Supplementary Material (ESI) for Photochemical & Photobiological Sciences

Supporting information (56 Pages)

6π-Photocyclization *O-tert*-butylacrylanilides. N-substitution dictates the regiochemistry of cyclization.

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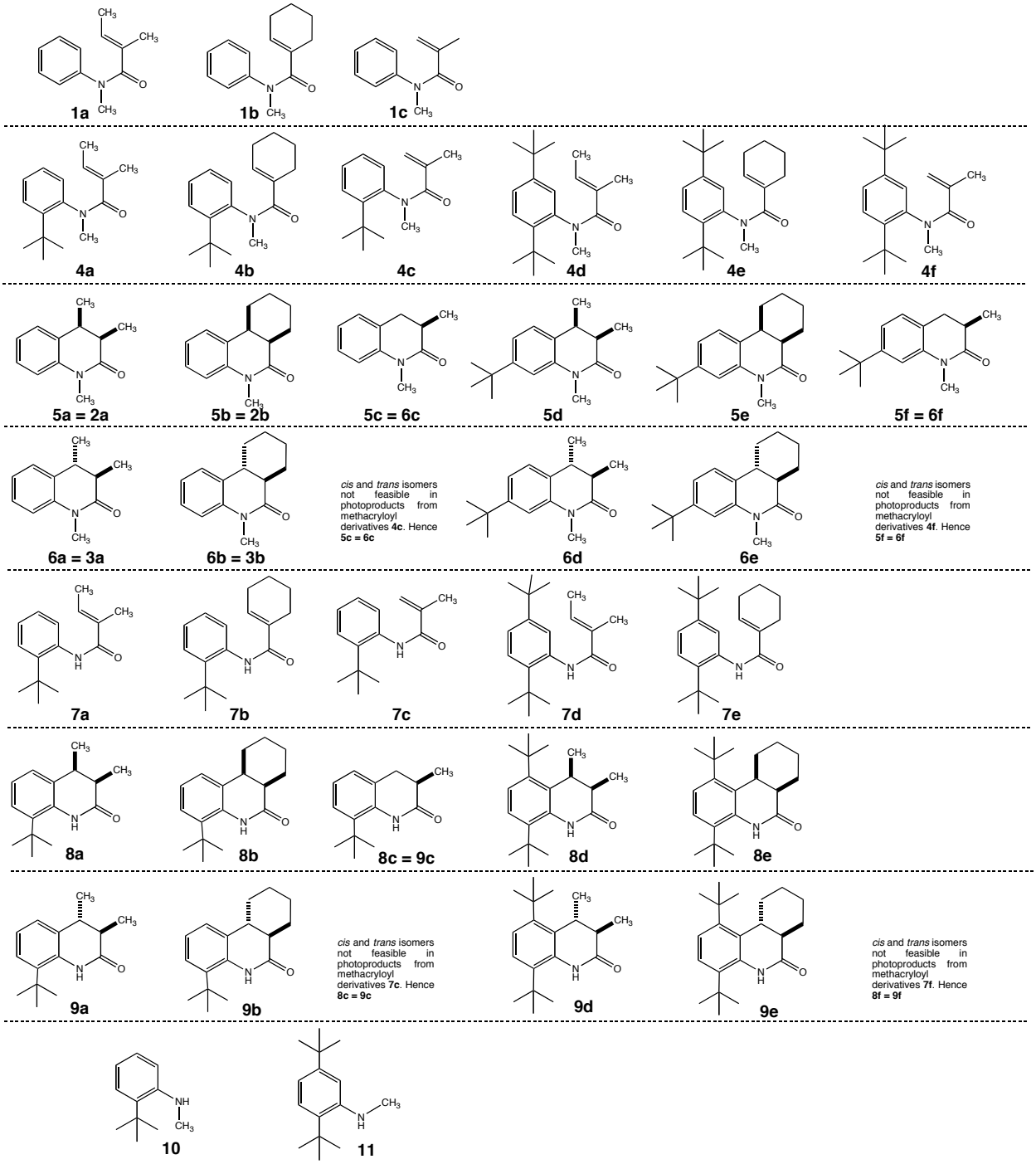
Contents

1. General methods

All solvents and chemicals were purchased from Alfa Aesar®, Sigma – Aldrich®, Across®, and Oakwood® Products, and were used as received without further purification. HPLC grade solvents (purchased from EMD®) were used for carrying out photoreactions. ^{1}H-NMR and ^{13}C-NMR spectra were obtained on Varian 400 MHz or 500 MHz spectrometer. Coupling constants (*J*) were reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s (singlet), b (broad), d (doublet), t (triplet), q (quartet), m (multiplet), virt (virtual), and ABq (AB quartet). Electrospray Ionization Spectra 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-prepaprative injections were perfomed on chiral stationary phase uisng (R,R) WHELK–01 columns: (25cm X 4.6 mm column for analytical injections, and 25 cm x 10mm for semi-preparative injections). Masslynx software version 4.1 was used to analyse the HPLC injections. Igor Pro® Sofware version 4.0 was used to process the chromatographic data. UV-Vis spectra were recored on a shimadzu 2501PC UV-Vis spectrometer using UV quality fluorimeter cells (with range until 190 nm) purchased from Luzchem. When necessary, the reactants and photoproducts were purified by chromatography on silica gel (Sorbent Technologies®, silica gel standard grade: Porosity 60 Å, Particle size: 230 x 400 mesh, Surface area: 500 – 600 m^2/g, Bulk density: 0.4 g/mL, pH range: 6.5 – 7.5). The Retention Factor (R*f*) values were recorded using a 30 % EtOAc-Hexanes as mobile phase (unless indicated) and on *Whatman*® flexible TLC plates (250 μ layer 20 x 20 cm, UV_{254}, PE SIL G/UV).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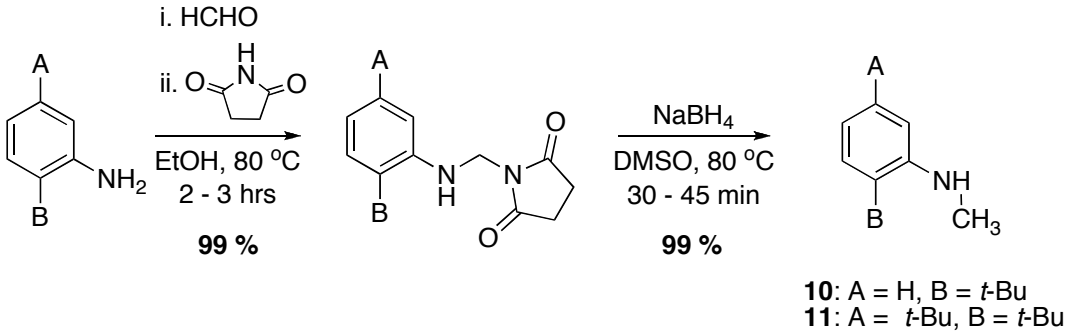
1b
1c
4a
4b
4c
4d
4e
4f
5a = 2a
5b = 2b
5c = 6c
5d
5e
5f = 6f
6a = 3a
6b = 3b
cis and trans isomers not feasible in photoproducts from methacryloyl derivatives 4c. Hence 5c = 6c
6d
6e
cis and trans isomers not feasible in photoproducts from methacryloyl derivatives 4f. Hence 5f = 6f
7a
7b
7c
7d
7e
8a
8b
8c = 9c
8d
8e
9a
9b
cis and trans isomers not feasible in photoproducts from methacryloyl derivatives 7c. Hence 8c = 9c
9d
9e
cis and trans isomers not feasible in photoproducts from methacryloyl derivatives 7f. Hence 8f = 9f
10
11

Chart 1

2. General procedure for synthesis of *N*-Methyl anilines 10 and 11



Scheme S1: Synthesis of *N*-Methyl substituted anilines

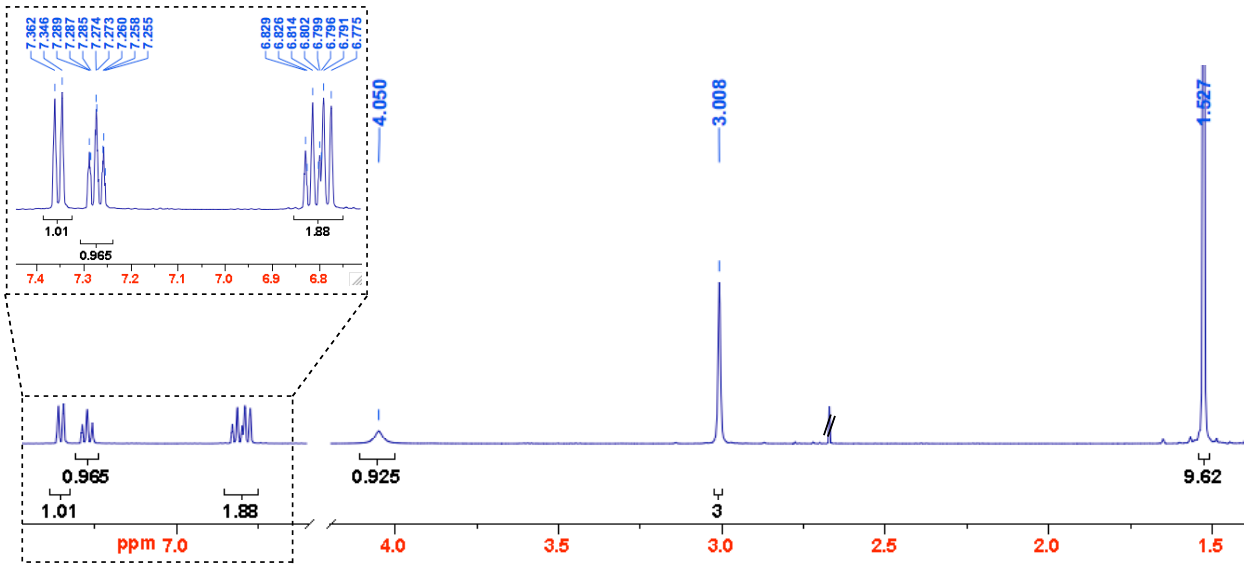
N-Methyl anilines **10** and **11** were synthesized using previously reported procedures. [1, 2] 1 equivalent of aniline (or substituted aniline) (5 g, 5.2 mL, 34 mmol, Sigma – Aldrich®) was dissolved in 15 mL of EtOH; then, 1.1 equivalent of 37.9 % formaldehyde solution (1.11g, 3 mL, 37 mmol, Mallinckrodt®) and 1.1 equivalent of succinimide (3.65 g, 37 mmol, TCI America) were respectively added to the aniline solution. The new mixture was allowed to reflux while stirring the reaction medium. After 2 to 3 hrs of reaction time, the solution was allowed to cool to room temperature and concentrated by removing the excess of solvent in a rotaovap. The concentrated solution was then kept aside to solidify/crystallize by adding a minimum amount (5 to 10 mL) of pentane to the reaction flask. A crystalline, powdered, or gelly succinamide derivative was collected by vacuum filtration, washed several times with cold ethanol, dried and was used without further purification.

Succinamide (8.85 g, 34 mmol; 1 equi.) was dissolved in 20 mL of dry DMSO under N_2 atmosphere. While heating the reaction flask and stirring the new solution, 1.1 equivalent (1.42 g, 37 mmol) of $NaBH_4$ (Aldrich®) was slowly added to the flask. The new mixture was allowed to reflux for 45 min under extremely dry conditions. The reaction mixture was cooled and the solution was transferred to a beaker containing cold DI water (about 200 mL). The organic layer was extracted with diethyl ether. The ether layer was then dried over anhydrous $NaSO_4$ (EMD™), filtered, and concentrated to obtain the expected *N*-Methyl substituted anilines. The purity (based on TLC, NMR, HPLC) of the synthesized compounds allowed us to employ them in subsequent reactions without further purification.

2.1 2-*tert*-butyl-*N*-methylaniline 10

^1H *NMR* (500 MHz, $CDCl_3$, δ ppm) 7.38 – 7.35 (d, J = 7.8, 1H), 7.30 – 7.24 (t, J = 7.6, 1H), 6.86 – 6.73 (m, 2H), 4.05 (bs, 1H), 3.01 (s, 3H), 1.53 (s, 9H)

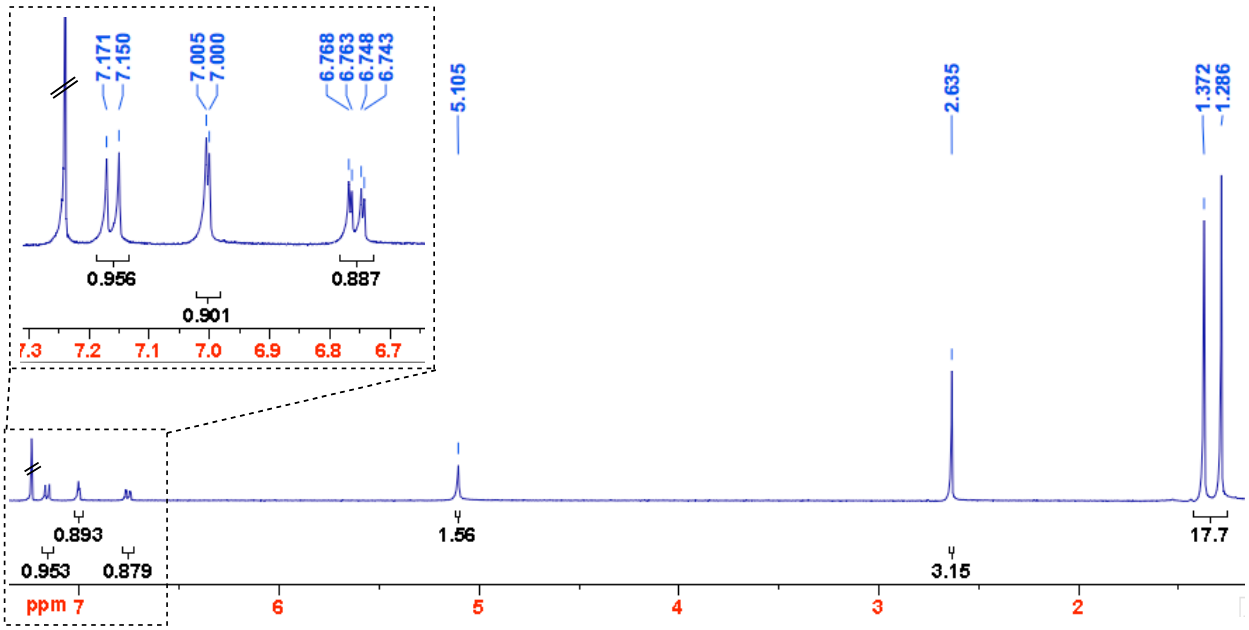
R*f* = 0.78



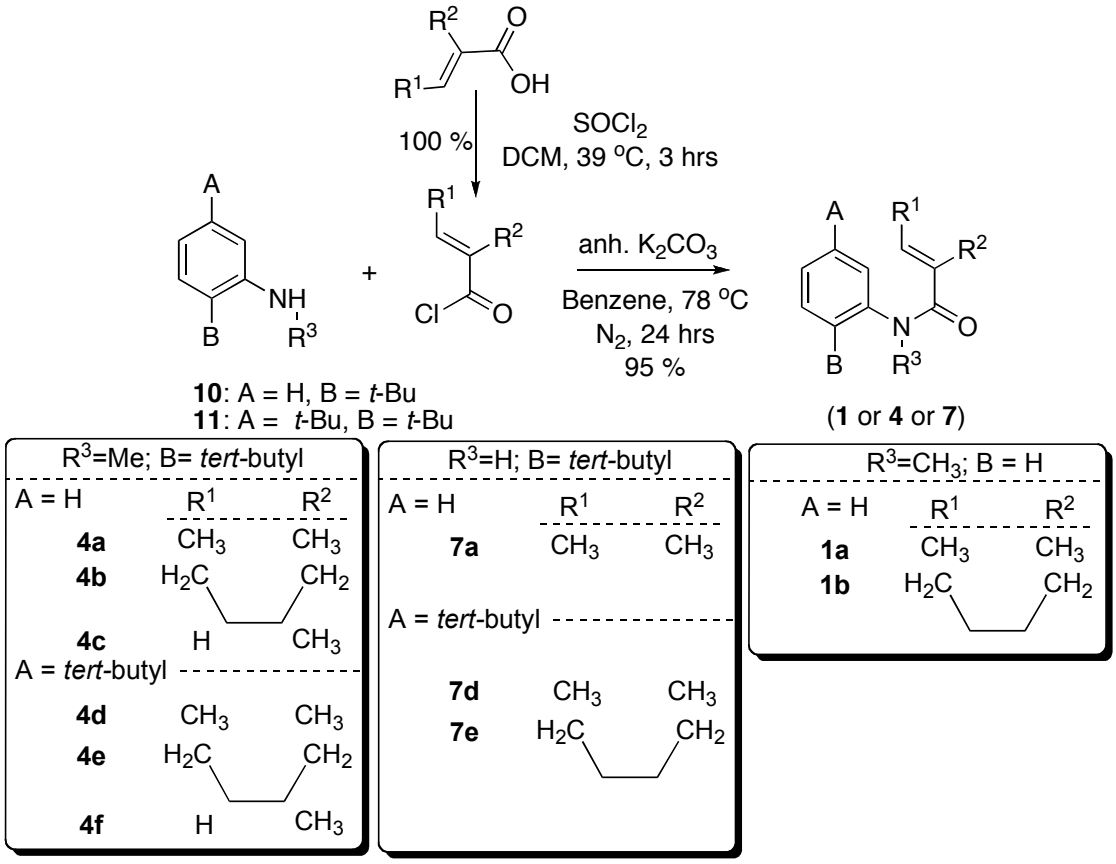
2.1 2,5-di-*tert*-butyl-*N*-methylaniline 11

^1H *NMR* (400 MHz, $CDCl_3$, δ ppm) 7.17 – 7.15 (d, J = 8, 1H), 7.00 (s, 1H), 6.77 – 6.75 (d, J = 8, 1H), 5.11 (bs, 1H), 2.64 (s, 3H), 1.37 (s, 9H), 1.29 (s, 9H)

R*f* = 0.89



3. General procedure for synthesis of acrylanilides 1, 4 and 7

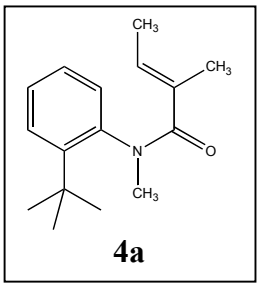


Scheme S2: Synthesis of acrylanilides **1**, **4** and **7**.

Acrylanilides **1**, **4** and **7** were prepared using procedures reported in literature (Scheme S2). [2-5] In a typical reaction, 1 equivalent of freshly synthesized aniline was dissolved in 20 mL of benzene. Then, the aniline solution was stirred and purged with N_2 gas; 1.5 equivalent of anhydrous K_2CO_3 (EMD^{TM}) was added to the reaction flask, and 1.5 equivalent of acyl (tigloyl, cyclohexyl, or methacryl) chloride (synthesized from the corresponding carboxylic acid or commercially available) was slowly added to the mixture in the flask constantly stirred and under N_2 atmosphere. The new solution was allowed to reflux (78 ^{o}C) overnight (24 hrs). After completion, the reaction was quenched (10 – 20 mL of water) and washed with water (2 x 20 mL) followed by extraction with EtOAc (2 x 20 mL). The organic layer was then dried over anhydrous $NaSO_4$ (EMD^{TM}) and concentrated by rotor evaporation. The expected amides were finally purified by flash chromatography on silica gel. Non-methylated amides (crystalline compounds) were recrystallizatized in pentane or diethyl ether.

4. Characterization of acrylanilides starting materials

4.1 Mono-*o-tert*-butyl acrylanilide 4a

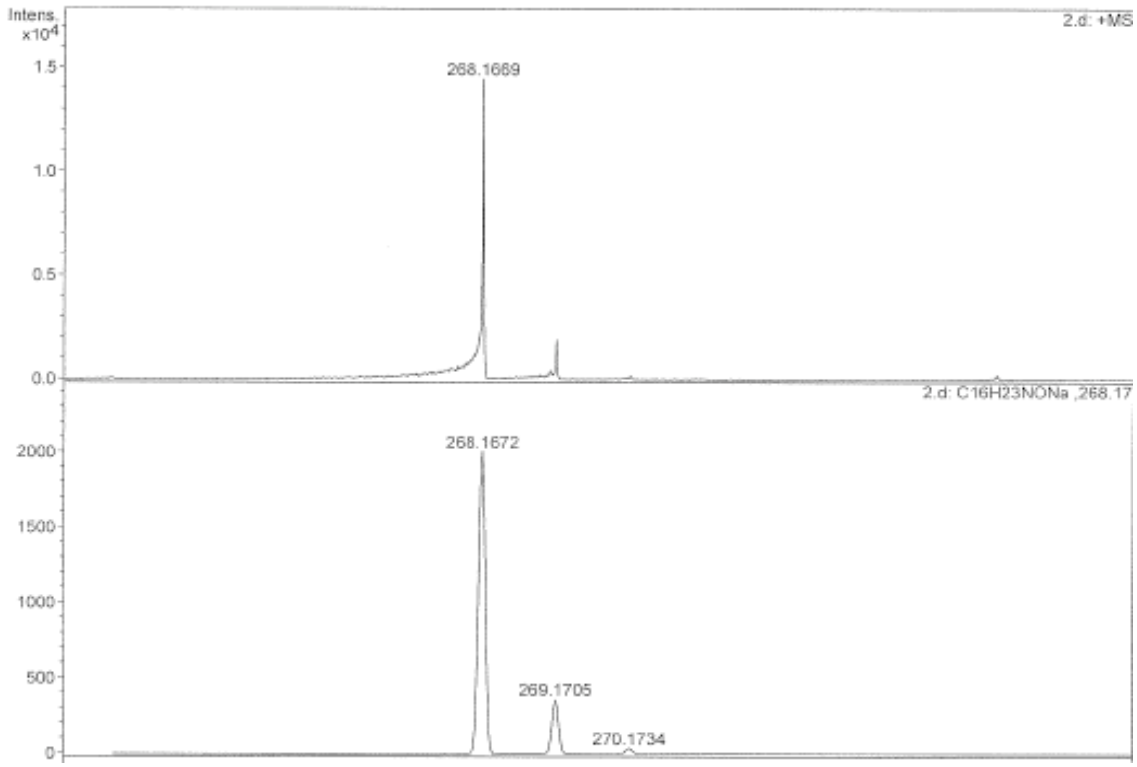


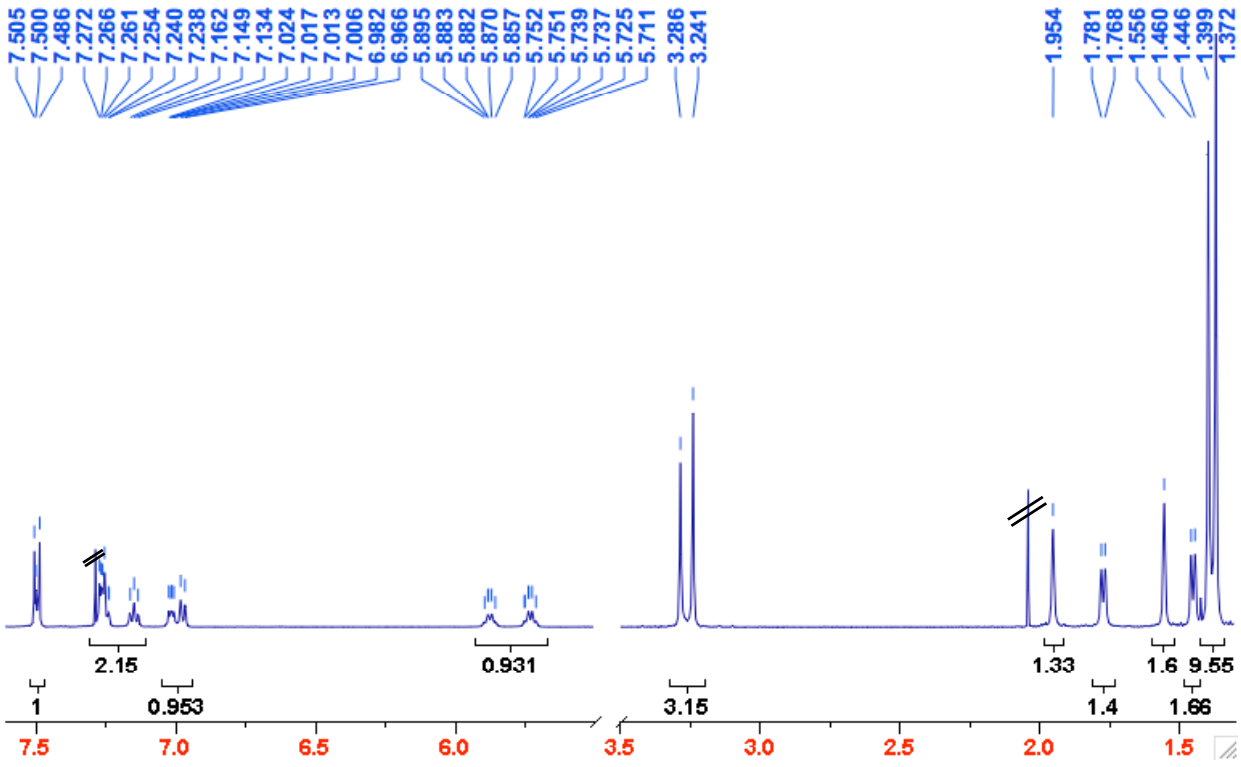
4a

^1H NMR (500 MHz, $CDCl_3$, δ ppm) 7.53 – 7.46 (m, 1H), 7.32 – 7.21 (m, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.06 – 6.93 (m, 1H), 5.87 and 5.73 (q, 1H, minor and major confomer), 3.29 and 3.24 (s, 3H, minor and major confomer) 1.95 and 1.55 (s, 3H, α-Me minor and major confomer), 1.77 and 1.45 (d, *J* = 6.5 Hz, β-Me minor and major confomer), 1.40 and 1.37 (s, 9H, ^{t}Bu minor and major confomer).

