Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information (74 Pages)

Engaging electronic effects for atropselective [5+2]-photocycloaddition of maleimides.

Ramya Raghunathan[a], Elango Kumarasamy[a], Steffen Jockusch,[b] Angel Ugrinov[a] and J. Sivaguru*,[a]

[a] *Department of Chemistry and Biochemistry, North Dakota State University, Fargo, ND 58108-6050, United States.*
[b] *Department of Chemistry, Columbia University, New York, New York 10027, United States.*
e-Mail: jayaraman.sivaguru@ndsu.edu

1. TABLE OF CONTENTS

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. ^{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). 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 Ultimate 3000 sample injector was used for injection on Dionex® HPLC. All HPLC injections 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) CHIRALCEL® 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® AD-H

a) 0.46 cm x 25 cm column for analytical injections.

b) 10 mm x 25 cm column for semi-preparative injections

iv) CHIRALPAK® IC

a) 0.46 cm x 25 cm column for analytical injections.

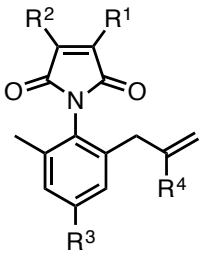
b) 10 mm x 25 cm column for semi-preparative injections

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. Optical activity values were recorded on JASCO® DIP – 370 digital polarimeter. When necessary, the

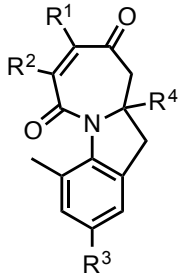
compounds were purified by combiflash equipped with dual wavelength UV-Vis absorbance detector (Teledyne ISCO) using hexanes:ethyl acetate as the mobile phase and Redisep® cartridge filled with silica (Teledyne ISCO) as stationary phase. In some cases, compounds were purified by column chromatography 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}). Absorbance measurements were performed using Agilent technologies® Cary 300 UV-Vis spectrophotometer.

2. Chemical structures of maleimides and synthetic protocol

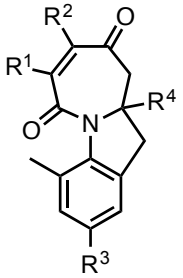
2.1. Chemical structures of maleimides



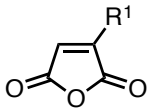
1(a-i)



2(a-h)

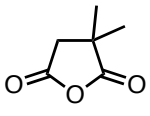


3(a-e), 3(g-h)

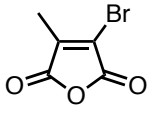


4a-e
a) R^1 = H; b) R^1 = Me; c) R^1 = Br;
d) R^1 = Ph; e) R^1 = CF_3

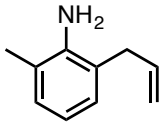
a) R^1-R^4 = H
b) R^1 = Me; R^2-R^4 = H
c) R^1 = Br; R^2-R^4 = H
d) R^1 = Ph; R^2-R^4 = H
e) R^1 = Ph; R^2 = H; R^3-R^4 = Me
f) R^1 = OMe; R^2-R^4 = H
g) R^1 = CF_3; R^2-R^4 = H
h) R^1 = Me; R^2 = Br; R^3-R^4 = H
i) R^1 = $(Me)_2$; R^2-R^4 = H



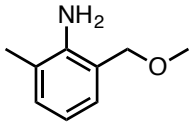
4f



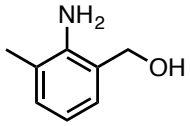
4h



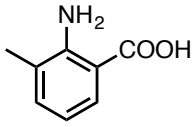
5



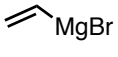
6



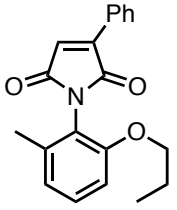
7



8

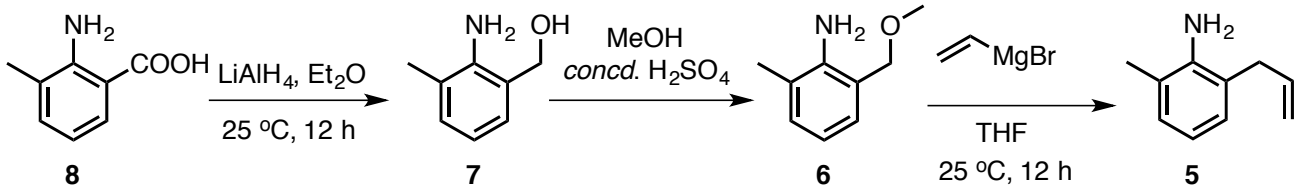


9

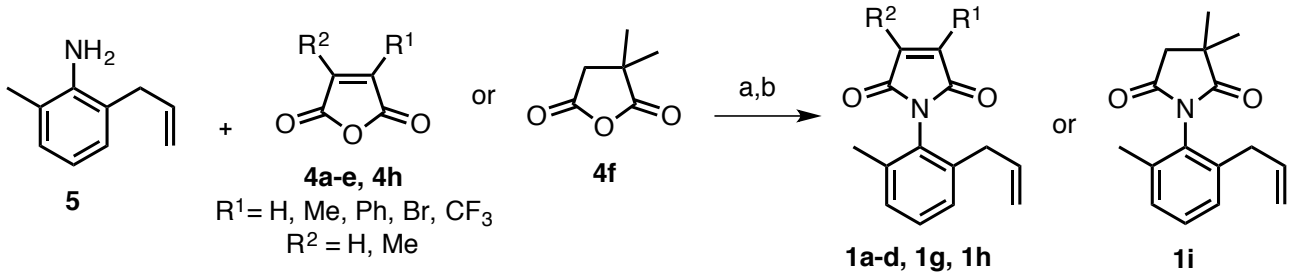


10

2.2. Synthetic protocol for aniline derivatives **5** and maleimides **1a-i**



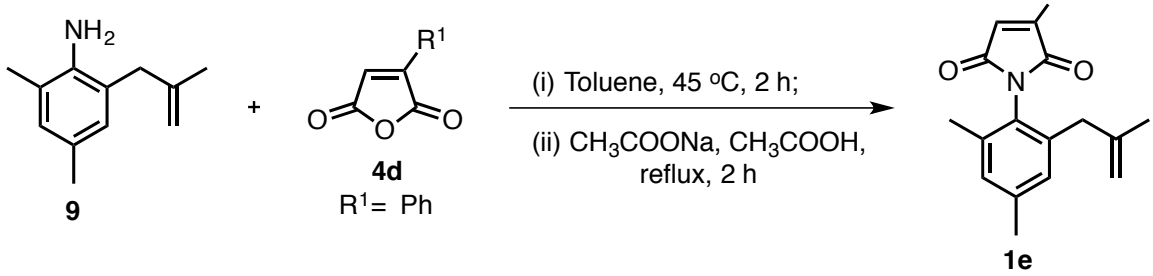
8 **7** **6** **5**



5 **4a-e, 4h** **4f** **1a-d, 1g, 1h** **1i**

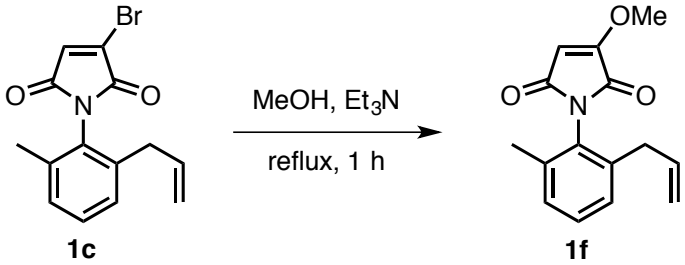
R^1= H, Me, Ph, Br, CF_3
R^2 = H, Me

(a) Toluene, 45 °C, 2 h; (b) CH_3COONa, CH_3COOH, reflux, 2 h



9 **4d** **1e**

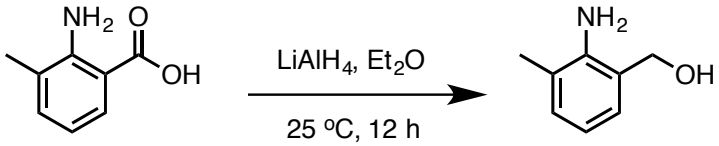
R^1= Ph



1c **1f**

3. General procedure for the synthesis atropisomeric maleimide 1a-i and their precursors

3.1. Synthesis of 2-amino benzyl alcohol **7**



8 **7**

Scheme S1: Synthesis of 2-amino benzyl alcohol derivative **7.**

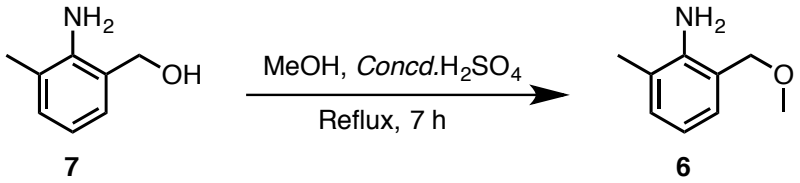
The benzyl alcohol derivative was synthesized according to a procedure reported in the literature.[1] To a slurry of lithium aluminum hydride (2.5 *equiv.*) in dry THF (50 mL) under N_2 atmosphere at 0 ^oC, a solution anthranillic acid derivative **8** (4.0 g, 1.0 *equiv.*) in dry THF (50 mL) was added over a period of 15 min without allowing the internal temperature to rise above 5 ^oC. The resulting mixture was allowed to warm to room temperature over 12 h. After the reaction, the mixture was cooled to 0 ^oC and quenched with saturated Na_2SO_4 solution over 15 min. To the resulting solid mixture DCM (CH_2Cl_2, 75 mL) was added, stirred for 15 min, filtered and the filtered solid residue was washed with DCM (50 mL). The combined organic layer was dried over *anhyd.* Na_2SO_4, filtered and the solvent was removed under reduced pressure to get the crude product. The crude product was directly taken to next step without further purification.

R*f* = 0.45 (50% hexanes: 50% ethyl acetate), Yield for **7** = 90%

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.03-7.01 (m, 1H), 6.92-6.90 (m, 1H), 6.65-6.61 (m, 1H), 4.61 (s, 2H), 3.40 (bs, 3H) and 2.15 (m, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 144.3, 130.7, 127.3, 124.4, 122.9, 117.9, 64.7 and 17.5.

3.2. Synthesis of 2-methoxymethylaniline **6**



7 **6**

Scheme S2: Synthesis of 2-methoxymethylaniline derivative **6.**

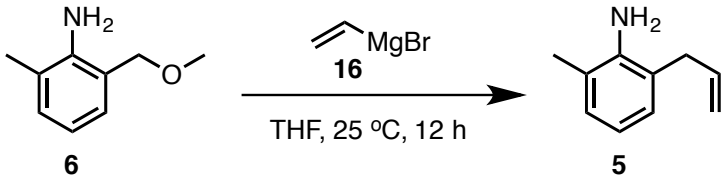
The methoxyaniline derivative was synthesized according to a procedure reported in the literature.[2] To a solution of aminobenzyl alcohol derivative **7** (5.0 g, 1.0 *equiv.*) in methanol (40 mL) at 0 ^{o}C, *concd*. H_2SO_4 (1.1 *equiv.*) was added over 5 min. The resulting mixture was heated to 50 ^{o}C for 7 h. After the reaction, the mixture was cooled to 10 ^{o}C and neutralized with saturated Na_2CO_3 solution carefully, during which a brisk effervescence was observed. The aqueous layer was extracted with DCM (3 × 40 mL). The combined organic layer was dried over *anhyd.* Na_2SO_4, filtered and the solvent was removed under reduced pressure to get the crude product. The crude product was purified by combiflash using a hexanes: ethyl acetate mixture.

R*f* = 0.80 (50% hexanes: 50% ethyl acetate), Yield for **6** = 77%

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.05-7.03 (m, 1H), 6.96-6.94 (m, 1H), 6.6-6.62 (m, 1H), 4.49 (s, 2H), 4.12 (bs, 2H), 3.33 (s, 3H) and 2.17 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 144.6, 130.7, 128.3, 122.5, 121.5, 117.5, 74.1, 57.6,and 17.5.

3.3. Synthesis of 2-(allyl)aniline **5**



6 **5**

Scheme S3: Synthesis of 2-(ally)aniline derivative **5.**

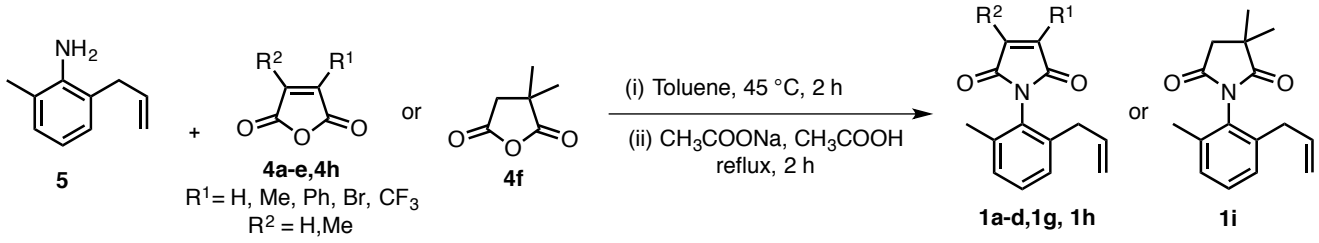
To a solution methoxyaniline derivative **6** (5.3 g, 1.0 *equiv.*) in dry THF (40 mL) at 0 °C, allyl magnesium halide (2.0 M in THF, 2.2 *equiv.*) was added slowly over 15 min. The resulting mixture was allowed to warm to room temperature over 12 h. After the reaction, the mixture was cooled to 0 °C and quenched with *dil.* HCl. The aqueous layer was extracted with DCM (3 × 50 mL). The combined organic layer was dried over *anhyd.* Na_2SO_4, filtered and the solvent was removed under reduced pressure to get the crude product. The crude product was purified by combiflash using a hexanes: ethyl acetate mixture.

R*f* = 0.40 (80% hexanes: 20% ethyl acetate), Yield for **5** = 55%

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.03-6.95 (m, 2H), 6.69-6.66 (m, 1H), 6.12-5.94 (m, 1H), 5.20-5.12 (m, 2H), 3.68 (bs, 2H), 3.38-3.34(m, 2H) and 2.22 (s, 3H).

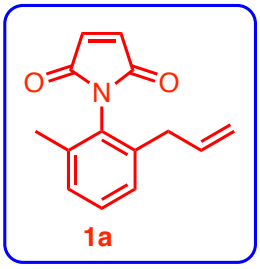
^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 143.0,136.1,128.8,128.0,123.3,122.3118.1,116.1,36.8 and 17.6.

3.4. Synthesis of atropisomeric maleimide derivatives **1a-d**, **1g**, **1i**



Scheme S4: Synthesis of atropisomeric maleimide derivatives **1a-d, 1g-1h** and **1i**.

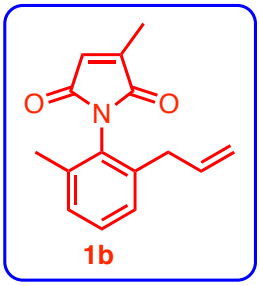
To a solution of aniline derivative **5** (500 mg, 1.1 *equiv.*) in toluene (5 mL) corresponding anhydride **4a-e, 4f, 4h** (1.0 *equiv.*) was added and the resulting mixture was heated to 50 ^{o}C for 2 h. After the reaction, the solvent was concentrated and the residue was directly taken to next step. To the residue from the above reaction in glacial acetic acid (5 mL), *anhyd.* sodium acetate (236 mg, 2.88 mmol) was added. The resulting mixture was refluxed for 2 h. After the reaction, the mixture was cooled to room temperature and diluted with ethyl acetate (20 mL). The organic layer was washed with DI water (2 x 15 mL), saturated $NaHCO_3$ solution (2 × 15 mL), dried over *anhyd.* Na_2SO_4, filtered and concentrated under reduced pressure to yield crude product. The crude product was purified by combiflash using a hexanes:ethyl acetate mixture.



TLC condition - R*f* = 0.45 (80% hexanes:20% ethyl acetate) for **1a** (Yield = 54 %)

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.27-7.23 (m, 1H), 7.16-7.12 (m, 2H), 5.81-5.71 (m, 1H), 4.98-4.93 (m, 2H), 3.19-3.17 (d, J = 6.4 Hz, 2H) and 2.07 (s, 3H).

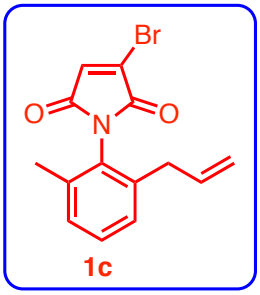
^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 169.9, 130.3, 137.6, 136.1, 134.5, 129.9, 129.4, 129.3, 128.3, 116.6, 36.9 and 18.1.



TLC condition - R*f* = 0.65 (80% hexanes:20% ethyl acetate) for **1b** (Yield = 60 %)

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.28-7.24 (m, 1H), 7.17-7.12 (m, 2H), 6.46-6.45 (q, J = 5.2 Hz 1H), 5.82-5.72 (m, 1H), 4.98-4.93 (m, 2H), 3.19-3.17 (d, J = 6.8 Hz, 2H), 2.14-2.14 (d, J = 2 Hz, 2H) and 2.09 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 170.9, 169.9, 146.1, 139.3, 137.5, 136.2, 129.7, 129.6, 129.3, 128.2, 127.8, 116.4, 36.9, 18.2 and 11.4.

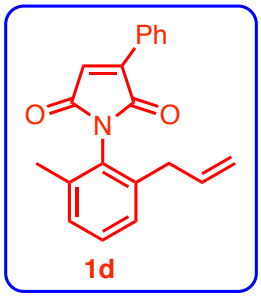


1c

TLC condition - R*f* = 0.50 (80% hexanes:20% ethyl acetate) for **1c** (Yield = 67 %)

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.30-7.26 (m, 1H), 7.18-7.14 (m, 2H), 6.99 (s,1H), 5.81-5.71 (m, 1H), 5.00-4.94 (m, 2H), 3.20-3.19 (d, J = 6.8 Hz, 2H) and 2.10 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 167.7, 164.4, 139.2, 137.5, 136.0, 132.3, 131.9, 130.2, 129.5, 129.1, 128.4, 116.7, 37.1 and 18.1.

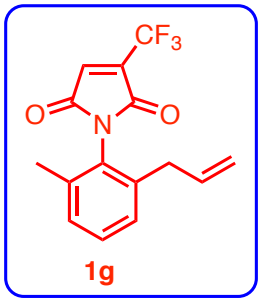


1d

TLC condition - R*f* = 0.50 (80% hexanes:20% ethyl acetate) for **1d** (Yield = 78 %)

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 8.03-8.00 (m, 2H), 7.49-7.48 (m, 3H), 7.32-7.29 (m, 1H), 7.23-7.21 (m, 2H), 6.90 (s, 1H), 5.91-5.80 (m, 1H), 5.04-5.00 (m, 2H), 3.31-3.29 (d, J = 6.4 Hz, 2H) and 2.1 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 169.9, 169.5, 144.1, 139.4, 137.7, 136.3, 131.6, 129.8, 129.8, 129.4, 129.3, 129.1, 128.9, 128.3, 124.3, 116.6, 37.1 and 18.3.

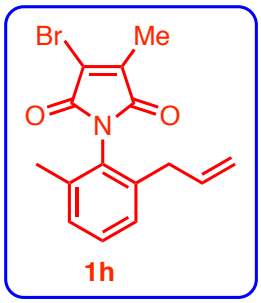


1g

TLC condition - R*f* = 0.60 (80% hexanes:20% ethyl acetate) for **1g** (Yield = 40 %)

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.32-7.28 (m, 1H), 7.21-7.15 (m, 2H), 7.09-7.08 (q, J = 5.2Hz, 1H), 5.79-5.69 (m, 1H), 4.99-4.92 (m, 2H), 3.22-3.20 (d, J = 6.8 Hz, 2H) and 2.10 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 166.2, 163.9, 139.0, 137.5, 136.0, 133.7, 130.3, 129.6, 128.7, 128.5, 120.8, 118.1, 116.5, 37.3 and 17.9.

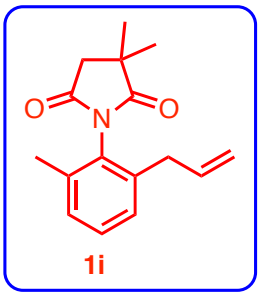


1h

TLC condition - R*f* = 0.50 (80% hexanes:20% ethyl acetate) for **1h** (Yield = 60 %)

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.29-7.25 (m, 1H), 7.18-7.15 (m, 2H), 5.81-5.71 (m, 1H), 4.99-4.93 (m, 2H), 3.20-3.18 (d, J = 6.8 Hz, 2H), 2.11 (s, 3H) and 2.09 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 168.5, 164.5, 142.8, 139.2, 137.6, 136.1, 129.9, 129.4, 128.3, 125.5, 116.5, 37.0, 18.2 and 11.2.

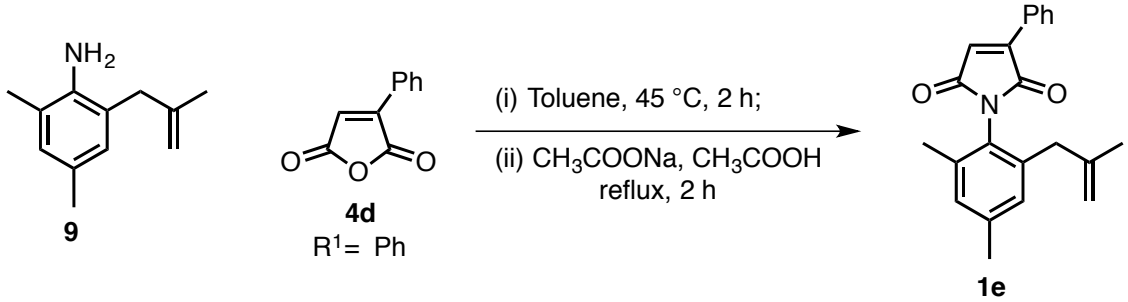


1i

TLC condition - R*f* = 0.80 (80% hexanes:20% ethyl acetate) for **1i** (Yield = 80 %)
^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.27-7.23 (m, 1H), 7.16-7.12 (m, 2H), 5.84-5.74 (m, 1H), 5.03-4.97 (m, 2H), 3.18 (d, *J*=6.8 Hz, 2H), 2.71 (s, 2H), 2.08 (s, 3H), 1.421 (s, 3H) and 1.42 (s, 3H).

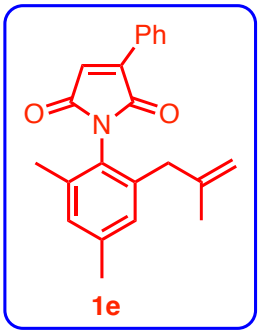
^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 182.2, 175.03, 137.97, 136.2, 136.1, 130.3, 129.8, 129.4,128.3, 116.6, 44.2, 40.8, 36.5, 26.4, 25.6, and 17.9.

3.5. Synthesis of atropisomeric maleimide derivative **1e**



Scheme S5: Synthesis of atropisomeric maleimide derivative **1e.**

To a solution of aniline derivative **9** (500 mg, 1.1 *equiv.*) in toluene (5 mL) corresponding anhydride **4d** (1.0 *equiv.*) was added and the resulting mixture was heated to 50 °C for 2 h. After the reaction, the solvent was concentrated and the residue was directly taken to next step. To the residue from the above reaction in glacial acetic acid (5 mL), *anhyd.* sodium acetate (236 mg, 2.88 mmol) was added. The resulting mixture was refluxed for 2 h. After the reaction, the mixture was cooled to room temperature and diluted with ethyl acetate (20 mL). The organic layer was washed with DI water (2 x 15 mL), saturated $NaHCO_3$ solution (2 × 15 mL), dried over *anhyd.* Na_2SO_4, filtered and concentrated under reduced pressure to yield crude product. The crude product was purified by combiflash using a hexanes:ethyl acetate mixture.



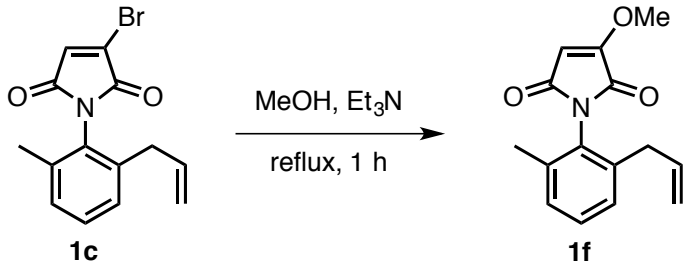
1e

TLC condition - R*f* = 0.2 (95% hexanes:5% ethyl acetate) for **1e** (Yield = 68 %)

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.98-7.96 (m, 2H), 7.48-7.46 (m, 3H), 7.02-6.98 (d, J = 16.4, 2H), 6.85 (s, 1H), 4.72 (s, 1H), 4.62 (s, 1H), 3.19 (s, 2H), 2.34 (s, 3H), 2.12 (s, 3H), and 1.59 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 169.7, 169.6, 144.0, 139.5, 138.5, 137.3, 131.5, 130.2, 129.6, 129.2, 129.0, 128.9, 42.6, 22.1, 21.4 and 18.1.

