

## Supporting Information (90 Pages)

# Light-induced stereospecific intramolecular [2+2]-cycloaddition of atropisomeric 3,4-dihydro-2-pyridones.

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## 1.0 GENERAL METHODS

All commercially obtained reagents/solvents were used as received; chemicals were purchased from Alfa Aesar<sup>®</sup>, Sigma-Aldrich<sup>®</sup>, Acros organics<sup>®</sup>, TCI America<sup>®</sup>, Mallinckrodt<sup>®</sup>, and Oakwood<sup>®</sup> Products, and were used as received without further purification. Unless stated otherwise, reactions were conducted in oven-dried glassware under nitrogen atmosphere. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on Varian 400 MHz (100 MHz for <sup>13</sup>C) and on 500 MHz (125 MHz for <sup>13</sup>C) spectrometers. Data from the <sup>1</sup>H-NMR spectroscopy are reported as chemical shift ( $\delta$  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 <sup>13</sup>C NMR spectra are reported in terms of chemical shift ( $\delta$  ppm). High-resolution mass spectrum data in Electrospray Ionization mode were recorded on a Bruker – Daltronics<sup>®</sup> BioTof mass spectrometer in positive (ESI+) ion mode. HPLC analyses were performed on Waters<sup>®</sup> HPLC equipped with 2525 pump. Waters<sup>®</sup> 2767 sample manager was used for automated sample injection. All HPLC injections were monitored using a Waters<sup>®</sup> 2487 dual wavelength absorbance detector at 254 and 270 nm. Analytical and semi-preparative injections were performed on chiral stationary phase using various columns as indicated below.

- i) Regis<sup>®</sup> 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<sup>®</sup> 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) CHIRALPACK<sup>®</sup> 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<sup>®</sup> 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 and to process HPLC traces. Igor Pro<sup>®</sup> 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<sup>®</sup> DIP – 370 digital polarimeter. CD spectra were recorded on JASCO<sup>®</sup> J-815 with JASCOPTC-423S/15 temperature controller maintained by liquid nitrogen. 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<sup>®</sup> cartridge filled with silica (Teledyne ISCO) as stationary phase. In some cases, compounds were purified by column chromatography on silica gel (Sorbent Technologies<sup>®</sup>, silica gel standard grade: porosity 60 Å, particle size: 230 x 400 mesh, surface area: 500 – 600 m<sup>2</sup>/g, bulk density: 0.4 g/mL, pH range: 6.5 – 7.5). Unless indicated, the Retardation Factor (R<sub>f</sub>) values were recorded using a 5-50% hexanes:ethyl acetate as mobile phase and on Sorbent Technologies<sup>®</sup>, silica Gel TLC plates (200 mm thickness w/UV<sub>254</sub>).

The plot of CD spectrum was carried out using molar ellipticity vs wavelength (nm) and the molar ellipticity was calculated using the formula,<sup>1</sup>

$$\text{Molar ellipticity } [\Delta\epsilon] = [\theta] / 32980cl$$

Where,

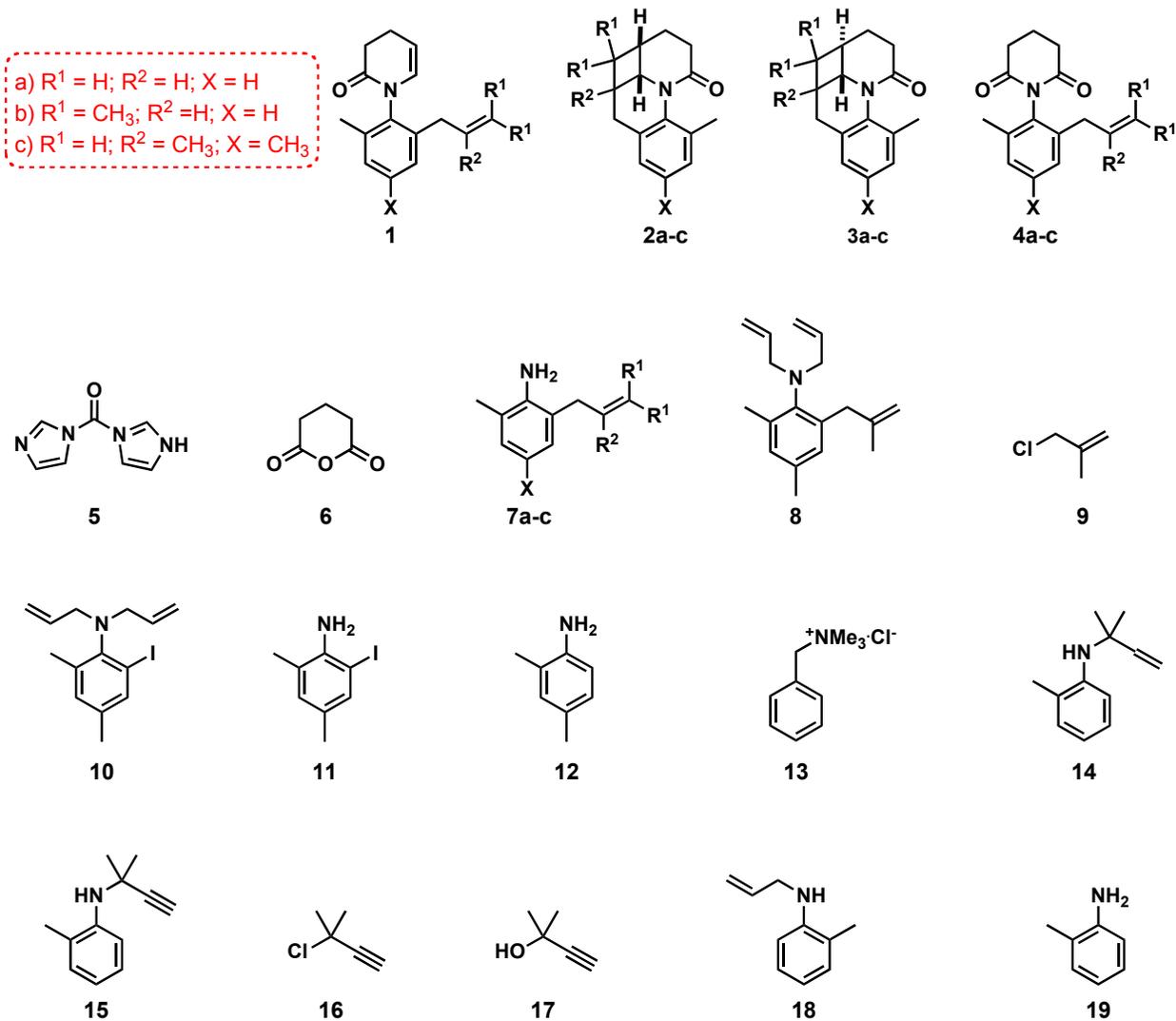
*c* = Concentration in mols/lit; *l* = Path length in cm;  $\theta$  = Ellipticity measured in millidegrees.

#### Photophysical Methods.

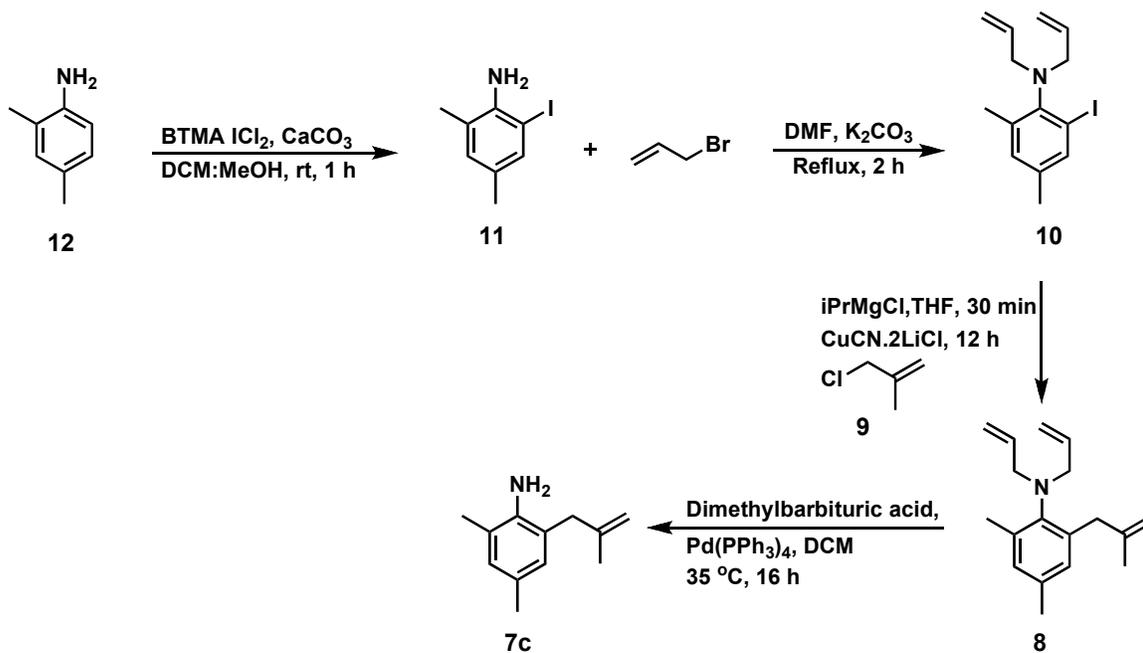
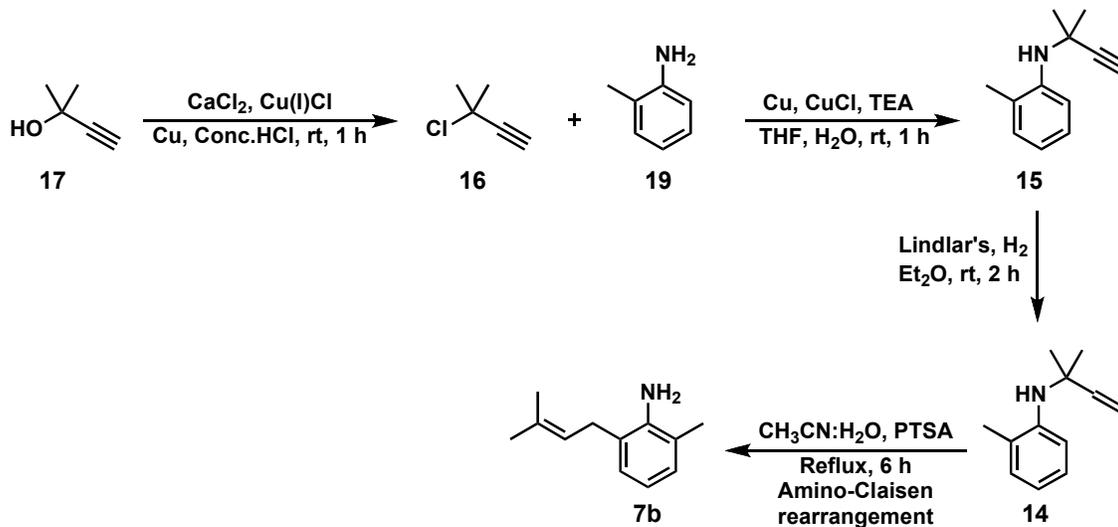
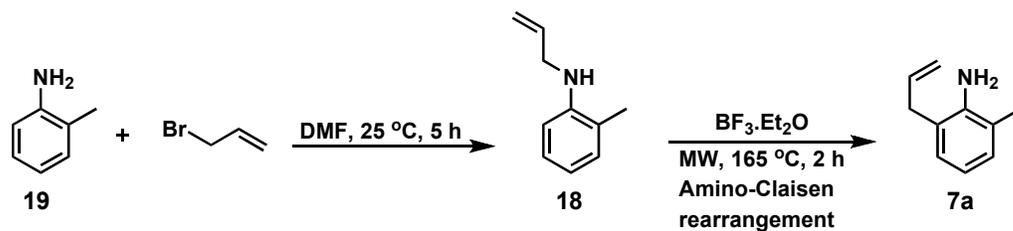
Spectrophotometric solvents (Sigma-Aldrich<sup>®</sup>) were used when ever necessary unless or otherwise mentioned. UV quality fluorimeter cells (with range until 190 nm) were purchased from Luzchem<sup>®</sup>. Absorbance measurements were performed using a Shimadzu<sup>®</sup> UV-2501PC UV-Vis spectrophotometer. Emission spectra were recorded on a Horiba Scientific<sup>®</sup> Fluorolog 3 spectrometer (FL3-22) equipped with double-grating monochromators, dual lamp housing containing a 450-watt CW xenon lamp and a UV xenon flash lamp (FL-1040), Fluorohub/MCA/MCS electronics and R928 PMT detector. Emission and excitation spectra were corrected in all the cases for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard instrument correction provided in the instrument software. Fluorescence (steady state) and phosphorescence (77 K) emission spectra were processed by FluorEssence<sup>®</sup> software. Phosphorescence lifetime measurements were performed using DAS6<sup>®</sup> V6.4 software. The goodness-of-fit was assessed by minimizing the reduced chi squared function and further judged by the symmetrical distribution of the residuals.

## 2. CHART AND SYNTHETIC PROTOCOLS

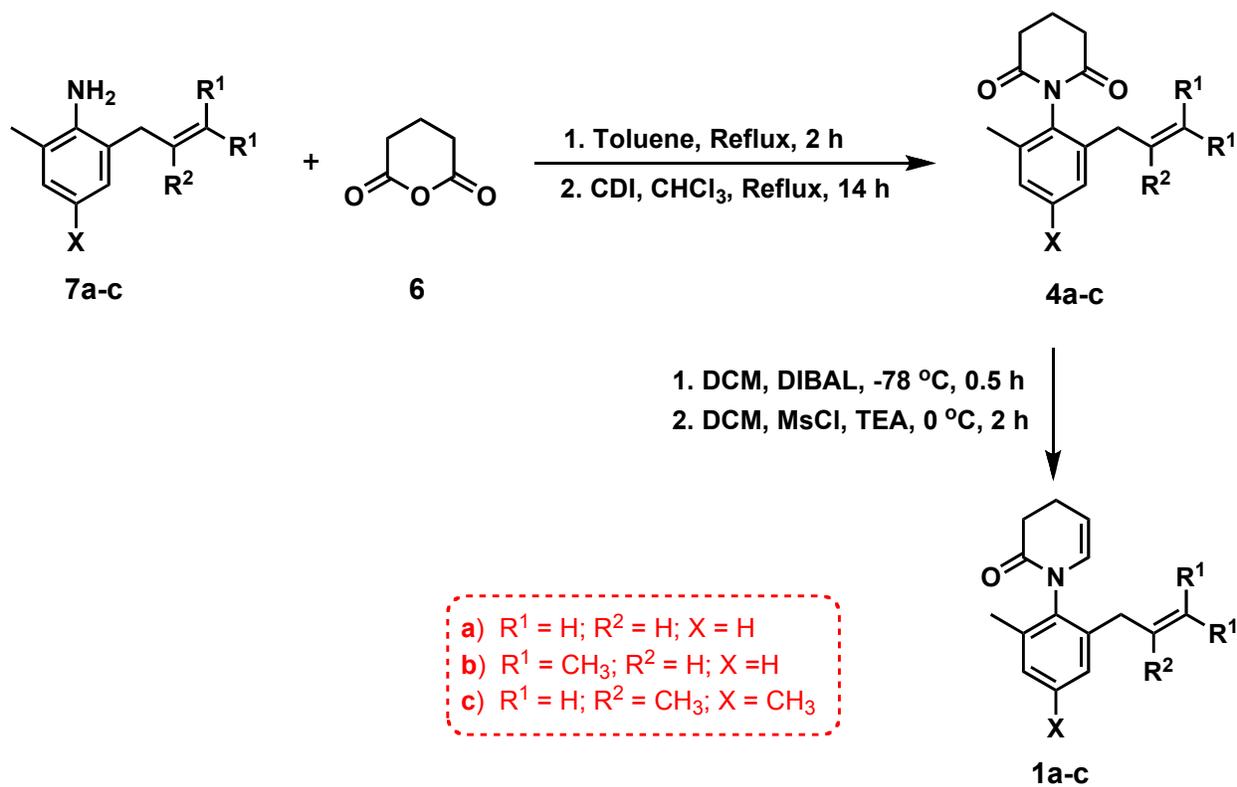
### 2.1 CHART



## 2.2 SYNTHETIC PROTOCOL FOR VARIOUS SUBSTITUTED ANILINE DERIVATIVES **7a-c**

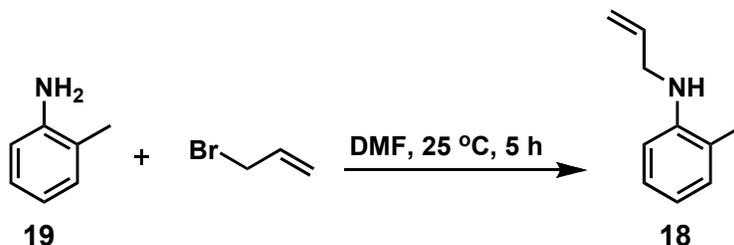


### 2.3 SYNTHETIC PROTOCOL FOR 3,4-DIHYDRO-2-PYRIDONE **1a-c**.



### 3. GENERAL PROCEDURE FOR SYNTHESIS OF SUBSTITUTED ANILINE DERIVATIVES **4a-c** AND THEIR PRECURSORS

#### 3.1 SYNTHESIS OF N-ALLYL-ANILINE DERIVATIVE **18**

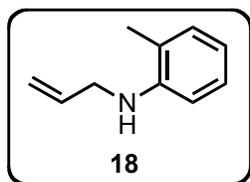


**Scheme S1:** Synthesis of N-allyl-aniline derivative **18**.

To a solution of O-toluidine **19** (2 g, 18.7 mmol) in DMF (60 mL) at room temperature allyl bromide (1.78 mL, 20.6 mmol) was added. The resulting mixture was stirred at room temperature for 5 h. After the reaction, DI water (50 mL) and diethyl ether (50 mL) was added to the mixture, stirred for 5 mins and the layers were separated. The aqueous layer was extracted with diethyl ether (2 X 20 mL). The combined organic layer was washed with DI water (2 X 30 mL) to remove traces of DMF, dried over *anhy.* Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was evaporated under reduced pressure to get the crude product. The crude product was purified by combiflash using hexanes:ethyl acetate mixture (95:5) to get the N-allylated derivative **18** in 60% yield.

TLC condition - R<sub>f</sub> = 0.80 (90% hexanes:10% ethyl acetate)

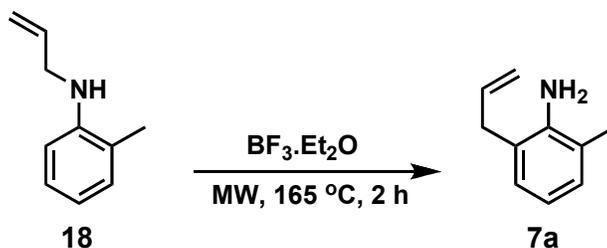
*Note:* The major side product was di-allylated aniline.



<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ ppm): 7.19 – 7.10 (m, 2H), 6.74 – 6.66 (m, 2H), 6.10 – 6.00 (m, 1H), 5.37 – 5.22 (m, 2H), 3.88 – 3.86 (d, J = 5.2 Hz, 2H), 3.66 (s, 1H) and 2.21 (s, 3H).

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, δ ppm): 146.3, 135.9, 130.3, 127.4, 122.2, 117.4, 116.4, 110.3, 46.8 and 17.8.

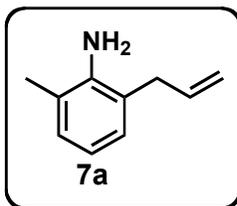
#### 3.2 SYNTHESIS OF 2-ALLYL-6-METHYL ANILINE **7a**



**Scheme S2:** Synthesis of 2-allyl-6-methyl aniline **7a**

The aniline derivative was synthesized according to the literature reported procedure.<sup>2</sup> To a solution of N-allyl-aniline derivative **18** (1.65 g, 11.2 mmol) in *O*-xylene at -10 °C added BF<sub>3</sub>.Et<sub>2</sub>O (48% in Et<sub>2</sub>O, 3.3 mL, 11.2 mmol). The resulting mixture was slowly warmed to room temperature and then moved to microwave, where it was maintained at 165 °C for 2 h. The mixture was cooled to 0-5 °C and the pH was adjusted to 8 by slowly adding 2N aq.NaOH solution. The layers were separated and the aqueous layer was extracted with diethyl ether (2 X 15 mL). The combined organic layers were washed with DI water (2 X 15 mL), dried over *anhy.* Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was evaporated under reduced pressure to get the crude product. The crude product was purified by combiflash using hexanes:ethyl acetate mixture (90:10) to get the 2-allyl-6-methyl aniline **7a** in 33% yield.

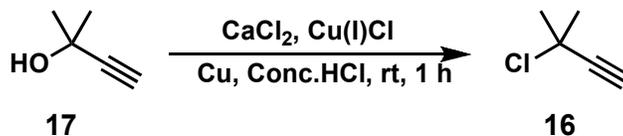
TLC condition - R<sub>f</sub> = 0.70 (80% hexanes:20% ethyl acetate)



<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ ppm): 7.02 – 6.96 (m, 2H), 6.73 – 6.69 (m, 1H), 6.04 – 5.94 (m, 1H), 5.17 – 5.13 (m, 2H), 3.65 (s, 2H), 3.36 – 3.34 (d, *J* = 6 Hz, 2H) and 2.21 (s, 3H).

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, δ ppm): 143.2, 136.1, 129.0, 128.2, 123.6, 122.6, 118.4, 116.3, 36.97 and 17.8.

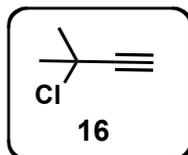
### 3.3 SYNTHESIS OF 3-CHLORO-3-METHYLBUT-1-YNE **16**



**Scheme S3:** Synthesis of 3-chloro-3-methylbut-1-yne **16**.

The 3-chloro-3-methylbut-1-yne was synthesized according to the literature reported procedure.<sup>3</sup> To a mixture of *anhy.* calcium chloride (3.3 g, 29.7 mmol) cuprous chloride (2.4 g, 24.2 mmol) copper powder (37.7 mg, 0.6 mmol) and *conc.* hydrochloric acid (25 mL) was added acetylinic alcohol (5 g, 59.4 mmol) at 0 °C over ten mins. The resulting mixture was stirred for 1 h at 0 °C. The phases were separated and the organic layer was washed with ice-cold *conc.* hydrochloric acid (2 X 20 mL). The organic layer was dried over *anhy.* potassium carbonate (5 g), filtered and the crude product was purified by distillation under reduced pressure to yield 65 % of the pure acetylinic chloride.

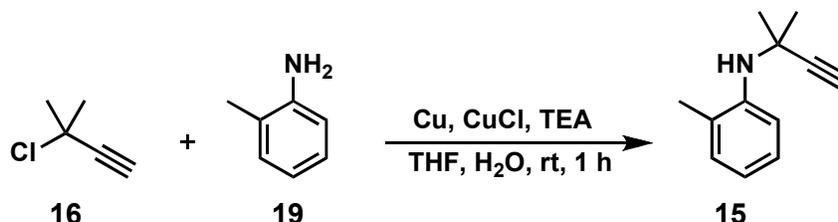
*Note:* As tertiary acetylinic chloride is highly acid and heat sensitive, distillation temperature was kept below 50 °C and small amount of *anhy.* K<sub>2</sub>CO<sub>3</sub> was kept in the distillation flask to avoid any decomposition or isomerization.



<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ ppm): 2.59 (s, 1H) and 1.83 (s, 6H).

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, δ ppm): 86.7, 72.0, 57.1, 34.7 and 32.3.

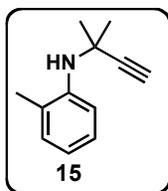
### 3.4 SYNTHESIS OF N-ACETYLINIC-ANILINE DERIVATIVE 15



**Scheme S4:** Synthesis of N-acetylinic-aniline derivative **15**.

The N-acetylinic-aniline derivative **15** was synthesized according to the literature reported procedure.<sup>4</sup> To a mixture of aniline (3 g, 30 mmol), cuprous chloride (85 mg), copper powder (85 mg), triethylamine (5.4 mL, 39 mmol), water (0.8 mL) and THF (8 mL) at room temperature added acetylinic chloride **16** (4.0 g, 39 mmol) in THF (8mL) slowly over 10 mins. The resulting mixture was stirred at room temperature over 1 h. To the reaction mixture DI water (10 mL) and DCM (20 mL) was added, stirred for 5 mins and the layers were separated. The aqueous layer was extracted with DCM (2 X 20 mL). The combined organic layer was dried over *anhy.* Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure to get the crude product. The crude product was purified by combiflash using hexanes:ethyl acetate mixture (95:5) to get the pure product in 40 % yield.

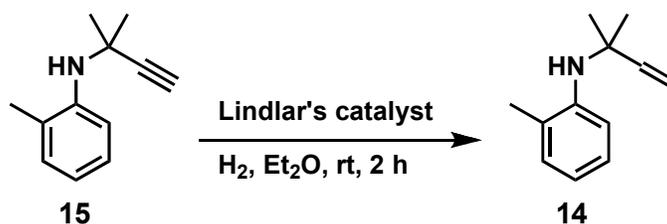
TLC condition - R<sub>f</sub> = 0.50 (95% hexanes:5% ethyl acetate)



<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ ppm): 7.33 – 7.31 (m, 1H), 7.12 – 7.08 (m, 2H), 6.75 – 6.72 (m, 1H), 3.54 (s, 1H), 2.38 (m, 1H), 2.15 (s, 3H) and 1.67 (s, 6H).

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, δ ppm): 143.7, 130.5, 126.7, 123.8, 118.3, 114.5, 88.9, 70.7, 47.8, 30.8 and 18.0.

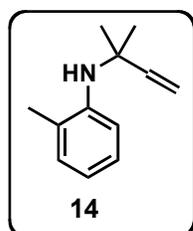
### 3.5 SYNTHESIS OF N-ALLYL-ANILINE DERIVATIVE **14**



**Scheme S5:** Synthesis of N-allyl-aniline derivative **14**.

In a flame dried flask charged Lindlar's catalyst (5% Pd on CaCO<sub>3</sub> poisoned with lead, 95 mg, 5 Wt%) under nitrogen atmosphere. To this added a solution of acetylinic aniline **15** (1.9 g, 11mmol) in dry diethyl ether (60 mL) through cannula. The nitrogen was evacuated and the flask was filled with H<sub>2</sub>. The mixture was stirred at room temperature for 2 h. After the reaction, the solution was filtered through celite bed and the bed was washed with diethyl ether (20 mL). The combined organic layer was concentrated to get the crude product. The crude product was purified by combiflash using hexanes:ethyl acetate mixture (95:5) to get pure product in 90% yield.

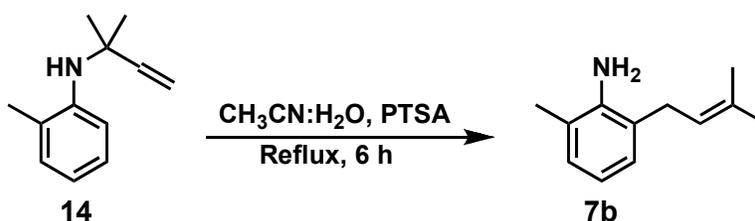
TLC condition - R<sub>f</sub> = 0.60 (95% hexanes:5% ethyl acetate)



<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ ppm): 7.03 – 6.99 (m, 2H), 6.83 – 6.81 (m, 1H), 6.63 – 6.59 (m, 1H), 6.01 – 5.99 (m, 1H), 5.21 – 5.16 (m, 1H), 5.12 – 5.09 (m, 2H), 3.56 (s, 1H), 2.13 (s, 3H) and 1.42 (s, 6H).

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, δ ppm): 146.5, 144.7, 130.4, 126.5, 122.7, 116.9, 113.7, 112.9, 54.6, 28.8 and 18.1.

### 3.6 SYNTHESIS OF 2-METHYL-6-ALLYL-ANILINE DERIVATIVE **7b**



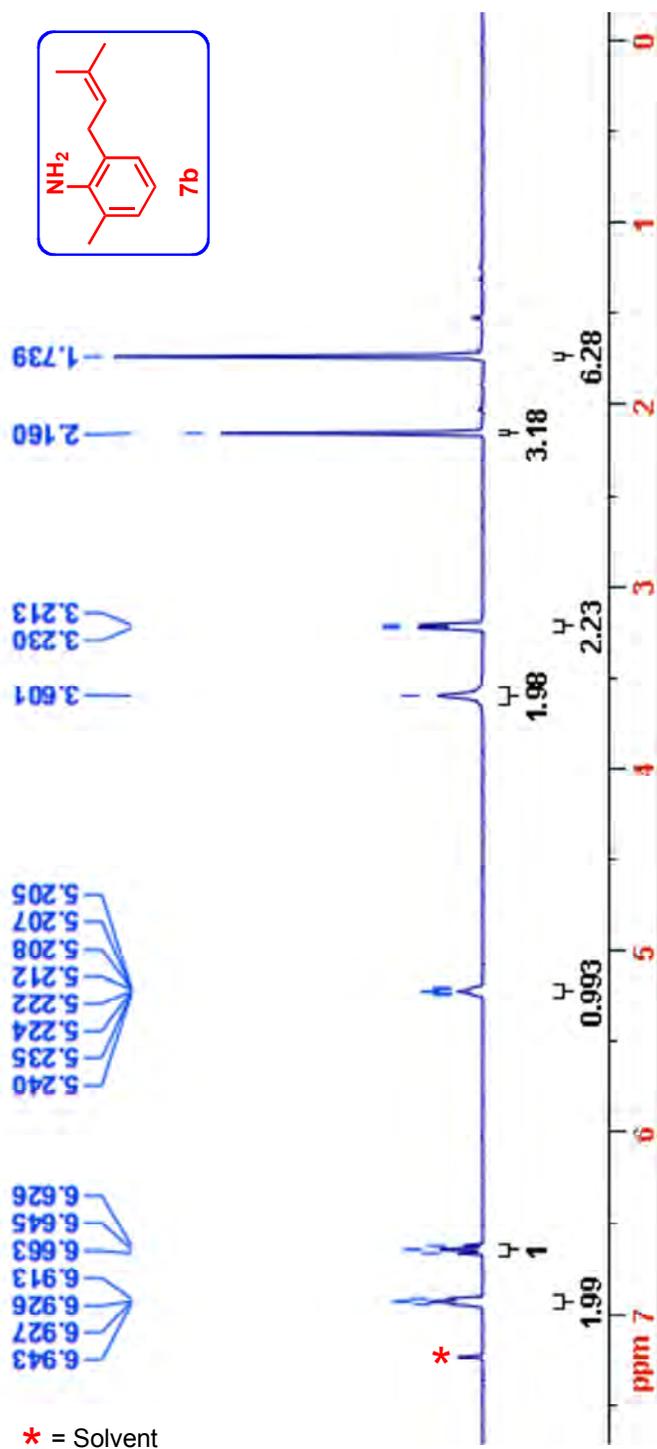
**Scheme S6:** Synthesis of 2-methyl-6-allyl-aniline derivative **7b**

A solution of 2-methyl-N-allyl-aniline derivative **14** (1.7 g, 9.7 mmol) and *p*-toluenesulfonic acid monohydrate (185 mg, 0.97 mmol) in 9:1 acetonitrile:water mixture (120 mL) was refluxed for 6 h. After the reaction, the mixture was cooled to room temperature and

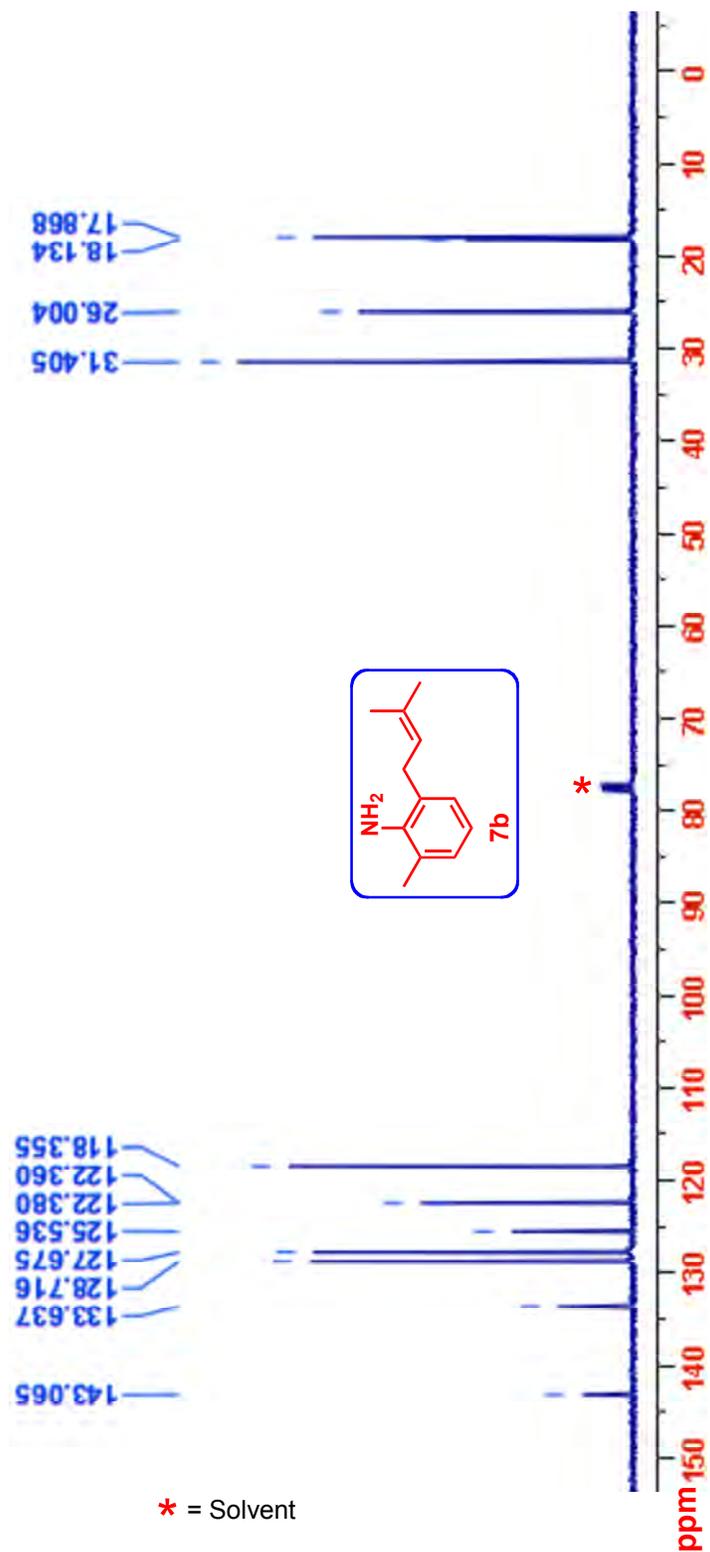
the solvent was removed under reduced pressure. The residue was taken up in DCM (50 mL) and the organic layer was washed with DI water (50 mL), dried over *anhy.* Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure to get the crude product. The crude product was purified by combiflash using hexanes:ethyl acetate mixture (90:10) to get the title product as a pale yellow liquid in 65% yield.

TLC condition -  $R_f = 0.30$  (90% hexanes:10% ethyl acetate)

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 6.94 – 6.91 (m, 2H), 6.66 – 6.63 (m, 1H) 5.24 – 5.21(m, 1H), 3.60 (s, 2H), 3.23 – 3.21 (d,  $J=6.8$  Hz, 2H), 2.16 (s, 3H) and 1.74 (s, 6H).



$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 143.1, 133.6, 128.7, 127.7, 125.5, 122.38, 122.36, 118.4, 31.4, 26.0, 18.1 and 17.9.

