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Supporting Information

Engaging hydrazine hydrate as a hydrogen source for cobalt(II) catalysed transfer hydrogenation of nitroaromatics

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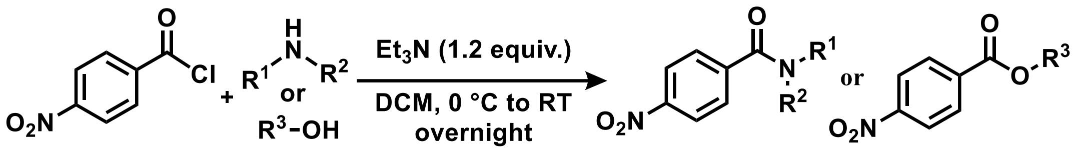
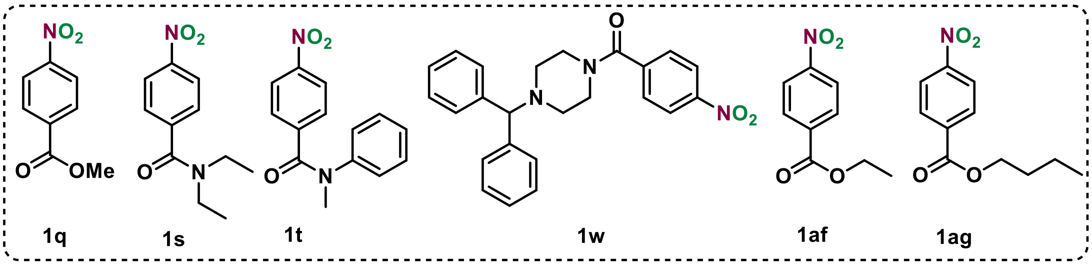
1. General information:

All the reactions were done in oven dried sealed tubes with screw caps. All the reagents, solvents, and substrates were obtained from commercial suppliers and used without any further purification or distillation. Thin layer chromatography (TLC) was performed on silica gel 60 F_{254} (Merck) with detection under UV-light. Chromatography separation was performed on silica gel (60-120) mesh. ^{1}H, ^{13}C NMR spectra were performed using Bruker 400 MHz spectrometers in ppm (parts per million). NMR spectra were recorded in $CDCl_3$ (referenced to 7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C) and DMSO-d_6 (referenced to 2.50 ppm for ^{1}H and 39.52 ppm for ^{13}C). Tetramethyl silane (TMS) was used as an internal standard in ^{1}H, ^{13}C NMR spectra, chemical shifts (δ) are reported in parts per million, coupling constant (*J*) in hertz. The abbreviations used for the peak multiplicity are as follows: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectra (HRMS) were recorded on the TOF-Q analyzer. All the Nitro compounds were purchased commercially and used without any purification.

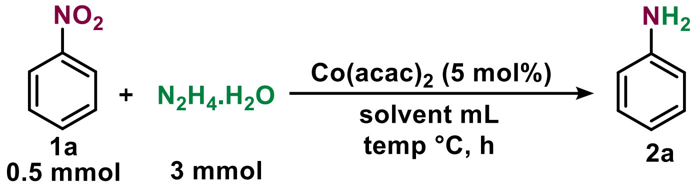
2. Synthesis of Amides and Esters containing Nitro compounds[1]:



4-Nitrobenzoyl chloride 1 g (1.0 equiv.) was added drop-wise to a rapidly stirred solution of the corresponding amines or alcohols (1.2 equiv.) and triethylamine (1.2 equiv.) in anhydrous CH_2Cl_2 at 0 °C. The reaction mixture was then allowed to warm up to RT and stirred overnight. The mixture was then diluted with an equivalent volume of CH_2Cl_2 before being transferred to a separation funnel. The combined CH_2Cl_2 layers were then washed with 20.0 mL of saturated $NaHCO_3$. The organic layer was collected, washed with an equivalent volume of brine and dried over anhydrous Na_2SO_4 before being concentrated under reduced pressure. The crude product was purified by silica gel (60-120 mesh) column chromatography to give pure products **1q, 1s, 1t, 1w, 1af, 1ag.**



3. Table.S1 Optimization of the reaction condition.[a]



Entry	Catalyst (5 mol%)	$N_2H_4.H_2O$ (equiv.)	Solvent (mL)	Temp. (°C)	Yield %[g]
1[b].	$Co(acac)_2$	4	Ethanol	100	17%
2[c].	$Co(acac)_2$	4	Ethanol	100	21%
3.	$Co(acac)_2$	4	Ethanol	100	31%
4.	$Co(acac)_2$	8	Ethanol	100	49%
5.	$Co(acac)_2$	8	Toluene	100	62%
6.	$Co(acac)_2$	8	Heptane	100	68%
7.	$Co(acac)_2$	8	*m*-Xylene	100	53%
8.	$Co(acac)_2$	8	CH_3CN	100	67%
9.	$Co(acac)_2$	8	CH_3CN: heptane (1:1)	100	30%
10.	$Co(acac)_2$	8	CH_3CN: H_2O (3:1)	100	91%
11.	$Co(acac)_2$	8	H_2O	100	42%
12.	$Co(acac)_2$	8	CH_3OH: H_2O (3:1)	100	28%
13.	$Co(OAc)_2.4H_2O$	8	CH_3CN: H_2O (3:1)	100	38%
14.	$[CoCp^*(CO)I_2]$	8	CH_3CN: H_2O (3:1)	100	75%
15[d].	$Co(acac)_2$	8	CH_3CN: H_2O (3:1)	100	42%
16[e].	$Co(acac)_2$	8	CH_3CN: H_2O (3:1)	100	90%
17.	-	8	CH_3CN: H_2O (3:1)	100	nd.
18.	$Co(acac)_2$	-	CH_3CN: H_2O (3:1)	100	nd.
19.	$Co(acac)_2$	2	CH_3CN: H_2O (3:1)	100	56%
20.	$Co(acac)_2$	4	CH_3CN: H_2O (3:1)	100	79%
21.	**$Co(acac)_2$**	**6**	**CH_3CN: H_2O (3:1)**	**100**	**89%**
22.	$Co(acac)_2$	6	CH_3CN: H_2O (3:1)	120	81%
23[f].	$Co(acac)_2$	6	CH_3CN: H_2O (3:1)	100	31%

[a]Reaction condition: 0.5 mmol Nitrobenzene, 6 equiv. $N_2H_4.H_2O$, 5 mol% $Co(acac)_2$ and CH_3CN: H_2O (3:1) 3 mL at 100 °C for 12 h. [b]KO^tBu (0.5 equiv.) used as a base. [c]K_2CO_3 (0.5 equiv.) used as a base. [d]2 mol% catalyst used. [e]10 mol% catalyst used. [f]Reaction proceeded for 6 h. [g]Isolated Yield.

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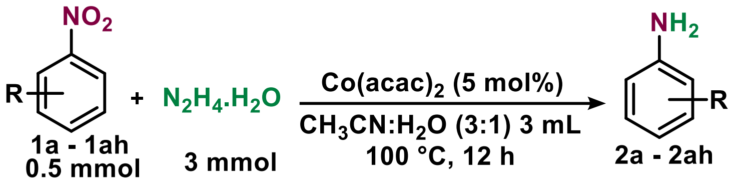
4. General procedure for transfer hydrogenation of nitroarenes.

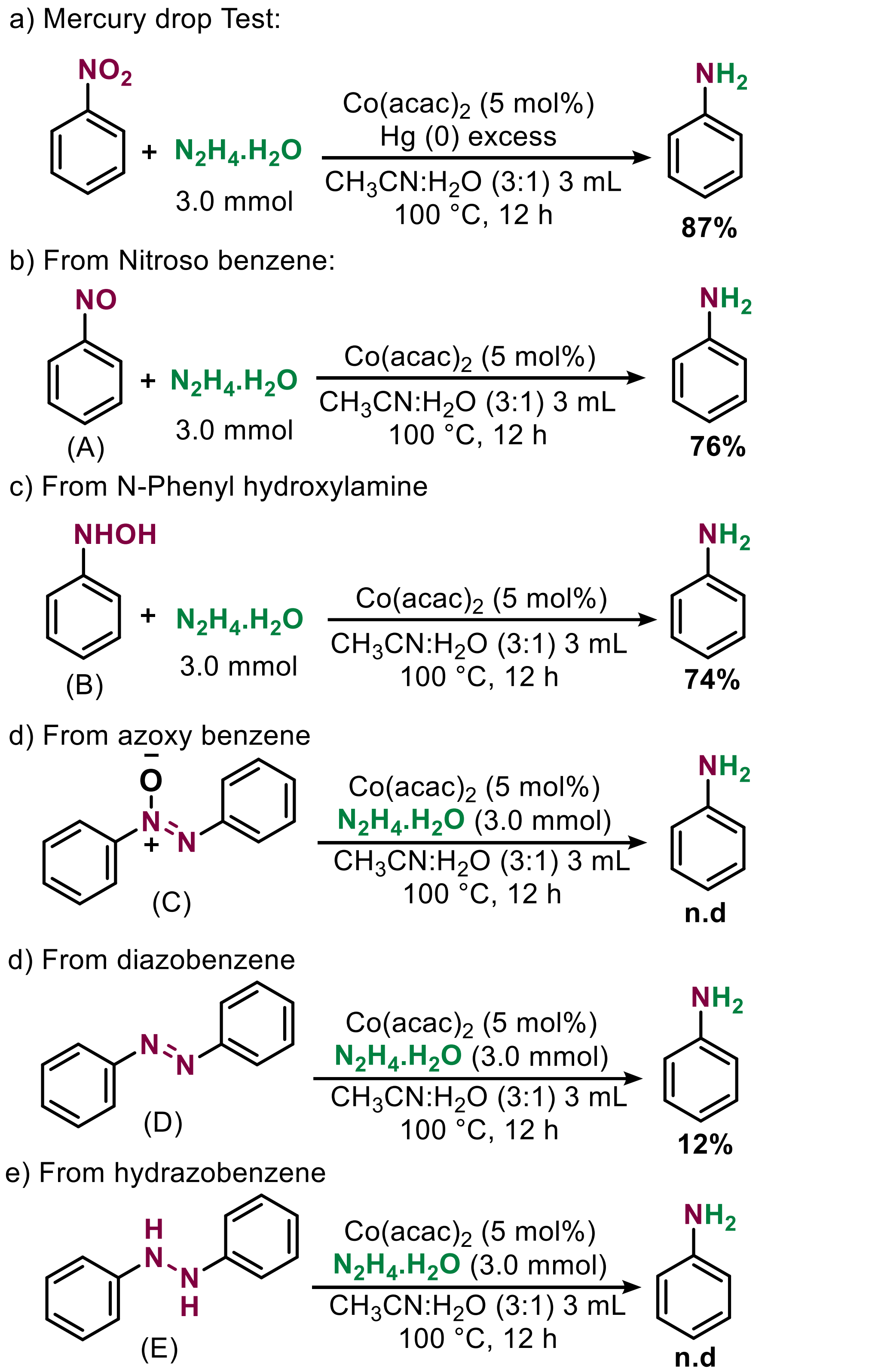


An oven dried, 20 mL screw-cap pressure tube was charged with a magnetic stir bar, 5 mol% $Co(acac)_2$ (6.4 mg), 6 equiv. hydrazine hydrate (75%) 200 µL and 0.5 mmol substrate (Nitro compounds). Then, CH_3CN: H_2O (3:1) 3 mL was added, and the tube was placed in a pre-heated oil bath at 100 °C for 12 hours. After the completion of the reaction, the pressure tube was allowed to cool, and workup was carried out with dichloromethane (3×15 mL) and concentrated. The crude mixture was purified by column chromatography using silica gel (60-120 mesh) with hexane and ethyl acetate as an eluent to obtain pure aniline derivatives **2a** – **2ah**.

5. Gram scale synthesis of aniline (2a)

An oven dried, 100 mL screw-cap pressure tube was charged with a magnetic stir bar, 5 mol% $Co(acac)_2$ (104.4 mg), 6 equiv. hydrazine hydrate (75%) 3.2 mL and 1g of nitrobenzene (8.12 mmol). Then, CH_3CN: H_2O (3:1) 30 mL was added, and the tube was placed in a pre-heated oil bath at (100 °C) for 12 hours. After the completion of the reaction, the pressure tube allowed to cool and the workup was carried out with dichloromethane (3×50 mL) and concentrated. The crude mixture was purified by column chromatography with hexane and ethyl acetate. The pure compound aniline **2a** was obtained 84% yield and further analysed by NMR analysis.

6. Mechanistic Studies



Scheme S1. Mechanistic studies of all possible intermediates in the reduction of Nitrobenzene. Reaction condition: 0.5 mmol of (a) or (b) or (c) or (d) or (e), 6 equiv. $N_2H_4.H_2O$, 5 mol% $Co(acac)_2$ and CH_3CN: H_2O (3:1) 3 mL at 100 °C for 12 h. n.d - Not detected.

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7. Computational Details:

All the computational calculations were performed using the Gaussian 16, Revision C.02 software[2] using M06-L[3] functional with the Def2-SVP[4] basis set using default spin. Based on the literature reports, we have chosen the M06-L functional to treat 3d transition metal systems for the transfer hydrogenation reactions.[5] Geometry optimizations are performed at M06-L level of theory. Following frequency calculations, ground states and transition states were identified by zero or one imaginary frequency, respectively.[6a] The Quadratic Synchronous Transit (QST3) method has been used to locate the transition state. Intrinsic reaction coordinate (IRC) calculations were carried out to verify transition states further. Thermally free energy-corrected electronic energy has been used to plot the reaction energy profile.

7.1 Mechanistic studies using DFT calculation:

To obtain detailed insights into the reaction mechanism, we performed computational studies. The oxidation state of the metal centre was analysed using orbital localization analysis *via* localizing occupied orbital analysis, orbital composition analysis, and evaluation of cobalt oxidation state by the localized orbital bonding analysis (LOBA) method.[6b] Initially, we optimize the structures of the catalyst, nitrobenzene, intermediates, and the hydrogen molecule to obtain the equilibrium structure in **Figure S1**.

First step, Co(acac)$_2$ underwent a reaction with the H_2 molecule produced from hydrazine hydrate led to the formation of reduced Co^{I}(acac)$_2$ complex (**IN1**) and the formation of Co-H[6c,6d] species occurring with the free energy of +8.36 kcal/mol, followed by nitrobenzene **1a** coordination to the **IN1** intermediate provided to **IN2** with the oxidation state of Co(I) and free energy would be a +12.28 kcal/mol**.** To identify the transition state (TS1), the QST3 method has been employed. This is further validated by IRC, both forward and backward direction connectivity of the two intermediates. First hydride transfer from the Co centre to the nitrobenzene **1a** is rendered transition state complex **TS1** with the energy of +36.44 kcal/mol. The calculated energy barrier for this step is found to be 24.16 kcal/mol, and this was the lowest among all, this would be the slowest step of the reaction and is considered to be the rate-determining step (RDS). From **TS1**, it is further transformed into **IN3** intermediate with -9.52 kcal/mol *via* oxygen coordination to the cobalt (III) state. Next step, the releasing of nitroso molecules **A** and a reaction of hydrogen molecules to the catalysis led to Co(I)-H complex with the association of nitroso complex at **IN4** intermediate with the free energy of -10.44 kcal/mol, followed by second transfer hydrogenation rendered **IN5** with Co-(III) state. Proton transfer at

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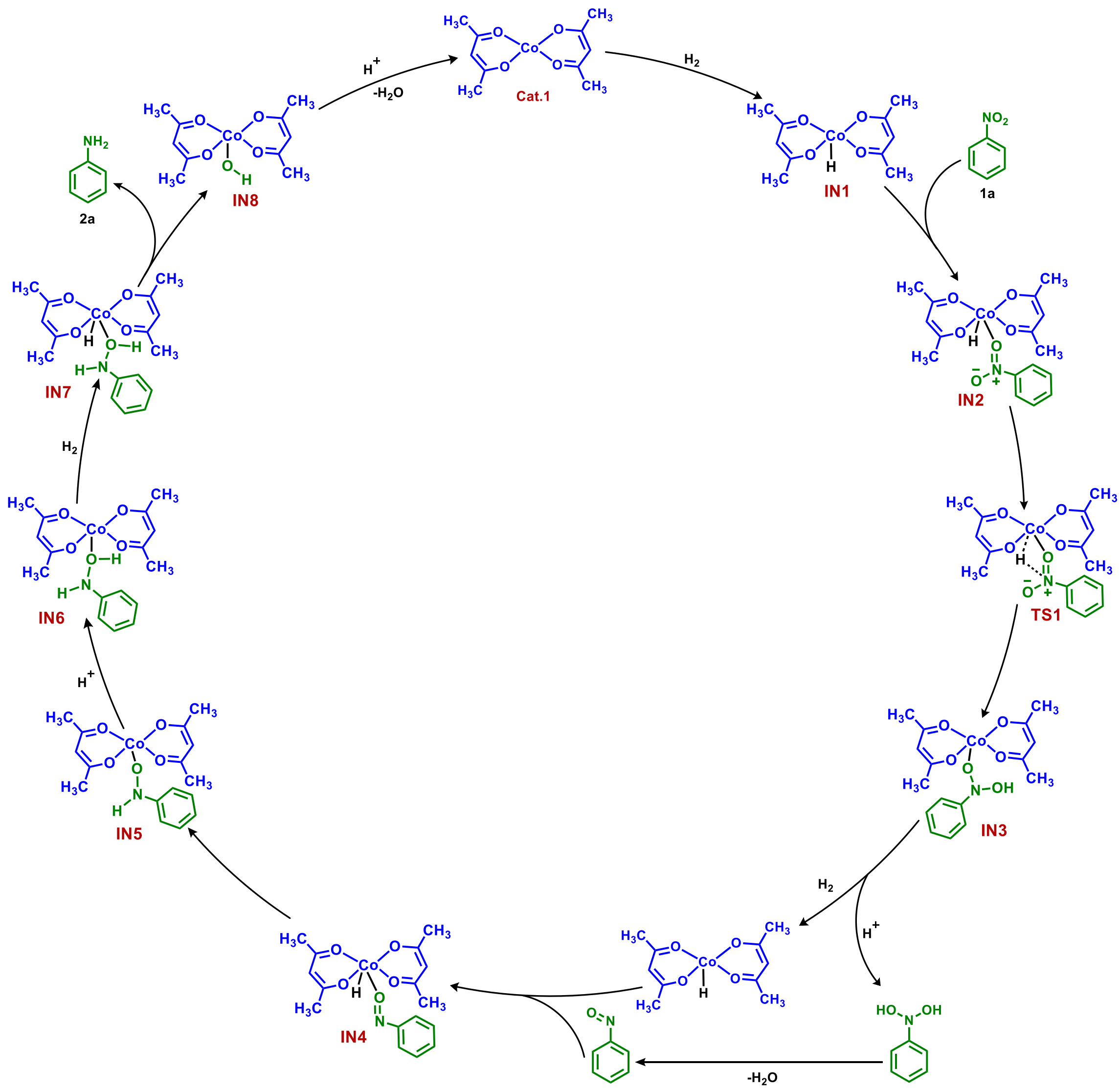
IN5 produced **IN6** with a free energy of -43.07 kcal/mol and the third hydride transfer to hydroxylamine **B** at **IN7** with a free energy of -26.03 kcal/mol produced aniline (**2a**) and formation of the intermediate **IN8** with a free energy of -77.32 Kcal/mol**.** The intermediate **IN8** underwent proton transfer and produced catalyst regeneration and water molecules, which completed the overall catalytic cycles in **Scheme S2**. Besides, the control experiments were conducted to trap the intermediates using the standard reaction conditions for a 1-hour duration, and the crude reaction mixture was analysed by ESI-HRMS. The major intermediate hydroxylamine **B** was found, and it suggested the transfer hydrogenation of nitro to amine derivatives *via* direct pathway (path a), which is aligned with the computationally predicted mechanistic pathways.



Scheme S2. Plausible reaction mechanism in detail for the transfer hydrogenation of nitro to amine.

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7.2 Energy profile diagram:

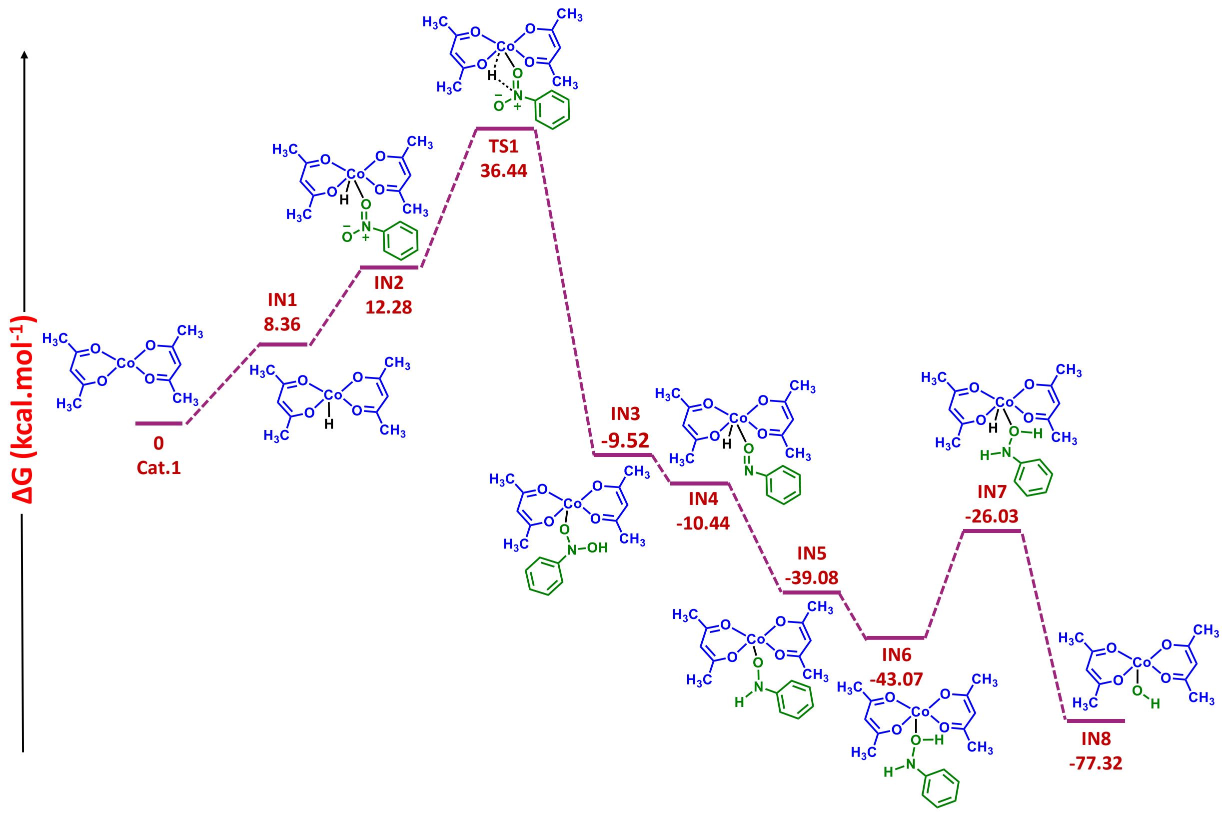

Figure S1. Free energy profile computed at M06-L/def2-SVP for cobalt-assisted hydrogenation of nitrobenzene derivatives. All the energy values in kcal/mol are with respect to Cat-1.

7.3 DFT insights for the condensation pathway for nitrobenzene reduction:

The nitrobenzene proceeds through the direct pathway via intermediates such as nitroso, hydroxylamine as supported by the experiments. The alternative pathway of the azoxybenzene **C**, azobenzene **D** route is not favorable. The initial and final geometries of the azobenzene interaction with the Co-catalyst are shown in **Figure S2**. As inferred from the final energy minimized structure of the azobenzene, the catalyst reveals that the azobenzene moiety has been detached from the catalyst and moved a little further from the active site. Since the azobenzene moiety is not in the vicinity of the catalytically active site, further the hydride transfer is unfavorable.

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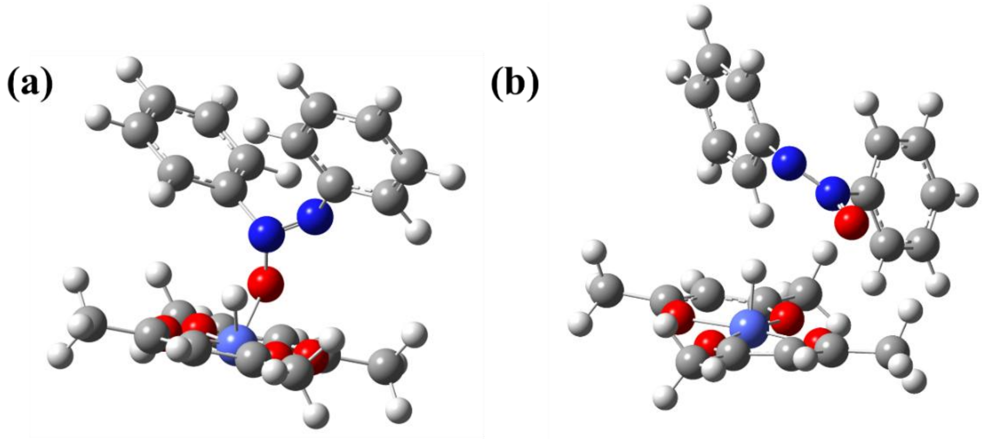
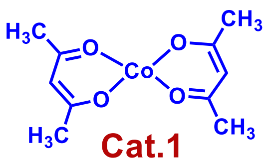


Figure S2. The initial structure used for the azobenzene binding with the catalyst (**a**). The final structure was obtained after the energy minimization (**b**).

7.4 Cartesian coordinates of all the optimized structures and the thermal free energy corrected electronic energy.

Table S2.



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H	-0.00069400	4.30354200	0.00000000
C	-0.00019200	-2.53992200	-1.23018900
C	-0.00022300	-3.21280600	0.00000000
C	-0.00019200	-2.53992200	1.23018900
H	-0.00062700	-4.30353700	0.00000000
O	0.00050500	1.27002200	-1.35885300
O	0.00050500	1.27002200	1.35885300
O	0.00042500	-1.27001800	-1.35885700
O	0.00042500	-1.27001800	1.35885700
Co	0.00061300	-0.00000500	0.00000000

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C -0.00061000 -3.30805600 -2.51484500

H 0.87790000 -3.03193200 -3.11438000

H -0.00081600 -4.39278900 -2.36122200

H -0.87916200 -3.03130100 -3.11399400

C -0.00061000 -3.30805600 2.51484500

H -0.00081600 -4.39278900 2.36122200

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H -0.87916200 -3.03130100 3.11399400

C -0.00073100 3.30805700 2.51484600

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H -0.00111700 4.39279000 2.36122400

H -0.87930100 3.03115000 3.11390200

C -0.00073100 3.30805700 -2.51484600

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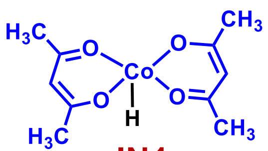
Table S3.



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O -0.09446500 1.27948700 -1.37700000

O -0.09443900 -1.27944800 1.37707600

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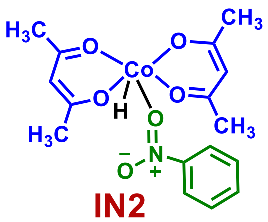
Table S4.



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C -1.27443400 2.91596700 0.56594800

C -1.28077700 1.91174400 1.55964600

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O	-0.84536200	1.58673500	-1.37772000
O	-1.09656600	0.68343600	1.35555400
Co	-0.85881700	-0.11369300	-0.49622700
C	-1.08092200	3.87585800	-1.73810300
H	-1.88824000	3.74736900	-2.47255100
H	-1.22027900	4.83190200	-1.22090000
H	-0.14547500	3.91011500	-2.31317600
C	-1.52081200	2.31345800	2.98968900
H	-1.64057300	3.39482700	3.12425900
H	-2.42145500	1.80759700	3.36510900
H	-0.69009600	1.96323300	3.61790700
C	-1.38702900	-3.87271400	1.22305600
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H	-2.26427100	-4.51022000	1.37852200
H	-0.64898500	-4.41810000	0.61908300
C	-4.93301300	-0.85930000	-0.64501200
H	-5.55967000	-1.69949900	-0.32665500
H	-5.27000000	0.05332300	-0.13476800
H	-5.08352600	-0.68616300	-1.71939800
H	-0.71067700	-0.76171500	-1.80219000
O	1.04530900	0.09376500	-0.25188100
N	1.91106200	-0.73202200	-0.61978300
C	3.27533200	-0.40853700	-0.22812900
C	4.29388300	-1.26824800	-0.63820600
C	3.52628200	0.73257200	0.53491100
C	5.60219200	-0.97093300	-0.27241400
H	4.04324000	-2.14680300	-1.23234600
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H	2.69859100	1.37448600	0.83471800

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C	5.87633400	0.16590400	0.49009200
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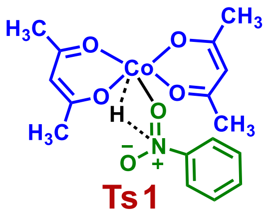
Table S5.



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C	-1.02992000	2.66308700	-0.66910100
C	-1.92451200	2.79732800	0.40545200
C	-2.20701600	1.79247900	1.35102200
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O	-0.78236100	-1.79418100	0.64511900
O	-0.37778200	1.61729300	-0.97339100
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H	-3.96376400	1.39283600	2.50231400
H	-2.59461600	1.96233600	3.44634500

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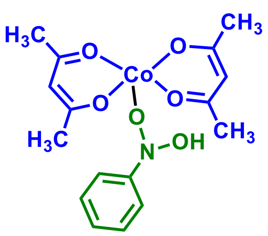
Table S6.



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C -0.55293200 2.57180600 -0.88840900

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C	3.01645500	-1.44508800	-0.33841600
C	3.74238200	-0.41000700	0.25506100
C	3.17172000	0.65325600	0.98813200
H	4.82984900	-0.45881700	0.19339200
O	0.83195900	0.70299400	-1.37734600
O	-0.70395300	1.07997900	0.96025100
O	1.74243200	-1.54070300	-0.34389600
O	1.93503600	0.85697300	1.14354200
Co	0.54178800	-0.18863400	0.29908600
C	3.73373600	-2.56858600	-1.01961600
H	3.40122300	-2.64223000	-2.06438400
H	4.82214800	-2.44991800	-0.99985100
H	3.47324500	-3.52262300	-0.54008300
C	4.07463200	1.63552900	1.67343400
H	5.13552300	1.46462800	1.46050900
H	3.80397200	2.65727200	1.37555200
H	3.91787500	1.57958600	2.75960400
C	-2.02865100	2.99353600	1.09782600
H	-1.70595000	3.14082500	2.13670000
H	-2.19534800	3.96711800	0.62420200
H	-2.98602000	2.45319600	1.14098100
C	0.73112200	2.34935600	-3.03410300
H	0.27977800	3.31981000	-3.26744800
H	1.82490100	2.44114900	-3.08244700
H	0.44830700	1.62705200	-3.81216500
H	0.37728900	-2.66613400	-0.62217700
O	-0.27956800	-1.52065300	1.44516400
N	-0.83493900	-1.53685300	0.24774500
C	-2.23421800	-1.19879200	0.14813000
C	-2.83526200	-1.18309300	-1.10981700

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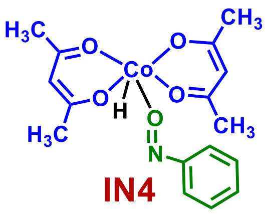
C	-2.92968900	-0.81960200	1.29262200
C	-4.16264400	-0.77776600	-1.21753200
H	-2.25775500	-1.48663000	-1.98374500
C	-4.26096900	-0.42904700	1.17076900
H	-2.40844800	-0.82934700	2.24922500
C	-4.87888500	-0.40149600	-0.07995000
H	-4.64230400	-0.75923000	-2.19860000
H	-4.81997000	-0.13990000	2.06395100
H	-5.92151900	-0.08851800	-0.16919000
O	-0.59822000	-2.70154900	-0.51413400

Table S7.



E = -2434.024836 Ha

C	-3.37638100	-1.08031500	-0.48908700
C	-2.96162700	-2.32599000	0.00574900
C	-1.62867500	-2.64268400	0.31896300
H	-3.72328000	-3.08582800	0.18344900
C	-0.99060700	2.70342900	-0.63826900
C	-1.23147700	2.81025000	0.73949400
C	-1.21321800	1.73791300	1.65822800
H	-1.43864600	3.80695500	1.13179100
O	-2.61660300	-0.09496800	-0.74198500
O	-0.63511600	-1.87139900	0.16732400
O	-0.73100000	1.64441800	-1.29042800
O	-0.99341500	0.53208400	1.36910200
Co	-0.73882600	-0.11922500	-0.53769600
C	-1.02419400	3.94639300	-1.48157200
H	-1.81487500	3.85266100	-2.23896900
H	-1.19830700	4.85658300	-0.89677100

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H	-0.08015300	4.04758400	-2.03413400
C	-1.46666500	2.02849400	3.11201500
H	-1.64787400	3.08973500	3.31804500
H	-2.33179200	1.44509400	3.45660300
H	-0.61054700	1.68895000	3.71140000
C	-1.30061800	-3.98649900	0.89680700
H	-0.84986600	-3.85882800	1.89061300
H	-2.17774600	-4.63676200	0.98522600
H	-0.54404600	-4.48310900	0.27442900
C	-4.83068600	-0.83108800	-0.75362900
H	-5.46183100	-1.69157400	-0.50627300
H	-5.16721000	0.03997200	-0.17509600
H	-4.97448600	-0.57297900	-1.81181700
H	-0.62648700	-0.67895400	-1.88793300
O	1.10663800	0.06960000	-0.37251200
N	1.90284900	-0.87762500	-0.47698800
C	3.23322300	-0.52036100	-0.24115700
C	4.16337000	-1.56458300	-0.38043000
C	3.65860900	0.77519300	0.11459600
C	5.51399200	-1.31731200	-0.16976700
H	3.78888600	-2.55276800	-0.65483200
C	5.00828400	1.00815200	0.32217100
H	2.91335500	1.56504600	0.22036600
C	5.93598900	-0.03319200	0.18073500
H	6.24248900	-2.12326700	-0.27723400
H	5.35315700	2.00693300	0.59882700
H	6.99766000	0.16234100	0.34793800

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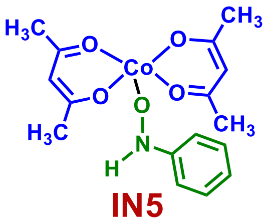
Table S8.



IN5

E = -2434.070476 Ha

C	-3.47012300	-0.13547100	0.57339700
C	-3.27109200	-1.53086900	0.63944800
C	-2.24126000	-2.21072900	-0.01969200
H	-3.99984100	-2.12676400	1.19007600
C	-0.04656900	2.80227900	-0.30389700
C	0.56232500	2.39862400	0.89905500
C	0.53856500	1.09067300	1.39895300
H	1.11142600	3.14802500	1.46955000
O	-2.70400900	0.67628000	-0.02101000
O	-1.31256000	-1.66324900	-0.70511800
O	-0.68115600	2.03424600	-1.08645600
O	-0.07844400	0.10247500	0.87706800
Co	-0.95797000	0.20787400	-0.76117000
C	0.04405700	4.23077800	-0.74297400
H	-0.96659300	4.64508000	-0.85951400
H	0.60817000	4.85513000	-0.04213500
H	0.51626200	4.28351400	-1.73336100
C	1.29540100	0.74444300	2.64263800
H	1.72060100	1.62603600	3.13406700
H	0.64351900	0.20989000	3.34588600
H	2.11376300	0.05663900	2.38189000
C	-2.18339900	-3.70654900	0.03147400
H	-1.24024600	-4.02393700	0.49887000
H	-3.01815300	-4.14670100	0.58734800
H	-2.17848700	-4.11514200	-0.98839900
C	-4.68000300	0.46658900	1.22298700

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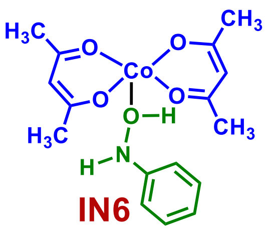
H	-5.30388600	-0.27073400	1.74004000
H	-4.36763300	1.23969600	1.93815100
H	-5.28826100	0.97855600	0.46458000
H	0.75303800	-2.05719500	-1.31075500
O	0.54578100	-0.15193500	-1.79587200
N	1.28190600	-1.19379100	-1.44574300
C	2.42919900	-1.01144600	-0.70156800
C	3.04583700	-2.11658100	-0.08531600
C	3.01657100	0.26091000	-0.57916500
C	4.21816300	-1.94533100	0.64093400
H	2.59032400	-3.10665500	-0.17756500
C	4.18818100	0.41295700	0.15334000
H	2.52935000	1.10773200	-1.06351600
C	4.79998200	-0.68108700	0.77089400
H	4.68236800	-2.81228800	1.11789000
H	4.63331400	1.40767800	0.24379900
H	5.72090000	-0.55230700	1.34293600

Table S9.



IN6

E= -2434.661175 Ha

C	-1.61544619	-2.76679263	-0.12229337
C	-0.32723355	-3.15062067	0.29292614
C	0.78512140	-2.29513769	0.29355904
H	-0.17712414	-4.18488638	0.60546315
C	-3.05362127	1.55264604	-0.71204318
C	-3.08717544	1.75143174	0.67792520
C	-2.09440723	1.34595560	1.59842174
H	-3.94230852	2.30038366	1.07570288
O	-1.94539099	-1.60267264	-0.51562581

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O	0.75066691	-1.06826809	-0.04868043
O	-2.14389488	0.93909608	-1.36122902
O	-1.05204377	0.69423472	1.30309014
Co	-0.77285226	-0.12147007	-0.57568121
C	-4.16136086	2.10743742	-1.55791633
H	-4.70441618	1.27942088	-2.03563206
H	-4.87430418	2.71497660	-0.98958869
H	-3.74435884	2.71102457	-2.37560030
C	-2.25617965	1.72085654	3.04487432
H	-3.19128314	2.25186952	3.25664717
H	-2.20921861	0.81582993	3.66628908
H	-1.41404004	2.35324669	3.36083858
C	2.13253098	-2.79974360	0.70684873
H	2.48289149	-2.24612697	1.58988987
H	2.13445215	-3.87120209	0.93552811
H	2.86580436	-2.59696593	-0.08670115
C	-2.72294527	-3.77705818	-0.13197028
H	-2.40578402	-4.76252112	0.22661246
H	-3.55564797	-3.42083459	0.49014582
H	-3.12304149	-3.88075997	-1.15026033
H	0.89546640	1.32748974	0.98488261
O	0.50647828	1.43625329	-0.93182142
N	1.36161686	1.74311264	0.17105524
C	2.65679958	1.24247913	-0.01858950
C	3.42700598	0.96848005	1.12127657
C	3.22433368	1.08419451	-1.28795039
C	4.74804703	0.55510891	0.98802977
H	2.97947816	1.08096048	2.11262610
C	4.54499101	0.65825715	-1.40601708
H	2.61961890	1.28047408	-2.17339767
C	5.31819574	0.39408077	-0.27577241
H	5.33548639	0.34646666	1.88559075

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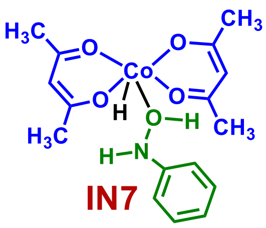
H 4.97496348 0.53121531 -2.40267289

H 6.35348504 0.06296970 -0.37755284

H -0.00288608 2.24627518 -1.08652605

Table S10.



