Supporting Information (54 Pages)

Intramolecular Paternò-Büchi reaction of atropisomeric α-oxoamides in solution and in the solid-state.

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1. GENERAL METHODS

All commercially obtained reagents/solvents were used as received; chemicals were purchased from Alfa Aesar®, Sigma-Aldrich®, Acros organics®, TCI America®, Mallinckrodt®, and Oakwood® Products, and were used as received without further purification. Unless otherwise stated, reactions were conducted in oven-dried glassware under nitrogen atmosphere. Unless otherwise state demineralized water (DM water) was used for work up procedures. ^{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 from the ^{1}H-NMR spectroscopy are reported as chemical shift (δ ppm) with the corresponding integration values. Coupling constants (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity are 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). High-resolution mass spectrum data in Electrospray Ionization mode 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 or on Dionex® Ultimate 3000 HPLC. Waters® 2767 sample manager was used for automated sample injection on Waters® HPLC or Ultimate 3000 sample injector was used for injection on Dionex® HPLC. All HPLC injections on Waters® HPLC were monitored using a Waters® 2487 dual wavelength absorbance detector at 254 and 270 nm or on Dionex®. HPLC were monitored using a diode array detector (DAD3000125). Analytical and semi-preparative injections were performed on chiral stationary phase using various columns as indicated below.

i) Regis® PIRKLE COVALENT (*R*,*R*) WHELK–01
   a) 25 cm x 4.6 mm column for analytical injections.
   b) 25 cm x 10 mm column for semi-preparative injections.
ii) CHIRACEL® OD-H
   a) 0.46 cm x 25 cm column for analytical injections.
   b) 10 mm x 25 cm column for semi-preparative injections.
iii) CHIRALPAK® IC
   a) 0.46 cm x 25 cm column for analytical injections.
   b) 10 mm x 25 cm column for semi-preparative injections
iv) CHIRALPAK® AD-H
   a) 0.46 cm x 15 cm column for analytical injections.
   b) 10 mm x 25 cm column for semi-preparative injections.
v) CHIRALCEL – OD-3

a) 0.46 cm x 15 cm column for analytical injections.

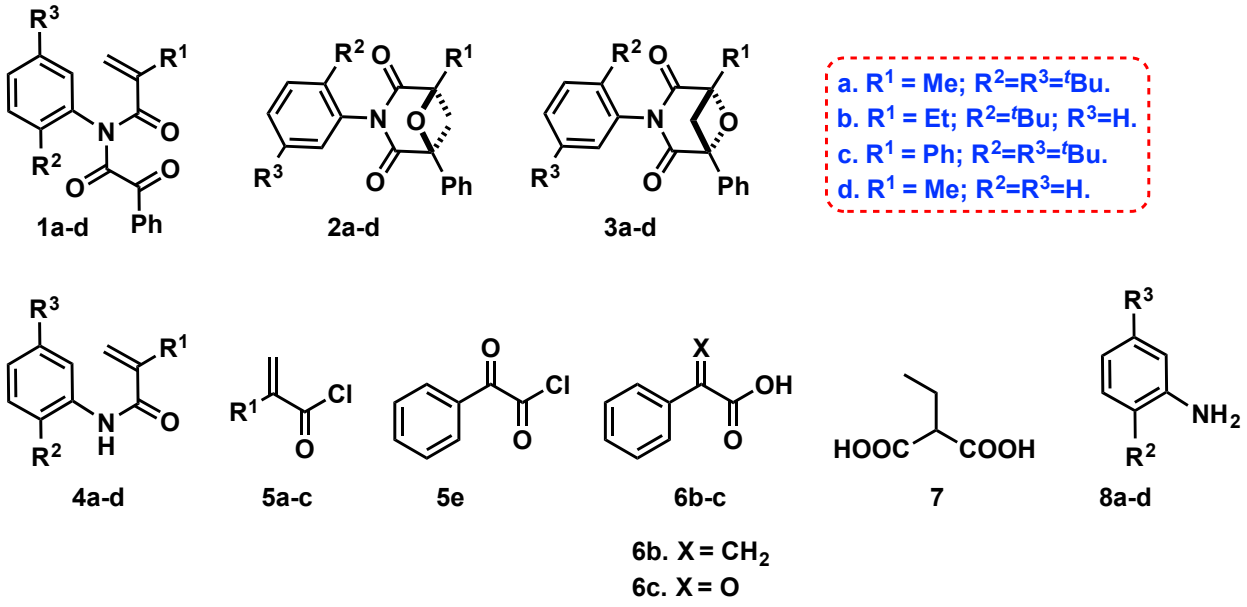
vi) CHIRAPAK – AD-3

a) 0.46 cm x 15 cm column for analytical injections.

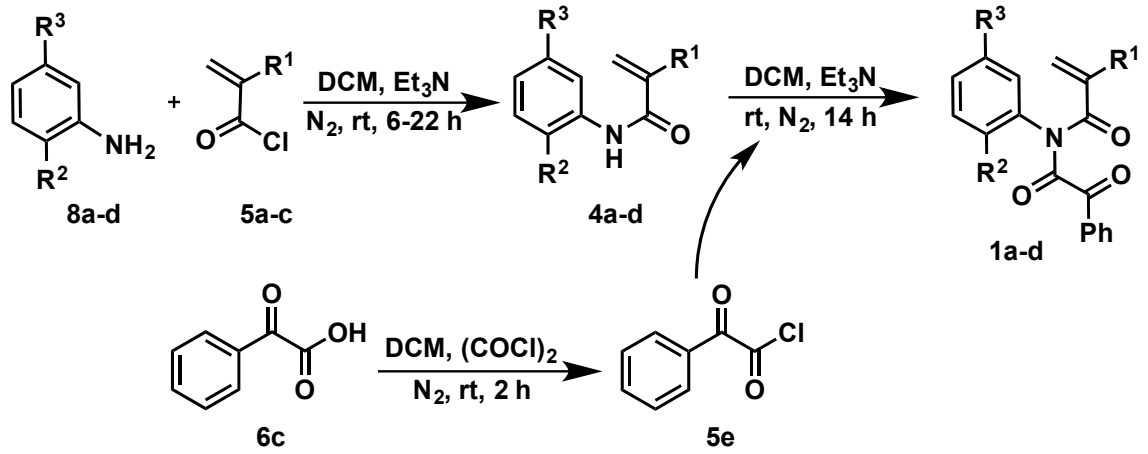
Masslynx software version 4.1 was used to monitor/analyze the HPLC injections on Waters® and to process HPLC traces. Chromeleon 7 software was used to monitor and process HPLC injections on Dionex® HPLC. Igor Pro® Software version 6.0 was used to process the HPLC graphics. UV-Vis spectra were recorded on 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. When necessary, the compounds were purified by combiflash equipped with dual wavelength UV-Vis absorbance detector (Teledyn ISCO) using hexanes:ethyl acetate as the mobile phase and Redisep® cartridge filled with silica (Teledyne ISCO) as stationary phase. In some cases, compounds were purified by column 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). Unless indicated, the Retardation Factor (R_f) values were recorded using a 5-50% hexanes:ethyl acetate as mobile phase and on Sorbent Technologies®, silica Gel TLC plates (200 mm thickness w/UV_{254}).

2. CHART AND SYNTHETIC PROTOCOLS

2.1 Chart

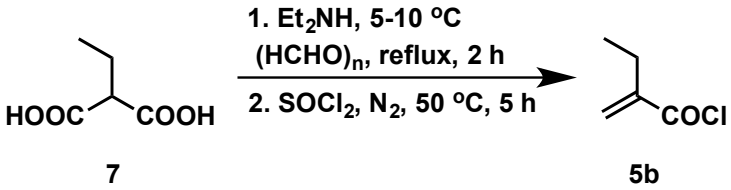


2.2 Synthetic protocol for α-oxoamides **1a-d**



3. General procedure for synthesis of α-oxoamides **1a-d** and their precursors

3.1 Synthesis of 2-methylenebutanoyl chloride **5b**



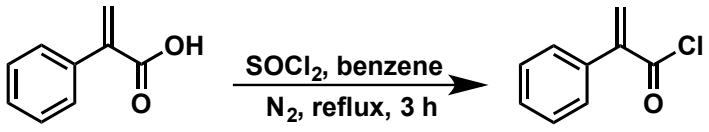
7 **5b**

Scheme S1: Synthesis of 2-methylenebutanoyl chloride **5b**

2-methylenebutanoyl chloride was synthesized according to the literature reported procedure.[1] To a solution of ethyl malonic acid (1.85 g, 1.0 equiv) in dry ethyl acetate (40 mL) at 0 °C under N_2 atmosphere diethylamine (2.17 mL, 1.5 equiv) was added. The mixture was stirred for 5 min followed by the addition of paraformaldehyde (0.67 g, 1.5 equiv) in 2 portions. The resulting mixture was stirred for 5 mins and then moved to oil bath where it was refluxed for 2 h. The mixture was cooled to room temperature and quenched with water. The pH of the solution was adjusted to 1 by carefully adding c*onc.* HCl and extracted with ethyl acetate (3 X 15 mL). The combined organic layer was dried over *anhy.* Na_2SO_4, filtered and the solvent was removed under reduced pressure to yield crude product as pale yellow oil. The crude product was directly taken to next stage without further purification.

To the crude product under N_2 atmosphere added thionyl chloride (1.54 mL, 1.0 equiv). The mixture was heated to 50 °C and maintained for 3 h. After 3 h, the excess thionyl chloride was removed under reduced pressure while the temperature was maintained at 25 °C. The vacuum was released under N_2 and the residue was taken up in DCM and directly taken to next step without further analysis or purification.

3.2 Synthesis of 2-phenylacryloyl chloride derivatives **5c**



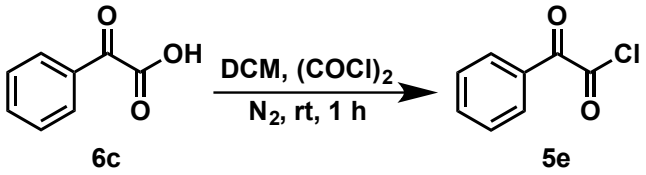
6b **5c**

Scheme S2: Synthesis of 2-phenylacryloyl chloride derivatives **5c**

To a solution of atropic acid **6b** (1.0 g, 6.74 mmol, 1.0 equiv) in dry benzene (15 mL) under N_2 atmosphere thionyl chloride (1 mL, 13.4 mmol, 2.0 equiv) was added and the resulting mixture was refluxed for 3 h. After the reaction the solvent and the excess thionyl chloride was removed under reduced pressure while the temperature was maintained at 25 °C. The vacuum

was released under N_2 and the residue was taken up in DCM and directly taken to next step without further analysis or purification.

3.3 Synthesis of phenylglyoxylyl chloride **5e**

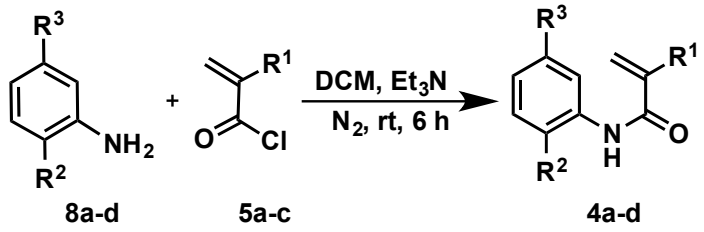


6c **5e**

Scheme S3: Synthesis of phenylglyoxylyl chloride **5e**.

To a solution of phenylglyoxylic acid **6c** (1.1 g, 7.33 mmol, 1.0 equiv) in DCM (10 mL) at room temperature added a two drops of DMF (catalytic). To this solution oxalyl chloride (2.5 equiv) was slowly added during which white effervescence was observed. The mixture was further stirred for 1 h and the solvent and excess oxalyl chloride was removed under reduced pressure while the temperature was maintained at 25 ^{o}C. The vacuum was released under N_2 and the residue was taken up in DCM and directly taken to next step without further analysis or purification.

3.4 Synthesis of substituted amide derivatives **4a-d**



8a-d **5a-c** **4a-d**

Scheme S4: Synthesis of substituted amide derivatives **4a-d.**

To a solution of aniline (1.0 g, 1.0 equiv), triethylamine (2.0 equiv) in dry DCM (15 mL) at 0 ^{o}C under N_2 atmosphere corresponding acyl chloride (1.1 equiv) was added. The resulting solution was slowly allowed to warm to room temperature over 6 h. After the reaction, water was added, stirred and the layers were separated. The organic layer was washed with DM water (2 X 15 mL), dried over *anhy.* Na_2SO_4, filtered and the solvent was removed under reduced pressure to yield crude product. The crude product was purified by combiflash using hexanes:ethyl acetate mixture.

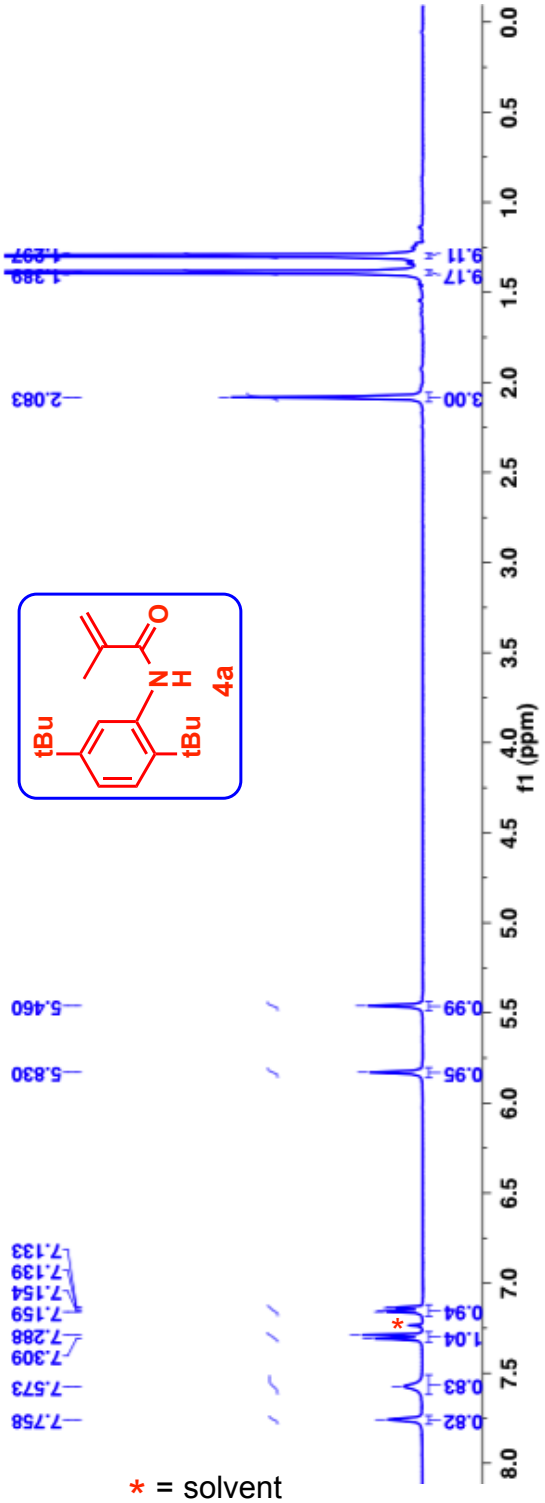
TLC condition - R_f = 0.32 (80% hexanes:20% ethyl acetate) for **4a** (Yield = 85 %)

TLC condition - R_f = 0.28 (50% hexanes:50% ethyl acetate) for **4b** (Yield = 76 %)

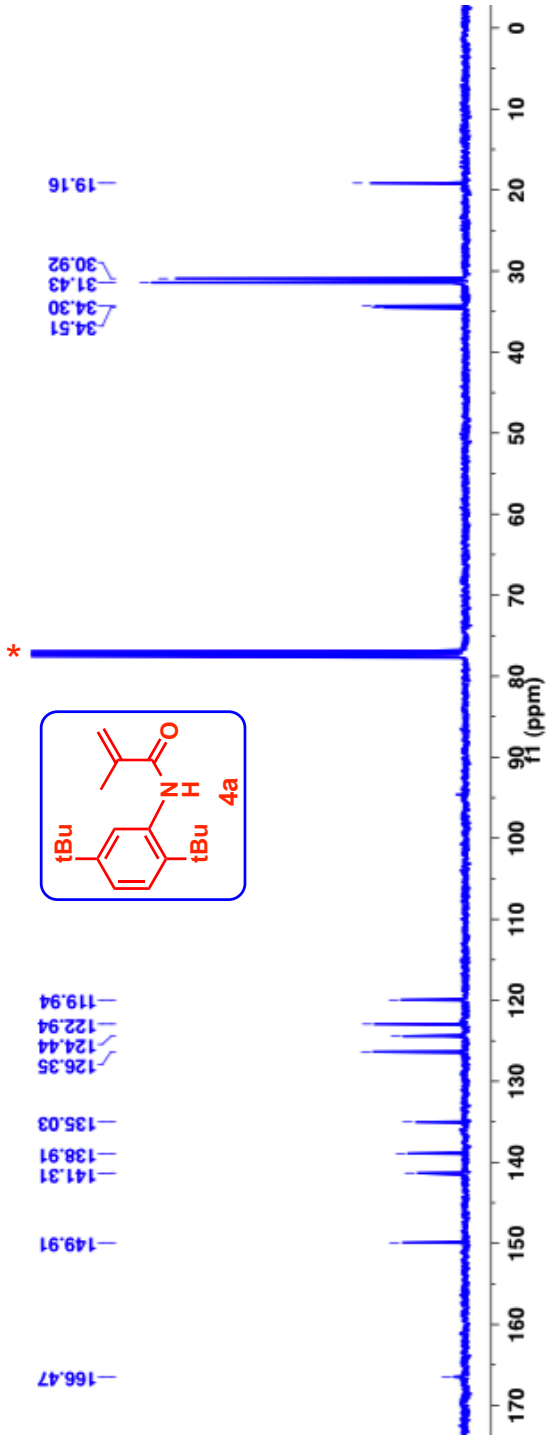
TLC condition - R_f = 0.30 (90% hexanes:10% ethyl acetate) for **4c** (Yield = 82 %)

TLC condition - R_f = 0.52 (50% hexanes:50% ethyl acetate) for **4d** (Yield = 93 %)

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.76 (s, 1H), 7.57 (bs, 1H), 7.31-7.29 (m, 1H), 7.17-7.13 (m, 1H), 5.83 (s, 1H), 5.46 (s, 1H), 2.08 (s, 3H), 1.39 (s, 9H) and 1.297 (s, 9H).

