Supporting Information

Green asymmetric synthesis of Warfarin and Coumachlor in pure water catalyzed by quinoline-derived 1,2-diamines

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General Information:

NMR spectra were recorded on a 300 MHz spectrometer. HRMS (high-resolution mass spectrometry) spectra were measured using electrospray ionization (ESI) and a time-of-flight (TOF) mass analyzer. Optical rotations were measured on a polarimeter and calibrated with pure solvent as a blank. HPLC analyses were performed on an HPLC system equipped with chiral stationary phase columns, detection at 220 or 254 nm. Silica gel (0.060−0.200 mm) was used for column chromatography. All reagents and solvents were purified and dried according to common methods.

1. General Procedure for the Preparation of Di-imines 7a-e: Corresponding quinolincarbaldehyde (1.57 g, 10.0 mmol) was added to a solution of (*R*,*R*) or (*S*,*S*)-HPEN (1.10 g, 5.00 mmol) in EtOH (96% w/w) (10 mL). The reaction mixture was stirred for 10 h at r.t. The solvent was evaporated under reduced pressure (10 Torr). The crude residue was washed with EtOH (3 x 5 mL) to afford pure compounds **7a-e**.

Schiff base ((*R*,*R*)-**7a**): Yellow solid, 217-220°C (dec), yield 1.44 g (55%), >99% *ee*. $[\alpha]_D^{20}$: +18.5 (c 1.0, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 13.56 (s, 2H), 8.36 (s, 2H), 8.06 (m, 4H), 8.08 - 8.01 (m, 4H), 7.70 (s, 2H), 7.29 (s, 2H), 7.17 (s, 2H), 7.02 (s, 2H), 7.06 (m, 4H), 6.82 (s, 2H), 5.71 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.9, 161.2, 159.1, 147.6, 136.6, 132.8, 131.8, 129.6, 129.1, 127.6, 126.5, 120.5, 118.7, 118.6, 117.2, 79.8 ppm. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{34}H_{27}N_4O_2^+$ 523.2129, found 523.2134.

Schiff base ((*R*,*R*)-**7b**): Yellow solid, Mp = >220°C (dec), yield 1.78 g (68%), >99% *ee*. $[\alpha]_D^{20}$: -71.3 (c 1.0, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 12.95 (s, 2H), 8.78 (s, 2H), 8.46 (s, 4H), 8.08 - 8.01 (m, 4H), 7.70 (s, 2H), 7.29 (s, 2H), 7.17 (s, 2H), 7.02 (s, 2H), 6.99 (s, 2H), 6.83 (s, 2H), 5.14 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.8, 160.6, 150.9, 147.4, 135.4, 133.3, 133.2, 132.3, 130.1, 129.1, 128.4, 127.7, 127.4, 119.4, 119.1, 117.0, 75.6 ppm. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{34}H_{27}N_4O_2^+$ 523.2129, found 523.2130.

Schiff base ((*S*,*S*)-**7c**): Yellow solid, Mp = 132-134°C, yield 2.43 g (93%), >99% *ee*. $[\alpha]_D^{20}$: -82.6 (c 0.35, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 13.07 (s (br), 2H), 8.77 (s, 2H), 8.24-8.08 (m, 6H), 7.72 - 7.58 (m, 6H), 7.34 (m, 2H), 7.08 (s, 4H), 6.83 (s, 2H), 5.76 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.3, 160.5, 150.2, 148.3, 145.4, 133.3, 132.3, 130.1, 129.6, 126.9, 126.0, 124.3, 121.7, 119.4, 119.0, 117.0, 71.9 ppm. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{34}H_{27}N_4O_2^+$ 523.2129, found 523.2122.

Schiff base ((*S*,*S*)-**7d**): Yellow solid, Mp = 145-151°C, yield 1.96 g (75%), >99% *ee*. $[\alpha]_D^{20}$: -89.4 (c 0.70, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 13.22 (s, 2H), 8.85 (s, 2H), 8.41 (s, 2H), 7.98 - 8.00 (m, 4H), 7.66-7.61 (m, 4H), 7.31-7.28 (m, 4H), 7.02 (m, 2H), 6.99 (m, 2H), 6.83 (m, 2H), 5.07 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.3, 160.6, 151.0, 147.5, 138.6, 136.3, 133.2, 132.3, 129.7, 129.5, 128.0, 127.6, 122.1, 119.3, 119.0, 116.9, 77.7 ppm. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{34}H_{27}N_4O_2^+$ 523.2129, found 523.2121.

Schiff base ((*S*,*S*)-**7e**): Yellow solid, Mp = 197-200°C, yield 2.30 g (88%), >99% *ee*. $[\alpha]_D^{20}$: -59.0 (c 1.0, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 13.81 (s, 2H), 8.96 (s, 2H), 8.52 (s, 2H), 8.00 - 7.98 (m, 4H), 7.52-7.50 (m, 2H), 7.17-7.10 (m, 6H), 6.95 (m, 2H), 6.90 (s, 2H), 6.88 (s, 2H), 6.79-6.74 (t, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 161.3, 149.3, 145.7, 137.8, 136.1, 132.2, 131.7, 129.3, 128.0, 127.1, 126.1, 120.8, 118.8, 118.4, 116.9, 70.5 ppm. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{34}H_{27}N_4O_2^+$ 523.2129, found 523.2124. The analytical data of (*R*,*R*)-**7e**) was identically.

2. General Procedure for the Preparation of Diamines 8b-e: The 10M HCl (2.0 mL) was added to a solution of Schiff base **7b-e** (1.50 g, 2.87 mmol) in THF (50.0 mL). After 10 h, orange precipitate was filtered and washed with THF (3 x 5 mL). Resulting solid was dissolved in 5M NaOH (10 mL) and extracted with DCM (3 x 20 mL). Combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure (10 Torr) to afford corresponding 1,2-diamine **8b-e**.

(1*R*,2*R*)**-1,2-di(quinolin-2-yl)ethane-1,2-diamine tetrahydrochloride** (*R*,*R*)-(**8a**)·4 HCl: Black oil. According to the ^1H NMR spectrum, the oil contained complex mixture of tar products.

(1*S*,2*S*)-**1,2-di(isoquinolin-4-yl)ethane-1,2-diamine** (*S*,*S*)-(**8b**): Yellow solid, Mp = 174-176°C, yield 0.79 g (88%), >99% *ee*. $[\alpha]_D^{20}$: -105.3 (c 0.5, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): 8.81 (s, 2H), 8.07-8.03 (m, 4H), 7.73 (m, 2H), 7.65-7.63 (m, 2H), 7.50-7.28 (m, 2H), 4.43 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): 146.9, 144.6, 140.3, 134.9, 130.2, 129.6, 128.0, 127.1, 123.1, 54.0 ppm. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{20}H_{19}N_4^+$ 315.1604, found 315.1609.

(1*S*,2*S*)-**1,2-di(quinolin-4-yl)ethane-1,2-diamine** (*S*,*S*)-(**8c**): Yellow solid, Mp = 114-118°C, yield 0.79 g (88%), >99% *ee*. $[\alpha]_D^{20}$: -102.2 (c 0.3, $CHCl_3$). ^1H NMR (300 MHz, DMSO d_6): 10.07 (s (br), 5H), 9.00 (d, *J* = 5.2 Hz, 2H), 8.76 (d, *J* = 5.6 Hz, 4H), 8.13 (d, *J* = 8.12 Hz, 2H), 7.94 (m, 5H), 7.50 (s (br), 3H), 6.71 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): 146.2, 145.8, 141.3, 133.4, 129.8, 126.5, 125.3, 127.1, 124.7, 122.4, 51.5 ppm. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{20}H_{19}N_4^+$ 315.1604, found 315.1613.

(1*S*,2*S*)-**1,2-di(quinolin-6-yl)ethane-1,2-diamine** (*S*,*S*)-(**8d**): Yellow solid, Mp = 97-100°C, yield 0.81 g (90%), >99% *ee*. $[\alpha]_D^{20}$: -94.7 (c 1.1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): 8.78 (s, 2H), 7.97 (m, 4H), 7.67 (s, 2H), 7.60 (d, *J* = Hz, 2H), 7.28 (m, 2H), 4.34 (s, 2H), 1.80 (s (br), 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): 151.3, 147.7, 141.5, 135.9, 129.5, 128.7, 128.0, 125.4, 121.3, 61.5 ppm. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{20}H_{19}N_4^+$ 315.1604, found 315.1607.

(1*S*,2*S*)-**1,2-di(quinolin-8-yl)ethane-1,2-diamine** (*S*,*S*)-(**8e**): Yellow solid, Mp = 85-87°C, yield 0.80 g (89%), >99% *ee*. $[\alpha]_D^{20}$: -148.1 (c 0.56, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): 8.90 (s, 2H), 8.06 (d, *J* = 8.17 Hz, 2H), 7.48 (d, *J* = 8.10 Hz, 2H), 7.36 (q, *J* = 4.10, 2H), 7.28 (s, 2H), 7.12 (t, *J* = 7.67 Hz, 2H), 5.38 (s, 2H), 2.90 (s (br), 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): 148.6, 146.5, 142.0, 136.3, 128.4, 128.3, 126.5, 125.9, 120.5, 60.2 ppm. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{20}H_{19}N_4^+$ 315,1604, found 315,1594.

(1*R*,2*R*)-**1,2-di(quinolin-8-yl)ethane-1,2-diamine** (*R*,*R*)-(**8e**): Yellow solid, (0.79 g, 88%; >99% *ee*). $[\alpha]_D^{20}$: +146.3 (c 0.75, $CHCl_3$). The analytical data for (*R*,*R*)-**8e** was identically to (*S*,*S*)-**8e**.

3. Asymmetric catalytic synthesis of compounds 3a-d. General procedure. The mixture of catalyst (*S*,*S*)-**8e** (18.8 mg, 0.06 mmol), (*R*)-MA (18.24 mg, 0.12 mmol), **1** (97.2 mg, 0.6 mmol) **2a-d** (0.72 mmol) and water (3.0 mL) was stirred at specified temperature for specified time (see Table 1). The reaction mixture was extracted with EtOAc (4 x 5 mL). The combined extracts were evaporated (10 Torr). The residue was purified by flash chromatography (*n*-hexane/ EtOAc 3:1 – 1:1) to afford corresponding Michael adducts **3a-d**.

(***S***)-**4-hydroxy-3-(3-oxo-1-phenylbutyl)-2H-chromen-2-one** (**3a**) (**Warfarin)** [1a,b]. Colorless solid, Mp = 155-158 °C (Lit. [1b] Mp = 156-159 °C), yield 159 mg (86 %), α_D^{20} = -9.46 (c 1, MeCN), 91 % *ee*. HPLC (Daicel Chiralcel AD-H; *n*-hexane/2-propanol, 70:30; flow rate = 0.8 mL/min; λ = 254 nm): t_1 = 5.2 (minor), t_2 = 10.2 (major) min. ^1H NMR (300 MHz, $CDCl_3$) δ 9.67 (s, 0.16H), 7.96 – 7.74 (m, 1.42H), 7.59-7.39 (m, 1.67H), 7.39-7.13 (m, 8.47H), 4.77 (d, *J* = 10.1 Hz, 0.16H), 4.30-4.13 (m, 1.23H), 3.90-3.78 (m, 0.36H), 3.37-3.30 (d, 0.19H), 2.53-2.35 (m, 1.50H), 2.29 (s, 0.32H) 2.07-1.95 (m, 0.74), 1.69-1.67 (m, 3H) ppm; ^{13}C NMR (75 MHz, DMSO d_6) δ 207.7, 166.1, 160.6, 159.9, 152.9, 144.4, 133.1, 132.3, 128.4, 128.3, 127.5, 124.3, 123.2, 116.9, 116.1, 115.8, 103.9, 102.4, 101.8, 100.1, 91.5, 45.4, 43.3, 42.0, 36.5, 35.7, 30.3, 27.5, 26.3 ppm.

(*S*)-3-(1-(4-chlorophenyl)-3-oxobutyl)-4-hydroxy-2H-chromen-2-one (**3b**) (**Coumachlor**) [2a,b]. Colorless solid, Mp = 175-176 °C (Lit. [2b] Mp = 174-176 °C), yield 133 mg (65 %), α_D^{20} = +11.86 (c 0.5, MeCN), 85 % *ee*. HPLC (Daicel Chiralcel AD-H; *n*-hexane/2-propanol, 70:30;

flow rate = 0.8 mL/min; λ = 254 nm): t_1 = 5.34, t_2 = 12.24 min. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.72 (0.18H), 7.90-7.81 (m, 1H), 7.59-7.44 (m, 1.29H), 7.37 – 7.14 (m, 6.64), 4.68 (d, *J* = 8.4 Hz, 0.16H), 4.38 (s(br), 0.41H), 4.16 (m, 1.10H), 3.83 (m, 0.55H), 3.32-3.26(m, 0.20H) 2.48-2.35 (m, 1.28H), 2.28 (s, 0.31H), 2.05 – 1.89 (m, 1.25H), 1.72 (s, 1.43H), 1.69 (s, 0.98H) ppm; ^{13}C NMR (75 MHz, DMSO d_6) δ 210.8, 152.8, 143.6, 132.1, 130.4, 129.9, 128.6, 127.7, 127.5, 124.0, 123.3, 116.6, 115.8, 103.3, 102.2, 101.6, 99.8, 42.9, 41.4, 35.4, 34.8, 31.6, 29.3, 28.2, 26.4 ppm.

(*S*)-4-hydroxy-3-(1-(4-methoxyphenyl)-3-oxobutyl)-2H-chromen-2-one (3c) [3]. Colorless solid, Mp = 165-167°C (No literature data are available), yield 91.0 mg (45 %), α_D^{20} = +4.75 (c 0.3, MeCN), 80 % *ee*. HPLC (Daicel Chiralcel AD-H; *n*-hexane/2-propanol, 70:30; flow rate = 0.8 mL/min; λ = 254 nm): t_1 = 6.5 (minor), t_2 = 14.9 (major) min. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.45 (s, 0.15H), 7.94-7.81 (m, 1.04H), 7.58-7.50 (m, 1.45H), 7.35- 7.14 (m, 4.59H), 6.89-6.83 (m, 2.15H), 4.66 (m, 0.17H), 4.26 (m, 0.50H), 4.13 (m, 0.53H), 3.79-3.78 (m, 3H), 2.57-2.38 (m, 1.83H), 2.29 (s, 0.53H), 1.72 - 1.69 (m, 2.70H) ppm; ^{13}C NMR (75 MHz, DMSO d_6) δ 160.7, 159.0, 158.0, 152.8, 143.7, 136.16, 132.3, 130.6, 128.7, 128.5, 125.5, 124.4, 123.2, 116.6, 116.2, 114.9, 114.1, 113.5, 104.1, 102.74, 101.8, 100.2, 55.4, 43.3, 42.2, 35.8, 34.8, 27.7, 26.2 ppm.

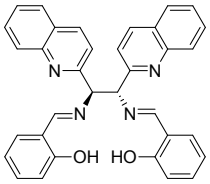
(*S*)-4-hydroxy-3-(3-oxocyclohexyl)-2H-chromen-2-one (3d) [3]. Colorless solid, Mp = 105-107 °C (No literature data are available), yield 123 mg (80 %), α_D^{20} = -26.45 (c 0.5, $CHCl_3$), 51 % *ee*. HPLC (Daicel Chiralcel AD-H; *n*-hexane/2-propanol, 80:20; flow rate = 1.0 mL/min; λ = 210 nm): t_1 = 6.0 (major), t_2 = 6.5 (minor) min. ^{1}H NMR (300 MHz, DMSO d_6) δ 12.32 (s (br), 0.47H) 7.83-7.74 (d, *J* = 7.6 Hz 1.00H), 7.61-7.56 (t, *J* = 7.8 Hz, 1.00H), 7.36-7.30 (m, 2.00H), 3.19 (s, 0.66H), 2.30-2.19 (m, 1.00H), 2.12-1.99 (m, 2.00H), 1.87-1.79 (m, 2.00H), 1.64-1.57 (m, 2.00H), 1.41-1.35 (m, 1.00H) ppm; ^{13}C NMR (75 MHz, DMSO d_6) δ 166.1, 161.1, 152.8, 133.0, 132.16, 124.4, 123.6, 122,7, 116.7, 103.4, 102.9, 91.5, 38.8, 35.9, 29.5, 28.3, 19.1 ppm.