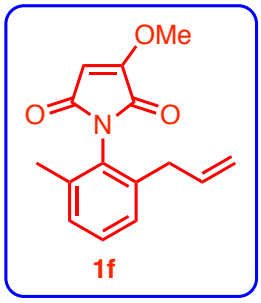
3.6. Synthesis of atropisomeric maleimide derivative **1f**



1c **1f**

Scheme S6: Synthesis of atropisomeric maleimide derivative **1f.**

To a solution of bromo maleimide derivative **1c** (500 mg, 1.0 *equiv.*) in MeOH (5 mL) triethylamine in MeOH (1.1 *equiv.*) was added and the resulting mixture refluxed for 1 h. After the reaction, the solvent was concentrated and the reaction mixture was quenched with DI water. The aqueous layer is extracted with DCM (20 mL). The combined organic layer was dried over *anhyd.* Na_2SO_4, filtered and concentrated under reduced pressure to yield crude product. The crude product was purified by combiflash using a hexanes:ethyl acetate mixture.



1f

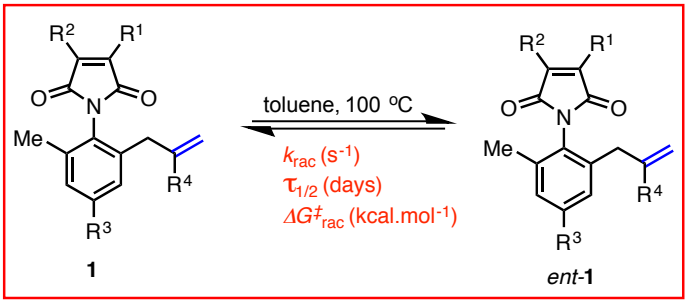
TLC condition - R*f* = 0.40 (50% hexanes:50% ethyl acetate) ,Yield = 63 %

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.27-7.23 (m, 1H), 7.15-7.11 (m, 2H), 5.83-5.72 (m, 1H), 5.54 (s, 1H), 4.99-4.95 (m, 2H), 3.96 (s, 3H), 3.20 (d, J = 6.8, 2H) and 2.10 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 169.3, 164.7, 161.0, 139.4, 137.7, 137.1, 129.8, 129.3, 129.0, 128.2, 116.5, 96.7, 59.2, 36.9 and 18.2.

4. Racemization kinetics of non-biaryl axially chiral maleimides 1c-f

Racemization kinetics of optically pure atropisomeric maleimides **1c-f** was performed at 100 °C in toluene. The racemization (% *ee*) was followed by HPLC analyses on a chiral stationary phase at different time intervals (Figures S1). The activation energy (Table S1) for racemization was computed from equations 1 and 2.[1]



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

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

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

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

$$\ln\left(\frac{R_0}{R_0 - x}\right) = k_{rac}t \qquad \textbf{Equation 2.}$$

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:

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

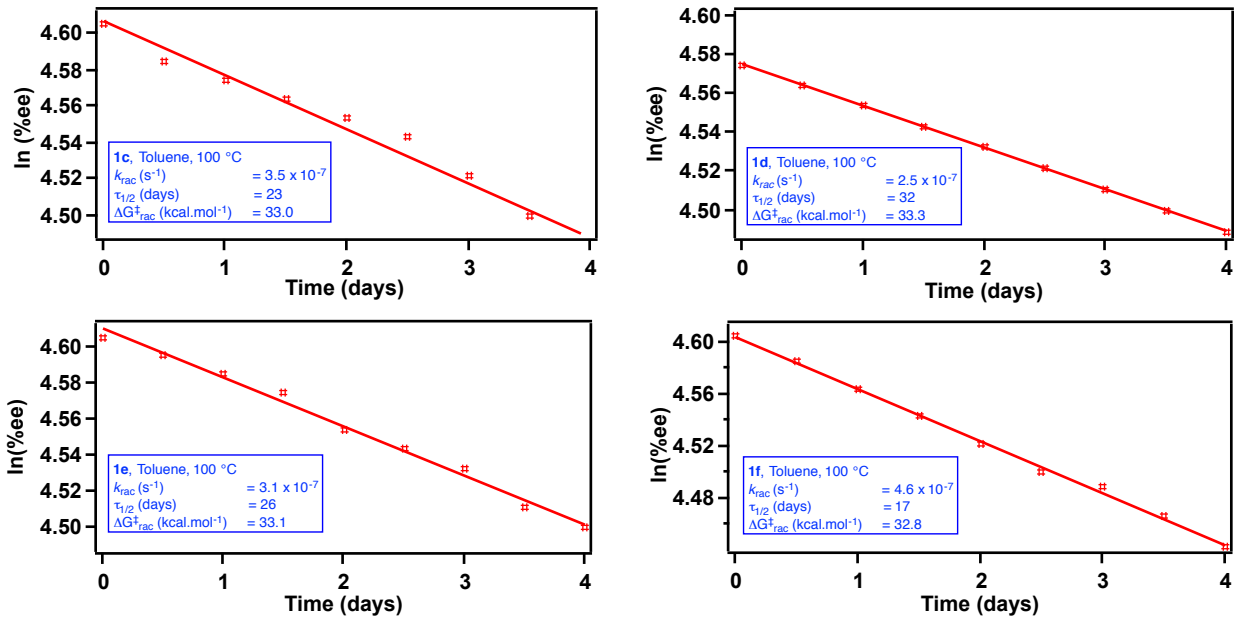


Figure S1: Racemization kinetics of maleimides **1c-f** in toluene at 100 °C.

Table S1: Half-life, activation energy and rate for racemization of maleimides **1c-f** in toluene at 100 °C.

Entry	Compound	Parameters		
		$\tau_{1/2rac}$ (days)	$\Delta G^{\ddagger}_{rac}$ (kcal·mol^{-1})	k_{rac} (s^{-1})
1	**1c**	23	33.0	3.5 X 10^{-7}
2	**1d**	32	33.3	2.5X 10^{-7}
3	**1e**	26	33.1	3.1 X 10^{-7}
4	**1f**	17	32.8	4.6 X 10^{-6}

Reported values carry an error of ±5%.

5. UV-Vis Spectrum of atropisomeric maleimides and its photoproducts

The UV-Vis spectra of atropisomeric maleimides and its photoproducts were measured in acetonitrile.

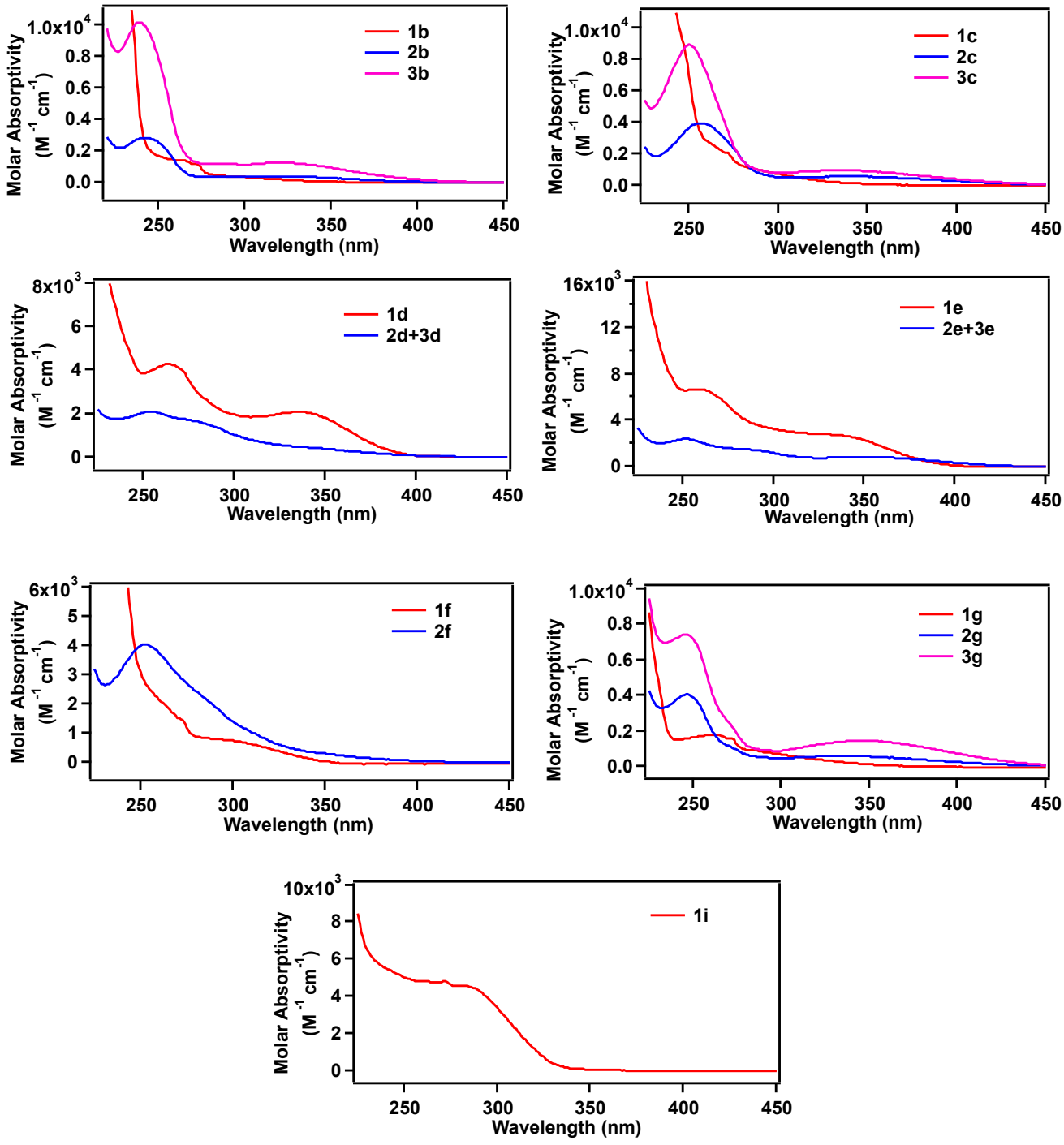
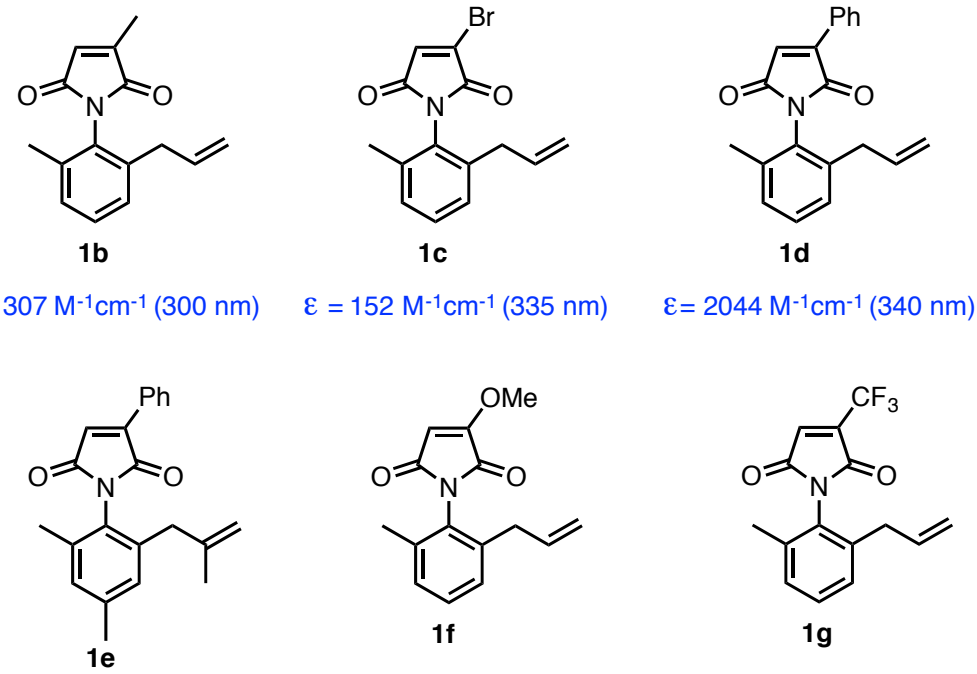


Figure S2: UV-Vis spectra of maleimides **1** and its photoproducts **2** and **3** in acetonitrile.



ε = 307 $M^{-1}cm^{-1}$ (300 nm) ε = 152 $M^{-1}cm^{-1}$ (335 nm) ε= 2044 $M^{-1}cm^{-1}$ (340 nm)

ε= 2644 $M^{-1}cm^{-1}$ (340 nm) ε= 759 $M^{-1}cm^{-1}$ (300 nm) ε=261 $M^{-1}cm^{-1}$ (335 nm)

Figure S3: Molar absorptivity of **1** for the longest absorption wavelength.

Solvatochromic effect: The UV-Vis spectra of atropisomeric maleimide **1d** in various solvent viz. Methyl cyclohexane (MCH), acetonitrile (MeCN) and methanol (MeOH).

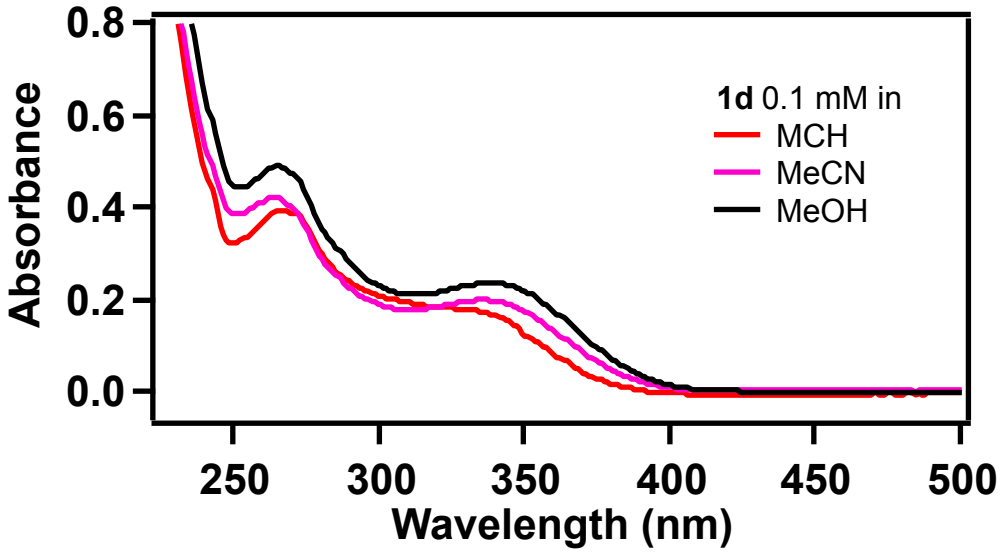


Figure S4: UV-Vis spectra of maleimides **1d** in various solvents.

6. General irradiation procedures and characterization of photoproducts.

6.1. Solvent optimization for photoreaction of maleimides **1a**

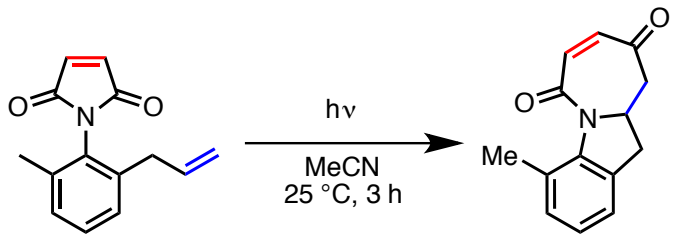
Several solvents were screened for the photoreaction of atropisomeric maleimide **1a**. In a typical experiment, maleimide **1a** in a given solvent (~3.9 mM concentration) was degassed with N_2 for 15 min and then sealed for photoreaction. This solution was irradiated in a Rayonet reactor (~300 nm or ~350 nm) for 3 h. After the reaction, a stock solution of internal standard (triphenylmethane) was added and this solution was concentrated under reduced pressure to obtain the crude reaction mixture. ^{1}H-NMR spectroscopy was recorded on the crude reaction mixture and from the integral values the conversion and mass balance were calculated (refer to section 7.3).

Table S2: Solvent screening for photoreaction of **1a**

Entry	Solvent	NMR Yield (%) (% mass balance)
1	Acetonitrile	26 (60)
2	Ethyl acetate	Decomposed
3	Dichloromethane	20 (59)
4	Chloroform	Decomposed
5	Benzene	33 (50)
6	MCH	35 (59)

Note: The reported value carry an error of ±5%.

6.2. Photoreaction of atropisomeric maleimides **1a** under various atmospheric conditions:



1a **2a**

Scheme 7: General irradiation procedure for maleimides **1a**

In a typical experiment, maleimide **1a** in MeCN (~3.9 mM concentration) was bubbled with Nitrogen or Oxygen for 8-10 min. For irradiation under air, the reaction mixture was irradiated without bubbling. The resultant solution was irradiated in a Rayonet reactor (~300 nm or ~350 nm) for 3 h. After the reaction, a stock solution of internal standard (triphenylmethane) was added and this solution was concentrated under reduced pressure to obtain the crude reaction mixture. ^{1}H-NMR

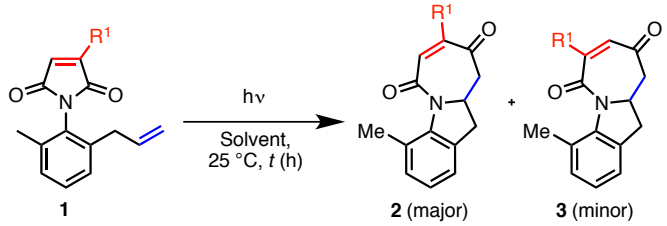
spectroscopy was recorded on the crude reaction mixture and from the integral values the conversion and mass balance were calculated (refer to section 7.3).

Table S3: Photoreaction of **1a** at various atmospheric conditions

Entry	Condition	NMR Yield (%)
1	Nitrogen	23
2	Oxygen	22
3	Air	26

Note: The reported value carry an error of ±5%.

6.3. Process for photoreaction of atropisomeric maleimides **1a-l**



Scheme 8: General irradiation procedure for maleimides **1a-l**

Enantiospecific reactions: A solution of optically pure atropisomeric maleimides obtained from HPLC preparative separation on a chiral stationary phase (2.5-4.0 mM or 1 mg/1 mL) in appropriate solvent was irradiated in a Rayonet reactor fitted with bulb of desired wavelength. After the 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, $[\alpha]_D$ and by HPLC. HPLC analysis of the photoproduct(s) on a chiral stationary phase gave the optical purity of the photoproducts.

Large-scale reactions: Large-scale reactions were carried out on racemic maleimides as batches (4 × 20 mL test tubes per batch). After the irradiation the solutions were combined and the solvent was evaporated under reduced pressure. The residue was purified by combiflash using a hexanes:ethyl acetate mixture as mobile phase. Conversion and mass balance were obtained from NMR integration of the crude reaction mixture against triphenylmethane as an internal standard using the following formula

$$\mathbf{mol_a = mol_i\ X \left(\frac{Integral\ of\ analyte}{Integral\ of\ Int.\ Std}\right)\ X\ \frac{N_a}{N_i}}$$

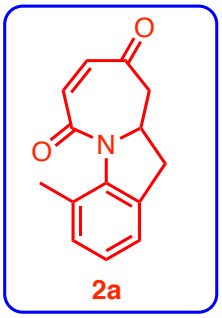
Where, N_a and N_i are the number of nuclei giving rise to the relevant analyte and internal standard signals respectively. Similarly mol_a and mol_i are the molarity of analyte and the internal standard in deuterated chloroform, respectively.

The *dr* of the photoproducts **2** and **3** were calculated from the crude reaction mixture after the photoreaction.

Table S4: Analysis of conversion and *dr* in the photoproducts

Entry	Compound	% NMR Yield (% mass balance)	*dr* (**2**:**3**)
1	**1a**	26 (60)	-
2	**1b**	16(76)	60:40
3	**1c**	20 (60)	65:35
4	**1d**	50(85)	70:30
5	**1e**	14(86)	74:26
6	**1f**	18(50)	99:1
7	**1g**	26(98)	45:55
8	**1h**	18(98)	69:31
9	**1i**	No reaction	

Note: The reported value carry an error of ±5%.

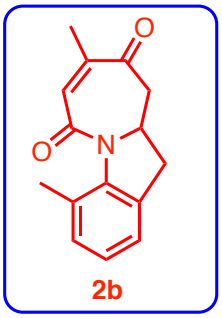


2a

TLC condition - R*f* = 0.30 (80% hexanes:20% ethyl acetate) for **2a**

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.05-7.01 (m, 3H), 6.58-6.6.55 (m, 1H), 6.39-6.36 (m, 1H), 5.08-5.02 (m, 1H), 3.66-3.59 (m, 1H), 3.08-2.99 (m, 1H), 2.78-2.72 (m, 2H) and 2.23 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 209.9, 172.5, 148.9, 146.3, 145.7, 141.5, 141.3, 138.2, 135.7, 132.4, 67.0, 60.9, 44.5 and 31.9.

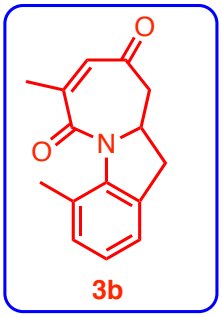


2b

TLC condition - R*f* = 0.15 (80% hexanes:20% ethyl acetate) for **2b**

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.03-6.99(m, 3H), 6.46-6.45 (m, 1H), 5.01-4.96 (m, 1H), 3.61-3.54 (m, 1H), 3.07-3.00 (m, 1H), 2.80-2.73 (m, 2H), 2.22 (s, 3H) and 2.05-2.04 (d, J = 4 Hz 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 200.9, 162.9, 145.3, 139.1, 132.3, 131.4, 131.2, 127.9, 125.4, 122.3, 56.6, 51.3, 34.3, 21.9 and 20.6.

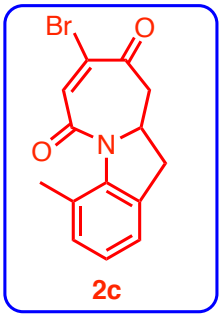


3b

TLC condition - R*f* = 0.2 (80% hexanes:20% ethyl acetate) for **3b**

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.07-7.02(m, 3H), 6.37 (s, 1H), 5.05-4.98 (m, 1H), 3.64-3.57 (m, 1H), 2.98-2.90 (m, 1H), 2.78-2.65 (m, 2H), 2.22 (s, 3H) and 2.18 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 199.7, 163.7, 145.1, 138.9, 133.1, 131.6, 131.2, 128.3, 125.5, 122.4, 56.9, 50.6, 34.1, 21.9 and 21.3.

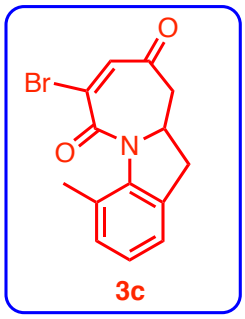


2c

TLC condition - R*f* = 0.30 (80% hexanes:20% ethyl acetate) for **2c**

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.19 (s, 1H), 7.05-7.02 (m, 3H), 5.07-4.99 (m, 1H), 3.65-3.58 (m, 1H), 3.19-3.11 (m, 1H), 2.92-2.75 (m, 2H) and 2.22 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 192.7, 160.3, 138.5, 137.5, 132.9, 131.4, 131.3, 128.2, 125.9, 122.5, 56.5, 50.3, 34.2 and 21.9.

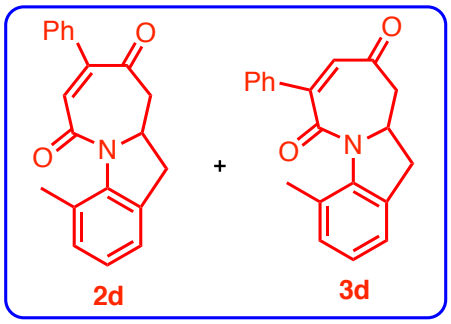


3c

TLC condition - R*f* = 0.2 (80% hexanes:20% ethyl acetate) for **3c**

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.08 (s, 1H), 7.07-7.04 (m, 3H), 5.13-5.06 (m, 1H), 3.68-3.61 (m, 1H), 2.99-2.91 (m, 1H), 2.79-2.70 (m, 2H) and 2.23 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 196.5, 158.1, 138.3, 137.7, 135.6, 131.4, 128.7, 126.2, 122.6, 57.2, 50.0, 34.1and 21.8.

