**Supplementary Materials**

# Efficacy of Selenourea Organocatalysts in Asymmetric Michael Reactions under Standard and Solvent-Free Conditions

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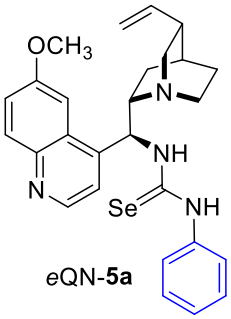
## S1. General

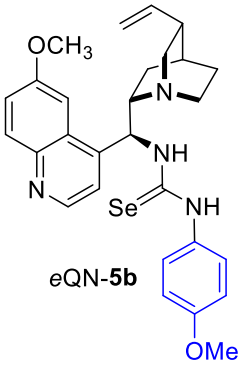
$^{1}H$ and $^{13}C$ NMR spectra (400 and 125 MHz or 600 and 151 MHz) were recorded in $CDCl_3$ on a JEOL ECZ400S instrument (Jeol Ltd., Tokyo, Japan) and Bruker Avance II 600 instrument (Bruker, Billerica, MA, USA), respectively. $^{1}H$ NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) and $CDCl_3$ (δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, etc.), coupling constants (Hz) and integration.
$^{13}C$ NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) or $CDCl_3$ (δ 77.16 ppm). High resolution mass spectra (HRMS) were measured on a Waters LCT Premier XE TOF instrument (Waters Corporation, Milford, MA, USA) with electrospray ionization.
HPLC analysis was performed on SHIMADZU NEXERA X2 apparatus (Chiral Technologies INC. West Chester, PA, USA) using CHIRALPAK IA-3, IB-3 and IC-3 chiral columns (4.6 mm × 25 cm) without guard column. Each HPLC analysis has been controlled by comparison with the pure sample and the racemate.
Optical rotations were measured using an Optical Activity Ltd. Model AA-5 automatic polarimeter (Optical Activity Ltd., Huntington, UK) at $\lambda$ = 589 nm (c g/100 mL).
Melting points were determined using a Boëtius hot-stage apparatus (PHMK VEB Analytic, Dresden, Germany).
Reactions were monitored by thin-layer chromatography (TLC) on silica gel 60 F-254 precoated plates (Merck, Darmstadt, Germany), and spots were visualized with a UV lamp or KMnO4 dip.
Catalytic reactions were performed in standard reaction tubes with PTFE stopper without any protection against moisture or air.
Ball milling was realized in a planetary ball mill PM-200 (Retsch GmbH, Haan, Germany) in a stainless steel 12 mL containers with stainless steel grinding balls with diameter 10 mm.

## S2. Catalysts

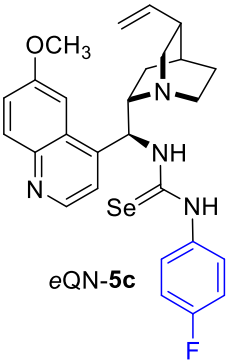
Selenoureas **5a–c**, **5f–h**, **5k** and thiourea **6a** were described in our previous publication [7]. Thiourea **6b** were prepared following the literature precedents [40,41]. Compounds **5d**, **5e**, **5i** and **5j** are novel.



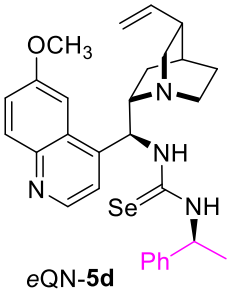
*e*QN-**5a**



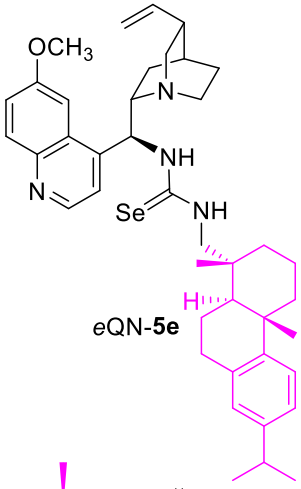
*e*QN-**5b**



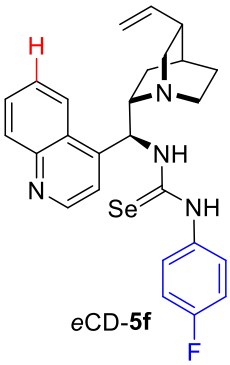
*e*QN-**5c**



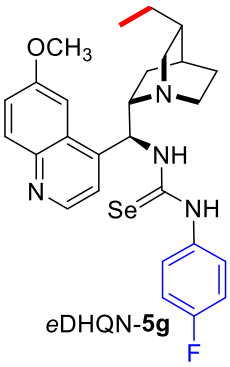
*e*QN-**5d**



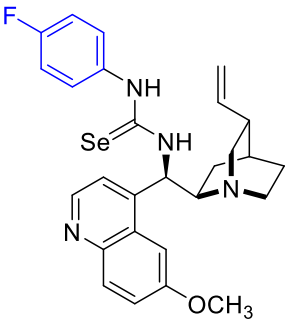
*e*QN-**5e**



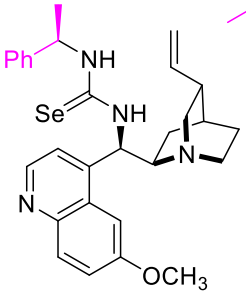
*e*CD-**5f**



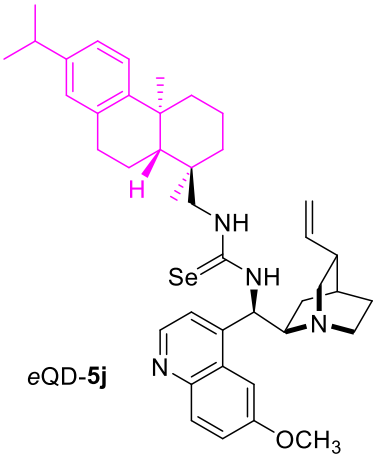
*e*DHQN-**5g**



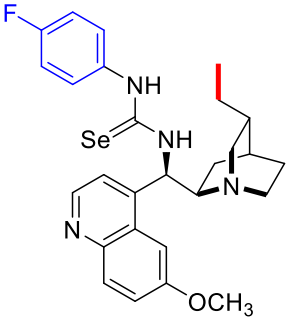
*e*QD-**5h**



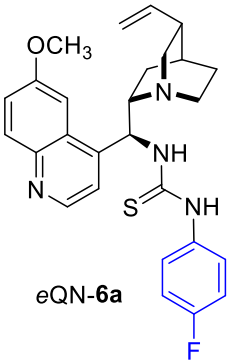
*e*QD-**5i**



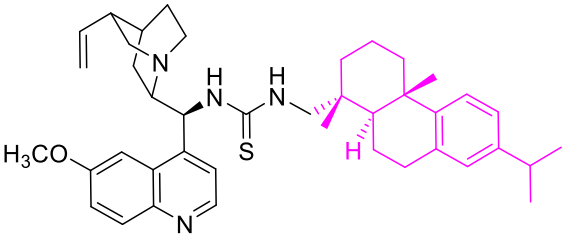
*e*QD-**5j**



*e*DHQD-**5k**



*e*QN-**6a**



*e*QN-**6b**

## S3. Spectral data

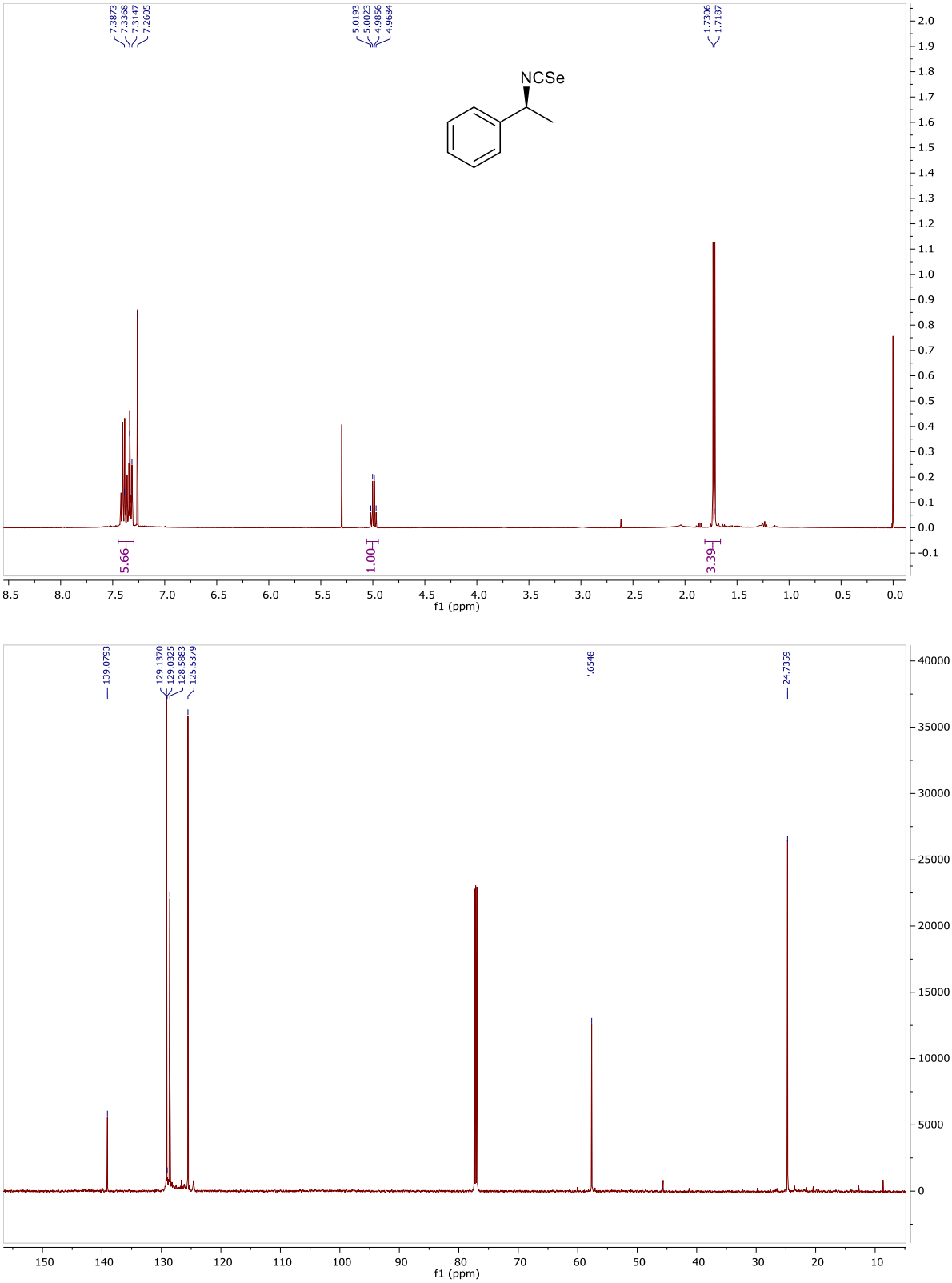



**Figure S1.** $^{1}$H and $^{13}$C NMR spectra of [(1*S*)-1-isoselenocyanatoethyl]benzene **3d**.

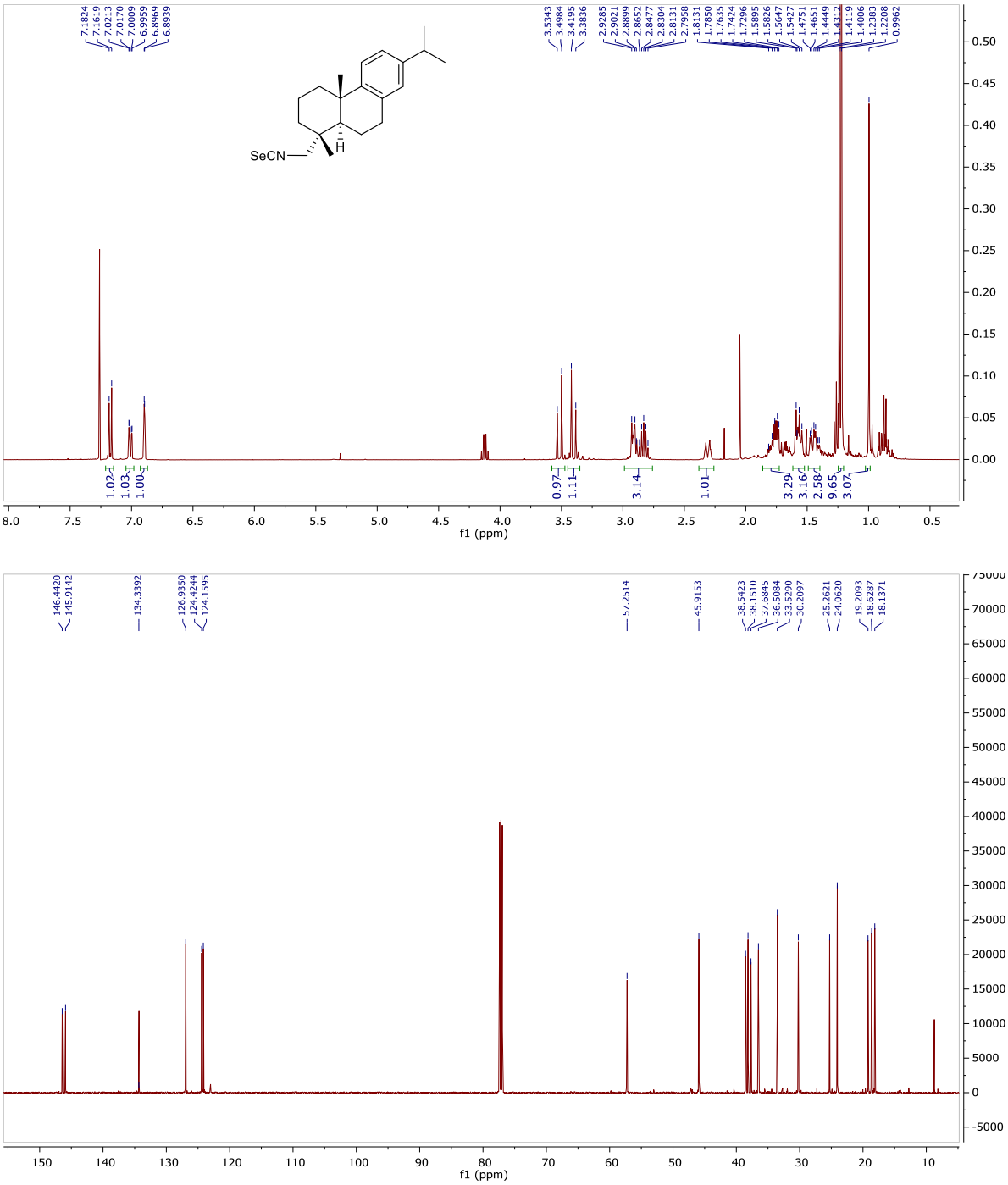



**Figure S2.** $^{1}$H and $^{13}$C NMR spectra of (1*R*,4a*S*,10a*R*)-1,4a-dimethyl-7-isopropyl-1-(isoselenocyanatomethyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene **3e**.

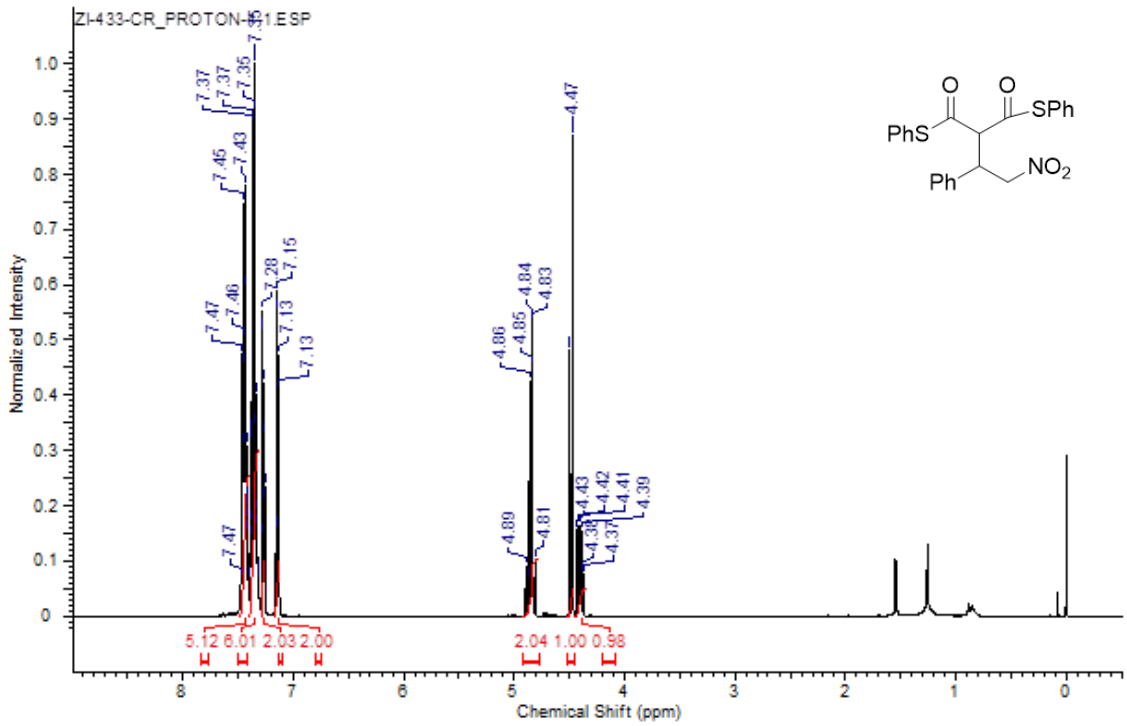



**Figure S3.** $^{1}$H NMR (400 MHz) spectrum of 2-(2-nitro-1-phenylethyl)-1,3-bis(phenylsulfanyl)propane-1,3-dione **9** in $CDCl_3$. The signal at 1.26 ppm refers to residual hexane and the signal at 1.56 ppm refers to residual water.

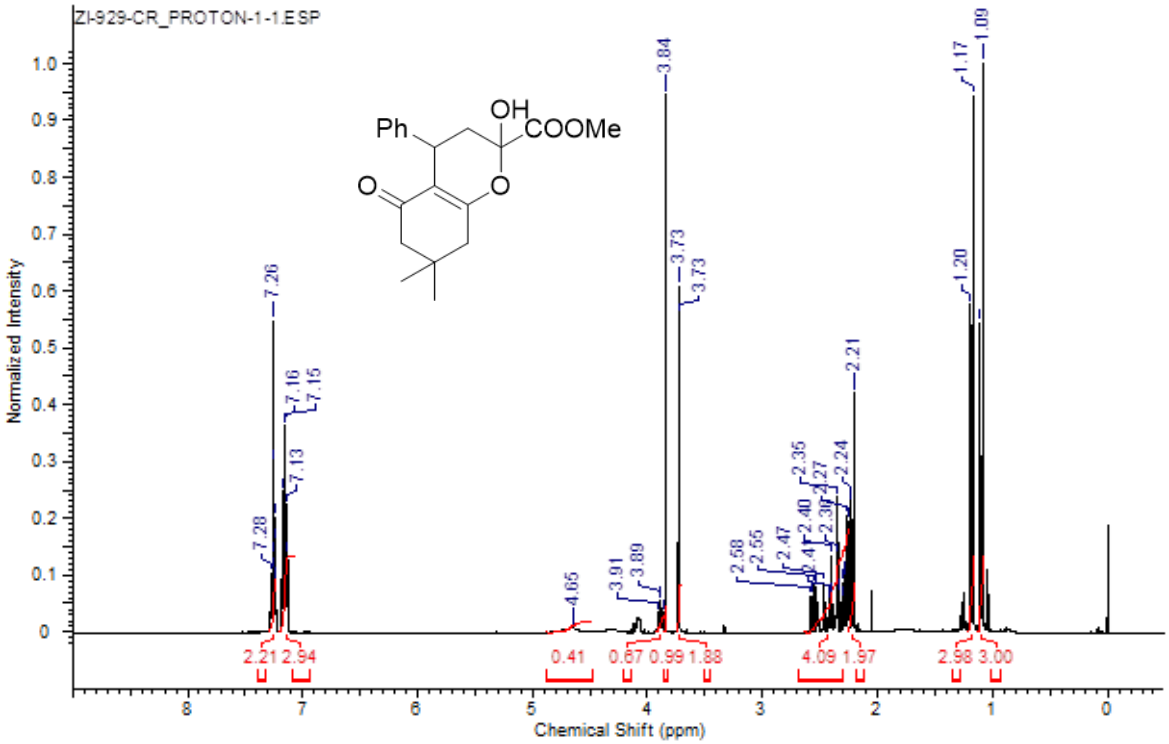



**Figure S4.** $^{1}$H NMR (400 MHz) spectra of 4-methyl-2-hydroxy-7,7-dimethyl-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2*H*-chromene-2-carboxylate **12** in $CDCl_3$. The signal at 2.04 ppm refers to residual ethyl acetate.

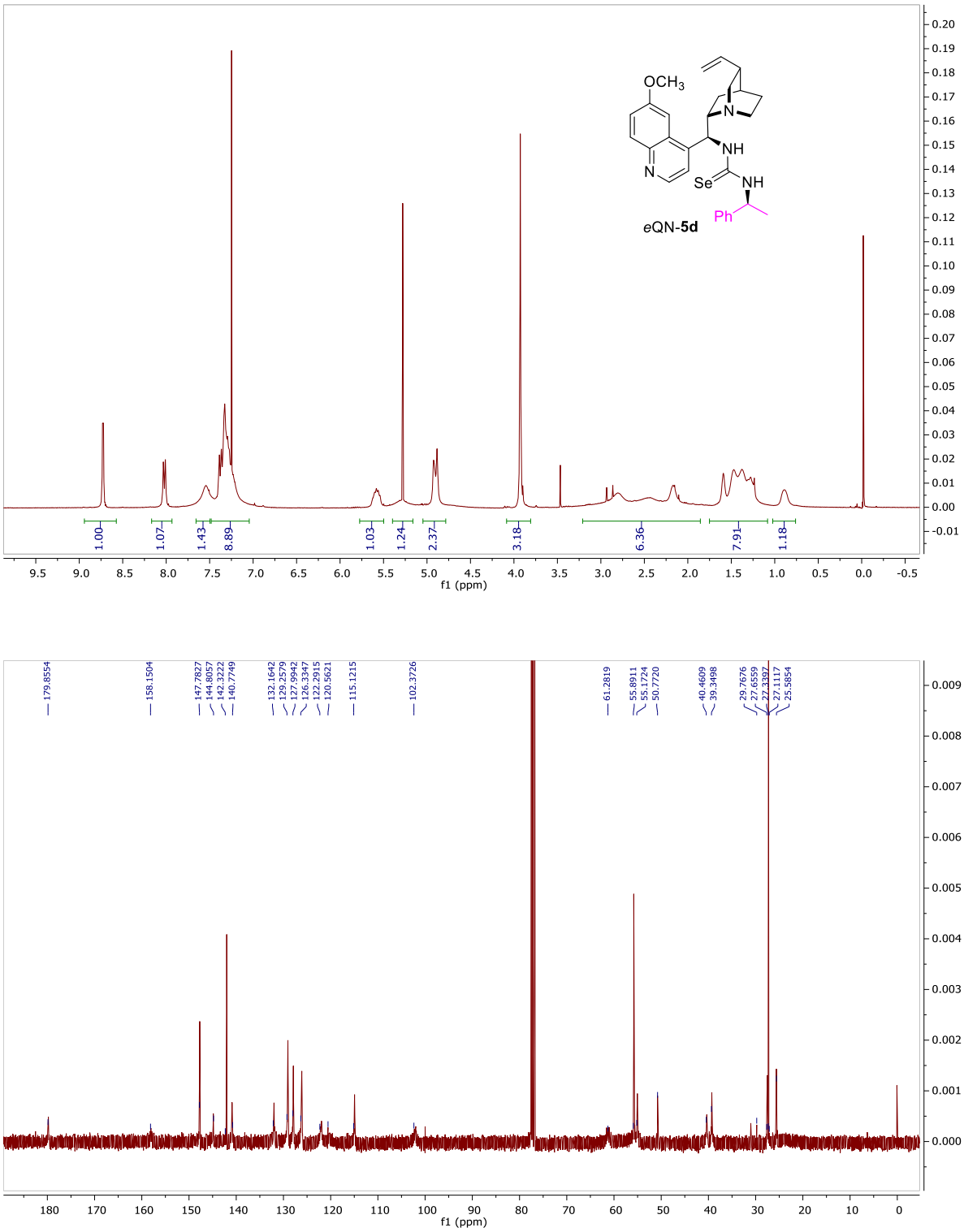



**Figure S5.** $^{1}$H and $^{13}$C NMR spectra of *N*-[(8*S*,9*S*)-6′-methoxycinchonan-9-yl]-*N*′-[(*S*)-1-phenylethyl]selenourea *e*QN-**5d.**

