

SUPPORTING INFORMATION

Highly Efficient Asymmetric [3+2] Cycloaddition Promoted by Chiral Aziridine-Functionalized Organophosphorus Compounds

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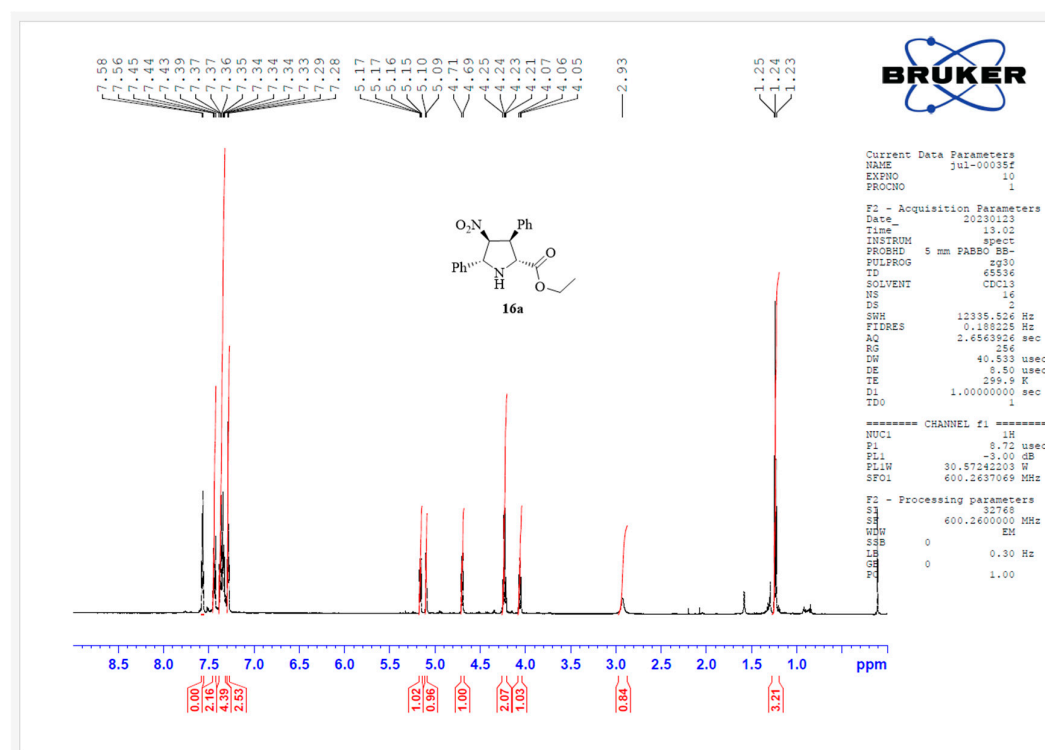
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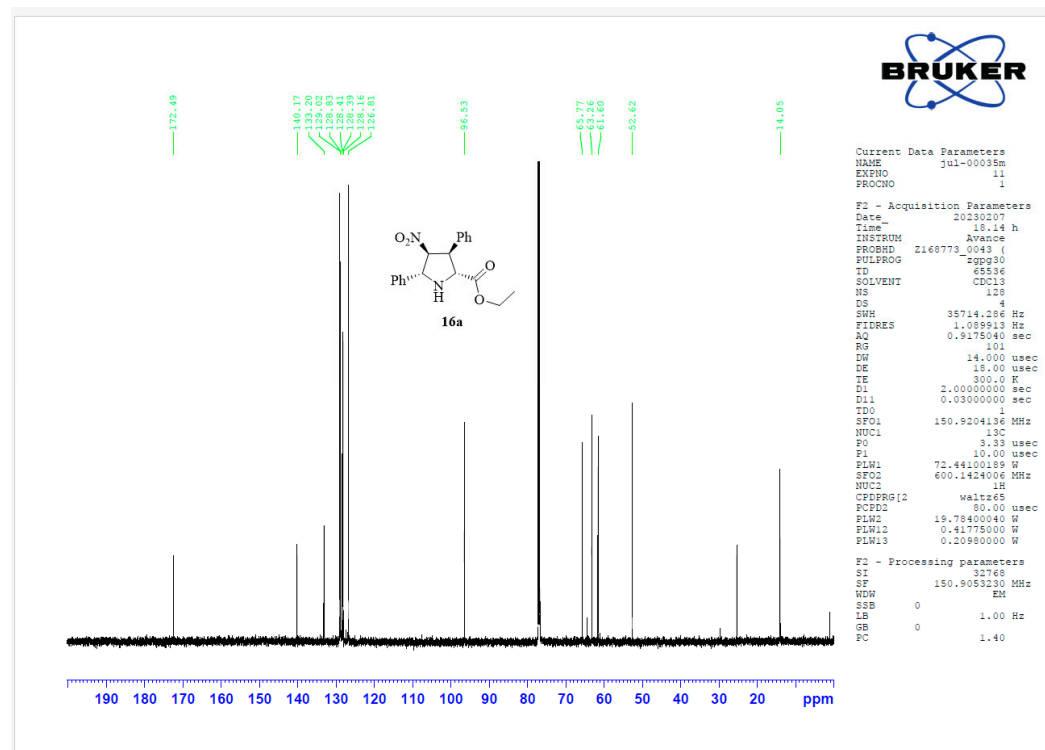
1. Copies of ^1H and ^{13}C NMR spectra

The ^1H and ^{13}C NMR of **16a**

^1H NMR (600 MHz, CDCl_3):

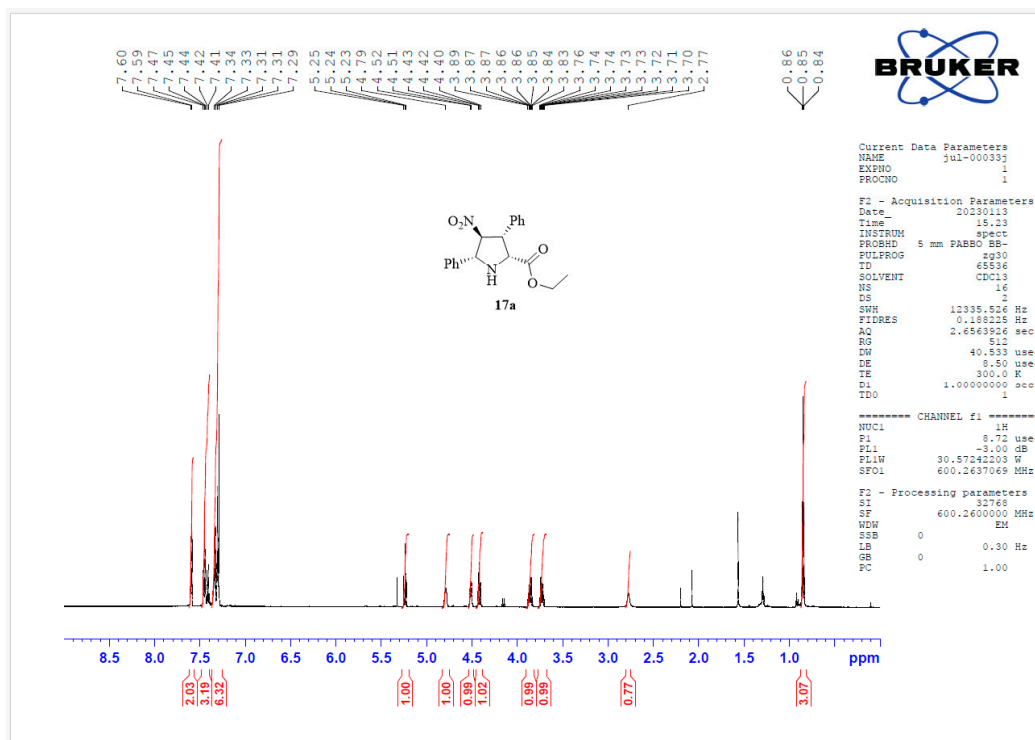


^{13}C NMR (150 MHz, CDCl_3):