IN7

E= -2435.123595 Ha

C -3.16299800 -1.25140800 -0.91307100

C -2.83338500 -2.41779000 -0.20541200

C -1.58912800 -2.64867500 0.40415900

H -3.58915900 -3.20052000 -0.13484300

C -1.10685500 2.67900600 -0.64670600

C -1.83026600 2.75609900 0.54593800

C -1.95266700 1.71013600 1.49309000

H -2.28181400 3.71764400 0.79410600

O -2.40359500 -0.24767000 -1.08660100

O -0.61151600 -1.83962400 0.39974000

O -0.50313400 1.64679600 -1.10328100

O -1.50275600 0.54485100 1.34700300

Co -0.68536700 -0.11487700 -0.36165800

C -0.97220000 3.89872000 -1.50875400

H -1.40718400 3.69779600 -2.49783900

H -1.45667800 4.78233500 -1.07898400

H 0.08988400 4.12183700 -1.68117600

C -2.64919400 1.99160500 2.79417900

H -3.06409600 3.00418500 2.85446900

H -3.45544400 1.26116500 2.94622700

H -1.94461800 1.84740100 3.62513400

C -1.34418800 -3.93506700 1.13222700

H -1.12430000 -3.72239500 2.18753800

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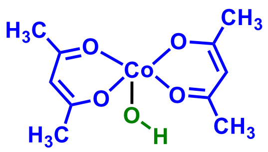
H	-2.19497800	-4.62272700	1.07766200
H	-0.45315800	-4.43236000	0.72572600
C	-4.51515900	-1.12160300	-1.54640700
H	-5.15701400	-1.98845000	-1.35616400
H	-5.01308300	-0.21595800	-1.17425200
H	-4.40456100	-0.98986800	-2.63151200
H	1.71513500	-1.44328000	-0.53218100
O	1.19451400	0.27860300	0.27991300
N	2.07855600	-0.82135100	0.19168400
C	3.41953000	-0.46425500	0.06794500
C	4.31080400	-1.37144300	-0.52889900
C	3.90774800	0.74654300	0.58106100
C	5.66572600	-1.07099500	-0.59723300
H	3.93075700	-2.31284600	-0.93387900
C	5.26791300	1.03575200	0.49296900
H	3.22232800	1.44467100	1.06380200
C	6.15578000	0.13493200	-0.09141700
H	6.34683800	-1.78641900	-1.06394300
H	5.63589100	1.98223900	0.89609300
H	7.21994800	0.36888400	-0.15535500
H	-0.08910400	-0.66919200	-1.60744600
H	1.41256800	0.91399400	-0.43639500

Table S11.



IN8

E= -2148.025769 Ha

C	-1.58533200	1.71643200	-0.26258500
C	-2.66281700	0.91629300	0.16516100
C	-2.69235100	-0.48157300	0.06970900
H	-3.56168900	1.41908000	0.52340900

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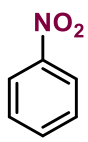
C	2.68059100	0.26235200	-0.46119700
C	2.59346500	0.24820600	0.94692100
C	1.44974400	-0.11036800	1.66258300
H	3.48055600	0.52468200	1.51673500
O	-0.47867800	1.27679600	-0.69366100
O	-1.73290300	-1.21789500	-0.33137200
O	1.73797600	-0.04260900	-1.24267300
O	0.32320700	-0.46016200	1.16900400
Co	0.03283200	-0.59759600	-0.65002300
C	3.96579800	0.65380800	-1.12209000
H	3.78084600	1.46248500	-1.84124100
H	4.73189700	0.97208400	-0.40723100
H	4.34935200	-0.19648900	-1.70246300
C	1.46868700	-0.10890000	3.16046600
H	2.42682300	0.23240900	3.56576400
H	0.66407600	0.53300000	3.54336200
H	1.26323000	-1.12181800	3.53269200
C	-3.94118500	-1.22586200	0.43013900
H	-3.72527500	-1.93657800	1.23981600
H	-4.75661200	-0.56462200	0.74227800
H	-4.27489200	-1.82687000	-0.42670300
C	-1.72473800	3.20903400	-0.25036100
H	-2.68680100	3.54693600	0.15003300
H	-0.91145000	3.65120700	0.34105500
H	-1.60776700	3.59783200	-1.27134200
O	0.50802200	-2.27997400	-1.05223600
H	-0.23091900	-2.84400700	-0.78052700

Table S12.



E = -436.313161 Ha

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C -0.24594300 0.00005600 -0.00013100

C 0.42638400 -1.21919900 -0.00006200

C 0.42653600 1.21926700 -0.00006100

C 1.81816000 -1.21122900 0.00014900

H -0.15020500 -2.14412200 0.00014800

C 1.81828100 1.21118200 -0.00008000

H -0.15002000 2.14419800 -0.00024300

C 2.51241100 -0.00006700 0.00007200

H 2.36467900 -2.15640400 -0.00004900

H 2.36497900 2.15626300 0.00021300

H 3.60458300 -0.00006000 0.00009300

N -1.72154600 0.00001200 -0.00032100

O -2.28233100 -1.08285300 0.00006100

O -2.28243900 1.08285000 0.00028400

Table S13.

H_2

E = -1.168684 Ha

H 0.00000000 0.00000000 0.37726400

H 0.00000000 0.00000000 -0.37726400

Table S14.

H_2O

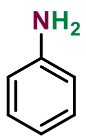
E=-76.346017 Ha

H 0.00000000 -0.75104600 -0.48176600

H 0.00000000 0.75104600 -0.48176600

O 0.00000000 0.00000000 0.12044200

Table S15.



E=-287.274325 Ha

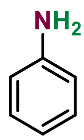
C -0.94320200 -0.00033800 -0.00758700

C -0.22130200 -1.20714600 -0.00312000

C	-0.22178700	1.20687800	-0.00319900
C	1.16976900	-1.20068200	0.00296100
H	-0.76588300	-2.15573200	-0.00776100
C	1.16926400	1.20099700	0.00306400
H	-0.76693200	2.15510000	-0.00880100
C	1.87999000	0.00029200	0.00593800
H	1.70630500	-2.15293200	0.00766200
H	1.70528700	2.15353100	0.00804300
H	2.97147800	0.00035500	0.01230200
N	-2.32593800	0.00001500	-0.07385400
H	-2.78235200	0.83940600	0.25938300
H	-2.78273300	-0.83984100	0.25780800

8. Spectroscopic Data (^{1}H and ^{13}C).

Aniline (2a)[7]



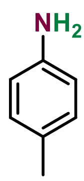
2a

Compound **2a** was prepared according to the general procedure of hydrogenation starting from **1a** (61.5 mg, 0.5 mmol) and purified by column chromatography (hexane: EtOAc = 90:10) affording 89 % yield (41.5 mg) as a yellow liquid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (t, *J* = 6.5 Hz, 2H), 6.65 (t, *J* = 6.6 Hz, 1H), 6.54 (d, *J* = 7.9 Hz, 2H), 3.39 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 129.2, 118.4, 115.1.

4-Methylaniline (2b)[7]



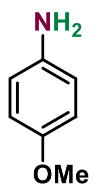
2b

Compound **2b** was prepared according to the general procedure of hydrogenation starting from **1b** (68.5 mg, 0.5 mmol) and purified by column chromatography (hexane: EtOAc = 90:10) afforded 85% yield (45.2 mg) as yellowish white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, *J* = 7.9 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 2H), 3.41 (s, 2H), 2.26 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 129.4, 127.4, 114.9, 20.0.

4-Methoxyaniline (2c)[8]



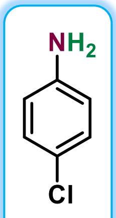
2c

Compound **2c** was prepared according to the general procedure of hydrogenation starting from **1c** (76.5 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 90:10) afforded 76% yield (47.1 mg) as brown solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 – 6.73 (m, 2H), 6.67 – 6.63 (m, 2H), 3.75 (s, 3H), 3.42 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 139.9, 116.5, 114.8, 55.8.

4-Chloroaniline (2d)[7]

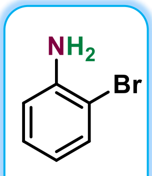


2d

Compound **2d** was prepared according to the general procedure of hydrogenation starting from **1d** (78.5 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 90:10) afforded 80% yield (50.8 mg) as yellow liquid.

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.2 Hz, 2H), 6.59 (d, *J* = 8.3 Hz, 2H), 3.60 (s, 2H).
^{13}**C NMR** (101 MHz, $CDCl_3$) δ 145.0, 129.2, 123.3, 116.3.

2-Bromoaniline (2e)[8]

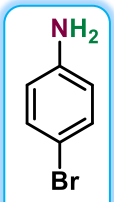


2e

Compound **2e** was prepared according to the general procedure of hydrogenation starting from **1e** (101 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 95:05) afforded 83% yield (72 mg) as brown solid.

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.10 (ddd, *J* = 8,7.6, 1.5 Hz, 1H), 6.76 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.62 (ddd, *J* = 8, 7.4, 1.5 Hz, 1H), 4.07 (s, 2H).
^{13}**C NMR** (101 MHz, $CDCl_3$) δ 144.2, 132.7, 128.4, 119.5, 115.9, 109.4.

4-Bromoaniline (2f)[7]

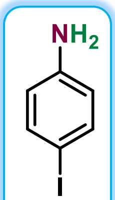


2f

Compound **2f** was prepared according to the general procedure of hydrogenation starting from **1f** (101 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 90:10) afforded 89% yield (76.5 mg) as white solid.

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.2 Hz, 2H), 6.56 (d, *J* = 8.2 Hz, 2H), 3.64 (s, 2H).
^{13}**C NMR** (101 MHz, $CDCl_3$) δ 145.4, 132.0, 116.7, 110.2.

4- Iodoaniline (2g)[8]

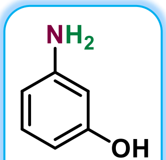


2g

Compound **2g** was prepared according to the general procedure of hydrogenation starting from **1g** (124.5 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 90:10) afforded 92 % yield (100.2 mg) as white solid.

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 2H), 6.50 – 6.43 (m, 2H), 3.54 (s, 2H).
^{13}**C NMR** (101 MHz, $CDCl_3$) δ 146.1, 137.9, 117.3, 79.4.

3-Aminophenol (2h)[7]



2h

Compound **2h** was prepared according to the general procedure of hydrogenation starting from **1h** (69.5 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 50:50) afforded 90% yield (49 mg) as brown solid.
^{1}**H NMR** (400 MHz, DMSO) δ 8.89 (s, 1H), 6.78 (t, *J* = 8.2 Hz, 1H), 6.03-6.00 (m, 2H), 5.95-5.93 (m, 1H), 4.85 (s, 2H).
^{13}**C NMR** (101 MHz, DMSO) δ 158.1, 149.8, 129.5, 105.6, 103.5, 101.1.

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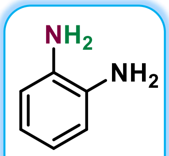
Benzene-1,2-diamine (2i)[8]

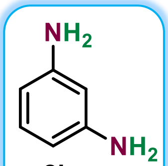


2i

Compound **2i** was prepared according to the general procedure of hydrogenation starting from **1i** (69 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 90:10) afforded 85% yield (46 mg) as brown solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75-6.70 (m, 4H), 3.39 (s, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 134.8, 120.4, 116.8.

Benzene-1,3-diamine (2j)[10]

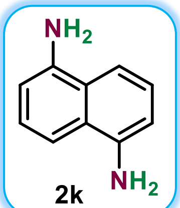


2j

Compound **2j** was prepared according to the general procedure of hydrogenation starting from **1j** (84 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 60:40) afforded 88% yield (47.5 mg) as brown liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (t, J = 7.9 Hz, 1H), 6.12 (dd, J = 7.9, 2.2 Hz, 2H), 6.03 (s, 1H), 3.34 (s, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 130.3, 106.1, 102.0.

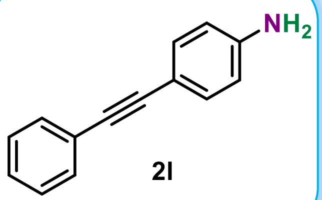
Napthalene-1,5-diamine (2k)[15]



2k

Compound **2k** was prepared according to the general procedure of hydrogenation starting from **1k** (109 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 70:30) afforded 81% yield (64 mg) as brown solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 4H), 6.81 – 6.75 (m, 2H), 4.13 (s, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 125.3, 124.5, 111.6, 109.9.

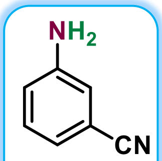
4-(2-Phenylethynyl)aniline (2l)[19]



2l

Compound **2l** was prepared according to the general procedure of hydrogenation starting from **1l** (111.5 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 80:20) afforded 74 % yield (71.5 mg) as off white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 6.8 Hz, 2H), 7.38 – 7.29 (m, 5H), 6.64 (d, J = 8.6 Hz, 2H), 3.78 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.77, 133.08, 131.47, 128.39, 127.78, 124.01, 114.87, 112.72, 90.24, 87.45.

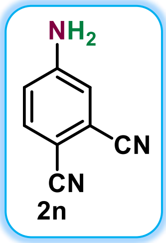
3-Aminobenzonitrile (2m)[9]



2m

Compound **2m** was prepared according to the general procedure of hydrogenation starting from **1m** (74 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 90:10) afforded 81% yield (48 mg) as yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, J = 7.8 Hz, 1H), 6.99 – 6.95 (m, 1H), 6.91 – 6.83 (m, 2H), 3.98 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.19, 129.9, 121.6, 119.3, 119.2, 117.2, 112.5.

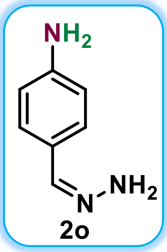
4-Aminopthalonitrile (2n)[13]



Compound **2n** was prepared according to the general procedure of hydrogenation starting from **1n** (86 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 50:50) afforded 76% yield (54.5 mg) as off-white solid.

^{1}H NMR (400 MHz, DMSO) δ 7.63 (d, *J* = 8.7 Hz, 1H), 7.01 (d, *J* = 2.3 Hz, 1H), 6.86 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.69 (s, 2H). **^{13}C NMR** (101 MHz, DMSO) δ 153.5, 135.4, 118.0, 117.7, 117.4, 116.9, 115.9, 98.2.

4-(Hydrazonomethyl)aniline (2o)



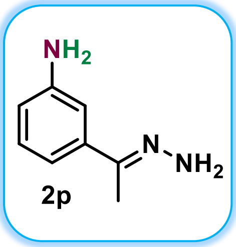
Compound **2o** was prepared according to the general procedure of hydrogenation starting from **1o** (75.5 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 20:80) afforded 77% yield (52 mg) as brown red solid.

^{1}H NMR (400 MHz, DMSO) δ 8.41 (s, 1H), 7.50 (d, *J* = 8.2 Hz, 2H), 6.61 (d, *J* = 8.4 Hz, 2H), 5.73 (s, 2H).

^{13}C NMR (101 MHz, DMSO) δ 159.87, 151.69, 129.81, 121.58, 113.57.

HR-MS: $[M + H]^+$ calculated for $C_7H_{10}N_3$, 136.0869; found 136.0870.

3-Ethyl Hydrazonoyl Aniline (2p)



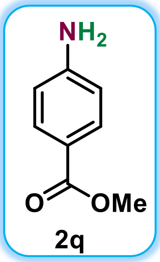
Compound **2p** was prepared according to the general procedure of hydrogenation starting from **1p** (82.5 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 60:40) afforded 69% yield (51.2 mg) as pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 1.7 Hz, 1H), 7.25 – 7.18 (m, 2H), 6.75 (dt, *J* = 7.0, 2.2 Hz, 1H), 3.73 (s, 2H), 2.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.45, 146.53, 139.66, 129.35, 117.36, 116.62, 113.07, 15.28.

HR-MS: $[M + H]^+$ calculated for $C_7H_{10}N_3$, 150.1026; found 150.1028.

Methyl-4-aminobenzoate (2q)[10]

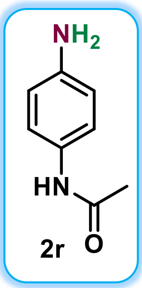


Compound **2q** was prepared according to the general procedure of hydrogenation starting from **1q** (90 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 80:20) afforded 78% yield (59 mg) as off white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.7 Hz, 2H), 6.63 (d, *J* = 8.7 Hz, 2H), 4.07 (s, 2H), 3.85 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 150.9, 131.7, 119.9, 113.9, 51.7.

N-(4-Aminophenyl)acetamide (2r)[10]

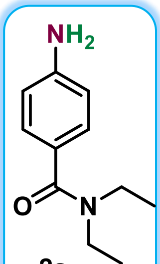


Compound **2r** was prepared according to the general procedure of hydrogenation starting from **1r** (90 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 50:50) afforded 72 % yield (54 mg) as white solid.

^{1}H NMR (400 MHz, DMSO) δ 9.47 (s, 1H), 7.19 (d, *J* = 8.7 Hz, 2H), 6.49 (d, *J* = 8.7 Hz, 2H), 4.81 (s, 2H), 1.96 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 167.9, 144.9, 128.8, 121.2, 114.1, 23.9.

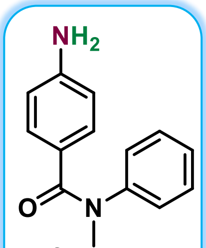
4-Amino-*N*,*N*-diethylbenzamide (2s)[16]


2s

Compound **2s** was prepared according to the general procedure of hydrogenation starting from **1s** (111 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 80:20) afforded 80% yield (77 mg) as white solid.

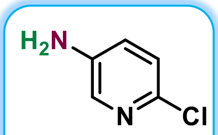
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.5 Hz, 2H), 6.64 (d, *J* = 8.3 Hz, 2H), 3.82 (s, 2H), 3.41 (s, 4H), 1.17 (t, *J* = 7.2 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 147.5, 128.3, 126.9, 114.29, 13.7.

4-Amino-*N*-methyl-*N*-phenylbenzamide (2t)[17]


2t

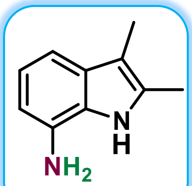
Compound **2t** was prepared according to the general procedure of hydrogenation starting from **1t** (128 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 80:20) afforded 82% yield (93.2 mg) as off white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.0 Hz, 2H), 7.17 – 7.09 (m, 3H), 7.04 (dd, *J* = 8.4, 1.3 Hz, 2H), 6.40 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 2H), 3.46 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 148.1, 145.9, 131.1, 129.2, 126.9, 126.1, 125.4, 113.7, 38.8.

5-Amino-2-chloropyridine (2u)[11]


2u

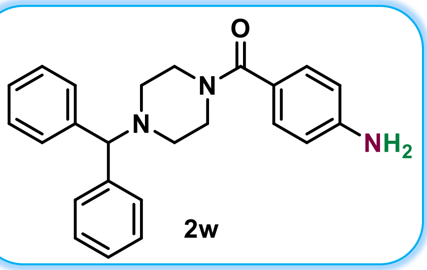
Compound **2u** was prepared according to the general procedure of hydrogenation starting from **1u** (79 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 75:25) afforded 81% yield (52.5 mg) as yellow crystaline solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 3.0 Hz, 1H), 7.07 (d, *J* = 8.5 Hz, 1H), 6.95 (dd, *J* = 8.5, 3.0 Hz, 1H), 3.15 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 140.3, 136.5, 124.9, 124.2.

2,3-dimethyl-1H-indol-7-amine (2v)


2v

Compound **2v** was prepared according to the general procedure of hydrogenation starting from **1v** (95 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 70:30) afforded 69% yield (56 mg) as black brown solid. Melting point:68-70°C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.52 (d, *J* = 7.3 Hz, 1H), 3.13 (s, 2H), 2.29 (s, 3H), 2.20 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 130.7, 130.7, 130.1, 126.1, 119.9, 110.4, 108.3, 108.1, 11.6, 8.8. **HR-MS:** $[M + H]^+$ calculated for $C_{10}H_{12}N_2$, 161.1073; found 161.1074.

(4-aminophenyl)(4-benzhydrylpiperazin-1-yl)methanone (2w)


2w

Compound **2w** was prepared according to the general procedure of hydrogenation starting from **1w** (200 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 80:25) afforded 85 % yield (158 mg) as pale yellow solid. Melting point: 152-154°C

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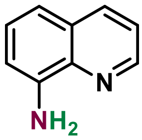
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.8 Hz, 4H), 7.23 (d, *J* = 6.1 Hz, 4H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.15 (t, *J* = 7.3 Hz, 2H), 6.57 (d, *J* = 8.5 Hz, 2H), 4.22 (s, 1H), 3.79 (s, 2H), 3.59 (s, 4H), 2.37 (s, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 148.0, 142.2, 129.3, 128.6, 127.9, 127.1, 114.1, 76.1, 52.1. **HR-MS:** $[M + H]^+$ calculated for $C_{24}H_{25}N_3O$, 372.2070; found 372.2072.

2,6-diamino benzothiazole (2x)[13]

2x

Compound **2x** was prepared according to the general procedure of hydrogenation starting from **1x** (97.5 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 30:70) afforded 84 % yield (69 mg) as off white solid.
^{1}H NMR (400 MHz, DMSO) δ 7.05 (d, *J* = 8.3 Hz, 1H), 6.94 (s, 2H), 6.82 (s, 1H), 6.51 (d, *J* = 8.3 Hz, 1H), 4.77 (s, 2H).
^{13}C NMR (101 MHz, DMSO) δ 162.8, 143.9, 143.6, 132.1, 118.3, 113.4, 105.7.

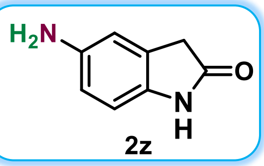
8-aminoquinoline(2y)[7]



2y

Compound **2y** was prepared according to the general procedure of hydrogenation starting from **1y** (87 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 90:10) afforded 78% yield (56.1 mg) as off white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (dd, *J* = 4.0, 1.2 Hz, 1H), 8.06 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.38 – 7.39 (m, 2H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.93 (dd, *J* = 7.5, 1.3 Hz, 1H), 4.99 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 144.0, 138.5, 136.1, 128.9,127.5, 121.4, 116.1, 110.2.

5-aminoindolin-2-one (2z)[18]

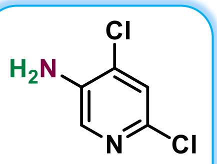


2z

Compound **2z** was prepared according to the general procedure of hydrogenation starting from **1z** (74 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 75:25) afforded 79 % yield (58.4 mg) as pale yellow solid.

^{1}H NMR (400 MHz, DMSO) δ 9.91 (s, 1H), 6.49 (d, *J* = 8.0 Hz, 2H), 6.37 (dd, *J* = 8.2, 2.2 Hz, 1H), 4.65 (s, 2H), 3.30 (s, 2H).
^{13}C NMR (101 MHz, DMSO) δ 175.9, 143.4, 133.5, 126.5, 112.3, 111.6, 109.3, 36.1.

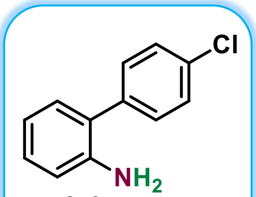
3-Amino-4,6-dichloropyridine (2aa)[14]



2aa

Compound **2aa** was prepared according to the general procedure of hydrogenation starting from **1aa** (96.5 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 75:25) afforded 73% yield (59.5 mg) as white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.23 (s, 1H), 4.12 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 139.3, 136.3, 129.7, 123.9.

4-Chloro-2′-aminobiphenyl (2ab)[12]



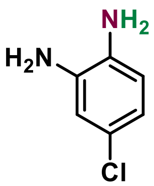
2ab

Compound **2ab** was prepared according to the general procedure of hydrogenation starting from **1ab** (116 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 90:10) afforded 80% yield (81 mg) as pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 4H), 7.19 (t, J = 7.6 Hz, 1H), 7.12 (d, J = 7.1 Hz, 1H), 6.85 (t, J = 7.4 Hz, 1H), 6.78 (d, J = 7.9 Hz, 1H), 3.73 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 138.0, 133.2, 130.5, 130.4, 129.1, 128.9, 126.3, 118.9, 115.8.

4-Chlorobenzene-1,2-diamine (2ac)[8]



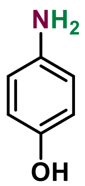
2ac

Compound **2ac** was prepared according to the general procedure of hydrogenation starting from **1ac** (86 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 60:40) afforded 87% yield (62 mg) as brick red solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.68 (d, J = 2.2 Hz, 1H), 6.66 (dd, J = 8.0, 2.3 Hz, 1H), 6.60 (d, J = 8.1 Hz, 1H), 3.16 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 133.1, 124.8, 119.6, 117.6, 116.3.

4-Aminophenol (2ad)[7]



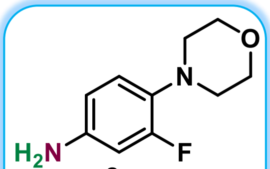
2ad

Compound **2ad** was prepared according to the general procedure of hydrogenation starting from **1ad** (69.5 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 50:50) afforded 79% yield (42.9 mg) as a yellowish white solid.

^{1}H NMR (400 MHz, DMSO) δ 8.35 (s, 1H), 6.50 – 6.41 (m, 4H), 4.36 (s, 2H).

^{13}C NMR (101 MHz, DMSO) δ 148.8, 140.6, 115.6, 115.3.

3-Fluoro-4-morpholinoaniline (2ae)[8]



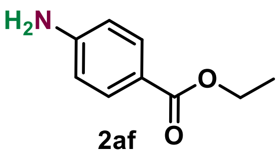
2ae

Compound **2ae** was prepared according to the general procedure of hydrogenation starting from **1ae** (113 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 60:40) afforded 86% yield (85 mg) as brown solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (dd, J = 10.0, 8.1 Hz, 1H), 6.47 – 6.37 (m, 2H), 3.89 – 3.83 (m, 4H), 3.55 (s, 2H), 2.99 – 2.93 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9 (d, $J_{C\text{-}F}$ = 244 Hz), 142.9 (d, $J_{C\text{-}F}$ = 10 Hz),131.9 (d, $J_{C\text{-}F}$ = 10 Hz), 120.4 (d, $J_{C\text{-}F}$ = 4 Hz), 110.8 (d, $J_{C\text{-}F}$ = 3 Hz), 104.1 (d, $J_{C\text{-}F}$ = 23 Hz), 67.3, 51.9(d, $J_{C\text{-}F}$ = 2 Hz).

Ethyl 4-aminobenzoate (2af)[8]



2af

Compound **2af** was prepared according to the general procedure of hydrogenation starting from **1af** (97.5 mg, 0.25 mmol) and purified by column chromatography (hexane:EtOAc = 80:20) afforded 72% yield (59.3 mg) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.7 Hz, 2H), 6.63 (d, J = 8.6 Hz, 2H), 4.31 (q, J = 7.1 Hz, 2H), 4.09 (s, 2H), 1.36 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 150.9, 131.6, 120.1, 113.9, 60.4, 14.5.

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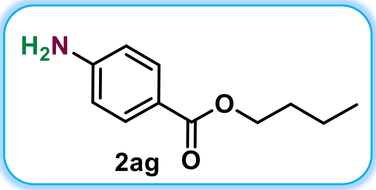
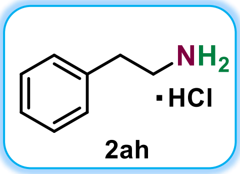
Butyl 4-aminobenzoate (2ag)[8]



Compound **2ag** was prepared according to the general procedure of hydrogenation starting from **1ag** (111.5 mg, 0.5 mmol) and purified by column chromatography (hexane:EtOAc = 85:15) afforded 81% yield (78.2 mg) as yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 8.7 Hz, 2H), 4.26 (t, *J* = 6.6 Hz, 2H), 4.06 (s, 2H), 1.74 – 1.69 (m, 2H), 1.46 (dq, *J* = 14.7, 7.4 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 150.9, 131.7, 120.2, 113.9, 64.5, 31.0, 19.4, 13.9.

2-Phenylethylamine hydrochloride (2ah)[7]



Compound **2ah** was prepared according to the general procedure of hydrogenation starting from **1ah** (75.5 mg, 0.5 mmol) afforded 35% yield (27.5 mg) as white solid after adding 2 ml of 1M HCl in ether.

^{1}H NMR (400 MHz, D_2O) δ 7.43 (dt, *J* = 29.6, 8.0 Hz, 5H), 3.33 (t, *J* = 7.2 Hz, 2H), 3.09 – 3.00 (m, 2H).
^{13}C NMR (101 MHz, D_2O) δ 136.6, 129.1, 128.9, 127.3, 40.6, 32.7.

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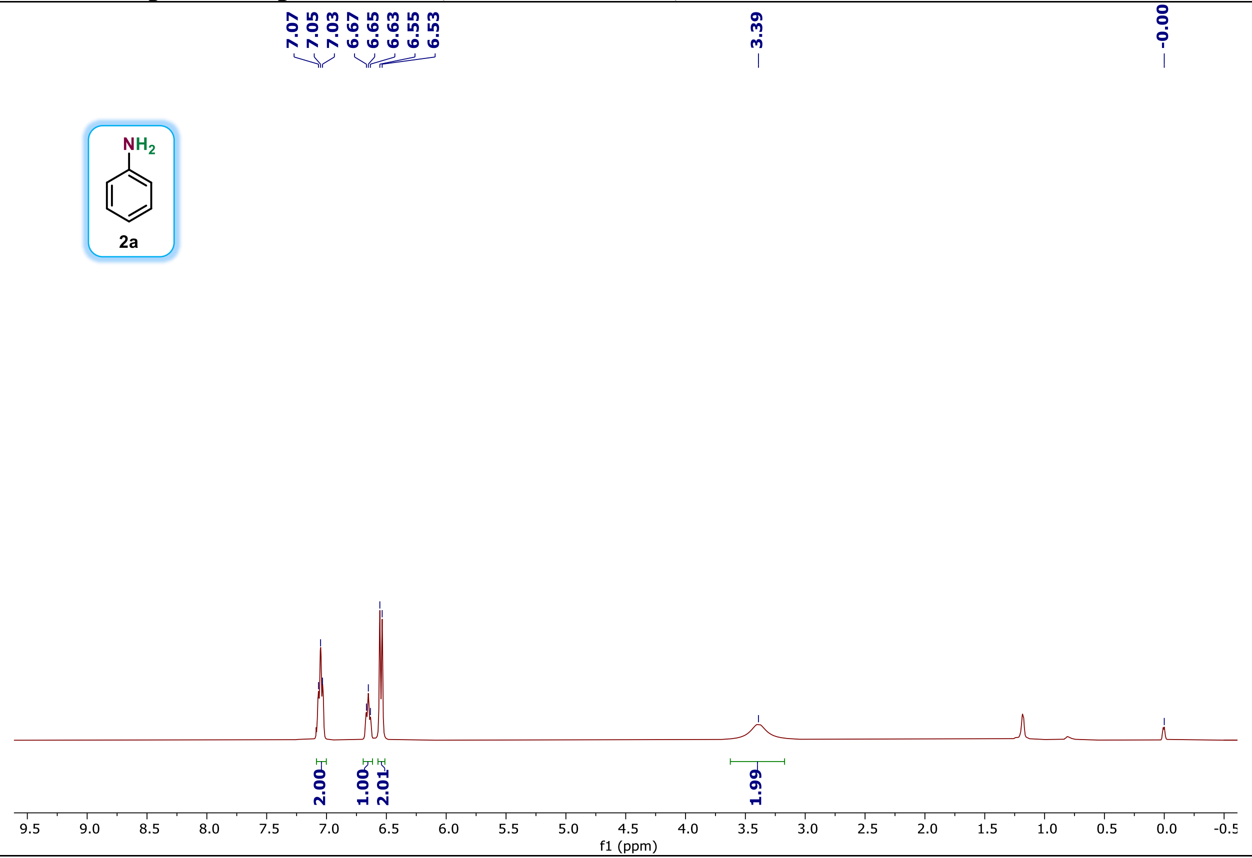
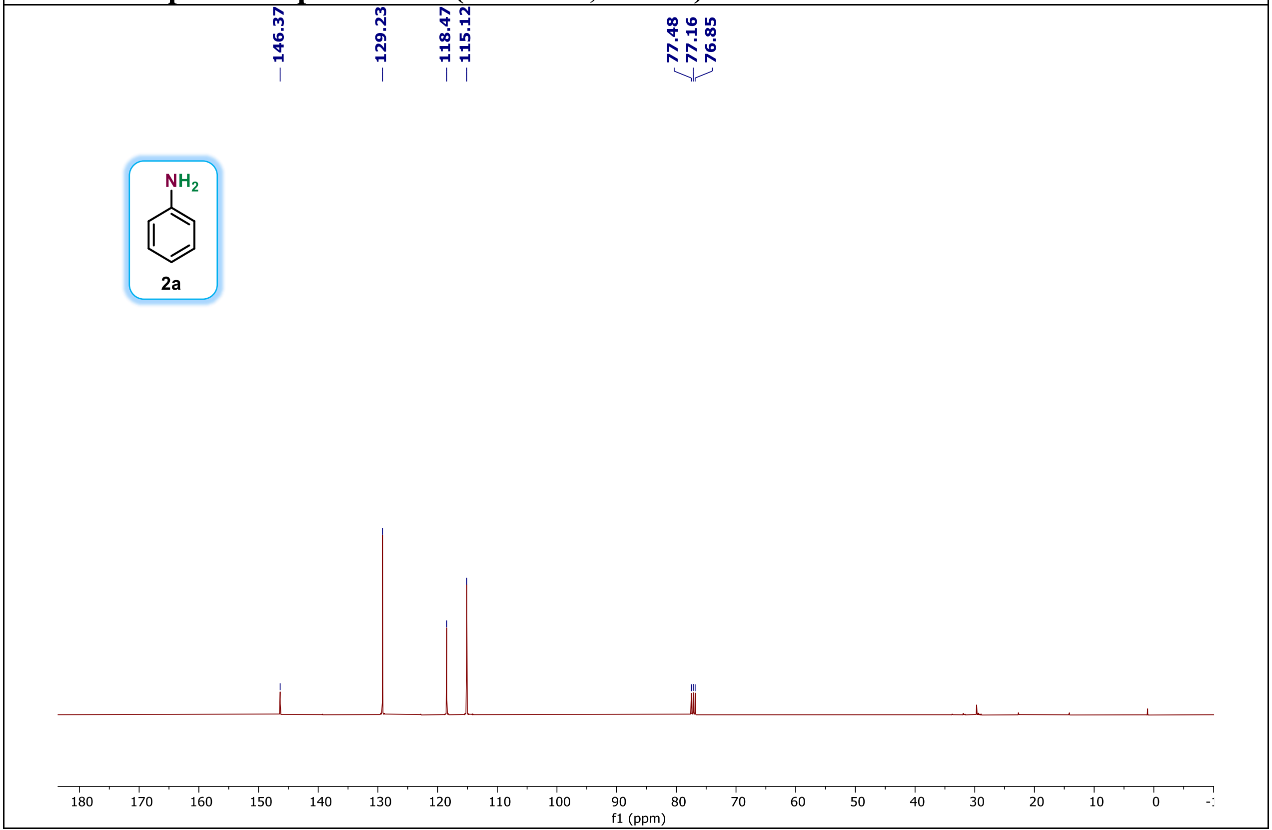
10. NMR Spectra

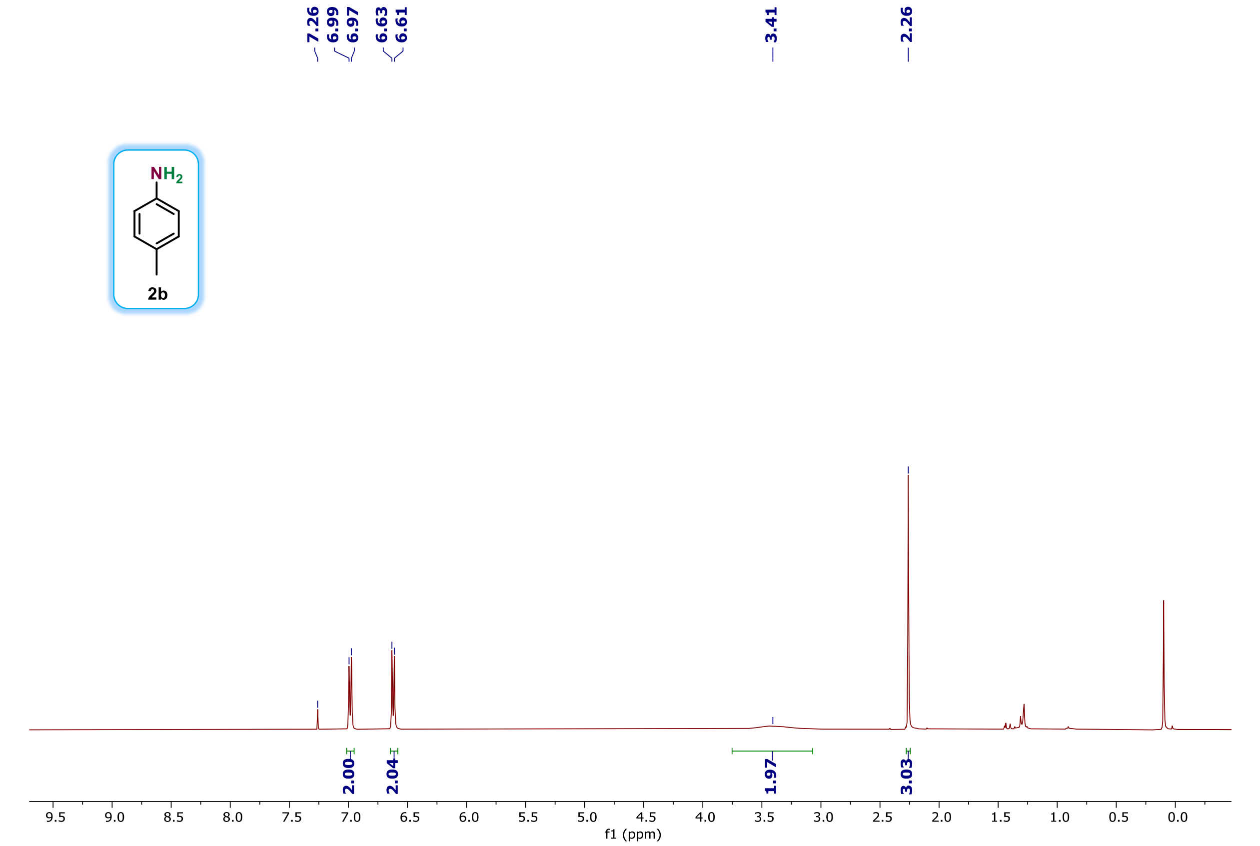
^{1}H NMR spectra of product 2a (400 MHz, $CDCl_3$)



