Supporting Information (50 Pages)

Photochemical Type II Reaction of Atropchiral Benzoylformamides To Point Chiral Oxazolidin-4-ones. Enantiomeric Resolution of Photoproducts.

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1.0 General methods.

All commercially obtained reagents/solvents were used as received; chemicals were purchased from Alfa Aesar®, Sigma – Aldrich®, Across®, TCI® America, Mallinckrodt®, and Oakwood® Products, and were used as received without further purification. Unless stated otherwise, reactions were conducted in oven-dried glassware under nitrogen atmosphere. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 400 MHz (100 MHz for ^{13}C) and on 500 MHz (125 MHz for ^{13}C) spectrometers. Data for ^{1}H NMR are reported as chemical shift (δ ppm) with the corresponding integration values. Coupling constants (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s (singlet), b (broad), d (doublet), t (triplet), q (quartet), m (multiplet) and virt (virtual). Data for ^{13}C NMR spectra are reported in terms of chemical shift (δ ppm). Electrospray Ionization Spectra were recorded on a Bruker – Daltronics® BioTof mass spectrometer in positive (ESI+) ion mode. HPLC analyses were performed on Waters® HPLC equipped with 2525 pump. Waters® 2767 sample manager was used for automated sample injection. All HPLC injections were monitored using a Waters® 2487 dual wavelength absorbance detector at 220, 254, and 270 nm. Analytical and semi-prepaprative injections were perfomed on chiral stationary phase using various columns as indicated below.

i) Regis® PIRKLE COVALENT (R,R) WHELK–01
   a) 0.46 mm x 25 cm column for analytical injections.
   b) 10 mm x 25 cm column for semi-preparative injections.
ii) CHIRALCEL® OD-H
   a) 0.46 cm Φ x 25 cm column for analytical injections.
   b) 10mm x 25 cm column for semi-preparative injections.
iii) CHIRALCEL® OD-3: 0.46 cm Φ x 15 cm column for analytical injections.
iv) CHIRALPAK® AD-H
   a) 0.46 cm Φ x 25 cm column for analytical injections.
   b) 10mm x 25 cm column for semi-preparative injections.
v) CHIRALPAK® AD-3: 0.46 cm Φ x 15 cm column for analytical injections.
vi) CHIRALPAK® AS-H: 0.46 cm Φ x 25 cm column for analytical injections.

Masslynx software version 4.1 was used to analyse the HPLC injections to process Hplc tracess. Igor Pro® Sofware version 4.0 was used to process the generate Hplc graphics. UV-Vis spectra were recorded on a Shimadzu 2501PC UV-Vis spectrometer using UV quality fluorimeter cells

(with range until 190 nm) purchased from Luzchem. Optical activity values were recorded on JASCO® DIP – 370 digital polarimeter. CD spectra were recorded on Applied Photophysics® π–180 spectrometer. When necessary, the compounds were purified by combiflash equiped with dual wavelength UV-Vis absorbance dectector (Teledyn ISCO) using ethylacetate-hexanes as the mobile phase and Redisep cartridge filled with silica (Teledyne ISCO) as stationary phase for seperation. In some cases, column were purified by chromatography on silica gel (Sorbent Technologies®, silica gel standard grade: Porosity 60 Å, Particle size: 230 x 400 mesh, Surface area: 500 – 600 m^2/g, Bulk density: 0.4 g/mL, pH range: 6.5 – 7.5). The Retention Factor (R*f*) values were recorded using a 5-30 % EtOAc-Hexanes as mobile phase and on Sorbent Technologies®,Silica Gel TLC plates (200 μm thickness w/UV_{254}).

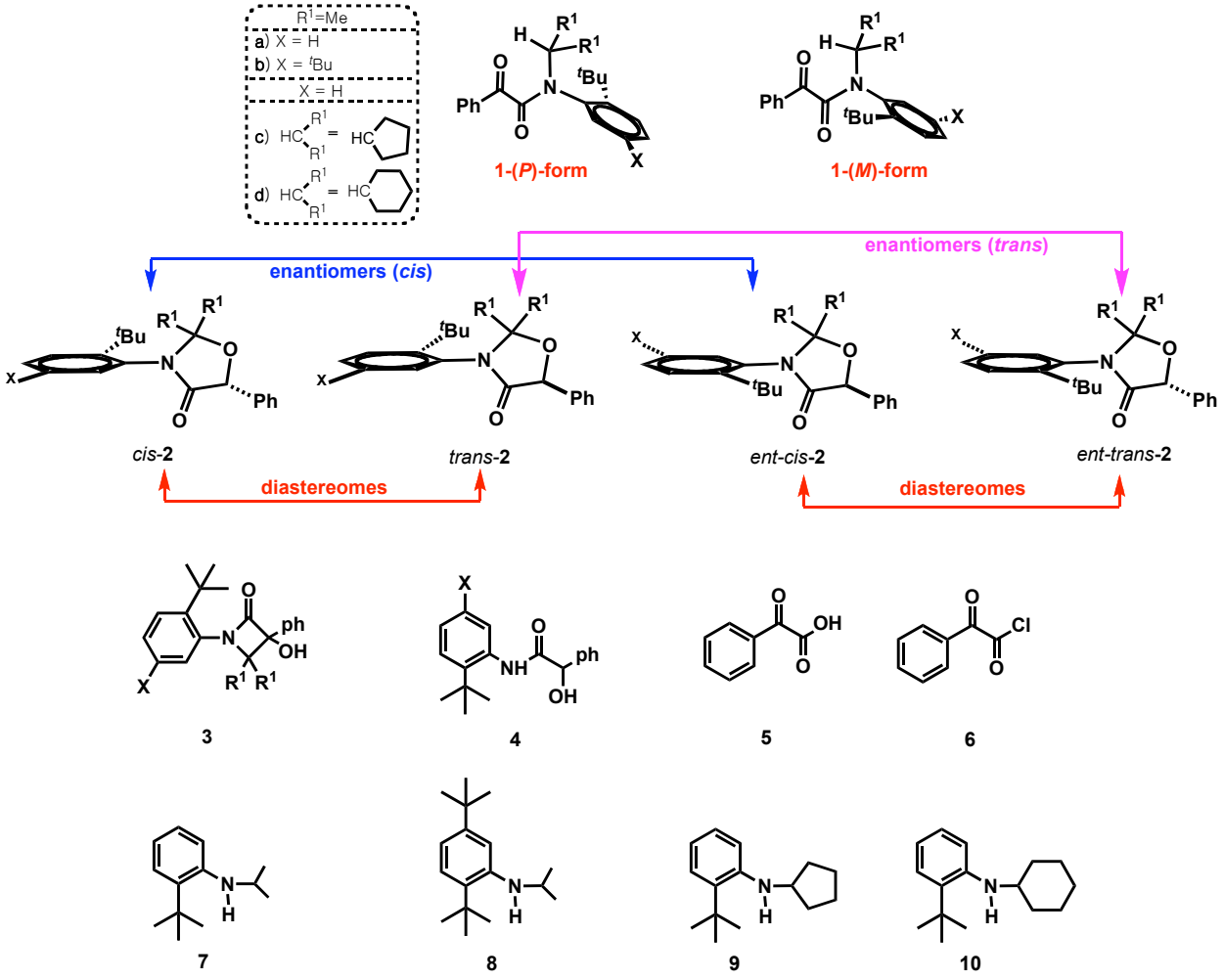
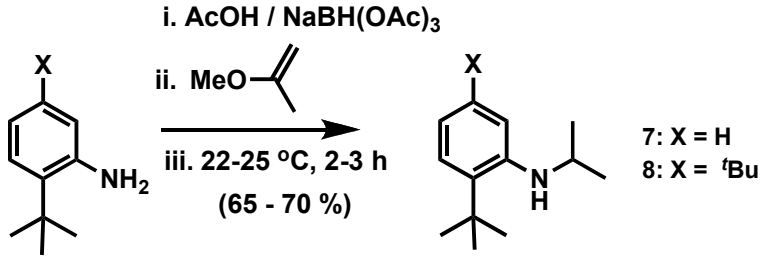


Chart-1

2. General procedure for synthesis of *N*-substituted anilines and benzoylformamide precursors.

2.1 Synthesis of *N*-isopropyl anilines **7** and **8**.



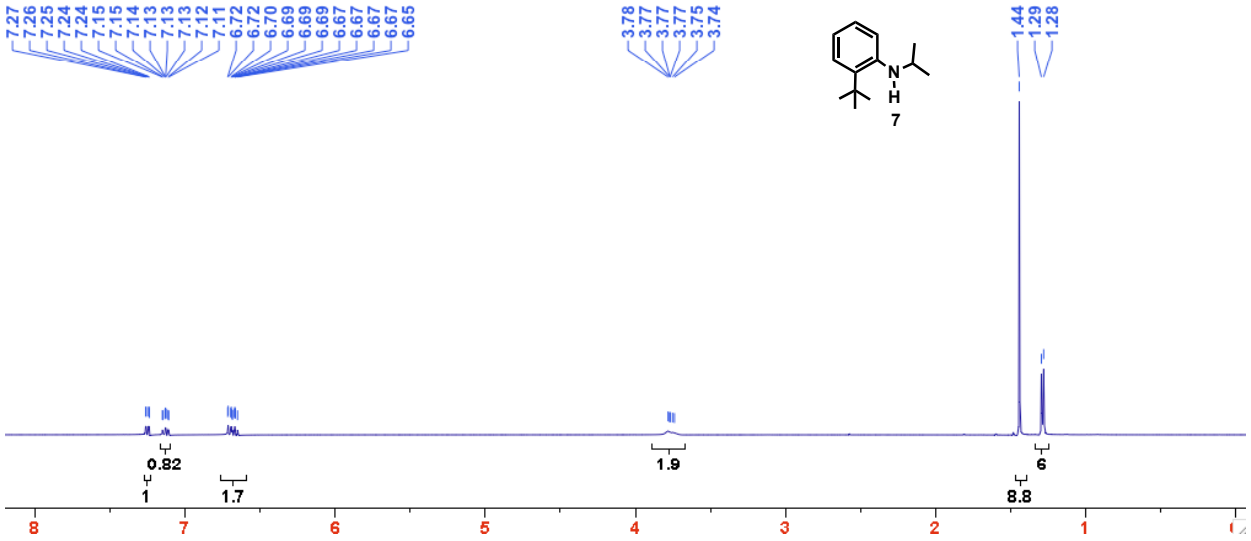
Scheme S1: Synthesis of *N*-isopropyl substituted anilines **7** and **8**.

N-Isopropyl anilines **7** and **8** were synthesized using previously reported procedures (Scheme S1).[1] To a stirred solution of *ortho*-*tert*-butyl substituted aniline (0.411 g, 2 mmol) in 6 mL of dichloromethane under nitrogen; 2-methoxypropene (0.287 mL, 3 mmol), acetic acid (0.114 mL, 2 mmol) and sodium triacetoxyborohydride (636 mg, 3mmol) were added sequentially. The reaction mixture was stirred at 22-25 ^{o}C for 2-3 h; the reaction was quenched with aqueous 1N KOH solution and extracted with dichloromethane (3 x 20 mL). The organic layer was washed with brine and dried over anhydrous sodium sulphate. Organic layer was filtered, and concentrated to obtain the expected *N*-Isopropyl-2, 5-di-*tert*-butyl aniline and purified by column chromatography (Isolate yield: 65-70%).

2.1a 2-*tert*-butyl-*N*-isopropylaniline **7**

R*f* = 0.78 (20 % EtOAc-80% Hexanes)

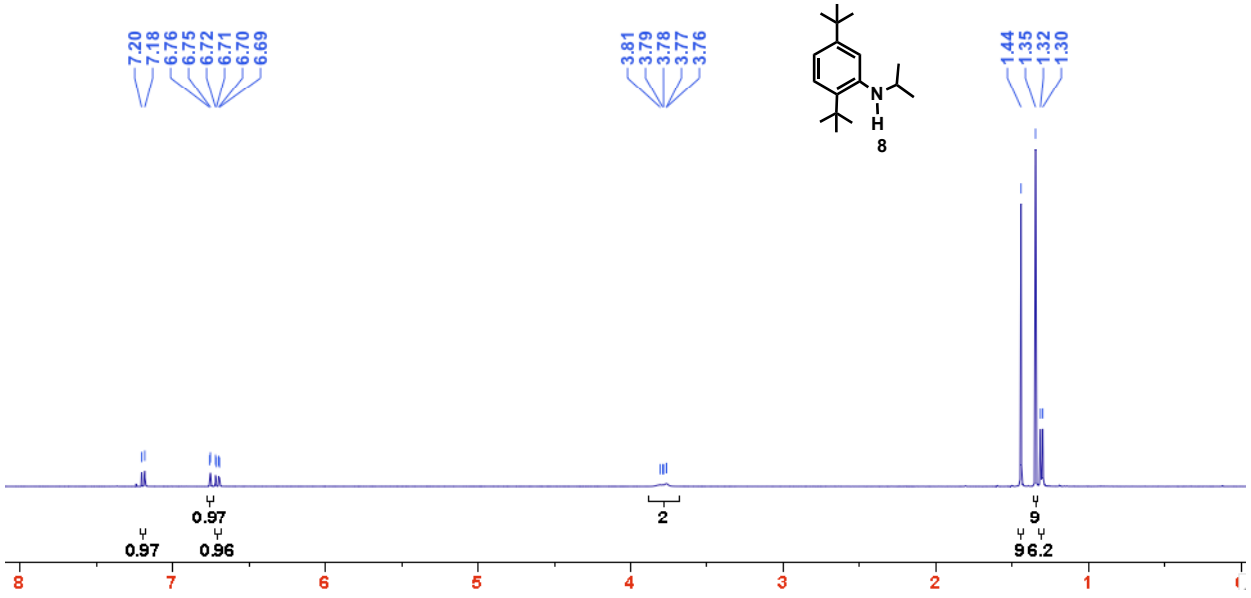
^{1}*H NMR* (400 MHz, $CDCl_3$, δ ppm): 7.27 – 7.24 (Ar, 1H), 7.15 – 7.11 (Ar, 1H), 6.72 – 6.65 (Ar, 2H), 3.78-3.74 (m, 2H), 1.44 (s, 9H), 1.29 -1.28 (d, *J* = 4 Hz, 6H)



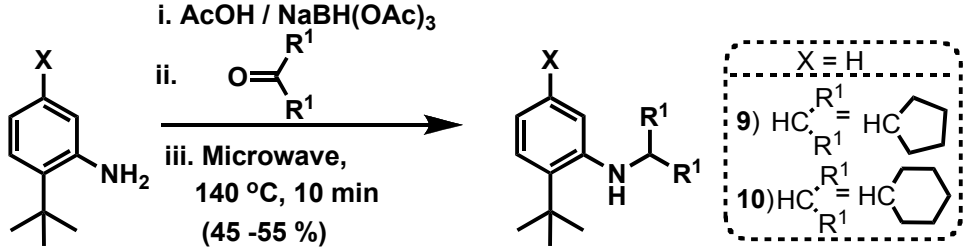
2.1b 2,5-di-*tert*-butyl-*N*-isopropylaniline **8**

R*f* = 0.89 (20 % EtOAc-80 %Hexanes)

^{1}*H NMR* (400 MHz, $CDCl_3$, δ ppm): 7.20 – 7.18 (Ar, 1H), 6.76-6.75 (Ar, 1H), 6.72 – 6.69 (Ar, 1H), 3.81-3.76 (m, 2H), 1.44 (s, 9H), 1.35 (s, 9H), 1.32 -1.30 (d, *J* = 8 Hz, 6H)



2.2 Synthesis of *N*-substituted anilines **9** and **10**.



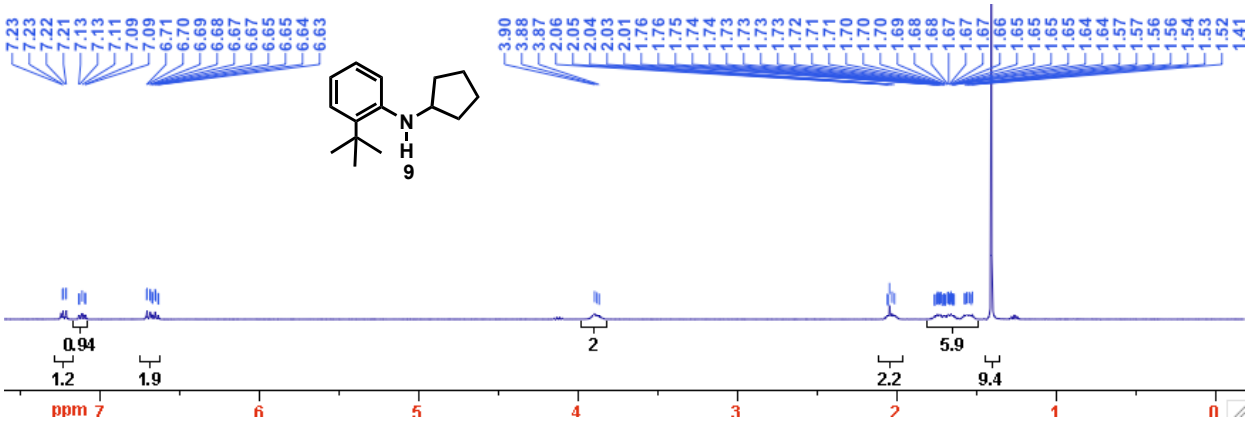
Scheme S2: Synthesis of *N*-substituted anilines **9** and **10**.

N-substituted anilines **9** and **10** were synthesized using previously reported procedures (Scheme S2).[2] In a 10 mL microwave test tube, *ortho-tert*-butyl substituted aniline (1 mmol; 1eq), the corresponding ketone (2 mmol; 2.0 eq), sodium triacetoxyborohydide (2.5 mmol; 2.5 eq) and acetic acid (3mmol) were mixed in 2 mL of 1,2-dicloroethane with magnetic bar. The mixture was irradiated in a microwave at 140 °C for 10 min. The reaction mixture was cooled to room temperature, quenched with saturated solution of ammonium chloride and extracted with chloroform (3 x 10 mL). Combined organic layer was dried over anhydrous sodium sulphate, filtered, concentrated and purified by flash column to yield **9** and **10** (Isolated yield: 45-55%).

2.2 2-*tert*-butyl-*N*-3-pentylaniline **9**

R*f* = 0.89 (20 % EtOAc-80% Hexanes)

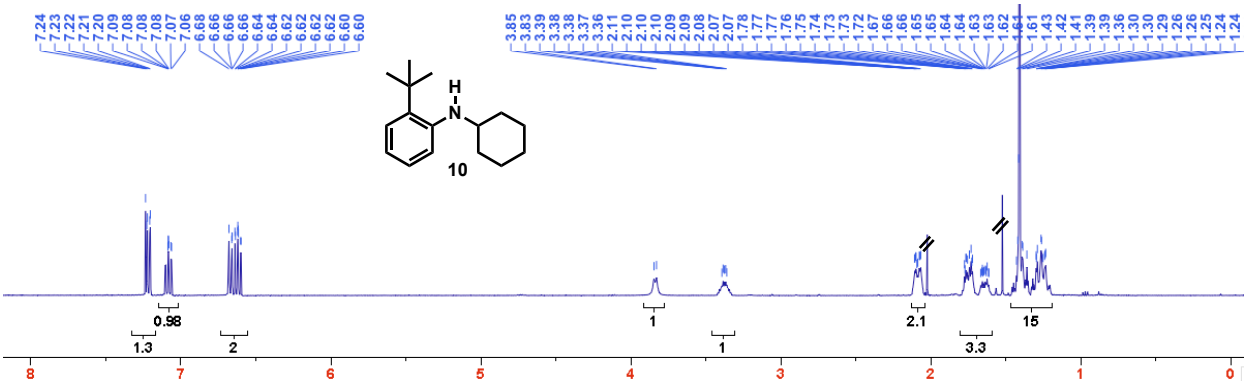
^1H *NMR* (400 MHz, $CDCl_3$, δ ppm): 7.23-7.21 (Ar, 1H), 7.13-7.09 (Ar, 1H), 6.71-6.63 (Ar, 2H), 3.90-3.87 (m, 2H), 2.06 -2.01 (m, 2H), 1.76 -1.52 (m, 6H), 1.41 (s, 9H).



2.2 2-*tert*-butyl-*N*-cyclohexylaniline **10**

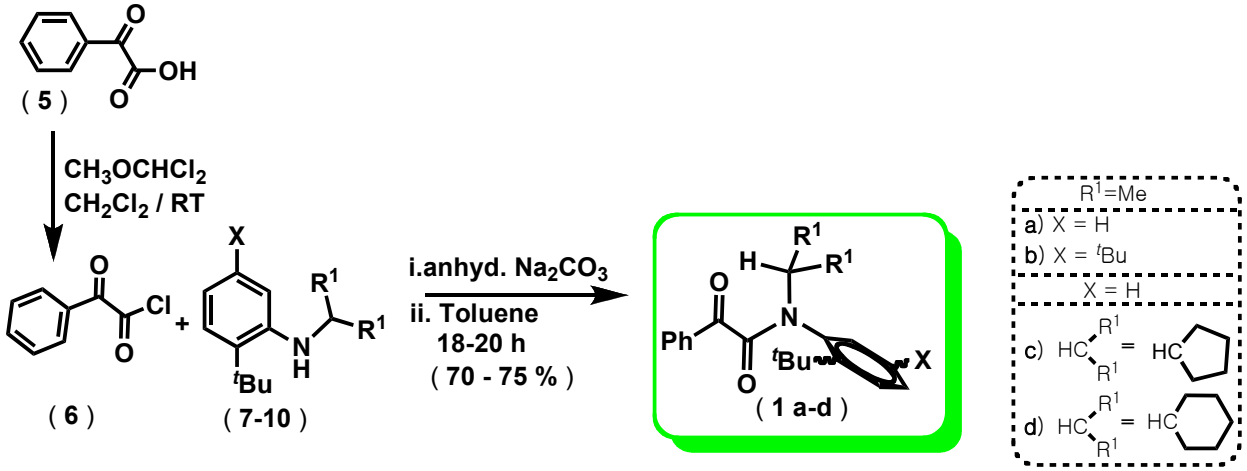
R*f* = 0.89 (20 % EtOAc-80 %Hexanes)

^{1}*H NMR* (400 MHz, $CDCl_3$, δ ppm) 7.24 – 7.20 (Ar, 1H), 7.08-7.06 (Ar, 1H), 6.62 – 6.58 (Ar, 2H), 3.85-3.83 (d, 1H), 3.39-3.36 (m, 1H), 2.11-2.07 (m, 2H), 1.78-1.61 (m, 3H), 1.43-1.42 (m, 14H).



3. General procedure for synthesis of benzoylformamides.

3.1 Synthesis of benzoylformamides **1a-d.**



Scheme S3: Preparation of benzoylformamides **1a-d**.