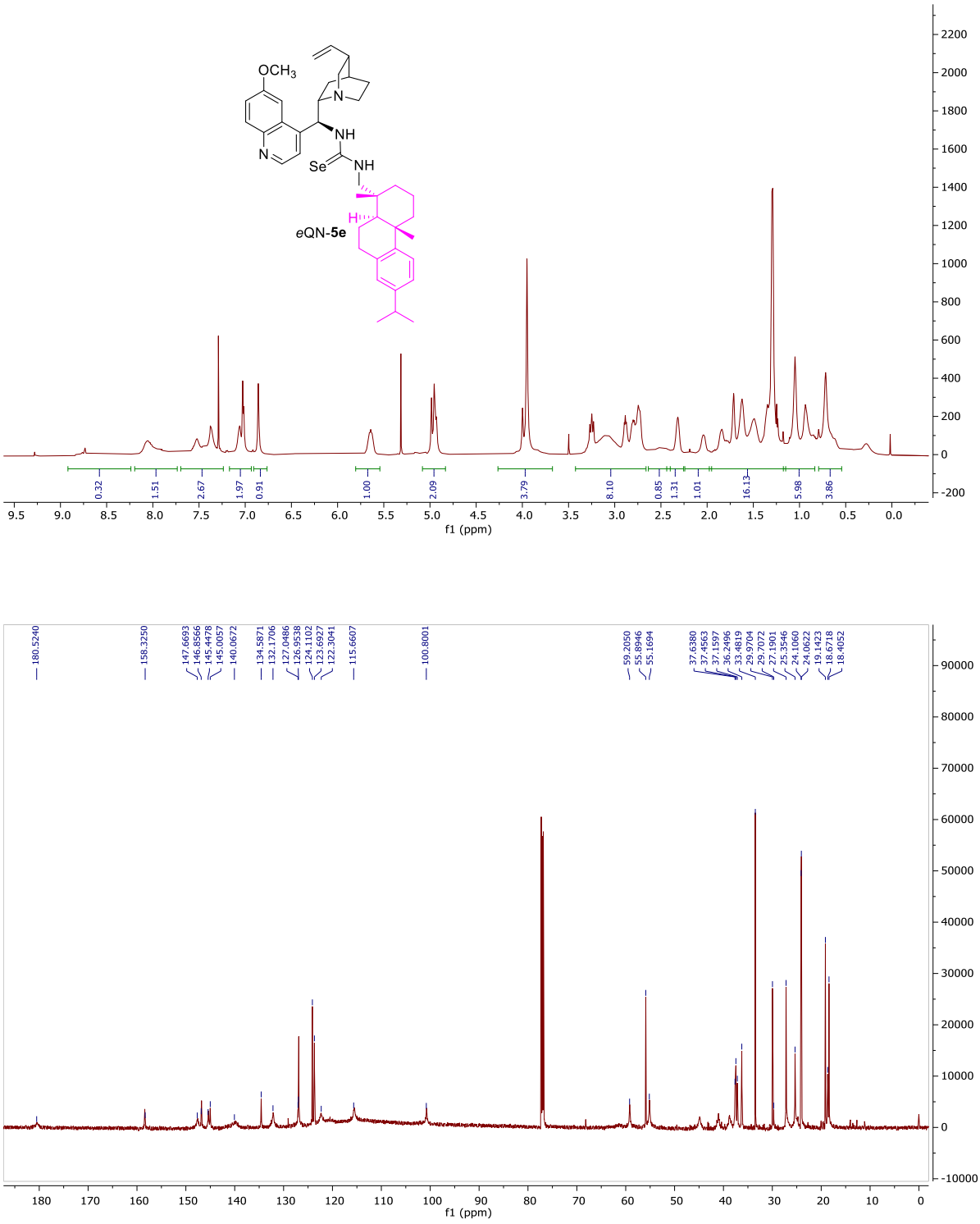



**Figure S6.** $^{1}$H and $^{13}$C NMR spectra of *N*-{[(1*R*,4a*S*,10a*R*)-1,4a-dimethyl-7-izopropyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-yl]methyl}-*N*′-[(8*S*,9*S*)-6′-methoxycinchonan-9-yl]selenourea *e*QN-**5e.**

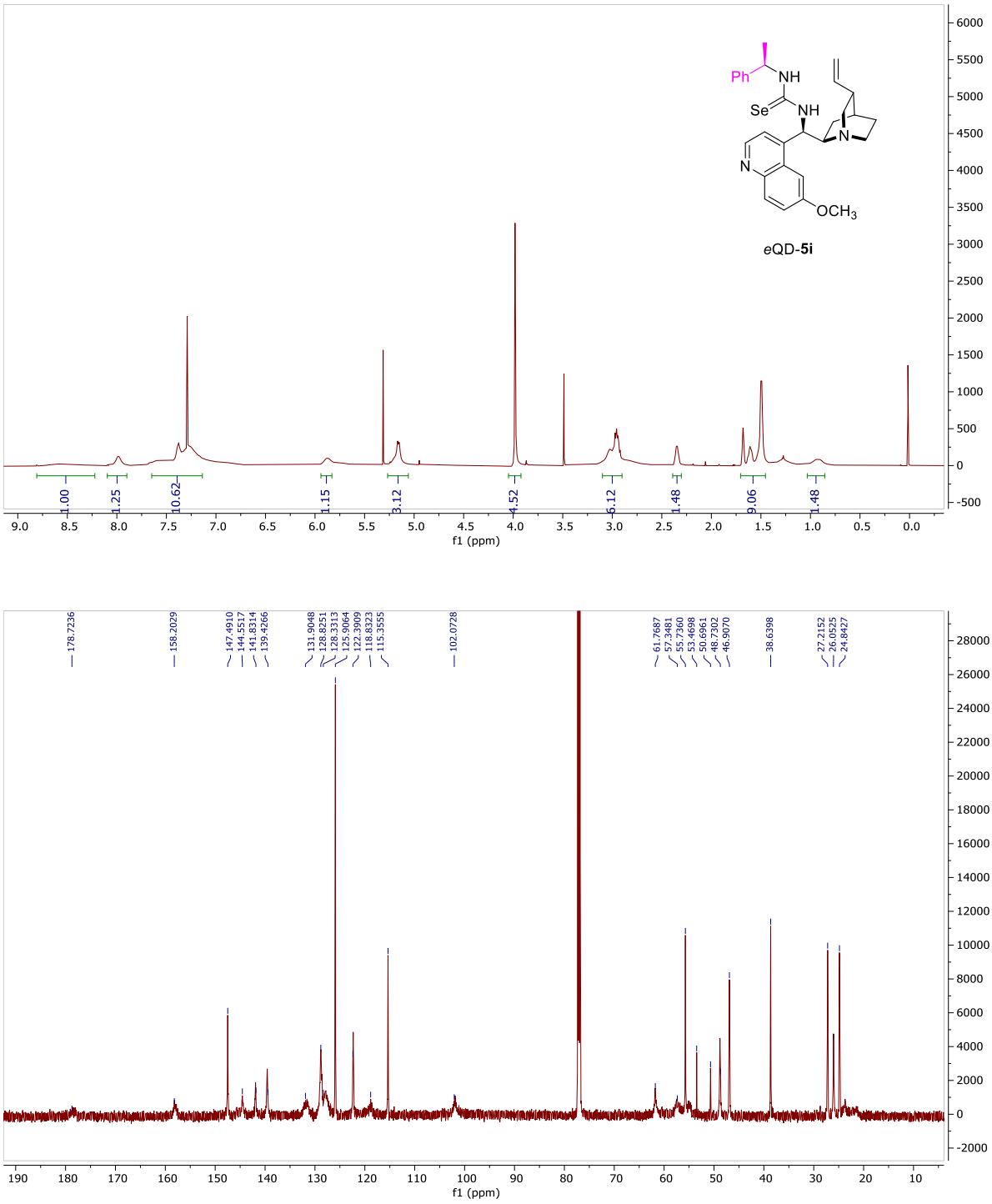



**Figure S7.** $^{1}$H and $^{13}$C NMR spectra of *N*-[(8*R*,9*R*)-6′-methoxycinchonan-9-yl]-*N*′-[(*S*)-1-phenylethyl]selenourea *e*QD-**5i.**

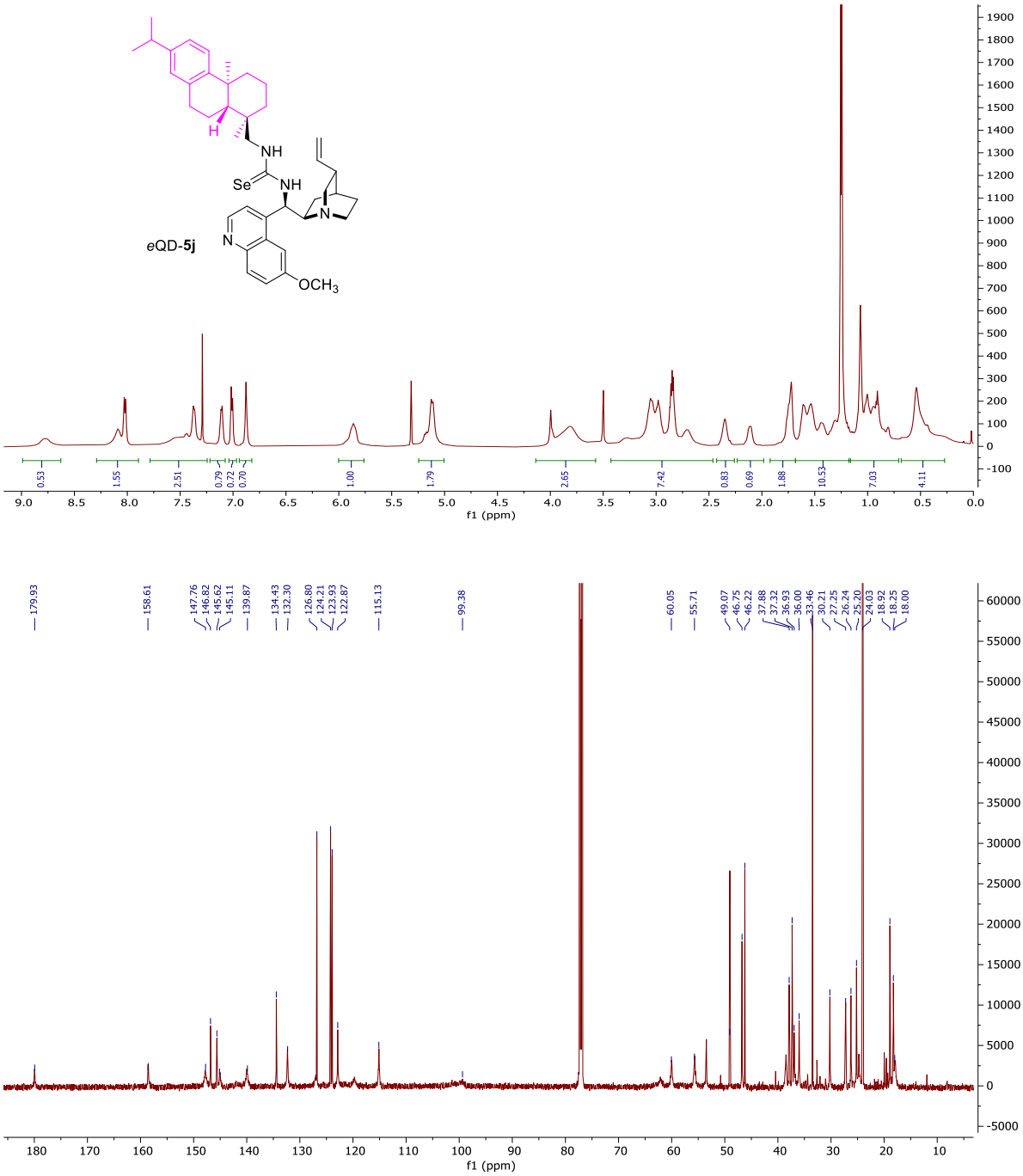
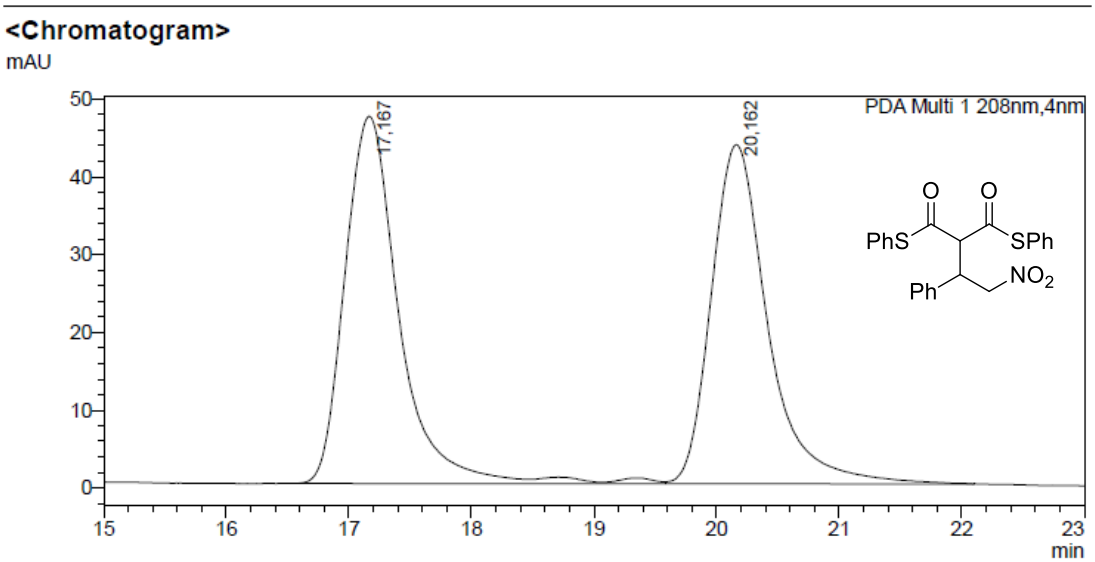



**Figure S8.** $^{1}$H and $^{13}$C NMR spectra of *N*-{[(1*R*,4a*S*,10a*R*)-1,4a-dimethyl-7-izopropyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-yl]methyl}-*N*′-[(8*R*,9*R*)-6′-methoxycinchonan-9-yl]selenourea *e*QD-**5j.**

## S4. HPLC chromatograms

### *S4.1.Michael Addition of S, S′-diphenyl dithiomalonate to trans-β-nitrostyrene.*

(Chiralcel IB-3, *n*-hexane/2-propanol, 9:1, flow rate 1mL/min, $\lambda$ = 205 nm)

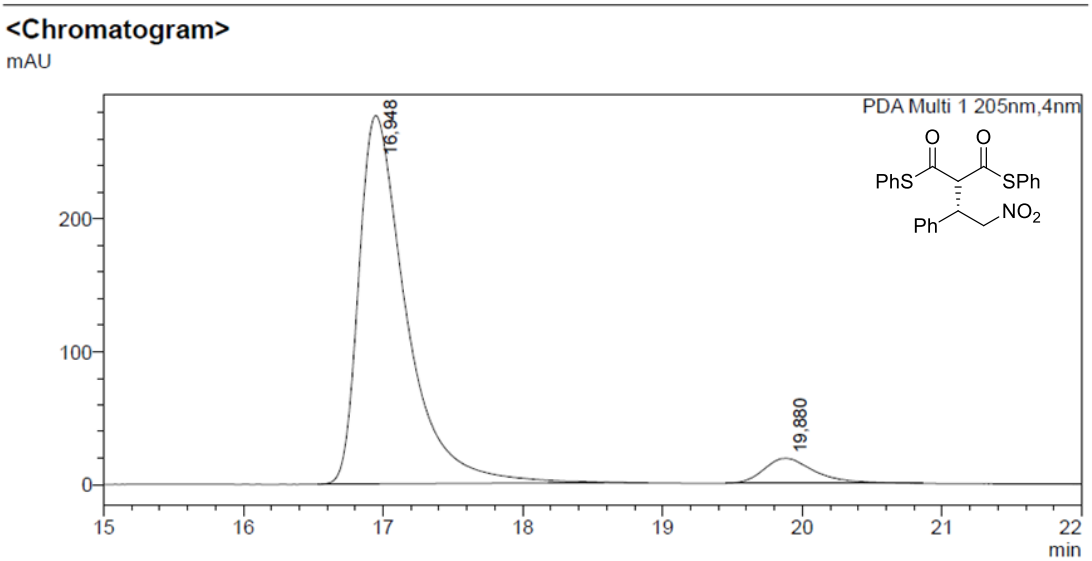



**<Peak Table>**

PDA Ch1 208nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 17,167 | 1451949 | 47230 | 50,915 |
| 2 | 20,162 | 1399774 | 43618 | 49,085 |
| Total | | 2851722 | 90848 | 100,000 |

**Figure S9.** HPLC chromatogram for racemic 2-(2-nitro-1-phenylethyl)-1,3-bis(phenylsulfanyl)propane-1,3-dione **9**.

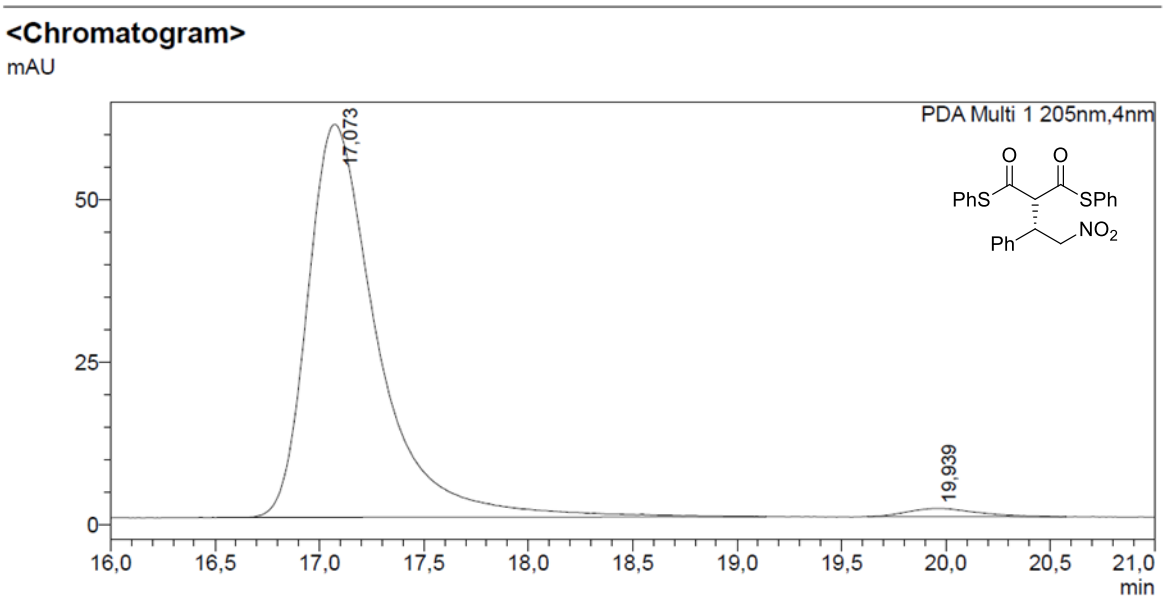



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 16,948 | 277480 | 6540106 | 93,241 |
| 2 | 19,880 | 18800 | 474053 | 6,759 |
| Total | | 296281 | 7014159 | 100,000 |

**Figure S10.** HPLC chromatogram for *S*-**9**: sample obtained with catalyst *e*QN-**5a** in a solution at 273 K (87% ee).

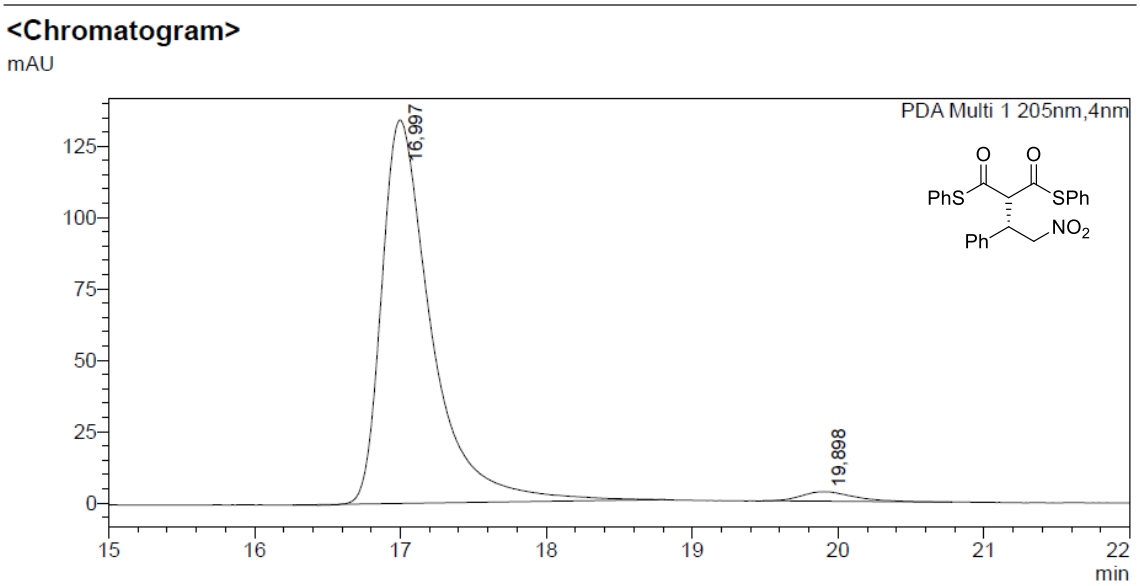



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 17,073 | 60341 | 1405426 | 98,020 |
| 2 | 19,939 | 1245 | 28389 | 1,980 |
| Total | | 61587 | 1433816 | 100,000 |

**Figure S11.** HPLC chromatogram for *S*-**9**: sample obtained with catalyst *e*QN-**5b** in a solution at 273 K (96% ee).

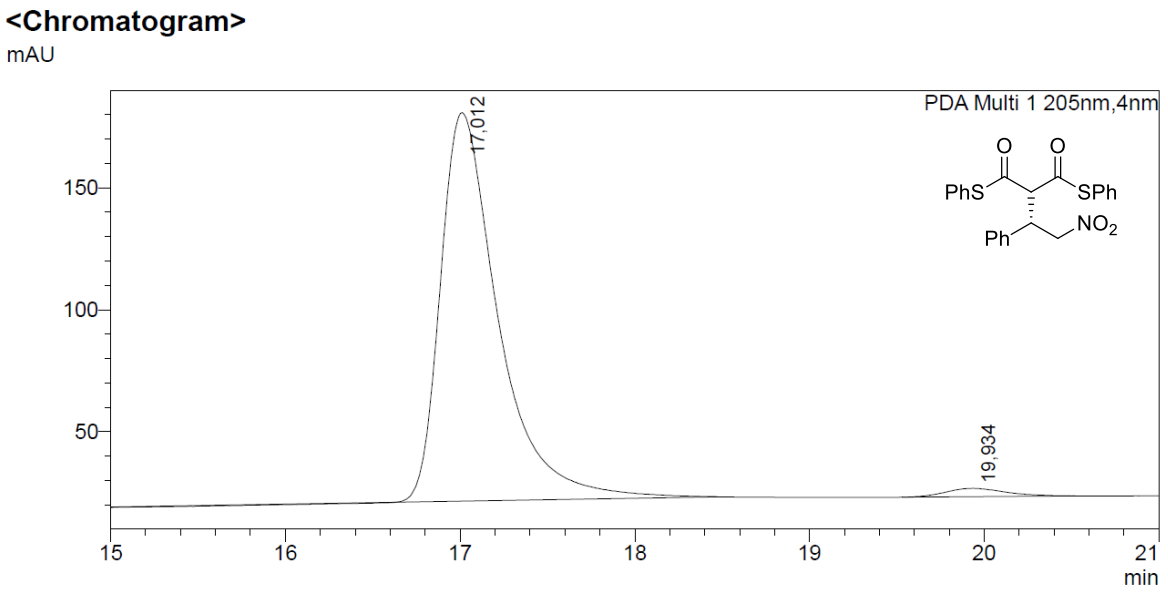



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 16,997 | 134255 | 3187870 | 97,395 |
| 2 | 19,898 | 3368 | 85276 | 2,605 |
| Total | | 137622 | 3273146 | 100,000 |

**Figure S12.** HPLC chromatogram for *S*-**9**: sample obtained with catalyst *e*QN-**5c** in a solution at 273 K (95% ee).

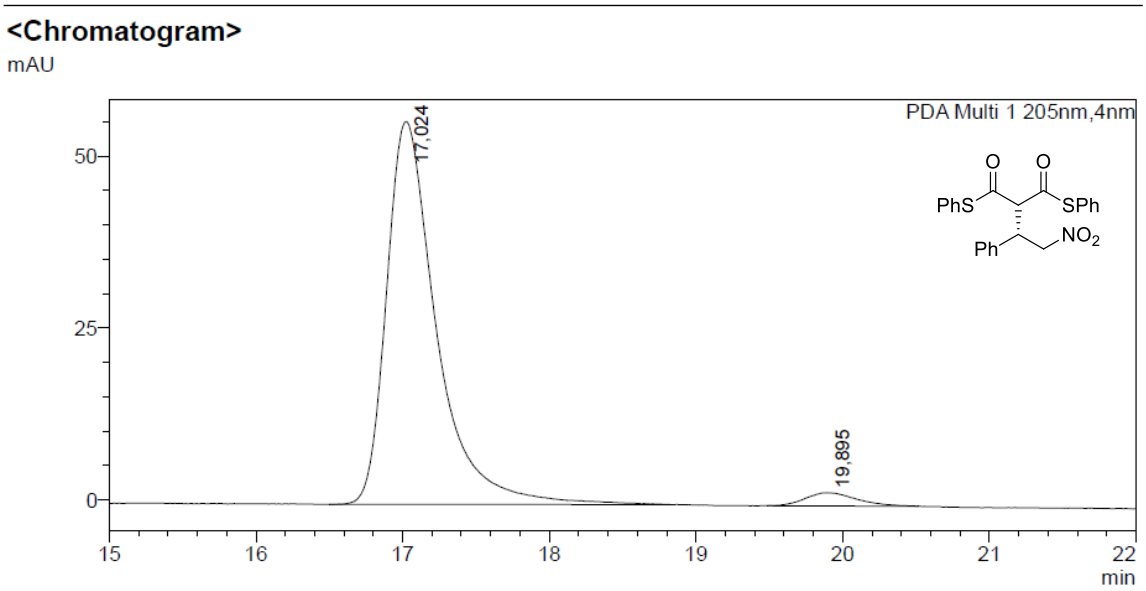



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 17,012 | 159270 | 3647067 | 97,839 |
| 2 | 19,934 | 3420 | 80554 | 2,161 |
| Total | | 162689 | 3727621 | 100,000 |

**Figure S13.** HPLC chromatogram for *S*-**9**: sample obtained with catalyst *e*QN-**5d** in a solution at 273 K (96% ee).

