SUPPORTING INFORMATION

Chiral Phosphoric Acid Catalyzed Enantioselective Annulation of Acyclic Enecarbamates to In Situ-Generated *ortho*-Quinone Methides

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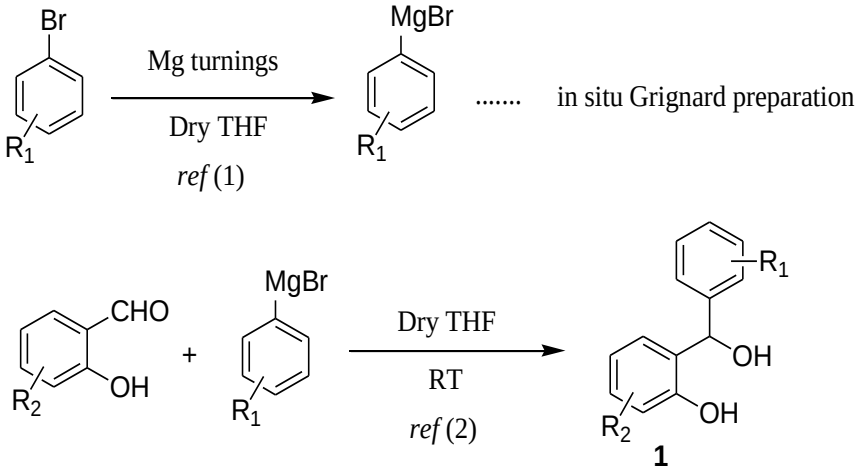
1. **General information:**

All reagents, chiral catalysts **I**, **IV** and **V** were purchased from Sigma Aldrich and the other chiral catalysts such as **II**, **III** and **VI** were prepared according to the reported procedures.[1,2,3] Solvents were purified according to standard procedures. Reactions were carried out and monitored by TLC analysis. For column chromatography, silica gel (60 − 120 mesh size) were used. ^{1}H NMR spectra were recorded on 400 MHz and 600 MHz spectrometer.^{13}C NMR spectra were recorded on 150 MHz. For ^{1}H and ^{13}C, $CDCl_3$ is used as reference NMR solvent. Chemical shifts and coupling constants were reported in parts per million (ppm) and Hertz (Hz) respectively. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), brs (broad singlet), dt (doublet of triplet). HRMS mass spectra were taken from mass spectrometer using +ESI mode. Enantiomeric ratios were determined by HPLC using stationary phase chiral column through the help of Dionex (Ultimate 3000) instrument.

2. **General Procedure for the synthesis of various o-hydroxybenzyl alcohols (1):**

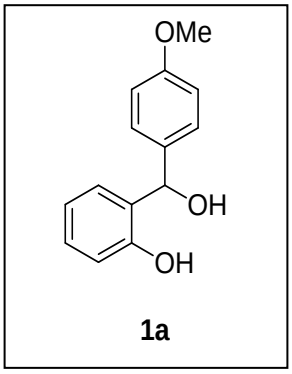
Various kinds of *o*-hydroxybenzyl alcohols **1** were prepared based on literature procedure.[4,5a]



First, a super dried 2-neck round-bottomed flask equipped with a stirbar was taken. It's one neck was closed with rubber septum and the other neck was fitted with a 2-way adapter (one side was linked with a argon balloon and other side was connected with a high vacuum pump). Then argon flash was done for 2-3 times. Thereafter a magnet and magnesium turnings (16 mmol) were charged under the stream of argon. Next, the flask was made vacuum and continued heating using heatgun for about 15 minutes. After heating, the whole flask was cooled under argon

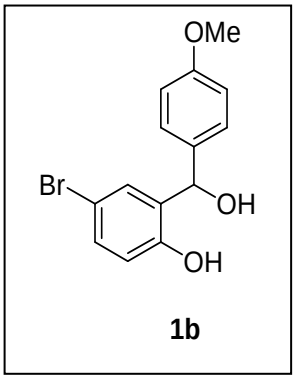
environment. Then 5 to 8 crystal of iodine was added through the septum quickly under the argon flow. Again the flask was made vacuum and argon flash. Thereafter, dry THF (5.3 ml) was added with the help of a dry syringe and the whole set up was placed in ice bath (0^oC). Aryl halide (16 mmol) was then added dropwise throughout 30 minutes. Finally, after completion of aryl bromide addition the reaction set up was shifted to room temperature and continued stirring for 3 hours. Reaction mixture was then turned to viscous and gray color, that indicated the formation of the Grignard reagent.

A separate dried 2 neck round-bottomed flask equipped with a stirbar was made vacuum and argon flashed. Then corresponding salicyldehyde (4 mmol, 1 equiv) and dry THF (4.4 ml) were added. Next, the whole set up was placed in an ice bath and consequently in situ prepared Grignard reagent (2.93 ml, 3M, 2.2 equiv) was added dropwise under argon. Finally the reaction set up was shifted at room temperature and continued stirring for overnight. Progress of the reaction was monitored by TLC analysis. Reaction mixture was quenched by using saturated NH_4Cl solution (15 ml). Work up was done by using diethyl ether and washed with brine solution. Organic layers were concentrated and purified by column chromatography using (Hexane / EtOAc) as solvent system to afford the corresponding desired o-hydroxybenzyl alcohol **1**.



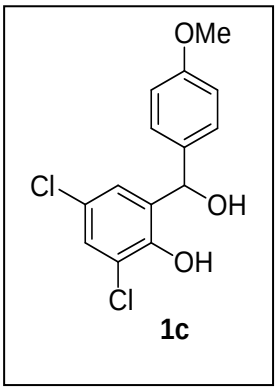
1a

This compound was prepared according to the general procedure **2**. Here, coupling of 2-hydroxy benzaldehyde (488 mg, 4 mmol) with insitu prepared 4-methoxy phenyl magnesium bromide was employed. The crude product was purified by column chromatography using 10% (Hexane / EtOAc) solvent system to get 435 mg (yield: 47%) of the desired compound **1a** as a pale orange sticky solid.



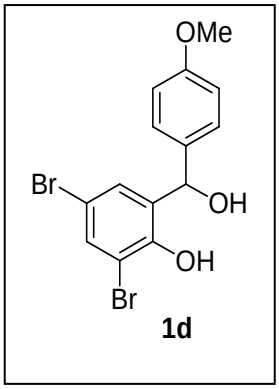
1b

This compound was prepared according to the general procedure **2**. Here, coupling of 5-bromo-2-hydroxy benzaldehyde (804 mg, 4 mmol) with insitu prepared 4-methoxy phenyl magnesium bromide was employed. The crude product was purified by column chromatography using 10% (Hexane / EtOAc) solvent system to get 523 mg (yield: 42%) of the desired compound **1b** as a colorless sticky solid.



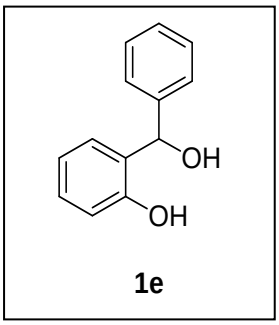
1c

This compound was prepared according to the general procedure **2**. Here, coupling of 3,5-dichloro-2-hydroxy benzaldehyde (764 mg, 4 mmol) with insitu prepared 4-methoxy phenyl magnesium bromide was employed. The crude product was purified by column chromatography using 10% (Hexane / EtOAc) solvent system to get 756 mg (yield: 63%) of the desired compound **1c** as an orange sticky solid.



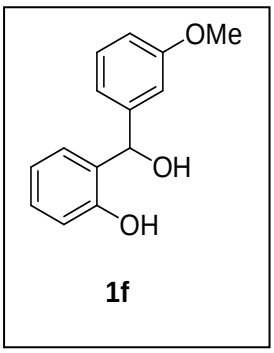
1d

This compound was prepared according to the general procedure **2**. Here, coupling of 3,5-dibromo-2-hydroxy benzaldehyde (1120 mg, 4 mmol) with insitu prepared 4-methoxy phenyl magnesium bromide was employed. The crude product was purified by column chromatography using 10% (Hexane / EtOAc) solvent system to get 1160 mg (yield: 75%) of the desired compound **1d** as a white solid.



1e

This compound was prepared according to the general procedure **2**. Here, coupling of 2-hydroxy benzaldehyde (488 mg, 4 mmol) with insitu prepared phenyl magnesium bromide was employed. The crude product was purified by column chromatography using 8% (Hexane / EtOAc) solvent system to get 642 mg (yield: 80%) of the desired compound **1e** as a colorless sticky liquid.

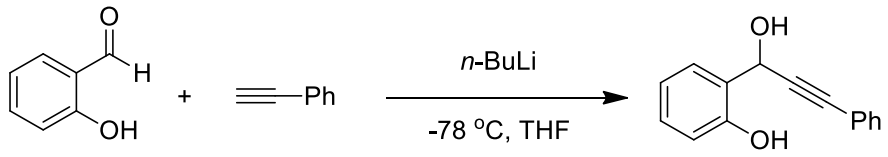


1f

This compound was prepared according to the general procedure **2**. Here, coupling of 2-hydroxy benzaldehyde (488 mg, 4 mmol) with insitu prepared 3-methoxy phenyl magnesium iodide was employed. The crude product was purified by column chromatography using 10% (Hexane/ EtOAc) solvent system to get 150 mg (yield: 16%) of the desired compound **1f** as an orange sticky liquid.

Synthesis of 2-(1-hydroxy-3-phenylprop-2-yn-1-yl) phenol:

2-(1-hydroxy-3-phenylprop-2-yn-1-yl) phenol was prepared based on literature procedure.[5b]

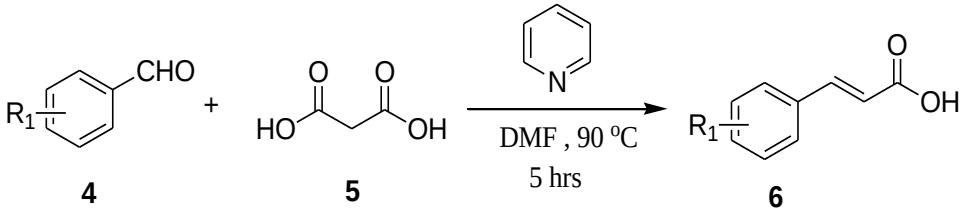


1g

Phenyl acetylene (460 mg, 4.5 mmol) was added in 2.5 ml dry THF. Then the solution was cooled to -78 ^{o}C. At that temperature *n*-BuLi (1.8 ml, 2.5 M in THF) was added dropwise. Resultant reaction mixture was shifted to -40 ^{o}C for 4 hours and again thereafter cooled to -78 ^{o}C. Then 2-hydroxy benzaldehyde (250 mg, 2.05 mmol) was added dropwise to the reaction mixture and continued stirring for 12 hours. After completion of the reaction, reaction mixture was quenched by saturated NH_4Cl. Finally, work up was done by DCM. The crude product was purified by column chromatography using 15% (Hexane/ EtOAc) solvent system to get 279 mg (yield: 61%) of the desired compound **1g** as white solid.

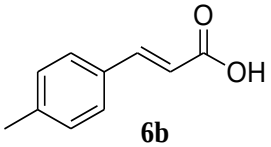
3. **Stepwise procedure for the synthesis of various enecarbamates (2):**

(A).Preparation of substituted cinnamic acids (6)



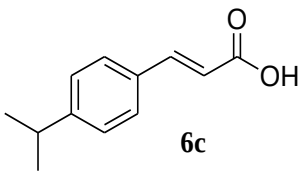
4 **5** **6**

To a solution of the corresponding substituted benzaldehyde **4** (3 mmol) and malonic acid **5** (9 mmol) in DMF (1.8 ml) was added pyridine (3 mmol) and stirred for 5 hrs at 90^{o}C. After adding water (4 ml), the reaction mixture was acidified (pH 1) with concentrated HCl and it was cooled to 0 ^{o}C. Resulting precipitate was filtered and washed with cold water for 2 to 3 times. Finally, crude solid product **6** was dried under vacuum pump for 3-4 hours. Thereafter substituted cinnamic acids (**6b** to **6o**), (Solid, white in color) were used directly without further purification for the preparation of substituted 3-phenyl-acryloyl azides **7**.



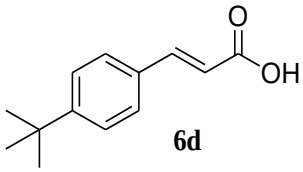
6b

Yield (452 mg, 93 %)



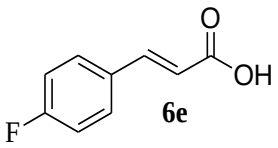
6c

Yield (458 mg, 80 %)



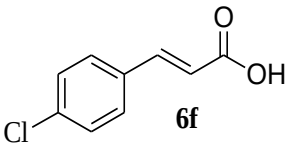
6d

Yield (580 mg, 95 %)



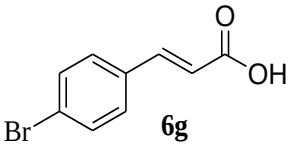
6e

Yield (473 mg, 95 %)



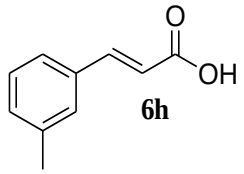
6f

Yield (521 mg, 95 %)



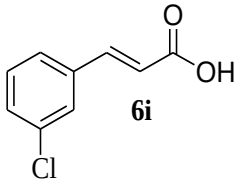
6g

Yield (573 mg, 84 %)



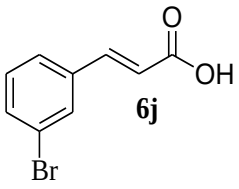
6h

Yield (460 mg, 95 %)



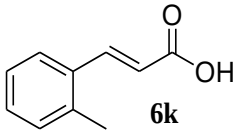
6i

Yield (495 mg, 90 %)



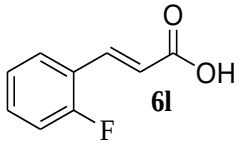
6j

Yield (660 mg, 97 %)



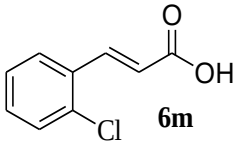
6k

Yield (413 mg, 85 %)



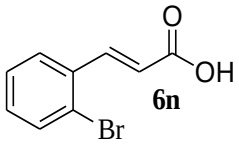
6l

Yield (468 mg, 94 %)



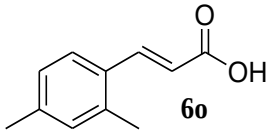
6m

Yield (520 mg, 95 %)



6n

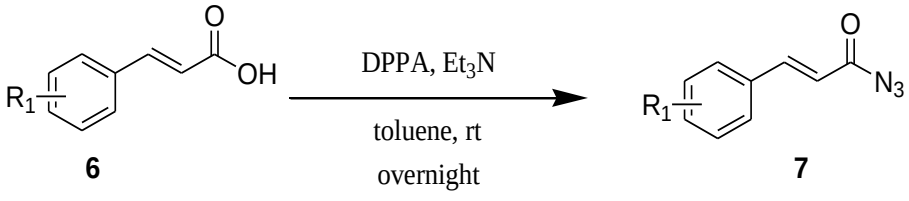
Yield (656 mg, 96 %)



6o

Yield (380 mg, 72 %)

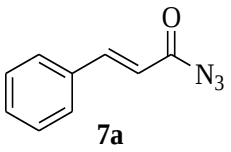
(B). <u>Preparation of substituted 3-phenyl-acryloyl azides (7) from cinnamic acids (6)</u>



6 **7**

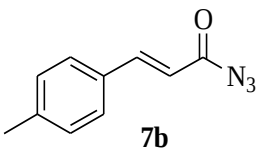
To the solution of corresponding cinnamic acid **6** (2 mmol) in toluene (13.3 ml), was added Et_3N (10 mmol) and diphenylphosphoryl azide (DPPA, 8 mmol) under argon balloon. Then the reaction mixture was stirred for overnight at room temperature. Progress of the reaction was monitored by TLC. Then work up was done by using DCM solvent and washed with brine solution. Organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. Finally the crude

acryloyl azides (**7a** to **7o**) were purified by column chromatography using 2% (Hexane / EtOAc). Thereafter substituted 3-phenyl-acryloyl azides (**7a** to **7o**), (Solid, white in color) were used directly for the preparation of various enecarbamates **2** without any characterization.



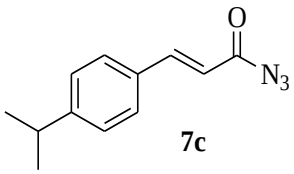
7a

Yield (277 mg, 80 %)



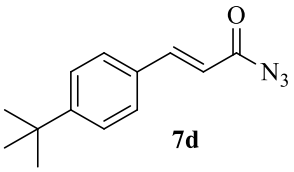
7b

Yield (220 mg, 59 %)



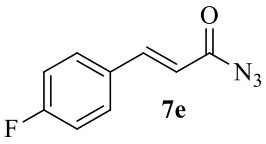
7c

Yield (332 mg, 77 %)



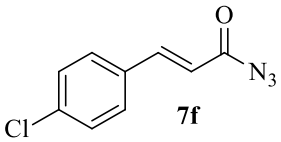
7d

Yield (360 mg, 79 %)



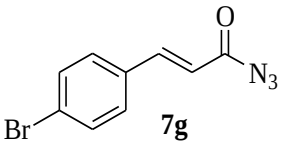
7e

Yield (311 mg, 81 %)



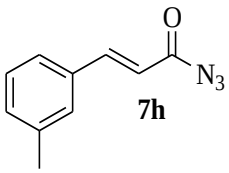
7f

Yield (333 mg, 80 %)



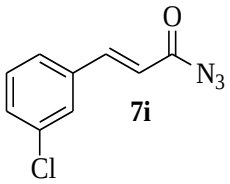
7g

Yield (452 mg, 90 %)



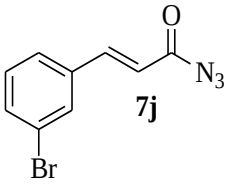
7h

Yield (312 mg, 83 %)



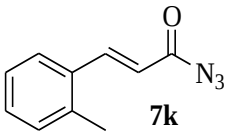
7i

Yield (342 mg, 82 %)



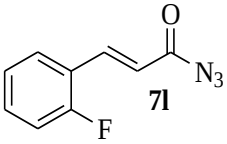
7j

Yield (430 mg, 85 %)



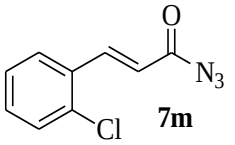
7k

Yield (183 mg, 49 %)



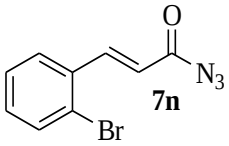
7l

Yield (335 mg, 88 %)



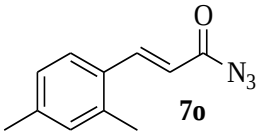
7m

Yield (375 mg, 90 %)



7n

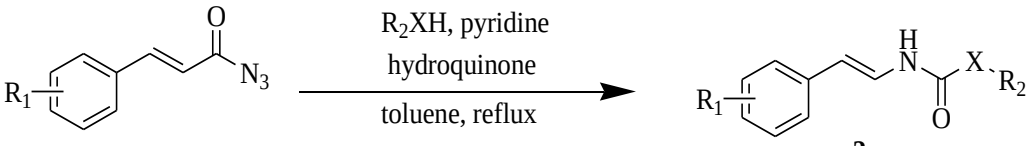
Yield (312 mg, 62 %)



7o

Yield (335 mg, 83 %)

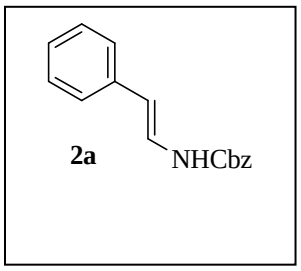
(C).<u>Preparation of enecarbamates (2) from substituted 3-phenyl-acryloyl azides (7) & characterization data for the enecarbamates (2)</u>



7 **2** X = O, S

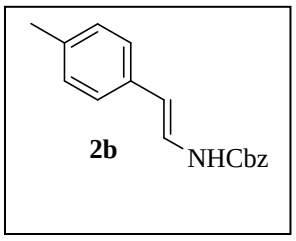
A solution of corresponding acryloyl azide **7** (1 mmol) in toluene (3 ml) was added dropwise to a stirred mixture of hydroquinone (0.05 mmol), pyridine (0.06 mmol) and corresponding alcohol or thiol (1.2 mmol) at 100 ^{o}C. The mixture was then stirred for 30 minutes under reflux condition and the toluene was removed by rotary evaporation. Finally the crude product was purified by doing column chromatography using (Hexane / EtOAc) as solvent system to afford the desired enecarbamates **2**.

Benzyl styrylcarbamate (2a)



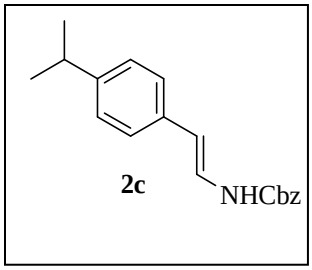
The procedure **3 (C)** was followed for the reaction of **7a** (173 mg, 1 mmol) to enecarbamate **2a**. The crude product was purified by column chromatography using 3% (Hexane / EtOAc) solvent system to get 225 mg (yield: 89%) of the desired compound **2a** as a white solid. **^{1}H NMR (600 MHz, CDCl3)**: δ 7.39 - 7.36 (m, 5H), 7.29 - 7.28 (m, 5H), 7.17 (d, *J* = 2.8 Hz, 1H), 6.77 (brs, 1H), 5.98 (d, *J* = 14.5 Hz, 1H), 5.20 (s, 2H); **^{13}C NMR (100 MHz, CDCl3)**: δ 153.8, 136.4, 136.0, 128.8, 128.8, 128.6, 128.5, 126.5, 125.5, 124.1, 111.2, 67.6.

Benzyl 4-methylstyrylcarbamate (2b)



The procedure **3 (C)** was followed for the reaction of **7b** (187 mg, 1 mmol) to enecarbamate **2b**. The crude product was purified by column chromatography using 4% (Hexane / EtOAc) solvent system to get 187 mg (yield: 70%) of the desired compound **2b** as a white solid. **^{1}H NMR (600 MHz, CDCl3)**: δ 7.38 (d, *J* = 4.2 Hz, 4H), 7.35 (dd, *J* = 8.3, 3.9 Hz, 1H), 7.18 (d, *J* = 7.7 Hz, 3H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.61 (brs, 1H), 5.94 (d, *J* = 14.6 Hz, 1H), 5.19 (s, 2H), 2.32 (s, 3H); **^{13}C NMR (100 MHz, CDCl3)**: δ 153.8, 136.2, 136.0, 133.5, 129.5, 128.7, 128.5, 128.4, 125.4, 123.3, 111.2, 67.5, 21.2.

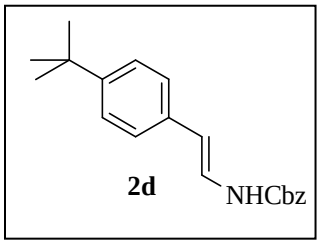
Benzyl 4-isopropylstyrylcarbamate (2c)



The procedure **3 (C)** was followed for the reaction of **7c** (215 mg, 1 mmol) to enecarbamate **2c**. The crude product was purified by column

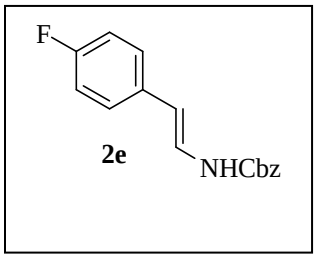
chromatography using 3% (Hexane / EtOAc) solvent system to get 248 mg (yield: 84%) of the desired compound **2c** as a white solid. **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.39 (d, *J* = 4.1 Hz, 4H), 7.35 (d, *J* = 5.0 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.78 (brs, 1H), 5.97 (d, *J* = 14.5 Hz, 1H), 5.20 (s, 2H), 2.90 – 2.87 (m, 1H), 1.26 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 153.9, 147.2, 136.0, 133.9, 128.7, 128.5, 128.3, 126.8, 125.4, 123.4, 111.2, 67.4, 33.8, 24.1.

Benzyl 4-tert-butylstyrylcarbamate (2d)



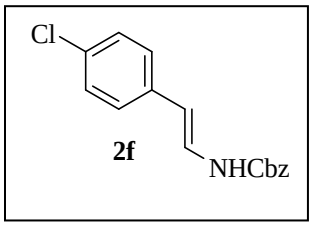
The procedure **3 (C)** was followed for the reaction of **7d** (229 mg, 1 mmol) to enecarbamate **2d**. The crude product was purified by column chromatography using 2.5% (Hexane / EtOAc) solvent system to get 270 mg (yield: 87%) of the desired compound **2d** as a white solid. **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.39 (d, *J* = 4.1 Hz, 4H), 7.35 (dd, *J* = 8.4, 4.0 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 3H), 6.63 (brs, 1H), 5.96 (d, *J* = 14.6 Hz, 1H), 5.19 (s, 2H), 1.31 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 153.9, 149.4, 136.0, 133.5, 128.7, 128.5, 128.4, 125.7, 125.2, 123.5, 111.1, 67.4, 34.6, 31.4.

Benzyl 4-fluorostyrylcarbamate (2e)



The procedure **3 (C)** was followed for the reaction of **7e** (191 mg, 1 mmol) to enecarbamate **2e**. The crude product was purified by column chromatography using 4% (Hexane / EtOAc) solvent system to get 188 mg (yield: 69%) of the desired compound **2e** as a white solid. **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.38 (d, *J* = 3.9 Hz, 4H), 7.22 (t, 2H), 7.16 (dd, *J* = 14.0, 11.6 Hz, 1H), 6.97 (t, *J* = 8.7 Hz, 3H), 6.74 (brs, 1H), 5.94 (d, *J* = 14.6 Hz, 1H), 5.19 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 162.8, 160.4, 153.9, 135.9, 132.4, 128.7, 128.5, 128.4, 126.8, 126.7, 123.9, 115.7, 115.5, 110.1, 67.5.

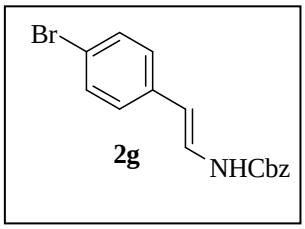
Benzyl 4-chlorostyrylcarbamate (2f)



The procedure **3 (C)** was followed for the reaction of **7f** (208 mg, 1 mmol) to enecarbamate **2f**. The crude product was purified by column chromatography using 3.5% (Hexane / EtOAc) solvent system to get 192 mg (yield: 67%) of the desired compound **2f** as a white solid. **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.40 – 7.34 (m, 5H), 7.23 (d, *J* = 8.5 Hz,

3H), 7.19 (d, *J* = 8.2 Hz, 2H), 6.73 (brs, 1H), 5.92 (d, *J* = 14.5 Hz, 1H), 5.19 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 153.7, 135.9, 134.9, 131.9, 128.9, 128.8, 128.7, 128.5, 126.6, 124.7, 109.9, 67.7.

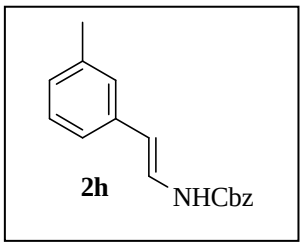
Benzyl 4-bromostyrylcarbamate (2g)



2g

The procedure **3 (C)** was followed for the reaction of **7g** (252 mg, 1 mmol) to enecarbamate **2g**. The crude product was purified by column chromatography using 4% (Hexane / EtOAc) solvent system to get 206 mg (yield: 62%) of the desired compound **2g** as a white solid. **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.38 (d, *J* = 8.1 Hz, 6H), 7.22 (d, *J* = 13.3 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 3H), 6.67 (d, *J* = 10.9 Hz, 1H), 5.90 (d, *J* = 14.5 Hz, 1H), 5.19 (s, 2H); **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 153.7, 135.8, 135.4, 131.8, 128.8, 128.6, 128.5, 126.9, 124.7, 119.9, 109.9, 67.7.

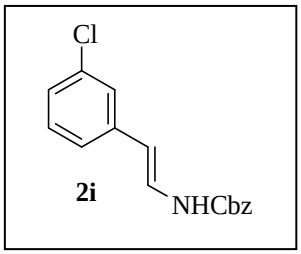
Benzyl 3-methylstyrylcarbamate (2h)



2h

The procedure **3 (C)** was followed for the reaction of **7h** (187 mg, 1 mmol) to enecarbamate **2h**. The crude product was purified by column chromatography using 4% (Hexane / EtOAc) solvent system to get 228 mg (yield: 85%) of the desired compound **2h** as a white solid. **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.36 – 7.30 (m, 5H), 7.21 (t, *J* = 12.7 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.08 (s, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 10.8 Hz, 1H), 5.90 (d, *J* = 14.5 Hz, 1H), 5.15 (s, 2H), 2.28 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 153.8, 138.2, 136.2, 136.0, 128.7, 128.6, 128.5, 128.3, 127.3, 126.1, 123.9, 122.6, 111.3, 67.5, 21.5.

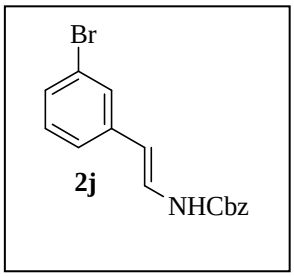
Benzyl 3-chlorostyrylcarbamate (2i)



2i

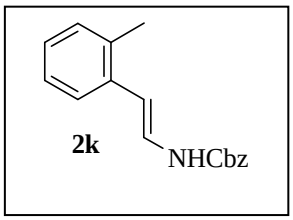
The procedure **3 (C)** was followed for the reaction of **7i** (208 mg, 1 mmol) to enecarbamate **2i**. The crude product was purified by column chromatography using 4% (Hexane / EtOAc) solvent system to get 187 mg (yield: 65%) of the desired compound **2i** as a white solid. **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.38 – 7.33 (m, 5H), 7.23 (d, *J* = 5.5 Hz, 2H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.11 (t, *J* = 9.3 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 1H), 5.88 (d, *J* = 14.5 Hz, 1H), 5.18 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 153.7, 138.3, 135.8, 134.6, 130.0, 128.8, 128.6, 128.4, 126.3, 125.4, 125.3, 123.4, 109.8, 67.7.

Benzyl 3-bromostyrylcarbamate (2j)



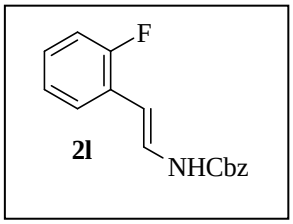
The procedure **3 (C)** was followed for the reaction of **7j** (252 mg, 1 mmol) to enecarbamate **2j**. The crude product was purified by column chromatography using 3.5% (Hexane / EtOAc) solvent system to get 294 mg, (yield: 89%) of the desired compound **2j** as a white solid. **^{1}H NMR (600 MHz, CDCl$_3$)**: δ 7.41 (s, 1H), 7.38 (brs, 5H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 6.88 (brs, 1H), 5.89 (d, *J* = 14.5 Hz, 1H), 5.20 (s, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 153.7, 138.6, 135.8, 130.2, 129.2, 128.8, 128.6, 128.4, 128.3, 125.3, 123.8, 122.9, 109.6, 67.7.

Benzyl 2-methylstyrylcarbamate (2k)



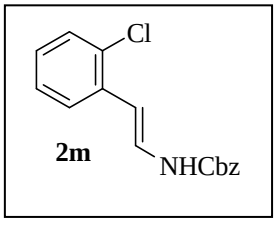
The procedure **3 (C)** was employed for the reaction of **7k** (187 mg, 1 mmol) to enecarbamate **2k**. The crude product was purified by column chromatography using 3% (Hexane / EtOAc) solvent system to get 212 mg, (yield: 79%) of the desired compound **2k** as a white solid. **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 7.41 – 7.34 (m, 6H), 7.17 – 7.09 (m, J = 17.5, 7.0 Hz, 4H), 6.70 (brs, 1H), 6.15 (d, *J* = 14.4 Hz, 1H), 5.20 (s, 2H), 2.29 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 153.7, 136.0, 135.1, 134.8, 130.5, 128.8, 128.6, 128.5, 126.7, 126.4, 124.9, 124.8, 109.0, 67.6, 20.2.

Benzyl 2-fluorostyrylcarbamate (2l)



The procedure **3 (C)** was followed for the reaction of **7l** (191 mg, 1 mmol) to enecarbamate **2l**. The crude product was purified by column chromatography using 3% (Hexane / EtOAc) solvent system to get 234 mg (yield: 86%) of the desired compound **2l** as a white solid. **^{1}H NMR (600 MHz, CDCl$_3$)**: δ 7.40 – 7.34 (m, 7H), 7.12 (dd, *J* = 13.2, 5.9 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 7.01 (dd, *J* = 10.2, 8.8 Hz, 1H), 6.85 (brs, 1H), 6.09 (d, *J* = 14.5 Hz, 1H), 5.20 (s, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 160.9, 158.5, 153.7, 135.9, 128.8, 128.6, 128.4, 127.6, 127.5, 126.4, 126.4, 126.2, 126.1, 124.3, 124.3, 124.2, 124.1, 115.9, 115.6, 103.7, 103.7, 67.7.

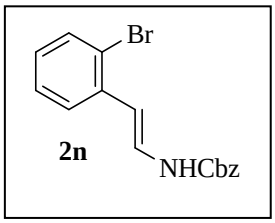
Benzyl 2-chlorostyrylcarbamate (2m)



The procedure **3 (C)** was followed for the reaction of **7m** (208 mg, 1 mmol) to enecarbamate **2m**. The crude product was purified by column chromatography using 2.5% (Hexane / EtOAc) solvent system to get 256

mg (yield: 89%) of the desired compound **2m** as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.48 (d, *J* = 7.6 Hz, 1H), 7.38 (brs, 5H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 5.5 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 8.6 Hz, 1H), 6.34 (d, *J* = 14.5 Hz, 1H), 5.20 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 153.6, 135.9, 134.4, 132.3, 129.9, 128.9, 128.7, 128.5, 127.6, 127.1, 126.1, 125.8, 107.3, 67.8.

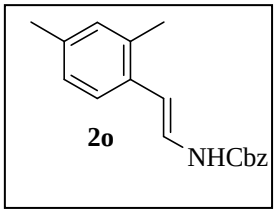
Benzyl 2-bromostyrylcarbamate (2n)



2n

The procedure **3 (C)** was followed for the reaction of **7n** (252 mg, 1 mmol) to enecarbamate **2n**. The crude product was purified by column chromatography using 3% (Hexane / EtOAc) solvent system to get 220 mg (yield: 66%) of the desired compound **2n** as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.52 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.38 (brs, 5H), 7.22 (dd, *J* = 16.1, 9.1 Hz, 2H), 7.03 (t, *J* = 6.9 Hz, 1H), 6.82 (brs, 1H), 6.32 (d, *J* = 14.5 Hz, 1H), 5.20 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 153.6, 136.2, 135.9, 133.1, 128.8, 128.7, 128.5, 127.9, 127.8, 126.2, 126.0, 123.0, 109.9, 67.8.

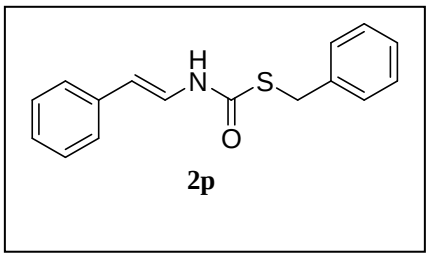
Benzyl 2,4-dimethylstyrylcarbamate (2o)



2o

The procedure **3 (C)** was followed for the reaction of **7o** (201 mg, 1 mmol) to enecarbamate **2o**. The crude product was purified by column chromatography using 4% (Hexane / EtOAc) solvent system to get 199 mg (yield: 71%) of the desired compound **2o** as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.39 (d, *J* = 4.1 Hz, 4H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.07 (dd, *J* = 22.1, 10.6 Hz, 2H), 6.97 (s, 1H), 6.95 (s, 1H), 6.63 (d, *J* = 10.2 Hz, 1H), 6.11 (d, *J* = 14.4 Hz, 1H), 5.19 (s, 2H), 2.29 (s, 3H), 2.25 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 153.7, 136.4, 136.1, 134.6, 132.2, 131.2, 128.8, 128.6, 128.5, 127.1, 124.9, 124.1, 109.0, 67.6, 21.2, 20.1.

S-benzyl N-styrylcarbamothioate (2p)

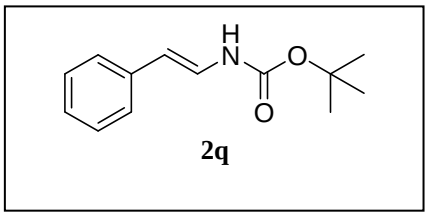


2p

The procedure **3 (C)** was followed for the reaction of **7p** (173 mg, 1 mmol) to enecarbamate **2p**. The crude product was purified by column chromatography using 4% (Hexane / EtOAc) solvent system to get 227 mg (yield: 84%) of the desired compound **2p** as a white solid. **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.43 (brs, 1H), 7.37 (d, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 4.3 Hz, 4H), 7.27 (s, 1H), 7.19 (dt, *J* = 8.6, 4.3 Hz, 1H), 7.11 (brs, 1H),

6.05 (d, *J* = 14.5 Hz, 1H), 4.25 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 165.2, 138.0, 136.3, 129.0, 128.7, 127.4, 126.6, 125.6, 123.3, 112.3, 34.2.

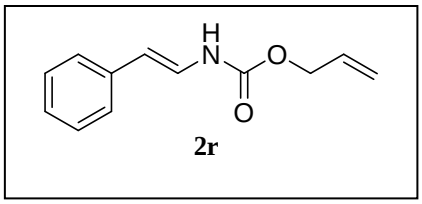
tert-butyl styrylcarbamate (2q)



2q

The procedure **3 (C)** was followed for the reaction of **7q** (173 mg, 1 mmol) to enecarbamate **2q**. The crude product was purified by column chromatography using 4% (Hexane / EtOAc) solvent system to get 94 mg (yield: 43%) of the desired compound **2q** as a white solid. **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.30 (d, *J* = 4.3 Hz, 5H), 7.18 (dt, *J* = 8.4, 4.1 Hz, 1H), 6.49 (brs, 1H), 5.94 (d, *J* = 14.5 Hz, 1H), 1.53 (s, 9H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 152.8, 136.7, 128.8, 126.2, 125.3, 124.5, 109.9, 81.1, 28.4.

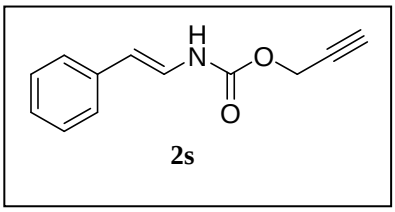
Allyl styrylcarbamate (2r)



2r

The procedure **3 (C)** was followed for the reaction of **7r** (173 mg, 1 mmol) to enecarbamate **2r**. The crude product was purified by column chromatography using 4% (Hexane / EtOAc) solvent system to get 177 mg (yield: 87%) of the desired compound **2r** as a white sticky solid. **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.30 – 7.27 (m, 5H), 7.23 (s, 1H), 7.16 (dd, *J* = 8.6, 5.0 Hz, 1H), 6.63 (d, *J* = 8.3 Hz, 1H), 5.98 (d, *J* = 14.6 Hz, 1H), 5.35 (d, *J* = 17.1 Hz, 1H), 5.26 (d, *J* = 10.3 Hz, 1H), 4.66 (d, *J* = 4.8 Hz, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 153.5, 136.2, 132.2, 128.6, 126.3, 125.3, 124.0, 118.4, 110.9, 66.2.

Prop-2-ynyl styrylcarbamate (2s)



2s

The procedure **3 (C)** was followed for the reaction of **7s** (173 mg, 1 mmol) to enecarbamate **2s**. The crude product was purified by column chromatography using 5% (Hexane / EtOAc) solvent system to get 175 mg (yield: 87%) of the desired compound **2s** as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.29 (d, *J* = 3.4 Hz, 4H), 7.23 (d, *J* = 2.8 Hz, 1H), 7.19 (s, 1H), 6.97 (brs, 1H), 6.03 (d, *J* = 14.5 Hz, 1H), 4.78 (s, 2H), 2.53 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 153.0, 136.1, 128.8, 126.6, 125.5, 123.7, 111.9, 77.8, 75.5, 53.3.

4. **<u>References</u>:**

1) (*a*) P. Wipf and J.-K. Jung, *J. Org. Chem.*, 2000, **65**, 6319; (*b*) J. Seayad, A.-M. Seayad and B. List, *J. Am. Chem. Soc.*, 2006, **128**, 1086.

2) (*a*) T. Akiyama, J. Itoh, K. Yokota and K. Fuchibe, *Angew. Chem. Int. Ed*., 2004, **43**, 1566; (*b*) T. Akiyama, H. Morita, J. Itoh and K. Fuchibe, *Org. Lett*., 2005, **7**, 2583; also see: (*c*) T. Akiyama, PCT Int. Appl. WO 200409675, 2004; (*d*) T. Akiyama, Y. Saitoh, H. Morita and K. Fuchibe, *Adv. Synth. Catal*., 2005, **347**, 1523.

3) (*a*) D. Uraguchi and M. Terada, *J. Am. Chem. Soc*., 2004, **126**, 5356; (*b*) D. Uraguchi, K. Sorimachi and M. Terada, *J. Am. Chem. Soc*., 2004, **126**, 11804; (*c*) D. Uraguchi, K. Sorimachi and M. Terada, *J. Am. Chem. Soc*., 2005, **127**, 9360; also see: (*d*) M. Terada, D. Uraguchi, K. Sorimachi and H. Shimizu, PCT Int. Appl. WO 2005070875, 2005.

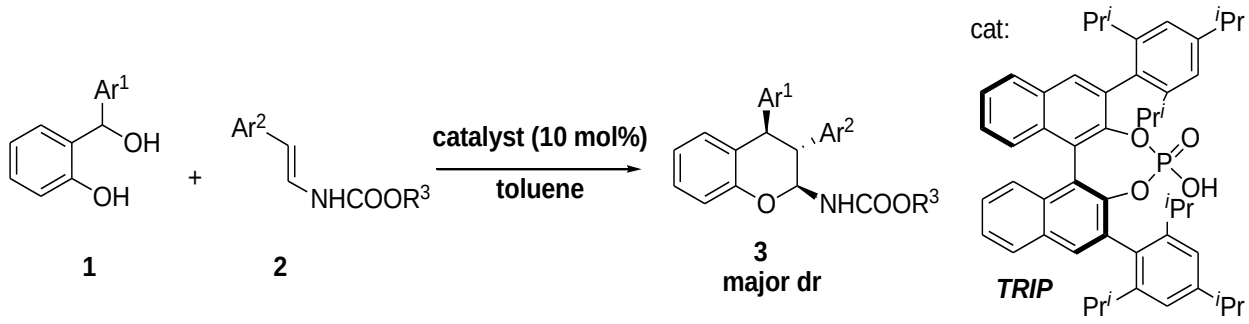
4) B. Meier, J.-N. Dumez, G. Stevanato, J. T. Hill-Cousins, S. S. Roy, P. Håkansson, S. Mamone, R. C. D. Brown, G. Pileio and M. H. Levitt, *J. Am. Chem. Soc*., 2013, **135**, 18746.

5) (*a*) M.-W. Chen, L.-L. Cao, Z.-S. Ye, G.-F. Jiang and Y.-G. Zhou, *Chem. Commun*., 2013, **49**, 1660; (*b*) S. Saha and C. Schneider, *Org. Lett*., 2015, **17**, 648.

6) X. Li, J. Sheng, G. Huang, F. Yin and D. Sang, *Eur. J. Med. Chem*., 2015, **97**, 32.

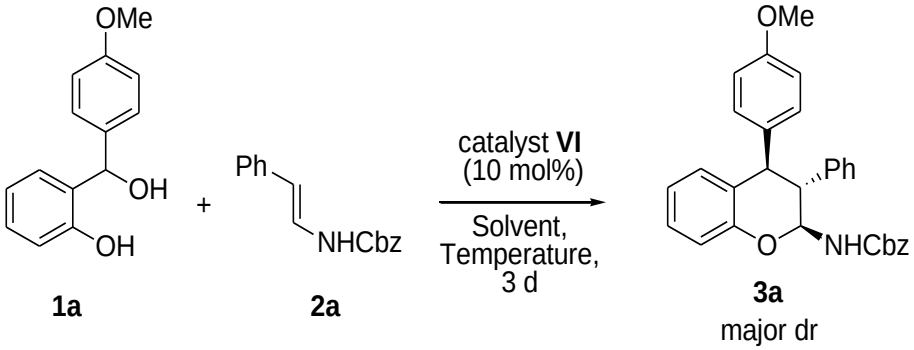
7) (*a*) A. Carboni, G. Dagousset, E. Magnier and G. Masson, *Org. Lett*., 2014, **16**, 1240; (*b*) T. Hashimoto, H. Nakatsu, Y. Takiguchi and K. Maruoka, *J. Am. Chem. Soc*., 2013, **135**, 16010.

5. **<u>General procedure for the synthesis of trisubstituted Chromans (3)</u>:**



To a solution of *o*-hydroxybenzyl alcohol **(1)** (0.08 mmol), enecarbamate **(2)** (0.12 mmol) in 0.4 ml dry toluene, catalyst **VI** (10 mol%) was added. Then the reaction mixture was stirred at room temperature for 3 to 4 days unless otherwise noted. After the completion of reaction, reaction mixture was directly subjected to the column using 5-7% (hexane/ ethyl acetate) to obtain the desired product (**3**).

6. **Solvent and temperature screening:**



1a **2a** **3a**
major dr

entry[a]	solvent	temperature	yield[b] %	ee[c] %
1	toluene	rt	81	90
2	DCM	rt	54	88
3[d]	DCM	rt	65	82
4	DMF	rt	n.d	-
5	DCE	rt	74	90
6	toluene	0 °C	82	88

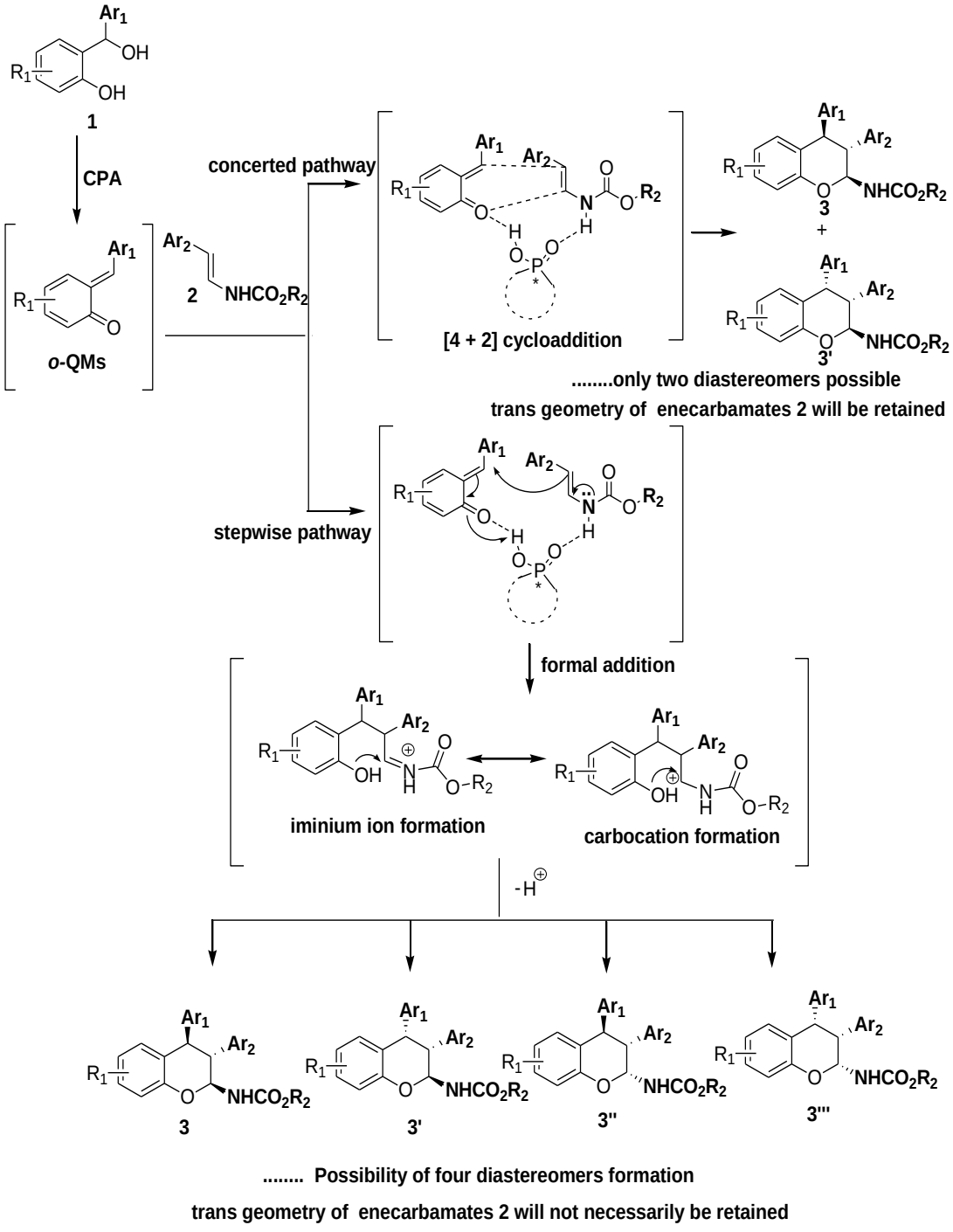
[a]Reaction condition: 0.04 mmol of **1a** and 0.06 mmol of **2a** in 0.2 mL solvent using 10 mol% catalyst for 3 days. [b]Isolated yield after silica gel column chromatography. [c]Determined by HPLC and of the major diastereomer. [d]5 mg 4A° MS was used.

7. **Possible mechanistic pathway involved in the synthesis of trisubstituted chromans (3):**

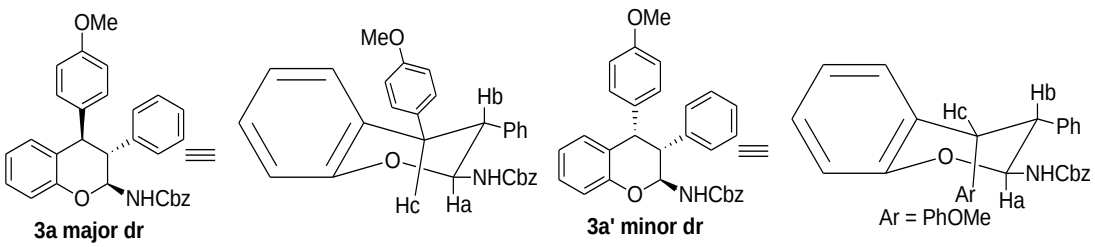
If the reaction underwent via concerted [4+2] mechanism then only two diastereomers **3** and **3'** can be formed, not only that but also *trans* geometry of enecarbamates **2** also will be retained in the tri-substituted chroman products. On the other hand, if the reaction underwent through stepwise path there might be a possibility of four diastereomers formation (diastereomer **3**, **3'**, **3''** & **3'''**). In that case *trans* geometry of enecarbamates **2** will not necessarily be retained in the tri-substituted chroman products. (**Scheme 1**).

In all of our experiments, we finely observed the presence of only two diastereomers **3** & **3'** with generally high diastereomeric ratio determined from **^{1}H NMR** experiment and **HPLC** analysis. Relative stereo chemistry of the product **3** & **3'** were confirmed from coupling constant value

and from **COSY** & **NOESY** experiment. However, we did not get any traces of product **3''** & **3'''**. These results might support the highly concerted nature of the concerned reaction.



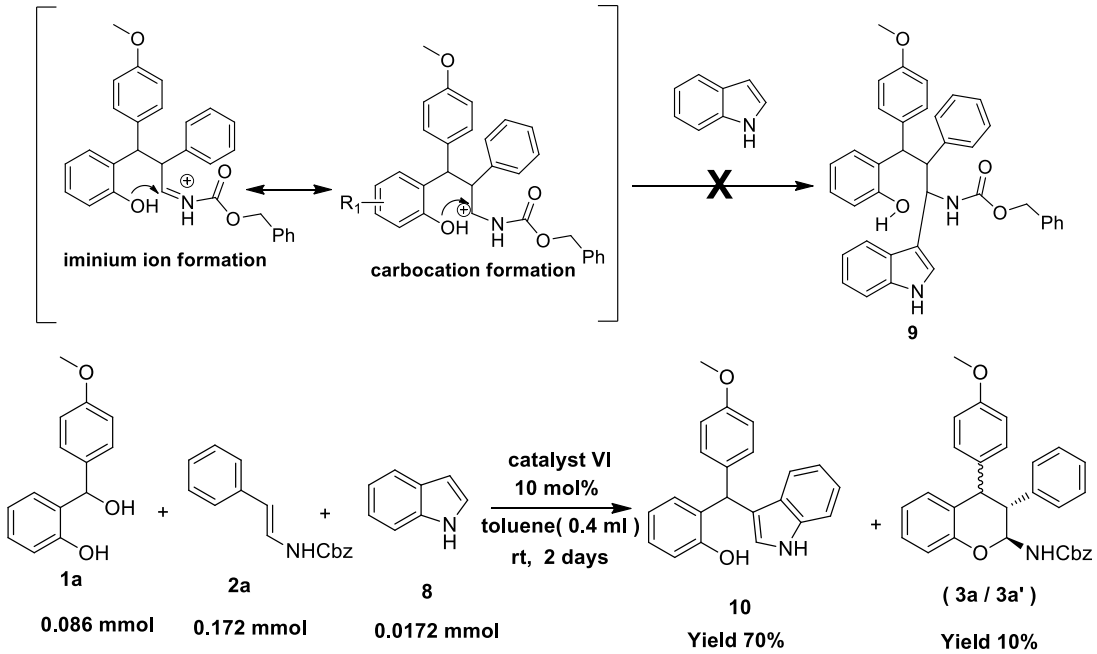
Scheme 1. Analysis of chroman formation based on Stepwise & concerted mechanism



Stereo specific addition of the enecarbamates **2** can also be supported by considering the coupling constant value of three characteristic protons H_a, H_b & H_c present in the chroman ring. As for example it is shown below for the compound **(3a/3a'), Diastereomeric ratio: 5.6:1**.

For **3a (major dr):** H_a: 5.97 (t, *J* = 9.6 Hz, 1H), H_b: 3.12 (t, *J* = 10.3 Hz, 1H), H_C: 4.31 (d, *J* = 10.9 Hz, 1H) & for **3a' (minor dr):** H_a: 6.14 (t, *J* = 10.3 Hz, 0.2H), H_b: 3.50 (dd, *J* = 10.2, 4.8 Hz, 0.2H), H_c: 4.25 (d, *J* = 5.2 Hz, 0.2H).

In addition, if the reaction proceeded via stepwise mechanism, then the iminium ion & carbocation intermediates might be captured by an external reactive nucleophile like indole for its stability as reported by *Shi et al.*[8] Hence, we carried out our reaction in presence of indole (**Scheme 2**. below) but the intercepted product **9** was not formed. Instead of that we got the product **10** as major along with trace amount of tri-substituted product **(3a/3a').** From this experiment we proposed that the concerned reaction possibly underwent via concerted pathway rather than stepwise way.

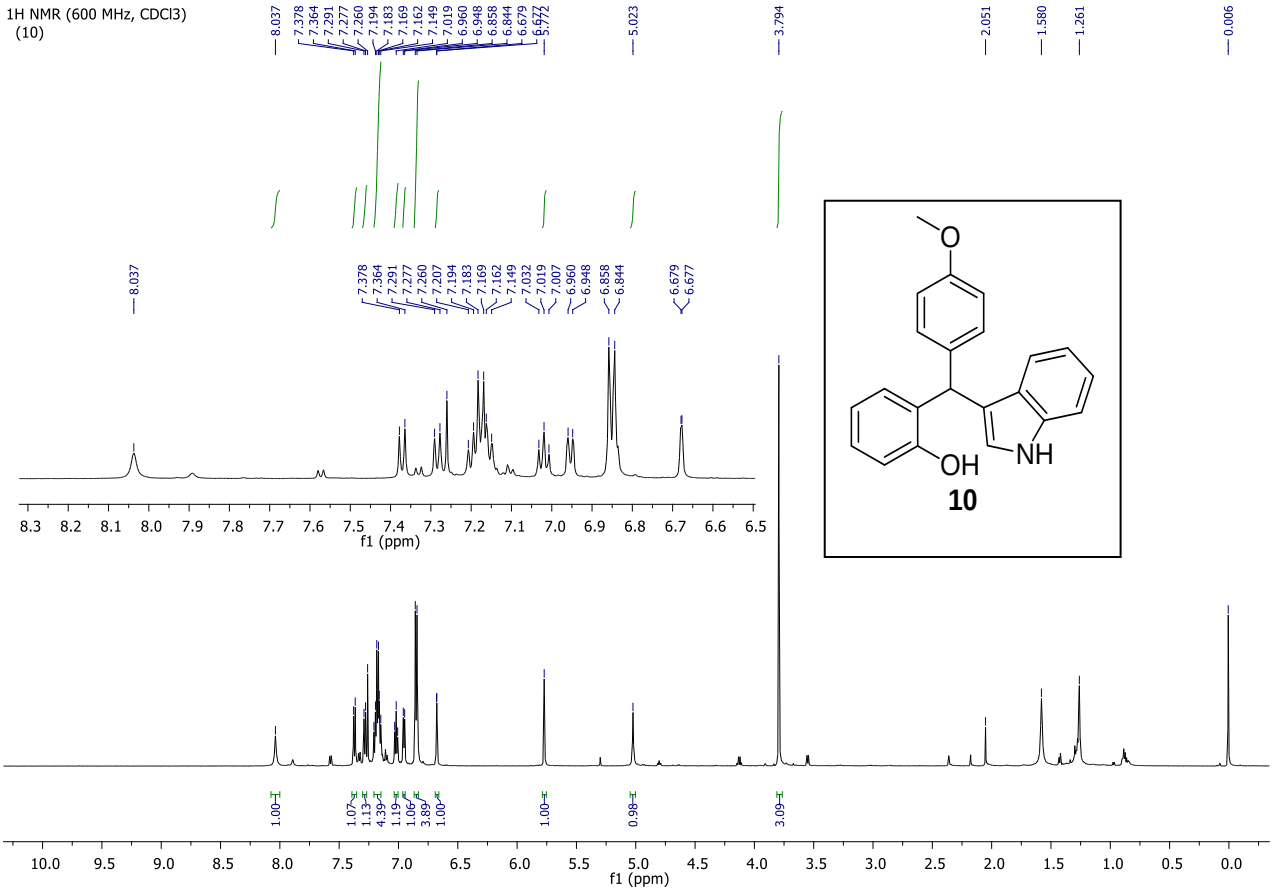


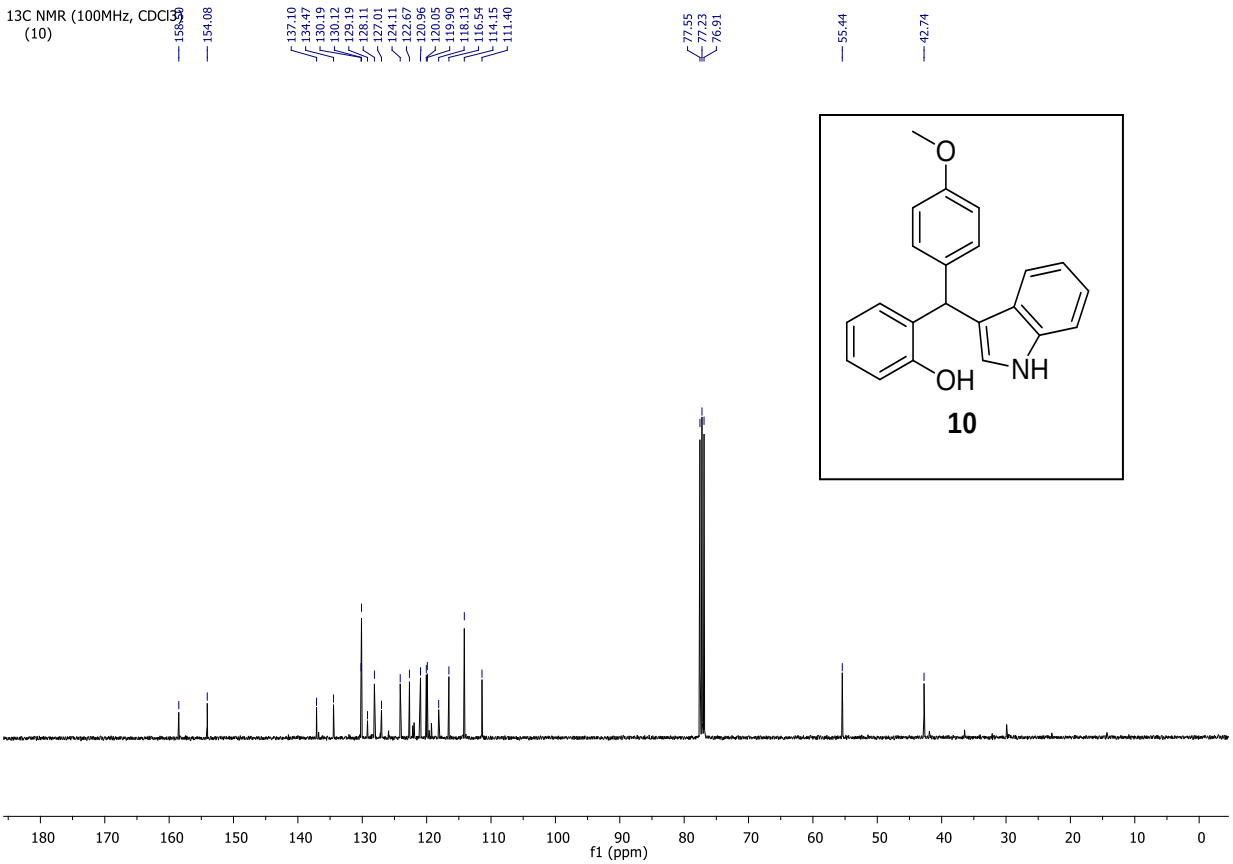
Scheme 2. Trapping experiment using indole as reactive nucleophile

8) J.-J. Zhao, S.-B. Sun, S.-H. He, Q. Wu and F. Shi, *Angew. Chem. Int. Ed*., 2015, **54**, 5460.

Characterization data of compound 10: **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 8.04 (s, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.21 – 7.15 (m, 4H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 6.9 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 4H), 6.68 (d, *J* = 1.4 Hz, 1H), 5.77 (s, 1H), 5.02 (s, 1H), 3.79 (s, 3H); **HRMS (-ESI):** Calc for $(C_{22}H_{19}NO_2\text{-}H)^-$ [M-H]- 328.1343; found: 328.1345, **^{13}C NMR (100 MHz, CDCl3)**: δ 158.5, 154.1, 137.1, 134.5, 130.2, 130.1, 129.2, 128.1, 127.0, 124.1, 122.7, 121.0, 120.1, 119.9, 118.1, 116.5, 114.2, 111.4, 55.4, 42.7.

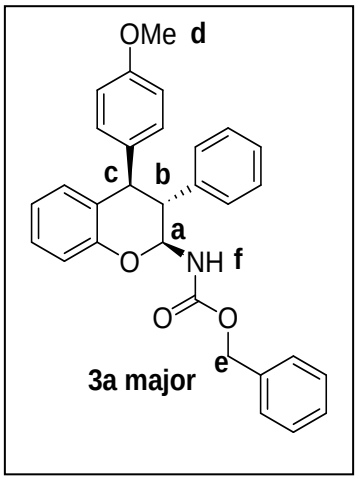
^{1}H NMR & ^{13}C NMR spectra of compound 10:





8. **<u>Characterization data for the trisubstituted chromans (3)</u>:**

Benzyl 3,4-dihydro-4-(4-methoxyphenyl)-3-phenyl-2H-chromen-2-ylcarbamate (3a/3a')

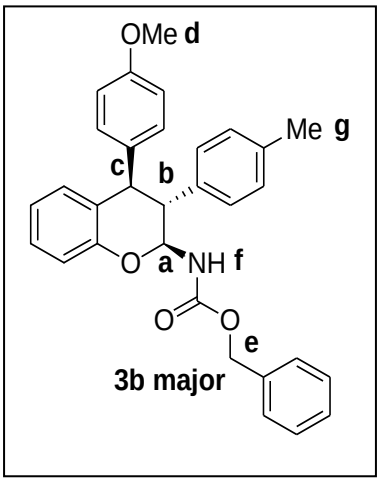


Compound **(3a/3a')** was prepared according to the general procedure **5**; **Reaction time**: 3 days; purified by column chromatography using 6% (Hexane / EtOAc) solvent system. White solid (30.2 mg, yield: 81%); **mp**: 114-116 ^{o}C; **Diastereomeric ratio:** 5.6:1; **^{1}H NMR (600 MHz, CDCl$_3$)**: δ 7.30 (brs, 3H), 7.23 – 7.13 (m, 7H), 7.03 (d, *J* = 8.2 Hz, 0.3H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.93 (d, *J* = 5.6 Hz, 2H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 2H), 6.74 (d, *J* = 7.7 Hz, 1H), 6.68 (d, *J* = 8.6 Hz, 2H), 6.63 (d, *J* = 8.6 Hz, 0.5H), 6.51 (d, *J* = 8.6 Hz, 0.4H), 6.14 (t, *J* = 10.3 Hz, 0.2H$_a$ *minor*), 5.97 (t, *J* = 9.6 Hz, 1H$_a$ *major*), 5.42 (d, *J* = 8.9 Hz, 1H$_f$), 5.03 (dd, *J* = 30.8, 11.1 Hz, 2.2H$_e$), 4.31 (d, *J* = 10.9 Hz, 1H$_c$ *major*), 4.25 (d, *J* = 5.2 Hz, 0.2H$_c$ *minor*), 3.73 (s, 0.5H$_d$ *minor*), 3.72 (s, 3H$_d$ *major*), 3.50 (dd, *J* = 10.2, 4.8 Hz, 0.2H$_b$ *minor*), 3.12 (t, *J* = 10.3 Hz, 1H$_b$ *major*); **^{13}C NMR (150 MHz, CDCl$_3$)**: δ 158.4, 155.5, 154.0, 138.8, 136.1, 134.6, 130.1, 128.9,

128.7, 128.4, 128.3, 128.1, 127.3, 126.2, 121.4, 117.2, 113.9, 82.1, 67.2, 55.3, 53.0, 50.8; **HRMS (+ESI):** Calc for $C_{30}H_{28}NO_4$ $[M+H]^+$ 466.2013; found: 466.2016.

HPLC: Chiralpak IC column. Flow rate 1 mL/min. UV detection at 254 nm for major diastereomer; τ(major) = 20.1 min., τ(minor) = 15.0 min. using hexane: isopropanol = 90:10 as eluent, ee 90%.

Benzyl 3,4-dihydro-4-(4-methoxyphenyl)-3-p-tolyl-2H-chromen-2-ylcarbamate (3b/3b')



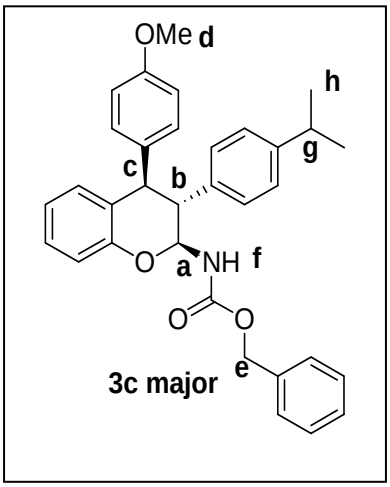
Compound **(3b/3b')** was prepared according to the general procedure **5**; **Reaction time**: 3 days; purified by column chromatography using 6% (Hexane / EtOAc) solvent system. White solid (32.2 mg, yield: 84%); **mp**: 53-55 ^oC; **Diastereomeric ratio:** 5:1; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.30 (brs, 3H), 7.20 (brs, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.97 (dd, *J* = 15.2, 7.8 Hz, 4H), 6.84 – 6.75 (m, 5H), 6.73 (d, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 8.5 Hz, 2H), 6.63 (d, *J* = 8.4 Hz, 0.4H), 6.52 (d, *J* = 8.4 Hz, 0.4H), 6.10 (t, *J* = 10.2 Hz, $0.2H_a$ *minor*), 5.93 (brs, $1H_a$ *major*), 5.34 (brs, $1H_f$), 5.04 (d, *J* = 19.8 Hz, $2.4H_e$), 4.29 (d, *J* = 11.0 Hz, $1H_c$ *major*), 4.22 (d, *J* = 5.3 Hz, $0.2H_c$ *minor*), 3.73 (s, $3.6H_d$), 3.07 (t, *J* = 9.6 Hz, $1H_b$ *major*), 2.29 (s, $0.5H_g$ *minor*), 2.27 (s, $3H_g$ *major*); **^{13}C NMR (150 MHz, $CDCl_3$)**: δ 158.4, 155.5, 154.0, 136.8, 136.2, 135.7, 134.8, 131.4, 130.2, 130.1, 129.6, 129.0, 129.0, 128.7, 128.3, 128.2, 128.0, 126.3, 124.7, 121.3, 121.1, 117.2, 117.0, 113.8, 113.3, 82.2, 82.2, 67.2, 67.2, 55.4, 55.3, 52.5, 50.7, 48.6, 48.4, 21.3; **HRMS (+ESI):** Calc for $C_{31}H_{30}NO_4$ $[M+H]^+$ 480.2169; found: 480.2172.

HPLC: Chiralpak IA column. Flow rate 1 mL/min. UV detection at 220 nm for major diastereomer; τ(major) = 33.6 min., τ(minor) = 58.2 min. using hexane: isopropanol = 90:10 as eluent, ee 92%.

Benzyl 3,4-dihydro-3-(4-isopropylphenyl)-4-(4-methoxyphenyl)-2H-chromen-2-ylcarbamate (3c/3c')

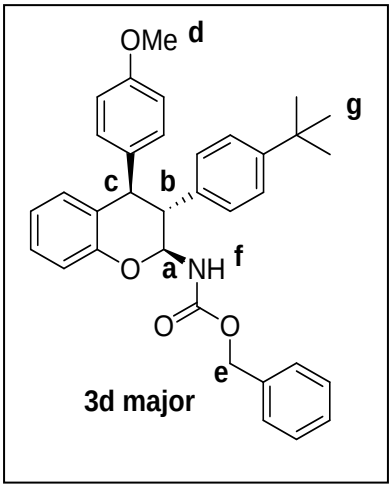
Compound **(3c/3c')** was prepared according to the general procedure **5**; **Reaction time**: 3 days; purified by column chromatography using 6% (Hexane / EtOAc) solvent system. Pale yellow solid (34.5 mg, yield: 85%); **mp**: 48-50 ^oC; **Diastereomeric ratio:** 8.3:1; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.30 (brs, 3H), 7.22 (brs, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 2H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.82 (dd, *J* = 12.8, 6.2 Hz, 3H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.74 (d, *J* = 7.7 Hz,

1H), 6.68 (d, *J* = 8.6 Hz, 2H), 6.61 (d, *J* = 8.5 Hz, 0.5H), 6.48 (d, *J* = 8.5 Hz, 0.3H), 6.11 (t, *J* = 10.2 Hz, 0.1H_a *minor*), 5.94 (brs, 1H_a *major*), 5.35 (d, *J* = 7.5 Hz, 1H_f), 5.04 (d, *J* = 19.8 Hz, 2.1H_e), 4.29 (d, *J* = 10.9 Hz, 1H_c *major*), 4.23 (d, *J* = 5.3 Hz, 0.12H_c *minor*), 3.73 (s, 3.4H_d), 3.08 (t, *J* = 9.8 Hz, 1H_b *major*), 2.83 (dt, *J* = 13.8, 6.9 Hz, 1.1H_g), 1.20 (dd, *J* = 6.9, 3.1 Hz, 6.7H_h); **^{13}C NMR (150 MHz, $CDCl_3$)**: δ 158.4, 155.56, 154.0, 147.7, 136.0, 134.9, 131.4, 130.2, 129.0, 128.7, 128.3, 128.2, 128.0, 126.8, 126.3, 121.3, 117.2, 113.8, 113.2, 82.2, 67.2, 55.3, 52.5, 50.7, 33.8, 24.1, 24.1; **HRMS (+ESI):** Calc for $C_{33}H_{34}NO_4$ $[M+H]^+$ 508.2482; found: 508.2483.



HPLC: Chiralpak IC column. Flow rate 1 mL/min. UV detection at 274 nm for major diastereomer; τ(major) = 24.8 min., τ(minor) = 20.0 min. using hexane: isopropanol = 93:7 up to τ = 30.0 min. thereafter, hexane: isopropanol = 86:14 as eluent, ee 88%.

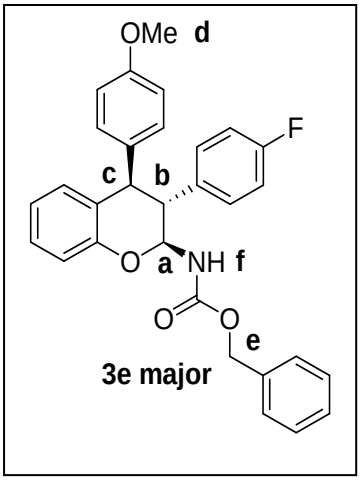
Benzyl 3-(4-tert-butylphenyl)-3,4-dihydro-4-(4-methoxyphenyl)-2H-chromen-2-ylcarbamate (3d/3d')



Compound **(3d/3d')** was prepared according to the general procedure **5**; **Reaction time**: 3 days; purified by column chromatography using 6% (Hexane / EtOAc) solvent system. White solid (36.3 mg, yield: 87%); **mp**: 56-58 ^oC; **Diastereomeric ratio:** 9.1:1; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.30 (brs, 4H), 7.23 (brs, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.82 (dd, *J* = 16.1, 8.0 Hz, 3H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.74 (d, *J* = 7.7 Hz, 1H), 6.68 (d, *J* = 8.7 Hz, 2H), 6.59 (d, *J* = 8.7 Hz, 0.3H), 6.47 (d, *J* = 8.5 Hz, 0.2H), 6.10 (t, *J* = 10.3 Hz, 0.1H_a *minor*), 5.93 (brs, 1H_a *major*), 5.34 (brs, 1H_f), 5.04 (d, *J* = 20.0 Hz, 2H_e), 4.29 (d, *J* = 10.8 Hz, 1H_c *major*), 4.23 (d, *J* = 5.2 Hz, 0.11H_c *minor*), 3.73 (s, 3.4H_d), 3.10 (t, *J* = 7.2 Hz, 1H_b *major*), 1.26 (s, 10H_g); **^{13}C NMR (150 MHz, $CDCl_3$)**: δ 158.4, 155.6, 154.0, 150.1, 136.2, 135.6, 135.0, 131.4, 130.2, 128.7, 128.3, 128.1, 128.0, 127.9, 126.3, 125.7, 125.1, 121.3, 117.2, 113.8, 113.1, 82.2, 67.2, 55.3, 52.4, 50.6, 34.6, 31.5; **HRMS (+ESI):** Calc for $C_{34}H_{36}NO_4$ $[M+H]^+$ 522.2639; found: 522.2639.

HPLC: Chiralpak IC column. Flow rate 1 mL/min. UV detection at 274 nm for major diastereomer; τ(major) = 23.9 min., τ(minor) = 19.9 min. using hexane: isopropanol = 93:7 up to τ = 55.1 min. thereafter, hexane: isopropanol = 88:12 as eluent, ee 88%.

Benzyl 3-(4-fluorophenyl)-3,4-dihydro-4-(4-methoxyphenyl)-2H-chromen-2-ylcarbamate (3e/3e')

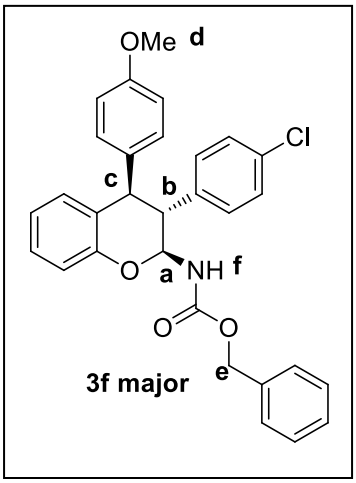


Compound **(3e/3e')** was prepared according to the general procedure **5**; **Reaction time**: 3 days; purified by column chromatography using 7% (Hexane / EtOAc) solvent system. White solid (28.6 mg, yield: 74%); **mp**: 53-55 ^{o}C; **Diastereomeric ratio: >20:1**; **^{1}H NMR (600 MHz, CDCl$_3$)**: δ 7.30 (brs, 3.2H), 7.19 (brs, 2H), 7.16 (t, *J* = 7.8 Hz, 1.3H), 6.95 (d, *J* = 8.2 Hz, 1.1H), 6.87 (d, *J* = 6.5 Hz, 4.3H), 6.82 (t, *J* = 7.4 Hz, 1.5H), 6.76 (d, *J* = 8.4 Hz, 2.3H), 6.72 (d, *J* = 7.7 Hz, 1.1H), 6.69 (d, *J* = 8.6 Hz, 2.2H), 6.08 (t, *J* = 10.3 Hz, 0.05H$_a$ *minor*), 5.93 (t, *J* = 9.9 Hz, 1H$_a$ *major*), 5.35 (brs, 1.1H$_f$), 5.04 (s, 2.1H$_e$), 4.25 (d, *J* = 11.1 Hz, 1.1H$_c$ *major*), 3.73 (s, 3.3H$_d$), 3.10 (t, *J* = 10.5 Hz, 1H$_b$ *major*); **^{13}C NMR (150 MHz, CDCl$_3$)**: δ 162.8, 161.2, 158.5, 155.5, 154.0, 136.0, 134.6, 134.3, 130.1, 129.8, 129.8, 128.7, 128.4, 128.2, 128.1, 125.9, 121.4, 117.2, 115.8, 115.7, 113.9, 82.0, 67.3, 55.3, 52.4, 50.9; **HRMS (+ESI):** Calc for $C_{30}H_{30}FN_2O_4$ $[M+NH_4]^+$ 501.2184; found: 501.2178; Specific rotation of **(3e/3e')** was found to be $[\alpha]^{26}_{589}$ = +134.4 (c = 0.25 g/100ml, $CHCl_3$).

HPLC: Chiralpak IC column. Flow rate 1 mL/min. UV detection at 254 nm for major diastereomer; τ(major) = 14.7 min., τ(minor) = 12.9 min. using hexane: isopropanol = 90:10 as eluent, ee 84%.

Benzyl 3-(4-chlorophenyl)-3,4-dihydro-4-(4-methoxyphenyl)-2H-chromen-2-ylcarbamate (3f/3f')

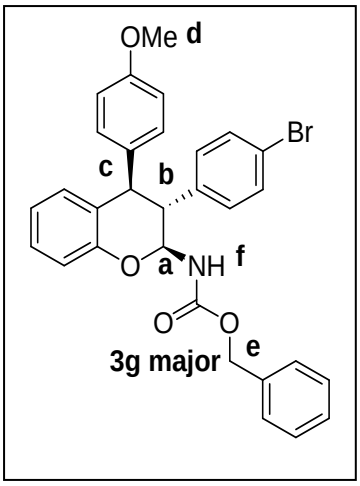
Compound **(3f/3f')** was prepared according to the general procedure **5**; **Reaction time**: 3 days; purified by column chromatography using 6-7% (Hexane / EtOAc) solvent system. White solid (19.2 mg, yield: 48%); **mp**: 56-58 ^{o}C; **Diastereomeric ratio:** 8.3:1; **^{1}H NMR (600 MHz, CDCl$_3$)**: δ 7.32 (d, *J* = 6.8 Hz, 3.3H), 7.20 (d, *J* = 5.8 Hz, 1.9H), 7.15 (t, *J* = 7.1 Hz, 3.4H), 6.95 (d, *J* = 8.2 Hz, 1.2H), 6.85 (d, *J* = 7.7 Hz, 1.9H), 6.82 (t, *J* = 7.5 Hz, 1.5H), 6.76 (d, *J* = 8.4 Hz, 2.3H), 6.71 (d, *J* = 7.8 Hz, 1.3H), 6.69 (d, *J* = 8.6 Hz, 2.2H), 6.65 (d, *J* = 8.6 Hz, 0.3H), 6.51 (d, J



= 8.6 Hz, 0.2H), 6.07 (t, *J* = 10.4 Hz, 0.12H_a *minor*), 5.93 (t, *J* = 10.0 Hz, 1H_a *major*), 5.28 (d, *J* = 9.3 Hz, 1H_f), 5.05 (s, 2.2H_e), 4.25 (d, *J* = 11.1 Hz, 1.2H_c), 3.74 (s, 3.4H_d), 3.10 (t, *J* = 10.5 Hz, 1H_b *major*); **^{13}C NMR (150 MHz, $CDCl_3$)**:δ 158.6, 155.4, 153.9, 137.5, 136.0, 134.2, 133.1, 130.1, 130.1, 129.7, 129.1, 128.8, 128.5, 128.2, 128.1, 125.9, 121.5, 117.2, 114.0, 81.9, 67.3, 55.4, 52.6, 50.8; **HRMS (+ESI):** Calc for $C_{30}H_{30}ClN_2O_4$ $[M+NH_4]^+$ 517.1889; found: 517.1895.

