Supplementary Material (ESI) for Chemical Communications

Supporting Information (47 pages)

Reactive Spin State Dependent Enantiospecific Photocyclization of Axially Chiral α-substituted Acrylanilides

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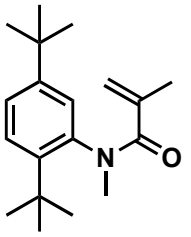
1. General Methods.

All commercially obtained reagents/solvents were used as received; chemicals were purchased from Alfa Aesar®, Sigma – Aldrich®, Across®, TCI® America, Mallinckrodt®, and Oakwood Products®, and were used as received without further purification. Unless stated otherwise, reactions were conducted in oven-dried glassware under an atmosphere of nitrogen using anhydrous solvents; Photoreactions were performed under N_2 or O_2 atmosphere. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 400 MHz (100 MHz) and on 500 MHz (125 MHz) spectrometers. Data for ^{1}H NMR spectra are reported relative to residual deuterated solvent signals, and are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Coupling constants (*J*) were reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: b (broad), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), virt (virtual), and ABq (AB quartet). Data for ^{13}C NMR spectra are reported relative to residual deuterated solvent signals. High-resolution mass spectra (HRMS) were recorded on a Bruker – Daltronics® BioTof mass spectrometer in positive (ESI+) ion mode. HPLC analyses were performed on Waters® HPLC equipped with 2525 pump. Waters® 2767 sample manager was used for automated sample injection. All HPLC injections were monitored using a Waters® 2487 dual wavelength absorbance detector at 254 nm and 270 nm. Analytical and semi-preparative injections were perfomed on chiral stationary phase using Regis® PIRKLE COVALENT (R,R) WHELK–O1 10/100 FEC columns‡. Masslynx software version 4.1 was used to analyse/process the HPLC injections. Igor Pro® Software version 4.0 was used to generate graphics of the chromatographic data. When necessary, the reactants and photoproducts were purified by chromatography: CombiFlash and/or on silica gel (Sorbent Technologies®, silica gel standard grade: Porosity 60 Å, Particle size: 230 x 400 mesh, Surface area: 500 – 600 m^2/g, Bulk density: 0.4 g/mL, pH range: 6.5 – 7.5). The Retention Factor (R*f*) values were recorded using a 20 % EtOAc-Hexanes as mobile phase (unless indicated) on SORBENT TECHNOLOGIES® Silica Gel TLC plates (200 μm thickness w/ UV_{254}). Optical activity values were recorded on JASCO® DIP – 370 digital polarimeter. CD spectra were recorded on JASCO® - 710 digital CD spectrometer.

‡ Regis® PIRKLE COVALENT (R,R) WHELK–O1 10/100 FEC columns: 25cm X 4.6 mm column for analytical injections, and 25 cm x 10.0 mm for semi-preparative injections.

2. Photophysical Methods.

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



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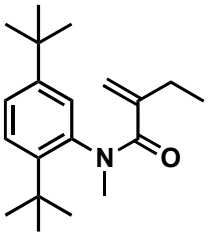

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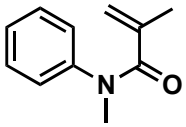

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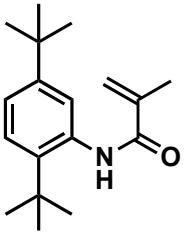

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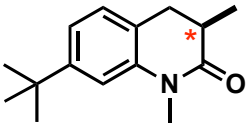

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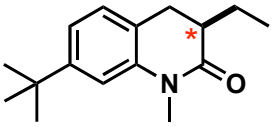

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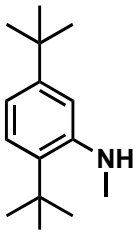

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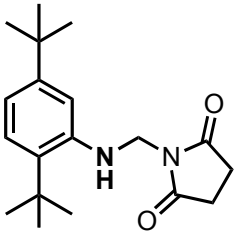

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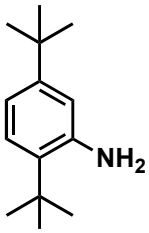

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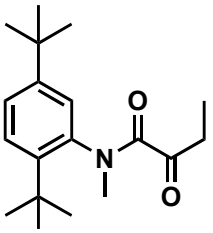

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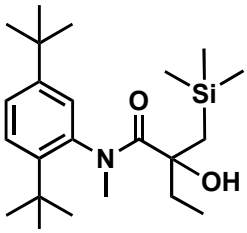

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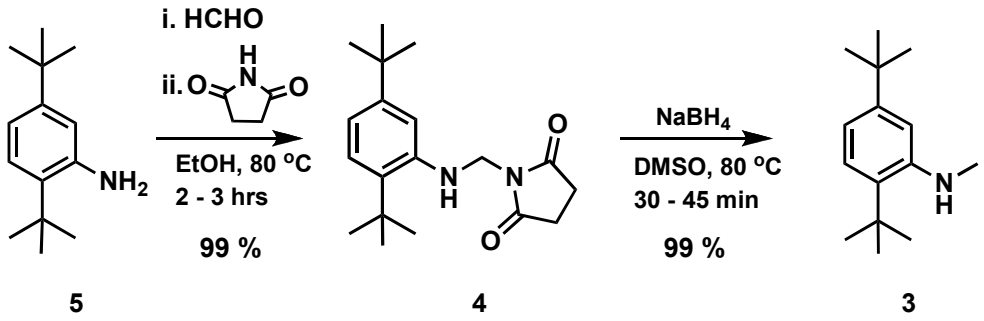
Chart 1

3. Procedure for synthesis and characterization of **3**, **6** and **7**.

3.1 Synthesis of aniline **3**.



Scheme S1: Synthesis of *N*-Methyl aniline **3**

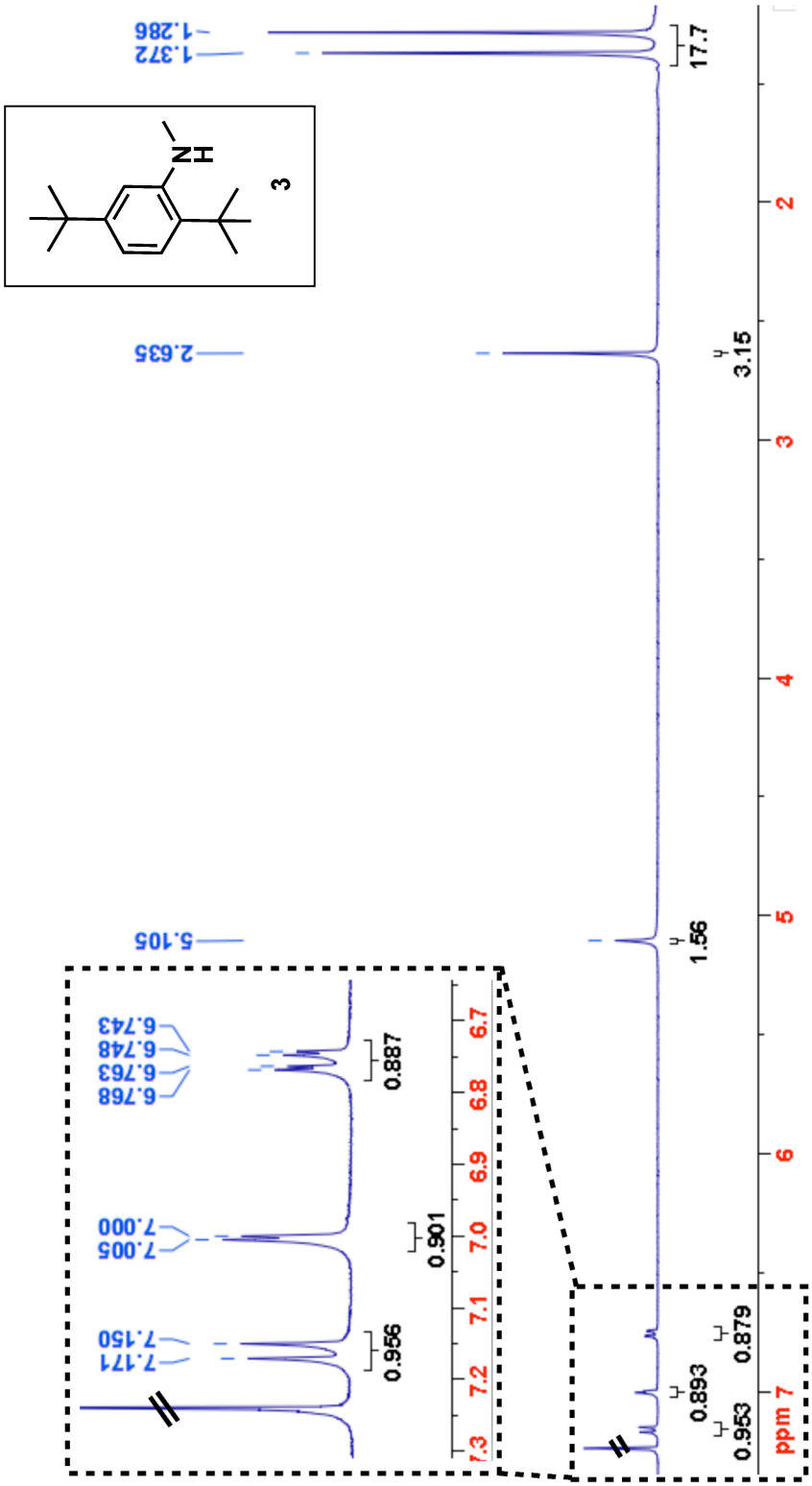
N-Methyl aniline **3** was synthesized using previously reported procedures.[1,2] 2,5-Di-*tert*-butylaniline **5** (1 equi., 5 g, 5.2 mL, 34 mmol) was dissolved in 15 mL of EtOH; 1.1 equi. of 37.9 % formaldehyde solution (1.11g, 3 mL, 37 mmol) and 1.1 equi. of succinimide (3.65 g, 37 mmol) were respectively added to the aniline solution. The new mixture was allowed to reflux with stirring. After 2-3 h, the solution was cooled to room temperature and further cooled in an ice bath. Amide **4** was collected by vacuum filtration, washed several times with cold ethanol, dried and was used without further purification.

The isolated succinimide derivative **4** (1 equiv., 8.85 g, 34 mmol) was dissolved in 20 mL of dry DMSO under N_2 atmosphere. $NaBH_4$ (1.1 equi., 1.42 g, 37 mmol) was slowly added to the flask. The new mixture was constantly stirred and heated at 80 ^oC for 45 min. The reaction mixture was cooled to room temperature and the solution was transferred into a beaker containing cold DI water (about 200 mL). The organic layer was extracted with diethyl ether; the combined organic fraction was then dried over anhydrous Na_2SO_4, filtered, and concentrated to obtain the expected *N*-Methyl aniline **3**. The purity (based on TLC, NMR, HPLC) of the synthesized aniline allowed us to employ it in subsequent reactions without further purification. However, **3** may be purified by chromatography (Solvent system: 100 % Hexane) to remove unreacted **4** (if any).

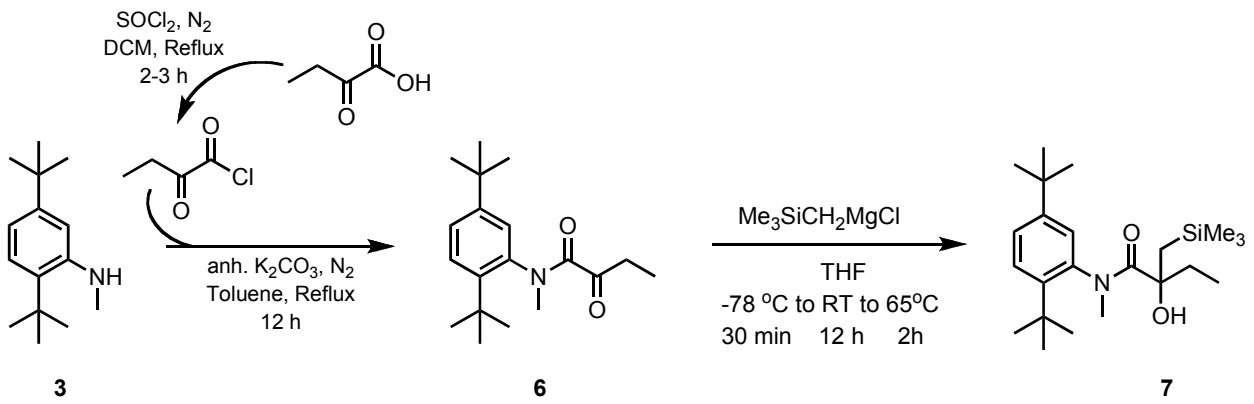
Purification Conditions:

(CombiFlash®) 24 g silica, flow rate: 30 mL/min, solvent system: 100% hexanes.

***^{1}H NMR* (400 MHz, $CDCl_3$, δ ppm)** 1.29 (s, 9H), 1.37 (s, 9H), 2.64 (s, 3H), 5.11 (b s, 1H), 6.74 - 6.77 (dd, J = 2 Hz and 8.4 Hz, 1H), 7.00 (d, J = 2 Hz, 1H), 7.16 (d, J = 8.4 Hz, 1H).



3.2 Synthesis of oxoamides **6**.



Scheme S2: Synthesis of **6** and **7**.

In a typical reaction, 2.09 g of 2-ketobutyric acid was dissolved in 10 mL of dry CH_2Cl_2; while the solution was kept under an atmosphere of N_2, thionyl chloride was slowly added to the flask, and the new mixture was allowed to reflux for 2-3 h. The excess CH_2Cl_2 and thionyl chloride was removed by roto-evaporation, and the acyl chloride was used in the subsequent step without further purification.

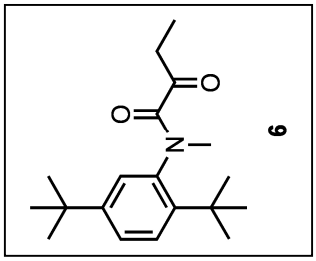
In a clean RB-flask, aniline **3** (3.35 g) initially prepared from reported procedure (*refer to procedure* 3.1) was dissolved in 20 mL of toluene. *Anhydrous* K_2CO_3 (1.5 equi.) of was added to the solution. The new mixture was vigorously stirred and kept under N_2 atmosphere. Acyl chloride (prepared as detailed above) was slowly added to the aniline reaction flask. The new mixture was allowed to reflux overnight (~12 h). The expected oxoamide **6** was isolated from the reaction mixture and was purified by chromatography using CombiFlash®.

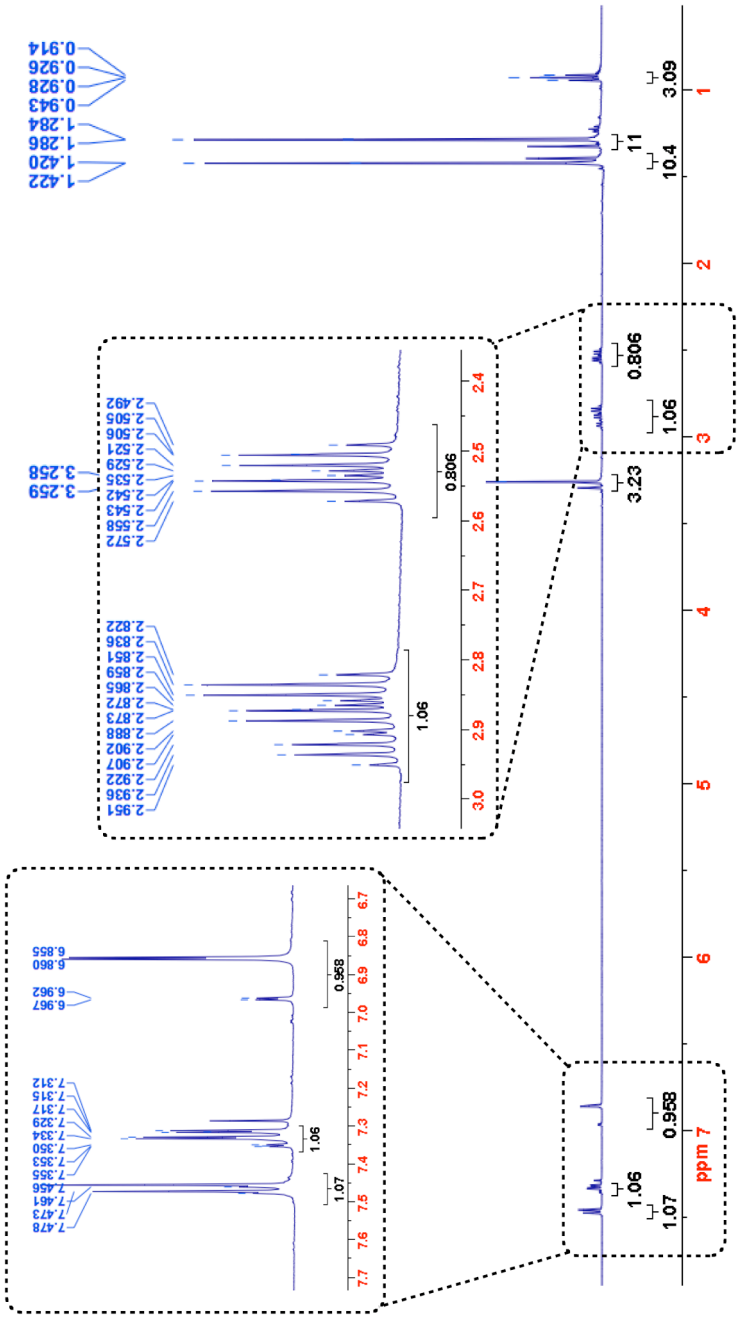
Purification Conditions:

(CombiFlash®) 24 g silica, flow rate: 25 mL/min. Solvent system: 16 % EtOAc – Hexanes. The overall yield: ~ 95 %.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm)