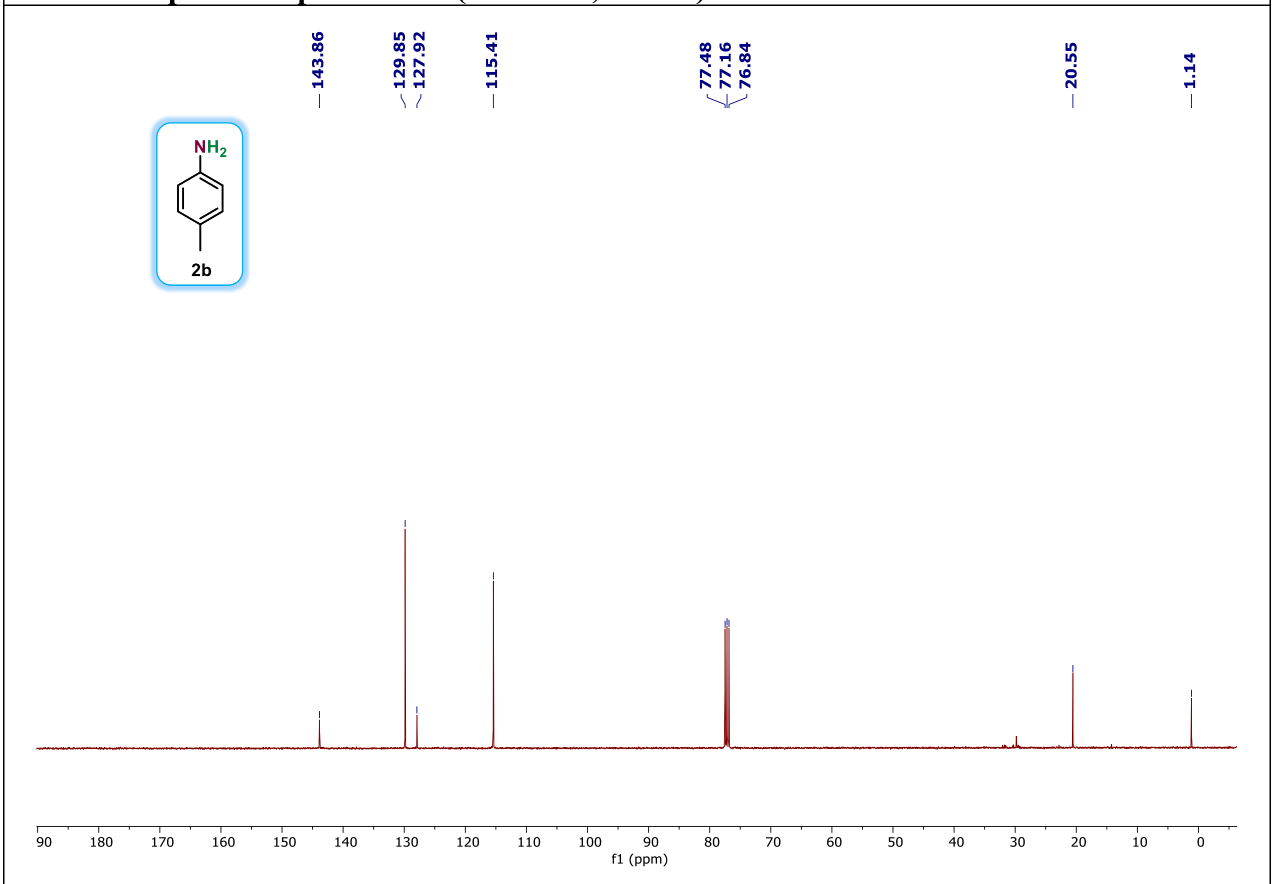
^{13}C NMR spectra of product 2a (101 MHz, $CDCl_3$)



^{1}H NMR spectra of product 2b (400 MHz, $CDCl_3$)



^{13}C NMR spectra of product 2b (101 MHz, $CDCl_3$)



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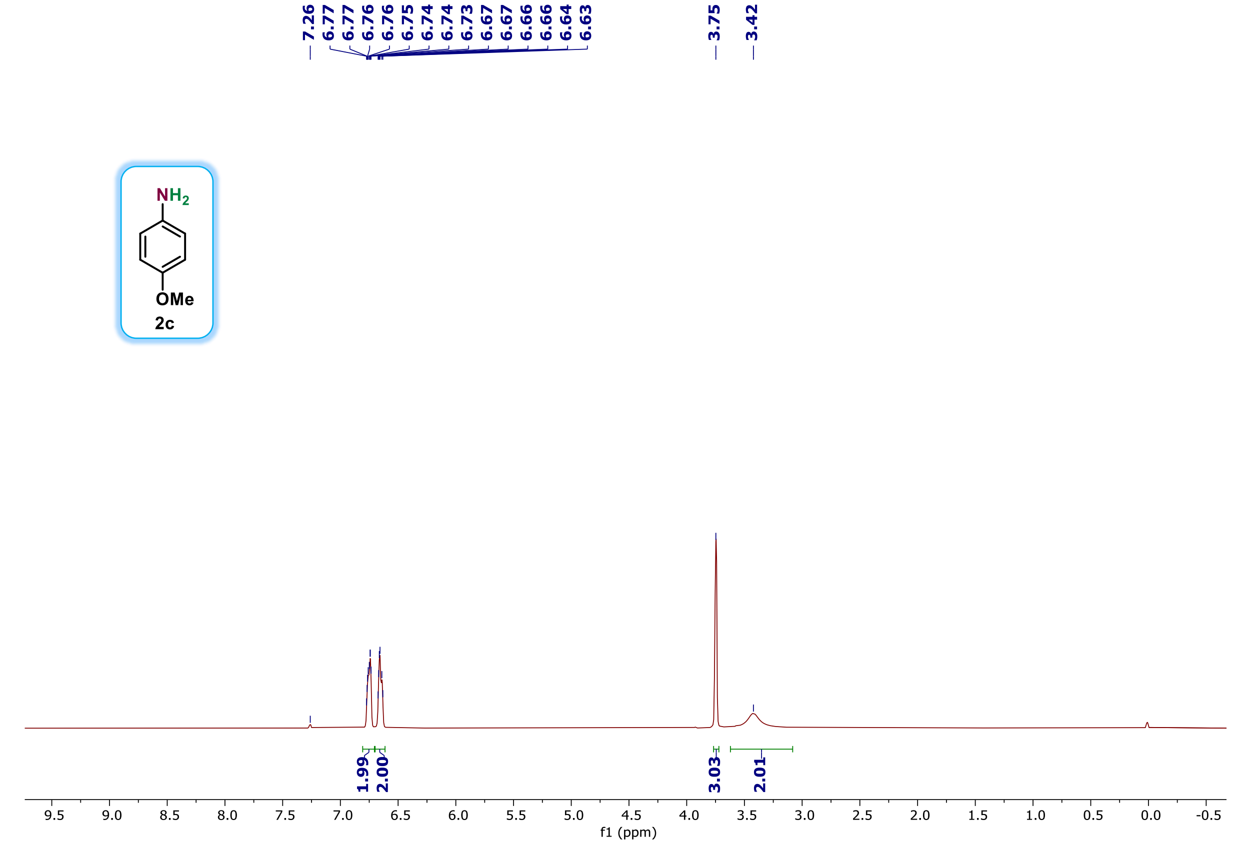
[1]H NMR spectra of product 2c (400 MHz, $CDCl_3$)



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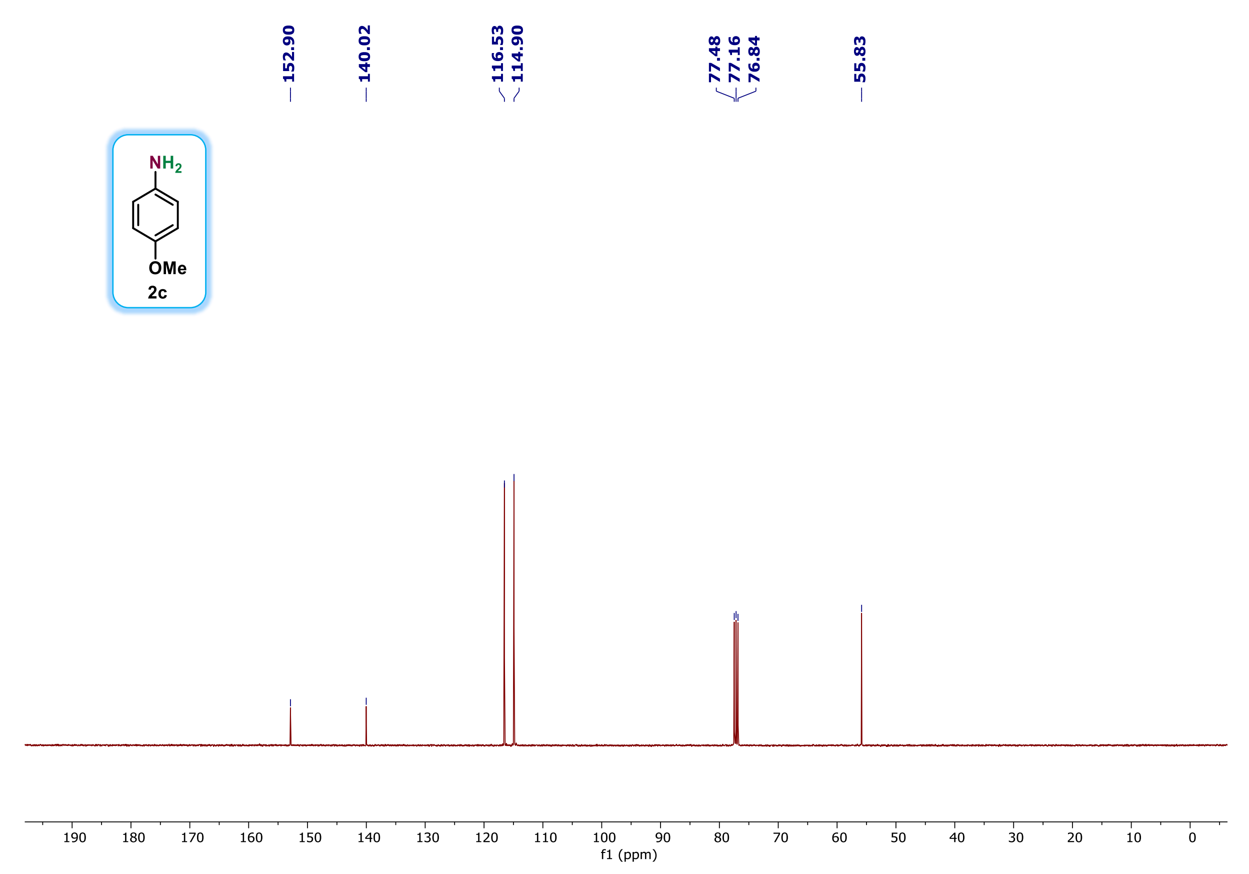

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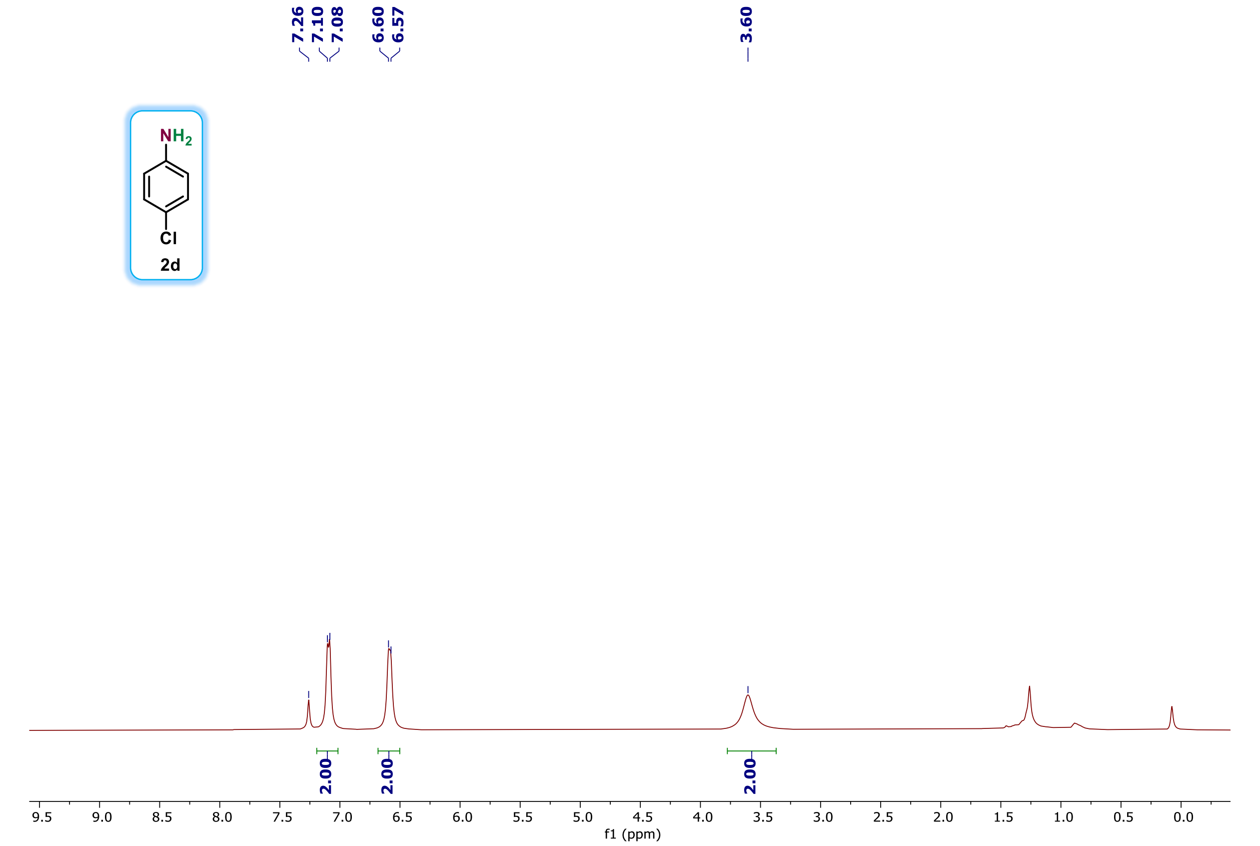
^{1}H NMR spectra of product 2d (400 MHz, $CDCl_3$)



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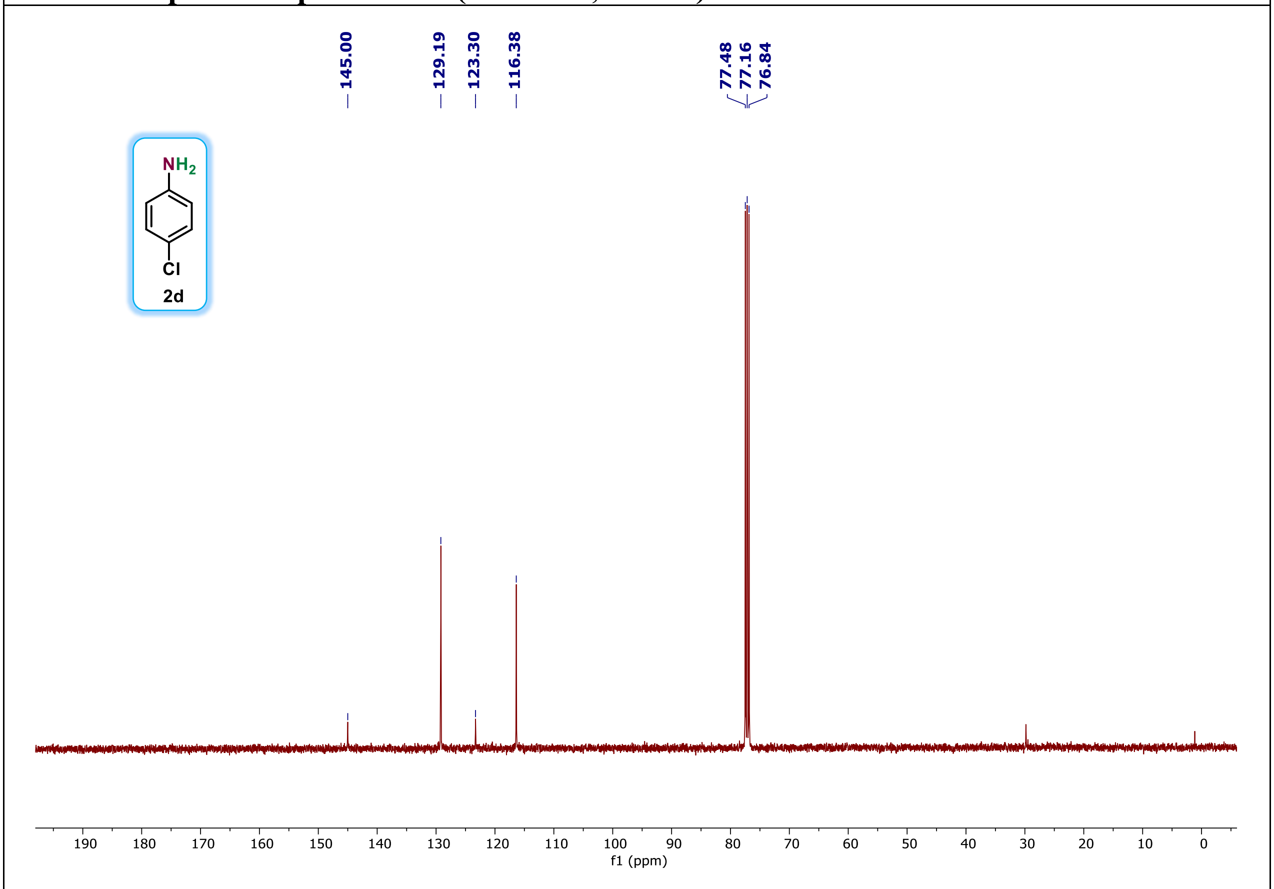

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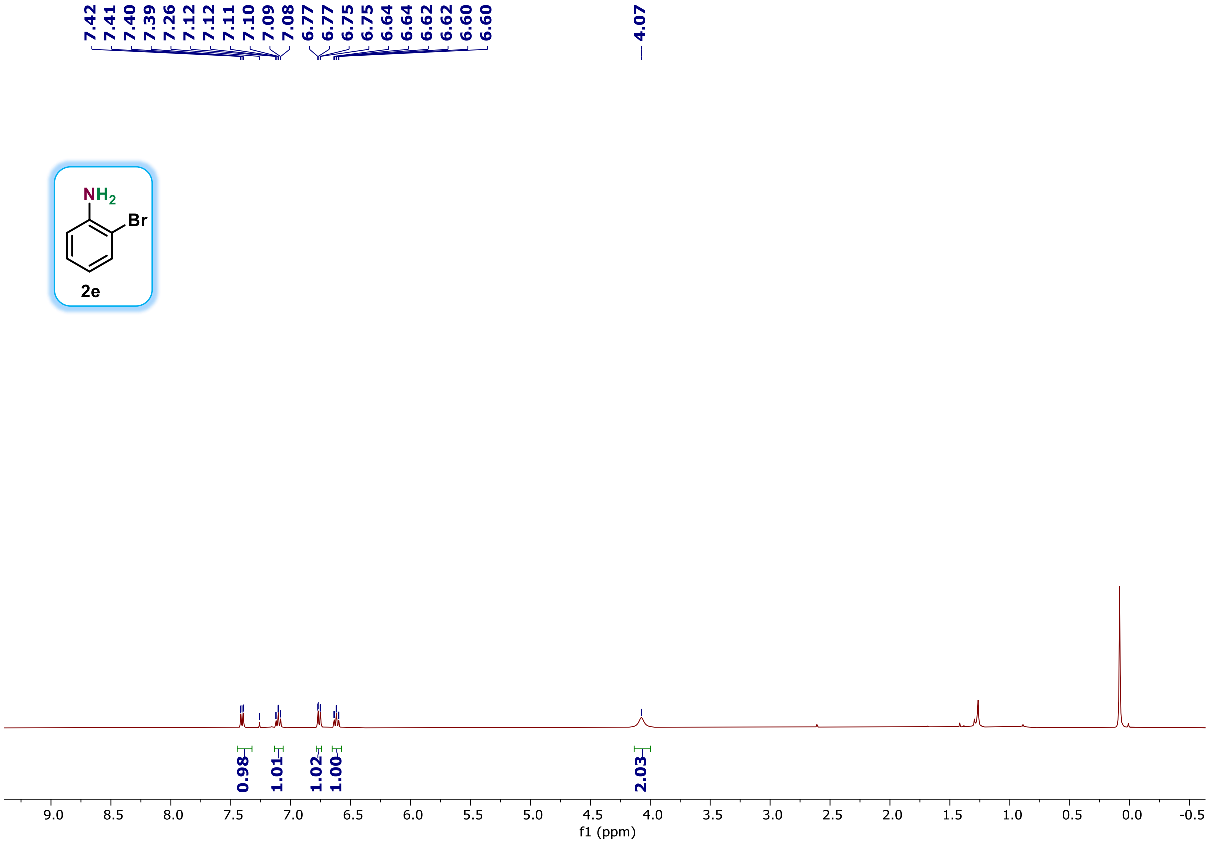
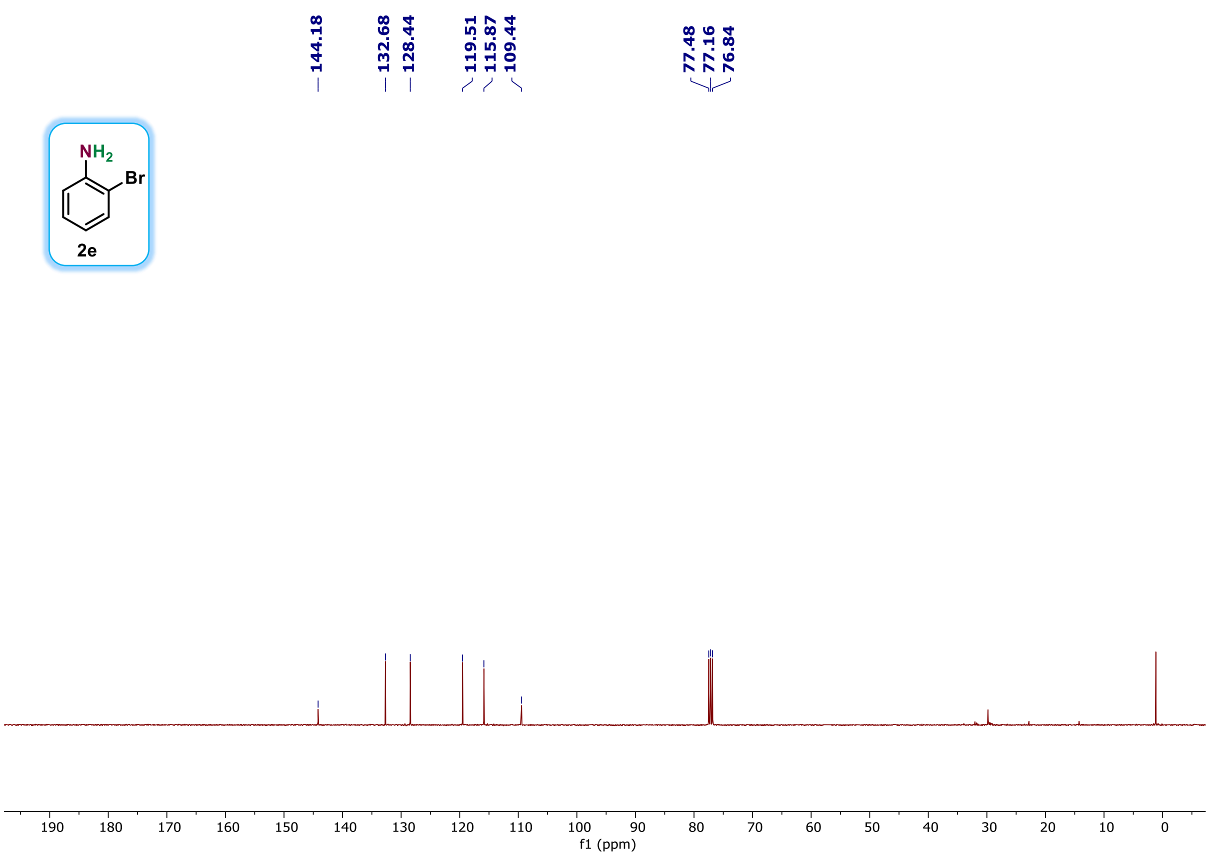
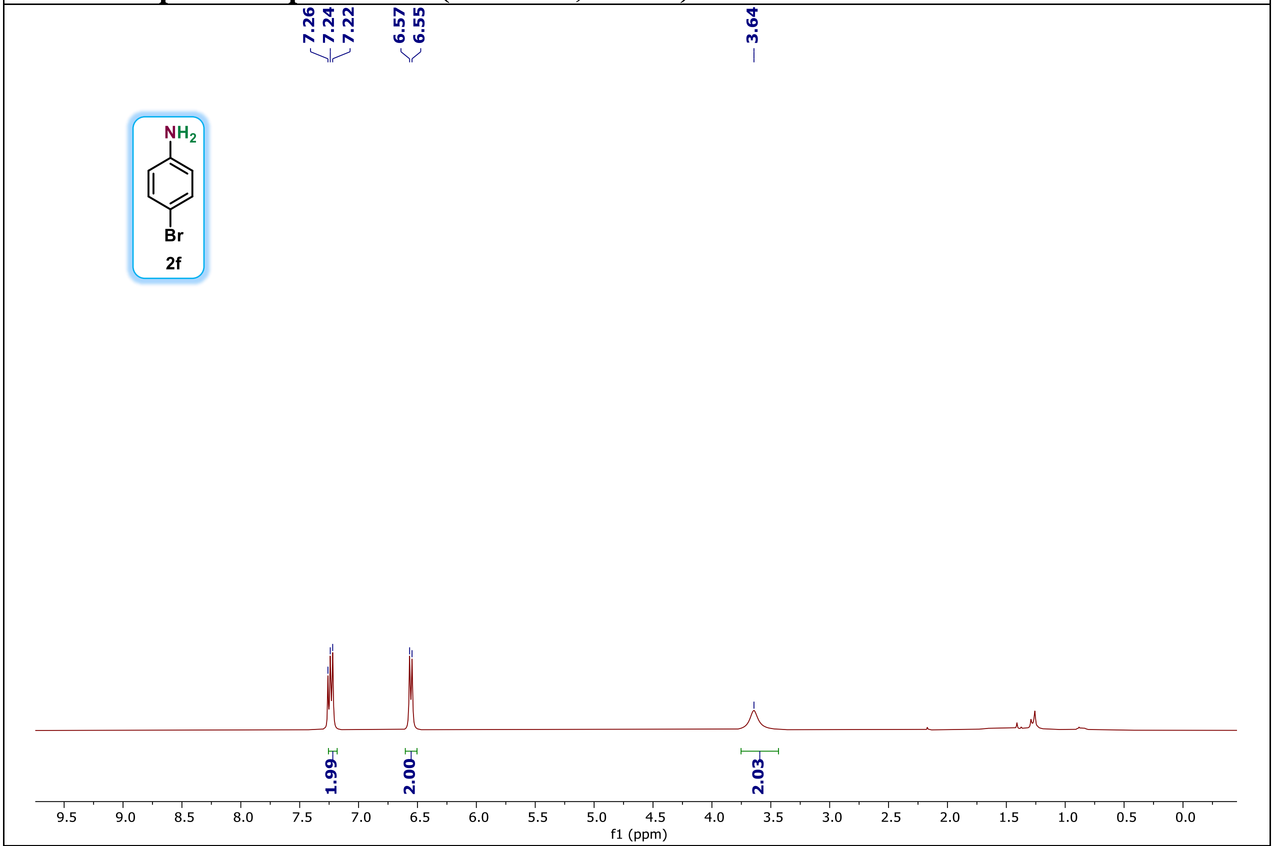
^{1}H NMR spectra of product 2e (400 MHz, $CDCl_3$)



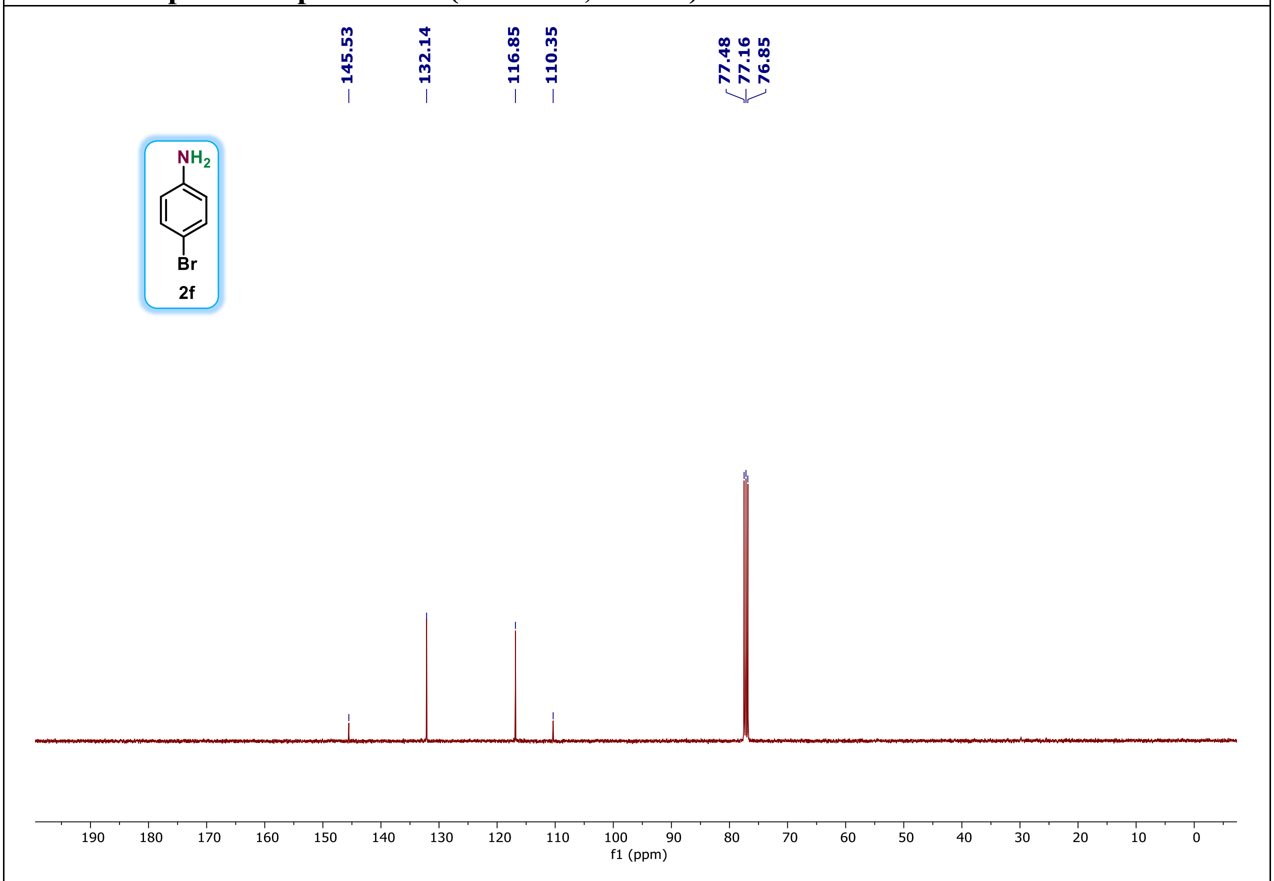
^{13}C NMR spectra of product 2e (101 MHz, $CDCl_3$)



[1]H NMR spectra of product 2f (400 MHz, $CDCl_3$)



[13]C NMR spectra of product 2f (101 MHz, $CDCl_3$)



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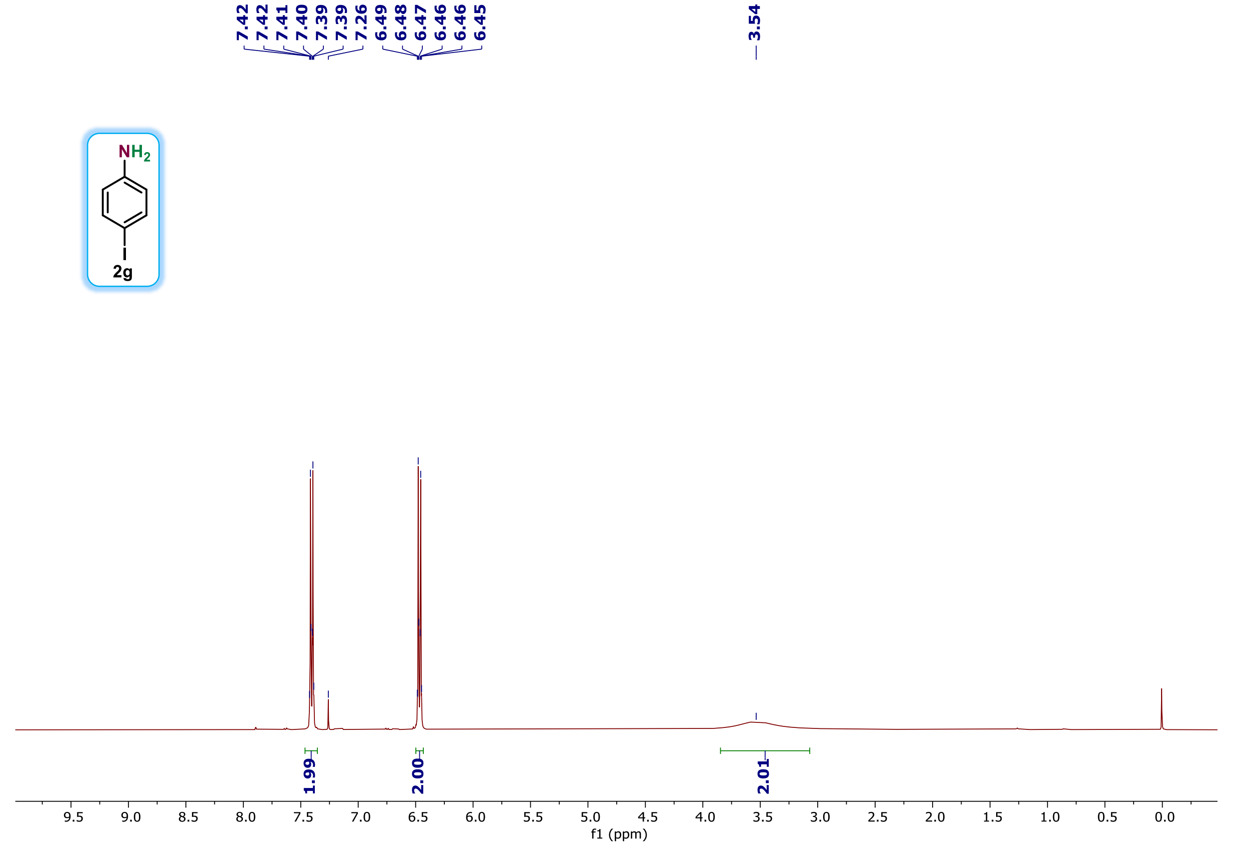
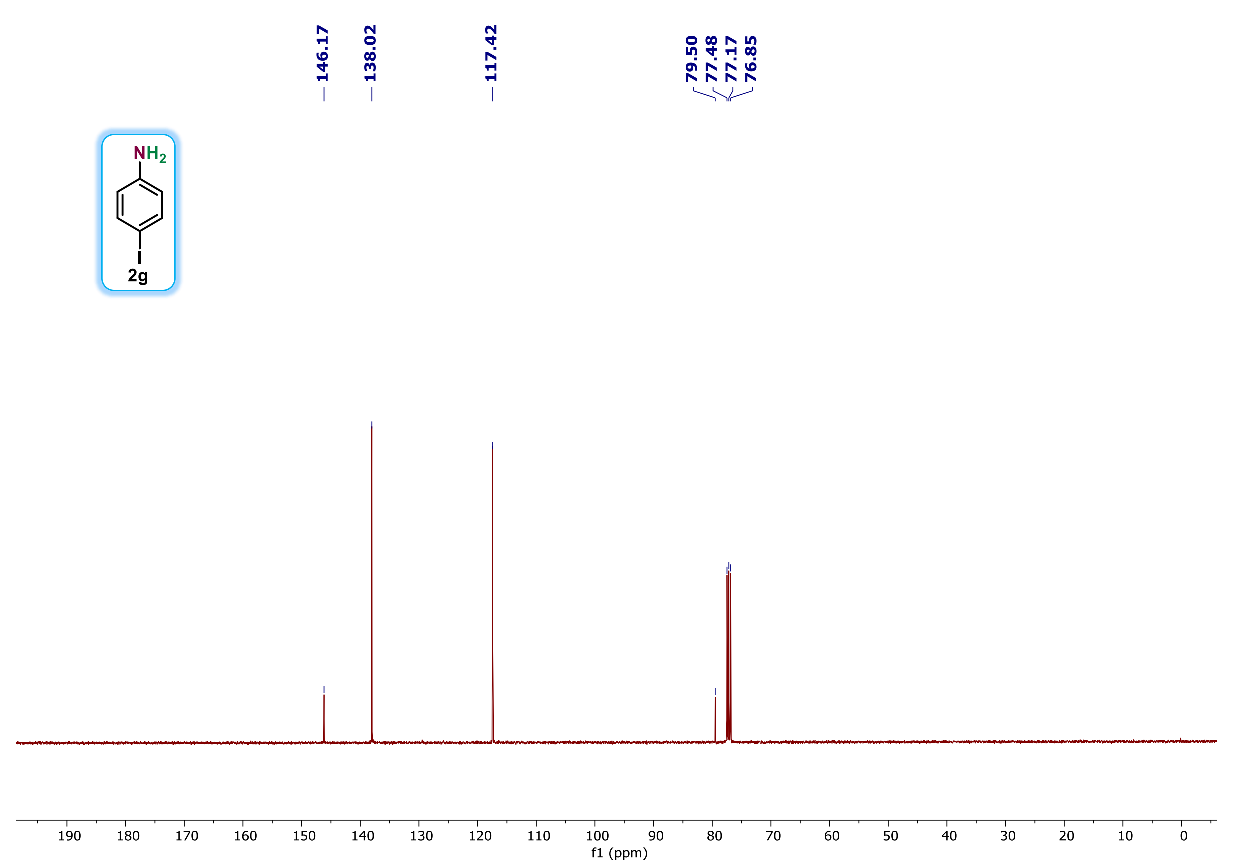
[1]H NMR spectra of product 2g (400 MHz, $CDCl_3$)



[13]C NMR spectra of product 2g (101 MHz, $CDCl_3$)