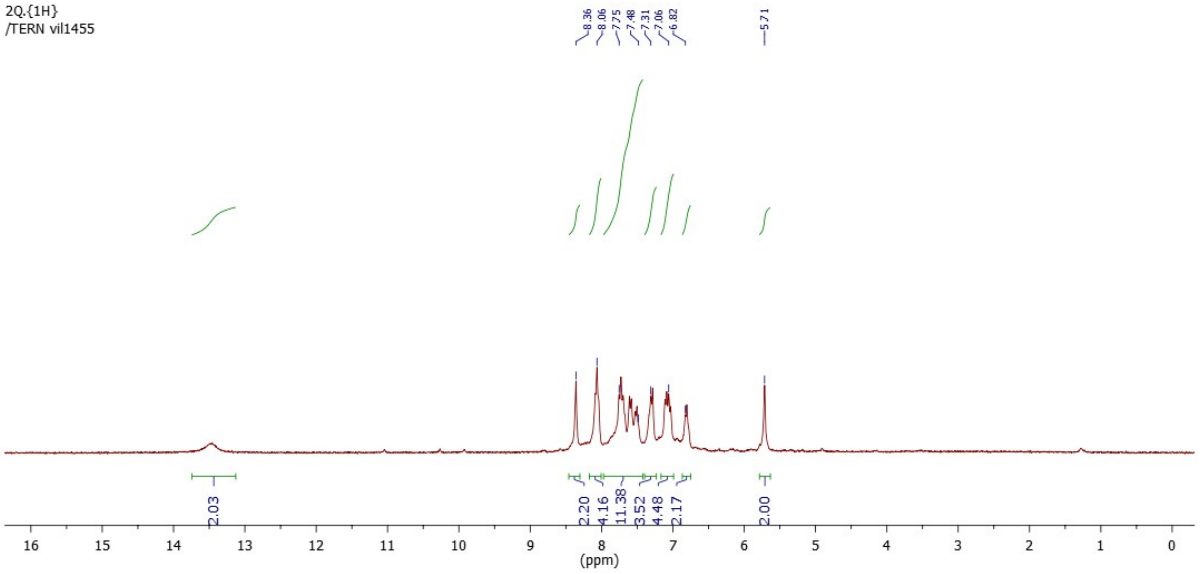
4. Scaling synthesis of Warfarin (3a) with catalyst recycling (conventional procedure). The mixture of (*S*,*S*)-**8e** (314 mg, 1.0 mmol), (*R*)-MA (304 mg, 2.0 mmol), **1** (1.62 g, 10.0 mmol), **2a** (1.75 g, 12.0 mmol), and water (30.0 mL) was stirred at r.t. for 24 h. The reaction mixture was extracted with EtOAc (3 x 50 mL). The combined extracts were evaporated (10 Torr). The residue was purified by flash chromatography (*n*-hexane/ EtOAc 3:1 – 1:1) to afford corresponding Michael adducts **3a** as colorless solid, yield 2.46 g (80 %), 90% *ee*. Then, fresh portions of **1** and **2a** were added to remaining aqueous solution of (*S*,*S*)-**8e** / (*R*)-MA and the reaction was re-performed at room temperature for the specified time (see Table 2).

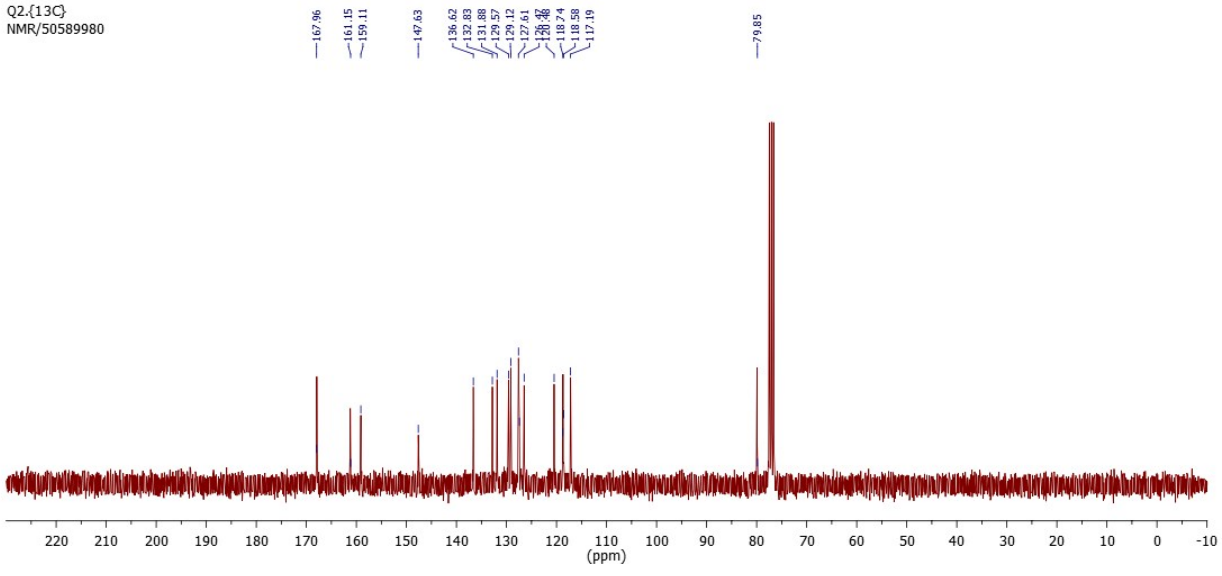
5. Scaling synthesis of warfarin (3a) with catalyst recycling (green procedure). The mixture of (*S*,*S*)-**8e** (314 mg, 1.0 mmol), (*R*)-MA (304 mg, 2.0 mmol), **1** (1.62 g, 10.0 mmol), **2a** (1.75 g, 12.0 mmol), and water (30.0 mL) was stirred at r.t. for 24 h. The aqueous phase was carefully decanted from the two-phase system and the remained solid organic phase was washed with water (2 x 30 mL) to completely remove the catalyst. Aqueous NaOH (1M, 10 mL) was added to the organic residue, the unsolved impurities were filtered off and the filtrate was acidified by aqueous HCl (1 M, 10 mL). The precipitate was filtered off, washed with water (2 x 10 mL) and dried under reduced pressure (10 Torr) at 50 ^{o}C for 1 h. Thus obtained sample of **3a** was recrystallized from *n*-hexane-EtOAc (3:1) mixture (100 mL) to afford 2.15 g (70%) of pure Warfarin as a colorless solid, Mp = 156-157 ^{o}C, >98.6% *ee*. The decanted aqueous layers were evaporated (10 Torr, 60 ^{o}C) affording recovered catalytic system (*S,S*)-**8e** / (*R*)-MA (1:3) (430 mg, ~70 %) which was identical, according to the ^{1}H NMR data, to corresponding system recovered after the 4th cycle of conventional procedure.

6. Pictures of ^{1}H and ^{13}C NMR spectra for novel compounds

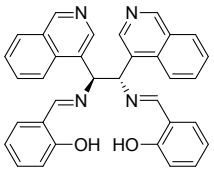
2,2'-({[(1*R*,2*R*)-1,2-di(quinolin-2-yl)ethane-1,2-diyl]bis(azanylylidene)}bis(methanylylidene))diphenol (*R*,*R*-**7a**).

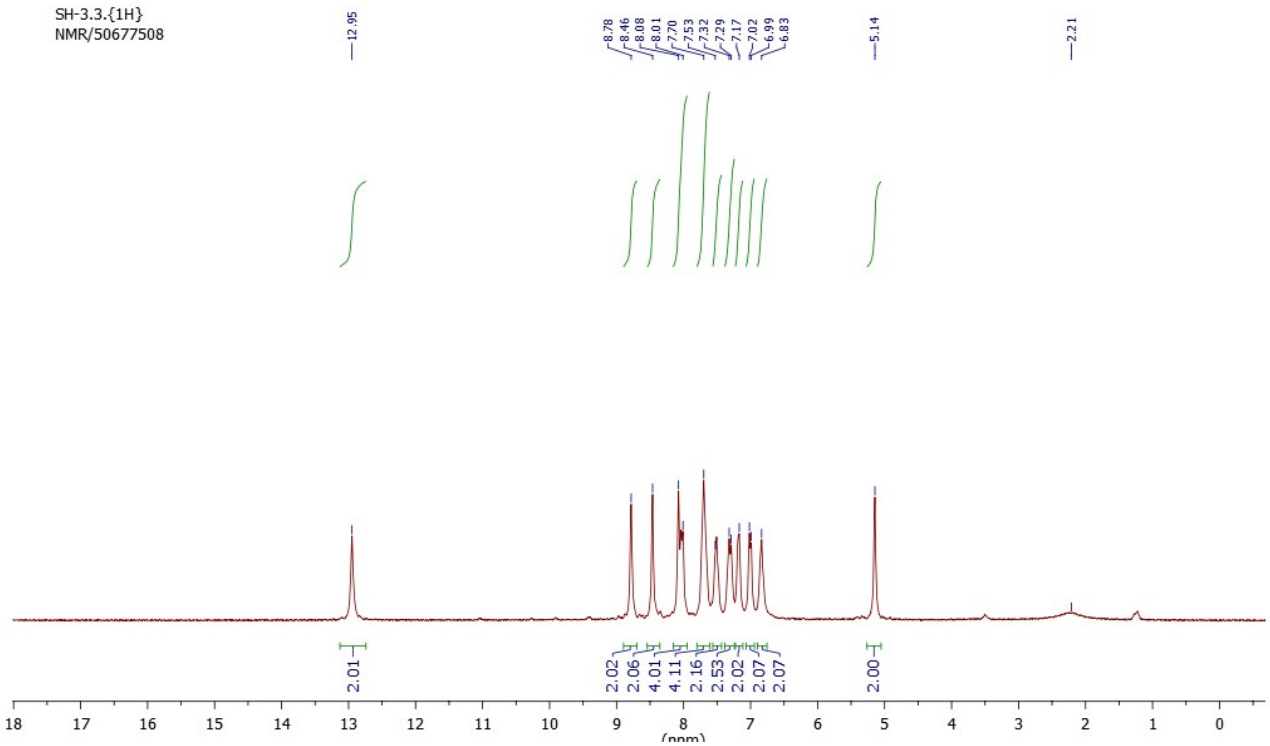


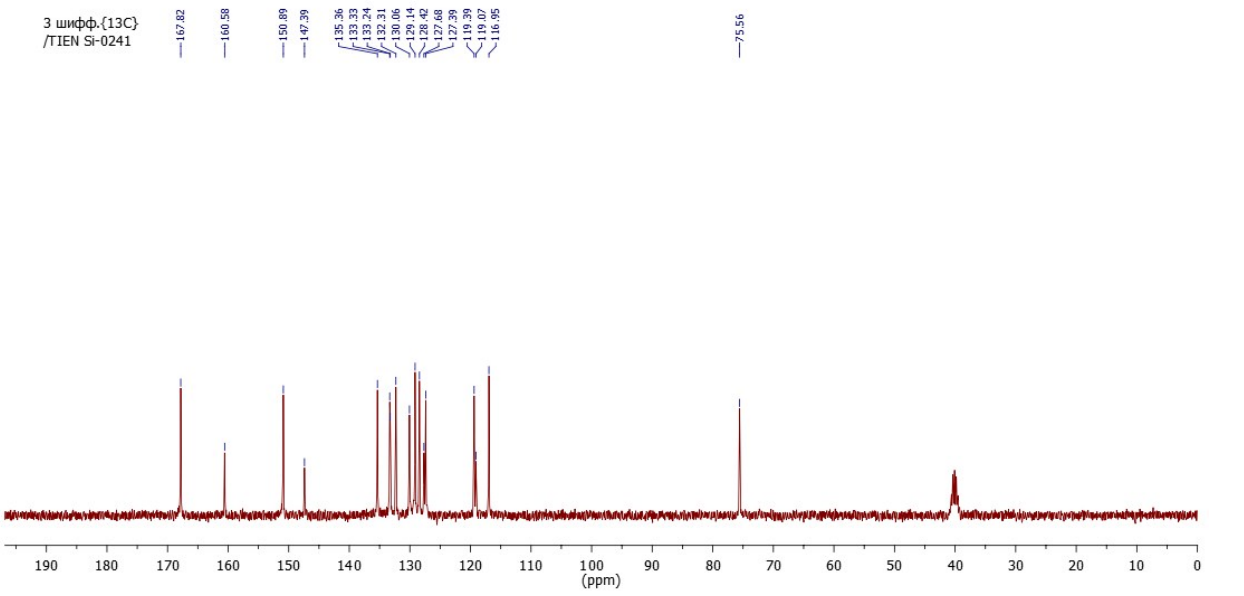




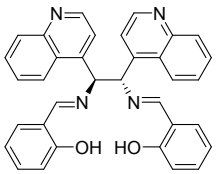
2,2'-({[(1*S*,2*S*)-1,2-di(isoquinolin-4-yl)ethane-1,2-diyl]bis(azanylylidene)}bis(methanylylidene))diphenol (*S*,*S*-**7b**).

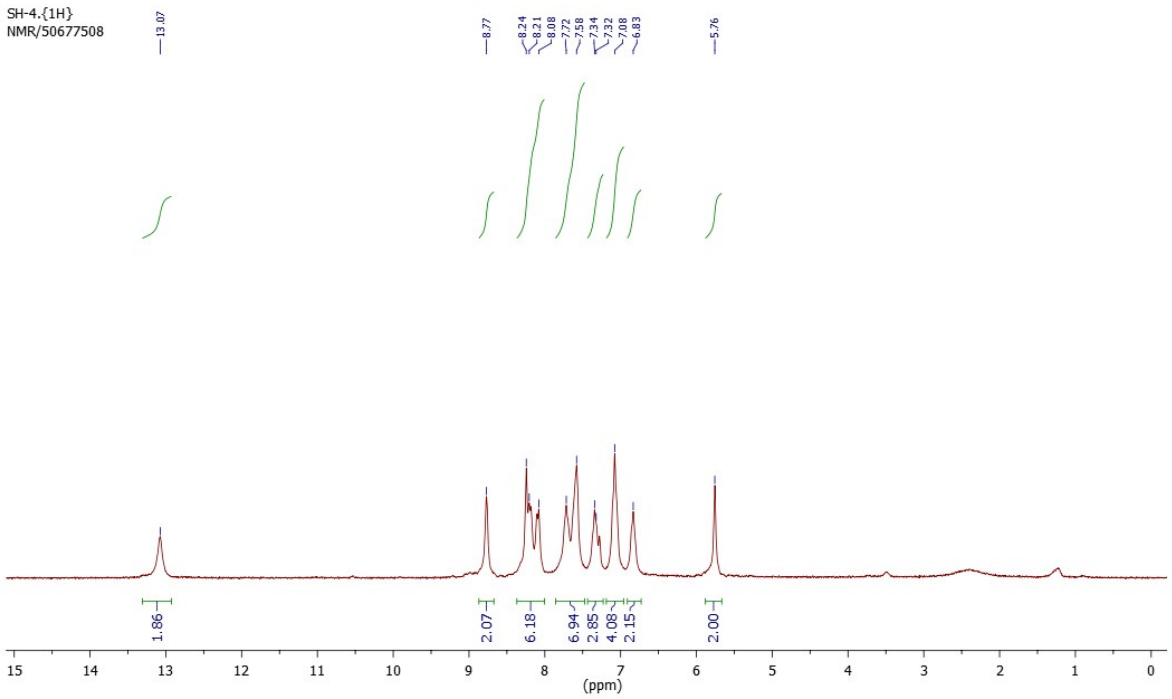


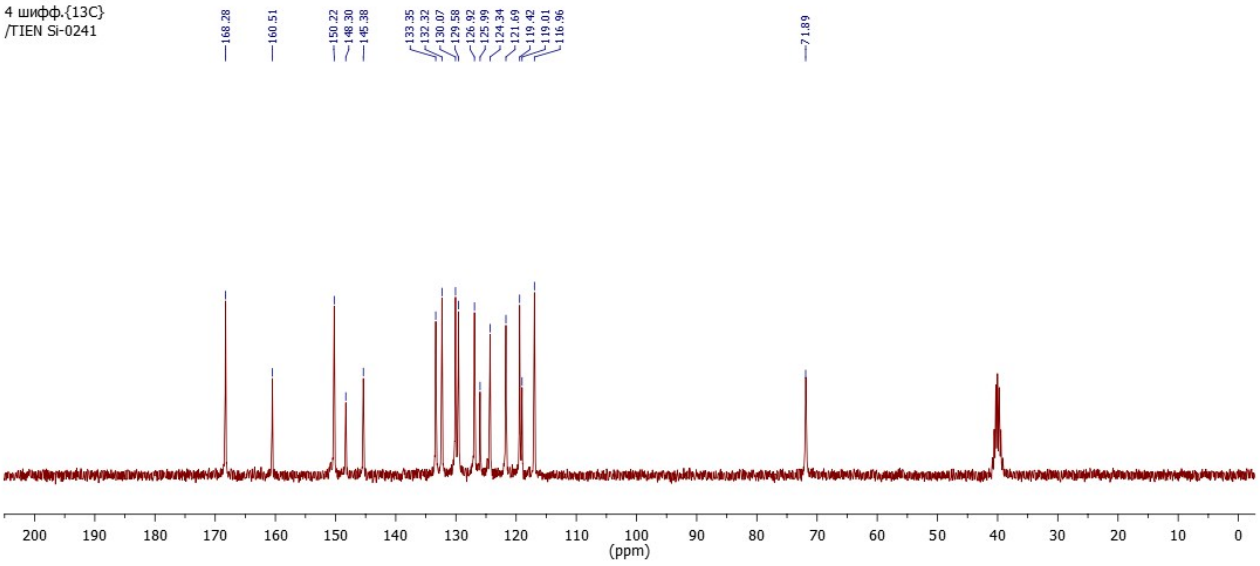




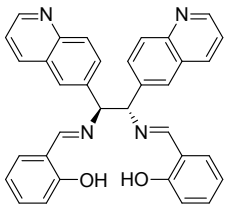
2,2'-({[(1*S*,2*S*)-1,2-di(quinolin-4-yl)ethane-1,2-diyl]bis(azanylylidene)}bis(methanylylidene))diphenol (*S*,*S*-**7c**).