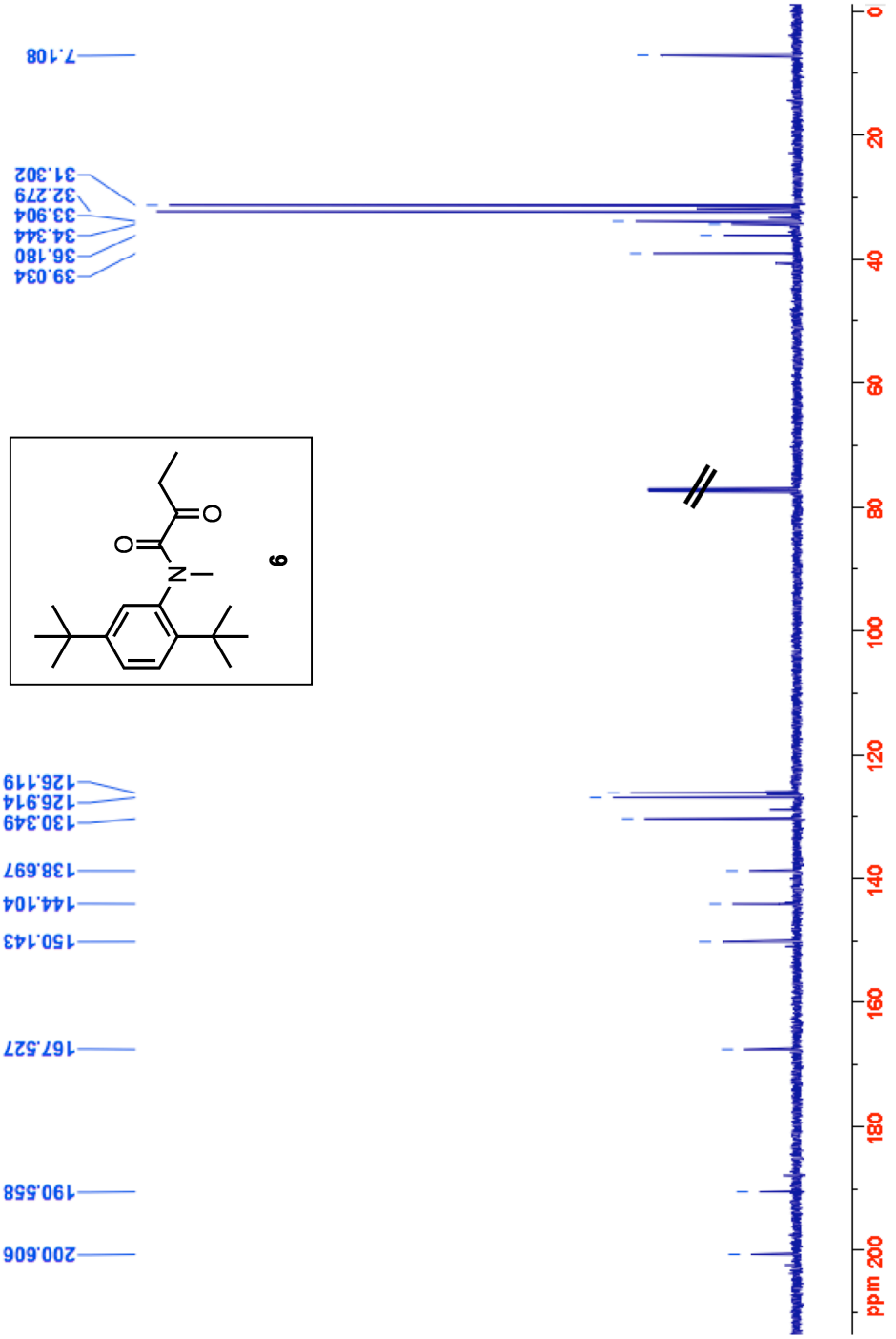
0.92 & 1.27 (t, *J* = 6 Hz, 3H, major and minor conformers), 1.28 & 1.29 (s, 9 H, major and minor conformers), 1.41 & 1.43 (s, 9 H, major and minor conformers), 2.48 – 2.58 (m, 1H, major and minor conformers), 2.82 – 2.97 (m, 1H, major and minor conformers), 3.25 & 3.26 (s, 3 H, major and minor conformers), 6.85 – 7.5 (Ar, 3H, major and minor conformers).



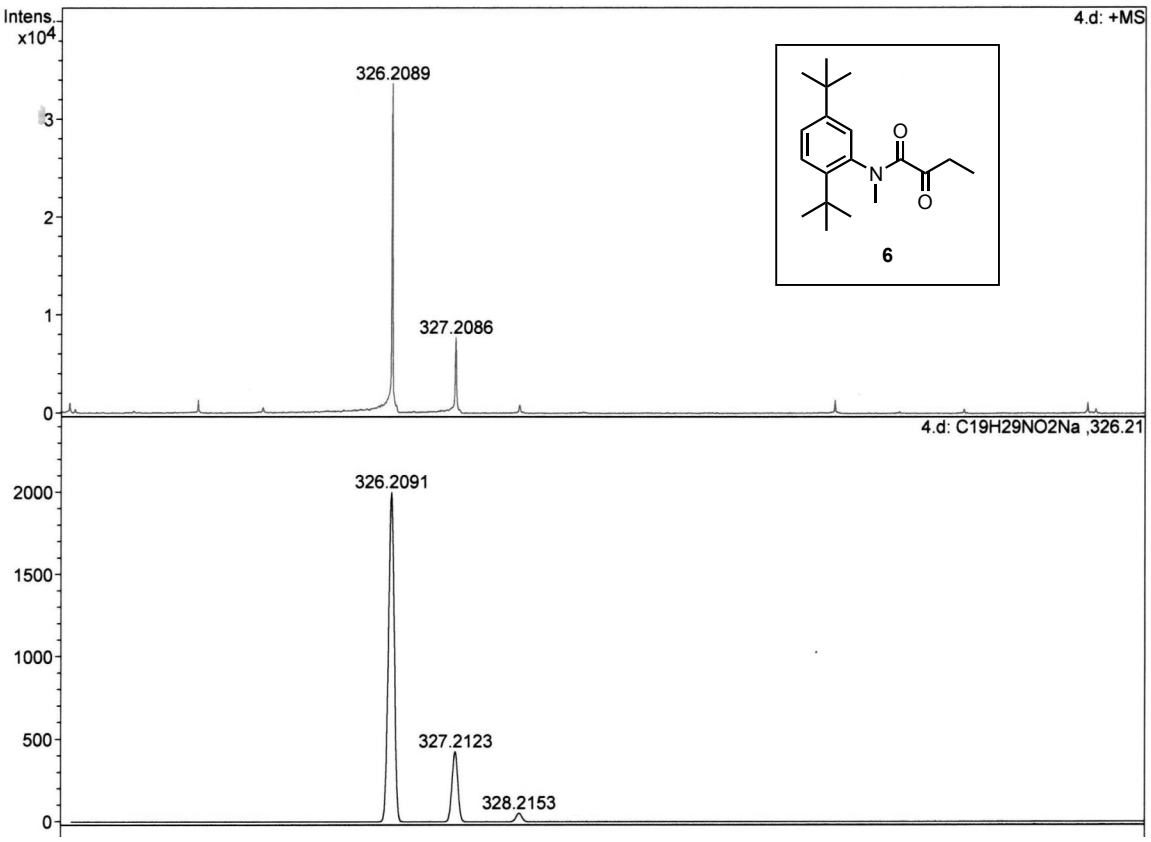


^{13}C NMR (125 MHz, $CDCl_3$, δ ppm)

δ for both *s-cis* and *s-trans* conformers (major and minor conformers) are observed for all carbon atoms.



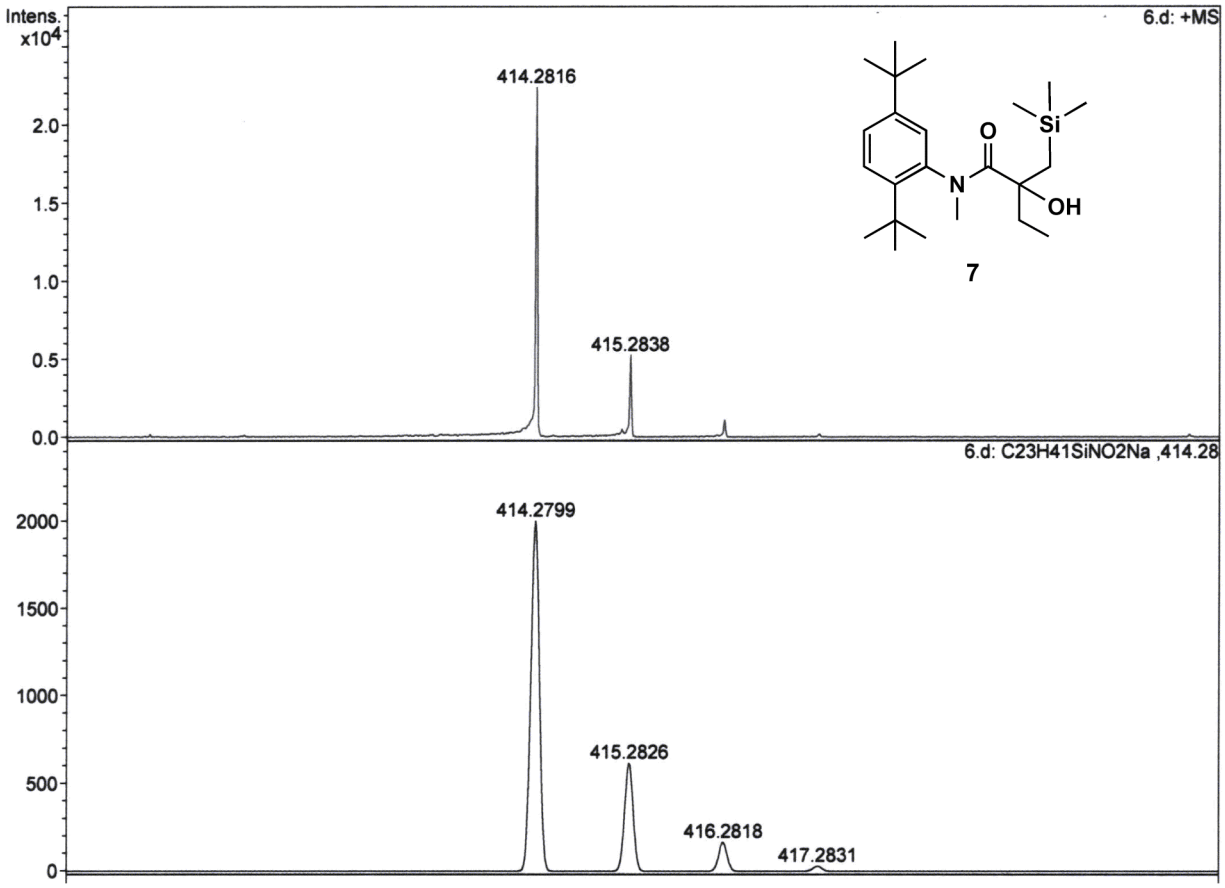
***ESI-MS* ([M + Na]$^+$):** Calculated: 326.2091; Observed: 326.2089; ΔM = 0.88 ppm.



3.3 Synthesis of silanol **7**.

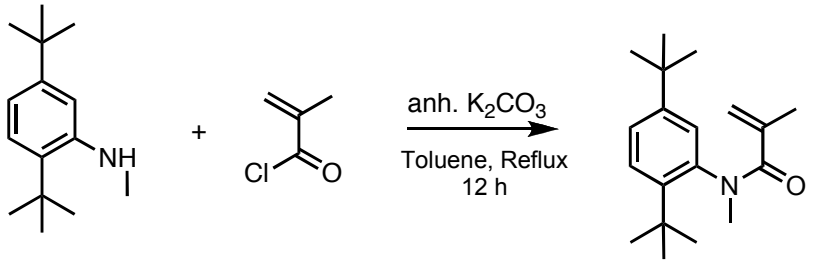
Silanol **7** was prepared according to a procedure reported in literature.[3] Oxoamide **6** in a minimum of dry THF was cooled to -78 ^{o}C; the solution was stirred for another 20 min at -78 ^{o}C and Me_3SiCH_2MgCl (5 equi.) was added to the reaction flask at -78 ^{o}C. The new mixture was stirred for 30 min at -78 ^{o}C, then for 12 h at RT, and finally for 2 h at 65 ^{o}C. The expected silanol **7** was not isolated, but a mass spectrometry analysis of an aliquot of the reaction mixture after the starting oxoamide **6** was completely consumed showed a major molecular ion peak at 414.2816 ($M + Na^+$) indicating the formation of intermediate **7**.

ESI-MS **([M + Na]$^+$):** Calculated: 414.2799; Observed: 414.2816; ΔM = 4 ppm



4. Procedure for synthesis and characterization of acrylanilides **1a-d**.

4.1 Synthesis of **1a**.



3 **1a**

Scheme S3: Synthesis of acrylanilide **1a**.

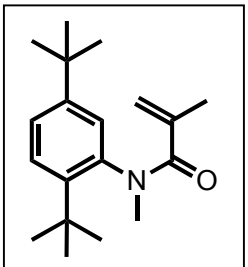
Acrylanilide **1a** was prepared using procedures reported in literature.[1,2,4,5] In a typical reaction, freshly synthesized aniline **3** (1 equi.) was dissolved in 20 mL of toluene. The aniline solution was then stirred and purged with N_2; *anhydrous* K_2CO_3 (1.5 equi.) and methacryloyl chloride (1.5 equi.) were respectively and slowly added to the solution with continuous stirring. The new solution was allowed to reflux (100 ^oC) overnight (~12 h). The reaction was quenched with 10 – 20 mL of water followed by extraction of the organic layer with EtOAc (3 x 20 mL). The organic layer was then dried over anhydrous Na_2SO_4 and concentrated by roto-evaporation. The expected amide were finally purified by chromatography (using CombiFlash®).

Purification Conditions:

(CombiFlash®) 24 g silica

Solvent system: 15 % EtOAc:Hexanes

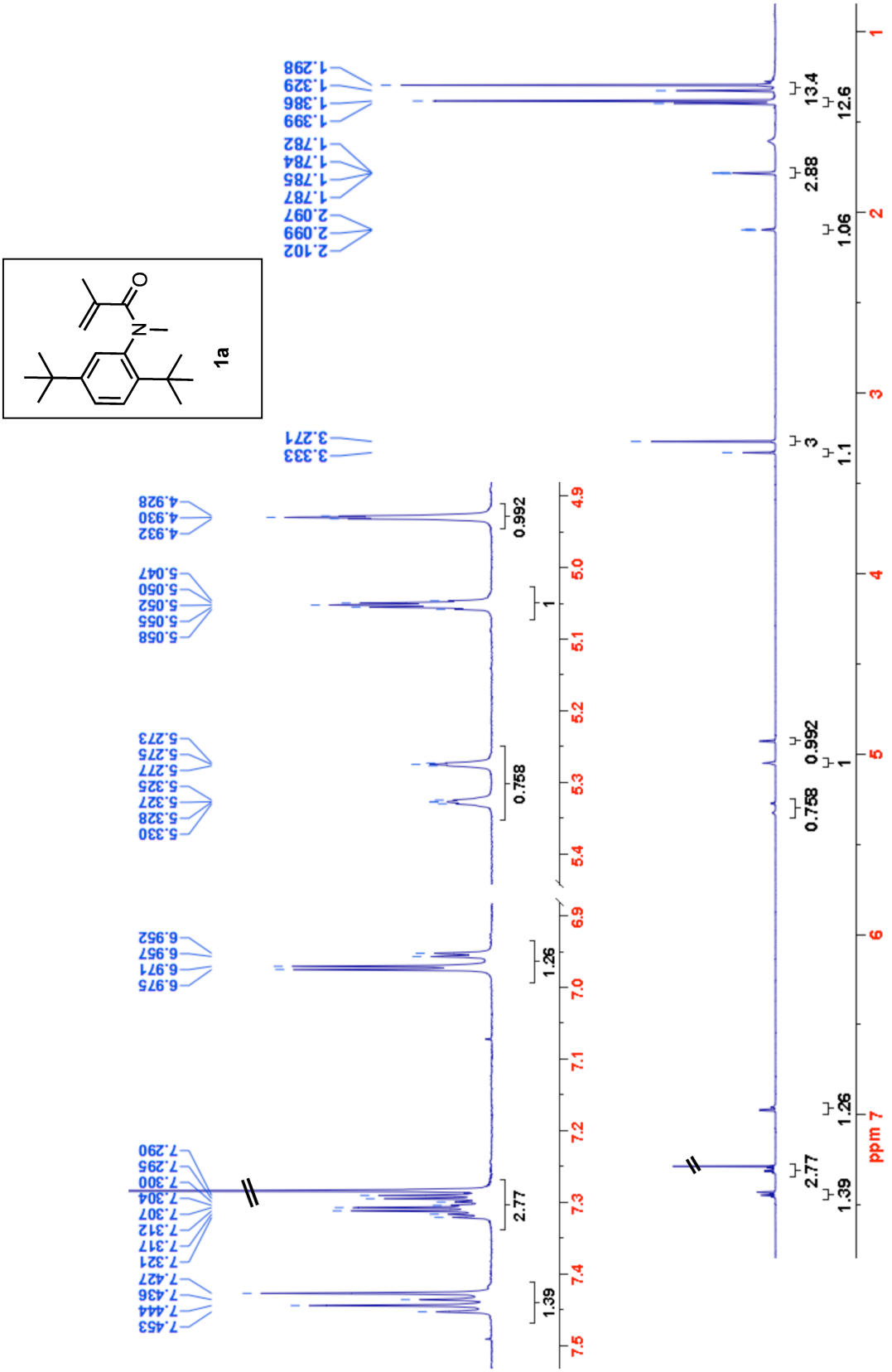
Flow rate: 22 mL/min



1a

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm)

1.29 & 1.33 (s, 9H, minor and major conformers), 1.39 & 1.4 (s, 9H, minor and major conformers), 1.78 & 2.1 (s, 3H, major and minor conformers), 3.27 & 3.33 (s, 3H, major and minor conformers), 4.92 – 5.06 & 5.27 – 5.33 (m, 2H, major and minor conformers, olefinic hydrogens), 6.94 - 7.46 (Ar, 3H, major and minor conformers).