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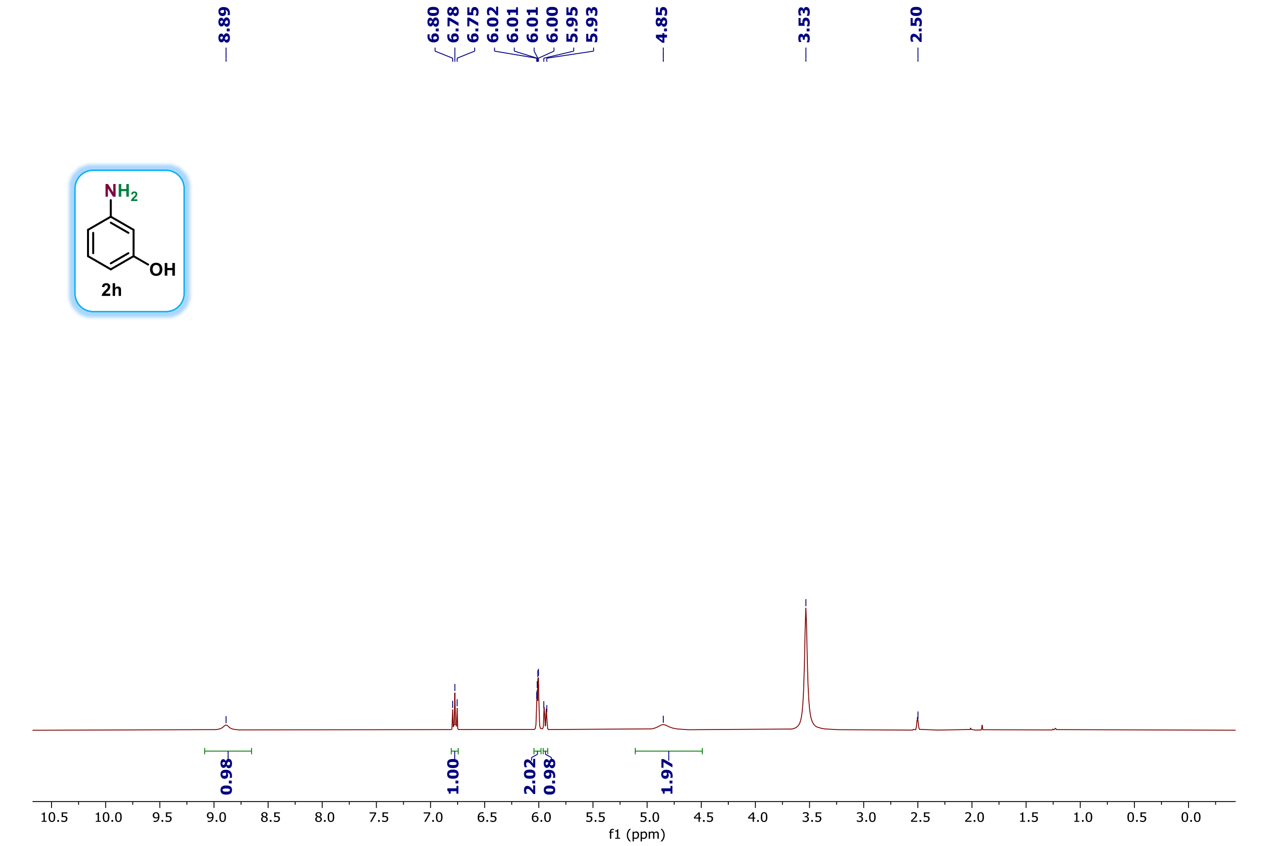
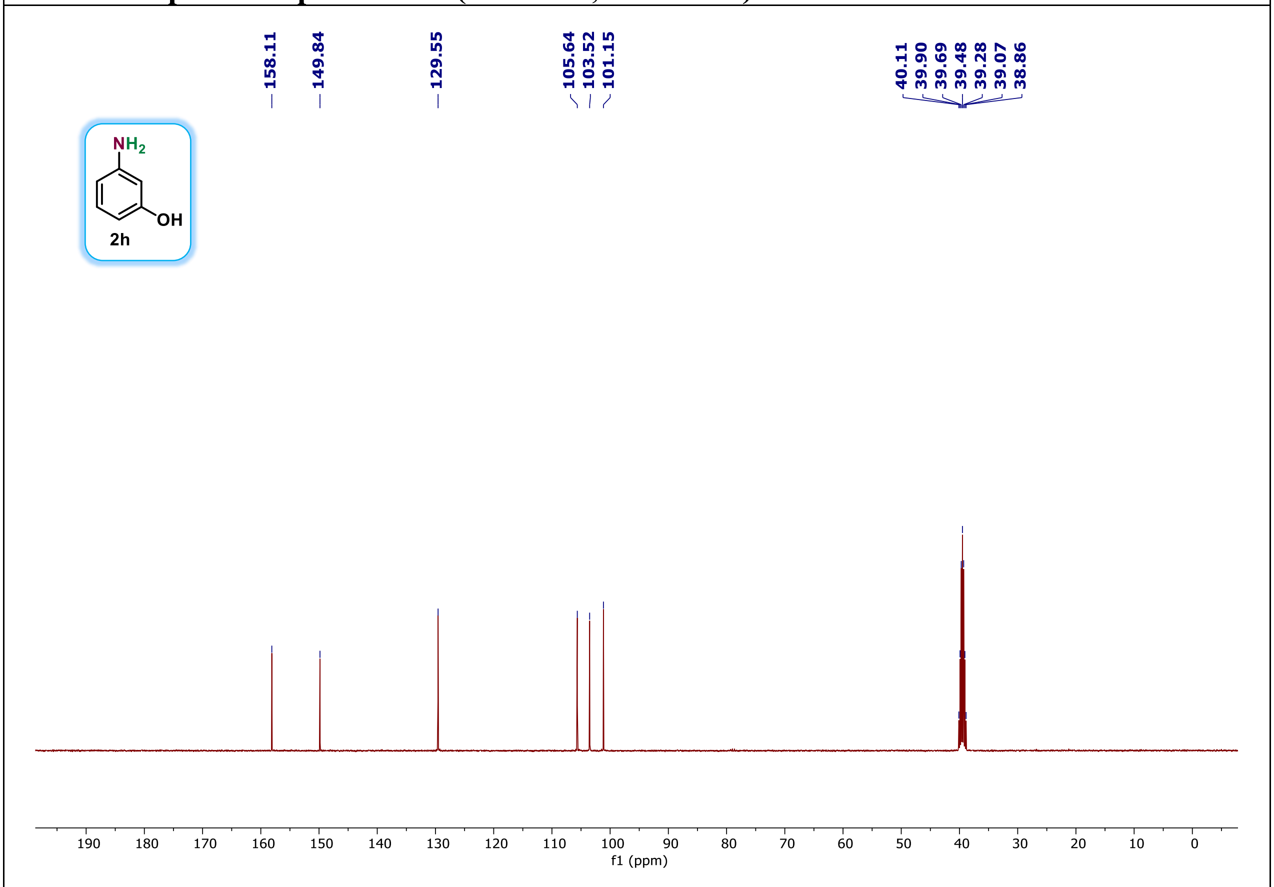
^{1}H NMR spectra of product 2h (400 MHz, DMSO-d_6)



^{13}C NMR spectra of product 2h (101 MHz, DMSO-d_6)



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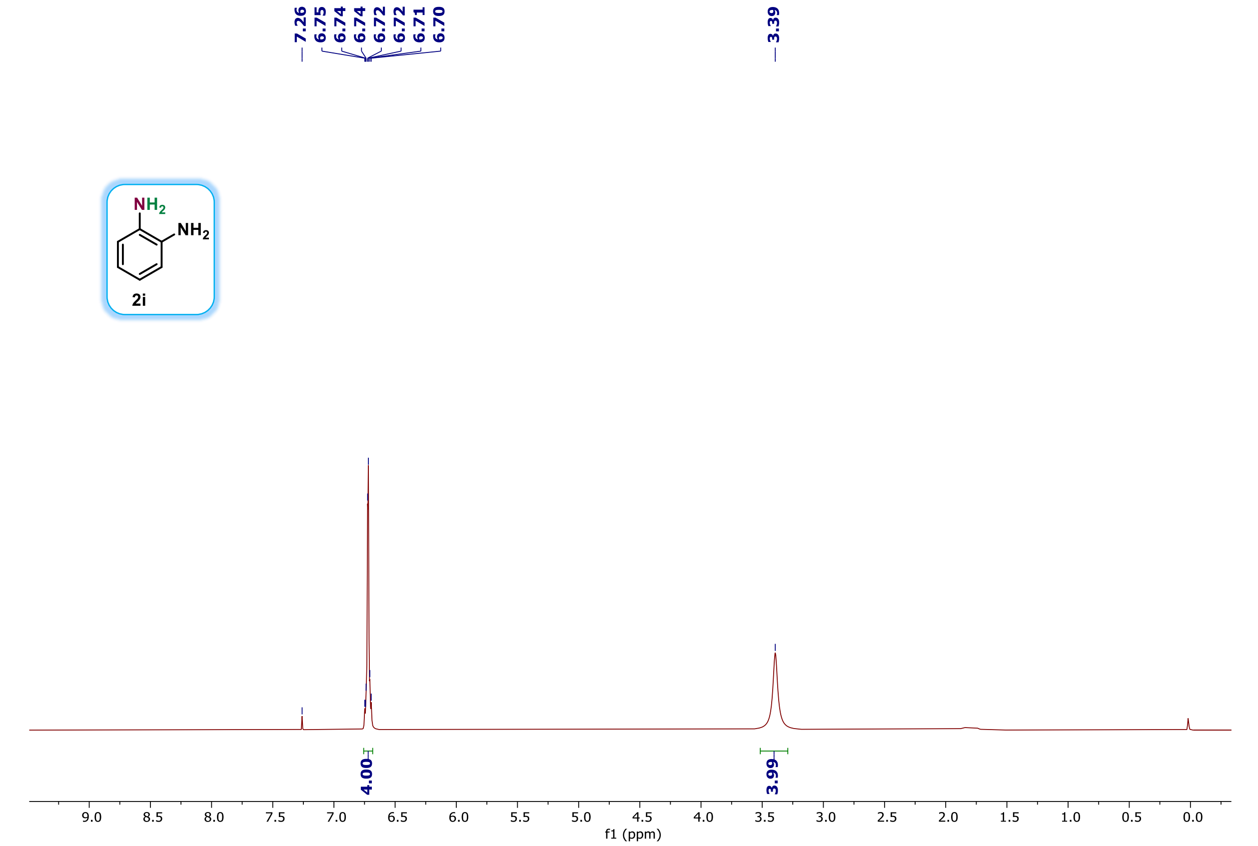
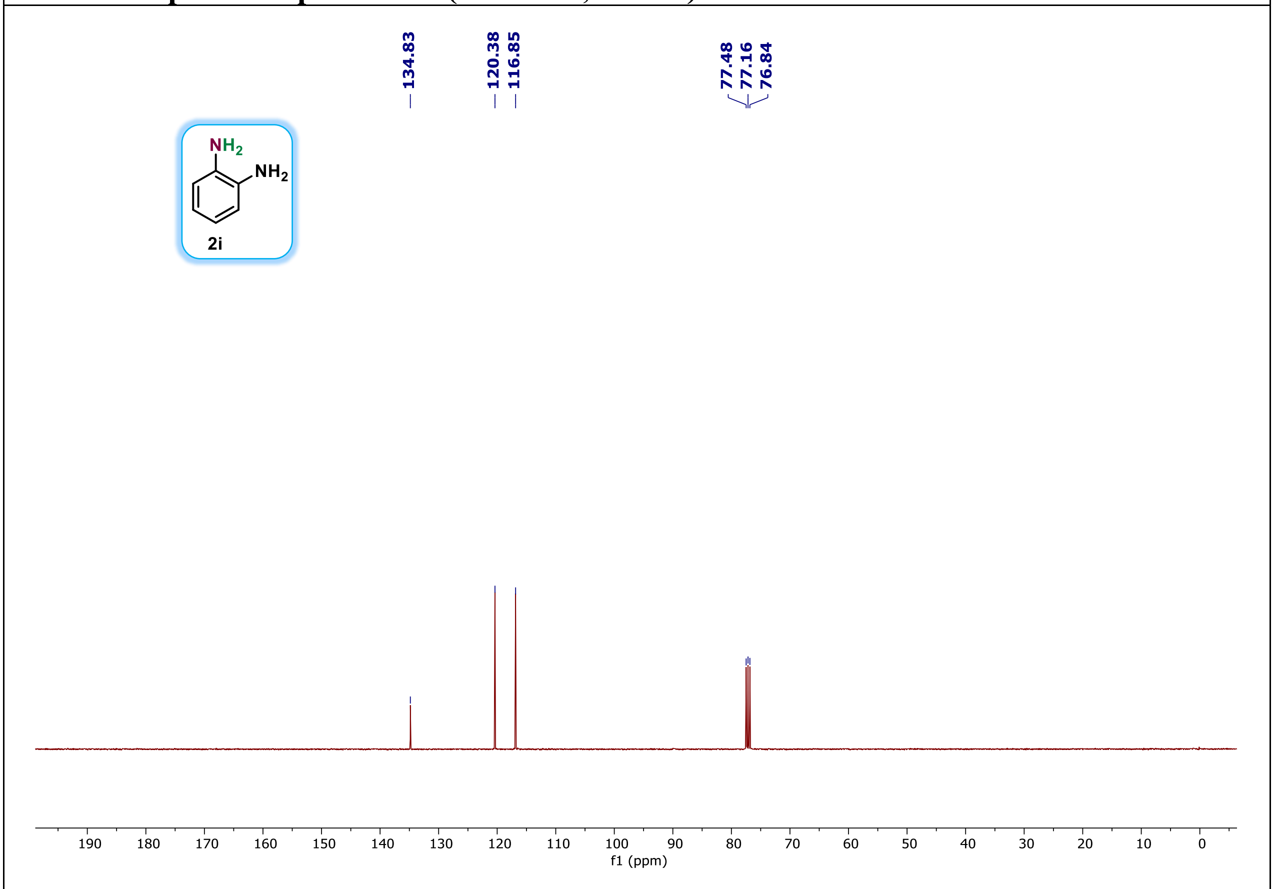
^1H NMR spectra of product 2i (400 MHz, $CDCl_3$)



^{13}C NMR spectra of product 2i (101 MHz, $CDCl_3$)



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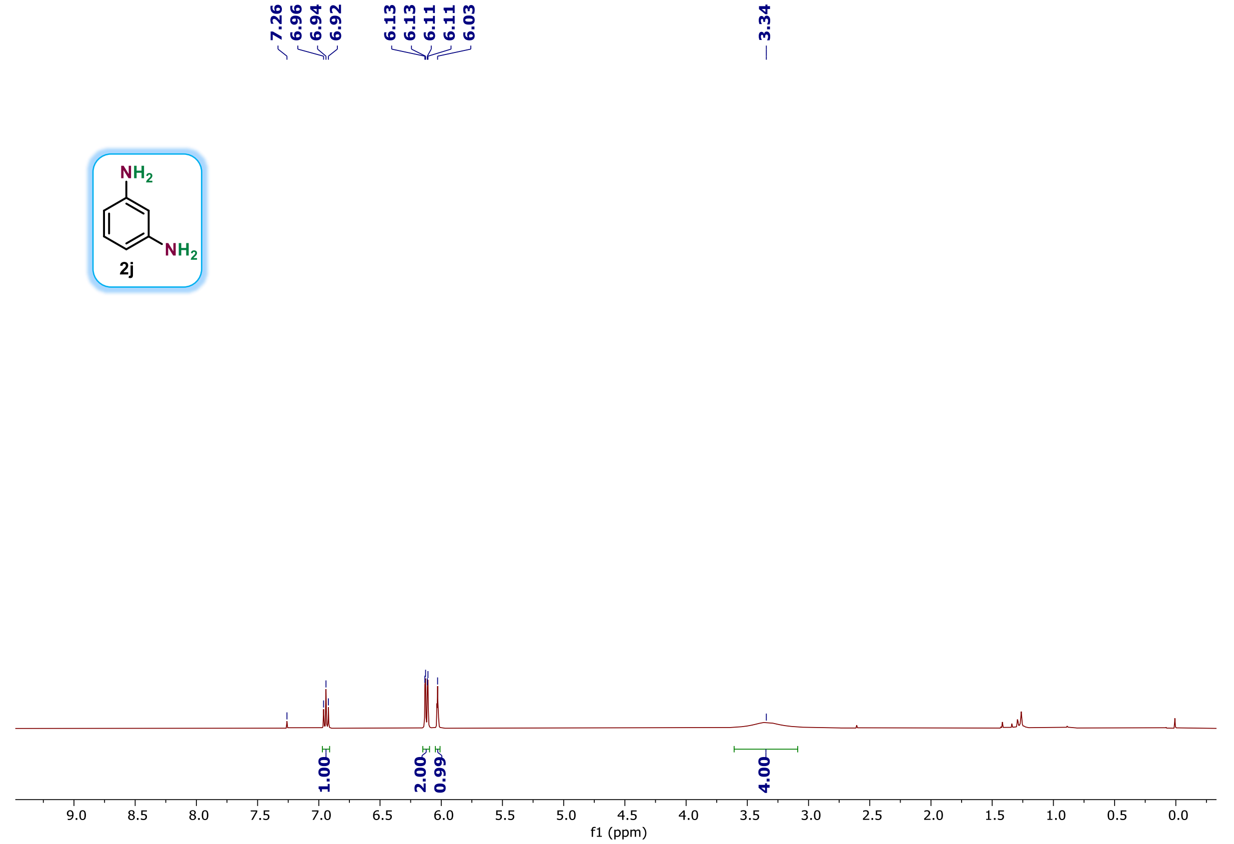

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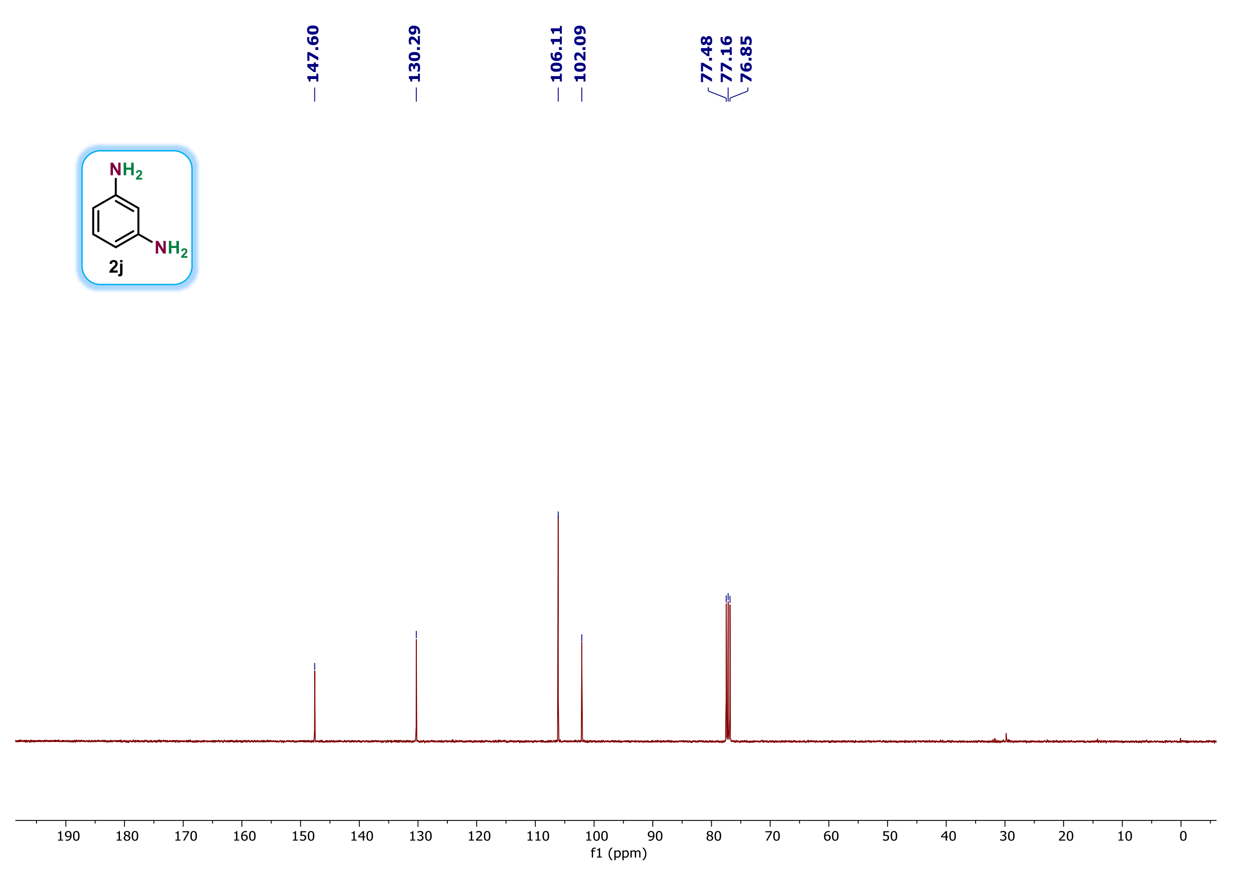

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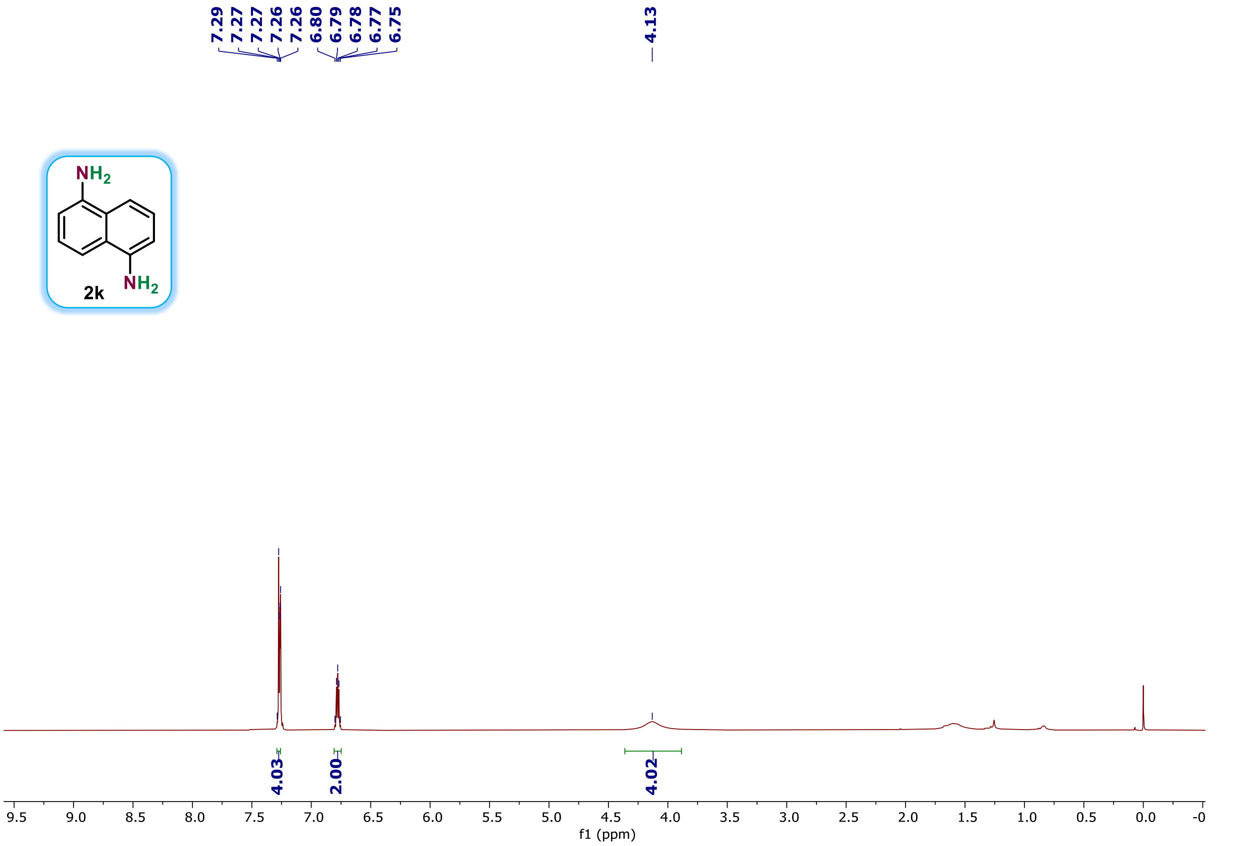
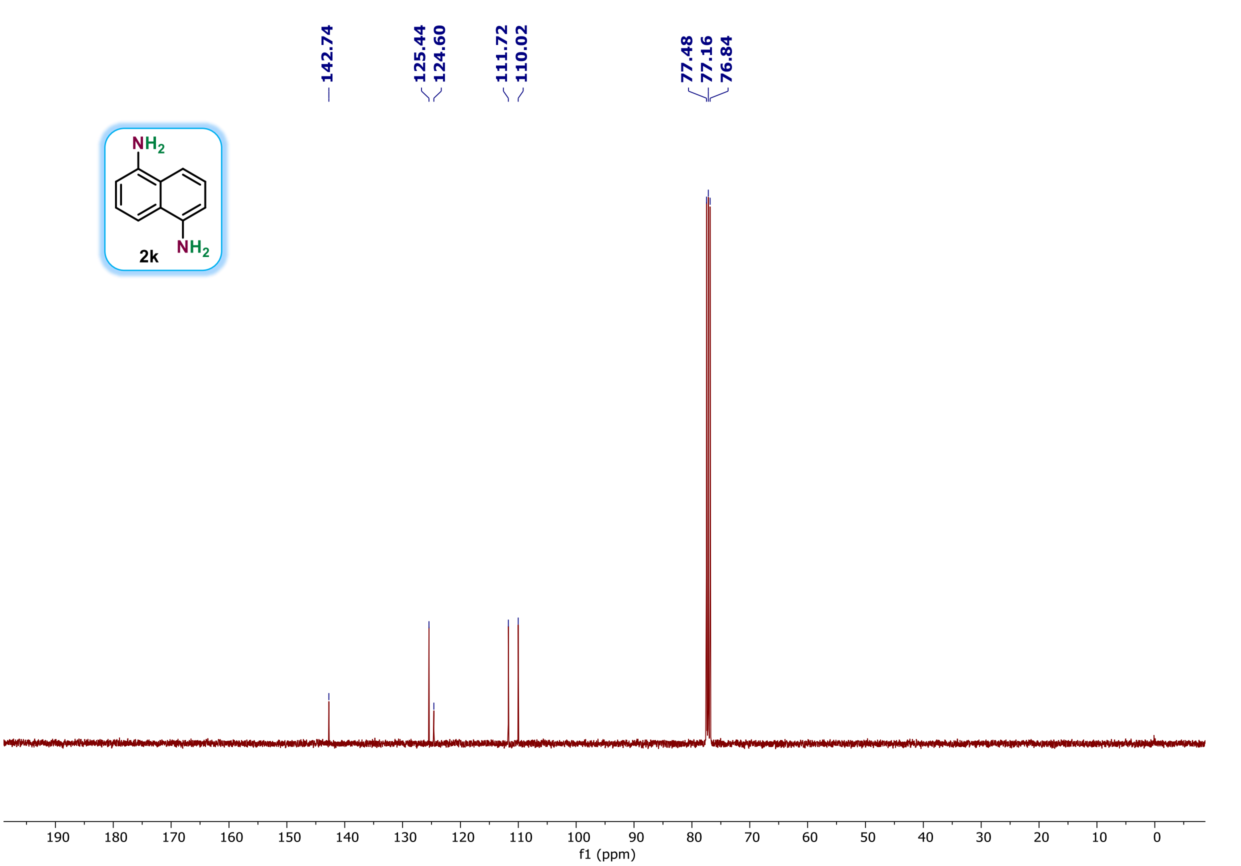
^{1}H NMR spectra of product 2k (400 MHz, $CDCl_3$)



^{13}C NMR spectra of product 2k (101 MHz, $CDCl_3$)



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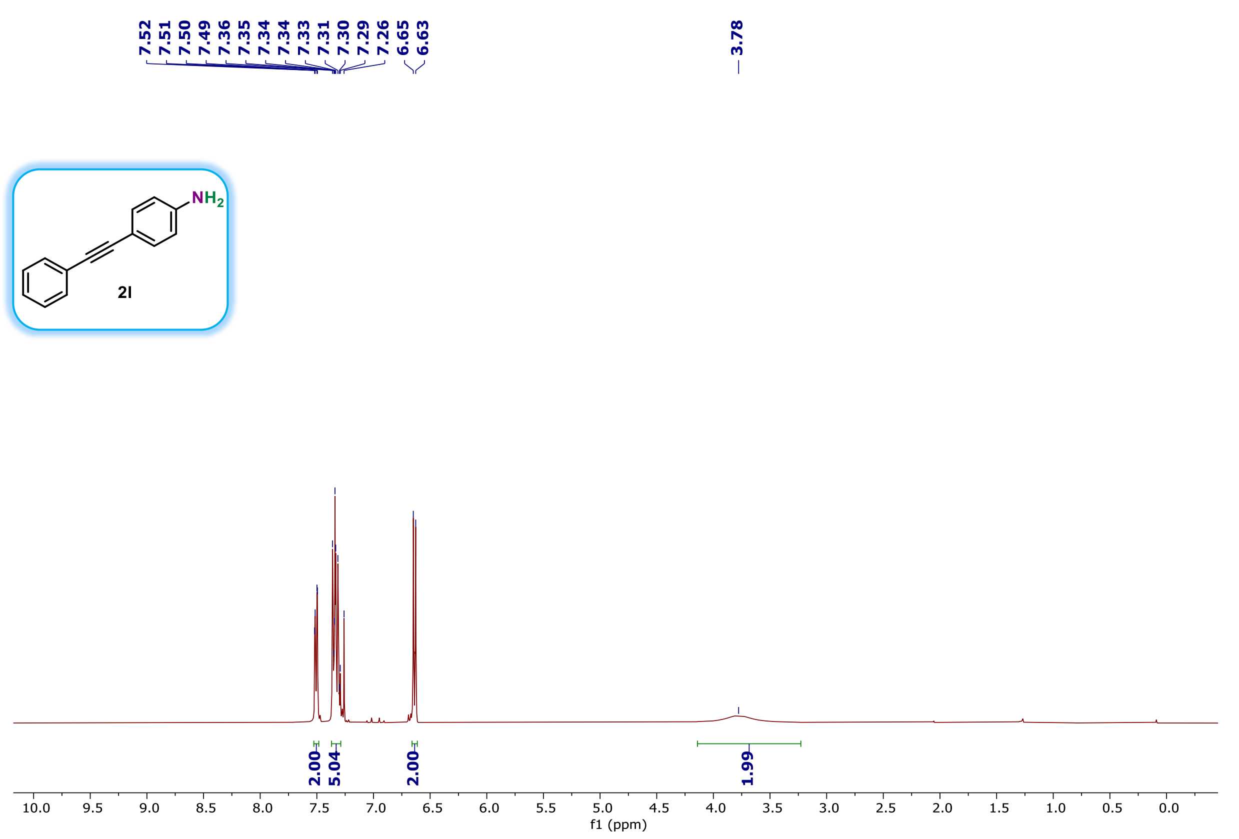
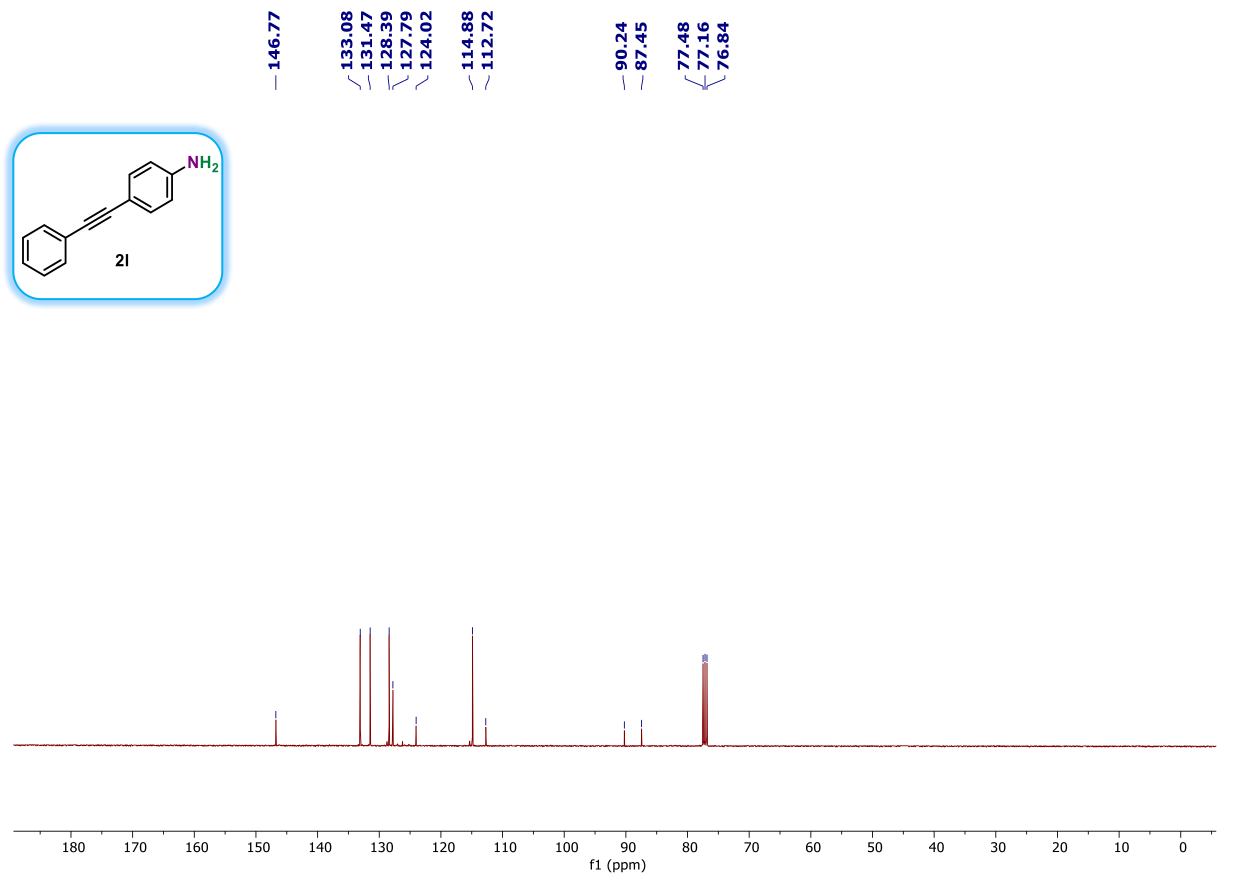
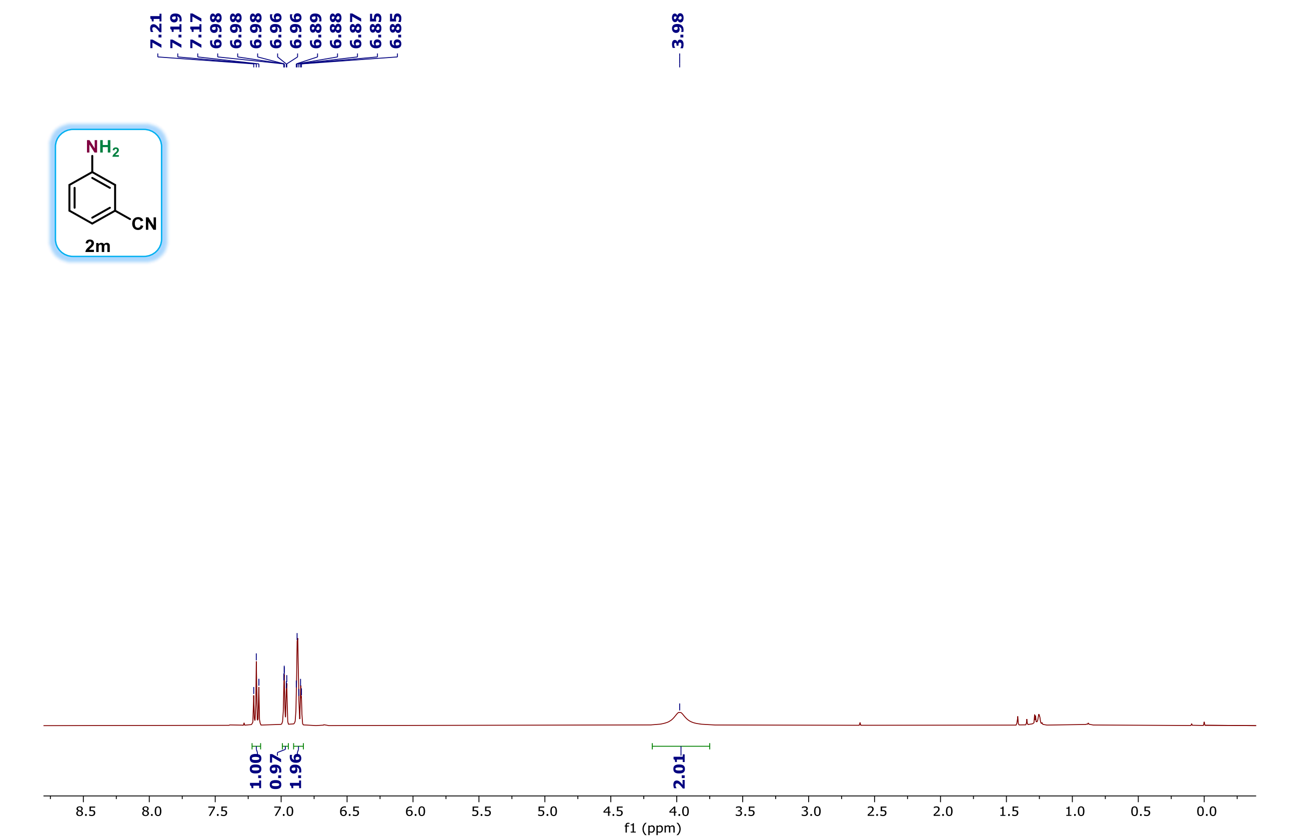
[1]H NMR spectra of product 2l (400 MHz, CDCl3)



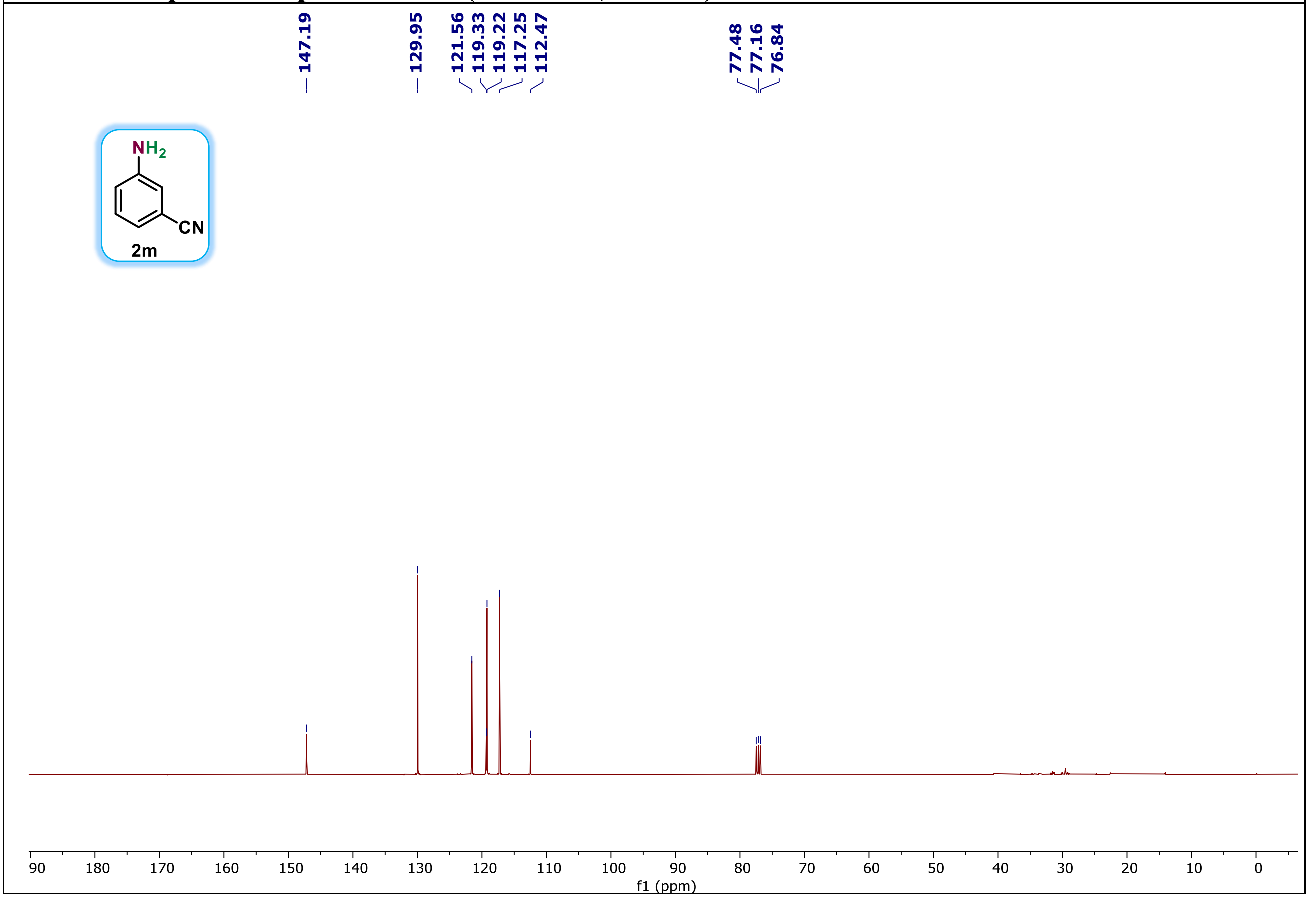
[13]C NMR spectra of product 2l (101 MHz, CDCl3)



