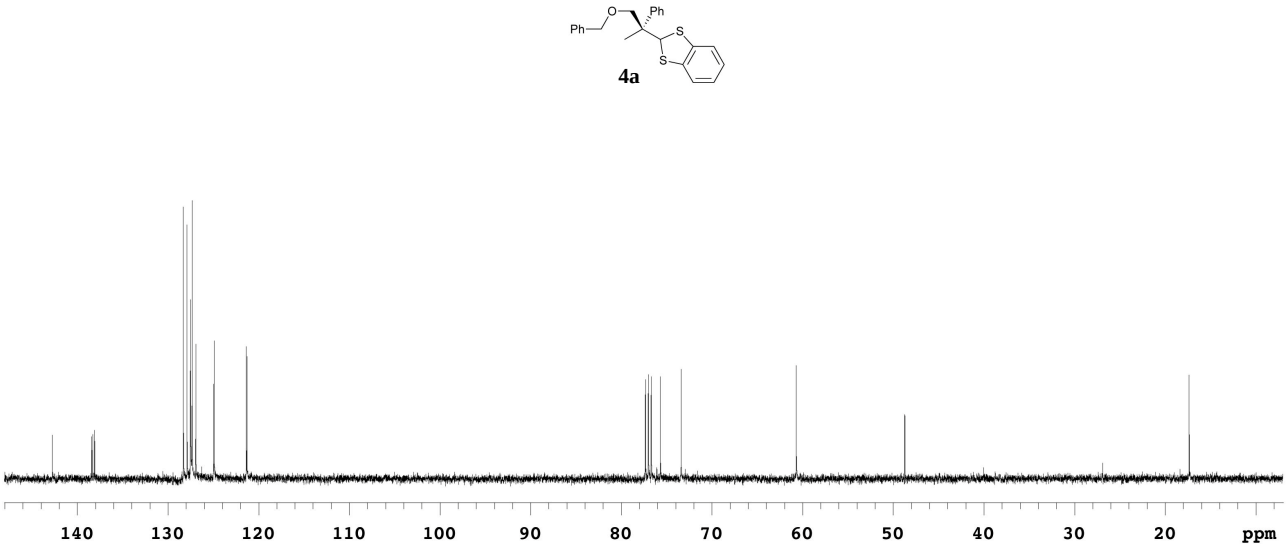
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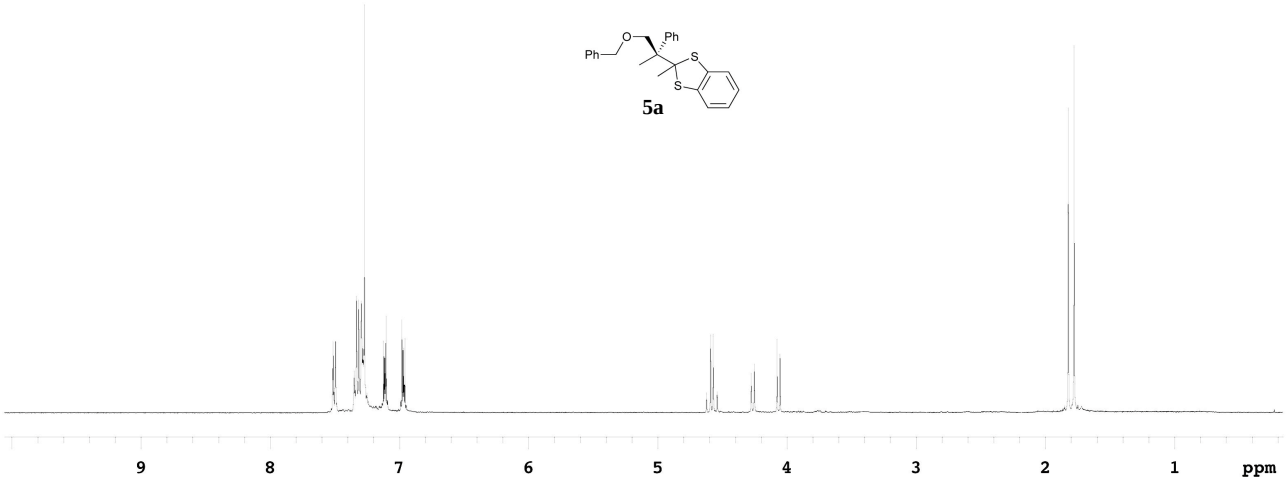
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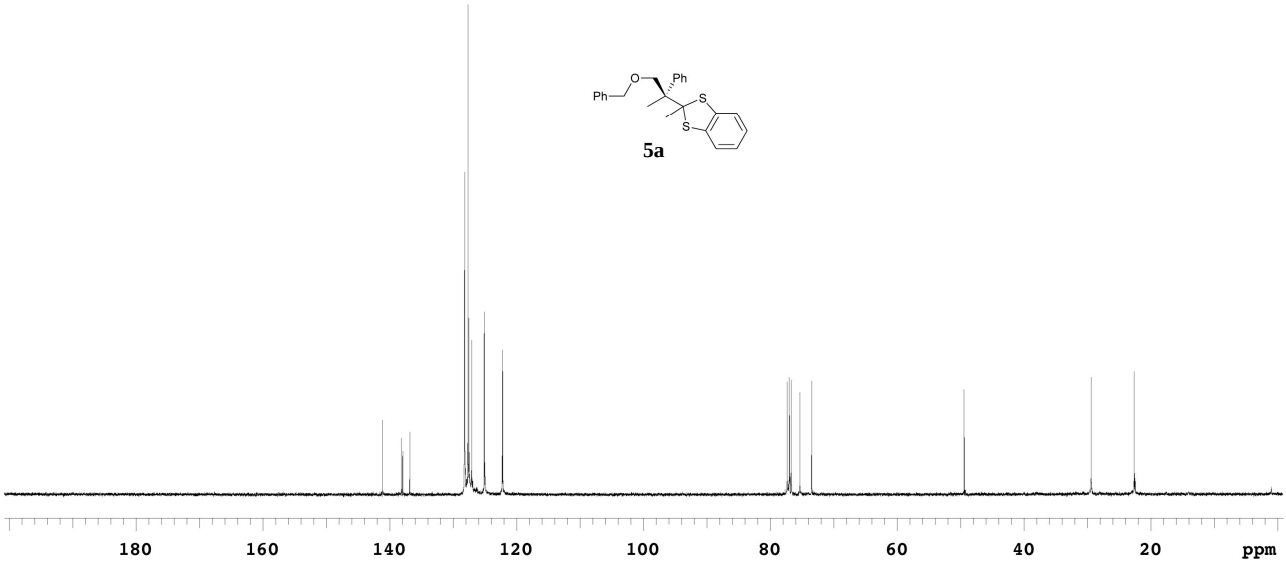
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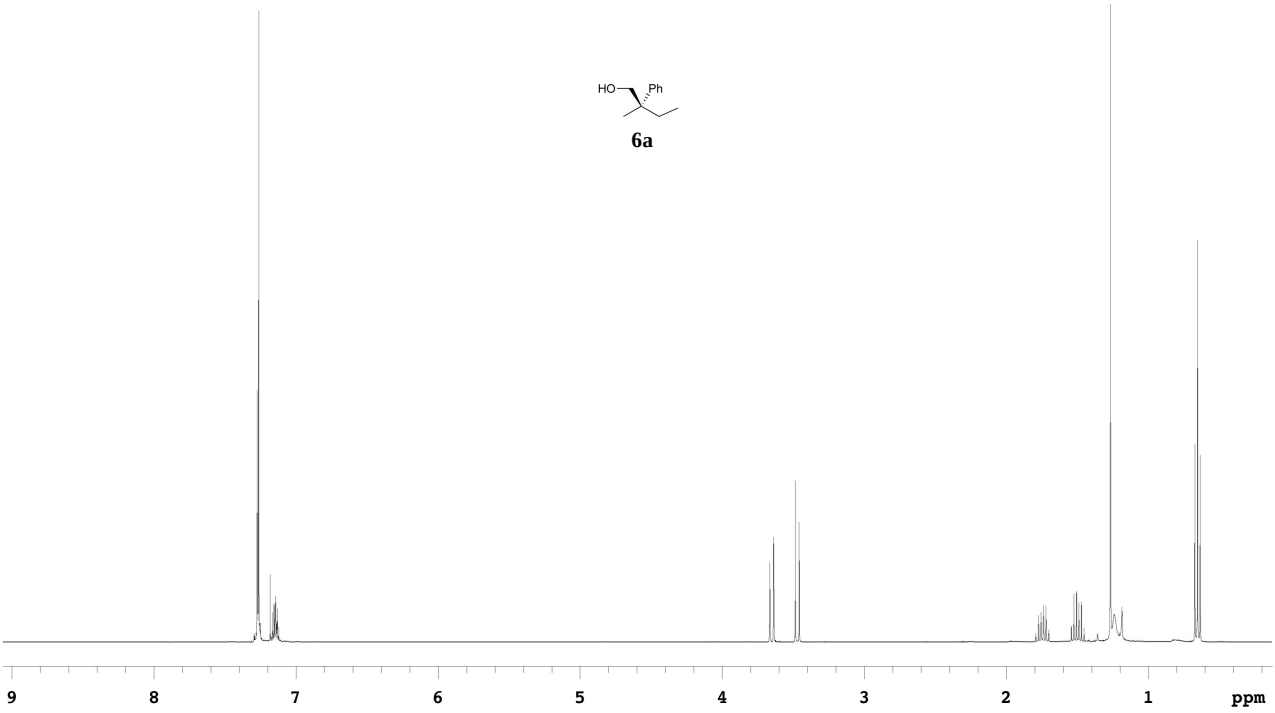
5a