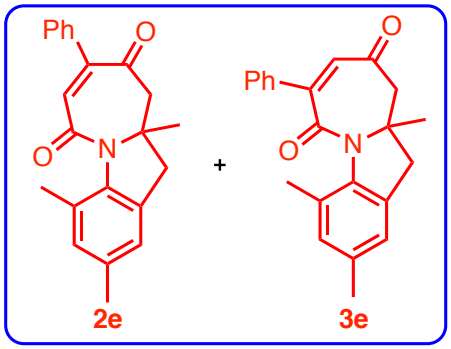


2d **3d**

TLC condition - R*f* = 0.40 (80% hexanes:20% ethyl acetate) for **2d** and **3d** (single spot)

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm), (Major **2d** + minor **3d**, 70:30): 7.50-7.27 (m, 16H), 7.06-7.04 (m, 9H), 6.67 (s, 2H), 6.62 (s, 1H), 5.23-5.13 (m, 3H), 3.64-3.58 (m, 3H), 3.18-3.11 (m, 2H), 3.01-2.95(m, 3H), 2.82-2.71 (m, 4H), 2.26 (s, 6H) and 2.25 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm), (Major **2d** + minor **3d**, 70:30): 201.9, 200.7, 163.7,162.9, 148.6, 146.6, 138.9, 138.7, 136.8, 135.5, 132.3, 131.8, 131.4, 131.2, 130.1, 129.8, 129.1, 128.8, 128.7, 128.5, 128.1, 128.0, 125.8, 125.5, 122.6, 122.54, 57.1, 57.0, 53.5, 50.8, 36.9, 33.9, 33.7, 29.9, 22.2 and 21.8

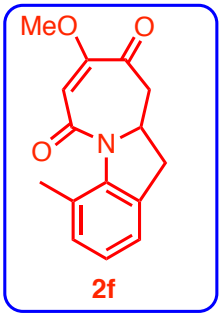


2e **3e**

TLC condition - R*f* = 0.20 (80% hexanes:20% ethyl acetate) for **2e** and **3e** (single spot)

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm), (Major **2e** + minor **3e**, 74:26): 7.57-7.54 (m, 2H), 7.41-7.38 (m, 10H), 7.06 (s, 1H), 6.89-6.87 (m, 5H), 6.48-6.47 (d, J = 2 Hz, 1H), 3.62-3.59 (d, J = 14 Hz, 2H), 3.48-3.45 (d, J = 15 Hz, 3H), 3.38-3.30 (m, 3H), 3.11-3.07 (d, J = 14 Hz, 2H), 2.99-2.92 (m, 2H), 2.86-2.82 (d, J = 15.2 Hz, 2H), 2.29-2.28 (m, 8H), 2.14 (s, 4H), 2.09 (s, 3H), 1.43 (s, 3H) and 1.33 (s, 4H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm), (Major **2e** + minor **3e**, 74:26): 196.5, 195.4, 163.9, 161.7, 152.1, 142.5, 139.4, 138.6, 138.2, 137.8, 135.8, 135.8, 135.4, 132.6, 131.6, 131.4, 131.2, 129.8, 129.2, 129.1, 128.9, 128.96, 128.7, 128.5, 128.48, 128.3, 122.96, 122.90, 64.84, 64.80, 54.2, 53.9, 47.6, 46.9, 23.2, 22.7, 21.8, 21.2, 21.1, 21.0

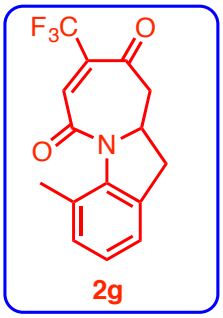


2f

TLC condition - R*f* = 0.20 (50% hexanes:50% ethyl acetate) for **2f**

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.03-6.99 (m, 3H), 5.74 (s, 1H), 5.07-5.02 (m, 1H), 3.76 (s, 3H), 3.65-3.58 (m, 1H), 3.09-3.02 (m, 1H), 2.86-2.70 (m, 2H), and 2.22 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 194.8, 163.1, 158.9, 139.2, 131.2, 130.9, 131.3, 127.9, 125.2, 122.4, 106.3, 56.4, 56.38, 34.1 and 21.8.

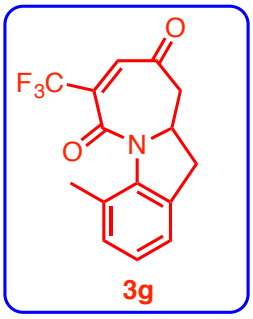


2g

TLC condition - R*f* = 0.20 (80% hexanes:20% ethyl acetate) for **2g**

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.13-7.09(m, 3H), 6.95 (s, 1H), 5.16-5.09 (m, 1H), 3.76-3.69 (m, 1H), 3.14-3.06 (m, 1H), 2.89-2.82 (m, 2H)) and 2.29 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 197.7, 157.7, 137.9, 135.7, 135.6, 131.3, 131.1, 128.5, 126.1, 122.4, 56.9, 50.6, 33.6, 29.7 and 21.7.

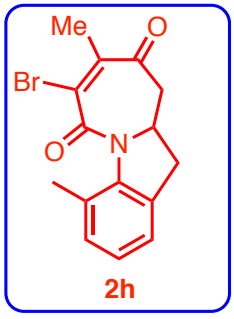


3g

TLC condition - R*f* = 0.10 (80% hexanes:20% ethyl acetate) for **3g**

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.12-7.09(m, 4H), 5.11-5.04 (m, 1H), 3.72-3.66 (m, 1H),3.22-3.15 (m, 1H), 2.99-2.85 (m, 2H) and 2.29 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 193.7, 159.9, 138.1, 135.9, 131.3, 131.2, 128.3, 126.2, 122.4, 119.8, 56.5, 51.6, 33.9, 29.7 and 21.7.

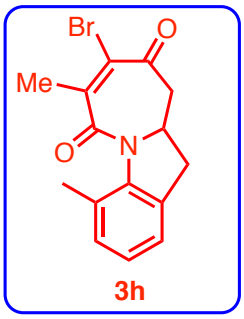


2h

TLC condition - R*f* = 0.40 (80% hexanes:20% ethyl acetate) for **2h**

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.05-7.02(m, 3H), 5.09-5.02 (m, 1H), 3.63-3.37 (m, 1H), 2.99-2.92 (m, 1H), 2.84-2.73 (m, 2H), 2.24 (s, 3H) and 2.21 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 199.7, 159.4, 145.9, 138.4, 131.4, 129.3, 128.4, 125.9, 122.6, 56.6, 50.9, 33.5, 22.9 and 21.8.



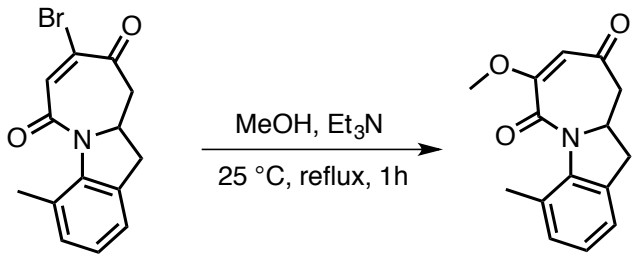
3h

TLC condition - R*f* = 0.2 (80% hexanes:20% ethyl acetate) for **3h**

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.05-7.02 (m, 3H), 5.04-4.97 (m, 1H), 3.62-3.56 (m, 1H), 3.07-2.99 (m, 1H), 2.89-2.84 (m,1H), 2.79-2.74 (m, 1H), 2.31 (s, 3H) and 2.19 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 195.2, 161.9, 142.2, 138.3, 131.3, 131.32, 129.4, 128.3, 125.9, 122.6, 56.4, 50.5, 33.5, 21.8 and 21.5.

6.4. Synthesis of minor methoxy maleimides photoproduct **3f**



2c **3f**

Scheme S9: Synthesis of minor methoxy maleimides photoproduct **3f**

To a solution of bromo maleimide derivative **2c** (10 mg, 1.0 *equiv.*) in MeOH (5 mL) triethylamine in MeOH (1.1 *equiv.*) was added and the resulting mixture refluxed for 1 h. After the reaction, the solvent was concentrated and the reaction mixture was quenched with DI water. The aqueous layer is extracted with DCM (20 mL). The combined organic layer was dried over *anhyd.* Na_2SO_4, filtered and concentrated under reduced pressure to yield crude product. The crude product was purified by combiflash using a hexanes:ethyl acetate mixture. Since the yield was very low (>0.5 mg was isolated) the product was characterized by mass spectrometry and HPLC.

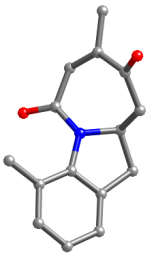
TLC condition - R*f* = 0.10 (50% hexanes:50% ethyl acetate) for **3f**

7. X-Ray crystal structure data for atropisomeric maleimides and its photoproducts

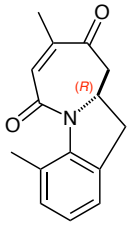
Structure determination: Single crystal X-ray diffraction data of the compounds **2** and **3** were collected on a Bruker Apex Duo diffractometer with a Apex 2 CCD area detector at T = 100K. Cu radiation was used. All structures were process with Apex 2 v2010.9-1 software package (SAINT v. 7.68A, XSHELL v. 6.3.1). 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

	(*10R*)-**2b** (PkA)	(*10S*)-**2b** (PkB)	**2c**	**3c**	**2f**	**2g**	**3g**
Formula	$C_{15}H_{15}NO_2$	$C_{15}H_{15}NO_2$	$C_{14}H_{12}BrNO_2$	$C_{14}H_{12}BrNO_2$	$C_{15}H_{15}NO_3$	$C_{15}H_{12}F_3NO_2$	$C_{15}H_{12}F_3NO_2$
FW	241.29	241.29	306.16	306.16	257.29	295.26	295.26
cryst. size_max [mm]	0.24	0.22	0.24	0.301	0.227	0.16	0.2
cryst. size_mid [mm]	0.17	0.20	0.166	0.23	0.221	0.11	0.182
cryst. size_min [mm]	0.14	0.12	0.06	0.21	0.045	0.05	0.075
cryst. system	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space Group, Z	'$P2_12_12_1$', 4	'$P2_12_12_1$', 4	'$P12_{1/n}1$', 4	'$P2_12_12_1$', 4	'$P12_{1/n}1$', 8	'$P\ 1\ 2_{1/c}\ 1$', 4	'$P12_11$', 2
a [Å]	7.9647(2)	7.9650(2)	18.1984(5)	8.5431(8)	16.9222(7)	9.6309(3)	8.7121(3)
b [Å]	9.5076(3)	9.5073(4)	7.3629(2)	9.8089(8)	7.6509(3)	7.8723(2)	11.7093 (3)
c [Å]	16.0492(5)	16.0506(4)	19.2858(5)	14.6636(12)	20.5384(8)	17.2740(3)	14.2353(4)
α [Å]	90	90	90	90	90	90	76.9998(11)
ß [Å]	90	90	108.4870(10)	90	109.285(2)	96.9200(12)	72.3793(11)
γ [Å]	90	90	90	90	90	90	69.8941(6)
V [$Å^3$]	1215.33(6)	1215.44(5)	2450.81(11)	1228.79(18)	2509.90(18)	1300.13(6)	1287.79(7)
ρ_{calc} [g/mm^3]	1.319	1.319	1.665	1.665	1.362	1.508	1.523
μ [mm^{-1}]	0.704	0.704	4.534	3.338	0.779	1.117	1.128
Radiation Type	Cu	Cu	Cu	Cu	Cu	Cu	Cu
F(000)	512	512	1236	616	1088	608	608
no of measured refl.	7249	9006	34112	9446	15458	15086	16410
no of indep. refl.	2119	2206	4323	2719	4309	2304	4407
no of refl. (I ≥ 2σ)	2077	2165	3735	2542	3820	2001	4025
Resolution [Å]	0.84	0.84	0.84	0.84	0.84	0.84	0.84
R1/wR2 (I ≥ 2σ)[a] [%]	2.77/6.79	2.66/6.56	3.21/7.78	0.00/4.25	0.000/28.73	4.50/11.28	3.51/8.72
R1/wR2 (all data) [%]	2.83/6.84	2.72/6.61	3.84/8.22	0.001/4.36	0.000/29.02	5.08/11.69	3.83/8.93

7.1. Photoproduct (*10R*)-**2b** (crystallized from hexanes:$CHCl_3$)

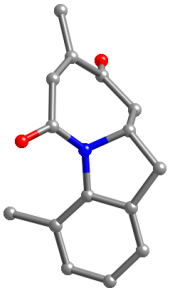


2b

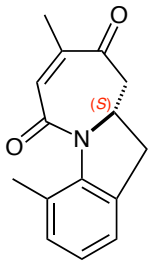


2b

7.2. Photoproduct (*10S*)-**2b** (crystallized from hexanes:$CHCl_3$)

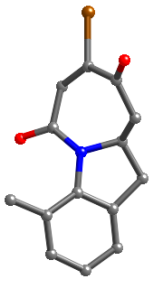


2b

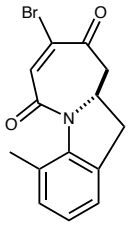


2b

7.3. Photoproduct **2c** (crystallized from hexanes:$CHCl_3$)

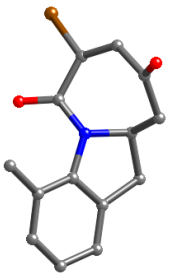


2c

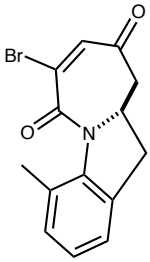


2c

7.4. Photoproduct **3c** (crystallized from hexanes:$CHCl_3$)

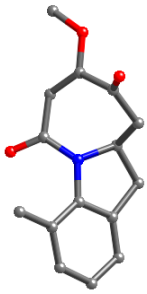


3c

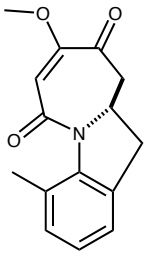


3c

7.5. Photoproduct **2f** (crystallized from hexanes:$CHCl_3$)



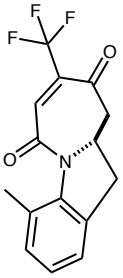
2f



2f

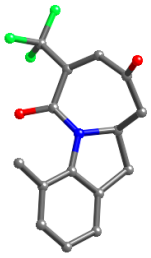
7.6. Photoproduct **2g** (crystallized from hexanes:$CHCl_3$)

2g

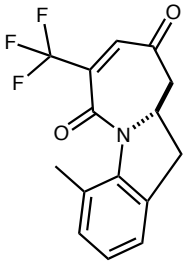


2g

7.7. Photoproduct **3g** (crystallized from hexanes:$CHCl_3$)



3g



3g

---

8. References:

1. Görl, C.; Alt, H. G. *J. Mol. Catal. A: Chem.* **2007**, *273*, 118.

2. Kumarasamy, E.; Raghunathan, R.; Jockusch, S.; Ugrinov. A.; Sivaguru. J. *J. Am. Chem. Soc.* **2014**, *136*, 8729.

3. Kajigaeshi, S.; Kakinami, T.; Yamasaki, H.; Fujisaki, S.; Okamoto, T. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 600.

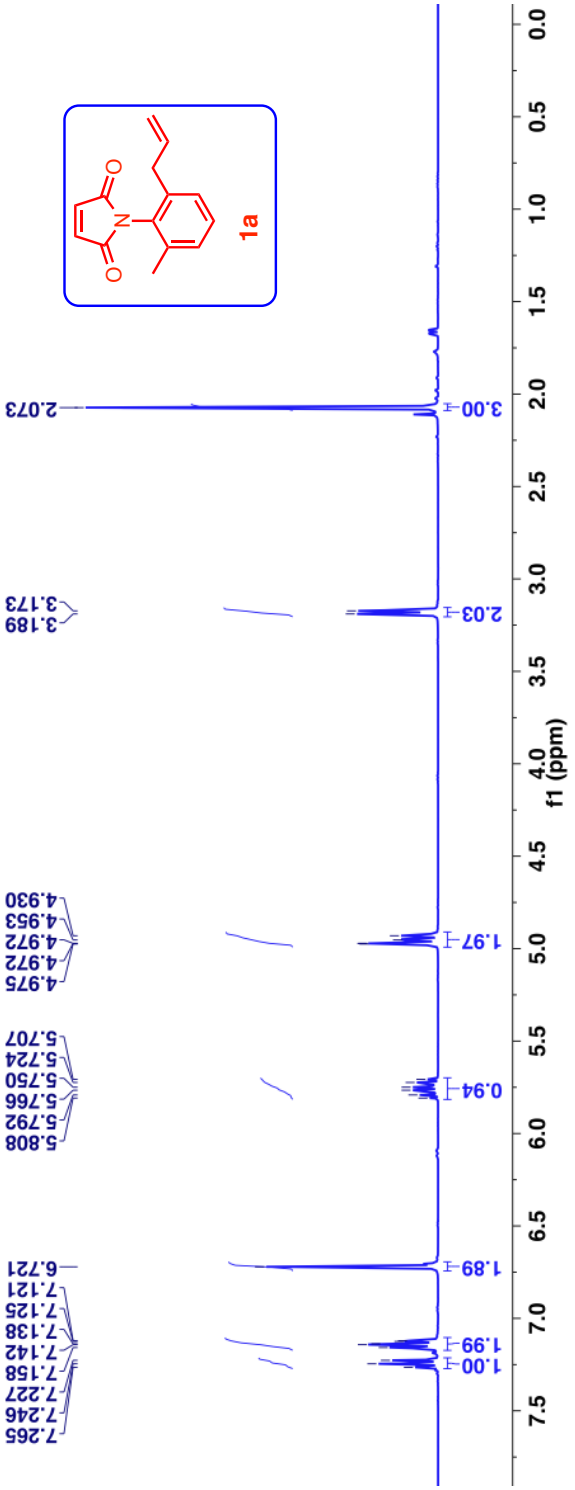
4. Tidwell, J. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 11797.

5. Yip, K.-T.; Yang, M.; Law, K.-L.; Zhu, N.-Y.; Yang, D. *J. Am. Chem. Soc.* **2006**, *128*, 3130.

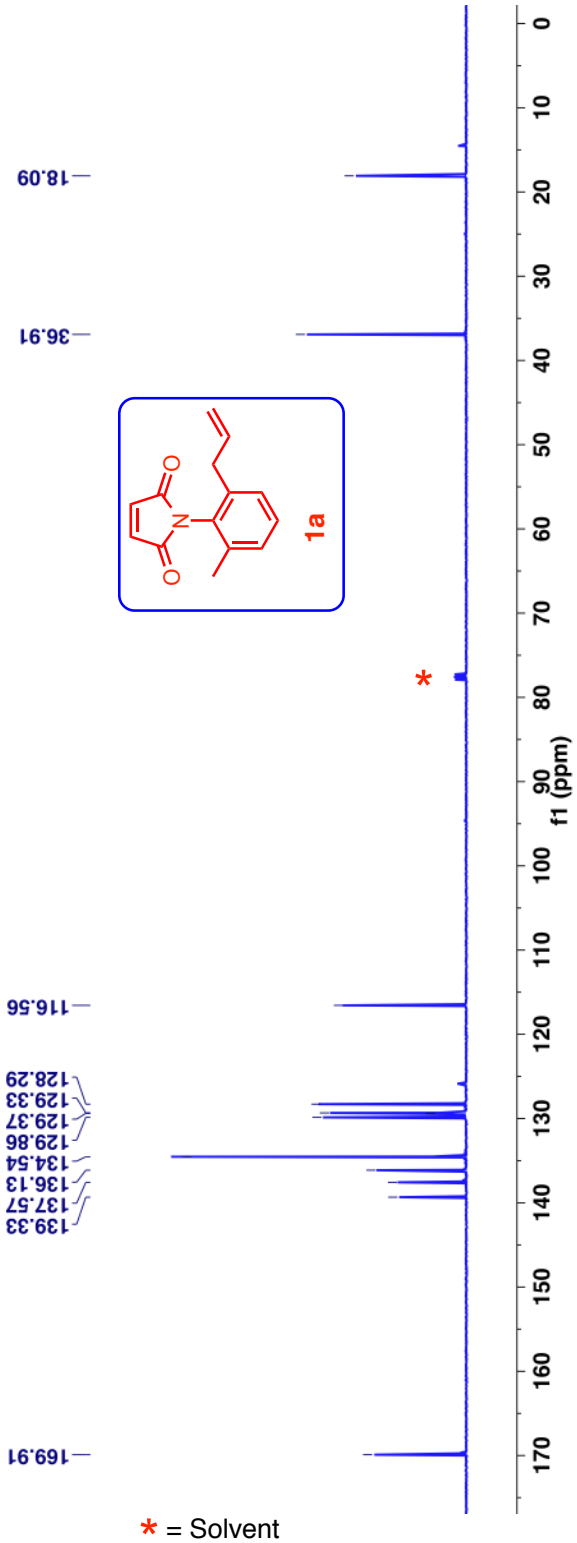
6. Kumarasamy, E.; Sivaguru. J Chem. Commun. **2013**, *49*, 4346.

9. NMR spectra, HPLC and specific rotation data of maleimides and its photoproducts.

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.27-7.23 (m, 1H), 7.16-7.12 (m, 2H), 5.81-5.71 (m, 1H), 4.98-4.93 (m, 2H), 3.19-3.17 (d, J = 6.4 Hz, 2H) and 2.07 (s, 3H).

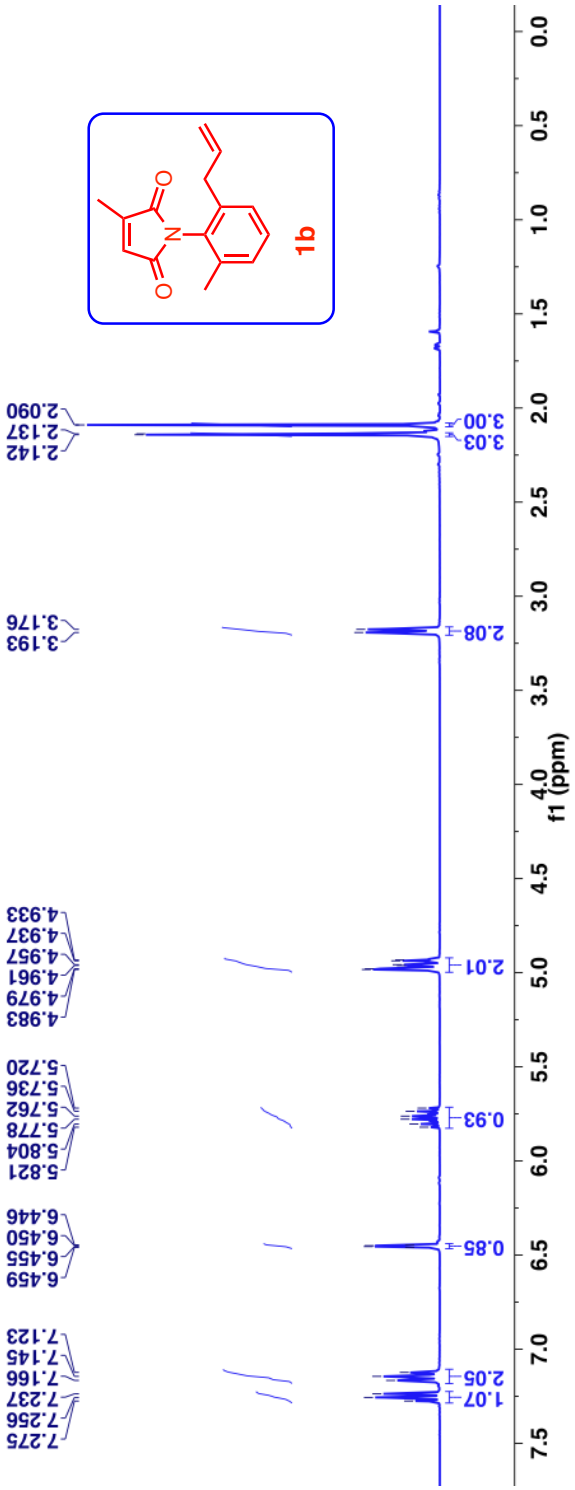


^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 169.9, 130.3, 137.6, 136.1, 134.5, 129.9, 129.4, 129.3, 128.3, 116.6, 36.9 and 18.1.