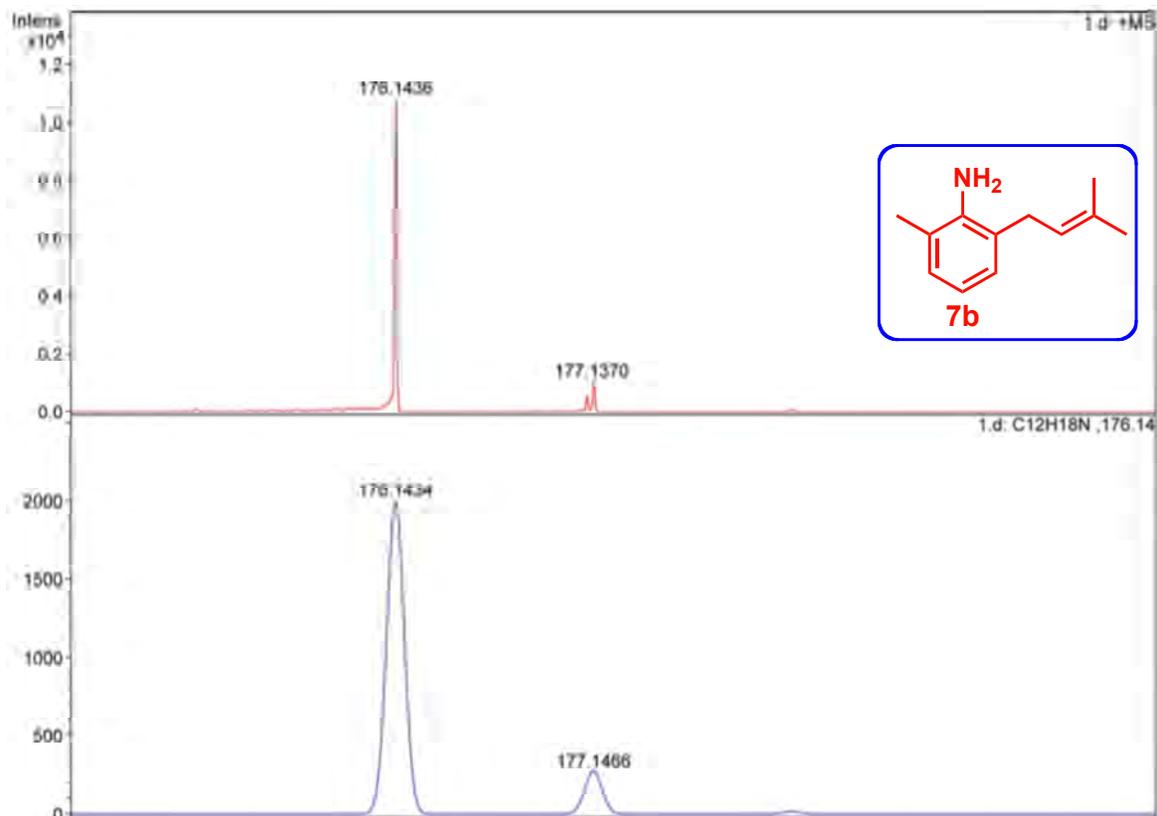


HRMS-ESI ( $m/z$ ) ( $[M + H]^+$ ):

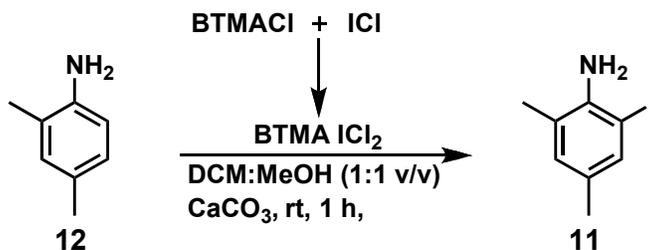
Calculated : 176.1434

Observed : 176.1436

$|\Delta m|$  : 1.1 ppm



### 3.7 SYNTHESIS OF 2-iodo-4,6-dimethylaniline **11**



**Scheme S7:** Synthesis of 2-iodo-4,6-dimethylaniline **11**

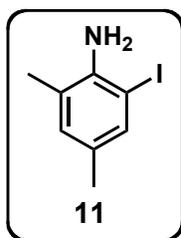
Synthesis of iodinating agent benzyltrimethylammonium dichloroiodate (**BTMA ICl<sub>2</sub>**): The compound was synthesized using previously reported procedure.<sup>5</sup> To a solution of iodine monochloride (3.0 g, 18.6 mmol) in DCM (37 mL) at room temperature added a solution of benzyltrimethylammonium chloride (3.5 g, 18.6 mmol) in DM water (22 mL) slowly over 10 mins.

The resulting mixture was stirred at room temperature for 30 mins. The layers were separated and the organic layer was washed with DM water (10 mL), dried over *anhy.* Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure to get the crude product as a brownish yellow solid. The crude product was directly used for iodination reaction without further purification (isolated crude product yield: 98%).

*Note:* The iodine monochloride was purchased as 1M solution in DCM, which was again diluted using required amount of DCM. The crude BTMA ICl<sub>2</sub> can also be recrystallized in DCM: Ether mixture.

To a mixture of aniline (1.0 g, 8.2 mmol) and calcium carbonate (1.4 g) in DCM:methanol (50:50 mixture, 50 mL) at room temperature added a solution of benzyltrimethylammonium dichloroiodate (2.9 g, 8.2 mmol) in DCM (30 mL) slowly over 30 mins. The resulting mixture was stirred at room temperature for 1 h. After the reaction, the mixture was filtered through celite bed under vacuum and the bed was washed with DCM (50 mL). The combined filtrate was concentrated under reduced pressure. The residue was taken up in 5% NaHSO<sub>3</sub> aqueous solution (40 mL) and the aqueous layer was extracted with diethyl ether (3 X 30 mL). The combined organic layer was dried over *anhy.* Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure to get the crude product. The crude product was purified by combiflash using hexanes:ethyl acetate mixture (95:5) to get the title compound as a brownish solid (isolated yield = 67%).

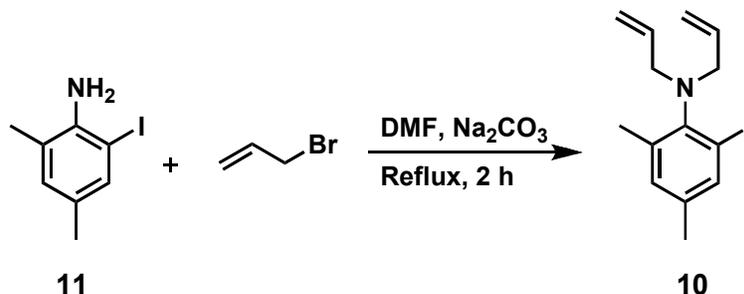
TLC condition - R<sub>f</sub> = 0.35 (95% hexanes:5% ethyl acetate)



<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, δ ppm): 7.34 (s, 1H) and 6.82 (s, 1H), 3.90 (bs, 2H), 2.18 (s, 3H), 2.16 (s, 3H).

<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, δ ppm): 142.5, 137.0, 131.6, 129.5, 122.7, 85.0, 20.0 and 19.1.

### 3.8 SYNTHESIS OF N-DIALLYL-2-iodo-4,6-DIMETHYLANILINE **10**

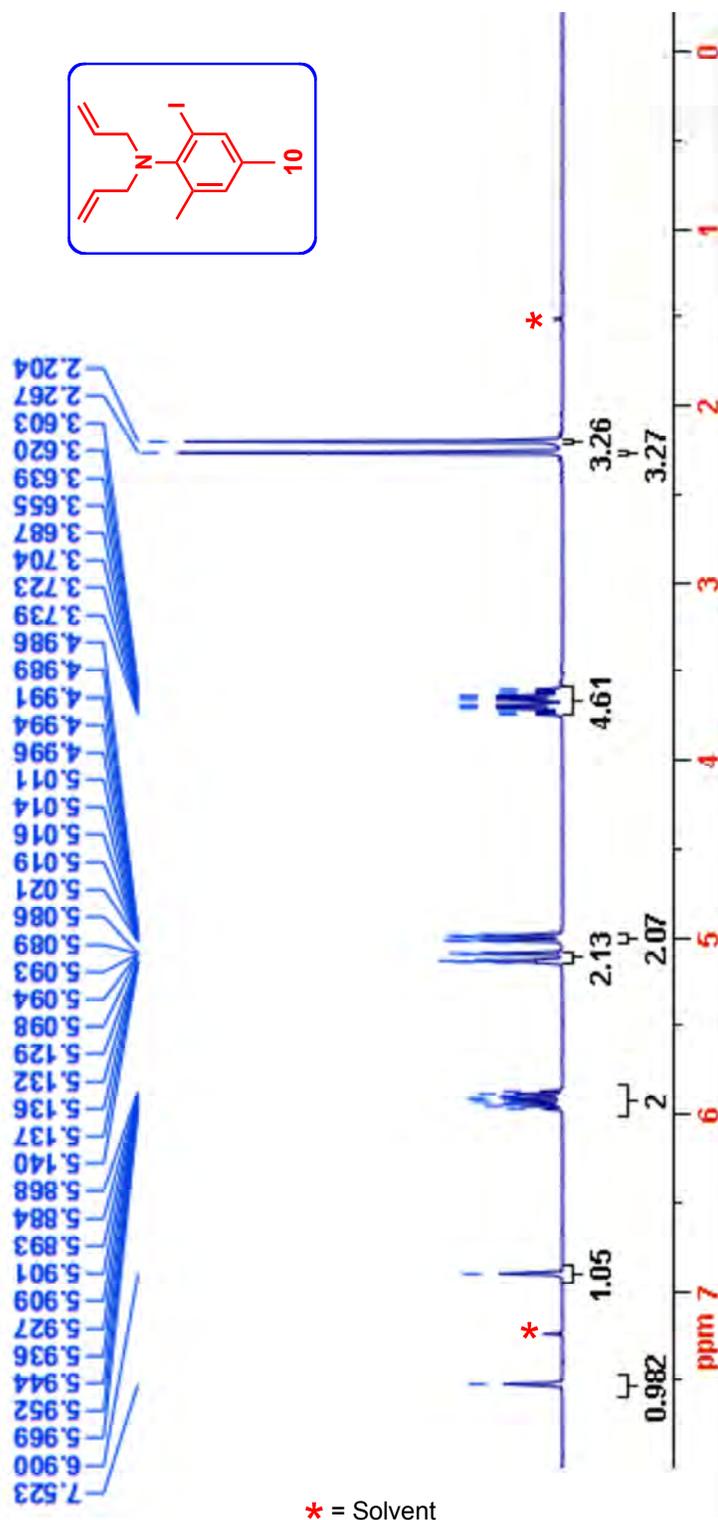


**Scheme S8:** Synthesis of 2-iodo-4,6-dimethylaniline **10**

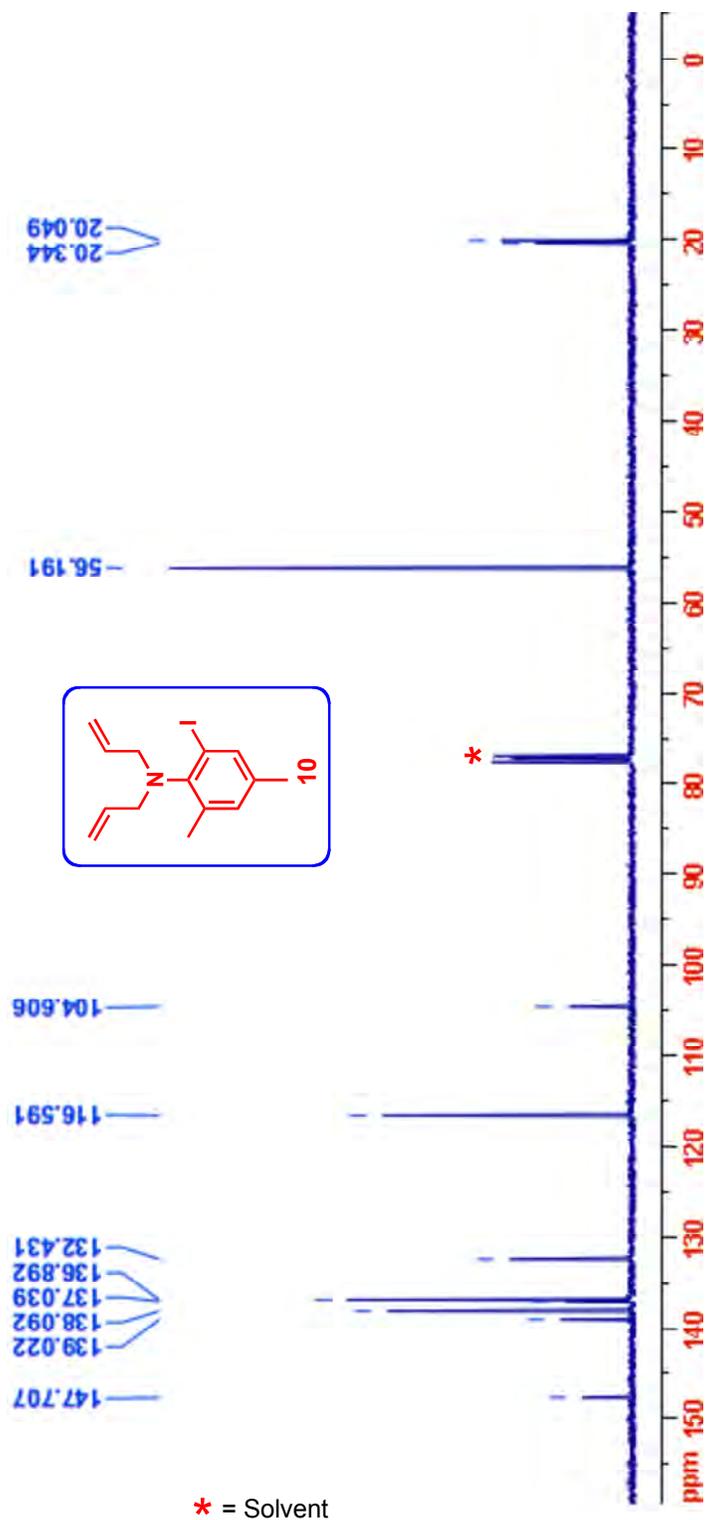
The compound was synthesized according to the literature reported procedure.<sup>6</sup> Mixture of aniline (5 g, 20.2 mmol), allyl bromide (4.4 mL, 50.9 mmol) and sodium carbonate (6.4 g, 60.6 mmol) in DMF (150 mL) was heated to 150 °C in a sealed tube and maintained for 2 h. After the reaction, the mixture was cooled to room temperature and poured into cold DI water (200 mL). The aqueous layer was extracted with diethyl ether (3 X 50 mL). The combined organic layer was washed with DI water (2 X 50 mL) to remove traces of DMF, dried over *anhy.* Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure to get the crude product. The crude product was purified by combiflash using hexanes:ethyl acetate mixture (98:2) to get the title compound as a pale yellow oil (isolated yield = 90%).

TLC condition - R<sub>f</sub> = 0.90 (90% hexanes:10% ethyl acetate)

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.52 (s, 1H), 6.90 (s, 1H), 5.97 - 5.87 (m, 2H), 5.14 - 5.09 (m, 2H), 5.02 - 4.99 (m, 2H), 3.74 - 3.60 (m, 4H), 2.27 (s, 3H) and 2.20 (s, 3H).



$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 147.7, 139.0, 138.1, 137.0, 136.9, 132.4, 116.6, 104.6, 56.2, 20.3 and 20.0.

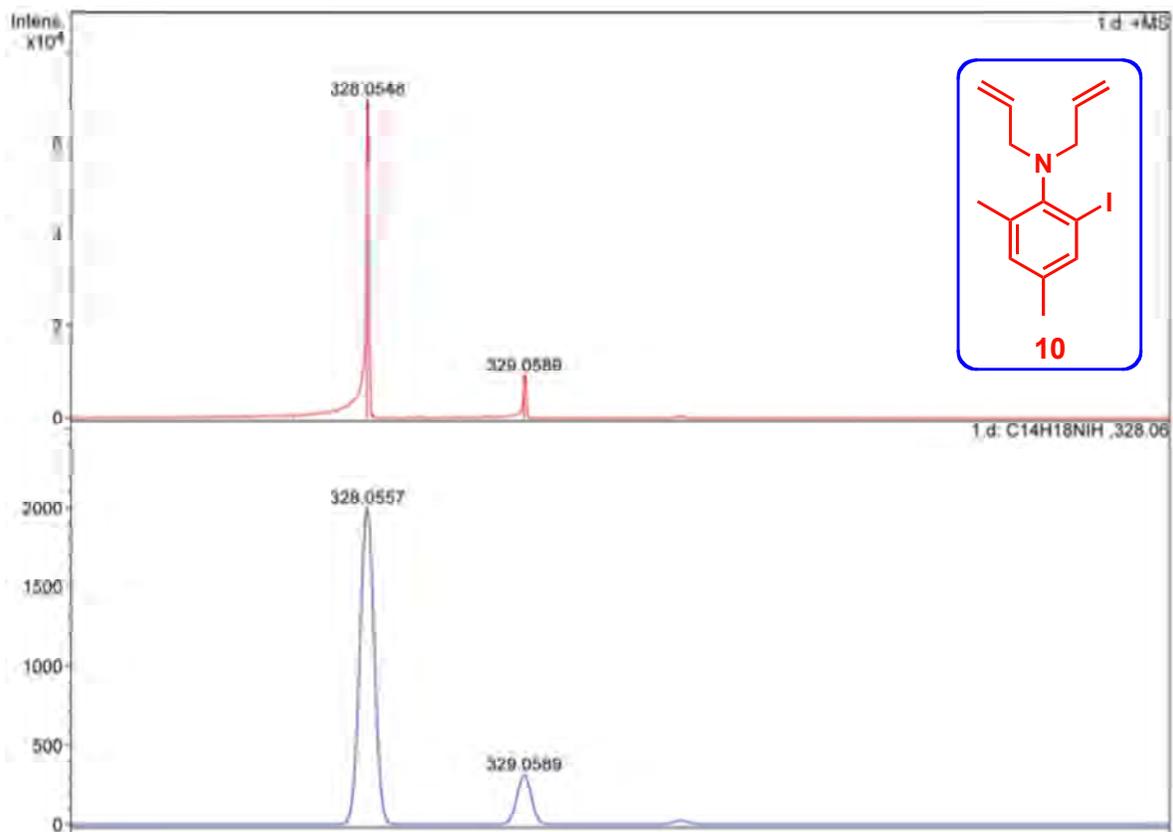


HRMS-ESI ( $m/z$ ) ( $[M + H]^+$ ):

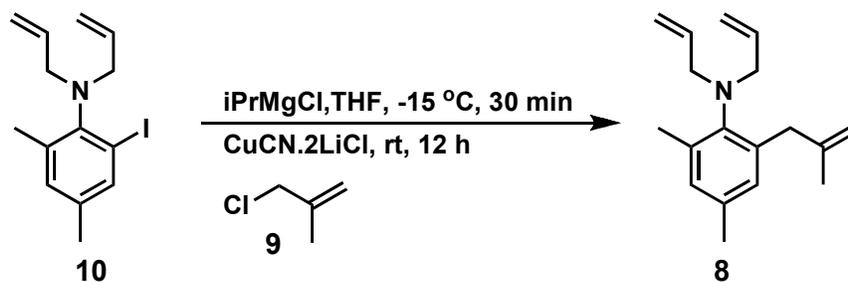
Calculated : 328.0557

Observed : 328.0548

$|\Delta m|$  : 2.7 ppm



### 3.9 SYNTHESIS OF N-DIALLYL-2,4-DIMETHYL-6-ALLYL-ANILINE DERIVATIVE **8**

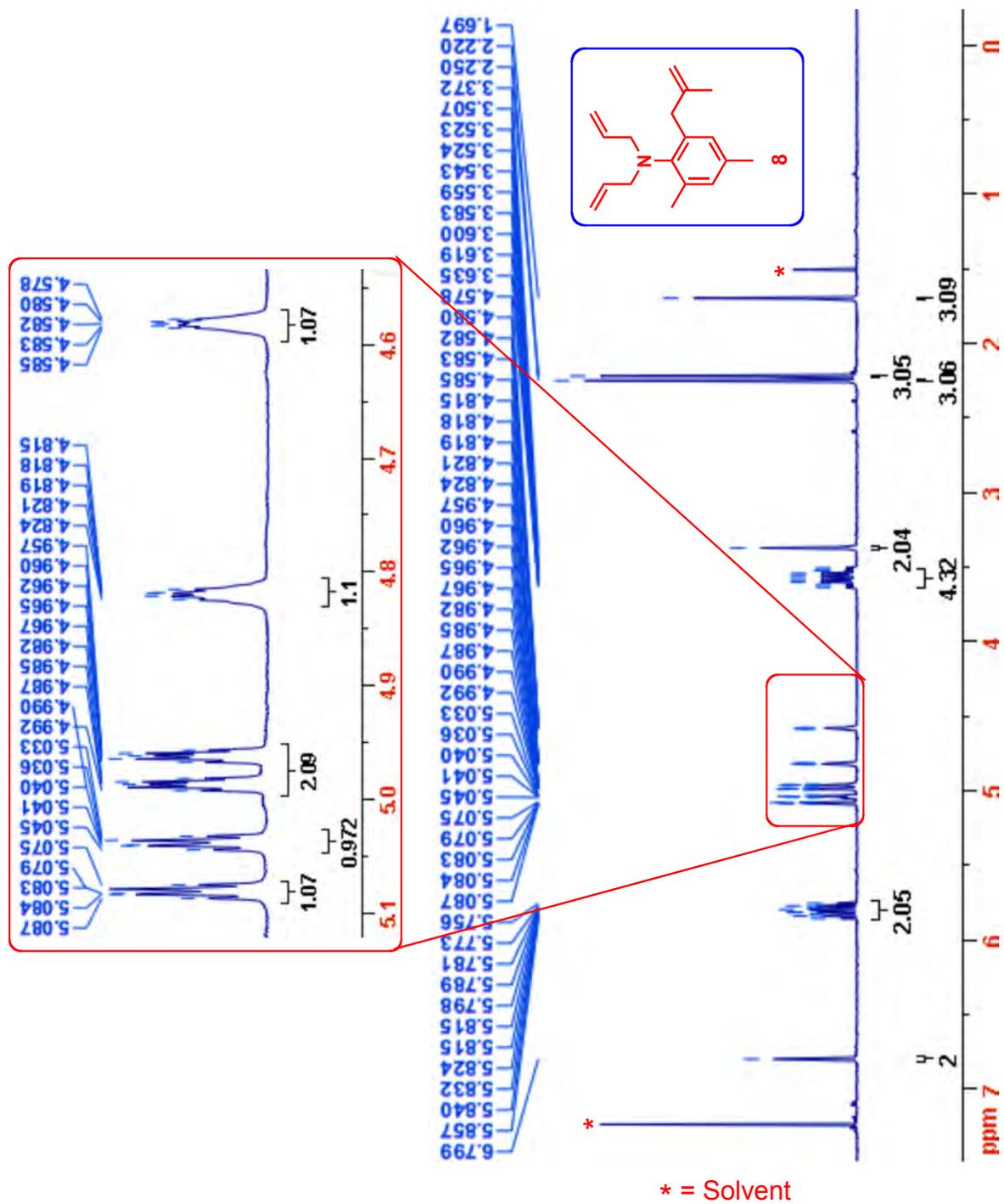


**Scheme S9:** Synthesis of N-Diallyl-2,4-Dimethyl-6-allyl-aniline derivative **8**.

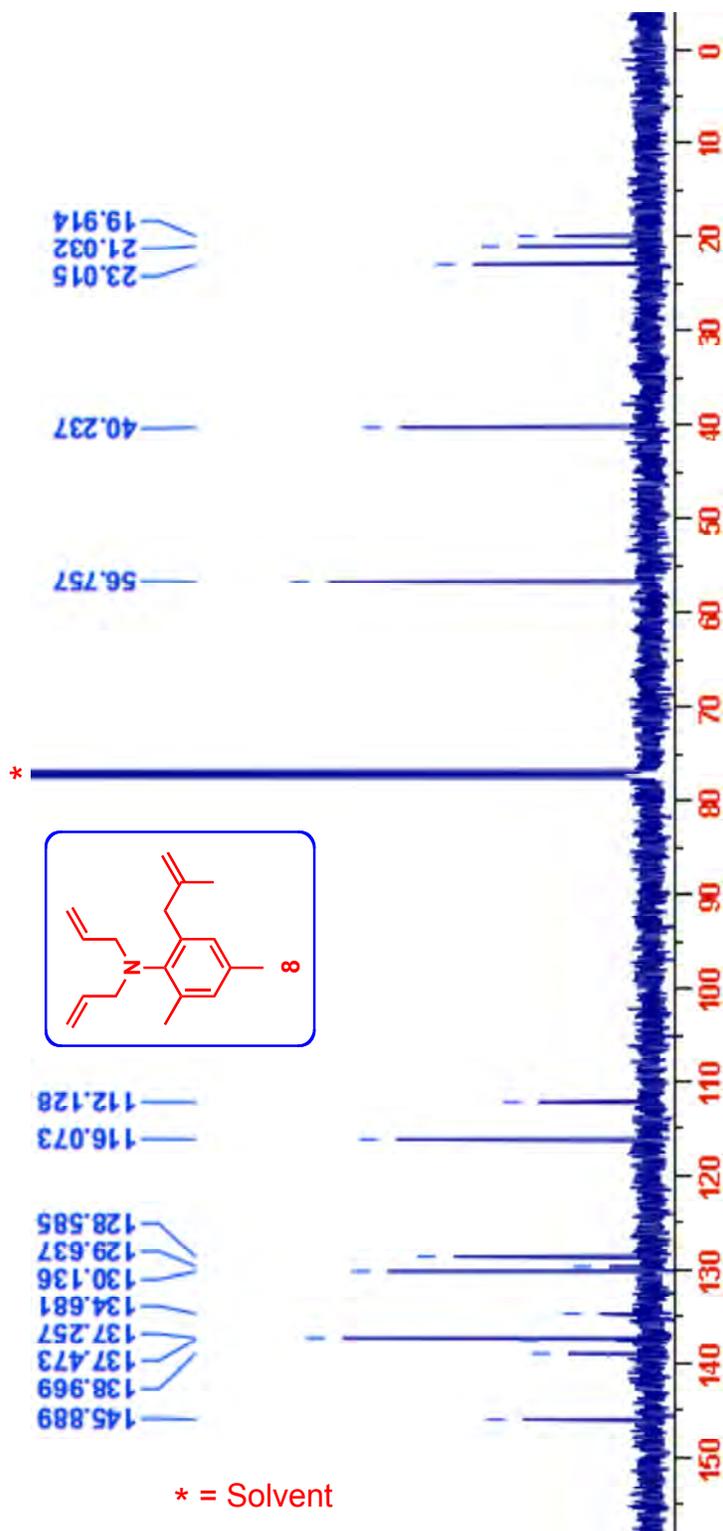
The compound was synthesized according to the literature reported procedure.<sup>7</sup> To a solution of N-diallyl-2-iodo aniline derivative **10** (5.9 g, 18.0 mmol) in dry THF (120 mL) at -15 °C under N<sub>2</sub> atmosphere added *i*PrMgCl.LiCl (1.3M in THF, 15.2 mL, 19.8 mmol) slowly over 10 mins. The mixture was maintained at -15 °C for 45 mins after which 3-chloro-2-methylpropene (2.13 mL, 21.6 mmol) and CuCN.2LiCl (0.16 mL, 0.9 mmol) was added. The reaction mixture was slowly allowed to warm to room temperature over 12 h. The reaction mixture was quenched with *Satd.* NH<sub>4</sub>Cl solution (50 mL), stirred and the layers were separated. The aqueous layer was extracted with diethyl ether (2 X 75 mL). The combined organic layer was dried over *anhy.* Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure to get the crude product. The crude product was purified by combiflash using hexanes:ethyl acetate mixture (95:5) to get the title compound as a pale yellow oil (isolated yield = 92%).

TLC condition - *R<sub>f</sub>* = 0.75 (100% hexanes)

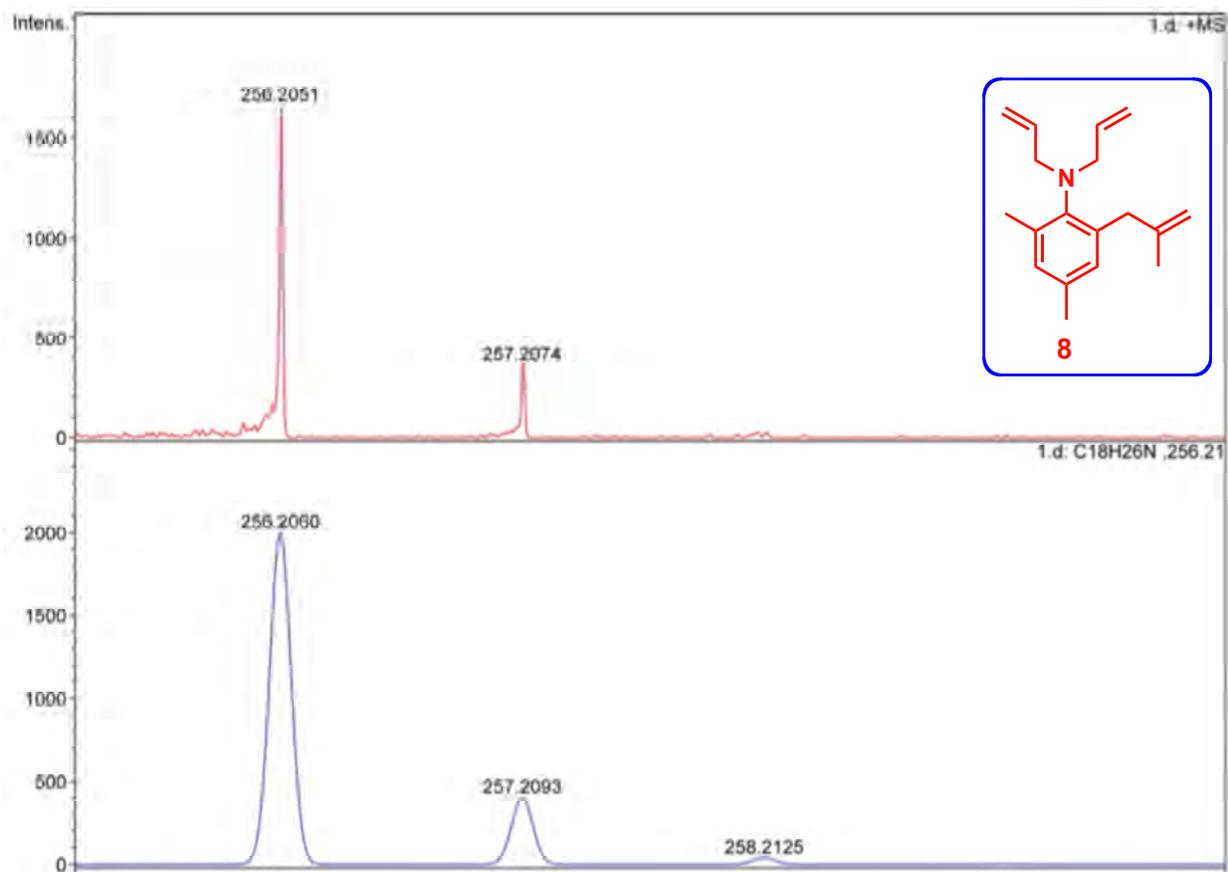
$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 6.79 (s, 2H), 5.86-5.76 (m, 2H), 5.09- 5.08 (m, 1H), 5.05-5.03 (m, 1H), 4.99-4.96 (m, 2H), 4.82-4.81 (m, 1H), 4.58- 4.578 (m, 1H), 3.64-3.51 (m, 4H), 3.37 (s, 2H), 2.25 (s, 3H), 2.22 (s, 3H) and 1.697 (s, 3H).



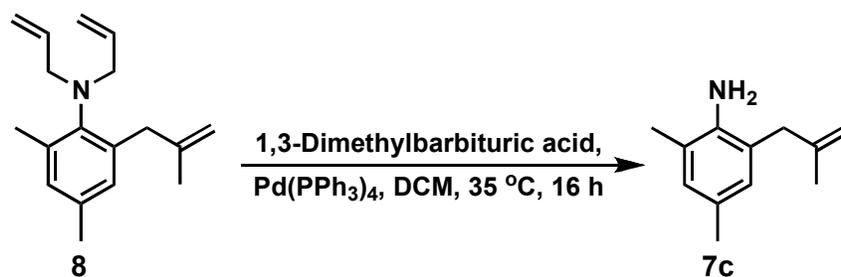
$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 145.9, 138.96, 137.5, 137.3, 134.7, 130.1, 129.6, 128.6, 116.1, 112.1, 56.8, 40.2, 23.0, 21.0 and 19.9.



HRMS-ESI ( $m/z$ ) ( $[M + H]^+$ ):  
Calculated : 256.2060  
Observed : 256.2051  
 $|\Delta m|$  : 3.5 ppm



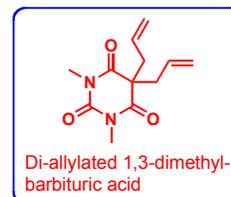
### 3.10 SYNTHESIS OF 2,4-DIMETHYL-6-ALLYL-ANILINE DERIVATIVE **7c**



**Scheme S10:** Synthesis of 2,4-Dimethyl-6-allyl-aniline derivative **7c**

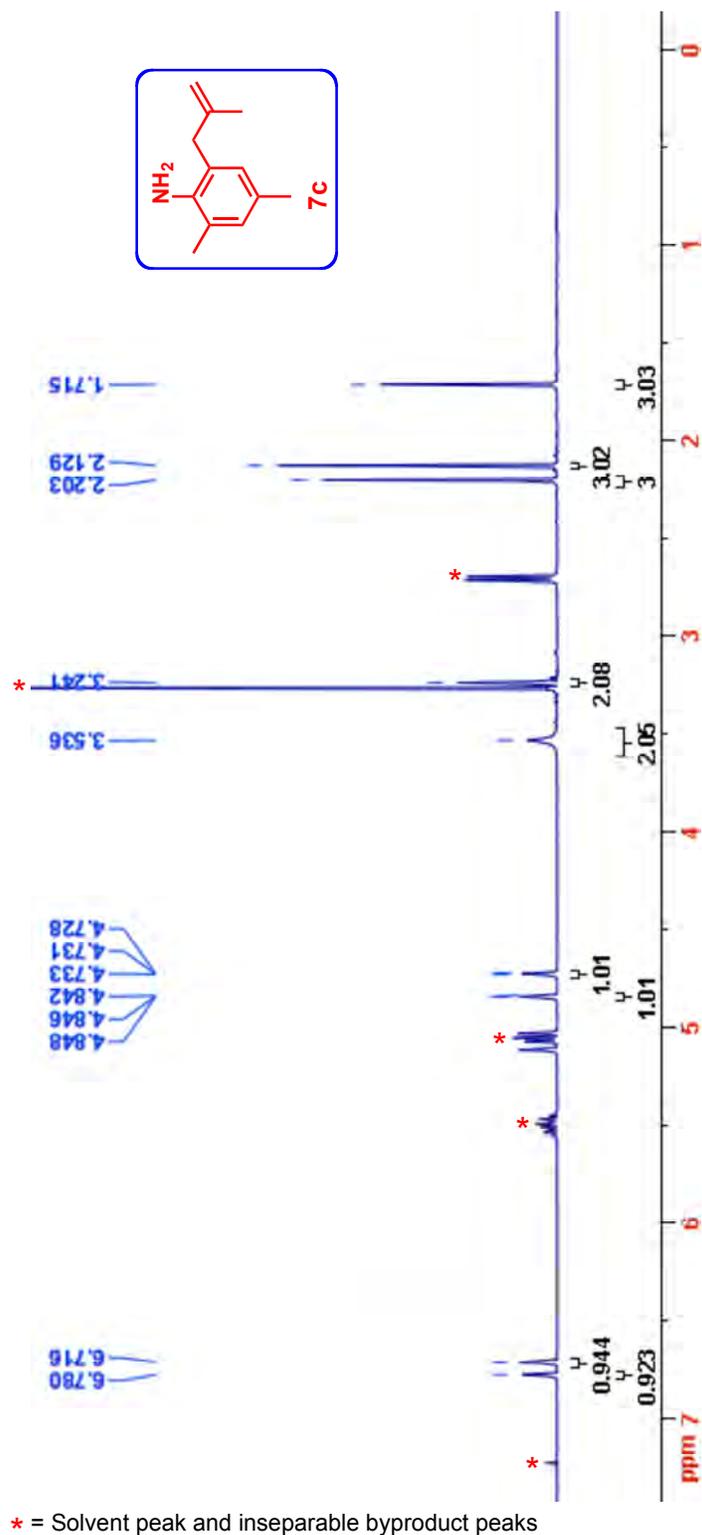
In a flame dried flask charged Pd(PPh<sub>3</sub>)<sub>4</sub> (183 mg, 0.16 mmol) and 1,3-dimethylbarbituric acid (12.8 g, 82 mmol). To this mixture added a solution of N-diallyl-6-(2-methylallyl)-aniline derivative **8** (4.2 g, 16.4 mmol) in dry DCM (100 mL) via cannula. The resulting solution was heated to 35 °C and maintained for 16 h. After the reaction the mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was taken in a *Satd.* Na<sub>2</sub>CO<sub>3</sub> solution (250 mL) and the aqueous layer was extracted with diethyl ether (3 X 75 mL). The combined organic layer was washed with *Satd.* Na<sub>2</sub>CO<sub>3</sub> solution (2 X 50 mL), dried over *anhy.* Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure to get the crude product. The crude product was purified by combiflash using hexanes:ethyl acetate mixture (95:5) to get the title compound as a pale yellow oil (isolated yield = 92%).

