Supplementary Information

Asymmetric 1,3-Dipolar Cycloaddition Reactions between Enals and Nitrones Catalysed by Half-Sandwich Rhodium or Iridium Diphosphane Complexes

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1. General Remarks

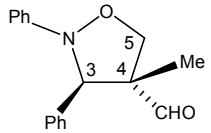
All solvents were dried over appropriate drying agents, distilled under argon and degassed prior to use. All preparations have been carried out under argon. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-300 spectrometer (300.13 MHz), Bruker AV-400 (400.16 MHz) or a Bruker AV-500 (500.13 MHz). Chemical shifts are expressed in ppm upfield from $SiMe_4$. Analytical HPLC was performed on an Alliance Waters (Waters 2996 PDA detector) instrument using a chiral column Daicel Chiralcel OD-H (0.46 cm × 25 cm) or Chiralpak AD-H (0.46 cm × 25 cm).

2. Starting Materials

The stereochemical purity of the enals was tested by NMR, after distillation under argon: methacrolein 95.5%, acrolein 99.9%, *trans*-crotonaldehyde 97.6% and *trans*-2-methyl-2-butenal 99.2%. The nitrones **Ia-e**,[1] **II**[2], **III**[3], **IV**[3], **V**[3], and the complexes $[(\eta^5\text{-}C_5Me_5)M(PP^*)(H_2O)][SbF_6]_2$ (**1-10**) were prepared according to literature procedures.[4]

3. Analytical Data for 1,3-Dipolar Cycloaddition Products

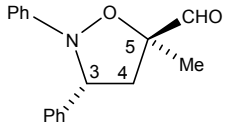
(3*R*,4*R*)-*endo*-4-methyl-2-*N*,3-diphenylisoxazolidine-4-carbaldehyde[5a,6a] (Table 1, Entries 1-10)



(3*R*,4*R*)-*endo*

^{1}H RMN (400.16 MHz, $CDCl_3$, 25 ºC): δ = 9.20 (s, 1H, CHO), 7.5-6.8 (m, 10H, H_{Ar}), 4.90 (s, 1H, H_3), 3,97 (d, J = 8.9 Hz, 1H, H_5), 3.56 (d, J = 8.9 Hz, 1H, H_5), 0.92 ppm (s, 3H, Me). ^{13}C RMN (100.62 MHz $CDCl_3$, 25 ºC): δ = 200.37 (CHO), 150-114 (12C, C^{Ar}), 73.19 (C^5), 72.48 (C^3), 63.11 (C^4), 15.49 ppm (Me). Enantiomeric excess was determined by ^{1}H NMR after the *in situ* formation of diastereomeric imines with (*R*)-(+)-α-methylbenzylamine (99%, Fluka). ^{1}H NMR (400.16 MHz, C_6D_6, RT): major isomer δ = 5.07 (s, O-N-C^3H), minor isomer δ = 5.03 ppm (s, O-N-C^3H).

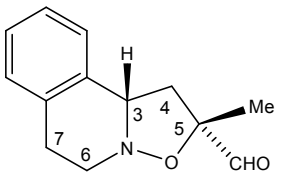
(3,5)-*endo*-4-methyl-2-*N*,3-diphenylisoxazolidine-4-carbaldehyde[5a,6a] (Table 1, Entries 1-10)



(3*R**,5*R**)-*endo*

^{1}H RMN (400.16 MHz, $CDCl_3$, 25 ºC): δ = 9.58 (d, J = 1.0 Hz, 1H, CHO), 7.5-6.8 (m, 10H, H_{Ar}), 4.61 (pt, J = 7.6 Hz, 1H, H_3), 3.04 (dd, J = 12.7, 7.6 Hz, 1H, H_4), 1.94 (dd, J = 12.7, 7.6 Hz, 1H, H_4), 1.16 ppm (s, 3H, Me). ^{13}C RMN (100.62 MHz $CDCl_3$, 25 ºC): δ = 201.37 (CHO), 150-114 (12C, C^{Ar}), 87.20 (C^5), 68.63 (C^3), 44.25 (C^4), 18.82 ppm (Me). Enantiomeric excess was determined by ^{1}H NMR after the *in situ* formation of diastereomeric imines with (*R*)-(+)-α-methylbenzylamine (99%, Fluka). ^{1}H NMR (400.16 MHz, C_6D_6, RT): major isomer δ = 4.84 (pt, O-N-C^3H), minor isomer δ = 5.16 ppm (pt, O-N-C^3H).

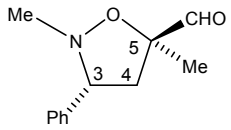
(3*S*,5*R*)-*endo*-2-methyl-1,5,6,10*b*-tetrahydro-*2H*-isoxazolo[3,2*a*]isoquinoline-2-carbaldehyde[5a] (Table 1, Entries 11-20)



(3*S*,5*R*)-*endo*

The oily residue was purified by column chromatography over silica gel with hexane/AcOEt (7/3, v/v) to provide the title compound as an oil. ^{1}H NMR (400.16 MHz, CD_2Cl_2, 25 ºC): δ = 9.51 (s, 1H, CHO), 7.1-6.9 (m, 4H, H_{Ar}), 4.62 (m, 1H, H_3), 3.21-2.84 (m, 2H, H_6), 2.94-2.74 (m, 2H, H_7), 2.48 (pt, J = 11.3 Hz, 1H, H_4), 2.35 (dd, J = 11.3, 7.0 Hz, 1H, H_4), 1.32 ppm (s, 3H, Me). ^{13}C NMR (100.62 MHz C_6D_6, 25 ºC): δ = 200.78 (CHO), 134.8-126.73 (6C, C^{Ar}), 87.85 (C^5), 63.77 (C^3), 50.02 (C^6), 43.82 (C^4), 29.0.2 (C^7), 21.30 ppm (Me). Enantiomeric excess of the adduct was checked by ^{1}H NMR with the use of the chiral shift reagent $Eu(hfc)_3$.^{1}H NMR (400.16 MHz, C_6D_6, 25 ºC): major isomer δ = 14.87 (s, CHO), minor isomer δ = 14.63 ppm (s, CHO).

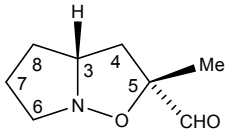
(3,5)-*endo*-5-methyl-2-*N*-methyl-3-phenylisoxazolidin-5-carbaldehyde[5d,6a] (Table 2, Entries 1-4)



(3*R**,5*R**)-*endo*

The oily residue was purified by column chromatography over silica gel with hexane/AcOEt (7/3, v/v) to provide the title compound as an oil. ^{1}H NMR (400.16 MHz, CD_2Cl_2, 25 ºC): δ = 9.55 (s, 1H, CHO), 7.3-7.1 (m, 5H, H_{Ar}), 3.58 (m, 1H, H_3), 2.84 (dd, J = 12.6, 7.1 Hz, 1H, H_4), 2.48 (s, 3H, NMe), 2.14 (dd, J = 12.6, 9.1 Hz, 1H, H_4), 1.34 ppm (s, 3H, Me). ^{13}C NMR (100.62 MHz CD_2Cl_2, 25 ºC): δ = 201.14 (CHO), 128 (6C, C^{Ar}), 85.11 (C^5), 73.58 (C^3), 48.00 (C^4), 43.73 (NMe), 21.19 ppm (Me). Enantiomeric excess was determined by ^{1}H NMR after the *in situ* formation of diastereomeric imines with (*R*)-(+)-α-methylbenzylamine (99%, Fluka). ^{1}H NMR (400.16 MHz, C_6D_6, RT): major isomer δ = 3.07 (t, O-N-C^3H), minor isomer δ = 3.23 ppm (t, O-N-C^3H).

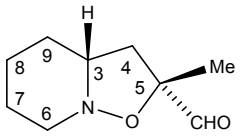
(3*R*,5*R*)-*endo*-hexahydropyrrolo[1,2*b*]isoxazolo-2-carbaldehyde[5a] (Table 2, Entries 5-8)



(3*R*,5*R*)-*endo*

The oily residue was purified by column chromatography over silica gel with hexane/AcOEt (7/3, v/v) to provide the title compound as an oil. ^{1}H NMR (400.16 MHz, CD_2Cl_2, 25 ºC): δ = 9.55 (s, 1H, CHO), 3.77 (m, 1H, H_3), 3.15-3.05 (m, 2H, H_6), 2.28 (d, J = 6.3 Hz, 2H, H_4), 1.97 (m, 2H, H_7, H_8), 1.72 (m, 1H, H_7), 1.59 (m, 1H, H_8) 1.34 ppm (s, 3H, Me). ^{13}C NMR (100.62 MHz CD_2Cl_2, 25 ºC): δ = 200.55 (CHO), 86.69 (C^5), 65.98 (C^3), 56.64 (C^6), 44.17 (C^4), 29.92 (C^7), 23.26 (C^8), 20.65 ppm (Me). Enantiomeric excess of adduct was checked by ^{1}H NMR with the use of the chiral shift reagent Eu(hfc)$_3$ (99%, Aldrich). ^{1}H NMR (400.16 MHz, C_6D_6, 25 ºC): major isomer δ = 11.30 (s, CHO), minor isomer δ = 12.32 ppm (s, CHO).

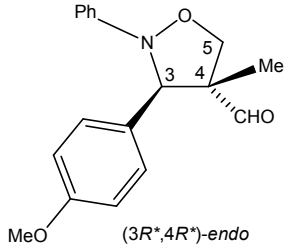
(3*R*,5*R*)-*endo*-hexahydroisoxazolo[2,3*a*]pyridine-2-carbaldehyde[5a] (Table 2, Entries 9-12)



(3*S*,5*R*)-*endo*

The oily residue was purified by column chromatography over silica gel with Et_2O/*n*-Pentane/MeOH (30/65/5, v/v/v) to provide the title compound as an oil. ^{1}H NMR (400.16 MHz, C_6D_6, 25 ºC): δ = 9.73 (s, 1H, CHO), 3.37 (m, 1H, H_6), 2.32 (m, 1H, H_6), 2.02 (pt, J = 11.4 Hz, 1H, H_4), 1.91 (m, 1H, H_3), 1.58 (dd, J = 11.4, 7.9 Hz, 1H, H_4), 1.44-1.04 (m, 2H, H_9), 1.34 (m, 2H, H_7), 1.30-0.85 (m, 2H, H_8), 1.11 ppm (s, 3H, Me). ^{13}C NMR (100.62 MHz C_6D_6, 25 ºC): δ = 204.18 (CHO), 83.12 (C^5), 66.66 (C^3), 55.17 (C^6), 42.94 (C^4), 29.37 (C^9), 24.75 (C^7), 23.97 (C^8), 19.57 ppm (Me). Enantiomeric excess was determined by ^{1}H NMR after the *in situ* formation of diastereomeric salts with (*S*)-(+)-mandelic acid (99%, Aldrich). ^{1}H NMR (400.16 MHz, $CDCl_3$, 25 ºC): major isomer δ = 9.60 (s, CHO), minor isomer δ = 9.56 ppm (s, CHO).

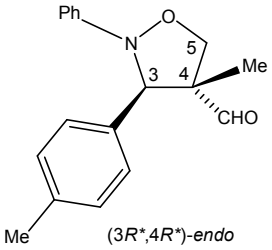
***Endo*-4-methyl-2-*N*-phenyl-3-(4-methoxyphenyl)-isoxazolidine-4-carbaldehyde[5b,c] (Table 2, Entry 13)**



(3*R**,4*R**)-*endo*

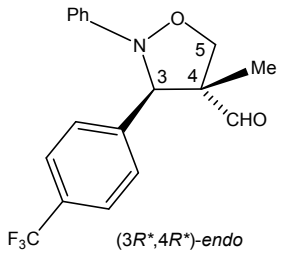
^{1}H NMR (400.16 MHz, $CDCl_3$, 25 ºC): δ = 9.66 (s, 1H, CHO), 7.4-6.8 (9H, H_{Ar}), 4.88 (s, 1H, H_3), 4.43 (d, J = 8.9 Hz, 1H, H_5), 3.98 (d, 1H, H_5), 3.82 (s, 3H, OMe), 0.91 ppm (s, 3H, Me). ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 ºC): δ = 200.63 (s, CHO), 159-114 (12C, C^{Ar}), 73.11 (s, C^5), 72.05 (s, C^3), 63.02 (s, C^4), 55.26 (s, OMe), 15.45 ppm (s, Me). Enantiomeric excess was determined by ^{1}H NMR after the *in situ* formation of diastereomeric imines with (*R*)-(+)-α-methylbenzylamine (99%, Fluka). ^{1}H NMR (400.16 MHz, C_6D_6, RT): major isomer δ = 4.93 (s, O-N-C^3H), minor isomer δ = 4.88 ppm (s, O-N-C^3H).

***Endo*-4-methyl-2-*N*-phenyl-3-(4-methylphenyl)-isoxazolidine-4-carbaldehyde[5b,c] (Table 2, Entry 14)**



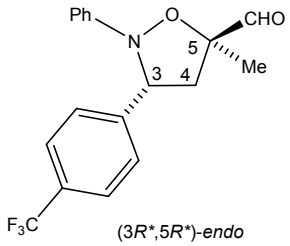
^{1}H NMR (400.16 MHz, $CDCl_3$, 25 ºC): δ = 9.69 (s, 1H, CHO), 7.4-6.9 (9H, H_{Ar}), 4.95 (s, 1H, H_3), 4.45 (d, J = 8.9 Hz, 1H, H_5), 4.01 (d, 1H, H_5), 2.43 (s, 3H, *Me*-Ar), 0.95 ppm (s, 3H, Me). ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 ºC): δ = 200.56 (s, CHO), 150-115 (12C, C^{Ar}), 73.15 (s, C^5), 72.35 (s, C^3), 63.05 (s, C^4), 21.25 (s, *Me*-Ar), 15.47 ppm (s, Me). Enantiomeric excess was determined by ^{1}H NMR after the *in situ* formation of diastereomeric imines with (*R*)-(+)-*α*-methylbenzylamine (99%, Fluka). ^{1}H NMR (400.16 MHz, C_6D_6, RT): major isomer δ = 5.00 (s, O-N-C^3H), minor isomer δ = 4.98 ppm (s, O-N-C^3H).