ESI-MS ($[M + Na]^+$): Calculated: 268.1672; Observed: 268.1669

R*f* = 0.11

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5.882
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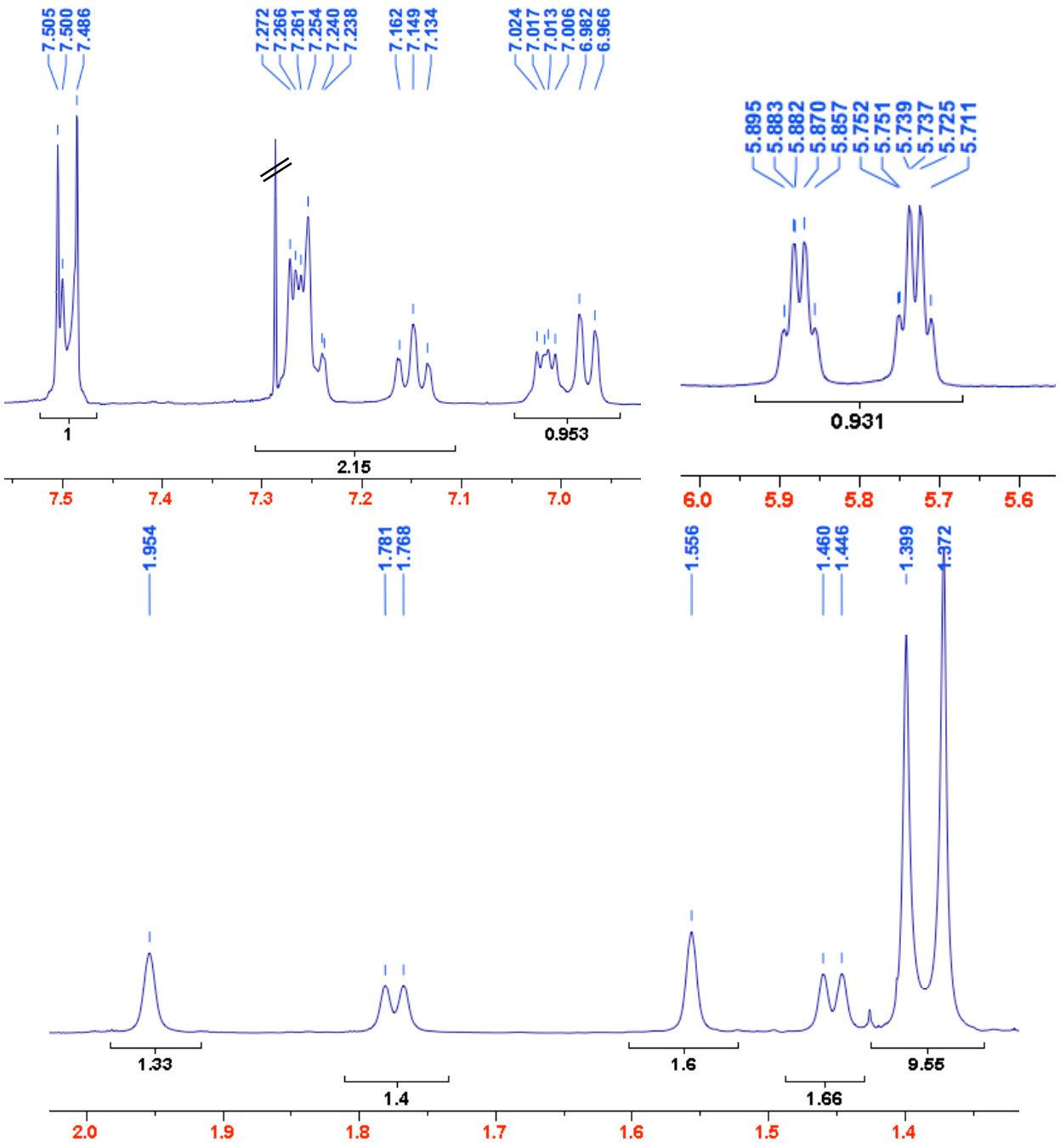
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1.33
1.4
1.6
1.66
9.55
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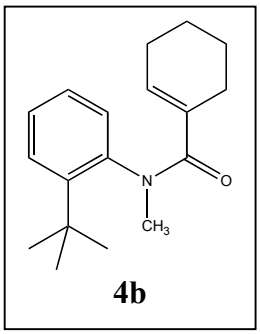
1.9
1.8
1.7
1.6
1.5
1.4

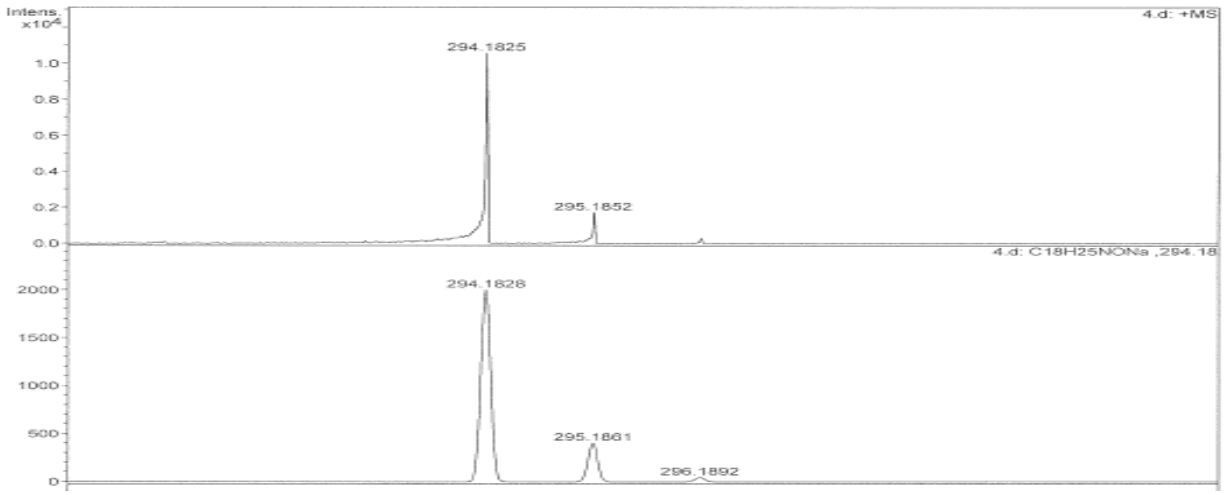
4.2 Mono-*o-tert*-butyl acrylanilide 4b

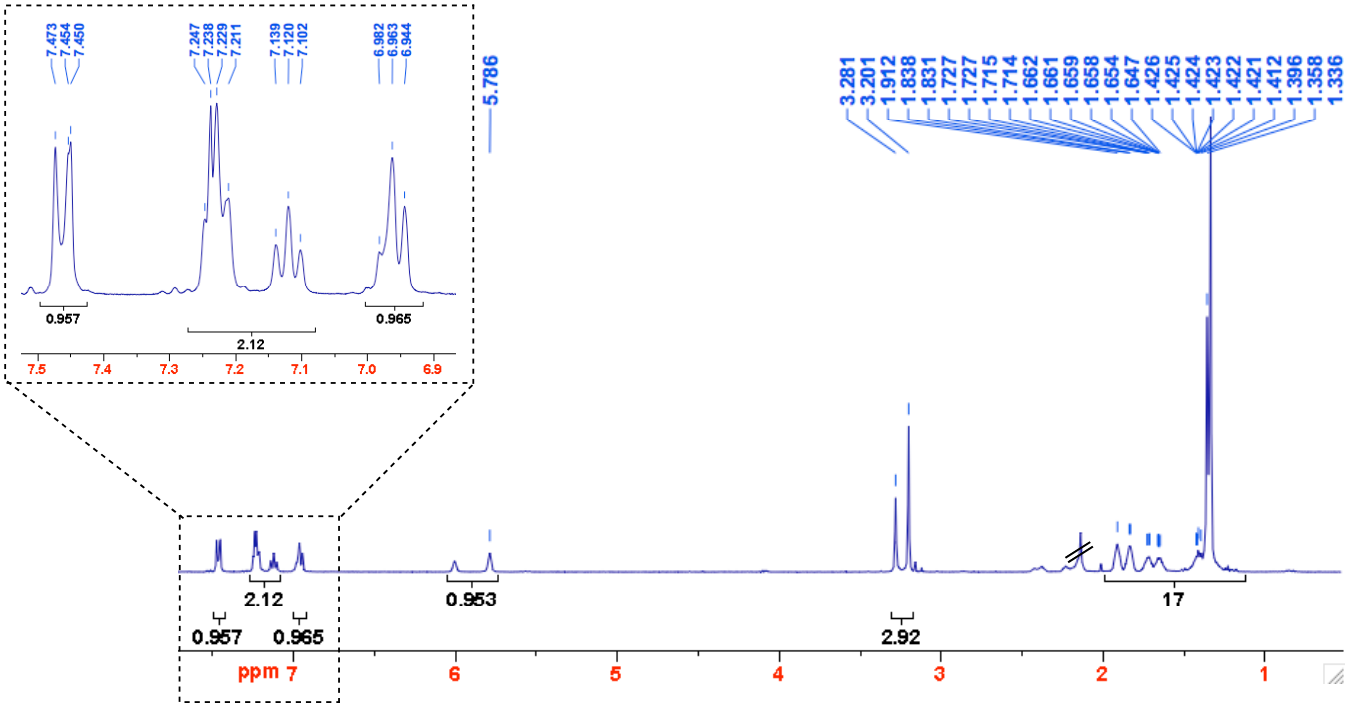


4b

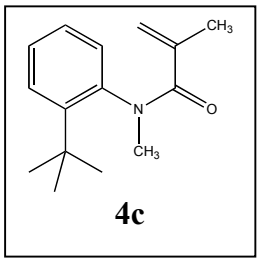
[1]H NMR (400 MHz, $CDCl_3$, δ ppm) 7.46 (d, *J* = 9.2 Hz, 1H), 7.26 – 7.17 (m, 1H), 7.10 (t, *J* = 8.4 Hz, 1H), 6.95 (m, 1H), 5.98 and 5.76 (s,1H, alkene H minor and major confomer), 3.30 and 3.22 (s, 3H, N-Me minor and major confomer), 2.44 -1.54 (m, 8H), 1.33 and 1.31 (s, 9H, ^{t}Bu minor and major confomer)

ESI-MS ($[M + Na]^+$): Calculated: 294.1828; Observed: 294.1825





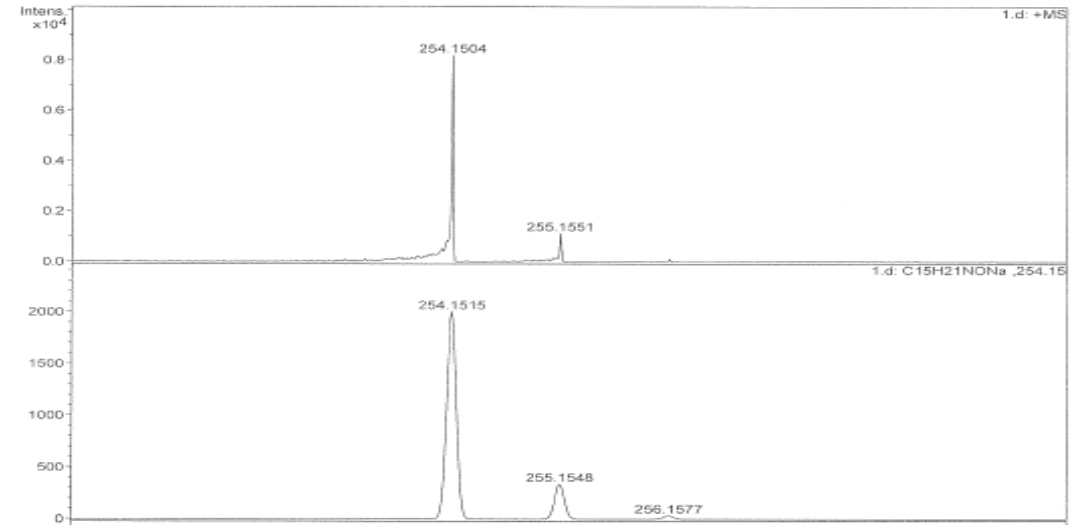
4.3 Mono-*o-tert*-butyl acrylanilide 4c

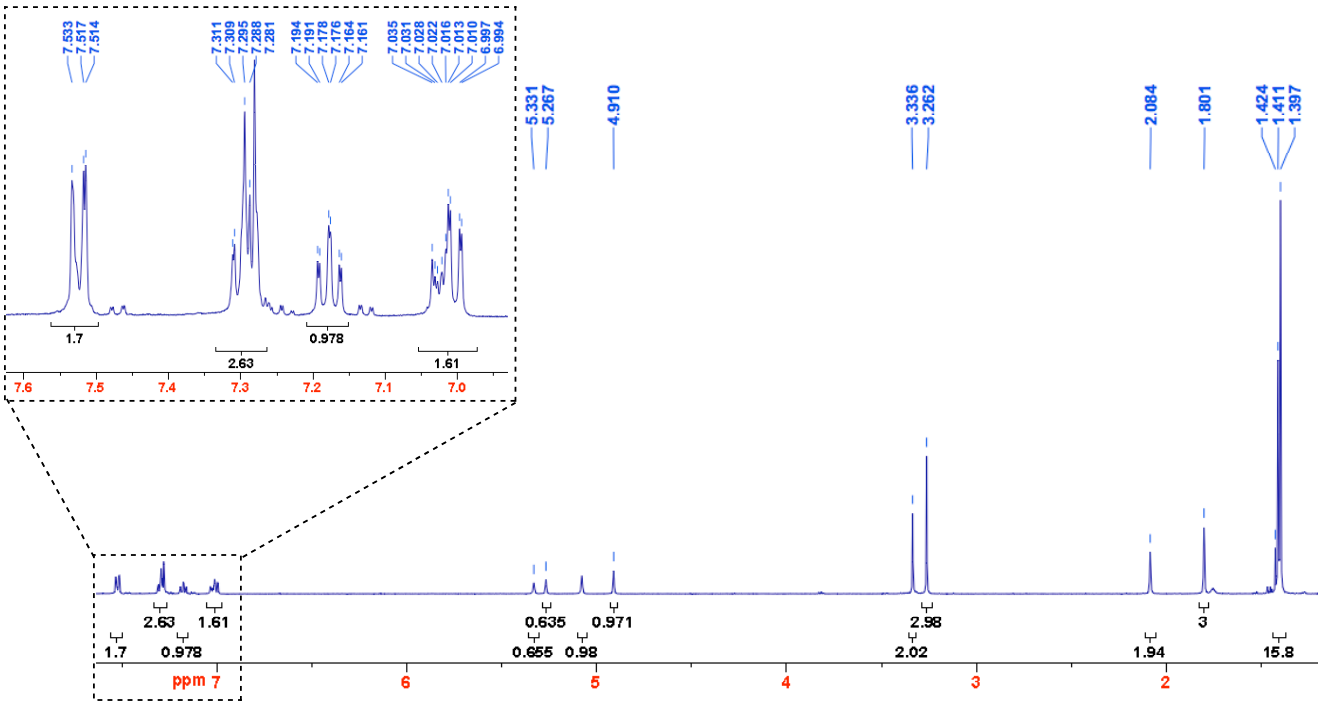


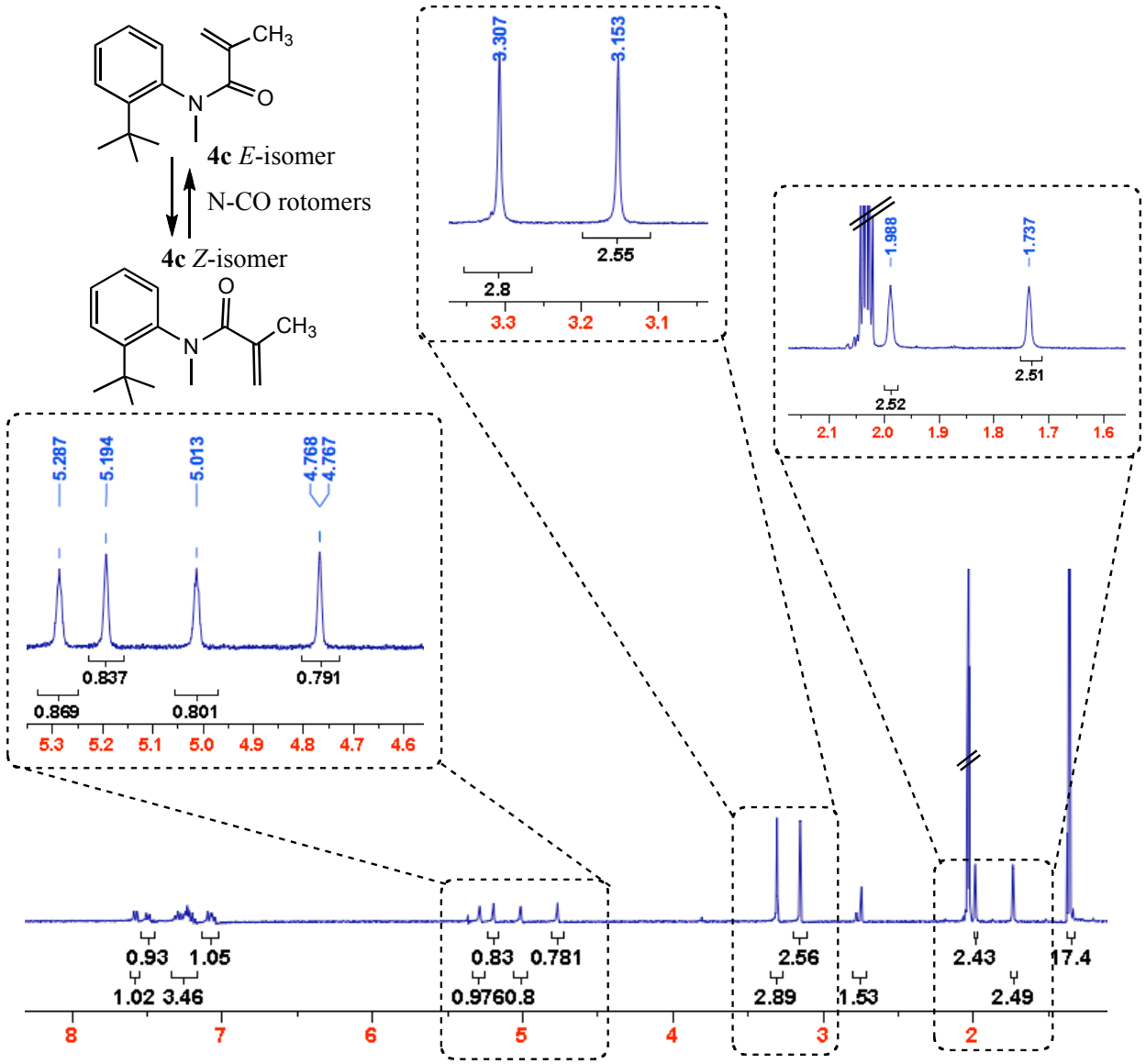
4c

^{1}H *NMR* (500 MHz, $CDCl_3$, δ ppm) 7.53-6.95 (Ar, 4 H), 5.29 and 5.04 (s, 1H, minor and major confomer), 5.23 and 4.87 (s, 1H, minor and major confomer), 3.30 and 3.22 (s, 3H, N-Me minor and major confomer), 2.04 and 1.76 (s, 3H, α-Me minor and major confomer), 1.37 and 1.36 (s, 9H, ^{t}Bu minor and major confomer)

ESI-MS ($[M + Na]^{+}$): Calculated: 254.1515; Observed: 254.1504

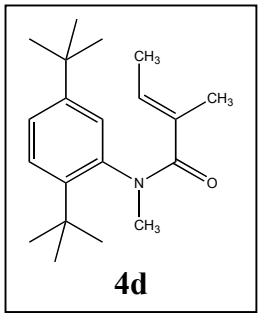






^{1}H NMR spectra of **4c** in acetone-d_6 (above). The *E:Z* N-CO rotomer ratio was close to 50:50. A comparison of rotomer ratio in acetone-d_6 and $CDCl_3$ shows that both E and Z isomers are present in solution.

4.4 Di-*tert*-butyl acrylanilide 4d

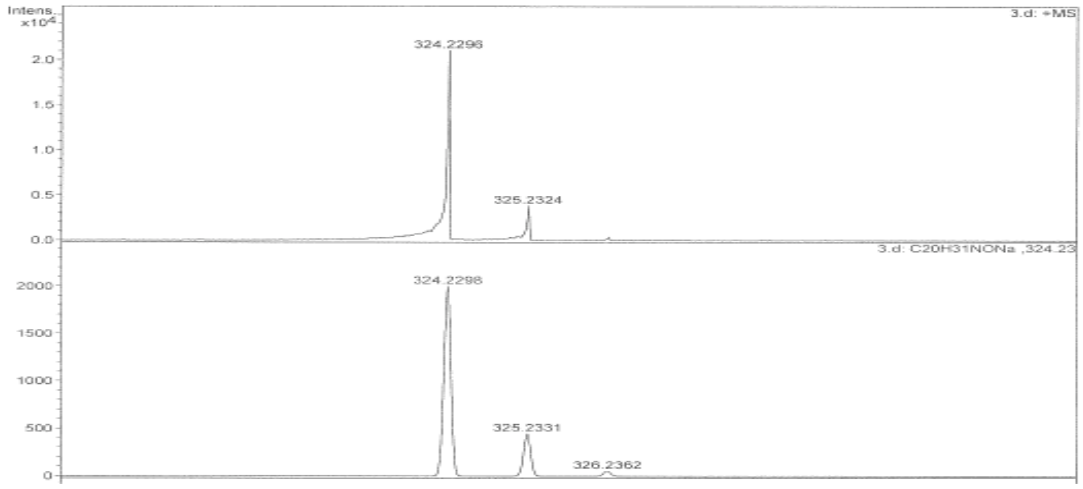


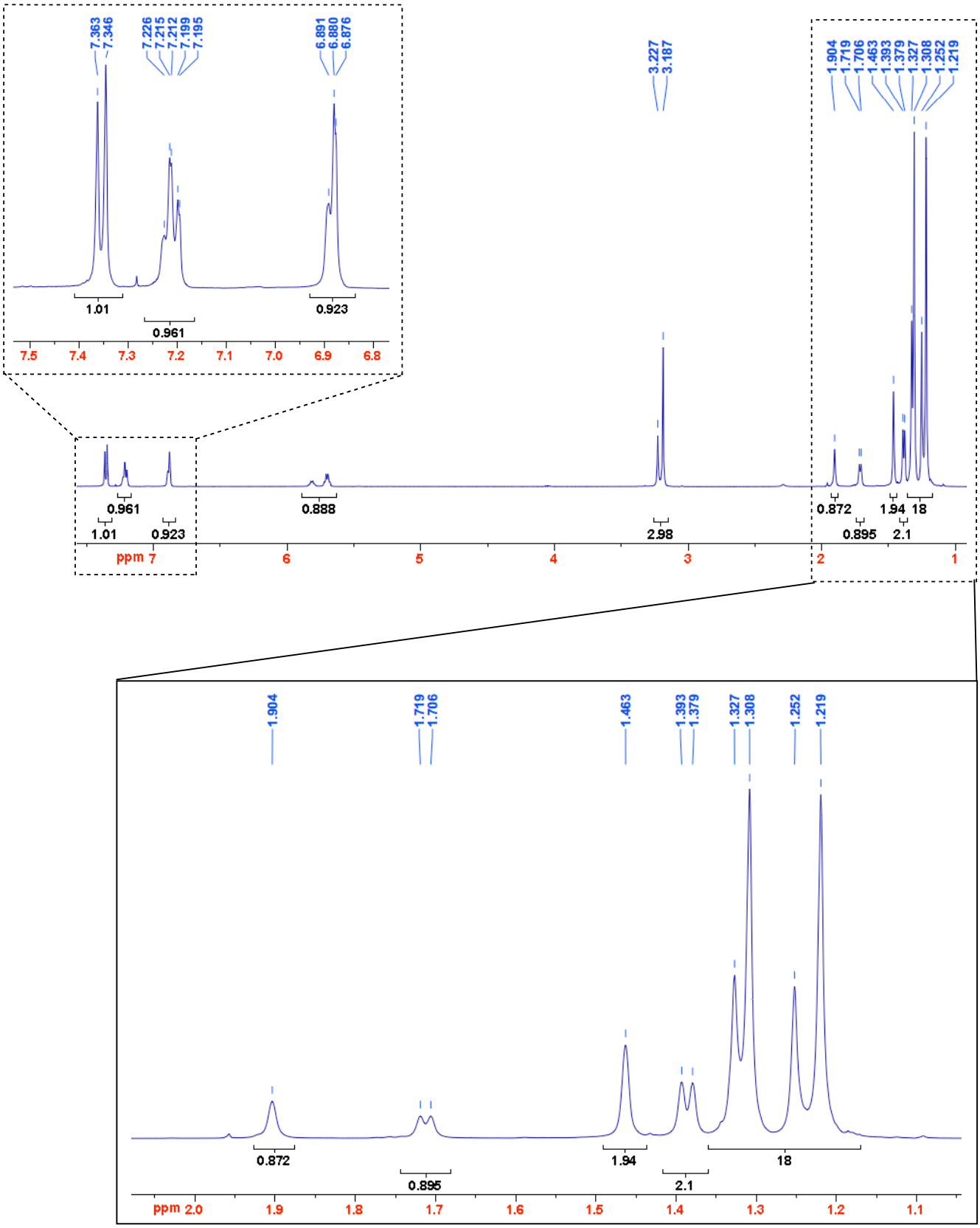
4d

^{1}H *NMR* (500 MHz, $CDCl_3$, δ ppm) 7.36 – 7.34 (m, 1H), 7.23 – 7.20 (m, 1H), 6.89 – 6.87 (m, 1H), 5.84 – 5.80 (q, alkene H minor confomer), 5.72 – 5.68 (q, alkene H major confomer), 3.23 (s, N-Me minor confomer), 3.19 (s, N-Me major confomer), 1.90 (s, α-Me minor confomer), 1.72 – 1.71 (d, β-Me minor confomer), 1.46 (s, α-Me major confomer), 1.39 – 1.38 (d, β-Me major confomer), 1.33 and 1.31 (^{t}Bu, 9H, minor and major confomer), 1.25 and 1.22 (^{t}Bu, 9H, minor and major confomer),.