In a typical reaction (Scheme S3), 1.25 equivalent of freshly synthesized benzoyl formyl chloride[3] **6** (from benzoylformic acid **5**) in a round-bottom-flask under N_2 atmosphere, 20 mL of dichloromethane was added. To the acyl chloride solution, 10 equivalent of anhydrous Na_2CO_3 was added with stirring. The appropriate *ortho-tert*-butyl substituted *N*-alkyl aniline **7-10** in toluene was slowly added and the reaction mixture was stirred over night (18-20 h) at 20-23 ^{o} C. The reaction was quenched by the addition of 20 mL of DI-water and extracted with

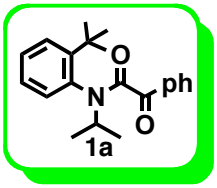
dichloromethane (2 x 30 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure in a rotory evaporator. The benzoylformamide **1a-d** was purified by flash chromatography on silica gel. (Isolated yield 70 – 75%).

4. Characterization of benzoylformamides.

4.1 Benzoylformamide **1a**

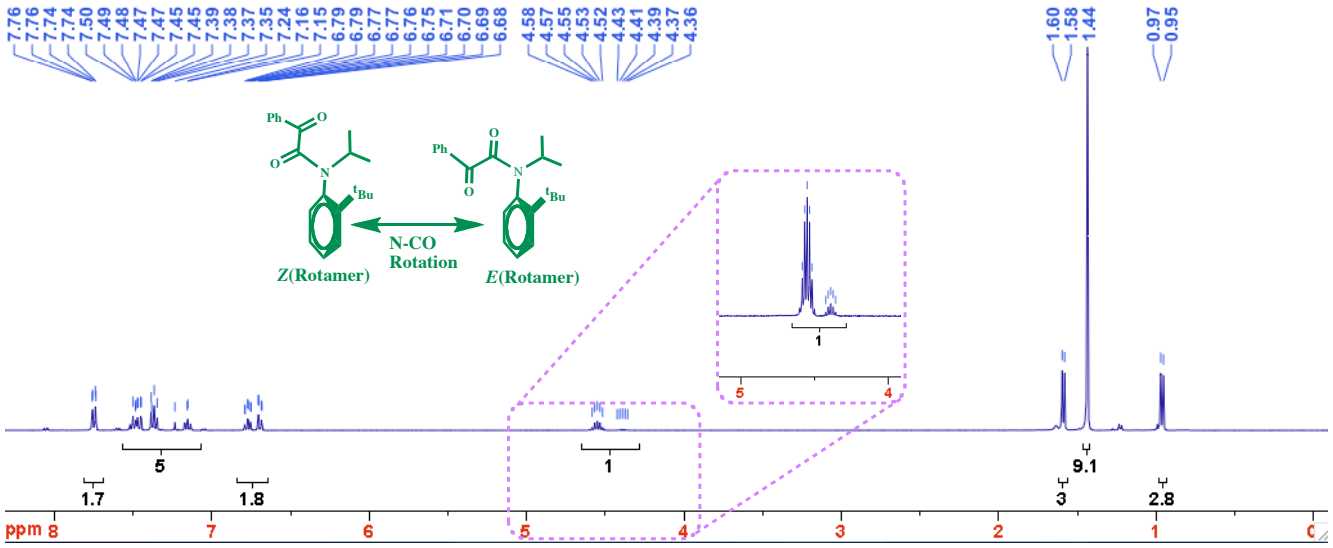
The title compound was purified by flash chromatography on silica gel with a solvent polarity 1-20% EtOAc-Hexanes as gradient.

R*f* = 0.4 (20 % EtOAc-80%Hexanes)

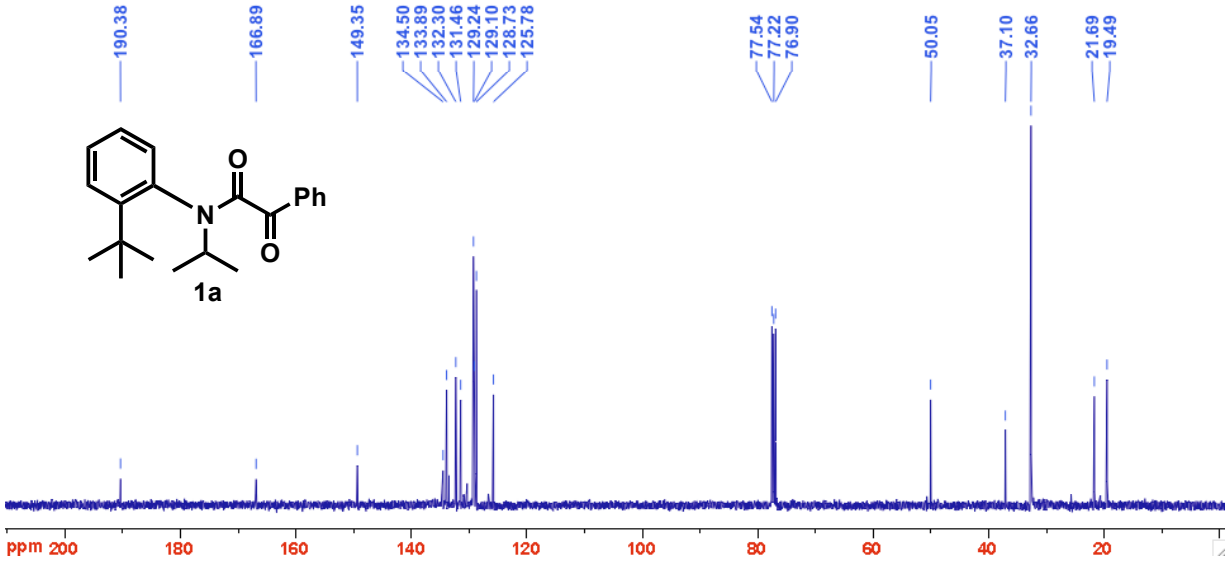


X-ray: see section 11 for details; see attached cif file.

^1H *NMR* (400 MHz, $CDCl_3$, δ ppm): 7.76-7.74 (Ar, 2H), 7.50-7.15 (Ar, 5H), 6.79-6.68 (Ar, 2H), 4.58-4.36 (m, 1H, N-CH, major and minor conformers), 1.60-1.58 (d, *J* = 8 Hz, 3H) 1.44 (s, 9H), 0.97-0.95 (d, *J* = 8 Hz, 3H).

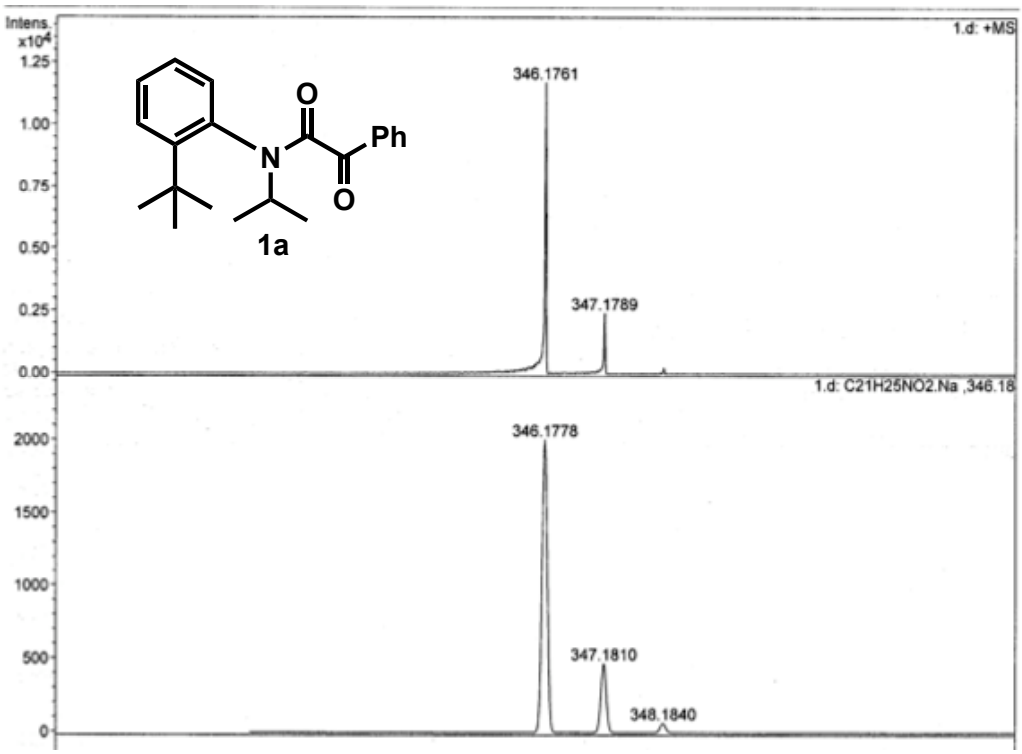


^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 190.38, 166.89, 149.35, 144.59, 134.50, 133.89, 132.30, 131.46, 129.24, 129.10, 128.73, 125.78, 50.05, 37.10, 32.66, 21.69, and 19.49.



HRMS-ESI (m/z) ($[M + Na]^+$): 346.1761

Calculated: 346.1778; Observed: 346.1761



HPLC analysis conditions:

For both analytical and preparative injections

Column: (AD-H); Abs. detector: 254 nm and 270 nm

Mobile phase: Hexanes: IPA = 96:04

Flow rate: 1 mL/min (Analytical), and 4.5 mL/min (Preparative).

Retention times (min): ~14.72 [(-)-**1a**] and ~22.37 [(+)-**1a**] (Analytical)

~6.99 [(-)-**1a**] and ~10.47 [(+)-**1a**] (Preparative / semi preparative).

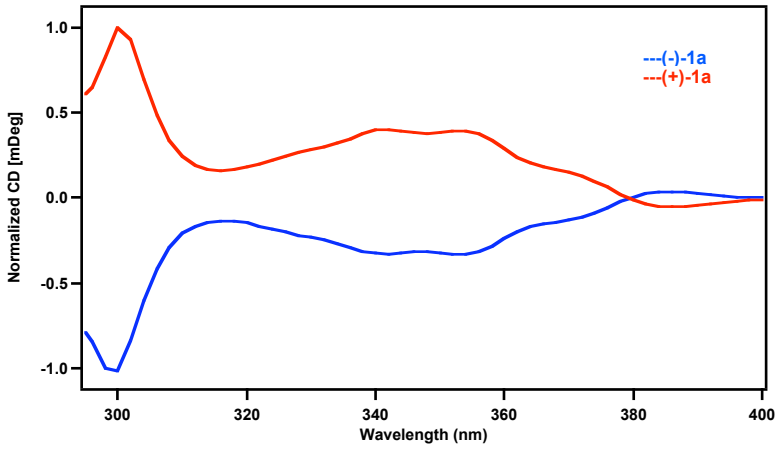
Optical Rotation $[\alpha]_D^{28}$:

HPLC peak retention time at ~14.72 min, (-)-**1a** (*c* = 0.1%, CH_3OH) = -109

HPLC peak retention time at ~22.37 min, (+)-**1a** (*c* = 0.1%, CH_3OH) = +110

CD Spectrum

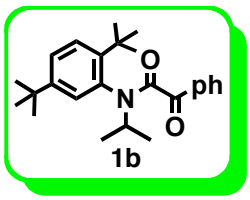
c = 0.1%, Methanol



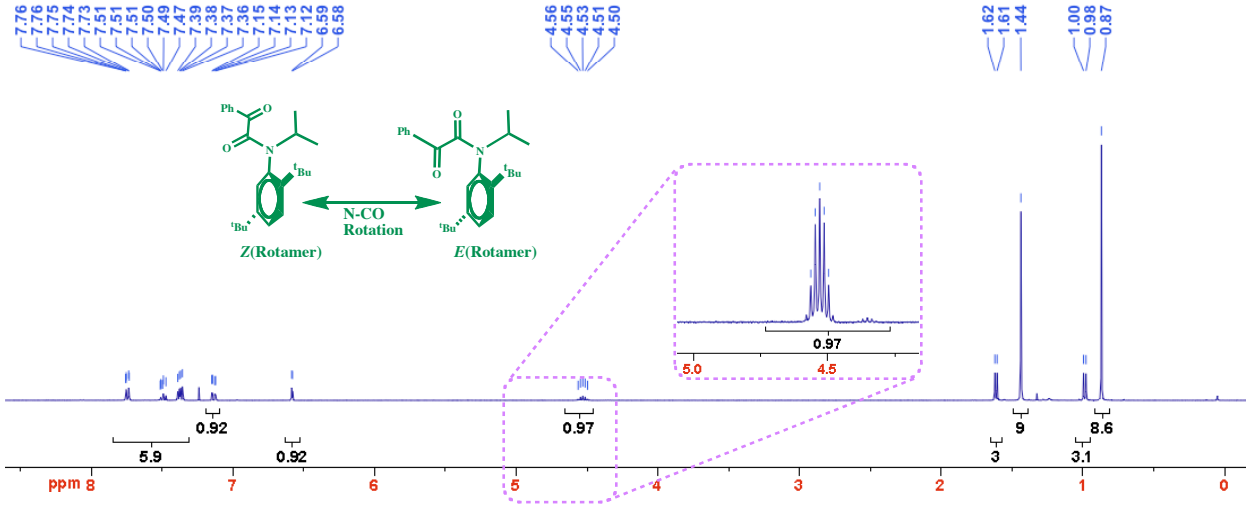
4.2 benzoylformamide **1b**

The title compound was purified by flash chromatography on silica gel with a solvent polarity of 1-20% EtOAc-Hexanes as gradient.

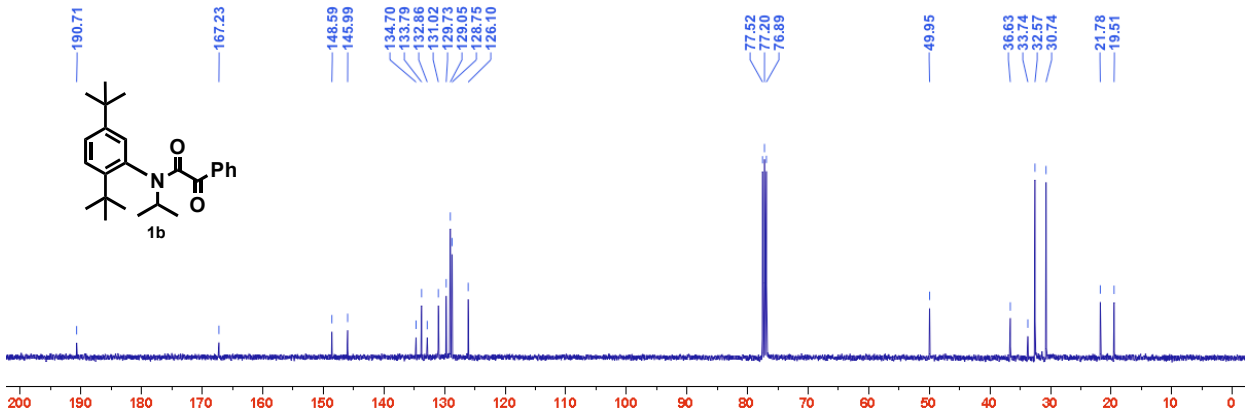
R*f* = 0.5 (20 % EtOAc-80%Hexanes)



[1]H NMR (400 MHz, $CDCl_3$, δ ppm): 7.76 – 6.58 (Ar, 8H), 4.56-4.50 (m, 1H, N-CH major and minor conformers), 1.62-1.61(d, *J* = 4 Hz, 3H,), 1.44 (s, 9H), 1.00-0.98 (d, *J* = 8 Hz, 3H,), and 0.87 (s, 9H).

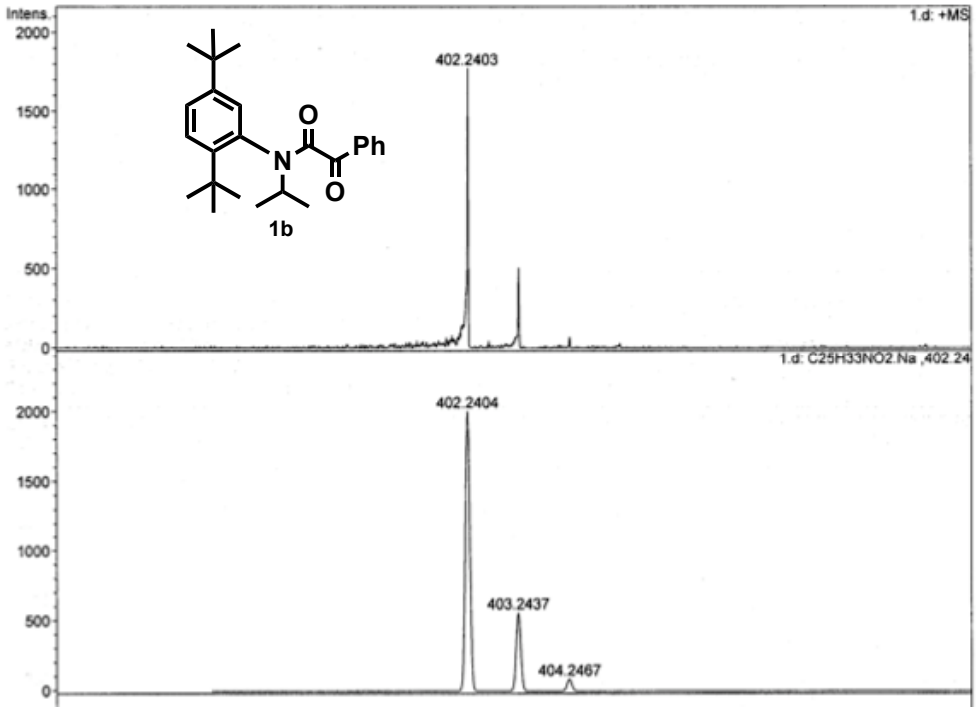


[13]C NMR (100 MHz, $CDCl_3$, δ ppm): 190.71, 167.23, 148.59, 145.99, 134.70, 133.70, 132.86, 131.02, 129.73, 129.05, 128.75, 126.10, 49.95, 36.63, 33.74, 32.57, 30.74, 21.78, and 19.51.



HRMS-ESI (m/z) ($[M + Na]^+$): 402.2404

Calculated: 402.2404; Observed: 402.2403



HPLC analysis conditions:

For both analytical and preparative injections

Column: (R,R) WHELK–01; Abs. detector: 254 nm and 270 nm

Mobile phase: Hexanes: IPA = 95:05 (Analytical), 98:02(Preparative /semi preparative).

Flow rate: 1 mL/min (Analytical), and 4.5 mL/min (Preparative /semi preparative).

Retention times (min): ~44.65 [(-)-**1b**] and ~51.80 [(+)-**1b**] (Analytical)

~50.22 [(-)-**1b**] and ~58.95 [(+)-**1b**] (Preparative / semi preparative).

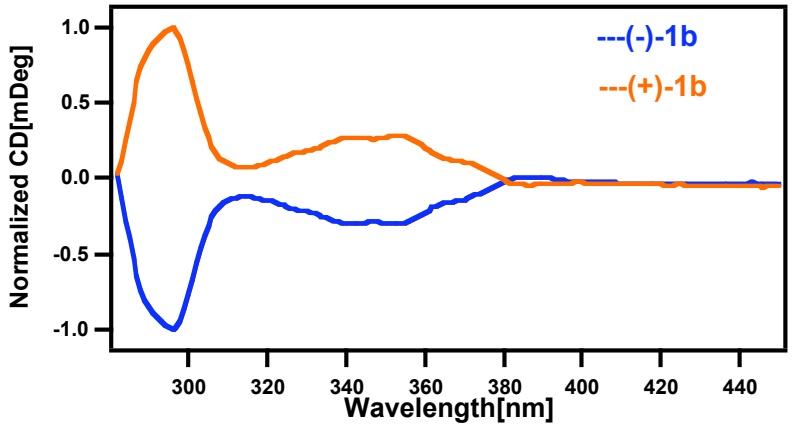
Optical Rotation $[\alpha]_D^{28}$:

HPLC peak retention time at ~44.65 min, (-)-**1b** (c = 0.1 %, $CHCl_3$) = -19

HPLC peak retention time at ~51.80 min, (+)-**1b** (c = 0.1 %, $CHCl_3$) = +21

CD Spectrum

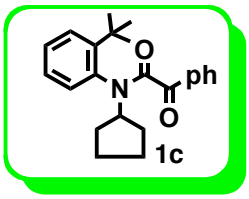
c = 0.1%, Methanol



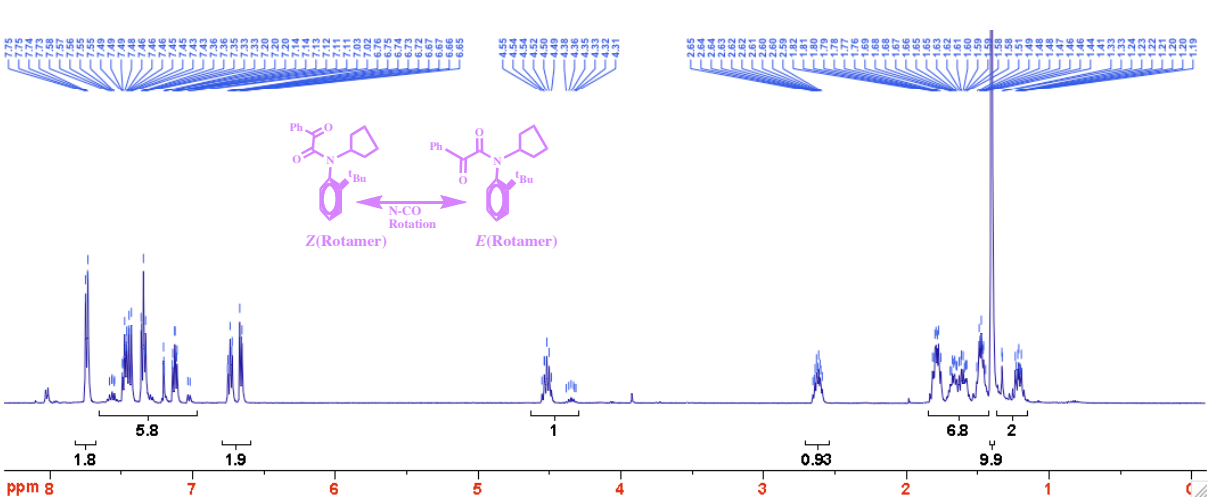
4.3 Benzoylformamide **1c**

The title compound was purified by flash chromatography on silica gel with a solvent polarity of 1-20% EtOAc-Hexanes as gradient.

