Supporting Information (115 Pages)

Photo-auxiliary approach for enabling excited state transformations with visible light

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1 GENERAL METHODS AND MATERIALS

All commercially obtained reagents/solvents were used as received; chemicals that were purchased from Alfa Aesar, Sigma – Aldrich®, Acros®, TCI® America, Mallinckrodt®, and Oakwood Products® were used as received without further purification. Spectroscopic grade acetonitrile purchased from EMD® were used for photoreactions and for recording absorbance spectra of various substrates. Unless otherwise stated dichloromethane and acetone were freshly distilled from CaH_2 and potassium carbonate before employing in a reaction. Unless stated otherwise, reactions were conducted in oven-dried glassware under an atmosphere of nitrogen using anhydrous solvents. For reactions that required temperature <-10 °C, a dry ice-acetone bath was utilized and the reaction was carried out under N_2 atmosphere.

^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 400 MHz (100 MHz for ^{13}C NMR) and on 500 MHz (125 MHz for ^{13}C NMR) spectrometers. The residual solvent signal was used as reference. ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.2 ppm). Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. In some instances, it was not possible to obtain a signal for the carbonyl carbon, despite of long relaxation times and concentrated samples. However, these signals are reported wherever possible. High-resolution mass spectrum data was recorded in Electrospray Ionization mode on a Bruker–Daltronics® BioTof mass spectrometer in positive (ESI+) ion mode.

The reactants and photoproducts were purified by flash chromatography using silica gel (by standard technique with solvents as indicated. RediSep®, silica gel standard grade: Porosity 60 Å, Particle size: 230 x 400 mesh, Average particle size: 60 to 70 micron). The Retardation Factor (R_f) values were recorded using various combination of solvent systems as mobile phase (as mentioned in the text) and on SORBENT TECHNOLOGIES® Silica Gel TLC plates (200 µm thickness w/UV_{254}).

1.1.0 Photophysical Methods

Spectrophotometric grade solvents were used wherever necessary unless otherwise mentioned. The compounds were purified by combiflash equipped with dual wavelength. UV-Vis spectra were recorded on Cary 300 series UV-Vis spectrometer using UV quality fluorimeter cells (with range until 190 nm) purchased from Luzchem. Low temperature luminescence experiments were performed using a quartz tube (3 mm inner diameter) that fitted in a quartz Dewar with an optical window. Emission spectra were recorded using Horiba Scientific®

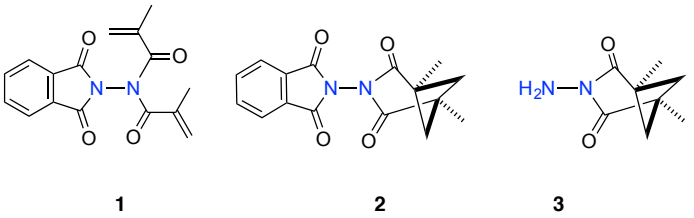
Fluorolog 3 spectrophotometer (FL3-22) equipped with double-grating monochromators, dual lamp housing containing a 450-watt CW xenon lamp and a UV xenon flash lamp (FL-1040), Fluorohub/MCA/MCS electronics and R928 PMT detector. Emission spectra were corrected in all the cases for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard instrument correction provided in the instrument software. Phosphorescence lifetime measurements were performed by multichannel scaling using a pulsed xenon lamp in conjunction with an OB920 spectrometer (Edinburgh Analytical Instruments). Laser flash photolysis experiments employed the pulses from a Spectra Physics GCR-150-30 Nd:YAG laser (355 nm, *ca.* 5 mJ/pulse, 7 ns pulse length or 266 nm, ca 5 mJ/pulse, 5 ns pulse length) and a computer controlled system that has been described elsewhere.[1]

1.2.0 Electrochemistry

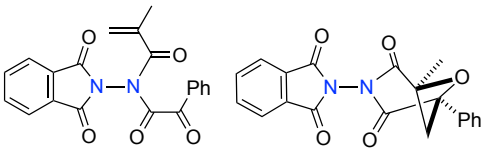
Cyclic voltammetry was performed using HPLC grade acetonitrile as the solvent on a CH instrument. Glassy carbon was utilized as the working electrode, silver chloride as the reference and platinum wire as the counter electrode. A solution of tetrabutylammonium hexafluorophosphate (TBAP) was used as the supporting electrolyte. The experiments were performed under constant flow of nitrogen. Measurements were made in MeCN Solvent. [**1**] = 1.0 mM; [**4**] = 0.83 mM; [**6**] = 0.49 mM; [**8**] = 0.49 mM; [**11a**] = 0.48 mM; [**11b**] = 1.68 mM; and [**11e**] = 0.76 mM.

2 CHART OF RELEVANT COMPOUNDS

2.1.0 Photoreactants and corresponding photoproducts



1 **2** **3**



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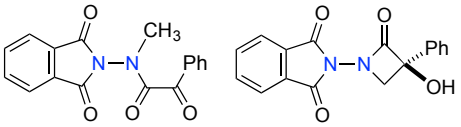

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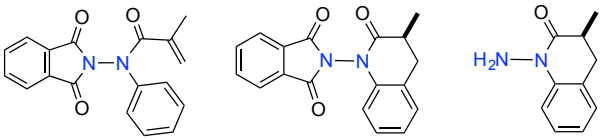
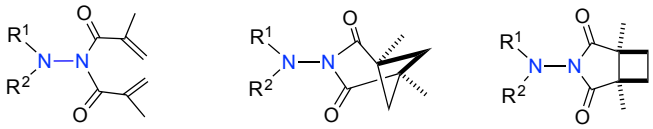


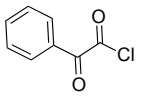
8 **9** **10**



11a-g **12** **13**

Imide	Amide	Carbamate	Amine
a) R^1 = PhCO; R^2 = CH_3CO	**b)** R^1 = PhCO, R^2 = CH_3	**d)** R^1 = CH_3, R^2 = Boc	**e)** R^1 = R^2 = CH_3
	c) R^1 = PhCO, R^2 = H		**f)** R^1 = CH_3, R^2 = H
			g) R^1 = R^2 = H

2.2.0 Other compounds utilized in synthesis



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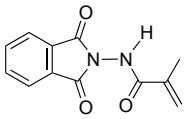

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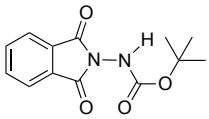

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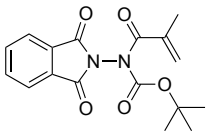

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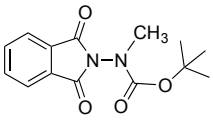

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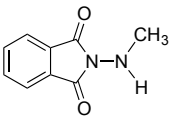

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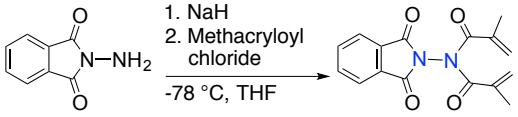
3 GENERAL PROCEDURE FOR THE SYNTHESIS OF REACTANTS

3.1.0 Synthetic route to acrylimide derivative **1**.



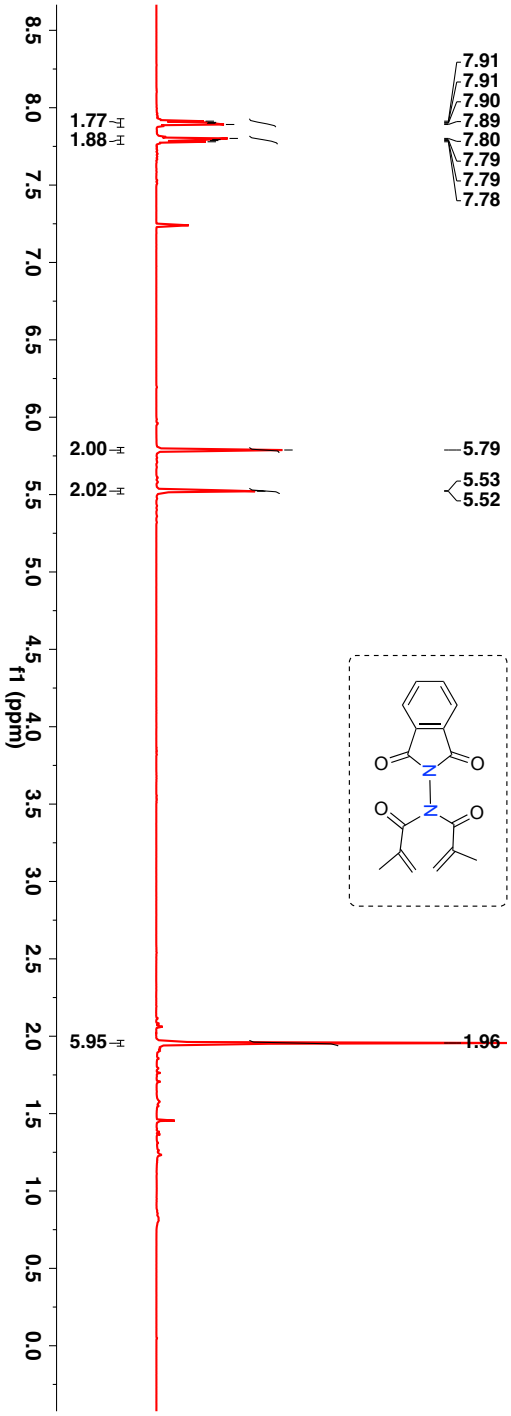
1

Scheme S1: Synthesis of acrylimide **1**.

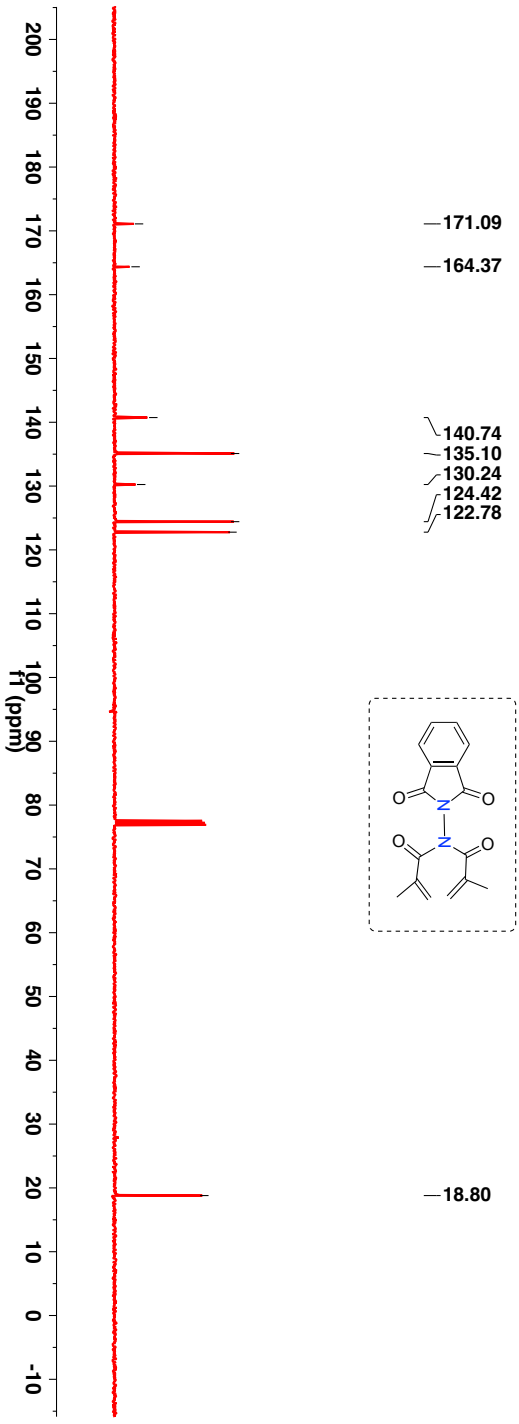
N-Aminophthalimide (1 *equiv*) was dissolved in freshly distilled THF under N_2 atmosphere. The reaction mixture was then cooled to -78 °C and this was followed by the addition of 5 *equiv* of NaH followed by the dropwise addition of methacryloyl chloride (2.2 *equiv*). After stirring for 1 h at this temperature, the mixture was brought to room temperature and stirred for 2.5 h (reaction was monitored by TLC). The reaction was quenched with 5 mL of NH_4Cl, stirred and the layers were separated. The organic layer was sequentially washed with DI water (2 × 10 mL), saturated $NaHCO_3$ (2 × 10 mL) and finally with brine. The organic layer was dried over *anhyd* Na_2SO_4, filtered and the solvent was removed under reduced pressure to yield crude product. The crude product was purified by combiflash using hexanes and ethyl acetate mixture to get the desired acrylimide. The product was characterized by NMR spectroscopy.

Crystalline solid (Yield = 35%). R_f = 0.8 (50% ethyl acetate:hexanes).

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 1.96 (s, 6H), 5.52-5.54 (m, 2H), 5.79 (bs, 2H), 7.78-7.80 (dd, *J* = 5.2 Hz, 2.8 Hz, 2H) and 7.89-7.91 (dd, *J* = 5.2 Hz, 3.2 Hz, 2H).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 18.8, 122.8, 124.4, 130.24, 135.1, 140.7, 164.4, and 171.1.



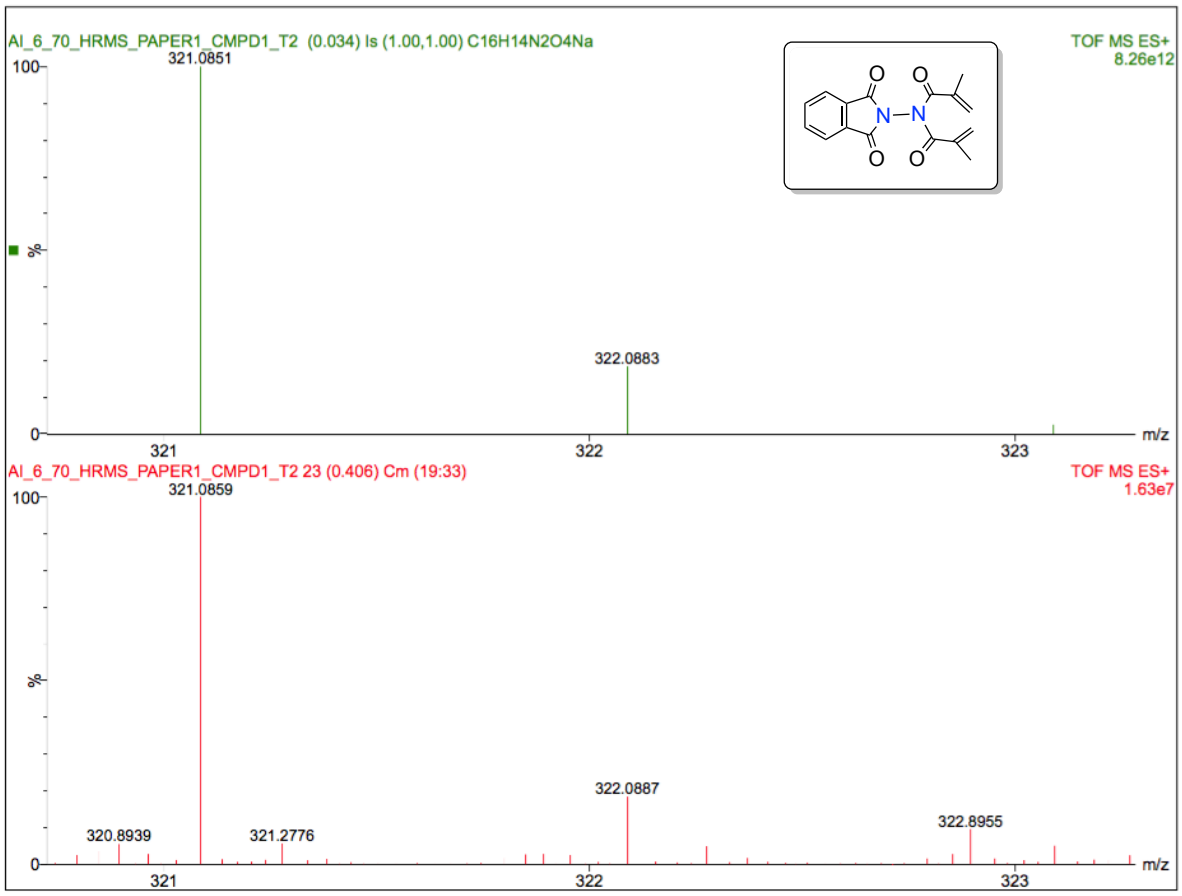
HRMS-ESI (m/z) ([M + Na]$^+$):

Chemical Formula : $C_{16}H_{14}N_2O_4$

Calculated : 321.0851

Observed : 321.0859

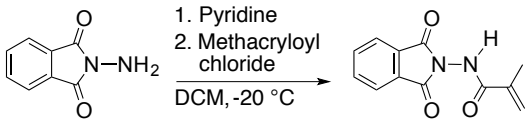
|Δm| : 2.5 ppm



3.1.1 Synthesis of phthalimide based amide derivative **15**.

The amide derivative **15** was synthesized by two different routes:

ROUTE 1



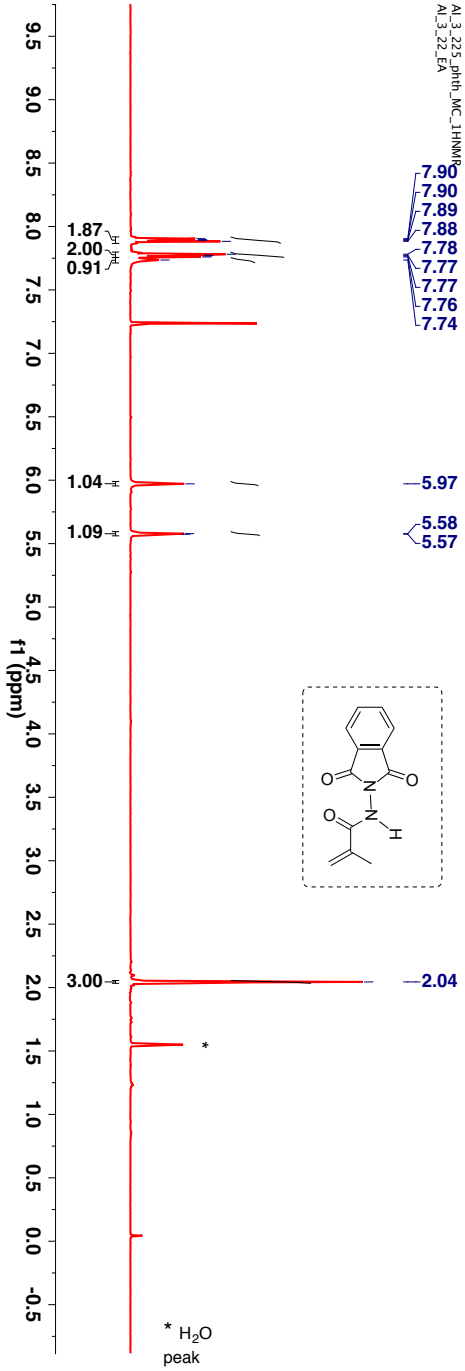
15

Scheme S2: Synthesis of amide **15**.

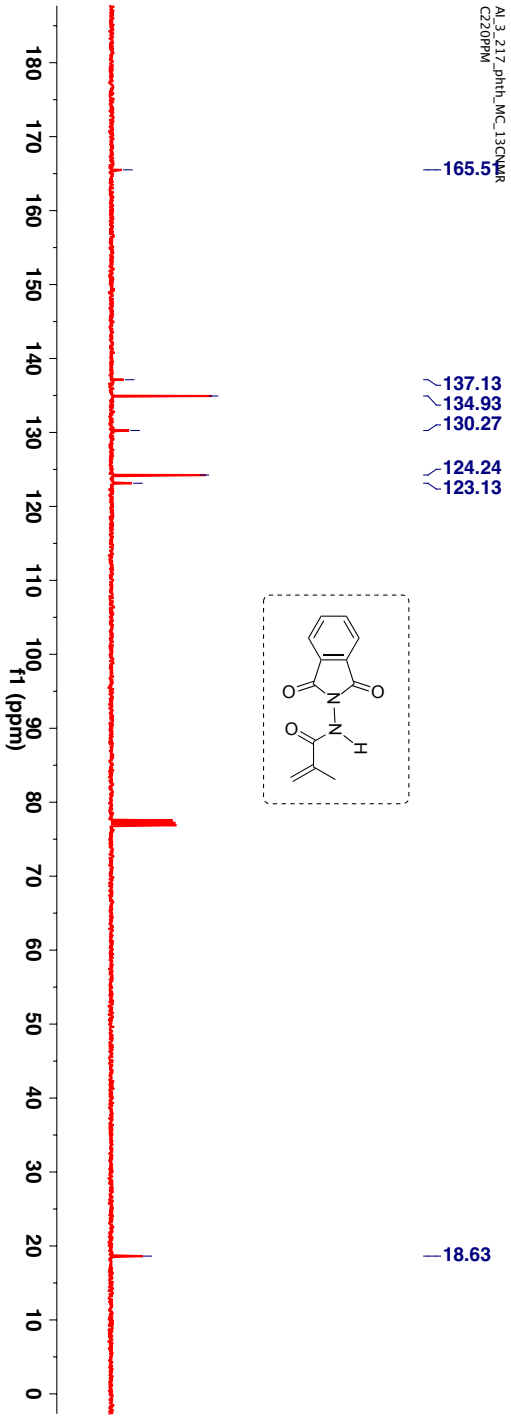
N-Aminophthalimide (1 *equiv*) was dissolved in freshly distilled DCM under N_2 atmosphere. To this solution, 1.5 *equiv* of pyridine was added and the reaction mixture was then cooled to -20 °C, followed by the dropwise addition of methacryloyl chloride (1.2 *equiv*). After stirring for 15 min, the mixture was brought to room temperature and stirred for 1 h (reaction was monitored by TLC). The reaction was quenched with 5 mL of H_2O, stirred and the organic layer was separated. The organic layer was sequentially washed with DI water (2 × 10 mL), saturated $NaHCO_3$ (2 × 10 mL) and finally with brine. The organic layer was dried over *anhyd* Na_2SO_4, filtered and the solvent was removed under reduced pressure to yield crude product. The crude product was purified by combiflash using hexanes and ethyl acetate as the eluting solvents. The product was characterized by NMR spectroscopy.

Crystalline solid (Yield = 65%). R_f = 0.7 (50% ethyl acetate:hexanes).

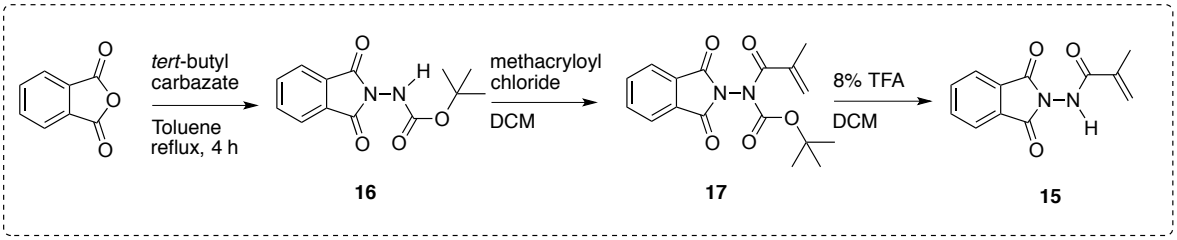
^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 2.04 (s, 3H), 5.57 (bs, 1H), 5.97 (bs, 1H), 7.74 (bs, 1H), 7.76-7.78 (dd, *J* = 5.6 Hz, 3.2 Hz, 2H) and 7.88-7.90 (dd, *J* = 5.6 Hz, 3.2 Hz, 2H).



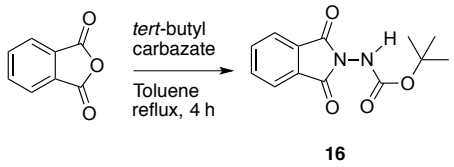
^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 18.6, 123.1, 124.2, 130.3, 134.9, 137.1, and 165.5.



ROUTE 2



ROUTE 2- STEP 1

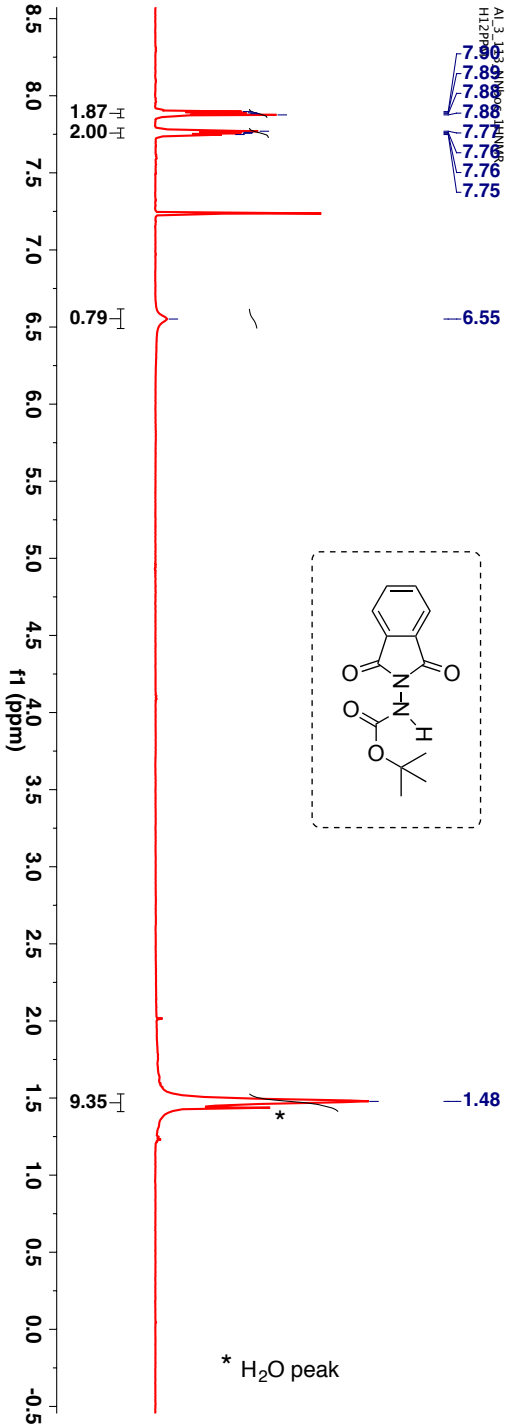


Scheme S3: Synthesis of amide derivative **16**.

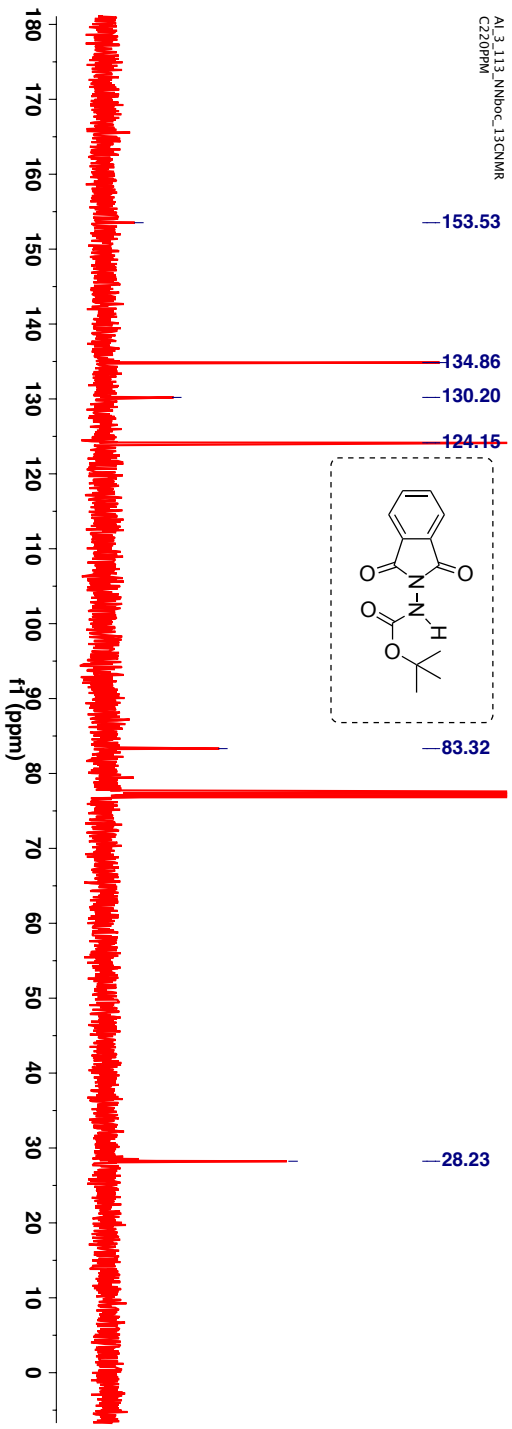
Modifying a procedure reported by Abbas *et. al.*[2] to a suspension *tert*-butylcarbazate (1 *equiv*) in toluene, phthalic anhydride (1 *equiv*) was added. The suspension was refluxed in a two-neck round bottom flask fitted with a Dean-Stark trap for 4 h. The mixture was cooled to room temperature and concentrated. The crude product was purified by column chromatography using hexanes and ethyl acetate as the eluting solvent and the product was characterized by NMR spectroscopy.

Crystalline solid (Yield = 94%). R_f = 0.5 (20% ethyl acetate:hexanes).

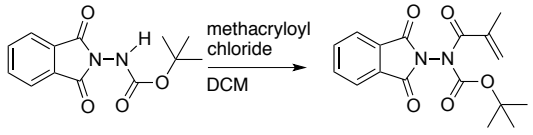
^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 1.48 (s, 9H), 6.55 (bs, 1H), 7.75-7.77 (dd, *J* = 5.6 Hz, 3.2 Hz, 2H) and 7.88-7.90 (dd, *J* = 5.6 Hz, 3.2 Hz, 2H).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 28.2, 83.3, 124.2, 130.2, 134.9 and 153.5.



ROUTE 2- STEP 2



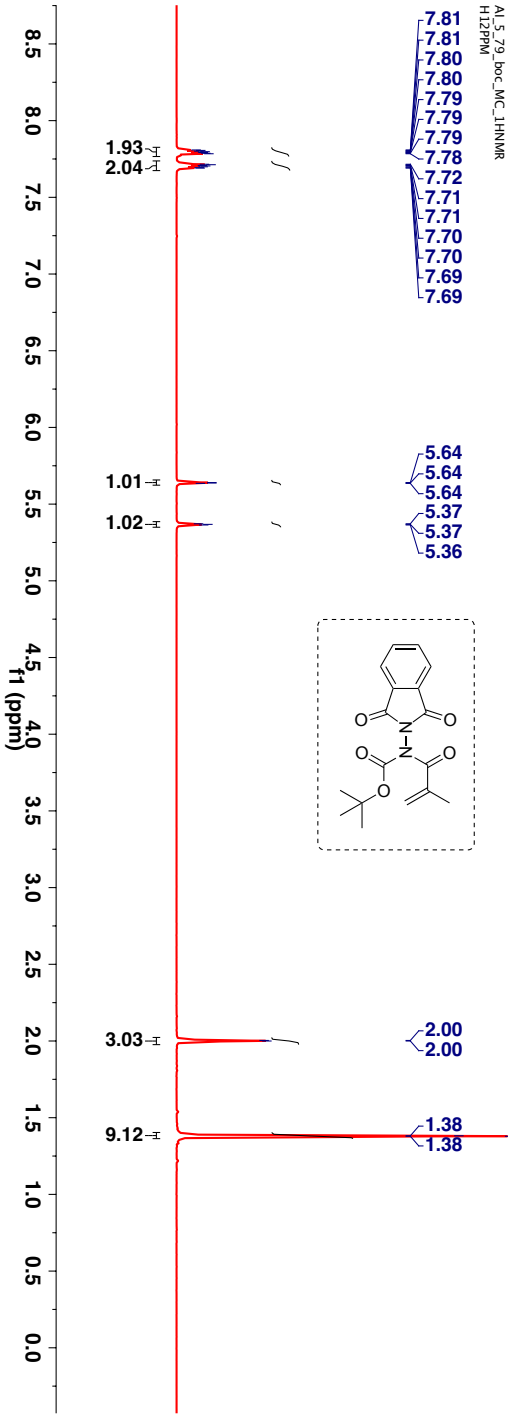
16 **17**

Scheme S4: Synthesis of imide derivative **17**.

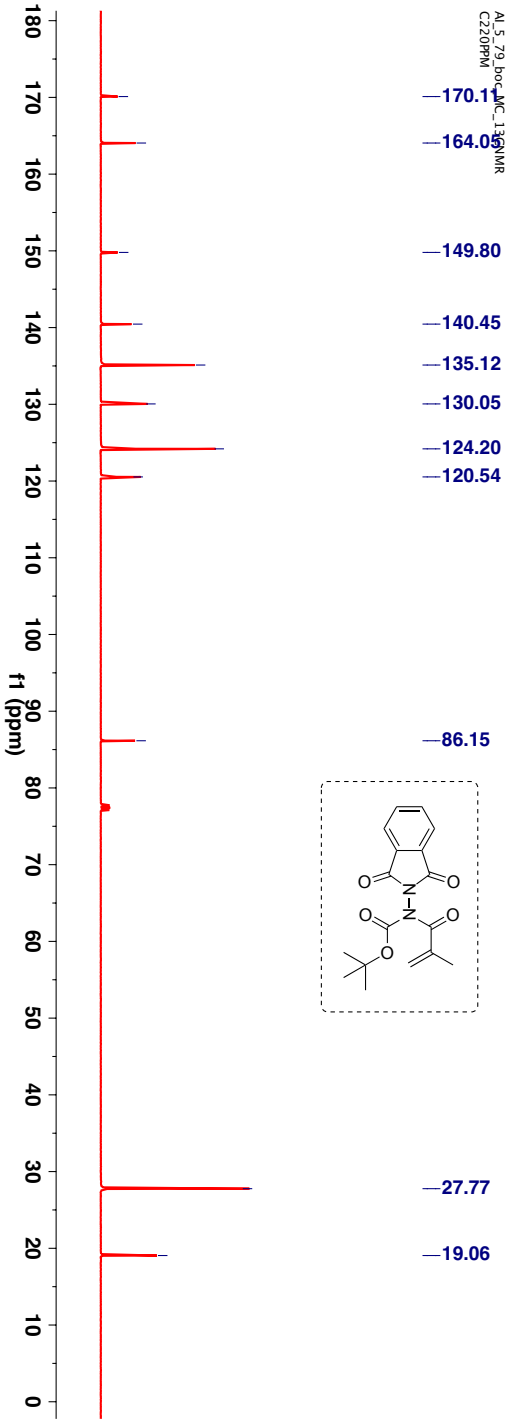
The amide derivative **16** (1 *equiv*) was taken in a round bottom flask under N_2 atmosphere, followed by the addition of anhydrous CH_2Cl_2. The solution was cooled to -20 °C and to this solution Et_3N (5 *equiv*) was added. To this solution 2.0 *equiv* of methacryloyl chloride was added slowly. The solution was stirred at -20 °C for 1 h and then at room temperature for 20 h. The reaction was quenched with 5 mL of H_2O, stirred and the layers were separated. The organic layer was sequentially washed with DI water (2 × 10 mL), saturated $NaHCO_3$ (2 × 10 mL) and finally with brine. The organic layer was dried over *anhyd* Na_2SO_4, filtered and the solvent was removed under reduced pressure to yield crude product. The crude product was purified by combiflash using hexanes and ethyl acetate as the eluting solvents.

