Supporting Information

Highly Selective Hydrolysis of Amides via Electroreduction

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1. General Information

NMR spectra: ^{1}H-NMR spectra were recorded on 400 or 600 MHz spectrophotometers, ^{13}C NMR spectra were recorded on 100 or 150 MHz with complete proton decoupling spectrophotometers using $CDCl_3$ as solvent. Data were reported in the following order: chemical shift (δ) values are reported in ppm with the solvent resonance as internal standard ($CDCl_3$: δ = 7.26 ppm for ^{1}H, TMS: δ = 0 ppm for ^{1}H, δ = 77.16 ppm for ^{13}C); multiplicities are indicated brs (broadened singlet), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (*J*) are given in Hertz (Hz). **High Resolution Mass Spectrometry (HRMS):** All were recorded on Agilent 6210 ESI/TOF using a positive electrospray ionization (ESI^{+}). Measured values are reported to 4 decimal places of the calculated value. The calculated values are based on the most abundant isotope. **Chromatography:** Analytical thin layer chromatography was performed using Qingdao Puke Parting Materials Co. silica gel plates (Silicagel 60 F254). Visualization was by ultraviolet fluorescence (λ = 254 nm) and/or staining with potassium permanganate ($KMnO_4$). Flash column chromatography was performed using 200-300 mesh silica gel.

All reactions were carried out under an air atmosphere using 5-5 mL H-type divided cell and Nafion 117 PFSA membranes. Electrolytes were dried in vacuum at 50 °C for at least 4 h. If not noted, other commercial reagents were used without further purification. All starting materials are commercially available or prepared by the reported method.[1] The electrochemical reactions were performed on a MESTEK DP3005B potentiostat (made in China) in constant current mode.

2. General Procedures

2.1 Preparation of Starting Materials

All starting materials were obtained from commercial sources or synthesized according to the reported literature.[1]

Substrates acquired after brief synthesis (generally in 10.0 mmol scale)

Substrate(s)	Method description
3, **5**, **45**, **46**, **48**, **49**	as described in *ref.* [1a] and [1c]
11	as described in *ref.* [1b] and [1c]
12, **14**	as described in *ref.* [1d]
27, 39, 40	as described in *ref.* [1e]
30	as described in *ref.* [1f]
32	as described in *ref.* [1g]
38	as described in *ref.* [1h]
41	as described in *ref.* [1i]
50	as described in *ref.* [1j]
54	as described in *ref.* [1k]
58	as described in *ref.* [1l]
60	as described in *ref.* [1m]

25, 26, 35 are commercially available. The rest of starting materials are also synthesized by the reported literature.[1c]

2.2 Photographic Guide for Electrochemical Reactions

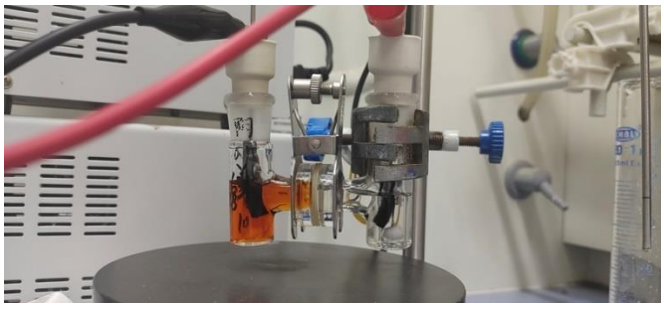
Overview of materials used: from left to right: (a) Graphite felt electrode (15 mm×10 mm×3 mm). (b) Electrochemical cell.

(a)

(b)

Assembling the cell:

Setting up the reaction:



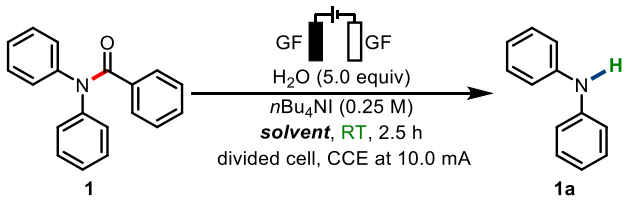
2.3 General Procedure: Electroreduction of Amides

An oven-dried H-type divided cell was equipped with a magnetic stir bar in each chamber. The cathodic chamber was charged with amides (0.3 mmol, 1.0 equiv), and

both chambers were charged with nBu$_4$NClO$_4$ (205 mg each, 0.15 M), DMF (4.0 mL each) and deionized H_2O (27 μL each, 5.0 equiv). Graphite felts (15 mm×10 mm×3 mm) were installed as the cathode and anode. Electrolysis was performed at room temperature with a constant current of 10.0 mA for 2-3 hours. Upon the reduction, the reaction mixture was transferred to 50 mL of ethyl acetate and subjected to washing with saturated brine (3 × 15 mL). The organic fractions were dried by Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by column chromatography on silica gel to furnish the corresponding products **1a** to **54a**.

3. Optimization of The Reaction Conditions

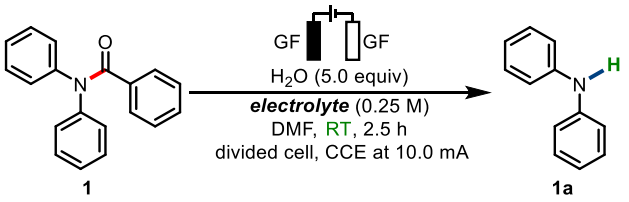
Table S-1: Evaluation of Solvents



Entry	Solvent	Yield (%)
1	**DMF**	**90**
2	Acetone	Trace
3	DMA	86
4	DMSO	87
5	MeCN	84
6	MeOH	N.D.
7	H_2O	N.D.
8	DCM	Trace

Reaction conditions: cathode: **1** (0.3 mmol), H_2O (1.5 mmol), nBu$_4$NI (0.25 M) in solvent (4.0 mL); anode: H_2O (1.5 mmol), nBu$_4$NI (0.25 M) in solvent (4.0 mL). Graphite felt as anode and cathode in an H-type divided cell, room temperature, 2.5 h, air atmosphere. Yields of isolated products. DMA = *N*,*N*-dimethylacetamide; DMF = *N*,*N*-dimethylformamide; GF = graphite felt; CCE = constant current electrolysis.

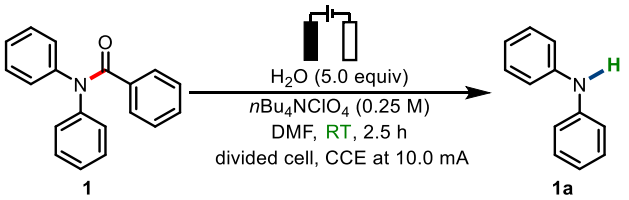
Table S-2: Evaluation of Electrolytes



Entry	Electrolyte	Yield (%)
1	*n*Bu$_4$NI	94
2	Et$_4$NI	84
3	NaI	45
4	*n*Bu$_4$NBr	79
5	*n*Bu$_4$NCl	77
6	*n*Bu$_4$NBF$_4$	73
7	***n*Bu$_4$NClO$_4$**	**95 (91)**
8	*n*Bu$_4$NPF$_6$	81

Reaction conditions: cathode: **1** (0.3 mmol), H_2O (1.5 mmol), electrolyte (0.25 M) in DMF (4.0 mL); anode: H_2O (1.5 mmol), electrolyte (0.25 M) in DMF (4.0 mL). Graphite as anode and cathode in an H-type divided cell, room temperature, 2.5 h, air atmosphere. Yields were determined by ^{1}H-NMR using $C_2H_2Cl_4$ as an internal standard. Isolated yield in parenthesis. GF = graphite felt; CCE = constant current electrolysis.

Table S-3: Evaluation of Electrodes

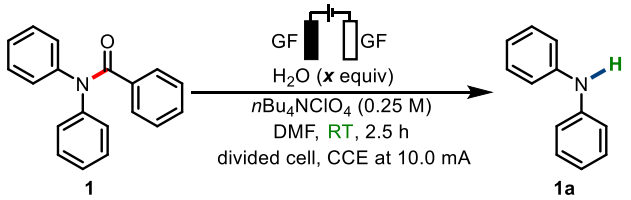


Entry	Anode	Cathode	Yield (%)
1	CC	GF	87
2	Graphite plate	GF	88
3	**GF**	**GF**	**95 (91)**
4	GF	Pt	78
5	GF	CC	80
6	GF	Graphite plate	83

Reaction conditions: cathode: **1** (0.3 mmol), H_2O (1.5 mmol), *n*Bu$_4$NClO$_4$ (0.25 M) in DMF (4.0 mL); anode: H_2O (1.5 mmol), *n*Bu$_4$NClO$_4$ (0.25 M) in DMF (4.0 mL), anode and cathode in an H-type divided cell, room temperature, 2.5 h, air atmosphere. Yields were determined by ^{1}H-NMR using $C_2H_2Cl_4$ as an

internal standard. Isolated yield in parenthesis. GF = graphite felt; CC = carbon cloth; CCE = constant current electrolysis.

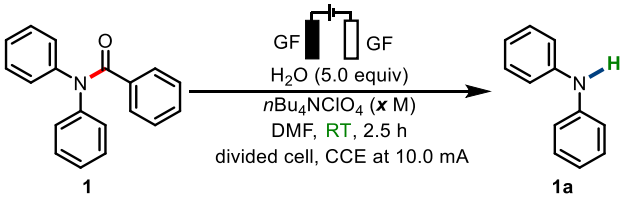
Table S-4: Optimization of Equivalent of H_2O



Entry	Equivalent of H_2O	Yield (%)
1	0.0	73
2	1.0	84
3	**5.0**	**95 (91)**
4	10.0	87
5	H_2O/DMF = 1:1	N.D.

Reaction conditions: cathode: **1** (0.3 mmol), H_2O (x mmol), nBu$_4$NClO$_4$ (0.25 M) in DMF (4.0 mL); anode: H_2O (x mmol), nBu$_4$NClO$_4$ (0.25 M) in DMF (4.0 mL). Graphite felt as anode and cathode in an H-type divided cell, room temperature, 2.5 h, air atmosphere. Yields were determined by ^{1}H-NMR using $C_2H_2Cl_4$ as an internal standard. Isolated yield in parenthesis. GF = graphite felt; CCE = constant current electrolysis.

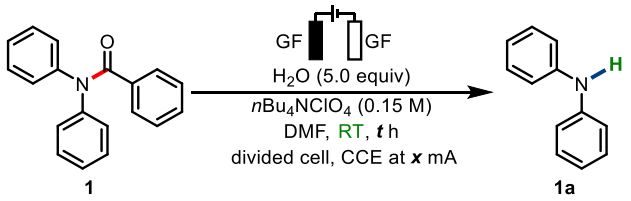
Table S-5: Concentration of Electrolyte for the Reactions



Entry	Concentration of electrolyte	Yield (%)
1	0	Trace
2	**0.15**	**96 (91)**
3	0.25	95
4	0.35	92

Reaction conditions: cathode: **1** (0.3 mmol), H_2O (1.5 mmol), nBu$_4$NClO$_4$ (x M) in DMF (4.0 mL); anode: H_2O (1.5 mmol), nBu$_4$NClO$_4$ (x M) in DMF (4.0 mL). Graphite felt as anode and cathode in an H-type divided cell, room temperature, 2.5 h, air atmosphere. Yields were determined by ^{1}H-NMR using $C_2H_2Cl_4$ as an internal standard. Isolated yield in parenthesis. GF = graphite felt; CCE = constant current electrolysis.

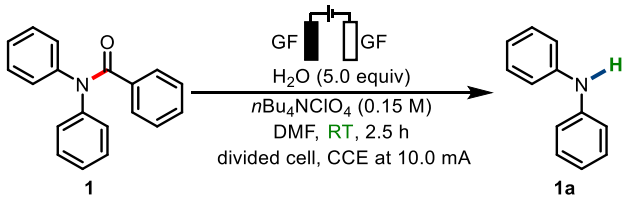
Table S-6: Evaluation of Current and Reaction Time



Entry	Constant Current	t (h)	Yield (%)
1	0 mA	2.5	N.D.
2	5 mA	5.0	75
3	**10 mA**	**2.5**	**96 (91)**
4	15 mA	1.7	90

Reaction conditions: cathode: **1** (0.3 mmol), H_2O (1.5 mmol), nBu$_4$NClO$_4$ (0.15 M) in DMF (4.0 mL); anode: H_2O (1.5 mmol), nBu$_4$NClO$_4$ (0.15 M) in DMF (4.0 mL). Graphite felt as anode and cathode in an H-type divided cell, room temperature, t h, air atmosphere. Yields were determined by ^{1}H-NMR using $C_2H_2Cl_4$ as an internal standard. Isolated yield in parenthesis. GF = graphite felt; CCE = constant current electrolysis.

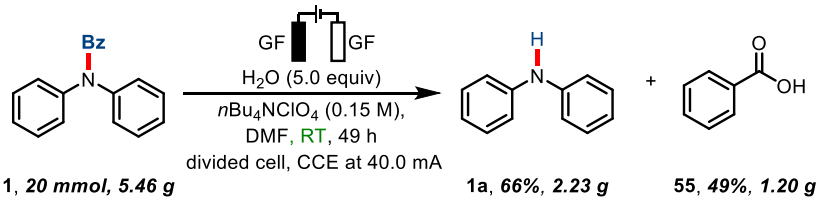
Table S-7: Variation from Optimal Conditions



Entry	Variation from optimal conditions	Yield (%)
1	none	91
2	undivided cell	N.D.
3	DMA as solvent	81
4	CH_3CN as solvent	42
5	electrolyte = nBu$_4$NI	87
6	electrolyte = nBu$_4$NBF$_4$	59
7	electrolyte = nBu$_4$NPF$_6$	77
8	CC (+)/GF (−)	83
9	GF (+)/Pt (−)	78
10	5 mA (5.0 h)	73
11	15 mA (1.7 h)	88
12	N_2 atmosphere	90
13	no electricity	N.D.

Reaction conditions: cathode: **1** (0.3 mmol), H_2O (1.5 mmol), nBu$_4$NClO$_4$ (0.15 M) in DMF (4.0 mL); anode: H_2O (1.5 mmol), nBu$_4$NClO$_4$ (0.15 M) in DMF (4.0 mL). Graphite felt as anode and cathode in an H-type divided cell, room temperature, 2.5 h, air atmosphere. Yields of isolated products. GF = graphite felt; CCE = constant current electrolysis.

4. Scalability of Electrochemical Reduction



An oven-dried H-type divided cell was equipped with a magnetic stir bar in each chamber. The cathodic chamber was charged with **1** (20 mmol, 5.46 g, 1.0 equiv), and both chambers were charged with nBu$_4$NClO$_4$ (7.56 g, each, 0.15 M), DMF (150 mL

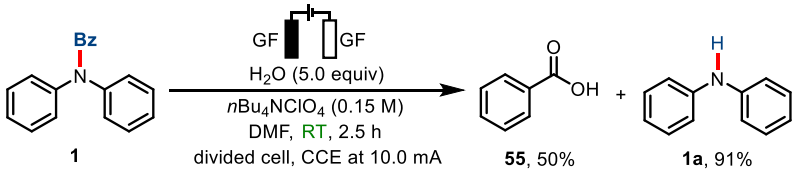
each) and H_2O (1.8 mL each, 5.0 equiv). Graphite felts (30 mm×30 mm×3 mm) were installed as the cathode and anode. Electrolysis was performed at room temperature with a constant current of 40 mA for 49 h. Upon the reduction, the reaction mixture was transferred to 150 mL of ethyl acetate and subjected to washing with saturated brine (3 × 150 mL). The organic fractions were dried by Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by column chromatography on silica gel to furnish the desired product **1a** (2.23 g) in 66% yield. The aqueous layer was acidified with HCl (1.0 M) to *p*H = 1-2. The aqueous layer was extracted with ethyl acetate (3 × 100 mL), and dried with anhydrous Na_2SO_4. Evaporation of the solvent subsequent column chromatography on silica gel afforded the corresponding product **55** (1.20 g) in 49% yield.

The Photographic Guide for Scale-up Electrochemical Reduction:

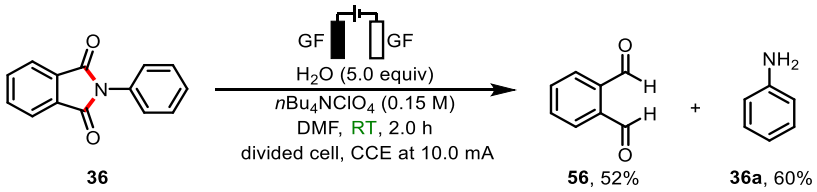
Figure S1 Reaction conditions: cathode: **1** (20 mmol), H_2O (5.0 equiv), *n*Bu_4NClO_4 (0.15 M) in DMF (150 mL); anode: H_2O (5.0 equiv), *n*Bu_4NClO_4 (0.15 M) in DMF (150 mL), graphite felt (GF) as anode and cathode in an H-type divided cell, room temperature, CCE = 40 mA, 49 h, air atmosphere. Yields of isolated products. GF = graphite felt; CCE = constant current electrolysis.

5. Mechanistic Studies

5.1 The Transformation of Benzoyl Functional Group

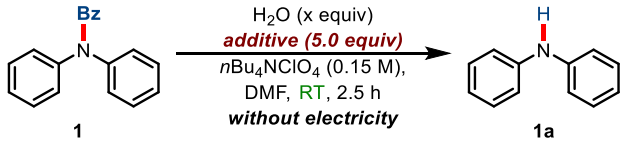


An oven-dried H-type divided cell was equipped with a magnetic stir bar in each chamber. The cathodic chamber was charged with **1** (0.3 mmol, 1.0 equiv), and both chambers were charged with *n*Bu$_4$NClO$_4$ (205 mg each, 0.15 M), DMF (4.0 mL each) and deionized H$_2$O (27 μL each, 5.0 equiv). Graphite felts (15 mm×10 mm×3 mm) were installed as the cathode and anode. Electrolysis was performed at room temperature with a constant current of 10.0 mA for 2.5 hours. Upon the reduction, the reaction mixture was transferred to 50 mL of ethyl acetate and subjected to washing with saturated brine (3 × 15 mL). The organic fractions were dried by Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude product was purified by column chromatography on silica gel to furnish the product **1a** in 91% yield. The aqueous layer was acidified with HCl (1.0 M) to pH = 1-2. The aqueous layer was extracted with ethyl acetate (3 × 15 mL), and dried with anhydrous Na$_2$SO$_4$. Evaporation of the solvent subsequent column chromatography on silica gel afforded the corresponding product **55** in 50% yield.



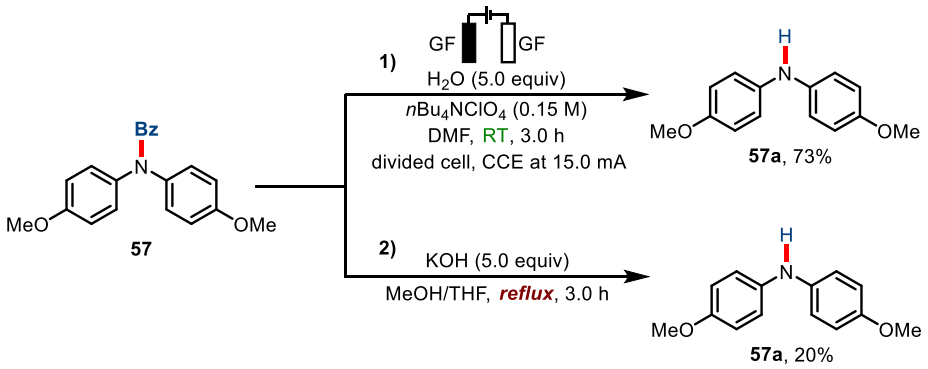
An oven-dried H-type divided cell was equipped with a magnetic stir bar in each chamber. The cathodic chamber was charged with **1** (0.3 mmol, 1.0 equiv), and both chambers were charged with *n*Bu4NClO4 (205 mg each, 0.15 M), DMF (4.0 mL each) and deionized H_2O (27 μL each, 5.0 equiv). Graphite felts (15 mm×10 mm×3 mm) were installed as the cathode and anode. Electrolysis was performed at room temperature with a constant current of 10.0 mA for 2.0 hours. Upon the reduction, the reaction mixture was transferred to 50 mL of ethyl acetate and subjected to washing with saturated brine (3 × 15 mL). The organic fractions were dried by Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by column chromatography on silica gel to furnish the product **56** in 52% yield and **36a** in 60% yield.

5.2 Contrast Experiments with Strong Base and Acid



An oven-dried 5 mL Schlenk tube equipped with a magnetic stir bar was charged with *n*Bu4NClO4 (205 mg, 0.15M), **1** (0.3 mmol), additive (5.0 equiv), DMF (4.0 mL) and indicated equivalent of H_2O. The solution was stirred at room temperature for 2.5 h.

Entry	Additive	H_2O (equiv)	Yield of **1a**
1	KOH	---	Trace
2	KOH	5.0	Trace
3	KOH	185.2	Trace
4	HCl	5.0	Trace



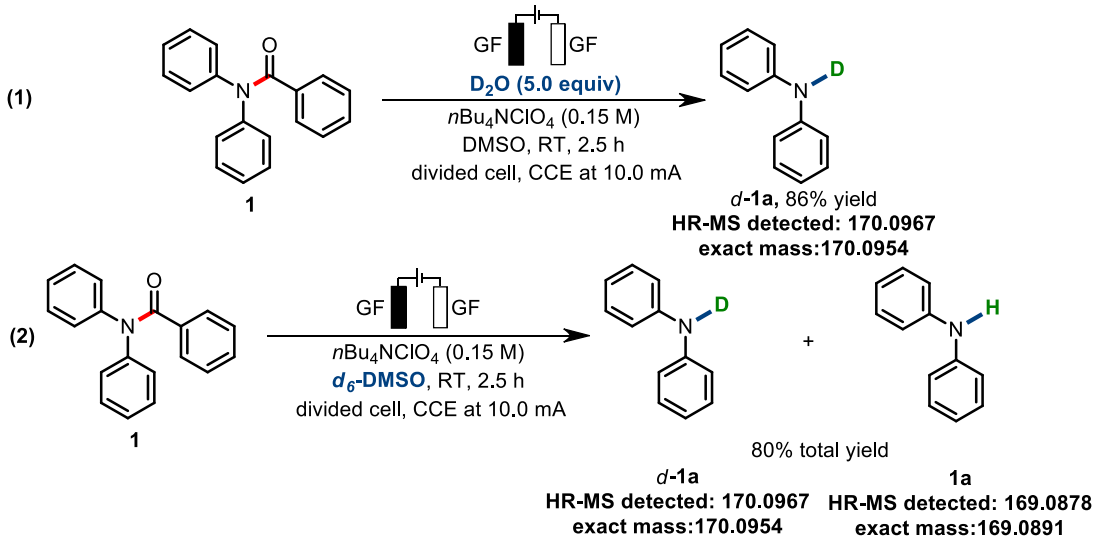
1) The general procedure was followed using **57** (0.3 mmol, 1.0 equiv) at room temperature with a constant current of 15.0 mA for 3.0 h. Isolated by column chromatography yield **57a** (73%).

2) An oven-dried 5 mL Schlenk tube equipped with a magnetic stir bar was charged with KOH (84 mg, 5.0 equiv), **57** (0.3 mmol), MeOH (2.0 ml), THF (2.0 mL). The solution was stirred at 70 °C for 3.0 h. After that, the reaction mixture was then cooled to room temperature and neutralized with 10% HCl solution. The aqueous layer was extracted with ethyl acetate (3 × 15 mL), and dried with anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by column chromatography on silica gel to furnish the product **57a** in 20% yield.

5.3 Detection of H Source

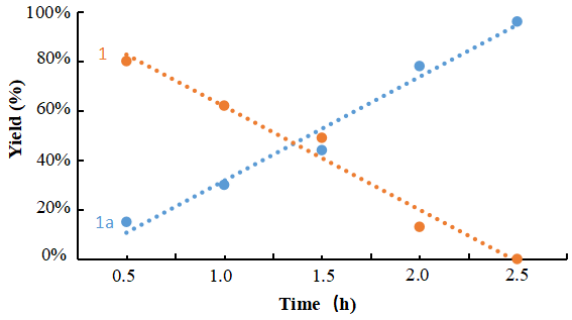
(1) An oven-dried H-type divided cell was equipped with a magnetic stir bar in each chamber. The cathodic chamber was charged with **1** (0.3 mmol, 1.0 equiv), and both chambers were charged with *n*Bu$_4$NClO$_4$ (205 mg each, 0.15 M), DMSO (4.0 mL each) and D$_2$O (27 μL each, 5.0 equiv). Graphite felts (15 mm×10 mm×3 mm) were installed as the cathode and anode. Electrolysis was performed at room temperature with a constant current of 10.0 mA for 2.0 hours. Upon the electroreduction, *d*-**1a** could be detected by HR-MS and isolated with 86% yield.

(2) An oven-dried H-type divided cell was equipped with a magnetic stir bar in each chamber. The cathodic chamber was charged with **1** (0.3 mmol, 1.0 equiv), and both chambers were charged with *n*Bu$_4$NClO$_4$ (205 mg each, 0.15 M), *d*$_6$-DMSO (4.0 mL each). Graphite felts (15 mm×10 mm×3 mm) were installed as the cathode and anode. Electrolysis was performed at room temperature with a constant current of 10.0 mA for 2.0 hours. Upon the electroreduction, *d*-**1a** and **1a** were detected by HR-MS and isolated with 80% total yield.



5.4 Kinetic Profiles Experiments

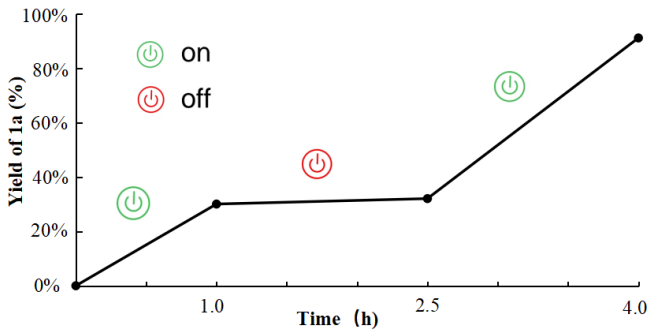
An oven-dried H-type divided cell was equipped with a magnetic stir bar in each chamber. The cathodic chamber was charged with **1** (0.3 mmol, 1.0 equiv), and both chambers were charged with *n*Bu_4NClO_4 (205 mg each, 0.15 M), DMF (4.0 mL each) and deionized H_2O (27 μL each, 5.0 equiv). Graphite felts (15 mm×10 mm×3 mm) were installed as the cathode and anode. Electrolysis was performed at room temperature with a constant current of 10.0 mA for indicated time. Upon the reduction, the reaction mixture was transferred to 50 mL of ethyl acetate and subjected to washing with saturated brine (3 × 15 mL). The organic fractions were dried by Na_2SO_4, filtered and concentrated in vacuo. The NMR yield of **1a** and **1** were determined by analysis of ^1H NMR with $C_2H_2Cl_4$ as internal standard.



Reaction time (h)	Yield of **1a** (%)	Yield of **1** (%)
0.5	15	80
1	30	62
1.5	44	49
2	78	13
2.5	96	0

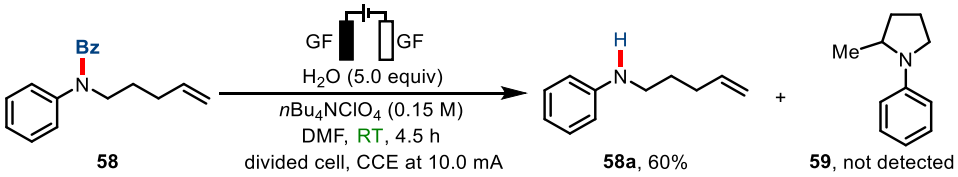
5.5 Electricity on/off Experiments

An oven-dried H-type divided cell was equipped with a magnetic stir bar in each chamber. The cathodic chamber was charged with **1** (0.3 mmol, 1.0 equiv), and both chambers were charged with *n*Bu$_4$NClO$_4$ (205 mg each, 0.15 M), DMF (4.0 mL each) and deionized H$_2$O (27 μL each, 5.0 equiv). Graphite felts (15 mm×10 mm×3 mm) were installed as the cathode and anode. Electrolysis was performed at room temperature with a constant current of 10.0 mA or without electricity for indicated time. Upon the reduction, the reaction mixture was transferred to 50 mL of ethyl acetate and subjected to washing with saturated brine (3 × 10 mL). The organic fractions were dried by Na_2SO_4, filtered and concentrated in vacuo. The NMR yield of **1a** and **1** were determined by analysis of ^{1}H NMR with $C_2H_2Cl_4$ as internal standard.



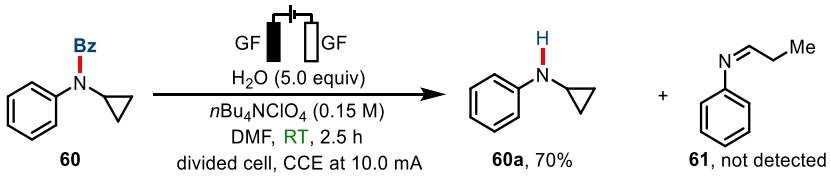
Reaction time (h)	Yield of **1a** (%)
0	0
1	30
2.5	32
4	91

5.6 Controlled Experiments for Exclusion of the Amidyl Radical



An oven-dried H-type divided cell was equipped with a magnetic stir bar in each chamber. The cathodic chamber was charged with **58** (0.3 mmol, 1.0 equiv), and both chambers were charged with *n*Bu$_4$NClO$_4$ (205 mg each, 0.15 M), DMF (4.0 mL each) and deionized H$_2$O (27 μL each, 5.0 equiv). Graphite felts (15 mm×10 mm×3 mm) were installed as the cathode and anode. Electrolysis was performed at room

temperature with a constant current of 10.0 mA. As the cell voltage increased to 31 V (compliance voltage of the DC power supply), the amide still can be detected by TLC and the current gradually decreased towards 0 mA.[2] The electrolysis lasted a total of 4.5 h. Upon the reduction, the reaction mixture was transferred to 50 mL of ethyl acetate and subjected to washing with saturated brine (3 × 15 mL). The organic fractions were dried by Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by column chromatography on silica gel to furnish the product **58a** in 60% yield.



An oven-dried H-type divided cell was equipped with a magnetic stir bar in each chamber. The cathodic chamber was charged with **60** (0.3 mmol, 1.0 equiv), and both chambers were charged with *n*Bu_4NClO_4 (205 mg each, 0.15 M), DMF (4.0 mL each) and deionized H_2O (27 μL each, 5.0 equiv). Graphite felts (15 mm×10 mm×3 mm) were installed as the cathode and anode. Electrolysis was performed at room temperature with a constant current of 10.0 mA for 2.5 h. Upon the reduction, the reaction mixture was transferred to 50 mL of ethyl acetate and subjected to washing with saturated brine (3 × 15 mL). The organic fractions were dried by Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by column chromatography on silica gel to furnish the product **60a** in 70% yield.

5.7 Cyclic Voltammetry Studies

Unless otherwise noted, the cyclic voltammetry was carried out with a Shanghai Chenhua CHI 700E instrument using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode, a Ag/AgCl reference electrode. The measurements were carried out at a scan rate of 50 mV/s.

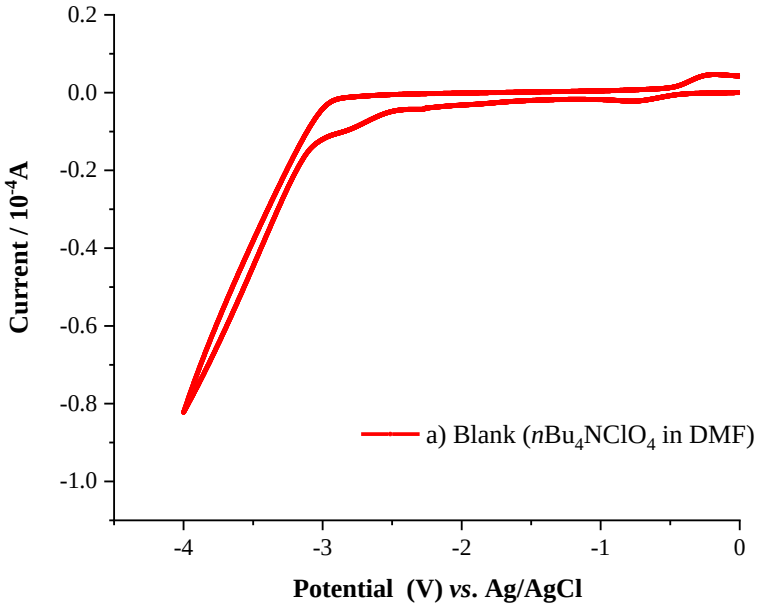


Figure S2. Cyclic voltammogram of *n*Bu4NClO4 (0.1 M) in DMF (5 mL) *vs.* Ag/AgCl.

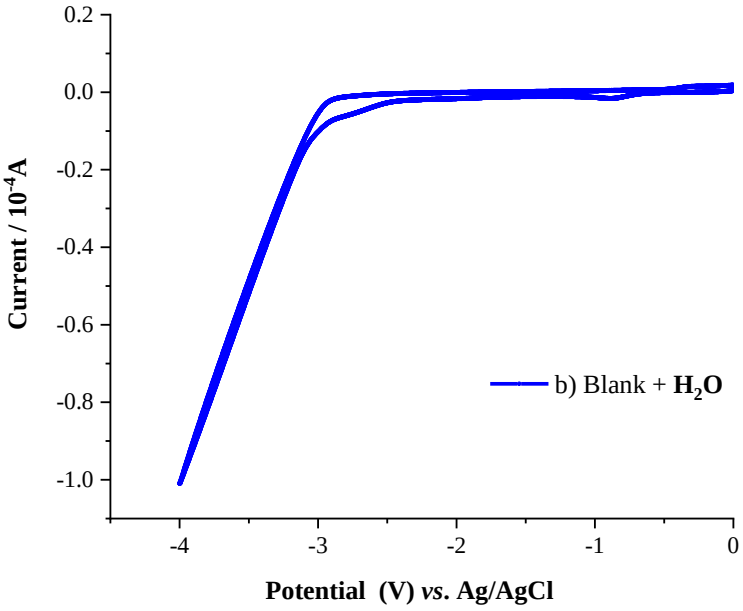


Figure S3. Cyclic voltammogram of **H_2O** (0.25 M) in an electrolyte of *n*Bu_4NClO_4 (0.1 M) in DMF (5 mL) *vs.* Ag/AgCl.

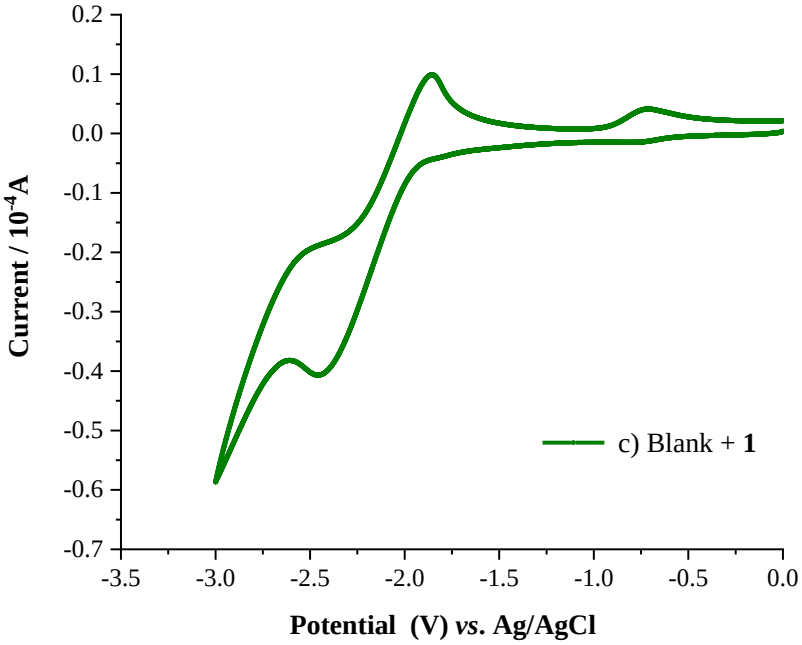


Figure S4. Cyclic voltammogram of **1** (0.05 M) in an electrolyte of *n*Bu_4NClO_4 (0.1 M) in DMF (5 mL). $E_{p/2}$ (**1**) = -2.46 V *vs.* Ag/AgCl.

