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1. General information

The reagents were purchased from Sigma Aldrich, Alfa Aesar or ABCR and used without further purification. All reactions involving air-and moisture-sensitive materials were carried out under argon atmosphere in oven-dried glassware with magnetic stirring. Solvents were dried prior to use. THF, PhMe was distilled from Na and benzophenone and CH_2Cl_2 from CaH_2. Column chromatography was performed with Kiesel gel (230-400 mesh). Analytical TLC was performed with Silica gel 60 F254 aluminum plates (Merck) with visualization by UV light and charring with aqueous $KMnO_4$ or Pancaldi reagent ($(NH_4)_6MoO_4$, $Ce(SO_4)_2$, H_2SO_4, H_2O). NMR analyses were performed with Bruker 400 MHz Avance III, Bruker DRX 500 Avance or Varian 200 MHz spectrometers. Chemical shifts are calibrated using residual solvents signals ($CDCl_3$: δ (H)= 7.26, δ (C)= 77.16) or TMS and are reported in ppm. Infrared spectra (IR) were recorded on a FT-IR-1600-Perkin Elmer spectrophotometer and are reported in frequency of absorption cm^{-1}). High-resolution mass spectra were in general recorded on ESI-MS-TOF (MicrOTOF II, Bruker, Germany).

2. Setup for photocatalytic reactions

The reaction setup is depicted in Figure 1. The reaction setup consists of a self-constructed light source configuration, made up of a rectangular box with a length of 200 mm and height of 40 mm. Inside of the box in central position, commercially available (CFL): DIALL SPIRAL, 23 W, 1450 LM light bulb is placed (light source can be replaced by any other lamp if necessary). Around the light source in distance of 50 mm there are 8 holes for placing a 4 mL reaction vials. Cooling of the setup is performed by W1209 digital temperature control switch connected with a commercially available 50 mm computer fan. During the first experiments the temperature was monitored inside the reactor and did not exceed the desired temperature of 35 °C. Reactor was placed on magnetic plate stirrer and stirring was performed with 400 rpm.

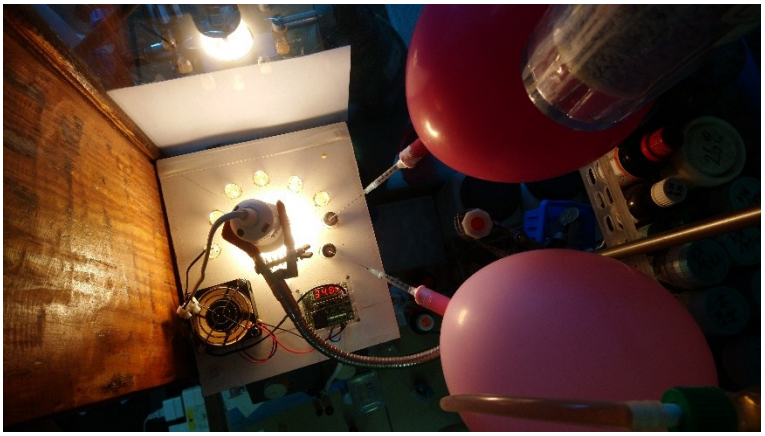


Figure 1 Reaction setup

3. Synthetic procedures

a) Synthesis of $[Ru(bpy)_3](PF_6)_2$

Prepared according to the modified literature procedure:[1] To a 250 mL round-bottomed flask $RuCl_3$ (540 mg, 2.6 mmol, 1.0 equiv.), 2,2'-bipyridine (2.5 g, 16.0 mmol, 6.1 equiv.) and EtOH (100 mL) were added. The reaction mixture was heated to reflux for 12h under argon. After cooling to room temperature, KPF_6 (1.9 g, 10.0 mmol, 3.8 equiv.) was added, and the solid was collected by vacuum filtration. The red solid was washed with water and then washed through the fritted funnel with acetone to removed excess ruthenium salts. The acetone eluent was diluted with Et_2O to precipitate the ruthenium complex. The resulting red solid was filtered and dried in vacuo. The product was obtained as an orange solid (1.0 g, 46%). $[M\text{-}2(PF_6)]^{2+}$ calcd for $C_{30}H_{24}N_6Ru$, 285.05; found, 285.2; $[M\text{-}PF_6]^+$ calcd for $C_{30}H_{24}F_6N_6PRu$, 714.6; found, 714.7.

b) General procedure A for synthesis of secondary amines

To a suspension of Pd/C (1.28 g, 1.1 mmol, 0.1 equiv.) in isopropyl alcohol (40 mL) aqueous solution (8 mL) of ammonium formate (4.01 g, 63.6 mmol, 6.0 equiv.) was added. The reaction mixture was stirred for 1 minute to activate Pd/C. Next, amine (10.6 mmol, 1.0 equiv.) and aldehyde (10.6 mmol, 1.0 equiv.) were added and the reaction mixture was stirred at room temperature (60 min). After completing the reaction based on TLC monitoring, the Pd/C catalyst was filtered off on celite and the solvent was removed by rotary evaporation. The reaction mixture was diluted with CH_2Cl_2 and washed with brine solution. The organic phase was collected, dried with anhydrous $MgSO_4$, and concentrated by rotary-evaporation. The residue was purified by silica flash column chromatography.

c) General procedure B for visible-light-mediated synthesis of imines 5a-5o

A vial was charged with $[Ru(bpy)_3](PF_6)_2$ (0.00125 mmol, 0.005 equiv.), and then *N*-substituted arylamine (0.25 mmol, 1.0 equiv.) and MS 4Å (30 mg) were added, followed by addition of 0.8 mL of dry, saturated with oxygen MeCN. The suspension was stirred 16h under oxygen atmosphere and irradiated using CFL at 35 °C. After specified time the crude was washed with pentane and filtered through the short pad of silica to obtain pure product.

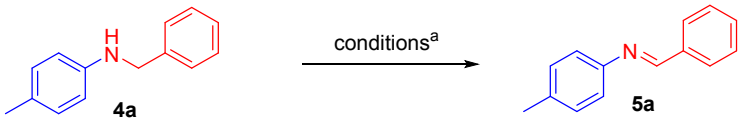
d) General procedure C for visible-light-mediated synthesis of imines 7a-7j

A vial was charged with $[Ru(bpy)_3](PF_6)_2$ (0.005 mmol, 0.02 equiv.), and then *N*-substituted arylamine (0.25 mmol, 1.0 equiv.) was added. Subsequently 30 mg of MS 4Å and anhydrous Na_3PO_4 (0.25 mmol, 1.0 equiv.) was added, followed by addition of 0.8 mL dry, saturated with oxygen MeCN. The suspension was stirred 16h under oxygen atmosphere and

irradiated using CFL at 35 °C. After specified time the crude was washed with pentane and filtered through the short pad of silica to obtain pure product.

4. Scope and limitations – dehydrogenation of *N*-benzyl anilines 4a-4o

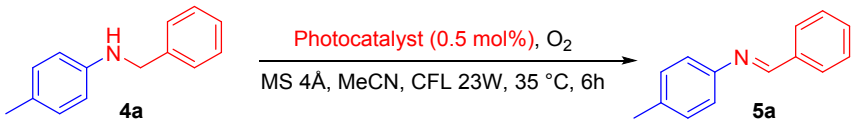
a) General optimization studies



No	Photocatalyst	Catalyst Loading	Additive	Oxidant	Yield [%]
1	$[Ru(bpy)_3](PF_6)_2$	2 mol%	—	O_2	50 [b]
2	$[Ru(bpy)_3](PF_6)_2$	2 mol%	—	O_2	75
3	$[Ru(bpy)_3](PF_6)_2$	2 mol%	—	air	trace
4	$[Ru(bpy)_3](PF_6)_2$	2 mol%	—	$^tBuO_2H$ [c]	86
5	$[Ru(bpy)_3](PF_6)_2$	2 mol%	MS 4Å [d]	O_2	> 99
6	**$[Ru(bpy)_3](PF_6)_2$**	**0.5 mol%**	**MS 4Å [d]**	**O_2**	**> 99 [e]**
7	$[Ru(bpy)_3](PF_6)_2$	0.5 mol%	MS 4Å [d]	$K_2S_2O_8$ [g]	—
8	$[Ru(bpy)_3](PF_6)_2$	0.5 mol%	$MgSO_4$ [g]	O_2	16 [e]
9	$[Ru(bpy)_3](PF_6)_2$	0.5 mol%	NaOH [g]	O_2	24 [e]
10	$[Ru(bpy)_3](PF_6)_2$	0.5 mol%	Na_3PO_4 [g]	O_2	90 [e]
11	$[Ru(bpy)_3](PF_6)_2$	0.5 mol%	K_2CO_3 [g]	O_2	42 [e]

[a] Unless otherwise indicated, all reactions were performed as follows: reaction scale: 0.25 mmol, 2 mol% of $[Ru(bpy)_3](PF_6)_2$, O_2 (balloon), MeCN 0.8 mL, temp. 35 °C, reaction time 16h, CFL 23W, isolated yield; [b] Blue LED; [c] 5 equiv; [d] additive amount: 30 mg; [e] reaction time 6h; [f] catalyst loading 5 mol%, reaction time 18h; [g] 1.0 equiv.

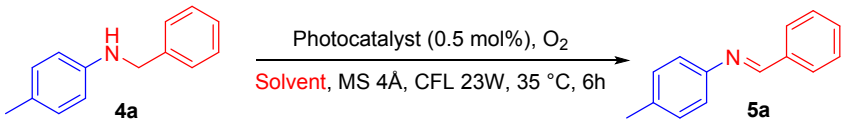
b) Photocatalyst screening



No	Photocatalyst	Additive	Yield [%]
1	**$[Ru(bpy)_3](PF_6)_2$**	**MS 4Å**	**> 99**
2	$[Ru(bpy)_3](Cl)_2$	MS 4Å	80
3	$Ir[dFFppy]_2$-(4,4'-dCF_3bpy)PF_6	MS 4Å	45
4	**Rose Bengal**	**MS 4Å**	**> 99 [a]**
5	Eosin Y	MS 4Å	58 [a]
6	Triphenylpyrylium	MS 4Å	— [a]
7	Methylene Blue	MS 4Å	— [a]

Unless otherwise indicated, all reactions were performed as follows: reaction scale: 0.25 mmol, 0.5 mol% of photocatalyst, 30 mg MS 4Å, O_2 (balloon), MeCN 0.8 mL, temp. 35 °C, reaction time 6h; CFL 23W; isolated yield; [a] catalyst loading 5 mol%, reaction time 18h.

c) Solvent screening

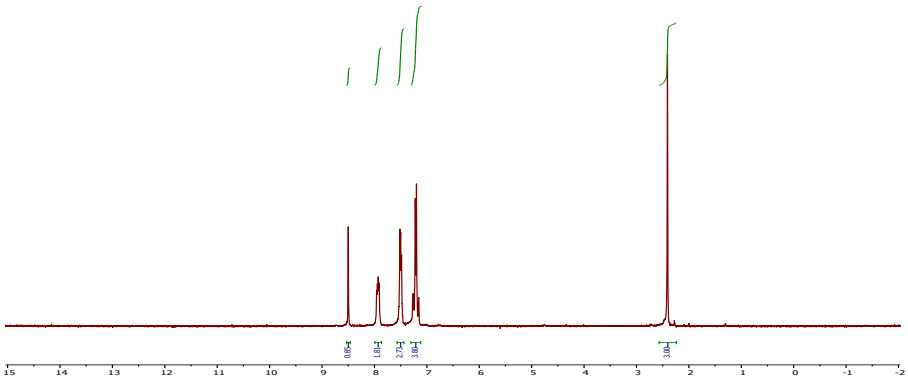


No	Photocatalyst	Additive	Solvent	Yield [%]
1	**$[Ru(bpy)_3](PF_6)_2$**	**MS 4Å**	**MeCN**	**> 99**
2	$[Ru(bpy)_3](PF_6)_2$	MS 4Å	DCE/MeCN (2/1)	78
3	$[Ru(bpy)_3](PF_6)_2$	MS 4Å	DMSO	—
4	$[Ru(bpy)_3](PF_6)_2$	MS 4Å	DCM	56
5	$[Ru(bpy)_3](PF_6)_2$	MS 4Å	$CHCl_3$	—
6	$[Ru(bpy)_3](PF_6)_2$	MS 4Å	MeOH	42
7	$[Ru(bpy)_3](PF_6)_2$	MS 4Å	PhMe	—
8	$[Ru(bpy)_3](PF_6)_2$	MS 4Å	DIOX	—
9	$[Ru(bpy)_3](PF_6)_2$	MS 4Å	DCE	25
10	$[Ru(bpy)_3](PF_6)_2$	MS 4Å	AcOEt	—

Unless otherwise indicated, all reactions were performed as follows: reaction scale: 0.25 mmol, 0.5 mol% of photocatalyst, 30 mg MS 4Å, O_2 (balloon), MeCN 0.8 mL, temp. 35 °C, reaction time 6h, CFL, isolated yield.

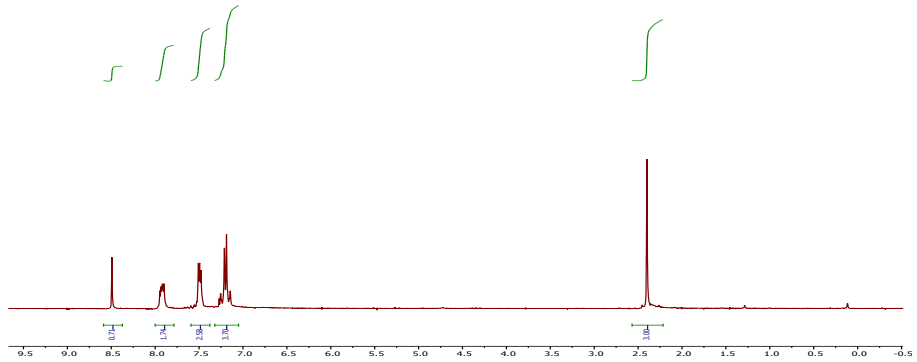
Our optimization studies showed that the best results were achieved using compact fluorescent lamp (CFL 23W) and $[Ru(bpy)_3](PF_6)_2$ as a catalyst (0.5 mol%) with the addition of molecular sieves (MS 4Å) in acetonitrile at 35 °C under oxygen atmosphere. In this conditions imine **5a** was obtained quantitatively after six hours. Rose Bengal catalyst proved to be also useful catalyst, however more catalyst (5 mol%) and longer reaction time (16h) was needed to get the same results. After given reaction time, reaction was washed with pentane and filtered to give pure product.

^{1}H NMR of crude reaction mixture in optimized reaction conditions after 6h (Ruthenium catalyst):

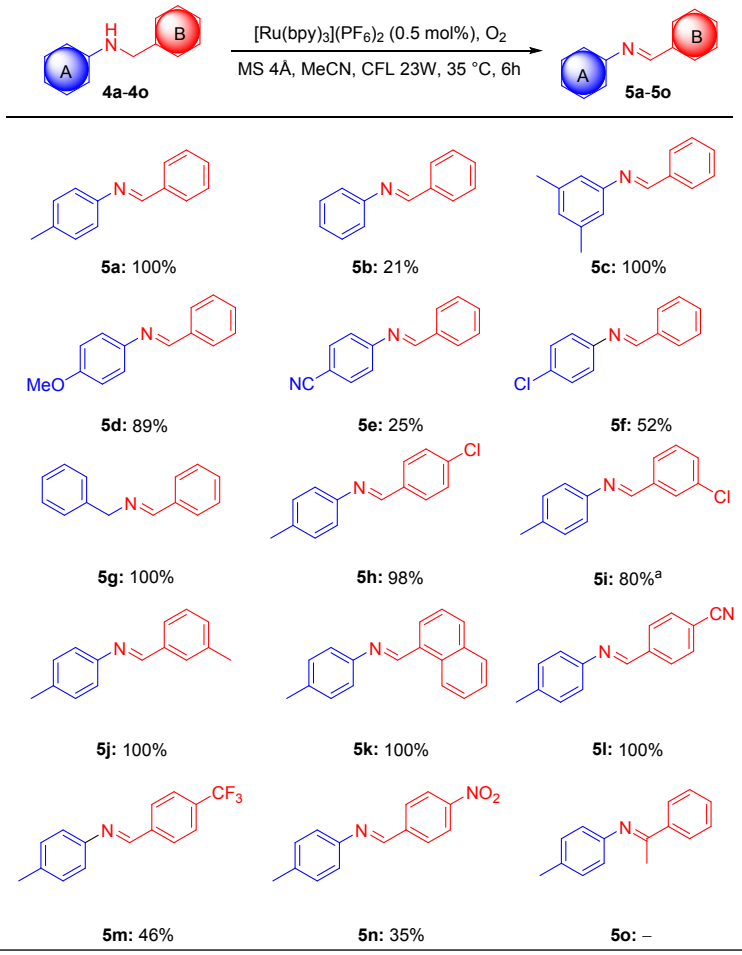


^{1}H NMR of crude reaction mixture in optimized reaction conditions after 16h (Rose

Bengal):



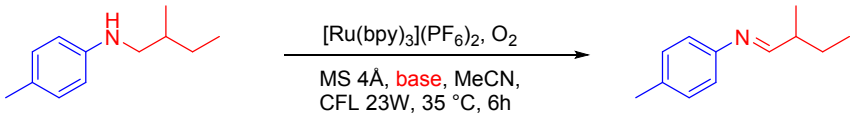
d) Reagents scope



Unless otherwise indicated, all reactions were performed as follows: reaction scale: 0.25 mmol, 0.5 mol% of photocatalyst, 30 mg MS 4Å, O_2 (balloon), MeCN 0.8 mL, temp. 35 °C, reaction time 16h, CFL 23W, isolated yield; [a] reaction time 48h.

5. Scope and limitations – dehydrogenation of *N*-alkyl aromatic amines 6a-6j

a) Optimization studies

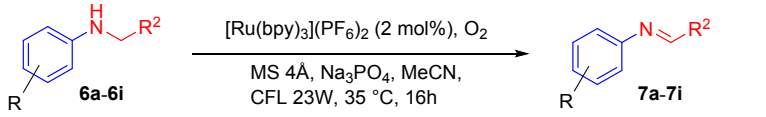


6a **7a**

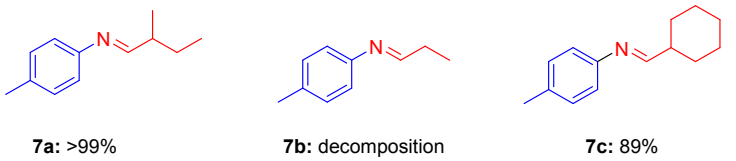
No	Catalyst	Catalyst loading	Additive	Base	Yield [%]
1	$[Ru(bpy)_3](PF_6)_2$	0.5 mol%	MS 4Å	—	—
2	$[Ru(bpy)_3](PF_6)_2$	0.5 mol%	MS 4Å	Na_3PO_4	48
3	**$[Ru(bpy)_3](PF_6)_2$**	**2 mol%**	**MS 4Å**	**Na_3PO_4**	**> 99** [a]
4	$[Ru(bpy)_3](PF_6)_2$	0.5 mol%	MS 4Å	K_2CO_3	33
5	$[Ru(bpy)_3](PF_6)_2$	0.5 mol%	MS 4Å	NaOH	—
6	$[Ru(bpy)_3](PF_6)_2$	0.5 mol%	MS 4Å	^{t}BuOK	—
7	$[Ru(bpy)_3](PF_6)_2$	0.5 mol%	MS 4Å	DBU	—
8	Rose Bengal	2 mol%	MS 4Å	—	—
9	Rose Bengal	2 mol%	MS 4Å	Na_3PO_4	— [a]
10	Rose Bengal	5 mol%	MS 4Å	Na_3PO_4	— [a]

Unless otherwise indicated, all reactions were performed as follows: reaction scale: 0.25 mmol, 2 mol% of photocatalyst, 30 mg of MS 4Å, base 1.0 equiv., O_2 (balloon), MeCN 0.8 mL, temp. 35 °C, reaction time 6h, CFL 23W, isolated yield; [a] reaction time 16h.

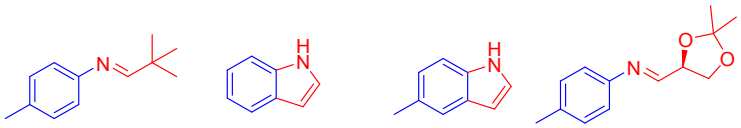
b) Reagents scope



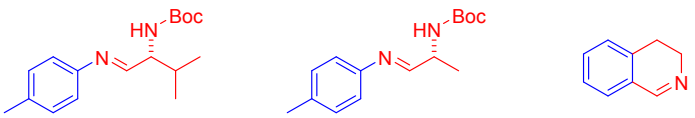
6a-6i **7a-7i**



7a: >99% **7b:** decomposition **7c:** 89%



7d: >99%[a] **7e:** 43%[a] **7f:** 76%[a] **7g:** >99%[a]



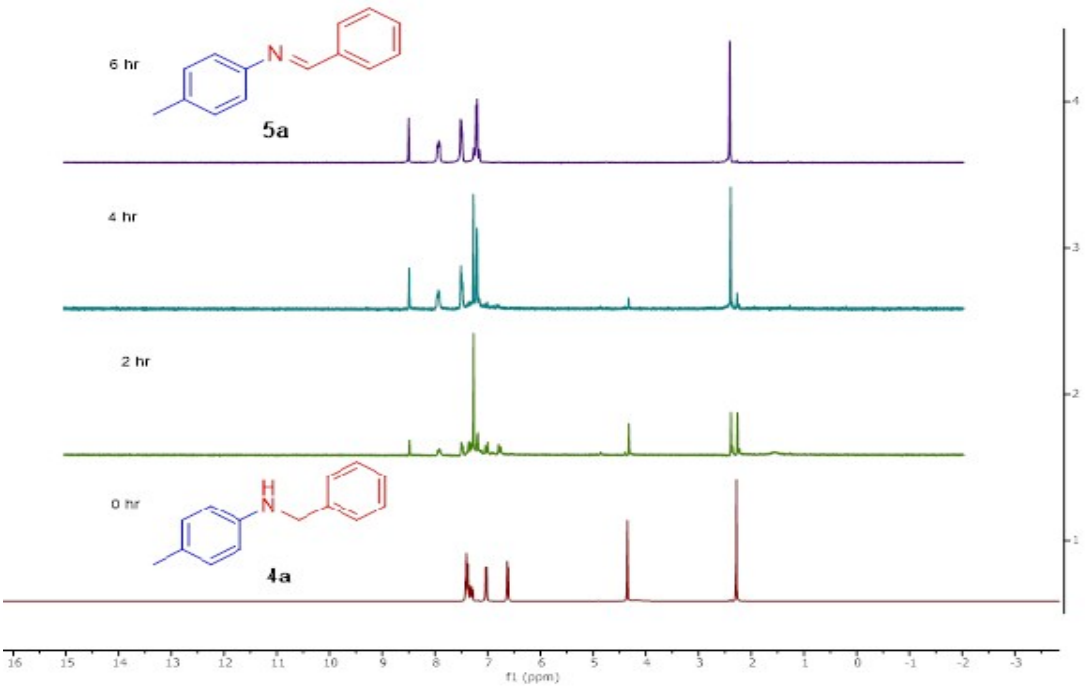
7h: >99%[a] **7i:** >99% **7j:** >99%[b] (43%[c])

Unless otherwise indicated, all reactions were performed as follows: reaction scale: 0.25 mmol, 2 mol% of photocatalyst, 30 mg MS 4Å, Na_3PO_4 1.0 equiv., O_2 (balloon), MeCN 0.8 mL, temp. 35 °C, reaction time 16h, CFL 23W, isolated yield; [a] reaction time 48h; [b] NMR yield; [c] isolated yield.

6. Mechanistic studies

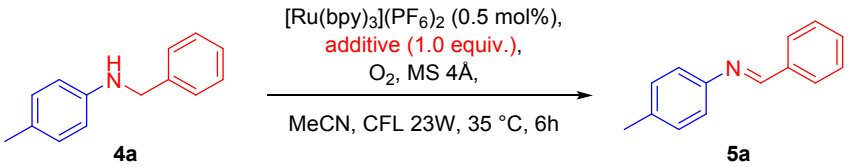
a) ^{1}H NMR of dehydrogenation of 4a in time (crude samples)

NMR experiments showed formation of only one product – imine **5a** in 100% conversion after 6h.



b) The influence of quencher additives

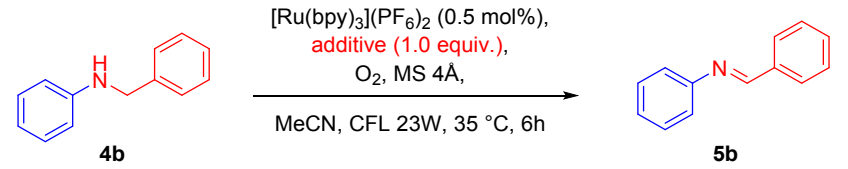
To gain more information about possible mechanistic path of the imine **5a** formation, several additional experiments were carried out. Control experiments showed no product formation without light source, photocatalyst or oxygen atmosphere indicating that some chemical quench occurs in the reaction between substrates, photocatalyst and oxygen (entries 2–4). To identify the existence of reactive oxygen intermediates, experiments with addition of different quenchers where investigated next (entries 4–8). Addition of TEMPO (entry 5) or 2,4,6-TTBP (entry 6) blocked reaction pointing likely on the radical mechanism. Additional experiments with benzoquinone demonstrated importance of the superoxide radical anion (entry 7). Furthermore, the addition of *tert*-butanol to the reaction mixture has no effect (entry 8), indicating no involvement of hydroxide radicals in the reaction mechanism. Moreover, no suppression of the oxidation reaction was observed in the presence of DABCO $^{1}O_2$ quencher (entry 9).



4a **5a**

No	Photocatalyst [0.5 mol%]	Additive [1.0 equiv.]	Yield [%]	Comment
1	$[Ru(bpy)_3](PF_6)_2$	—	100	model reaction
2	—	—	—	photo-induced reaction
3	—	— [b]	—	photo-induced reaction
4	$[Ru(bpy)_3](PF_6)_2$	— [c]	—	importance of oxygen intermediates
5	$[Ru(bpy)_3](PF_6)_2$	TEMPO	20	radical mechanism
6	$[Ru(bpy)_3](PF_6)_2$	2,4,6-TTBP	—	radical mechanism
7	$[Ru(bpy)_3](PF_6)_2$	Benzoquinone	—	superoxide radical involvement
8	$[Ru(bpy)_3](PF_6)_2$	^{t}BuOH	100	no hydroxide radical dependence
9	$[Ru(bpy)_3](PF_6)_2$	DABCO	100	no $^1O_2$ involvement

Unless otherwise indicated, all reactions were performed as follows: reaction scale: 0.25 mmol, 0.5 mol% of $[Ru(bpy)_3](PF_6)_2$, 30 mg MS 4Å, O_2 (balloon), MeCN 0.8 mL, temp. 35 °C, reaction time 6h, CFL 23W, isolated yield; [b] no light; [c] no oxygen.