*Note:* The product accompanied by inseparable Di-allylated 1,3-dimethylbarbituric acid byproduct. So the mixture was taken to next step where it gets removed by filtration after the reaction. The relative percentage of the product was determined by <sup>1</sup>H-NMR spectroscopy.

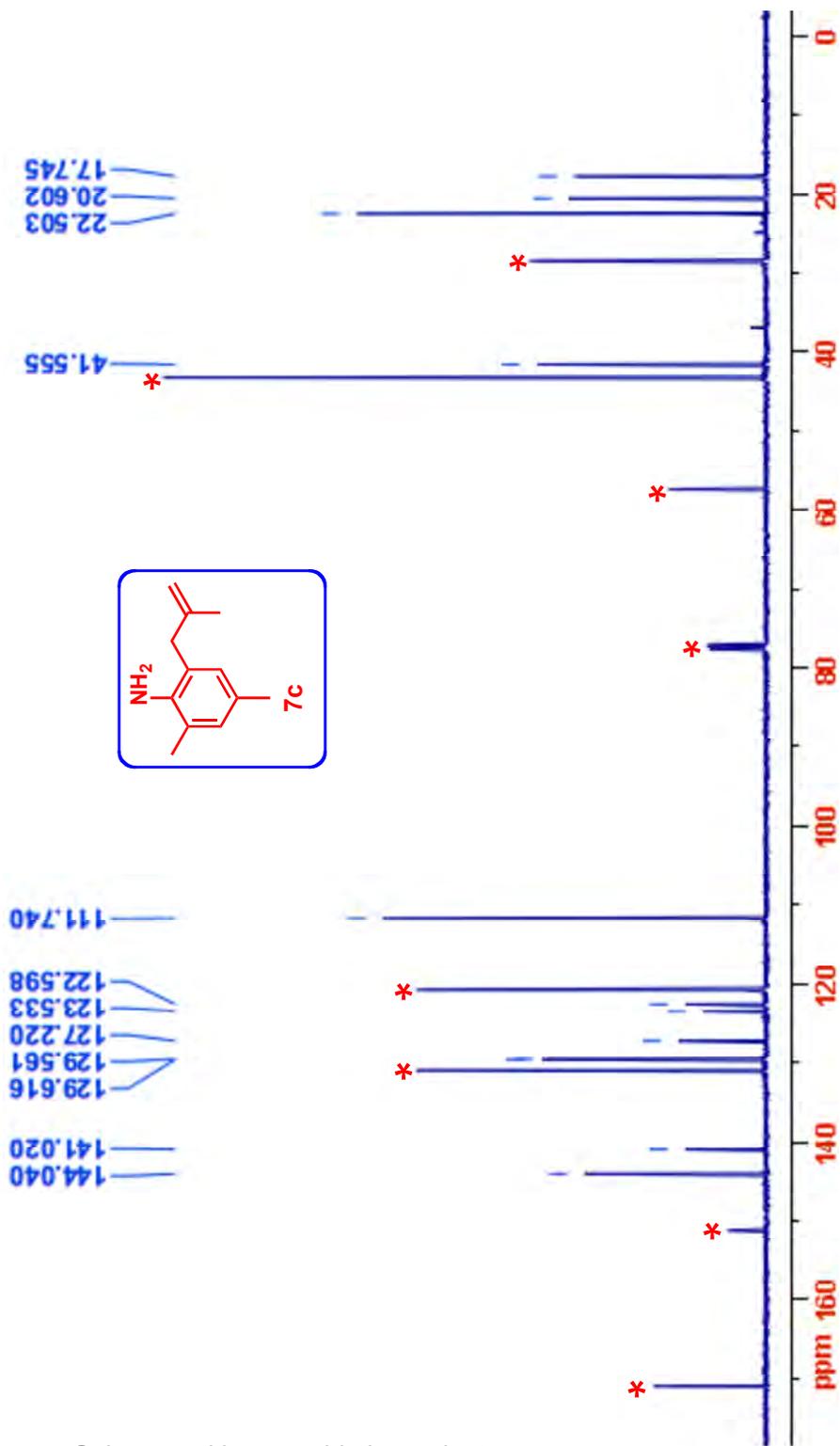


TLC condition - R<sub>f</sub> = 0.35 (100% hexanes)

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 6.78 (s, 1H), 6.72 (s, 1H), 4.85 – 4.84 (m, 1H), 4.73 – 4.728 (m, 1H), 3.54 (bs, 2H), 3.24 (s, 2H), 2.20 (s, 3H), 2.13 (s, 3H) and 1.71 (s, 3H).



$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 144.0, 141.0, 129.61, 129.56, 127.2, 123.5, 122.6, 111.7, 41.6, 22.5, 20.6 and 17.7.



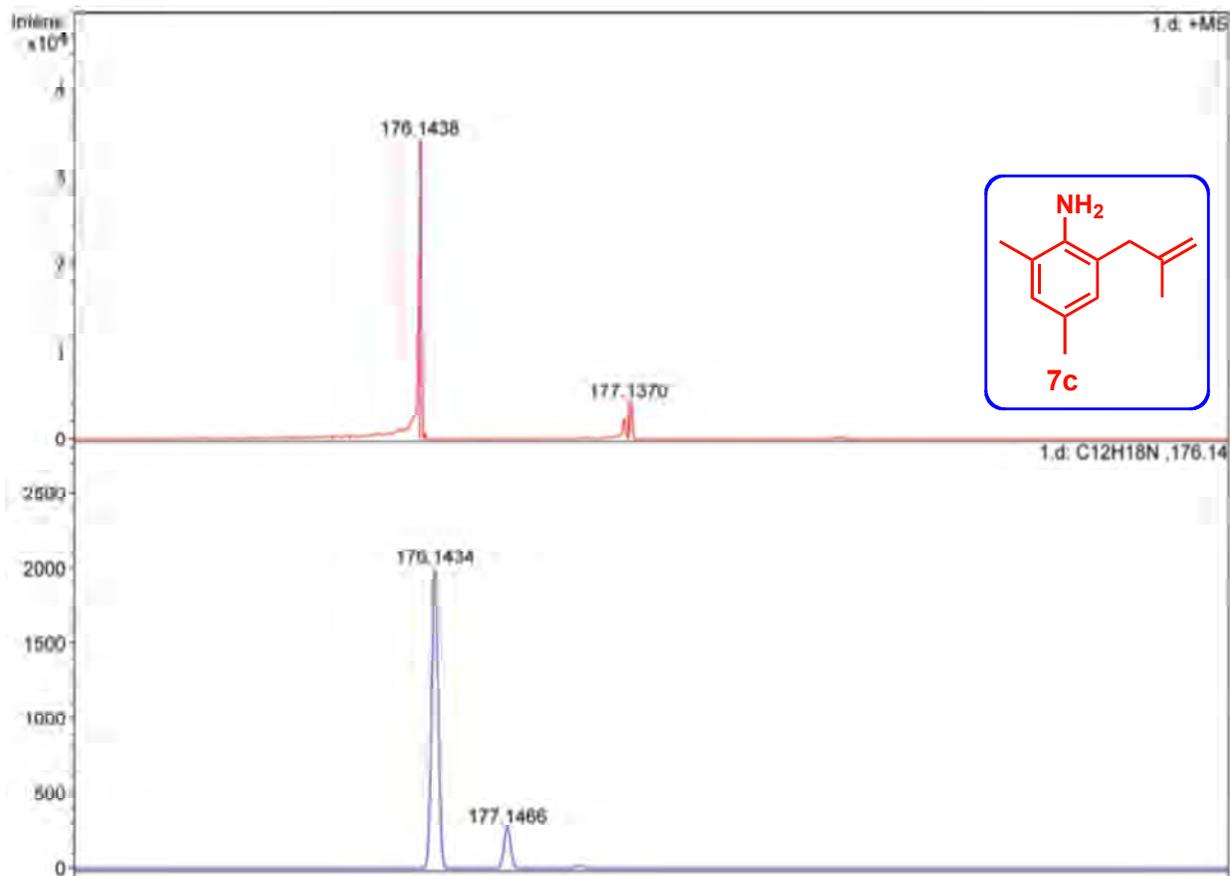
\* = Solvent and inseparable byproduct

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

Calculated : 176.1434

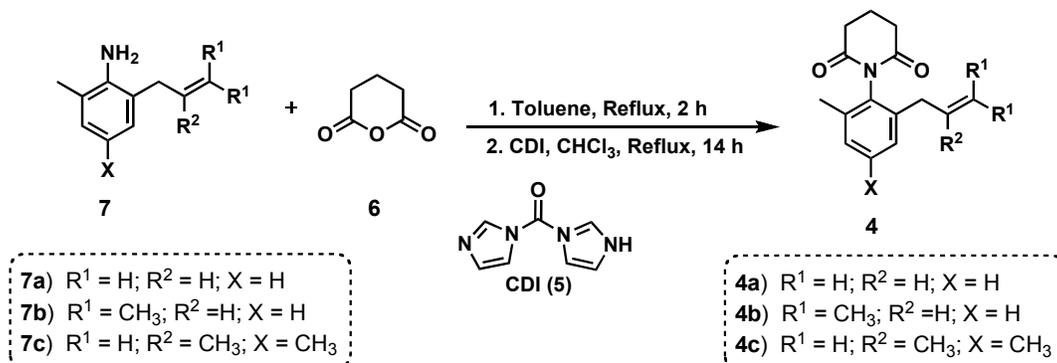
Observed : 176.1438

$|\Delta m|$  : 2.3 ppm



#### 4. GENERAL PROCEDURE FOR SYNTHESIS OF 3,4-DIHYDRO-2-PYRIDONE **1a-c**.

##### 4.1 SYNTHESIS OF PIPERIDINE-2,6-DIONE DERIVATIVES **4a-c**



#### **Scheme S11:** Synthesis of piperidine-2,6-dione derivatives **4a-c**.

The Piperidine-2,6-dione derivatives **4** (7.6 mmol) were synthesized according to the literature reported procedure.<sup>8</sup> To a solution of corresponding aniline derivative **7** (10 mmol) in toluene (20 mL) at 25 °C, glutaric anhydride **6** (9.1 mmol) was added. The resulting mixture was refluxed for 2 h. The reaction mixture was cooled to room temperature and the residue was diluted with n-pentane (50 mL). The precipitated solid was filtered and washed with n-pentane (20 mL) and dried under vacuum. The crude product was directly taken to next step without further purification.

To the crude product from above reaction dissolved in chloroform under N<sub>2</sub> atmosphere 1,1'-carbonyldiimidazole **5** (12 mmol) was added. To resulting solution was refluxed for 14 h. After the reaction, the solution was cooled to room temperature and DI water was added. The mixture was stirred and the layers were separated. The organic layer was washed with DI Water (2 X 100 mL), cold aqueous 2N HCl (2 X 75 mL or until the imidazole byproduct is removed) and brine solution (1 X 100 mL). The organic layer was dried over *anhy.* Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was evaporated under reduced pressure to get the crude product. The crude product was purified by combiflash using hexanes:ethyl acetate mixture (80:20) to get the title product **4** in 76% yield over two steps.

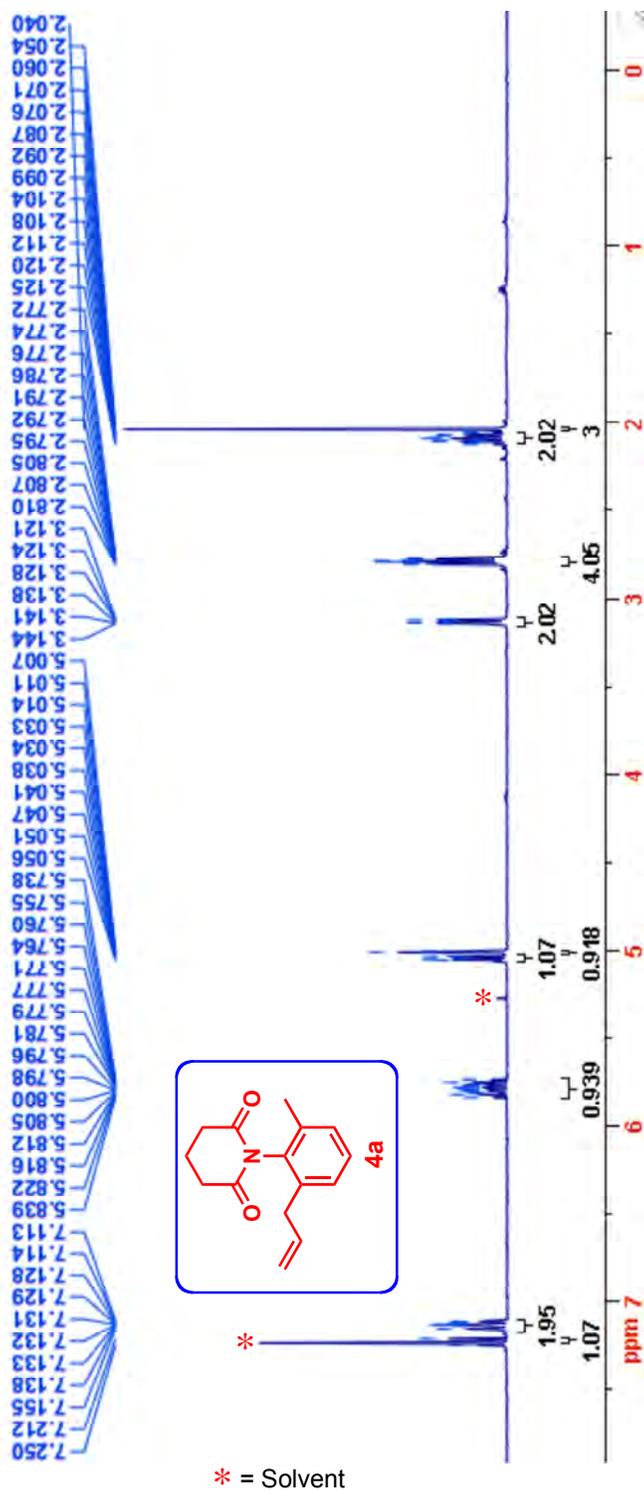
Note: During the addition of 1,1'-carbonyldiimidazole evolution of CO<sub>2</sub> gas was observed.

R<sub>f</sub> = 0.60 (50% hexanes:50% ethyl acetate) for **4a**.

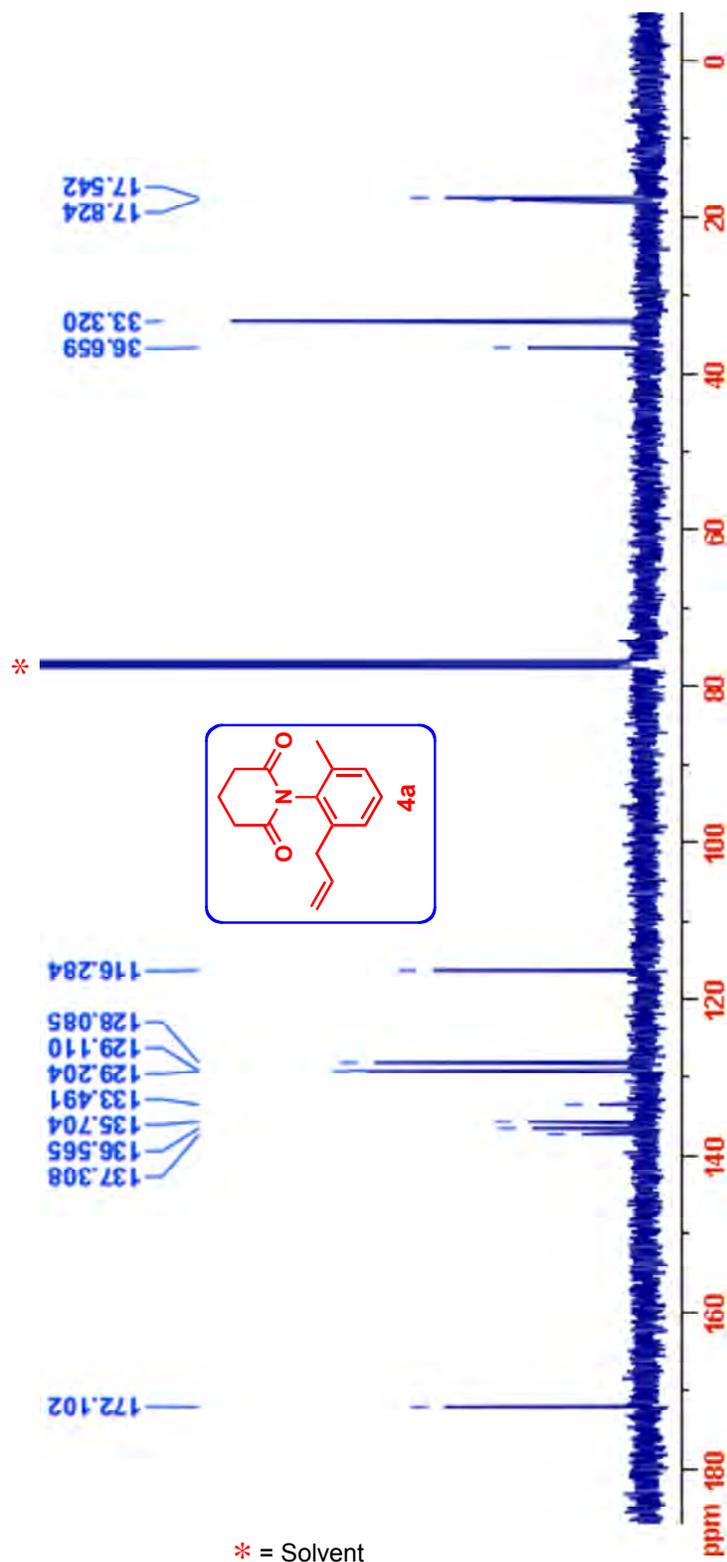
R<sub>f</sub> = 0.60 (50% hexanes:50% ethyl acetate) for **4b**.

R<sub>f</sub> = 0.70 (50% hexanes:50% ethyl acetate) for **4c**.

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.25 - 7.12 (m, 1H), 7.15 - 7.11 (m, 2H), 5.84 - 5.74 (m, 1H), 5.06 - 5.03 (m, 1H), 5.01 - 5.00 (m, 1H) 3.14 - 3.12 (m, 2H), 2.81 - 2.77 (m, 4H), 2.12 - 2.05 (m, 2H), 2.04 (s, 3H).



$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 172.1, 137.3, 136.6, 135.7, 133.5, 129.2, 129.1, 128.1, 116.3, 36.6, 33.3, 17.8 and 17.5.

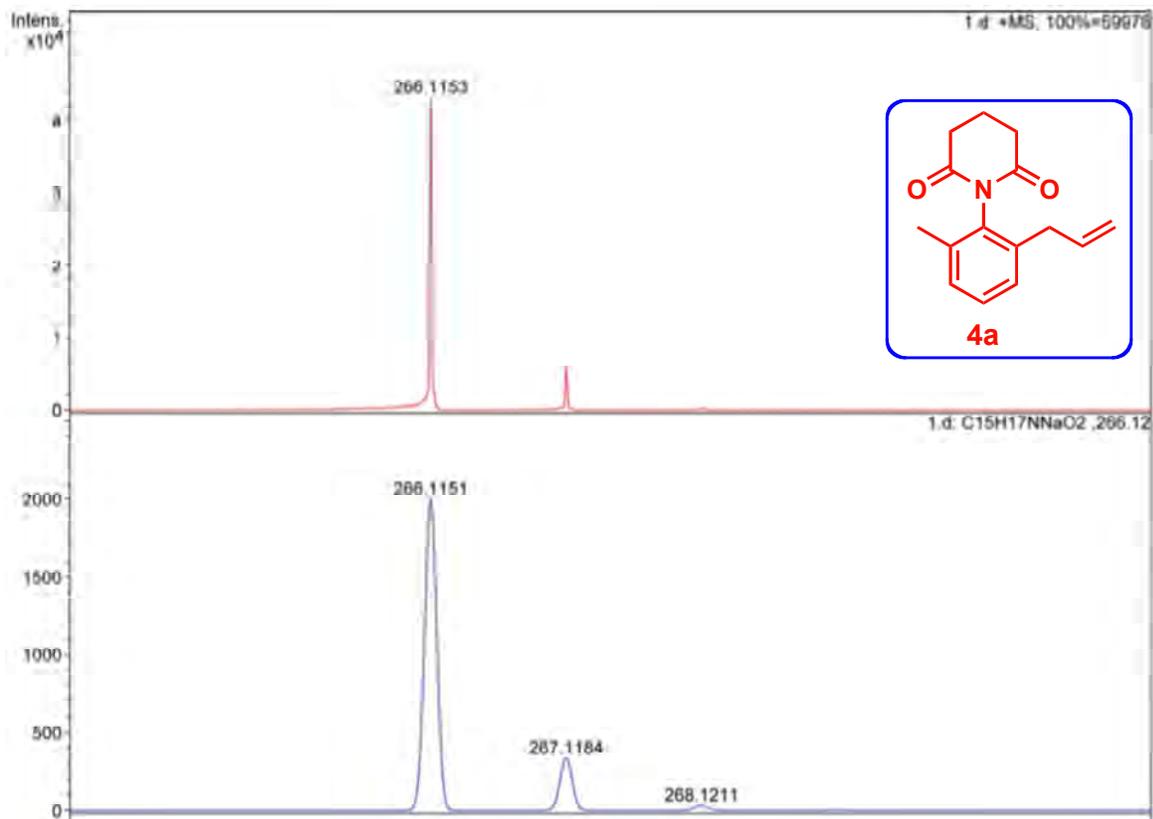


HRMS-ESI ( $m/z$ ) ( $[M + Na]^+$ ):

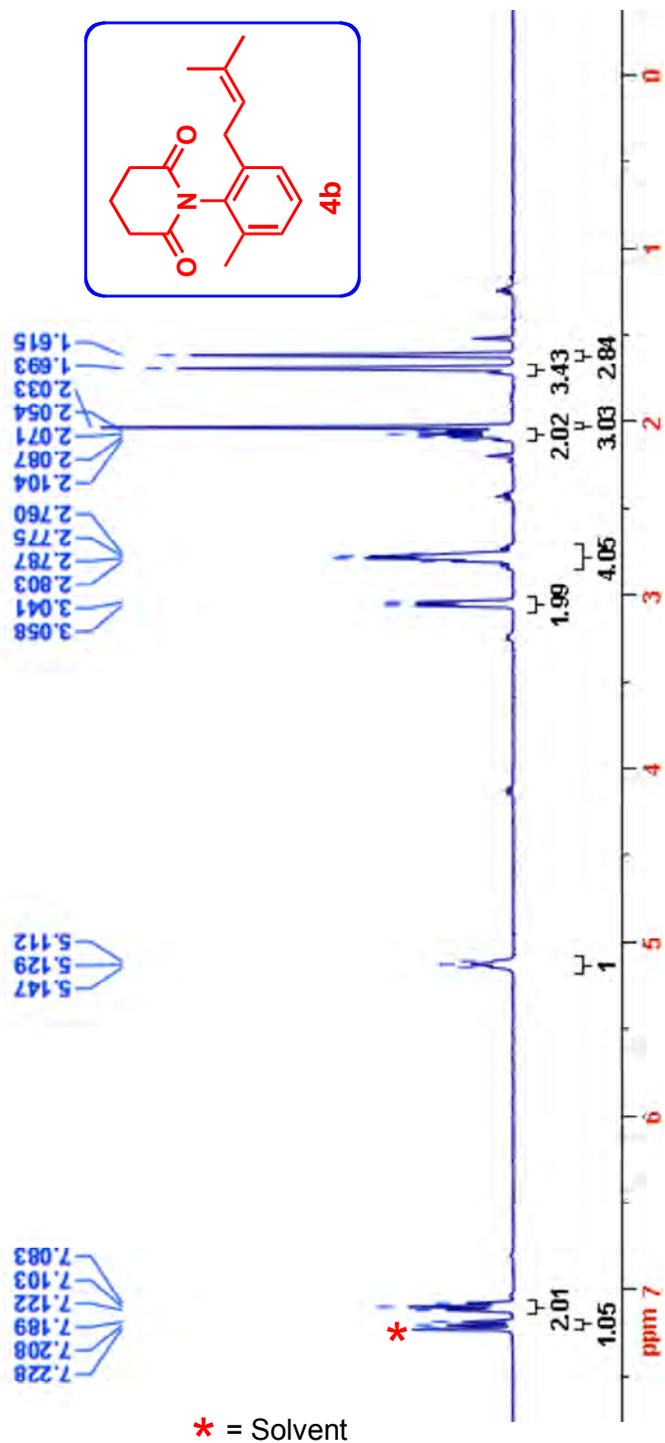
Calculated : 266.1151

Observed : 266.1153

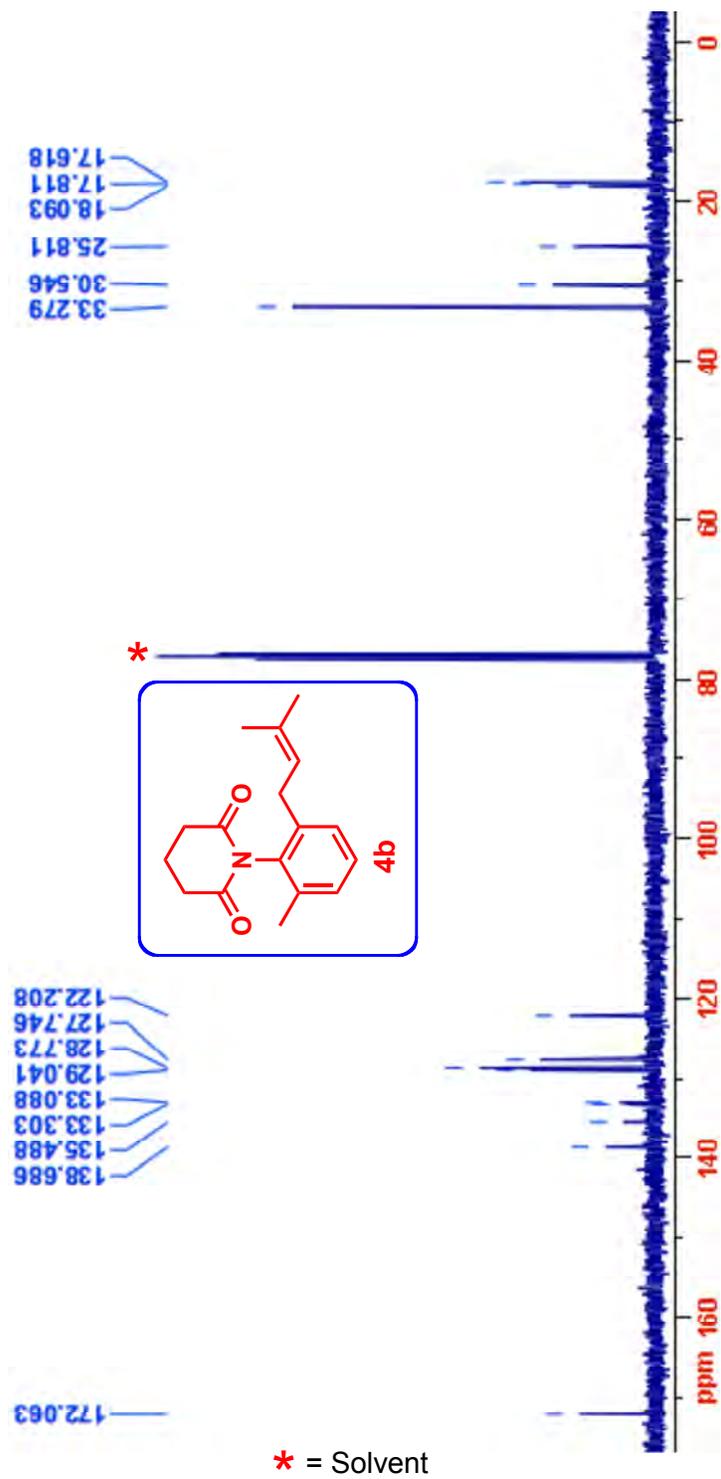
$|\Delta m|$  : 0.7 ppm



$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.23 – 7.19 (m, 1H), 7.12 – 7.08 (m, 2H), 5.15 – 5.11 (m, 1H), 3.06 – 3.04 (d,  $J = 6.8$  Hz, 2H), 2.8 – 2.76 (m, 4H), 2.10 – 2.05 (m, 2H), 2.03 (s, 3H), 1.69 (s, 3H) and 1.61 (s, 3H).



$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 172.1, 138.7, 135.5, 133.3, 133.1, 129.0, 128.8, 127.7, 122.2, 33.3, 30.5, 25.8, 18.1, 17.8 and 17.6.

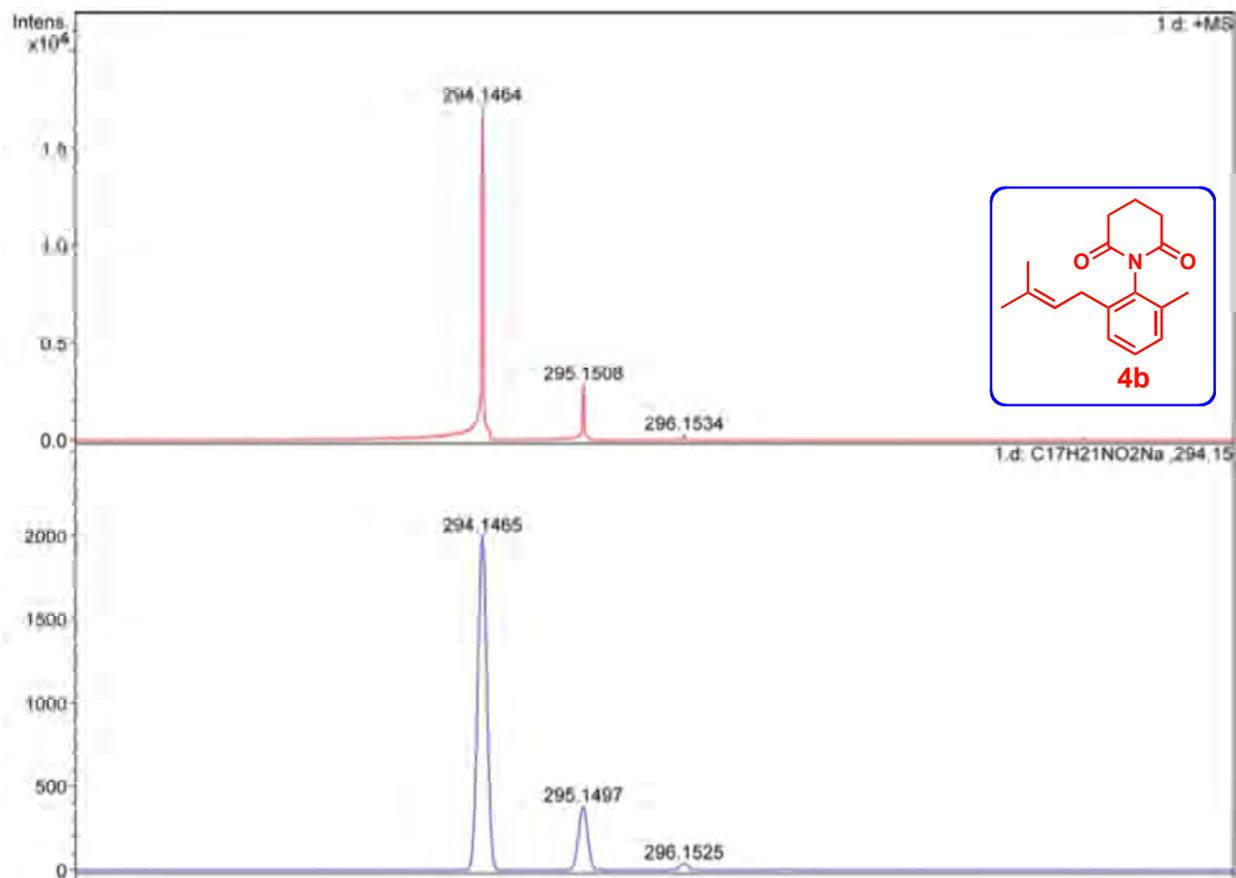


HRMS-ESI ( $m/z$ ) ( $[M + Na]^+$ ):

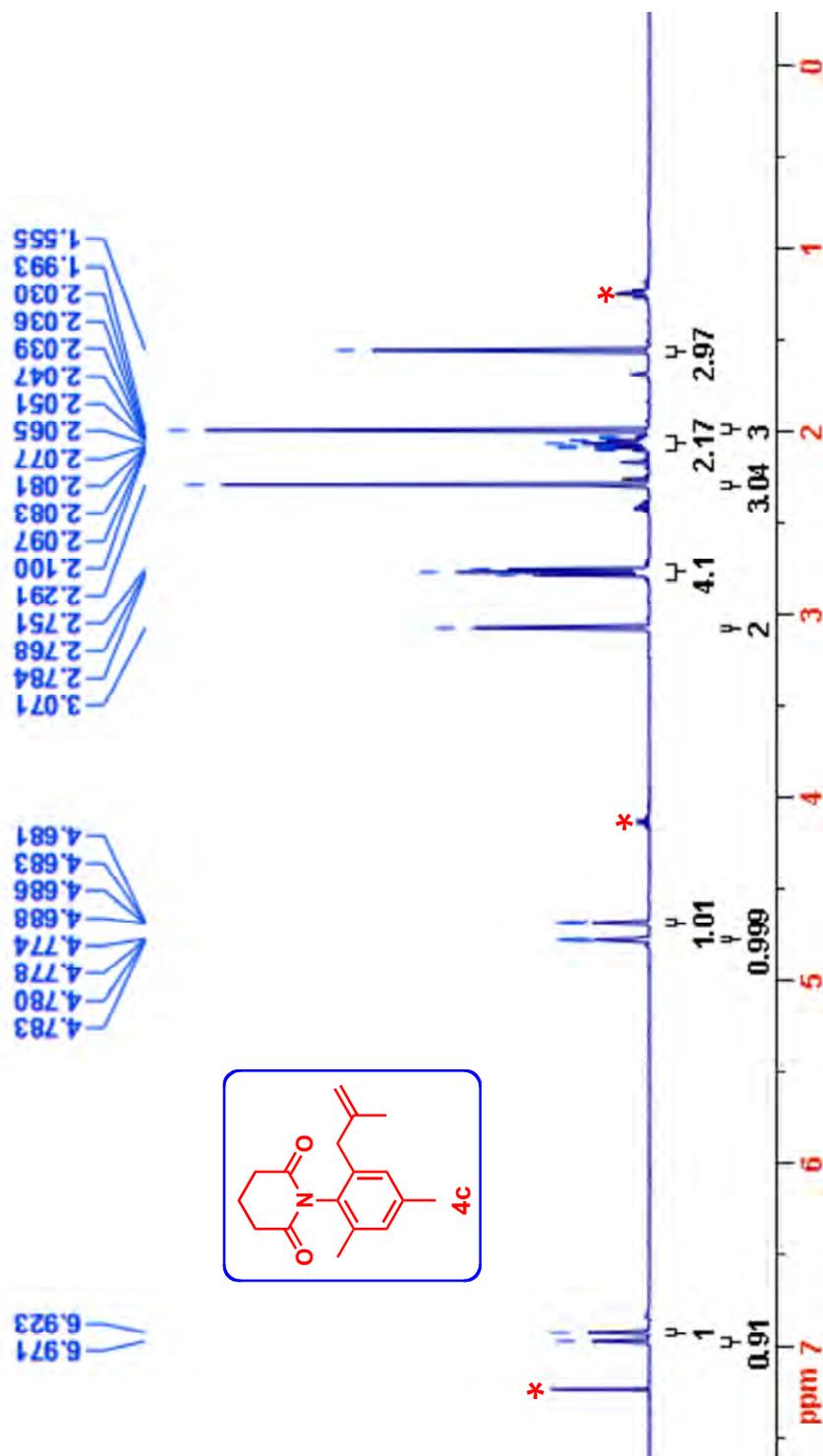
Calculated : 294.1465

Observed : 294.1464

$|\Delta m|$  : 0.3 ppm

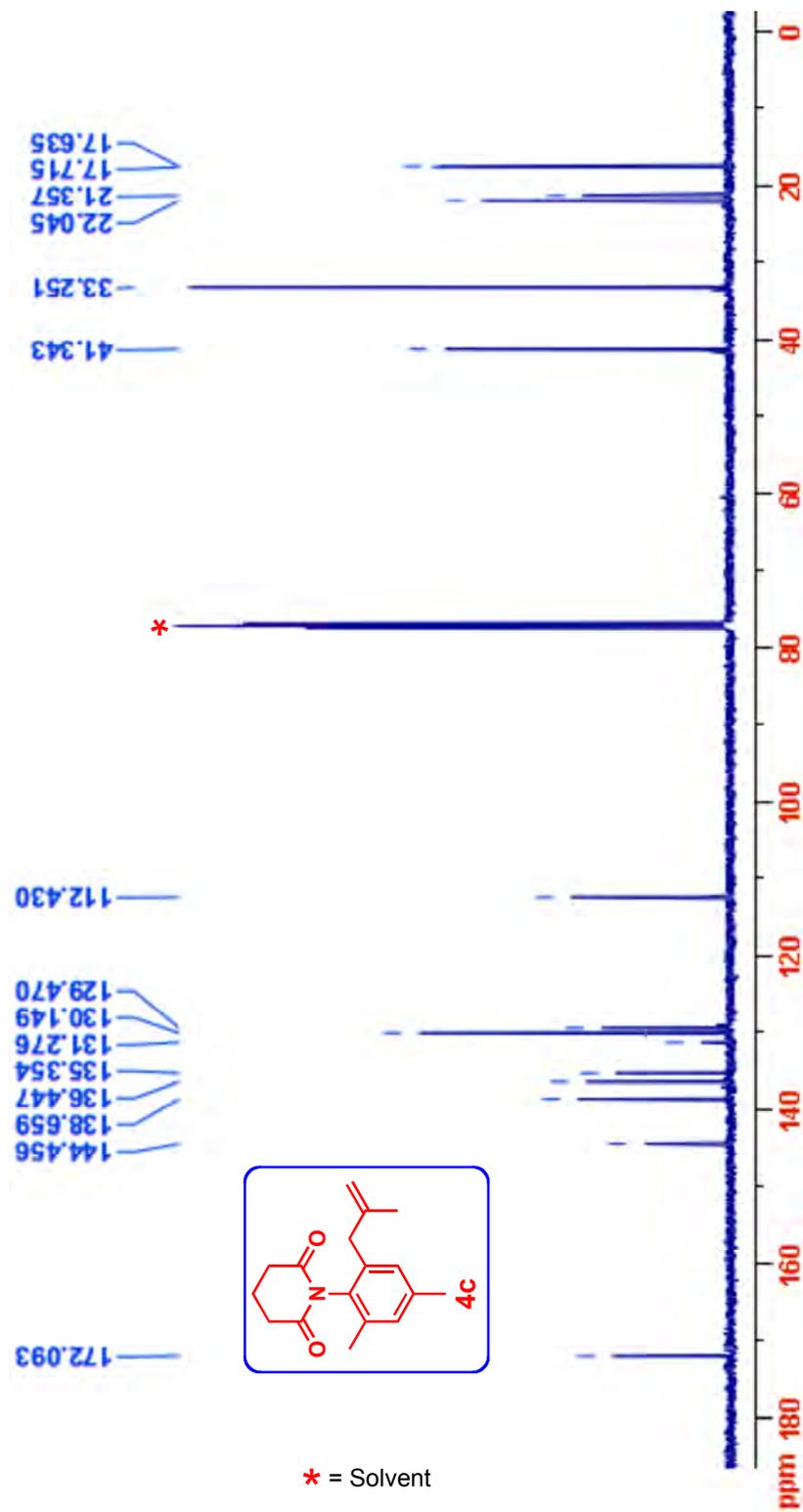


$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 6.97 (s, 1H), 6.92 (s, 1H), 4.78 – 4.77 (m, 1H), 4.69 – 4.68 (m, 1H), 3.07 (s, 2H), 2.78 – 2.75 (m, 4H), 2.29 (s, 3H), 2.10 – 2.03 (m, 2H), 1.99 (s, 3H) and 1.55 (s, 3H).