1a
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1.329
1.386
1.399
1.782
1.784
1.785
1.787
2.097
2.099
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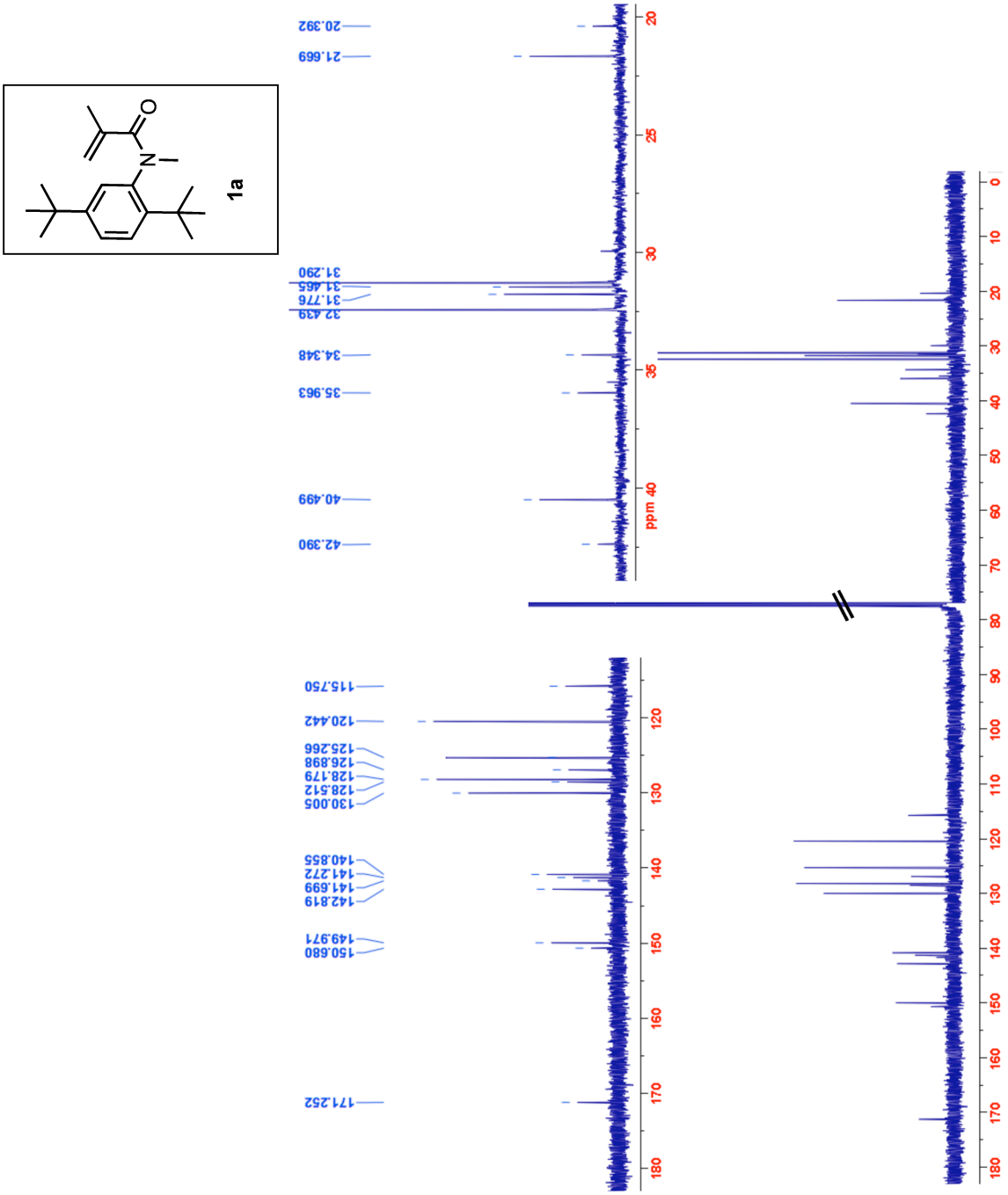
3.271
3.333
4.928
4.930
4.932
5.047
5.050
5.052
5.055
5.058
5.273
5.275
5.277
5.325
5.327
5.328
5.330
6.952
6.957
6.971
6.975
7.290
7.295
7.300
7.304
7.307
7.312
7.317
7.321
7.427
7.436
7.444
7.453
0.992
1
0.758
1.26
2.77
1.39
13.4
12.6
2.88
1.06
3
1.1
0.992
1
0.758
1.26
2.77
1.39
ppm 7

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm)

δ for both *s-cis* and *s-trans* conformers (major and minor conformers) are observed for all carbon atoms.



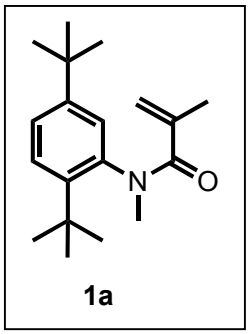
CD Spectroscopy

Optically pure isomers of **1a** were separated by HPLC and dissolved in spectrophotometric grade methylcyclohexane.

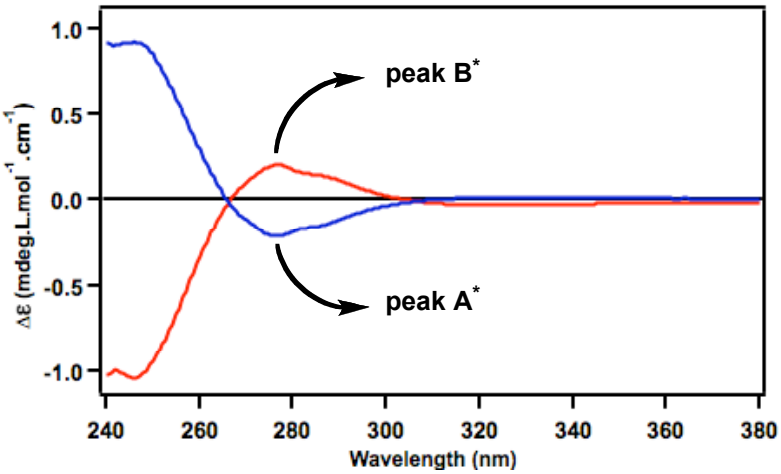
c_A = 1.25 mM

c_B = 1.04 mM

Path length = 1 cm



1a



***** *peak A and B refers to the first and second peak respectively that elute from the HPLC chiral stationary phase analysis/separation.*

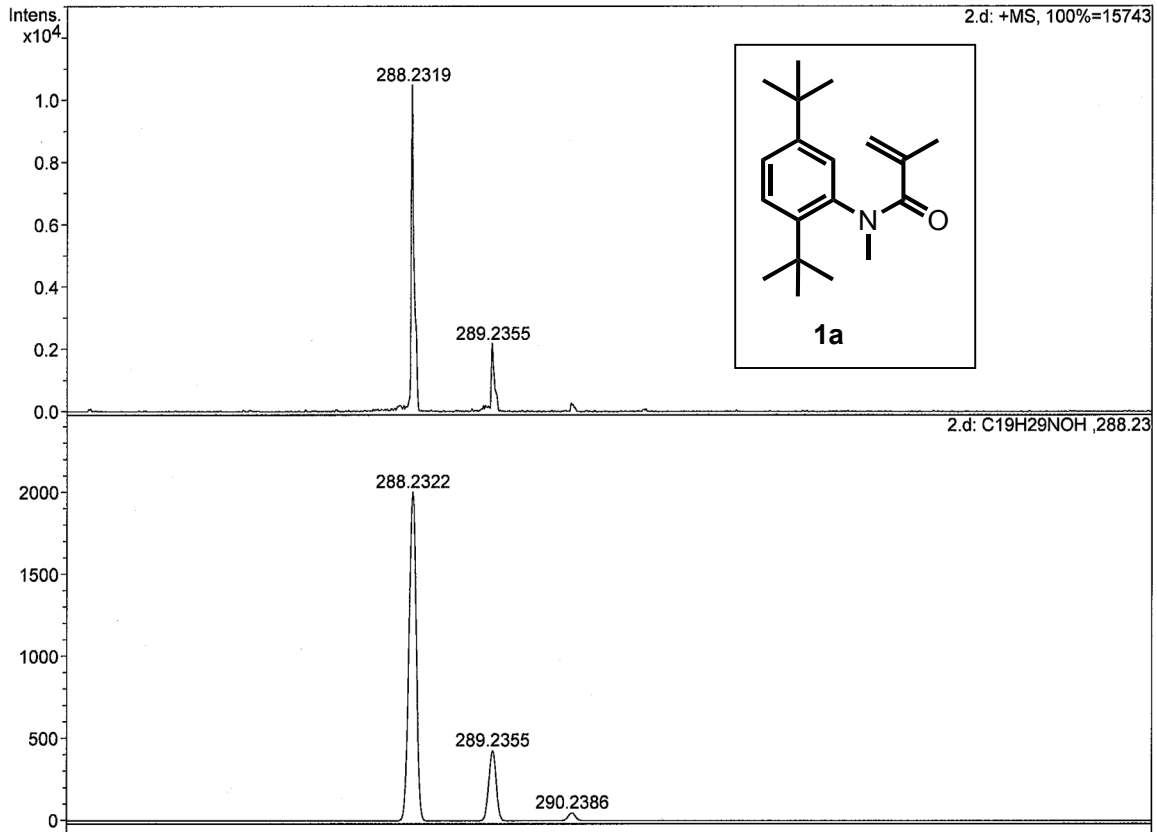
Note: (-) and (+) are assigned based on the sign of CD spectra at 285 nm to the optically pure isomers peak A and peak B that elute from the HPLC chiral stationary phase analysis/separation. In the present case (with **1a**), peak A was assigned as the (-) isomer and peak B was assigned as the (+) isomer based on their CD spectra.

Optical Rotation $[\alpha]_D^{25}$

Peak A (**1a**) = - 29.05 (c = 0.210 %, $CHCl_3$),

Peak B: (**1a**) = + 25.35 (c = 0.213 %, $CHCl_3$)

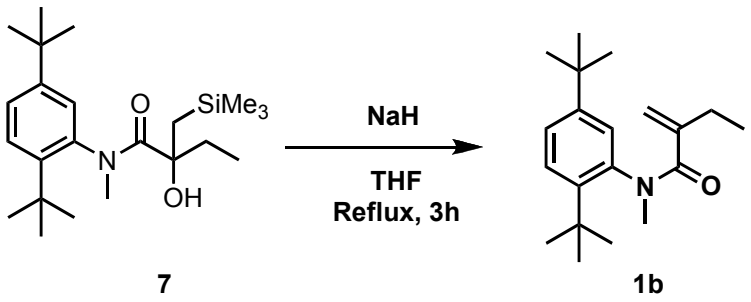
***ESI-MS* ([M + H]$^+$):** Calculated: 288.2322; Observed: 288.2319; ΔM = 1 ppm.



HPLC analysis conditions:

Column: (R,R) WHELK–O1; Abs. detector: 254 nm and 270 nm
Mobile phase: Hexanes:IPA = 98:2; Flow rate: 1 mL/min
Retention time (min): **Peak A:** ~ 47.50
Peak B: ~ 53.75

4.2 Synthesis of Acrylanilide **1b**.



7 **1b**

Scheme S4: Synthesis of acrylanilide **1b**.

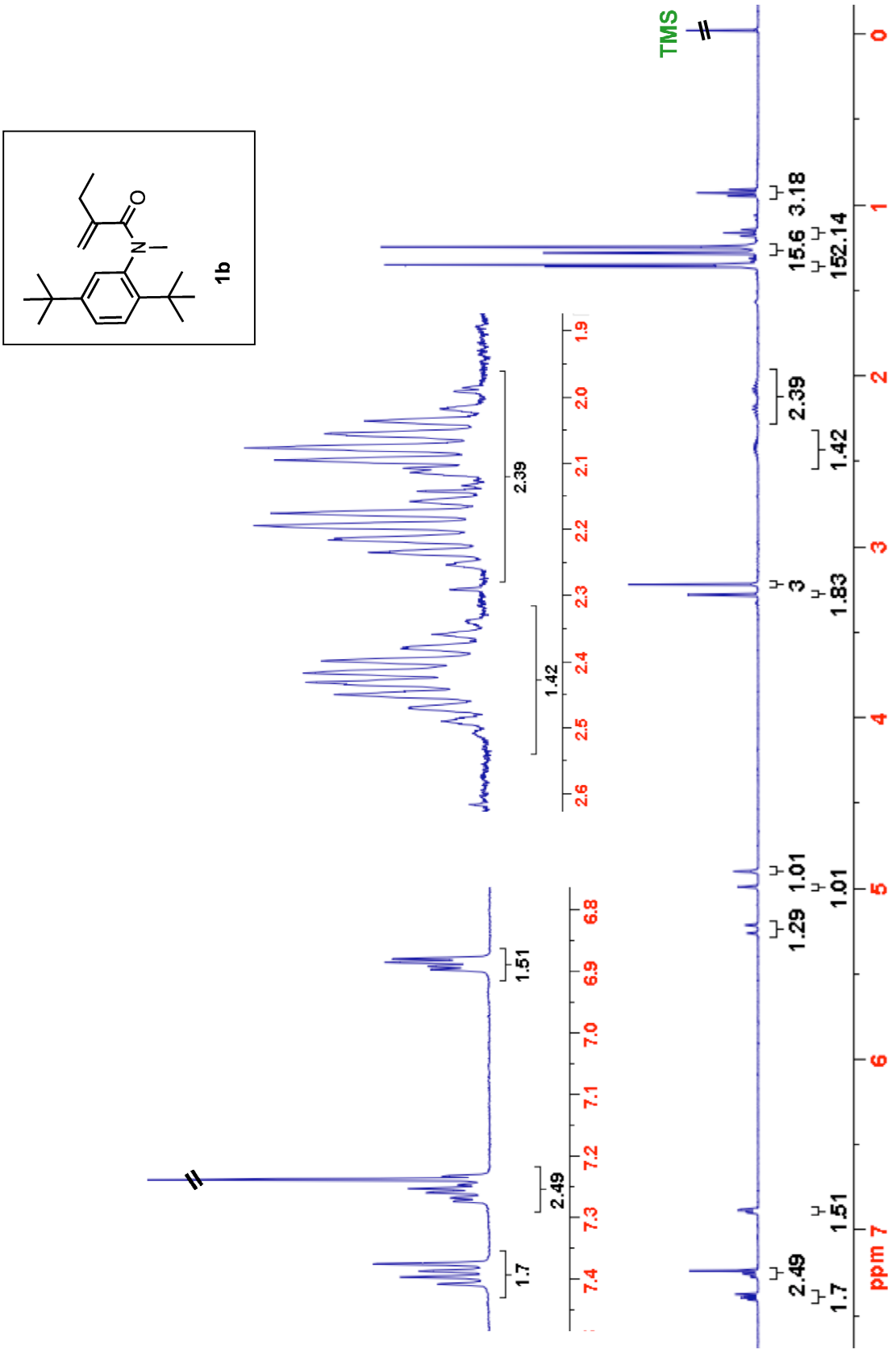
Silanol **7** was dissolved in a minimum (~ 20 mL) of THF and NaH (excess) was added to the solution. The new mixture was constantly stirred and allowed to reflux for 3 h. After, the reaction mixture was slowly quenched with DI water (while the flask was immersed into an ice bath). The insoluble by-products were filtered off on celite. The recovered filtrate was washed with DI water, and the expected crude **1b** was extracted with EtOAc (3 x 20 mL). The combined organic fractions were concentrated and purified by CombiFlash®.

Purification Conditions:

Silica gel (24 g) at 18 % EtOAc – Hexanes with a flow rate of 25 mL/min.

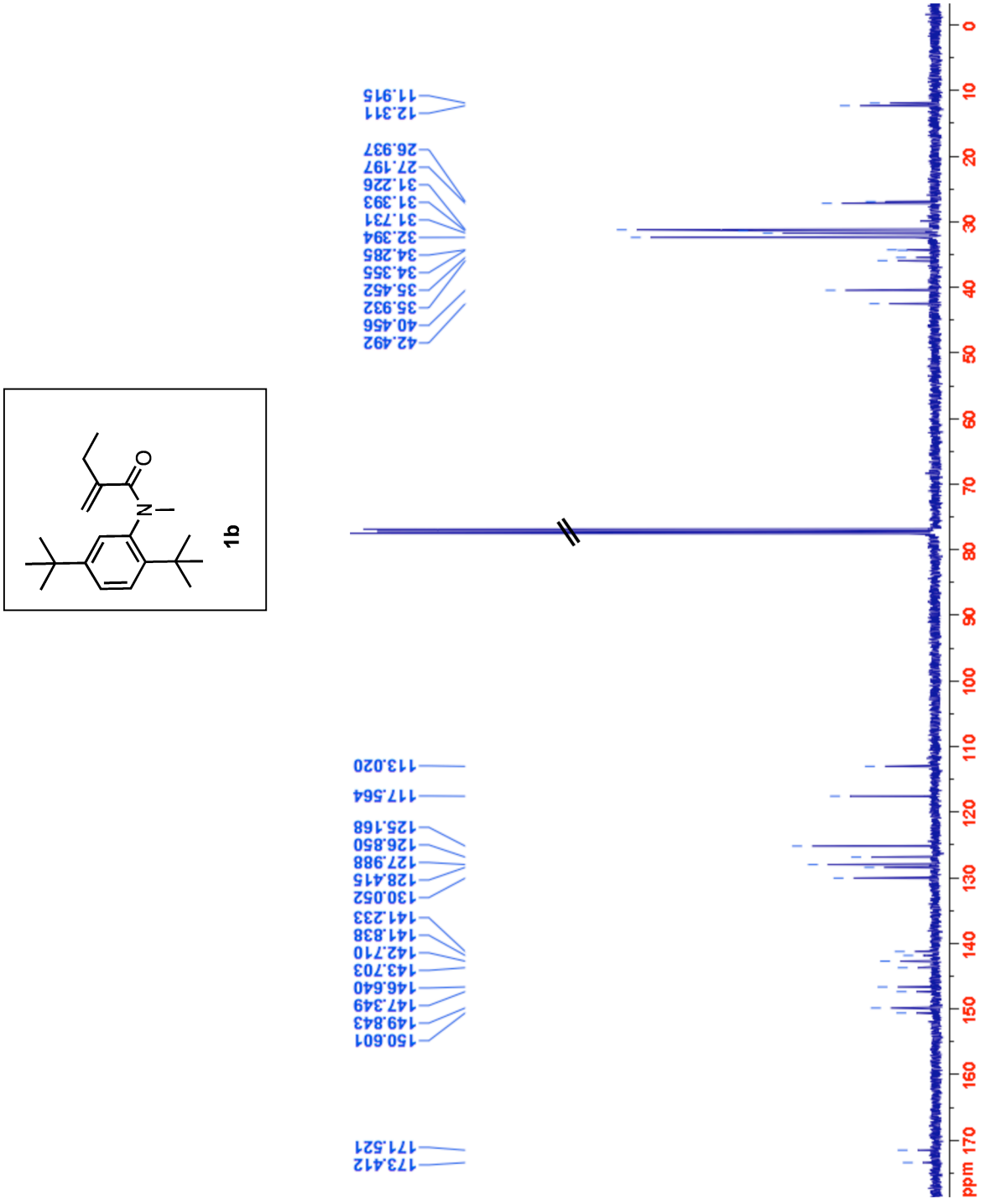
^{1}H NMR, 400 MHz, $CDCl_3$, δ ppm

0.93 & 1.16 (t, J = 7.2 Hz, 3H, major and minor conformers, α-CH_2-CH_3) 1.24 & 1.27 (s, 9H, minor and major conformers, ^{t}Bu), 1.34 & 1.35(s, 9H, minor and major conformers, ^{t}Bu), 1.96 - 2.28 & 2.32 – 2.54 (m, 2H, major and minor conformers, α-CH_2), 3.22 & 3.28 (s, 3H, major and minor conformers, N-CH_3), 4.85 – 5.05 & 5.15 – 5.3 (2H, major and minor conformers, olefinic H), 6.86 – 7.43 (Ar, 3H, contribution from major and minor conformers).