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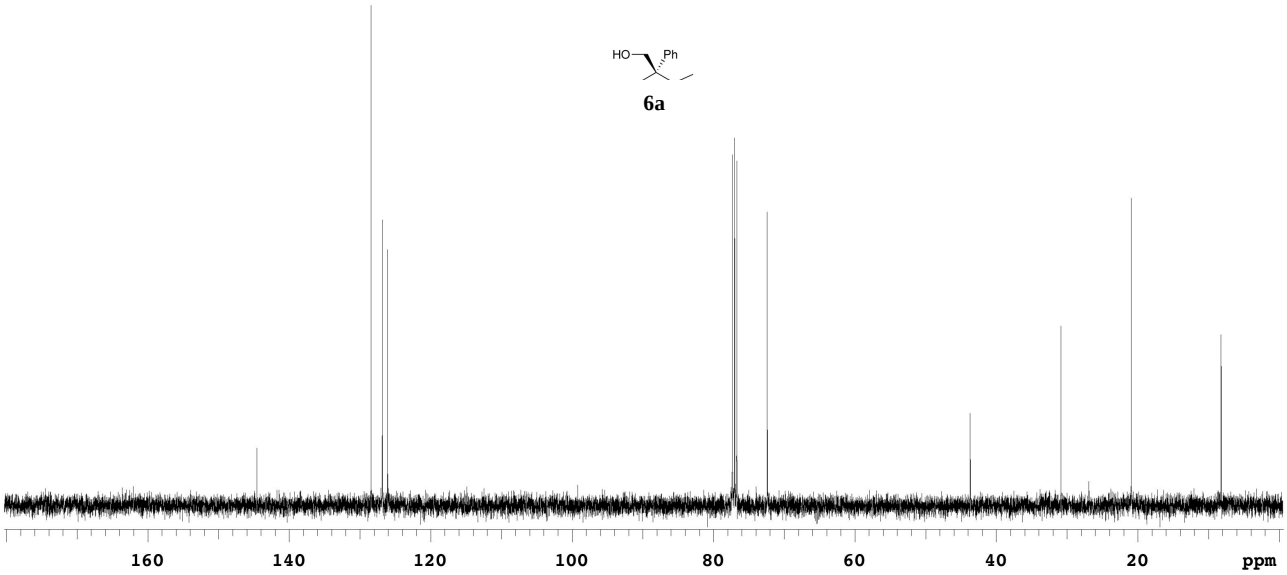

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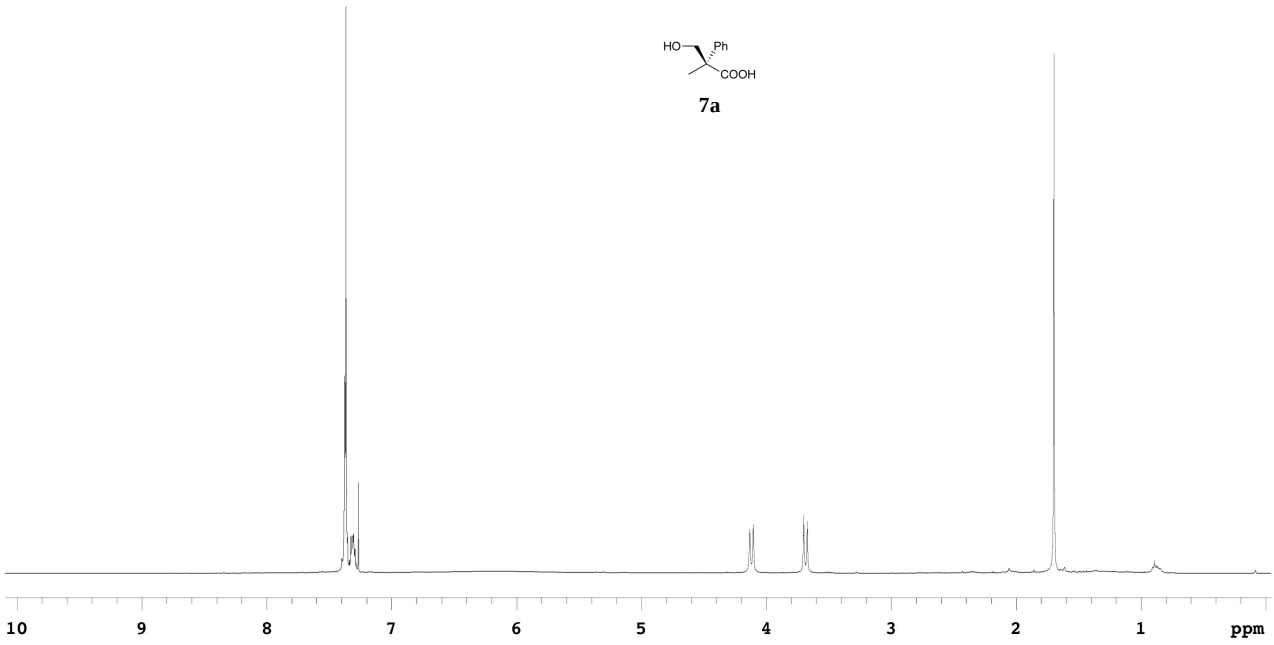

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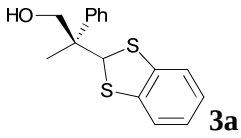
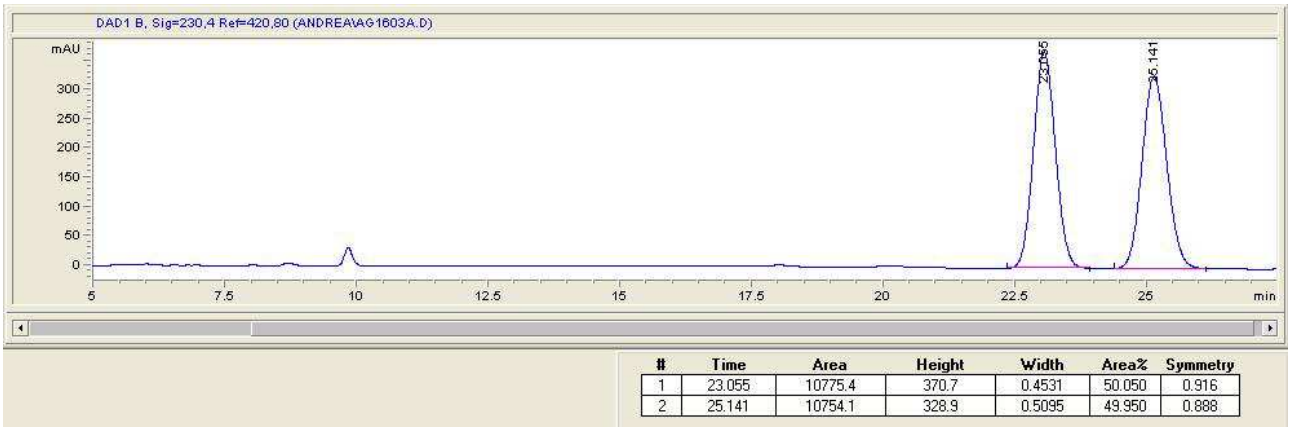
HPLC Traces