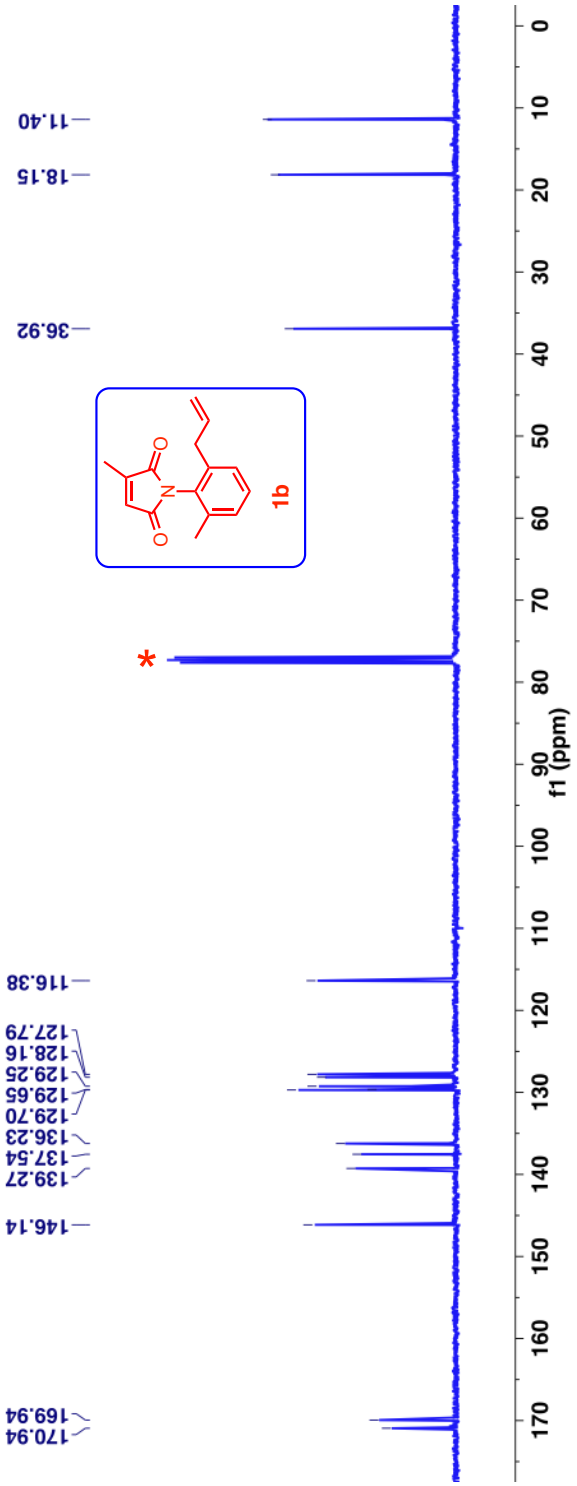


* = Solvent

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.28-7.24 (m, 1H), 7.17-7.12 (m, 2H), 6.46-6.45 (q, J = 5.2 Hz 1H), 5.82-5.72 (m, 1H), 4.98-4.93 (m, 2H), 3.19-3.17 (d, J = 6.8 Hz, 2H), 2.14-2.14 (d, J = 2 Hz, 2H) and 2.09 (s, 3H).

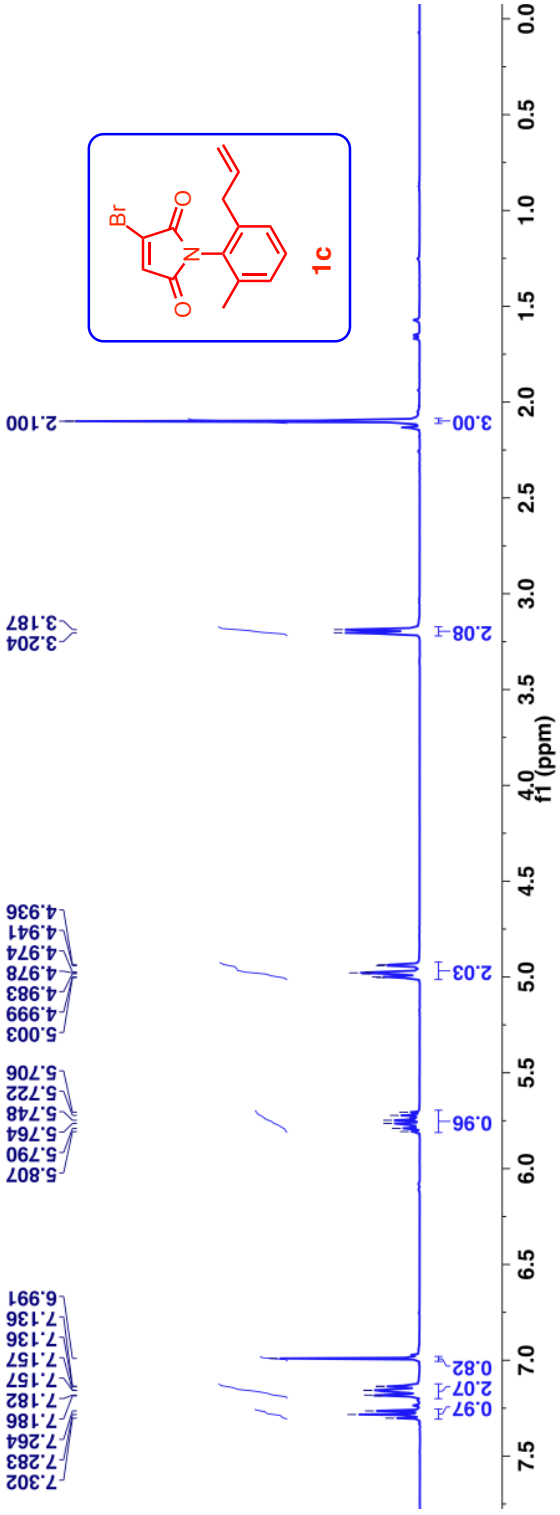


^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 170.9, 169.9, 146.1, 139.3, 137.5, 136.2, 129.7, 129.6, 129.3, 128.2, 127.8, 116.4, 36.9, 18.2 and 11.4.

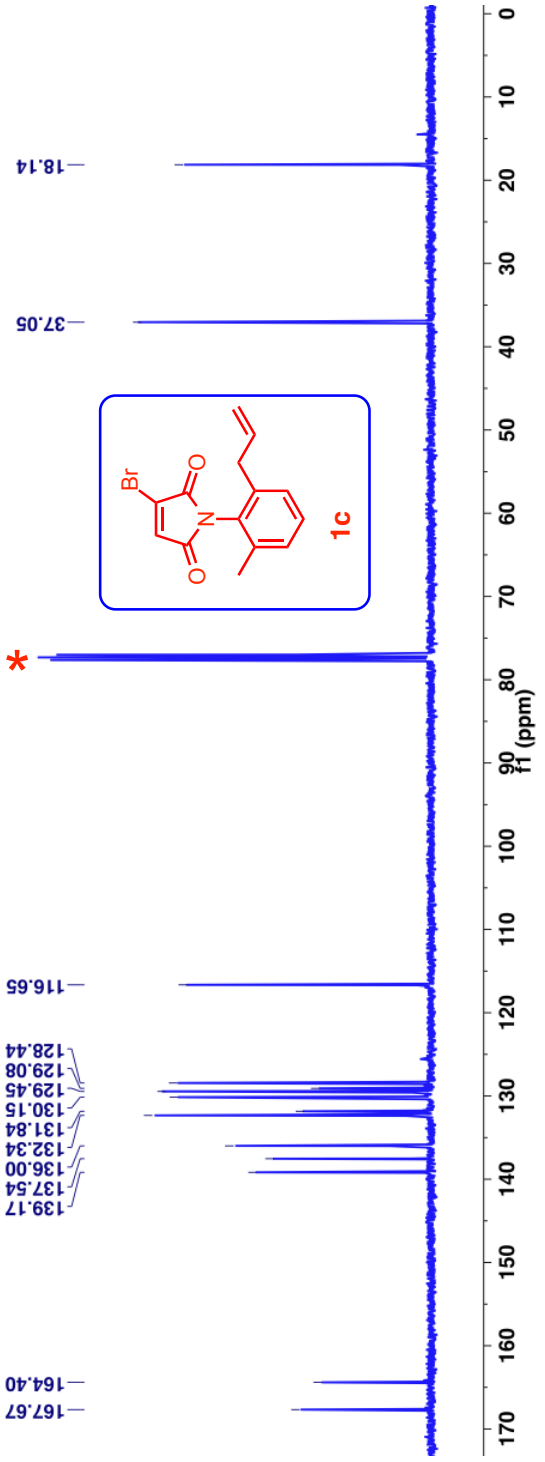


* = Solvent

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.30-7.26 (m, 1H), 7.18-7.14 (m, 2H), 6.99 (s, 1H), 5.81-5.71 (m, 1H), 5.00-4.94 (m, 2H), 3.20-3.19 (d, J = 6.8 Hz, 2H) and 2.10 (s, 3H).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 167.7, 164.4, 139.2, 137.5, 136.0, 132.3, 131.9, 130.2, 129.5, 129.1, 128.4, 116.7, 37.1 and 18.1.



* = Solvent

HPLC analysis conditions:

For analytical conditions,

I). Column	: CHIRALPAK-IC
Abs. detector wavelength	: 254 nm and 270 nm
Mobile phase	: Hexanes:2-propanol = 98:2
Flow rate	: 1.0 mL/min
Retention times (min)	: ~ 6.72 [(+)-**1c**] and ~ 7.40 [(-)-**1c**]

For preparative conditions,

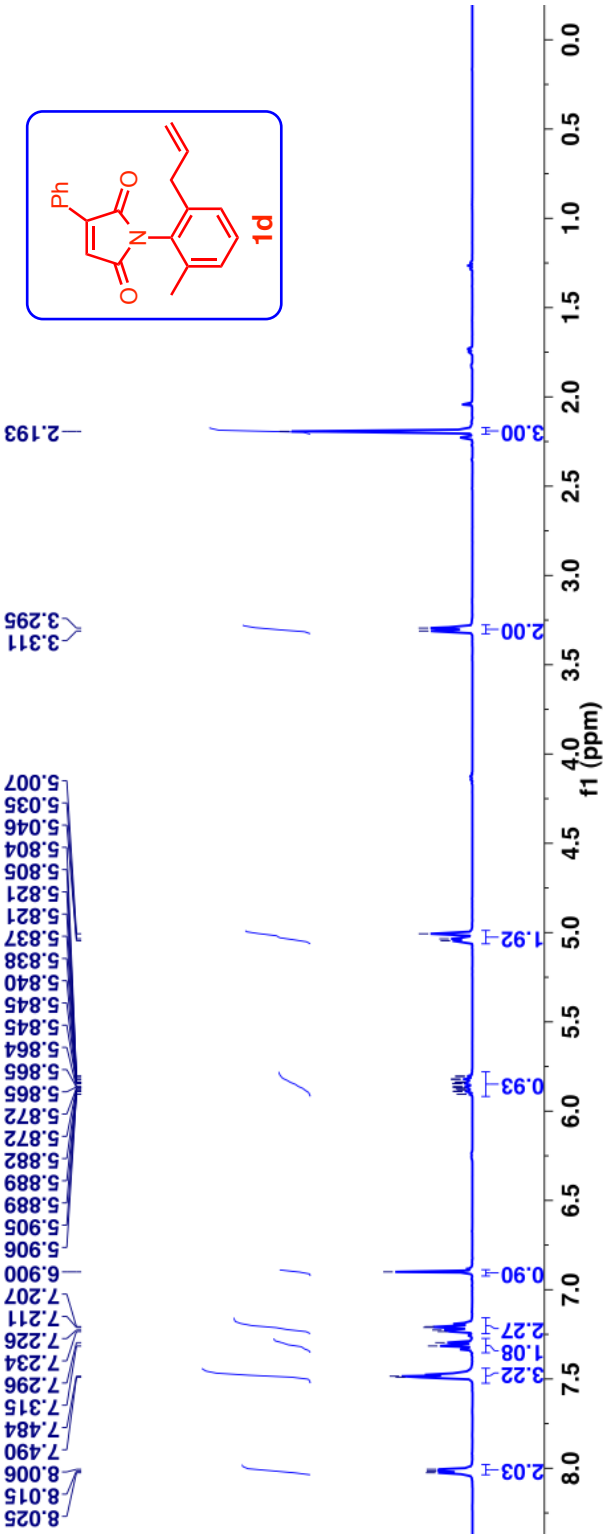
I). Column	: CHIRALPAK-IC
Abs. detector wavelength	: 254 nm and 270 nm
Mobile phase	: Hexanes:2-propanol = 99:1
Flow rate	: 3.0 mL/min
Retention times (min)	: ~ 13.05 [(+)-**1c** and ~ 15.30 [(-)-**1c**]

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

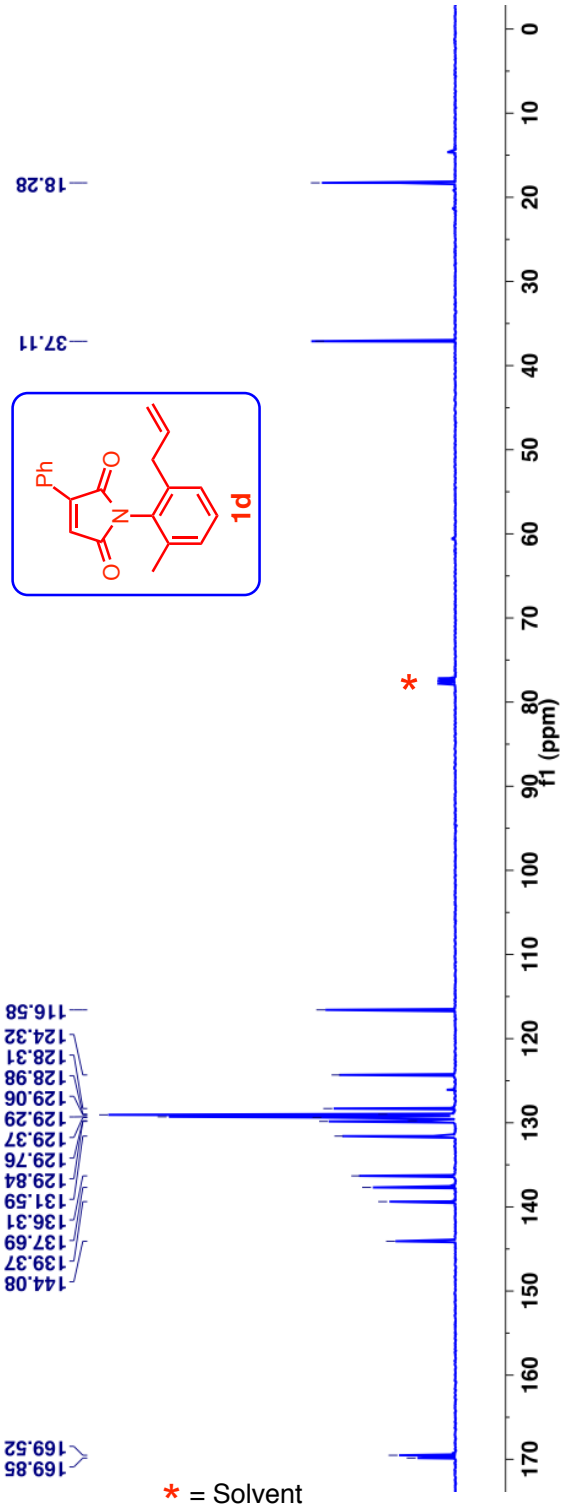
HPLC retention time (CHIRALPAK-IC) at ~ 6.72 min, (*c* ≈ 0.383 %, $CHCl_3$) = +8.33 deg

HPLC retention time (CHIRALPAK-IC) at ~ 7.40 min, (*c* ≈ 0.383 %, $CHCl_3$) = -8.85 deg.

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 8.03-8.00 (m, 2H), 7.49-7.48 (m, 3H), 7.32-7.29 (m, 1H), 7.23-7.21 (m, 2H), 6.90 (s, 1H), 5.91-5.80 (m, 1H), 5.04-5.00 (m, 2H), 3.31-3.29 (d, J = 6.4 Hz, 2H) and 2.1 (s, 3H).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 169.9, 169.5, 144.1, 139.4, 137.7, 136.3, 131.6, 129.8, 129.8, 129.4, 129.3, 129.1, 128.9, 128.3, 124.3, 116.6, 37.1 and 18.3.



* = Solvent

HPLC analysis conditions:

For analytical conditions,

I). Column	: CHIRALPAK-ADH
Abs. detector wavelength	: 254 nm and 270 nm
Mobile phase	: Hexanes:2-propanol = 95:5
Flow rate	: 1.0 mL/min
Retention times (min)	: ~ 7.17 [(+)-**1d**] and ~ 7.72 [(-)-**1d**]

For preparative conditions,

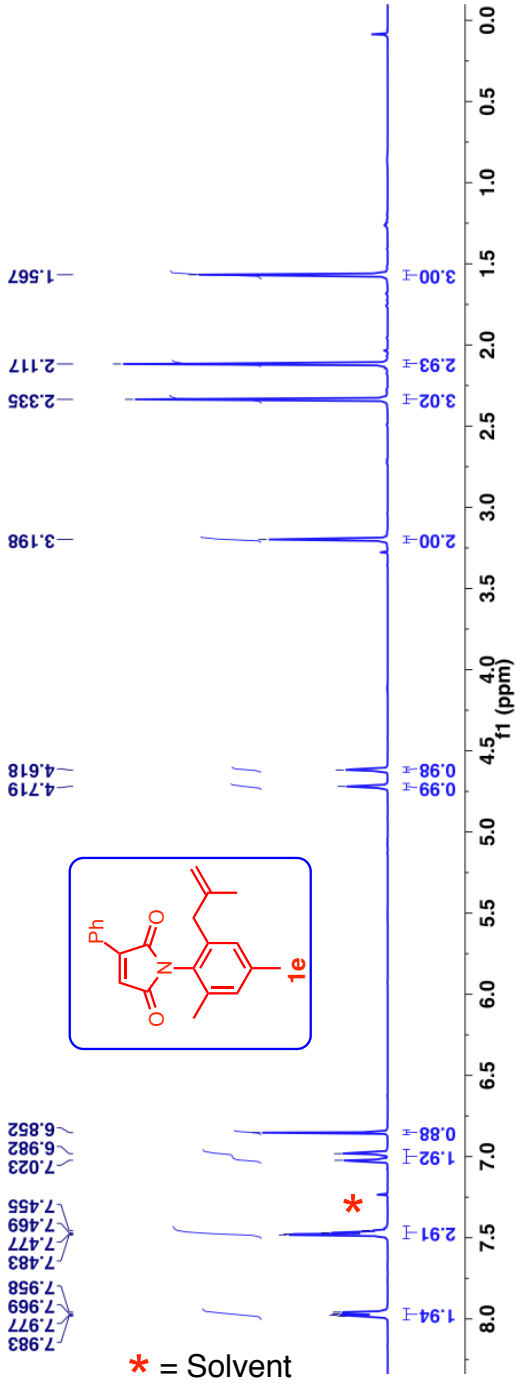
I). Column	: CHIRALPAK-ADH
Abs. detector wavelength	: 254 nm and 270 nm
Mobile phase	: Hexanes:2-propanol = 99:1
Flow rate	: 3.0 mL/min
Retention times (min)	: ~ 31.95 [(+)-**1d** and ~ 36.02 [(-)-**1d**]

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

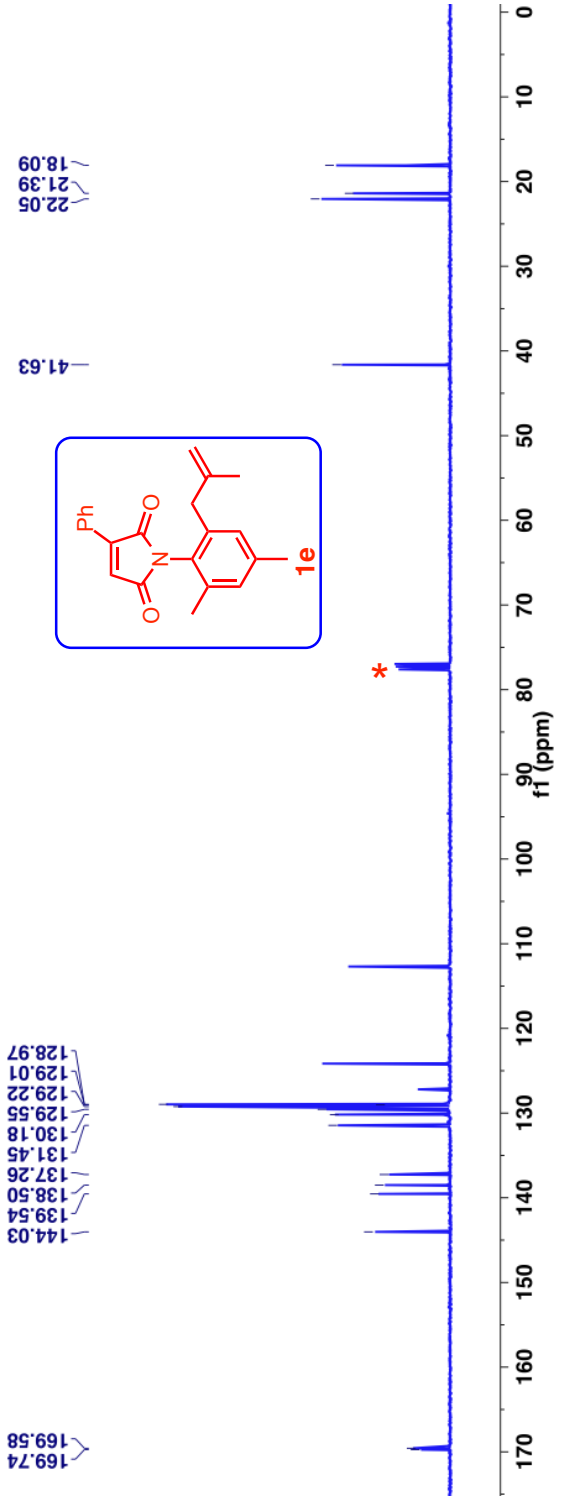
HPLC retention time (CHIRALPAK-ADH) at ~ 7.17 min, (*c* ≈ 0.231 %, $CHCl_3$) = +7.10 deg

HPLC retention time (CHIRALPAK-ADH) at ~ 7.72 min, (*c* ≈ 0.231 %, $CHCl_3$) = -7.45 deg.

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.98-7.96 (m, 2H), 7.48-7.46 (m, 3H), 7.02-6.98 (d, J = 16.4, 2H), 6.85 (s, 1H), 4.72 (s, 1H), 4.62 (s, 1H), 3.19 (s, 2H), 2.34 (s, 3H), 2.12 (s, 3H), and 1.59 (s, 3H).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 169.7, 169.6, 144.0, 139.5, 138.5, 137.3, 131.5, 130.2, 129.6, 129.2, 129.0, 128.9, 42.6, 22.1, 21.4 and 18.1.



* = Solvent

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)	: ~ 6.12 [(+)-**1e**] and ~ 6.64 [(-)-**1e**]

For preparative conditions,

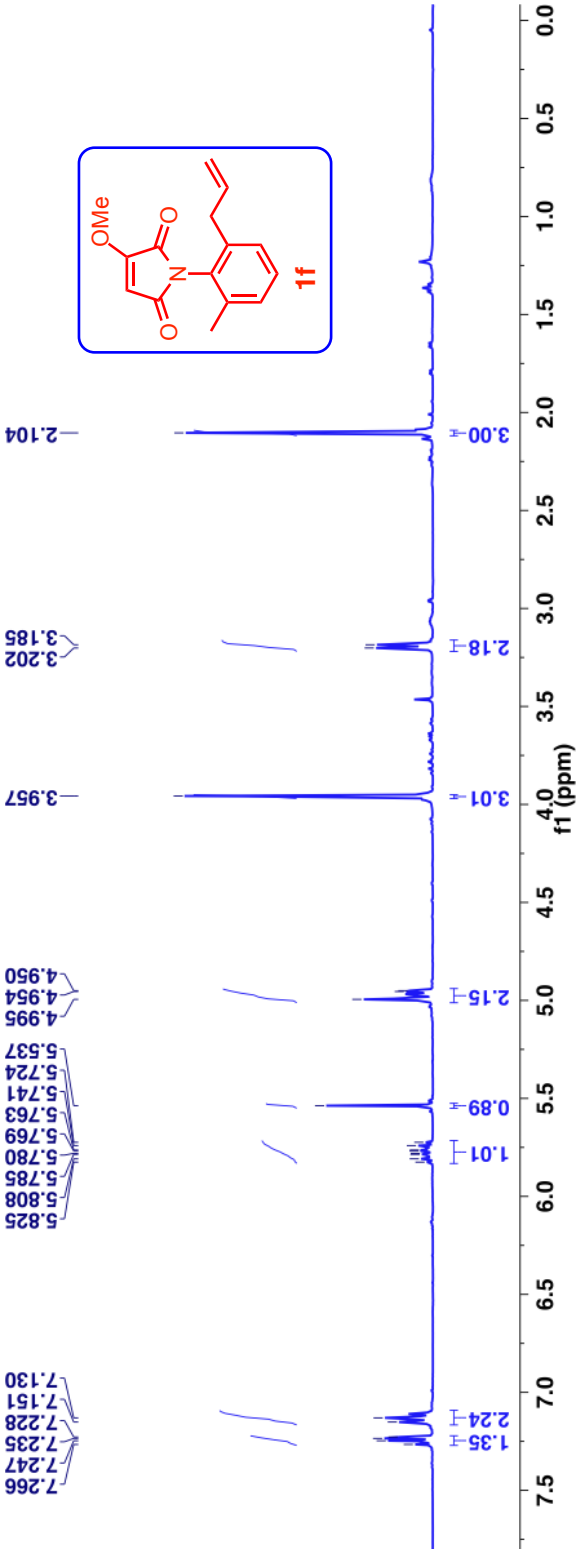
I). Column	: CHIRALPAK-IC
Abs. detector wavelength	: 254 nm and 270 nm
Mobile phase	: Hexanes:2-propanol = 99:1
Flow rate	: 3.0 mL/min
Retention times (min)	: ~ 19.53 [(+)-**1e** and ~ 22.10 [(-)-**1e**]

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

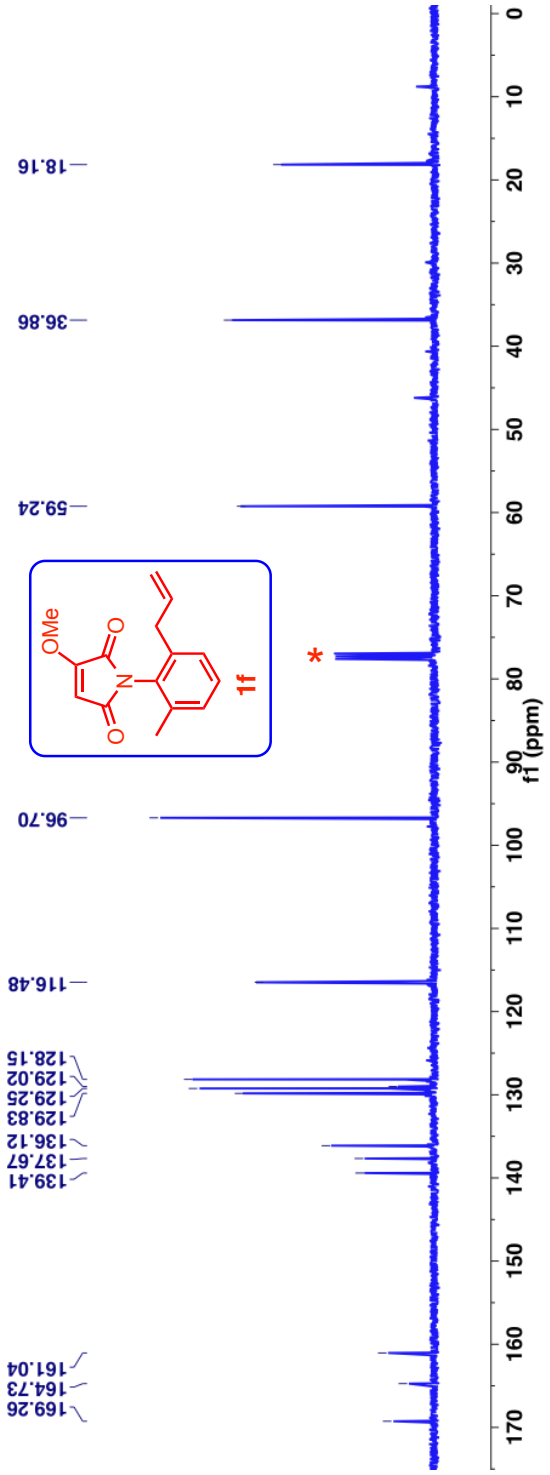
HPLC retention time (CHIRALPAK-IC) at ~ 6.12 min, ($c \approx 1.364$ %, $CHCl_3$) = +7.88 deg

HPLC retention time (CHIRALPAK-IC) at ~ 6.64 min, ($c \approx 1.364$ %, $CHCl_3$) = -7.74 deg.