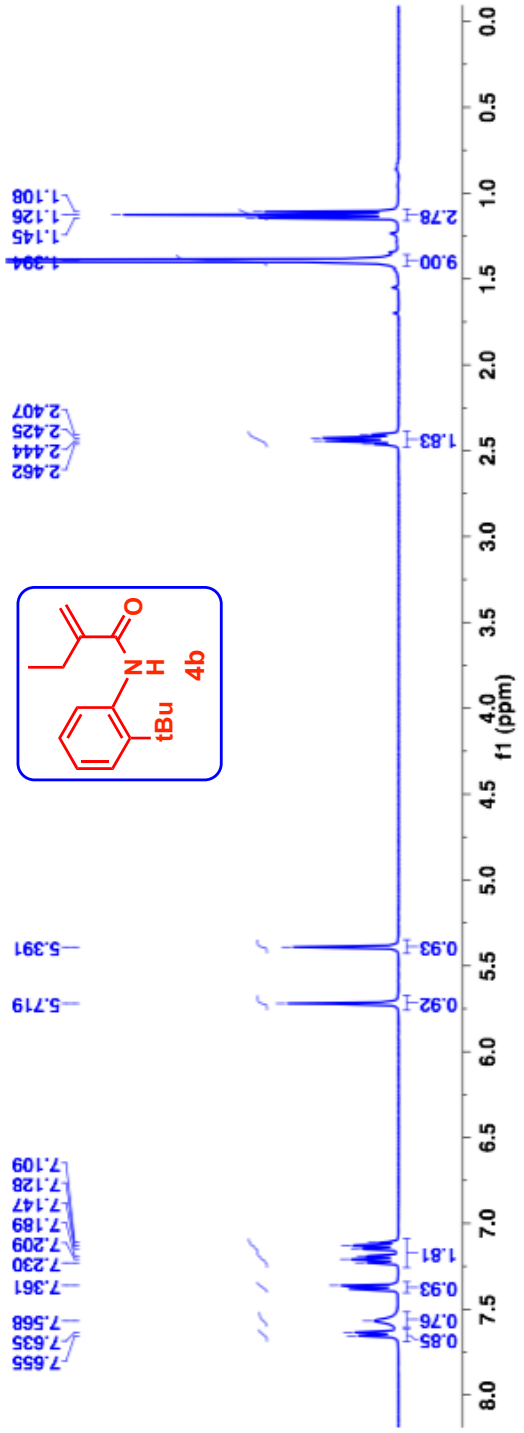


^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 166.5, 149.9, 141.3, 138.9, 135.0, 126.3, 124.4, 122.9, 119.9, 34.5, 34.3, 31.4, 30.9 and 19.2.

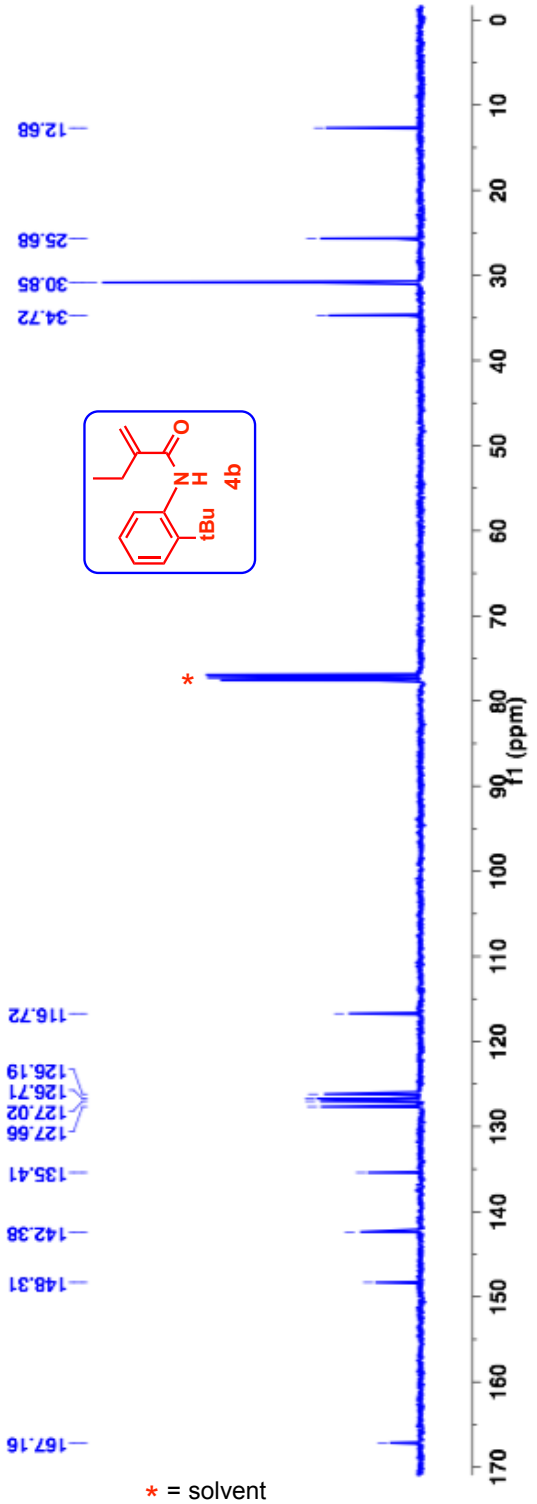


* = solvent

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.65-7.63 (m, 1H), 7.57 (bs, 1H), 7.38-7.36 (m, 1H), 7.23-7.11 (m, 2H), 5.72 (s, 1H), 5.39 (s, 1H), 2.43 (q, *J*=7.2 Hz, 2H) 1.39 (s, 9H) and 1.13 (t, *J*=7.2 Hz, 3H).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 167.2, 148.3, 142.4, 135.4, 127.7, 127.0, 126.7, 126.2, 116.7, 34.7, 30.8, 25.7 and 12.7.



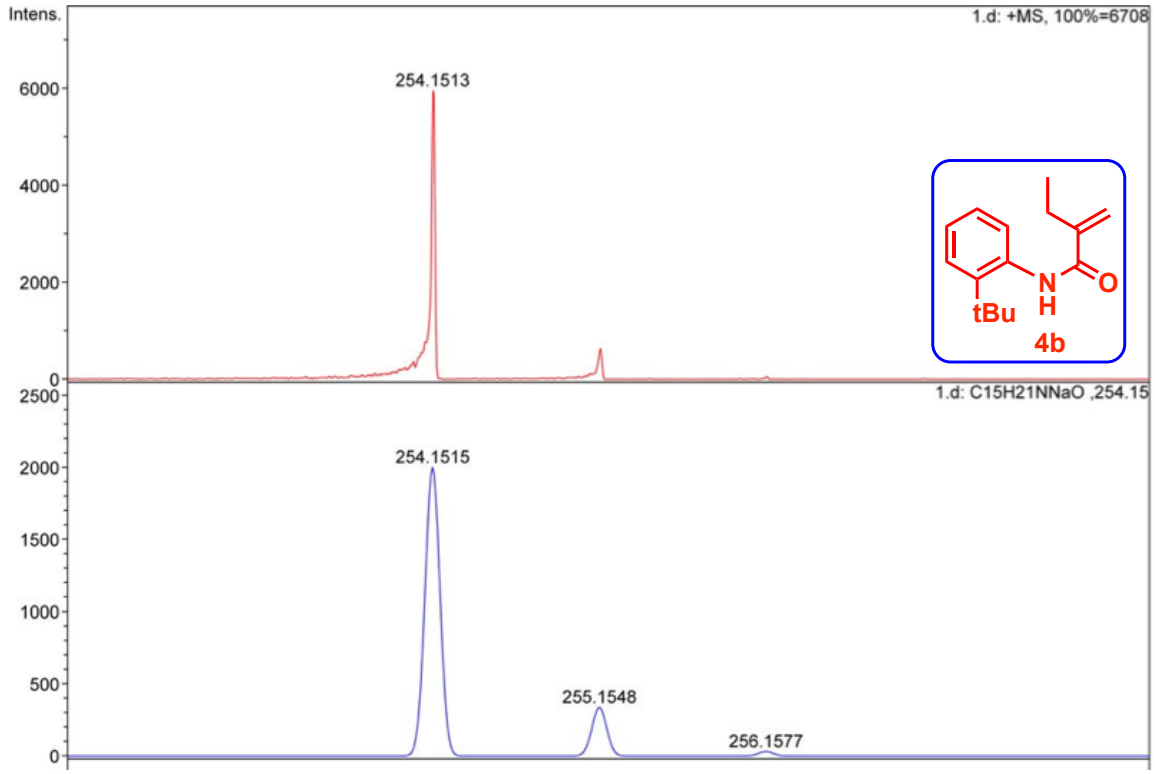
* = solvent

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

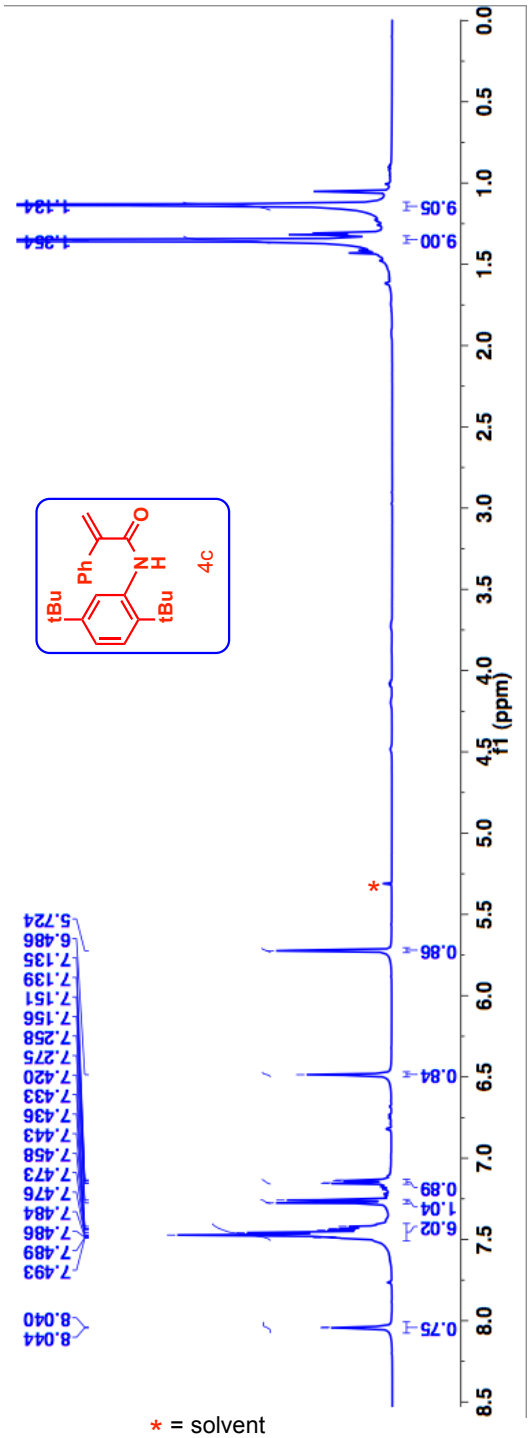
Calculated : 254.1515

Observed : 254.1513

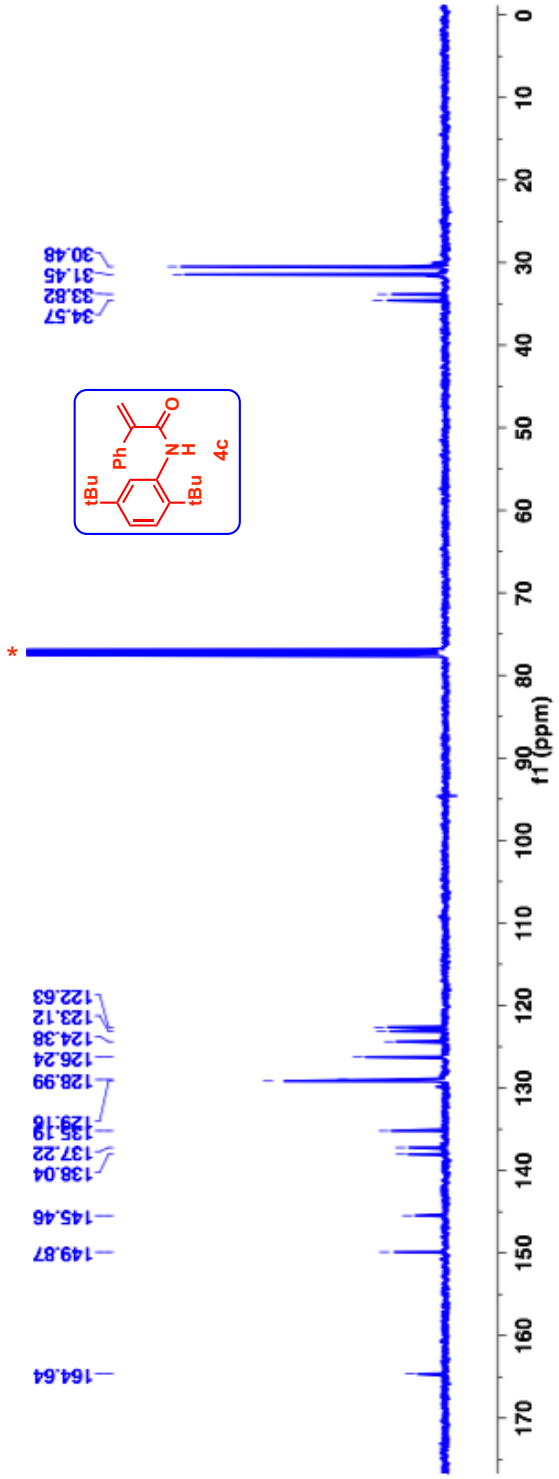
|Δm| : 0.8 ppm



^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 8.05-8.04 (m, 1H), 7.49-7.42 (m, 6H), 7.27-7.26 (m, 1H), 7.16-7.13 (m, 1H), 6.49 (s, 1H), 5.72 (s, 1H), 1.35 (s, 9H) and 1.34 (s, 9H).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 164.6, 149.9, 145.5, 138.0, 137.2, 135.2, 129.2, 129.1, 128.99, 126.2, 124.4, 123.1, 122.6, 34.6, 33.8, 31.4 and 30.5.

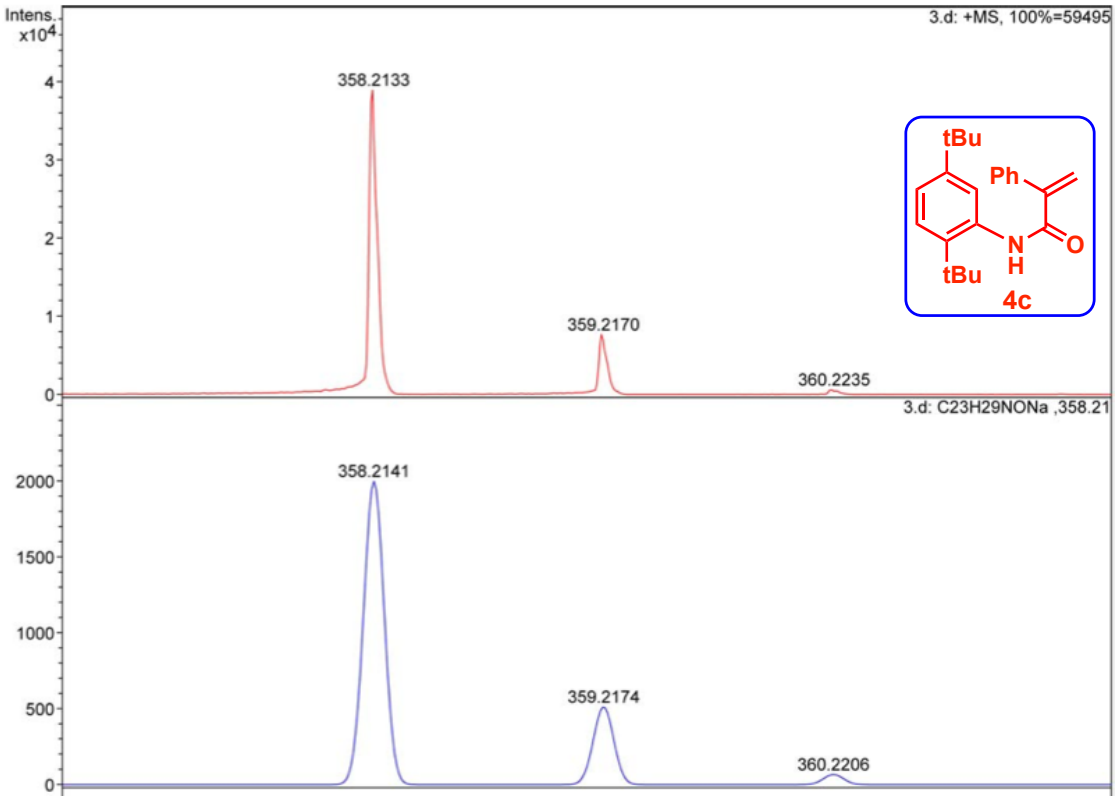


HRMS-ESI (m/z) ([M + Na]$^+$):