Crystalline solid (Yield = 65%). R_f = 0.5 (20% ethyl acetate:hexanes).

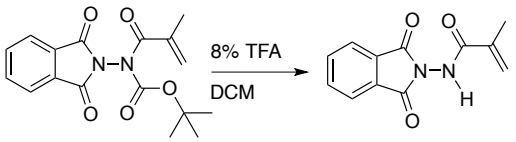
^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 1.38 (s, 9H), 2.0 (s, 3H), 5.36 (bs, 1H), 5.64 (bs, 1H), 7.70-7.72 (m, 2H) and 7.78-7.81 (m, 2H).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 19.1, 27.8, 86.2, 120.5, 124.2, 130.1, 135.1, 140.5, 149.8, 164.1 and 170.1.



ROUTE 2-STEP 3



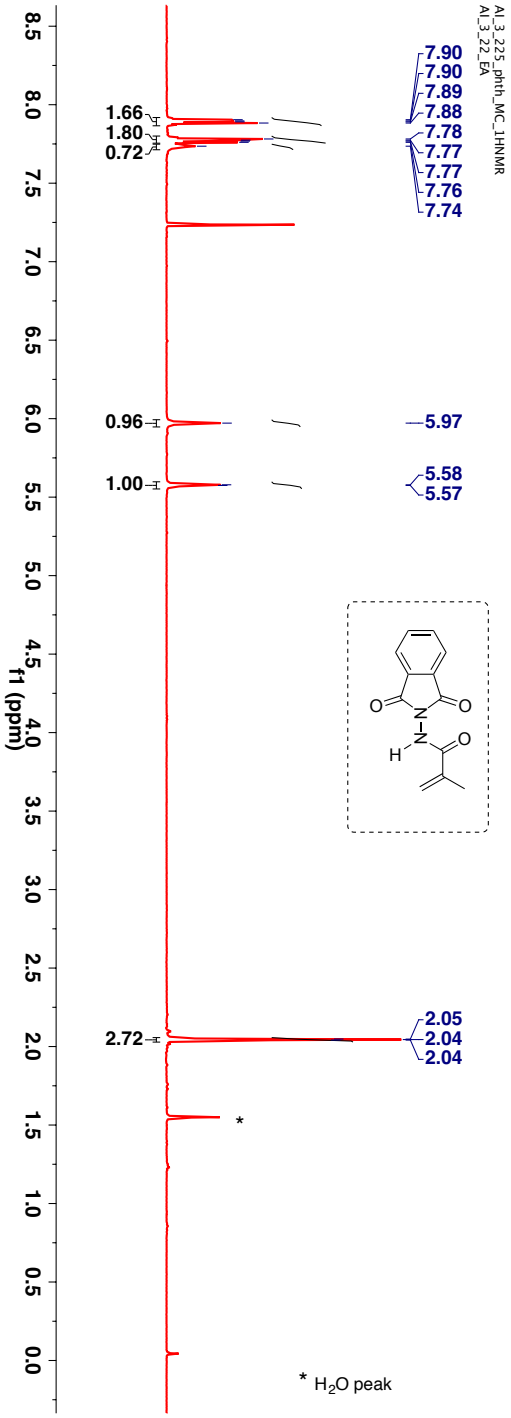
17 **15**

Scheme S5: Synthesis of amide derivative **15**.

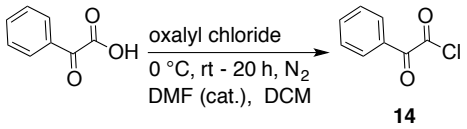
Modifying a procedure reported by Abbas *et. al.*,[2] to a solution of *N*-acyl-*N*-*tert*-butyloxycarbonylaminophthalimide (1 *equiv*) in anhydrous CH_2Cl_2 was added small volumes of trifluoroacetic acid (8% TFA in CH_2Cl_2) (25 *equiv*) at 0°C. The mixture was slowly brought to room temperature and stirred overnight. More TFA was added until complete consumption of starting material was observed. The solution was concentrated under vacuum. The crude was dissolved in ethyl acetate and the organic layer was sequentially washed with DI water (2 × 10 mL), saturated $NaHCO_3$ (2 × 10 mL) and finally with brine. The organic layer was dried over *anhyd* Na_2SO_4, filtered and the solvent was removed under reduced pressure to yield crude product. After concentrating the organic layer, the crude product was purified by combiflash using hexanes and ethyl acetate as the eluting solvents.

Crystalline solid (Yield = 90%). R_f = 0.4 (20% ethyl acetate:hexanes).

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 2.04 (s, 3H), 5.57 (bs, 1H), 5.97 (bs, 1H), 7.74 (bs, 1H), 7.76-7.78 (dd, *J* = 5.6 Hz, 3.2 Hz, 2H) and 7.88-7.90 (dd, *J* = 5.6 Hz, 3.2 Hz, 2H).



3.2.0 Synthesis of acyl chloride derivative **14**.

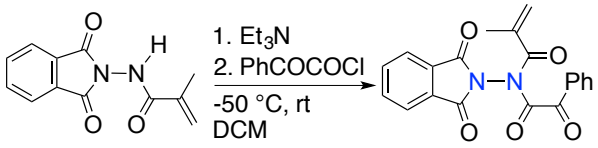


14

Scheme S6: Synthesis of acyl chloride **14**.

Following a reported procedure by Iyer *et. al.*,[3] phenylgloxylic acid (1 *equiv*) was dissolved in dichloromethane (10 mL) at 0 °C under N_2 atmosphere. To this solution oxalyl chloride (2.5 *equiv*) was added slowly. After complete addition, two drops of DMF was added during which effervescence was observed. After stirring for 15 min in an ice bath, the mixture was brought to room temperature and stirred for 3 h. The crude was concentrated to remove volatile impurities under reduced pressure while the temperature was maintained at 25 ^{o}C. After vacuum was released under N_2 atmosphere and the crude was taken to the next step without further purification.

3.2.1 Synthesis of α-oxoamide derivative **4**.



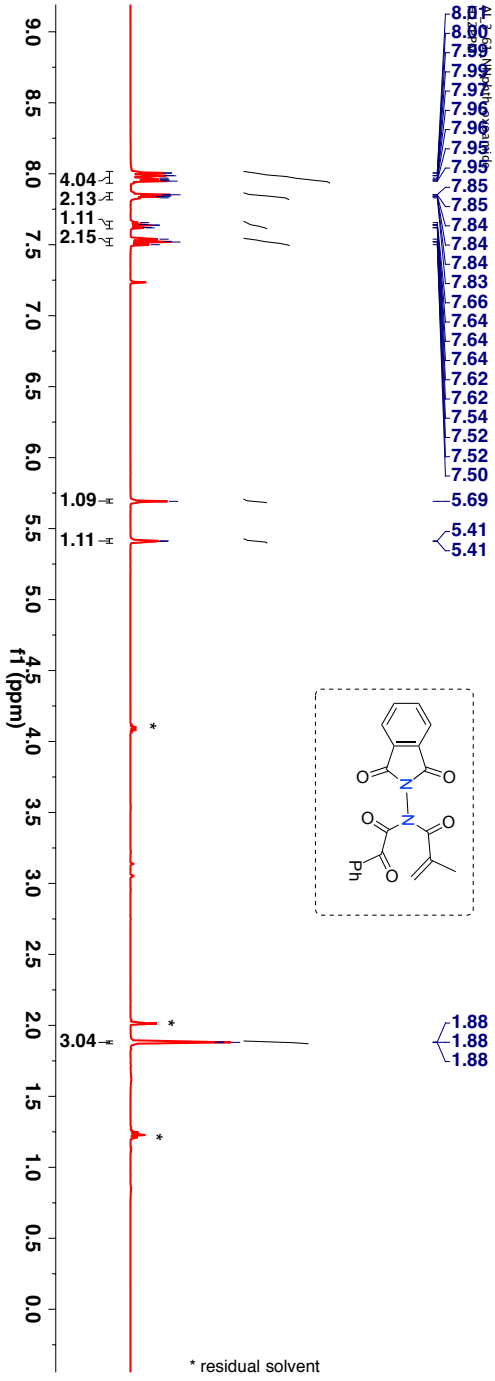
15 **4**

Scheme S7: Synthesis of α-oxoamide derivative **4**.

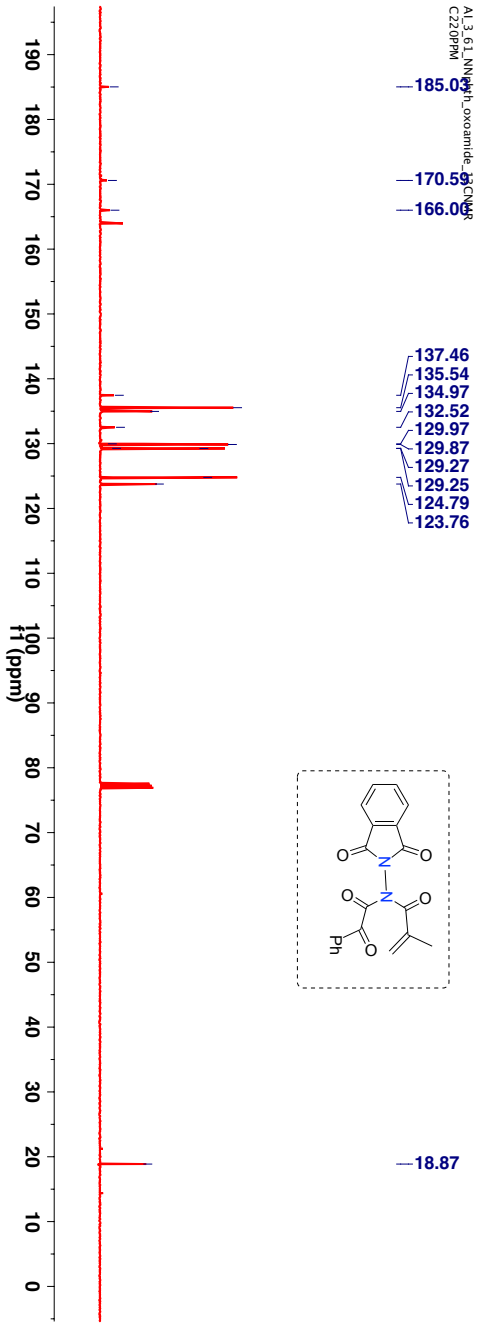
The amide derivative **15** (1 *equiv*) was taken in a round bottom flask under N_2 atmosphere. This was followed by the addition of dry CH_2Cl_2 and the solution was cooled to -50 °C. To this solution Et_3N (5 *equiv*) was added. To this solution was added freshly prepared acyl chloride **14** (2.0 *equiv*). The solution was stirred at -50 °C for 1 h and then at room temperature for 20 h. The reaction was quenched with 5 mL of H_2O, stirred and the layers were separated. The organic layer was sequentially washed with DI water (2 × 10 mL), saturated $NaHCO_3$ (2 × 10 mL) and finally with brine. The solvent was evaporated. The crude was purified by chromatography (20% EA in hexane).

Pale yellow solid (Yield = 42%). R_f = 0.5 (50% ethyl acetate:hexanes).

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 1.88 (s, 3H), 5.41 (s, 1H), 5.69 (s, 1H), 7.50-7.54 (m, 2H), 7.62-7.64 (m, 1H), 7.83-7.85 (m, 2H), 7.95-8.01 (m, 4H).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 18.9, 123.8, 124.8, 129.3, 129.8, 129.9, 132.5, 134.9, 135.5, 137.5, 166.0, 163.8, 170.6 and 185.0.



* residual solvent

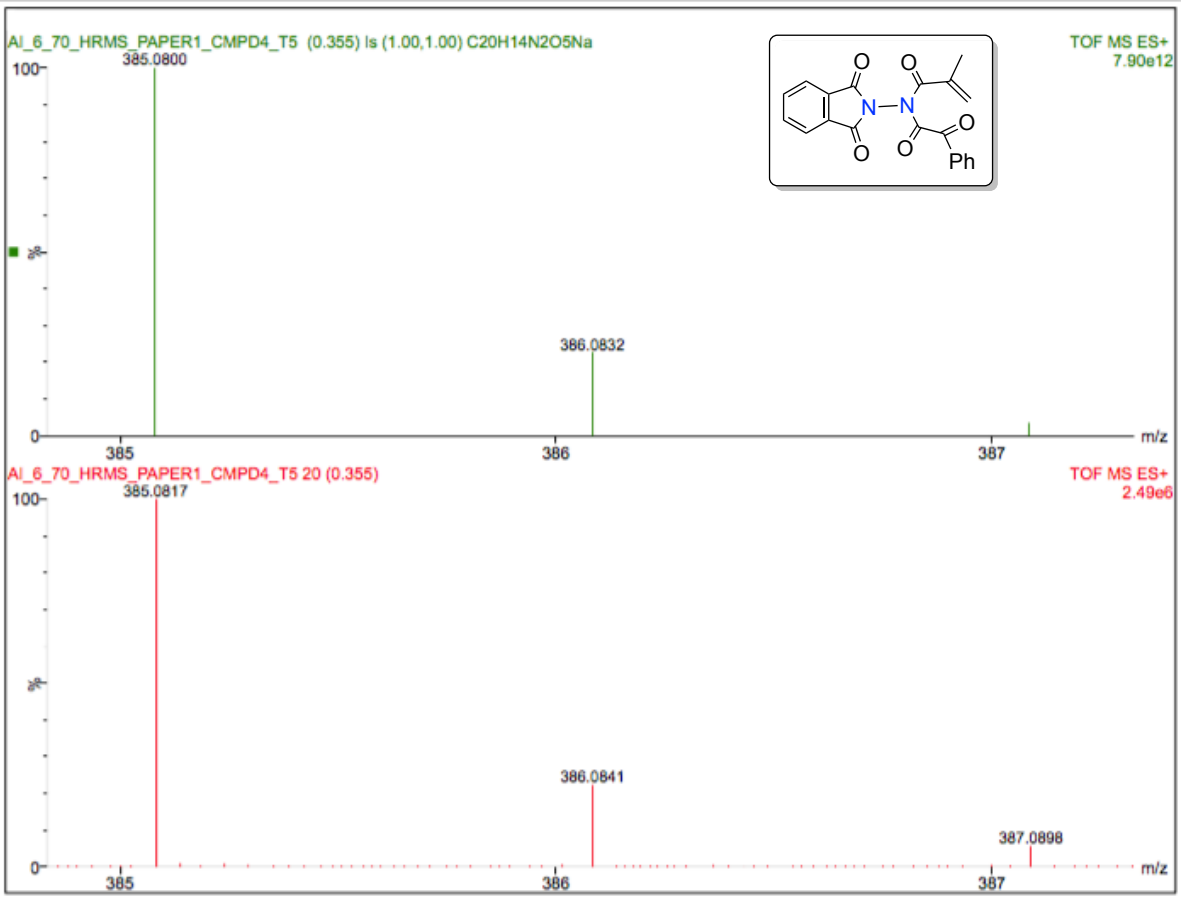
HRMS-ESI (m/z) ([M + Na]$^+$):

Chemical Formula : $C_{20}H_{14}N_2O_5$

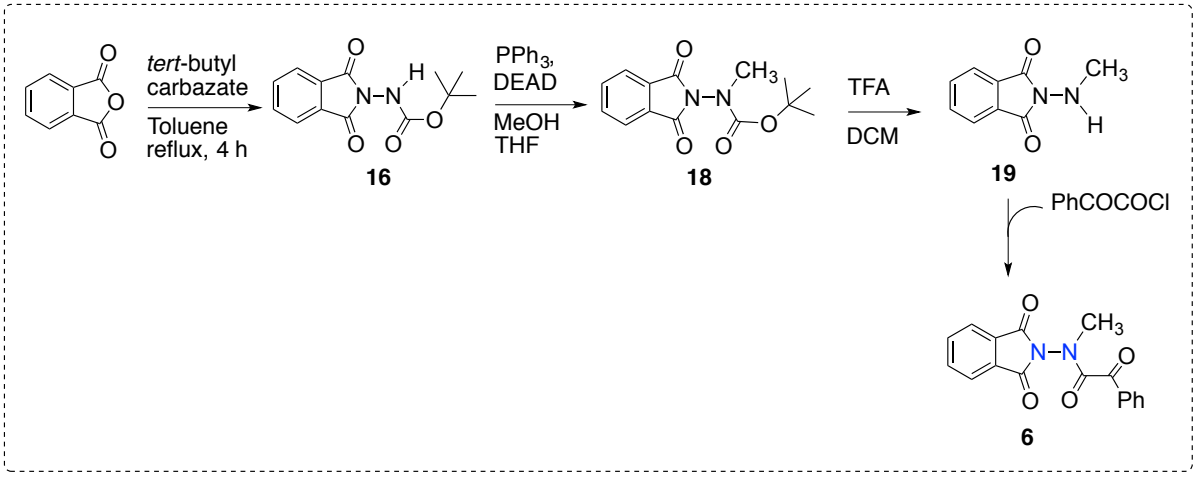
Calculated : 385.0800

Observed : 385.0817

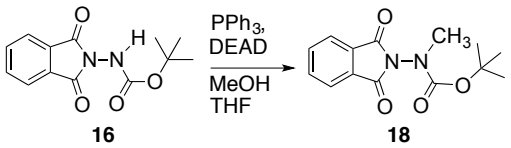
|Δm| : 4.4 ppm



3.3.0 Synthesis of α-oxoamide derivative **6**.



STEP 1

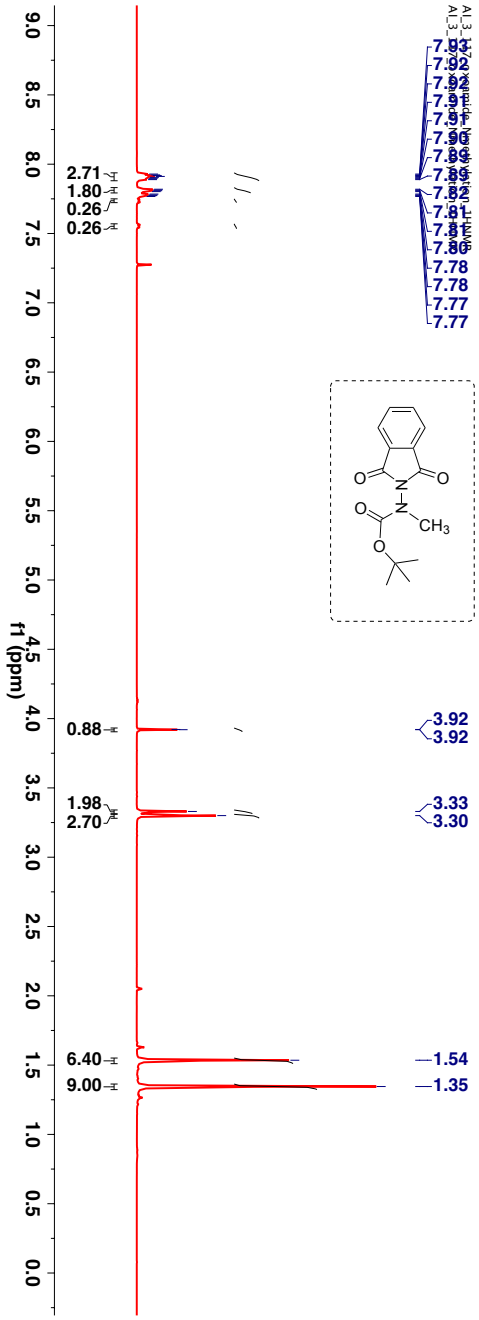


Scheme S8: Synthesis of α-oxoamide derivative **18**.

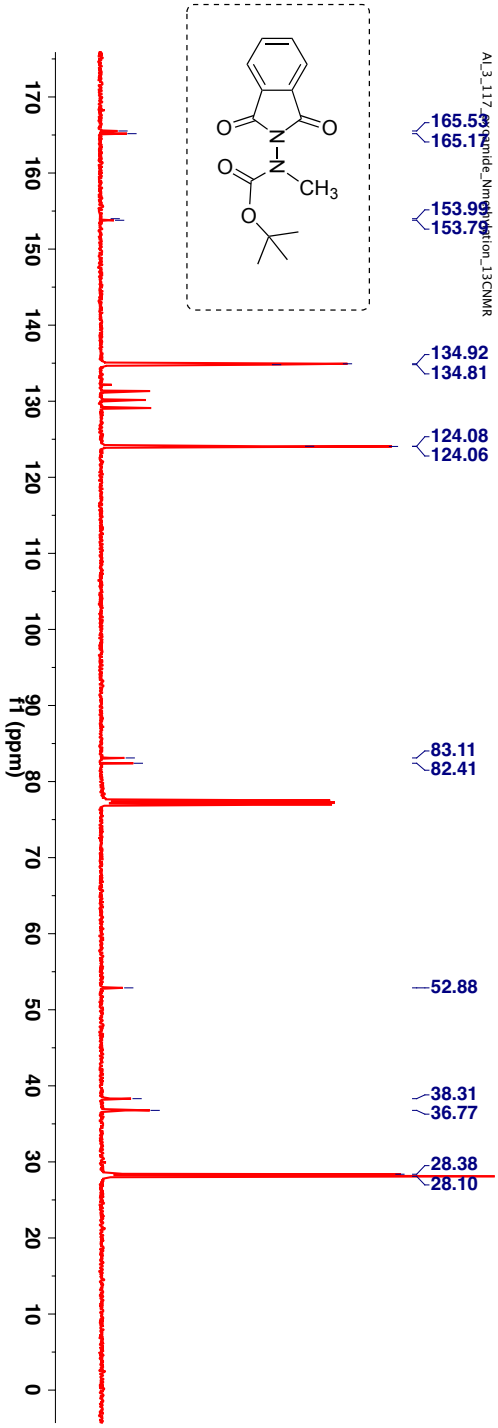
Modifying a procedure reported by Abbas *et. al.*,[2] to a solution of *N-tert*-butyloxycarbonylaminophthalimide **16** (1 *equiv*), PPh_3 (1.5 *equiv*) and methanol (3 *equiv*) in anhydrous THF and under N_2 atmosphere was added one portion of Diethyl azodicarboxylate (DEAD) (1.5 *equiv*) under stirring at 0-5 °C. The resulting solution was stirred overnight and concentrated under vacuum. The crude was purified by column chromatography on silica gel using hexanes and ethyl acetate. The product was characterized by NMR spectroscopy.

Clear solid (Yield = 87%). R_f = 0.6 (50% ethyl acetate:hexanes).

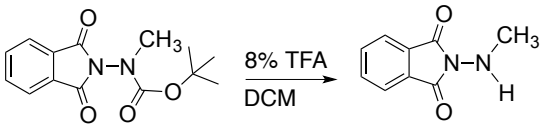
^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm, mixture of rotamers): 1.35 (s, 9H), 1.54 (s), 3.30 (s, 3H), 3.33 (s), 3.92 (s), 7.54-7.56 (m), 7.73-7.78 (m), 7.77-7.78 (m), 7.80-7.82 (m, 2H) and 7.89-7.93 (m, 2H).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm, mixture of rotamers): 28.1, 28.4, 36.8, 38.3, 52.9, 82.4, 83.1, 124.1, 124.1, 129.1, 130.3, 131.3, 132.2, 134.8, 134.9, 153.8, 153.9, 165.2 and 165.5.



STEP 2



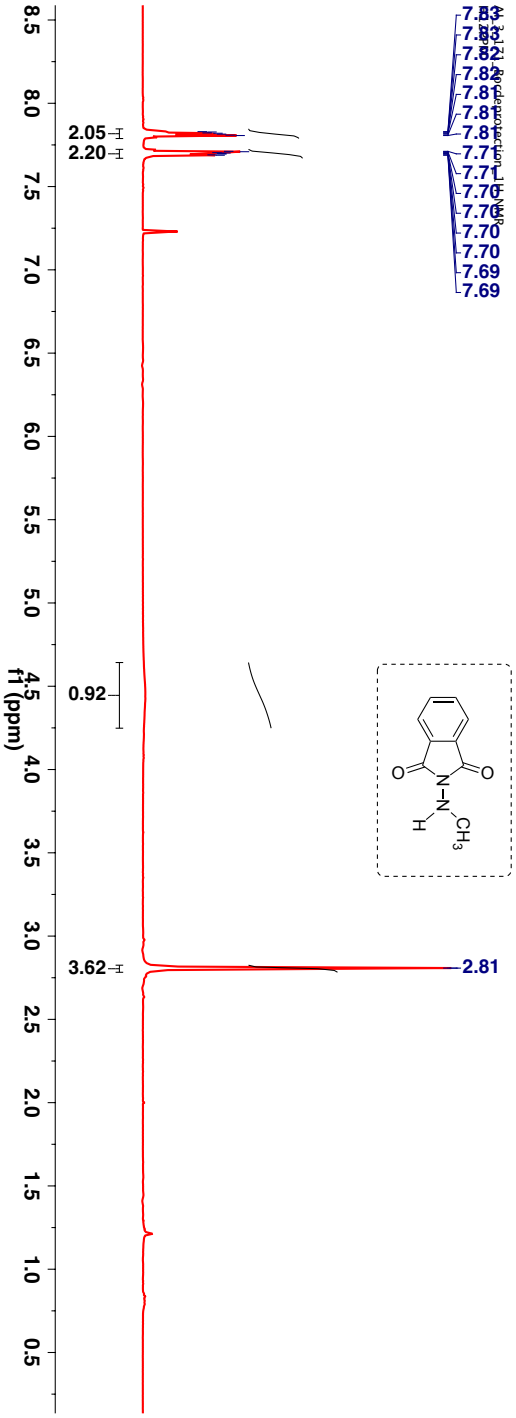
18 **19**

Scheme S9: Synthesis of hydrazide derivative **19.**

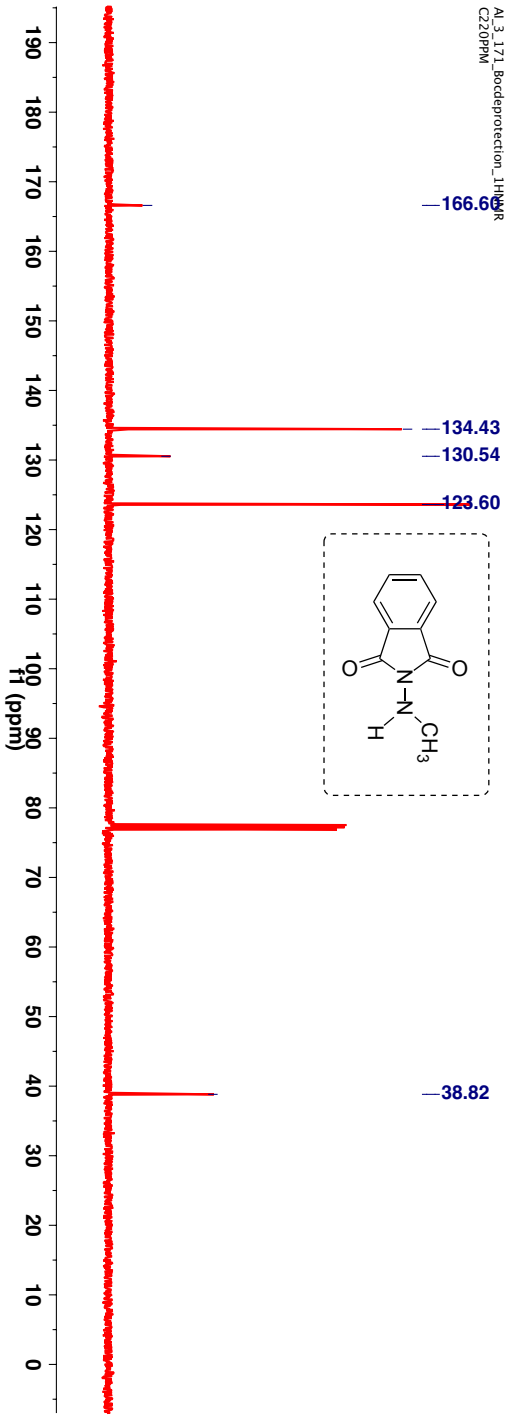
Modifying a procedure reported by Abbas *et. al.*,[2] to a solution of *N*-alkyl-*N*-*tert*-butyloxycarbonylaminophthalimide **18** (1 *equiv*) in anhydrous CH_2Cl_2 was added small portions of trifluoroacetic acid (8% TFA in CH_2Cl_2) (25 *equiv*) at 0°C. The mixture was brought to room temperature and stirred overnight. More TFA was added until complete consumption of starting material was observed. The solution was concentrated under vacuum. The crude was dissolved in ethyl acetate and the organic layer was sequentially washed with DI water (2 × 10 mL), saturated $NaHCO_3$ (2 × 10 mL) and finally with brine. The organic layer was dried over *anhyd* Na_2SO_4, filtered and the solvent was removed under reduced pressure to yield crude product. After concentrating the organic layer, the desired compound was purified by combiflash using hexanes and ethyl acetate mixture.

Colorless solid (Yield = 77%). R_f = 0.3 (50% ethyl acetate:hexanes).

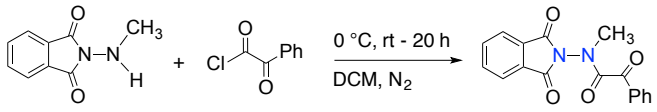
^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 2.81 (s, 3H), 4.47 (bs, 1H), 7.69-7.71(m, 2H) and 7.81-7.83 (m, 2H).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 38.8, 123.6, 130.5, 134.4 and 166.6.



STEP 3



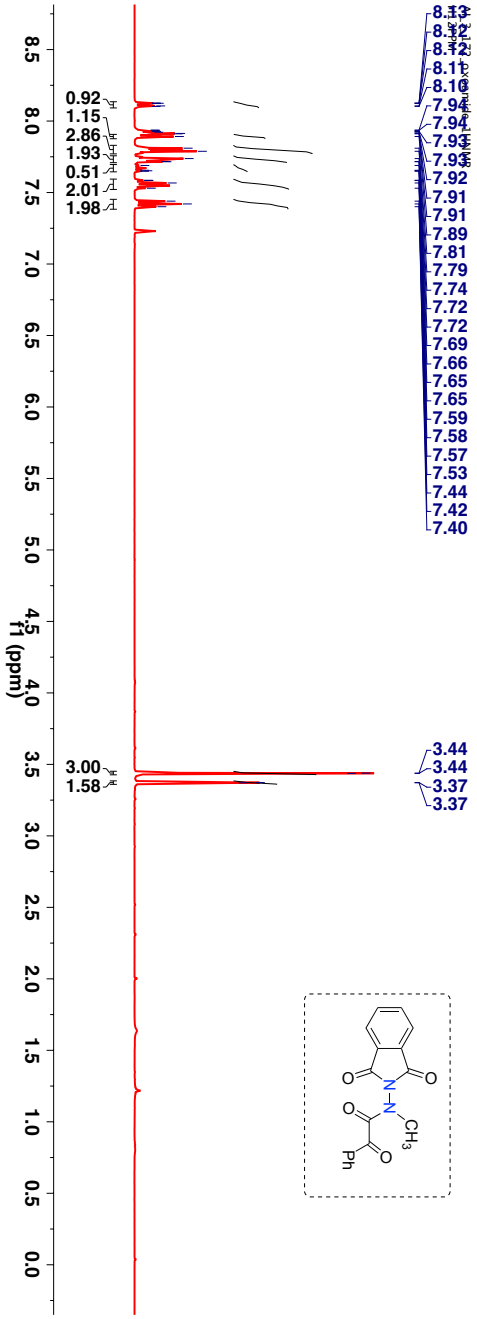
19 **14** **6**

Scheme S10: Synthesis of oxoamide derivative **6**

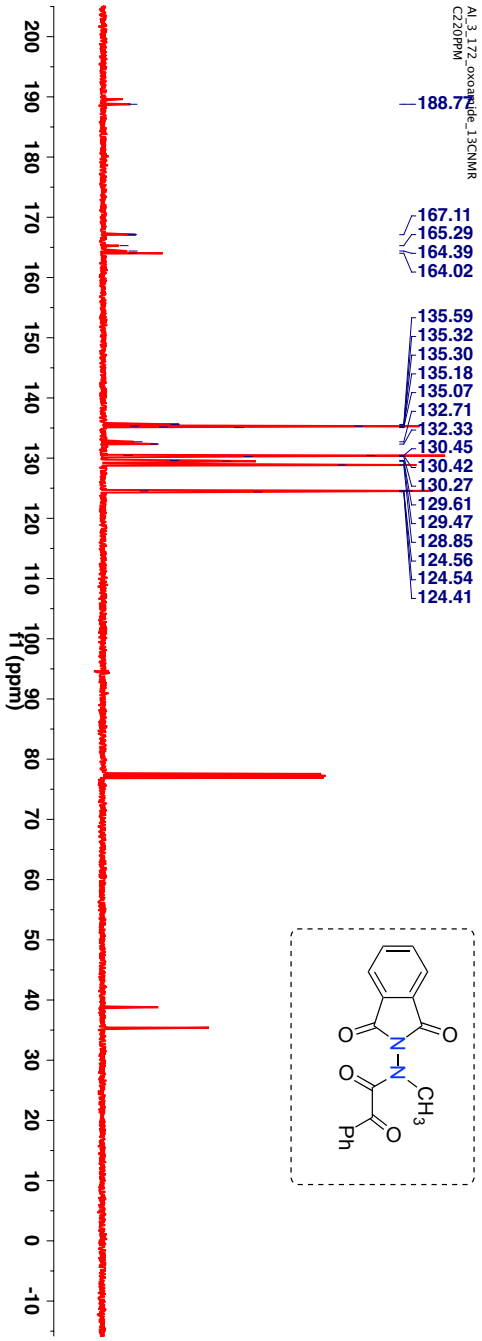
To the hydrazide derivative **19** (1 *equiv*) in a round bottom flask under N_2 atmosphere, dry CH_2Cl_2 was added and the solution was cooled to -20 °C. To this solution Et_3N (5 *equiv*) was added followed by the addition of freshly prepared acyl chloride **14** (2 *equiv*). The solution was stirred at -20 °C for 1 h and then at room temperature for 20 h. The reaction was quenched with 5 mL of H_2O, stirred and the layers were separated. The organic layer was sequentially washed with DI water (2 × 10 mL), saturated $NaHCO_3$ (2 × 10 mL) and finally with brine. The organic layer was dried over *anhyd* Na_2SO_4, filtered and the solvent was removed under reduced pressure to yield crude product. After concentrating the organic layer, the desired compound was purified by combiflash using hexanes and ethyl acetate as the eluting solvent.