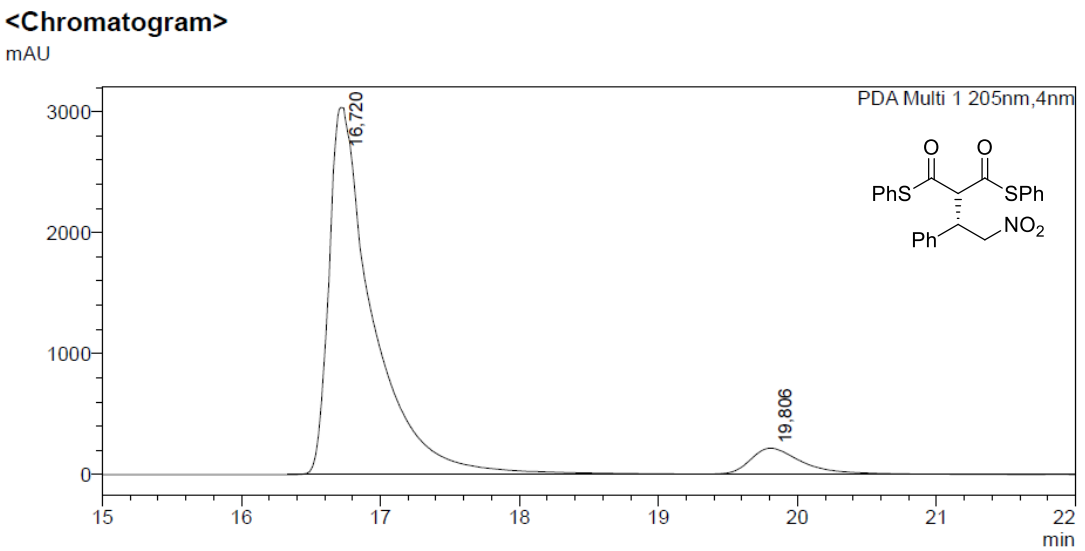



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 17,024 | 55701 | 1321649 | 96,572 |
| 2 | 19,895 | 1918 | 46921 | 3,428 |
| Total | | 57619 | 1368570 | 100,000 |

**Figure S14.** HPLC chromatogram for *S*-**9**: sample obtained with catalyst *e*QN-**5e** in a solution at 273 K (93% ee).

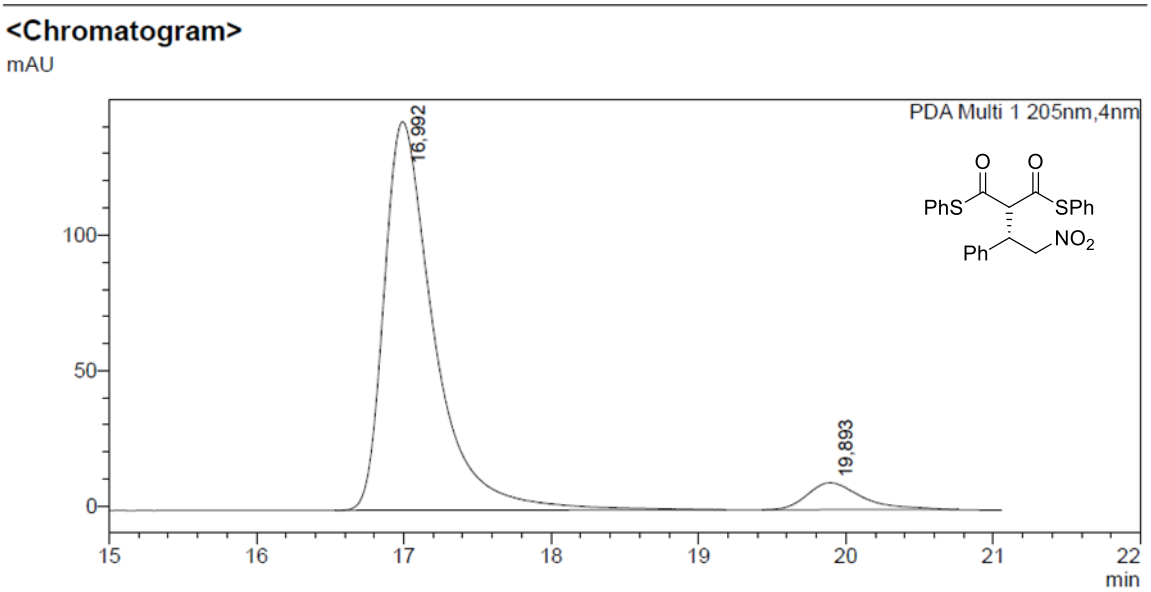



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 16,720 | 3033117 | 67223172 | 92,391 |
| 2 | 19,806 | 213659 | 5536411 | 7,609 |
| Total | | 3246776 | 72759584 | 100,000 |

**Figure S15.** HPLC chromatogram for *S*-**9**: sample obtained with catalyst *e*CD-**5f** in a solution at 273 K (85% ee).

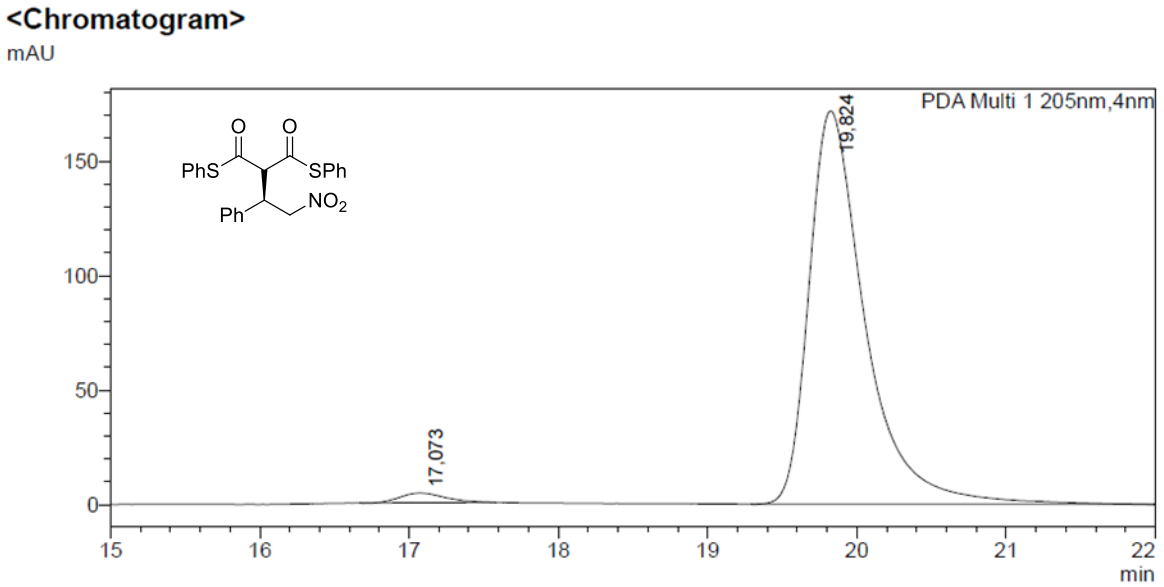



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 16,992 | 143305 | 3377740 | 92,939 |
| 2 | 19,893 | 9946 | 256605 | 7,061 |
| Total | | 153251 | 3634345 | 100,000 |

**Figure S16.** HPLC chromatogram for *S*-**9**: sample obtained with catalyst *e*DHQN-**5g** in a solution at 273 K (86% ee).

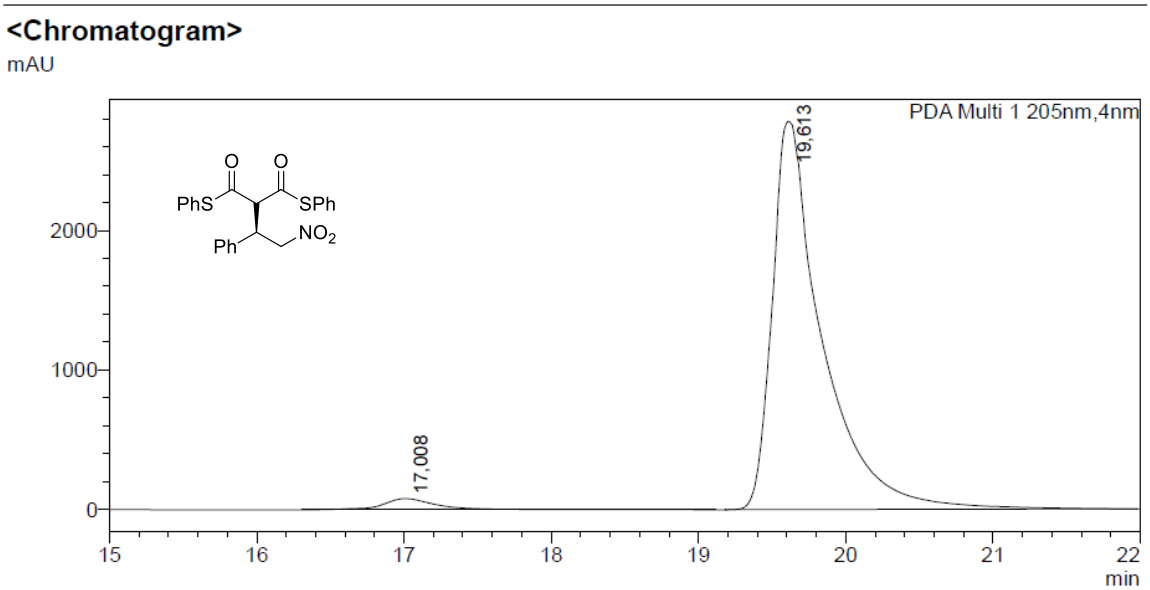



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 17,073 | 4291 | 90214 | 1,968 |
| 2 | 19,824 | 171787 | 4492951 | 98,032 |
| Total | | 176078 | 4583165 | 100,000 |

**Figure S17.** HPLC chromatogram for *R*-**9**: sample obtained with catalyst *e*QD-**5h** in a solution at 273 K (96% ee).

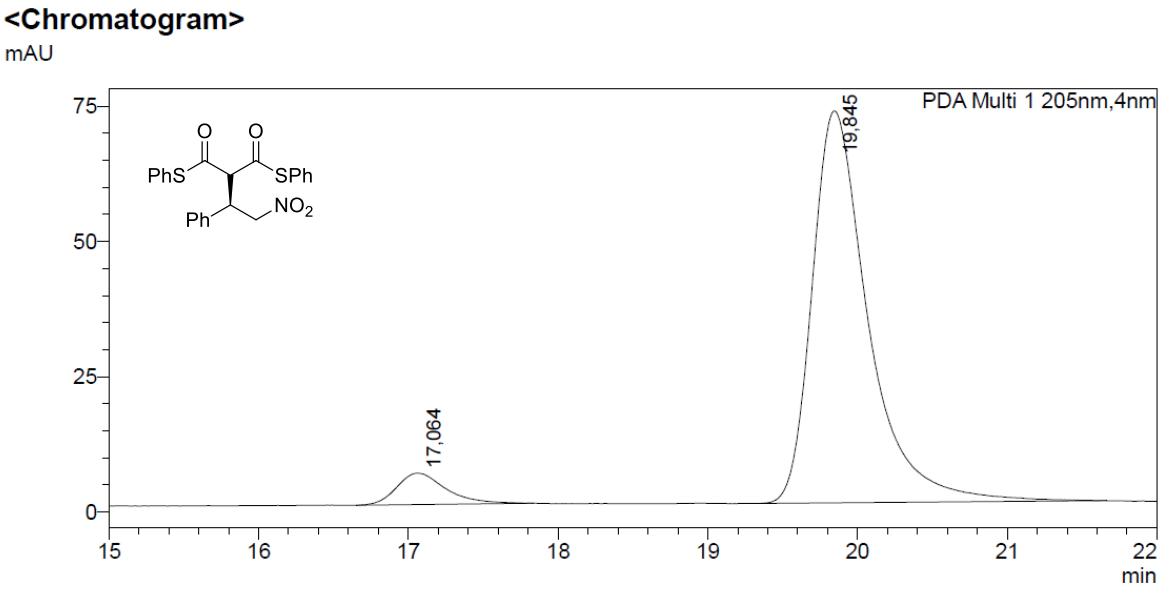



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 17,008 | 78936 | 1974337 | 2,913 |
| 2 | 19,613 | 2785797 | 65808578 | 97,087 |
| Total | | 2864733 | 67782915 | 100,000 |

**Figure S18.** HPLC chromatogram for *R*-**9**: sample obtained with catalyst *e*QD-**5i** in a solution at 273 K (94% ee).

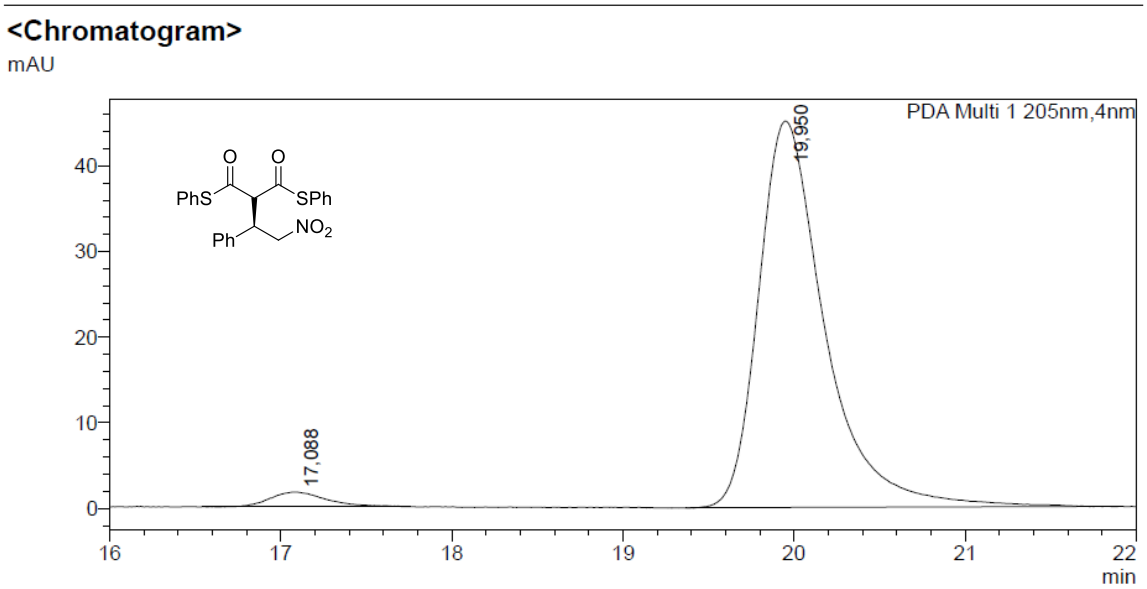



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 17,064 | 5818 | 132206 | 6,546 |
| 2 | 19,845 | 72434 | 1887444 | 93,454 |
| Total | | 78253 | 2019650 | 100,000 |

**Figure S19.** HPLC chromatogram for *R*-**9**: sample obtained with catalyst *e*QD-**5j** in a solution at 273 K (87% ee).

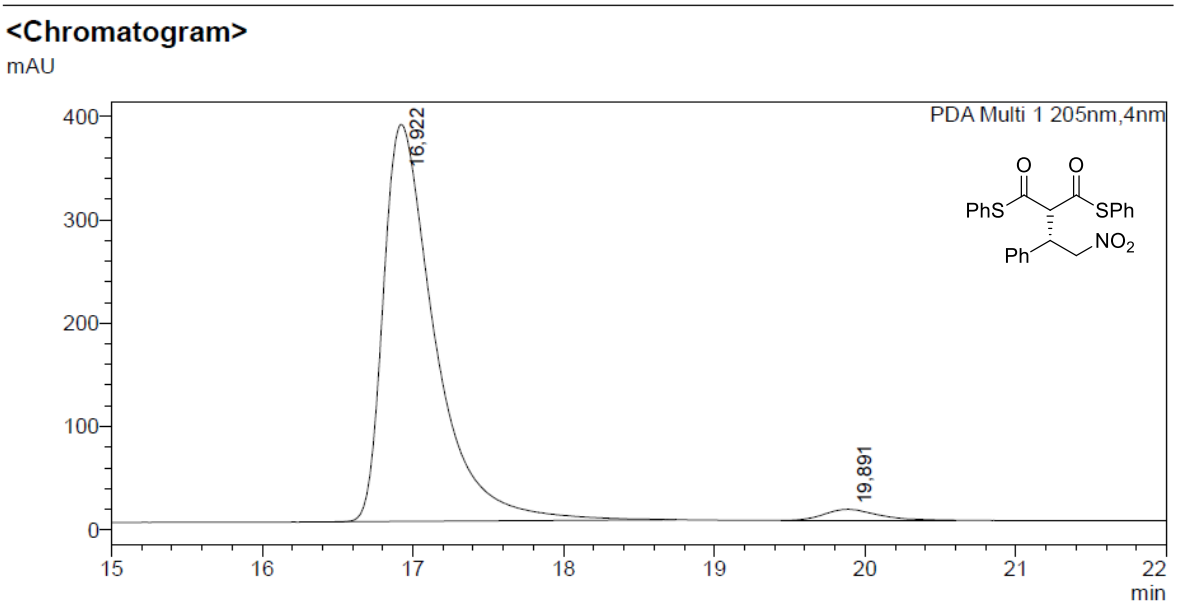



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 17,088 | 1708 | 39236 | 3,124 |
| 2 | 19,950 | 45123 | 1216567 | 96,876 |
| Total | | 46831 | 1255803 | 100,000 |

**Figure S20.** HPLC chromatogram for *R*-**9**: sample obtained with catalyst *e*DHQD-**5k** in a solution at 273 K (94% ee).

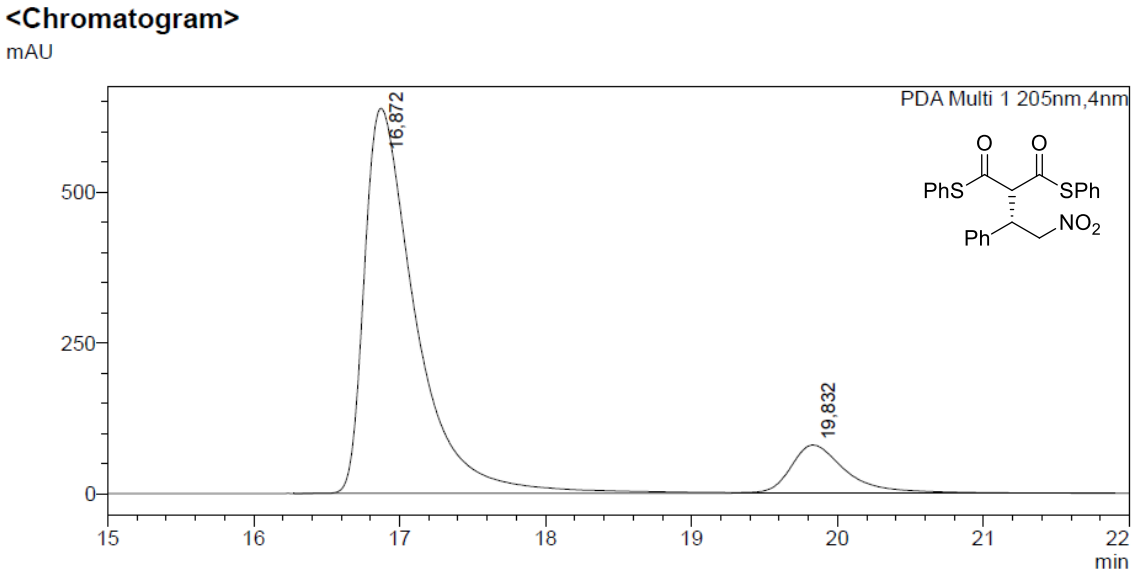



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 16,922 | 384266 | 9123943 | 97,228 |
| 2 | 19,891 | 10637 | 260096 | 2,772 |
| Total | | 394903 | 9384039 | 100,000 |

**Figure S21.** HPLC chromatogram for *S*-**9**: sample obtained with catalyst *e*QN-**6a** in a solution at 273 K (95% ee).

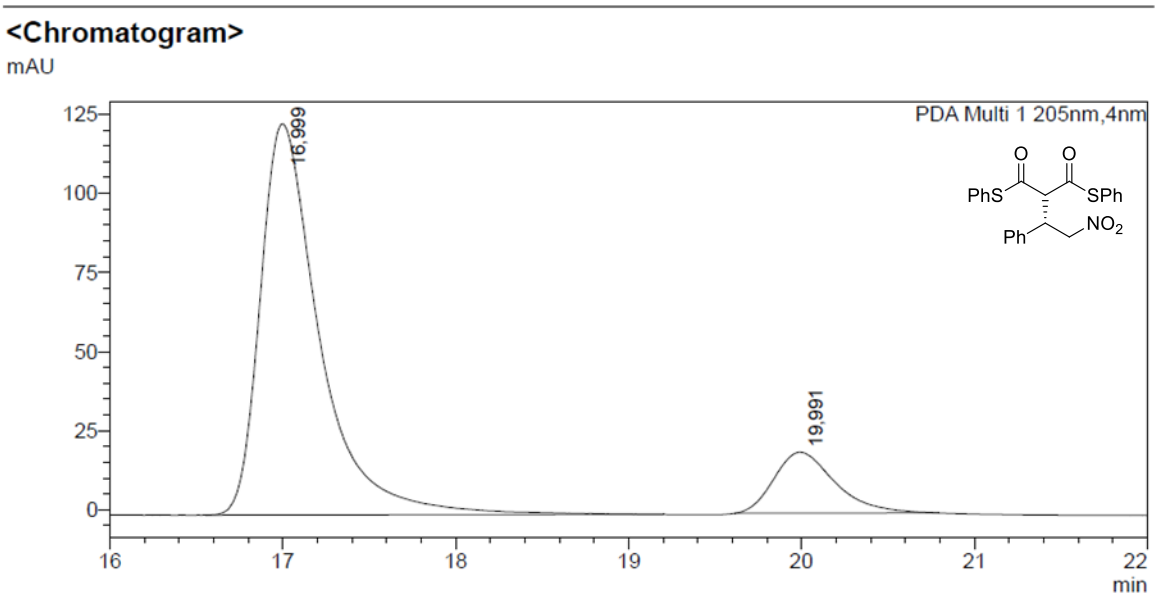



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 16,872 | 637452 | 15566419 | 87,961 |
| 2 | 19,832 | 79798 | 2130531 | 12,039 |
| Total | | 717251 | 17696949 | 100,000 |

**Figure S22.** HPLC chromatogram for *S*-**9**: sample obtained with catalyst *e*QN-**6b** in a solution at 273 K (76% ee).

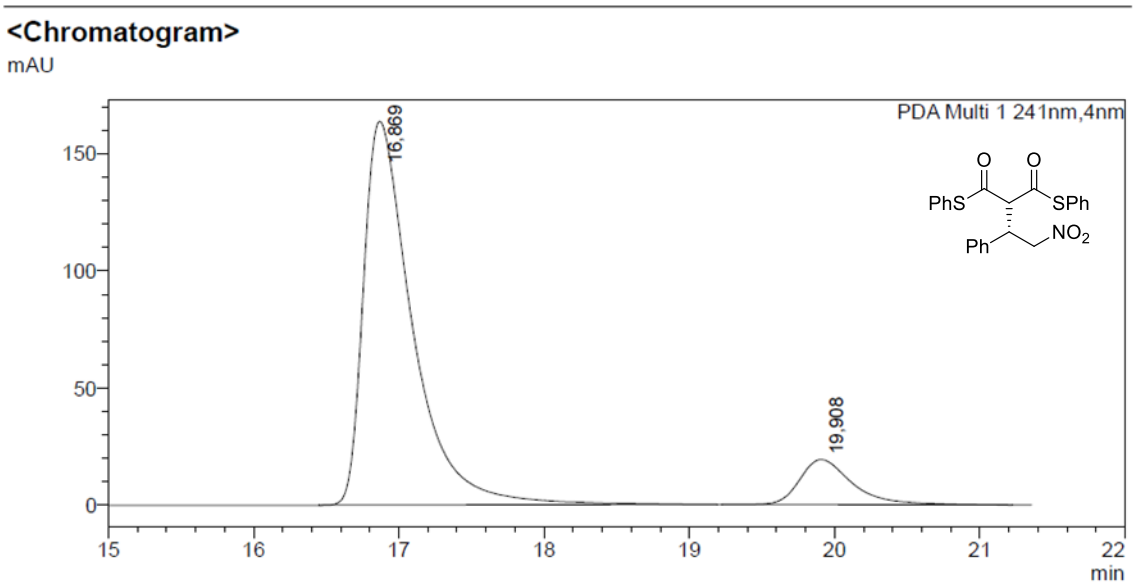



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 16,999 | 123587 | 2958165 | 86,201 |
| 2 | 19,991 | 19270 | 473529 | 13,799 |
| Total | | 142857 | 3431694 | 100,000 |

**Figure S23.** HPLC chromatogram for *S*-**9**: sample obtained with catalyst *e*QN-**5c** in a solution at 298 K (72% ee).