4b **5b**

No	Photocatalyst [0.5 mol%]	Additive [1.0 equiv.]	Yield [%]	Comment
1	$[Ru(bpy)_3](PF_6)_2$	—	21	model reaction
2	$[Ru(bpy)_3](PF_6)_2$	DABCO	—	$^1O_2$ involvement
3	$[Ru(bpy)_3](PF_6)_2$	TEMPO	—	$^1O_2$ involvement

Unless otherwise indicated, all reactions were performed as follows: reaction scale: 0.25 mmol, 0.5 mol% of $[Ru(bpy)_3](PF_6)_2$, 30 mg MS 4Å, O_2 (balloon), MeCN 0.8 mL, temp. 35 °C, reaction time 6h, CFL 23W, isolated yield.

c) Stern-Volmer experiments: Quenching of Ru^{2+} by arylamines, and O_2

Stern-Volmer analyses for each of the reaction components (Figure 2, Figure 3) clearly showed that arylamine exhibit strong quench of $Ru(bpy)_3^{2+}$ (Figure 2). Samples were prepared by adding solutions of substrates to $[Ru(bpy)_3](PF_6)_2$ solution in MeCN (total volume 2 mL) and degassed with Ar. The concentration of $[Ru(bpy)_3](PF_6)_2$ in MeCN was 1.17×10^{-5} M. Samples were irradiated at 453 nm, and emission was detected at 608 nm. For oxygen quenching experiment sample was initially degassed with Ar and oxygenated over 30 min by bubbling O_2 through the solution.

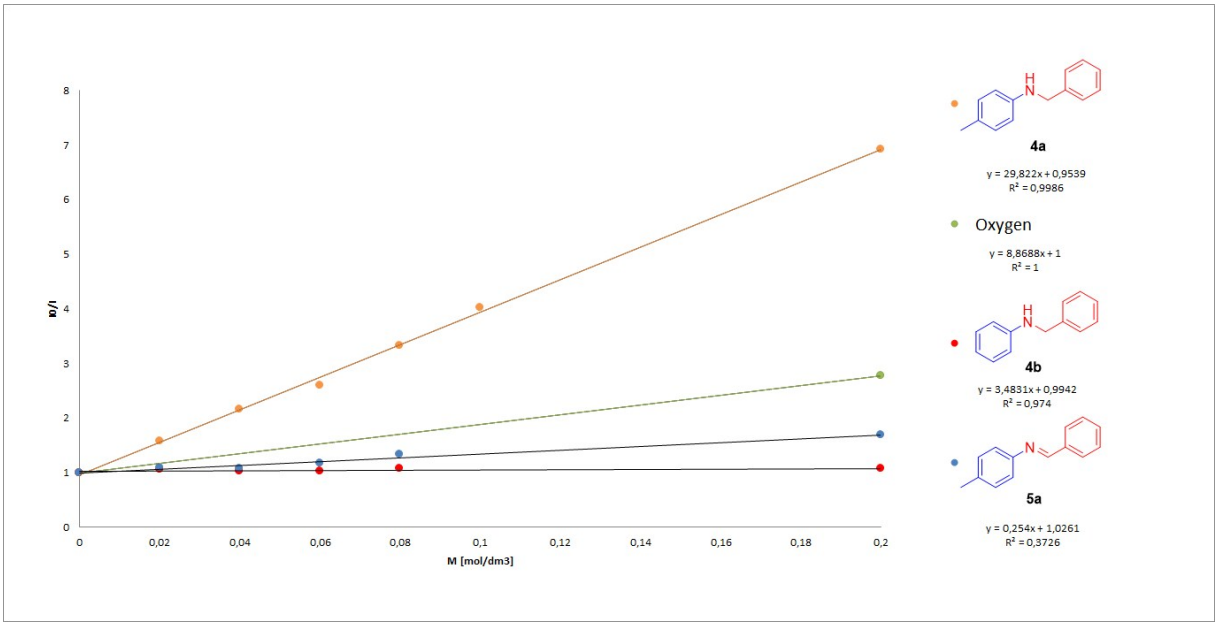


*Figure 2 Stern-Volmer quenching experiments of $Ru(bpy)_3^{2+}$ for **4a**, **4b**, **5a** and oxygen*

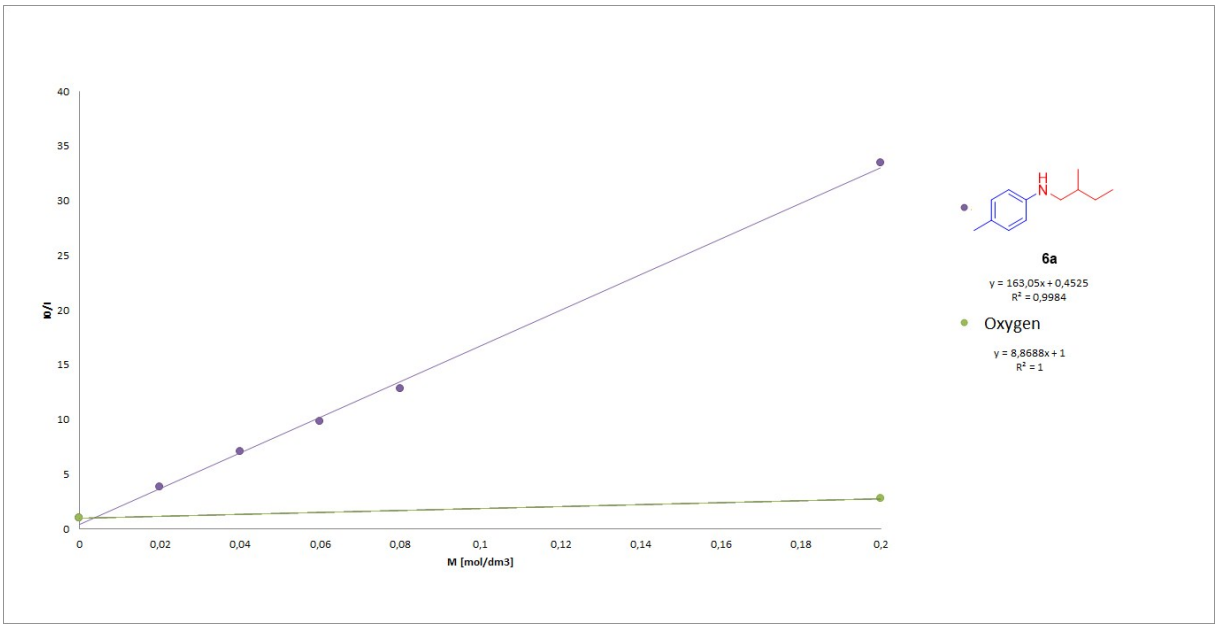


*Figure 3 Stern-Volmer quenching experiments of $Ru(bpy)_3^{2+}$ for **6a** and oxygen*

The quenching rates for each of the photocatalysts were determined using following equation:

$$\frac{I_0}{I} = k_q \cdot \tau \cdot [quencher]$$

I_0 – emission intensity without the quencher

I – emission intensity in the presence of the quencher

τ – the lifetime of the photocatalyst in the excited state

Determined quenching rates (k_q):

τ = 890 ns in acetonitrile [2]

N-Benzyl-4-methylaniline **4a**:	$k_q = 8.87 \cdot 10^7\ s^{-1} \cdot M^{-1}$
N-Benzylaniline **4b**:	$k_q = 5.28 \cdot 10^7\ s^{-1} \cdot M^{-1}$
Benzal-4-methylaniline **5a**:	$k_q = 5.14 \cdot 10^7\ s^{-1} \cdot M^{-1}$
4-Methyl-*N*-(2-methylbutyl)aniline **6a**	$k_q = 2.16 \cdot 10^8\ s^{-1} \cdot M^{-1}$
Oxygen:	$k_q = 6.61 \cdot 10^7\ s^{-1} \cdot M^{-1}$

Stern–Volmer analyses for each of the reaction components clearly showed that starting material (*N*-Benzyl-4-methylaniline **4a**) exhibit strong quench of $Ru(bpy)_3^{2+}$, with quenching rate constant of $k_q = 8.87 \cdot 10^7\ s^{-1} \cdot M^{-1}$ indicating Ru^+ formation rather than involvement of singlet oxygen reaction pathway. However, it can be seen that not substituted *N*-benzylaniline **4b** indicates much lower quench of $Ru(bpy)_3^{2+}$ ($k_q = 5.69 \cdot 10^7\ s^{-1} \cdot M^{-1}$) than oxygen ($k_q = 6.61 \cdot 10^7\ s^{-1} \cdot M^{-1}$) indicating in this case rather type II of the reaction pathway and explain poor results generated by the **4b** amine. Aliphatic 4-Methyl-*N*-(2-methylbutyl)aniline **6a** also exhibit strong quench of $Ru(bpy)_3^{2+}$, with quenching rate constant of $k_q = 2.16 \cdot 10^8\ s^{-1} \cdot M^{-1}$.

d) Proposed mechanism

A proposed reaction mechanism for the imine **5a** formation begins with SET to the amine **4a** from the excited state of $[Ru(bpy)_3]^{2+}$, generated by the visible light irradiation (Figure 4). This process leads to the formation of cation radical **9**. Subsequent oxidation of $[Ru(bpy)_3]^+$ by SET from the oxygen regenerates ruthenium catalyst along with the superoxide radical formation. Subsequent loss of the α-proton from the **9** followed by the oxidation of the resulting radical produces the imine **5a**. In *N*-alkyl anilines α-proton of the cation radical is less acidic than in *N*-benzyl anilines, therefore addition of stronger base facilitate proton loss from **9** intermediate (pKb of Na_3PO_4 is 1.65; pKb of superoxide is 9.12).[3, 4]

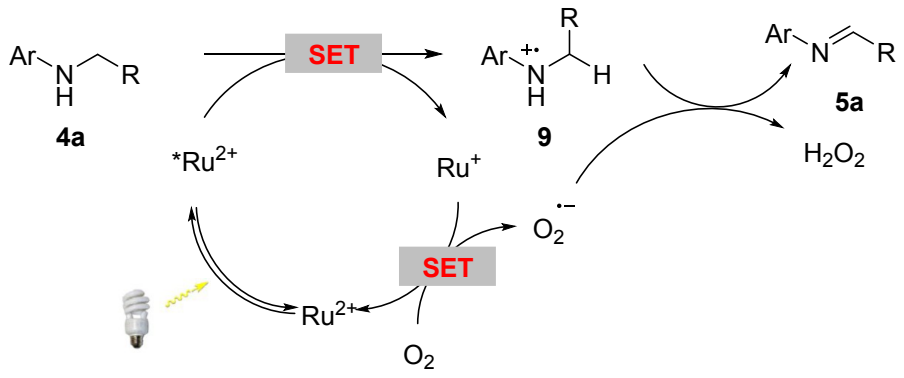
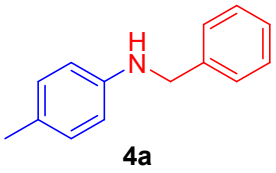


Figure 4 Proposed reaction mechanism

7. Characteristic of the obtained compounds

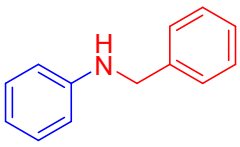
_N_-Benzyl-4-methylaniline (4a)



4a

Prepared according to the general procedure A. The product was obtained as a yellow oil (1.25 g, 70%, eluent: Hexane/AcOEt = 95/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, 5H), 7.05 – 7.00 and 6.65 – 6.60 (m, 4H, AA'XX'), 4.34 (s, 2H), 2.27 (s, 3H) and correspond to literature data.[5]

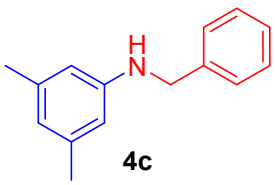
_N_-Benzylaniline (4b)



4b

Prepared according to the general procedure A. The product was obtained as a white solid (1.26 g, 76%, eluent: Hexane/AcOEt = 95/5). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.42 – 7.12 (m, 7H), 6.84 – 6.57 (m, 3H), 4.35 (s, 2H) and correspond to literature data.[5]

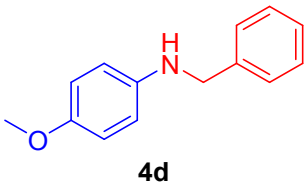
_N_-Benzyl-3,5-dimethylaniline (4c)



4c

Prepared according to the general procedure A. The product was obtained as a colorless solid (1.87 g, 88%, eluent: Hexane/AcOEt = 9/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.24 (m, 5H), 6.95 (d, J = 6.6 Hz, 2H), 6.58 (d, J = 6.6 Hz, 1H), 4.40 (s, 2H), 3.78 (bs, 1H), 2.28 (s, 3H), 2.19 (s, 3H) and correspond to literature data.[6]

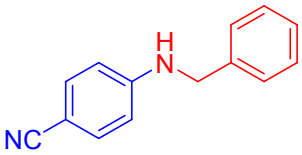
_N_-Benzyl-4-methoxyaniline (4d)



4d

Prepared according to the general procedure A. The product was obtained as a yellow oil (1.75 g, 89%, eluent: Hexane/AcOEt = 95/5). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.42 – 7.23 (m, 5H), 6.84 – 6.73 and 6.69 – 6.55 (m, 4H, AA'XX'), 4.29 (s, 2H), 3.75 (s, 3H) and correspond to literature data.[5]

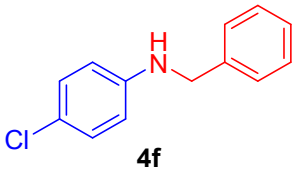
4-Cyano-*N*-benzylaniline (4e)



4e

Prepared according to the general procedure A. The product was obtained as white powder (1.92 g, 79 %, Eluent: Hexane/AcOEt = 9/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 5H), 7.42 – 7.38 and 6.65 – 6.56 (m, 4H, AA'XX'), 4.73 (bs, 1H), 4.38 (s, 2H) correspond to literature data.[7]

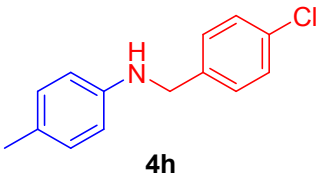
4-Chloro-*N*-benzylaniline (4f)



4f

Prepared according to the general procedure A. The product was obtained as a brown solid (1.42 g, 73%, eluent: Hexane/AcOEt = 95/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H), 7.14 – 7.08 and 6.58 – 6.51 (m, 4H, AA'XX'), 4.31 (s, 2H), 4.09 (bs, 1H) and correspond to literature data.[8]

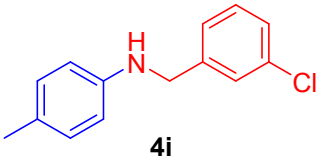
4-Methyl-*N*-(4-chlorobenzyl)aniline (4h)



4h

Prepared according to the general procedure A. The product was obtained as a yellow oil (1.52 g, 75%, eluent: Hexane/AcOEt = 95/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (m, 4H), δ 7.10 – 7.13 and 6.50 – 6.60 (m, 4H, AA'XX'), 4.30 (s, 2H), 3.94 (bs, 1H), 2.25 (s, 3H) and correspond to literature data.[9]

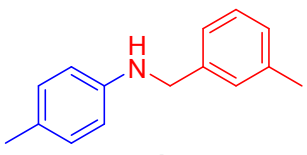
4-Methyl-*N*-(3-chlorobenzyl)aniline (4i)



4i

Prepared according to the general procedure A. The product was obtained as a colorless oil (1.80 g, 78%, eluent: Hexane/AcOEt = 9/1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.27 (s, 3H), 7.00 (d, J = 8.4 Hz, 2H), 6.55 (d, J = 8.4 Hz, 2H), 4.31 (s, 2H), 2.26 (s, 3H) and correspond to literature data.[8]

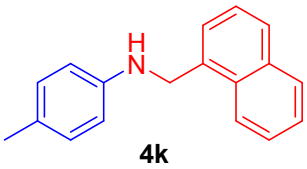
4-Methyl-*N*-(3-methylbenzyl)aniline (4j)



4j

Prepared according to the general procedure A. The product was obtained as a brown oil (1.75 g, 77%, eluent: Hexane/AcOEt = 9/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.17 (m, 3H), 7.13 (d, J = 7.3 Hz, 1H), 7.03 – 7.00 and 6.59 – 6.65 (m, 4H, AA'XX'), 4.31 (s, 2H), 3.91 (bs, 1H), 2.39 (s, 3H), 2.29 (s, 3H) and correspond to literature data.[10]

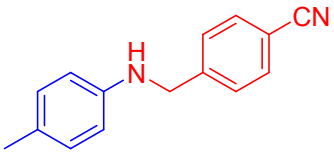
4-Methyl-*N*-(naphthalen-1-ylmethyl)aniline (4k)



4k

Prepared according to the general procedure A. The product was obtained as a brown oil (1.50 g, 61%, eluent: Hexane/AcOEt = 95/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (t, *J* = 8.7 Hz, 4H), 7.58 – 7.41 (m, 3H), 7.02-7.00 and 6.73 – 6.56 (m, 4H, AA'XX'), 4.51 (s, 2H), 4.04 (bs, 1H), 2.27 (s, 3H) and correspond to literature data.[11]

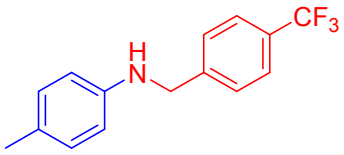
4-Methyl-*N*-(4-cyanobenzyl)aniline (4l)



4l

Prepared according to the general procedure A. The product was obtained as a white solid (1.80 g, 81%, eluent: Hexane/AcOEt = 95/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.58 and 7.55 – 7.45 (m, 4H, AA'XX'), δ 7.10 – 6.81 and 6.65 – 6.45 (m, 4H, AA'XX'), 4.43 (s, 2H), 4.12 (bs, 1H), 2.27 (s, 3H) and correspond to literature data.[12]

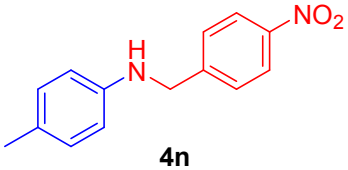
4-Methyl-*N*-(4-trifluoromethylbenzyl)aniline (4m)



4m

Prepared according to the general procedure A. The product was obtained as a yellow solid (1.78 g, 85%, eluent: Hexane/AcOEt = 4/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.51 (m, 4H, AA'XX'), 7.02 – 6.57 (m, 4H, AA'XX'), 4.42 (s, 2H), 4.05 (bs, 1H), 2.27 (s, 3H) and correspond to literature data.[13]

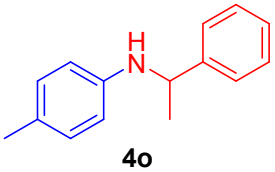
***N*-(4-Nitrobenzylidene)-4-methylaniline (4n)**



4n

Prepared according to the general procedure A. The product was obtained as a white solid (1.92 g, 79%, eluent: Hexane/AcOEt = from 9/1 to 4/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.53 (d, *J* = 8.0 Hz, 2H), 4.46 (s, 2H), 4.17 (bs, 1H), 2.26 (s, 3H) and correspond to literature data.[7]

***N*-(1-Phenyl-ethylidene)-4-methylaniline (4o)**

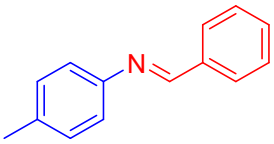


4o

Prepared according to the general procedure A. The product was obtained as a yellow oil (2.04 g, 96%, eluent: Hexane:AcOEt 9/1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.45 – 7.13 (m, 5H), δ 6.98 – 6.81 and 6.60

– 6.50 (m, 4H, AA'XX'), 4.46 (q, J = 6.8 Hz, 1H), 2.19 (s, 3H), 1.54 (d, J = 6.8 Hz, 4H) and correspond to literature data.[10]

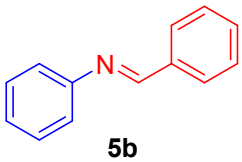
Benzal-4-methylaniline (5a)



5a

Prepared according to the general procedure B. The product was obtained as a brown solid (49 mg, 100%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.97 – 7.82 (m, 2H), 7.57 – 7.39 (m, 3H), 7.33 – 7.06 (m, 4H), 2.36 (d, J = 11.0 Hz, 3H) and correspond to literature data.[7]

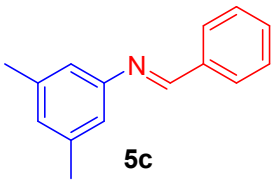
Benzylidene phenylamine (5b)



5b

Prepared according to the general procedure B. The product was obtained as a brown solid (10 mg, 21%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 4.7 Hz, 1H), 7.97 – 7.85 (m, 2H), 7.52 – 7.45 (m, 3H), 7.44 – 7.37 (m, 2H), 7.25 – 7.19 (m, 3H) and correspond to literature data.[7]

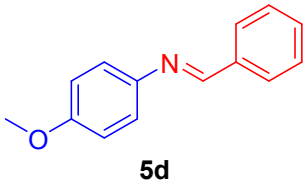
3,5-Dimethyl-*N*-benzylideneaniline (5c)



5c

Prepared according to the general procedure B. The product was obtained as a yellow oil (52 mg, 99%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.04 – 7.81 (m, 2H), 7.62 – 7.39 (m, 3H), 6.97 (m, 3H), 2.42 – 2.22 (m, 6H) and correspond to literature data.[14]

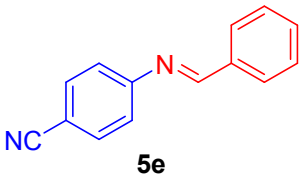
[4-(Benzylideneamino)phenyl]methanol (5d)



5d

Prepared according to the general procedure B. The product was obtained as a solid (47 mg, 89%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.02 – 7.85 (m, 2H), 7.50 (m, 2H), 7.39 (m, 2H), 7.30 (d, J = 2.4 Hz, 1H), 7.00 – 6.94 (m, 1H), 6.82 (d, J = 8.8 Hz, 1H), 3.89 – 3.80 (m, 3H) and correspond to literature data.[7]

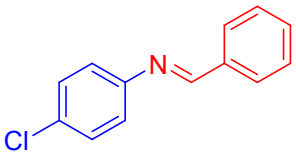
1-(4-Cyanophenyl)-*N*-phenylmethanimine (5e)



5e

Prepared according to the general procedure B. The product was obtained as a solid (14 mg, 25%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.93 – 7.68 (m, 4H, AA'XX'), 7.57 – 7.49 (m, 3H), 7.25 (d, J = 8.4 Hz, 2H) correspond to literature data.[7]

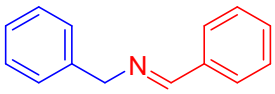
1-(4-Chlorophenyl)-*N*-phenylmethanimine (5f)



5f

Prepared according to the general procedure B. The product was obtained as a yellow oil (28 mg, 52%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.90 (m, 2H), 7.55 – 7.44 (m, 3H), 7.42 – 7.09(m, 4H, AA'XX') and correspond to literature data.[14]

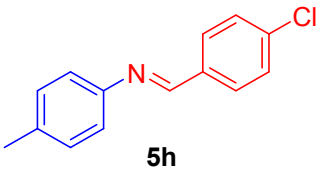
***N*-Benzylidenebenzylamine (5g)**



5g

Prepared according to the general procedure B. The product was obtained as an orange oil (49 mg, 99%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.90 – 7.75 (m, 2H), 7.54 – 7.20 (m, 8H), 4.86 (d, J = 1.2 Hz, 2H) and correspond to literature data.[7]

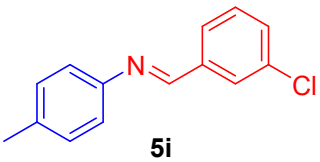
***N*-(4-Chlorobenzylidene)-4-methylaniline (5h)**



5h

Prepared according to the general procedure B. The product was obtained as an orange oil (56 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.84 – 7.45 (m, 4H, AA'XX'), 7.38 – 6.95 (m, 4H), 2.54 – 2.25 (m, 3H) and correspond to literature data.[15]

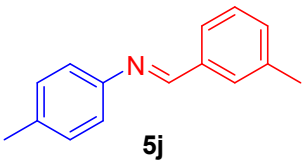
***N*-(3-Chlorobenzylidene)-4-methylaniline (5i)**



5i

Prepared according to the general procedure B. The product was obtained as an oil (46 mg, 80%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.00 (s, 1H), 7.80 (d, J = 6.5 Hz, 1H), 7.58 – 7.39 (m, 2H), 7.35 – 7.10 (m, 4H), 2.44 (s, 3H) and correspond to literature data.[16]

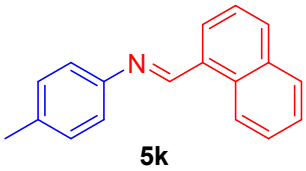
_N_-(3-Methyl-benzylidene)-4-methylaniline (5j)



5j

Prepared according to the general procedure B. The product was obtained as an oil (52 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.77 (s, 1H), 7.68 (m, 1H), 7.41 – 7.27 (m, 2H), 7.21 – 7.15 (m, 4H, AA'XX'), 2.43 (d, J = 8.6 Hz, 3H), 2.39 (s, 3H) and correspond to literature data.[17]

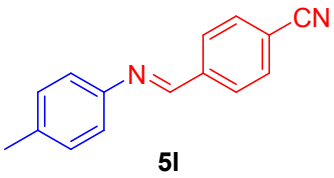
1-Napthyliden-*p*-methylanilin (5k)



5k

Prepared according to the general procedure B. The product was obtained as a yellowish solid (49 mg, 99%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.26 – 8.08 (m, 2H), 8.03 – 7.74 (m, 3H), 7.69 – 7.44 (m, 2H), 7.33 – 7.09 (m, 4H), 2.39 (s, 3H) and correspond to literature data.[11]

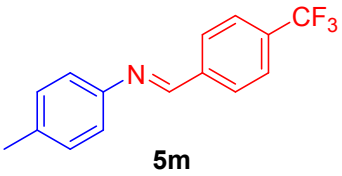
_N_-(4-Cyanobenzylidene)-4-methylaniline (5l)



5l

Prepared according to the general procedure B. The product was obtained as an oil (55 mg, 99%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.13 –7.64 (m, 4H, AA'XX'), 7.34 – 7.08 (m, 4H), 2.39 (s, 3H) and correspond to literature data.[18]

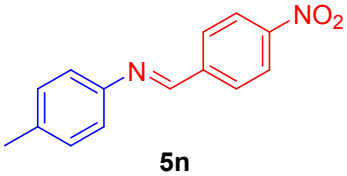
_N_-(4-Trifluoromethylbenzylidene)-4-methylaniline (5m)



5m

Prepared according to the general procedure B. The product was obtained as a yellow oil (30 mg, 46%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.02 – 7.73 (m, 4H, AA'XX'), 7.36 – 6.97 (m, 4H), 2.40 (s, 3H) and correspond to literature data.[13]

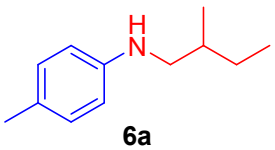
_N_-(4-Nitrobenzylidene)-4-methylaniline (5n)



5n

Prepared according to the general procedure B. The product was obtained as a yellow solid (21 mg, 35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.37 –7.99 (m, 4H, AA'XX'), 7.27 – 7.17 (m, 4H), 2.45 (s, 3H) and correspond to literature data.[19]

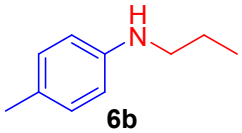
4-Methyl-*N*-(2-methylbutyl)aniline (6a)



6a

Prepared according to the general procedure A. The product was obtained as a yellow oil (1.49 g, 85%, eluent: Hexane/AcOEt = 95/5). IR ($CHCl_3$, cm^{-1}) 3416, 3015, 2960, 2922, 2872, 1521, 1461, 806; ^1H NMR (400 MHz, $CDCl_3$) δ 7.01 – 6.57 (m, 4H, AA'XX'), 3.65 (bs, 1H), 3.07 (dd, *J* = 12.2, 6.0 Hz, 1H), 2.91 (dd, *J* = 12.2, 6.0 Hz, 1H), 2.27 (s, 3H), 1.81 – 1.62 (m, 1H), 1.62 – 1.44 (m, 1H), 1.35 – 1.14 (m, 1H), 1.07 – 0.86 (m, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 146.4, 129.7, 126.1, 112.8, 50.3, 34.5, 27.3, 20.5, 17.6, 11.3; HRMS (EI) m/z [M+]: calcd for $C_{12}H_{19}N$ 177.1517, found 177.1519.