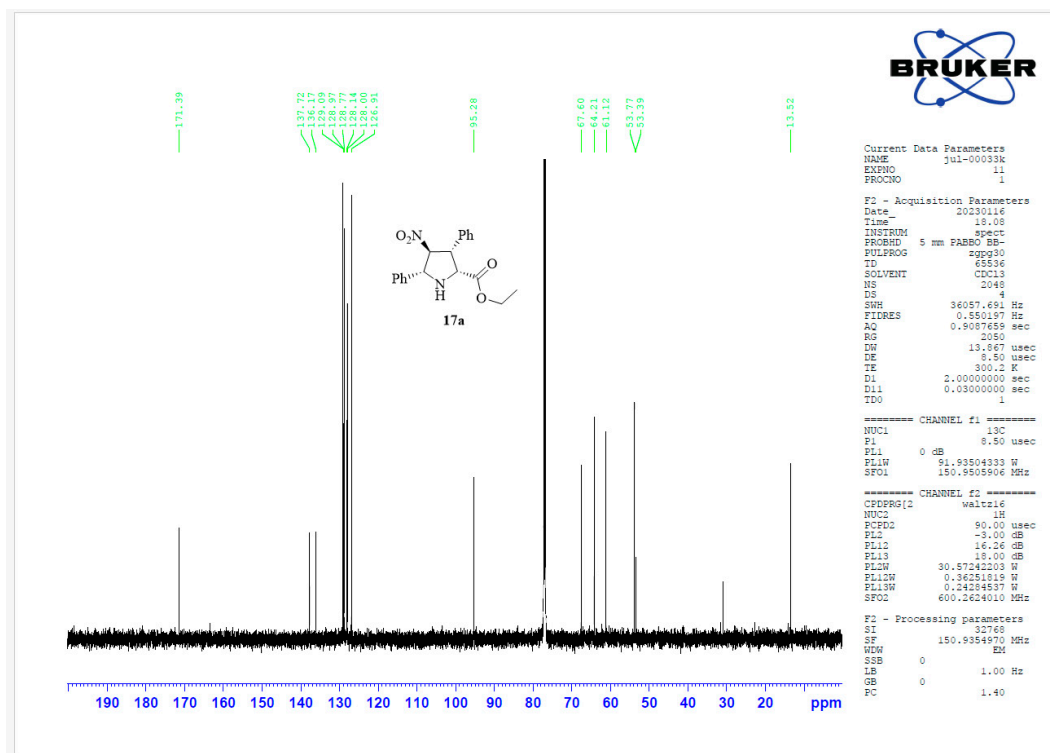


The ^1H and ^{13}C NMR of **17a**

^1H NMR (600 MHz, CDCl_3):

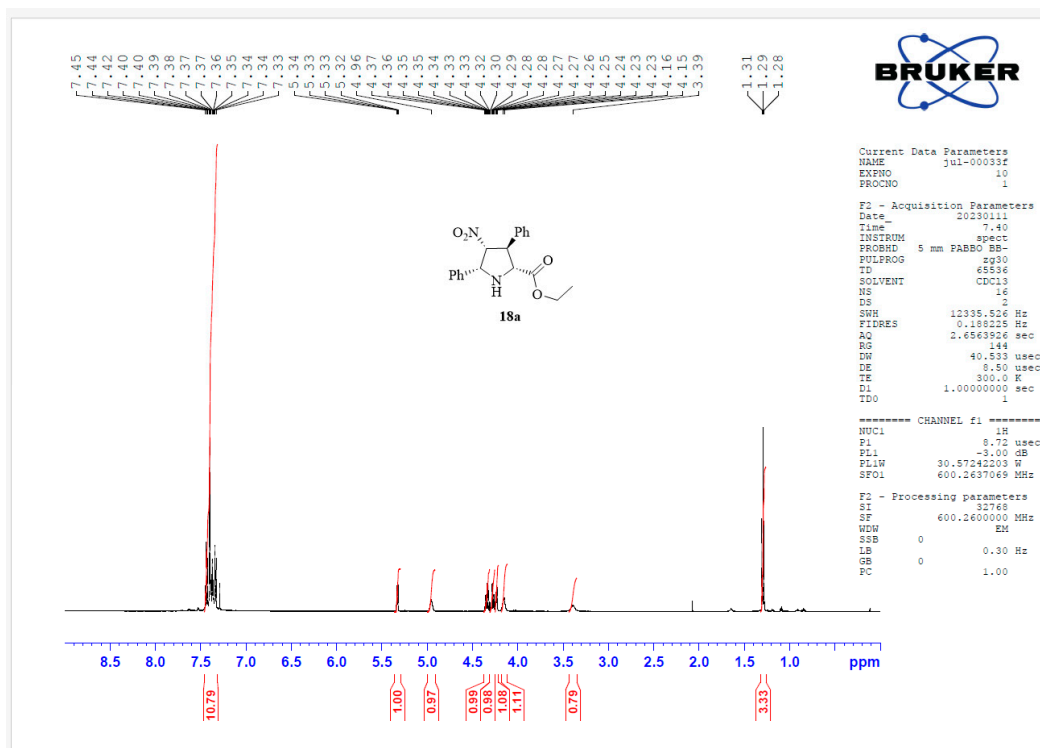


^{13}C NMR (150 MHz, CDCl_3):

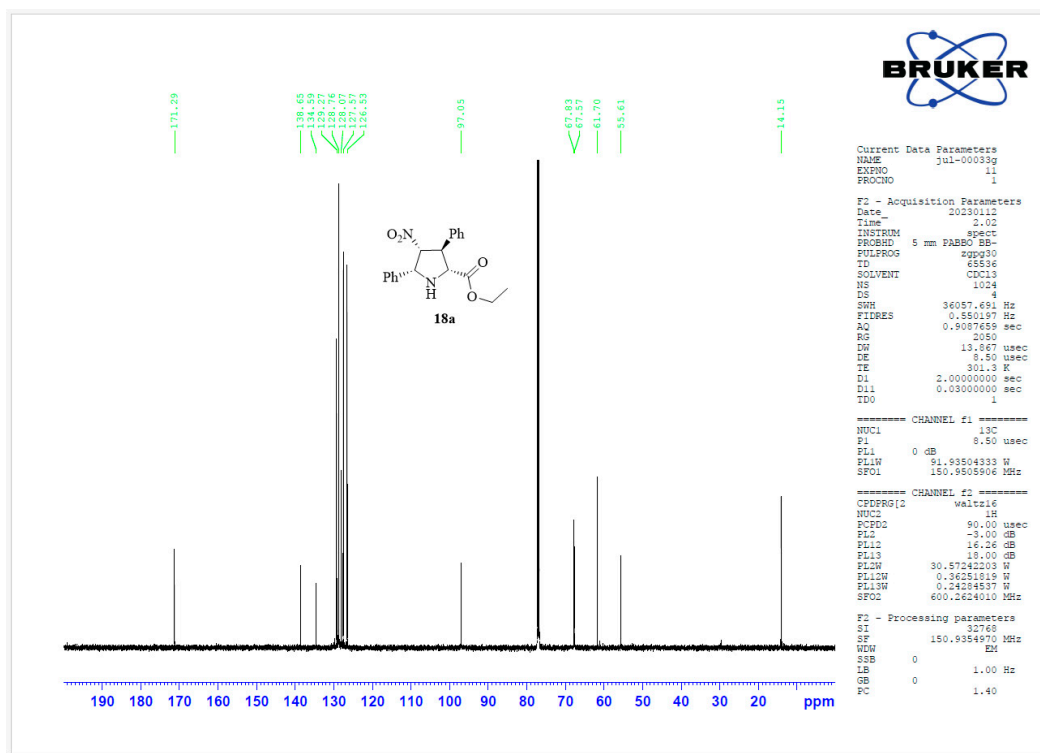


The ^1H and ^{13}C NMR of **18a**

^1H NMR (600 MHz, CDCl_3):

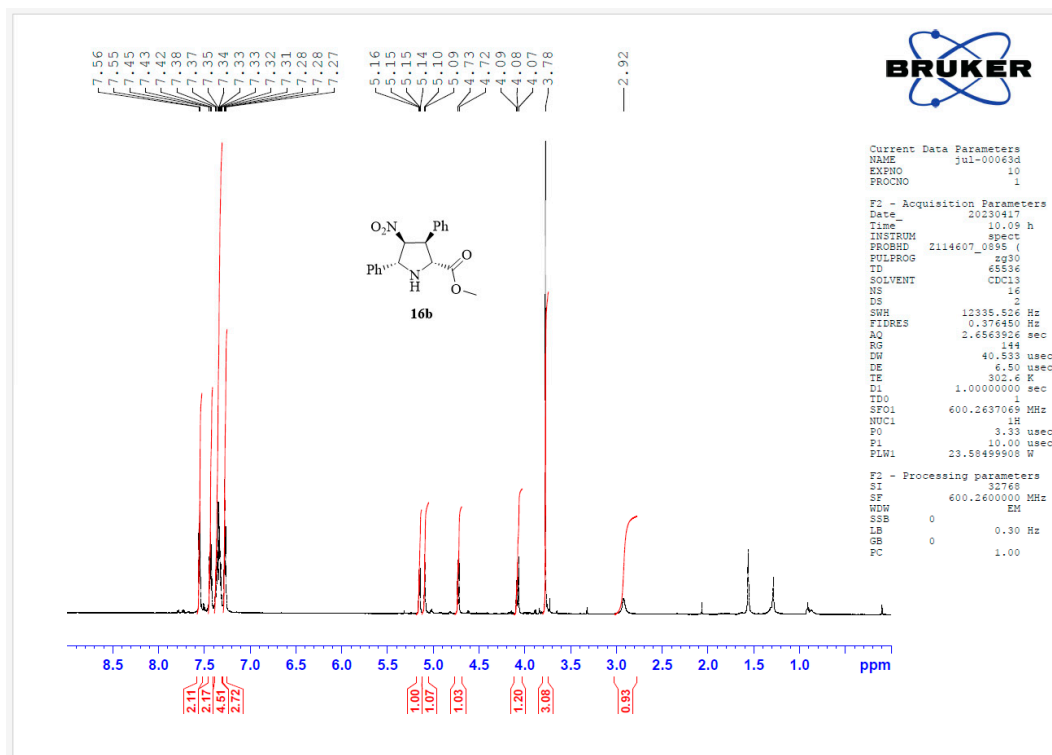


^{13}C NMR (150 MHz, CDCl_3):