Yellow solid (Yield = 68%). R_f = 0.6 (50% ethyl acetate:hexanes).

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm, 1.9 : 1.0 rotamer ratio, mixture of rotamers): 3.37 (s), 3.44 (s, 3H), 7.40-7.44 (m, 2H), 7.53-7.59 (m, 2H), 7.65-7.69 (m), 7.72-7.74 (m, 2H), 7.79-7.81 (m, 2H), 7.89-7.93 (m, 3H) and 8.10-8.13 (m, 1H).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm, all peaks are reported together as it is difficult to assign certain peaks in aromatic region to minor rotamer peaks): 35.4, 38.8, 124.4, 124.6, 128.9, 129.5, 129.6, 130.1, 130.3, 130.5, 132.3, 132.7, 135.1, 135.2, 135.3, 135.6, 164.0, 164.4, 165.3, 167.1, 188.8 and 189.8.



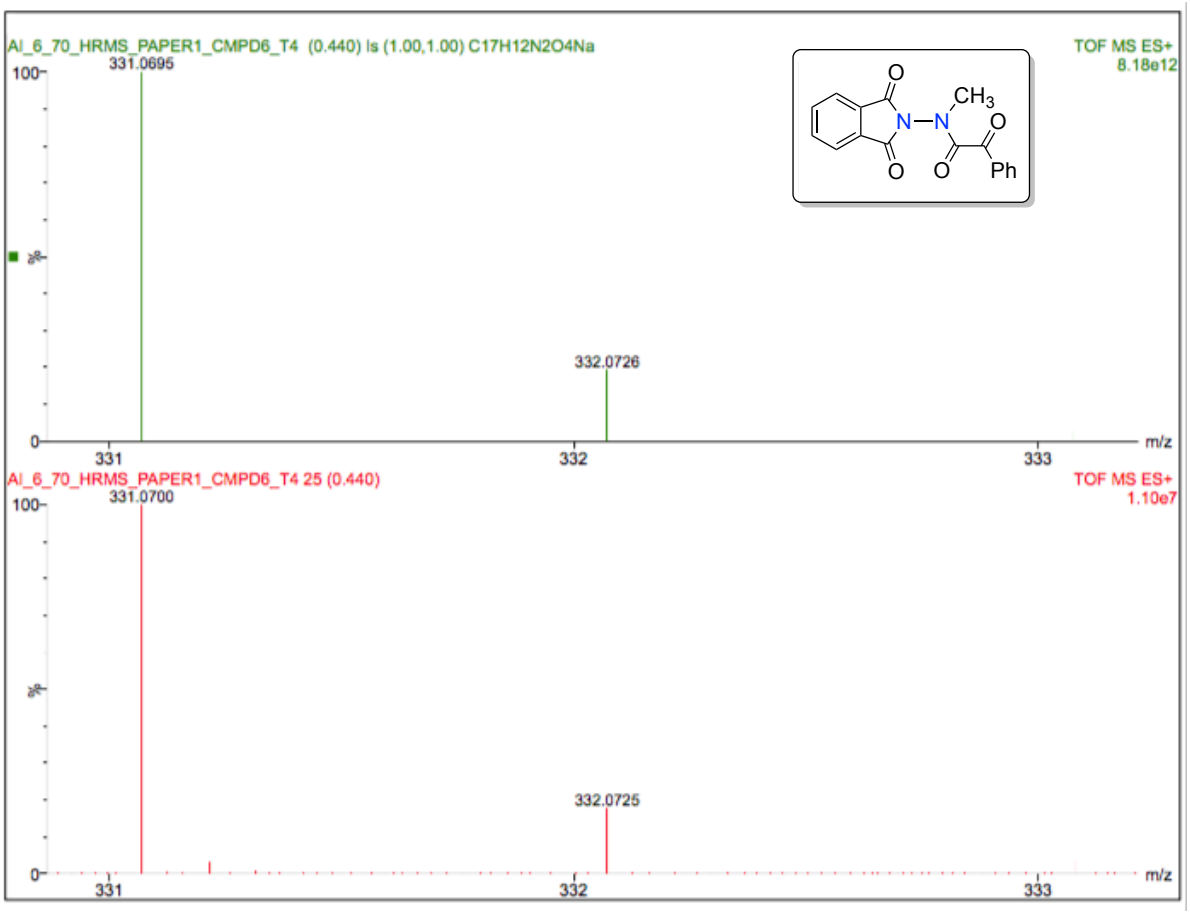
HRMS-ESI (m/z) ([M + Na]$^+$):

Chemical Formula : $C_{17}H_{12}N_2O_4$

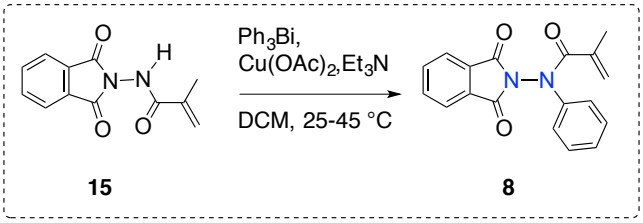
Calculated : 331.0695

Observed : 331.0700

|Δm| : 1.5 ppm



3.4.0 Synthesis of acrylanilide derivative **8**.

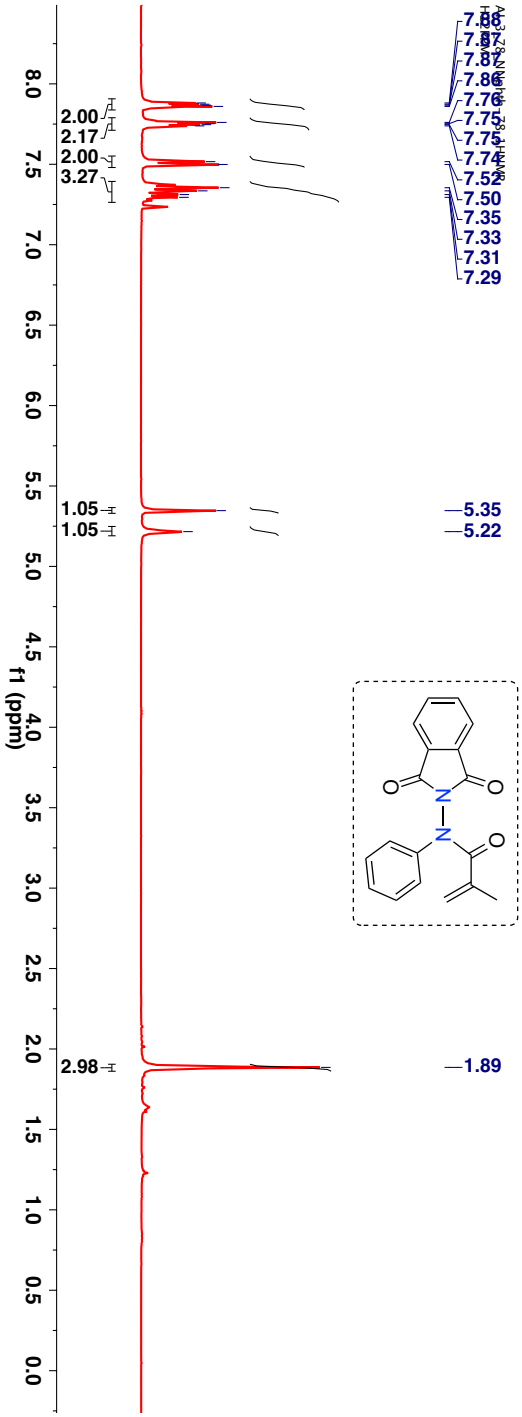


Scheme S11: Synthesis of acrylanilide derivative **8.**

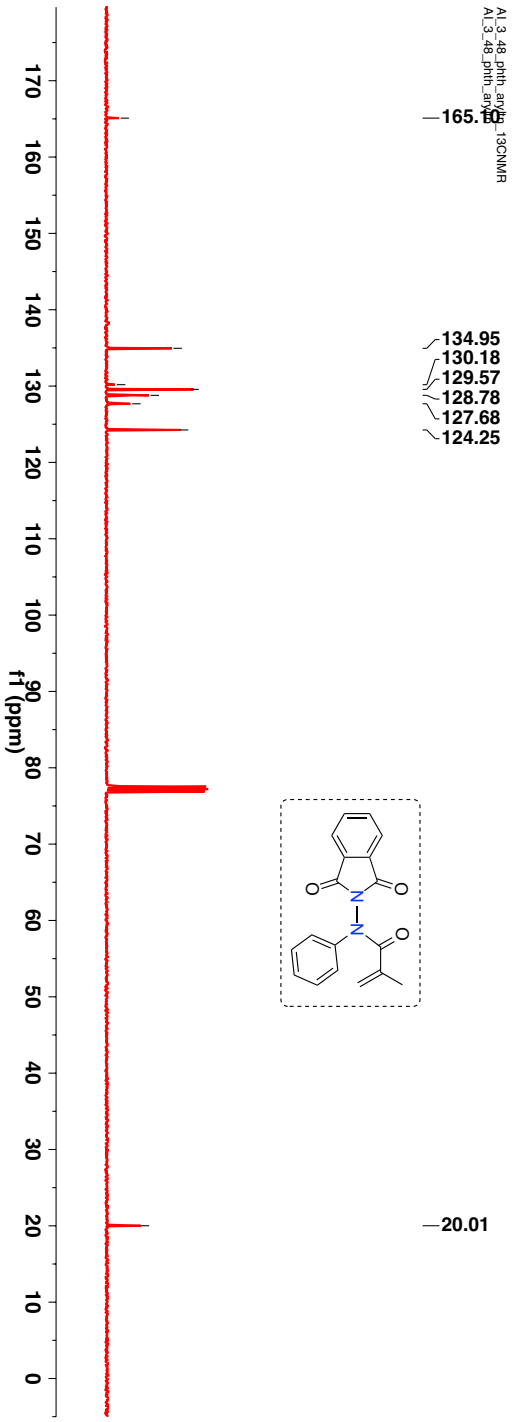
Following the modified procedure reported by Kikugawa *et. al.*[4] a mixture of amide **15** (1 *equiv*), triphenylbismuth (2 *equiv*), cupric acetate (1.5 *equiv*), and triethylamine (1.5 *equiv*) was stirred in anhydrous CH_2Cl_2 for 1.5 h at room temperature under N_2 atmosphere and then refluxed for 20 h. After completion of the reaction, the solution was diluted with ethyl acetate (20 mL) and filtered through a short celite plug. The filtrate was evaporated under reduced pressure. The crude product was chromatographed with a flash column using ethyl acetate and hexanes as the eluting solvent. The desired product was obtained as a white solid.

Crystalline solid (Yield = 33%). R_f = 0.7 (50% ethyl acetate:hexanes).

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 1.89 (s, 3H), 5.22 (s, 1H), 5.35 (s, 1H), 7.28-7.37 (m, 3H), 7.50-7.52 (m, 2H), 7.74-7.76 (m, 2H), and 7.86-7.88 (m, 2H).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 20.0, 124.3, 127.7, 128.8, 129.6, 130.2, 134.9 and 165.1.



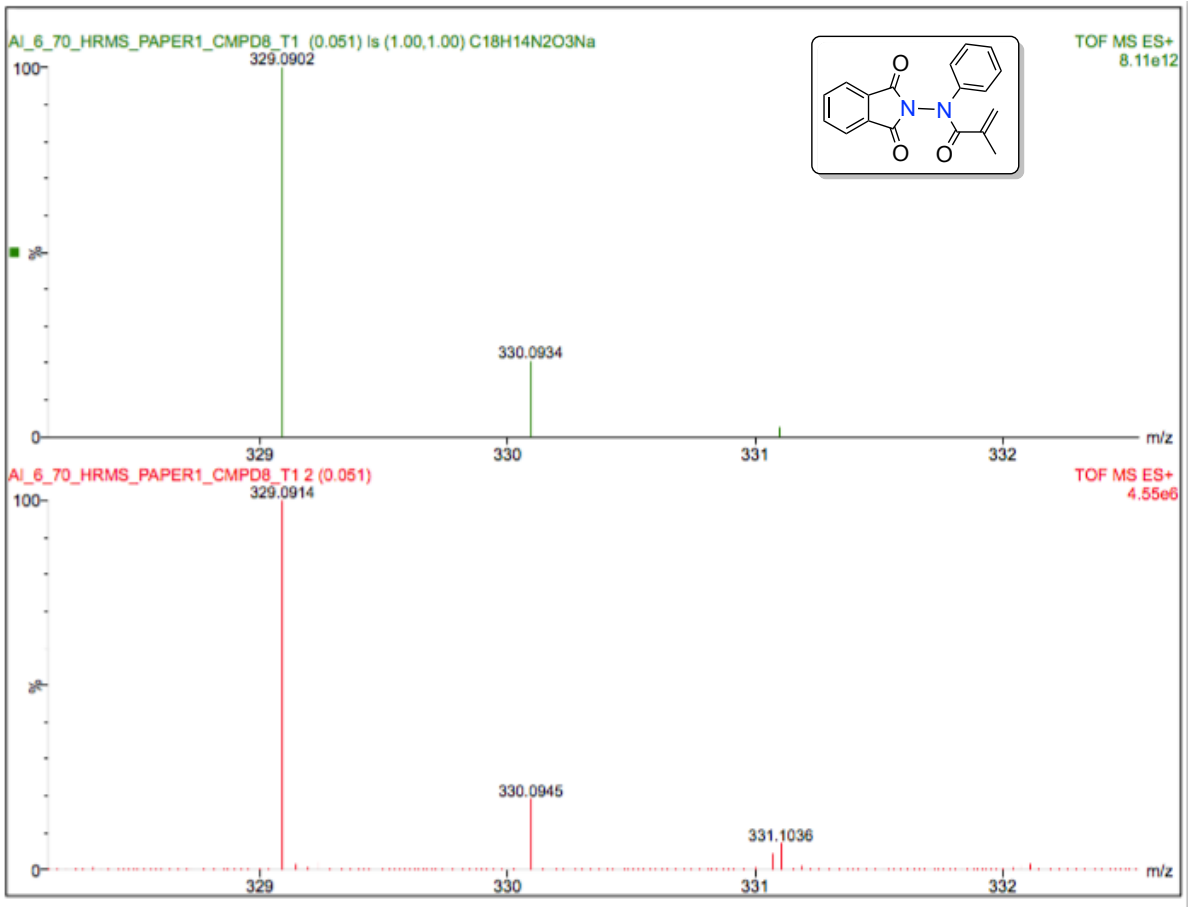
HRMS-ESI (m/z) ([M + H]):

Chemical Formula : $C_{18}H_{14}N_2O_3$

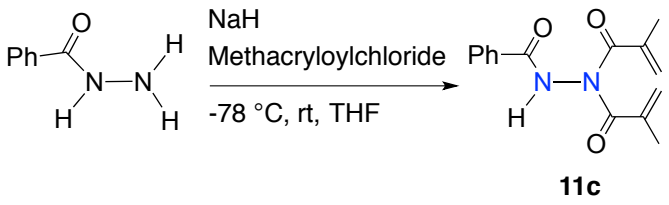
Calculated : 329.0902

Observed : 329.0914

|Δm| : 3.6 ppm



3.5.0 Synthesis of amide based hydrazide derivative **11c**.



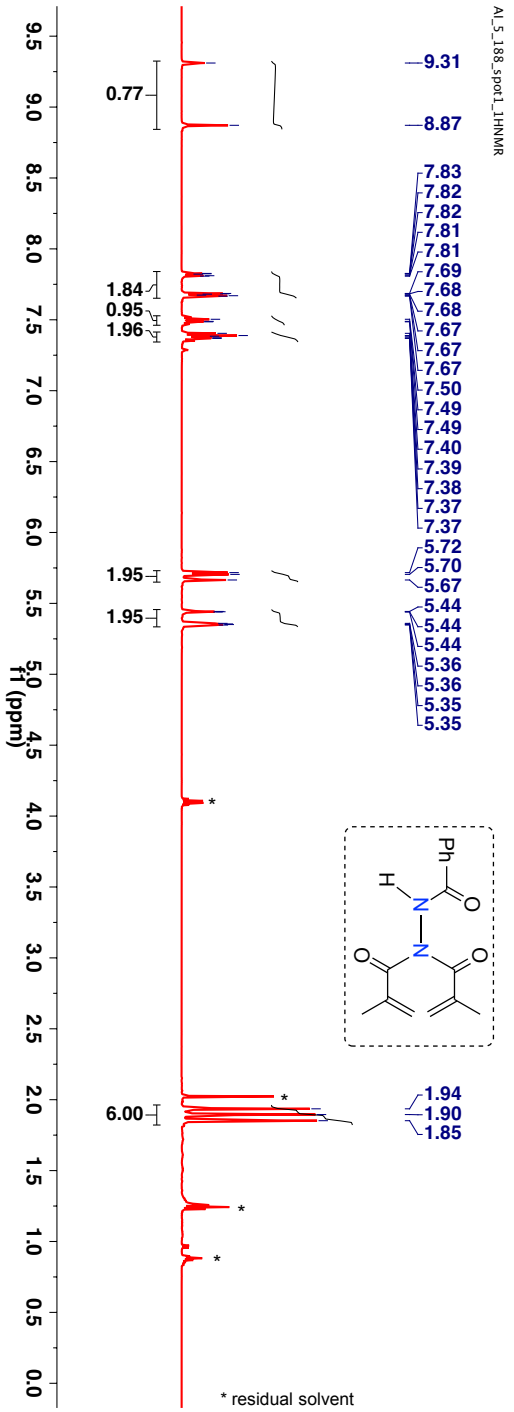
11c

Scheme S12: Synthesis of amide based hydrazide derivative **11c**.

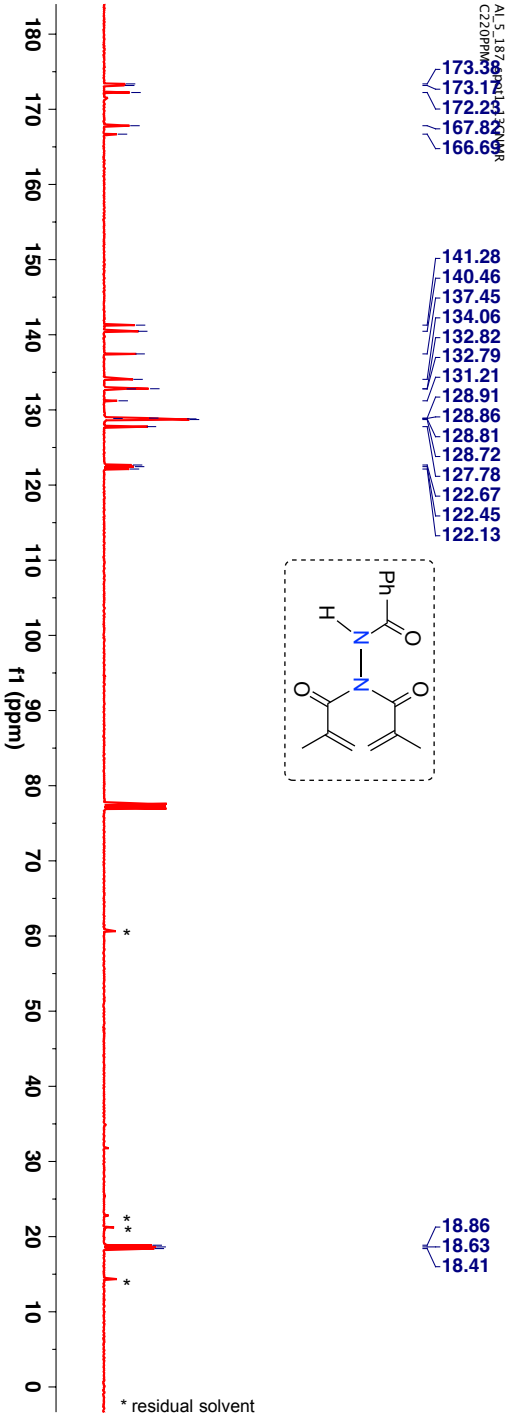
Benzhydrazine (1 *equiv*) was taken in a round bottom flask under N_2 atmosphere and dissolved in in freshly distilled THF. The solution was cooled to -78 °C. To this solution NaH (5 *equiv*) was added slowly in portions. To this solution was added methacryloyl chloride (2.0 *equiv*). The solution was stirred at -50 °C for 2 h and then at room temperature for 20 h. The reaction was quenched with 5 mL of H_2O, stirred and the layers were separated. The organic layer was sequentially washed with DI water (2 × 10 mL), saturated $NaHCO_3$ (2 × 10 mL) and finally with brine. The organic layer was dried over *anhyd* Na_2SO_4, filtered and the solvent was removed under reduced pressure to yield crude product. After concentrating the organic layer, the desired compound was purified by combiflash using hexanes and ethyl acetate as the eluting solvent.

Viscous clear liquid (Yield = 44%). R_f = 0.5 (50% ethyl acetate:hexanes).

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm, mixture of rotamers): 1.85 (s), 1.90 (s), 1.94 (s), 5.35-5.36 (m), 5.44 (s), 5.67 (s), 5.70-5.72 (m), 7.37-7.40 (m), 7.49-7.50 (m), 7.67-7.69 (m), 7.81-7.83 (m), 8.87 (bs) and 9.31 (bs).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm, mixture of rotamers): 18.4, 18.6, 18.9, 122.1, 122.5, 122.7, 127.8, 128.7, 128.8, 128.8, 128.9, 131.2, 132.8, 132.8, 134.1, 137.5, 140.5, 141.3, 166.7, 167.8, 172.2, 173.2 and 173.4.



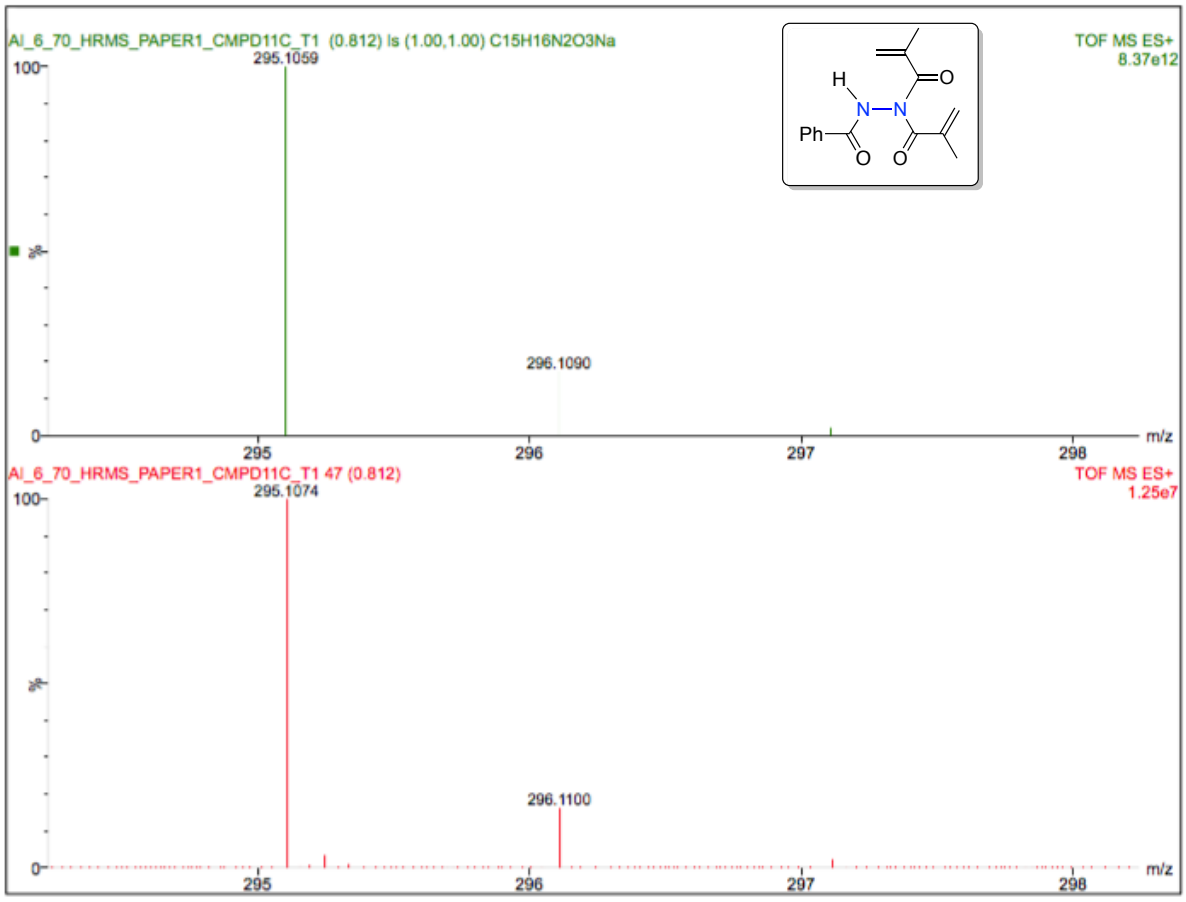
HRMS-ESI (m/z) ([M + H]):

Chemical Formula : $C_{15}H_{16}N_2O_3$

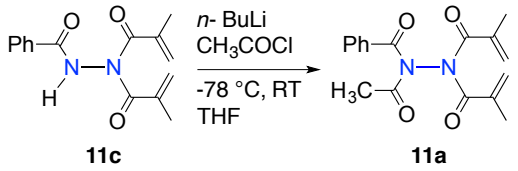
Calculated : 295.1059

Observed : 295.1074

|Δm| : 1.6 ppm



3.5.1 Synthesis of amide based hydrazide derivative **11a**.

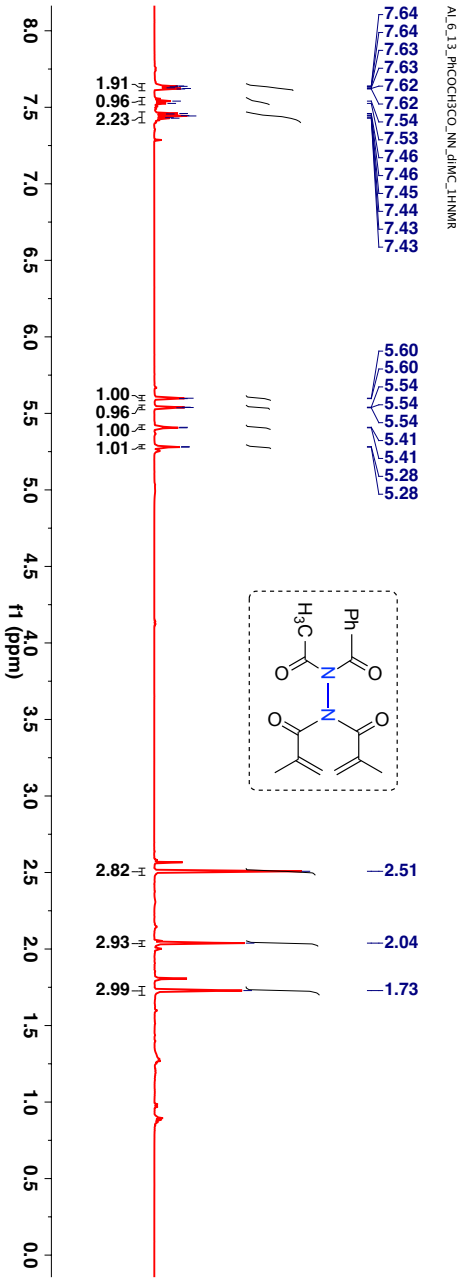


Scheme S13: Synthesis of amide based hydrazide derivative **11a**.

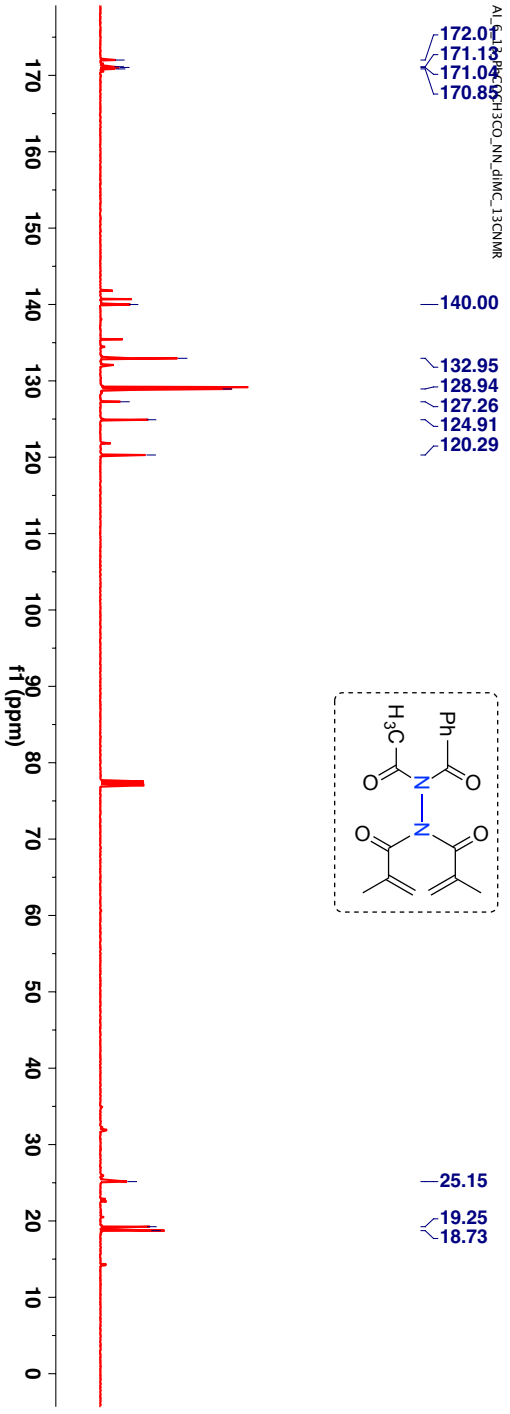
The amide based hydrazide derivative **11c** (1 *equiv*) was taken in a round bottom flask under N_2 atmosphere and dissolved in freshly distilled THF. The solution was cooled to -78 °C. To this solution *n*-BuLi (1 *equiv*) was added dropwise over a period of 10 minutes. This was followed by addition of freshly distilled acetyl chloride (1.1 *equiv*). The solution was stirred at -78 °C for 2 h after which TLC showed complete consumption of starting material. The reaction was quenched with 5 mL of H_2O, stirred and the layers were separated. The organic layer was sequentially washed with DI water (2 × 10 mL), saturated $NaHCO_3$ (2 × 10 mL) and finally with brine. The organic layer was dried over *anhyd* Na_2SO_4, filtered and the solvent was removed under reduced pressure to yield crude product. After concentrating the organic layer, the desired compound was purified by combiflash using hexanes and ethyl acetate as the eluting solvent.

Viscous liquid that became solid on standing (Yield = 71%). R_f = 0.6 (50% ethyl acetate:hexanes).

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm, mixture of rotamers): 1.73 (s, 3H), 2.04 (s, 3H), 2.51 (s, 3H), 5.28 (s, 1H), 5.41 (s, 1H), 5.54 (s, 1H), 5.60 (s, 1H), 7.43-7.46 (m, 2H), 7.53-7.56 (m, 1H) and 7.62-7.64 (m, 2H).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm, mixture of rotamers): 18.7, 19.2, 25.2, 120.3, 124.9, 127.3, 128.9, 133.0, 140.0, 141.1, 142.0, 170.8, 171.0, 171.1 and 172.0.