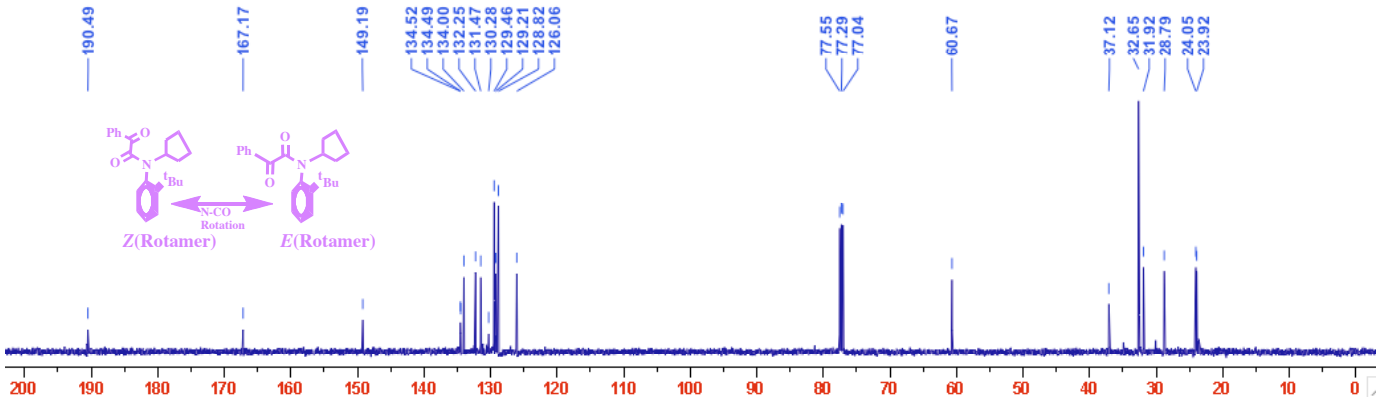
R*f* = 0.4 (20 % EtOAc-80%Hexanes)



^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.75 – 6.65 (Ar, 9H), 4.55-4.31 (m, 1H, N-CH, major and minor conformers), 2.65-2.59 (m, 1H) and 1.82-1.19 (m, 16H).

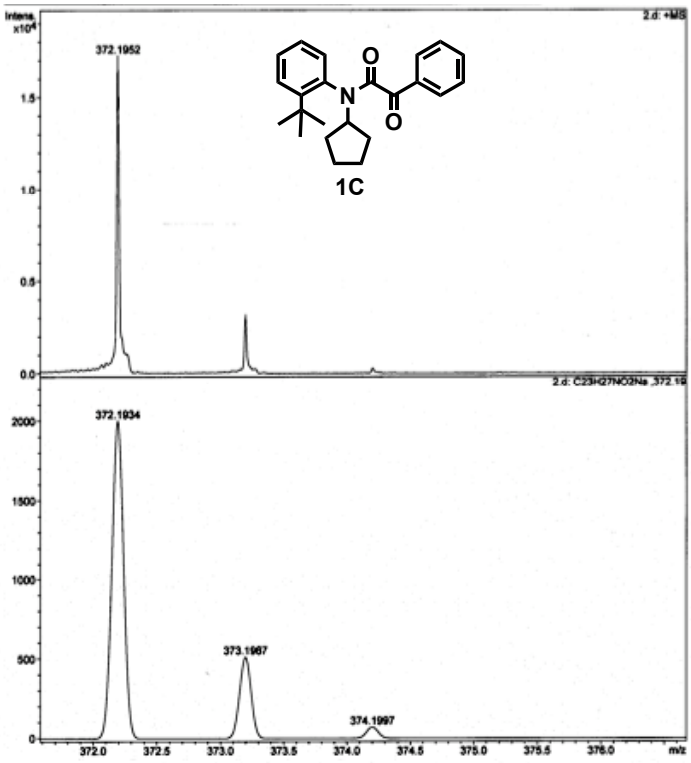


^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 190.49, 167.17, 149.19, 134.52, 134.49, 134.00, 132.25, 131.47, 130.28, 129.46, 129.21, 128.82, 126.06, 60.67, 37.12, 32.65, 31.92, 28.79, 24.05 and 23.92.



HRMS-ESI (m/z) ($[M + Na]^+$): 372.1934

Calculated: 372.1934; Observed: 372.1952



HPLC analysis conditions:

For both analytical and preparative injections

Column: (AD-H); Abs. detector: 254 nm and 270 nm

Mobile phase: Hexanes: IPA = 96:04

Flow rate: 0.5 mL/min (Analytical), and 4.5 mL/min (Preparative / semi preparative).

Retention times (min): ~13.94 [(-)-**1c**] and ~19.82 [(+)-**1c**] (Analytical)

~9.02 [(-)-**1c**] and ~11.95 [(+)-**1c**] (Preparative / semi preparative).

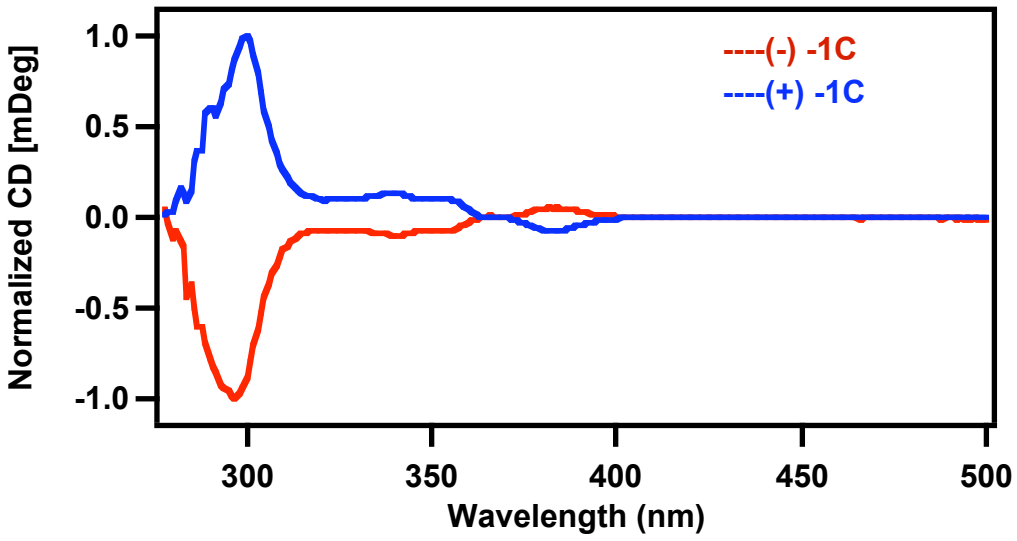
Optical Rotation $[\alpha]_D^{28}$:

HPLC peak retention time at ~13.94 min, (-)-**1c** (c = 0.1 %, CH_3OH) = -98

HPLC peak retention time at ~19.82 min, (+)-**1c** (c = 0.1 %, CH_3OH) = +101

CD Spectrum

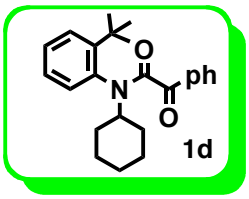
c = 0.1%, Methanol



4.4 Benzoylformamide **1d**

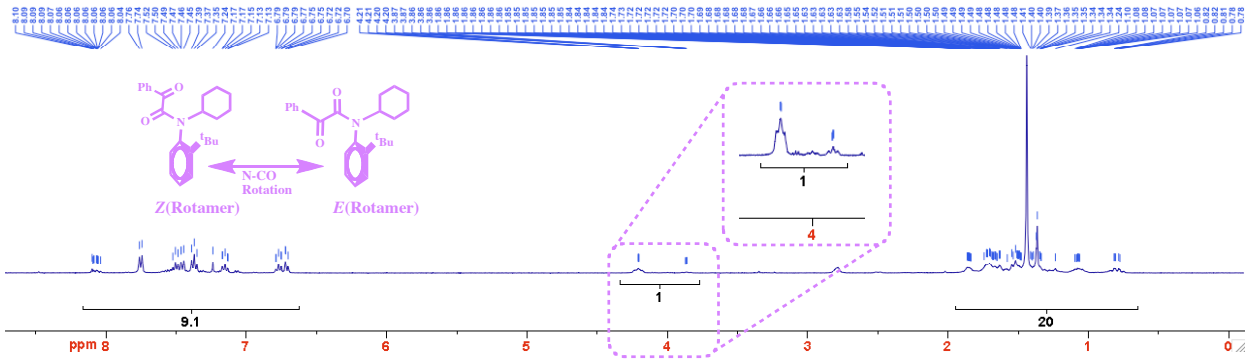
The title compound was purified by flash chromatography on silica gel with a solvent polarity of 1-20% EtOAc-Hexanes as gradient.

R*f* = 0.5 (20 % EtOAc-80%Hexanes)

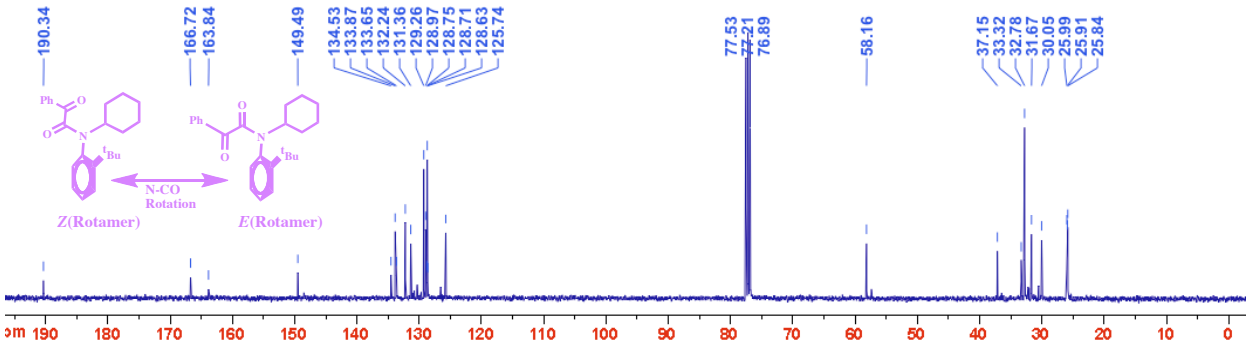


X-ray: see section 11 for details; see attached cif file.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.10 -6.70 (m, 9H), 4.21 -3.65(m, 1H, N-CH, major and minor conformers), 1.86 -0.78(m, 19H).

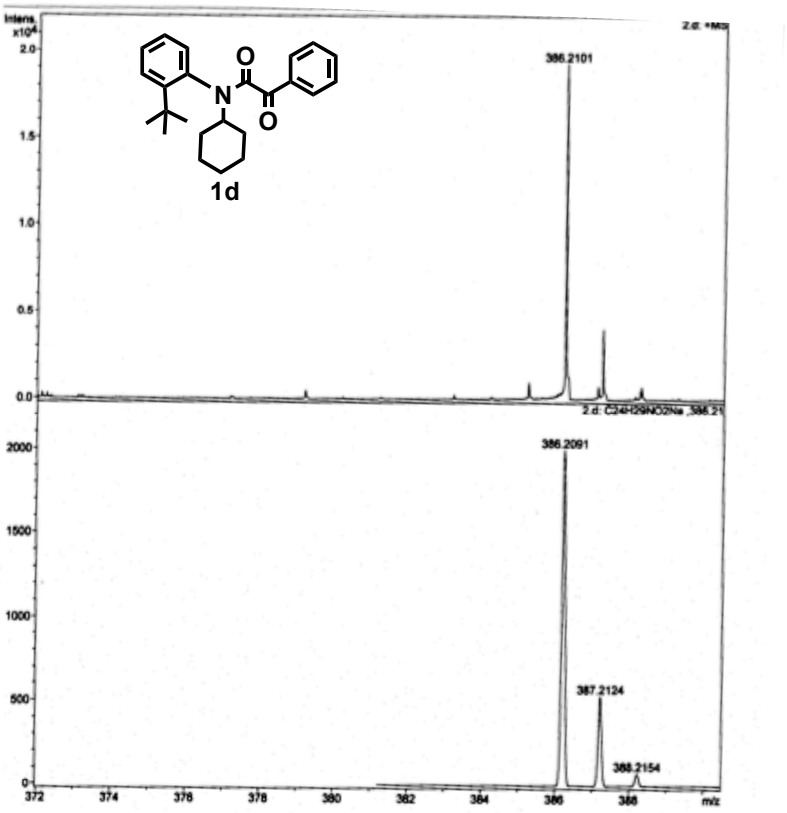


^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 190.34, 166.72, 163.84, 149.49, 134.53, 133.87, 133.65, 132.24, 131.36, 129.26, 128.97, 128.75,128.71,128.63, 125.74, 58.16, 37.15, 33.32, 32.78, 31.67, 30.05, 25.99, 25.91 and 25.84.



HRMS-ESI (m/z) ([M + Na]$^+$): 386.2091

Calculated: 386.2091; Observed: 386.2101



HPLC analysis conditions:

For both analytical and preparative injections

Column: (AD-H); Abs. detector: 254 nm and 270 nm

Mobile phase: Hexanes: IPA = 96:04

Flow rate: 0.5 mL/min (Analytical), and 4.5 mL/min (Preparative).

Retention times (min): ~12.94 [(-)-**1d**] and ~20.49 [(+)-**1d**] (Analytical)

~8.53 [(-)-**1d**] and ~13.35 [(+)-**1d**] (Preparative / semi preparative).

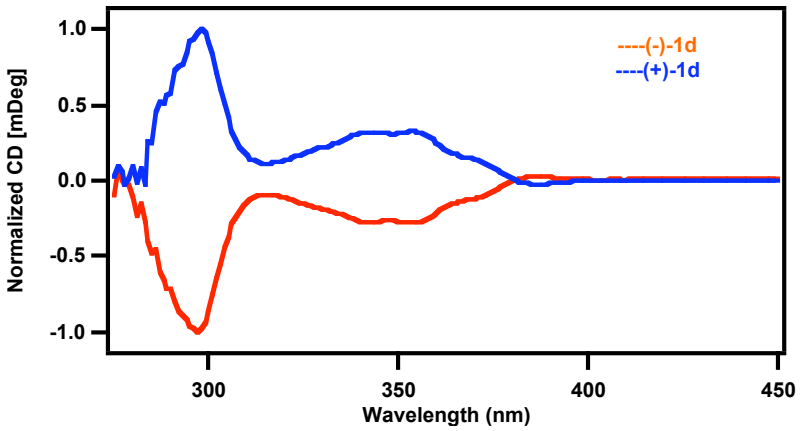
Optical Rotation $[\alpha]_D^{28}$:

HPLC peak retention time at ~12.94 min, (-)-**1d** (c = 0.1 %, CH_3OH) = -31

HPLC peak retention time at ~20.49 min, (+)-**1d** (c = 0.1 %, CH_3OH) = +30

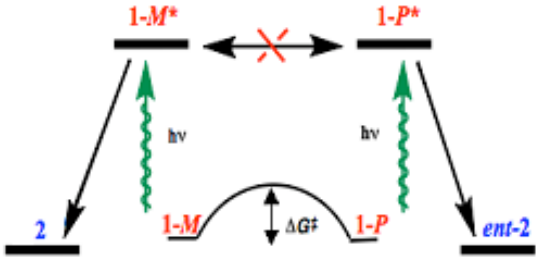
CD Spectrum

c = 0.1%, Methanol



5. Enantiomerization kinetics of non-biaryl atropisomeric benzoylformamides.

Racemization of optically pure non-biaryl atropisomeric benzoylformamides was followed at 75 °C in 2-propanol for **1a** and **1b** and at 110 °C in octane/2-propanol 97/3 (v/v) for **1d**. The racemization rate was followed by HPLC analysis at different time intervals (Figure S-1). The activation energy (Table S1) for racemization was computed from equation 1.



$$k_{rac} = \kappa\left(\frac{k_B T}{h}\right)e^{-\Delta G^{\neq}/RT}$$

$$\Delta G^{\neq} = -RT\ln\left(\frac{hk_{rac}}{\kappa hTk_B}\right)$$

The half-life of racemization, $\tau_{1/2}$, can be calculated using the rate constant of enantiomerization k_{enant} (assuming **1-*P*$_0$** = 0 at t = 0).

$$\ln\left(\frac{x_{eq}}{x_{eq}-x}\right) = \ln\left(\frac{R_0}{2R-R_0}\right) = \ln\left(\frac{R+S}{R-S}\right) = 2k_{enant}t \qquad \textbf{Equation 1.}$$

$$\ln\left(\frac{R_0}{R_0-x}\right) = k_{rac}t$$

Where R_0 is the initial concentration of the (*R*)-enantiomer; $x = R_0 - R,S$ (concentration of the racemate at time *t*); and k_{rac} is the rate of constant of racemization.

Note: $R_0 = R + S$
At 50% ee, the equation becomes:

$$\tau_{1/2} = \frac{\ln 2}{2k_{enant}} \text{ or } \tau_{1/2} = \frac{\ln 2}{k_{rac}}$$

Table S1: Activation energy ($\Delta G^{\ddagger}_{enant}$) and half-life ($\tau_{1/2}$) for enantiomerization of optically pure non-biaryl atropisomeric benzoylformamides.

Compd.	Temp.	Solvent	$\Delta G^{\ddagger}_{enant}$ (kcal.mol^{-1})	k_{enant} (sec^{-1})	$(\tau_{1/2})_{enant}$
(-)-1a	75 ^{o}C	2-propanol	30.52	4.92x10^{-7}	8.16days
(+)-1a	75 ^{o}C	2-propanol	30.52	4.92x10^{-7}	8.16 days
(-)-1b	75 ^{o}C	2-propanol	30.79	3.31x10^{-7}	12.1 days
(+)-1b	75 ^{o}C	2-propanol	30.79	3.42x10^{-7}	11.7 days
(-)-1d	110 ^{o}C	Octane / 2-propanol 97/3 (v/v)	31.38	9.8x10^{-6}	0.41 days (9.84 h)
(+)-1d	110 ^{o}C	Octane / 2-propanol 97/3 (v/v)	31.41	9.54x10^{-6}	0.42 days (10.08 h)

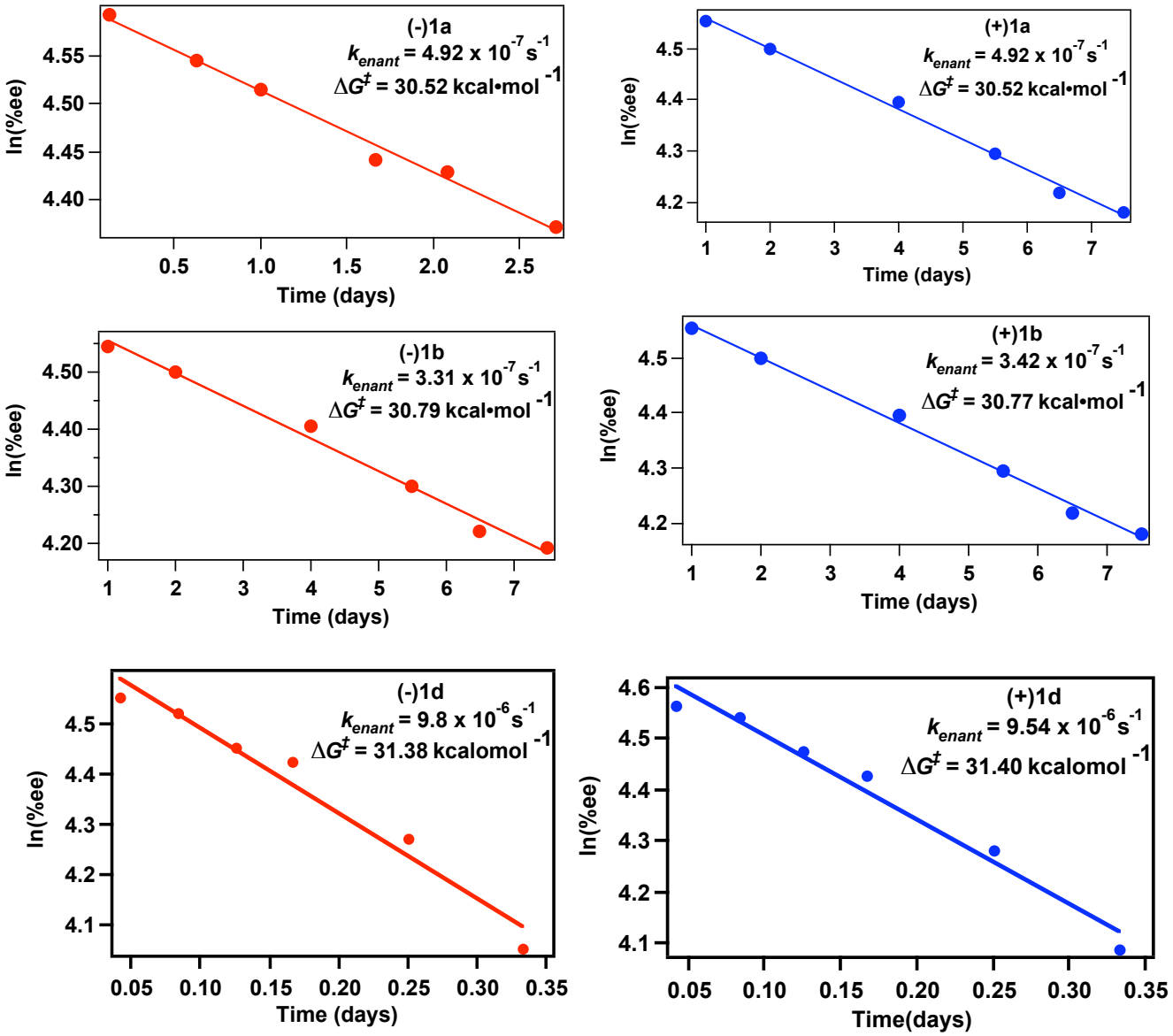
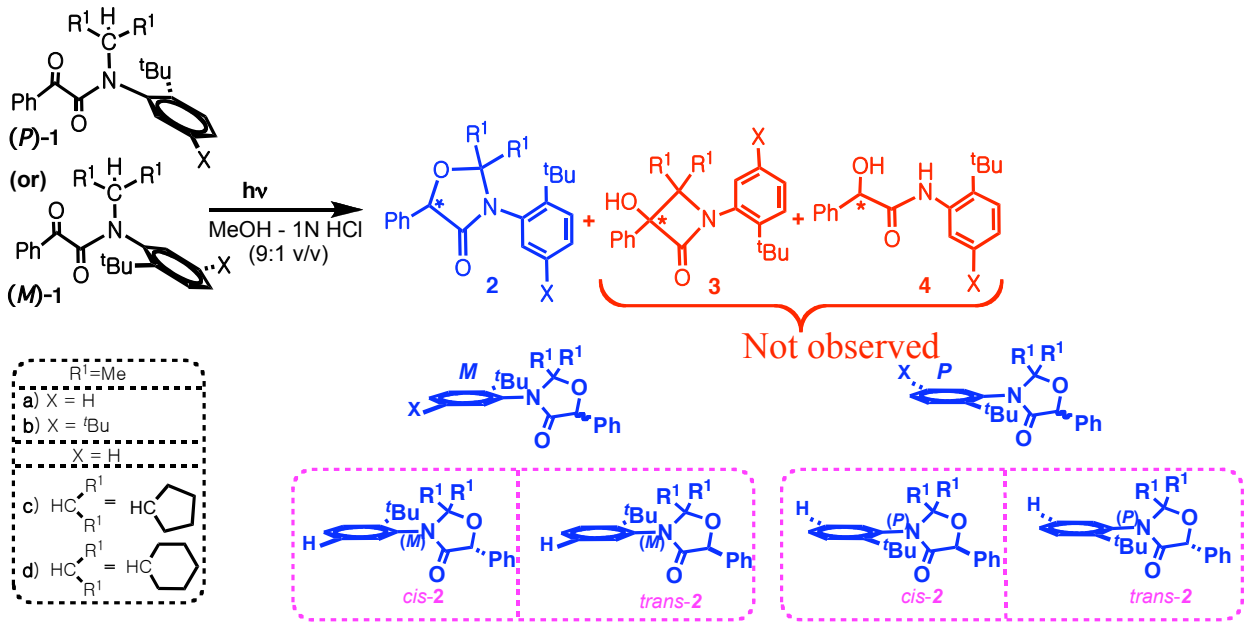


Figure S1: Enantiomerization kinetics of optically pure non-biaryl atropisomeric benzoylformamides **1a, 1b** and **1c**.