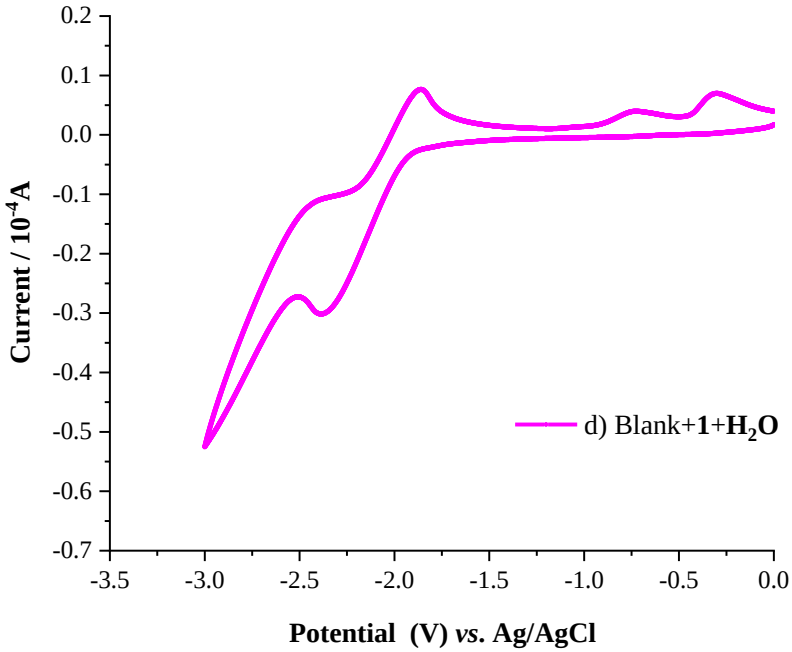
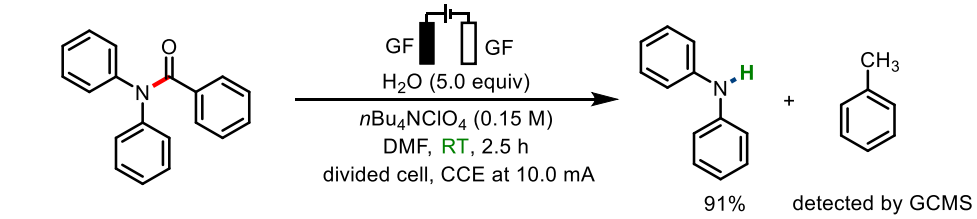
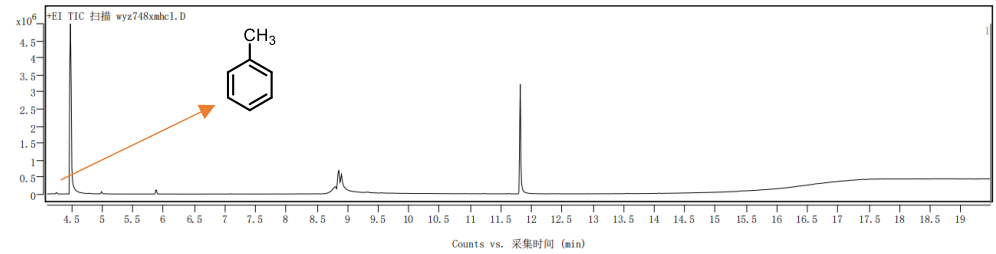


Figure S5. Cyclic voltammogram of **1** (0.05 M) and **H_2O** (0.25 M) in an electrolyte of *n*Bu4NClO4 (0.1 M) in DMF (5 mL). $E_{p/2}$ (**1**+ H_2O) = -2.39 V *vs.* Ag/AgCl.

5.8 The Detection of Benzyl Alcohol



样品色谱图



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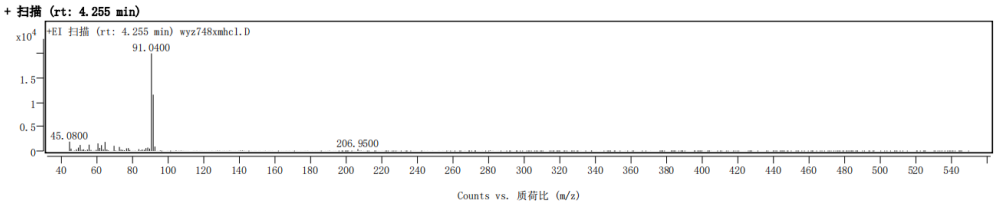
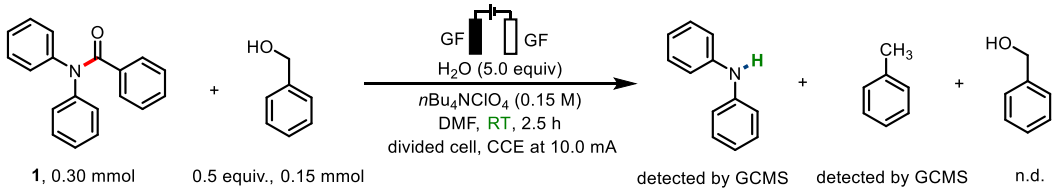
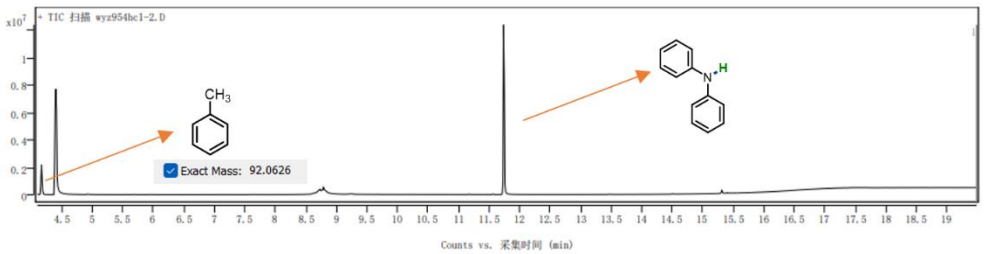
+ 扫描 (rt: 4.255 min)







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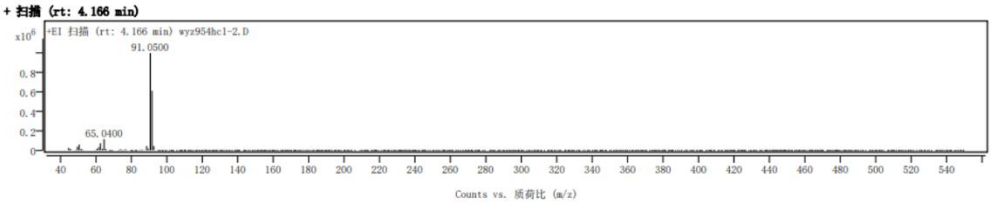
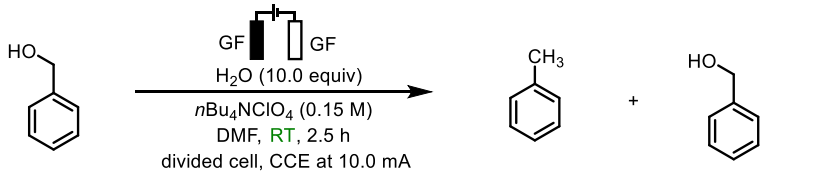
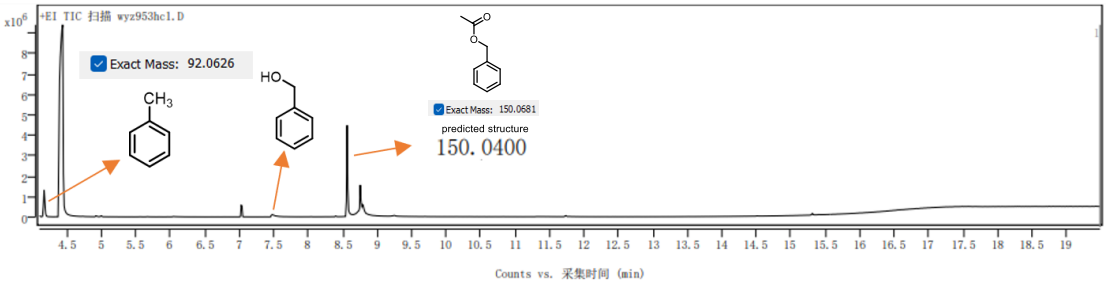
+ 扫描 (rt: 4.166 min)



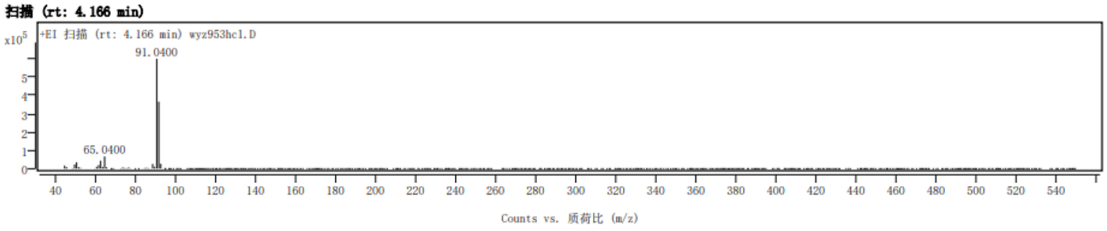


0.15 mmol detected by GCMS detected by GCMS



样品谱图

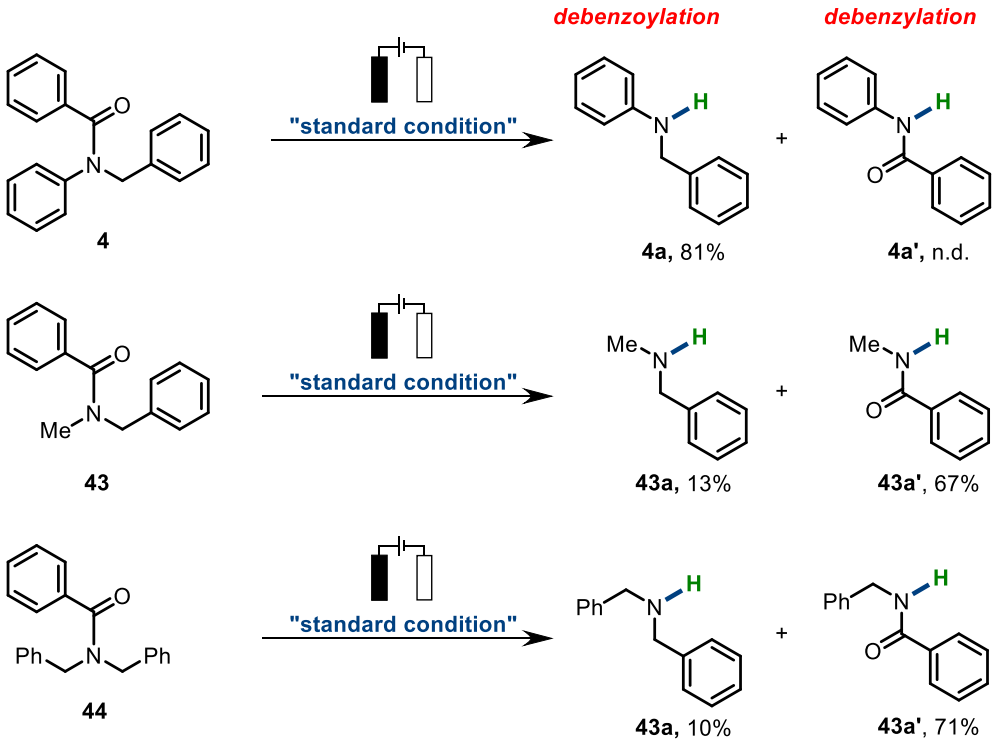
扫描 (rt: 4.166 min)



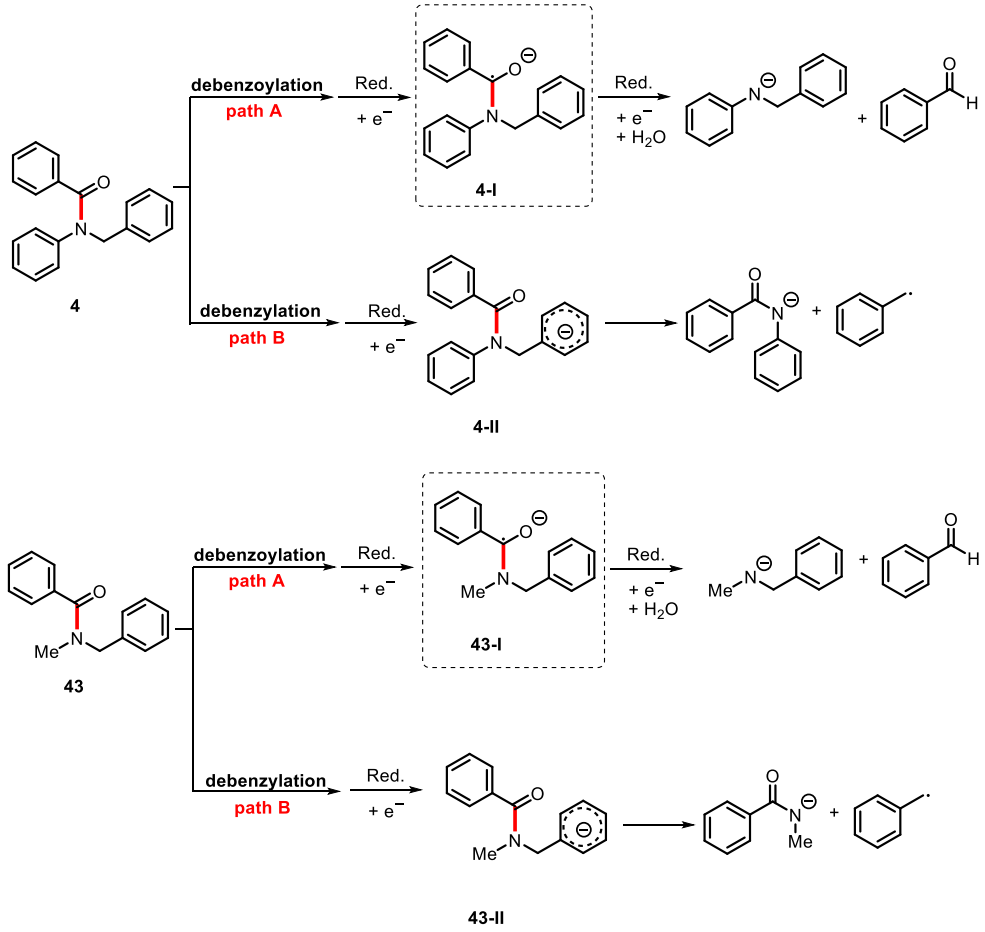
5.9 Studies of Selective Electroreduction

5.9.1. Firstly, we conducted this electroreduction deprotection on *N*-aryl benzamilides **3**, *N*-alkyl benzamilides **43** and **44** to compare the selectivity of debenzoylation and debenzylation. It is evident that *N*-aryl benzamilides (**3**, **4** and **5**) predominantly undergo debenzoylation, while *N*-alkyl benzamilides (**43**, **44** and **53**) primarily undergo debenzylation (Scheme S1). Based on our mechanistic studies and previous literature report,[3] we propose two pathways for *N*-aryl benzamilides **4** and *N*-alkyl benzamilides **43**. In the debenzoylation pathway A, the initial reduction of amides forms the radical anion species **4-I** and **43-I**, respectively, with **4-I** being more stable than **43-I**. This increased stability is attributed to the conjugative effect of the phenyl group on the radical anion (Scheme S2). Therefore, *N*-aryl benzamilides favor the debenzoylation pathway A.

Scheme S1. Selective electroreduction of compound **4**, **43** and **44**



Scheme S2. The two proposed pathways for compound **4** and **43**



In addition, we conducted cyclic voltammetry (CV) experiments on *N*-aryl benzamilides **1**, *N*-alkyl benzamilides **7** and *N,N*-dimethylbenzamide (Figure S6). The reductive peak were observed at $E_{p/2}$(**1**) = -2.45 V *vs.* Ag/AgCl, $E_{p/2}$(**7**) = -2.57 V *vs.* Ag/AgCl, $E_{p/2}$(*N,N*-dimethylbenzamide) = -2.64 V *vs.* Ag/AgCl. We can conclude that the phenyl group decreases the absolute value of reduction potential of amides through a conjugative effect. These results further support our proposed mechanistic studies.

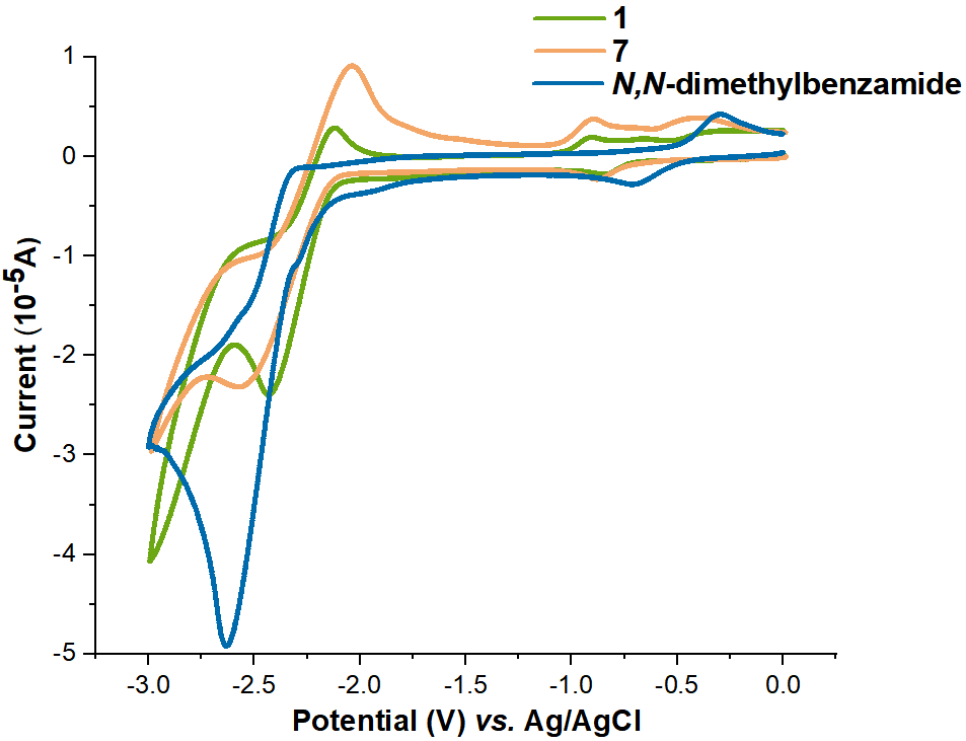
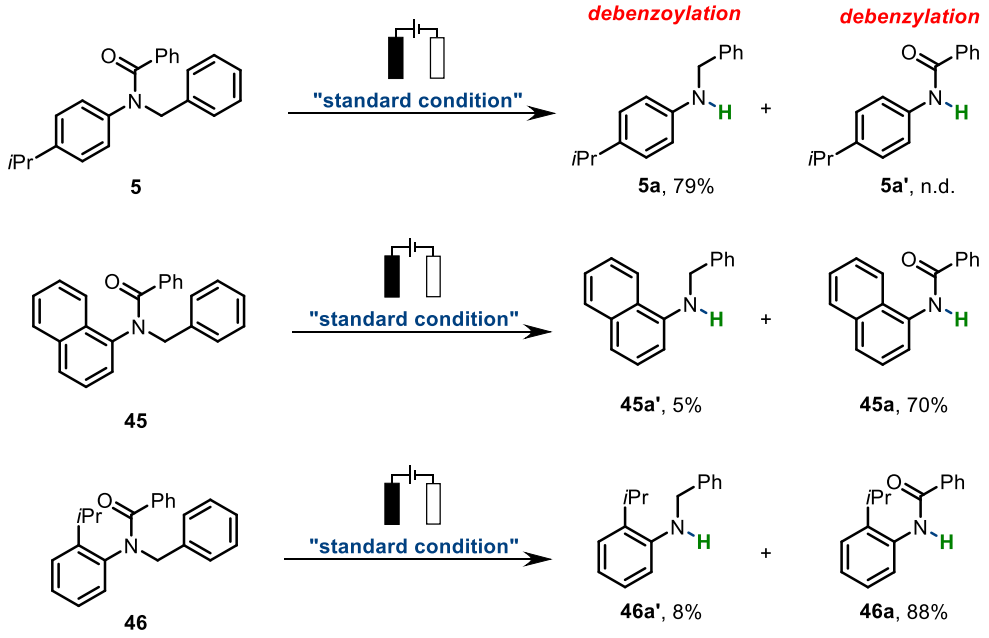


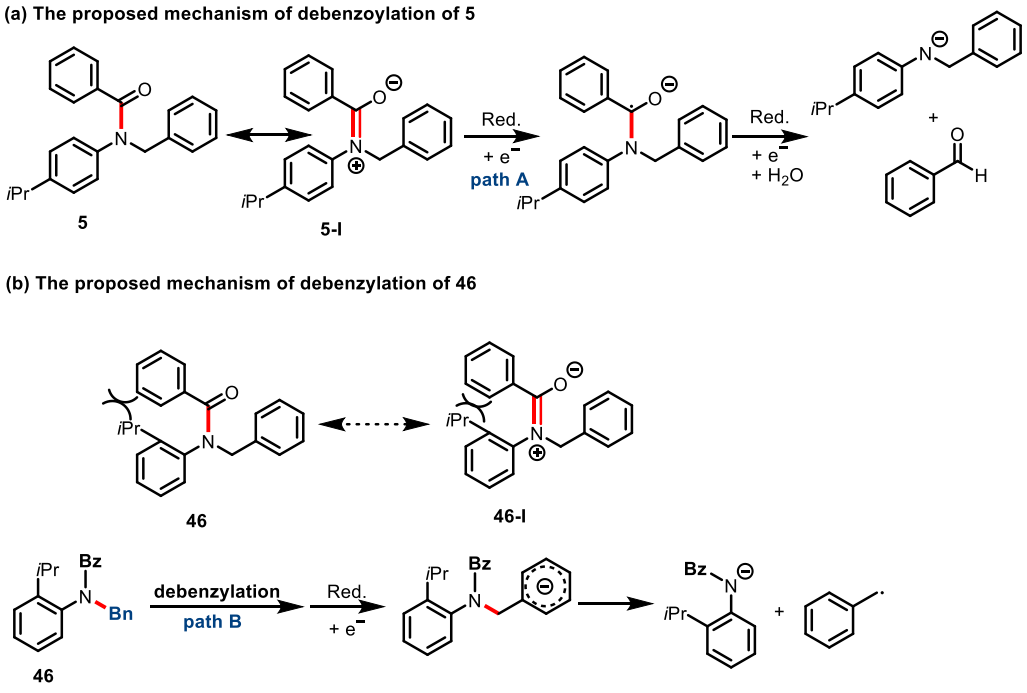
Figure S6. Cyclic voltammetry of substrate **1** (0.05 M), **7** (0.05 M), *N,N*-dimethylbenzamide (0.05 M) in DMF (5 mL) with nBu$_4$NClO$_4$ (0.1 M) as supporting electrolyte. $E_{p/2}$(**1**) = -2.45 V *vs.* Ag/AgCl, $E_{p/2}$(**7**) = -2.57 V *vs.* Ag/AgCl, $E_{p/2}$(*N,N*-dimethylbenzamide) = -2.64 V *vs.* Ag/AgCl.

5.9.2. Regarding the selectivity of *N*-aryl benzamilides **5**, **45** and **46**, we observed that benzamides with more steric hinderance tend to undergo debenzylation (Scheme S3). The *para*-*i*Pr-substituted *N*-benzyl-*N*-phenylbenzamide **5** can proceed through the proposed debenzoylation path A as shown in Scheme S4a. Compound **5** forms the tautomerization intermediate **5-I**, which readily undergoes reduction to generate the radical anions species. However, the *ortho*-*i*Pr-substituted *N*-benzyl-*N*-phenylbenzamide **46** is unable to form the resonance structure **46-I** due to steric hindrance, which prevents the amide groups from conjugating in a planar manner (Scheme S4b). Consequently, compound **46** undergoes debenzylation to afford the corresponding *N*-phenylbenzamide (path B).

Scheme S3. Selective electroreduction of compound **5**, **45** and **46**



Scheme S4. The debenzoylation of **5** and debenzylation of **46**



In addition, CV studies of compounds **1**, **5** and **46** further illustrate that *ortho*-substituted bulky groups will increase the absolute value of reduction potential of benzamilides ($E_{p/2}$(**5**) = -2.43 V *vs.* Ag/AgCl, $E_{p/2}$(**46**) = -2.58 V *vs.* Ag/AgCl) (Figure S7). Based on our mechanistic studies and previous literature report,[4] we conclude

that *ortho*-substituted function group weaken the conjugative effect between the phenyl and amide groups, resulting in different selectivities in electroreduction.

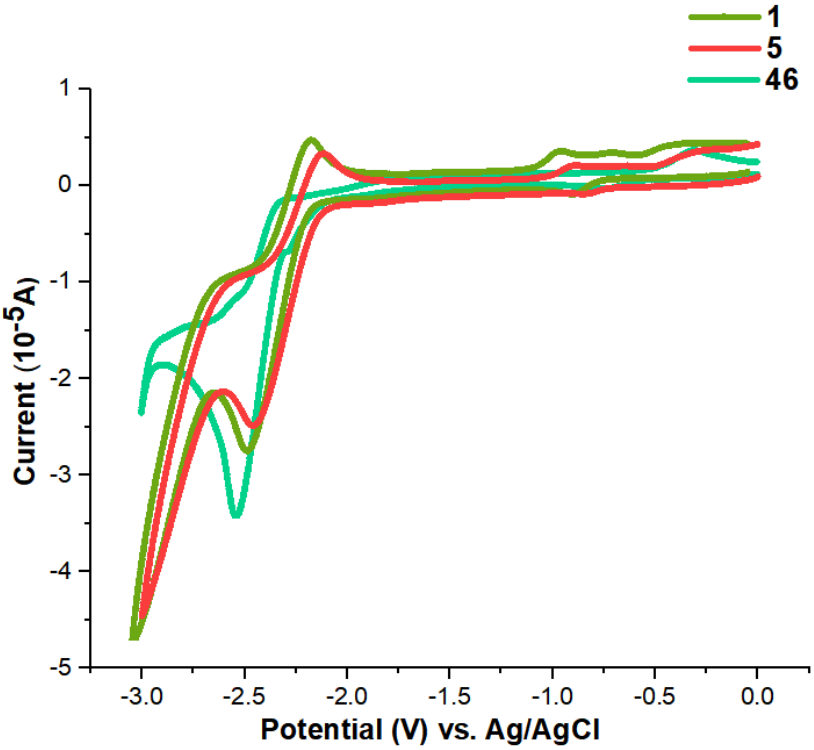
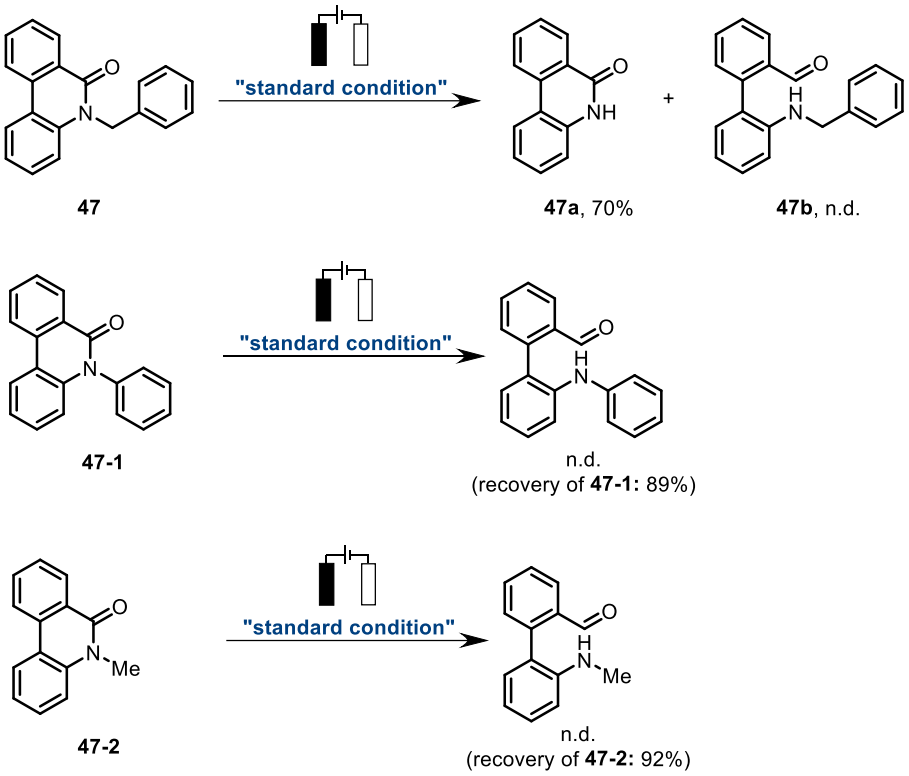


Figure S7. Cyclic voltammetry of substrate **1** (0.05 M), **5** (0.05 M), **46** (0.05 M) in DMF (5 mL) with nBu$_4$NClO$_4$ (0.1 M) as supporting electrolyte. $E_{p/2}$(**1**) = -2.45 V *vs.* Ag/AgCl, $E_{p/2}$(**5**) = -2.43 V *vs.* Ag/AgCl, $E_{p/2}$(**46**) = -2.58 V *vs.* Ag/AgCl.

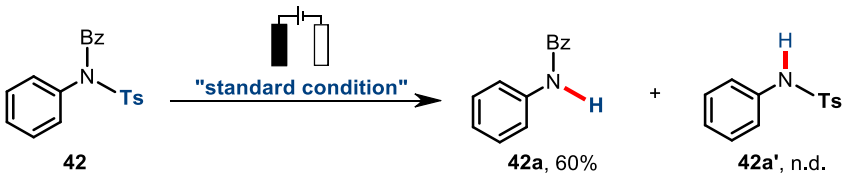
5.9.3. Regarding the selective electroreduction of 5-benzylphenanthridin-6(5*H*)-one **47**, we only observed the debenzylation product **47a** without the debenzoylation product **47b**. Moreover, we conducted the control experiments with **47-1** and **47-2**. Unfortunately, no deprotected products were achieved, and only the starting materials were recovered. These dates indicate that the phenanthridin-6(5*H*)-one moiety is a quite stable cyclic structure, making it difficult to deprotect under this electroreduction condition.

Scheme S5. Selective electroreduction of compound **47**, **47-1** and **47-2**

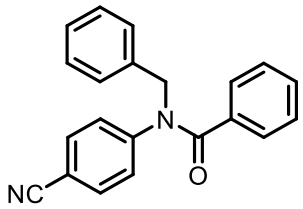


5.9.4. Regarding the selective electroreduction of *N*-phenyl-*N*-tosylbenzamide **42**, we only detected desulfonation product **42a** under standard electroreduction condition. We assume this is because the more electro-withdrawing functional group is more likely to be removed under these conditions. Moreover, previous literature reports also support this viewpoint.[5]

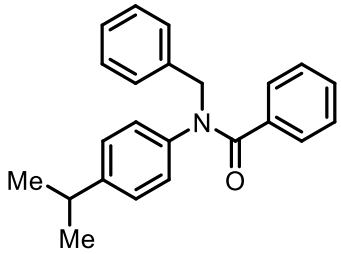
Scheme S6. Selective electroreduction of compound **42**



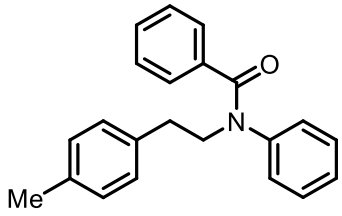
6. Characterization Data of Substrates



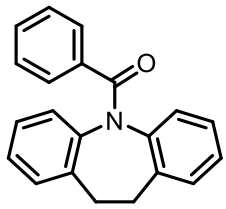
***N*-Benzyl-*N*-(4-cyanophenyl)benzamide (3)**: Prepared from 4-(benzylamino)benzonitrile and benzoyl chloride following the reported literature procedure[1c] and obtained as a colourless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 7.1 Hz, 2H), 7.31–7.26 (m, 6H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 5.17 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 147.8, 136.9, 135.1, 133.0, 130.6, 128.9, 128.8, 128.3, 128.1, 127.8(3), 127.8(0), 118.2, 110.0, 53.6. **HR-MS** (ESI) *m/z* calcd for $C_{21}H_{17}N_2O$ $[M+H]^+$ 313.1335, found 313.1330.



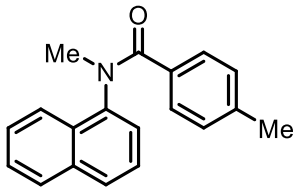
***N*-Benzyl-*N*-(4-isopropylphenyl)benzamide (5)**: Prepared from *N*-benzyl-4-isopropylaniline and benzoyl chloride following the reported literature procedure[1c] and obtained as a colourless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (s, 4H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 6.6 Hz, 1H), 7.23 (d, *J* = 6.6 Hz, 1H), 7.19 (d, *J* = 7.2 Hz,2H), 7.02 (d, *J* = 7.8 Hz, 2H), 6.88 (d, *J* = 7.8 Hz, 2H), 5.17 (s, 2H), 2.82 (hept, *J* = 6.8 Hz, 1H), 1.19 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 147.3, 141.2, 137.7, 136.0, 129.5, 128.7, 128.4, 128.2, 127.6, 127.4, 127.2, 126.9, 53.9, 33.4, 23.8. **HR-MS** (ESI) *m/z* calcd for $C_{23}H_{24}NO$ $[M+H]^+$ 330.1852, found 330.1869.



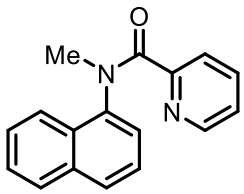
***N*-(4-Methylphenethyl)-*N*-phenylbenzamide (11)**: Prepared from *N*-(4-methylphenethyl)aniline and benzoyl chloride following the reported literature procedure[1c] and obtained as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34–7.31 (m, 2H), 7.29–7.27 (m, 1H), 7.25–7.18 (m, 5H), 7.17–7.13 (m, 4H), 6.95 (d, *J* = 7.6 Hz, 2H), 4.17–4.13 (m, 2H), 3.03–2.99 (m, 2H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 143.8, 136.3, 135.9(7), 135.9(5), 129.6, 129.3, 129.2, 129.0, 128.8, 127.8, 126.7, 52.7, 33.5, 21.2. **HR-MS** (ESI) *m/z* calcd for $C_{22}H_{22}NO$ $[M+H]^+$ 316.1696, found 316.1710.



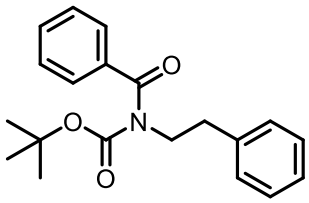
(10,11-Dihydro-5H-dibenzo[b,f]azepin-5-yl)(phenyl)methanone (18): Prepared from iminodibenzyl and benzoyl chloride following the reported literature procedure[1c] and obtained as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.4 Hz, 3H), 7.23 (m, 10H), 3.66–3.61 (m, 2H), 2.98–2.95 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.7, 141.8, 135.9, 135.7, 130.2, 129.8, 128.7, 128.6, 128.5, 127.9, 127.8, 126.9. **HR-MS** (ESI) *m/z* calcd for $C_{21}H_{17}NNaO$ $[M+Na]^+$ 322.1202, found 322.1205.



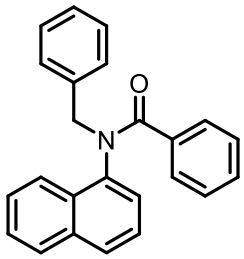
***N*-4-Dimethyl-*N*-(naphthalen-1-yl)benzamide (33)**: Prepared from *N*-methylnaphthalen-1-amine and 4-methylbenzoyl chloride following the reported literature procedure[1c] and obtained as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.55–7.51 (m, 1H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.79 (d, *J* = 7.9 Hz, 2H), 3.52 (s, 3H), 2.13 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0, 141.5, 139.9, 134.6, 132.9, 130.0, 128.8, 128.3, 127.9(9), 127.9(6), 127.4, 126.6, 126.5, 125.7, 122.9, 38.7, 21.3. **HR-MS** (ESI) *m/z* calcd for $C_{19}H_{18}NO$ $[M+H]^+$ 276.1383, found 276.1385.



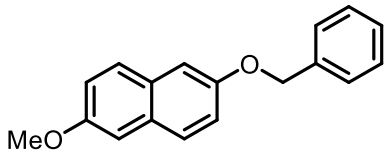
***N*-Methyl-*N*-(naphthalen-1-yl)picolinamide (34)**: Prepared from *N*-methylnaphthalen-1-amine and picolinoyl chloride following the reported literature procedure[1c] and obtained as a brown solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 1.6 Hz, 1H), 8.31 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.64–7.60 (m, 1H), 7.55–7.51 (m, 2H), 7.30–7.26 (m, 1H), 7.14–7.12 (m, 1H), 6.95–6.92 (m, 1H), 3.55 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.4, 150.5, 148.6, 140.4, 135.1, 134.7, 131.8, 129.9, 128.9, 128.8, 127.8, 126.8, 126.6, 125.6, 122.6, 122.4, 38.5. **HR-MS** (ESI) *m/z* calcd for $C_{17}H_{15}N_2O$ $[M+H]^+$ 263.1179, found 263.1182.



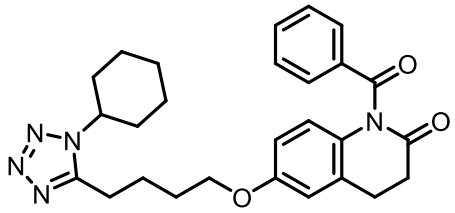
Tert-butyl benzoyl(phenethyl)carbamate (40): Prepared from *N*-phenethylbenzamide and di-tert-butyl dicarbonate following the reported literature procedure[1e] and obtained as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.42–7.39 (m, 3H), 7.35–7.31 (m, 2H), 7.27–7.26 (m, 4H), 7.22–7.16 (m, 1H), 4.04–4.00 (m, 2H), 3.02–2.98 (m, 2H), 1.10 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.3, 153.4, 138.7, 138.0, 131.0, 129.2, 128.6, 128.0, 127.4, 126.5, 83.0, 47.0, 35.1, 27.4. **HR-MS** (ESI) *m/z* calcd for $C_{20}H_{24}NO_3$ $[M+H]^+$ 326.1751, found 326.1756.



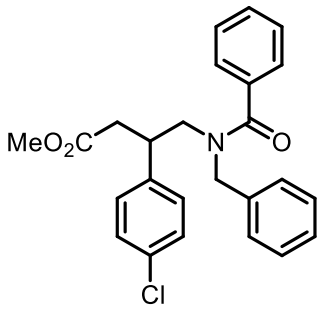
***N*-Benzyl-*N*-(naphthalen-1-yl)benzamide (45)**: Prepared from *N*-benzylnaphthalen-1-amine and benzoyl chloride following the reported literature procedure[1c] and obtained as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.26 (s, 7H), 7.15–7.00 (m, 2H), 6.97 (t, *J* = 7.3 Hz, 2H), 6.76 (d, *J* = 7.1 Hz, 1H), 5.90 (d, *J* = 14.0 Hz, 1H), 4.48 (d, *J* = 14.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.6, 138.8, 137.4, 136.2, 134.5, 130.2, 129.6, 129.5, 128.8, 128.4, 128.3, 127.6, 127.6, 127.5, 127.3, 126.4, 125.2, 122.8, 53.4. **HR-MS** (ESI) *m/z* calcd for $C_{24}H_{20}NO$ $[M+H]^+$ 338.1539, found 338.1545.