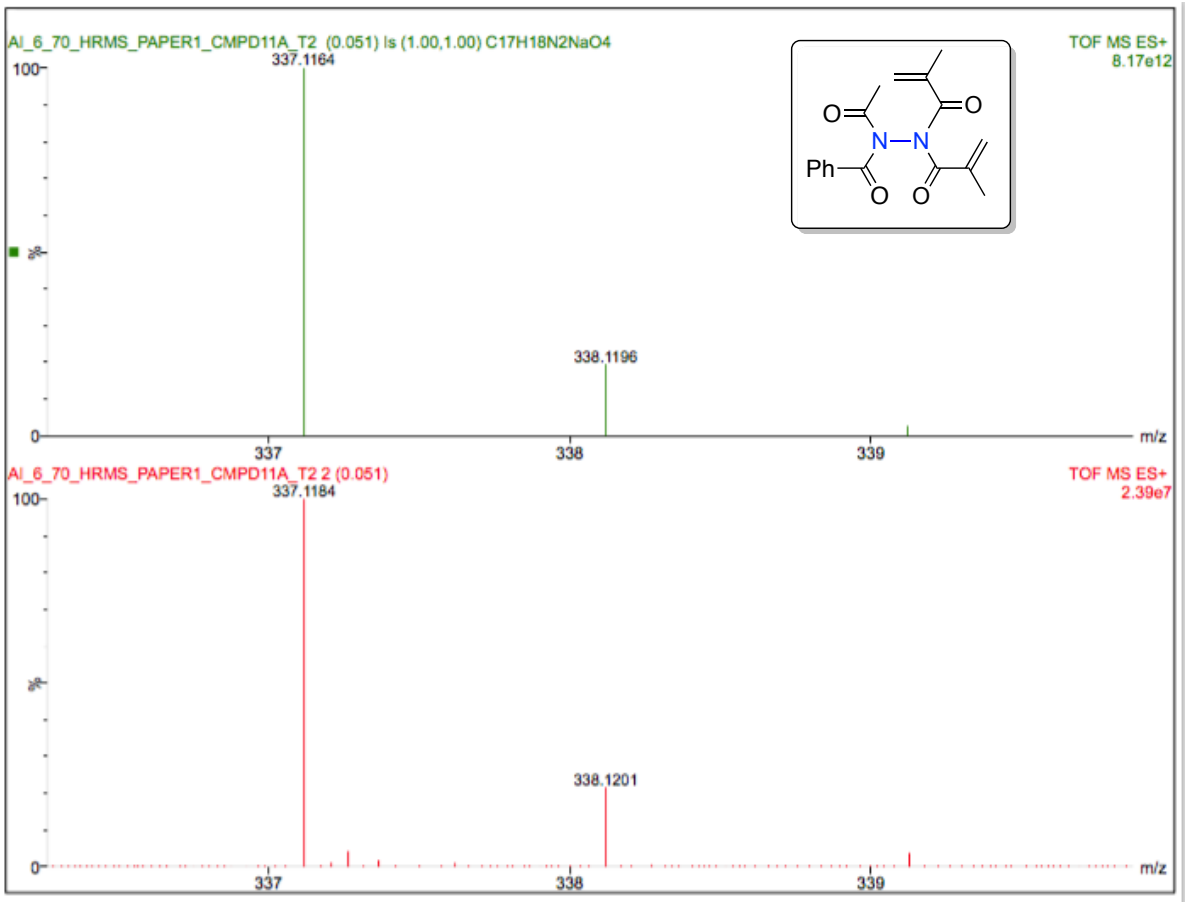
HRMS-ESI (m/z) ([M + Na]$^+$):

Chemical Formula : $C_{17}H_{18}N_2O_4$

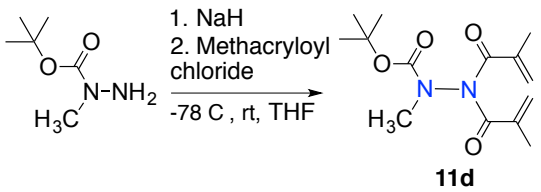
Calculated : 337.1164

Observed : 337.1184

|Δm| : 5.9 ppm



3.5.2 Synthesis of secondary carbamate based hydrazide derivative **11d**.

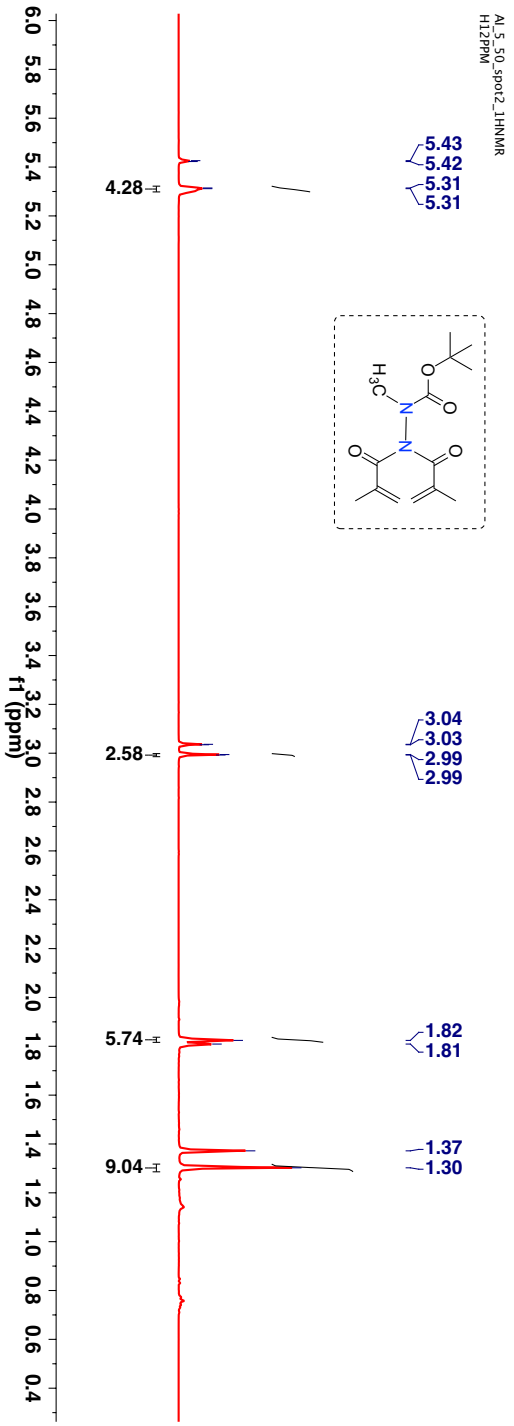


Scheme S14: Synthesis of carbamate based hydrazide derivative **11d**.

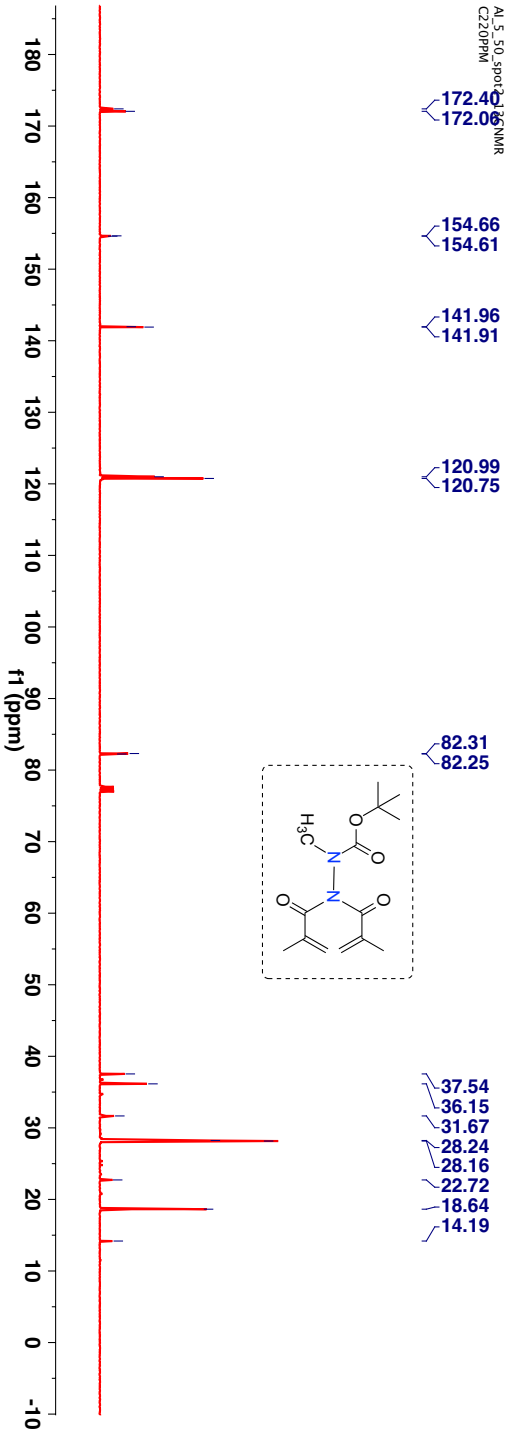
1-Boc-1-methylhydrazine (1 *equiv*) was dissolved in freshly distilled THF under N_2 atmosphere. The reaction mixture was then cooled to -78 °C and this was followed by the addition of 5 *equiv* of NaH followed by the dropwise addition of methacryloyl chloride (2.5 *equiv*). After stirring for 1 h, the mixture was brought to room temperature and stirred for 20 h. The reaction was quenched with 5 mL of NH_4Cl, stirred and the layers were separated. The organic layer was sequentially washed with DI water (2 × 10 mL), saturated $NaHCO_3$ (2 × 10 mL) and finally with brine. The organic layer was dried over *anhyd* Na_2SO_4, filtered and the solvent was removed under reduced pressure to yield crude product. The crude product was purified by combiflash using hexanes and ethyl acetate as the eluting solvents.

Viscous liquid (Yield = 32%). R_f = 0.4 (50% ethyl acetate:hexanes).

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm, 1.9 : 1.0 rotamer ratio, mixture of rotamer): 1.30 (s, 9H), 1.37 (s), 1.82 (s, 6H), 1.81 (s), 2.99(s, 3H), 3.04 (s), 5.31 (m, 4H) and 5.42 (s).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm, mixture of rotamer): 14.2, 18.6, 22.8, 28.2, 28.2, 31.7, 36.2, 37.5, 82.3, 82.3, 120.8, 120.9, 141.9, 141.9, 154.6, 154.7, 172.1 and 172.4.



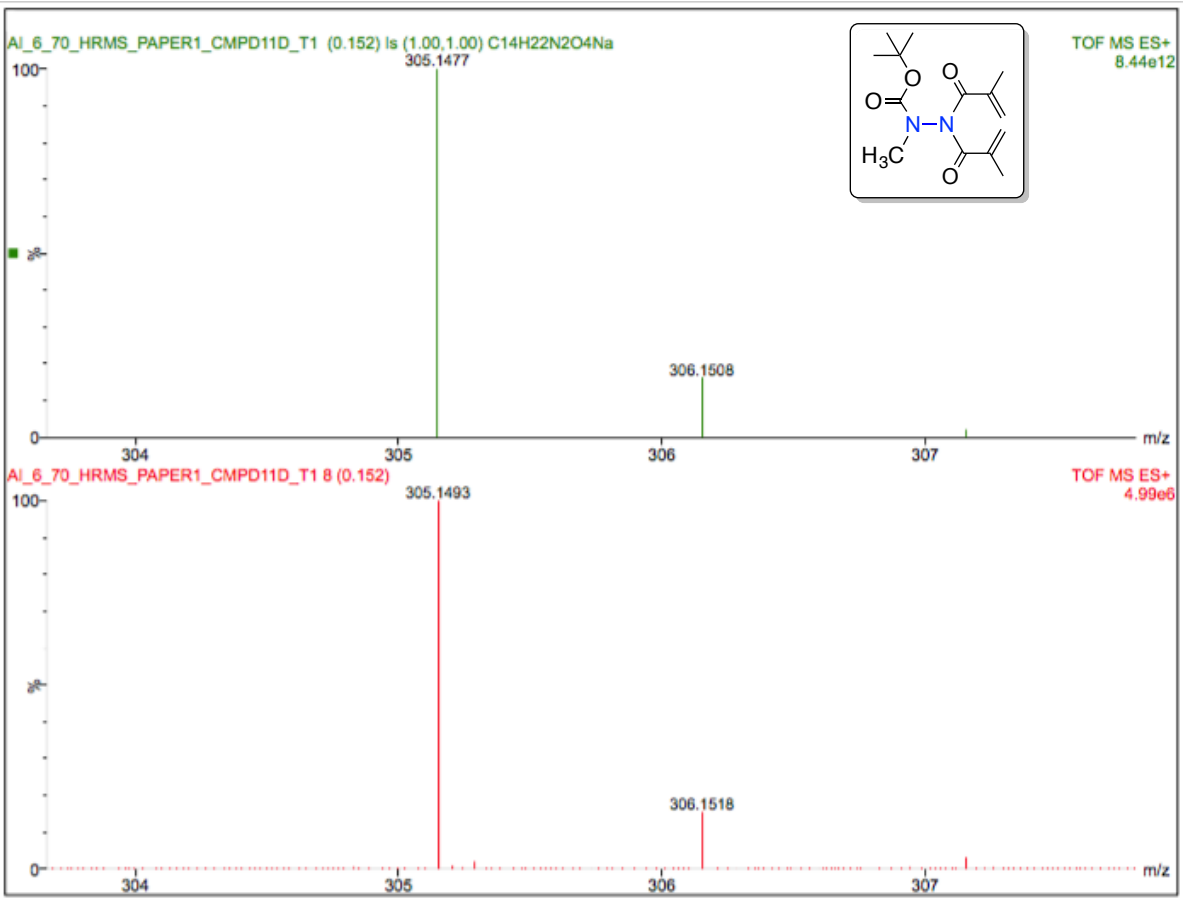
HRMS-ESI (m/z) ([M + Na]$^+$):

Chemical Formula : $C_{14}H_{22}N_2O_4$

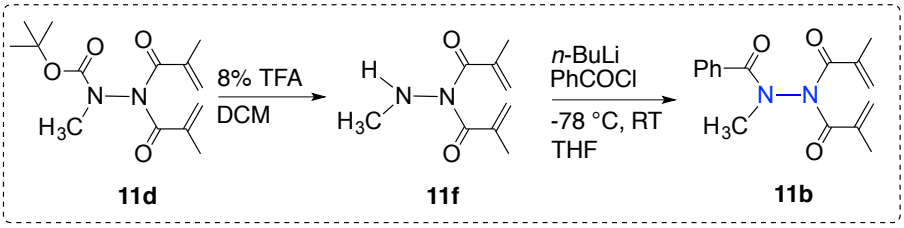
Calculated : 305.1477

Observed : 305.1493

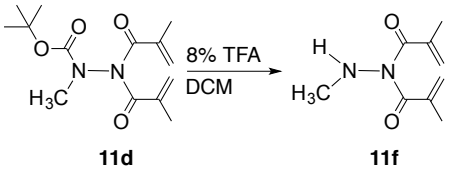
|Δm| : 5.2 ppm



3.5.3 Synthesis of amide based hydrazide derivative **11b**.



STEP1

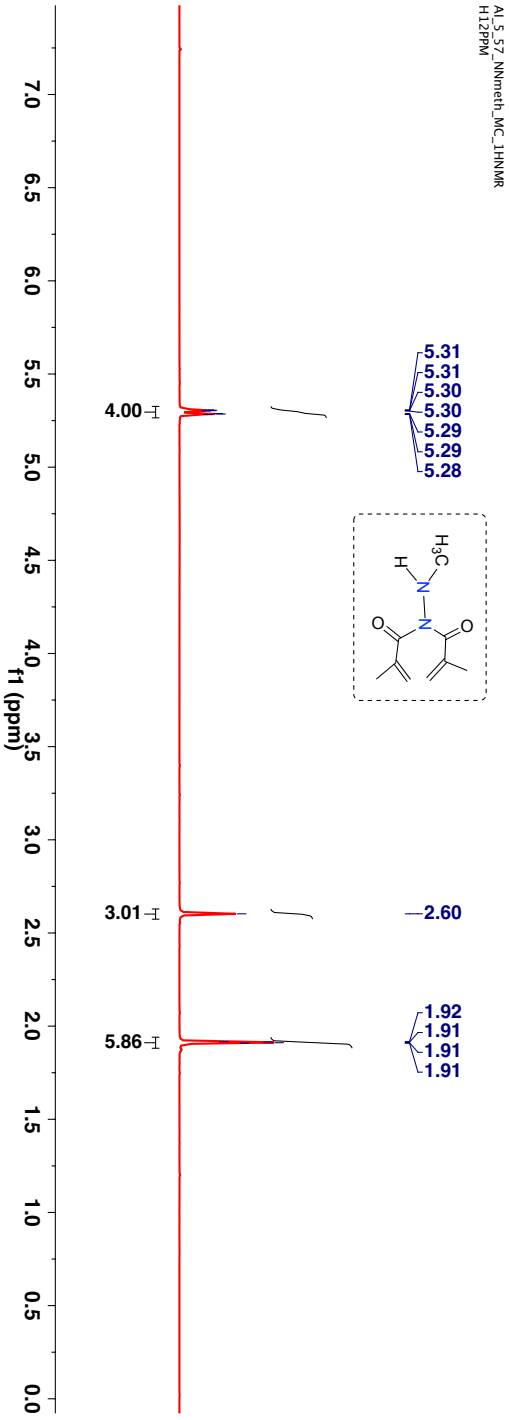


Scheme S15: Synthesis of amine based hydrazide derivative **11f**.

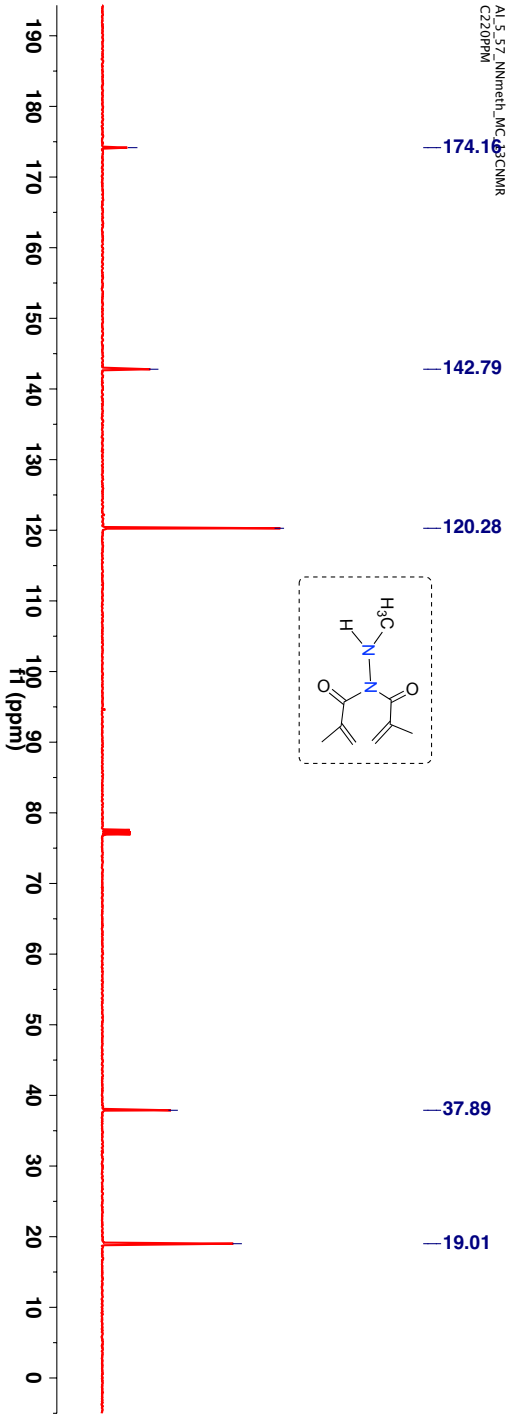
To a solution of imide derivative **11d** (1 *equiv*) in anhydrous CH_2Cl_2 was added small portions of trifluoroacetic acid (8% TFA in CH_2Cl_2) (25 *equiv*) at 0°C. The mixture was stirred overnight. More TFA was added until complete consumption of starting material was observed. The solution was concentrated under vacuum. The crude was dissolved in ethyl acetate and the organic layer was sequentially washed with DI water (2 × 10 mL), saturated $NaHCO_3$ (2 × 10 mL) and finally with brine. The organic layer was dried over *anhyd* Na_2SO_4, filtered and the solvent was removed under reduced pressure to yield crude product. After concentrating the organic layer, the crude product was purified by combiflash using hexanes and ethyl acetate and ethyl acetate as eluting solvents.

Viscous clear liquid (Yield = 38%). R_f = 0.4 (20% ethyl acetate:hexanes).

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 1.91 (s, 6H), 2.60 (s, 3H) and 5.28-5.31 (m, 4H).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 19.0, 37.9, 120.3, 142.8 and 174.2.



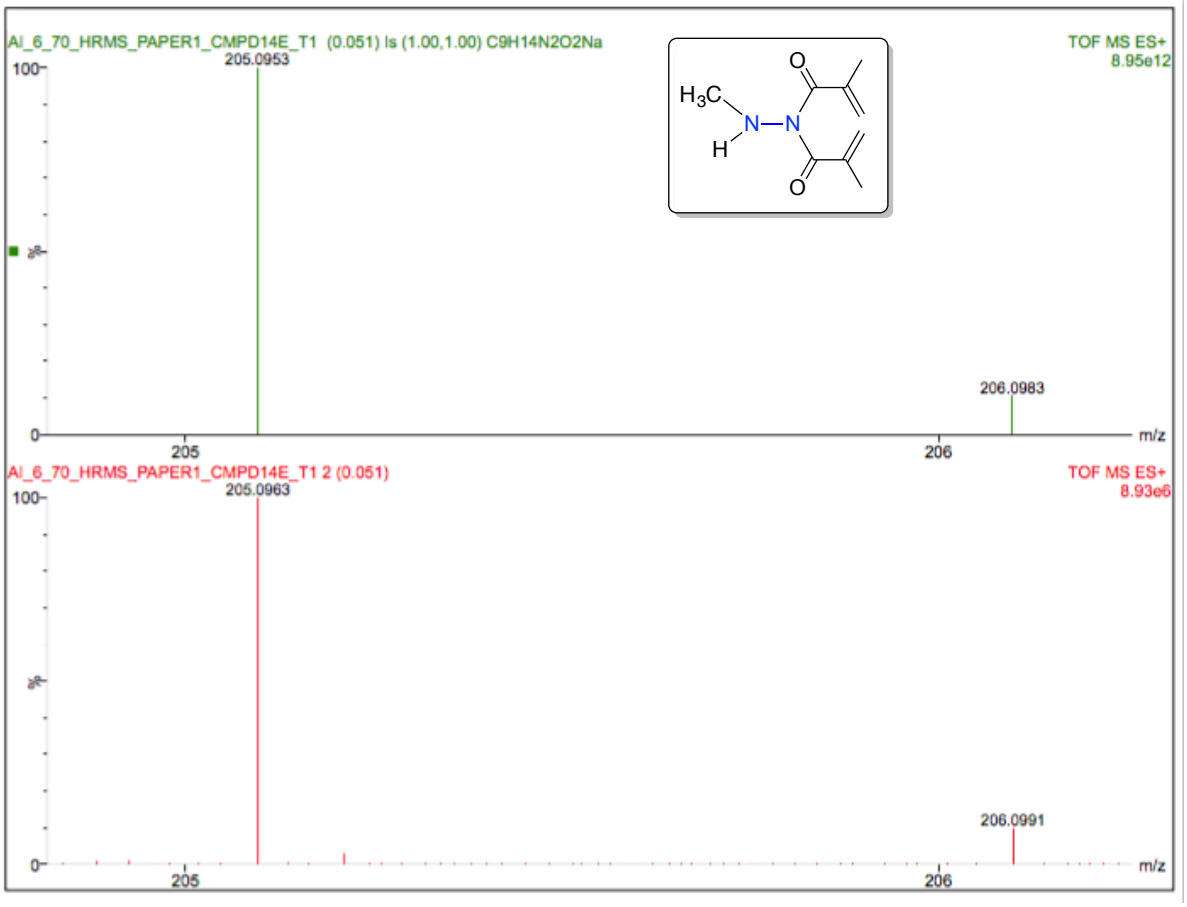
HRMS-ESI (m/z) ([M + Na]$^+$):

Chemical Formula : $C_9H_{14}N_2O_2$

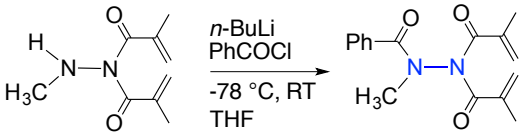
Calculated : 205.0953

Observed : 205.0963

|Δm| : 4.9 ppm



STEP 2



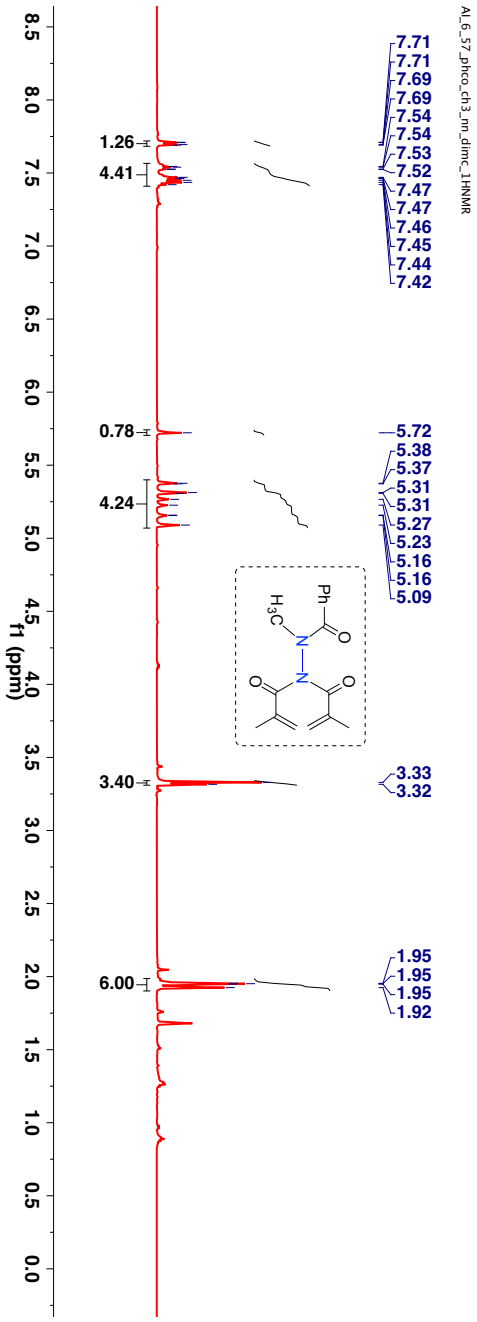
11f **11b**

Scheme S16: Synthesis of amide based hydrazide derivative **11b**.

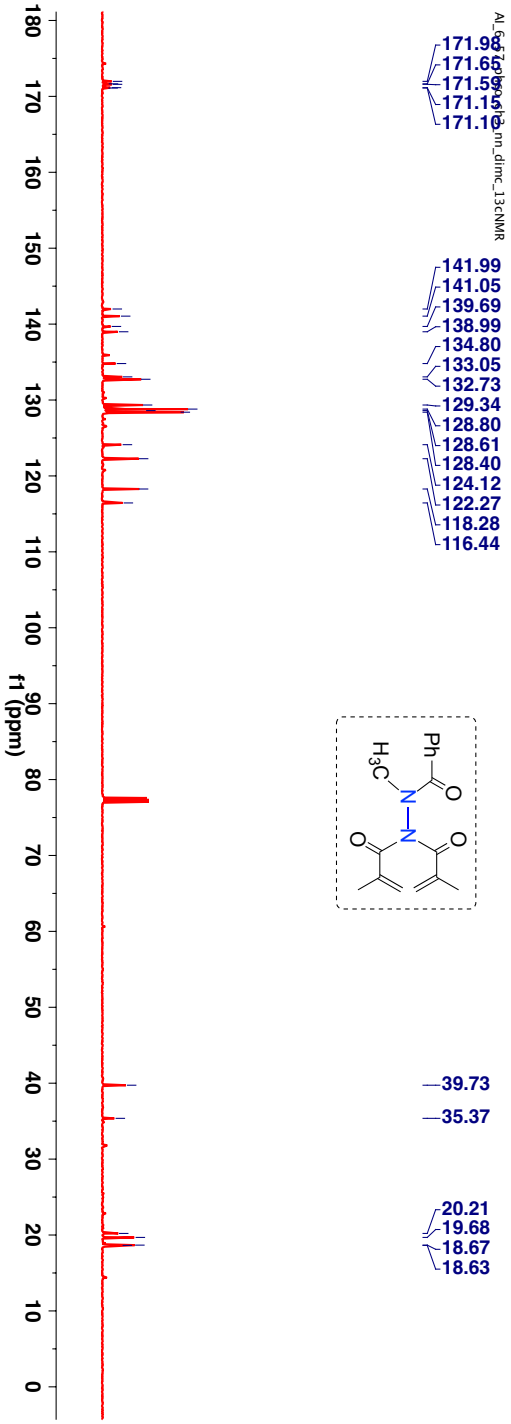
The hydrazide derivative **11f** (1 *equiv*) was taken in a round bottom flask under N_2 atmosphere and dissolved in freshly distilled THF. The solution was cooled to -78 °C. To this solution *n*-BuLi (1 *equiv*) was added dropwise over a period of 10 minutes. This was followed by addition of freshly benzoyl chloride (1.1 *equiv*). The solution was stirred at -78 °C for 3 h after which TLC showed complete consumption of starting material. The reaction was quenched with 5 mL of H_2O, stirred and the layers were separated. The organic layer was sequentially washed with DI water (2 × 10 mL), saturated $NaHCO_3$ (2 × 10 mL) and finally with brine. The organic layer was dried over *anhyd* Na_2SO_4, filtered and the solvent was removed under reduced pressure to yield crude product. After concentrating the organic layer, the crude product was purified by combiflash using hexanes and ethyl acetate and ethyl acetate as eluting solvents.

Clear oil (Yield = 20%). R_f = 0.3 (20% ethyl acetate:hexanes).

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm, mixture of rotamers): 1.92 (s), 1.96 (s), 3.32 (s), 3.33 (s), 5.09 (s), 5.16 (s), 5.23 (s), 5.27 (s), 5.31 (s), 5.38 (s), 5.72 (s), 7.42-7.54 (m) and 7.69-7.71 (m).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm, mixture of rotamers): 18.6, 18.7, 19.7, 20.2, 35.4, 39.7, 116.4, 118.3, 122.3, 124.1, 128.4, 128.6, 128.8, 129.3, 132.7, 133.0, 134.8, 139.0, 139.7, 141.1, 142.0, 171.1, 171.2 and 171.6.



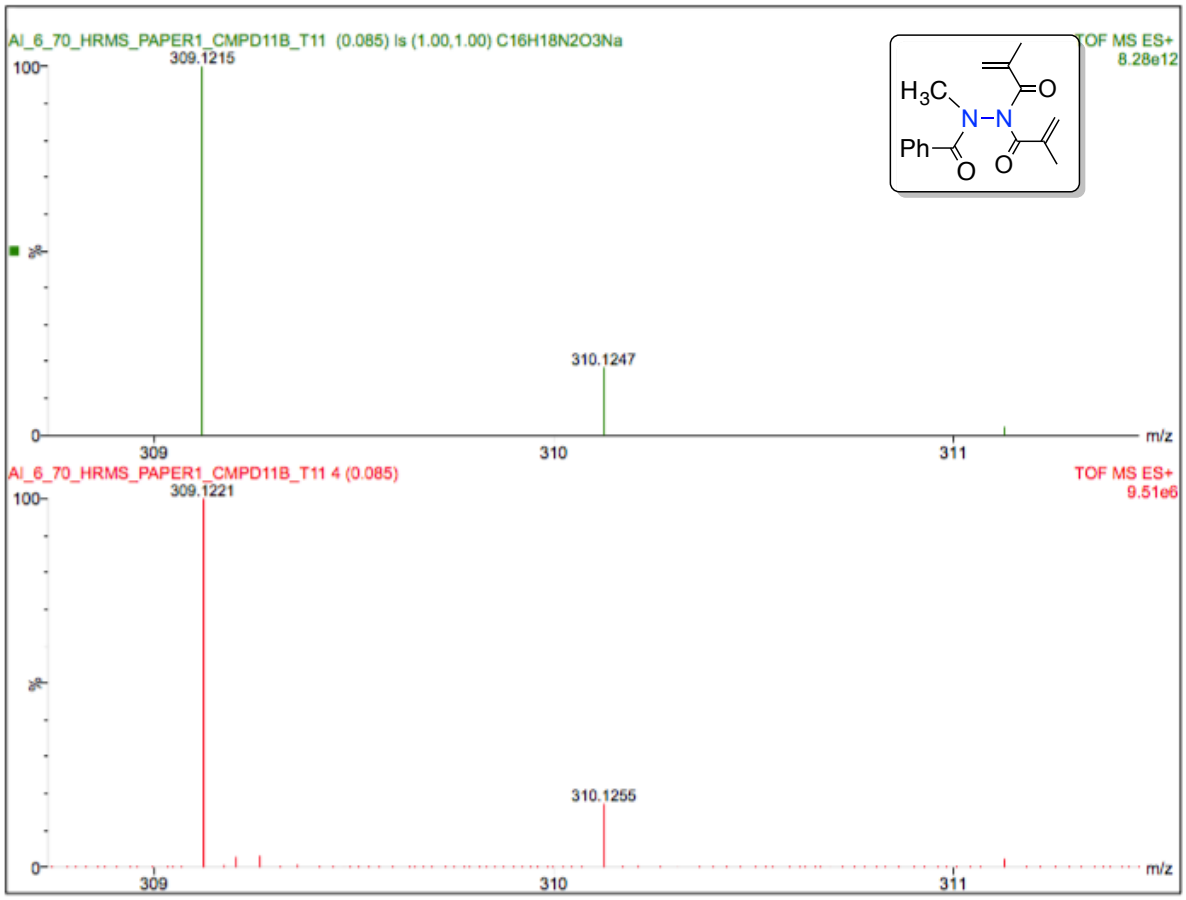
HRMS-ESI (m/z) ([M + Na]$^+$):

Chemical Formula : $C_{16}H_{18}N_2O_3$

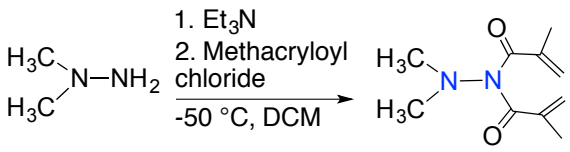
Calculated : 309.1215

Observed : 309.1221

|Δm| : 1.9 ppm



3.5.4 Synthesis of tertiary amine based hydrazide derivative **11e**.



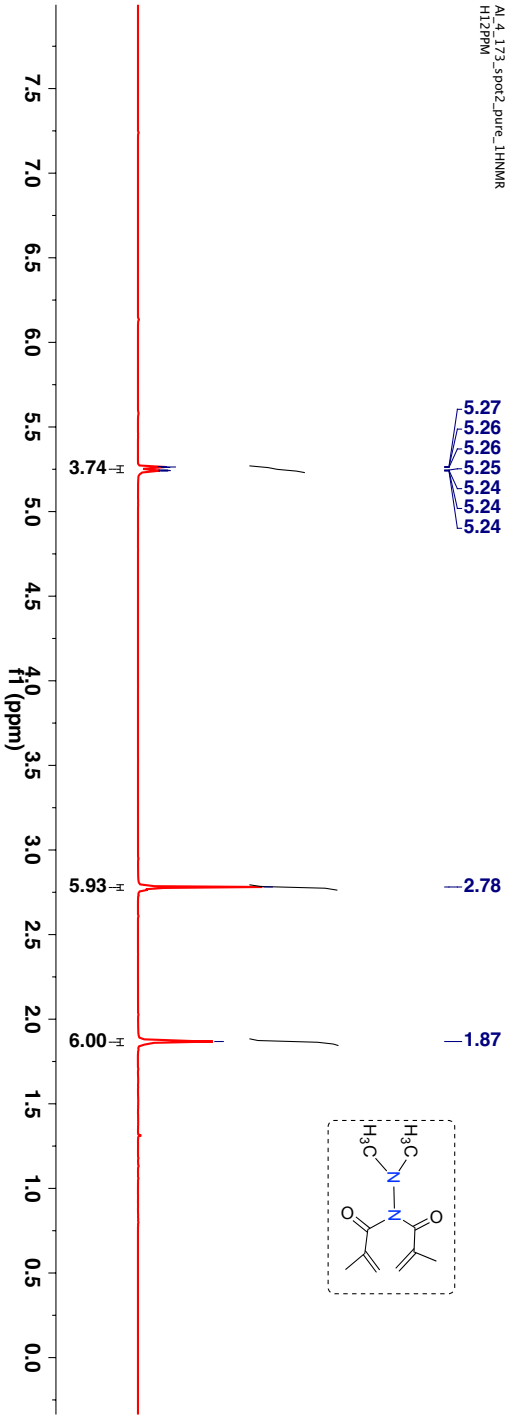
11e

Scheme S17: Synthesis of acrylimide derivative **11e**.