HPLC: Chiralpak IA column. Flow rate 1 mL/min. UV detection at 220 nm for major diastereomer; τ(major) = 50.8 min., τ(minor) = 109.5 min. using hexane: isopropanol = 92:8 as eluent, ee 92%.

Benzyl 3-(4-bromophenyl)-3,4-dihydro-4-(4-methoxyphenyl)-2H-chromen-2-ylcarbamate (3g/3g')

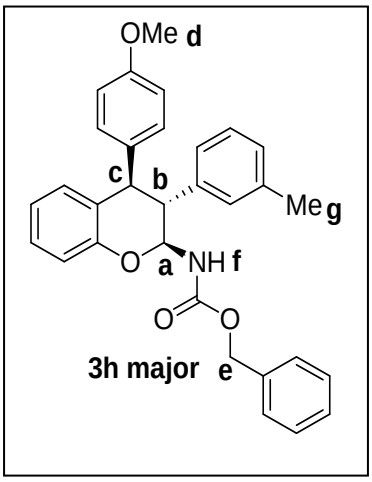


Compound **(3g/3g')** was prepared according to the general procedure **5**; **Reaction time**: 3 days; purified by column chromatography using 6% (Hexane / EtOAc) solvent system. White amorphous solid (23.1 mg, yield: 53%); **Diastereomeric ratio:** 9:1; **^{1}H NMR (600 MHz, CDCl3)**: δ 7.30 (d, J = 4.9 Hz, 1H), 7.24 (d, J = 8.4 Hz, 4H), 7.19 (s, 1H), 7.13 (d, J = 6.0 Hz, 2H), 7.08 (t, J = 7.6 Hz, 1H), 6.88 (d, J = 8.1 Hz, 1H), 6.75 (d, J = 7.7 Hz, 1H), 6.74 – 6.71 (m, 2H), 6.69 (d, J = 8.5 Hz, 2H), 6.63 (t, J = 9.6 Hz, 3H), 6.58 (d, J = 8.7 Hz, 1H), 6.45 (d, J = 8.6 Hz, 1H), 6.00 (t, J = 10.5 Hz, 0.11H_a *minor*), 5.86 (t, J = 9.9 Hz, 1H_a *major*), 5.25 (d, J = 9.9 Hz, 1H_f), 4.98 (s, 2.2H_e), 4.17 (d, J = 11.1 Hz, 1.1H_c), 3.67 (s, 3.4H_d), 3.02 (t, J = 10.5 Hz, 1H_b *major*); **^{13}C NMR (150 MHz, $CDCl_3$)**: δ 158.6, 155.4, 153.9, 138.0, 136.0, 134.2, 132.0, 130.1, 130.1, 130.0, 128.8, 128.5, 128.2, 128.1, 125.9, 121.5, 121.3, 117.2, 114.0, 81.8, 67.3, 55.4, 52.6, 50.8; **HRMS (+ESI):** Calc for $C_{30}H_{30}BrN_2O_4$ $[M+NH_4]^+$ 561.1383; found: 561.1377.

HPLC: Chiralpak IA column. Flow rate 1 mL/min. UV detection at 220 nm for major diastereomer; τ(major) = 57.1 min., τ(minor) = 108.3 min. using hexane: isopropanol = 92:8 up to τ = 45.1 min. thereafter, hexane: isopropanol = 90:10 as eluent, ee 94%.

Benzyl 3,4-dihydro-4-(4-methoxyphenyl)-3-m-tolyl-2H-chromen-2-ylcarbamate (3h/3h')

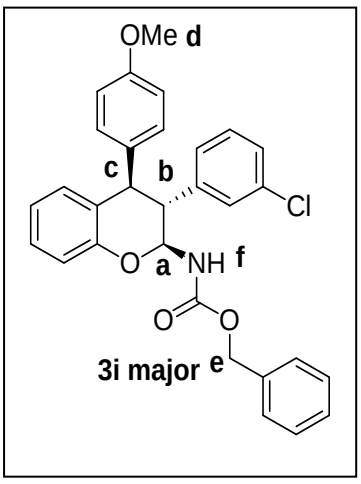
Compound **(3h/3h')** was prepared according to the general procedure **5**; **Reaction time**: 3 days; purified by column chromatography using 6% (Hexane / EtOAc) solvent system. Pale yellow solid (26.9 mg, yield: 70%); **mp**: 52–54 °C; **Diastereomeric ratio:** 10:1; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.30 (brs, 3H), 7.20 (brs, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.07 (t, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 0.3H), 6.97 (t, *J* = 8.2 Hz, 2H), 6.88 (d, *J* = 7.9 Hz, 0.2H), 6.82 (t, *J* = 7.1 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 2H), 6.73 (d, *J* = 7.6 Hz, 3H), 6.69 (d, *J* = 8.7 Hz, 2H), 6.63 (d, *J* = 8.6 Hz, 0.3H), 6.50 (d, *J* = 8.6 Hz, 0.3H), 6.10 (t, *J* = 10.3 Hz, 0.1H_a *minor*), 5.93 (t, *J* = 9.3 Hz, 1H_a *major*), 5.34 (d, *J* = 8.9 Hz, 1H_f), 5.04 (dd, *J* = 24.5, 11.5 Hz, 2H_e), 4.31 (d, *J* = 11.1 Hz, 1H_c *major*), 4.23 (d, *J* = 5.3 Hz, 0.1H_c *minor*), 3.73 (s, 3.3H_d), 3.06 (t, *J* = 10.2 Hz, 1H_b *major*), 2.23 (s, 3H_g *major*), 2.19 (s, 0.3H_g *minor*); **^{13}C NMR (150 MHz, $CDCl_3$)**: δ 158.4, 155.5, 154.0, 138.7, 138.3, 136.1, 134.8, 131.4, 130.1, 129.0, 128.7, 128.3, 128.1, 128.0, 126.3, 125.4, 124.6, 121.4, 117.2, 113.8, 82.1, 67.2, 55.3, 52.9, 50.6, 21.6; **HRMS (+ESI):** Calc for $C_{31}H_{30}NO_4$ $[M+H]^+$ 480.2169; found: 480.2170.



HPLC: Chiralpak IC column. Flow rate 1 mL/min. UV detection at 274 nm for major diastereomer; τ(major) = 19.0 min., τ(minor) = 14.3 min. using hexane: isopropanol = 90:10 as eluent, ee 92%.

Benzyl 3-(3-chlorophenyl)-3,4-dihydro-4-(4-methoxyphenyl)-2H-chromen-2-ylcarbamate (3i/3i')

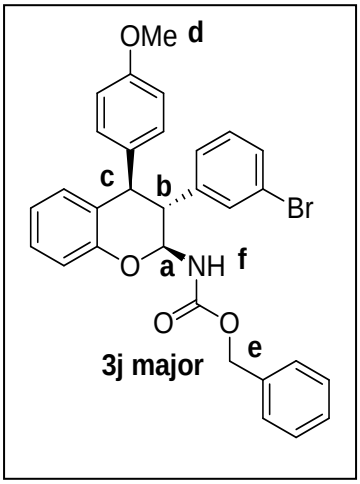
Compound **(3i/3i')** was prepared according to the general procedure **5**; **Reaction time**: 4 days; purified by column chromatography using 6-7% (Hexane / EtOAc) solvent system. White semi solid (19.2 mg, yield: 48%); **Diastereomeric ratio:** 5:1; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.32 (d, *J* = 6.9 Hz, 4H), 7.22 (d, *J* = 6.4 Hz, 2H), 7.18 – 7.10 (m, 4H), 7.01 (d, *J* = 8.1 Hz, 0.3H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.92 (s, 1H), 6.82 (dd, *J* = 11.0, 3.9 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 2H), 6.71 (dd, *J* = 12.7, 8.3 Hz, 3H), 6.65 (d, *J* = 8.6 Hz, 0.4H), 6.52 (d, *J* = 8.5 Hz, 0.3H), 6.07 (t, *J* = 10.3 Hz, 0.2H_a *minor*), 5.92 (t, *J* = 9.8 Hz, 1H_a *major*), 5.31 (d, *J* = 9.9



Hz, 1H_f), 5.06 (brs, 2.1H_e), 4.28 (d, *J* = 11.0 Hz, 1H_c *major*), 4.24 (d, *J* = 5.3 Hz, 0.2H_c *minor*), 3.74 (s, 3.6H_d), 3.10 (t, *J* = 10.4 Hz, 1H_b *major*); **^{13}C NMR (150 MHz, $CDCl_3$)**: δ 158.6, 155.4, 153.9, 141.0, 136.0, 134.6, 134.1, 131.4, 130.1, 130.1, 129.5, 128.7, 128.4, 128.2, 128.2, 127.7, 126.5, 125.8, 121.5, 117.2, 114.0, 81.8, 67.4, 55.4, 52.8, 50.6; **HRMS (+ESI):** Calc for $C_{30}H_{30}ClN_2O_4$ $[M+NH_4]^+$ 517.1889; found: 517.1907.

HPLC: Chiralpak IA column. Flow rate 1 mL/min. UV detection at 254 nm for major diastereomer; τ(major) = 29.3 min., τ(minor) = 48.7 min. using hexane: isopropanol = 90:10 as eluent, ee 94%.

Benzyl 3-(3-bromophenyl)-3,4-dihydro-4-(4-methoxyphenyl)-2H-chromen-2-ylcarbamate (3j/3j')

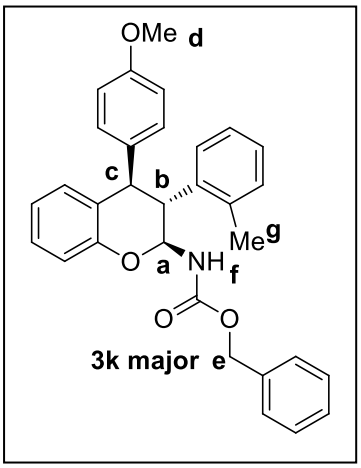


Compound **(3j/3j')** was prepared according to the general procedure **5**; **Reaction time**: 4 days; purified by column chromatography using 6% (Hexane / EtOAc) solvent system. Yellow white solid (34.8 mg, yield: 80%); **mp**: 64-66 ^oC; **Diastereomeric ratio:** 20:1; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.31 (t, *J* = 6.9 Hz, 4H), 7.22 (brs, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.09 – 7.02 (m, 2H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.87 (d, *J* = 6.8 Hz, 1H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.71 (dd, *J* = 11.7, 8.5 Hz, 3H), 6.08 (t, *J* = 10.3 Hz, 0.03H_a *minor*), 5.92 (t, *J* = 9.7 Hz, 1H_a *major*), 5.41 (d, *J* = 9.2 Hz, 1H_f), 5.05 (d, *J* = 6.1 Hz, 2H_e), 4.27 (d, *J* = 11.0 Hz, 1H_c *major*), 4.21 (d, *J* = 5.3 Hz, 0.05H_c *minor*), 3.74 (s, 3.1H_d), 3.09 (t, *J* = 10.6 Hz, 1H_b *major*); **^{13}C NMR (150 MHz, $CDCl_3$)**: δ 158.6, 155.5, 153.9, 141.3, 136.0, 134.1, 131.5, 130.5, 130.4, 130.1, 130.1, 128.7, 128.4, 128.2, 128.1, 126.9, 125.8, 122.8, 121.5, 117.2, 114.0, 81.8, 67.3, 55.4, 52.7, 50.6; **HRMS (+ESI):** Calc for $C_{30}H_{30}BrN_2O_4$ $[M+NH_4]^+$ 561.1383; found: 561.1428.

HPLC: Chiralpak IA column. Flow rate 1 mL/min. UV detection at 254 nm for major diastereomer; τ(major) = 30.1 min., τ(minor) = 48.0 min. using hexane: isopropanol = 90:10 as eluent, ee 94%.

Benzyl 3,4-dihydro-4-(4-methoxyphenyl)-3-o-tolyl-2H-chromen-2-ylcarbamate (3k/3k')

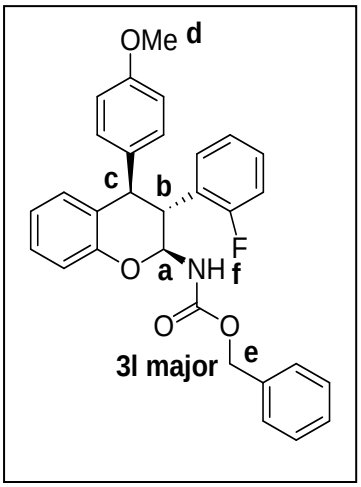
Compound **(3k/3k')** was prepared according to the general procedure **5**; **Reaction time**: 3 days; purified by column chromatography using 6% (Hexane / EtOAc) solvent system. White



amorphous solid (27.6 mg, yield: 72%); **mp**: 71-73 °C; **Diastereomeric ratio:** 4.2:1; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.30 (brs, 4H), 7.25 – 7.15 (m, 5H), 7.08 (t, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 0.3H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.89 (t, *J* = 7.5 Hz, 0.3H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 8.6 Hz, 2H), 6.60 (d, *J* = 8.5 Hz, 0.5H), 6.45 (d, *J* = 8.3 Hz, 0.5H), 6.14 (t, *J* = 10.1 Hz, 0.2H_a *minor*), 5.93 (brs, 1H_a *major*), 5.24 (d, *J* = 7.3 Hz, 1H_f), 5.01 (dd, *J* = 31.1, 16.0 Hz, 2.4H_e), 4.34 (d, *J* = 10.6 Hz, 1H_c *major*), 4.27 (d, *J* = 4.9 Hz, 0.24H_c *minor*), 3.73 (s, 3H_d *major*), 3.72 (s, 0.6H_d *minor*), 3.45 (t, *J* = 9.7 Hz, 1H_b *major*), 2.42 (s, 0.7H_g *minor*), 1.73 (s, 3H_g *major*); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 158.5, 158.5, 155.7, 155.5, 154.3, 153.9, 137.5, 136.9, 136.1, 134.7, 132.9, 131.3, 130.4, 130.3, 130.2, 130.1, 128.7, 128.5, 128.3, 128.1, 126.9, 126.8, 126.3, 125.7, 124.6, 121.4, 121.2, 117.3, 117.1, 113.7, 113.1, 82.7, 78.5, 67.2, 55.3, 51.2, 47.5, 45.9, 44.0, 19.8, 19.7; **HRMS (+ESI):** Calc for $C_{31}H_{30}NO_4$ $[M+H]^+$ 480.2169; found: 480.2189.

HPLC: Chiralpak IA column. Flow rate 1 mL/min. UV detection at 220 nm for major diastereomer; τ(major) = 38.0 min., τ(minor) = 73.6 min. using hexane: isopropanol = 95:5 as eluent, ee 88%.

Benzyl 3-(2-fluorophenyl)-3,4-dihydro-4-(4-methoxyphenyl)-2H-chromen-2-ylcarbamate (3l)

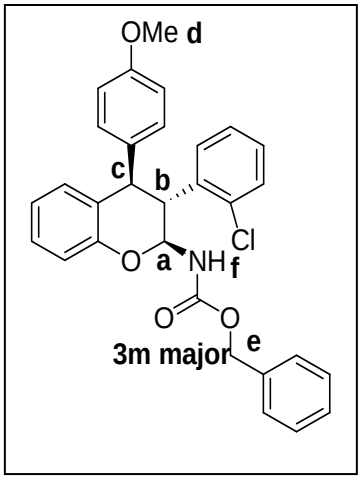


Compound **(3l)** was prepared according to the general procedure **5**; **Reaction time**: 3 days; purified by column chromatography using 7% (Hexane / EtOAc) solvent system. White solid (32.1 mg, yield: 83%); **mp**: 60-62 °C; **Diastereomeric ratio:**>20:1; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.31 (d, *J* = 6.0 Hz, 3H), 7.21 (d, *J* = 5.9 Hz, 2H), 7.15 (dd, *J* = 14.6, 7.7 Hz, 2H), 7.09 (brs, 1H), 7.03 (t, *J* = 7.0 Hz, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.90 (t, *J* = 9.3 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.82 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 7.7 Hz, 1H), 6.69 (d, *J* = 8.5 Hz, 2H), 6.01 (t, *J* = 9.9 Hz, 1H_a *major*), 5.47 (d, *J* = 8.8 Hz, 1H_f), 5.07 (d, *J* = 12.3 Hz, 1H_e), 5.01 (d, *J* = 12.3 Hz, 1H_e), 4.46 (d, *J* = 11.3 Hz, 1H_c *major*), 3.73 (s, 3H_d *major*), 3.58 (t, *J* = 10.6 Hz, 1H_b *major*); **^{13}C NMR (150 MHz, $CDCl_3$)**: δ 161.9, 160.3, 158.5, 155.5, 153.9, 136.1, 134.1, 130.0, 130.0, 128.9,

128.9, 128.7, 128.3, 128.2, 128.1, 125.89, 124.7, 121.4, 117.2, 115.7, 115.6, 113.9, 81.7, 67.2, 55.3, 48.7, 32.1; **HRMS (+ESI):** Calc for $C_{30}H_{30}FN_2O_4$ $[M+NH_4]^+$ 501.2184; found: 501.2187; Specific rotation of **(3l)** was found to be $[\alpha]^{25}_{589}$ = +87.2 (c = 0.25 g/100ml, $CHCl_3$).

HPLC: Chiralpak IA column. Flow rate 1 mL/min. UV detection at 220 nm for major diastereomer; τ(major) = 28.4 min., τ(minor) = 56.7 min. using hexane: isopropanol = 90:10 as eluent, ee 94%.

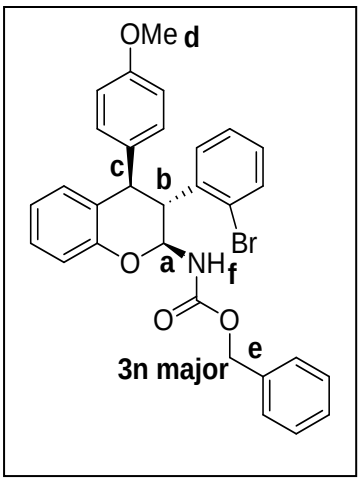
Benzyl 3-(2-chlorophenyl)-3,4-dihydro-4-(4-methoxyphenyl)-2H-chromen-2-ylcarbamate (3m)



Compound **(3m)** was prepared according to the general procedure **5**; **Reaction time**: 3 days; purified by column chromatography using 6% (Hexane / EtOAc) solvent system. White solid (35.2 mg, yield: 88%); **mp**: 70-72 ^oC; **Diastereomeric ratio:**>20:1; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.31 (d, *J* = 6.5 Hz, 5H), 7.21 (d, *J* = 5.3 Hz, 3H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.10 (t, *J* = 8.3 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.83 (t, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 8.5 Hz, 2H), 5.89 (brs, $1H_a$ *major*), 5.50 (d, *J* = 8.4 Hz, $1H_f$ *major*), 5.03 (dd, *J* = 41.7, 12.3 Hz, $2H_e$ *major*), 4.40 (brs, $1H_c$ *major*), 4.03 (brs, $1H_b$ *major*), 3.73 (s, $3H_d$ *major*); **^{13}C NMR (150 MHz, $CDCl_3$):** δ 158.6, 155.5, 153.8, 136.5, 136.1, 133.4, 130.2, 129.9, 129.7, 128.7, 128.4, 128.3, 128.2, 128.1, 127.7, 126.0, 121.4, 117.2, 113.9, 82.7, 67.2, 55.3, 49.5, 46.6; **HRMS (+ESI):** Calc for $C_{30}H_{27}ClNO_4$ $[M+H]^+$ 500.1623; found: 500.1604; Specific rotation of **(3m)** was found to be $[\alpha]^{28}_{589}$ = +68.8 (c = 0.25 g/100ml, $CHCl_3$).

HPLC: Chiralpak IA column. Flow rate 1 mL/min. UV detection at 220 nm for major diastereomer; τ(major) = 19.6 min., τ(minor) = 65.3 min. using hexane: isopropanol = 90:10 as eluent, ee 94%.

Benzyl 3-(2-bromophenyl)-3,4-dihydro-4-(4-methoxyphenyl)-2H-chromen-2-ylcarbamate (3n)

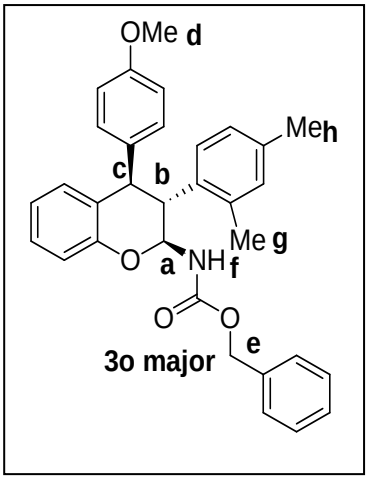


Compound **(3n)** was prepared according to the general procedure **5**; **Reaction time**: 3 days; purified by column chromatography using 6% (Hexane / EtOAc) solvent system. White solid (38.8 mg, yield: 89%); **mp**: 72-74 ^oC; **Diastereomeric ratio:**>20:1; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.38 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.29 (m, 5H), 7.21 (d, *J* = 5.7 Hz, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.03 (t, *J* =

8.4 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.89 (d, *J* = 7.9 Hz, 2H), 6.83 (t, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 8.4 Hz, 2H), 5.88 (t, *J* = 9.4 Hz, $1H_a$ *major*), 5.54 (d, *J* = 9.6 Hz, $1H_f$ *major*), 5.07 (d, *J* = 12.3 Hz, $1H_e$ *major*), 4.99 (d, *J* = 12.3 Hz, $1H_e$ *major*), 4.40 (d, *J* = 10.7 Hz, $1H_c$ *major*), 4.04 (t, *J* = 10.0 Hz, $1H_b$ *major*), 3.73 (s, $3H_d$ *major*); **^{13}C NMR (150 MHz, $CDCl_3$)**: δ 158.6, 155.5, 153.7, 138.2, 136.1, 133.2, 133.0, 130.3, 129.9, 128.7, 128.7, 128.4, 128.3, 128.2, 128.1, 126.4, 126.0, 121.4, 117.1, 113.9, 82.8, 67.2, 55.3, 49.7, 49.3; **HRMS (+ESI):** Calc for $C_{30}H_{27}BrNO_4$ $[M+H]^+$ 544.1118; found: 544.1148; Specific rotation of **(3n)** was found to be $[\alpha]^{28}_{589}$ = +64.0 (c = 0.25 g/100ml, $CHCl_3$).

HPLC: Chiralpak IB column. Flow rate 1 mL/min. UV detection at 220 nm for major diastereomer; τ(major) = 10.6 min., τ(minor) = 16.8 min. using hexane: isopropanol = 90:10 as eluent, ee 94%.

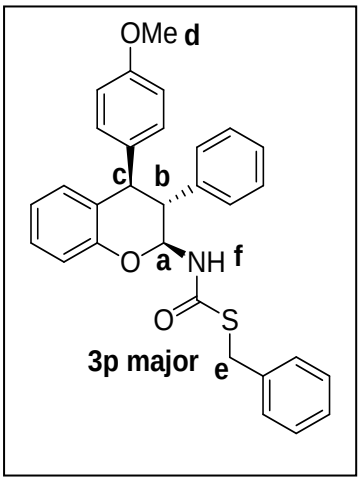
Benzyl 3,4-dihydro-4-(4-methoxyphenyl)-3-(2,4-dimethylphenyl)-2H-chromen-2-ylcarbamate (3o/3o')



Compound **(3o/3o')** was prepared according to the general procedure **5**; **Reaction time**: 3 days; purified by column chromatography using 6% (Hexane / EtOAc) solvent system. White solid (24.9 mg, yield: 63%); **mp**: 95-97 ^oC; **Diastereomeric ratio:** 4.3:1; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.30 (brs, 4H), 7.24 – 7.19 (m, 2H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.10 (s, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 7.00 – 6.96 (m, 2H), 6.88 (t, *J* = 7.3 Hz, 0.3H), 6.84 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 8.3 Hz, 3H), 6.66 (d, *J* = 8.6 Hz, 2H), 6.61 (d, *J* = 8.6 Hz, 1H), 6.46 (d, *J* = 8.4 Hz, 0.5H), 6.11 (t, *J* = 10.1 Hz, $0.2H_a$ *minor*), 5.89 (brs, $1H_a$ *major*), 5.21 (brs, $1H_f$), 5.03 (dd, *J* = 46.0, 9.0 Hz, $2.5H_e$), 4.31 (d, *J* = 10.4 Hz, $1H_c$ *major*), 4.25 (d, *J* = 4.9 Hz, $0.23H_c$ *minor*), 3.73 (s, $3.7H_d$), 3.40 (t, *J* = 9.7 Hz, $1H_b$ *major*), 2.37 (s, $0.6H_g$ *minor*), 2.25 (s, $3.7H_h$), 1.69 (s, $3H_g$ *major*); **^{13}C NMR (150 MHz, $CDCl_3$)**: δ 158.5, 158.5, 155.5, 154.3, 154.0, 136.6, 136.2, 134.9, 134.4, 133.0, 131.4, 131.1, 130.2, 130.2, 128.7, 128.4, 128.3, 128.0, 127.7, 126.4, 124.7, 121.4, 121.1, 117.3, 117.1, 113.7, 113.2, 82.7, 78.6, 67.2, 60.6, 55.3, 51.2, 46.0, 43.8, 21.2, 21.1, 19.7, 19.6; **HRMS (+ESI):** Calc for $C_{32}H_{32}NO_4$ $[M+H]^+$ 494.2326; found: 494.2324.

HPLC: Chiralpak IC column. Flow rate 1 mL/min. UV detection at 254 nm for major diastereomer; τ(major) = 24.1 min., τ(minor) = 22.5 min. using hexane: isopropanol = 92:8 as eluent, ee 92%.

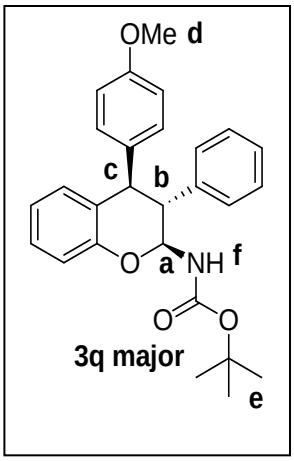
S-benzyl N-3,4-dihydro-4-(4-methoxyphenyl)-3-phenyl-2H-chromen-2-ylcarbamothioate (3p/3p')



Compound **(3p/3p')** was prepared according to the general procedure **5**; **Reaction time**: 3 days; purified by column chromatography using 6% (Hexane / EtOAc) solvent system. White solid (28.5 mg, yield: 74%); **mp**: 79-81 ^{o}C; **Diastereomeric ratio:** 20:1; **^{1}H NMR (600 MHz, CDCl$_3$)**: δ 7.27 (d, *J* = 7.0 Hz, 1H), 7.25 (brs, 1H), 7.24 – 7.14 (m, 7H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.93 (d, *J* = 6.1 Hz, 2H), 6.83 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 8.6 Hz, 2H), 6.74 (d, *J* = 7.7 Hz, 1H), 6.69 (d, *J* = 8.7 Hz, 2H), 6.13 (brs, 1H$_a$ *major*), 5.88 (d, *J* = 8.8 Hz, 1H$_f$ *major*), 4.31 (d, *J* = 10.9 Hz, 1H$_c$ *major*), 4.24 (d, *J* = 5.2 Hz, 0.1H$_c$ *minor*), 4.10 (brs, 2.1H$_e$), 3.73 (s, 3.2H$_d$), 3.12 (t, *J* = 10.4 Hz, 1H$_b$ *major*); **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 168.1, 158.4, 153.8, 138.4, 137.7, 134.5, 131.3, 130.1, 129.0, 128.8, 128.7, 128.3, 128.1, 127.4, 126.0, 121.5, 117.2, 113.9, 113.3, 80.8, 55.3, 52.8, 50.4, 34.3, 29.9; **HRMS (+ESI):** Calc for $C_{30}H_{28}NO_3S$ $[M+H]^+$ 482.1784; found: 482.1780; Specific rotation of **(3p/3p')** was found to be $[\alpha]^{29}_{589}$ = +111.2 (c = 0.25 g/100ml, $CHCl_3$).

HPLC: Chiralpak IA column. Flow rate 1 mL/min. UV detection at 220 nm for major diastereomer; τ(major) = 32.4 min., τ(minor) = 57.1 min. using hexane: isopropanol = 90:10 as eluent, ee 95%.

tert-butyl 3,4-dihydro-4-(4-methoxyphenyl)-3-phenyl-2H-chromen-2-ylcarbamate (3q/3q')

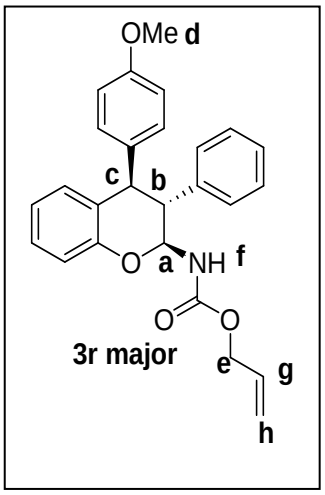


Compound **(3q/3q')** was prepared according to the general procedure **5**; **Reaction time**: 3 days; purified by column chromatography using 6-7% (Hexane / EtOAc) solvent system. White amorphous solid (26.9 mg, yield: 78%); **mp**: 55-57 ^{o}C; **Diastereomeric ratio:** 1.5:1; **^{1}H NMR (600 MHz, CDCl$_3$)**: δ 7.21 – 7.13 (m, 7H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 3H), 6.86 (t, *J* = 7.3 Hz,

1H), 6.81 (d, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 6.9 Hz, 2H), 6.68 (d, *J* = 8.5 Hz, 2H), 6.60 (d, *J* = 8.1 Hz, 1H), 6.48 (d, *J* = 8.0 Hz, 1H), 6.09 (t, *J* = 10.4 Hz, 0.7H_a *minor*), 5.90 (brs, 1H_a *major*), 5.07 (dd, *J* = 17.9, 9.1 Hz, 2H_f), 4.30 (d, *J* = 11.1 Hz, 1H_c *major*), 4.24 (d, *J* = 5.3 Hz, 0.7H_c *minor*), 3.73 (s, 3H_d *major*), 3.72 (s, 2H_d *minor*), 3.47 (t, *J* = 4.8 Hz, 0.7H_b *minor*), 3.08 (t, *J* = 9.9 Hz, 1H_b *major*), 1.36 (s, 6H_e *minor*), 1.33 (s, 9H_e *major*); **^{13}C NMR (150 MHz, $CDCl_3$)**: δ 158.5, 158.4, 155.0, 154.6, 154.2, 154.0, 139.0, 138.1, 134.8, 132.7, 131.3, 130.2, 130.1, 130.0, 129.2, 128.7, 128.5, 128.4, 128.2, 128.0, 127.2, 127.1, 126.2, 124.6, 121.2, 121.0, 117.2, 117.1, 113.8, 113.3, 81.9, 80.6, 77.8, 55.3, 55.3, 53.2, 53.2, 50.8, 48.8, 28.4, 28.3; **HRMS (+ESI):** Calc for $C_{27}H_{30}NO_4$ $[M+H]^+$ 432.2169; found: 432.2167.

HPLC: Chiralpak IA column. Flow rate 1 mL/min. UV detection at 220 nm for major diastereomer; τ(major) = 17.4 min., τ(minor) = 27.6 min. using hexane: isopropanol = 92:8 as eluent, ee 90%.

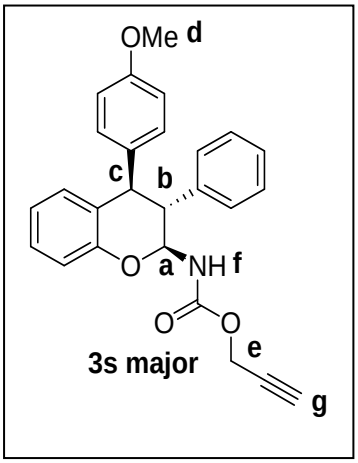
Allyl 3,4-dihydro-4-(4-methoxyphenyl)-3-phenyl-2H-chromen-2-ylcarbamate (3r/3r')



Compound **(3r/3r')** was prepared according to the general procedure **5**; **Reaction time**: 3 days; purified by column chromatography using 6% (Hexane / EtOAc) solvent system. White semi solid (20.3 mg, yield: 61%); **Diastereomeric ratio:** 6.7:1; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.24 – 7.12 (m, 5H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.93 (d, *J* = 6.8 Hz, 2H), 6.81 (t, *J* = 7.1 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 7.3 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 7.7 Hz, 0.3H), 6.49 (d, *J* = 7.8 Hz, 0.3H), 6.11 (t, *J* = 9.7 Hz, 0.1H_a *minor*), 5.94 (brs, 1H_a *major*), 5.80 (brs, 1H_g), 5.27 (brs, 1H_f), 5.13 (d, *J* = 12.3 Hz, 2H_h), 4.50 (d, *J* = 23.1 Hz, 2H_e), 4.31 (d, *J* = 11.0 Hz, 1H_c *major*), 4.25 (d, *J* = 4.5 Hz, 0.2H_c *minor*), 3.73 (s, 3.3H_d), 3.10 (t, *J* = 9.2 Hz, 1H_b *major*); **^{13}C NMR (150 MHz, $CDCl_3$)**: δ 158.4, 155.4, 154.0, 138.8, 134.6, 132.5, 131.4, 130.1, 129.2, 128.9, 128.3, 128.1, 127.3, 126.2, 121.4, 118.0, 117.2, 113.9, 113.3, 82.0, 66.1, 55.3, 53.0, 50.8; **HRMS (+ESI):** Calc for $C_{26}H_{26}NO_4$ $[M+H]^+$ 416.1856; found: 416.1890.

HPLC: Chiralpak IC column. Flow rate 1 mL/min. UV detection at 220 nm for major diastereomer; τ(major) = 28.6 min., τ(minor) = 22.1 min. using hexane: isopropanol = 95:5 as eluent, ee 90%.

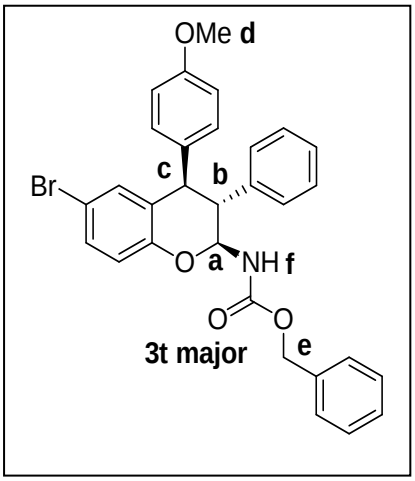
Prop-2-ynyl 3,4-dihydro-4-(4-methoxyphenyl)-3-phenyl-2H-chromen-2-ylcarbamate(3s/3s')



Compound **(3s/3s')** was prepared according to the general procedure **5**; **Reaction time**: 3 days; purified by column chromatography using 7% (Hexane / EtOAc) solvent system. White semi solid (29.4 mg, yield: 89%); **Diastereomeric ratio:** 12.5:1; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.23 – 7.12 (m, 4H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.92 (d, *J* = 6.9 Hz, 2H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 8.6 Hz, 2H), 6.73 (d, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 8.7 Hz, 2H), 6.09 (t, *J* = 10.3 Hz, 0.1H_a *minor*), 5.92 (t, *J* = 9.8 Hz, 1H_a *major*), 5.41 (brs, 1H_f), 4.60 (dd, *J* = 57.5, 15.5 Hz, 2.1H_e), 4.31 (d, *J* = 11.1 Hz, 1H_c *major*), 4.24 (d, *J* = 5.3 Hz, 0.1H_c *minor*), 3.72 (s, 3.2H_d), 3.11 (t, *J* = 10.4 Hz, 1H_b *major*), 2.42 (s, 1H_g *major*); **^{13}C NMR (150 MHz, $CDCl_3$)**: δ 158.5, 154.7, 153.9, 138.7, 134.6, 131.4, 130.1, 128.9, 128.3, 128.1, 127.4, 126.1, 121.4, 117.2, 113.9, 113.3, 82.0, 77.8, 75.2, 55.3, 53.1, 52.9, 50.7; **HRMS (+ESI):** Calc for $C_{26}H_{24}NO_4$ $[M+H]^+$ 414.170; found: 414.1693.

HPLC: Chiralpak IC column. Flow rate 1 mL/min. UV detection at 220nm for major diastereomer; τ(major) =17.4 min., τ(minor) = 12.7 min. using hexane: isopropanol = 90:10 as eluent, ee 90%.

Benzyl 6-bromo-3,4-dihydro-4-(4-methoxyphenyl)-3-phenyl-2H-chromen-2-ylcarbamate (3t/3t')

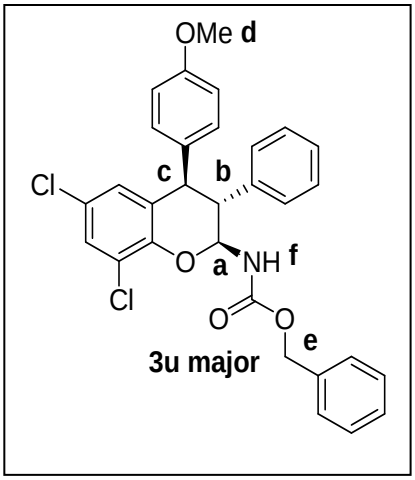


Compound **(3t/3t')** was prepared according to the general procedure **5**; **Reaction time**: 3 days; purified by column chromatography using 6-7% (Hexane / EtOAc) solvent system. White semi solid (37.5 mg, yield: 86%); **Diastereomeric ratio:** 2.6:1; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.29 (brs, 5H), 7.26 – 7.11 (m, 8H), 7.08 (s, 0.4H), 6.90 (brs, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 6.69 (d, *J* = 8.5 Hz, 2H), 6.63 (d, *J* = 8.6 Hz, 1H), 6.48 (d, *J* = 8.5 Hz, 1H), 6.11 (t, *J* = 10.1 Hz, 0.3H_a *minor*), 5.93 (t, *J* = 8.6 Hz, 1H_a *major*), 5.34 (brs, 1.1H_f), 5.03 (d, *J* = 20.1 Hz, 2.6H_e), 4.25 (d, *J* = 11.0 Hz, 1H_c *major*), 4.19 (d, *J* = 5.2 Hz, 0.38H_c *minor*), 3.74 (s, 4.1H_d), 3.08 (t, *J* = 10.1 Hz, 1H_b *major*); **^{13}C NMR (150 MHz, $CDCl_3$)**: δ

158.8, 158.7, 155.5, 155.4, 153.2, 153.0, 138.4, 136.1, 133.7, 132.6, 131.9, 131.5, 131.3, 131.1, 130.1, 129.1, 128.9, 128.7, 128.4, 128.4, 128.3, 128.1, 127.5, 127.4, 126.7, 119.1, 118.9, 114.2, 113.6, 113.5, 113.3, 82.4, 67.4, 67.3, 55.4, 55.3, 52.6, 50.6, 48.5, 48.4; **HRMS (+ESI):** Calc for $C_{30}H_{27}BrNO_4$ $[M+H]^+$ 544.1118; found: 544.1101.

HPLC: Chiralpak IA column. Flow rate 1 mL/min. UV detection at 220 nm for major diastereomer; τ(major) = 41.7 min., τ(minor) = 62.4 min. using hexane: isopropanol = 90:10 as eluent, ee 84%.

Benzyl 6,8-dichloro-3,4-dihydro-4-(4-methoxyphenyl)-3-phenyl-2H-chromen-2-ylcarbamate (3u/3u')

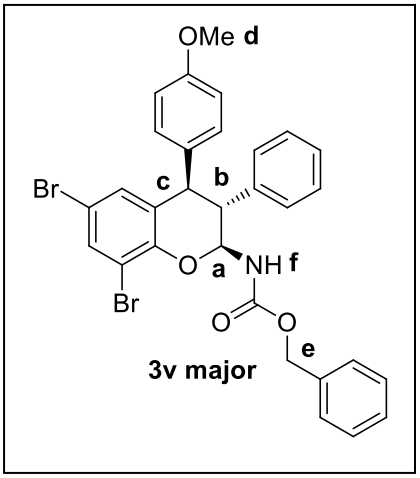


Compound **(3u/3u')** was prepared according to the general procedure **5**; **Reaction time**: 6 days; purified by column chromatography using 6% (Hexane / EtOAc) solvent system. White semi solid (12.8 mg, yield: 30%); **Diastereomeric ratio:** >20:1; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.29 (brs, 3H), 7.24 (d, *J* = 1.8 Hz, 1H), 7.18 (brs, 5H), 6.89 (brs, 2H), 6.74 (d, *J* = 8.4 Hz, 2H), 6.69 (d, *J* = 8.5 Hz, 2H), 6.61 (s, 1H), 6.18 (brs, 0.03H_a *minor*), 6.00 (t, *J* = 8.9 Hz, 1H_a *major*), 5.36 (d, *J* = 8.5 Hz, 1H_f *major*), 5.05 (s, 2H_e *major*), 4.27 (d, *J* = 11.1 Hz, 1H_c *major*), 3.74 (s, 3H_d *major*), 3.12 (t, *J* = 10.1 Hz, 1H_b *major*); **^{13}C NMR (150 MHz, $CDCl_3$)**: δ 158.8, 155.4, 148.8, 139.5, 137.9, 136.0, 133.1, 130.1, 129.3, 129.0, 128.7, 128.5, 128.4, 128.3, 128.0, 127.6, 125.9, 122.9, 114.2, 83.1, 67.4, 55.4, 52.4, 51.0; **HRMS (+ESI):** Calc for $C_{30}H_{26}Cl_2NO_4$ $[M+H]^+$ 534.1233; found: 534.1232; Specific rotation of **(3u/3u')** was found to be $[\alpha]^{27}_{589}$ = +106.0 (c = 0.10 g/100ml, $CHCl_3$).

HPLC: Chiralpak IA column. Flow rate 1 mL/min. UV detection at 220 nm for major diastereomer; τ(major) = 40.4 min., τ(minor) = 70.8 min. using hexane: isopropanol = 93:7 as eluent, ee 88%.

Benzyl 6,8-dibromo-3,4-dihydro-4-(4-methoxyphenyl)-3-phenyl-2H-chromen-2-ylcarbamate (3v/3v')

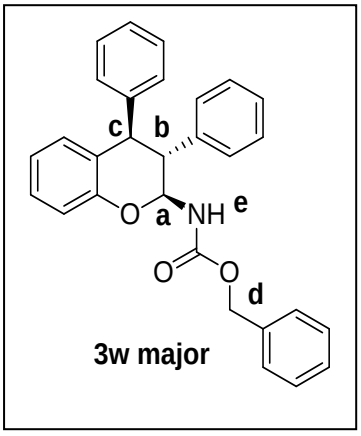
Compound **(3v/3v')** was prepared according to the general procedure **5**; **Reaction time**: 3 days; **Temperature**: 50 ^{o}C; purified by column chromatography using 6% (Hexane / EtOAc) solvent system. White solid (16.5 mg, yield: 33%); **mp**: 66-68 ^{o}C; **Diastereomeric ratio:** 11:1; **^{1}H NMR**



(600 MHz, $CDCl_3$): δ 7.54 (d, *J* = 1.8 Hz, 1H), 7.29 (brs, 3H), 7.18 (brs, 5H), 6.89 (brs, 2H), 6.79 (s, 1H), 6.73 (d, *J* = 8.5 Hz, 2H), 6.69 (d, *J* = 8.6 Hz, 2H), 6.18 (t, *J* = 10.8 Hz, 0.1H_a *minor*), 5.99 (brs, 1H_a *major*), 5.34 (brs, 1H_f), 5.07 (d, *J* = 11.9 Hz, 2H_e), 4.28 (d, *J* = 10.7 Hz, 1H_c *major*), 4.21 (d, *J* = 5.1 Hz, 0.1H_c *minor*), 3.74 (s, 3.1H_d), 3.11 (t, *J* = 9.8 Hz, 1H_b *major*); **^{13}C NMR (150 MHz, $CDCl_3$)**: δ 158.9, 155.3, 150.2, 139.5, 137.9, 136.1, 134.1, 133.2, 131.9, 131.3, 130.1, 129.7, 129.0, 128.7, 128.4, 128.3, 128.0, 127.7, 114.3, 113.6, 113.4, 112.2, 83.4, 67.4, 55.4, 52.6, 50.9; **HRMS (+ESI):** Calc for $C_{30}H_{26}Br_2NO_4$ $[M+H]^+$ 622.0223; found: 622.0226.

HPLC: Chiralpak IA column. Flow rate 1 mL/min. UV detection at 220 nm for major diastereomer; τ(major) = 19.9 min., τ(minor) = 48.6 min. using hexane: isopropanol = 88:12 as eluent, ee 92%.

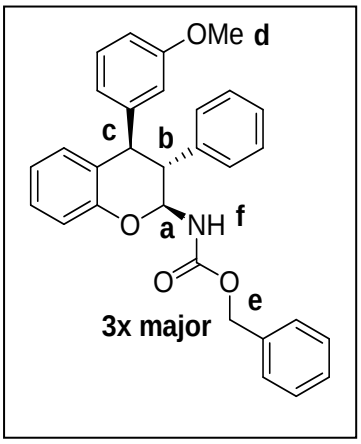
Benzyl 3,4-dihydro-3,4-diphenyl-2H-chromen-2-ylcarbamate (3w/3w')



Compound **(3w/3w')** was prepared according to the general procedure **5**; **Reaction time**: 3 days; purified by column chromatography using 5% (Hexane / EtOAc) solvent system. White solid (13.2 mg, yield: 38%); **mp**: 95-97 ^oC; **Diastereomeric ratio:** 14.3:1; **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.30 (brs, 3H), 7.18 (brs, 5H), 7.14 (d, *J* = 4.1 Hz, 4H), 7.08 (t, *J* = 7.4 Hz, 0.2H), 7.03 (d, *J* = 8.2 Hz, 0.1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.92 (d, *J* = 4.9 Hz, 2H), 6.86 (d, *J* = 3.9 Hz, 2H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 6.9 Hz, 0.1H), 6.60 (d, *J* = 7.5 Hz, 0.2H), 6.16 (t, *J* = 10.2 Hz, 0.1H_a *minor*), 5.98 (t, *J* = 9.4 Hz, 1H_a *major*), 5.33 (d, *J* = 8.7 Hz, 1H_e), 5.04 (dd, *J* = 29.0, 12.0 Hz, 2H_d), 4.37 (d, *J* = 11.0 Hz, 1H_c *major*), 4.30 (d, *J* = 5.4 Hz, 0.07H_c *minor*), 3.15 (t, *J* = 10.2 Hz, 1H_b *major*); **^{13}C NMR (150 MHz, $CDCl_3$)**: δ 155.5, 154.1, 142.6, 139.5, 138.6, 136.1, 130.4, 130.2, 129.2, 128.9, 128.7, 128.5, 128.3, 128.2, 128.1, 127.4, 126.9, 125.9, 121.4, 117.2, 114.3, 82.1, 67.2, 53.0, 51.6; **HRMS (+ESI):** Calc for $C_{29}H_{26}NO_3$ $[M+H]^+$ 436.1907; found: 436.1909.

HPLC: Chiralpak IC column. Flow rate 1 mL/min. UV detection at 220 nm for major diastereomer; τ(major) = 17.0 min., τ(minor) = 14.6 min. using hexane: isopropanol = 93:7 as eluent, ee 88%.

Benzyl 3,4-dihydro-4-(3-methoxyphenyl)-3-phenyl-2H-chromen-2-ylcarbamate (3x/3x')

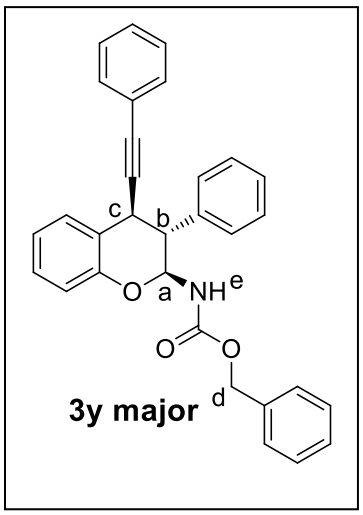


Compound **(3x/3x')** was prepared according to the general procedure **5**; **Reaction time**: 3 days; purified by column chromatography using 6% (Hexane / EtOAc) solvent system. White solid (26.1 mg, yield: 70%); **mp**: 48-50 ^{o}C; **Diastereomeric ratio:** 2.2:1; **^{1}H NMR (600 MHz, CDCl$_3$)**: δ 7.30 (brs, 4H), 7.23 – 7.14 (m, 8H), 7.06 (t, *J* = 7.9 Hz, 1H), 7.04 – 7.00 (m, 1H), 6.97 (d, *J* = 9.1 Hz, 2H), 6.94 (d, *J* = 6.1 Hz, 2H), 6.88 (t, *J* = 7.4 Hz, 0.6H), 6.83 (t, *J* = 7.1 Hz, 1H), 6.76 (d, *J* = 7.7 Hz, 1H), 6.71 (d, *J* = 7.1 Hz, 1H), 6.69 (d, *J* = 2.4 Hz, 1H), 6.67 (d, *J* = 2.6 Hz, 1H), 6.47 (d, *J* = 7.5 Hz, 1H), 6.39 (s, 1H), 6.26 (d, *J* = 7.5 Hz, 0.5H), 6.17 (t, *J* = 10.3 Hz, 0.4H$_a$ *minor*), 6.02 (s, 0.5H), 5.96 (t, *J* = 9.8 Hz, 1H$_a$ *major*), 5.36 (d, *J* = 9.7 Hz, 1.2H$_f$), 5.03 (dd, *J* = 29.0, 10.1 Hz, 2.7H$_e$), 4.34 (d, *J* = 11.0 Hz, 1H$_c$ *major*), 4.27 (d, *J* = 5.5 Hz, 0.46H$_c$ *minor*), 3.63 (s, 3H$_d$ *major*), 3.51 (s, 1.5H$_d$ *minor*), 3.15 (t, *J* = 10.4 Hz, 1H$_b$ *major*); **^{13}C NMR (150MHz, CDCl$_3$)**: δ 159.6, 159.0, 155.7, 155.5, 154.0, 153.8, 144.2, 142.0, 139.5, 138.7, 137.7, 136.1, 130.1, 129.4, 129.1, 128.9, 128.7, 128.3, 128.3, 128.2, 128.1, 127.4, 127.2, 125.6, 124.0, 122.8, 121.6, 121.4, 121.2, 117.2, 117.1, 115.9, 115.0, 114.3, 112.9, 112.3, 82.0, 78.1, 67.3, 67.2, 55.3, 55.2, 52.8, 51.6, 49.4, 48.6; **HRMS (+ESI):** Calc for $C_{30}H_{28}NO_4$ $[M+H]^+$ 466.2013; found: 466.2014.

HPLC: Chiralpak IA column. Flow rate 1 mL/min. UV detection at 220 nm for major diastereomer; τ(major) = 66.0 min., τ(minor) = 45.6 min. using hexane: isopropanol = 90:10 as eluent, ee 86%.

Benzyl (3-phenyl-4-(phenylethynyl)chroman-2-yl)carbamate (3y/3y')

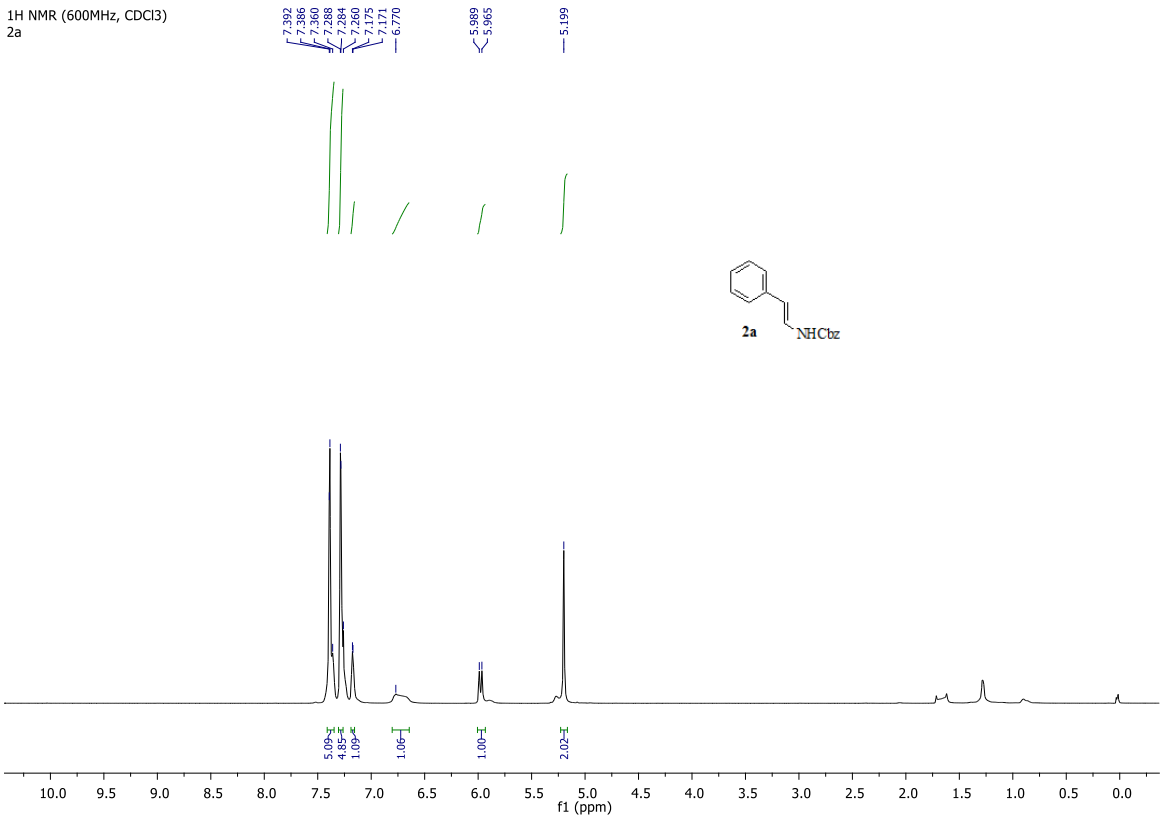
Compound **(3y/3y')** was prepared according to the general procedure **5**; **Reaction time**: 2 days; purified by column chromatography using 5% (Hexane / EtOAc) solvent system. White solid (22.4 mg, yield: 61%); **mp**: 176-178 ^{o}C; **Diastereomeric ratio:** 2.5:1; **^{1}H NMR (600 MHz, CDCl$_3$)**: δ 7.58 (d, *J* = 7.6 Hz, 1.1H), 7.36 (d, *J* = 6.5 Hz, 4.2H), 7.32 (brs, 6.3H), 7.28 (d, *J* = 7.6 Hz, 5.2H), 7.23 (dd, *J* = 14.7, 8.1 Hz, 7H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.98 – 6.92 (m, 2H), 6.42 (t,

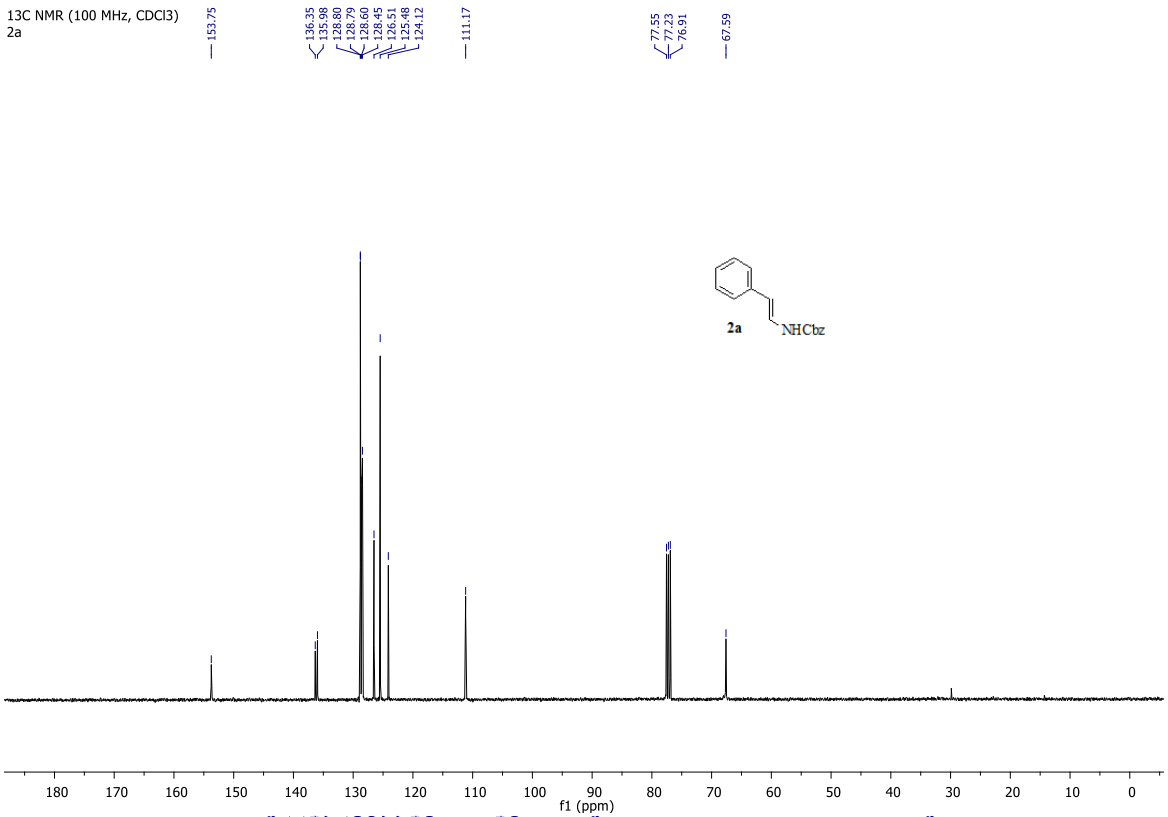


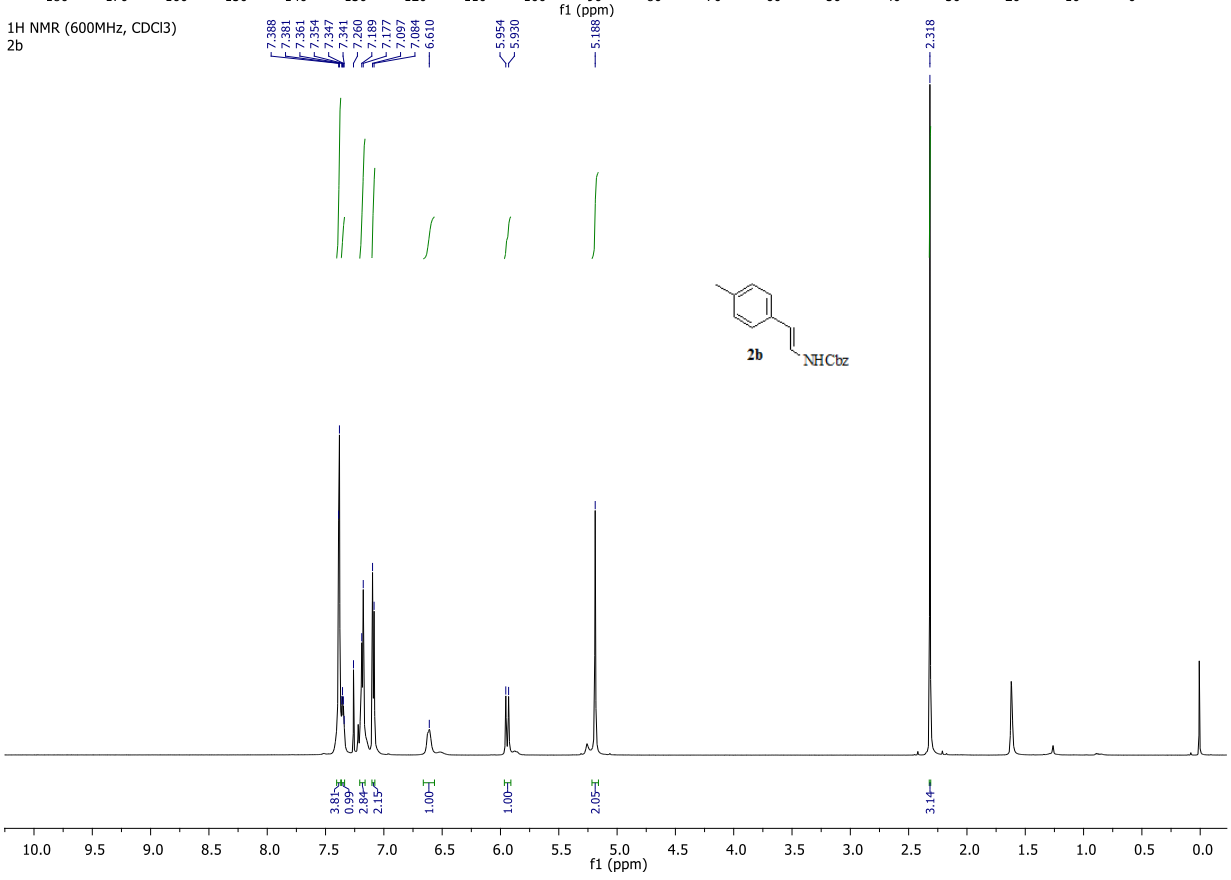
J = 9.8 Hz, 0.3H_a *minor*), 5.97 (t, *J* = 9.4 Hz, 1H_a *major*), 5.69 (d, *J* = 9.8 Hz, 1H_e *major*), 5.42 (d, *J* = 9.7 Hz, 0.4H_e *minor*), 5.09 (d, *J* = 28.8 Hz, 2.8H_d), 4.38 (d, *J* = 9.9 Hz, 1H_c *major*), 4.21 (d, *J* = 4.5 Hz, 0.4H_c *minor*), 3.39 (dd, *J* = 8.9, 4.3 Hz, 0.4H_b *minor*), 3.24 (t, *J* = 9.3 Hz, 1H_b *major*); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 155.5, 152.7, 152.6, 138.7, 136.1, 131.8, 131.7, 129.3, 129.3, 129.2, 129.1, 129.0, 128.7, 128.6, 128.4, 128.3, 128.2, 127.9, 127.9, 123.2, 123.1, 122.0, 121.7, 121.4, 121.4, 117.5, 117.4, 84.0, 81.5, 67.4, 49.6, 47.0, 37.3, 36.9; **HRMS (+ESI):** Calc for $C_{31}H_{26}NO_3$ $[M+H]^+$ 460.1907; found: 460.1912.

HPLC: Chiralpak ID column. Flow rate 1 mL/min. UV detection at 254 nm for major diastereomer; τ(major) = 89.4 min., τ(minor) = 70.7 min. using hexane: isopropanol = 95:5 up to τ = 50.1 min. thereafter, hexane: isopropanol = 90:10 as eluent, ee 52%.

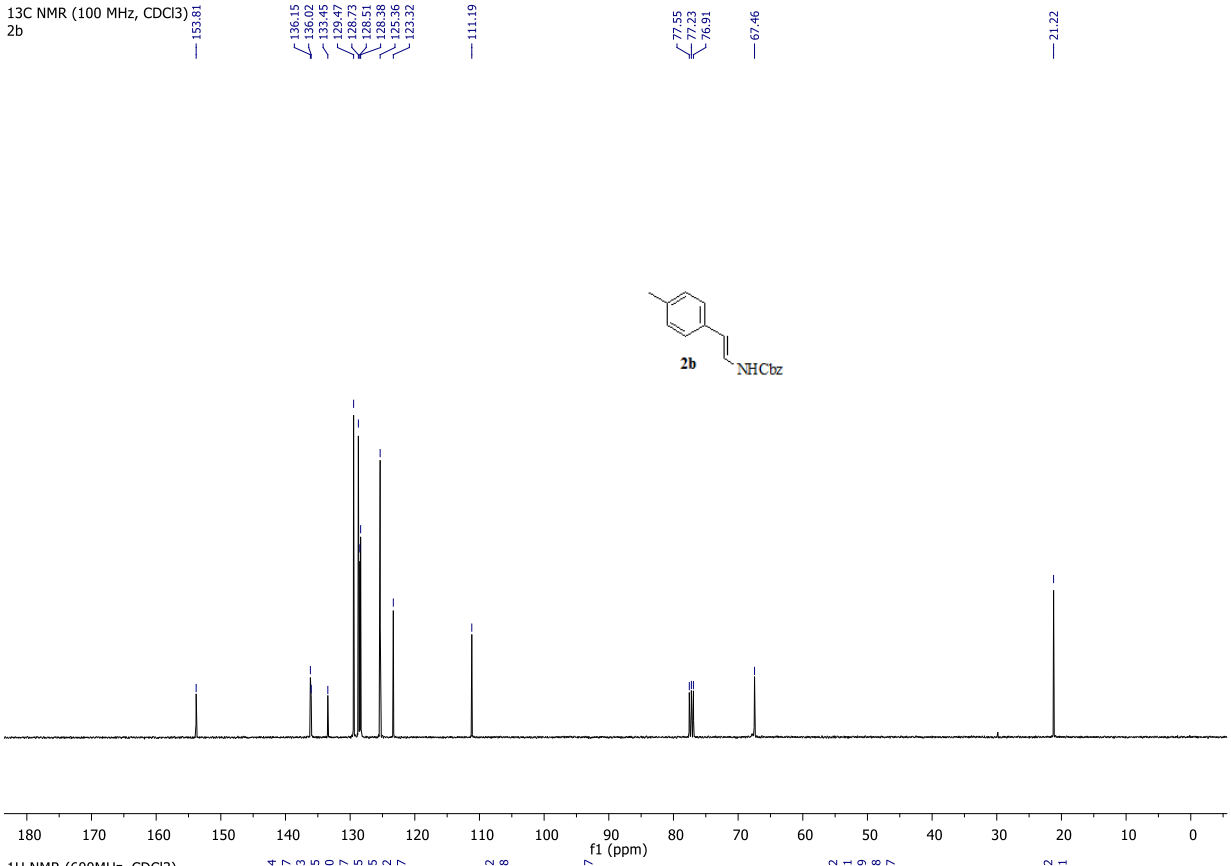
9. **<u>NMR Spectra of enecarbamates (2) & trisubstituted chromans (3)</u>:**



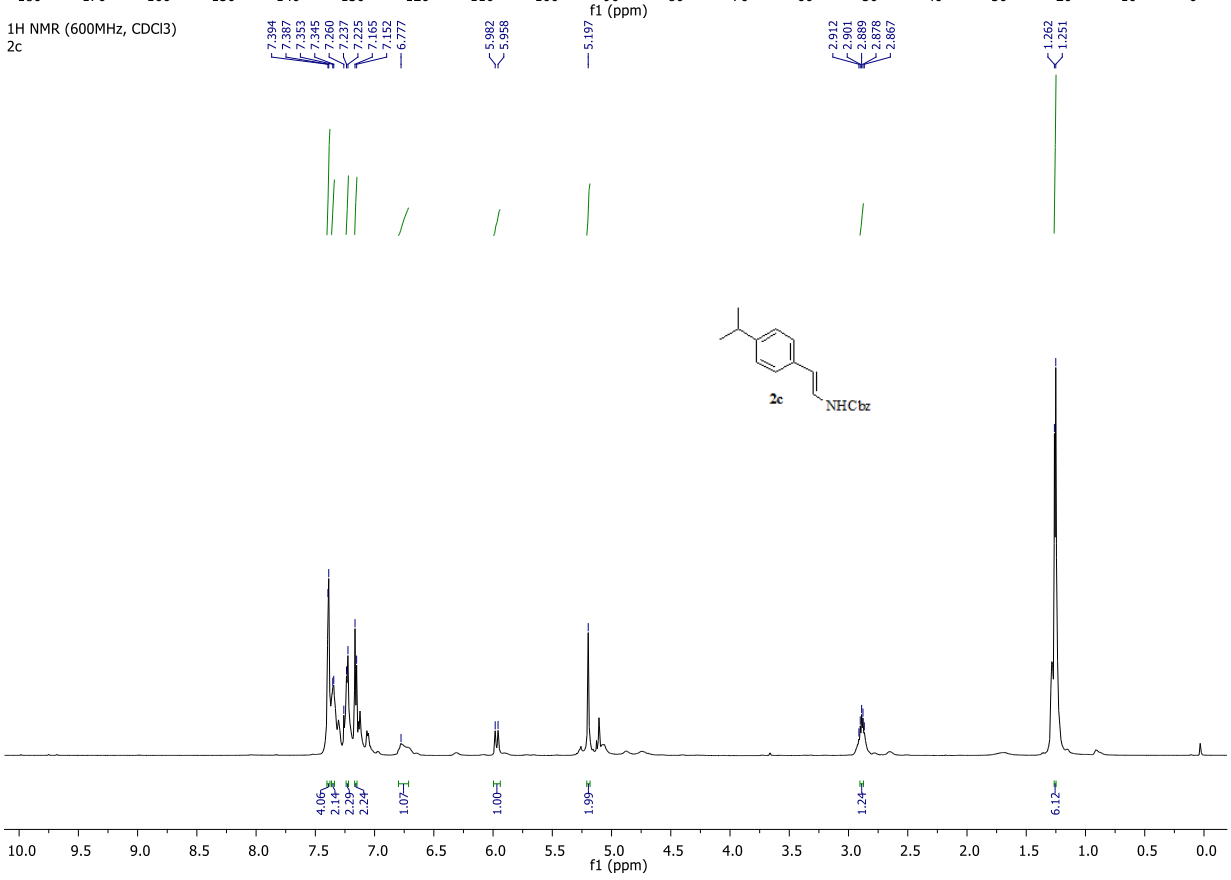

13C NMR (100 MHz, CDCl3)
2a
153.75
136.35
135.98
128.80
128.79
128.60
128.45
126.51
125.48
124.12
111.17
77.55
77.23
76.91
67.59
2a
NHCbz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

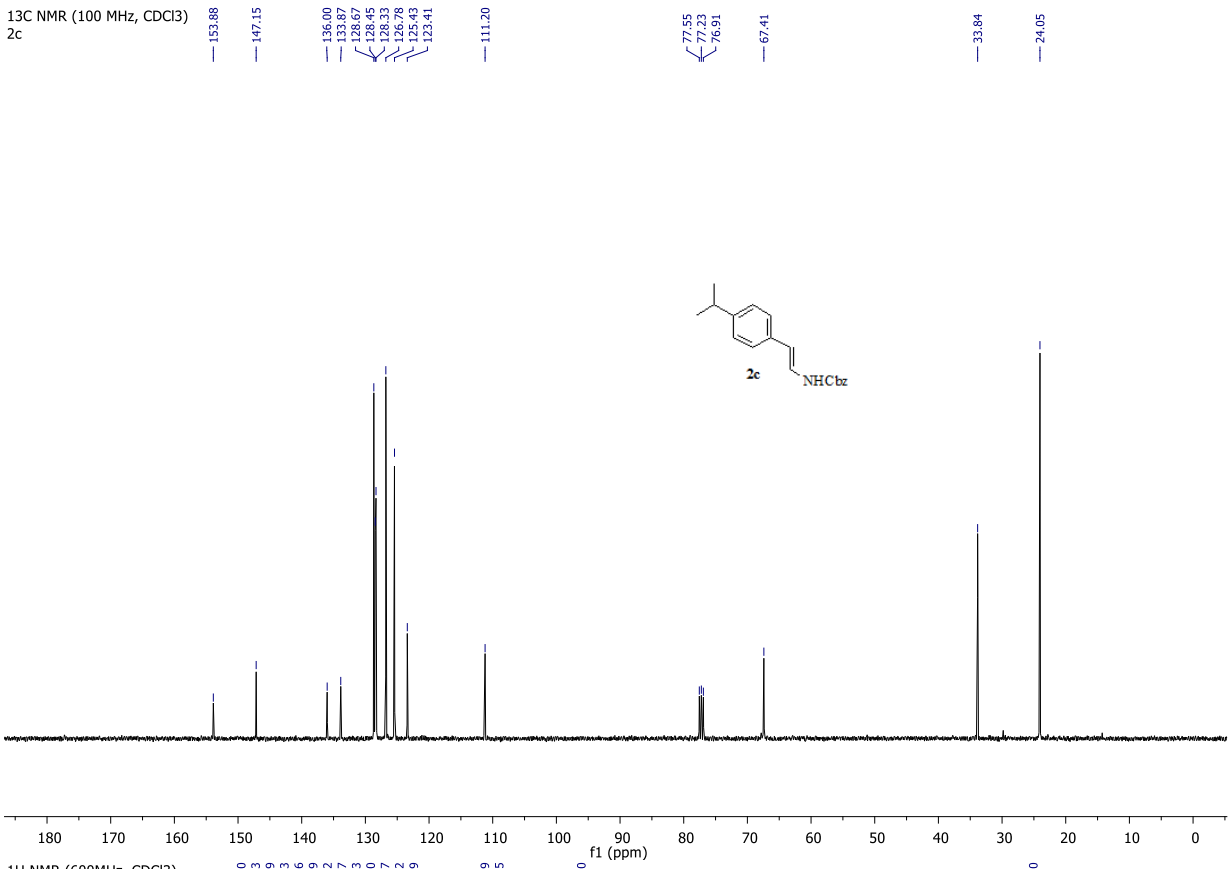

1H NMR (600MHz, CDCl3)
2b
7.388
7.381
7.361
7.354
7.347
7.341
7.260
7.189
7.177
7.097
7.084
6.610
5.954
5.930
5.188
2.318
2b
NHCbz
3.81
0.99
2.84
2.15
1.00
1.00
2.05
3.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

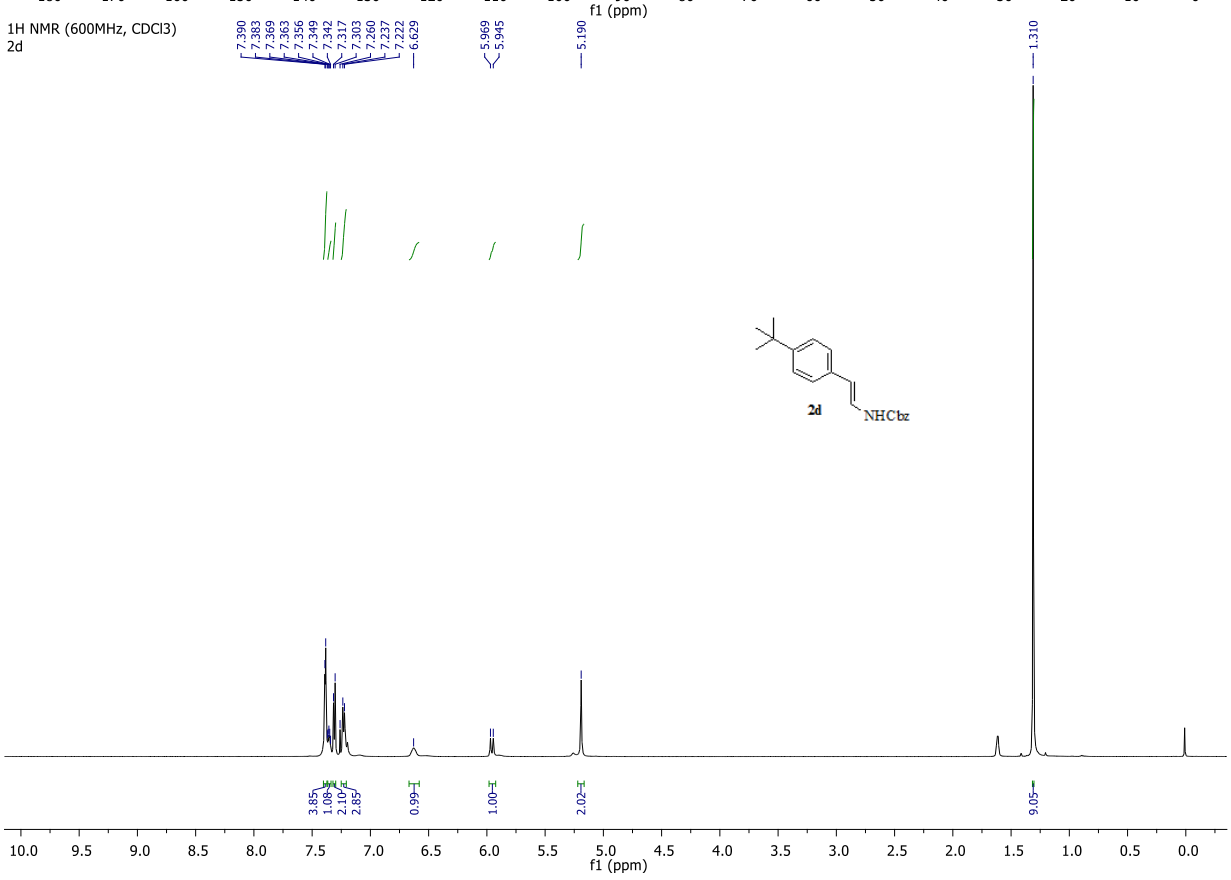
13C NMR (100 MHz, CDCl3)
2b



1H NMR (600MHz, CDCl3)
2c

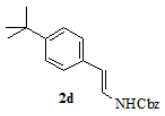


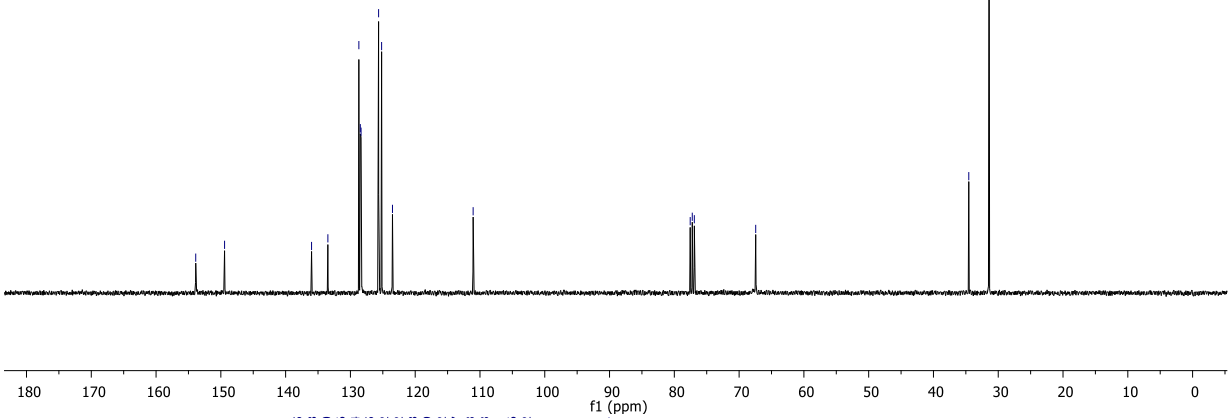

13C NMR (100 MHz, CDCl3)
2c
153.88
147.15
136.00
133.87
128.67
128.45
128.33
126.78
125.43
123.41
111.20
77.55
77.23
76.91
67.41
33.84
24.05
2c
NHCbz
f1 (ppm)


1H NMR (600MHz, CDCl3)
2d
7.390
7.383
7.369
7.363
7.356
7.349
7.342
7.317
7.303
7.260
7.237
7.222
6.629
5.969
5.945
5.190
1.310
2d
NHCbz
3.85
1.08
2.10
2.85
0.99
1.00
2.02
9.05
f1 (ppm)

13C NMR (100 MHz, CDCl3)
2d

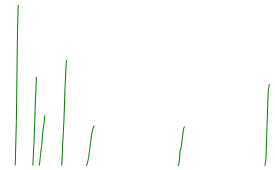
153.88
149.43
136.00
133.48
128.70
128.47
128.36
125.65
125.18
123.51
111.06
77.55
77.23
76.91
67.44
34.55
31.41