\* = Solvent

$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 172.1, 144.4, 138.6, 136.4, 135.3, 131.3, 130.1, 129.5, 112.4, 41.3, 33.2, 22.0, 21.3, 17.7 and 17.6.

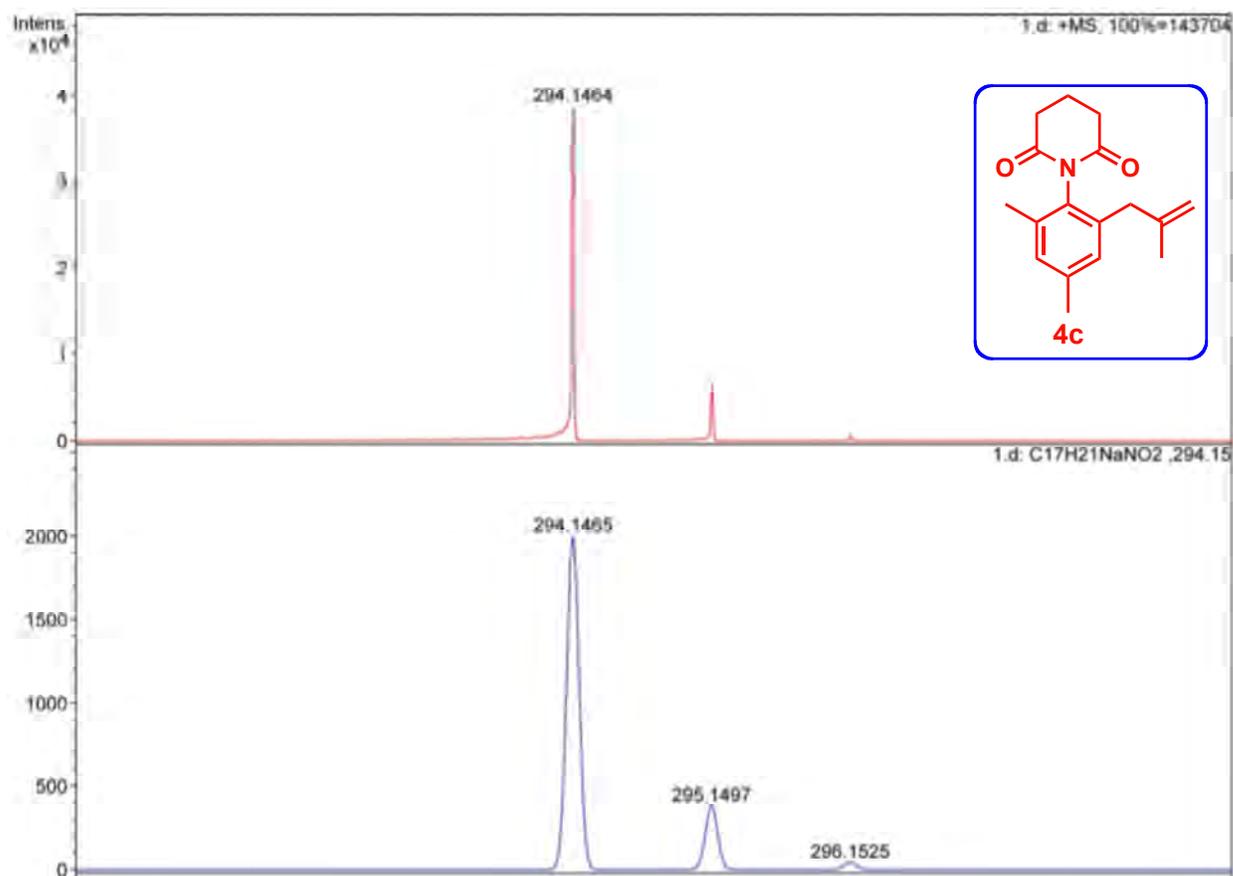


HRMS-ESI ( $m/z$ ) ( $[M + Na]^+$ ):

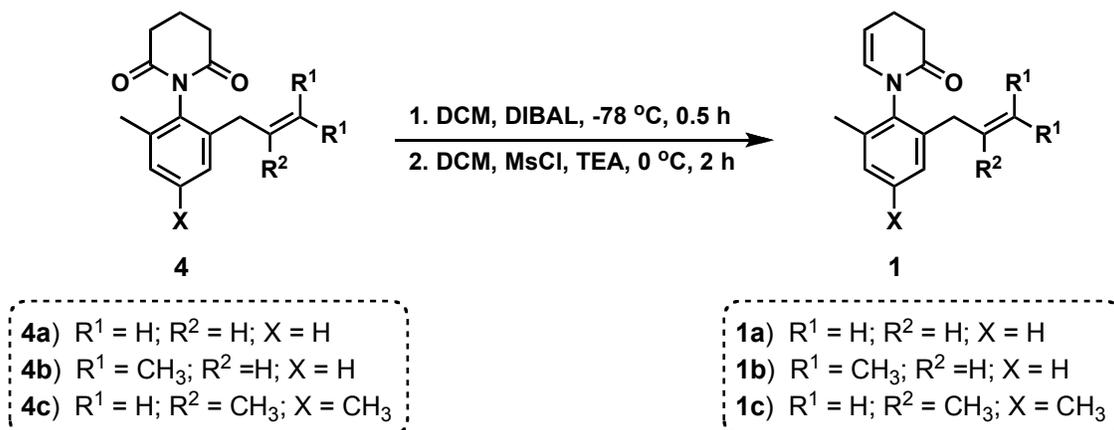
Calculated : 294.1465

Observed : 294.1464

$|\Delta m|$  : 0.3 ppm



#### 4.2 SYNTHESIS OF 3,4-DIHYDRO-2-PYRIDONE **1a-c**



**Scheme S12:** Synthesis of 3,4-dihydro-2-pyridone **1a-c**.

To a solution of corresponding piperidine-2,6-dione derivative **4** (7.6 mmol) in DCM (25 mL) under  $\text{N}_2$  atmosphere at  $-78\text{ }^\circ\text{C}$  was added DIBAL (25% Wt/Wt in hexanes, 13.7 mmol). The mixture was stirred at  $-78\text{ }^\circ\text{C}$  for 30 mins. The reaction mixture was quenched with DI water (10 mL) followed by the addition of *aq.* 2N NaOH solution (10 mL). The reaction mixture was slowly warmed to room temperature and the mixture was poured into saturated solution of Rochelle's salt (sodium potassium tartarate, 200 mL). The aqueous layer was extracted with DCM (3 X 75 mL). The combined organic layer was dried over *anhy.*  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was evaporated under reduced pressure to get the crude product. The crude product was directly taken to next step without further purification.

To the crude product from above reaction dissolved in DCM (75 mL) at  $0\text{ }^\circ\text{C}$  under  $\text{N}_2$  atmosphere was added methanesulfonyl chloride (12.16 mmol) and triethylamine (22.8 mmol). The resulting solution was stirred at  $0\text{ }^\circ\text{C}$  for 2 h. After the reaction, DI water (50 mL) was added and the mixture was stirred for 10 mins and the layers were separated. The aqueous layer was extracted with of DCM (2 X 20 mL). The combined organic layer was dried over *anhy.*  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was evaporated under reduced pressure to get the crude product. The crude product was purified by combiflash using hexanes:ethyl acetate mixture (80:20) to get the title product **1** in 65% yield over two steps.

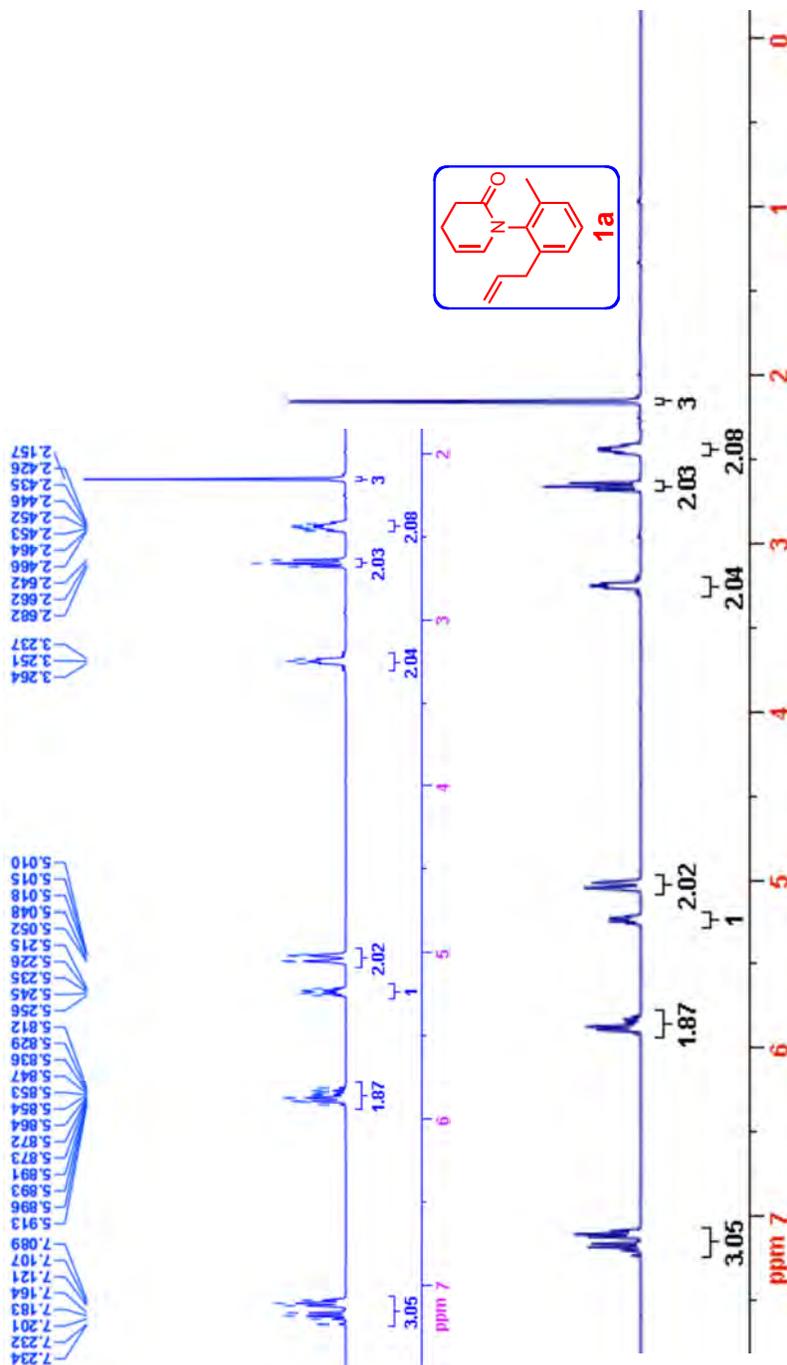
$R_f = 0.40$  (50% hexanes:50% ethyl acetate) for **1a**.

$R_f = 0.40$  (50% hexanes:50% ethyl acetate) for **1b**.

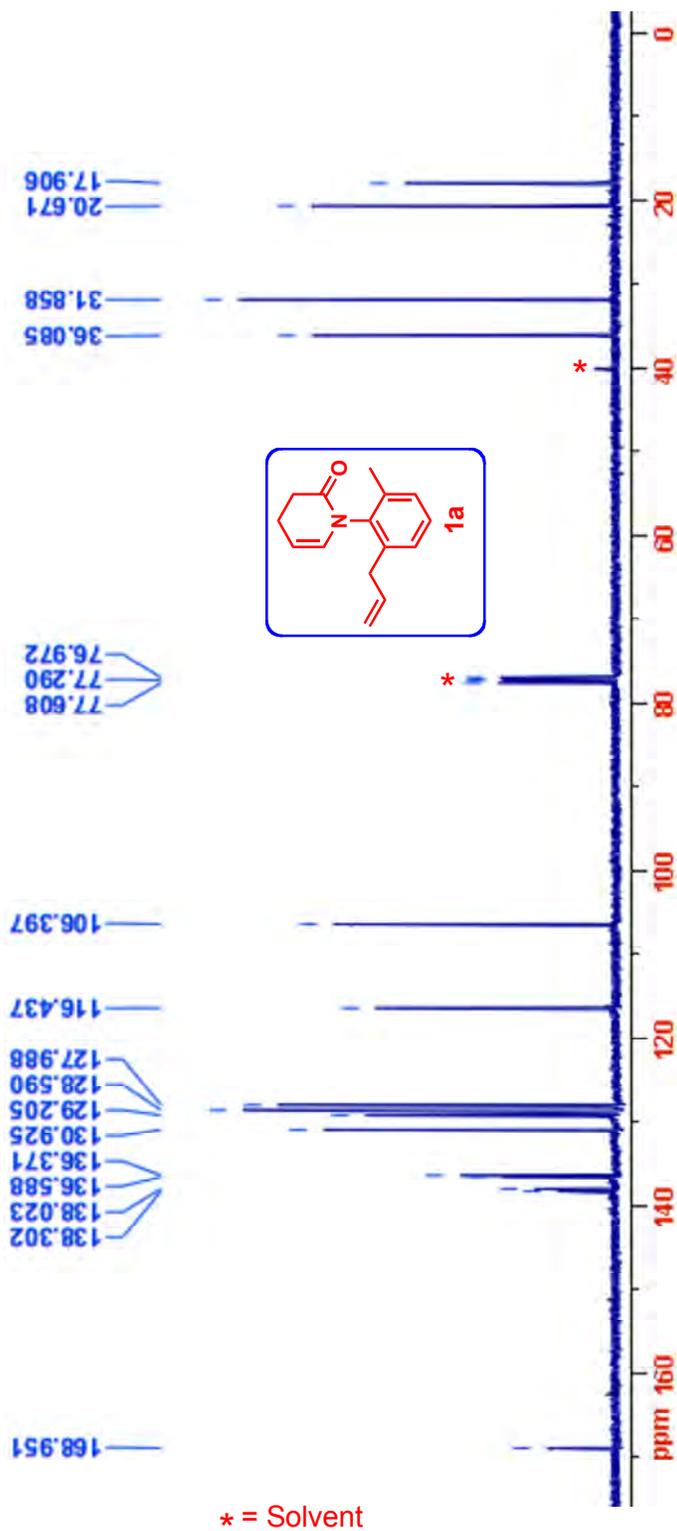
$R_f = 0.50$  (50% hexanes:50% ethyl acetate) for **1c**.

*Note:* The samples turn dark brown over time, so they were stored in amber vials in freezer.

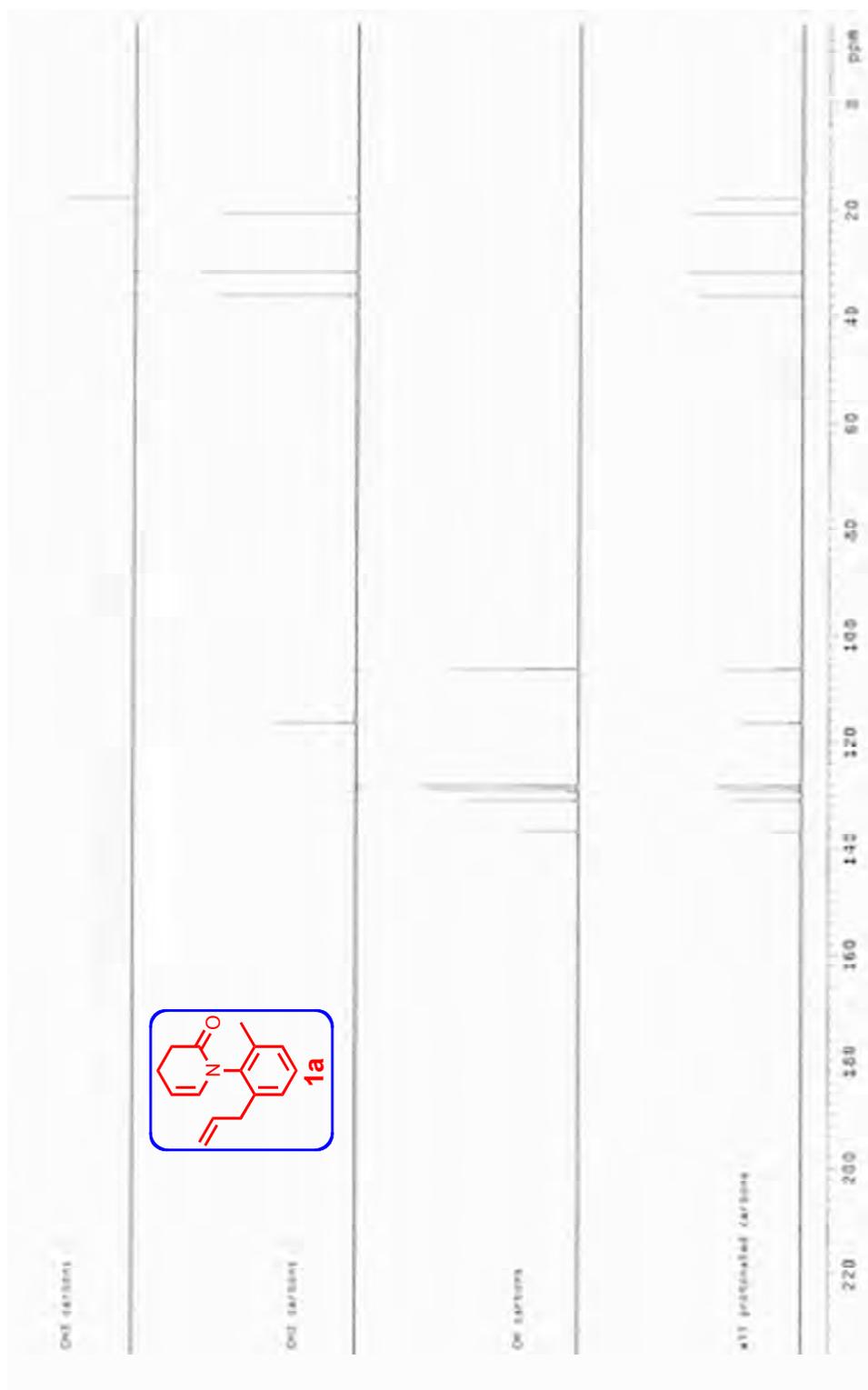
$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.23 - 7.09 (m, 3H), 5.91- 5.81 (m, 2H), 5.26 - 5.22 (m, 1H), 5.05 - 5.01 (m, 2H), 3.26 - 3.24 (m, 2H), 2.68 - 2.64 (t,  $J = 8$  Hz, 2H), 2.47 - 2.43 (m, 2H), 2.16 (s, 3H).



$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 168.95, 138.3, 138.0, 136.6, 136.4, 130.9, 129.2, 128.6, 127.98, 116.4, 106.4, 36.1, 31.9, 20.7 and 17.9.



$^{13}\text{C}$  DEPT spectra:

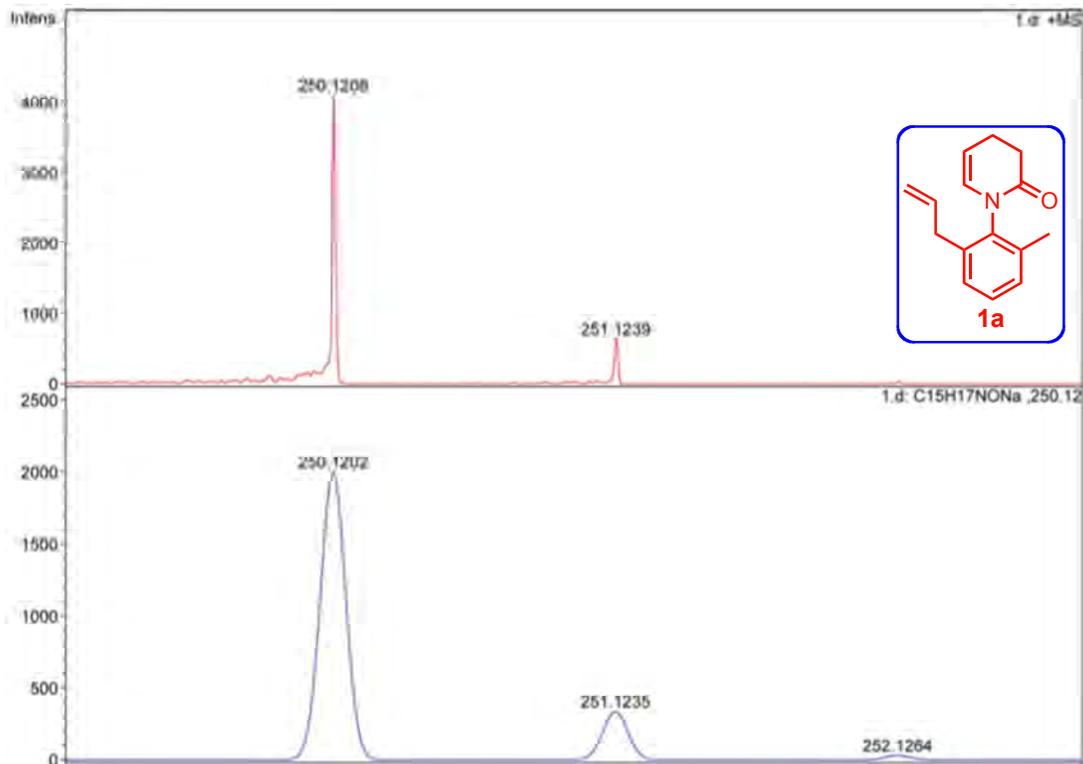


HRMS-ESI ( $m/z$ ) ( $[M + Na]^+$ ):

Calculated : 250.1202

Observed : 250.1208

$|\Delta m|$  : 2.4 ppm



HPLC analysis conditions:

For analytical conditions,

- I). Column : RR-WHELK-01 10/100 FEC  
Abs. detector wavelength : 254 nm and 270 nm  
Mobile phase : Hexanes:2-propanol = 95:5  
Flow rate : 1.0 mL/min  
Retention times (min) : ~ 28.92 [(+)-**1a**] and ~ 32.13 [(-)-**1a**]
- II). Column : CHIRALPAK-IC  
Abs. detector wavelength : 254 nm and 270 nm  
Mobile phase : Hexanes:2-propanol = 90:10  
Flow rate : 1.0 mL/min  
Retention times (min) : ~ 16.24 [(-)-**1a**] and ~ 19.64 [(+)-**1a**]

For preparative conditions,

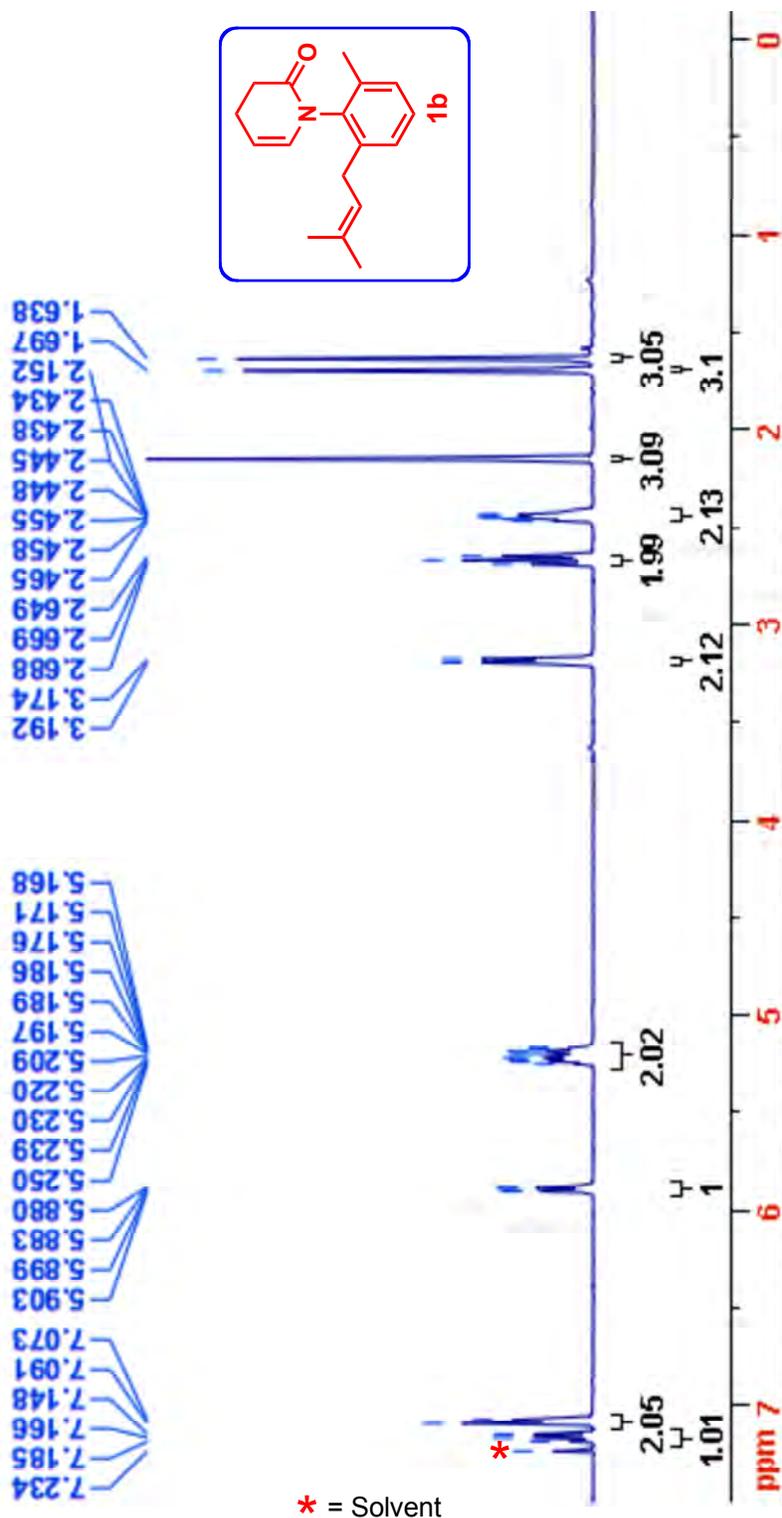
l). Column : CHIRALPAK-IC  
Abs. detector wavelength : 254 nm and 270 nm  
Mobile phase : Hexanes:2-propanol = 95:5  
Flow rate : 3.0 mL/min  
Retention times (min) : ~ 32.72 [(-)-**1a** and ~ 40.62 [(+)-**1a**]

Optical rotation  $[\alpha]_D^{26}$  :

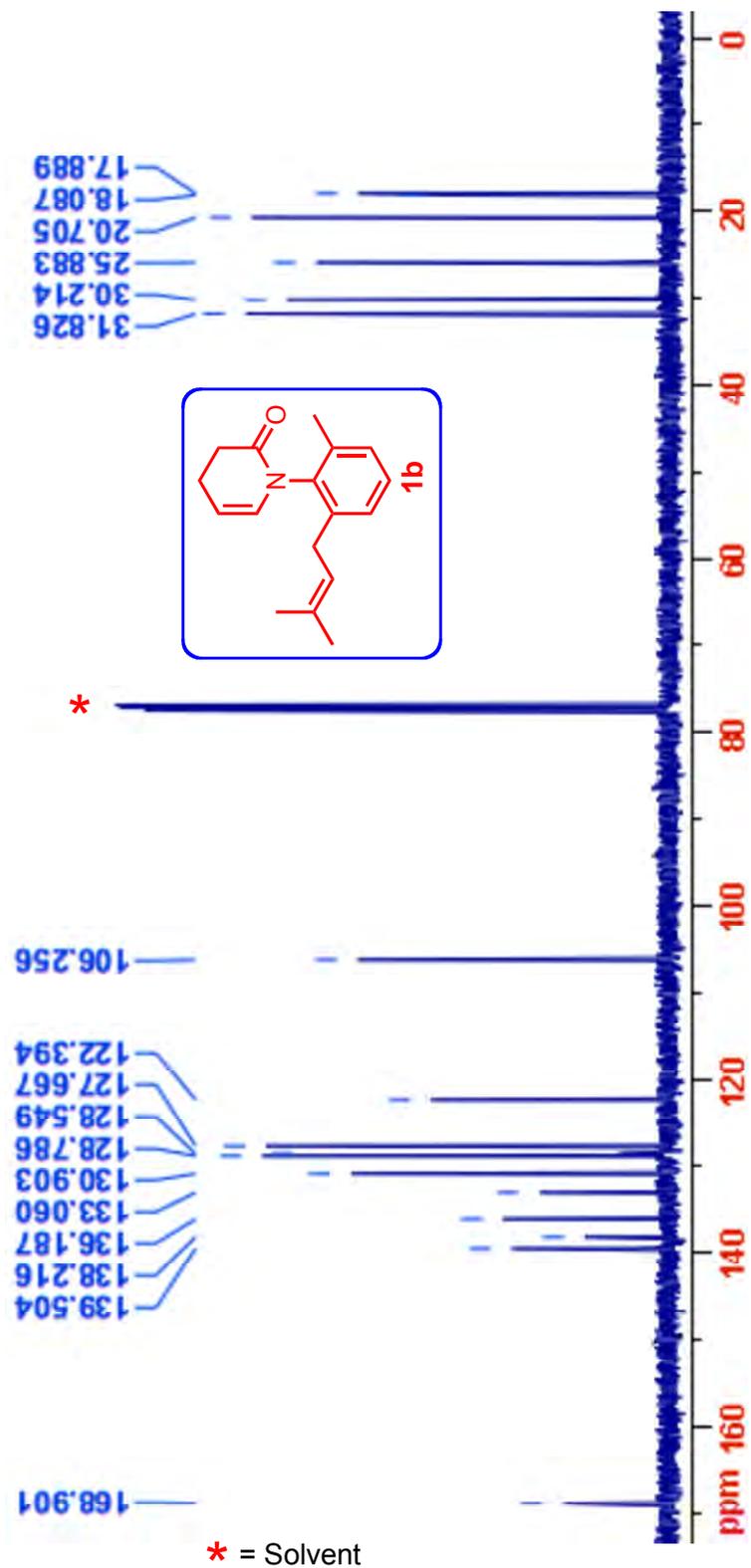
HPLC retention time (RR-WHELK-01) at ~ 28.92 min, (c = 0.725%, MeOH) = +34.37 deg

HPLC retention time (RR-WHELK-01) at ~ 32.13 min, (c = 0.725%, MeOH) = -32.27 deg.