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.27-7.23 (m, 1H), 7.15-7.11 (m, 2H), 5.83-5.72 (m, 1H), 5.54 (s, 1H), 4.99-4.95 (m, 2H), 3.96 (s, 3H), 3.20 (d, J = 6.8, 2H) and 2.10 (s, 3H).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 169.3, 164.7, 161.0, 139.4, 137.7, 137.1, 129.8, 129.3, 129.0, 128.2, 116.5, 96.7, 59.2, 36.9 and 18.2.



* = Solvent

HPLC analysis conditions:

For analytical conditions,

I). Column	: CHIRALPAK-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)	: ~ 13.59 [(-)-**1f**] and ~ 15.34 [(+)-**1f**]

For preparative conditions,

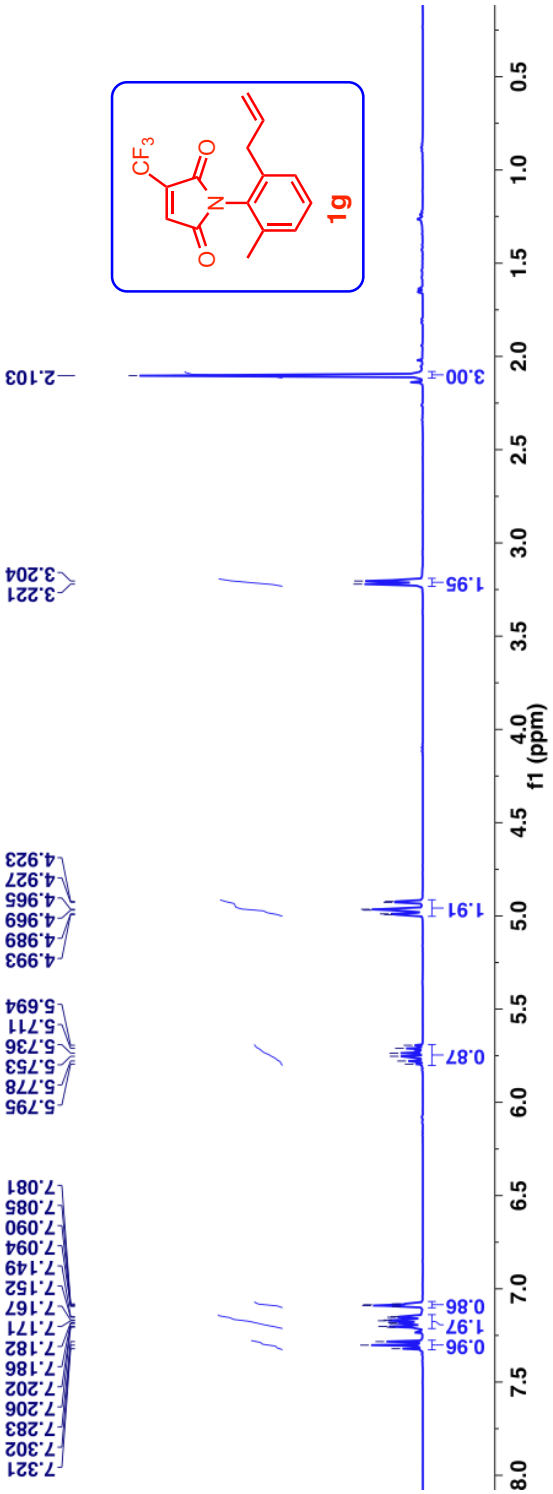
I). Column	: CHIRALPAK-IC
Abs. detector wavelength	: 254 nm and 270 nm
Mobile phase	: Hexanes:2-propanol = 99:1
Flow rate	: 3.0 mL/min
Retention times (min)	: ~ 5.64 [(-)**1f** and ~ 18.89 (+)**1f**]

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

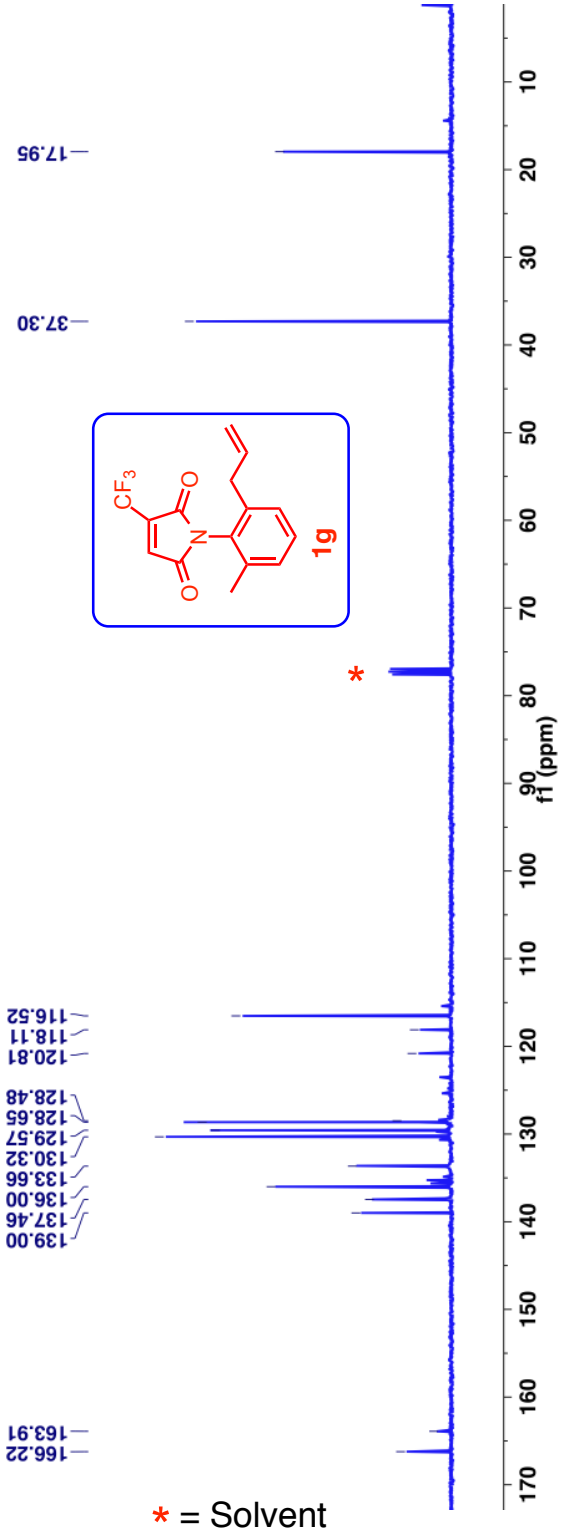
HPLC retention time (CHIRALPAK-IC) at ~ 13.59 min, (*c* ≈ 0.408 %, $CHCl_3$) = - 3.69 deg

HPLC retention time (CHIRALPAK-IC) at ~ 15.35 min, (*c* ≈ 0.408 %, $CHCl_3$) = +1.89 deg.

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.32-7.28 (m, 1H), 7.21-7.15 (m, 2H), 7.09-7.08 (q, J = 5.2Hz, 1H), 5.79-5.69 (m, 1H), 4.99-4.92 (m, 2H), 3.22-3.20 (d, J = 6.8 Hz, 2H) and 2.10 (s, 3H).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 166.2, 163.9, 139.0, 137.5, 136.0, 133.7, 130.3, 129.6, 128.7, 128.5, 120.8, 118.1, 116.5, 37.3 and 17.9.



* = Solvent

HPLC analysis conditions:

For analytical conditions,

I). Column : CHIRALPAK-ADH

Abs. detector wavelength : 254 nm and 270 nm

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

Flow rate : 1.0 mL/min

Retention times (min) : ~ 4.30 [(A)-**1g**] and ~ 5.30 [(B)-**1g**]

For preparative conditions,

I). Column : CHIRALPAK-ADH

Abs. detector wavelength : 254 nm and 270 nm

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

Flow rate : 3.0 mL/min

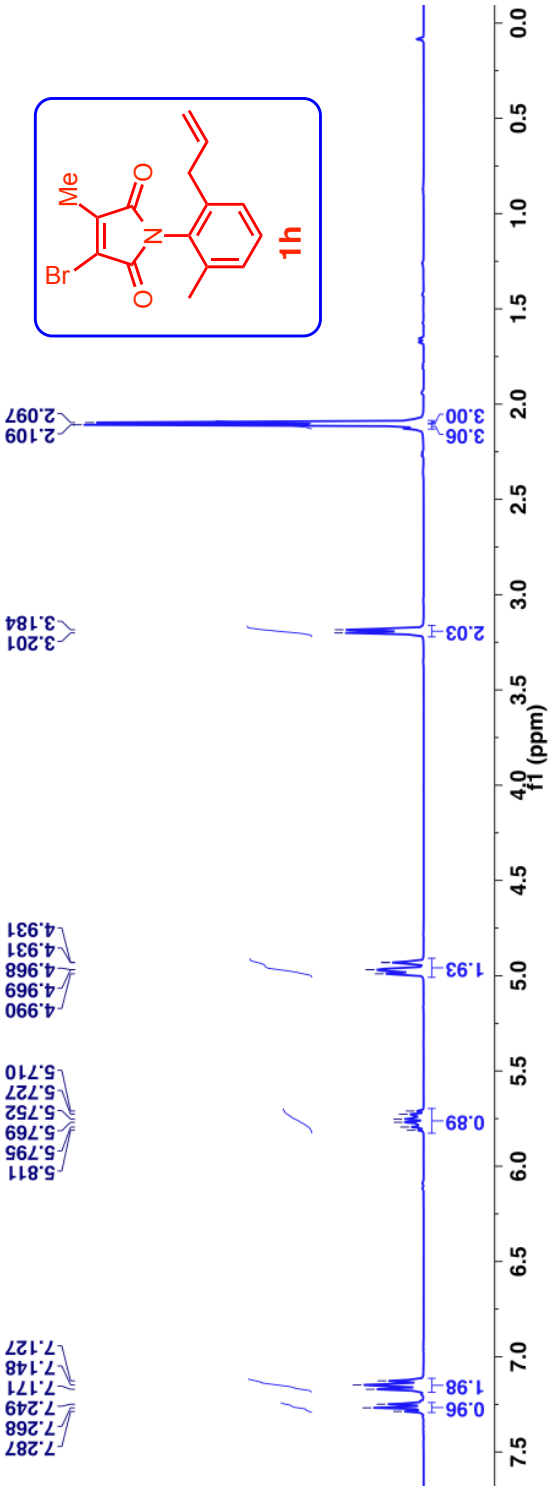
Retention times (min) : ~ 10.42 [(A)-**1g**] and ~ 12.42 [(B)-**1g**]

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

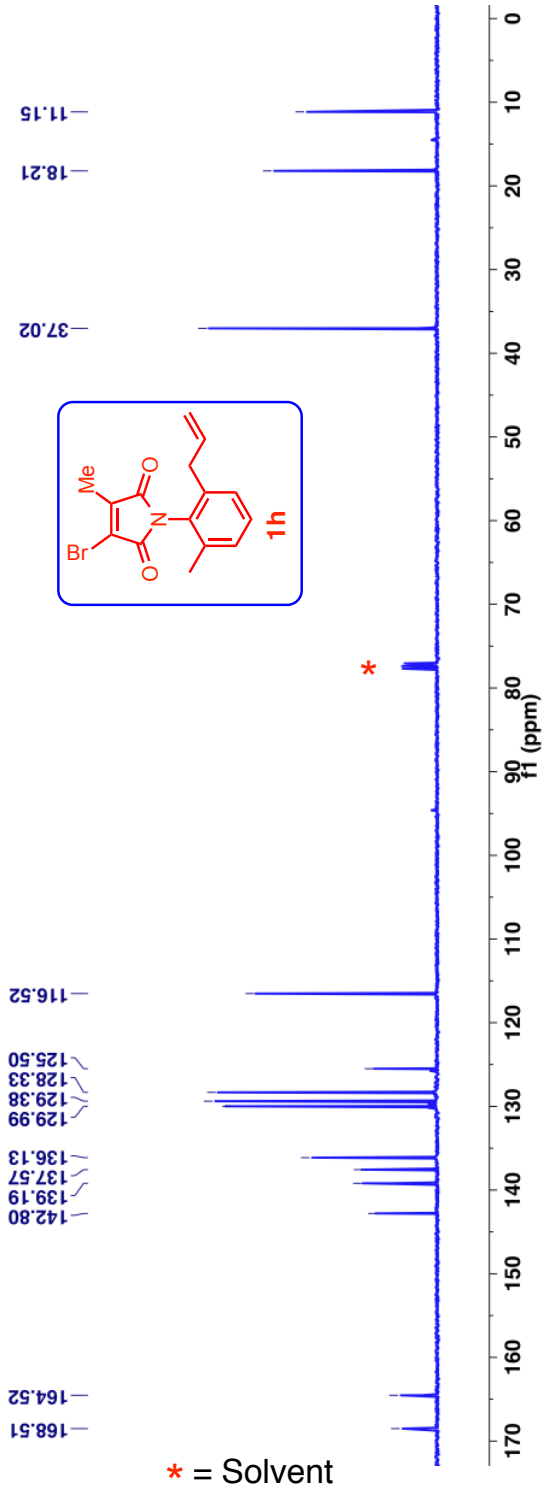
HPLC retention time (CHIRALPAK-ADH) at ~ 10.42 min, (*c* ≈ 0.283 %, $CHCl_3$) = +7.47 deg

HPLC retention time (CHIRALPAK-ADH) at ~ 12.42 min, (*c* ≈ 0.283 %, $CHCl_3$) = -7.21 deg.

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.29-7.25 (m, 1H), 7.18-7.15 (m, 2H), 5.81-5.71 (m, 1H), 4.99-4.93 (m, 2H), 3.20-3.18 (d, J = 6.8 Hz, 2H), 2.11 (s, 3H) and 2.09 (s, 3H).

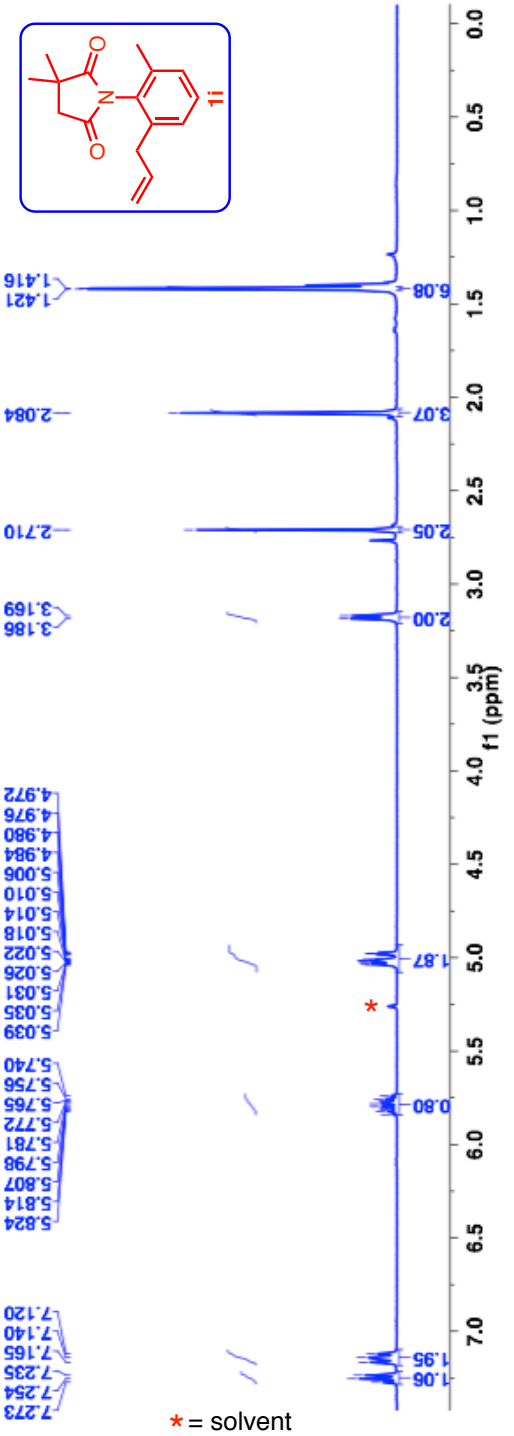


^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 168.5, 164.5, 142.8, 139.2, 137.6, 136.1, 129.9, 129.4, 128.3, 125.5, 116.5, 37.0, 18.2 and 11.2.

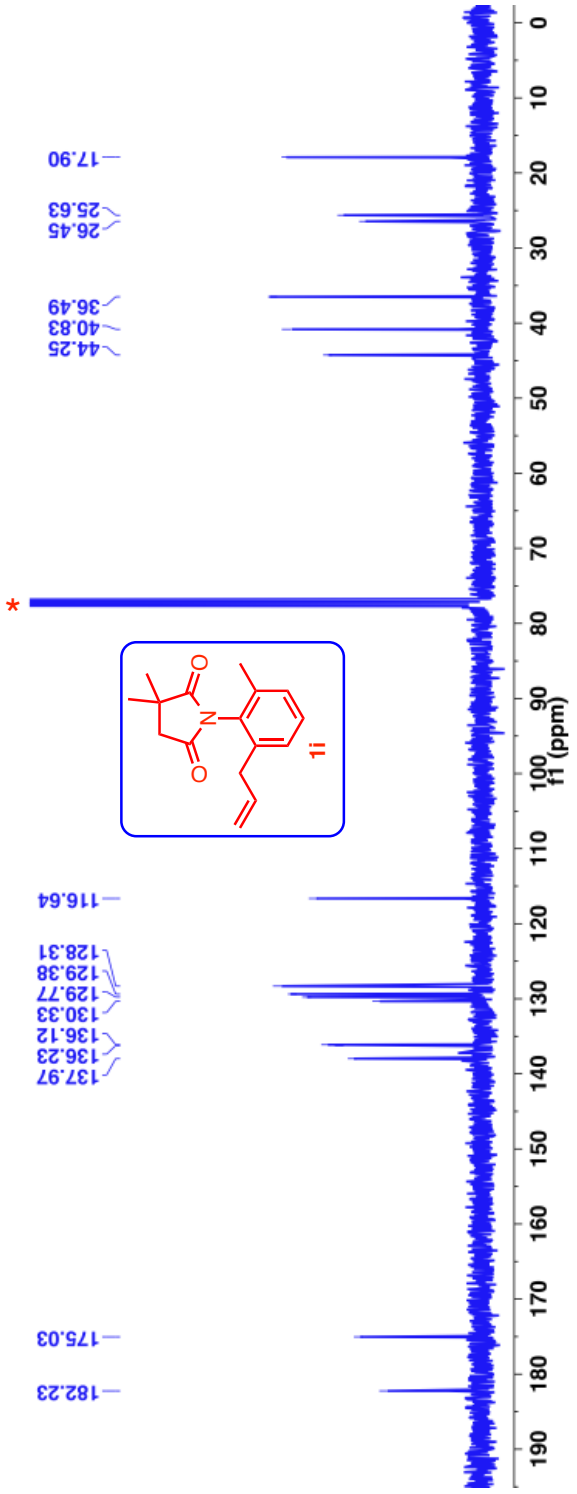


* = Solvent

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.27-7.23 (m, 1H), 7.16-7.12 (m, 2H), 5.84-5.74 (m, 1H), 5.03-4.97 (m, 2H), 3.18 (d, *J*=6.8 Hz, 2H), 2.71 (s, 2H), 2.08 (s, 3H), 1.421 (s, 3H) and 1.42 (s, 3H).

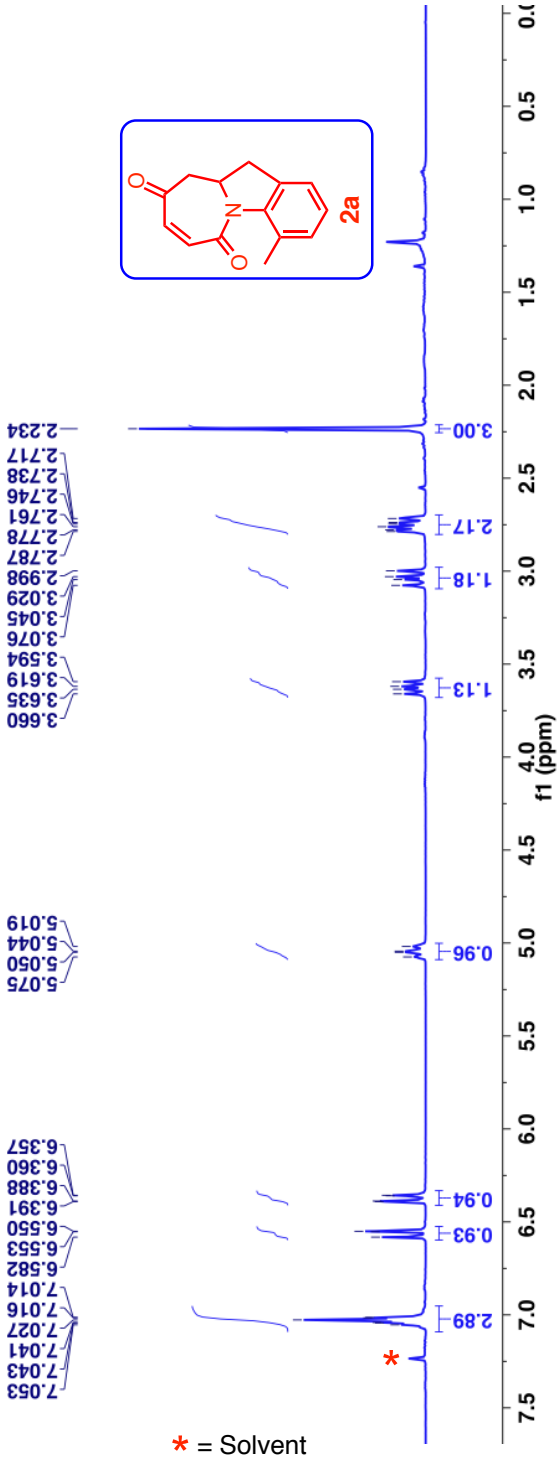


^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 182.2, 175.03, 137.97, 136.2, 136.1, 130.3, 129.8, 129.4,128.3, 116.6, 44.2, 40.8, 36.5, 26.4, 25.6, and 17.9.