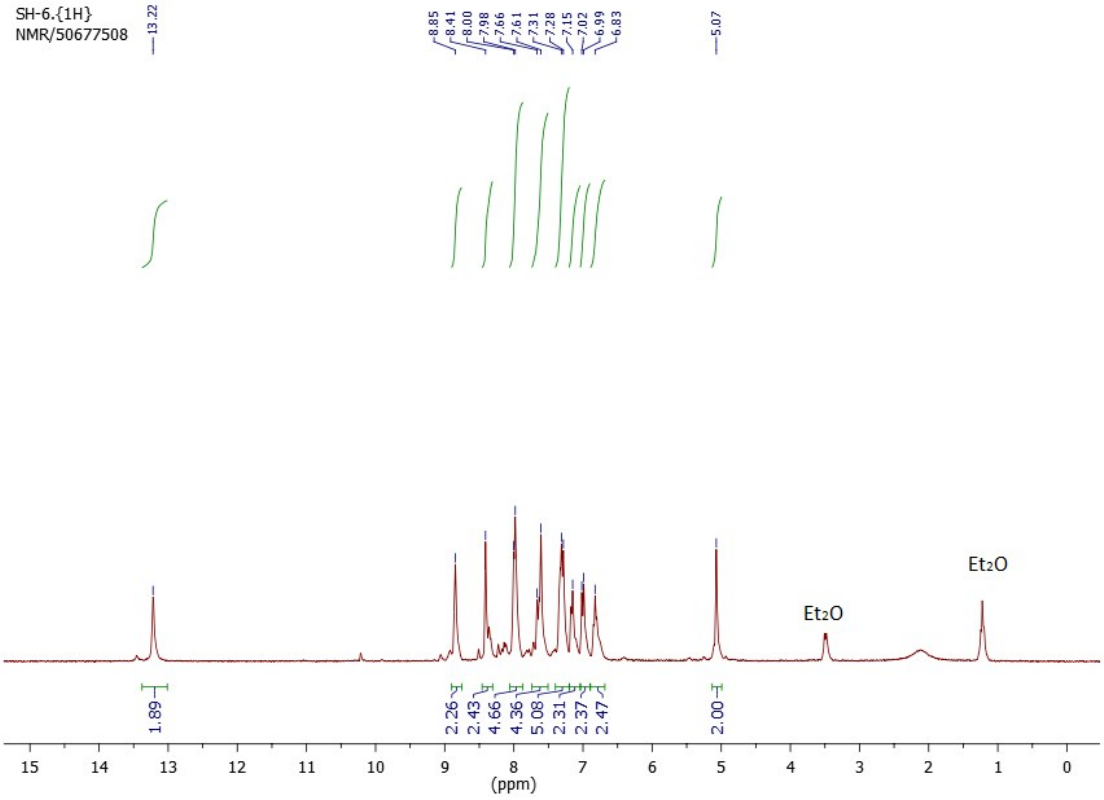


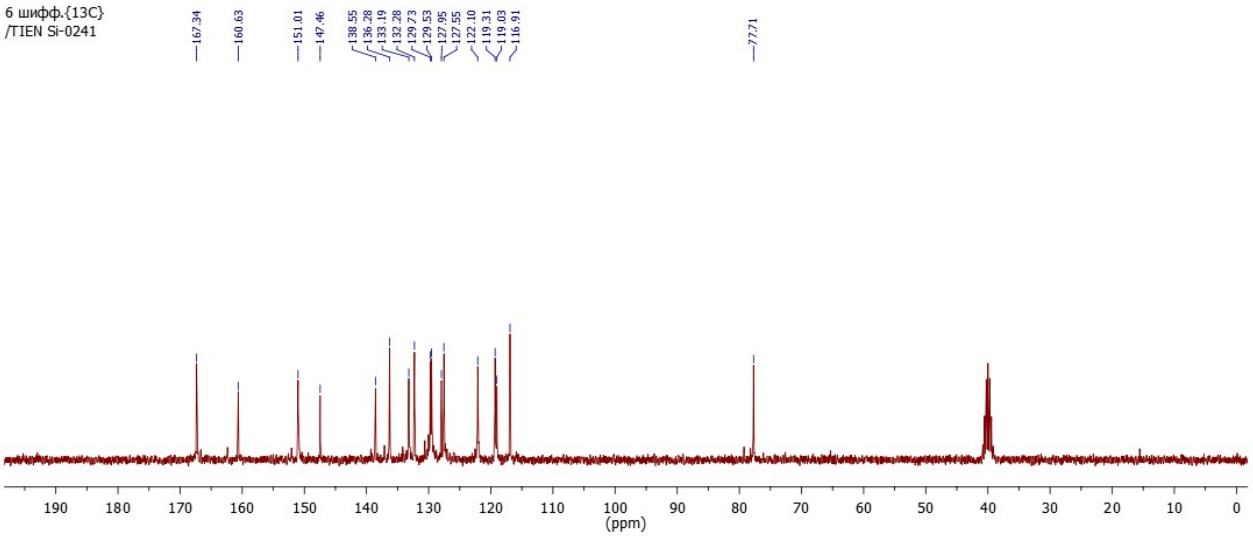




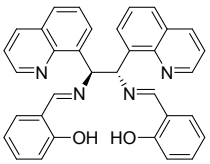
2,2'-({[(1*S*,2*S*)-1,2-di(quinolin-6-yl)ethane-1,2-diyl]bis(azanylylidene)}bis(methanylylidene))diphenol (*S*,*S*-**7d**).

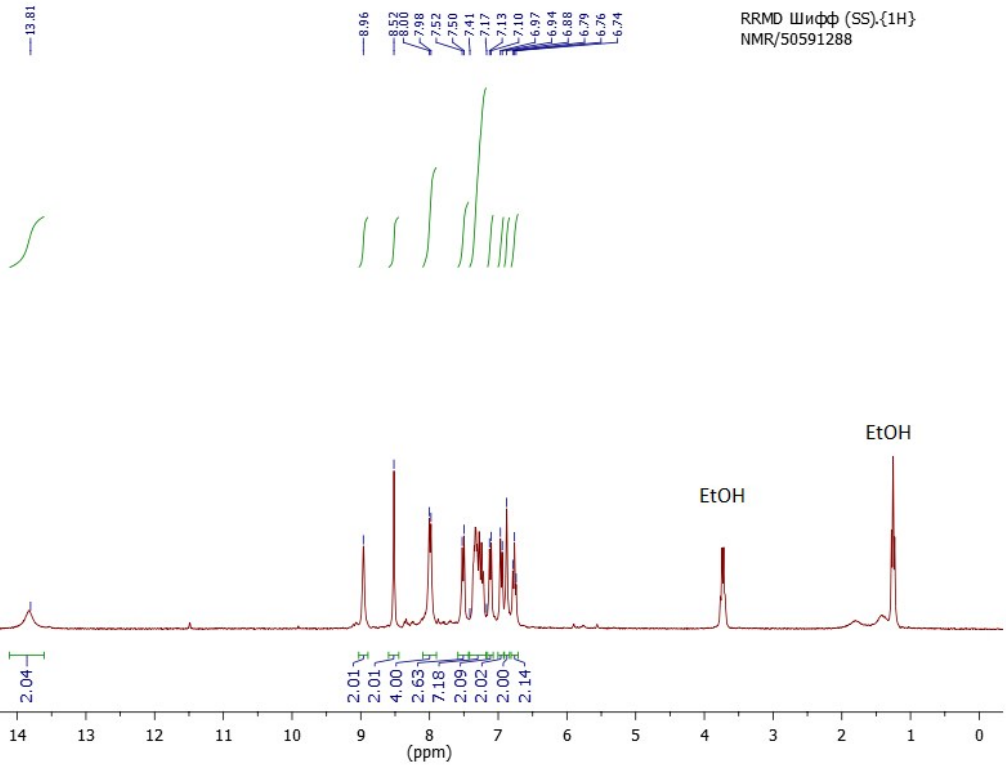


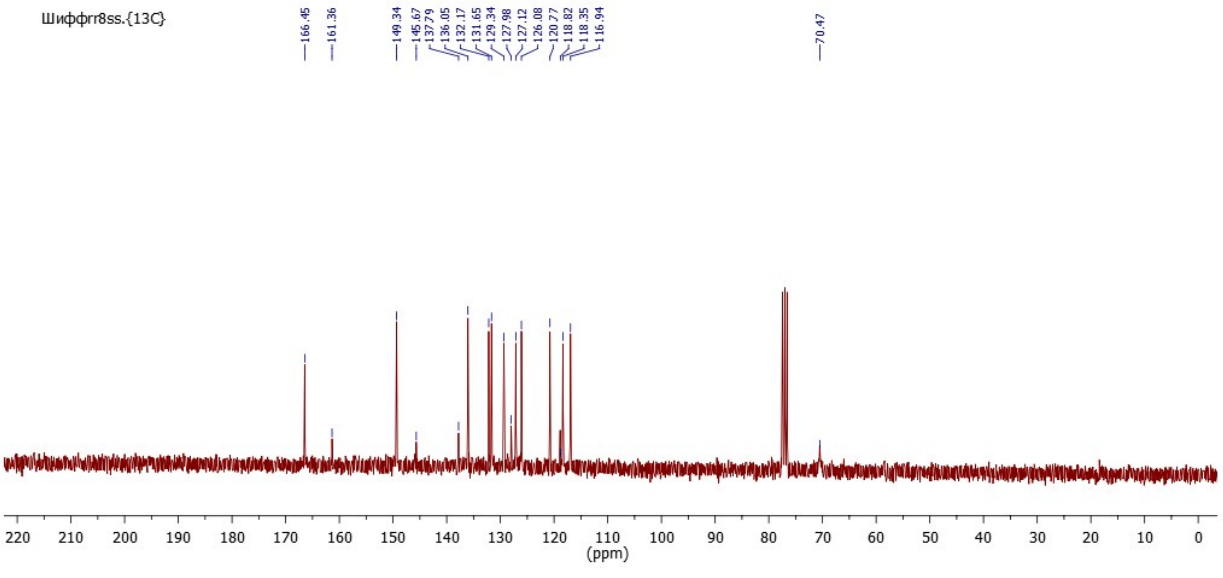




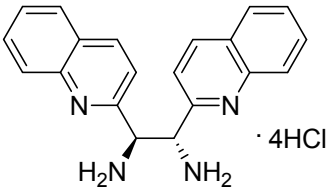
2,2'-({[(1*S*,2*S*)-1,2-di(quinolin-8-yl)ethane-1,2-diyl]bis(azanylylidene)}bis(methanylylidene))diphenol (*S*,*S*-**7e**).



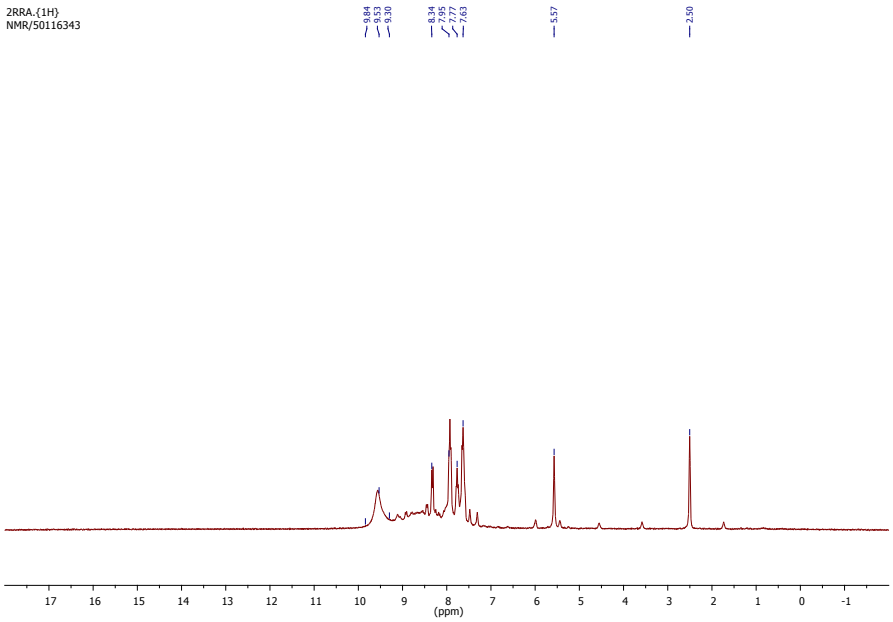




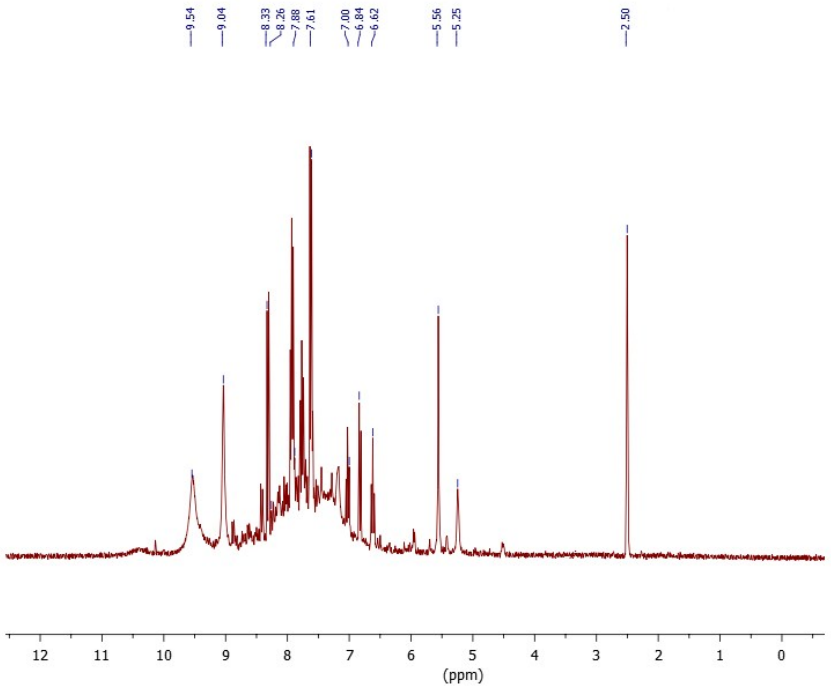
(1*R*,2*R*)-1,2-di(quinolin-2-yl)ethane-1,2-diamine ((*R*,*R*)-**8a** tetrahydrochloride).