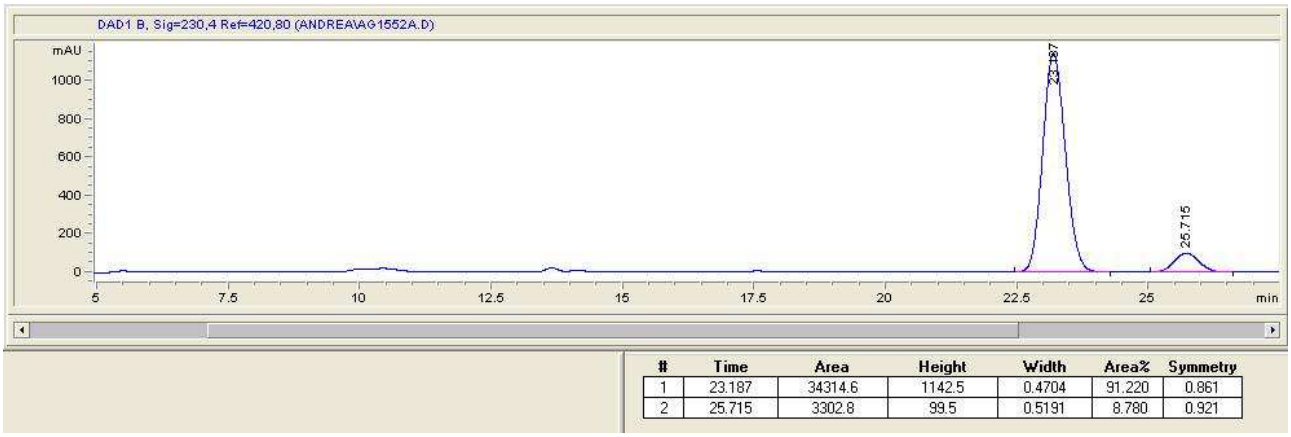
3a

Racemic



#	Time	Area	Height	Width	Area%	Symmetry
1	23.055	10775.4	370.7	0.4531	50.050	0.916
2	25.141	10754.1	328.9	0.5095	49.950	0.888

Enantioselective



#	Time	Area	Height	Width	Area%	Symmetry
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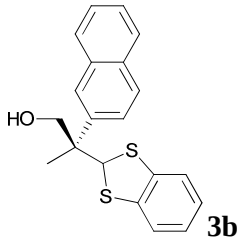
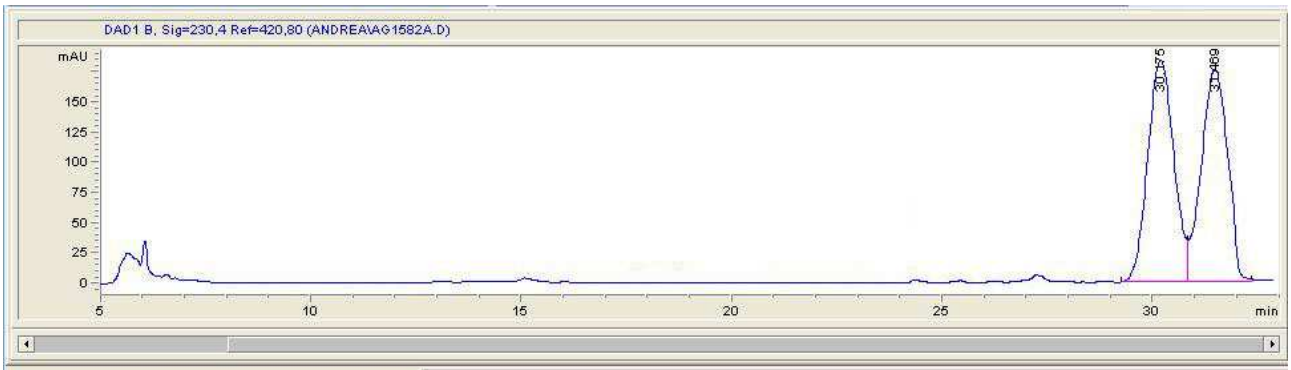
2	25.715	3302.8	99.5	0.5191	8.780	0.921



3b

Racemic



#	Time	Area	Height	Width	Area%	Symmetry
1	30.175	7953.7	184.2	0.6738	51.267	0.918
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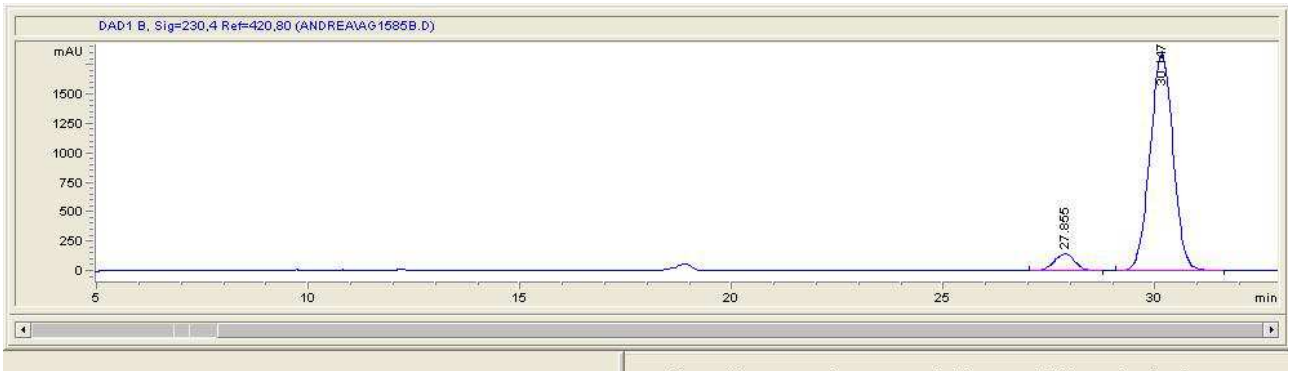
Enantioselective



#	Time	Area	Height	Width	Area%	Symmetry
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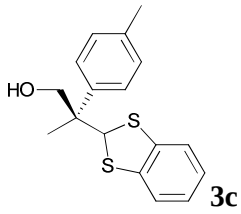
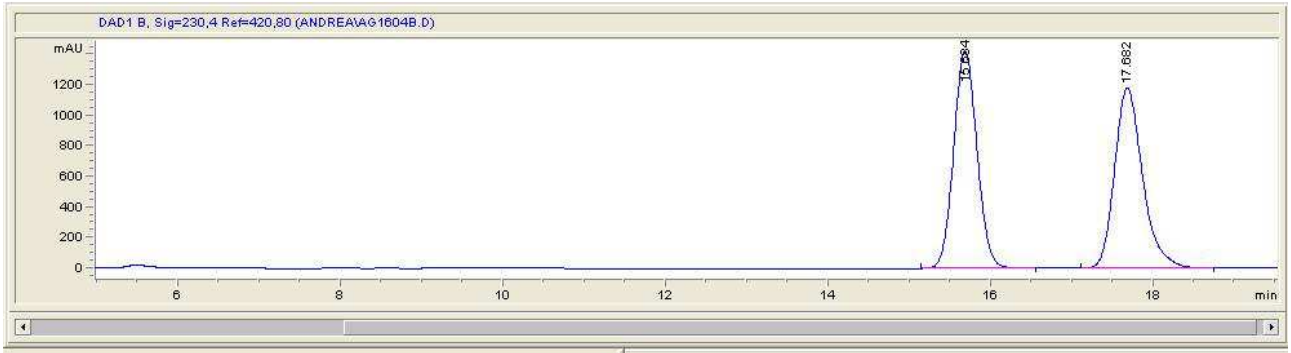
2	30.147	69852.9	1837.3	0.5916	93.399	1.025



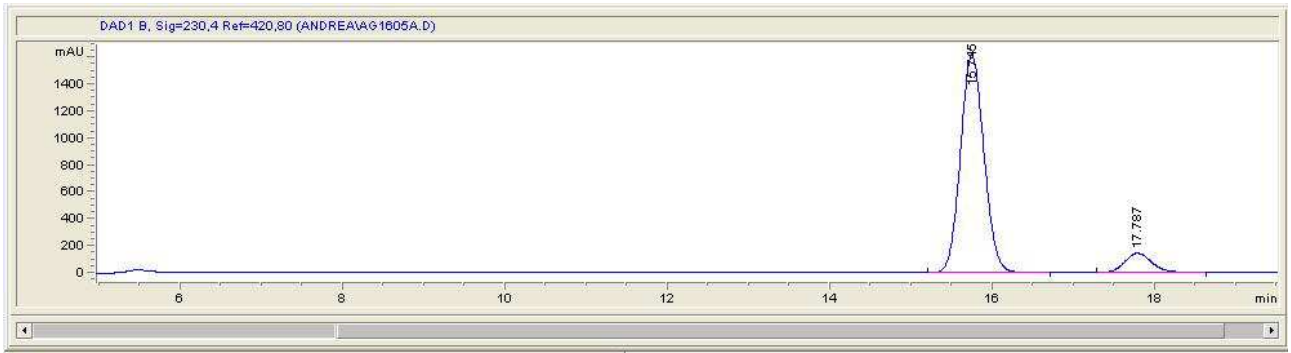
3c

Racemic



#	Time	Area	Height	Width	Area%	Symmetry
1	15.684	28365.3	1421.5	0.3108	50.081	0.902
2	17.682	28274	1178.9	0.3678	49.919	0.774

