Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Direct Conversion of Phenols into Primary Anilines with Hydrazine Catalyzed by Palladium

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Contents

I. General Experimental Information

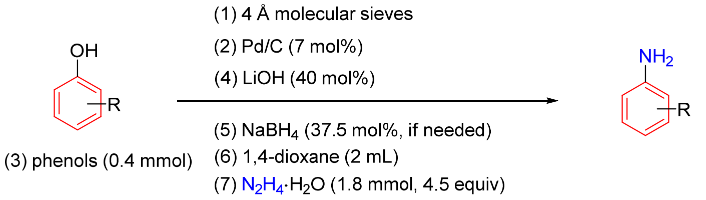
All reactions were carried out under an atmosphere of argon, unless otherwise stated. All reported reaction temperatures corresponded to oil bath temperatures. Solvents and reagents were purchased from Sigma-Aldrich chemical company and Fisher Scientific and were used without further purification unless otherwise specified. 1,4-Dioxane and toluene were purified by the *Pure Solvent MD-7* purification system (Innovative Technology). Pentane was distilled under atmosphere pressure prior to use. 4 Å molecular sieves were purchased from Sigma-Aldrich chemical company and were freshly activated in the oven for 12 h at 380 ^{o}C prior to use. HCO_2Na (sodium formate) was purchased from Merck chemical company. Product purifications were performed either with preparative chromatography on a Biotage Isolera One automated chromatography system on silica gel or with preparative analytical thin-layer chromatography (TLC) using E. Merck silica gel 60 F_{254} pre-coated plates (0.25 mm).

NMR Spectroscopy: Nuclear magnetic resonance (^{1}H, ^{13}C, ^{19}F) spectra were recorded on a Bruker AV500 equipped with a 60-position Sample Xpress sample changer (^{1}H, 500 MHz; ^{13}C, 125 MHz). Chemical shifts are expressed in parts per million (ppm) units downfield from TMS, with the solvent residue peak as the chemical shift standard ($CDCl_3$: δ 7.26 ppm in ^{1}H NMR, δ 77.16 ppm in ^{13}C NMR; DMSO-d_6 δ 2.50 ppm in ^{1}H NMR, δ 39.52 ppm in ^{13}C NMR; acetone-d_6 δ 2.04 ppm in ^{1}H NMR, δ 206.3 ppm in ^{13}C NMR). Data are reported as following: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, td = triplet of doublets, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet, br = broad singlet), coupling constants *J* (Hz), and integration.

Mass Spectrometry: EI-MS was obtained from the Agilent GC-MS system. High Resolution Mass (HRMS) spectra was performed by the McGill Chemistry Department Mass Spectrometry Facility and was recorded using electrospray ionization (ESI+) and/or atmospheric pressure chemical ionization APCI(+/-), performed either on "Exactive Plus Orbitrap" a ThermoScientific high resolution accurate mass (HR/AM) FT mass spectrometer, or a Bruker Daltonics Maxis Impact quadrupole-time of flight (QTOF) mass spectrometer. Protonated molecular ions $(M+H)^{+}$, $(M-H)^{-}$ or sodium adducts $(M+Na)^{+}$, were used for empirical formula confirmation.

Caution*: hydrazine monohydrate is potentially hazardous, and pressure can be built up at high temperature. Therefore appropriate personal protections should be performed running this transformation.*

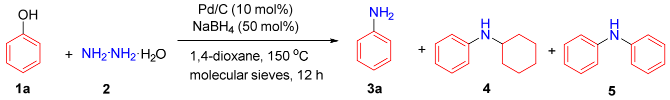
II. Experimental Procedure



General procedures: Freshly activated 4 Å molecular sieves (100 mg 4 Å molecular sieves per 0.3 mmol N_2H_4•H_2O) was added into a flame-dried 15 mL Synthware™ cylindrical heavy wall pressure vessel, charged with a magnetic stir bar; followed by the addition of Pd/C (5 wt%, 7 mol%, 59.6 mg). The vessel was then vacuumed, stirred and heated in an oil-bath at 140 °C for 1 h to pre-activate the Pd/C. Next, phenols (0.4 mmol, 1 equiv) and LiOH (0.16 mmol, 40 mol%, 3.8 mg) ($NaBH_4$ (0.15 mmol, 37.5 mol%, 5.7 mg), if needed) were added into the vessel under argon protection. After three cycles of evacuation/backfilling sequence with argon, 1,4-dioxane (2.0 mL) and N_2H_4•H_2O (1.8 mmol, 4.5 equiv, 87.3 µL) were added. Then the vessel was sealed, allowed to stir at room temperature for 20 mins and then stirred at 170 °C in the pre-heated oil bath at 750 rpm for 16 h. After completion, the reaction mixture was diluted with EtOAc or MeOH and filtered through a pad of celite. The filtrate was then concentrated *in vacuo*, and the resulting residue was purified by column chromatography on silica gel or preparative TLC (EtOAc/hexanes, DCM/MeOH, *etc*.) to afford the corresponding products.