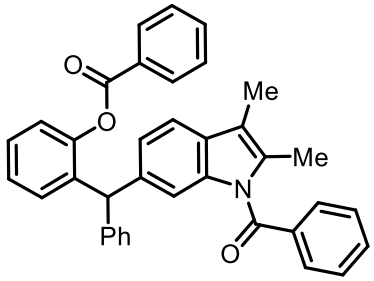
1-(Benzyloxy)-6-methoxynaphthalene (49): Prepared from 6-methoxynaphthalen-1-ol and benzyl bromide following the reported literature procedure[1a] and obtained as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61–7.56 (m, 2H), 7.43 (d, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.18–7.13 (m, 2H), 7.08–7.04 (m, 2H), 5.09 (s, 2H), 3.83 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.3, 155.4, 137.2, 130.0, 129.8, 128.7, 128.3, 128.1, 127.7, 119.4, 119.1, 107.6, 106.2, 70.2, 55.4. **HR-MS** (ESI) *m/z* calcd for $C_{18}H_{17}O_2$ $[M+H]^+$ 265.1223, found 265.1228.



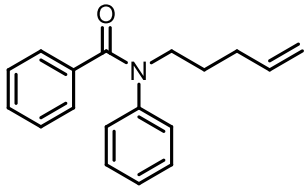
1-Benzoyl-6-(4-(1-cyclohexyl-1H-tetrazol-5-yl)butoxy)-3,4-dihydroquinolin-2(1H)-one (51): Prepared from cilostazol and benzoyl chloride following the reported literature procedure[1c] and obtained as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 6.78–6.74 (m, 2H), 6.64 (dd, *J* = 8.8, 2.1 Hz, 1H), 4.14–4.09 (m, 1H), 3.98 (t, *J* = 5.7 Hz, 2H), 3.06–3.02 (m, 2H), 2.90 (t, *J* = 7.3 Hz, 2H), 2.78–2.74 (m, 2H), 2.06–1.95 (m, 8H), 1.92–1.86 (m, 2H), 1.77 (d, *J* = 11.4 Hz, 1H), 1.47–1.30 (m, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.6, 170.7, 155.7, 153.6, 134.1, 133.9, 131.7, 130.0, 129.0, 128.0, 119.2, 114.5, 113.2, 67.6, 57.7, 33.0, 32.8, 28.6, 26.2, 25.4, 24.9, 24.1, 23.1. **HR-MS** (ESI) *m/z* calcd for $C_{27}H_{32}N_5O_3$ $[M+H]^+$ 474.2500, found 474.2507.



Methyl-4-(*N*-benzylbenzamido)-3-(4-chlorophenyl)butanoate (53): Prepared from Baclon following the reported literature procedure and obtained as a white solid **^{1}H NMR** (400 MHz, CD_3OD) *δ* 7.51–7.49 (m, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.23–7.18 (m, 4H), 7.14–7.10 (m, 2H), 7.07 (m, 5H), 4.71 (s, 3H), 4.34 (s, 2H), 3.41–3.33 (m, 3H), 2.64 (dd, *J* = 15.8, 5.3 Hz, 1H), 2.47 (dd, *J* = 15.8, 8.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 172.6, 167.6, 139.9, 137.9, 134.2, 133.1, 131.7, 129.1, 129.0, 128.9, 128.7, 128.5, 126.9, 52.0, 45.0, 41.4, 38.5, 33.7. **HR-MS** (ESI) *m/z* calcd for $C_{25}H_{24}ClNO_3$ $[M+H]^+$ 422.1517, found 422.1526.

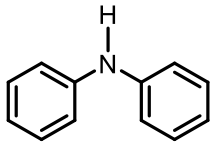


2-((1-Benzoyl-2,3-dimethyl-1H-indol-6-yl)(phenyl)methyl)phenyl benzoate (54): Prepared from 2,3-dimethyl-1*H*-indole and 2-(hydroxy(phenyl)methyl)phenol following the reported literature procedure[1j] and obtained as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.7 Hz, 2H), 7.59–7.26 (m, 8H), 7.23–7.11 (m, 7H), 7.07–7.06 (m, 2H), 6.98 (d, J = 7.6 Hz, 1H), 6.84–6.82 (m, 2H), 5.75 (s, 1H), 2.27 (s, 3H), 2.18 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.5, 164.9, 149.0, 143.5, 137.1, 135.4, 135.4, 135.3, 133.5, 133.2, 131.5, 131.0, 130.9, 130.2, 129.5, 129.4, 129.0, 128.4, 128.2, 128.0, 127.4, 126.2, 125.8, 122.6, 121.1, 117.7, 111.2, 106.7, 51.3, 11.5, 8.6. **HR-MS** (ESI) *m/z* calcd for $C_{37}H_{30}NO_3$ $[M+H]^+$ 536.2220, found 536.2229.

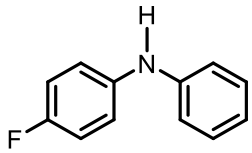


***N*-(pent-4-en-1-yl)-*N*-phenylbenzamide (58)**: Prepared from *N*-phenylbenzamide and 5-bromopent-1-ene following the reported literature procedure[1j] and obtained as a colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, J = 7.2 Hz, 2H), 7.26–7.22 (m, 3H), 7.18–7.15 (m, 3H), 7.05 (d, J = 7.7 Hz, 2H), 5.87–5.77 (m, 1H), 5.05–4.96 (m, 2H), 3.98–3.94 (m, 2H), 2.14 (q, J = 7.1 Hz, 2H), 1.77 (p, J = 7.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.4, 143.5, 137.8, 136.4, 129.5, 129.2, 128.7, 127.9, 127.8, 126.7, 115.1, 50.1, 31.2, 26.9. **HR-MS** (ESI) *m/z* calcd for $C_{18}H_{20}NO$ $[M+H]^+$ 266.1539, found 266.1547.

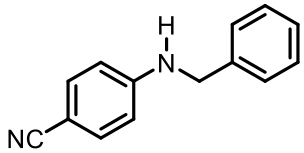
7. Characterization Data of the Products



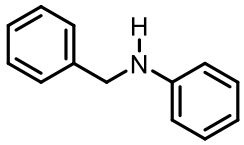
Diphenylamine (1a): Followed general procedure with **1** (0.3 mmol) for 2.5 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) yielded 91% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.28 (m, 4H), 7.16–7.06 (m, 4H), 6.99 (m, 2H), 5.73 (brs, 1H). The product is known and the characterization is in consistence with the reported literature.[6]



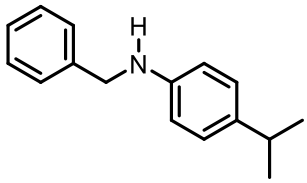
4-Fluoro-*N*-phenylaniline (2a): Followed general procedure with **2** (0.3 mmol) for 3.0 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) yielded 64% as a brown solid.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26–7.22 (m, 2H), 7.08–7.02 (m, 2H), 6.99–6.95 (m, 4H), 6.89 (t, *J* = 7.3 Hz, 1H), 5.56 (brs, 1H). The product is known and the characterization is in consistence with the reported literature.[7]



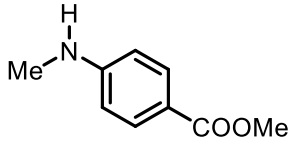
4-(Benzylamino)benzonitrile (3a): Followed general procedure with **3** (0.3 mmol) for 2.5 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) yielded 64% as a yellow solid. **^{1}H NMR** (400 MHz, CDCl3) δ 7.42–7.39 (m, 2H), 7.37–7.29 (m, 5H)., 6.60–6.58 (m, 2H), 4.64 (brs, 1H), 4.38 (d, *J* = 5.4 Hz, 2H). The product is known and the characterization is in consistence with the reported literature.[8]



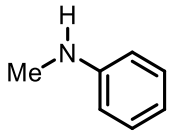
***N*-Benzylaniline (4a)**: Followed general procedure with **4** (0.3 mmol) for 2.5 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) yielded 81% as a yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44–7.37 (m, 4H), 7.34–7.30 (m, 1H), 7.25–7.21 (m, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.68 (d, *J* = 7.7 Hz, 2H), 4.37 (s, 2H), 4.06 (brs, 1H). The product is known and the characterization is in consistence with the reported literature.[9]



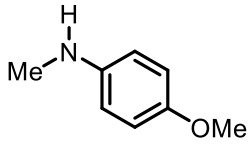
***N*-Benzyl-4-isopropylaniline (5a)**: Followed general procedure with **5** (0.3 mmol) under 10 mA, the cell voltage increased to 31 V (compliance voltage of the DC power supply), and the current gradually decreased towards 0 mA for 15.5 h, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) yielded 79% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45–7.38 (m, 4H), 7.33 (t, *J* = 6.9 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.66 (d, *J* = 8.2 Hz, 2H), 4.36 (s, 2H), 3.97 (brs, 1H), 2.93–2.82 (m, 1H), 1.28 (d, *J* = 6.9 Hz, 6H). The product is known and the characterization is in consistence with the reported literature.[10]



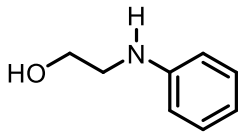
Methyl 4-(methylamino)benzoate (6a): Followed general procedure with **6** (0.3 mmol) for 2.0 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) yielded 62% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88–7.86 (m, 2H), 6.57–6.53 (m, 2H), 4.19 (brs, 1H), 3.85 (s, 3H), 2.88 (d, *J* = 5.2 Hz, 3H). The product is known and the characterization is in consistence with the reported literature.[11]



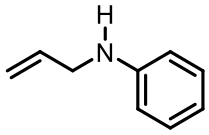
***N*-Methylaniline (7a)**: Followed general procedure with **7** (0.3 mmol) for 2.5 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) yielded 66% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.9 Hz, 2H), 6.73 (t, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 2H), 3.67 (s, 1H), 2.85 (s, 3H). The product is known and the characterization is in consistence with the reported literature.[11]



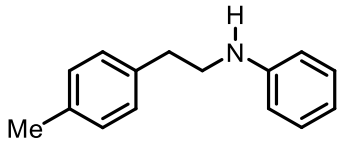
4-Methoxy-*N*-methylaniline (8a): Followed general procedure with **8** (0.3 mmol) for 3.0 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) yielded 83% as a brown solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.85–6.79 (m, 2H), 6.62–6.58 (m, 2H), 3.76 (s, 3H), 2.81 (s, 3H). The product is known and the characterization is in consistence with the reported literature.[11]



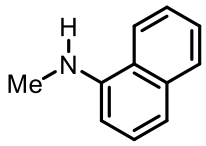
2-(Phenylamino)ethan-1-ol (9a): Followed general procedure with **9** (0.3 mmol) for 3.0 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded 61% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22–7.17 (m, 2H), 6.77–6.73 (m, 1H), 6.68–6.65 (m, 2H), 3.83–3.81 (m, 2H), 3.30 (t, *J* = 5.2 Hz, 2H), 2.77 (brs, 2H). The product is known and the characterization is in consistence with the reported literature.[12]



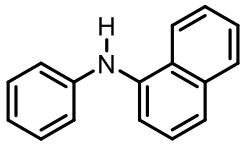
***N*-Allylaniline (10a):** Followed general procedure with **10** (0.3 mmol) for 2 h 50 min under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) yielded 56% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22–7.18 (m, 2H), 6.76–6.72 (m, 1H), 6.66–6.64 (m, 2H), 6.03–5.94 (m, 1H), 5.33–5.29 (m, 1H), 5.20–5.18 (m, 1H), 3.80 (d, *J* = 4.0 Hz, 3H). The product is known and the characterization is in consistence with the reported literature.[13]



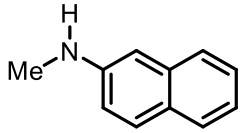
***N*-(4-Methylphenethyl)aniline (11a):** Followed general procedure with **11** (0.3 mmol) for 2 h 50 min under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) yielded 79% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20–7.12 (m, 6H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J* = 7.9 Hz, 2H), 3.64 (brs, 1H), 3.36 (t, *J* = 7.0 Hz, 2H), 2.87 (t, *J* = 7.0 Hz, 2H), 2.34 (s, 3H). The product is known and the characterization is in consistence with the reported literature.[14]



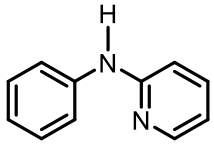
***N*-Methylnaphthalen-1-amine (12a):** Followed general procedure with **12** (0.3 mmol) for 5.5 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) yielded 74% as a brown oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86–7.79 (m, 2H), 7.52–7.41 (m, 3H), 7.30 (d, *J* = 8.2 Hz, 1H), 6.64 (d, *J* = 7.6 Hz, 1H), 4.42 (brs, 1H), 3.04 (s, 3H). The product is known and the characterization is in consistence with the reported literature.[15]



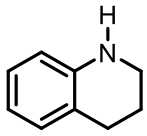
***N*-Phenylnaphthalen-1-amine (13a):** Followed general procedure with **13** (0.3 mmol) for 2.5 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) yielded 88% as a brown solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.95–7.88 (m, 1H), 7.62 (d, *J* = 7.3 Hz, 1H), 7.57–7.49 (m, 2H), 7.47–7.40 (m, 2H), 7.33–7.28 (m, 2H), 7.03 (d, *J* = 7.7 Hz, 2H), 6.97 (t, *J* = 7.3 Hz, 1H), 5.96 (brs, 1H). The product is known and the characterization is in consistence with the reported literature.[6]



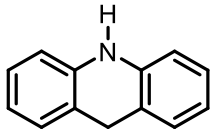
***N*-Methylnaphthalen-2-amine (14a):** Followed general procedure with **14** (0.3 mmol) for 2.5 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) yielded 84% as a brown oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73–7.64 (m, 3H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.25–7.22 (m, 1H), 6.89 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.83 (s, 1H), 3.50 (brs, 1H), 2.94 (s, 3H). The product is known and the characterization is in consistence with the reported literature.[16]



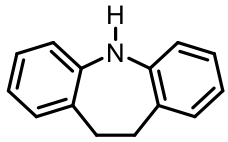
***N*-Phenylpyridin-2-amine (15a):** Followed general procedure with **15** (0.3 mmol) for 2.5 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) yielded 84% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22–8.21 (m, 1H), 7.51–7.46 (m, 1H), 7.37 (brs, 1H), 7.35–7.33 (m, 4H), 7.08–7.04 (m, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.74–6.71 (m, 1H). The product is known and the characterization is in consistence with the reported literature.[17]



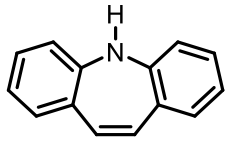
1,2,3,4-Tetrahydroquinoline (16a): Followed general procedure with **16** (0.3 mmol) for 2.0 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) yielded 81% as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.02–6.97 (m, 2H), 6.65 (td, *J* = 7.4, 1.2 Hz, 1H), 6.52 (d, *J* = 7.9 Hz, 1H), 3.68 (brs, 1H), 3.34–3.31 (m, 2H), 2.79 (t, *J* = 6.4 Hz, 2H), 2.00–1.94 (m, 2H). The product is known and the characterization is in consistence with the reported literature.[18]



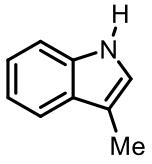
9,10-Dihydroacridine (17a): Followed general procedure with **17** (0.3 mmol) for 4.0 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) yielded 67% as a yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.12–7.07 (m, 4H), 6.86 (t, *J* = 7.4 Hz, 2H), 6.67 (d, *J* = 7.9 Hz, 2H), 5.95 (brs, 1H), 4.07 (s, 2H). The product is known and the characterization is in consistence with the reported literature.[6]



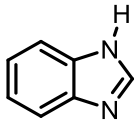
10,11-Dihydro-5*H*-dibenzo[b,f]azepine (18a): Followed general procedure with **17** (0.3 mmol) for 2.0 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) yielded 61% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14–7.08 (m, 4H), 6.82 (t, *J* = 7.3 Hz, 2H), 6.76 (d, *J* = 7.9 Hz, 2H), 6.02 (brs, 1H), 3.12 (s, 4H). The product is known and the characterization is in consistence with the reported literature.[6]



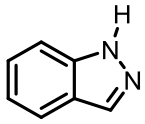
5*H*-Dibenzo[b,f]azepine (19a): Followed general procedure with **19** (0.3 mmol) for 4 h 10 min under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) yielded 58% as a yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.03 (td, *J* = 7.8, 2.0 Hz, 2H), 6.88–6.81 (m, 4H), 6.50 (d, *J* = 7.9 Hz, 2H), 6.32 (s, 2H), 4.95 (s, 1H). The product is known and the characterization is in consistence with the reported literature.[6]



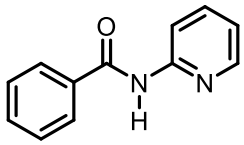
3-Methyl-1H-indole (20a): Followed general procedure with **20** (0.3 mmol) for 2.5 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) yielded 79% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (brs, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 6.98 (s, 1H), 2.36 (s, 3H). The product is known and the characterization is in consistence with the reported literature.[19]



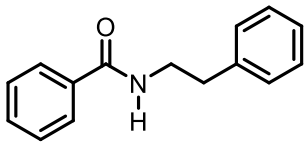
1*H*-Benzo[d]imidazole (21a): Followed general procedure with **21** (0.3 mmol) for 1.5 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 1:1) yielded 58% as a white solid. **^{1}H NMR** (400 MHz, DMSO) δ 12.45 (brs, 1H), 8.21 (s, 1H), 7.59 (s, 2H), 7.20–7.16 (m, 2H). The product is known and the characterization is in consistence with the reported literature.[6]



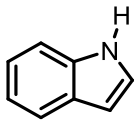
1*H*-Indazole (22a): Followed general procedure with **22** (0.3 mmol) for 2.5 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded 81% as a white solid. **^{1}H NMR** (400 MHz, CDCl3) δ 8.12 (s, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.42–7.38 (m, 1H), 7.20–7.17 (m, 1H). The product is known and the characterization is in consistence with the reported literature.[20]



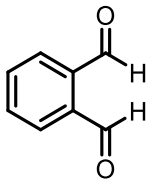
***N*-(Pyridin-2-yl)benzamide (23a):** Followed general procedure with **23** (0.3 mmol) for 2.5 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) yielded 61% as a yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.15 (brs, 1H), 8.40 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 4.2 Hz, 1H), 7.93–7.91 (m, 2H), 7.76–7.71 (m, 1H), 7.57–7.55 (m, 1H), 7.48–7.45 (m, 2H), 7.04–7.00 (m, 1H). The product is known and the characterization is in consistence with the reported literature.[21]



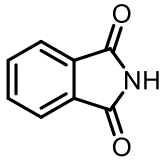
***N*-Phenethylbenzamide (24a):** Followed general procedure with **24** (0.3 mmol) for 1.5 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 4:1) yielded 79% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 3H), 6.33 (brs, 1H), 3.71 (q, *J* = 6.6 Hz, 2H), 2.93 (t, *J* = 6.9 Hz, 2H). The product is known and the characterization is in consistence with the reported literature.[22]



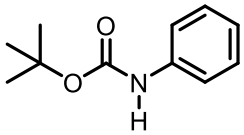
1*H*-Indole (35a): Followed general procedure with **35** (0.3 mmol) for 2.5 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded 44% as a brown solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (brs, 1H), 7.69–7.66 (m, 1H), 7.42–7.40 (m, 1H), 7.24–7.20 (m, 1H), 7.16–7.12 (m, 1H), 6.59–6.57 (m, 1H). The product is known and the characterization is in consistence with the reported literature.[9]



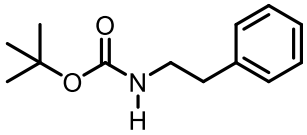
Phthalaldehyde (56): Followed general procedure with **36** (0.3 mmol) for 2.5 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded 52% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 10.53–10.52 (m, 2H), 7.99–7.96 (m, 2H), 7.79–7.76 (m, 2H). The product is known and the characterization is in consistence with the reported literature. [23]



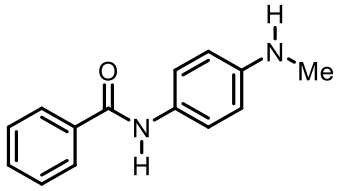
Phthalimide (37a): Followed general procedure with **37** (0.3 mmol) for 2.5 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded 42% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.88 (dd, J = 5.4, 3.1 Hz, 2H), 7.77 (dd, J = 5.4, 3.1 Hz, 2H). The product is known and the characterization is in consistence with the reported literature.[24]



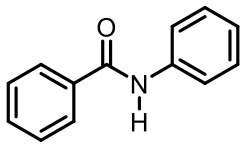
***tert*-Butyl phenylcarbamate (39a)**: Followed general procedure with **39** (0.3 mmol) for 2.0 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) yielded 74% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37–7.35 (m, 2H), 7.30–7.28 (m, 2H), 7.05–7.01 (m, 1H), 6.57 (s, 1H), 1.52 (s, 9H). The product is known and the characterization is in consistence with the reported literature.[25]



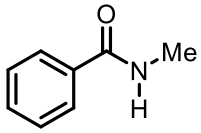
***tert*-Butyl phenethylcarbamate (40a):** Followed general procedure with **40** (0.3 mmol) for 3.0 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded 72% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32–7.28 (m, 2H), 7.24–7.18 (m, 3H), 4.61 (brs, 1H), 3.40–3.35 (m, 2H), 2.79 (t, J = 6.7 Hz, 2H), 1.44 (s, 9H). The product is known and the characterization is in consistence with the reported literature. [26]



***N*-(4-(Methylamino)phenyl)benzamide (41a):** Followed general procedure with **41** (0.3 mmol) for 5 h 40 min under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded 76% as a white solid. **^{1}H NMR** (400 MHz, DMSO) δ 9.91 (s, 1H), 7.94–7.92 (m, 2H), 7.57–7.46 (m, 5H), 6.54–6.52 (m, 2H), 5.50 (q, *J* = 5.2 Hz, 1H), 2.67 (d, *J* = 4.9 Hz, 3H). The product is known and the characterization is in consistence with the reported literature.[1h]

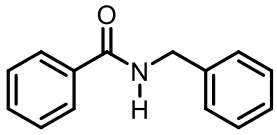


***N*-Phenylbenzamide (42a):** Followed general procedure with **42** (0.3 mmol) for 5 h 40 min under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded 60% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.86 (d, *J* = 7.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.55–7.52 (m, 1H), 7.48–7.44 (m, 2H), 7.37–7.34 (m, 2H), 7.17–7.13(m, 1H). The product is known and the characterization is in consistence with the reported literature.[9]

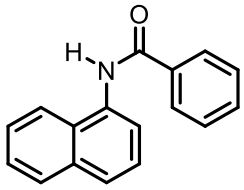


***N*-Methylbenzamide (43a)**: Followed general procedure with **43** (0.3 mmol) under 10 mA, the cell voltage gradually increased to 31 V (compliance voltage of the DC power supply), and the current gradually decreased towards 0 mA for 5 h 40 min, purification by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) yielded 67% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77–7.74 (m, 2H), 7.49–7.45 (m, 1H),

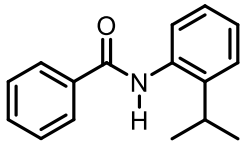
7.41–7.38 (m, 2H), 6.44 (s, 1H), 2.98 (d, J = 4.7 Hz, 3H). The product is known and the characterization is in consistence with the reported literature.[27]



***N*-Benzylbenzamide (44a):** Followed general procedure with **44** (0.3 mmol) for 6 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded 71% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.5 Hz, 2H), 7.49–7.46 (m, 1H), 7.41–7.37 (m, 2H), 7.33–7.25 (m, 5H), 6.69 (brs, 1H), 4.60 (d, J = 5.7 Hz, 2H). The product is known and the characterization is in consistence with the reported literature.[27]

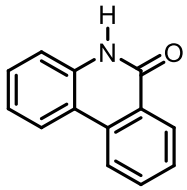


***N*-(Naphthalen-1-yl)benzamide (45a):** Followed general procedure with **45** (0.3 mmol) for 2.5 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded 70% as a brown solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (brs, 1H), 8.01–7.96 (m, 3H), 7.92–7.87 (m, 2H), 7.74 (d, J = 8.3 Hz, 1H), 7.61–7.57 (m, 1H), 7.53–7.48 (m, 5H). The product is known and the characterization is in consistence with the reported literature.[28]

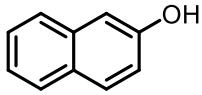


***N*-(2-Isopropylphenyl)benzamide (46a):** Followed general procedure with **46** (0.3 mmol) for 4.0 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) yielded 88% as a white solid. **^{1}H NMR** (400 MHz,

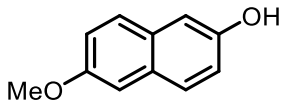
$CDCl_3$) δ 7.87 (d, *J* = 7.3 Hz, 2H), 7.81 (d, *J* = 6.9 Hz, 1H), 7.75 (brs, 1H), 7.57–7.53 (m, 1H), 7.51–7.47 (m, 2H), 7.33–7.31 (m, 1H), 7.24–7.19 (m, 2H), 3.10 (hept, *J* = 6.8 Hz, 1H), 1.28 (d, *J* = 6.8 Hz, 6H). The product is known and the characterization is in consistence with the reported literature.[29]



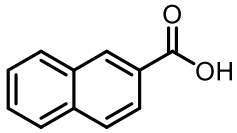
Phenanthridin-6-one (47a): Followed general procedure with **47** (0.3 mmol) for 6 h 10 min under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded 85% as a white solid. **^{1}H NMR** (400 MHz, DMSO) δ 11.69 (brs, 1H), 8.50 (d, *J* = 8.1 Hz, 1H), 8.38 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.32 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.87–7.83 (m, 1H), 7.66–7.62 (m, 1H), 7.51–7.46 (m, 1H), 7.38–7.36 (m, 1H), 7.28–7.24 (m, 1H). The product is known and the characterization is in consistence with the reported literature.[30]



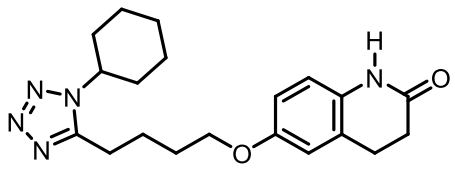
Naphthalen-2-ol (48a): Followed general procedure with **48** (0.3 mmol) for 3.0 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded 87% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (t, *J* = 7.8 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.46–7.42 (m, 1H), 7.36–7.32 (m, 1H), 7.16–7.10 (m, 2H), 5.09 (s, 1H). The product is known and the characterization is in consistence with the reported literature.[31]



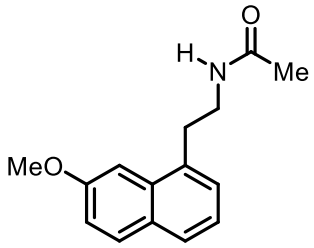
6-Methoxynaphthalen-2-ol (49a): Followed general procedure with **49** (0.3 mmol) for 3.0 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded 75% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.7 Hz, 1H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.13–7.07 (m, 4H), 4.91 (brs, 1H), 3.90 (s, 3H). The product is known and the characterization is in consistence with the reported literature.[32]



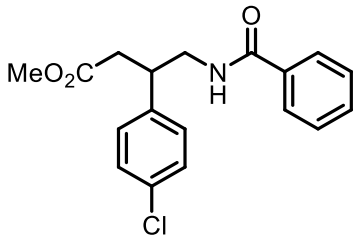
2-Naphthoic acid (50a): Followed general procedure with **50** (0.3 mmol) for 3.0 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 15:1) yielded 63% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.14 (dd, *J* = 8.6, 1.4 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.92 (t, *J* = 7.8 Hz, 2H), 7.65–7.56 (m, 2H). The product is known and the characterization is in consistence with the reported literature.[33]



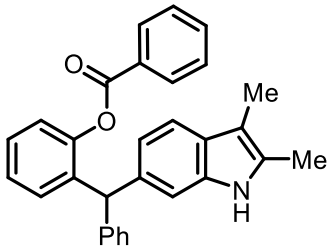
Cilostazol (51a): Followed general procedure with **51** (0.2 mmol) and H_2O (7.5 equiv) for 3.0 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded 67% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 6.69–6.66 (m, 2H), 4.15–4.08 (m, 1H), 3.96 (t, *J* = 6.0 Hz, 2H), 2.91 (t, *J* = 7.5 Hz, 4H), 2.59 (t, 2H), 2.06–1.93 (m, 8H), 1.90–1.84 (m, 2H), 1.76 (d, *J* = 11.9 Hz, 1H), 1.44–1.30 (m, 3H). The product is known and the characterization is in consistence with the reported literature.[34]



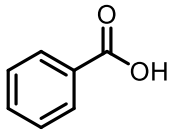
***N*-(2-(7-Methoxynaphthalen-1-yl)ethyl)acetamide (52a):** Followed general procedure with **52** (0.2 mmol) and H_2O (7.5 equiv) for 2 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:2) yielded 83% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.9 Hz, 1H), 7.72–7.67 (m, 1H), 7.49 (d, *J* = 2.3 Hz, 1H), 7.30–7.28 (m, 2H), 7.18 (dd, *J* = 8.9, 2.5 Hz, 1H), 5.74 (brs, 1H), 4.00 (s, 3H), 3.65–3.59 (m, 2H), 3.26 (t, *J* = 7.3 Hz, 2H), 1.96 (s, 3H). The product is known and the characterization is in consistence with the reported literature.[35]



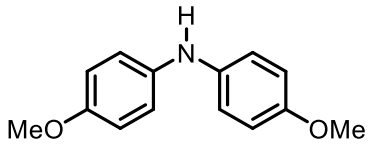
Methyl-4-benzamido-3-(4-chlorophenyl)butanoate (53a): Followed general procedure with **53** (0.3 mmol) for 2.0 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded 43% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* = 7.67–7.65 (m, 2H), 7.50–7.46 (m, 1H), 7.41–7.38 (m, 2H), 7.32–7.29 (m, 2H), 7.21–7.17 (m, 2H), 6.36 (brs, 1H), 3.81 (dt, *J* = 12.9, 6.6 Hz, 1H), 3.57 (s, 3H), 3.55–3.45 (m, 2H), 2.77 (dd, *J* = 15.9, 6.6 Hz, 1H), 2.66 (dd, *J* = 15.9, 7.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* = 172.6, 167.6, 139.9, 134.2, 133.1, 131.7, 129.1, 129.0, 128.7, 126.9, 52.0, 45.1, 41.4, 38.5. **HR-MS** (ESI) *m/z* calcd for $C_{18}H_{18}ClNNaO_3$ $[M+Na]^+$ 354.0867, found 354.0878.



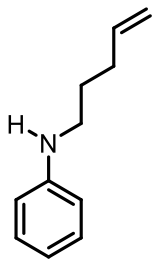
2-((2,3-Dimethyl-1H-indol-6-yl)(phenyl)methyl)phenyl benzoate (54a): Followed general procedure with **54** (0.3 mmol) for 2.0 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) yielded 52% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.94–7.92 (m, 2H), 7.61 (t, J = 6.9 Hz, 1H), 7.54 (brs, 1H), 7.45–7.38 (m, 3H), 7.37–7.33 (m, 1H), 7.30–7.26 (m, 2H), 7.24–7.17 (m, 3H), 7.12 (d, J = 6.7 Hz, 2H), 7.03 (d, J = 7.7 Hz, 1H), 6.89 (d, J = 8.8 Hz, 2H), 5.81 (s, 1H), 2.33 (s, 3H), 2.24 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 164.9, 149.0, 143.5, 137.1, 135.5, 135.3, 133.5, 131.0, 130.8, 130.2, 129.5, 129.4, 128.4, 128.2, 128.0, 127.5, 126.2, 125.9, 122.6, 121.2, 117.7, 111.2, 106.9, 51.3, 11.6, 8.6. **HR-MS** (ESI) *m/z* calcd for $C_{30}H_{26}NO_2$ $[M+H]^+$ 432.1958, found 432.1964.



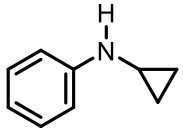
Benzoic acid (55): Followed the procedure (5.1 the transformation of benzoyl functional group) with **1** (0.3 mmol) for 2.5 h under 10 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 1:1) yielded 49% as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, J = 7.7 Hz, 2H), 7.62 (t, J = 7.3 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H). The product is known and the characterization is in consistence with the reported literature.[36]



Bis(4-methoxyphenyl)amine (57a): Followed general procedure with **57** (0.3 mmol) for 3.0 h under 15 mA, purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) yielded 73% as a white solid.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.96 (d, *J* = 8.6 Hz, 4H), 6.84 (d, *J* = 8.6 Hz, 4H), 5.33 (brs, 1H), 3.79 (s, 6H). The product is known and the characterization is in consistence with the reported literature.[7]



***N*-(Pent-4-en-1-yl)aniline (58a):** Followed general procedure with **58** (0.3 mmol) under 10 mA, the cell voltage gradually increased to 31 V (compliance voltage of the DC power supply), and the current gradually decreased towards 1 mA for 4.5 h, purification by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) yielded 60% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22–7.18 (m, 2H), 6.74–6.70 (m, 1H), 6.64–6.61 (m, 2H), 5.92–5.81 (m, 1H), 5.11– 5.01 (m, 2H), 3.62 (brs, 1H), 3.15 (t, *J* = 7.1 Hz, 2H), 2.20 (q, *J* = 7.1 Hz, 2H), 1.74 (p, *J* = 7.3 Hz, 2H). The product is known and the characterization is in consistence with the reported literature.[37]



***N*-Cyclopropylaniline (60a):** Followed general procedure with **60** (0.3 mmol) for 2.5 h under 10 mA, purification by column chromatography on silica gel (petroleum

ether/EtOAc = 20:1) yielded 70% as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11–7.07(m, 2H), 6.70–6.62 (m, 3H), 4.05 (brs, 1H), 2.34–2.29 (m, 1H), 0.64–0.60 (m, 2H), 0.43–0.39 (m, 2H). The product is known and the characterization is in consistence with the reported literature.[38]

8. References

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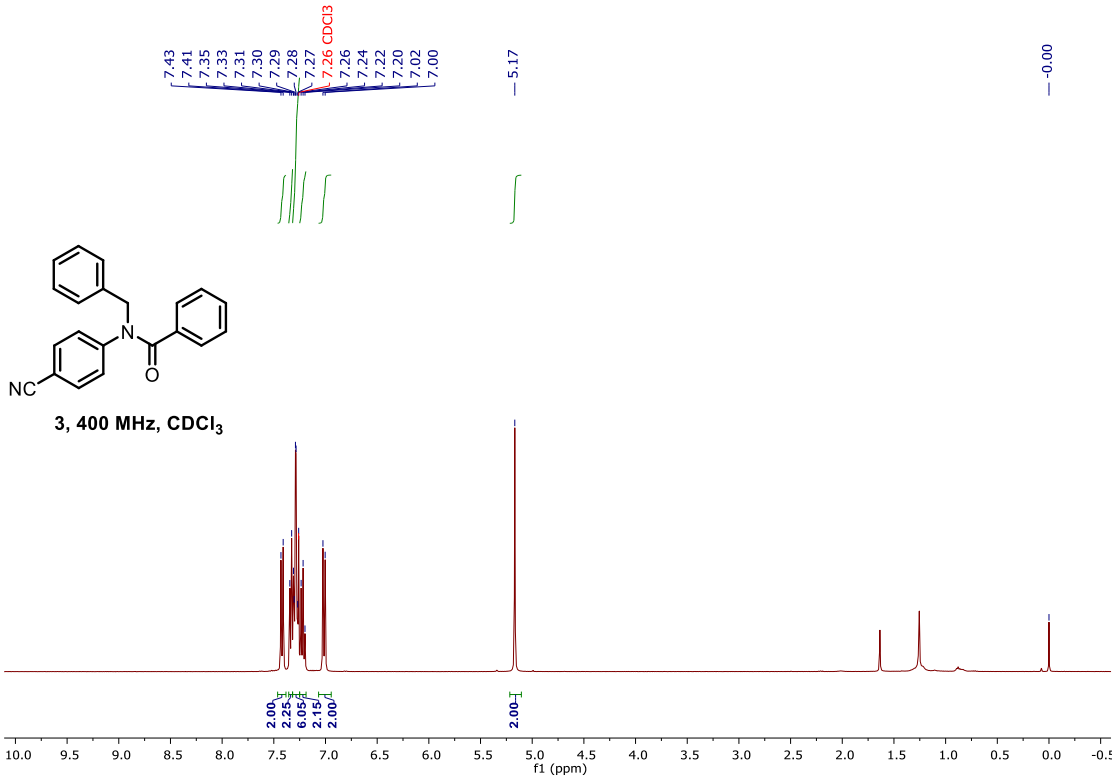
9. ^{1}H and ^{13}C NMR Spectra of Unreported Starting Materials