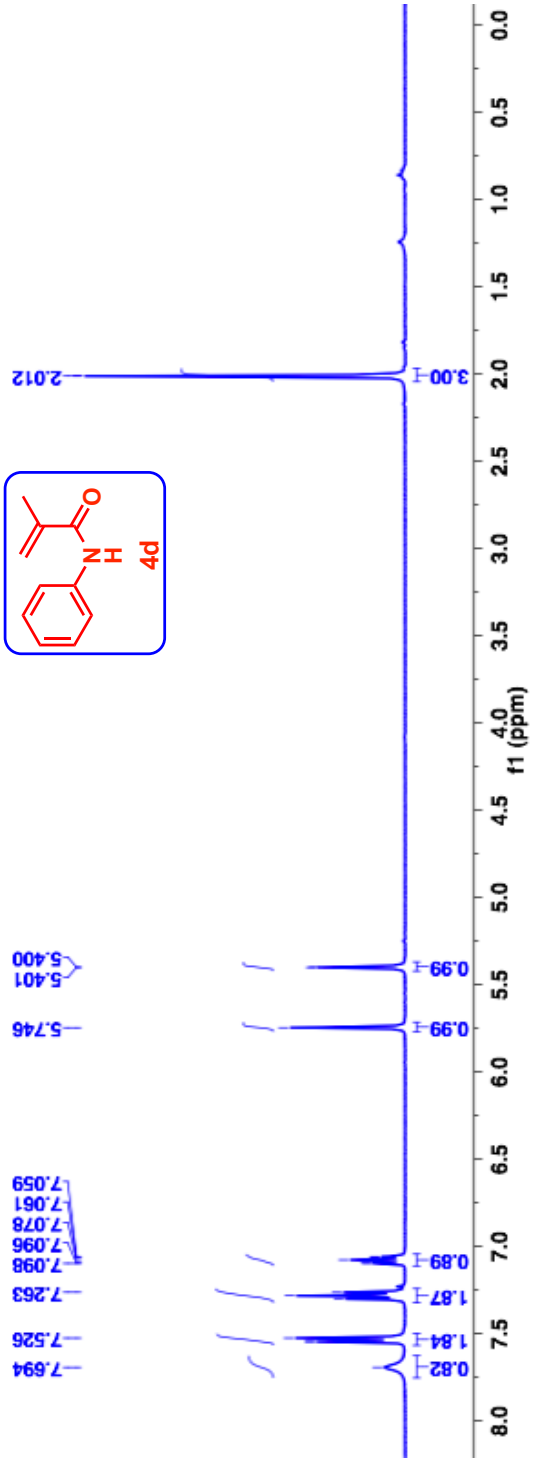
Calculated : 358.2141

Observed : 358.2133

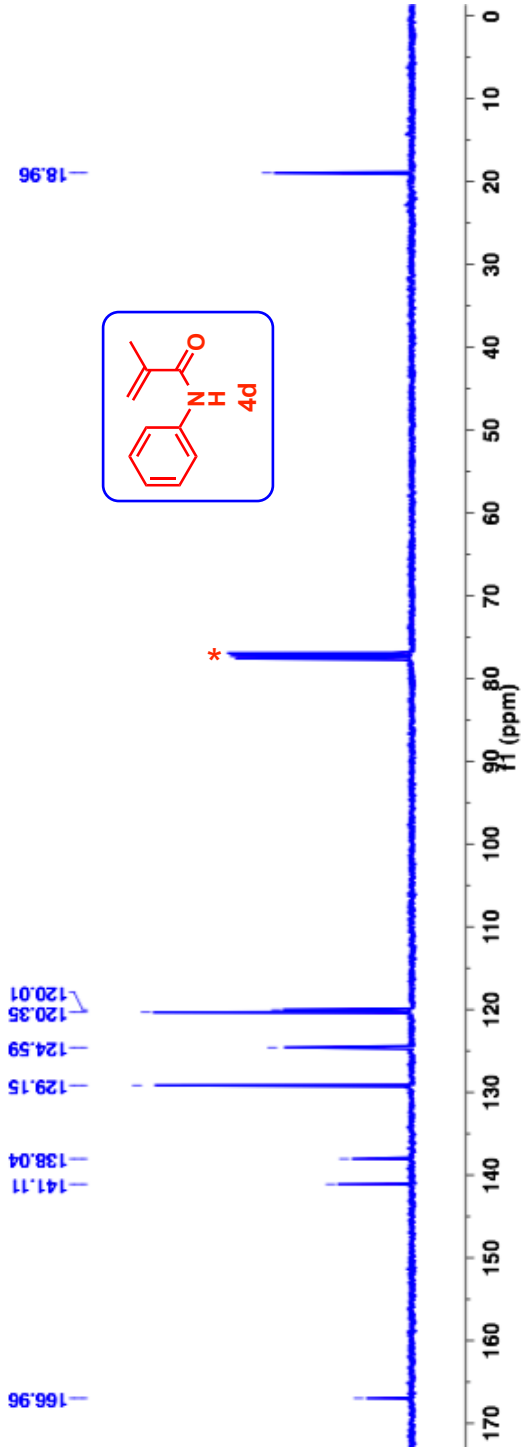
|Δm| : 2.2 ppm



^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.69 (bs, 1H), 7.55-7.53 (m, 2H), 7.30-7.26 (m, 2H), 7.098-7.06 (m, 1H), 5.75 (s, 1H), 5.40 (s, 1H) and 2.01 (s, 3H).

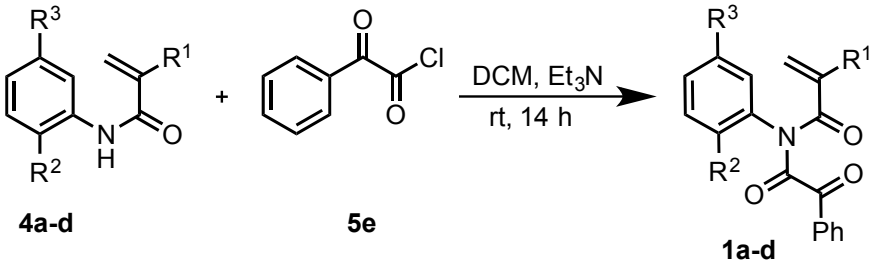


^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 166.96, 141.1, 138.0, 129.1, 124.6, 120.3, 120.0 and 18.96.



* = solvent

3.5 Synthesis of α-oxoamides derivatives **1a-d**

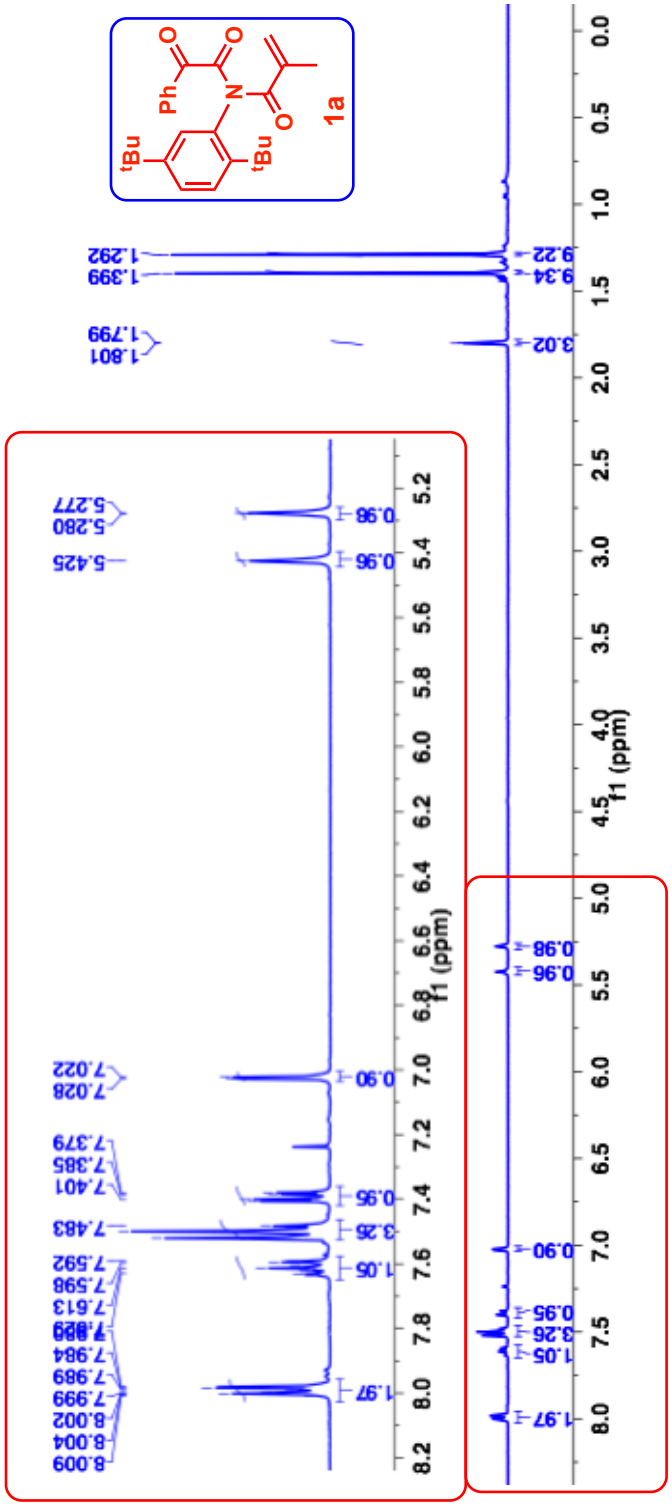


Scheme S5: Synthesis of α-oxoamides derivatives **1a-d.**

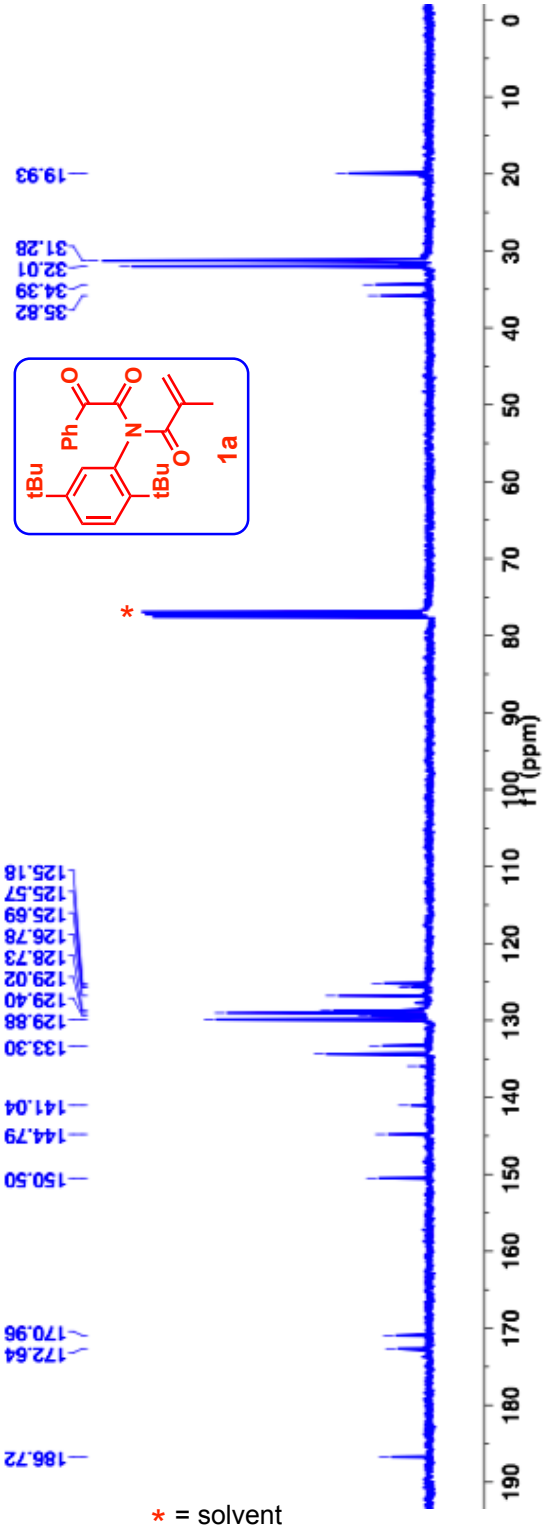
To a solution of corresponding amide (1.0 g, 1.0 equiv) in dry DCM (15 mL) at 0 ^{o}C under N_2 atmosphere triethylamine (2.3 equiv) was added followed by the addition of corresponding acid chloride (2.0 equiv). The resulting solution was slowly allowed to warm to room temperature over 14 h. After the reaction, water was added, stirred and the layers were separated. The organic layer was washed with DM water (2 X 15 mL), dried over *anhy.* Na_2SO_4, filtered and the solvent was removed under reduced pressure to yield crude product. The crude product was purified by combiflash using hexanes:ethyl acetate mixture.

TLC condition - R_f = 0.43 (80% hexanes:20% ethyl acetate) for **1a** (Yield = 84 %)
TLC condition - R_f = 0.33 (50% hexanes:50% ethyl acetate) for **1b** (Yield = 64 %)
TLC condition - R_f = 0.40 (90% hexanes:10% ethyl acetate) for **1c** (Yield = 58 %)
TLC condition - R_f = 0.32 (50% hexanes:50% ethyl acetate) for **1d** (Yield = 70 %)

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 8.01-7.98 (m, 2H), 7.62-7.59 (m, 1H), 7.52-7.48 (m, 3H), 7.41-7.38 (m, 1H), 5.42 (s, 1H), 5.28- 5.28 (m, 1H), 1.80-1.799 (m, 3H), 1.399 (s, 9H) and 1.29 (s, 9H).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 186.7, 172.6, 170.96, 150.5, 144.8, 141.0, 135.9, 134.4, 133.3, 129.9, 129.4, 129.0, 128.7, 126.8, 125.7, 125.6, 125.2, 35.8, 34.4, 32.0, 31.3 and 19.9.



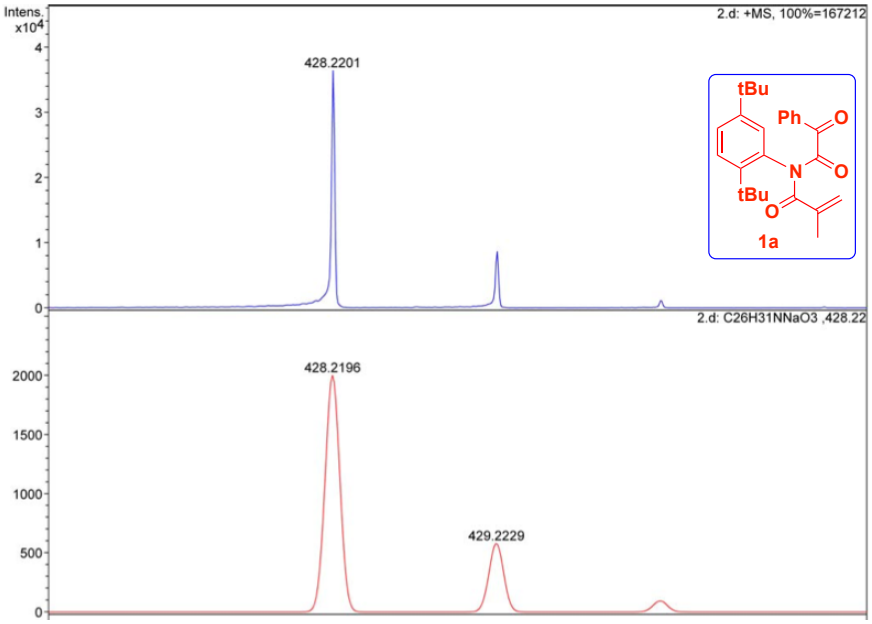
* = solvent

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

Calculated : 428.2196

Observed : 428.2201

|Δm| : 1.2 ppm



HPLC analysis conditions:

For analytical conditions,

I). Column : (*R*,*R*) WHELK–01

Abs. detector wavelength : 254 nm and 270 nm

Mobile phase : Hexanes:2-propanol = 95:5

Flow rate : 1.0 mL/min

Retention times (min) : ~ (-)-9.44 and ~ (+)-11.98

For preparative conditions,

I). Column : (*R*,*R*) WHELK–01

Abs. detector wavelength : 254 nm and 270 nm

Mobile phase : Hexanes:2-propanol = 95:5

Flow rate : 3.0 mL/min

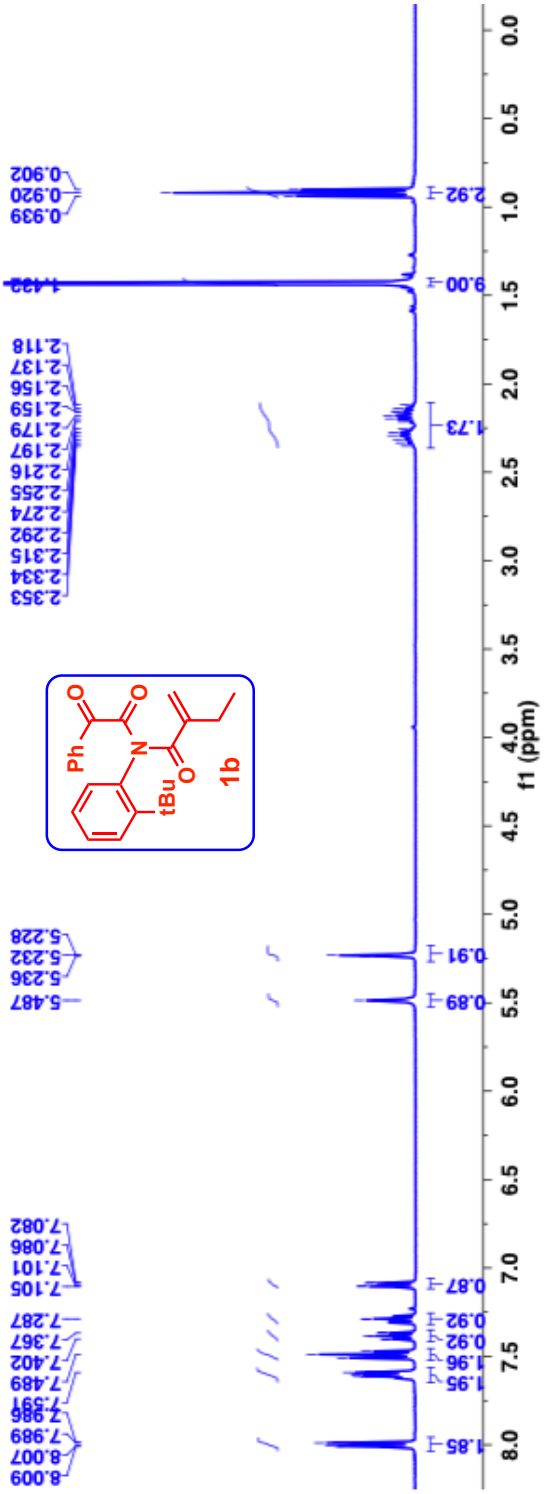
Retention times (min) : ~ (-)-14.0 and ~ (+)-17.37