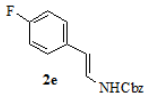


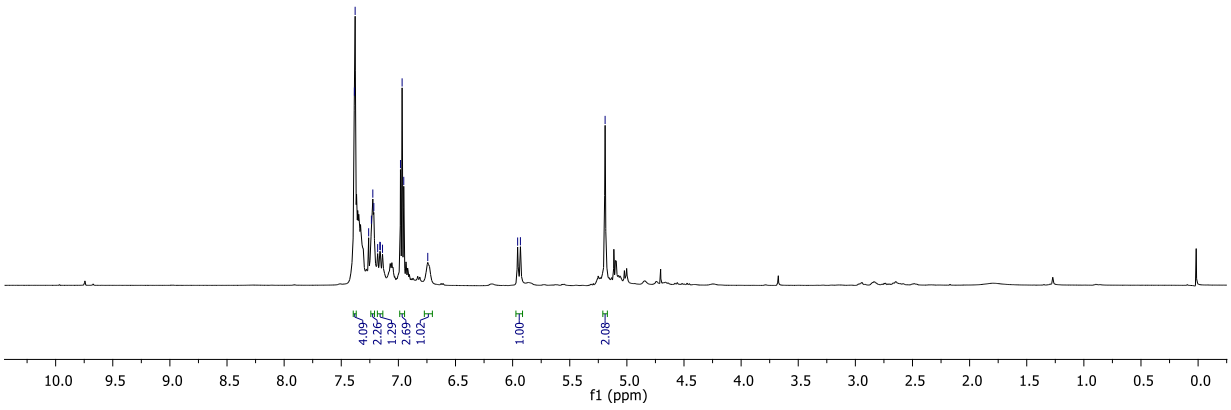


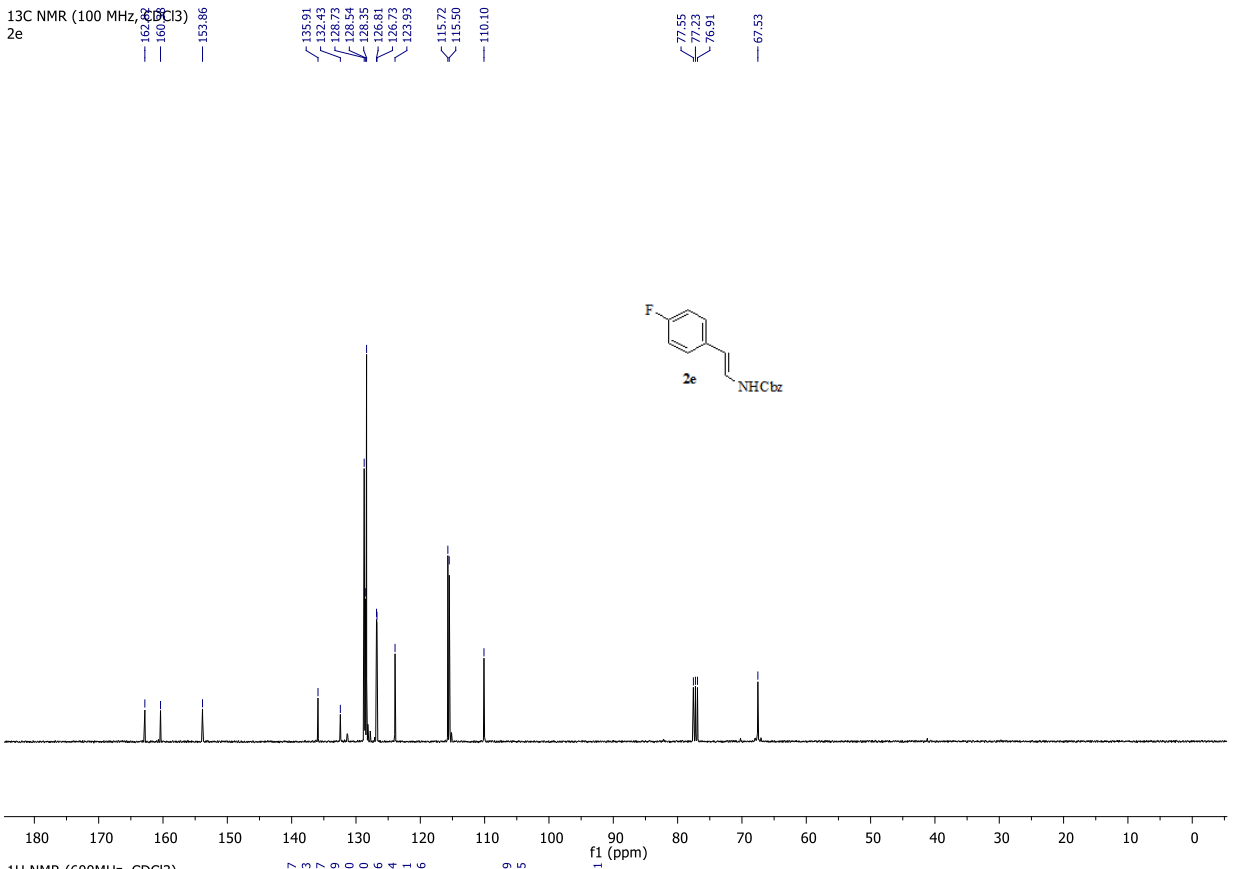
1H NMR (600MHz, CDCl3)
2e

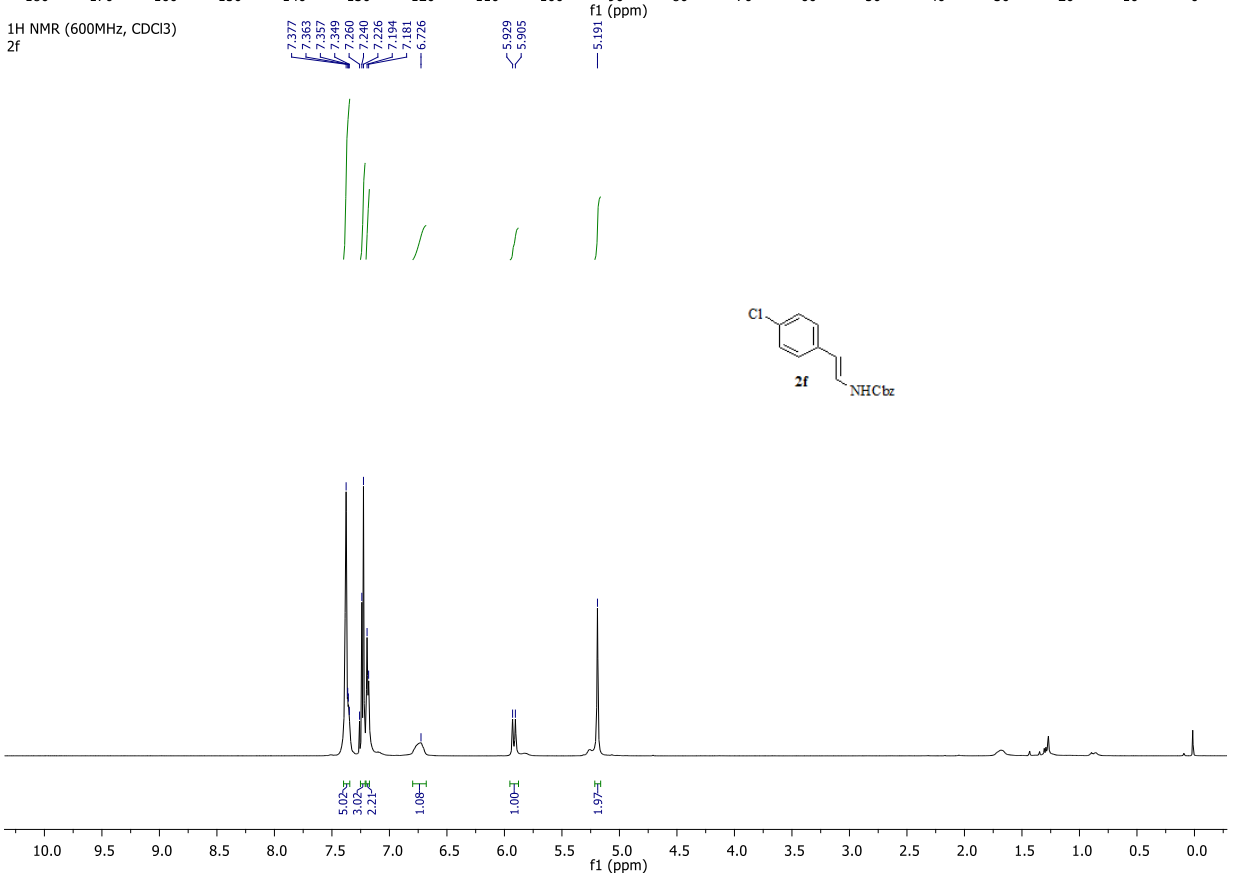
7.385
7.378
7.260
7.236
7.224
7.215
7.182
7.162
7.158
7.139
6.982
6.967
6.953
6.743
5.956
5.932
5.191



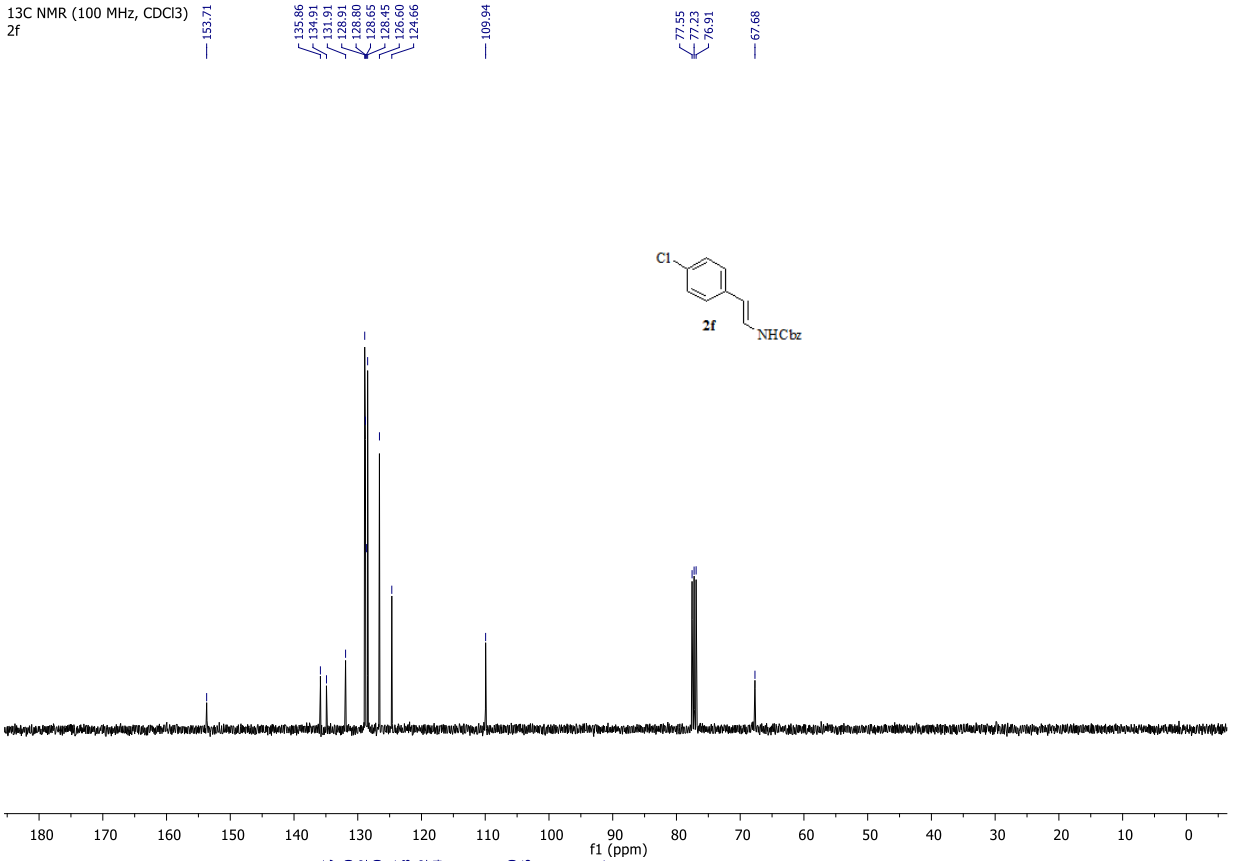




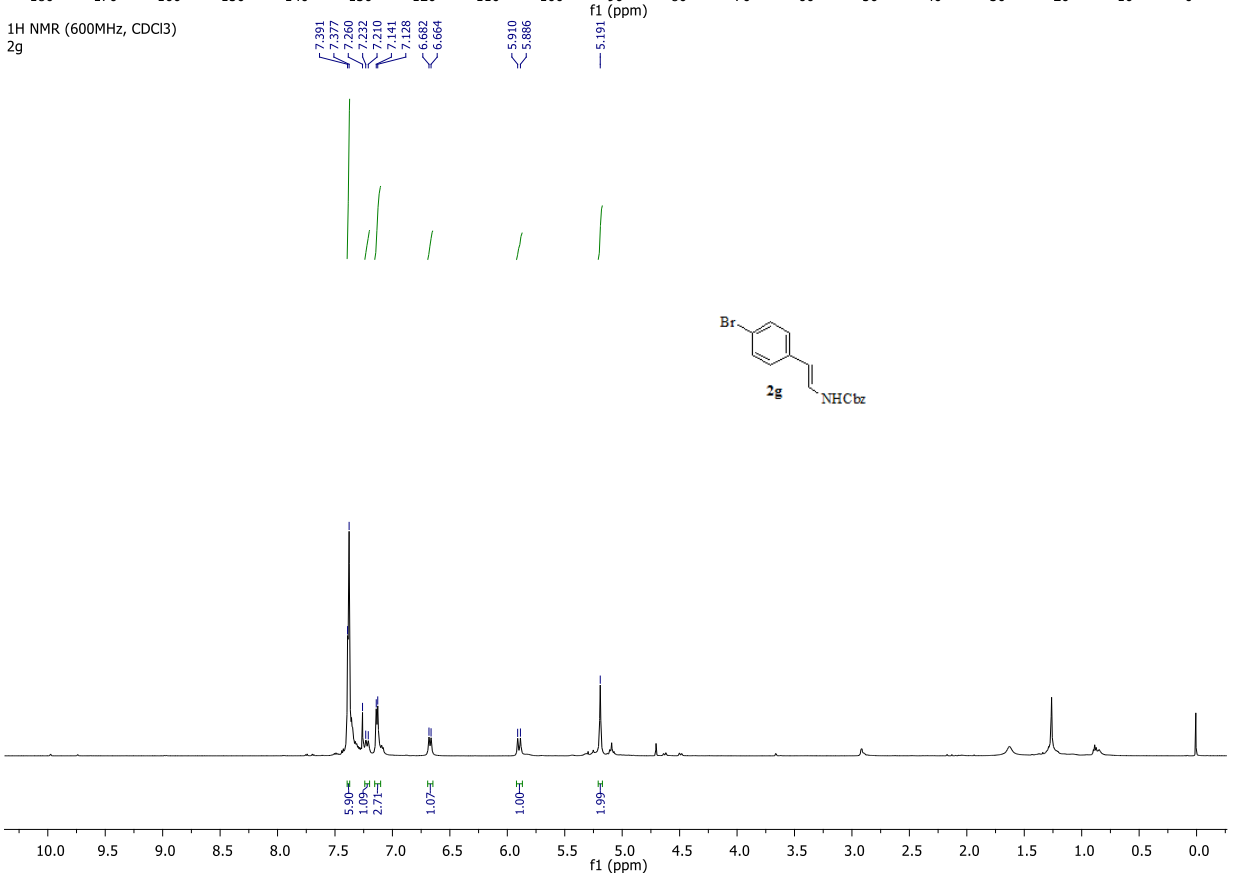

13C NMR (100 MHz, CDCl3)
2e
162.86
160.07
153.86
135.91
132.43
128.73
128.54
128.35
126.81
126.73
123.93
115.72
115.50
110.10
77.55
77.23
76.91
67.53
F
2e
NHCbz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


1H NMR (600MHz, CDCl3)
2f
7.377
7.363
7.357
7.349
7.260
7.240
7.226
7.194
7.181
6.726
5.929
5.905
5.191
Cl
2f
NHCbz
5.02
3.02
2.21
1.08
1.00
1.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

13C NMR (100 MHz, CDCl3)
2f

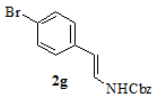


1H NMR (600MHz, CDCl3)
2g

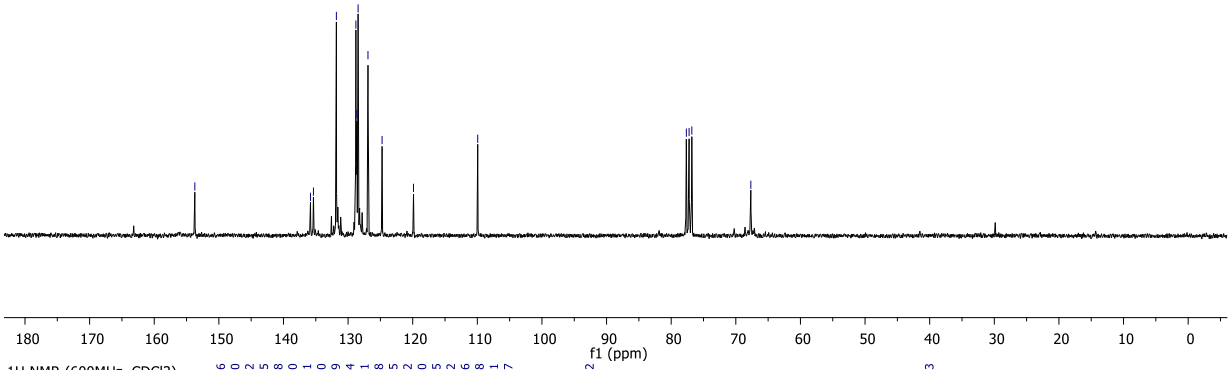


13C NMR (75 MHz, CDCl3)
2g

153.72
135.82
135.36
131.81
128.79
128.64
128.45
126.92
124.74
119.88
109.94
77.65
77.23
76.81
67.68

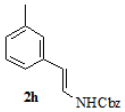


2g



1H NMR (600MHz, CDCl3)
2h

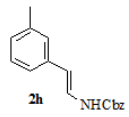
7.346
7.340
7.322
7.315
7.308
7.260
7.231
7.210
7.189
7.144
7.131
7.118
7.075
7.052
7.040
6.955
6.942
6.716
6.698
5.911
5.887
5.152
2.283

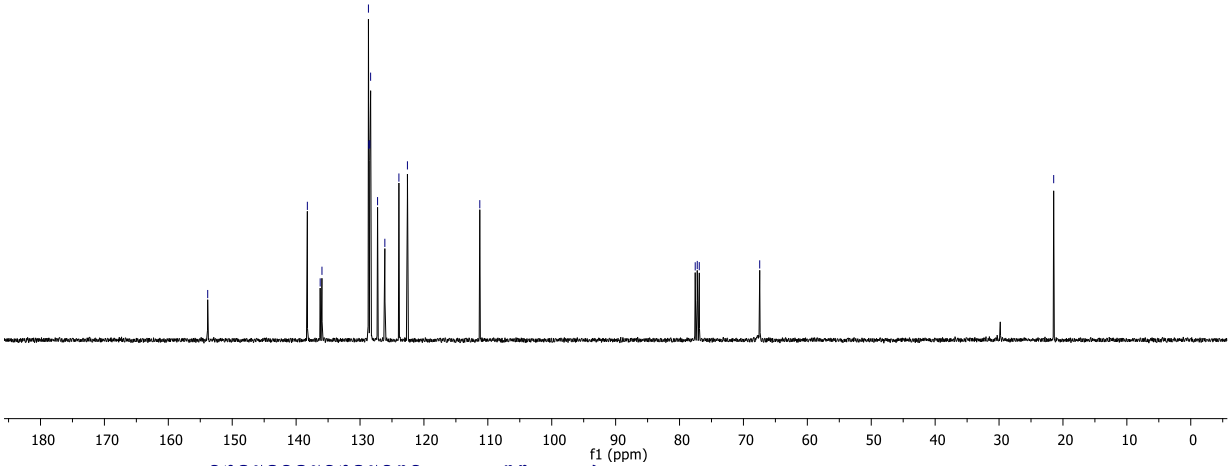


2h

13C NMR (100 MHz, CDCl3)
2h

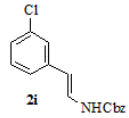
153.84
138.24
136.24
135.96
128.68
128.63
128.48
128.34
127.26
126.12
123.91
122.58
111.26
77.55
77.23
76.91
67.45
21.45

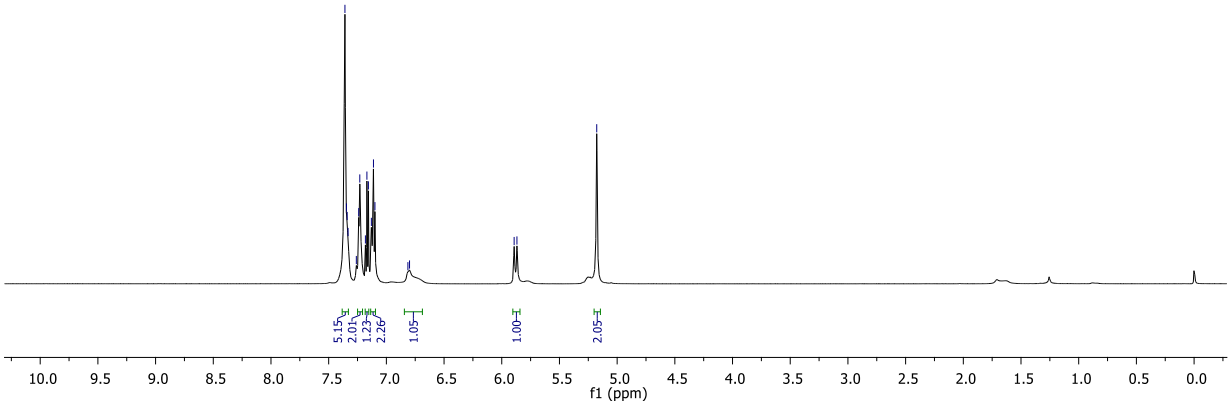




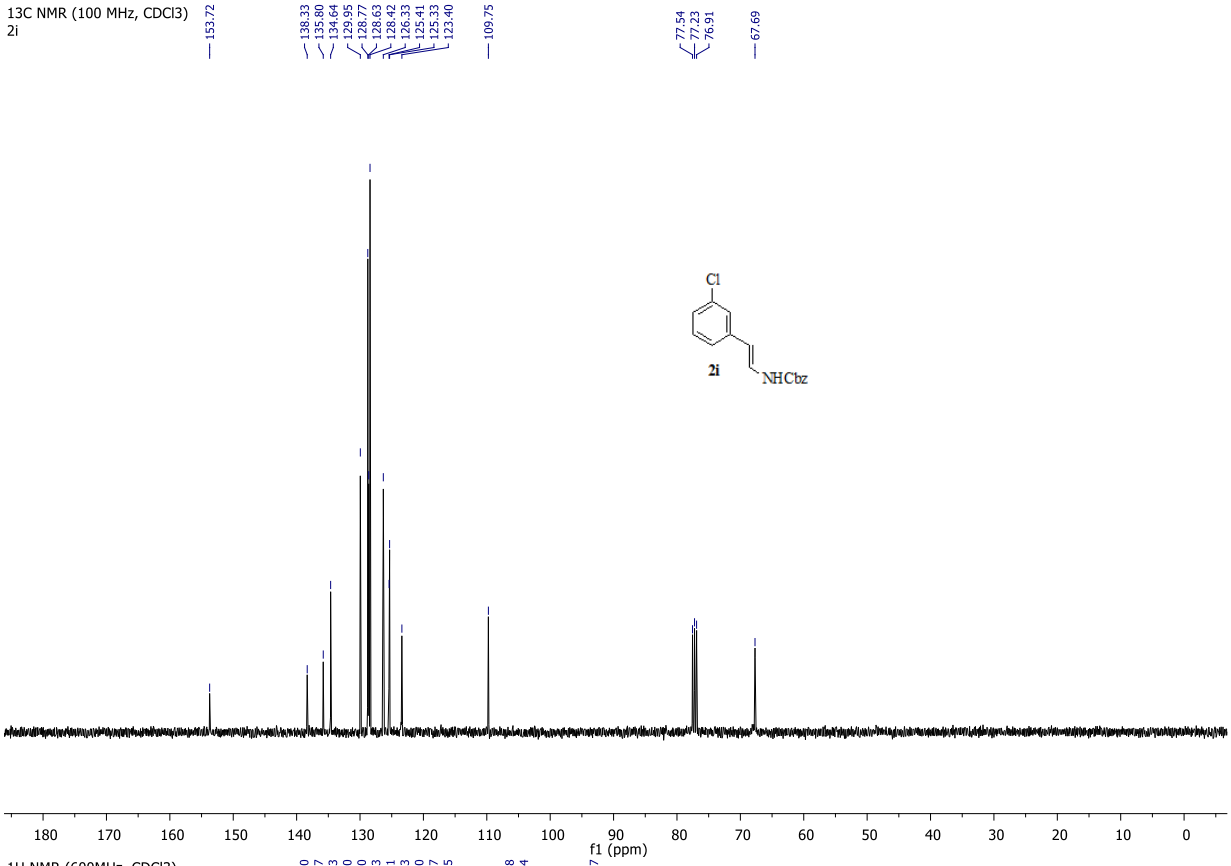
1H NMR (600MHz, CDCl3)
2i

7.359
7.346
7.340
7.332
7.260
7.239
7.230
7.182
7.169
7.156
7.130
7.112
7.099
6.813
6.799
5.893
5.868
5.177

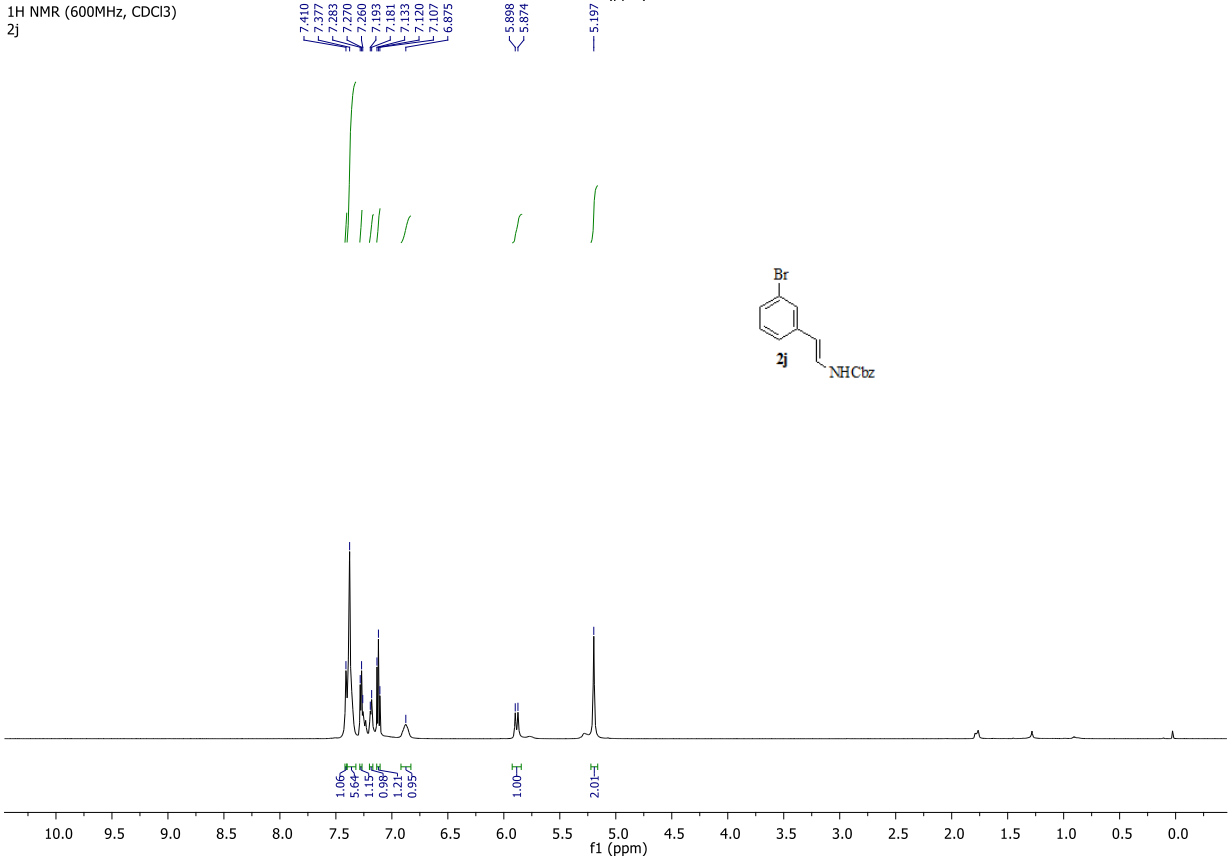


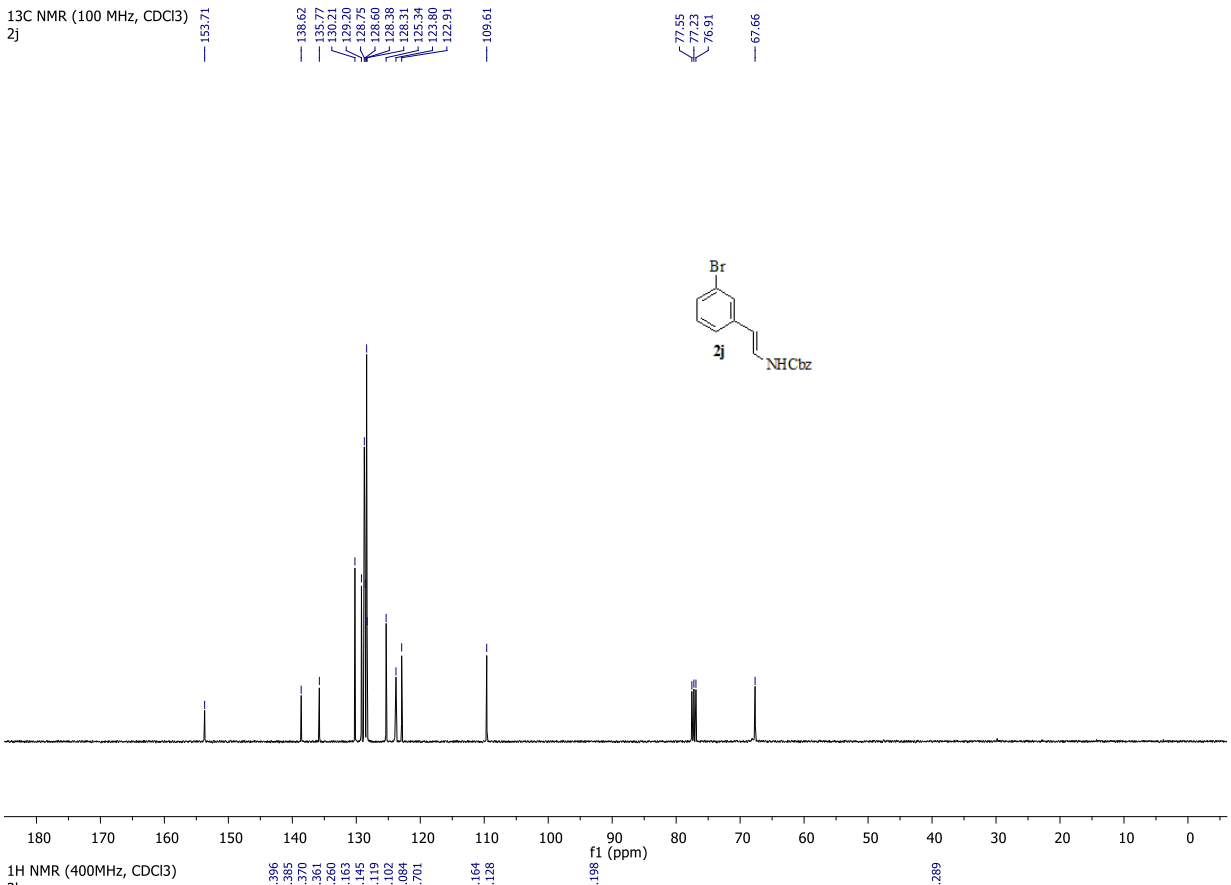


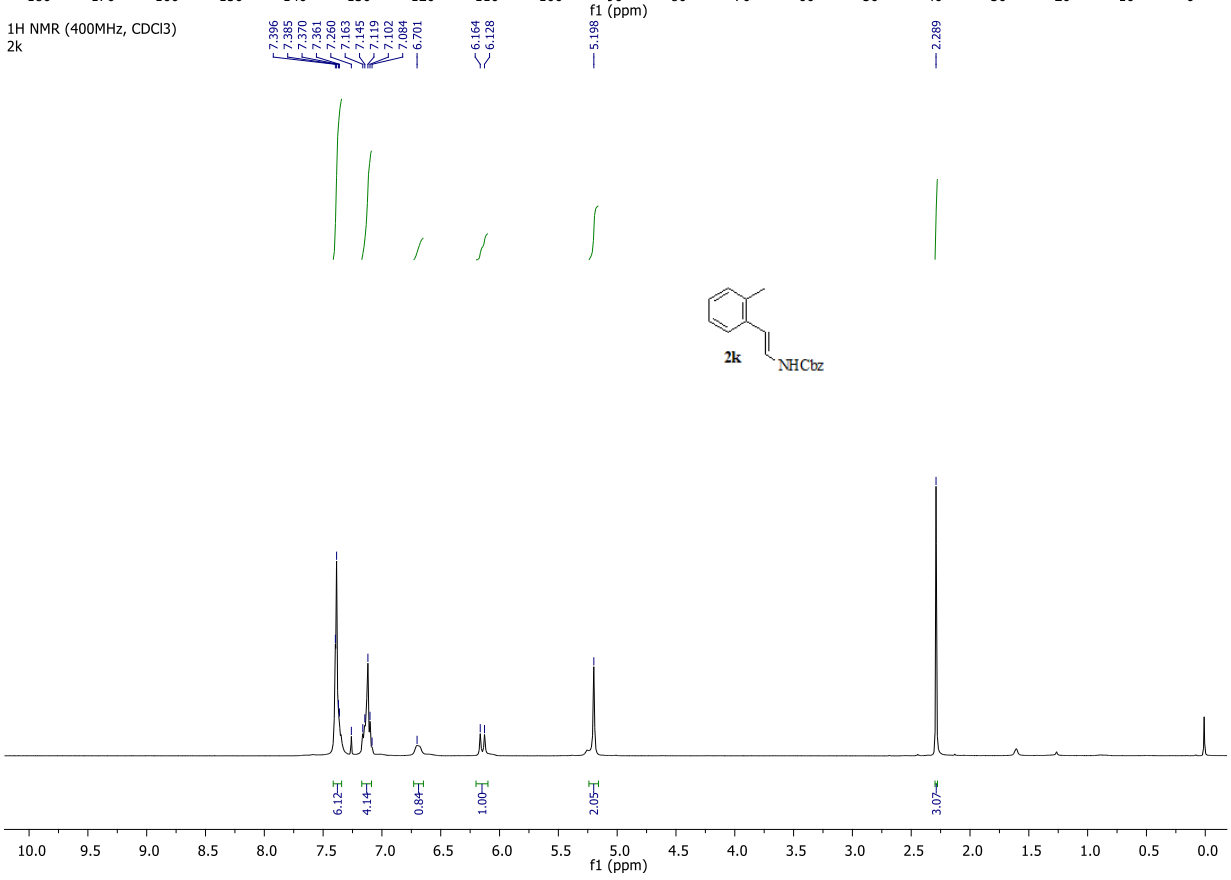
13C NMR (100 MHz, CDCl3)
2i

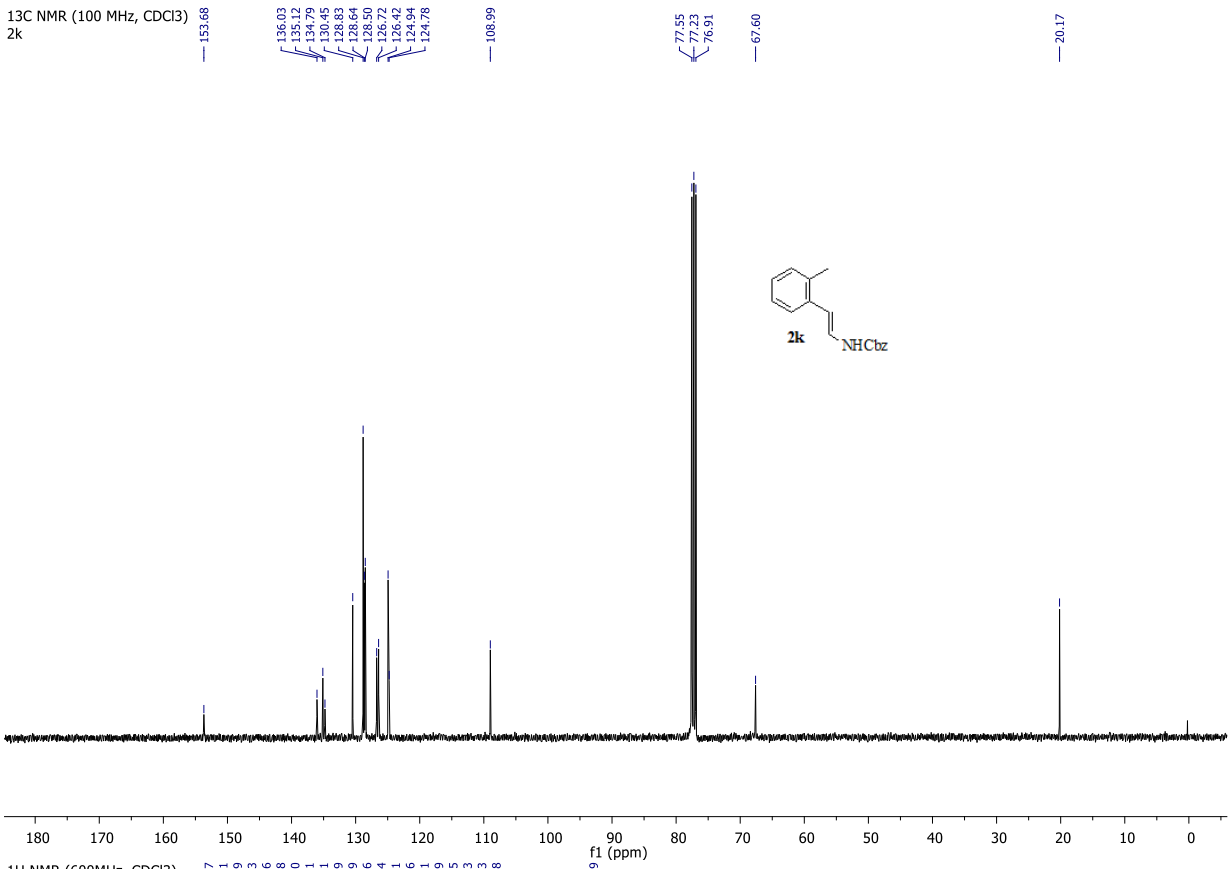


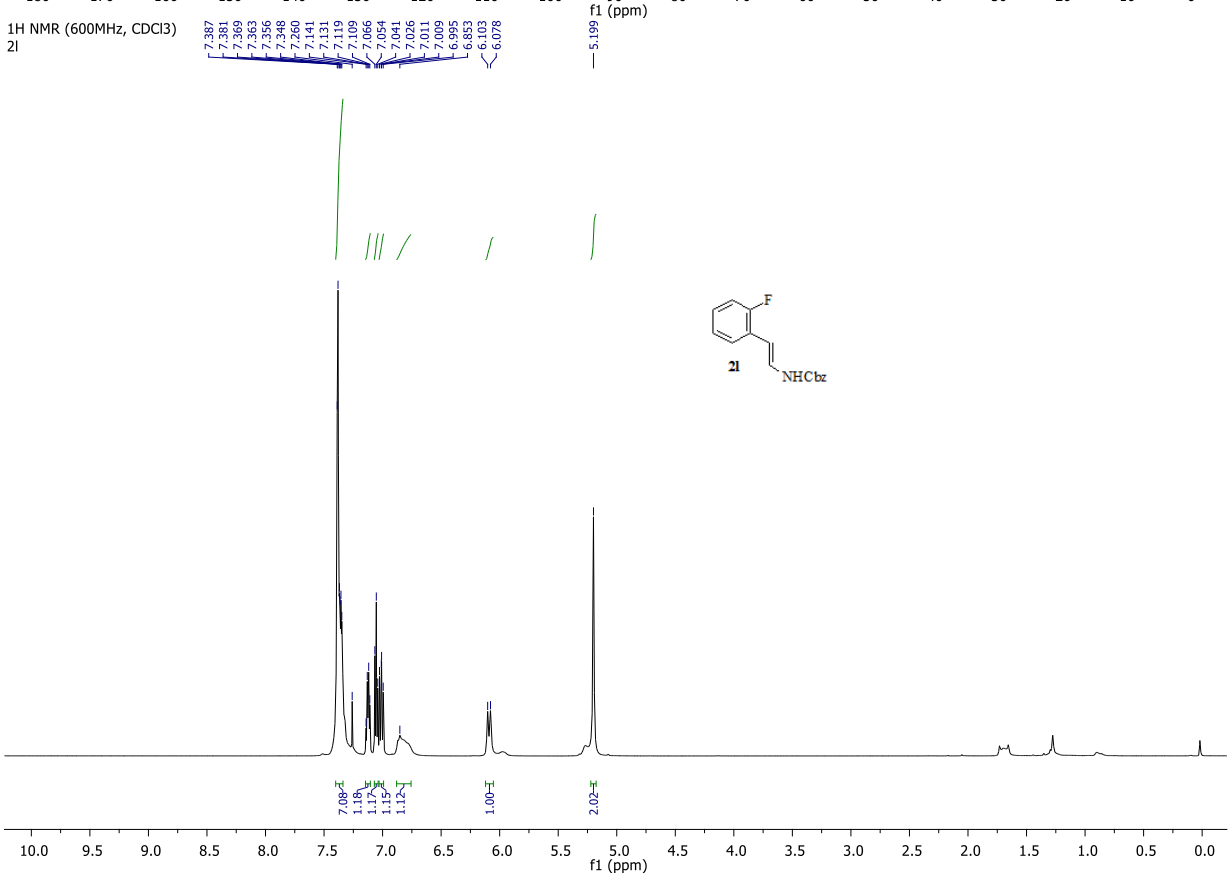
1H NMR (600MHz, CDCl3)
2j

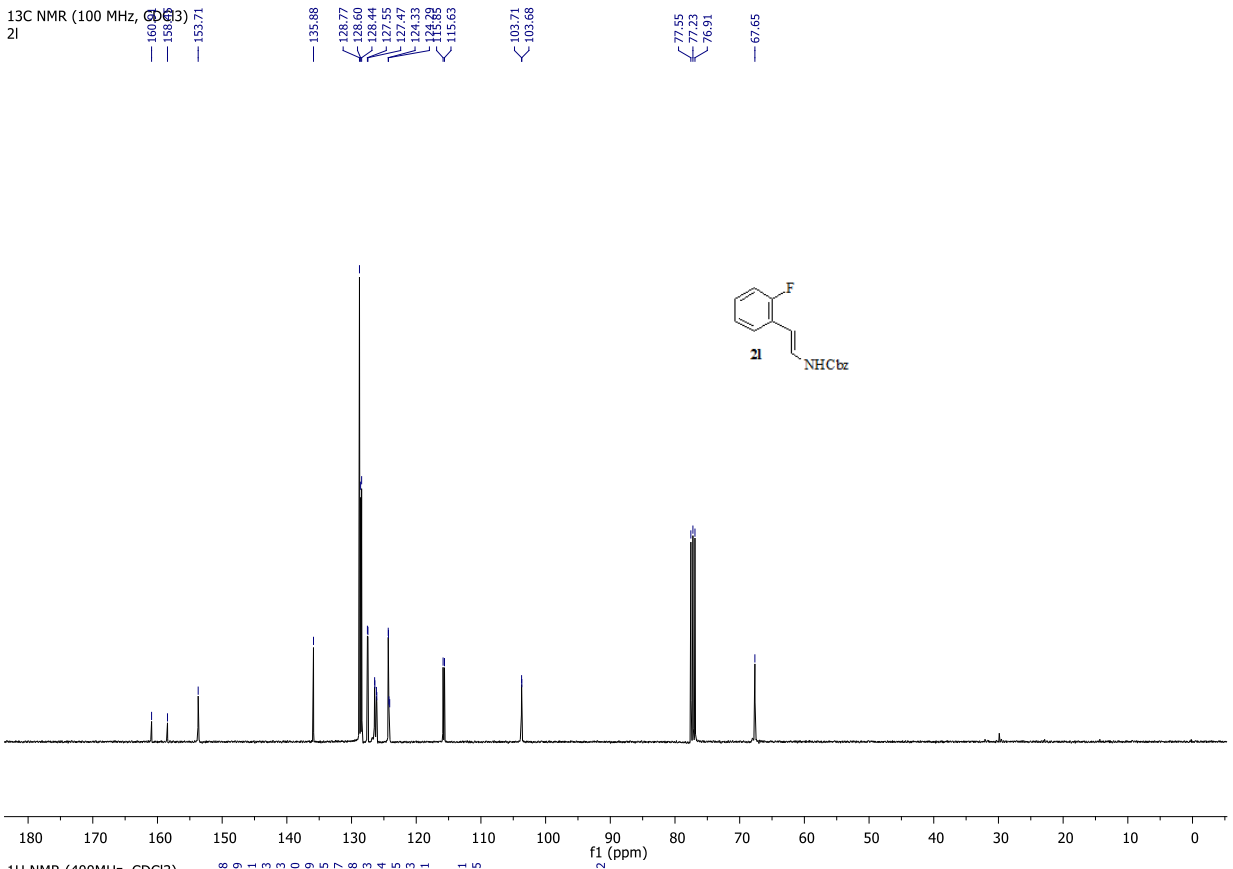


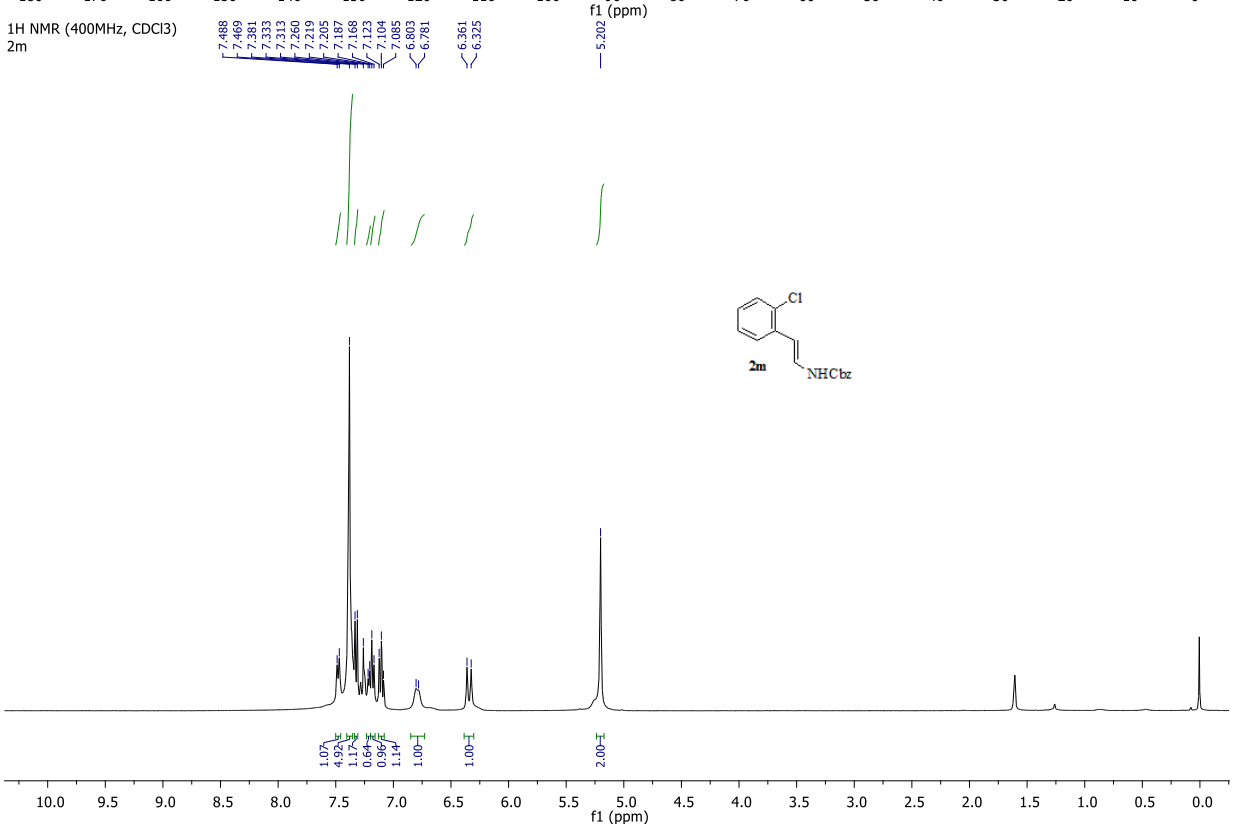

13C NMR (100 MHz, CDCl3)
2j
153.71
138.62
135.77
130.21
129.20
128.75
128.60
128.38
128.31
125.34
123.80
122.91
109.61
77.55
77.23
76.91
67.66
Br
2j
NHCbz
f1 (ppm)

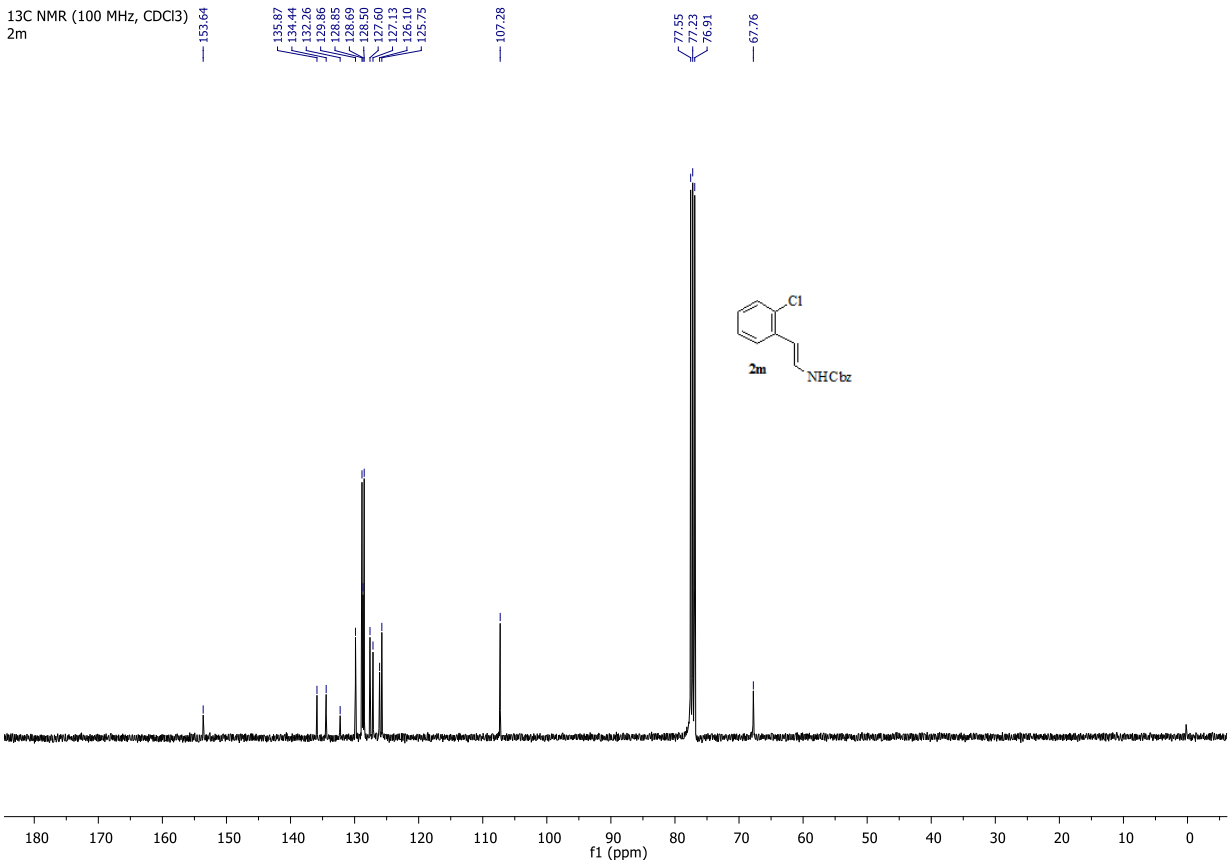

1H NMR (400MHz, CDCl3)
2k
7.396
7.385
7.370
7.361
7.260
7.163
7.145
7.119
7.102
7.084
6.701
6.164
6.128
5.198
2.289
2k
NHCbz
6.12
4.14
0.84
1.00
2.05
3.07
f1 (ppm)

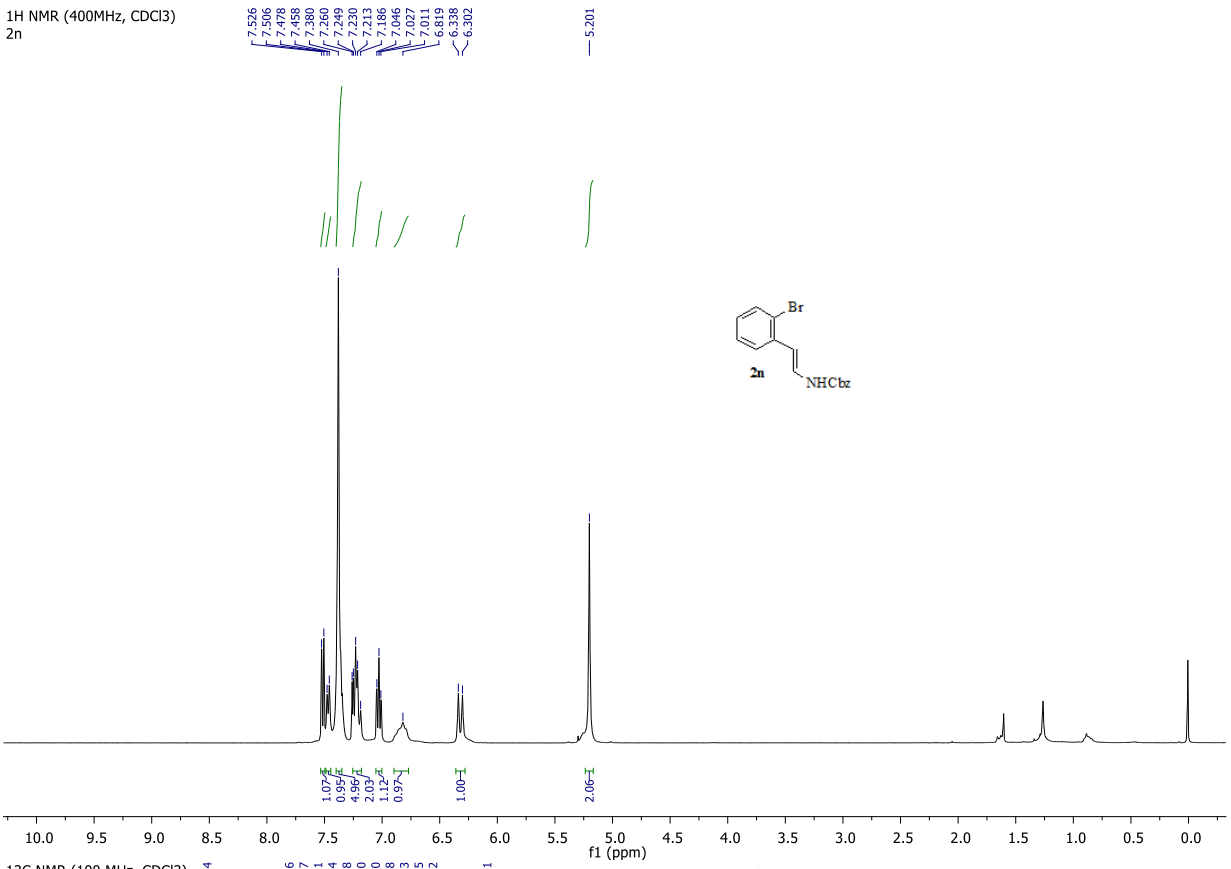

13C NMR (100 MHz, CDCl3)
2k
153.68
136.03
135.12
134.79
130.45
128.83
128.64
128.50
126.72
126.42
124.94
124.78
108.99
77.55
77.23
76.91
67.60
20.17
2k
NHCbz
f1 (ppm)

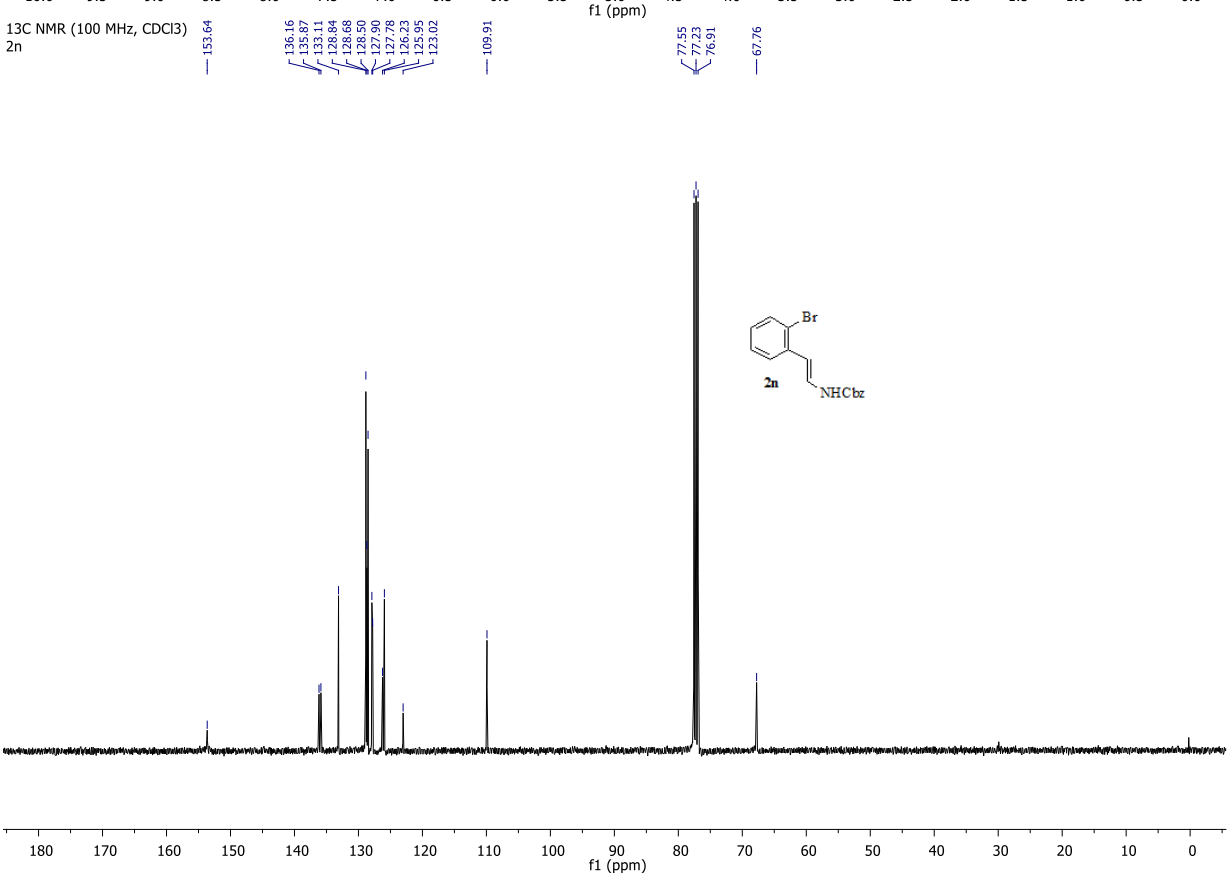

1H NMR (600MHz, CDCl3)
2l
7.387
7.381
7.369
7.363
7.356
7.348
7.260
7.141
7.131
7.119
7.109
7.066
7.054
7.041
7.026
7.011
7.009
6.995
6.853
6.103
6.078
5.199
F
2l
NHCbz
7.08
1.18
1.17
1.15
1.12
1.00
2.02
f1 (ppm)

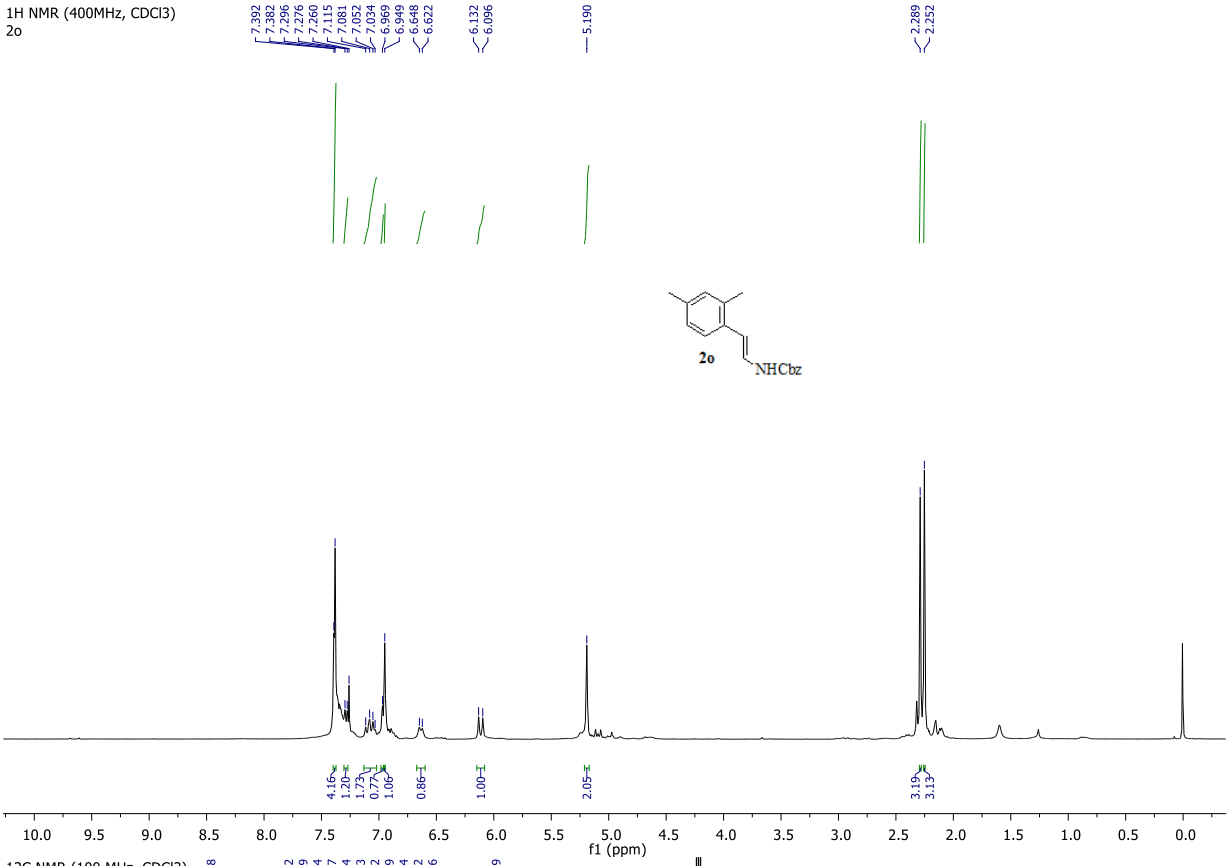

13C NMR (100 MHz, CDCl3)
2l
160.61
158.23
153.71
135.88
128.77
128.60
128.44
127.55
127.47
124.33
124.29
115.85
115.63
103.71
103.68
77.55
77.23
76.91
67.65
F
2l
NHCbz
f1 (ppm)

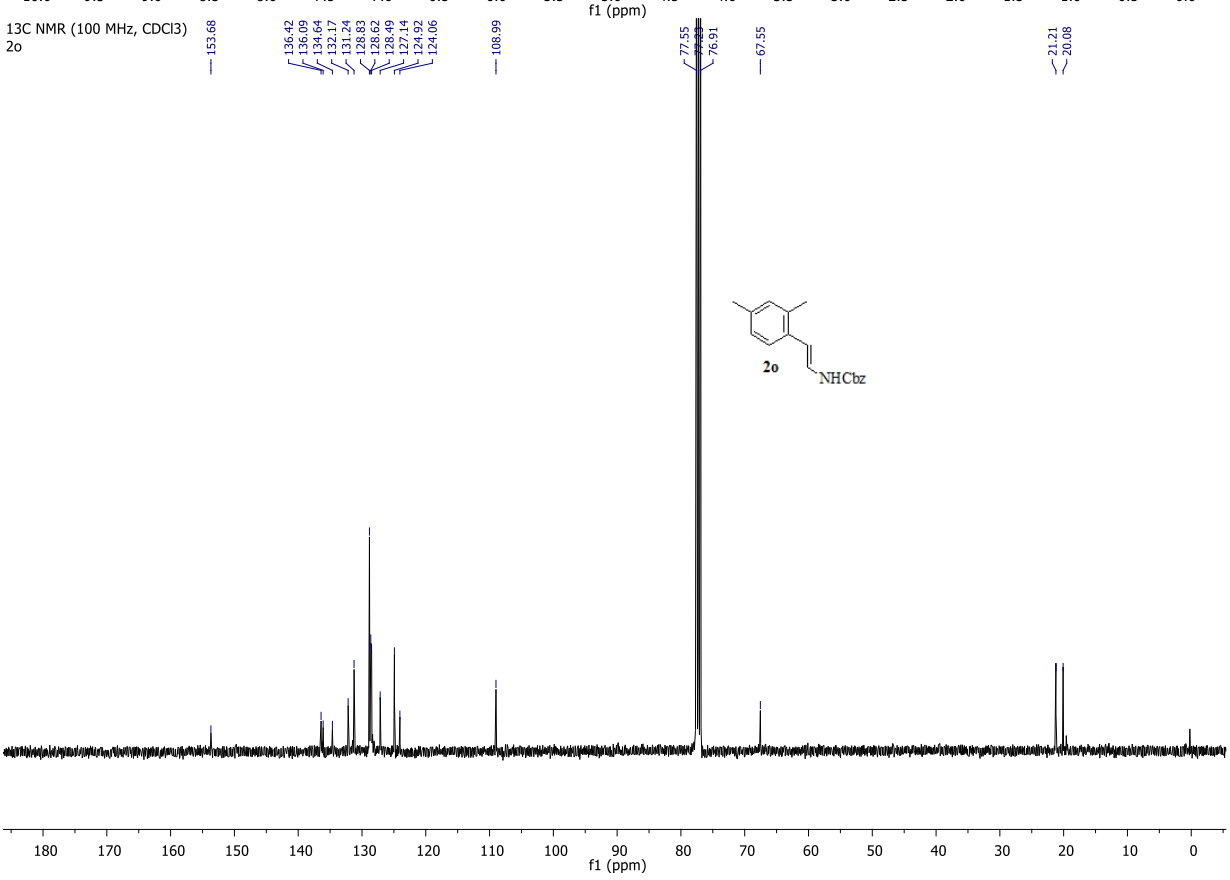

1H NMR (400MHz, CDCl3)
2m
7.488
7.469
7.381
7.333
7.313
7.260
7.219
7.205
7.187
7.168
7.123
7.104
7.085
6.803
6.781
6.361
6.325
5.202
Cl
2m
NHCbz
1.07
4.92
1.11
0.64
0.98
1.14
1.00
1.00
2.00
f1 (ppm)

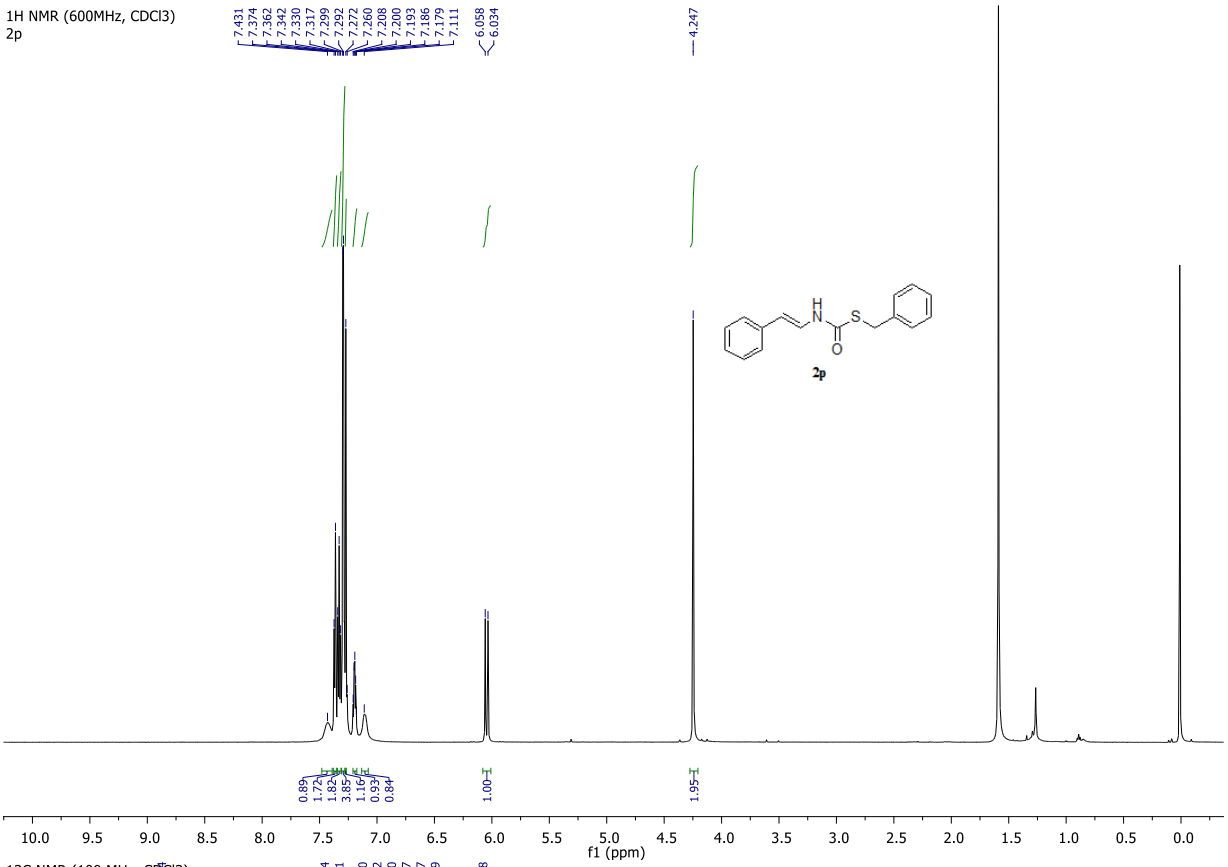

13C NMR (100 MHz, CDCl3)
2m
153.64
135.87
134.44
132.26
129.86
128.85
128.69
128.50
127.60
127.13
126.10
125.75
107.28
77.55
77.23
76.91
67.76
Cl
2m
NHCbz
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

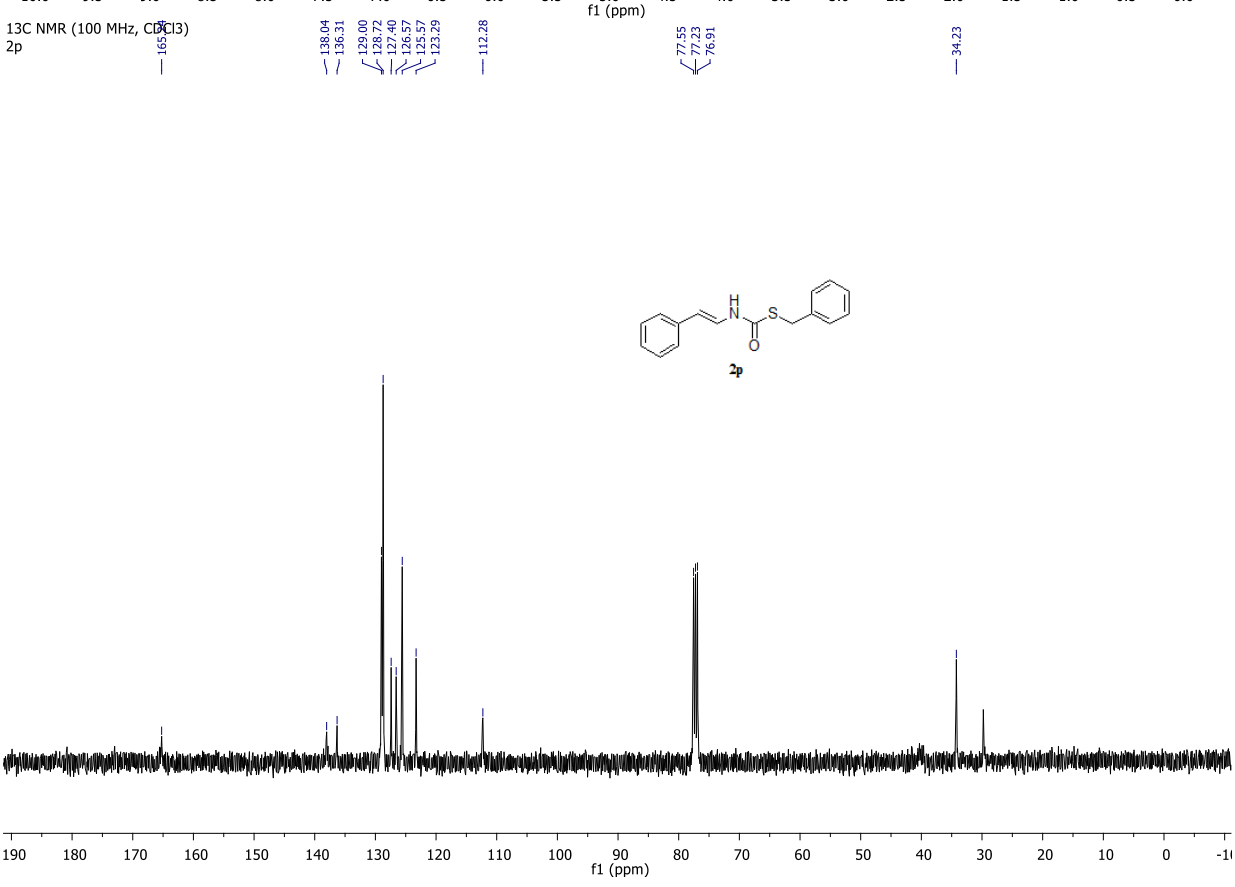

1H NMR (400MHz, CDCl3)
2n
7.526
7.506
7.478
7.458
7.380
7.260
7.249
7.230
7.213
7.186
7.046
7.027
7.011
6.819
6.338
6.302
5.201
Br
2n
NHCbz
1.07
0.95
4.96
2.03
1.12
0.97
1.00
2.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

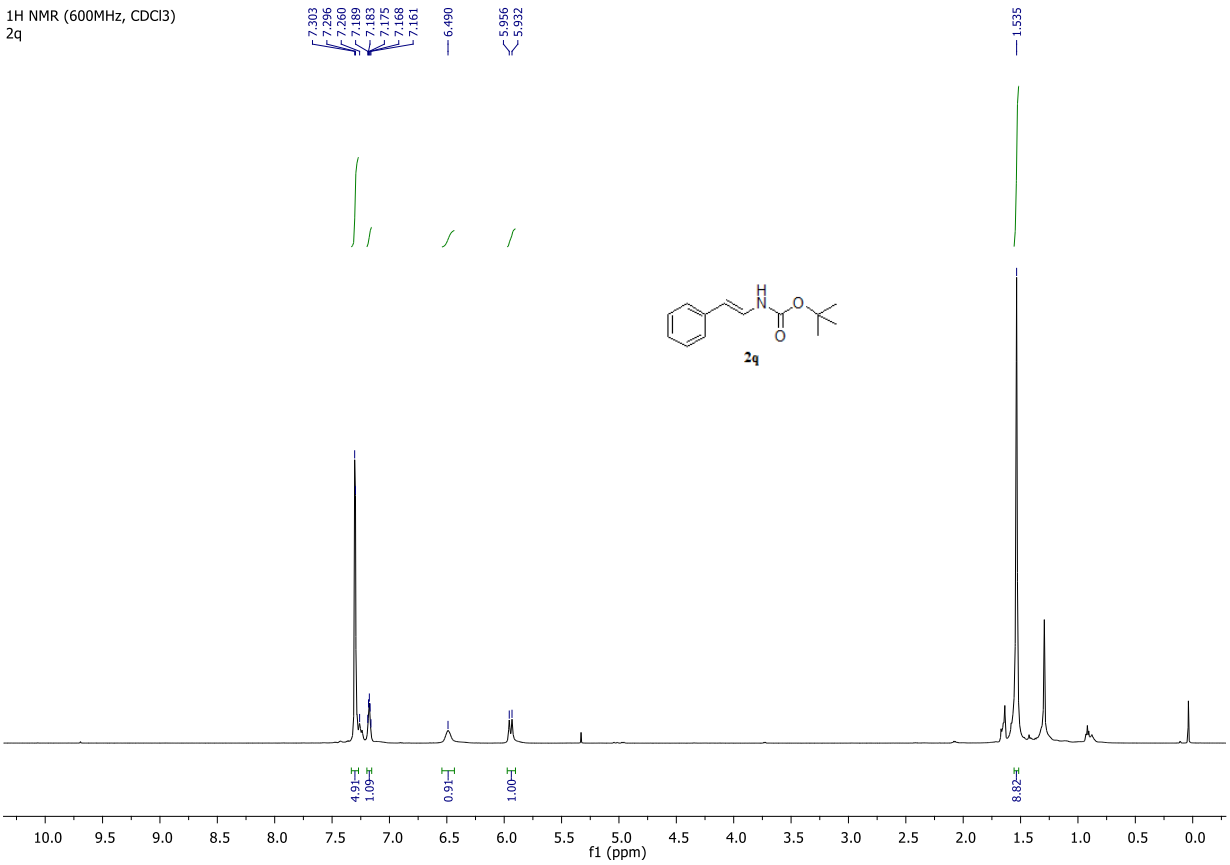

13C NMR (100 MHz, CDCl3)
2n
153.64
136.16
135.87
133.11
128.84
128.68
128.50
127.90
127.78
126.23
125.95
123.02
109.91
77.55
77.23
76.91
67.76
Br
2n
NHCbz
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

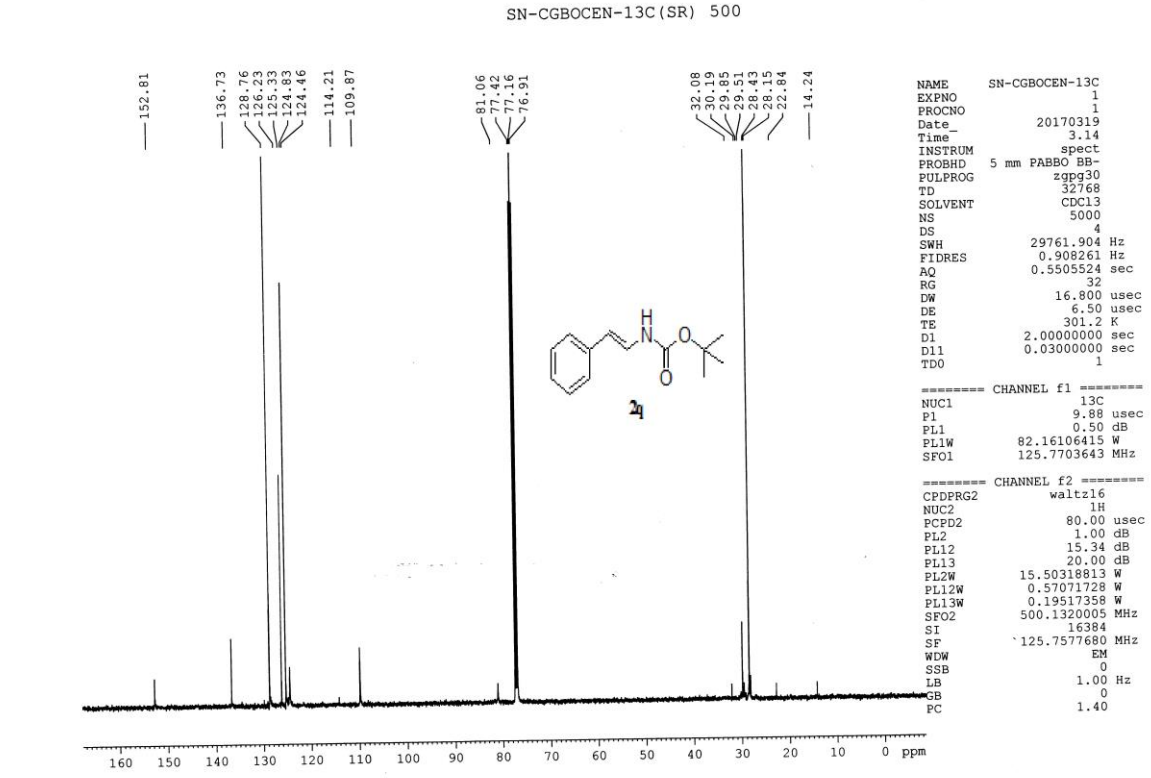

1H NMR (400MHz, CDCl3)
2o
7.392
7.382
7.296
7.276
7.260
7.115
7.081
7.052
7.034
6.969
6.949
6.648
6.622
6.132
6.096
5.190
2.289
2.252
2o
NHCbz
4.16
1.20
1.73
0.77
1.06
0.86
1.00
2.05
3.19
3.13
f1 (ppm)