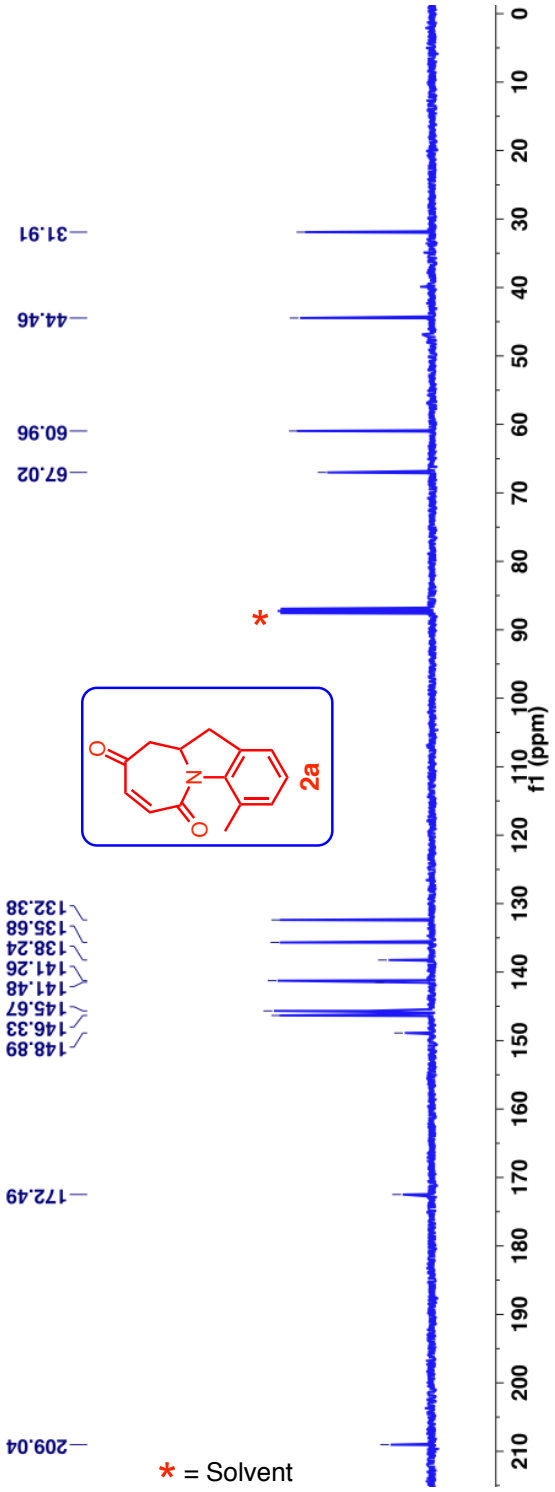


* = solvent

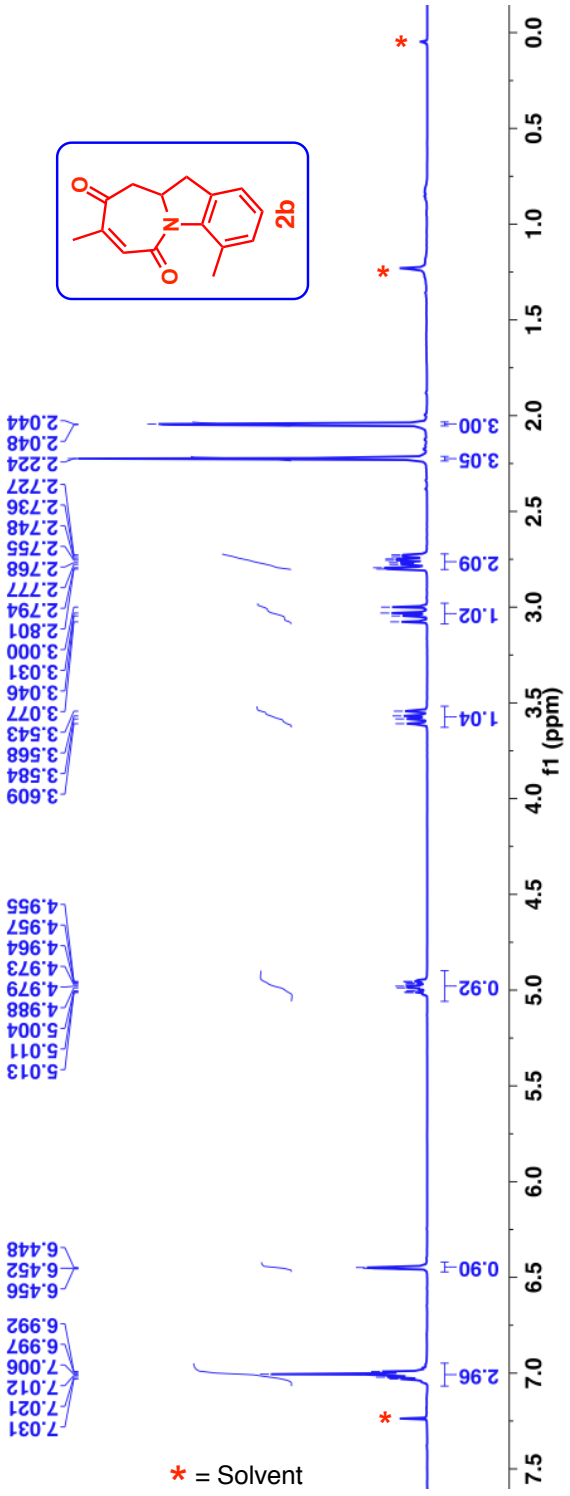
^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.05-7.01 (m, 3H), 6.58-6.6.55 (m, 1H), 6.39-6.36 (m, 1H), 5.08-5.02 (m, 1H), 3.66-3.59 (m, 1H), 3.08-2.99 (m, 1H), 2.78-2.72 (m, 2H) and 2.23 (s, 3H).



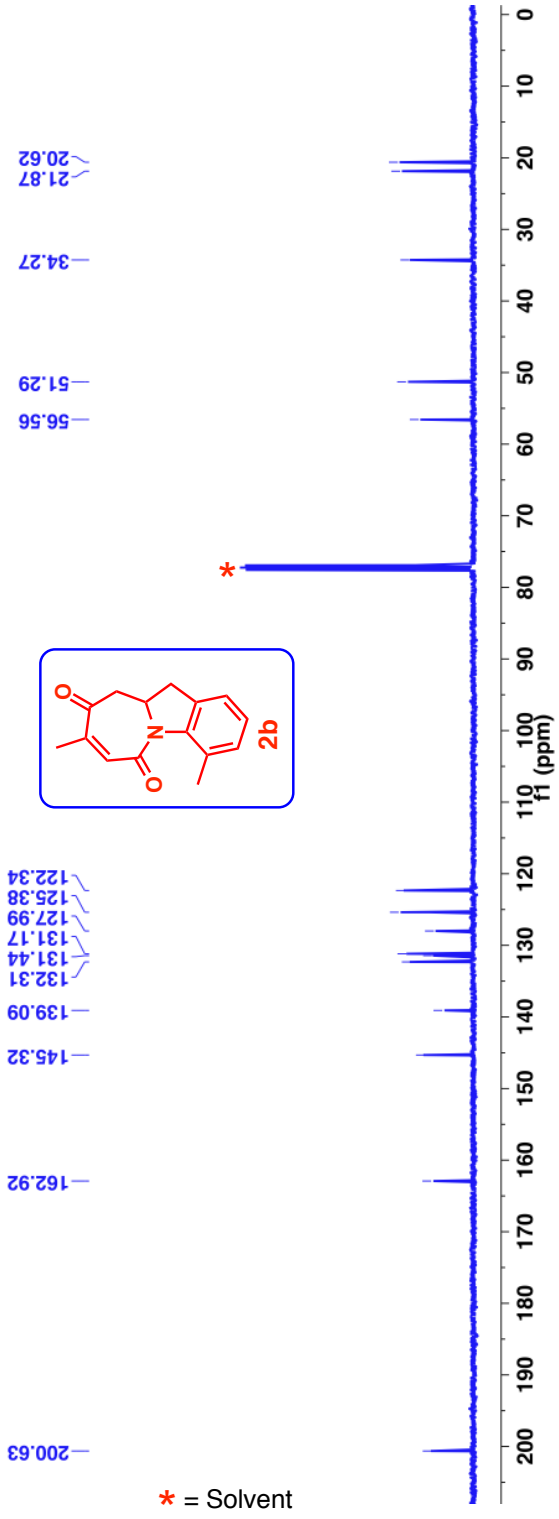
^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 209.9, 172.5, 148.9, 146.3, 145.7, 141.5, 141.3, 138.2, 135.7, 132.4, 67.0, 60.9, 44.5 and 31.9.



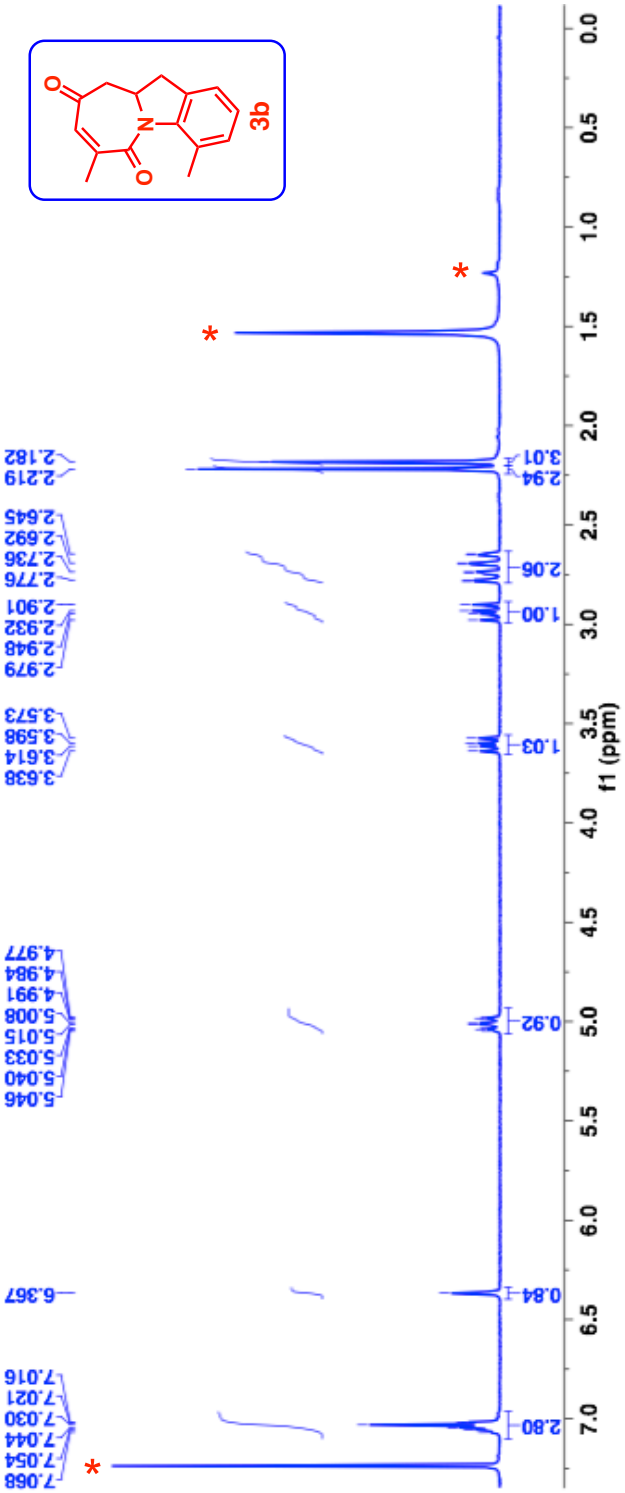
^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.03-6.99(m, 3H), 6.46-6.45 (m, 1H), 5.01-4.96 (m, 1H), 3.61-3.54 (m, 1H), 3.07-3.00 (m, 1H), 2.80-2.73 (m, 2H), 2.22 (s, 3H) and 2.05-2.04 (d, J = 4 Hz 3H).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 200.9, 162.9, 145.3, 139.1, 132.3, 131.4, 131.2, 127.9, 125.4, 122.3, 56.6, 51.3, 34.3, 21.9 and 20.6.

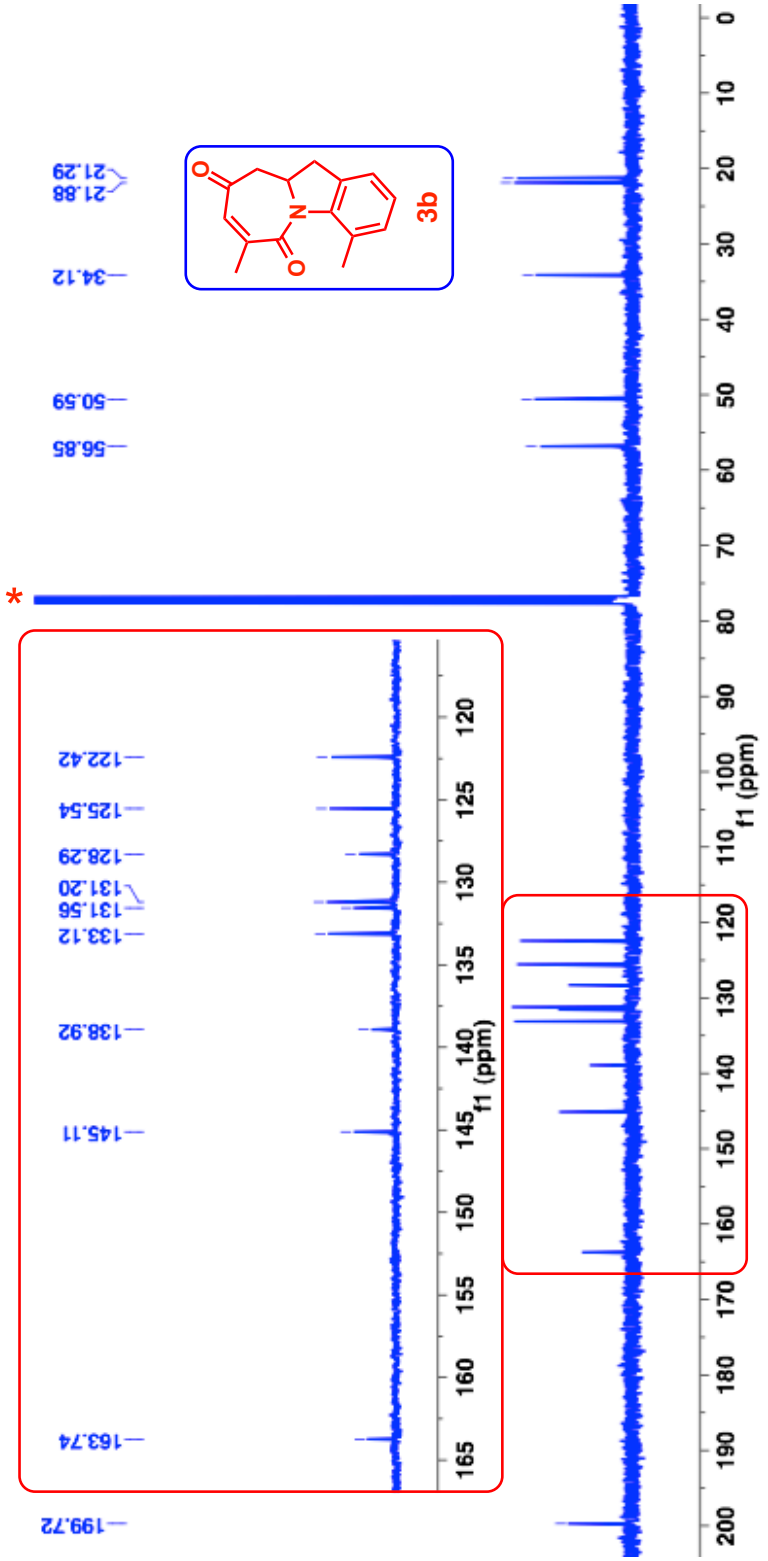


^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.07-7.02(m, 3H), 6.37 (s, 1H), 5.05-4.98 (m, 1H), 3.64-3.57 (m, 1H), 2.98-2.90 (m, 1H), 2.78-2.65 (m, 2H), 2.22 (s, 3H) and 2.18 (s, 3H).

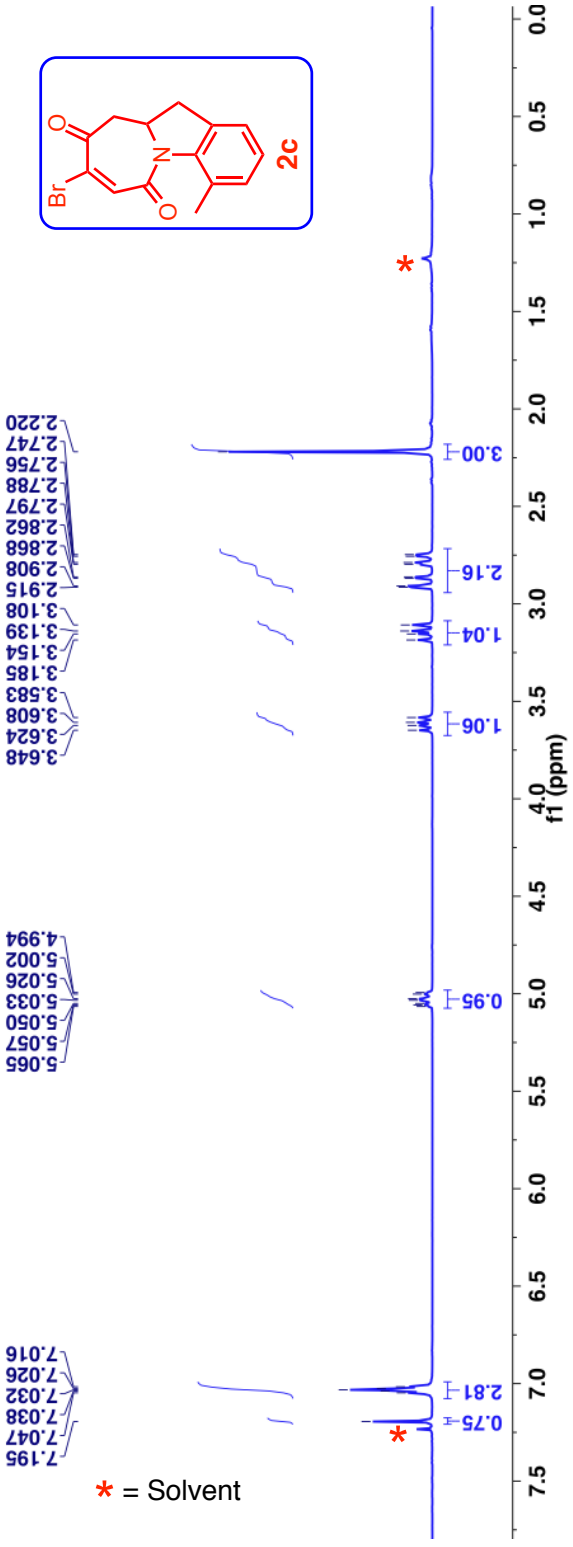


* = Solvent

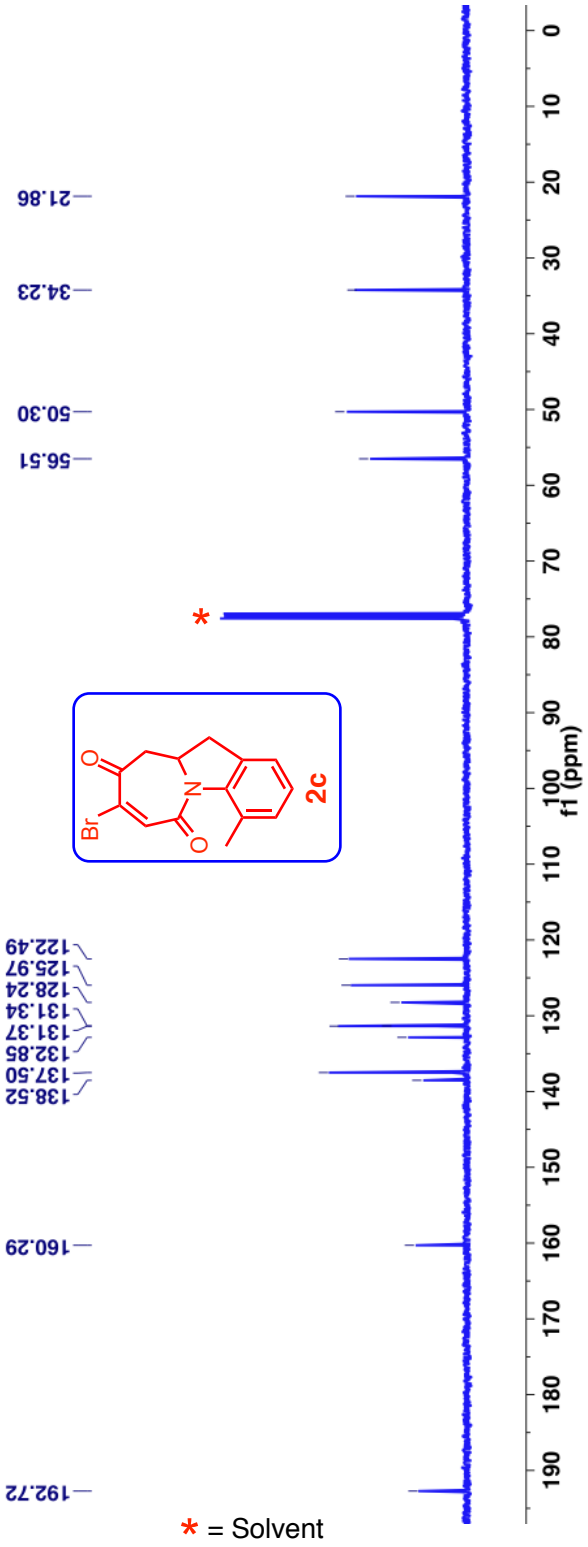
^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 199.7, 163.7, 145.1, 138.9, 133.1, 131.6, 131.2, 128.3, 125.5, 122.4, 56.9, 50.6, 34.1, 21.9 and 21.3.



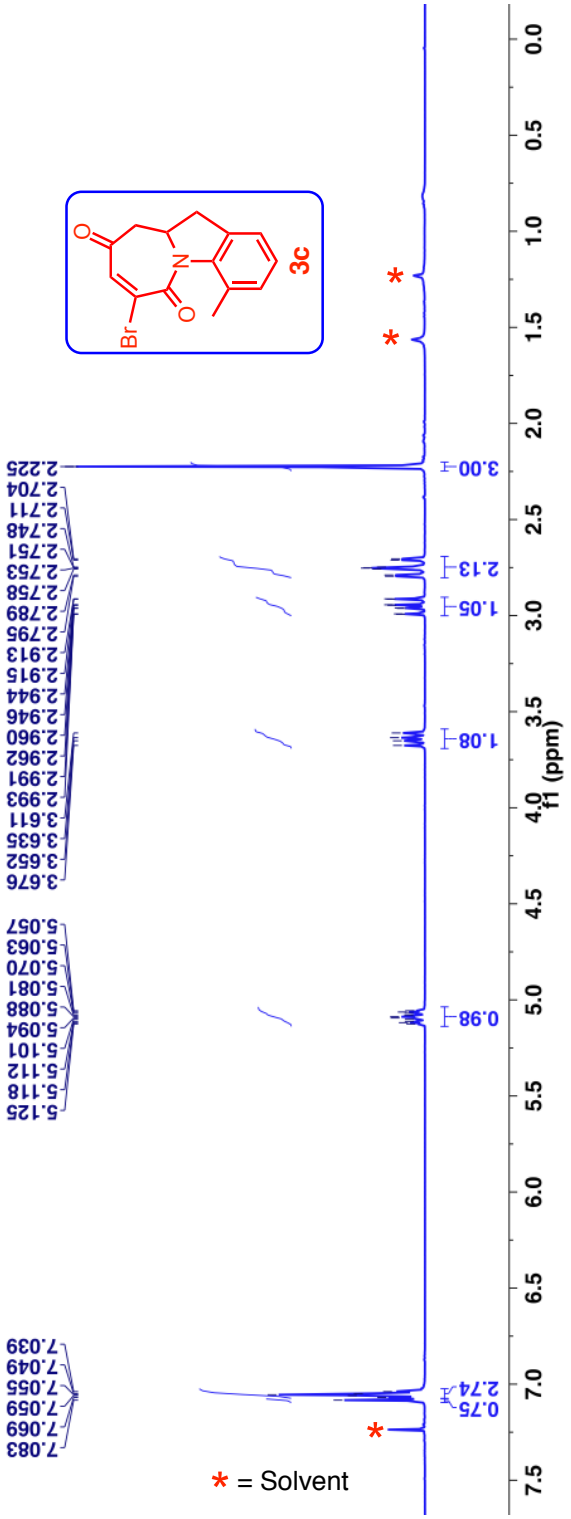
^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.19 (s, 1H), 7.05-7.02 (m, 3H), 5.07-4.99 (m, 1H), 3.65-3.58 (m, 1H), 3.19-3.11 (m, 1H), 2.92-2.75 (m, 2H) and 2.22 (s, 3H).