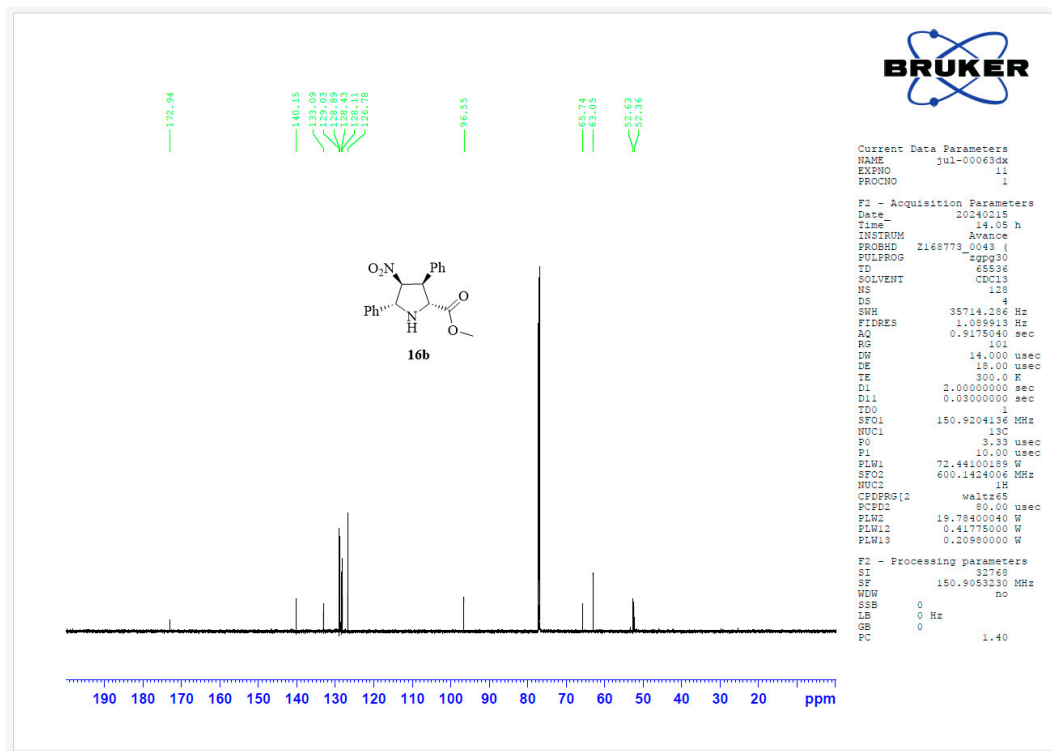


The ^1H and ^{13}C NMR of **16b**

^1H NMR (600 MHz, CDCl_3):

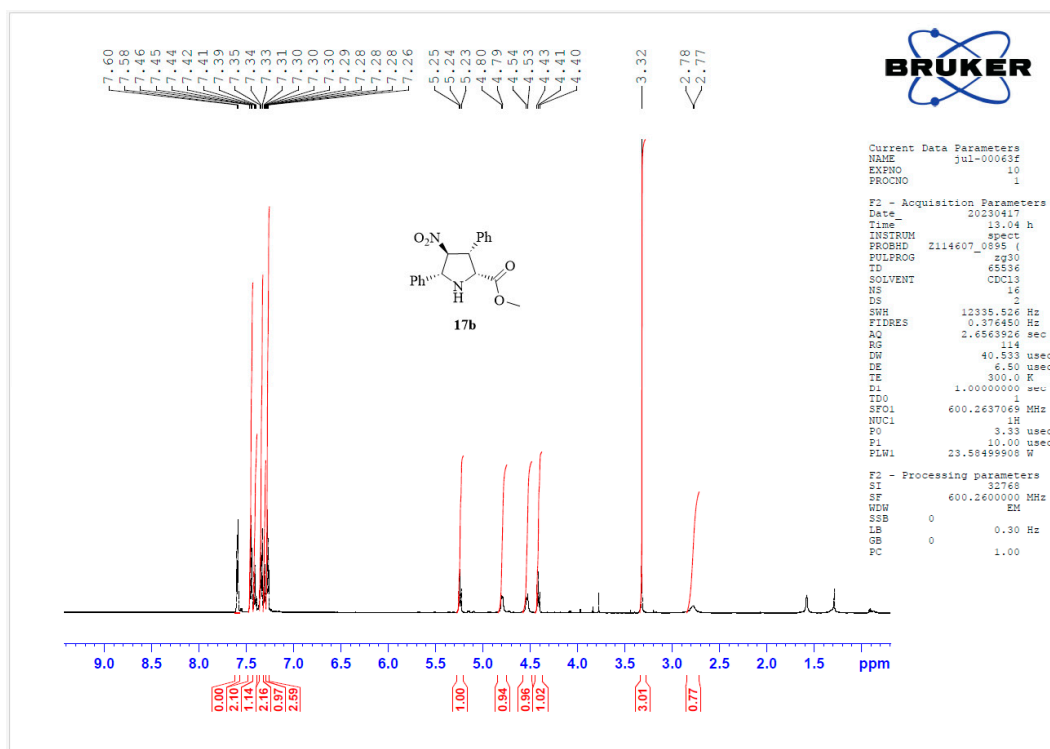


^{13}C NMR (150 MHz, CDCl_3):

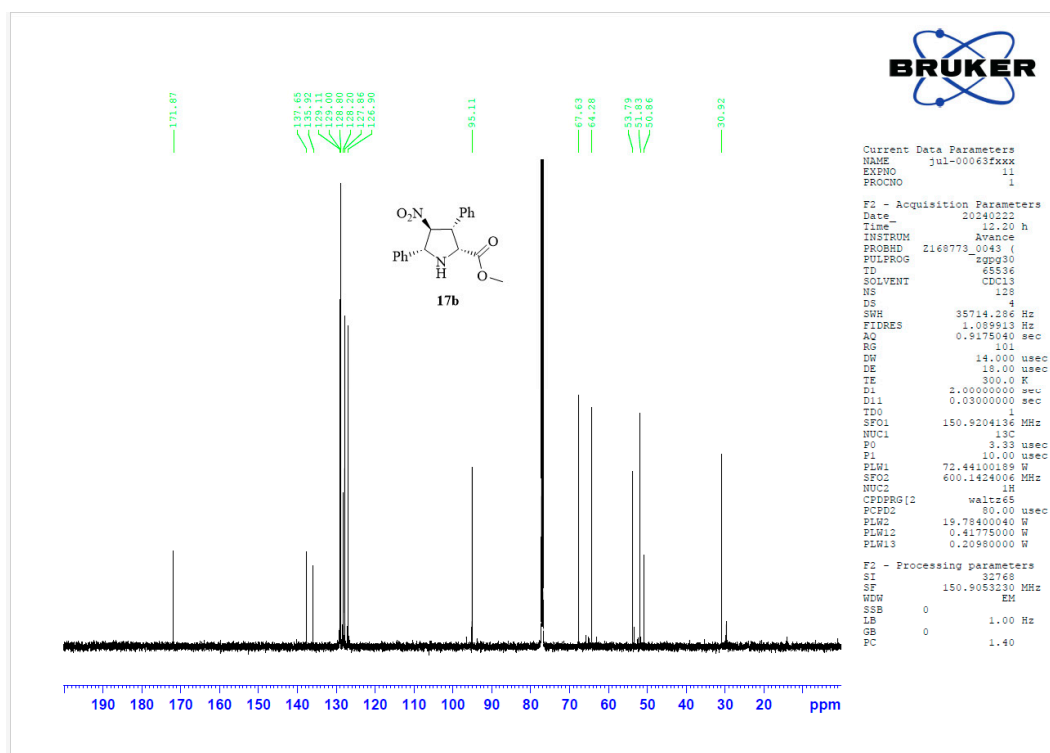


The ^1H and ^{13}C NMR of **17b**

^1H NMR (600 MHz, CDCl_3):