ESI-MS ($[M + Na]^{+}$): Calculated: 324.2298; Observed: 324.2296

Purified at 20% EtOAc/Hexanes by flash chromatography on silica gel. R*f* = 0.59

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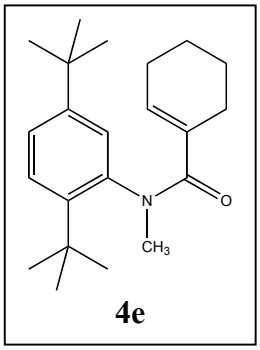
4.5 Di-*tert*-butyl acrylanilide 4e



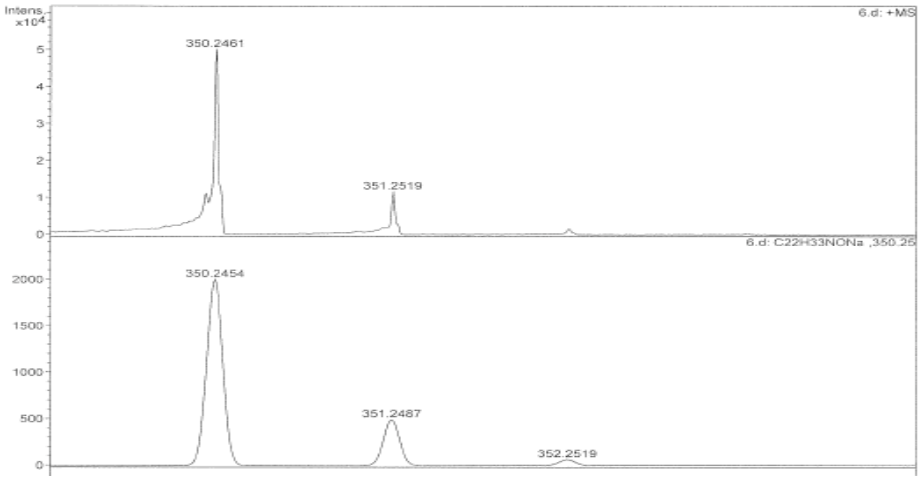
4e

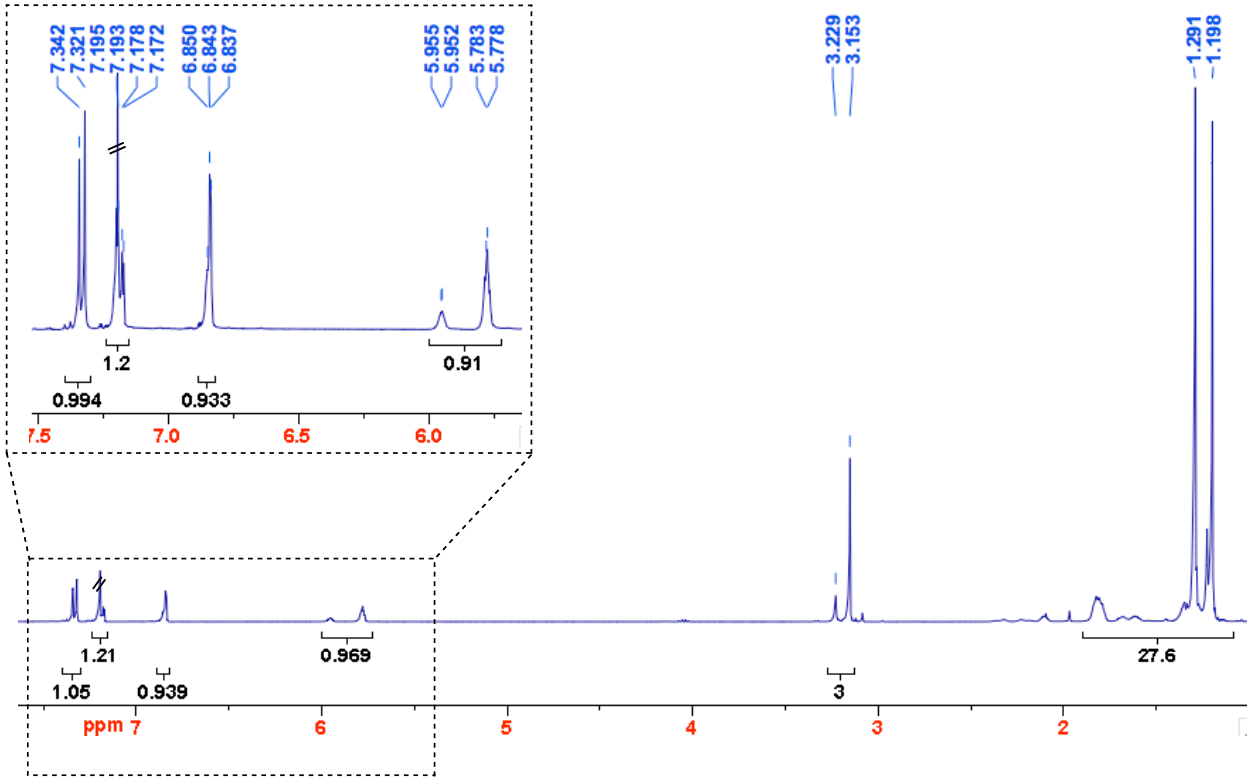
^{1}H *NMR* (400 MHz, $CDCl_3$, δ ppm) 7.41 – 7.35 (m, 1H), 7.27 – 7.20 (m, 1H), 6.92 – 6.86 (m, 1H), 6.03 – 5,96 (m, alkene H minor confomer), 5.86 – 5.79 (m, alkene H, major confomer), 3.23 (s, N-Me minor confomer), 3.15 (s, N-Me major confomer), 1.99 – 1.04 (m, 26H)

^{13}C *NMR* (100 MHz, $CDCl_3$ ppm): 21.57, 22.45, 25.28, 26.67, 31.27, 32.40, 40.51, 124.95, 128.26, 129.94, 133.27, 172.16.

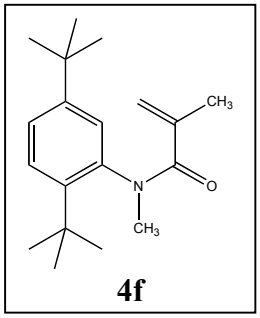
Purified at 15% EtOAc/Hexanes by flash chromatography on silica gel R*f* = 0.60

ESI-MS ($[M + Na]^+$): Calculated: 350.2454; Observed: 350.2461





4.6 Di-*tert*-butyl acrylanilide 4f



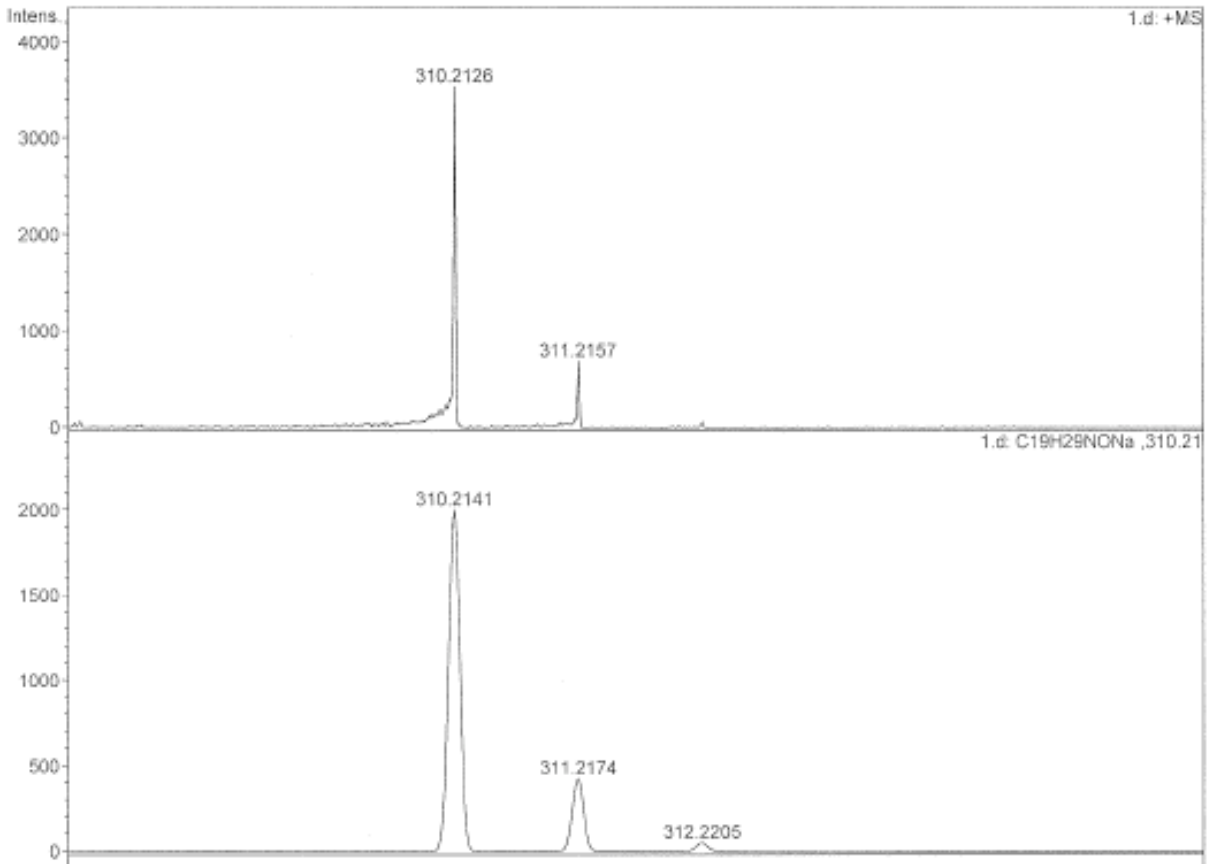
4f

Crude **4f** crystallized upon standing after the reaction was completed; the compound was characterized by NMR spectroscopy

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 7.17 – 7.14 (d, 1H), 7.01 (s, 1H), 6.77 – 6.74 (d, 1H), 5.10 (s, 2H), 2.63 (s, 3H), 1.37 (s, 9H), 1.29 (s, 9H)

ESI-MS ($[M + Na]^+$): Calculated: 310.2141; Observed: 310.2126

R*f* = 0.38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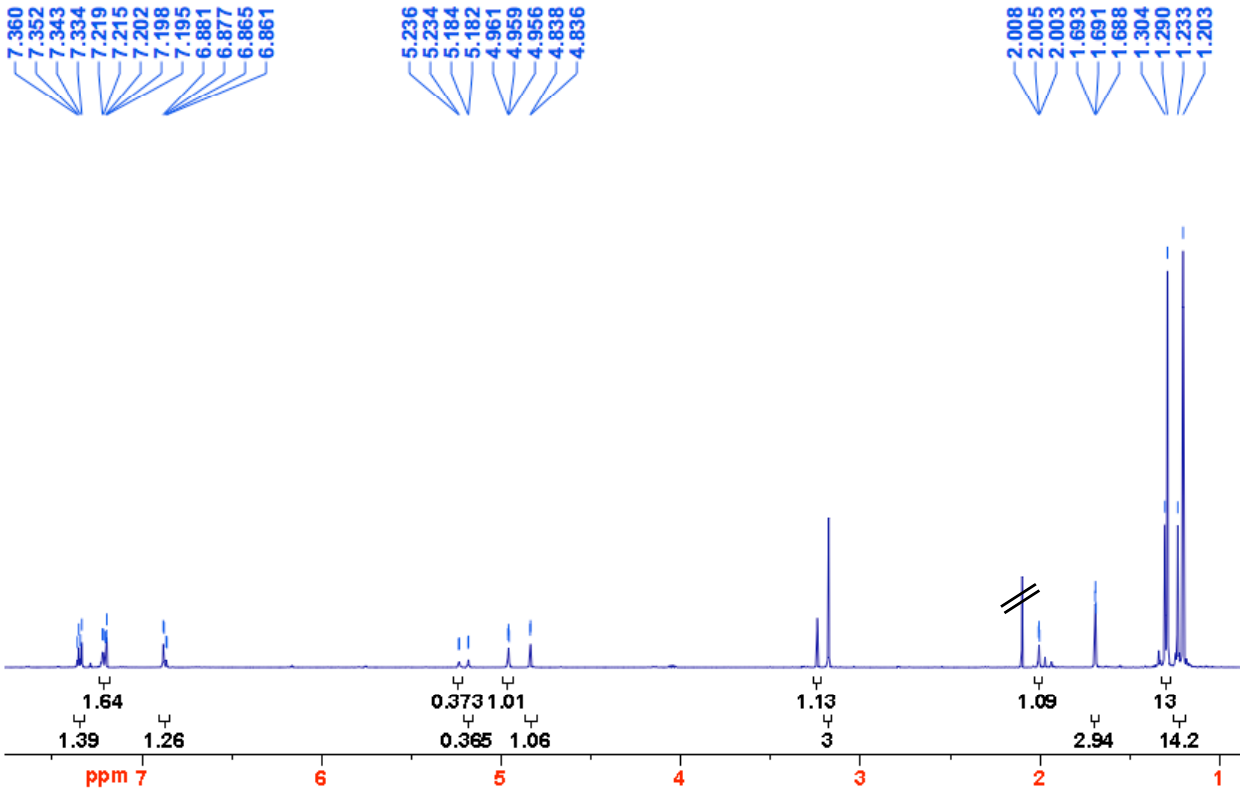
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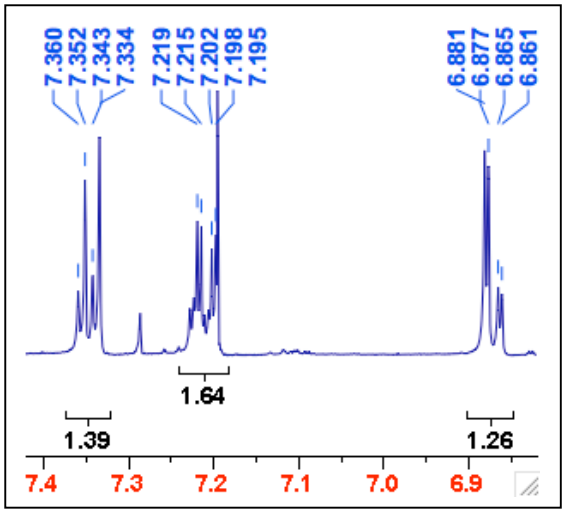
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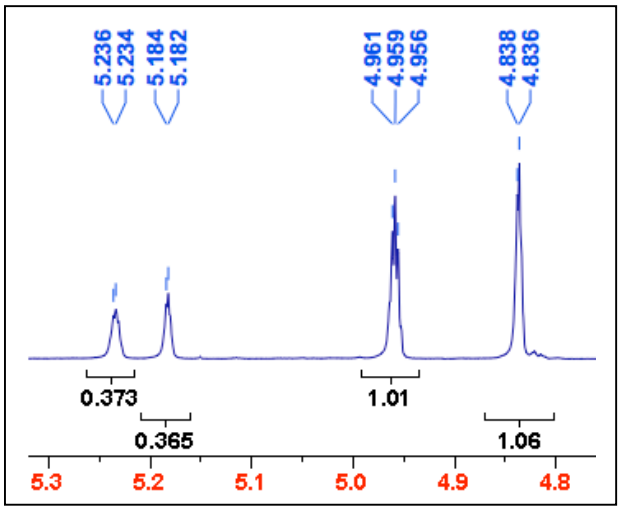
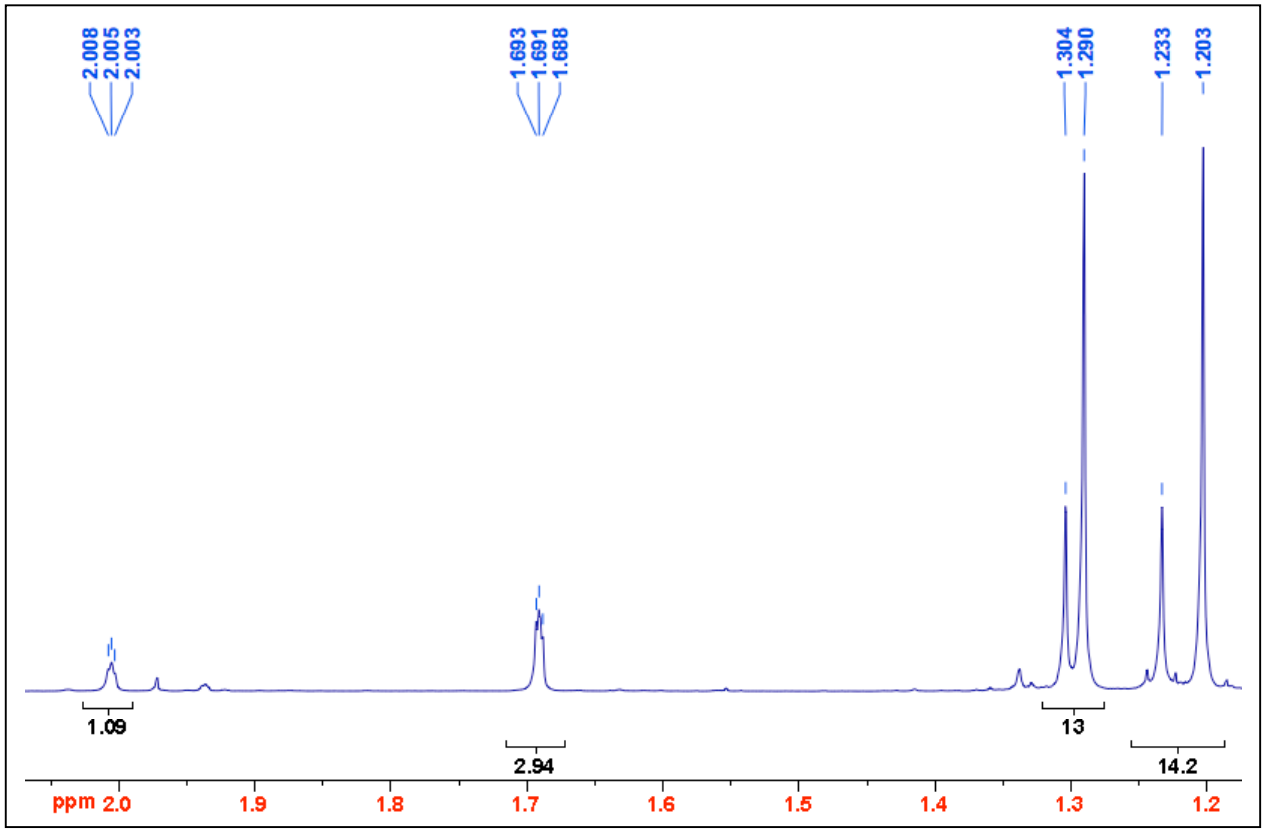
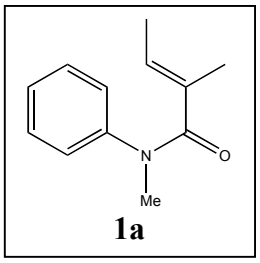
7.0
6.9


5.236
5.234
5.184
5.182
4.961
4.959
4.956
4.838
4.836
0.373
0.365
1.01
1.06
5.3
5.2
5.1
5.0
4.9
4.8



4.7 Parent acrylanilide 1a [3-5]

1a was purified at 30 % EtOAc/Hexanes by flash chromatography on silica gel (R*f* = 0.20); pure **1a** formed upon standing to give white needle like crystals.

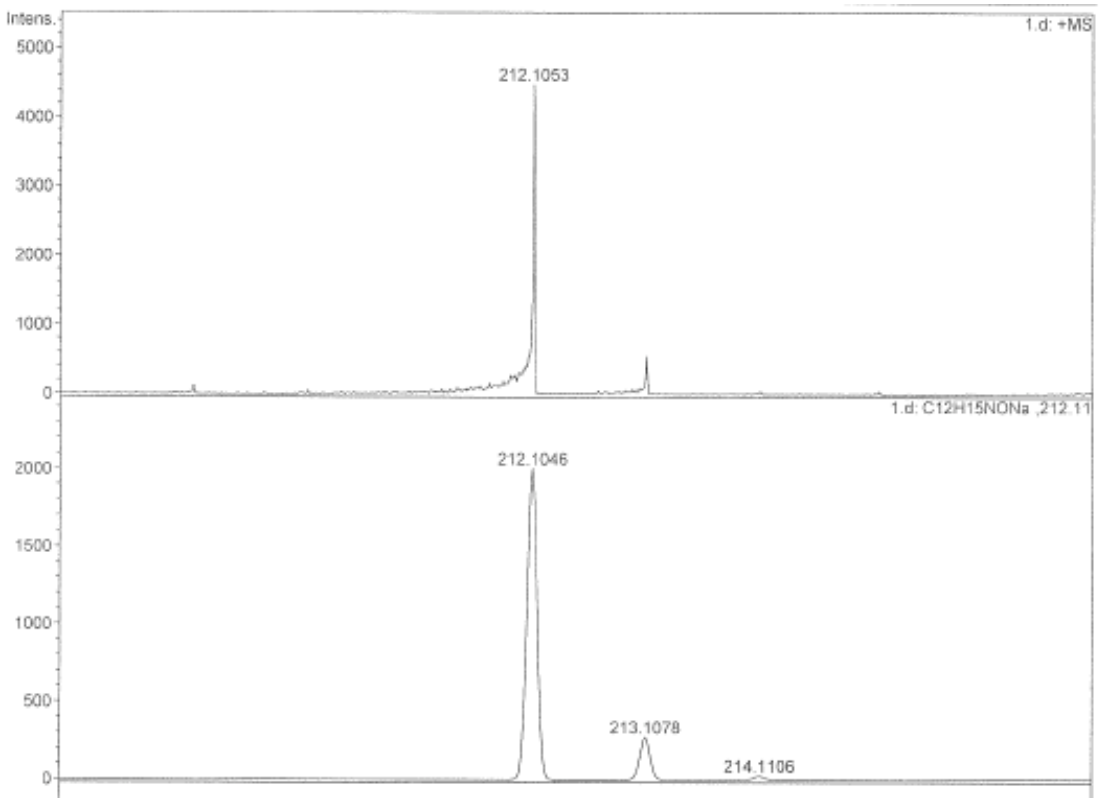


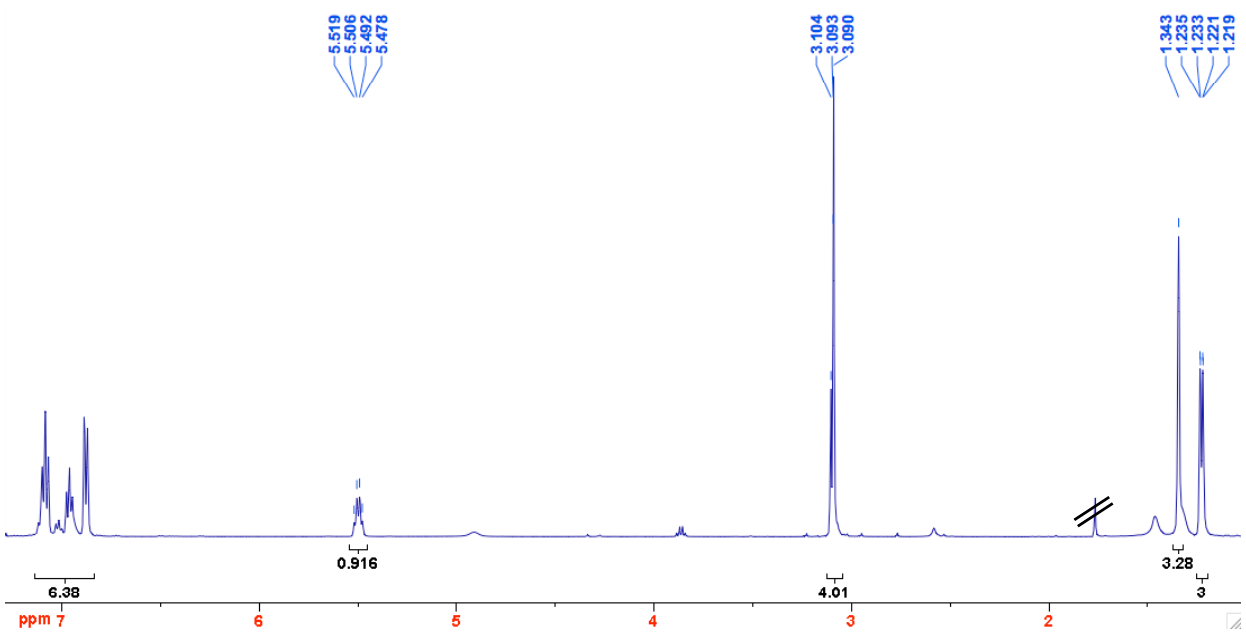
1a

[1]H NMR (500 MHz, $CDCl_3$, δ ppm) 7.14 – 7.05 (t, 2H), 7.00 – 691 (t, 1H), 6.91 – 6.83 (d, 2H), 5.58 – 5.40 (m, 1H), 3.13 – 3.05 (virt. s, 3H). 1.40 – 1.28 (s, 3H), 1.27 – 1.17 (d, *J* = 7, 3H)

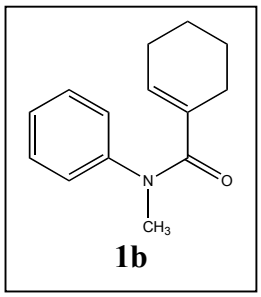
[13]C NMR (125 MHz, $CDCl_3$, δ ppm), 13.29, 14.03, 37.72, 126.34, 126.44, 128.98, 129.14, 130.30, 132.66, 173.09.