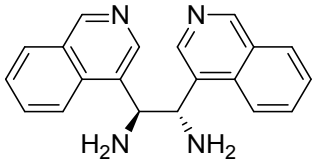
Freshly prepared (*R*,*R*)-**8a** tetrahydrochloride (300 MHz, DMSO-d_6).

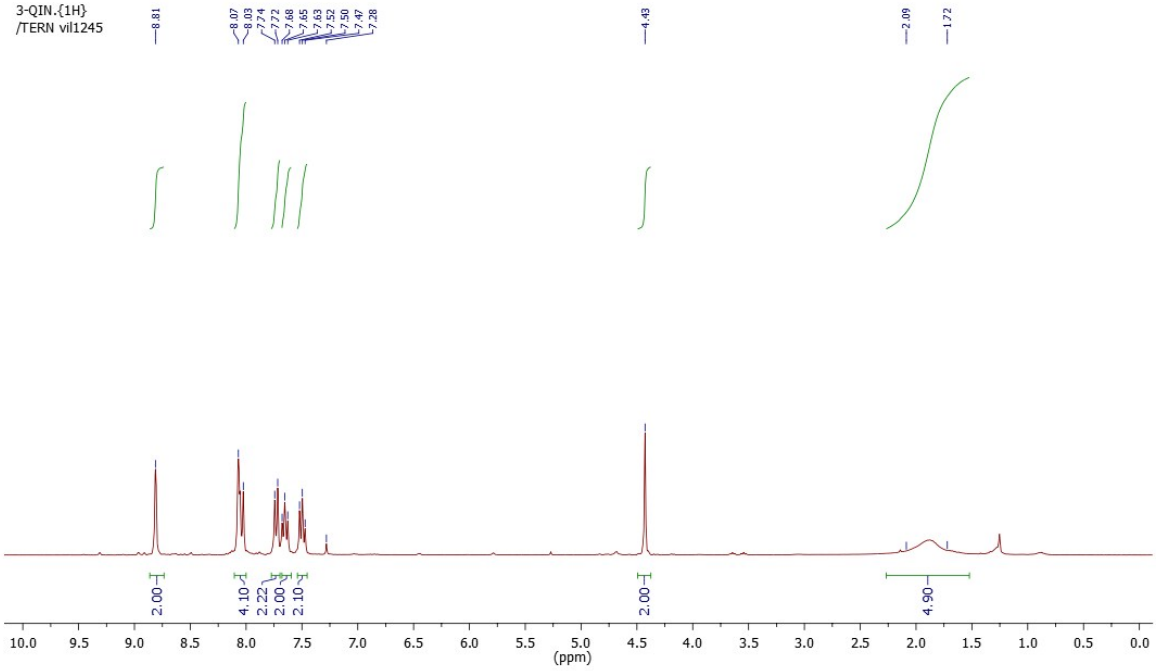


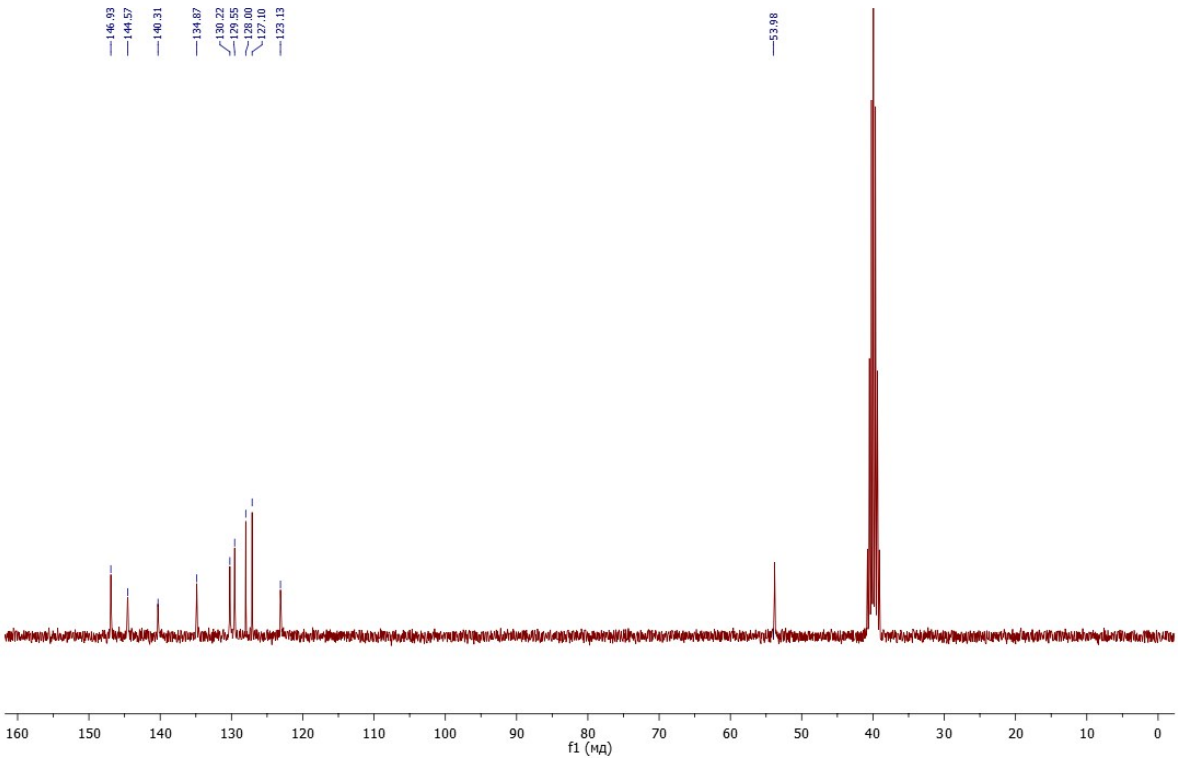
The spectrum of (*R*,*R*)-**8a** tetrahydrochloride solution in DMSO-d_6 after 6 h (300 MHz).



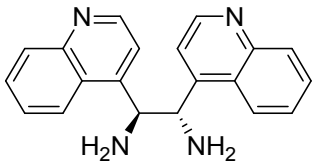
(1*S*,2*S*)-1,2-di(isoquinolin-4-yl)ethane-1,2-diamine ((*S*,*S*)-**8b**).

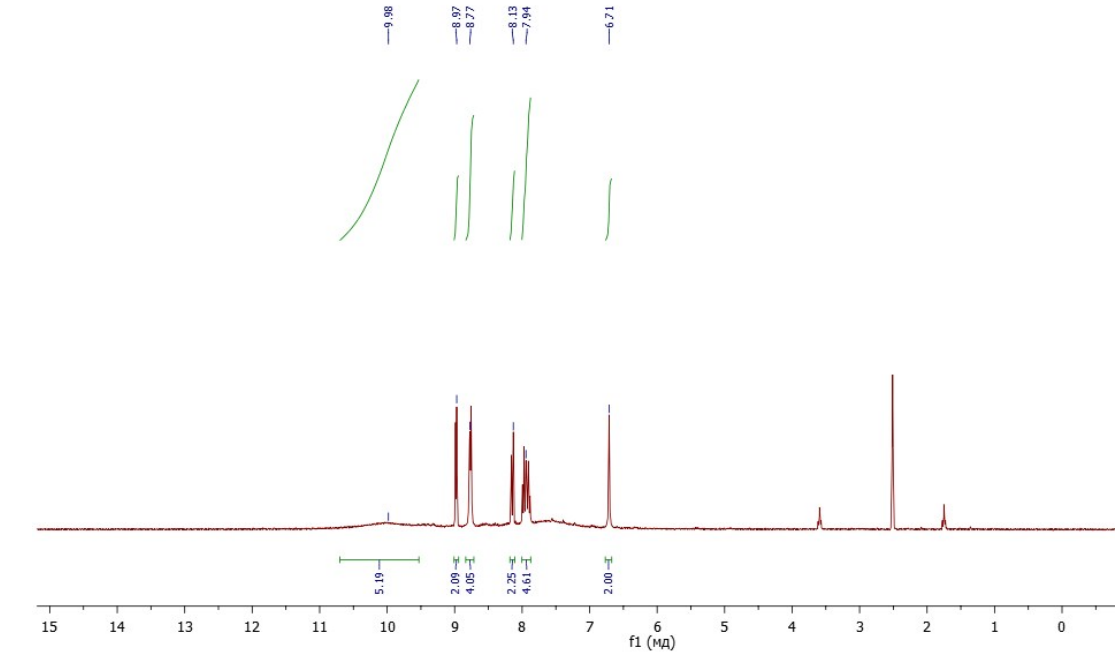


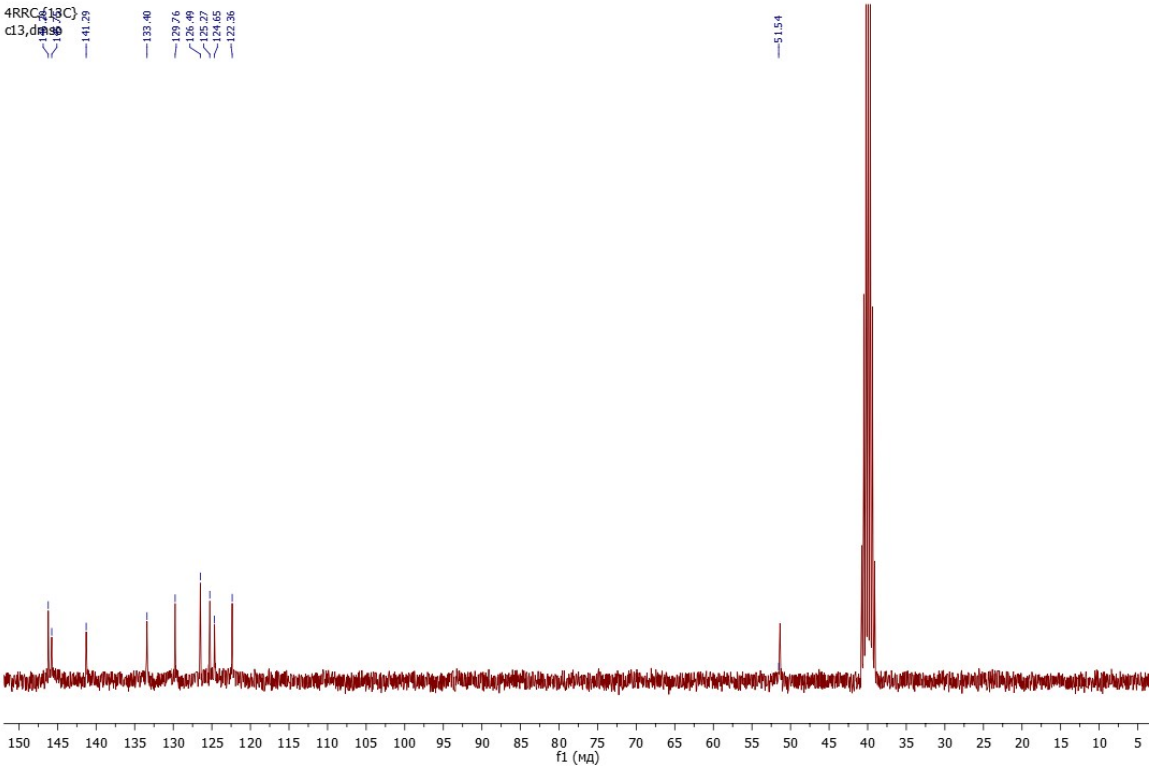




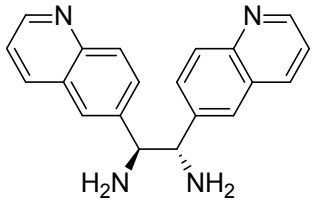
(1*S*,2*S*)-1,2-di(quinolin-4-yl)ethane-1,2-diamine ((*S*,*S*)-**8c**).

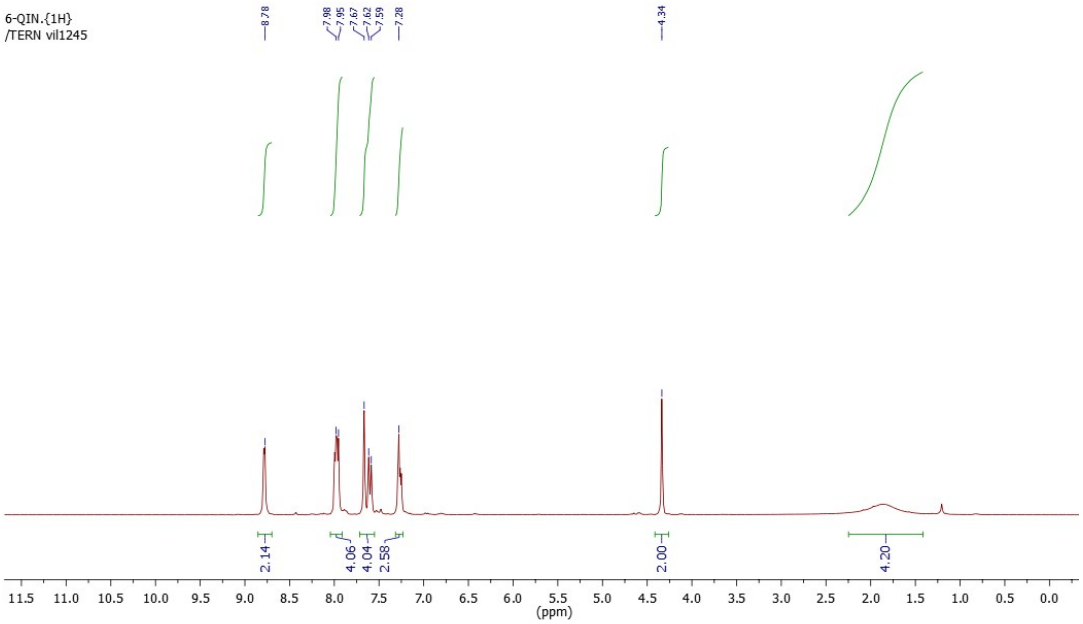


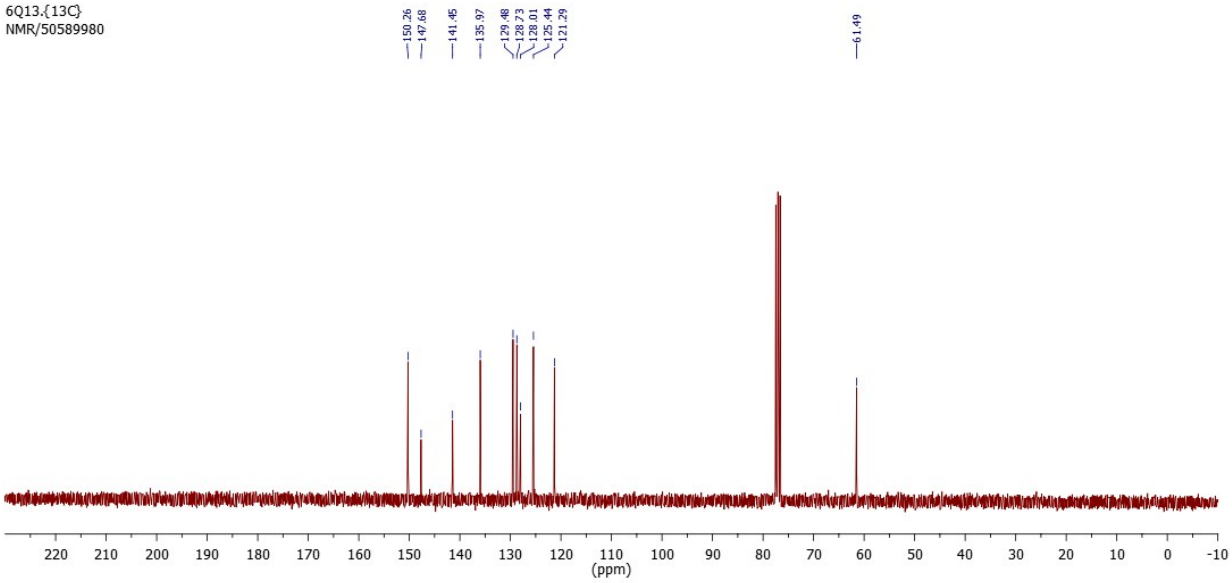




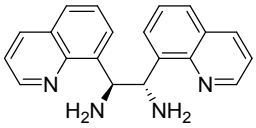
(1*S*,2*S*)-1,2-di(quinolin-6-yl)ethane-1,2-diamine (*S*,*S*-**8d**).