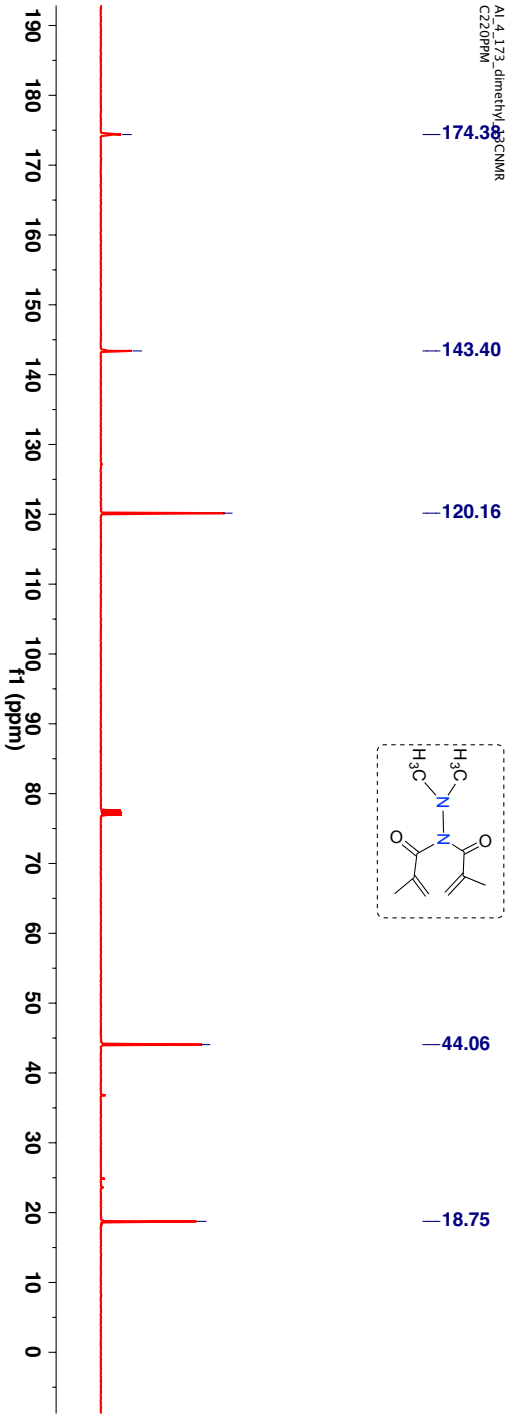
To *N,N*-dimethylhydrazine (1 *equiv*) in a round bottom flask under N_2 atmosphere, anhydrous CH_2Cl_2 was added and the solution was cooled to -50 °C. To this solution Et_3N (5 *equiv*) was added. To this solution was added methacryloyl chloride (2.0 *equiv*). The solution was stirred at -50 °C for 2 h and then at room temperature for 20 h. The reaction was quenched with 5 mL of H_2O, stirred and the layers were separated. The organic layer was sequentially washed with DI water (2 × 10 mL), saturated $NaHCO_3$ (2 × 10 mL) and finally with brine. The organic layer was dried over *anhyd* Na_2SO_4, filtered and the solvent was removed under reduced pressure to yield crude product. After concentrating the organic layer, the crude product was purified by combiflash using hexanes and ethyl acetate and ethyl acetate as eluting solvents.

Viscous clear liquid (Yield = 15%). R_f = 0.5 (20% ethyl acetate:hexanes).

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 1.87 (s, 6H), 2.78 (s, 6H) and 5.24-5.27 (m, 4H).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 18.8, 44.1, 120.2 143.4 and 174.4.



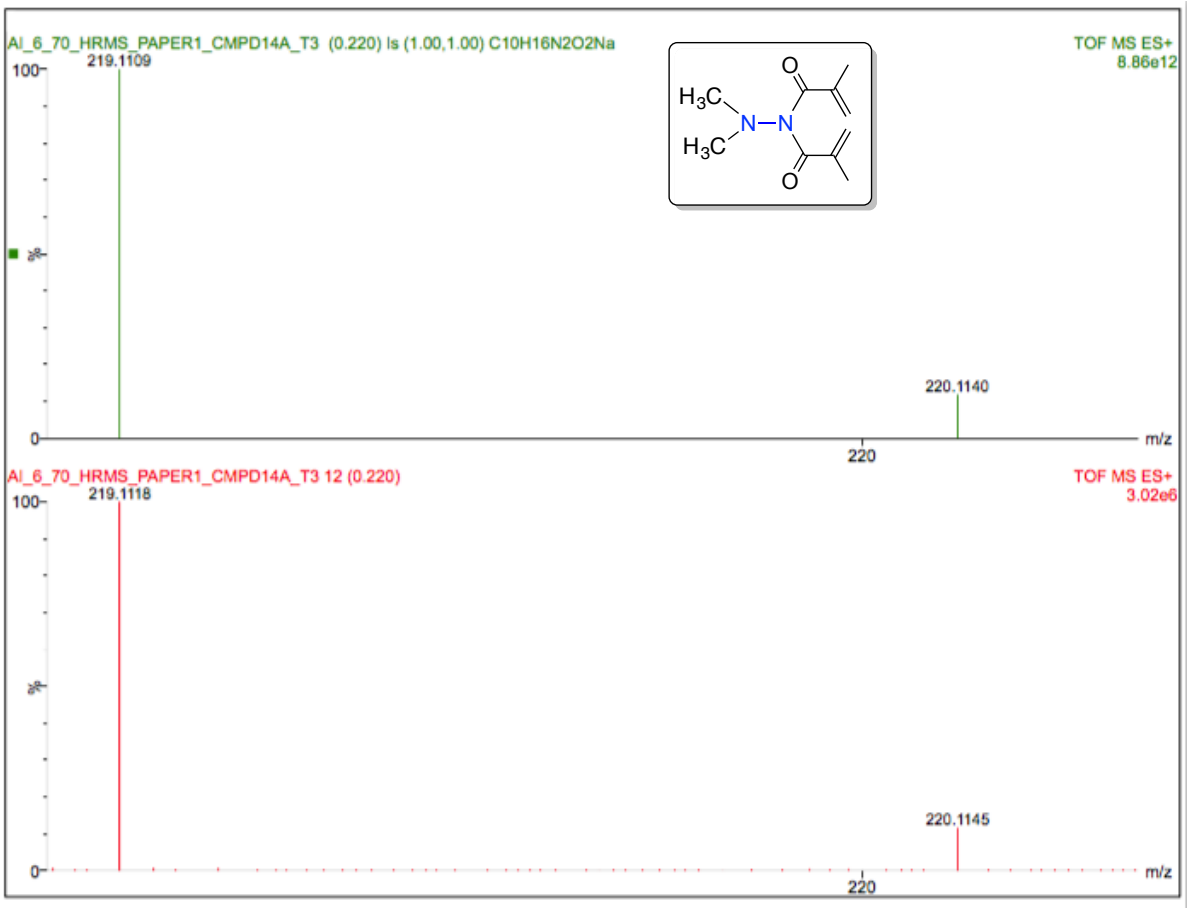
HRMS-ESI (m/z) ([M + Na]$^+$):

Chemical Formula : $C_{10}H_{16}N_2O_2$

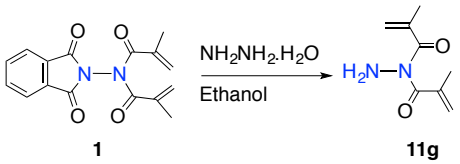
Calculated : 219.1109

Observed : 219.1118

|Δm| : 4.1 ppm



3.5.5 Synthesis of primary amine derivative **11g**.



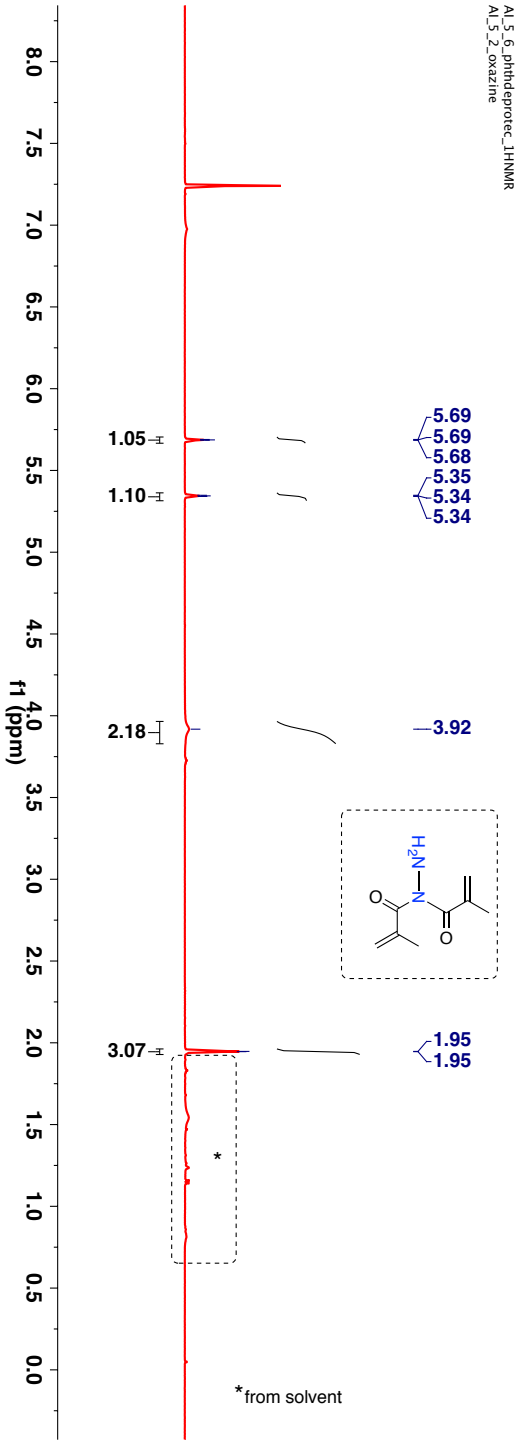
1 **11g**

Scheme S18: Synthesis of acrylimide derivative **11g**.

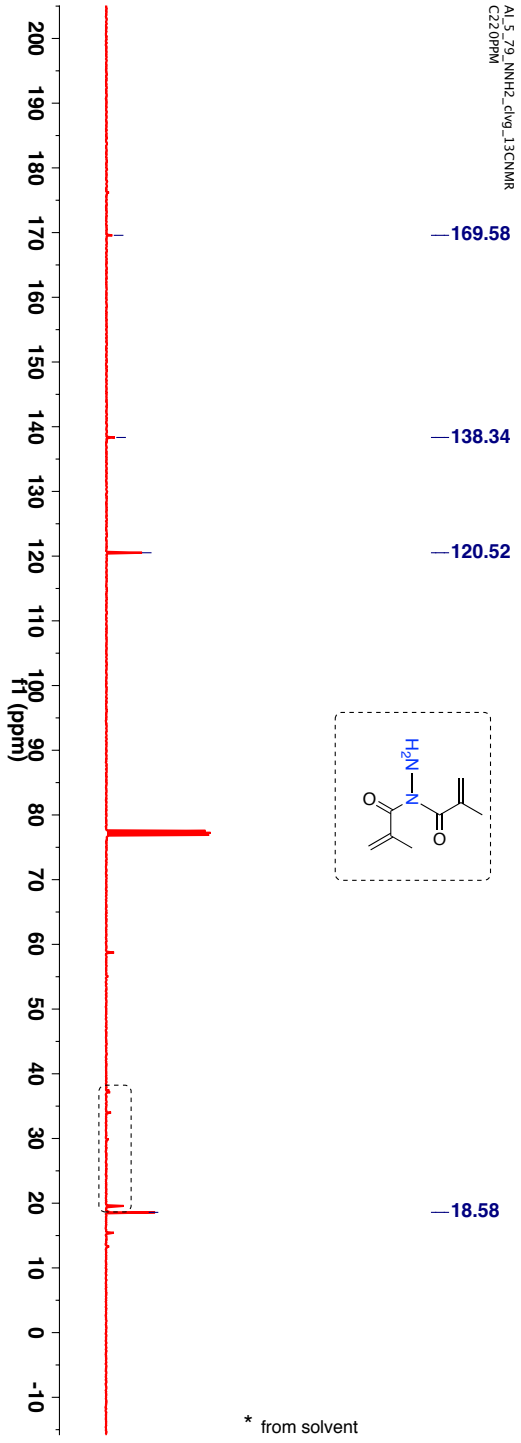
Imide derivative **1** (1 *equiv*) was dissolved in absolute ethanol. To the reaction mixture hydrazine hydrate (11 *equiv*) was added and the mixture was refluxed for 45 minutes (monitored by TLC). The solution was filtered through a short celite plug. The crude was diluted with ethyl acetate and was washed with 1M HCl. The aqueous layer was separated and washed with 1N NaOH and the organic layer was washed with brine (2 × 10 mL). The organic layer was dried over *anhyd* Na_2SO_4, filtered and the solvent was removed under reduced pressure to yield product. The compound was used without further purification.

Clear solid (Yield = 16%)

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 1.95 (s, 3H), 3.92 (bs, 2H), 5.34 (s, 1H) and 5.69 (s, 1H).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 18.6, 120.5, 138.3 and 169.6.



4. GENERAL PROCEDURE FOLLOWED FOR IRRADIATION OF SUBSTRATES AND CHARACTERIZATION OF PHOTOPRODUCTS

Procedure for photoreaction:

The substrate was dissolved in an appropriate solvent in a Pyrex test-tube, followed by the addition of the triplet sensitizer (thioxanthone). The solution was deoxygenated by nitrogen bubbling. The deoxygenated solution was irradiated at ambient condition in a Rayonet reactor equipped with ~420 nm tubes (16 tubes x 14 Watt) (Figure S1). In case of Norrish-Yang cyclization of α-oxamide derivative the irradiation was performed with Rayonet reactor/CFL lamp (compact fluorescent lamp, 13 W)/purple LED's. For the LED photoreaction, a visible light photoreactor was used which was constructed from a commercial purple LED tape (300 LEDs, 4.8 W, 16.4 ft) wound around a beaker wound (Figure S1-middle).

After irradiation, triphenylmethane was added as internal standard and the solvent was evaporated under reduced pressure. Conversion and mass balance was determined using the following equation by NMR spectroscopy:

$$mol_a = mol_i \times \left(\frac{Integral\ of\ analyte}{Integral\ of\ internal\ standard}\right) \times \frac{N_a}{N_i}$$

Where, N_a and N_i are the number of nuclei giving rise to the relevant analyte and internal standard peaks respectively. Similarly, mol_a and mol_i are the number of moles of analyte and the internal standard respectively.

Figure S1. (left) Rayonet Reactor equipped with ~420 nm tube lights. (middle) The visible light photoreactor constructed from a commercial purple LED tape wound around a beaker and (right) household CFL lamp irradiation.

Characterization of photoproduct after photoreaction:

In case of large-scale photoreactions, after irradiation the mixture was purified by combiflash using hexanes/ethyl acetate mixtures. The photoproducts were then characterized by NMR spectroscopy and/or single crystal XRD.

In case of control substrates *viz*., tertiary/secondary/primary amine (acrylimide) derivatives, the mixture was purified by preparative thin layer chromatography. These substrates showed very weak/negligible fluorescence under UV-light illumination, so by utilizing preparative thin layer chromatography the sensitizer band was removed and remaining band was taken for analyzing with NMR spectroscopy.

In some of the cases, the R_f of substrate and the photoproduct did not show appreciable difference during the course of photoreaction. So in order to avoid ambiguity the photoreactions were monitored by ^{1}H-NMR spectroscopy.

Concentrations of hydrazides and irradiation time employed for sensitizer loading studies.

Solvent = MeCN;

[**1**] ≈ 3.35 mM, irradiation time ≈ 5.5 h;
[**4**] ≈ 3.33 mM, irradiation time = 2 h;
[**8**] ≈ 3.26 mM, irradiation time ≈ 40 h.

Concentrations of hydrazides and irradiation time employed for solvent effects.

Sensitizer = 10 mol% TX.
[**1**] = 3.35 mM, irradiation time = 5.5 h;
[**4**] = 3.33 mM, irradiation time = 2 h;
[**6**] = 5.1 mM, irradiation time = 7 h;
[**8**] = 3.26 mM, irradiation time = 40 h;

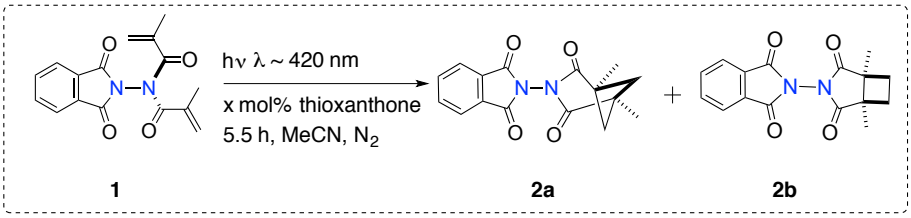
Concentrations of control substrates and irradiation time employed for solvent effects.

Irradiation time for **11a**-**11g** = 8 h

[**11a**] = 3.18 mM; [**11b**] = 3.49 mM; [**11c**] = 3.67 mM; [**11d**] = 3.54 mM;

[**11e**] = 5.1 mM; [**11f**] = 5.49 mM; and [**11g**] = 2.38 mM.

4.1.0 Reaction optimization for [2+2] photoreaction of acrylimide derivative **1**.



Scheme S19: Photoreaction of acrylimide derivative **1**.

Table S1. Sensitizer/Catalyst loading studies for intramolecular [2+2] photoreaction of *N-N* bond based acrylimide derivative **1**.[a]

Entry	Tx (x mol%)	Conversion/%
1	0	0
2	1	8
3	5	39
4	10	100

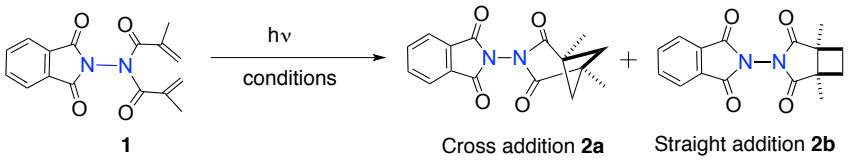
[a] [**1**] = 3.35 mM, Tx: Thioxanthone

Table S2. Solvent screening studies for intramolecular [2+2] photoreaction of *N-N* bond based acrylimide derivative **1**.[a]

Entry	Solvent	Conversion/%
1	Methanol	100
2	Acetonitrile	100
3	Ethyl acetate	<7
4	Benzene	63
6	Methylcyclohexane	0

[a] [**1**] = 3.35 mM. The photoreactions were performed with 10 mol% thioxanthone loading.

4.1.1 [2+2] Photoreaction of acrylimide derivative **1** under different conditions.



Scheme S20: Photoreaction of acrylimide derivative **1**.

Table S3. Intramolecular [2+2] photoreaction of *N-N* bond based acrylimide derivative **1** under different conditions.[a]

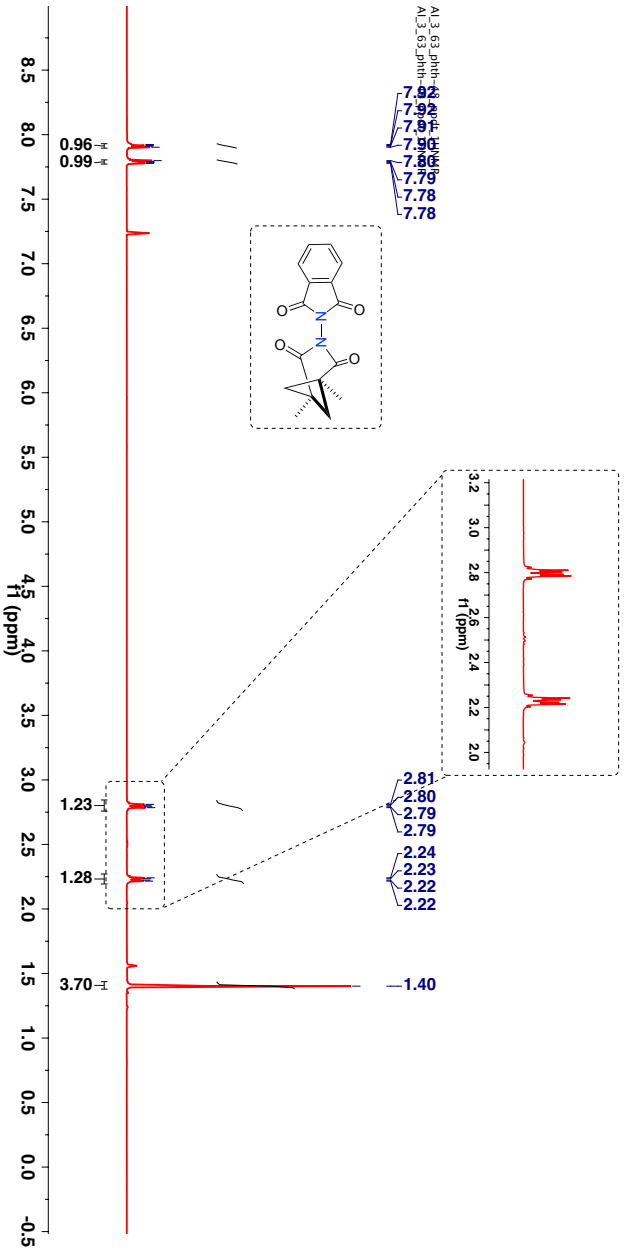
Entry	Conditions	Conversion/%[b]	2a:2b[c]
1	λ > 290 nm, Acetone, 3h	100	>99:1
2	λ > 290 nm, MeCN, 3h	100	95:5
3	λ ~ 350 nm, 10 mol% benzophenone, MeCN, 5.5h	100	96:4
4	λ ~ 350 nm, 10 mol% xanthone, MeCN, 8h	100	96:4
5	λ ~ 420 nm, 10 mol% thioxanthone, MeCN, 8h	100	91:9

[a] Irradiations were performed at room temperature unless otherwise noted. The solvent utilized for irradiation was HPLC grade with no optical density at irradiation wavelength performed with 10 mol% of thioxanthone as sensitizer. [**1**] = 3.35 mM, Rayonet reactor equipped ~420 nm (16 tubes × 14 W each). [b] % conversion/NMR yield (±5% error) calculated by ^{1}H-NMR spectroscopy using triphenylmethane as internal standard. [c] Ratios determined from crude NMR.

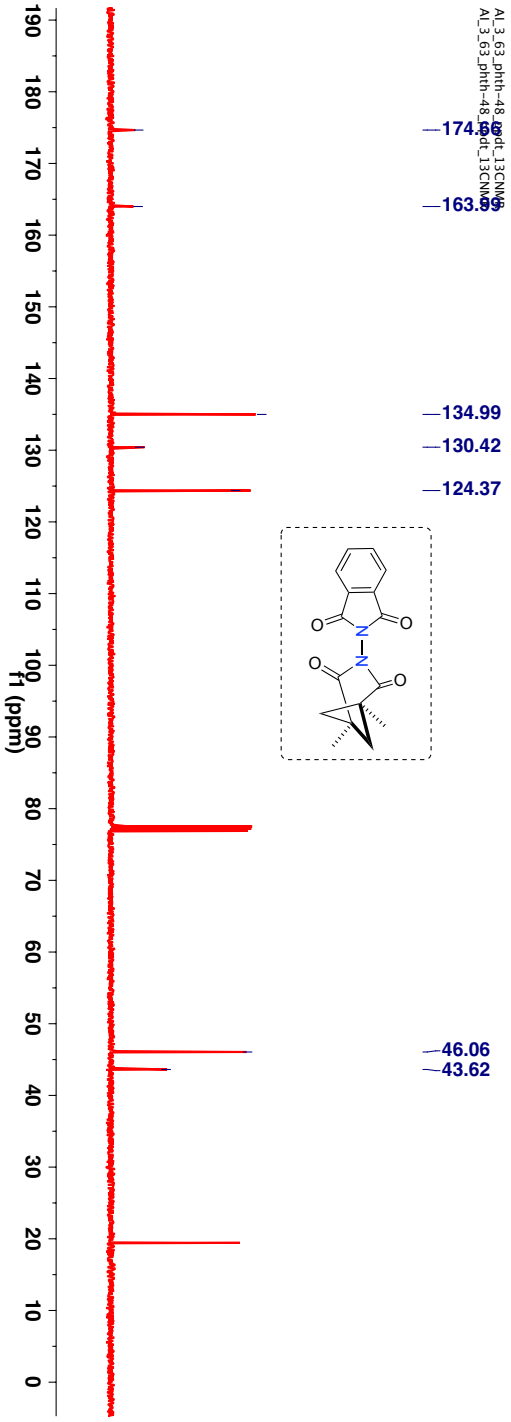
4.1.2 Characterization of photoproduct **2**.

Crystalline solid (Yield = 71%). R_f = 0.4 (20% ethyl acetate:hexanes).

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 1.40 (s, 6H), 2.22-2.41 (m, 2H), 2.79-2.81 (m, 2H), 7.77-7.79 (dd, 2H, J_1 5.6Hz, J_2 3.2Hz) and 7.90-7.92 (dd, 2H, J_1 5.6Hz, J_2 3.2Hz).

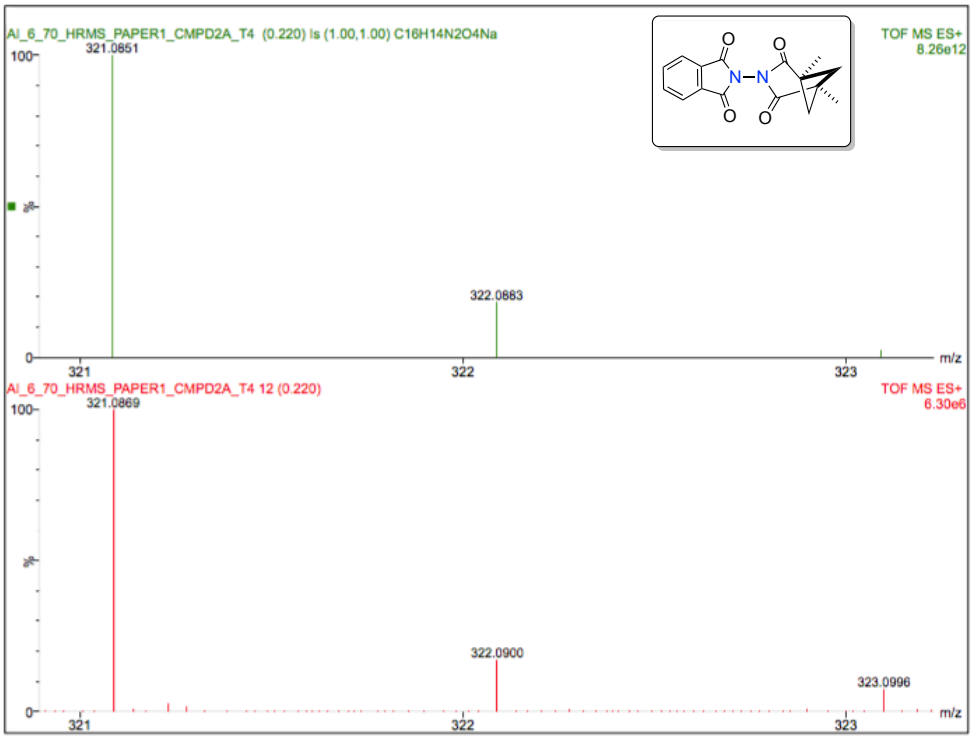


^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 19.5, 43.6, 46.0, 124.4, 130.4, 134.9, 163.9 and 174.7.



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

Chemical Formula	: $C_{16}H_{14}N_2O_4$
Calculated	: 321.0851
Observed	: 321.0869
|Δm|	: 5.6 ppm



4.1.3 UV-VIS spectra of acrylimide derivative **1**.

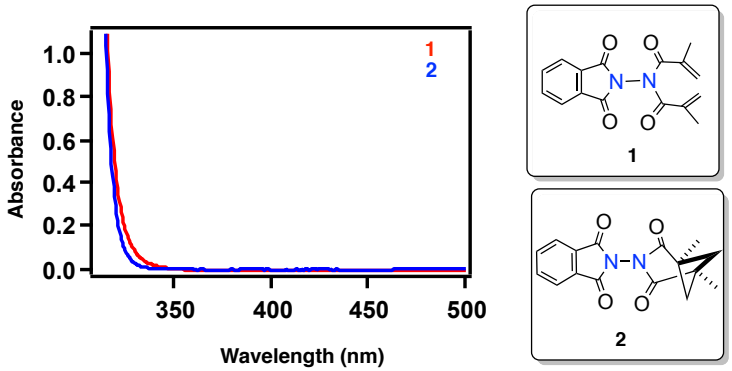
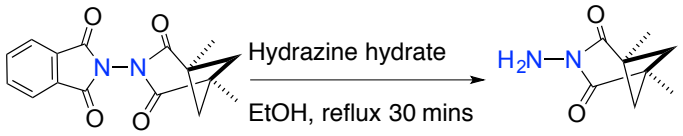


Figure S2. UV-Vis spectra of *N-N* bond based acrylimide derivative **1** (conc. = 3.35 mM) and photoproduct **2** (conc. = 3.35 mM) recorded at the reaction concentration in acetonitrile.

4.1.4 Removal of phthalimide ring in acrylimide based photoproduct **2**.



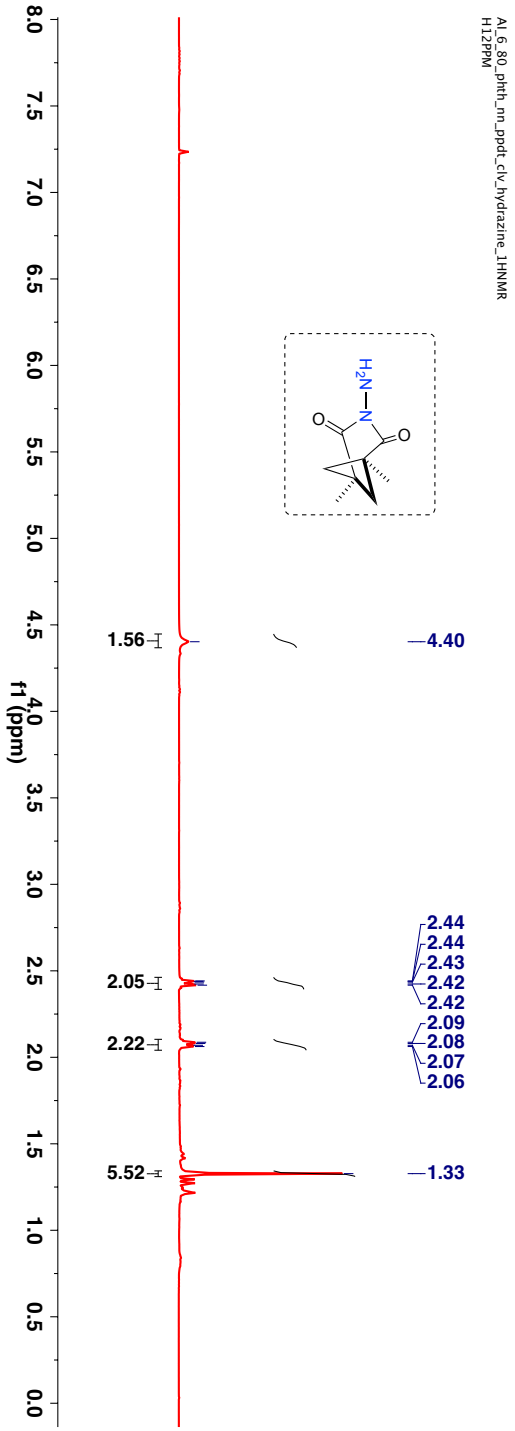
2 **3**

Scheme S21: Removal of phthalimide ring of acrylimide based photoproduct **2**.