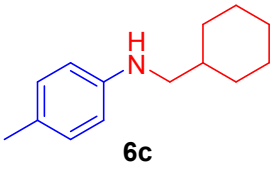
4-Methyl-*N*-(ethyl)aniline (6b)



6b

Prepared according to the general procedure A. The product was obtained as a brown oil (1.50 g, 73%, eluent: Hexane/AcOEt = 95/5). ^1H NMR (400 MHz, $CDCl_3$) δ 7.02 – 6.51 (m, 4H, AA'XX'), 3.60 (bs, 1H), 3.09 (t, *J* = 7.1 Hz, 2H), 2.28 (d, *J* = 6.5 Hz, 3H), 1.76 – 1.57 (m, 2H), 1.09 – 0.96 (t, 3H) and correspond to literature data.[20]

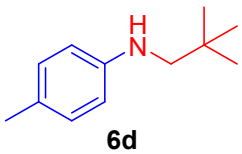
***N*-(Cyclohexylmethyl)-4-methylaniline (6c)**



6c

Prepared according to the general procedure A. The product was obtained as a yellowish solid (1.50 g, 70%, eluent: Hexane/AcOEt = 95/5). ^1H NMR (400 MHz, $CDCl_3$) δ 7.05– 6.48 (m, 4H, AA'XX'), 3.62 (bs, 1H), 2.97 (d, *J* = 6.7 Hz, 2H), 2.27 (s, 3H), 1.75 (m, 5H), 1.66 – 1.52 (m, 1H), 1.40 – 1.11 (m, 3H), 1.10 – 0.90 (m, 2H) and correspond to literature data.[5]

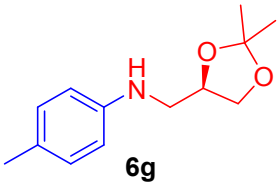
***N*-Neopentylaniline (6d)**



6d

Prepared according to the general procedure A. The product was obtained as a reddish solid (1.50 g, 80%, eluent: Hexane/AcOEt = 95/5). ^1H NMR (400 MHz, $CDCl_3$) δ 7.01 – 6.58 (m, 4H, AA'XX'), 3.51 (bs, 1H), 2.90 (s, 2H), 2.26 (s, 3H), 1.01 (s, 9H) and correspond to literature data.[10]

***N*-(2-Methyl-1,3-dioxolan-5-ylmethyl)-4-methylaniline (6g)**

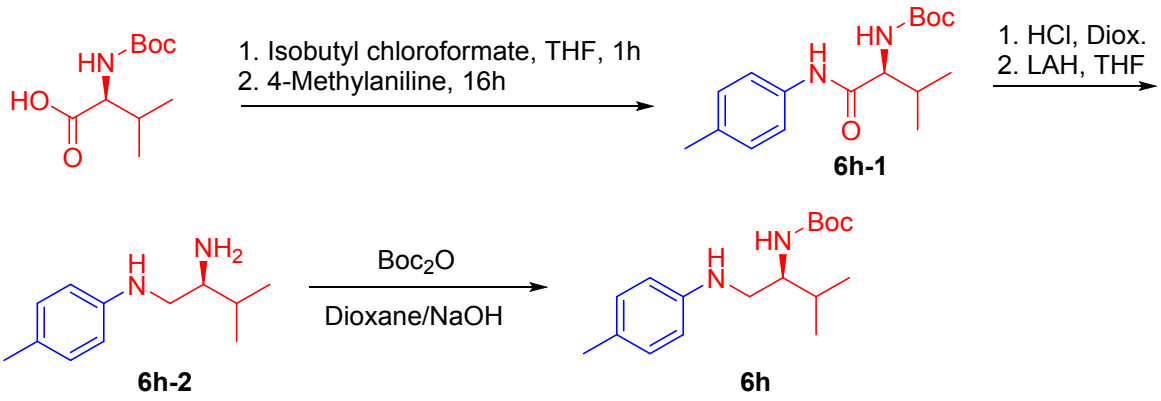


6g

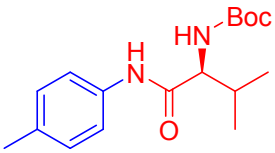
Prepared according to the general procedure A. The product was obtained as colorless oil (1.60 g, 72%, eluent: Hexane/AcOEt = 9/1). $[\alpha]^{25}_D$ = - 5.0 (c 1.0, EtOH); IR ($CHCl_3$, cm^{-1}) 3384, 2986, 2932, 2878,

1518, 1070, 614, 511; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 – 6.56 (m, 4H, AA'XX'), 4.35 (qd, *J* = 6.4, 4.5 Hz, 1H), 4.08 (dd, *J* = 8.2, 6.4 Hz, 1H), 3.82 (bs, 1H), 3.76 (dd, *J* = 8.2, 6.4 Hz, 1H), 3.28 (dd, *J* = 12.6, 4.5 Hz, 1H), 3.22 – 3.12 (m, 1H), 2.24 (s, 3H), 1.45 (s, 3H), 1.37 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 145.7, 129.7, 127.0, 113.2, 109.4, 74.6, 67.3, 47.0, 26.9, 25.4, 20.4; HRMS (EI) m/z [M+]: calcd for $C_{13}H_{19}NO_2$ 221.1416, found 221.1423.

Synthesis of *tert*-butyl (2*S*)-3-methyl-1-[(4-methylphenyl)amino]butan-2-ylcarbamate (6h)



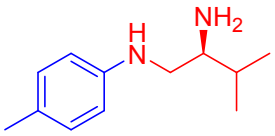
(2*S*)-2-Amino-3-methyl-*N*-(4-methylphenyl)butanamide (6h-1)



6h-1

To a cold solution (-15 °C) of *N*-Boc-L-Valine (42.0 mmol) and 4-methylmorpholine (4.16 g, 4.56 mL, 42.0 mmol, 1.0 equiv.) in dry THF (120 mL) isobutyl chloroformate (5.74 g, 5.45 mL, 42.0 mmol, 1.0 equiv.) in dry THF (20 mL) was added dropwise over 15 min. After the mixture was stirred for another 15 min, 4-methylaniline (4.50 g, 42.0 mmol) was added. Then the mixture was allowed to slowly warm to room temperature and stirred for 16h. After evaporation of the solvent in vacuo, the residue was diluted with AcOEt and the organic phase was washed with 10% aq Na_2CO_3, 0.1 M HCl, brine and dried over anhydrous Na_2SO_4. Evaporation of the solvents gave crude (2*S*)-2-amino-3-methyl-*N*-(4-methylphenyl)butanamide **6h-1**, which was used for the subsequent acid hydrolysis without further purification. The product was obtained as a yellow solid (12.00 g, 93%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (bs, 1H), 7.35 – 6.99 (m, 4H, AA'XX'), 5.62 (d, *J* = 8.7 Hz, 1H), 4.15 (bs, 1H), 2.28 (d, *J* = 12.9 Hz, 3H), 2.16 (d, *J* = 5.4 Hz, 1H), 1.43 (s, 9H), 1.02 (t, *J* = 8.7 Hz, 6H) and correspond to literature data.[21]

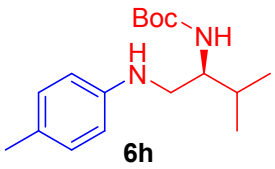
(2*S*)-*N*^{1}-(4-Methylphenyl)-3-methyl-1,2-butanediamine (6h-2)



6h-2

(2*S*)-2-Amino-3-methyl-*N*-(4-methylphenyl)butanamide **6h-1** (1,18 g, 4.0 mmol, 1 equiv.) was dissolved in 5 mL HCl (4.0 M in dioxane) and the mixture was stirred at room temperature until TLC showed the disappearance of the starting material. Then the mixture was treated with 1 M aq NaOH and extracted with DCM. The organic phase was washed with brine and dried over anhydrous Na_2CO_3. Evaporation of the solvent in vacuo gave the crude of (2*S*)-2-amino-3-methyl-*N*-(4-methylphenyl)butanamide, which was purified by column chromatography. The product was obtained as a yellow solid (0.55 g, 71%, eluent: CH_3Cl/MeOH 5%); ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.43 (bs, 1H), 7.67 – 7.13 (m, 4H, AA'XX'), 3.36 (d, *J* = 3.6 Hz, 1H), 2.50 – 2.27 (m, 4H), 1.48 (bs, 2H), 1.04 (d, *J* = 6.9 Hz, 3H), 0.87 (d, *J* = 6.9 Hz, 3H). and correspond to literature data.[21] To a stirred solution of 5.3 g (2*S*)-2-Amino-3-methyl-*N*-(4-methylphenyl)butanamide (15.0 mmol, 1.0 equiv) in dry THF (60 mL) under Ar atmosphere lithium aluminium hydride (1.65 g, 45.0 mmol, 3.0 equiv) was added portion-wise at 0 °C. The reaction mixture was then refluxed for 12h. Thereafter it was cooled and slowly quenched with aq NaOH and residue slurry was filtered through the celite. The filtrate was taken in ethyl acetate, washed with brine, and dried. The product **6h-2** was obtained as a white solid (2.67 g, 55%, eluent: DCM/MeOH 10%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 – 6.56 (m, 4H, AA'XX'), 3.23 (m, 1H), 2.84 (m, 1H), 2.79 – 2.70 (m, 1H), 2.23 (s, 3H), 1.73 – 1.62 (m, 1H), 1.37 – 1.20 (m, 1H), 0.96 (dd, *J* = 9.1, 6.8 Hz, 6H) and correspond to literature data.[21]

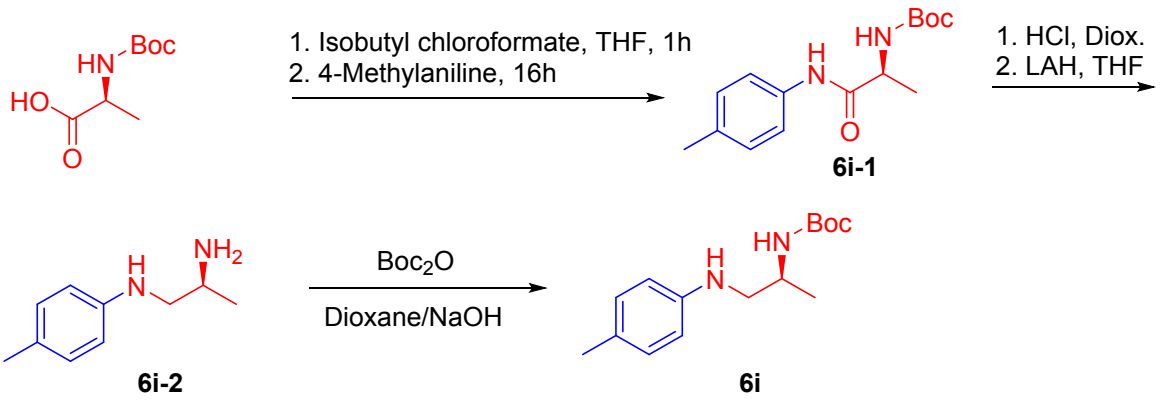
***tert*-Butyl (2*S*)-3-methyl-1-[(4-methylphenyl)amino]butan-2-ylcarbamate (6h)**



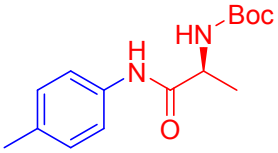
6h

To a stirred solution of (2*S*)-*N*^{1}-(4-Methylphenyl)-3-methyl-1,2-butanediamine **6h-2** (0.63 g, 3.45 mmol, 1.0 equiv) in dioxane (3 mL) 1M NaOH (3 mL) was added. The reaction mixture was cooled to 5 °C and Boc_2O (0.75 g, 3.62 mmol, 1.05 equiv) was added. The reaction mixture was stirred overnight at rt. Thereafter solution was washed with DCM (3x10 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent in vacuo gave the crude **6h**, which was purified by column chromatography. The product was obtained as a white solid (1.08 g, 59%, eluent: Hexane/AcOEt = 9/1). $[\alpha]^{25}_D$ = - 16.0 (c 1.0, DCM); m.p. 66.7 – 67.4 °C; IR ($CHCl_3$, cm^{-1}) 3386, 2965, 2930, 1690, 1523, 1173, 807, 507; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 -6.56 (m, 4H, AA'XX'), 4.53 (bs, 1H), 3.68 (bs, 1H), 3.24 (m, 1H), 3.08 – 2.96 (m, 1H), 2.24 (s, 3H), 1.86 (m, 1H), 1.46 (s, 9H), 0.97 (dd, *J* = 14.4, 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 156.5, 146.2, 129.7, 126.5, 112.8, 79.4, 55., 47.3, 30.5, 28.3, 20.3, 19.4, 18.0; HRMS (ESI) m/z [M+H]$^+$: calcd. for $C_{17}H_{28}N_2O_2$ 293.2229, found 293.2229.

Synthesis of *tert*-butyl (2*S*)-1-[(4-methylphenyl)amino]butan-2-ylcarbamate (6i)



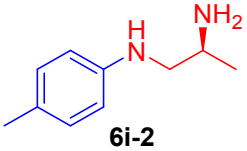
***tert*-Butyl *N*-[(1*S*)-1-Methyl-2-oxo-2-(4-toluidino)ethyl]carbamate (6i-1)**



6i-1

To a cold solution (-15 °C) of *N*-Boc-L-alanine (8.0 g, 42.0 mmol) and 4-methylmorpholine (4.16 g, 4.56 mL, 42.0 mmol, 1.0 equiv.) in dry THF (120 mL) isobutyl chloroformate (5.74 g, 5.45 mL, 42.0 mmol, 1.0 equiv.) in dry THF (20 mL) was added dropwise over 15 min. After the mixture was stirred for another 15 min, 4-methylaniline (4.50 g, 42.0 mmol, 1.0 equiv.) was added. Then the mixture was allowed to slowly warm to room temperature and stirred 16h. After evaporation of the solvent in vacuo, the residue was diluted with AcOEt and the organic phase was washed with 10% aq Na_2CO_3, 0.1 M HCl, and brine and dried over anhydrous Na_2SO_4. Evaporation of the solvents gave crude *N*-Boc-(*R*)-amino amide, which was purified by column chromatography. The product was obtained as a white solid (5.50 g, 49%, eluent: Hexane/AcOEt 95/5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.41 – 7.13 (m, 4H, AA'XX'), 5.02 (bs, 1H), 4.31 (bs, 1H), 2.33 (s, 3H), 1.53 – 1.36 (m, 12H) and correspond to literature data.[21]

(2*S*)-*N*^{1}-(4-methylphenyl)-1,2-propanediamine (6i-2)

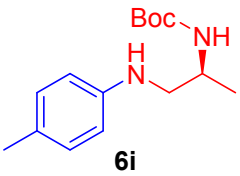


6i-2

tert-Butyl *N*-[(1*S*)-1-Methyl-2-oxo-2-(4-toluidino)ethyl]carbamate **6i-1** (2.78 g, 10.0 mmol, 1 equiv.) was solved in 10 mL of Dioxane/HCl solution (4.05 M in dioxane). The mixture was stirred at room temperature until TLC showed the disappearance of the starting material. Then the mixture was treated with 1M aq. NaOH and extracted with DCM. The organic phase was washed with brine and dried

over anhydrous Na_2SO_4. Evaporation of the solvent in vacuo gave the crude of (2*S*)-2-amino-*N*-(4-methylphenyl)propanamide, which was purified by column chromatography. The product was obtained as a yellow solid (2.4 g, 71%, eluent: DCM/MeOH 5%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 5.02 (s, 1H), 4.31 (s, 1H), 2.33 (s, 3H), 1.53 – 1.36 (m, 12H) and correspond to literature data.[21] To a stirred solution of 5.3 g (2*S*)-2-amino-3-methyl-*N*-(4-methylphenyl)butanamide (15.0 mmol, 1.0 equiv) in dry THF (60 mL) and under Ar atmosphere lithium aluminium hydride (1.65 g, 45.0 mmol, 3.0 equiv.) was slowly added at 0 °C. The reaction mixture was then refluxed for 12h. Thereafter it was cooled and slowly quenched with 1M NaOH and residue slurry was filtered through celite. The filtrate was taken in ethyl acetate, washed with brine, and dried. The product **6i-2** was obtained as a white solid (2.67 g, 55%, eluent: DCM/MeOH 10%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02– 6.51 (m, 4H, AA'XX') 3.25 – 3.08 (m, 2H), 2.95 – 2.80 (m, 1H), 2.27 (s, 3H), 1.23 – 1.08 (m, 3H) and correspond to literature data.[21]

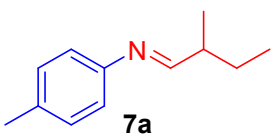
tert-Butyl (2*S*)-1-[(4-methylphenyl)amino]butan-2-ylcarbamate (6i)



6i

To a stirred solution of (2*S*)-*N*-(4-methylphenyl)-1,2-propanediamine **6i-2** (0.78 g, 4.76 mmol, 1.0 equiv) in dioxane (5 mL) and 1M NaOH (5 mL) was added. The reaction mixture was cooled to 5 °C and Boc_2O (1.09 g, 5.00 mmol, 1.05 equiv.) was added portion-wise. The reaction mixture was stirred overnight at rt. Thereafter solution was washed with DCM (3x10 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent in vacuo gave the crude **6i**, which was purified by column chromatography. The product was obtained as a yellowish solid (0.78 g, 62%, eluent: Hexane/AcOEt = 95/5); $[\alpha]^{25}_D$ = - 14.0 (c 1.0, DCM). m.p. 93.3 – 94.1 °C; IR ($CHCl_3$, cm^{-1}) 3378, 2976, 2870, 1693, 1522, 1168, 1054, 807; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.96 – 6.52 (m, 4H, AA'XX'), 4.60 (bs, 1H), 3.90 (bs, 2H), 3.11 (m, 1H), 3.04 (m, 1H), 2.22 (s, 3H), 1.44 (s, 9H), 1.18 (d, *J* = 6.6 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 155.8, 145.7, 129.7, 126.3, 112.8, 79.6, 50.6, 46.3, 28.2, 19.0, 19.0; HRMS (ESI) m/z $[M+H]^+$: calcd. for $C_{15}H_{24}N_2O_2$ 287.1735, found 287.1729.

2-Methylbutyraldehyde-4-methylaniline (7a)

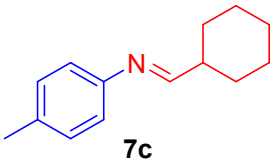


7a

Prepared according to the general procedure C. The product was obtained as a yellow oil (44 mg, 100%). IR ($CHCl_3$, cm^{-1}) 3269, 2965, 2873, 1687, 1520, 1302, 815; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 5.8 Hz, 1H), 7.12 – 6.95 (m, 4H, AA'XX'), 2.48 – 2.38 (m, 1H), 2.33 (s, 3H), 1.66 (m, 1H), 1.58 – 1.45 (m, 1H), 1.17 (d, *J* = 6.8 Hz, 3H), 1.03 – 0.94 (t, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR

(151 MHz, $CDCl_3$) δ 170.0, 149.8, 134.9, 129.5, 120.5, 41.5, 27.0, 20.9, 16.8, 11.6; HRMS (EI) m/z [M+]: calcd for $C_{12}H_{17}N$ 175.1361, found 175.1365.

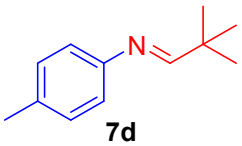
_N_-(Cyclohexylmethylene)-4-methylaniline (7c)



7c

Prepared according to the general procedure C. The product was obtained as a solid (45 mg, 89%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.70 (d, J = 5.1 Hz, 1H), 7.13 – 6.93 (m, 4H, AA'XX'), 2.33 (s, 3H), 2.03 – 1.66 (m, 6H), 1.41 – 1.27 (m, 4H) and correspond to literature data.[22]

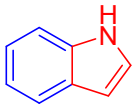
***N-tert*-Butyl-1-phenylmethanimine (7d)**



7d

Prepared according to the general procedure C. The product was obtained as an oil (44 mg, 100%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.15 – 7.05 and 6.95 – 6.85 (m, 4H, AA'XX'), 2.33 (s, 3H), 1.18 (s, 9H) and correspond to literature data.[7]

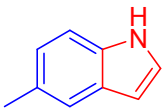
Indole (7e)



7e

Prepared according to the general procedure C. The product was obtained as a brown solid (13 mg, 43%, eluent: Hexane/AcOEt = 95/5). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.81 – 7.64 (m, 1H), 7.51 – 7.33 (m, 1H), 7.34 – 7.11 (m, 3H), 6.70 – 6.51 (m, 1H) and correspond to literature data.[7]

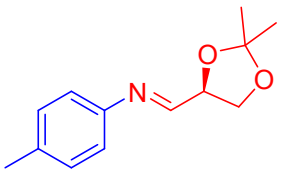
5-Methylindole (7f)



7f

Prepared according to the general procedure C. The product was obtained as a brown solid (25 mg, 76%), eluent: Hexane/AcOEt = 95/5). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.46 (dd, J = 1.6, 0.8 Hz, 1H), 7.34 – 7.22 (m, 1H), 7.21 – 7.12 (m, 1H), 7.05 (m, 1H), 6.49 (m, 1H), 2.47 (s, 3H) and correspond to literature data.[7]

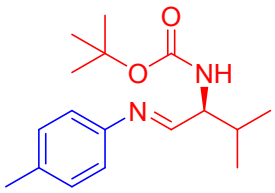
_N_-Phenyl-2,3-O-Isopropyliden-_D_-glyceraldimin (7g)



7g

Prepared according to the general procedure C. The product was obtained as an oil (58 mg, 99%). $[\alpha]^{25}_{D}$ = 7.6 (c 1.0, EtOH; IR ($CHCl_3$, cm^{-1}) 3384, 3380, 2986, 2932, 2878, 1518, 1070, 614; ^1H NMR (200 MHz, $CDCl_3$) δ 7.85 (d, *J* = 5.0 Hz, 1H), 7.16 – 7.00 (m, 4H, AA'XX'), 4.83 – 4.68 (m, 1H), 4.35 – 4.24 (m, 1H), 4.07 (dd, *J* = 8.5, 6.1 Hz, 1H), 2.35 (s, 3H), 1.50 – 1.43 (m, 6H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 162.85, 136.5, 129.9, 120.8, 110.6, 77.7, 67.7, 26.8, 25.7, 21.2; HRMS (EI) m/z [M+]: calcd for $C_{13}H_{17}NO_2$ 219.1261, found 219.1259.

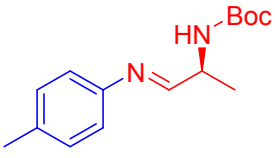
***tert*-Butyl (2*S*)-3-methyl-1-[(4-methylphenyl)imino]butan-2-ylcarbamate (7h)**



7h

Prepared according to the general procedure C. The product was obtained as an oil (73 mg, 99%). $[\alpha]^{25}_{D}$ = 11.4 (c 1.0, DCM); IR ($CHCl_3$, cm^{-1}) 3386, 2965, 2930, 1698, 1523, 1365,1173, 807; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.15 – 6.98 (m, 4H, AA'XX'), 5.74 (bs, 1H), 4.39 (bs, 1H), 2.41 (s, 3H), 2.31 (m, 1H), 1.49 (s, 9H), 1.07 – 0.98 (m, 6H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) 200.3, 162.1, 135.6, 129.65, 120.4, 114.2, 82.4, 28.7, 28.0, 20.9, 19.0, 18.9, 18.1; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{17}H_{26}N_2O_2Na$ 313.1892, found 313.1895.

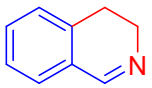
***tert*-Butyl (2*S*)-1-[(4-methylphenyl)imino]butan-2-ylcarbamate (7i)**



7i

Prepared according to the general procedure C. The product was obtained as an oil (66 mg, 99%). $[\alpha]^{25}_{D}$ = 6.2 (c 0.7, DCM); IR ($CHCl_3$, cm^{-1}) 3347, 2977, 1708 1505, 1366, 1169, 1057, 816; ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.11 – 6.96 (m, 4H, AA'XX'), 5.74 (bs, 1H), 4.43 (bs, 1H), 2.29 (s, 3H), 1.53 – 1.28 (m, 12H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 162.8, 155.3, 148.2, 135.6, 129.6, 120.5, 79.4, 49.9, 28.4, 20.9, 18.5; HRMS (ESI) m/z $[M+Na]^+$: calcd for $C_{15}H_{22}N_2O_2Na$ 285.1579, found 285.1568.