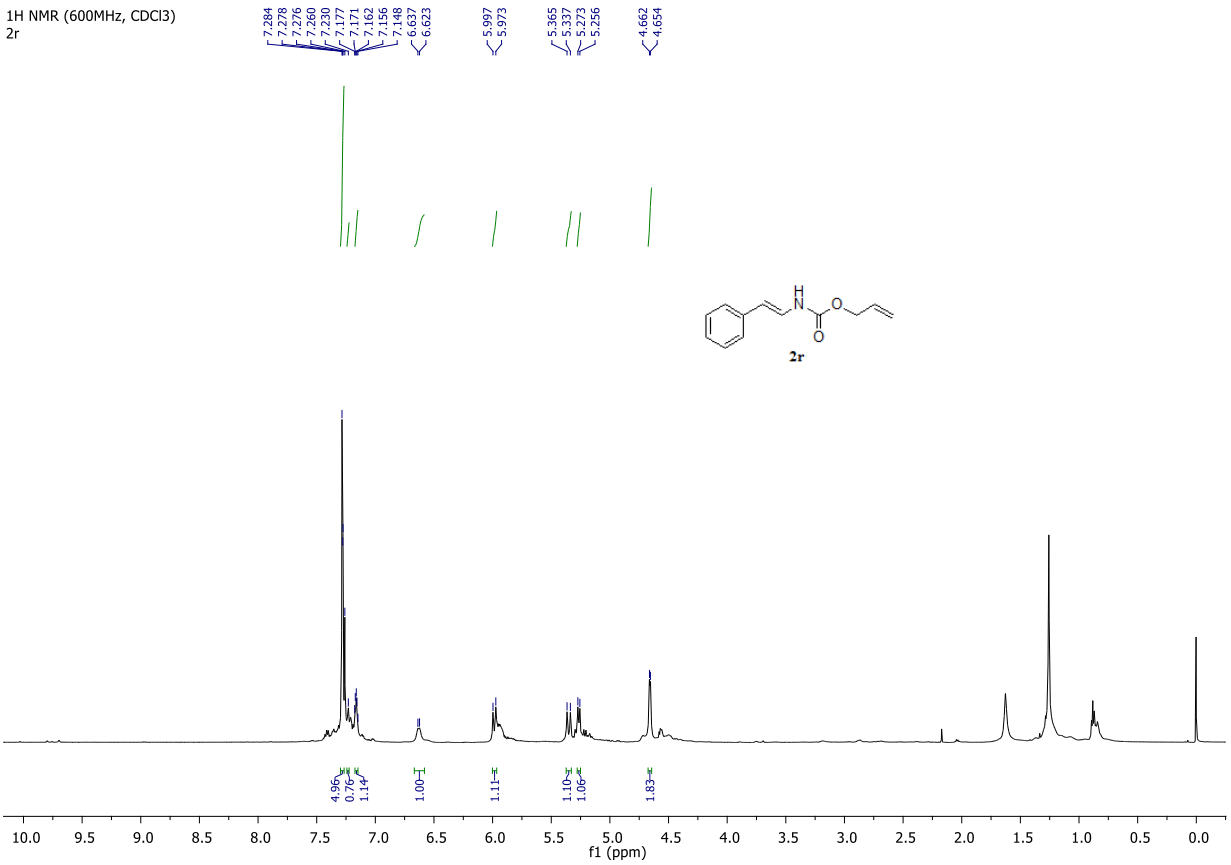

13C NMR (100 MHz, CDCl3)
2o
153.68
136.42
136.09
134.64
132.17
131.24
128.83
128.62
128.49
127.14
124.92
124.06
108.99
77.55
77.23
76.91
67.55
21.21
20.08
2o
NHCbz
f1 (ppm)

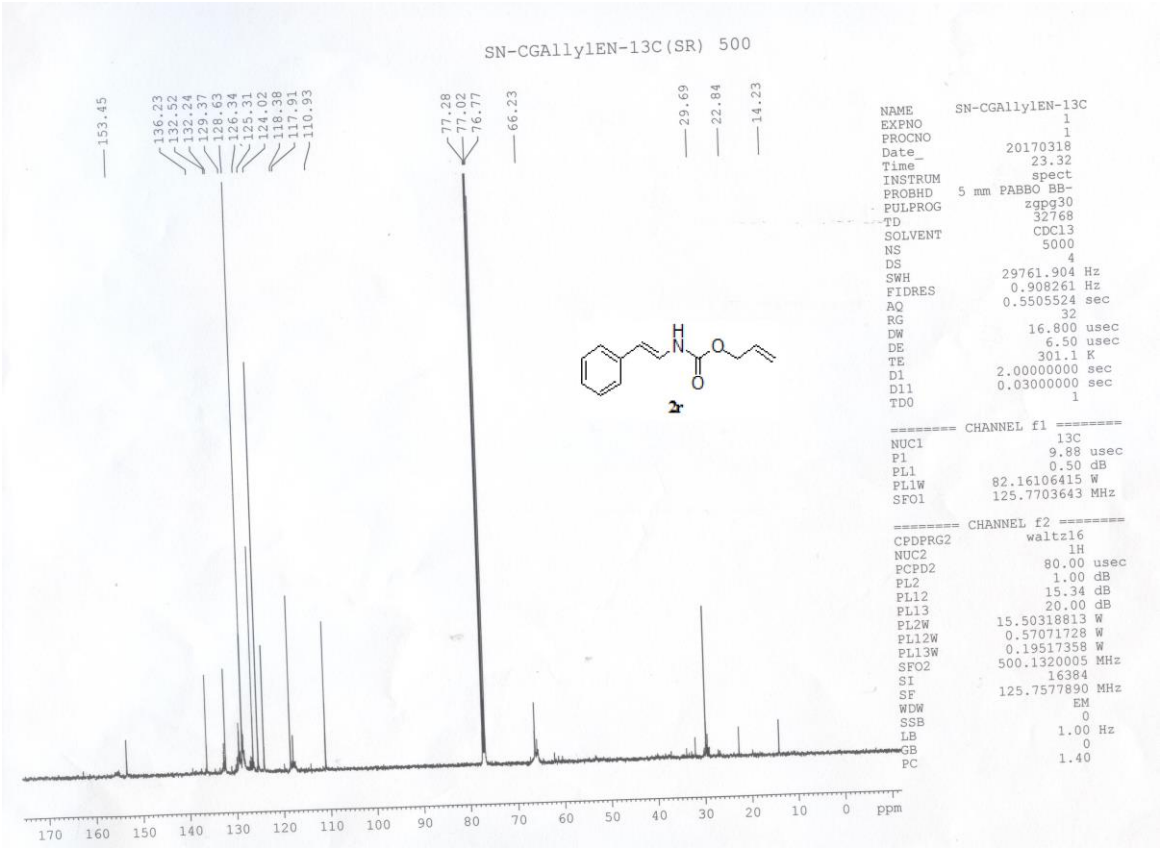

1H NMR (600MHz, CDCl3)
2p
7.431
7.374
7.362
7.342
7.330
7.317
7.299
7.292
7.272
7.260
7.208
7.200
7.193
7.186
7.179
7.111
6.058
6.034
4.247
0.89
1.72
1.82
3.85
1.16
0.93
0.84
1.00
1.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
2p

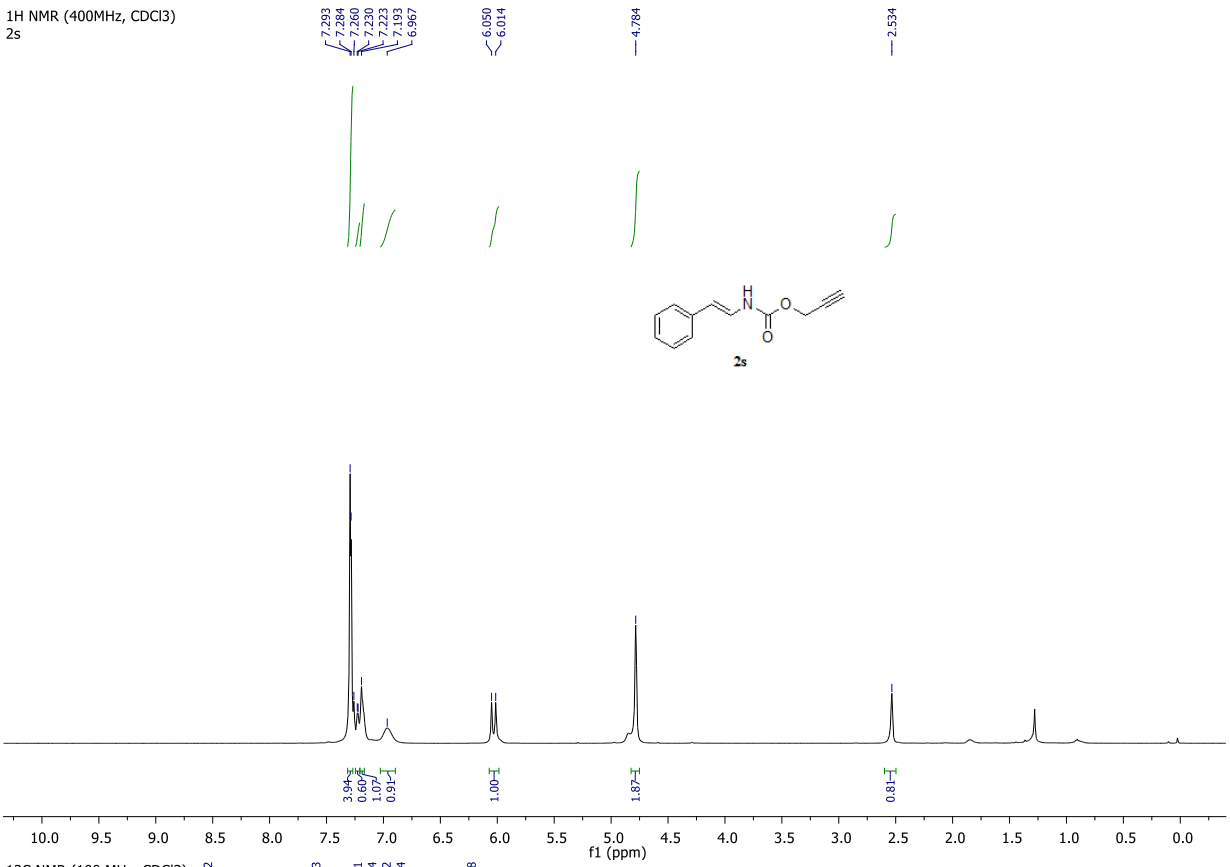

13C NMR (100 MHz, CDCl3)
2p
165.51
138.04
136.31
129.00
128.72
127.40
126.57
125.57
123.29
112.28
77.55
77.23
76.91
34.23
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
2p

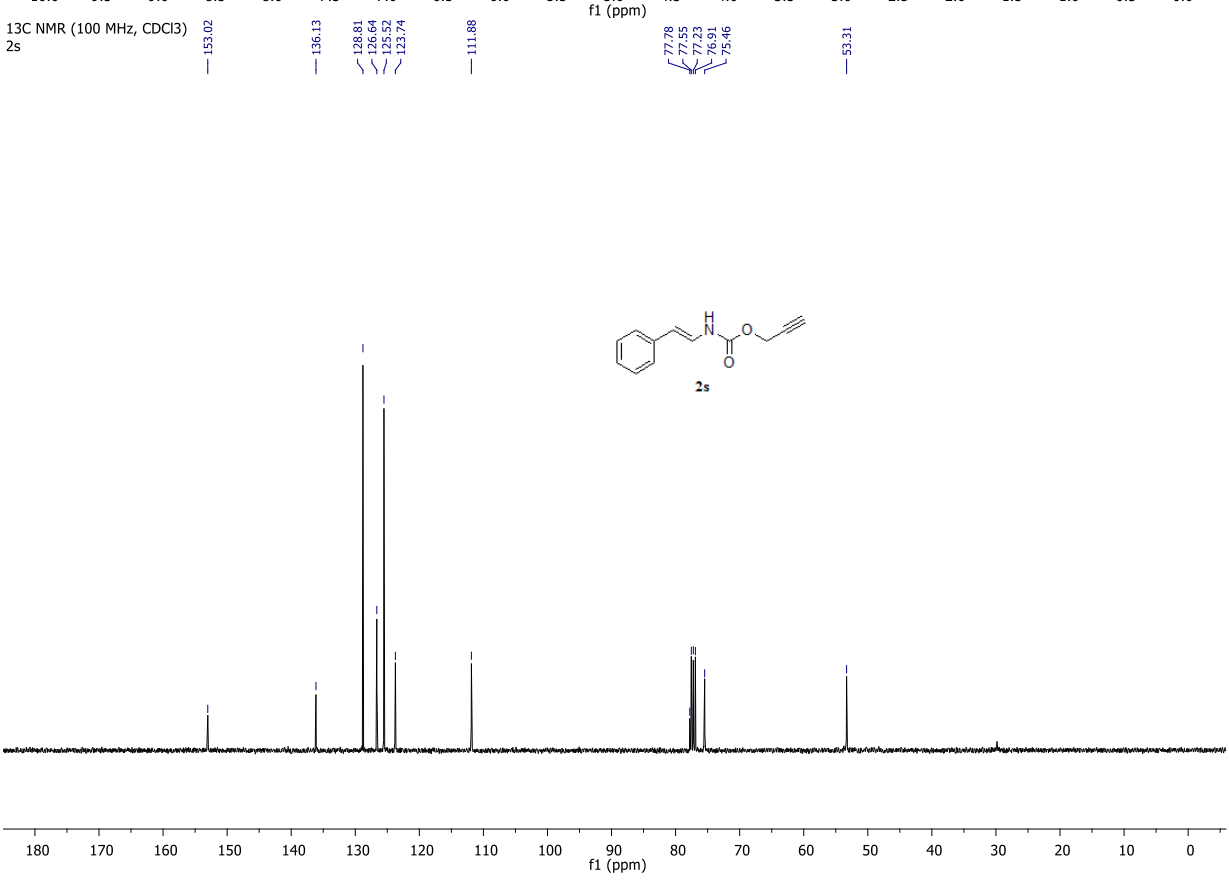

1H NMR (600MHz, CDCl3)
2q
7.303
7.296
7.260
7.189
7.183
7.175
7.168
7.161
6.490
5.956
5.932
1.535
2q
4.91
1.09
0.91
1.00
8.82
f1 (ppm)

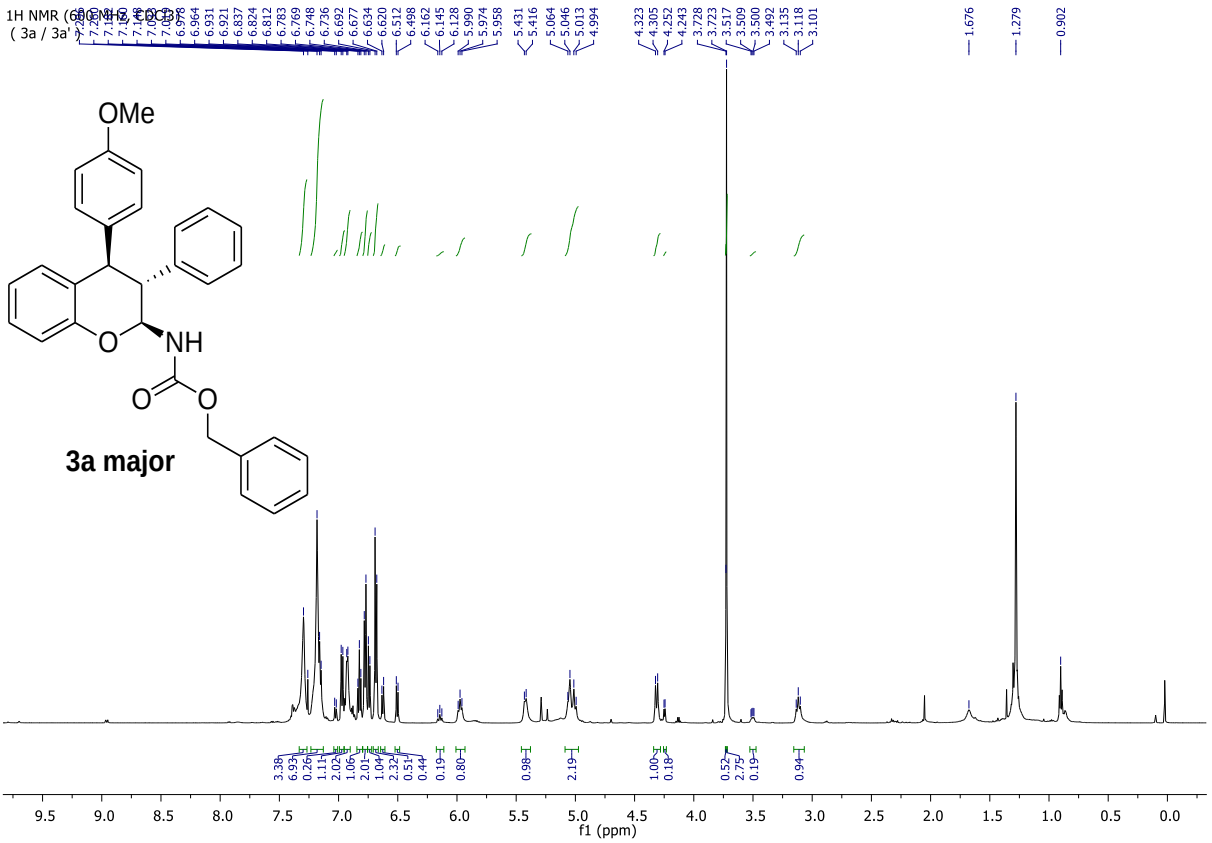

SN-CGBOCEN-13C(SR) 500
152.81
136.73
128.76
126.23
125.33
124.83
124.46
114.21
109.87
81.06
77.42
77.16
76.91
32.08
30.19
29.85
29.51
28.43
28.15
22.84
14.24
2q
NAME SN-CGBOCEN-13C
EXPNO 1
PROCNO 1
Date_ 20170319
Time 3.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 5000
DS 4
SWH 29761.904 Hz
FIDRES 0.908261 Hz
AQ 0.5505524 sec
RG 32
DW 16.800 usec
DE 6.50 usec
TE 301.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.88 usec
PL1 0.50 dB
PL1W 82.16106415 W
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 15.34 dB
PL13 20.00 dB
PL2W 15.50318813 W
PL12W 0.57071728 W
PL13W 0.19517358 W
SFO2 500.1320005 MHz
SI 16384
SF 125.7577680 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

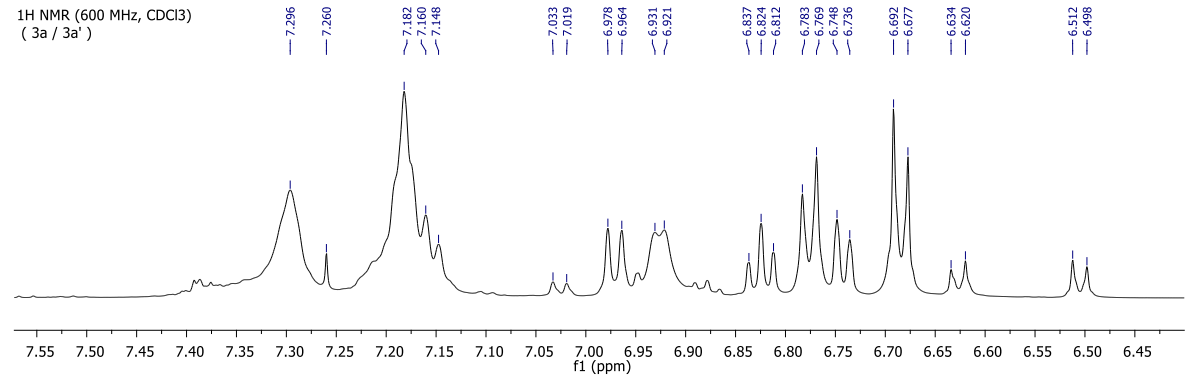

1H NMR (600MHz, CDCl3)
2r
7.284
7.278
7.276
7.260
7.230
7.177
7.171
7.162
7.156
7.148
6.637
6.623
5.997
5.973
5.365
5.337
5.273
5.256
4.662
4.654
2r
4.96
0.76
1.14
1.00
1.11
1.10
1.06
1.83
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

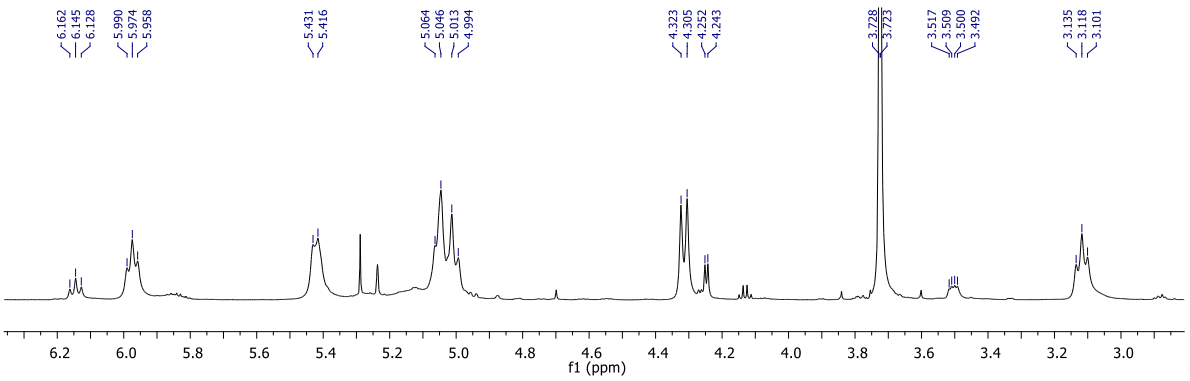

SN-CGAllylEN-13C(SR) 500
153.45
136.23
132.52
132.24
129.37
128.63
126.34
125.31
124.02
118.38
117.91
110.93
77.28
77.02
76.77
66.23
29.69
22.84
14.23
2r
NAME SN-CGAllylEN-13C
EXPNO 1
PROCNO 1
Date_ 20170318
Time 23.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 5000
DS 4
SWH 29761.904 Hz
FIDRES 0.908261 Hz
AQ 0.5505524 sec
RG 32
DW 16.800 usec
DE 6.50 usec
TE 301.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.88 usec
PL1 0.50 dB
PL1W 82.16106415 W
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 15.34 dB
PL13 20.00 dB
PL2W 15.50318813 W
PL12W 0.57071728 W
PL13W 0.19517358 W
SFO2 500.1320005 MHz
SI 16384
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

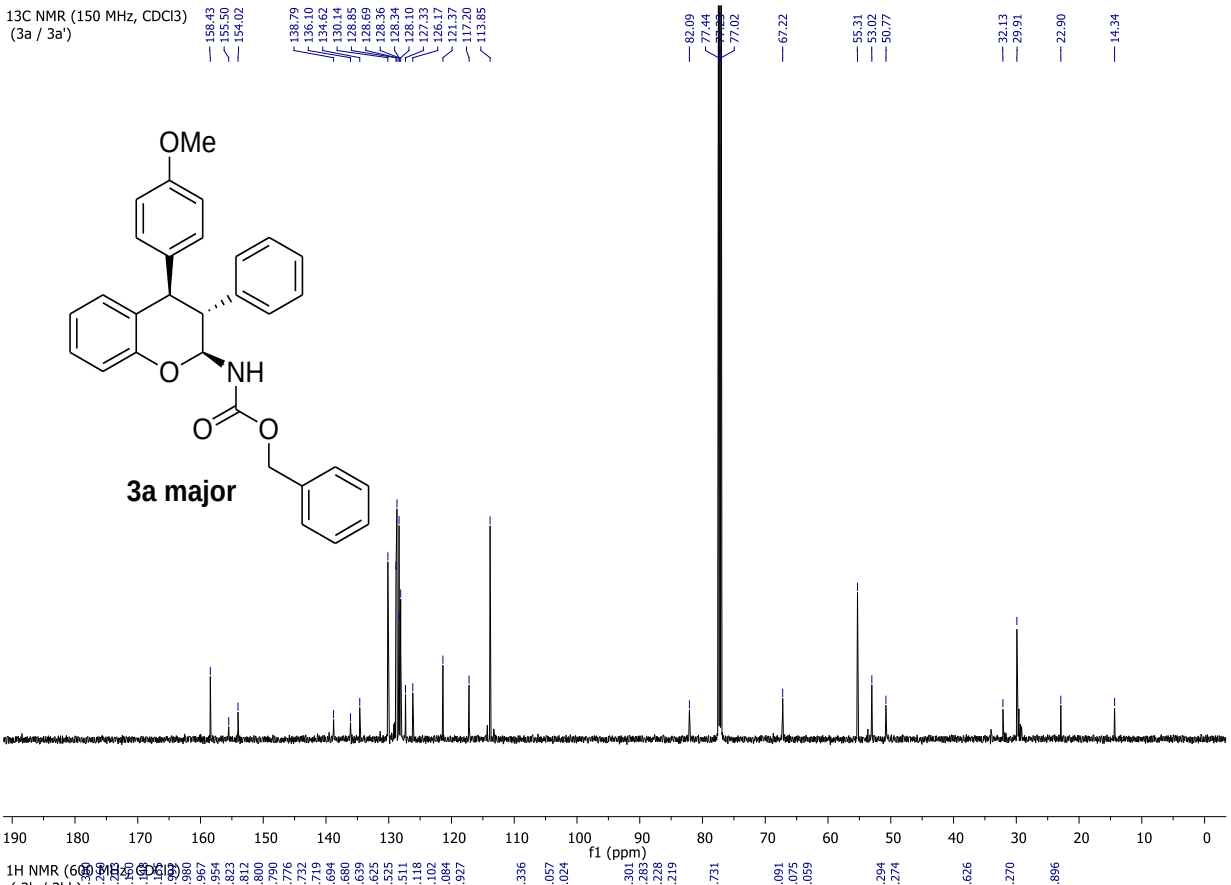

1H NMR (400MHz, CDCl3)
2s
7.293
7.284
7.260
7.230
7.223
7.193
6.967
6.050
6.014
4.784
2.534
2s
3.94
0.60
1.07
0.91
1.00
1.87
0.81
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

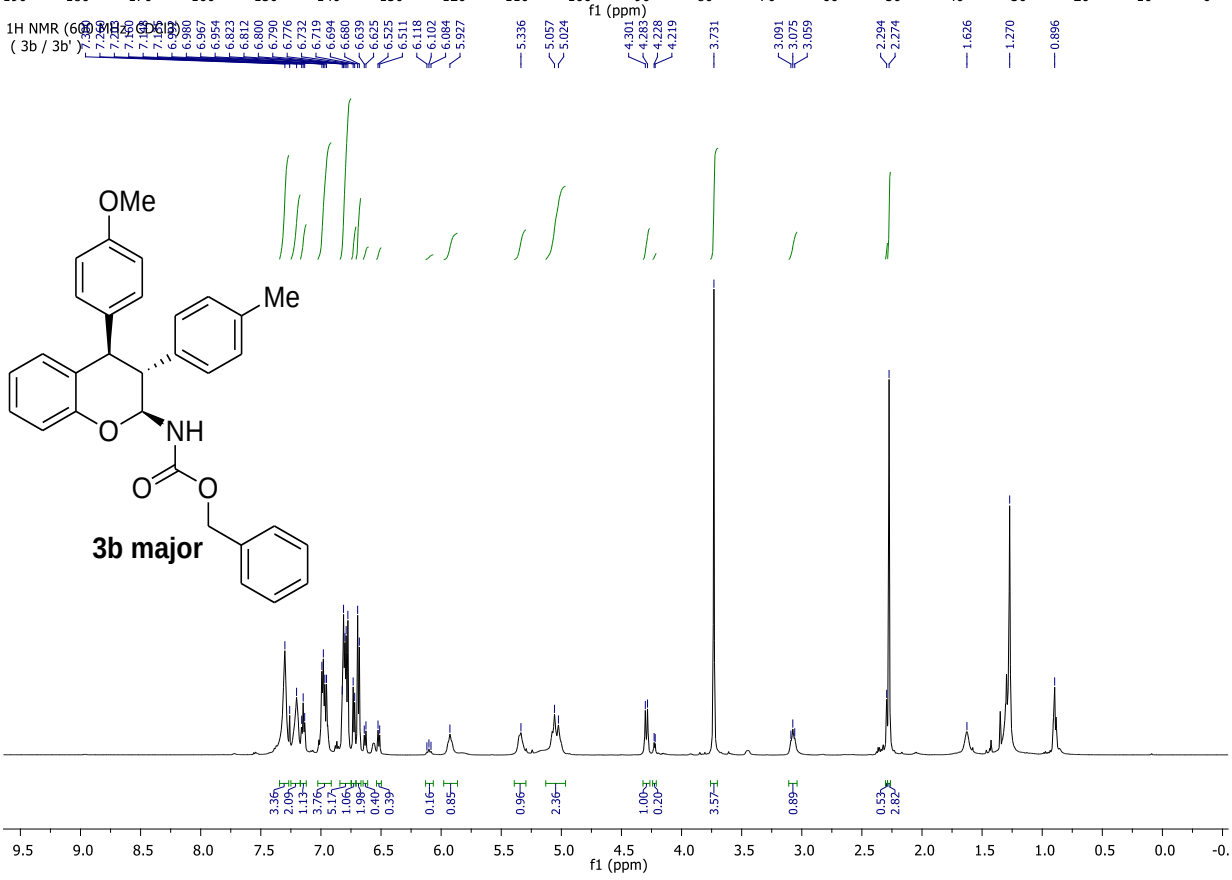

13C NMR (100 MHz, CDCl3)
2s
153.02
136.13
128.81
126.64
125.52
123.74
111.88
77.78
77.55
77.23
76.91
75.46
53.31
2s
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

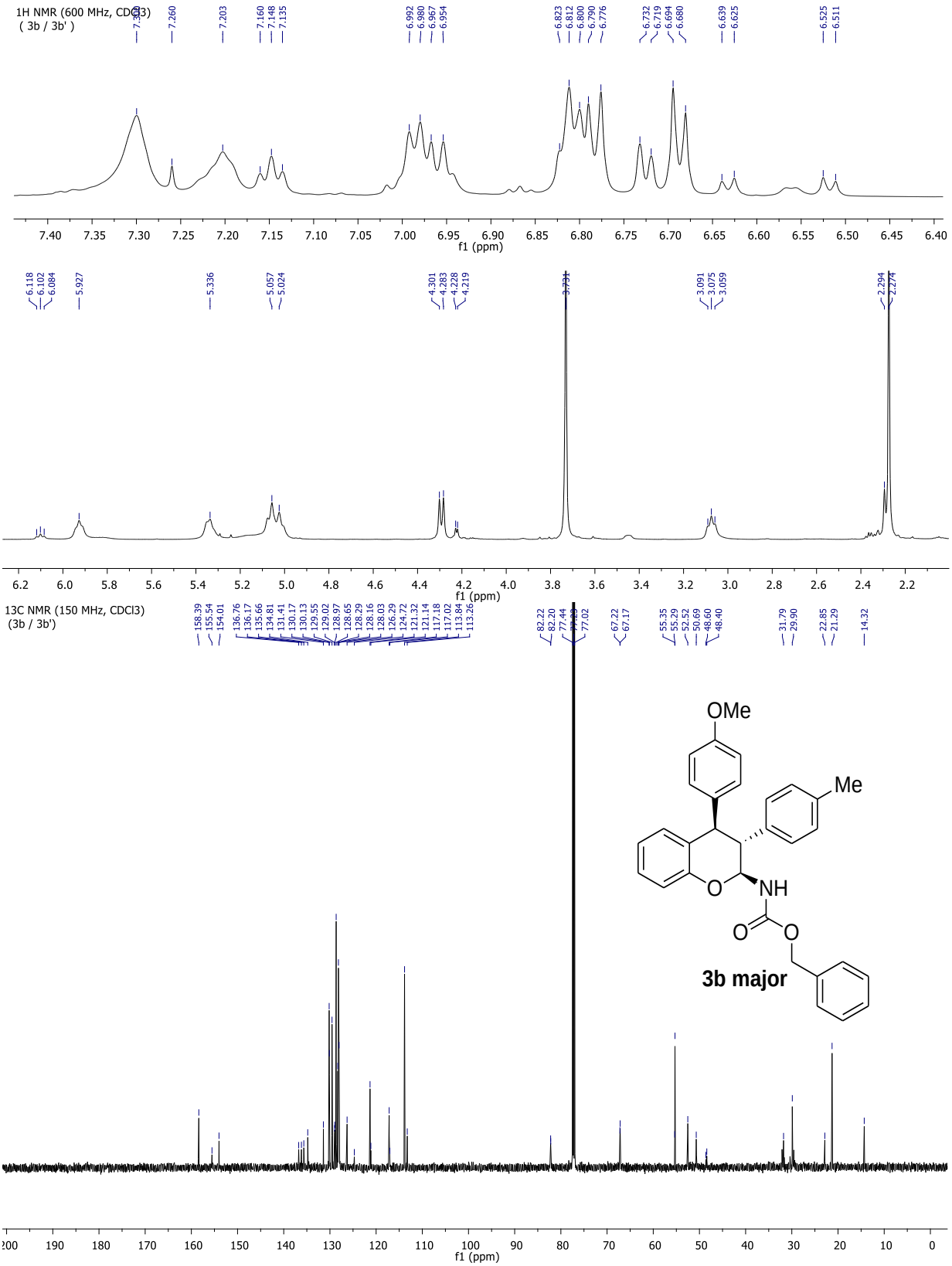

1H NMR (600 MHz, CDCl3)
(3a / 3a')
OMe
O
NH
O
O
3a major
f1 (ppm)

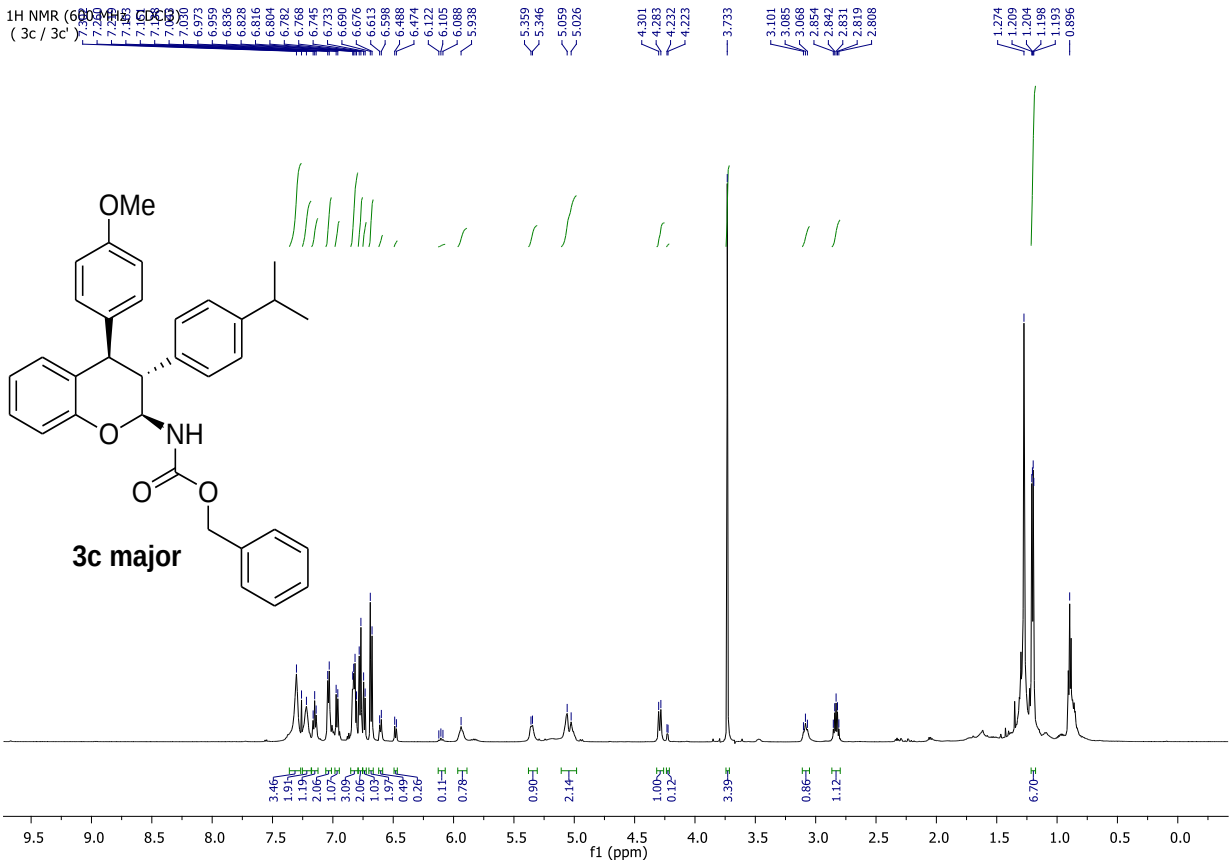

1H NMR (600 MHz, CDCl3)
(3a / 3a')
f1 (ppm)

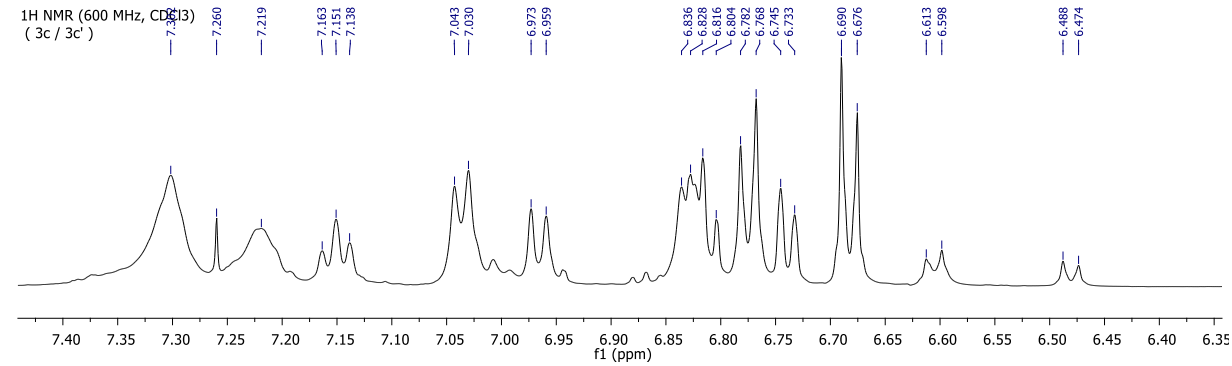

f1 (ppm)

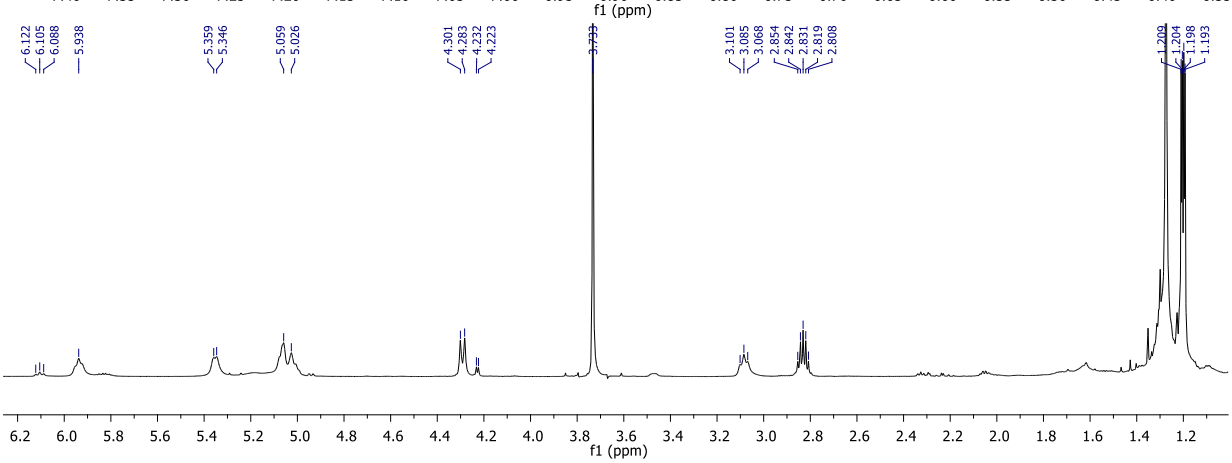

13C NMR (150 MHz, CDCl3)
(3a / 3a')
158.43
155.50
154.02
138.79
136.10
134.62
130.14
128.85
128.69
128.36
128.34
128.10
127.33
126.17
121.37
117.20
113.85
82.09
77.44
77.02
67.22
55.31
53.02
50.77
32.13
29.91
22.90
14.34
OMe
NH
O
O
O
3a major
f1 (ppm)

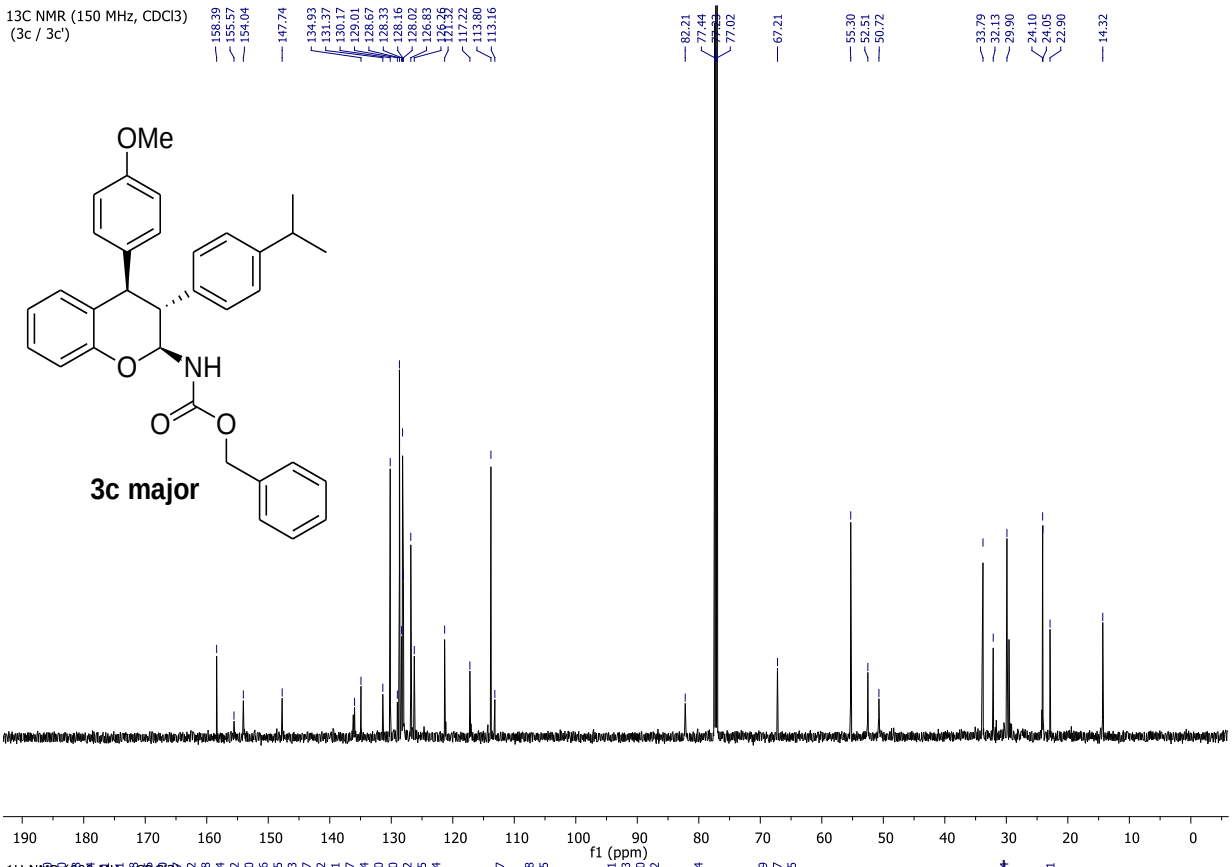

1H NMR (600 MHz, CDCl3)
(3b / 3b')
5.336
5.057
5.024
4.301
4.283
4.228
4.219
3.731
3.091
3.075
3.059
2.294
2.274
1.626
1.270
0.896
OMe
Me
NH
O
O
O
3b major
3.36
2.09
1.13
3.76
5.17
1.06
1.98
0.40
0.39
0.16
0.85
0.96
2.36
1.00
0.20
3.57
0.89
0.53
2.82
f1 (ppm)

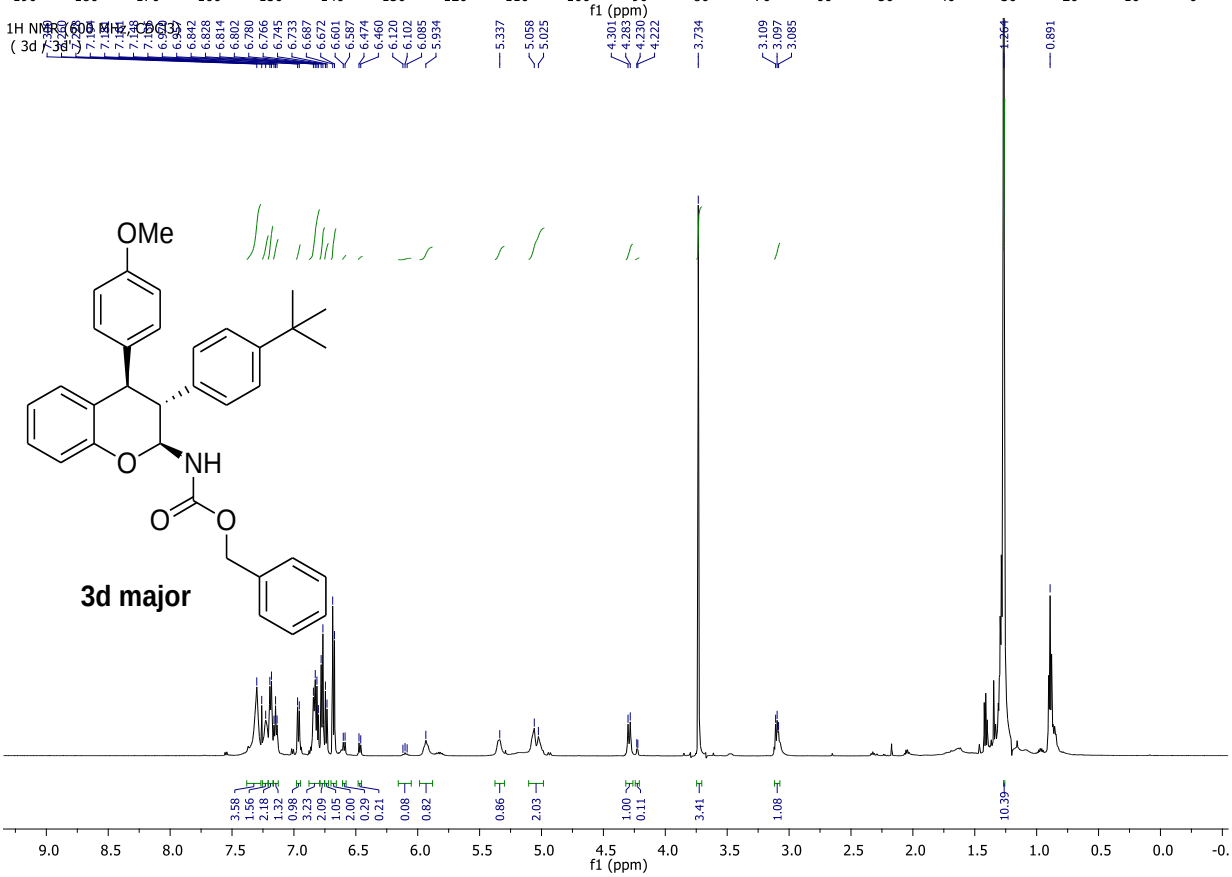

1H NMR (600 MHz, CDCl3)
(3b / 3b')
7.260
7.203
7.160
7.148
7.135
6.992
6.980
6.967
6.954
6.823
6.812
6.800
6.790
6.776
6.732
6.719
6.694
6.680
6.639
6.625
6.525
6.511
f1 (ppm)
6.118
6.102
6.084
5.927
5.336
5.057
5.024
4.301
4.283
4.228
4.219
3.731
3.091
3.075
3.059
2.294
2.274
13C NMR (150 MHz, CDCl3)
(3b / 3b')
158.39
155.54
154.01
136.76
136.17
135.66
134.81
131.41
130.17
130.13
129.55
129.02
128.97
128.65
128.29
128.16
128.03
126.29
124.72
121.32
121.14
117.18
117.02
113.84
113.26
82.22
82.20
77.44
77.23
77.02
67.22
67.17
55.35
55.29
52.52
50.69
48.60
48.40
31.79
29.90
22.85
21.29
14.32
OMe
Me
O
NH
O
O
3b major

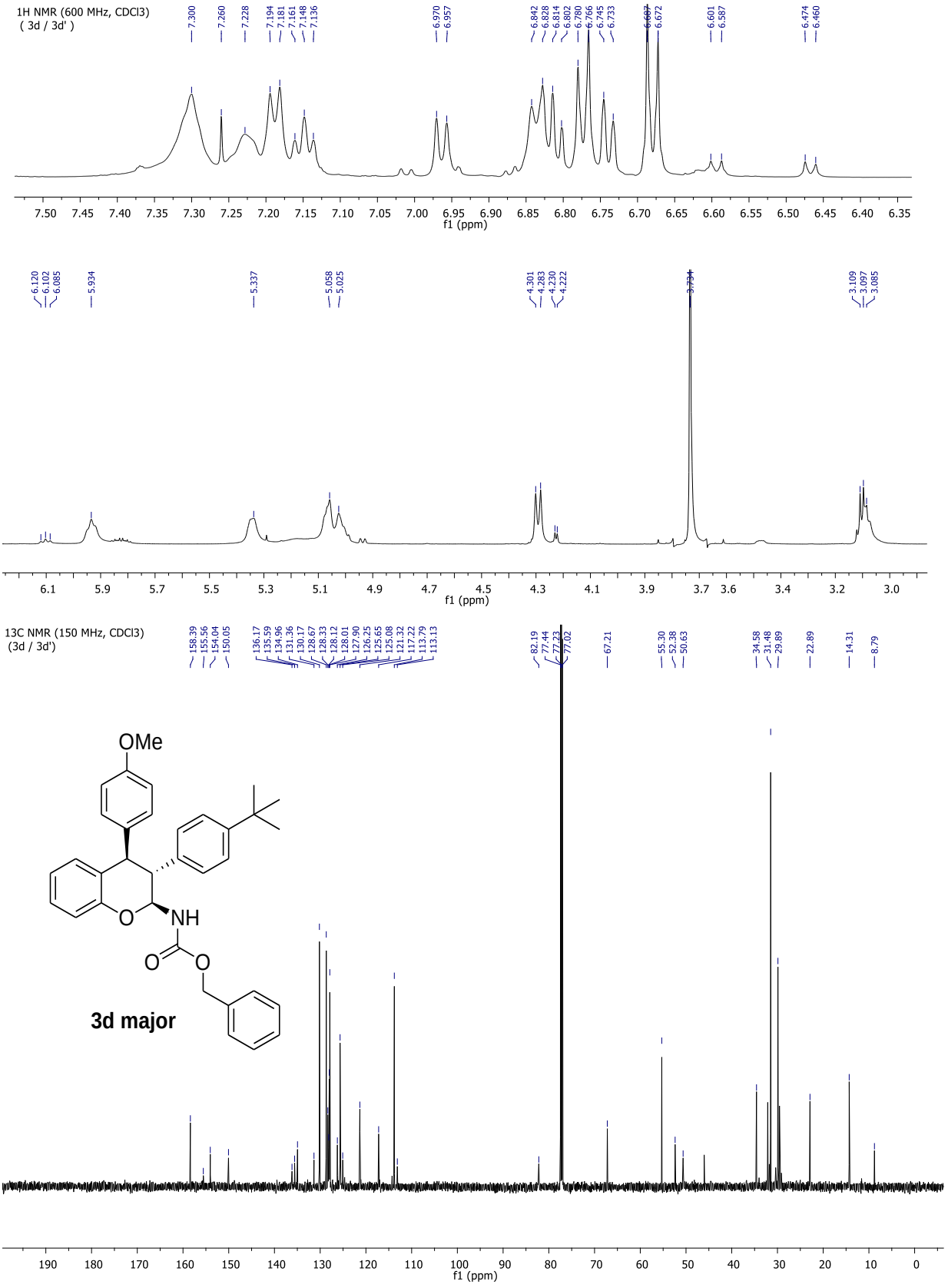

1H NMR (600 MHz, CDCl3)
(3c / 3c')
OMe
O
NH
O
O
3c major
f1 (ppm)

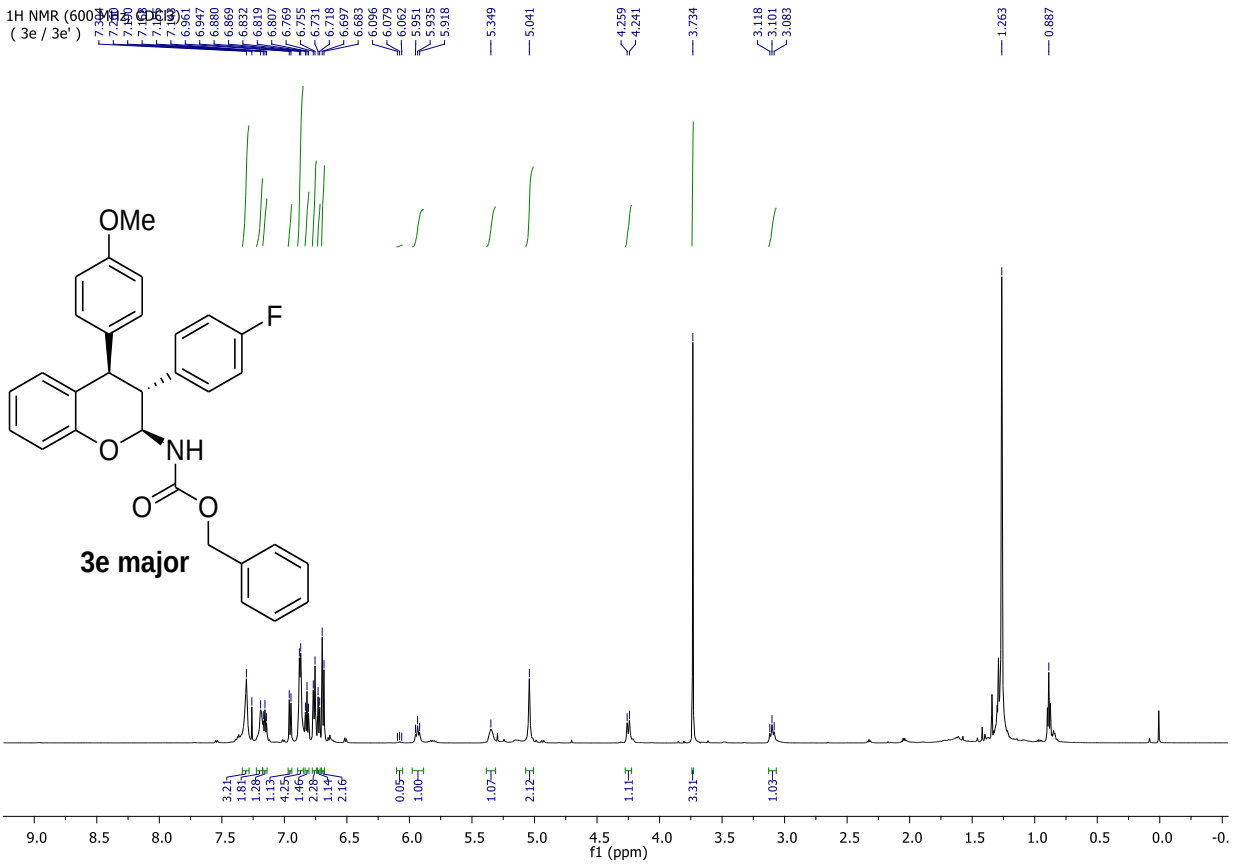

1H NMR (600 MHz, CDCl3)
(3c / 3c')
f1 (ppm)

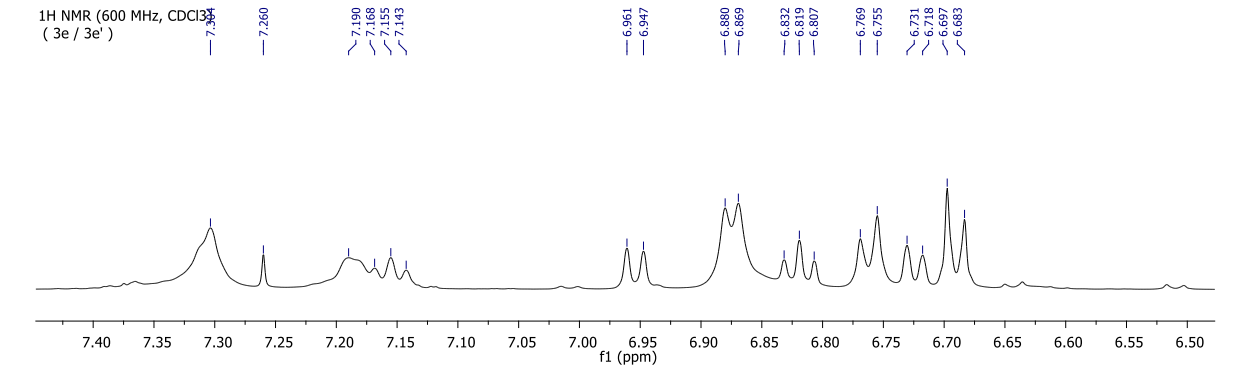

f1 (ppm)

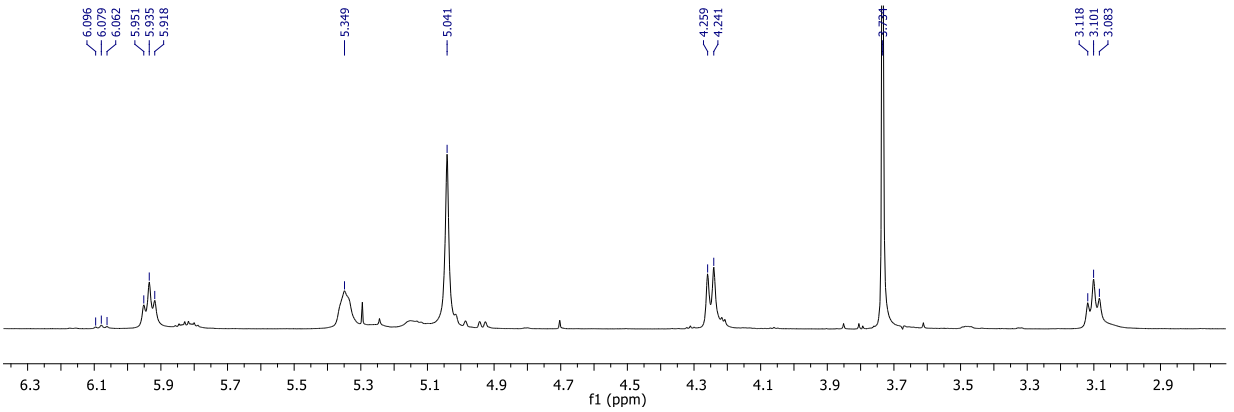

13C NMR (150 MHz, CDCl3)
(3c / 3c')
158.39
155.57
154.04
147.74
134.93
131.37
130.17
129.01
128.67
128.33
128.16
128.02
126.83
117.22
113.80
113.16
82.21
77.44
77.23
77.02
67.21
55.30
52.51
50.72
33.79
32.13
29.90
24.10
24.05
22.90
14.32
OMe
NH
O
O
O
3c major
f1 (ppm)

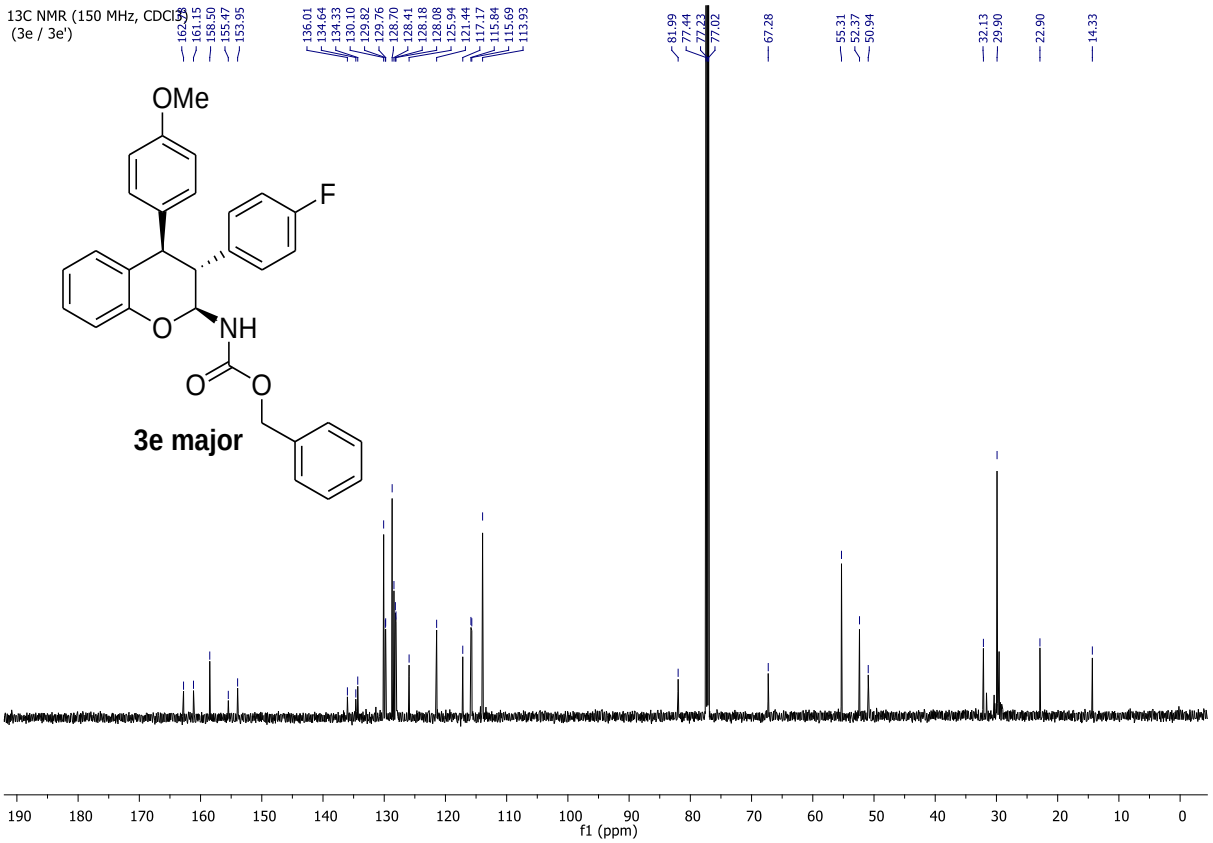

1H NMR (600 MHz, CDCl3)
(3d / 3d')
5.337
5.058
5.025
4.301
4.283
4.230
4.222
3.734
3.109
3.097
3.085
1.264
0.891
OMe
NH
O
O
O
3d major
3.58
1.56
2.18
1.32
0.98
3.23
2.09
1.05
2.00
0.29
0.21
0.08
0.82
0.86
2.03
1.00
0.11
3.41
1.08
10.39
f1 (ppm)

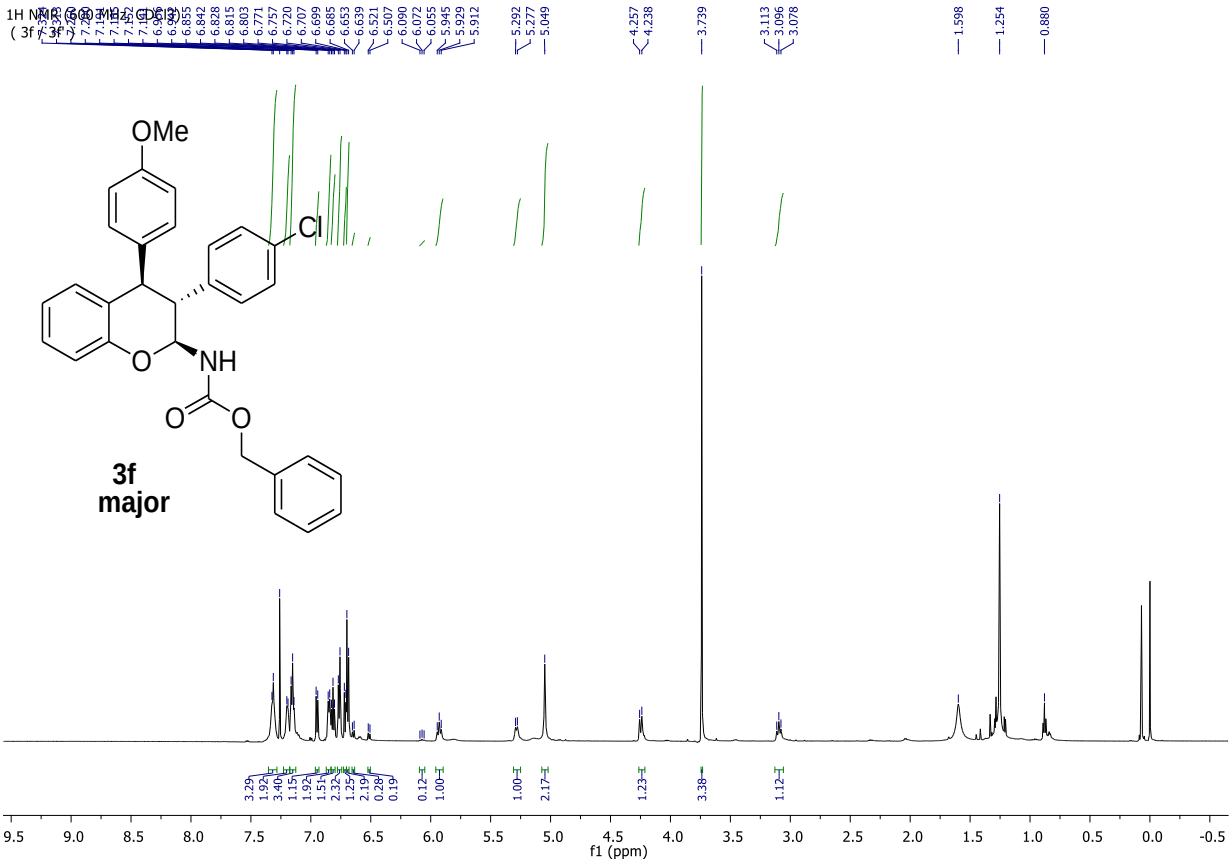

1H NMR (600 MHz, CDCl3)
(3d / 3d')
7.300
7.260
7.228
7.194
7.181
7.161
7.148
7.136
6.970
6.957
6.842
6.828
6.814
6.802
6.780
6.766
6.745
6.733
6.687
6.672
6.601
6.587
6.474
6.460
f1 (ppm)
6.120
6.102
6.085
5.934
5.337
5.058
5.025
4.301
4.283
4.230
4.222
3.734
3.109
3.097
3.085
f1 (ppm)
13C NMR (150 MHz, CDCl3)
(3d / 3d')
158.39
155.56
154.04
150.05
136.17
135.59
134.96
131.36
130.17
128.67
128.33
128.12
128.01
127.90
126.25
125.65
125.08
121.32
117.22
113.79
113.13
82.19
77.44
77.23
77.02
67.21
55.30
52.38
50.63
34.58
31.48
29.89
22.89
14.31
8.79
OMe
O
NH
O
O
3d major
f1 (ppm)

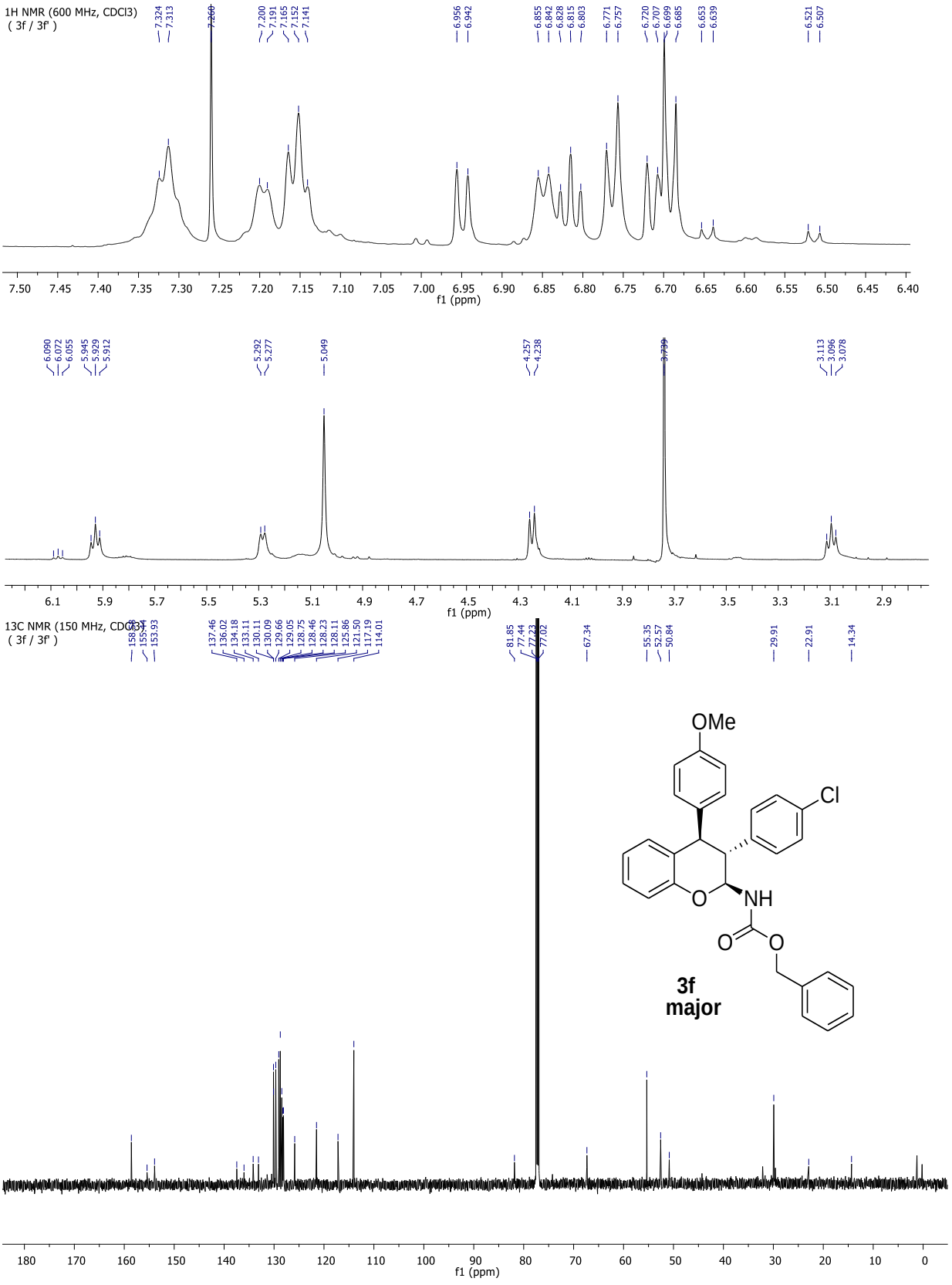

1H NMR (600 MHz, CDCl3)
(3e / 3e')
OMe
F
O
NH
O
O
3e major
f1 (ppm)

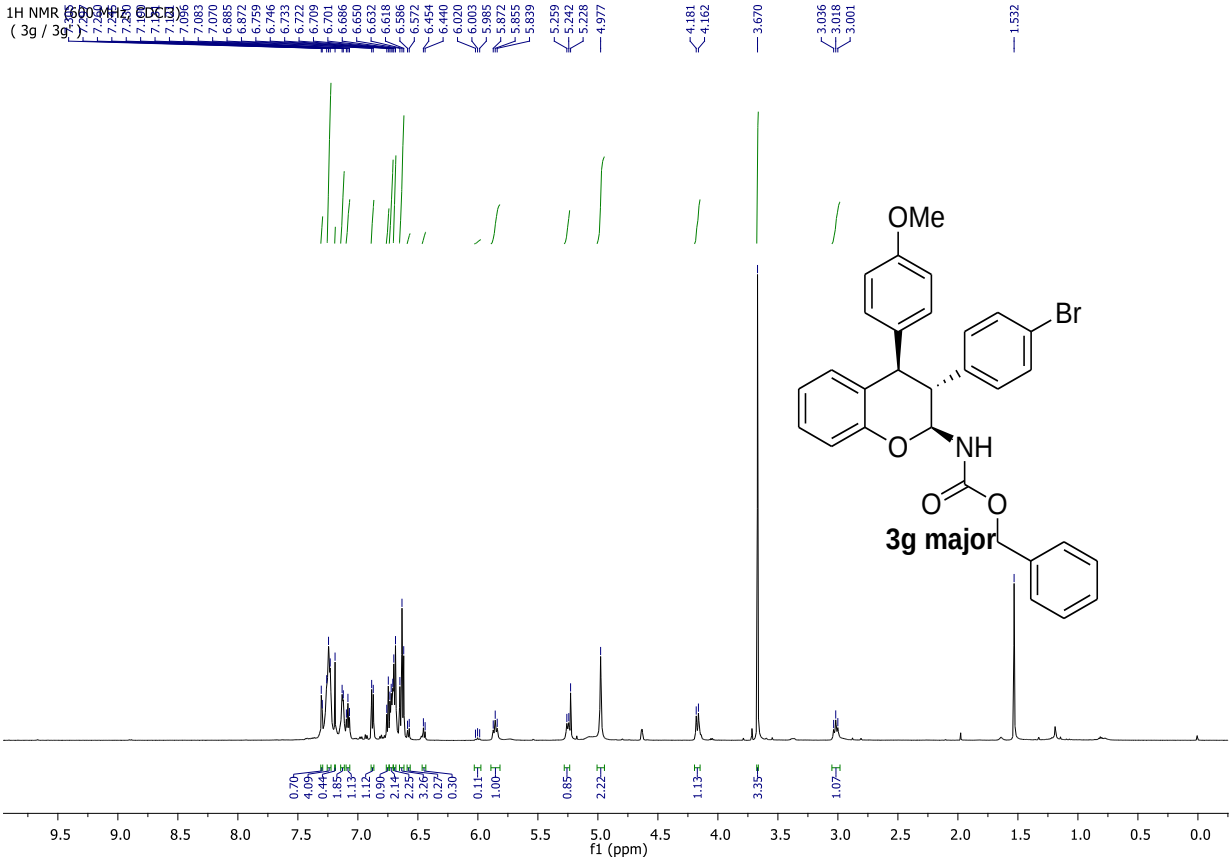

1H NMR (600 MHz, CDCl3)
(3e / 3e')
f1 (ppm)

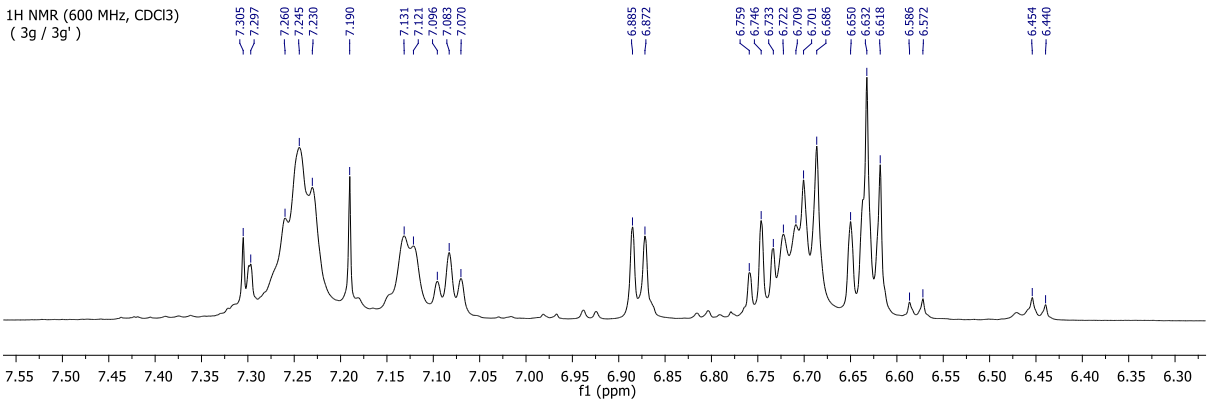

f1 (ppm)

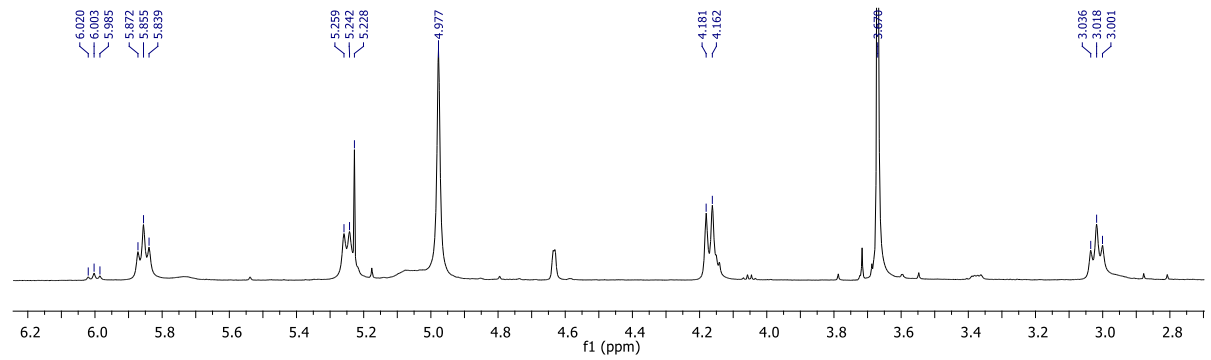

13C NMR (150 MHz, CDCl3)
(3e / 3e')
OMe
F
O
NH
O
O
3e major
f1 (ppm)

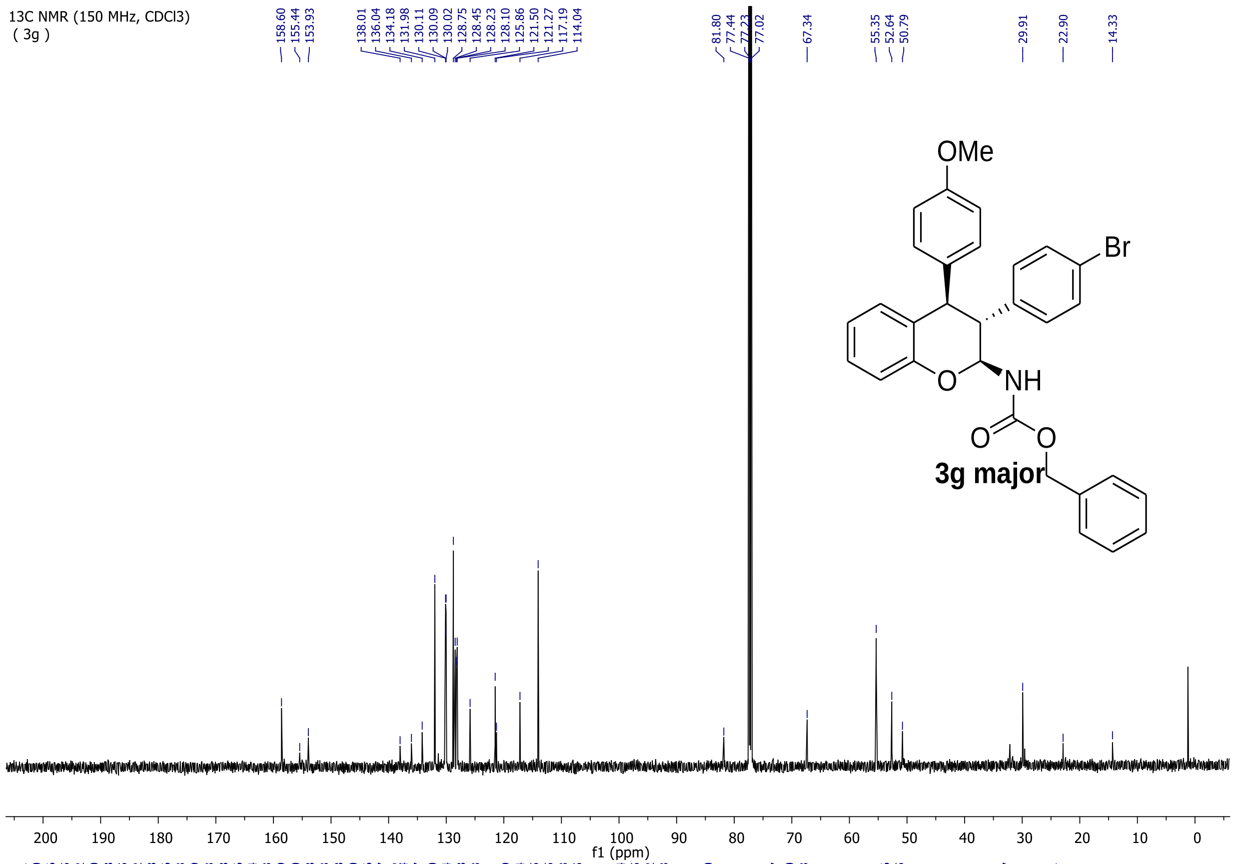

1H NMR (600 MHz, CDCl3)
(3f / 3f')
OMe
Cl
O
NH
O
O
3f
major
f1 (ppm)