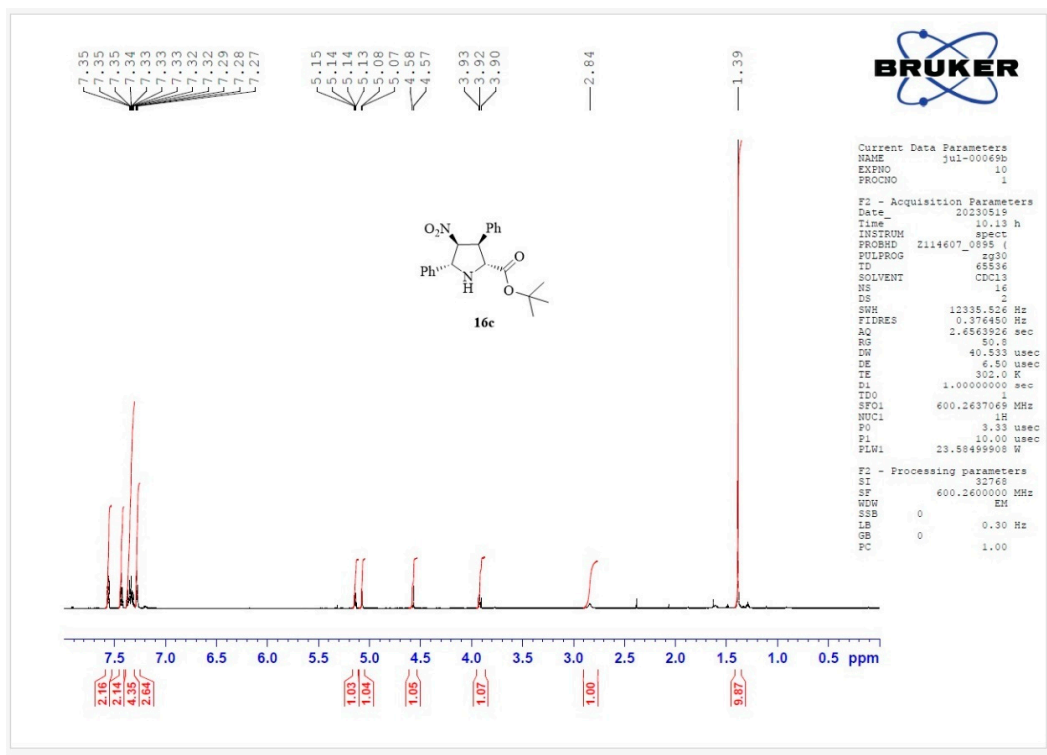


^{13}C NMR (150 MHz, CDCl_3):

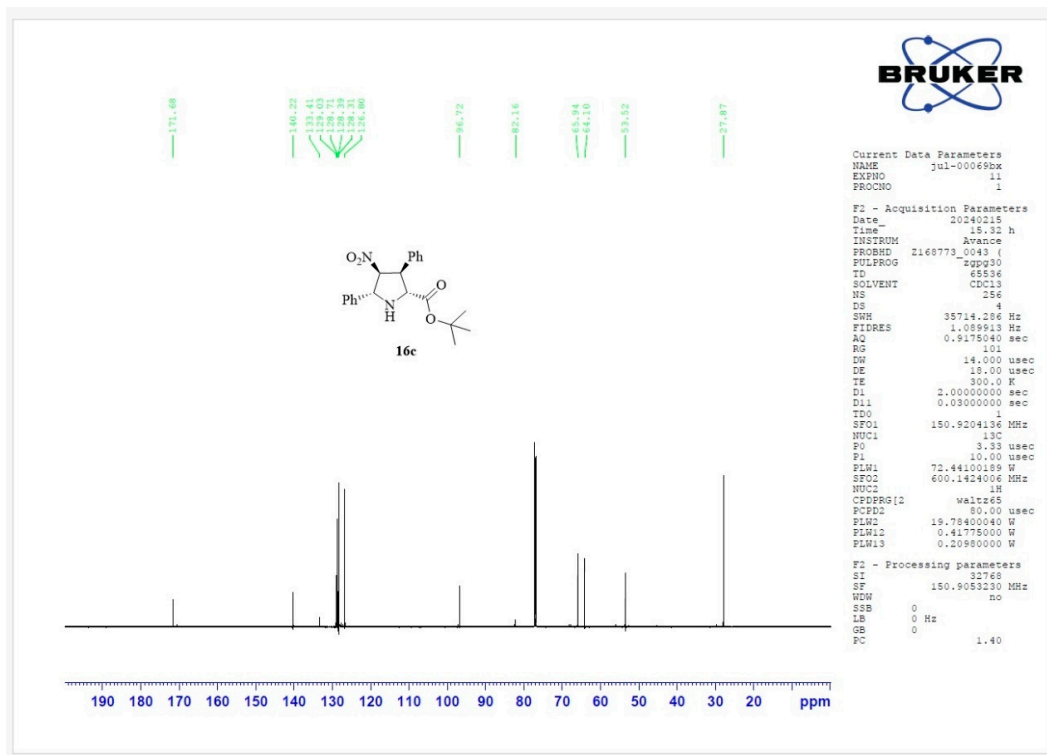


The ^1H and ^{13}C NMR of **16c**

^1H NMR (600 MHz, CDCl_3):

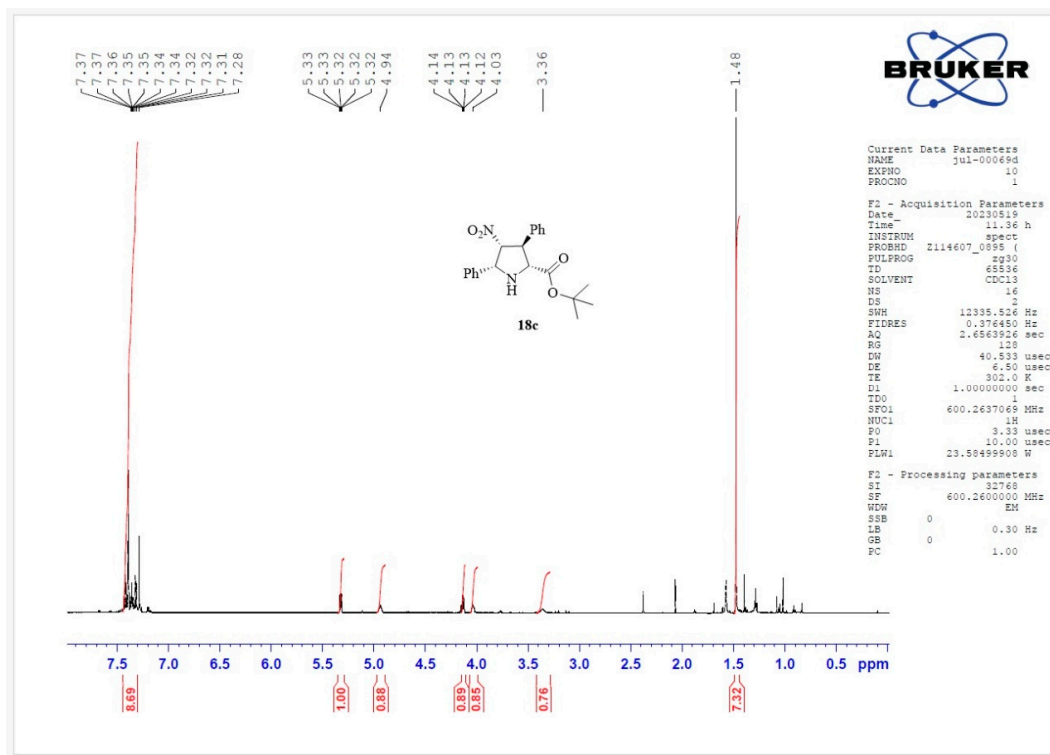


^{13}C NMR (150 MHz, CDCl_3):

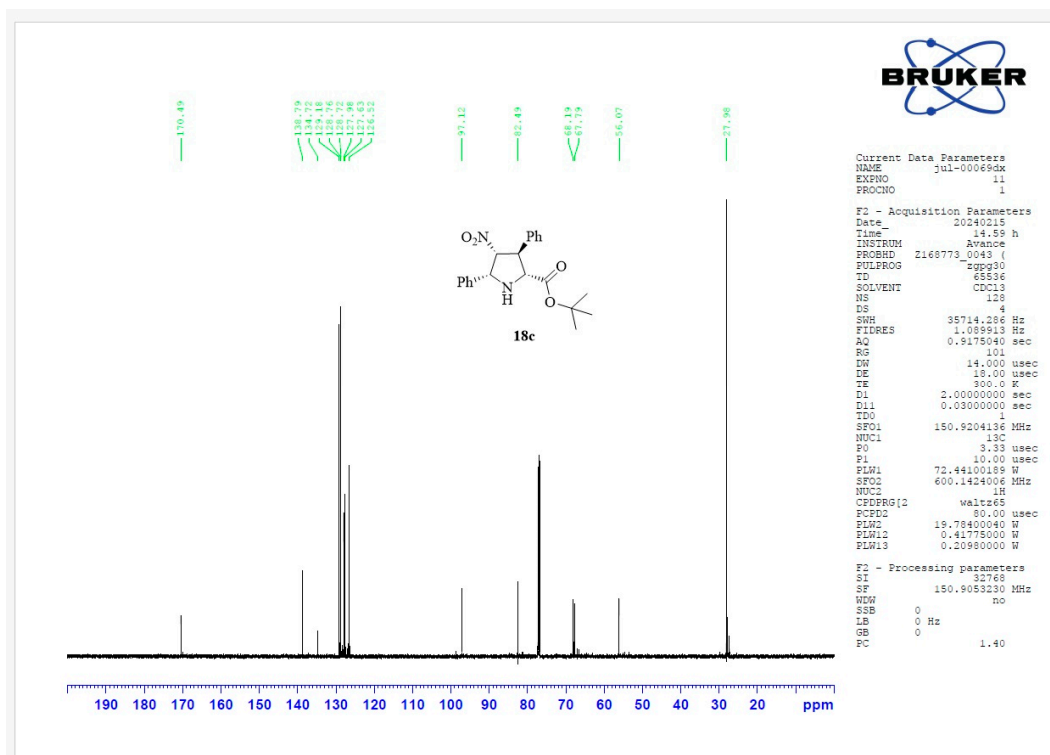


The ^1H and ^{13}C NMR of **18c**

^1H NMR (600 MHz, CDCl_3):