6. General irradiation procedures.



Scheme S5: General irradiation procedure for benzoylformamides **1**

Optically pure (*P* or *M* isomer) of benzoylformamides **1a-d** (0.001 mM of **1a**; 0.008 mM of **1b**; 0.003 mM of **1c**; 0.003 mM of **1d**) in MeOH-1N HCl (9:1v/v) was irradiated for a given time interval in Pyrex tube with a 450 W high-pressure mercury lamp, at various temperatures and under constant flow of nitrogen. The reaction was monitored by ^{1}H NMR spectroscopy. After irradiation, the reaction mixture was basified with triethylamine and concentrated under reduced pressure and the photoproducts were isolated by chromatography and characterized by NMR spectroscopy, mass spectrometry, single crystal XRD and by HPLC. HPLC analysis of the photolysate on chiral stationary phases gave the optical purity of the photoproducts.

7. Monitoring photochemical Type II reaction of axially chiral benzoylformamide 1a leading to Oxazolidine-4-one 2a by ^{1}H NMR spectroscopy

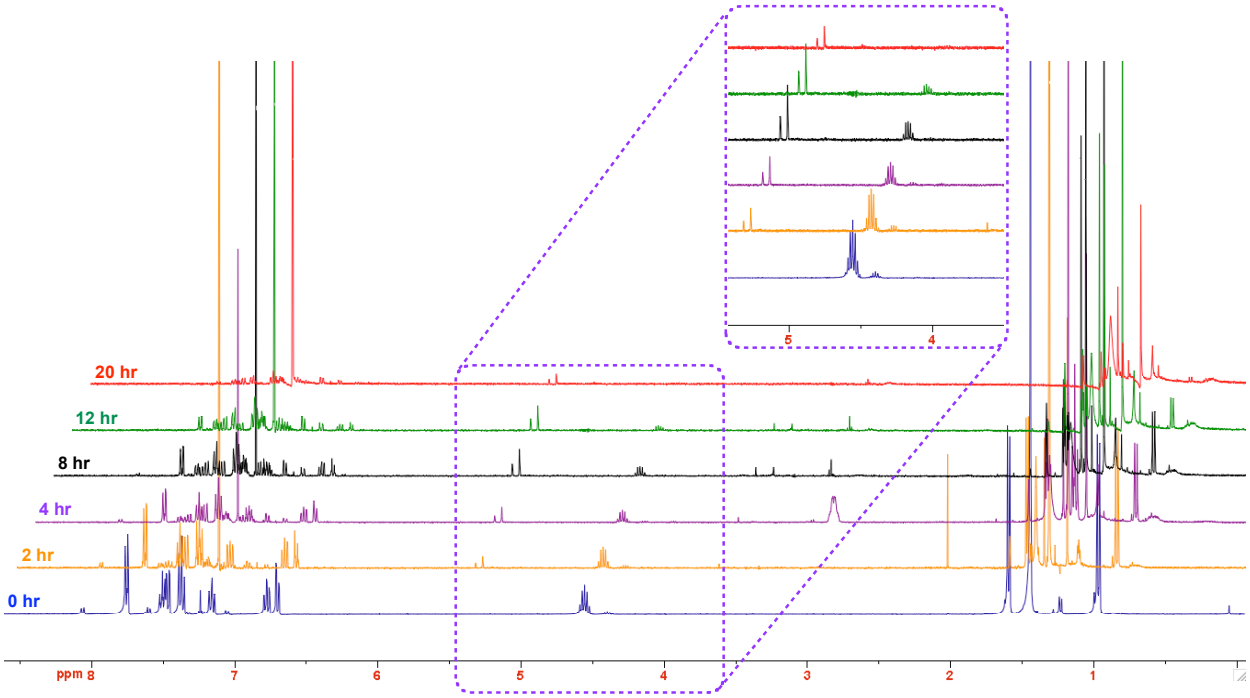


Figure S2: Time dependent irradiation of benzoylformamide **1a** in 9/1 v/v of MeOH-1N HCl followed by followed by ^{1}H NMR spectroscopy (400 MHz; ^{1}H NMR recorded in $CDCl_3$)

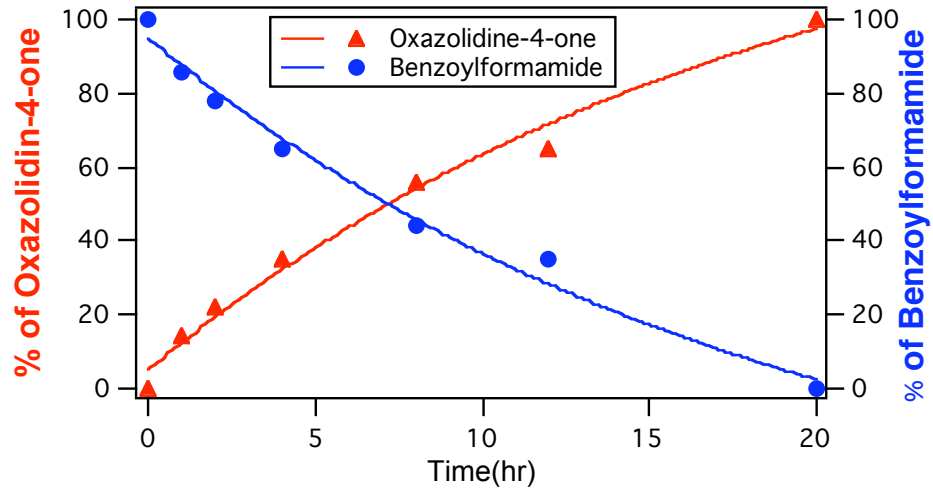
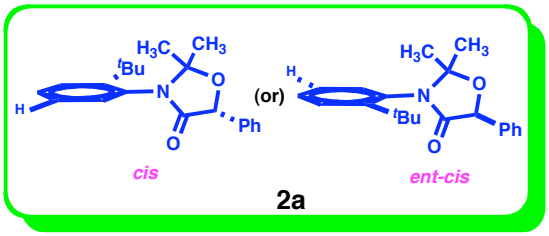


Figure S3: Time dependent irradiation to monitor the reaction progress. Formation of Oxazolidine-4-one **2a** [mixture of *cis* and *trans* (Red)] and disappearance of the reactant benzoylformamide **1a** (Blue)

8. Characterization of photoproducts.

8.1 *cis*-oxazolidine-4-one **2a**

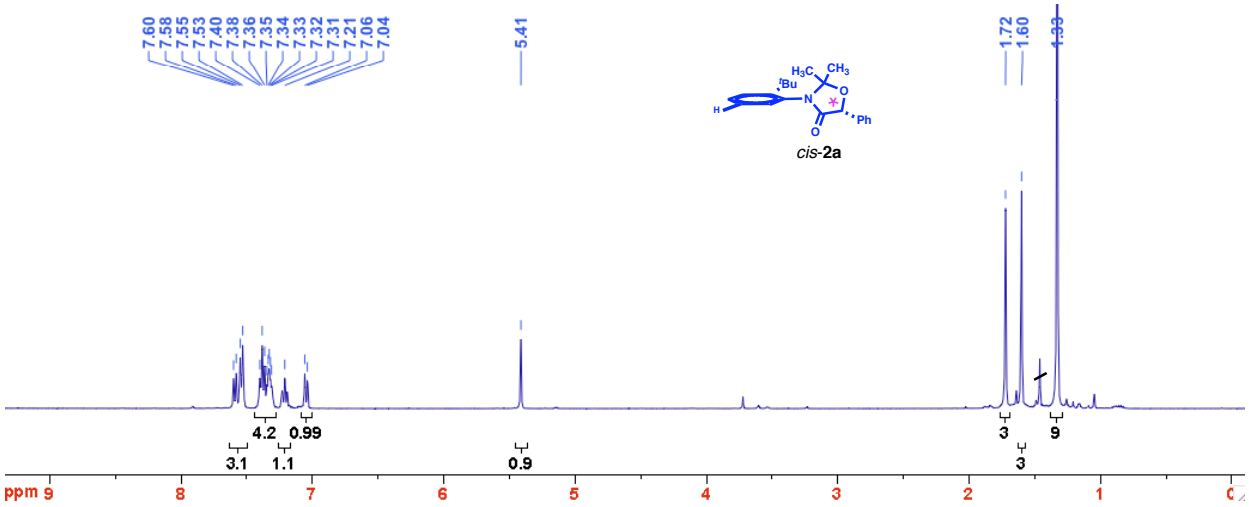


The title compound was purified by preparative thin layer chromatography using S20% EtOAc-80% Hexanes as the mobile phase.

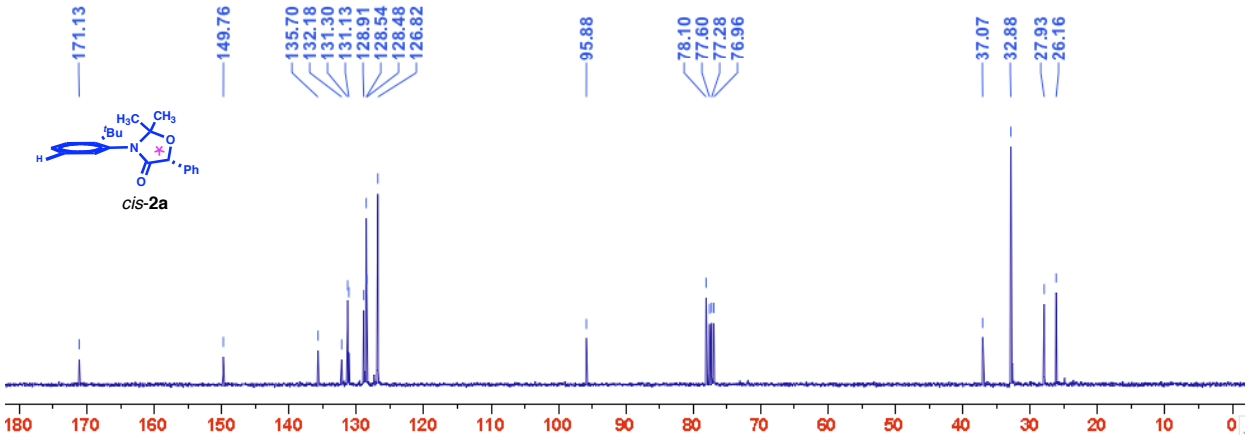
R*f* = 0.25 (20 % EtOAc-80%Hexanes)

X-ray: see section 11 for details; see attached cif file.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.60 – 7.04 (Ar, 9H), 5.41 (s, 1H), 1.72 (s, 3H), 1.60 (s, 3H) and 1.33 (s, 9H).

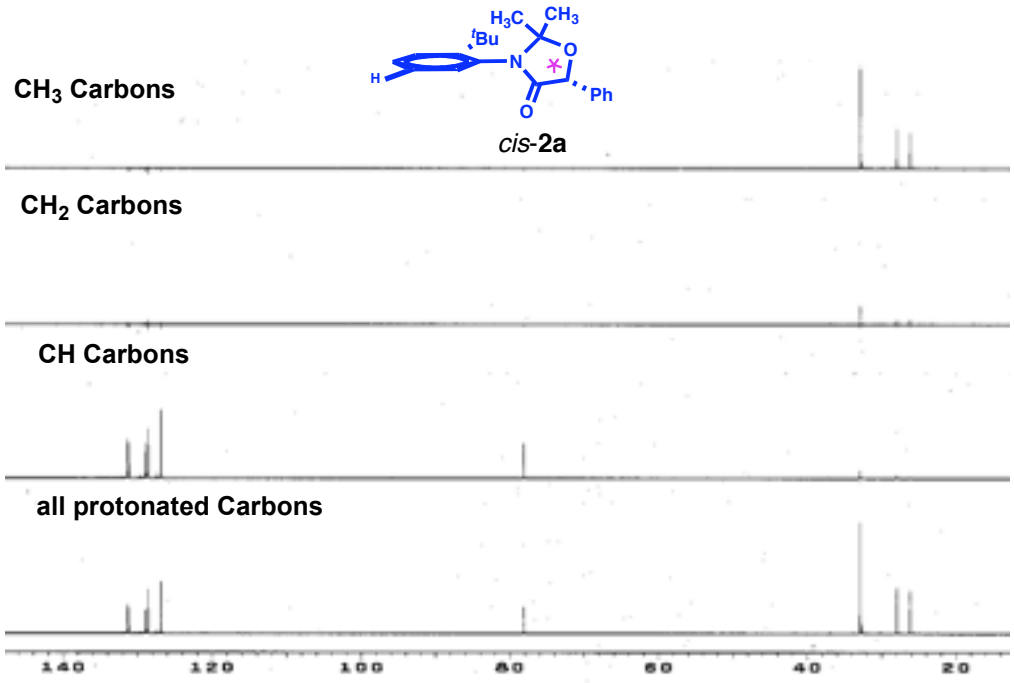


^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 171.13, 149.76, 135.70, 132.18, 131.30, 131.13, 128.91, 128.54, 128.48, 126.82, 95.88, 78.10, 37.07, 32.88, 27.93 and 26.16



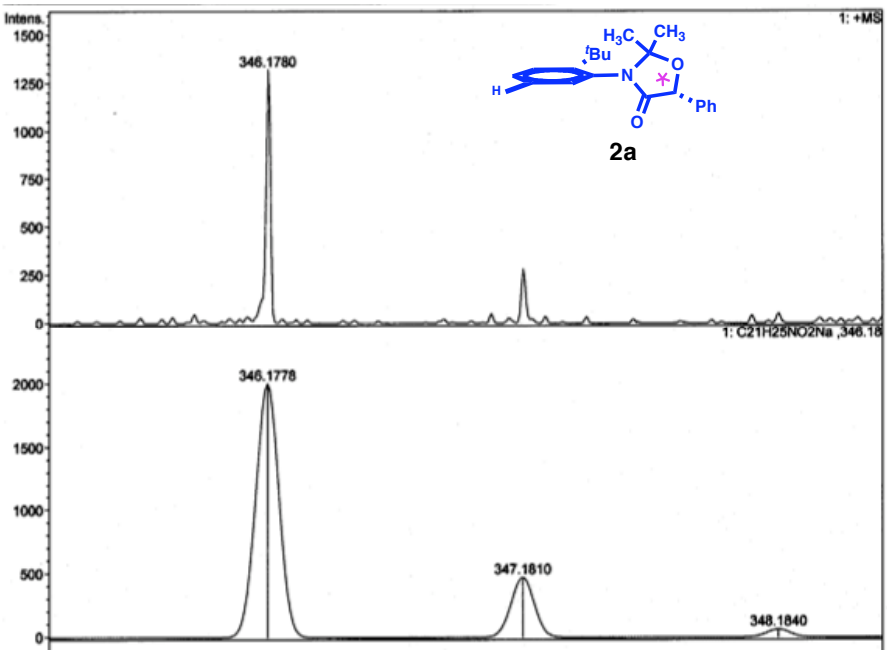
^{13}C DEPT spectra:

Analysis of ^{13}C DEPT shows C-5 hydrogen corresponding to the carbocycle (apart from aromatic hydrogen and methyl / *tert*- butyl hydrogens). This confirms the formation of the 5-membered oxoazolidine-4-one *cis*-**2a**.



HRMS-ESI (m/z) ([M + Na]$^+$): 346.1778

Calculated: 346.1778; Observed: 346.1780



HPLC analysis conditions:

Chiralpak OD-3 and Chiralpak OD-H (both the columns were combined and used for analytical seperation. Abs. detector: 220 nm and 254 nm; Mobile phase: Hexanes: IPA = 96:04. Flow rate: 1 mL/min (Analytical); Retention times (min): ~36.57 [(+)-*cis*-**2a**] and ~55.19 [(-)-*cis*-**2a**]

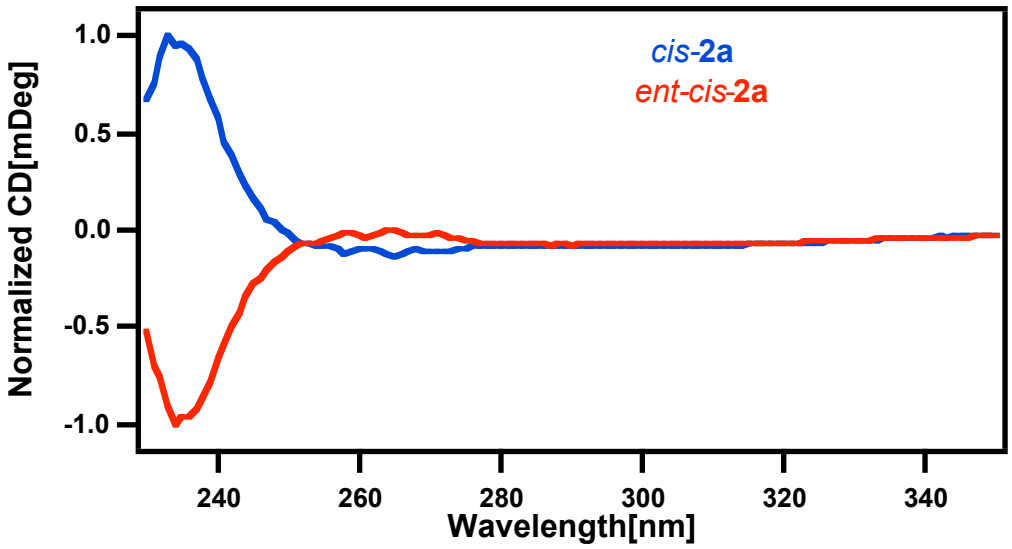
Optical Rotation $[\alpha]_D^{28}$:

HPLC peak retention time at ~36.57 min, (*cis*-**2a**) (*c* = 0.1 %, CH_3OH) = +29

HPLC peak retention time at ~ 55.19 min, (*ent-cis*-**2a**) (*c* = 0.1 %, CH_3OH) = -31

CD Spectrum

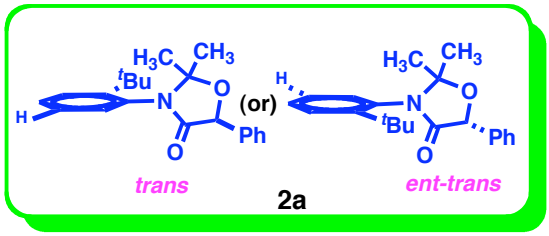
c = 0.1%, Methanol



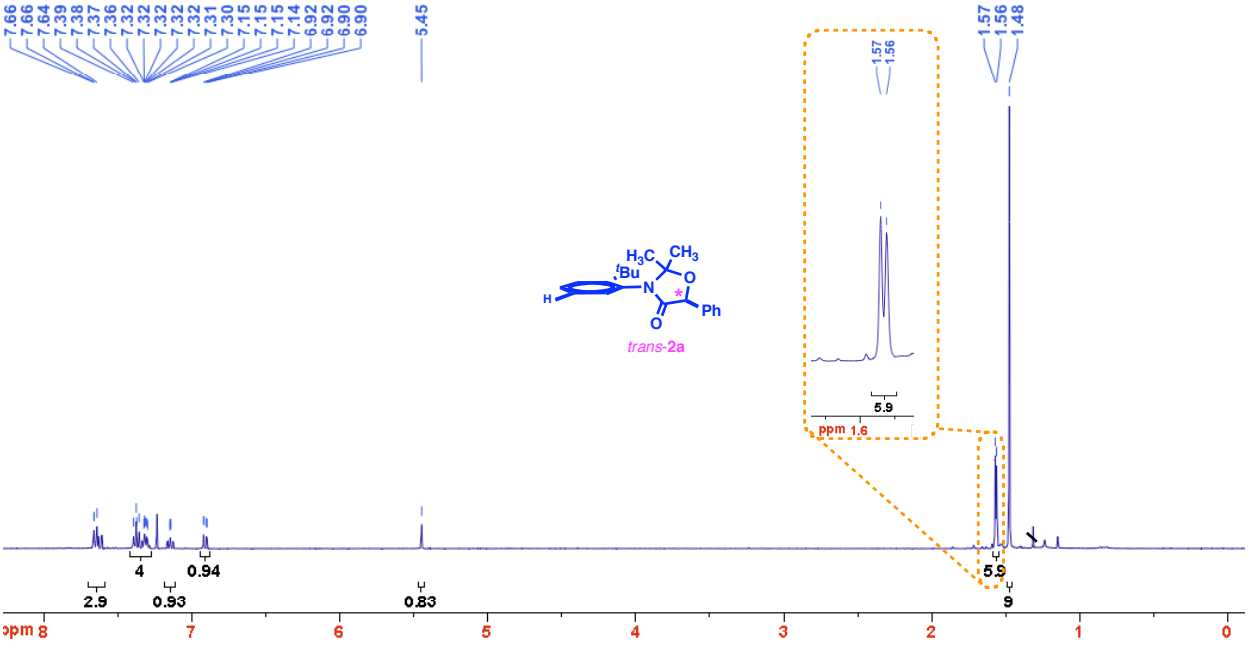
8.2 *trans*-oxazolidine-4-one **2a** [*trans*-**2a**]

The title compound was purified by preparative thin layer chromatography using 20% EtOAc-80% Hexanes as the mobile phase.

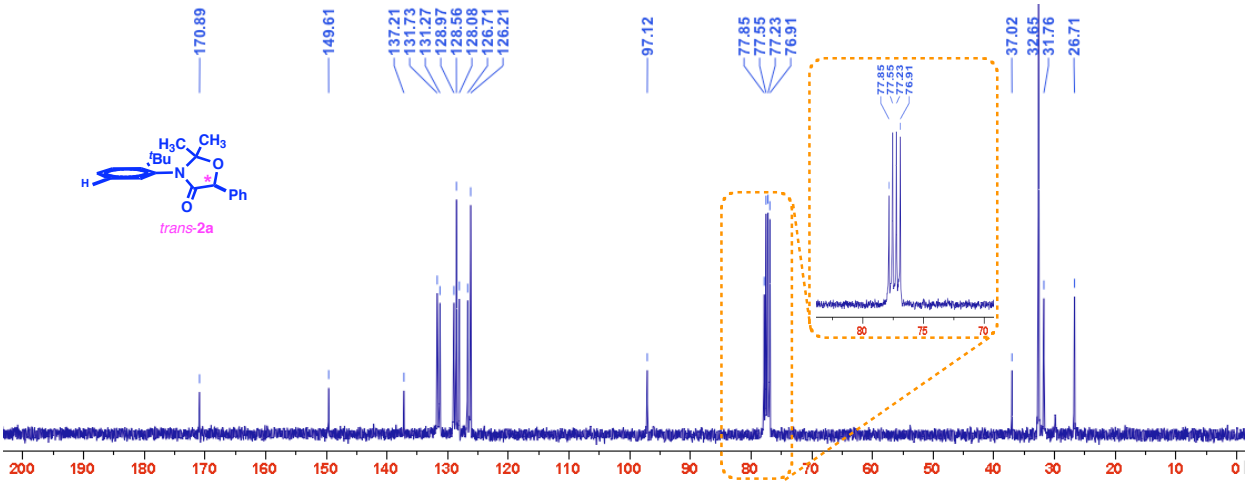
R*f* = 0.25 (20 % EtOAc-80%Hexanes)



[1]H NMR (400 MHz, $CDCl_3$, δ ppm): 7.66-7.64 (Ar, 3H), 7.39-7.30 (Ar, 4H), 7.15 (Ar, 1H), 6.90 (Ar, 1H), 5.45 (s, 1H), 1.57-1.56 (partially merged singlets, 6H) and 1.48 (s, 9H).