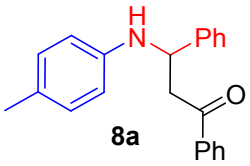
3,4-dihydroisoquinoline (7j)



7j

Prepared according to the general procedure C. The product was obtained as a pale yellow oil (14 mg, 43%), eluent: Hexane/AcOEt = 2/3). ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.38 – 7.15 (m, 4H), 3.78 (t, *J* = 8.2 Hz, 2H), 2.76 (t, *J* = 8.2 Hz, 2H) and correspond to literature data.[28]

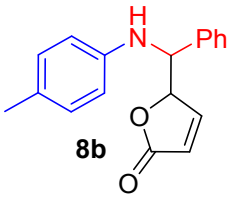
1,3-Diphenyl-3-(4-methylphenylamino)propan-1-one (8a)



8a

To a suspension of *N*-benzyl-*N*-(4-methylphenyl)amine (39.50 mg, 0.200 mmol, 1.00 equiv.), $[Ru(bpy)_3](PF_6)_2$ (3.40 mg,0.004 mmol, 0.02 equiv.) and molecular sieves 4Å in MeOH (1 mL), respectively 1-styrenyloxytrimethylsilane (77.00 mg, 0.400 mmol, 2.00 equiv.) and $Zn(OTf)_2$ (14.50 mg, 0.040 mmol; 0.20 equiv.) were added. Stirring was continued for 18h at 35 °C under oxygen atmosphere and irradiated using 23 W CFL. Solvent was evaporated and residue was submitted to column chromatography (eluent: Hexane/AcOEt = 9/1) to afford pure product as yellow oil (36 mg, 57%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.92 (d, *J* = 6.8 Hz, 2H), 7.41 – 7.62 (m, 5H), 7.19 – 7.37 (m, 3H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.51 (d, *J* = 8.7 Hz, 2H), 4.99 (t, *J* = 7.4 Hz, 1H), 3.49 (t, *J* = 5.2 Hz, 2H), 2.19 (s, 3H) and correspond to literature data.[23]

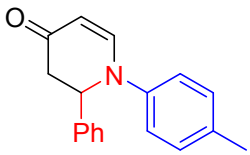
5-[(4-Methoxy-phenylamino)-phenyl-methyl]-5*H*-furan-2-one (8b)



8b

To a suspension of *N*-benzyl-*N*-(4-methylphenyl)amine (39.50 mg, 0.200 mmol, 1.00 equiv.), $[Ru(bpy)_3](PF_6)_2$ (3.40 mg, 0.004 mmol, 0.02 equiv.) and molecular sieves 4Å in MeCN (1 mL), respectively 2-(trimethylsiloxy)furan (37.50 mg, 0.240 mmol, 1.20 equiv.) and $Zn(OTf)_2$ (14.50 mg, 0.040 mmol; 0.20 equiv.) were added. Stirring was continued for 48h at 35 °C under oxygen atmosphere and irradiated using 23 W CFL. Solvent was evaporated and residue was submitted to column chromatography (eluent: Hexane/AcOEt = 8/2) to afford pure product as yellow oil (23 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 – 7.43 (m, 6H), 6.9 (d, *J* = 8.3 Hz, 2H), 6.48 (d, *J* = 8.4 Hz, 2H), 6.16 (dd, *J*= 2.0, 5.8 Hz, 1H), 5.23 (dt, *J* = 1.8, 6.8 Hz, 1H), 4.45 (d, *J* = 6.8 Hz, 1H), 2.18 (s, 3H) and correspond to literature data.[24]

1-(4-Methylphenyl)-2-phenyl-2,3-dihydro-1H-pyridin-4-one (8c)

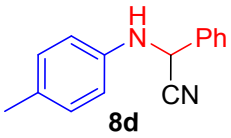


8c

Suspension of *N*-benzyl-*N*-(4-methylphenyl)amine (39.50, 0.200 mmol, 1.00 equiv.), $[Ru(bpy)_3](PF_6)_2$ (3.40 mg, 0.004 mmol, 0.02 equiv.) and 4 Å molecular sieves in MeCN (1 mL), was stirred at 35 °C and irradiated using 23 W CFL. After 6h lamp was turned off and respectively trans-1-methoxy-3-trimethylsiloxy-1,3-butadiene (41.50 mg, 2.400 mmol, 1.20 equiv.) and $Zn(OTf)_2$ (14.50 mg, 0.040 mmol; 0.20 equiv.) were added. Stirring at rt. was continued for 18h at darkness. Solvent was evaporated and residue was submitted to column chromatography (eluent: Hexane/AcOEt = 7/3) to afford pure product as yellow oil (47 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dd, *J* = 1.2, 7,6 Hz, 1H), 7.23 – 7.34 (m, 5H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.25 – 5.27 (m, 2H), 3.28 (dd, *J* = 7.2, 16.4 Hz, 1H), 2.78 (ddd, *J* =

1.2, 3.2, 16.4 Hz, 1H), 2.29 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 190.1, 148.7, 142.4, 138.1, 134.3, 130.0, 128.9, 127.8, 126.2, 118.9, 102.3, 61.9, 43.4, 20.7; IR ($CHCl_3$, cm^{-1}) 3029, 1647, 1590, 1575, 1512, 1308, 1275, 1206; HR-EI-MS m/z $[M]^+$: calc. for: $C_{18}H_{17}NO$ 286.1208, found: 286.1200.

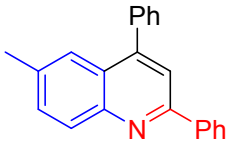
2-Phenyl-2-(4-methylphenylamino)acetonitrile (8d)



8d

To a suspension of *N*-benzyl-*N*-(4-methylphenyl)amine (39.50 mg, 0.200 mmol, 1.00 equiv.), $[Ru(bpy)_3](PF_6)_2$ (3.40 mg, 0.004 mmol, 0.02 equiv.) and 4 Å molecular sieves in MeCN (1 mL), respectively trimethylsilyl cyanide (24.00 mg, 0.240 mmol, 1.20 equiv.) and $Zn(OTf)_2$ (14.50 mg, 0.040 mmol; 0.20 equiv.) were added. Stirring was continued for 18h at 35 °C under oxygen atmosphere and irradiated using 23 W CFL. Solvent was evaporated and residue was submitted to column chromatography (eluent: Hexane/AcOEt = 8/2) to afford pure product as white solid (28 mg, 63%).^{1}H NMR (200 MHz, $CDCl_3$): δ 7.59 – 7.64 (m, 2H), 7.44 – 7.49 (m, 3H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.72 (d, *J* = 7.8 Hz, 2H), 5.42 (s, 1H), 2.29 (s, 3H) and correspond to literature data.[25]

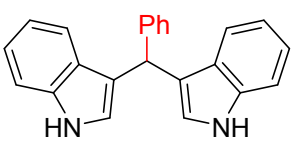
2,4-Diphenyl-6-methylquinoline (8e)



8e

A mixture of *N*-substituted arylamine (0.25 mmol, 1.0 equiv.), phenylacetylene (125 µL, 1.12 mmol, 4.5 equiv.), $[Ru(bpy)_3](PF_6)_2$ (0.004 mmol, 0.02 mmol.), $Bi(OTf)_3$ (32 mg, 0.05mmol, 0.2 equiv.) and 30 mg MS 4Å in 0.8 mL dry, saturated with oxygen MeCN was stirred for 48h under oxygen atmosphere at 80 ^{0}C and irradiated using 23 W CFL. Afterward, the reaction mixture was quenched by addition 200 µL *N*,*N*,*N*′,*N*′-tetramethylethylenediamine. Thereafter solution was washed with DCM (3x10 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent in vacuo gave the crude of 2,4-diphenyl-6-methylquinoline, which was purified by column chromatography. The product was obtained as a yellowish solid (55.0 mg, 73%, Hexane/DCM = 4/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 – 8.11 (m, 3H), 7.78 (s, 1H), 7.66 (s, 1H), 7.60 – 7.49 (m, 8H), 7.46 (m, 1H), 2.48 (s, 3H) and correspond to literature data.[26]

3,3'-Bis-indolyl(phenyl)methane (8f)

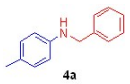


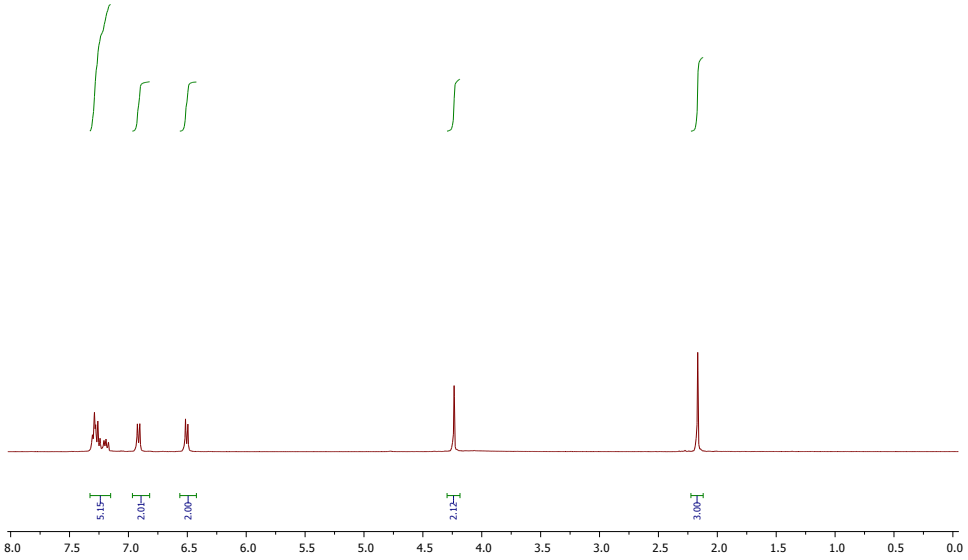
8f

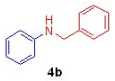
A suspension of *N*-benzyl-*N*-(4-methylphenyl)amine (39.50 mg, 0.200 mmol, 1.00 equiv.), $[Ru(bpy)_3](PF_6)_2$ (3.40 mg, 0.004 mmol,

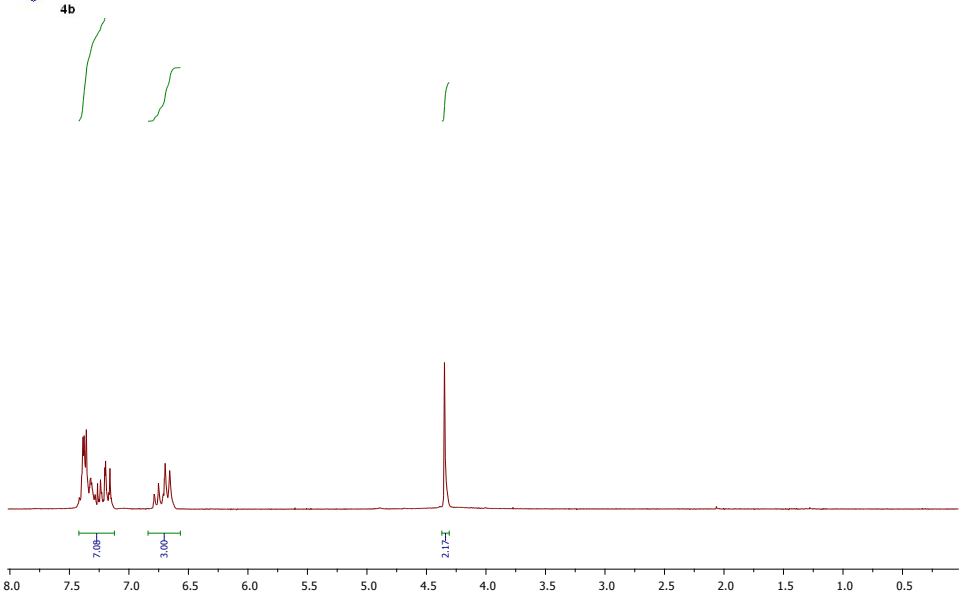
0.02 equiv.), indole (58.50 mg, 0.500 mmol; 2.50 equiv.), $Zn(OTf)_2$ (14.50 mg, 0.040 mmol; 0.20 equiv.) and molecular sieves 4 Å in MeCN/DCE (*v*/*v*: 1/2; 1 mL), was stirred for 18h at 35 °C under oxygen atmosphere and irradiated using 23 W CFL. Solvent was evaporated and residue was submitted to column chromatography (eluent: Hexane/AcOEt = 8/2) to afford pure product as red-brown solid (33 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 2H), 7.32 – 7.42 (m, 6H), 7.27 – 7.31 (m, 2H), 7.13 – 7.22 (m, 3H), 6.66 (s, 2H), 5.89 (s, 1H) and correspond to literature data.[27]

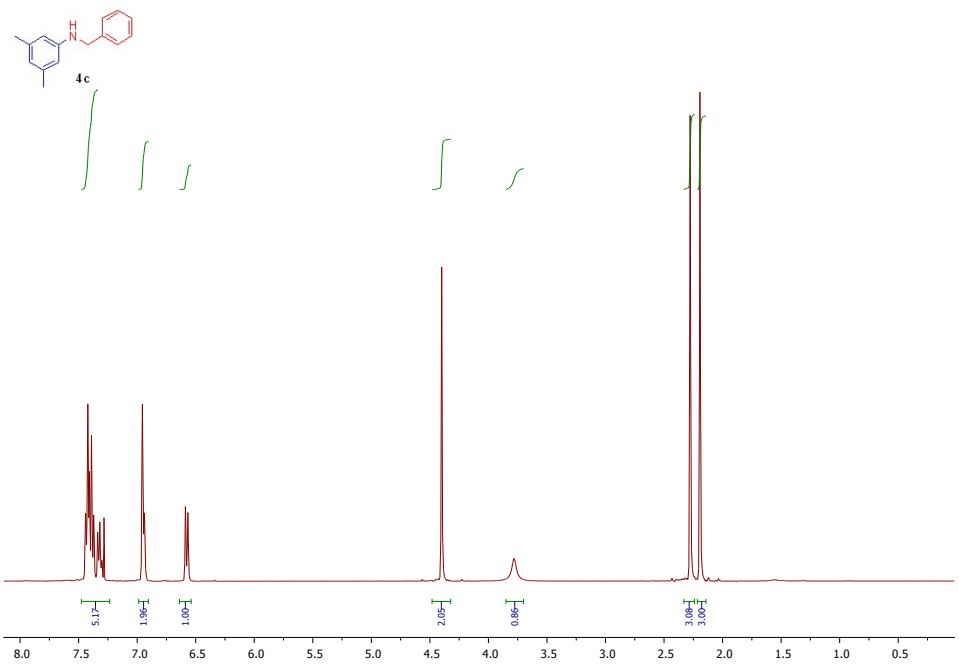
8. Copies of ^{1}H and ^{13}C NMR spectra's