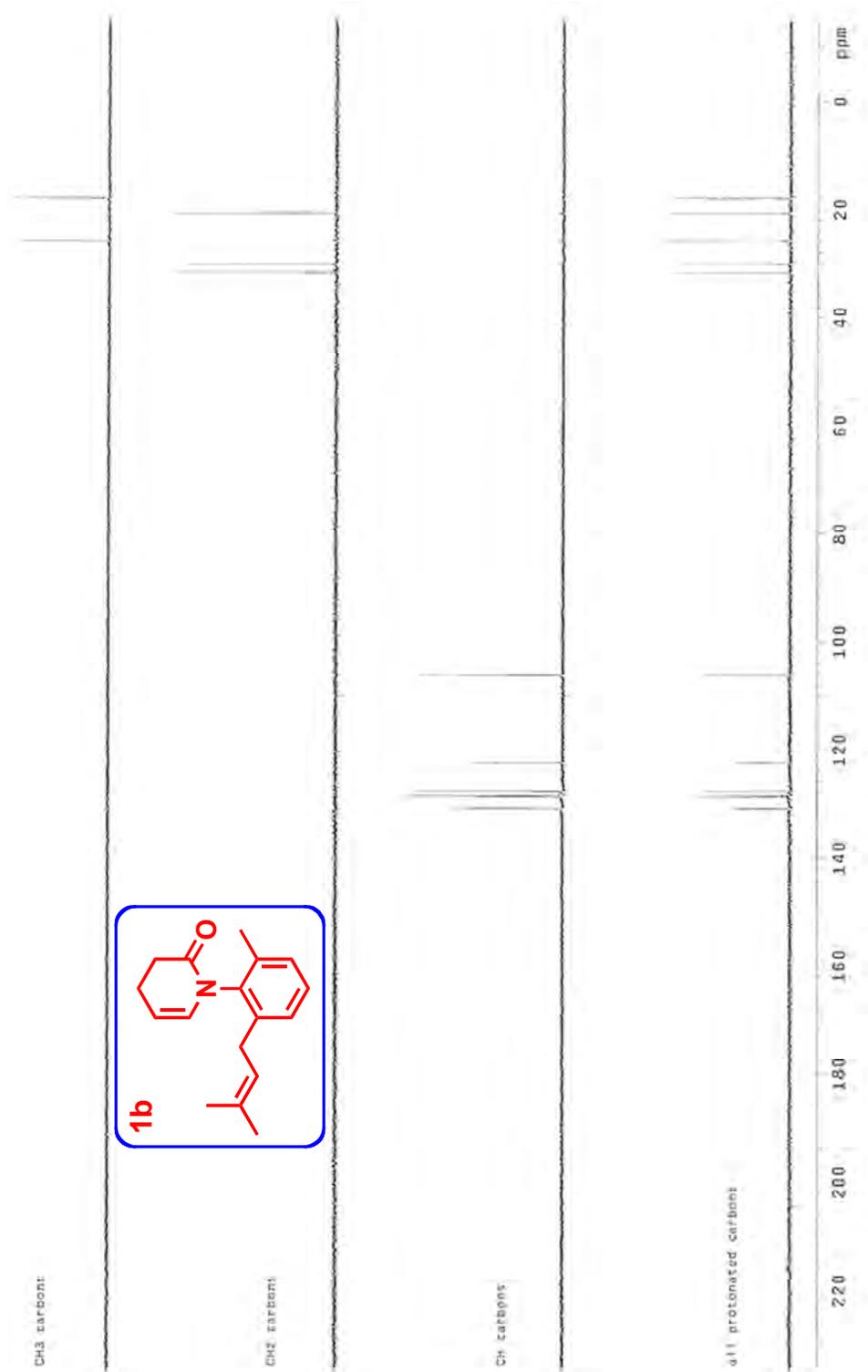
$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.18 – 7.15 (m, 1H), 7.09 – 7.07 (m, 2H), 5.90 – 5.88 (m, 1H), 5.25 – 5.17 (m, 2H), 3.19 – 3.17 (d,  $J = 7.2$  Hz, 2H), 2.69 – 2.65 (m, 2H), 2.46 – 2.42 (m, 2H), 2.15 (s, 3H), 1.69 (m, 3H) and 1.64 (m, 3H).



$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 168.9, 139.5, 138.2, 136.2, 133.1, 130.9, 128.8, 128.5, 127.7, 122.4, 106.2, 31.8, 30.2, 25.9, 20.7, 18.1 and 17.9.



$^{13}\text{C}$  DEPT spectra:

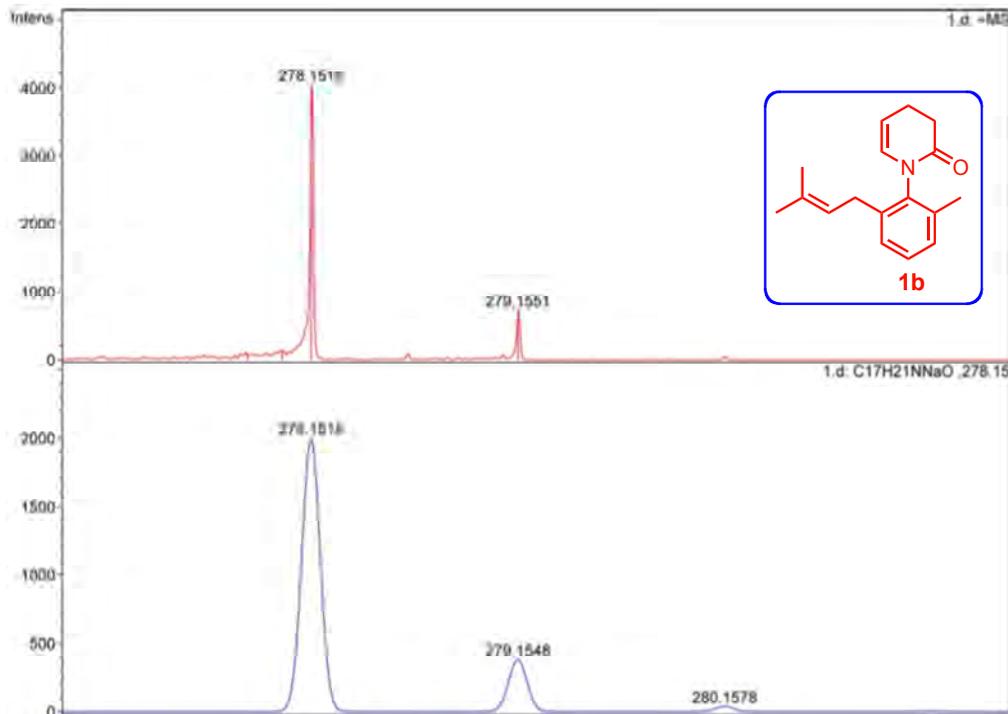


HRMS-ESI ( $m/z$ ) ( $[M + Na]^+$ ):

Calculated : 278.1515

Observed : 278.1516

$|\Delta m|$  : 0.4 ppm



HPLC analysis conditions:  
For analytical conditions,

I). Column : CHIRALPAK-IC  
Abs. detector wavelength : 254 nm and 270 nm  
Mobile phase : Hexanes:2-propanol = 90:10  
Flow rate : 1.5 mL/min  
Retention times (min) : ~ 8.94 [(-)-**1b** and ~ 10.89 [(+)-**1b**]

For preparative conditions,

I). Column : CHIRALPAK-IC  
Abs. detector wavelength : 254 nm and 270 nm  
Mobile phase : Hexanes:2-propanol = 95:5  
Flow rate : 3.0 mL/min  
Retention times (min) : ~ 28.39 [(-)-**1b** and ~ 35.92 [(+)-**1b**]

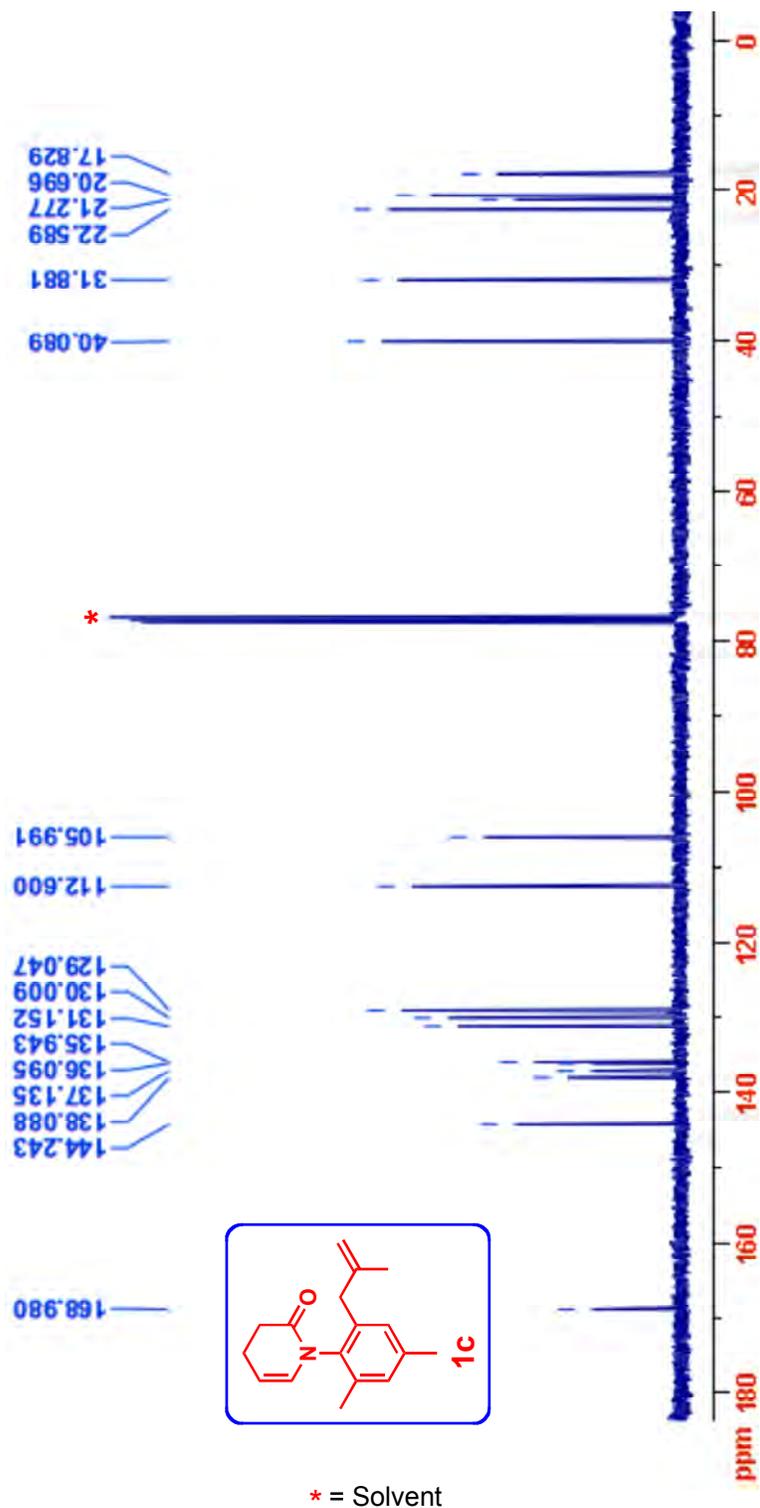
Optical rotation  $[\alpha]_D^{26}$ :

HPLC retention time (CHIRALPACK® IC) at ~ 8.94 min, ( $c = 0.369\%$ , MeOH) = -70.90 deg.

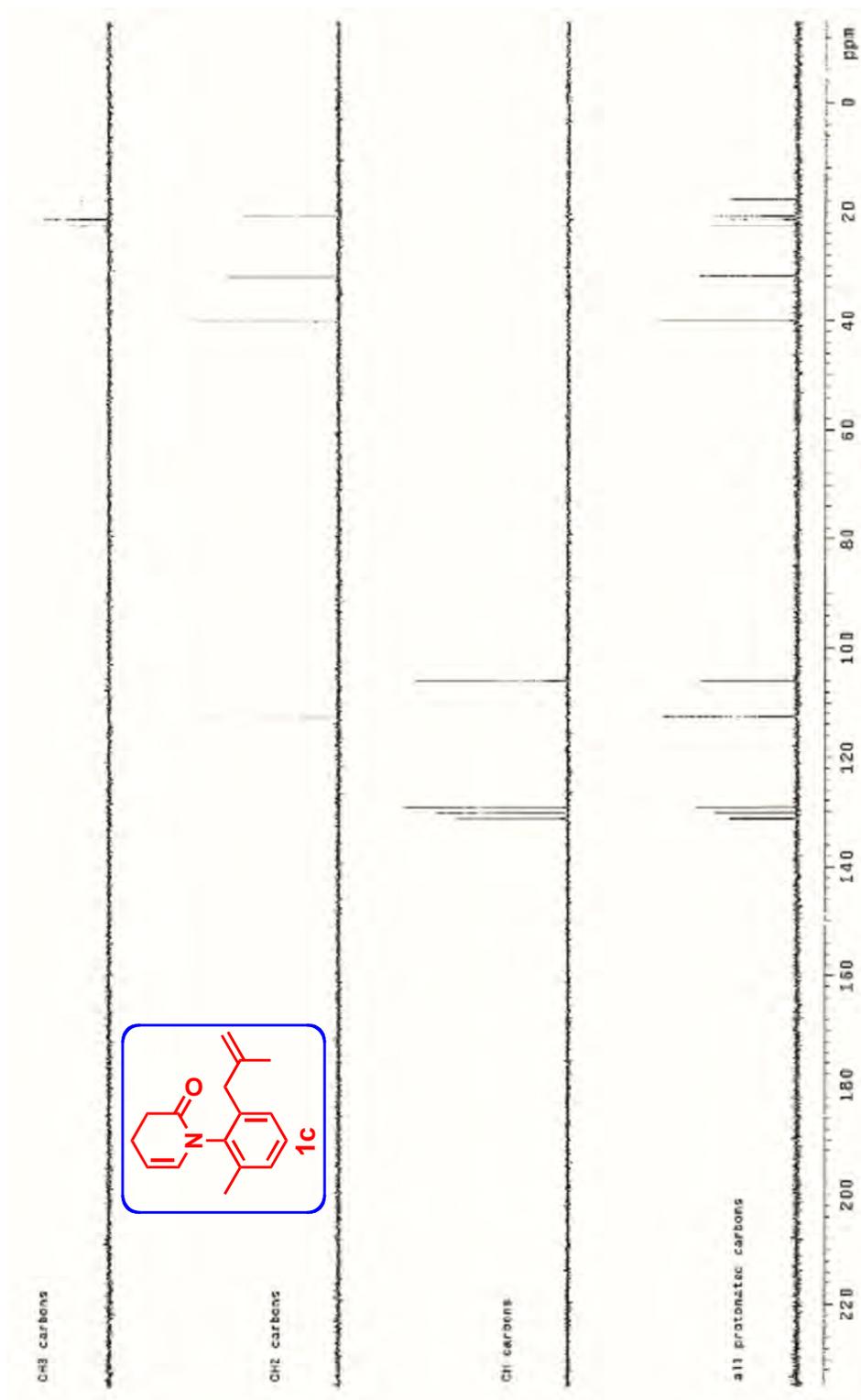
HPLC retention time (CHIRALPACK® IC) at ~ 10.89 min, ( $c = 0.369\%$ , MeOH) = +70.63 deg.



$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 168.98, 144.2, 138.1, 137.1, 136.1, 135.9, 131.1, 130.0, 129.0, 112.6, 105.99, 40.1, 31.9, 22.6, 21.3, 20.7 and 17.8.



$^{13}\text{C}$  DEPT Spectra:

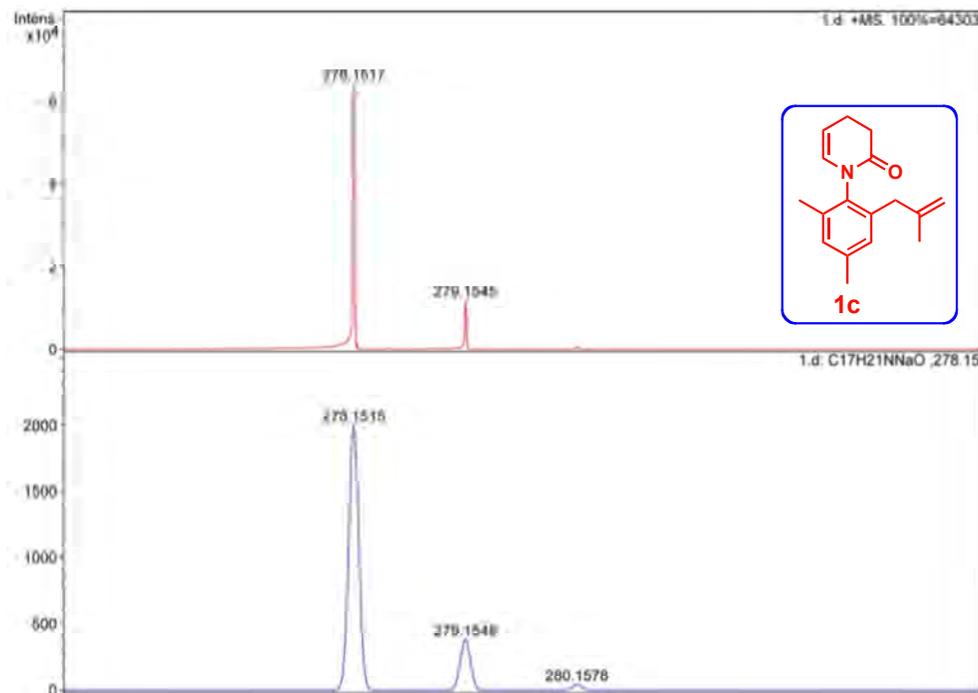


HRMS-ESI ( $m/z$ ) ( $[M + Na]^+$ ):

Calculated : 278.1515

Observed : 278.1517

$|\Delta m|$  : 0.7 ppm



HPLC analysis conditions:

For analytical conditions,

I). Column	: CHIRALPACK® IC
Abs. detector wavelength	: 254 nm and 270 nm
Mobile phase	: Hexanes:2-propanol = 90:10
Flow rate	: 1.0 mL/min
Retention times (min)	: ~ 15.55 [(-)- <b>1c</b> and ~ 17.83 [(+)- <b>1c</b>

For preparative conditions,

I). Column	: CHIRALPAK-IC
Abs. detector wavelength	: 254 nm and 270 nm
Mobile phase	: Hexanes:2-propanol = 95:5
Flow rate	: 3.0 mL/min
Retention times (min)	: ~ 33.97 [(-)- <b>1c</b> and ~ 40.57 [(+)- <b>1c</b>

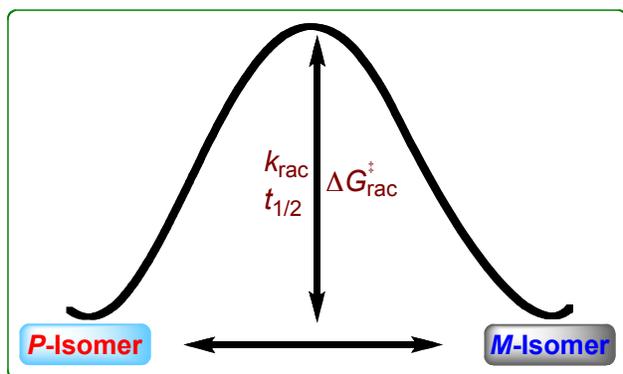
Optical rotation  $[\alpha]_D^{26}$  :

HPLC retention time (CHIRALPACK® IC) at ~ 15.55 min, ( $c = 0.700\%$ , MeOH) = -48.07 deg.

HPLC retention time (CHIRALPACK® IC) at ~ 17.83 min, ( $c = 0.700\%$ , MeOH) = +48.80 deg.

### 5. RACEMIZATION KINETICS OF NON-BIARYL ATROPISOMERIC 3,4-DIHYDRO-2-PYRIDONES **1a-c**.

Racemization kinetics of optically pure atropisomeric 3,4-dihydro-2-pyridones **1a-c** was followed at various temperatures (50 and 75 °C) and in different solvents (2-propanol, methanol and acetone). 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 equations 1 and 2.<sup>9</sup>



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

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

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  $t = 0$ ).

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

$$\ln \left( \frac{R_0}{R_0 - x} \right) = \ln \left( \frac{R+S}{R-S} \right) = k_{rac} t \quad \text{Equation 2.}$$

Where,  $k_{rac} = 2 \cdot k_{enant}$ ;  $R_0$  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:

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

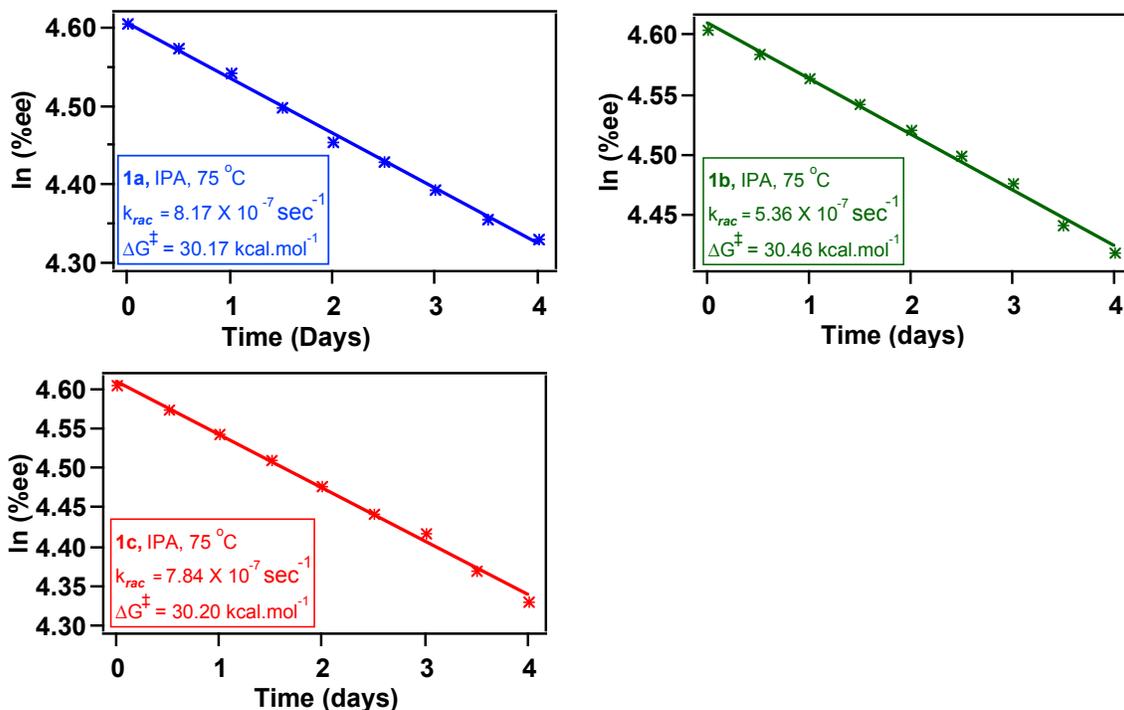


Figure S1: Racemization kinetics of 3,4-dihydro-2-pyridones **1a-c** in 2-propanol at 75 °C.

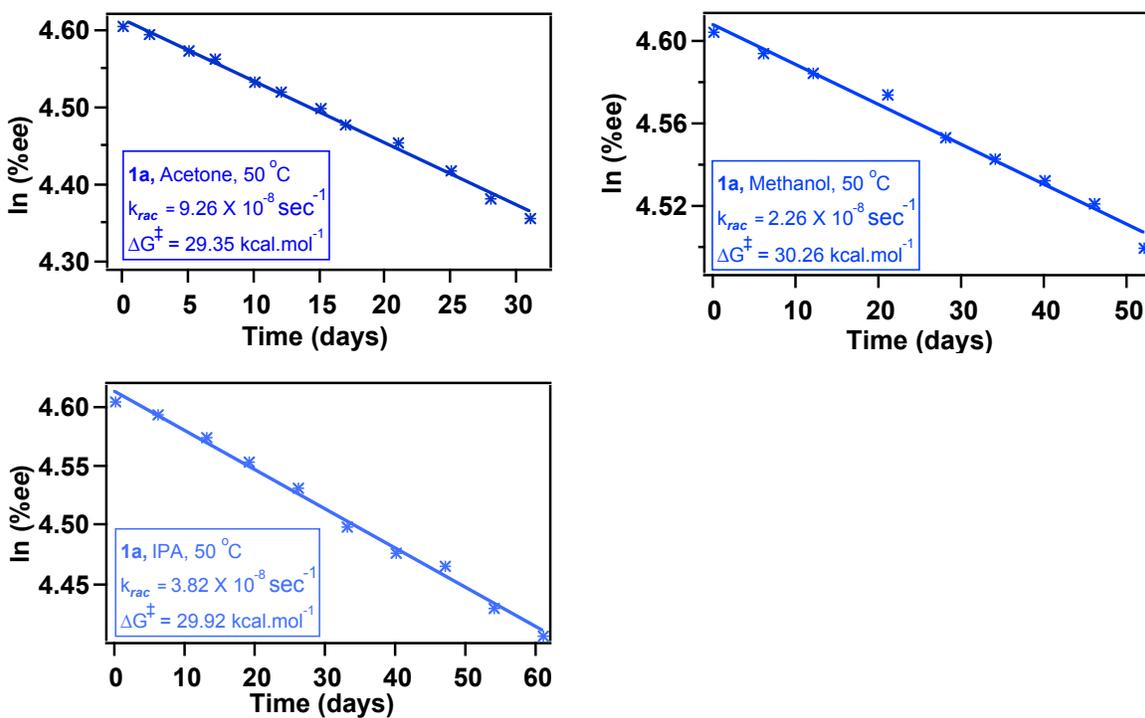


Figure S2: Racemization kinetics of 3,4-dihydro-2-pyridones **1a** in 2-propanol, methanol and acetone at 50 °C respectively.

**Table S1:** Activation energy, rate and half-life for racemization of optically pure non-biaryl atropchiral 3,4-dihydro-2-pyridones **1a-c**.

Entry	T (°C)	Parameters	Compound	Solvent		
				2-propanol	Methanol	Acetone
1	75	$\tau_{1/2rac}$ (days)	<b>1a</b>	9.82	b	b
2			<b>1b</b>	15.0	b	b
3			<b>1c</b>	10.2	b	b
4		$\Delta G_{rac}^\ddagger$ (kcal•mol <sup>-1</sup> )	<b>1a</b>	30.17	b	b
5			<b>1b</b>	30.46	b	b
6			<b>1c</b>	30.20	b	b
7		$k_{rac}$ (s <sup>-1</sup> )	<b>1a</b>	8.17 X 10 <sup>-7</sup>	b	b
8			<b>1b</b>	5.36 X 10 <sup>-7</sup>	b	b
9			<b>1c</b>	7.84 X 10 <sup>-7</sup>	b	b
10	50	$\tau_{1/2rac}$ (days)	<b>1a</b>	210	355	86.6
11			<b>1b</b>	a	a	177
12			<b>1c</b>	284	a	176
13		$\Delta G_{rac}^\ddagger$ (kcal•mol <sup>-1</sup> )	<b>1a</b>	29.92	30.26	29.35
14			<b>1b</b>	a	a	29.81
15			<b>1c</b>	30.11	a	29.81
16		$k_{rac}$ (s <sup>-1</sup> )	<b>1a</b>	3.82 X 10 <sup>-8</sup>	2.26 X 10 <sup>-8</sup>	9.26 X 10 <sup>-8</sup>
17			<b>1b</b>	a	a	4.54 X 10 <sup>-8</sup>
18			<b>1c</b>	2.82 X 10 <sup>-8</sup>	a	4.56 X 10 <sup>-8</sup>

Reported values carry an error of  $\pm 5\%$ . <sup>a</sup> The compound did not racemize even after 60 days, hence data not provided. <sup>b</sup> above the boiling point of the solvent, hence racemization kinetics were not performed.

## 6. PHOTOPHYSICAL STUDIES ON NON-BIARYL ATROPISOMERIC 3,4-DIHYDRO-2-PYRIDONE **1a-c**

The photophysical studies on 3,4-dihydro-2-pyridone **1a-c** were carried out in two spectrometric grade solvents *viz* ethanol (EtOH) and methylcyclohexane (MCH). The standard reference for fluorescence quantum yield was phenol in water ( $\phi_r = 0.14$ ) and the fluorescence quantum yield was calculated using the following equation,<sup>10</sup>

$$\phi_s = \phi_r (I_s/I_r)(A_r/A_s)(\eta_s^2/\eta_r^2)$$

Where,

$\phi_s$  is the fluorescence quantum yield of the sample **1a-c**,

$\phi_r$  is the fluorescence quantum yield for the reference solution (i.e. phenol in water),

$I_s$  is the fluorescence intensity of the sample **1a-c**,

$I_r$  is the fluorescence intensity of the reference solution (phenol in water),

$A_s$  is the absorbance value of the sample **1a-c**,

$A_r$  is the absorbance value of the reference solution (phenol in water),

$\eta_s$  is the refractive index of the solvent (ethanol = 1.361 and MCH = 1.422) for the sample **1a-c**, and

$\eta_r$  is the refractive index of the solvent (water = 1.333) for the reference (phenol in water).

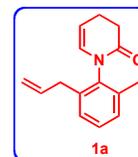
### 6.1 EMISSION MEASUREMENTS OF 3,4-DIHYDRO-2-PYRIDONE **1a**.

The following parameters were maintained during Fluorescence acquisition.

Excitation slit-width = 1 nm; Emission slit-width = 2 nm;

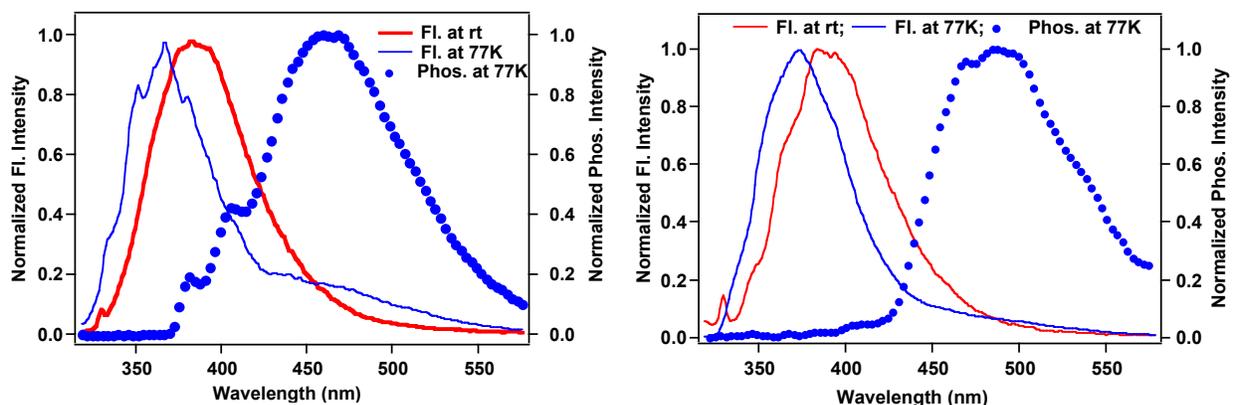
Integration time = 0.1 sec; Wavelength increment = 1 nm;

The fluorescence quantum yield ( $\phi_f$ ) of **1a** was ~ 0.094 in EtOH and ~ 0.103 in MCH.



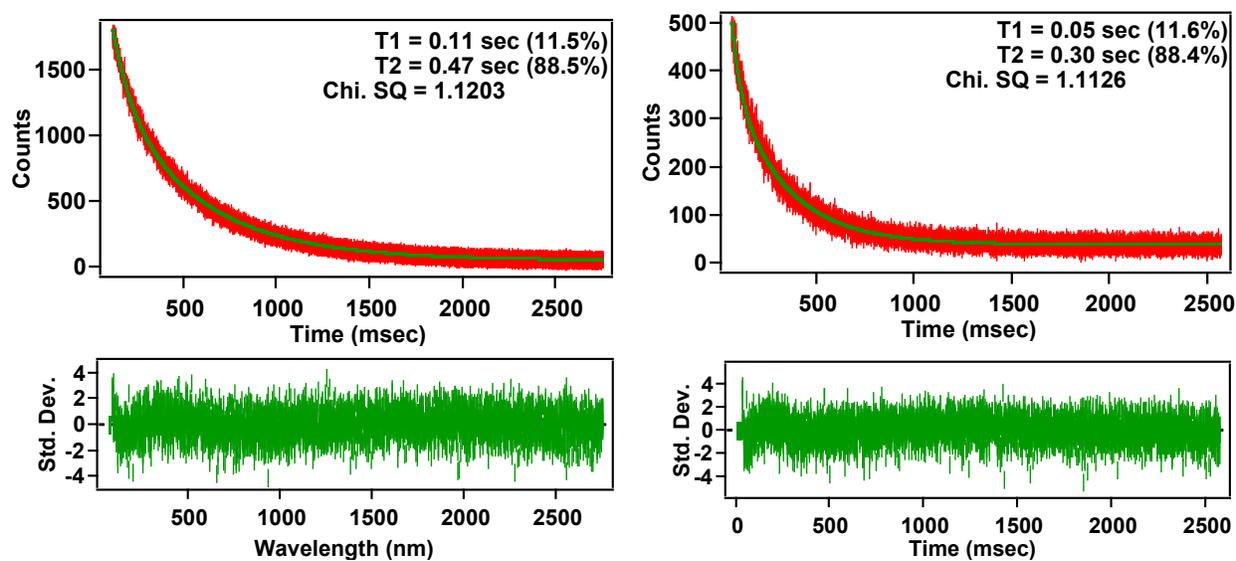
The phosphorescence spectra were recorded at 77 K in EtOH and MCH glass. The following parameters were employed during acquisition:

Excitation: 298 nm for EtOH and 299 nm for MCH; emission: 318-576 nm for EtOH and 319-578 nm for MCH; excitation slit-width: 5 nm; emission slit-width: 8 nm; time per flash: 3000 msec for EtOH and 2500 msec for MCH; flash per count: 10, delay time: 100 msec; wavelength increment: 3 nm; sample window: 2500 msec for EtOH and 2000 msec for MCH.



**Figure S3:** Fluorescence at room temperature (—), fluorescence at 77 K (—) and phosphorescence at 77 K (•) for **1a** recorded in EtOH (left) and MCH (right) ( $c \sim 1.03 \times 10^{-3}$  M).

The phosphorescence decay profiles were recorded at 77 K in EtOH and MCH using a PhosLamp with a trigger pulse delay of 1%. The sample in EtOH was excited at 298 nm and the emission was monitored at 462 nm. The sample in MCH was excited at 299 nm and the emission was monitored at 491 nm. Following parameters were maintained during acquisition: Excitation slit-width = 5 nm; emission slit-width = 8 nm; time (phosphorescence) range = 2.8 sec; number of sweeps = 200.



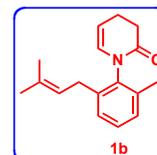
**Figure S4:** Phosphorescence decay profile of **1a** in EtOH (left) and MCH (right) at 77 K ( $c \sim 1.03 \times 10^{-3}$  M).

## 6.2 EMISSION MEASUREMENTS OF 3,4-DIHYDRO-2-PYRIDONE **1b**.

The following parameters were maintained during Fluorescence acquisition.

Excitation slit-width = 1 nm; Emission slit-width = 2 nm;

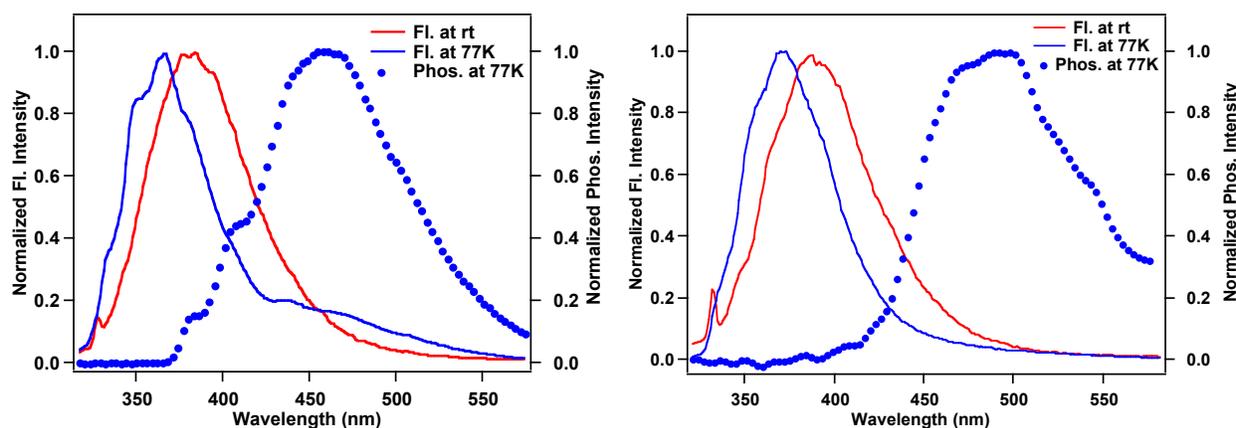
Integration time = 0.1 sec; Wavelength increment = 1 nm;



The fluorescence quantum yield ( $\phi_f$ ) of **1b** was  $\sim 0.057$  in EtOH and  $\sim 0.067$  in MCH.