1b
TMS
ppm

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm)

δ for both *s-cis* and *s-trans* conformers (major and minor conformers) are observed for all carbon atoms.



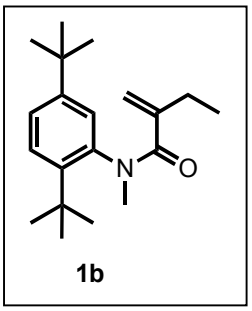
CD Spectrometry:

Optically pure isomers of **1b** were separated by HPLC and dissolved in spectrophotometric grade methylcyclohexane.

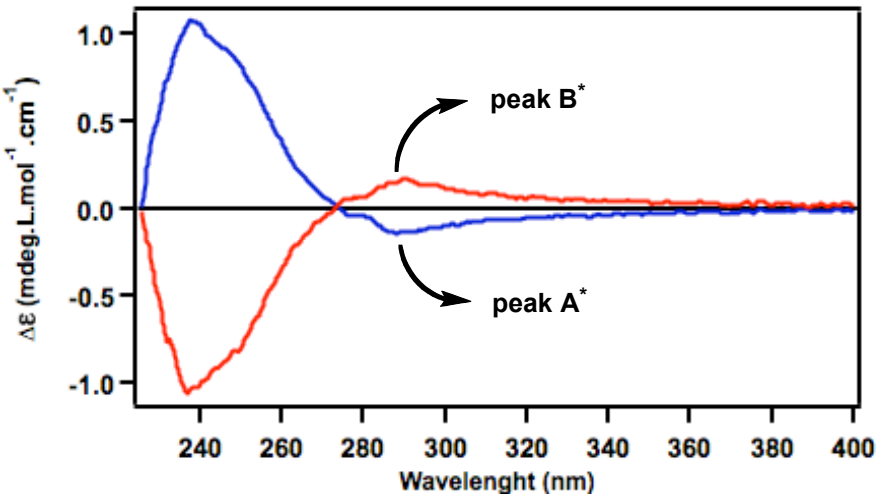
c_A = 4.64 x 10^{-4} M.

c_B = 5.97 x 10^{-4} M.

Path length = 1 cm



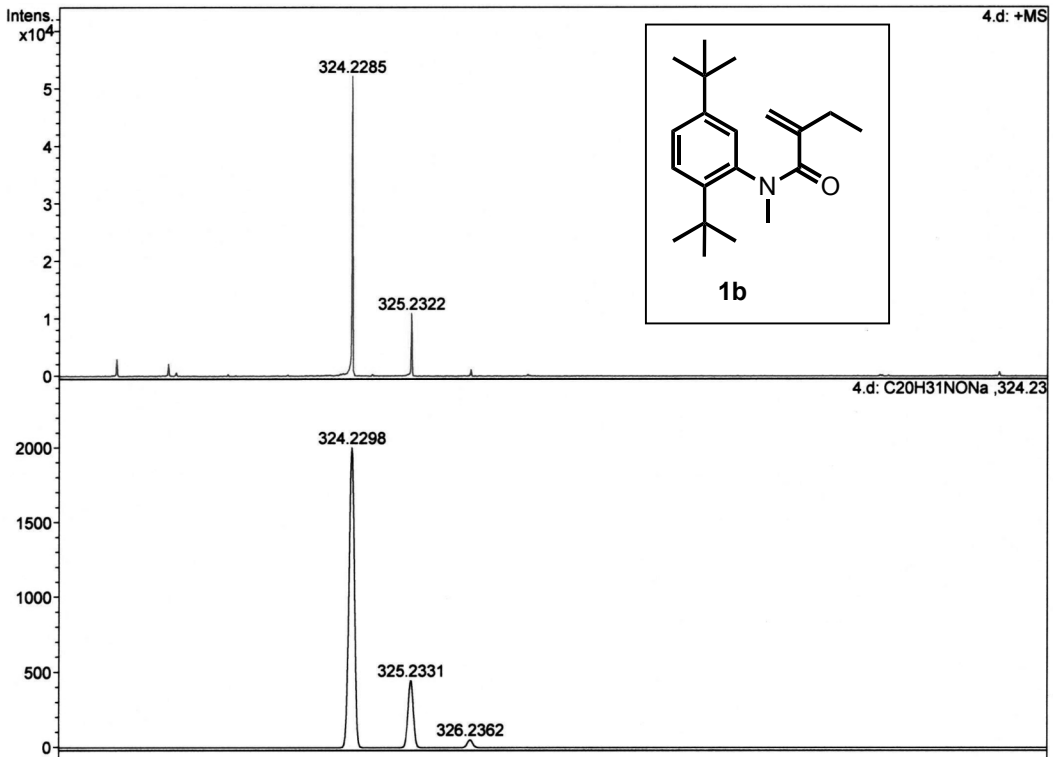
1b



** peak A and B refers to the first and second peak respectively that elute from the HPLC chiral stationary phase analysis/separation.*

Note: (-) and (+) are assigned based on the sign of CD spectra at 285 nm to the optically pure isomers peak A and peak B that elute from the HPLC chiral stationary phase analysis/separation. In the present case (with **1b**), peak A was assigned as the (-) isomer and peak B was assigned as the (+) isomer based on their CD spectra.

***ESI-MS* ([M + Na]$^+$):** Calculated: 324.2298; Observed: 324.2285; ΔM = 4 ppm.



HPLC analysis conditions:

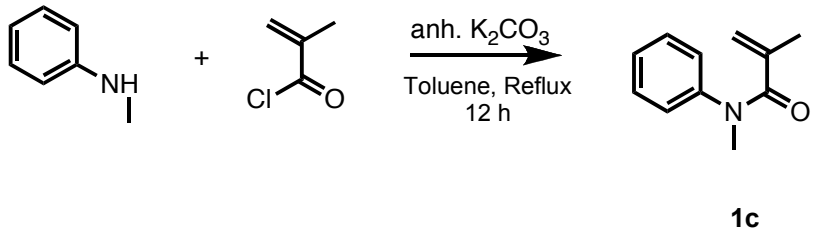
Column: (R,R) WHELK–O1; Abs. detector: 254 nm and 270 nm

Mobile phase: Hexanes:IPA = 98:2; Flow rate: 1 mL/min

Retention time (min): **Peak A:** ~ 36.75

Peak B: ~ 45.47

4.3 Synthesis of **1c**.



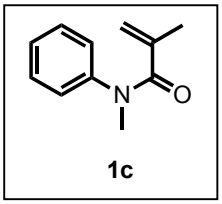
1c

Scheme S5: Synthesis of acrylanilide **1c**.

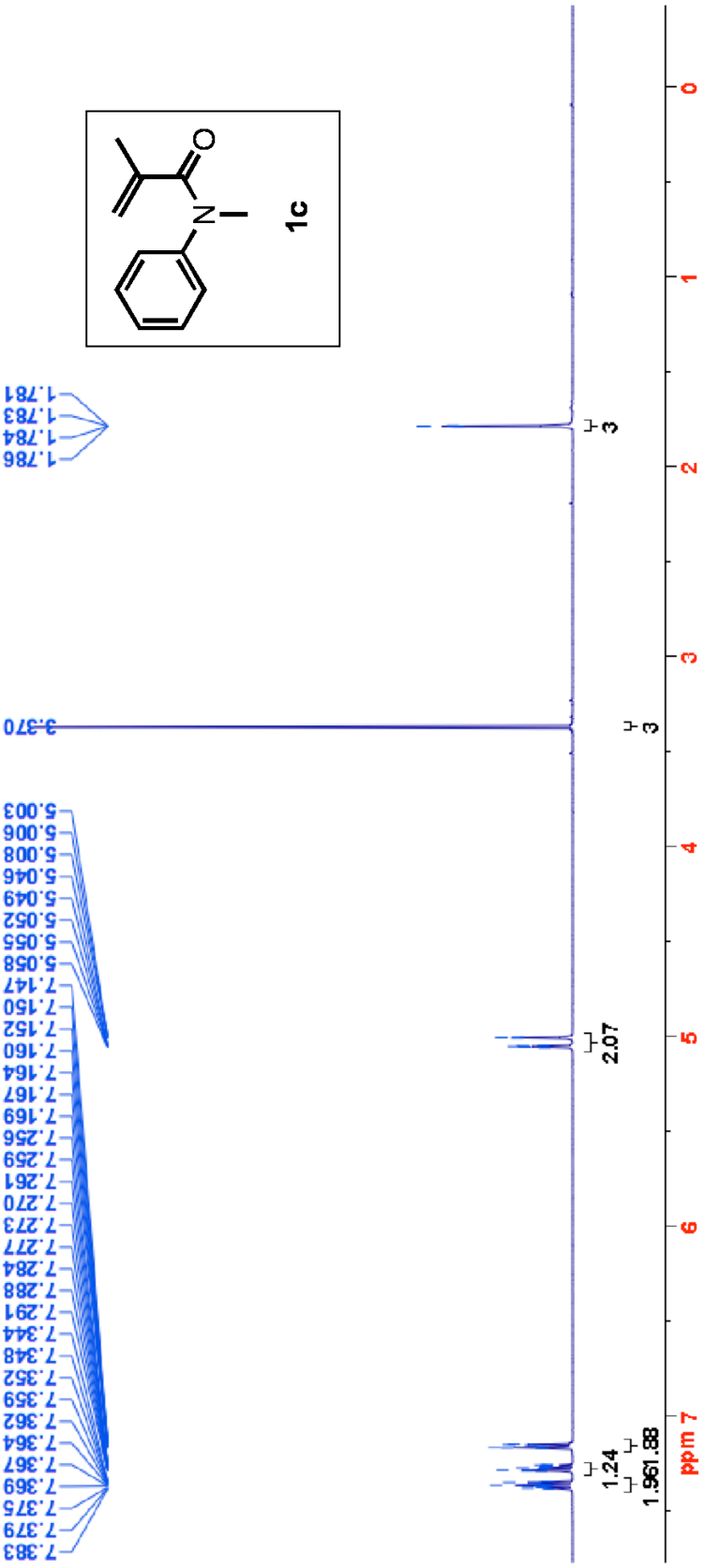
Note: Procedure as detailed in section 4.1 was followed for the synthesis of **1c**. (Yield: 99 %); No further purification was required. **1c** upon standing formed white needle like crystals at room temperature.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm)

1.78 (s, 3H), 3.37 (s, 3H), 5.00 – 5.06 (2H, olefinic H), 7.14 – 7.38 (Ar, 5H)

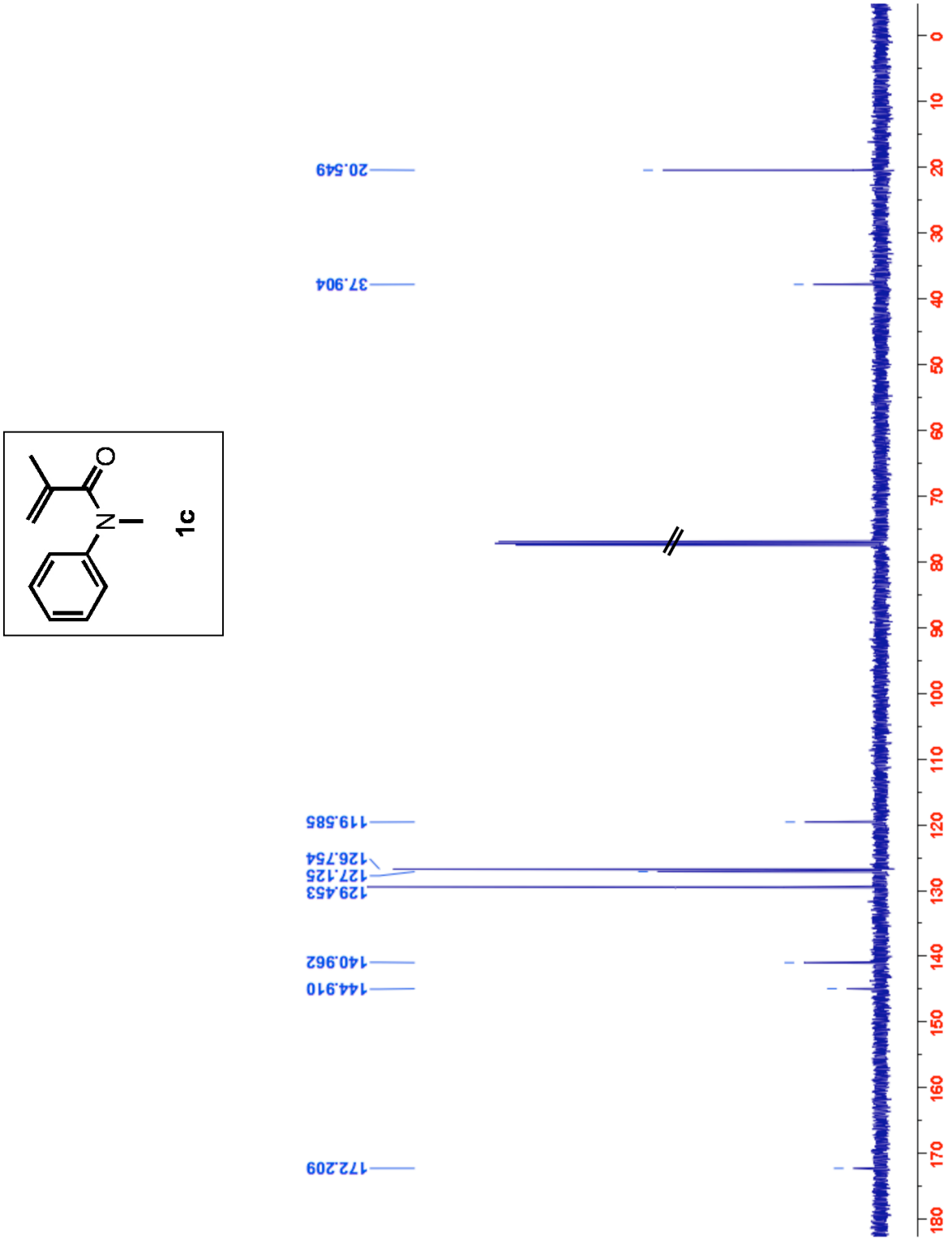


1c

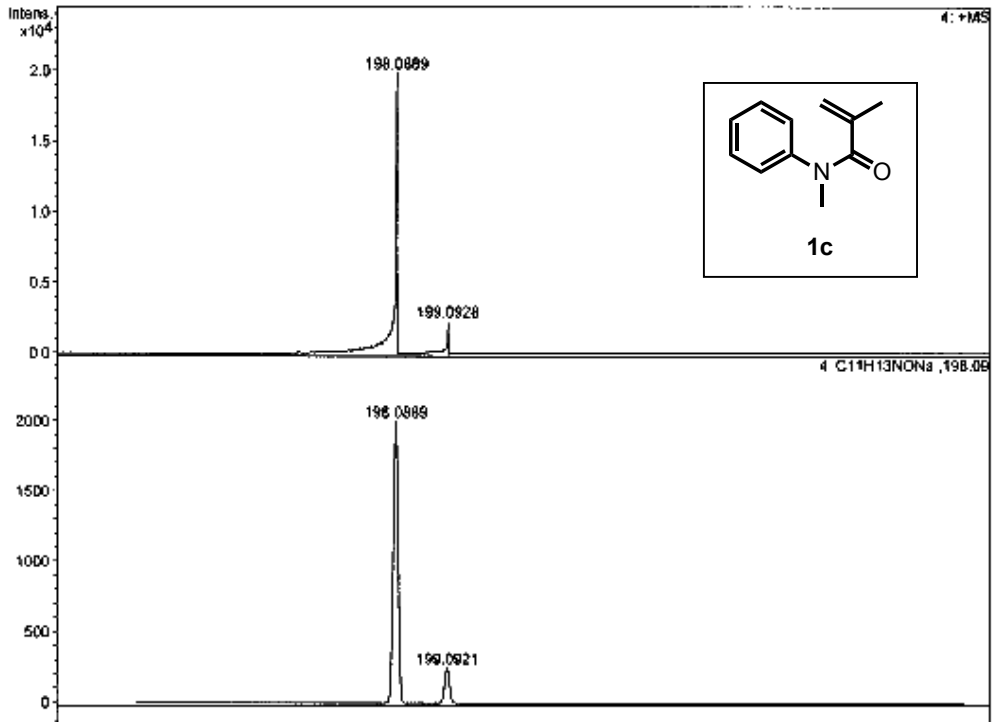

1c
1.781
1.783
1.784
1.786
3.370
5.003
5.006
5.008
5.046
5.049
5.052
5.055
5.058
7.147
7.150
7.152
7.160
7.164
7.167
7.169
7.256
7.259
7.261
7.270
7.273
7.277
7.284
7.288
7.291
7.344
7.348
7.352
7.359
7.362
7.364
7.367
7.369
7.375
7.379
7.383
3
3
2.07
1.24
1.96
1.88
0
1
2
3
4
5
6
ppm 7

^{13}C NMR (125 MHz, $CDCl_3$, δ ppm)

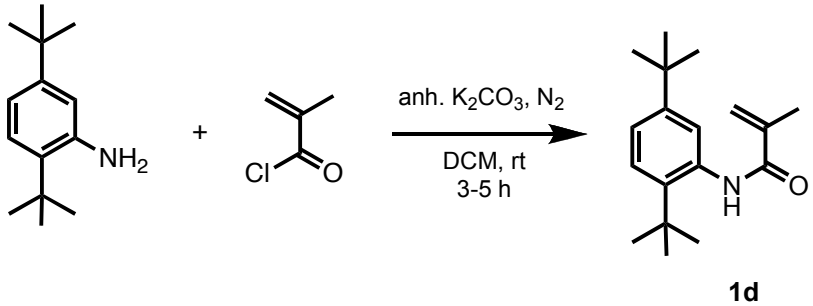
δ 20.55, 37.90, 119.58, 126.75, 127.12, 129.45, 140.96, 144.91, 172.21.