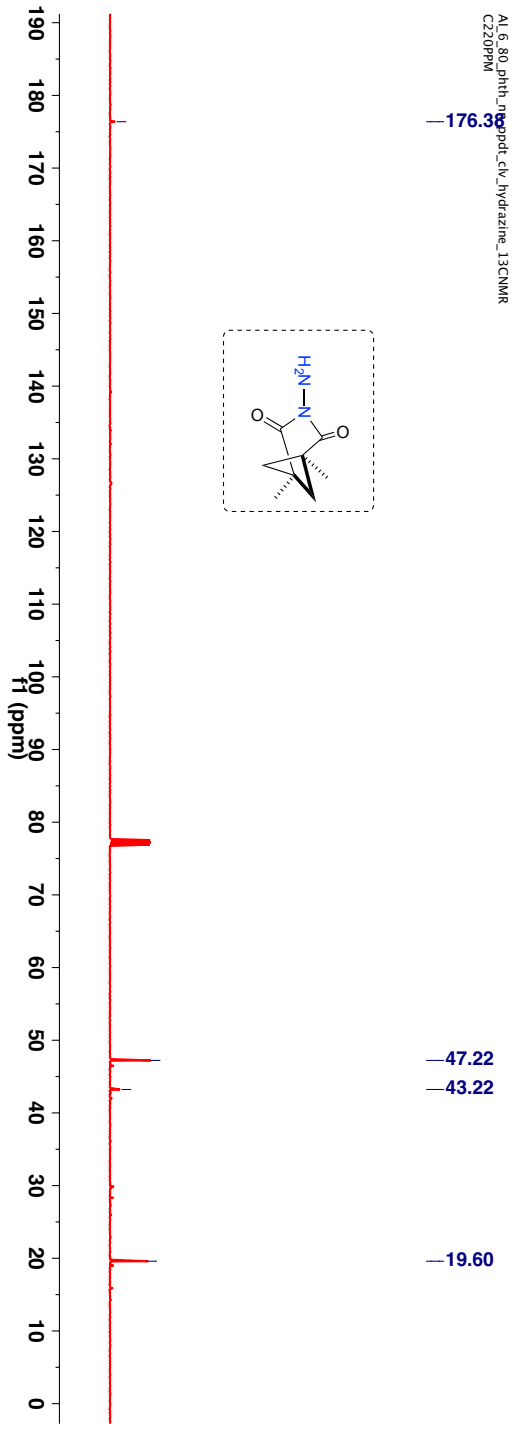
Following the modified procedure reported by Michael et al.[5] the photoproduct **2** (1 *equiv*) was charged in a vial equipped with a teflon cap. The compound was dissolved in absolute ethanol (5mL per 100mg of photoproduct) and hydrazine monohydrate (11.9 *equiv*) was added. The solution was stirred for 5 min and refluxed for 30 min (until TLC showed complete consumption of starting material). The solution was brought to room temperature and diluted with ethyl acetate. The solution was sonicated for 15 min and then filtered through a short celite plug. The filtrate was concentrated under reduced pressure to obtain the crude product. The crude product was purified using a prep TLC with hexanes and ethyl acetate mixture as eluting solvents to obtain *N*-amino photoproduct.

4.1.5 Characterization of product **3**.

Crystalline solid (Yield = 81%). ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 1.33 (s, 6H), 2.06-2.09 (m, 2H), 2.42-2.44 (m, 2H) and 4.40 (bs).

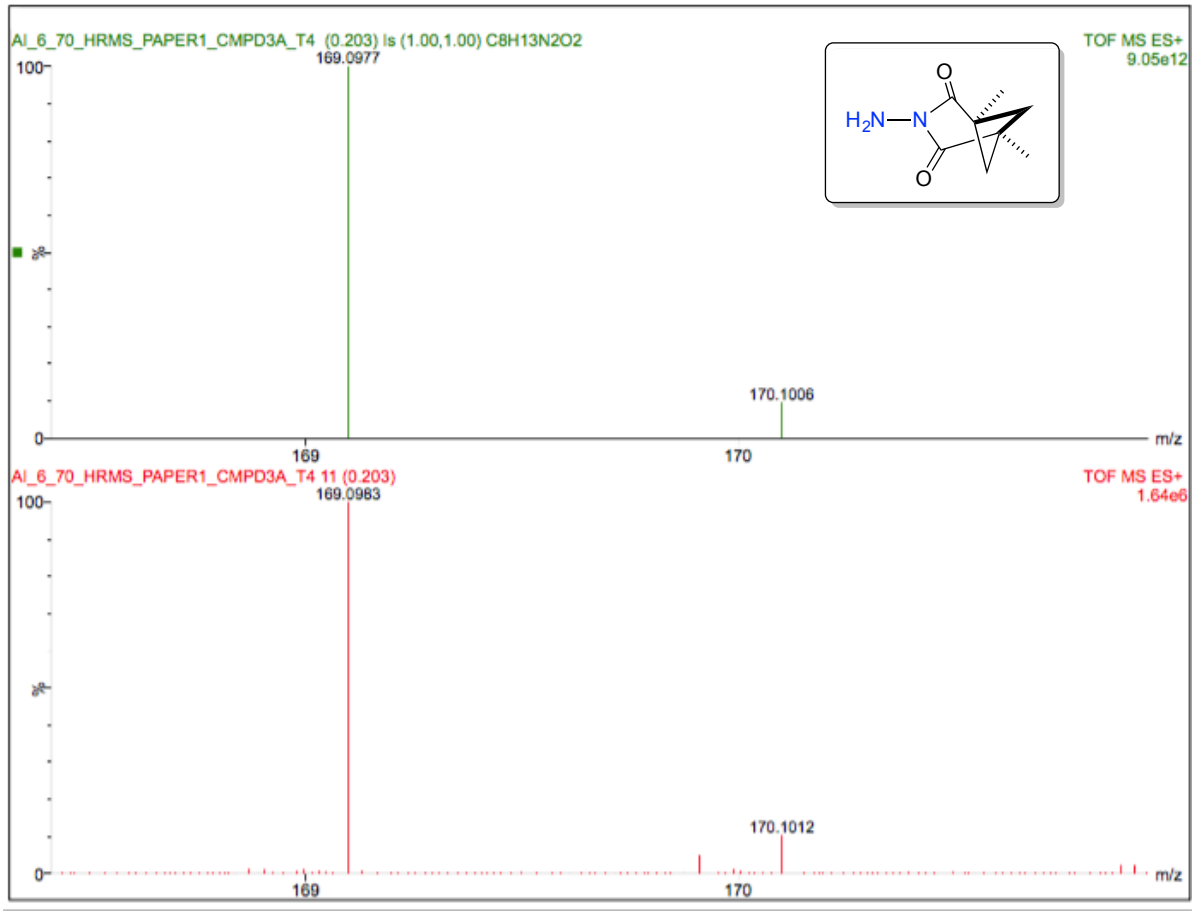


^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 19.6, 43.2, 47.2 and 176.4.

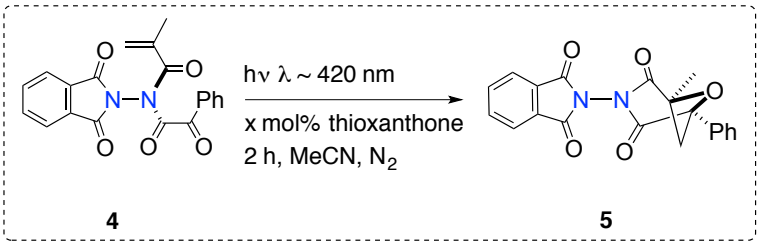


HRMS-ESI (m/z) ([M + H]$^+$):

Chemical Formula	: $C_8H_{12}N_2O_2$
Calculated	: 169.0977
Observed	: 169.0963
|Δm|	: 2.0 ppm



4.2.0 Reaction optimization for Paternò-Büchi reaction of α-oxoamide derivative **4**.



Scheme S22: Photoreaction of α-oxoamide derivative **4**.

Table S4. Sensitizer/Catalyst loading studies for Paternò-Büchi reaction of *N-N* bond based α-oxoamide derivative **5**.[a]

Entry	Tx (x mol%)	Conversion/%
1	0	19
2	1	26
3	5	100
4	10	100

[a] [**4**] = 3.33 mM, Tx : Thioxanthone

Table S5. Solvent screening studies for Paternò-Büchi reaction of N-N bond based α-oxoamide derivative **5**.[a]

Entry	Solvent	Conversion/%
1	Methanol	Decomposition
2	Acetonitrile	100
3	Ethyl acetate	78
4	Benzene	100
6	Methylcyclohexane	71

[a] [**4**] = 3.33 mM. The photoreactions were performed with 10 mol% thioxanthone loading.

Table S6. Effect of reaction atmosphere on Paternò-Büchi reaction of *N*-*N* bond based α-oxoamide derivative **5**.[a]

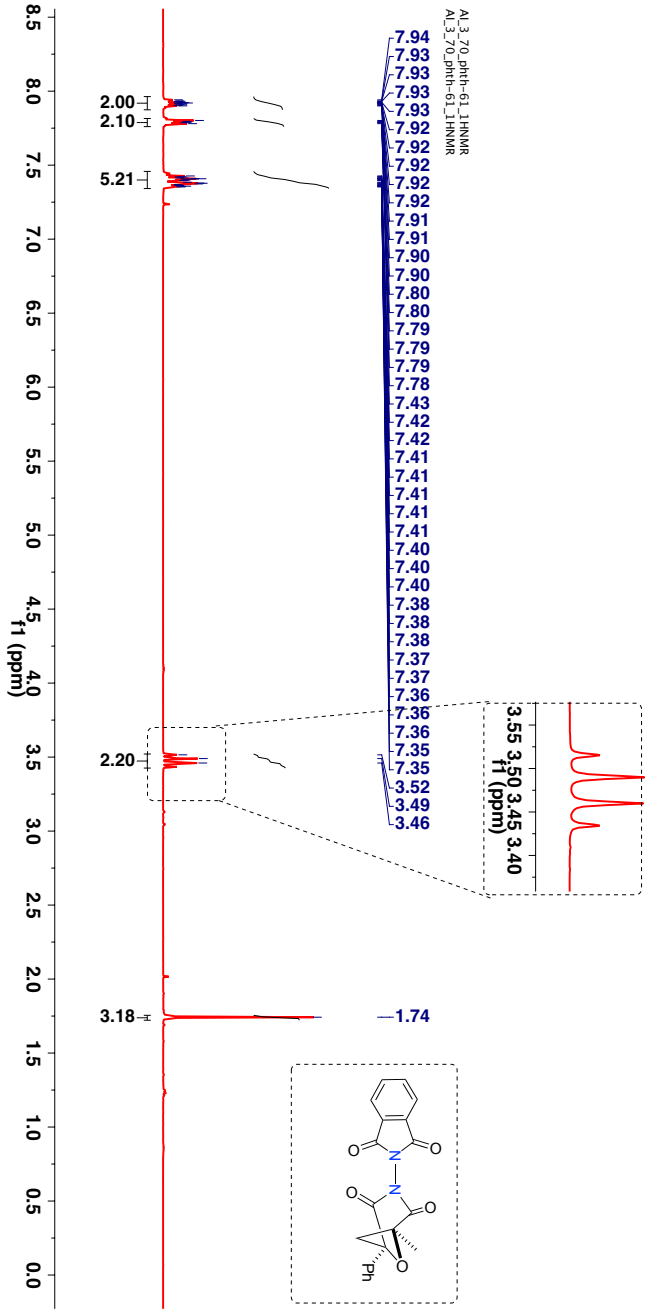
Entry	Conditions	Conversion/%
1	λ ~ 420 nm, MeCN, N_2, 2h	19
2	λ ~ 420 nm, MeCN, O_2, 2h	23

[a] [**4**] = 3.33 mM.

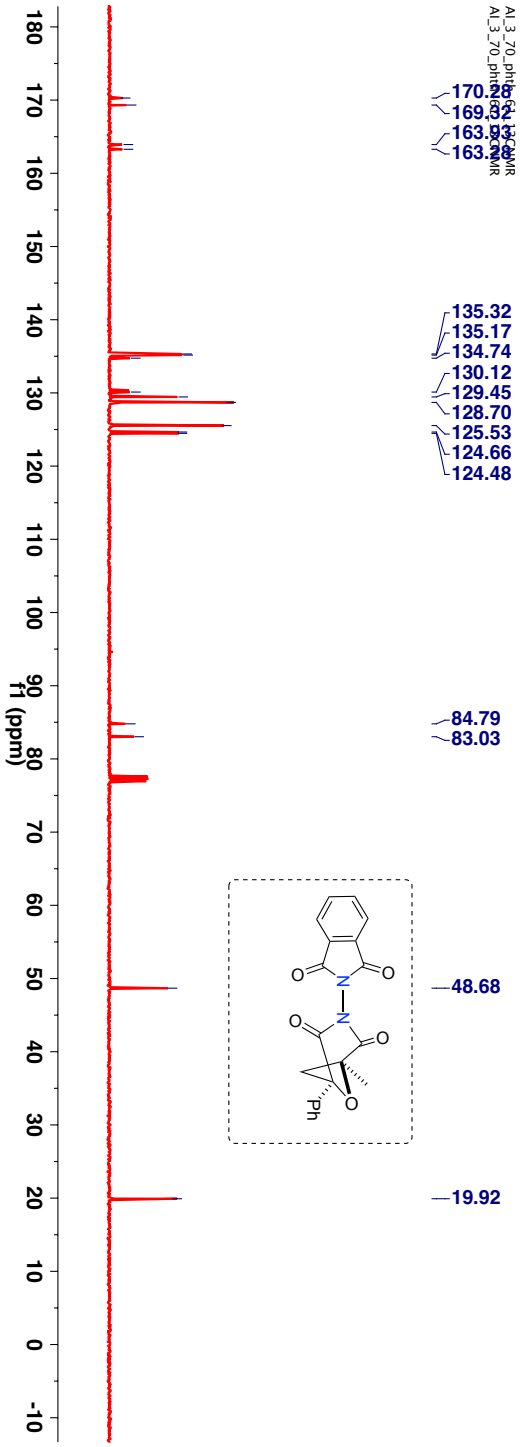
4.2.1 Characterization of photoproduct **5**.

Pale yellow solid (Yield = 88%). R_f = 0.5 (50% ethyl acetate:hexanes).

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 1.74 (s, 3H), 3.43-3.52 (ABq, 2H), 7.36-7.44 (m, 5H), 7.78-7.80 (m, 2H), and 7.90-7.94 (m, 2H).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 19.9, 48.7, 83.0, 84.8, 124.5, 124.7, 125.5, 129.5, 130.1, 135.2, 135.3, 163.3, 163.9, 169.3 and 170.3.



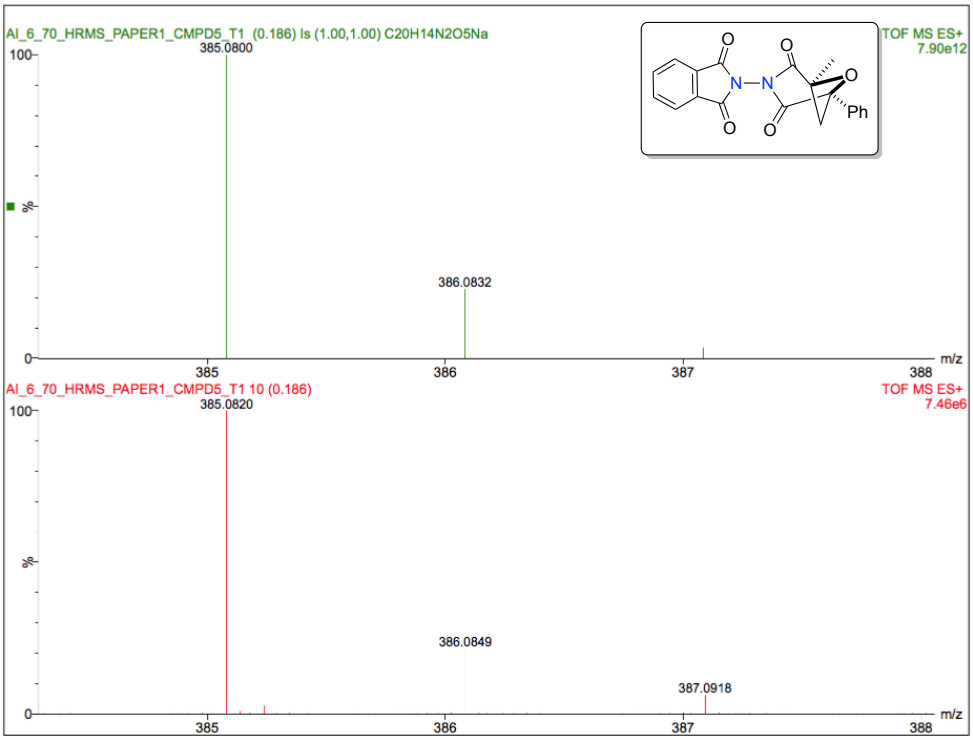
HRMS-ESI (m/z) ([M + Na]$^+$):

Chemical Formula : $C_{20}H_{14}N_2O_5$

Calculated : 385.0800

Observed : 385.0820

|Δm| : 5.2 ppm



4.2.2 UV-VIS spectra of α–oxoamide derivative **4**.

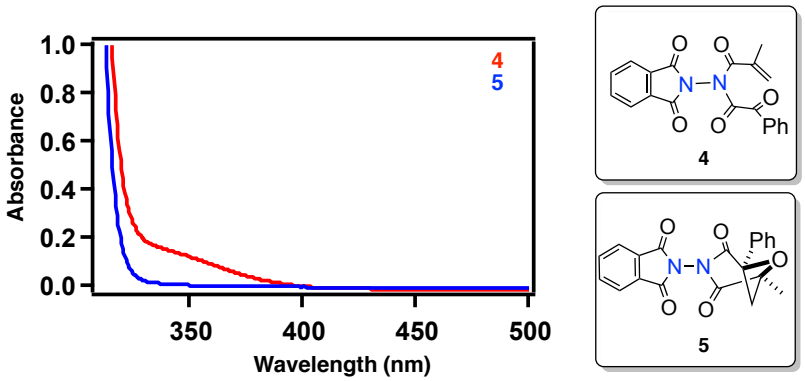
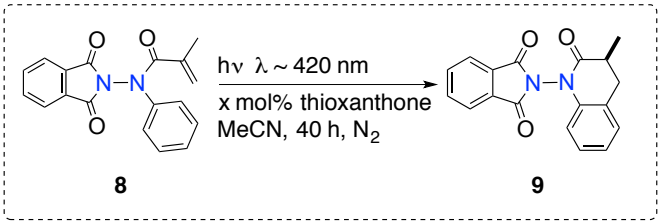


Figure S3. UV-Vis spectra of *N-N* bond based α–oxoamide derivative **4** (conc. = 1.32 mM) and photoproduct **5** (conc. = 1.32 mM) recorded in acetonitrile.

4.3.0 Reaction optimization for 6π photocyclization of acrylanilide derivative **8**.



Scheme S23: Photoreaction of 6π photocyclization of acrylanilide derivative **8**.

Table S7. Sensitizer/Catalyst loading studies for 6π photocyclization of acrylanilide derivative of *N-N* bond based acrylanilide derivative **8**.[a]

Entry	Tx (x mol%)	Conversion/%
1	0	7
2	1	88
3	5	46
4	10	90

[a] [**8**] = 3.26 mM, Tx: thioxanthone

Table S8. Solvent screening studies for 6π photocyclization of acrylanilide derivative of *N-N* bond based acrylanilide derivative **8**.[a]

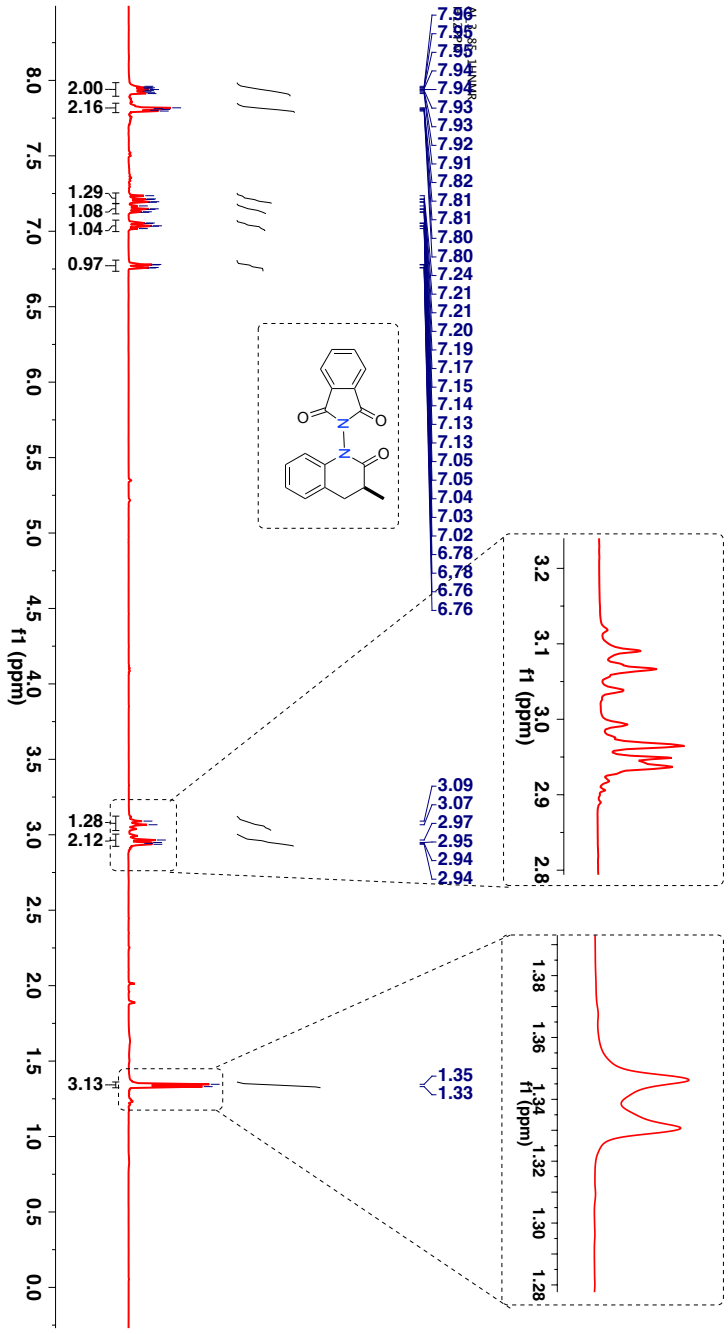
Entry	Solvent	Conversion/%
1	Methanol	91
2	Acetonitrile	90
3	Ethyl acetate	100
4	Benzene	60
6	Methylcyclohexane	71

[a] [**8**] = 3.26 mM.

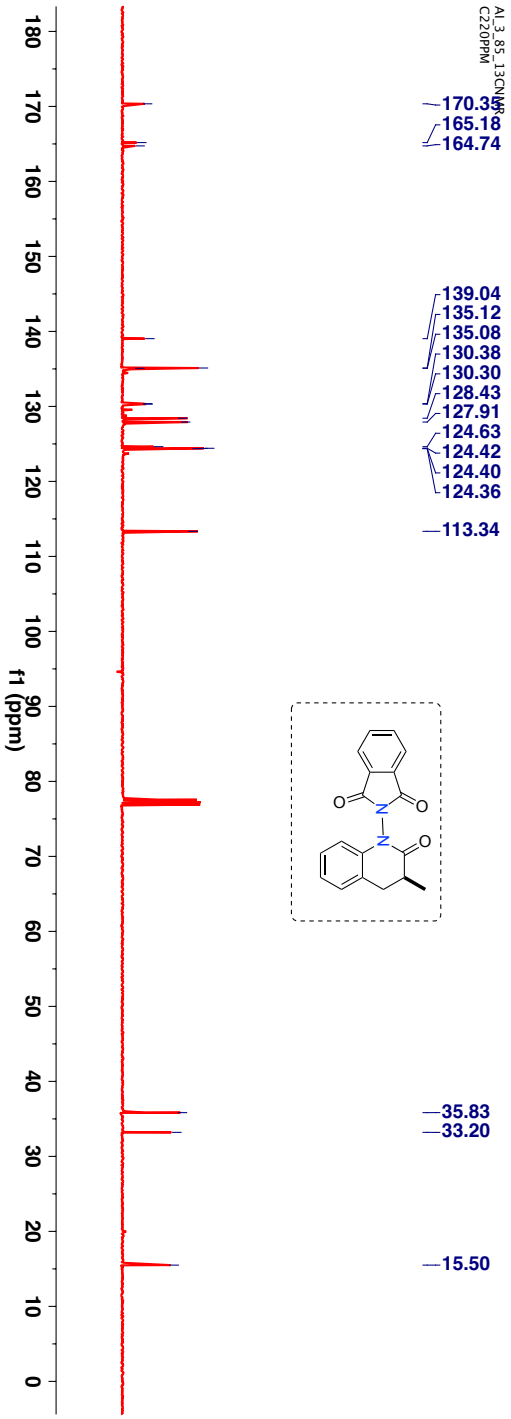
4.3.1 Characterization of photoproduct **9**.

Crystalline solid (Yield = 62%). R_f = 0.4 (50% ethyl acetate:hexanes).

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 1.34 (d, 3H), 2.94-3.12 (m, 3H), 6.67 (d, 1H, *J* 8Hz), 7.02-7.06 (m, 1H), 7.13-7.17 (m, 1H), 7.21 (d, 1H, *J* 8Hz), 7.79-7.82 (m, 2H) and 7.91-7.96 (m, 2H).

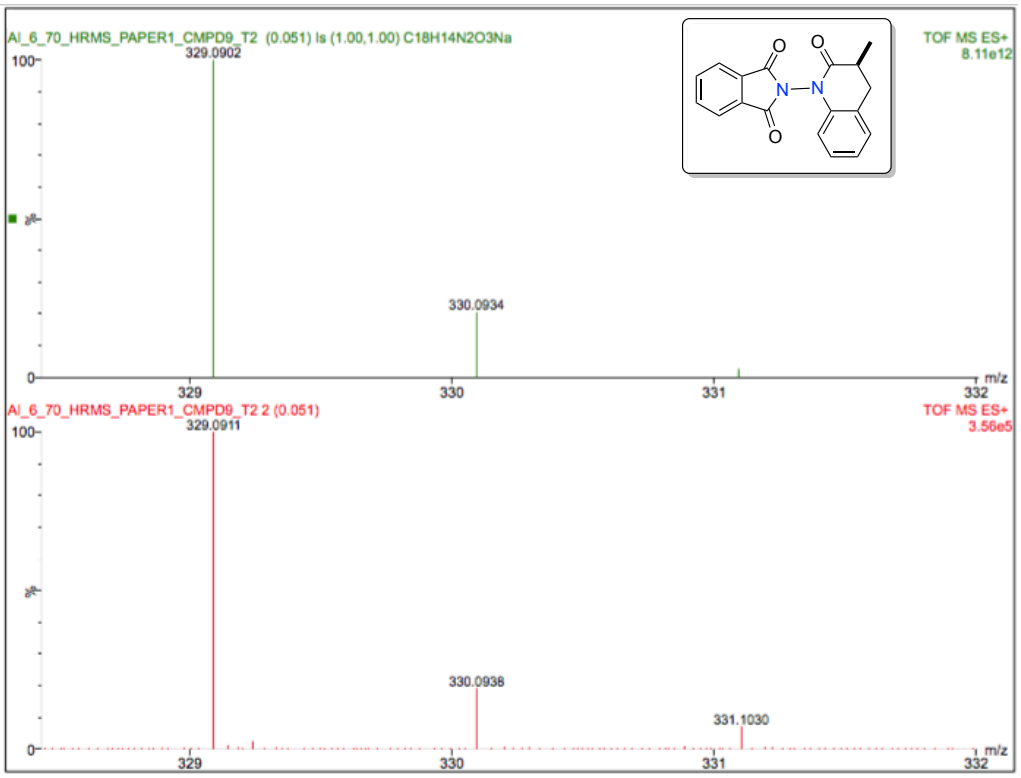


^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 15.5, 33.2, 35.8, 113.3, 124.4, 124.4, 124.4, 124.6, 127.9, 128.4, 130.3, 130.4, 135.1, 135.1, 139.0, 164.7, 165.2 and 170.4.



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

Chemical Formula	: $C_{18}H_{14}N_2O_3$
Calculated	: 329.0902
Observed	: 329.0911
|Δm|	: 2.7 ppm



4.3.2 UV-VIS spectra of acrylanilide derivative **8**.

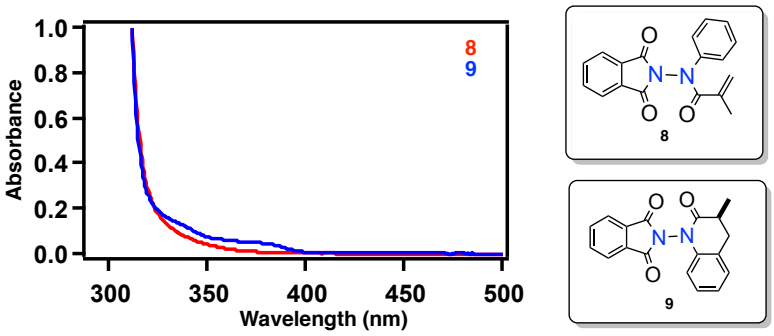
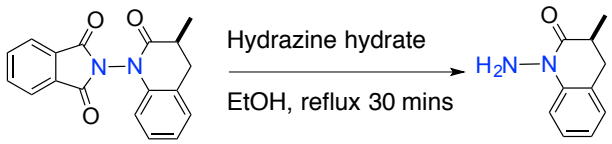


Figure S4. UV-Vis spectra of *N-N* bond based acrylanilide derivative **8** (conc. = 1.24 mM) and photoproduct **9** (conc. = 1.24 mM) recorded in acetonitrile.

4.3.3 Removal of phthalimide ring in acrylanilide based photoproduct **9**.



9 **10**

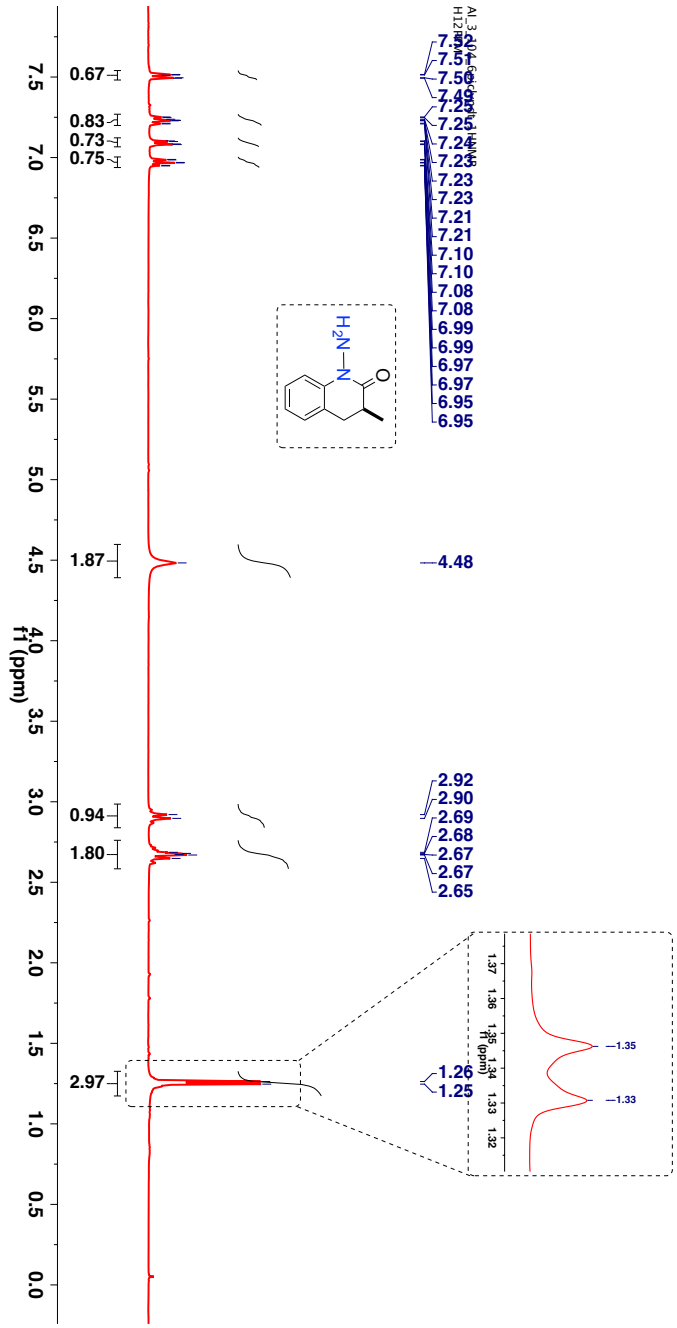
Scheme S24: Removal of phthalimide ring in acrylanilide based photoproduct **9**.

Following the modified procedure reported by Michael et al.[5] the photoproduct **9** (1 *equiv*) was charged in a vial equipped with a teflon cap. The compound was dissolved in absolute ethanol (5 mL per 100 mg of photoproduct) and hydrazine monohydrate (11.9 *equiv*) was added. The solution was stirred for 5 min and refluxed for 30 min (until TLC showed complete consumption of starting material). The solution was brought to room temperature and diluted with ethyl acetate. The solution was sonicated for 15 min and then filtered through a short celite plug. The filtrate was concentrated under reduced pressure to obtain the crude product. The crude product was purified using a prep TLC with hexanes and ethyl acetate mixture as eluting solvent to obtain i.e. *N*-amino dihydroquinolinone derivative **10**.