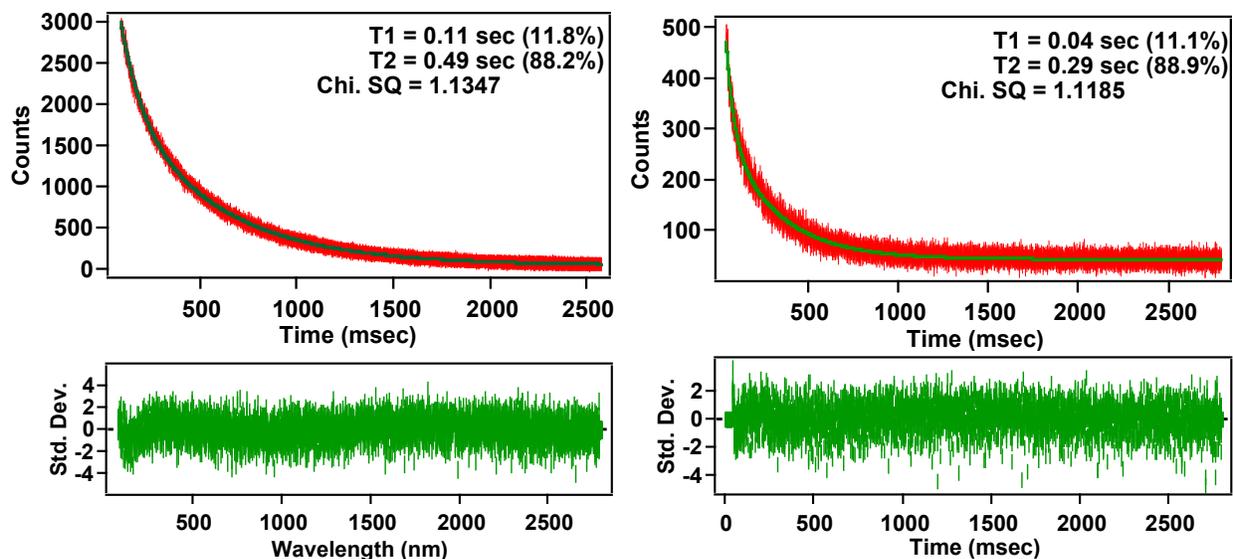
The phosphorescence spectra were recorded at 77 K in EtOH and MCH glass. The following parameters were employed during acquisition:

Excitation: 297 nm for EtOH and 301 nm for MCH; Emission: 317-574 nm for EtOH and 321-582 nm for MCH; excitation slit-width: 5 nm; emission slit-width: 8 nm; time per flash: 3000 msec for EtOH and 2500 msec for MCH; flash per count: 10; delay time: 100 msec; wavelength increment: 3 nm; sample window: 2500 msec for EtOH and 2000 msec for MCH.



**Figure S5:** Fluorescence at room temperature (—), fluorescence at 77 K (—) and phosphorescence at 77 K (•) for **1b** recorded in EtOH (left) and MCH (right) ( $c \sim 9.13 \times 10^{-4}$  M).

The phosphorescence decay profiles were recorded at 77 K in EtOH and MCH using a PhosLamp with a trigger pulse delay of 1%. The sample in EtOH was excited at 297 nm and the emission was monitored at 460 nm. The sample in MCH was excited at 301 nm and the emission was monitored at 488 nm. Following parameters were maintained during acquisition: Excitation slit-width = 5 nm; emission slit-width = 8 nm; time (phosphorescence) range = 2.8 sec; number of sweeps = 200.



**Figure S6:** Phosphorescence decay profile of **1c** in EtOH (left) and MCH (right) at 77 K ( $c \sim 9.13 \times 10^{-4}$  M).

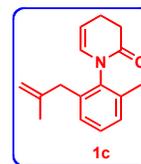
### 6.3 EMISSION MEASUREMENTS OF 3,4-DIHYDRO-2-PYRIDONE **1c**.

The following parameters were maintained during Fluorescence acquisition.

Excitation slit-width = 1nm; Emission Slit-width = 2 nm;

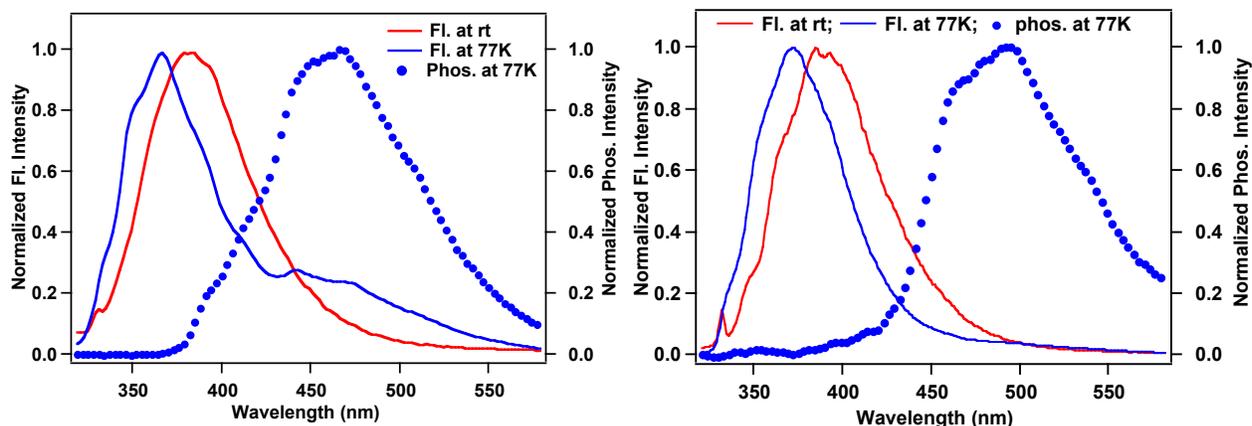
Integration time = 0.1 sec; Wavelength increment = 1 nm;

The fluorescence quantum yield ( $\phi_f$ ) of **1c** was  $\sim 0.082$  in EtOH and  $\sim 0.098$  in MCH.



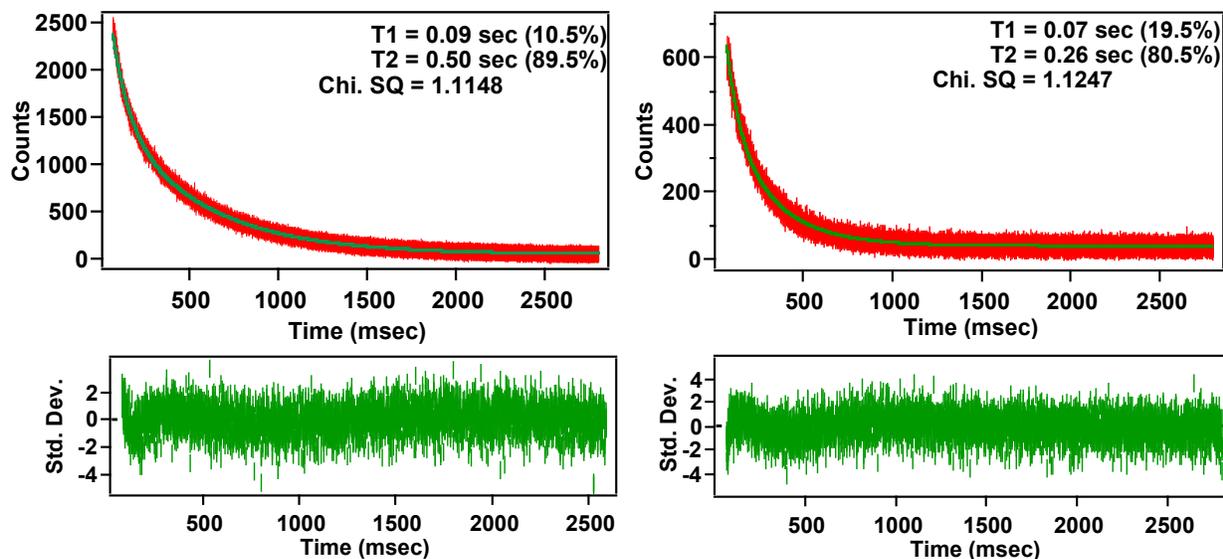
The phosphorescence spectra were recorded at 77 K in EtOH and MCH glass. The following parameters were employed during acquisition:

Excitation: 297 nm for EtOH and 301 nm for MCH; Emission: 317-574 nm for EtOH and 321-582 nm for MCH; excitation slit-width: 5 nm; emission slit-width: 8 nm; time per flash: 3000 msec for EtOH and 2500 msec for MCH; flash per count: 10, delay time: 100 msec; wavelength increment: 3 nm; sample window: 2500 msec for EtOH and 2000 msec for MCH.



**Figure S7:** Fluorescence at room temperature (—), fluorescence at 77 K (—) and phosphorescence at 77 K (•) for **1c** recorded in EtOH (left) and MCH (right) ( $c \sim 9.13 \times 10^{-4}$  M).

The phosphorescence decay profiles were recorded at 77 K in EtOH and MCH using a PhosLamp with a trigger pulse delay of 1%. The sample in EtOH was excited at 297 nm and the emission was monitored at 467 nm. The sample in MCH was excited at 301 nm and the emission was monitored at 492 nm. Following parameters were maintained during acquisition: Excitation slit-width = 5 nm; emission slit-width = 8 nm; time (phosphorescence) range = 2.8 sec; number of sweeps = 200.



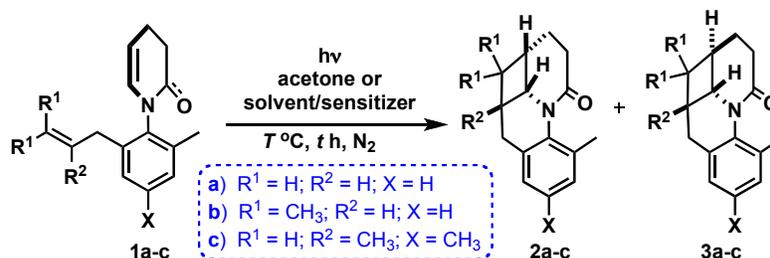
**Figure S8:** Phosphorescence decay profile of **1c** in EtOH (left) and MCH (right) at 77 K ( $c \sim 9.13 \times 10^{-4}$  M).

**Table S2:** Fluorescence quantum yield, phosphorescence lifetime and triplet energy of atropchiral 3,4-dihydro-2-pyridones **1a-c** in ethanol and methylcyclohexane.

Entry	Compd	Solvent	Fluorescence quantum yield ( $\phi_f$ )	Phosphorescence life time (sec)	Triplet energy (kcal.mol <sup>-1</sup> )
1	<b>1a</b>	EtOH	~ 0.094	~ 0.47	~ 73.88
2		MCH	~ 0.103	~ 0.30	~ 72.56
3	<b>1b</b>	EtOH	~ 0.057	~ 0.49	~ 74.07
4		MCH	~ 0.067	~ 0.29	~ 73.3
5	<b>1c</b>	EtOH	~ 0.082	~ 0.50	~ 75.44
6		MCH	~ 0.098	~ 0.26	~ 73.88

## 7. GENERAL IRRADIATION PROCEDURES AND CHARACTERIZATION OF PHOTOPRODUCTS

### 7A. PROCESS FOR PHOTOREACTION OF 3,4-DIHYDRO-2-PYRIDONES **1a-c**



**Scheme S13:** General irradiation procedure for 3,4-dihydro-2-pyridone **1a-c**

A solution of optically pure atropisomeric 3,4-dihydro-2-pyridones **1a-c** (2.0 mM **1a** and 2.2 mM of **1b-c**) in acetone or with the combination of methanol and the sensitizer (xanthone or acetophenone) were irradiated at -30 °C for a given time interval in Pyrex tube with a 450 W medium-pressure mercury lamp under constant flow of nitrogen. After irradiation, the solvent was evaporated under reduced pressure and the photoproducts were isolated by preparative thin layer chromatography and characterized by NMR spectroscopy, mass spectrometry, single crystal XRD, CD,  $[\alpha]_D$  and by HPLC. HPLC analysis of the photolysate on chiral stationary phases gave the optical purity of the photoproducts.

### 7B. CONVERSION AND MASS BALANCE AFTER PHOTOREACTIONS IN 3,4-DIHYDRO-2-PYRIDONES

Conversion and mass balance was obtained by irradiating the racemic mixture of 3,4-dihydro-2-pyridones (2.23 mM for **1a** and 1.95 mM **1b-c**) in acetone or with the combination of methanol and the sensitizer (xanthone or acetophenone) in Pyrex test tube with a 450 W medium-pressure mercury lamp for given time interval and temperature under constant flow of

nitrogen. After irradiation, a stock solution of internal standard in chloroform (triphenylmethane, 4.09 mM) was added to the reaction mixture. The solvent from the mixture with the internal standard was completely evaporated under reduced pressure. The residue was dissolved in 1 mL of deuterated chloroform and <sup>1</sup>H-NMR was recorded. From the integral value of respective peaks, the % conversion and mass balance was calculated using the formula given below.

$$\text{mol}_a = \text{mol}_i \times \left( \frac{\text{Integral (analyte)}}{\text{Integral (Int.Std)}} \right) \times \frac{N_i}{N_a}$$

Where,  $N_a$  and  $N_i$  are the number of nuclei giving rise to the relevant analyte and internal standard signals respectively. Similarly  $\text{mol}_a$  and  $\text{mol}_i$  are the molarity of analyte and the internal standard in deuterated chloroform respectively.

**Table S3:** Conversion and mass balance<sup>a</sup> in photoreactions of 3,4-dihydro-2-pyridones **1a-c**.

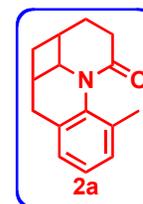
Entry	Compd	Solvent	Sensitizer	t (°C)	Time (h)	(%) Convn	(%) MB
1	<b>1a</b>	Acetone	Acetone	-30	3	70	96 <sup>b</sup>
2		Methanol	xanthone	-30	3	76	89
3		Methanol	Acetophenone	-30	3	29	92
4	<b>1b</b>	Acetone	Acetone	-30	24	39	79
5		Methanol	xanthone	-30	3	21	82
6		Methanol	Acetophenone	-30	12	20	87
7	<b>1c</b>	Acetone	Acetone	25	2.5	90	77
8		Methanol	xanthone	25	2.5	92	84
9		Methanol	Acetophenone	25	12	33	86

<sup>a</sup> Reported values carry an error of ±5%. <sup>b</sup> 8-10 % of uncharacterized impurity was observed in case of **1a** and **1c**. Convn – conversion; MB- mass balance. Longer irradiation of xanthone sensitizer leads to decomposition, so the irradiation time was limited to 3 h.

While the ee values in the photoproducts remained the same at both -30 °C and at 25 °C, the conversion and mass balance of the photoreaction was affected significantly. For compounds **1a-b**, the reactions at 25 °C showed good conversion with poor mass balance. On the other hand, at -30 °C there was excellent mass balance and conversion. In the case of **1c** the uncharacterized side product was higher at -30 °C than the photoproduct. But at -30 °C the uncharacterized side product was less than 8%. Prolonged irradiation after consumption of the reactants **1a-c** (>80% conversion) led to decomposition.

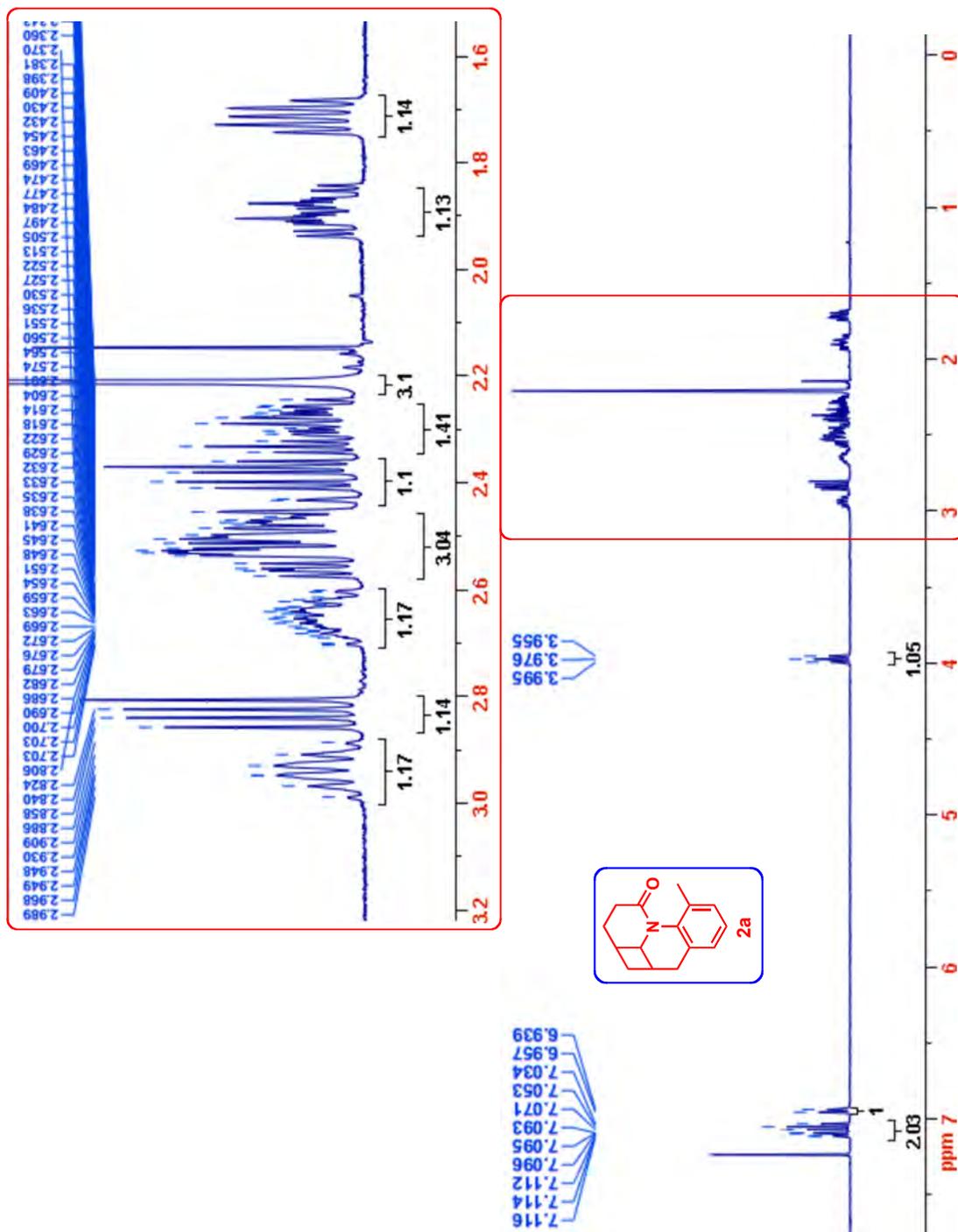
#### 7C. CHARACTERIZATION OF PHOTOPRODUCT **2a**

The title compound was purified by preparative thin layer chromatography using solvents hexanes:ethyl acetate mixture (50:50) as the mobile phase.

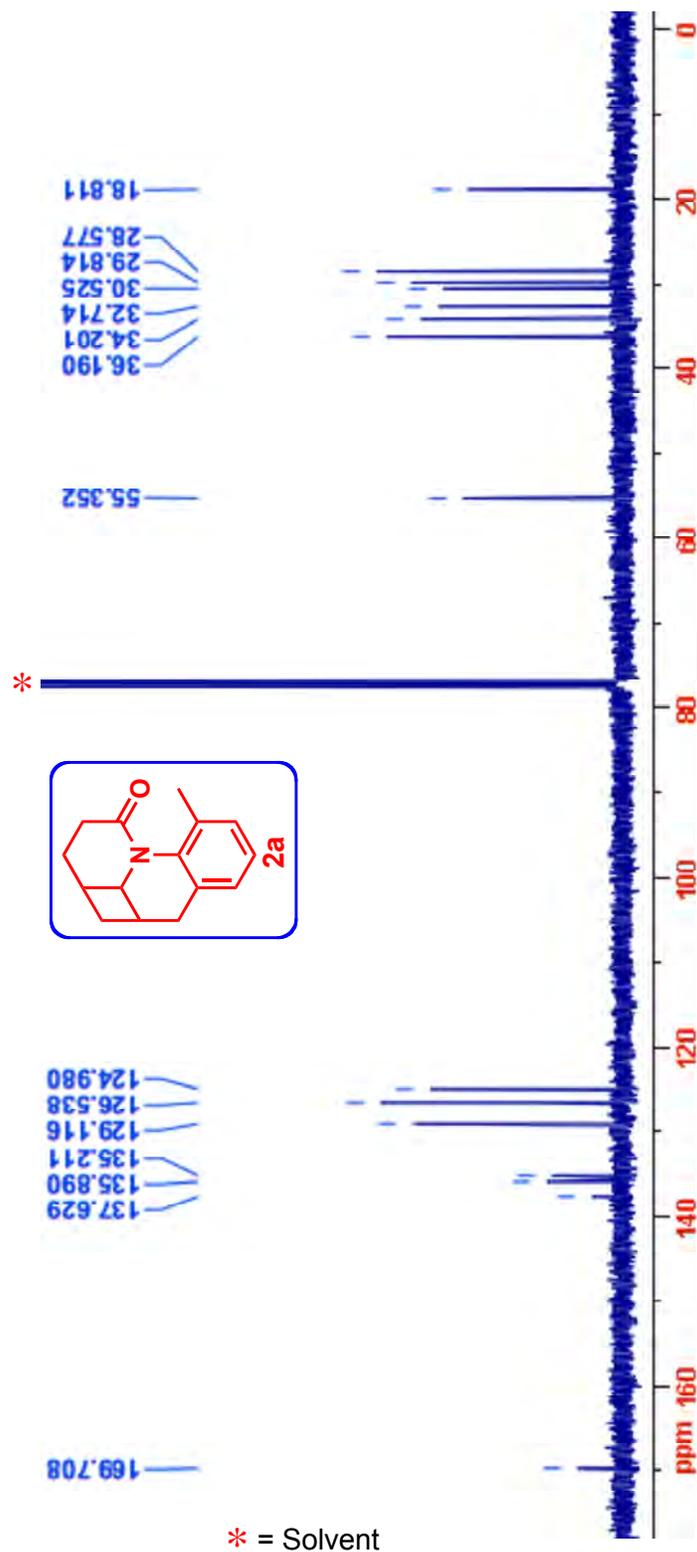


$R_f = 0.40$  (50% hexanes:50% ethyl acetate).

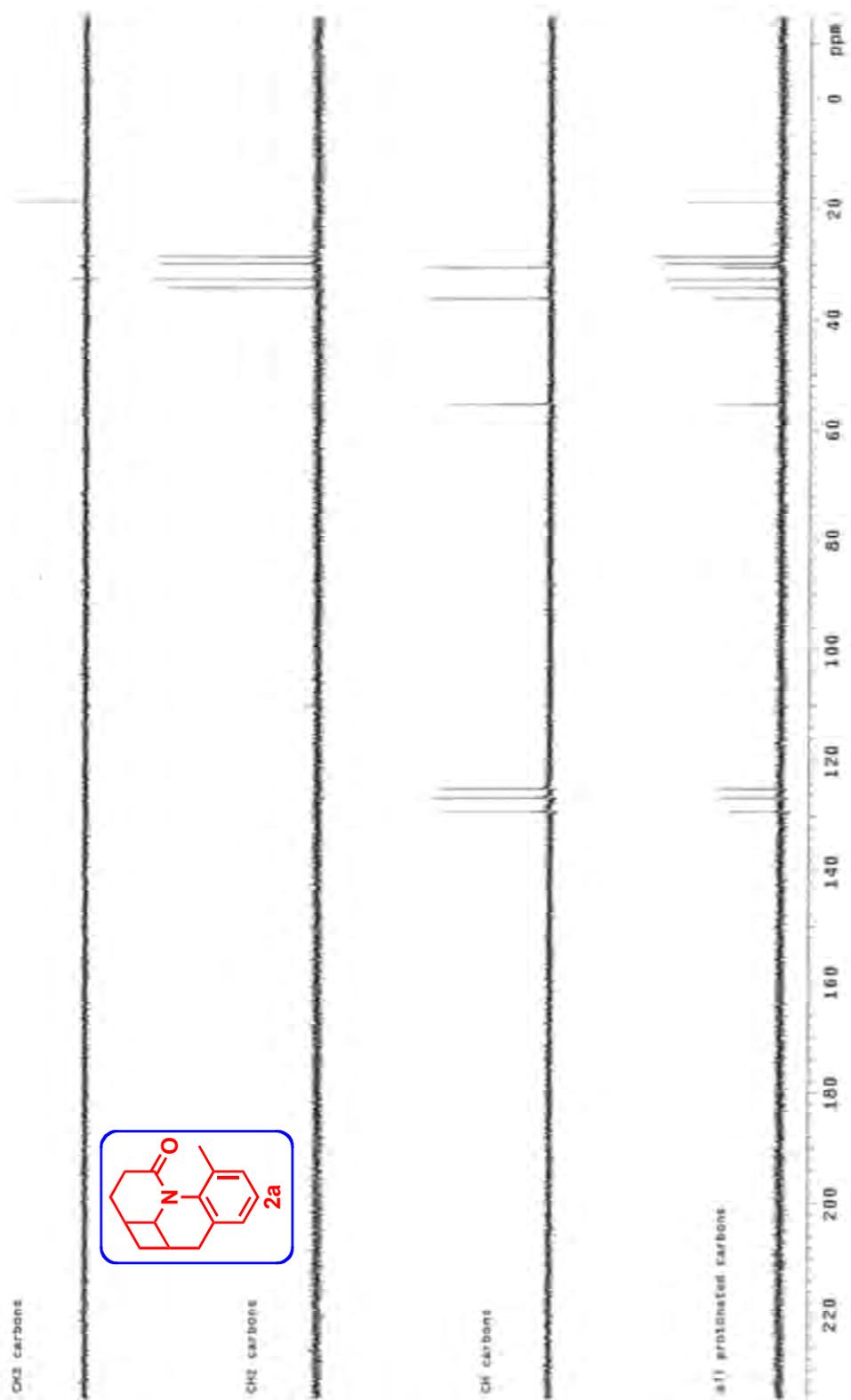
$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.12 – 7.03 (m, 2H), 6.96 – 6.94 (m, 1H), 3.99 – 3.96 (t,  $J = 8.4$  Hz, 1H), 2.99 – 2.89 (m, 1H), 2.86 – 2.81 (m, 1H), 2.70 – 2.60 (m, 1H), 2.57 – 2.45 (m, 3H), 2.43 – 2.36 (m, 1H), 2.34 – 2.24 (m, 1H), 2.21 (s, 3H), 1.94 – 1.84 (m, 1H) and 1.74 – 1.68 (m, 1H).



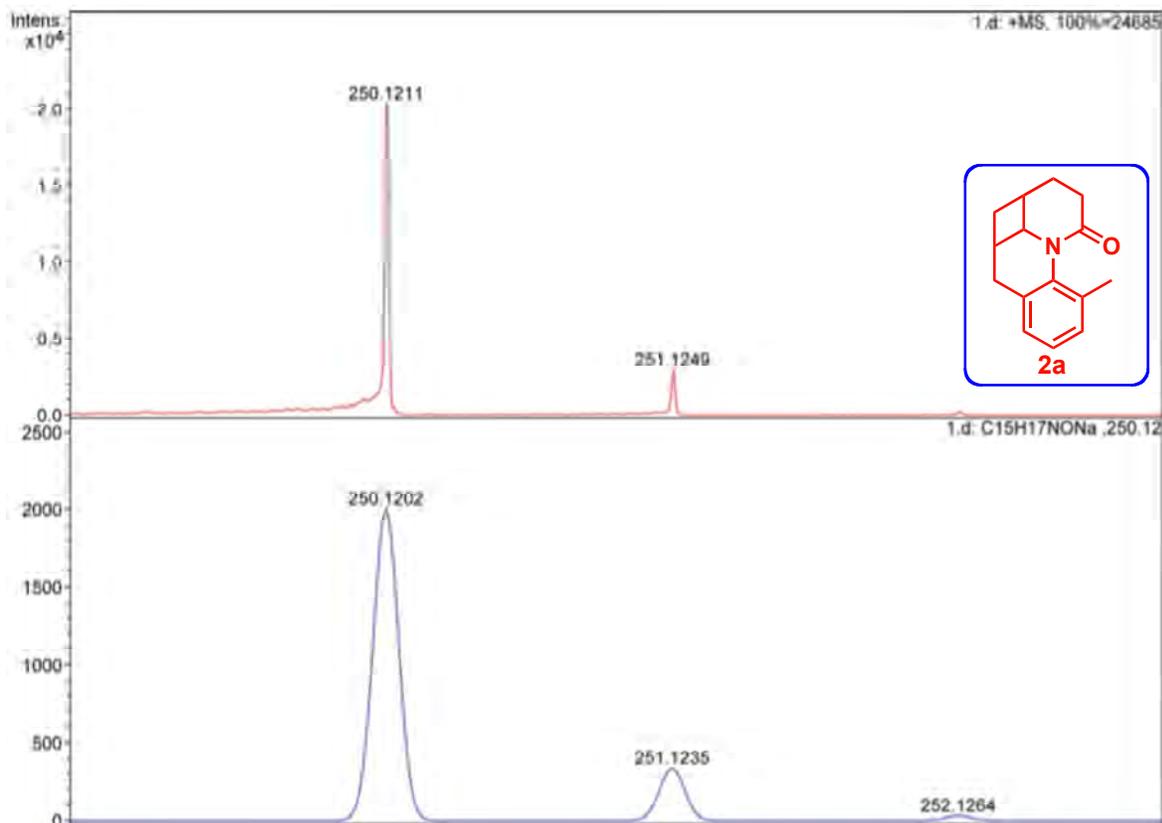
$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 169.7, 137.6, 135.9, 135.2, 129.1, 126.5, 124.98, 55.3, 36.2, 34.2, 32.7, 30.5, 29.8, 28.6 and 18.8.



$^{13}\text{C}$  DEPT Spectra:



HRMS-ESI ( $m/z$ ) ( $[M + Na]^+$ ):  
Calculated : 250.1202  
Observed : 250.1211  
 $|\Delta m|$  : 3.6 ppm



HPLC analysis conditions:

For analytical conditions,

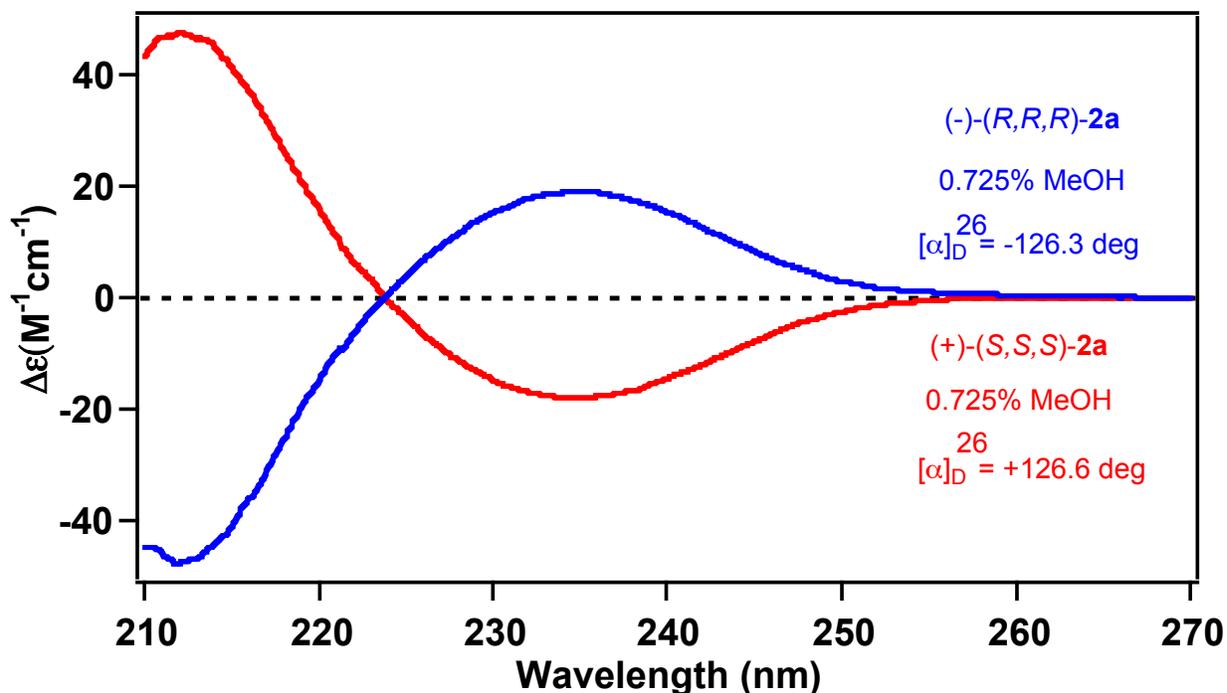
- l). Column : RR-WHELK-01 10/100 FEC
- Abs. detector wavelength : 254 nm and 270 nm
- Mobile phase : Hexanes:2-propanol = 80:20
- Flow rate : 1.0 mL/min
- Retention times (min) : ~ 19.20 [(+)-(S,S,S)-2a] and ~ 34.63 [(-)-(R,R,R)-2a]

Compound **2a**: Optical Rotation  $[\alpha]_D^{26}$  :

HPLC retention time (RR-WHELK-01 10/100 FEC) at ~ 19.20 min, (c = 0.725%, MeOH) = +126.6 deg.

HPLC retention time (RR-WHELK-01 10/100 FEC) at ~ 34.63 min, (c = 0.725%, MeOH) = -126.3 deg.

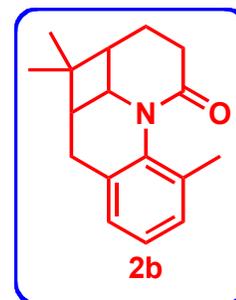
The CD spectra was measured in methanol (concentration: 0.048 mM)



#### 7D. CHARACTERIZATION OF PHOTOPRODUCT **2b**

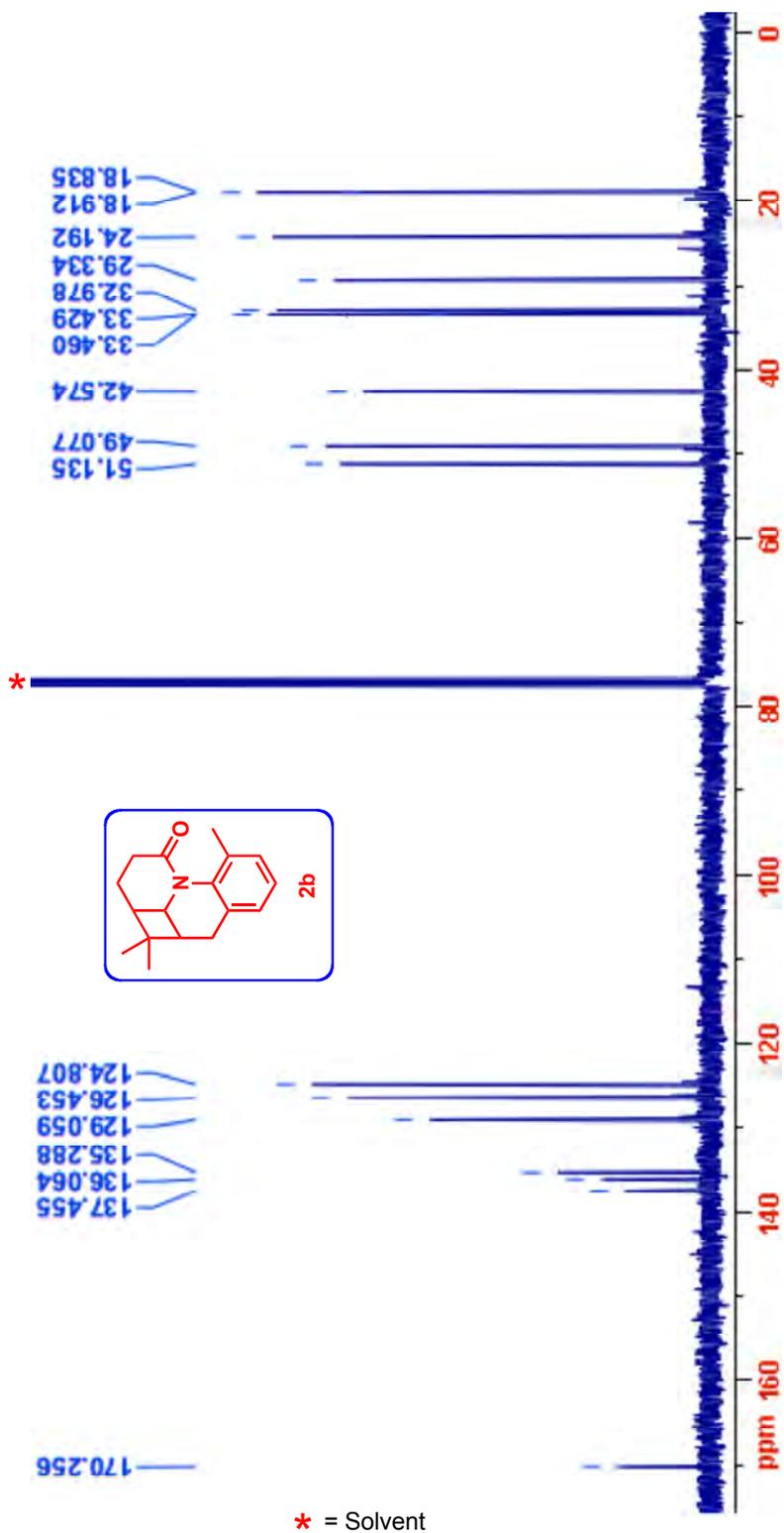
The title compound was purified by preparative thin layer chromatography using solvents hexanes:ethyl acetate mixture (50:50) as the mobile phase.