***ESI-MS* ([M + Na]$^+$):** Calculated: 198.0889; Observed: 198.0889; ΔM = 0 ppm.



4.4 Synthesis of **1d**.

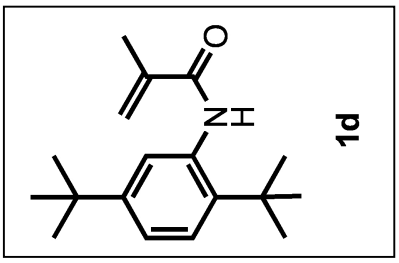


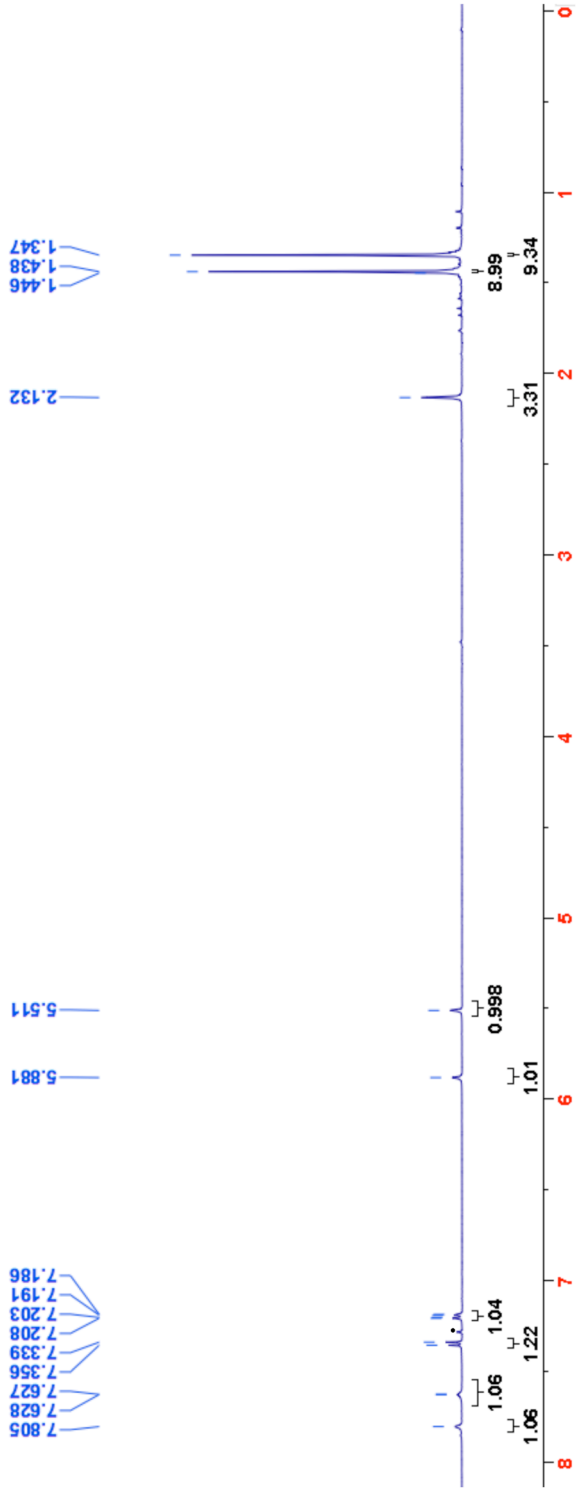
Scheme S6: Synthesis of acrylanilide **1d**.

Note: Procedure as detailed in section 4.1 was followed for the synthesis of **1d**. The reaction was performed at ambient temperature in CH_2Cl_2 for 3-5 h. The reaction was quenched with DI water, and the crude expected product **1d** was extracted from the aqueous fraction with chloroform (3 x 20 mL). The organic fraction was concentrated by roto-evaporation; and **1d** was purified by recrystallization in *n*-pentane.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm)

1.35 (s, 9H), 1.44 (s, 9H), 2.13 (s, 3H), 5.51 (s, 1H), 5.88 (s, 1H), 7.18 – 7.21 (dd, 1H), 7.33 – 7.36 (d, 1H), 7.62 – 7.63 (b s, N-H), 7.80 (s, 1H).

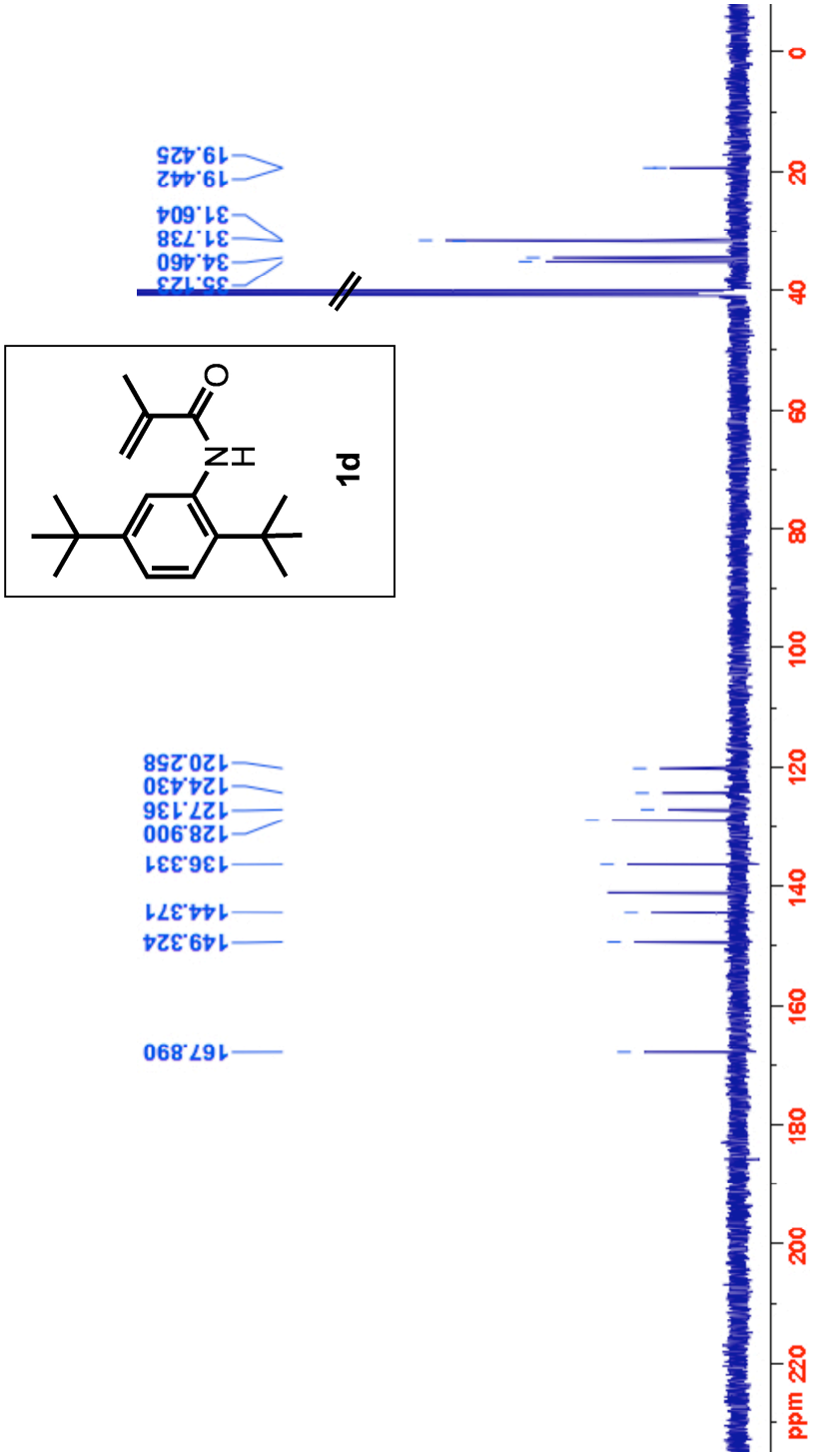




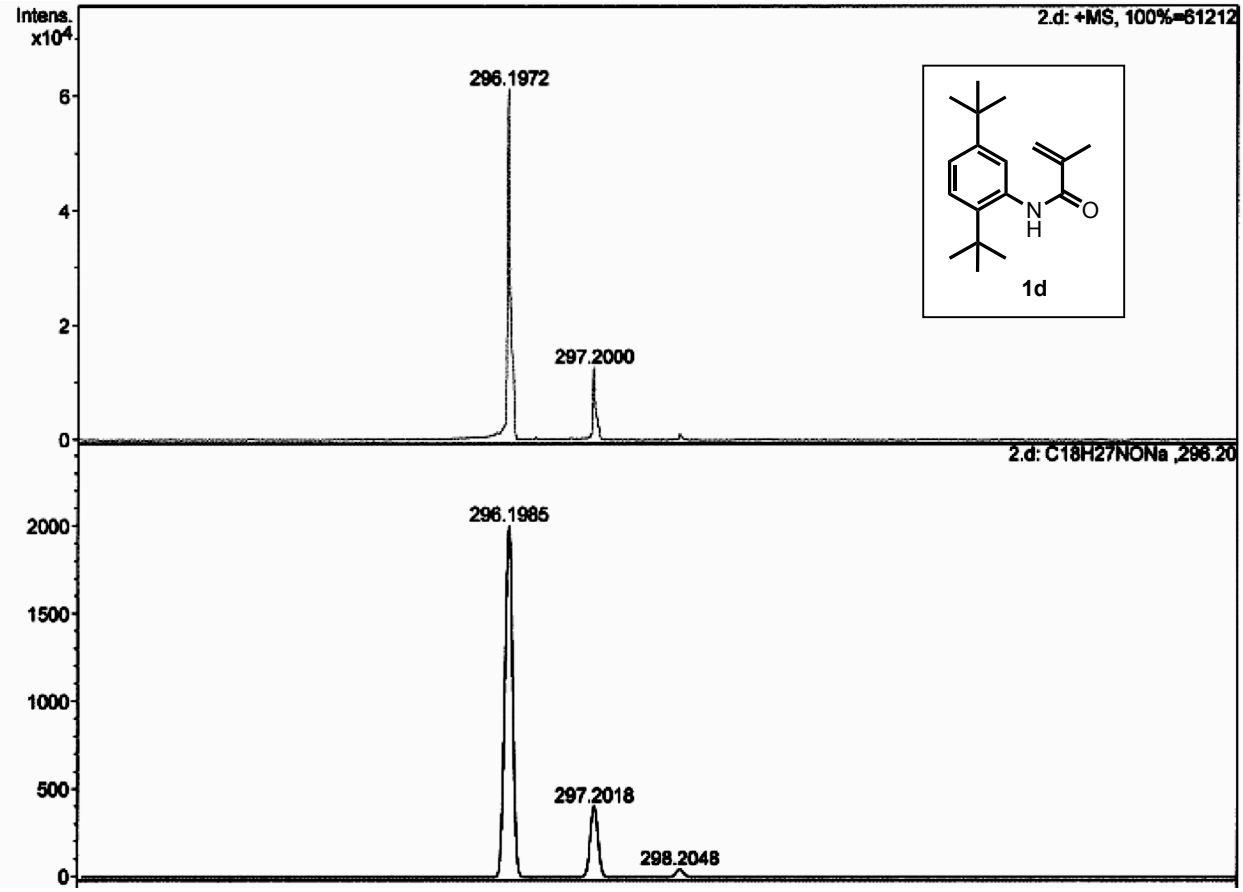
(*=Solvent)

^{13}C NMR [125 MHz, DMSO (Temp. = 45 ^{o}C), δ ppm]

δ 19.42, 19.44, 31.60, 31.73, 34.46, 35.12, 120.25, 124.43, 127.13, 128.90, 136.33, 144.37, 149.32, 167.89. (Note: To observe the amide carbonyl resonance, the solvent was changed from $CDCl_3$ to DMSO-d_6 and the NMR was recorded at 45 ^{o}C).



***ESI-MS* ([M + Na]$^+$):** Calculated: 296.1985; Observed: 296.1972; ΔM = 4.3 ppm.

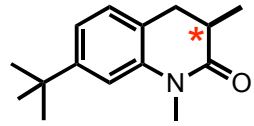


5. General Irradiation procedures.

HPLC purified/optically pure samples of **1a,b** (3.5 mg/mL) in acetone or 2,2,2-trifluoroethanol (TFE) or in methanol (MeOH) in 13 mm Pyrex tube were deaerated with N_2 for 15 min and irradiated at room temperature (27±1 ^oC) or at 20 ^oC for specified time. The samples were kept under a N_2 atmosphere during the irradiation period. After irradiation, the samples were concentrated and analyzed by spectroscopy and chromatography.

5. Characterization of Photoproducts.

5.1 Photoproduct **2a** = *ent*-**2a**.



2a = *ent*-**2a**

Purification Conditions:

Compound **2a** was purified by chromatography using CombiFlash®: RediSep column: 12 g silica

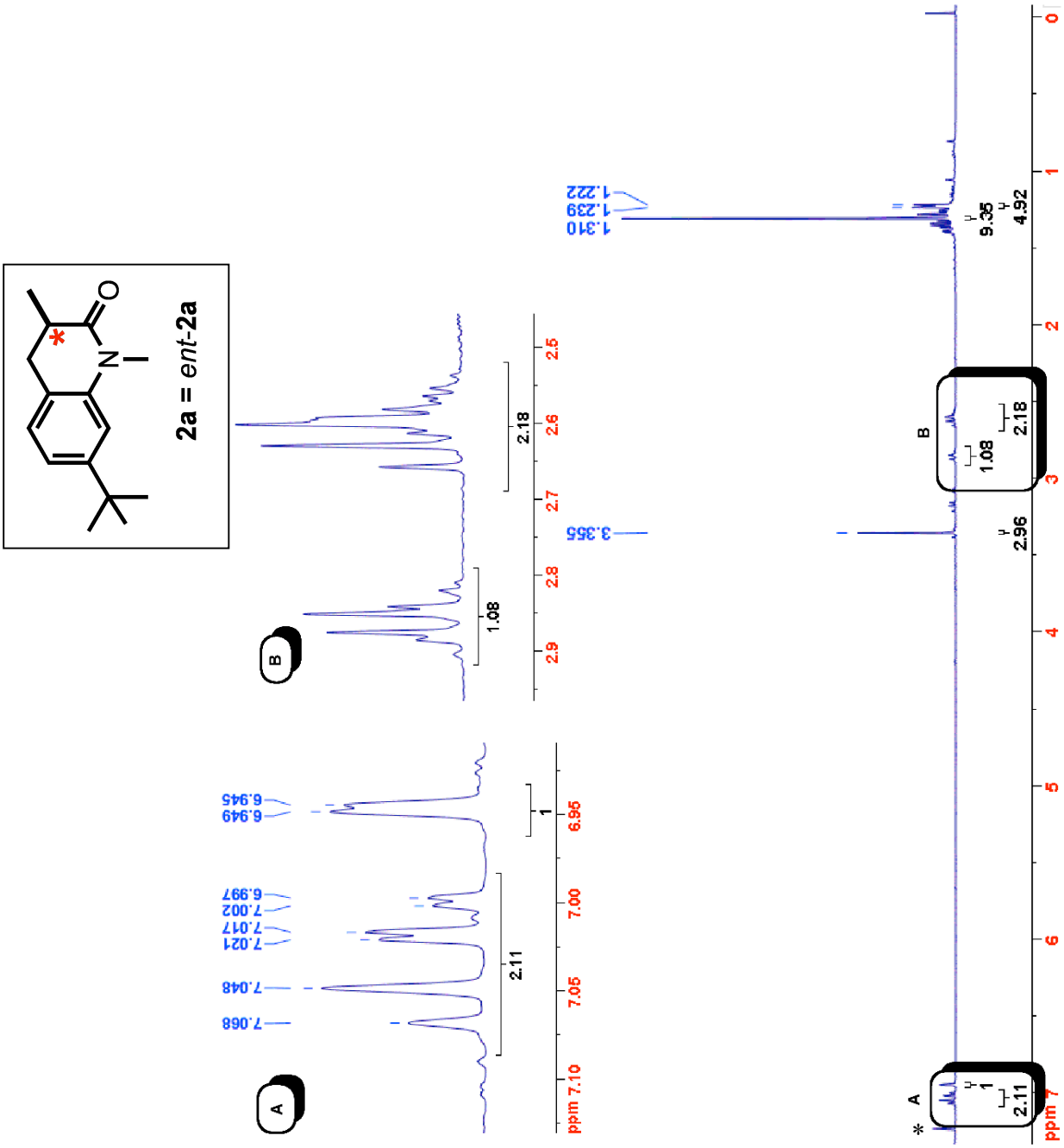
Flow rate: 21 mL/min

Equilibration volume: 50.4 mL

Solvent system: 22 % diethyl ether:*n*-pentane

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm)

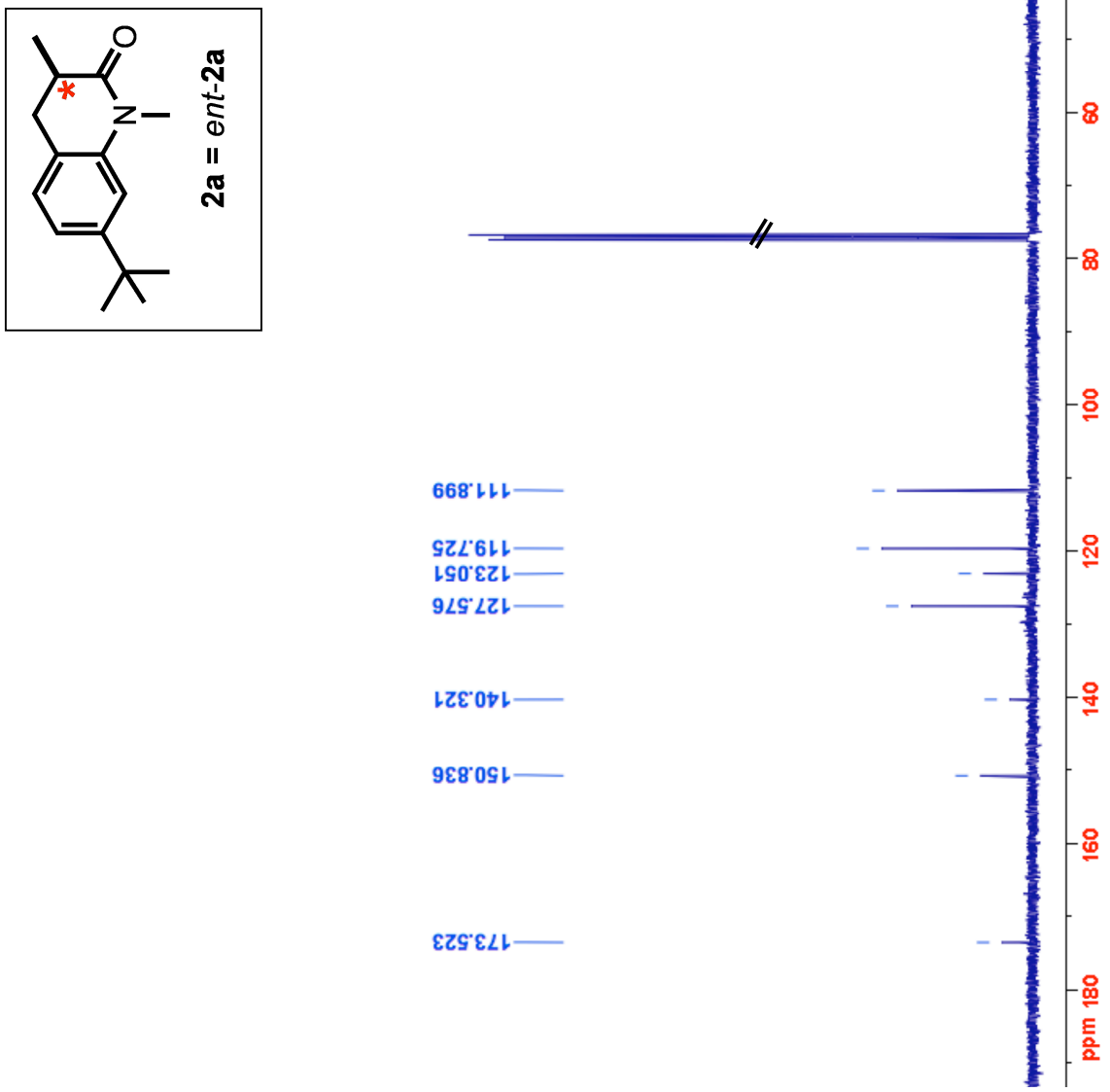
1.23 (d, *J* = 6.8 Hz, 3H), 1.31 (s, 9H), 2.5 – 2.7 (m, 2H), 2.8 – 2.93 (m, 1H), 3.36 (s, 3H), 6.94 – 7.1 (Ar, 3H).