***Endo*-4-methyl-2-*N*-phenyl-3-(4-trifluoromethyl-phenyl)-isoxazolidine-4-carbaldehyde[5a,c] (Table 2, Entry 16)**



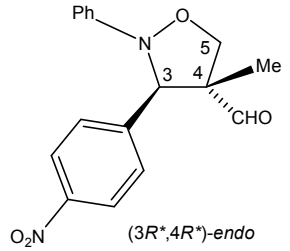
^{1}H NMR (400.16 MHz, $CDCl_3$, 25 ºC): δ = 9.70 (s, 1H, CHO), 7.7-6.9 (9H, H_{Ar}), 5.08 (s, 1H, H_3), 4.45 (d, J = 8.9 Hz, 1H, H_5), 4.02 (d, 1H, H_5), 0.92 ppm (s, 3H, Me). ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 ºC): δ = 199.82 (s, CHO), 150-114 (12C, C^{Ar}), 124.18 (q, $J_{F\text{-}C}$ = 272.0 Hz, CF_3), 73.18 (s, C^5), 71.78 (s, C^3), 63.24 (s, C^4), 15.53 ppm (s, Me). ^{19}F NMR (282.2 MHz, $CDCl_3$, 25 ºC): δ = -62.28 ppm (s, CF_3). Enantiomeric excess was determined by ^{1}H NMR after the *in situ* formation of diastereomeric imines with (*R*)-(+)-*α*-methylbenzylamine (99%, Fluka). ^{1}H NMR (400.16 MHz, C_6D_6, RT): major isomer δ = 5.09 (s, O-N-C^3H), minor isomer δ = 4.98 ppm (s, O-N-C^3H).

***Endo*-5-methyl-2-*N*-phenyl-3-(4-trifluoromethyl-phenyl)-isoxazolidine-5-carbaldehyde[5a,c] (Table 2, Entry 16)**



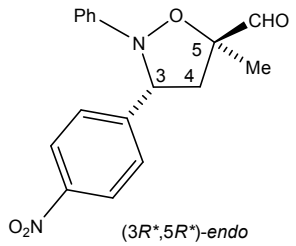
^{1}H NMR (400.16 MHz, $CDCl_3$, 25 ºC): δ = 9.65 (s, 1H, CHO), 7.7-6.9 (9H, H_{Ar}), 4.94 (pt, J = 7.5 Hz, 1H, H_3), 3.37 (dd, J = 8.2, 12.6 Hz, 1H, H_4), 2.27 (dd, J = 6.8 Hz, 1H, H_4), 1.52 ppm (s, 3H, Me). ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 ºC): δ = 200.75 (s, CHO), 150-114 (12C, C^{Ar}), 124.22 (q, $J_{F\text{-}C}$ = 272.0 Hz, CF_3), 87.40 (s, C^5), 67.93 (s, C^3), 45.59 (s, C^4), 18.56 ppm (s, Me). ^{19}F NMR (282 MHz, $CDCl_3$, 25 ºC): δ = -62.32 ppm (s, CF_3). Enantiomeric excess was determined by ^{1}H NMR after the *in situ* formation of diastereomeric imines with (*R*)-(+)-α-methylbenzylamine (99%, Fluka). ^{1}H NMR (400.16 MHz, C_6D_6, RT): major isomer δ = 4.71 (pt, O-N-C^3H), minor isomer δ = 5.03 ppm (pt, O-N-C^3H).

***Endo*-4-methyl-2-*N*-phenyl-3-(4-nitro-phenyl)-isoxazolidine-4-carbaldehyde[5a] (Table 2, Entry 17)**



^{1}H NMR (400.16 MHz, $CDCl_3$, 25 ºC): δ = 9.69 (s, 1H, CHO), 8.4-6.8 (9H, H_{Ar}), 5.07 (s, 1H, H_3), 4.46 (d, J = 8.9 Hz, 1H, H_5), 4.03 (d, 1H, H_5), 0.92 ppm (s, 3H, Me). ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 ºC): δ = 199.39 (s, CHO), 149-114 (12C, C^{Ar}), 73.34 (s, C^5), 71.42 (s, C^3), 63.39 (s, C^4), 15.82 ppm (s, Me). Enantiomeric excess was determined by ^{1}H NMR after the *in situ* formation of diastereomeric imines with (*R*)-(+)-α-methylbenzylamine (99%, Fluka). ^{1}H NMR (400.16 MHz, C_6D_6, RT): major isomer δ = 5.12 (s, O-N-C^3H), minor isomer δ = 4.97 ppm (s, O-N-C^3H).

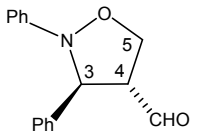
***Endo*-5-methyl-2-*N*-phenyl-3-(4-nitro-phenyl)-isoxazolidine-5-carbaldehyde[5a] (Table 2, Entry 17)**



(3*R**,5*R**)-*endo*

^{1}H NMR (400.16 MHz, $CDCl_3$, 25 ºC): δ = 9.66 (d, J = 0.9 Hz, 1H, CHO), 8.4-6.8 (9H, H_{Ar}), 4.94 (pt, J = 6.7 Hz, 1H, H_3), 3.39 (dd, J = 8.3, 12.6 Hz, 1H, H_4), 2.24 (dd, J = 6.6 Hz, 1H, H_4), 1.51 ppm (s, 3H, Me). ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 ºC): δ = 200.76 (s, CHO), 149-114 (12C, C^{Ar}), 87.32 (s, C^5), 67.47 (s, C^3), 45.45 (s, C^4), 18.61 ppm (s, Me). Enantiomeric excess was determined by ^{1}H NMR after the *in situ* formation of diastereomeric imines with (*R*)-(+)-α-methylbenzylamine (99%, Fluka). ^{1}H NMR (400.16 MHz, C_6D_6, RT): major isomer δ = 4.68 (pt, O-N-C^3H), minor isomer δ = 5.01 ppm (pt, O-N-C^3H).

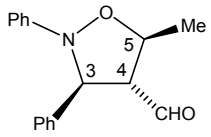
(3,4)-*endo*-2,3-diphenylisoxazolidine-4-carbaldehyde[6b] (Table 3, Entries 1-4)



(3*R**,4*R**)-*endo*

The oily residue was purified by column chromatography over silica gel with hexane/AcOEt (7/3, v/v) to provide the title compound as an oil. ^{1}H NMR (400.16 MHz, CD_2Cl_2, 25 ºC): δ = 9.70 (d, J = 1.5 Hz, 1H, CHO), 7.5-6.8 (m, 10H, H_{Ar}), 4.99 (d, J = 4.6 Hz, 1H, H_3), 4.42 (m, 2H, H_5), 3.53 ppm (m, 1H, H_4). ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 ºC): δ = 197.98 (CHO), 150-115 (12C, C^{Ar}), 70.04 (C^3), 66.33 (C^4), 65.59 ppm (C^5). Enantiomeric excess was determined by HPLC analysis of the primary alcohol obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel OD-H column (*n*-hexane/2-propanol: 95/5, 0.5 mL/min); major isomer: t_r = 18.2 min. and minor isomer: t_r = 28.4 min.

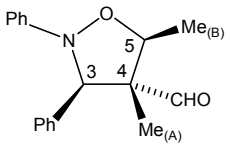
(3*S*,4*R*,5*S*)-*endo*-5-methyl-2,3-diphenylisoxazolidine-4-carbaldehyde[6b] (Table 3, Entries 5-8)



(3*S*,4*R*,5*S*)-*endo*

The oily residue was purified by column chromatography over silica gel with hexane/AcOEt (7/3, v/v) to provide the title compound as an oil. ^{1}H NMR (400.16 MHz, CD_2Cl_2, 25 ºC): δ = 9.63 (d, J = 2.5 Hz, 1H, CHO), 7.4-6.8 (m, 10H, H_{Ar}), 5.01 (d, J = 6.3 Hz, 1H, H_3), 4.43 (dq, J = 8.6, 6.1 Hz, 1H, H_5), 3.15 (m, 1H, H_4), 1.45 ppm (s, 3H, Me). ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 ºC): δ = 197.67 (CHO), 151.2-114.1 (12C, C^{Ar}), 75.37 (C^5), 72.90 (C^4), 71.41 (C^3), 17.84 ppm (Me). Enantiomeric excess was determined by HPLC analysis of the primary alcohol obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel OD-H column (*n*-hexane/2-propanol: 95/5, 1 mL/min); major isomer: t_r = 13.7 min. and minor isomer: t_r = 20.9 min.

(3,4)-*endo*-5-methyl-2,3-diphenylisoxazolidine-4-methyl-4-carbaldehyde[6b] (Table 3, Entries 9, 10)



(3*S**,4*R**,5*S**)-*endo*

The oily residue was purified by column chromatography over silica gel with hexane/AcOEt (7/3, v/v) to provide the title compound as an oil. ^{1}H NMR (400.16 MHz, CD_2Cl_2, 25 ºC): δ = 9.57 (s, 1H, CHO), 7.4-6.8 (m, 10H, H_{Ar}), 5.01 (s, 1H, H_3), 4.42 (q, J = 6.3 Hz, 1H, H_5), 1.23 (s, 3H, $Me_{(B)}$), 0.80 ppm (s, 3H, $Me_{(A)}$). ^{13}C NMR (100.62 MHz, $CDCl_3$, 25 ºC): δ = 200.45 (CHO), 152-113 (12C, C^{Ar}), 77.75 (C^3), 75.53 (C^5), 65.76 (C^4), 12.79 ($Me_{(A)}$), 11.06 ppm ($Me_{(B)}$). Enantiomeric excess was determined by HPLC analysis of the primary alcohol obtained by $NaBH_4$ reduction of the aldehyde, using a Chiracel OD-H column (*n*-hexane/2-propanol: 95/5, 0.75 mL/min); major isomer: t_r = 13.8 min. and minor isomer: t_r = 29.5 min.

4. References

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5. (*a*) F. Viton, G. Bernardinelli and E. P. Kündig, *J. Am. Chem. Soc*. 2002, **124**, 4968-4969; (*b*) A. Bädoiu, G. Bernardinelli, J. Mareda, E. P. Kündig and F. Viton, *Chem. Asian J.* 2008, **3**, 1298; (*c*) X. Wang, C. Weigl and M. P. Doyle, *J. Am. Chem. Soc.* 2011, **133**, 9572; (*d*) A. Badoiu, G. Bernardinelli and E. P. Kündig, *Synthesis* 2010, 2207-2212.