III. Optimization of the Reaction Conditions

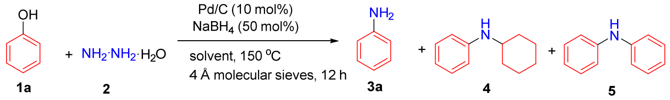
Table S1. Evaluation of molecular sieves[a]



entry	molecular sieve type	molecular sieve amount (mg)	conv. (%)	yield (%)		
				3a	**4**	**5**
1	-	-	100	10	46	1
2	4 Å	50	100	48	25	3
3	4 Å	75	100	46	26	5
4	**4 Å**	**100**	**100**	**58**	**8**	**2**
5	4 Å	150	100	57	11	3
6	4 Å	300	96	53	10	2
7	3 Å	100	100	44	22	4
8	5 Å	100	58	24	4	6

[a] Reaction conditions: phenol (0.2 mmol, 1 equiv), $N_2H_4{\cdot}H_2O$ (0.3 mmol, 1.5 equiv), 10 mol% of 5 wt% Pd/C with $NaBH_4$ (50 mol%) in 1,4-dixoane (1 mL) were stirred under argon for 12 h; Starting material conversion and NMR yields were given with 1,3,5-trimethoxylbenzene as the internal standard, and yields were calculated based on phenol.

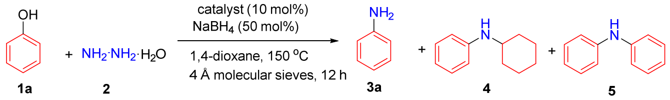
Table S2. Evaluation of solvents[a]



entry	various solvents (1 mL)	conv. (%)	yield (%)		
			3a	**4**	**5**
1	**1,4-dioxane**	**100**	**58**	**8**	**2**
2	heptane	99	35	15	11
3	*m*-xylene	78	24	6	1<
4	toluene	81	43	8	1<
5	trihexyltetradecylphosphonium dicyanamide (Ionic liquid)	-	-	-	-
6	diglyme	-	-	-	-
7	NMP	70	15	1<	1<
8	CPME	100	30	30	10

[a] Reaction conditions: phenol (0.2 mmol, 1 equiv), $N_2H_4{\cdot}H_2O$ (0.3 mmol, 1.5 equiv), 10 mol% of 5 wt% Pd/C, $NaBH_4$ (50 mol%) with 100 mg 4 Å molecular sieve in various solvents above (1 mL) were stirred under argon for 12 h; Starting material conversion and NMR yields were given with 1,3,5-trimethoxylbenzene as the internal standard, and yields were calculated based on phenol.

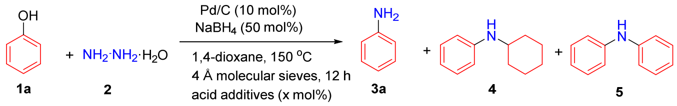
Table S3. Evaluation of catalysts[a]



entry	catalyst (10 mol%)	conv. (%)	yield (%)		
			3a	**4**	**5**
1	**Pd/C (5 wt%)**	**100**	**58**	**8**	**2**
2	Pd/C (10 wt%)	100	52	22	5
3	Pd/Al_2O_3(5 wt%)	100	42	<1	<1
4	Ru/C (5 wt%)	-	-	-	-

[a] Reaction conditions: phenol (0.2 mmol, 1 equiv), $N_2H_4{\cdot}H_2O$ (0.3 mmol, 1.5 equiv), 10 mol% catalyst, $NaBH_4$ (50 mol%), 100 mg 4 Å molecular sieve with additives in 1,4-dixoane (1 mL) were stirred under argon for 12 h; Starting material conversion and NMR yields were given with 1,3,5-trimethoxylbenzene as the internal standard, and yields were calculated based on phenol.