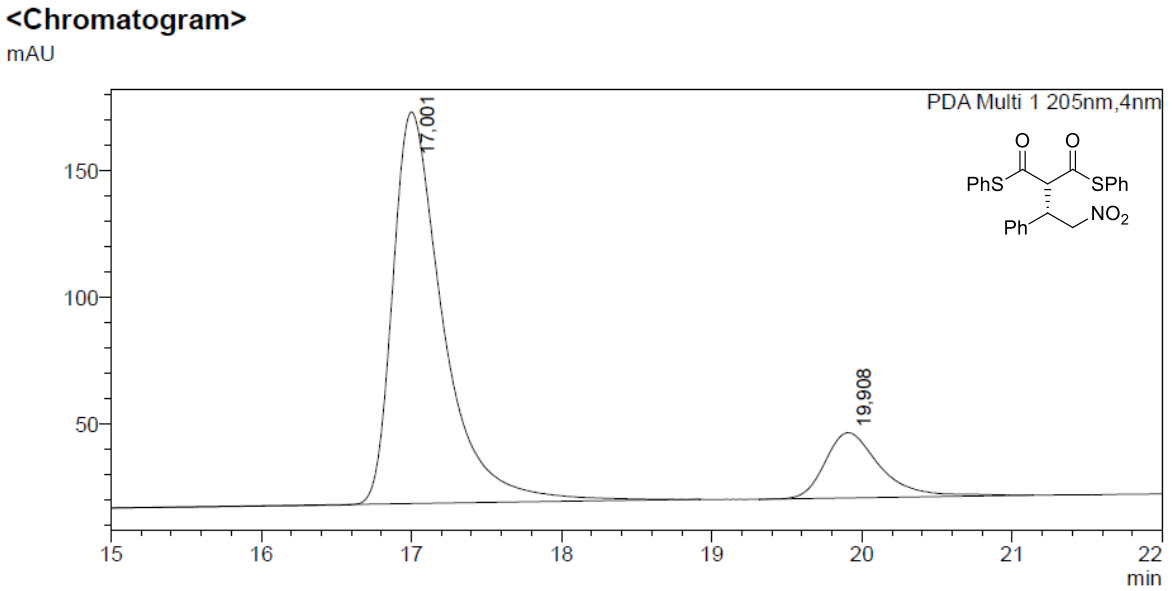



**<Peak Table>**

PDA Ch1 241nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 16,869 | 163734 | 89,492 | 3847695 | 88,827 |
| 2 | 19,908 | 19225 | 10,508 | 483955 | 11,173 |
| Total | | 182959 | 100,000 | 4331650 | 100,000 |

**Figure S24.** HPLC chromatogram for *S*-**9**: sample obtained with catalyst *e*QN-**5d** in a solution at 298 K (78% ee).

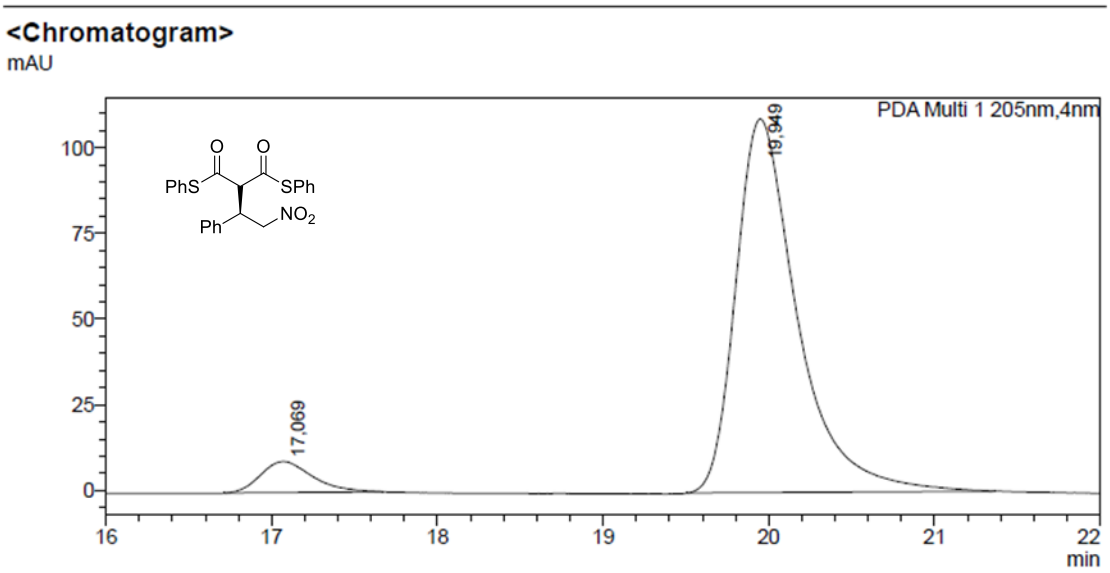



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 17,001 | 154644 | 3589373 | 84,520 |
| 2 | 19,908 | 25780 | 657379 | 15,480 |
| Total | | 180424 | 4246751 | 100,000 |

**Figure S25.** HPLC chromatogram for *S*-**9**: sample obtained with catalyst *e*QN-**5e** in a solution at 298 K (69% ee).

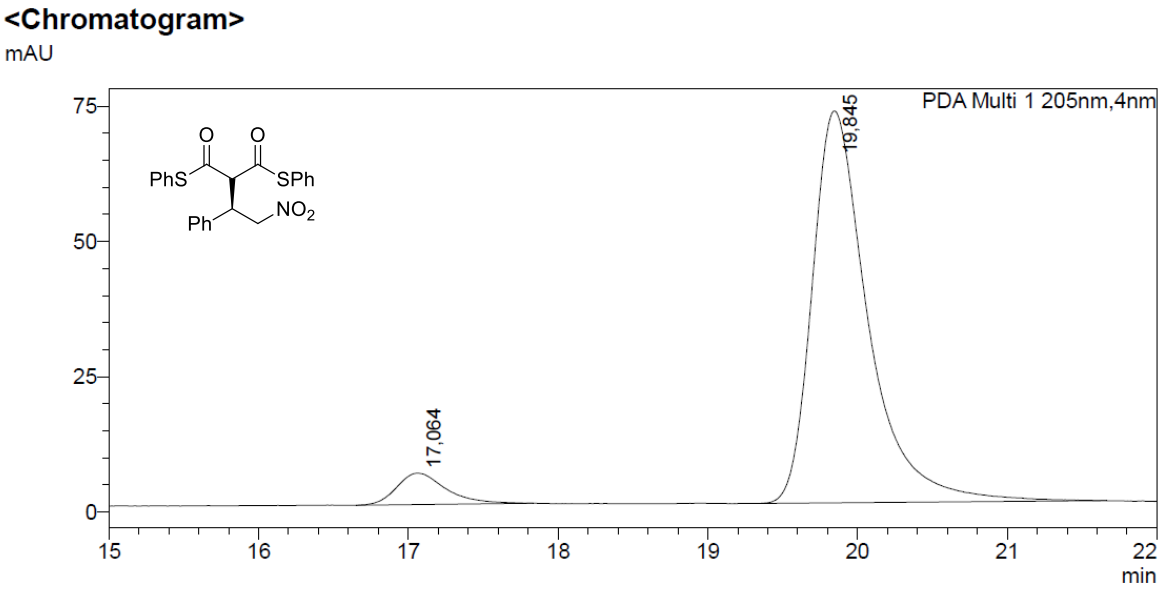



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 17,069 | 9045 | 197039 | 6,535 |
| 2 | 19,949 | 109101 | 2817944 | 93,465 |
| Total | | 118147 | 3014983 | 100,000 |

**Figure S26.** HPLC chromatogram for *R*-**9**: sample obtained with catalyst *e*QD-**5h** in a solution at 298 K (87% ee).

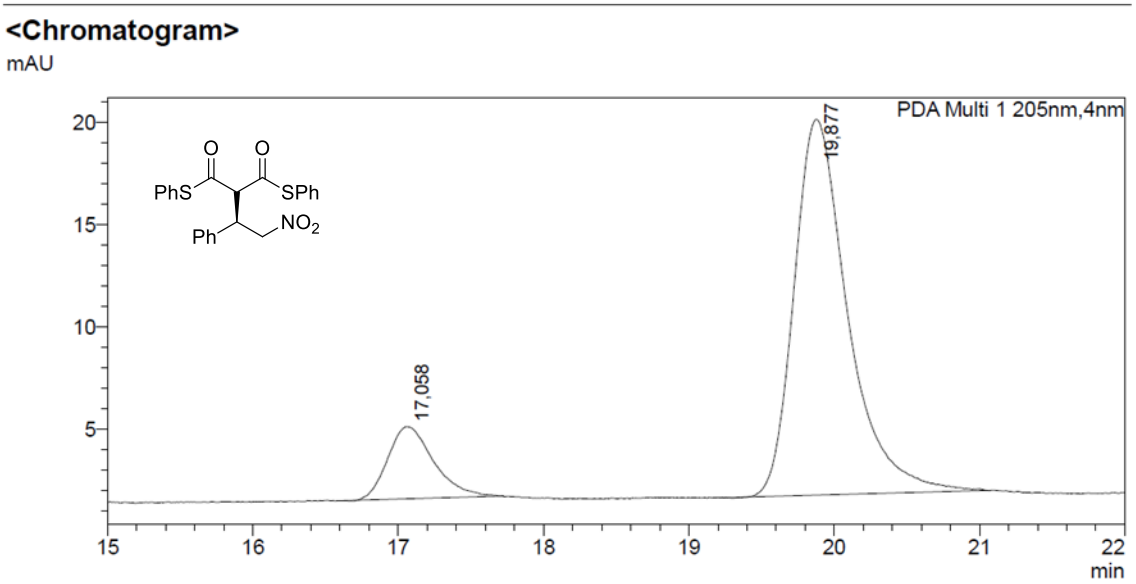



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 17,064 | 5818 | 132206 | 6,546 |
| 2 | 19,845 | 72434 | 1887444 | 93,454 |
| Total | | 78253 | 2019650 | 100,000 |

**Figure S27.** HPLC chromatogram for *R*-**9**: sample obtained with catalyst *e*QD-**5i** in a solution at 298 K (89% ee).

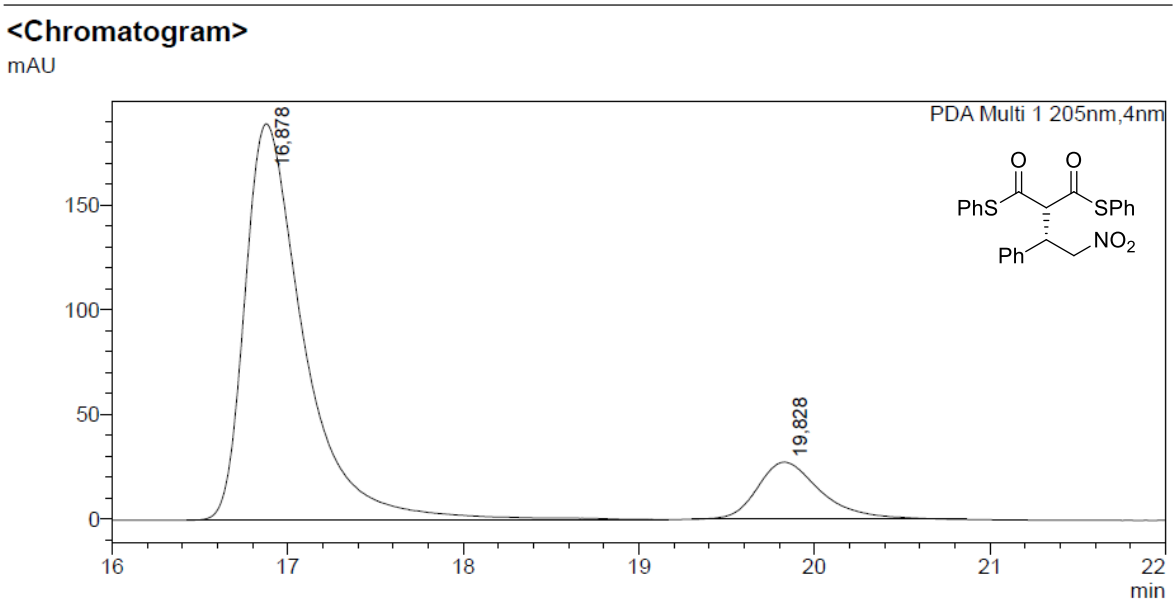



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 17,058 | 3537 | 77408 | 14,109 |
| 2 | 19,877 | 18372 | 471229 | 85,891 |
| Total | | 21908 | 548638 | 100,000 |

**Figure S28.** HPLC chromatogram for *R*-**9**: sample obtained with catalyst *e*QD-**5j** in a solution at 298 K (72% ee).

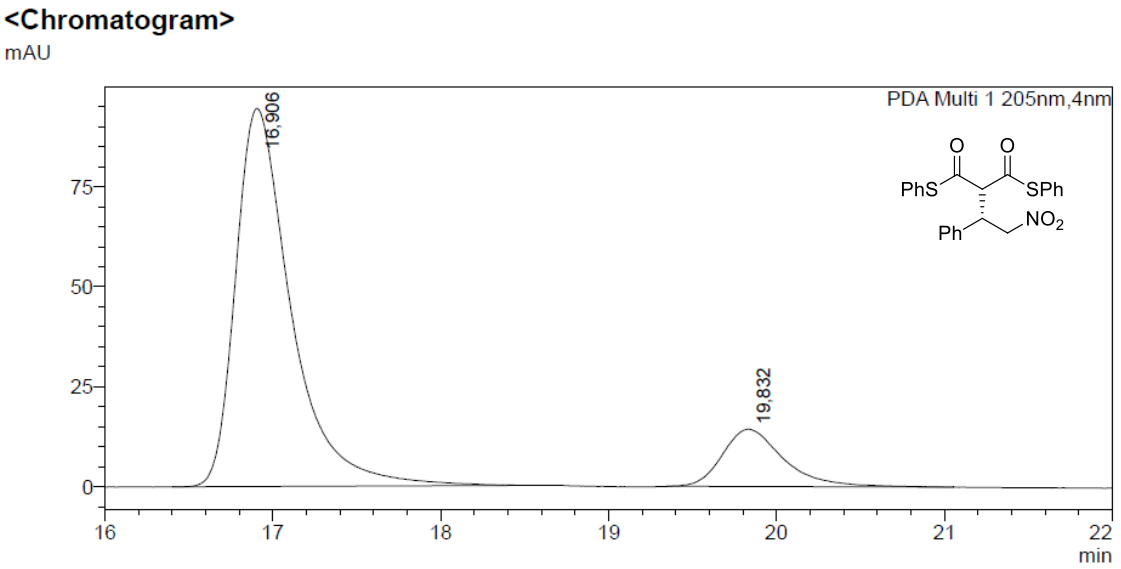



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 16,878 | 189594 | 4445119 | 86,582 |
| 2 | 19,828 | 27354 | 688880 | 13,418 |
| Total | | 216948 | 5133999 | 100,000 |

**Figure S29.** HPLC chromatogram for *S*-**9**: sample obtained with catalyst *e*QN-**5a** in a planetary ball mill (73% ee).

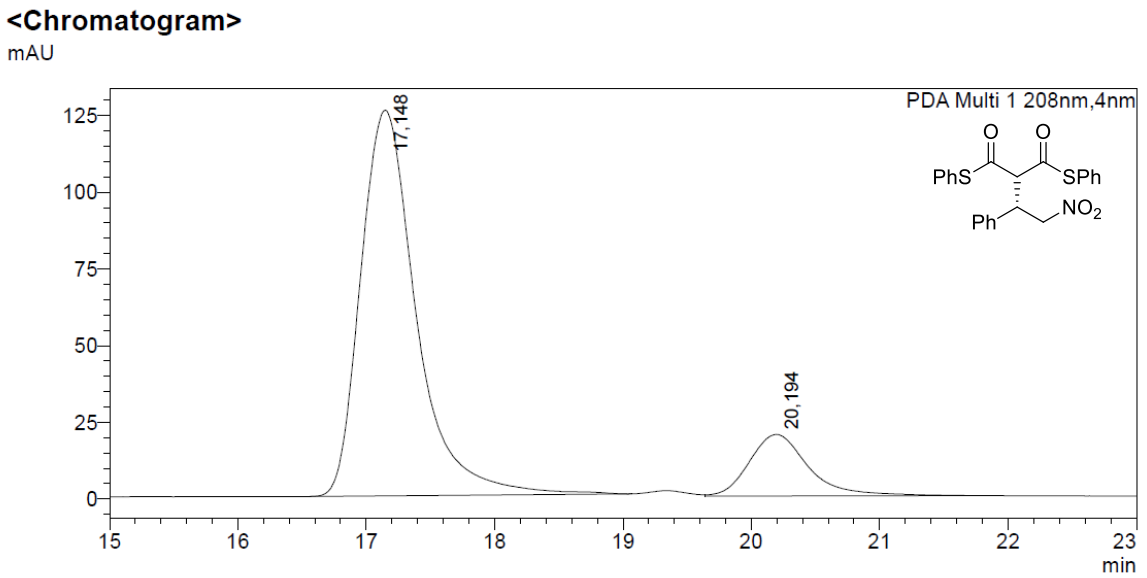



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 16,906 | 94501 | 2173387 | 85,615 |
| 2 | 19,832 | 14317 | 365166 | 14,385 |
| Total | | 108818 | 2538553 | 100,000 |

**Figure S30.** HPLC chromatogram for *S*-**9**: sample obtained with catalyst *e*QN-**5b** in a planetary ball mill (71% ee).

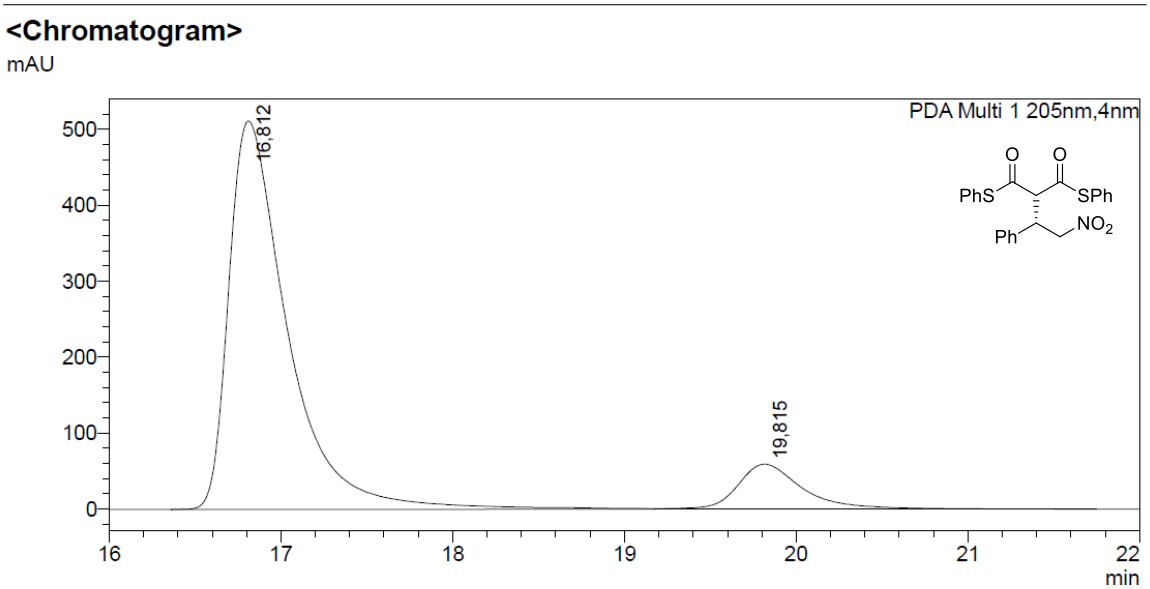



**<Peak Table>**

PDA Ch1 208nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 17,148 | 3787395 | 125716 | 85,489 |
| 2 | 20,194 | 642853 | 20040 | 14,511 |
| Total | | 4430248 | 145756 | 100,000 |

**Figure S31.** HPLC chromatogram for *S*-**9**: sample obtained with catalyst *e*QN-**5c** in a planetary ball mill (71% ee).

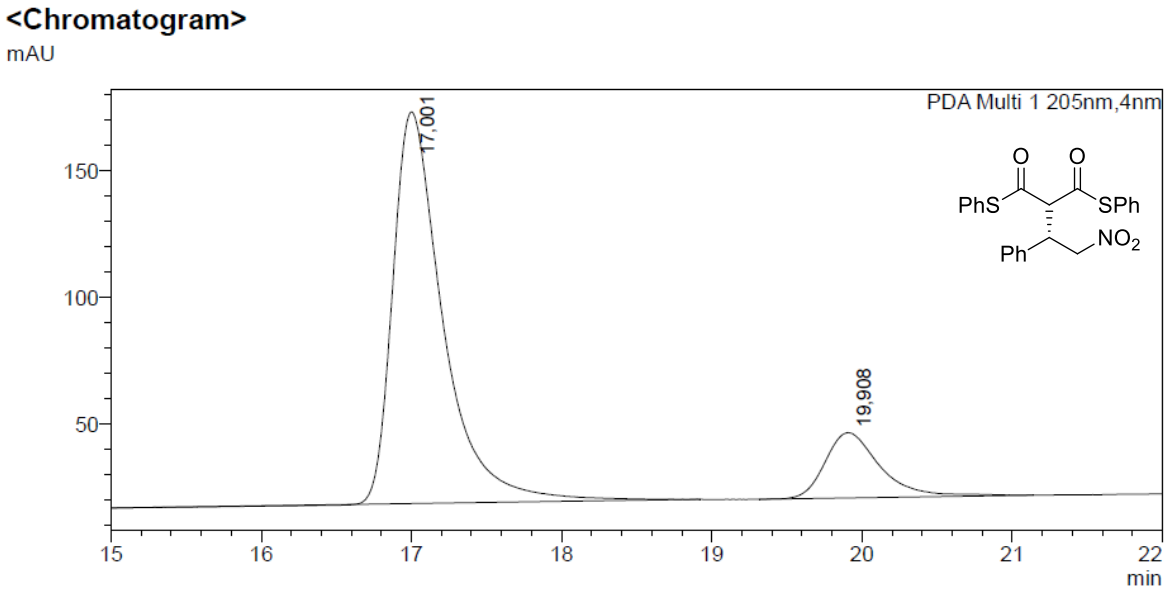



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 16,812 | 511710 | 89,592 | 12208380 | 88,469 |
| 2 | 19,815 | 59444 | 10,408 | 1591303 | 11,531 |
| Total | | 571154 | 100,000 | 13799683 | 100,000 |

**Figure S32.** HPLC chromatogram for *S*-**9**: sample obtained with catalyst *e*QN-**5d** in a planetary ball mill (77% ee).

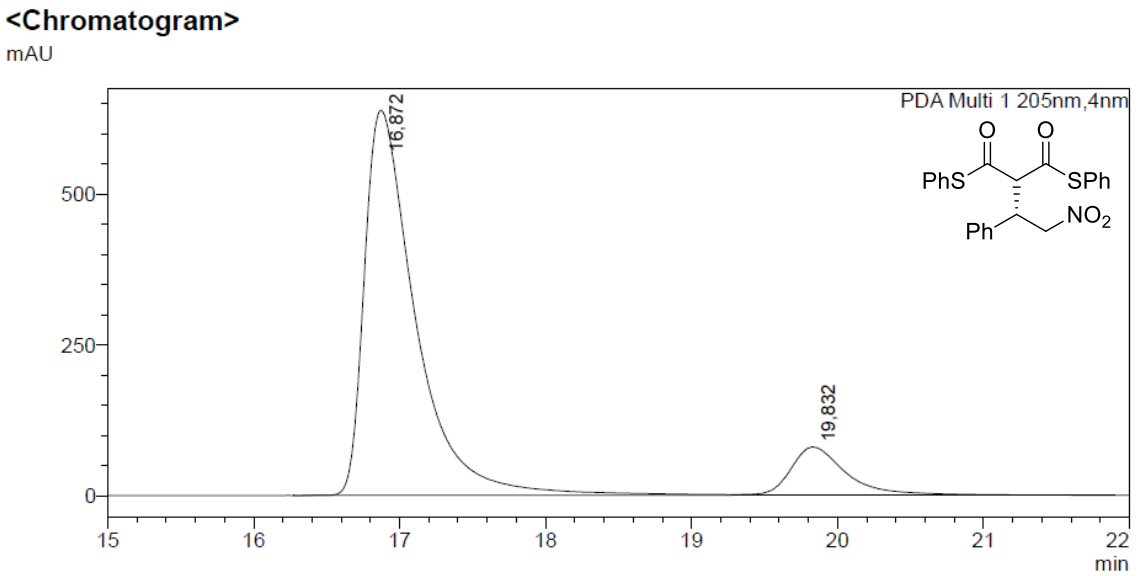



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 17,001 | 154644 | 3589373 | 84,520 |
| 2 | 19,908 | 25780 | 657379 | 15,480 |
| Total | | 180424 | 4246751 | 100,000 |

**Figure S33.** HPLC chromatogram for *S*-**9**: sample obtained with catalyst *e*QN-**5e** in a planetary ball mill (69% ee).