$R_f = 0.35$  (50% hexanes:50% ethyl acetate).

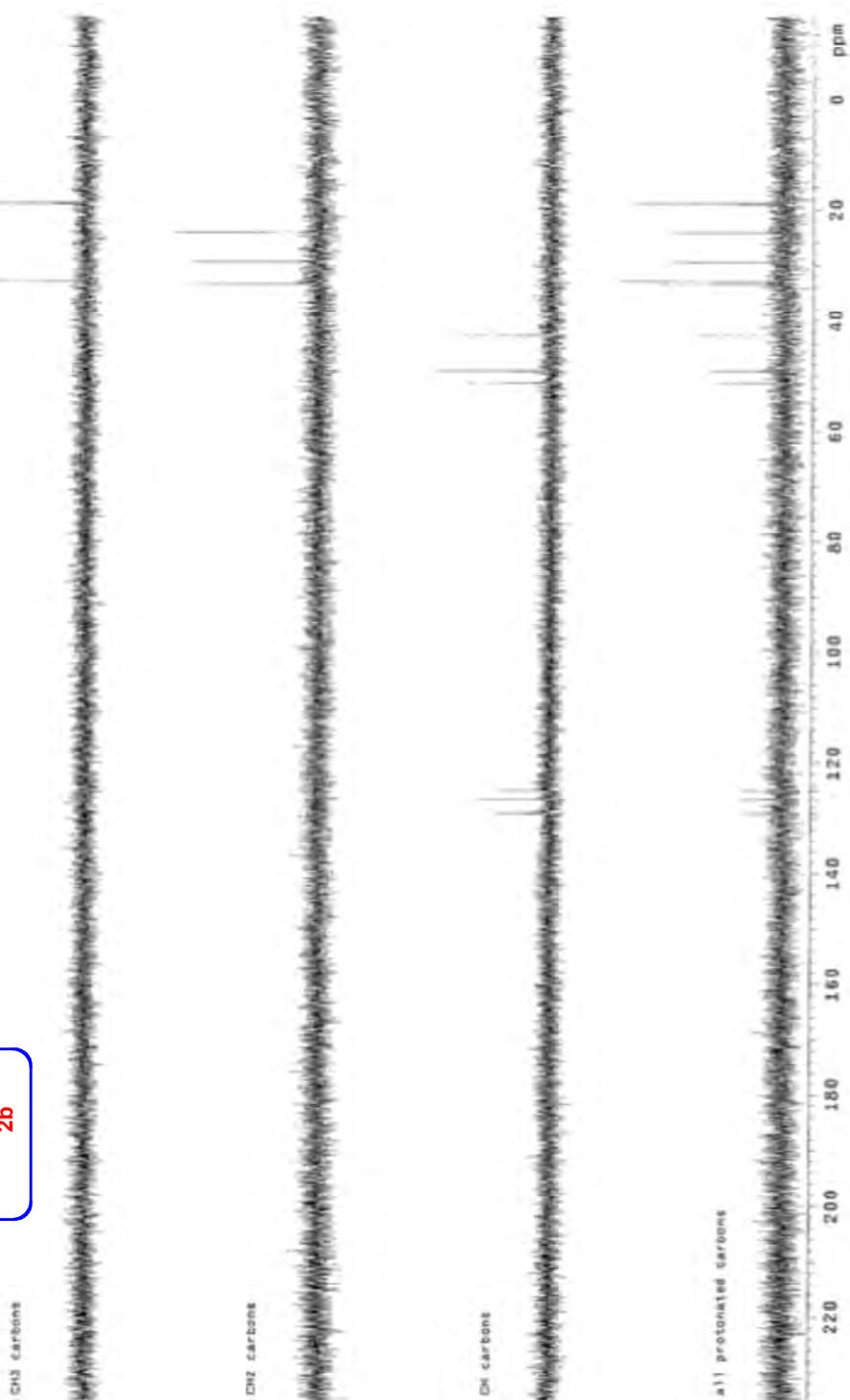
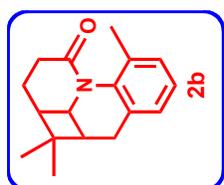




$^{13}\text{C}$ -NMR 100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 170.2, 137.4, 136.1, 135.3, 129.0, 126.4, 124.8, 51.1, 49.1, 42.6, 33.5, 33.4, 32.97, 29.3, 24.2, 18.9 and 18.8.



$^{13}\text{C}$  DEPT Spectra:

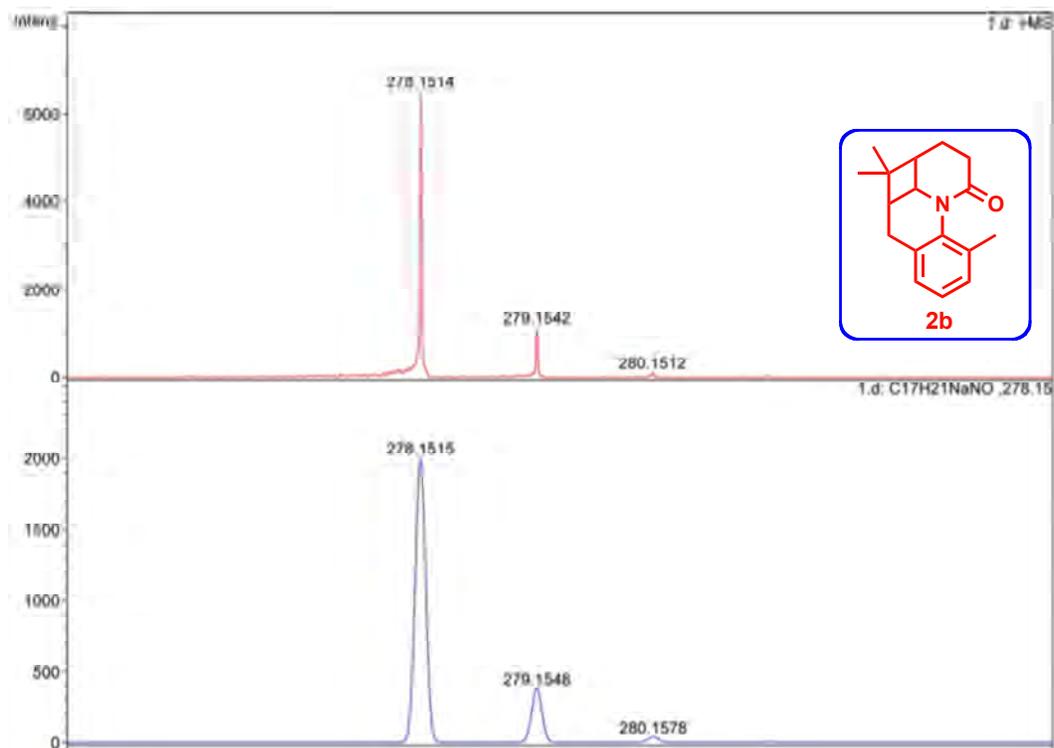


HRMS-ESI ( $m/z$ ) ( $[M + Na]^+$ ):

Calculated : 278.1515

Observed : 278.1514

$|\Delta m|$  : 0.4 ppm



HPLC analysis conditions:

For analytical conditions,

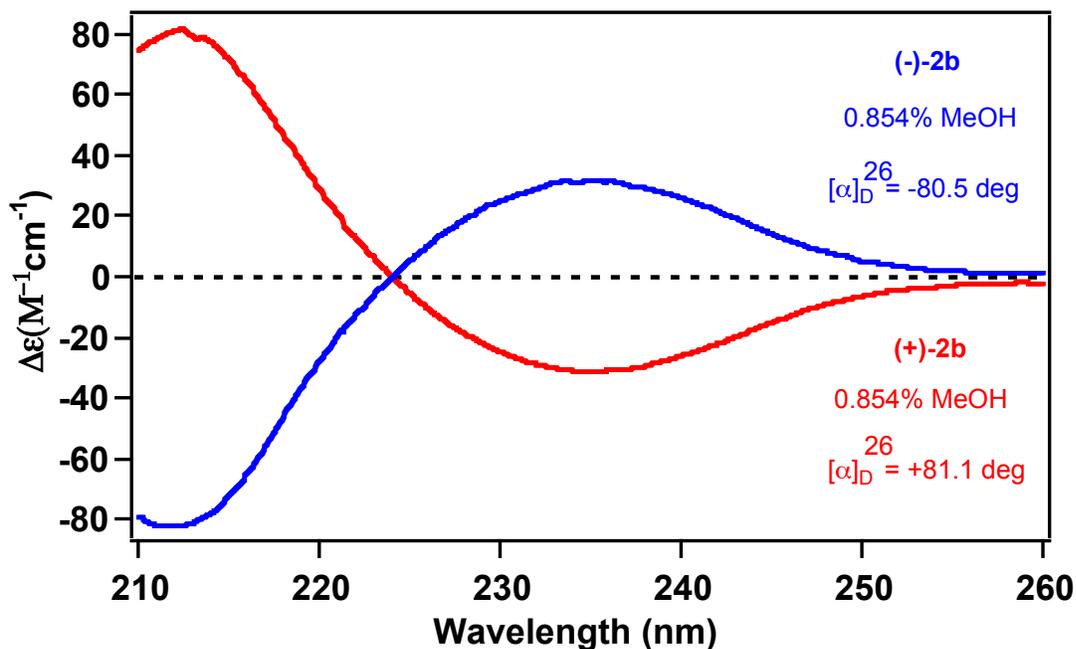
- I). Column : CHIRALPACK® IC
- Abs. detector wavelength : 254 nm and 270 nm
- Mobile phase : Hexanes:2-propanol = 95:5
- Flow rate : 1.0 mL/min
- Retention times (min) : ~ 55.32 [(+)-**2b**] and ~ 57.64 [(-)-**2b**]

Compound **2b**: Optical Rotation  $[\alpha]_D^{26}$  :

HPLC retention time (CHIRALPACK<sup>®</sup> IC) at ~ 55.32 min, (c = 0.854%, MeOH) = +81.1 deg

HPLC retention time (CHIRALPACK<sup>®</sup> IC) at ~ 57.64 min, (c = 0.854%, MeOH) = -80.5 deg.

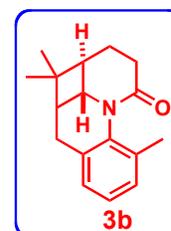
The CD spectra was measured in methanol (concentration: 0.035 mM)



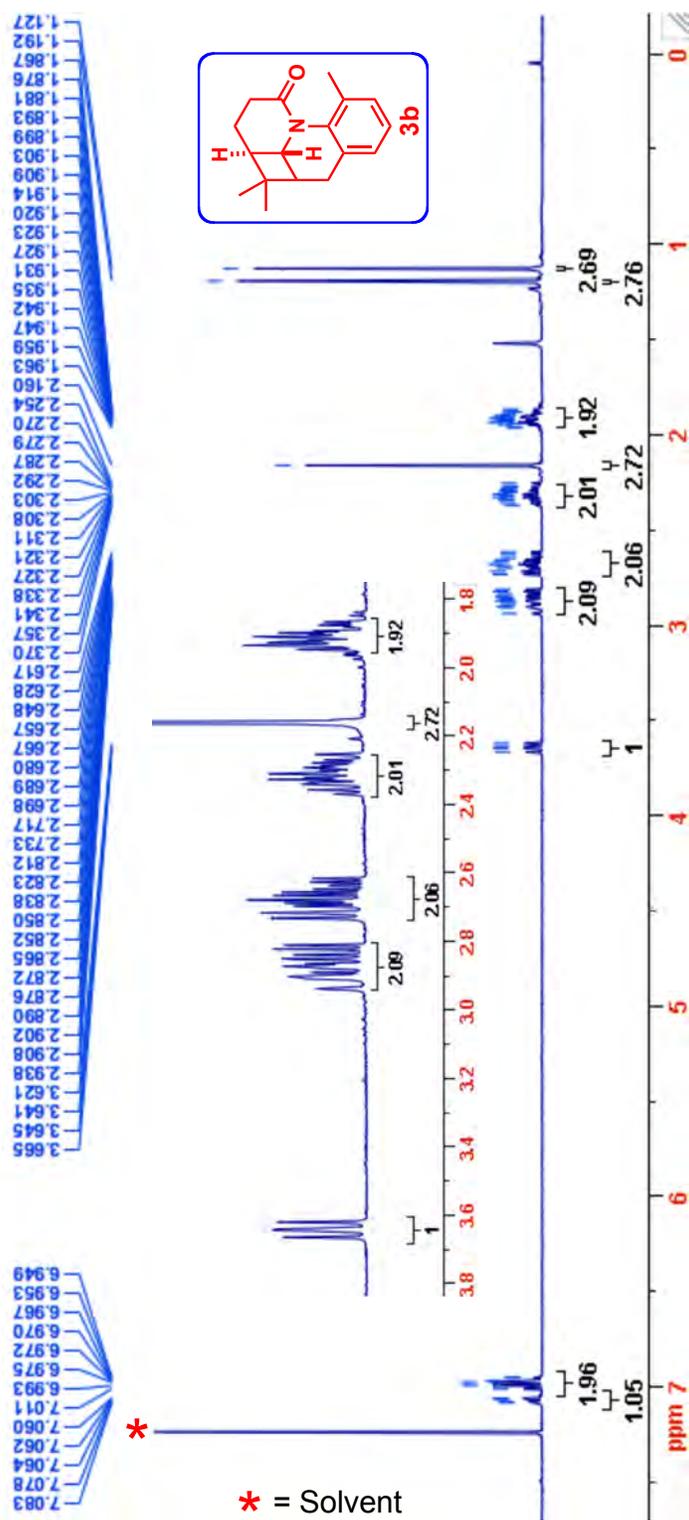
#### 7E. CHARACTERIZATION OF PHOTOPRODUCT **3b**

The title compound was purified by preparative thin layer chromatography using solvents hexanes:ethyl acetate mixture (50:50) as the mobile phase.

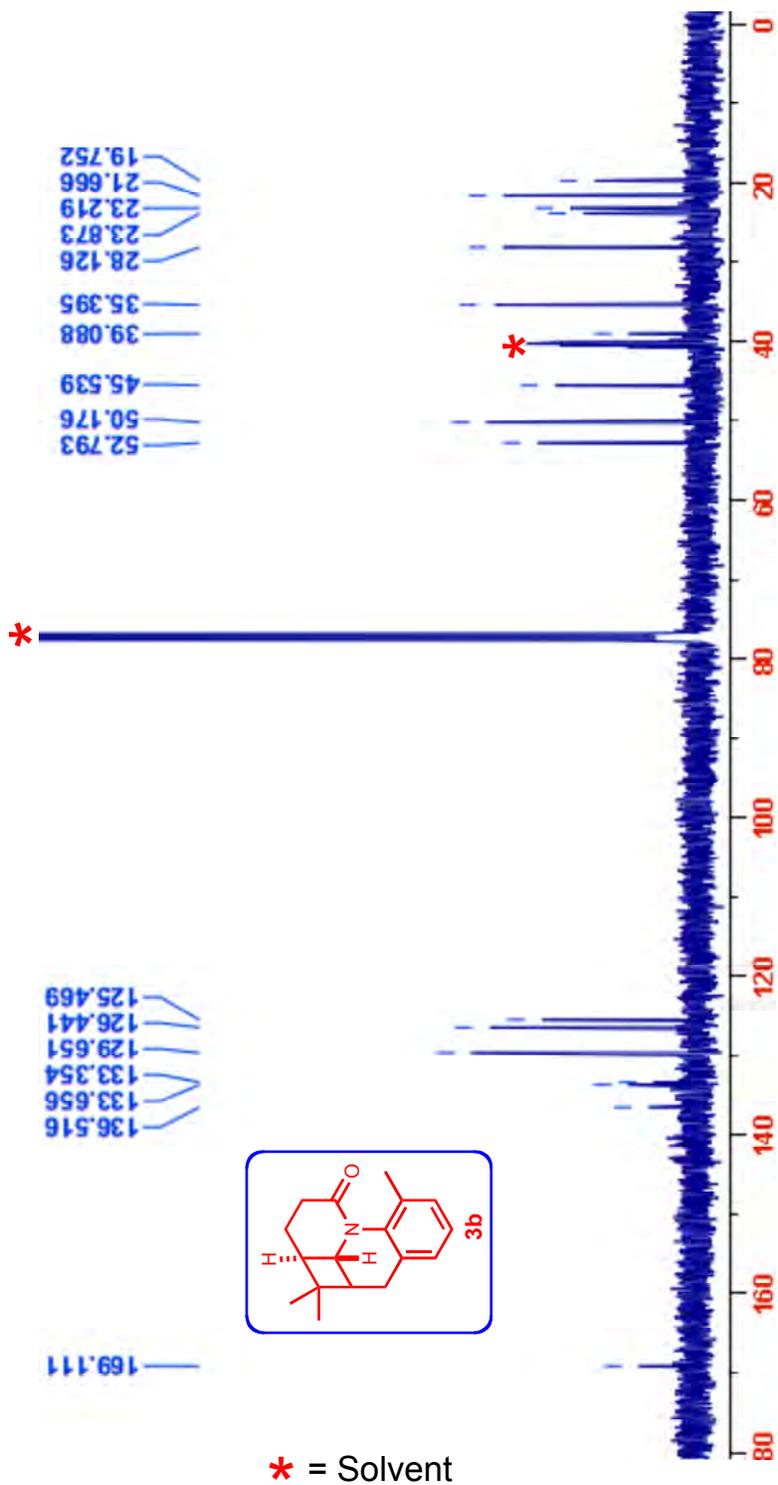
$R_f = 0.55$  (50% hexanes:50% ethyl acetate).



$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.08 - 7.06 (m, 1H), 7.01 - 6.95 (m, 2H), 3.66 - 3.62 (m, 1H), 2.94 - 2.81 (m, 2H), 2.73 - 2.62 (m, 2H), 2.37 - 2.25 (m, 2H), 2.16 (s, 3H) 1.96 - 1.84 (m, 2H), 1.19 (s, 3H), 1.13 (s, 3H).



$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$  and DMSO,  $\delta$  ppm): 169.1, 136.5, 133.6, 133.3, 126.6, 126.4, 125.5, 52.8, 50.2, 45.5, 39.1, 35.4, 28.1, 23.9, 23.2, 21.7 and 19.8.

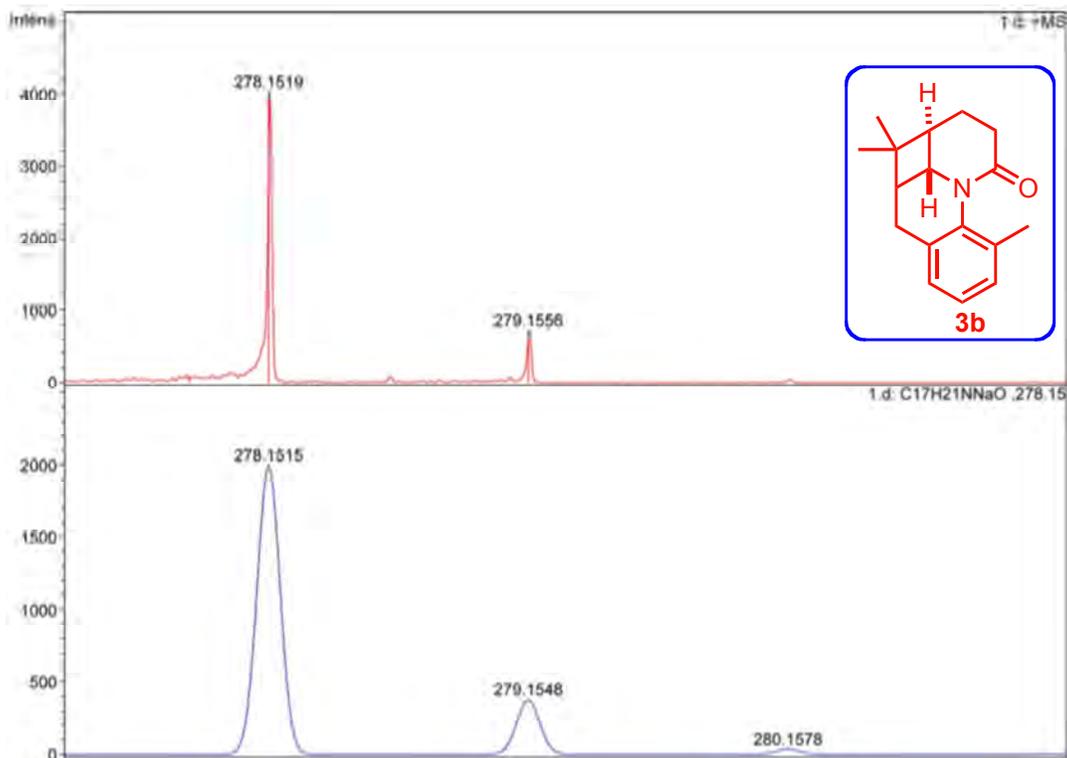


HRMS-ESI ( $m/z$ ) ( $[M + Na]^+$ ):

Calculated : 278.1515

Observed : 278.1519

$|\Delta m|$  : 1.4 ppm



HPLC analysis conditions:

For analytical conditions,

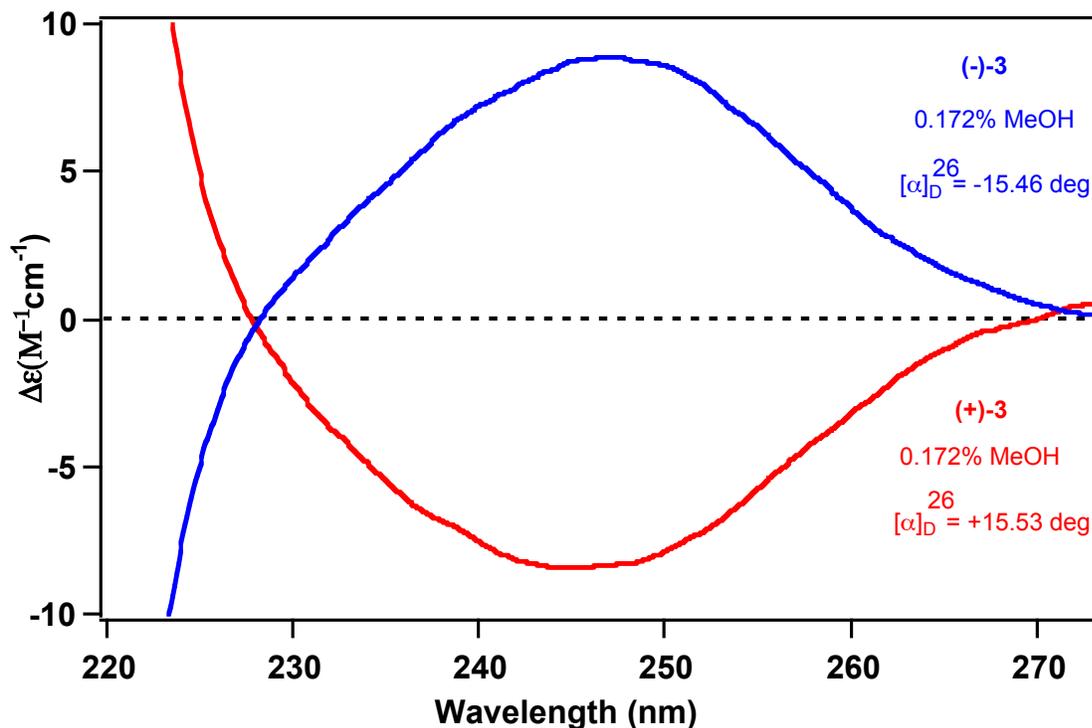
I). Column	: CHIRALPACK® IC
Abs. detector wavelength	: 254 nm and 270 nm
Mobile phase	: Hexanes:2-propanol = 95:5
Flow rate	: 1.0 mL/min
Retention times (min)	: ~ 37.62 [(+)- <b>3b</b> ] and ~ 54.03 [(-)- <b>3b</b> ]

Compound **3b**: Optical Rotation  $[\alpha]_D^{26}$  :

HPLC retention time (CHIRALPACK<sup>®</sup> IC) at ~ 37.62 min, (c = 0.172%, MeOH) = +15.53 deg

HPLC retention time (CHIRALPACK<sup>®</sup> IC) at ~ 57.64 min, (c = 0.172%, MeOH) = -15.46 deg.

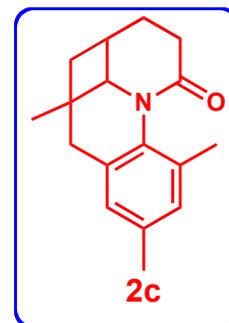
The CD spectra was measured in methanol (concentration: 0.086 mM)



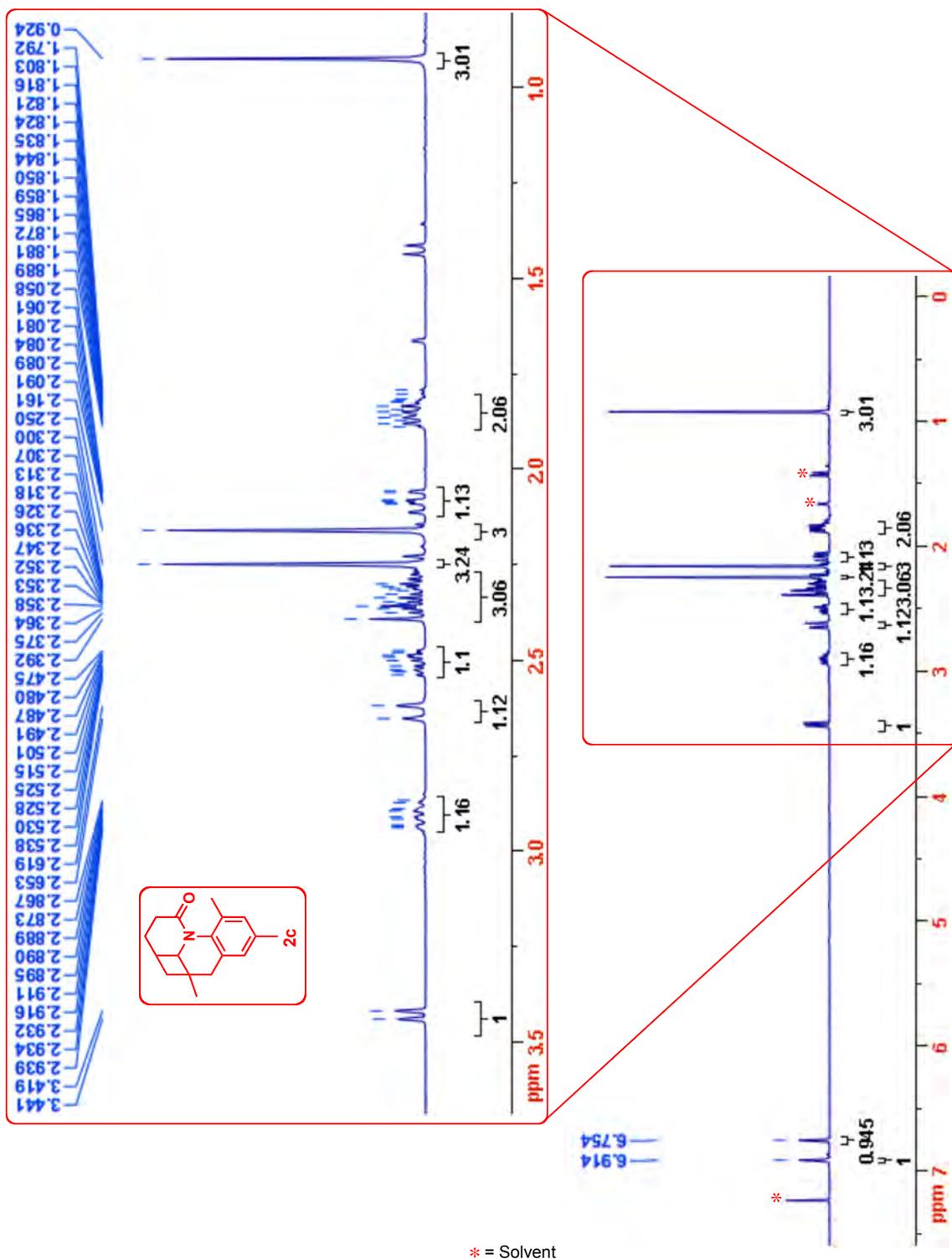
#### 7F. CHARACTERIZATION OF PHOTOPRODUCT **3**

The title compound was purified by preparative thin layer chromatography using solvents hexanes:ethyl acetate mixture (50:50) as the mobile phase.

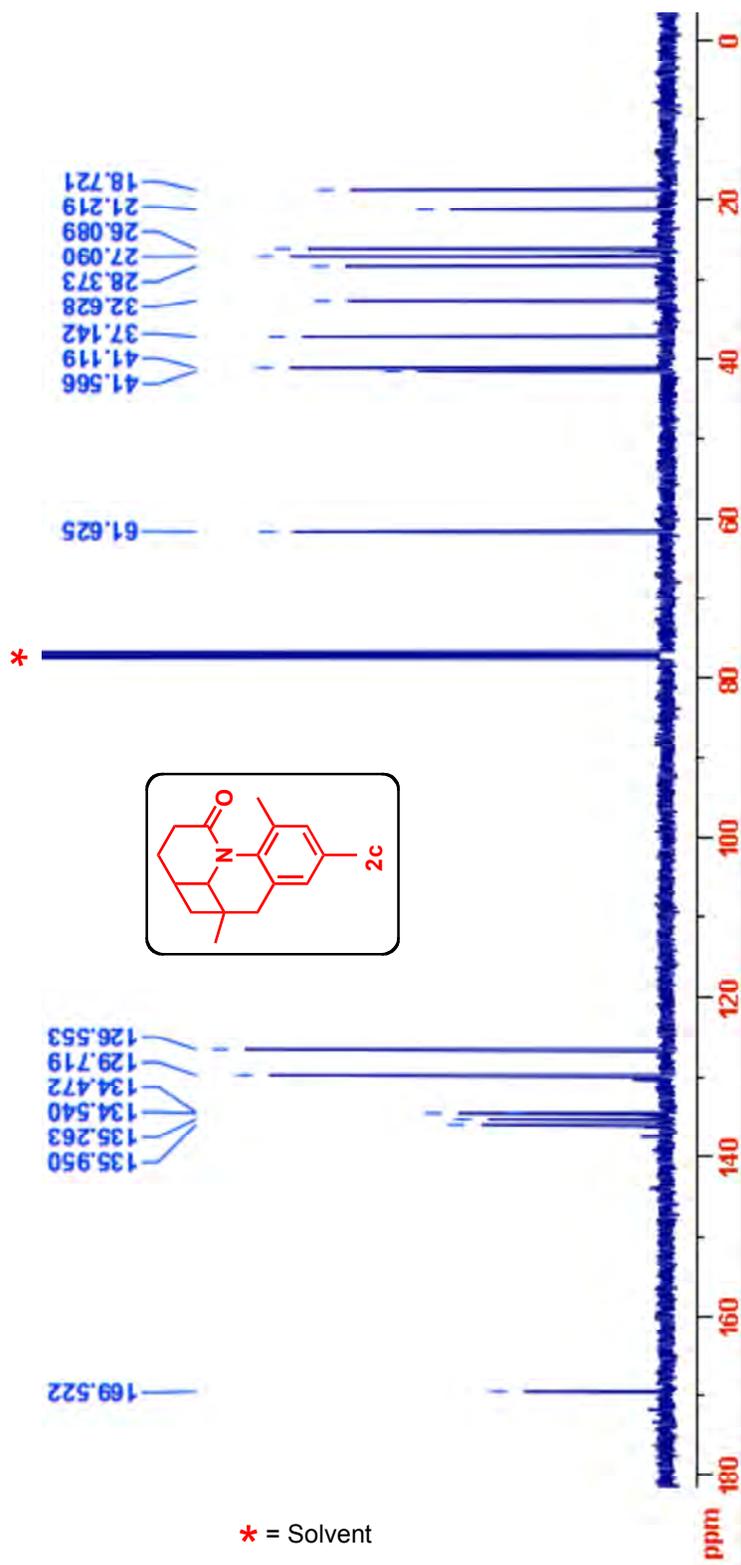
$R_f = 0.50$  (50% hexanes:50% ethyl acetate).



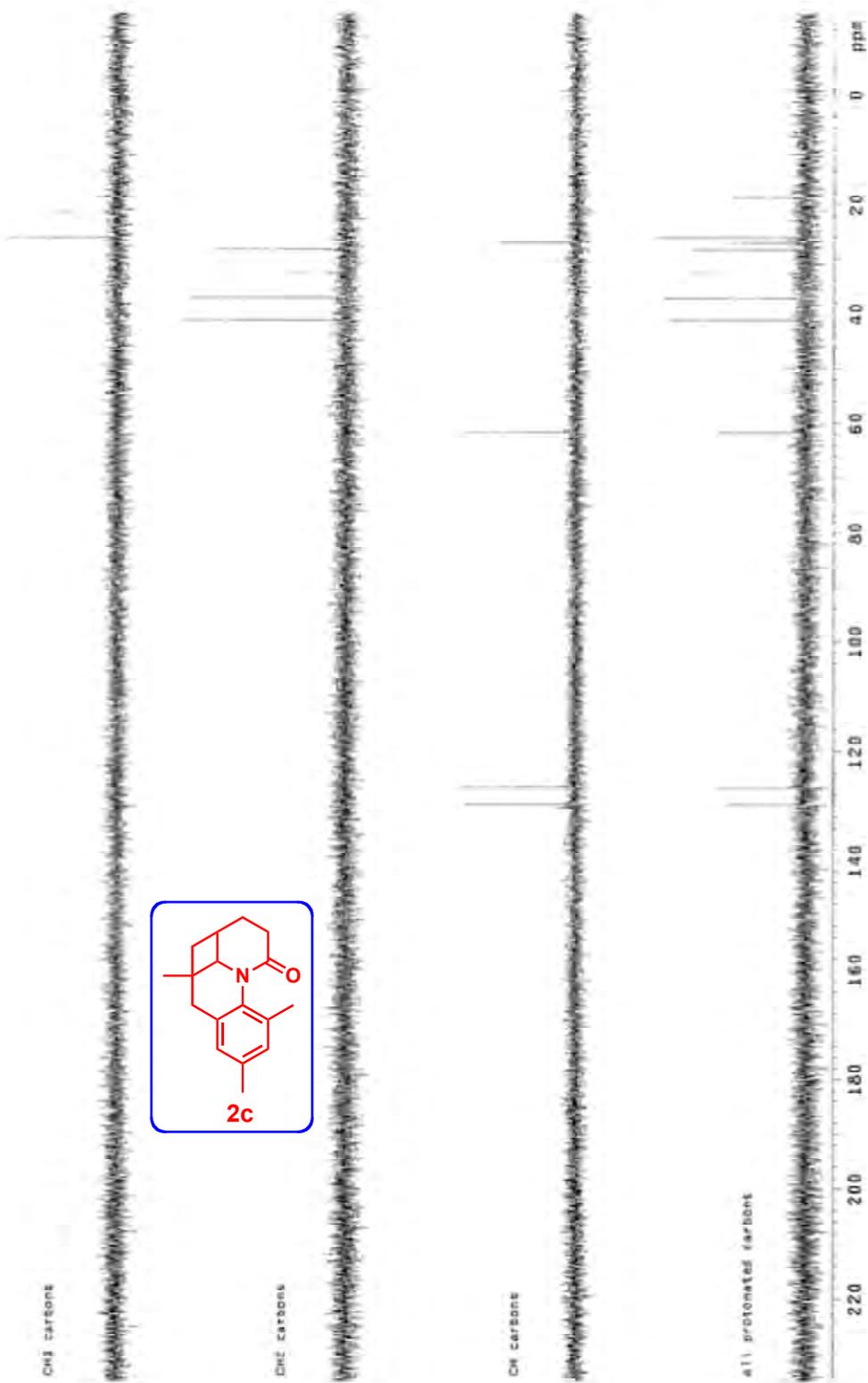
$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 6.92 (s, 1H), 6.75 (s, 1H), 3.44 – 3.42 (d,  $J = 8.4$  Hz, 1H), 2.94 – 2.87 (m, 1H), 2.65 – 2.62 (m, 1H), 2.54 – 2.48 (m, 1H), 2.39 – 2.26 (m, 3H), 2.25 (s, 3H), 2.16 (s, 3H), 2.12 – 2.06 (m, 1H), 1.89 – 1.82 (m, 2H) and 0.93 (s, 3H).