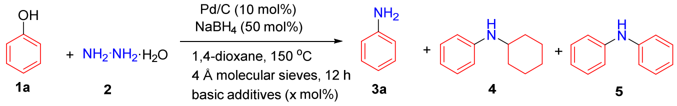
Table S4. Evaluation of acid additives[a]



entry	acid additives (x mol%)	conv. (%)		yield (%)	
			3a	**4**	**5**
1	**-**	**100**	**58**	**8**	**2**
2	$NiCl_2$ (10)	87	27	46	5
3	ZnF_2 (10)	100	30	36	11
4	$ZnCl_2$ (10)	55	10	4	1<
5	CuCl (10)	97	27	36	14
6	$In(OAc)_3$ (10)	100	21	48	9
7	$MnCl_2$ (10)	100	47	22	8
8	Al_2O_3 (10)	100	51	17	3
9	$SnCl_2$ (10)	-	-	-	-
10	$B_2(OH)_4$ (10)	100	51	17	4
11	$B(OH)_3$ (10)	100	34	34	11
12	HCO_2H (10)	100	36	40	8
13	HOAc (10)	81	41	12	3
14	TFA (10)	100	52	15	3
15[b]	CO_2	87	13	46	14

[a] Reaction conditions: phenol (0.2 mmol, 1 equiv), $N_2H_4 \cdot H_2O$ (0.3 mmol, 1.5 equiv), 10 mol% of 5 wt% Pd/C, $NaBH_4$ (50 mol%), 100 mg 4 Å molecular sieve with additives in 1,4-dixoane (1 mL) were stirred under argon for 12 h; Starting material conversion and NMR yields were given with 1,3,5-trimethoxylbenzene as the internal standard, and yields were calculated based on phenol; [b] The reaction was run under the atmosphere of sealed CO_2 instead of Argon.

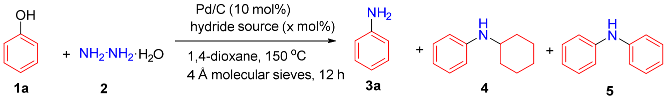
Table S5. Evaluation of base additives[a]



entry	basic additives (x mol%)	conv. (%)		yield (%)	
			3a	**4**	**5**
1	**-**	**100**	**58**	**8**	**2**
2	LiO^{t}Bu (10)	100	58	7	1
3	NaO^{t}Bu (10)	100	59	6	1
4	NaO^{t}Bu (20)	100	55	3	1<
5	KO^{t}Bu (10)	100	59	10	2
6	CaO (10)	100	60	8	1<
7	CaO (20)	100	53	7	1<
8	NaOAc (20)	100	50	6	1<
9	Na_2CO_3 (10)	100	55	16	4
10	K_2CO_3 (10)	100	51	21	4
11	Cs_2CO_3 (10)	100	54	17	2
12	$Mg(OH)_2$ (10)	100	54	14	3
13	Na_3PO_4 (10)	100	60	12	2
14	Na_3PO_4 (20)	100	50	22	5
15	Na_2HPO_4 (20)	100	51	17	6
16	NaH_2PO_4 (20)	100	40	24	6
17	K_3PO_4 (20)	100	60	10	2
18	K_3PO_4 (40)	100	52	12	3
19	K_2HPO_4 (20)	100	51	22	4

[a] Reaction conditions: phenol (0.2 mmol, 1 equiv), $N_2H_4 \cdot H_2O$ (0.3 mmol, 1.5 equiv), 10 mol% of 5 wt% Pd/C, $NaBH_4$ (50 mol%), 100 mg 4 Å molecular sieve with additives in 1,4-dixoane (1 mL) were stirred under argon for 12 h; Starting material conversion and NMR yields were given with 1,3,5-trimethoxylbenzene as the internal standard, and yields were calculated based on phenol.

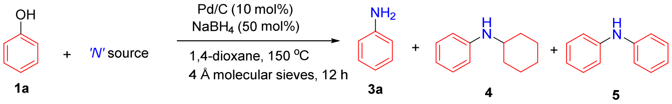
Table S6. Evaluation of hydride source[a]



entry	hydride source (x mol%)	conv. (%)		yield (%)	
			3a	**4**	**5**
1	**$NaBH_4$ (50)**	**100**	**58**	**8**	**2**
2	HCO_2Na (100)	97	34	30	18
3	H_2 (sealed in 10 mL tube)	100	18	38	12
4	1,4-cyclohexadiene (200)	23	12	1<	1<

[a] Reaction conditions: phenol (0.2 mmol, 1 equiv), $N_2H_4\cdot H_2O$ (0.3 mmol, 1.5 equiv), 10 mol% of 5 wt% Pd/C, various hydride sources with 100 mg 4 Å molecular sieve in 1,4-dioxane (1 mL) were stirred under argon for 12 h; Starting material conversion and NMR yields were given with 1,3,5-trimethoxybenzene as the internal standard, and yields were calculated based on phenol; For entry 3, the reaction was run under hydrogen gas sealed in the reaction tube.