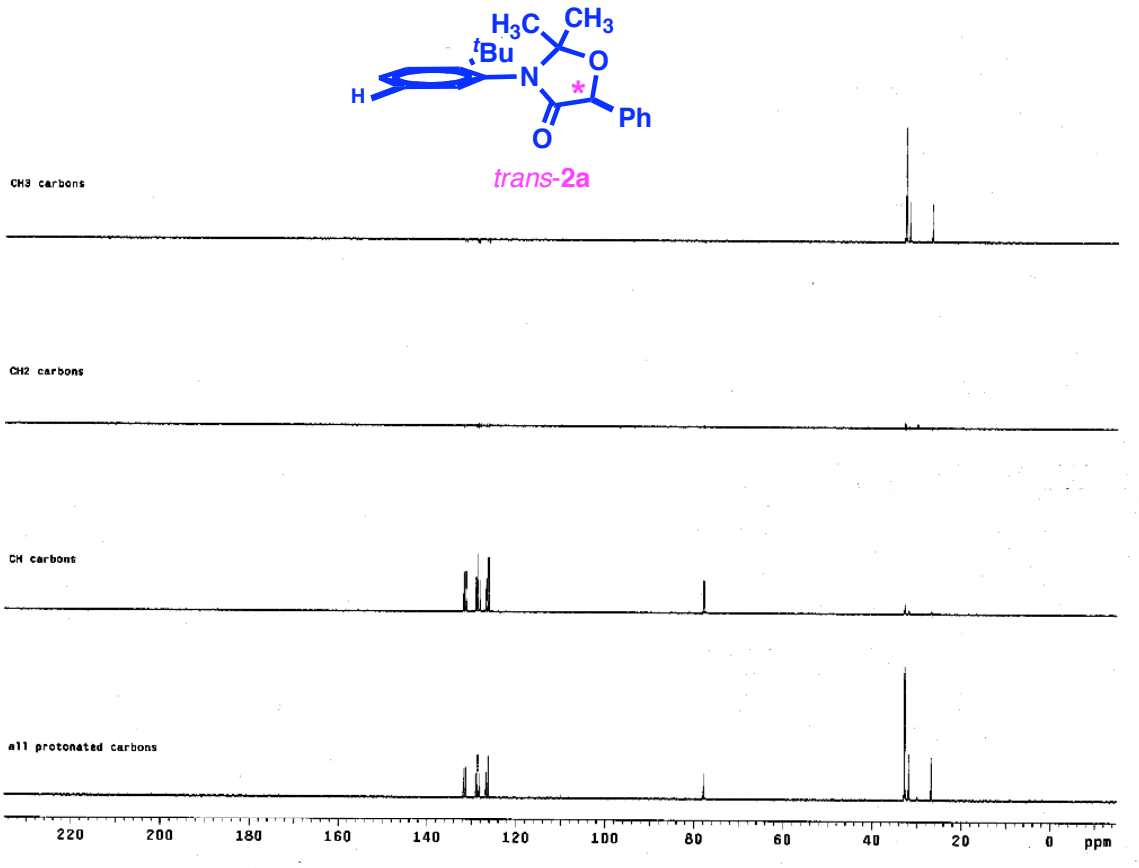


[13]C NMR (100 MHz, $CDCl_3$, δ ppm): 170.89, 149.61, 137.73, 131.27, 128.97, 128.56, 128.08, 126.71, 126.21, 97.12, 77.85, 37.02, 32.65, 31.76 and 26.71.



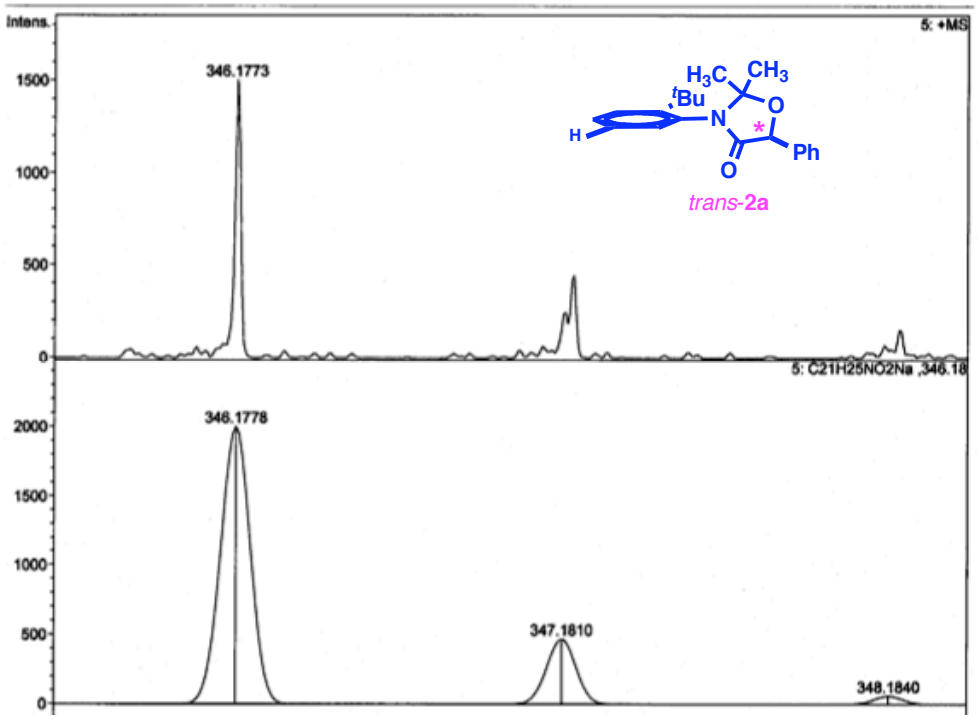
^{13}C DEPT spectra:

Analysis of ^{13}C DEPT shows C-5 hydrogen corresponding to the carbocycle (apart from aromatic hydrogen and methyl / *tert*-butyl hydrogens). This confirms the formation of the 5-membered oxoazolidine-4-one *trans*-**2a**.



HRMS-ESI (m/z) ([M + Na]$^+$): 346.1778

Calculated: 346.1778; Observed: 346.1773



HPLC analysis conditions:

For analytical injections

Column: Chiralpak OD-3 and Chiralpak OD-H (both the columns were combined and used for analytical seperation).

Abs. detector: 220 nm and 254 nm

Mobile phase: Hexanes: IPA = 96:04

Flow rate: 0.5 mL/min (Analytical)

Retention times (min): ~23.82 [(+)-*trans*-**2a**] and ~24.72 [(-)-*ent*-*trans*-**2a**] (Analytical)

Optical Rotation $[\alpha]_D^{28}$:

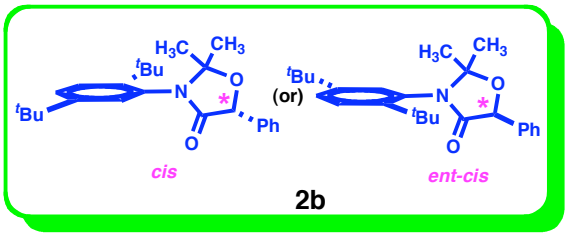
HPLC peak retention time at ~23.82 min, (*trans*-**2a**) (*c* = 0.1 %, CH_3OH) = -67

HPLC peak retention time at ~ 24.72 min, (*ent*-*trans*-**2a)** (*c* = 0.1 %, CH_3OH) = 71

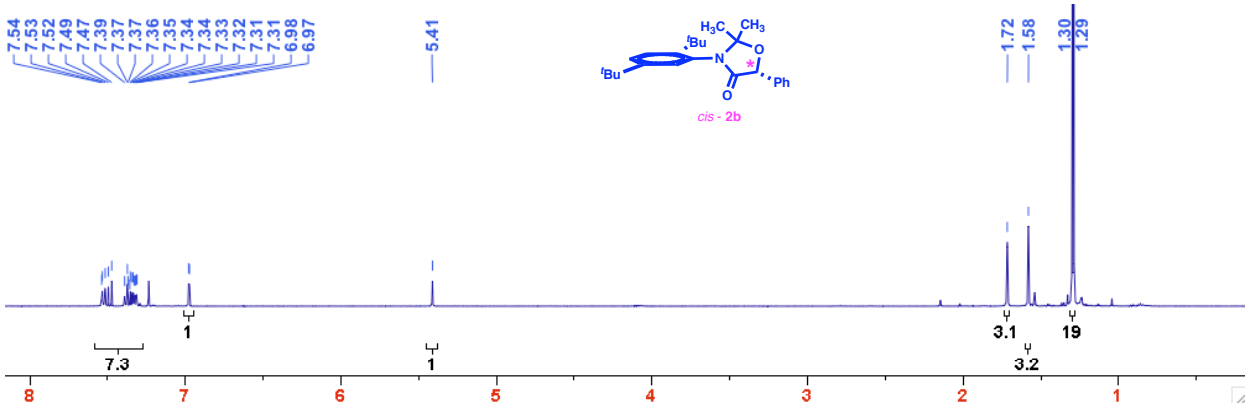
8.3 *cis*-oxazolidine-4-one- **2b** [*cis*-**2b**]

The title compound was purified by preparative thin layer chromatography wit 30% EtOAc-70% Hexanes as the mobile phase.

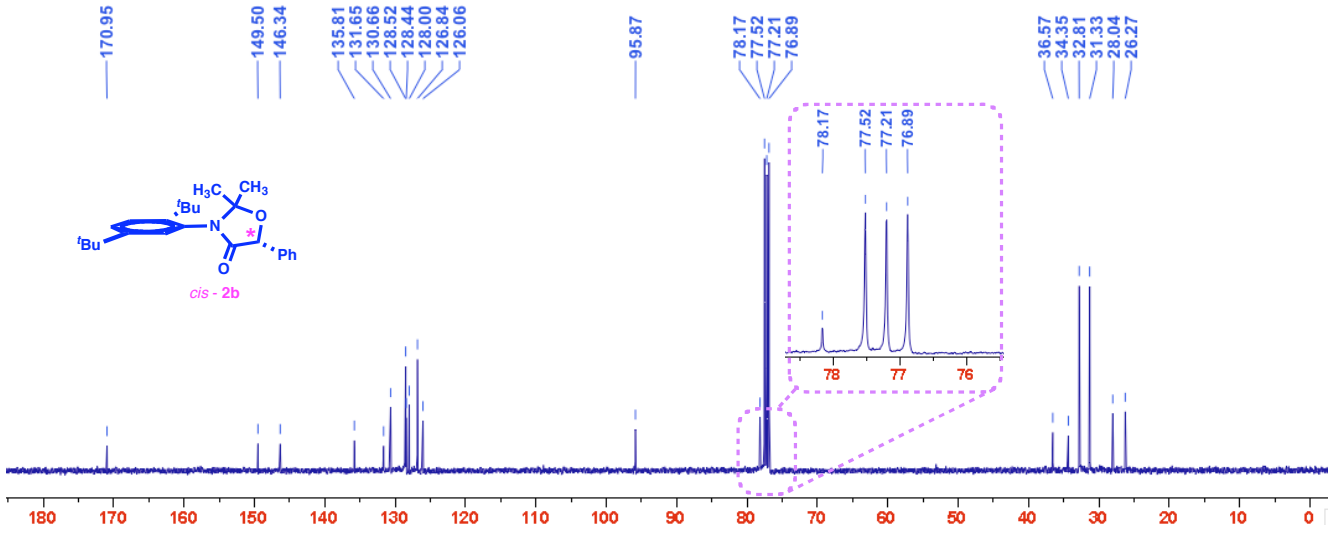
R*f* = 0.3 (30 % EtOAc-70%Hexanes)



[1]H NMR (400 MHz, $CDCl_3$, δ ppm): 7.54 – 7.31 (m, 7H), 6.98 (m, 1H), 5.41 (s, 1H), 1.72(s, 3H), 1.58 (s, 3H) and 1.30-1.29 (two merged singlets, 18H).

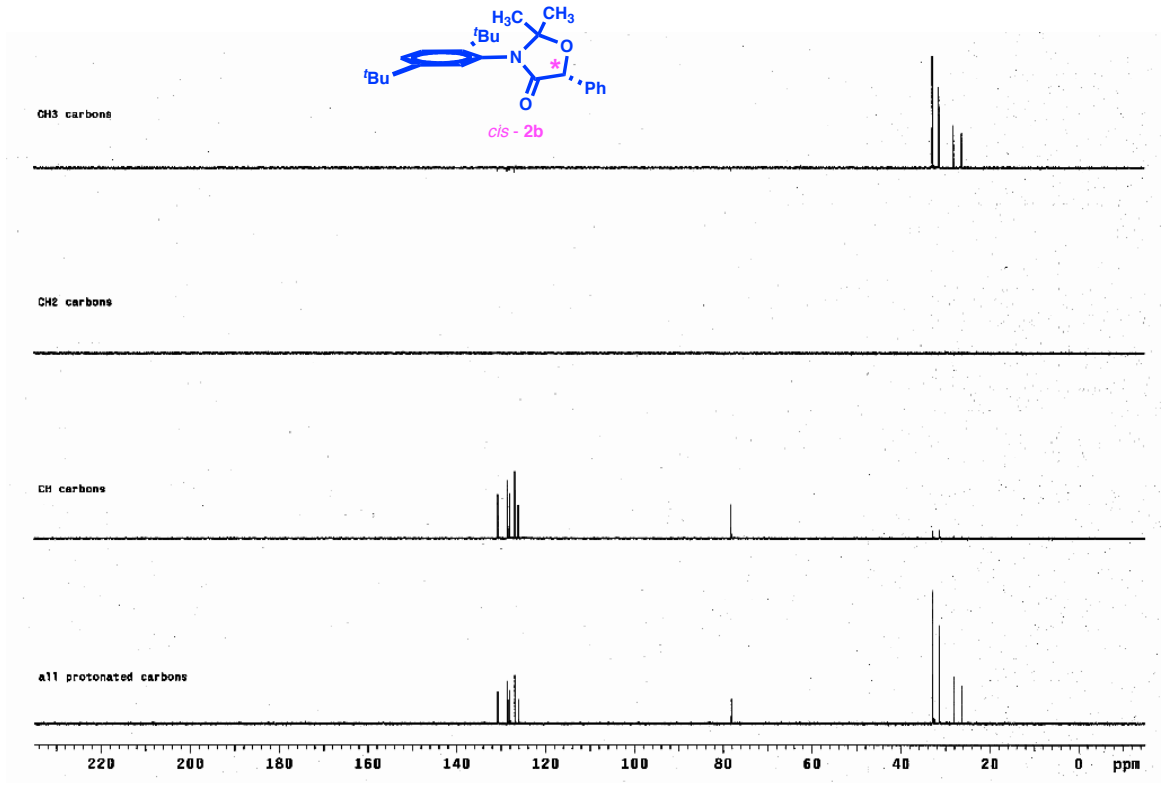


[13]C NMR (100 MHz, $CDCl_3$, δ ppm): 170.95, 149.50, 146.34, 135.81, 131.65, 130.66, 128.52, 128.44, 128.00, 126.84, 126.06, 95.87, 78.17, 36.57, 34.35, 32.81, 31.33, 28.04 and 26.27.



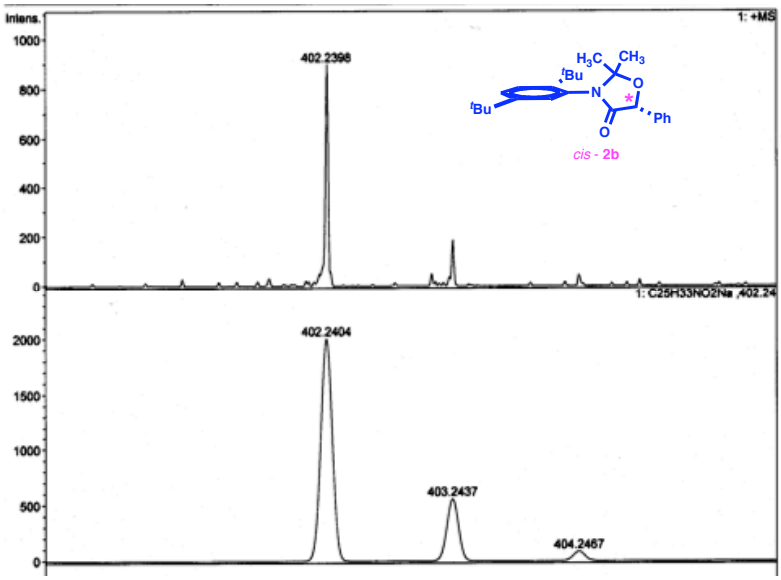
^{13}C DEPT spectra:

Analysis of ^{13}C DEPT shows C-5 hydrogen corresponding to the carbocycle (apart from aromatic hydrogen and methyl / *tert*- butyl hydrogen). This confirms the formation of the 5-membered oxoazolidine-4-one *cis*-**2b**.



HRMS-ESI (m/z) ([M + Na]$^+$): 402.2404

Calculated: 402.2404; Observed: 402.2398



HPLC analysis conditions:

For analytical injections

Column: Chiralpak OD-3 and Chiralpak OD-H (both the columns were combined and used for analytical seperation

Abs. detector: 220 nm and 254 nm

Mobile phase: Hexanes: IPA = 96:04

Flow rate: 1 mL/min (Analytical)

Retention times (min): ~14.42 [(-)-*cis*-**2b]** and ~21.52 [(+)-*ent-cis*-2**b**] (Analytical)

Optical Rotation $[\alpha]_D^{28}$:

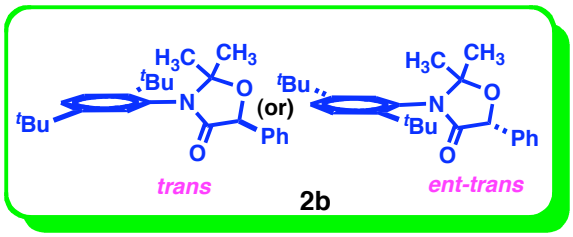
HPLC peak retention time at ~14.42 min, (*cis*-**2b**) (*c* = 0.1 %, CH_3OH) = -38

HPLC peak retention time at ~ 21.52 min, (*ent-cis*-**2b)** (*c* = 0.1 %, CH_3OH) = +35

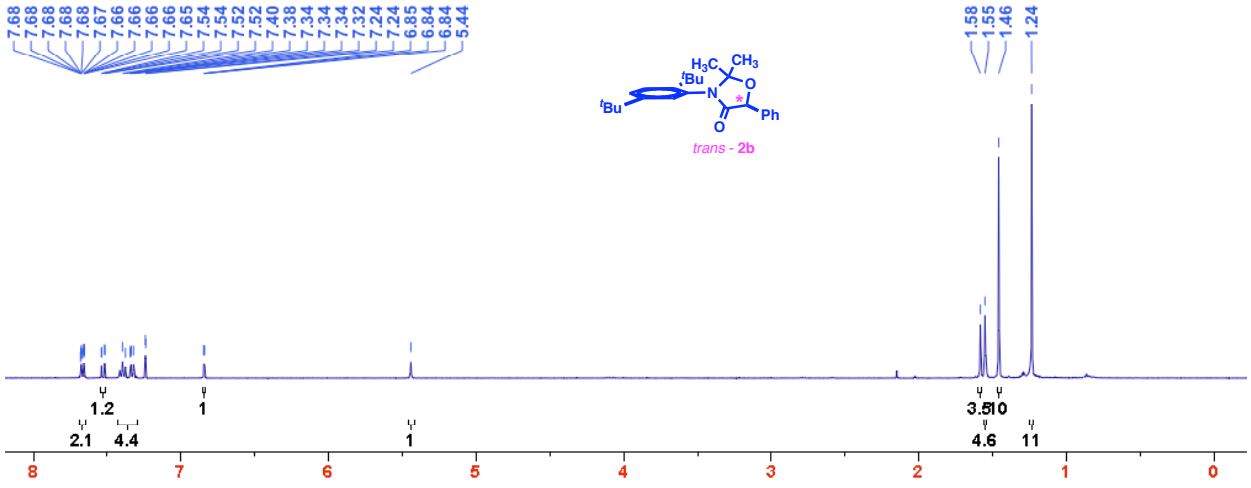
8.4 *trans*-oxazolidine-4-one- **2b** [*trans*-**2b**]

The title compound was purified by preparative thin layer chromatography with 30% EtOAc-70% Hexanes as the mobile phase.

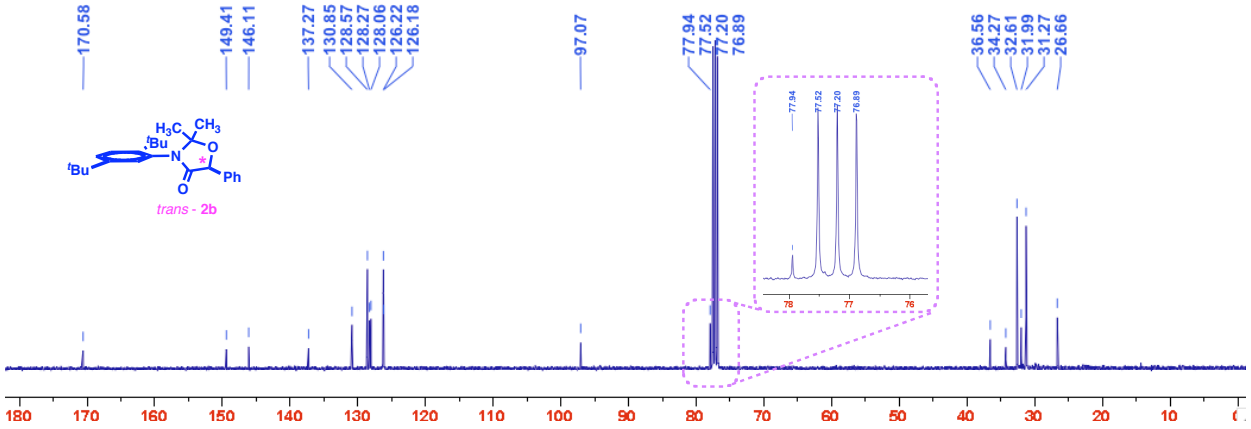
R*f* = 0.5 (30 % EtOAc-70%Hexanes)



^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.68 – 7.24 (Ar, 7H), 6.85 - 6.84 (Ar, 1H), 5.44 (s, 1H), 1.58(s, 3H), 1.55(s, 3H), 1.46 (s, 9H) and 1.24 (s, 9H).