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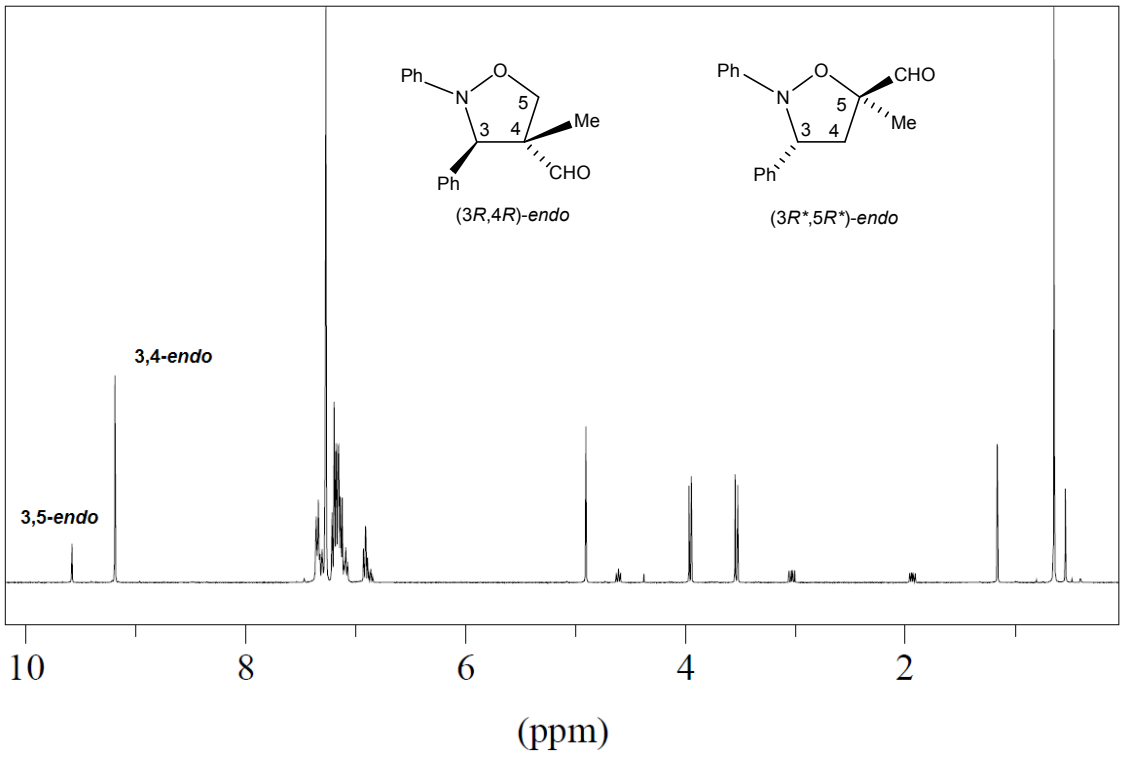
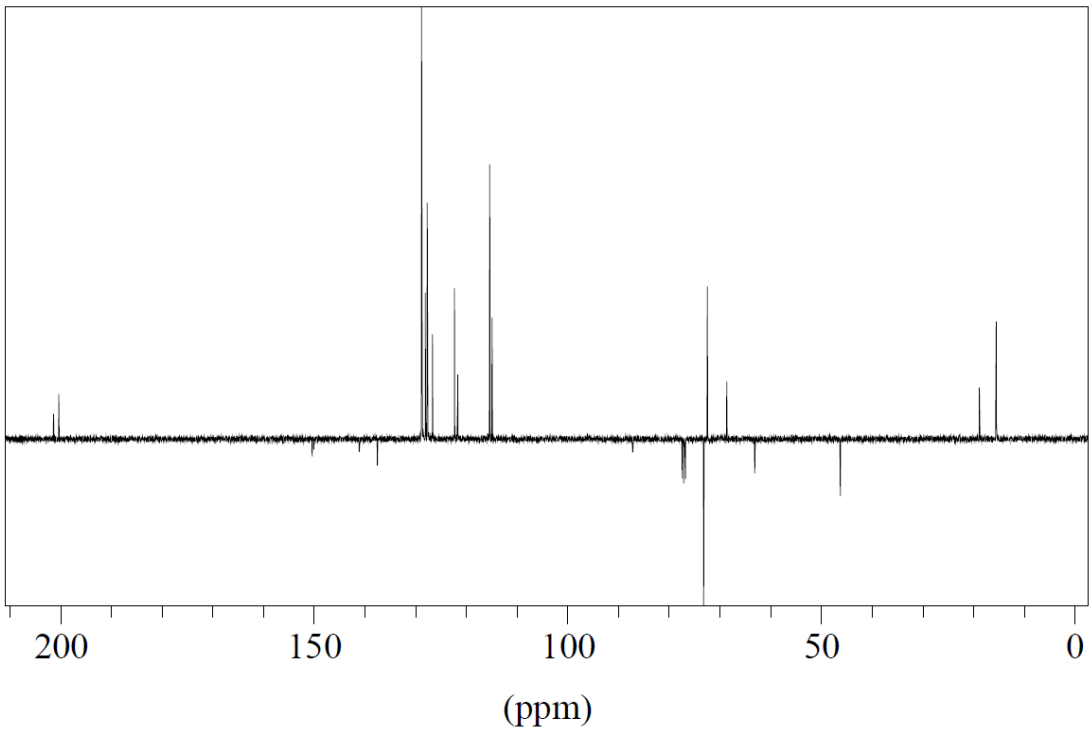
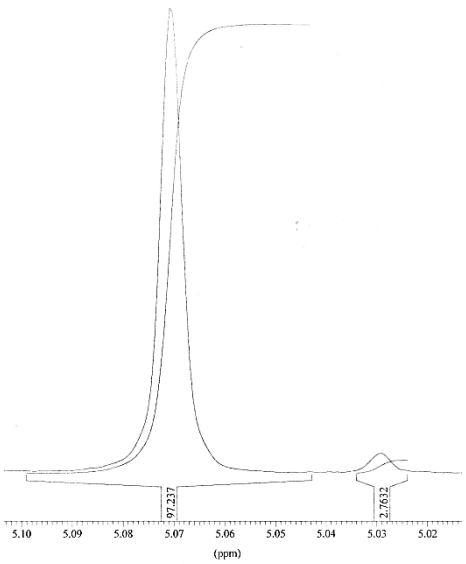
5. ^{1}H and ^{13}C NMR Spectra and Chromatograms of the Adducts

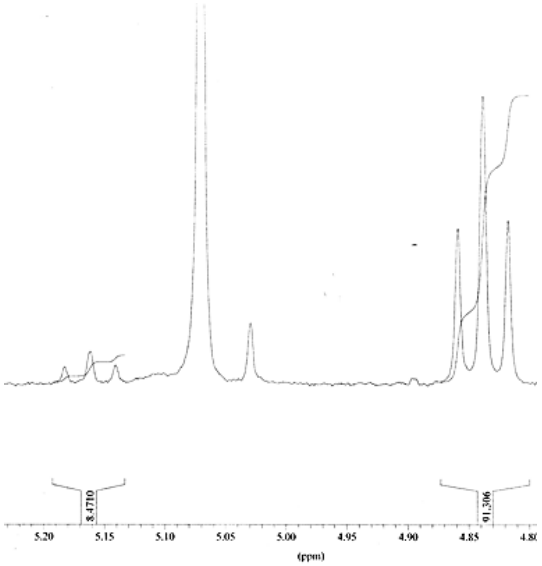
Mixture of (3,4)-*endo*-4-methyl-2-*N*,3-diphenylisoxazolidine-4-carbaldehyde/(3,5)-*endo*-4-methyl-2-*N*,3-diphenylisoxazolidine-5-carbaldehyde: 1/5 molar ratio (Table 1, Entries 1-10)



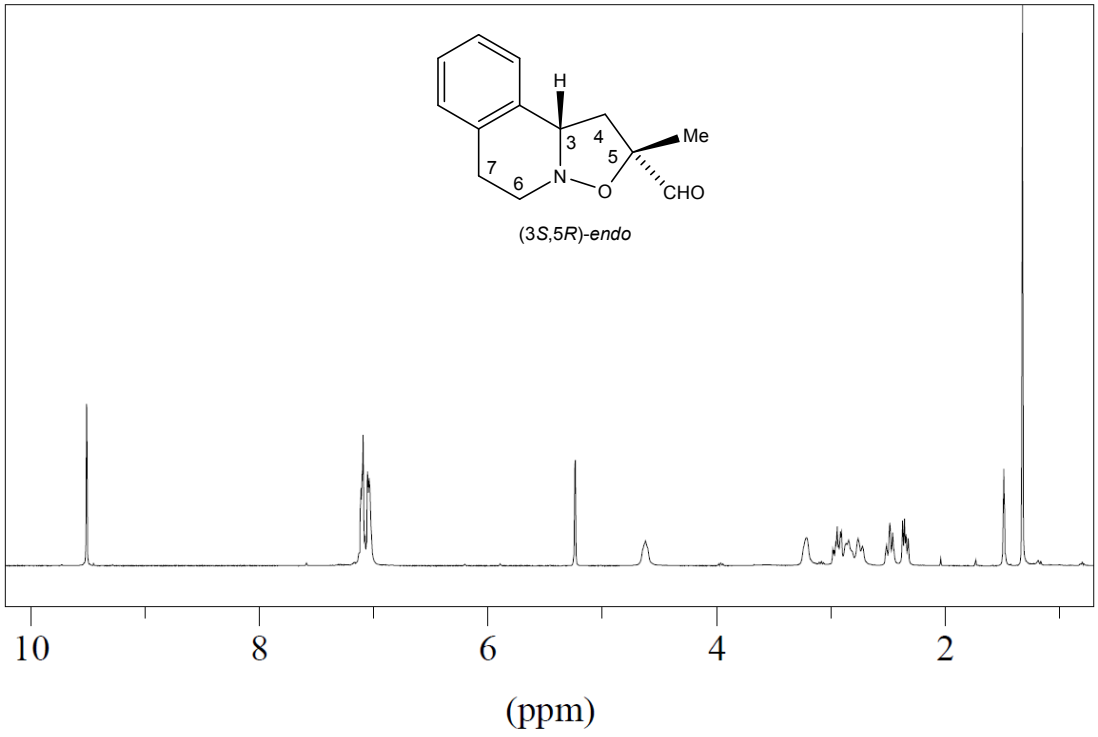


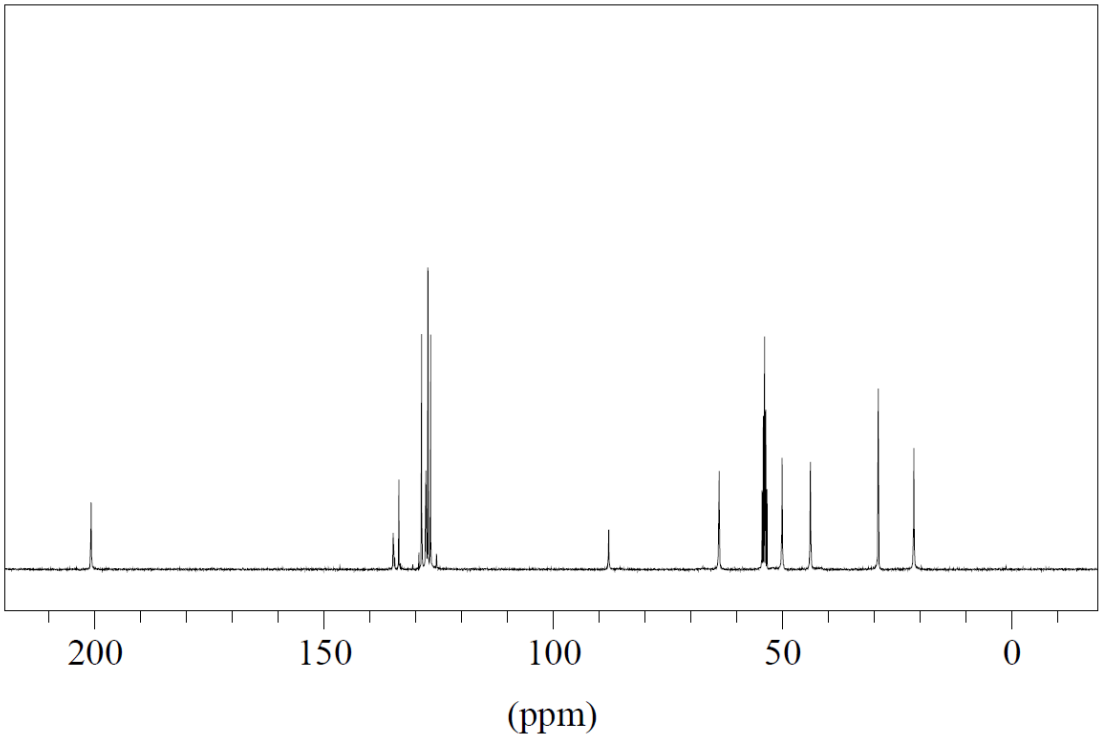
Ee (3,4)-*endo* **Ee (3,5)-*endo***



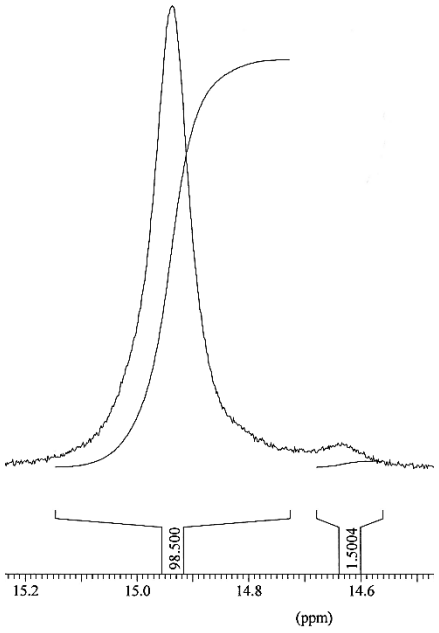


(3,5)-*endo*-2-methyl-1,5,6,10*b*-tetrahydro-*2H*-isoxazolo[3,2*a*]isoquinoline-2-carbaldehyde (Table 1, Entries 11-20)