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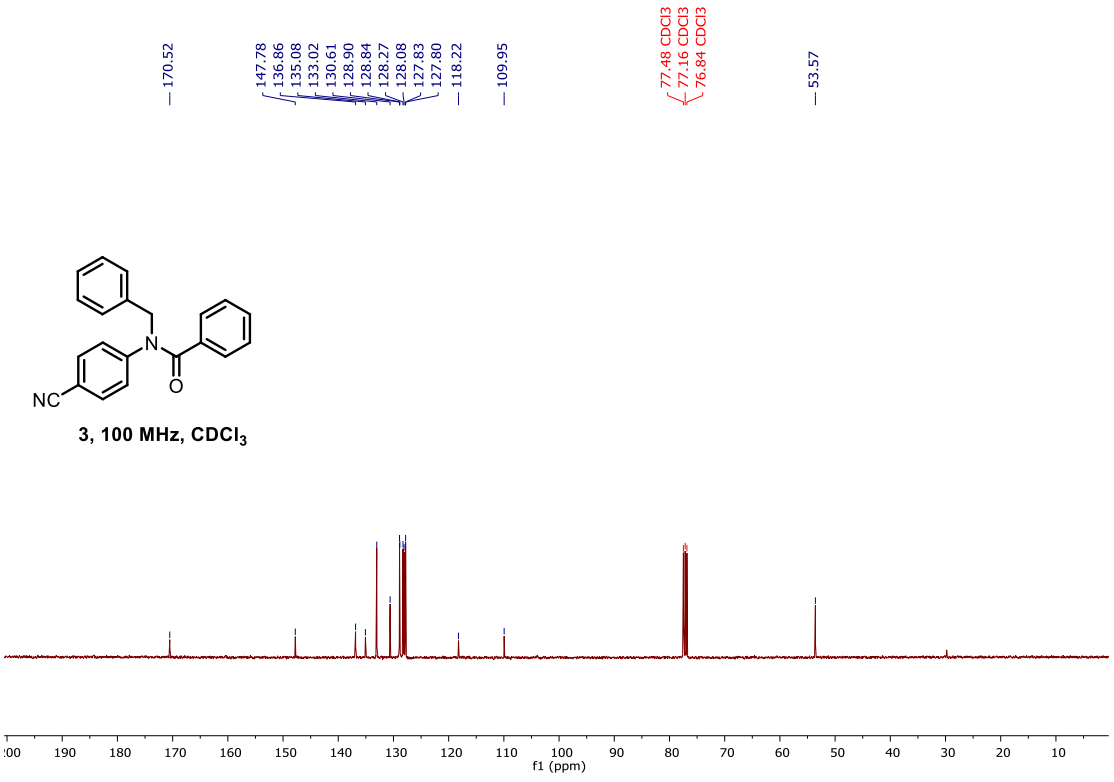

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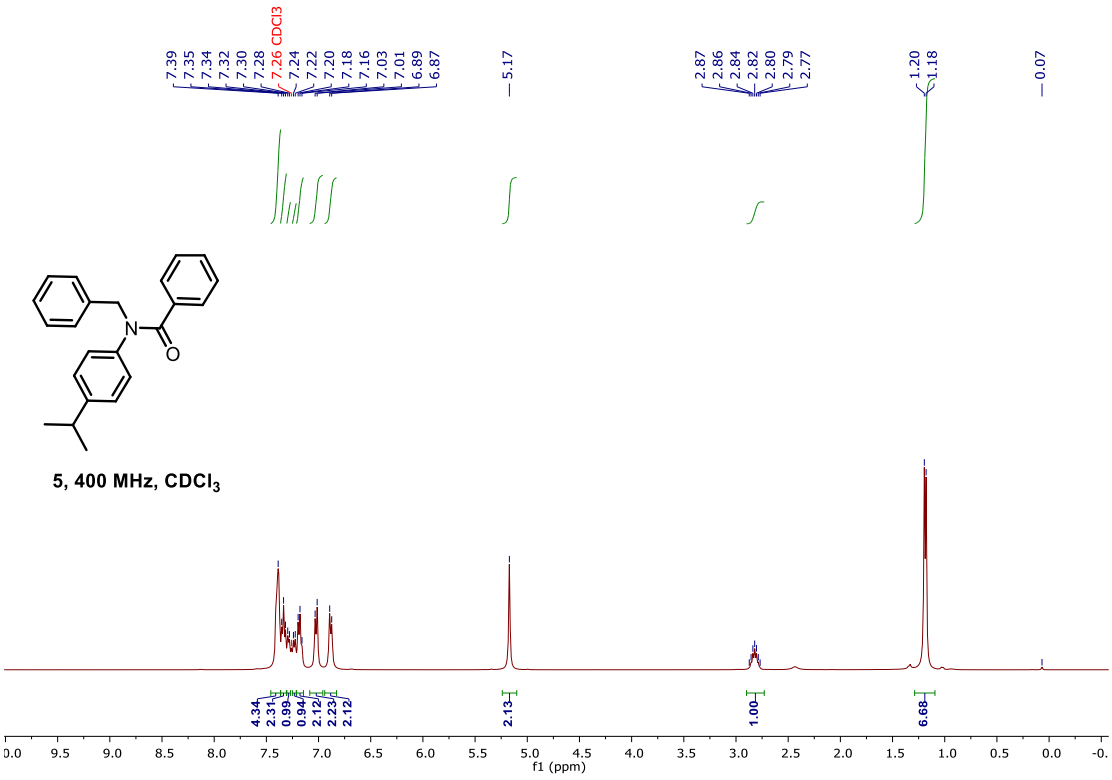

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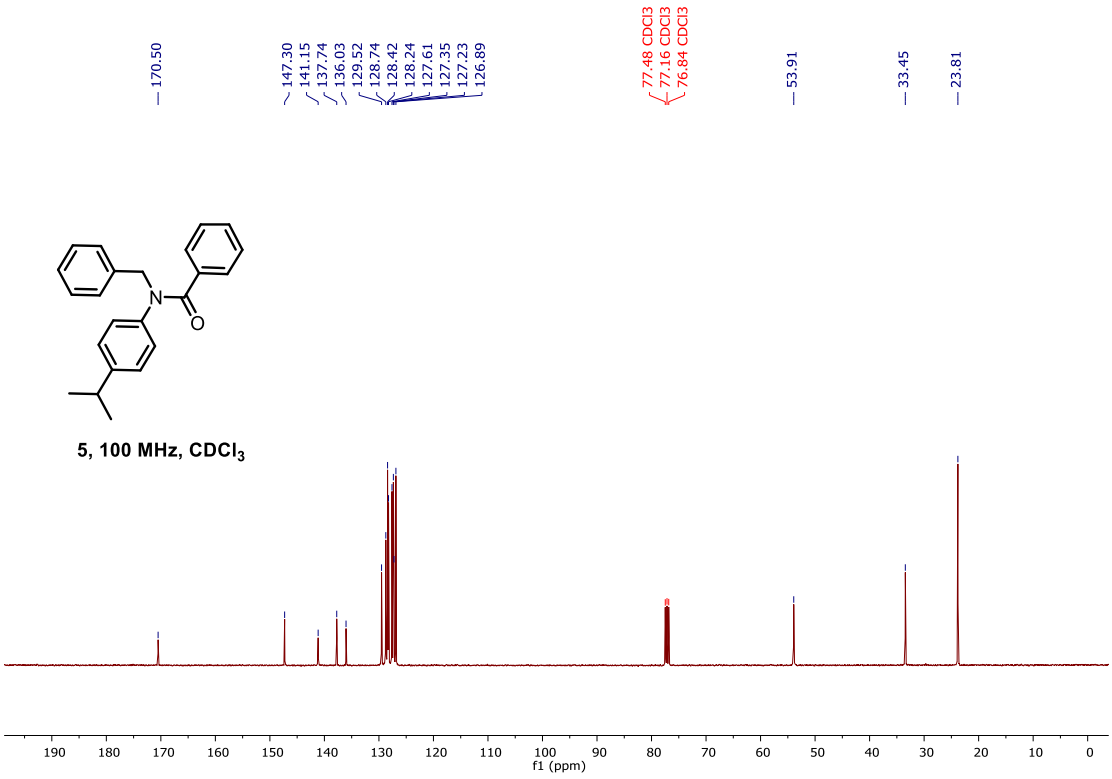

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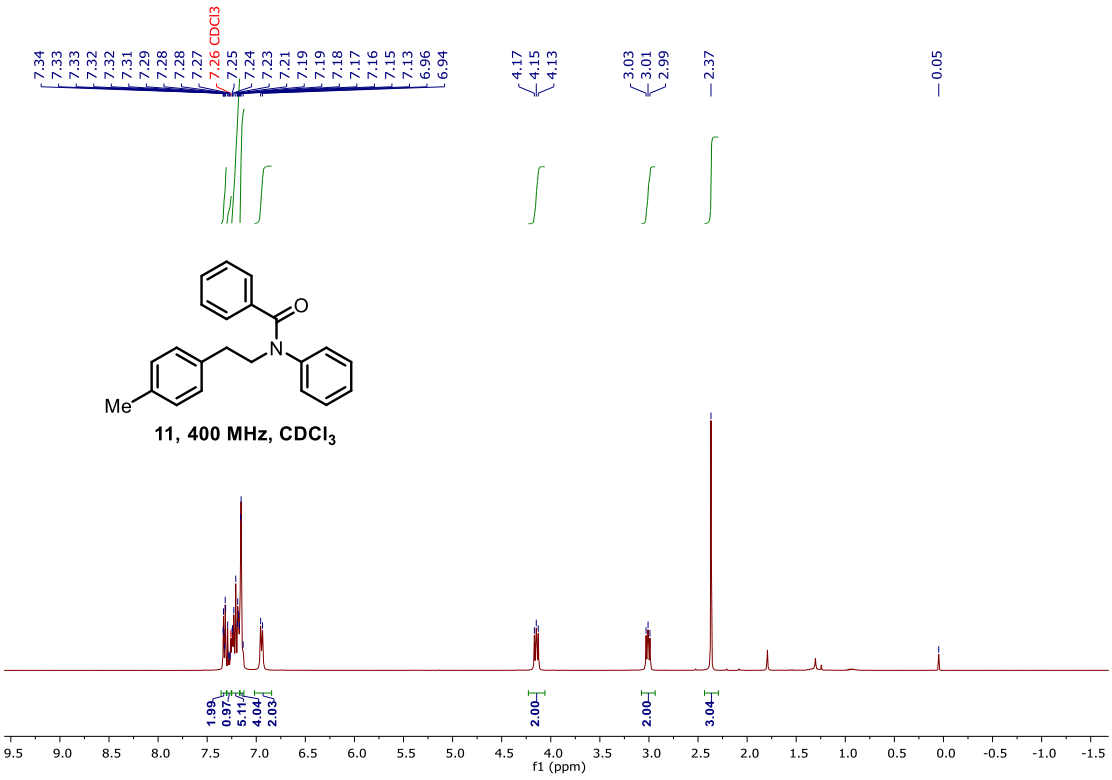
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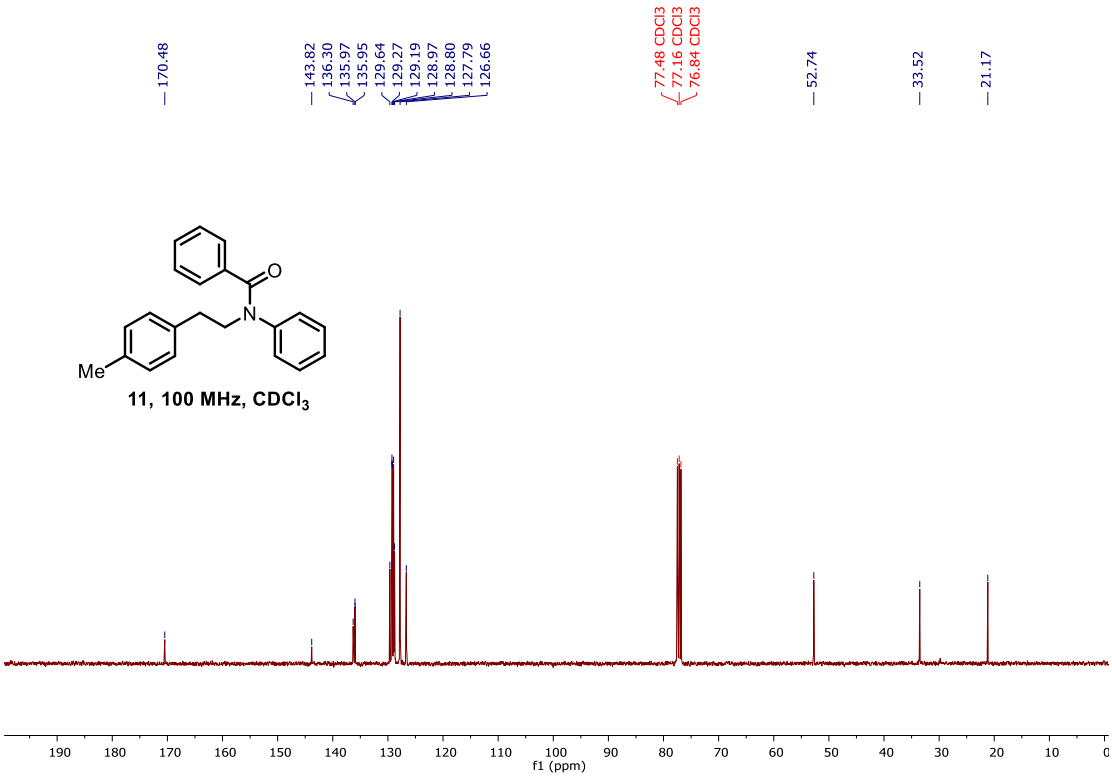
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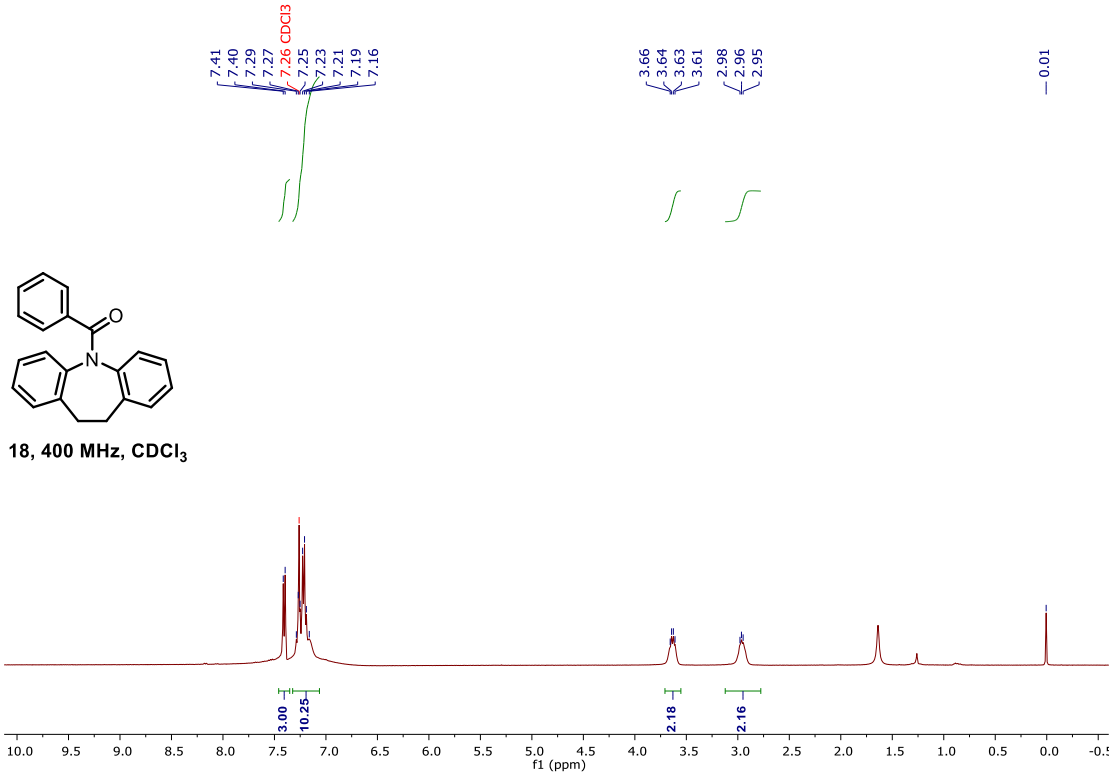
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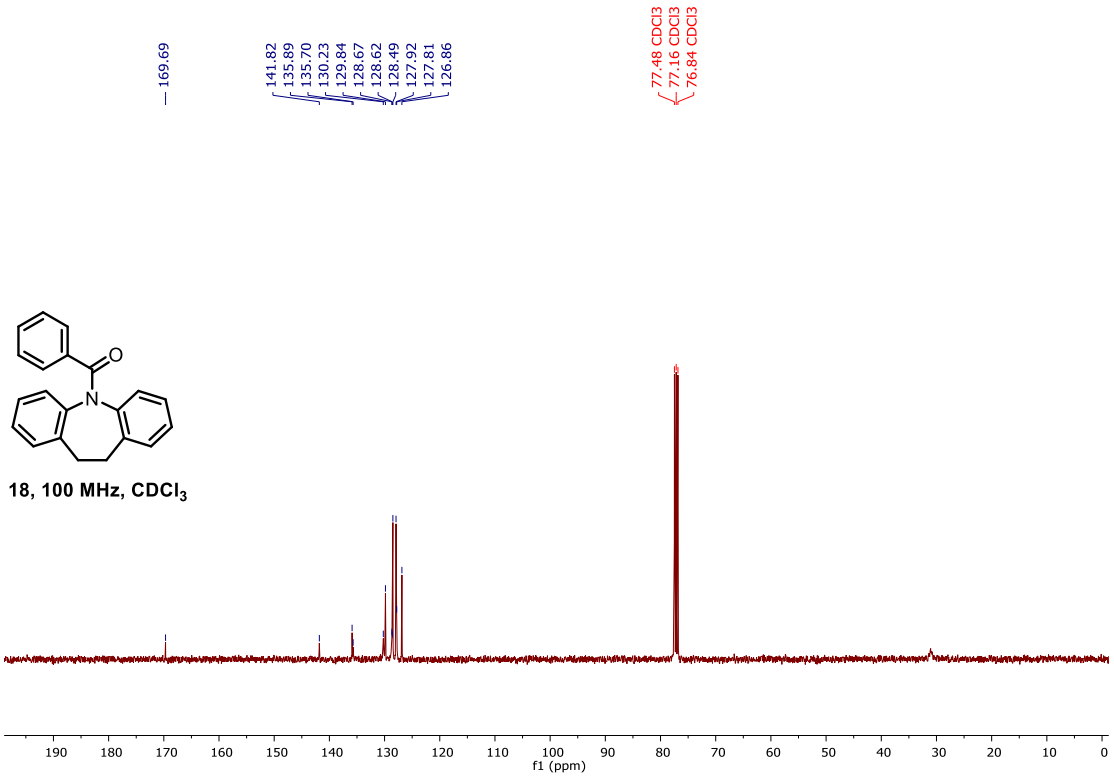
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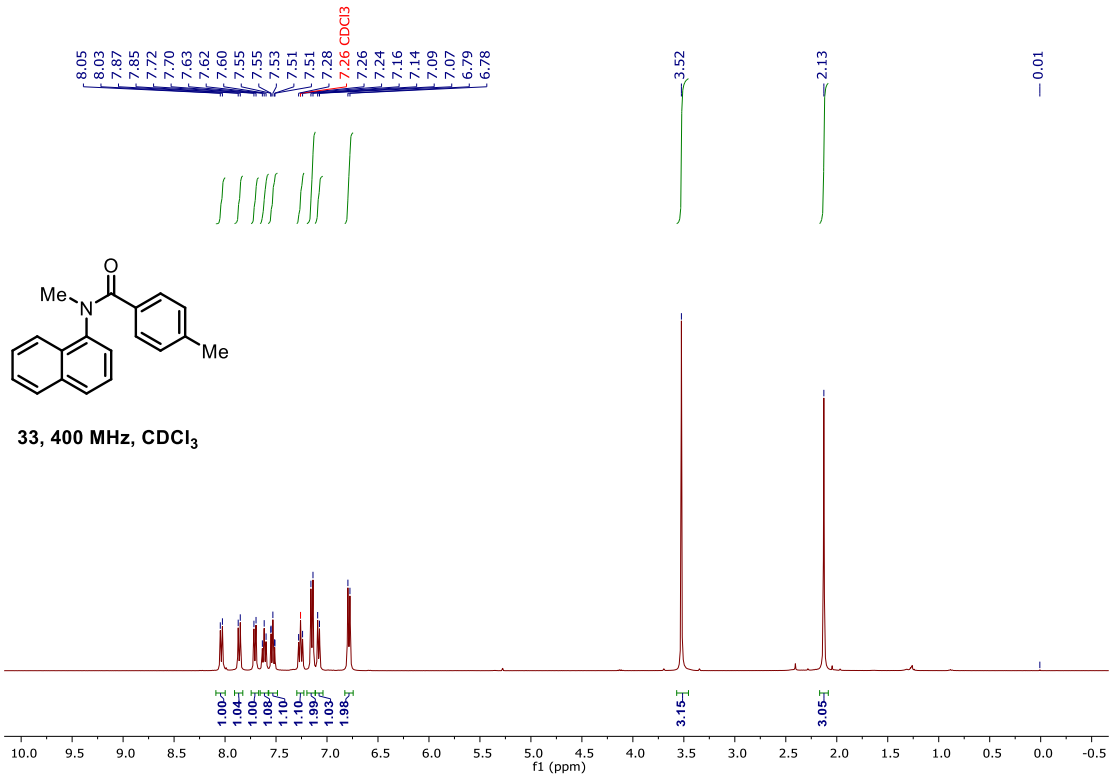
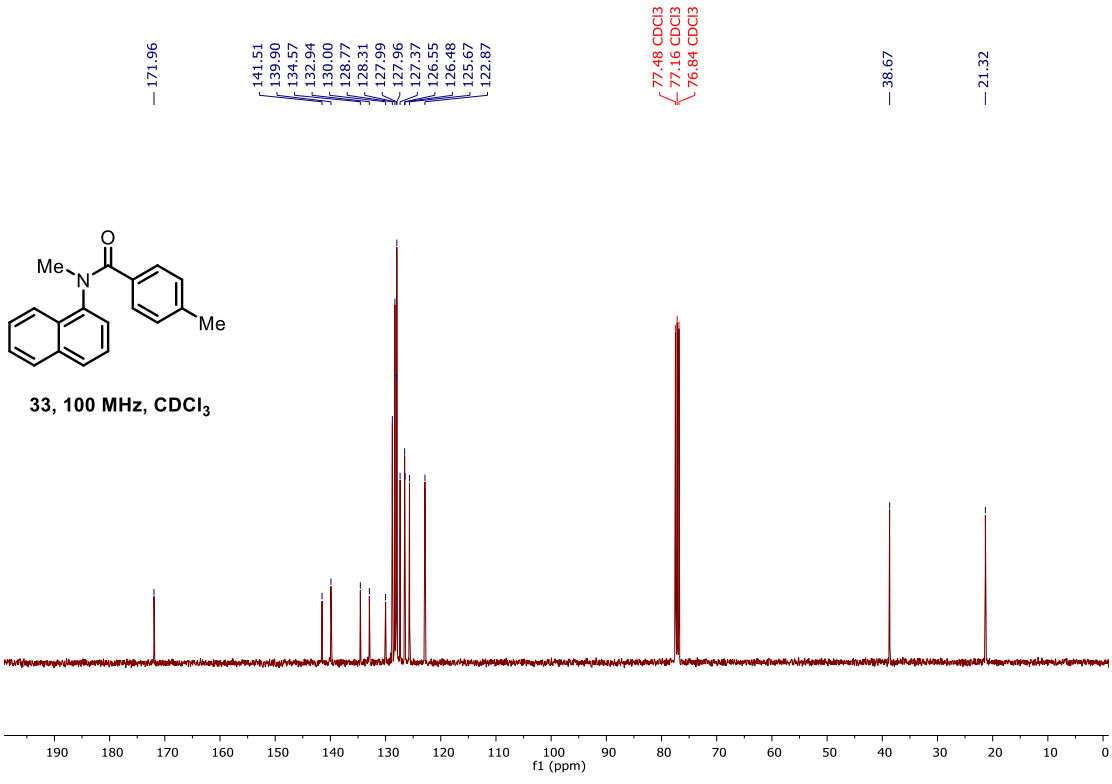
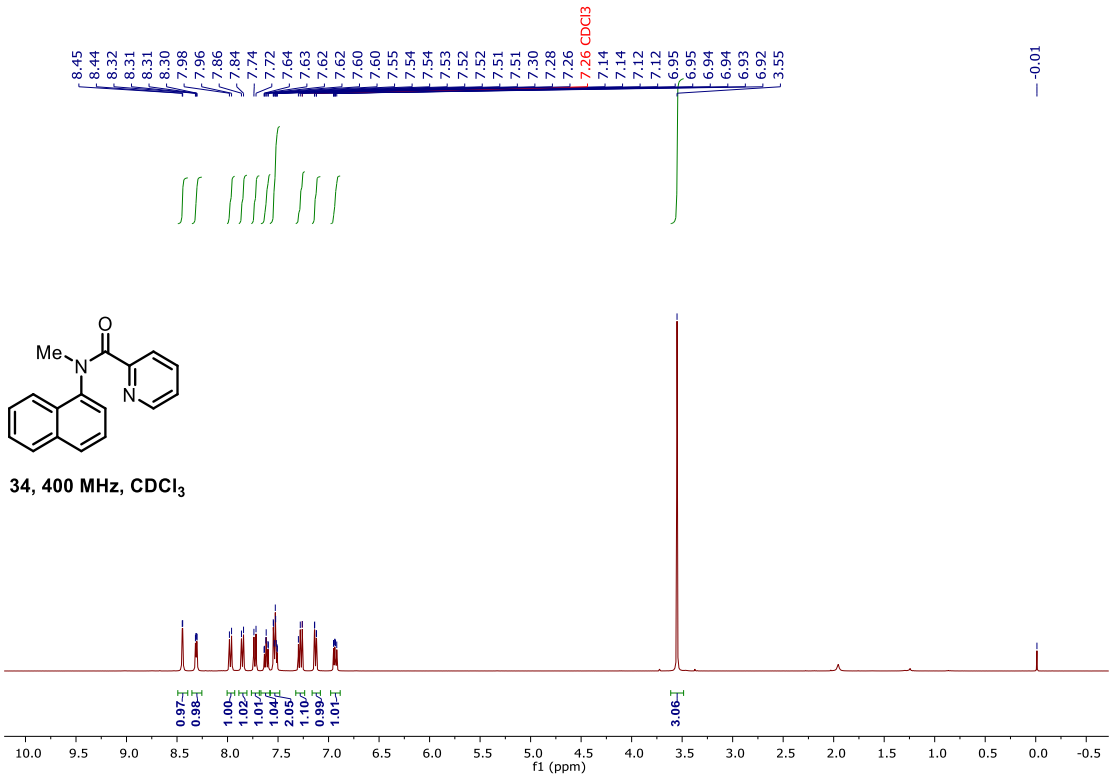
128.67
128.62
128.49
127.92
127.81
126.86
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
O
N
18, 100 MHz, CDCl3
f1 (ppm)

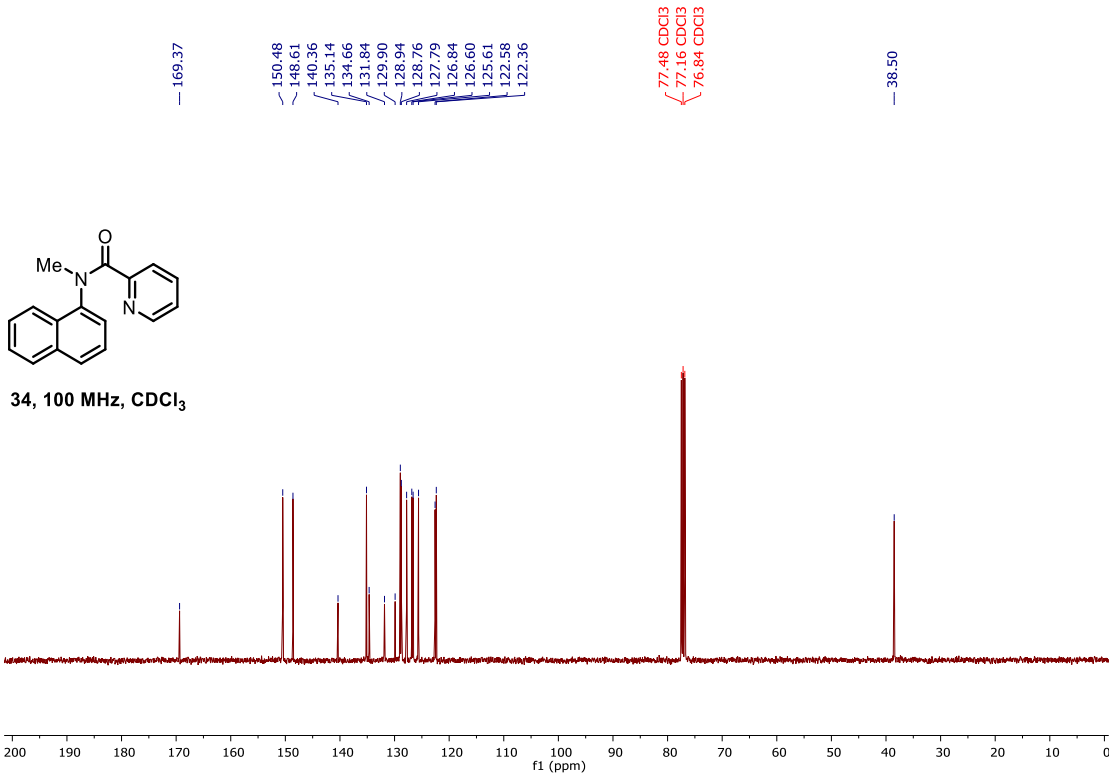


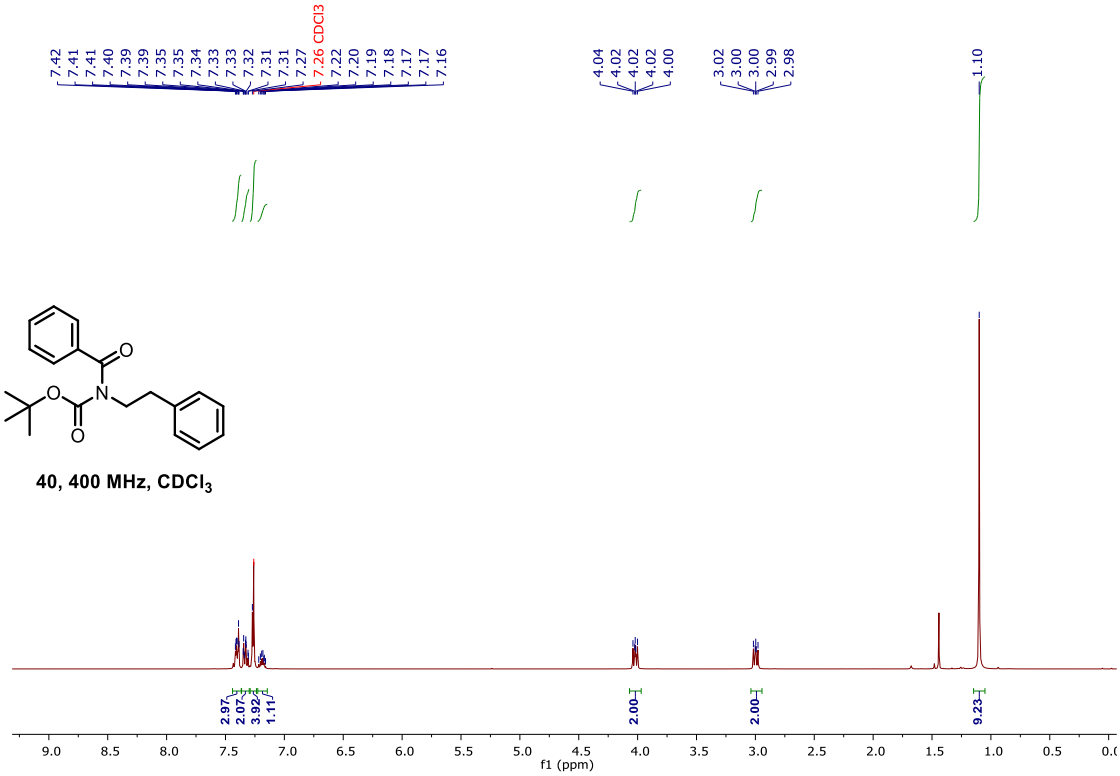
33, 400 MHz, $CDCl_3$



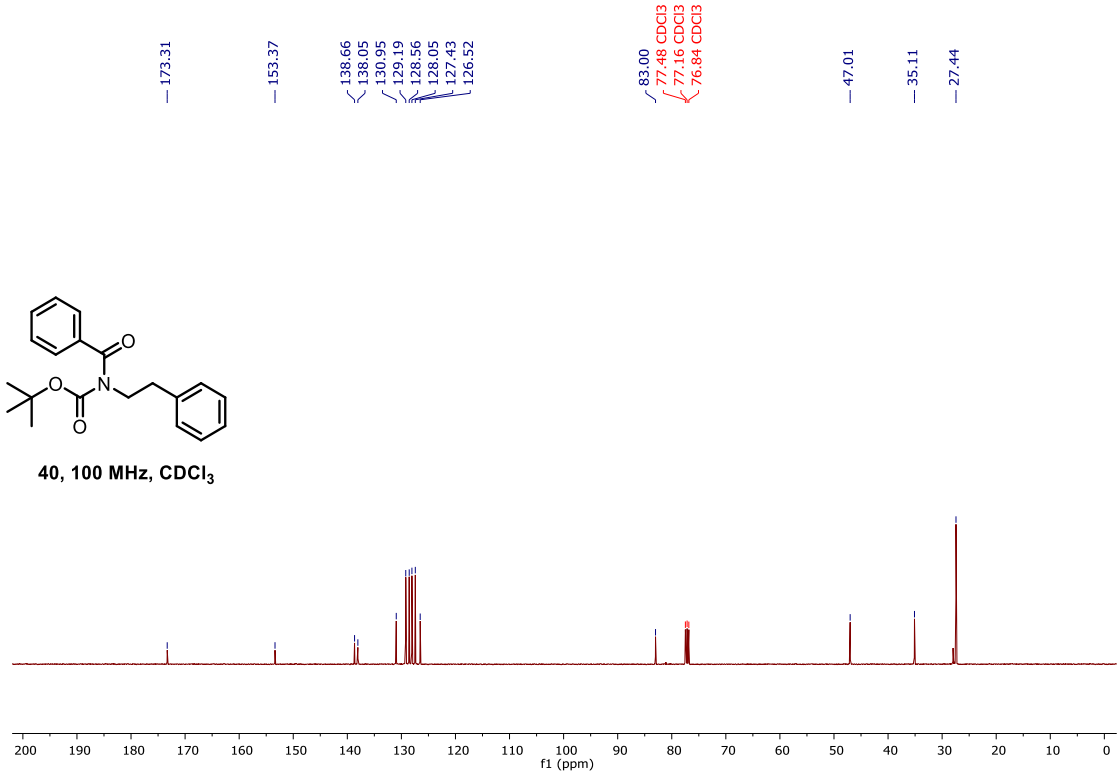
33, 100 MHz, $CDCl_3$


8.45
8.44
8.32
8.31
8.31
8.30
7.98
7.96
7.86
7.84
7.74
7.72
7.64
7.63
7.62
7.62
7.60
7.60
7.55
7.54
7.54
7.53
7.52
7.52
7.51
7.51
7.30
7.28
7.26
7.26 CDCl3
7.14
7.14
7.12
7.12
6.95
6.95
6.94
6.94
6.93
6.92
3.55
-0.01
Me
N
O
N
34, 400 MHz, CDCl3
0.97
0.98
1.00
1.02
1.01
1.04
2.05
1.10
0.99
1.01
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

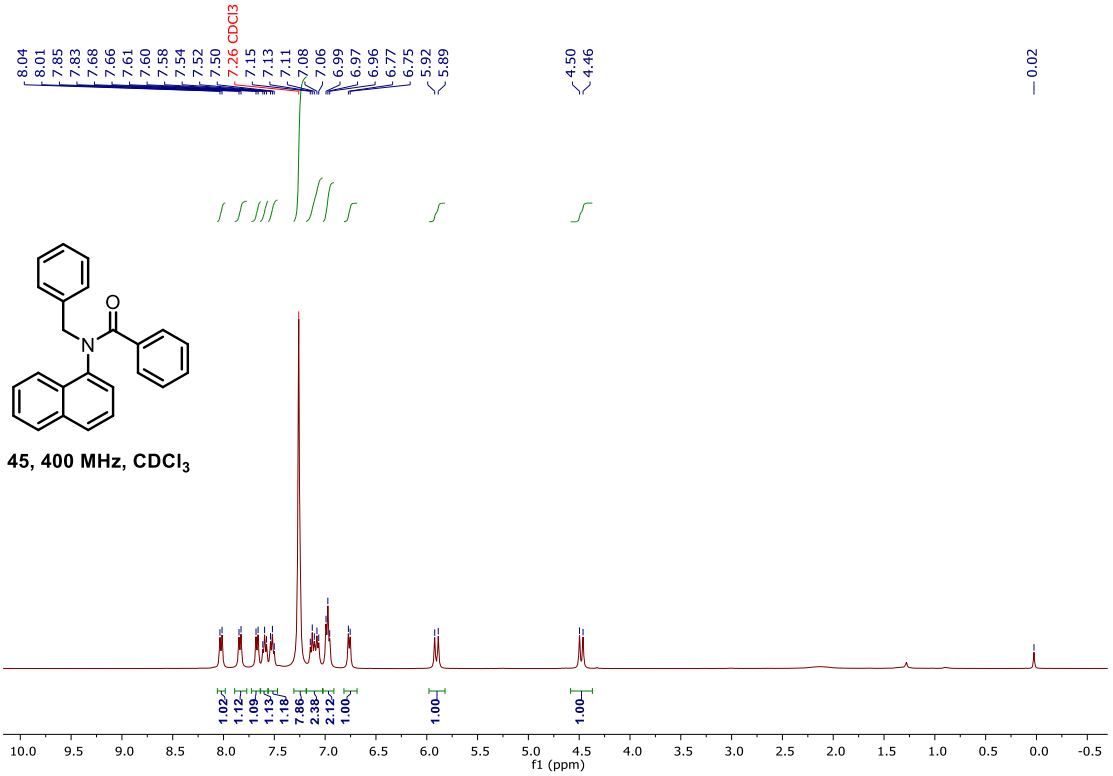

169.37
150.48
148.61
140.36
135.14
134.66
131.84
129.90
128.94
128.76
127.79
126.84
126.60
125.61
122.58
122.36
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
38.50
Me
N
O
N
34, 100 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