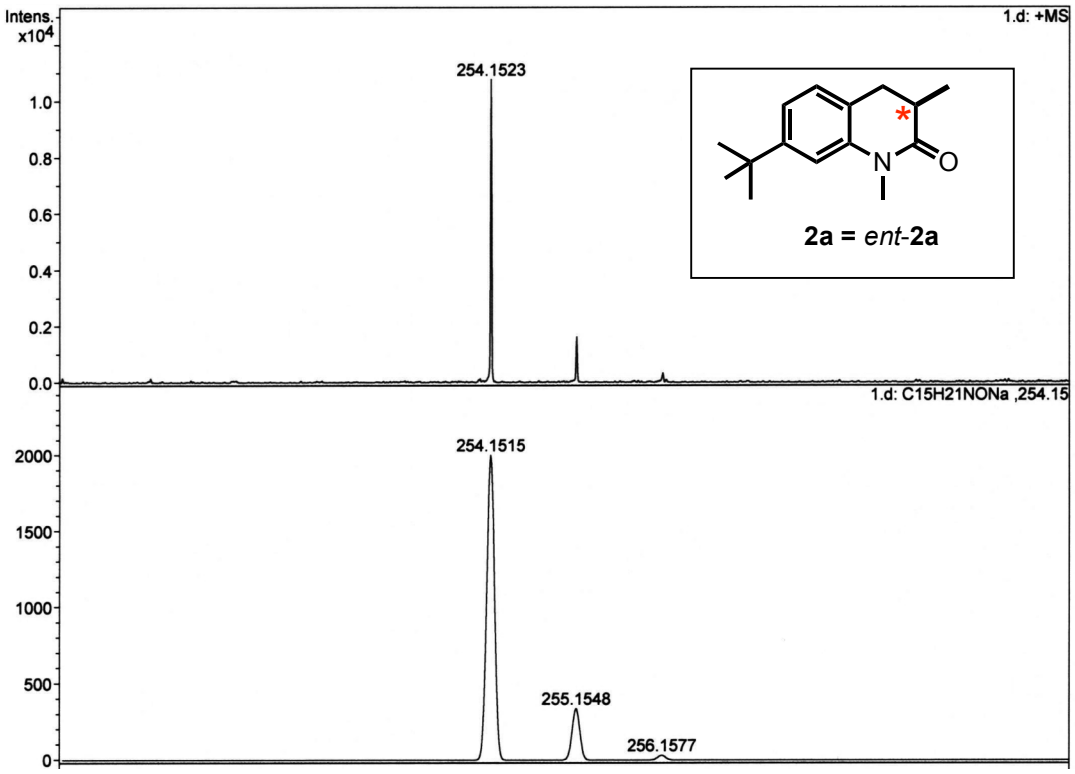
*=residual solvent peak

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm)

δ 15.94, 29.97, 31.59, 33.07, 34.97, 35.82, 111.9, 119.72, 123.05, 127.57, 140.32, 150.83, 173.52.



***ESI-MS* ([M + Na]$^+$):** Calculated: 254.1515; Observed: 254.1523; ΔM = 3 ppm.



HPLC analysis conditions:

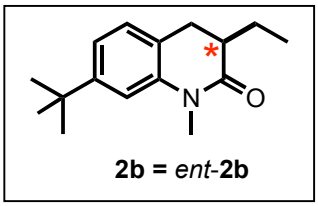
Column: (R,R) WHELK–O1; Abs. detector: 254 nm and 270 nm

Mobile phase: Hexanes:IPA = 98:2; Flow rate: 1 mL/min

Retention time (min): **2a:** ~30.70

ent-**2a:** ~32.07

5.2 Photoproduct **2b** = *ent*-**2b**.



2b = *ent*-**2b**

Purification Conditions:

Compound **2b** was purified by chromatography using CombiFlash®: RediSep column: 12 g silica

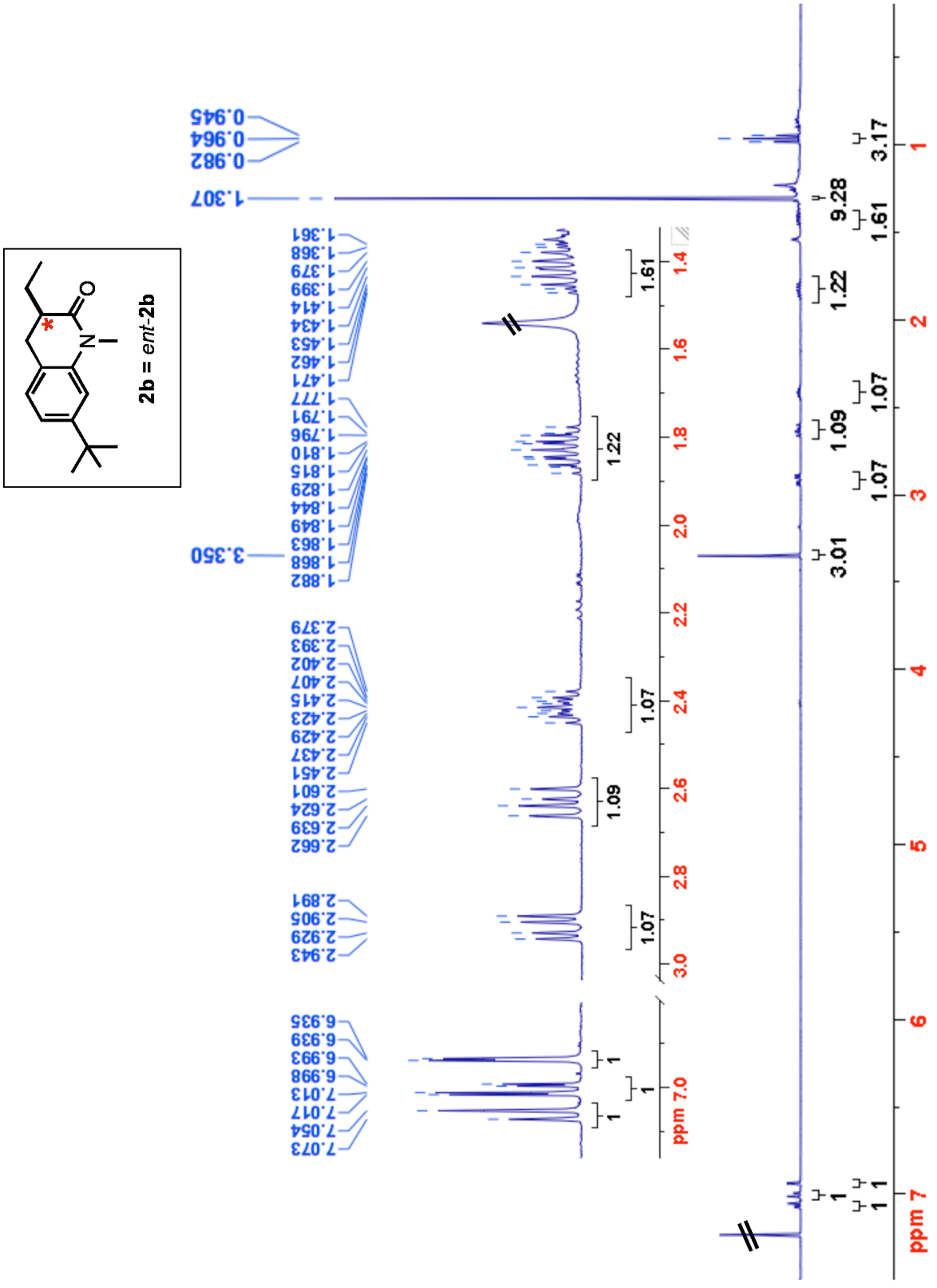
Flow rate: 21 mL/min

Equilibration volume: 50.4 mL

Solvent system: 22 % diethyl ether:*n*-pentane

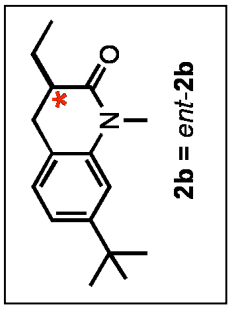
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm)

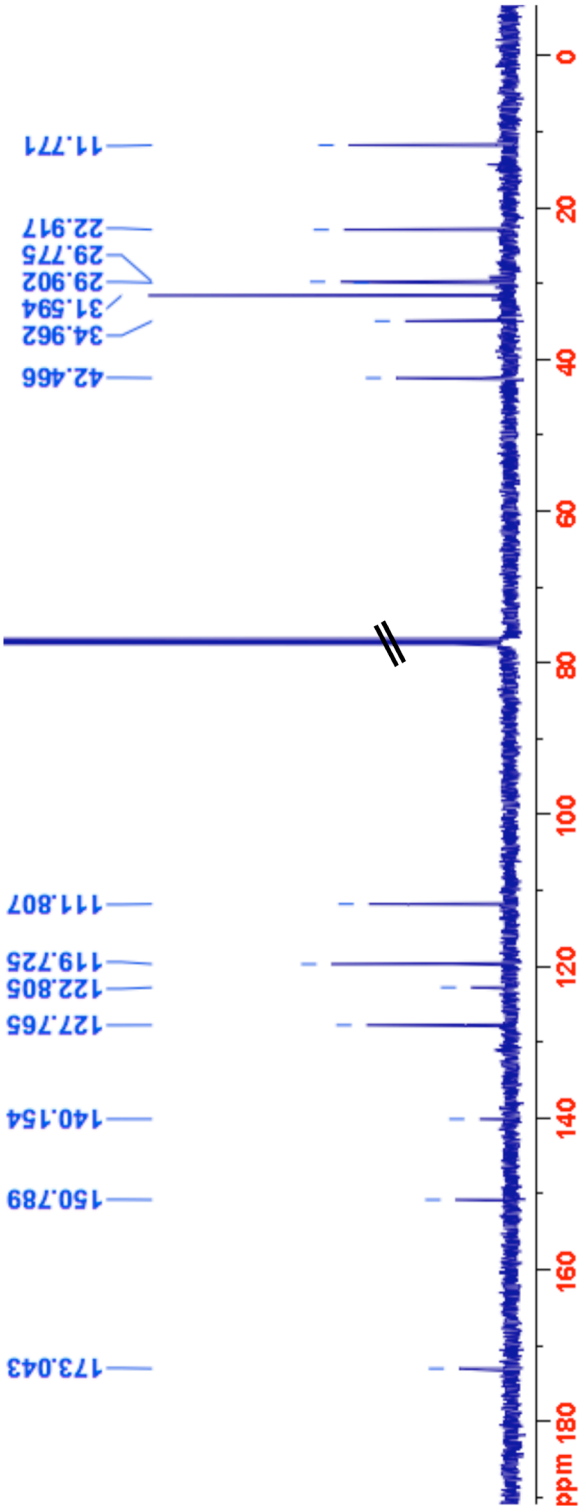
0.96 (t, *J* = 7.2 Hz, 3H), 1.30 (s, 9H), 1.36 – 1.48 (m, 1H), 1.77 – 1.89 (m, 1H), 2.37 – 2.46 (m, 1H), 2.60 – 2.67 (m, 1H), 2.89 – 2.95 (m, 1H), 3.35 (s, 3H), 6.93 – 7.08 (Ar, 3H).


2b = ent-2b
O
N
*
0.945
0.964
0.982
1.307
1.361
1.368
1.379
1.399
1.414
1.434
1.453
1.462
1.471
1.777
1.791
1.796
1.810
1.815
1.829
1.844
1.849
1.863
1.868
1.882
3.350
2.379
2.393
2.402
2.407
2.415
2.423
2.429
2.437
2.451
2.601
2.624
2.639
2.662
2.891
2.905
2.929
2.943
6.935
6.939
6.993
6.998
7.013
7.017
7.054
7.073
ppm 7.0
ppm 7
1.61
1.22
1.09
1.07
3.01
9.28
3.17

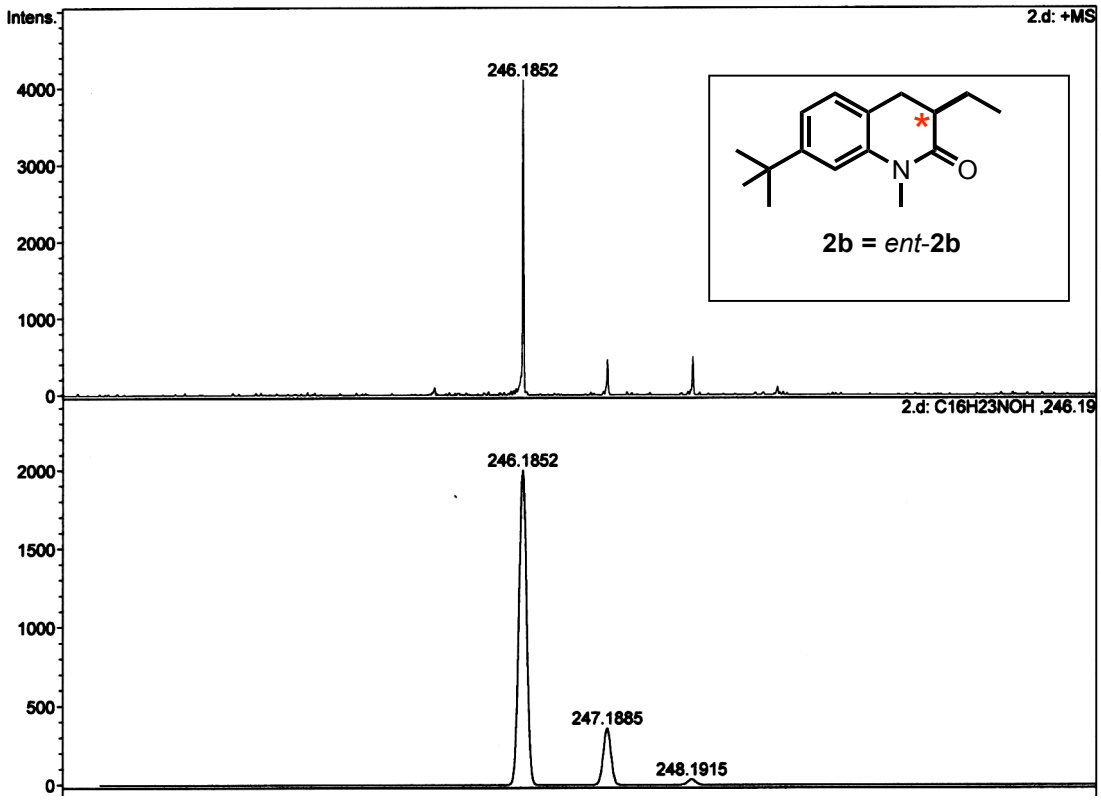
***^{13}C NMR* (100 MHz, $CDCl_3$, δ ppm)**

δ 11.77, 22.92, 29.77, 29.90, 31.59, 34.96, 42.46, 111.81, 119.72, 122.80, 127.76, 140.15, 150.79, 173.04.