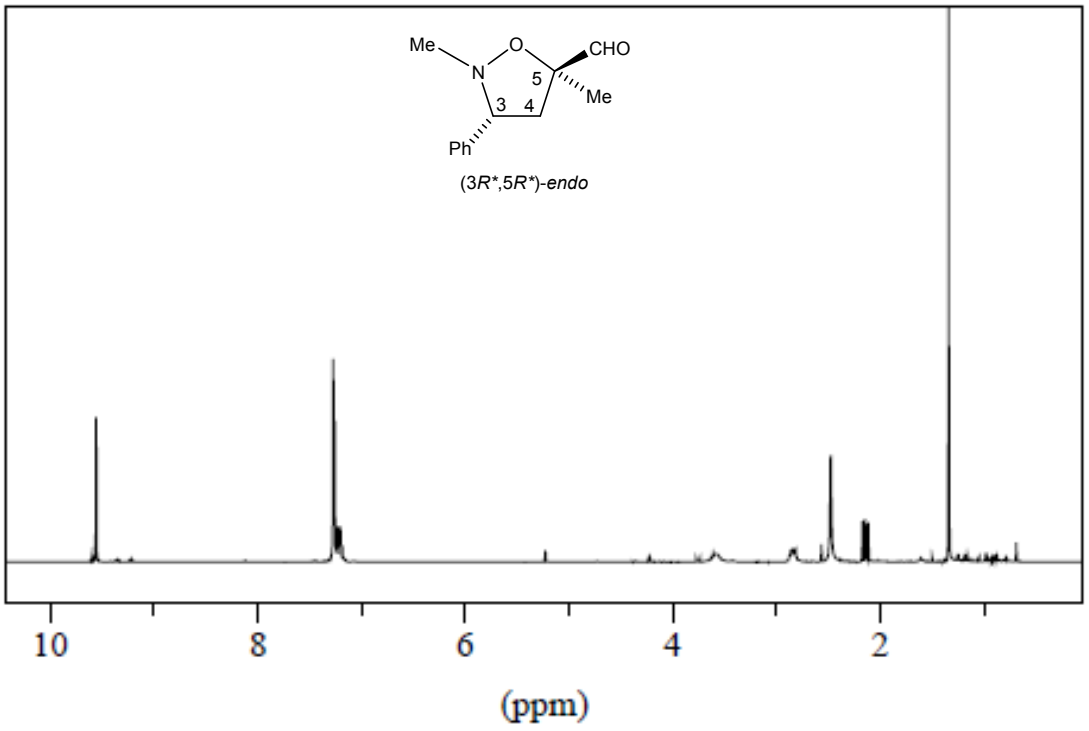


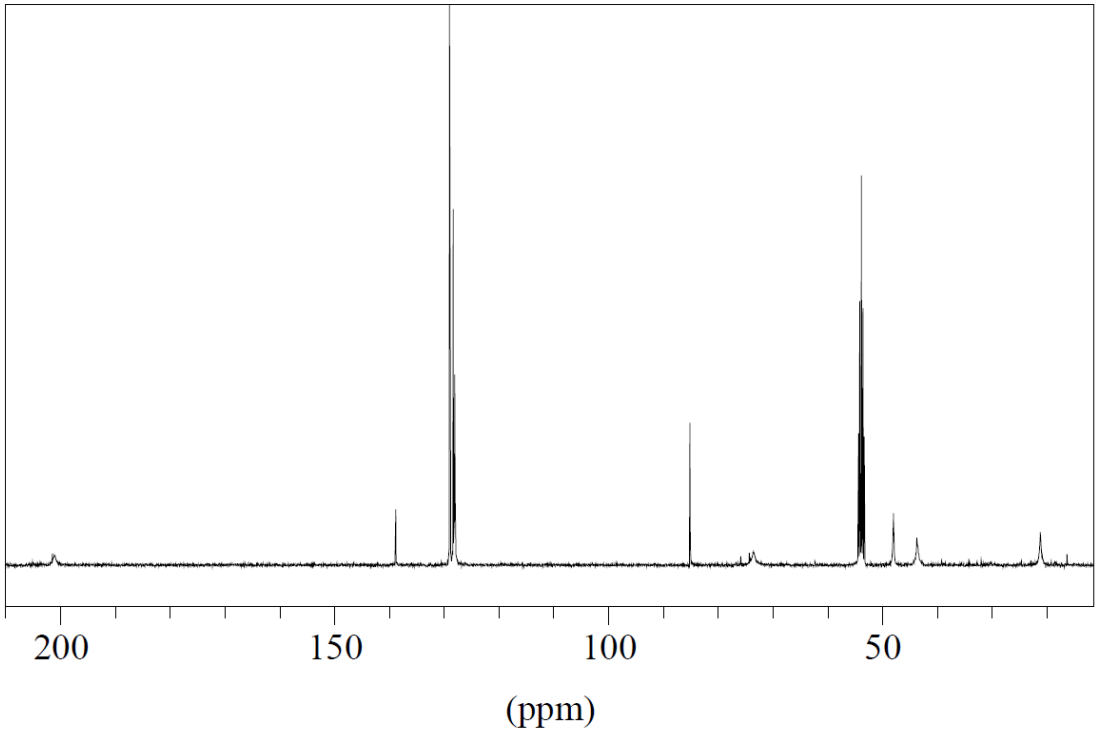


Ee (3,5)-*endo*

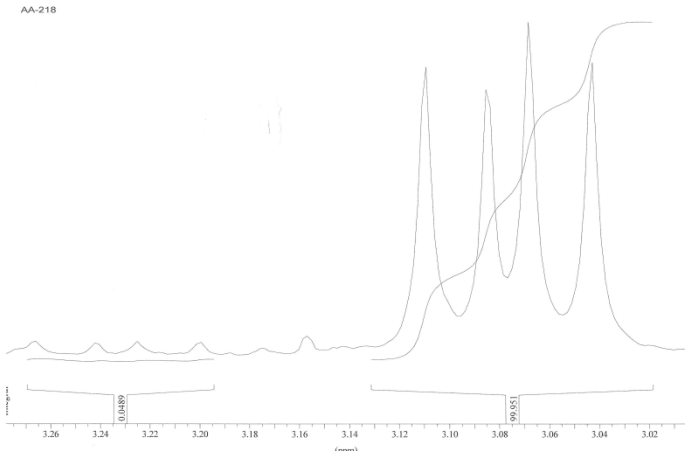


(3,5)-*endo*-5-methyl-2-*N*-methyl-3-phenylisoxazolidine-5-carbaldehyde (Table 2, Entries 1-4)

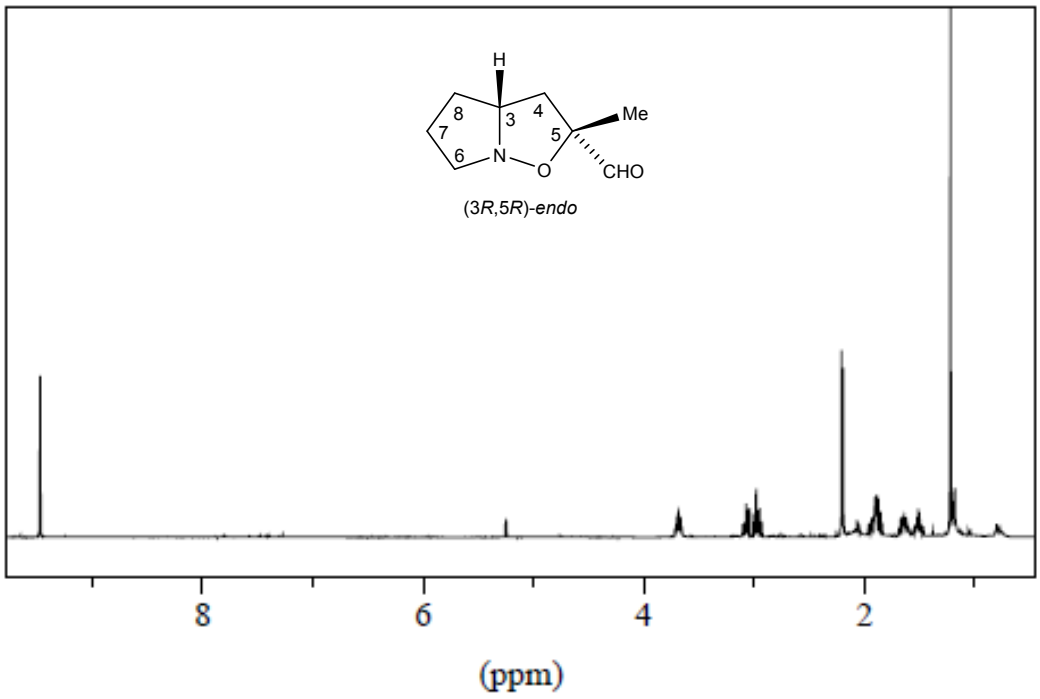


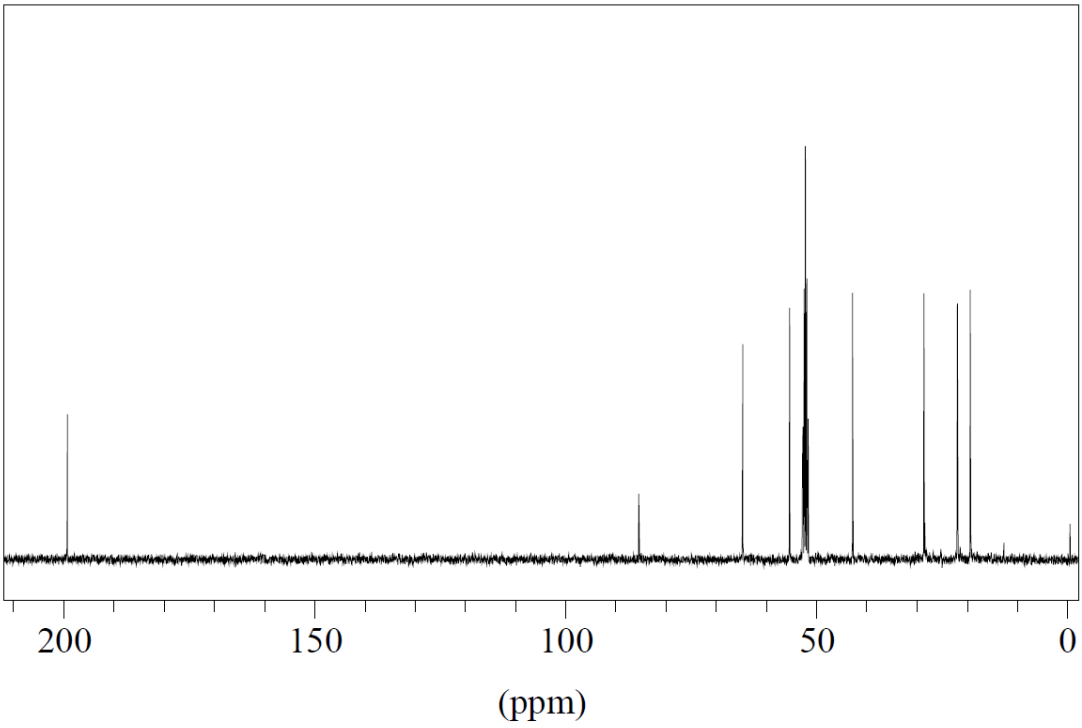


Ee (3,5)-*endo*

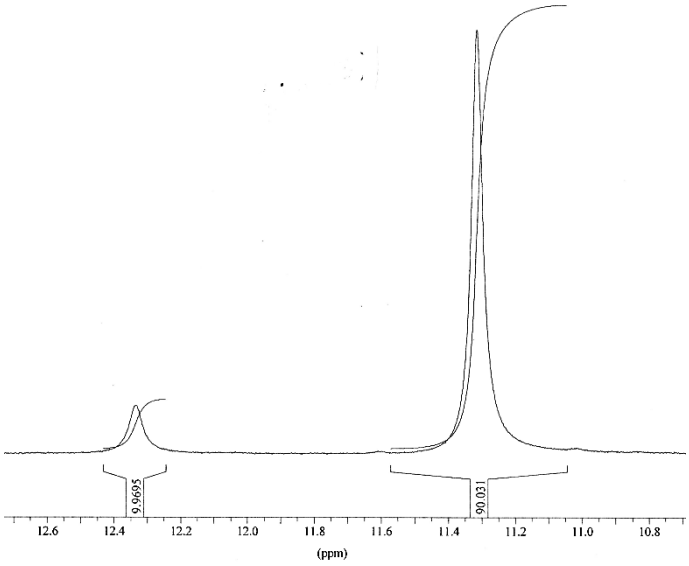


(3*R*,5*R*)-*endo*-hexahydropyrrolo[1,2*b*]isoxazolo-2-carbaldehyde (Table 2, Entries 5-8)