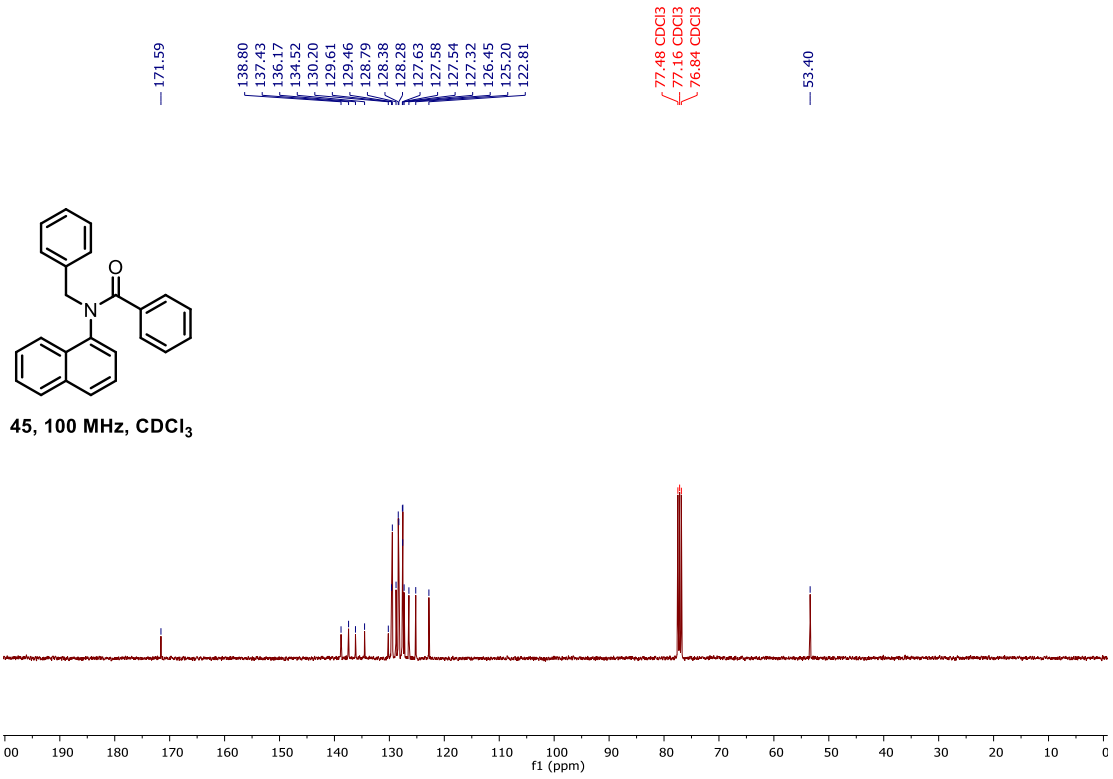
40, 400 MHz, $CDCl_3$



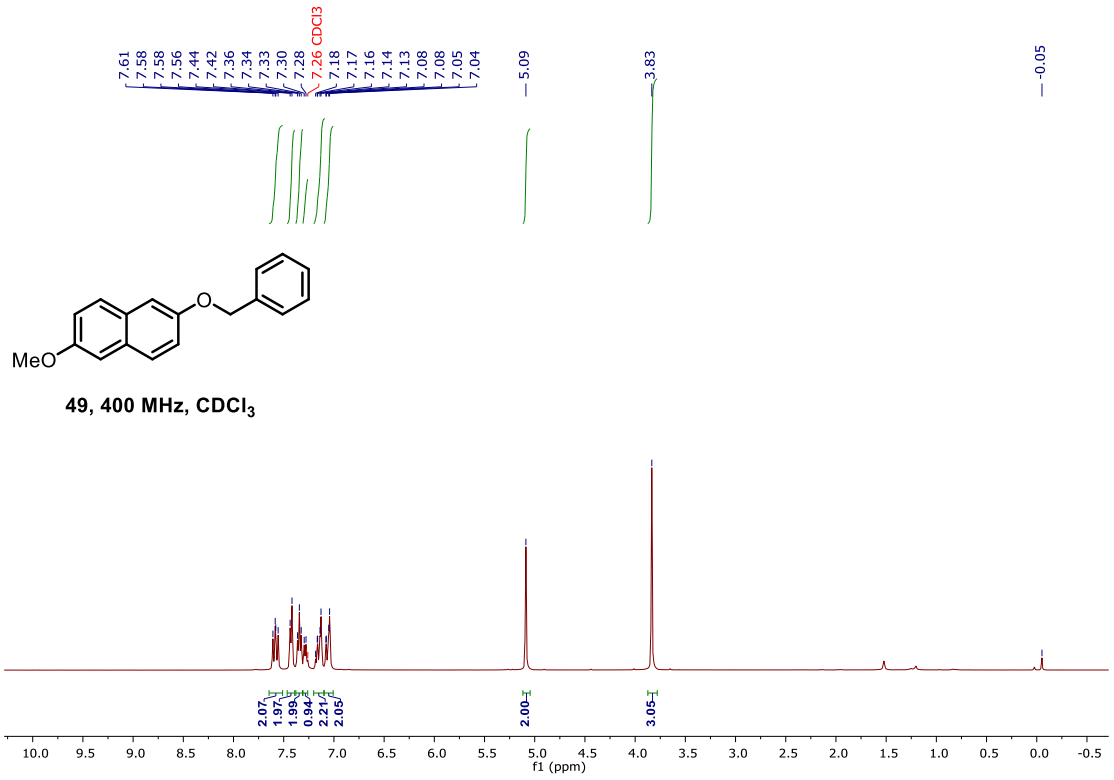
40, 100 MHz, $CDCl_3$



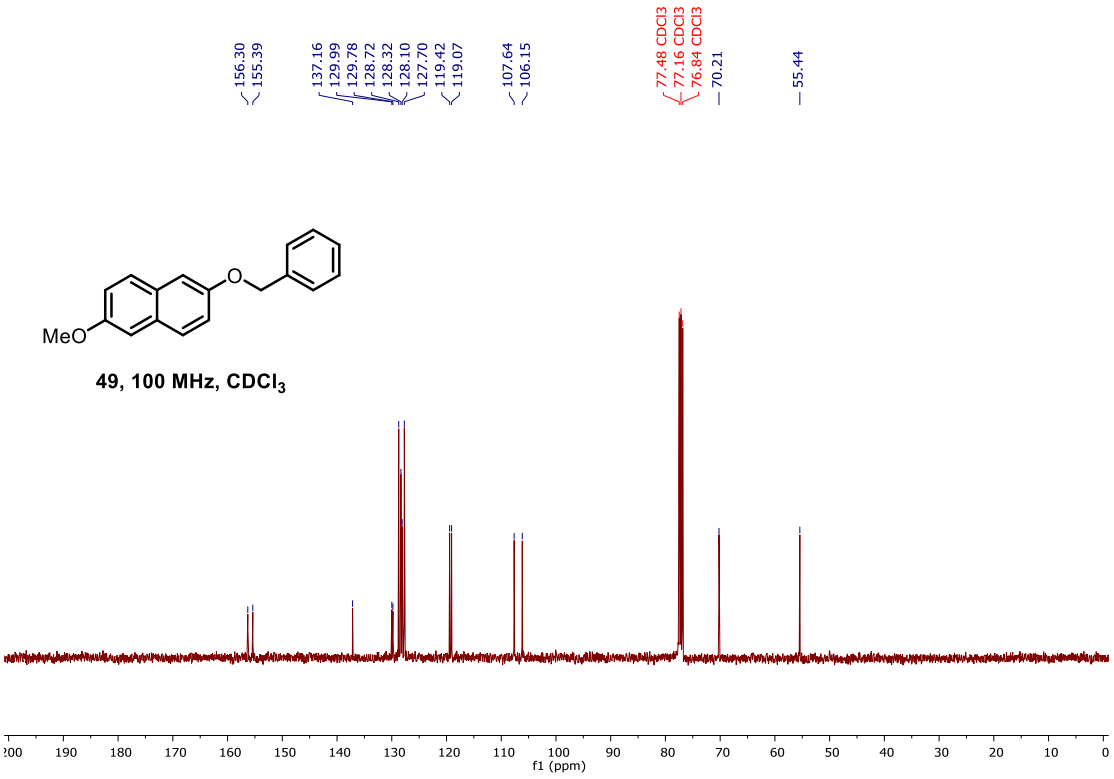
45, 400 MHz, $CDCl_3$



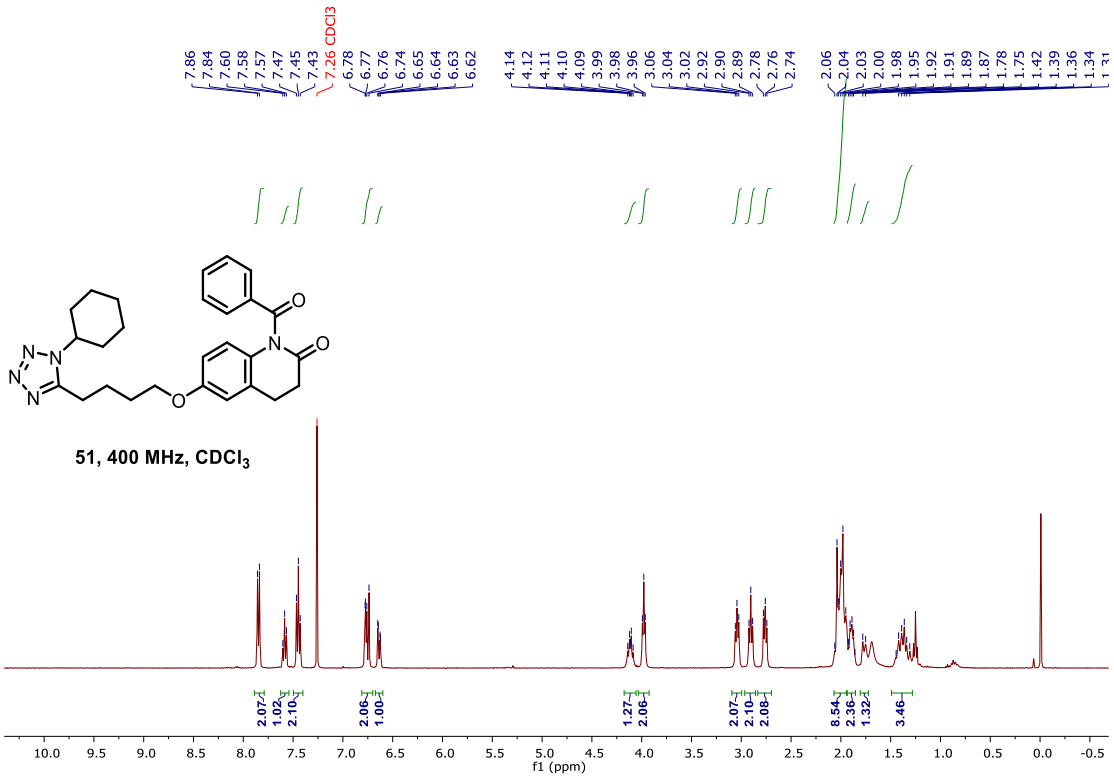
45, 100 MHz, $CDCl_3$



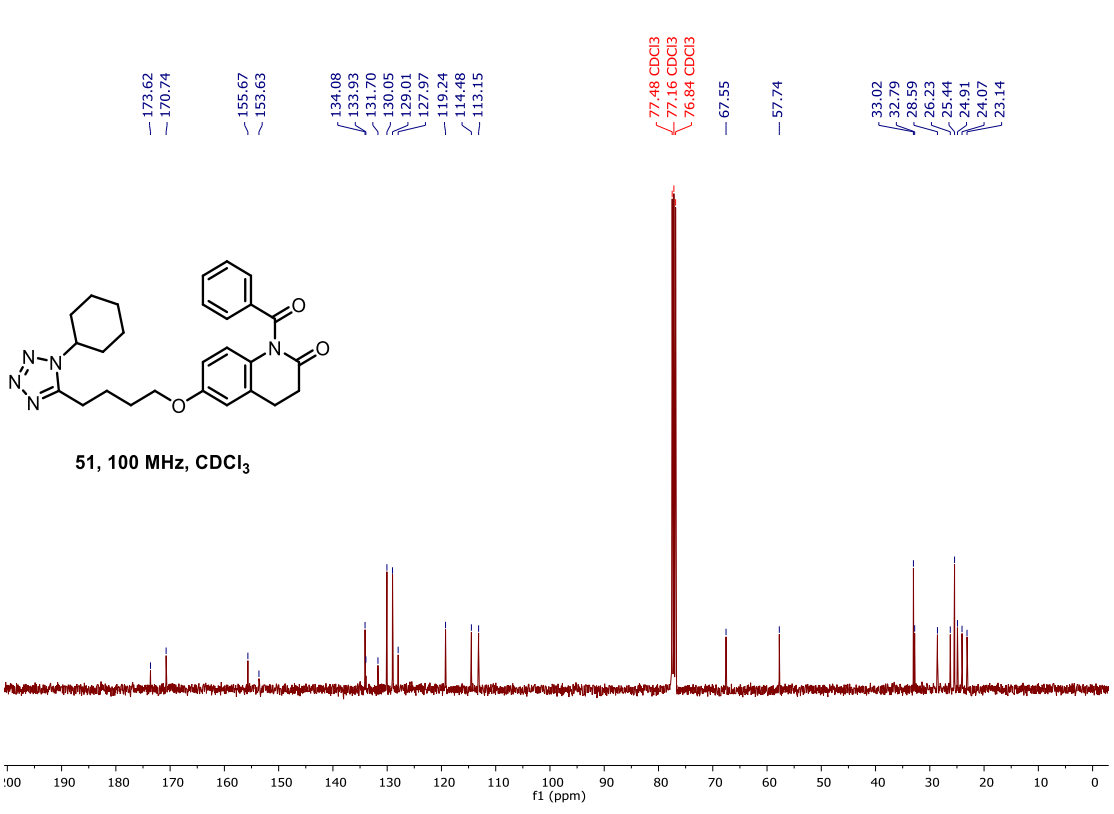
49, 400 MHz, $CDCl_3$



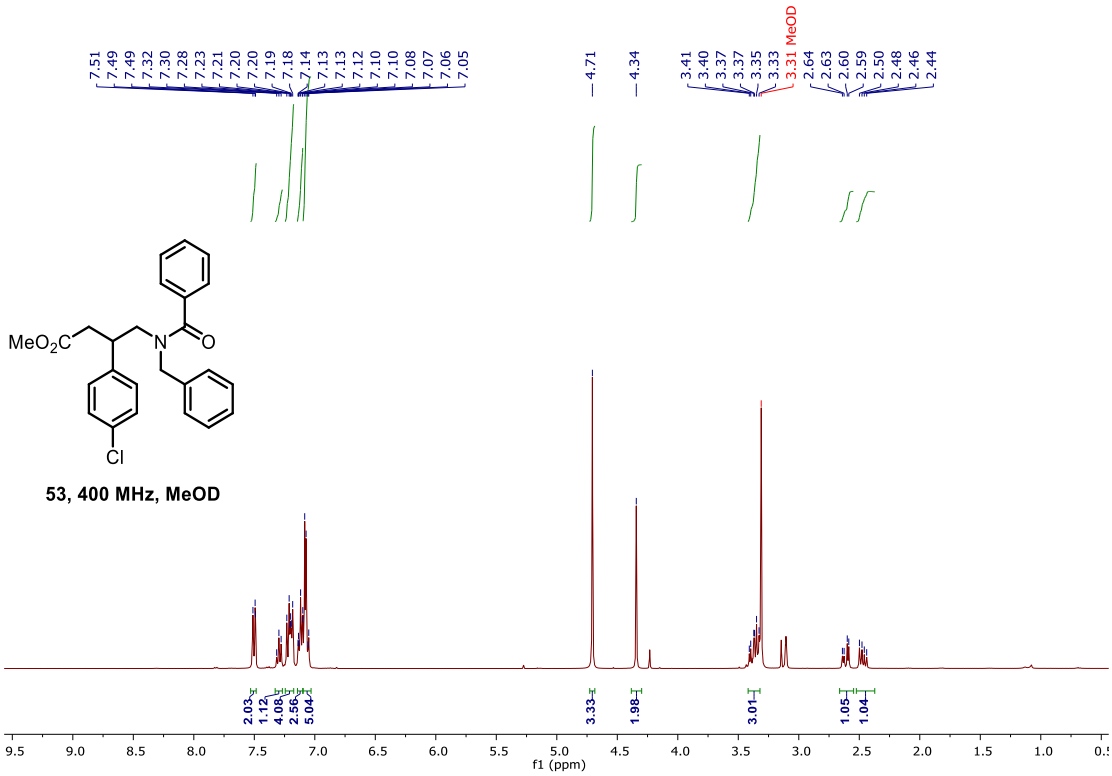
49, 100 MHz, $CDCl_3$



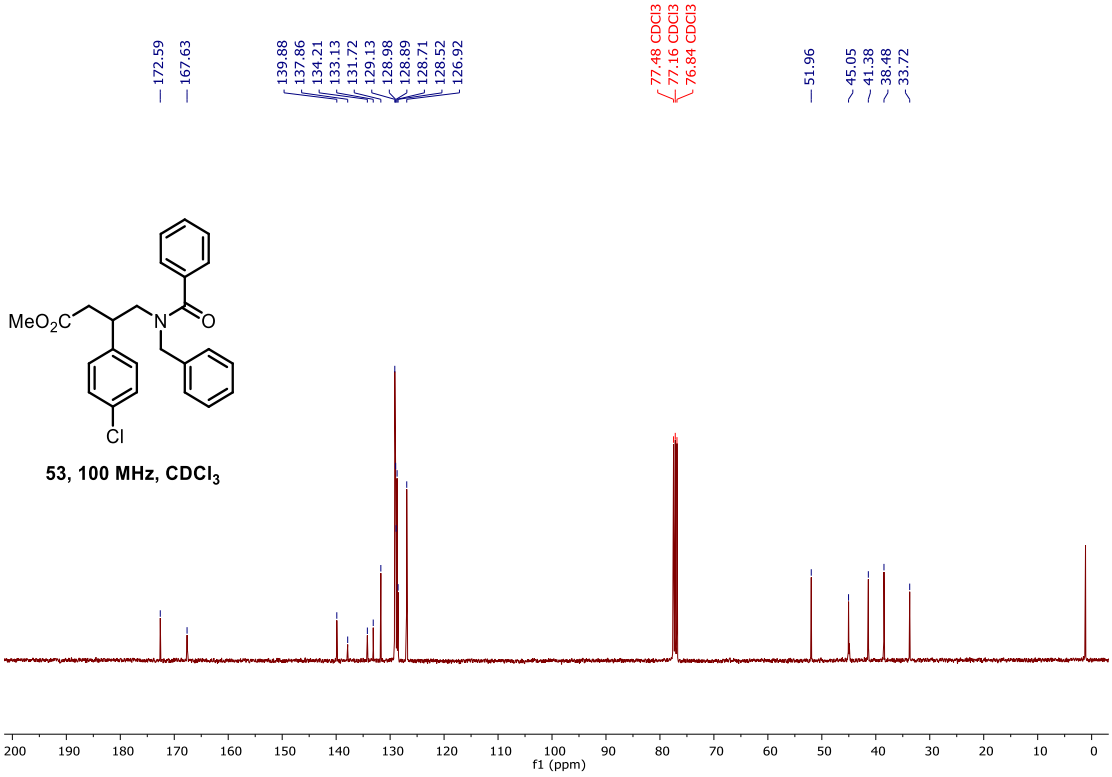
51, 400 MHz, $CDCl_3$



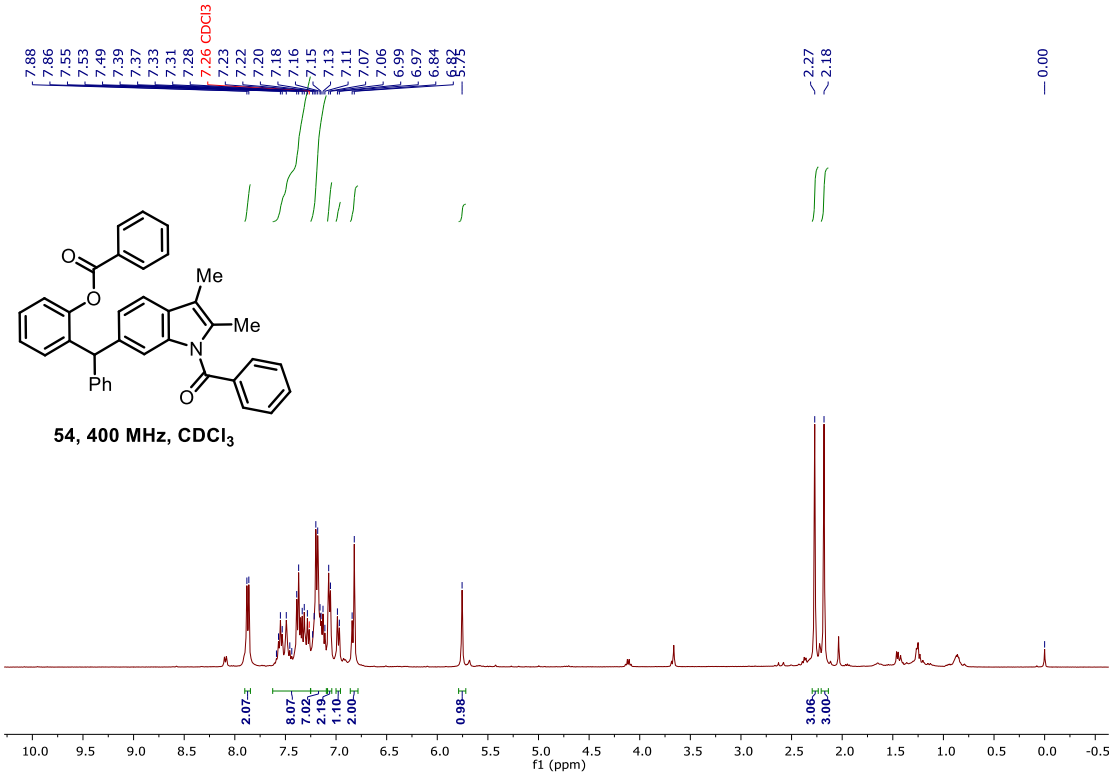
51, 100 MHz, $CDCl_3$



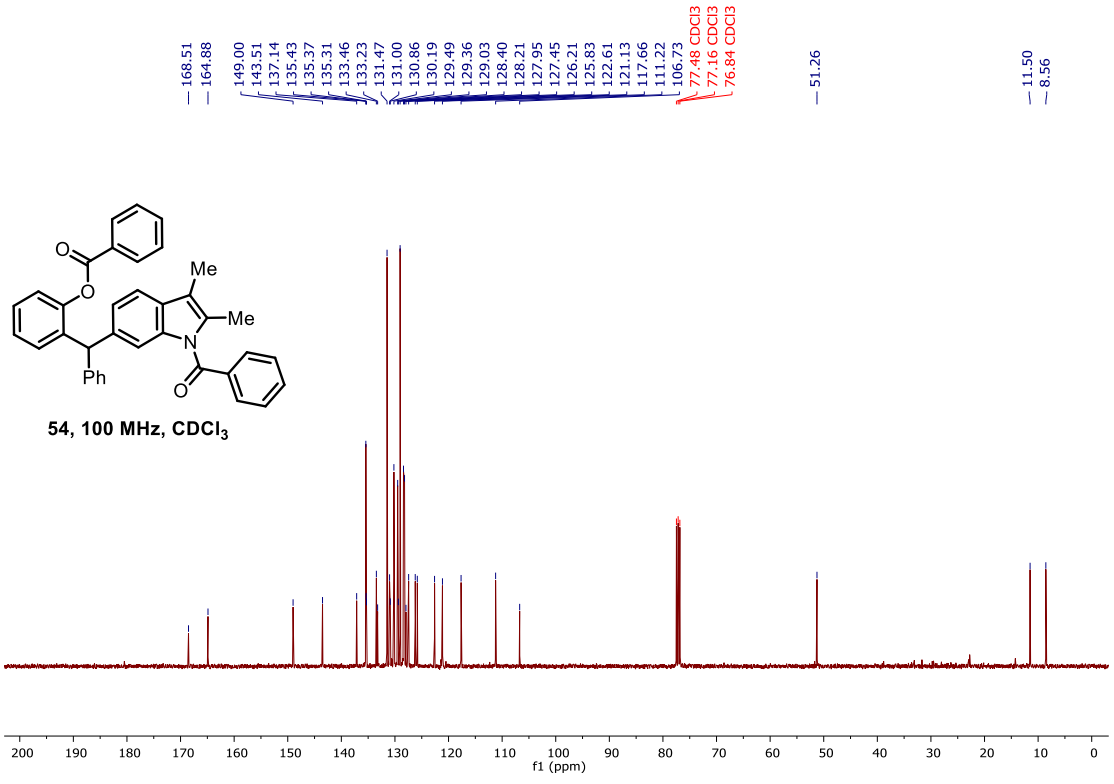
53, 400 MHz, MeOD



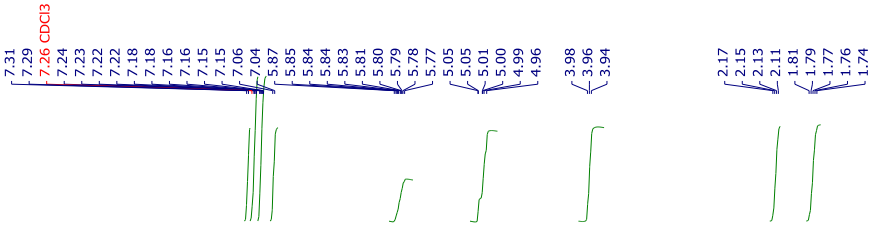
53, 100 MHz, $CDCl_3$

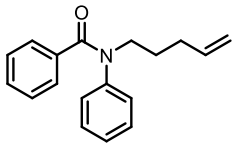


54, 400 MHz, $CDCl_3$

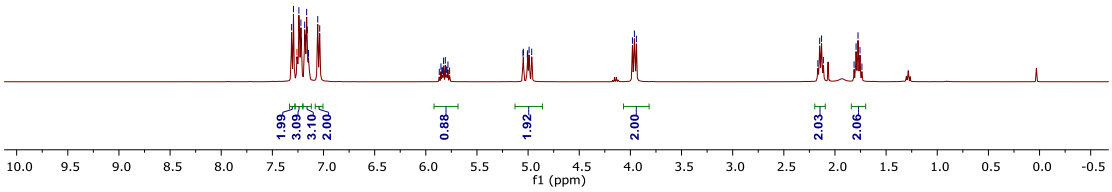


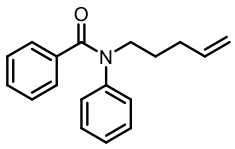
54, 100 MHz, $CDCl_3$



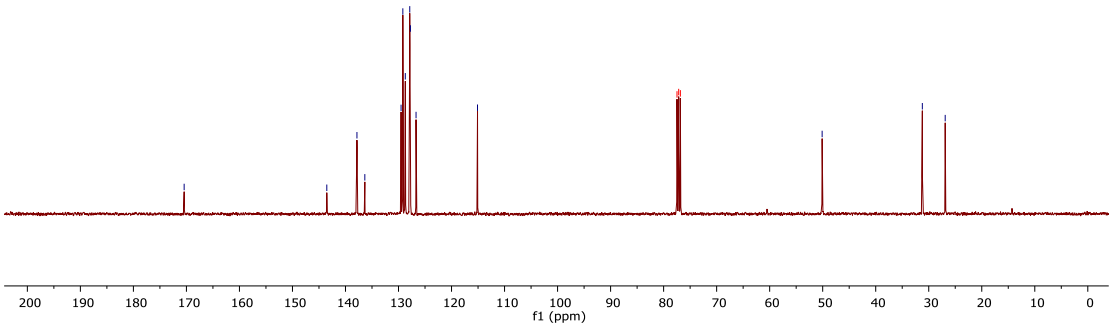


58, 400 MHz, $CDCl_3$

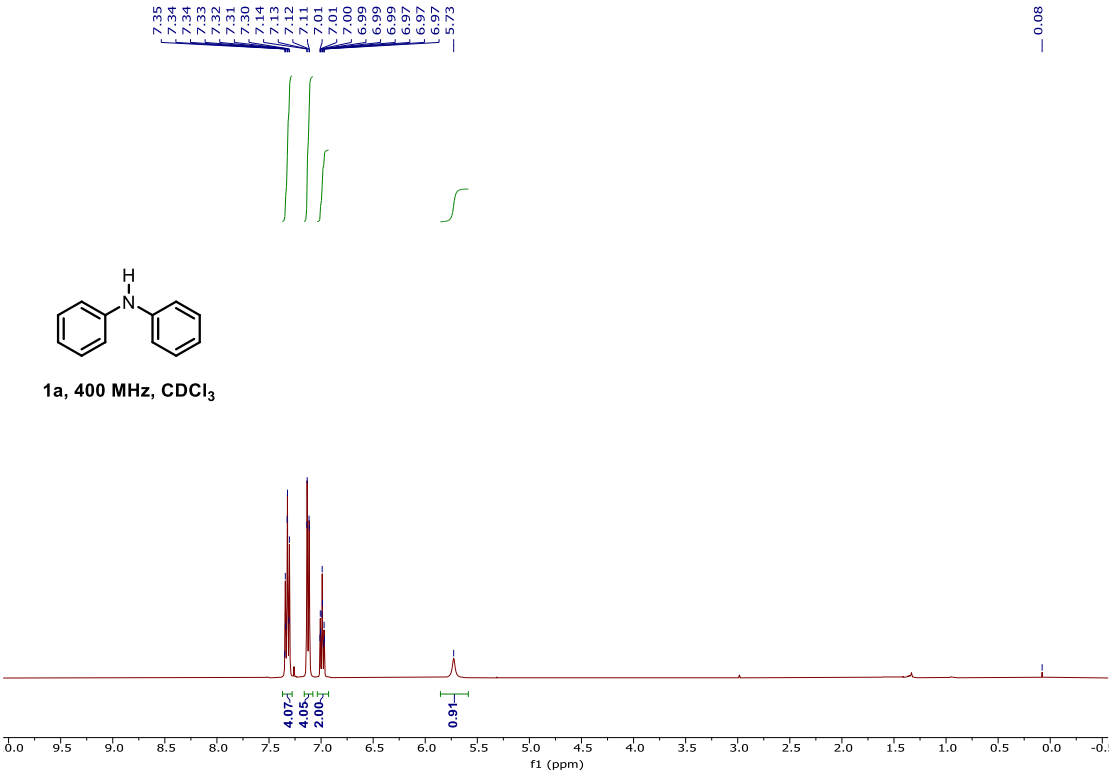




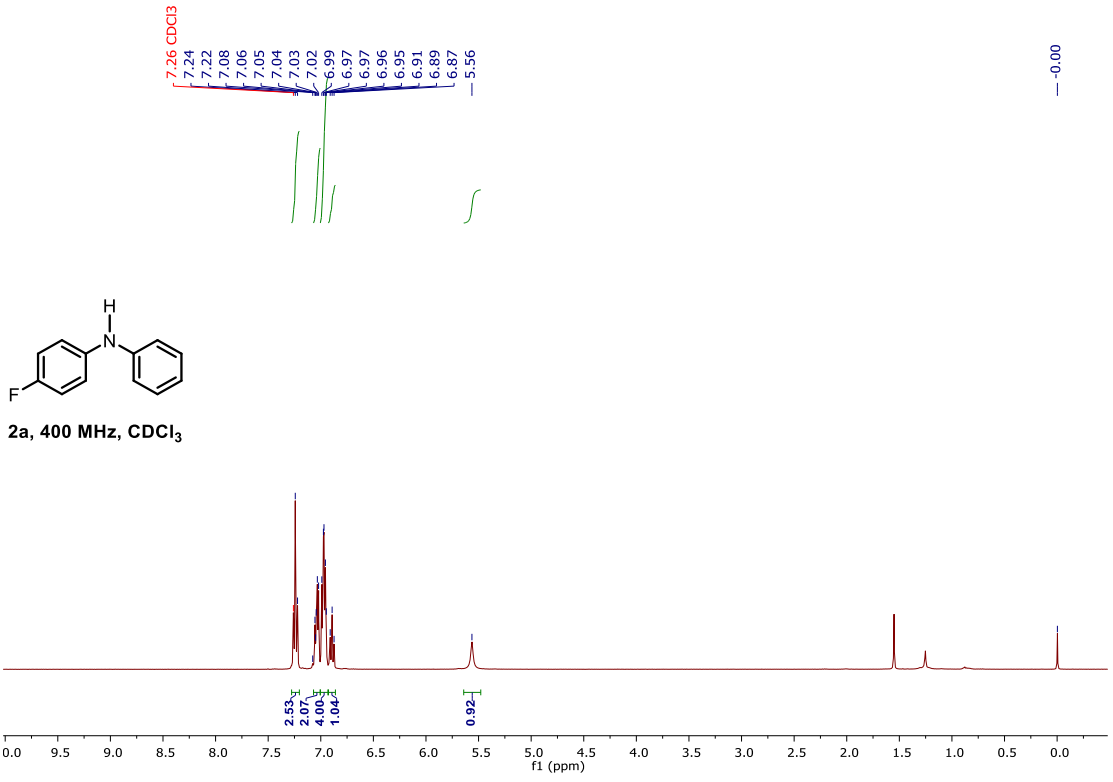
58, 100 MHz, $CDCl_3$



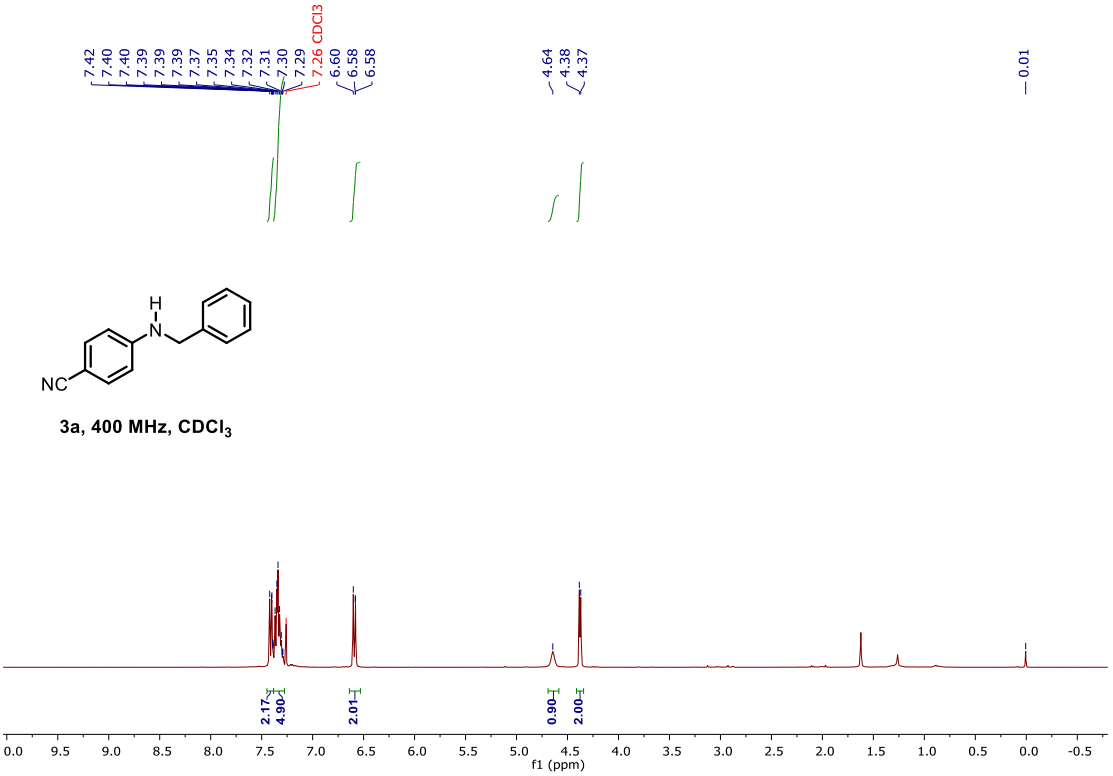
10. NMR Spectra of Products



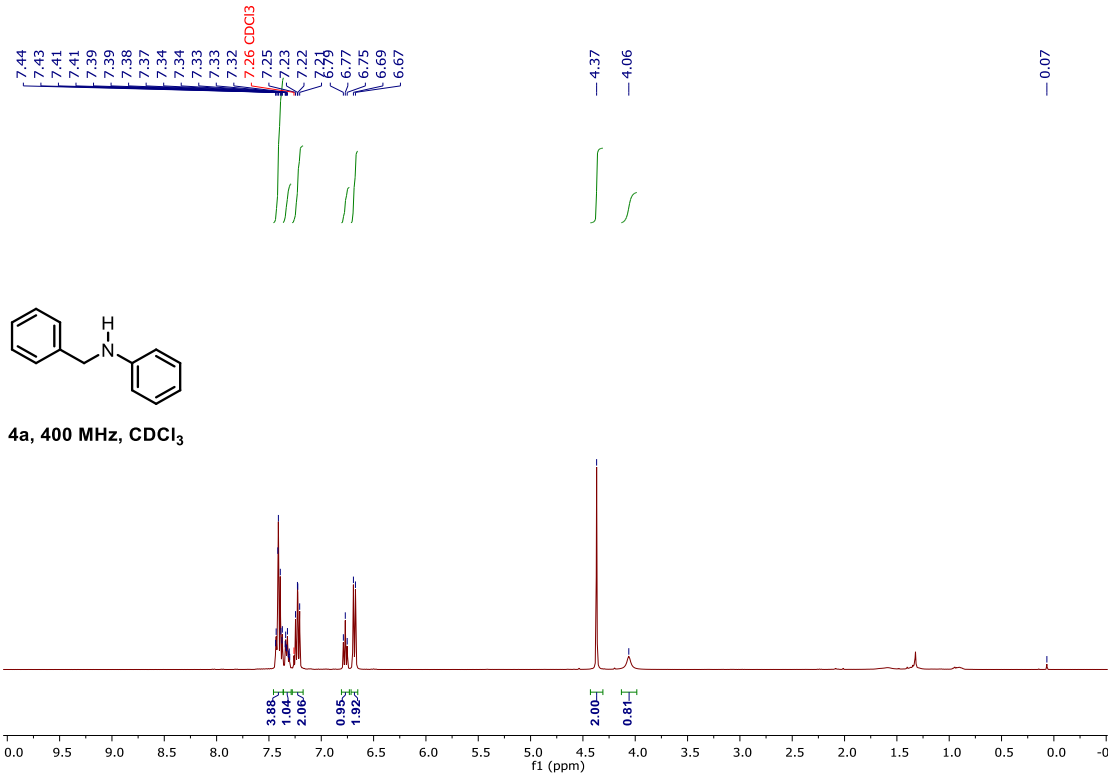
1a, 400 MHz, $CDCl_3$



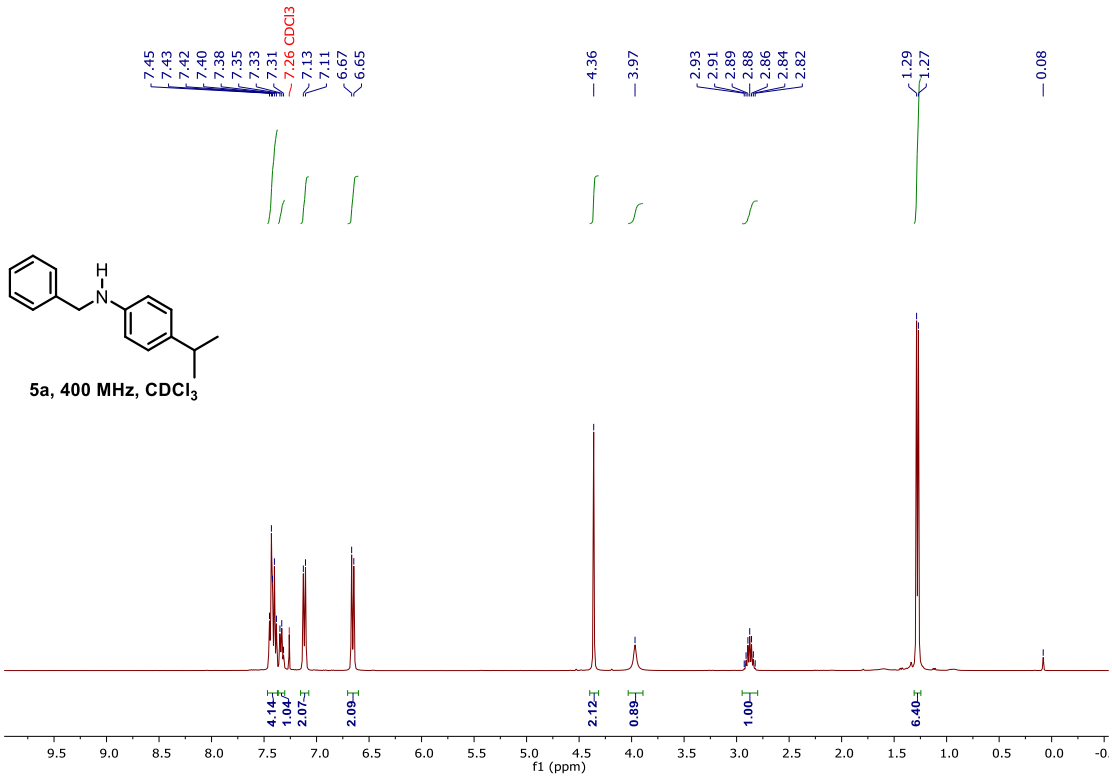
2a, 400 MHz, $CDCl_3$



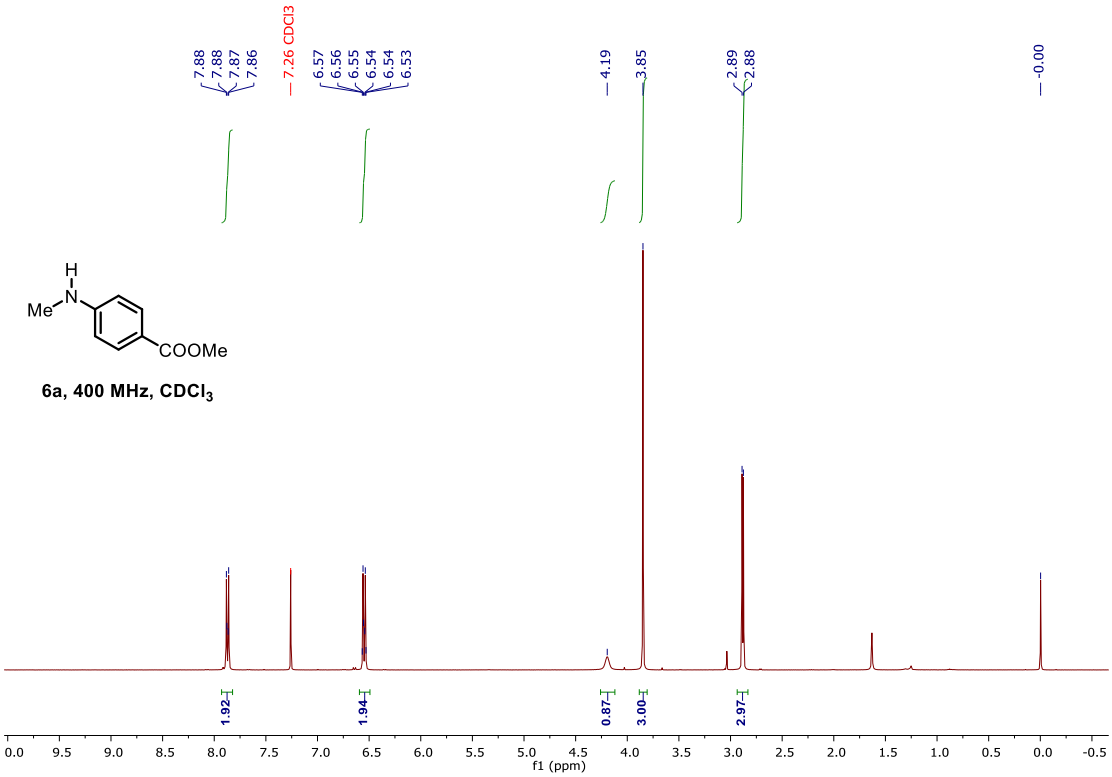
3a, 400 MHz, $CDCl_3$



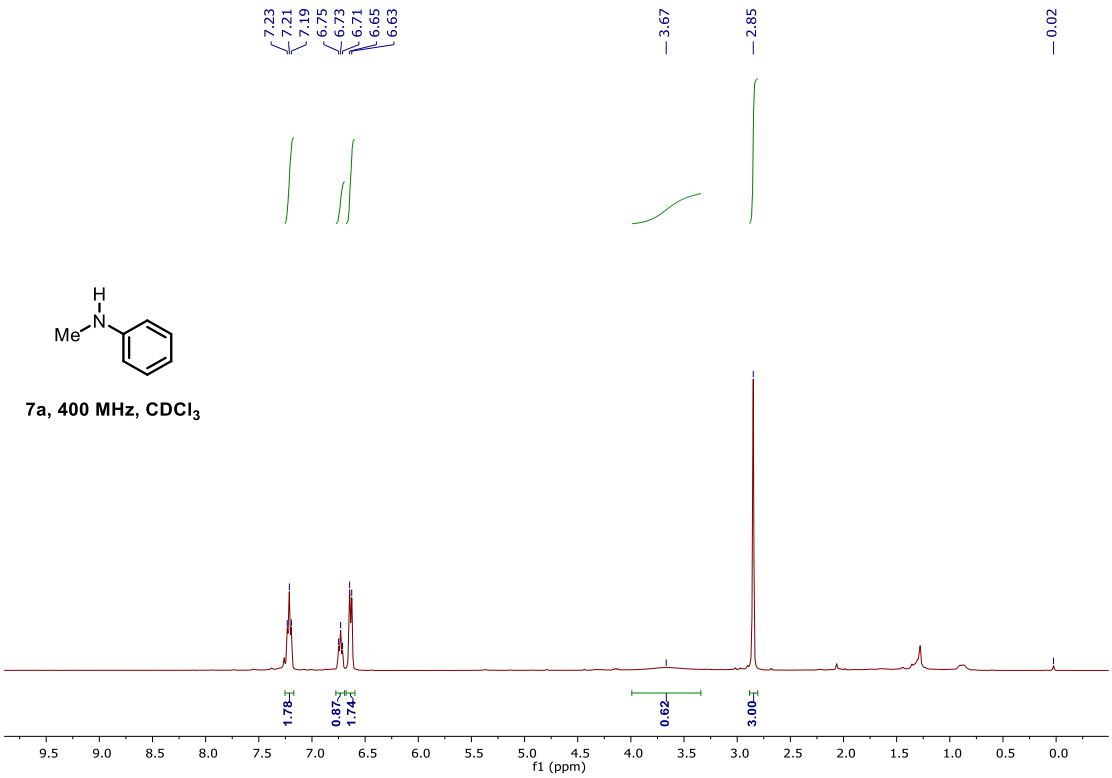
4a, 400 MHz, $CDCl_3$



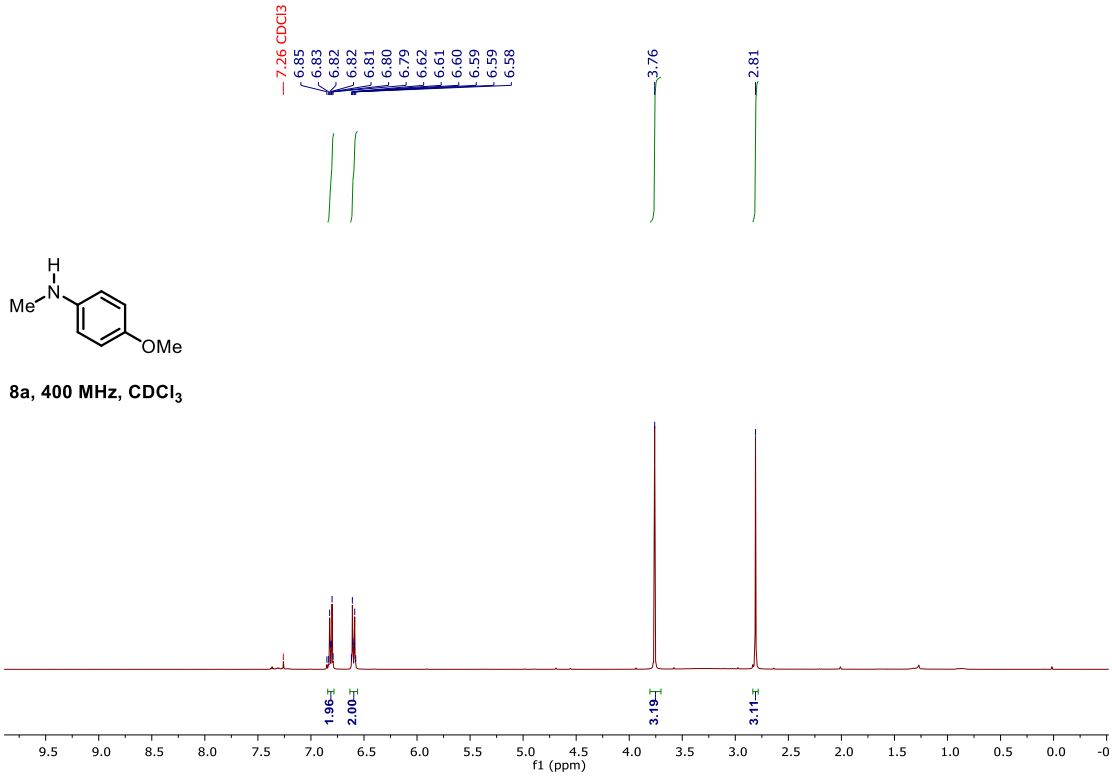
5a, 400 MHz, $CDCl_3$