[1]H NMR spectra of product 2m (400 MHz, CDCl3)



[13]C NMR spectra of product 2m (101 MHz, CDCl3)



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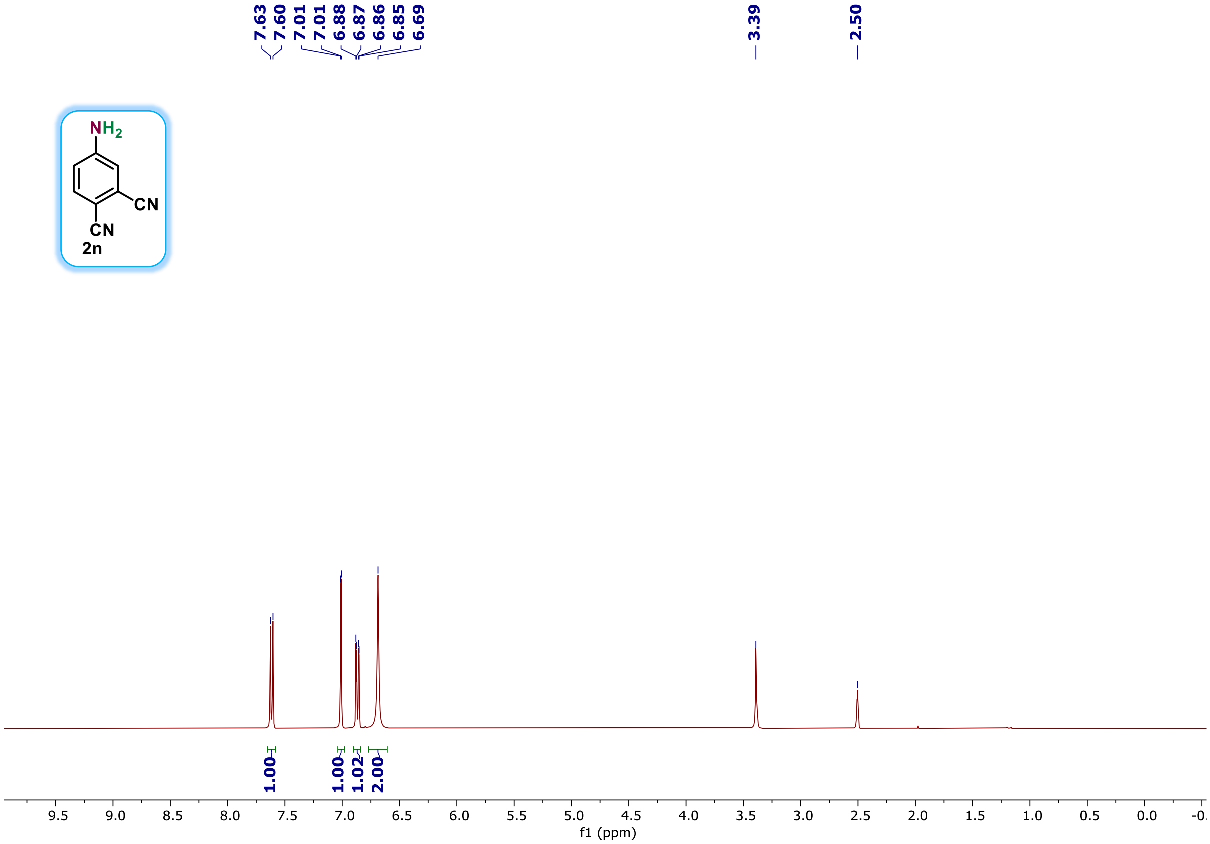
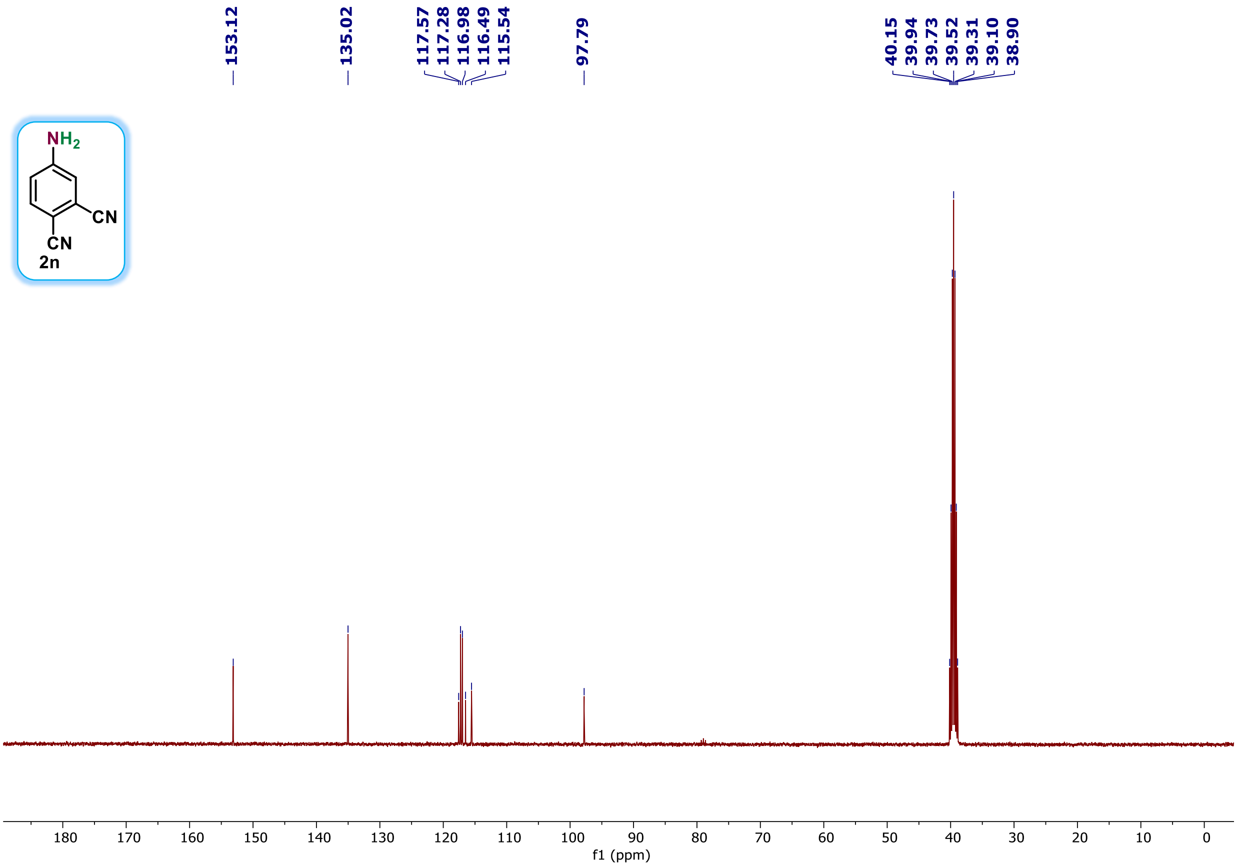
^{1}H NMR spectra of product 2n (400 MHz, DMSO-d_6)



^{13}C NMR spectra of product 2n (101 MHz, DMSO-d_6)



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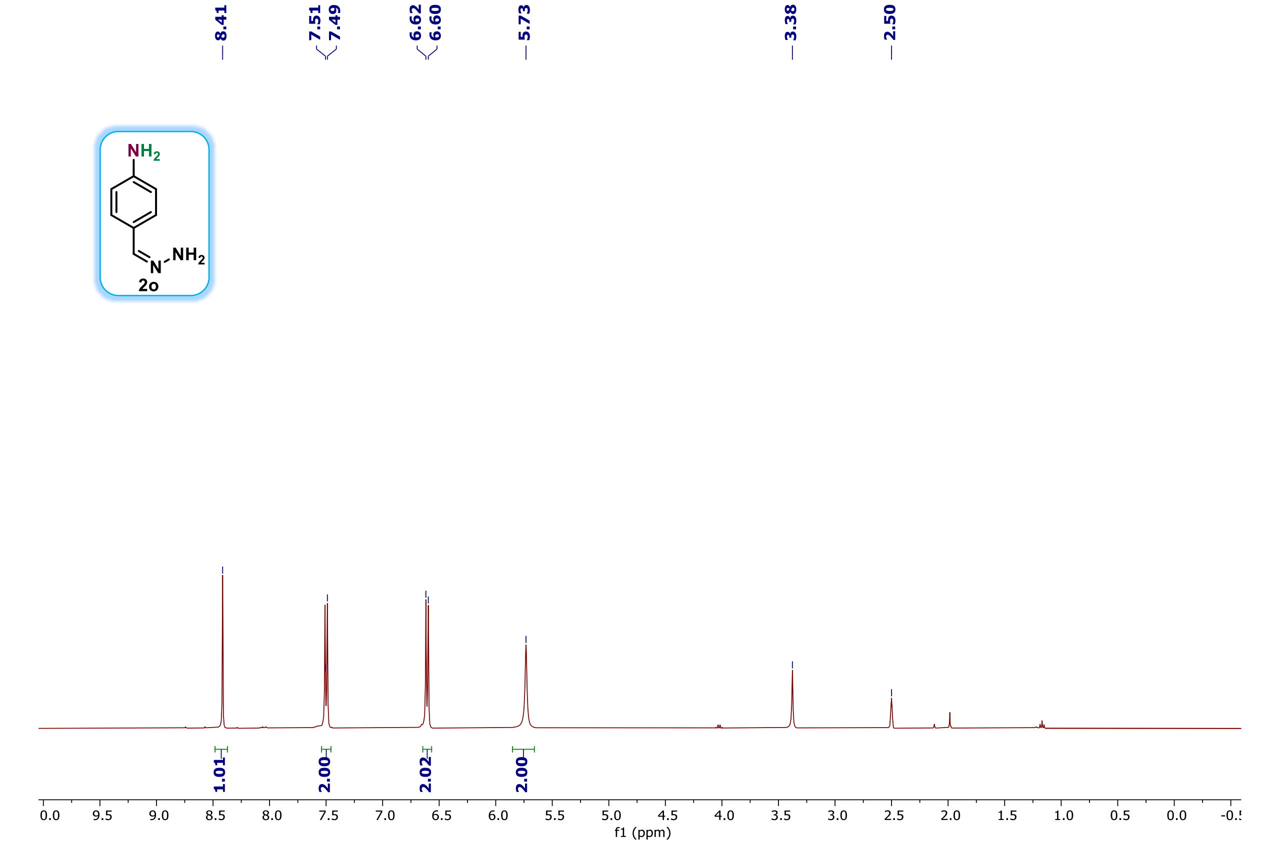
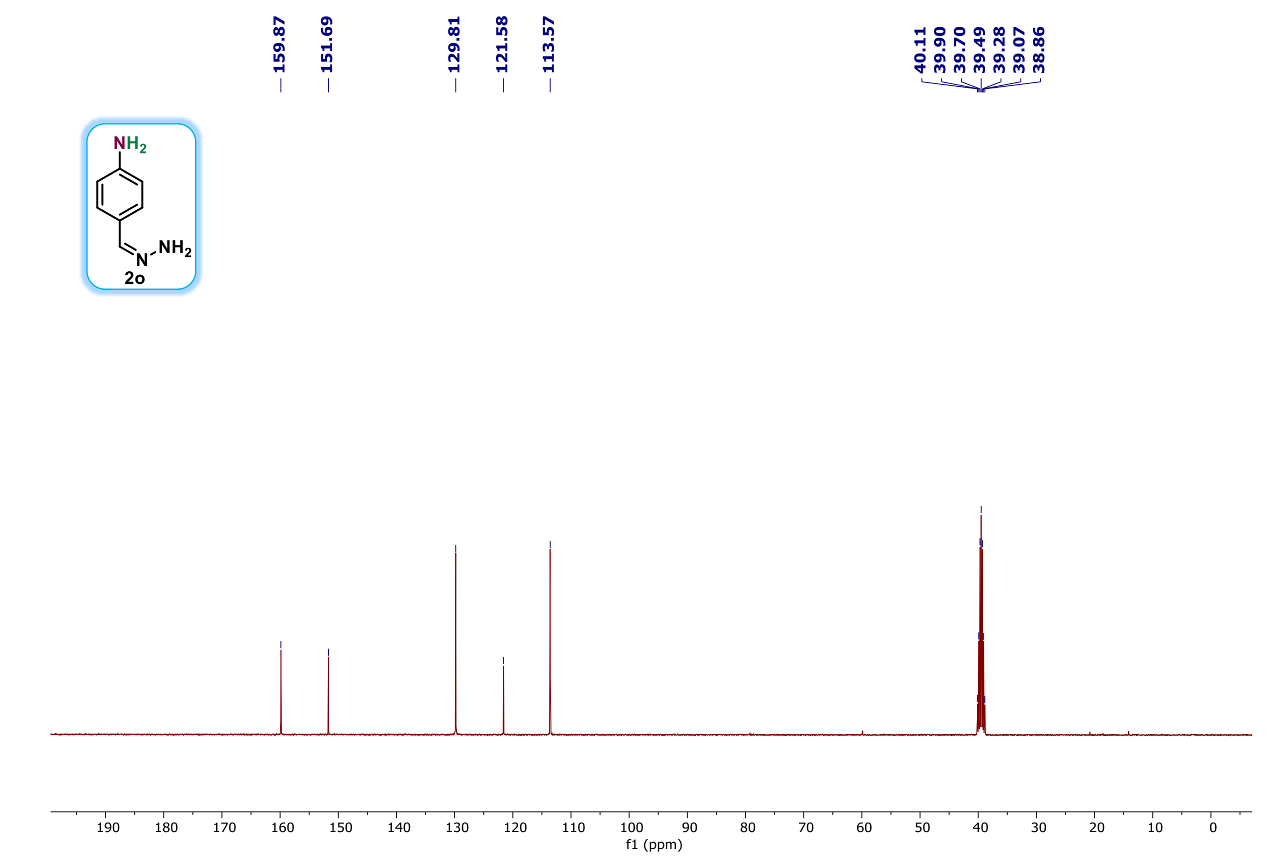
[1]H NMR spectra of product 2o (400 MHz, DMSO-d6)



[13]C NMR spectra of product 2o (101 MHz, DMSO-d6)



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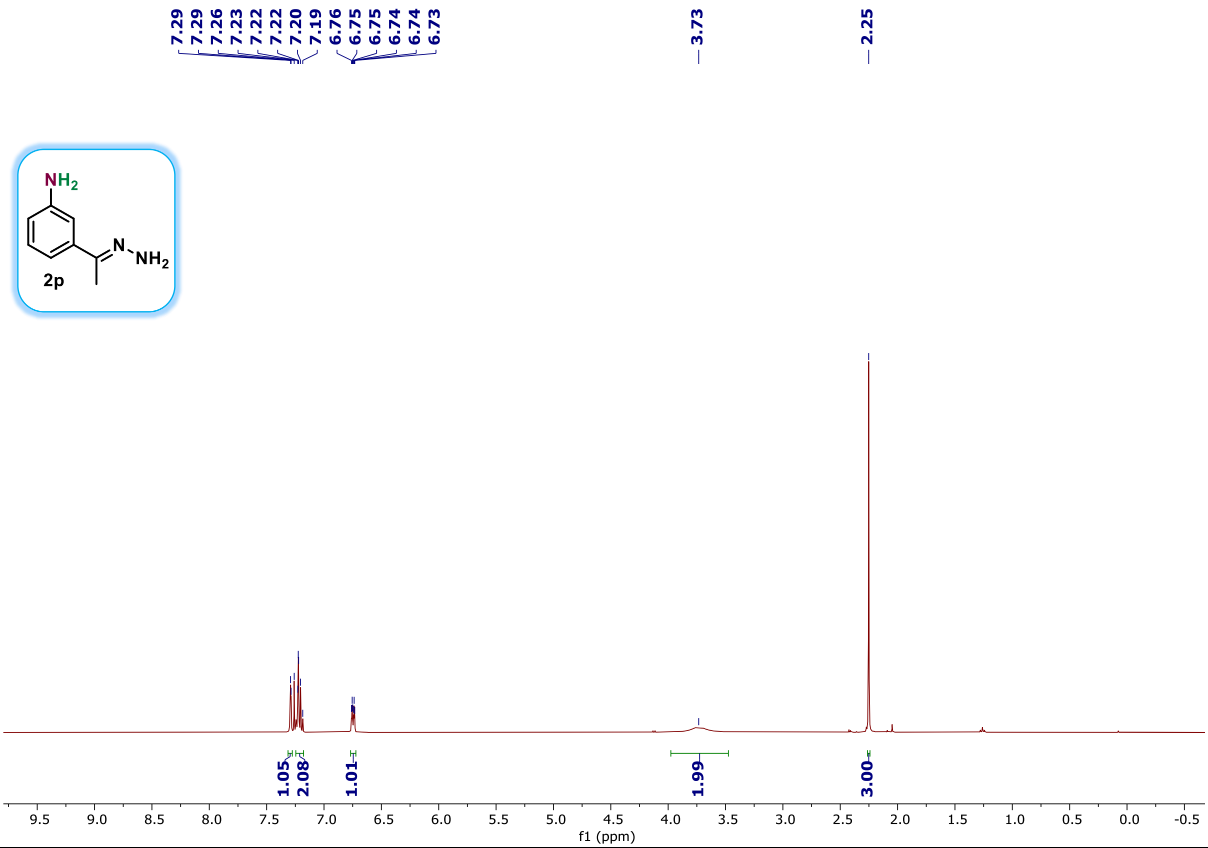
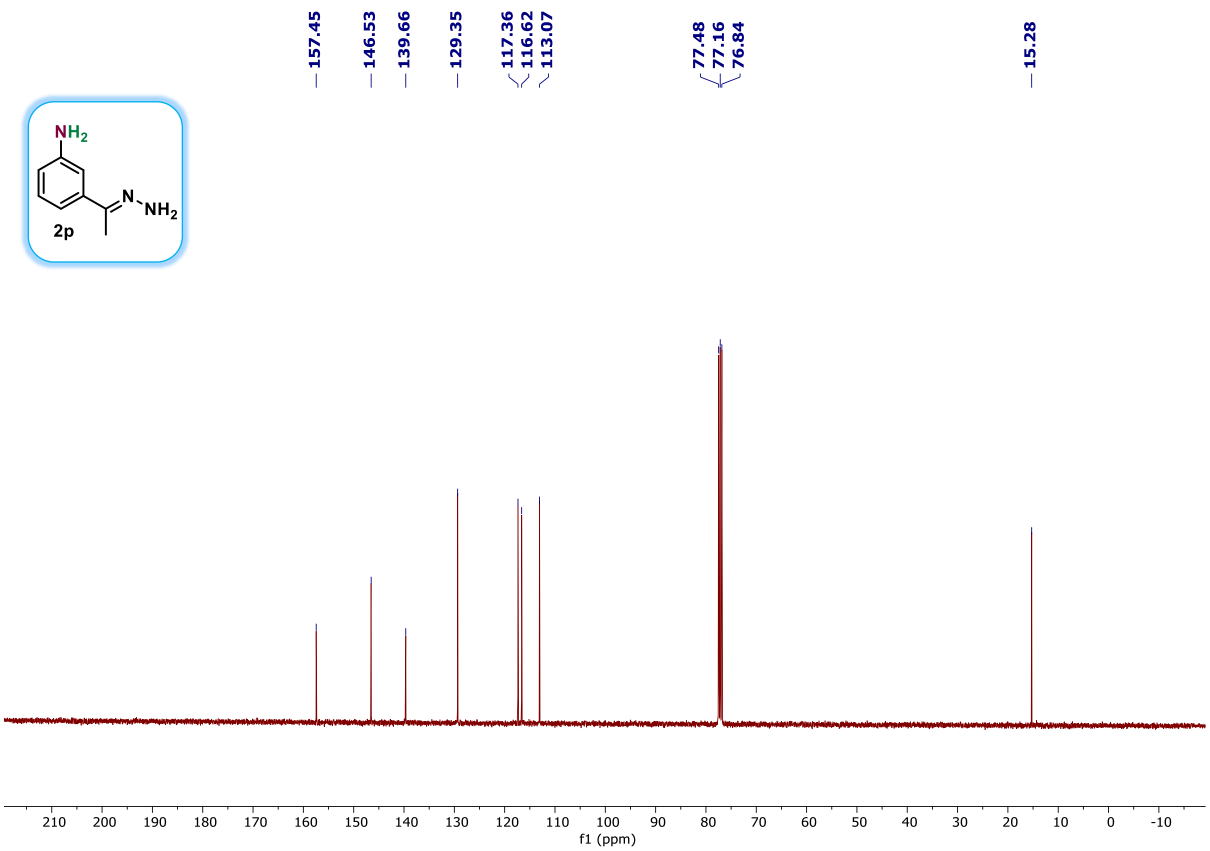
^{1}H NMR spectra of product 2p (400 MHz, $CDCl_3$)



^{13}C NMR spectra of product 2p (101 MHz, $CDCl_3$)



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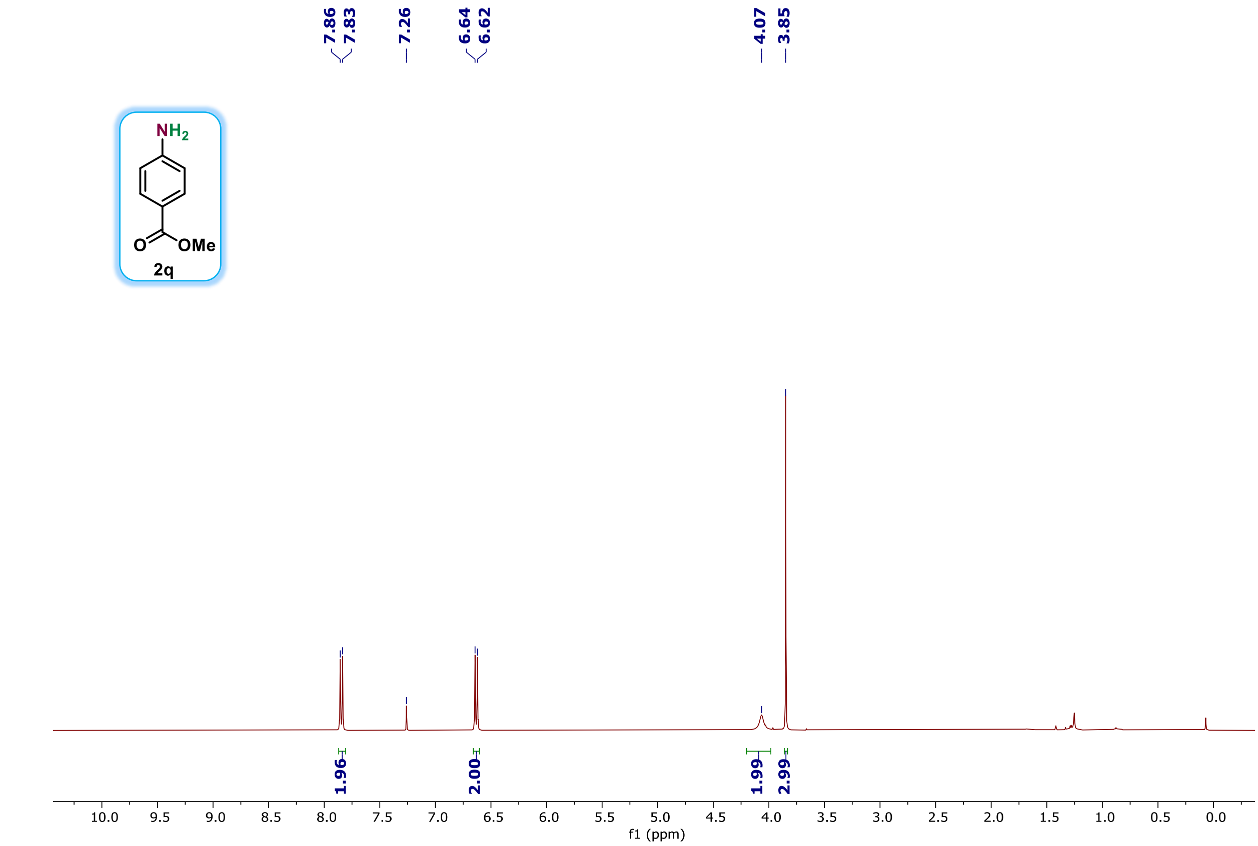
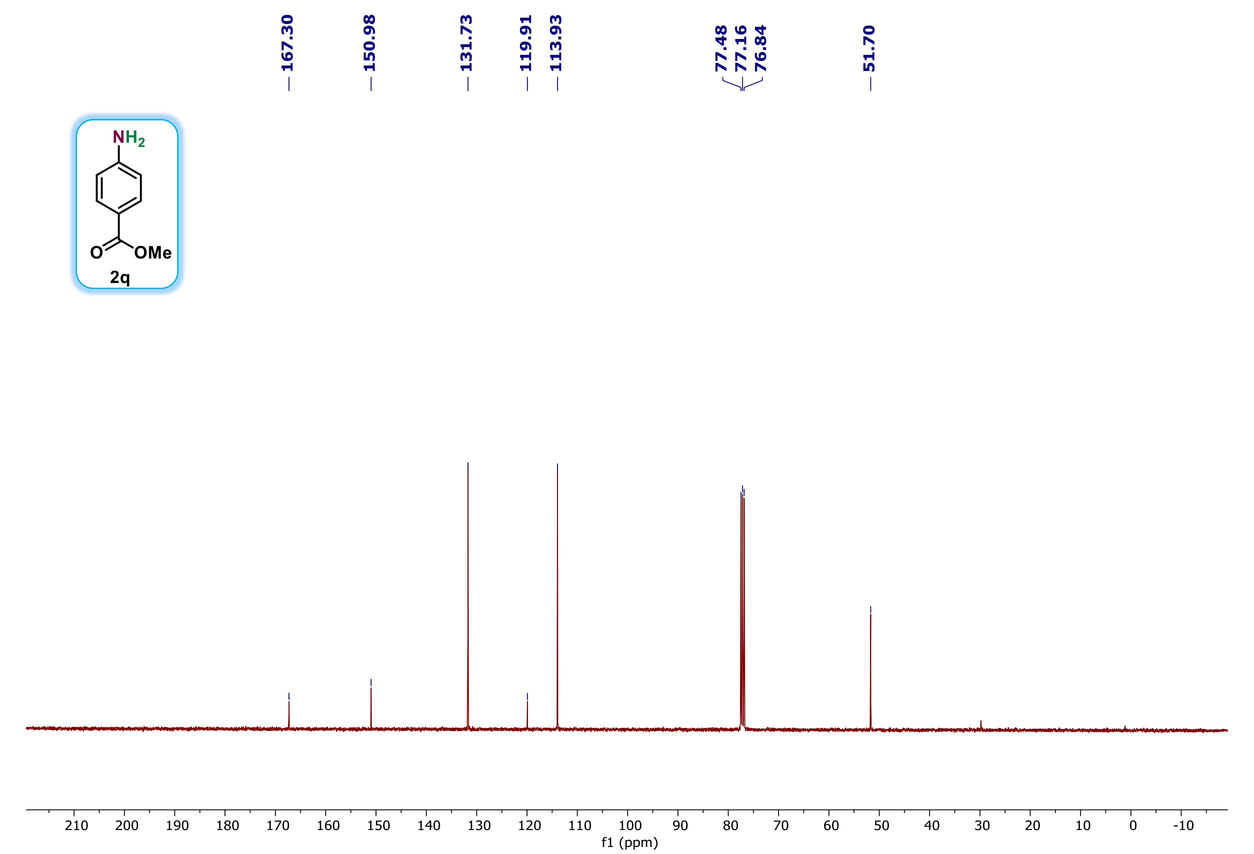
^1H NMR spectra of product 2q (400 MHz, $CDCl_3$)



^{13}C NMR spectra of product 2q (101 MHz, $CDCl_3$)



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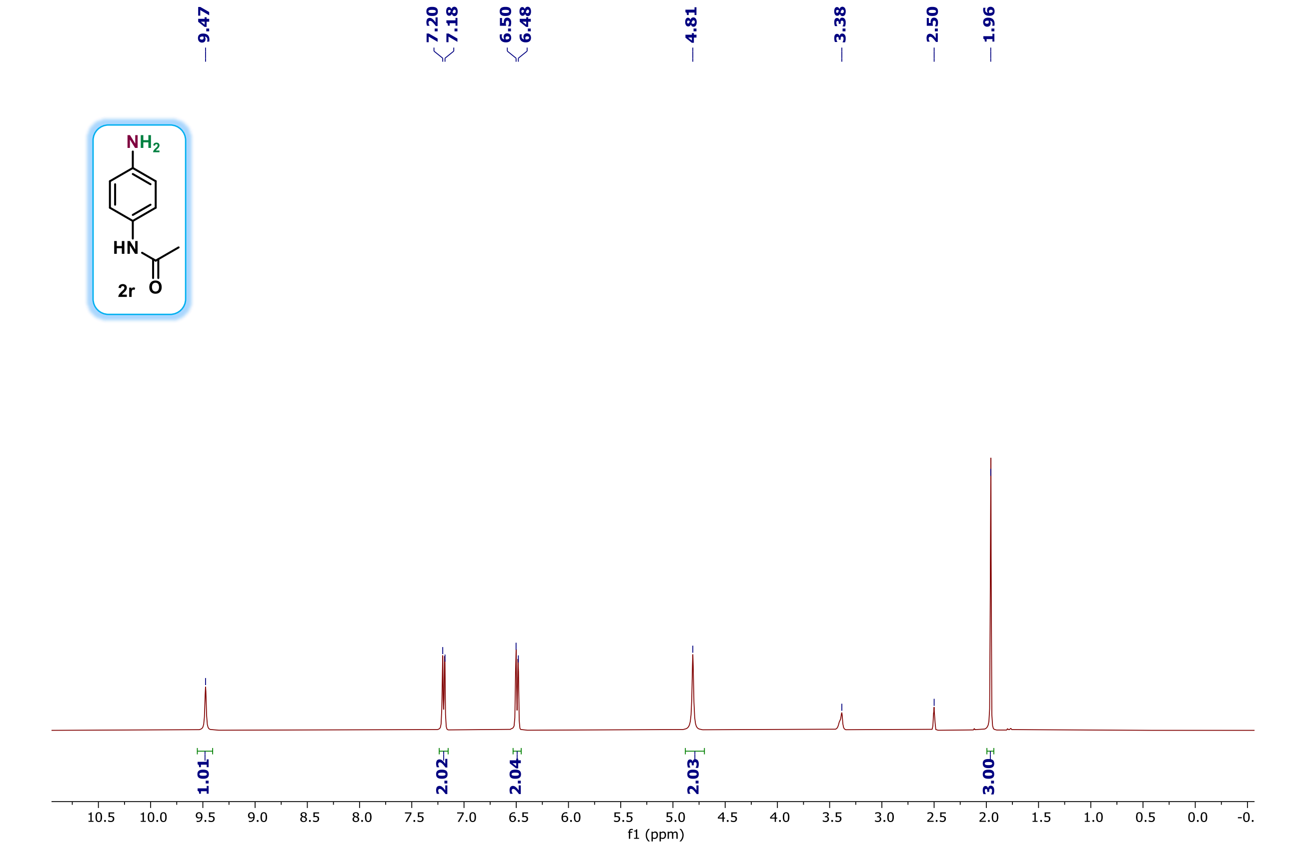
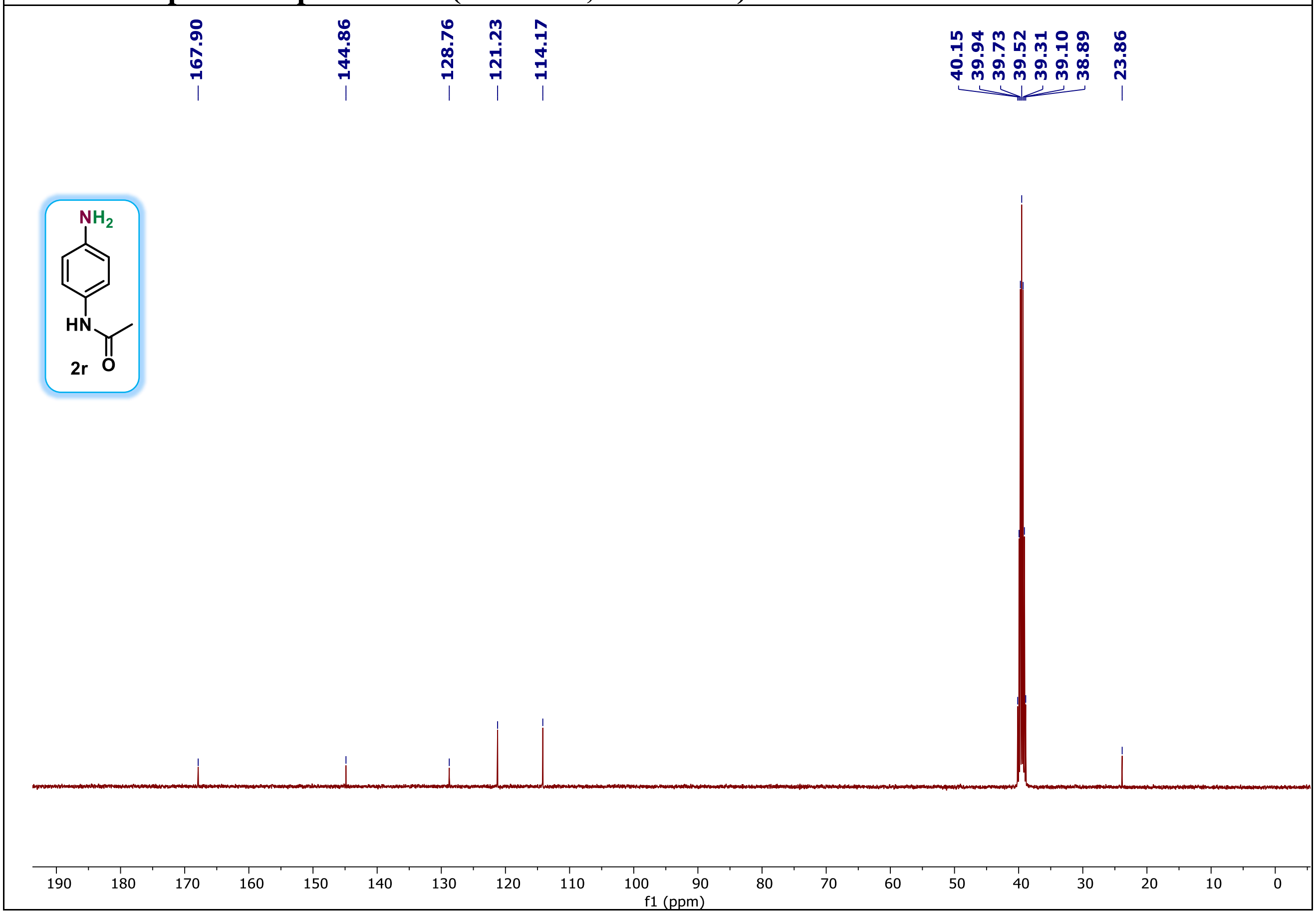
^{1}H NMR spectra of product 2r (400 MHz, DMSO-d$_6$)



^{13}C NMR spectra of product 2r (101 MHz, DMSO-d$_6$)