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7.5
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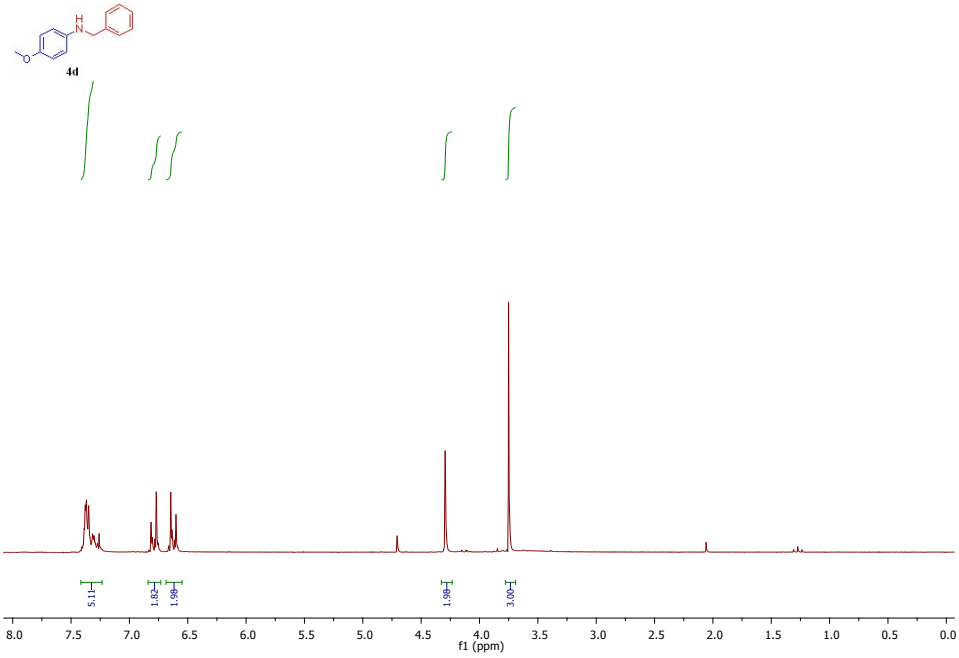
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5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6.5
6.0
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4.5
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3.5
3.0
2.5
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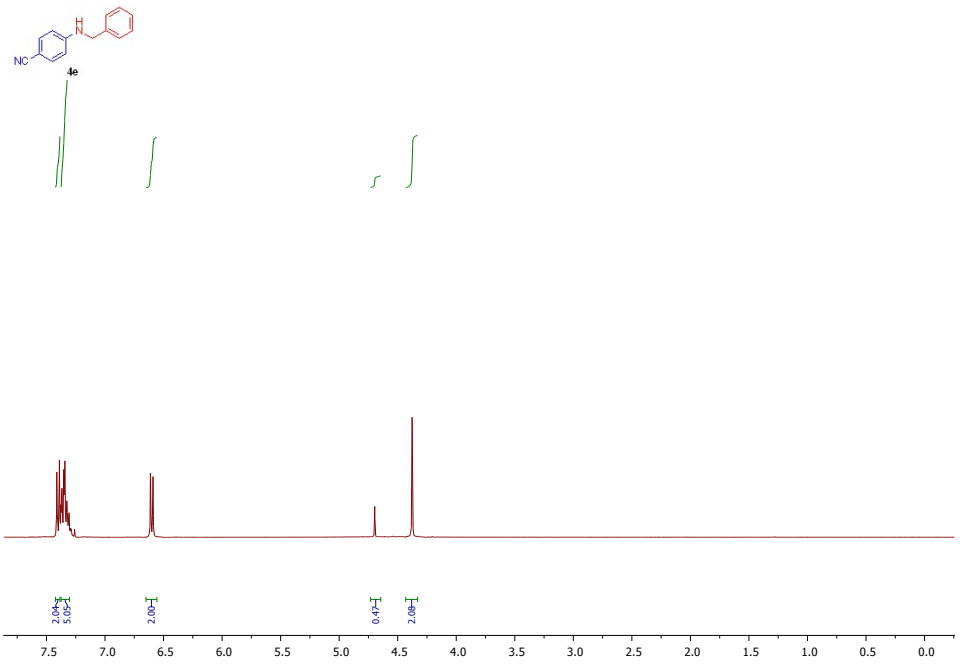
1.5
1.0
0.5
0.0
f1 (ppm)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N
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7.0
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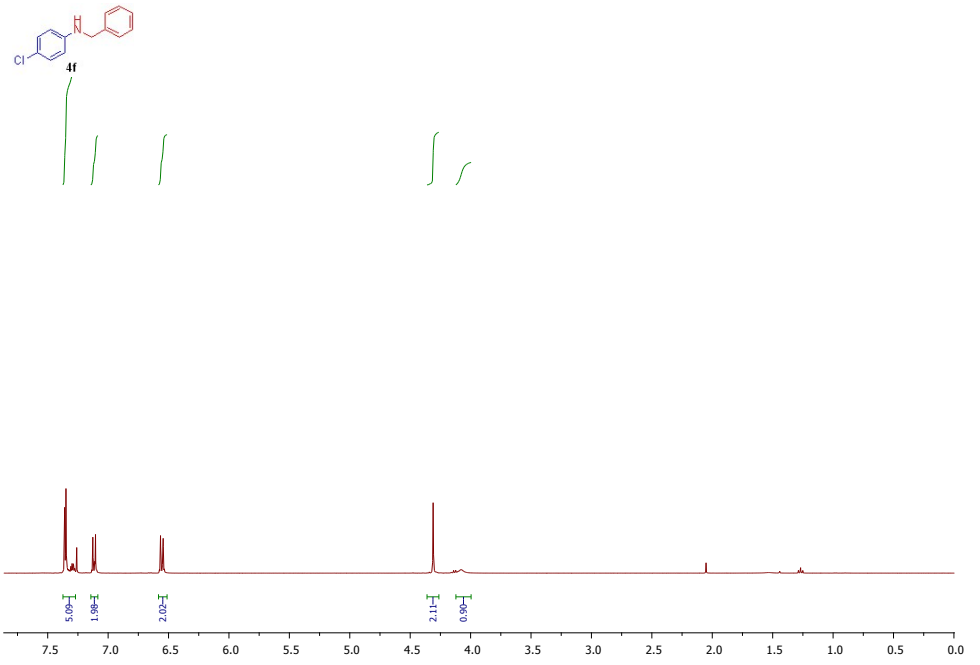
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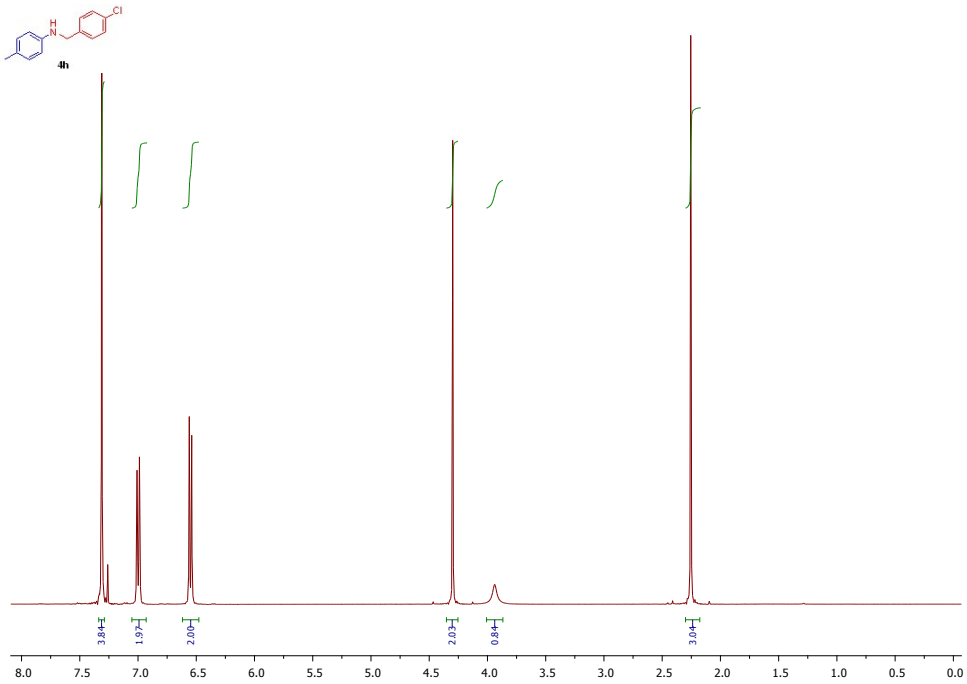
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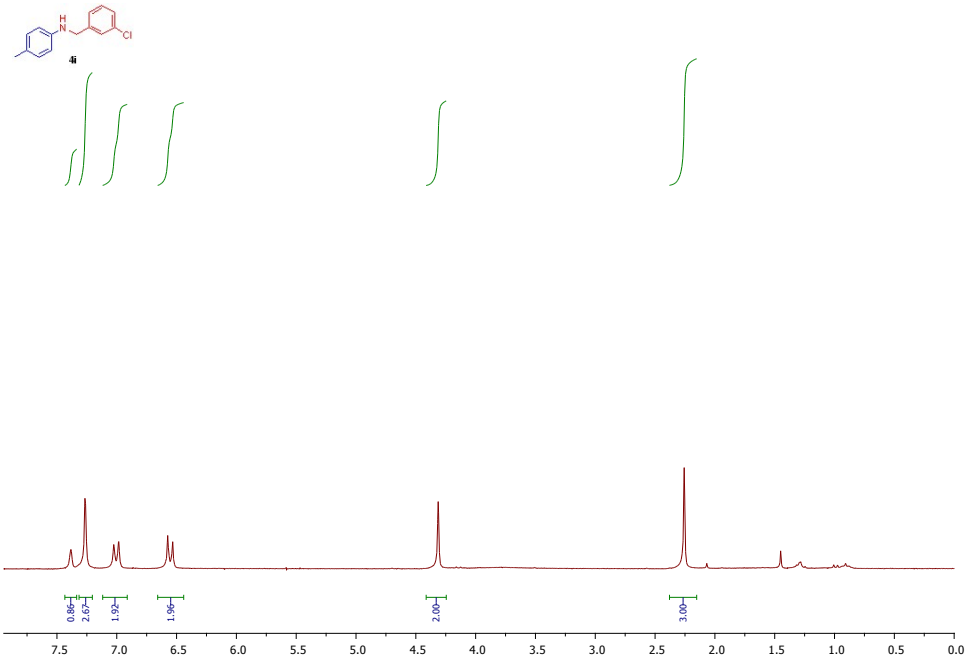
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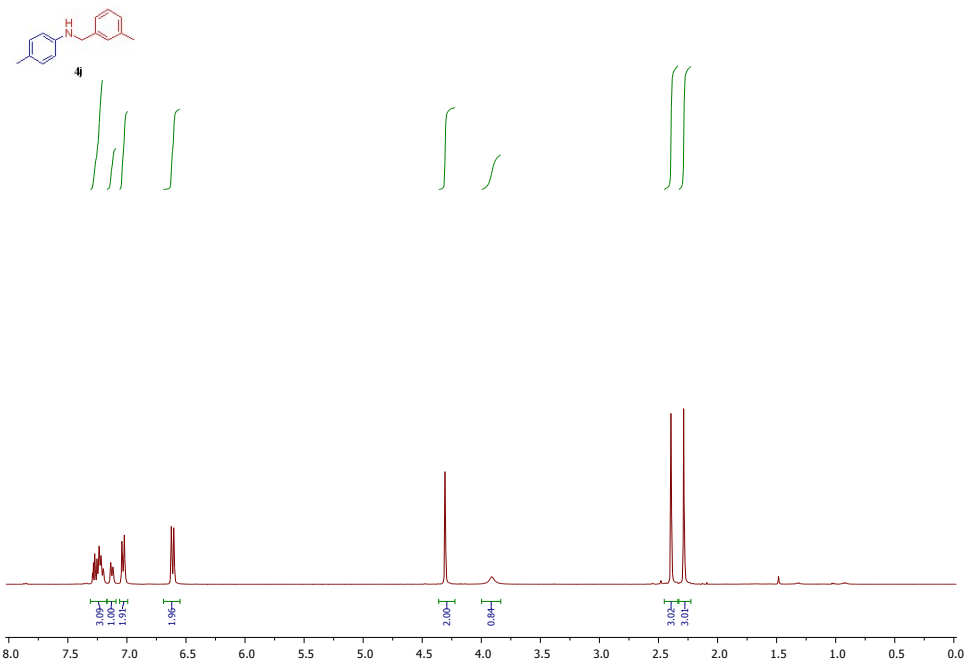
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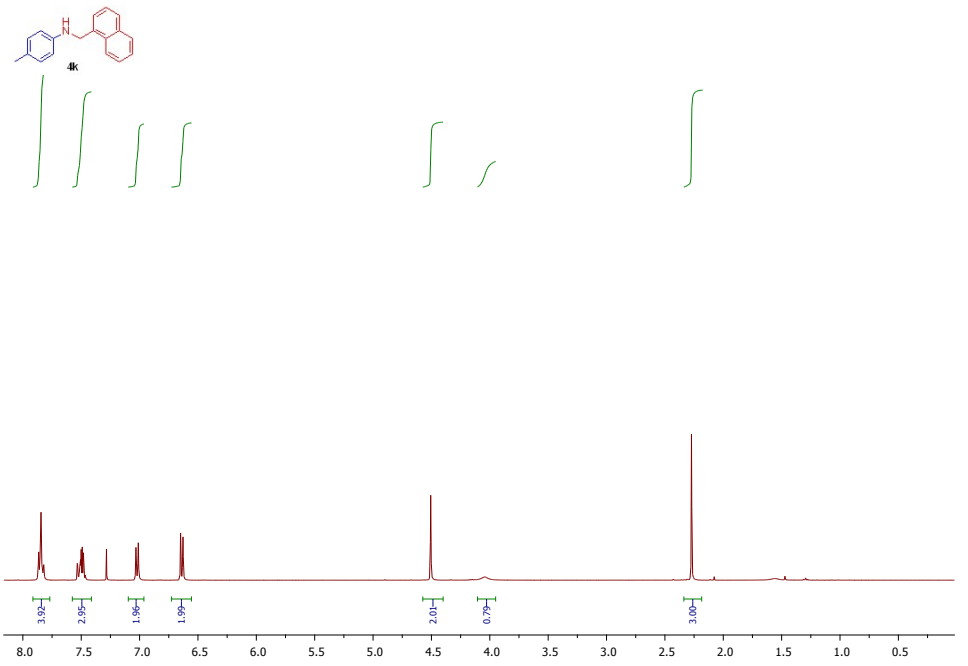
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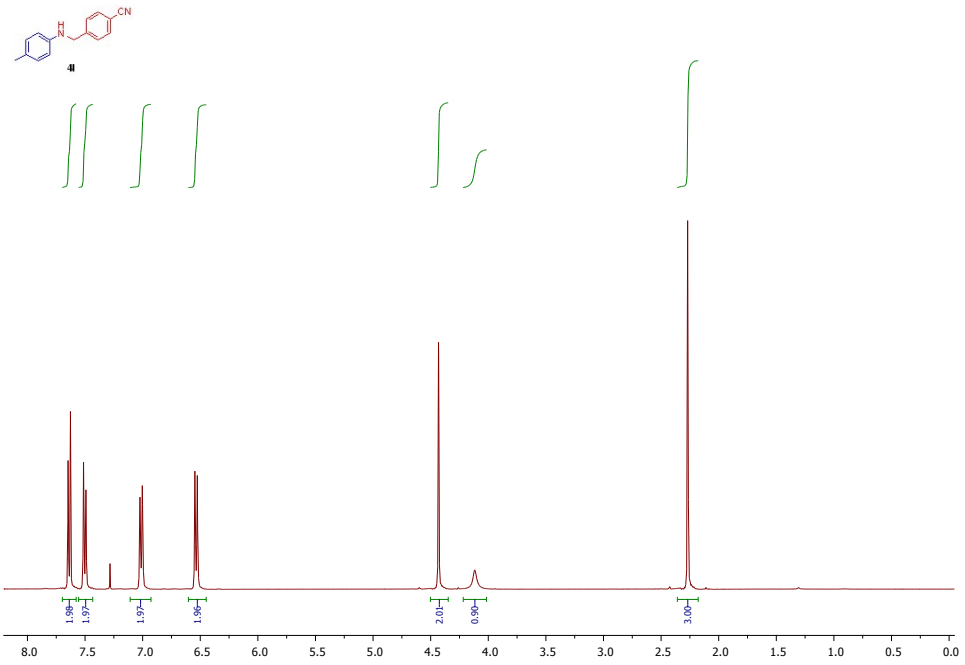
0.5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H
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6.5
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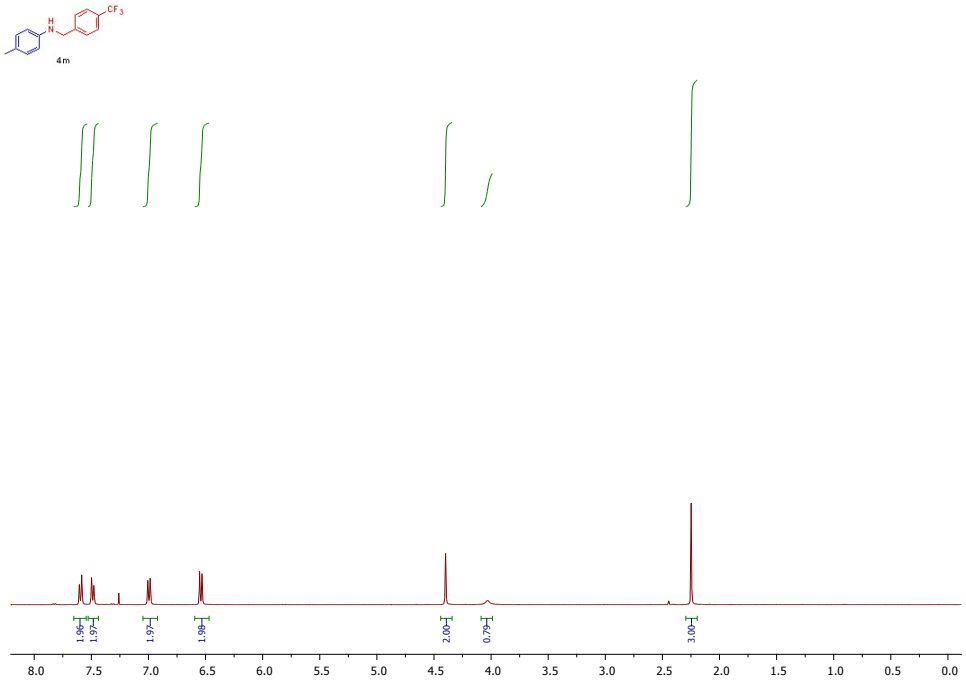
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H
N
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8.0
7.5
7.0
6.5
6.0
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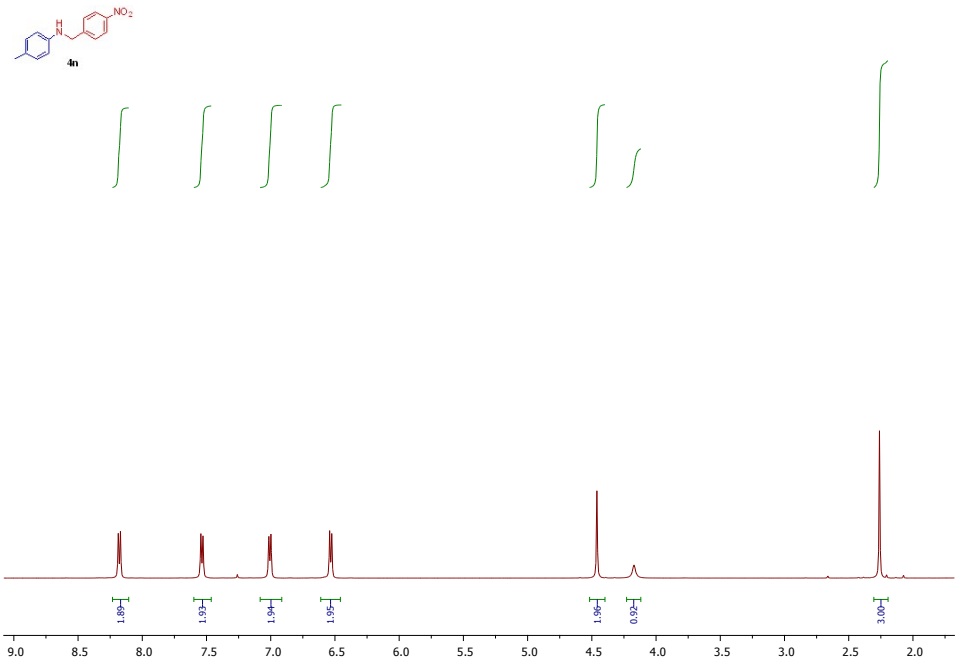
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8.5
8.0
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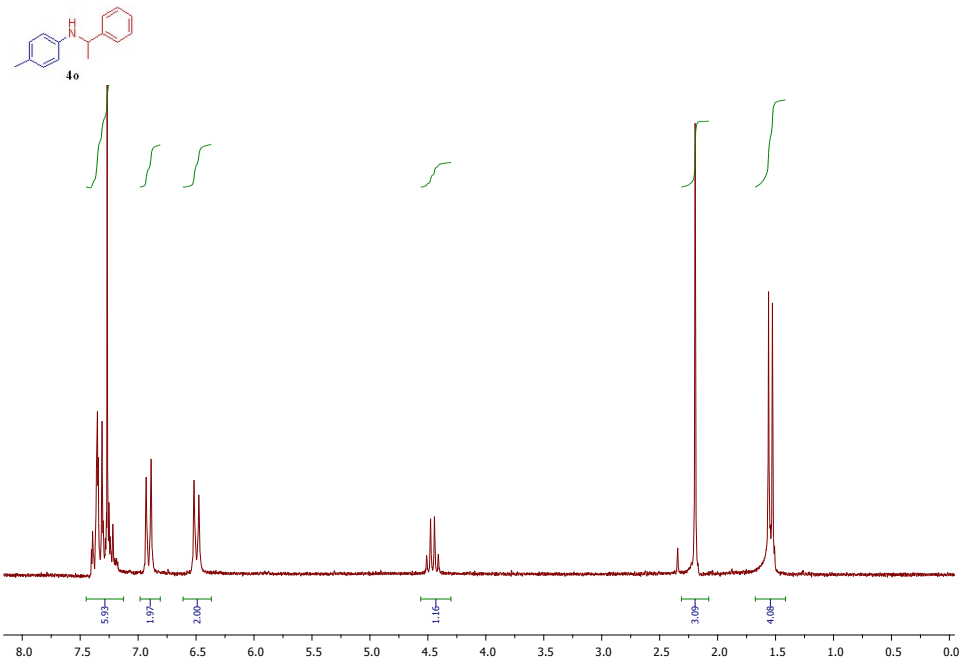
2.0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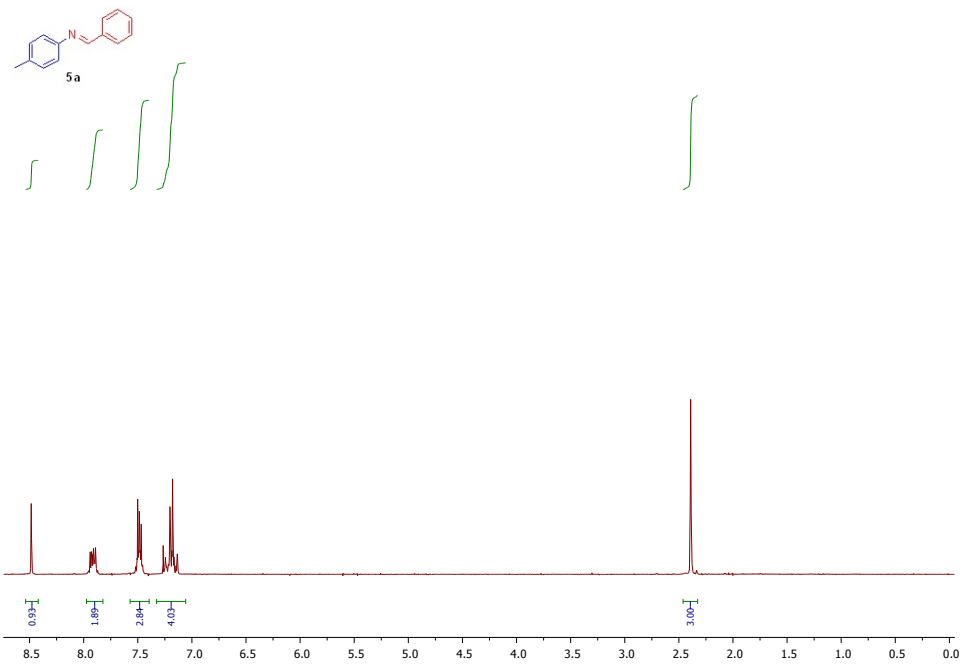
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7.0
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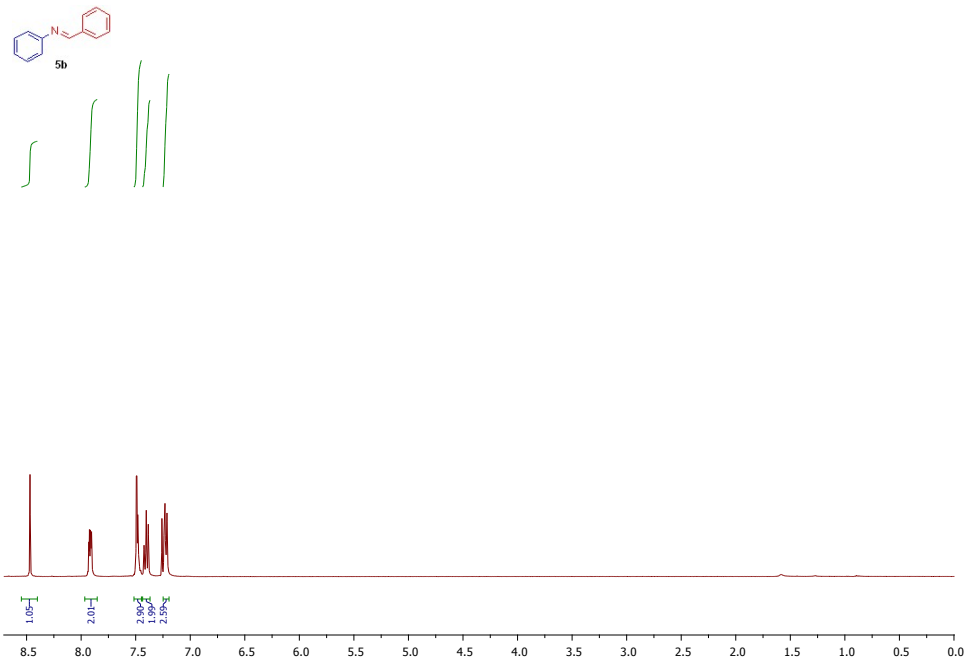
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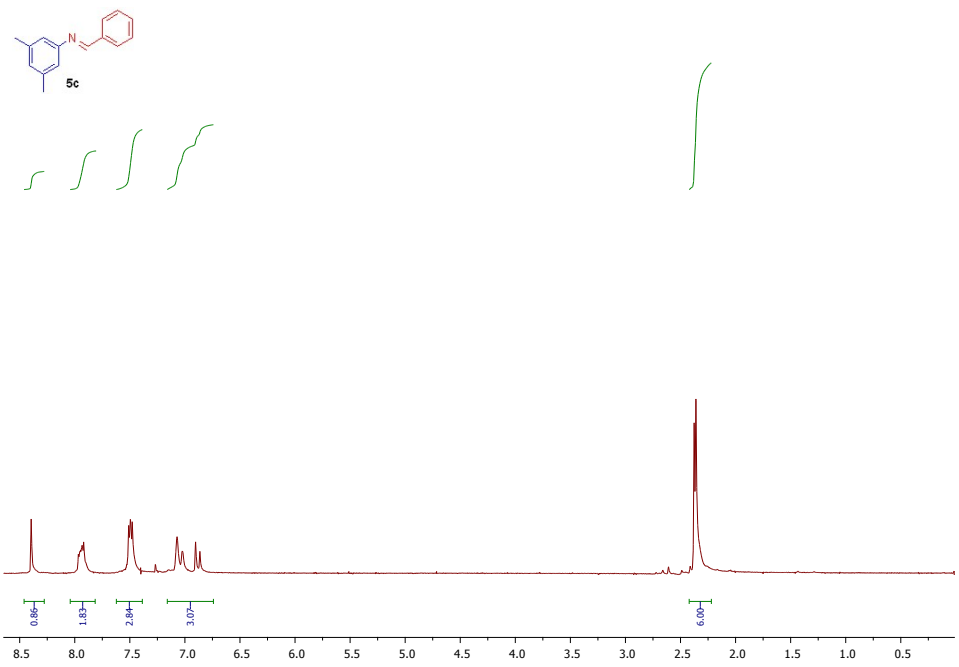
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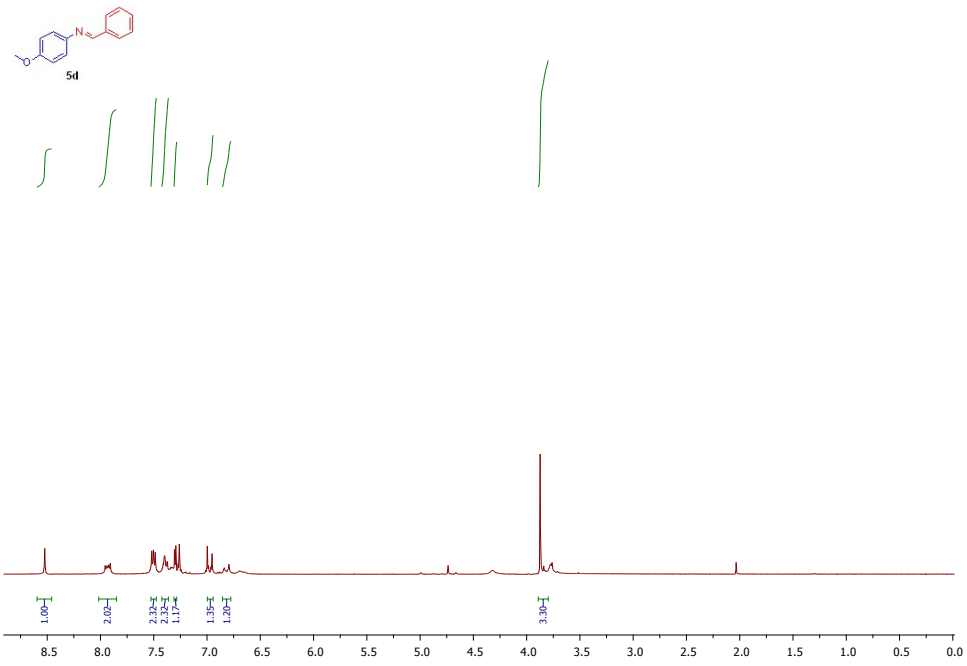
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6.5
6.0
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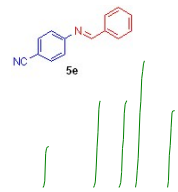
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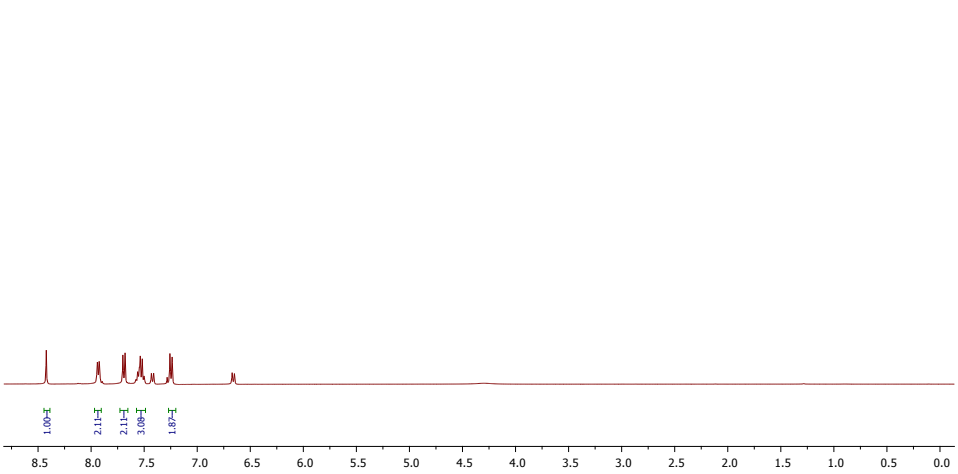
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7.5
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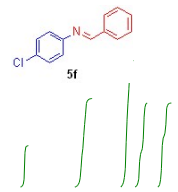
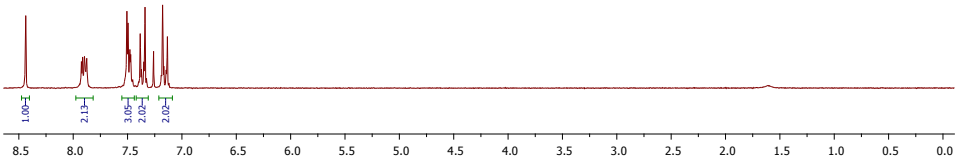