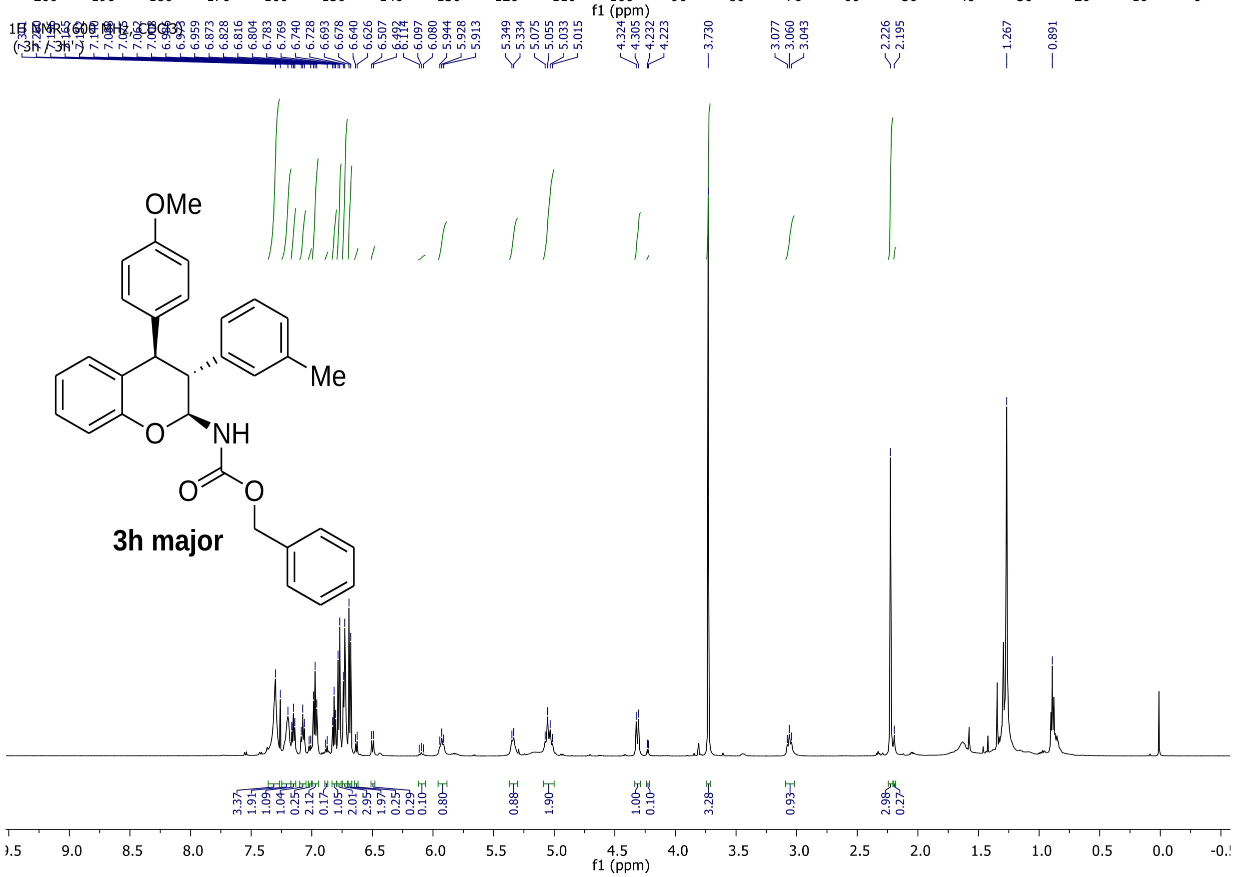

1H NMR (600 MHz, CDCl3)
(3f / 3f')
7.324
7.313
7.266
7.200
7.191
7.165
7.152
7.141
6.956
6.942
6.855
6.842
6.828
6.815
6.803
6.771
6.757
6.720
6.707
6.699
6.685
6.653
6.639
6.521
6.507
f1 (ppm)
6.090
6.072
6.055
5.945
5.929
5.912
5.292
5.277
5.049
4.257
4.238
3.739
3.113
3.096
3.078
f1 (ppm)
13C NMR (150 MHz, CDCl3)
(3f / 3f')
158.84
155.34
153.93
137.46
136.02
134.18
133.11
130.11
130.09
129.66
129.05
128.75
128.46
128.23
128.11
125.86
121.50
117.19
114.01
81.85
77.44
77.23
77.02
67.34
55.35
52.57
50.84
29.91
22.91
14.34
f1 (ppm)
OMe
Cl
O
NH
O
O
3f
major

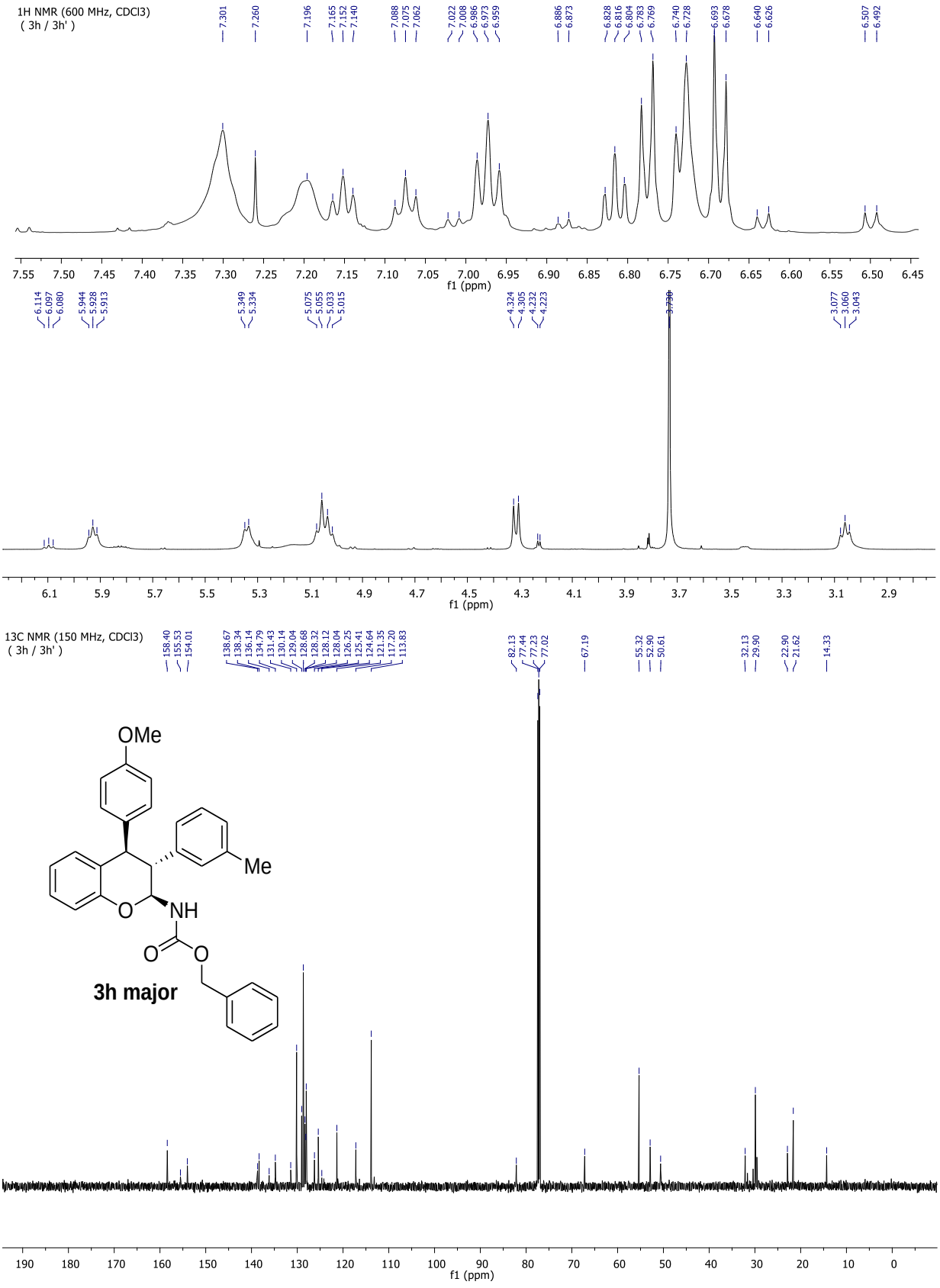

1H NMR (600 MHz, CDCl3)
(3g / 3g')
OMe
Br
O
NH
O
O
3g major
f1 (ppm)

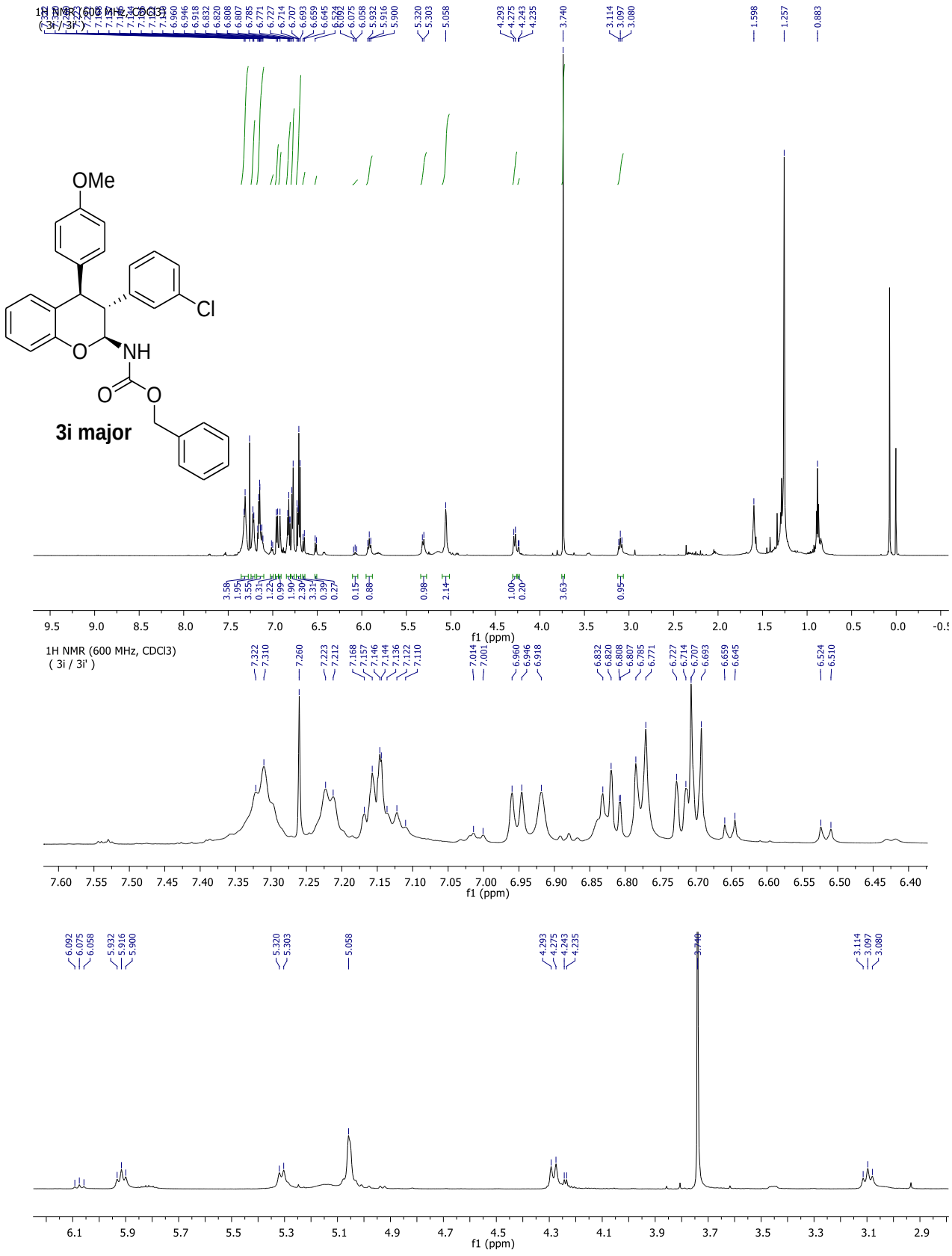

1H NMR (600 MHz, CDCl3)
(3g / 3g')
f1 (ppm)

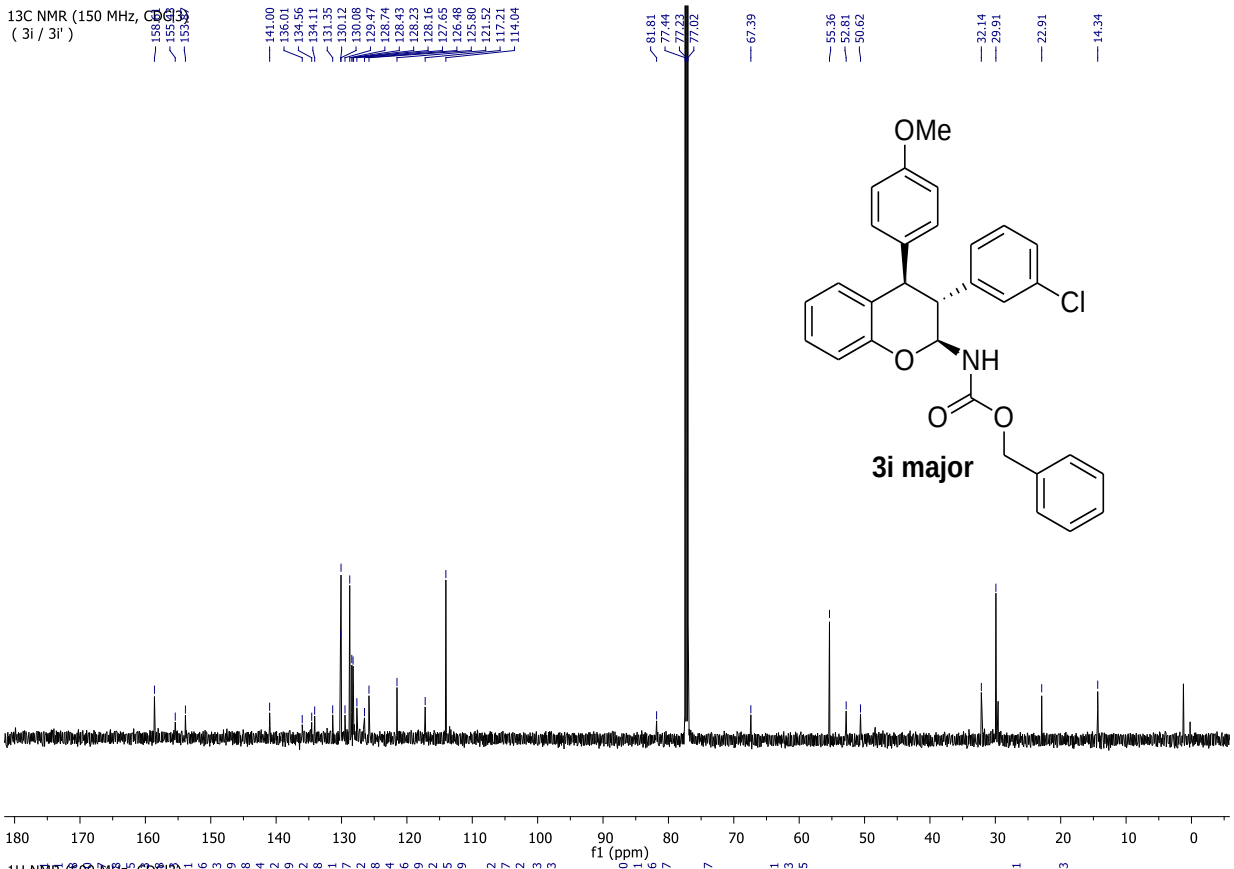

f1 (ppm)

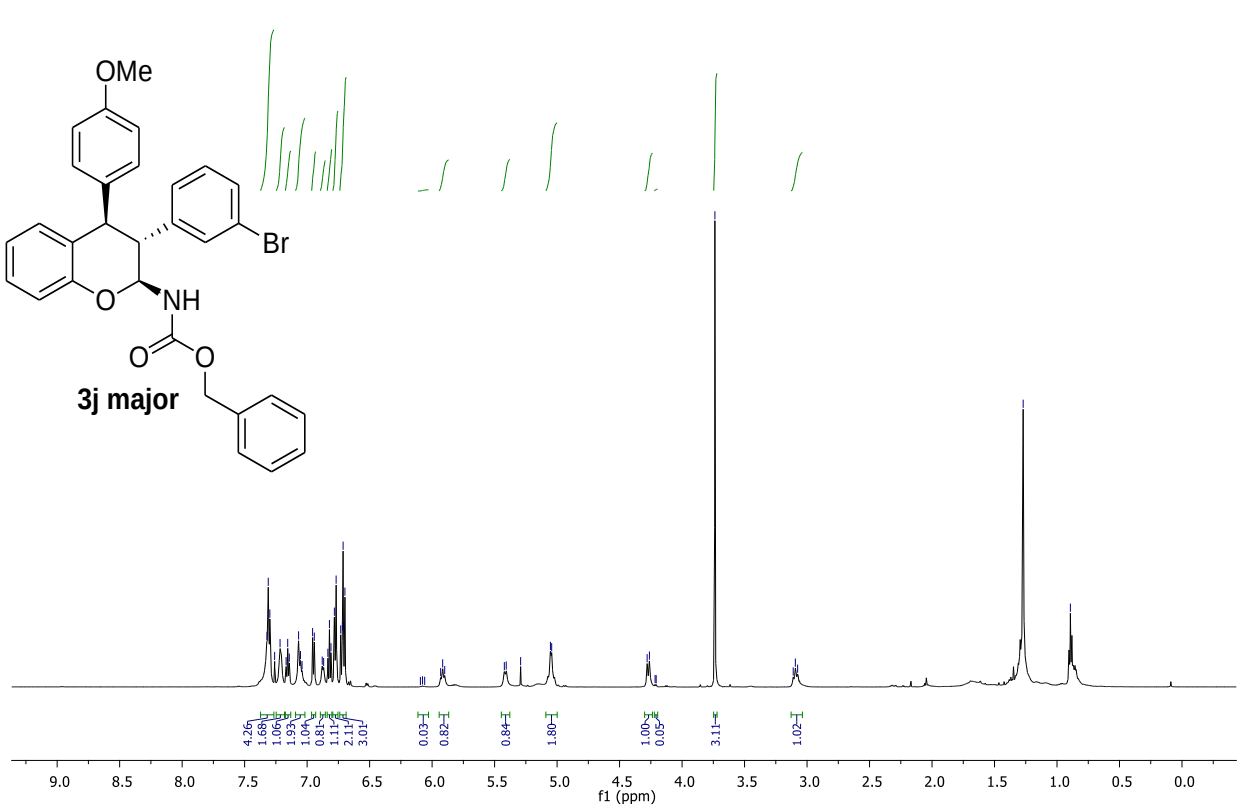

13C NMR (150 MHz, CDCl3)
(3g)
158.60
155.44
153.93
138.01
136.04
134.18
131.98
130.11
130.09
130.02
128.75
128.45
128.23
128.10
125.86
121.50
121.27
117.19
114.04
81.80
77.44
77.23
77.02
67.34
55.35
52.64
50.79
29.91
22.90
14.33
OMe
Br
O
NH
O
O
3g major
f1 (ppm)

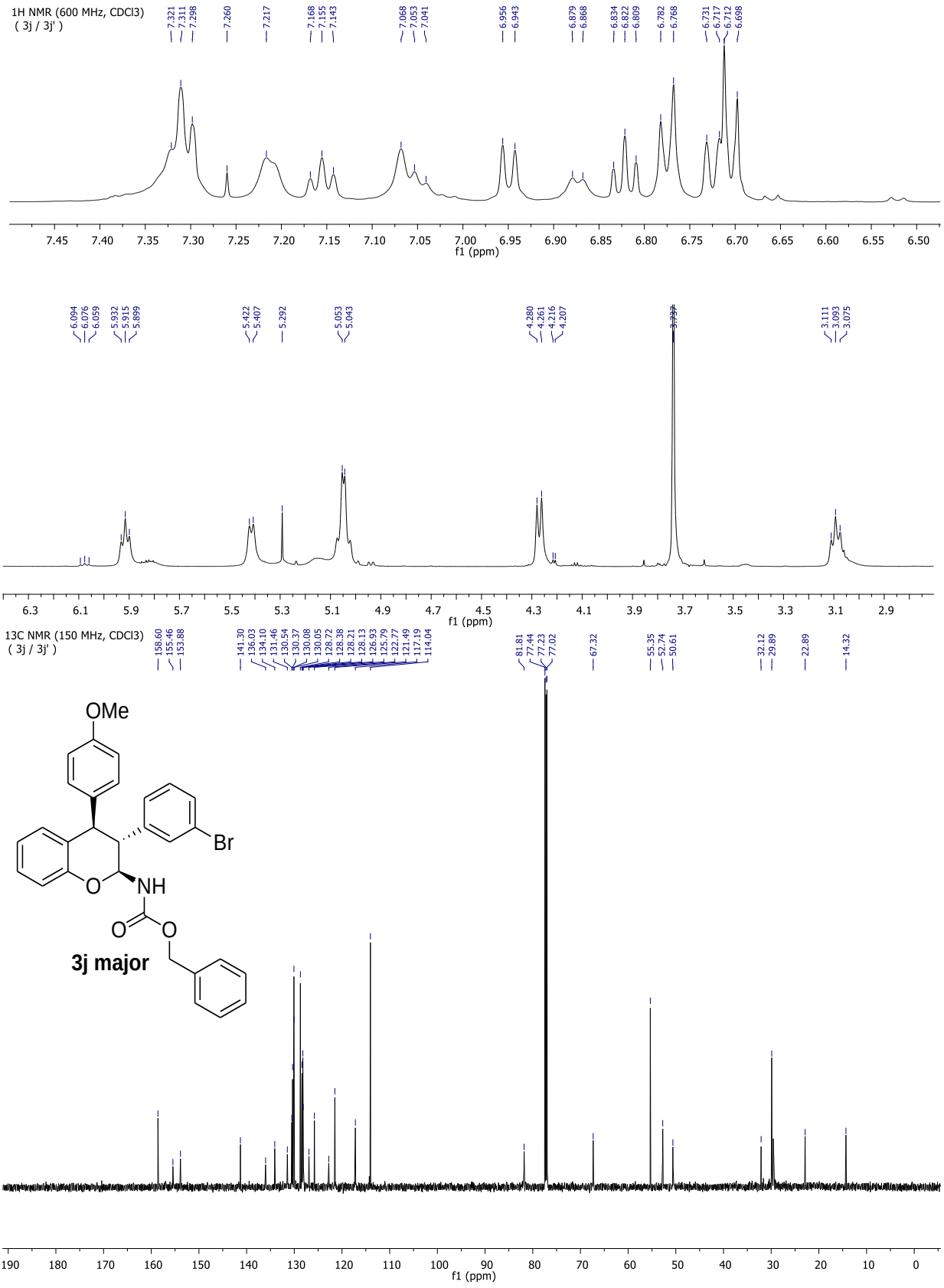

6.959
6.873
6.828
6.816
6.804
6.783
6.769
6.740
6.728
6.693
6.678
6.640
6.626
6.507
6.097
6.080
5.944
5.928
5.913
5.349
5.334
5.075
5.055
5.033
5.015
4.324
4.305
4.232
4.223
3.730
3.077
3.060
3.043
2.226
2.195
1.267
0.891
OMe
Me
O
NH
O
O
3h major
3.37
1.91
1.09
1.04
0.25
2.12
0.17
1.05
2.01
2.95
1.97
0.25
0.29
0.10
0.80
0.88
1.90
1.00
0.10
3.28
0.93
2.98
0.27
f1 (ppm)

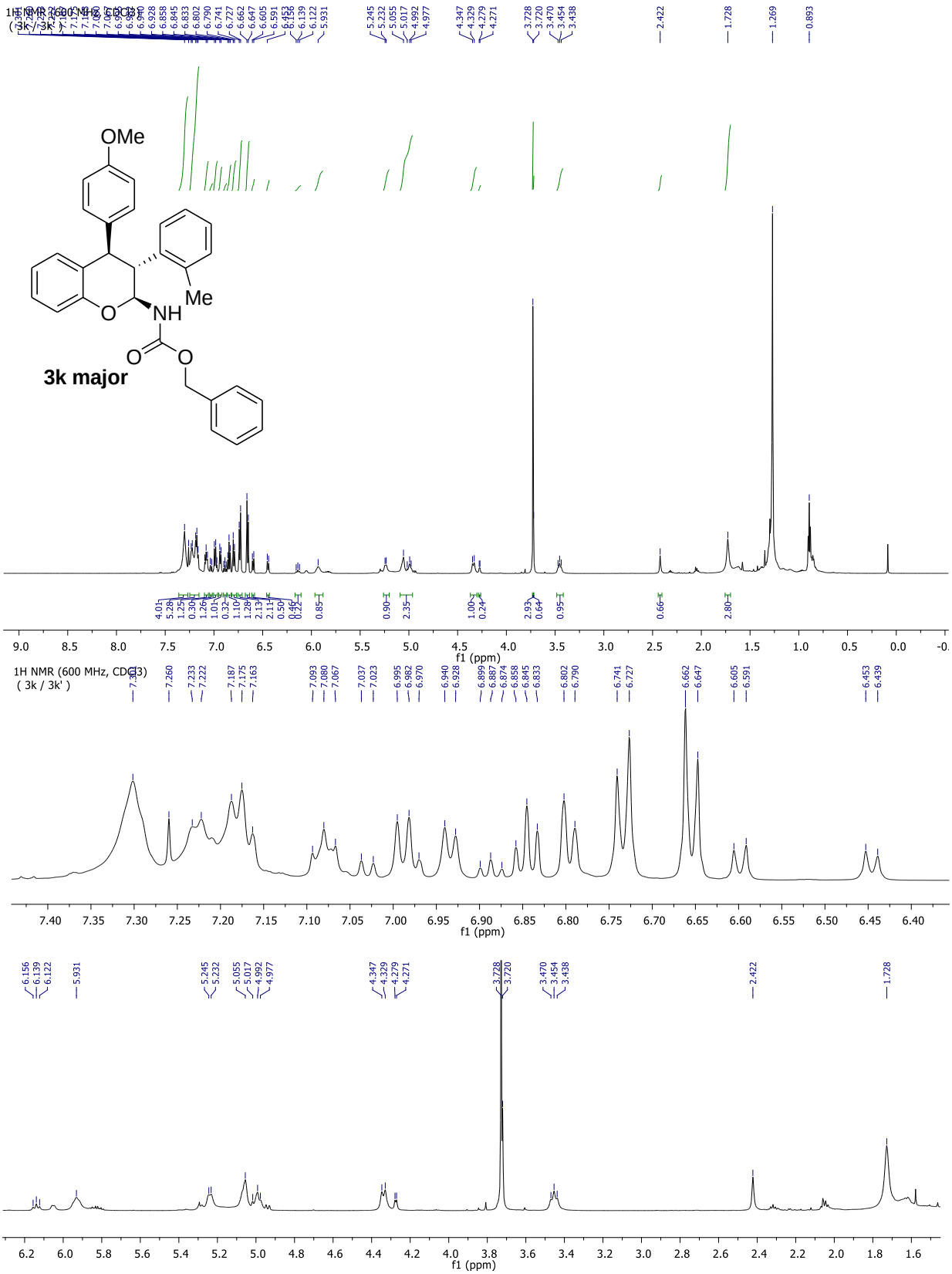

1H NMR (600 MHz, CDCl3)
(3h / 3h')
7.301
7.260
7.196
7.165
7.152
7.140
7.088
7.075
7.062
7.022
7.008
6.986
6.973
6.959
6.886
6.873
6.828
6.816
6.804
6.783
6.769
6.740
6.728
6.693
6.678
6.640
6.626
6.507
6.492
f1 (ppm)
6.114
6.097
6.080
5.944
5.928
5.913
5.349
5.334
5.075
5.055
5.033
5.015
4.324
4.305
4.232
4.223
3.730
3.077
3.060
3.043
f1 (ppm)
13C NMR (150 MHz, CDCl3)
(3h / 3h')
158.40
155.53
154.01
138.67
138.34
136.14
134.79
131.43
130.14
129.04
128.68
128.32
128.12
128.04
126.25
125.41
124.64
121.35
117.20
113.83
82.13
77.44
77.23
77.02
67.19
55.32
52.90
50.61
32.13
29.90
22.90
21.62
14.33
OMe
Me
O
NH
O
O
3h major
f1 (ppm)

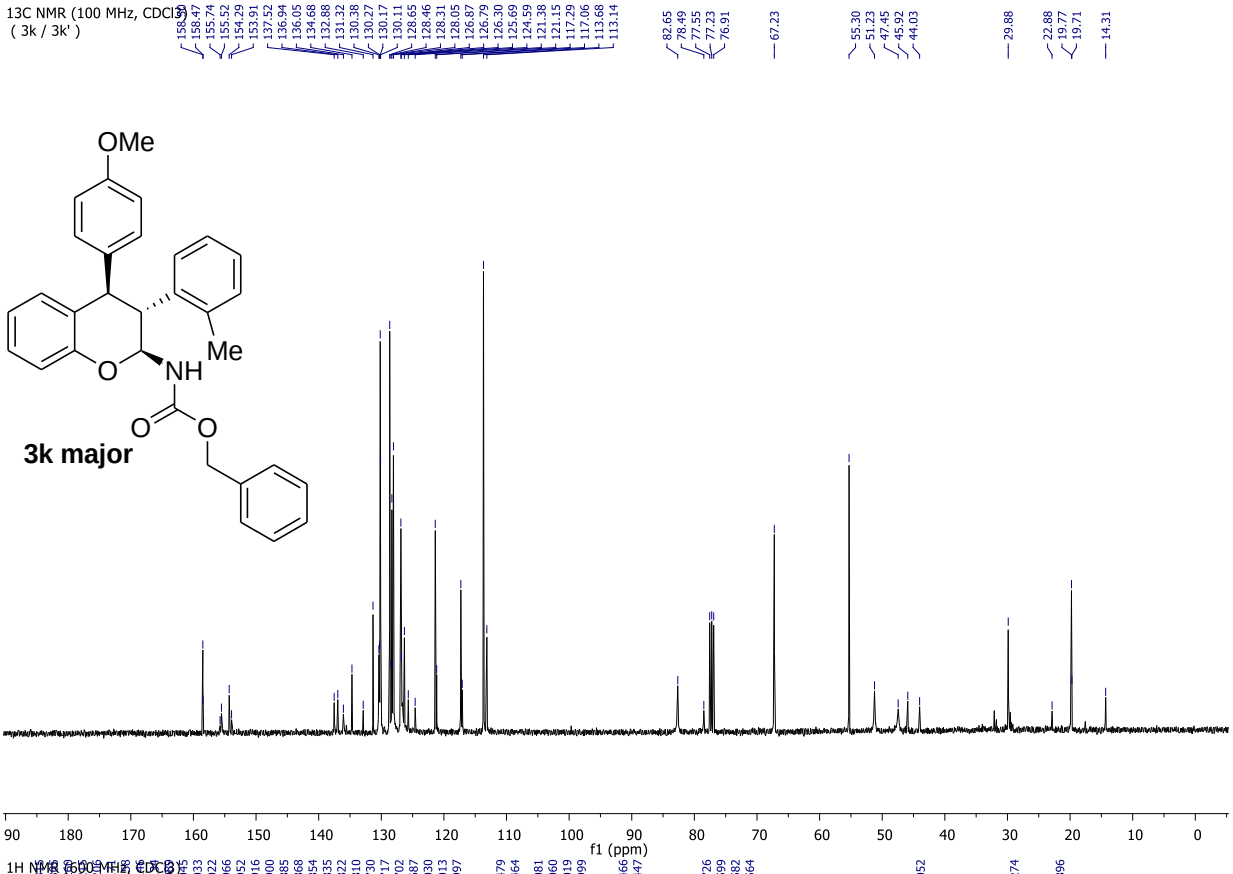

1H NMR (600 MHz, CDCl3)
(3i / 3i')
OMe
Cl
O
NH
O
O
3i major
f1 (ppm)

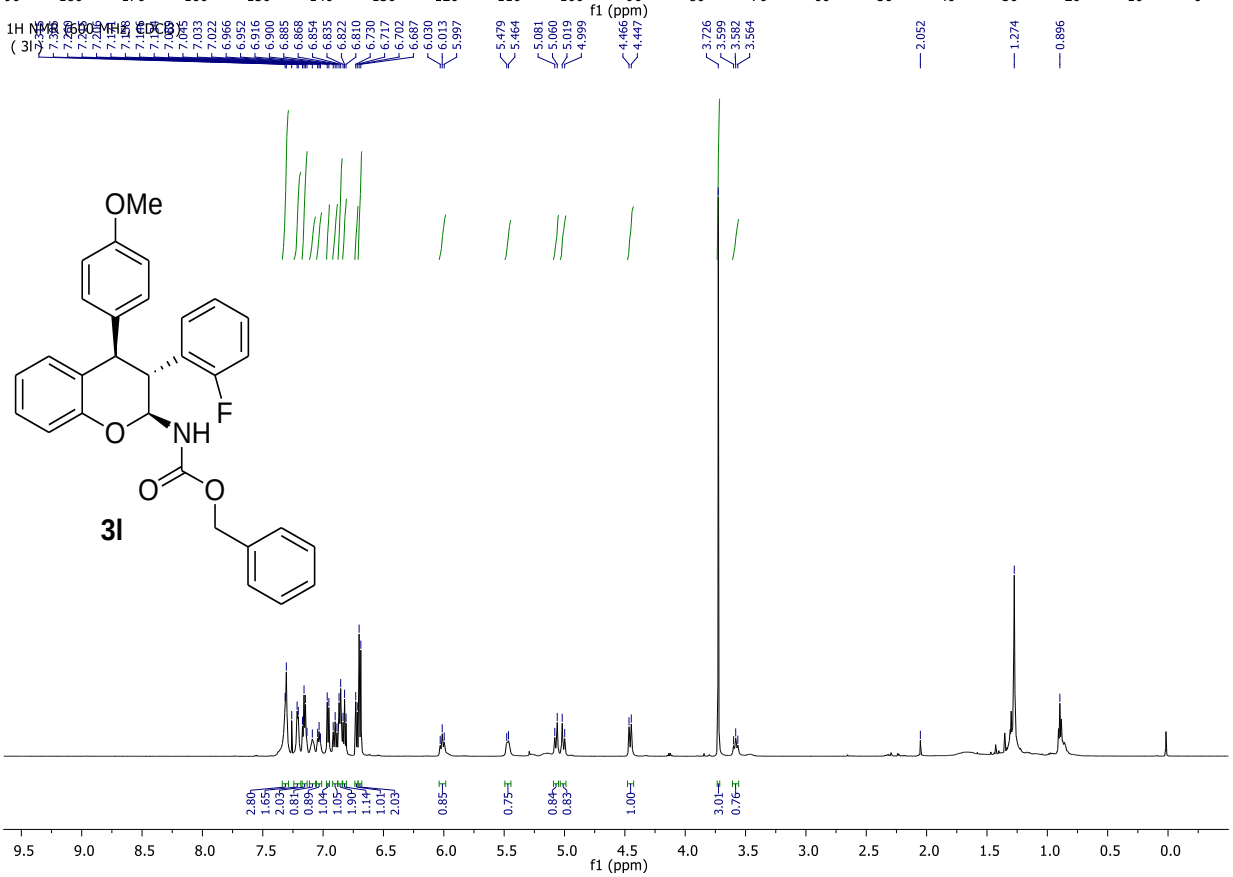

13C NMR (150 MHz, CDCl3)
(3i / 3i')
OMe
Cl
O
NH
O
O
3i major
f1 (ppm)

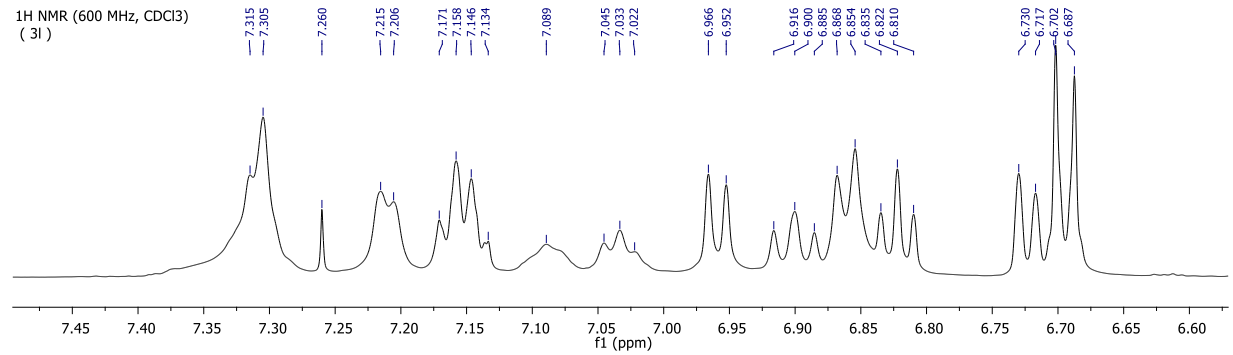

1H NMR (600 MHz, CDCl3)
(3j / 3j')
OMe
Br
O
NH
O
O
3j major
f1 (ppm)

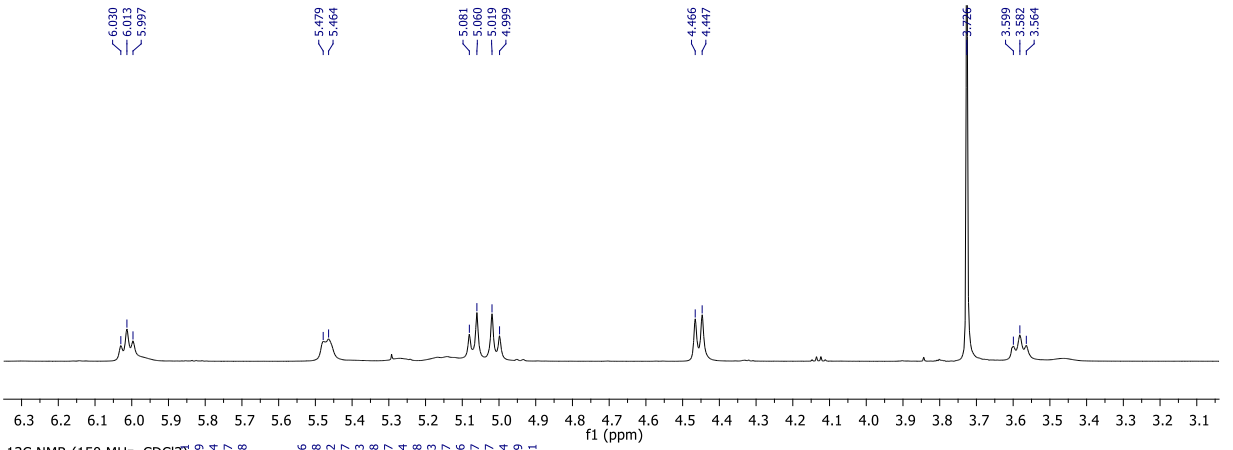

1H NMR (600 MHz, CDCl3)
(3j / 3j')
7.321
7.311
7.298
7.260
7.217
7.168
7.155
7.143
7.068
7.053
7.041
6.956
6.943
6.879
6.868
6.834
6.822
6.809
6.782
6.768
6.731
6.717
6.712
6.698
f1 (ppm)
6.094
6.076
6.059
5.932
5.915
5.899
5.422
5.407
5.292
5.053
5.043
4.280
4.261
4.216
4.207
3.737
3.111
3.093
3.075
f1 (ppm)
13C NMR (150 MHz, CDCl3)
(3j / 3j')
158.60
155.46
153.88
141.30
136.03
134.10
131.46
130.54
130.37
130.08
130.05
128.72
128.38
128.21
128.13
126.93
125.79
122.77
121.49
117.19
114.04
81.81
77.44
77.23
77.02
67.32
55.35
52.74
50.61
32.12
29.89
22.89
14.32
OMe
Br
O
NH
O
O
3j major
f1 (ppm)

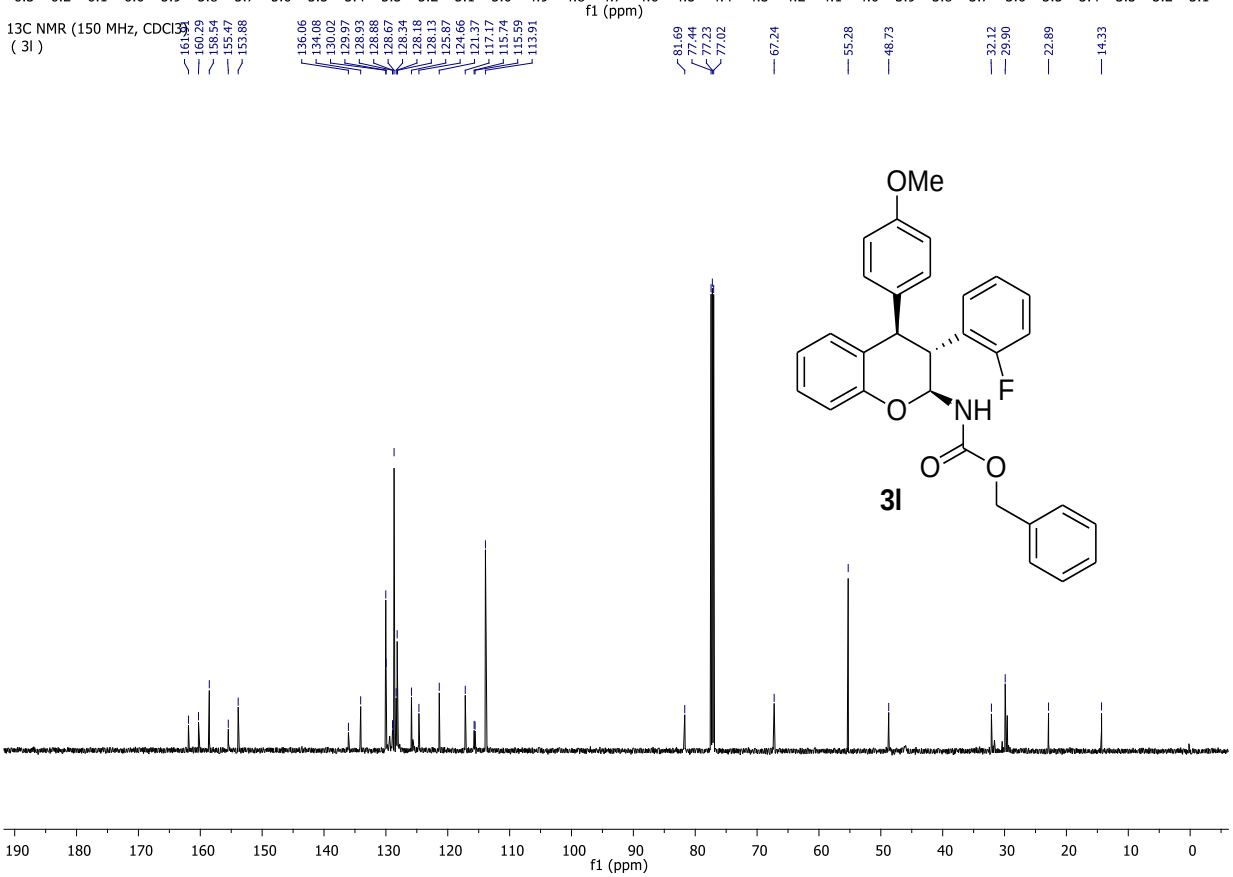

1H NMR (600 MHz, CDCl3)
(3k / 3k')
OMe
Me
NH
O
O
O
3k major
f1 (ppm)


13C NMR (100 MHz, CDCl3)
(3k / 3k')
OMe
Me
NH
O
O
O
3k major
f1 (ppm)


1H NMR (600 MHz, CDCl3)
(3l / 3l')
OMe
F
NH
O
O
O
3l
f1 (ppm)

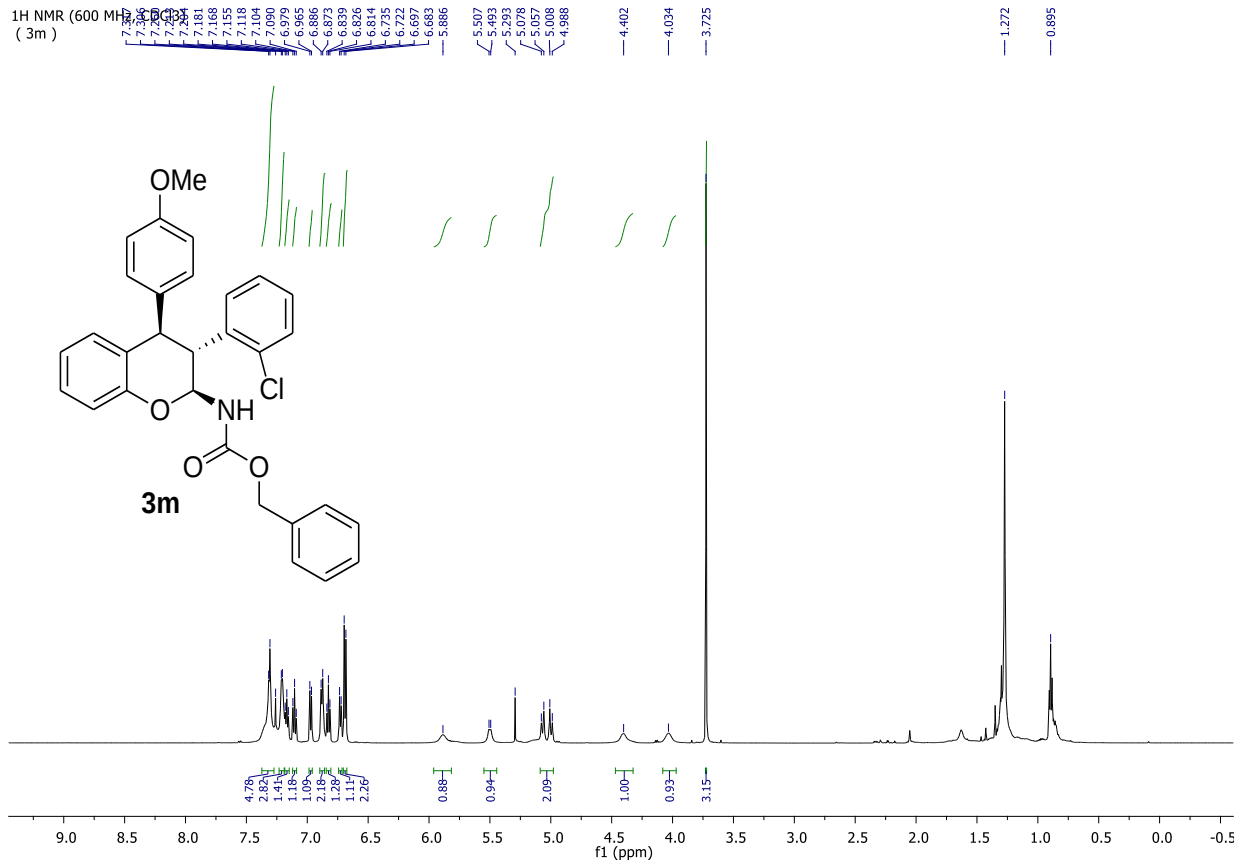

1H NMR (600 MHz, CDCl3)
(3l)
7.315
7.305
7.260
7.215
7.206
7.171
7.158
7.146
7.134
7.089
7.045
7.033
7.022
6.966
6.952
6.916
6.900
6.885
6.868
6.854
6.835
6.822
6.810
6.730
6.717
6.702
6.687
f1 (ppm)

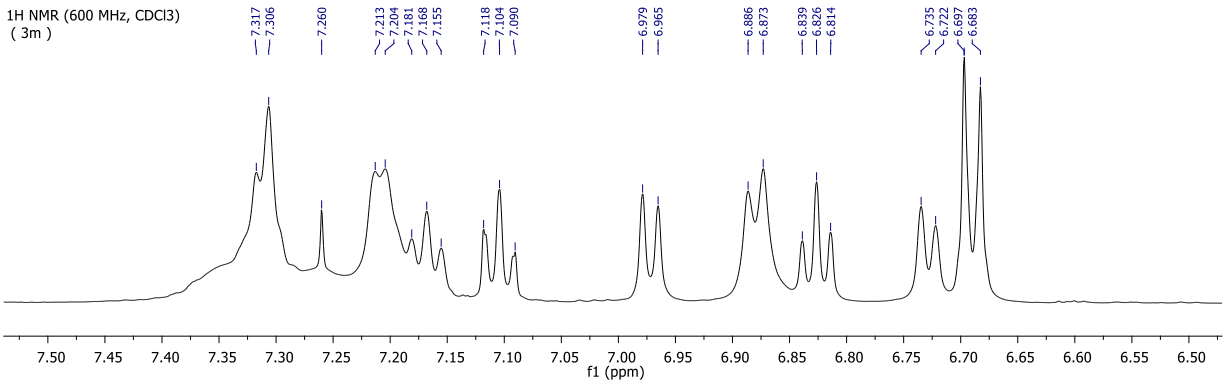

6.030
6.013
5.997
5.479
5.464
5.081
5.060
5.019
4.999
4.466
4.447
3.726
3.599
3.582
3.564
f1 (ppm)

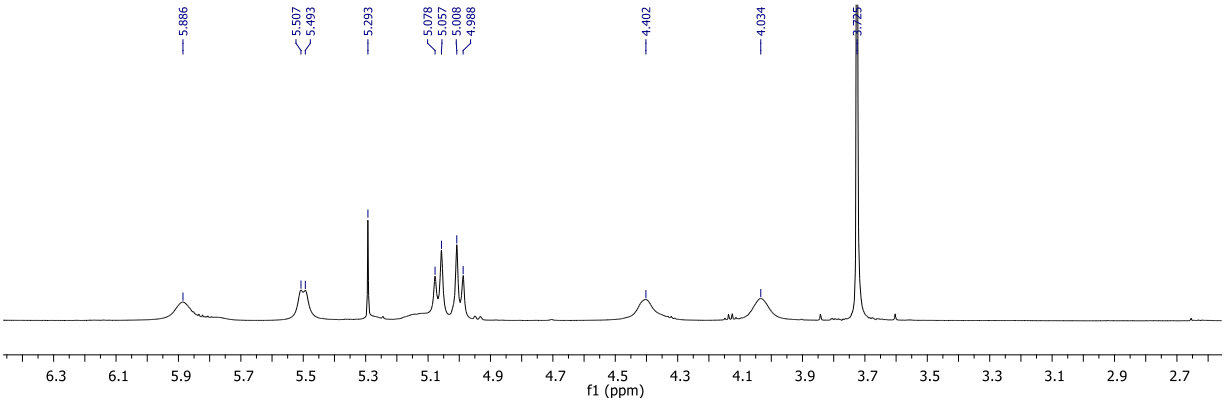

13C NMR (150 MHz, CDCl3)
(3l)
161.97
160.29
158.54
155.47
153.88
136.06
134.08
130.02
129.97
128.93
128.88
128.67
128.34
128.18
128.13
125.87
124.66
121.37
117.17
115.74
115.59
113.91
81.69
77.44
77.23
77.02
67.24
55.28
48.73
32.12
29.90
22.89
14.33
f1 (ppm)

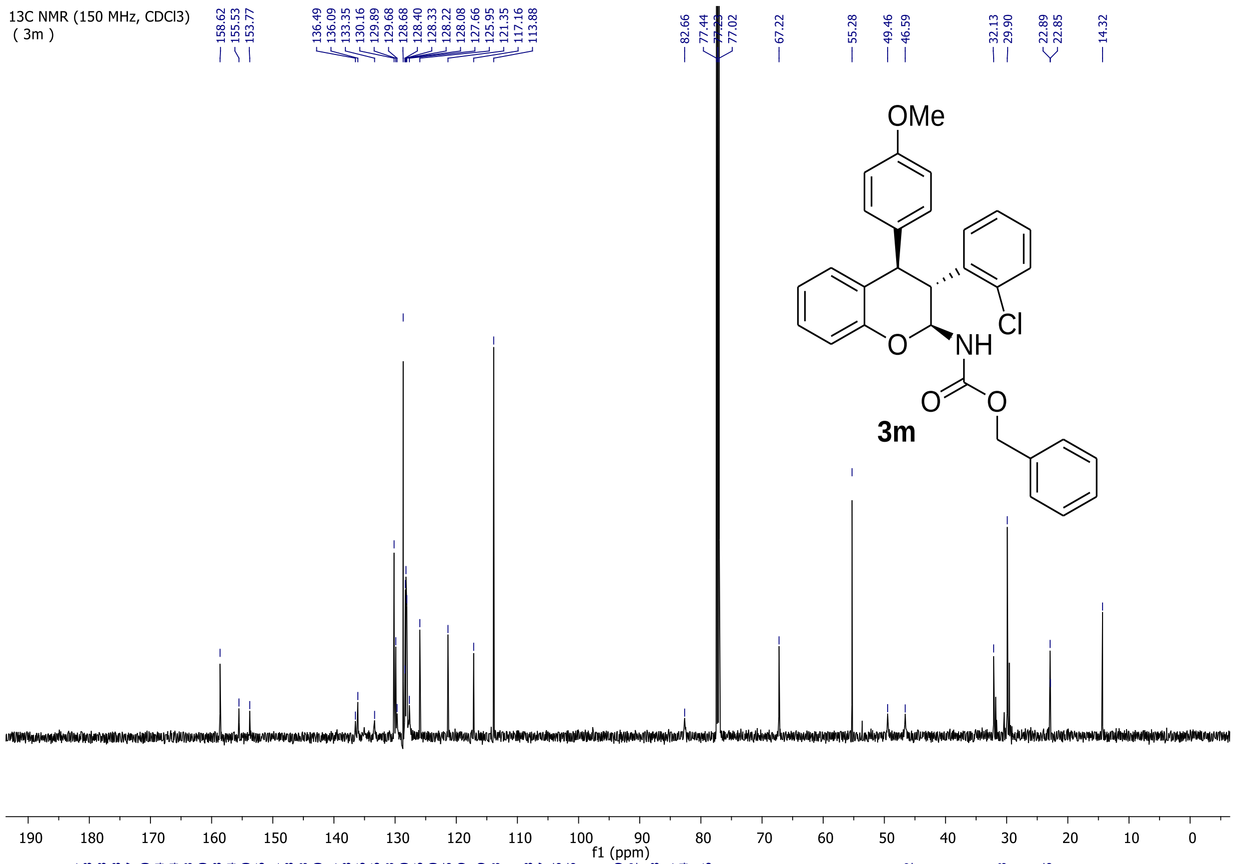
OMe
F
O
NH
O
O

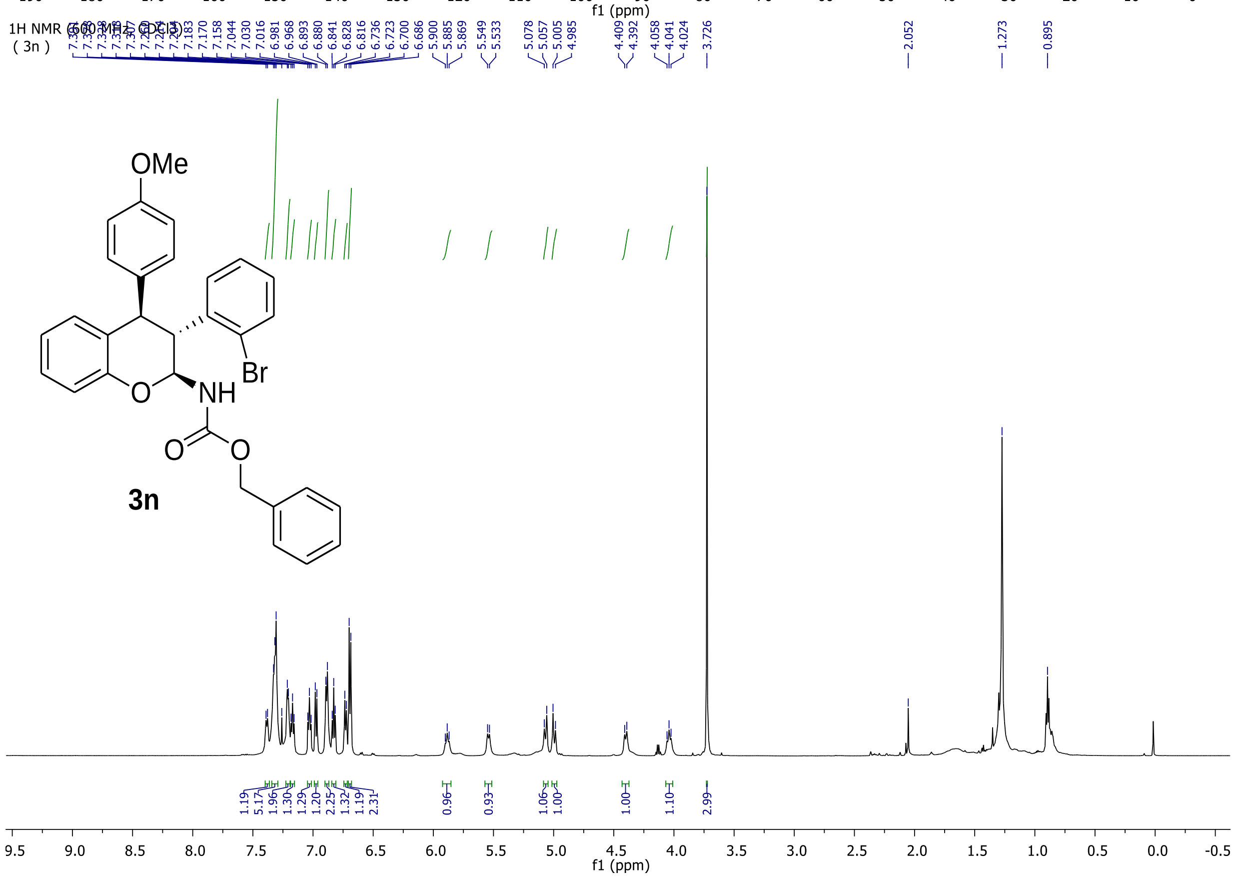
3l

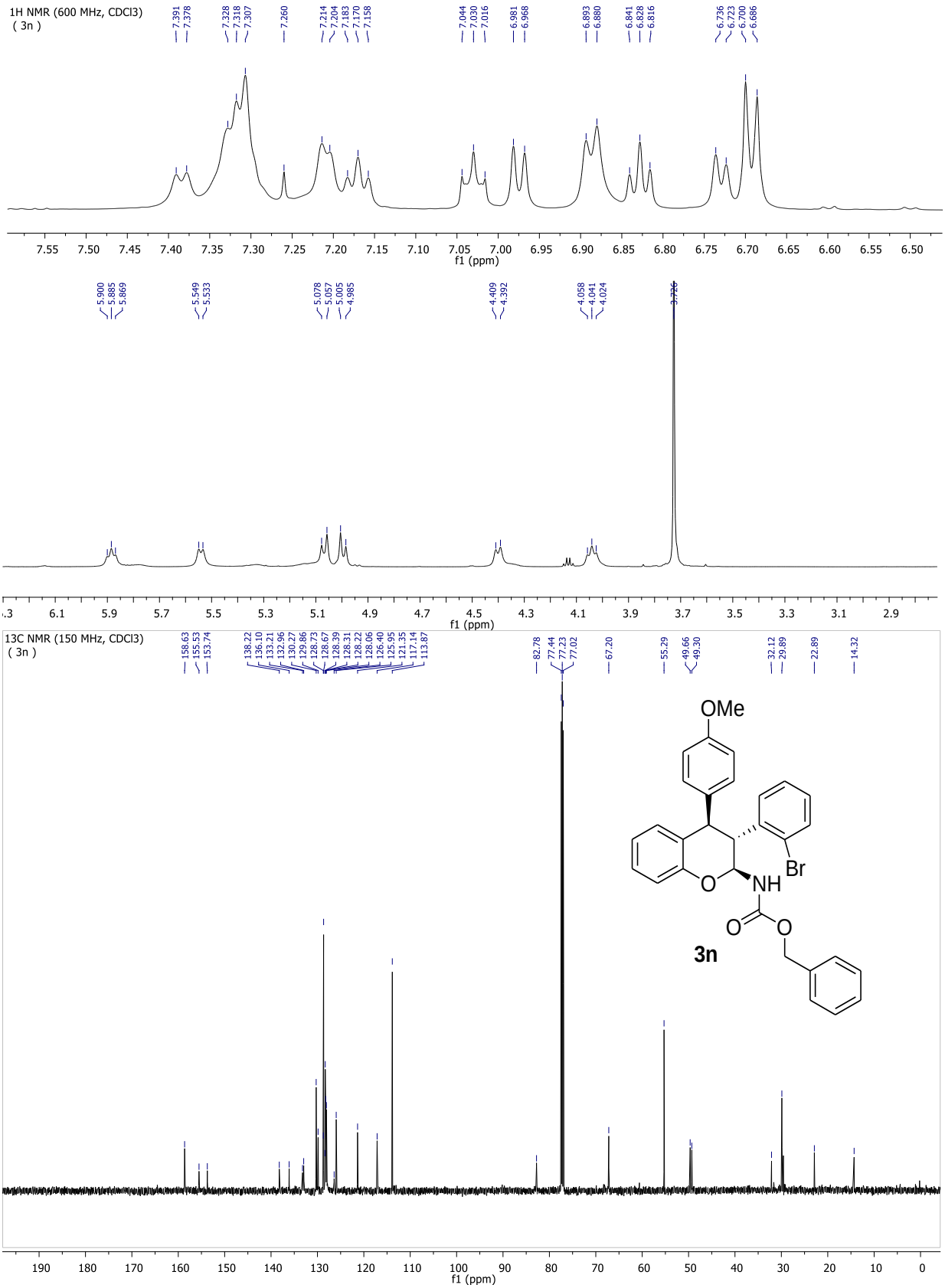

1H NMR (600 MHz, CDCl3)
(3m)
OMe
Cl
O
NH
O
O
3m
f1 (ppm)

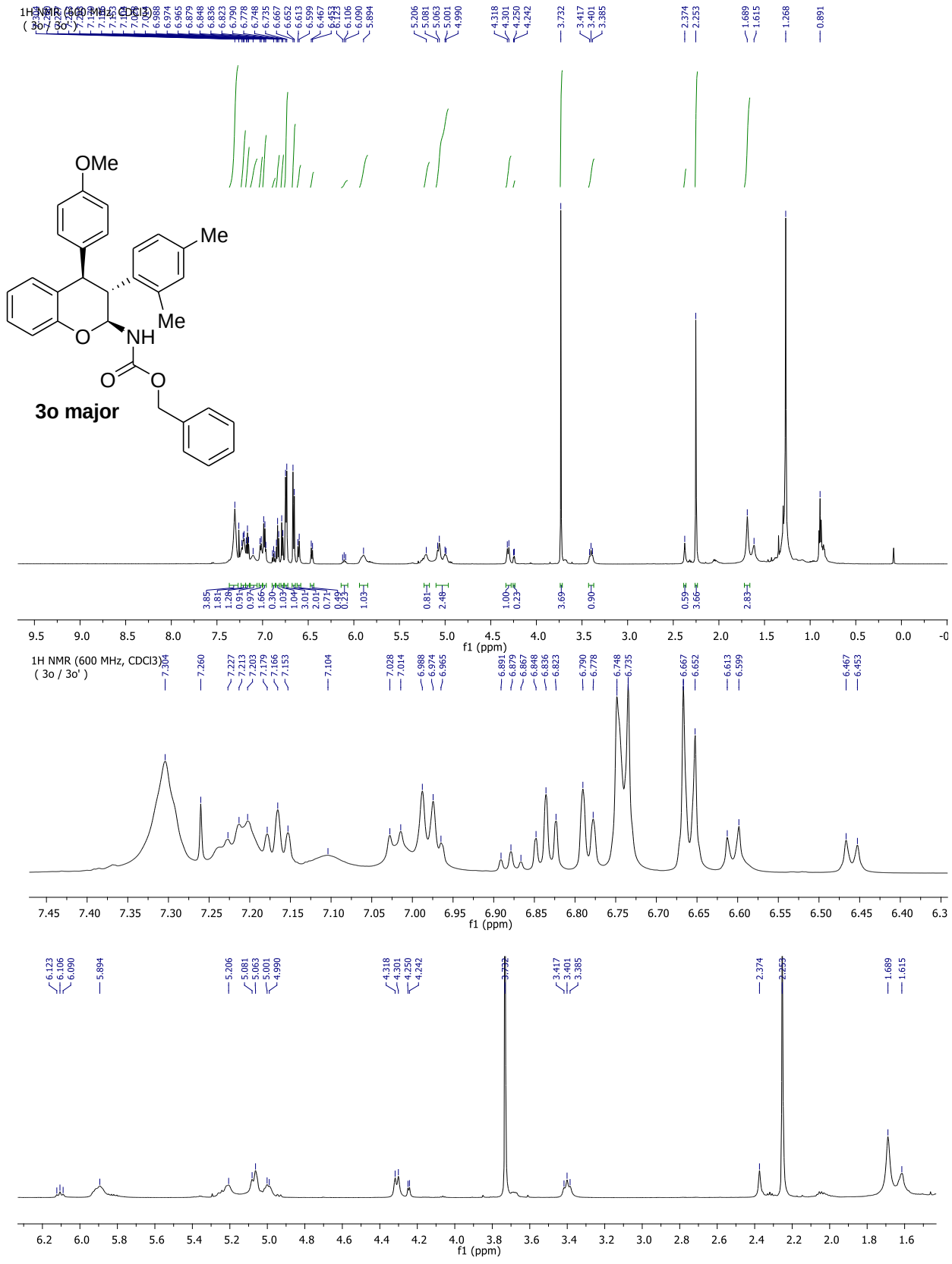

1H NMR (600 MHz, CDCl3)
(3m)
f1 (ppm)

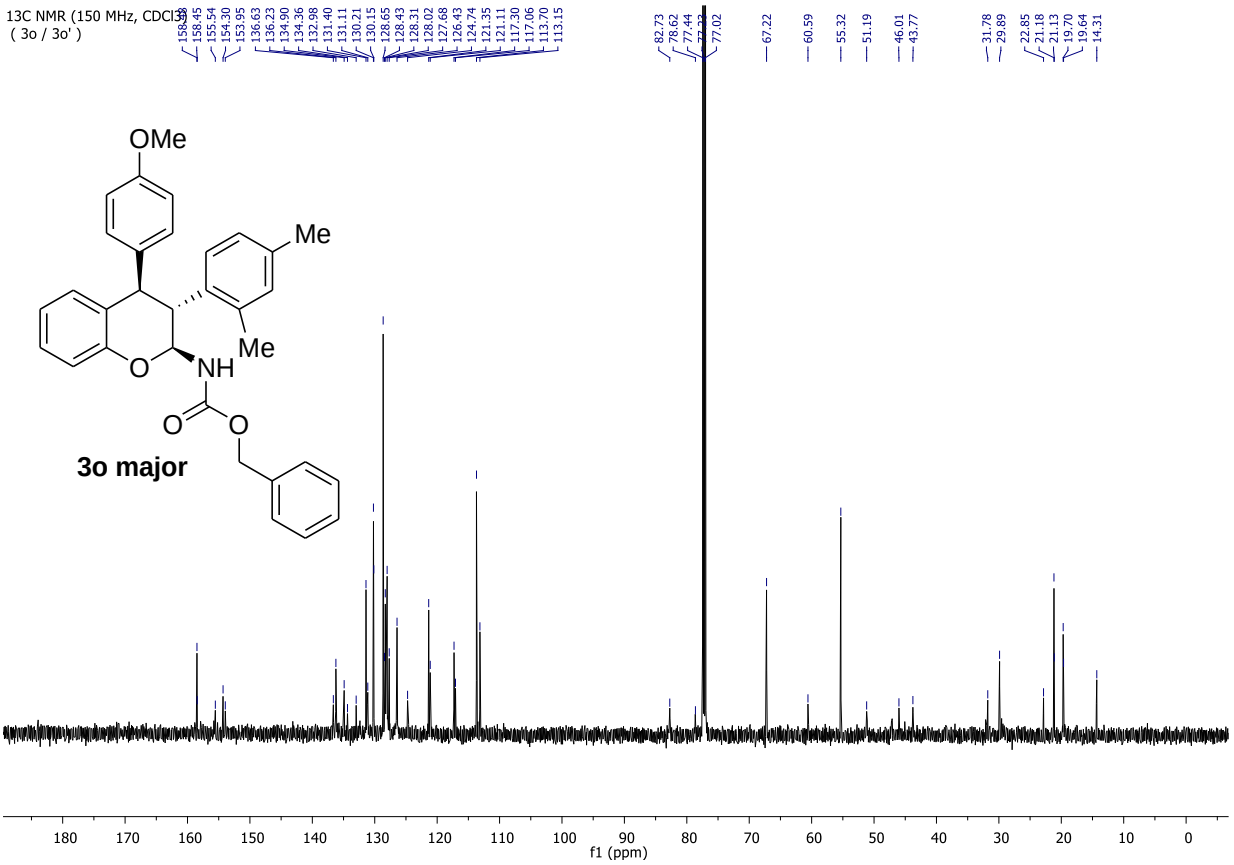

f1 (ppm)

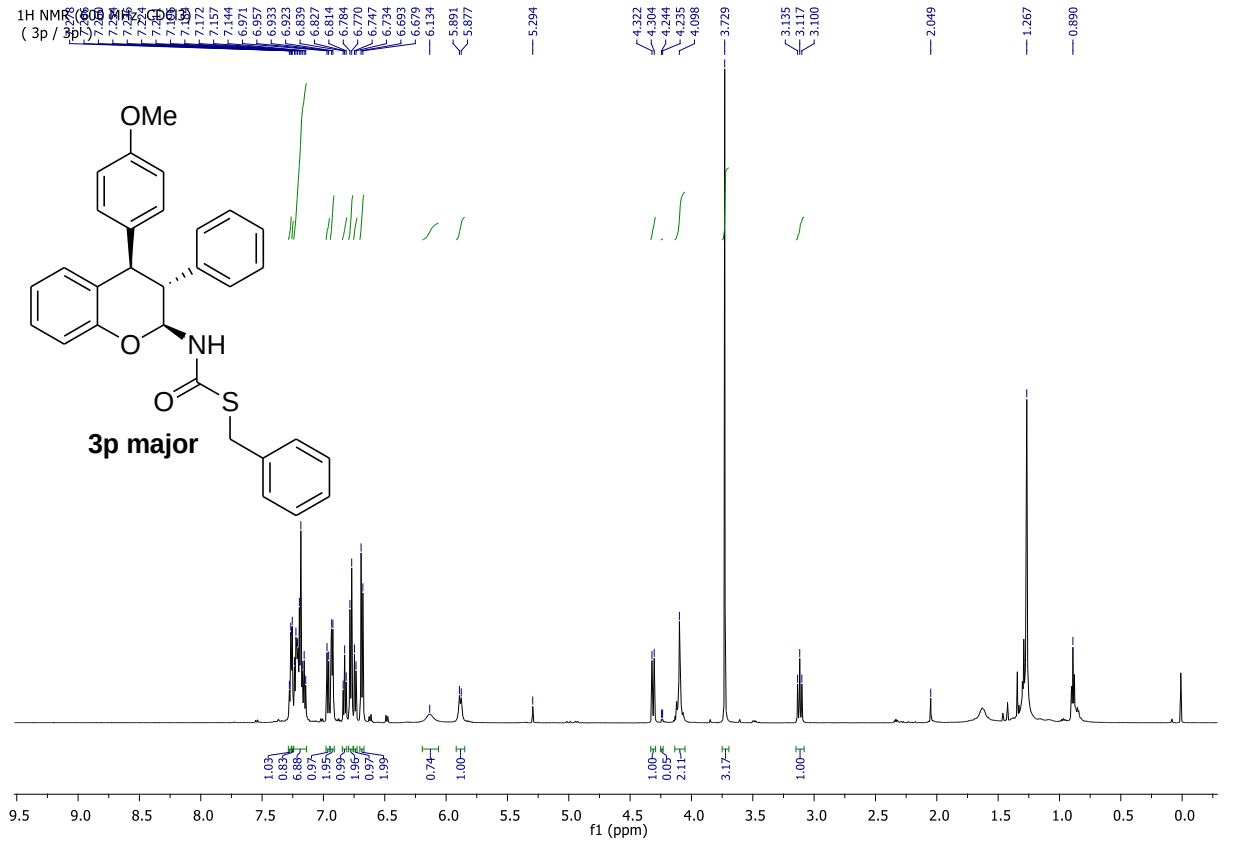

13C NMR (150 MHz, CDCl3)
(3m)
158.62
155.53
153.77
136.49
136.09
133.35
130.16
129.89
129.68
128.68
128.40
128.33
128.22
128.08
127.66
125.95
121.35
117.16
113.88
82.66
77.44
77.02
67.22
55.28
49.46
46.59
32.13
29.90
22.89
22.85
14.32
OMe
Cl
O
NH
O
O
3m
f1 (ppm)

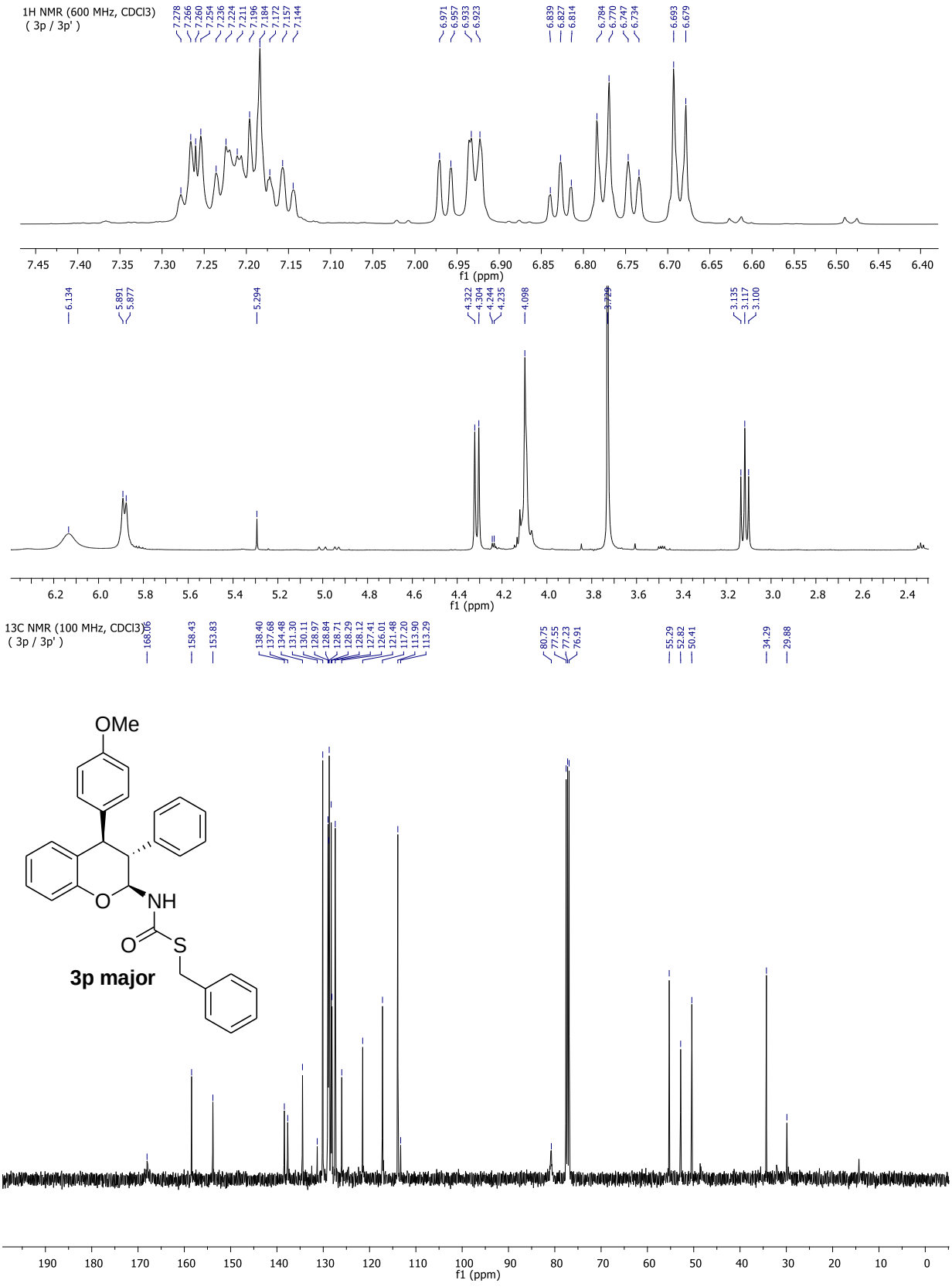

1H NMR
(3n)
7.307
7.183
7.170
7.158
7.044
7.030
7.016
6.981
6.968
6.893
6.880
6.841
6.828
6.816
6.736
6.723
6.700
6.686
5.900
5.885
5.869
5.549
5.533
5.078
5.057
5.005
4.985
4.409
4.392
4.058
4.041
4.024
3.726
2.052
1.273
0.895
OMe
Br
O
NH
O
O
3n
1.19
5.17
1.96
1.30
1.29
1.20
2.25
1.32
1.19
2.31
0.96
0.93
1.06
1.00
1.00
1.10
2.99
f1 (ppm)