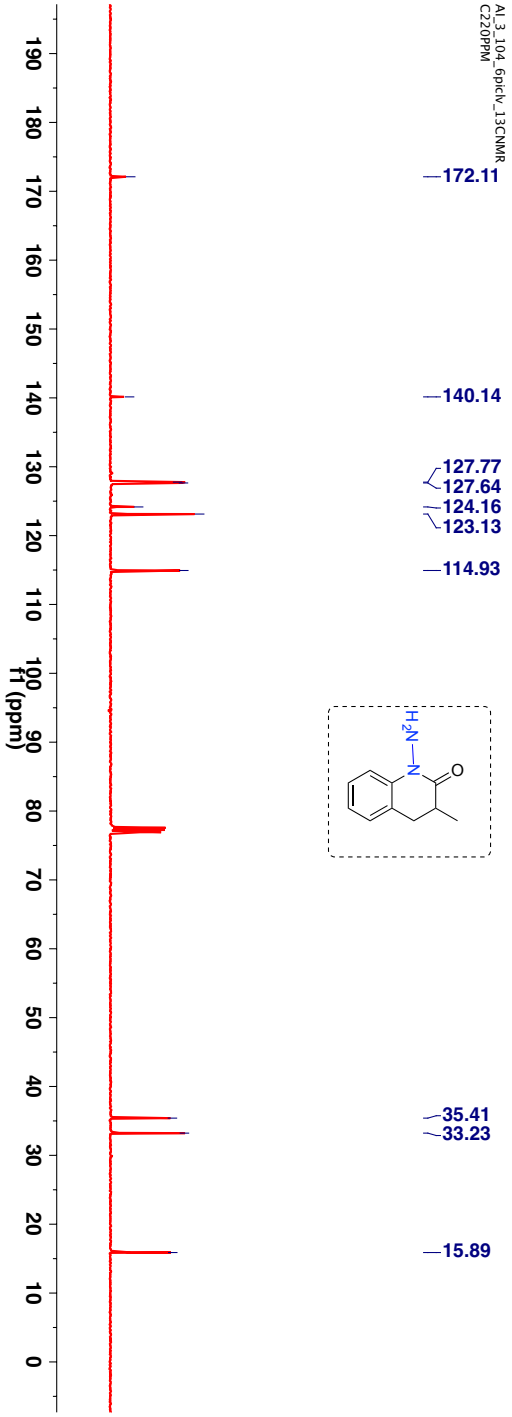
4.3.4 Characterization of product **10**.

Crystalline solid (Yield = 74%).

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 1.25 (d, 3H, *J* 6.4Hz), 2.62-2.72 (m, 2H), 2.87-2.95 (m, 1H), 4.48 (bs, 2H), 6.95-6.97 (m, 1H), 7.06-7.10 (m, 1H), 7.21-7.25 (m, 1H) and 7.49-7.52 (m, 1H).

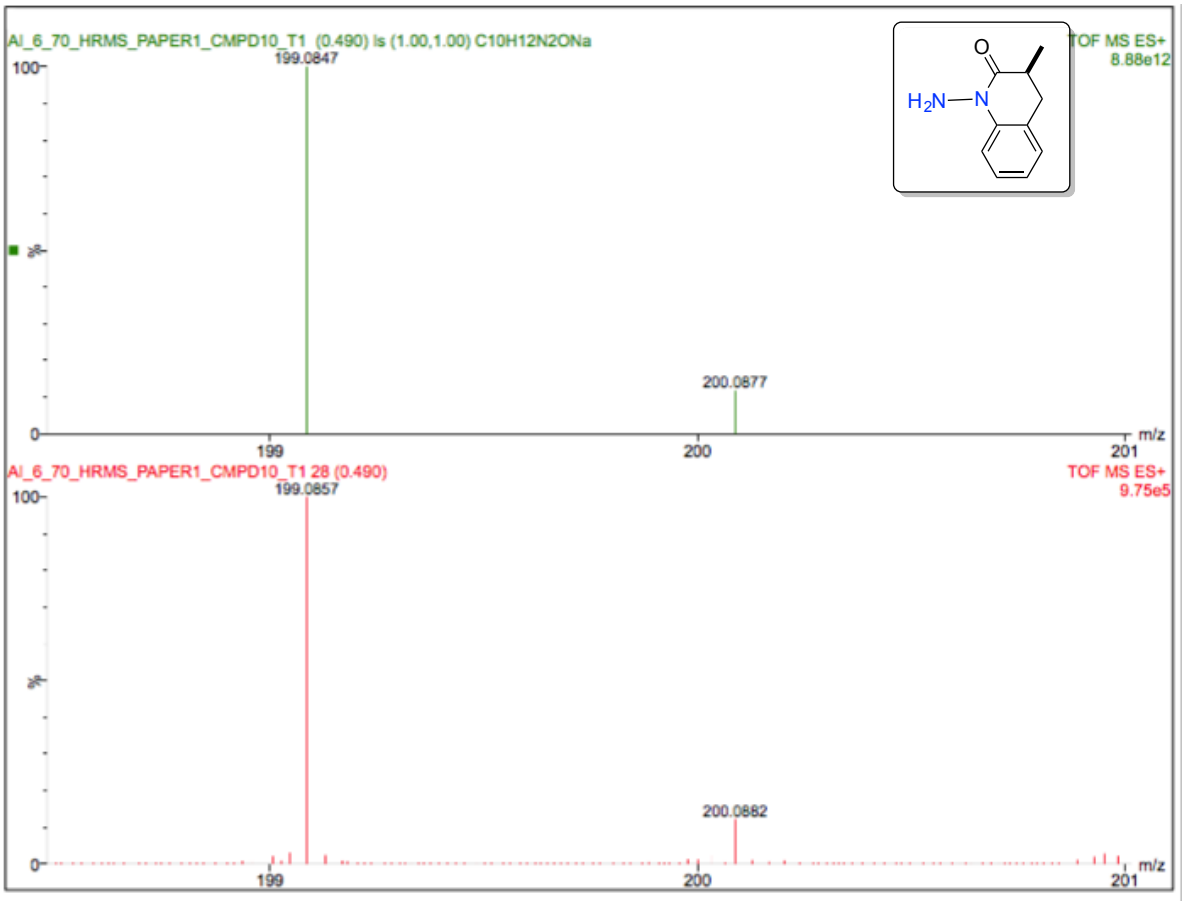


^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 15.9, 33.2, 35.8, 114.9, 123.1, 124.2, 127.6, 127.8, 140.1, and 172.1.

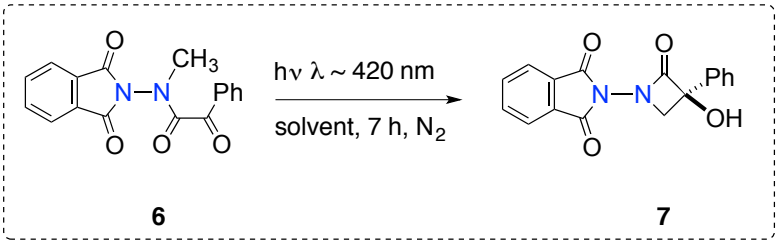


HRMS-ESI (m/z) ([M + Na]$^+$):

Chemical Formula	: $C_{10}H_{12}N_2O$
Calculated	: 199.0847
Observed	: 199.0857
|Δm|	: 5.0 ppm



4.4.0 Reaction optimization for Norrish-Yang cyclization of α-oxoamide derivative **6**.



Scheme S25: Photoreaction of α-oxoamide derivative **6**.

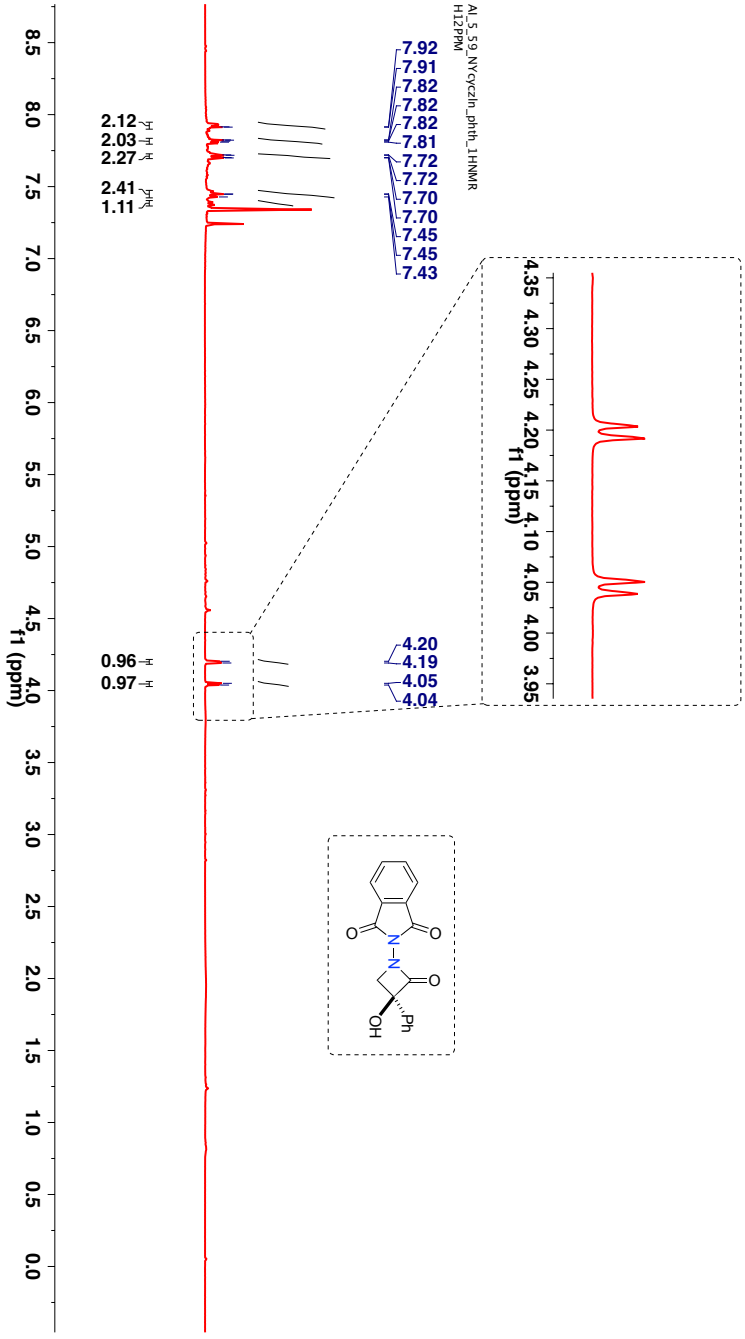
Table S9. Solvent screening studies for Norrish-Yang cyclization of α-oxoamide derivative **6**.[a]

Entry	Solvent	Conversion/%
1	Methanol	decomposition
2	Acetonitrile	16
3	Ethyl acetate	55
4	Benzene	80
6	Methylcyclohexane	No reaction

[a] [**6**] = 3.24 mM.

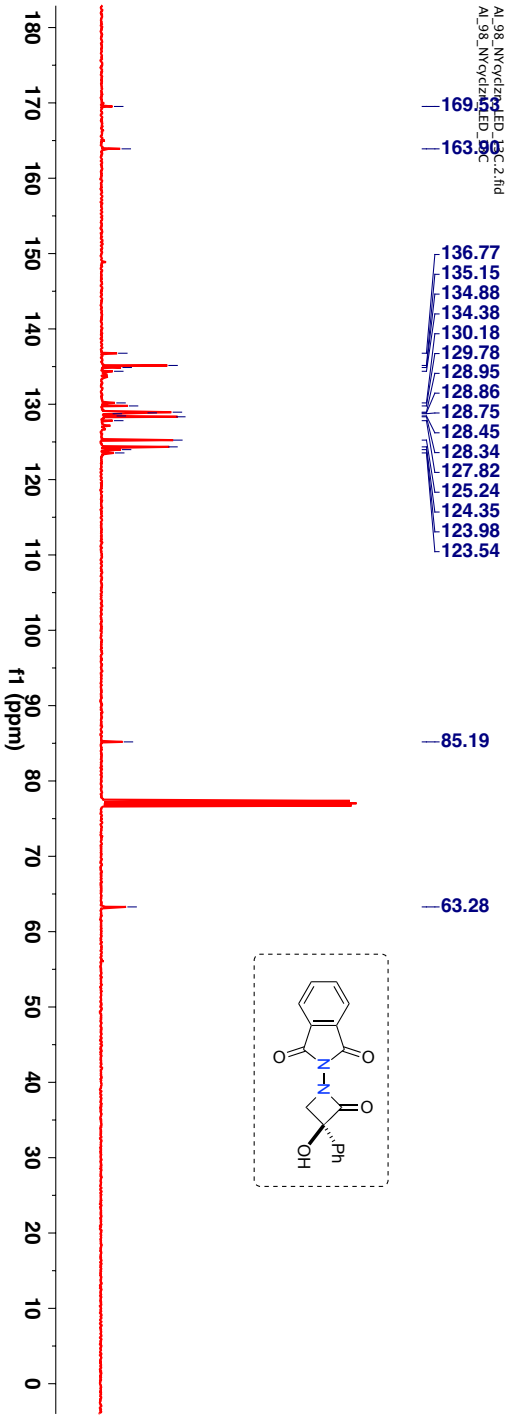
4.4.1 Characterization of photoproduct **7**.

Crude NMR for **7**. Photoreaction performed with purple LED as the light source. ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 4.04-4.20 (ABq, 2H), 7.37-7.47 (m, 3H), 7.69-7.72 (m, 2Hz), 7.80-7.82 (m, 2H) and 7.91-7.93 (m, 2H).



Crude NMR aromatic region has thioxanthone peaks (sensitizer)

^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 63.3, 85.2, 123.5, 123.9, 124.4, 125.3, 127.8, 128.3, 128.5, 128.9, 128.9, 129.8, 130.2, 134.4, 134.9, 135.2, 136.8, 163.9 and 169.5.



4.4.2 UV-VIS spectra of α–oxoamide derivative **6**.

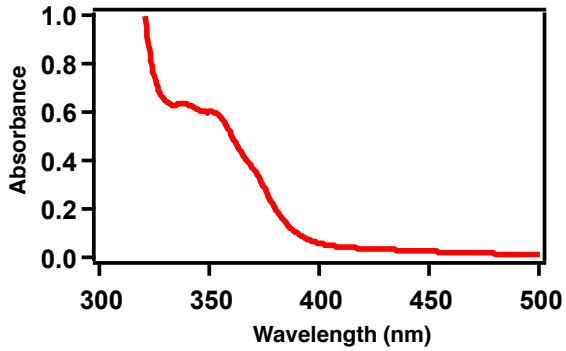


Figure S5. UV-Vis spectra of *N-N* bond based α–oxoamide derivative **6** (conc. = 3.2 mM) recorded at the reaction concentration in benzene.

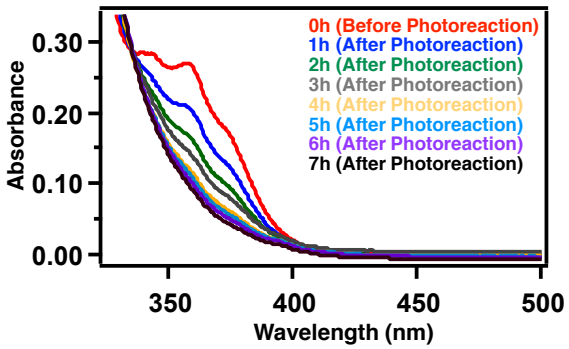


Figure S6. UV-Vis spectra of *N-N* bond based α–oxoamide derivative **6** recorded in benzene during the course of photoreaction under CFL lamp illumination; [**6**] = 3.2 mM (before photoreaction).

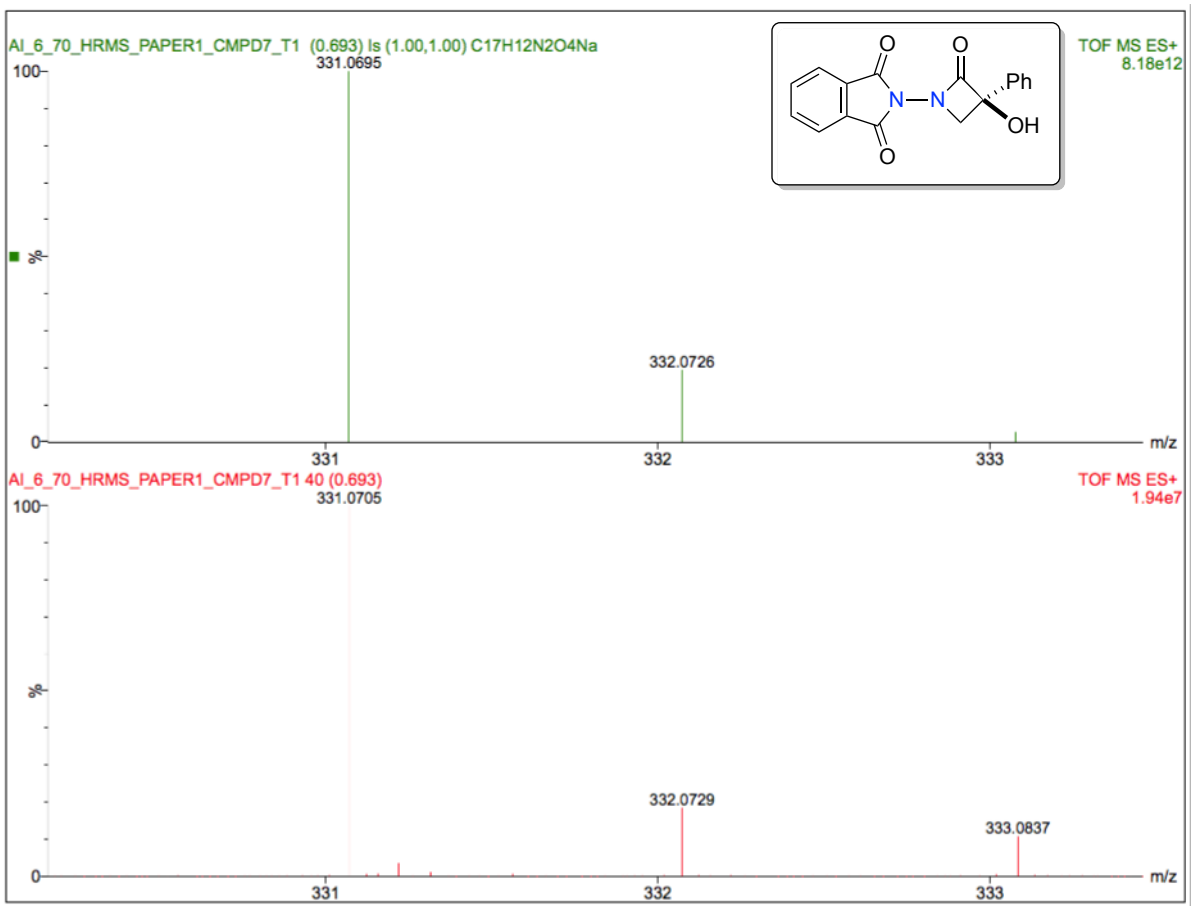
HRMS-ESI (m/z) ([M + Na]$^+$):

Chemical Formula : $C_{17}H_{12}N_2O_4$

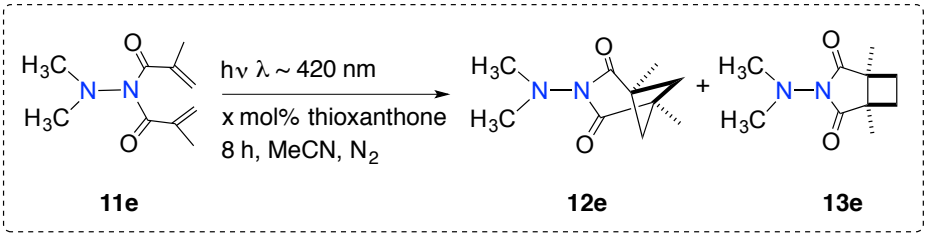
Calculated : 331.0695

Observed : 331.0705

|Δm| : 3.0 ppm



4.5.0 Reaction optimization for [2+2] photoreaction of tertiary amine derivative **11e**.



Scheme S26: Photoreaction of [2+2] photoreaction of tertiary amine (acrylimide) derivative **11e**.

Table S10. Sensitizer/catalyst loading studies for [2+2] photoreaction of tertiary amine derivative **11e**.[a]

Entry	Tx (x mol%)	Conversion/%
1	0	0
2	1	74
3	5	93
4	10	95

[a] [**11e**] = 5.1 mM, Tx: Thioxanthone

Table S11. Solvent screening studies for [2+2] photoreaction of tertiary amine derivative **11e**.[a]

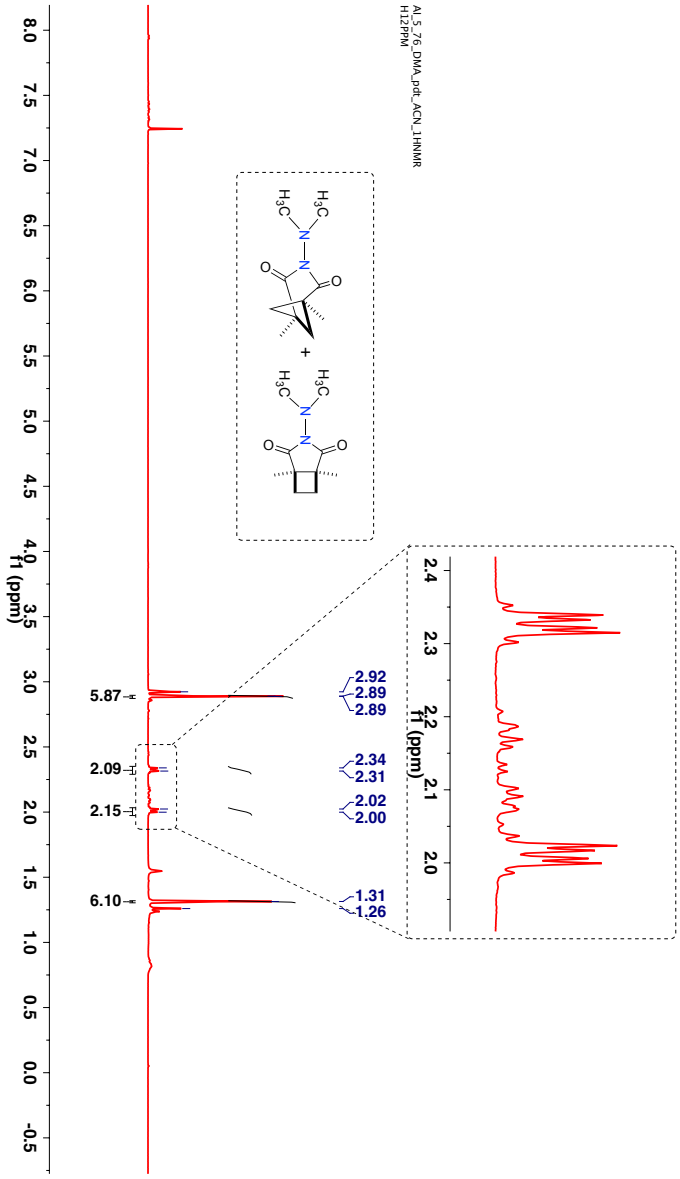
Entry	Solvent	Conversion/%	NMR yield/%	12e:13e
1	Methanol	-[b]	-	-
2	Acetonitrile	95	40	70:30
3	Ethyl acetate	55	27	75:25
4	Benzene	52	28	75:25
6	Methylcyclohexane	Decomposition	-	-

[a] [**11e**] = 5.1 mM. [b] Difficult to interpret because of overlapping peaks

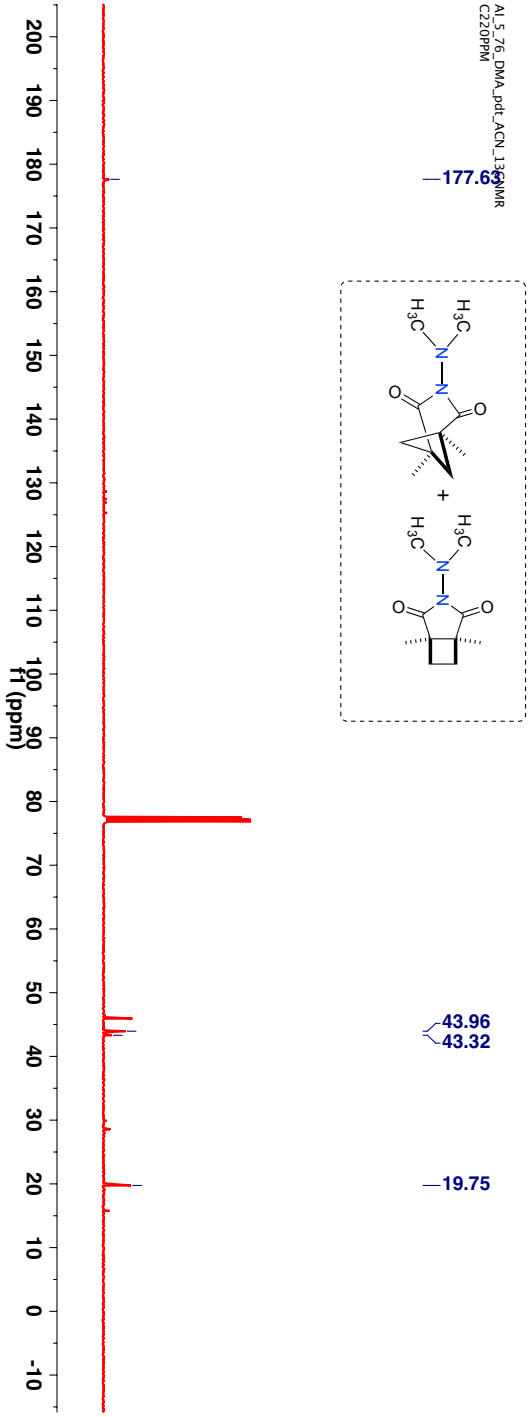
4.5.1 Characterization of photoproduct **12e** and **13e**.

Solid (Yield = 24%). R_f = 0.2 (20% ethyl acetate:hexanes).

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm, mixture of regioisomers): 1.26 (s), 1.31 (s, 6H), 2.00-2.02 (m, 2H), 2.03-2.20 (m), 2.31-2.34 (m, 2H), 2.89 (s, 6H) and 2.92 (s).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm, mixture of regioisomers): 15.8, 19.8, 28.6, 43.3, 43.9, 44.0 and 177.6.



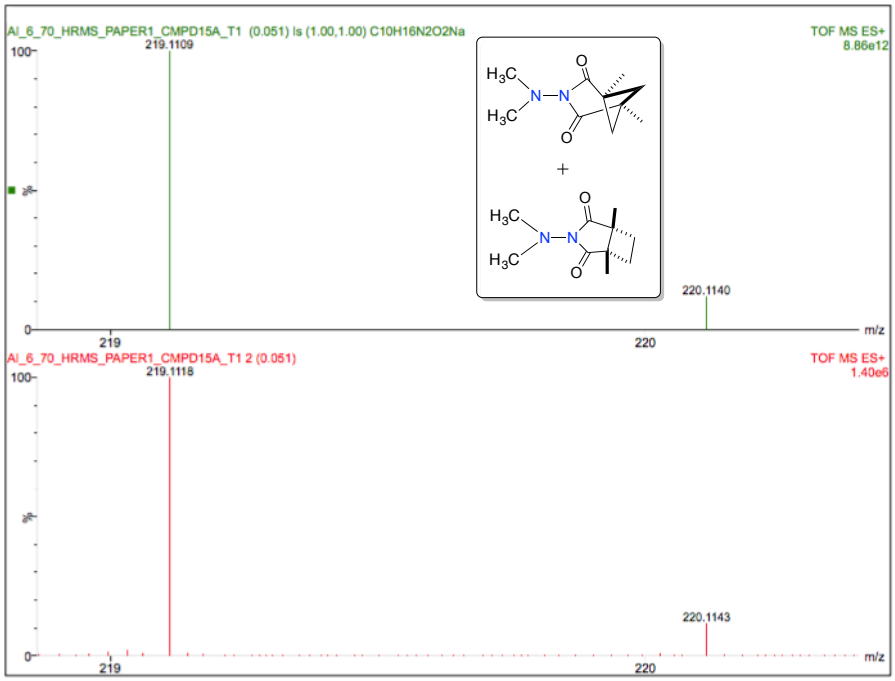
HRMS-ESI (m/z) ([M + Na]$^+$):

Chemical Formula : $C_{10}H_{16}N_2O_2$

Calculated : 219.1109

Observed : 219.1118

|Δm| : 4.1 ppm



4.5.2 UV-VIS spectra of tertiary amine derivative **11e**.

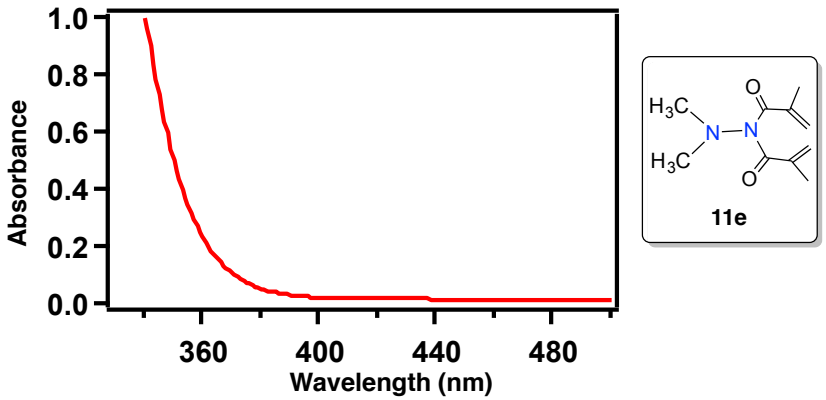
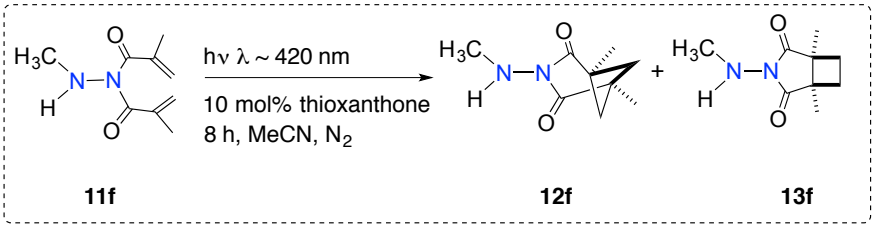


Figure S7. UV-Vis spectra of tertiary amine derivative **11e** (conc. = 5.1 mM) recorded at the reaction concentration in acetonitrile.

4.6.0 Reaction optimization for [2+2] photoreaction of secondary amine derivative **11f**.



Scheme S27: Photoreaction of [2+2] photoreaction of secondary amine derivative **11f**.

Table S12. [2+2]-Photoreaction of secondary amine derivative **11f**.[a]

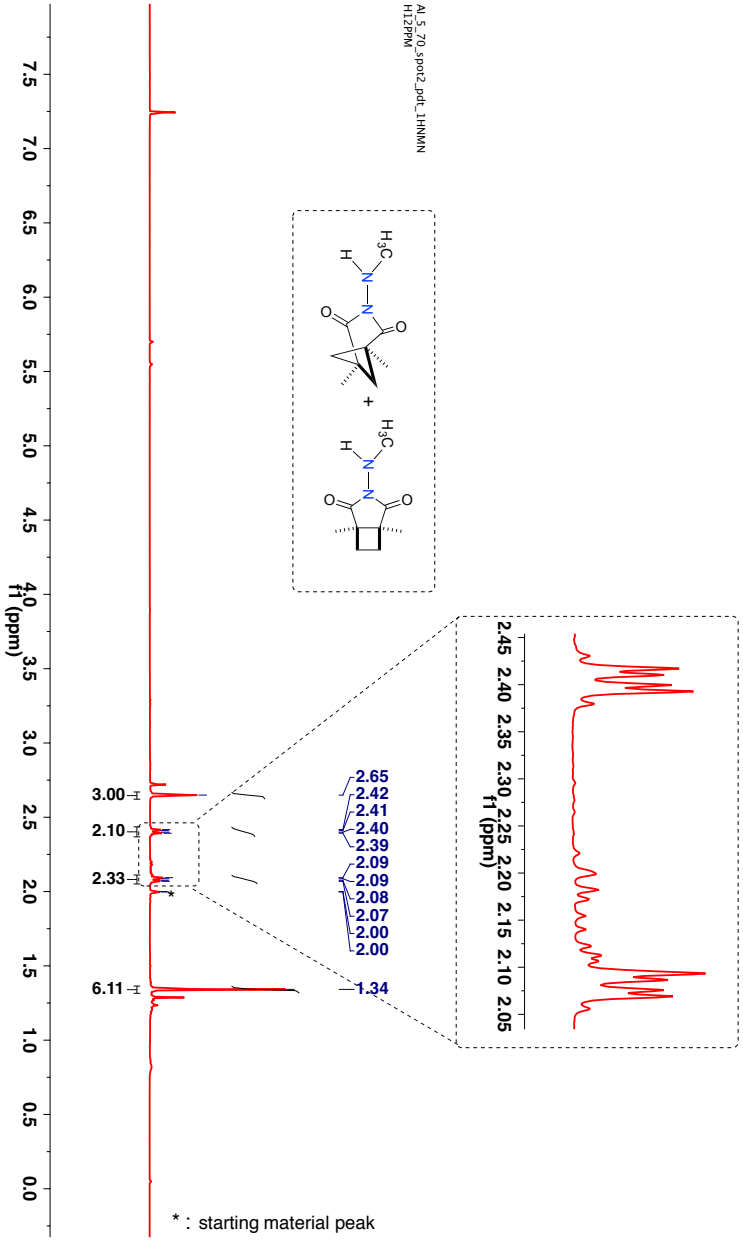
Entry	Solvent	Conversion/%	NMR yield/%	12f:13f
1	Acetonitrile	>99	40	80:20

[a] [**11f**] = 5.49 mM.