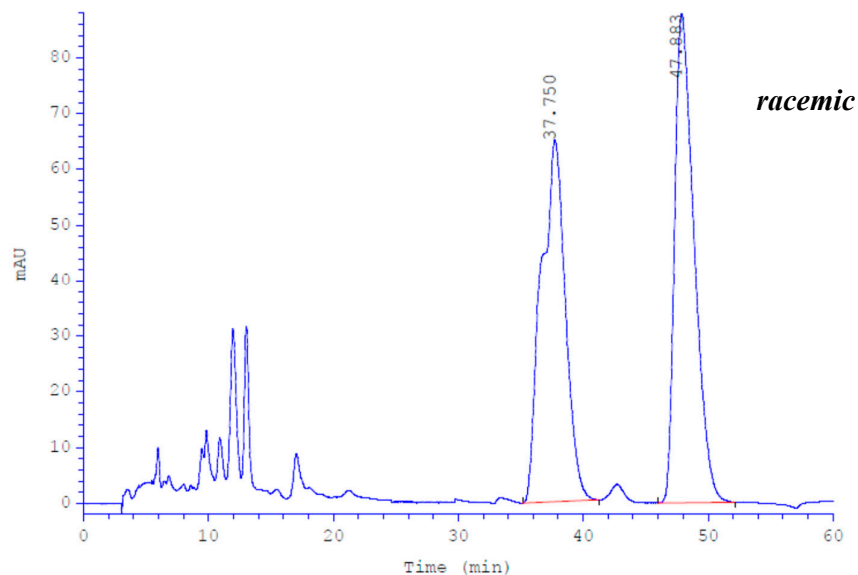
^{13}C NMR (150 MHz, CDCl_3):



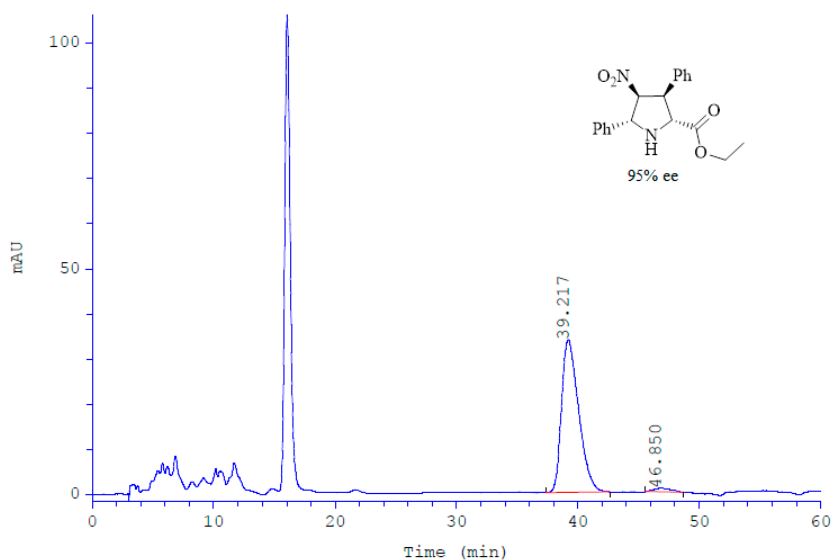
2. HPLC chromatograms

(2*R*,3*S*,4*S*,5*R*)-Ethyl 4-Nitro-3,5-diphenylpyrrolidine-2-carboxylate (4-*epi-endo*) **16a**

ee (95%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : *i*PrOH = 90:10, flow = 1.0 mL/min, λ = 254 nm, retention times (min): 39.2 (major), 46.8 (minor).



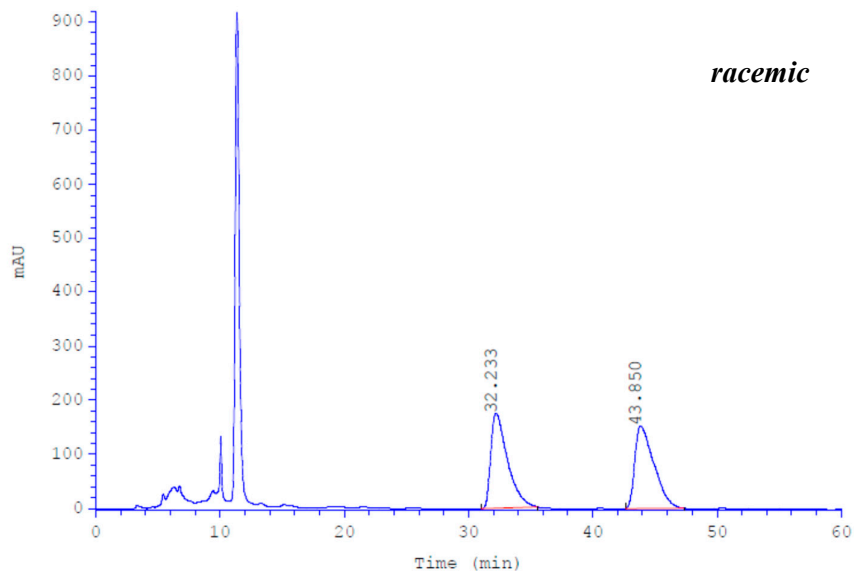
| | Ret time [min] | Start [min] | End [min] | Compound | Amount | Units | Area [mAU*min] | Height [mAU] | % Area | Width [min] | Type |
|---|----------------|-------------|-----------|----------|--------|-------|----------------|--------------|---------|-------------|------|
| 1 | 37.750 | 35.17 | 41.30 | | 0 | | 145.739 | 64.913 | 47.8549 | 2.358 | BB |
| 2 | 47.883 | 46.02 | 52.18 | | 0 | | 158.805 | 87.8865 | 52.1451 | 1.686 | BB |



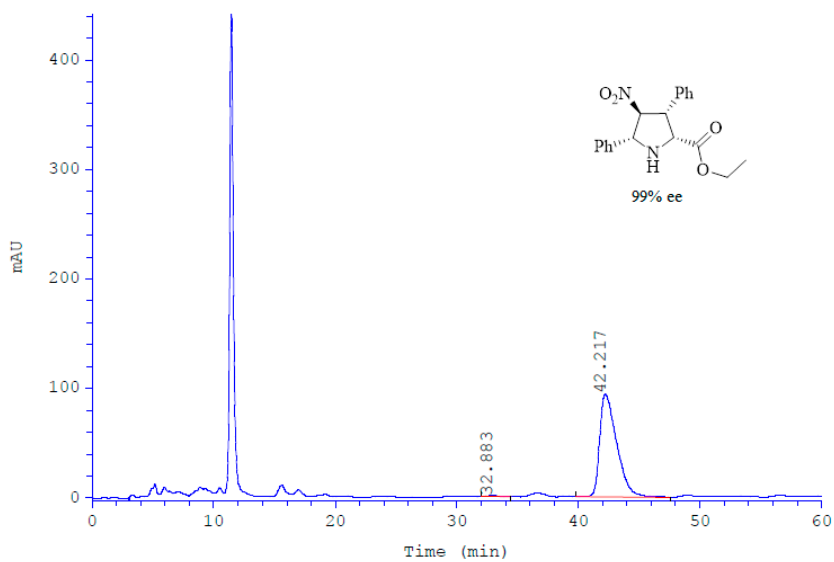
| | Ret time [min] | Start [min] | End [min] | Compound | Amount | Units | Area [mAU*min] | Height [mAU] | % Area | Width [min] | Type |
|---|----------------|-------------|-----------|----------|--------|-------|----------------|--------------|---------|-------------|------|
| 1 | 39.217 | 37.38 | 42.63 | | 0 | | 54.9899 | 33.8001 | 97.5331 | 1.513 | BB |
| 2 | 46.850 | 45.59 | 48.73 | | -1 | | 1.39087 | 0.839868 | 2.4669 | 1.641 | BB+ |

(2*R*,3*R*,4*S*,5*R*)- Ethyl 4-Nitro-3,5-diphenylpyrrolidine-2-carboxylate (*exo*) **17a**

ee (99%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : *i*PrOH = 90:10, flow = 1.0 mL/min, λ = 254 nm, retention times (min): 32.9 (minor), 42.2 (major).