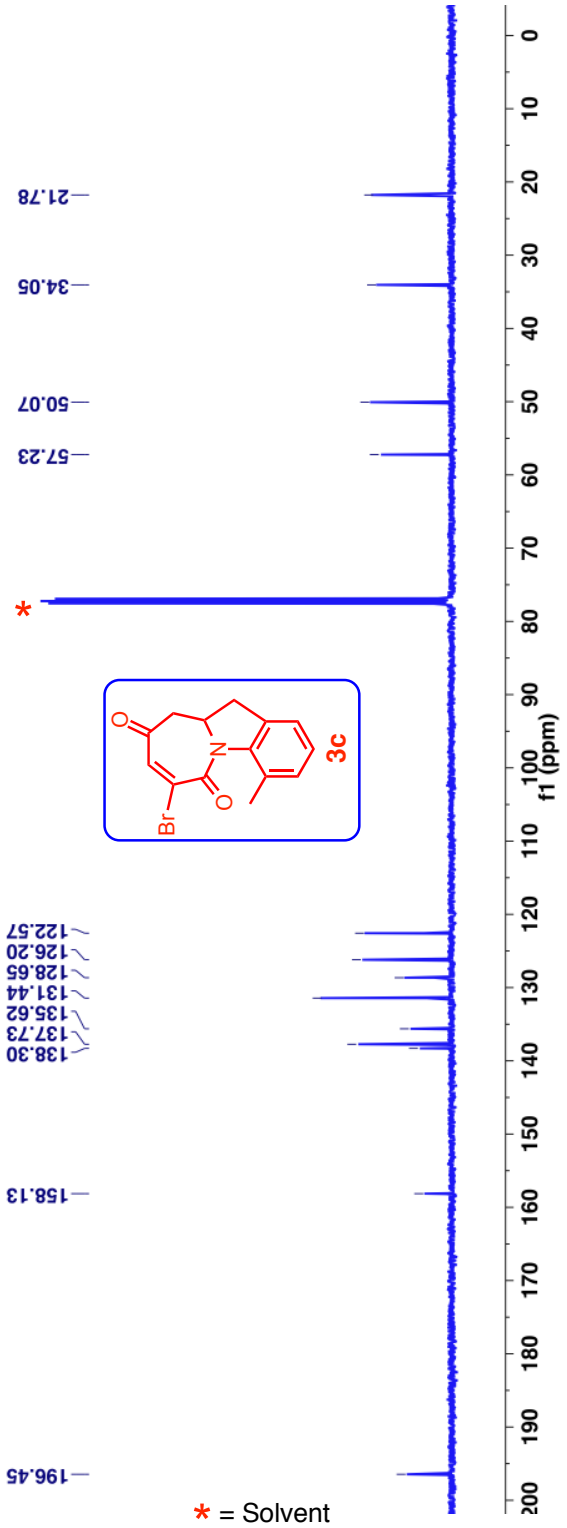
^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 192.7, 160.3, 138.5, 137.5, 132.9, 131.4, 131.3, 128.2, 125.9, 122.5, 56.5, 50.3, 34.2 and 21.9.



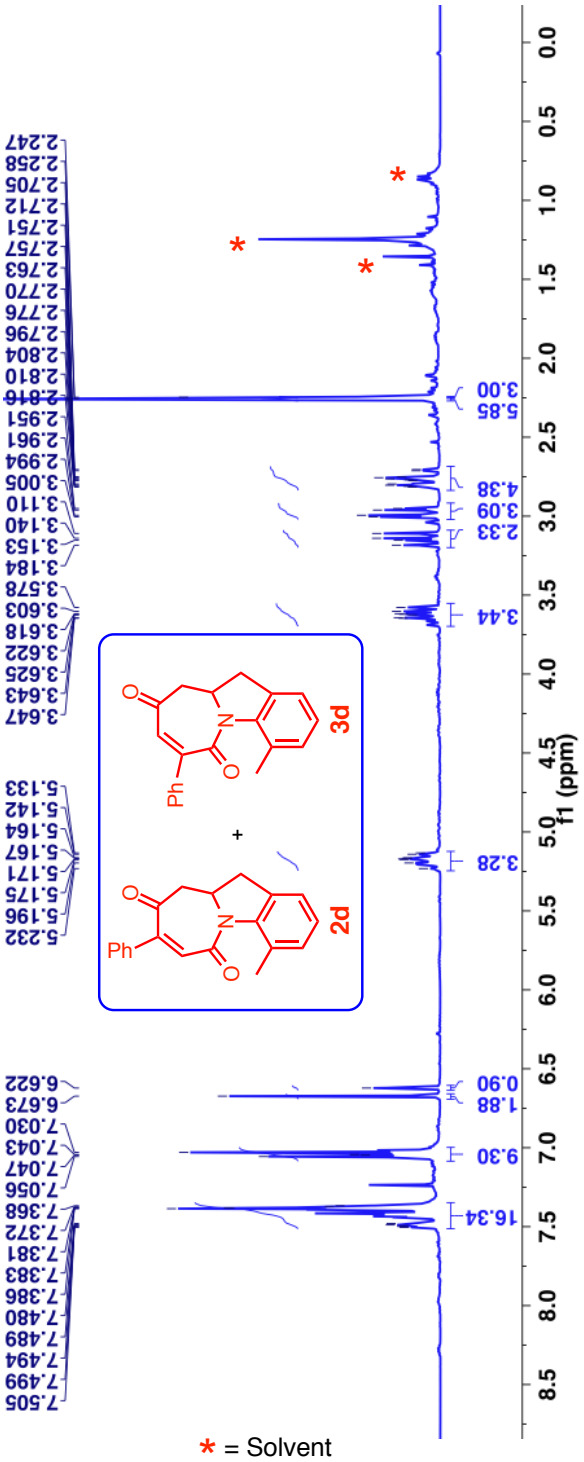
^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.08 (s, 1H), 7.07-7.04 (m, 3H), 5.13-5.06 (m, 1H), 3.68-3.61 (m, 1H), 2.99-2.91 (m, 1H), 2.79-2.70 (m, 2H) and 2.23 (s, 3H).



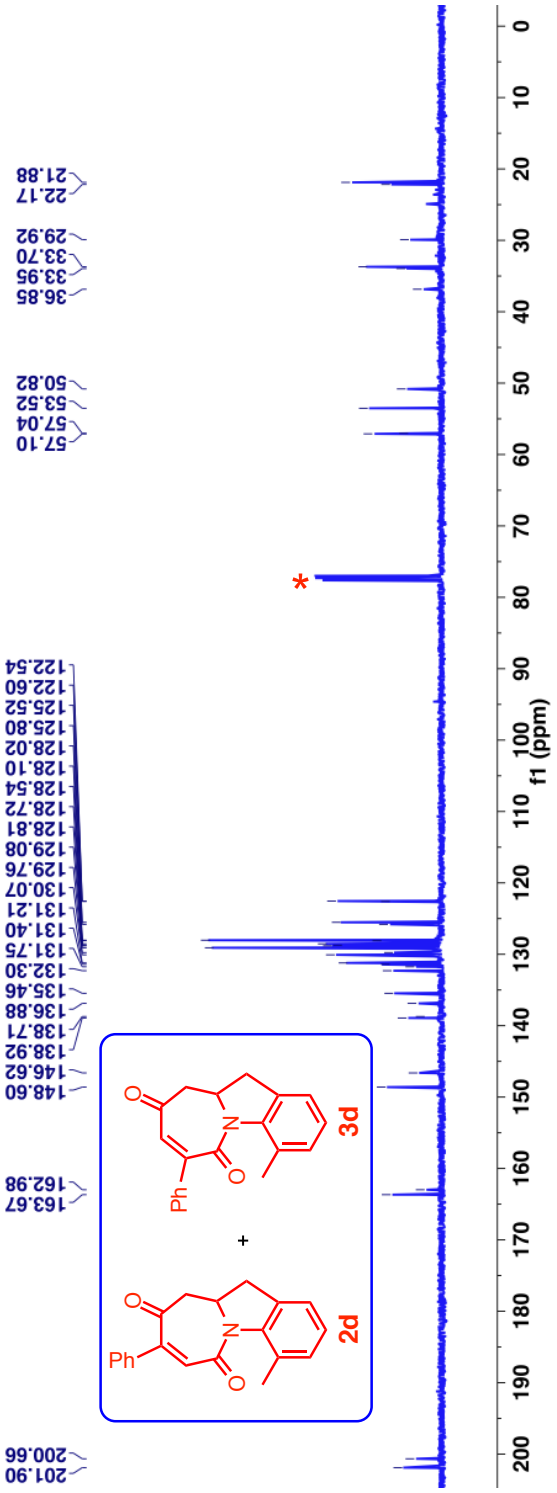
^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 196.5, 158.1, 138.3, 137.7, 135.6, 131.4, 128.7, 126.2, 122.6, 57.2, 50.0, 34.1and 21.8.



^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm), (Major 2d + minor 3d, 70:30): 7.50-7.27 (m, 16H), 7.06-7.04 (m, 9H), 6.67 (s, 2H), 6.62 (s, 1H), 5.23-5.13 (m, 3H), 3.64-3.58 (m, 3H), 3.18-3.11 (m, 2H), 3.01-2.95(m, 3H), 2.82-2.71 (m, 4H), 2.26 (s, 6H) and 2.25 (s, 3H).

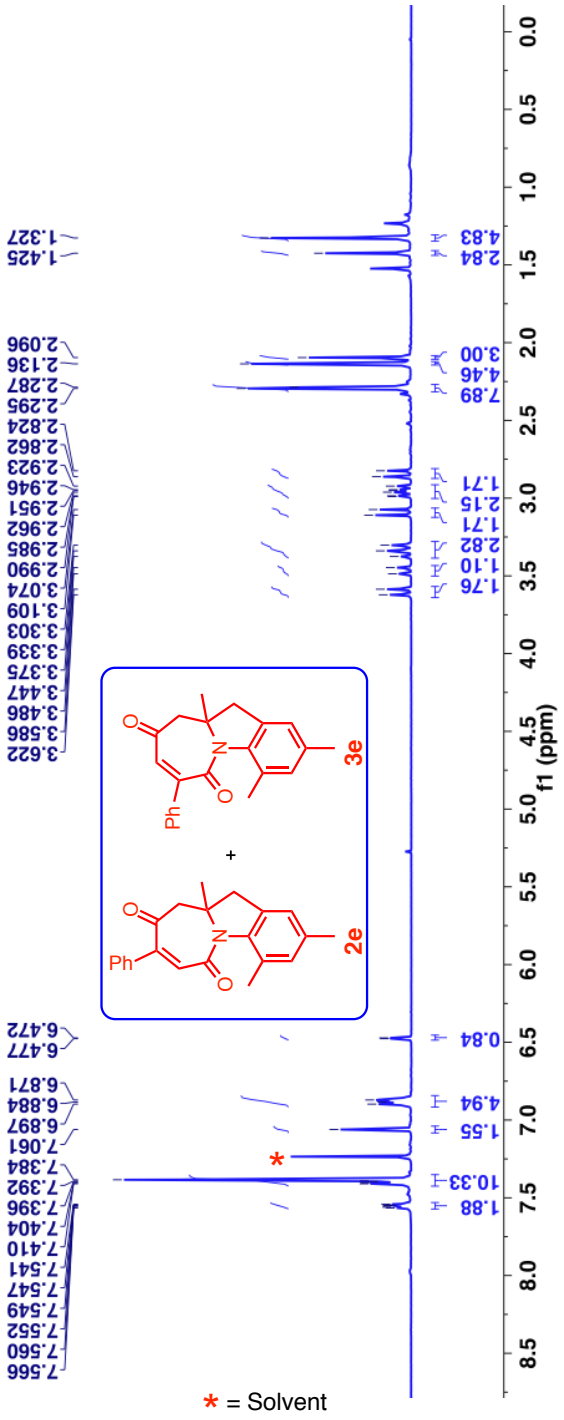


^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm), (Major **2d** + minor **3d**, 70:30): 201.9, 200.7, 163.7,162.9, 148.6, 146.6, 138.9, 138.7, 136.8, 135.5, 132.3, 131.8, 131.4, 131.2, 130.1, 129.8, 129.1, 128.8, 128.7, 128.5, 128.1, 128.0, 125.8, 125.5, 122.6, 122.54, 57.1, 57.0, 53.5, 50.8, 36.9, 33.9, 33.7, 29.9, 22.2 and 21.8

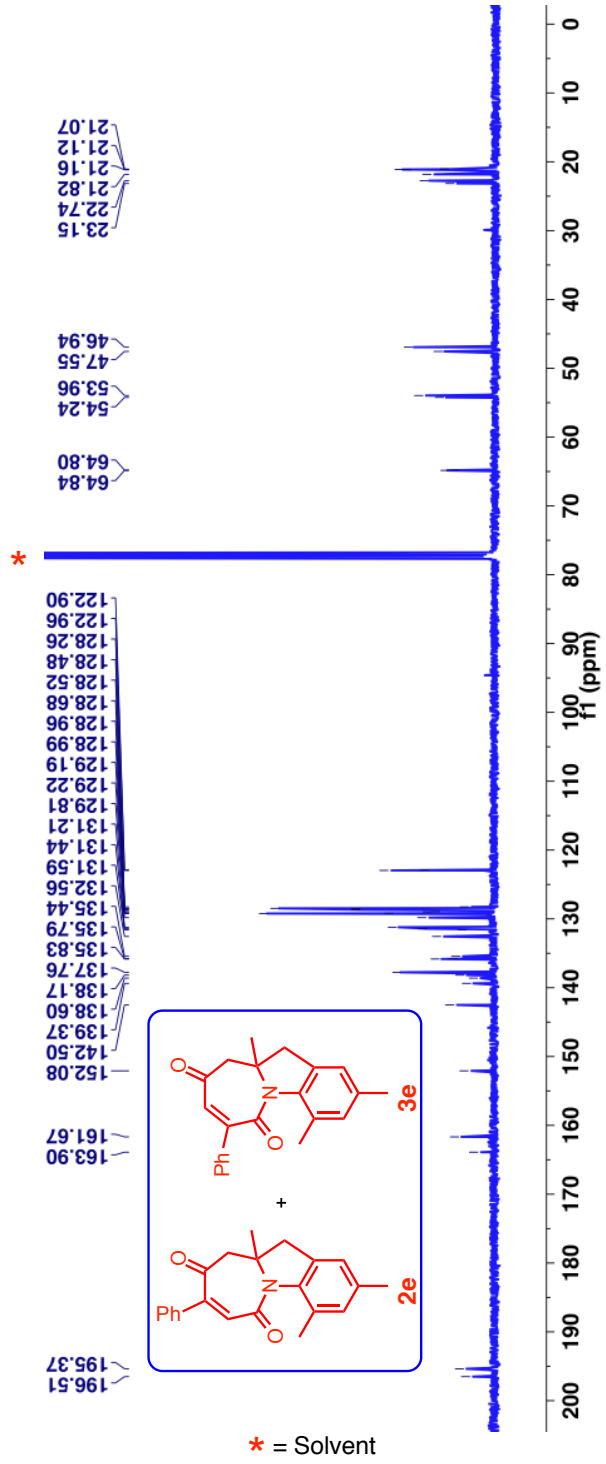


= Solvent

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm), (Major **2e** + minor **3e**, 74:26): 7.57-7.54 (m, 2H), 7.41-7.38 (m, 10H), 7.06 (s, 1H), 6.89-6.87 (m, 5H), 6.48-6.47 (d, J = 2 Hz, 1H), 3.62-3.59 (d, J = 14 Hz, 2H), 3.48-3.45 (d, J = 15 Hz, 3H), 3.38-3.30 (m, 3H), 3.11-3.07 (d, J = 14 Hz, 2H), 2.99-2.92 (m, 2H), 2.86-2.82 (d, J = 15.2 Hz, 2H), 2.29-2.28 (m, 8H), 2.14 (s, 4H), 2.09 (s, 3H), 1.43 (s, 3H) and 1.33 (s, 4H).

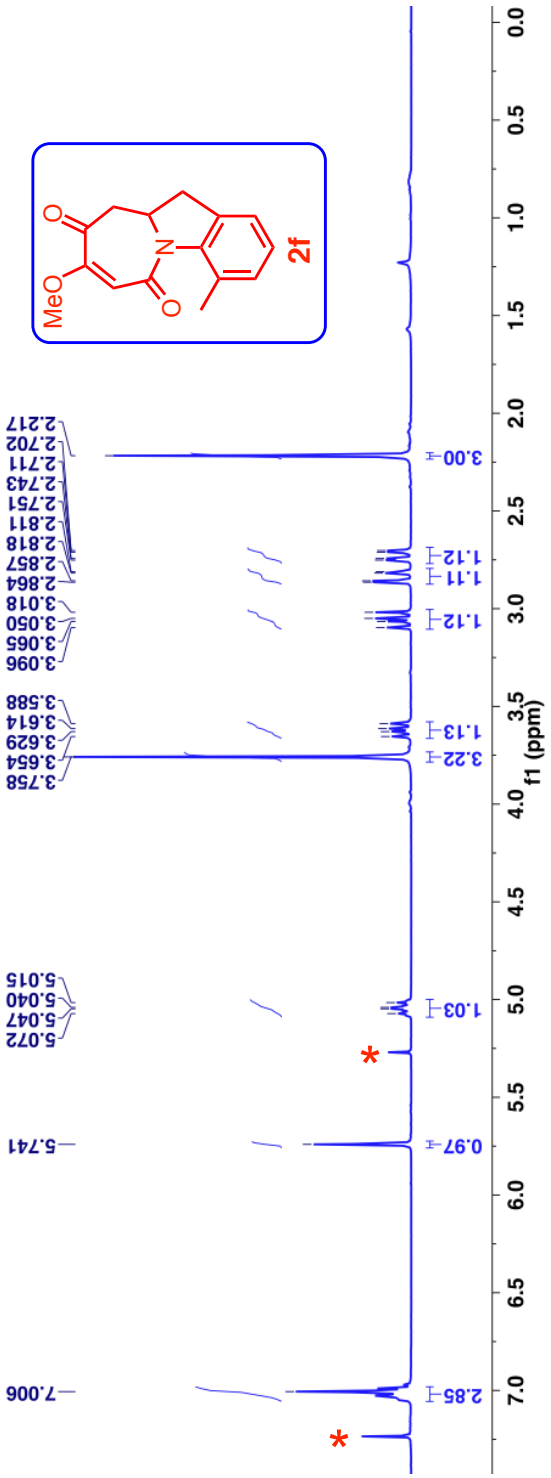


^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm), (Major **2e** + minor **3e**, 74:26): 196.5, 195.4, 163.9, 161.7, 152.1, 142.5, 139.4, 138.6, 138.2, 137.8, 135.8, 135.8, 135.4, 132.6, 131.6, 131.4, 131.2, 129.8, 129.2, 129.1, 128.9, 128.96, 128.7, 128.5, 128.48, 128.3, 122.96, 122.90, 64.84, 64.80, 54.2, 53.9, 47.6, 46.9, 23.2, 22.7, 21.8, 21.2, 21.1, 21.0

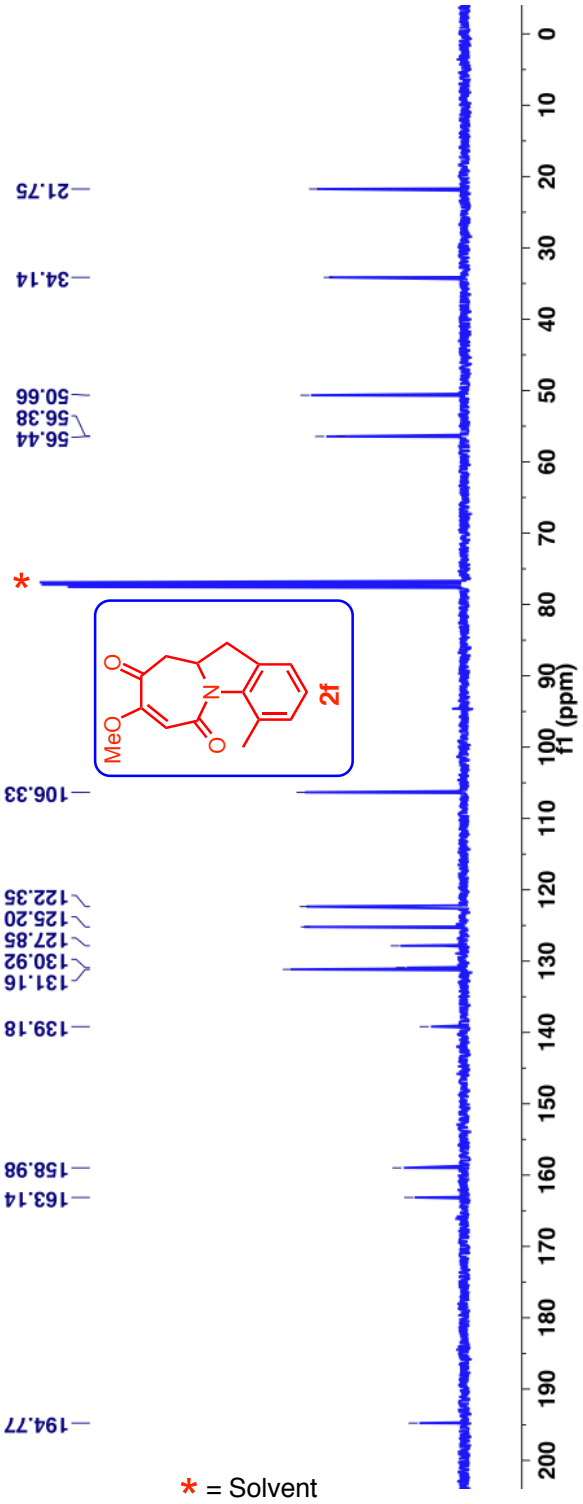


* = Solvent

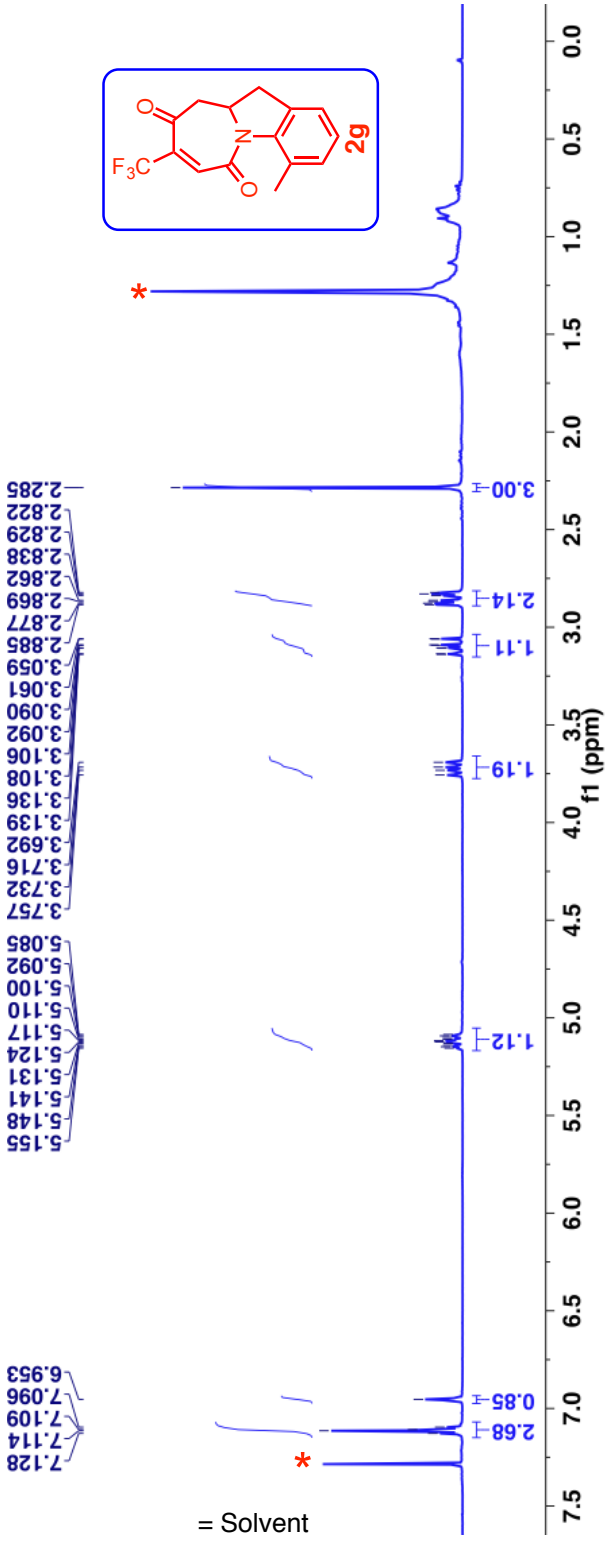
^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.03-6.99 (m, 3H), 5.74 (s, 1H), 5.07-5.02 (m, 1H), 3.76 (s, 3H), 3.65-3.58 (m, 1H), 3.09-3.02 (m, 1H), 2.86-2.70 (m, 2H), and 2.22 (s, 3H).