Optical rotation $[\alpha]_D^{22}$:

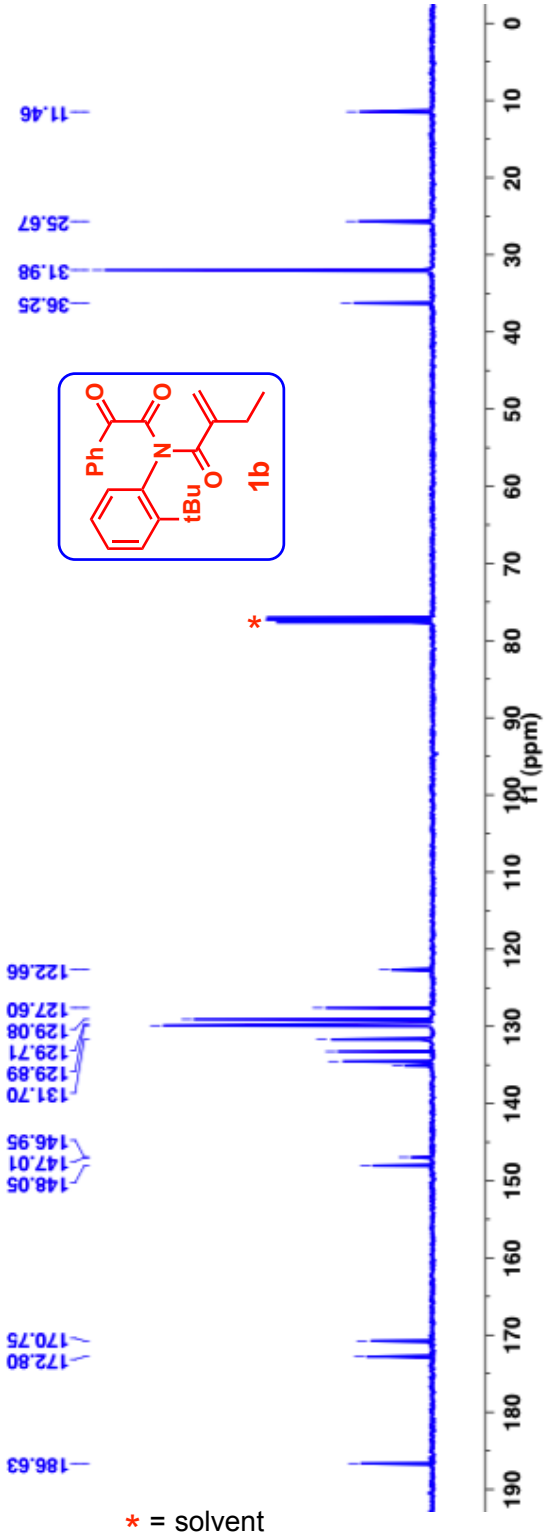
HPLC retention time (*R*,*R*) WHELK–01 at ~ 9.44 min, (*c* = 0.772 %, MeOH) = -22.05 deg.

HPLC retention time (*R*,*R*) WHELK–01 at ~ 11.98 min, (*c* = 0.772 %, MeOH) = +22.91 deg.

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 8.01-7.99 (m, 2H), 7.61-7.59 (m, 2H), 7.51-7.47(m, 2H), 7.41-7.36 (m, 1H), 7.29-7.287 (m, 1H), 7.10-7.08 (m, 1H), 5.49 (s, 1H), 5.23 (t, *J*=1.6 Hz, 1H) 2.35-2.12 (m, 2H), 1.43 (s, 9H) and 0.92 (t, *J*= 7.4 Hz, 3H).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 186.6, 172.8, 170.7, 148.0, 147.0, 146.9, 135.1, 134.5, 133.3, 131.7, 129.9, 129.7, 129.1, 127.6, 122.7, 36.2, 31.98, 25.7 and 11.5.



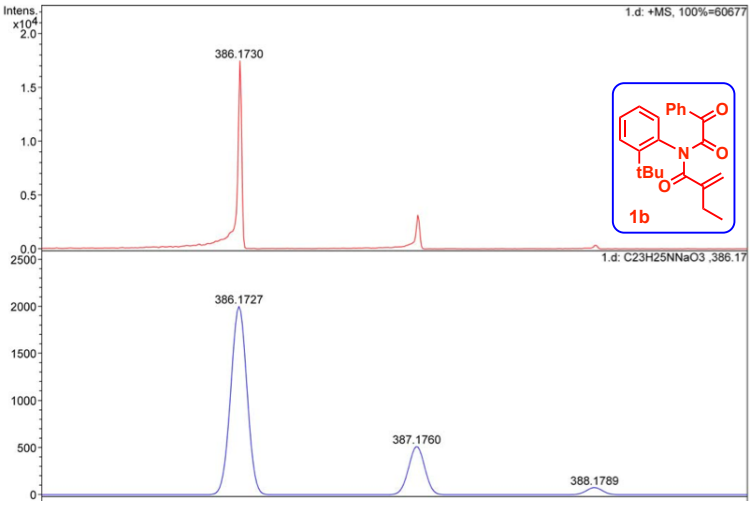
* = solvent

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

Calculated : 386.1727

Observed : 386.1730

|Δm| : 0.8 ppm



HPLC analysis conditions:

For analytical conditions,

I). Column : CHIRALPAK-AD-H

Abs. detector wavelength : 254 nm and 270 nm

Mobile phase : Hexanes:2-propanol = 90:10

Flow rate : 1.0 mL/min

Retention times (min) : ~ 5.66 [*M*-(-)-**1b**] and 13.58 [*P*-(+)-**1b**]

For preparative conditions,

I). Column : CHIRALPAK-AD-H

Abs. detector wavelength : 254 nm and 270 nm

Mobile phase : Hexanes:2-propanol = 95:5

Flow rate : 3.0 mL/min

Retention times (min) : ~ 10.80 [*M*-(-)-**1b**] and ~ 29.77 [*P*-(+)-**1b**]

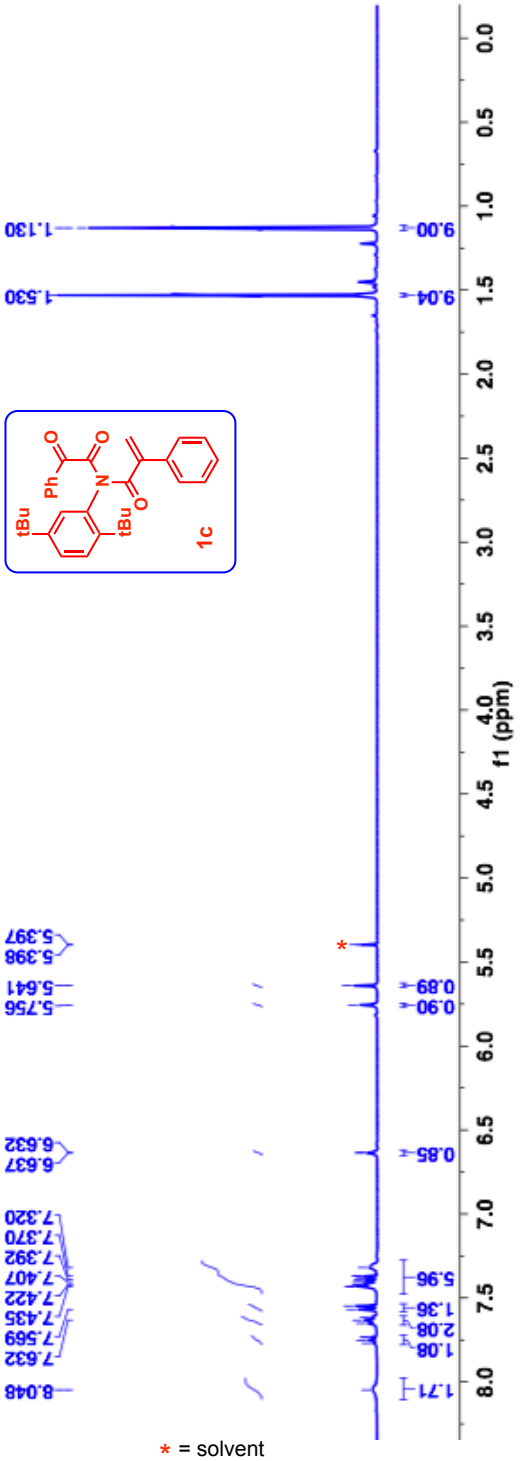
(The absolute crystal structure was obtained by single crystal XRD using Flack parameters)

Optical rotation $[\alpha]_D^{22}$:

HPLC retention time CHIRALPAK-AD-H at ~ 5.66 min, (*c* = 2.00 %, MeOH) = -65.06 deg.

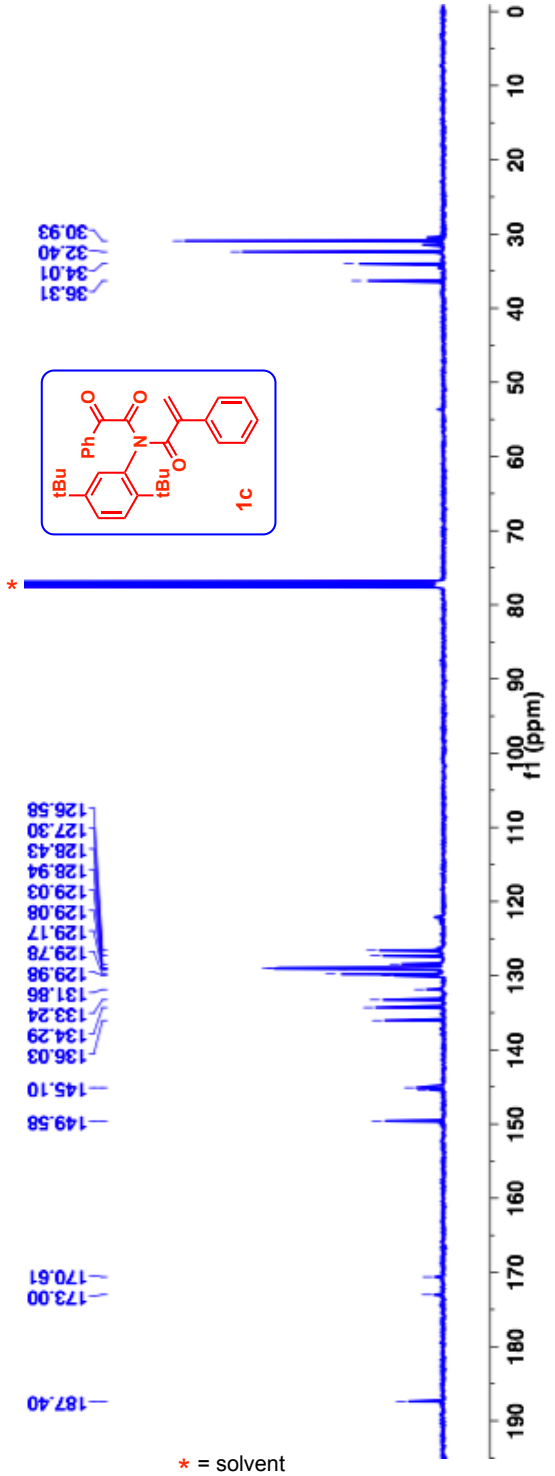
HPLC retention time CHIRALPAK-AD-H at ~ 13.58 min, (*c* = 2.00 %, MeOH) = +64.08 deg.

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 8.05-8.04 (m, 2H), 7.77-7.73 (m, 1H), 7.65-7.61 (m, 2H), 7.57-7.55 (m, 1H), 7.43-7.32 (m, 6H), 6.64-6.63 (m, 1H), 5.76 (s, 1H), 5.64 (s, 1H), 1.53 (s, 9H) and 1.13 (s, 9H)



* = solvent

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 187.4, 173.0, 170.6, 149.6, 145.4, 145.1, 136.0, 134.3, 133.2, 131.9, 129.98, 129.8, 129.2, 129.0, 129.1, 128.9, 128.4, 127.3, 126.6, 36.3, 34.0, 32.4 and 30.9.

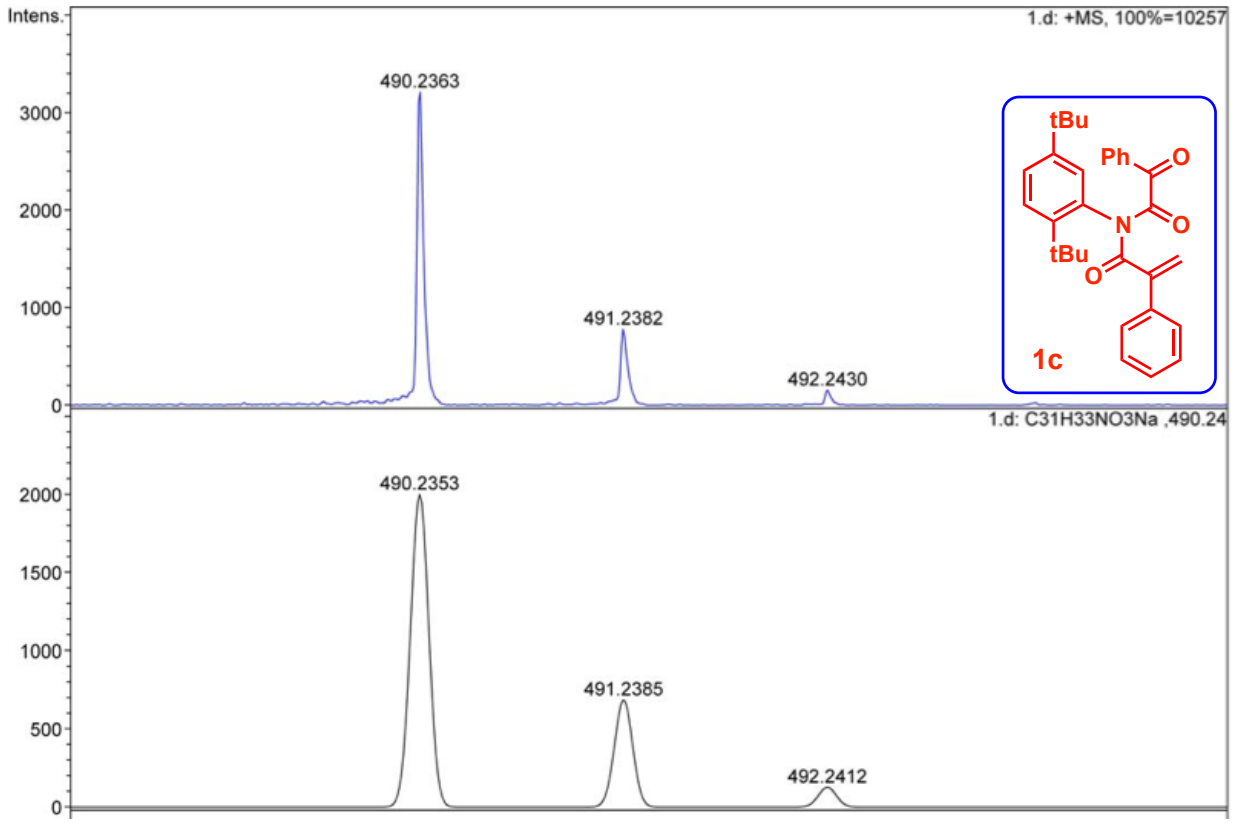


HRMS-ESI (m/z) ([M + Na]$^+$):