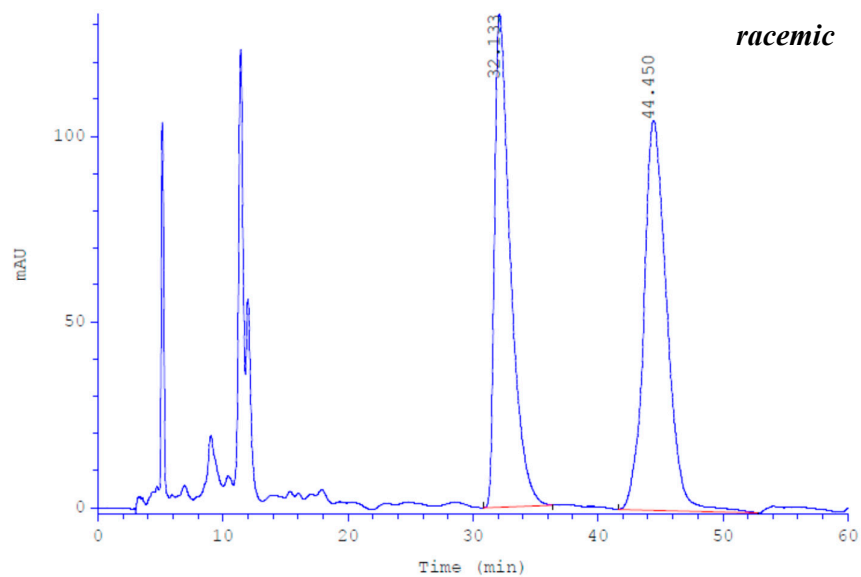
| | Ret.time [min] | Start [min] | End [min] | Compound | Amount | Units | Area [mAU*min] | Height [mAU] | % Area | Width [min] | Type |
|---|-------------------|----------------|--------------|----------|--------|-------|-------------------|-----------------|---------|----------------|------|
| 1 | 32.233 | 31.05 | 35.59 | | -1 | | 273.815 | 175.718 | 50.2509 | 1.391 | BB+ |
| 2 | 43.850 | 42.66 | 47.33 | | -1 | | 271.081 | 152.259 | 49.7491 | 1.711 | BB+ |



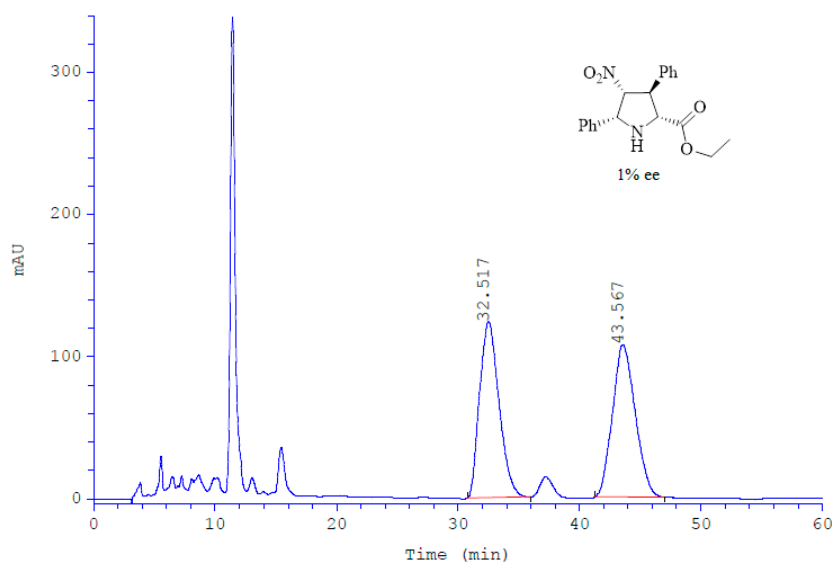
| | Ret.time [min] | Start [min] | End [min] | Compound | Amount | Units | Area [mAU*min] | Height [mAU] | % Area | Width [min] | Type |
|---|-------------------|----------------|--------------|----------|--------|-------|-------------------|-----------------|---------|----------------|------|
| 1 | 32.883 | 31.99 | 34.45 | | -1 | | 1.06041 | 0.920395 | 0.6873 | 1.135 | BB+ |
| 2 | 42.217 | 39.80 | 47.57 | | 0 | | 153.231 | 94.0342 | 99.3127 | 1.484 | BB |

(2*R*,3*S*,4*R*,5*R*)- Ethyl 4-Nitro-3,5-diphenylpyrrolidine-2-carboxylate (*endo*) **18a**

ee (1%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : *i*PrOH = 90:10, flow = 1.0 mL/min, λ = 254 nm, retention times (min): 32.5 (major), 43.6 (minor).



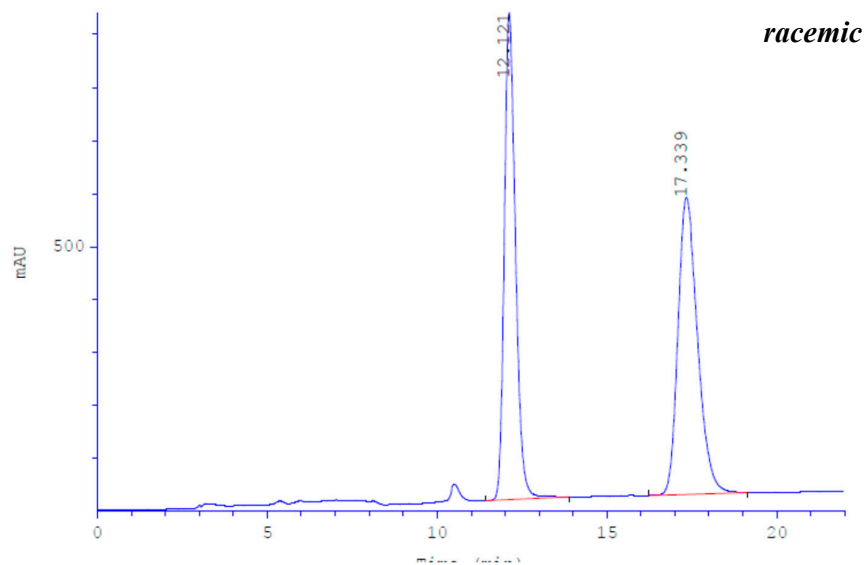
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|---|-------------------|----------------|--------------|----------|--------|-------|-------------------|-----------------|---------|----------------|------|
| 1 | 32.133 | 30.87 | 36.42 | | 0 | | 195.835 | 132.827 | 46.6754 | 1.300 | BB |
| 2 | 44.450 | 41.65 | 52.78 | | 0 | | 223.733 | 105.061 | 53.3246 | 1.892 | BB |



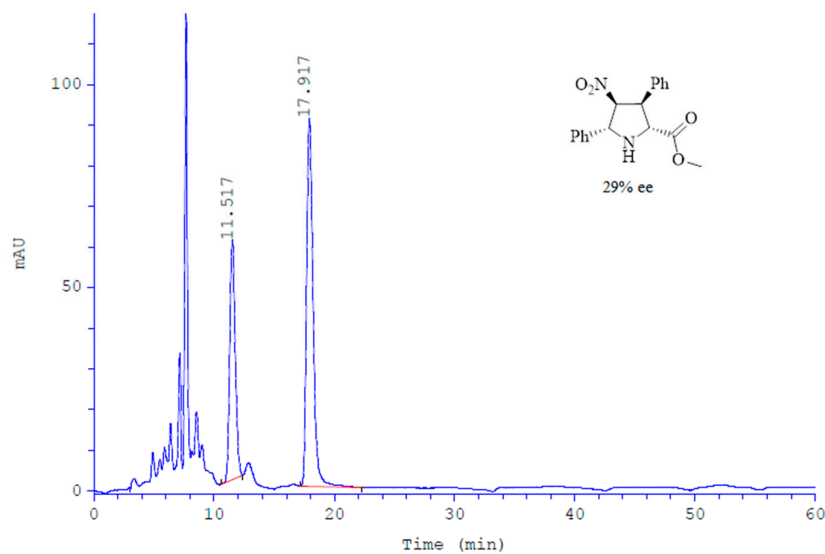
| | Ret.time [min] | Start [min] | End [min] | Compound | Amount | Units | Area [mAU*min] | Height [mAU] | % Area | Width [min] | Type |
|---|-------------------|----------------|--------------|----------|--------|-------|-------------------|-----------------|---------|----------------|------|
| 1 | 32.517 | 30.78 | 35.99 | | -1 | | 229.755 | 123.791 | 49.6830 | 1.785 | BB+ |
| 2 | 43.567 | 41.32 | 46.99 | | -1 | | 232.687 | 107.314 | 50.3170 | 2.029 | BB+ |

(2*R*,3*S*,4*S*,5*R*)-Methyl 4-Nitro-3,5-diphenylpyrrolidine-2-carboxylate (*4-epi-endo*) **16b**

ee (29%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : *i*PrOH = 90:10, flow = 1.0 mL/min, λ = 254 nm, retention times (min): 11.5 (minor), 17.9 (major).