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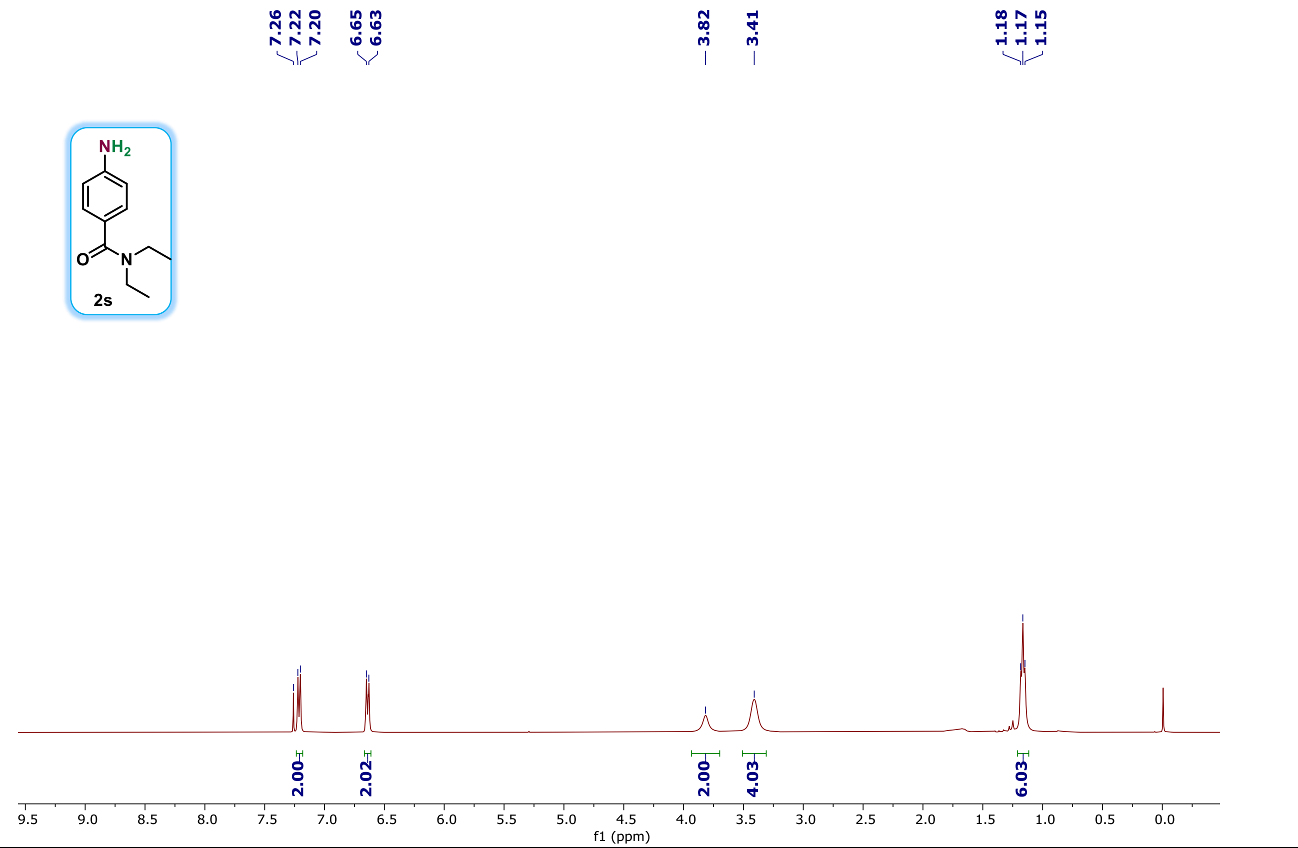
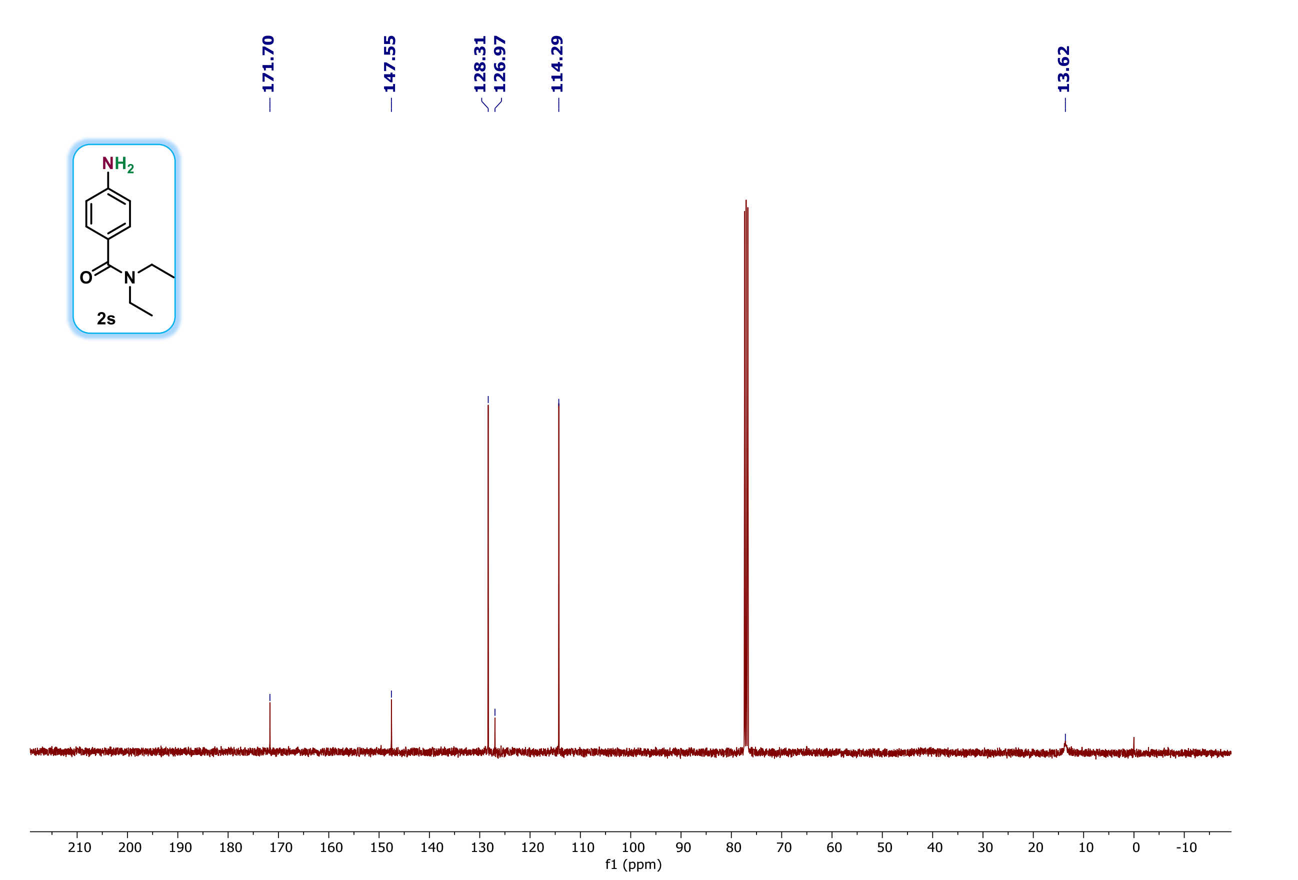
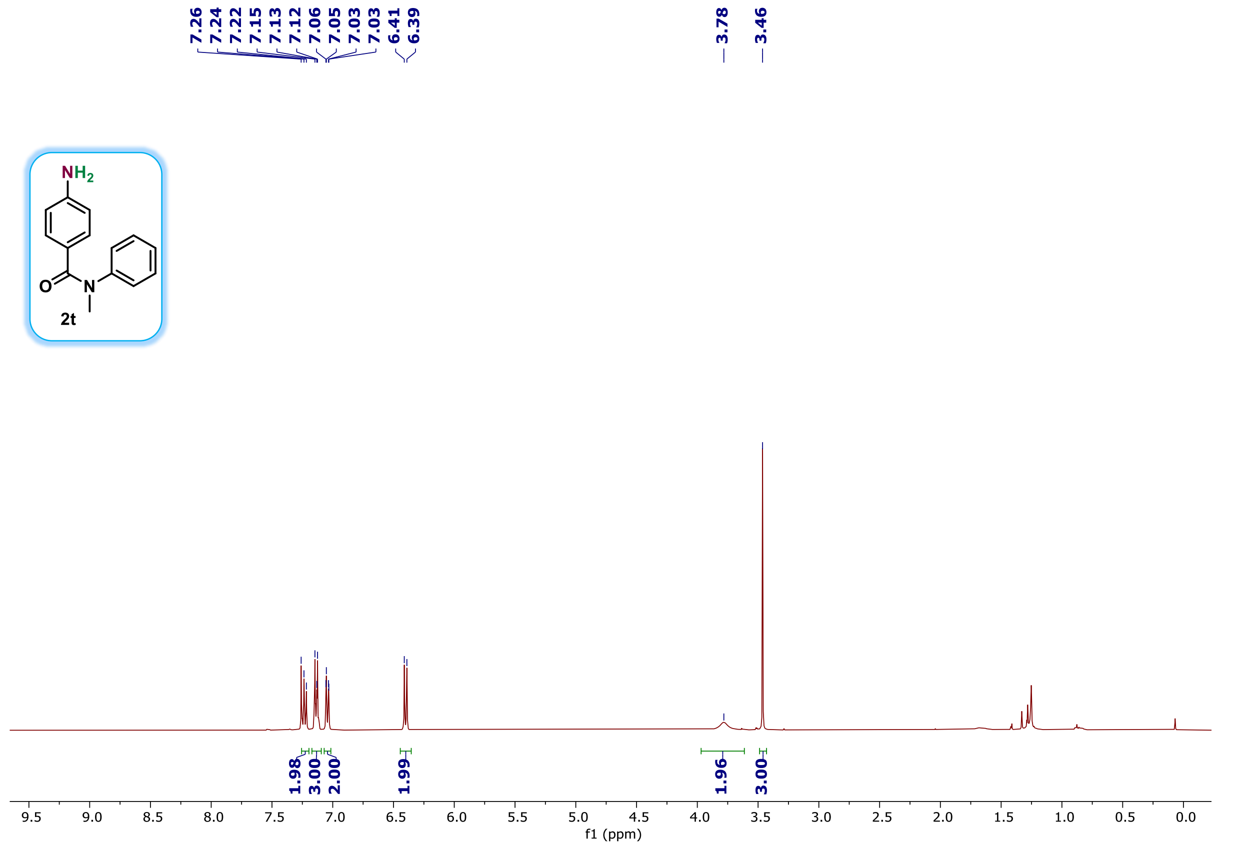
[1]H NMR spectra of product 2s (400 MHz, $CDCl_3$)



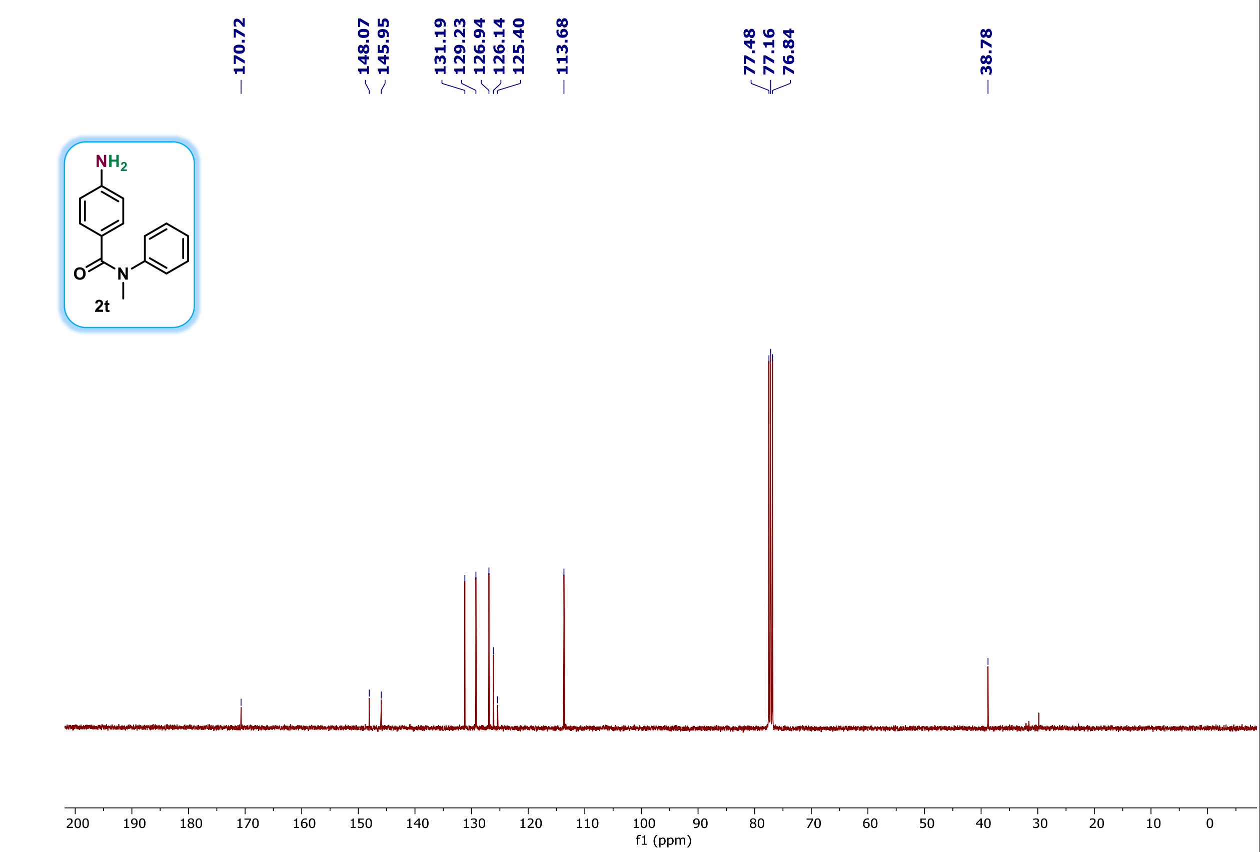
[13]C NMR spectra of product 2s (101 MHz, $CDCl_3$)



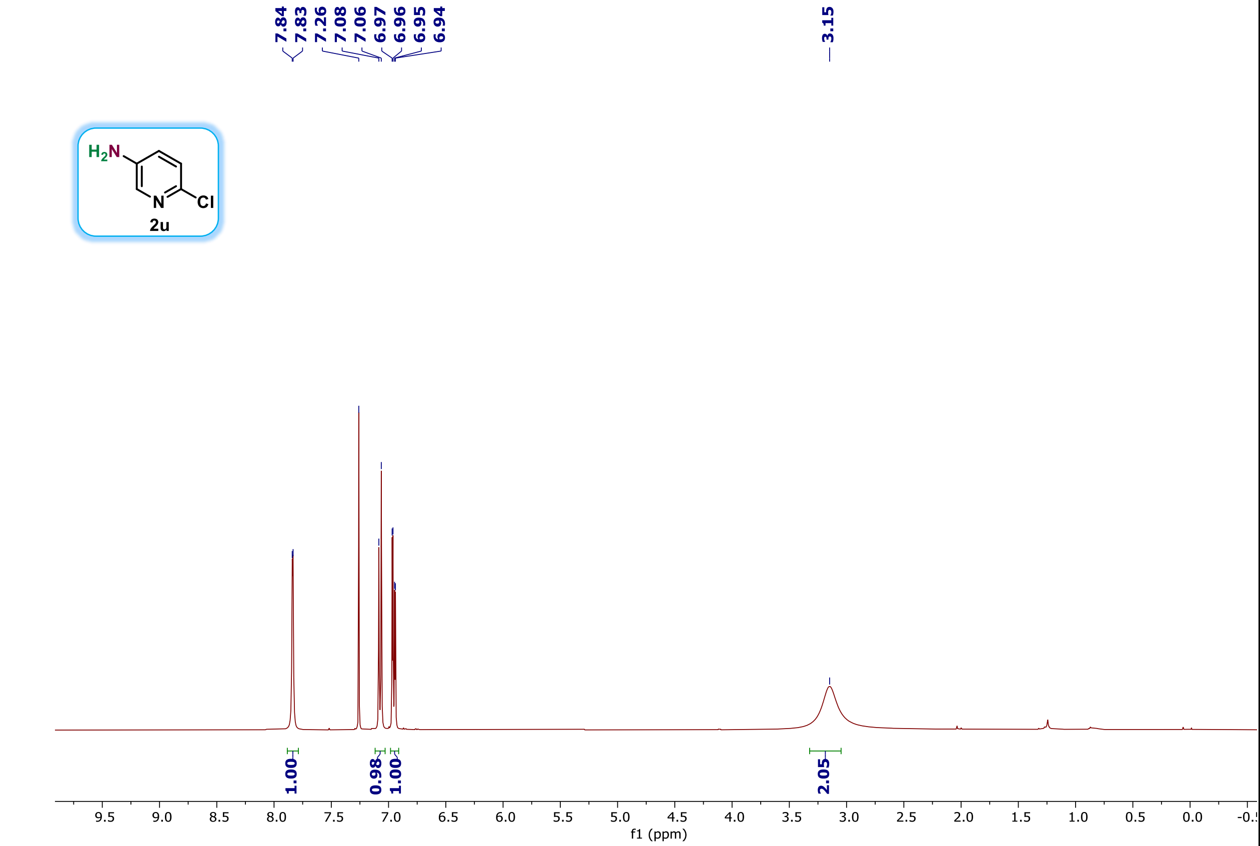
[1]H NMR spectra of product 2t (400 MHz, $CDCl_3$)



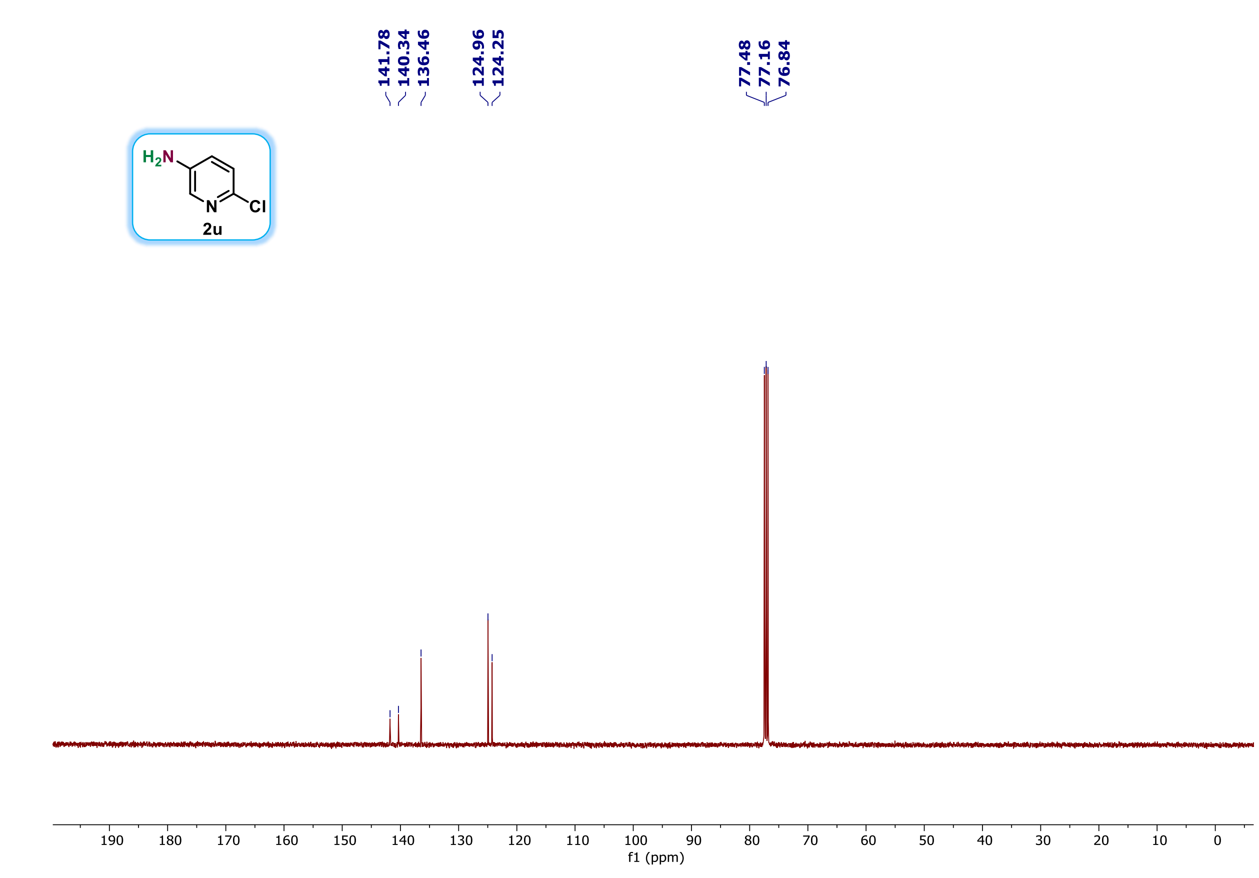
[13]C NMR spectra of product 2t (101 MHz, $CDCl_3$)



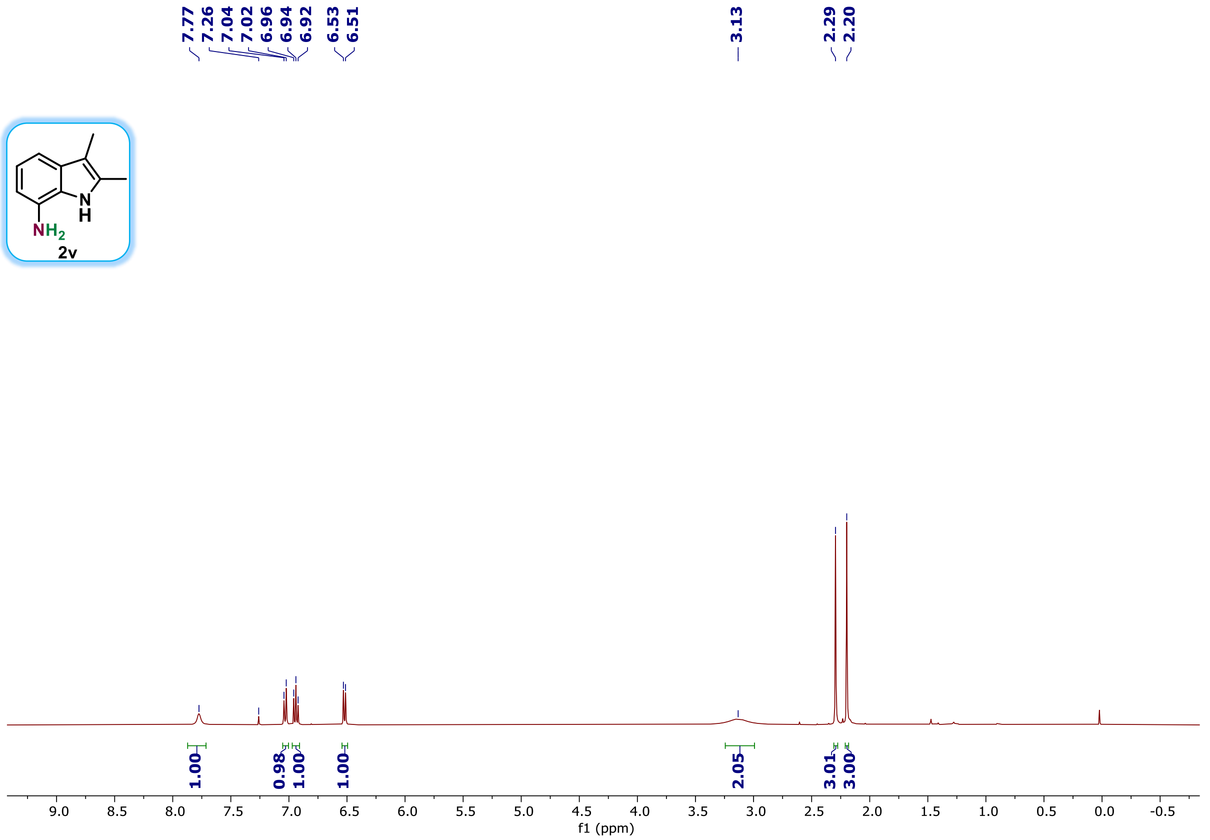
^{1}H NMR spectra of product 2u (400 MHz, $CDCl_3$)



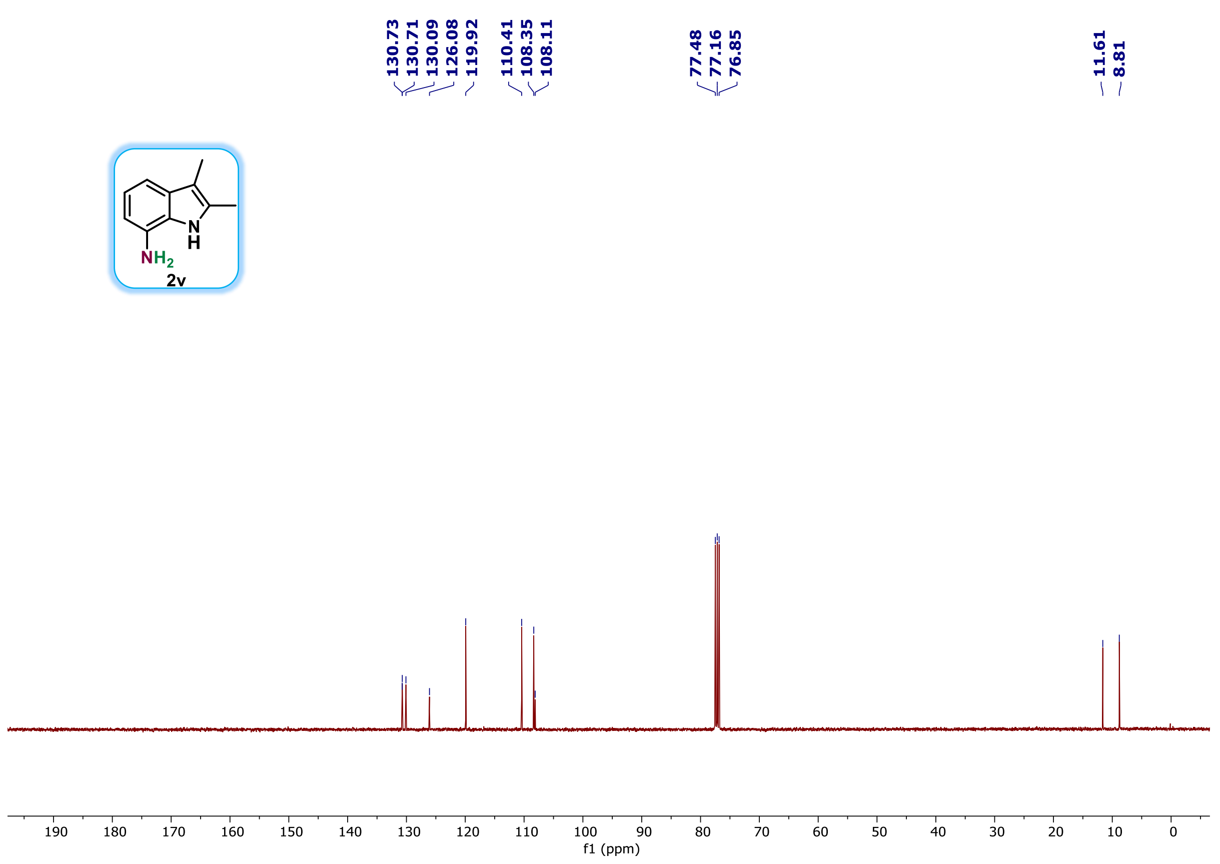
^{13}C NMR spectra of product 2u (101 MHz, $CDCl_3$)



^{1}H NMR spectra of product 2v (400 MHz, $CDCl_3$)



^{13}C NMR spectra of product 2v (101 MHz, $CDCl_3$)



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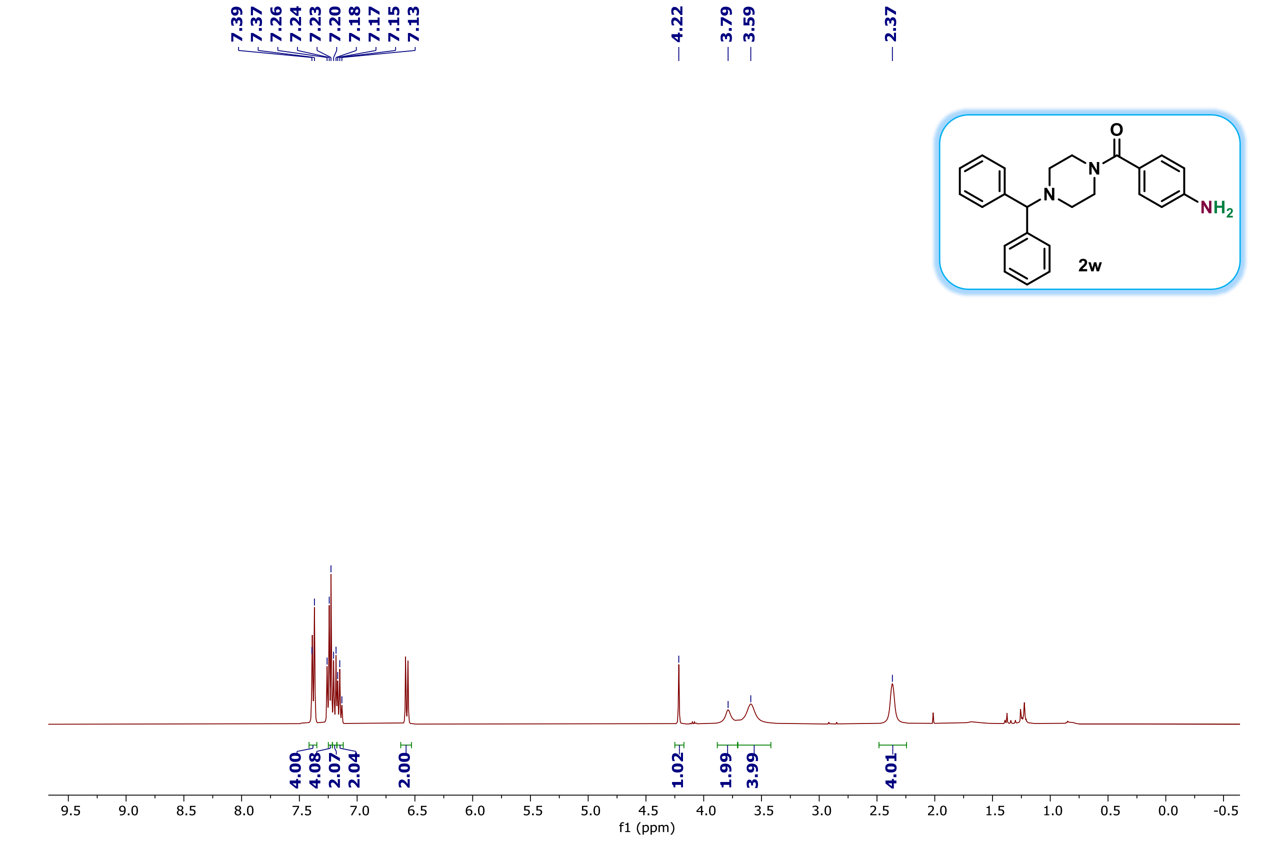
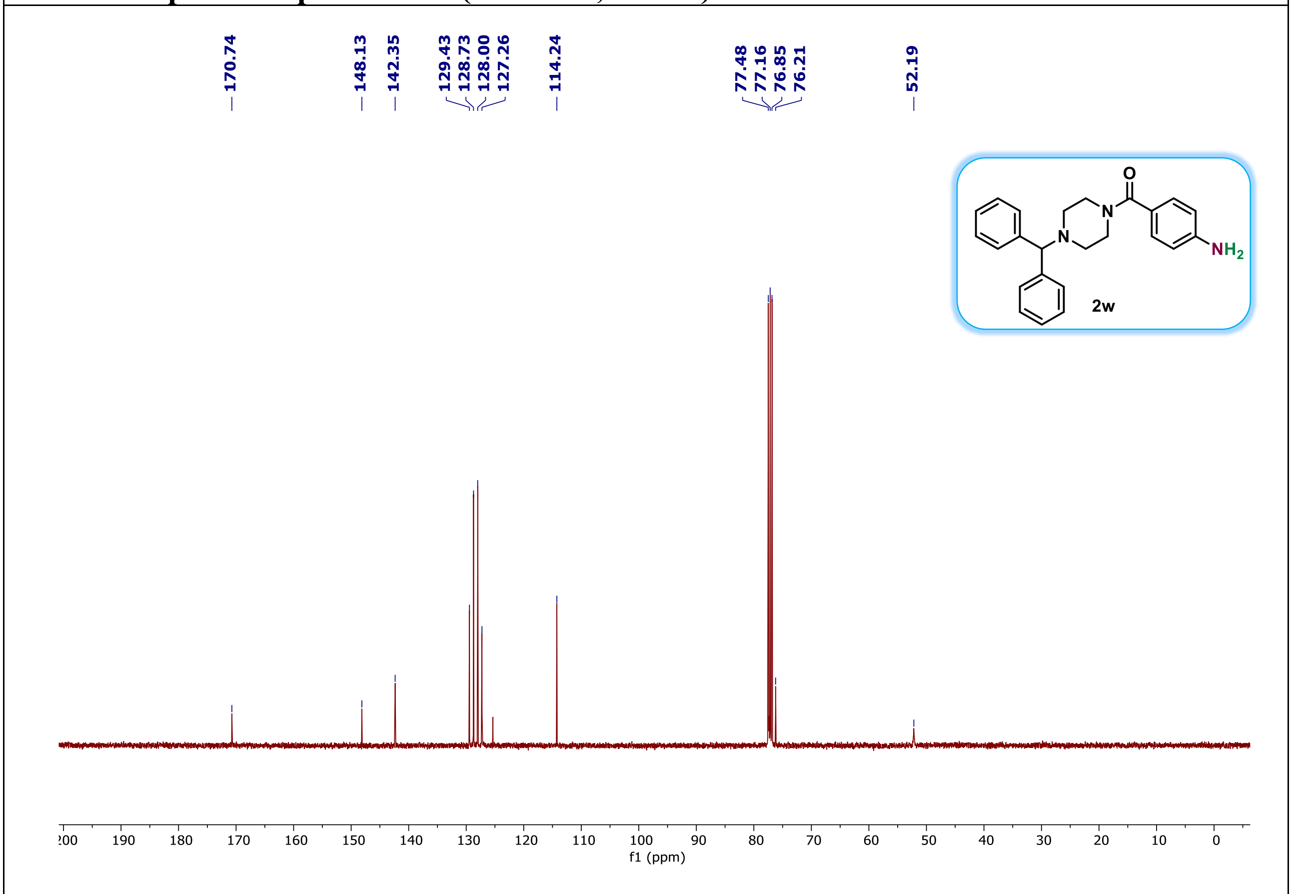
^{1}H NMR spectra of product 2w (400 MHz, $CDCl_3$)



^{13}C NMR spectra of product 2w (101 MHz, $CDCl_3$)



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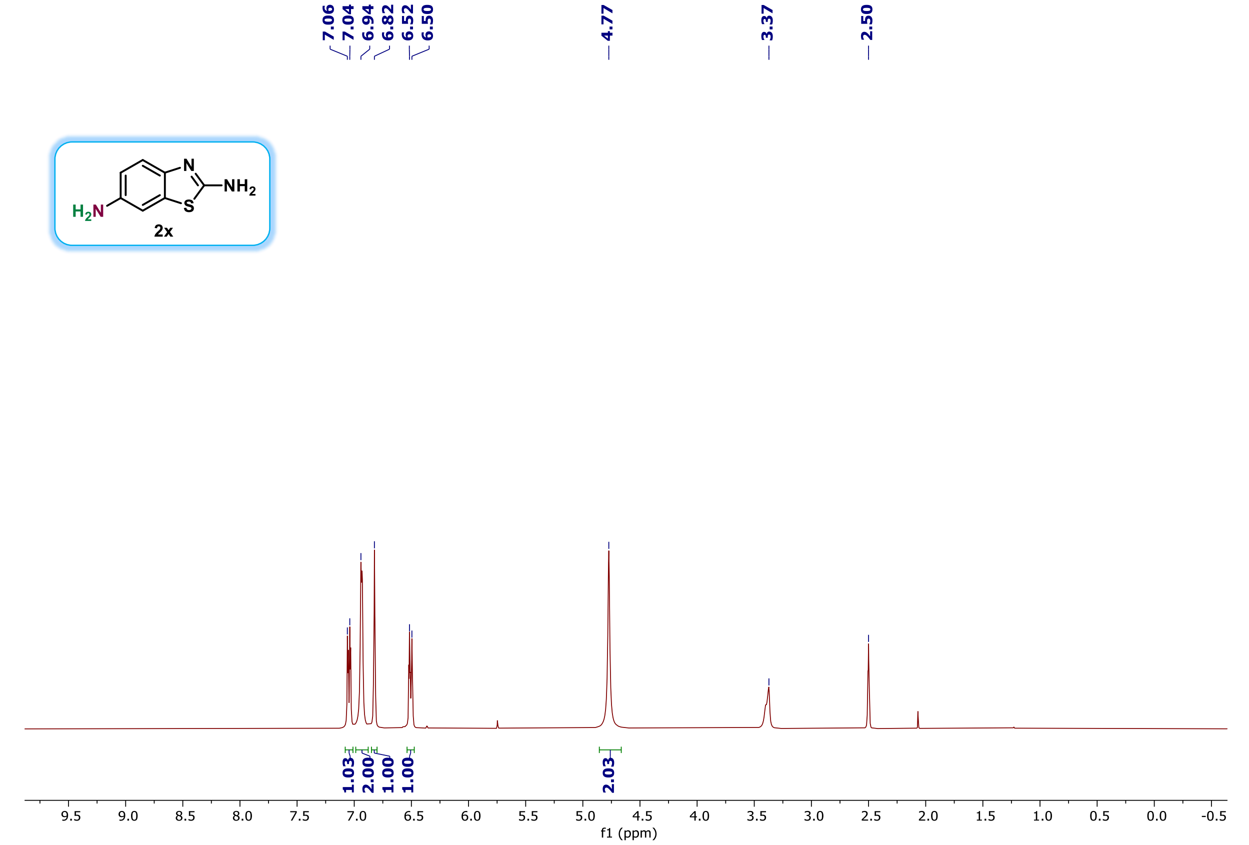
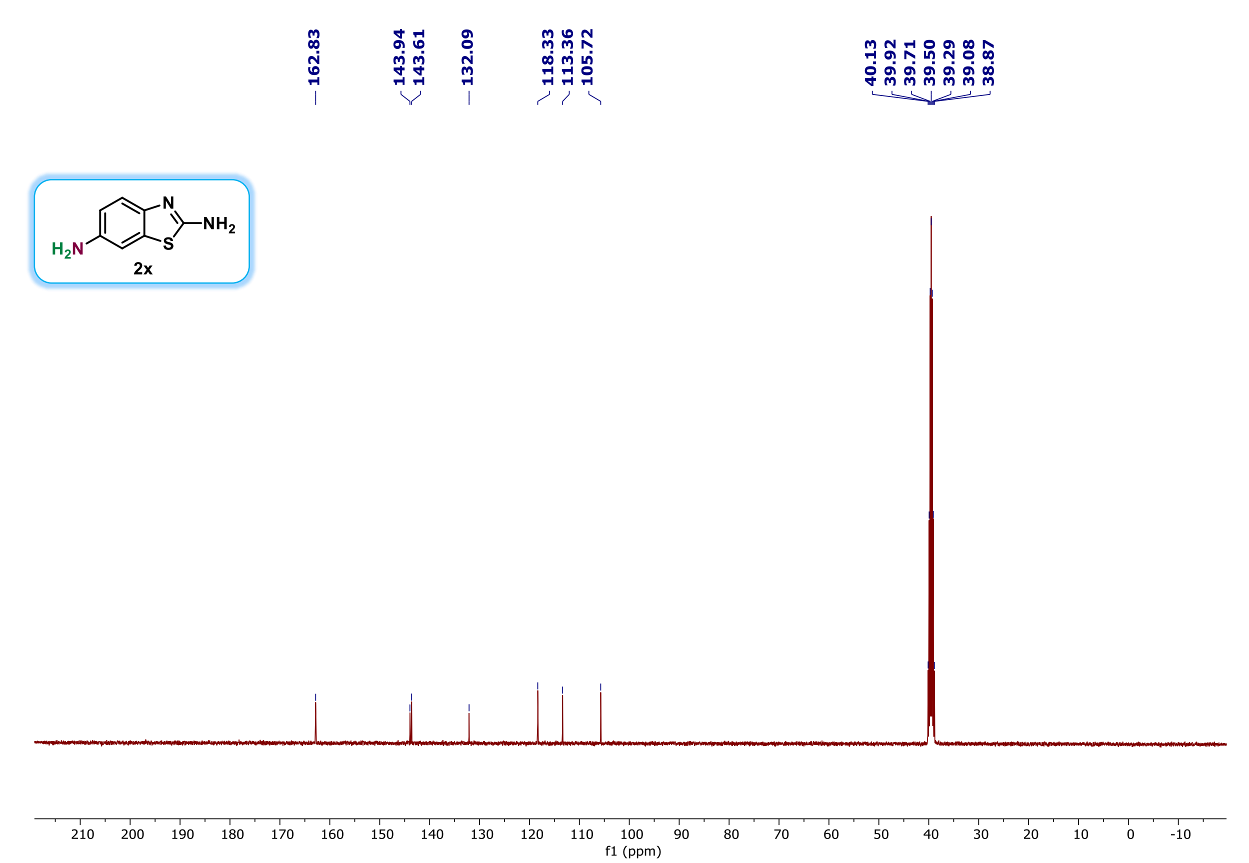
^{1}H NMR spectra of product 2x (400 MHz, DMSO-d_6)



^{13}C NMR spectra of product 2x (101 MHz, DMSO d^6)