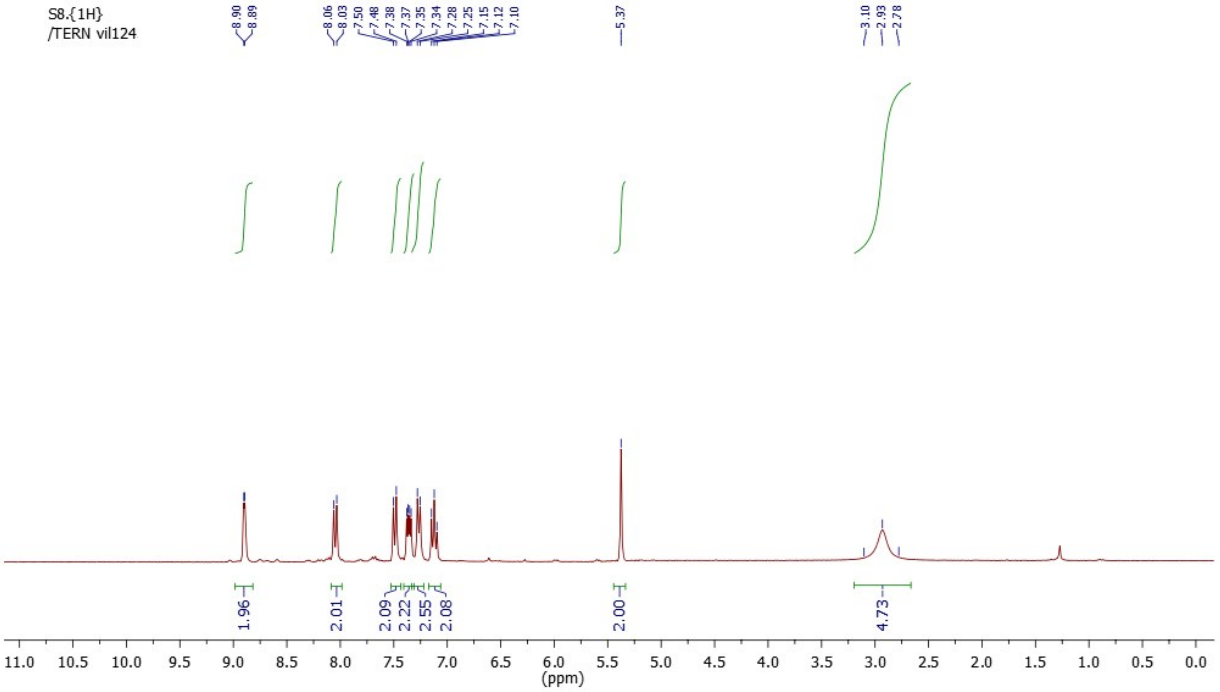


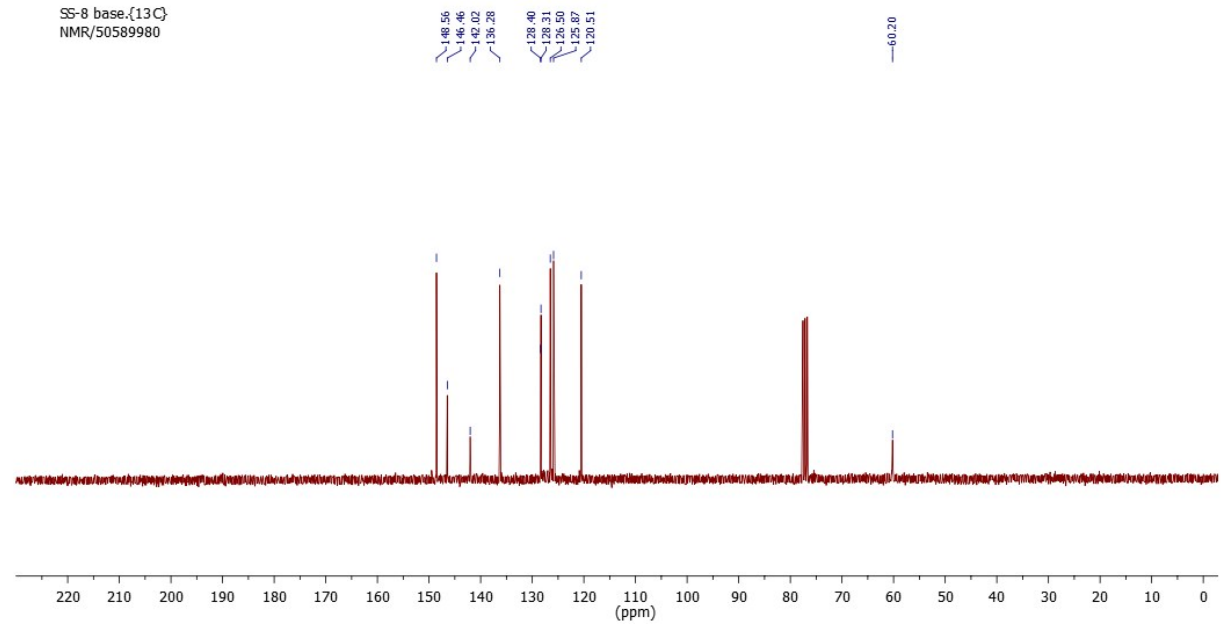




(1*S*,2*S*)-1,2-di(quinolin-8-yl)ethane-1,2-diamine (*S*,*S*-**8e**).

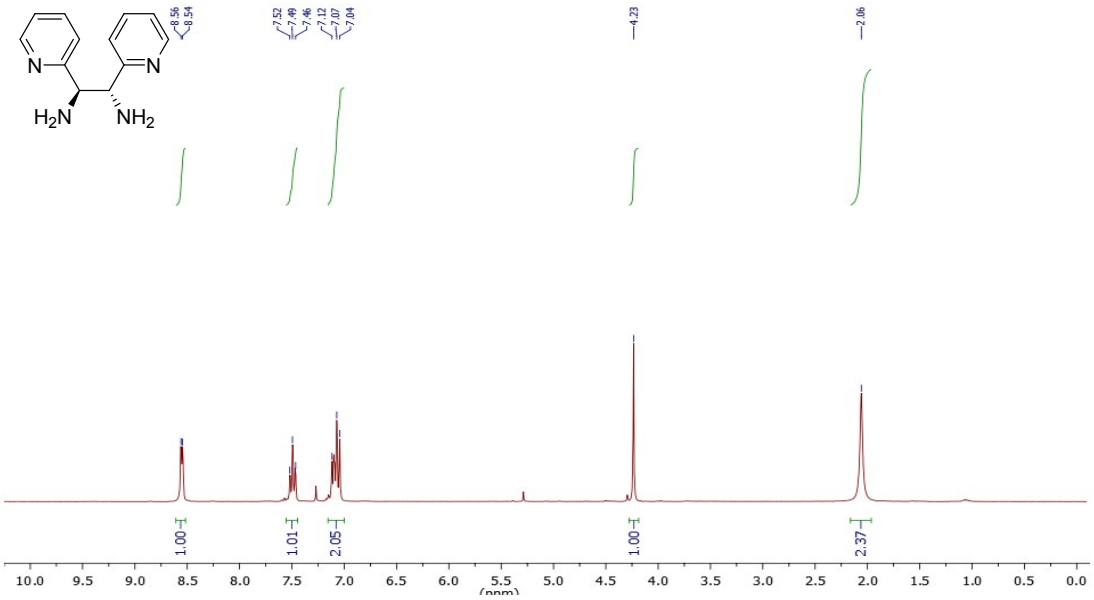




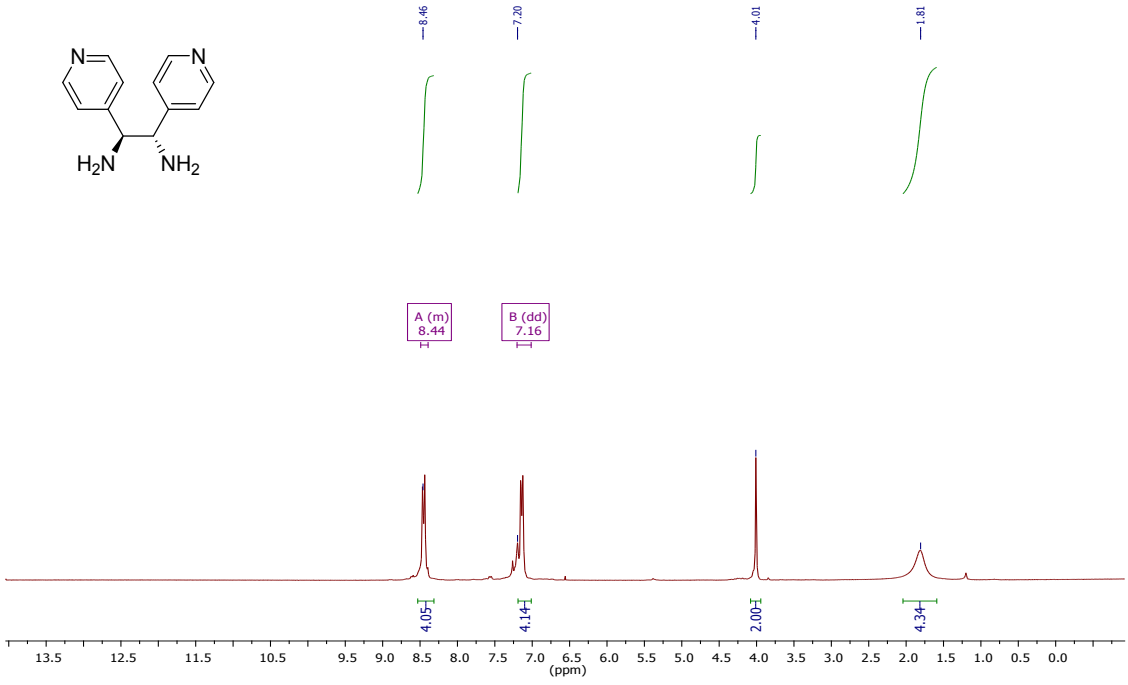


7. Pictures of ^{1}H NMR and ^{13}C NMR spectra for known compounds

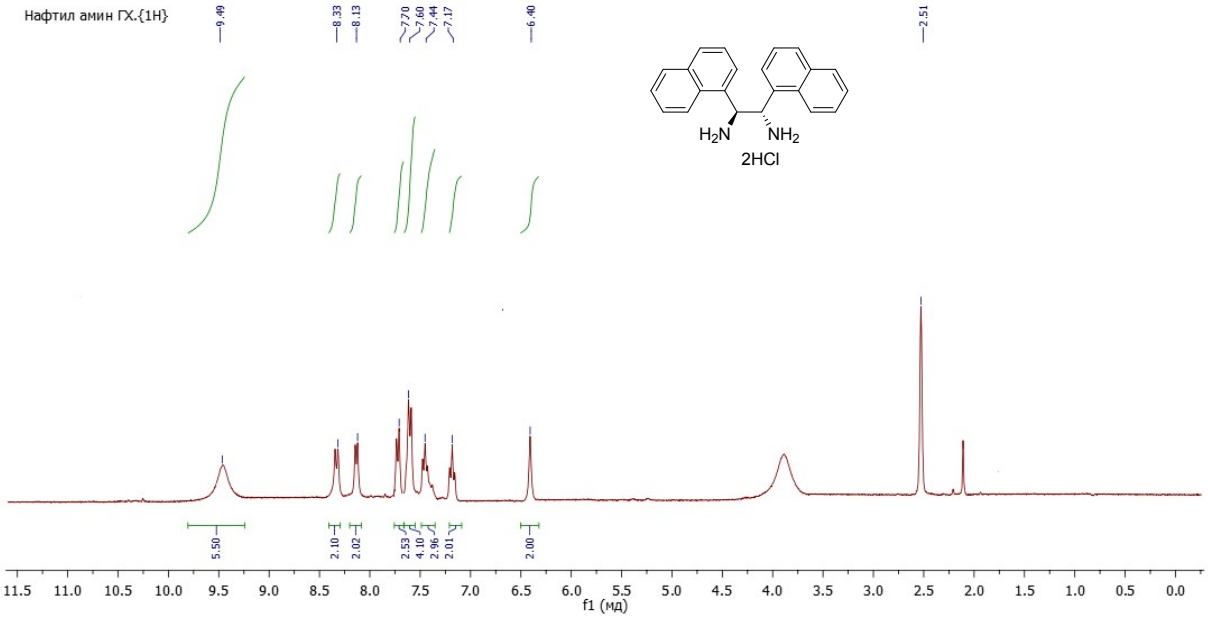
(1*R*,2*R*)-1,2-di(pyridin-2-yl)ethane-1,2-diamine (*R*,*R*-**8f**) [4]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.55 (d, J = 4.3 Hz, 2H), 7.52-7.46 (td, J = 7.7, 1.5 Hz, 2H), 7.12 −7.04 (m, 4H), 4.23 (s, 2H), 2.06 (s (*br*), 4H) ppm.



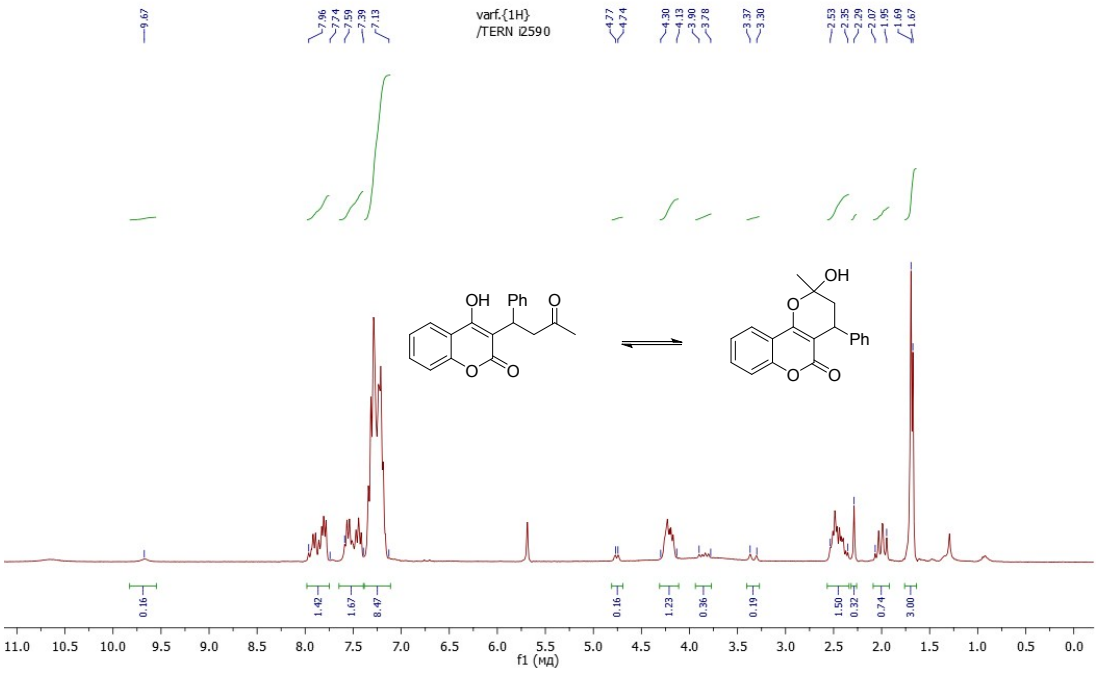
(1*S*,2*S*)-1,2-di(pyridin-4-yl)ethane-1,2-diamine (*S*,*S*-**8g**) [5].^{1}H NMR (300 MHz, $CDCl_3$): δ 8.46 (d, J = 8.44 Hz, 4H), 7.20 (d, J = 7.16 Hz, 4H), 4.01 (s, 2H), 1.81 (s, (*br*), 4H) ppm.