$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 169.5, 135.9, 135.3, 134.5, 134.47, 129.7, 126.5, 61.6, 41.6, 41.1, 37.1, 32.6, 28.4, 27.1, 26.1, 21.2 and 18.7.



$^{13}\text{C}$  DEPT:

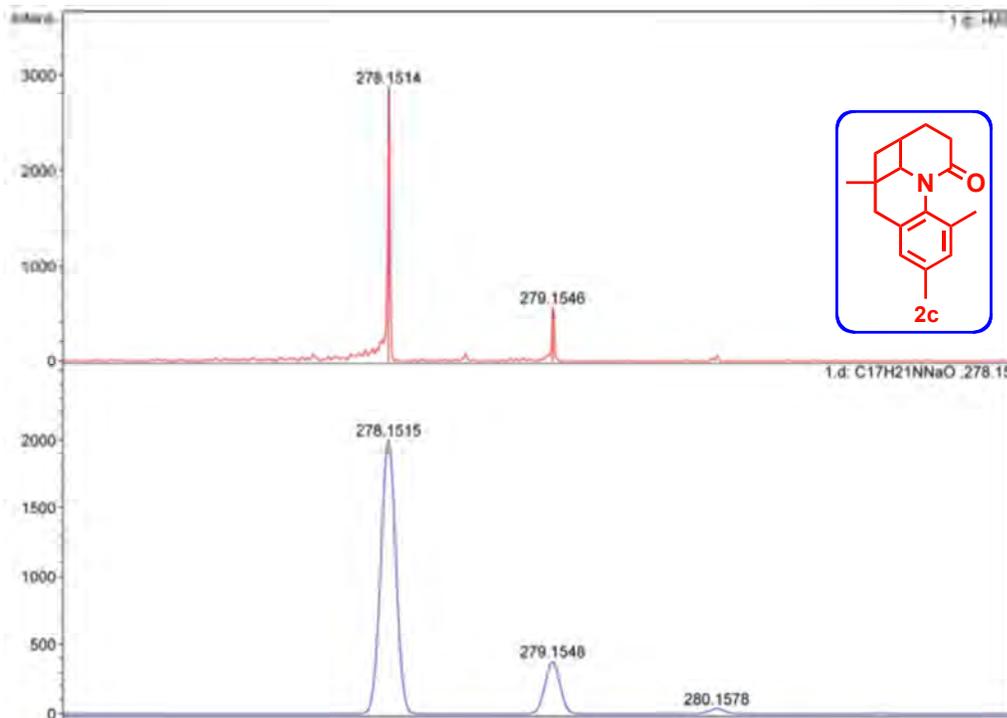


HRMS-ESI ( $m/z$ ) ( $[M + Na]^+$ ):

Calculated : 278.1515

Observed : 278.1514

$|\Delta m|$  : 0.4 ppm



HPLC analysis conditions:

For analytical conditions,

- I). Column : CHIRALPAK IC  
Abs. detector wavelength : 254 nm and 270 nm  
Mobile phase : Hexanes:2-propanol = 90:10  
Flow rate : 1.0 mL/min  
Retention times (min) : ~ 81.63 [(+)-S,S,S-**2c**] and ~ 89.90 [(-)-R,R,R-**2c**]

(Note: Above analytical condition were employed to ascertain the enantiomeric excess reported in table 1 in the manuscript).

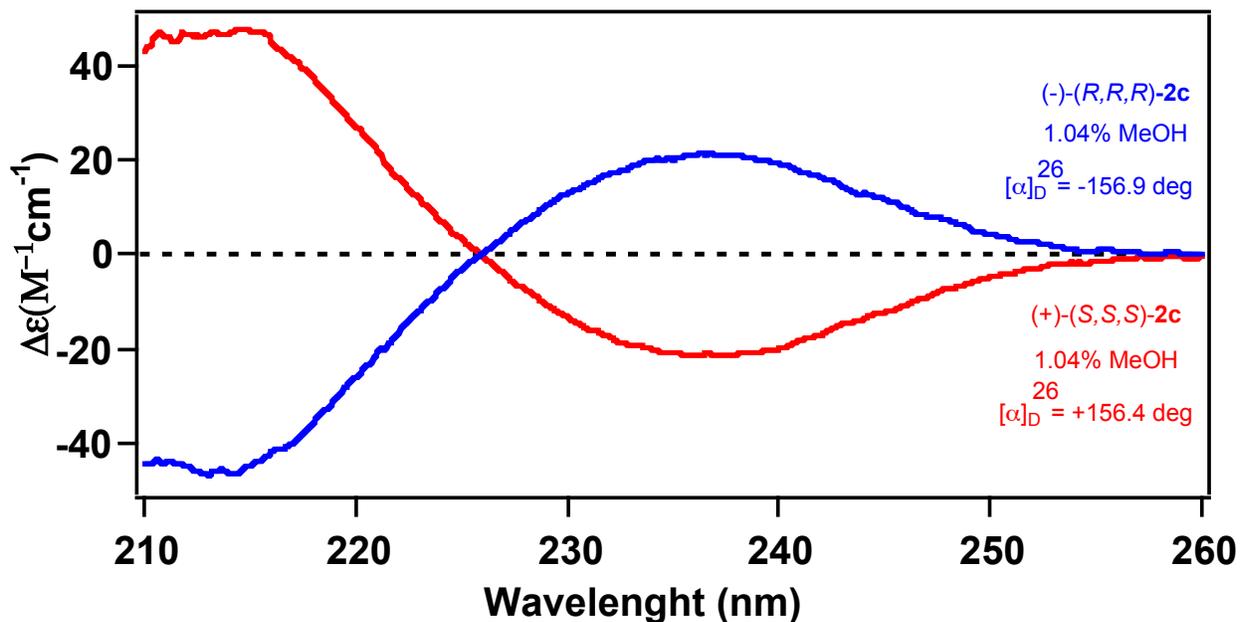
- II). Column : RR-WHELK-01 10/100 FEC  
Abs. detector wavelength : 254 nm and 270 nm  
Mobile phase : Hexanes:2-propanol = 90:10  
Flow rate : 1.0 mL/min  
Retention times (min) : ~ 39.35 [(+)-S,S,S-**2c**] and ~ 79.74 [(-)-R,R,R-**2c**]

Compound **2c**: Optical Rotation  $[\alpha]_D^{26}$  :

HPLC retention time (CHIRALPACK® IC) at ~ 39.35 min, ( $c = 1.04\%$ , MeOH) = +156.9 deg

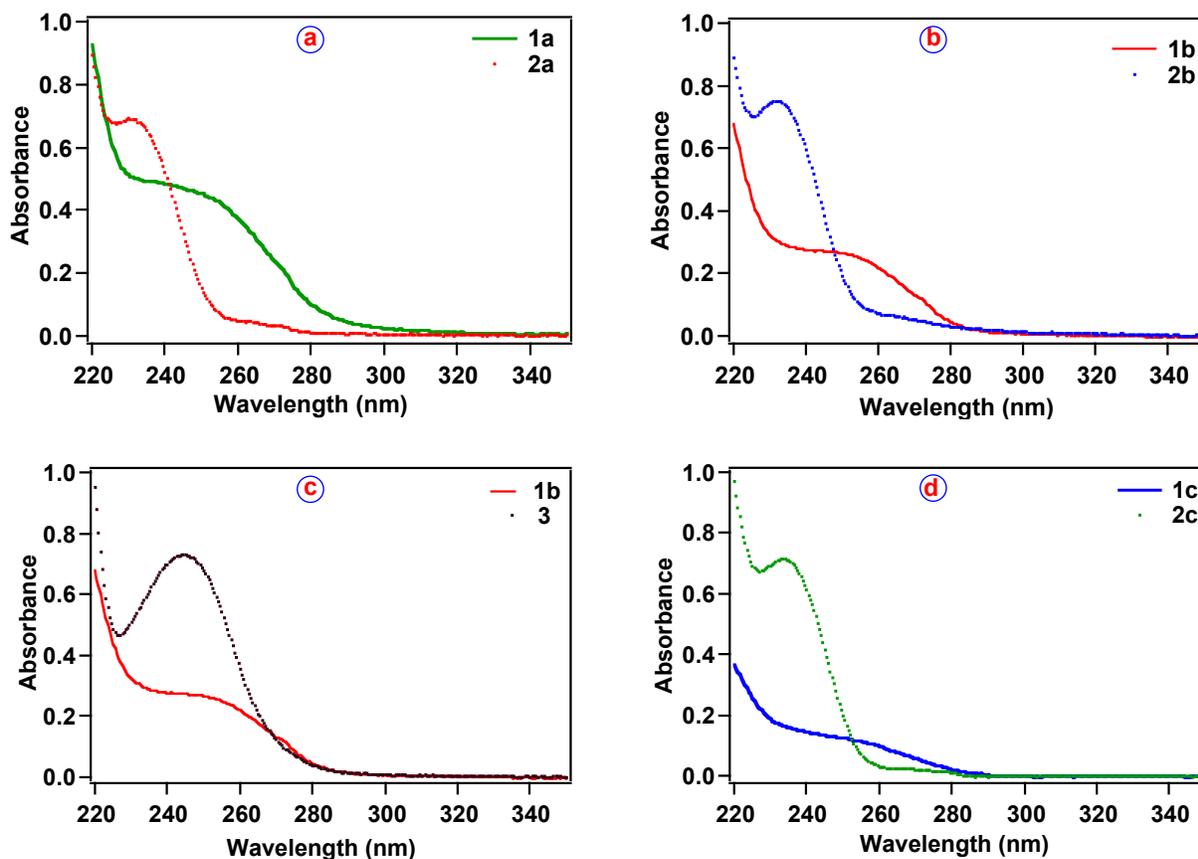
HPLC retention time (CHIRALPACK® IC) at ~ 79.74 min, ( $c = 1.04\%$ , MeOH) = -156.4 deg.

The CD spectra was measured in methanol (concentration: 0.052 mM)



## 7. UV-VIS SPECTRUM OF NON-BIARYL ATROPISOMERIC 3,4-DIHYDRO-2-PYRIDONES **1a-c** AND ITS PHOTOPRODUCTS.

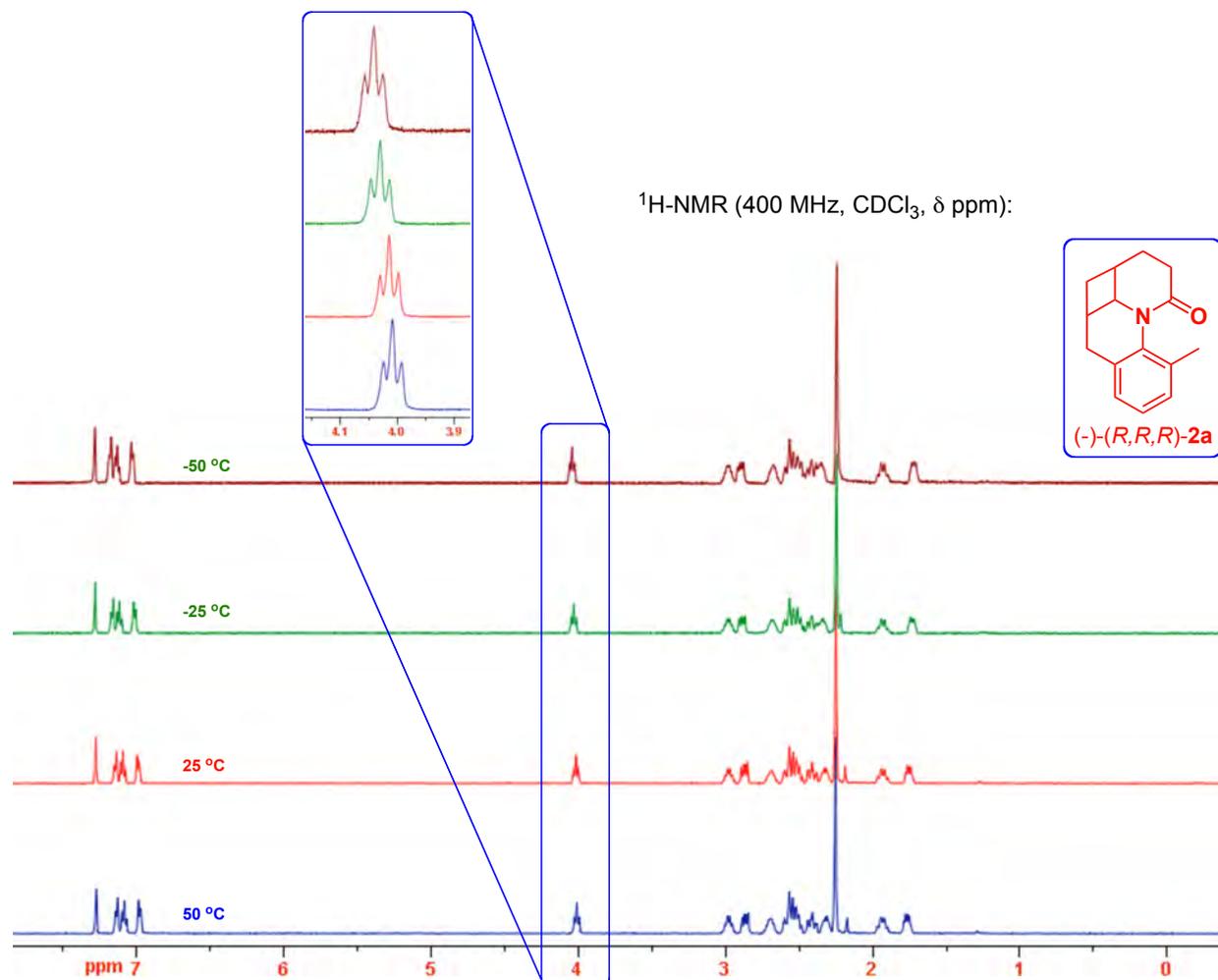
The UV-Vis spectra of 3,4-dihydropyridones and its photoproducts were measured in methanol ( $c \sim 0.1$  mM).



**Figure S9:** UV-Vis spectra of **1a-c**, **2a-c** and **3** in methanol ( $c \sim 0.1$  mM).

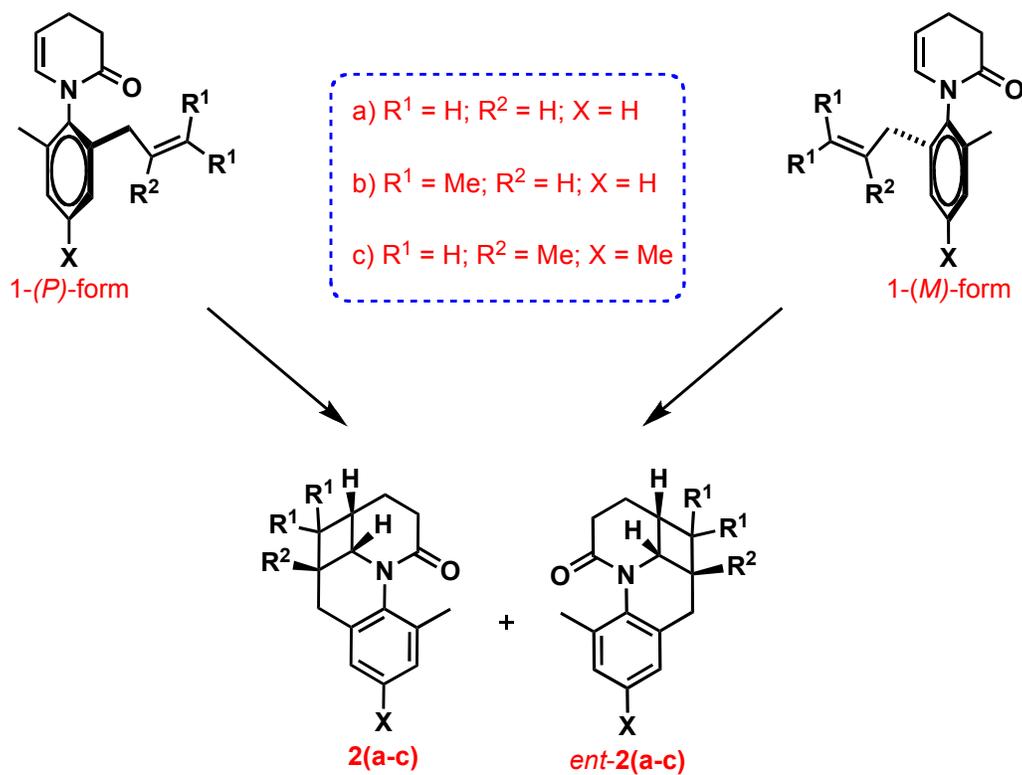
### 9. VARIABLE TEMPERATURE NMR (VT-NMR) OF 2,3-DIHYDRO-2-PYRIDONE PHOTOPRODUCT **2a**.

To ascertain the enantiomeric nature of the individual photoproduct **2**, variable temperature  $^1\text{H-NMR}$  was carried out. Enantiopure photoproduct  $[(-)-(R,R,R)\text{-}2\text{a}]$  was dissolved in  $\text{CDCl}_3$  and  $^1\text{H-NMR}$  was recorded at different temperatures *viz*, 50, 25, -25 and -50 °C. There was no observable diastereomeric protons in the temperature range investigated (50 to -50 °C) indicating the lack of chiral conformers in the photoproduct.

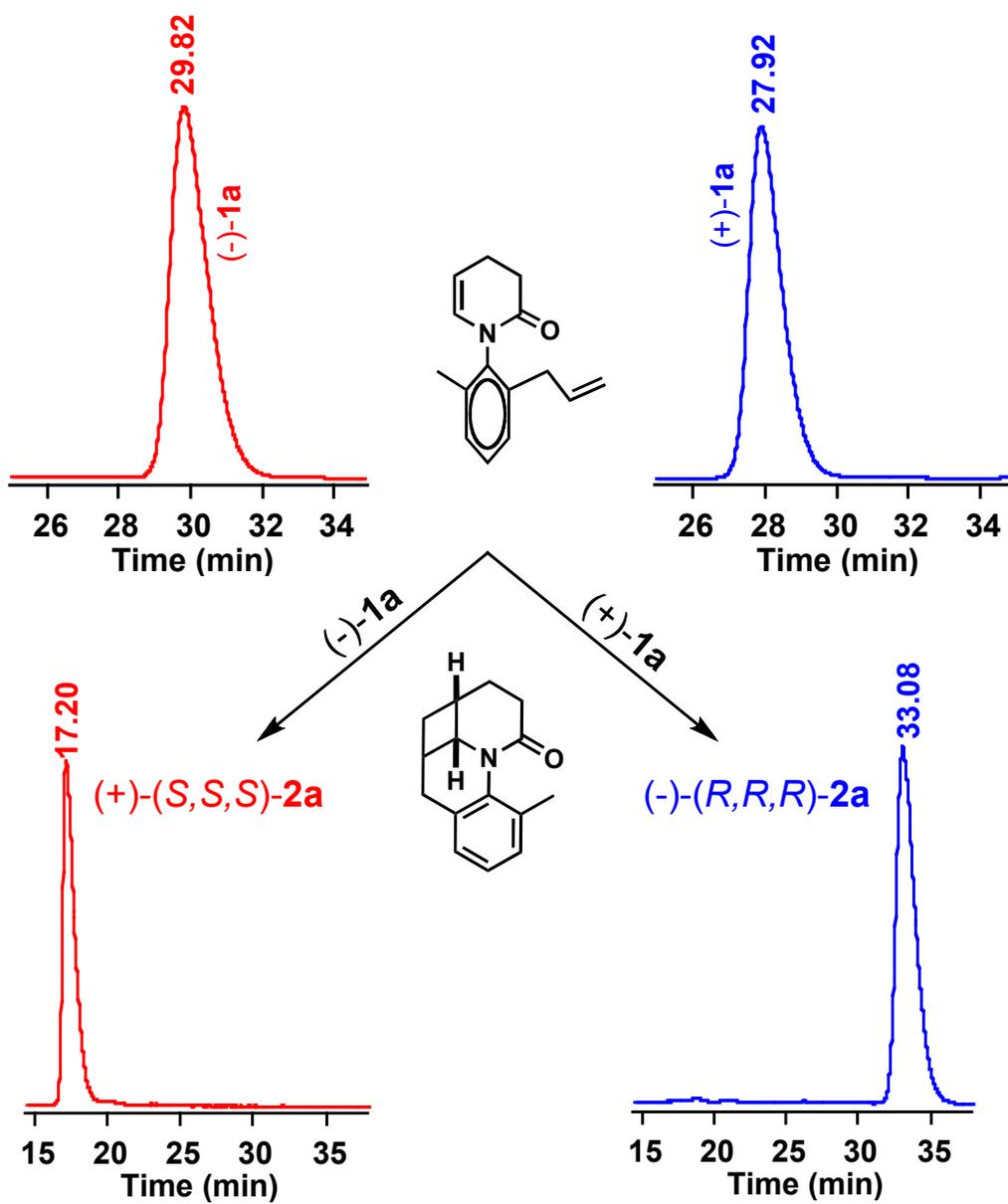


**Figure S10:** Variable temperature  $^1\text{H-NMR}$  on enantiopure  $(-)-(R,R,R)\text{-}2\text{a}$  at various temperatures.

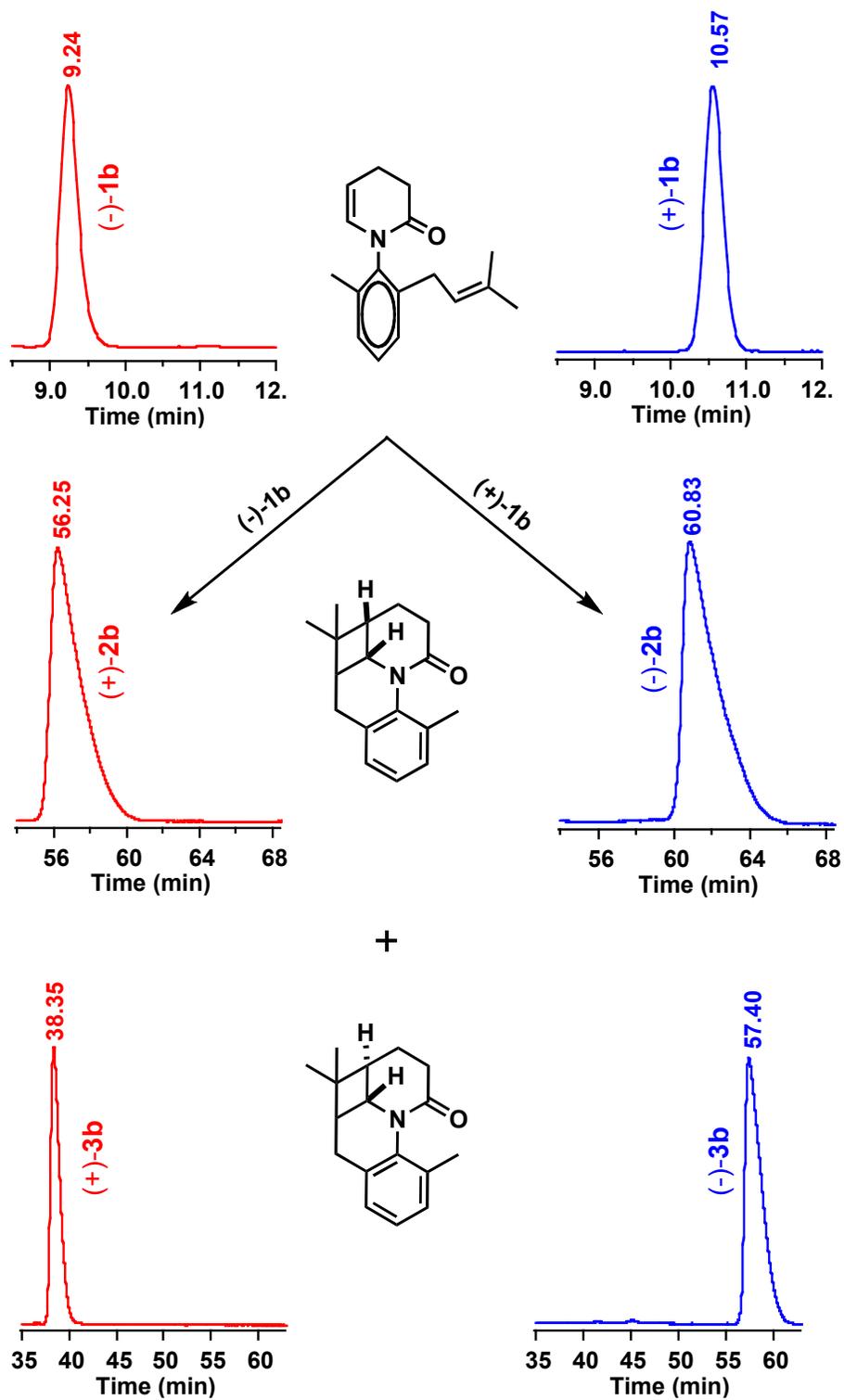
10. HPLC ANALYSIS AFTER PHOTOREACTION OF ATROPISOMERIC 3,4-DIHYDRO-2-PYRIDONES.



### 10.1 HPLC ANALYSIS OF PHOTOPRODUCTS UPON IRRADIATION OF (+)-**1a** AND (-)-**1a**.



### 10.2 HPLC ANALYSIS OF PHOTOPRODUCTS UPON IRRADIATION OF (+)-**1b** AND (-)-**1b**.

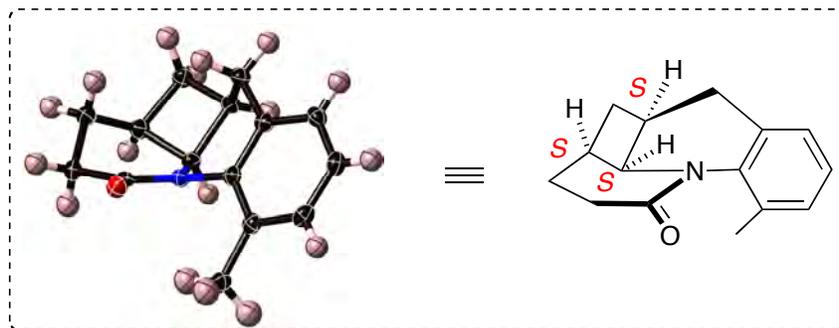


## 11. X-RAY STRUCTURAL PARAMETERS

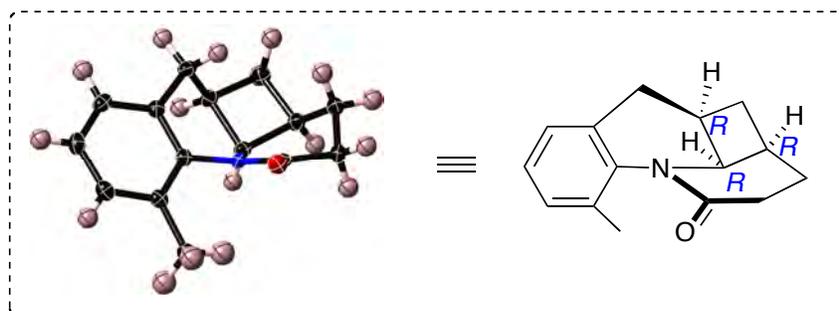
*Structure determination:* Single crystal X-ray diffraction data of the compounds **2a**, **2c** and **3b** were collected on a Bruker Apex Duo diffractometer with a Apex 2 CCD area detector at T = 100K. Cu radiation was used. All structures were processed with Apex 2 v2011.4-1 software package (SAINT v. 7.68A, XSELL v. 6.14). Direct method was used to solve the structures after multi-scan absorption corrections. Details of data collection and refinement are given in the table below.

Entry	<b>2a-(S,S,S)</b>	<b>2a-(R,R,R)</b>	<b>2c-(R,R,R)</b>	<b>2c-(S,S,S)</b>	<b>3b</b>
<b>Formula</b>	C <sub>15</sub> H <sub>17</sub> NO	C <sub>15</sub> H <sub>17</sub> NO	C <sub>17</sub> H <sub>21</sub> NO	C <sub>17</sub> H <sub>21</sub> NO	C <sub>17</sub> H <sub>21</sub> NO
<b>FW</b>	227.30	227.30	255.35	255.35	255.35
<b>cryst. size_max [mm]</b>	.37	.20	.34	.37	.33
<b>cryst. size_mid [mm]</b>	.14	.16	.28	.35	.17
<b>cryst. size_min [mm]</b>	.04	.04	.23	.09	.03
<b>cryst. system</b>	Hexagonal	Hexagonal	Monoclinic	Monoclinic	Triclinic
<b>Space Group, Z</b>	P6 <sub>1</sub> , 6	P6 <sub>5</sub> , 6	P2 <sub>1</sub> , 2	P2 <sub>1</sub> , 2	P-1, 4
<b>a [Å]</b>	7.3117(2)	7.3171(2)	6.8497(2)	6.8456(2)	9.3999(7)
<b>b [Å]</b>	7.3117(2)	7.3171(2)	13.0702(3)	13.0609(2)	9.6886(6)
<b>c [Å]</b>	37.2526(9)	37.2390(11)	7.9554(2)	7.9584(2)	16.2607(10)
<b>α [Å]</b>	90	90	90	90	100.574(3)
<b>β [Å]</b>	90	90	105.727(1)	105.815(1)	98.903(3)
<b>γ [Å]</b>	120	120	90	90	103.446(3)
<b>V [Å<sup>3</sup>]</b>	1724.74(8)	1726.66(8)	685.56(3)	684.62(3)	1385.48(16)
<b>ρ<sub>calc</sub> [g/cm<sup>3</sup>]</b>	1.313	1.312	1.237	1.239	1.224
<b>μ [cm<sup>-1</sup>]</b>	0.639	.638	0.589	0.590	.583
<b>Radiation Type</b>	Cu	Cu	Cu	Cu	Cu
<b>F(000)</b>	732	732	276	276	552
<b>no of measured refl.</b>	14783	13311	8534	7269	34128
<b>no of indep. refl.</b>	1958	1966	2442	2403	4965
<b>no of refl. (I ≥ 2σ)</b>	1949	1930	2426	2376	4361
<b>Resolution [Å]</b>	.84	.84	.84	.84	.84
<b>R1/wR2 (I ≥ 2σ)<sup>a</sup> [%]</b>	2.99/7.73	2.87/7.51	2.83/7.83	2.79/7.32	4.32/10.58
<b>R1/wR2 (all data) [%]</b>	3.01/7.74	2.93/7.56	2.85/7.85	2.81/7.35	4.97/11.01

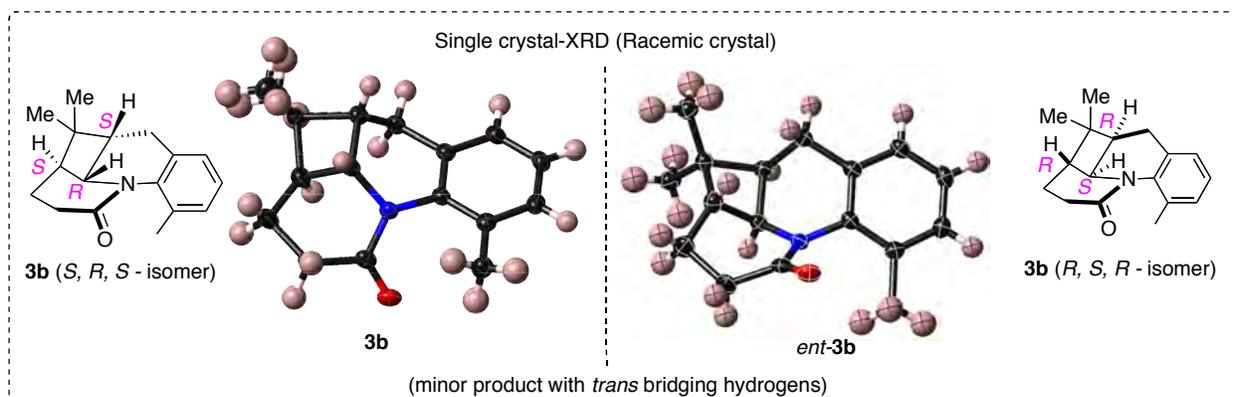
11.1 X-RAY STRUCTURE OF PHOTOPRODUCT (+)-(S,S,S)-**2a** (CRYSTALLIZED FROM: HEXANES:2-PROPANOL)



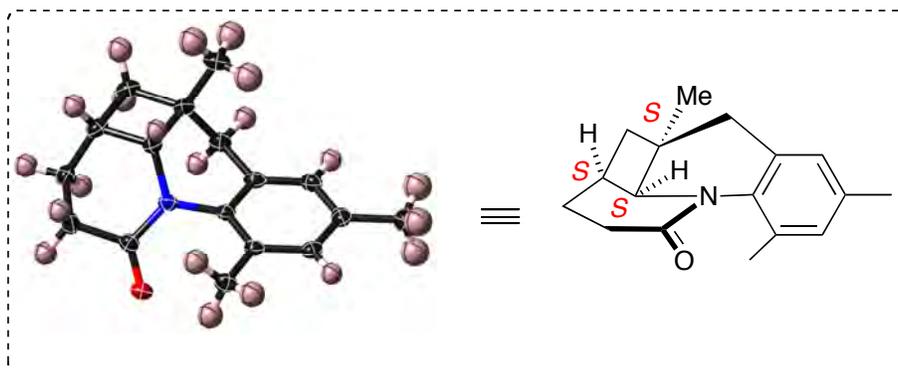
11.2 X-RAY STRUCTURE OF PHOTOPRODUCT (-)-(R,R,R)-**2a** (CRYSTALLIZED FROM: HEXANES:2-PROPANOL)



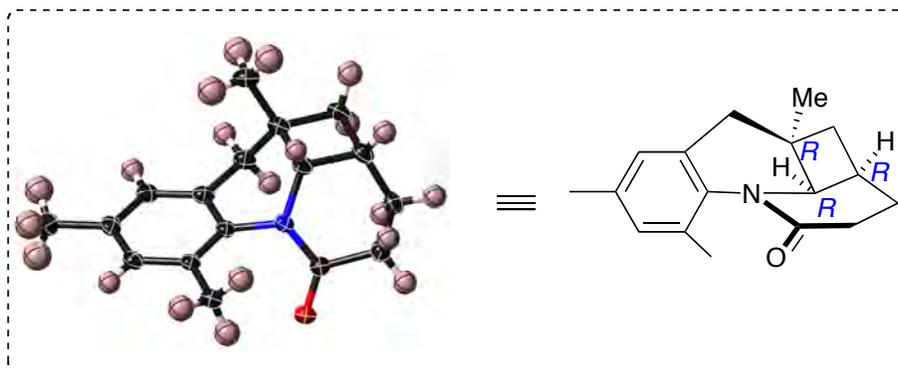
11.3 X-RAY STRUCTURE OF PHOTOPRODUCT **3** (CRYSTALLIZED FROM: HEXANES:CHLOROFORM)



11.4 X-RAY STRUCTURE OF PHOTOPRODUCT (+)-(S,S,S)-**2c** (CRYSTALLIZED FROM:  
HEXANES:CHLOROFORM)



11.5 X-RAY STRUCTURE OF PHOTOPRODUCT (-)-(R,R,R)-**2c** (CRYSTALLIZED FROM:  
HEXANES:CHLOROFORM)



## 12. REFERENCES

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