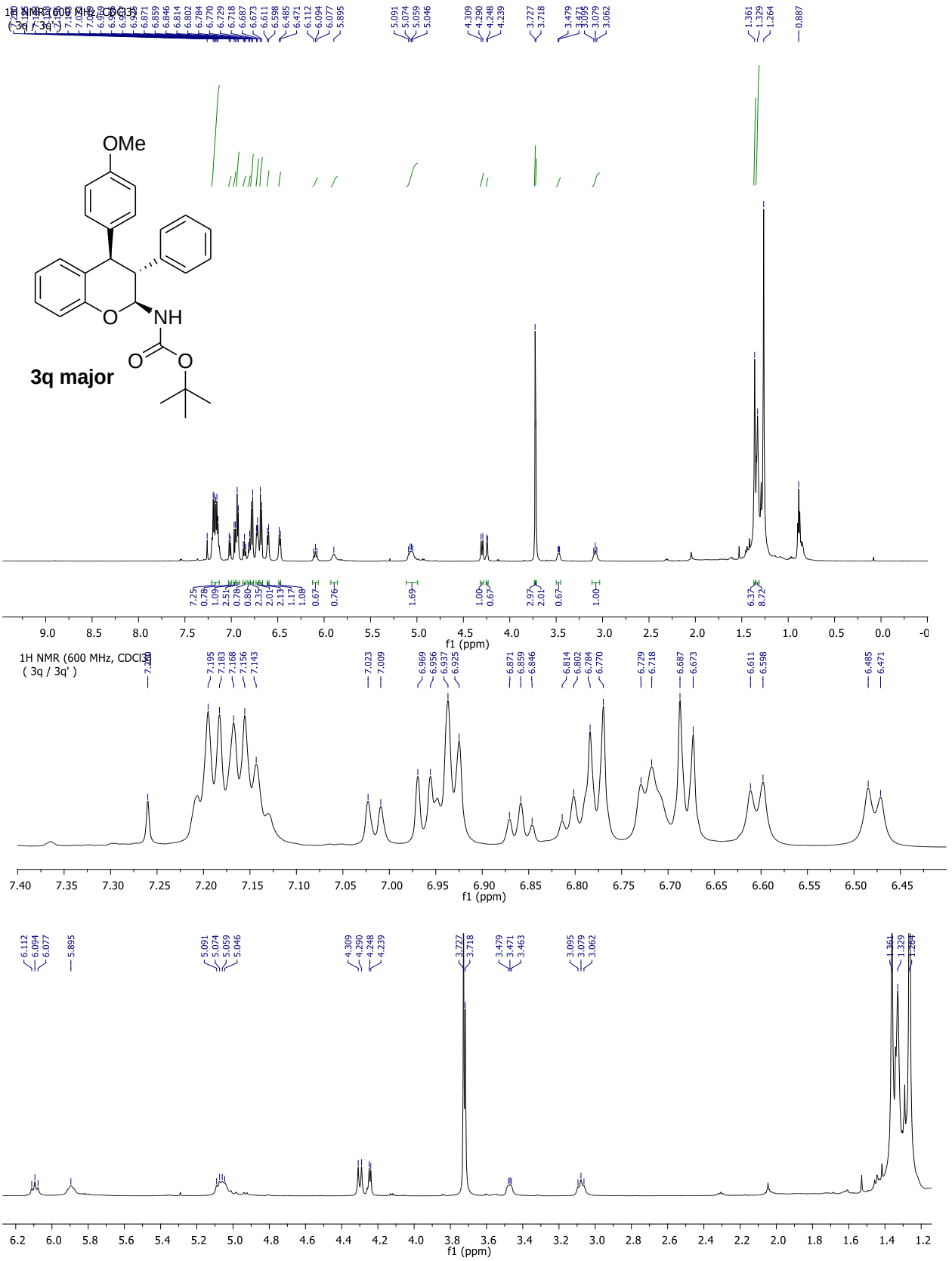

1H NMR (600 MHz, CDCl3)
(3n)
7.391
7.378
7.328
7.318
7.307
7.260
7.214
7.204
7.183
7.170
7.158
7.044
7.030
7.016
6.981
6.968
6.893
6.880
6.841
6.828
6.816
6.736
6.723
6.700
6.686
f1 (ppm)
5.900
5.885
5.869
5.549
5.533
5.078
5.057
5.005
4.985
4.409
4.392
4.058
4.041
4.024
3.726
f1 (ppm)
13C NMR (150 MHz, CDCl3)
(3n)
158.63
155.53
153.74
138.22
136.10
133.21
132.96
130.27
129.86
128.73
128.67
128.39
128.31
128.22
128.06
126.40
125.95
121.35
117.14
113.87
82.78
77.44
77.23
77.02
67.20
55.29
49.66
49.30
32.12
29.89
22.89
14.32
OMe
Br
NH
O
O
O
3n
f1 (ppm)

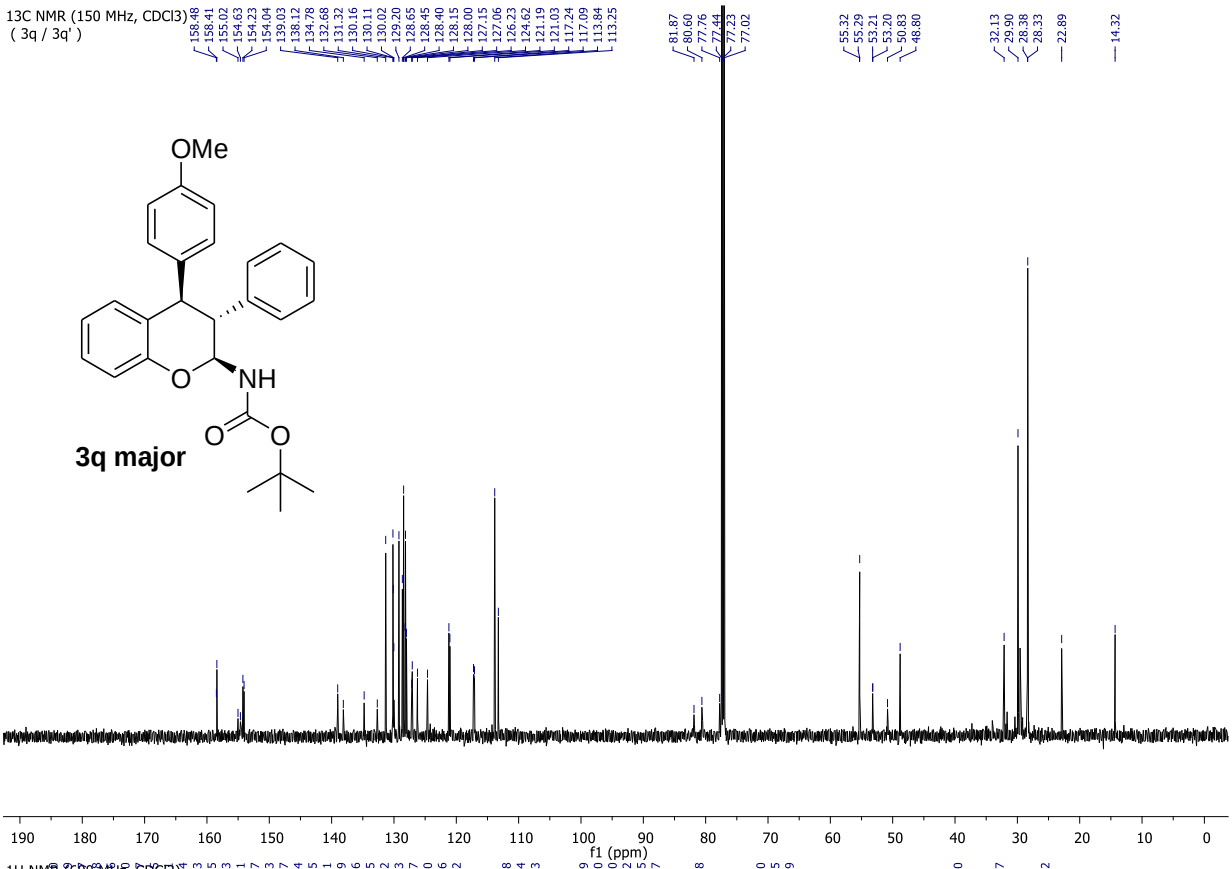

1H NMR (600 MHz, CDCl3)
(3o / 3o')
OMe
Me
Me
O
NH
O
O
3o major
f1 (ppm)

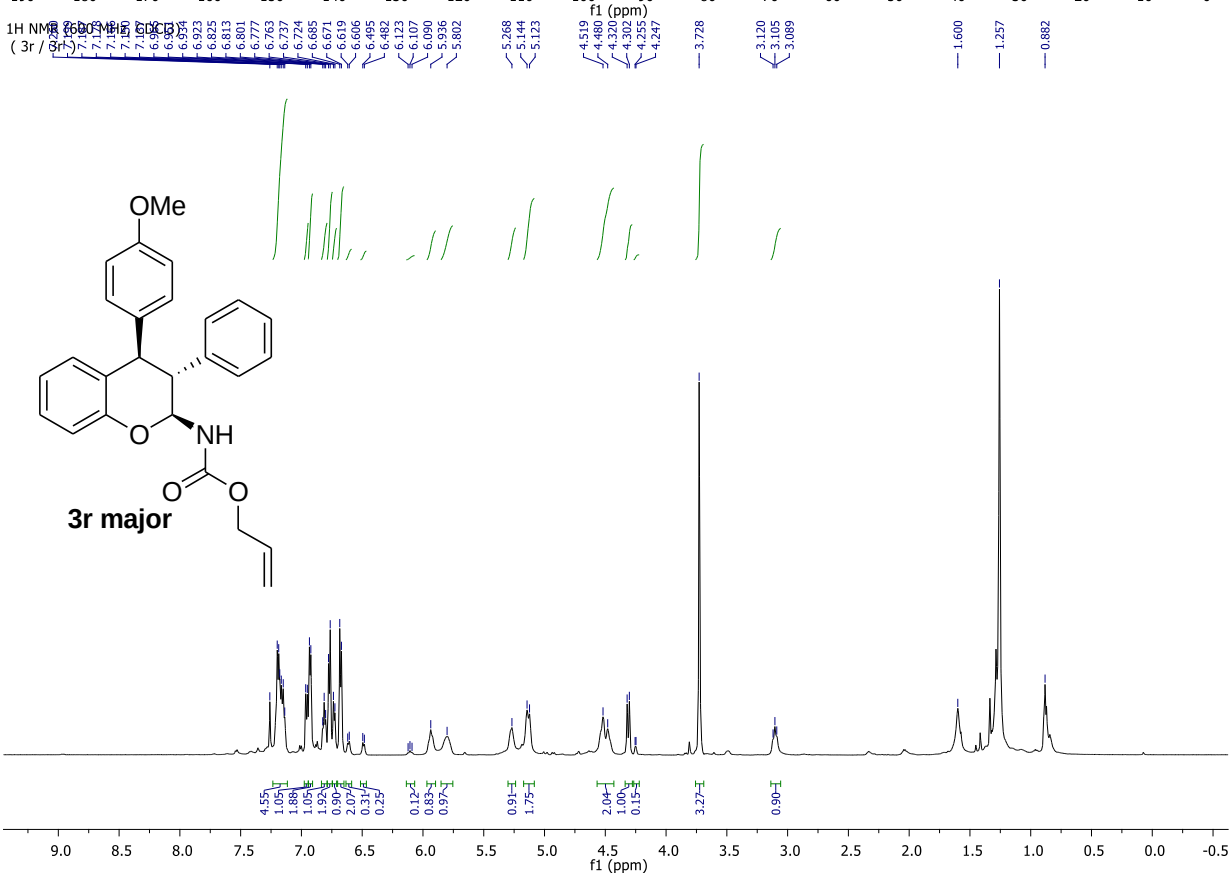

13C NMR (150 MHz, CDCl3)
(3o / 3o')
OMe
Me
Me
NH
O
O
O
3o major
f1 (ppm)

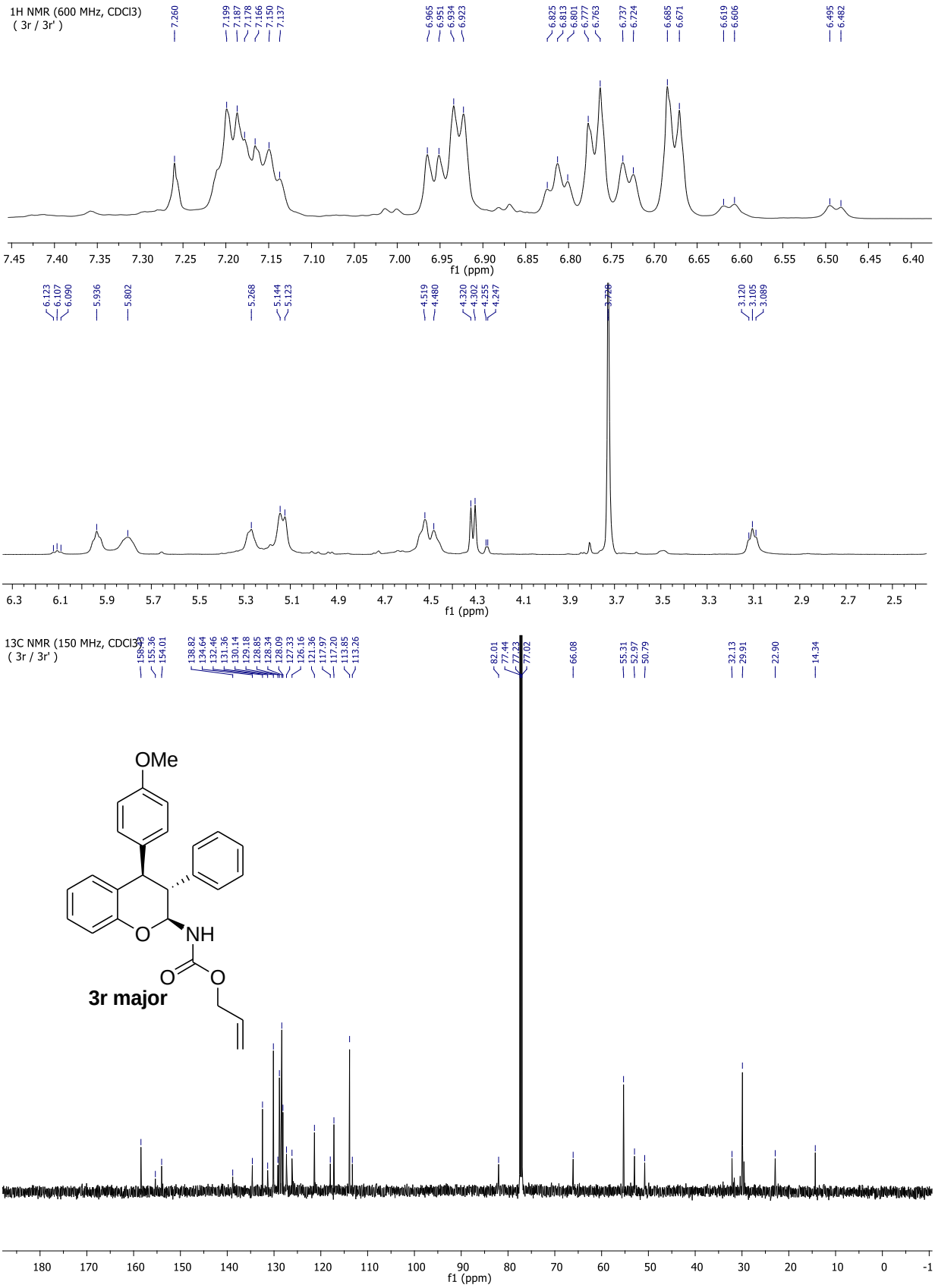

1H NMR (600 MHz, CDCl3)
(3p / 3p')
OMe
NH
O
O
S
3p major
f1 (ppm)

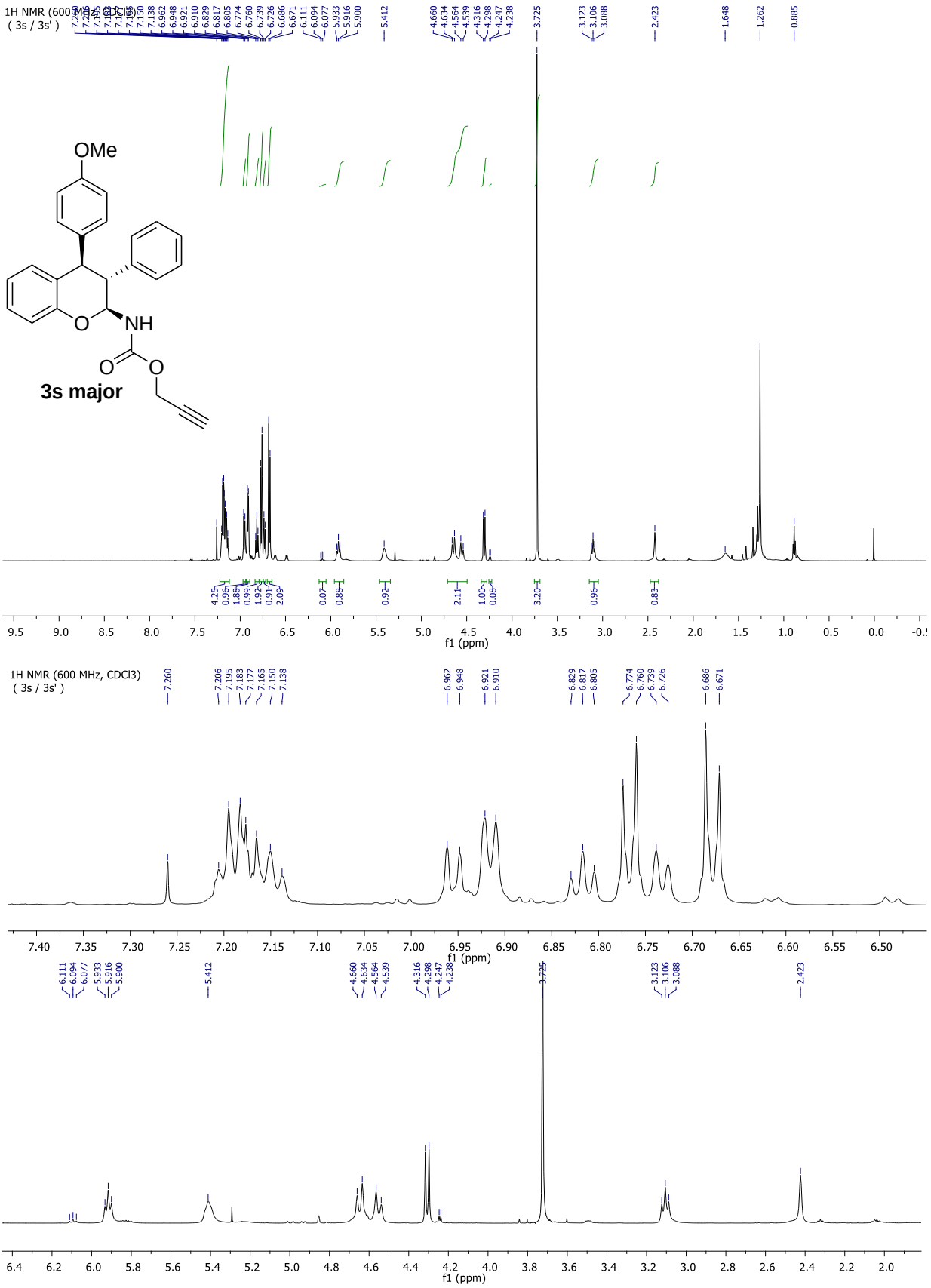

1H NMR (600 MHz, CDCl3)
(3p / 3p')
7.278
7.266
7.260
7.254
7.236
7.224
7.211
7.196
7.184
7.172
7.157
7.144
6.971
6.957
6.933
6.923
6.839
6.827
6.814
6.784
6.770
6.747
6.734
6.693
6.679
f1 (ppm)
6.134
5.891
5.877
5.294
4.322
4.304
4.244
4.235
4.098
3.729
3.135
3.117
3.100
f1 (ppm)
13C NMR (100 MHz, CDCl3)
(3p / 3p')
168.06
158.43
153.83
138.40
137.68
134.48
131.30
130.11
128.97
128.84
128.71
128.29
128.12
127.41
126.01
121.48
117.20
113.90
113.29
80.75
77.55
77.23
76.91
55.29
52.82
50.41
34.29
29.88
OMe
O
NH
O
S
3p major
f1 (ppm)

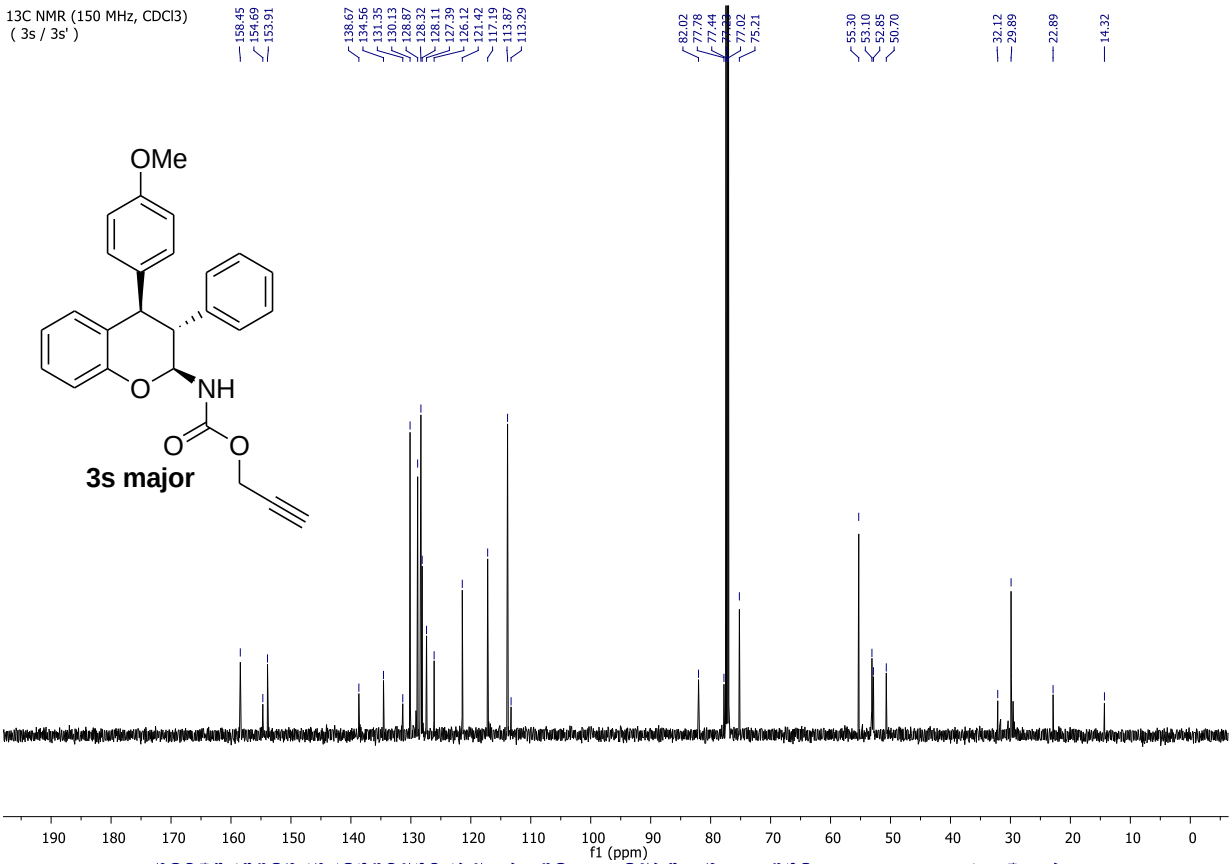

OMe
O
NH
O
O
3q major
1H NMR (600 MHz, CDCl3)
(3q / 3q')
f1 (ppm)

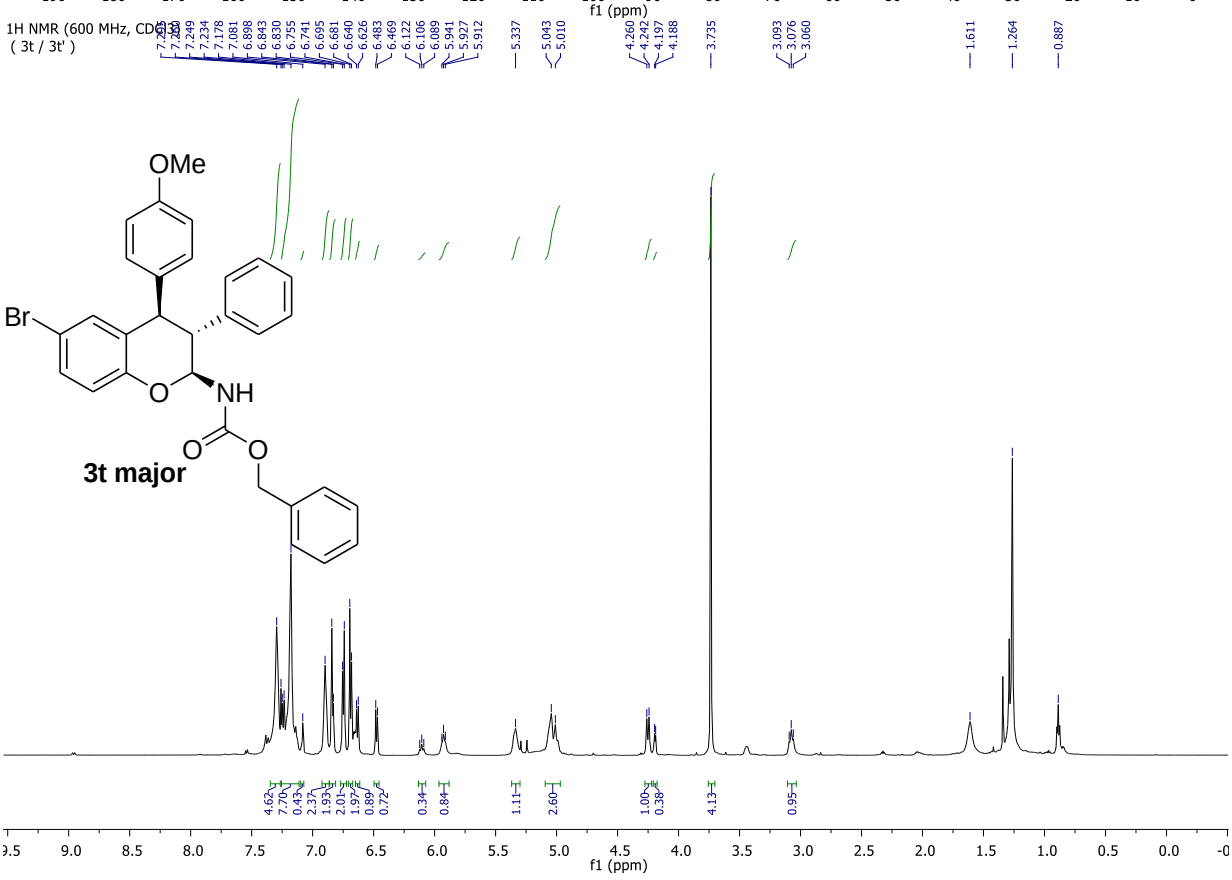

13C NMR (150 MHz, CDCl3)
(3q / 3q')
OMe
NH
O
O
O
3q major
f1 (ppm)

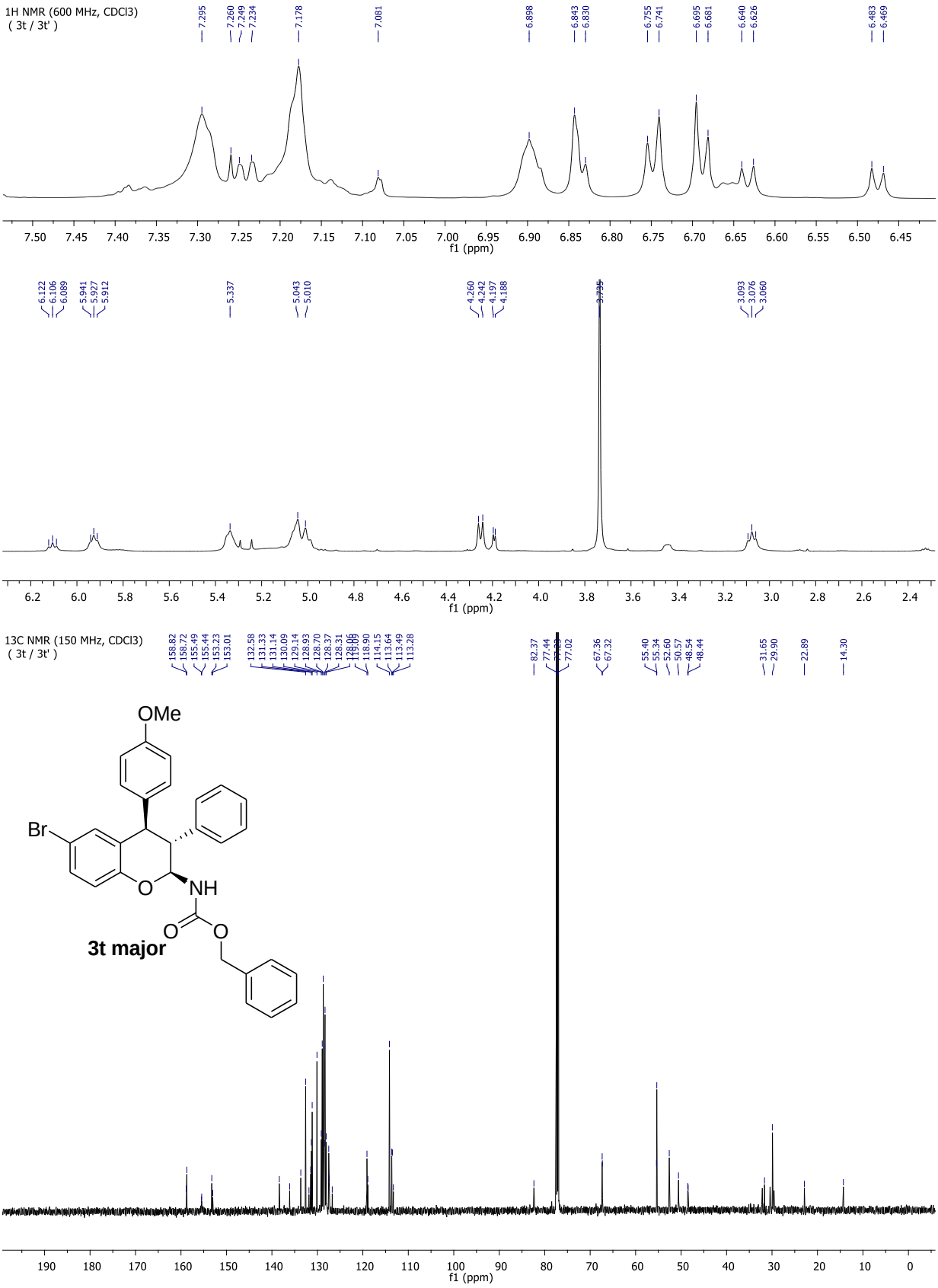

1H NMR (600 MHz, CDCl3)
(3r / 3r')
OMe
NH
O
O
O
3r major
f1 (ppm)

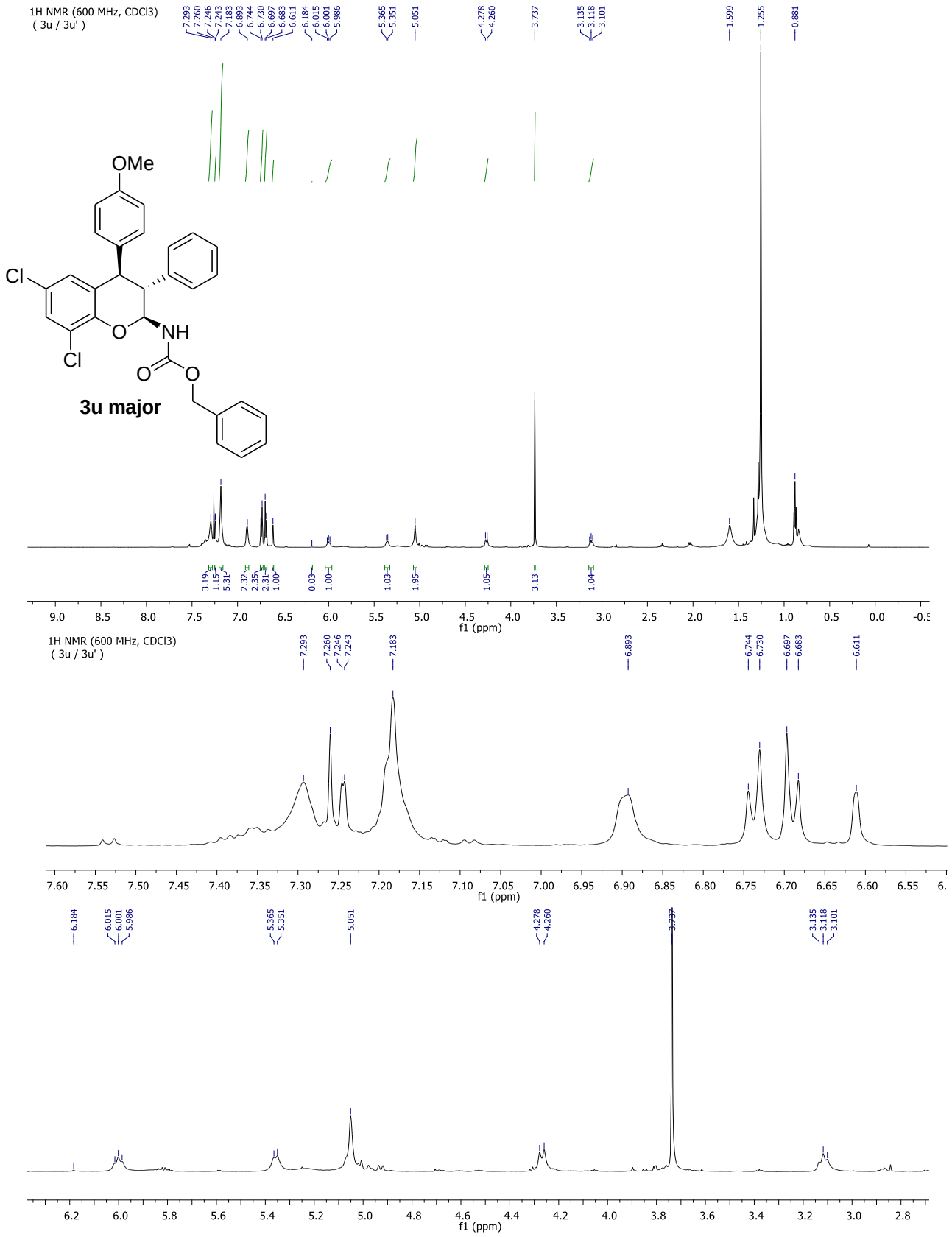

1H NMR (600 MHz, CDCl3)
(3r / 3r')
13C NMR (150 MHz, CDCl3)
(3r / 3r')
OMe
O
NH
O
O
3r major
f1 (ppm)

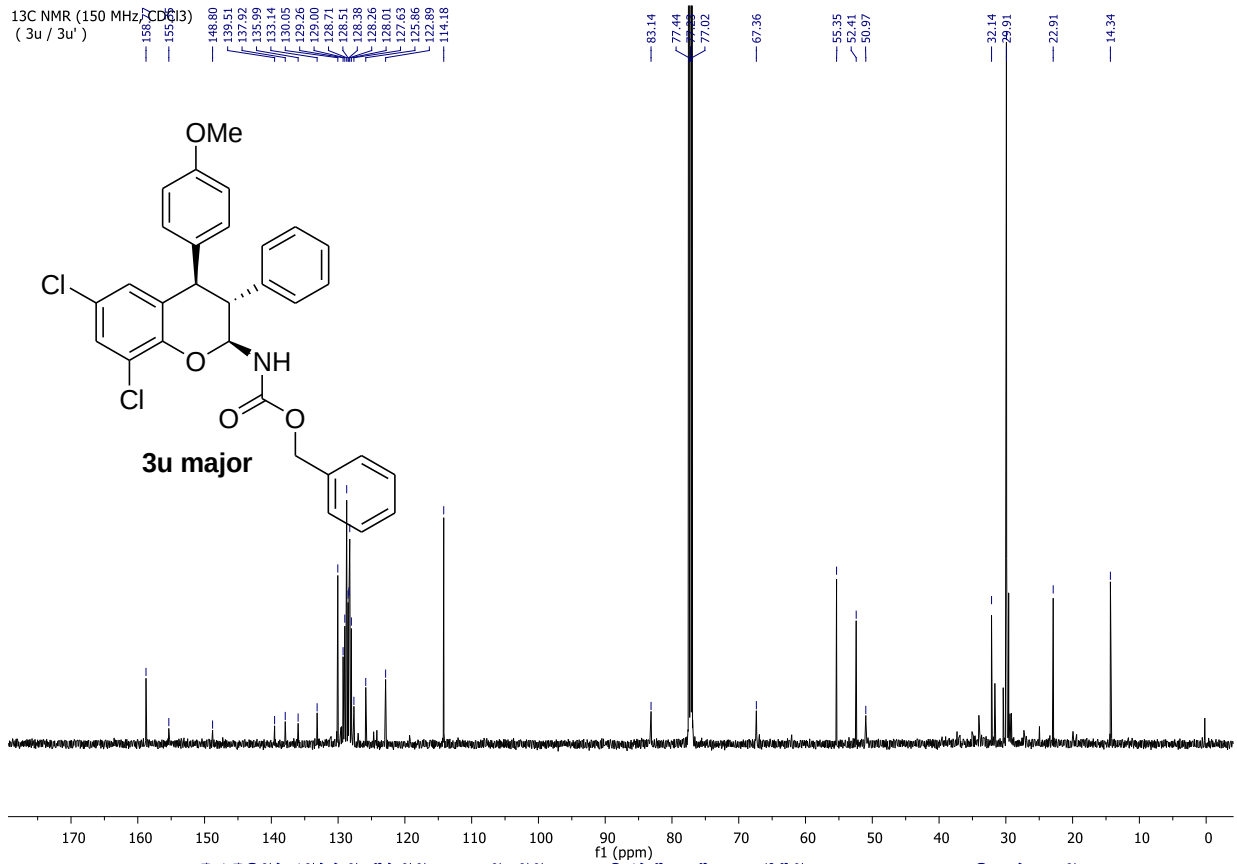

1H NMR (600 MHz, CDCl3)
(3s / 3s')
OMe
O
NH
O
O
3s major
f1 (ppm)
1H NMR (600 MHz, CDCl3)
(3s / 3s')
f1 (ppm)
f1 (ppm)

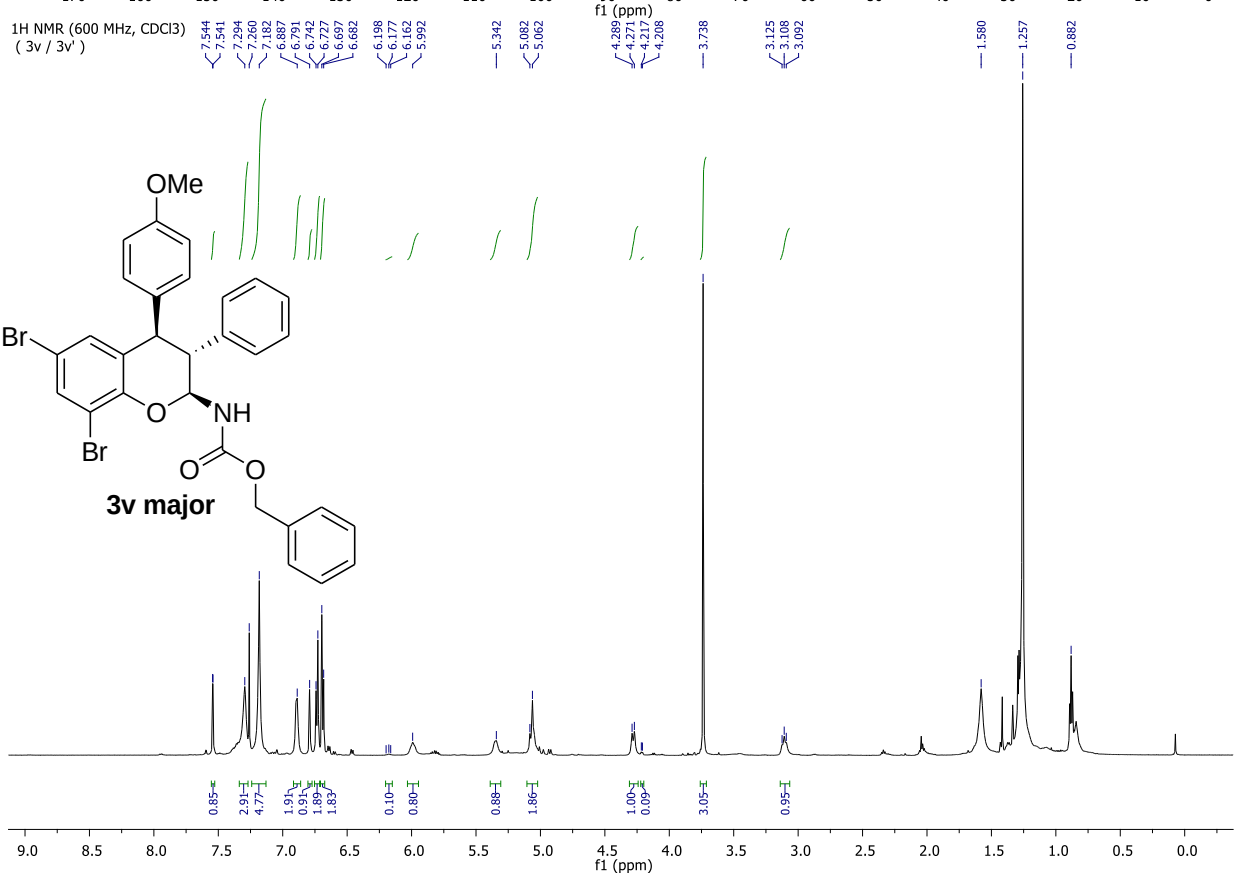

13C NMR (150 MHz, CDCl3)
(3s / 3s')
OMe
O
NH
O
O
3s major
f1 (ppm)

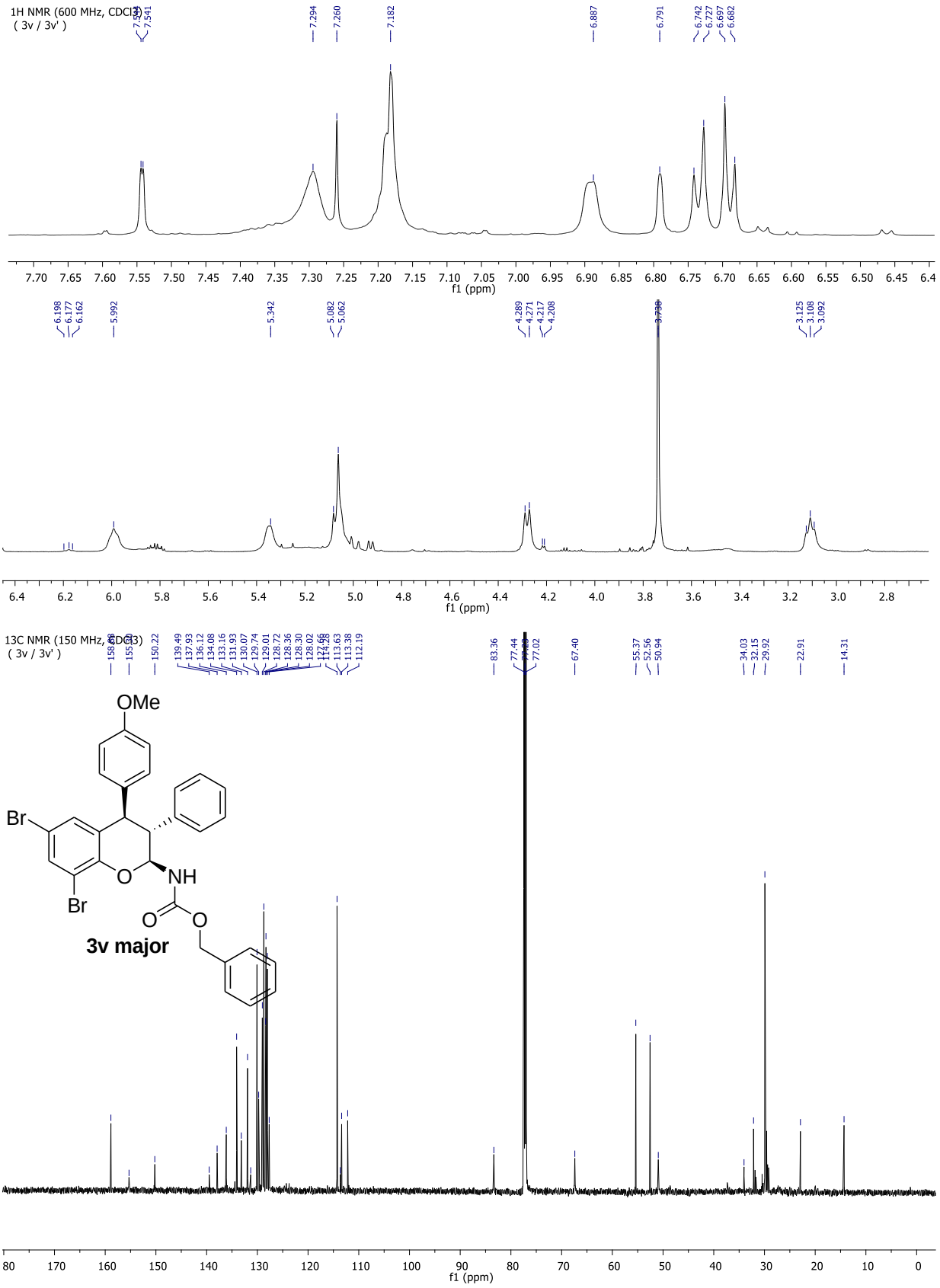

1H NMR (600 MHz, CDCl3)
(3t / 3t')
OMe
Br
O
NH
O
O
3t major
f1 (ppm)

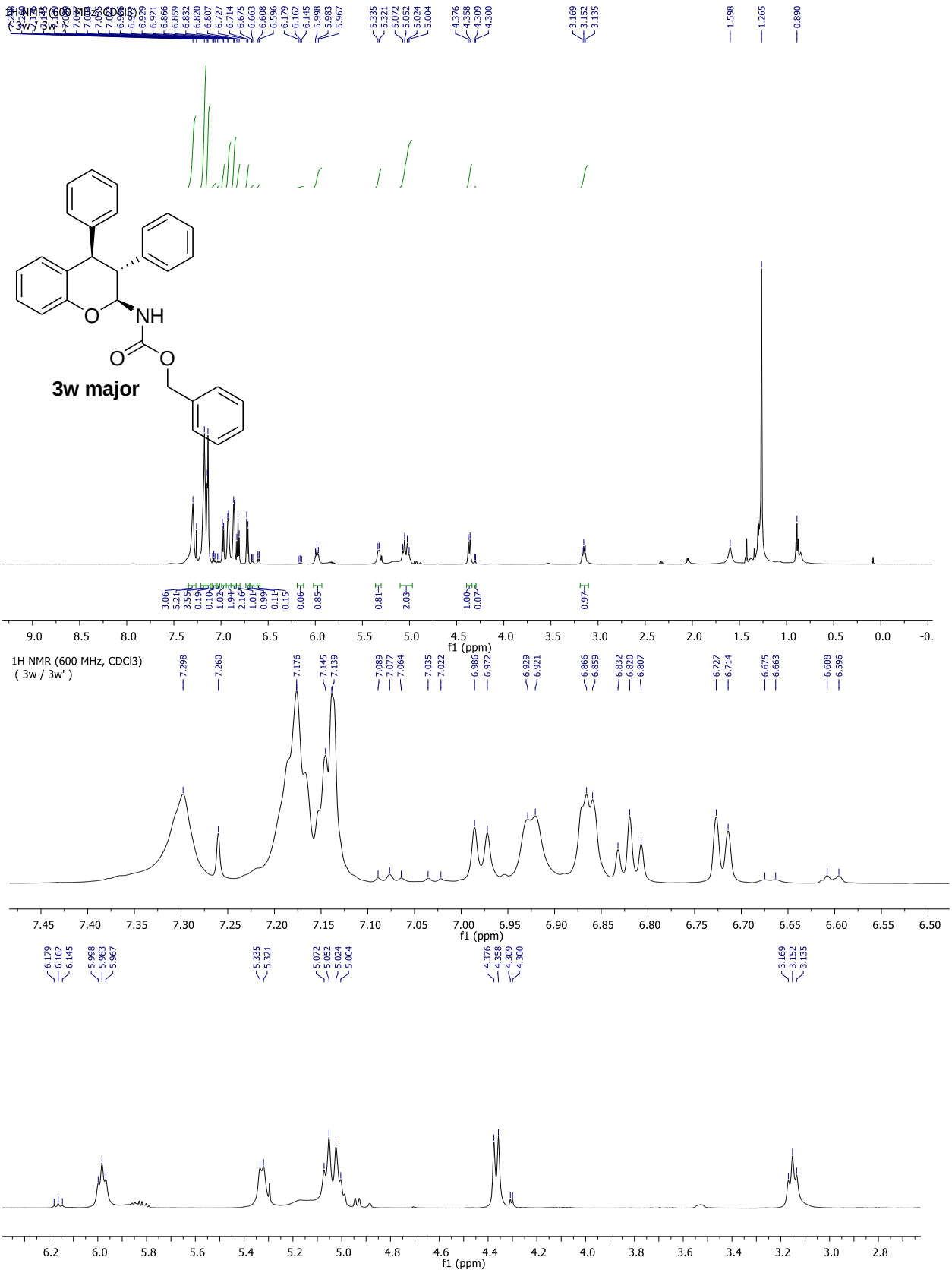

1H NMR (600 MHz, CDCl3)
(3t / 3t')
7.295
7.260
7.249
7.234
7.178
7.081
6.898
6.843
6.830
6.755
6.741
6.695
6.681
6.640
6.626
6.483
6.469
f1 (ppm)
6.122
6.106
6.089
5.941
5.927
5.912
5.337
5.043
5.010
4.260
4.242
4.197
4.188
3.735
3.093
3.076
3.060
f1 (ppm)
13C NMR (150 MHz, CDCl3)
(3t / 3t')
158.82
158.72
155.49
155.44
153.23
153.01
132.58
131.33
131.14
130.09
129.14
128.93
128.70
128.37
128.31
118.90
114.15
113.64
113.49
113.28
82.37
77.44
77.02
67.36
67.32
55.40
55.34
52.60
50.57
48.54
48.44
31.65
29.90
22.89
14.30
OMe
Br
O
NH
O
O
3t major
f1 (ppm)

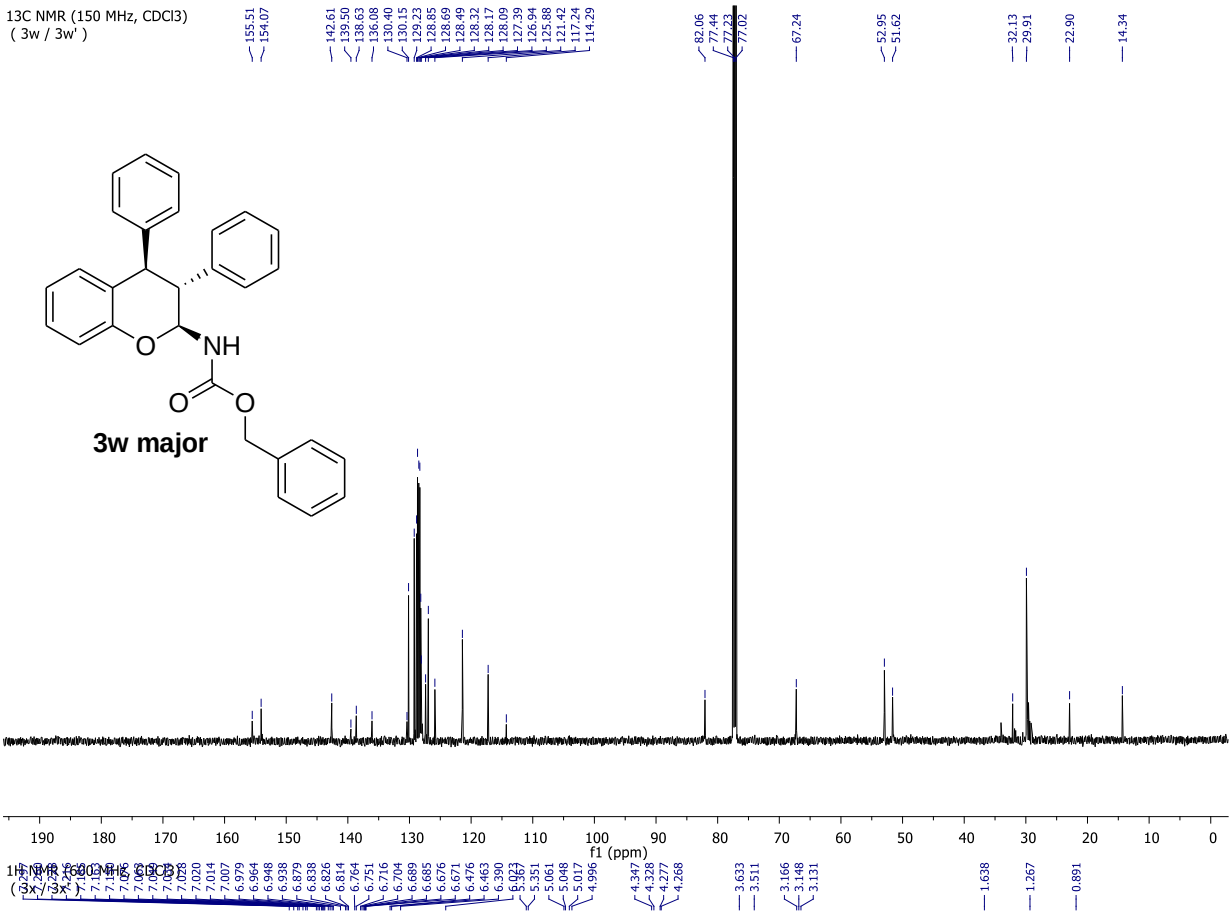

1H NMR (600 MHz, CDCl3)
(3u / 3u')
OMe
Cl
Cl
O
NH
O
O
3u major
f1 (ppm)
1H NMR (600 MHz, CDCl3)
(3u / 3u')
f1 (ppm)
f1 (ppm)

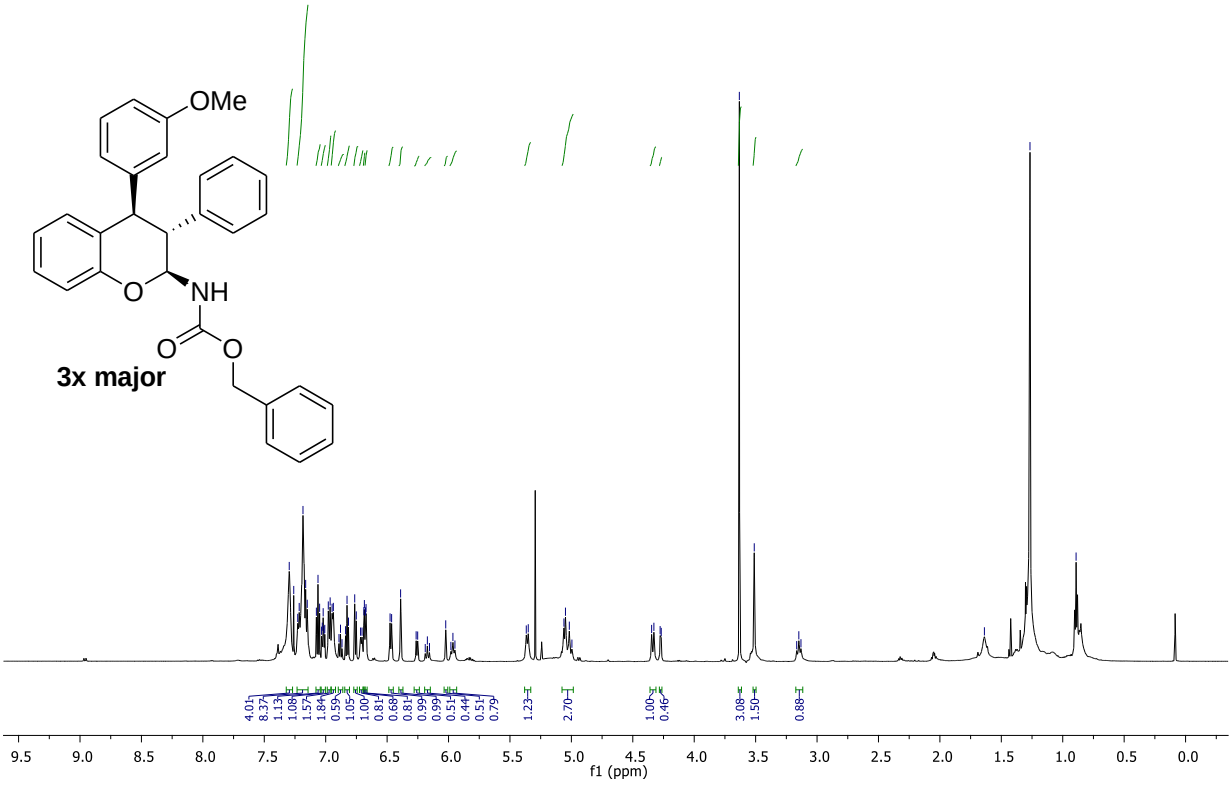

13C NMR (150 MHz, CDCl3)
(3u / 3u')
158.47
155.07
148.80
139.51
137.92
135.99
133.14
130.05
129.26
129.00
128.71
128.51
128.38
128.26
128.01
127.63
125.86
122.89
114.18
83.14
77.44
77.23
77.02
67.36
55.35
52.41
50.97
32.14
29.91
22.91
14.34
OMe
Cl
Cl
O
NH
O
O
3u major
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

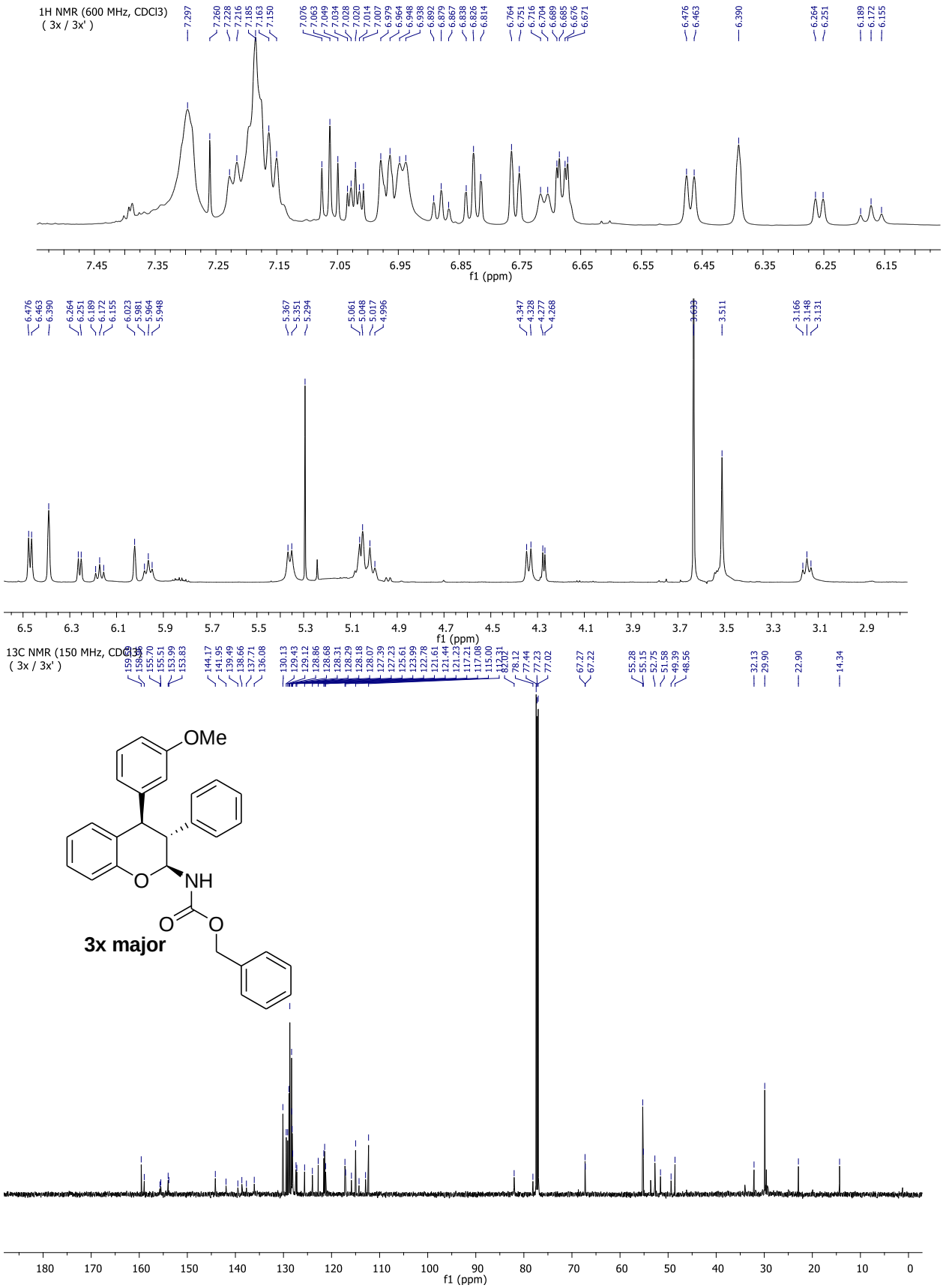

1H NMR (600 MHz, CDCl3)
(3v / 3v')
7.544
7.541
7.294
7.260
7.182
6.887
6.791
6.742
6.727
6.697
6.682
6.198
6.177
6.162
5.992
5.342
5.082
5.062
4.289
4.271
4.217
4.208
3.738
3.125
3.108
3.092
1.580
1.257
0.882
OMe
Br
Br
O
NH
O
O
3v major
0.85
2.91
4.77
1.91
0.91
1.89
1.83
0.10
0.80
0.88
1.86
1.00
0.09
3.05
0.95
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

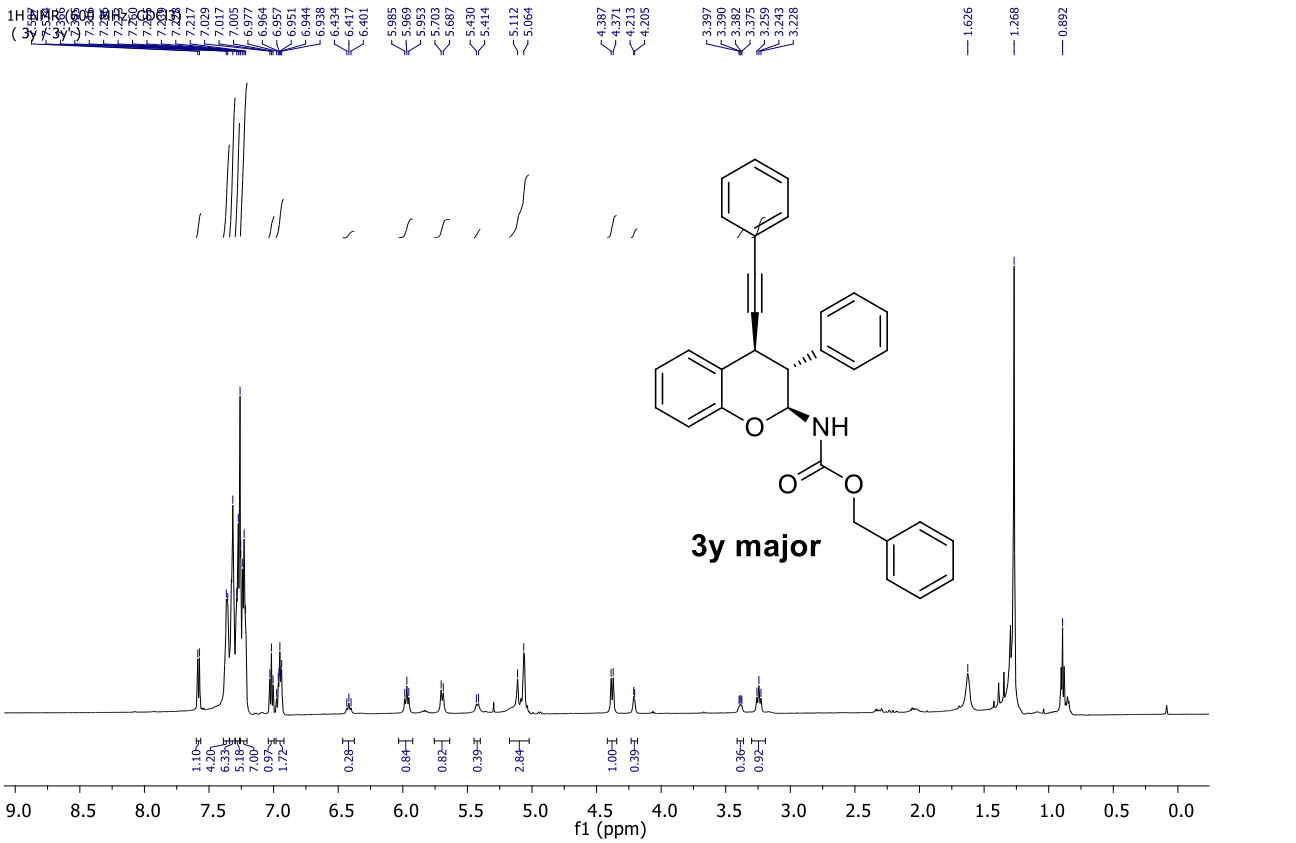

1H NMR (600 MHz, CDCl3)
(3v / 3v')
7.541
7.294
7.260
7.182
6.887
6.791
6.742
6.727
6.697
6.682
f1 (ppm)
6.198
6.177
6.162
5.992
5.342
5.082
5.062
4.289
4.271
4.217
4.208
3.730
3.125
3.108
3.092
f1 (ppm)
13C NMR (150 MHz, CDCl3)
(3v / 3v')
150.22
139.49
137.93
136.12
134.08
133.16
131.93
130.07
129.74
129.01
128.72
128.36
128.30
128.02
114.28
113.63
113.38
112.19
83.36
77.44
77.23
77.02
67.40
55.37
52.56
50.94
34.03
32.15
29.92
22.91
14.31
OMe
Br
O
NH
Br
O
O
3v major
f1 (ppm)

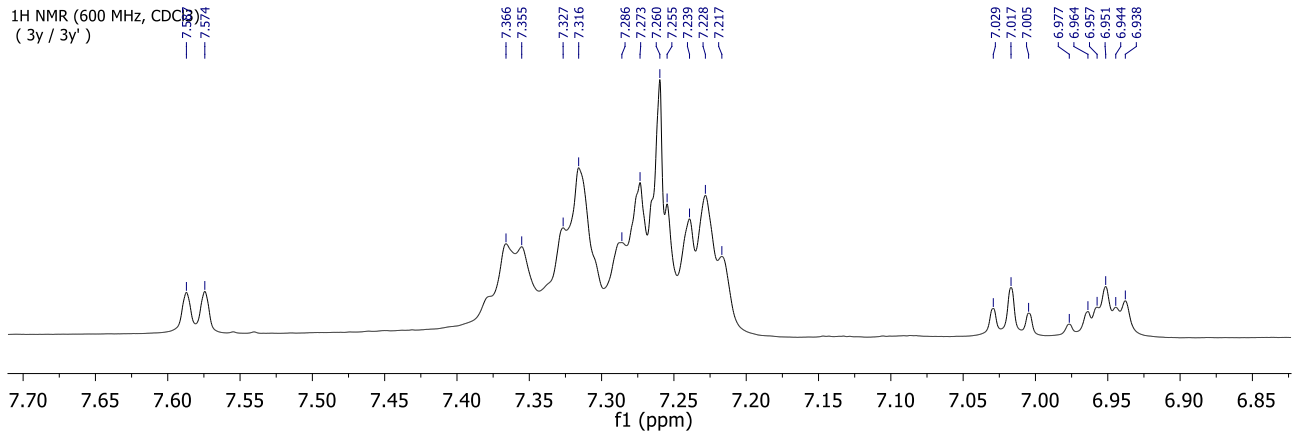

1H NMR (600 MHz, CDCl3)
(3w / 3w')
3w major
f1 (ppm)

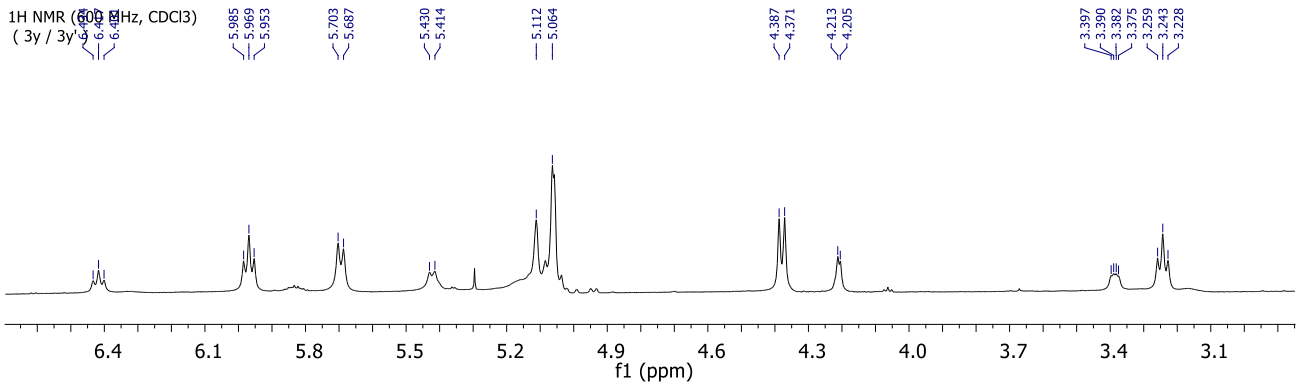

13C NMR (150 MHz, CDCl3)
(3w / 3w')
155.51
154.07
142.61
139.50
138.63
136.08
130.40
130.15
129.23
128.85
128.69
128.49
128.32
128.17
128.09
127.39
126.94
125.88
121.42
117.24
114.29
82.06
77.44
77.23
77.02
67.24
52.95
51.62
32.13
29.91
22.90
14.34
O
NH
O
O
3w major
f1 (ppm)

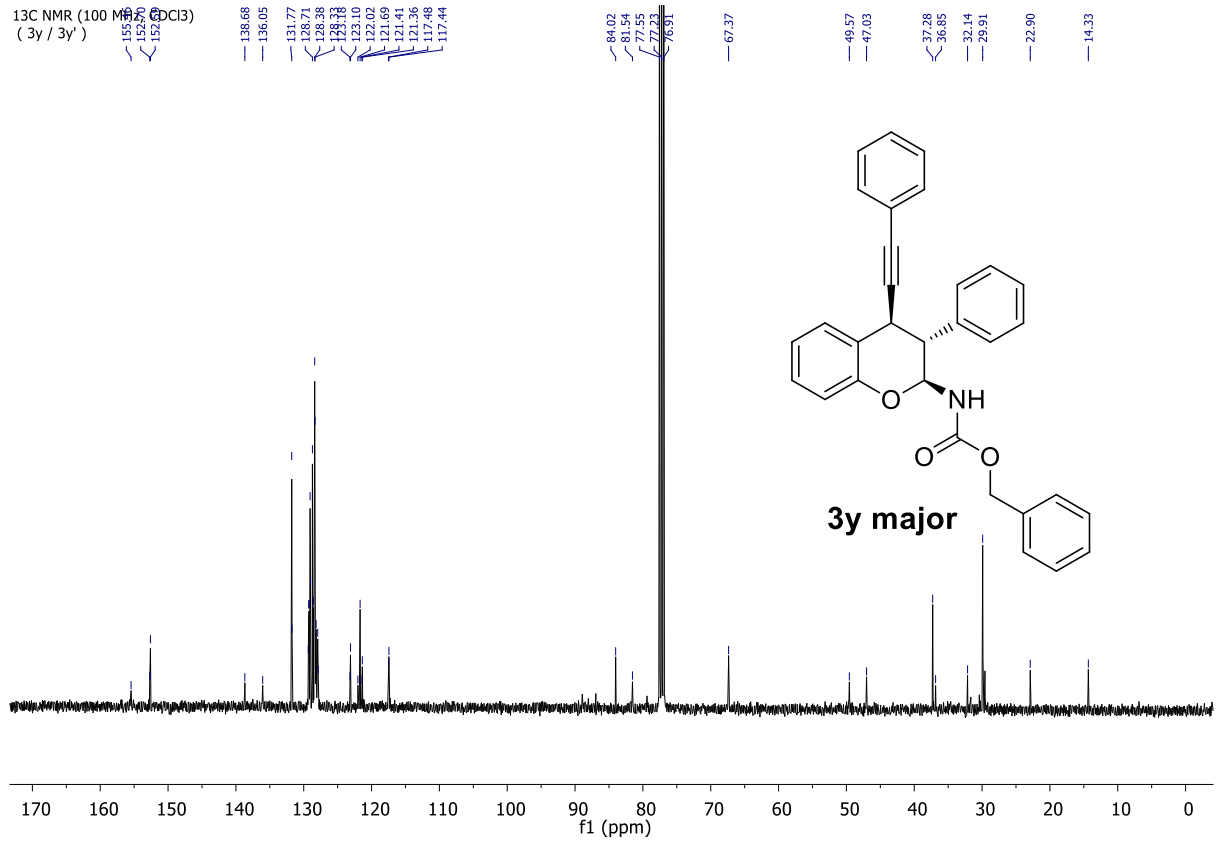

1H NMR (600 MHz, CDCl3)
(3x / 3x')
3.633
3.511
3.166
3.148
3.131
1.638
1.267
0.891
OMe
O
NH
O
O
3x major
4.01
8.37
1.13
1.08
1.57
1.84
0.59
1.05
1.00
0.81
0.68
0.81
0.99
0.99
0.51
0.44
0.51
0.79
1.23
2.70
1.00
0.46
3.08
1.50
0.88
f1 (ppm)


1H NMR (600 MHz, CDCl3)
(3x / 3x')
f1 (ppm)
13C NMR (150 MHz, CDCl3)
(3x / 3x')
f1 (ppm)
OMe
NH
O
O
O
3x major

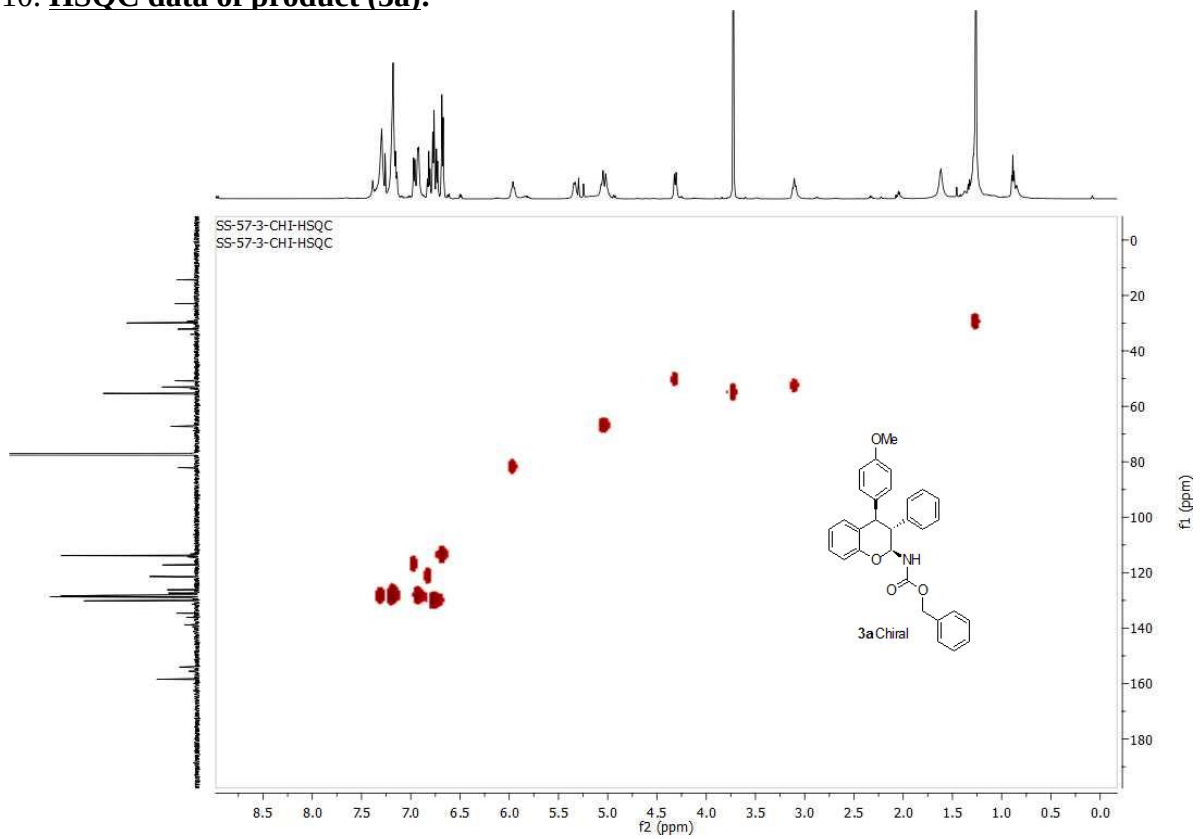

1H NMR (600 MHz, CDCl3)
(3y / 3y')
3y major
f1 (ppm)


1H NMR (600 MHz, CDCl3)
(3y / 3y')
f1 (ppm)

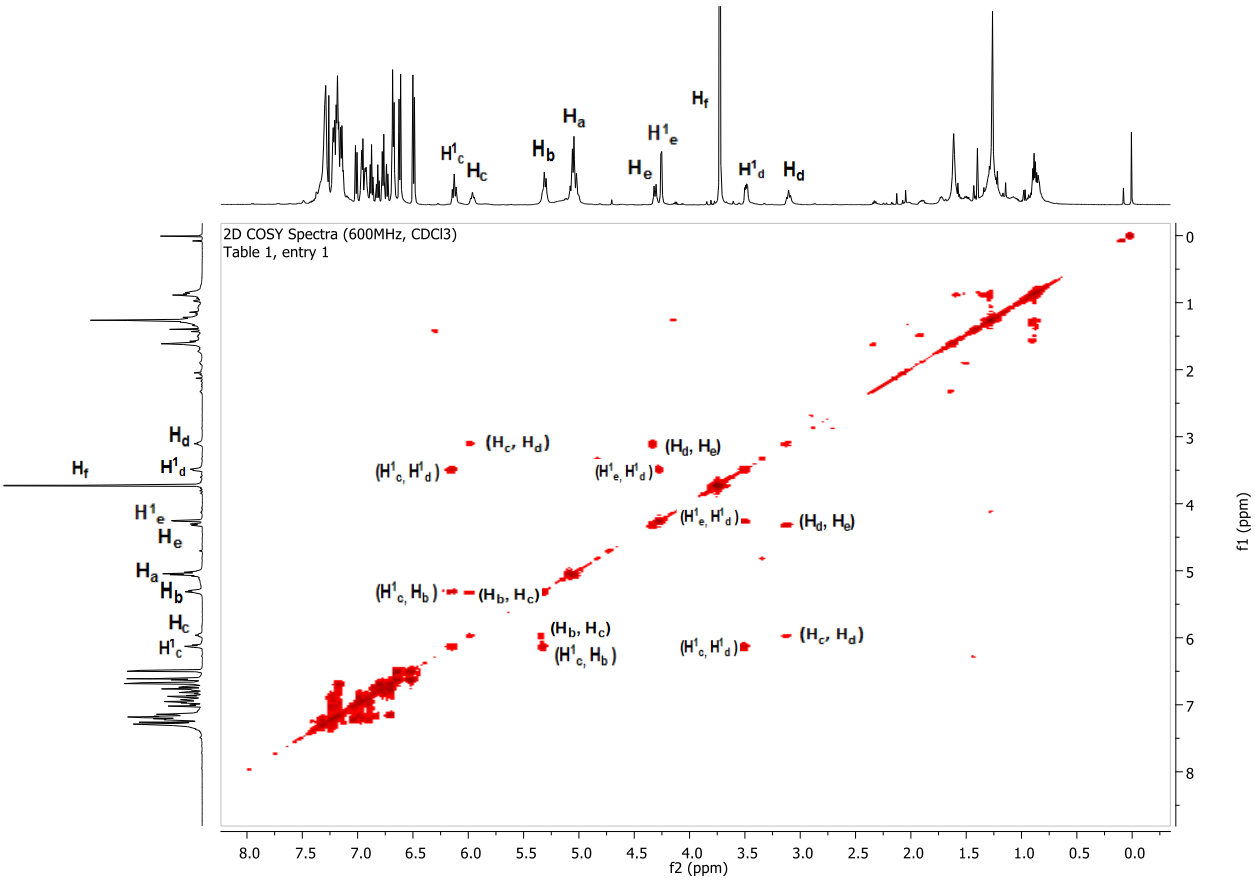

1H NMR (600 MHz, CDCl3)
(3y / 3y')
f1 (ppm)