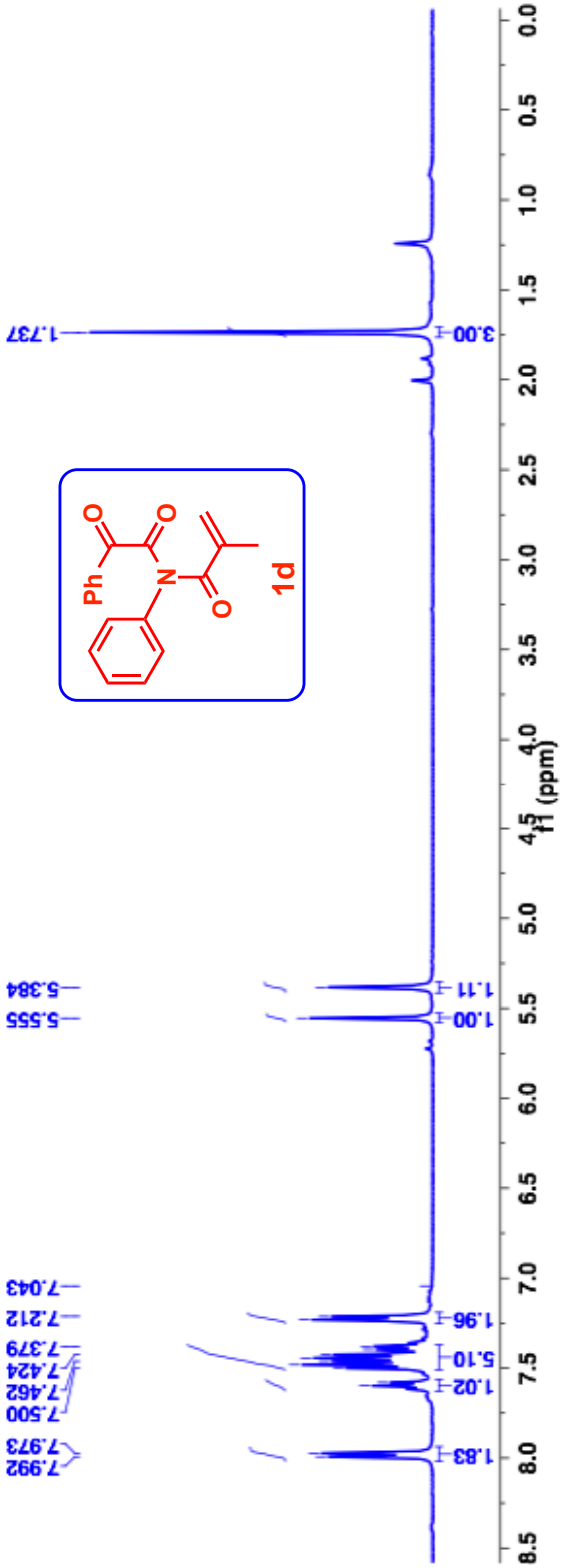
Calculated : 490.2353

Observed : 490.2363

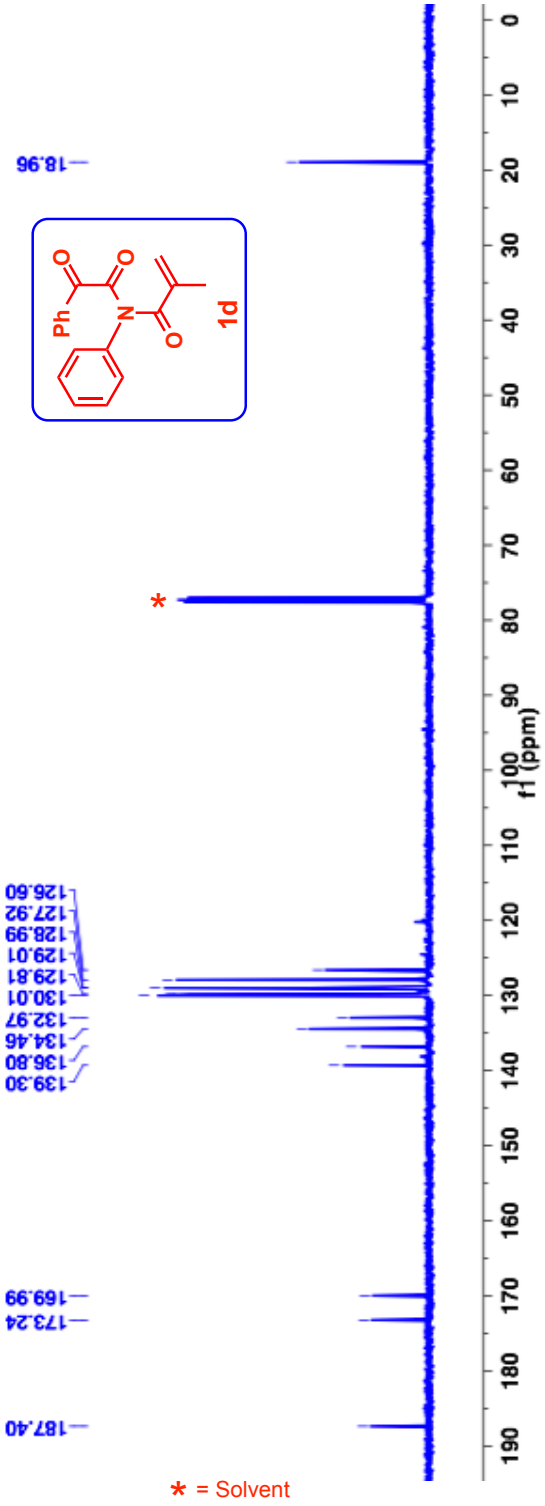
|Δm| : 2.0 ppm



^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.99-7.97 (m, 2H), 7.598-7.58 (m, 1H), 7.50-7.38 (m, 5H), 7.23-7.21 (m, 2H), 5.55 (s, 1H), 5.38 (s, 1H) and 1.74 (m, 3H).

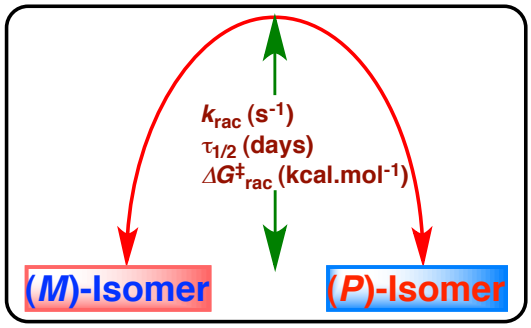


^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 187.4, 173.2, 169.99, 139.3, 136.8, 134.5, 132.97, 130.0, 129.8, 129.0, 128.99, 127.9, 126.6 and 18.96.



4. RACEMIZATION KINETICS OF NON-BIARYL AXIALLY CHIRAL α-OXOAMIDES **1a-b**

Racemization of optically pure non-biaryl axially chiral α-oxoamides **1a-b** was followed at 50 °C in different solvents (benzene and acetonitrile). The racemization rate was followed by HPLC analyses on a chiral stationary phase at different time intervals (Figures S1 and S2). The activation energy (Table S1) for racemization was computed from equation 1.[2]



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

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

The half-life of racemization, $t_{1/2}$, can be calculated using the rate constant of racemization k_{rac} (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, $k_{rac} = 2.k_{enant}$; 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 constant for racemization.

Note: $R_0 = R + S$

At 50% ee, the equation becomes:

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

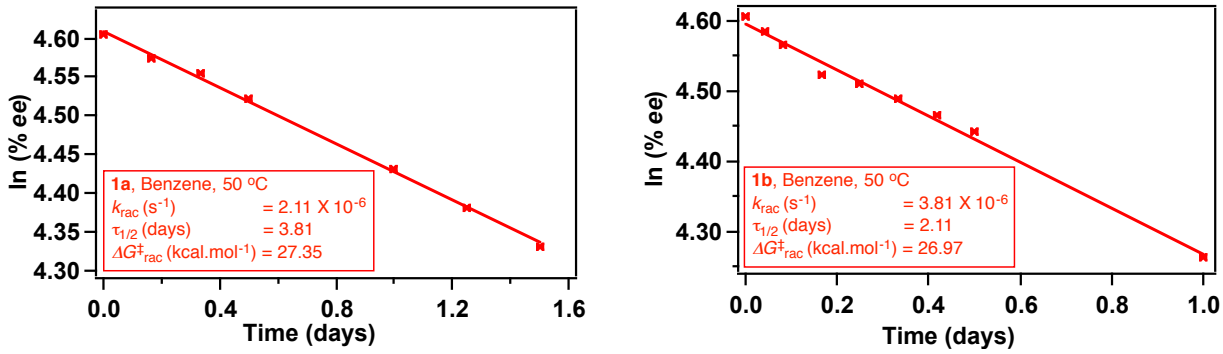


Figure S1: Racemization kinetics of axially chiral α-oxoamides **1a-b** in benzene at 50 °C.

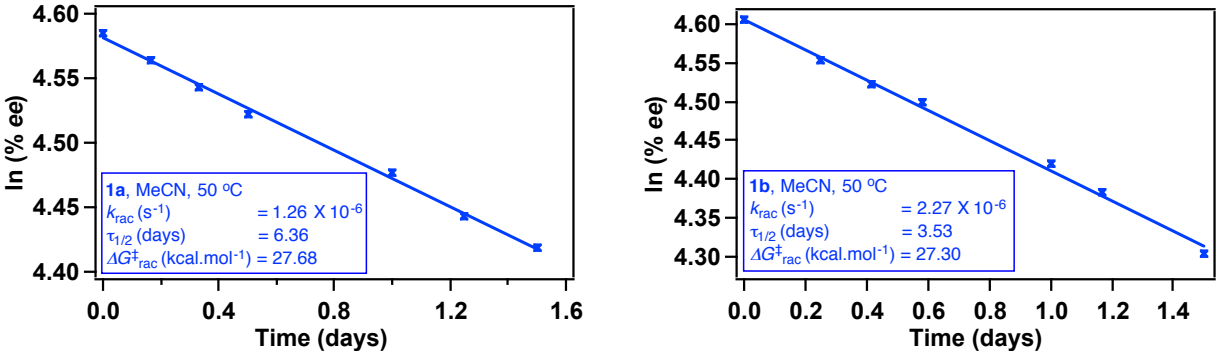


Figure S2: Racemization kinetics of axially chiral α-oxoamides **1a-b** in acetonitrile at 50 °C.

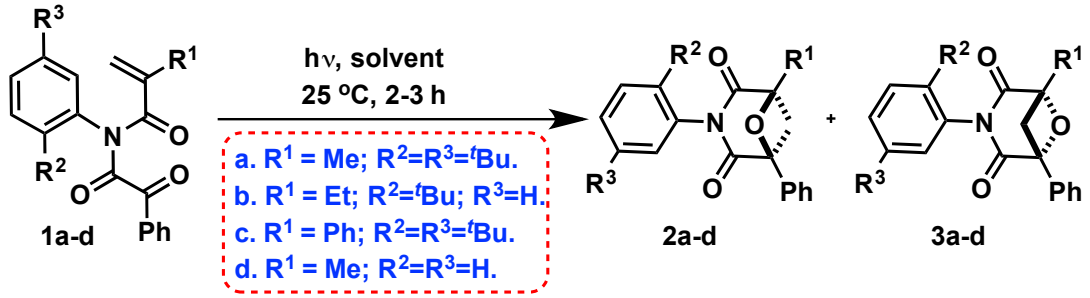
Table S1: Activation energy, rate and half-life for racemization of optically pure non-biaryl axially chiral α-oxoamides **1a-b**.

Entry	T (°C)	Compound	Solvent	Physical parameters		
				$\tau_{1/2rac}$ (days)	$\Delta G^{\ddagger}_{rac}$ (kcal•mol^{-1})	k_{rac} (s^{-1})
1	50	**1a**	Benzene	3.81	27.35	2.11 X 10^{-6}
2	50		MeCN	6.36	27.68	1.26 X 10^{-6}
3	50	**1b**	Benzene	2.11	26.97	3.81 X 10^{-6}
4	50		MeCN	3.53	27.30	2.27 X 10^{-6}

[a] Reported values carry an error of ±5%. MeCN – acetonitrile.

5. General irradiation procedures and characterization of photoproducts

5a. Procedure for photoreaction of α-oxoamides **1a-d**



Scheme S6: Photoreaction of α-oxoamides derivatives **1a-d.**

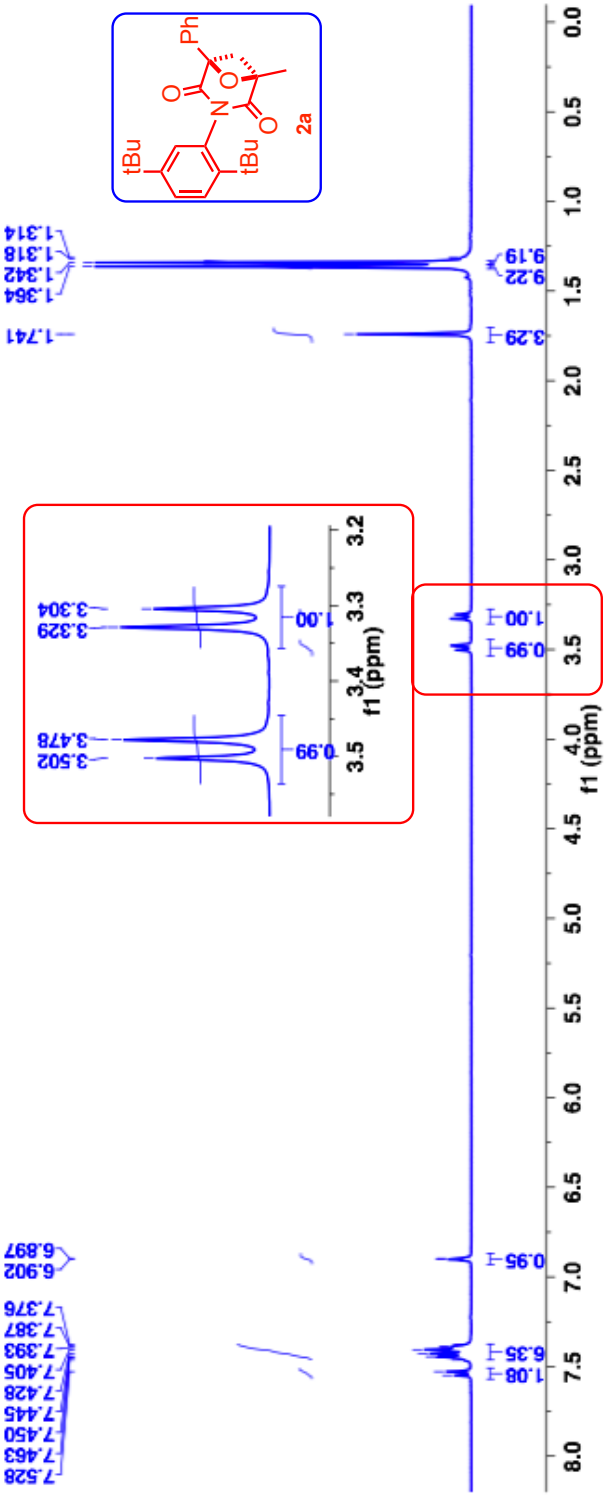
A solution (~ 3 mM concentration/1mg in 1mL) of optically pure axially chiral α-oxoamides **1a-b** and **1c-d** (racemic **1c** and achiral **1d**) in benzene or acetonitrile were irradiated at 25 °C for a given time interval in Pyrex tube with a 450 W medium pressure mercury lamp placed inside a water cooled quartz well under a constant flow of nitrogen or in a rayonet reactor equipped with 16 (12 Watt) ~350 nm bulbs under constant flow of nitrogen. After irradiation, the solvent was evaporated under reduced pressure and the photoproducts were isolated by preparative thin layer chromatography. For large scale reactions, the photosylate was purified by combiflash using hexanes:ethyl acetate mixtures. The photoproducts were then characterized by NMR spectroscopy, mass spectrometry, single crystal XRD, $[\alpha]^{T}_{D}$ and HPLC analysis of the photosylate on a chiral stationary phase gave the optical purity of the photoproducts.

Note: For some compounds (**1a** and **1c**), the reaction was monitored by ^{1}H-NMR spectroscopy, as TLC monitoring was difficult due to the overlap of R_f for starting material and the product.

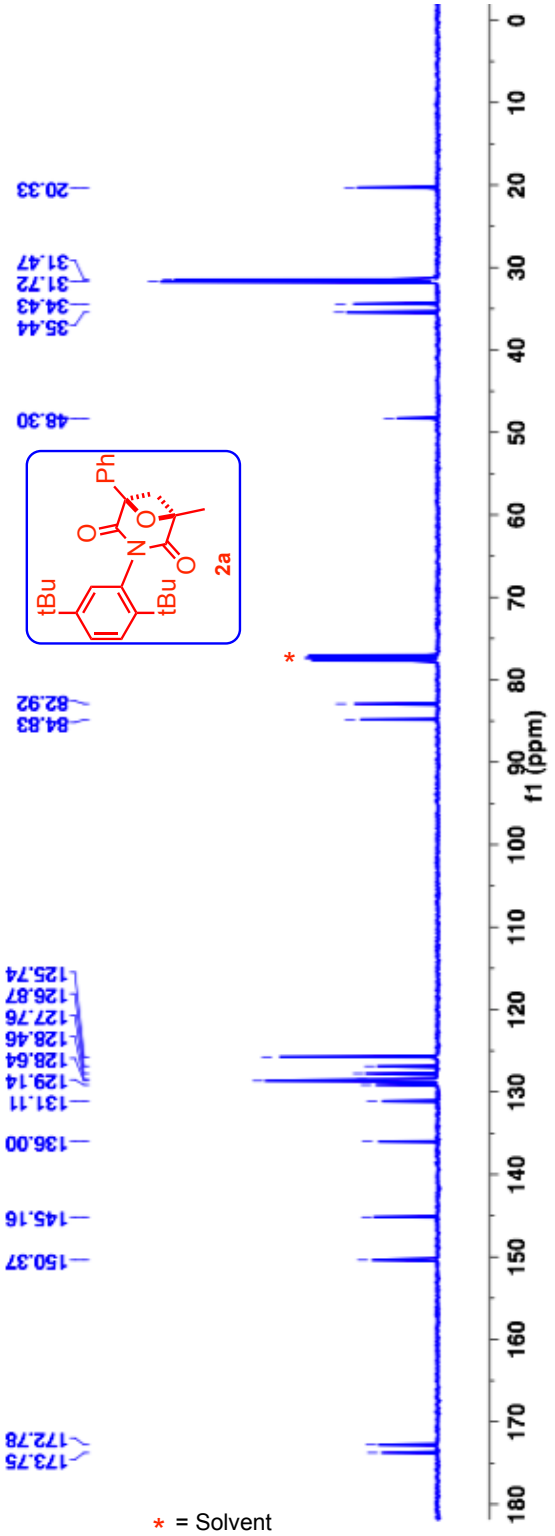
TLC condition - R*f* = 0.56 for **2a** and 0.73 for **3a** respectively (80% hexanes:20% ethyl acetate)
TLC condition - R*f* = 0.46 for **2b** and 0.59 for **3b** respectively (80% hexanes:20% ethyl acetate)
TLC condition - R*f* = 0.50 for **2c** (50% hexanes:50% DCM)
TLC condition - R*f* = 0.24 for **2d** (50% hexanes:50% ethyl acetate)

5b. Characterization of photoproducts **2** and **3**

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.55-7.53 (m, 1H), 7.46-7.38 (m, 6H), 6.90 (d, *J*=2 Hz, 1H), 3.50-3.30 (ABq, 2H), 1.74 (s, 3H), 1.36 (s, 9H) and 1.34 (s, 9H).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 173.7, 172.8, 150.4, 145.2, 136.0, 131.1, 129.1, 128.6, 128.5, 127.8, 126.9, 125.7, 84.8, 82.9, 48.3, 35.4, 34.4, 31.7, 31.5 and 20.3.