ESI-MS ($[M + Na]^+$): Calculated: 212.1046; Observed: 212.1053


Intens.
5000
4000
3000
2000
1000
0
1.d: +MS
212.1053
1.d: C12H15NONa ,212.11
2000
1500
1000
500
0
212.1046
213.1078
214.1106


5.519
5.506
5.492
5.478
3.104
3.093
3.090
1.343
1.235
1.233
1.221
1.219
0.916
3.28
6.38
4.01
3
ppm 7
6
5
4
3
2

4.8 Parent acrylanilide 1b [3-5]

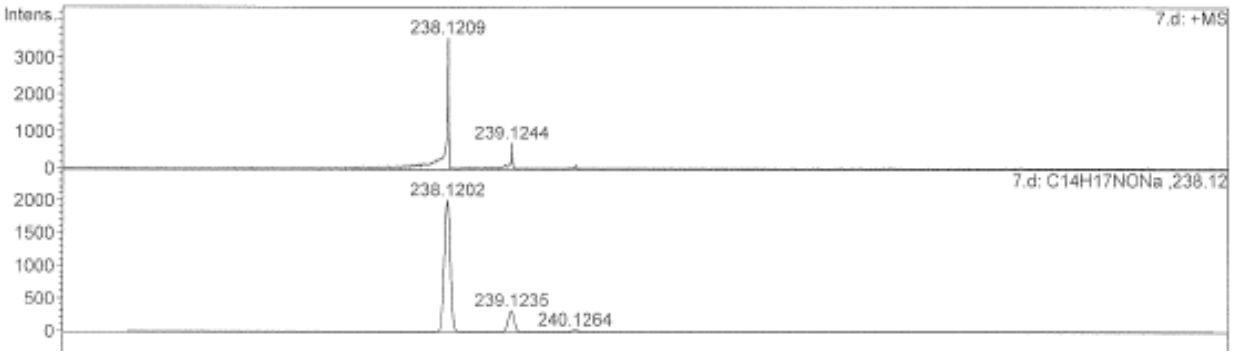


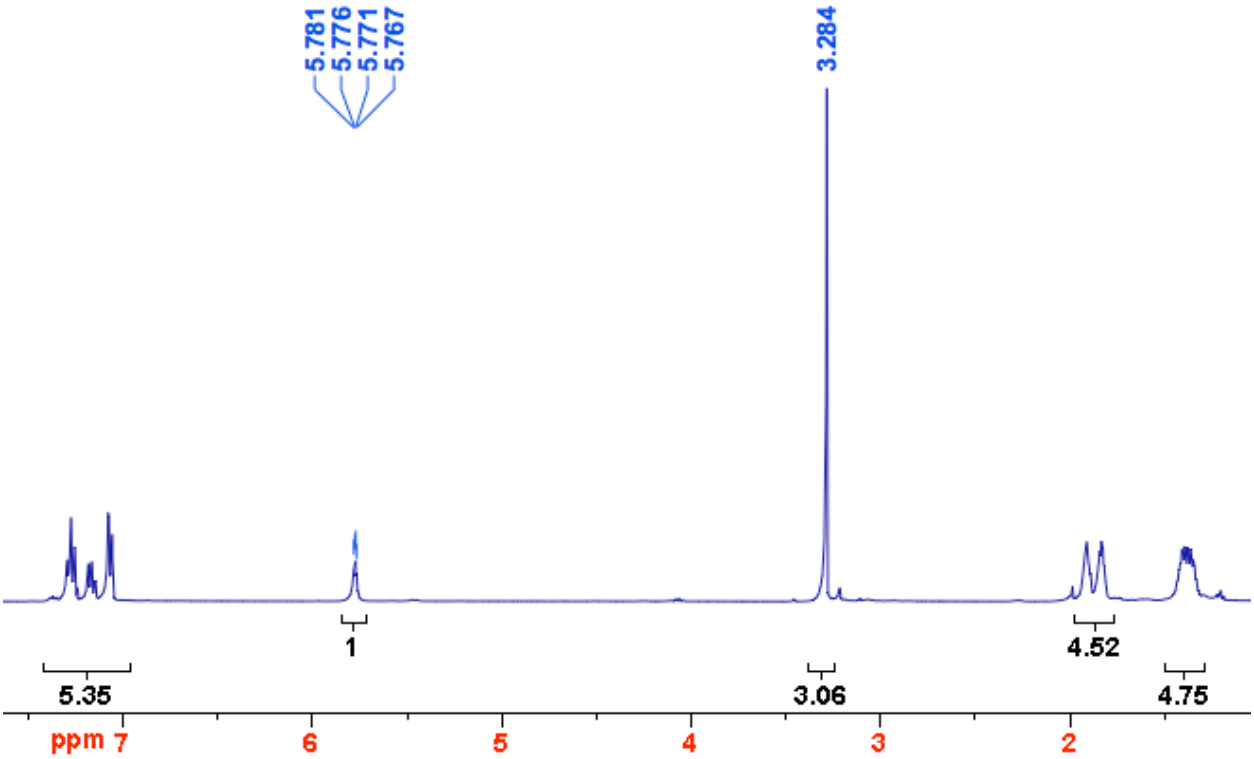
1b

1b was purified at 12 % EtOAc/Hexanes by flash chromatography on silica gel. (R*f* = 0.49)

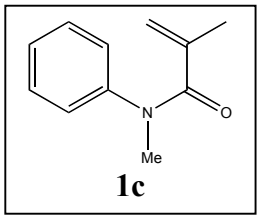
^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) 7.34 – 7.28 (t, 2H), 7.23 – 7.17 (t, 1H), 7.13 – 7.08 (d, 2H), 5.83 – 5.79 (m, 1H), 3.32 (s, 3H), 1.98 – 1.82 (m, 4H), (1.47 – 1.34 (m, 4H)

ESI-MS ($[M + Na]^+$) ($C_{14}H_{17}NO$): Calculated: 238.1202; Observed: 238.1193.





4.9 Parent acrylanilide 1c [3-5]

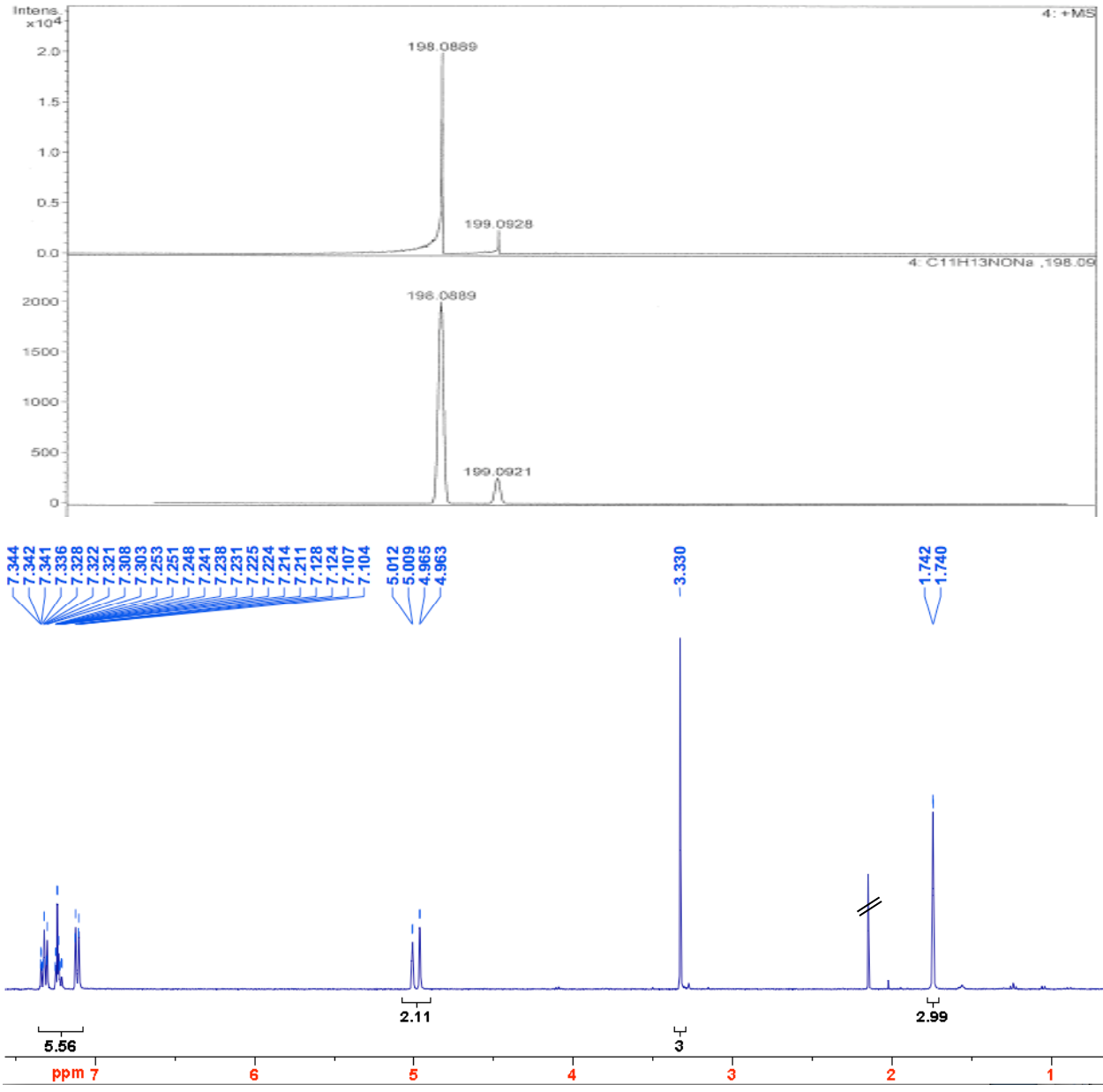


1c

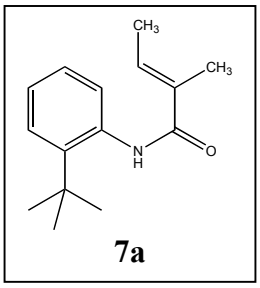
The reaction that led to the formation of **1c** was totally driven to completion (conversion yield: 99 %); thus, no further purification was required. Also, **1c** upon standing formed white needle like crystals at room temperature. R*f* = 0.37

[1]H NMR (500 MHz, $CDCl_3$, δ ppm) 7.35 – 7.27 (t, 2H), 7,25 – 7.18 (t, 1H), 7.14 – 7.07 (d, 2H), 5.02 – 4.91 (d, 2H), 3.31 (s, 3H), 1.76 – 1.69 (s, 3H)

ESI-MS ($[M + Na]^+$): Calculated: 198.0889; Observed: 198.0889



4.10 mono-*o-tert*-butyl-NH acrylanilide 7a



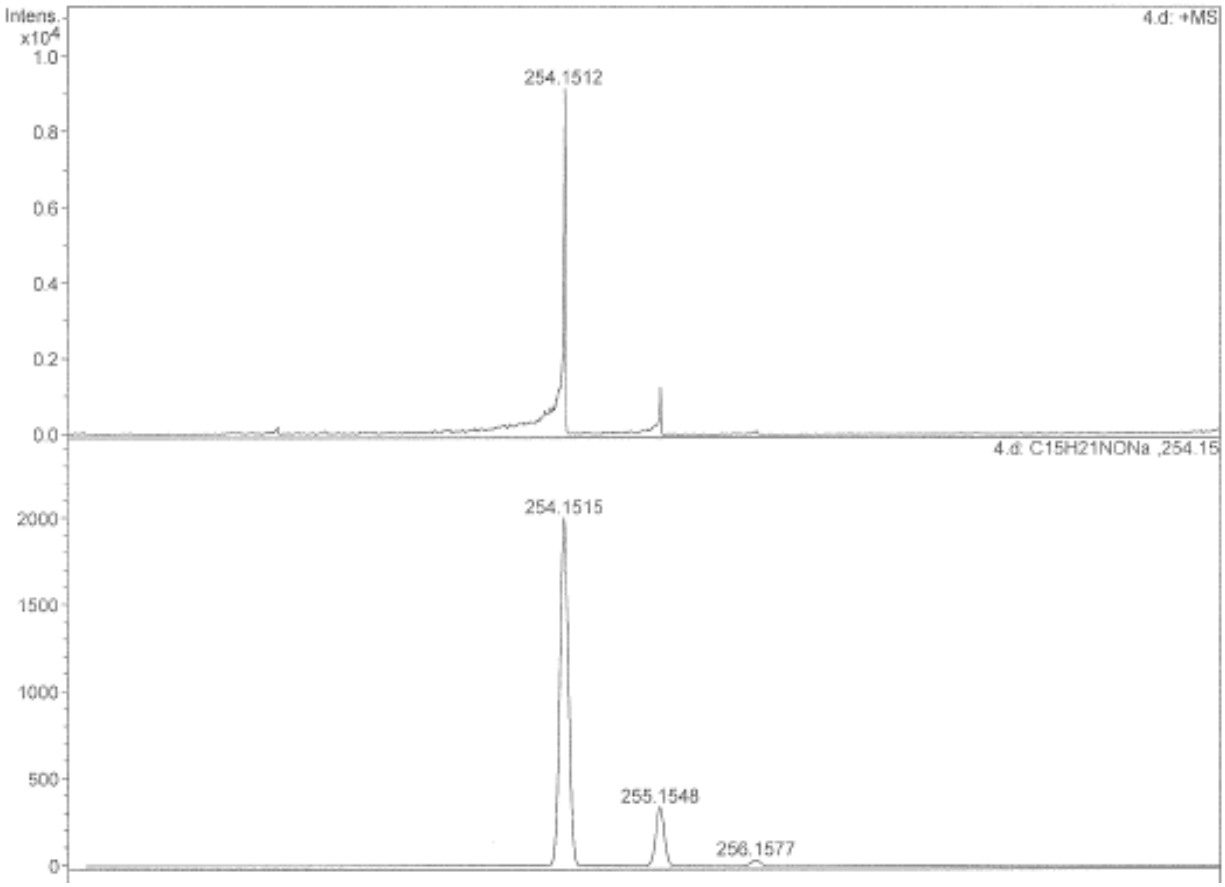
7a

R*f* = 0.45

[1]H NMR (400 MHz, $CDCl_3$, δ ppm) 7.68 – 7.61 (d, *J* = 8.0, 1H), 7.44 (bs, 1H), 7.40 – 7.33 (d, *J* = 8.0, 1H), 7.26 – 7.18 (t, *J* = 7.0, 1H), 7.18 – 7.09 (t, *J* = 7.2, 1H), 6.65 – 6.54 (m, 1H), 2.01 – 1.94 (m, 3H), 1.86 – 1.78 (m, 3H), 1.40 (s, 9H)

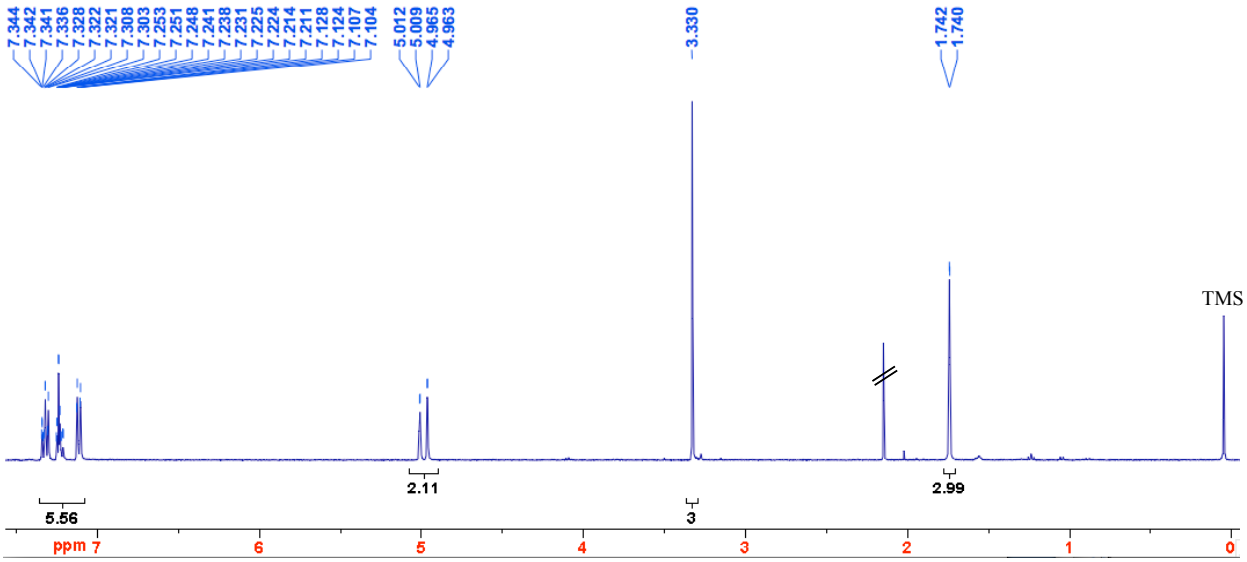
[13]C NMR (125 MHz, $CDCl_3$, δ ppm) 167.62, 142.51, 135.74, 132.75, 131.79, 127.95, 127.07, 126.72, 126.12, 34.80, 30.92, 14.43, 12.91

ESI-MS ($[M + Na]^+$): Calculated: 254.1515; Observed: 254.1512

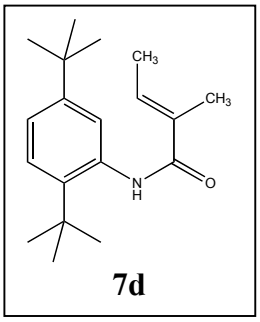


HPLC analysis conditions:

Column: (R,R) WHELK–01; Abs. detector: 254 nm and 270 nm
Mobile phase: Hexanes: IPA = 93:07; Flow rate: 1 mL/min
Retention time (min): ~ 35.55


7.344
7.342
7.341
7.336
7.328
7.322
7.321
7.308
7.303
7.253
7.251
7.248
7.241
7.238
7.231
7.225
7.224
7.214
7.211
7.128
7.124
7.107
7.104
5.012
5.009
4.965
4.963
3.330
1.742
1.740
TMS
2.11
2.99
5.56
3
ppm 7
6
5
4
3
2
1
0

4.11 Mono-*o-tert*-butyl-NH acrylanilide 7d



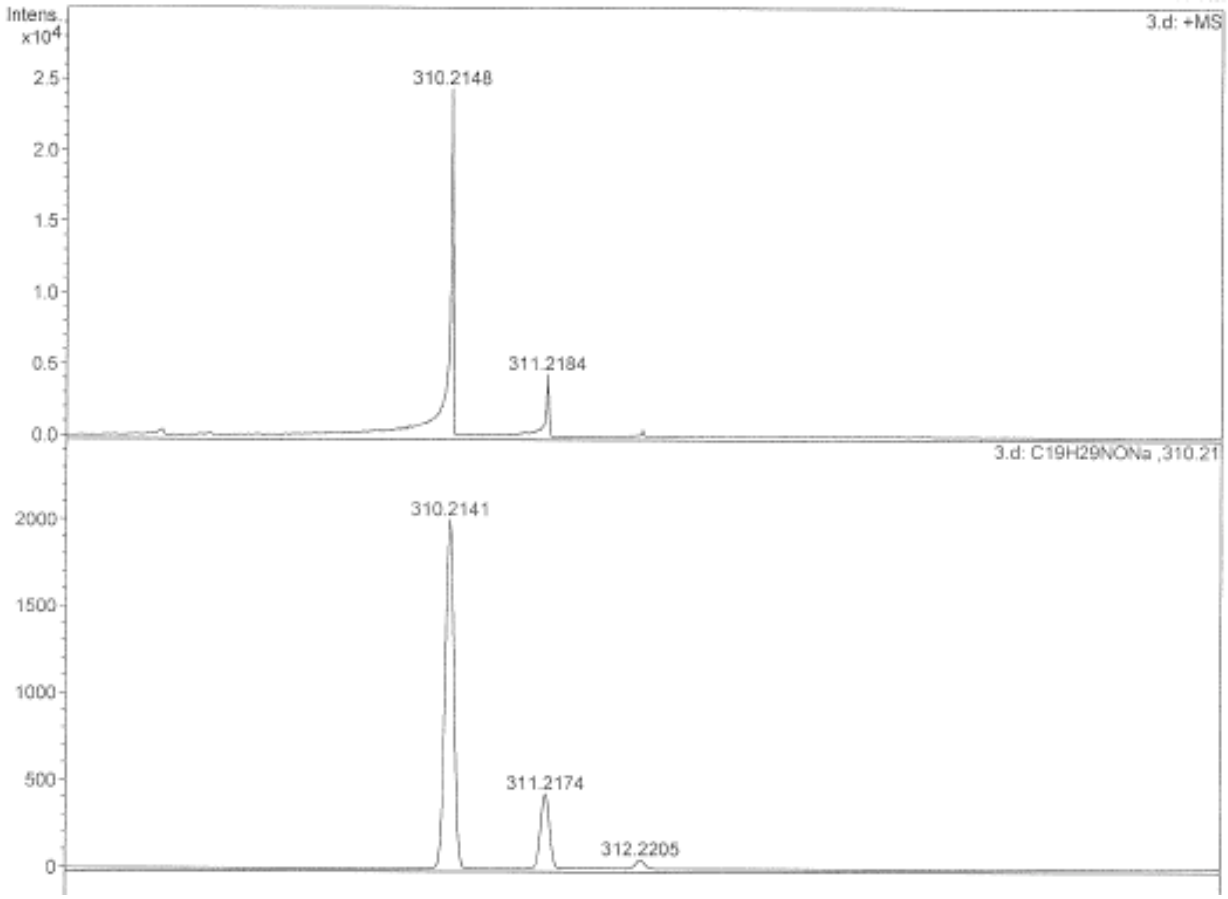
7d

R*f* = 0.56

^{1}H *NMR* (500 MHz, $CDCl_3$, δ ppm) 7.75 (Ar, 1H), 7.49 (bs, 1H), 7.57 – 7.42 (d, *J* = 8.5, 1H), 7.38 – 7.31 (d, *J* = 8.5, 1H), 6.69 – 6.59 (m, 1H), 2.01 (s, 3H), 1.90 – 1.84 (d, *J* = 7, 3H), 1.43 (s, 9H), 1.34 (s, 9H)

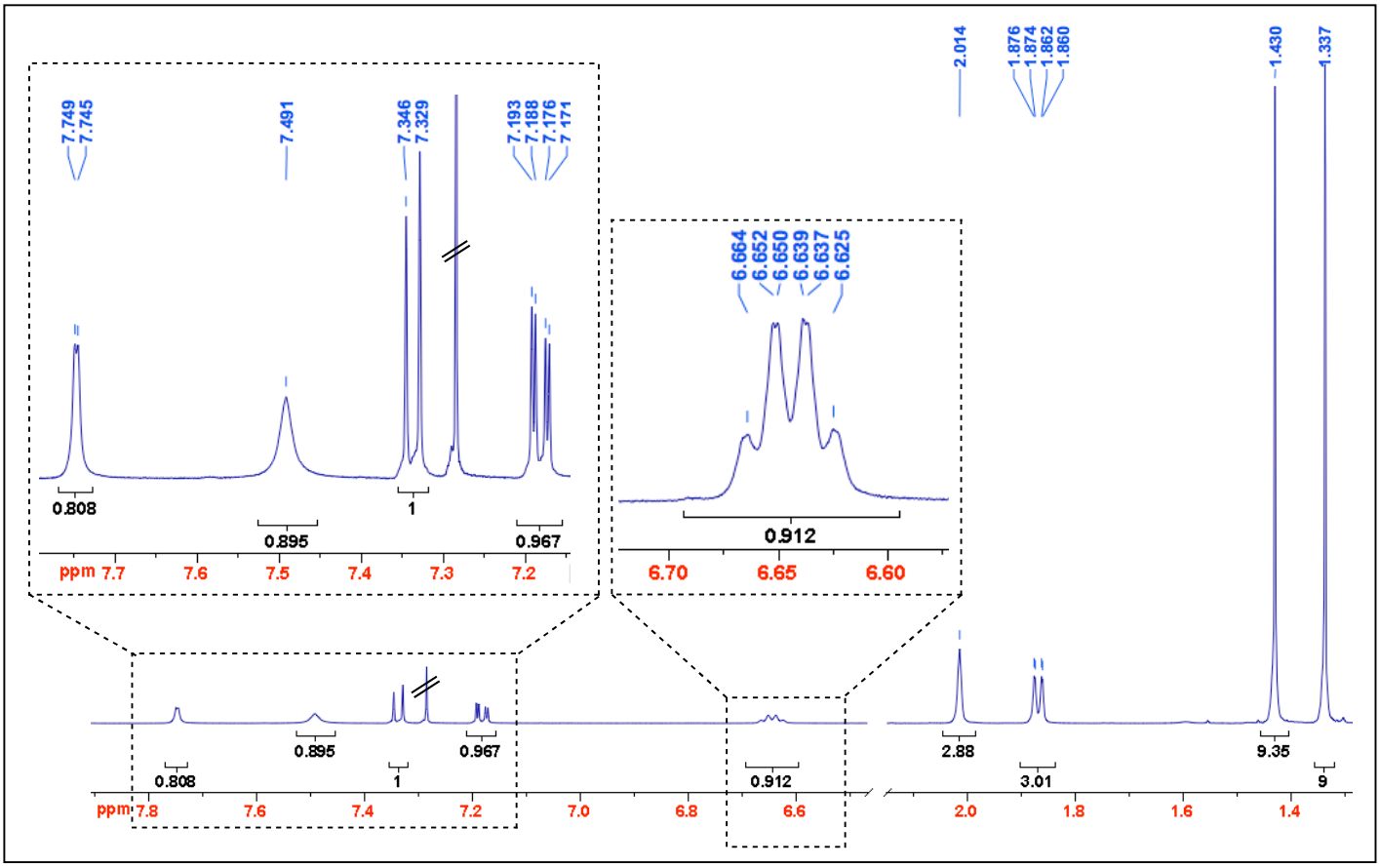
^{13}C *NMR* (125 MHz, $CDCl_3$, δ ppm) 187.84, 149.89, 139.19, 135.37, 131.69, 126.37, 124.87, 122.89, 34.55, 34.39, 31.48, 30.98, 14.43, 12.91

ESI-MS ($[M + Na]^+$): Calculated: 310.2148; Observed: 310.2141

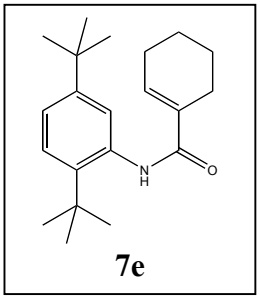


HPLC analysis conditions:

Column: (R,R) WHELK–01; Abs. detector: 254 nm and 270 nm
Mobile phase: Hexanes: IPA = 93:07; Flow rate: 1 mL/min
Retention time (min): ~13.69


7.749
7.745
7.491
7.346
7.329
7.193
7.188
7.176
7.171
6.664
6.652
6.650
6.639
6.637
6.625
2.014
1.876
1.874
1.862
1.860
1.430
1.337
0.808
0.895
1
0.967
0.912
2.88
3.01
9.35
9
ppm