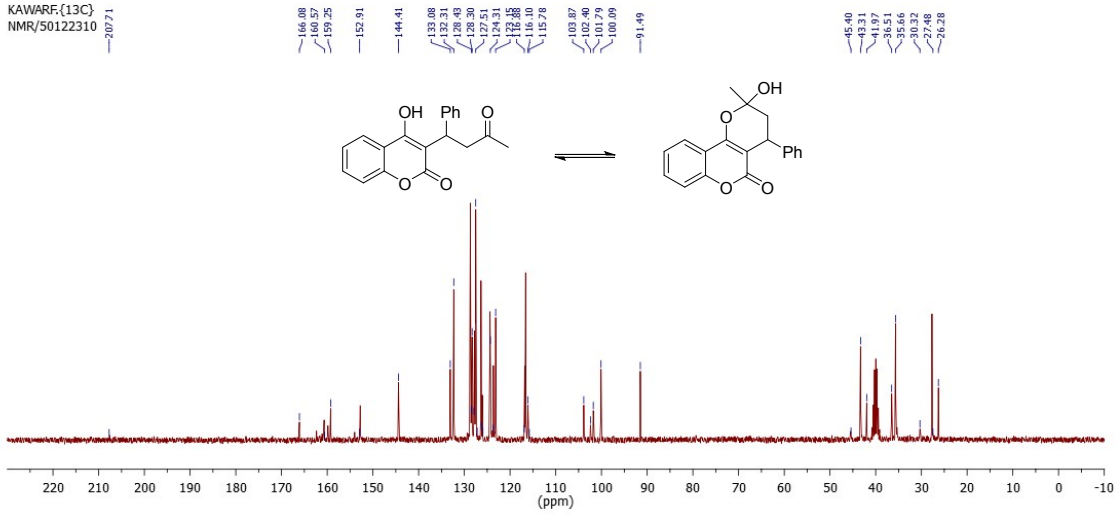


(1*S*,2*S*)-1,2-di(naphthalen-1-yl)ethane-1,2-diamine (*S*,*S*-**8h**) [6]. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.63-9.32 (s (br), 6H, $2NH_3^+$), 8.33 (d, J = 8.30 Hz, 2H), 8.13 (d, J = 7.04 Hz, 2H), 7.70 (m, 2H), 7.58 (m, 4H), 7.44 (m, 2H), 7.17 (t, J = 7.64 Hz, 2H), 6.40 (s, 2H) ppm.

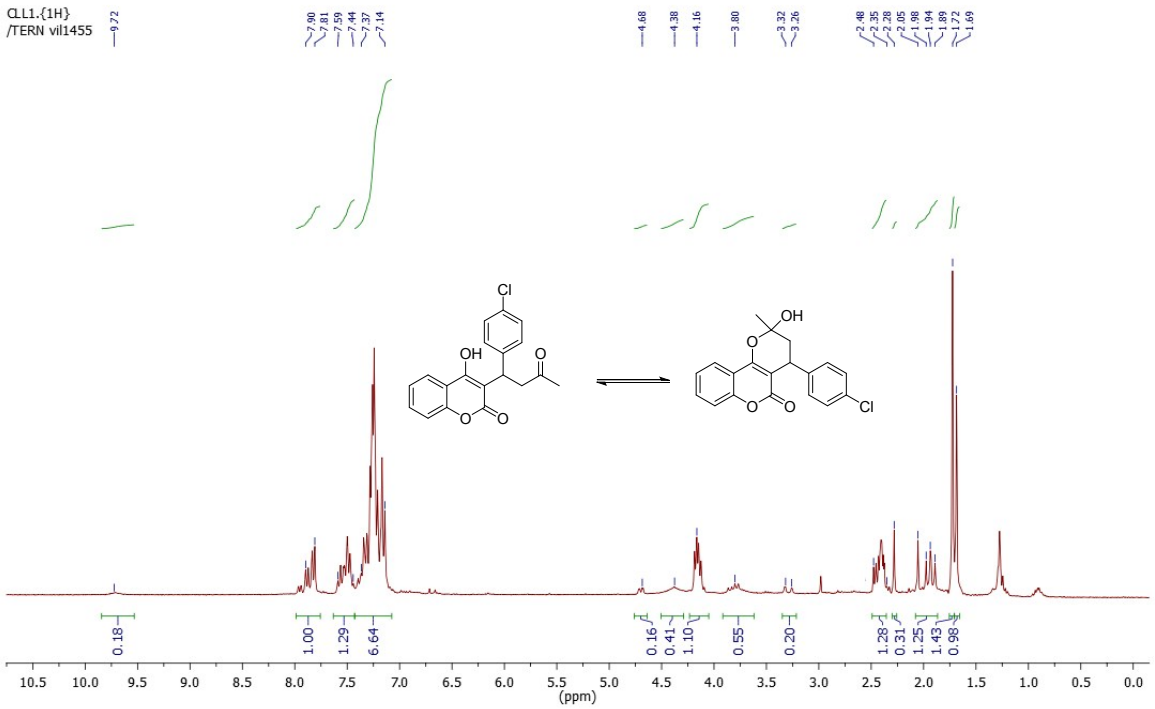


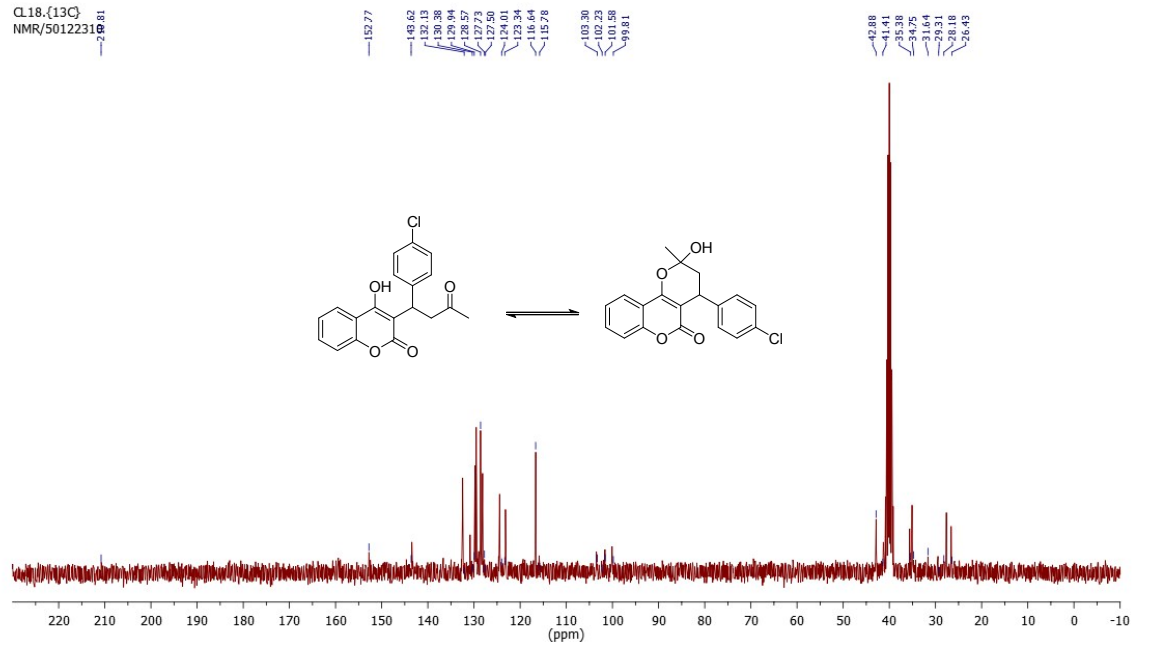
(***S***)**-4-hydroxy-3-(3-oxo-1-phenylbutyl)-2H-chromen-2-one** (**3a**).



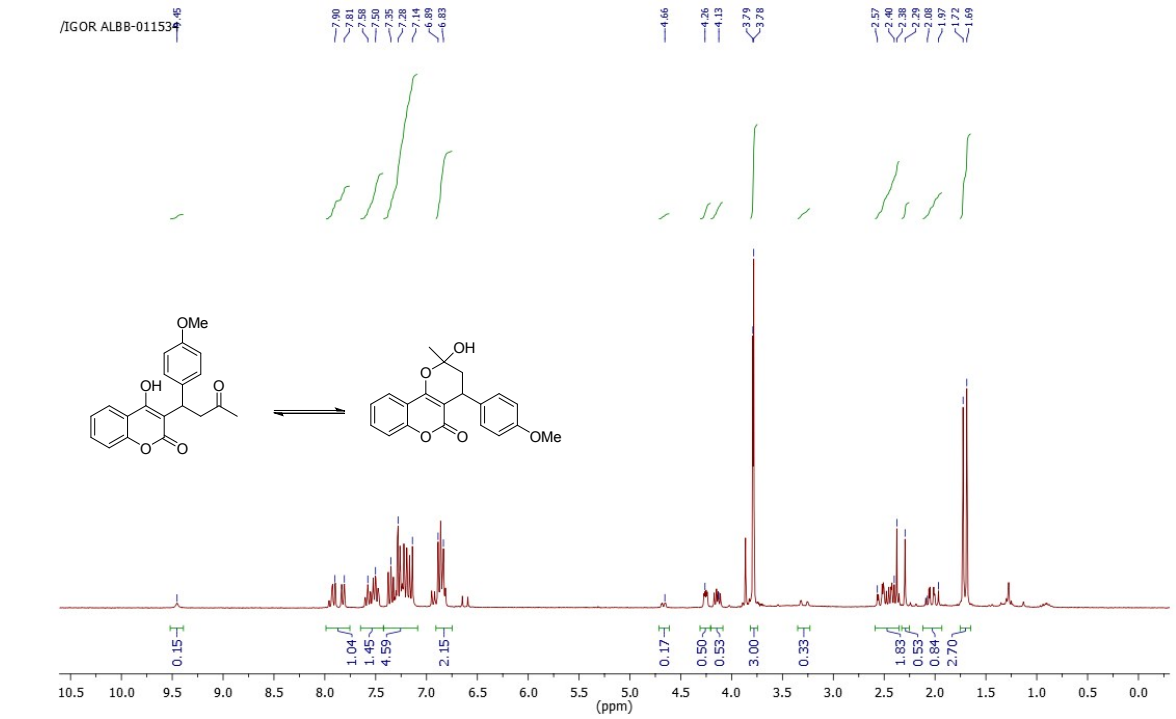


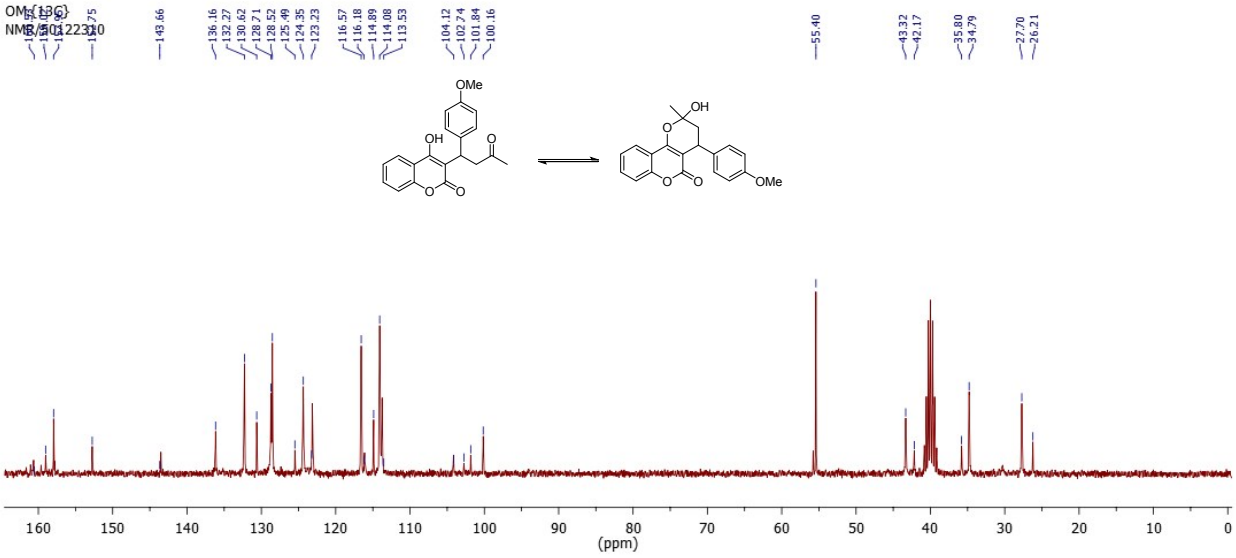
(*S*)-3-(1-(4-chlorophenyl)-3-oxobutyl)-4-hydroxy-2H-chromen-2-one (3b).



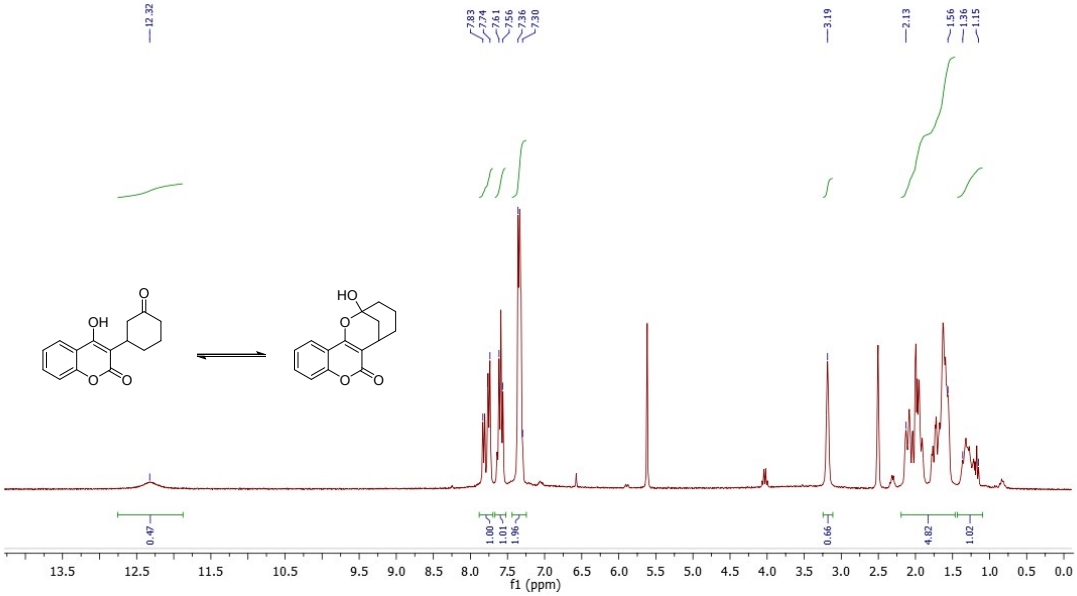


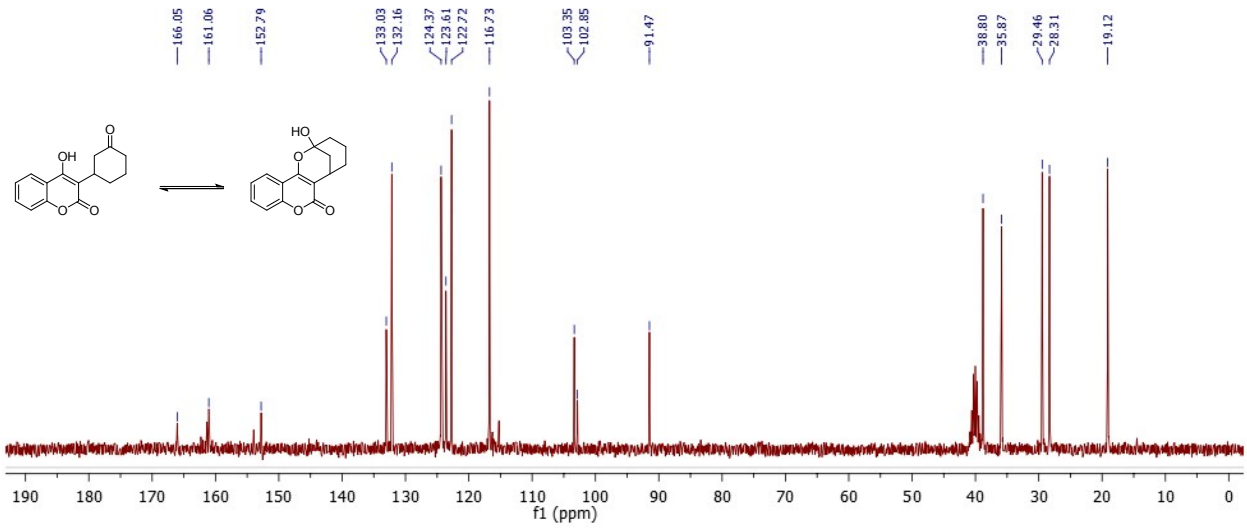
(*S*)-4-hydroxy-3-(1-(4-methoxyphenyl)-3-oxobutyl)-2H-chromen-2-one (3c).