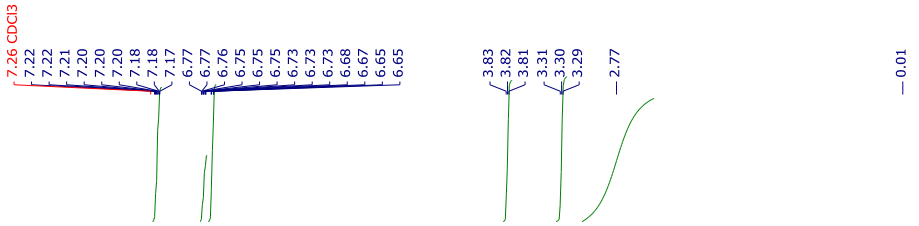
6a, 400 MHz, $CDCl_3$

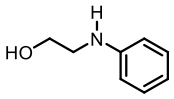


7a, 400 MHz, $CDCl_3$

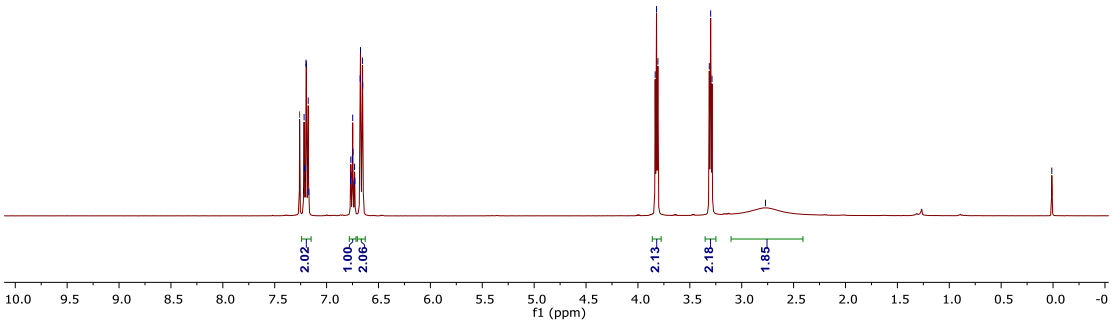


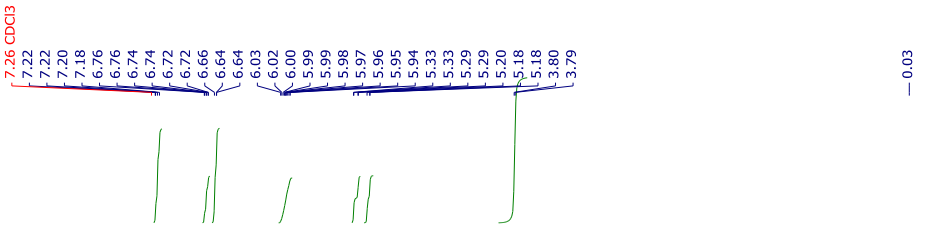
8a, 400 MHz, $CDCl_3$

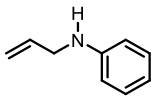




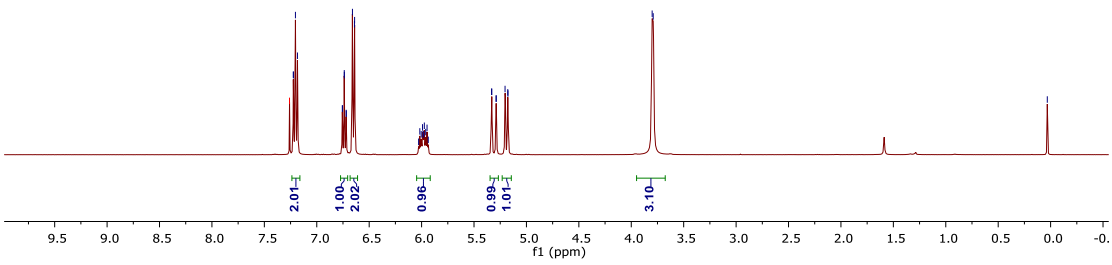
9a, 400 MHz, $CDCl_3$

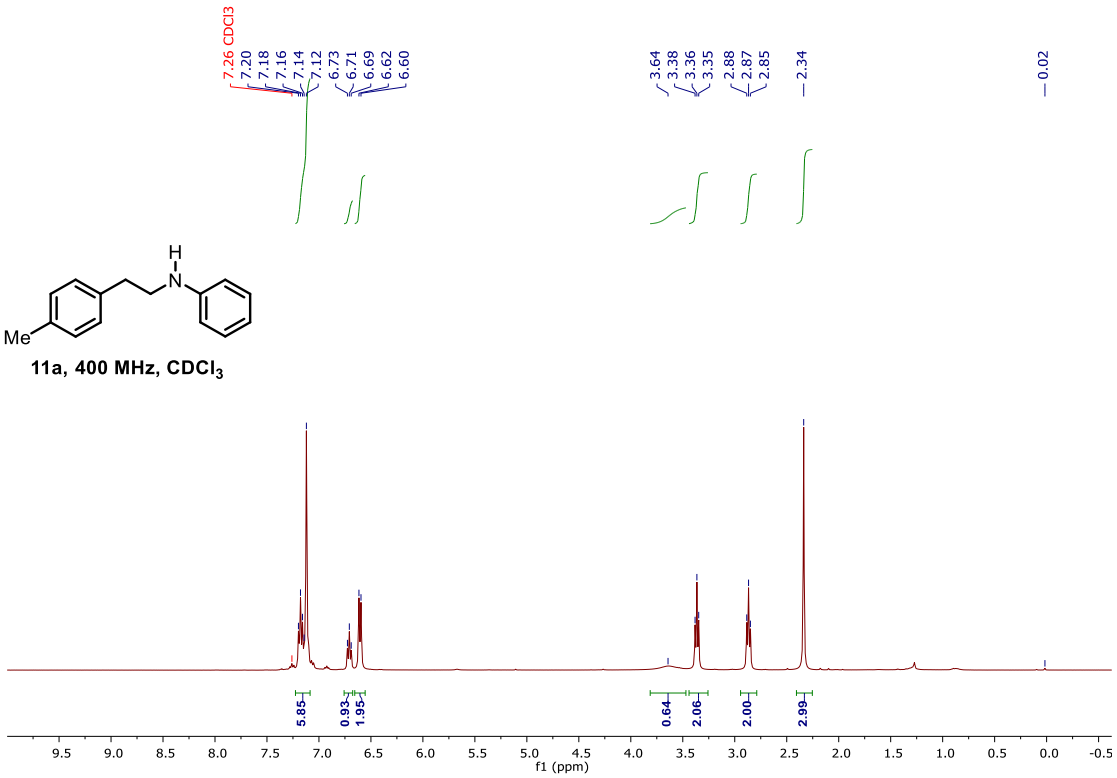




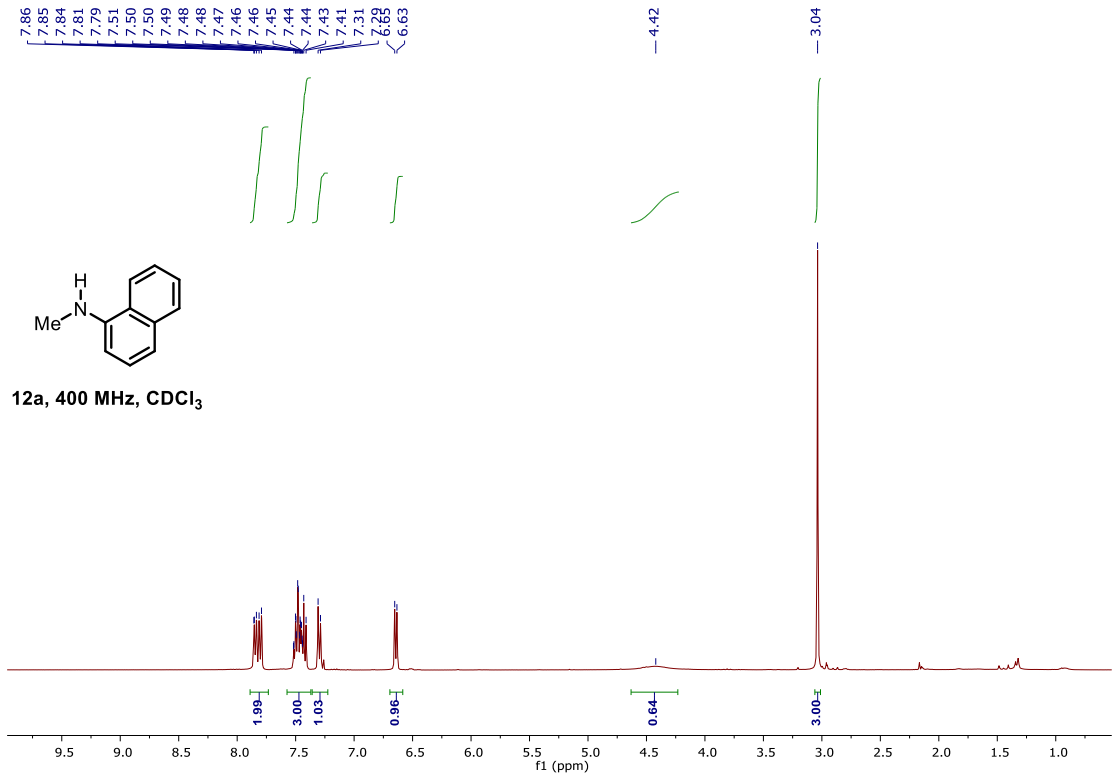


10a, 400 MHz, $CDCl_3$

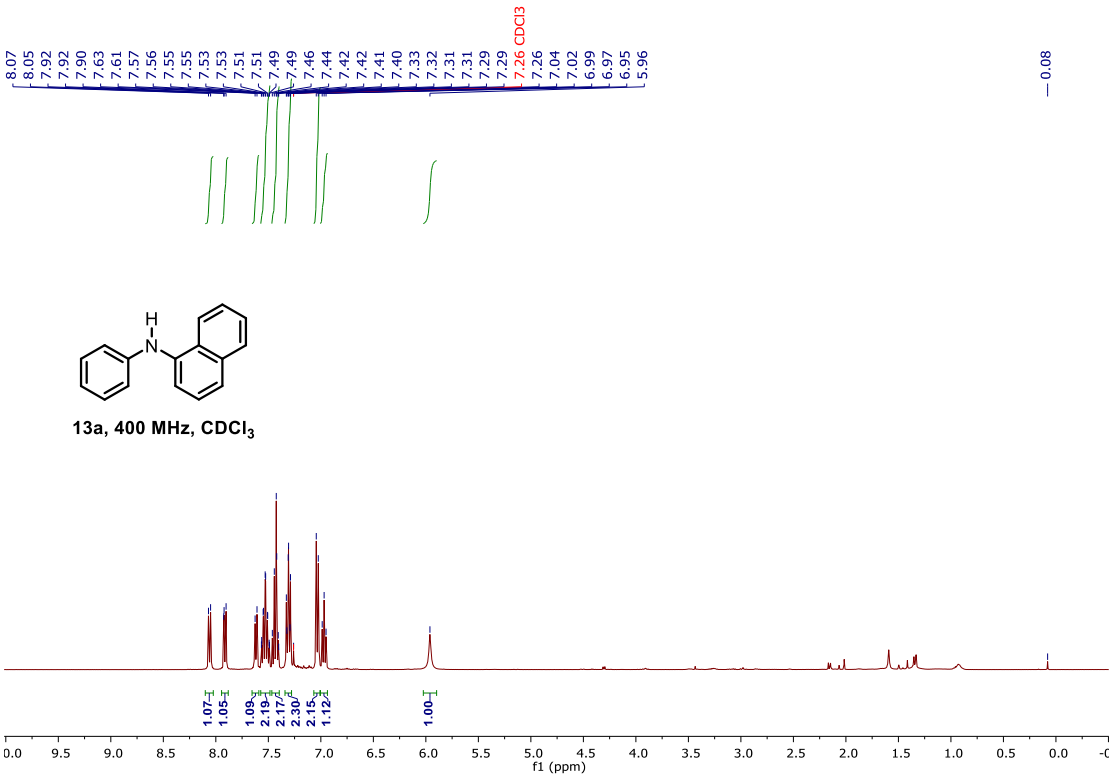




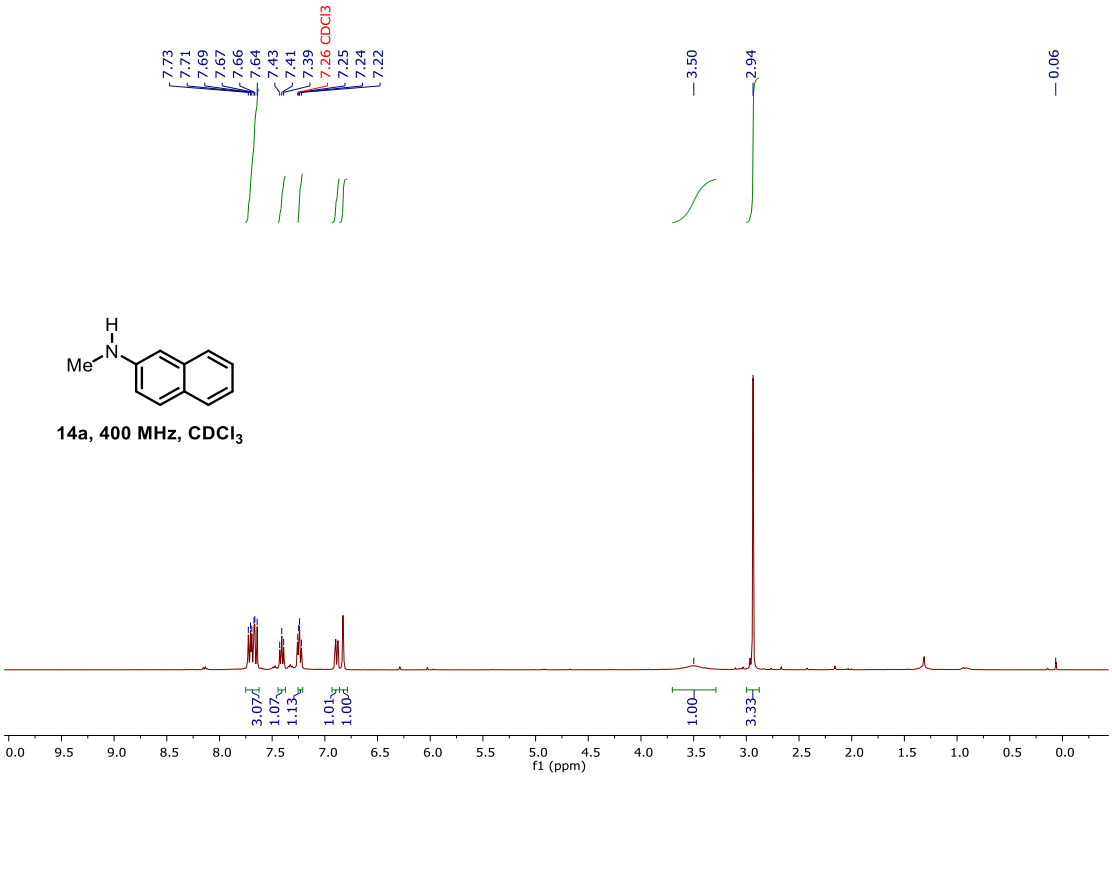
11a, 400 MHz, $CDCl_3$



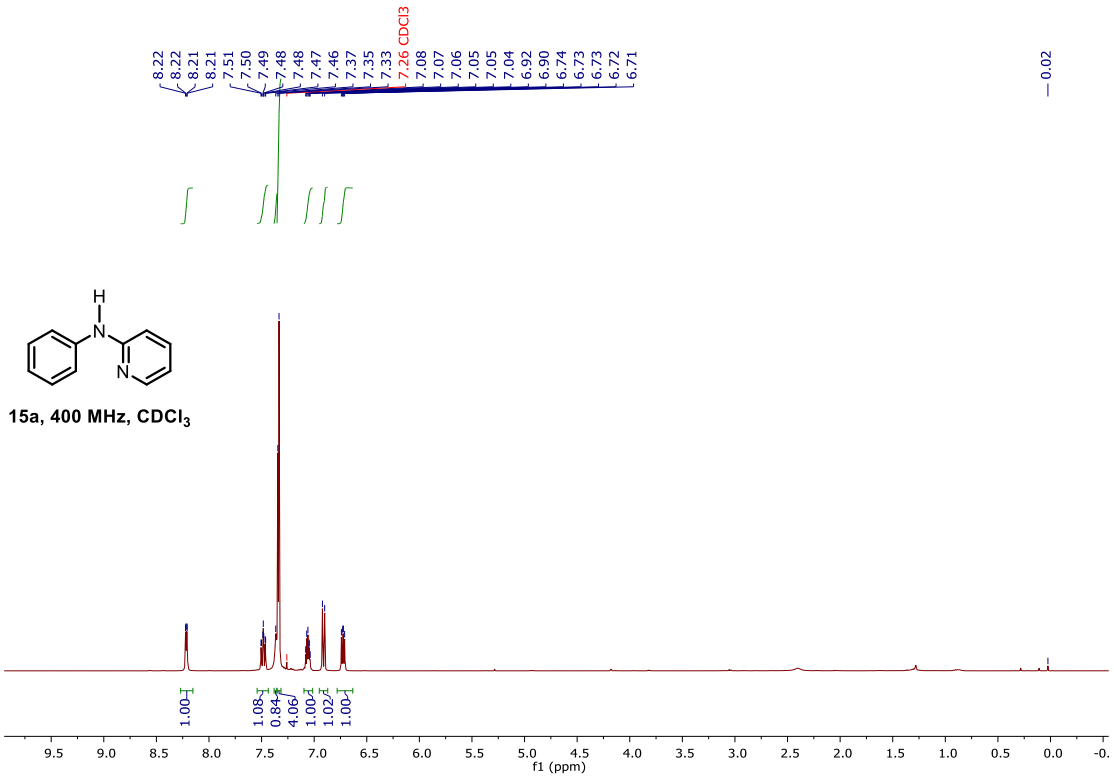
12a, 400 MHz, $CDCl_3$



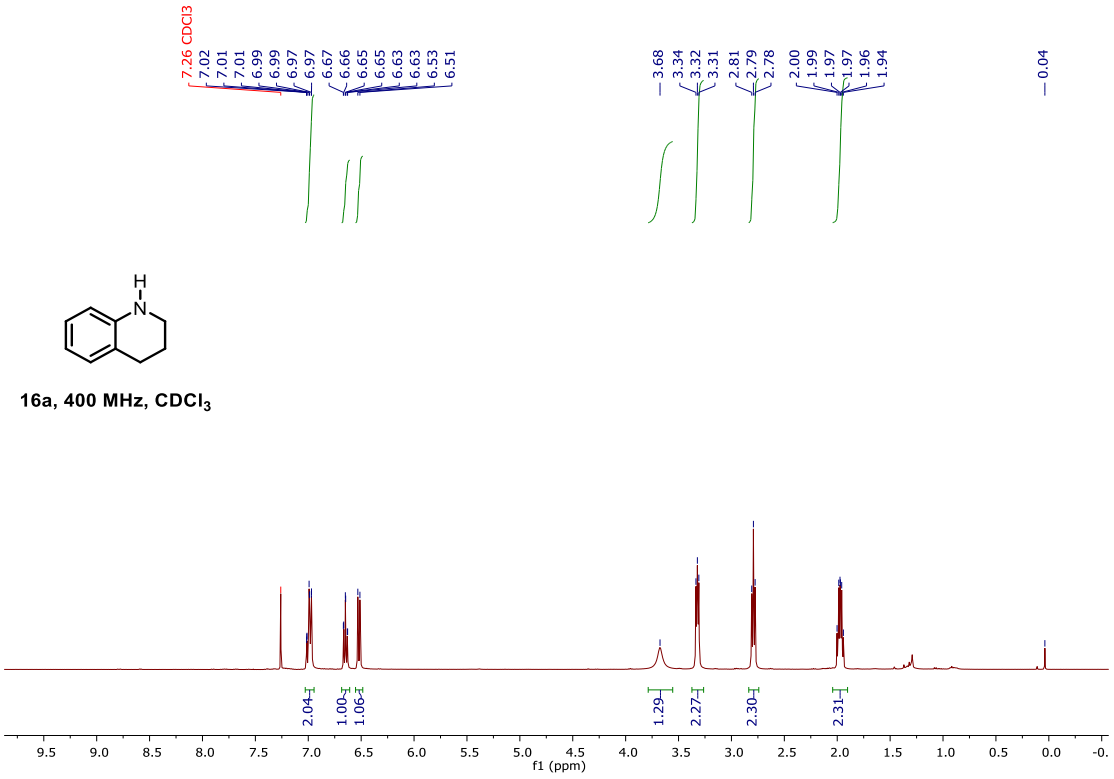
13a, 400 MHz, $CDCl_3$



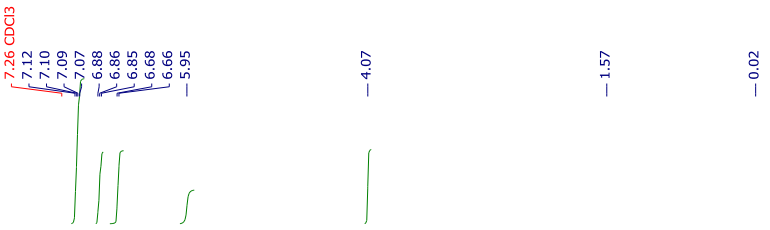
14a, 400 MHz, $CDCl_3$

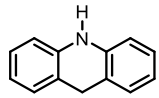


15a, 400 MHz, $CDCl_3$

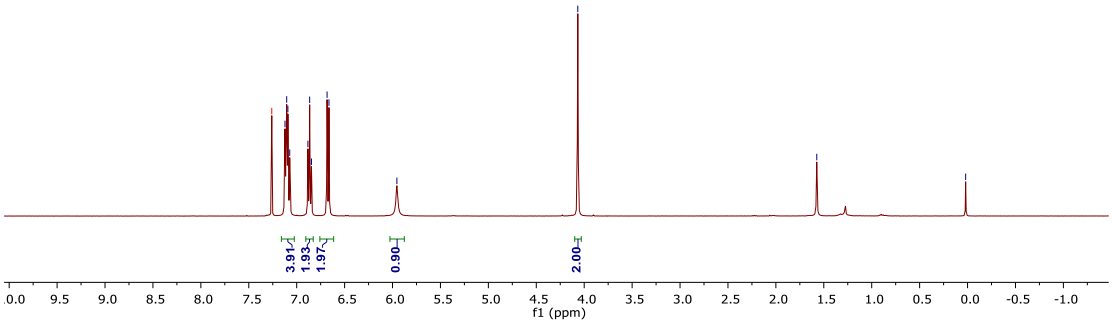


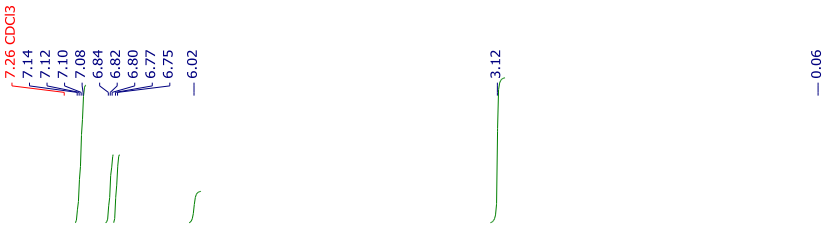
16a, 400 MHz, $CDCl_3$

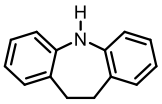




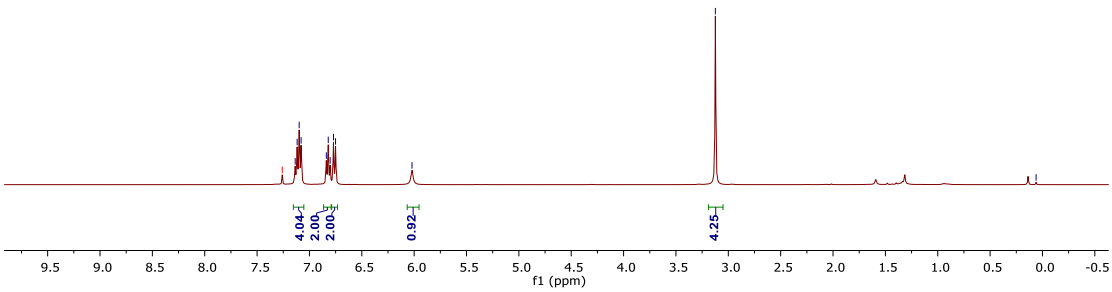
17a, 400 MHz, $CDCl_3$

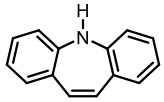




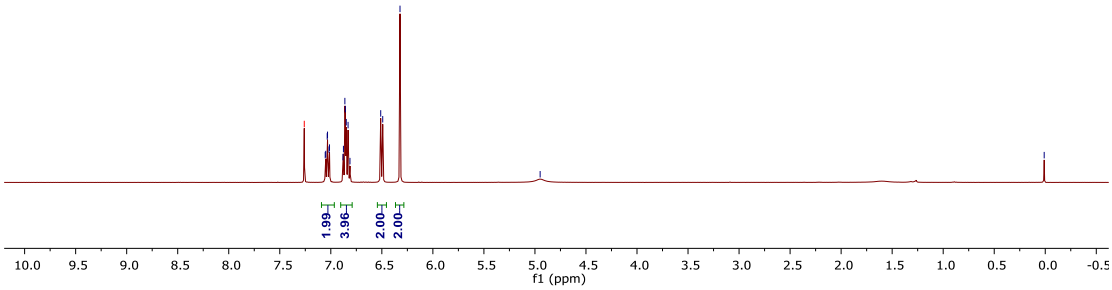


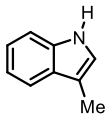
18a, 400 MHz, $CDCl_3$



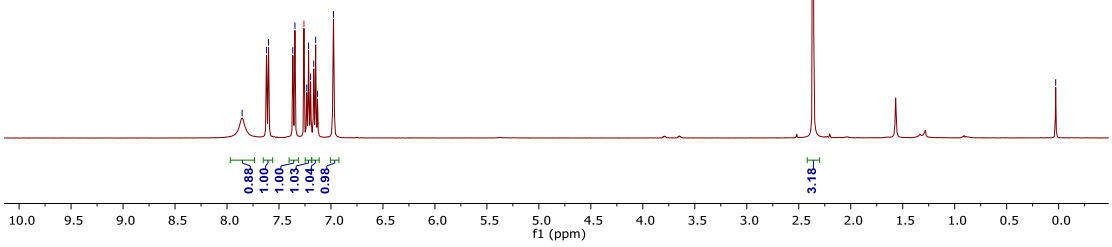


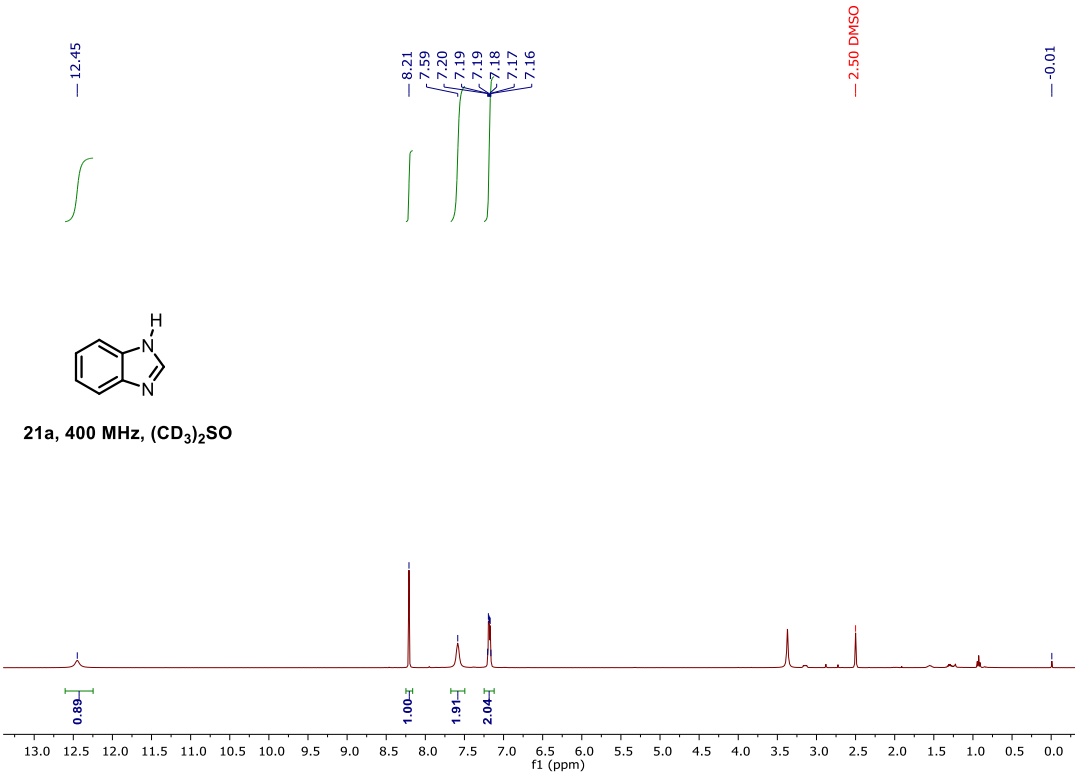
19a, 400 MHz, $CDCl_3$



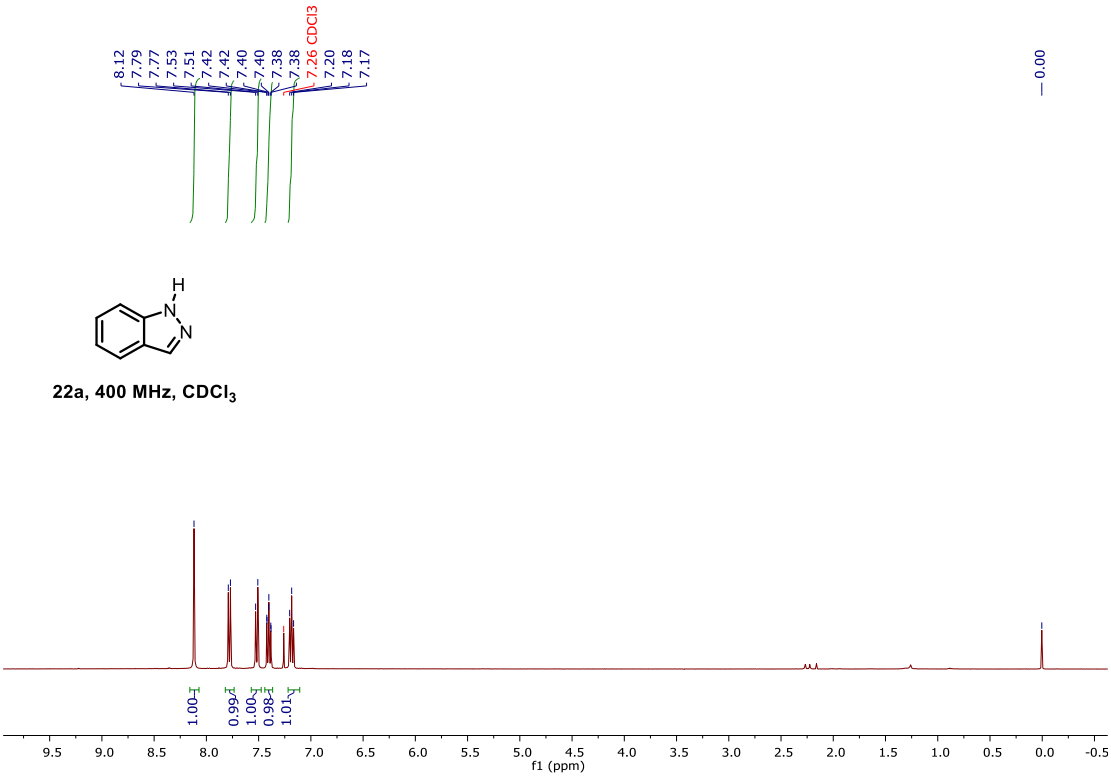


20a, 400 MHz, $CDCl_3$

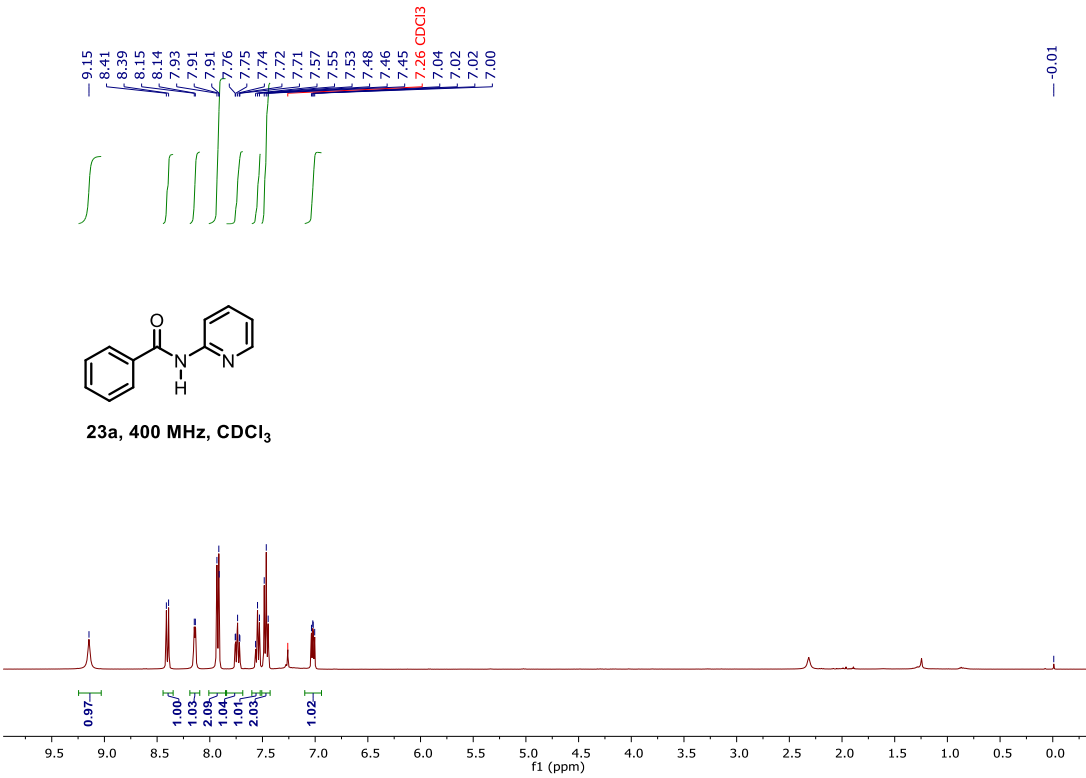