Ennatioselective



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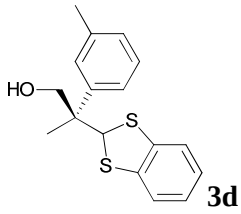
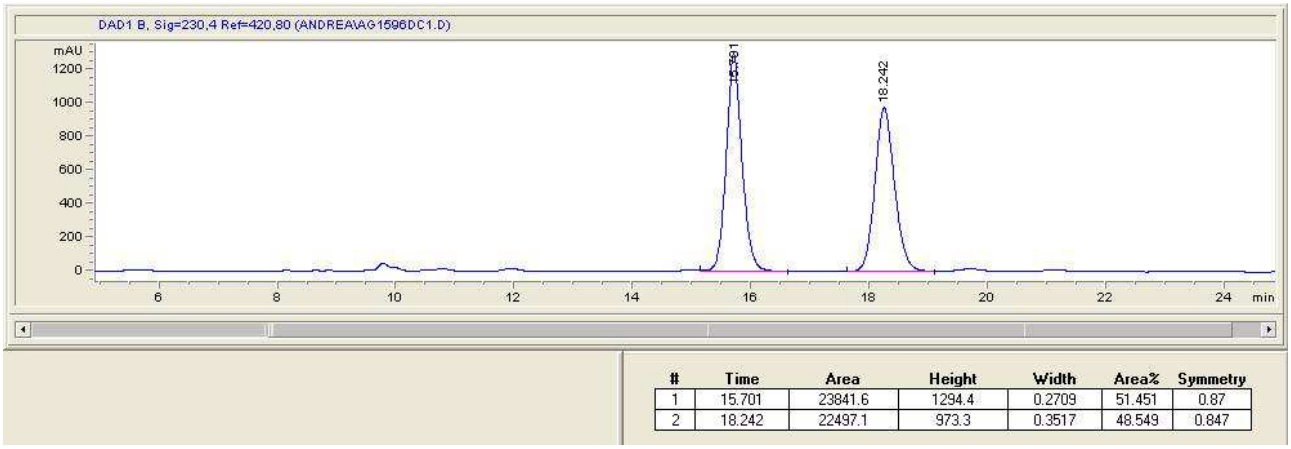
1	15.745	32581.1	1620.6	0.3126	90.499	0.893
2	17.787	3420.6	144.6	0.362	9.501	0.834



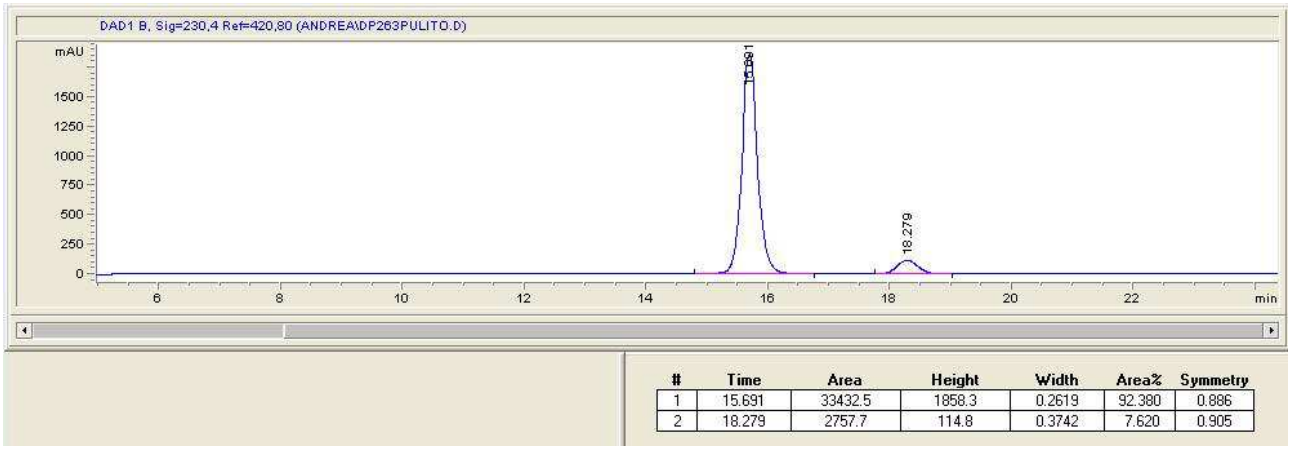
3d

Racemic

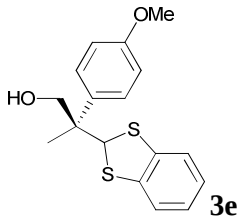


#	Time	Area	Height	Width	Area%	Symmetry
1	15.701	23841.6	1294.4	0.2709	51.451	0.87
2	18.242	22497.1	973.3	0.3517	48.549	0.847

Enantioselective

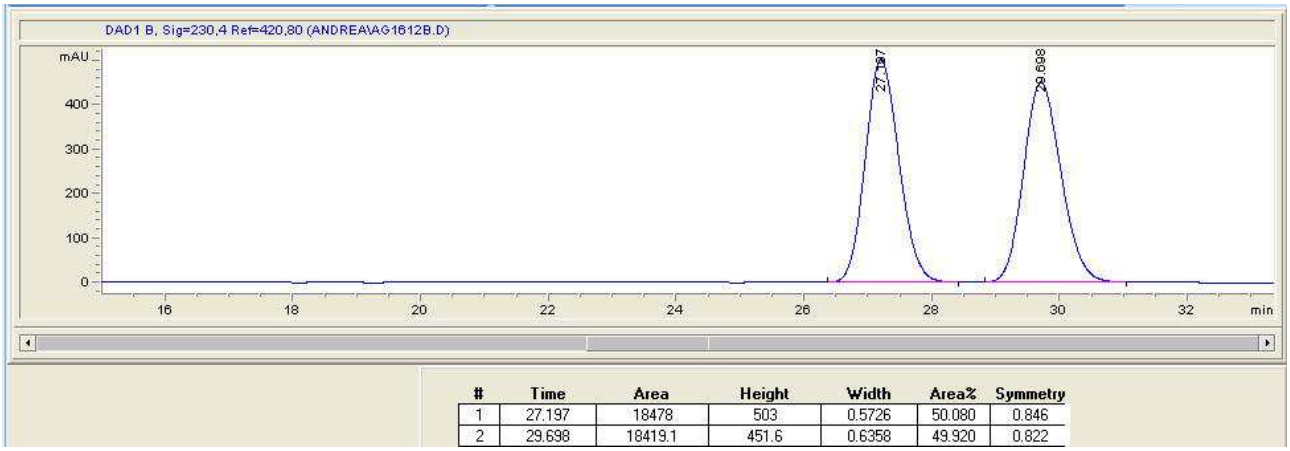


#	Time	Area	Height	Width	Area%	Symmetry
1	15.691	33432.5	1858.3	0.2619	92.380	0.886
2	18.279	2757.7	114.8	0.3742	7.620	0.905



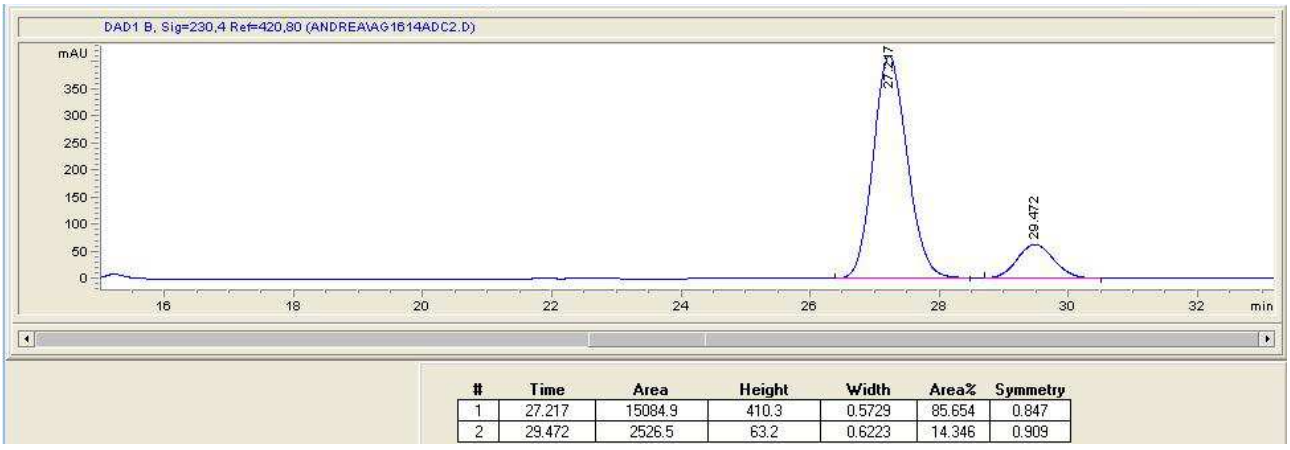
3e

Racemic

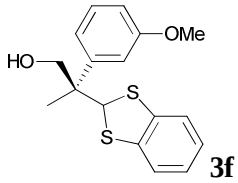


#	Time	Area	Height	Width	Area%	Symmetry
1	27.197	18478	503	0.5726	50.080	0.846
2	29.698	18419.1	451.6	0.6358	49.920	0.822