***ESI-MS* ([M + H]$^+$):** Calculated: 246.1852; Observed: 246.1852; ΔM = 0 ppm.



HPLC analysis conditions:

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

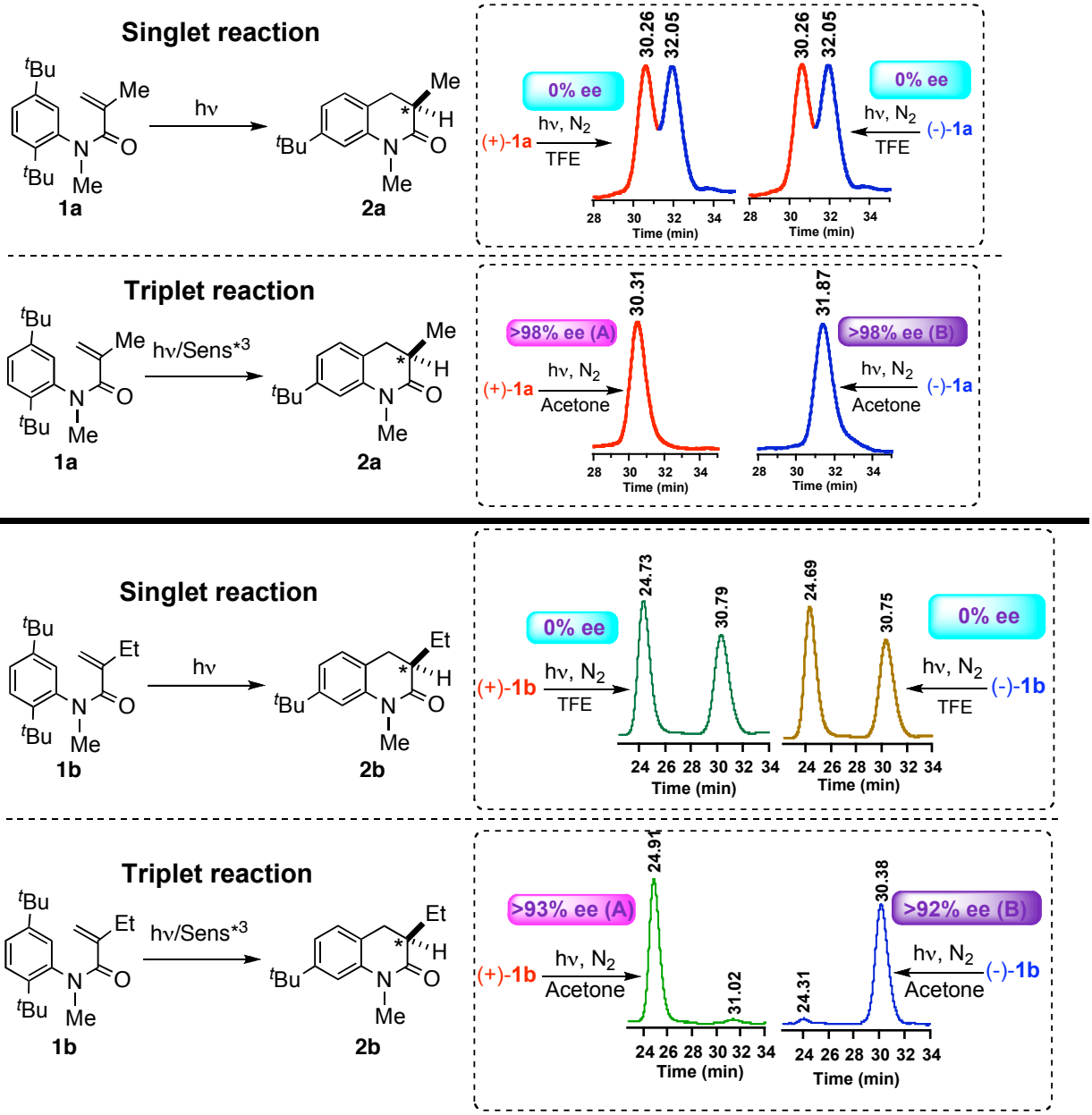
Mobile phase: Hexanes:IPA = 98:2; Flow rate: 1 mL/min

Retention time (min): **2b:** ~27.05

ent-**2b:** ~33.37

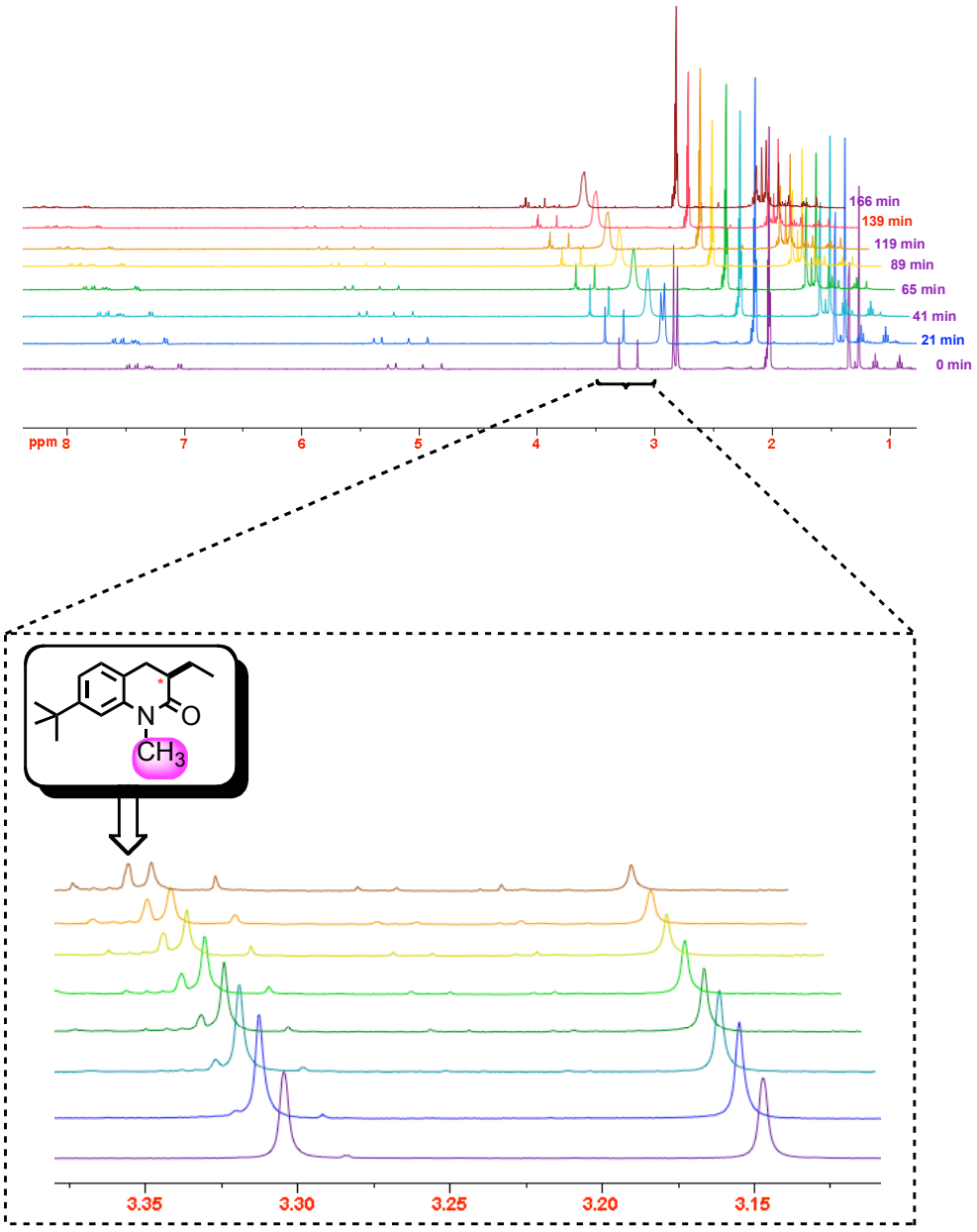
7.0 Photoproduct analysis by chiral stationary phase separation on HPLC and by NMR.

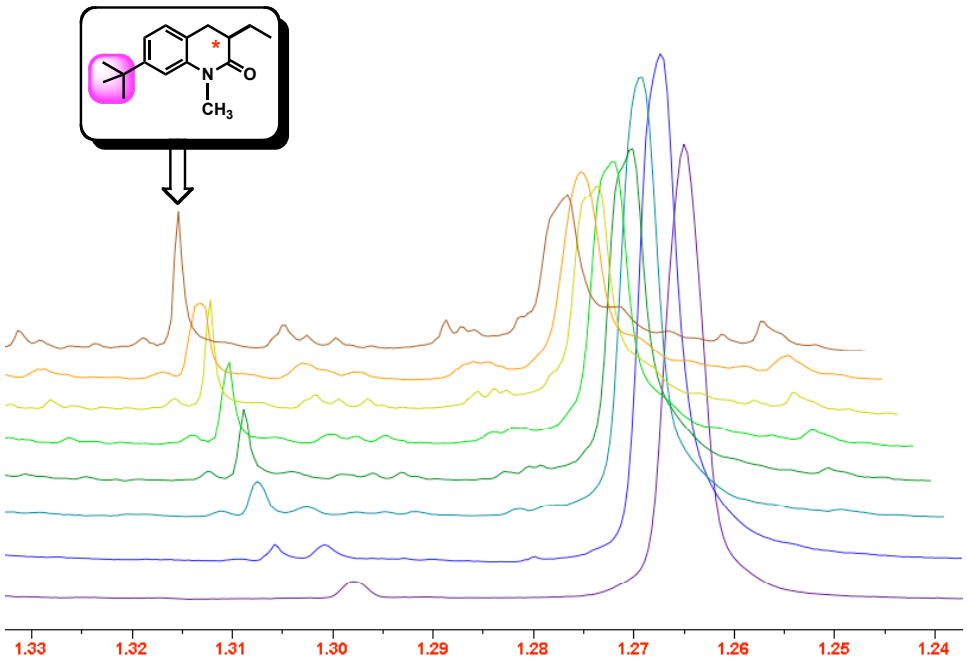
7.1 Photoproduct analysis by chiral stationary phase separation on HPLC.



7.2 Monitoring photoreaction and conversion by ^{1}H NMR.

HPLC purified acrylanilide (3.5 mg) was dissolved in 1 ml of acetone-d_6 in a NMR tube. The sample was exposed to UV-VIS light (medium pressure Hg lamp); the reaction was followed by ^{1}H NMR spectroscopy. Represented below is the reaction profile at different intervals for **1b**. The N-Methyl group or the *tert*-butyl group was used as an NMR handle to follow the reaction.





7.3 Absolute Conversion by ^{1}H NMR.

HPLC purified **1a-b** (3.5 mg) was dissolved in 1 ml of acetone or TFE in a 13 mm Pyrex test tube. The samples were exposed to UV-VIS light (medium pressure Hg lamp) for specified time; each sample was then analyzed by ^{1}H NMR spectroscopy with α,α'-dichloro-*p*-xylene, as an internal standard.

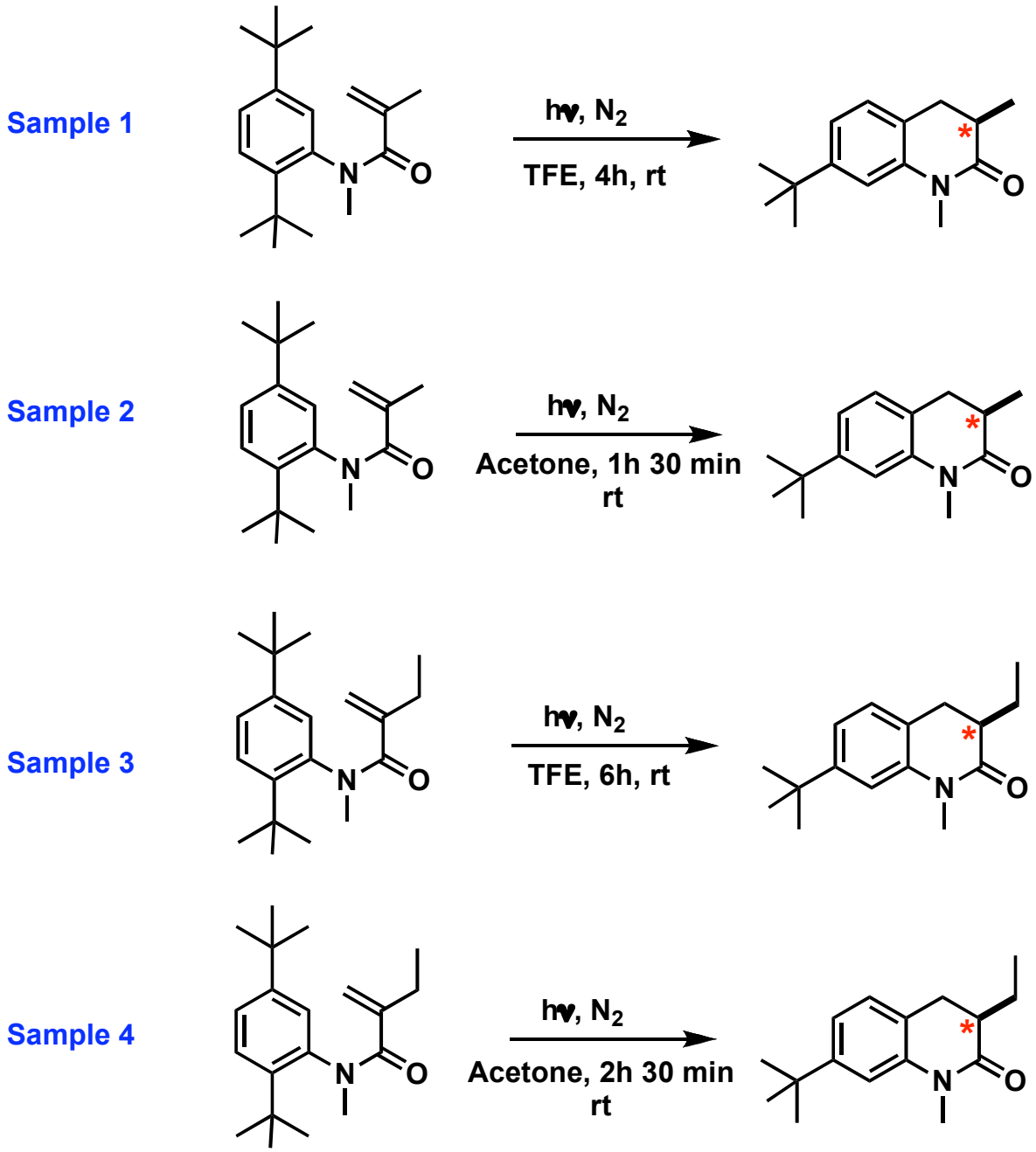
The number of moles of analyte (product or starting material) in the NMR aliquot is given by the following equation:[6,7]

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

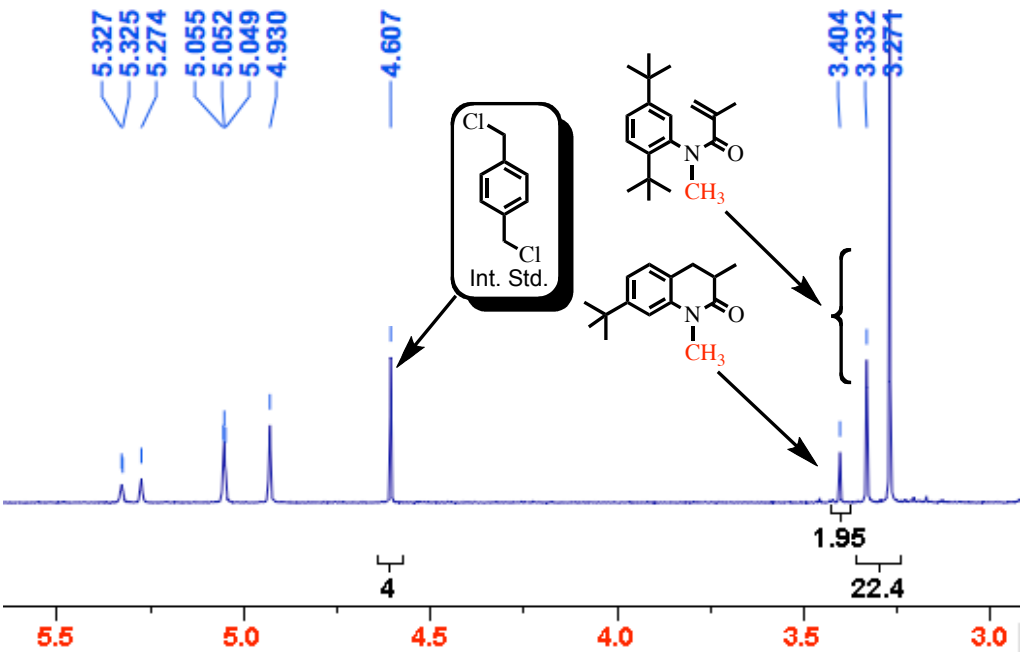
Where N_a and N_i are the number of nuclei giving rise to the relevant analyte and standard signals respectively.[6,7]

For triplet sensitization, the conversion was ~30% for **1a-b** irradiation (90 min for **1a** and 150 min for **1b**) in acetone. Higher irradiation time resulted in higher conversion but the reactivity slowed due to decomposition products from the solvent acetone. The mass balance was >88% for all irradiations.

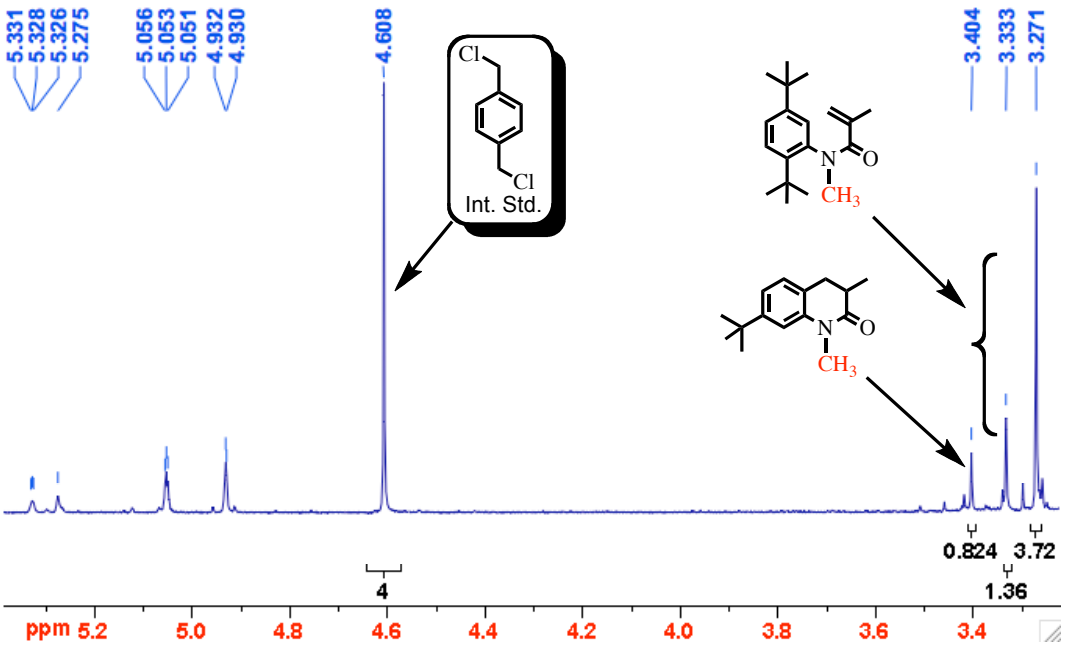
For singlet irradiation (in TFE or methanol) of **1a-b** the conversion was 10-20% for 6 h irradiations with >90% mass balance. Higher irradiation time led to an increase in conversion.