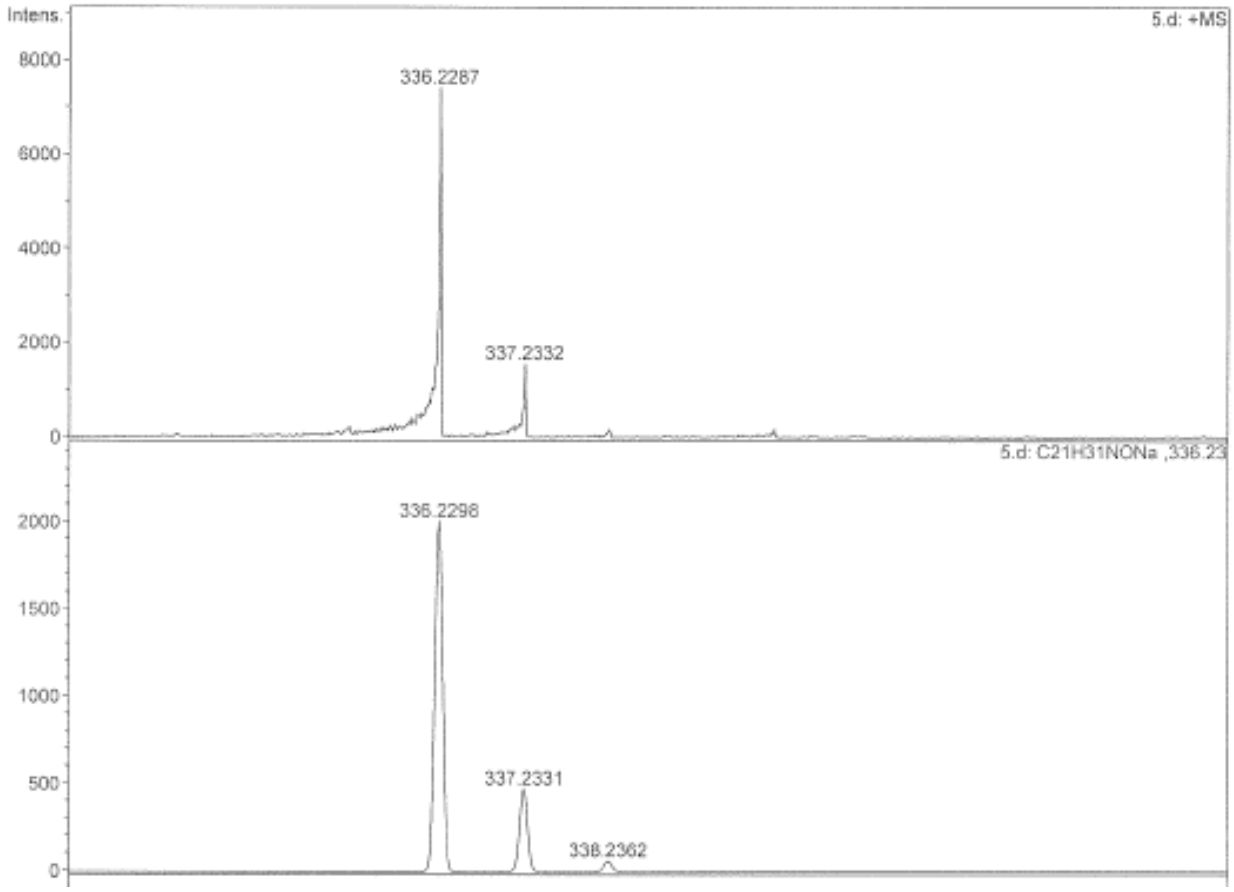
4.12 Mono-*o-tert*-butyl-NH acrylanilide 7e
R*f* = 0.64



7e

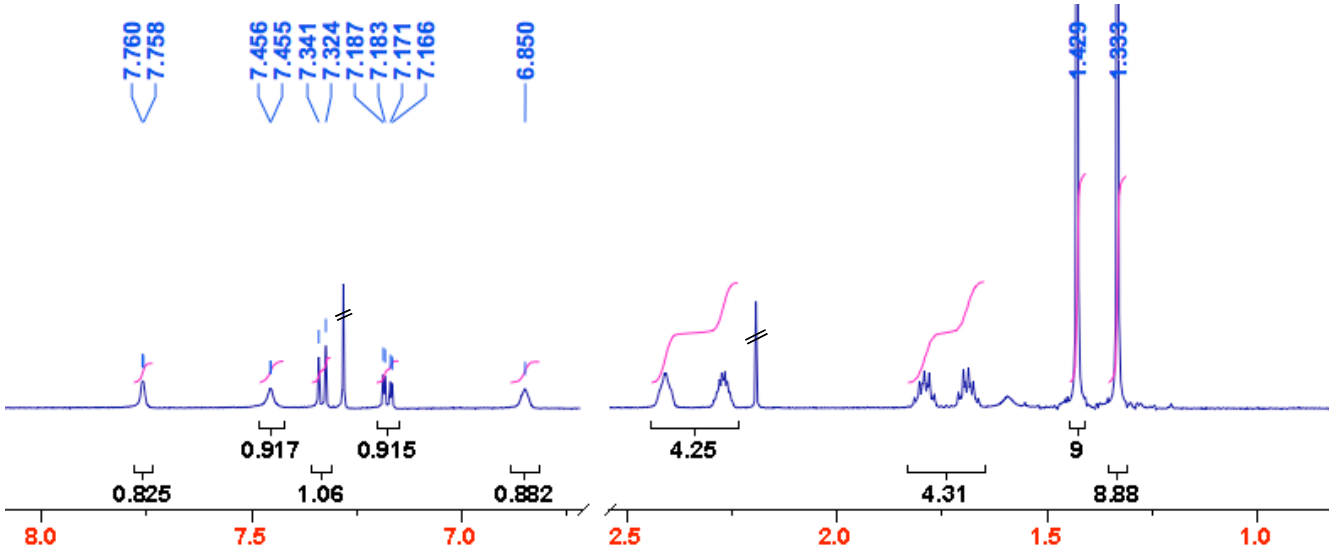
[1]H NMR (400 MHz, $CDCl_3$, δ ppm) 7.76 (Ar, 1H), 7.45 (bs, 1H), 7.36 – 7.32 (d, *J* = 6.8, 1H), 7.20 – 7.15 (d, *J* = 6.4, 1H), 6.85 (dd, 1H), 2.46 – 2.23 (m, 4H), 1.84 – 1.64 (m 4H), 1.43 (s, 9H), 1.33 (s, 9H)

ESI-MS ($[M + Na]^+$): Calculated: 336.2298; Observed: 336.2287

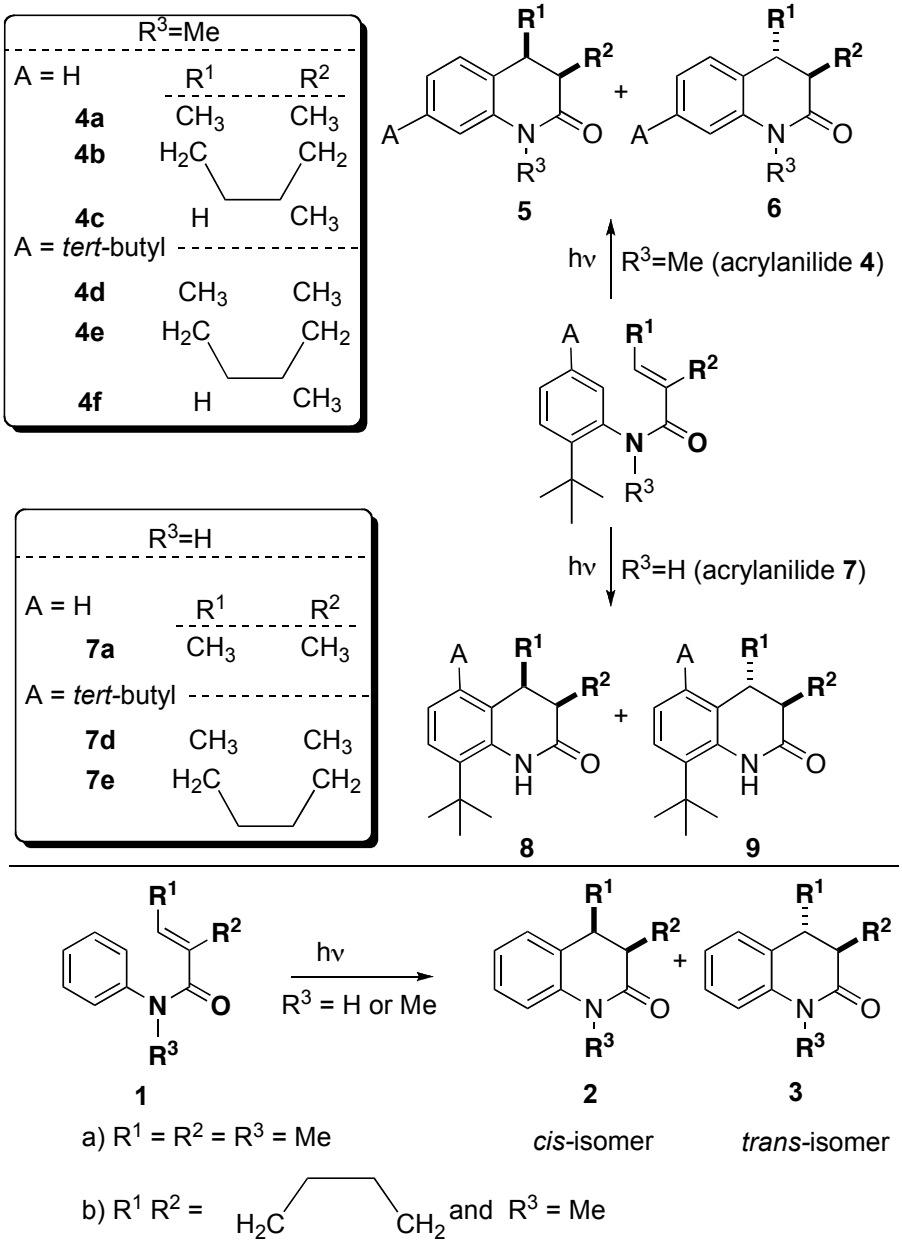


HPLC analysis conditions:

Column: (R,R) WHELK–01; Abs. detector: 254 nm and 270 nm
Mobile phase: Hexanes: IPA = 90:10; Flow rate: 1 mL/min
Retention time (min): ~ 13.09


7.760
7.758
7.456
7.455
7.341
7.324
7.187
7.183
7.171
7.166
6.850
1.429
1.333
0.825
0.917
1.06
0.915
0.882
4.25
4.31
9
8.88
8.0
7.5
7.0
2.5
2.0
1.5
1.0

5. General Irradiation Procedures for acrylanilides 1, 4 and 7

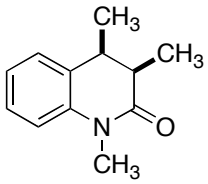


Scheme S3

Solutions of acrylanilides (0.1mmol) in 15 mL of the selected solvent were irradiated for 3 - 5 h in Pyrex tubes with a 450 W) at room temperature and under constant flow of nitrogen. The reaction was monitored by TLC. After 5 h of irradiation, the solvent was removed under reduced pressure and the photoproducts were characterized by NMR spectroscopy. The *cis/trans* ratio in the photoproducts was calculated from NMR and from chromatographic analysis (HPLC / GC) of the photolysate.

6. Characterization of photoproducts

6.1 *cis*-Photoproduct 2a (= 5a)



2a (= **5a**)

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) 7.29 – 7.22 (Ar, 1H), 7.19 – 7.13 (Ar, 1H), 7.07 – 7.01 (Ar, 1H), 7.00 – 6.94 (Ar, 1H), 3.36 (s, 3H), 3.02 – 2.92 (m, 1H), 2.81 – 2.71 (m, 1H), 1.21 – 1.16 (d, J = 7, 3H), 1.15 – 1.10 (d, J = 7, 3H)

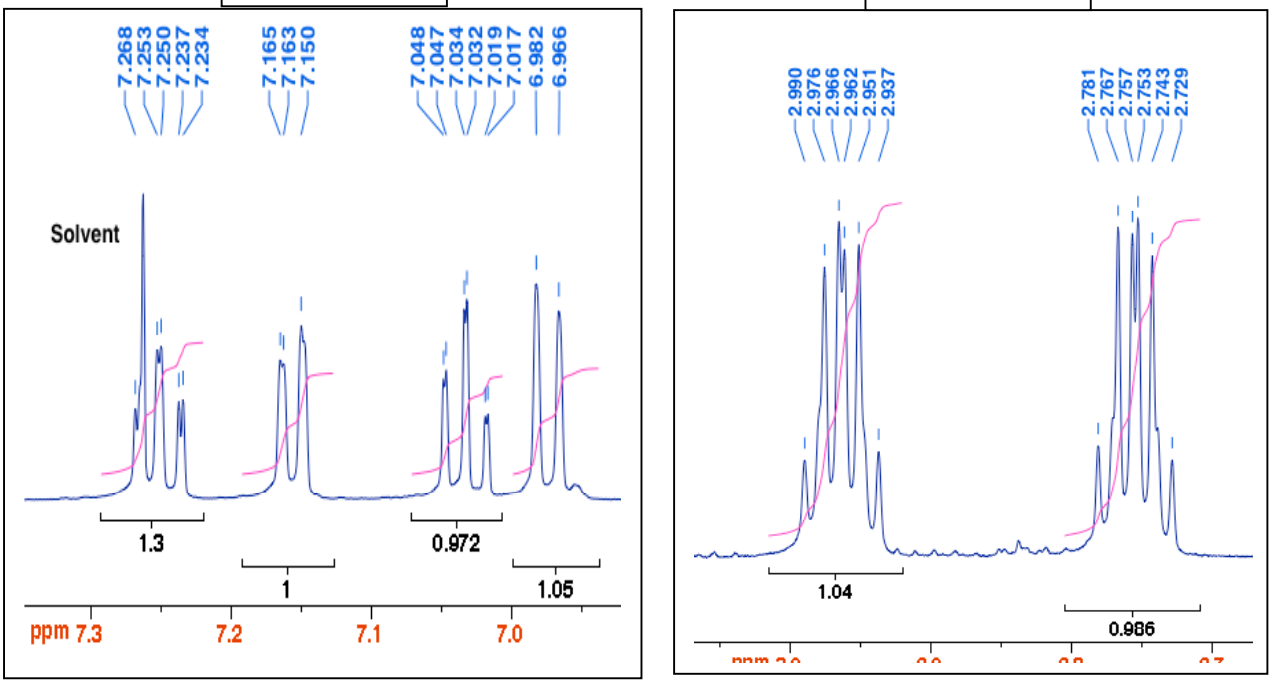
Rf = 0.54

ESI-MS ([M + Na]$^+$): Calculated: 212.1046; Observed: 212.1034

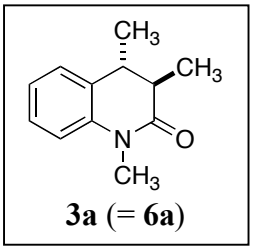
Note: The photoproducts were separated from the starting material **1a** by preparative chromatography on TLC plate (Eluting Solvent: 8 % EtOAc/Hexanes).

HPLC analysis conditions: Column: (R,R) WHELK–01; Abs. detector: 254 nm and 270 nm
Mobile phase: Hexanes: IPA = 93: 07; Flow rate: 1 mL/min
Retention time (min): ~16.9 (**2a**)
(*ent*-**2a** does not resolve in the condition employed)

^{1}H NMR (Aromatic hydrogens (left) and α and β hydrogens (right) of compound **2a** (= **5a**).



6.2 *trans*-Photoproduct 3a (= 6a)



3a (= 6a)

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) 7.29 – 7.23 (Ar, 1H), 7.21 – 7.16 (Ar, 1H), 7.09 – 7.02 (Ar, 1H), 7.01 – 6.97 (Ar, 1H), 3.37 (s, 3H), 2.75 – 2.67 (m, 1H), 2.59 – 2.51 (m, 1H), 1.25 – 1.21 (d, J = 7.5, 3H), 1.14 – 1.10 (d, J = 7, 3H)

ESI-MS ($[M + Na]^+$): Calculated: 212.1046; Observed: 212.1034

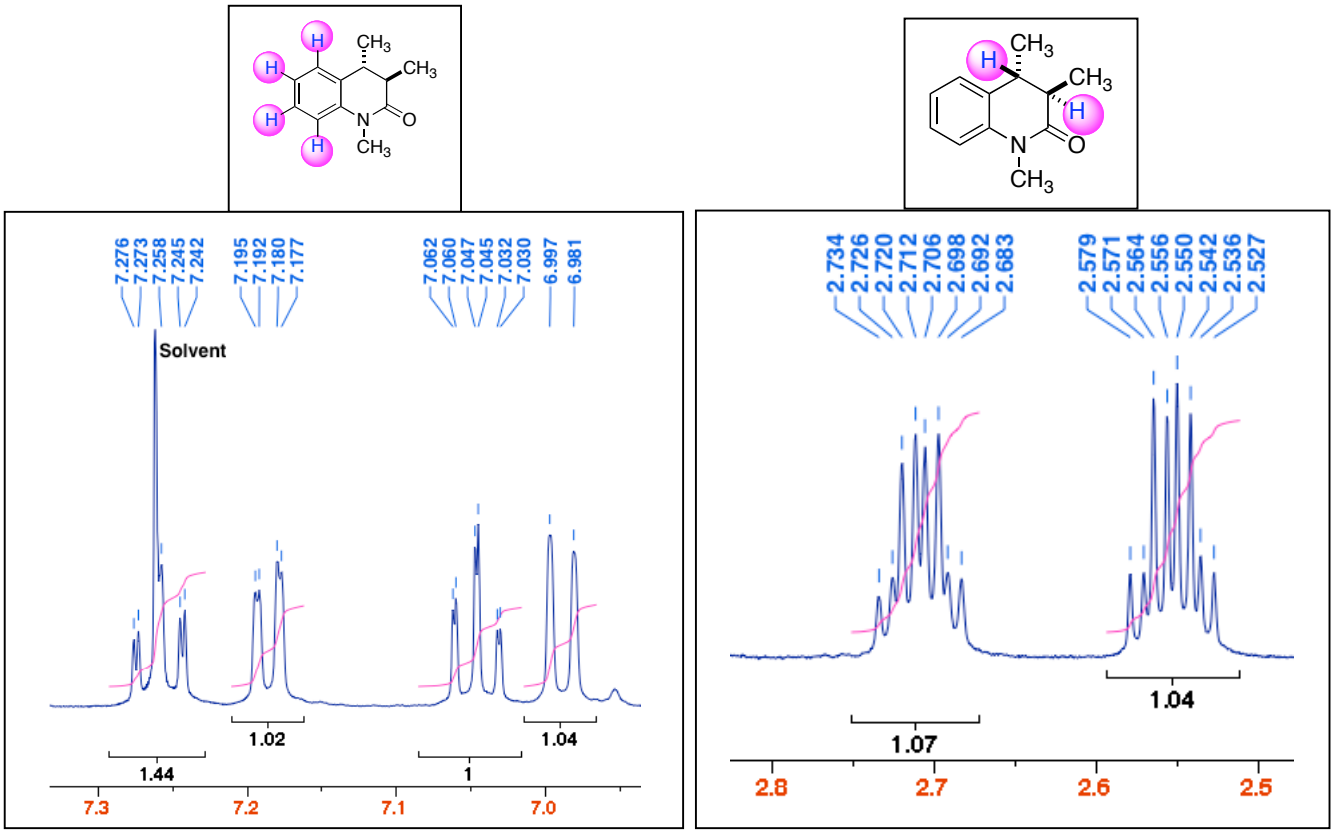
Rf = 0.46

HPLC analysis conditions:

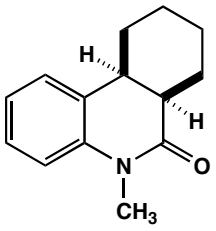
Column: (R,R) WHELK–01; Abs. detector: 254 nm and 270 nm
Mobile phase: Hexanes:IPA = 93:07; Flow rate: 1 mL/min
Retention time (min): ~17.5 (**3a**) and ~20.3 (*ent*-**3a**)

^{1}H NMR (Aromatic hydrogens (left) and α and β hydrogens (right) of compound **3a** (= **6a**).

Note: The *trans* photoproducts were separated from the starting material by chromatography (Eluting Solvent: 8 % EtOAc/Hexanes).



6.3 *cis*-Photoproduct 2b (= 5b)



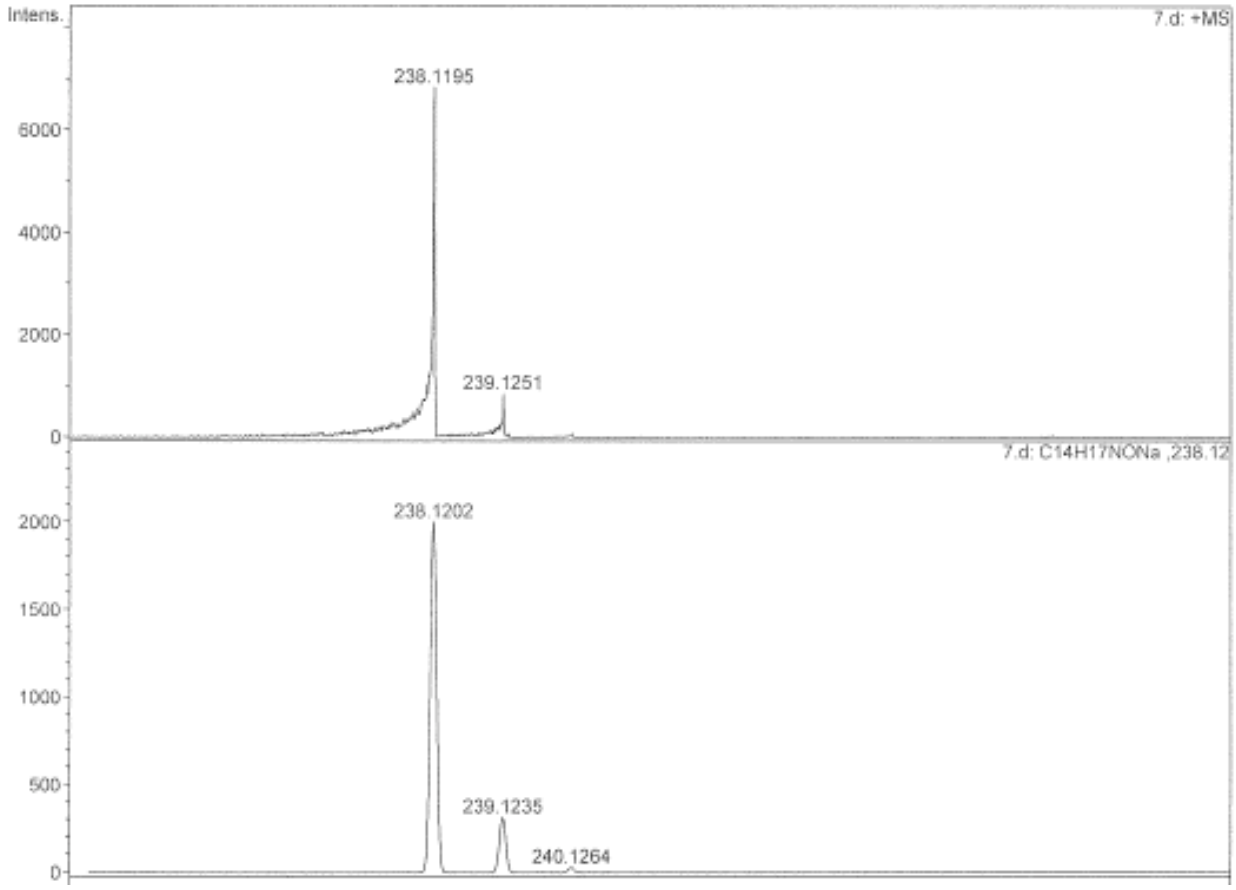
2b (= **5b**)

^{1}H *NMR* (500 MHz, $CDCl_3$, δ ppm) 7.31 – 7.24 (Ar, 1H), 7.21 – 7.16 (Ar, 1H), 7.09 – 7.03 (Ar, 1 H), 7.01 – 6.97 (Ar, 1H), 3.4 (s, 3H), 2.96 – 2.87 (m, 1H), 2.86 – 2.77 (m, 1H), 1.83 – 1.14 (m, 8H)

^{13}C *NMR* (100 MHz, $CDCl_3$ δ ppm) 25.36, 25.42, 27.10, 29.00, 30.06, 37.23, 43.68, 114.65, 123.00, 124.13, 127.43, 130.77, 172.67

ESI-MS ($[M + Na]^+$): Calculated: 238.1202; Observed: 238.1195

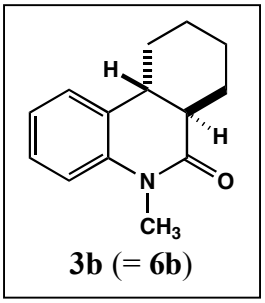
R*f* = 0.67



HPLC analysis conditions:

Column: (R,R) WHELK–01; Abs. detector: 254 nm and 270 nm
Mobile phase: Hexanes : IPA = 90:10; Flow rate: 1 mL/min
Retention time (min): ~14.87 (**2b**) and ~15.89 (*ent*-**2b**)

6.4 *trans*-Photoproduct 3b (= 6b)



3b (= **6b**)

^{1}H *NMR* (500 MHz, $CDCl_3$, δ ppm) 7.32 – 723 (Ar, 2H), 7.12 – 7.06 (Ar, 1H), 7.03 – 7.6.97 (Ar, 1H), 3.39 (s, 3H), 2.63 – 2.53 (m, 1H), 2.52 – 2.45 (m, 1H), 2.11 – 1.84 (m, 4H), 1.48 – 1.31 (m, 4H)

^{13}C NMR (100 MHz, $CDCl_3$ δ ppm) 25.36, 25.42, 27.10, 29.00, 30.06, 37.23, 43.68, 114.65, 123.00, 124.13, 127.43, 130.77, 172.67

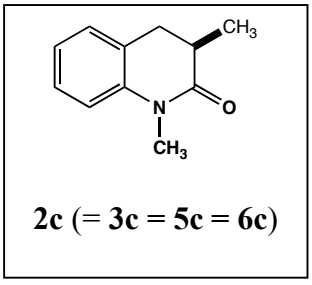
ESI-MS ($[M + Na]^+$): Calculated: 238.1202; Observed: 238.1195

R*f* = 0.63

HPLC analysis conditions:

Column: (R,R) WHELK–01; Abs. detector: 254 nm and 270 nm
Mobile phase: Hexanes:IPA = 90:10; Flow rate: 1 mL/min
Retention time (min): ~24.15 (**3b**) and ~29.52 (*ent*-**3b**)

6.5 Photoproduct 2c (= 3c = 5c = 6c)

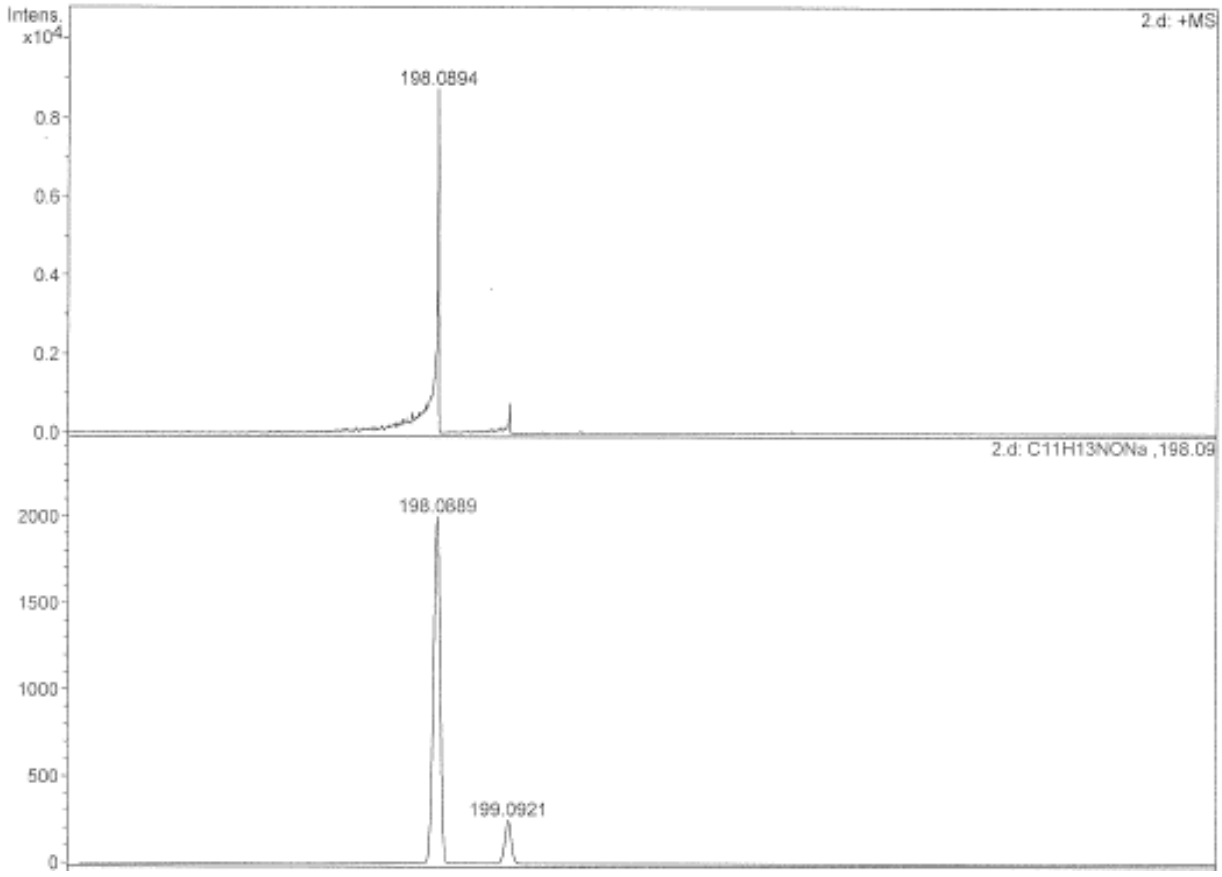


2c (= **3c = 5c = 6c**)

cis and *trans* isomers not feasible in photoproducts from methacryloyl derivatives **4c**. Hence **2c = 3c = 5c = 6c.**
R*f* = 0.44 (Eluting Solvent: 10 % EtOAc/Hexanes).