Enantioselective

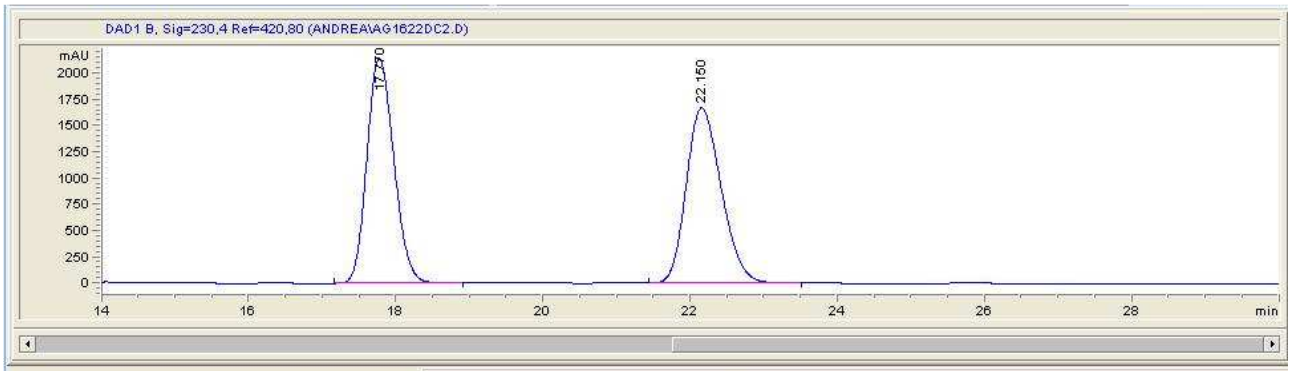


#	Time	Area	Height	Width	Area%	Symmetry
1	27.217	15084.9	410.3	0.5729	85.654	0.847
2	29.472	2526.5	63.2	0.6223	14.346	0.909



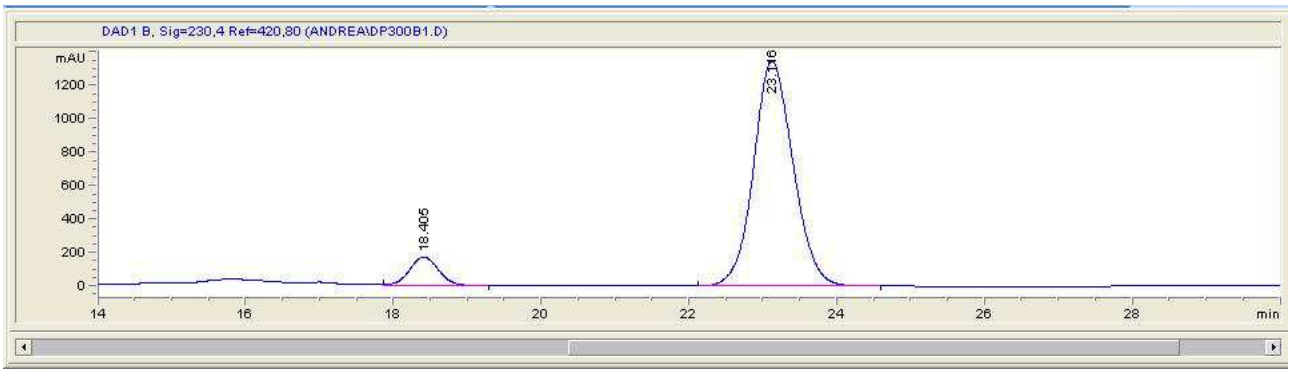
3f

Racemic

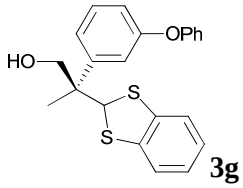


#	Time	Area	Height	Width	Area%	Symmetry
1	17.77	54483.9	2139.7	0.3991	49.623	0.812
2	22.15	55311.4	1668.7	0.5167	50.377	0.75

Enantioselective

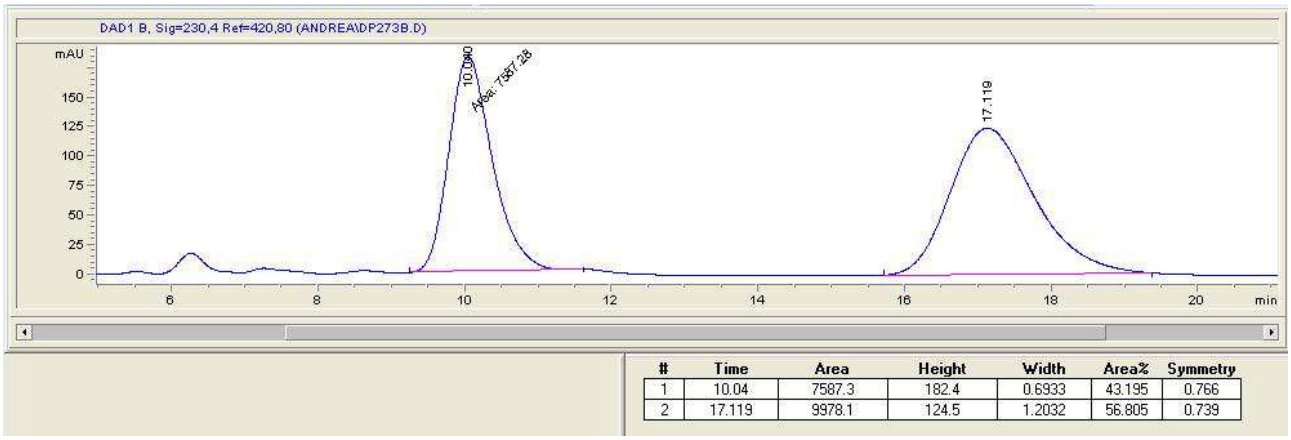


#	Time	Area	Height	Width	Area%	Symmetry
1	18.405	4767.7	172.5	0.4265	8.683	0.934
2	23.116	50138.8	1346.2	0.5725	91.317	0.838



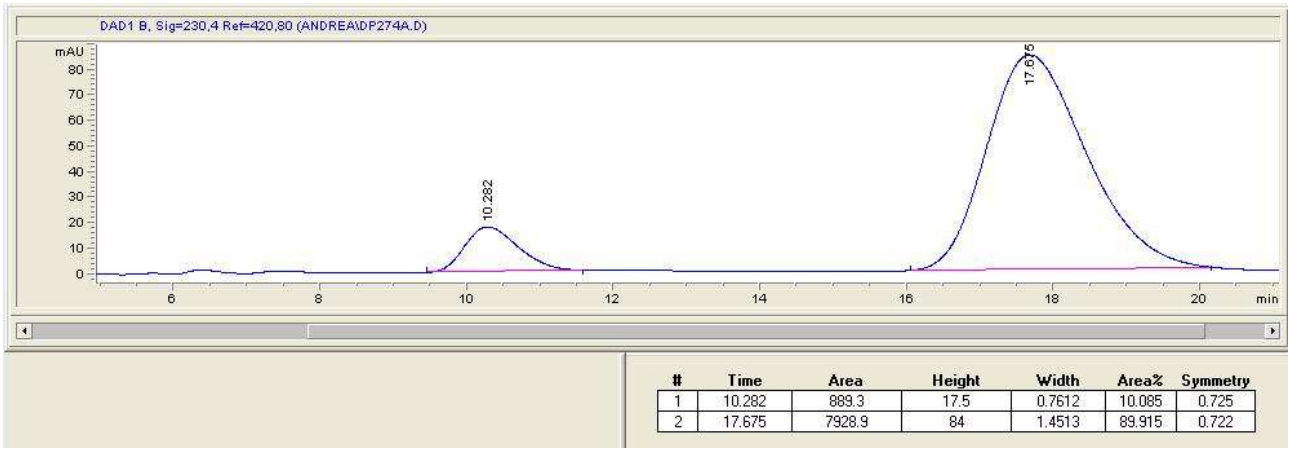
3g

Racemic

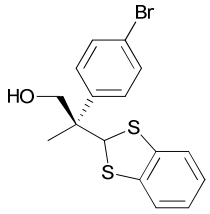


#	Time	Area	Height	Width	Area%	Symmetry
1	10.04	7587.3	182.4	0.6933	43.195	0.766
2	17.119	9978.1	124.5	1.2032	56.805	0.739