Cl
N
5f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2.02
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7.5
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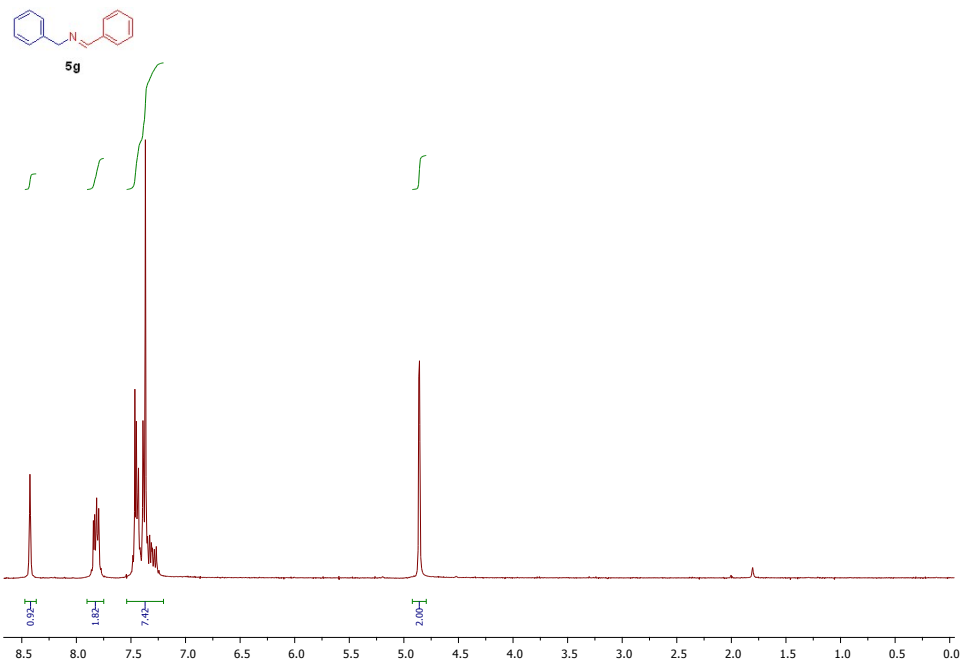
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6.0
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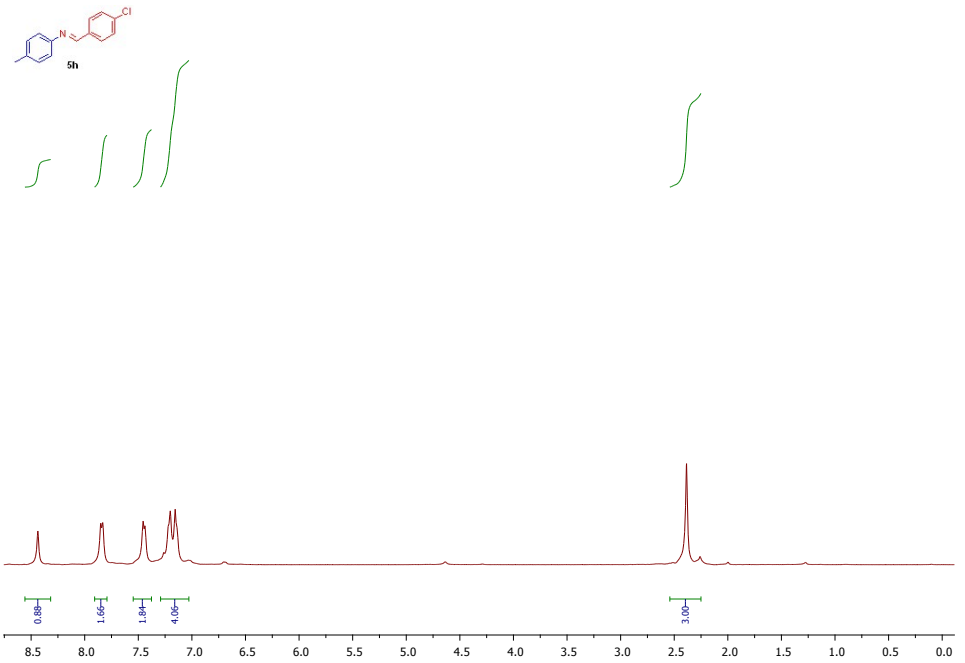
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Cl
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8.0
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6.0
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3.0
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2.0
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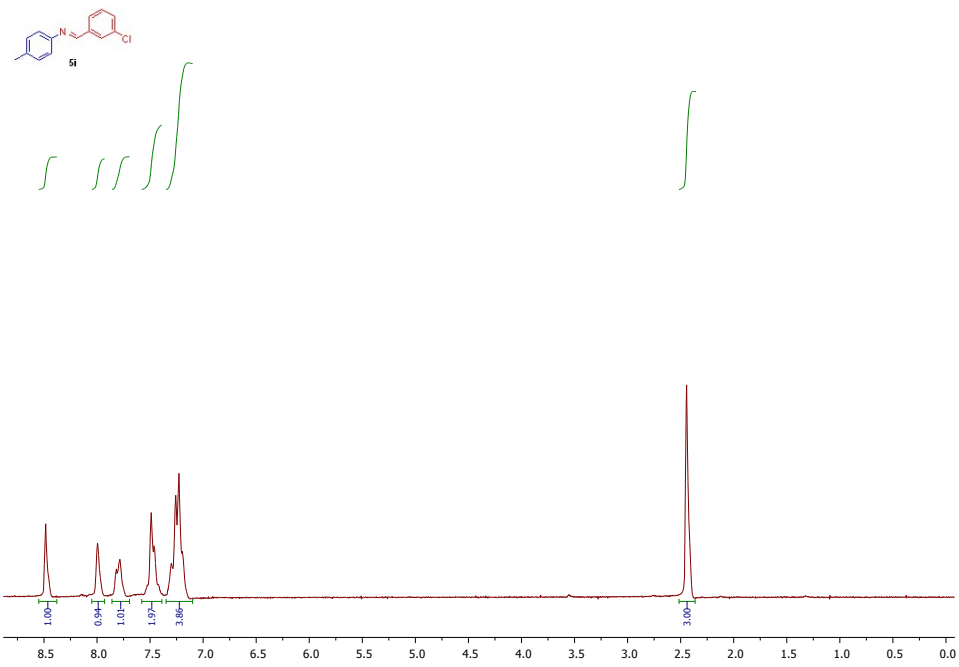
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1.97
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8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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3.0
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2.0
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1.0
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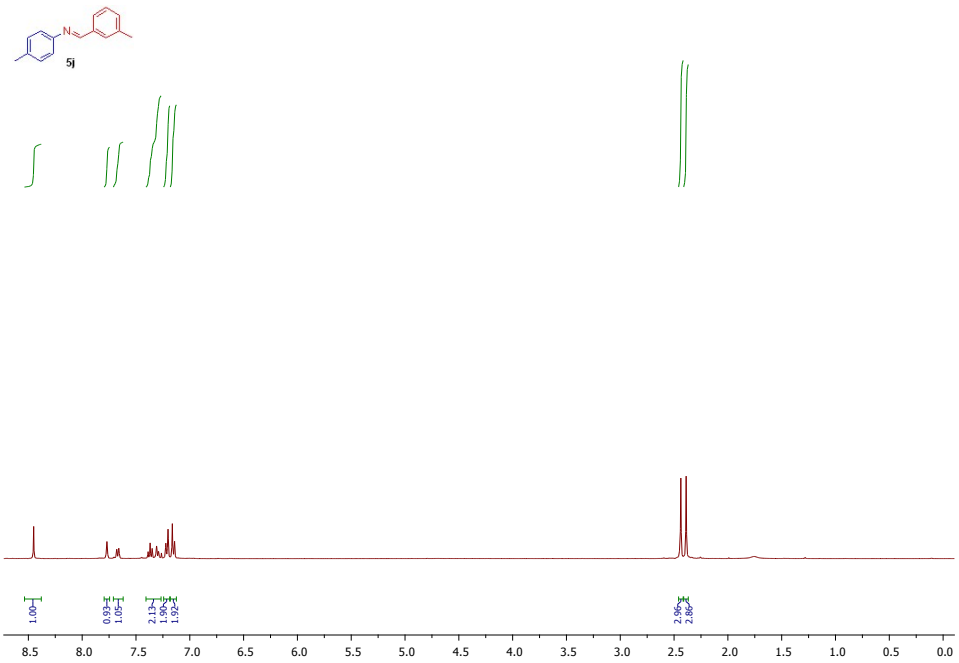
0.0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0.93
1.05
2.13
1.96
1.92
2.96
2.86
8.5
8.0
7.5
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6.5
6.0
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4.5
4.0
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3.0
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2.0
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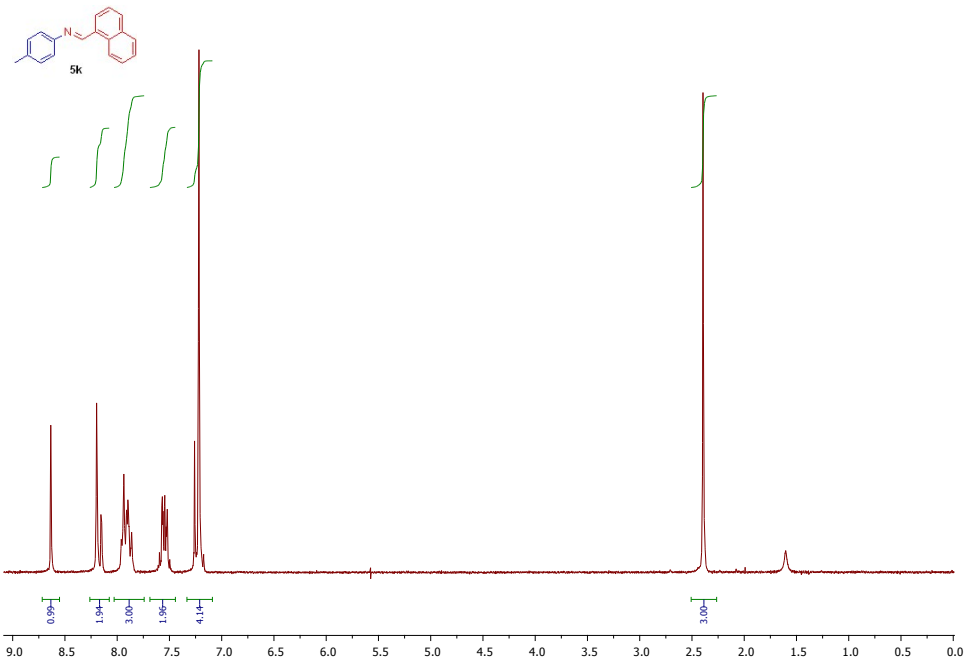
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1.96
4.14
3.00
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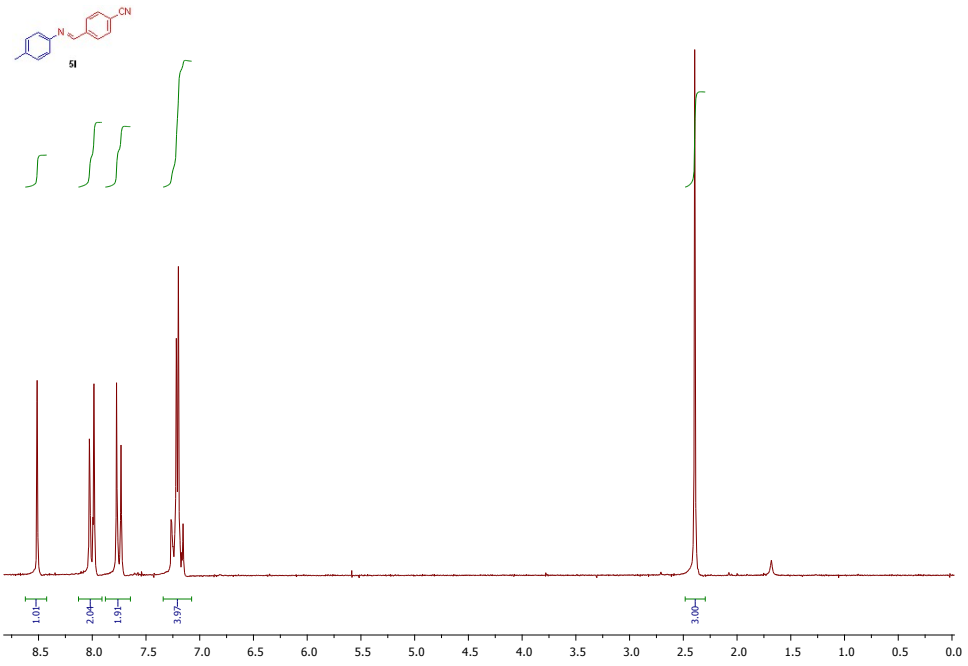
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CN
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2.04
1.91
3.97
3.00
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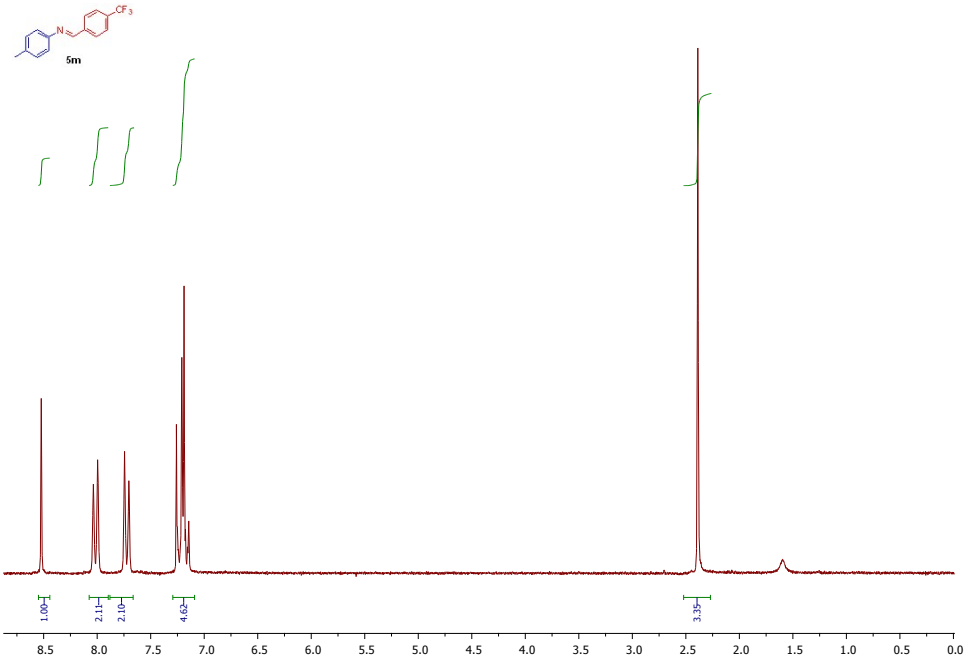
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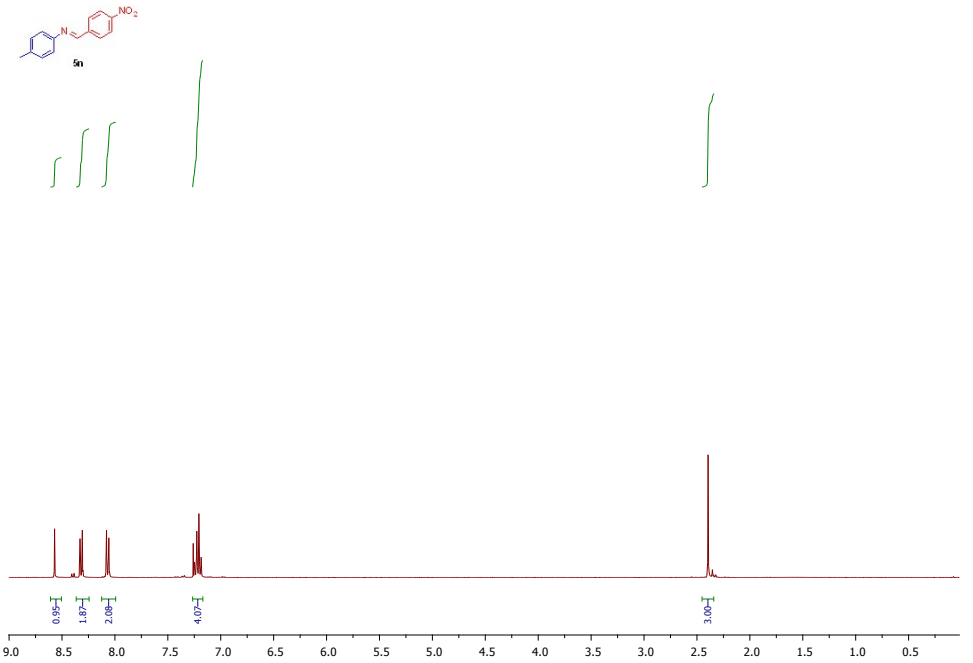
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4.07
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7.5
7.0
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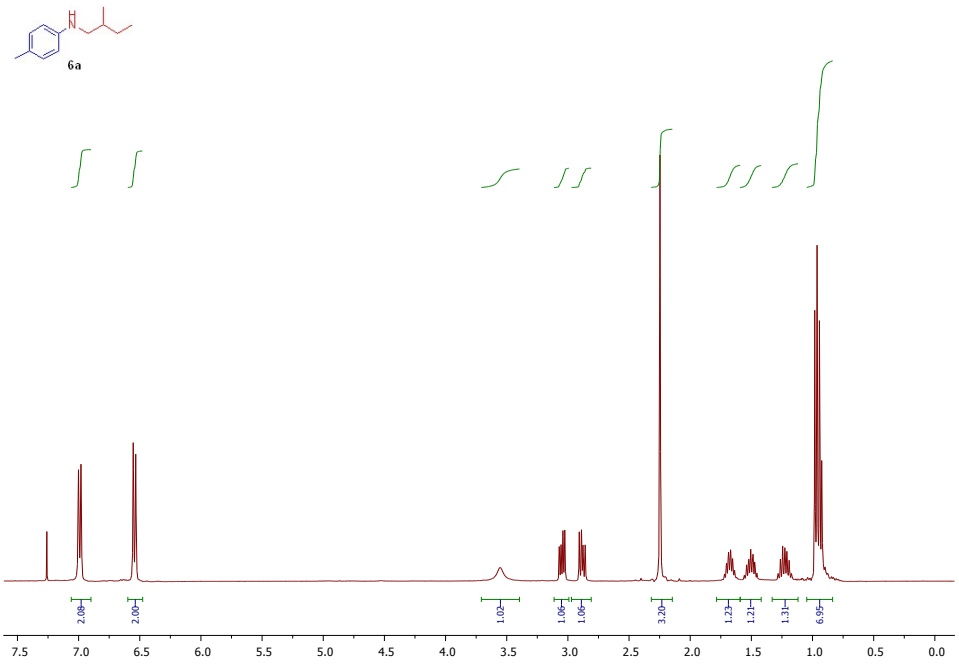
1.0
0.5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1.02
1.06
1.06
3.20
1.23
1.21
1.31
6.95
7.5
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6.5
6.0
5.5
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4.5
4.0
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3.0
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2.0
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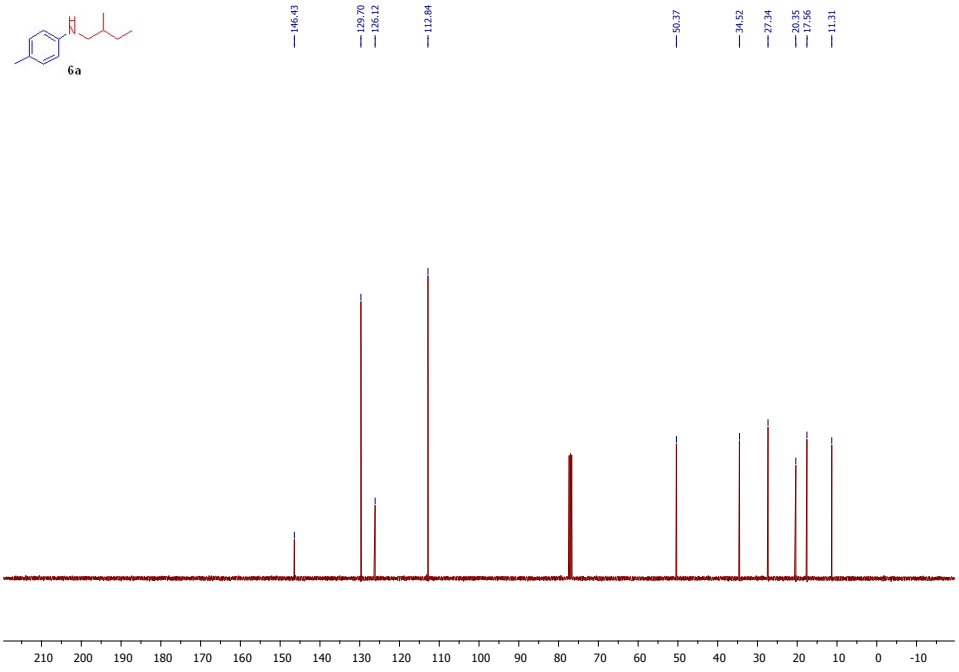
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27.34
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17.56
11.31
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200
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10
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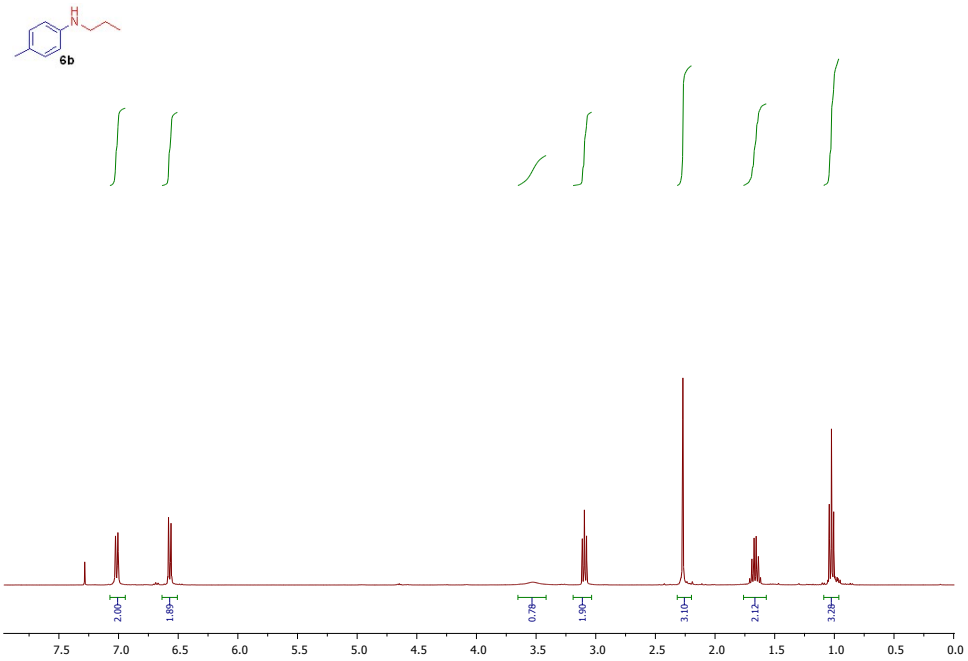
-10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2.12
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7.0
6.5
6.0
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5.0
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2.0
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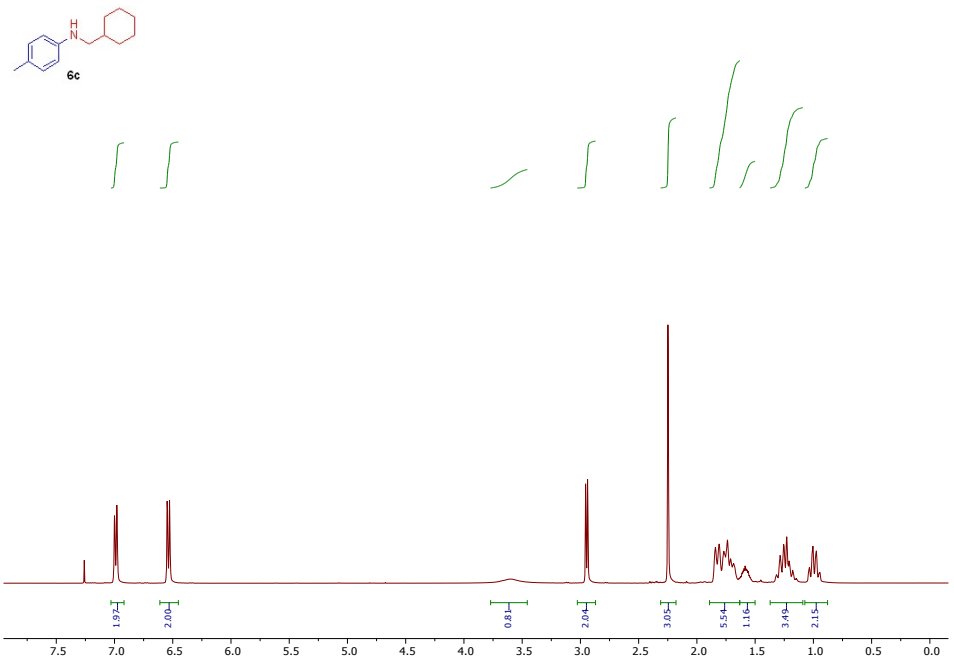
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3.05
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3.49
2.15
7.5
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6.5
6.0
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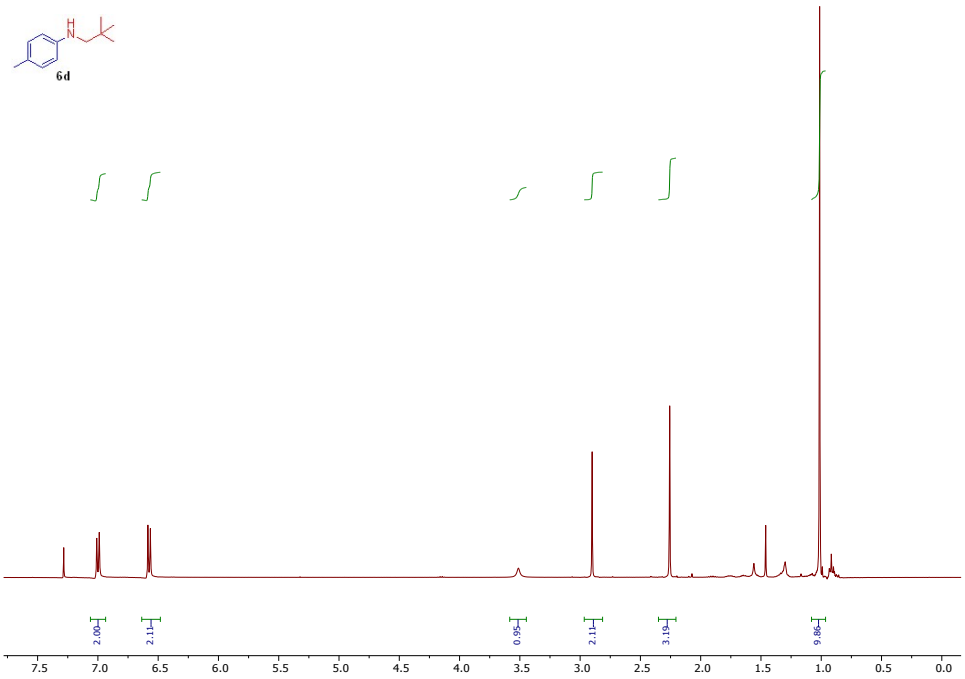
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2.11
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7.5
7.0
6.5
6.0
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2.0
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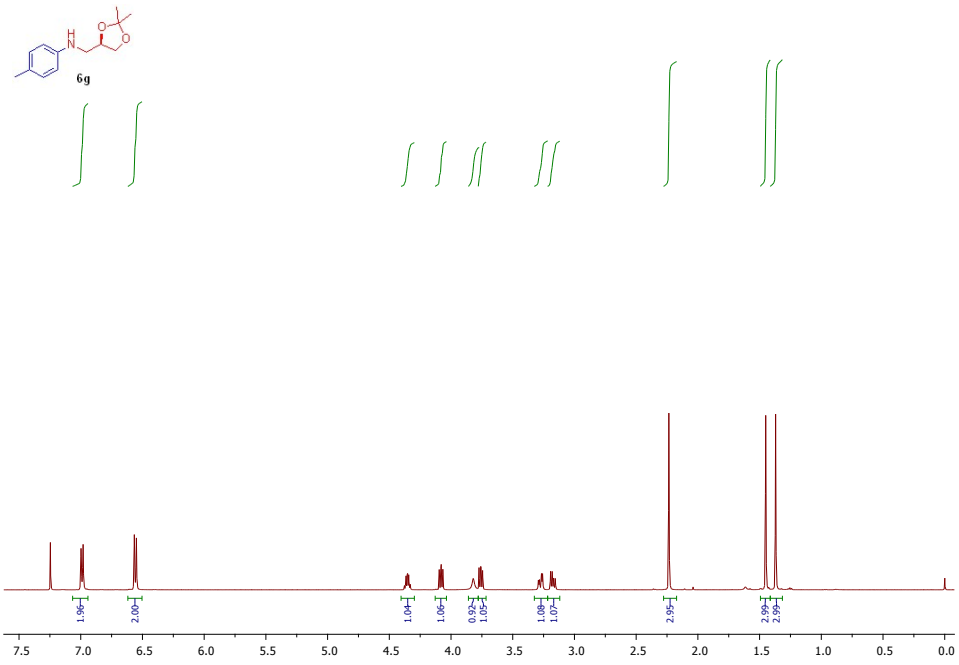
0.0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1.06
0.92
1.05
1.08
1.07
2.95
2.99
2.99
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7.0
6.5
6.0
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2.0
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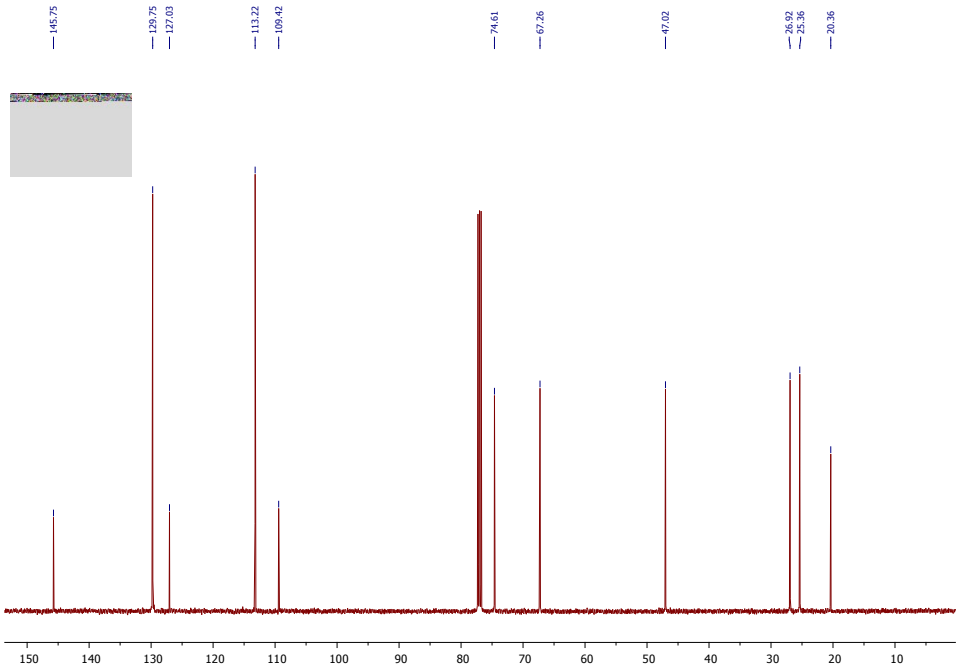
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74.61
67.26
47.02
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20.36
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80
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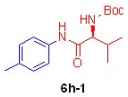
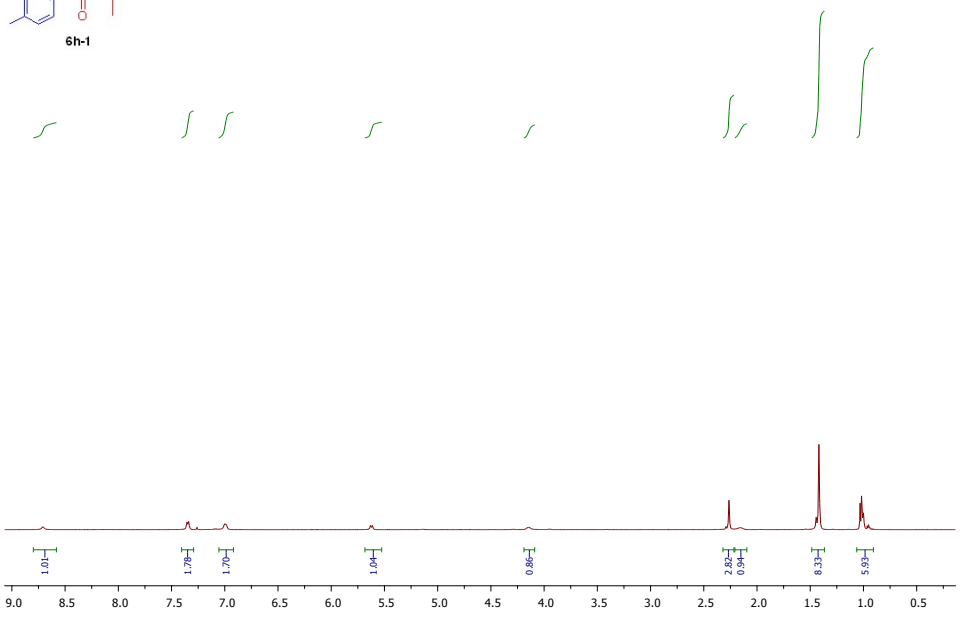
20
10