^{1}H *NMR* (500 MHz, $CDCl_3$, δ ppm) 7.28 – 7.23 (Ar, 1H), 7.18 – 7.14 (Ar, 1H), 7.04 – 6.99 (Ar, 1H), 6.99 – 6.95 (Ar, 1H), 3.36 (s, 3H), 2.97 – 2.89 (m, 1H), 2.74 – 2.55 (m, 2H), 1.29 – 1.23 (d, *J* = 7, 3H)
^{13}C-*NMR* (100 MHz, $CDCl_3$ δ ppm): 15.89, 30.0, 33.52, 35.70, 114.67, 122.88, 125.94, 127.58, 128.05, 140.62, 173.40

ESI-MS ($[M + Na]^+$): Calculated: 198.0889; Observed: 198.0894



HPLC analysis conditions:

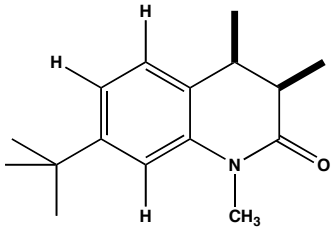
Column: (R,R) WHELK–01; Abs. detector: 254 nm and 270 nm
Mobile phase: Hexanes:IPA = 98:02; Flow rate: 1 mL/min
Retention time (min): ~34.50 (**2c**) and ~39.30 (*ent*-**2c**)

6.6 *cis*-Photoproduct 5d

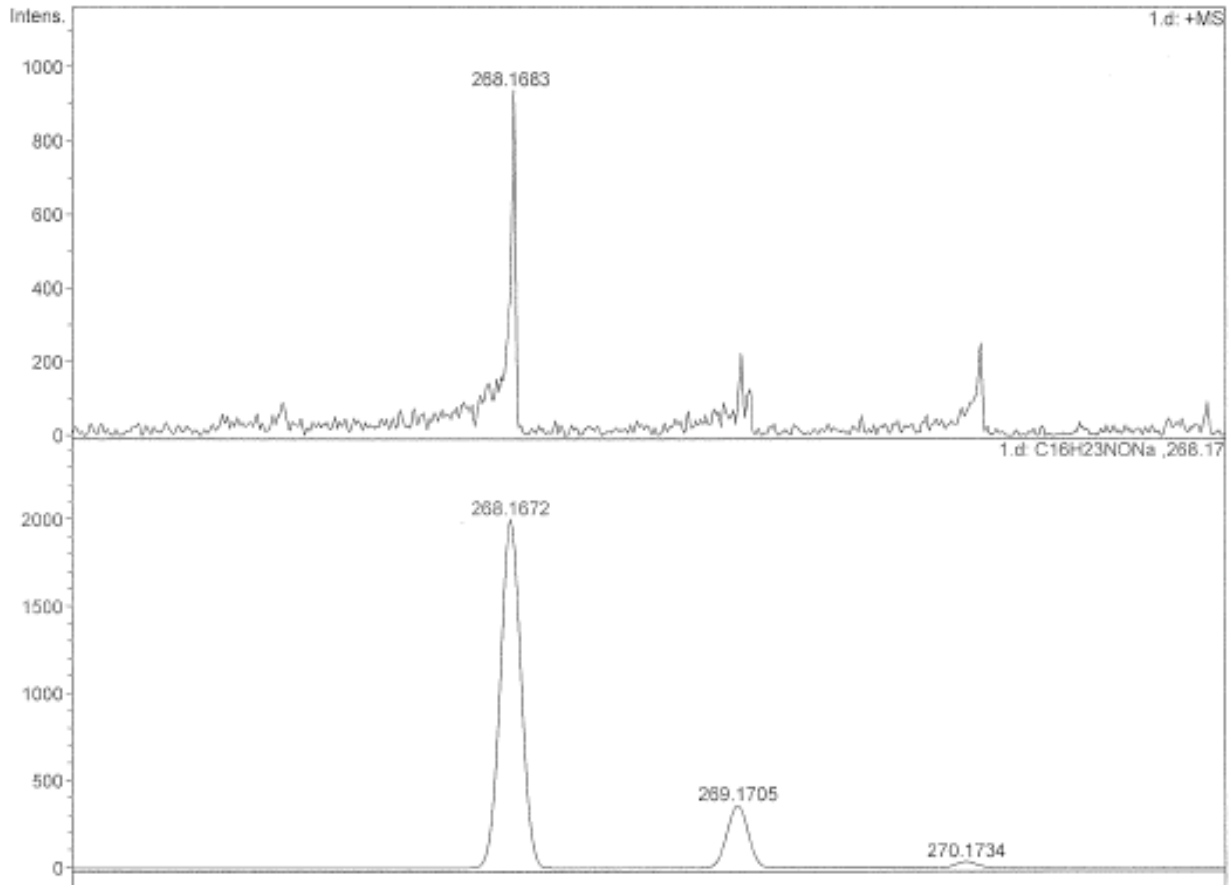
^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) 7.10 – 6.96 (Ar, 3H), 3.38 (s, 3H), 2.97 – 2.88 (m, 1H), 2.78 – 2.69 (m, 1H), 1.33 (s, 9H), 1.19 – 1.15 (d, *J* = 7, 3H), 1.12 – 1.08 (d, *J* = 7, 3H)

ESI-MS ($[M + Na]^+$): Calculated: 268.1672; Observed: 268.1683

R*f* = 0.83



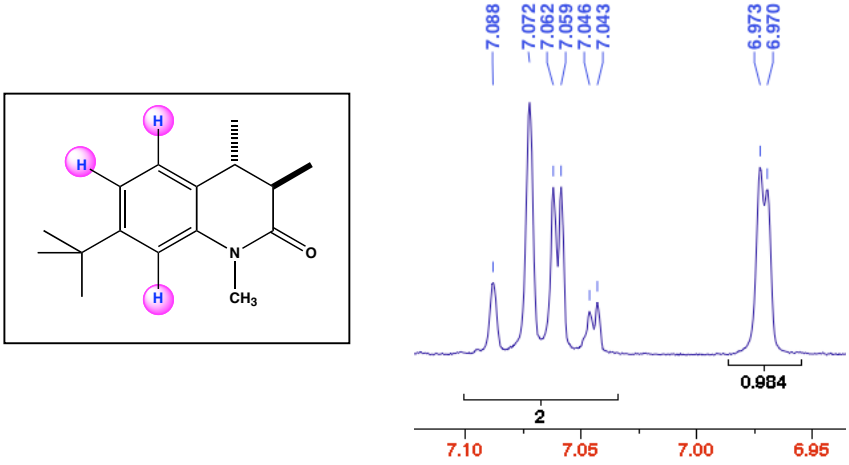
5d

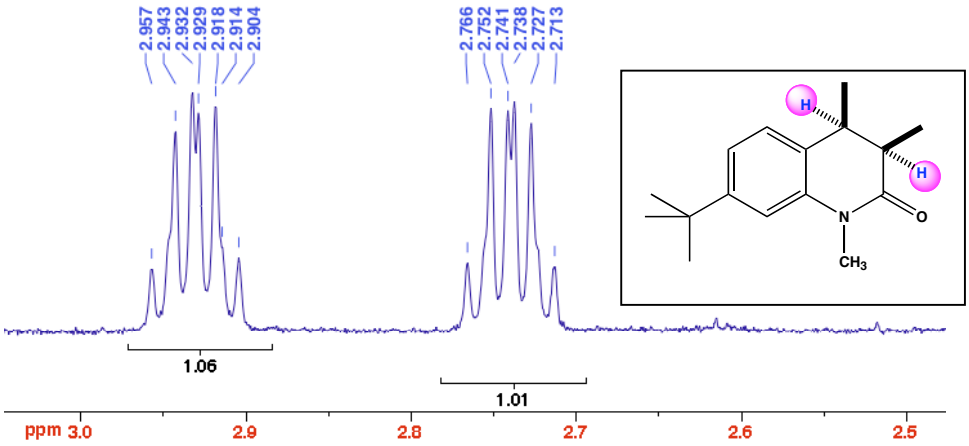


HPLC analysis conditions:

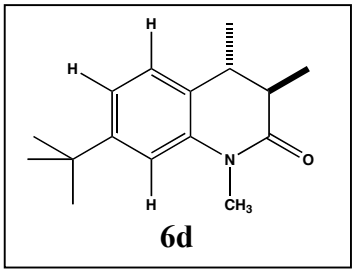
Column: (R,R) WHELK–01; Abs. detector: 254 nm and 270 nm
Mobile phase: Hexanes:IPA = 93:7; Flow rate: 1mL/min
Retention time (min): ~13.25 (**5d**)
(*ent*-**5d** does not resolve in the condition employed)

^1H NMR (Aromatic hydrogens (top) and α and β hydrogens (bottom) of compound **5d**.





6.7 *trans*-Photoproduct 6d



^1H *NMR* (500 MHz, $CDCl_3$, δ ppm) 7.13 – 6.96 (Ar, 3H), 3.39 (s, 3H), 2.70 – 2.63 (m, 1H), 2.55 – 2.47 (m, 1H), 1.34 (s, 9H), 1.24 – 1.21 (d, *J* = 7, 3H), 1.15 – 1.11 (d, *J* = 7.5, 3H)

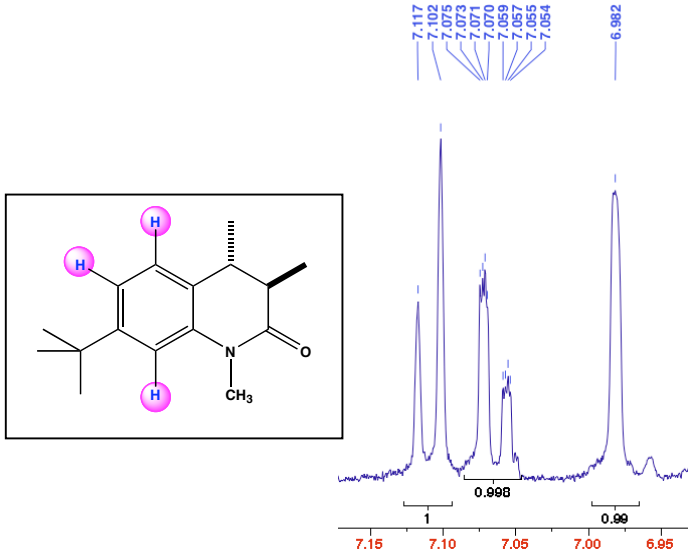
ESI-MS ($[M + H]^+$): Calculated: 268.1672; Observed: 268.1683

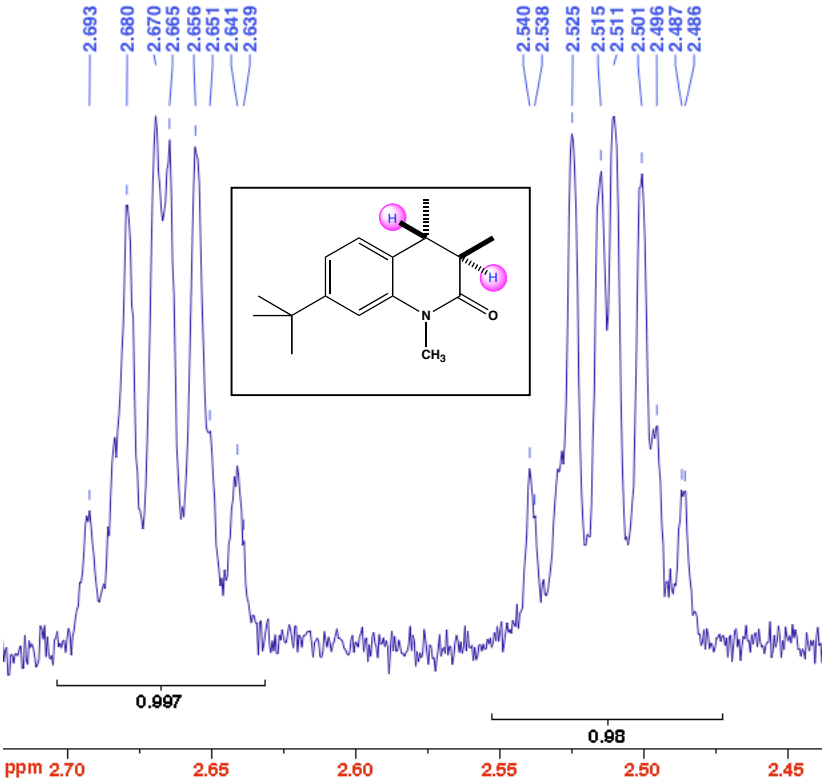
R*f* = 0.77

HPLC analysis conditions:

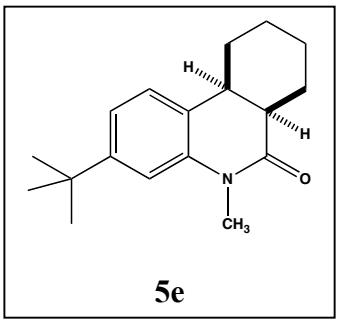
Column: (R,R) WHELK–01; Abs. detector: 254 nm and 270 nm
Mobile phase: Hexanes:IPA = 93:07; Flow rate: 1 mL/min
Retention time (min): ~15.23 (**6d**) and ~16.40 (*ent* **- 6d**)

^1H *NMR* (Aromatic hydrogens (top) and α and β hydrogens (bottom) of compound **5d**.





6.8 *cis*-Photoproduct 5e



5e

^{1}H *NMR* (400 MHz, $CDCl_3$, δ ppm) 7.04 – 6.87 (Ar, 3H), 3.32 (s, 3H), 2.84 – 2.73 (m, 1H), 2.72 – 2.64 (q, 1H), 1.1-2.1 (m, 17H)

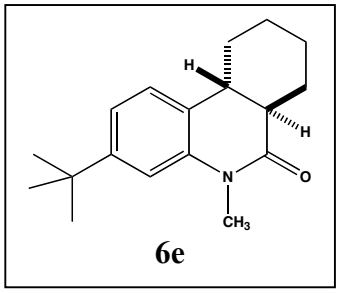
ESI-MS ($[M + Na]^+$): Calculated: 294.1828; Observed: 294.1825

R*f* = 0.66

HPLC analysis conditions:

Column: (R,R) WHELK–01; Abs. detector: 254 nm and 270 nm
Mobile phase: Hexanes:IPA = 90 : 10; Flow rate: 1 mL/min
Retention time (min): ~12.53 (**5e**) and ~13.39 (*ent*-**5e**)

6.9 *trans*-Photoproduct 6e



6e

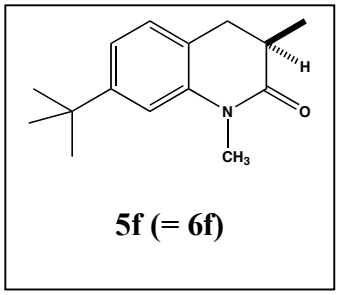
As the R*f* is identical with the starting isomer the isolation to characterize by NMR was not feasible. NMR analysis was performed on the crude mixture and was analyzed by HPLC.
R*f* = 0.66

ESI-MS ([M + Na] $^{+}$): Calculated: 294.1828; Observed: 294.1825

HPLC analysis conditions:

Column: (R,R) WHELK–01; Abs. detector: 254 nm and 270 nm
Mobile phase: Hexanes:IPA = 90 : 10; Flow rate: 1 mL/min
Retention time (min): ~20.45 (**6e**) and ~22.74 (*ent*-**6e**)

6.10. Photoproduct 5f (= 6f)



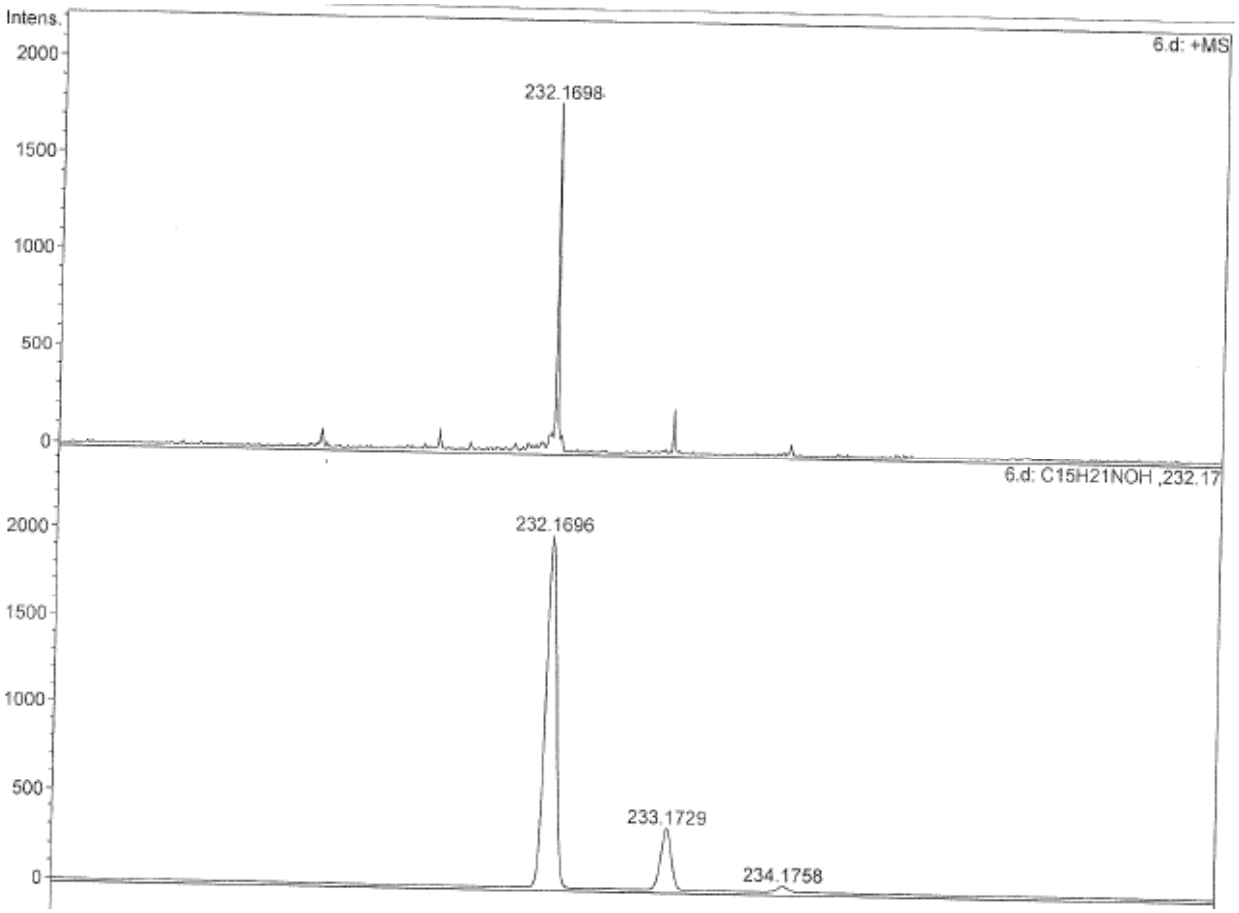
5f (= 6f)

cis and *trans* isomers not feasible in photoproducts from methacryloyl derivatives **4f** (and **1c**). Hence **5f = 6f.**
R*f* = 0.36 (Solvent System: 10 % EtOAc/Hexanes).
^{1}*H NMR* (500 MHz, $CDCl_3$) δ 7.13 – 7.09 (Ar, 1H), 7.08 – 7. 04 (Ar, 1H), 7.01 – 6.98 (Ar, 1H), 3.40 (s, 3H), 2.95 – 2.87 (m, 1H), 2.74 – 2.57 (m, 2H), 1.36 (s, 9H), 1.24 – 1.29 (d, 3H)

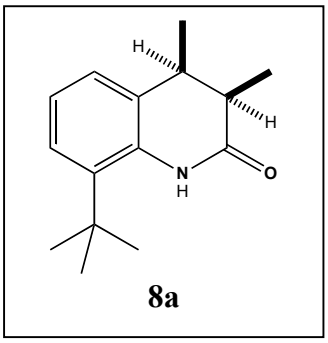
HPLC analysis conditions:

Column: (R,R) WHELK–01; Abs. detector: 254 nm and 270 nm
Mobile phase: Hexanes:IPA = 90:02; Flow rate: 1 mL/min
Retention time (min): **5f** (= **6f**): ~31.03
ent-**5f** (=*ent*-**6f**): ~32.42

ESI-MS ([M + H] $^{+}$): Calculated: 232.1696; Observed: 232.1698



6.11. *cis*-Photoproduct 8a



8a

^{1}H *NMR* (500 MHz, $CDCl_3$, δ ppm) 7.64 (bs, 1H), 7.32 – 7.20 (Ar, 1H), 7.10 – 7.04 (Ar, 1H), 7.03 – 6.94 (Ar, 1H), 3.06 – 2.94 (m, *J* = 2.5 and 7, 1H), 2.84 – 2.273 (m, *J* = 2.5 and 7, 1H), 1.45 (s, 9H), 1.27 – 1.19 (d, *J* = 7, 3H), 1.19 – 1.11 (d, *J* = 7, 3H)

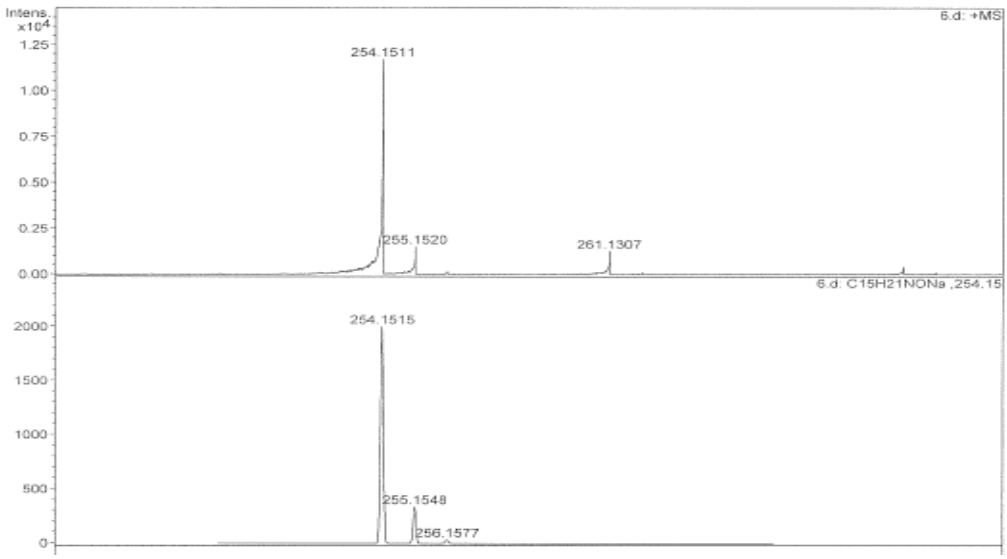
^{13}C-*NMR* (125 MHz, $CDCl_3$ δ ppm): 173.25, 135.06, 134.48, 131.86, 125.06, 125.23, 123.12, 39.08, 37.50, 34.33, 30.78, 14.92, 11.39