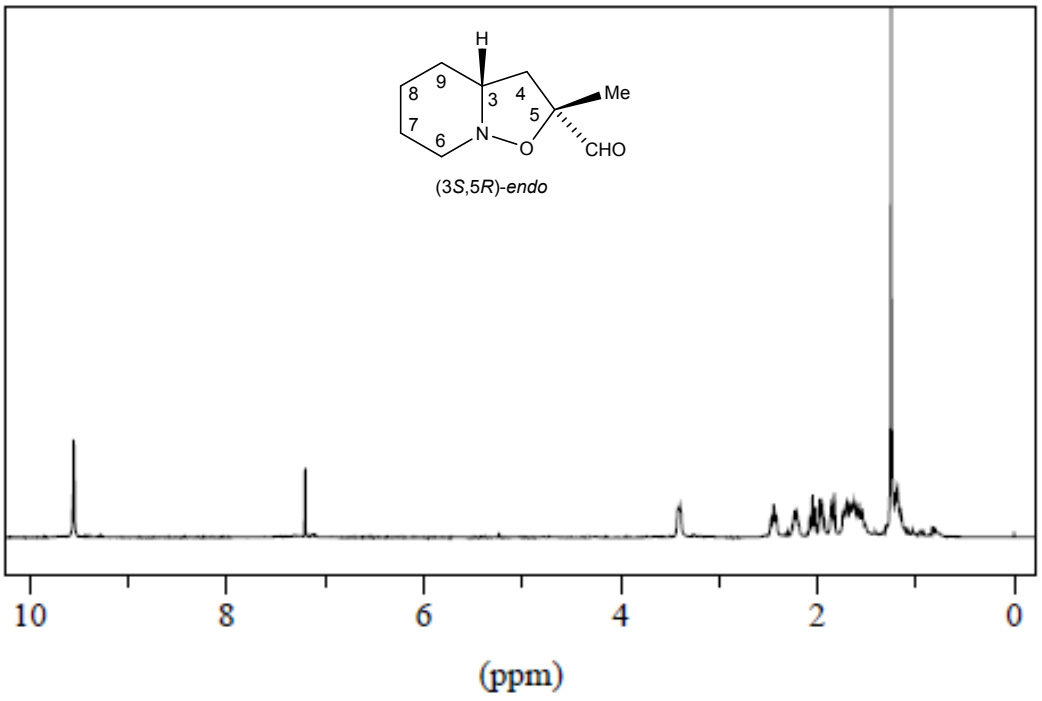


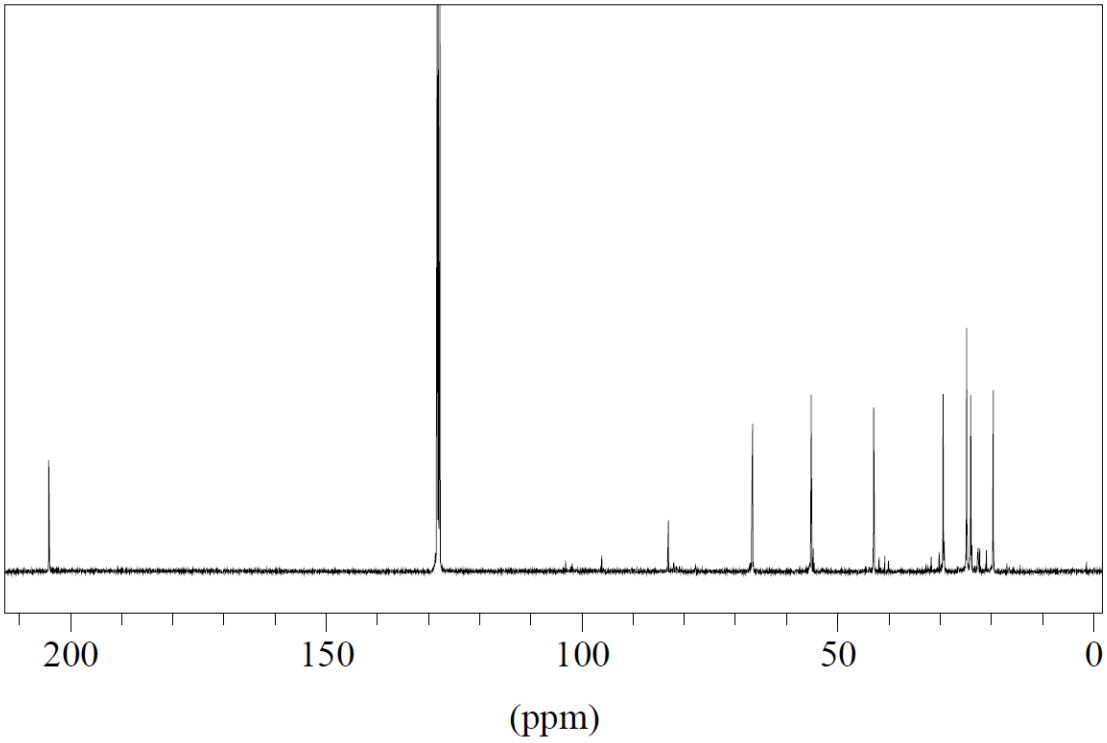

200
150
100
50
0
(ppm)

Ee (3,5)-*endo*

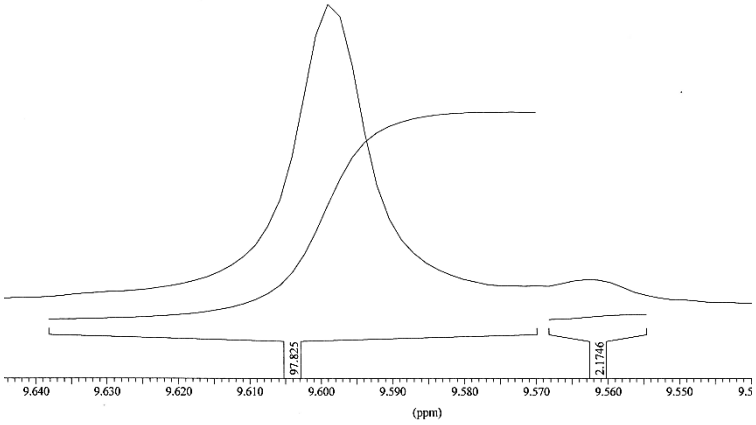

9.9695
90.031
12.6
12.4
12.2
12.0
11.8
11.6
11.4
11.2
11.0
10.8
(ppm)

(3*R*,5*R*)-*endo*-hexahydroisoxazolo[2,3*a*]pyridine-2-carbaldehyde (Table 2, Entries 9-12)

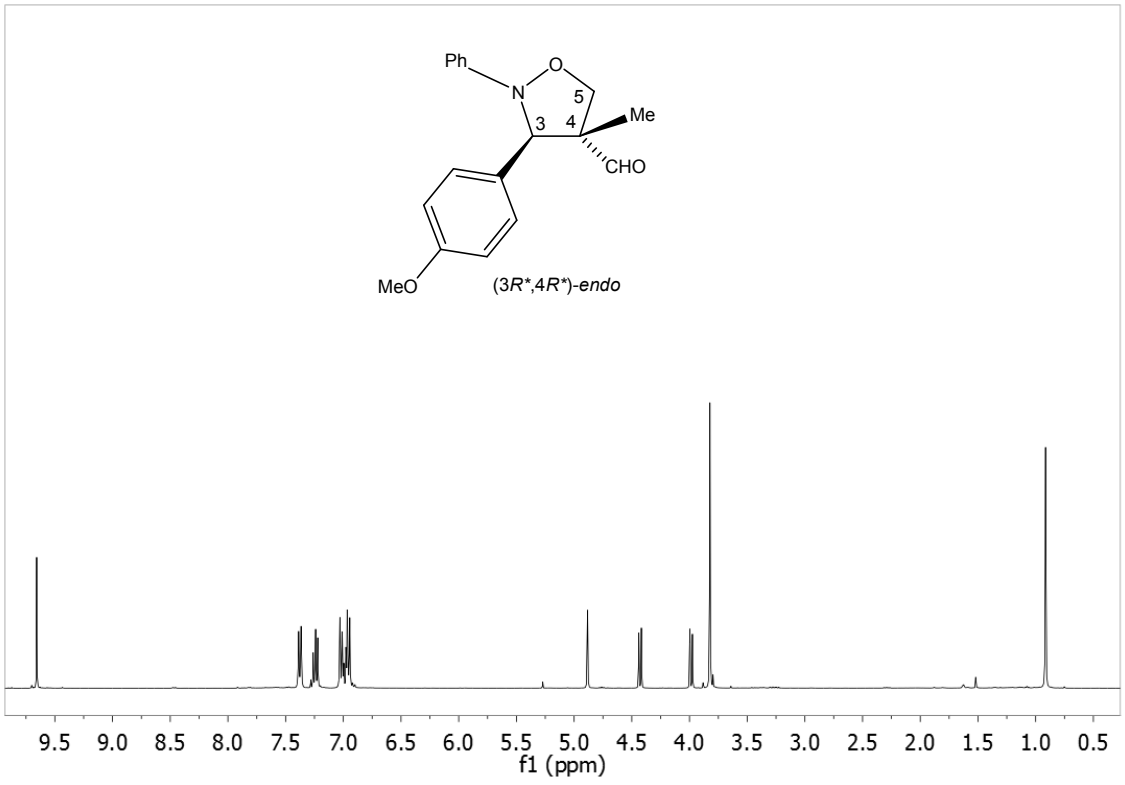


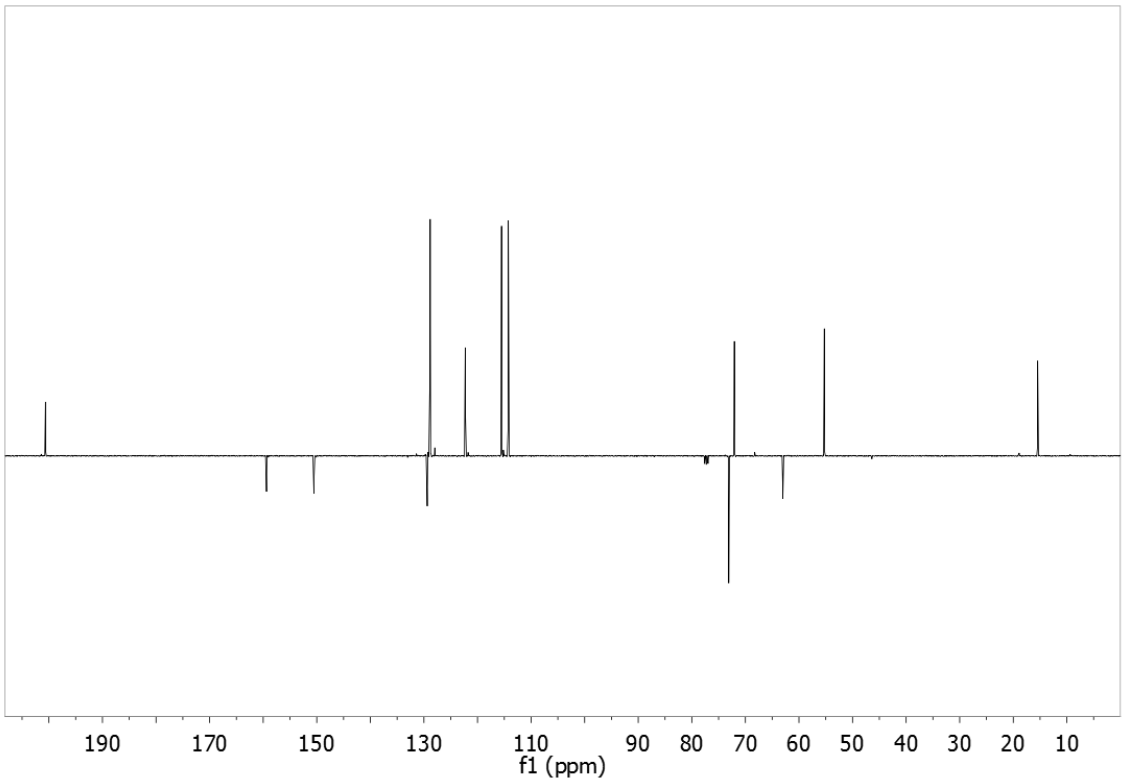


Ee (3,5)-*endo*

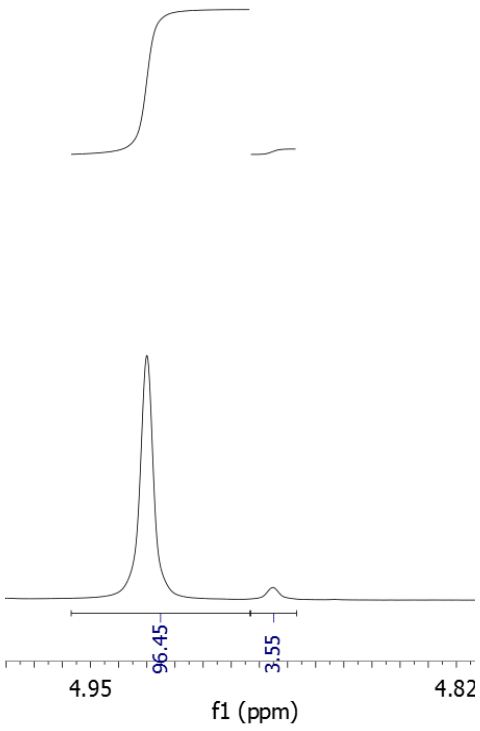


(3,4)-*endo*-4-methyl-2-*N*-phenyl-3-(4-methoxyphenyl)-isoxazolidine-4-carbaldehyde (Table 2, Entry 13)