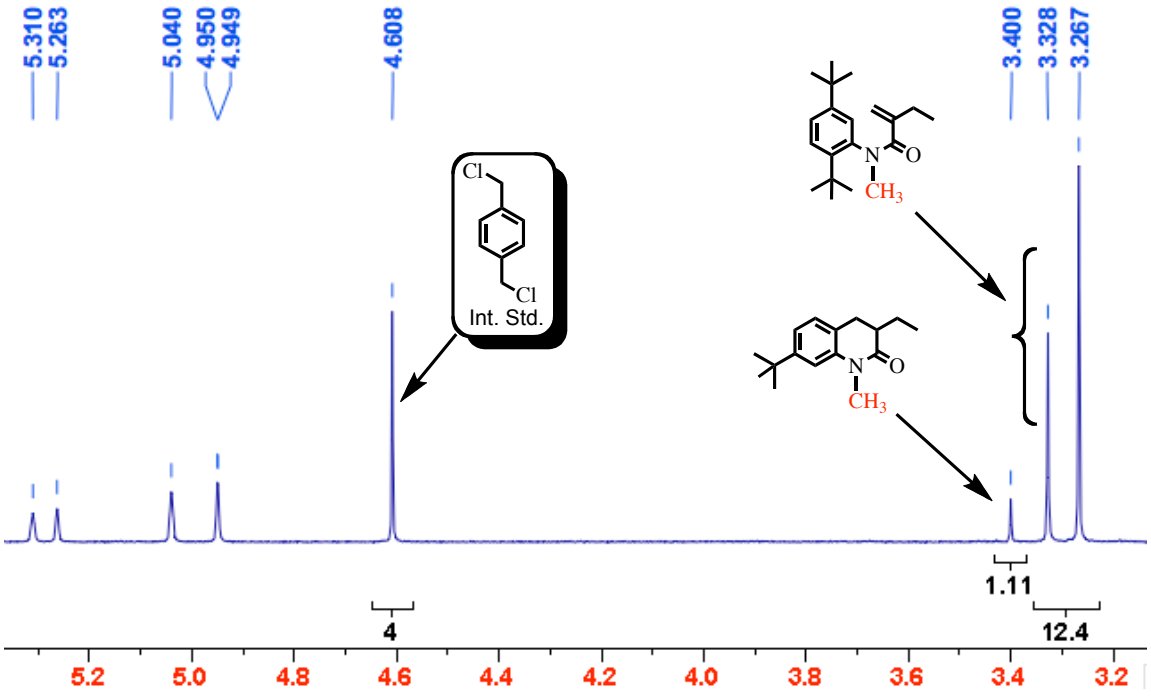
Scheme S4: Monitoring conversion by ^{1}H NMR. The representative ^{1}H NMR traces of sample reactions (samples 1-4) is given below.



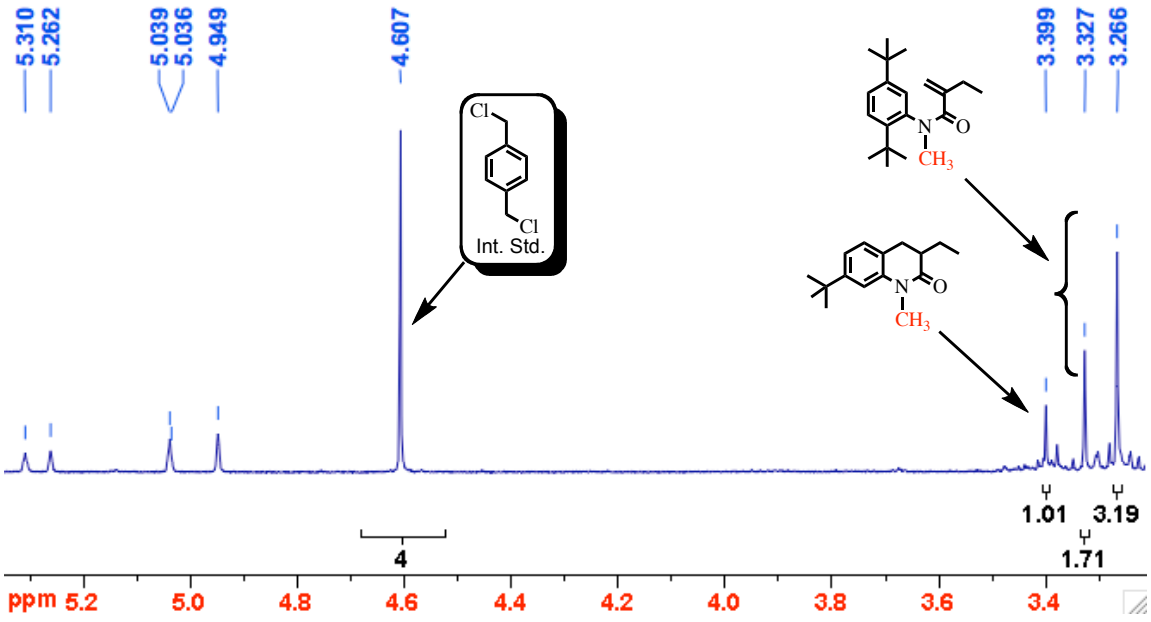
Sample 1: Photoreaction of **1a** in TFE for 4h. ^{1}H NMR of the crude sample from 3.0 to 5.5 ppm.



Sample 2: Photoreaction of **1a** in acetone for 1h 30 min. ^{1}H NMR of the crude sample from 3.0 to 5.5 ppm.



Sample 3: Photoreaction of **1b** in TFE for 6h. ^{1}H NMR of the crude sample from 3.0 to 5.5 ppm.



Sample 4: Photoreaction of **1b** in acetone for 2h 30min. ^{1}H NMR of the crude sample from 3.0 to 5.5 ppm.

8. Photophysical Measurements

8.1 UV – VIS profile of chromophores **1a-d**.

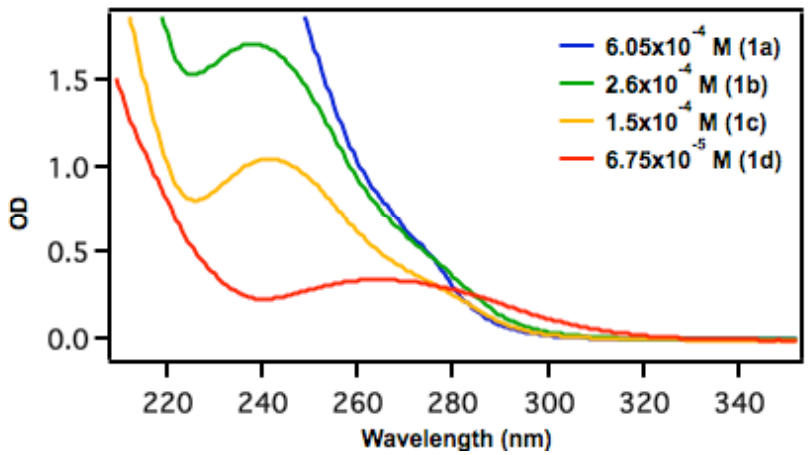


Figure S1: UV-VIS absorption spectra of **1a-c** in methylcyclohexane (MCH). Concentration of the substrates are [**1a**] = 6.05 x 10^{-4} M; [**1b**] = 2.6 x 10^{-4} M; [**1c**] = 1.5 x 10^{-4} M; and [**1d**] = 6.75 x 10^{-4} M.

8.2 Fluorescence Measurements at Room Temperature.

The following parameters were maintained during acquisition.

Excitation slit-width = 1 nm; emission slit-width = 5.0 nm;

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

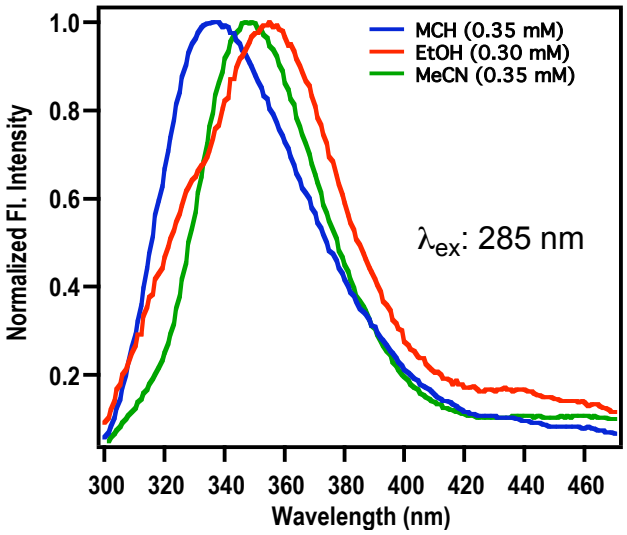


Figure S2: Fluorescence spectra of **1a** in non-polar methycyclohexane (MCH) and polar solvents acetonitrile (MeCN) and ethanol (EtOH). Concentration of **1a** given in brackets.

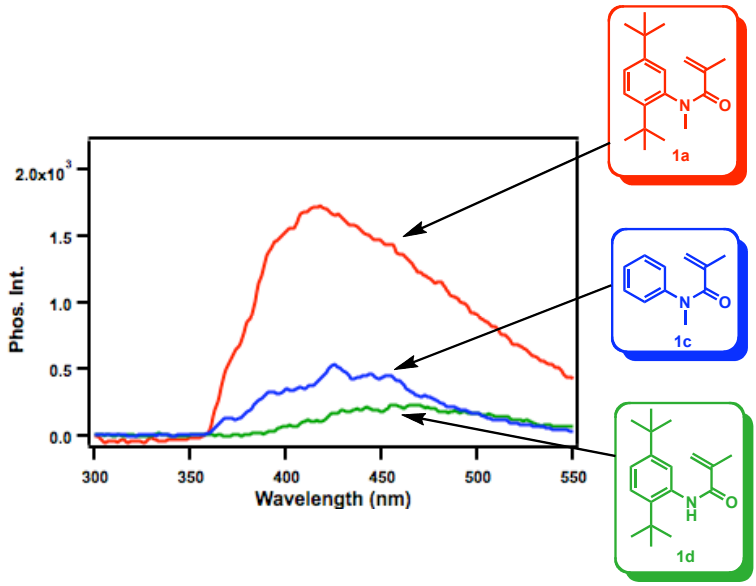
8.3 Phosphorescence measurements at 77 K in Methylcyclohexane (MCH).

The phosphorescence spectra were recorded at 77 K in Methylcyclohexane (MCH) by exciting the samples at 285 nm using a pulsed Xenon lamp and monitoring the emission from 330-550 nm. The following parameters were employed during acquisition:

Time window 1: (acquisition from 10 to 20 msec)

Excitation slit-width 5 nm, emission slit-width = 8 nm; time per flash = 61 msec; flash per count = 10, delay time = 10 msec, wavelength increment = 1 nm; sample window = 10 msec.

Time Window 1: 10 – 20 msec



Time window 2: (acquisition from 0.3 to 0.9 sec)

Excitation slit-width = 5 nm, emission slit-width = 8 nm; time per flash = 1 sec; flash per count = 10, delay time = 300 msec; wavelength increments = 1 nm; sample window = 600 msec.

Time Window 2: 0.3 – 0.9 sec

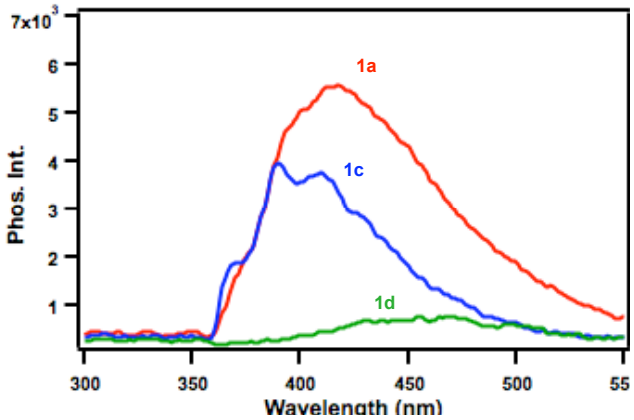


Figure S3: Phosphorescence emission of **1a** (c = 6.05 x 10^{-4} M), **1c** (c = 1.5 x 10^{-4} M), and **1d** (c = 6.75 x 10^{-4} M) in MCH at 77 K.

*Note: There is no emission from **1d*** (N-H derivative). *Only* N-Me derivatives ***1a-c*** *showed observable phosphorescence.*

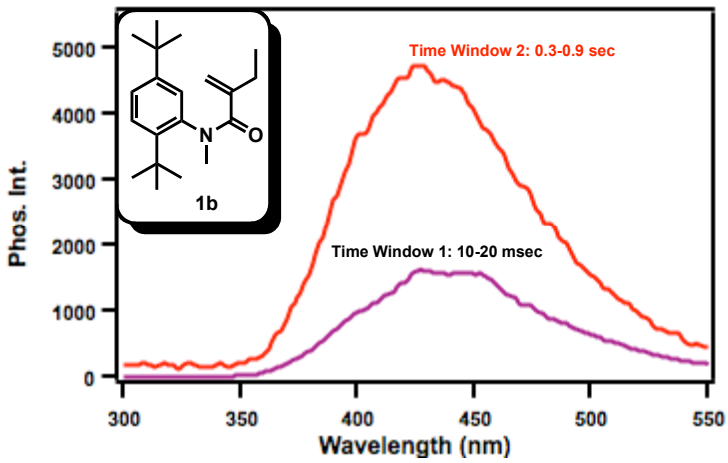


Figure S4: Phosphorescence emission of **1b** at different time gates (time window 1 and time window 2)

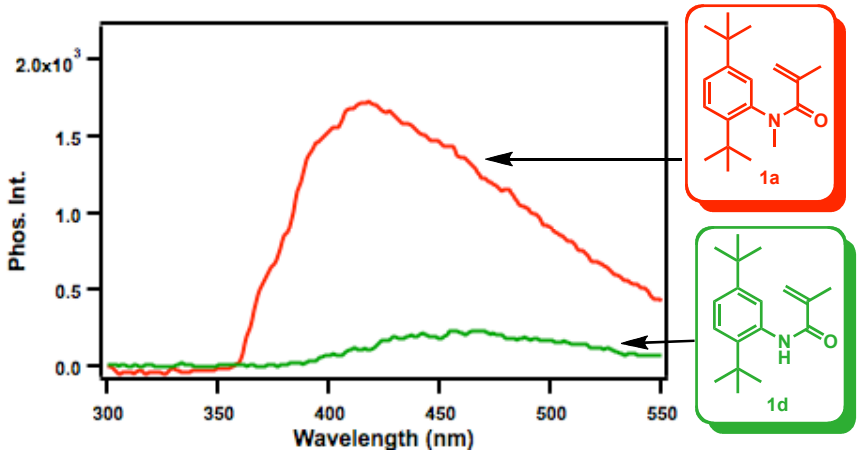


Figure S5: Phosphorescence emission of **1a** and **1d** at time window: 10 to 20 msec

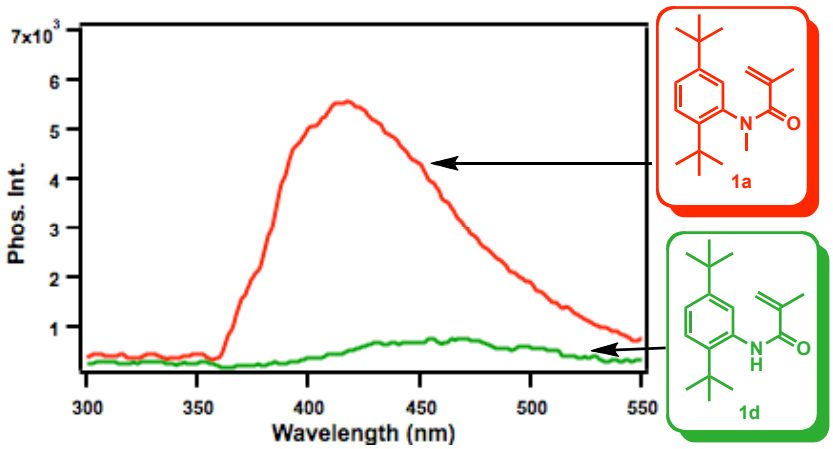


Figure S6: Phosphorescence emission of **1a** and **1d** at time window: 0.3 to 0.9 sec

Note: There is no phosphorescence emission from N-H *derivative **1d**.*

8.4 Phosphorescence decay/lifetime profile of **1a,b**.

The decay profiles were recorded at 77 K in Methylcyclohexane (MCH).by exciting the samples at 285 nm using a PhosLamp with a trigger pulse delay of 1%. The emission was monitored at 415 nm for **1a** and at 430 nm for **1b**.

The following parameters were maintained during acquisition:

Excitation slit-width = 8 nm, Emission slit-width = 8 nm

Time (phosphorescence) range = 11 sec, number of sweeps = 100

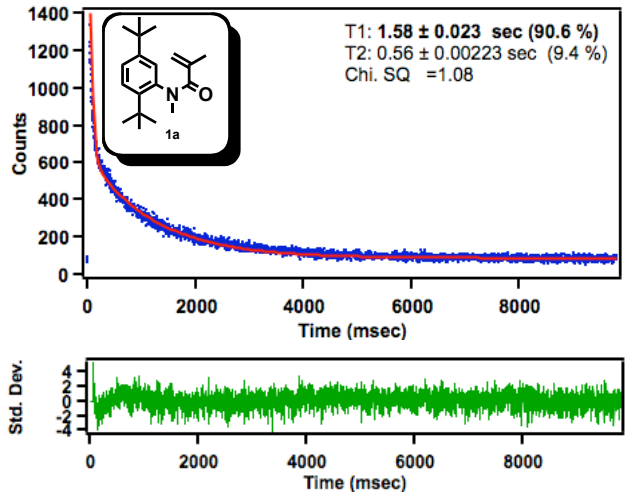


Figure S7: Phosphorescence decay of **1a**; c = 6.05 x 10^{-4} M in MCH at 77 K in MCH.

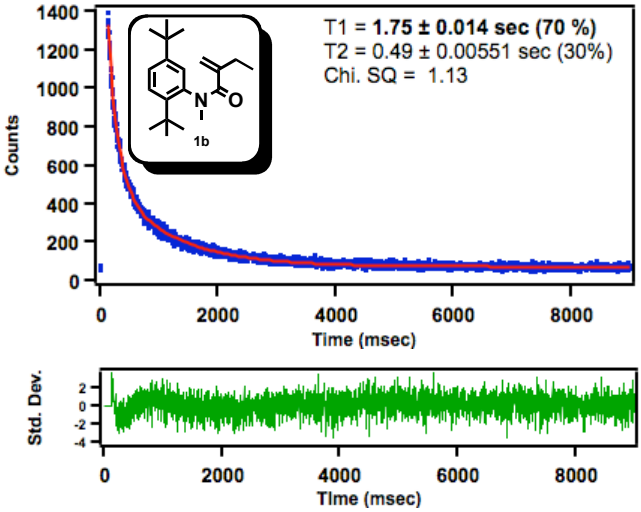


Figure S8: Phosphorescence decay of **1b**; c = 2.6 x 10^{-4} M in MCH at 77 K in MCH.

9. Reference

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