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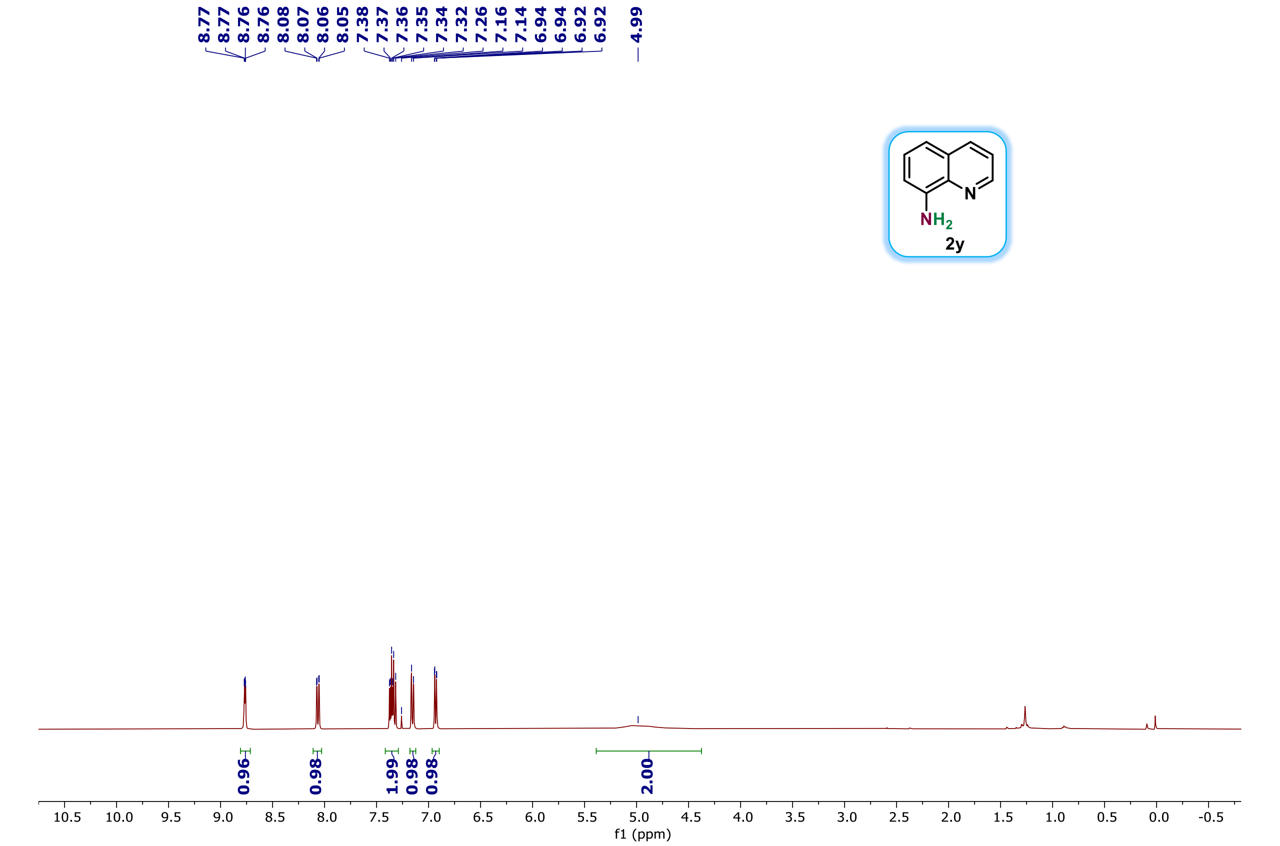
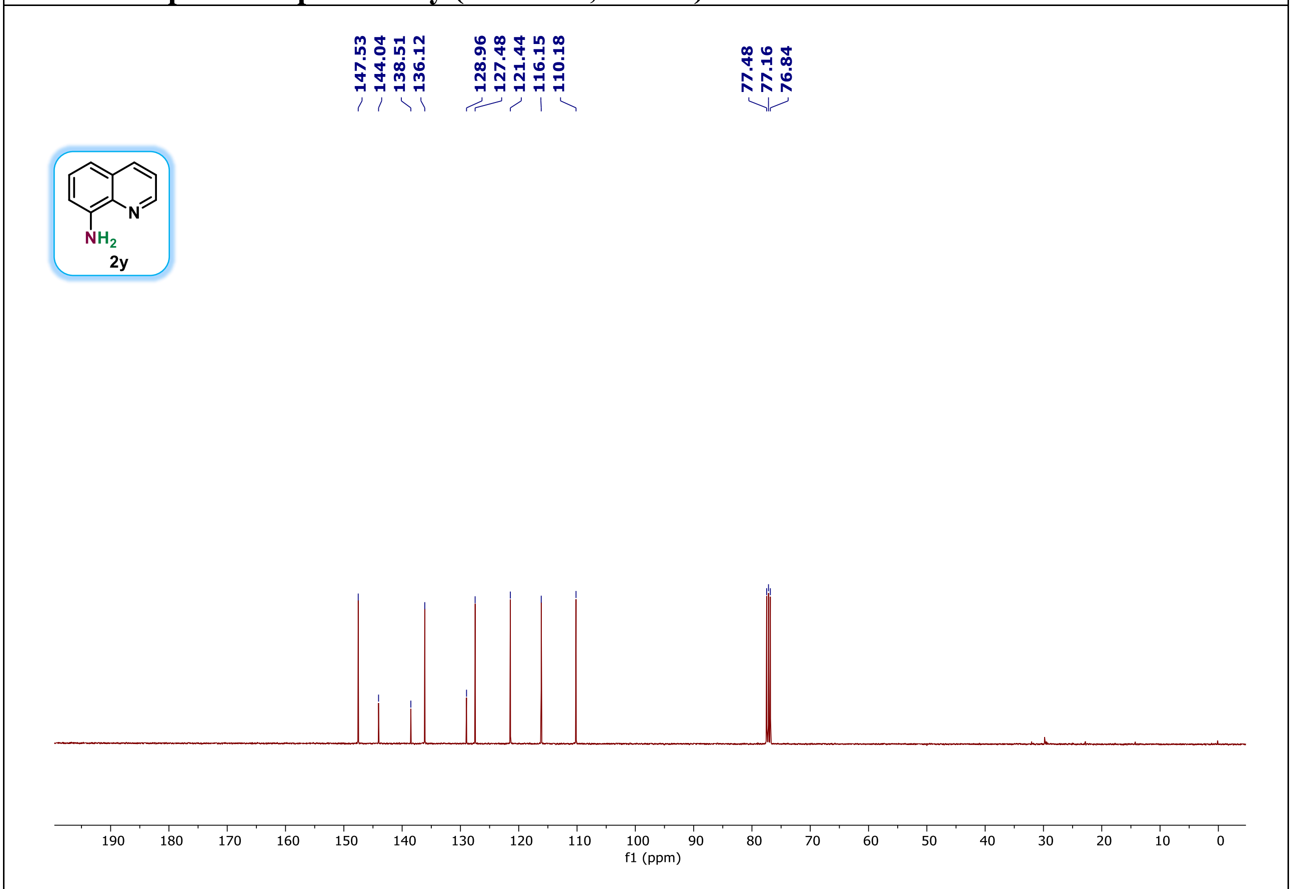
^{1}H NMR spectra of product 2y (400 MHz, $CDCl_3$)



^{13}C NMR spectra of product 2y (101 MHz, $CDCl_3$)



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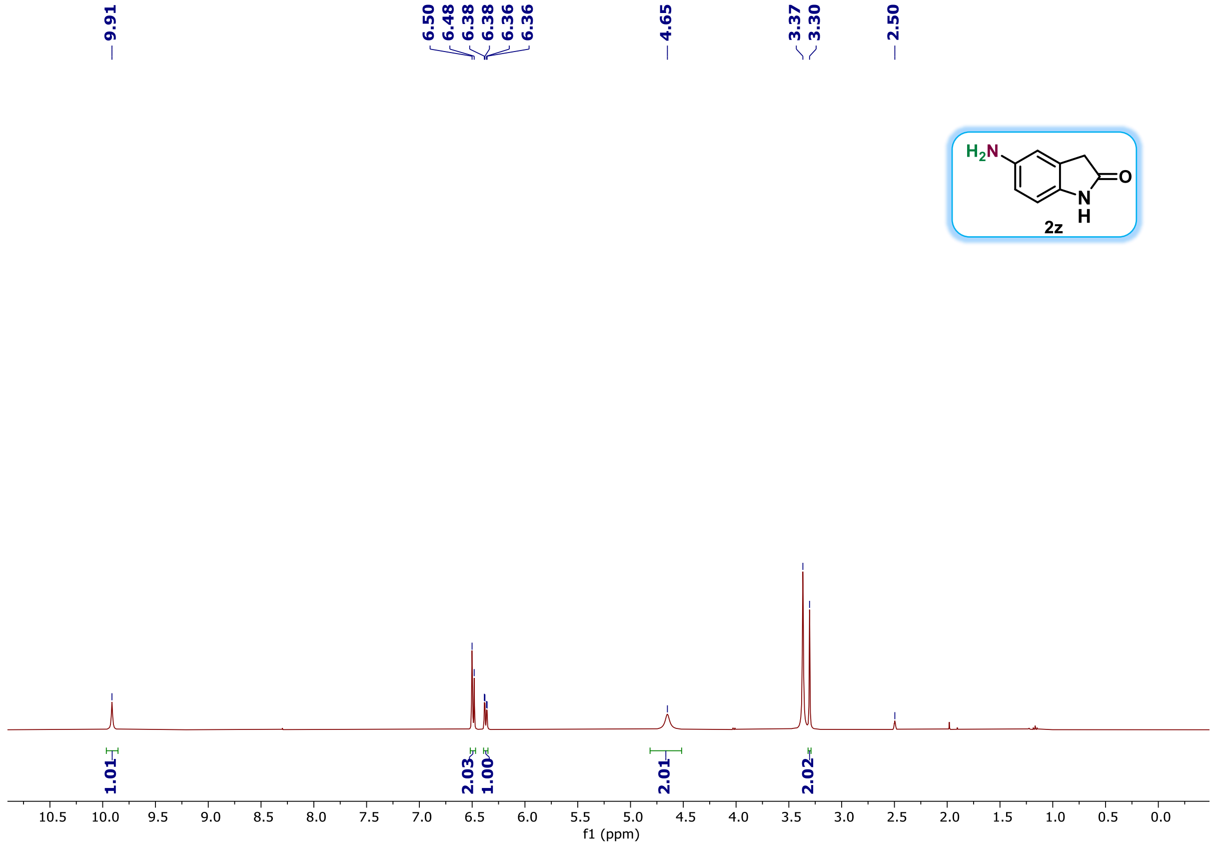
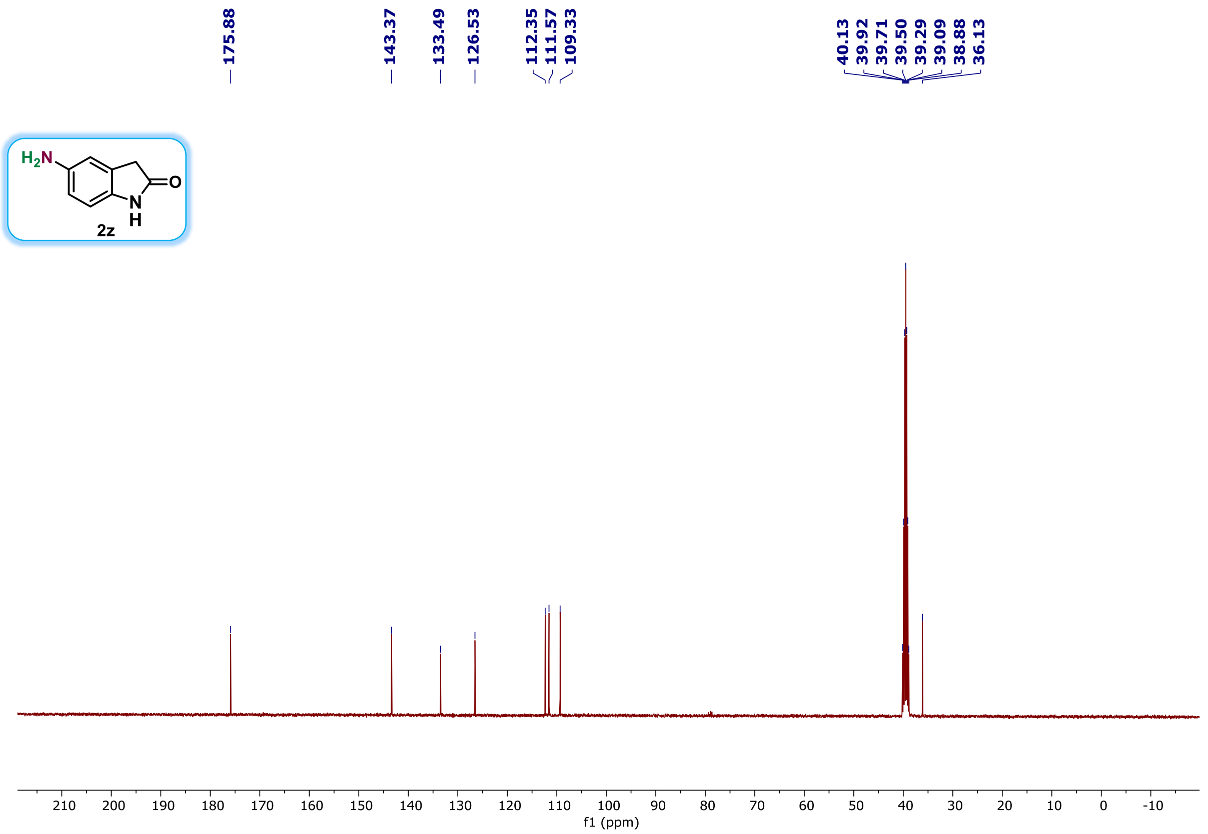
^{1}H NMR spectra of product 2z (400 MHz, DMSO-d_6)



^{13}C NMR spectra of product 2z (101 MHz, DMSO-d_6)



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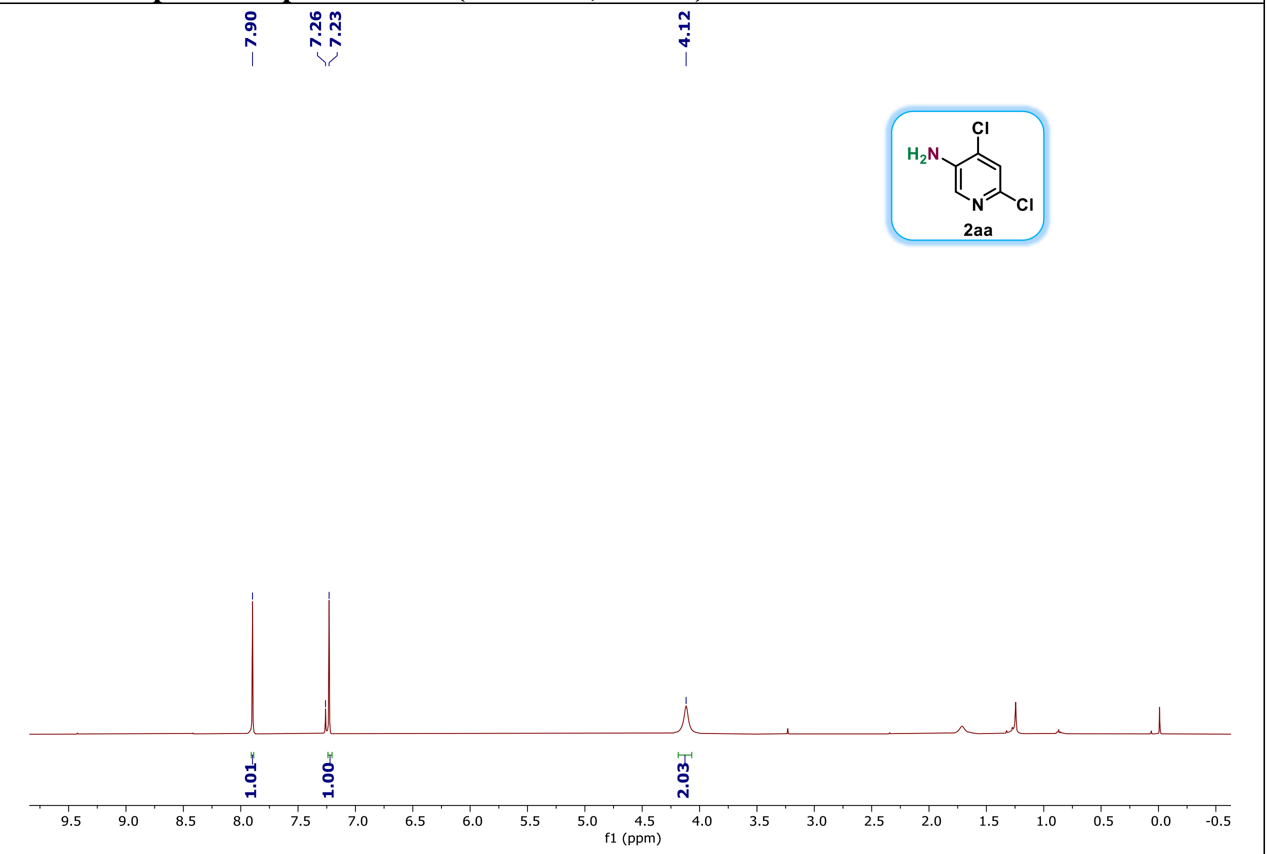
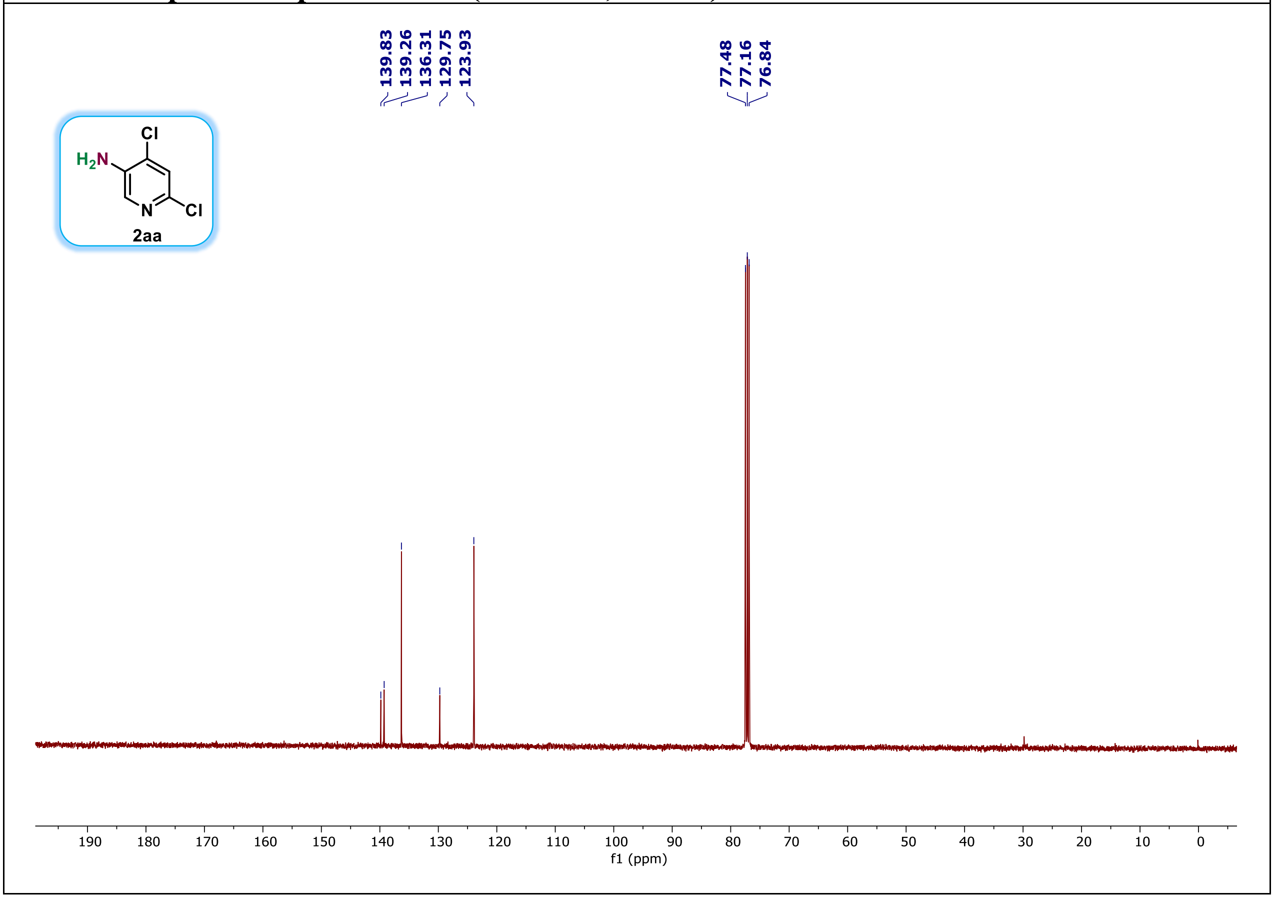
[1]H NMR spectra of product 2aa (400 MHz, $CDCl_3$)



[13]C NMR spectra of product 2aa (101 MHz, $CDCl_3$)



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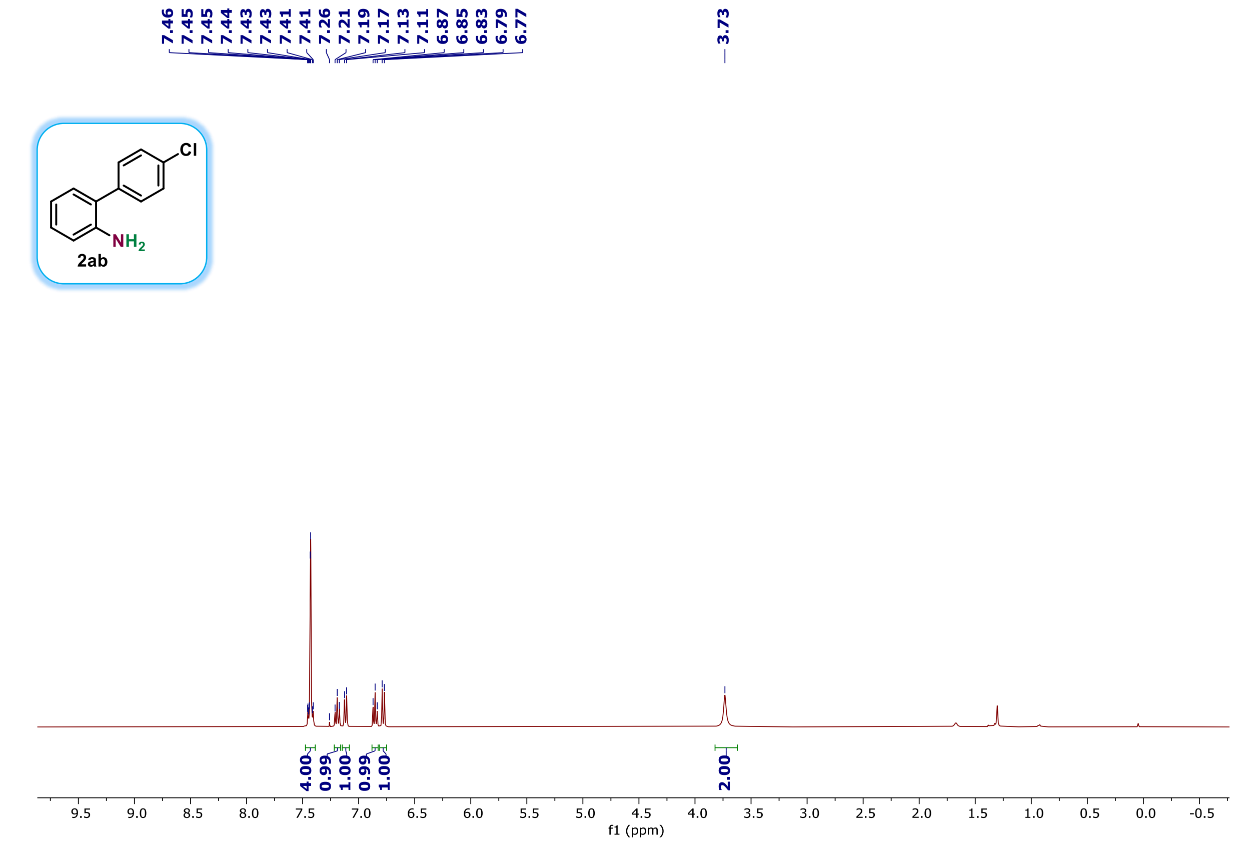
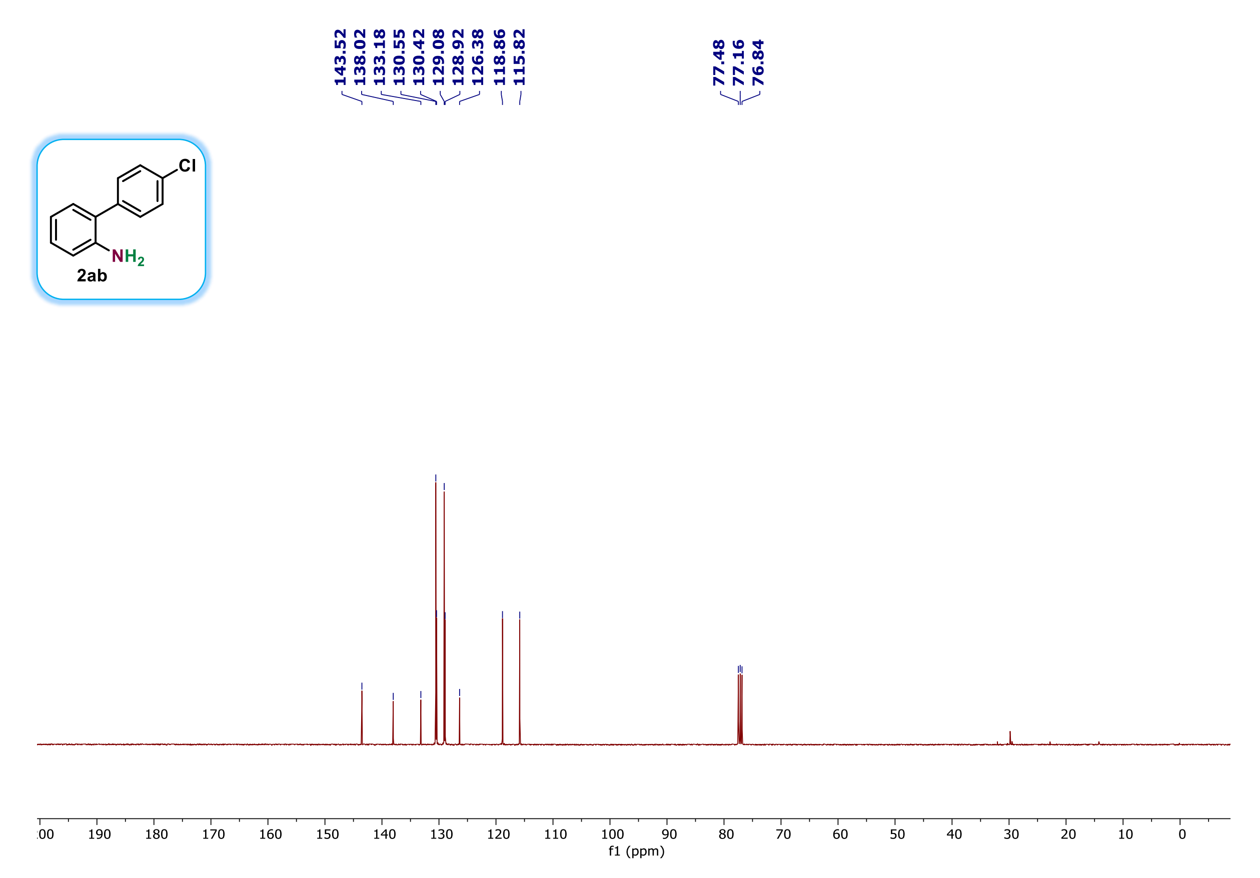
[1]H NMR spectra of product 2ab (400 MHz, $CDCl_3$)



[13]C NMR spectra of product 2ab (101 MHz, $CDCl_3$)



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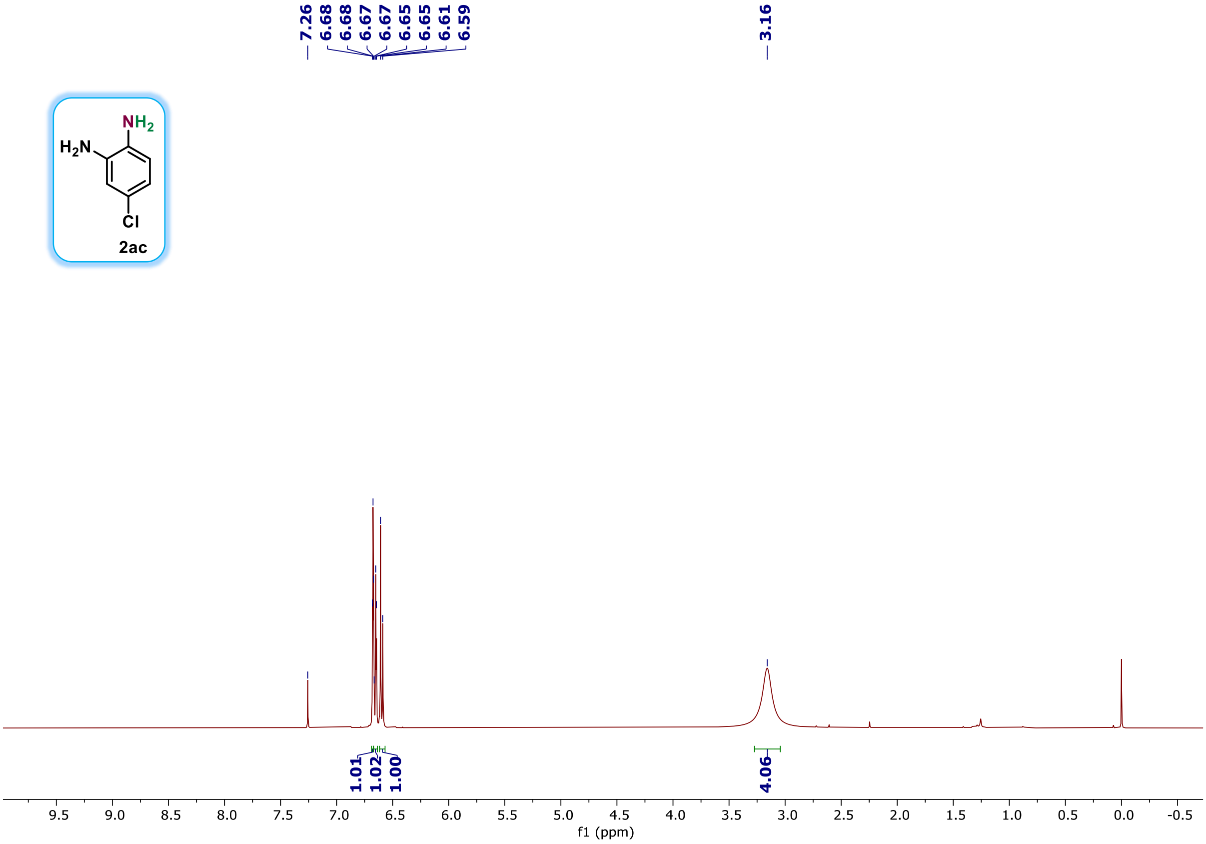
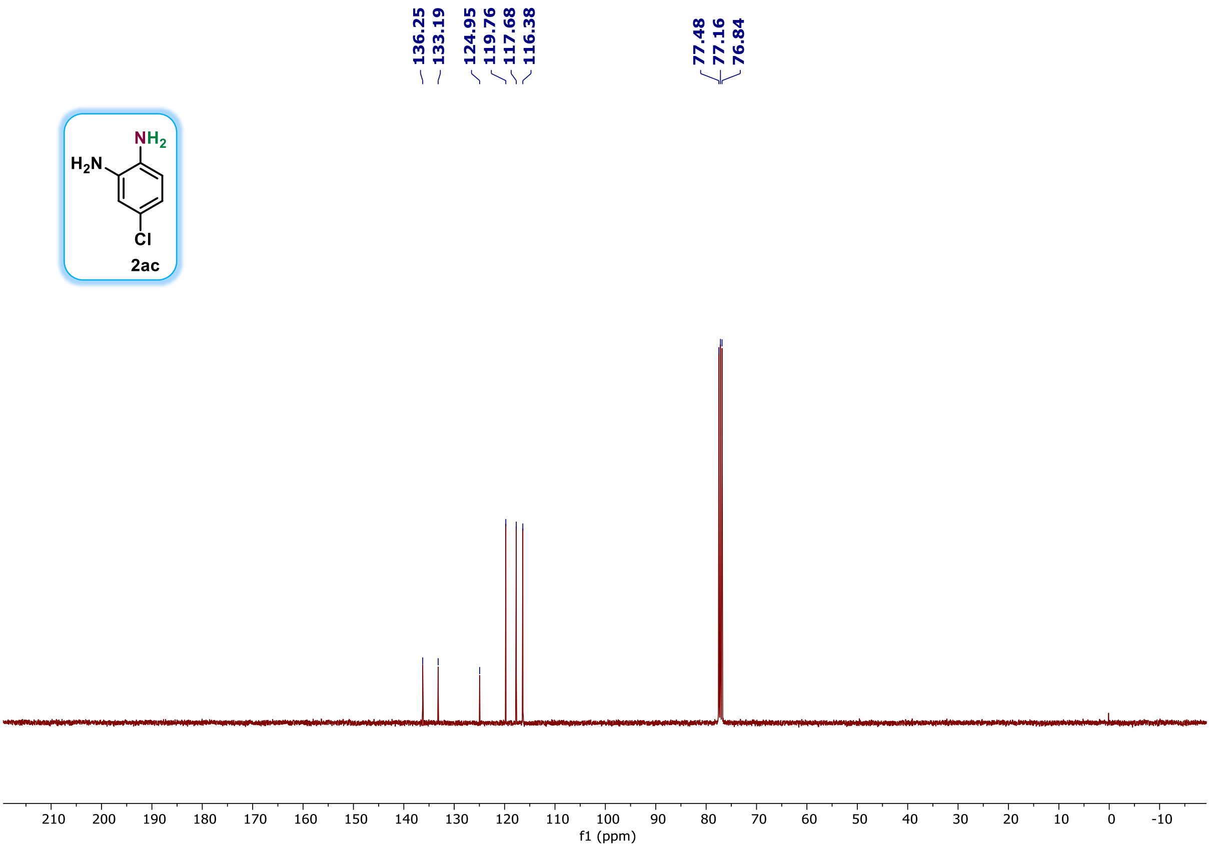
[1]H NMR spectra of product 2ac (400 MHz, CDCl3)



[13]C NMR spectra of product 2ac (101 MHz, CDCl3)



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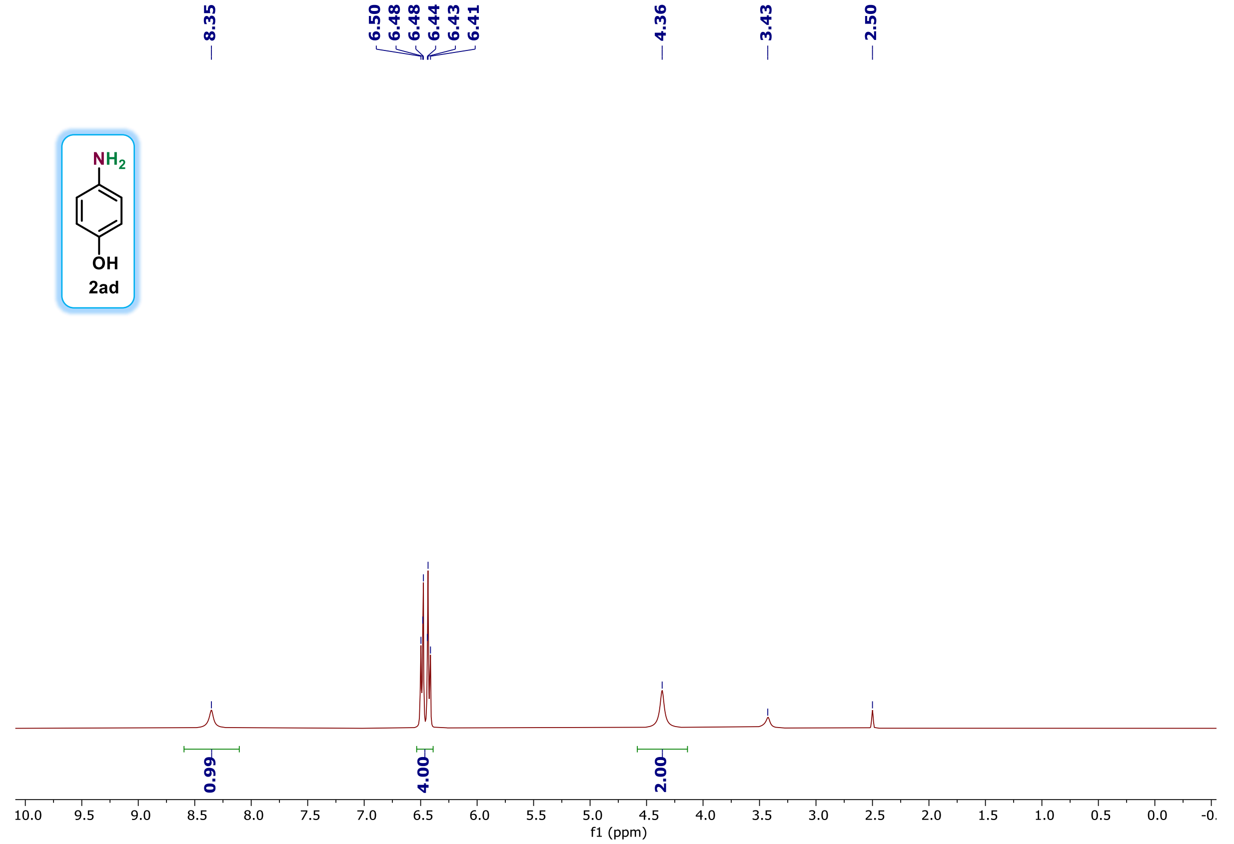
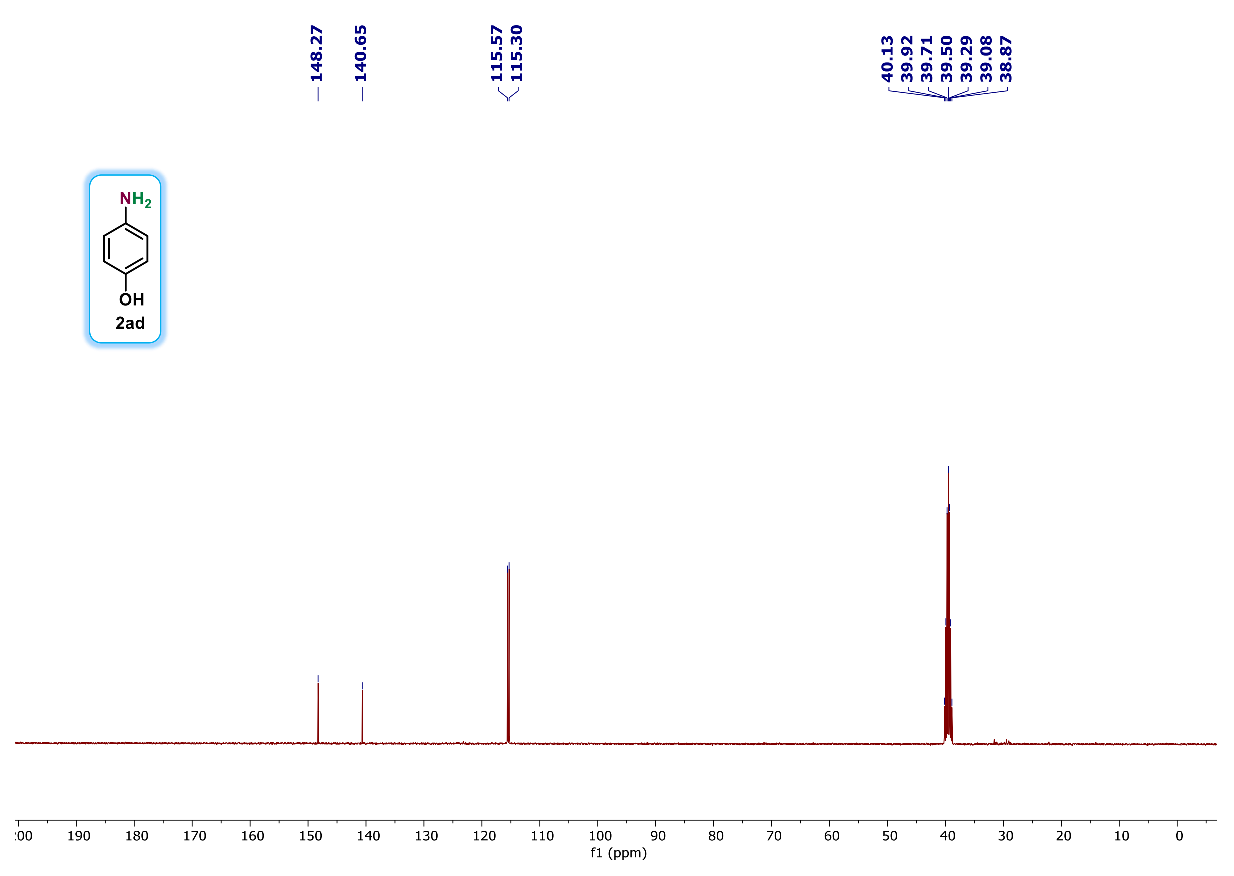
^{1}H NMR spectra of product 2ad (400 MHz, DMSO-d$_6$)