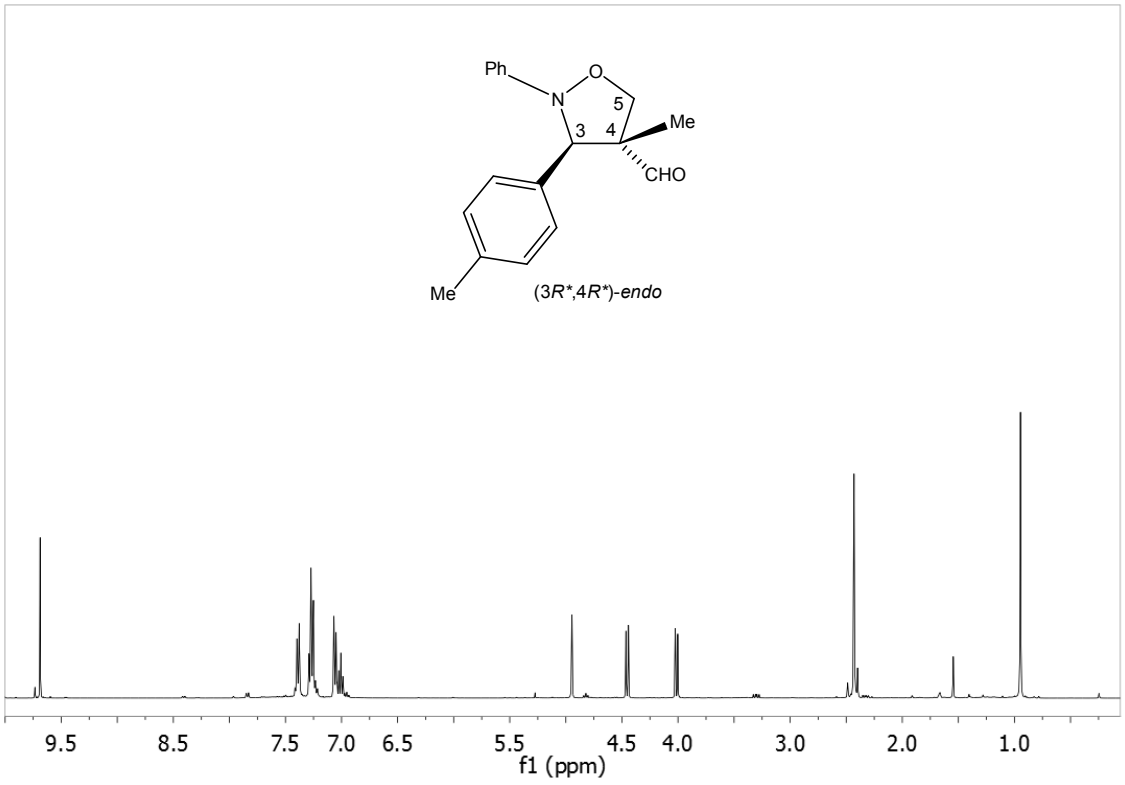


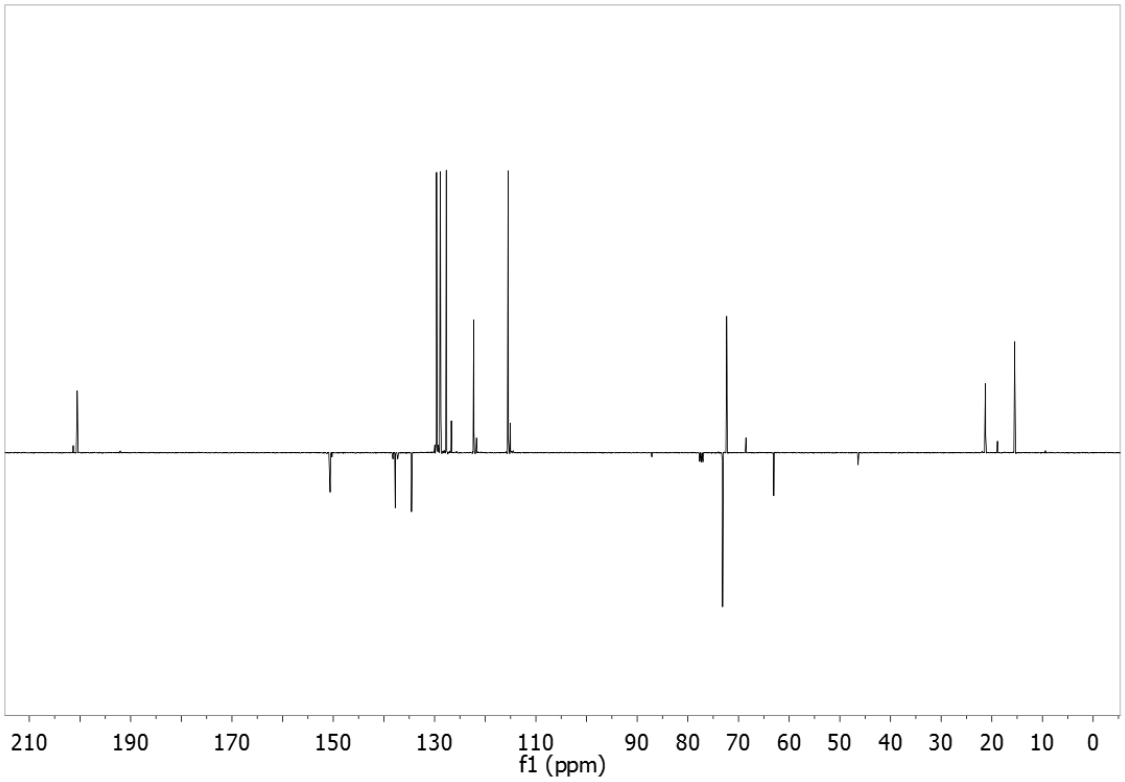

190
170
150
130
110
90
80
70
60
50
40
30
20
10
f1 (ppm)

Ee (3,4)-*endo*

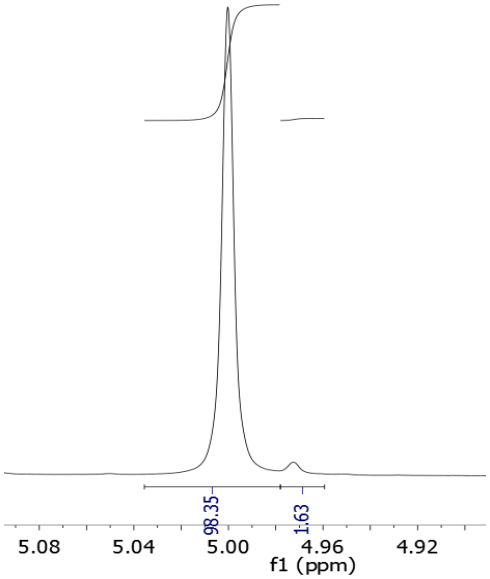

96.45
3.55
4.95
4.82
f1 (ppm)

(3,4)-*endo*-4-methyl-2-*N*-phenyl-3-(4-methylphenyl)-isoxazolidine-4-carbaldehyde (Table 2, Entry 14)

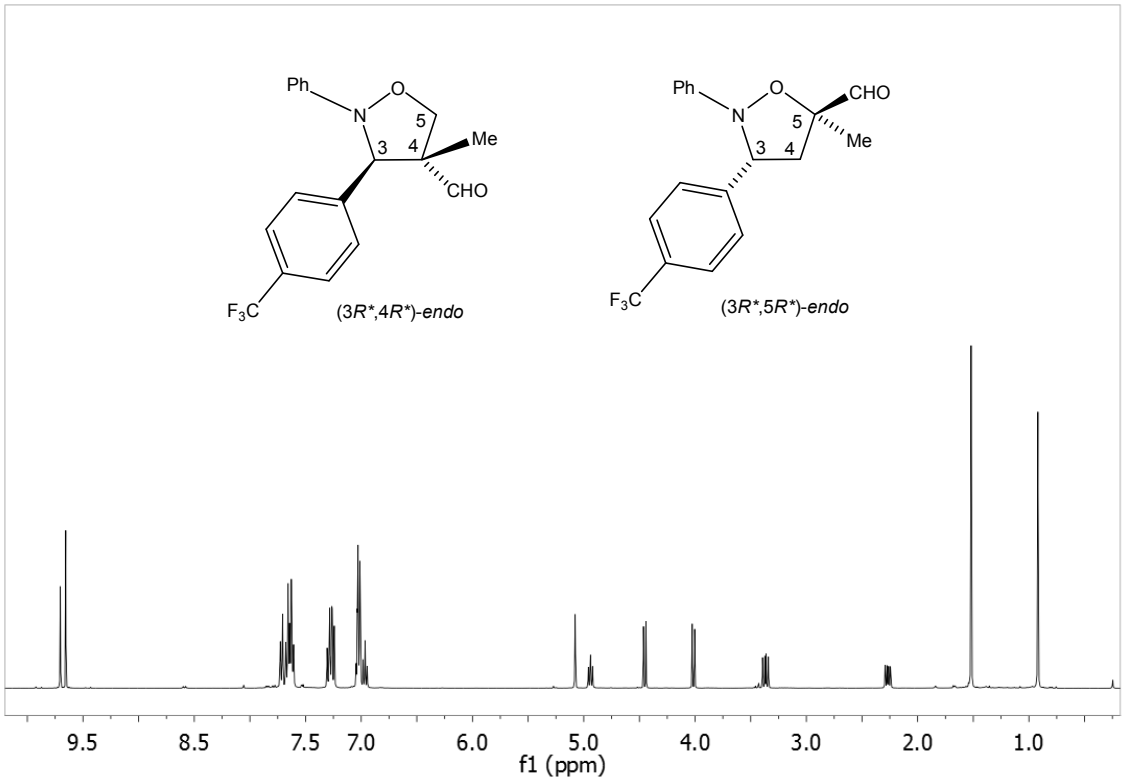


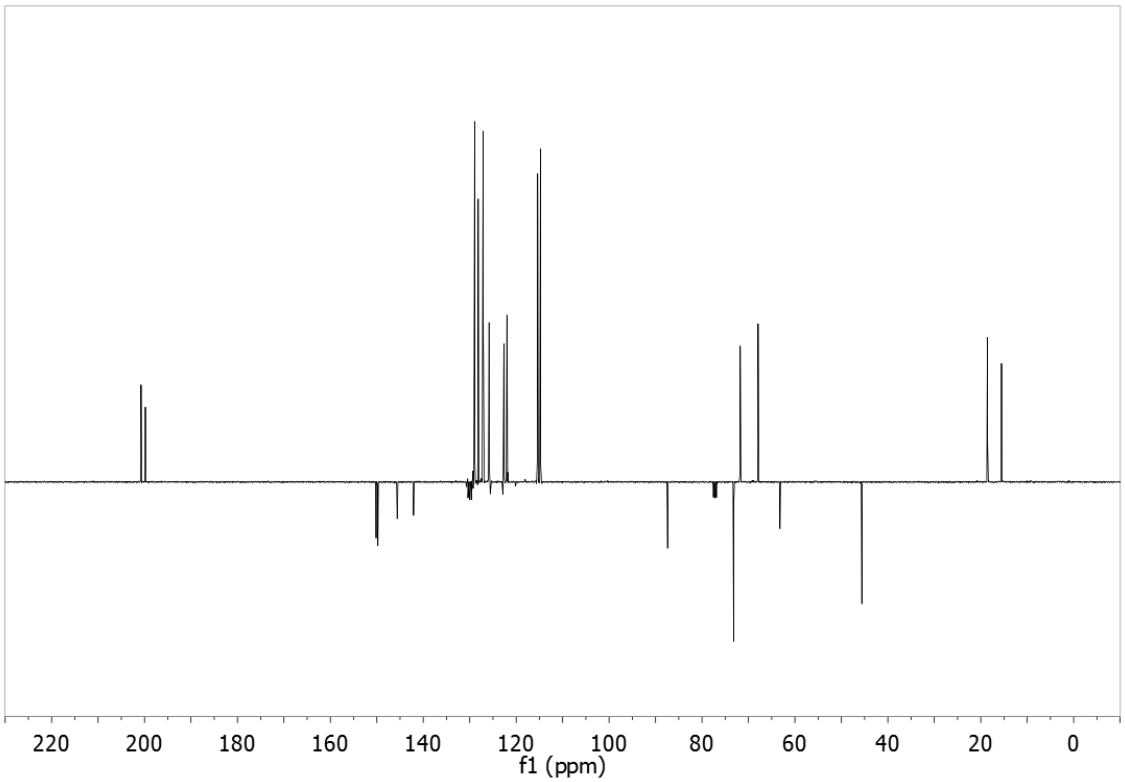


Ee (3,4)-*endo*

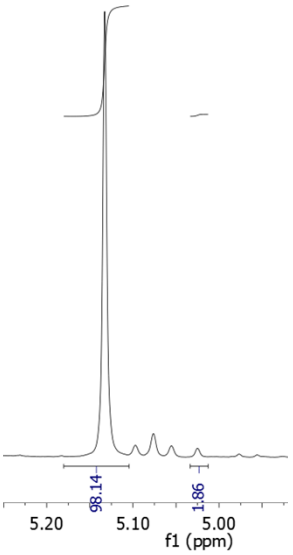


Mixture of (3,4)-*endo*-4-methyl-2-*N*-phenyl-3-(4-trifluoromethylphenyl)-isoxazolidine-4-carbaldehyde and (3,5)-*endo*-5-methyl-2-*N*-phenyl-3-(4-trifluoromethyl-phenyl)-isoxazolidine-5-carbaldehyde (Table 2, Entry 16): 46/54 molar ratio