Enantioselective

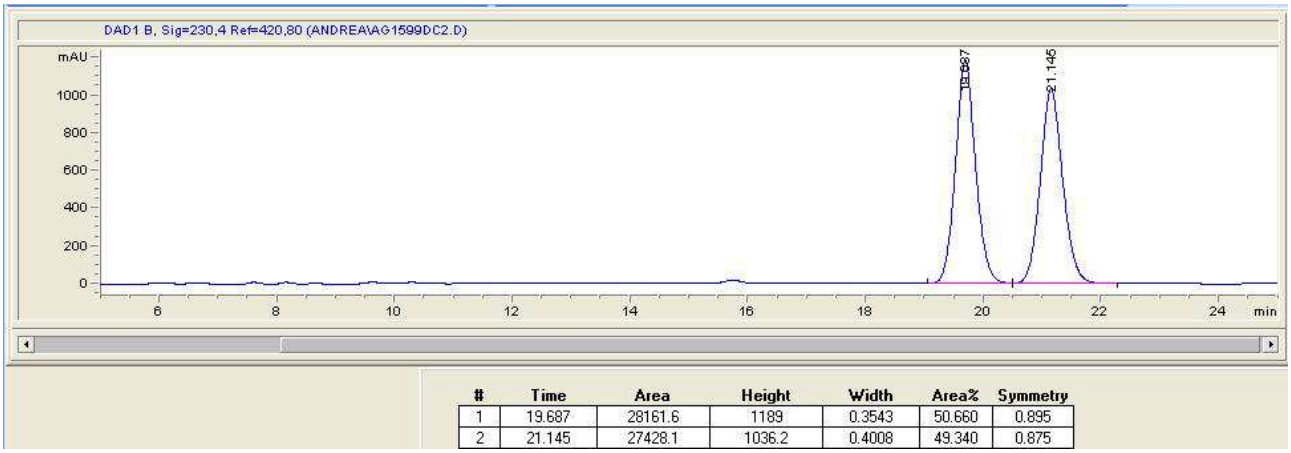


#	Time	Area	Height	Width	Area%	Symmetry
1	10.282	889.3	17.5	0.7612	10.085	0.725
2	17.675	7928.9	84	1.4513	89.915	0.722



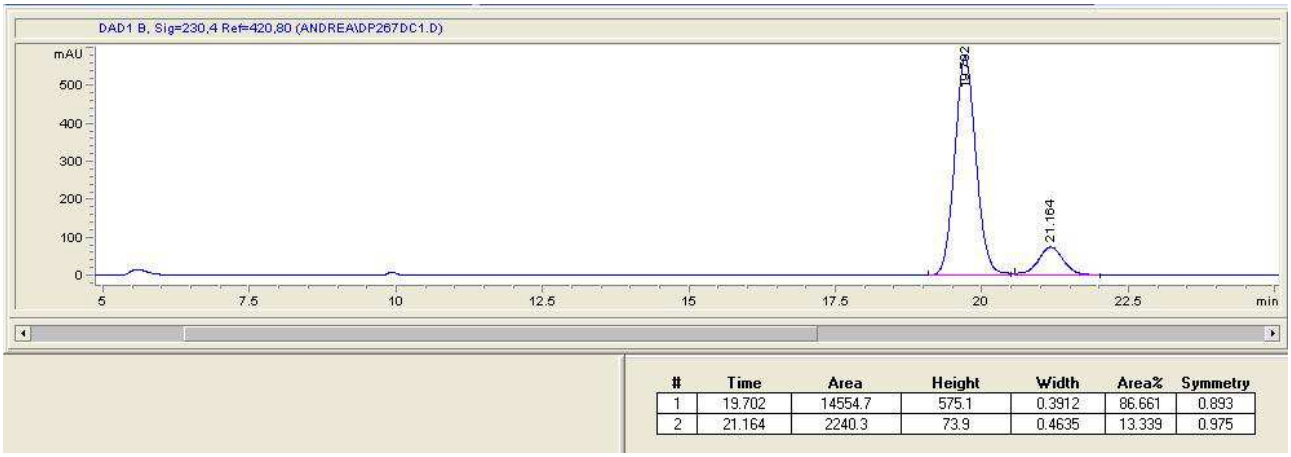
3h

Racemic

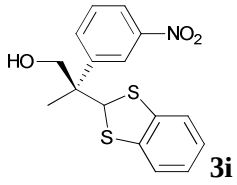


#	Time	Area	Height	Width	Area%	Symmetry
1	19.687	28161.6	1189	0.3543	50.660	0.895
2	21.145	27428.1	1036.2	0.4008	49.340	0.875

Enantioselective

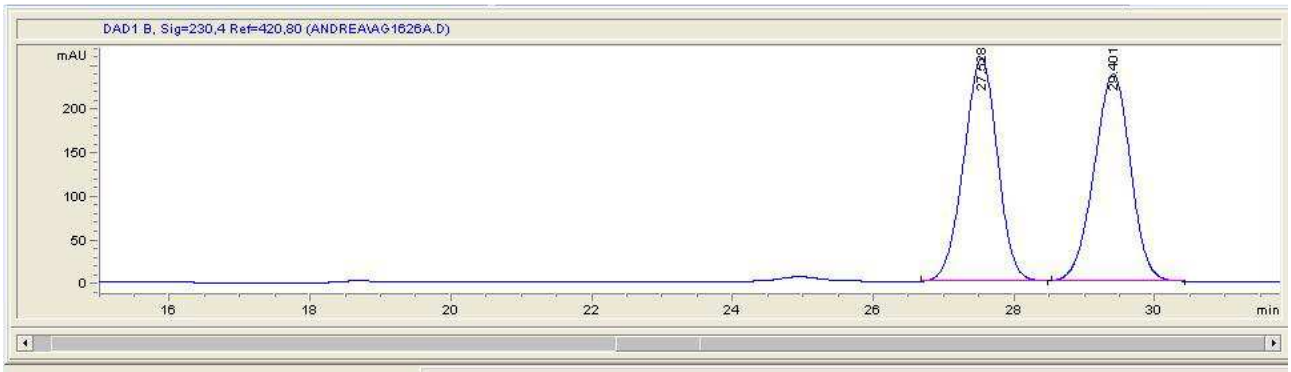


#	Time	Area	Height	Width	Area%	Symmetry
1	19.702	14554.7	575.1	0.3912	86.661	0.893
2	21.164	2240.3	73.9	0.4635	13.339	0.975



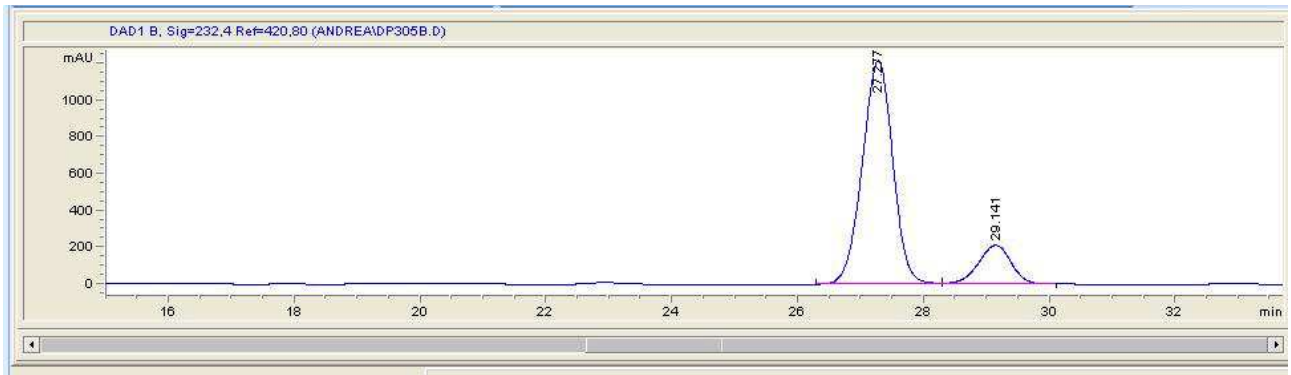
3i

Racemic

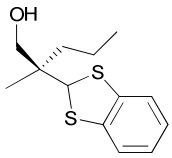


#	Time	Area	Height	Width	Area%	Symmetry
1	27.528	8603.7	255.9	0.5222	50.027	1.067
2	29.401	8594.6	238.3	0.5609	49.973	1.085