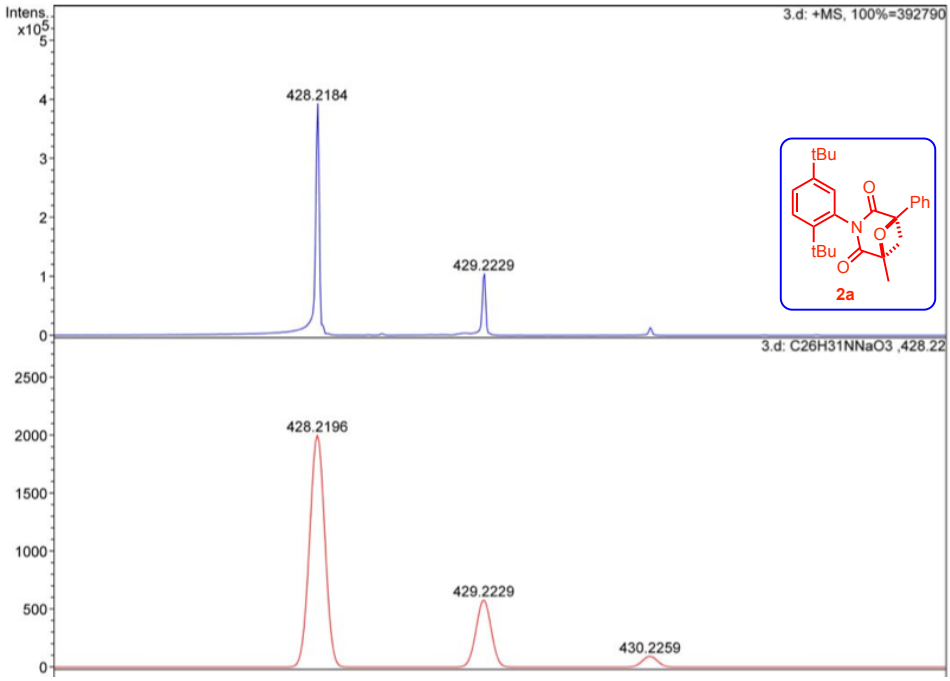


HRMS-ESI (m/z) ($[M + Na]^+$):

Calculated : 428.2196

Observed : 428.2184

$|\Delta m|$: 2.8 ppm



HPLC analysis conditions:

For analytical conditions,

I). Column : CHIRALPAK-AD-H

Abs. detector wavelength : 254 nm and 270 nm

Mobile phase : Hexanes:2-propanol = 98:2

Flow rate : 1.0 mL/min

Retention times (min) : ~ (+)-4.64 and (-)-7.95

For preparative conditions,

I). Column : CHIRALPAK-AD-H

Abs. detector wavelength : 254 nm and 270 nm

Mobile phase : Hexanes:2-propanol = 99:1

Flow rate : 3.0 mL/min

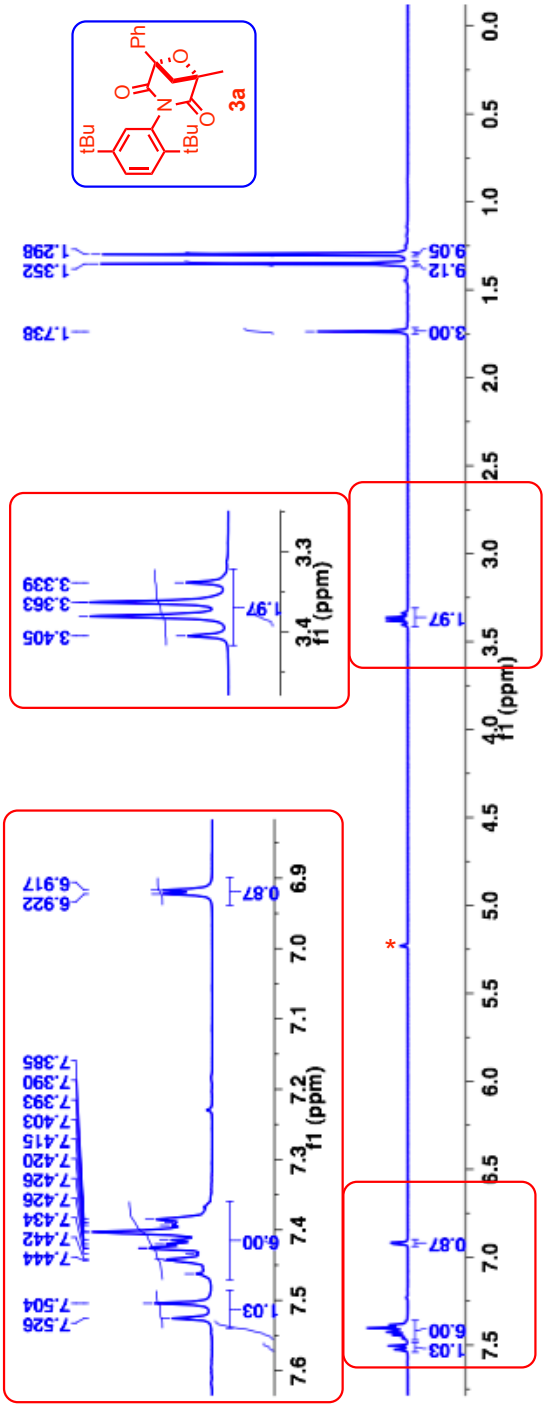
Retention times (min) : ~ (+)-7.53 and (-)-15.10

Optical rotation $[\alpha]_D^{22}$:

HPLC retention time CHIRALPAK-AD-H at ~ 4.64 min, (*c* = 1.10 %, MeOH) = +22.27 deg.

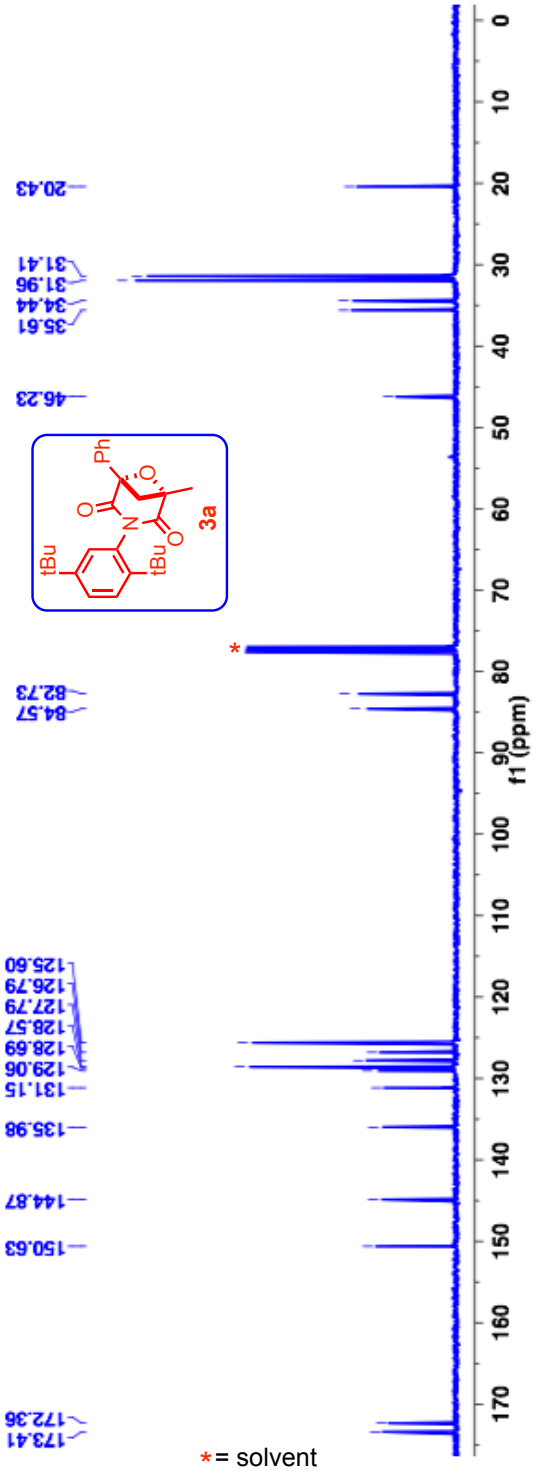
HPLC retention time CHIRALPAK-AD-H at ~ 7.95 min, (*c* = 1.10 %, MeOH) = -23.41 deg.

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.53-7.50 (m, 1H), 7.46-7.38 (m, 6H), 6.92 (d, *J*=2 Hz, 1H), 3.40-3.339 (ABq, 2H), 1.74 (s, 3H), 1.35 (s, 9H) and 1.298 (s, 9H).



* = solvent

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 173.4, 172.4, 150.6, 144.9, 135.98, 131.1, 129.1, 128.7, 128.6, 127.8, 126.8, 125.6, 84.6, 82.7, 46.2, 35.6, 34.4, 31.96, 31.4 and 20.4.



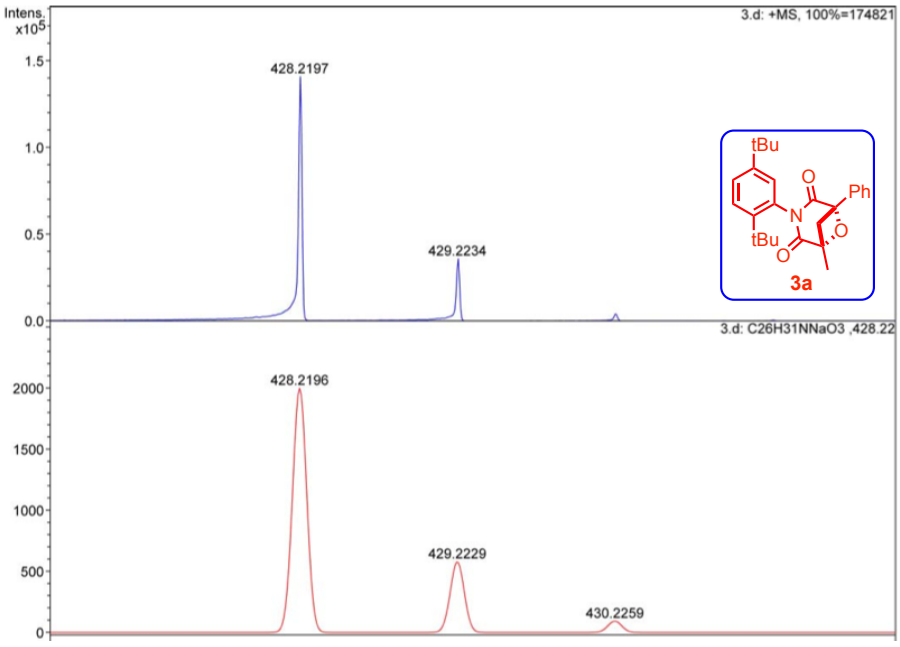
* = solvent

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

Calculated : 428.2196

Observed : 428.2197

|Δm| : 0.2 ppm



HPLC analysis conditions:

For analytical conditions,

I). Column : (*R*,*R*) WHELK–01

Abs. detector wavelength : 254 nm and 270 nm

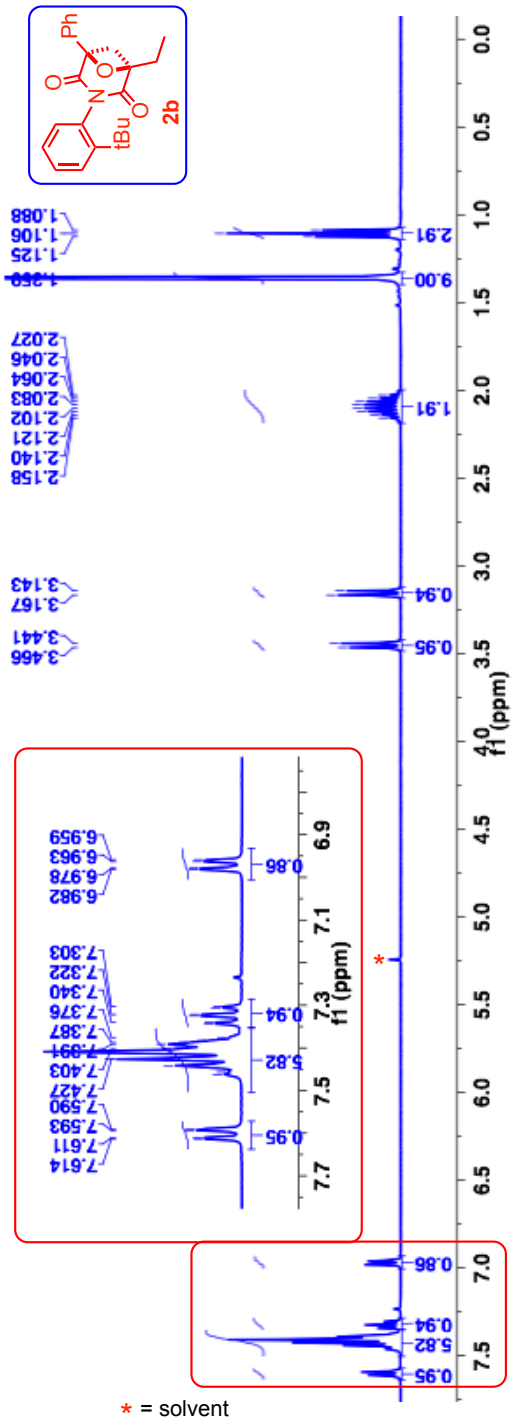
Mobile phase : Hexanes:2-propanol = 98:2

Flow rate : 1.0 mL/min

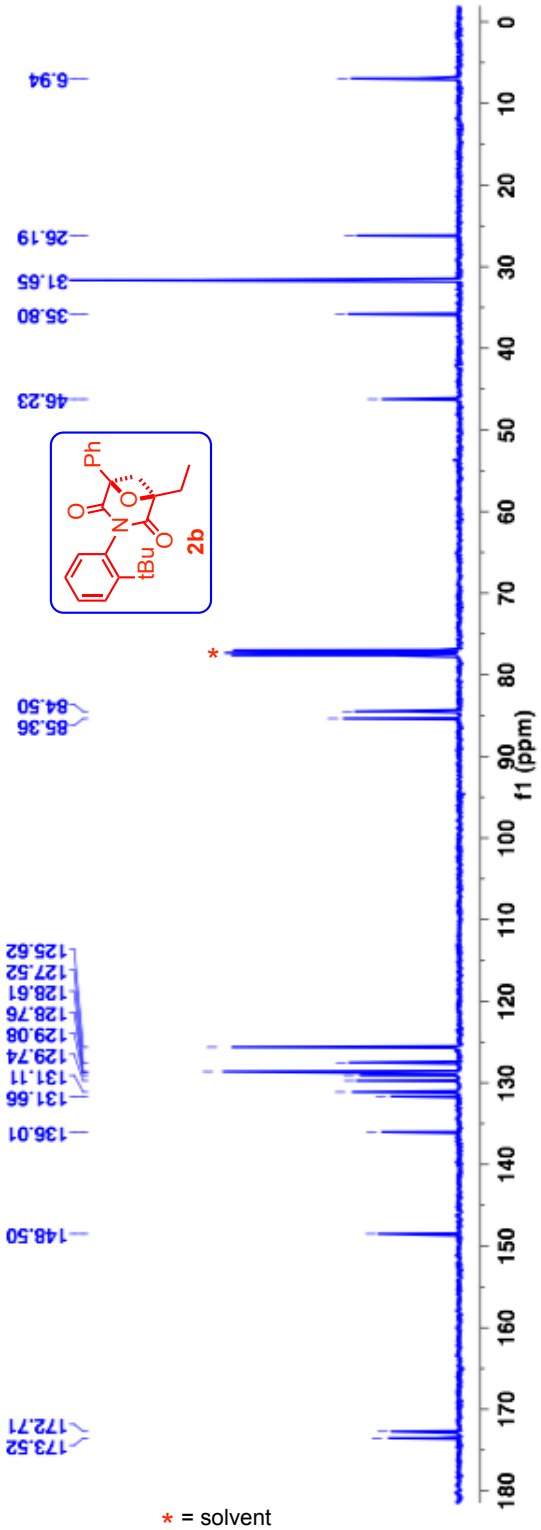
Retention times (min) : ~ 10.25 [**PkA**] and ~ 20.52 [**PkB**]

(**PkA** and **PkB** refers to the order of elution of the isomers in the HPLC on the chiral stationary phase)

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.61-7.59 (m, 1H), 7.46-7.38 (m, 6H), 7.32-7.30 (m, 1H), 6.98-6.96 (m, 1H), 3.47-3.14 (ABq, 2H), 2.16-2.03 (m, 2H), 1.36 (s, 9H) and 1.11 (t, *J*=7.46 Hz, 3H)



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 173.5, 172.7, 148.5, 136.0, 131.7, 131.1, 129.7, 129.1, 128.8, 128.6, 127.5, 125.6, 85.4, 84.5, 46.2, 35.8, 31.6, 26.2 and 6.9.