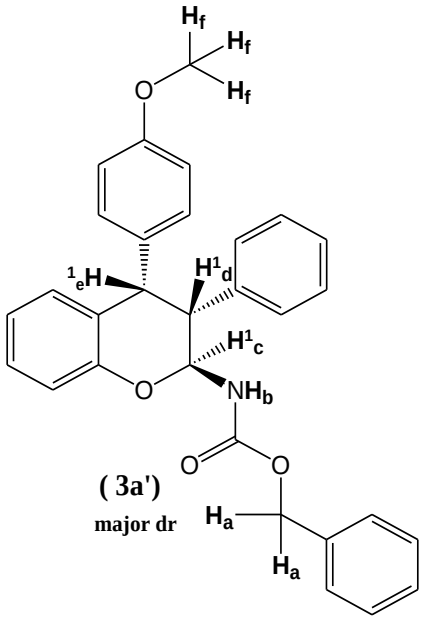


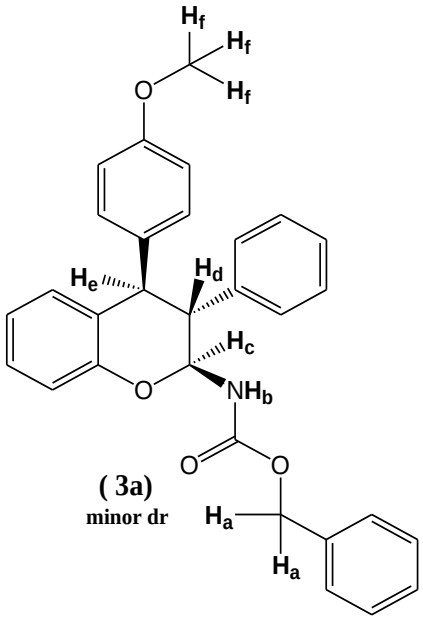
10. **HSQC data of product (3a):**

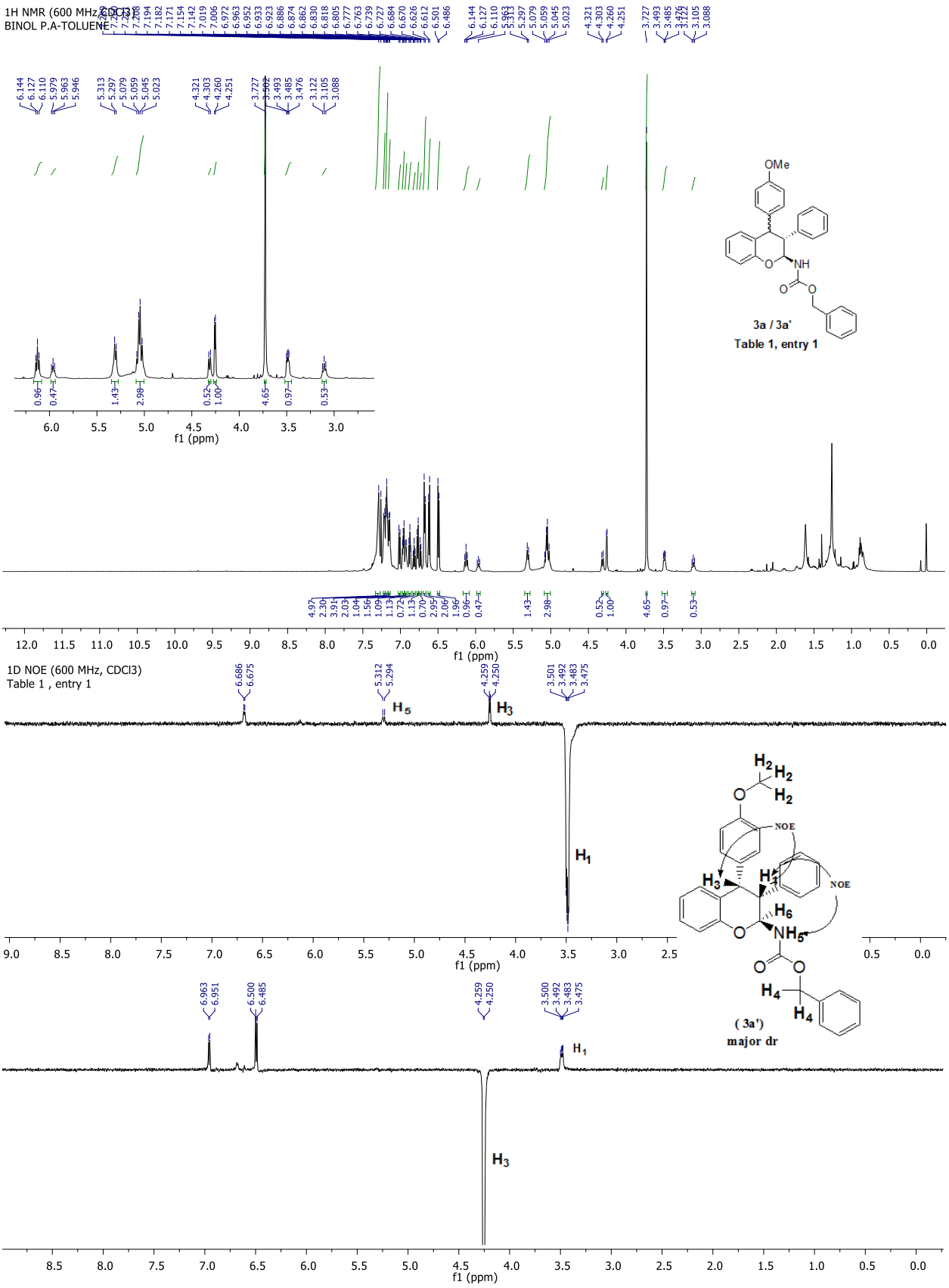


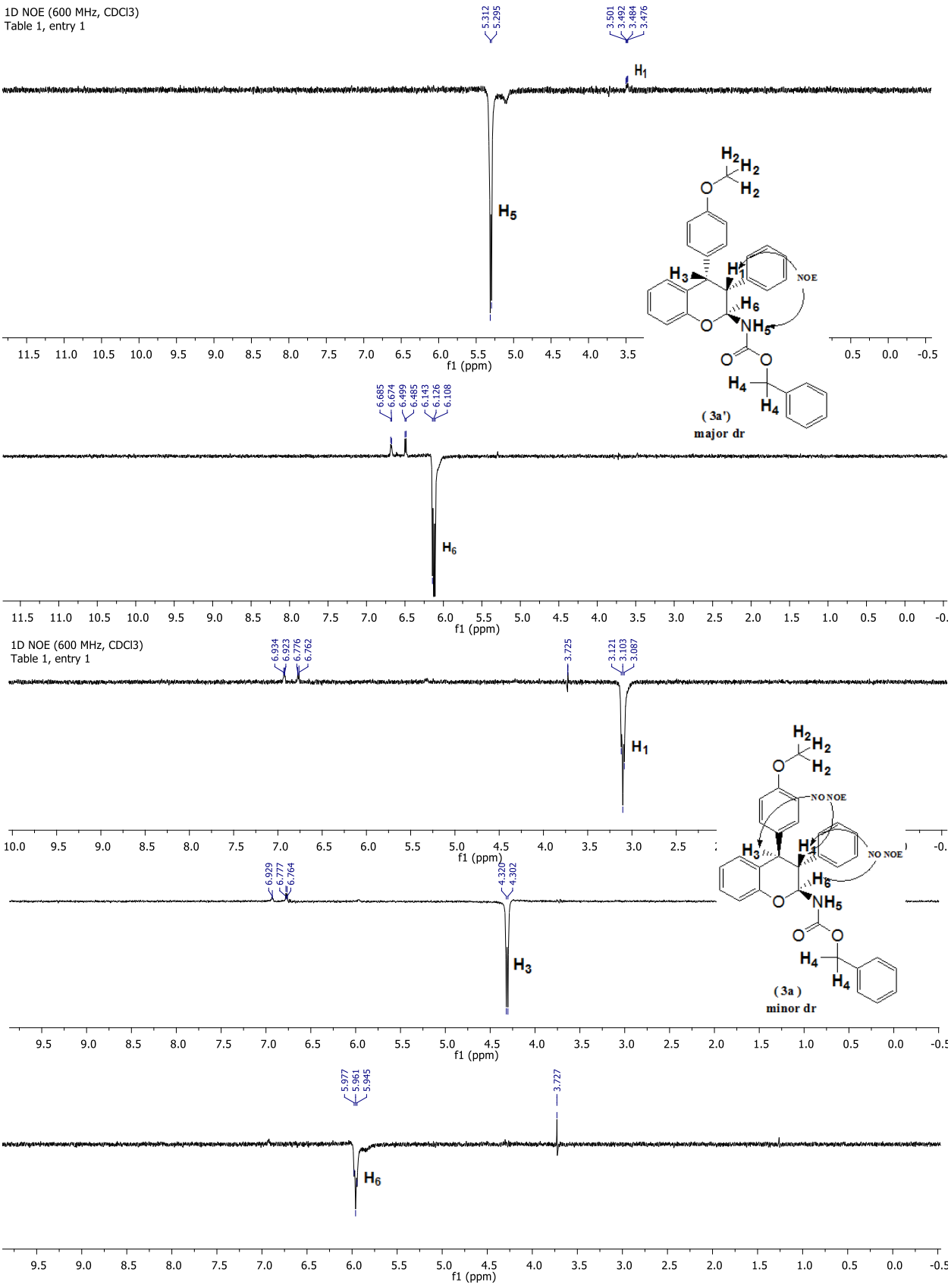
11. **<u>COSY and 1D NOE spectra for relative stereo chemistry of product (Table 1, entry 1) (3a/3a')</u>**



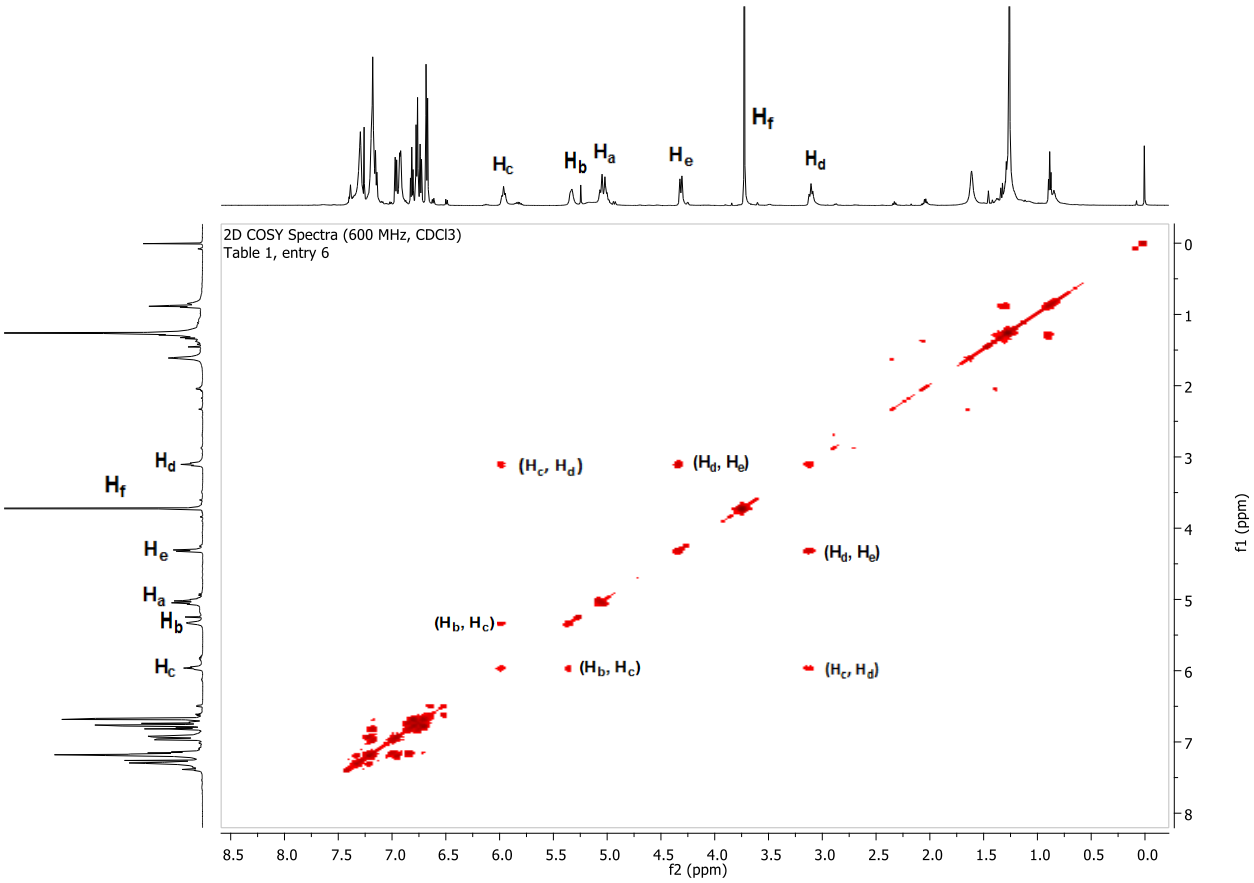


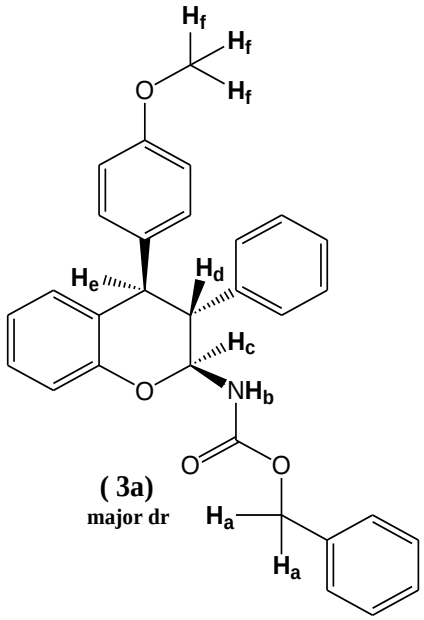



1H NMR (600 MHz, CDCl3)
BINOL P.A-TOLUENE
f1 (ppm)
OMe
NH
O
3a / 3a'
Table 1, entry 1
1D NOE (600 MHz, CDCl3)
Table 1 , entry 1
H5
H3
H1
NOE
H2
H6
H4
(3a')
major dr

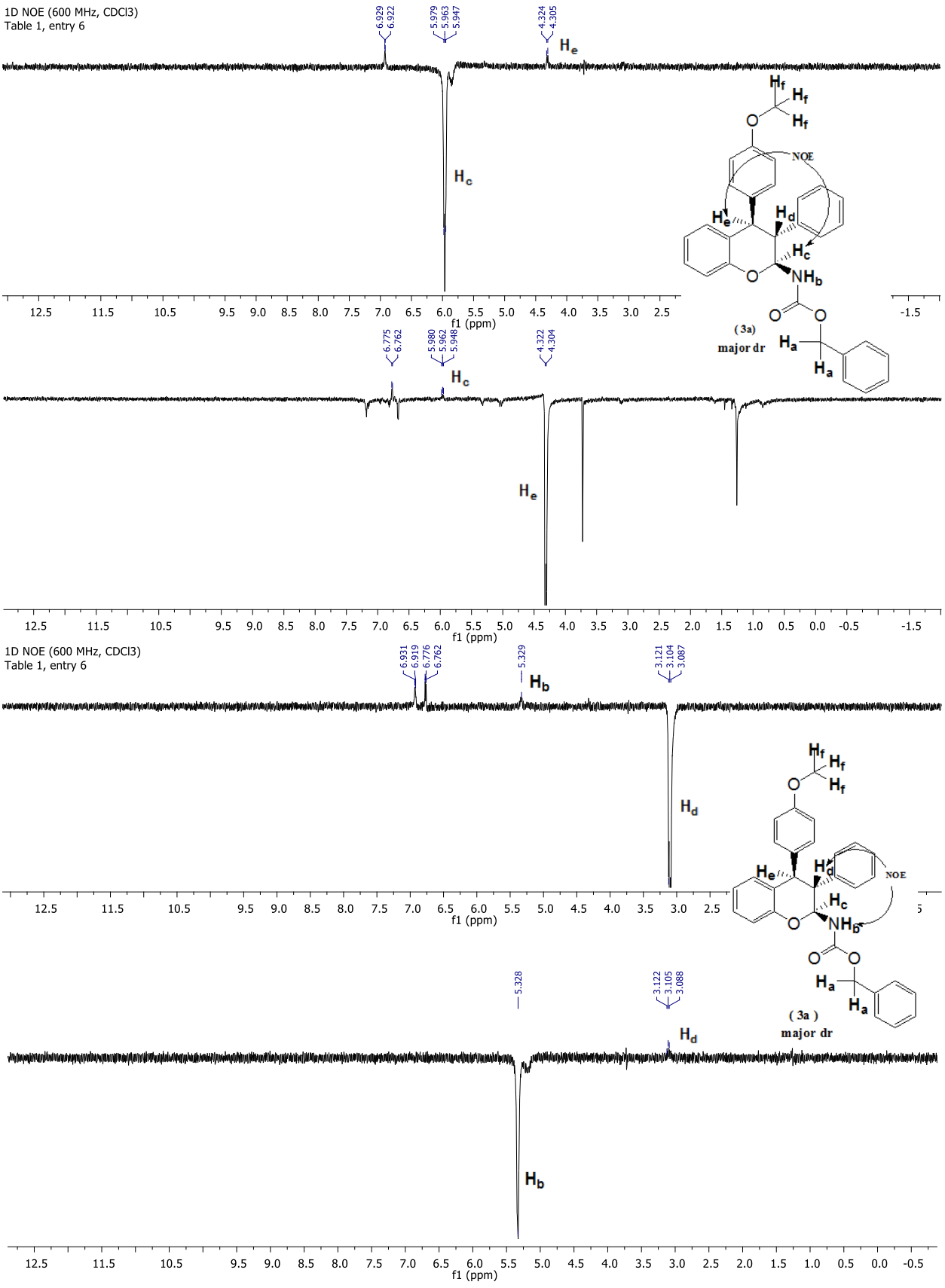

1D NOE (600 MHz, CDCl3)
Table 1, entry 1
5.312
5.295
3.501
3.492
3.484
3.476
H1
H5
f1 (ppm)
H2
H2
H2
O
H3
H1
NOE
H6
NH5
O
O
H4
H4
(3a')
major dr
6.685
6.674
6.499
6.485
6.143
6.126
6.108
H6
f1 (ppm)
1D NOE (600 MHz, CDCl3)
Table 1, entry 1
6.934
6.923
6.776
6.762
3.725
3.121
3.103
3.087
H1
f1 (ppm)
H2
H2
H2
O
NO NOE
H3
H1
NO NOE
H6
NH5
O
O
H4
H4
(3a)
minor dr
6.929
6.777
6.764
4.320
4.302
H3
f1 (ppm)
5.977
5.961
5.945
3.727
H6
f1 (ppm)

COSY and 1D NOE spectra for relative stereo chemistry of product (3a), (Table 1, entry 6)

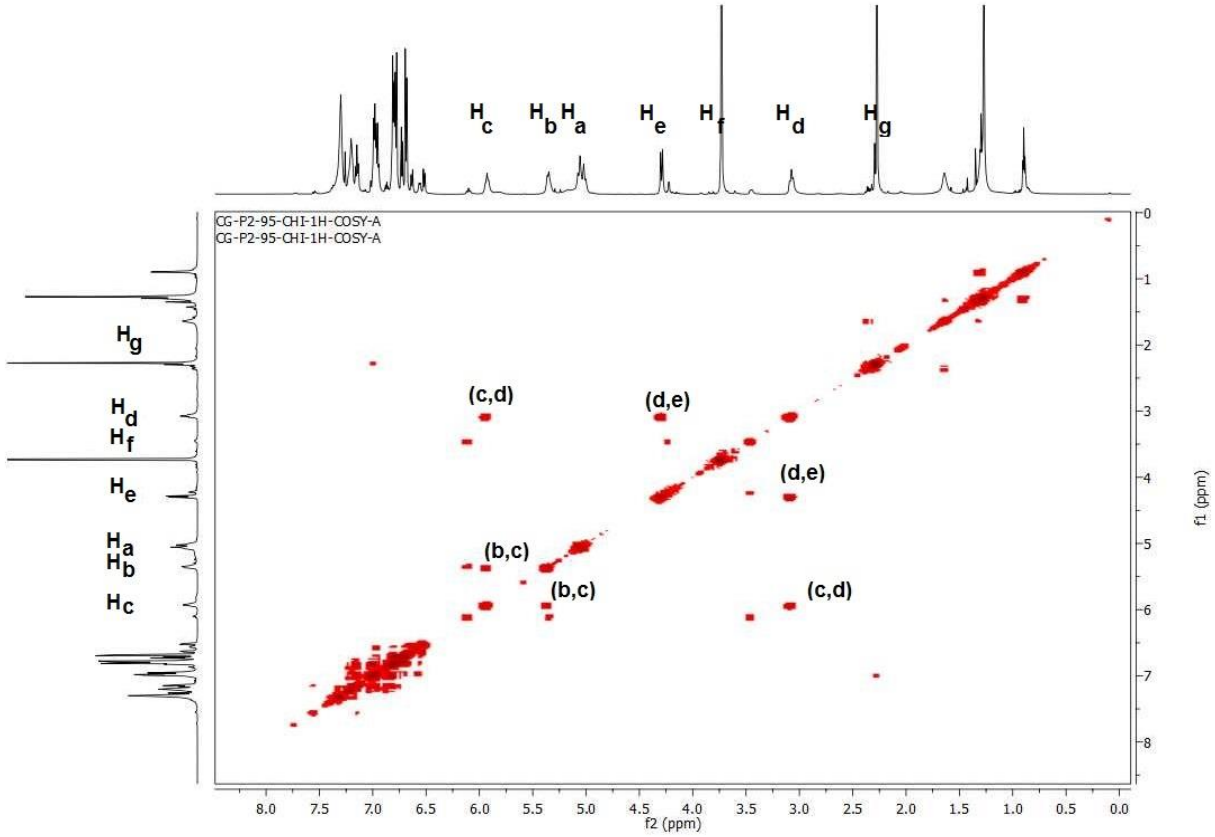


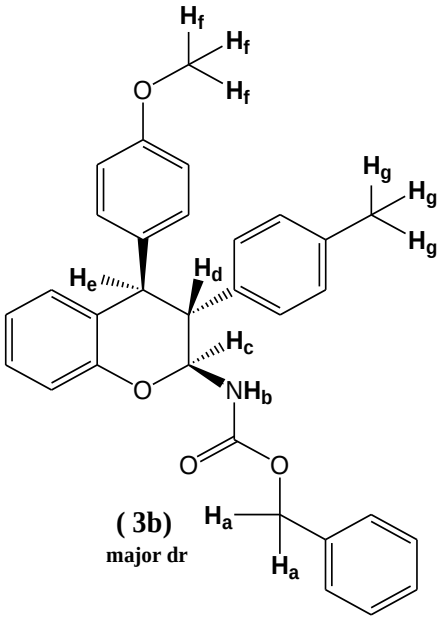


(3a)
major dr

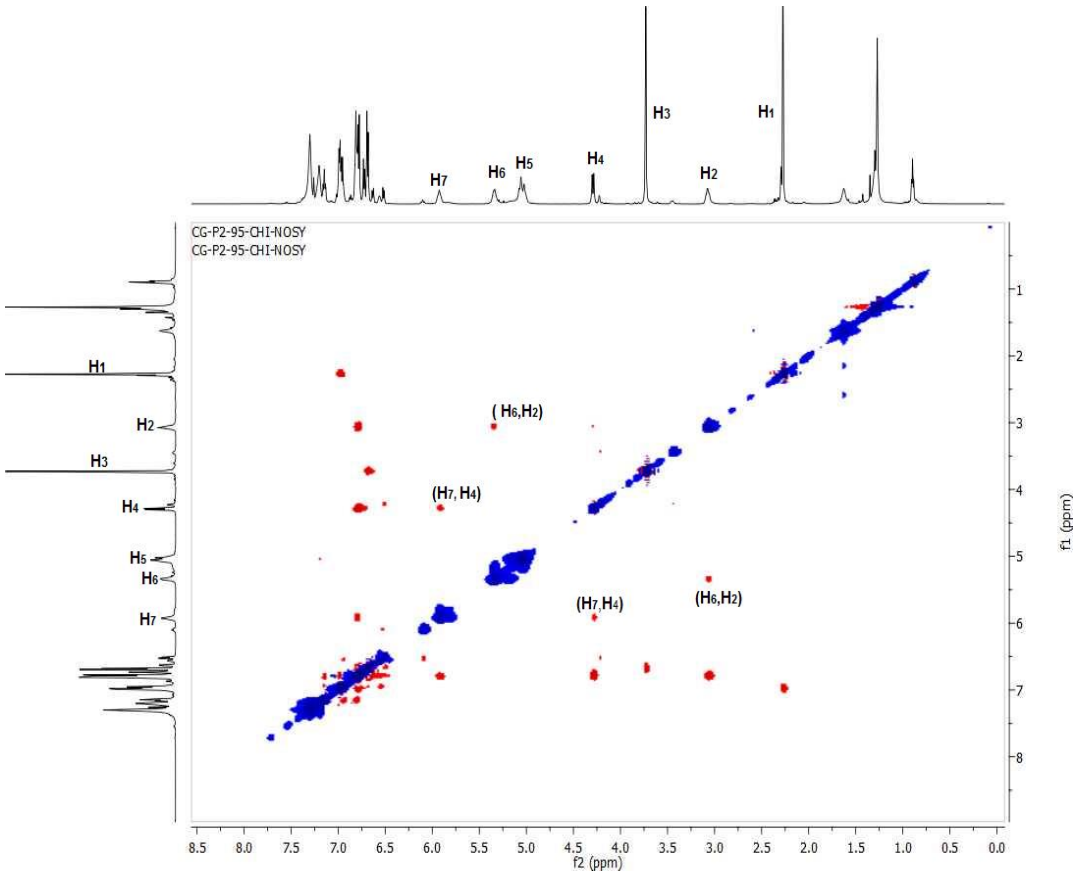

1D NOE (600 MHz, CDCl3)
Table 1, entry 6
6.929
6.922
5.979
5.963
5.947
4.324
4.305
He
Hc
Hf
Hf
Hf
O
NOE
He
Hd
Hc
O
NHb
O
O
(3a)
major dr
Ha
Ha
f1 (ppm)
6.775
6.762
5.980
5.962
5.948
4.322
4.304
Hc
He
1D NOE (600 MHz, CDCl3)
Table 1, entry 6
6.931
6.919
6.776
6.762
5.329
Hb
3.121
3.104
3.087
Hd
5.328
3.122
3.105
3.088
Hd
Hb
(3a)
major dr

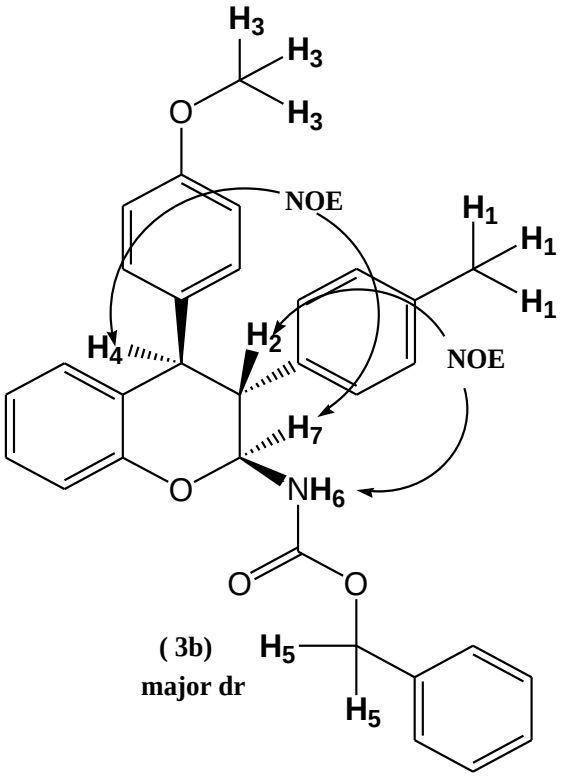
COSY and NOESY spectra for relative stereo chemistry of product (3b)





(3b)
major dr

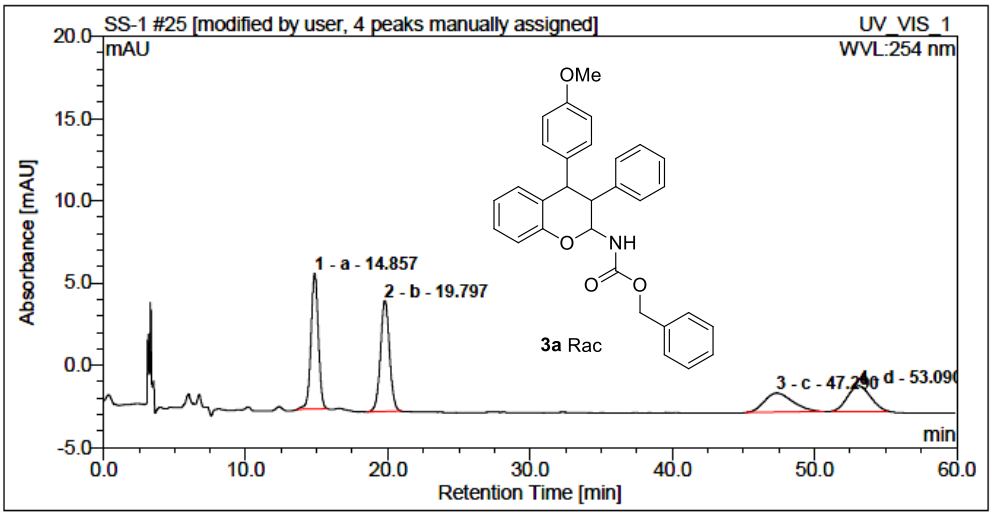

CG-P2-95-CH1-NOSY
CG-P2-95-CH1-NOSY
H3
H1
H7
H6
H5
H4
H2
(H6,H2)
(H7, H4)
(H7, H4)
(H6,H2)
f2 (ppm)
f1 (ppm)


H3
H3
H3
O
NOE
H1
H1
H1
H4
H2
NOE
H7
O
NH6
O
O
H5
H5

(3b)
major dr

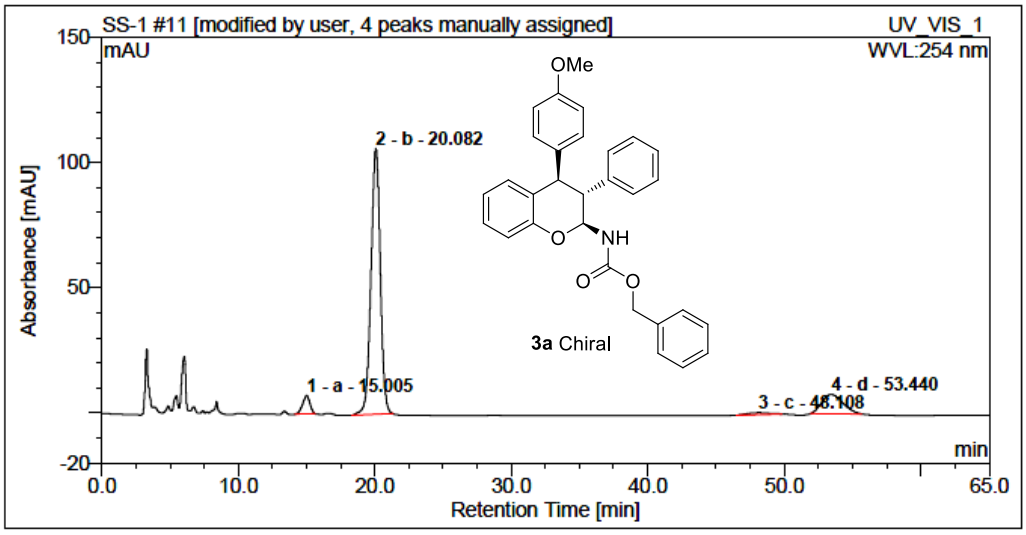
12. **HPLC Chromatogram:**

SS-57-RAC-IC



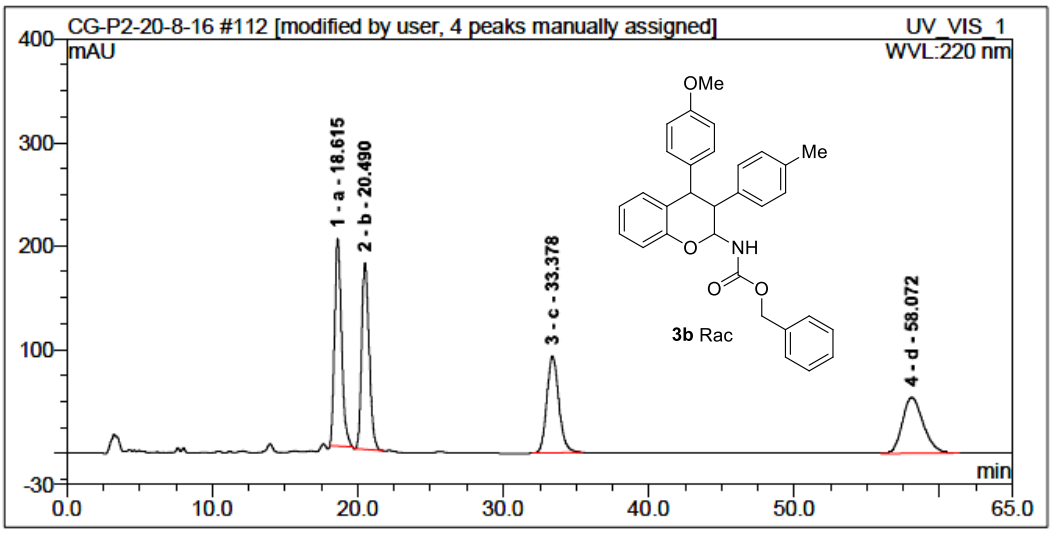
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	14.86	4.923752	32.0145676	8.24147	n.a.
2	b	19.80	4.9754	32.35038778	6.75735	n.a.
3	c	47.29	2.682175	17.43967992	1.16426	n.a.
4	d	53.09	2.798	18.19536471	1.524	n.a.

SS-57-CHI-IC



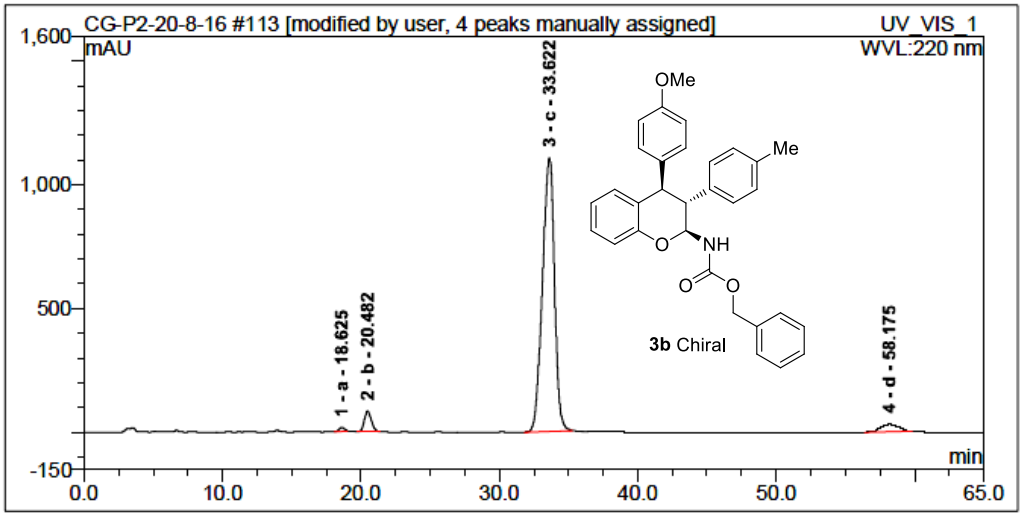
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	15.01	4.623583	4.472750321	7.364	n.a.
2	b	20.08	83.6376	80.90914224	106.2197	n.a.
3	c	48.11	1.329568	1.286194158	0.75086	n.a.
4	d	53.44	13.781	13.33191328	7.645	n.a.

P2-90-RAC-IA



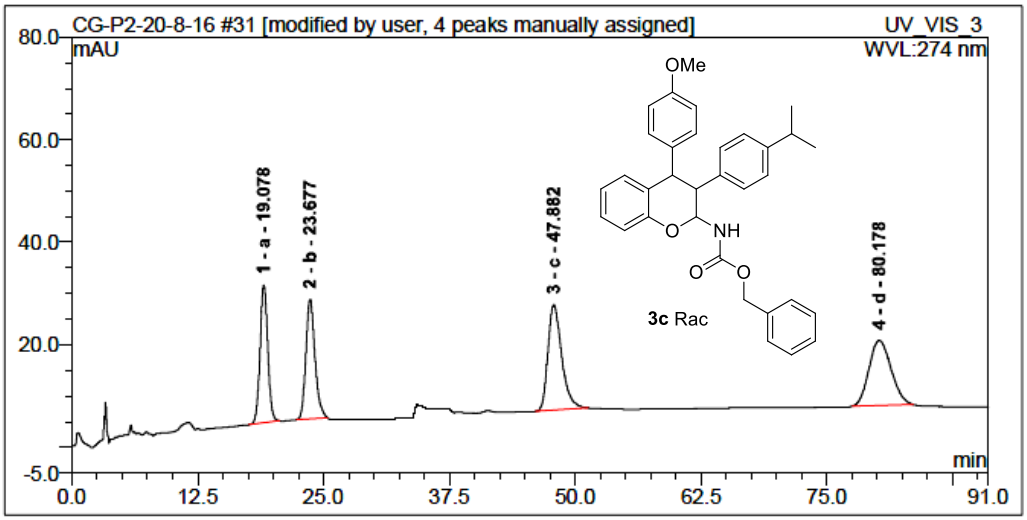
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	18.62	111.2762	27.86351322	200.5874	n.a.
2	b	20.49	107.369	26.88515748	180.3395	n.a.
3	c	33.38	90.33453	22.6197375	93.59877	n.a.
4	d	58.07	90.382	22.6315918	54.159	n.a.

P2-90-CHI-IA



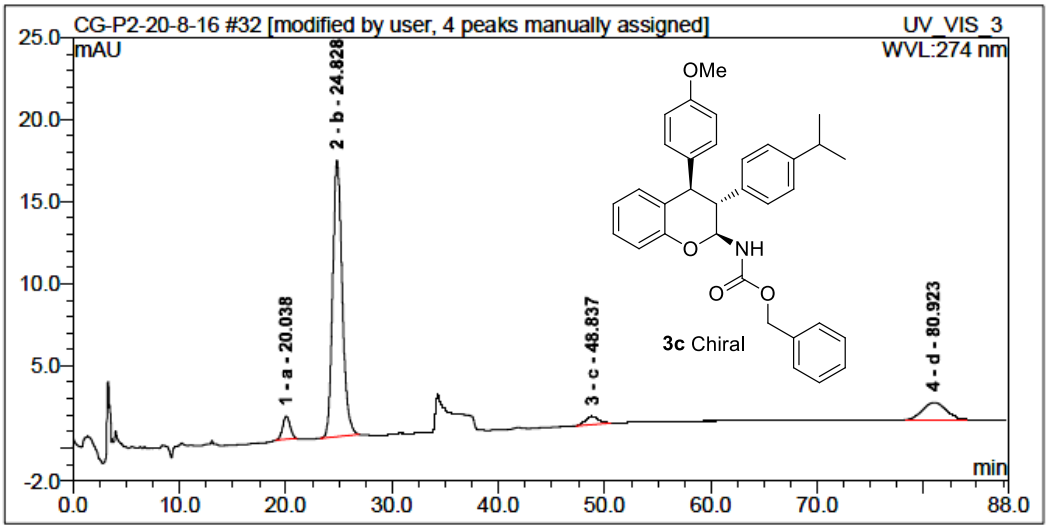
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	18.63	7.463579	0.614450587	15.95955	n.a.
2	b	20.48	49.41242	4.067953051	84.40162	n.a.
3	c	33.62	1111.585	91.51293701	1105.709	n.a.
4	d	58.18	46.214	3.80465935	30.689	n.a.

P2-118-RAC-IC



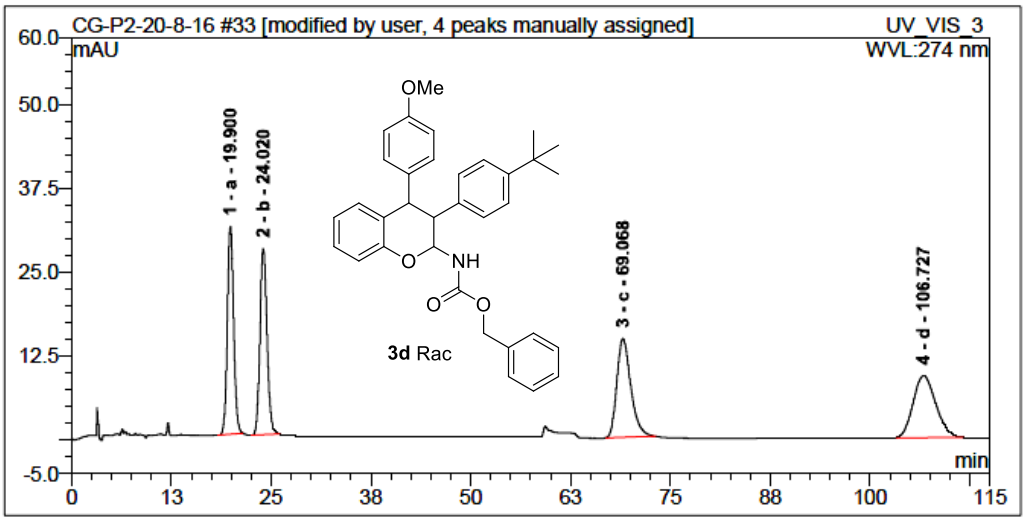
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	19.08	23.90745	21.12592507	26.87354	n.a.
2	b	23.68	24.39004	21.55237399	23.27715	n.a.
3	c	47.88	32.67547	28.87382799	20.57732	n.a.
4	d	80.18	32.193	28.44787295	12.662	n.a.

P2-118-CHI-IC



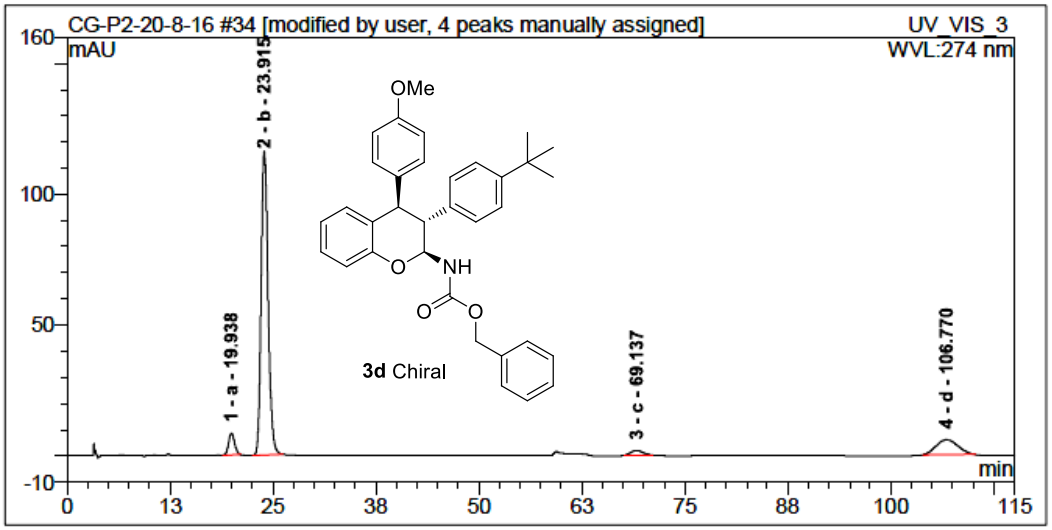
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	20.04	1.13983	5.194469459	1.39749	n.a.
2	b	24.83	17.44175	79.48605306	16.82985	n.a.
3	c	48.84	0.727118	3.313645701	0.49335	n.a.
4	d	80.92	2.634	12.00583178	1.046	n.a.

P2-119-RAC-IC



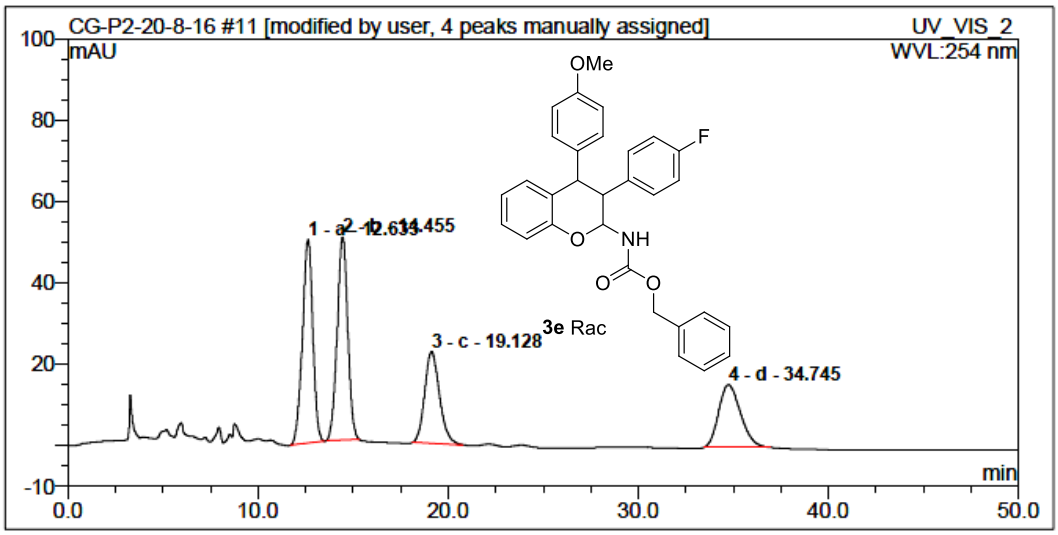
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	19.90	28.15766	24.07601897	31.01408	n.a.
2	b	24.02	28.45199	24.32768432	27.79985	n.a.
3	c	69.07	29.98324	25.63697075	14.73311	n.a.
4	d	106.73	30.360	25.95932596	9.243	n.a.

P2-119-CHI-IC



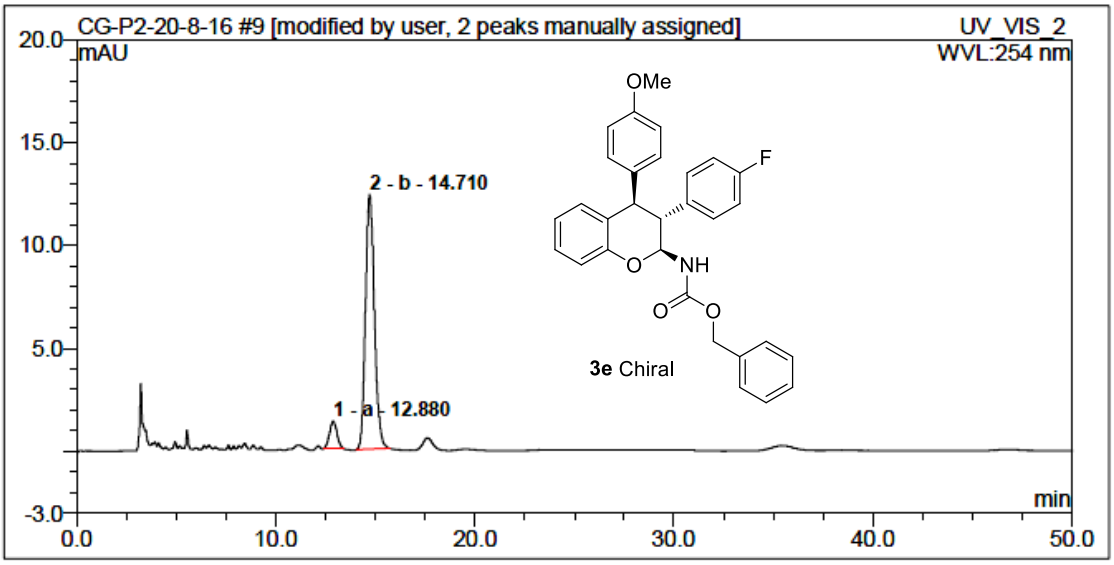
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	19.94	6.943547	4.928667947	8.34682	n.a.
2	b	23.92	113.2806	80.40881082	116.0163	n.a.
3	c	69.14	3.10418	2.203408777	1.76834	n.a.
4	d	106.77	17.552	12.45911245	5.717	n.a.

CG-P2-94-RAC-IC



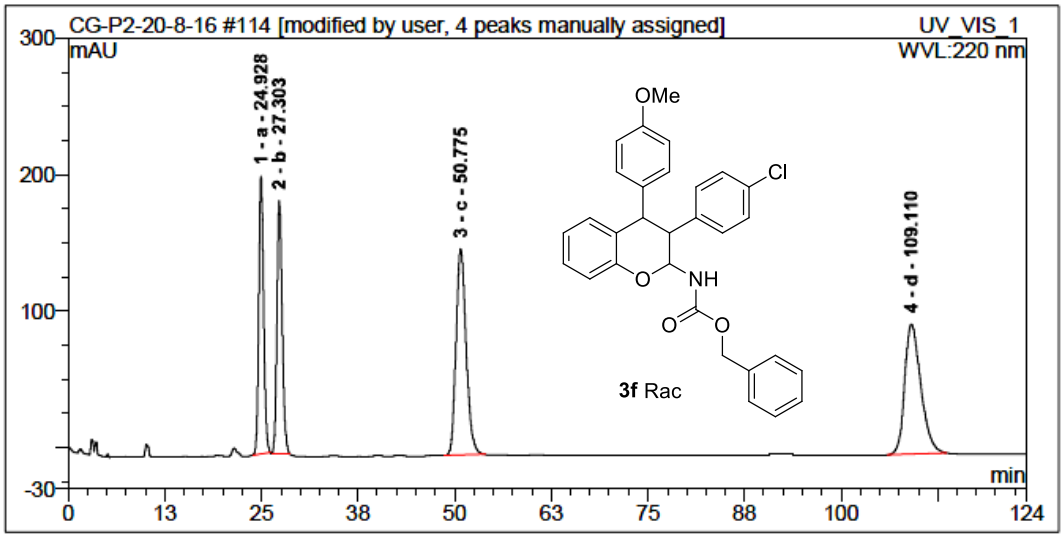
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	12.63	31.77363	30.33795604	50.14325	n.a.
2	b	14.46	32.11443	30.66336476	49.92436	n.a.
3	c	19.13	20.40716	19.48507418	22.57763	n.a.
4	d	34.75	20.437	19.51360502	15.382	n.a.

CG-P2-94-CHI-IC



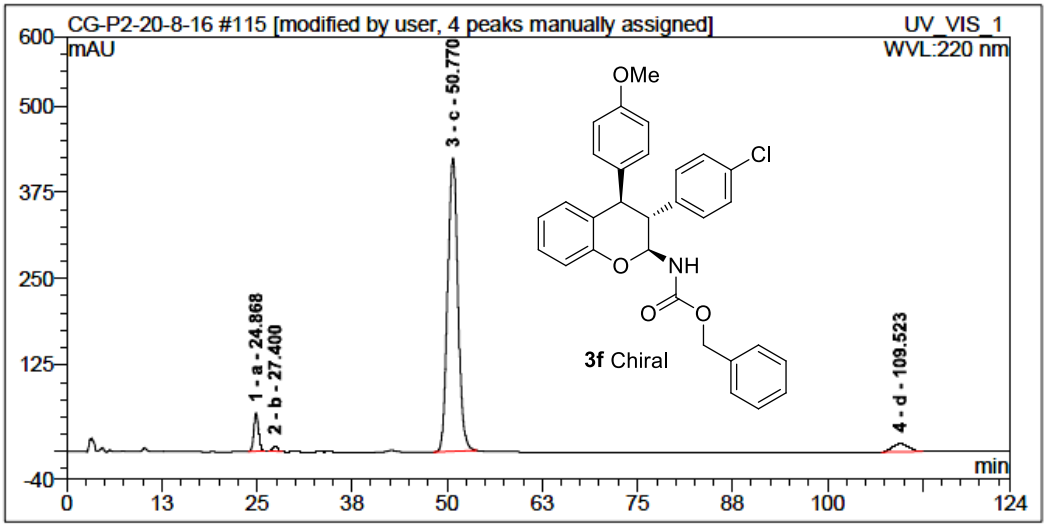
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	12.88	0.564734	8.053995858	1.3117	n.a.
2	b	14.71	6.447	91.94600414	12.379	n.a.

P2-4-CI-RAC-IA



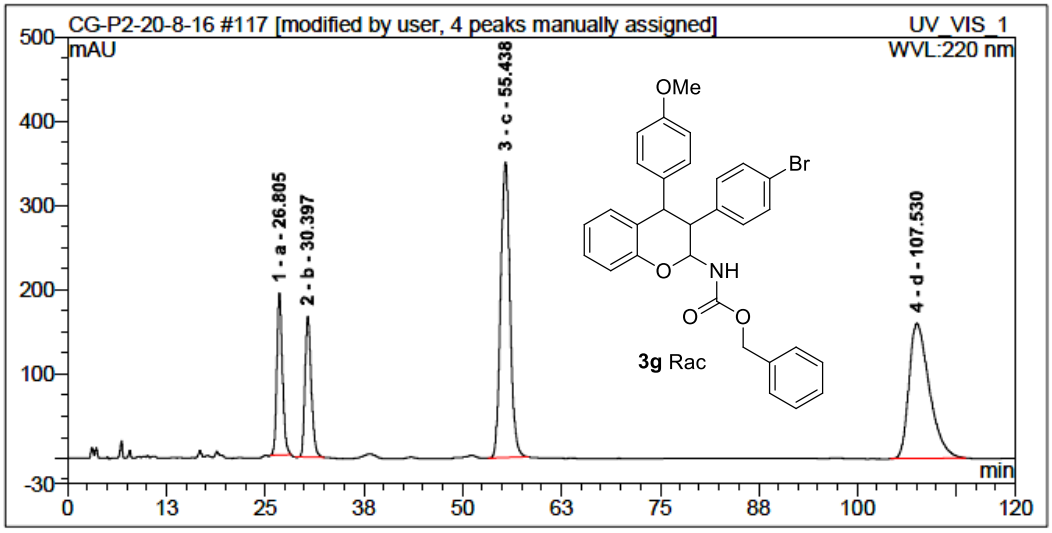
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	24.93	148.0496	19.61442014	203.7602	n.a.
2	b	27.30	146.6591	19.43020275	185.2691	n.a.
3	c	50.78	229.0662	30.34793624	150.9963	n.a.
4	d	109.11	231.025	30.60744086	95.175	n.a.

P2-4-CI-CHI-IA



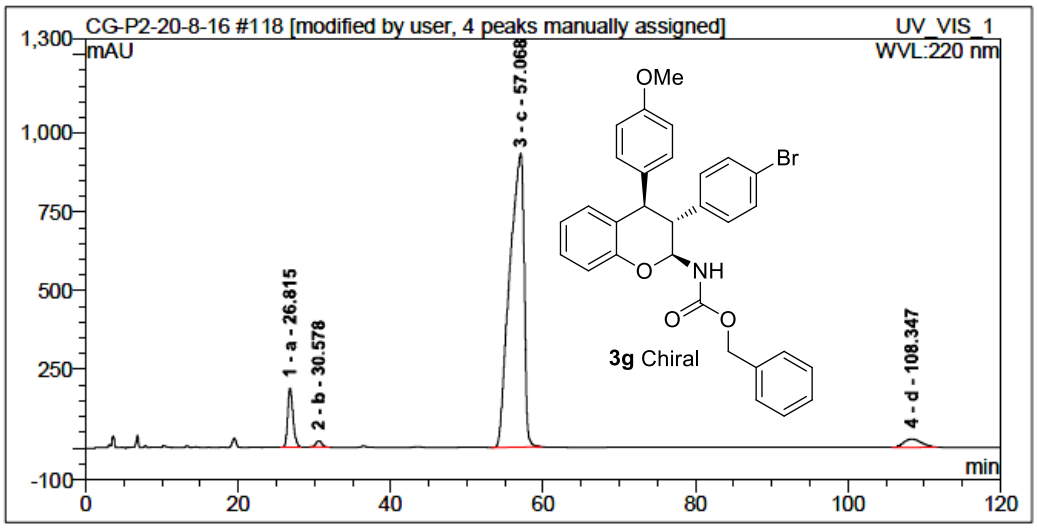
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	24.87	40.42519	5.4598504	55.78375	n.a.
2	b	27.40	6.344182	0.8568489824	8.22721	n.a.
3	c	50.77	665.6114	89.89787616	424.6394	n.a.
4	d	109.52	28.028	3.785424457	12.034	n.a.

P2-4-Br-RAC-IA



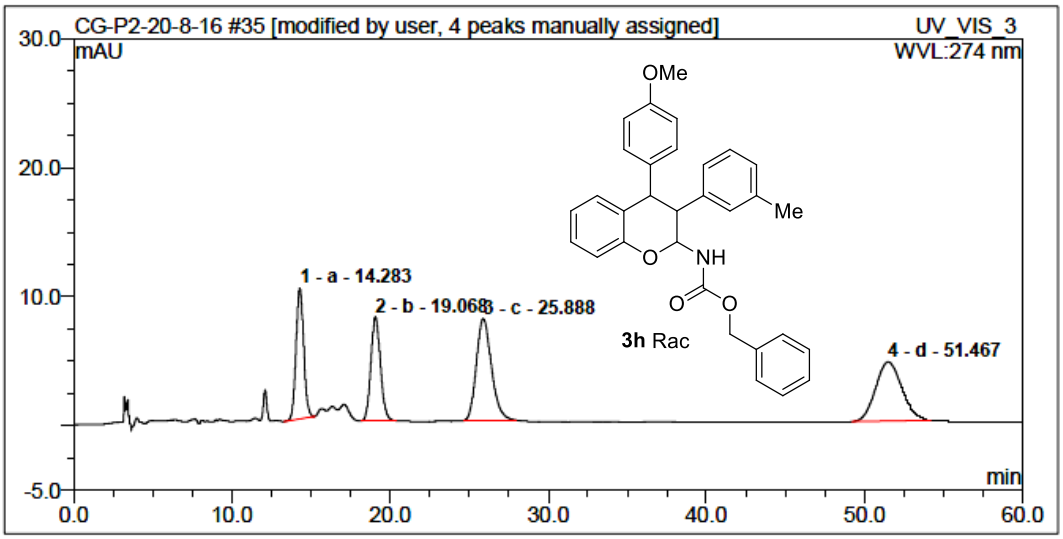
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	26.81	156.5554	12.27670464	192.3728	n.a.
2	b	30.40	154.0161	12.07758383	167.0487	n.a.
3	c	55.44	484.1258	37.96400547	351.3359	n.a.
4	d	107.53	480.526	37.68170605	160.531	n.a.

P2-4-Br-CHI-IA



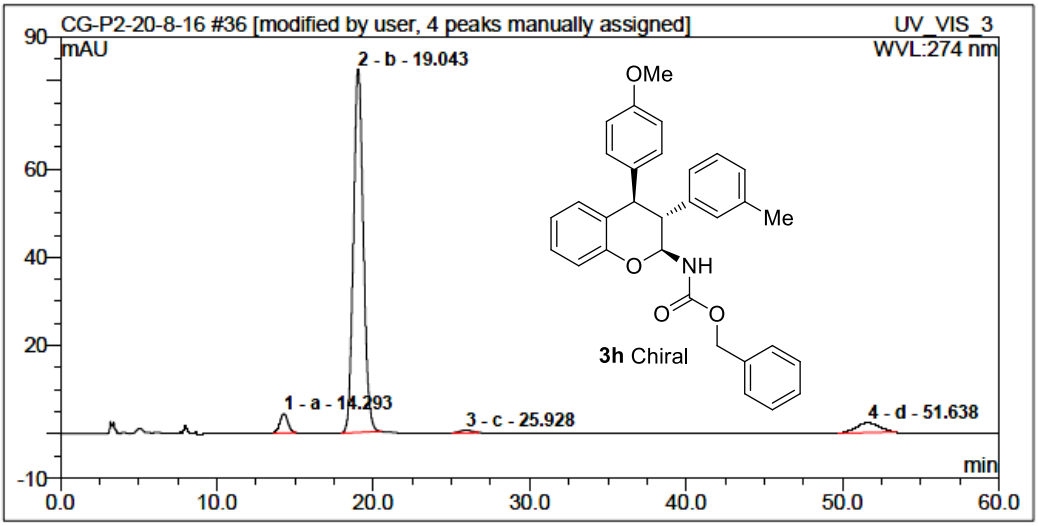
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	26.82	151.9812	6.684382704	186.8681	n.a.
2	b	30.58	18.65361	0.8204163376	19.74184	n.a.
3	c	57.07	2032.319	89.38469344	932.6104	n.a.
4	d	108.35	70.723	3.110507522	26.400	n.a.

CG-P2-116-RAC-IC



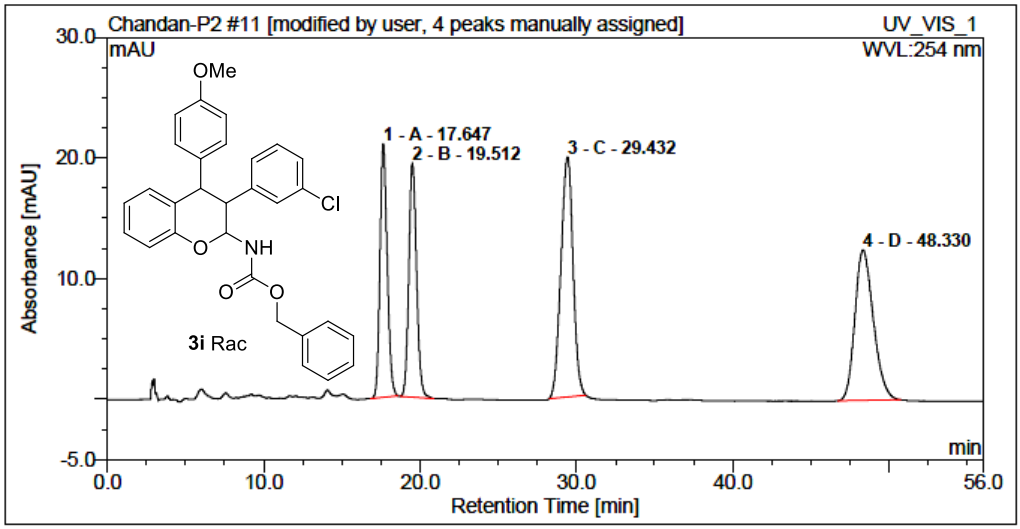
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	14.28	5.702252	19.70840519	10.14883	n.a.
2	b	19.07	5.664433	19.57769223	8.06497	n.a.
3	c	25.89	8.745237	30.22571746	7.88011	n.a.
4	d	51.47	8.821	30.48818512	4.568	n.a.

CG-P2-116-CHI-IC



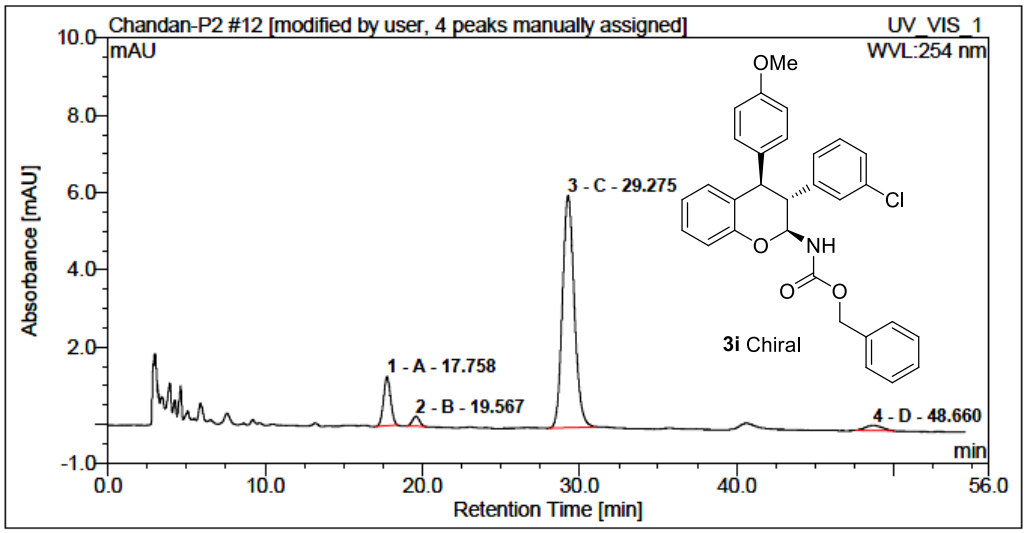
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	14.29	2.581352	3.818377377	4.34313	n.a.
2	b	19.04	60.56322	89.58610924	82.40843	n.a.
3	c	25.93	0.524569	0.7759508608	0.57698	n.a.
4	d	51.64	3.934	5.819562518	2.179	n.a.

CG-P2-3-Cl-RAC-IA



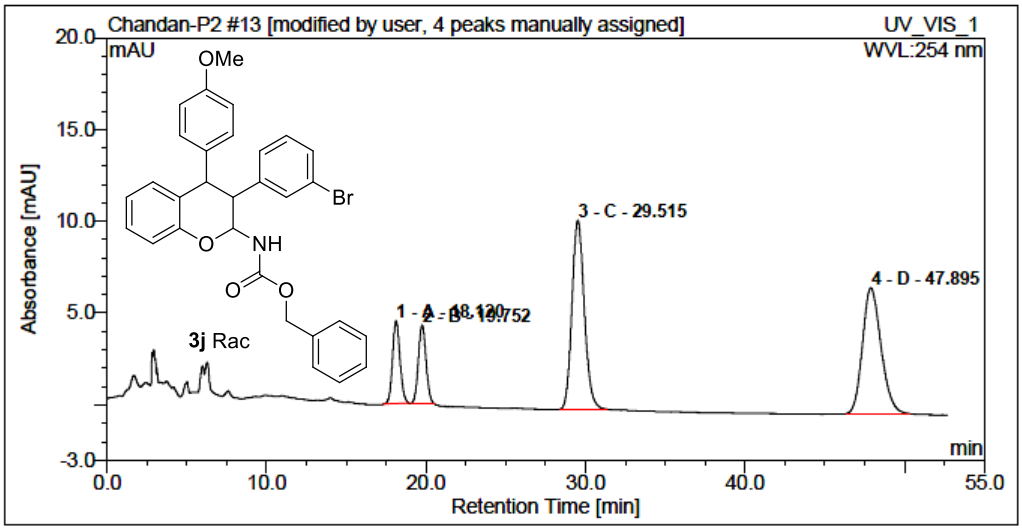
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	A	17.65	11.29361	19.69576151	21.00427	n.a.
2	B	19.51	11.12418	19.4002911	19.38132	n.a.
3	C	29.43	17.84009	31.11266225	19.8574	n.a.
4	D	48.33	17.082	29.79128514	12.451	n.a.

CG-P2-3-Cl-CHI-IA



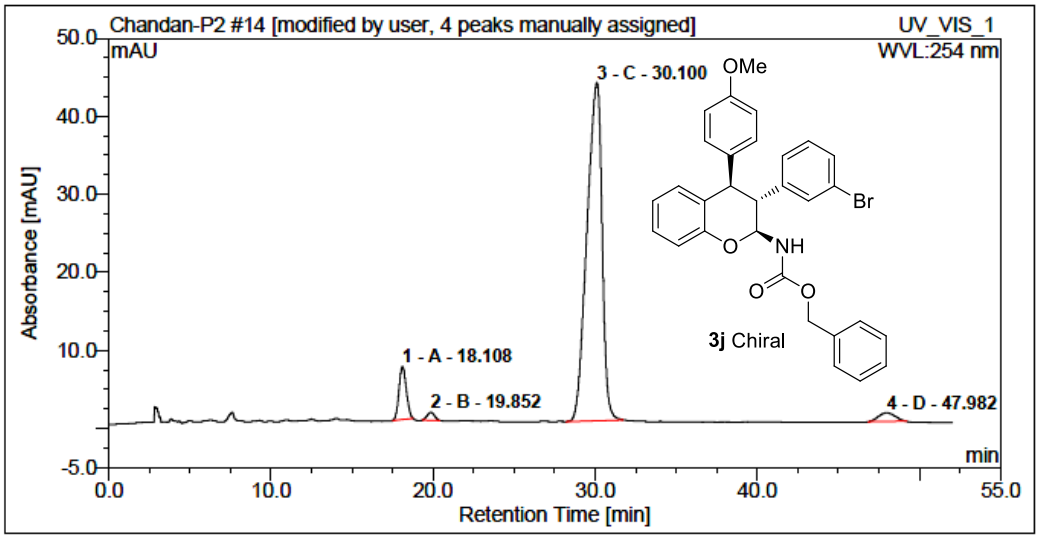
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	A	17.76	0.666523	10.69907697	1.27349	n.a.
2	B	19.57	0.131742	2.11473516	0.25702	n.a.
3	C	29.28	5.265687	84.52516869	6.00873	n.a.
4	D	48.66	0.166	2.661019174	0.135	n.a.

CG-P2-120-RAC-IA



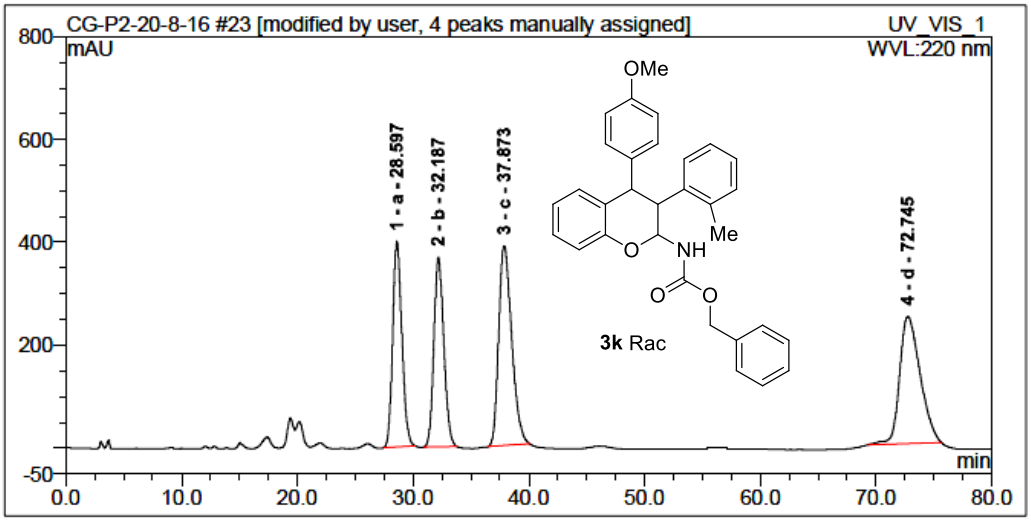
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	A	18.12	2.433539	10.44255962	4.49546	n.a.
2	B	19.75	2.375028	10.19148148	4.25907	n.a.
3	C	29.52	9.260104	39.73603186	10.29364	n.a.
4	D	47.90	9.235	39.62992704	6.850	n.a.

CG-P2-120-CHI-IA



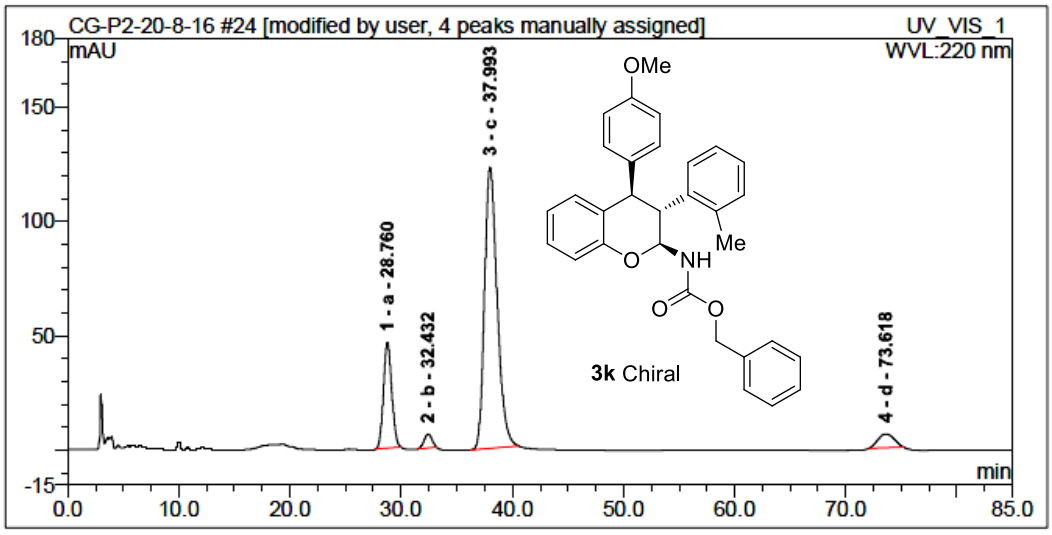
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	A	18.11	3.525821	6.776238368	6.78591	n.a.
2	B	19.85	0.531681	1.021832404	1.03218	n.a.
3	C	30.10	46.64533	89.64718009	43.25883	n.a.
4	D	47.98	1.329	2.554749136	1.115	n.a.

P2-115-RAC-IA



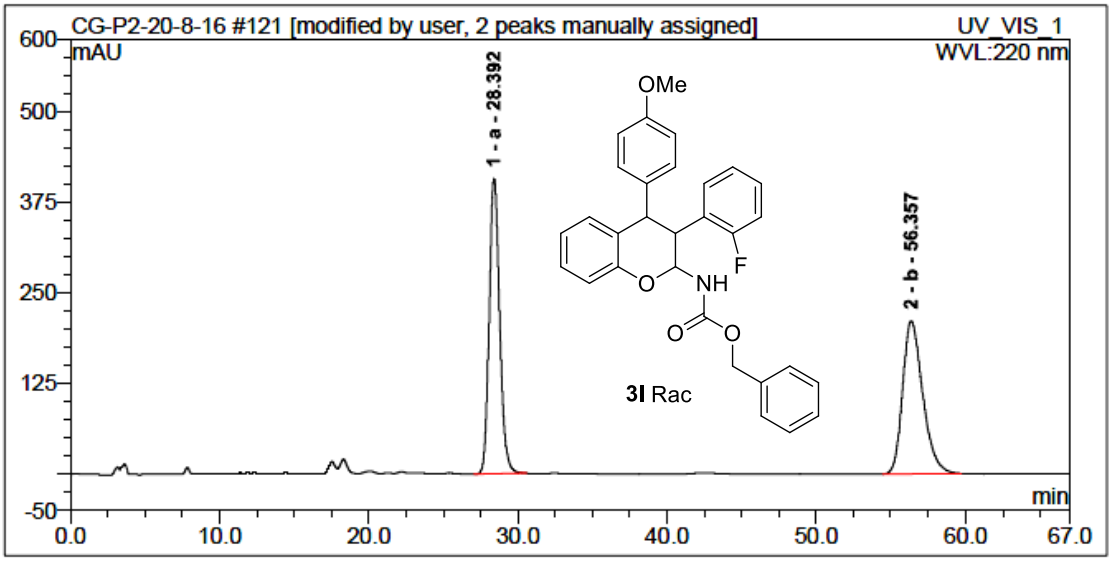
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	28.60	367.9948	21.02953021	399.8376	n.a.
2	b	32.19	367.2679	20.98799162	369.2401	n.a.
3	c	37.87	507.5938	29.0070946	388.9667	n.a.
4	d	72.75	507.039	28.97538357	247.474	n.a.

P2-115-CHI-IA



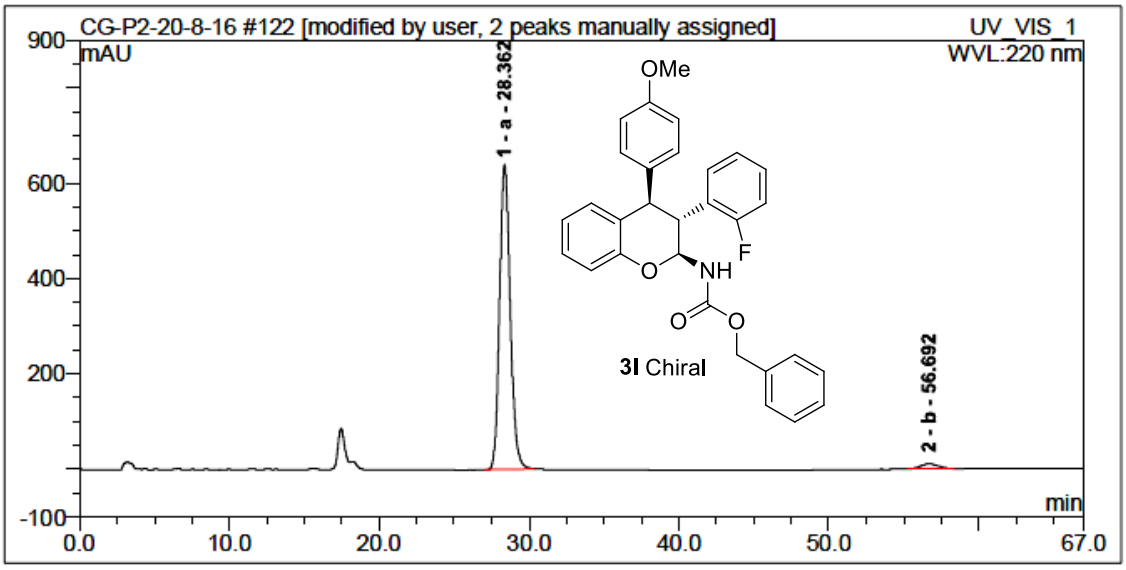
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	28.76	39.84976	18.38879231	46.21871	n.a.
2	b	32.43	4.939181	2.279200452	6.01822	n.a.
3	c	37.99	161.7102	74.62166627	122.923	n.a.
4	d	73.62	10.208	4.710340967	6.092	n.a.

P2-125-RAC-IA



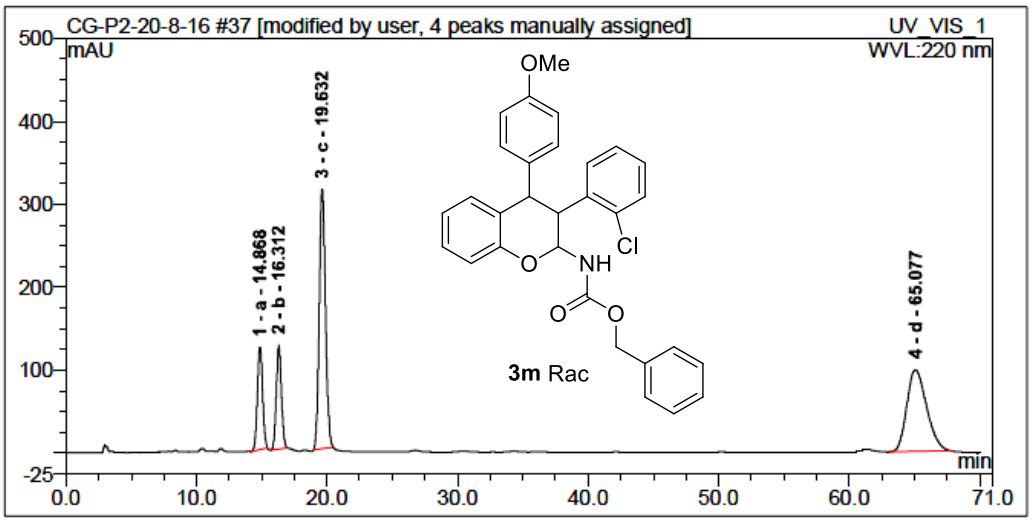
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	28.39	330.5729	50.09363685	407.1227	n.a.
2	b	56.36	329.337	49.90636315	210.862	n.a.

P2-125-CHI-IA



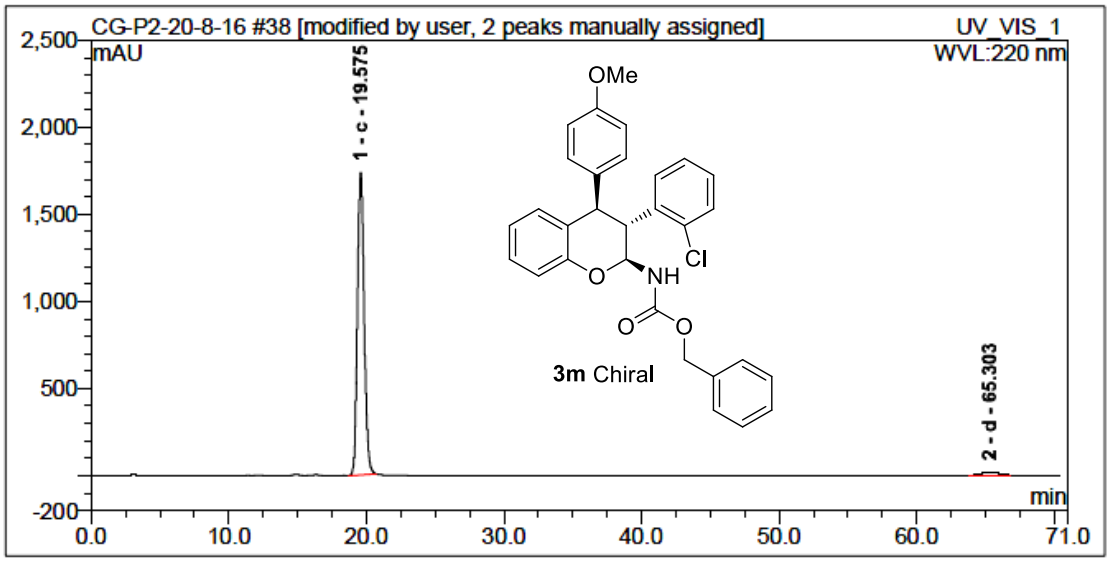
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	28.36	525.4879	97.27833622	639.5804	n.a.
2	b	56.69	14.702	2.721663784	10.320	n.a.