Enantioselective

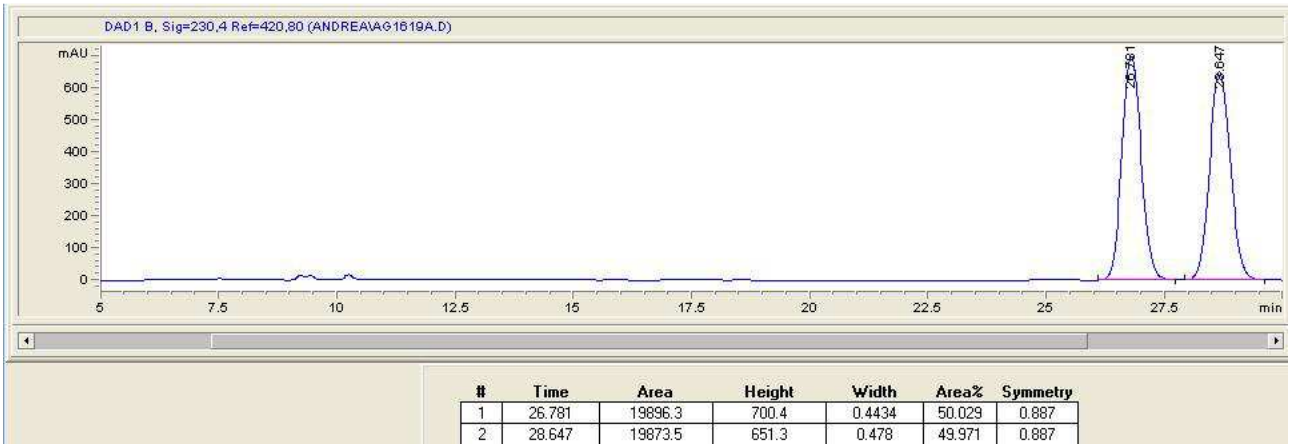


#	Time	Area	Height	Width	Area%	Symmetry
1	27.277	41093.5	1216.6	0.5241	84.180	1.065
2	29.141	7722.8	211.7	0.5657	15.820	1.113



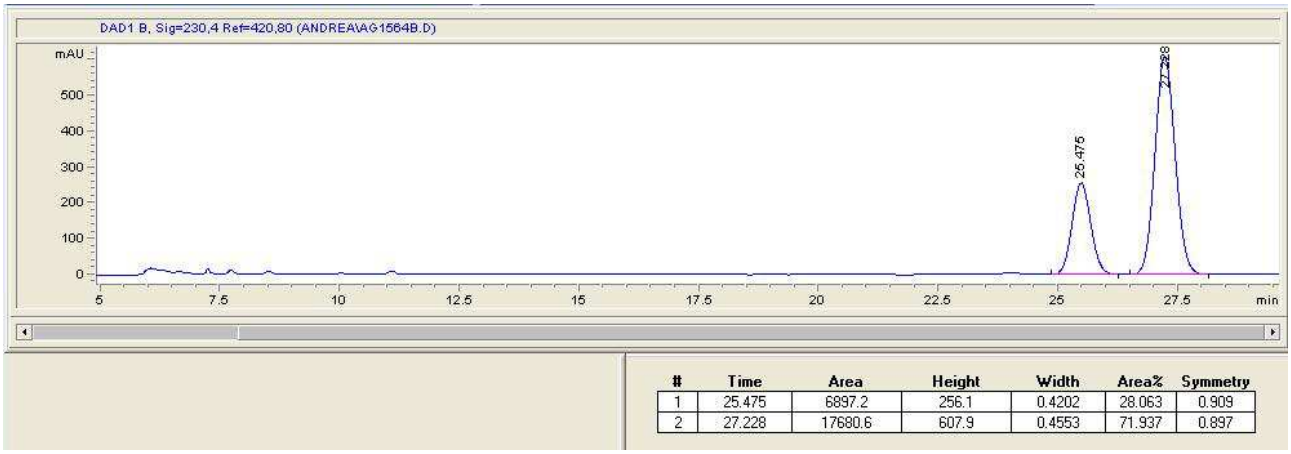
3j

Racemic

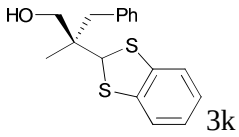


#	Time	Area	Height	Width	Area%	Symmetry
1	26.781	19896.3	700.4	0.4434	50.029	0.887
2	28.647	19873.5	651.3	0.478	49.971	0.887

Enantioselective

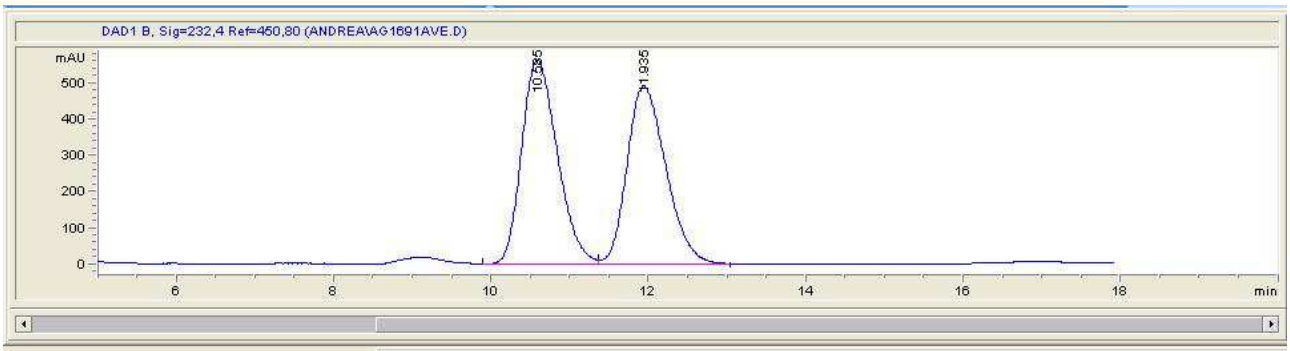


#	Time	Area	Height	Width	Area%	Symmetry
1	25.475	6897.2	256.1	0.4202	28.063	0.909
2	27.228	17680.6	607.9	0.4553	71.937	0.897



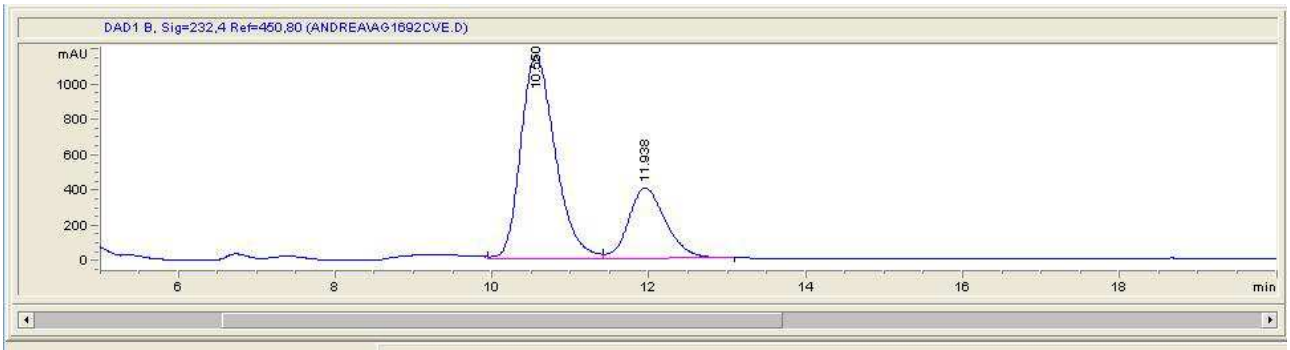
3k

Racemic

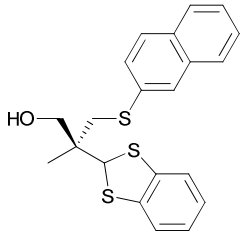


#	Time	Area	Height	Width	Area%	Symmetry
1	10.585	17868.5	564.7	0.4619	51.253	0.762
2	11.935	16994.9	492.6	0.4313	48.747	0.738