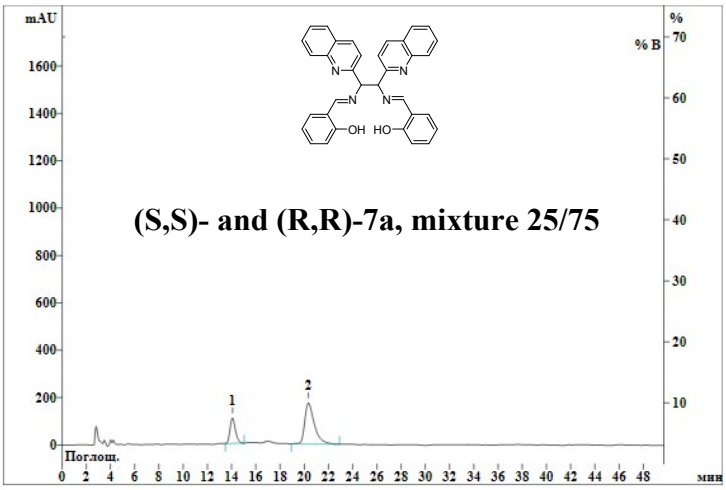
(*S*)-4-hydroxy-3-(3-oxocyclohexyl)-2H-chromen-2-one (3d).



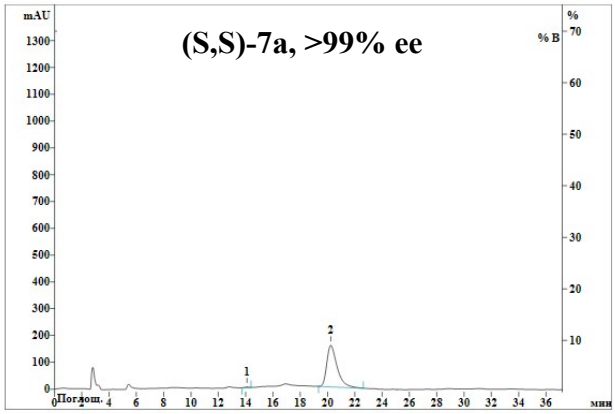


8. **HPLC data**

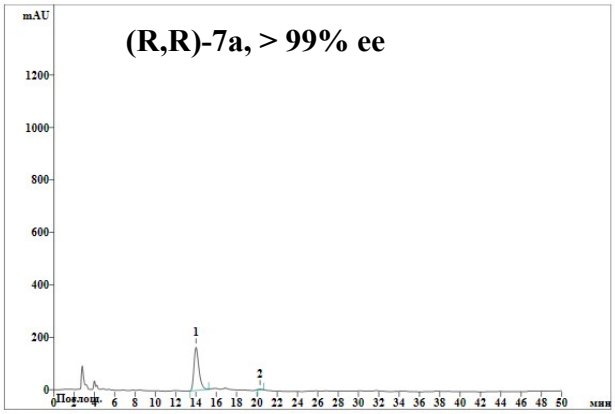
2,2'-({[(1*R*,2*R*)-1,2-di(quinolin-2-yl)ethane-1,2-diyl]bis(azanylylidene)}bis(methanylylidene))diphenol (*R*,*R*-**7a**). HPLC (Daicel Chiralcel AD-H; *n*-hexane/2-propanol, 70:30; flow rate = 1.0 mL/min; λ = 254 nm): t_1 = 14.1, t_2 = 20.3 min.



Пик	Время мин	Площадь mAU*сек	Площадь %
1	14.07	3329.45	25.92
2	20.34	9514.33	74.08
2	49.69	12843.78	100.00

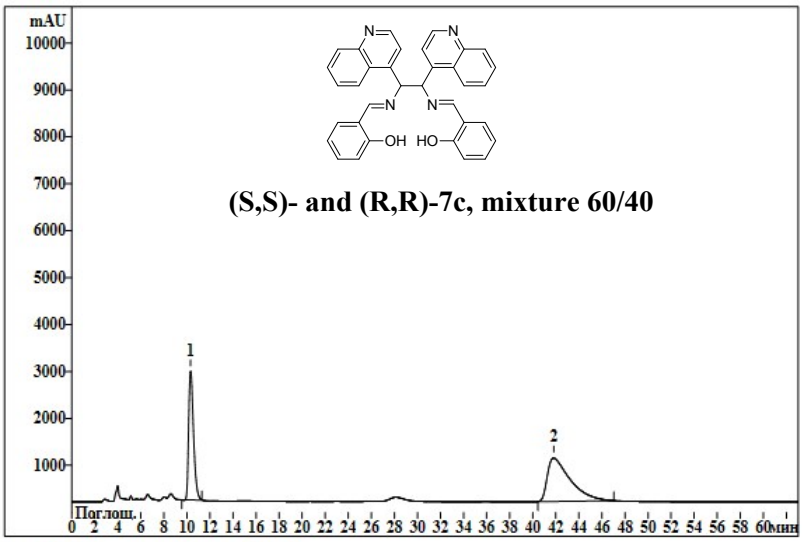


Пик	Время мин	Площадь mAU*сек	Площадь %
1	14.1	40.64	0.49
2	20.24	8176.08	99.51
2	37.19	8216.72	100.00



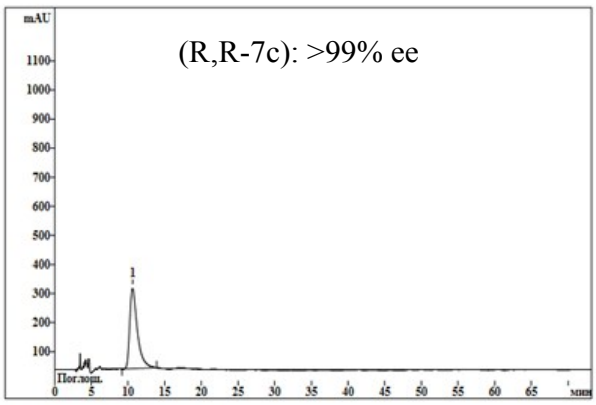
Пик	Время мин	Площадь mAU*сек	Площадь %
1	14.01	5558.80	99.52
2	20.3	26.91	0.48
2	49.98	5585.71	100.00

2,2'-({[(1*S*,2*S*)-1,2-di(quinolin-4-yl)ethane-1,2-diyl]bis(azanylylidene)}bis(methanylylidene))diphenol (*S*,*S*-**7c**). HPLC (Daicel Chiralcel OD-H; *n*-hexane/2-propanol, 70:30; flow rate = 1.0 mL/min; λ = 220 nm): t_1 = 10.3, t_2 = 41.8 min.



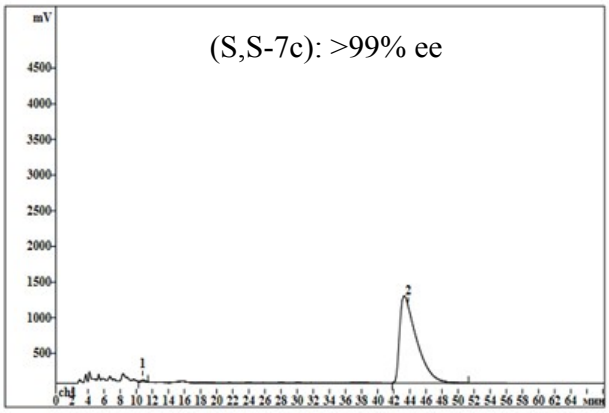
(S,S)- and (R,R)-7c, mixture 60/40

No	Время мин	Площадь mAU*сек	Площадь %
1	10.32	80326.53	38.64
2	41.81	127579.43	61.36
2	63.04	207905.96	100.00



(R,R-7c): >99% ee

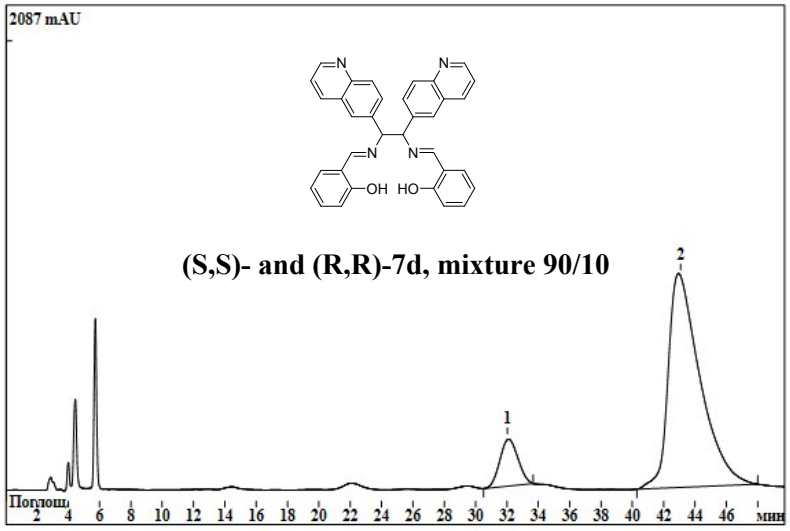
No	Время мин	Площадь mAU*сек	Площадь %
1	10.61	20077.66	100.00
1	73.23	20077.66	100.00



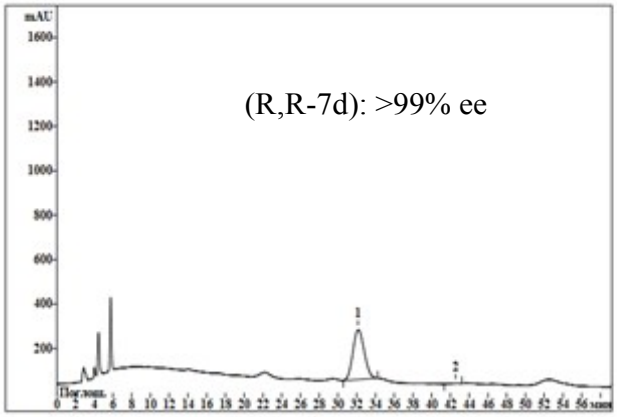
(S,S-7c): >99% ee

No	Retention мин	Width/2 мин	Height mV	Height %	Area mV*сек	Area %
1	10.8	0.480	25.02	2.28	783.23	0.44
2	43.8	2.422	1074.27	97.72	178187.62	99.56
2	68.23	1.451	1099.29	100.00	178970.84	100.00

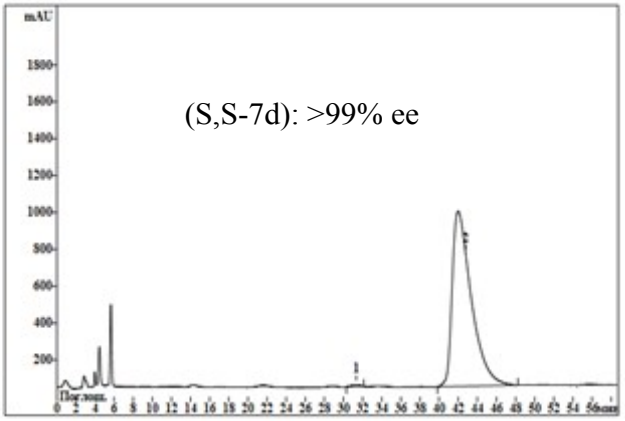
2,2'-({[(1*S*,2*S*)-1,2-di(quinolin-6-yl)ethane-1,2-diyl]bis(azanylylidene)}bis(methanylylidene))diphenol (*S*,*S*-**7d**). Daicel Chiralcel AD-H; *n*-hexane/2-propanol, 70:30; flow rate = 1.0 mL/min; λ = 220 nm): t_1 = 32.0, t_2 = 43.1 min.



No	Время мин	Площадь mAU*сек	Площадь %
1	32.02	17071.28	11.11
2	43.07	136556.47	88.89
2	56.18	153627.75	100.00

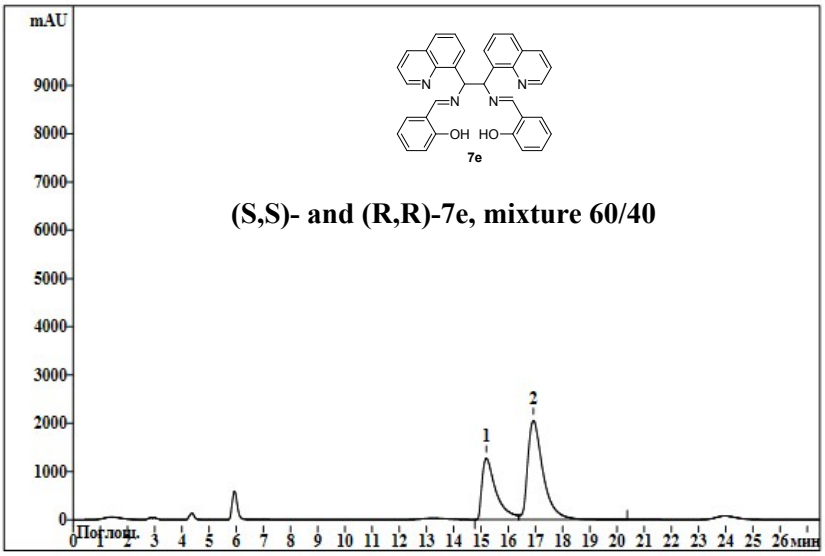


No	Время мин	Площадь mAU*сек	Площадь %
1	32.12	18809.22	99.65
2	42.53	66.36	0.35
2	59.23	18875.58	100.00

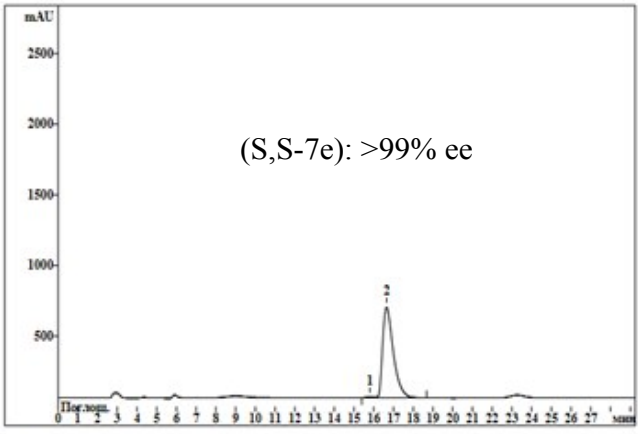


No	Время мин	Площадь mAU*сек	Площадь %
1	31.28	570.65	0.43
2	42.77	132280.08	99.57
2	58.87	132850.73	100.00

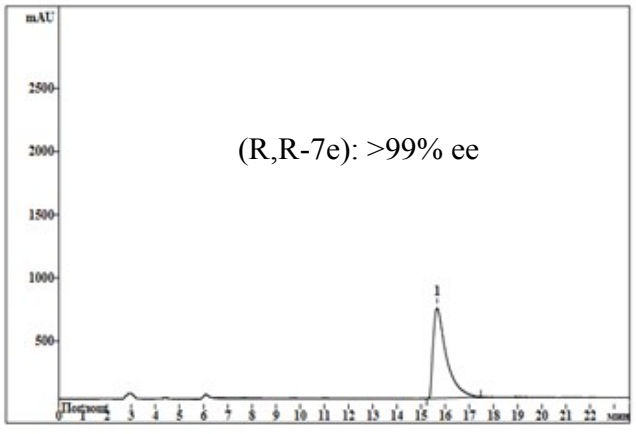
2,2'-({[(1S,2S)-1,2-di(quinolin-8-yl)ethane-1,2-diyl]bis(azanylylidene)}bis(methanylylidene))diphenol (*S*,*S*-**7e**). Daicel Chiralcel AD-H; *n*-hexane/2-propanol, 70:30; flow rate = 1.0 mL/min; λ = 220 nm): t_1 = 15.2, t_2 = 16.9 min.