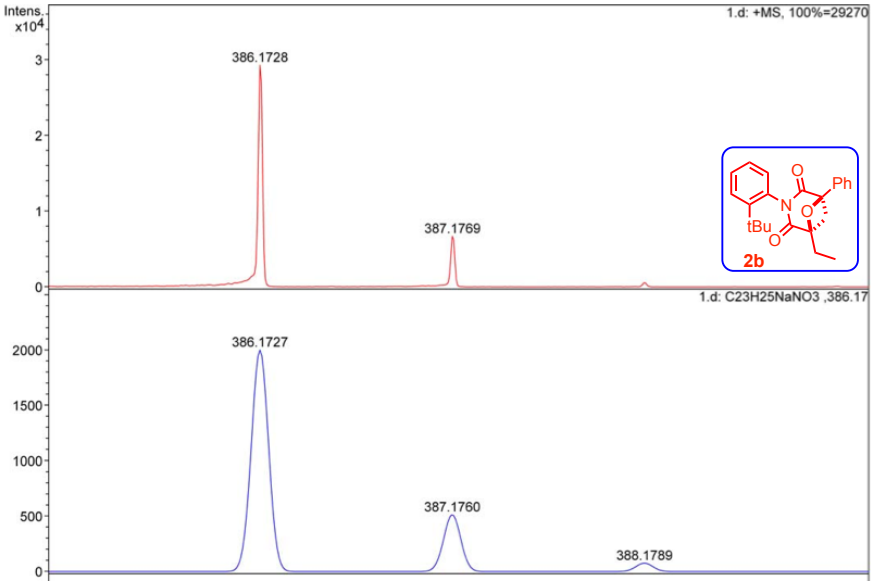


HRMS-ESI (m/z) ($[M + Na]^+$):

Calculated : 386.1727

Observed : 386.1728

$|\Delta m|$: 0.3 ppm



HPLC analysis conditions:

For analytical conditions,

I). Column : CHIRALPAK-AD-H

Abs. detector wavelength : 254 nm and 270 nm

Mobile phase : Hexanes:2-propanol = 90:10

Flow rate : 1.0 mL/min

Retention times (min) : ~ (-)-6.34 and (+)-10.92

For preparative conditions,

I). Column : (*R*,*R*) WHELK–01

Abs. detector wavelength : 254 nm and 270 nm

Mobile phase : Hexanes:2-propanol = 98:2

Flow rate : 3.0 mL/min

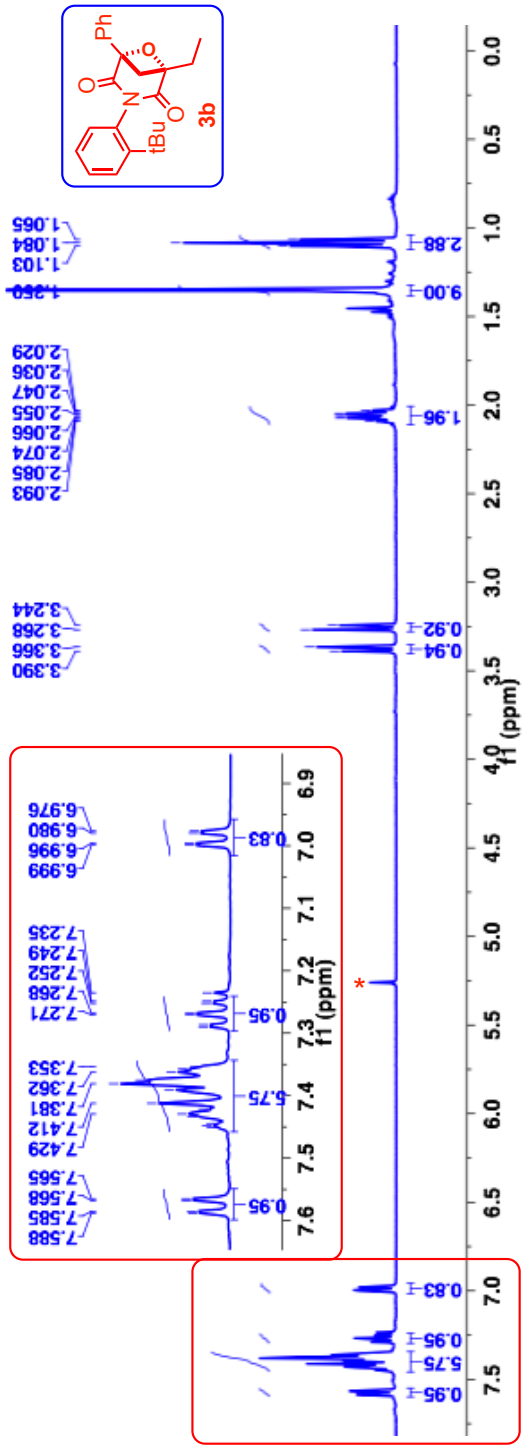
Retention times (min) : ~ (+)-21.00 and (-)-28.14

Optical rotation $[\alpha]_D^{24}$:

HPLC retention time CHIRALPAK-AD-H at ~ 6.34 min, (*c* = 1.83 %, $CHCl_3$) =-11.91 deg.

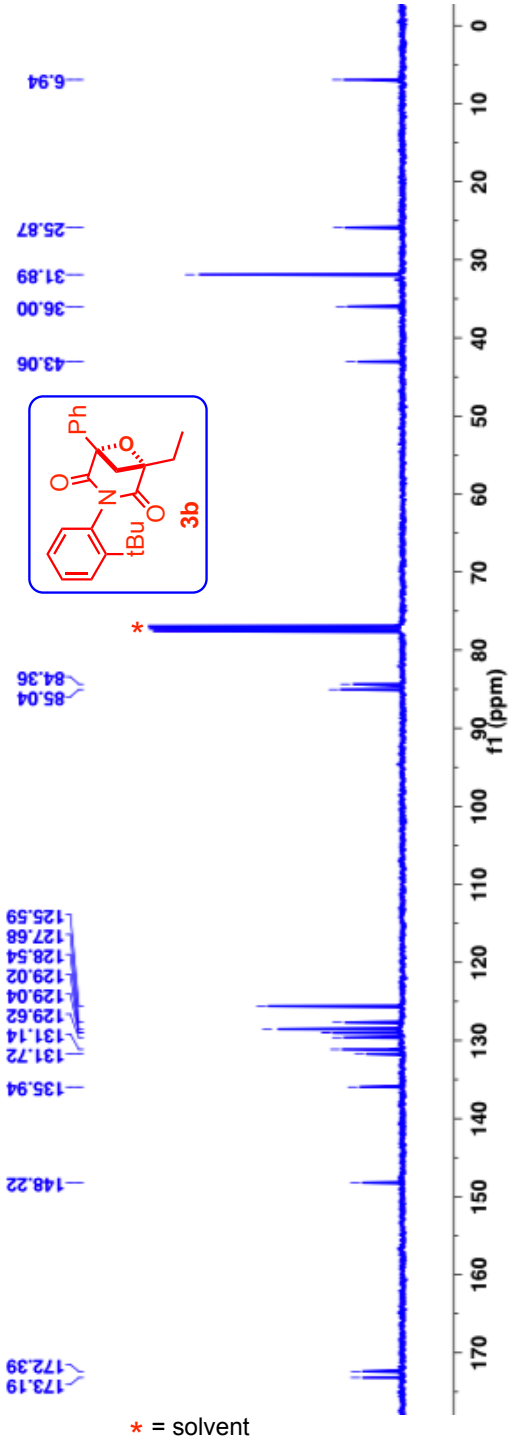
HPLC retention time CHIRALPAK-AD-H at ~ 10.92 min, (*c* = 1.83 %, $CHCl_3$) = +11.92 deg.

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.59 (m, 1H), 7.43-7.35 (m, 6H), 7.27-7.23 (m, 1H), 6.999-6.98 (m, 1H), 3.39-3.24 (ABq, 2H), 2.09-2.03 (m, 2H), 1.35 (s, 9H) and 1.08 (t, *J*= 7.6 Hz, 3H).



* = solvent

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 173.2, 172.4, 148.2, 135.9, 131.7, 131.1, 129.6, 129.0, 129.0, 128.5, 127.7, 125.6, 85.0, 84.4, 43.1, 36.0, 31.9, 25.9 and 6.94.



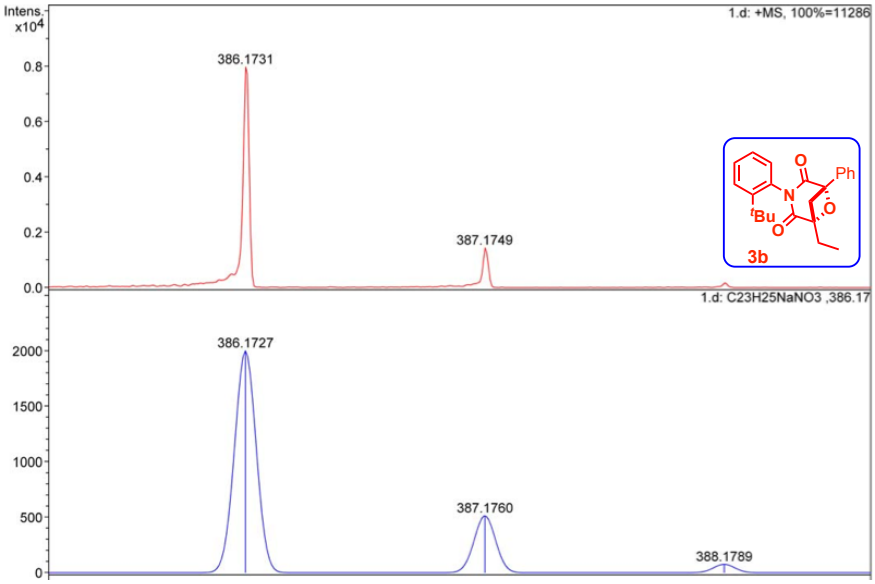
* = solvent

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

Calculated : 386.1727

Observed : 386.1731

|Δm| : 1.0 ppm



HPLC analysis conditions:

For analytical conditions,

I). Column : (*R*,*R*) WHELK–01

Abs. detector wavelength : 254 nm and 270 nm

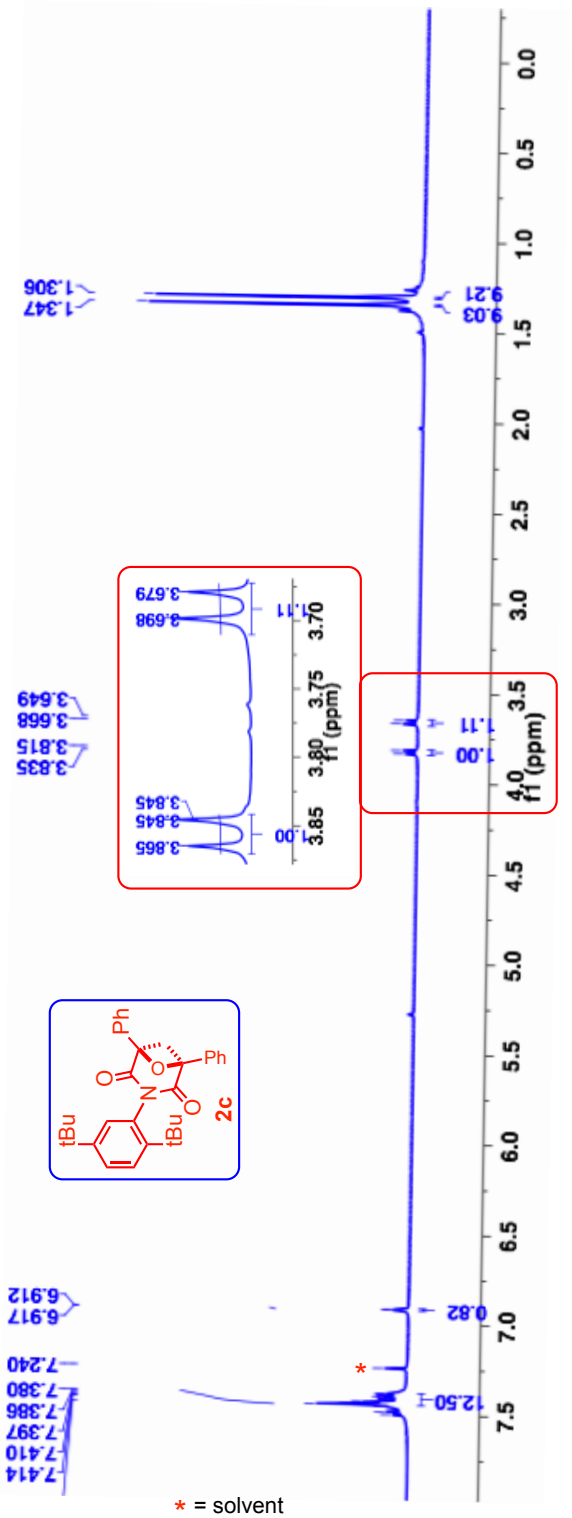
Mobile phase : Hexanes:2-propanol = 90:10

Flow rate : 1.0 mL/min

Retention times (min) : ~ 9.15 (**PkA**) and 11.72 (**PkB**)

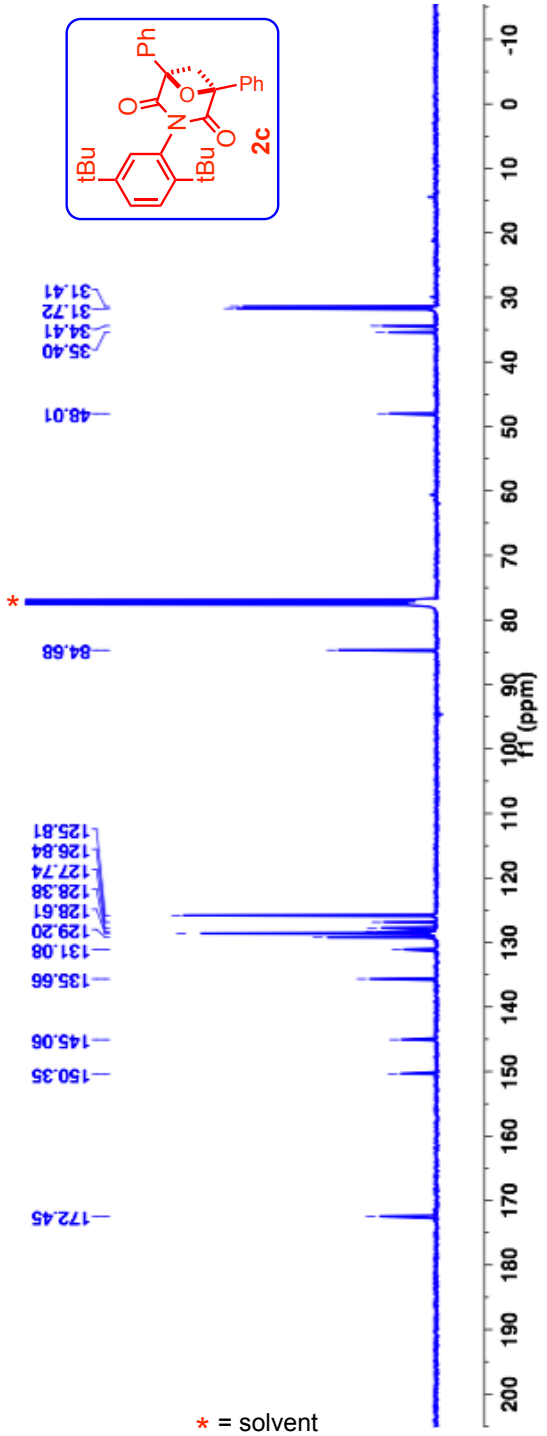
(**PkA** and **PkB** refers to the order of elution of the isomers in the HPLC on the chiral stationary phase)

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.74-7.38 (m, 12H), 6.92-6.91 (m, 1H), 3.87-3.68 (ABq, 2H), 1.35 (s, 9H) and 1.31 (s, 9H).



* = solvent

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 172.4, 150.3, 145.1, 135.7, 131.1, 129.2, 128.6, 128.4, 127.7, 126.8, 125.8, 84.7, 48.0, 35.4, 34.4, 31.7 and 31.4.

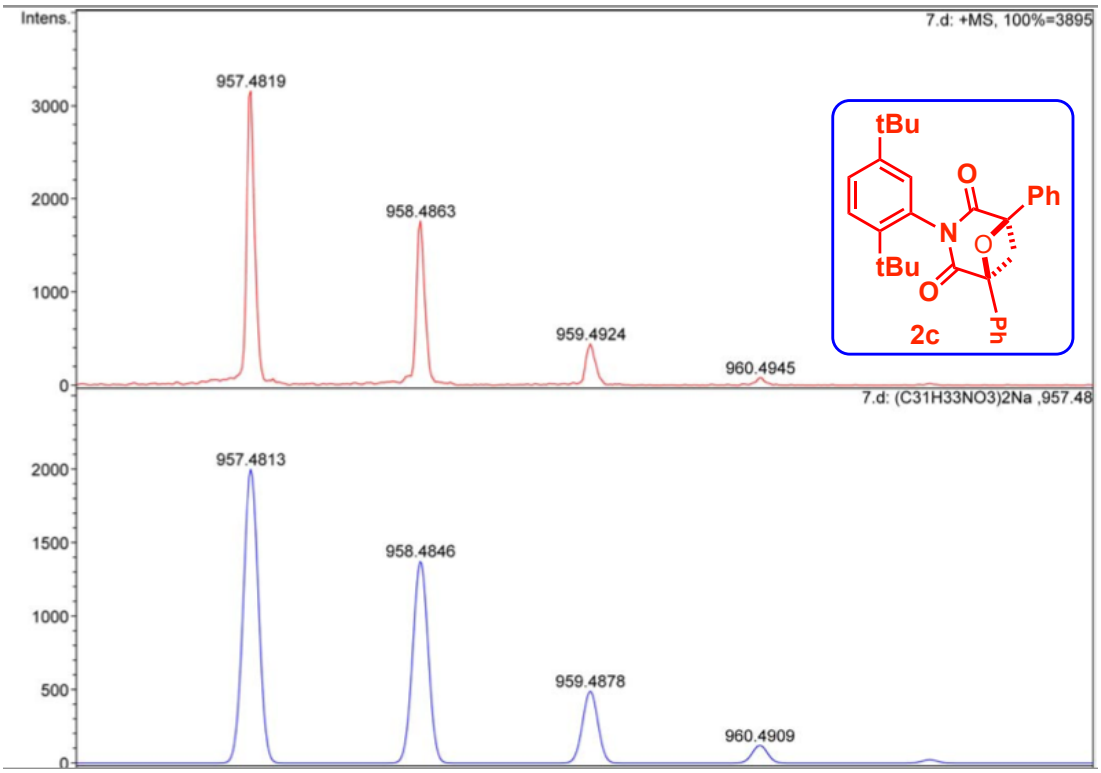


HRMS-ESI (m/z) ($[2M+Na]^+$):