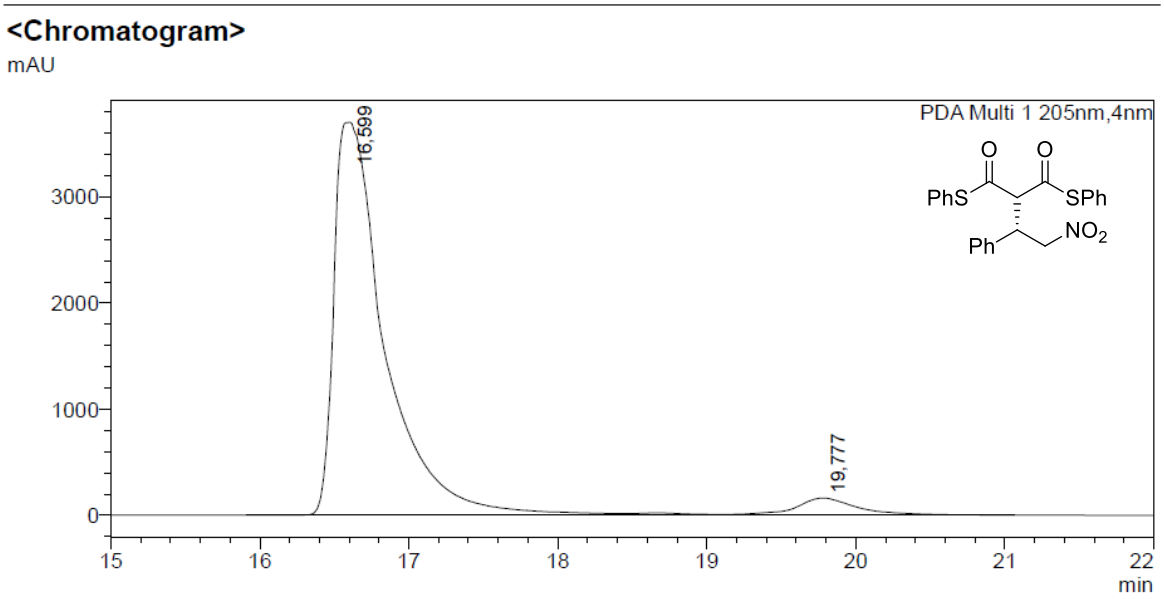



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 16,872 | 637452 | 15566419 | 87,961 |
| 2 | 19,832 | 79798 | 2130531 | 12,039 |
| Total | | 717251 | 17696949 | 100,000 |

**Figure S34.** HPLC chromatogram for *S*-**9**: sample obtained with catalyst *e*CD-**5f** in a planetary ball mill (76% ee).

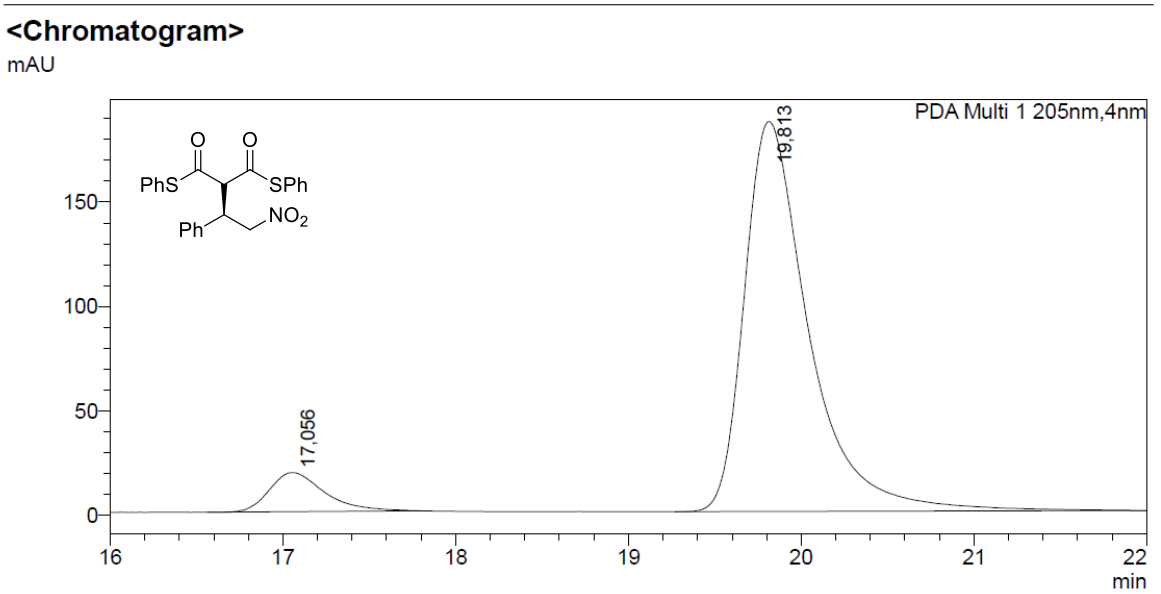



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 16,599 | 3700182 | 95,838 | 88370769 | 94,928 |
| 2 | 19,777 | 160698 | 4,162 | 4721399 | 5,072 |
| Total | | 3860880 | 100,000 | 93092167 | 100,000 |

**Figure S35.** HPLC chromatogram for *S*-**9**: sample obtained with catalyst *e*DHQN-**5g** in a planetary ball mill (90% ee).

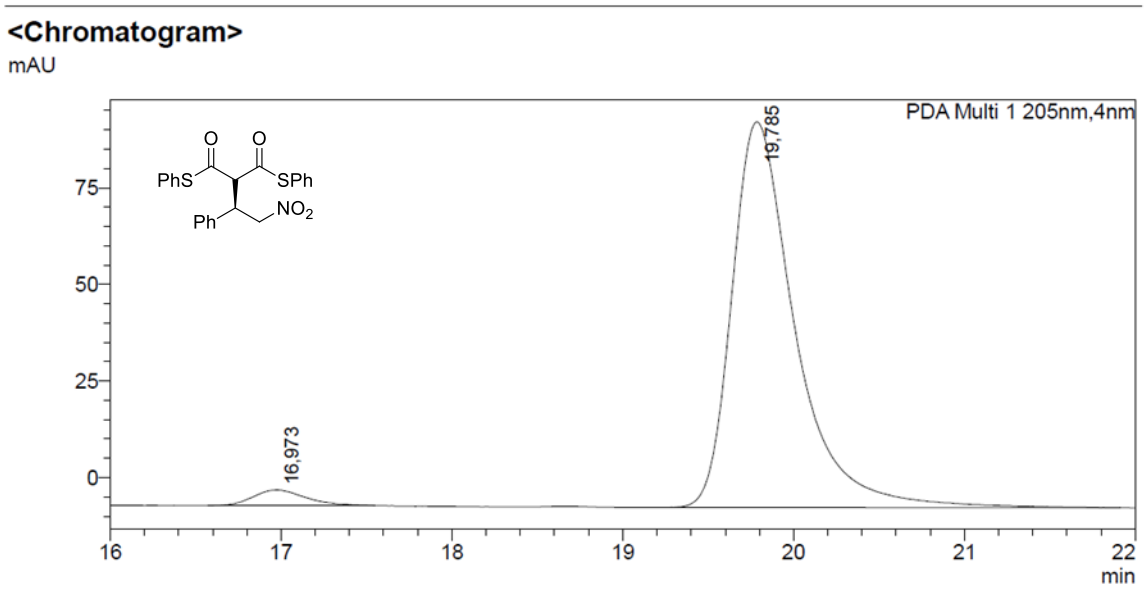



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 17,056 | 18711 | 413528 | 7,865 |
| 2 | 19,813 | 186635 | 4844052 | 92,135 |
| Total | | 205346 | 5257580 | 100,000 |

**Figure S36.** HPLC chromatogram for *R*-**9**: sample obtained with catalyst *e*QD-**5h** in a planetary ball mill (84% ee).

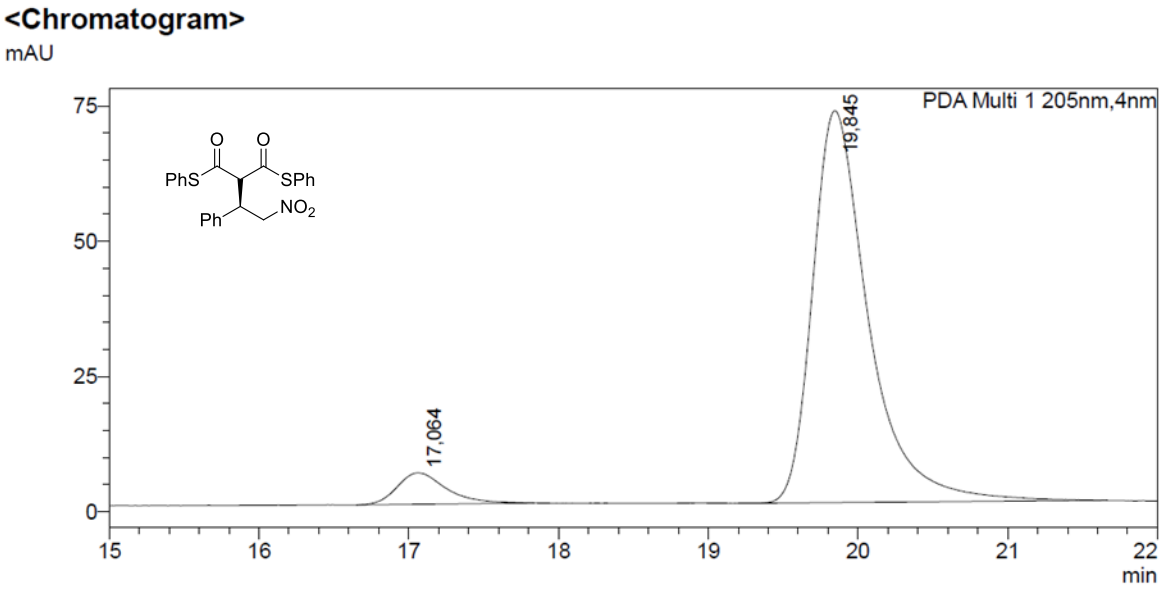



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 16,973 | 4056 | 87109 | 3,282 |
| 2 | 19,785 | 99873 | 2566932 | 96,718 |
| Total | | 103929 | 2654041 | 100,000 |

**Figure S37.** HPLC chromatogram for *R*-**9**: sample obtained with catalyst *e*QD-**5i** in a planetary ball mill (93% ee).

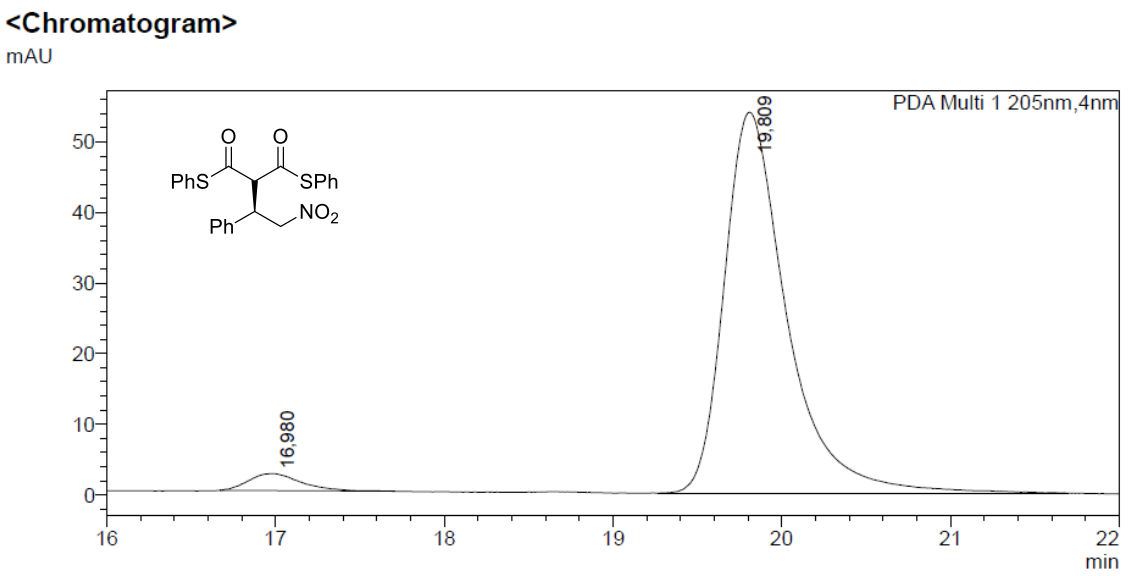



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 17,064 | 5818 | 132206 | 6,546 |
| 2 | 19,845 | 72434 | 1887444 | 93,454 |
| Total | | 78253 | 2019650 | 100,000 |

**Figure S38.** HPLC chromatogram for *R*-**9**: sample obtained with catalyst *e*QD-**5j** in a planetary ball mill (87% ee).

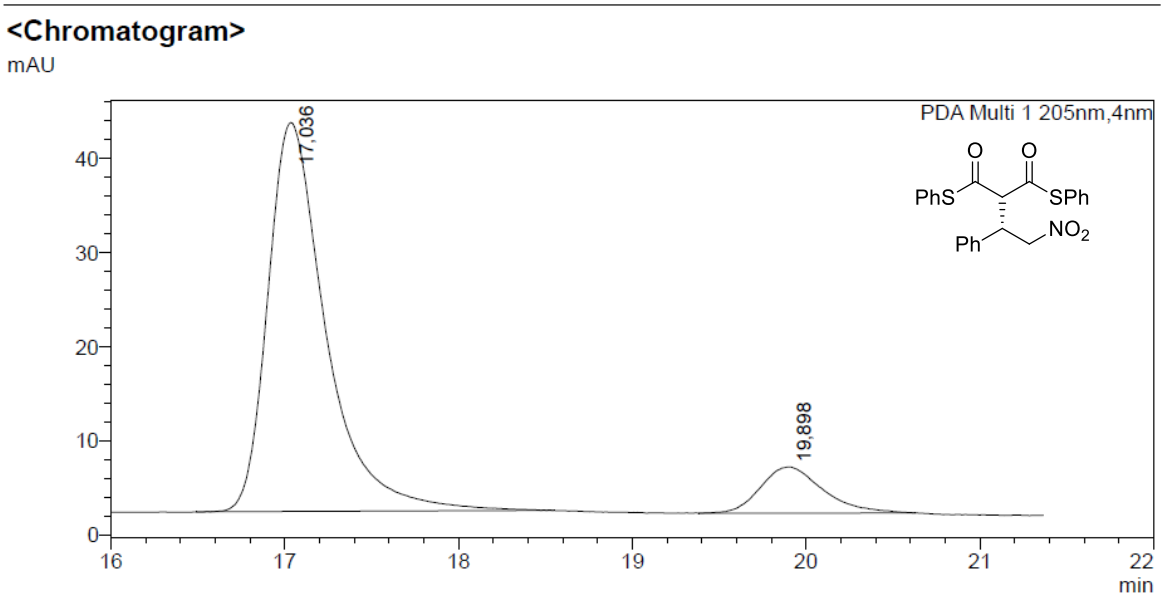



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 16,980 | 2425 | 51669 | 3,578 |
| 2 | 19,809 | 53946 | 1392537 | 96,422 |
| Total | | 56370 | 1444206 | 100,000 |

**Figure S39.** HPLC chromatogram for *R*-**9**: sample obtained with catalyst *e*DHQD-**5k** in a planetary ball mill (93% ee).

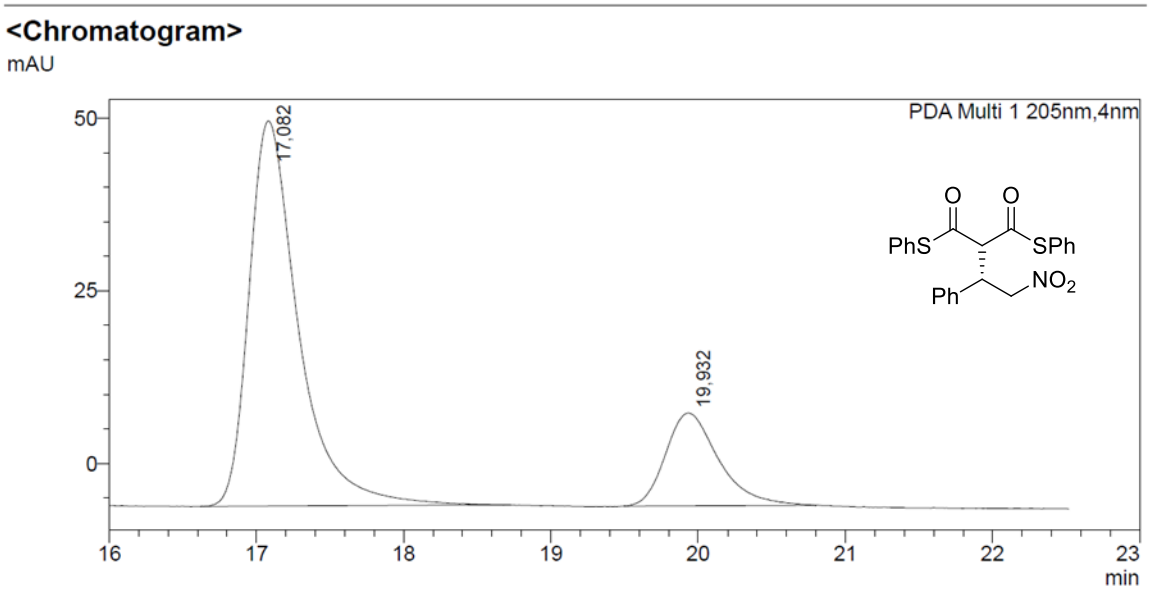



**<Peak Table>**

PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 17,036 | 41302 | 960308 | 88,670 |
| 2 | 19,898 | 4904 | 122704 | 11,330 |
| Total | | 46206 | 1083012 | 100,000 |

**Figure S40.** HPLC chromatogram for *S*-**9**: sample obtained with catalyst *e*QN-**6a** in a planetary ball mill (77% ee).




**<Peak Table>**

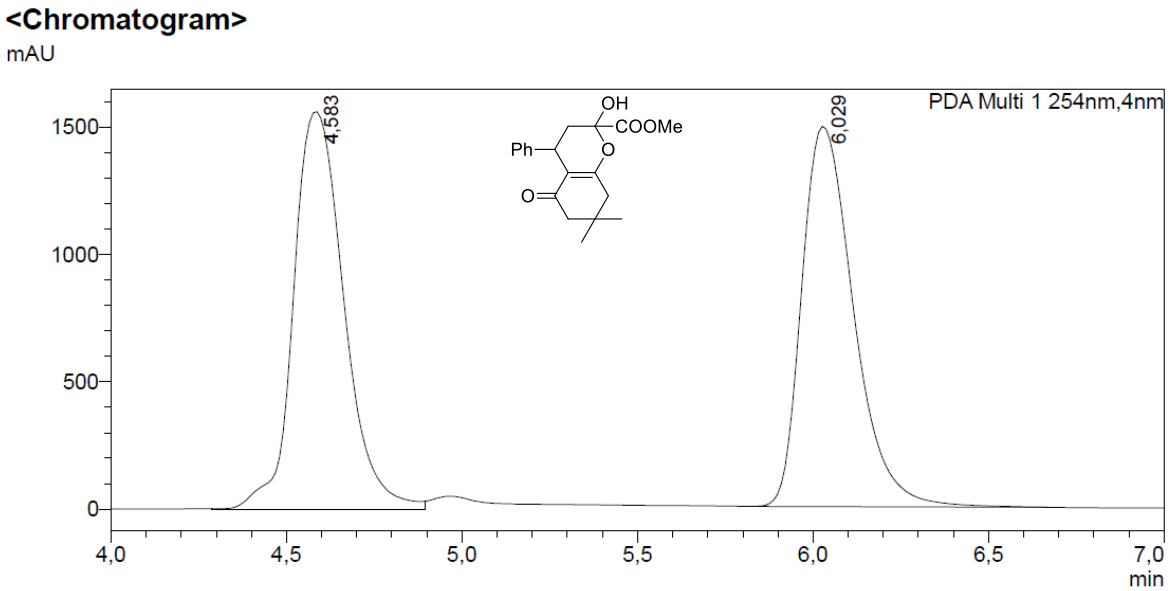
PDA Ch1 205nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 17,082 | 55746 | 1304014 | 79,476 |
| 2 | 19,932 | 13427 | 336744 | 20,524 |
| Total | | 69173 | 1640759 | 100,000 |

**Figure S41.** HPLC chromatogram for *S*-**9**: sample obtained with catalyst *e*QN-**6b** in a planetary ball mill (59% ee).

### *S4.2. Asymmetric Michael hemiacetalization reaction of benzylidenepyruvate and dimedone*

(Chiralcel IA-3, n-hexane/2-propanol, 7:3, flow rate 1mL/min, $\lambda$=254 nm)

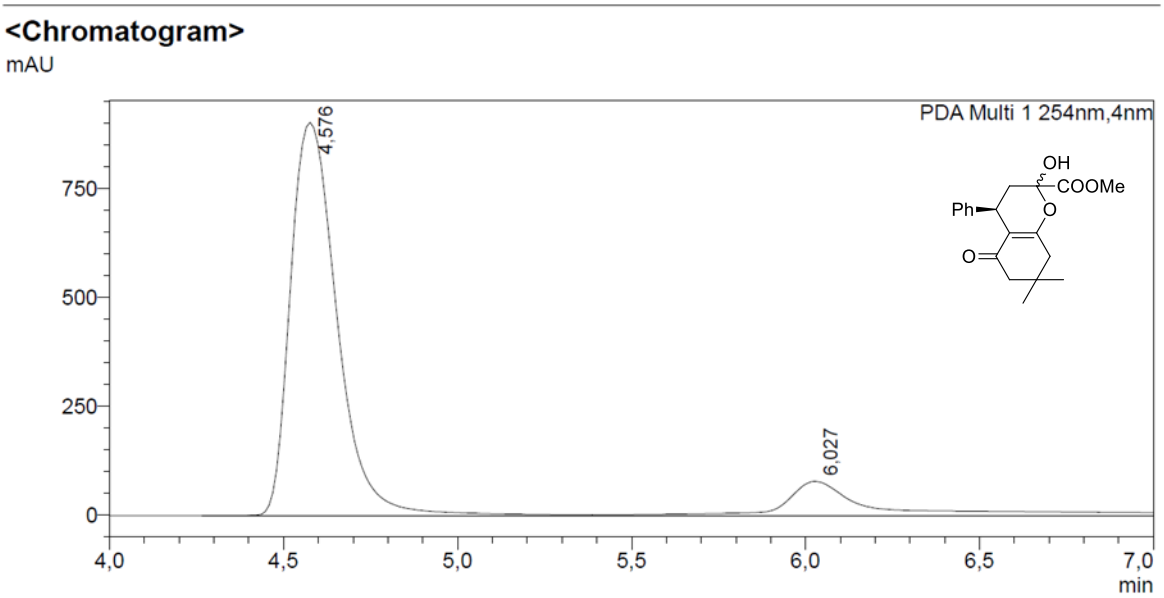



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,583 | 1559716 | 51,085 | 15576963 | 50,373 |
| 2 | 6,029 | 1493435 | 48,915 | 15346567 | 49,627 |
| Total | | 3053151 | 100,000 | 30923529 | 100,000 |

**Figure S42**. HPLC chromatogram for racemic 4-methyl-2-hydroxy-7,7-dimethyl-5-oxo-4-phenyl-3,4,5,6,7,8-hexahydro-2*H*-chromene-2-carboxylate **12.**

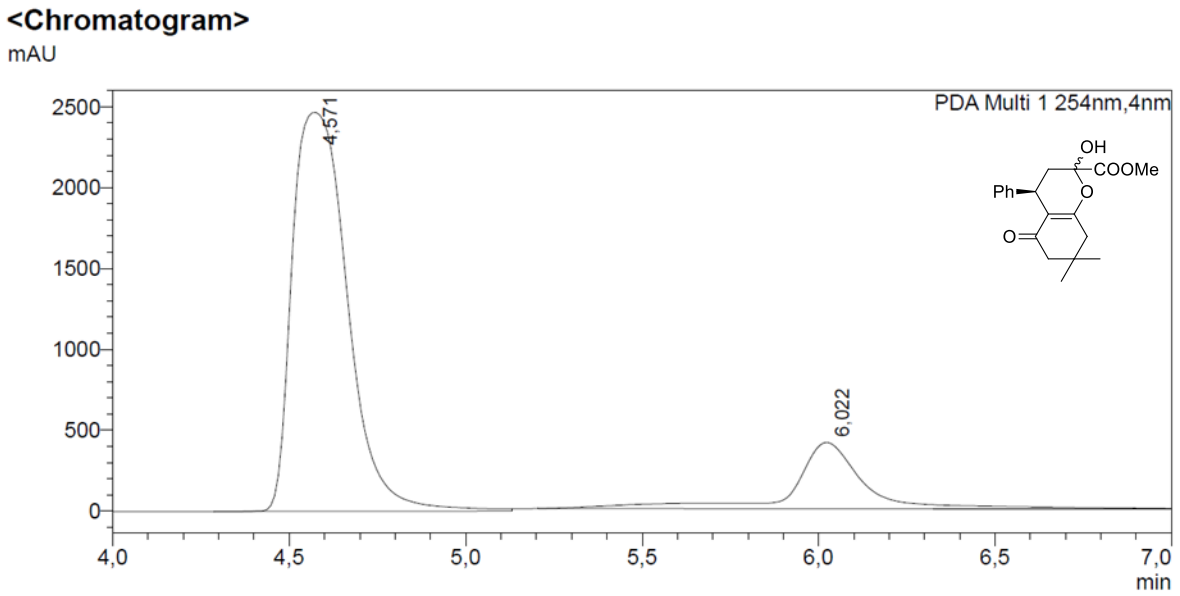



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,576 | 902212 | 92,039 | 8408378 | 83,272 |
| 2 | 6,027 | 78042 | 7,961 | 1689103 | 16,728 |
| Total | | 980254 | 100,000 | 10097481 | 100,000 |

**Figure S43.** HPLC chromatogram for *R*-**12**: sample obtained with catalyst *e*QN-**5a** in a solution at 298 K (67% ee).