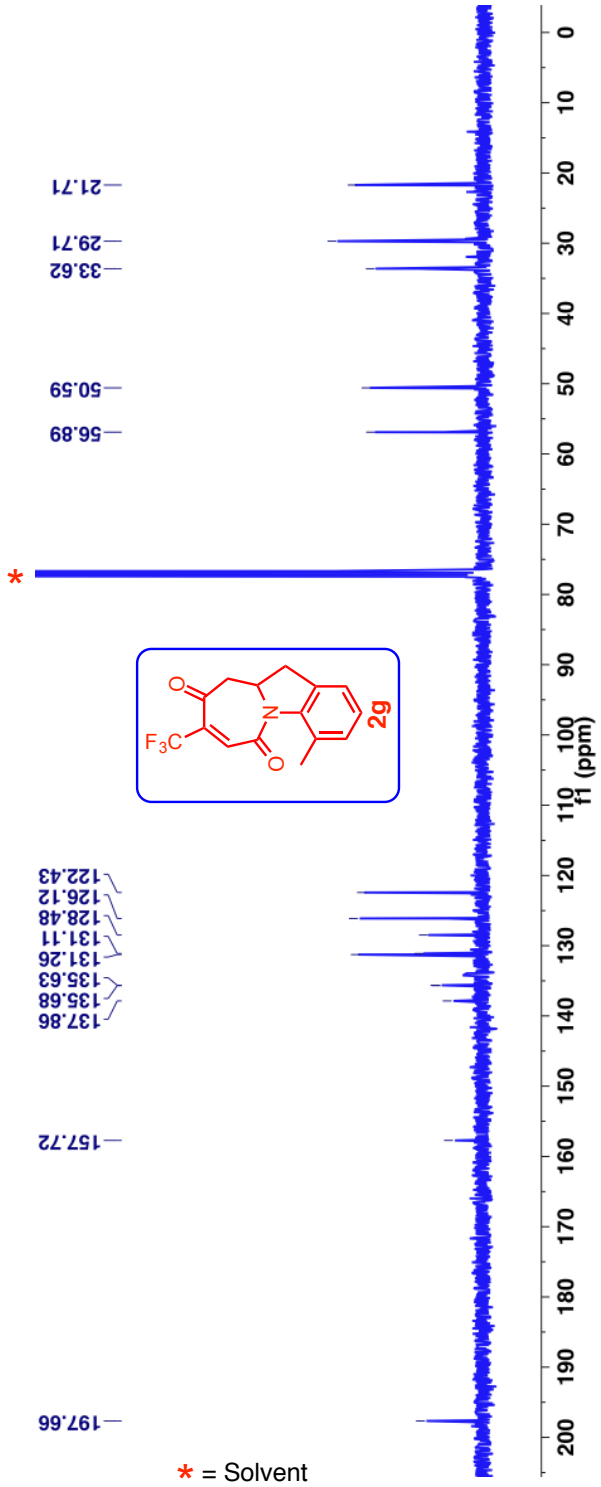
^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 194.8, 163.1, 158.9, 139.2, 131.2, 130.9, 131.3, 127.9, 125.2, 122.4, 106.3, 56.4, 56.38, 34.1 and 21.8.



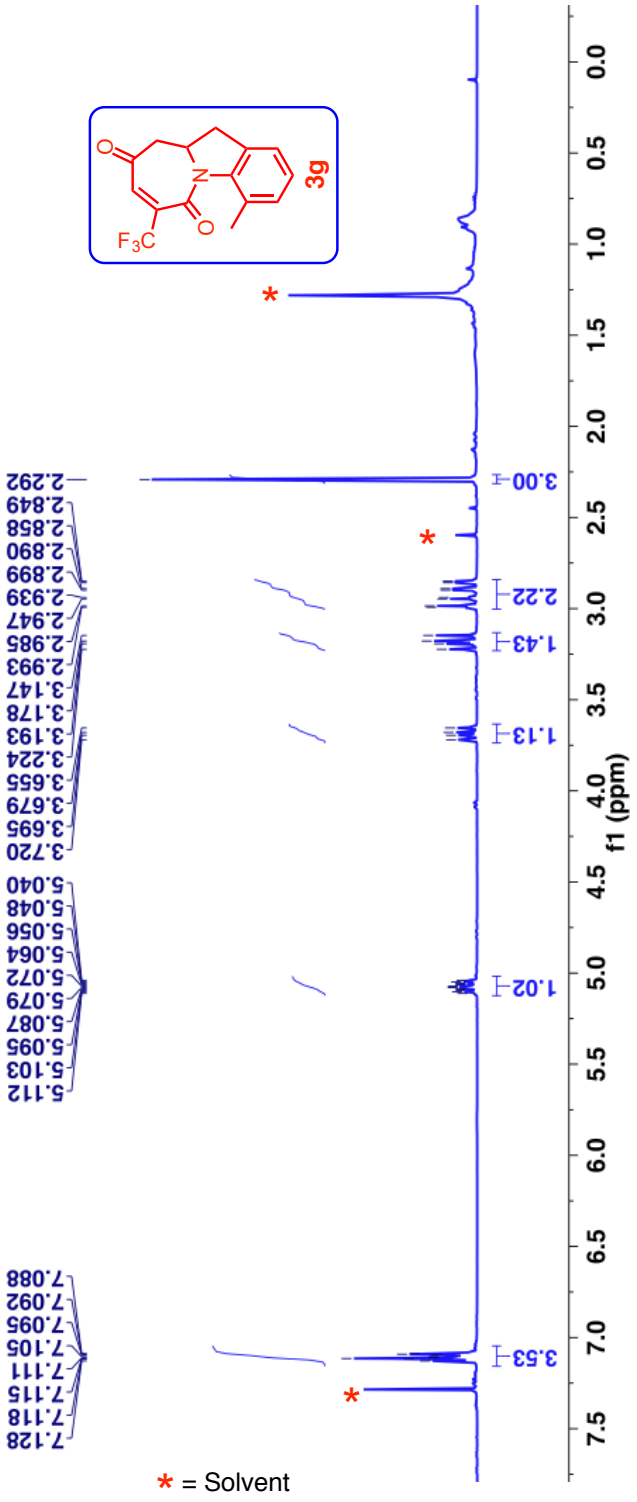
^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.13-7.09(m, 3H), 6.95 (s, 1H), 5.16-5.09 (m, 1H), 3.76-3.69 (m, 1H), 3.14-3.06 (m, 1H), 2.89-2.82 (m, 2H)) and 2.29 (s, 3H).



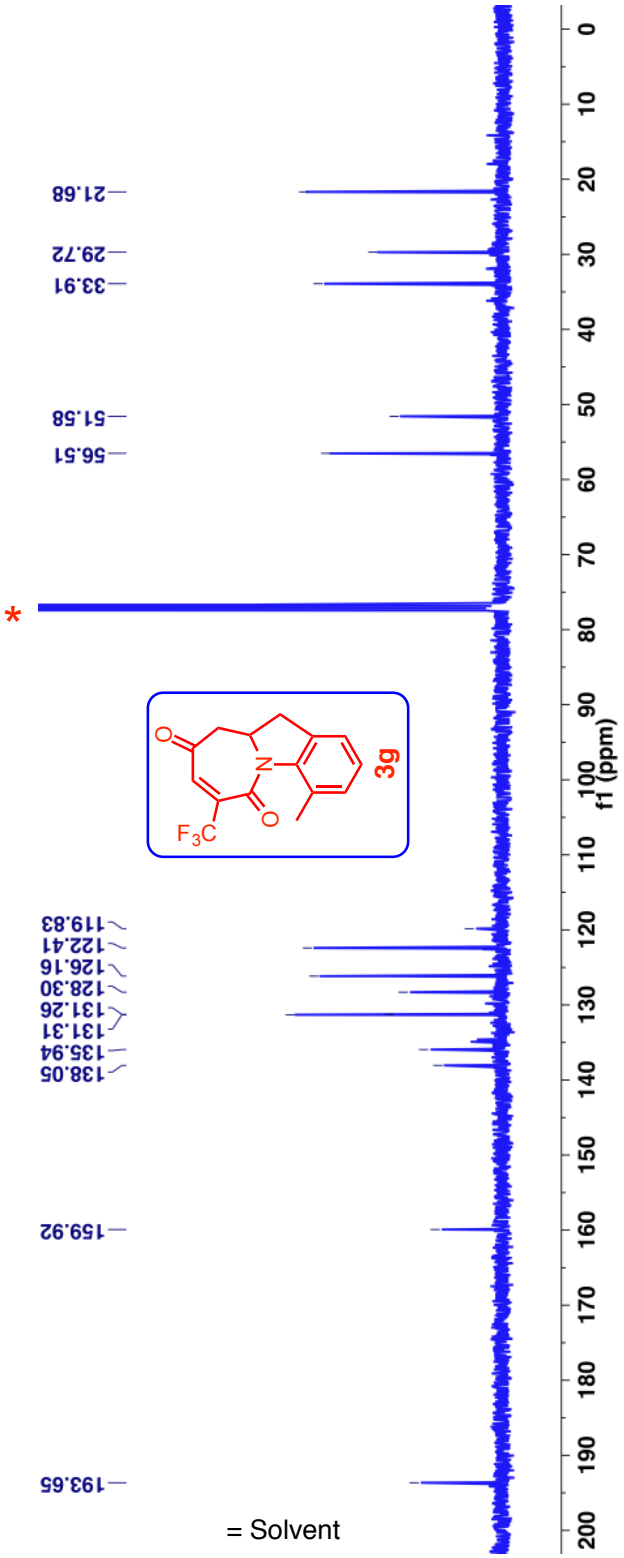
^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 197.7, 157.7, 137.9, 135.7, 135.6, 131.3, 131.1, 128.5, 126.1, 122.4, 56.9, 50.6, 33.6, 29.7 and 21.7.



^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.12-7.09(m, 4H), 5.11-5.04 (m, 1H), 3.72-3.66 (m, 1H),3.22-3.15 (m, 1H), 2.99-2.85 (m, 2H) and 2.29 (s, 3H).

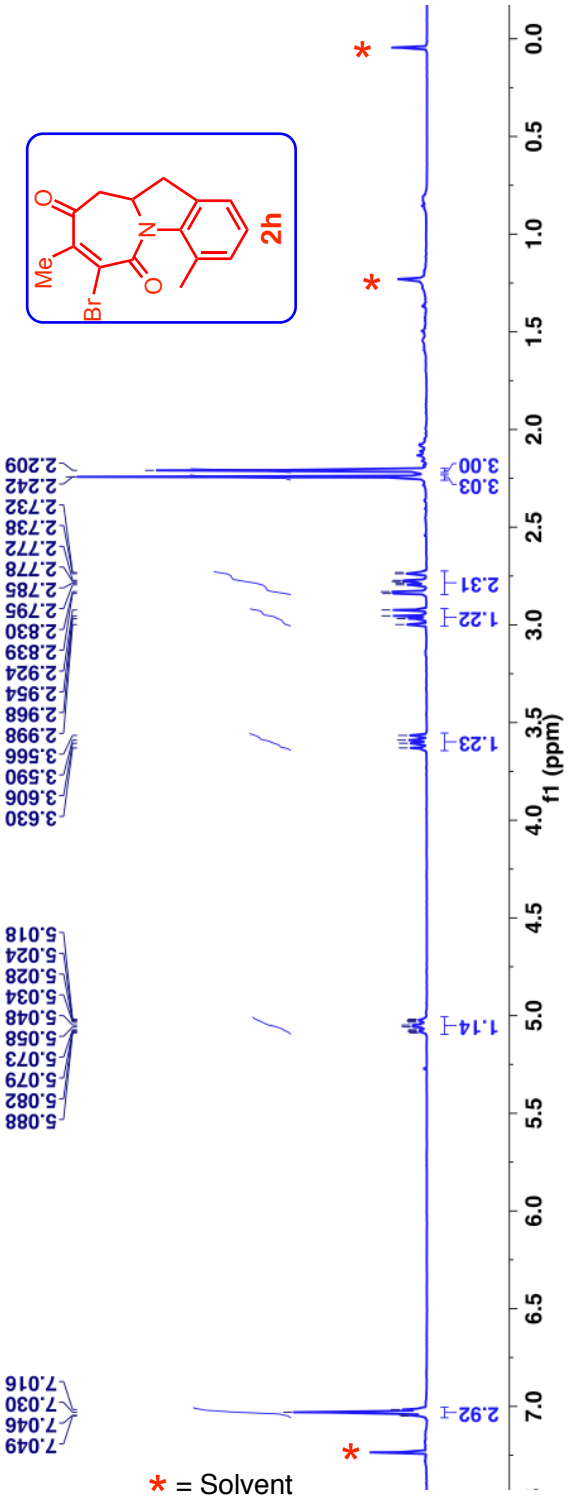


^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 193.7, 159.9, 138.1, 135.9, 131.3, 131.2, 128.3, 126.2, 122.4, 119.8, 56.5, 51.6, 33.9, 29.7 and 21.7.

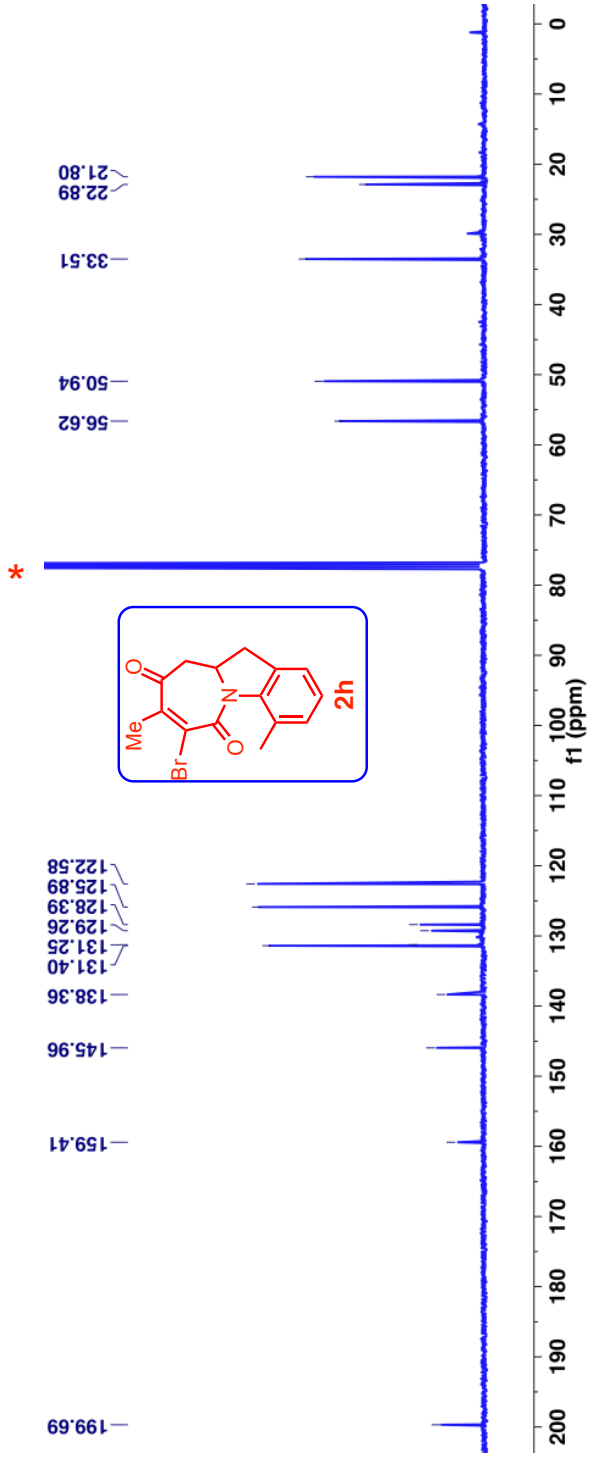


= Solvent

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.05-7.02(m, 3H), 5.09-5.02 (m, 1H), 3.63-3.37 (m, 1H), 2.99-2.92 (m, 1H), 2.84-2.73 (m, 2H), 2.24 (s, 3H) and 2.21 (s, 3H).

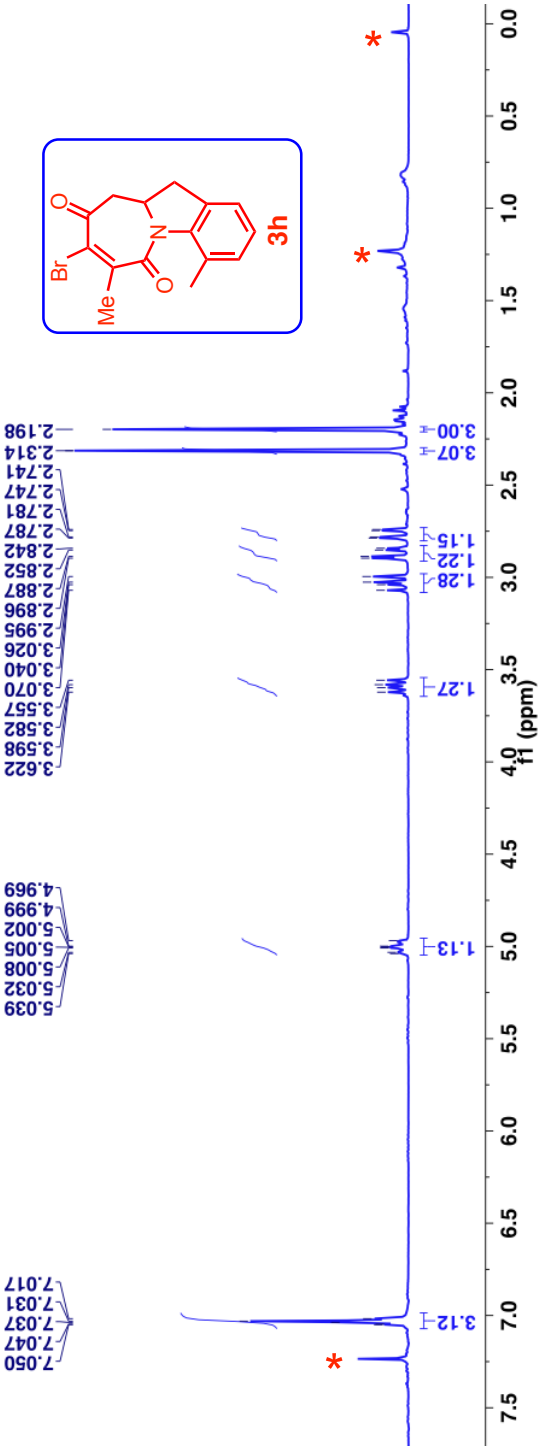


^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 199.7, 159.4, 145.9, 138.4, 131.4, 129.3, 128.4, 125.9, 122.6, 56.6, 50.9, 33.5, 22.9 and 21.8.



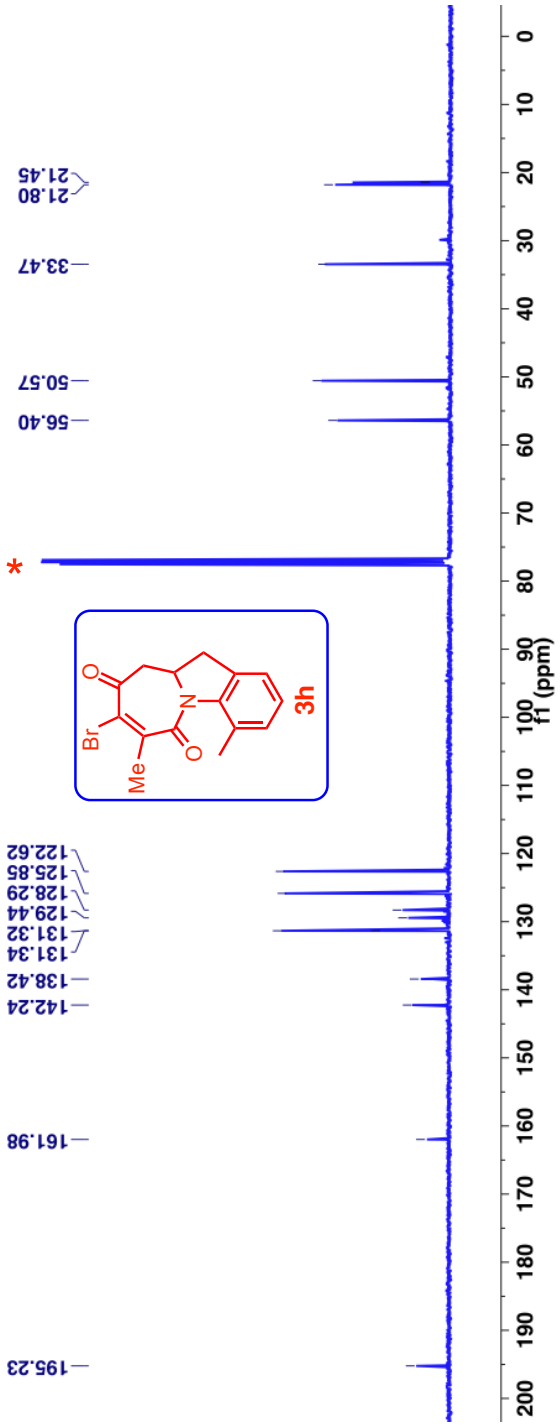
* = Solvent

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.05-7.02 (m, 3H), 5.04-4.97 (m, 1H), 3.62-3.56 (m, 1H), 3.07-2.99 (m, 1H), 2.89-2.84 (m, 1H), 2.79-2.74 (m, 1H), 2.31 (s, 3H) and 2.19 (s, 3H).



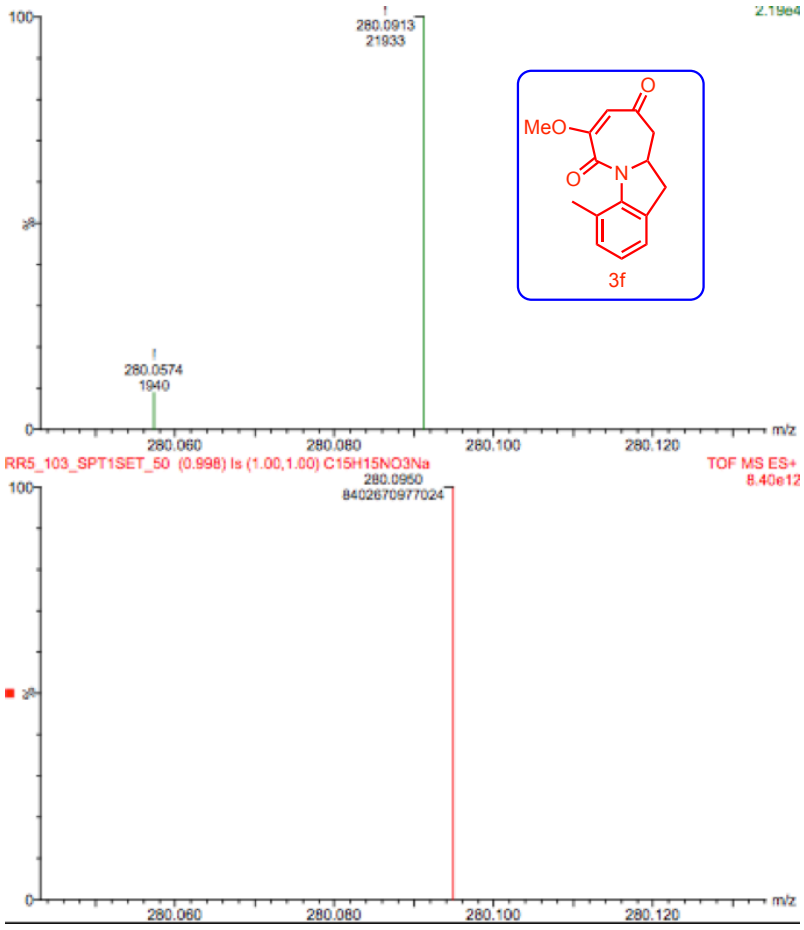
* = Solvent

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 195.2, 161.9, 142.2, 138.3, 131.3, 131.32, 129.4, 128.3, 125.9, 122.6, 56.4, 50.5, 33.5, 21.8 and 21.5.



* = Solvent

HRMS-ESI (m/z) ([M + Na]$^+$): Calculated: 280.0950; Observed: 280.0913; |Δm|: 11 ppm.



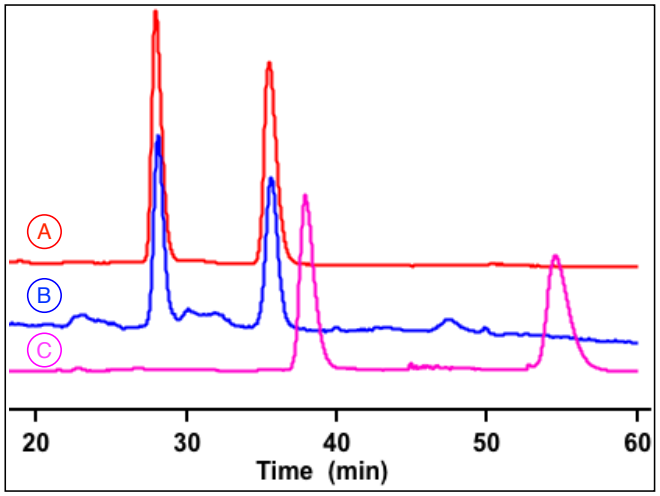


Figure S5: HPLC trace of A) Pure major methoxy maleimide photoproduct **2f**; B) Crude photoreaction of **1f** and C) HPLC trace of thermally synthesized **3f**.