HN
Boc
H
N
O

6h-1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8.0
7.5
7.0
6.5
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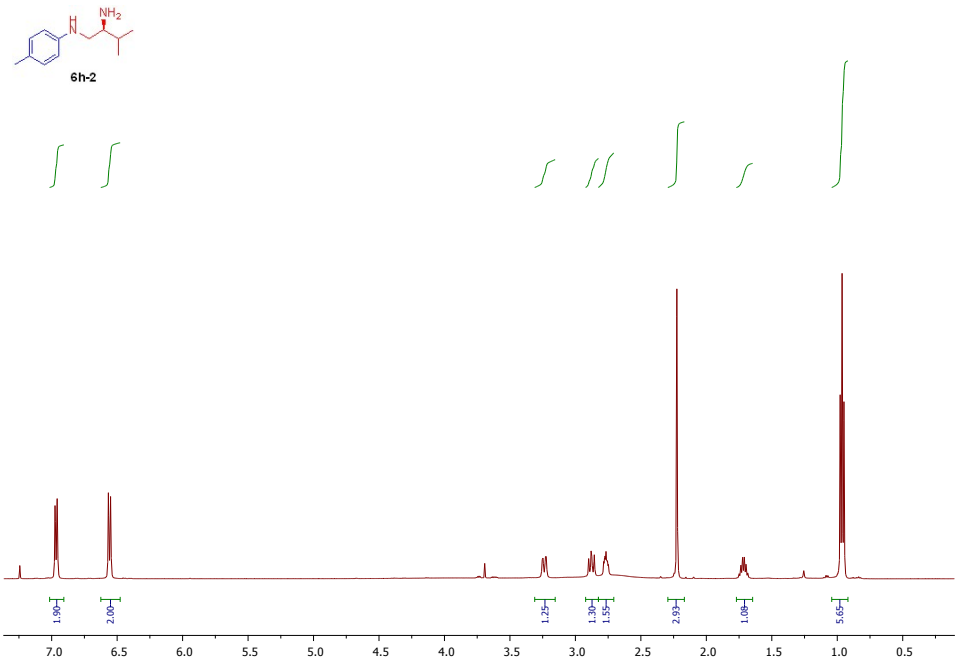
2.5
2.0
1.5
1.0
0.5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2.93
1.08
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7.0
6.5
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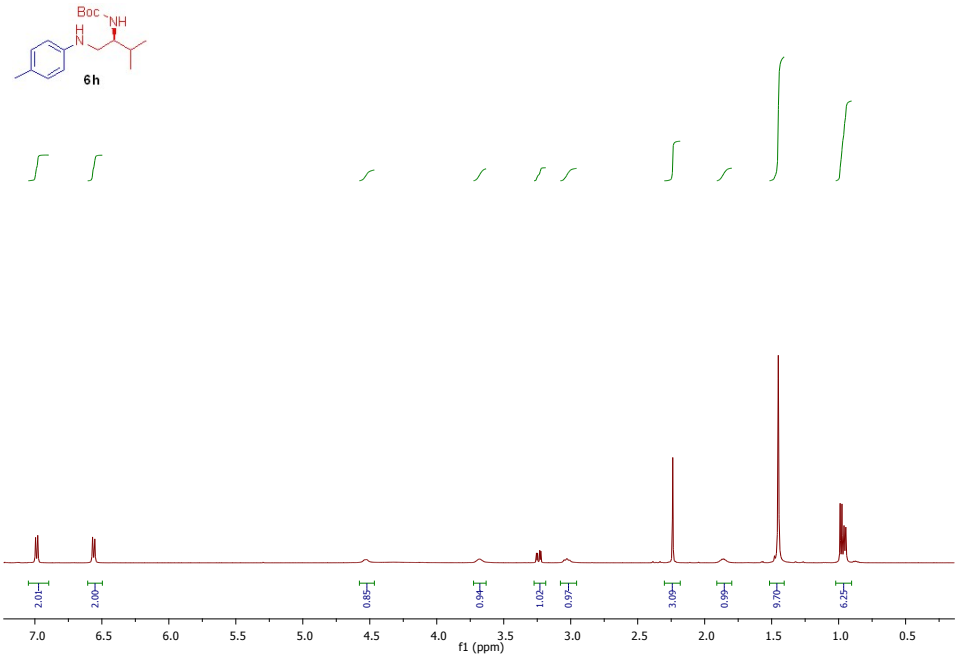
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


6h
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2.00
0.85
0.94
1.02
0.97
3.09
0.99
9.70
6.25
7.0
6.5
6.0
5.5
5.0
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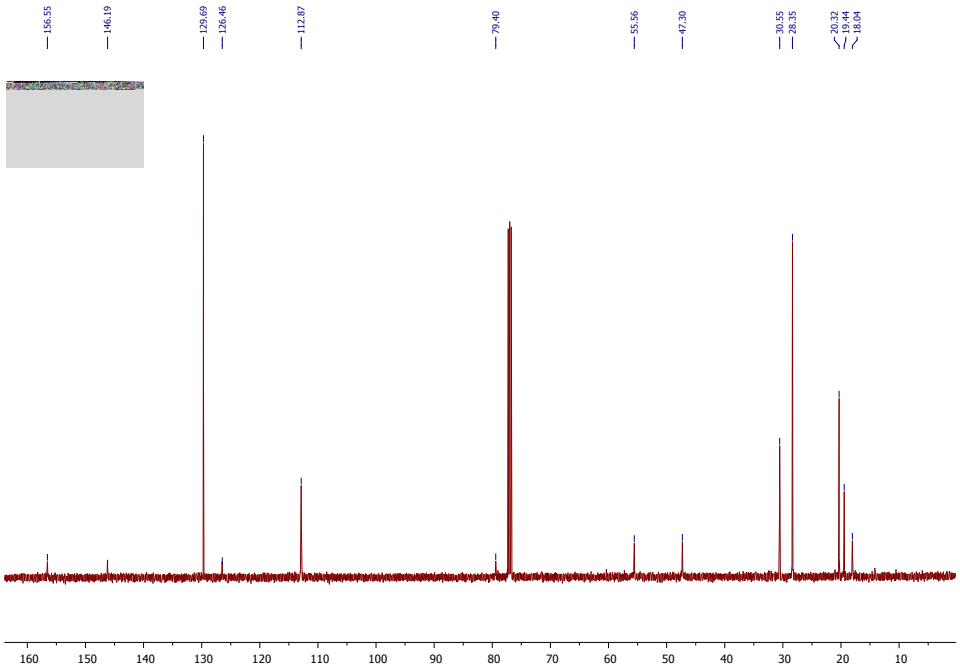
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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47.30
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28.35
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120
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80
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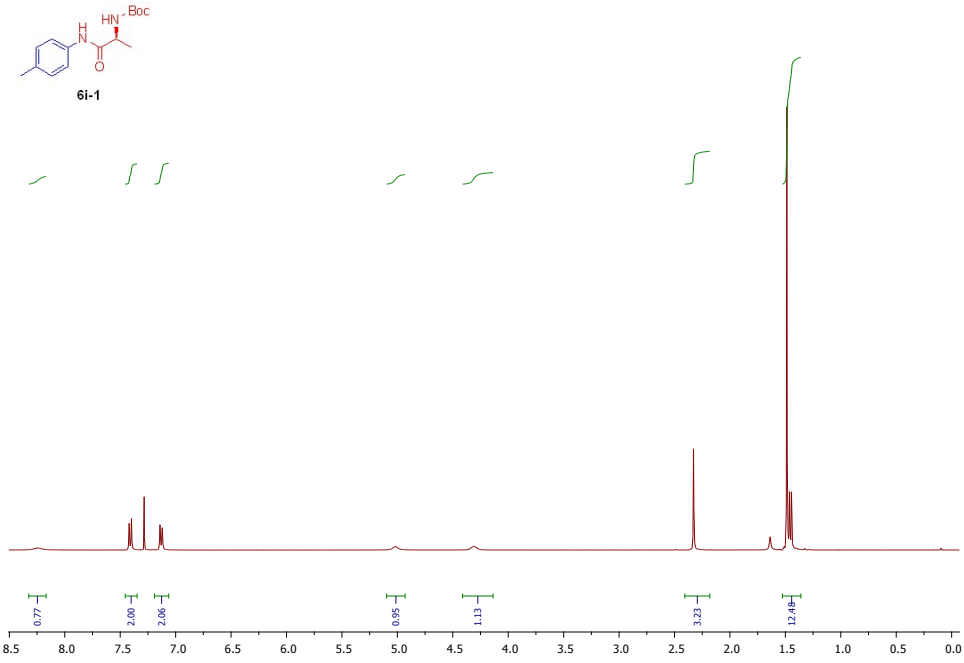
20
10


HN
Boc
H
N
O
6i-1
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2.06
0.95
1.13
3.23
12.48
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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2.0
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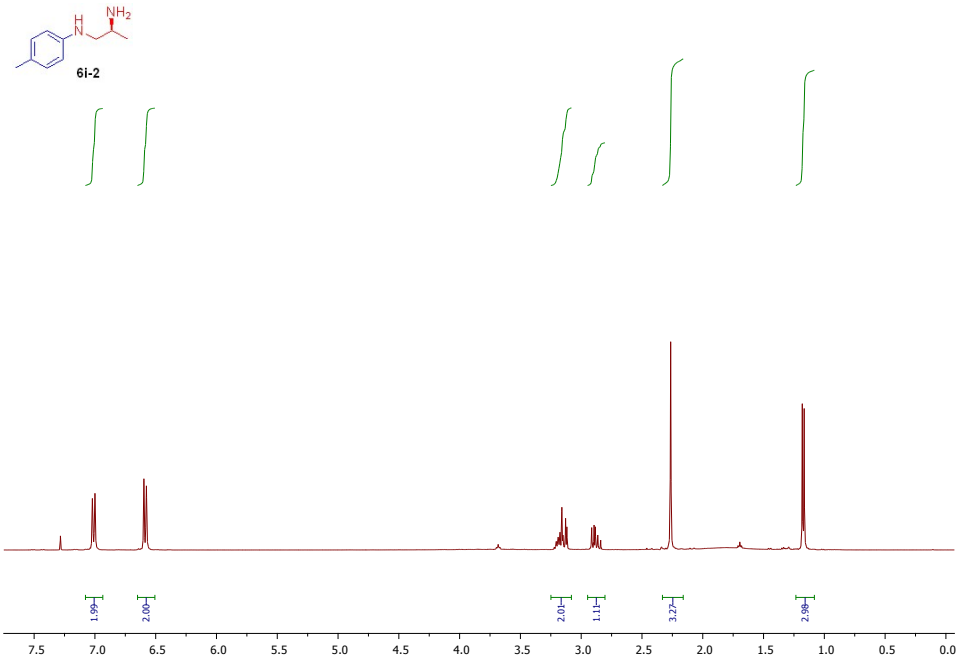
0.0


6i-2
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2.00
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1.11
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2.98
7.5
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6.5
6.0
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3.0
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2.0
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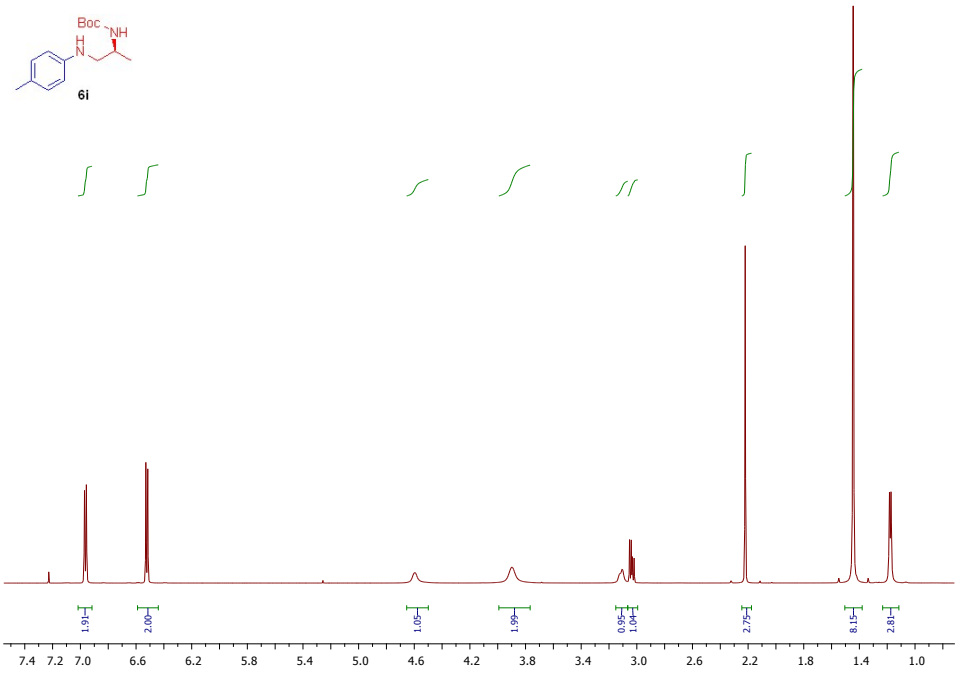
1.0
0.5
0.0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1.05
1.99
0.95
1.04
2.75
8.15
2.81
7.4
7.2
7.0
6.6
6.2
5.8
5.4
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4.6
4.2
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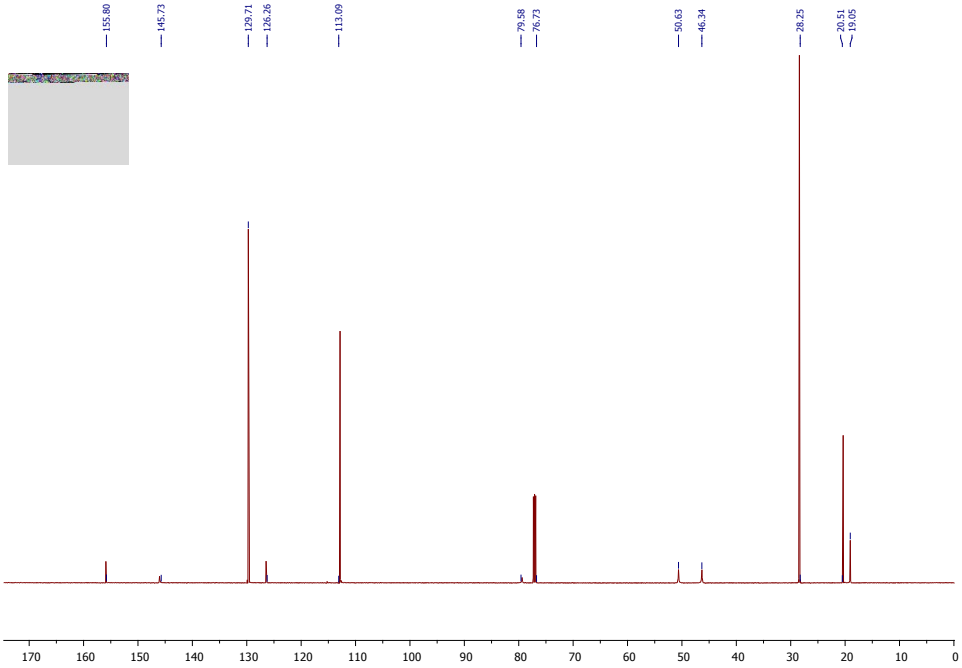
3.4
3.0
2.6
2.2
1.8
1.4
1.0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79.58
76.73
50.63
46.34
28.25
20.51
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100
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70
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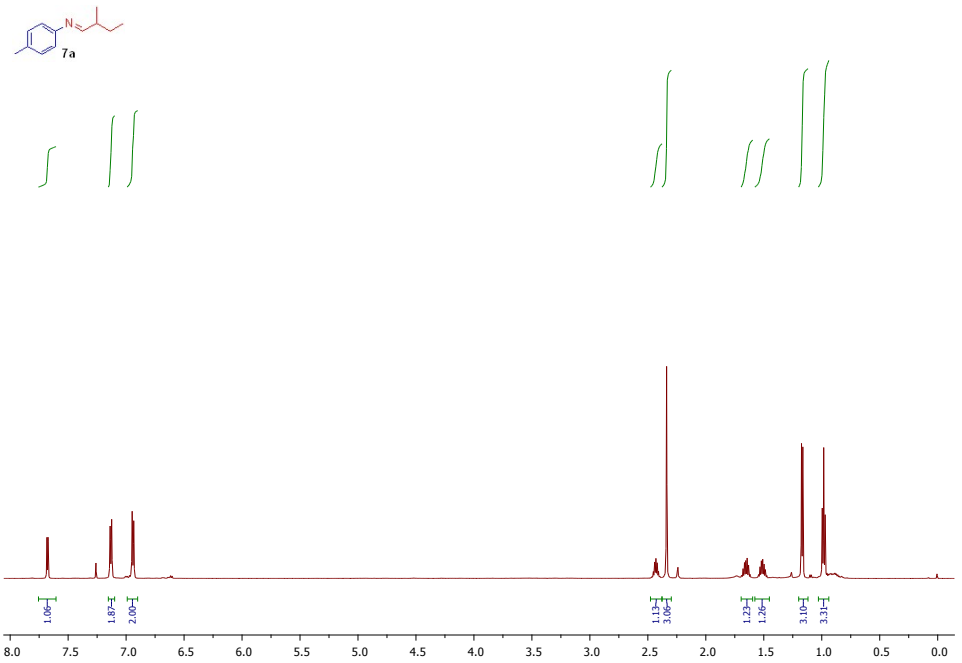
10
0


7a
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1.87
2.00
1.13
3.06
1.23
1.26
3.10
3.31
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
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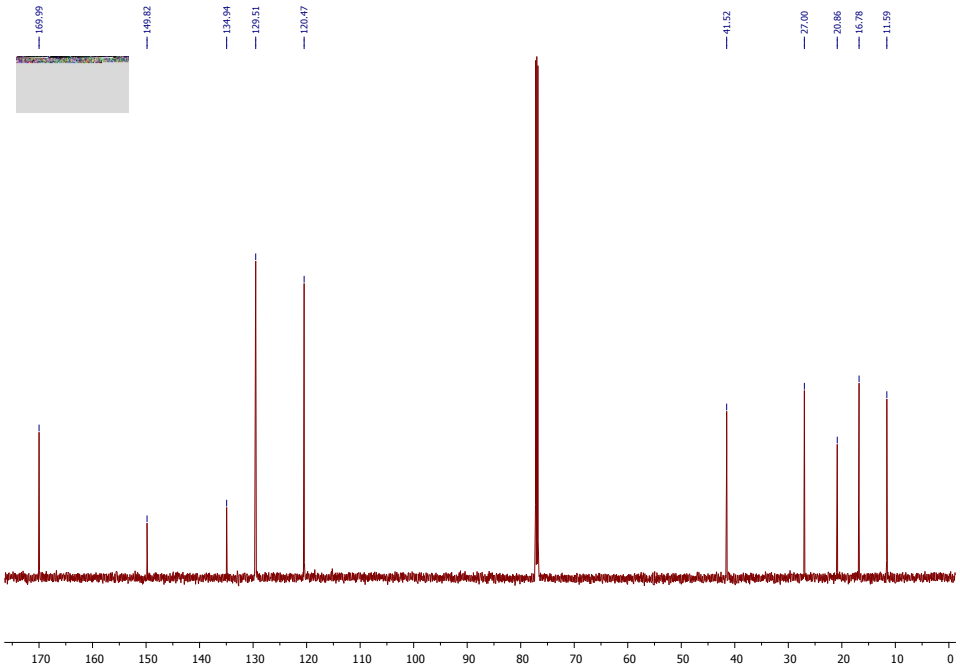
0.0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149.82
134.94
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20.86
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150
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130
120
110
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90
80
70
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30
20
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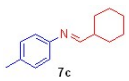
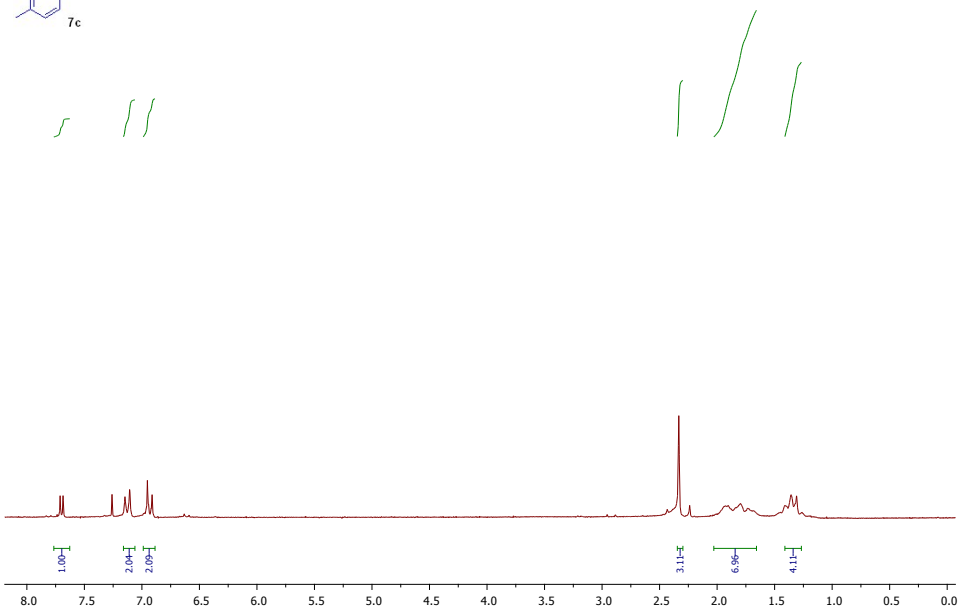
0