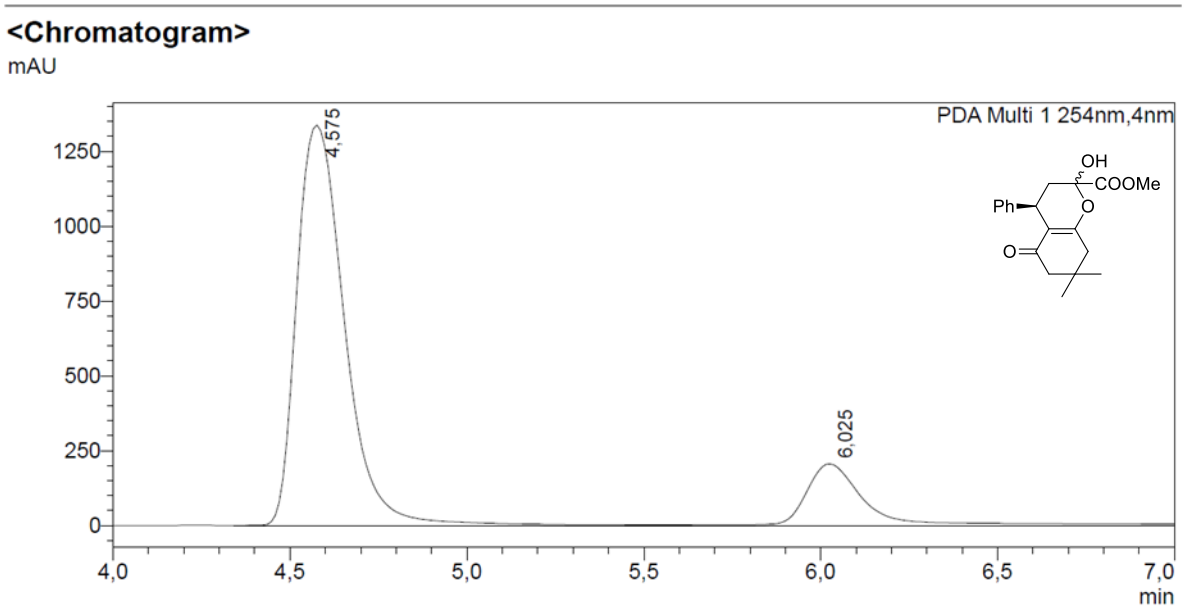



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,571 | 2465931 | 85,755 | 26895481 | 81,877 |
| 2 | 6,022 | 409621 | 14,245 | 5953244 | 18,123 |
| Total | | 2875552 | 100,000 | 32848725 | 100,000 |

**Figure S44.** HPLC chromatogram for *R*-**12**: sample obtained with catalyst *e*QN-**5b** in a solution at 298 K (64% ee).

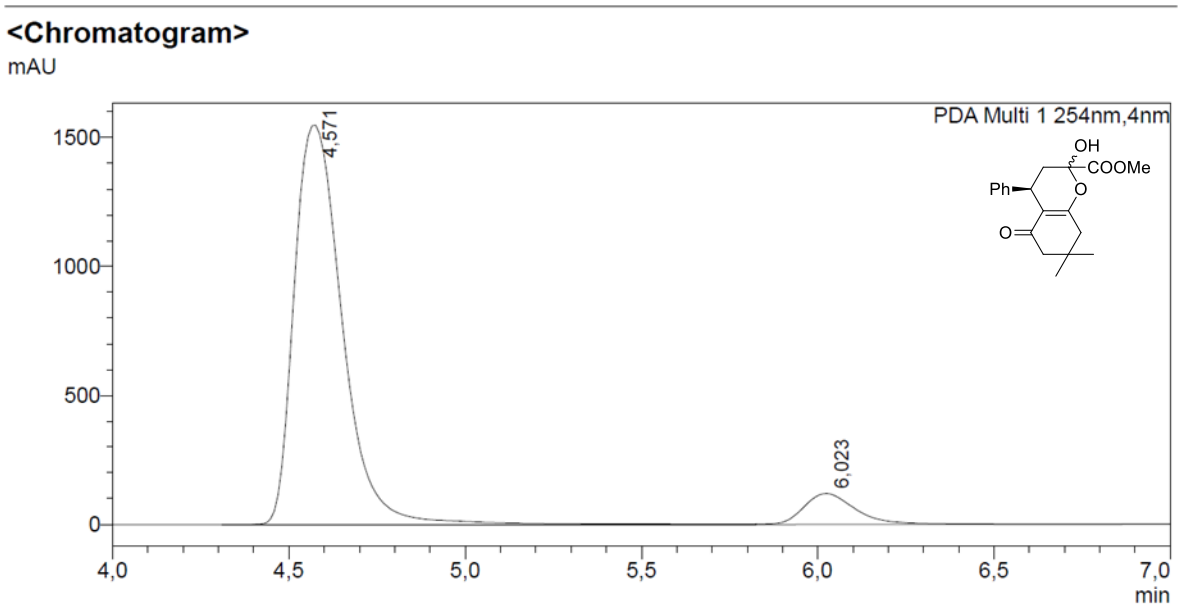



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,575 | 1337383 | 86,659 | 12598230 | 82,444 |
| 2 | 6,025 | 205891 | 13,341 | 2682791 | 17,556 |
| Total | | 1543273 | 100,000 | 15281022 | 100,000 |

**Figure S45.** HPLC chromatogram for *R*-**12**: sample obtained with catalyst *e*QN-**5c** in a solution at 298 K (65% ee).

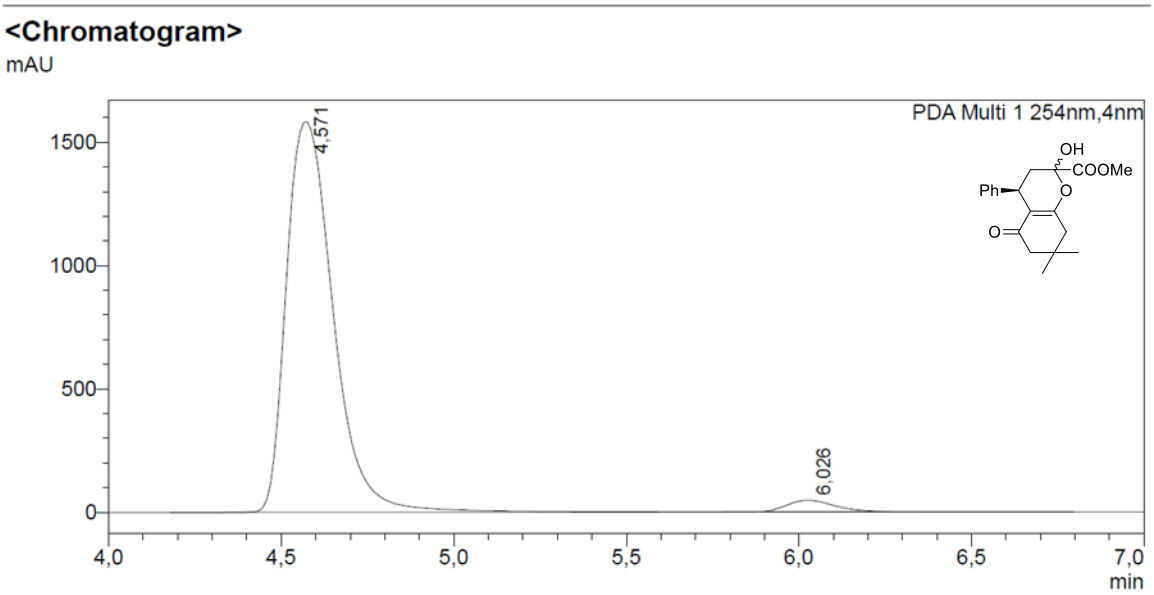



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,571 | 1547690 | 92,827 | 14697718 | 92,200 |
| 2 | 6,023 | 119596 | 7,173 | 1243343 | 7,800 |
| Total | | 1667287 | 100,000 | 15941061 | 100,000 |

**Figure S46.** HPLC chromatogram for *R*-**12**: sample obtained with catalyst *e*QN-**5d** in a solution at 298 K (84% ee).

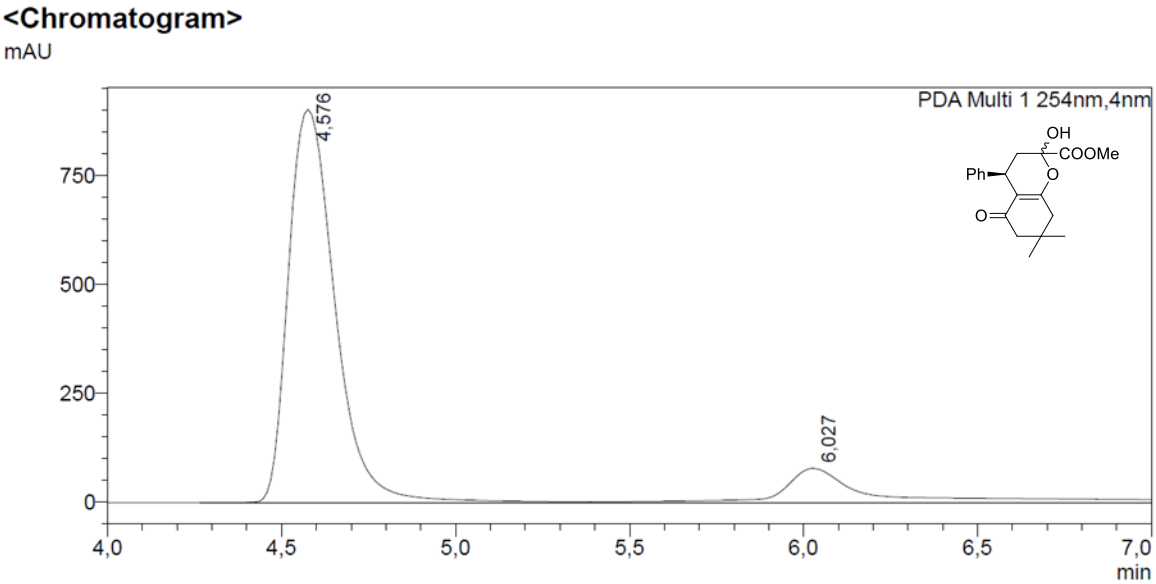



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,571 | 1582090 | 97,053 | 14985419 | 96,856 |
| 2 | 6,026 | 48037 | 2,947 | 486491 | 3,144 |
| Total | | 1630128 | 100,000 | 15471910 | 100,000 |

**Figure S47.** HPLC chromatogram for *R*-**12**: sample obtained with catalyst *e*QN-**5e** in a solution at 298 K (94% ee).

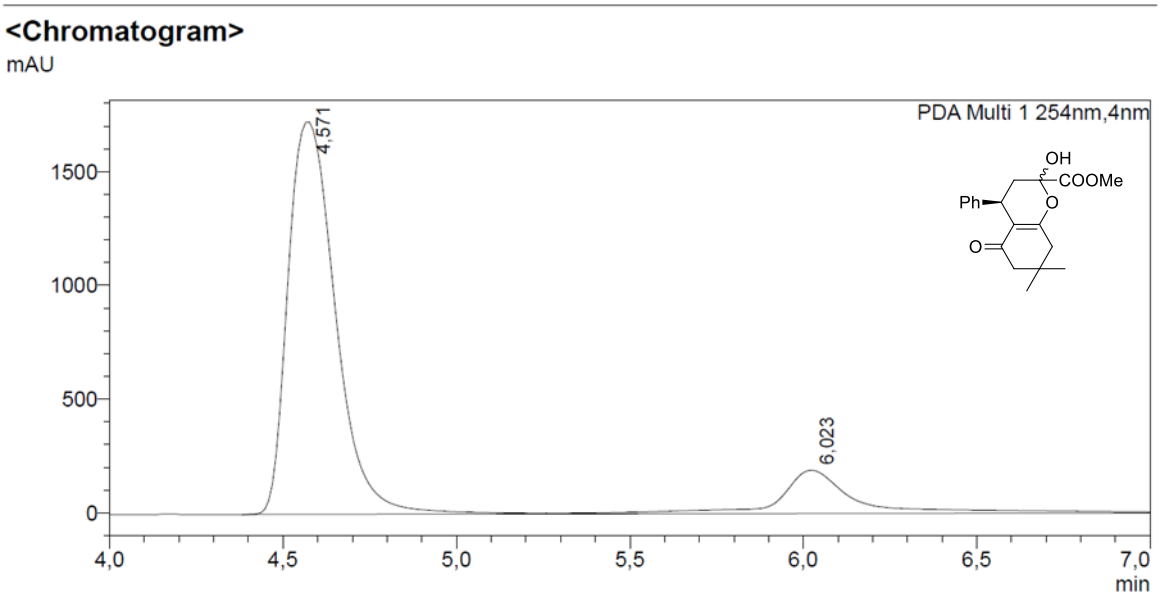



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,576 | 902212 | 92,039 | 8408378 | 83,272 |
| 2 | 6,027 | 78042 | 7,961 | 1689103 | 16,728 |
| Total | | 980254 | 100,000 | 10097481 | 100,000 |

**Figure S48.** HPLC chromatogram for *R*-**12**: sample obtained with catalyst *e*CD-**5f** in a solution at 298 K (66% ee).

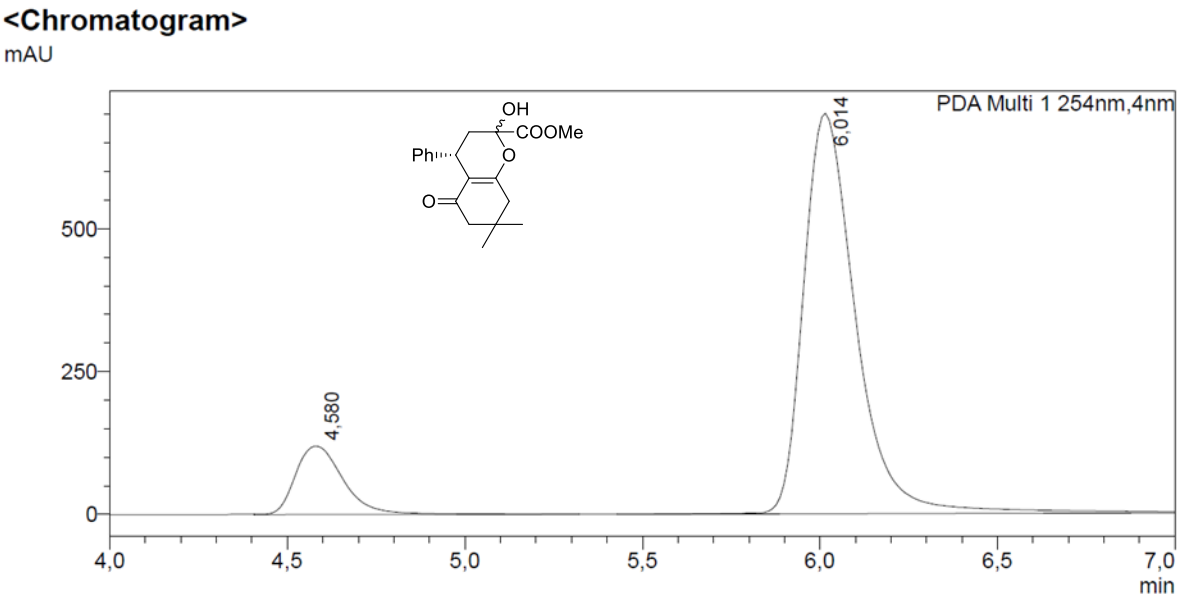



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,571 | 1724053 | 90,063 | 16464213 | 84,351 |
| 2 | 6,023 | 190219 | 9,937 | 3054525 | 15,649 |
| Total | | 1914272 | 100,000 | 19518738 | 100,000 |

**Figure S49.** HPLC chromatogram for *R*-**12**: sample obtained with catalyst *e*DHQN-**5g** in a solution at 298 K (69% ee).

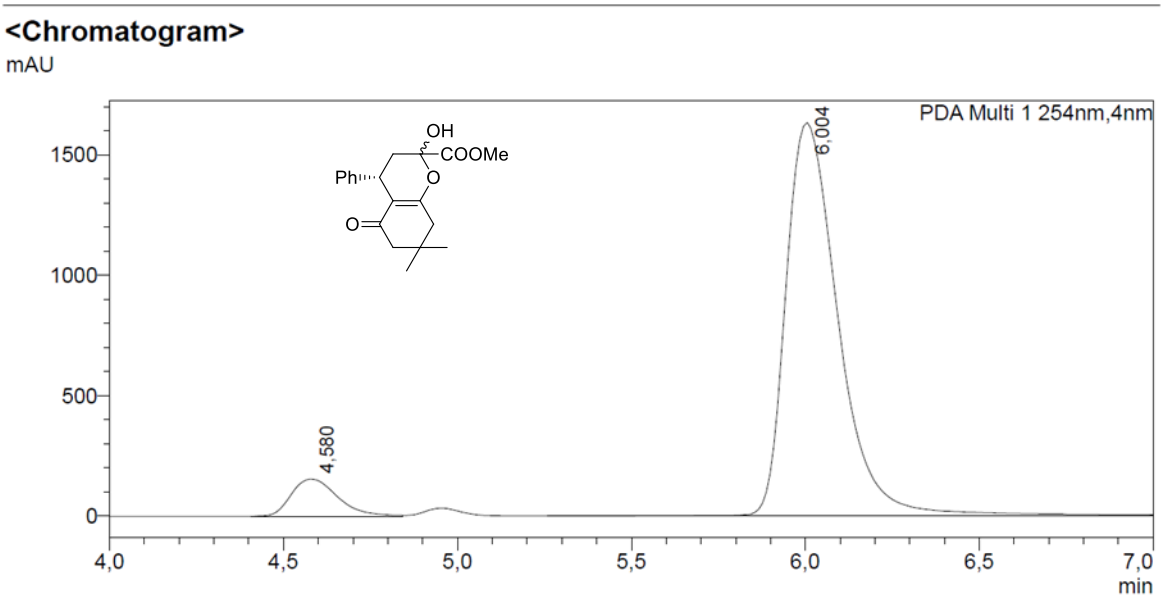



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,580 | 119665 | 14,577 | 1120225 | 13,329 |
| 2 | 6,014 | 701251 | 85,423 | 7283971 | 86,671 |
| Total | | 820917 | 100,000 | 8404196 | 100,000 |

**Figure S50.** HPLC chromatogram for *S*-**12**: sample obtained with catalyst *e*QD-**5h** in a solution at 298 K (73% ee).

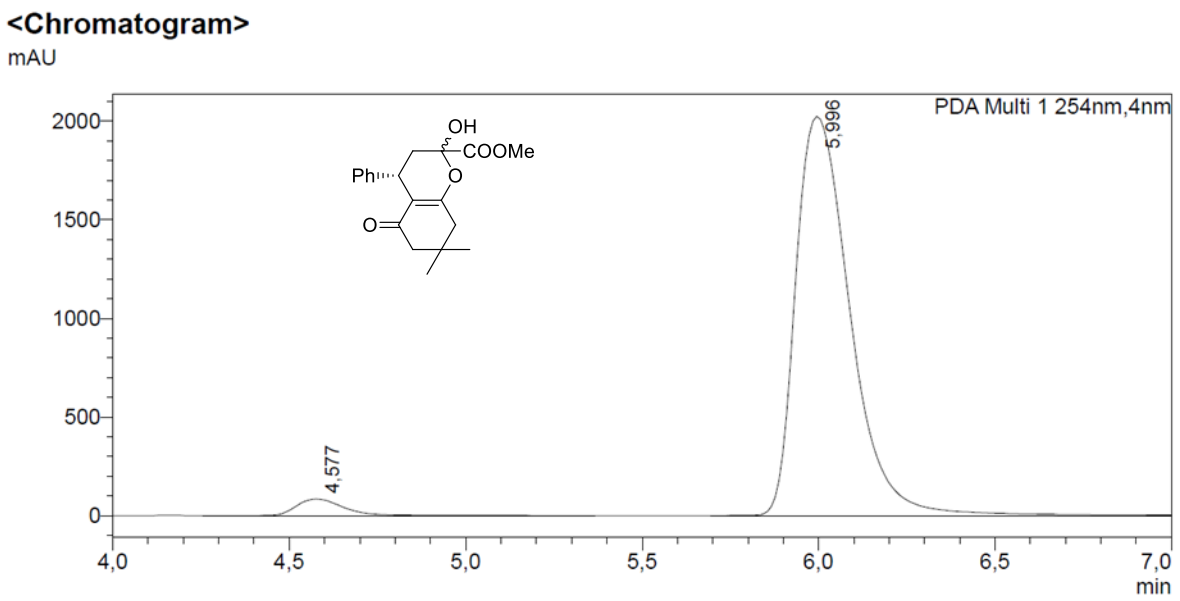



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 4,580 | 1424606 | 7,567 |
| 2 | 6,004 | 17401201 | 92,433 |
| Total | | 18825806 | 100,000 |

**Figure S51.** HPLC chromatogram for *S*-**12**: sample obtained with catalyst *e*QD-**5i** in a solution at 298 K (85% ee).

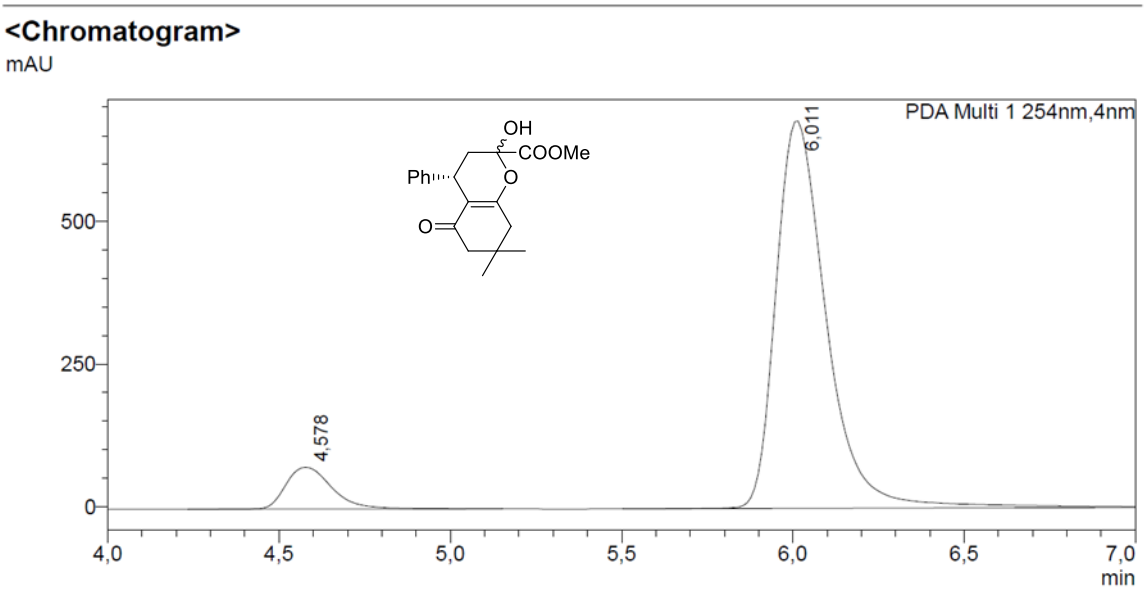



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,577 | 83457 | 3,958 | 780476 | 3,454 |
| 2 | 5,996 | 2025155 | 96,042 | 21815039 | 96,546 |
| Total | | 2108613 | 100,000 | 22595515 | 100,000 |

**Figure S52.** HPLC chromatogram for *S*-**12**: sample obtained with catalyst *e*QD-**5j** in a solution at 298 K (93% ee).

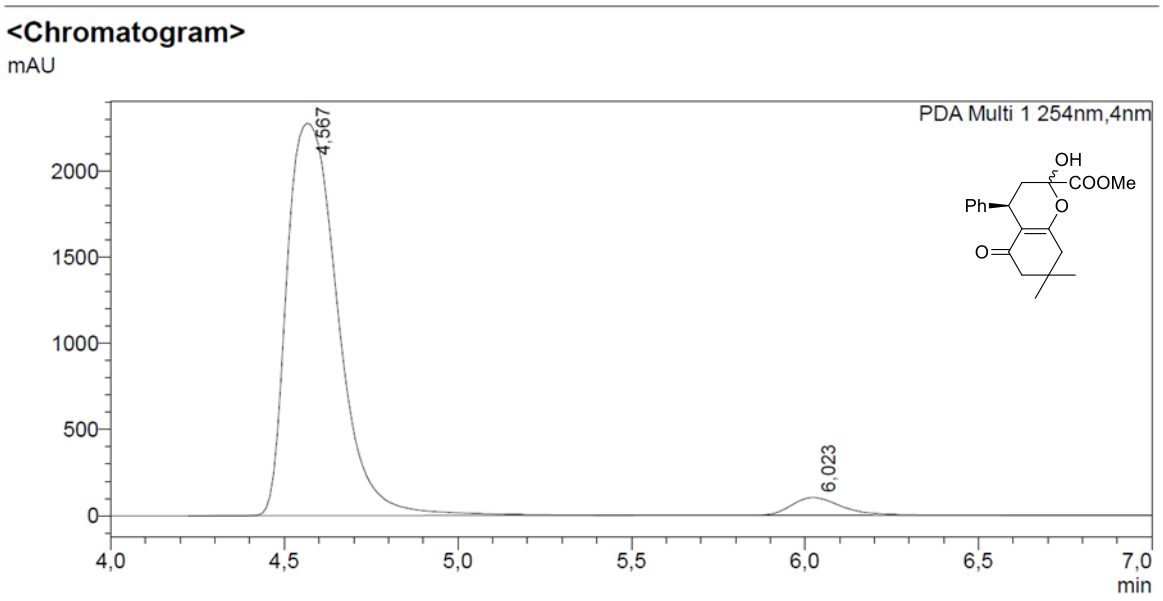



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,578 | 73209 | 9,738 | 684076 | 8,888 |
| 2 | 6,011 | 678538 | 90,262 | 7012609 | 91,112 |
| Total | | 751746 | 100,000 | 7696686 | 100,000 |

**Figure S53.** HPLC chromatogram for *S*-**12**: sample obtained with catalyst *e*DHQD-**5k** in a solution at 298 K (82% ee).