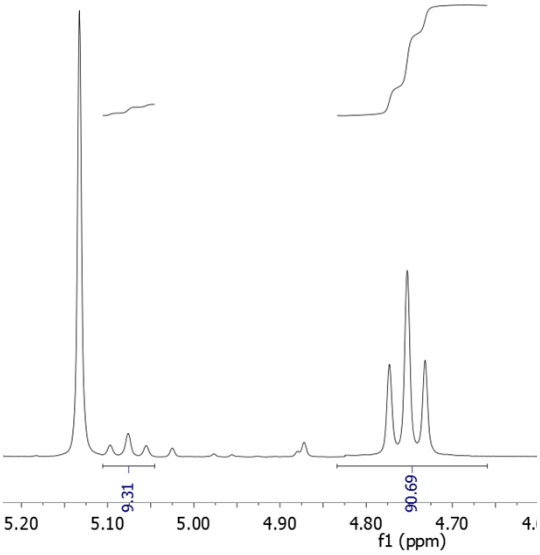




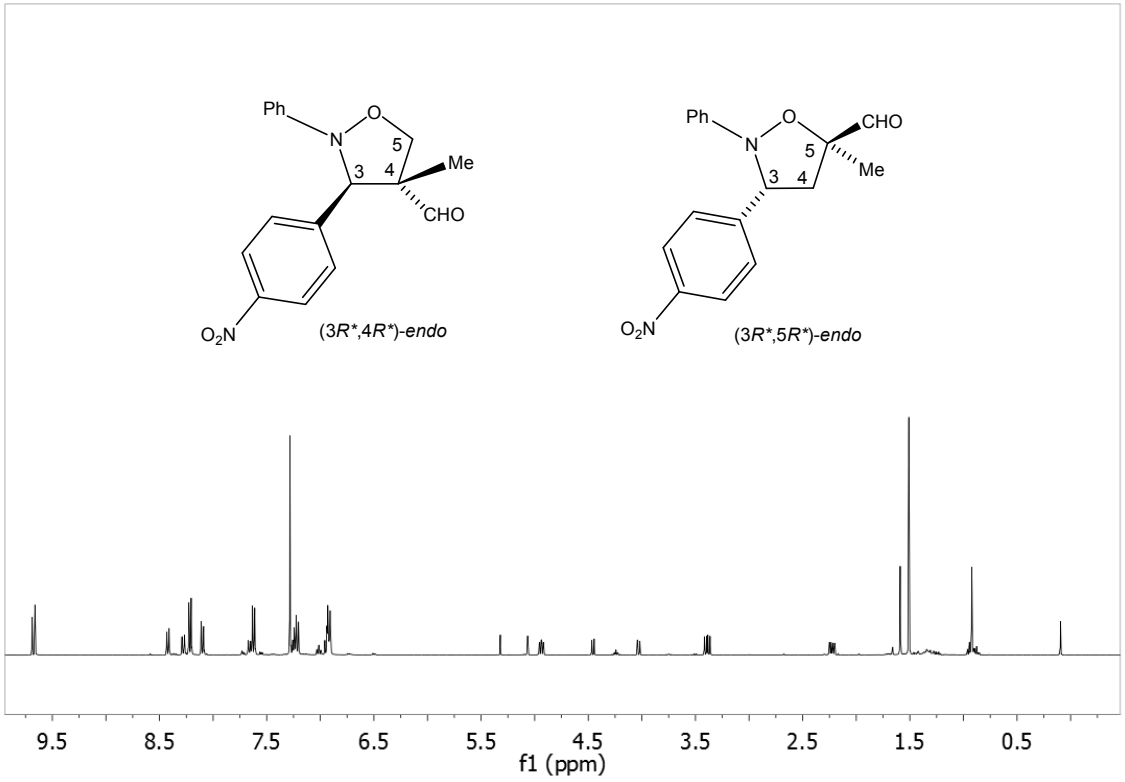
Ee (3,4)-*endo*

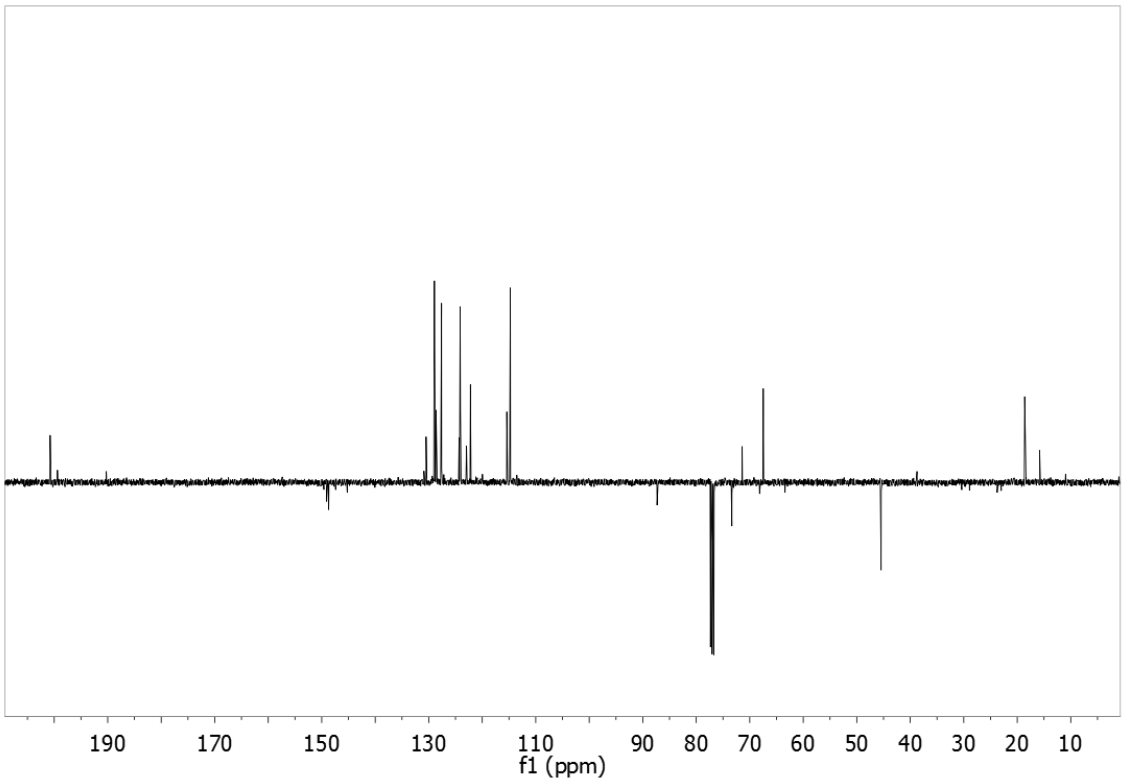


Ee (3,5)-*endo*

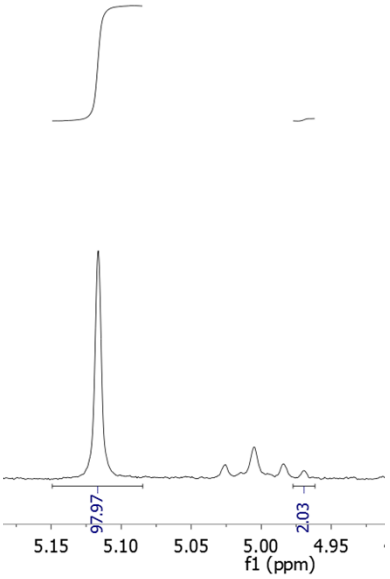


Mixture of (3,4)-*endo*-4-methyl-2-*N*-phenyl-3-(4-nitro-phenyl)-isoxazolidine-4-carbaldehyde and (3,5)-*endo*-5-methyl-2-*N*-phenyl-3-(4-nitro-phenyl)-isoxazolidine-5-carbaldehyde (Table 2, Entry 17): 30/70 molar ratio

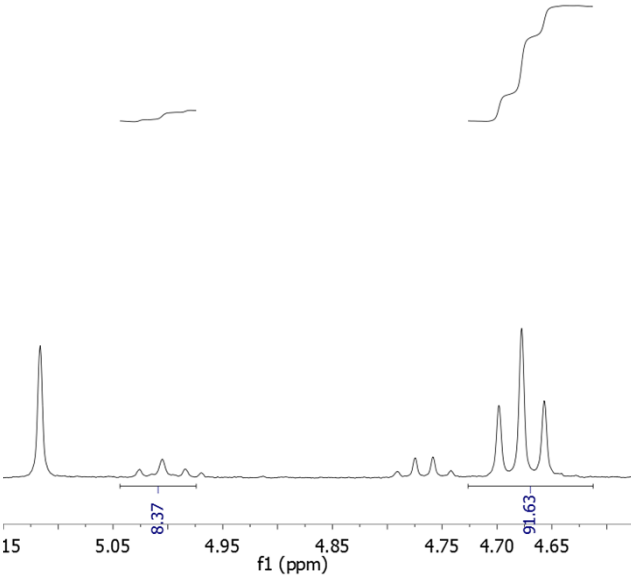




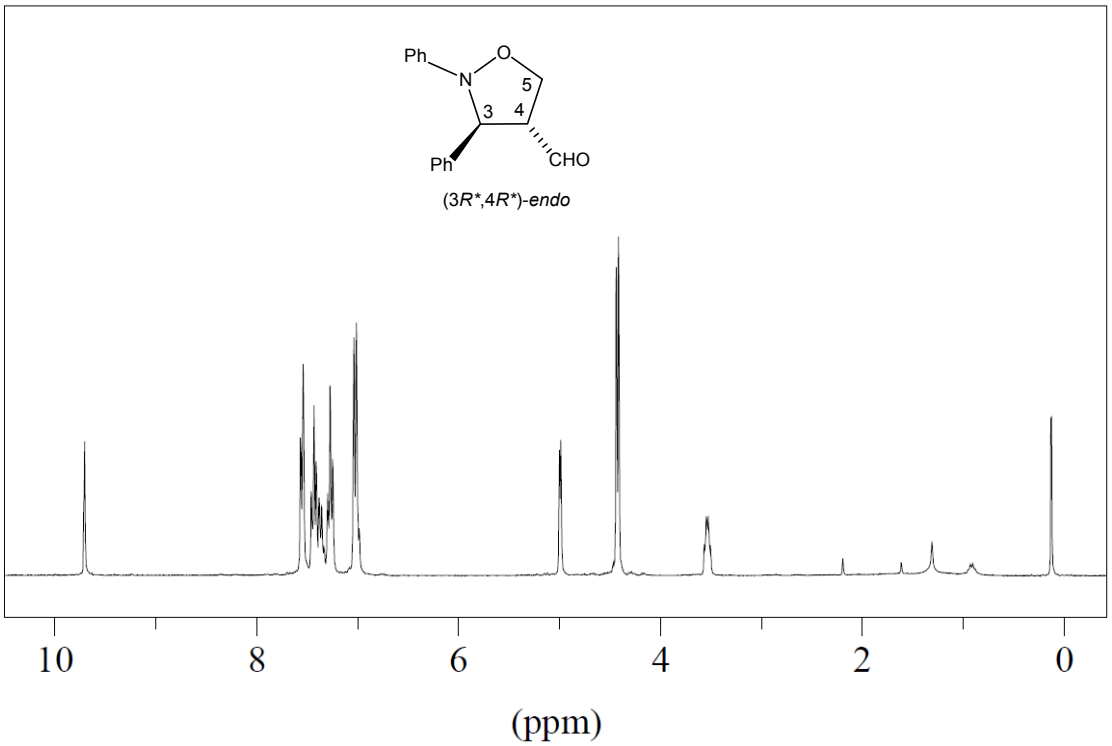
Ee (3,4)-*endo*

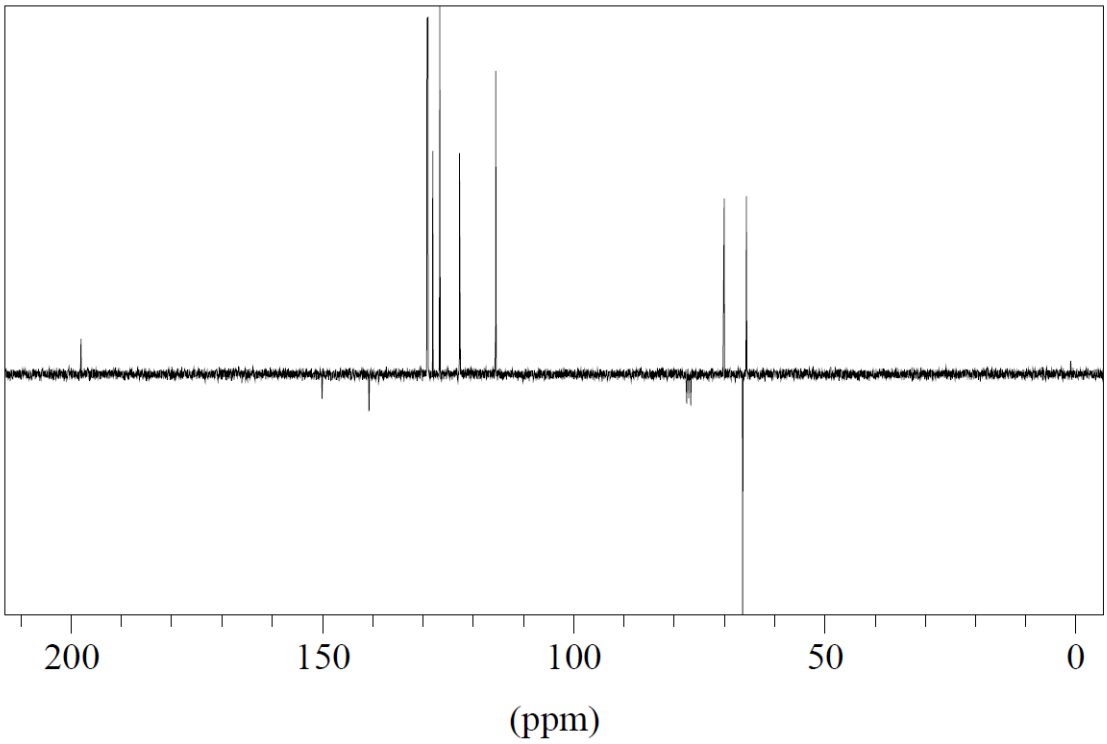


Ee (3,5)-*endo*

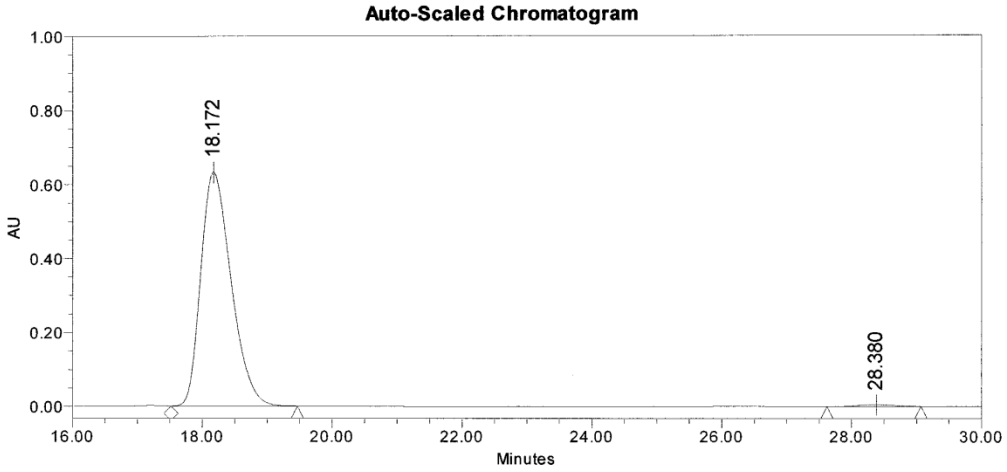


(3,4)-*endo*-2,3-diphenylisoxazolidine-4-carbaldehyde (Table 3, Entries 1-4)