^{13}C NMR spectra of product 2ad (101 MHz, DMSO-d$_6$)



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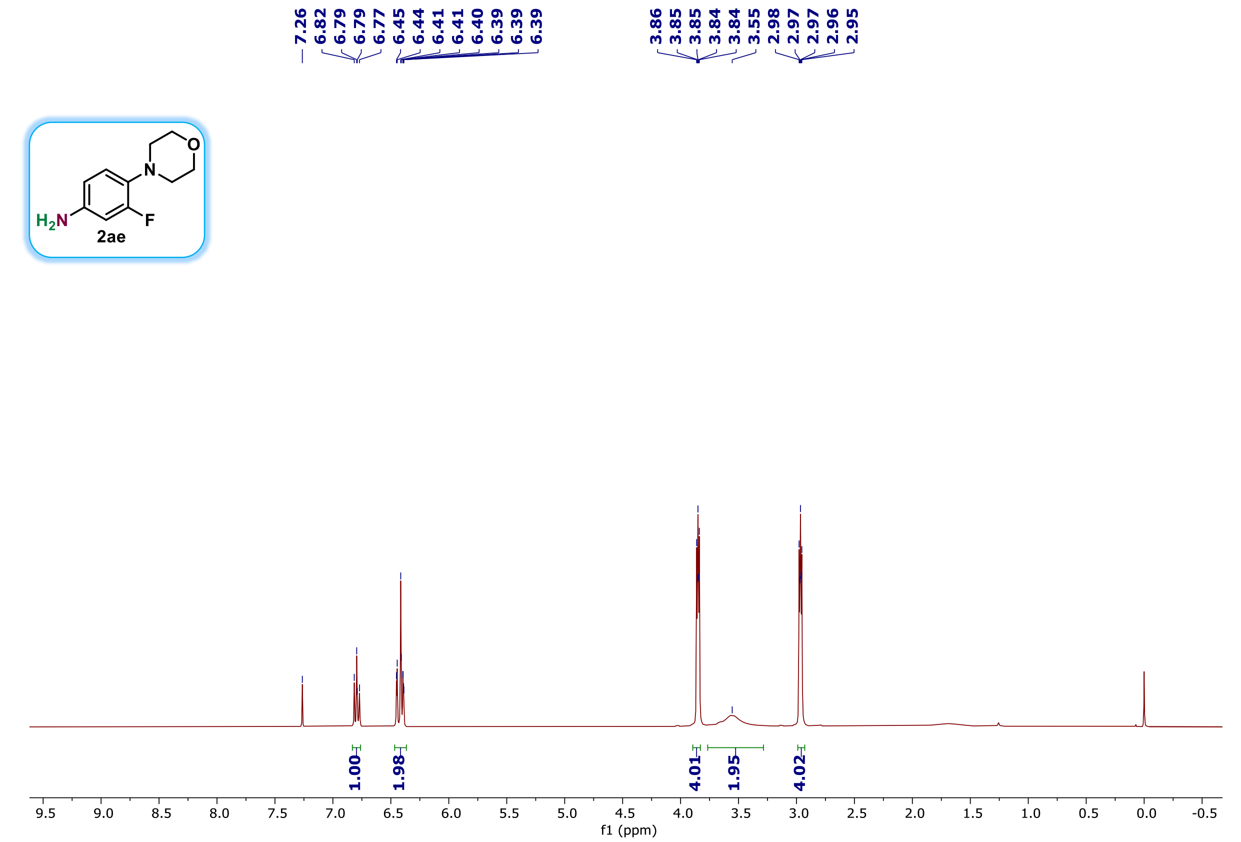
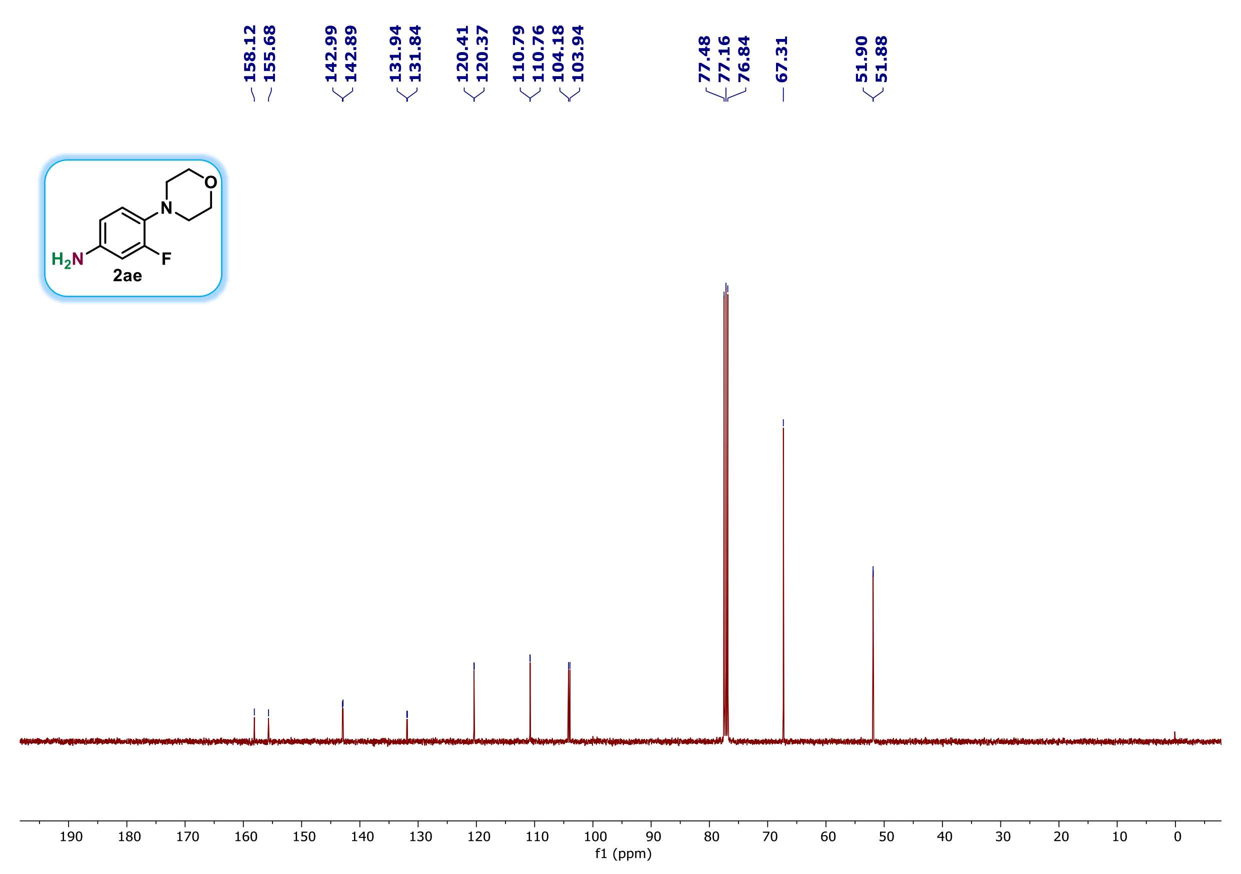
[1]H NMR spectra of product 2ae (400 MHz, CDCl3)



[13]C NMR spectra of product 2ae (101 MHz, CDCl3)



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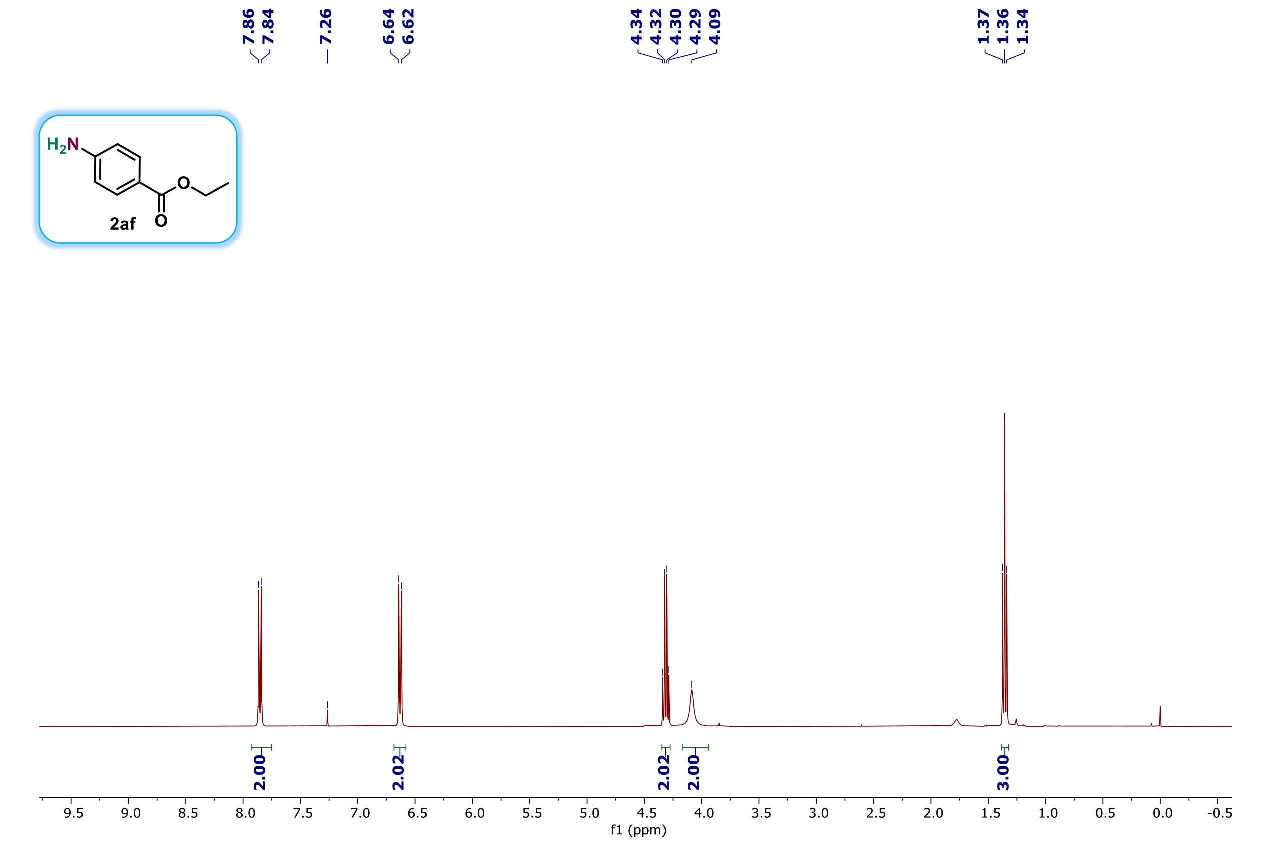
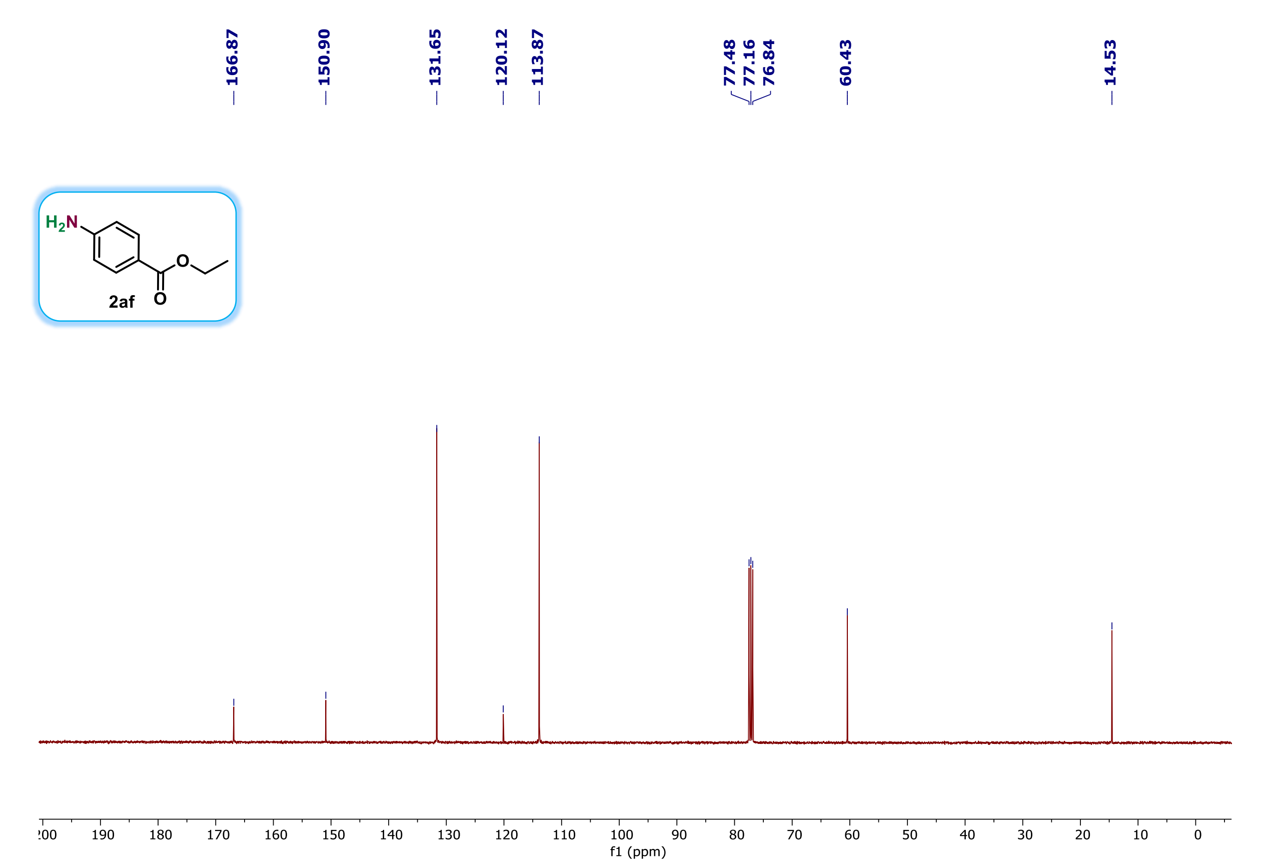
[1]H NMR spectra of product 2af (400 MHz, $CDCl_3$)



[13]C NMR spectra of product 2af (101 MHz, $CDCl_3$)



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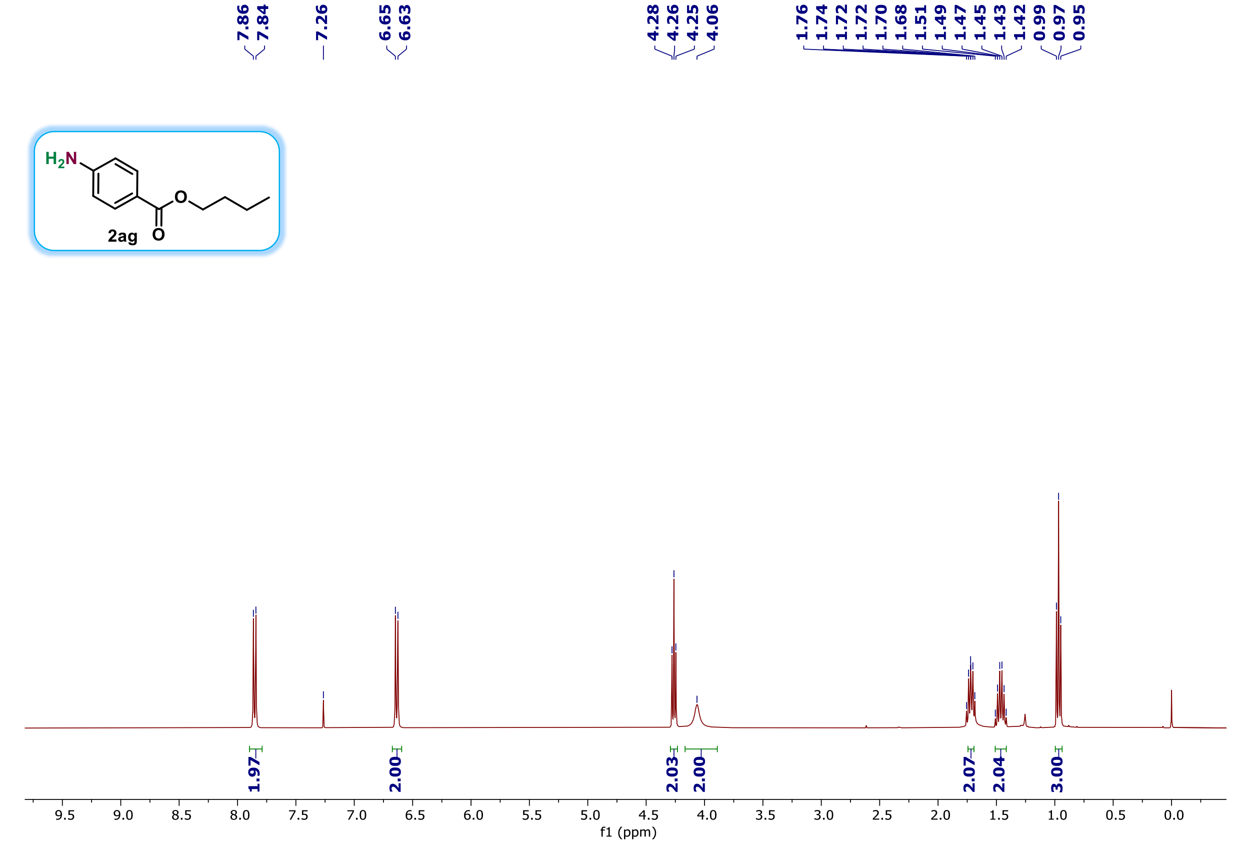
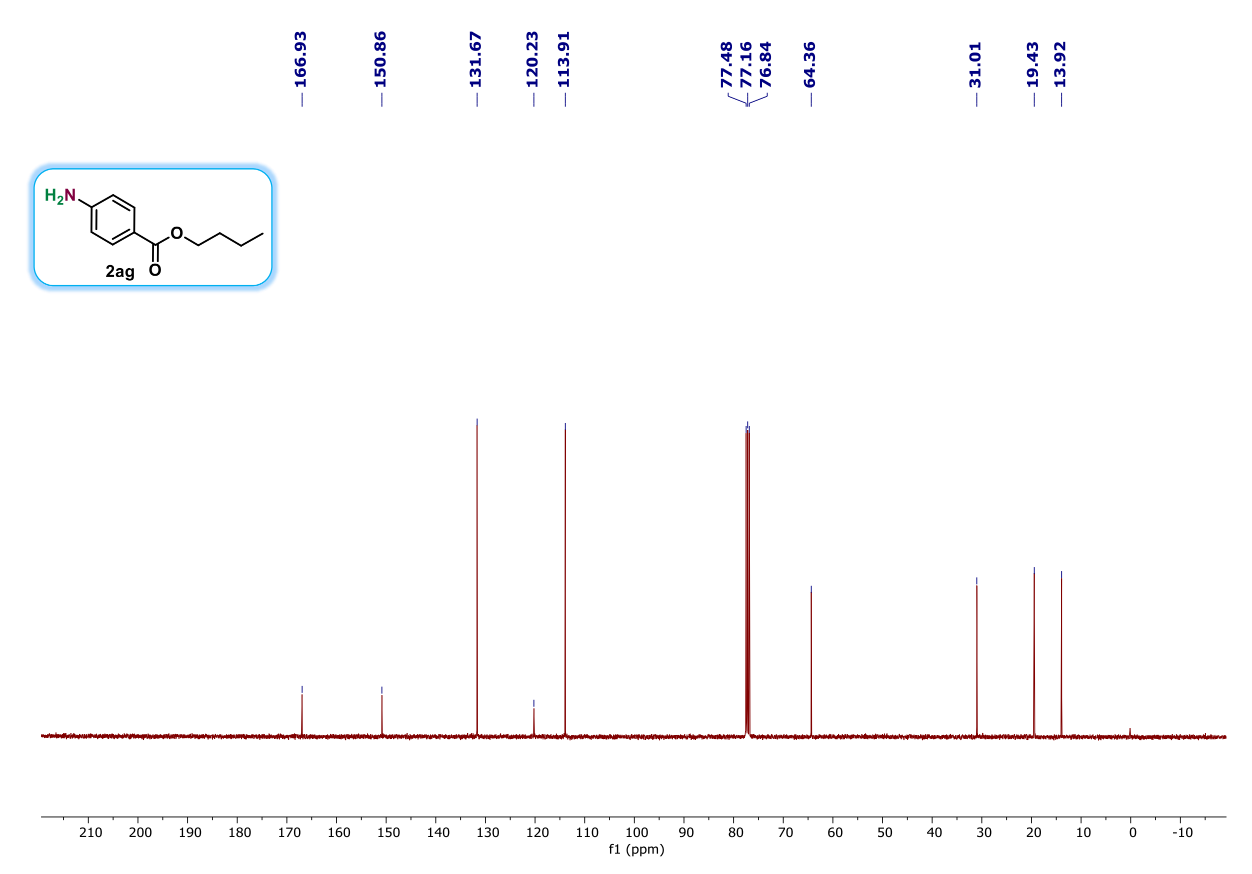
^{1}H NMR spectra of product 2ag (400 MHz, $CDCl_3$)



^{13}C NMR spectra of product 2ag (101 MHz, $CDCl_3$)



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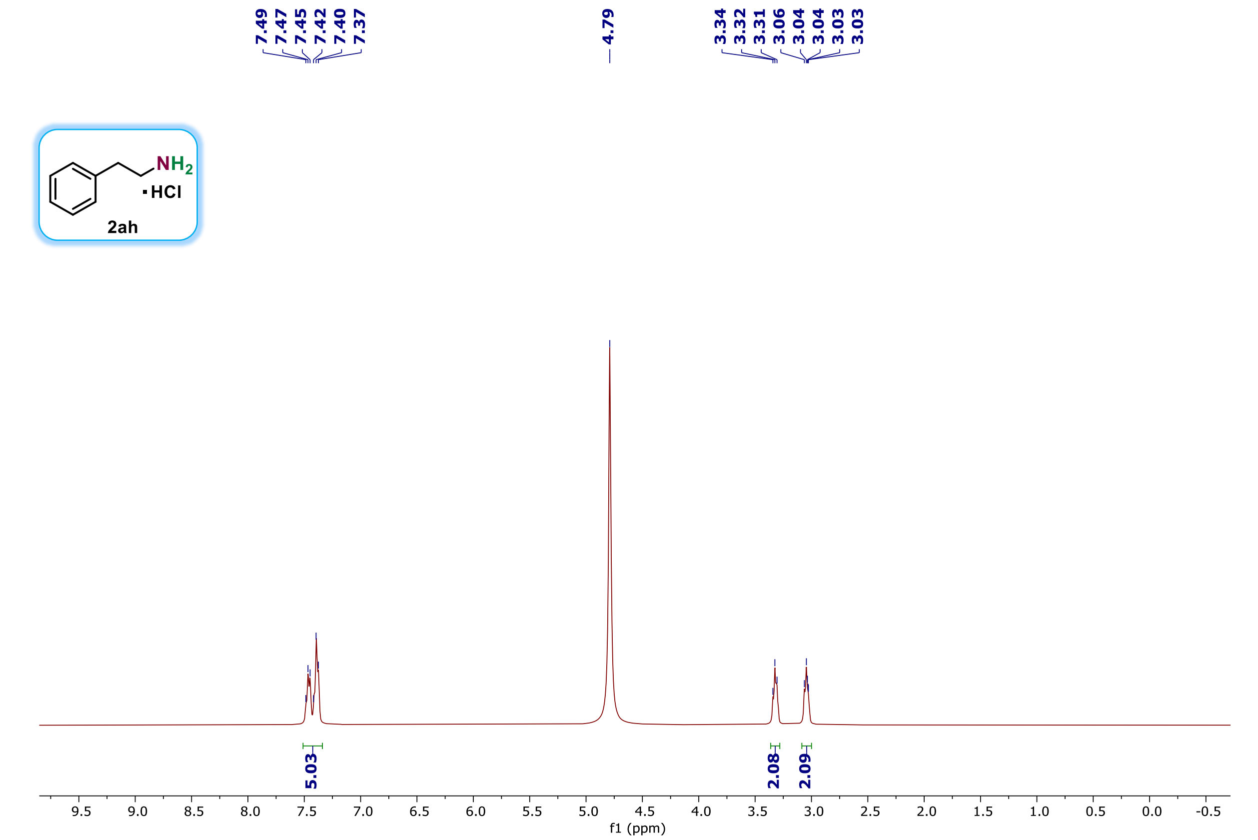
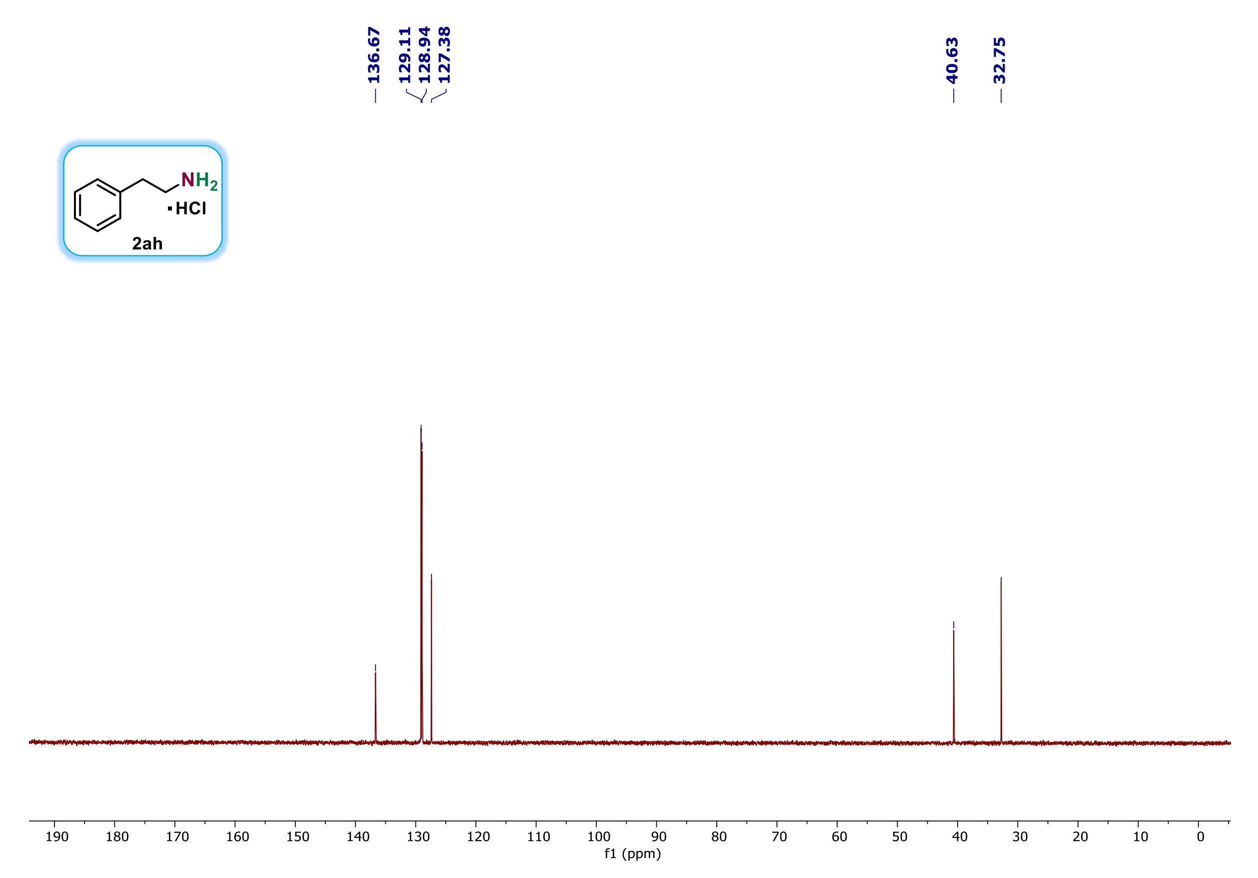
^{1}H NMR spectra of product 2ah (400 MHz, D_2O)



^{13}C NMR spectra of product 2ah (101 MHz, D_2O)



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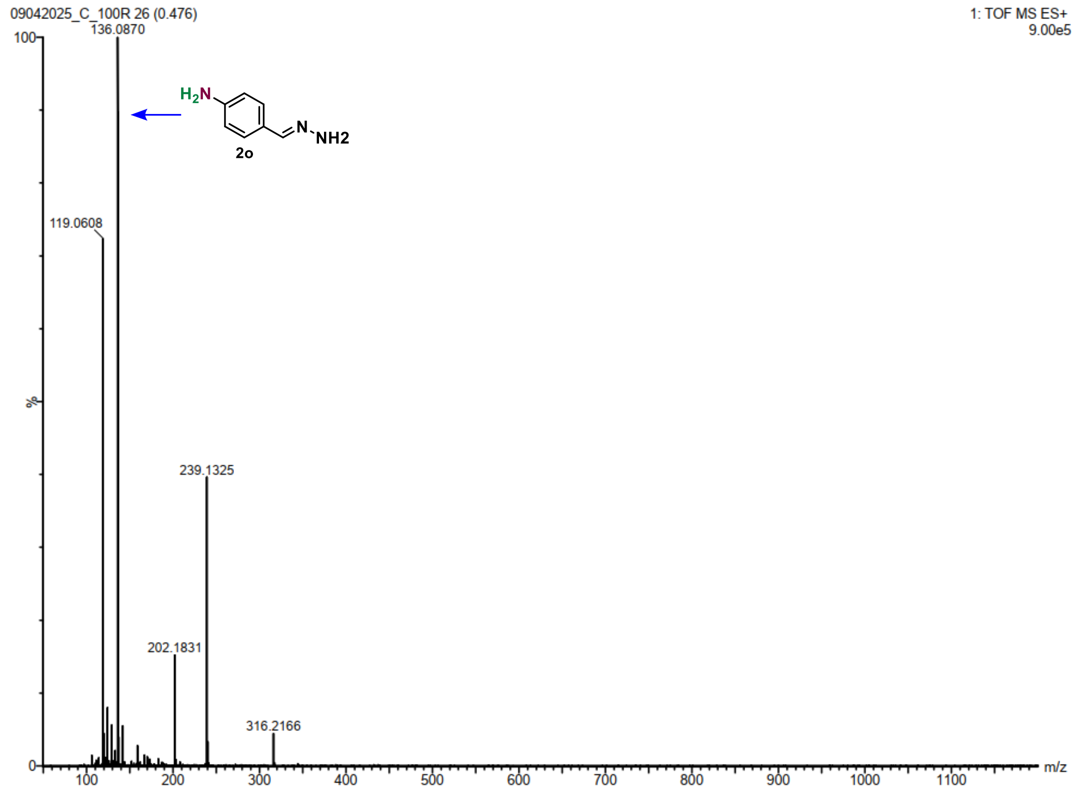
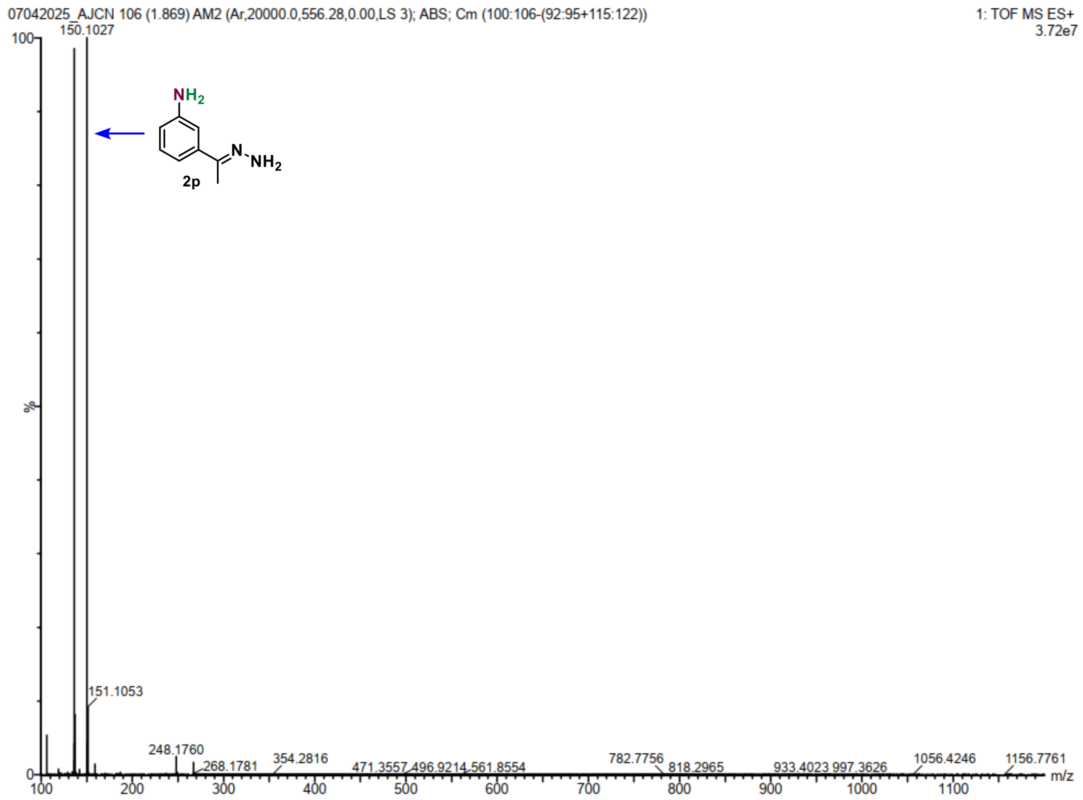
11. HRMS Data

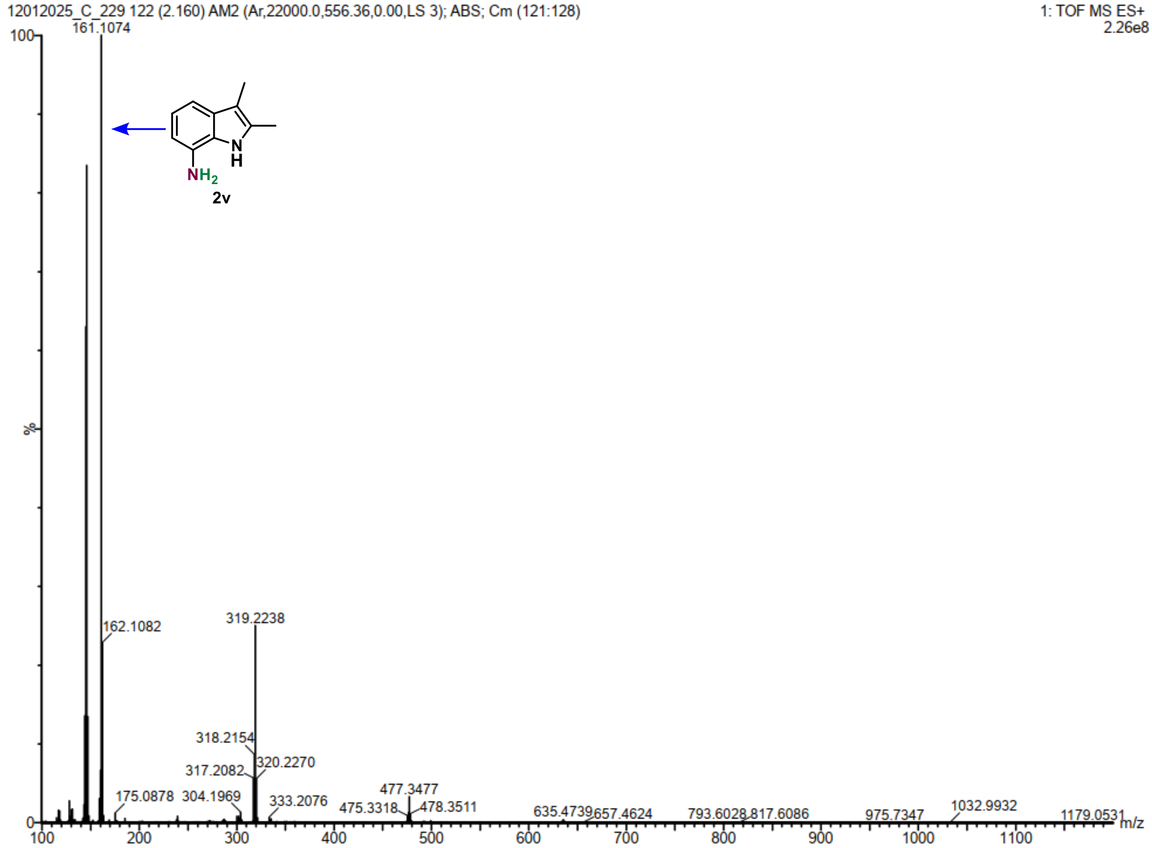
HR-MS spectra of product 2o



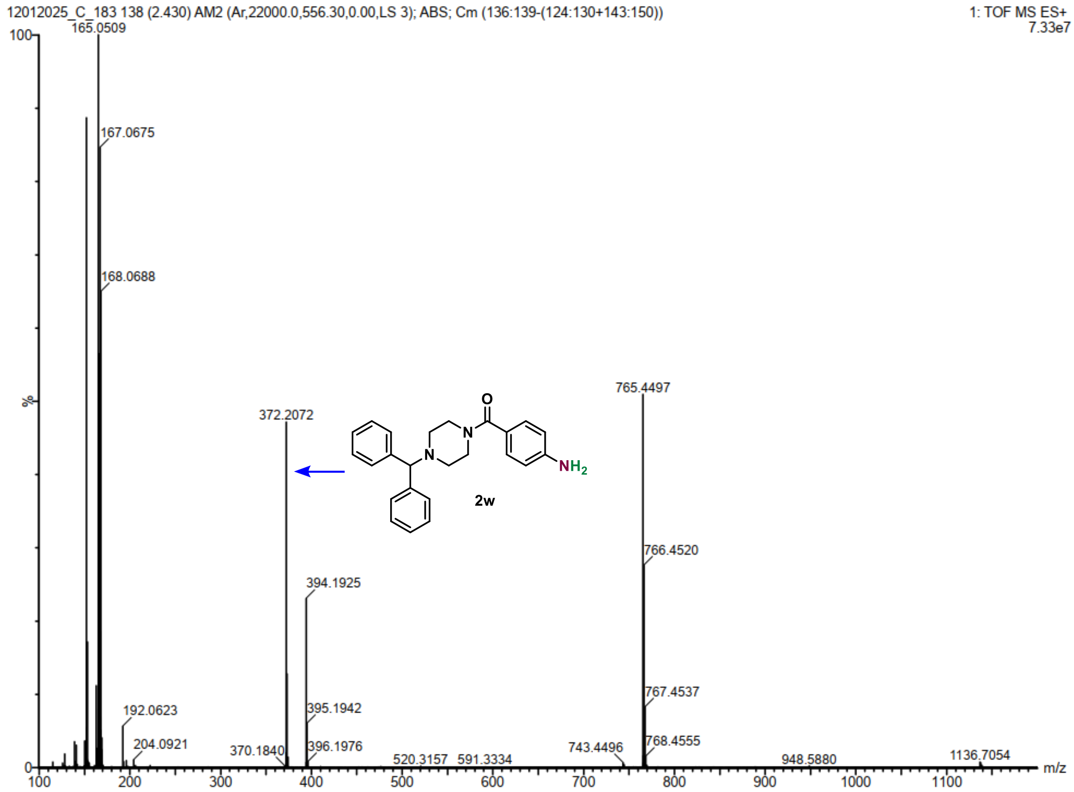
HR-MS spectra of product 2p



HR-MS spectra of product 2v



HR-MS spectra of compound 2w



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HR-MS spectra of intermediate hydroxyl amine