P2-123-RAC-IA



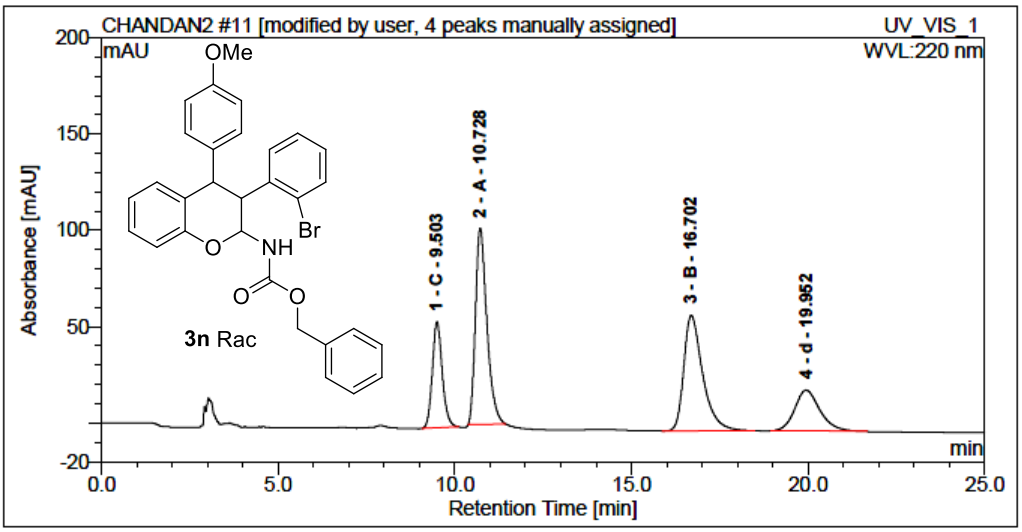
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	14.87	57.11314	12.37340689	122.9452	n.a.
2	b	16.31	57.23118	12.39898069	125.5152	n.a.
3	c	19.63	173.2538	37.53497361	312.6897	n.a.
4	d	65.08	173.982	37.69263881	98.800	n.a.

P2-123-CHI-IA



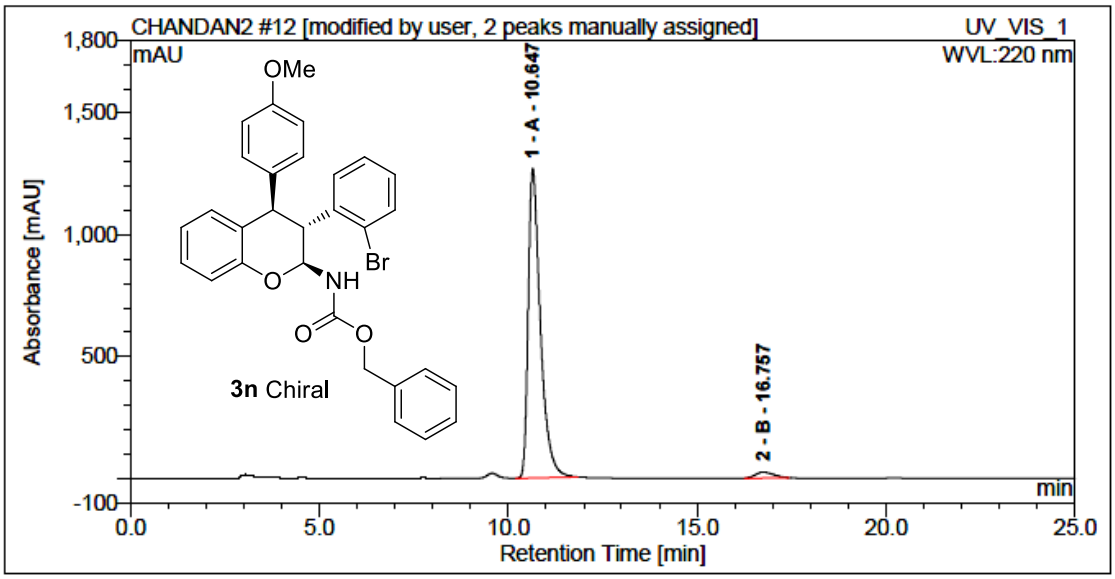
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	c	19.58	981.9319	97.10596771	1735.308	n.a.
2	d	65.30	29.264	2.894032292	19.107	n.a.

P2-124-RAC-IB-10%



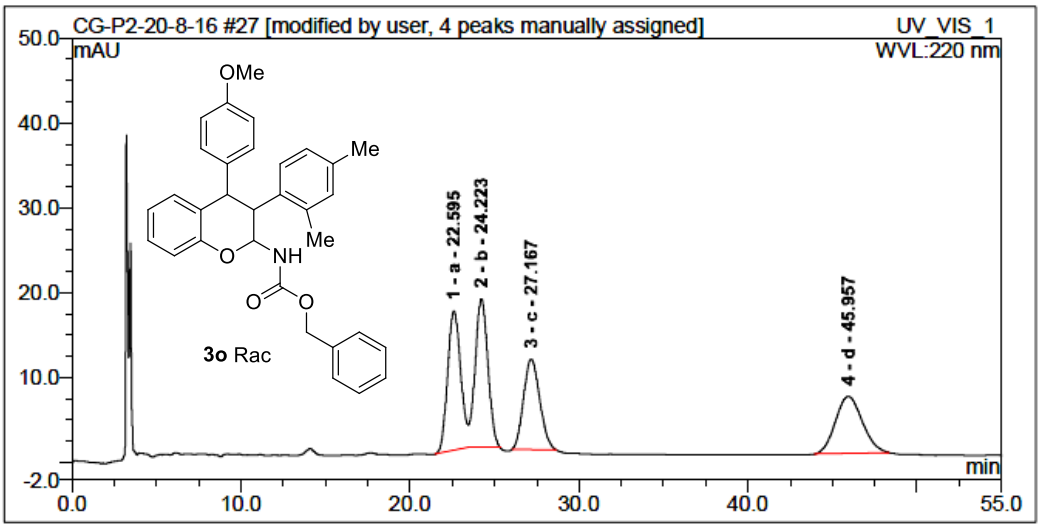
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	C	9.50	17.90306	16.14172743	55.08396	n.a.
2	A	10.73	38.10233	34.35376126	101.7302	n.a.
3	B	16.70	37.27505	33.60787627	60.00693	n.a.
4	d	19.95	17.631	15.89663504	21.222	n.a.

P2-124-CHI-IB-10%



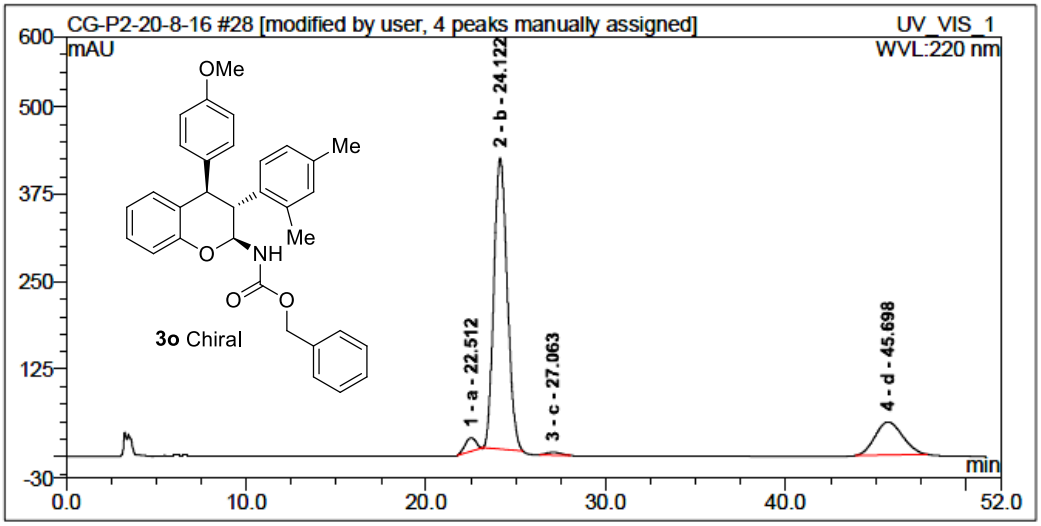
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	A	10.65	474.1742	97.39590396	1271.7	n.a.
2	B	16.76	12.678	2.604096036	23.287	n.a.

P2-117-RAC-IC-220nm



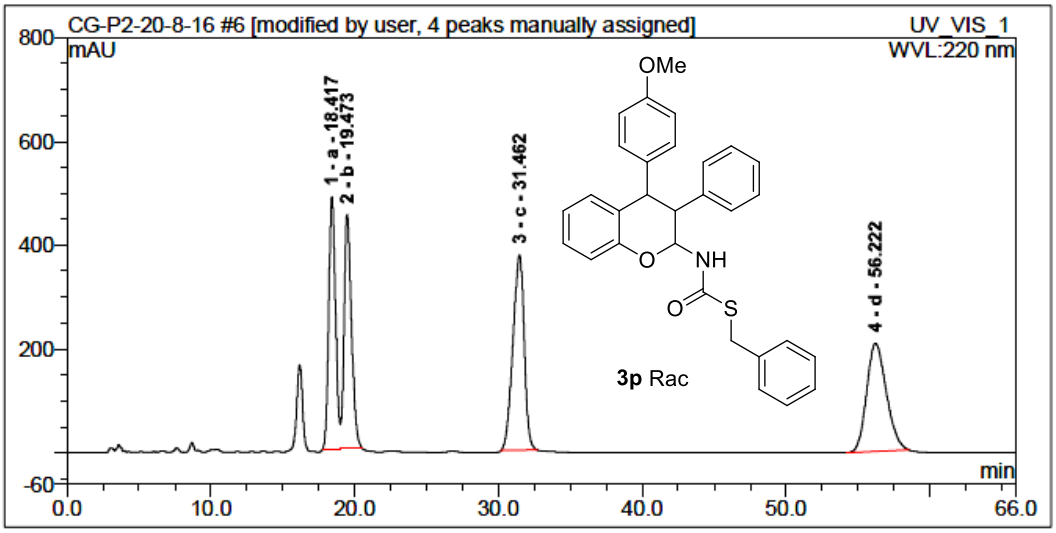
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	22.60	14.78724	27.27064381	16.43579	n.a.
2	b	24.22	15.15087	27.94123432	17.47955	n.a.
3	c	27.17	11.90276	21.95107653	10.66413	n.a.
4	d	45.96	12.383	22.83704534	6.702	n.a.

P2-117-CHI-IC-220nm



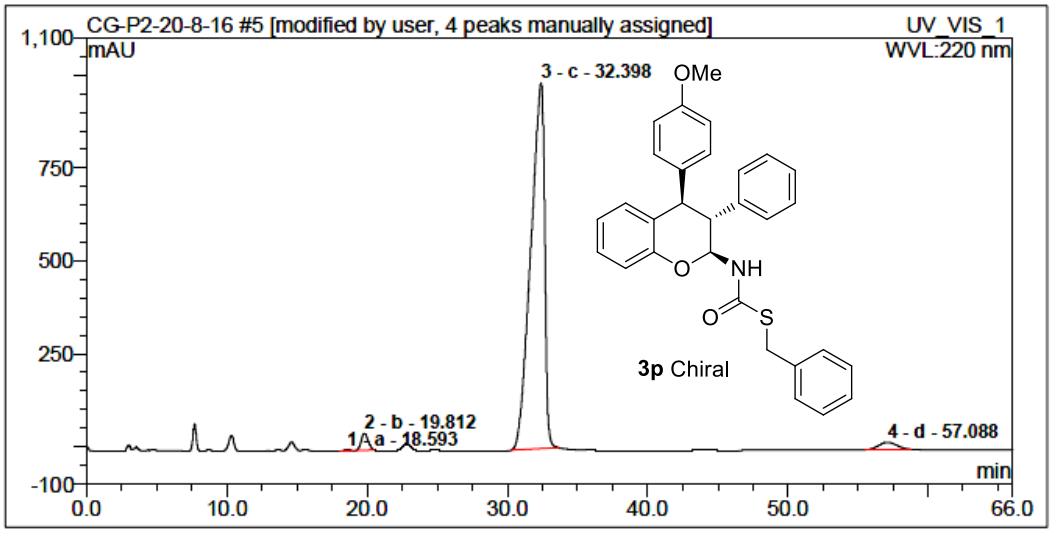
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	22.51	13.4591	2.925383688	19.21198	n.a.
2	b	24.12	358.7869	77.98362152	415.7659	n.a.
3	c	27.06	3.834732	0.8334927585	4.1381	n.a.
4	d	45.70	83.999	18.25750203	47.135	n.a.

P2-92-RAC-IA-220nm



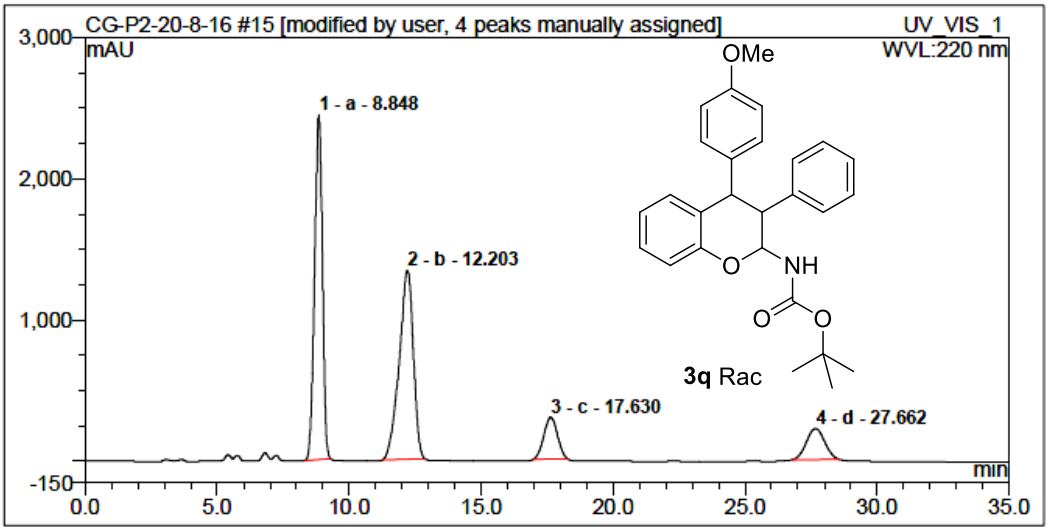
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	18.42	263.8636	21.88590033	486.0072	n.a.
2	b	19.47	267.3652	22.17633327	450.1063	n.a.
3	c	31.46	343.6043	28.49991428	376.9113	n.a.
4	d	56.22	330.800	27.43785212	208.059	n.a.

CG-P2-92-CHI-IA-220nm



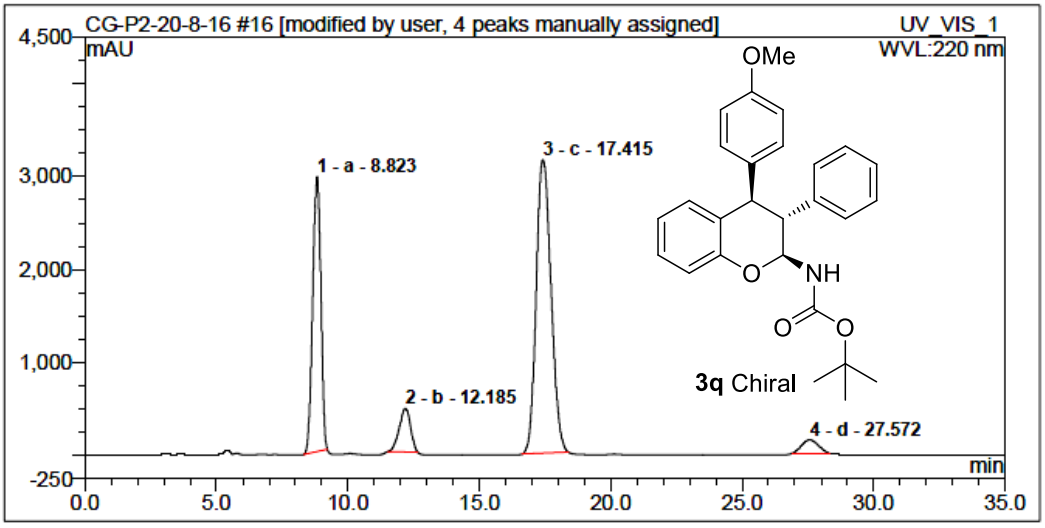
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	18.59	1.280049	0.1086115573	2.88478	n.a.
2	b	19.81	25.98498	2.204813764	45.64207	n.a.
3	c	32.40	1122.805	95.26949738	983.7086	n.a.
4	d	57.09	28.487	2.417077297	19.020	n.a.

CG-P2-105-RAC-IA



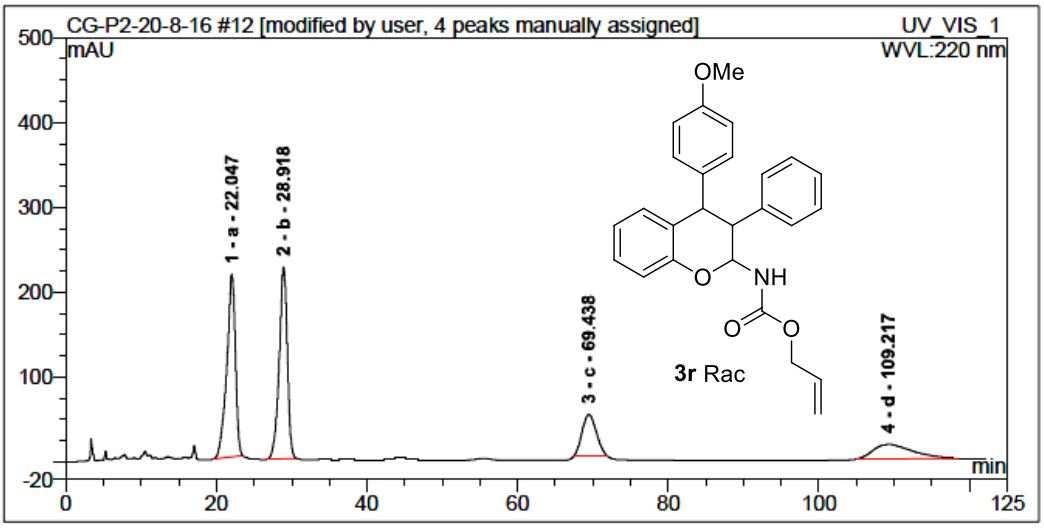
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	8.85	837.0718	41.45018565	2439.305	n.a.
2	b	12.20	829.8984	41.09497274	1336.618	n.a.
3	c	17.63	176.5708	8.74344643	295.6571	n.a.
4	d	27.66	175.924	8.711395187	219.514	n.a.

CG-P2-105-CHI-IA



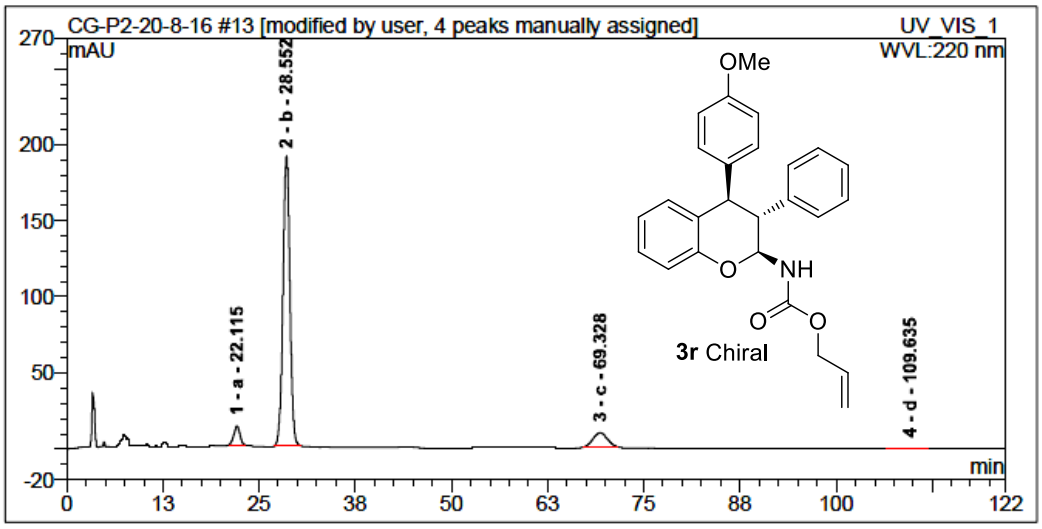
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	8.82	1064.605	30.70509015	2959.643	n.a.
2	b	12.19	232.3893	6.702518659	467.9652	n.a.
3	c	17.42	2063.344	59.5104979	3156.738	n.a.
4	d	27.57	106.855	3.081893293	144.328	n.a.

P2-104-RAC-IC



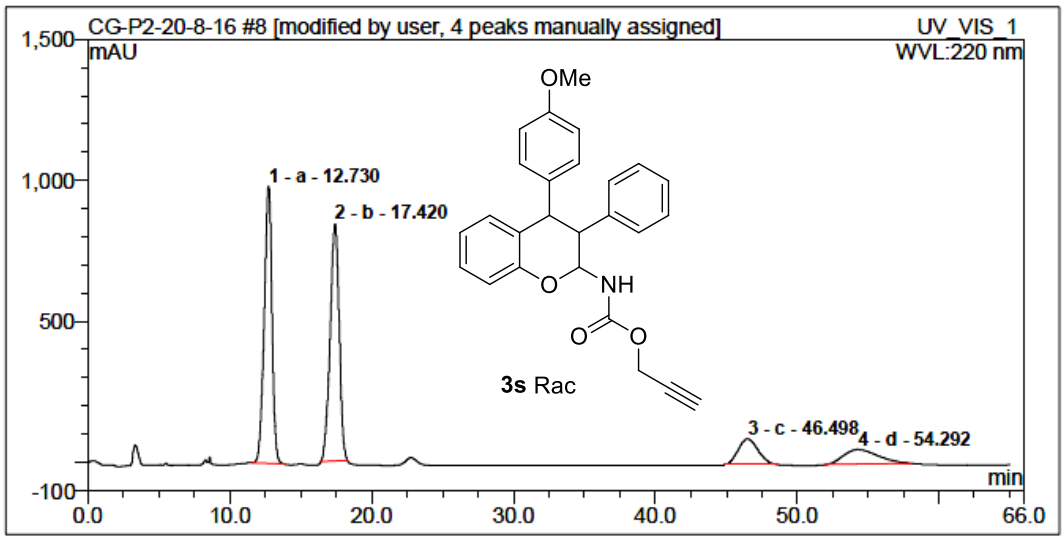
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	22.05	285.3055	36.73892854	215.1022	n.a.
2	b	28.92	282.4755	36.3745154	226.0451	n.a.
3	c	69.44	107.4398	13.83508308	48.9813	n.a.
4	d	109.22	101.355	13.05147297	16.990	n.a.

P2-104-CHI-IC



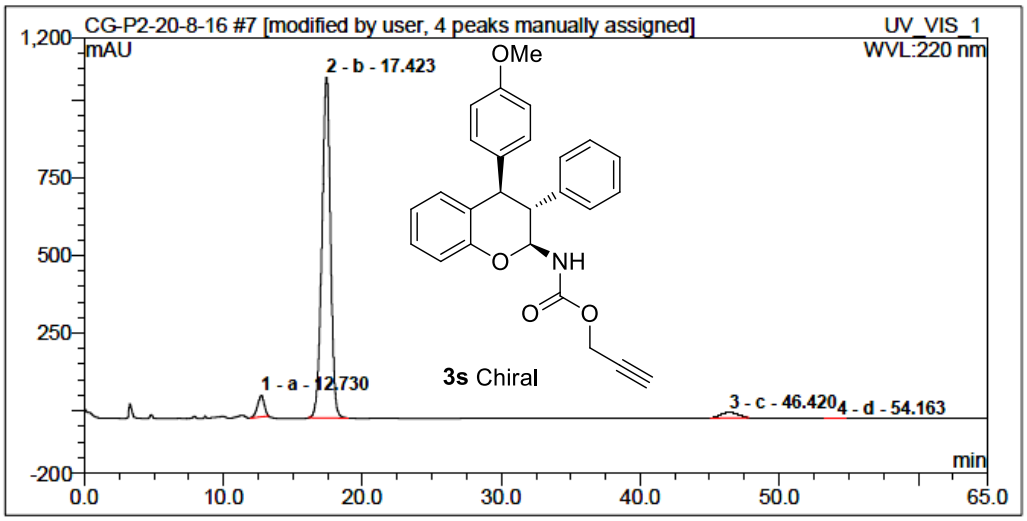
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	22.12	11.25596	4.911304057	12.44959	n.a.
2	b	28.55	197.6632	86.24622426	190.6015	n.a.
3	c	69.33	19.66433	8.580121857	9.21862	n.a.
4	d	109.64	0.601	0.2623498287	0.228	n.a.

CG-P2-91-RAC-IC



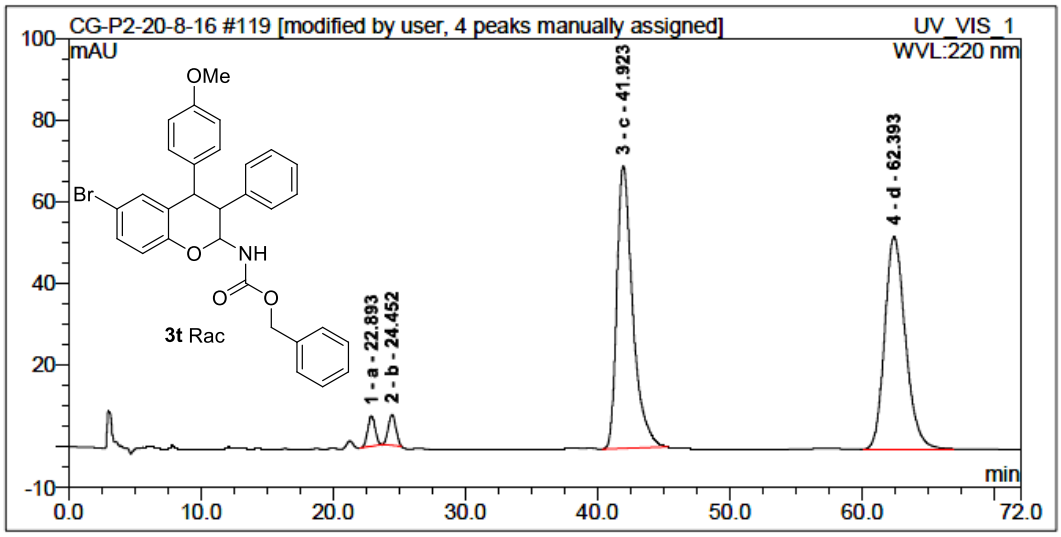
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	12.73	625.5126	40.43267097	984.0171	n.a.
2	b	17.42	622.9537	40.26726806	840.0671	n.a.
3	c	46.50	149.8669	9.687285938	91.30396	n.a.
4	d	54.29	148.714	9.612775029	51.740	n.a.

CG-P2-91-CHI-IC



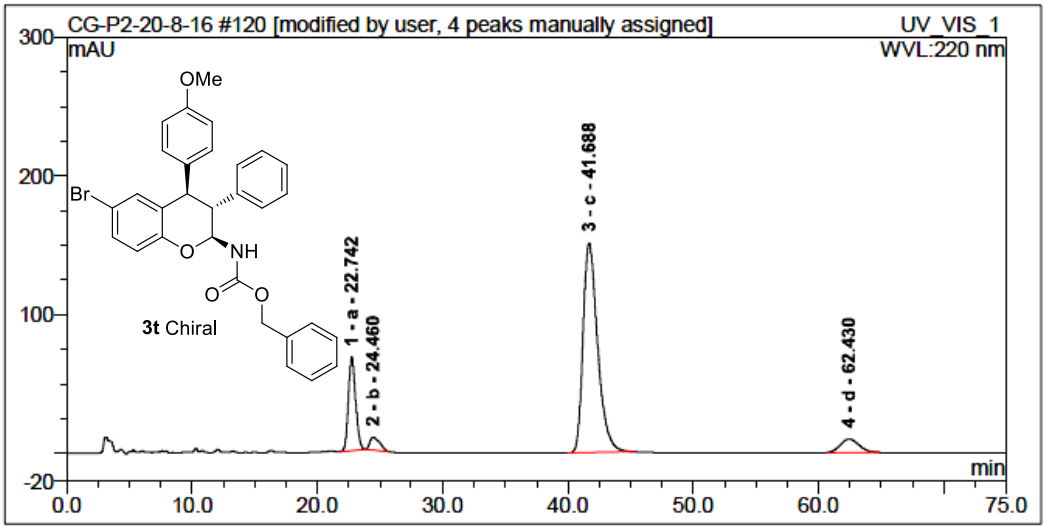
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	12.73	38.41023	4.502455275	68.77119	n.a.
2	b	17.42	787.8372	92.35043288	1096.236	n.a.
3	c	46.42	26.7598	3.136789625	18.17993	n.a.
4	d	54.16	0.088	0.01032221854	0.107	n.a.

P2-128-RAC-IA



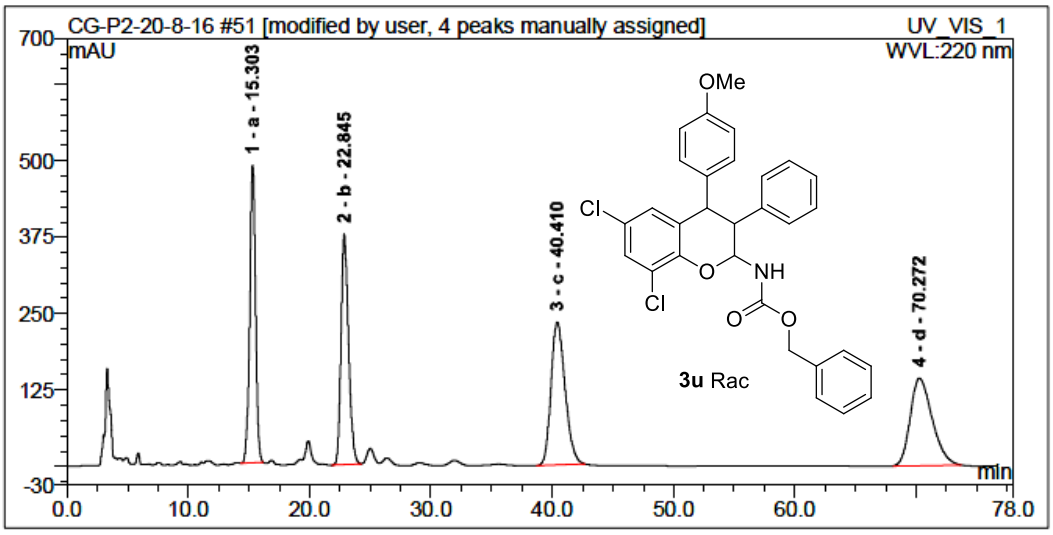
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	22.89	4.883249	2.432611102	7.44096	n.a.
2	b	24.45	4.986246	2.483919357	7.54736	n.a.
3	c	41.92	96.11367	47.8794303	69.28723	n.a.
4	d	62.39	94.758	47.20403924	52.121	n.a.

P2-128-CHI-IA



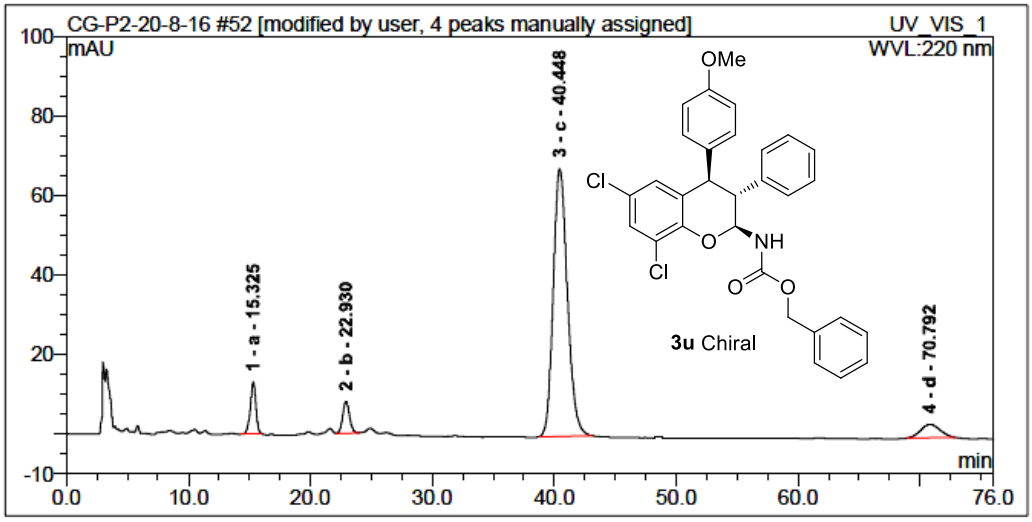
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	22.74	45.16302	16.43523008	67.54441	n.a.
2	b	24.46	8.380591	3.049772399	9.21115	n.a.
3	c	41.69	204.2788	74.33890436	151.3428	n.a.
4	d	62.43	16.972	6.17609316	9.803	n.a.

P2-131-RAC4-IA



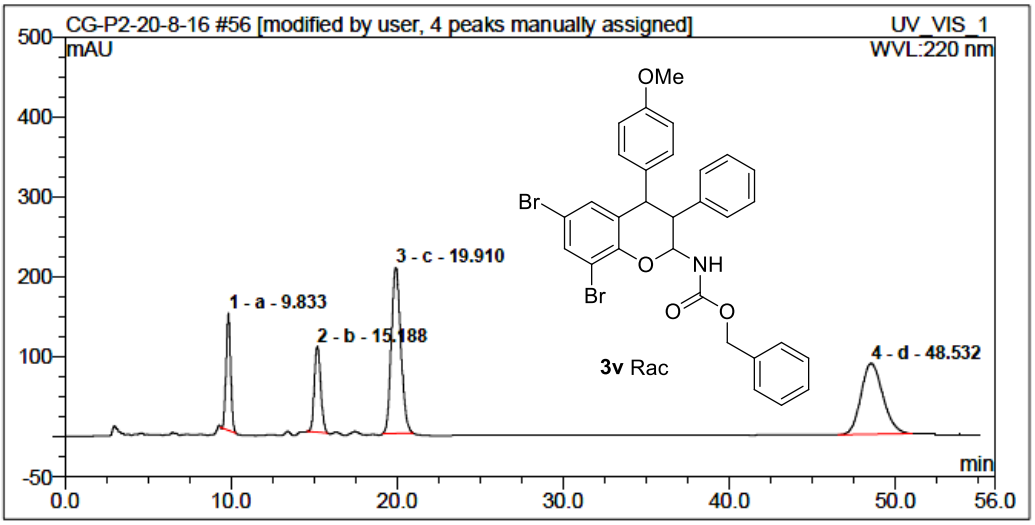
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	15.30	268.9275	23.34876201	486.8136	n.a.
2	b	22.85	270.213	23.46037002	377.3908	n.a.
3	c	40.41	313.8436	27.2484555	233.8065	n.a.
4	d	70.27	298.801	25.94241248	142.760	n.a.

P2-131-CHI-IA



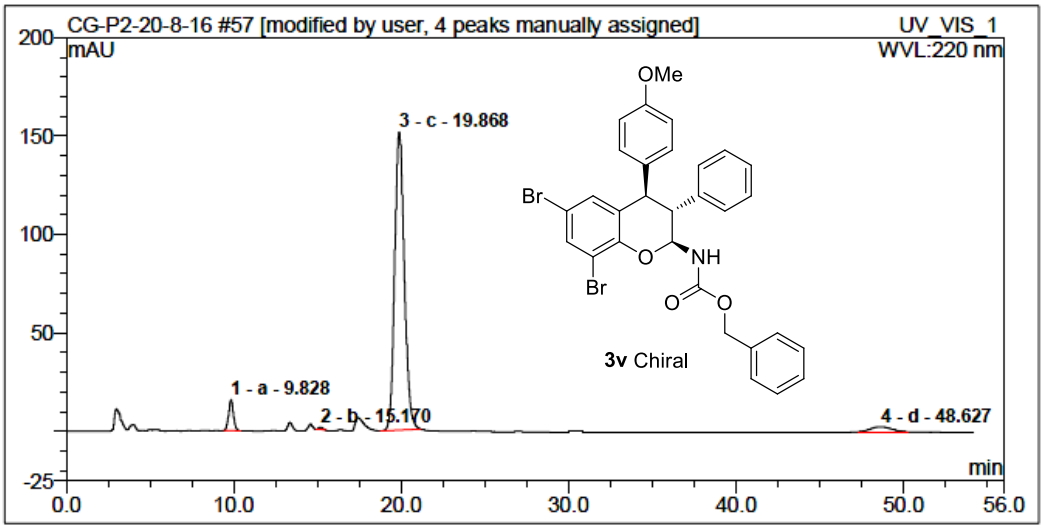
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	15.33	6.925702	6.369125655	13.06066	n.a.
2	b	22.93	5.176035	4.760069058	7.97671	n.a.
3	c	40.45	90.45156	83.18252279	67.41469	n.a.
4	d	70.79	6.185	5.688282497	3.324	n.a.

CG-P2-133-RAC-IA



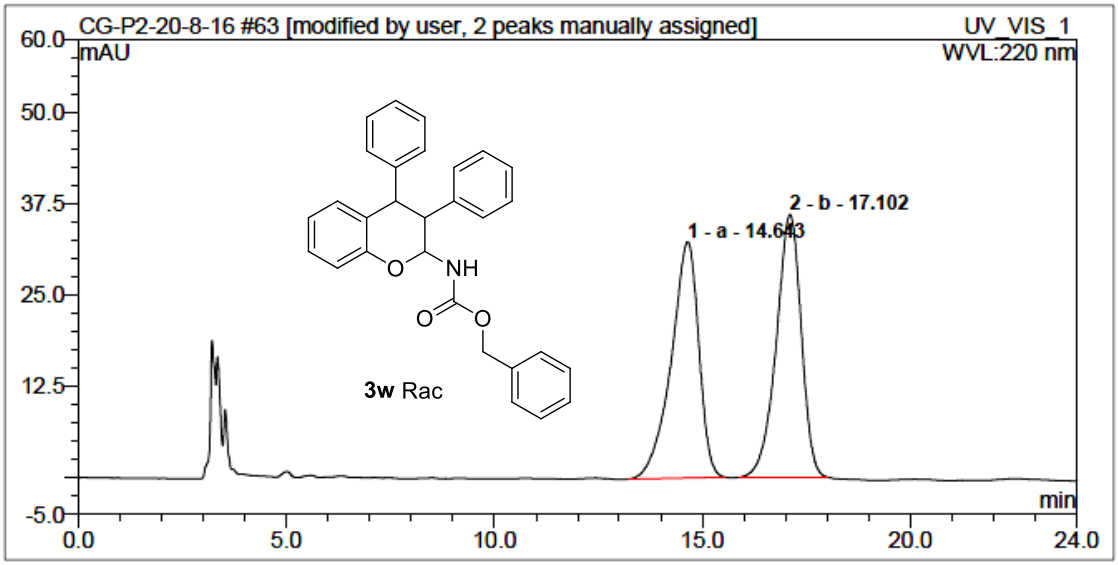
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	9.83	47.09253	12.80056024	146.7983	n.a.
2	b	15.19	47.7081	12.96788443	107.5648	n.a.
3	c	19.91	136.9508	37.2255851	207.387	n.a.
4	d	48.53	136.143	37.00597023	88.776	n.a.

CG-P2-133-CHI-50*C-IA



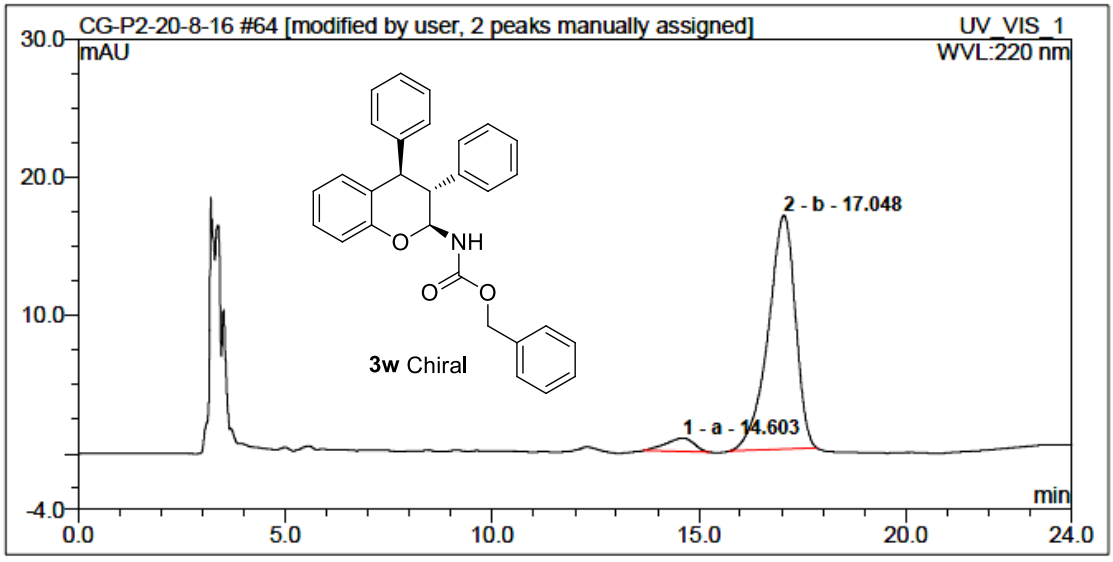
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	9.83	5.247845	4.771339934	15.82508	n.a.
2	b	15.17	0.337903	0.3072211404	1.07585	n.a.
3	c	19.87	100.6834	91.54137965	151.467	n.a.
4	d	48.63	3.718	3.380059279	2.608	n.a.

CG-P2-135-RAC-IC



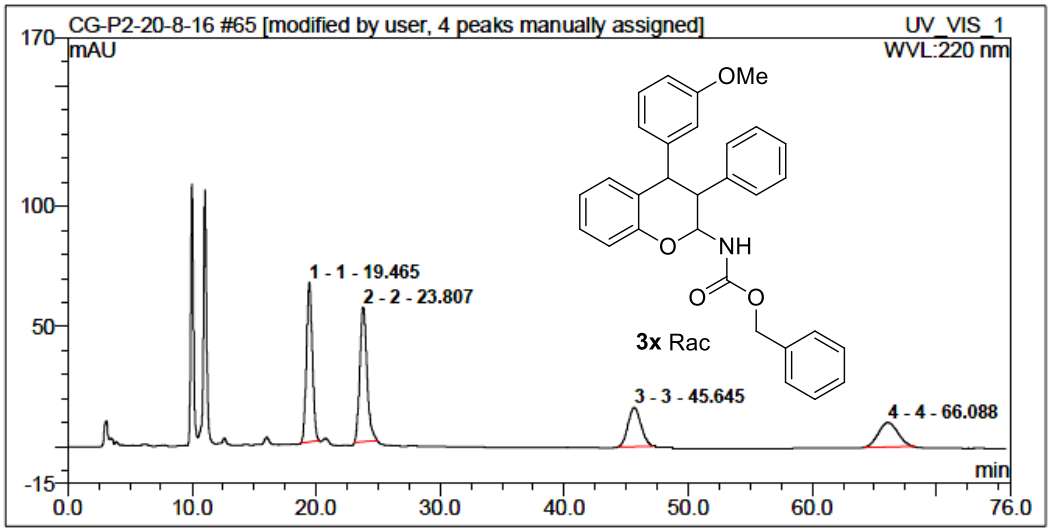
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	14.64	24.85738	49.88748612	32.35206	n.a.
2	b	17.10	24.970	50.11251388	35.991	n.a.

CG-P2-135-CHI-IC



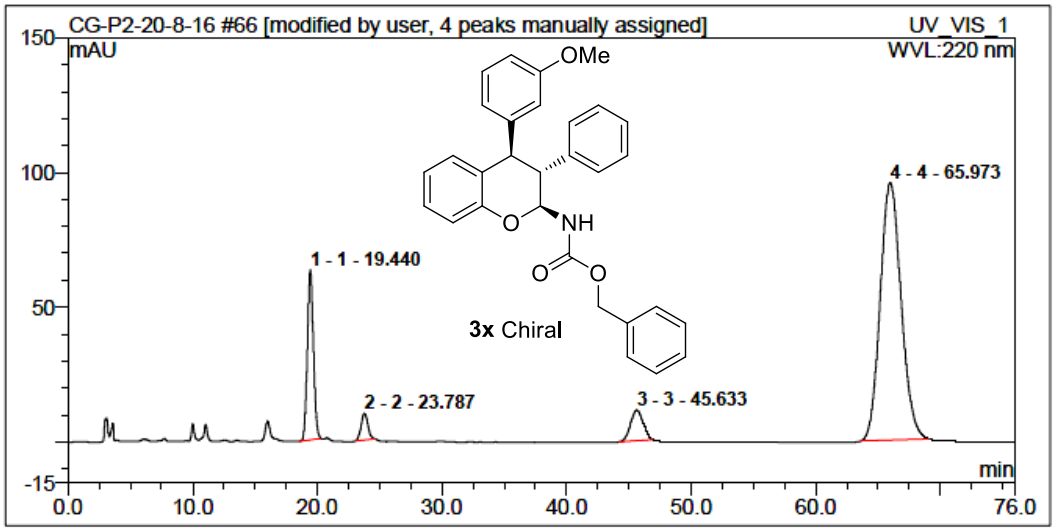
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	14.60	0.76758	5.624082129	0.97671	n.a.
2	b	17.05	12.881	94.37591787	16.910	n.a.

CG-P2-136-RAC-IA



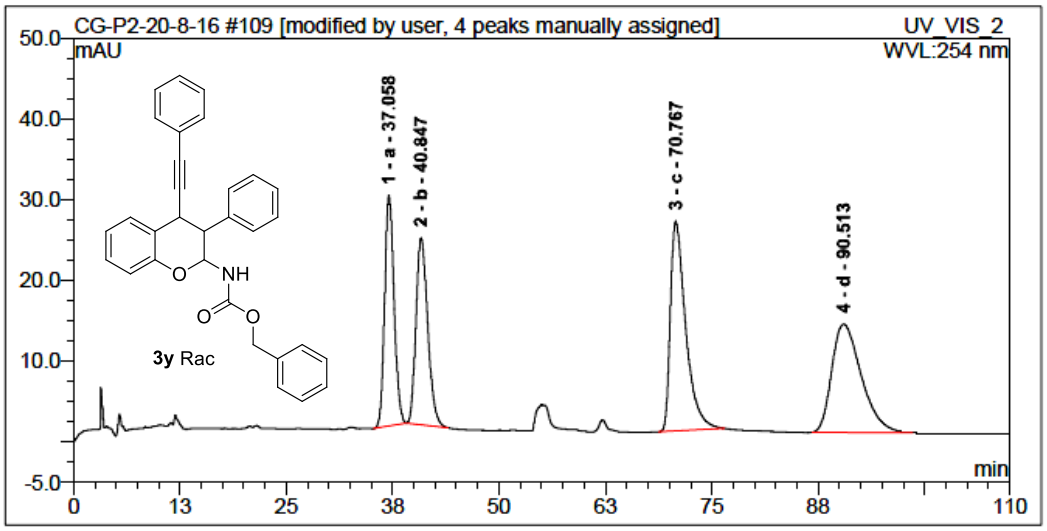
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	19.47	36.7884	32.77396314	66.21447	n.a.
2	2	23.81	37.5221	33.42759788	55.85455	n.a.
3	3	45.65	19.43095	17.31059456	16.15091	n.a.
4	4	66.09	18.507	16.48784443	10.140	n.a.

CG-P2-136-CHI-IA



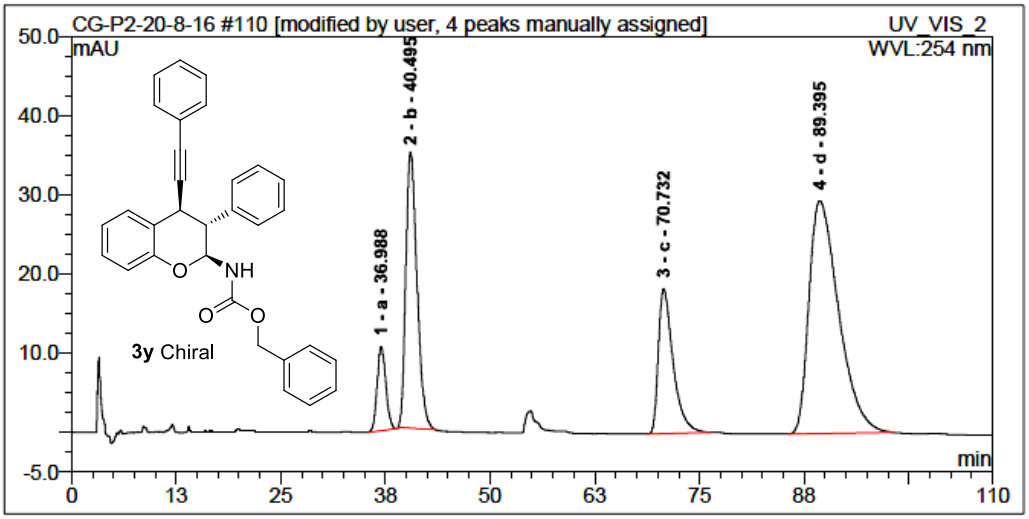
No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	1	19.44	35.66993	14.81954743	63.11569	n.a.
2	2	23.79	6.097993	2.533492877	9.76617	n.a.
3	3	45.63	13.41393	5.572995539	11.36742	n.a.
4	4	65.97	185.513	77.07396415	95.583	n.a.

Ph-AC-CBZ-RAC-ID



No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	37.06	36.73943	20.19240744	28.578	n.a.
2	b	40.85	36.97069	20.31950913	23.15838	n.a.
3	c	70.77	54.26093	29.82242605	26.01006	n.a.
4	d	90.51	53.976	29.66565738	13.404	n.a.

Ph-AC-CBZ-CHI-ID

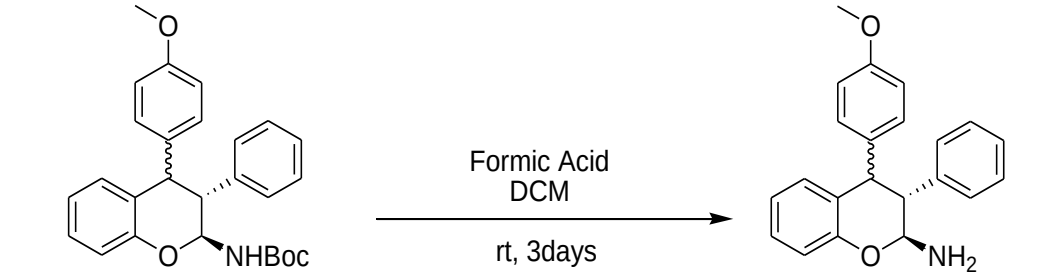


No.	Peak Name	Ret.Time (detected) min	Area mAU*min	Rel.Area(ident.) %	Height mAU	Amount
1	a	36.99	12.71044	5.646231492	10.59519	n.a.
2	b	40.50	53.77161	23.8864242	34.9062	n.a.
3	c	70.73	37.4655	16.64292537	18.35106	n.a.
4	d	89.40	121.166	53.82441893	29.424	n.a.

13. Determination of absolute stereochemistry for the compound (3q) from Mosher amides:

For the determination of absolute configuration, we initially tried to recrystallize most of the synthesized trisubstituted chroman products. But unfortunately, because of the semisolid nature & for few cases amorphous, high powder nature of the substrate we were unable to get the crystal structure. In this situation, we then focused our attention towards an alternative method for assignment of absolute configuration i.e. Mosher experiment, a procedure for derivatizing and analyzing through the help of **^{1}H NMR** of an optically active amine. For this purpose, we have chosen the substrate **(3q/3q')** because conversion into corresponding chiral amine led to no change in configuration at the same time deprotection of Boc group present in this substrate was comparatively easier than Cbz deprotection present in other substrates.

Boc group deprotection of substrate (3q):

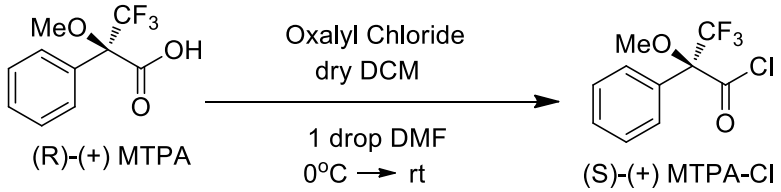


(3q/3q')
dr: 1.5:1
Relative stereochemistry: Known
Absolute stereochemistry: Unknown

(11q/11q')
dr: 1.4:1
no change in configuration

160 mg (0.37 mmol) of **(3q/3q')** was deprotected to corresponding chiral amine **(11q/11q')** with 5 ml of 98% formic acid and 1.5 ml dry DCM solvent. The reaction was continued for 3 days. Progress of the reaction was monitored by TLC. Formic acid was evaporated and then 5 ml water was added. pH ~8 was maintained by the addition of Na_2CO_3. Organic phase was extracted with DCM and washed with brine. Finally purified by column chromatography.

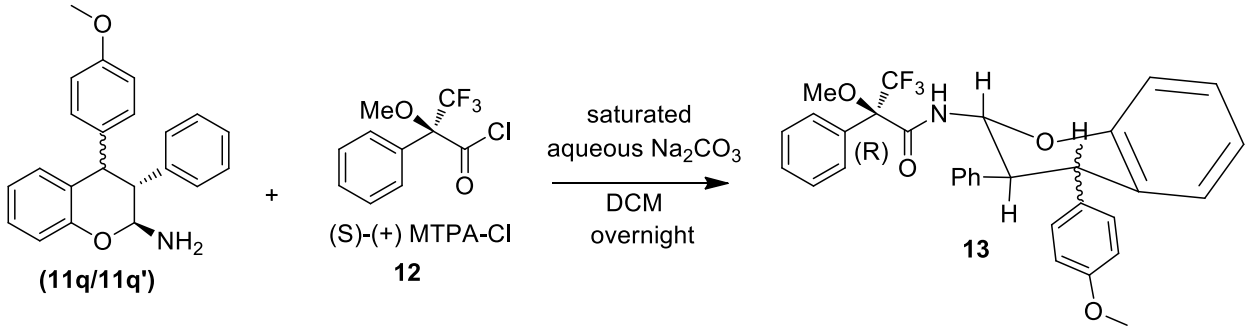
Preparation of (S)-(+) MTPA-Cl & compound (13):



(R)-(+) MTPA

(S)-(+) MTPA-Cl

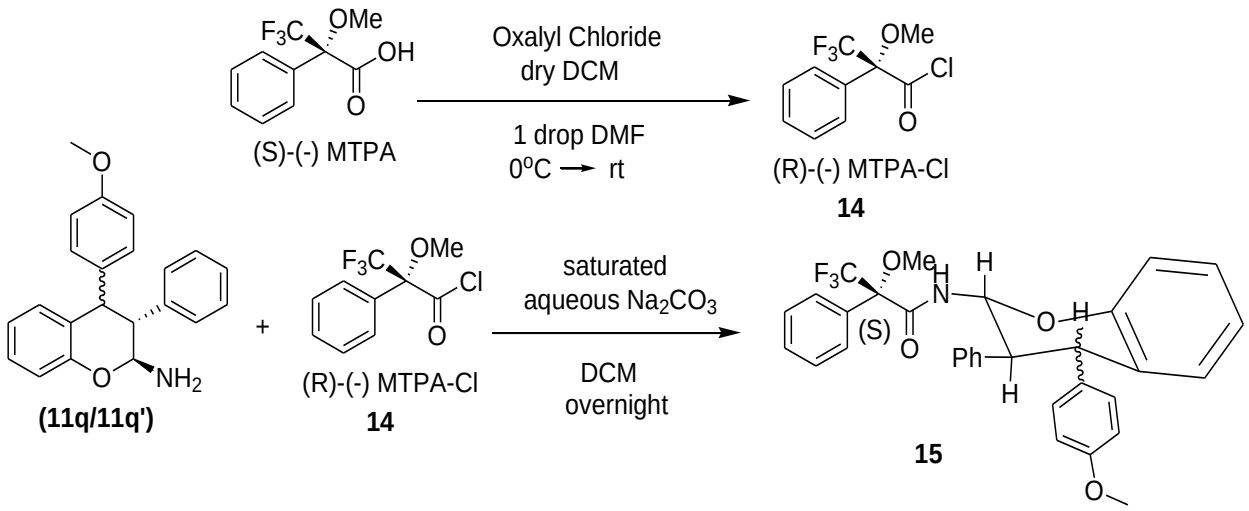
12



(S)-(+) MTPA-Cl **(12)** was prepared according to literature procedure.[6] (R)-(+) MTPA, Moshers acid (121 mg, 0.52 mmol) was dissolved in 2.4 ml dry DCM and cooled to 0 ^{o}C. Then oxalyl chloride (0.5 ml, 5.2 mmol) was added followed by the addition of one drop DMF. Thereafter, the reaction mixture was continued to stir for 1 hour. Progress of the reaction was then monitored by TLC analysis. The reaction mixture was concentrated in *vacuo.* After this, residue was suspended in hexane and concentrated it again in *vacuo*. Finally, product (S)-(+) MTPA-Cl was dissolved in required amount of dry DCM to prepare 0.21 M solution of corresponding Moshers acid chloride **(12).**

In the next step **(11q/11q')** amine (16 mg, 0.048 mmol) was dissolved in 1.2 ml DCM and then previously prepared Moshers acid chloride **(12)** was added followed by the addition of 1.21 ml saturated aqueous Na_2CO_3. The reaction mixture was stirred for overnight. Organic phase was extracted with DCM & concentrated in *vacuo*. Finally purified by column chromatography using (hexane/ EtOAc) as solvent system to afford the desired product **(13).**

Preparation of (R)-(-) MTPA-Cl & compound (15):



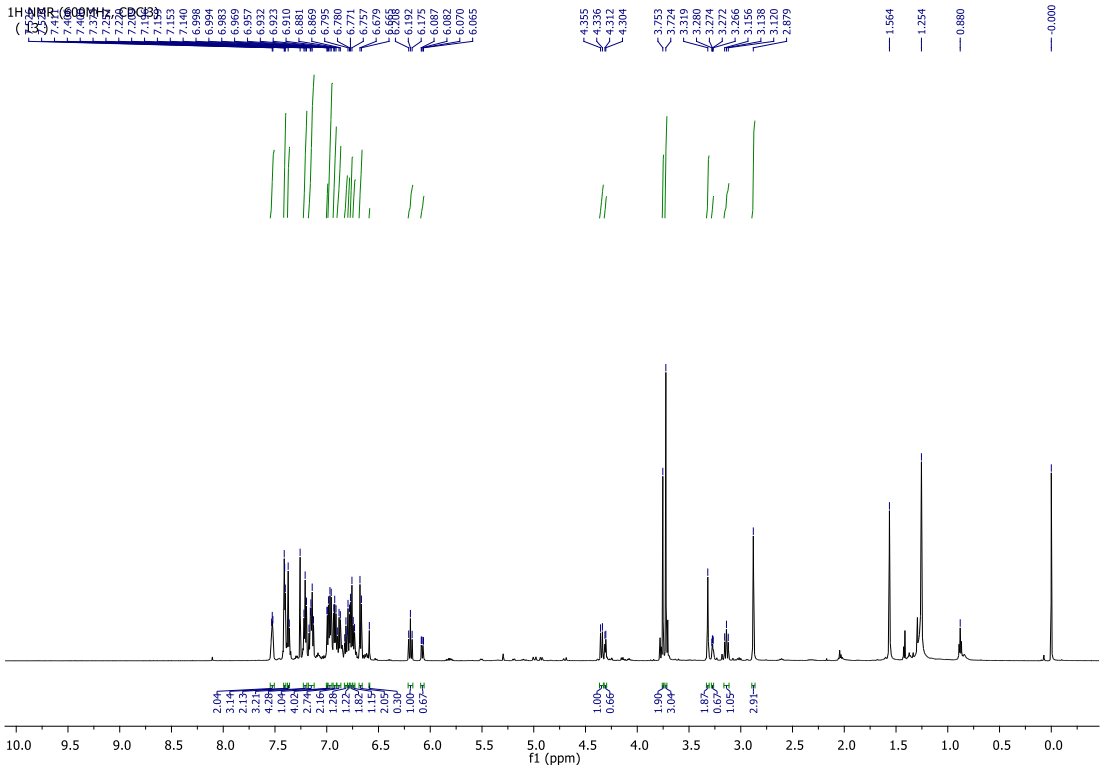
(R)-(-) MTPA-Cl **(14)** was prepared according to literature procedure.[9] (S)-(-) MTPA, Moshers acid (121 mg, 0.52 mmol) was dissolved in 2.4 ml dry DCM and cooled to 0 ^{o}C. Then oxalyl chloride (0.5 ml, 5.2 mmol) was added followed by the addition of one drop DMF. Thereafter, the reaction mixture was continued to stir for 1 hour. Progress of the reaction was then monitored by TLC analysis. The reaction mixture was concentrated in *vacuo.* After this, residue was suspended in hexane and concentrated it again in *vacuo*. Finally, product (R)-(-) MTPA-Cl was dissolved in required amount of dry DCM to prepare 0.21 M solution of corresponding Moshers acid chloride **(14).**

In the next step **(11q/11q')** amine (16 mg, 0.048 mmol) was dissolved in 1.2 ml DCM and then previously prepared Moshers acid chloride **(14)** was added followed by the addition of 1.21 ml saturated aqueous Na_2CO_3. The reaction mixture was stirred for overnight. Organic phase was extracted with DCM & concentrated in *vacuo*. Finally purified by column chromatography using (hexane/ EtOAc) as solvent system to afford the desired product **(15).**

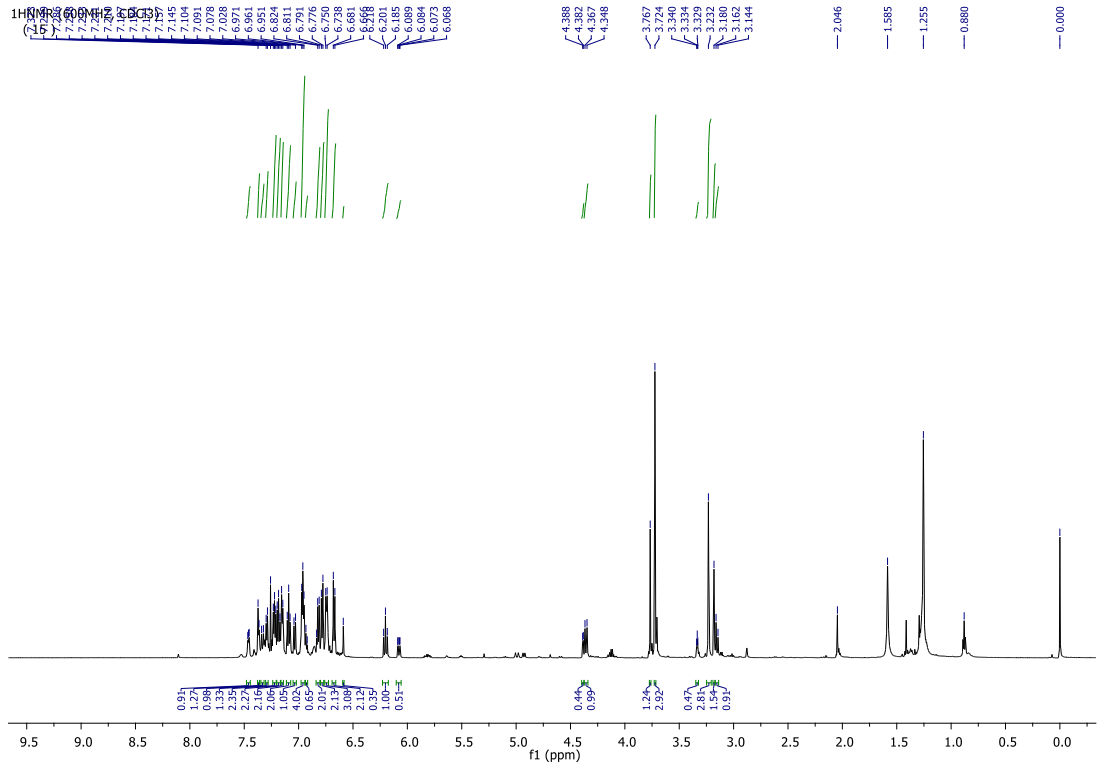
Characterization data for (13): **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.55 – 7.51 (m, 2H), 7.42 – 7.40 (m, 3H), 7.37 (d, *J* = 6.4 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 3H), 7.15 (dt, *J* = 15.2, 7.5 Hz, 4H), 7.00 (d, *J* = 2.2 Hz, 1H), 6.99 – 6.95 (m, 4H), 6.94 – 6.91 (m, 3H), 6.90 – 6.86 (m, 2H), 6.81 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 8.7 Hz, 1H), 6.76 (d, *J* = 8.6 Hz, 2H), 6.74 (d, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 8.6 Hz, 2H), 6.59 (s, 0.3H), 6.19 (t, *J* = 10.0 Hz, 1H), 6.08 (dd, *J* = 9.9, 3.1 Hz, 0.7H), 4.35 (d, *J* = 11.0 Hz, 1H), 4.31 (d, *J* = 5.0 Hz, 0.7H), 3.75 (s, 1.9H), 3.72 (s, 3H), 3.32 (s, 1.88H), 3.27 (dd, *J* = 4.8, 3.3 Hz, 0.7H), 3.14 (t, *J* = 10.6 Hz, 1H), 2.88 (s, 3H), **HRMS (+ESI):** Calc for $C_{32}H_{29}F_3NO_4$ $[M+H]^+$ 548.2043; found: 548.2021.

Characterization data for (15): **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 7.48 – 7.44 (m, 1H), 7.37 (d, *J* = 5.3 Hz, 1H), 7.33 (d, *J* = 10.2 Hz, 1H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.24 – 7.21 (m, 2H), 7.20 – 7.17 (m, 2H), 7.15 (d, *J* = 6.9 Hz, 2H), 7.09 (t, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 8.6 Hz, 1H), 6.98 – 6.94 (m, 4H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.84 – 6.80 (m, 2H), 6.78 (d, *J* = 8.5 Hz, 2H), 6.74 (d, *J* = 7.7 Hz, 3H), 6.67 (d, *J* = 8.5 Hz, 2H), 6.59 (s, 0.4H), 6.20 (t, *J* = 10.1 Hz, 1H), 6.08 (dd, *J* = 9.8, 3.0 Hz, 0.5H), 4.38 (d, *J* = 3.5 Hz, 0.4H), 4.36 (d, *J* = 11.2 Hz, 1H), 3.77 (s, 1.2H), 3.72 (s, 3H), 3.33 (t, *J* = 3.3 Hz, 0.5H), 3.23 (s, 3H), 3.18 (s, 1.5H), 3.15 (d, *J* = 10.7 Hz, 1H); **HRMS (+ESI):** Calc for $C_{32}H_{29}F_3NO_4$ $[M+H]^+$ 548.2043; found: 548.2036.

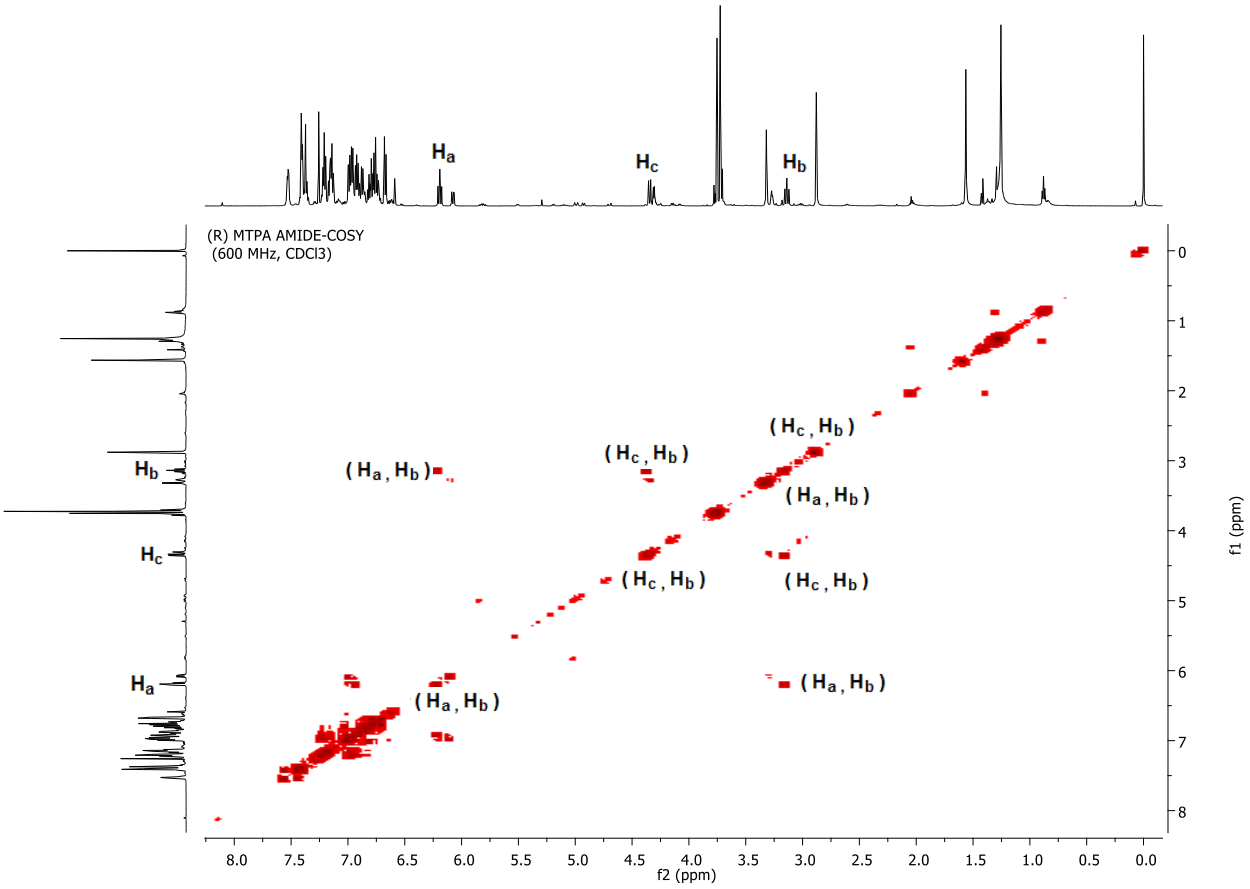
^{1}H NMR spectra of (13):

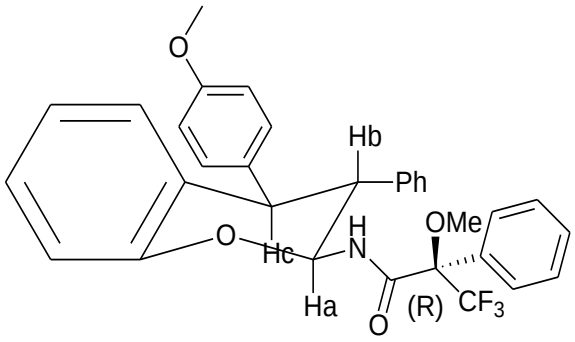


^{1}H NMR spectra of (15):



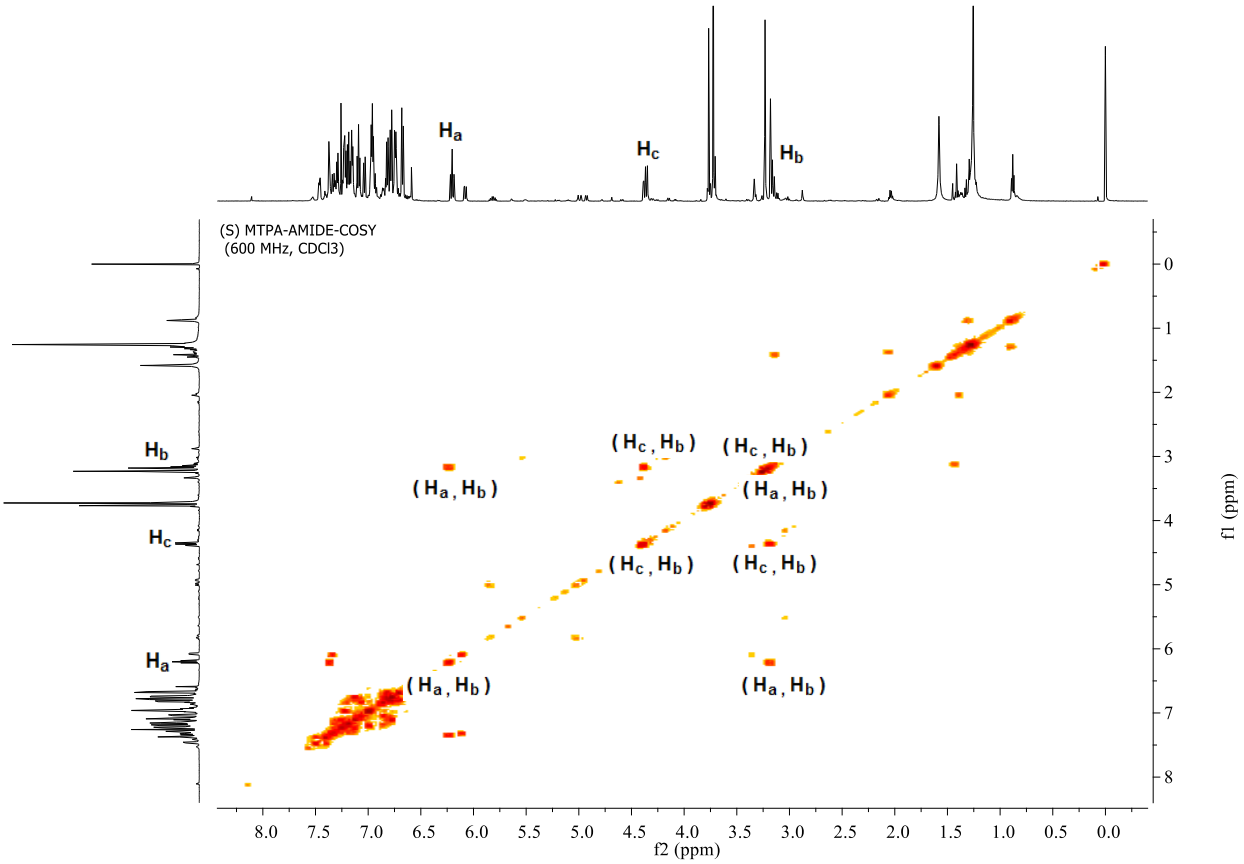
COSY spectra of (13):

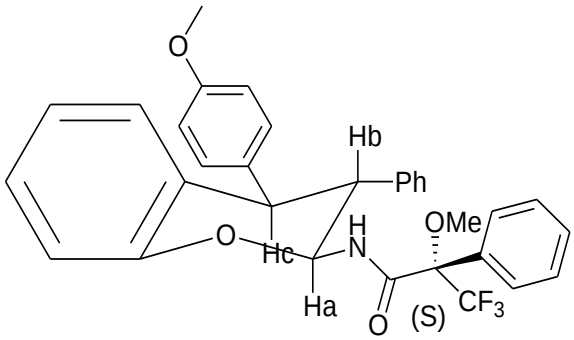




(13) major dr

COSY spectra of (15):



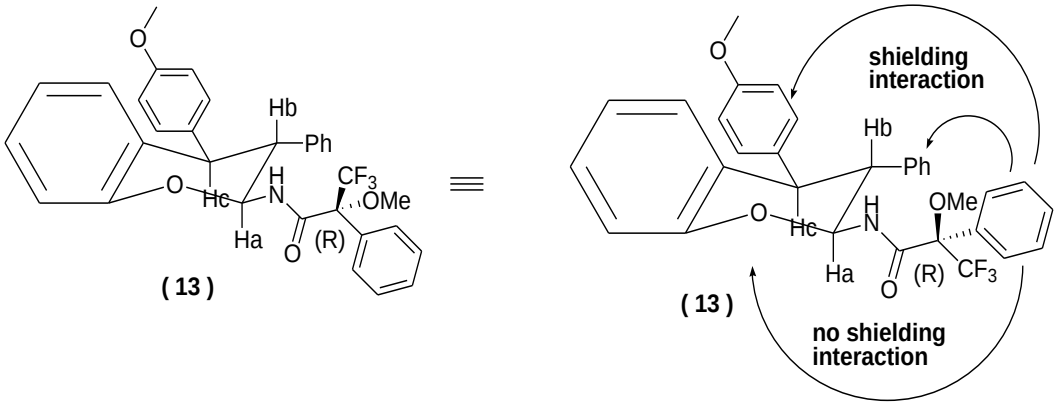


(15) major dr

Analysis for the absolute configuration of the major diastereomer of the substrate (3q /3q'):

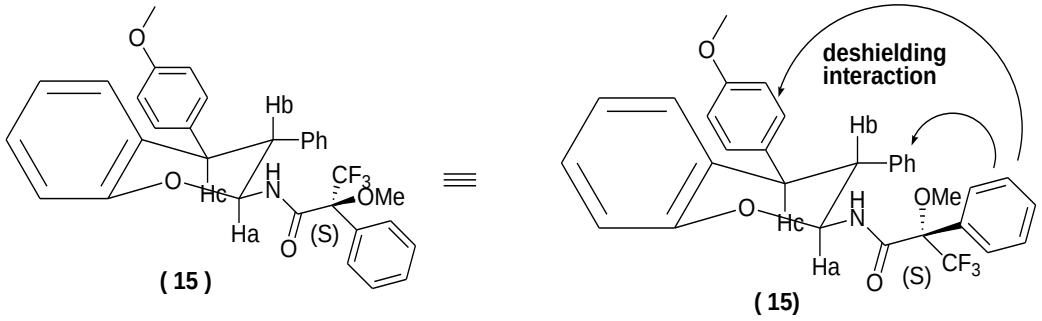
From the Mosher's methodology,[9,10] it is known that, in the most stable conformation of the MTPA amide, the trifluromethyl group is always *syn* periplanar with respect to carbonyl group. Furthermore, N-H bond and the carbonyl group prefers *anti* orientation amongst themselves from energy point of view.

Accordingly, we envisioned the molecular models of our trisubstituted chroman moiety. Analysis of **(13) & (15)** reveals that H_a, H_b, H_c protons of the major dr are shielded in MTPA-amide **(13)** compared to MTPA-amide **(15).** This clearly indicates that shielding interaction is present between the phenyl group of the Mosher part and the three adjacent protons. Thus, it can be predicted that the phenyl group adjacent to H_b must be coplanar with the phenyl group of Mosher part. Also, for our concerted mechanism, H_a and H_b must be *trans* to each other as dienophile enecarbamates are in *trans* conformation. In addition, coupling constant value & NOESY, COSY analysis (for compound **(3a/3a')**) revealed that H_b and H_c are also *trans* to each for the major diastereomer as shown in page no-S.17 & page no- S.96 to S.97.



Compound **(13)**	H_a: δ 6.19 (t, *J* = 10.0 Hz, 1H)	shielded
	H_b: δ 3.14 (t, *J* = 10.6 Hz, 1H)	shielded
	H_c: δ 4.35 (d, *J* = 11.0 Hz, 1H)	shielded

9) D. J. Fox, S. Parris, D. S. Pedersen, C. R. Tyzack and S. Warren, *Org. Biomol. Chem*., 2006, **4**, 3108; 10) J. M. Seco, E. Quinoa and R. Riguera, *Chem. Rev*., 2004, **104**, 17.



	H_a: δ 6.20 (t, *J* = 10.1 Hz, 1H)	deshielded
Compound **(15)**	H_b: δ 3.15 (d, J = 10.7 Hz, 1H)	deshielded
	H_c: δ 4.36 (d, *J* = 11.2 Hz, 1H)	deshielded

Thus, the absolute configuration for the major diastereomer of compound **(3q)** was determined as