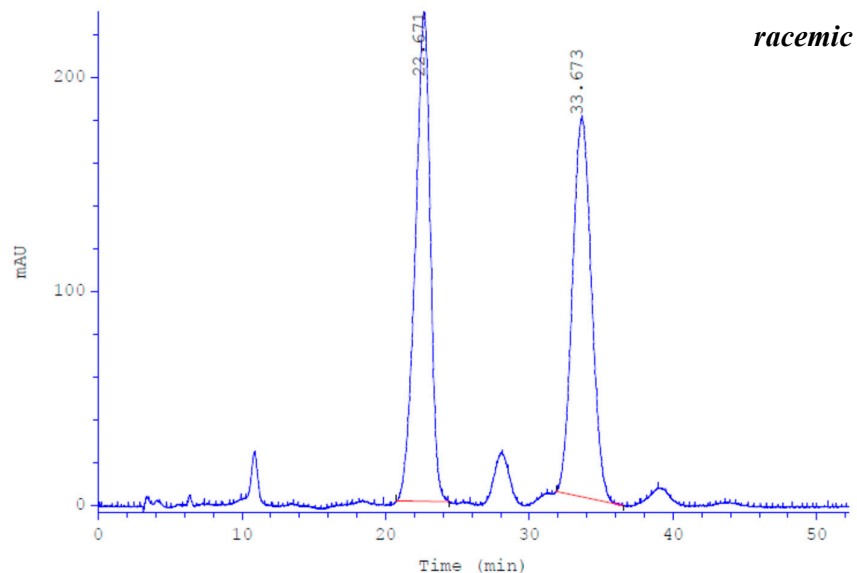
| | Ret.time [min] | Start [min] | End [min] | Compound | Amount | Units | Area [mAU*min] | Height [mAU] | % Area | Width [min] | Type |
|---|----------------|-------------|-----------|----------|--------|-------|----------------|--------------|---------|-------------|------|
| 1 | 12.121 | 11.42 | 13.90 | | 0 | | 350.615 | 919.297 | 48.3905 | 0.345 | BB |
| 2 | 17.339 | 16.24 | 19.14 | | 0 | | 373.938 | 561.96 | 51.6095 | 0.611 | BB |



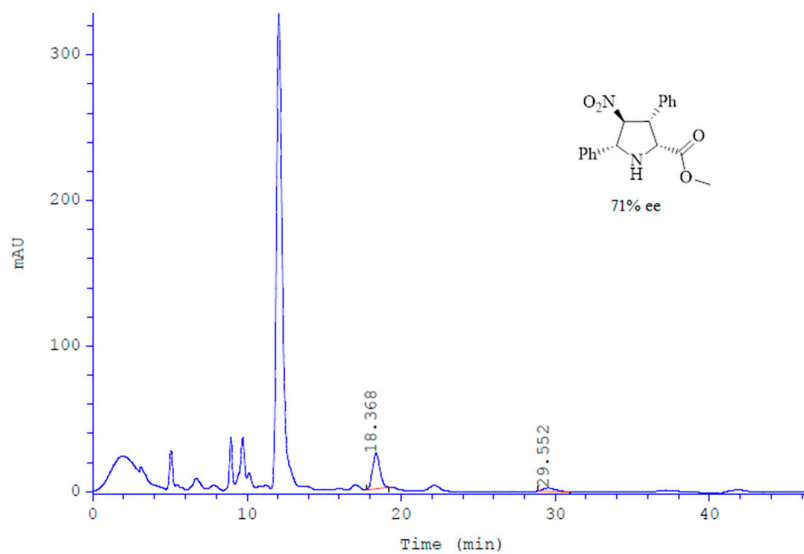
| | Ret.time [min] | Start [min] | End [min] | Compound | Amount | Units | Area [mAU*min] | Height [mAU] | % Area | Width [min] | Type |
|---|----------------|-------------|-----------|----------|--------|-------|----------------|--------------|---------|-------------|------|
| 1 | 11.517 | 10.62 | 12.37 | | 0 | | 30.9541 | 59.0456 | 35.4339 | 0.482 | BB |
| 2 | 17.917 | 17.13 | 22.25 | | 0 | | 56.4034 | 90.6417 | 64.5661 | 0.551 | BB |

(2*R*,3*R*,4*S*,5*R*)-Methyl 4-Nitro-3,5-diphenylpyrrolidine-2-carboxylate (*exo*) **17b**

ee (71%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : *i*PrOH = 90:10, flow = 1.0 mL/min, λ = 254 nm, retention times (min): 18.4 (major), 29.5 (minor).



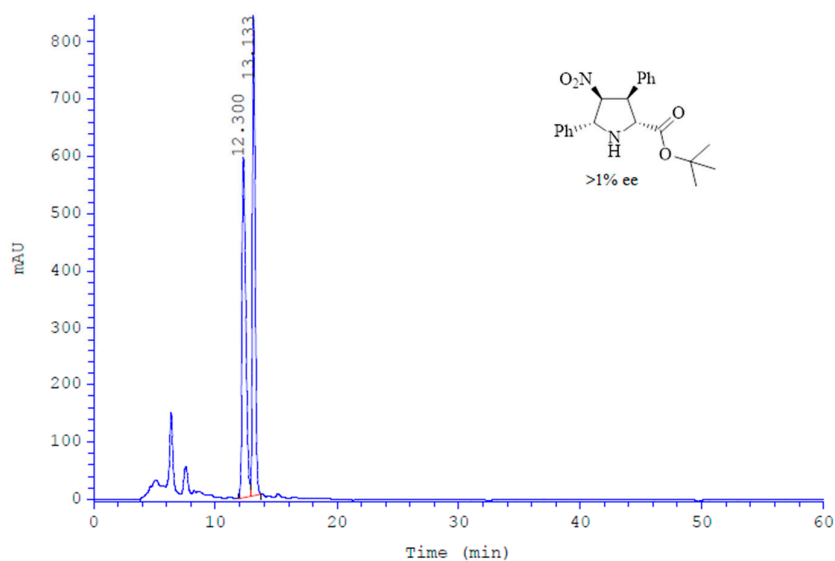
| | Ret.time [min] | Start [min] | End [min] | Compound | Amount | Units | Area [mAU*min] | Height [mAU] | % Area | Width [min] | Type |
|---|-------------------|----------------|--------------|----------|--------|-------|-------------------|-----------------|---------|----------------|------|
| 1 | 22.671 | 20.74 | 24.40 | | -1 | | 276.407 | 228.727 | 50.3573 | 1.120 | BB+ |
| 2 | 33.673 | 31.88 | 36.53 | | -1 | | 272.485 | 178.233 | 49.6427 | 1.450 | BB+ |



| | Ret.time [min] | Start [min] | End [min] | Compound | Amount | Units | Area [mAU*min] | Height [mAU] | % Area | Width [min] | Type |
|---|-------------------|----------------|--------------|----------|--------|-------|-------------------|-----------------|---------|----------------|------|
| 1 | 18.368 | 17.75 | 19.23 | | 0 | | 13.3866 | 24.1825 | 85.4035 | 0.516 | BB |
| 2 | 29.552 | 28.88 | 30.96 | | -1 | | 2.28794 | 2.2623 | 14.5965 | 1.007 | BB+ |

(2*R*,3*S*,4*S*,5*R*)-*Tert*-butyl 4-Nitro-3,5-diphenylpyrrolidine-2-carboxylate (4-*epi-endo*) **16c**

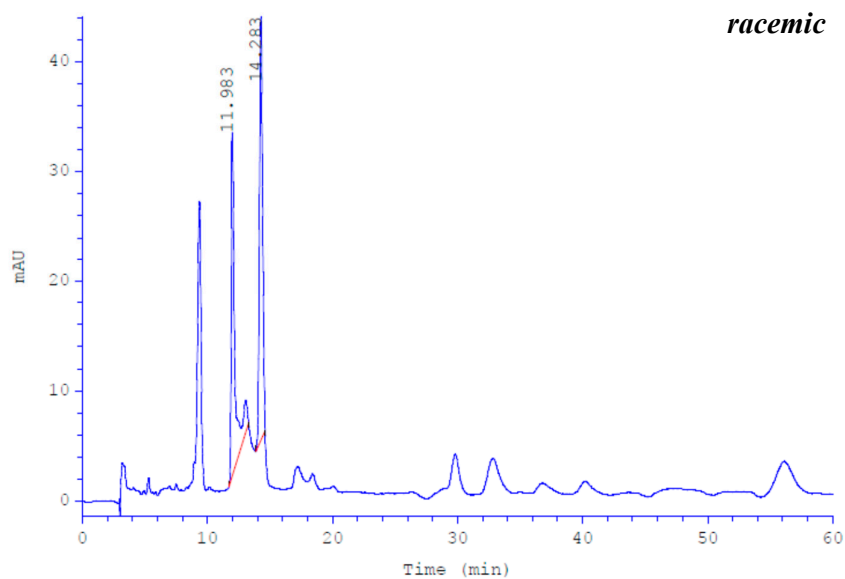
ee (>1%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : *i*PrOH = 90:10, flow = 1.0 mL/min, λ = 254 nm, retention times (min): 12.3, 13.1.