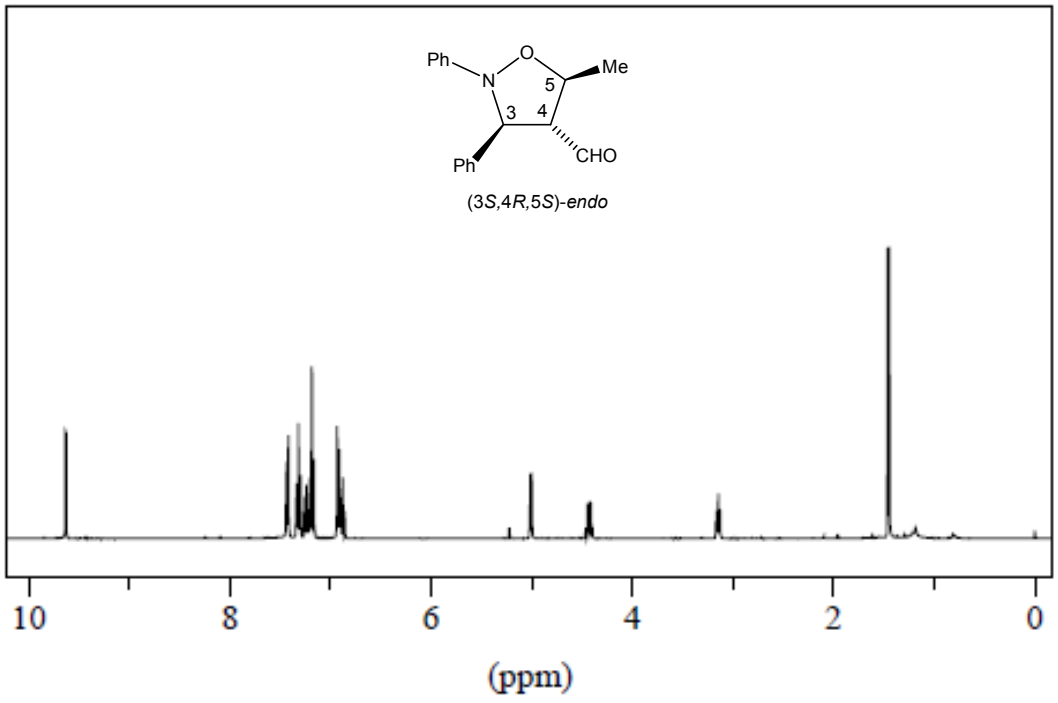
Ee 3,4-*endo*

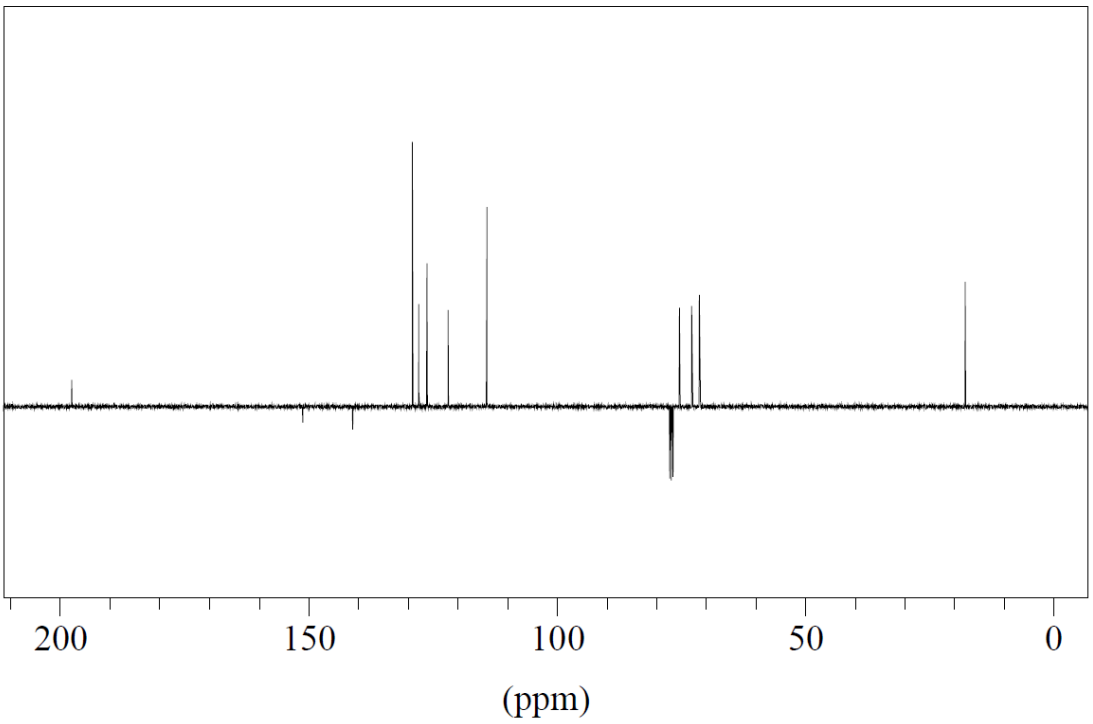


Peak Results

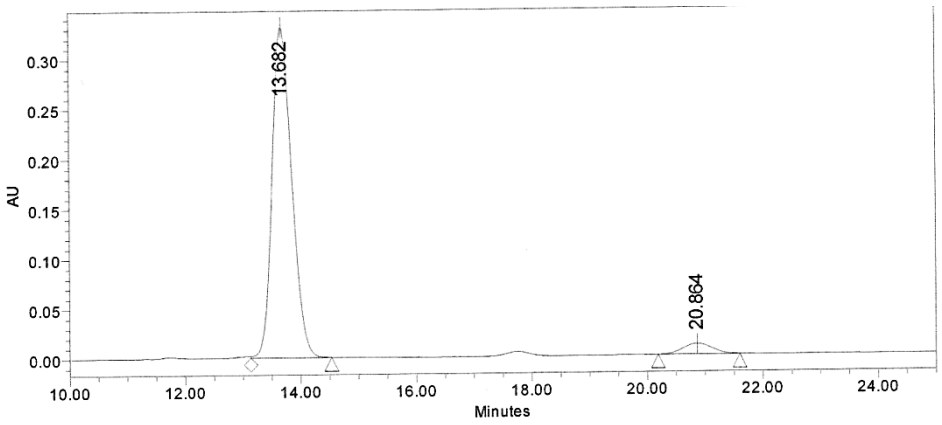
	Name	RT	Area	Height	% Area	Purity1 Angle	Purity1 Threshold
1		18.172	20482085	633071	99.08	2.106	4.679
2		28.380	189818	4677	0.92	3.424	10.237

(3*R*,4*R*,5*S*)-*endo*-5-methyl-2,3-diphenylisoxazolidine-4-carbaldehyde (Table 3, Entries 5-8)





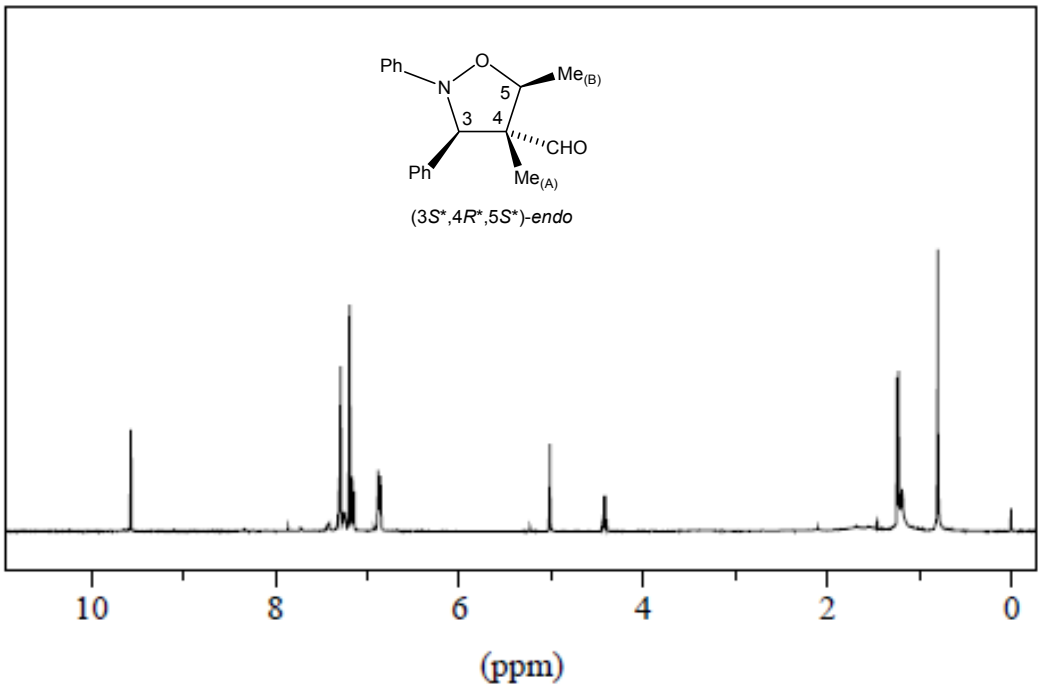
Ee 3,4-*endo*

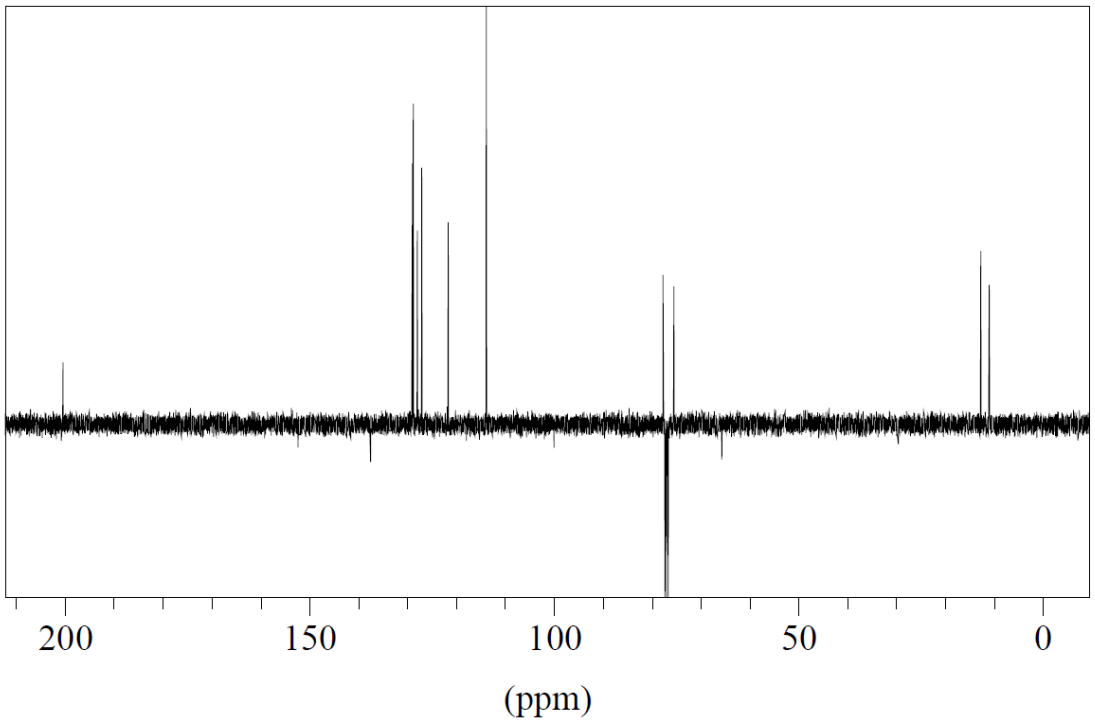


Peak Results

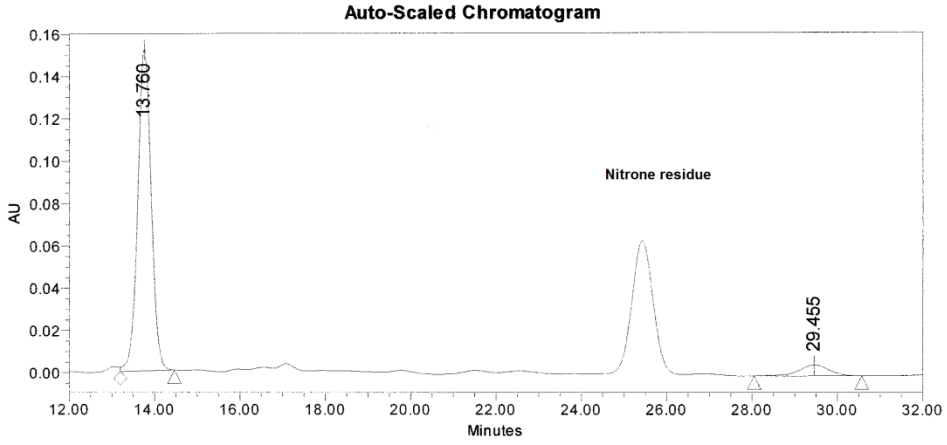
	Name	RT	Area	Height	% Area	Purity1 Angle	Purity1 Threshold
1		13.682	7849118	330563	95.46	0.316	0.300
2		20.864	373323	10659	4.54	0.559	0.968

(3,4)-*endo*-5-methyl-2,3-diphenylisoxazolidine-4-methyl-4-carbaldehyde (Table 3, Entries 9, 10)





Ee 3,4-*endo*



Peak Results

	Name	RT	Area	Height	% Area	Purity1 Angle	Purity1 Threshold
1		13.760	3339167	151860	92.82	5.194	22.466
2		29.455	258238	5224	7.18	60.078	90.000