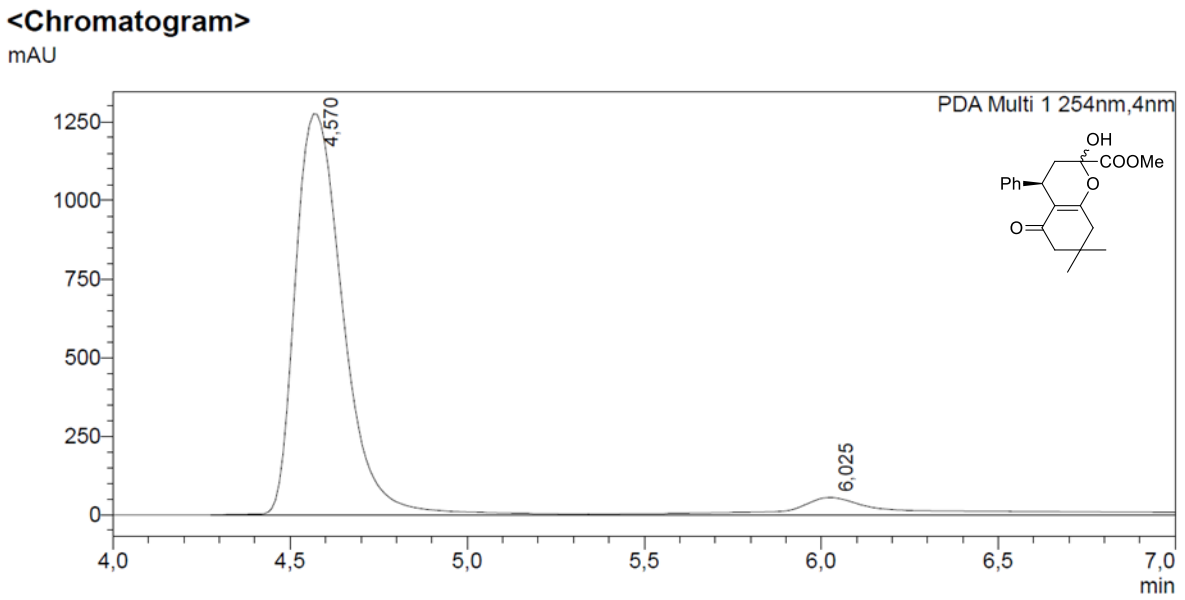



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,567 | 2277554 | 95,652 | 23245479 | 95,345 |
| 2 | 6,023 | 103522 | 4,348 | 1135007 | 4,655 |
| Total | | 2381075 | 100,000 | 24380486 | 100,000 |

**Figure S54.** HPLC chromatogram for *R*-**12**: sample obtained with catalyst *e*QN-**6a** in a solution at 298 K (91% ee).

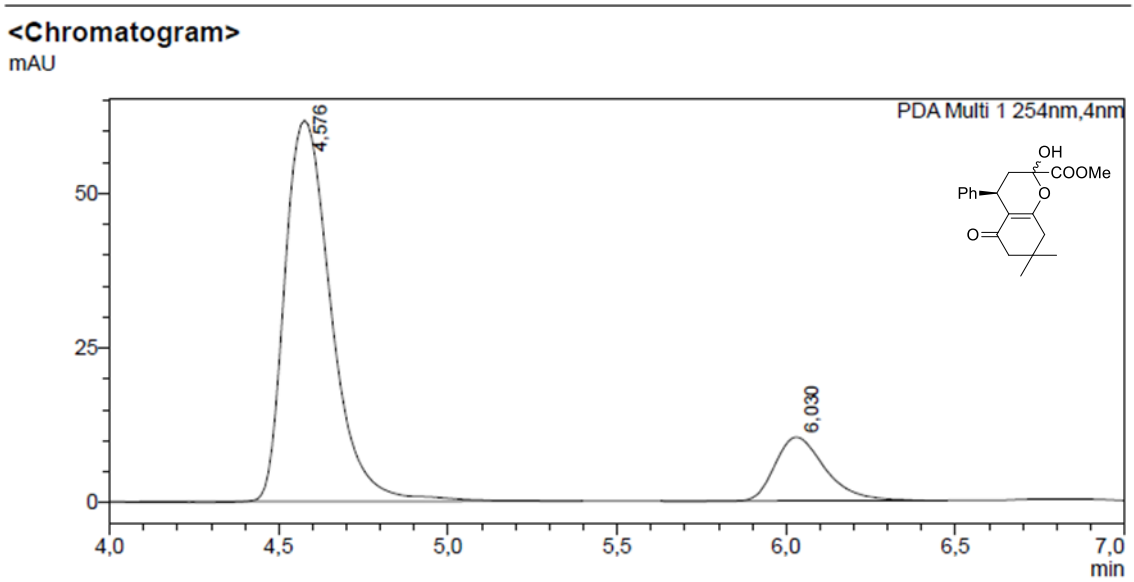



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,570 | 1274846 | 95,895 | 11964344 | 87,764 |
| 2 | 6,025 | 54568 | 4,105 | 1668130 | 12,236 |
| Total | | 1329414 | 100,000 | 13632473 | 100,000 |

**Figure S55.** HPLC chromatogram for *R*-**12**: sample obtained with catalyst *e*QN-**6b** in a solution at 298 K (76% ee).

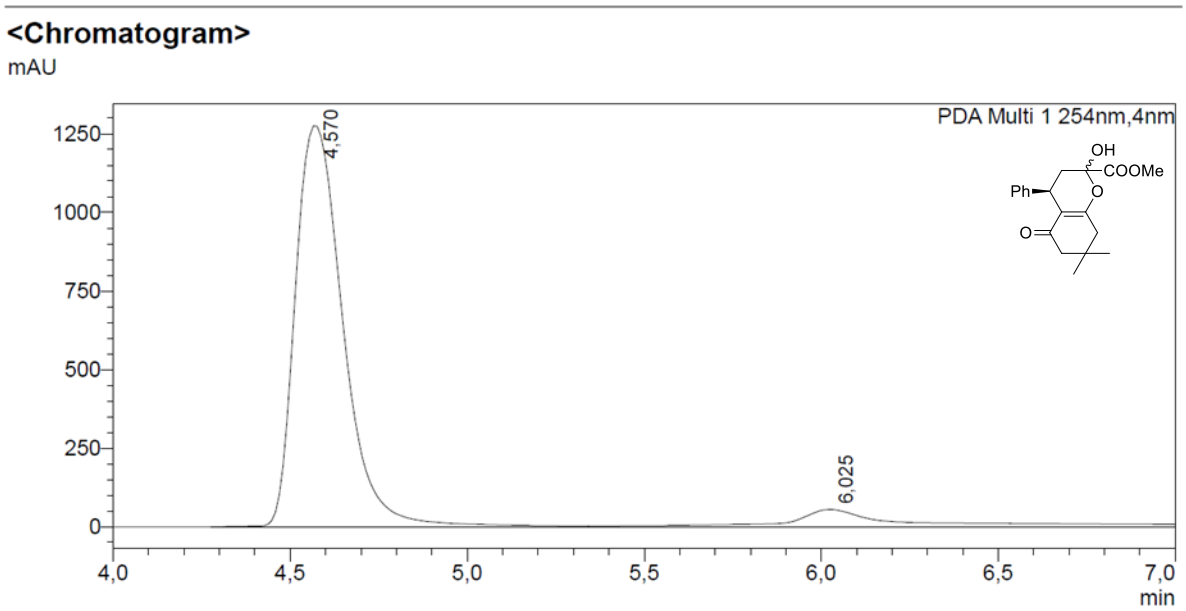



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,576 | 61671 | 85,698 | 586220 | 84,703 |
| 2 | 6,030 | 10292 | 14,302 | 105870 | 15,297 |
| Total | | 71963 | 100,000 | 692091 | 100,000 |

**Figure S56.** HPLC chromatogram for *R*-**12**: sample obtained with catalyst *e*QN-**5c** in a solution at 273 K (69% ee).

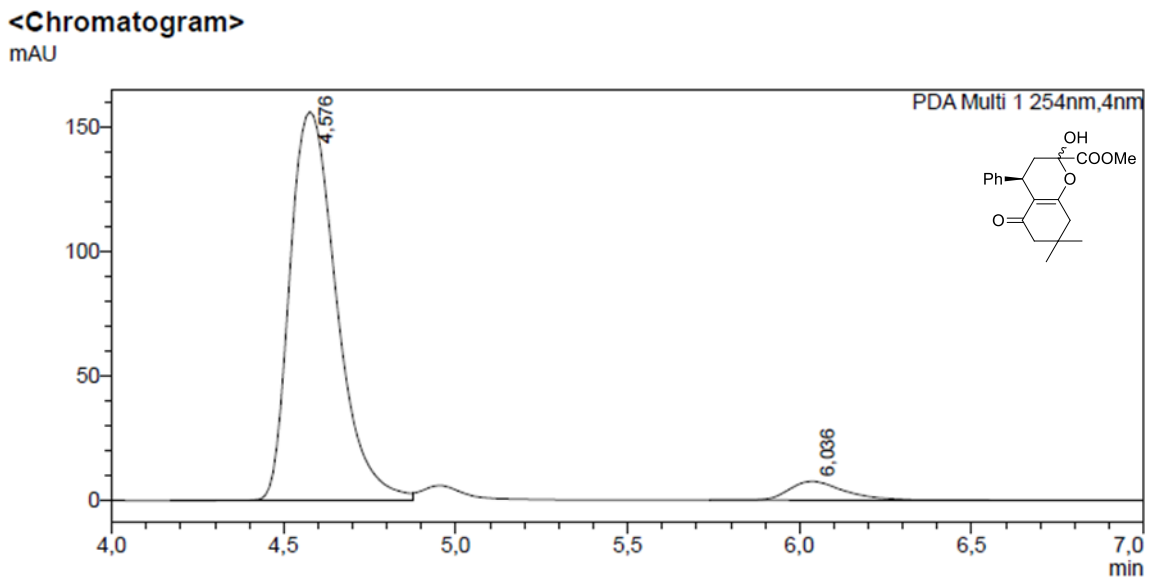



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,570 | 1274846 | 95,895 | 11964344 | 87,764 |
| 2 | 6,025 | 54568 | 4,105 | 1668130 | 12,236 |
| Total | | 1329414 | 100,000 | 13632473 | 100,000 |

**Figure S57.** HPLC chromatogram for *R*-**12**: sample obtained with catalyst *e*QN-**5d** in a solution at 273 K (76% ee).

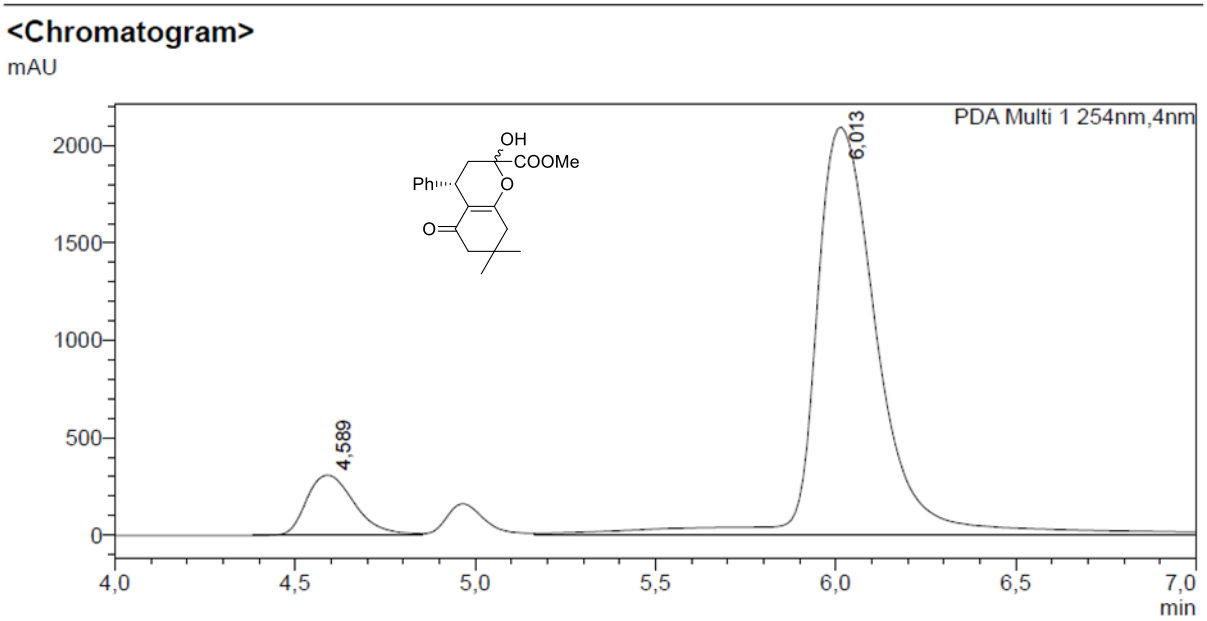



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,576 | 156343 | 95,391 | 1475819 | 94,623 |
| 2 | 6,036 | 7554 | 4,609 | 83869 | 5,377 |
| Total | | 163897 | 100,000 | 1559688 | 100,000 |

**Figure S58.** HPLC chromatogram for *R*-**12**: sample obtained with catalyst *e*QN-**5e** in a solution at 273 K (89% ee).

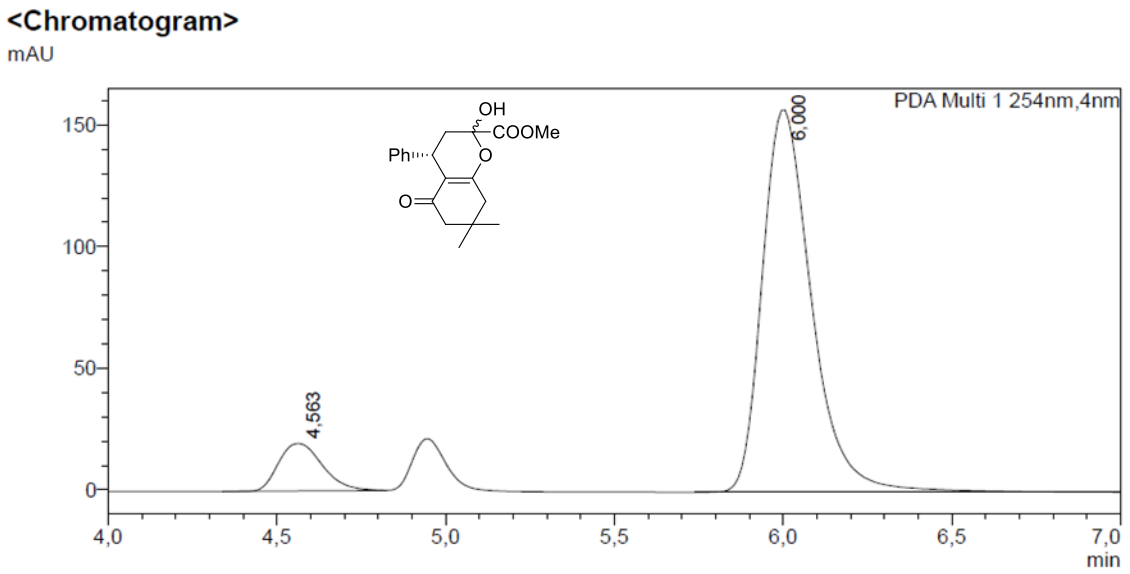



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,589 | 308434 | 12,831 | 2858669 | 9,778 |
| 2 | 6,013 | 2095348 | 87,169 | 26377099 | 90,222 |
| Total | | 2403782 | 100,000 | 29235768 | 100,000 |

**Figure S59.** HPLC chromatogram for *S*-**12**: sample obtained with catalyst *e*QD-**5h** in a solution at 273 K (80% ee).

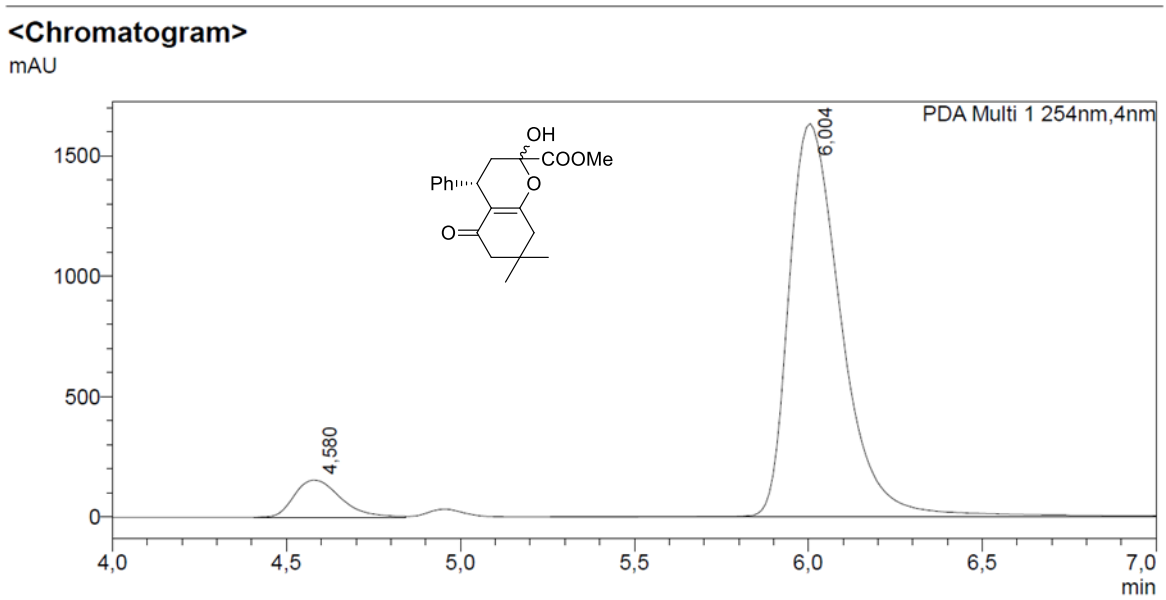



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 4,563 | 19552 | 175414 | 9,873 |
| 2 | 6,000 | 157113 | 1601303 | 90,127 |
| Total | | 176665 | 1776716 | 100,000 |

**Figure S60.** HPLC chromatogram for *S*-**12**: sample obtained with catalyst *e*QD-**5i** in a solution at 273 K (80% ee).

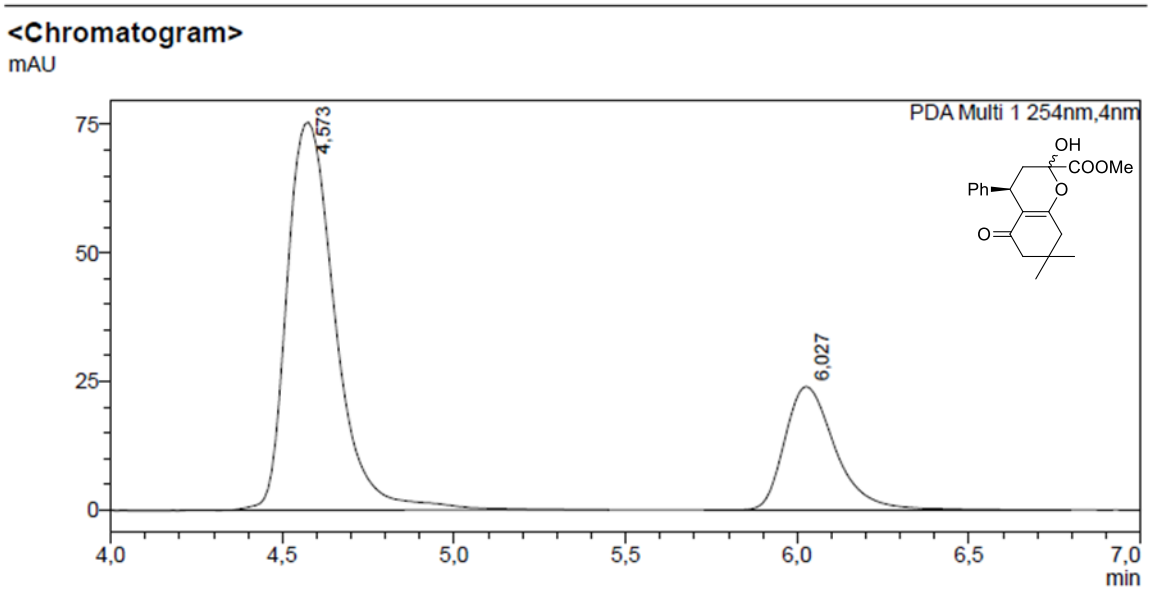



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 4,580 | 1424606 | 7,567 |
| 2 | 6,004 | 17401201 | 92,433 |
| Total | | 18825806 | 100,000 |

**Figure S61.** HPLC chromatogram for *S*-**12**: sample obtained with catalyst *e*QD-**5j** in a solution at 273 K (85% ee).

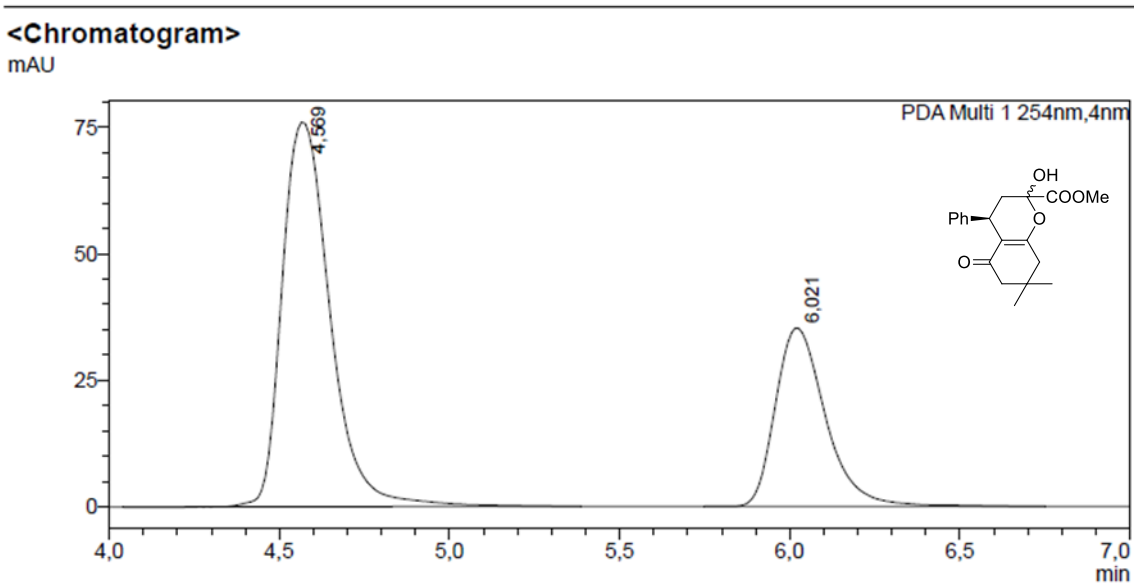



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,573 | 75418 | 75,853 | 735167 | 74,876 |
| 2 | 6,027 | 24009 | 24,147 | 246680 | 25,124 |
| Total | | 99427 | 100,000 | 981847 | 100,000 |

**Figure S62.** HPLC chromatogram for *R*-**12**: sample obtained with catalyst *e*QN-**5a** in a planetary ball mill (50% ee).

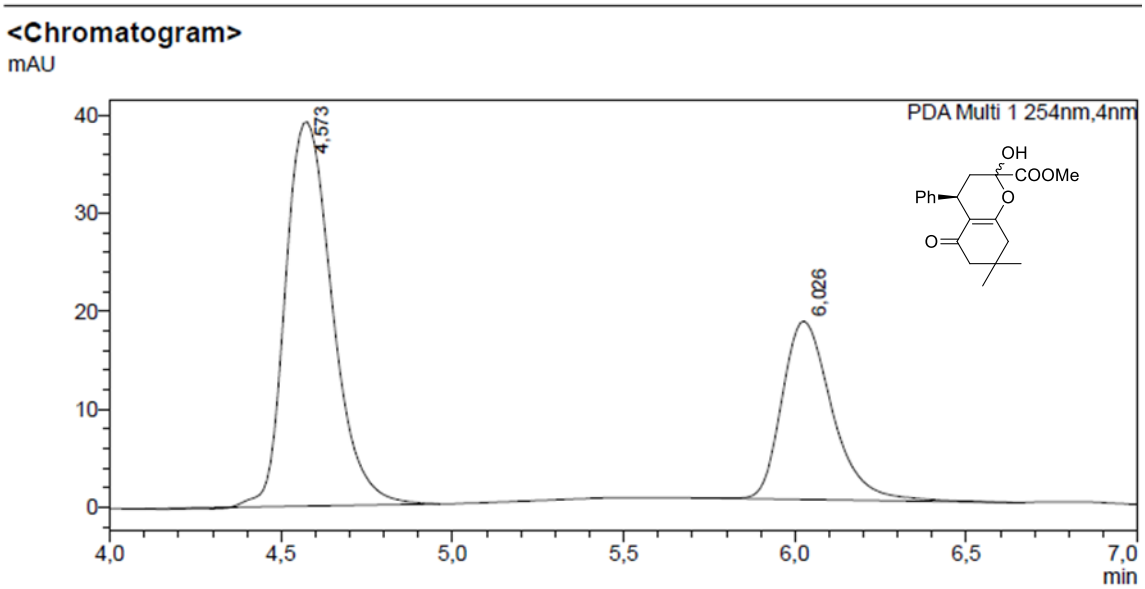



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,569 | 76073 | 68,320 | 746696 | 67,304 |
| 2 | 6,021 | 35275 | 31,680 | 362746 | 32,696 |
| Total | | 111348 | 100,000 | 1109442 | 100,000 |

**Figure S63.** HPLC chromatogram for *R*-**12**: sample obtained with catalyst *e*QN-**5b** in a planetary ball mill (35% ee).