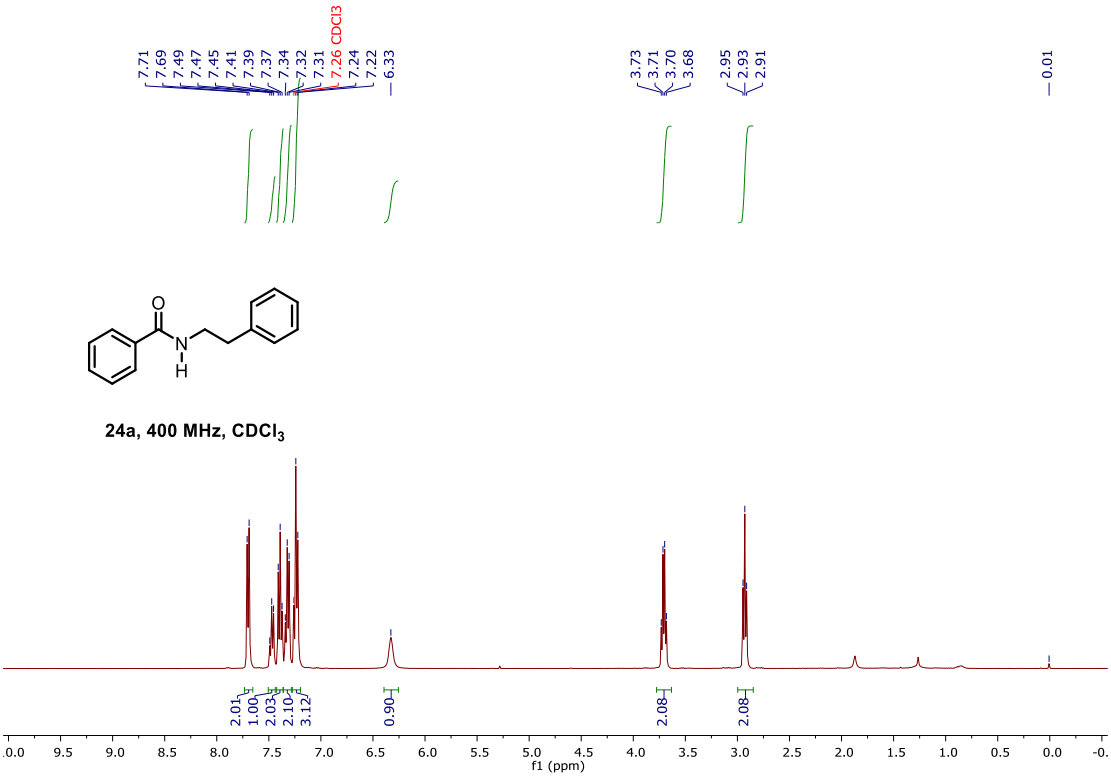
21a, 400 MHz, $(CD_3)_2SO$



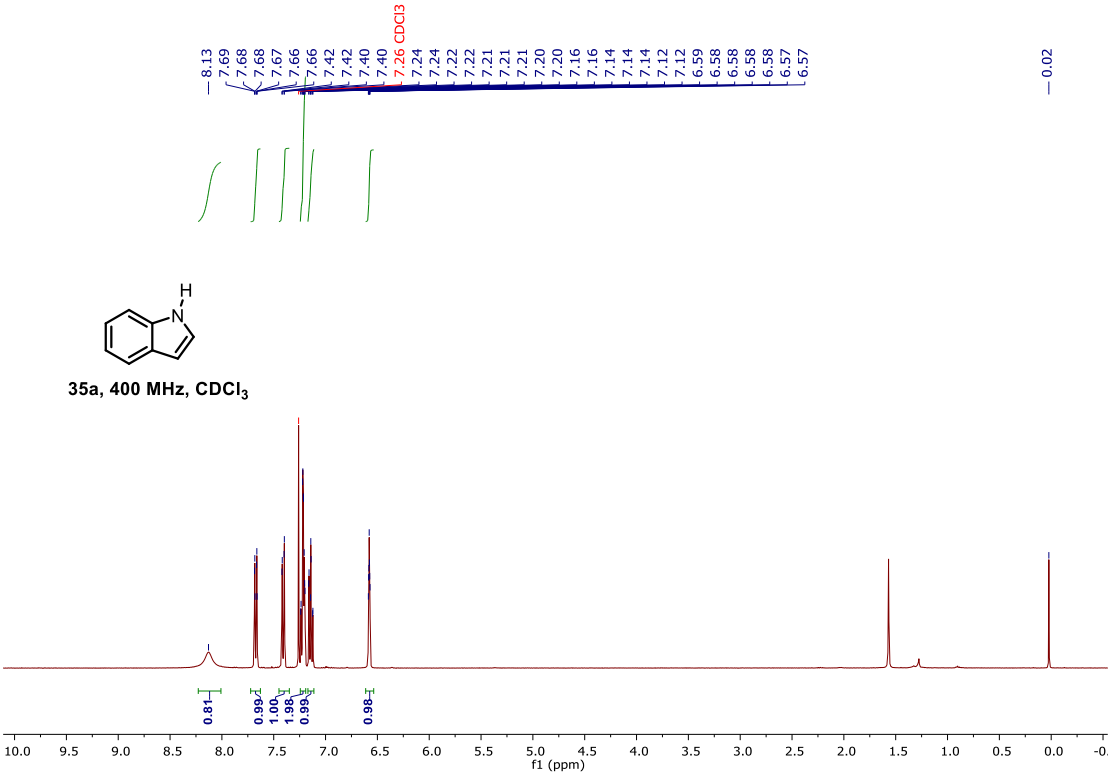
22a, 400 MHz, $CDCl_3$



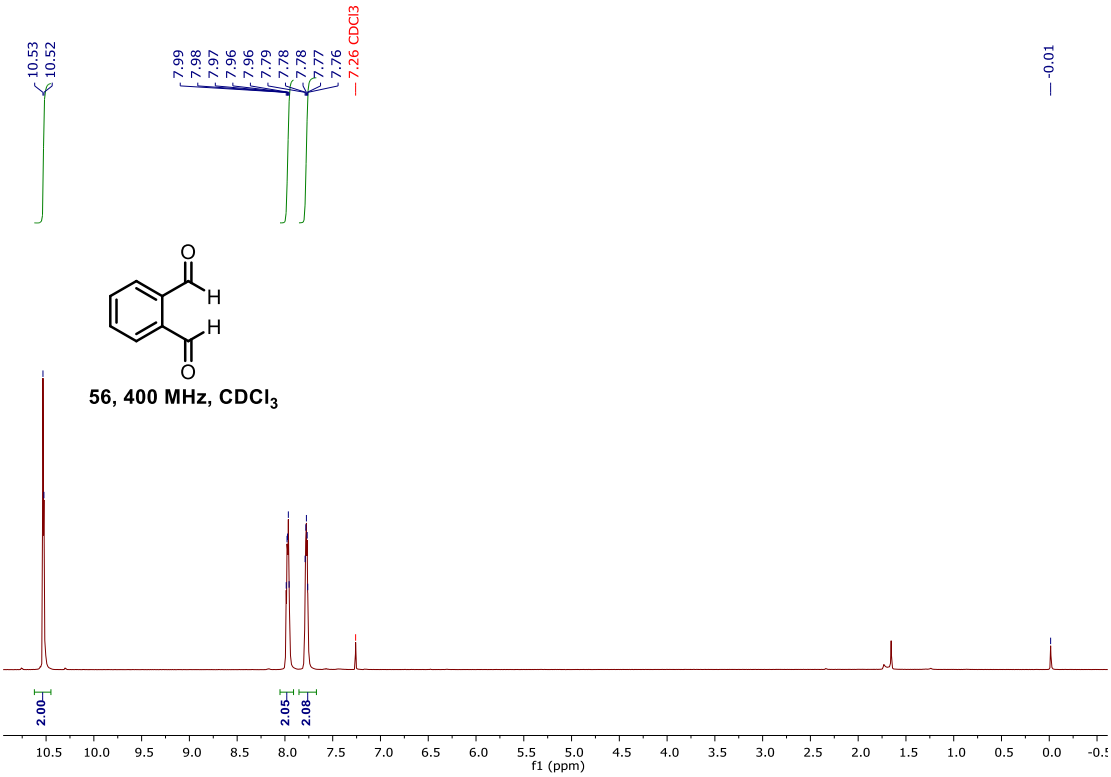
23a, 400 MHz, $CDCl_3$



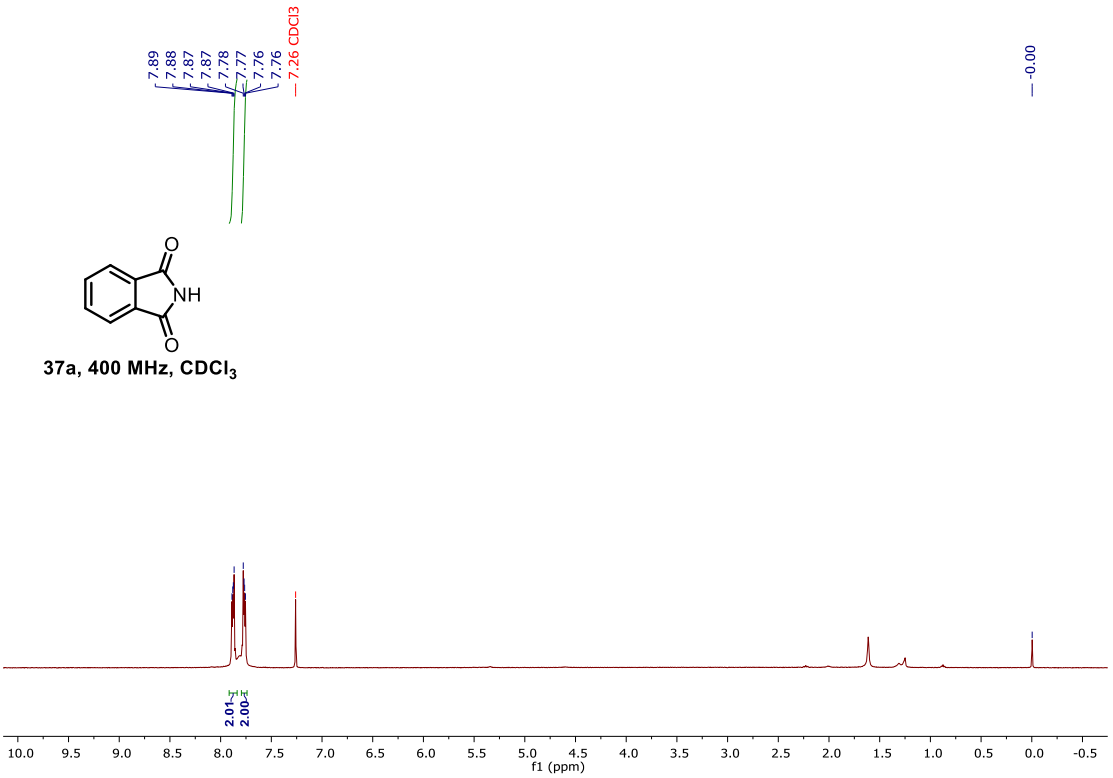
24a, 400 MHz, $CDCl_3$



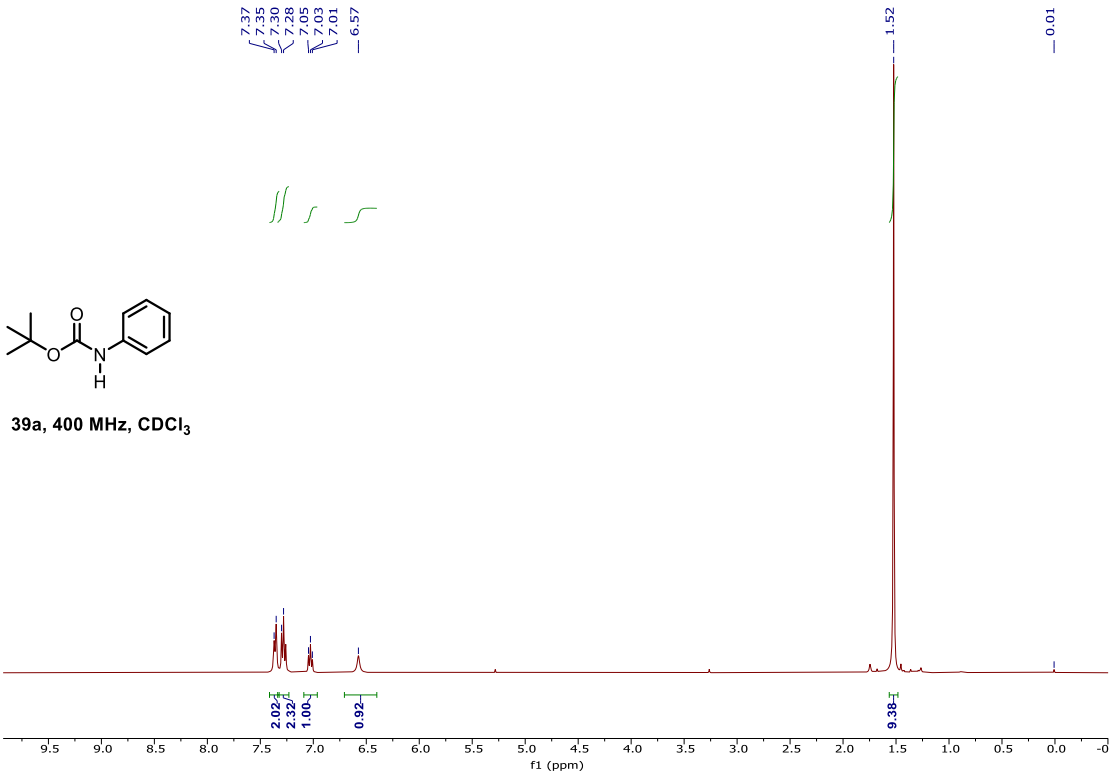
35a, 400 MHz, $CDCl_3$



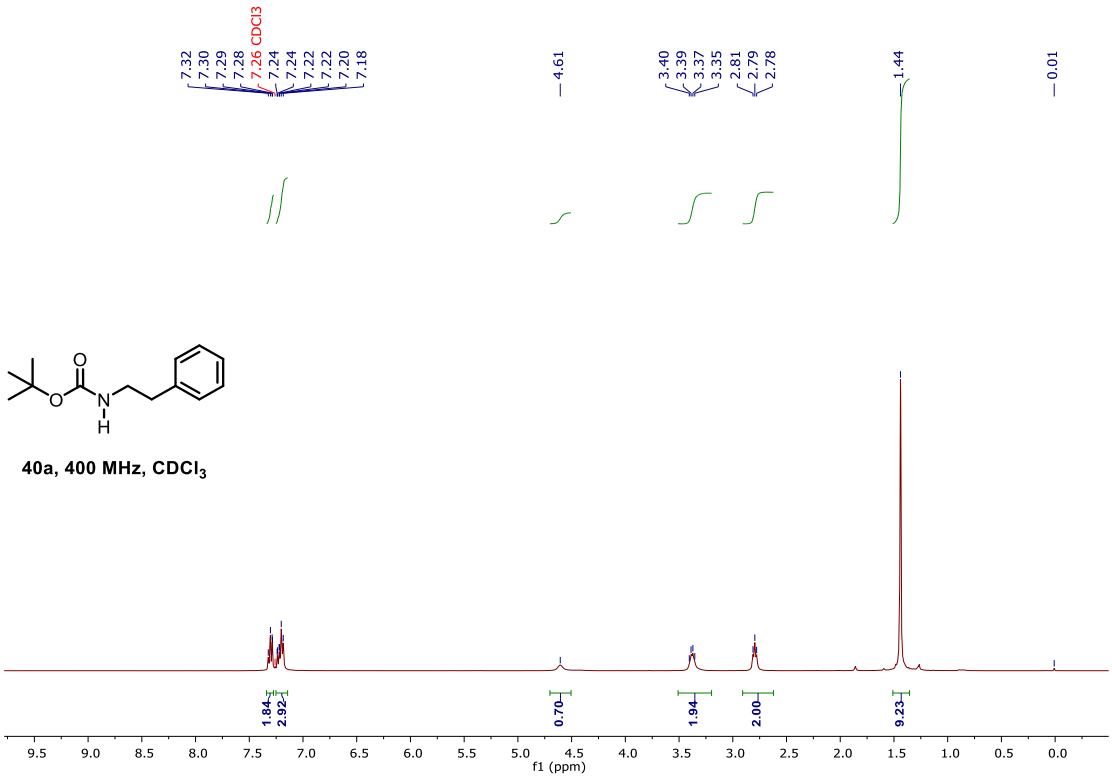
56, 400 MHz, $CDCl_3$



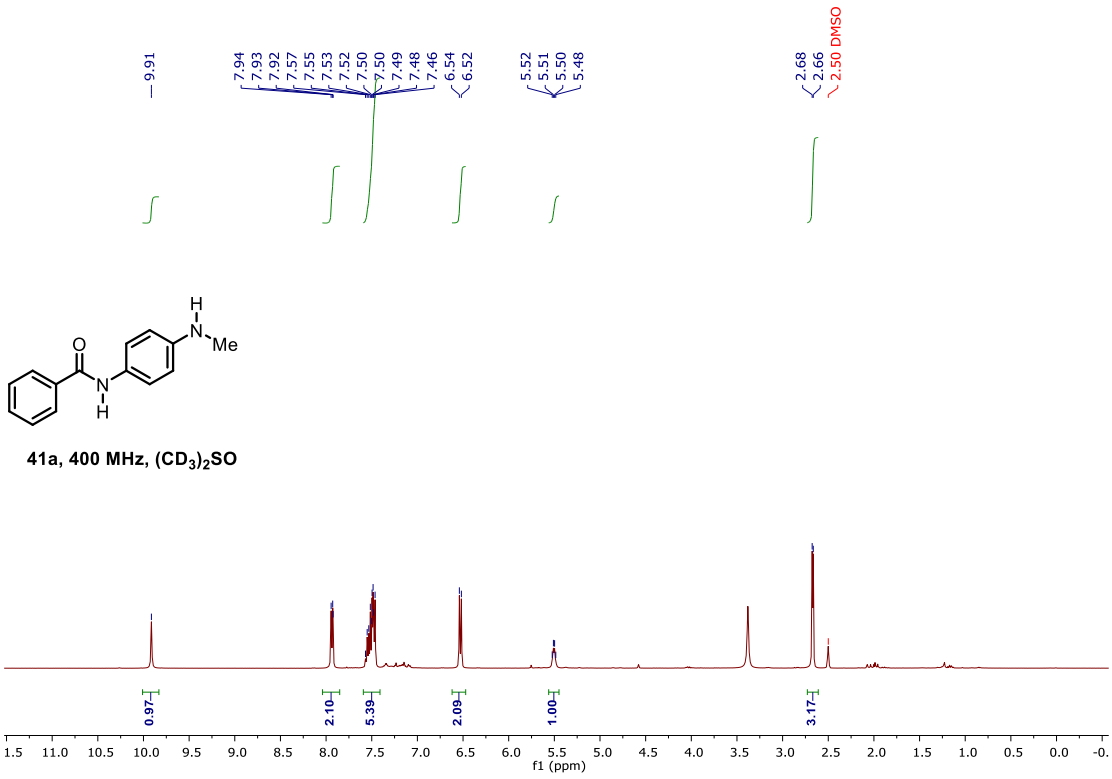
37a, 400 MHz, $CDCl_3$



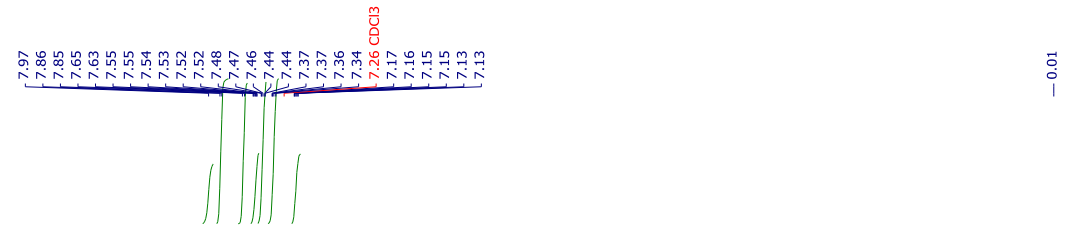
39a, 400 MHz, $CDCl_3$

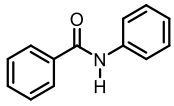


40a, 400 MHz, $CDCl_3$

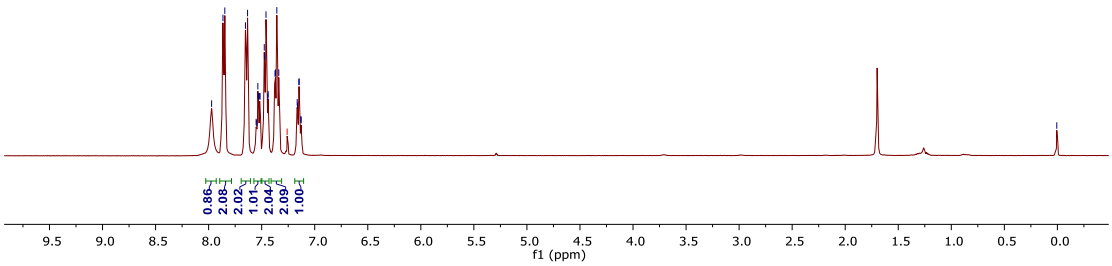


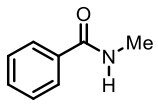
41a, 400 MHz, $(CD_3)_2SO$



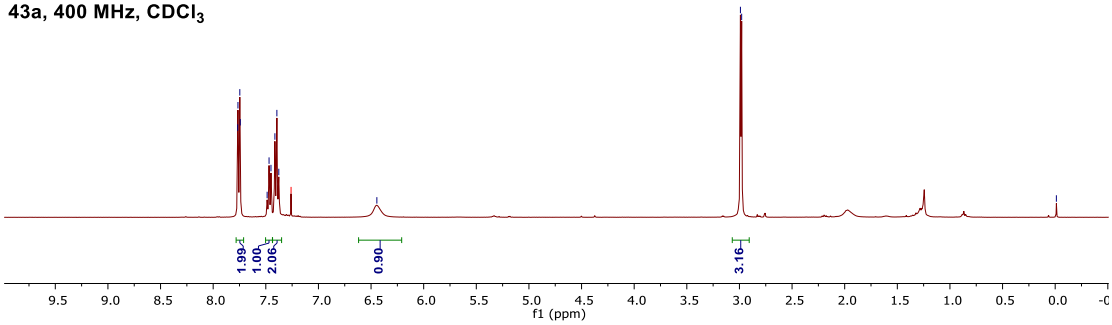


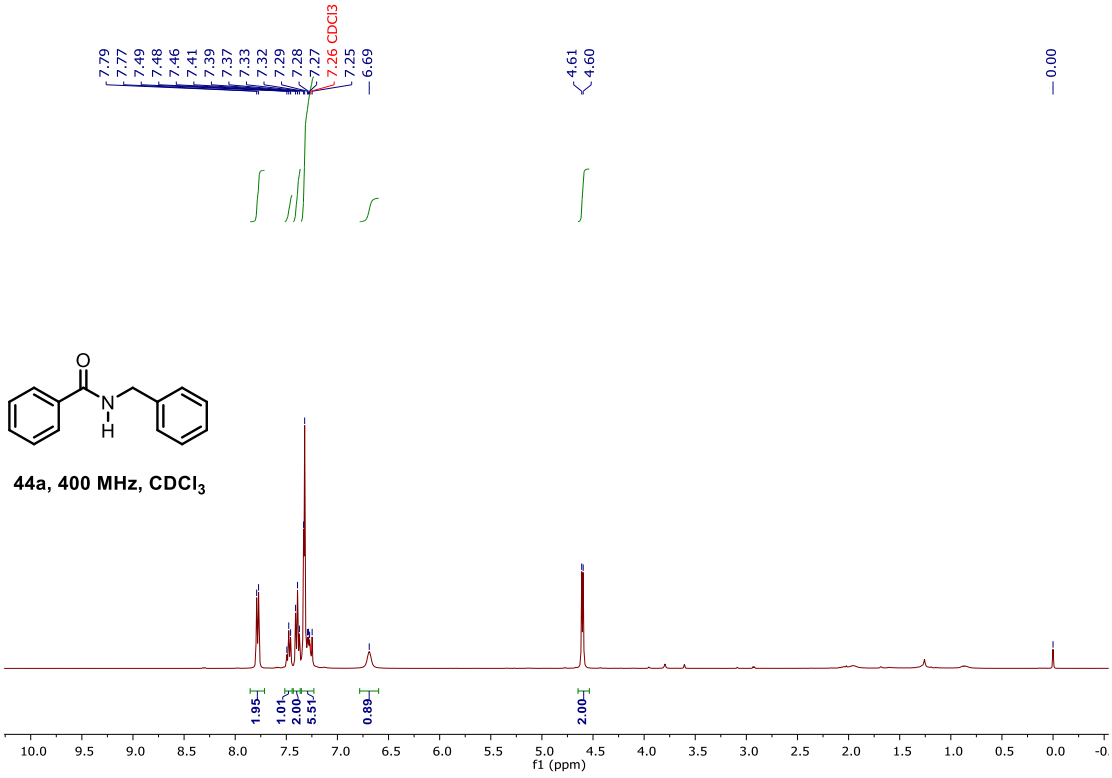
42a, 400 MHz, $CDCl_3$



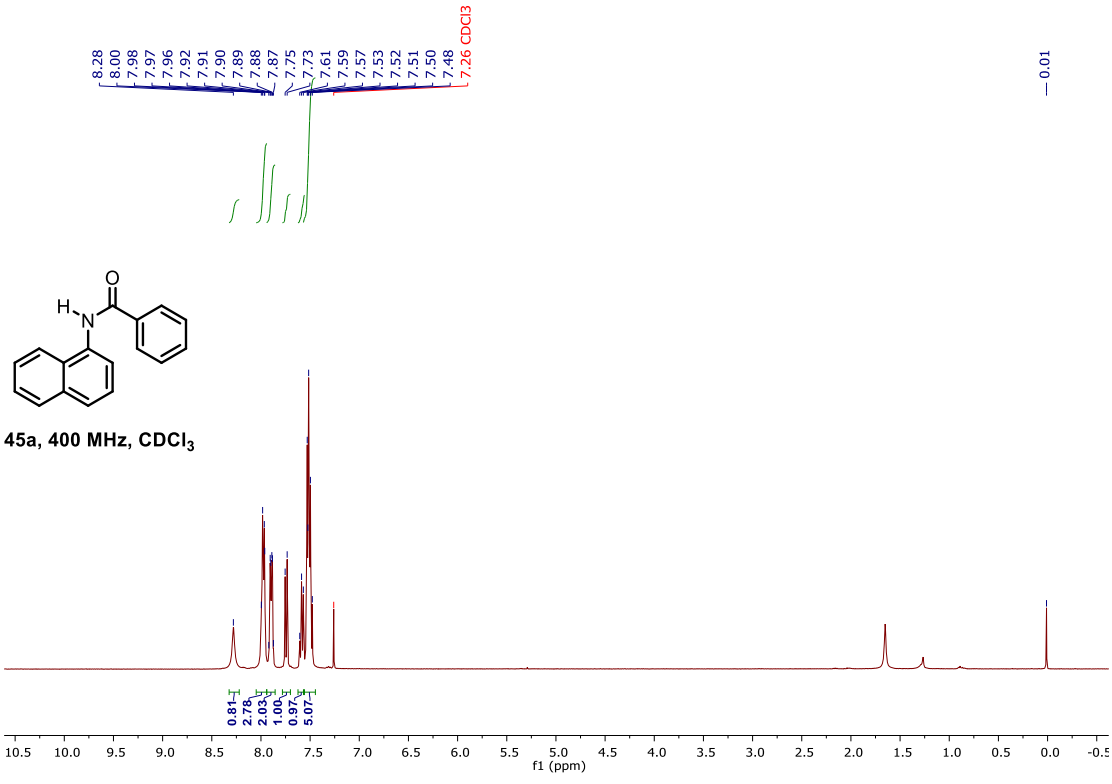


43a, 400 MHz, $CDCl_3$

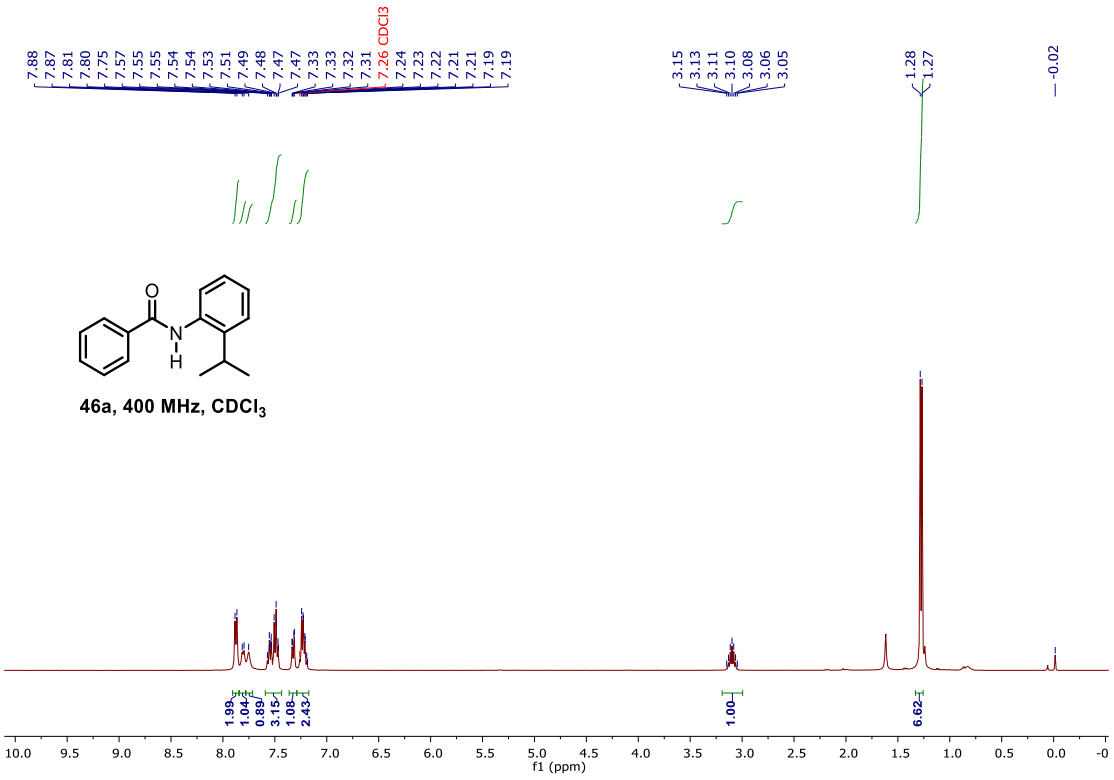




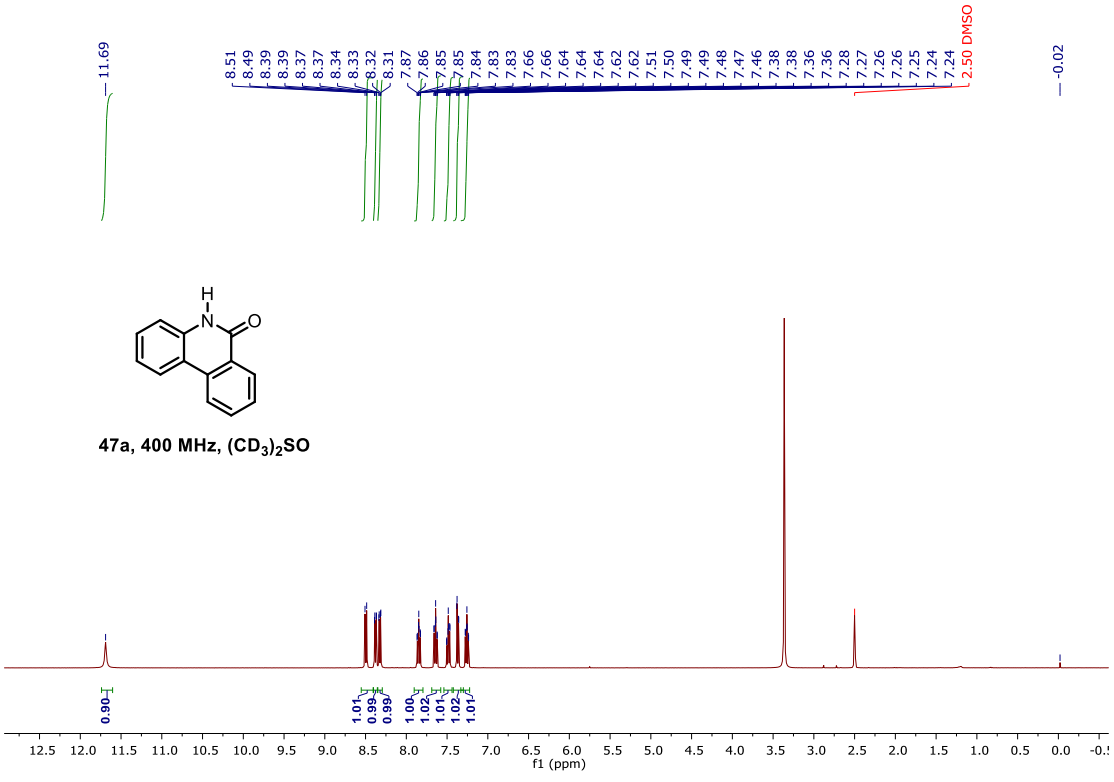
44a, 400 MHz, $CDCl_3$



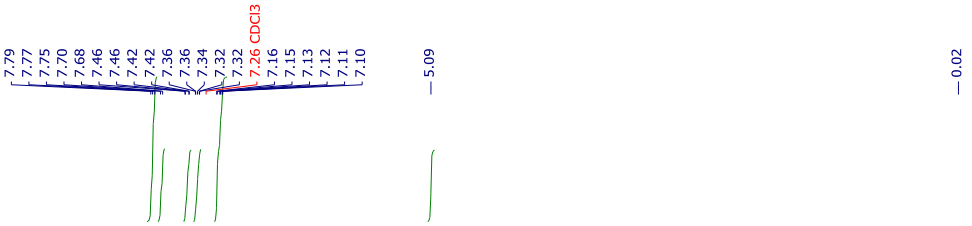
45a, 400 MHz, $CDCl_3$

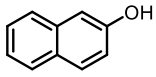


46a, 400 MHz, $CDCl_3$

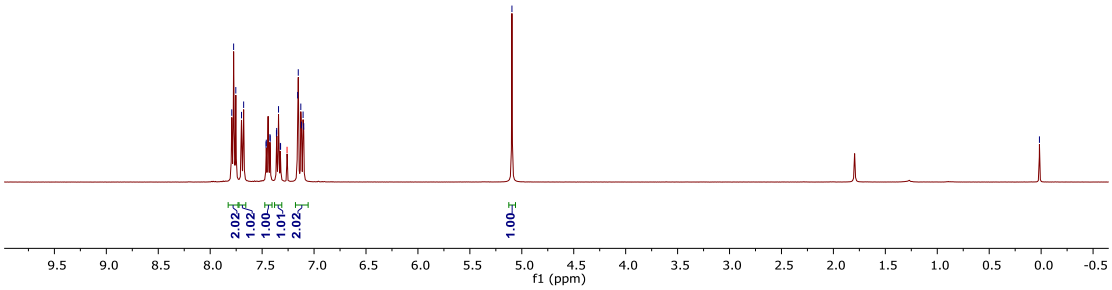


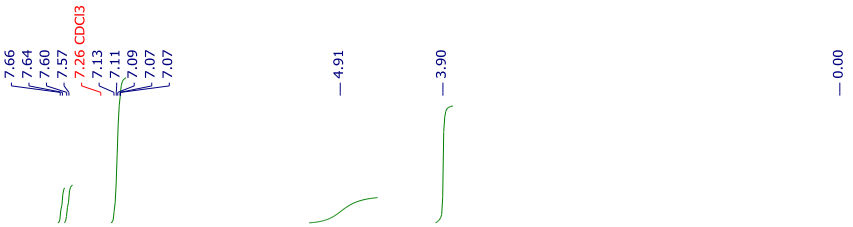
47a, 400 MHz, $(CD_3)_2SO$

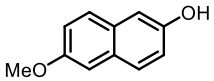




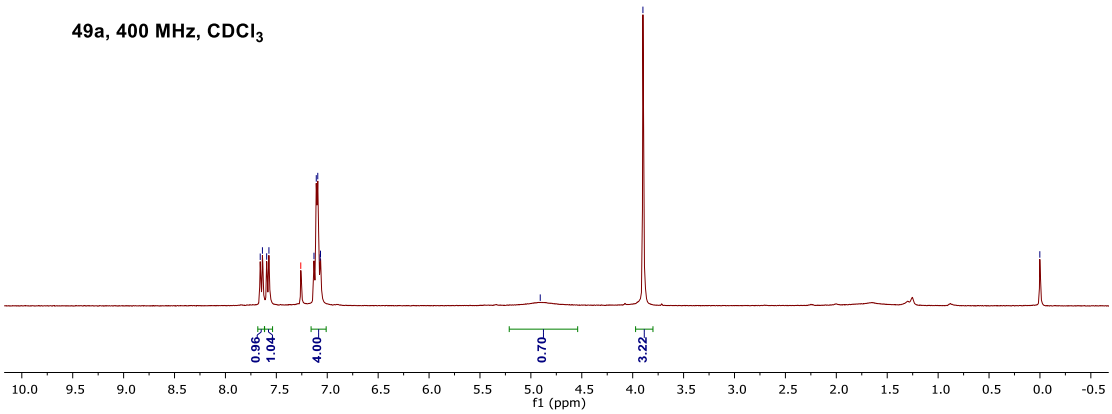
48a, 400 MHz, $CDCl_3$

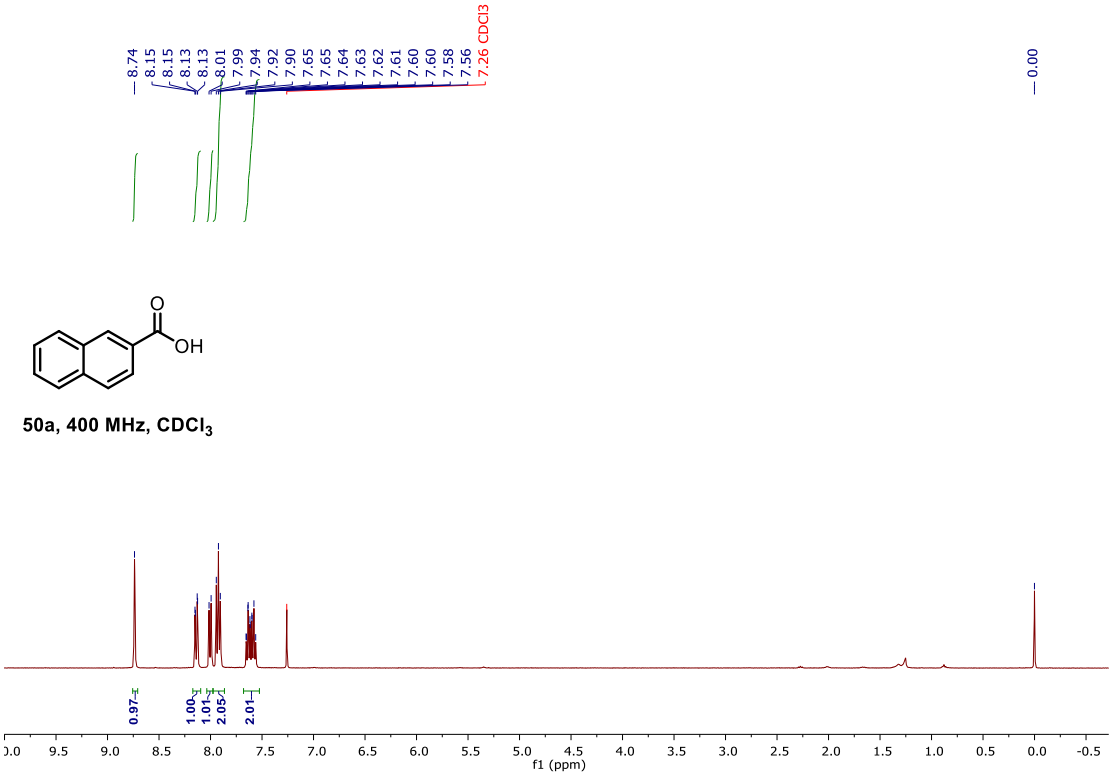