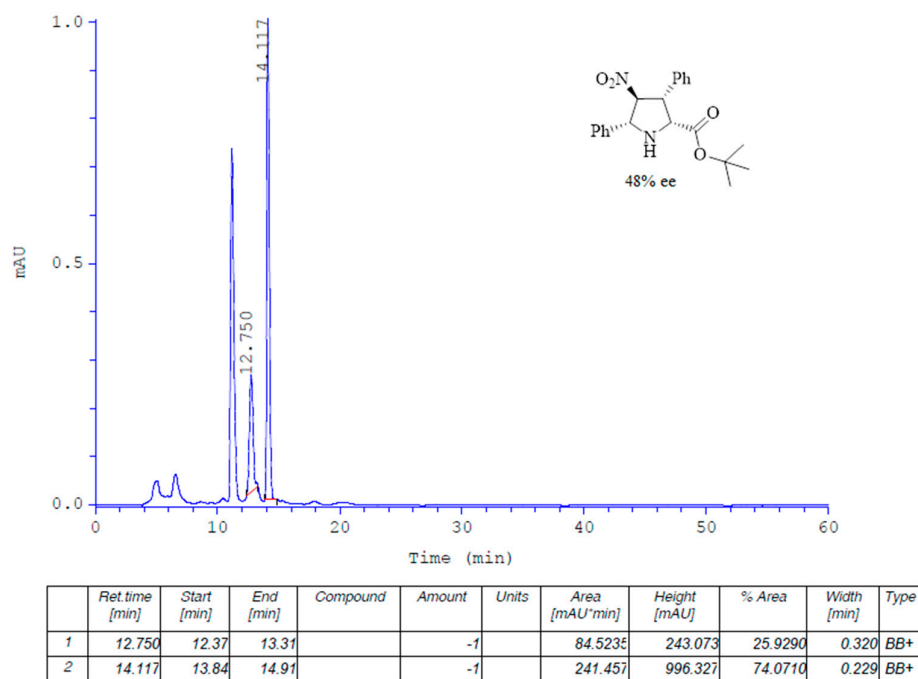
| | Ret.time [min] | Start [min] | End [min] | Compound | Amount | Units | Area [mAU*min] | Height [mAU] | % Area | Width [min] | Type |
|---|-------------------|----------------|--------------|----------|--------|-------|-------------------|-----------------|---------|----------------|------|
| 1 | 12.300 | 11.88 | 12.85 | | 0 | | 218.559 | 595.778 | 49.7338 | 0.338 | BP |
| 2 | 13.133 | 12.85 | 13.72 | | 0 | | 220.898 | 839.701 | 50.2662 | 0.246 | PB |

(2*R*,3*R*,4*S*,5*R*)-*Tert*-butyl 4-Nitro-3,5-diphenylpyrrolidine-2-carboxylate (*exo*) **17c**

ee (48%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : *i*PrOH = 90:10, flow = 1.0 mL/min, λ = 254 nm, retention times (min): 12.7 (minor), 14.1 (major).

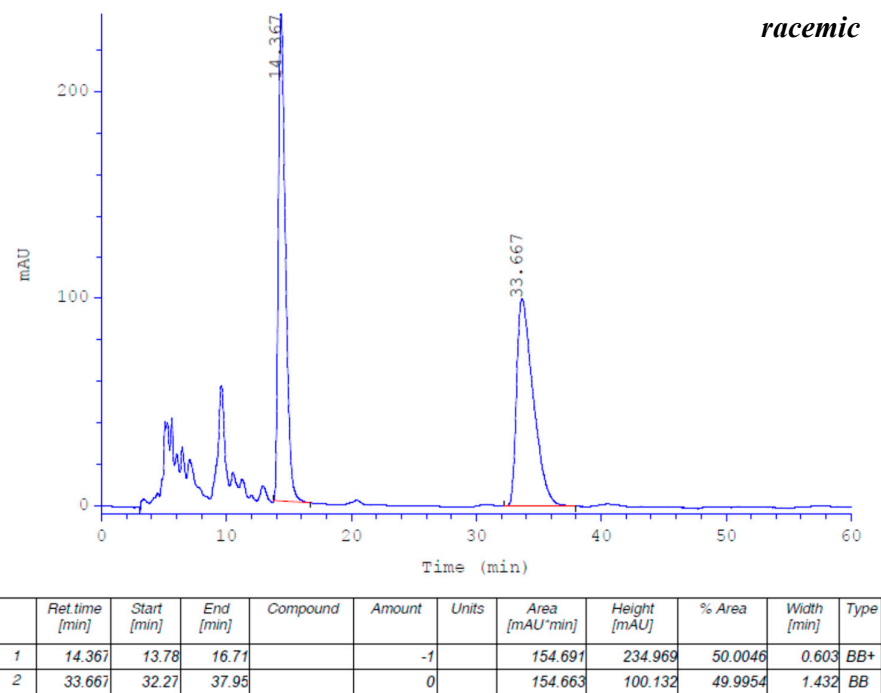


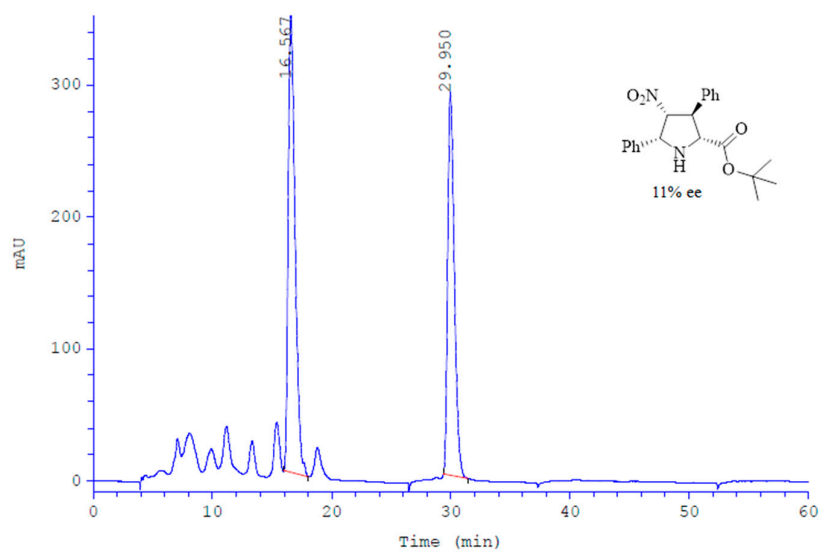
| | Ret.time [min] | Start [min] | End [min] | Compound | Amount | Units | Area [mAU*min] | Height [mAU] | % Area | Width [min] | Type |
|---|-------------------|----------------|--------------|----------|--------|-------|-------------------|-----------------|---------|----------------|------|
| 1 | 11.983 | 11.71 | 13.29 | | -1 | | 10.0194 | 31.1951 | 47.6487 | 0.210 | BB+ |
| 2 | 14.283 | 13.88 | 14.61 | | -1 | | 11.0082 | 38.3994 | 52.3513 | 0.272 | BB+ |



(2R,3S,4R,5R)-Tert-butyl 4-Nitro-3,5-diphenylpyrrolidine-2-carboxylate (*endo*) **18c**

ee (11%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : *i*PrOH = 90:10, flow = 1.0 mL/min, λ = 254 nm, retention times (min): 16.6 (major), 29.9 (minor).





| | Ret.time [min] | Start [min] | End [min] | Compound | Amount | Units | Area [mAU*min] | Height [mAU] | % Area | Width [min] | Type |
|---|-------------------|----------------|--------------|----------|--------|-------|-------------------|-----------------|---------|----------------|------|
| 1 | 16.567 | 15.98 | 18.04 | | -1 | | 232.172 | 345.385 | 55.3214 | 0.628 | BB+ |
| 2 | 29.950 | 29.38 | 31.45 | | -1 | | 187.507 | 290.122 | 44.6786 | 0.604 | BB+ |