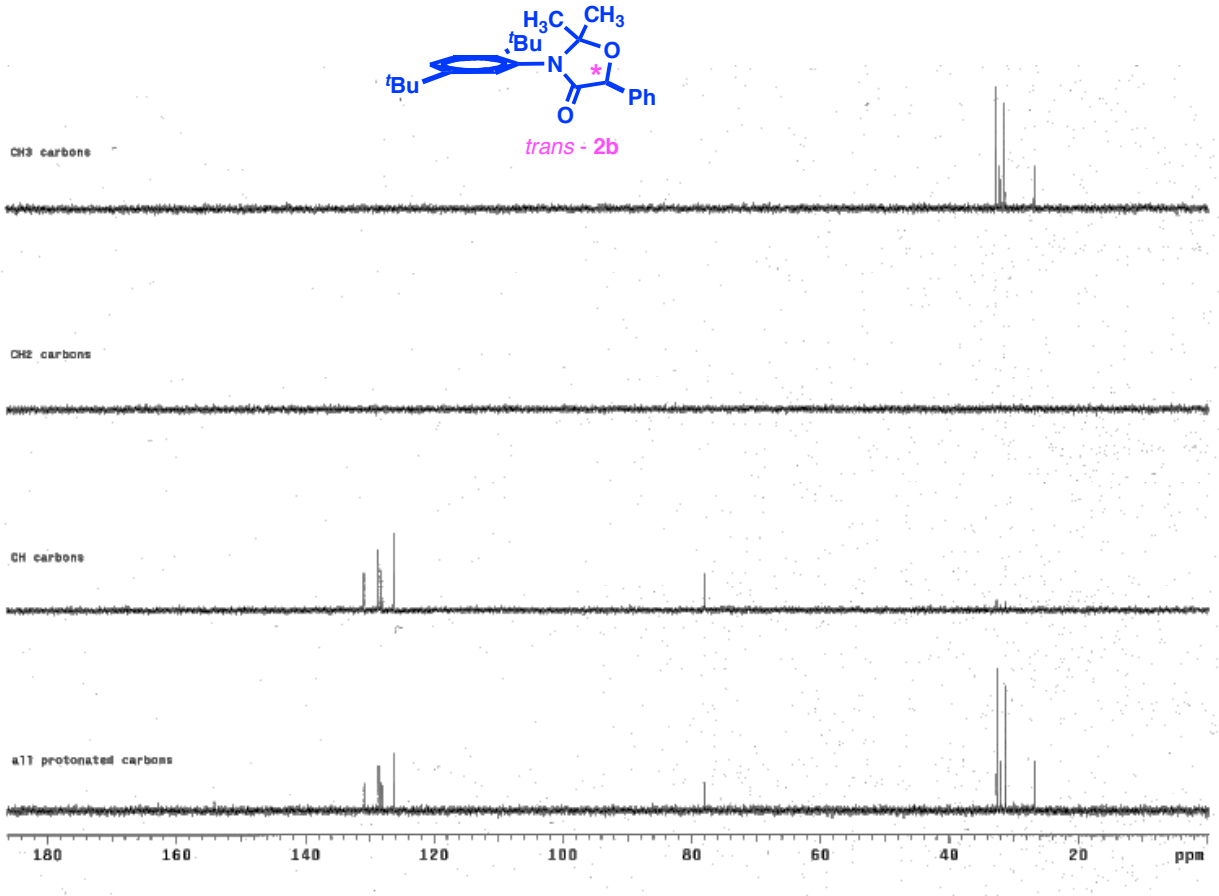


^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 178.58, 149.41, 146.11, 137.27, 130.85, 128.57, 128.27, 128.06, 126.22, 126.18, 97.07, 77.94, 36.56, 34.27, 32.61, 31.99, 31.27 and 26.66.



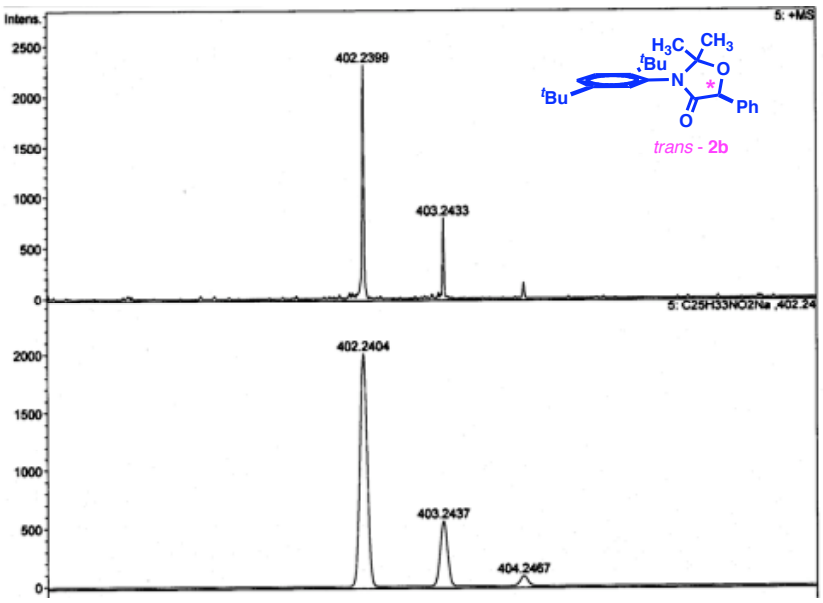
^{13}C DEPT spectra:

Analysis of ^{13}C DEPT shows C-5 hydrogen corresponding to the carbocycle (apart from aromatic hydrogen and methyl / *tert*- butyl hydrogens). This confirms the formation of the 5-membered oxoazolidine-4-one *trans*-**2b**.



HRMS-ESI (m/z) ($[M + Na]^+$): 402.2404

Calculated: 402.2404; Observed: 402.2399



HPLC analysis conditions:

For analytical injections

Column: Chiralpak OD-3 and Chiralpak OD-H (both the columns were combined and used for analytical seperation

Abs. detector: 220 nm and 254 nm

Mobile phase: Hexanes: IPA = 96:04

Flow rate: 1 mL/min (Analytical)

Retention times (min): ~13.45 [(-)-*trans*-**2b**] and ~14.42 [(+)-*ent-trans*-2**b**] (Analytical)

Optical Rotation $[\alpha]_D^{28}$:

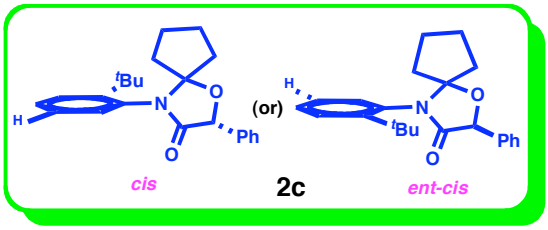
HPLC peak retention time at ~13.45 min, (*trans*-**2b**) (*c* = 0.1 %, CH_3OH) = -15

HPLC peak retention time at ~ 14.42 min, (*ent-trans*-**2b)** (*c* = 0.1 %, CH_3OH) = +13

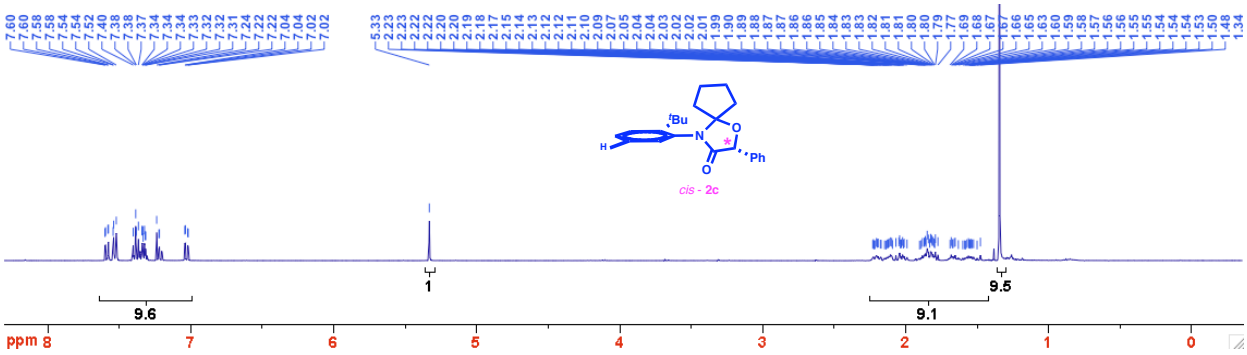
8.5 *cis*-oxazolidine-4-one- **2c** [*cis*-**2c**]

The title compound was purified by preparative thin layer chromatography with 30% EtOAc-70% Hexanes as the mobile phase.

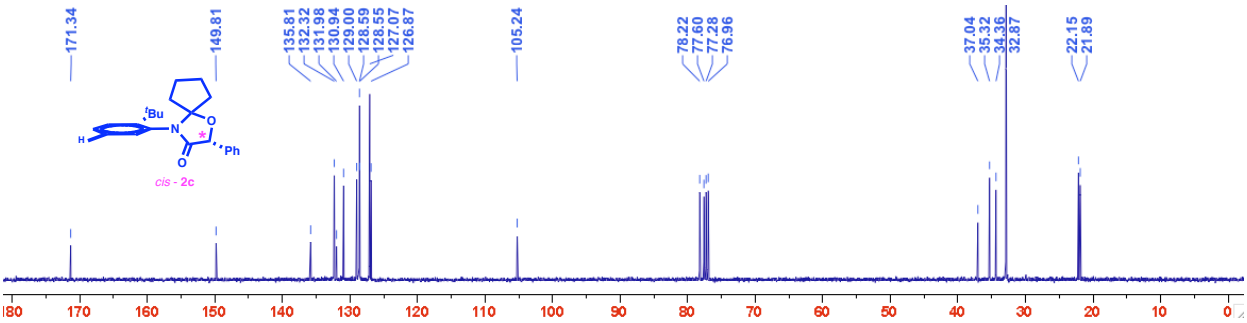
R*f* = 0.30 (30 % EtOAc-70%Hexanes)



[1]H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.60 -7.02 (Ar, 9H), 5.33(s, 1H), 2.23 -1.48(m, 8H), 1.34(s, 9H).

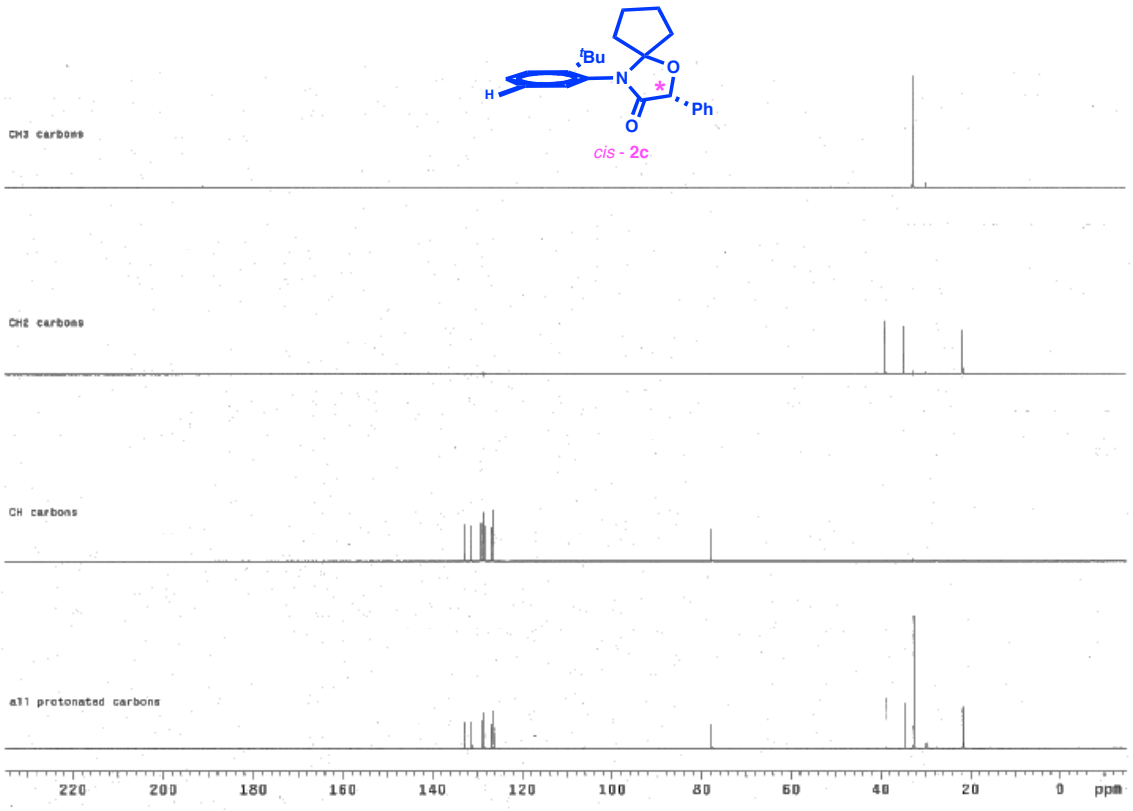


[13]C NMR (100 MHz, $CDCl_3$, δ ppm): 171.34, 149.81, 135.81, 132.32, 131.98, 130.94, 129.00, 128.59, 128.55, 127.07, 126.67, 105.24, 78.22, 37.04, 35.32, 34.36, 32.87, 22.15 and 21.89.



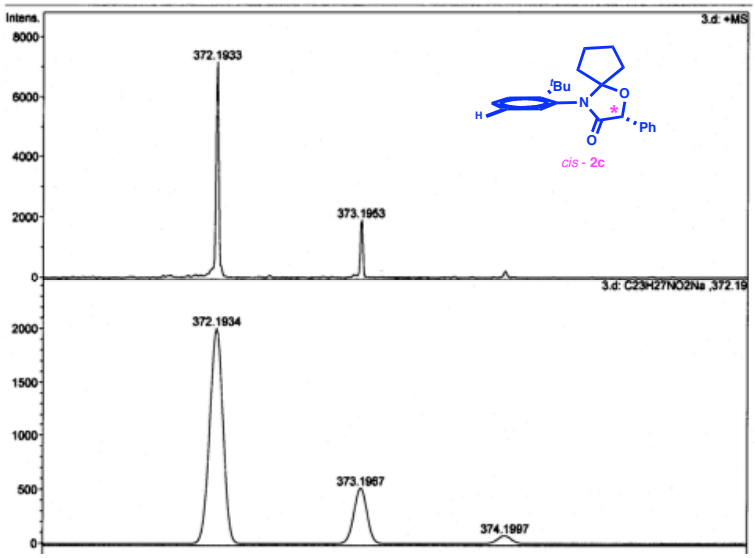
[13]C DEPT spectra:

Analysis of [13]C DEPT shows C-5 hydrogen corresponding to the carbocycle (apart from aromatic hydrogen and methyl / *tert*- butyl hydrogens). This confirms the formation of the 5-membered oxoazolidine-4-one *cis*-**2c**.



HRMS-ESI (m/z) ($[M + Na]^+$): 372.1934

Calculated: 372.1934; Observed: 372.1933



HPLC analysis conditions:

For analytical injections

Column: Chiralpak AS-H

Abs. detector: 220 nm and 254 nm

Mobile phase: Hexanes: IPA = 96:04

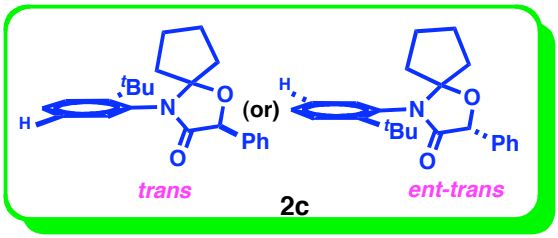
Flow rate: 0.5 mL/min (Analytical)

Retention times (min): ~12.67 [(+)-*cis*-**2c**] and ~18.22 [(-)-*ent*-*cis*-**2c**] (Analytical)

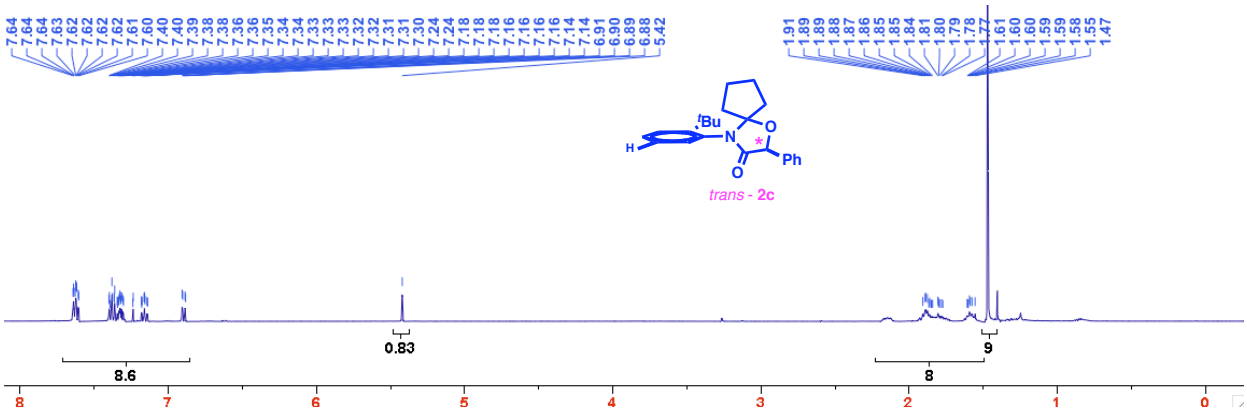
8.6 *trans*-oxazolidine-4-one **2c** [*trans*-**2c**]

The title compound was purified by preparative thin layer chromatography with 30% EtOAc-70% Hexanes as the mobile phase.

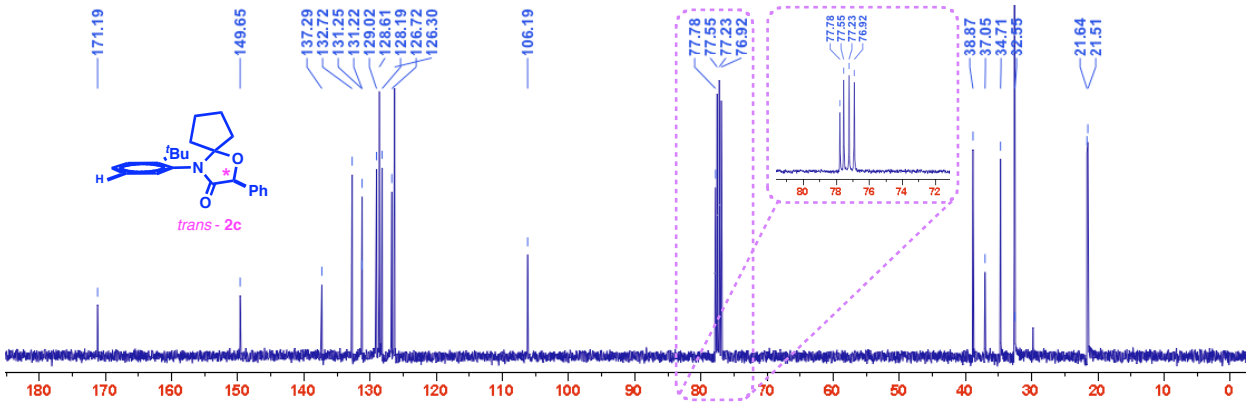
R*f* = 0.6 (30 % EtOAc-70%Hexanes)



^{1}*H-NMR* (400 MHz, $CDCl_3$, δ ppm): 7.64 -6.88 (Ar, 9H), 5.42(s, 1H), 1.91 -1.55(m, 8H), 1.47(s, 9H).

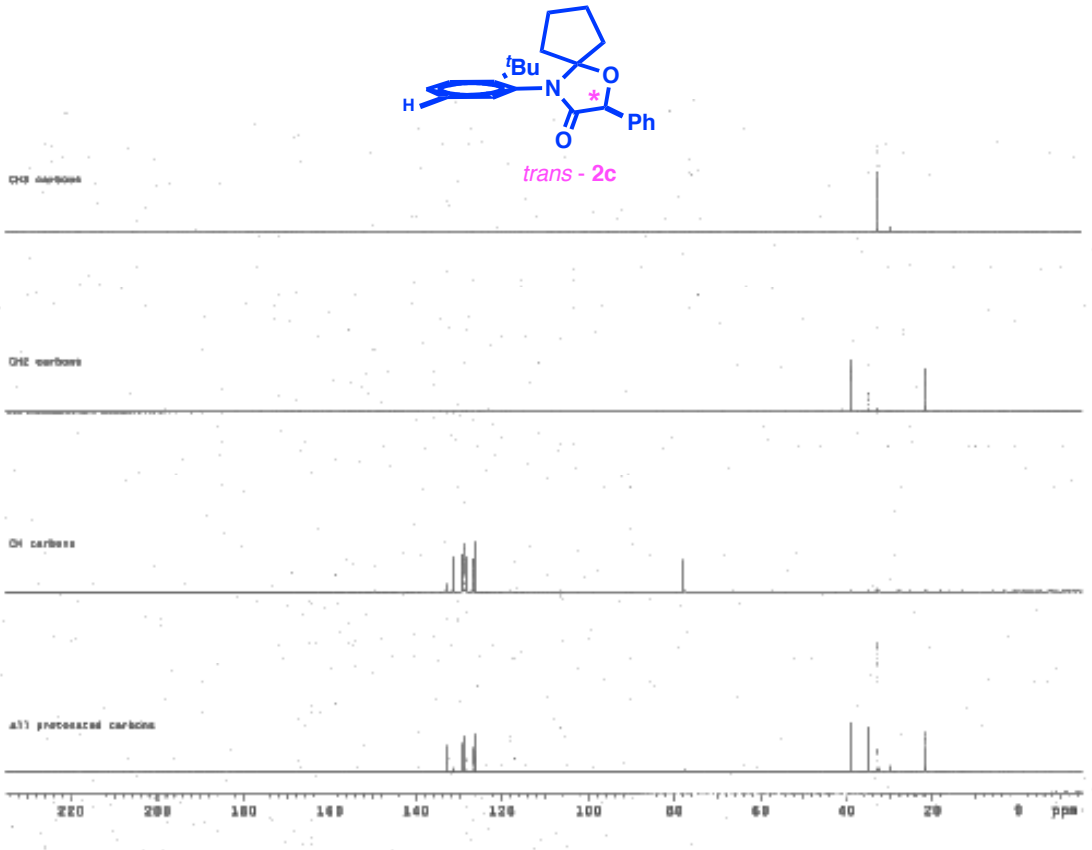


^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 171.19, 149.65, 137.29, 132.72, 131.25, 131.22, 129.02, 128.61, 128.19, 126.72, 126.30, 106.19, 77.78, 38.87, 37.05, 34.71, 32.55, 21.64 and 21.51.