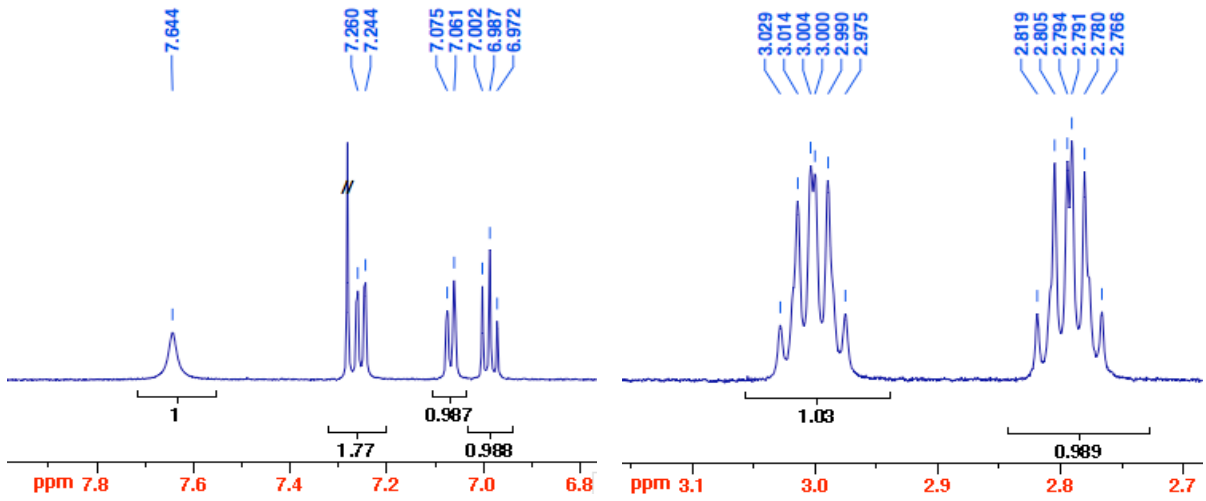
R*f* = 0.53

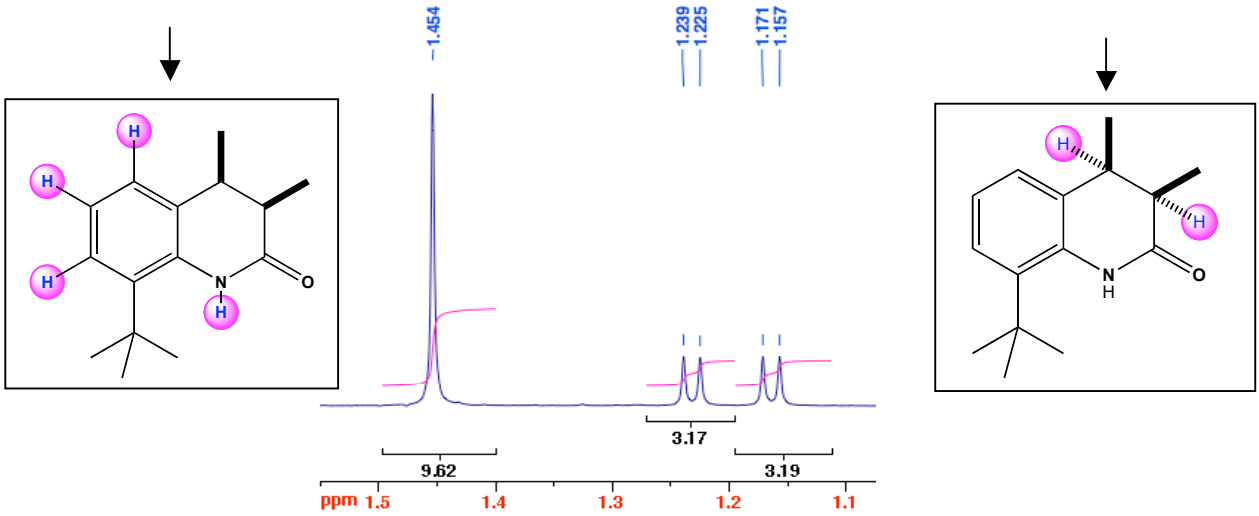
HPLC analysis conditions:

Column: (R,R) WHELK–01; Abs. detector: 254 nm and 270 nm
Mobile phase: Hexanes:IPA = 93:07; Flow rate: 1 mL/min
Retention time (min): ~8.14 (**8a**) and ~10.44 (*ent*-**8a**)

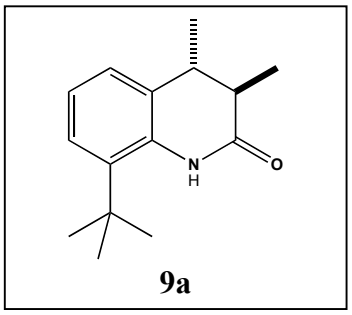
ESI-MS ($[M + Na]^+$): Calculated: 254.1515; Observed: 254.1511


Intens.
x10^4
1.25
1.00
0.75
0.50
0.25
0.00
254.1511
255.1520
261.1307
6.d: +MS
6.d: C15H21NONa ,254.15
2000
1500
1000
500
0
254.1515
255.1548
256.1577


7.644
7.260
7.244
7.075
7.061
7.002
6.987
6.972
3.029
3.014
3.004
3.000
2.990
2.975
2.819
2.805
2.794
2.791
2.780
2.766
1
0.987
1.77
0.988
1.03
0.989
ppm 7.8
7.6
7.4
7.2
7.0
6.8
ppm 3.1
3.0
2.9
2.8
2.7


1.454
1.239
1.225
1.171
1.157
H
N
O
3.17
9.62
3.19
ppm 1.5
1.4
1.3
1.2
1.1

6.12. *trans*-Photoproduct 9a



9a

^{1}H *NMR* (500 MHz, $CDCl_3$, δ ppm) 7.66 (bs, 1H), 7.30 – 7.21 (Ar, 1H), 7.13 – 7.06 (Ar, 1H), 7.03 – 6.95 (Ar, 1H), 2.83 – 273 (m, 1H), 2.54 – 2.43 (m, 1H), 1.45 (s, 9H), 1.30 – 1.26 (d, J = 7, 3H), 1.19 - 1.14 (d, J = 7.5, 3H)

^{13}C-*NMR* (125 MHz, $CDCl_3$ δ ppm): 173.25, 135.06, 134.48, 131.86, 125.06, 125.23, 123.12, 39.08, 37.50, 34.33, 30.78, 14.92, 11.39

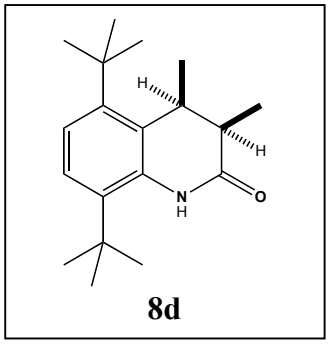
ESI-MS ($[M + Na]^+$): Calculated: 254.1515; Observed: 254.1511

Rf = 0.46

HPLC analysis conditions:

Column: (R,R) WHELK–01; Abs. detector: 254 nm and 270 nm
Mobile phase: Hexanes:IPA = 93:07; Flow rate: 1 mL/min
Retention time (min): ~9.82 (**9a** and *ent*-**9a**)

6.13. *cis*-Photoproduct 8d



8d

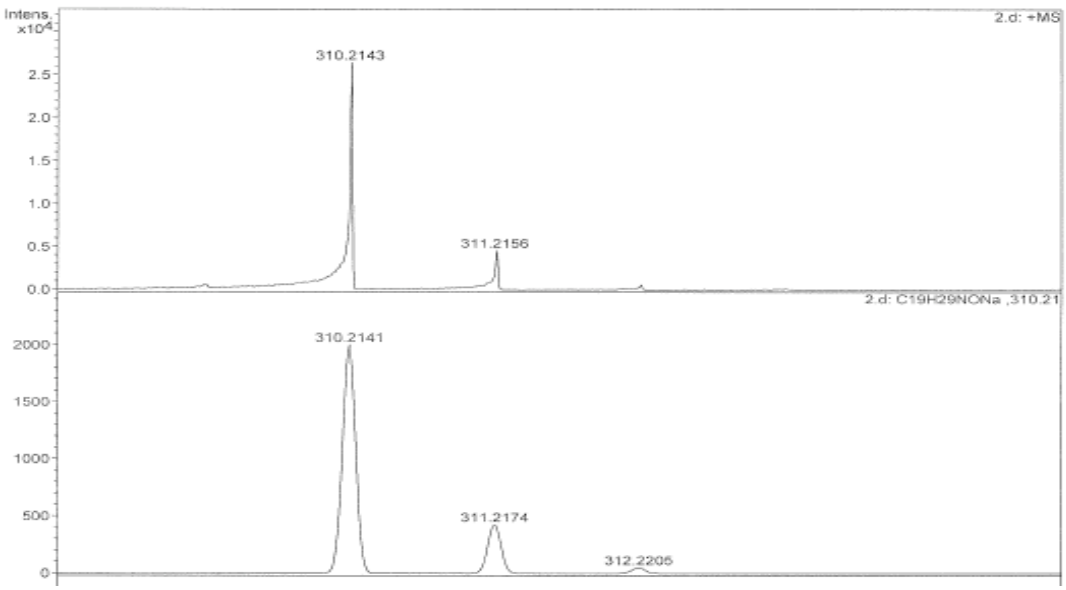
^{1}H *NMR* (500 MHz, $CDCl_3$, δ ppm) 7.68 (bs, 1H), 7.22 – 7.08 (ABq, 2H), 3.64 – 3.48 (m, 1H), 2.65 – 2.52 (m, 1H), 1.46 (s, 18H), 1.31 – 1.26 (d, J = 7, 3H), 1.13 – 1.09 (d, J = 7.5, 3H)

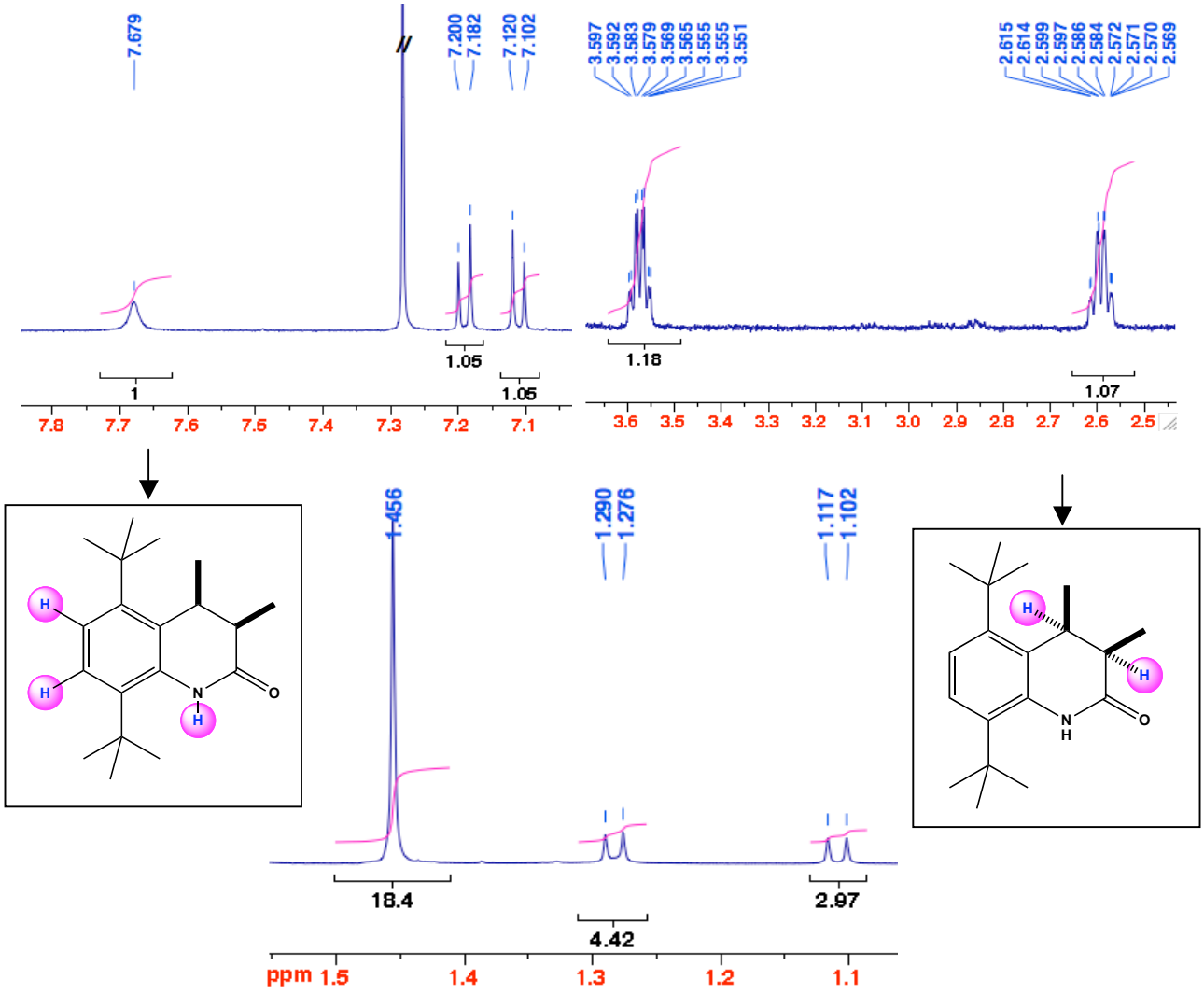
HPLC analysis conditions:

Column: (R,R) WHELK–01; Abs. detector: 254 nm and 270 nm
Mobile phase: Hexanes:IPA = 93:07; Flow rate: 1 mL/min
Retention time (min): 9.52 (**8d**) and 10.48 (*ent*-**8d**)

ESI-MS ($[M + Na]^+$): Calculated: 310.2141; Observed: 310.2143

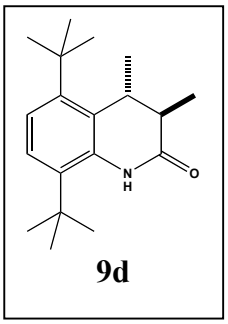
Rf = 0.39


Intens.
x10^4
2.5
2.0
1.5
1.0
0.5
0.0
310.2143
311.2156
2.d: +MS
2.d: C19H29NONa ,310.21
2000
1500
1000
500
0
310.2141
311.2174
312.2205


7.679
7.200
7.182
7.120
7.102
3.597
3.592
3.583
3.579
3.569
3.565
3.555
3.555
3.551
2.615
2.614
2.599
2.597
2.586
2.584
2.572
2.571
2.570
2.569
1.05
1.18
1
1.05
1.07
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
1.456
1.290
1.276
1.117
1.102
18.4
4.42
2.97
ppm 1.5
1.4
1.3
1.2
1.1
H
H
N
H
O
H
H
N
H
O

6.14. *trans*-Photoproduct 9d

The isolation of **9d** by chromatography not possible due to its close R*f* with the starting material (**7a** R*f* = 0.56) and hence NMR characterization not provided.

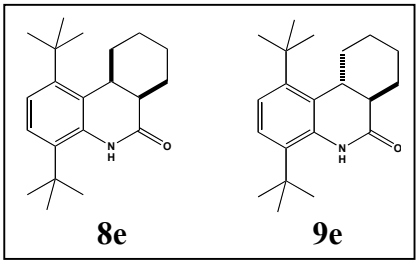


9d

ESI-MS ([M + Na]$^+$): Calculated: 310.2141; Observed: 310.2143
R*f* = 0.61

HPLC analysis conditions:
Column: (R,R) WHELK–01; Abs. detector: 254 nm and 270 nm
Mobile phase: Hexanes:IPA = 93:07; Flow rate: 1 mL/min
Retention time (min): 10.00 (**9d** *ent*-**9d**)

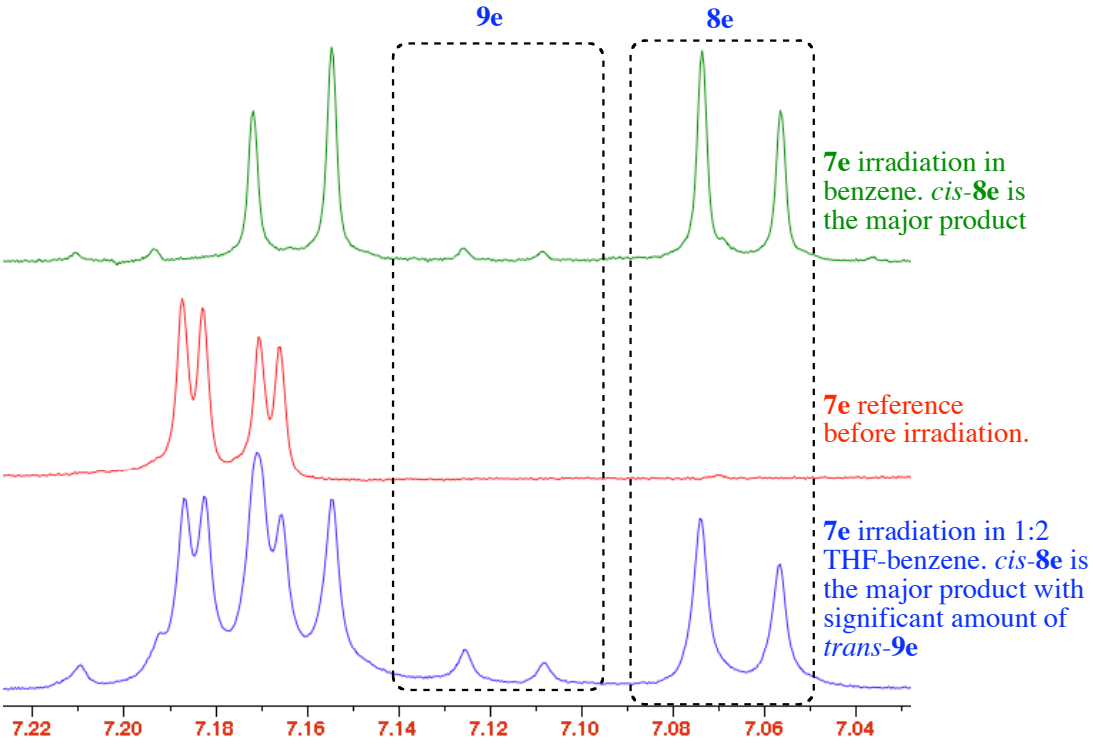
6.15. Mixture of Photoproducts [*cis*-8e *and trans*- 9e]



8e **9e**

cis-**8e** *and trans*- **9e** are not separable by PTLC. The major photoproduct formed in benzene irradiations was assigned based on previous trends in the NMR shifts. The characterization provided below is from the mixture of isomers in comparison with the starting material (Figure S1). The cis:trans ratio was cross-verified on HPLC.

^{1}*H NMR* of **8e** (500 MHz, $CDCl_3$, δ ppm) 7.45 (bs, 1H), 7.18 – 7.05 (ABq, 2H), 3.48- 3.41 (m, 1H), 2.76 – 2.70 (m, 1H), 1.84 -1.50 (m, 8H), 1.46 (s, 9H), 1.44 (s, 9H).



Comparision of the aromatic region in **7e** and its photoproduct irradiation mixture

Figure S1: NMR analysis of *cis*-**8e** and *trans*-**9e** photoproducts.

HPLC analysis conditions:

Column: (R,R) WHELK–01; Abs. detector: 254 nm and 270 nm
Mobile phase: Hexanes:IPA = 90:10; Flow rate: 1 mL/min
Retention time (min): ~4.90 (**9e**) and 5.10 (*ent*-**9e** not separable)
~6.37 (**8e**) and ~7.95 (*ent*-**8e**)

7. Verifying *cis:trans* ratio by NMR and HPLC analysis.

In general NMR analysis showed that crude reaction mixture can be employed to ascertain the *cis:trans* ratio as the *cis*-isomer resonates slightly downfield than the corresponding *trans*-isomer. For example the ratio of **5a:6a** (**2a:3a**) can be identified from the crude reaction mixture (**5a** resonate at ~3.00 and 2.76 ppm; **6**: resonate at 2.74 and 2.52).

5a (=**2a**) and **6a** (=**3a**) can be separated by chromatography and were characterized independently as indicated before (sections 6.1 and 6.2).

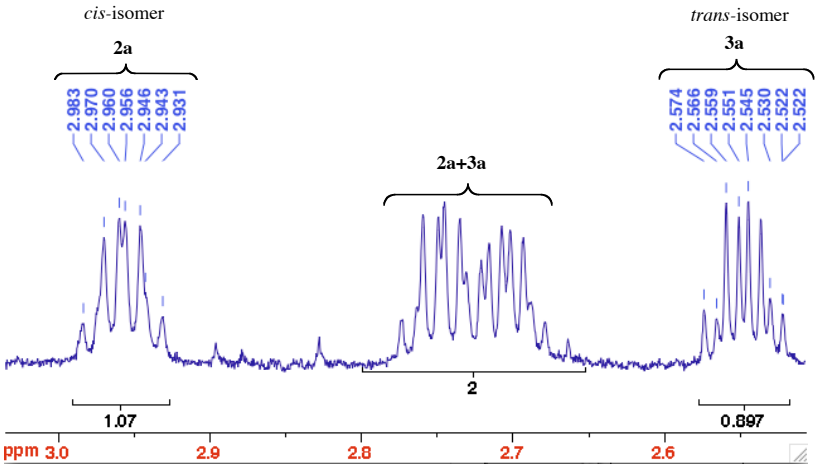


Figure S2: NMR analysis to determine *cis:trans* ratio. The proton resonances of the quinolinone hydrogens are shown.

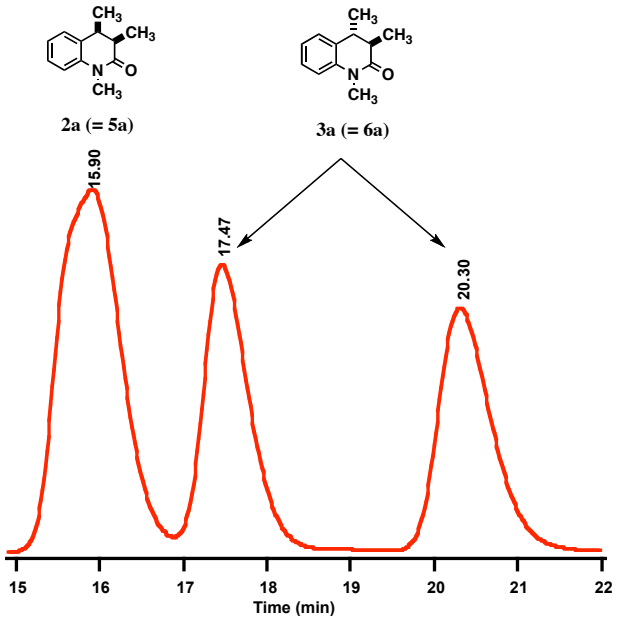


Figure S3: HPLC analysis to verify *cis:trans* ratio. (Note: **2a**) and *ent*-**2a** are not resolved on a chiral stationary phase HPLC separation and elutes as a single peak at ~15.9 min.

8. Product verification by independent synthesis

As photoproducts from **1a** and **4a** are identical, the products were verified by HPLC analysis that showed identical retention time. The *cis* product **5a** (= **2a**) did not resolve under our analysis condition. On the other hand, the *trans* product **6a** (= **3a**) was resolved with the two enantiomers having different retention time. The *cis* and *trans* ratio from HPLC analysis (Figure S4) correlated with ^{1}H NMR spectroscopic analysis (see section 7).

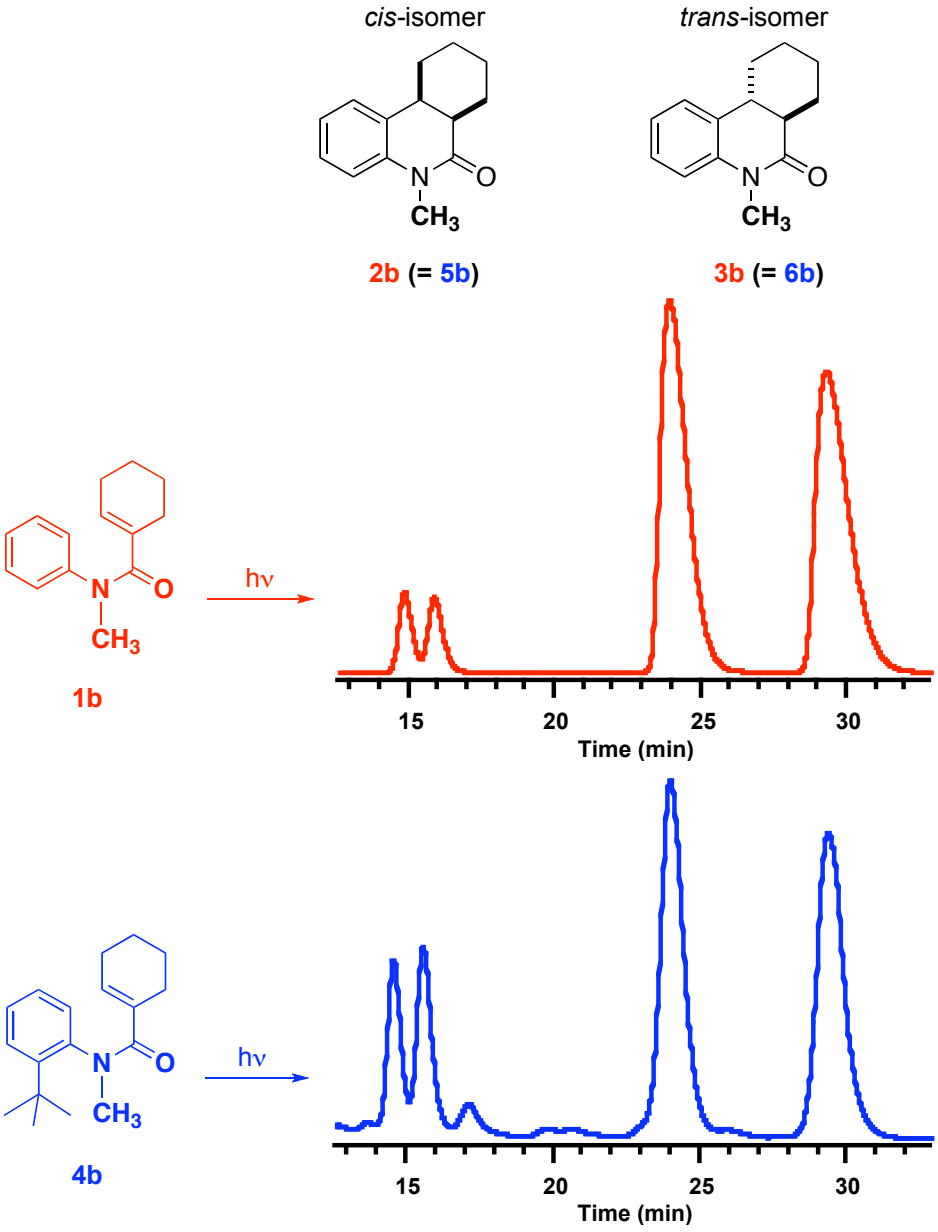


Figure S4: Product verification by independent synthesis.