No	Время мин	Площадь mAU*сек	Площадь %
1	15.19	45829.86	36.14
2	16.93	80978.93	63.86
2	27.47	126808.79	100.00

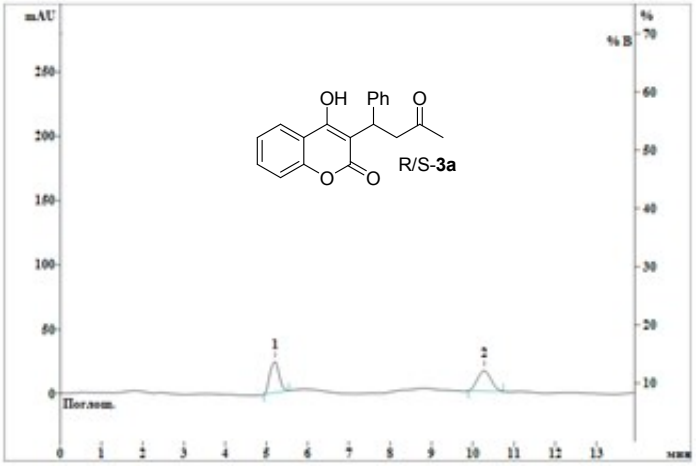


No	Время мин	Площадь mAU*сек	Площадь %
1	15.8	115.01	0.47
2	16.65	24204.87	99.53
2	29.26	24319.88	100.00

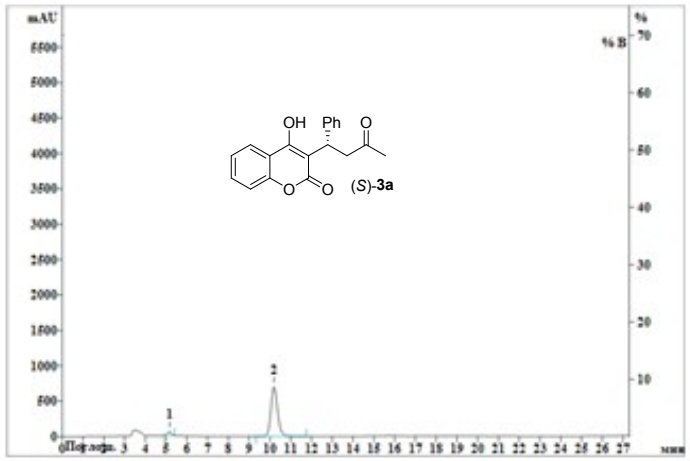


No	Время мин	Площадь mAU*сек	Площадь %
1	15.66	27375.69	100.00
1	23.64	27375.69	100.00

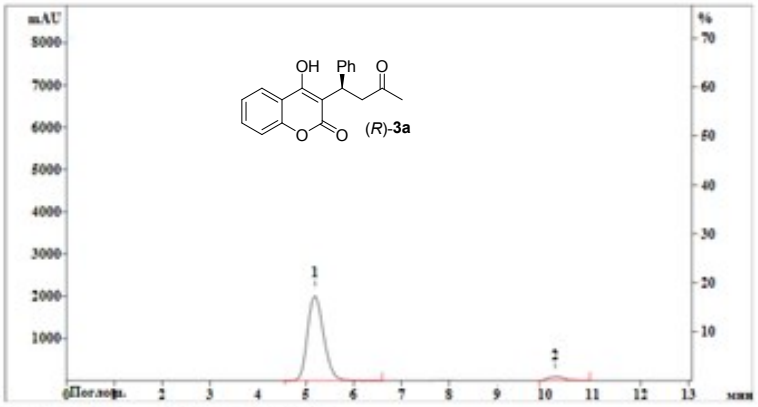
(***S***)**-4-hydroxy-3-(3-oxo-1-phenylbutyl)-2H-chromen-2-one** (**3a**). HPLC (Daicel Chiralcel AD-H; *n*-hexane/2-propanol, 70:30; flow rate = 0.8 mL/min; λ = 254 nm): t_1 = 5.2 (minor), t_2 = 10.2 (major) min.



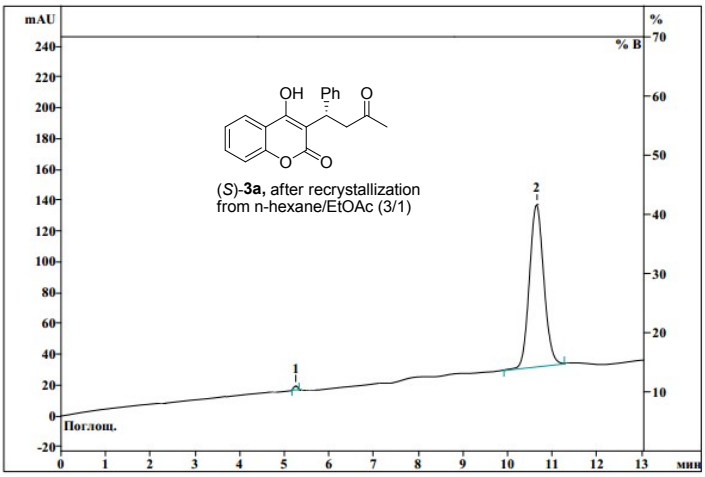
Пик	Время мин	Площадь mAU*сек	Площадь %
1	5.203	375.46	50.75
2	10.28	364.41	49.25
2	13.93	739.87	100.00



Пик	Время мин	Площадь mAU*сек	Площадь %
1	5.166	746.03	4.56
2	10.2	15604.86	95.44
2	27.29	16350.90	100.00



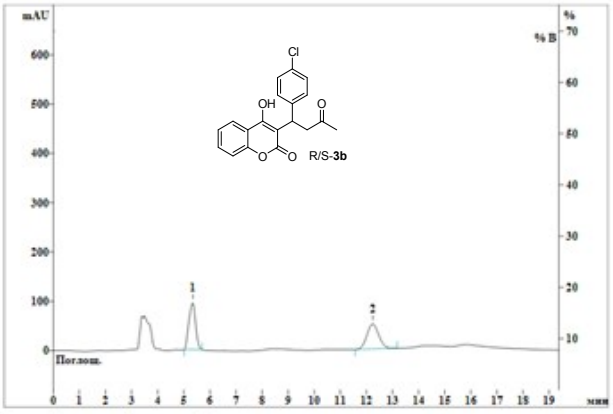
Пик	Время мин	Площадь mAU*сек	Площадь %
1	5.332	46826.98	95.78
2	10.18	2069.70	4.22
2	13.09	48890.68	100.00



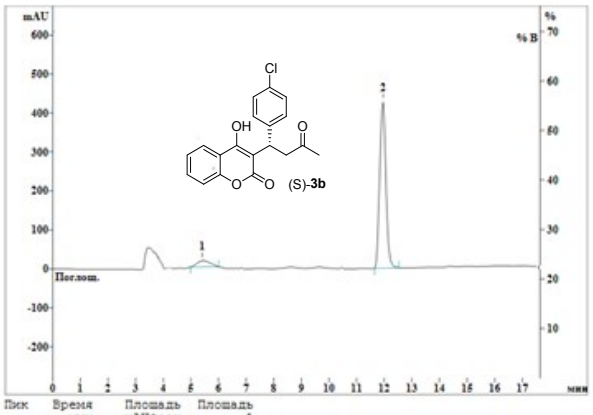
Пик	Время мин	Площадь mAU*сек	Площадь %
1	5.259	15.53	0.66
2	10.65	2334.21	99.34
2	13.05	2349.74	100.00

(*S*)-3-(1-(4-chlorophenyl)-3-oxobutyl)-4-hydroxy-2H-chromen-2-one (**3b**).

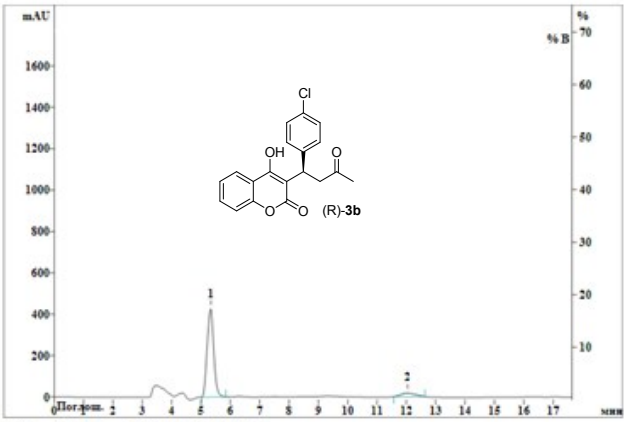
HPLC (Daicel Chiralcel AD-H; *n*-hexane/2-propanol, 70:30; flow rate = 0.8 mL/min; λ = 254 nm): t_1 = 5.34 (minor), t_2 = 12.24 (major) min.



Пик	Время мин	Площадь mAU*сек	Площадь %
1	5.34	1698.32	51.70
2	12.24	1586.81	48.30
2	19.38	3285.13	100.00

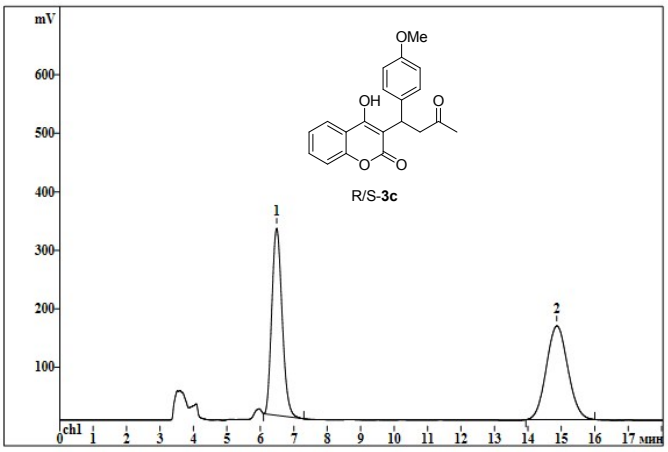


Пик	Время мин	Площадь mAU*сек	Площадь %
1	5.64	546.04	7.59
2	12.09	6645.75	92.41
2	17.64	7191.80	100.00

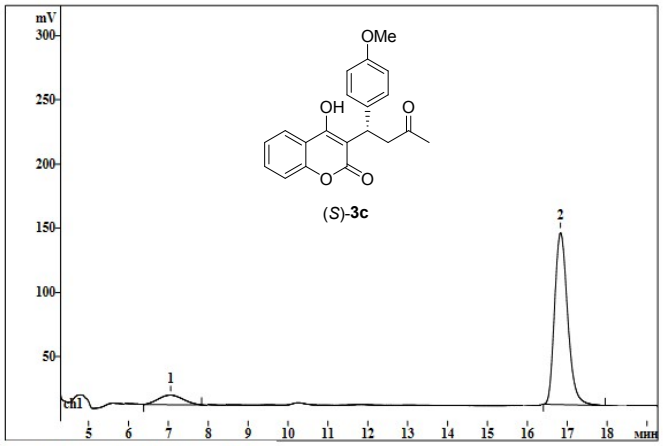


Пик	Время мин	Площадь mAU*сек	Площадь %
1	5.33	6630.44	92.02
2	12.1	575.19	7.98
2	17.64	7205.63	100.00

4-hydroxy-3-(1-(4-methoxyphenyl)-3-oxobutyl)-2H-chromen-2-one (3c). HPLC (Daicel Chiralcel AD-H; *n*-hexane/2-propanol, 70:30; flow rate = 0.8 mL/min; λ = 254 nm): t_1 = 6.5 (minor), t_2 = 14.9 (major) min.

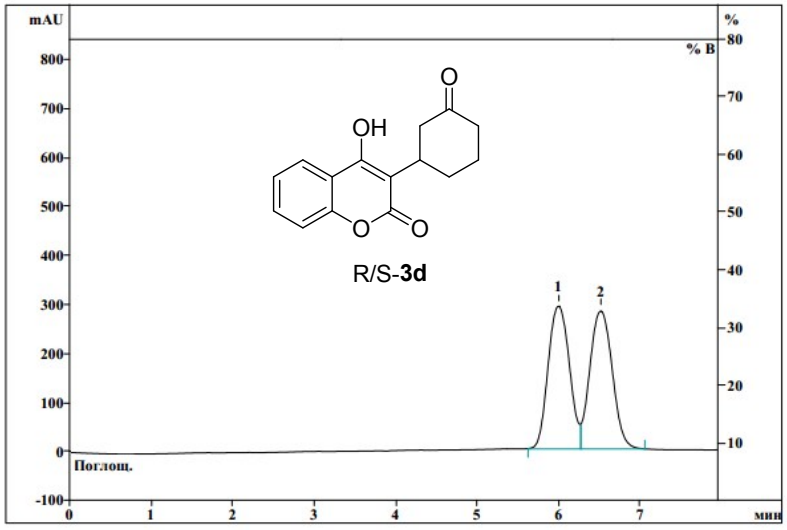


No	Retention мин	Width/2 мин	Height mV	Height %	Area mV*сек	Area %
1	6.486	0.334	319.56	66.63	6851.49	48.87
2	14.87	0.698	160.06	33.37	7169.73	51.13
2	18.04	0.516	479.61	100.00	14021.22	100.00

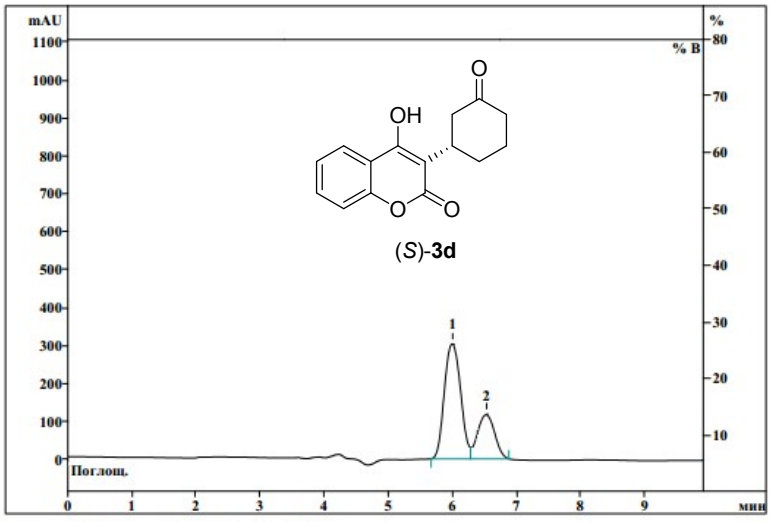


No	Retention мин	Height %	Area %
1	7.074	5.29	9.56
2	16.84	94.71	90.44
2	23.07	100.00	100.00

(*S*)-4-hydroxy-3-(3-oxocyclohexyl)-2H-chromen-2-one (3d). HPLC (Daicel Chiralcel AD-H; *n*-hexane/2-propanol, 80:20; flow rate = 1.0 mL/min; λ = 210 nm): t_1 = 6.0 (major), t_2 = 6.5 (minor) min.



Пик	Время мин	Площадь mAU*сек	Площадь %
1	5.999	5272.65	49.41
2	6.52	5397.97	50.59
2	7.95	10670.62	100.00



Пик	Время мин	Площадь mAU*сек	Площадь %
1	6.002	5654.13	75.44
2	6.528	1840.50	24.56
2	9.917	7494.63	100.00

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