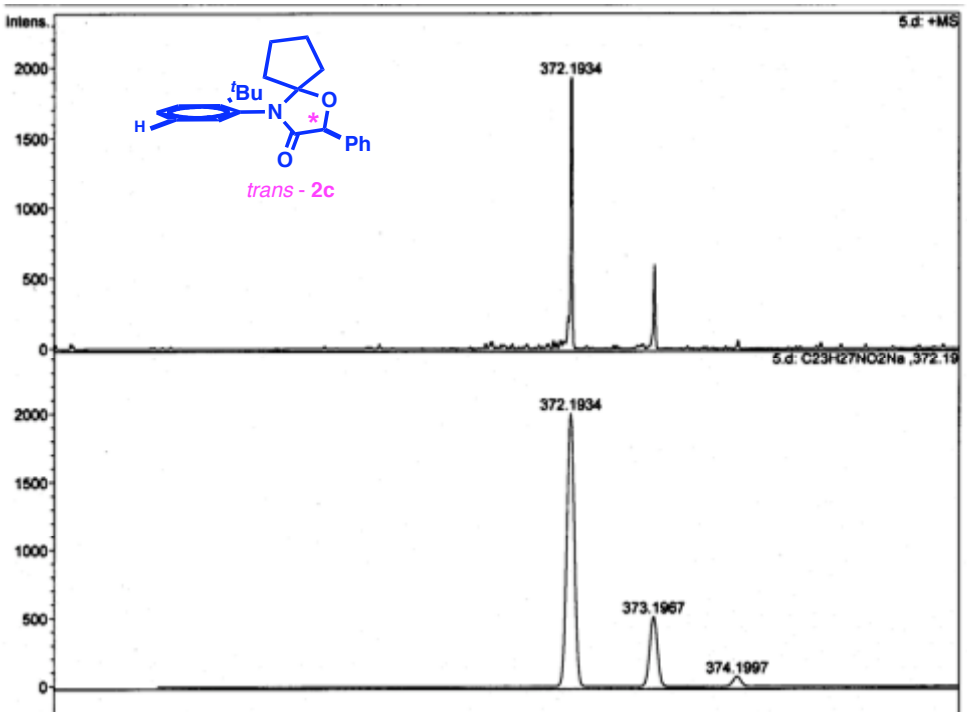
^{13}C DEPT spectra:

Analysis of ^{13}C DEPT shows C-5 hydrogen corresponding to the carbocycle (apart from aromatic hydrogen and methyl / *tert*- butyl hydrogens). This confirms the formation of the 5-membered oxoazolidine-4-one *trans*-**2c**.



HRMS-ESI (m/z) ([M + Na]$^+$): 372.1934

Calculated: 372.1934; Observed: 372.1934



HPLC analysis conditions:

For analytical injections

Column: Chiralpak AS-H

Abs. detector: 220 nm and 254 nm

Mobile phase: Hexanes: IPA = 96:04

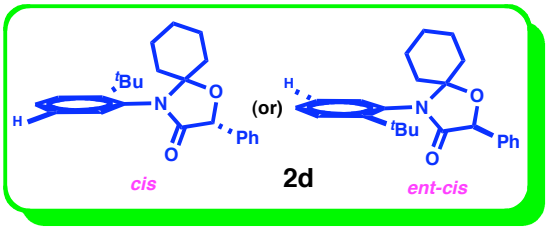
Flow rate: 0.5 mL/min (Analytical)

Retention times (min): ~11.34 [(+)-*trans*-**1c**] and ~12.44 [(-)-*ent*-*trans*-**1c**] (Analytical)

8.7 *cis*-oxazolidine-4-one-**2d** [*cis*-**2d**]

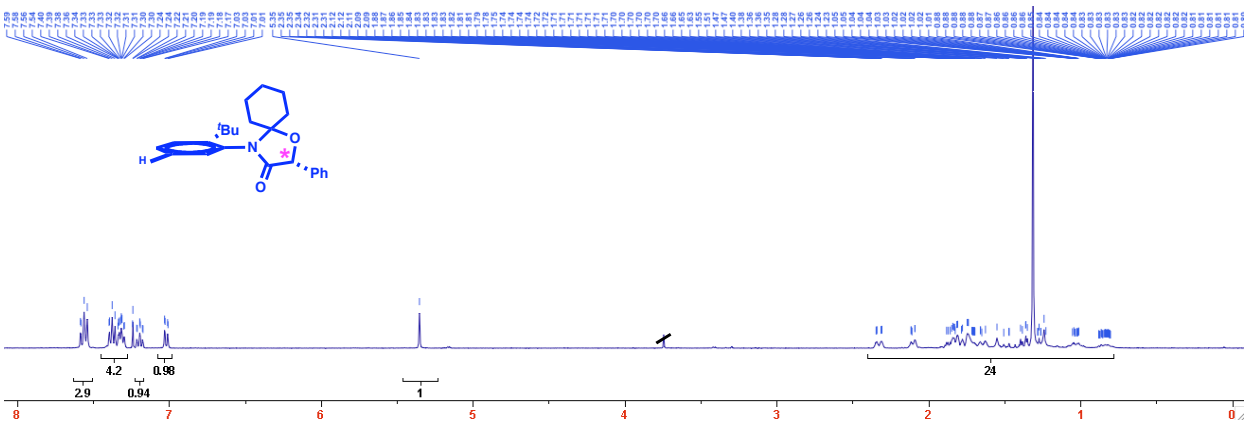
The title compound was purified by preparative thin layer chromatography with 30% EtOAc-70% Hexanes as the mobile phase.

R*f* = 0.3 (30 % EtOAc-70%Hexanes)

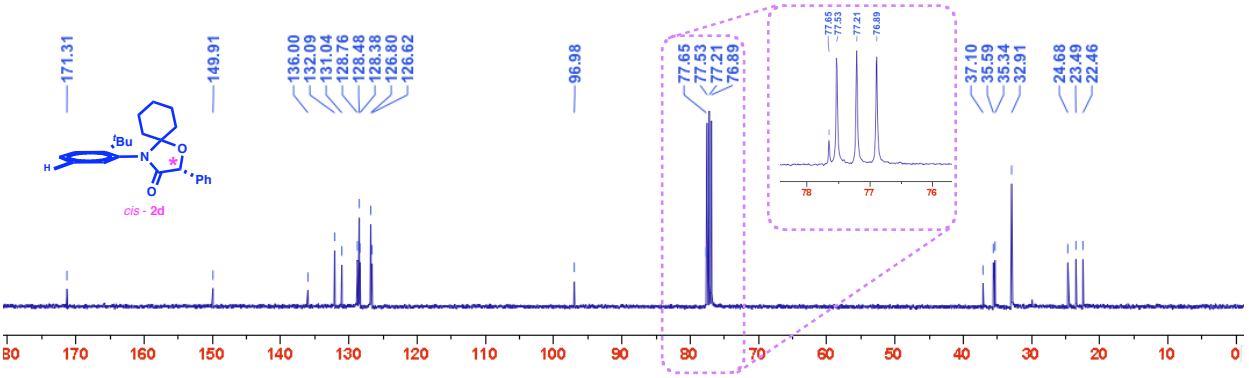


X-ray: see section 11 for details; see attached cif file.

[1]H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.59 - 7.01 (Ar, 9H), 5.35(s, 1H), 2.35 -0.80(m, 19H).

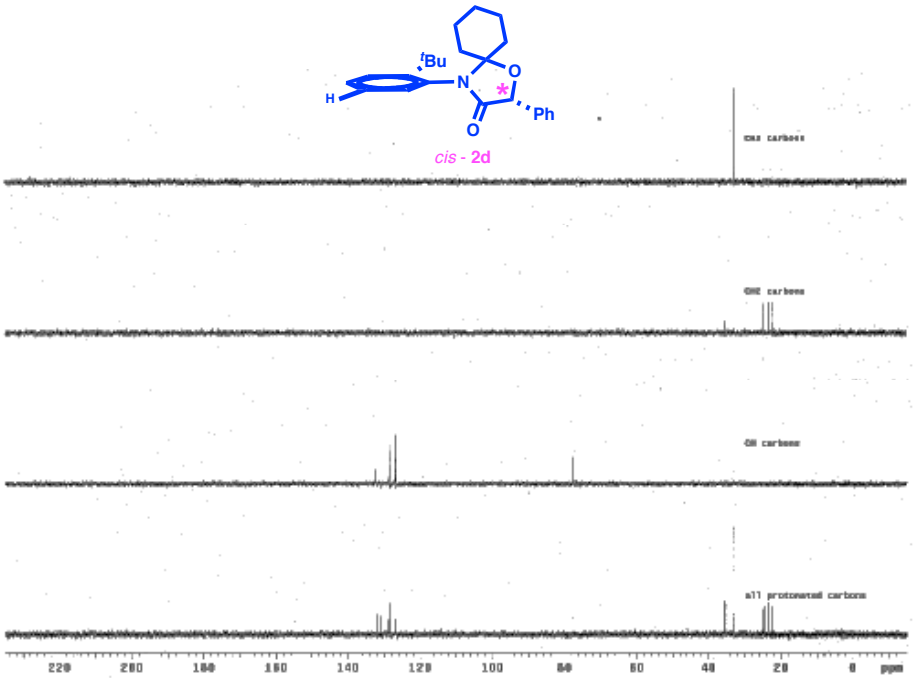


[13]C NMR (100 MHz, $CDCl_3$, δ ppm): 171.31, 149.91, 136.00, 132.09, 131.04, 128.76, 128.48, 128.38, 126.80, 126.62, 96.98, 77.65, 37.10, 35.59, 35.34, 32.91, 24.68, 23.49 and 22.46.



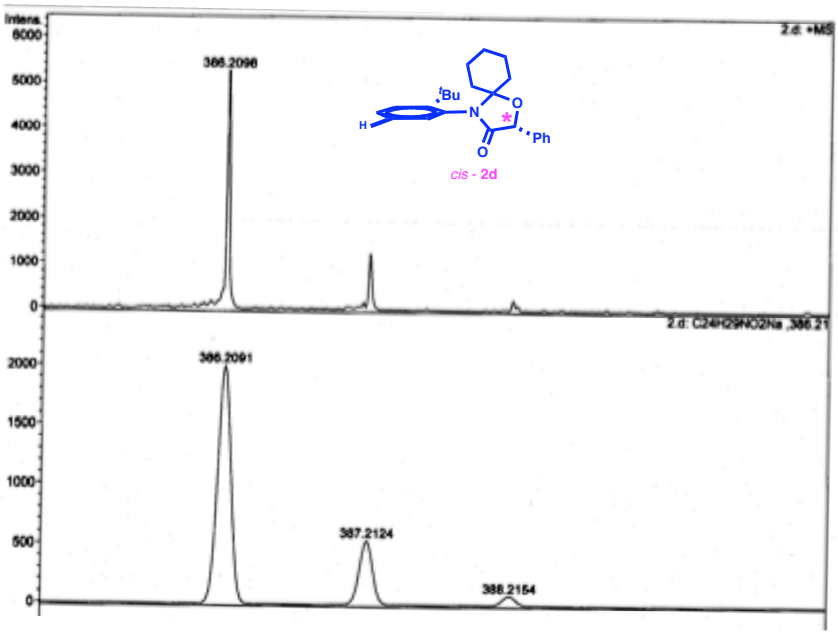
[13]C DEPT spectra:

Analysis of [13]C DEPT shows C-5 hydrogen corresponding to the carbocycle (apart from aromatic hydrogen and methyl / *tert*- butyl hydrogens). This confirms the formation of the 5-membered oxoazolidine-4-one *cis*-**2d**.



HRMS-ESI (m/z) ($[M + Na]^+$): 386.2091

Calculated: 386.2091; Observed: 386.2098



HPLC analysis conditions:

For analytical injections

Column: Chiralpak AS-H

Abs. detector: 220 nm and 254 nm

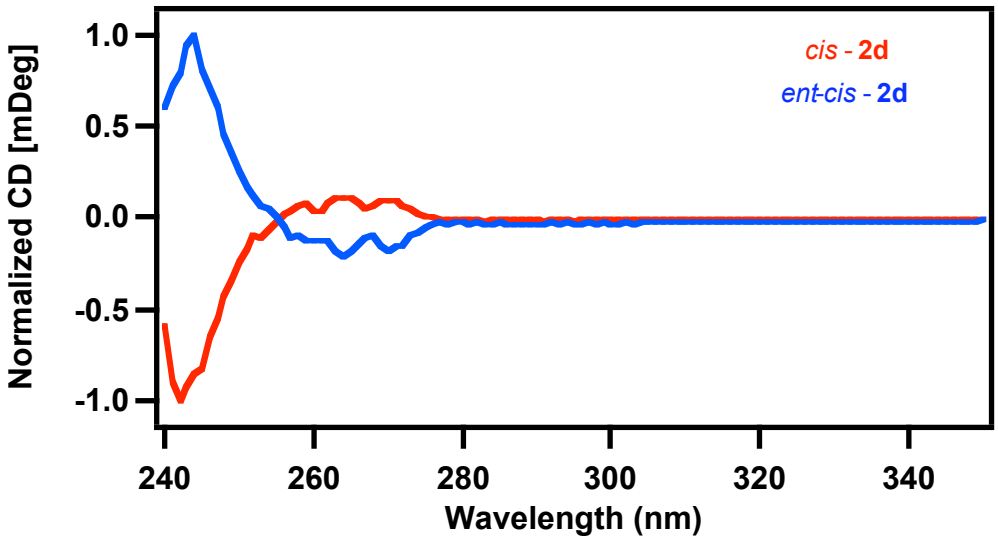
Mobile phase: Hexanes: IPA = 96:04

Flow rate: 1 mL/min (Analytical)

Retention times (min):~6.59 *cis*-**2d** and ~11.09 *ent-cis*-**2d** (Analytical)

CD Spectrum

c = 0.1%, Methanol

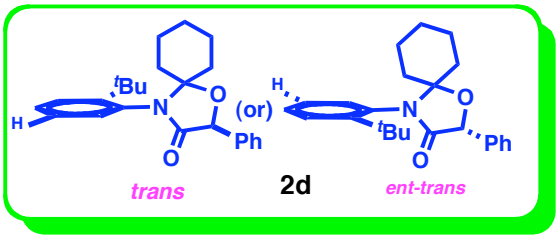


8.8 *trans*-oxazolidine-4-one-**2d** [*trans*-**2d**]

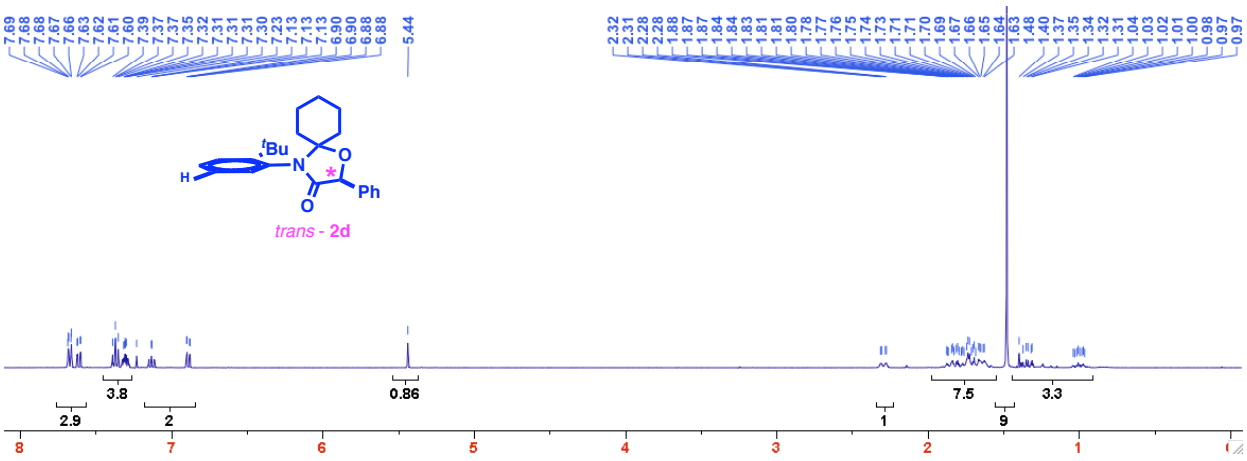
The title compound was purified by preparative thin layer chromatography Solvent polarity: 30% EtOAc-70%Hexanes.

R*f* = 0.45 (30 % EtOAc-70%Hexanes)

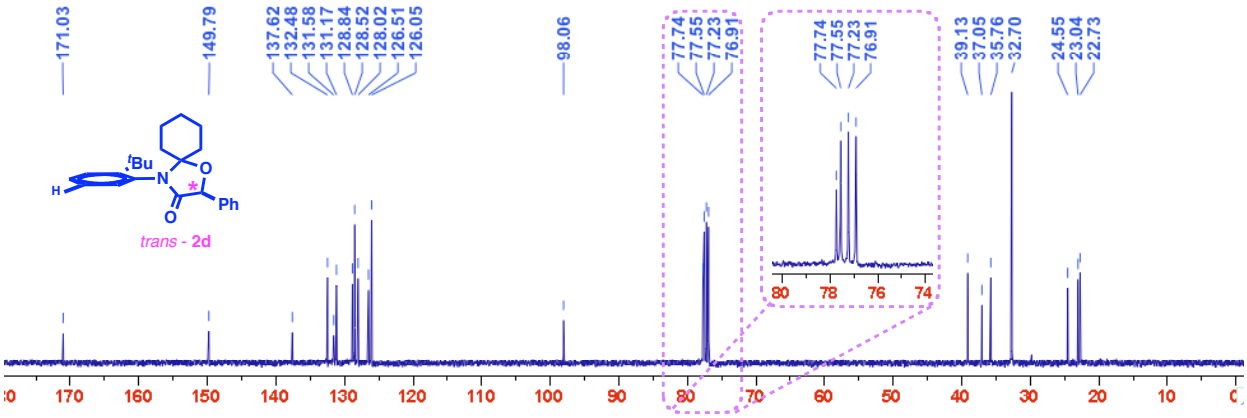
X-ray: see section 11 for details; see attached cif file.



[1]H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.69 -6.88 (Ar, 9H), 5.44(s, 1H), 2.32 -0.97(m, 19H).

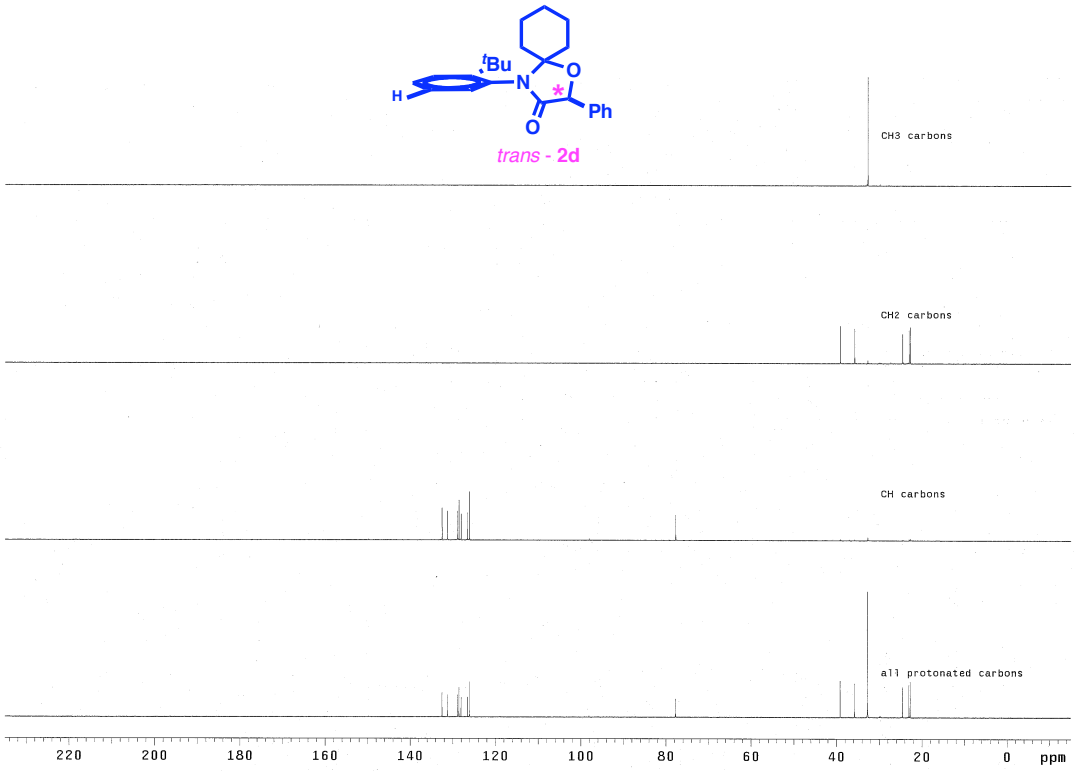


[13]C NMR (100 MHz, $CDCl_3$, δ ppm): 171.03, 149.79, 137.62, 132.48, 131.58, 131.17, 128.84, 128.52, 128.02, 126.51, 126.05, 98.06, 77.74, 39.13, 37.05, 35.76, 32.70, 24.55, 23.04 and 22.73.



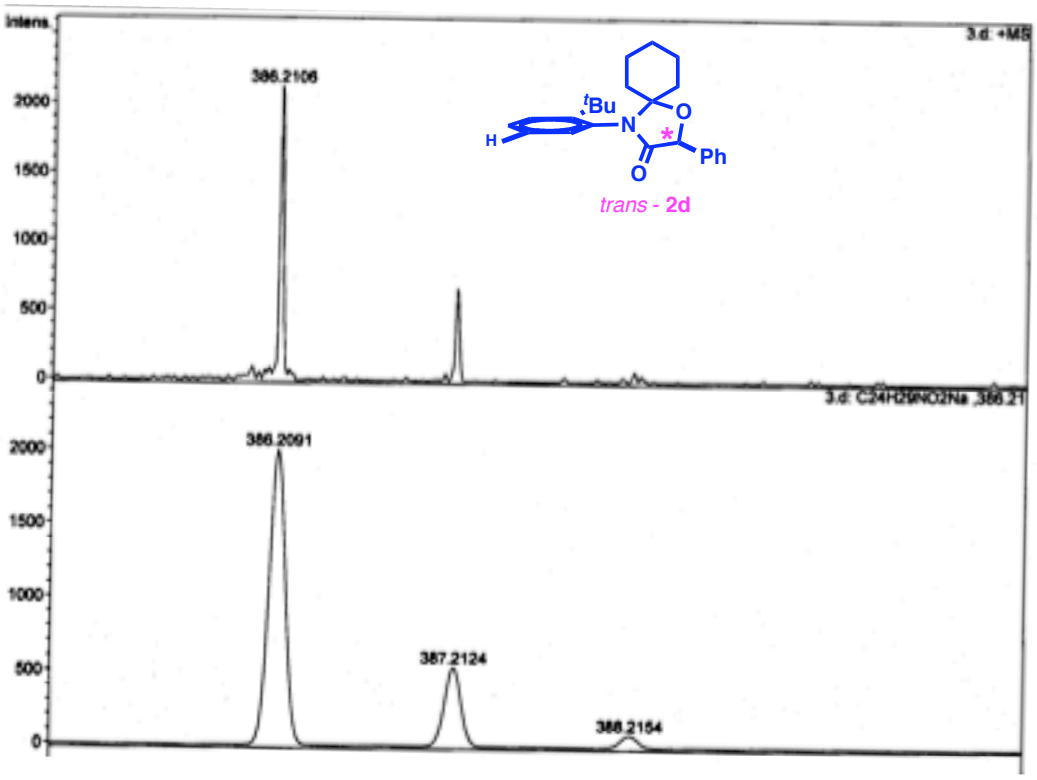
[13]C DEPT spectra:

Analysis of [13]C DEPT shows C-5 hydrogen corresponding to the carbocycle (apart from aromatic hydrogen and methyl / *tert*- butyl hydrogens). This confirms the formation of the 5-membered oxoazolidine-4-one *trans*-**2d**.