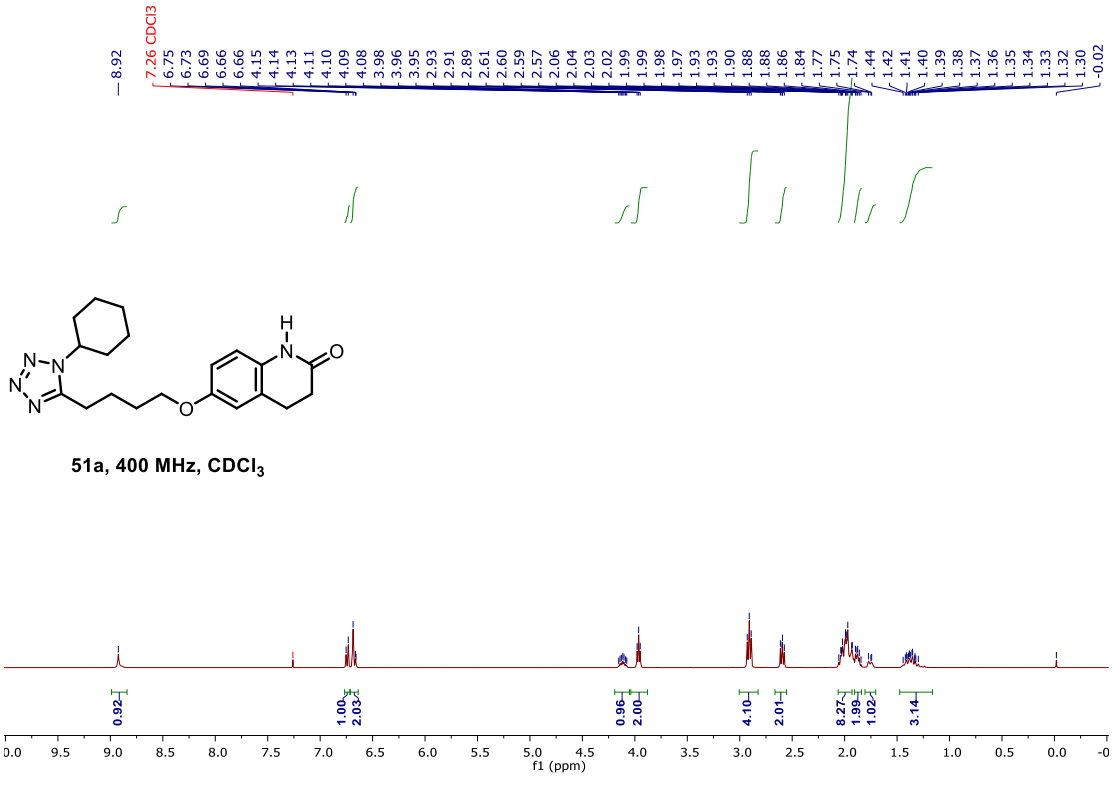


49a, 400 MHz, $CDCl_3$

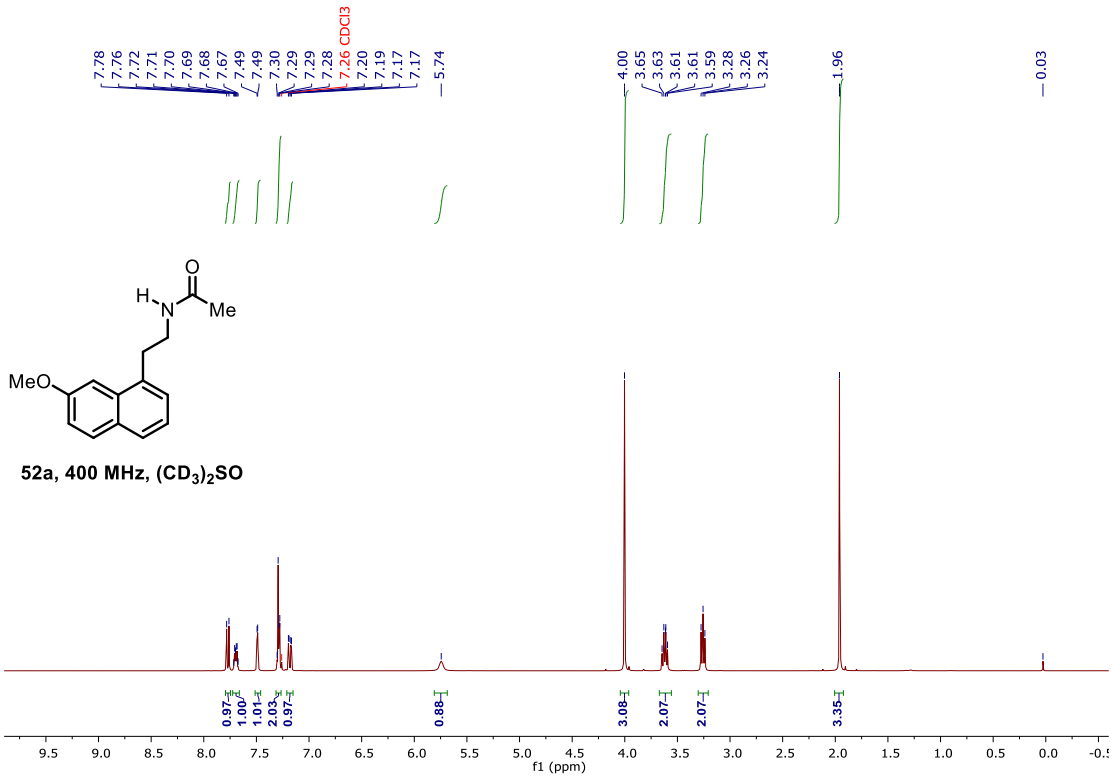




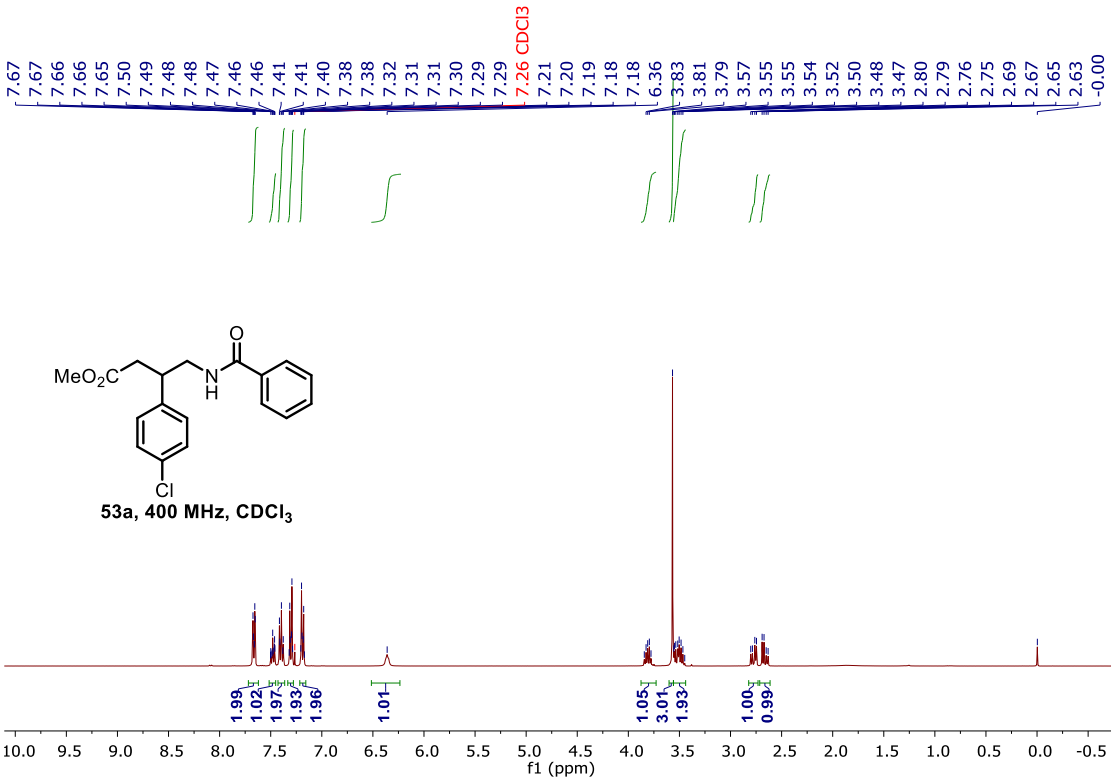
50a, 400 MHz, $CDCl_3$

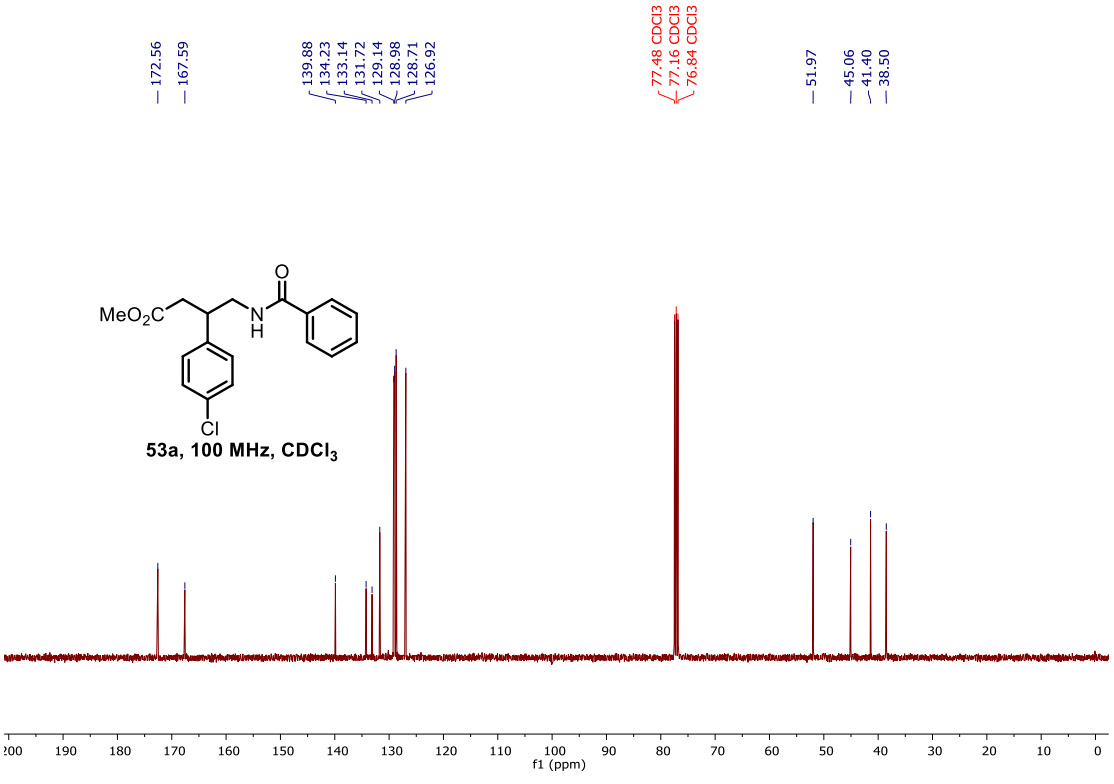


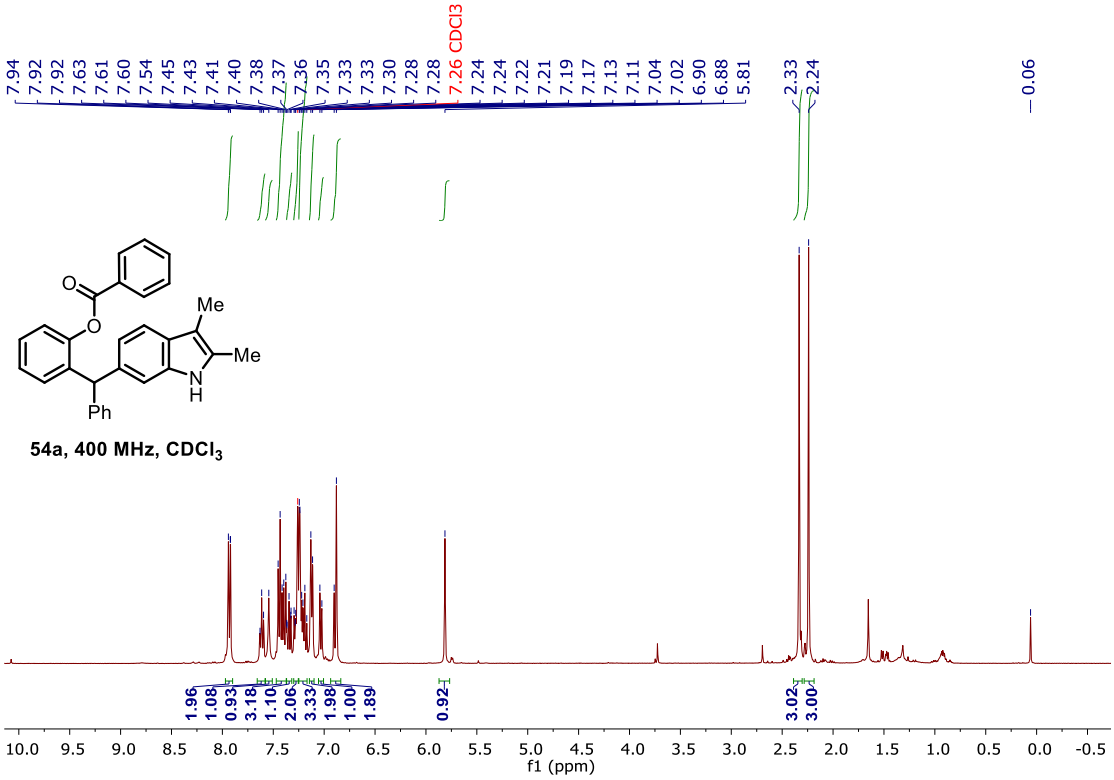
51a, 400 MHz, $CDCl_3$



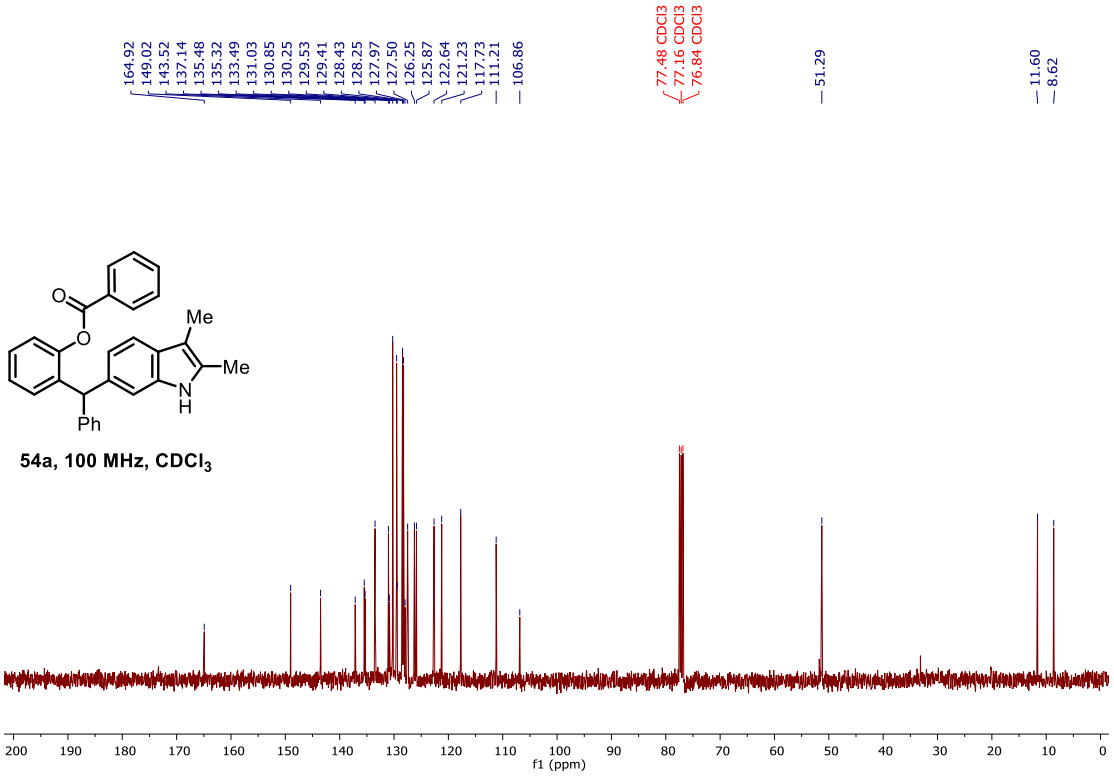
52a, 400 MHz, $(CD_3)_2SO$


7.67 7.67 7.66 7.66 7.65 7.50 7.49 7.48 7.48 7.47 7.46 7.46 7.41 7.41 7.40 7.38 7.38 7.32 7.31 7.31 7.30 7.29 7.29 7.26 CDCl3 7.21 7.20 7.19 7.18 7.18 6.36 3.83 3.81 3.79 3.57 3.55 3.55 3.54 3.52 3.50 3.48 3.47 2.80 2.79 2.76 2.75 2.69 2.67 2.65 2.63 -0.00
MeO2C
N
H
O
Cl
53a, 400 MHz, CDCl3
1.99 1.02 1.97 1.93 1.96 1.01 1.05 3.01 1.93 1.00 0.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

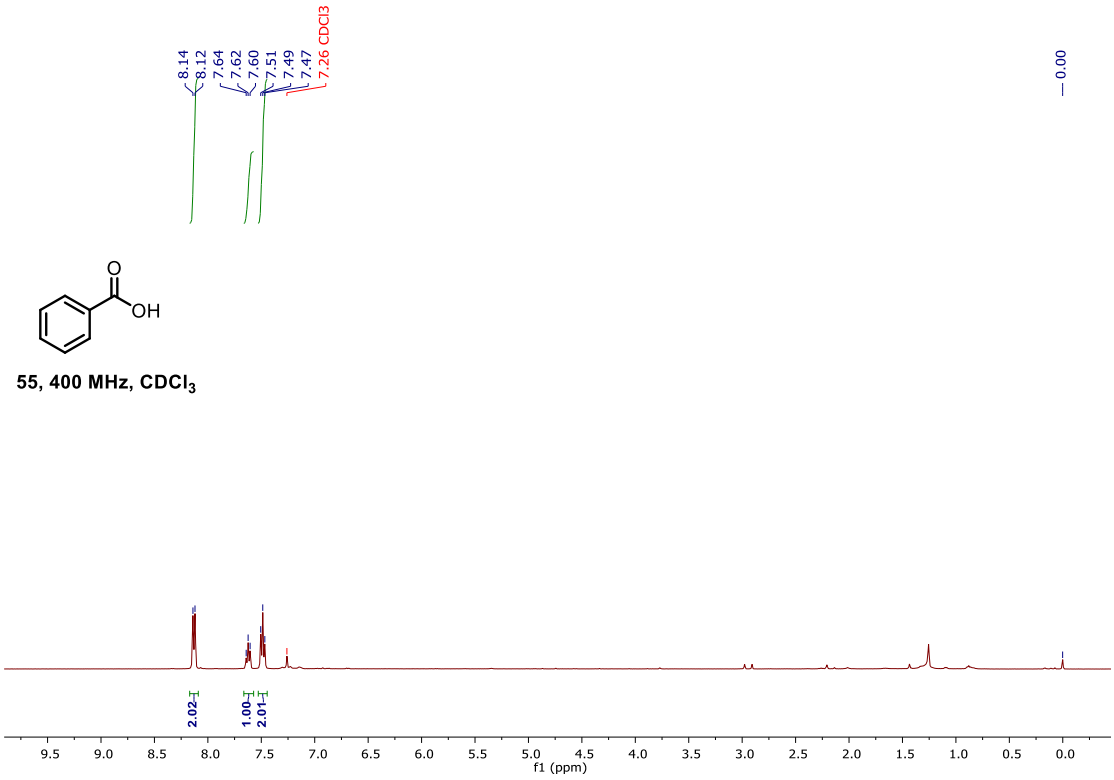

172.56 167.59 139.88 134.23 133.14 131.72 129.14 128.98 128.71 126.92 77.48 CDCl3 77.16 CDCl3 76.84 CDCl3 51.97 45.06 41.40 38.50
MeO2C
N
H
O
Cl
53a, 100 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



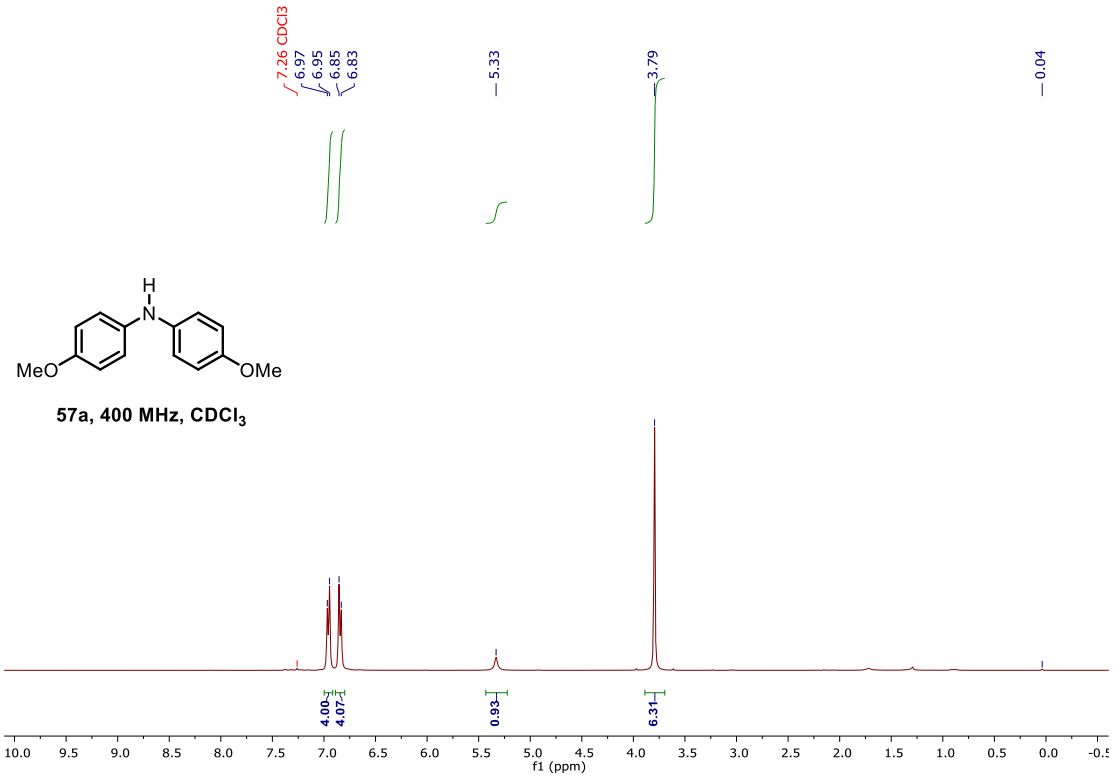
54a, 400 MHz, $CDCl_3$



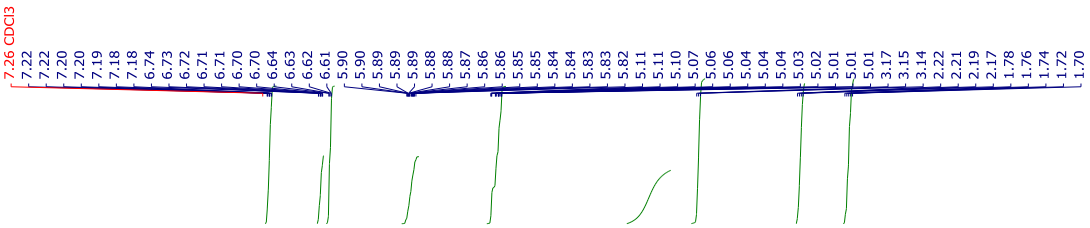
54a, 100 MHz, $CDCl_3$

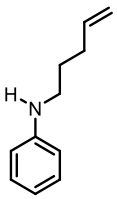


55, 400 MHz, $CDCl_3$

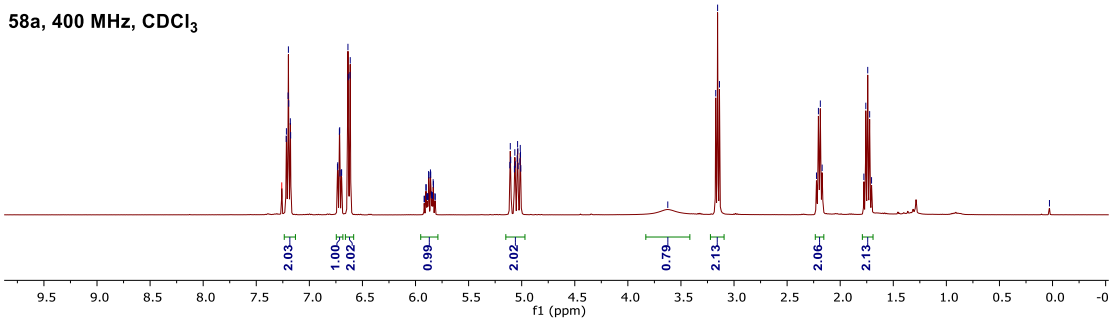


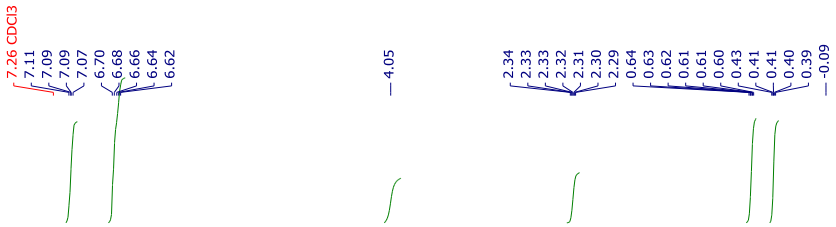
57a, 400 MHz, $CDCl_3$

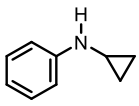




58a, 400 MHz, $CDCl_3$







60a, 400 MHz, $CDCl_3$