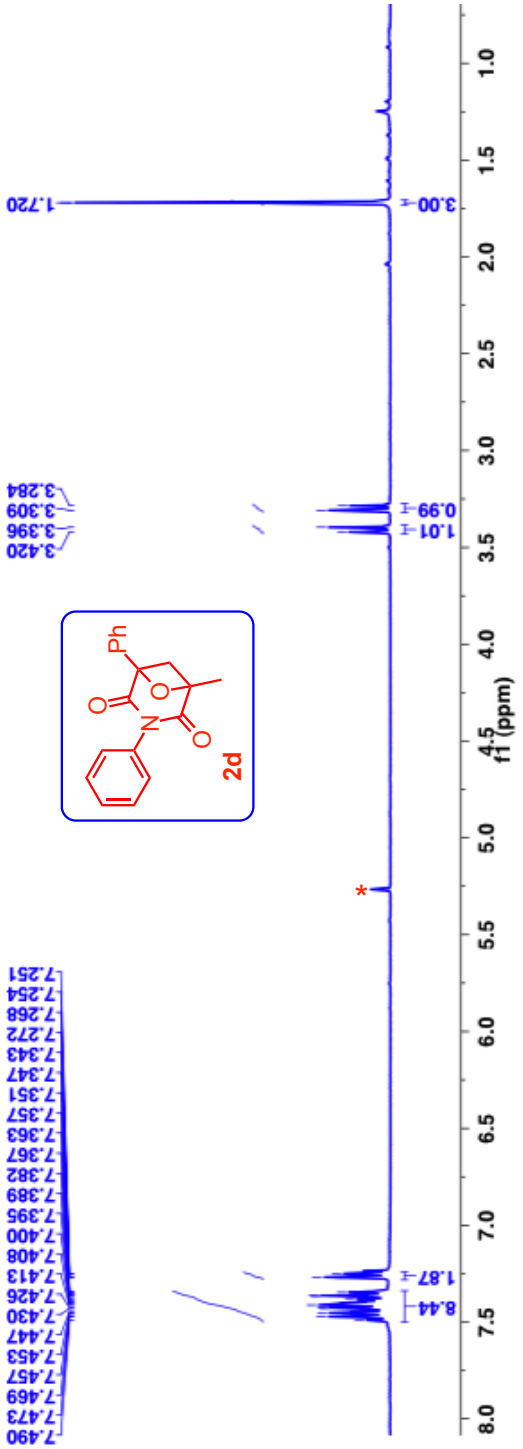
Calculated : 957.4813

Observed : 957.4819

|Δm| : 0.6 ppm

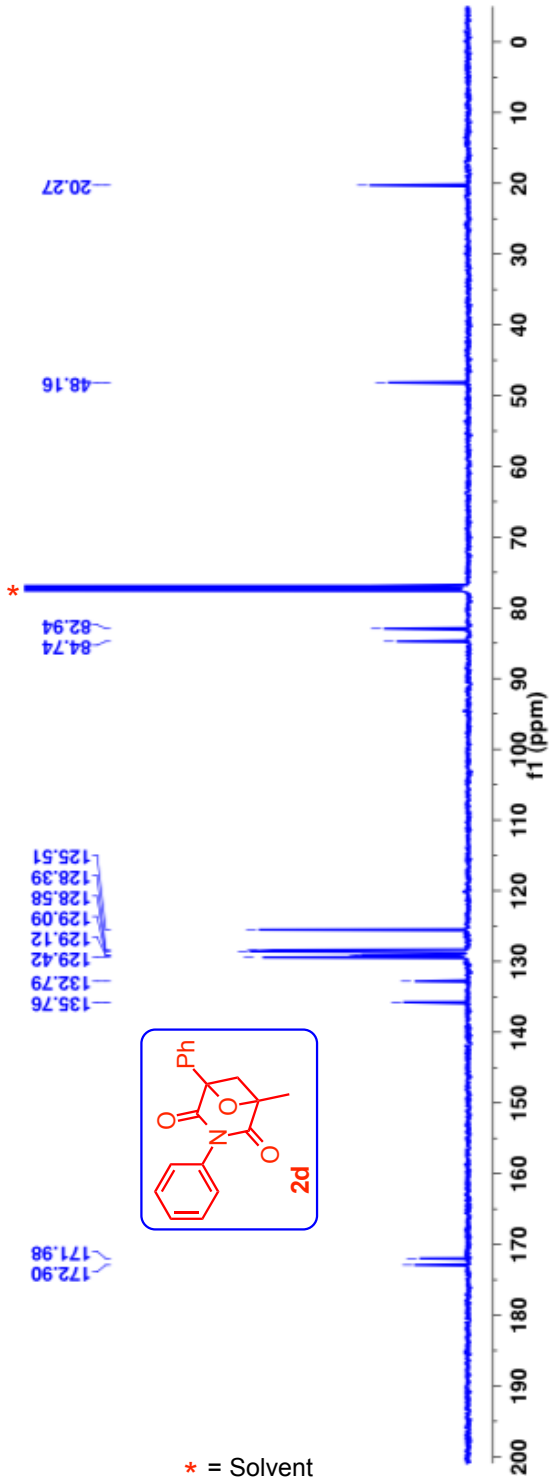


^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.49-7.34 (m, 8H), 7.27-7.25 (m, 2H), 3.42-3.31 (ABq, 2H) and 1.72 (s, 3H).



* = Solvent

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 172.9, 171.98, 135.8, 132.8, 129.4, 129.1, 129.09, 128.6, 128.4, 125.5, 84.7, 82.9, 48.2 and 20.3.



6. UV-Vis spectrum of α-oxoamides **1a-d** and its photoproducts.

The UV-Vis spectra of oxoamides **1a-d** and its photoproducts **2** and **3** were measured in acetonitrile.

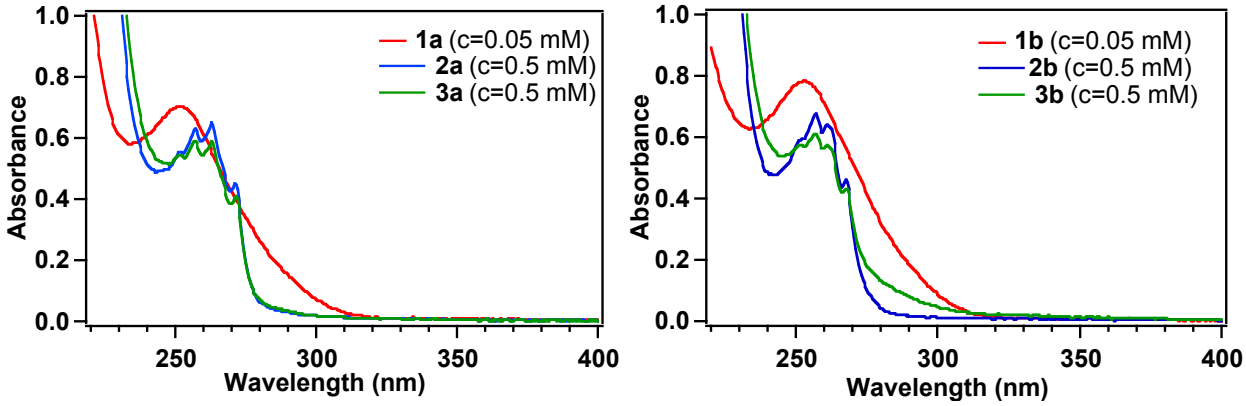


Figure S3: UV-Vis spectra of axially chiral oxoamides and its photoproducts in acetonitrile.

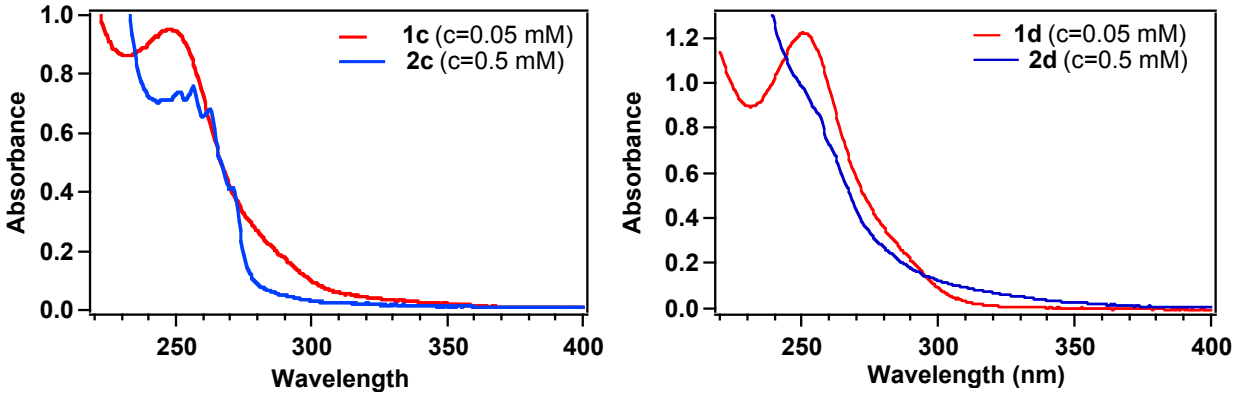
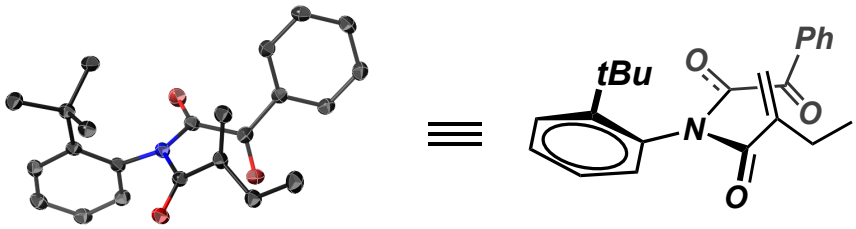


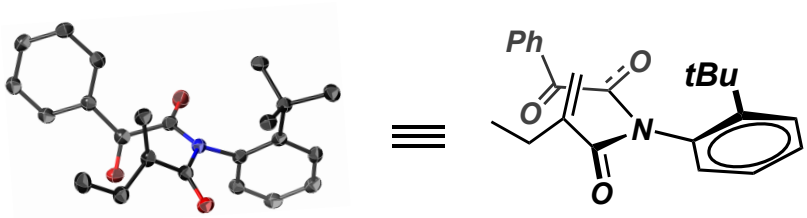
Figure S4: UV-Vis spectra of oxoamides and its photoproducts in acetonitrile.

7. X-RAY STRUCTURES AND STRUCTURAL PARAMETERS:

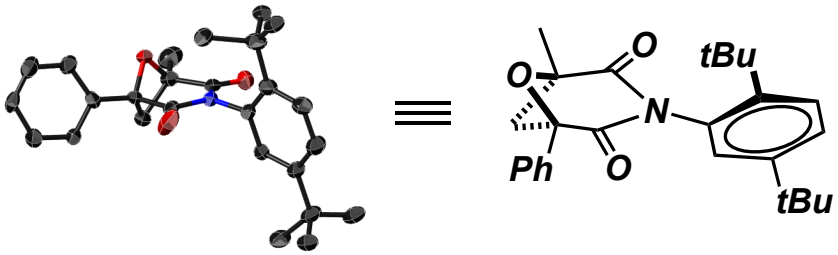
7.1 X-ray structure of (-)-(*M*)-**1b** (Crystallized from: hexanes/2-propanol)



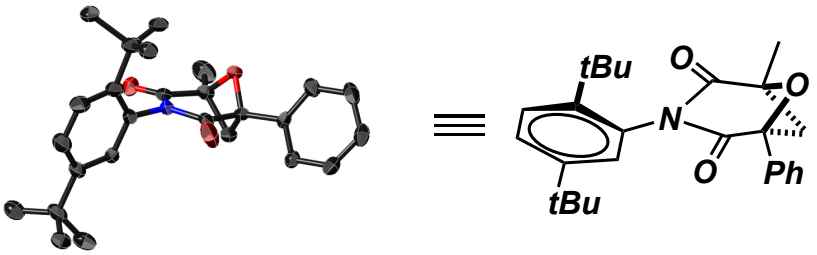
7.2 X-ray structure of (+)-(*P*)- **1b** (Crystallized from: hexanes/chloroform)



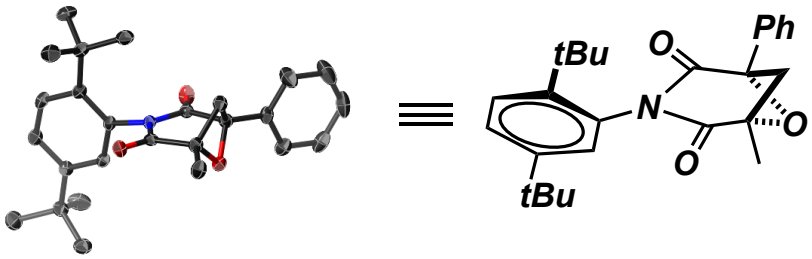
7.3 X-ray structure of (-)-(*R,R,M*)-**2a** (crystallized from: hexanes/chloroform)



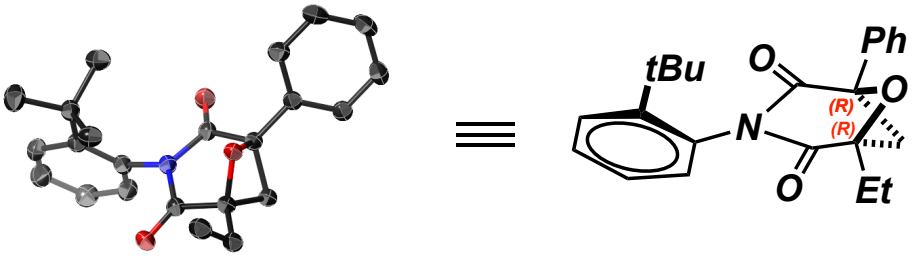
7.4 X-ray structure of (+)-(*S,S,P*)-**2a** (crystallized from: hexanes/2-propanol)



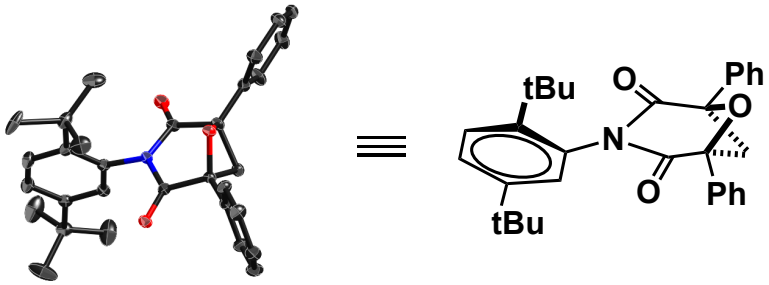
7.5 X-ray structure of **3a** (crystallized from: hexanes/chloroform)



7.6 X-ray structure of (+)-(*R,R,M*)-**2b** (crystallized from: hexanes/chloroform)



7.8 X-ray structure of **2c** (crystallized from: hexanes/ethylacetate)



7.6 Structural parameters table

TABLE S2: STRUCTURAL PARAMETERS OF COMPOUNDS (*M*)-**1b**, (*P*)-**1b**, (*R, R, M*)-**2a**, (*S, S, P*)-**2a**, (*R, R, M*)-**2b**, **3a** and **2c**.

Crystals	(*M*)_**1b**	(*P*)_**1b**	(*R,R,M*)_**2a**	(*S,S,P*)_**2a**	(*R,R,M*)_**2b**	**3a**	**2c**
Formula	$C_{23}H_{25}NO_3$	$C_{23}H_{25}NO_3$	$C_{26}H_{31}NO_3$	$C_{26}H_{31}NO_3$	$C_{23}H_{25}NO_3$	$C_{26}H_{31}NO_3$	$C_{31}H_{33}NO_3$
FW	363.44	363.44	405.52	405.52	363.44	405.52	467.58
Cryst. Size [mm]	.24, .24, .06	.18, .16, .12	.25, .17, .07	.25, .17, .07	.24, .17, .07	.16, 06, .03	.43, .21, .04
Space Group, Z	$P2_12_12_1$, 4	$P2_12_12_1$, 4	$P2_1$, 2	$P2_1$, 2	$P2_1$, 2	P-1, 4	Cc, 4
a (Å)	7.6205(2)	7.6186(2)	9.4837(3)	9.4836(3)	8.4687(3)	9.7846(4)	11.5834(4)
b (Å)	10.6084(3)	10.6097(3)	11.0800(3)	11.0788(3)	8.4682(3)	12.0025(6)	22.5492(7)
c (Å)	24.2862(7)	24.3166(7)	11.5198(3)	11.5270(3)	14.3425(5)	20.5396(9)	11.4549(4)
α (^{o})	90	90	90	90	90	89.213(2)	90
β (^{o})	90	90	106.749(1)	106.817(2)	103.349(2)	76.836(2)	120.314(2)
γ (^{o})	90	90	90	90	90	78.502(2)	90
V (Å^3)	1963.33(9)	1965.54(8)	1159.14(6)	1159.31(6)	1000.78(6)	2300.37(18)	2582.89(15)
ρcalc [g/cm^3]	1.230	1.228	1.162	1.162	1.206	1.171	1.202
μ [mm^{-1}]	.646	.645	.594	.594	.633	.599	.603
Radiation Type	Cu	Cu	Cu	Cu	Cu	Cu	Cu
F(000)	776	776	436	436	388	872	1000
No of measured refl.	8473	15043	12752	16291	9615	27607	18163
No of independent refl.	3399	3429	3872	4117	3355	7861	3923
No of refl. (I ≥ 2σ)	3337	3403	3856	3957	3282	6654	3087
R1/wR2 (I ≥ 2σ) [%]	2.52/6.40	2.56/6.58	5.64/14.36	5.13/11.00	3.12/8.27	3.68/9.02	6.95/17.74
R1/wR2 (all data) [%]	2.58/6.45	2.58/6.59	5.66/14.37	5.38/11.13	3.21/8.37	4.55/9.54	10.93/23.25

8. REFERENCES

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2. C. Wolf, *Dynamic Stereochemistry of Chiral Compounds. Principles and Applications*, RSC publishing: Cambridge, UK., 2008.