HRMS-ESI (m/z) ([M + Na]$^{+}$): 386.2091

Calculated: 386.2091; Observed: 386.2106



HPLC analysis conditions:

For analytical injections

Column: Chiralpak AD-3 (or) Chiralpak AS-H

Abs. detector: 220 nm and 254 nm

Mobile phase: Hexanes: IPA = 96:04

Flow rate: 0.5 mL/min (Analytical), 4.5 mL/min (Preparative/ semi preparative)

Retention times (min):

For AS-H column

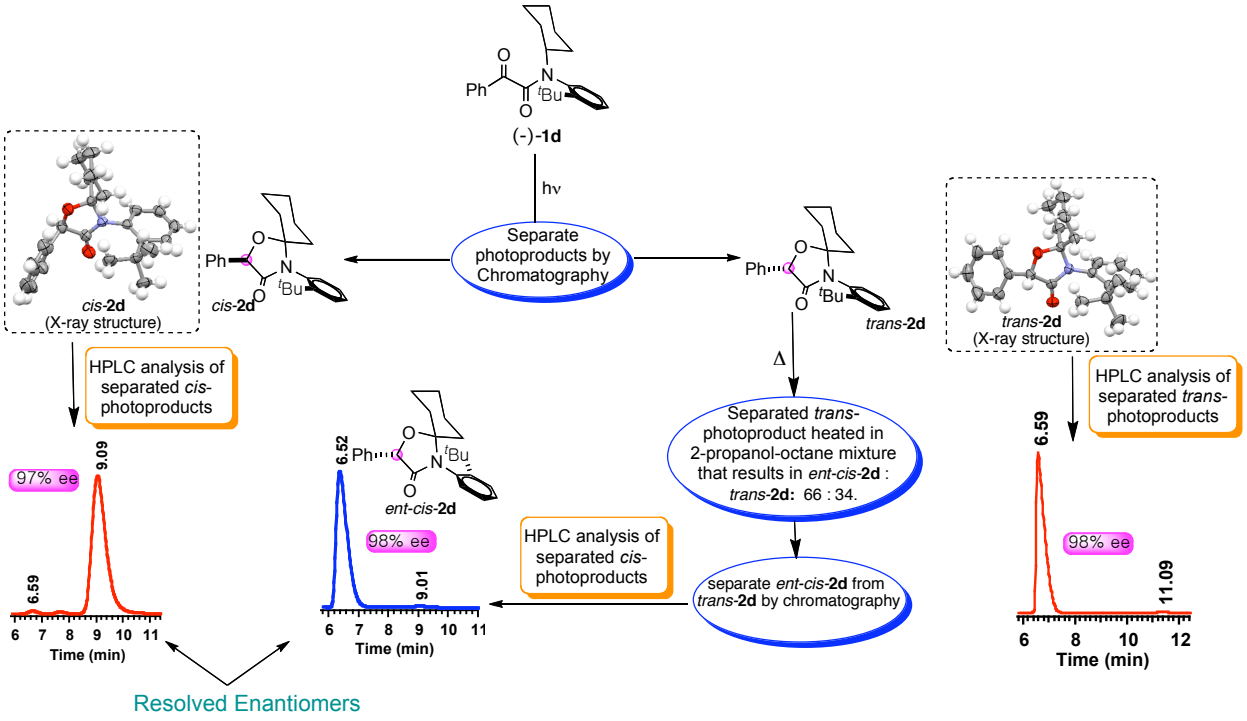
~11.40 min, *trans*-**2d** and ~12.00 min, *ent*-*trans*-**2d** (Analytical)

For AD-3 column

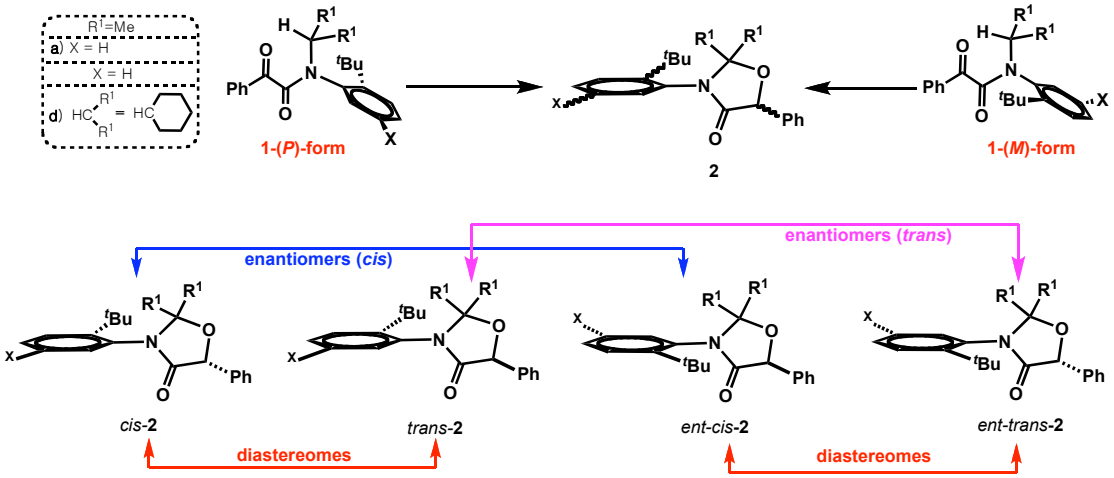
~6.59 min, *trans*-**2d** and ~11.09 min, *ent*-*trans*-**2d** (Analytical)

9. Kinetic Resolution of photoproducts

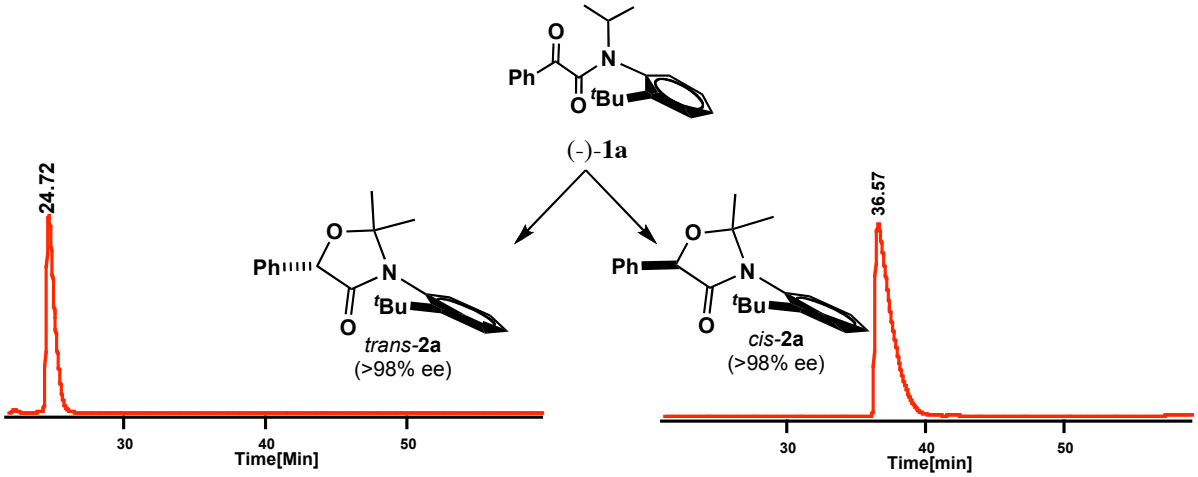
Pure *trans*-**2d** (1mg) was dissolved in 1 mL isopropyl alcohol and again diluted with 4 mL of *n*-octane. This diluted solution was refluxed at 120 ^{o}C for 5 h, concentrated and analyzed by Hplc, Hplc analysis indicate as *ent-cis*-**2d** (65)**:** *trans*-**2d** (35), then *ent-cis*-**2d** and *trans*-**2d** purified by thin layer chromatography and purity was determined by Hplc(>97% ee).



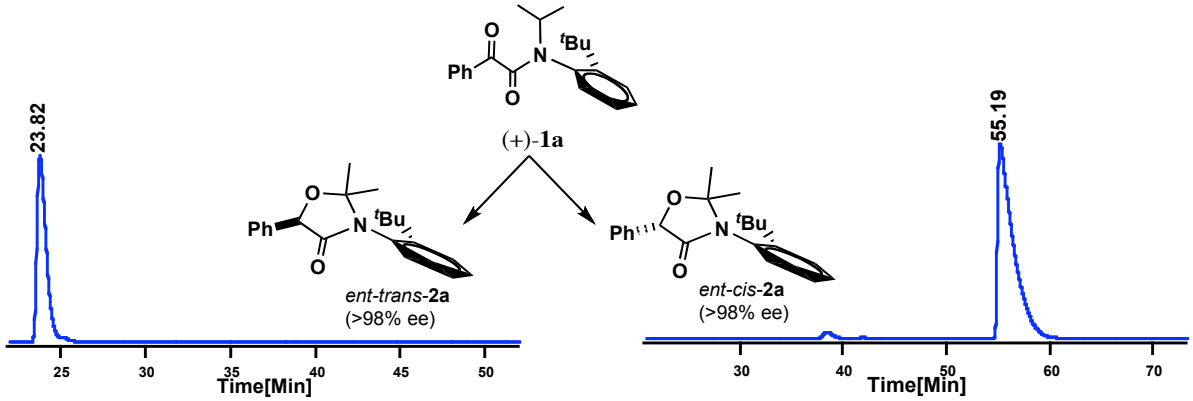
10. HPLC analysis after photoreaction of atropchiral benzoylformamides



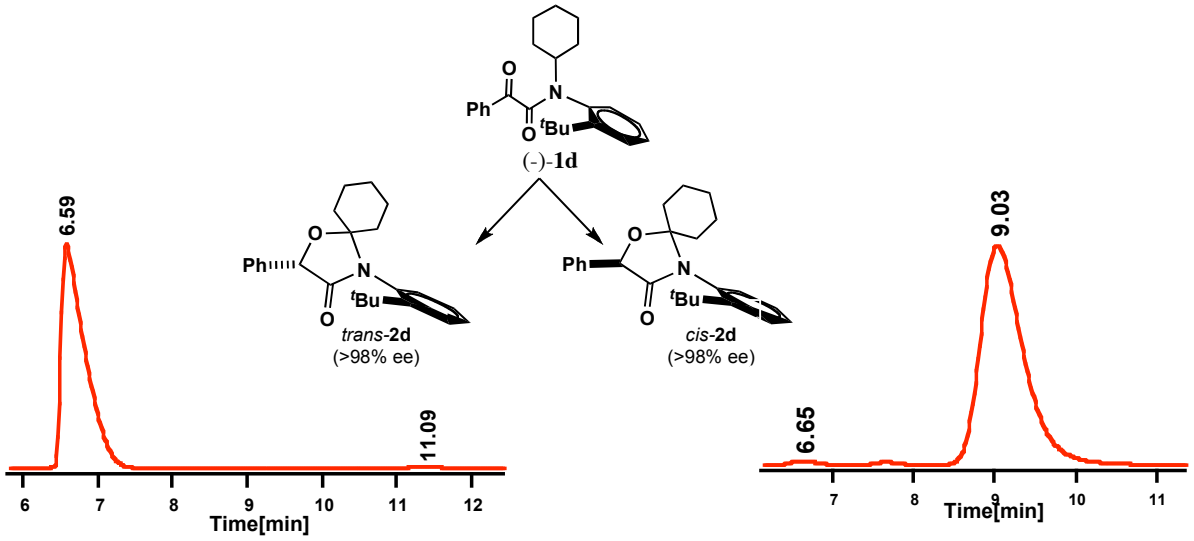
10.1 HPLC analysis of photoproducts upon irradiation of (-)-1a.



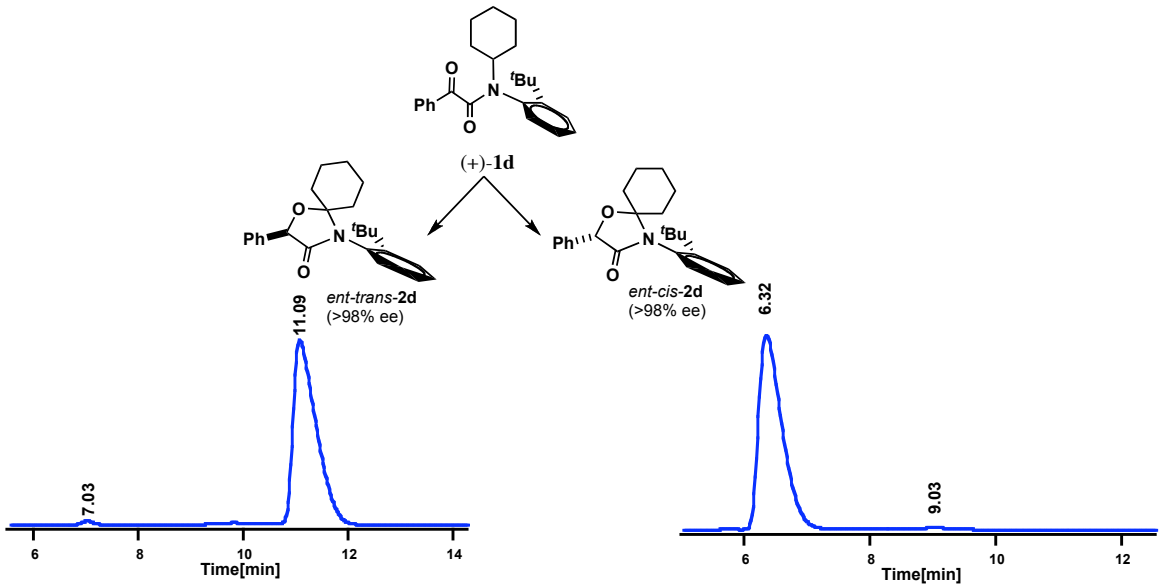
10.2 HPLC analysis of photoproducts upon irradiation of (+)-1a. Note the optical antipode of the *cis* and *trans* photoproducts are enhanced indicating the system is well behaved.



10.3 HPLC analysis of photoproducts upon irradiation of (-)-1d.



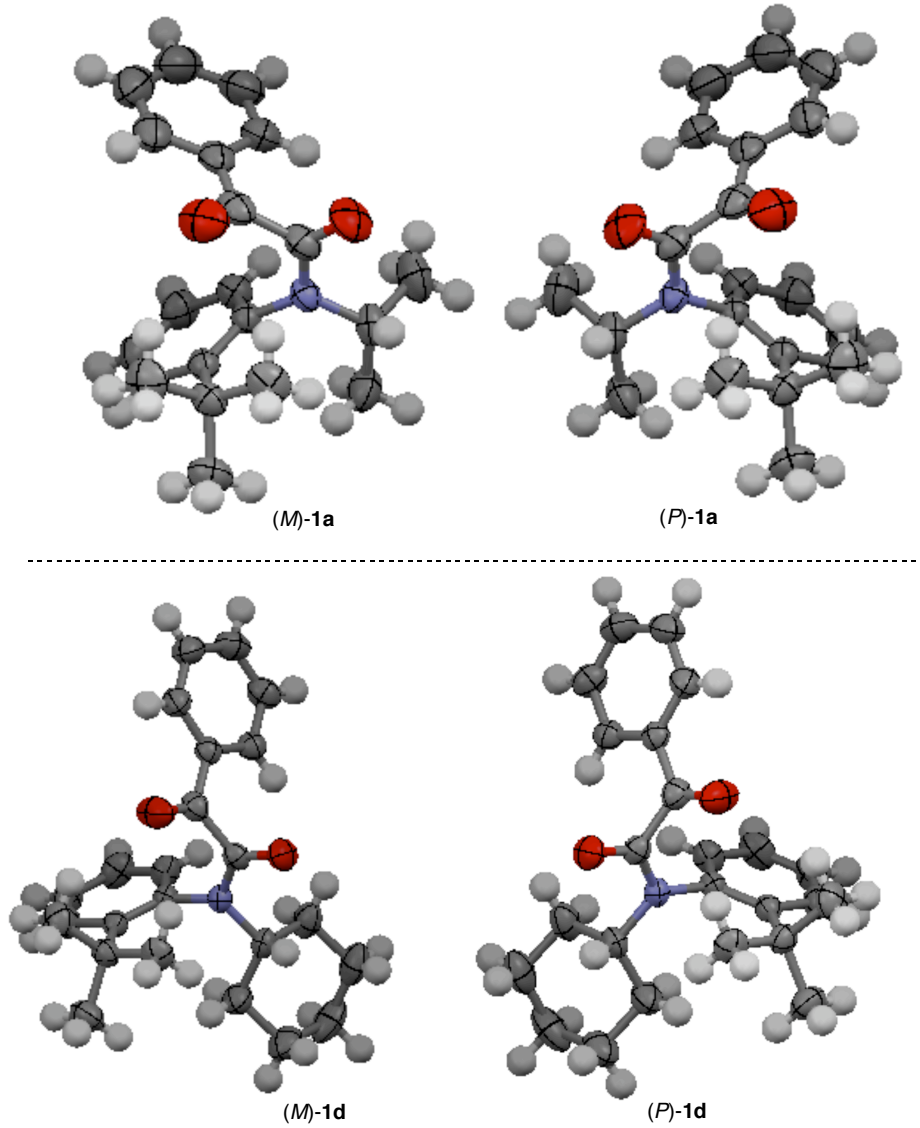
10.4 HPLC analysis of photoproducts upon irradiation of (+)-1d. Note the optical antipode of the *cis* and *trans* photoproducts are enhanced indicating the system is well behaved.



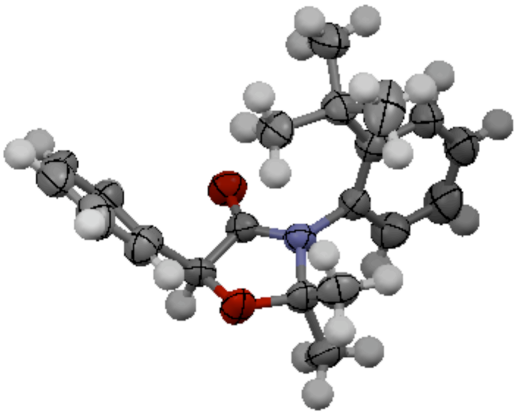
11. X-ray structural parameters

The crystal structure have been deposited at the Cambridge crystallographic data centre and allocated the deposition numbers [CCDC 759989 to 759993]. Single crystal X-ray diffraction data sets were collected on a SIEMENS diffractometer with a 1K CCD area detector (graphite-monochromated Mo Kα radiation, crystals protected with Parathone-N oil). All structures, except *cis*-**2a**, were solved by direct methods and refined on F^2 using the SHELXL, after integration and absorption corrections with SAINT 6.45A. Compound *cis*-**2a** was solved by direct method, but the integrations and absorption corrections were performed with SAINT 7.34A and SADABS version 2007/4.

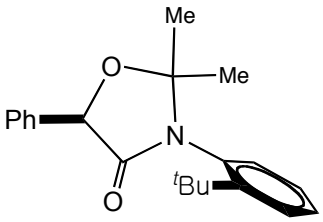
11.1 X-ray structure of benzoylformamide **1a** and **1d**.

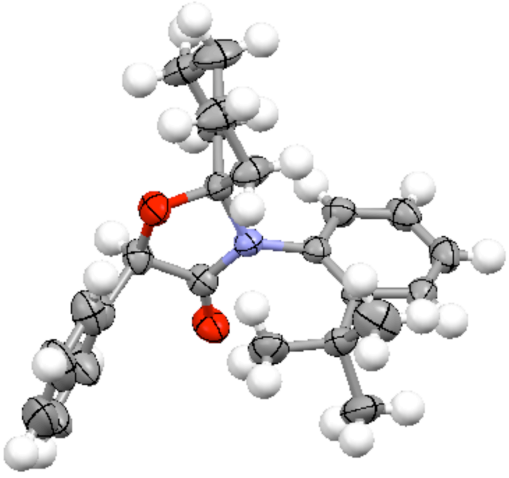


11.2 X-ray structure of oxazolidin-4-one photoproducts *cis*-**2a**, *cis*-**2d** and *trans*-**2d**.

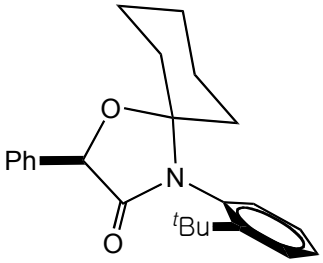


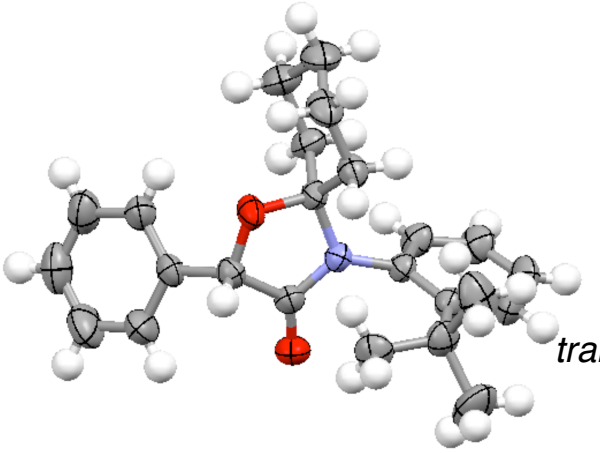
cis-**2a**



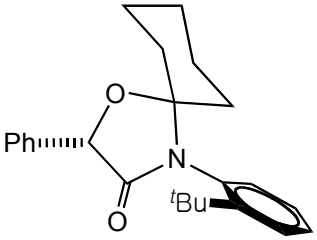


cis-**2d**





trans-**2d**



12. Reference

(1) Reddy, T. J.; Leclair, M.; Proulx, M. *Synlett* **2005**, 583-586.

(2) Bailey, H. V.; Heaton, W.; Vicker, N.; Potter, B. V. L. *Synlett* **2006**, 2444-2448.

(3) Heaney, F.; Fenlon, J.; McArdleb, P.; Cunninghamb, D. *Org. Biomol. Chem.* **2003**, 1122-1132.