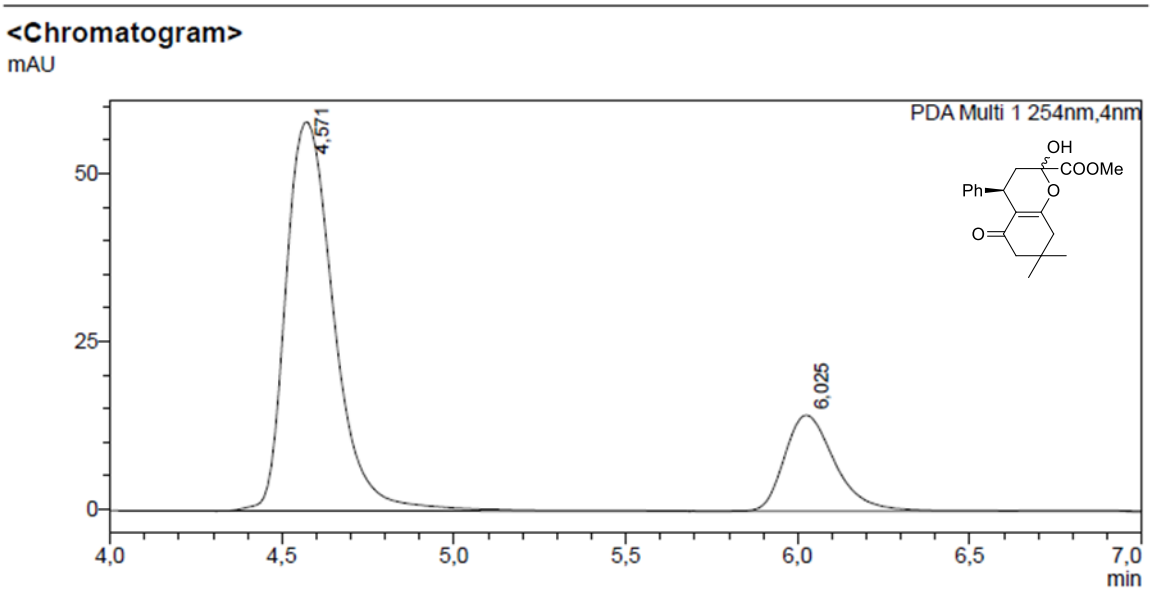



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,573 | 39171 | 68,272 | 372081 | 66,775 |
| 2 | 6,026 | 18204 | 31,728 | 185132 | 33,225 |
| Total | | 57375 | 100,000 | 557213 | 100,000 |

**Figure S64.** HPLC chromatogram for *R*-**12**: sample obtained with catalyst *e*QN-**5c** in a planetary ball mill (34% ee).

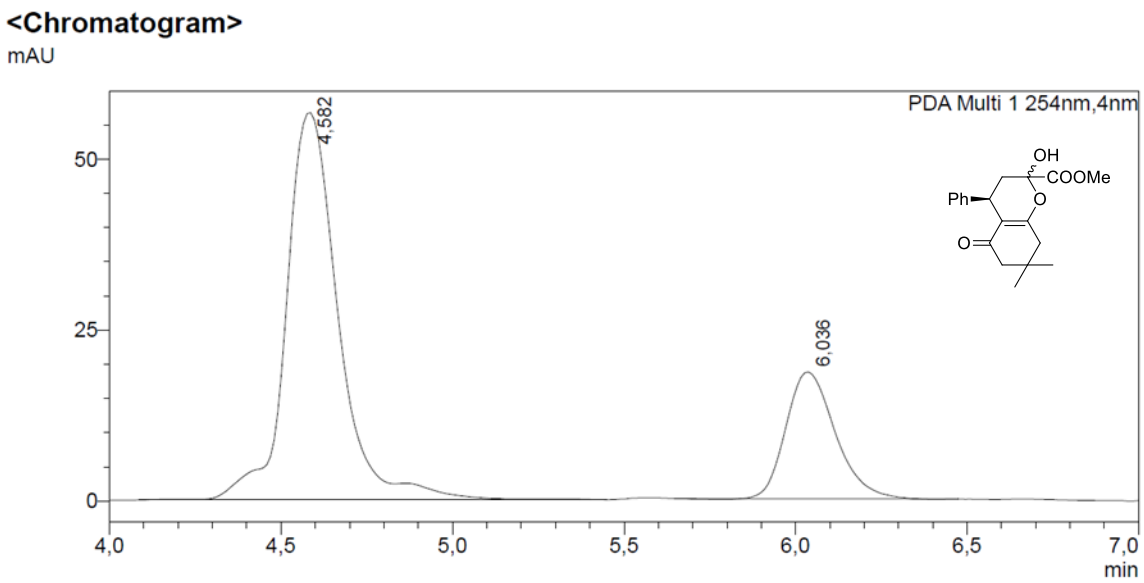



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,571 | 57853 | 80,176 | 565868 | 79,073 |
| 2 | 6,025 | 14305 | 19,824 | 149757 | 20,927 |
| Total | | 72158 | 100,000 | 715625 | 100,000 |

**Figure S65.** HPLC chromatogram for *R*-**12**: sample obtained with catalyst *e*QN-**5d** in a planetary ball mill (58% ee).

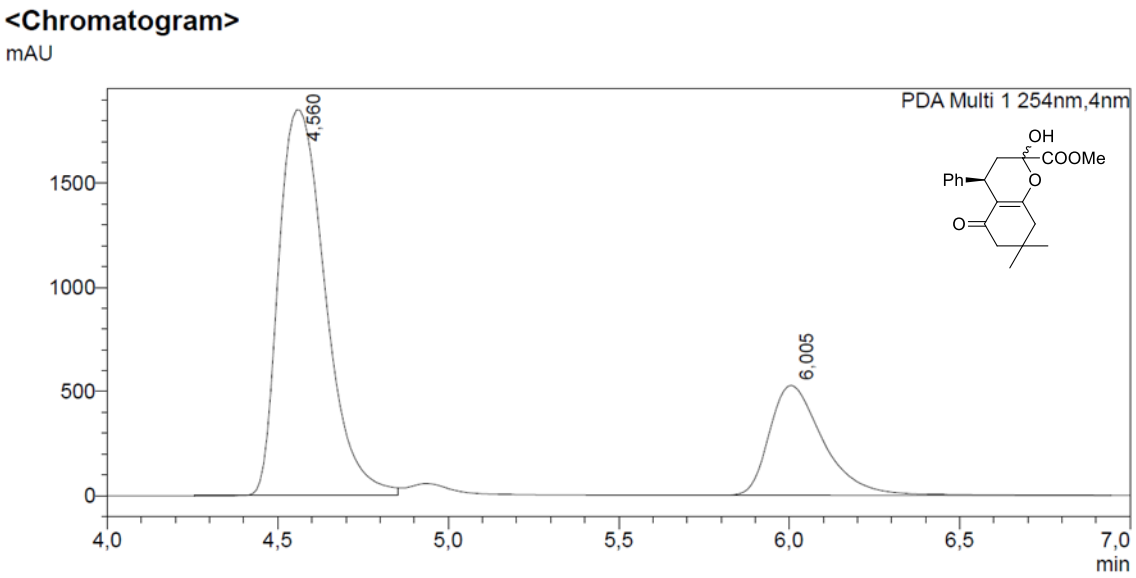



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,582 | 56624 | 75,278 | 599438 | 76,311 |
| 2 | 6,036 | 18595 | 24,722 | 186087 | 23,689 |
| Total | | 75219 | 100,000 | 785525 | 100,000 |

**Figure S66.** HPLC chromatogram for *R*-**12**: sample obtained with catalyst *e*QN-**5e** in a planetary ball mill (53% ee).

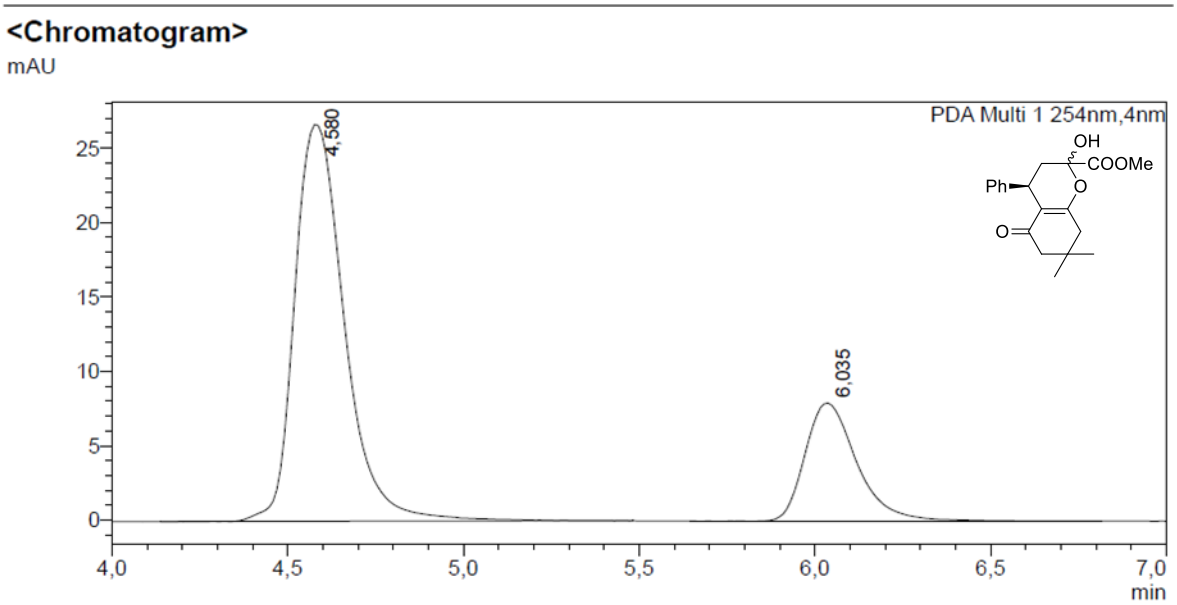



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,560 | 1849248 | 77,771 | 17607255 | 75,155 |
| 2 | 6,005 | 528551 | 22,229 | 5820726 | 24,845 |
| Total | | 2377799 | 100,000 | 23427982 | 100,000 |

**Figure S67.** HPLC chromatogram for *R*-**12**: sample obtained with catalyst *e*QN-**5f** in a planetary ball mill (50% ee).

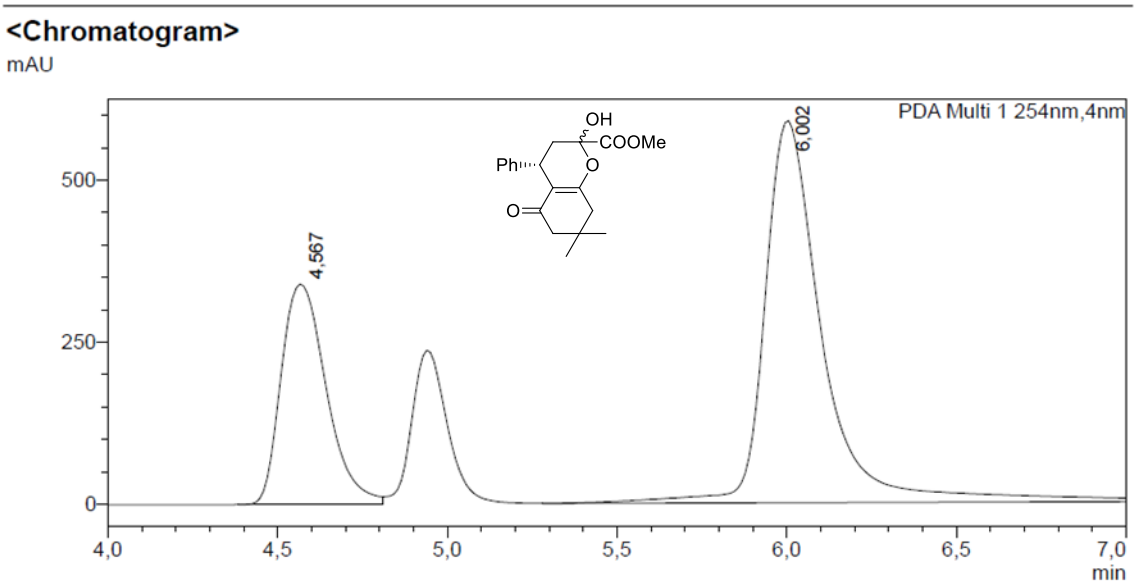



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,580 | 26656 | 77,059 | 263296 | 76,457 |
| 2 | 6,035 | 7936 | 22,941 | 81073 | 23,543 |
| Total | | 34592 | 100,000 | 344370 | 100,000 |

**Figure S68.** HPLC chromatogram for *R*-**12**: sample obtained with catalyst *e*DHQN-**5g** in a planetary ball mill (53% ee).

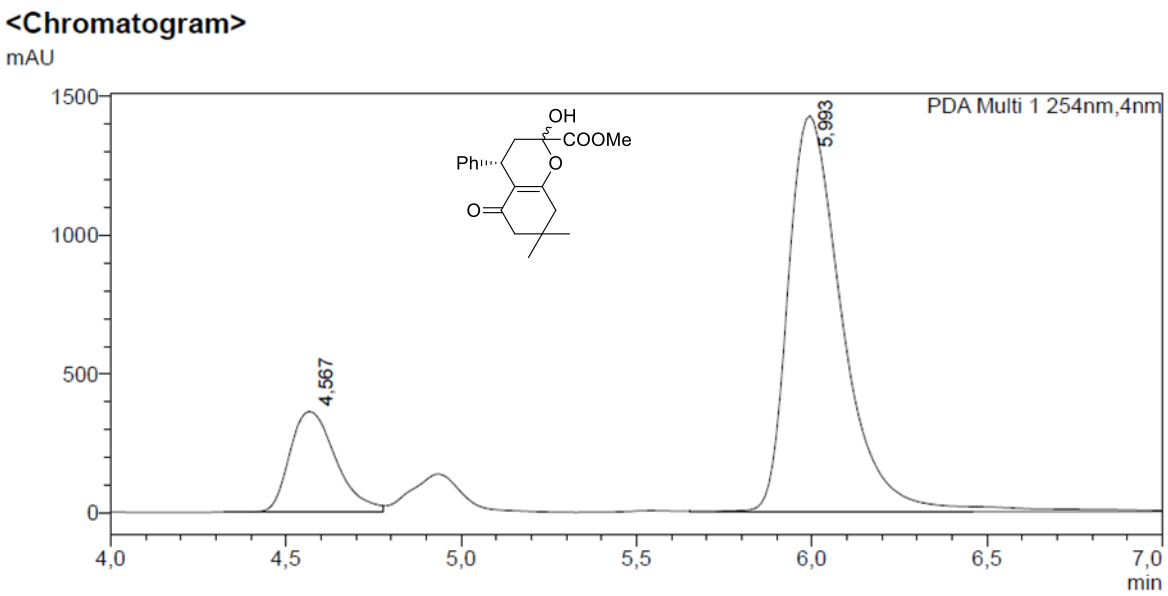



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,567 | 339511 | 36,561 | 3141300 | 30,669 |
| 2 | 6,002 | 589100 | 63,439 | 7101403 | 69,331 |
| Total | | 928611 | 100,000 | 10242703 | 100,000 |

**Figure S69.** HPLC chromatogram for *S*-**12**: sample obtained with catalyst *e*QD-**5h** in a planetary ball mill (39% ee).

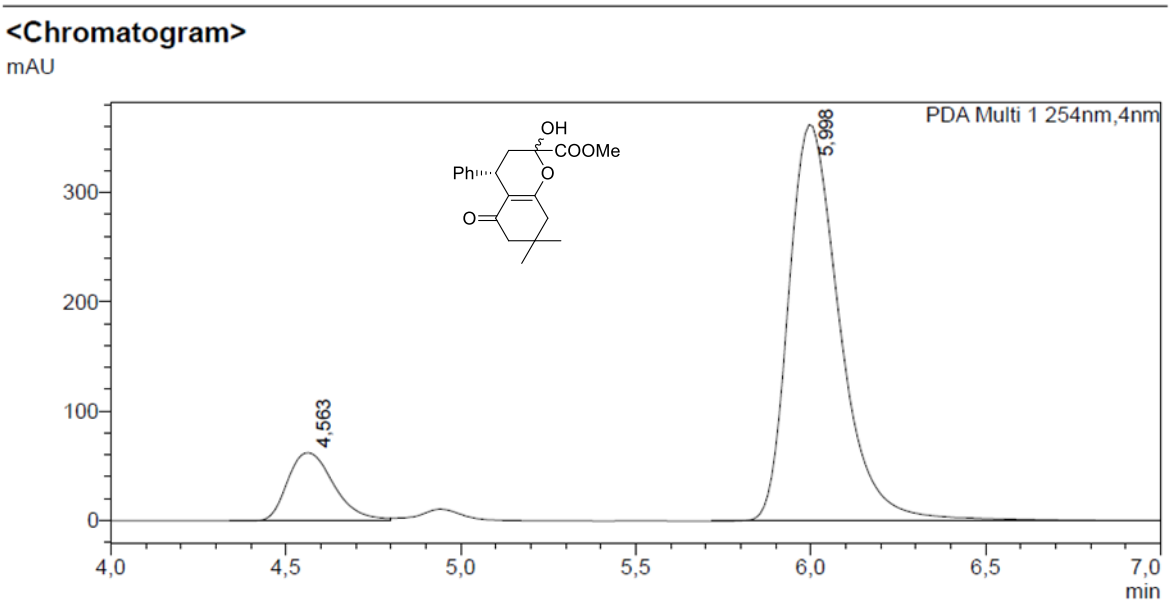



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,567 | 363379 | 20,302 | 3355393 | 17,791 |
| 2 | 5,993 | 1426529 | 79,698 | 15504737 | 82,209 |
| Total | | 1789907 | 100,000 | 18860131 | 100,000 |

**Figure S70.** HPLC chromatogram for *S*-**12**: sample obtained with catalyst *e*QD-**5i** in a planetary ball mill (64% ee).

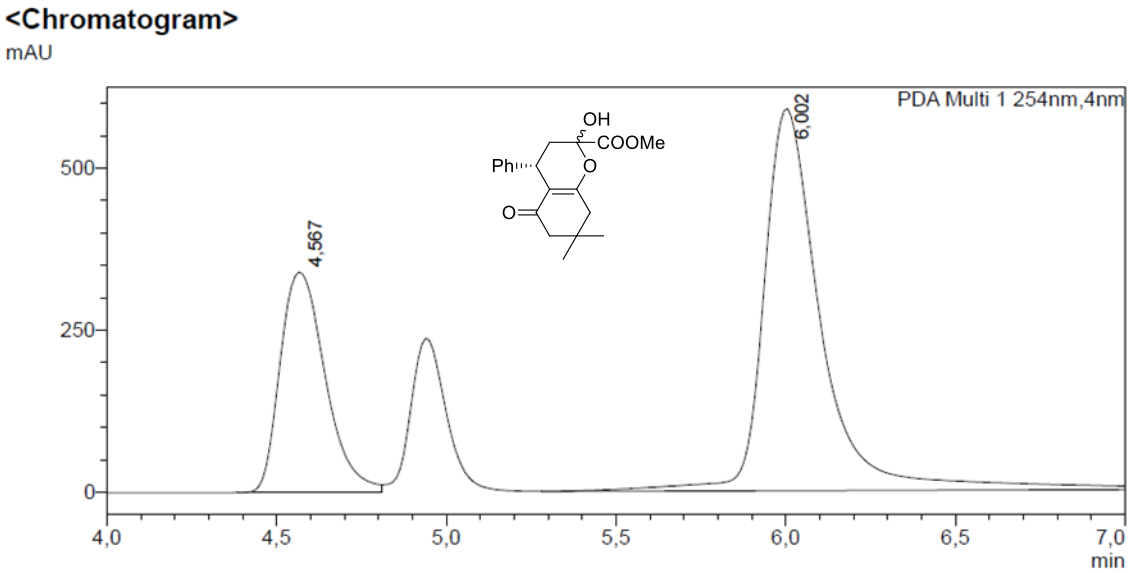



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Area | Area% |
|---|---|---|---|---|
| 1 | 4,563 | 62316 | 575093 | 13,492 |
| 2 | 5,998 | 362447 | 3687265 | 86,508 |
| Total | | 424763 | 4262358 | 100,000 |

**Figure S71.** HPLC chromatogram for *S*-**12**: sample obtained with catalyst *e*QD-**5j** in a planetary ball mill (73% ee).

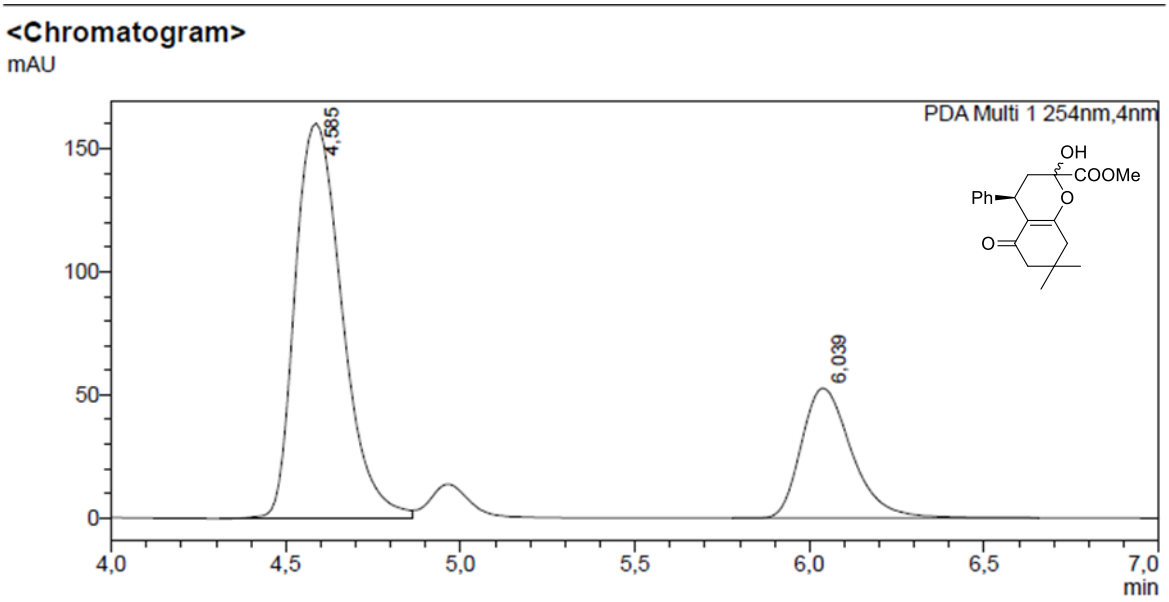



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,567 | 339511 | 36,561 | 3141300 | 30,669 |
| 2 | 6,002 | 589100 | 63,439 | 7101403 | 69,331 |
| Total | | 928611 | 100,000 | 10242703 | 100,000 |

**Figure S72.** HPLC chromatogram for *S*-**12**: sample obtained with catalyst *e*DHQD-**5k** in a planetary ball mill (39% ee).

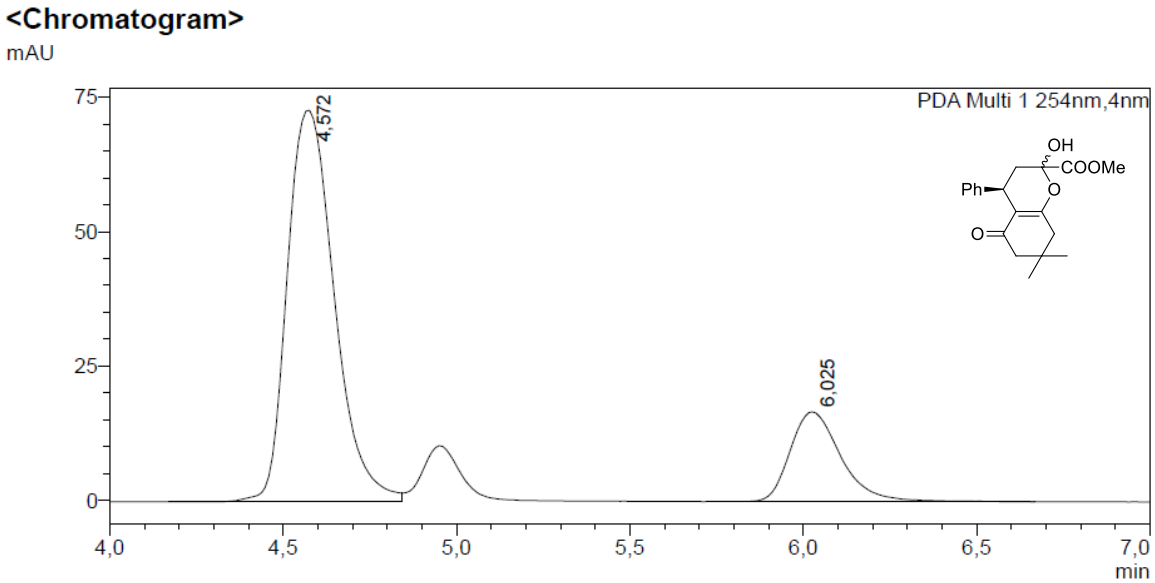



**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,585 | 160406 | 75,262 | 1508683 | 74,003 |
| 2 | 6,039 | 52724 | 24,738 | 529995 | 25,997 |
| Total | | 213130 | 100,000 | 2038678 | 100,000 |

**Figure S73.** HPLC chromatogram for *R*-**12**: sample obtained with catalyst *e*QN-**6a** in a planetary ball mill (48% ee).




**<Peak Table>**

PDA Ch1 254nm

| Peak# | Ret. Time | Height | Height% | Area | Area% |
|---|---|---|---|---|---|
| 1 | 4,572 | 72814 | 81,377 | 689692 | 80,356 |
| 2 | 6,025 | 16664 | 18,623 | 168603 | 19,644 |
| Total | | 89478 | 100,000 | 858295 | 100,000 |

**Figure S74.** HPLC chromatogram for *R*-**12**: sample obtained with catalyst *e*QN-**6b** in a planetary ball mill (61% ee).