N

7c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2.09
3.11
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4.11
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7.5
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6.0
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4.5
4.0
3.5
3.0
2.5
2.0
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1.0
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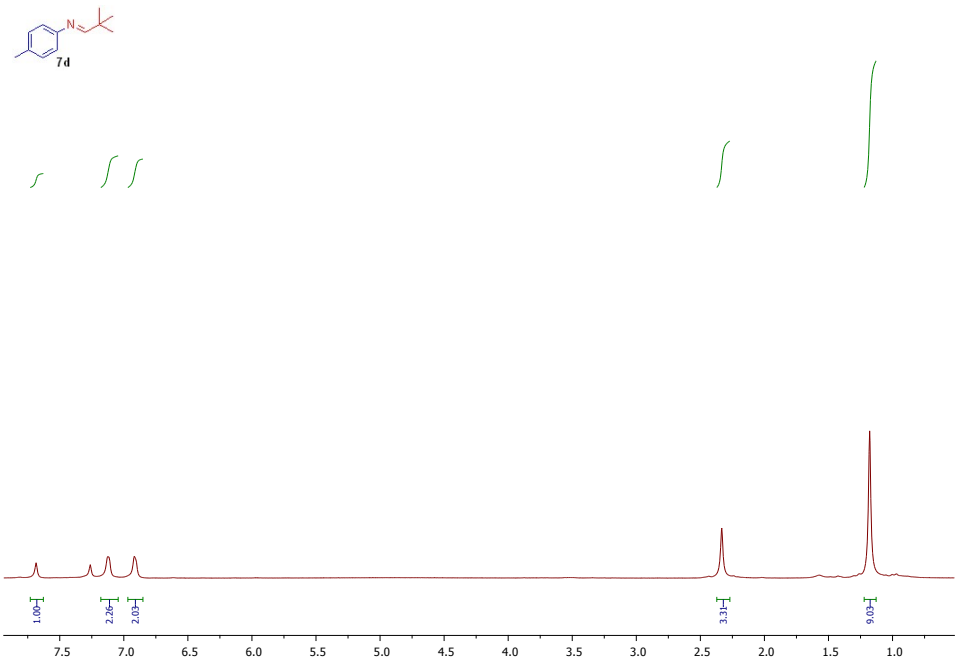
0.0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1.00
2.26
2.03
3.31
9.03
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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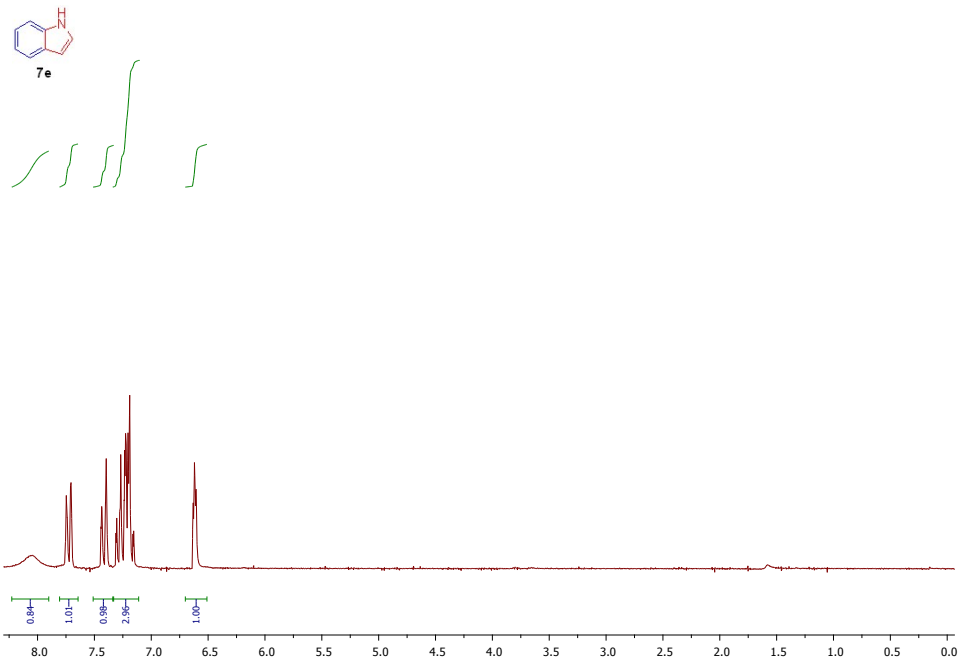
2.0
1.5
1.0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1.00
8.0
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7.0
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6.0
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4.5
4.0
3.5
3.0
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2.0
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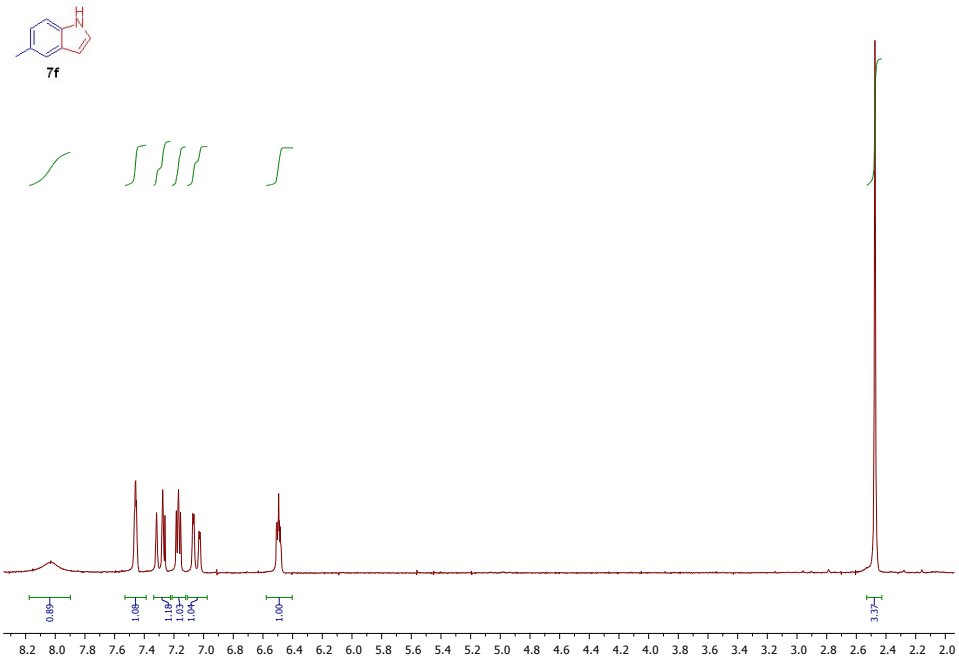
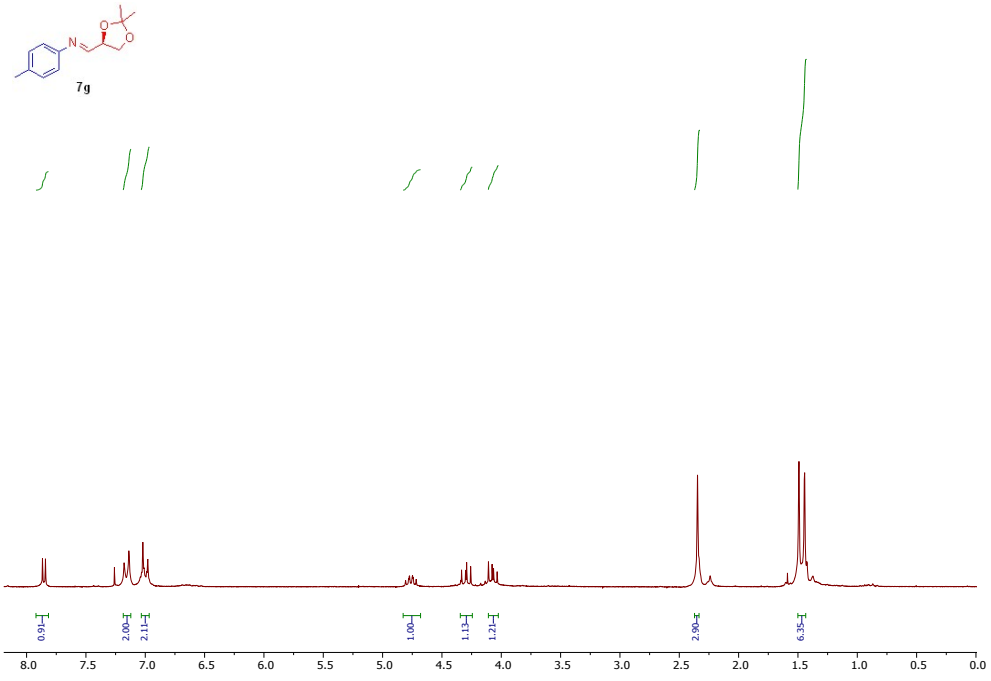
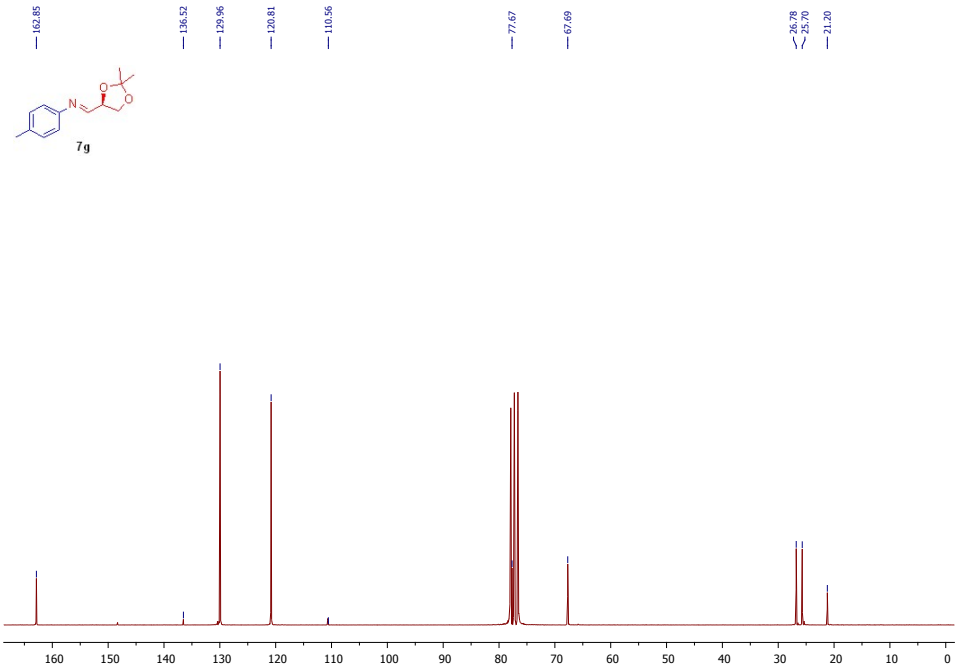
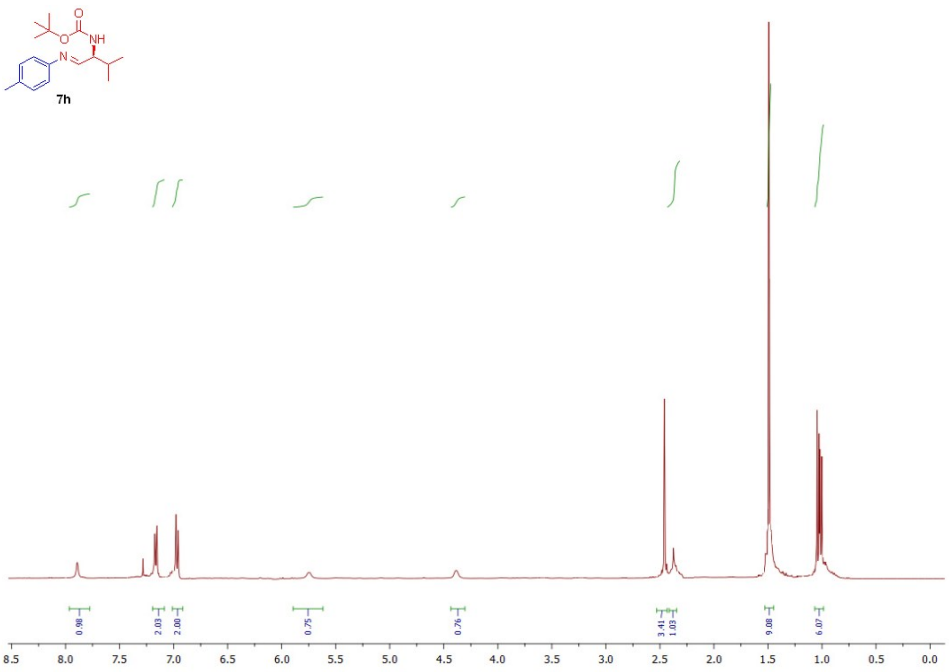
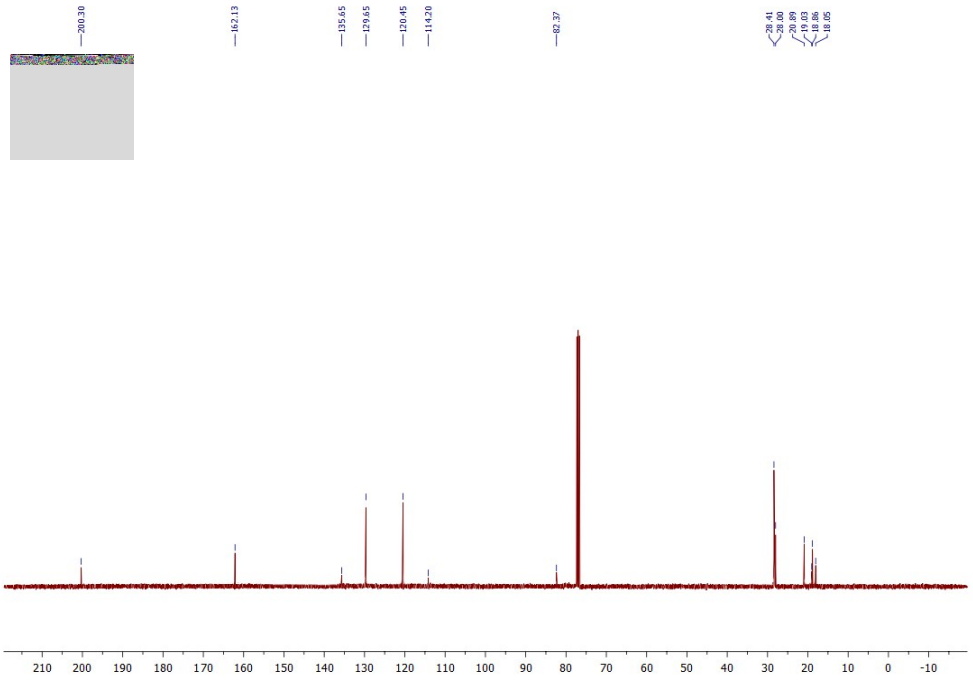
1.0
0.5
0.0

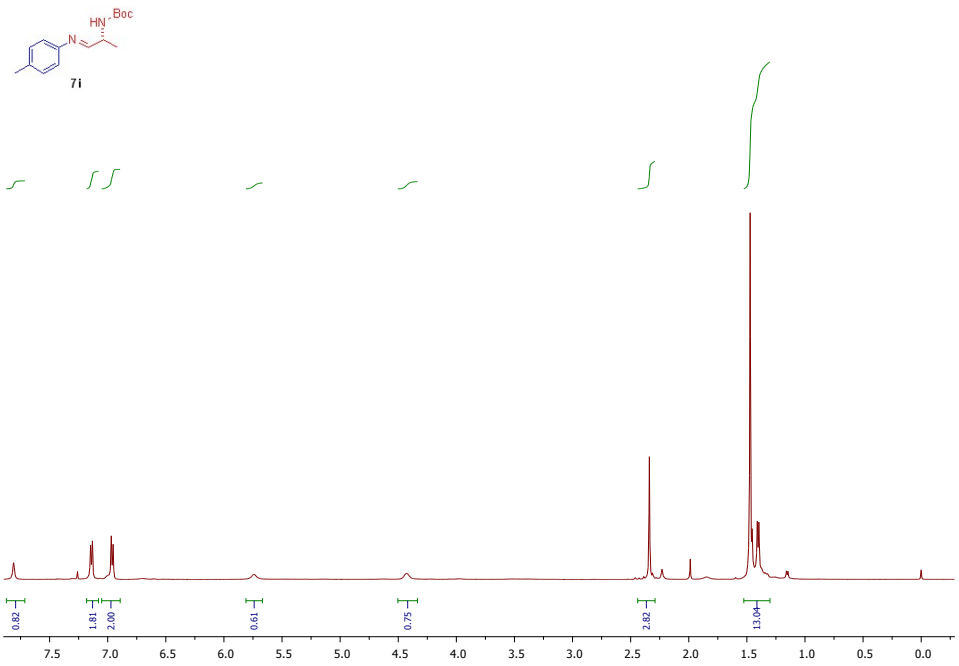

7f
0.89
1.08
1.18
1.03
1.04
1.00
3.37
8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0

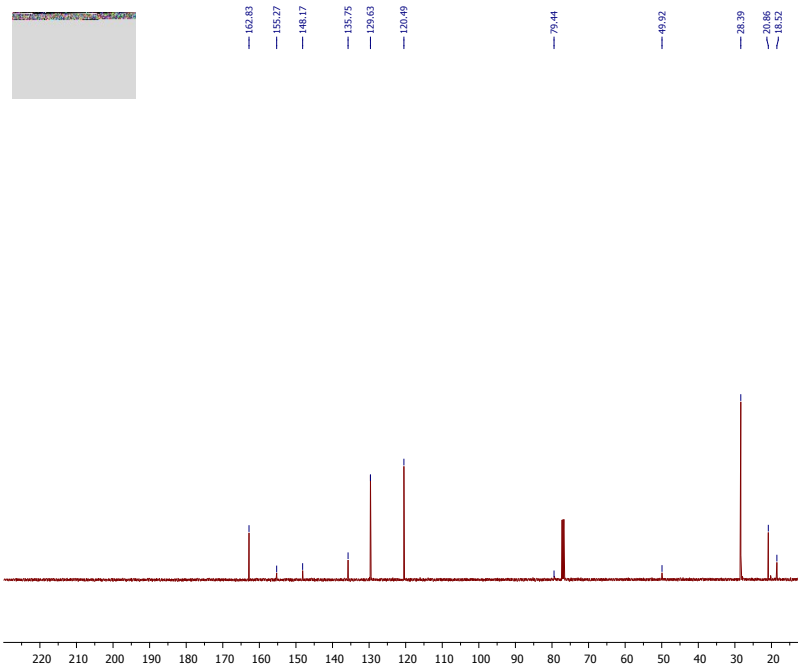

7g
0.91
2.00
2.11
1.00
1.13
1.21
2.90
6.35
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


162.85
136.52
129.96
120.81
110.56
77.67
67.69
26.78
25.70
21.20
7g
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7h
0.98
2.03
2.00
0.75
0.76
3.41
1.03
9.08
6.07
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


200.30
162.13
135.65
129.65
120.45
114.20
82.37
28.41
28.00
20.89
19.03
18.86
18.05
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


HN
Boc
N
7i
0.82
1.81
2.00
0.61
0.75
2.82
13.04
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


162.83
155.27
148.17
135.75
129.63
120.49
79.44
49.92
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20.86
18.52
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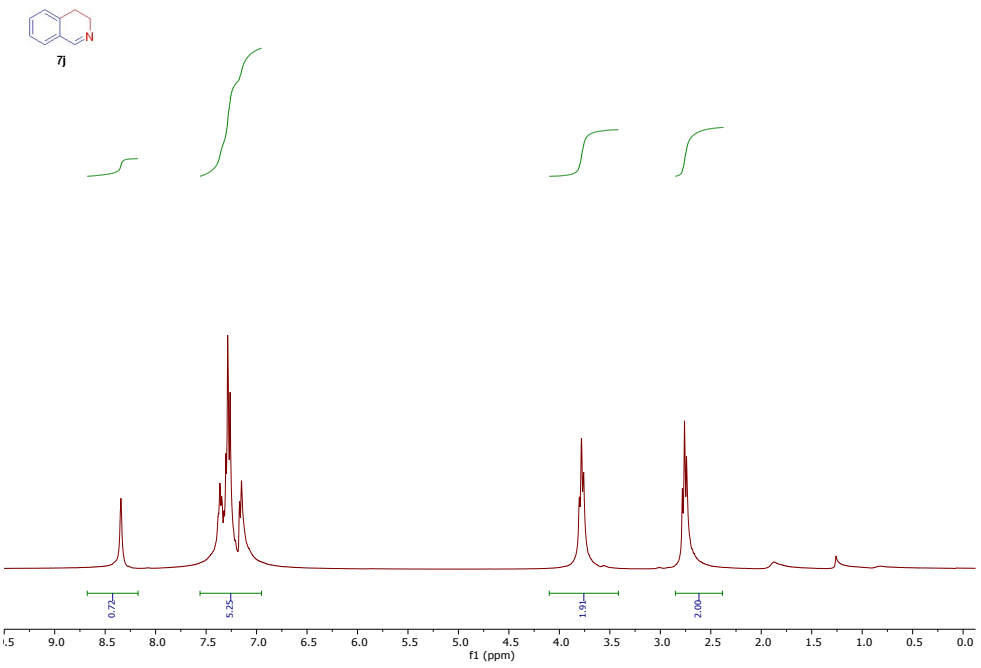
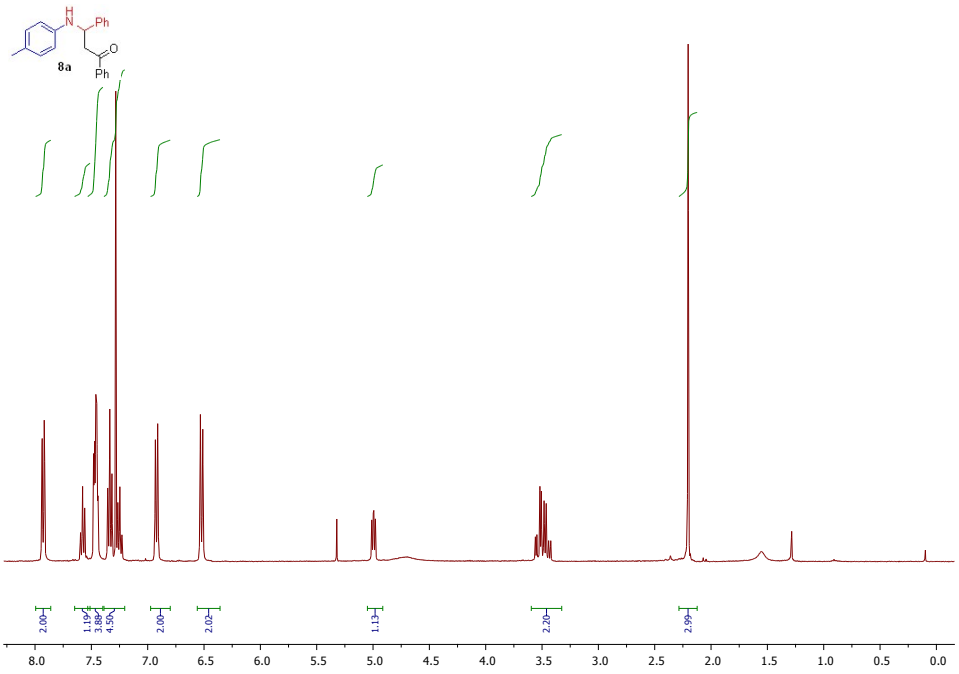
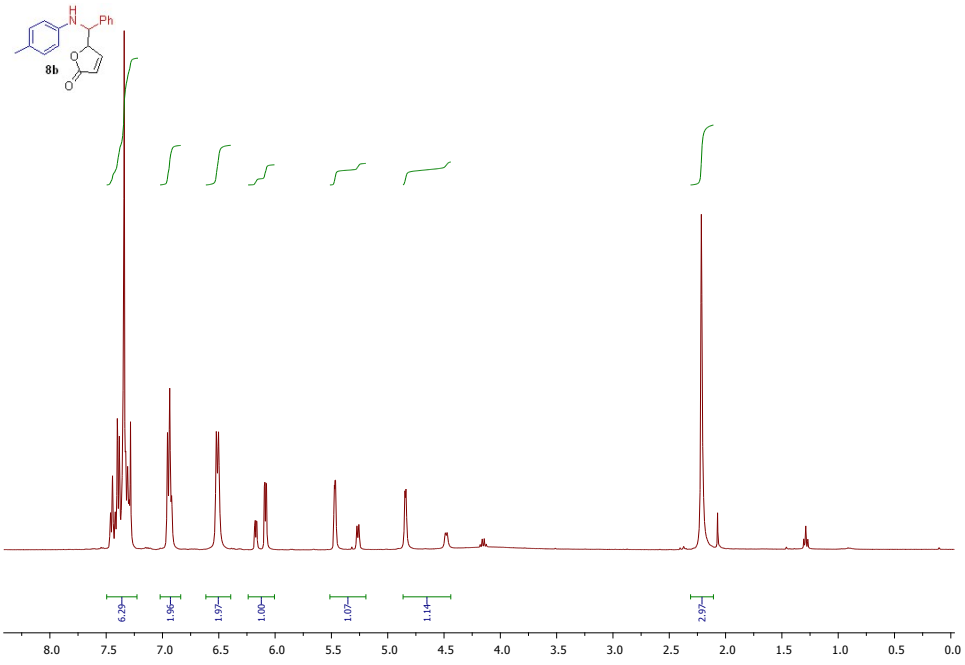

7j
0.72
5.25
1.91
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


8a
2.00
1.19
3.88
4.95
2.00
2.00
1.13
2.20
2.99
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


8b
6.29
1.96
1.97
1.00
1.07
1.14
2.97
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
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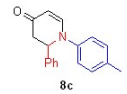
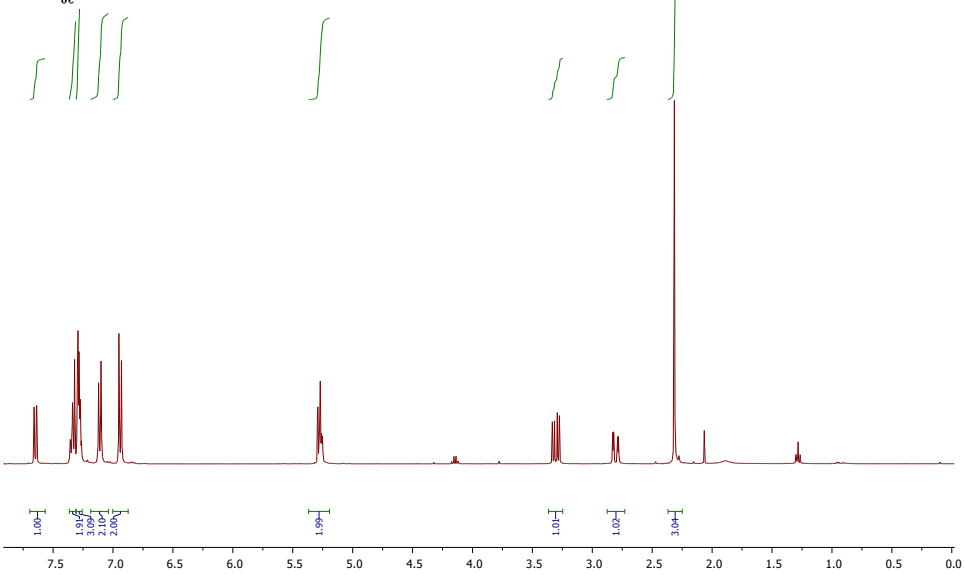
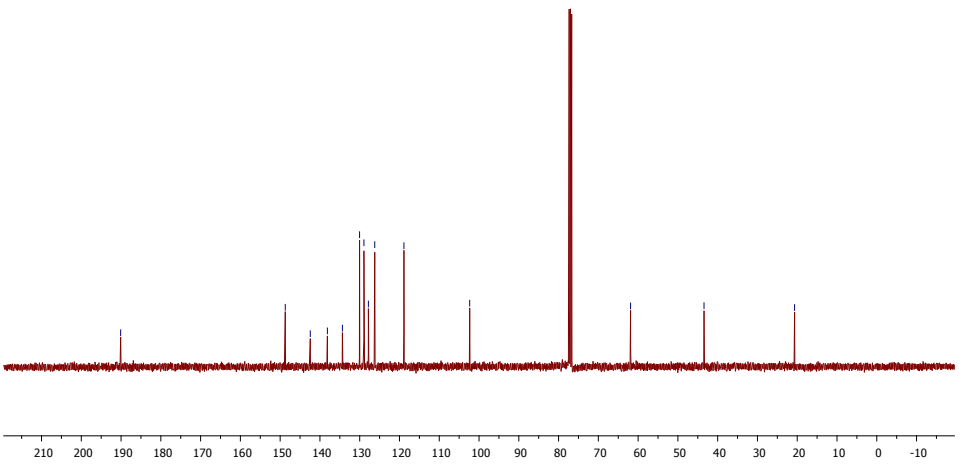


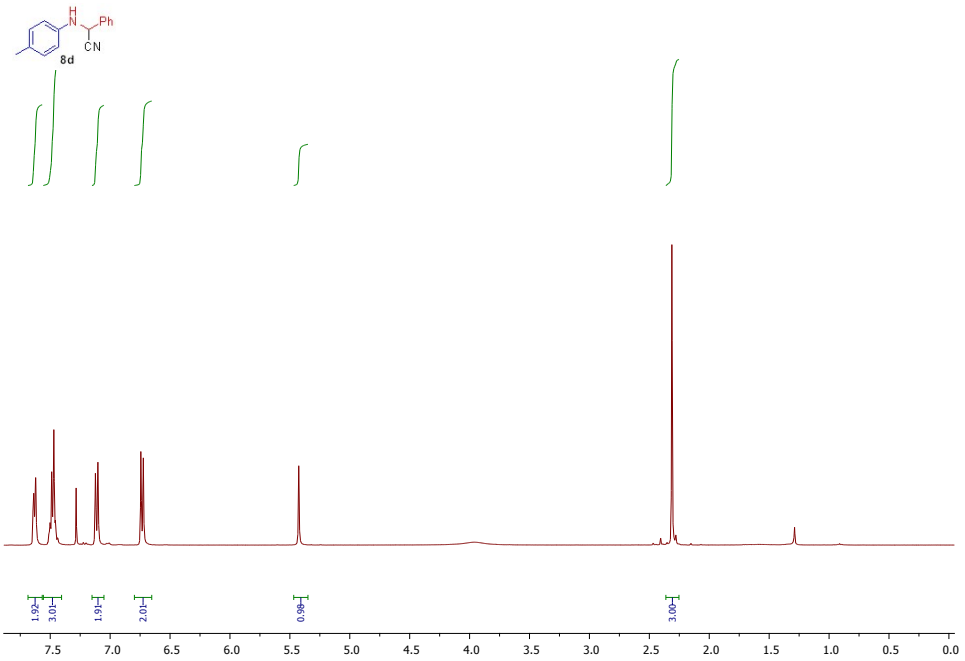
8c

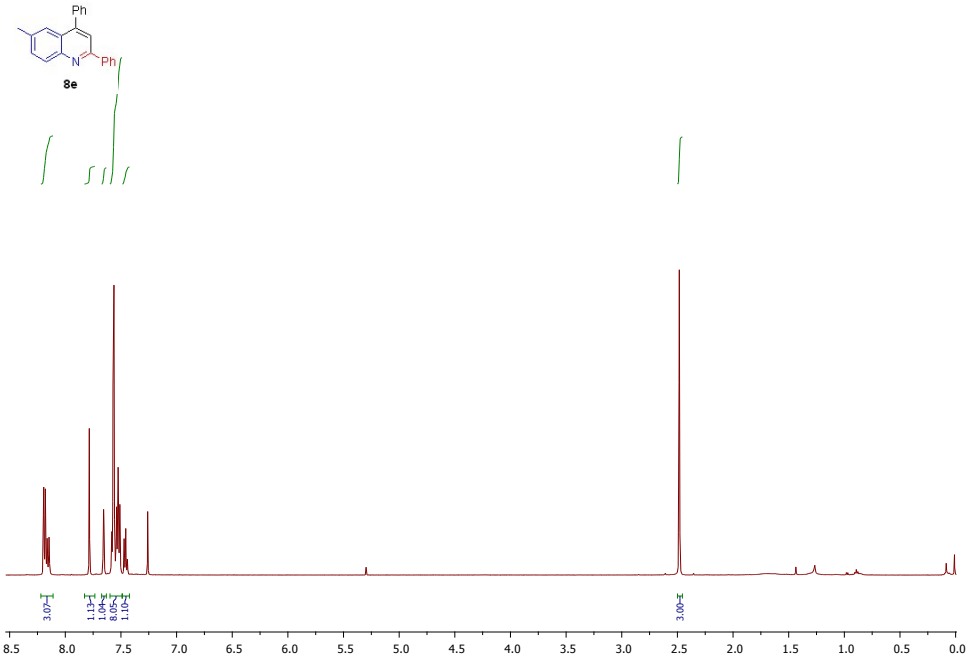

1.00
1.91
3.09
2.10
2.06
1.99
1.01
1.02
3.04
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

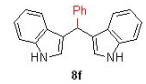

190.10
148.72
142.43
138.13
134.35
130.04
128.94
127.33
126.22
118.88
102.35
61.90
43.43
20.66

8c

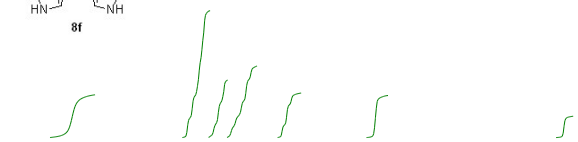

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

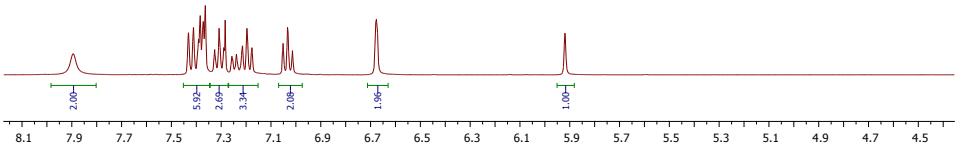

8d
Ph
CN
1.92
3.01
1.91
2.01
0.98
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


Ph
N
Ph
8e
3.07
1.13
1.04
8.05
1.10
3.00
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


Ph
HN
NH

8f




2.00
5.93
2.69
3.34
2.08
1.96
1.00
8.1
7.9
7.7
7.5
7.3
7.1
6.9
6.7
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5.5
5.3
5.1
4.9
4.7
4.5

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