Enantioselective

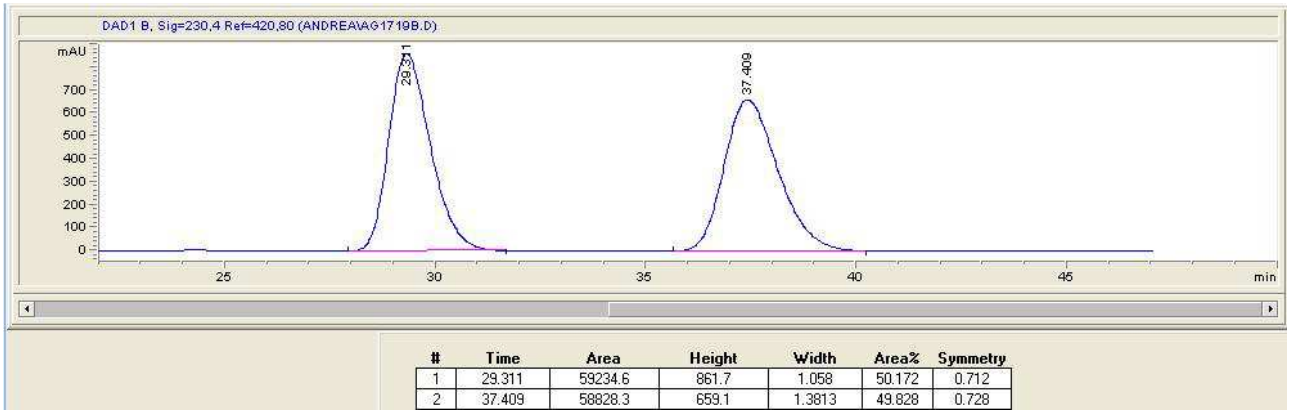


#	Time	Area	Height	Width	Area%	Symmetry
1	10.55	35411.8	1150.9	0.3718	72.920	0.75
2	11.938	13150.5	399.6	0.4191	27.080	0.706



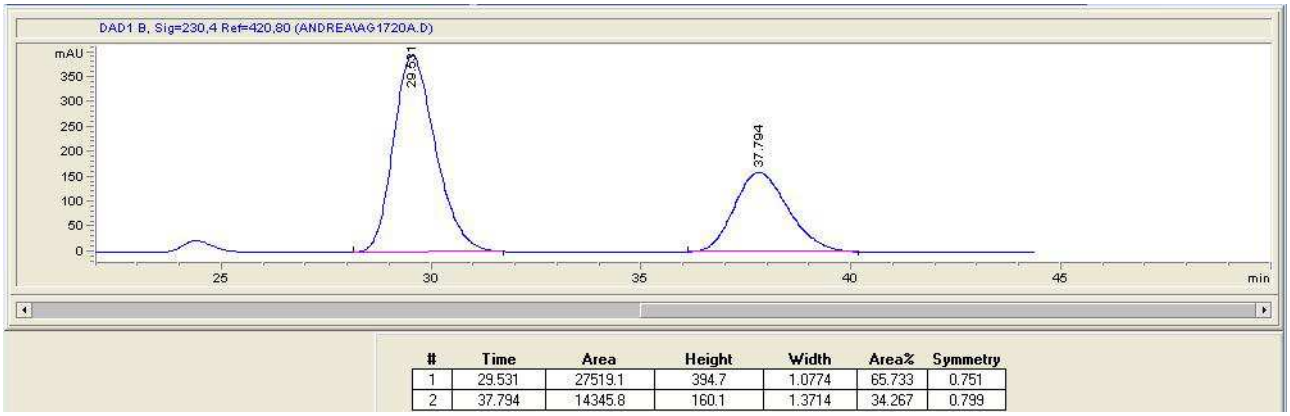
3l

Racemic

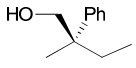


#	Time	Area	Height	Width	Area%	Symmetry
1	29.311	59234.6	861.7	1.058	50.172	0.712
2	37.409	58828.3	659.1	1.3813	49.828	0.728

Enantioselective

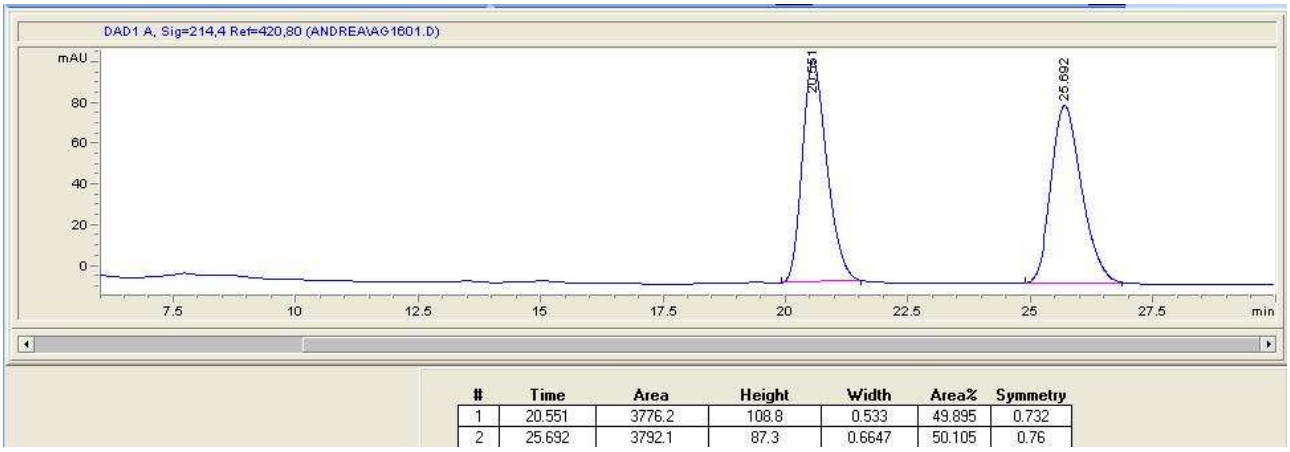


#	Time	Area	Height	Width	Area%	Symmetry
1	29.531	27519.1	394.7	1.0774	65.733	0.751
2	37.794	14345.8	160.1	1.3714	34.267	0.799



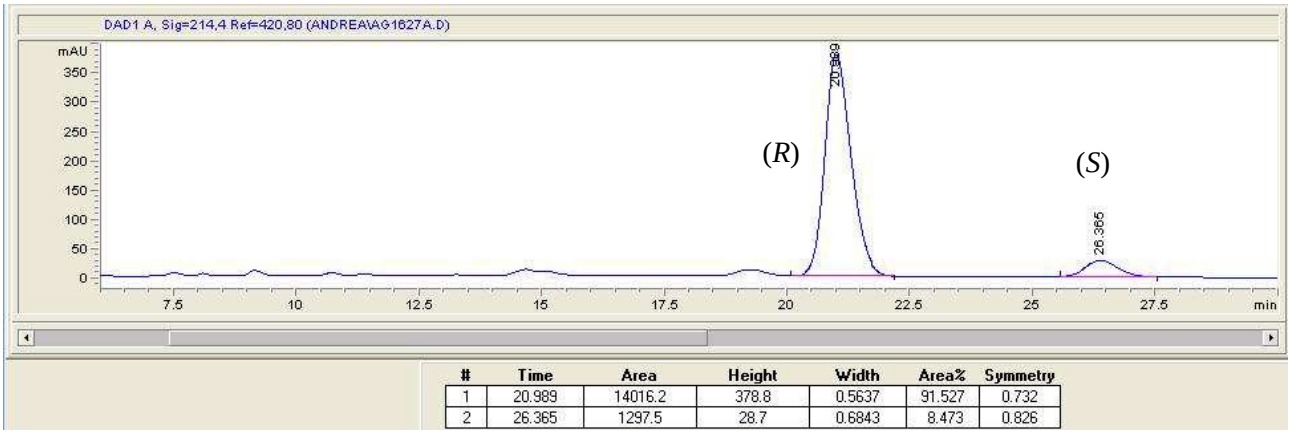
6a

Racemic



#	Time	Area	Height	Width	Area%	Symmetry
1	20.551	3776.2	108.8	0.533	49.895	0.732
2	25.692	3792.1	87.3	0.6647	50.105	0.76

Enantioselective



#	Time	Area	Height	Width	Area%	Symmetry
1	20.989	14016.2	378.8	0.5637	91.527	0.732
2	26.365	1297.5	28.7	0.6843	8.473	0.826