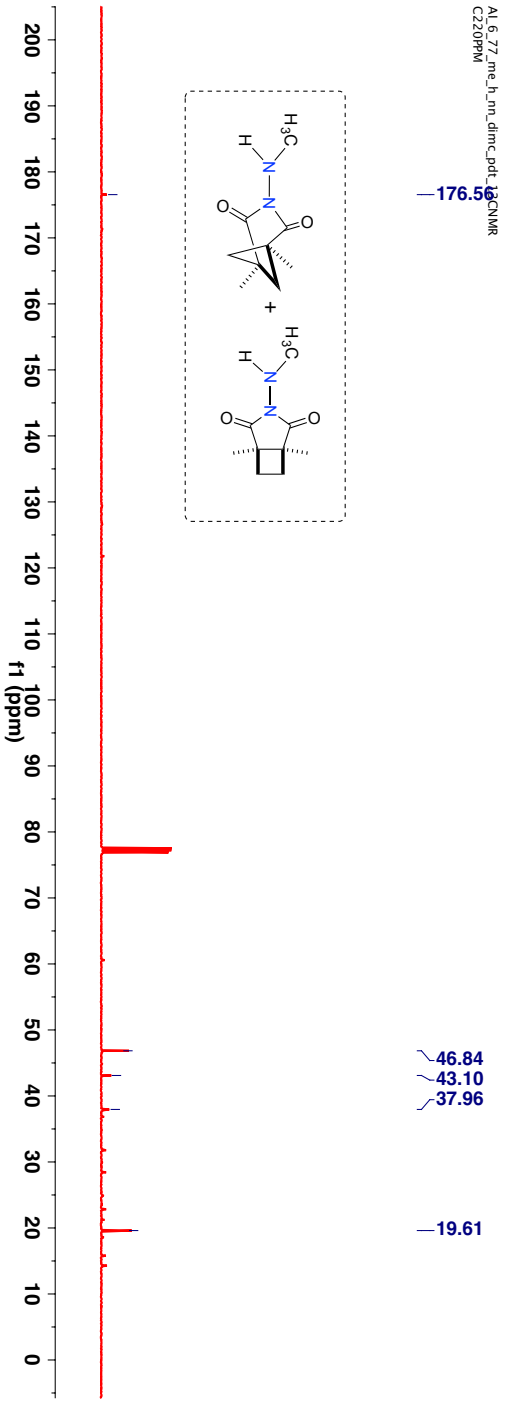
4.6.1 Characterization of photoproduct **12f** and **13f**.

Thick oil (Yield = 35%).

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm, mixture of regioisomers): 1.29 (s), 1.34 (s, 6H), 2.07-2.09 (m, 2H), 2.10-2.20 (m), 2.39-2.42 (m, 2H), 2.65 (s, 3H) and 2.72 (s).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm, mixture of regioisomers): 19.6, 37.9, 43.1, 46.8 and 176.6.



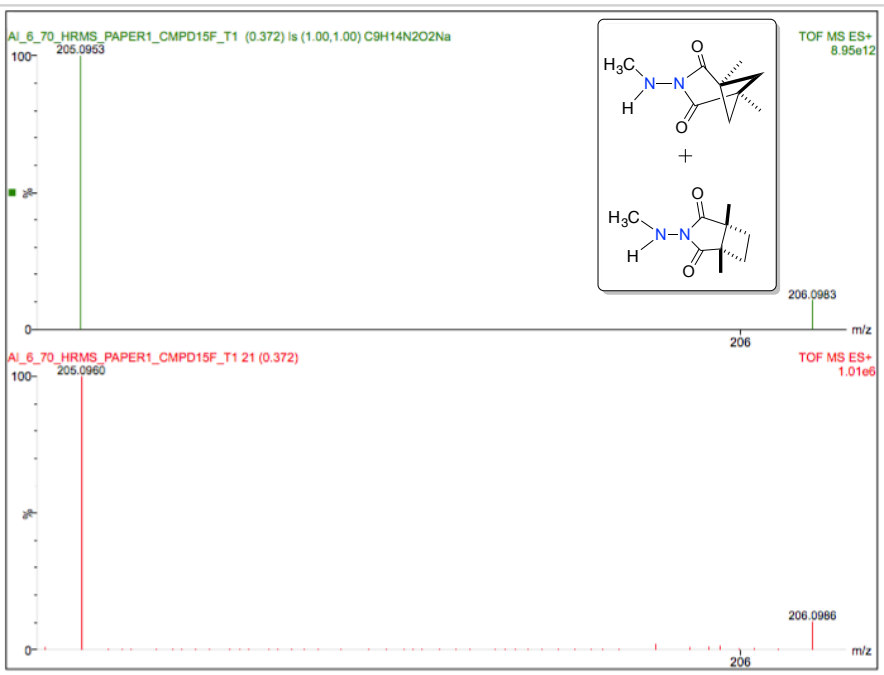
HRMS-ESI (m/z) ([M + Na]$^+$):

Chemical Formula : $C_9H_{14}N_2O_2$

Calculated : 205.0963

Observed : 205.0960

|Δm| : 1.5 ppm



4.6.2 UV-VIS spectra of secondary amine derivative **11f**.

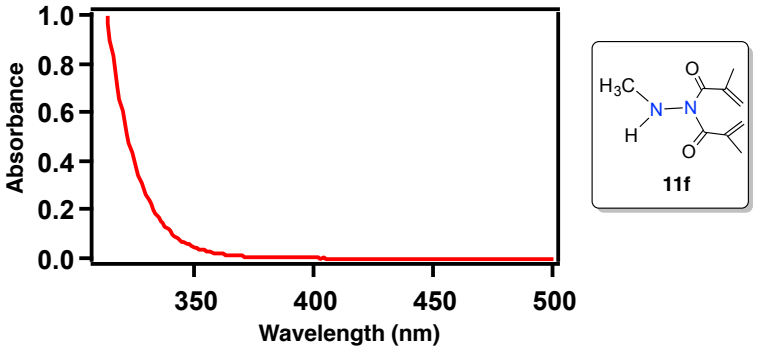
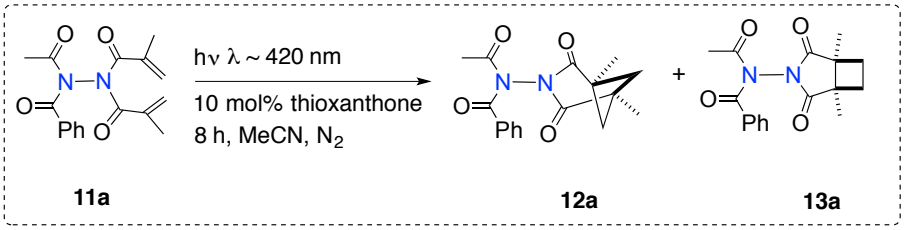


Figure S8. UV-Vis spectra of secondary amine derivative **11f** (conc. = 5.49 mM) recorded at the reaction concentration in acetonitrile.

4.7.0 Reaction optimization for [2+2] photoreaction of imide based derivative **11a**.



Scheme S28: Photoreaction of [2+2] photoreaction of imide based derivative **11a**.

Table S13. [2+2]-Photoreaction of imide based derivative **11a**.[a]

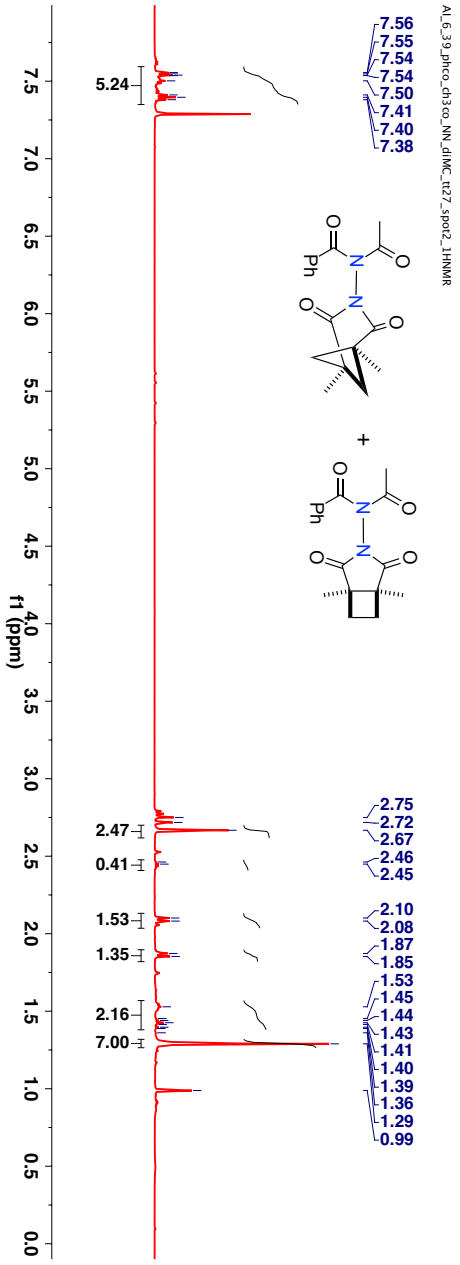
Entry	Solvent	Conversion/%	NMR yield/%	12a:13a
1	Acetonitrile	56	52	-[b]

[a] [**11a**] =3.18 mM. [b] Ratios were difficult to determine because of overlapping peaks by ^{1}H NMR spectroscopy

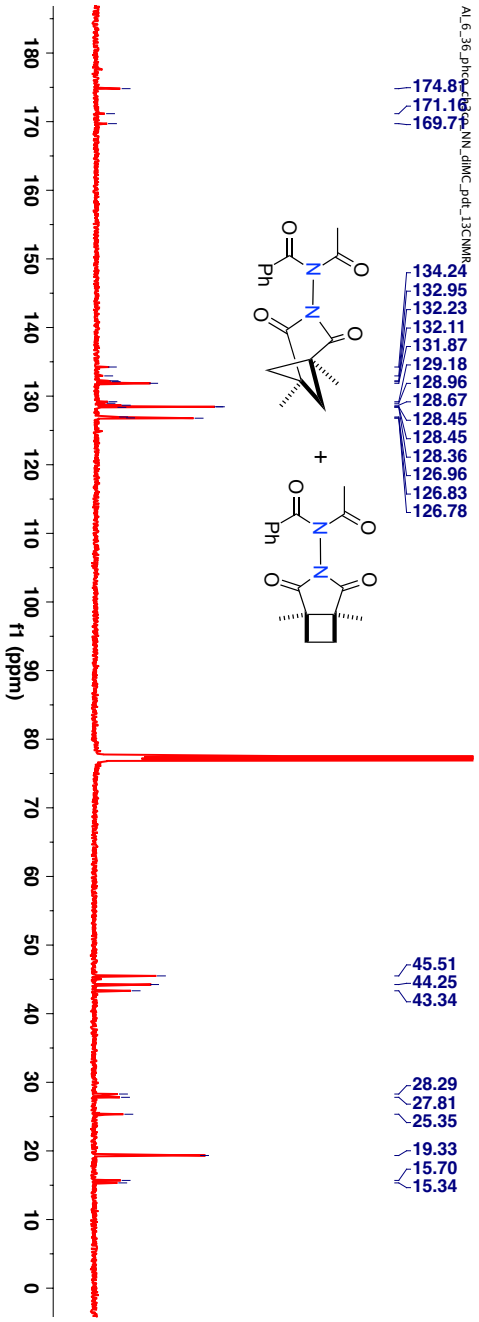
4.7.1 Characterization of photoproduct **12a** and **13a**.

Thick oil (Yield = 45%). R_f = 0.2 (10% ethyl acetate:hexanes).

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm, mixture of rotamers): 0.99 (s), 1.29 (s), 1.30 (s), 1.39-1.45 (m), 1.51-1.55 (m), 1.85-1.88 (m), 2.08-2.11 (m), 2.42-2.46 (m), 2.67 (s), 2.72-2.79 (m) and 7.39-7.56 (m).



^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm, all peaks are reported together): 15.3, 15.7, 19.3, 25.3, 25.5, 27.8, 28.3, 43.3, 44.2, 45.5, 126.8, 126.8, 127.0, 128.4, 128.4, 128.4, 128.7, 129.0, 129.2, 131.9, 132.1, 132.2, 132.9, 134.2, 169.7, 171.2 and 174.8.



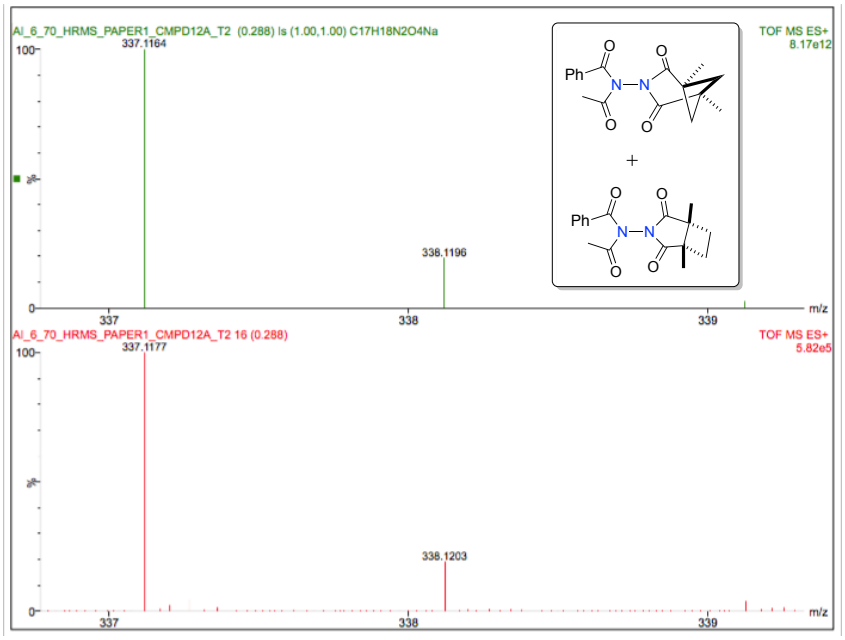
HRMS-ESI (m/z) ([M + Na]$^+$):

Chemical Formula : $C_{17}H_{18}N_2O_4$

Calculated : 337.1177

Observed : 337.1164

|Δm| : 3.8 ppm



4.7.2 UV-VIS spectra of imide based derivative **11a**.

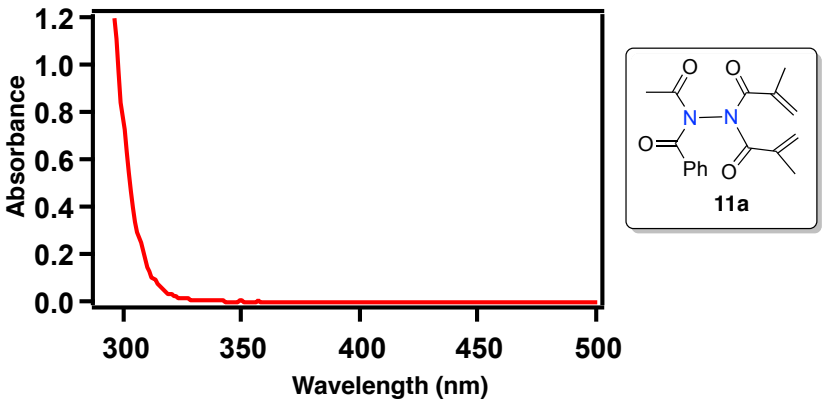
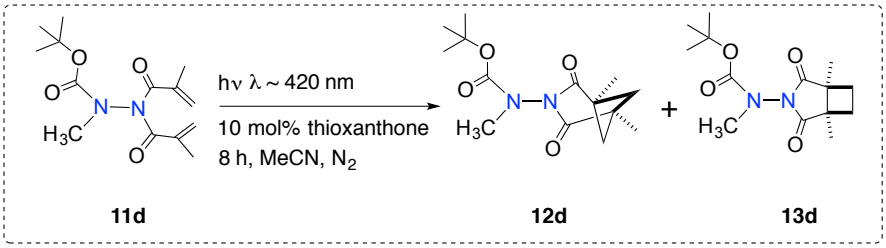


Figure S9. UV-Vis spectra of imide based derivative **11a** (conc. = 3.18 mM) recorded at the reaction concentration in acetonitrile.

4.8.0 Reaction optimization for [2+2] photoreaction of carbamate derivative **11d**.



Scheme S29: Photoreaction of [2+2] photoreaction of carbamate derivative **11d**.

Table S14. [2+2]-Photoreaction of carbamate derivative **11d**.[a]

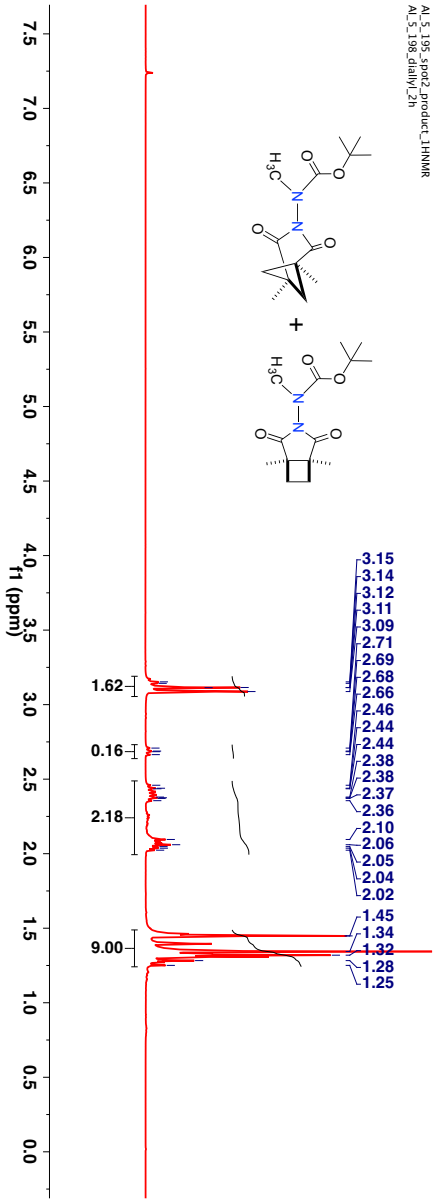
Entry	Solvent	Conversion/%	12d:13d
1	Acetonitrile	82	-[b]

[a] [**11d**] = 3.54 mM. [b] Difficult to determine due to overlapping peaks

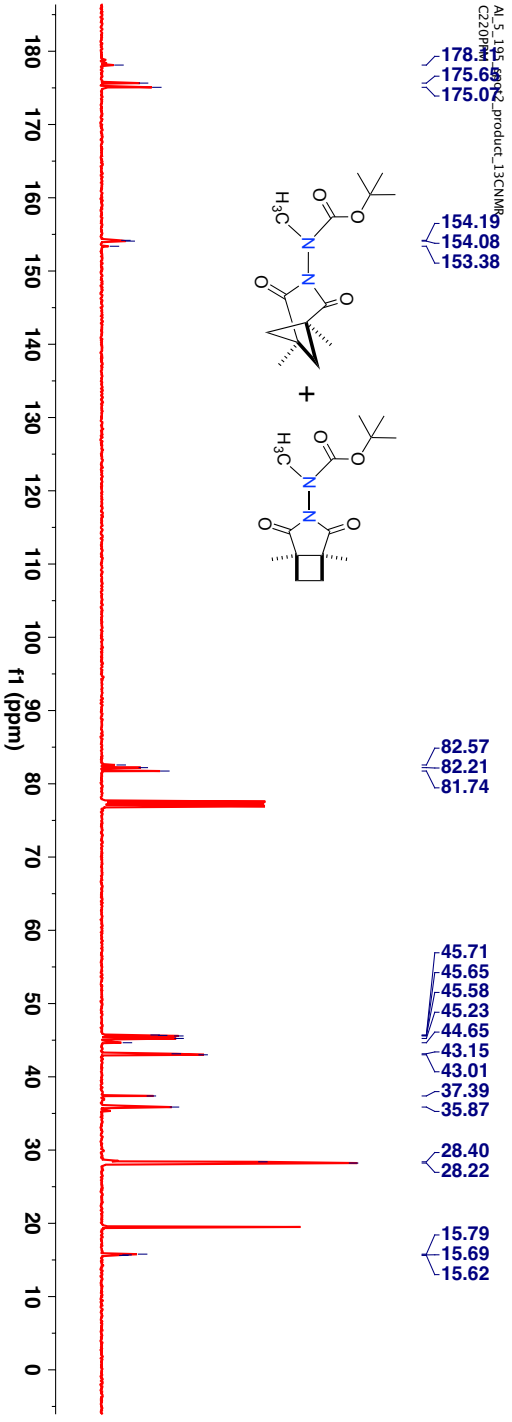
4.8.1 Characterization of photoproduct **12d** and **13d**.

Thick oil (Yield = 73%). R_f = 0.3 (20% ethyl acetate:hexanes).

^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm, mixture of regioisomers): 1.25 (s), 1.28 (s), 1.32 (s), 1.34 (s), 1.36 (s), 1.45 (s), 2.02-2.10 (m), 2.36-2.46 (m), 2.66-2.71 (m), 3.10 (s), 3.11 (s), 3.14 (s), 3.15 (s).

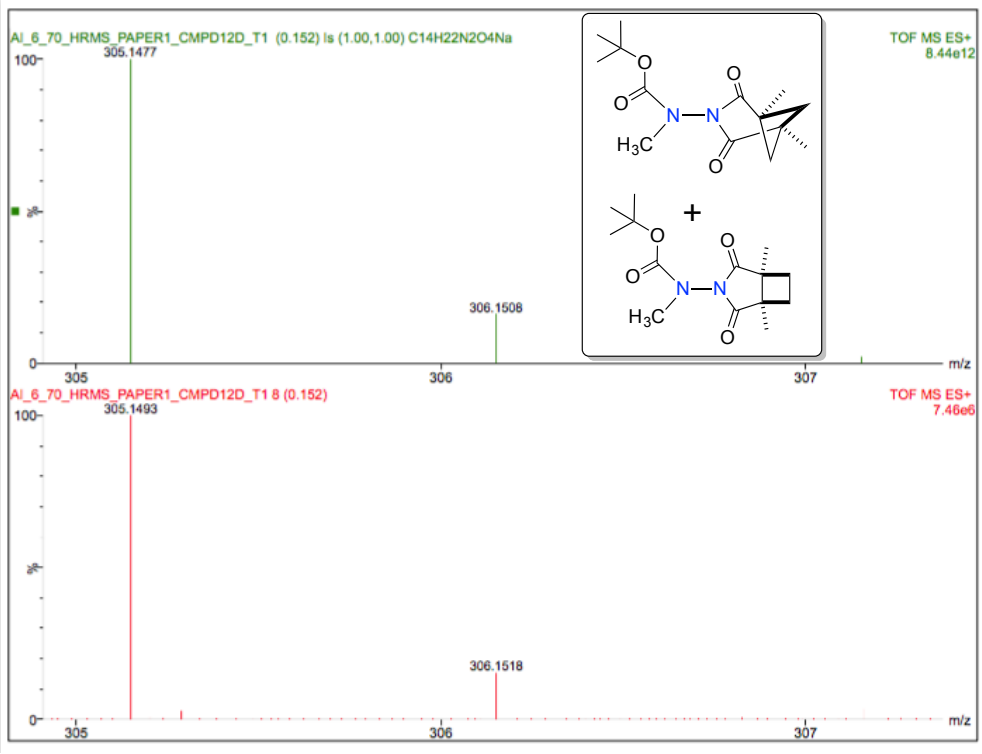


^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm, mixture of regioisomers): 15.6, 15.7, 15.8, 19.5, 28.2, 28.4, 35.9, 37.4, 43.0, 43.1, 44.7, 45.2, 45.6, 45.7, 45.7, 81.7, 82.2, 82.6, 153.4, 154.1, 154.2, 175.1, 175.7 and 178.1.



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

Chemical Formula	: $C_{14}H_{22}N_2O_4$
Calculated	: 305.1477
Observed	: 305.1493
|Δm|	: 5.6 ppm



4.8.2 UV-VIS spectra of carbamate derivative **11d**.

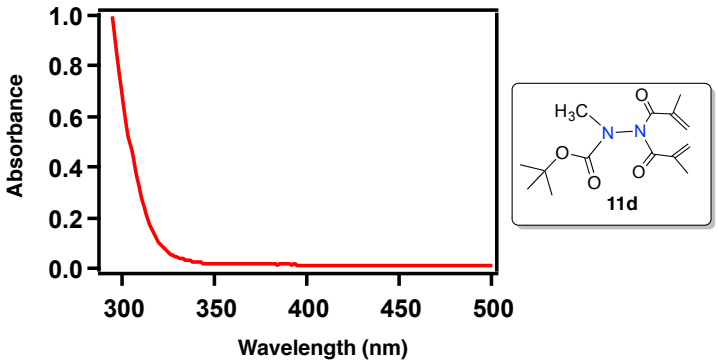
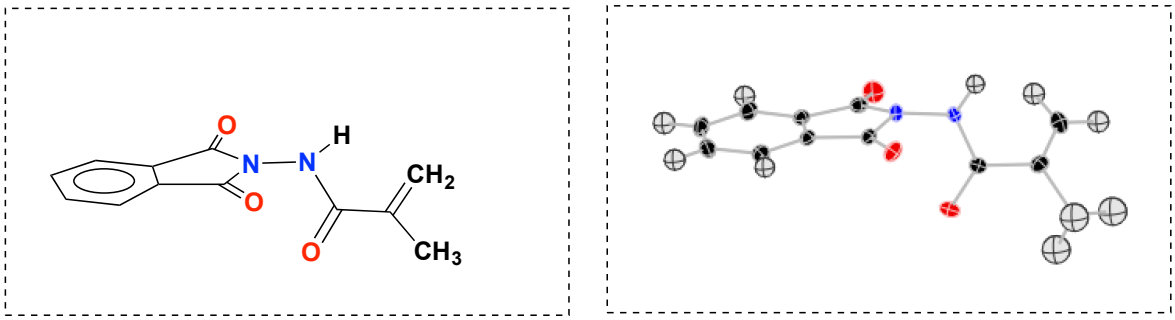


Figure S10. UV-Vis spectra of carbamate derivative, **11d** recorded at the reaction concentration in acetonitrile (conc.= 3.5 mM).

5 XRD STRUCTURES AND STRUCTURAL PARAMETERS

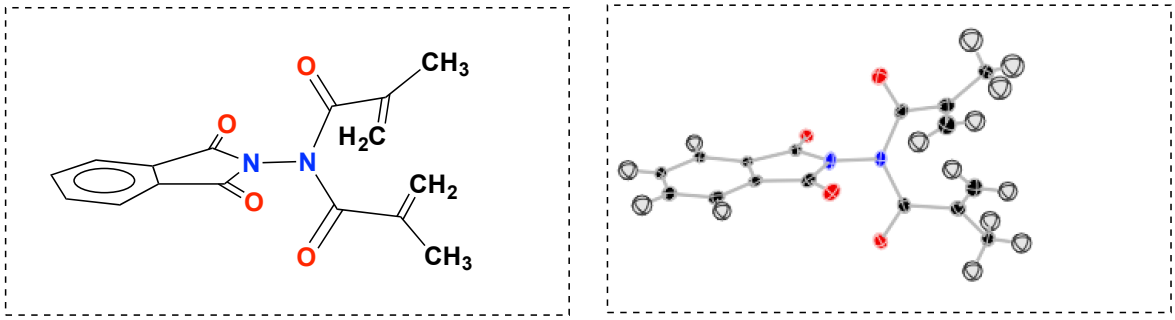
5.1.0 Single crystal XRD structure of phthalimide based amide derivative **15**.

(Crystallization solvent(s): hexanes/chloroform)



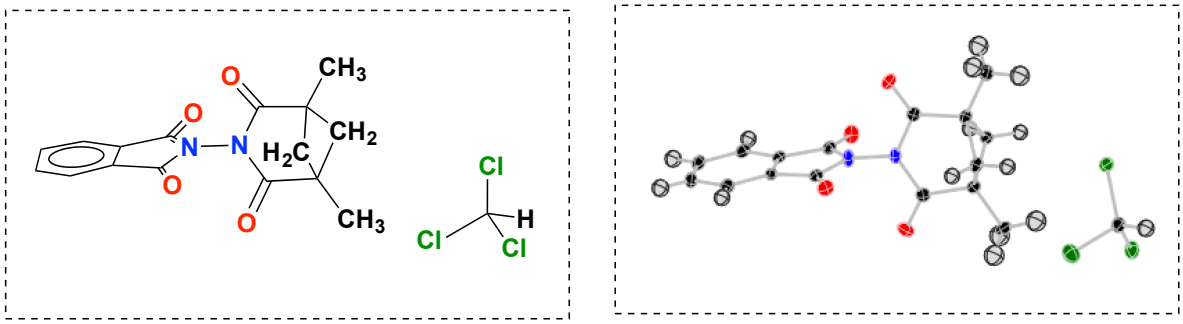
5.1.1 Single crystal XRD structure of phthalimide based acrylimide derivative **1**.

(Crystallization solvent(s): hexanes/ethylacetate)



5.1.2 Single crystal XRD structure of acrylimide based photoproduct **2**.

(Crystallization solvent: chloroform)

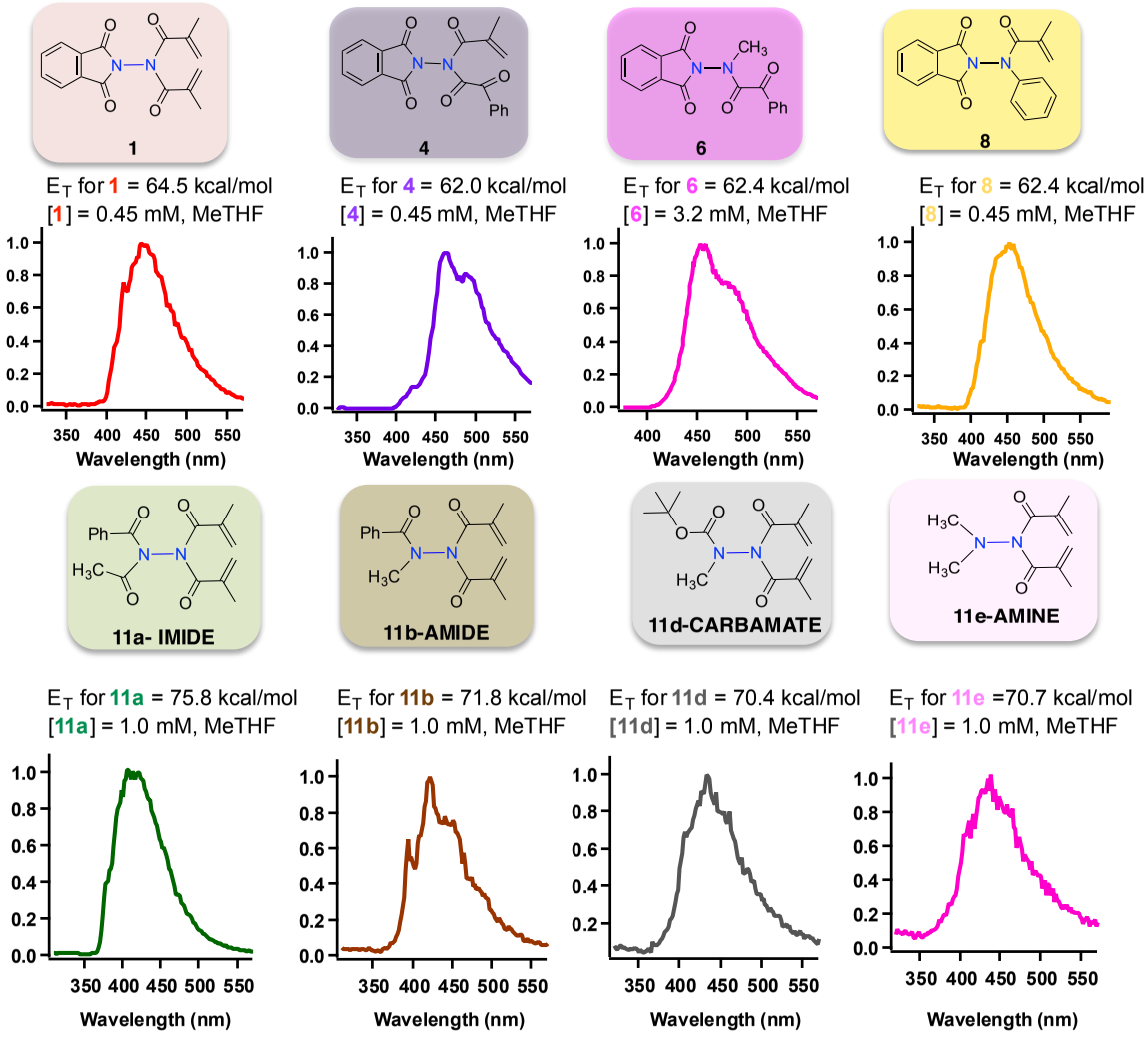


5.1.3 Structural parameters table for hydrazides **15**, **1** and **2**.

Crystals	**15**	**1**	**2**
Formula	$C_{12}H_{10}N_2O_3$	$C_{16}H_{14}N_2O_4$	$C_{16}H_{14}N_2O_4$, $CHCl_3$
Formula Weight	230.22	298.29	417.66
Space Group, Z	P 21/c	P 21/c	P -1
a/Å	8.5484(3)	32.0290(13)	7.9595(3)
b/Å	34.4488(11)	11.6208(5)	15.2345(5)
c/Å	15.2307(4)	16.5874(7)	16.7559(6)
α /°	90	90	110.399
β/°	101.098(2)	103.875(2)	100.744
γ /°	90	90	97.410
V ($Å^3$)	4401.3(3)	5993.7(4)	1829.03(11)
h, k , l_{max}	10,41,18	38,13,19	9,18,19
ρ_{calc} [mg/mm^3]	1.390	1.322	1.517
μ [mm^{-1}]	0.852	0.803	4.772
Radiation type	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
F(000)	1920.0	2504.35	856.0
No. of measured reflections	7716	10593	6332
No. of independent reflections	6487	9800	5905
Final R indexes ($I \geq 2\sigma$)	R_1 = 0.0363, wR_2 = 0.0941	R_1 = 0.0612, wR_2 = 0.1768	R_1 = 0.0295, wR_2 = 0.0748
R1/wR2 ($I \geq 2\sigma$) [%]	0.0363/0.0941	0.0612/0.1768	0.0295/0.0748

6 PHOTOPHYSICAL DATA

6.1.0 Phosphorescence spectra of substrates recorded at 77K.



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