9. Deuteration Experiment to ascertain intermolecular vs. intramolecular Hydrogen migration.

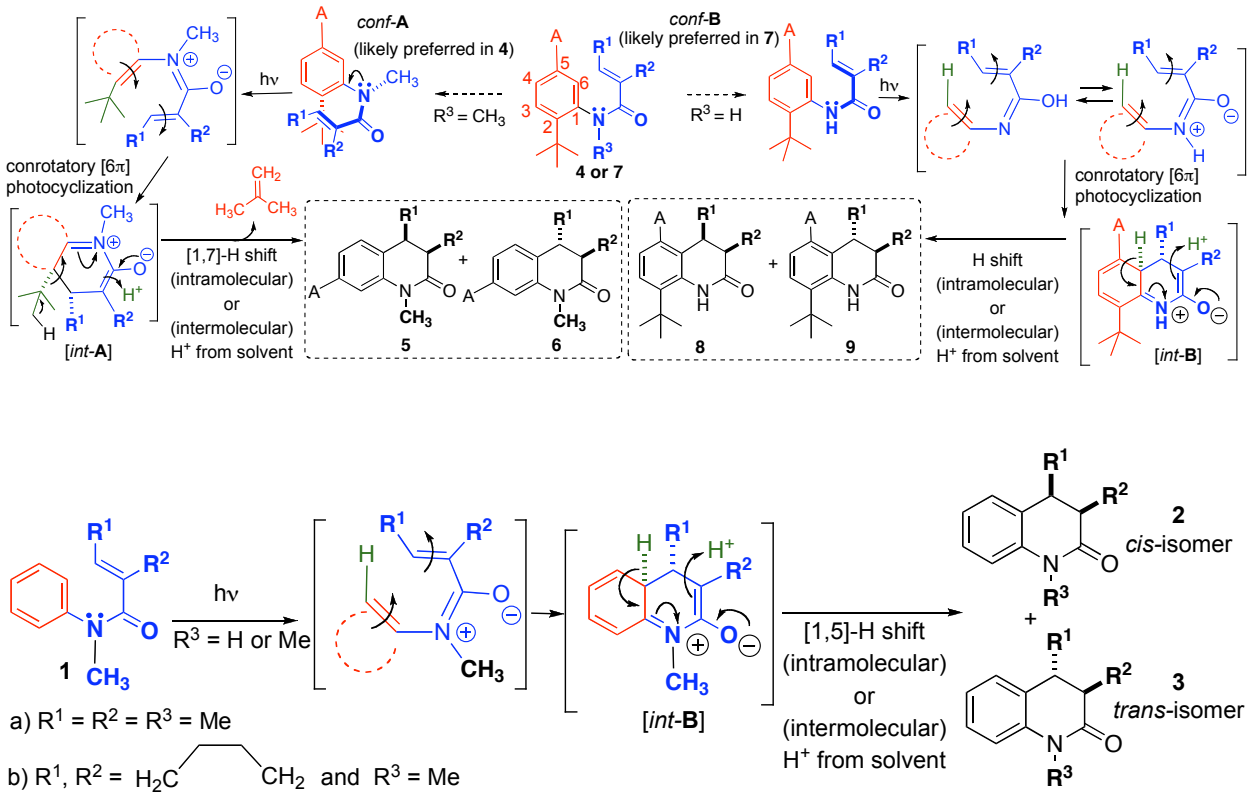


Figure S5: Mechanism of photocyclization of parent acrylanilides **1** (bottom) and molecularly chiral acrylanilides **4** (top).

Photocyclization of **4d** was performed in methanol-*d* (Refer to general procedure insection 5 for photocyclization in methanol-*d*) to ascertain the intermolecular vs intramolecular [1,7]-H migration from the intermediate *int*-**A** leading to photocyclized *cis* and *trans* products. It is well established in literature [3-5] that in protic solvents, the zwitterionic intermediate *int*-**1** (Figure S5-bottom) from the N-Methyl substituted parent acrylanilides **1** undergoesintramolecular [1,5]-H shift and yields the *trans* product, whereas the *cis* isomer is formed by intermolecular H migration. Photocyclization of **4d** in methanol-*d* clearly showed (based on deuterium incorporation in *d*-*cis*-**5d**, Figures S6-blue and S7) that the proton is incorporated in the *cis* isomer by intermolecular hydrogen transfer to the zwitterionic intermediate *int*-**A** (Figures S5-top, S6 and S7) from the protic solvent. On the other hand, proton was delivered intramolecularly by a [1,7]-H shift leading to the *trans*-**6d** product (no deuterium incorporation in the *trans*-**6d** photoproduct, Figures S5-top, S6 and S7). *trans*-**6d** and *d*-*cis*-**5d**

were not separable by chromatography, hence their characterization were done as a mixture by ^{1}H NMR (Figure 6)and HRMS (Figure S7) that clearly established the formation of photoproducts by intramolecular path way in the case of *trans* isomer and intermolecular pathway in the case of *cis* isomer.

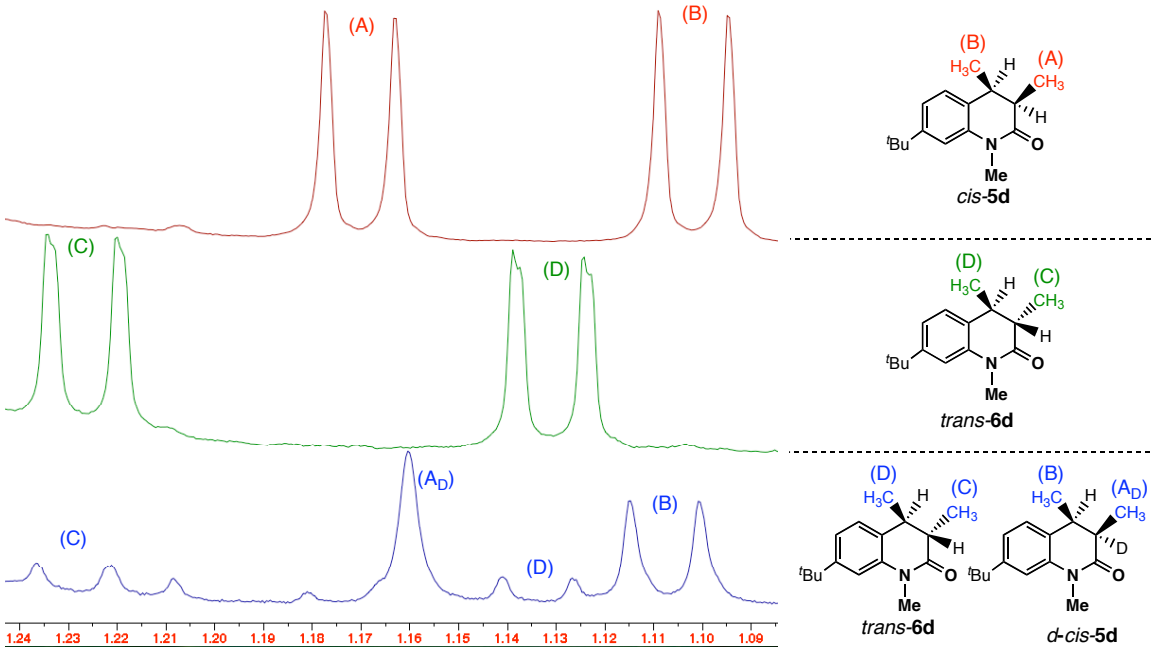


Figure S6: ^{1}H NMR upon photocyclization of **4d** in methanol-*d* (Blue). The methyl resonances in *cis*-**5d** (red), *trans*-**6d** (green) are given for comparison.

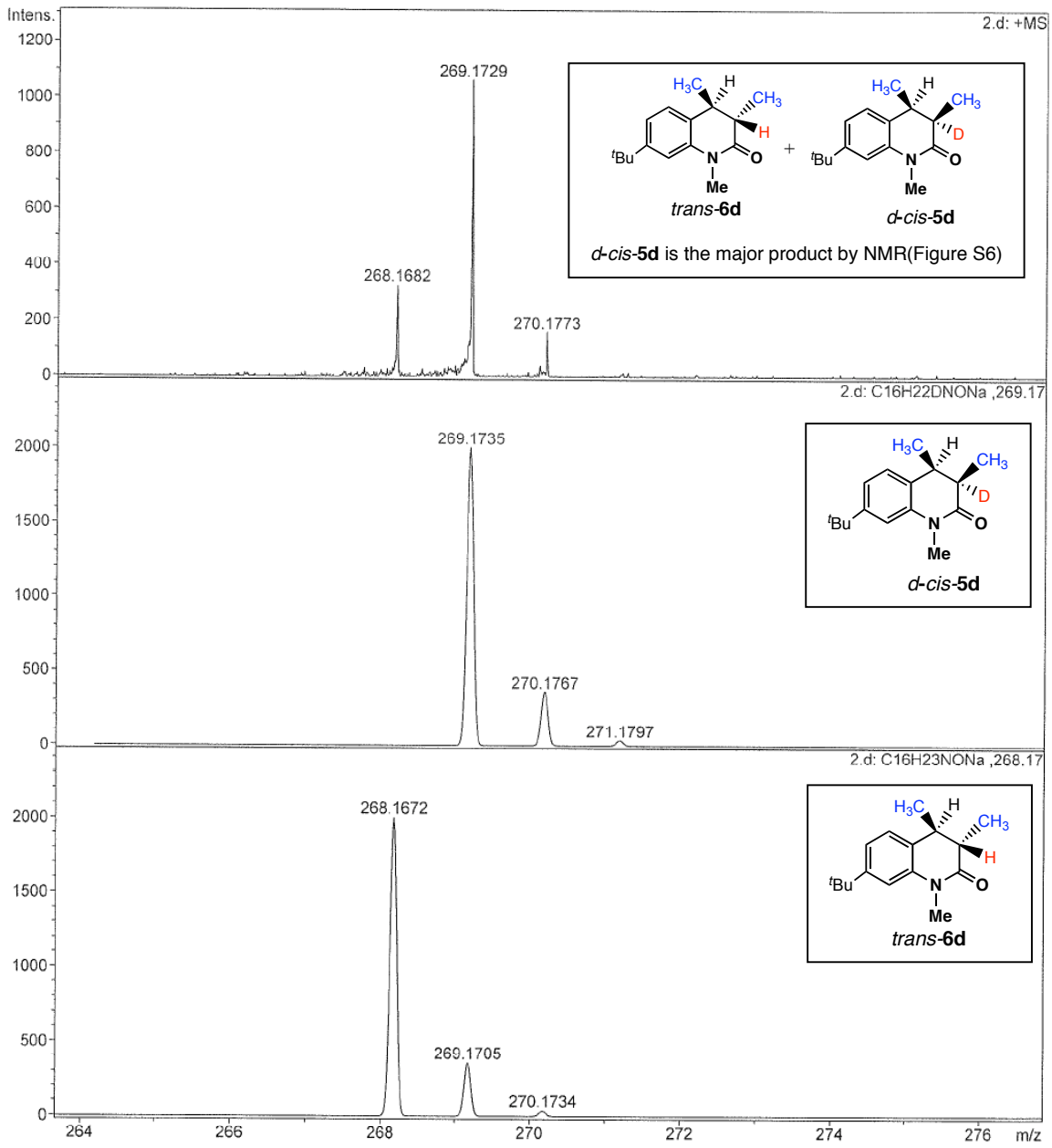


Figure S7: Top: ESI-MS of *d-cis*-**5d** and *trans*-**6d** mixture from photocyclization of **4d** in methanol-*d*; Middle: simulation of ESI-MS spectra for *d-cis*-**5d**; Bottom: simulation of ESI-MS spectra for *trans*-**5d**.

10. UV-Vis absorption spectra of reactants and photoproducts.

UV-Vis absorption spectra of N-Methyl-*O*-*tert*-butyl-acrylanilides **4** and its photoproducts were recorded either in HPLC grade methanol or in HPLC grade hexanes. The molar absorptivity of N-Methyl *O*-*tert*-butyl-acrylanilides **4** were similar to the parent acryl anilides **1** reported in literature (Reference 5). For spectral changes during irradiation of acrylanilides refer to Reference 5 for discussion.

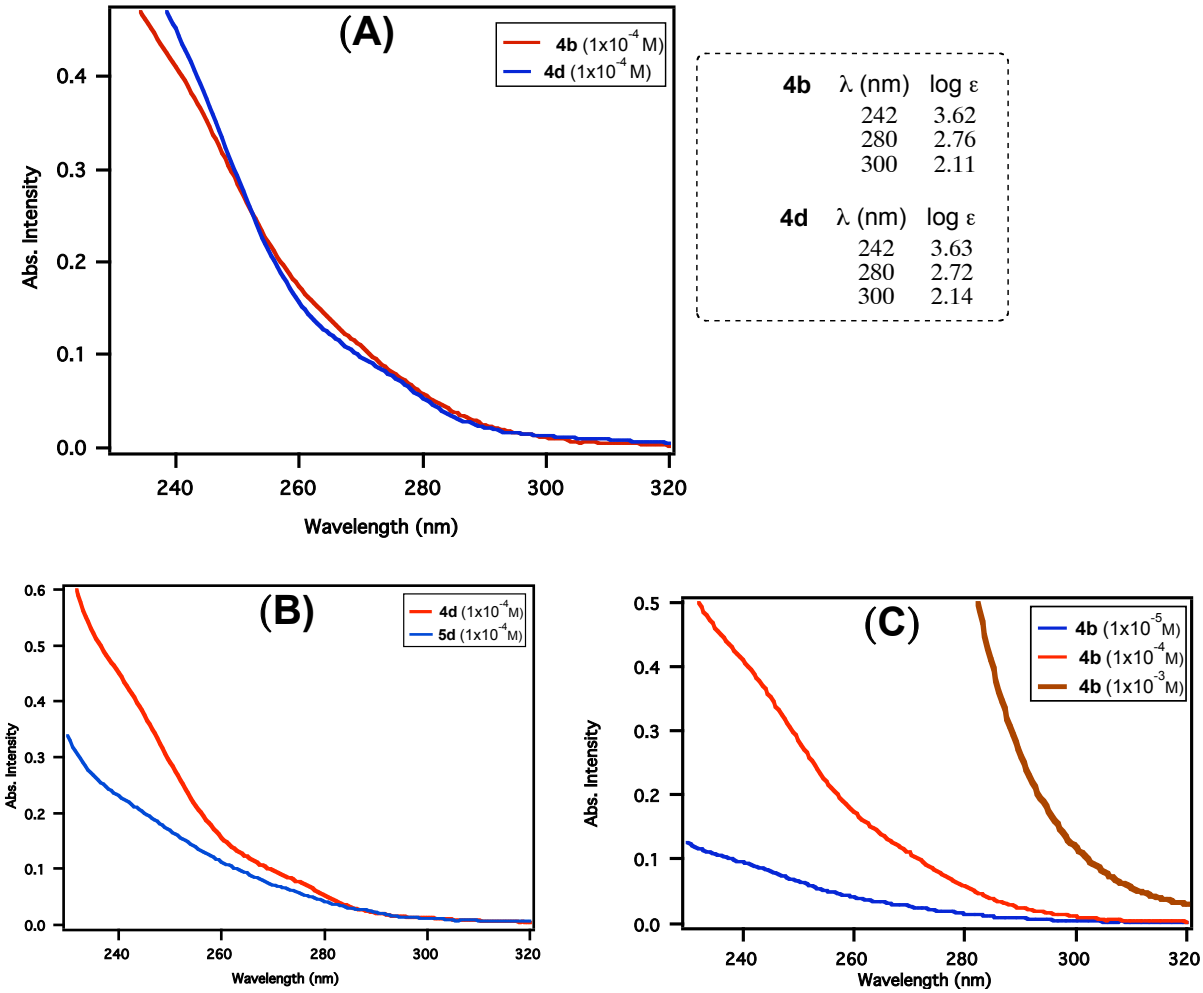


Figure S8: (A): UV-Vis spectra of N-Methyl-*O*-*tert*-butyl-acrylanilides **4b** and **4d**; (B) UV-Vis spectra of N-Methyl-*O*-*tert*-butyl-acrylanilides **4d** and the corresponding photoproduct **5d**; (C) (B) UV-Vis spectra of N-Methyl-*O*-*tert*-butyl-acrylanilides **4b** at various concentrations.

11. Photocyclization of 4c at elevated temperatures in methanol and acetone-d_6.

Photocyclization of **4c** was performed in methanol (at 58±2 °C) and in acetone (at 40±2 °C) to ascertain reactivity at elevated temperatures.

Solution of **4c** (0.01 mmol) in 1 mL of acetone-d_6 was irradiated for 4 h in a Pyrex tube with a 450 W Hg lamp at room temperature and at 40±2 °C under constant flow of nitrogen. The reaction was monitored by ^{1}H NMR spectroscopy that did not show any observable photoproducts.

Solution of **4c** (0.1 mmol) in 15 mL of methanol was irradiated for 5 h and 13 h in Pyrex tube with a 450 W Hg lamp at room temperature and at 58±2 °C under constant flow of nitrogen. The reaction mixture was analyzed after 5h and 13 h irradiations on a HPLC and retention times were compared with authentic sample prepared from the parent acrylanilide **1c**. No photoproducts were detected (Figure S9).

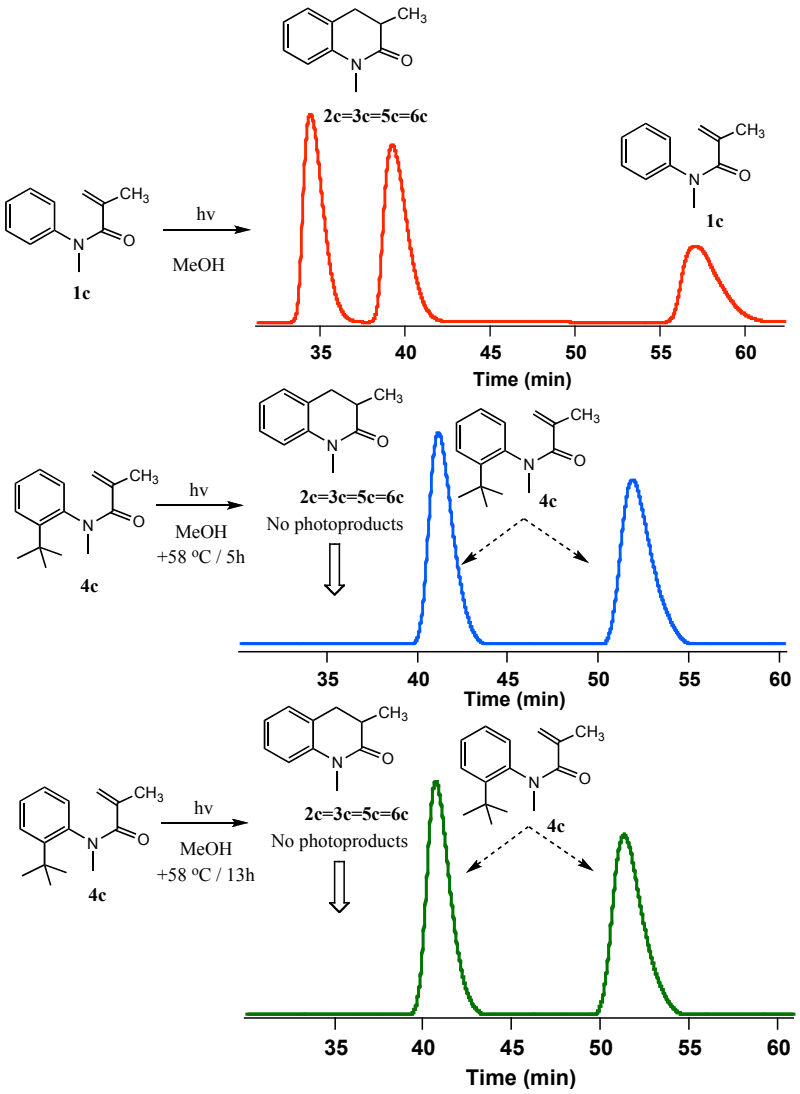


Figure S9: HPLC analysis after photoirradiation of **4c** at RT (middle) and +58 °C (bottom). The authentic photoproduct form **1c** (top) is provided as reference.

12. Photocyclization of 4e in acetone under N_2, O_2 and Et_3N to ascertain the reactive spin states.

Photoirradiation of **4e** was carried out (Figure 2) in acetone under a) N_2 atmosphere; b) O_2 atmosphere; and c) in the presence of triethylamine under N_2 atmosphere.

Solution of **4e** (0.1 mmol) and Et_3N (0.25 mmol) in 15 mL of acetone was irradiated for 5 h in a Pyrex tube with a 450 W Hg lamp at room temperature and under constant flow of nitrogen. The photolysate was analyzed on a HPLC (Figure – bottom) and compared with the irradiation done under N_2 without Et_3N (Figure – top).

Solutions of **4e** (0.1 mmol) in 15 mL of acetone was irradiated for 5 h in Pyrex tube with a 450 W Hg lamp at room temperature and under constant flow of oxygen. The photolysate was analyzed on a HPLC (Figure – middle) and compared with the irradiation done under N_2 (Figure – top).

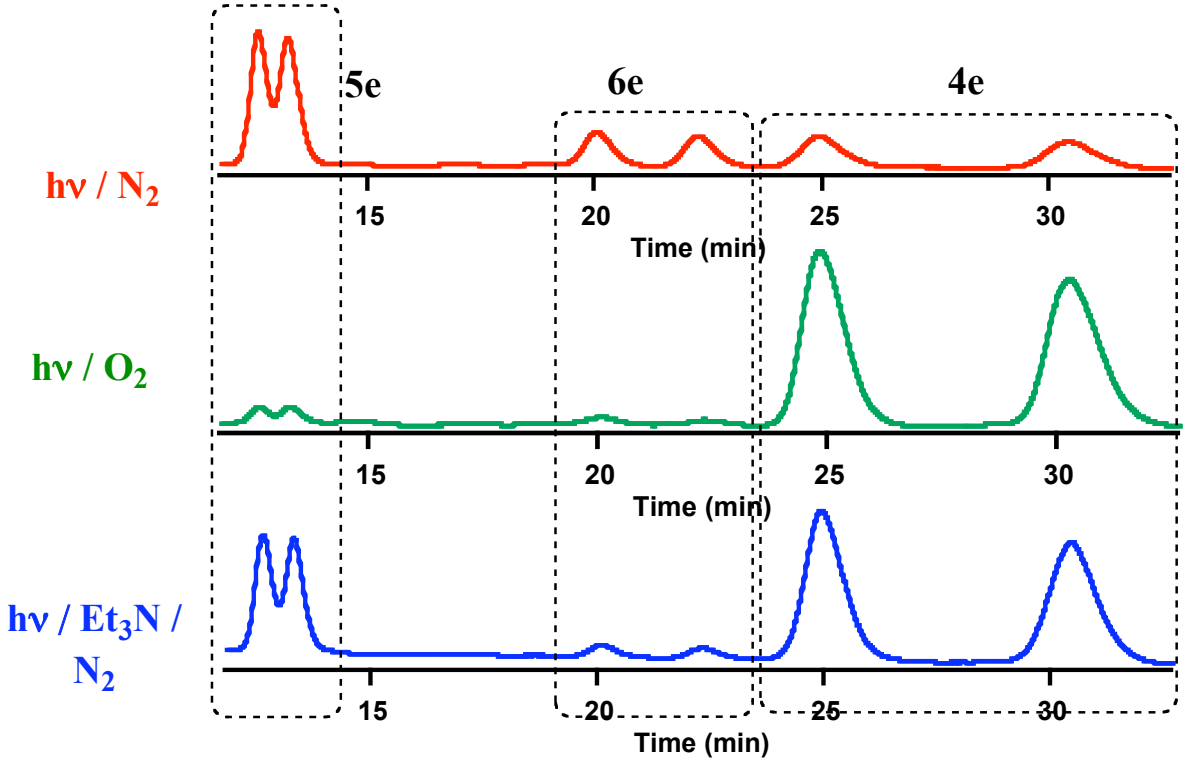


Figure S10: HPLC analysis after photoirradiation of **4e** in acetone under N_2 (top); O_2 (middle); under N_2 in the presence of Et_3N (bottom).

13. X-ray structural parameters

Structure determination: Single crystal X-ray diffraction data sets were collected on a SIEMENS diffractometer with a 1K CCD area detector (graphite-monochromated Mo Ka radiation, crystals protected with Parathone-N oil). The structures were solved by direct methods and refined on F^2 using the SHELXTL V6.14 package (after absorption corrections with SADABS). Details of the data collections and refinements are given in the table S1.

Structure_4c: $C_{15}H_{21}NO$, M=231.33, Monoclinic, P21/c (no.14), a = 11.120(16), b = 10.165(15), c = 12.745(18), β = 108.04(3), V = 1370 (3) $Å^3$, 298K, Z = 4, 6779 reflections measured, 2388 unique reflections (R_{int} = 0.0575) which were used in all calculations. R_1/wR_2 = 6.01/18.72, R_1/wR_2 (all) = 7.26/20.29

Structure_7a: $C_{15}H_{21}NO$, M=231.33, Tetragonal, I-4 (no.82), a = 17.588(12), c = 8.963(13), V = 2773 (5) $Å^3$, 250K, Z = 8, 7197 reflections measured, 1463 unique reflections (R_{int} = 0.0444) which were used in all calculations. R_1/wR_2 = 5.62/16.52, R_1/wR_2 (all) = 7.53/19.64

Structure_4f: $C_{19}H_{29}NO$, M=287.43, Triclinic, P-1 (no.2), a = 11.073(10), b = 14.119(13), c = 14.351(13), α = 115.446(14), β = 96.908(16), γ = 107.764(15), V = 1845 (3) $Å^3$, 298K, Z = 4, 13641 reflections measured, 6418 unique reflections (R_{int} = 0.0380) which were used in all calculations. R_1/wR_2 = 8.54/25.23, R_1/wR_2 (all) = 11.61/28.64

The A-errors reported for structure_4f are regarding structural disorder in the t-butyl groups. The observed disorder is not unusual for such molecules and it has no influence on the subject of interest discussed in the paper.

Table S1: Crystallography parameters of **4c**, **4f**, and **7a**

Structure	**4c**	**4f**	**7a**
Formula	$C_{15}H_{21}NO$	$C_{19}H_{29}NO$	$C_{15}H_{21}NO$
FW	231.33	287.43	231.33
space group, Z	P2(1)/c, 4	P-1, 4	I-4, 8
a [Å]	11.120(16)	11.073(10)	17.588(12)
b [Å]	10.165(15)	14.119(13)	17.588(12)
c [Å]	12.745(18)	14.351(13)	8.963(13)
α [°]	90.0	115.446(14)	90.0
β [°]	108.04(3)	96.908(16)	90.0
γ [°]	90.0	107.764(15)	90.0
V [Å^3]	1370(3)	1845(3)	2773(5)
ρcalc [g•cm^{-3}]	1.122	1.035	1.108
No. of measured refl.	6779	13641	7197
No. of indep. refl.	2388	6418	1463
No. of used refl.	1905	4199	1101
μ [cm^{-1}]	0.069	0.063	0.069
$2\theta_{max}$ [°]	50	50	52
R1/wR2 ($I \geq 2\sigma_1$)* [%]	6.01/18.72	8.54/25.23	5.62/16.52
R1/wR2 (all data) [%]	7.26/20.29	11.61/28.64	7.53/19.64

[*] $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$, $wR2 = \{[\Sigma[(F_o)^2 - (F_c)^2]^2] / [\Sigma w(F_o^2)^2]\}^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$, $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$ where $P = [(F_o)^2 + 2(F_c)^2] / 3$; A (B) = 0.1325 (0.24) for 4c, A (B) = 0.1185 (0.0) for 4f, A (B) = 0.1673 (0.7359) 7a.

14. Reference

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