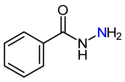
Table S7. Evaluation of *N* source[a]



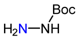
entry	*N* source	conv. (%)		yield (%)	
			3a	**4**	**5**
1	***N1***	**100**	**58**	**8**	**2**
2	*N2*	-	-	-	-
3	*N3*	49	21	1<	1<
4	*N4*	-	-	-	-
5	*N5*	-	-	-	-
6	*N6*	-	-	-	-
7	*N7*	60	11	24	1<
8	*N8*	87	18	56	1<

$NH_2{-}NH_2\cdot H_2O$

N1

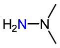


N2

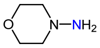


$H_2N{-}NH(Boc)$

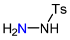
N3



N4

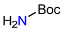


N5



$H_2N{-}NH(Ts)$

N6



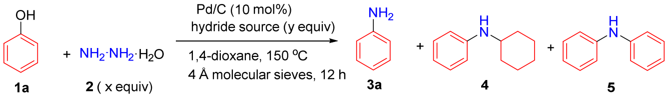
N7

$NH_3\ H_2O$

N8

[a] Reaction conditions: phenol (0.2 mmol, 1 equiv), *N* sources (0.3 mmol, 1.5 equiv), 10 mol% of 5 wt% Pd/C, $NaBH_4$ (50 mol%) with 100 mg 4 Å molecular sieve in 1,4-dioxane (1 mL) were stirred under argon for 12 h; Starting material conversion and NMR yields were given with 1,3,5-trimethoxybenzene as the internal standard, and yields calculated were based on phenol; For entry 8, 10.5 equiv ammonia water was used with 200 mg 4 Å molecular sieve.

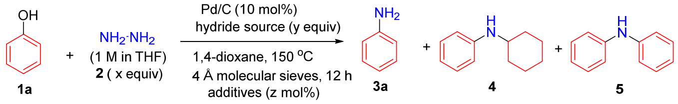
Table S8. Optimization of hydride and hydrazine amount[a]



entry	$N_2H_4\cdot H_2O$ (x equiv)	hydride source (y equiv)	conv. (%)		yield (%)	
				3a	**4**	**5**
1	**1.5**	**$NaBH_4$ (0.5)**	**100**	**58**	**8**	**2**
2	1.5	-	67	25	4	10
3	4.5	-	78	51	2	2
4	6.0	-	82	49	2	2
5	4.5	$NaBH_4$ (0.5)	100	49	6	1<
6	4.5	$NaBH_4$ (0.25)	100	58	2	2
7	3.0	$NaBH_4$ (0.25)	100	58	4	2
8	3.0	HCO_2Na (1.0)	100	61	10	7
9	**N_2H_4 (THF) (3.0)**	**HCO_2Na (1.0)**	**100**	**64**	**3**	**1<**

[a] Reaction conditions: phenol (0.2 mmol, 1 equiv), $N_2H_4\cdot H_2O$ (x equiv), 10 mol% of 5 wt% Pd/C, various hydride sources with 4 Å molecular sieve (100 mg per 0.3 mmol $N_2H_4\cdot H_2O$) in 1,4-dioxane (1 mL) were stirred under argon for 12 h; Starting material conversion and NMR yields were given with 1,3,5-trimethoxybenzene as the internal standard, and yields were calculated based on phenol.

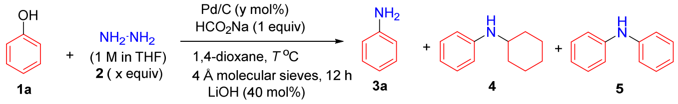
Table S9. Optimization of hydride, additives, and hydrazine amount in N_2H_4 in THF solution (1M)[a]



entry	N_2H_4 in THF (x equiv)	hydride source (y equiv)	additives (z mol%)	conv. (%)	yield (%)		
					3a	4	5
1	**3.0**	**HCO_2Na (1.0)**	**-**	**100**	**64**	**3**	**1<**
2	3.0	HCO_2Na (1.0)	LiOH (20)	97	54	2	1<
3	**3.0**	**HCO_2Na (1.0)**	**LiOH (40)**	**100**	**68**	**2**	**1<**
4	3.0	HCO_2Na (1.0)	LiOH (50)	89	57	2	1<
5	3.0	HCO_2Na (1.0)	LiOH (80)	96	57	1	1<
6	3.0	HCO_2Na (1.0)	LiOH (160)	95	43	1<	1<
7	3.0	HCO_2Na (1.0)	$LiOH\cdot H_2O$ (40)	89	63	2	1<
8	3.0	HCO_2Na (1.0)	LiF (40)	91	58	2	1<
9	3.0	HCO_2Na (1.0)	LiCl (40)	100	56	5	2
10	3.0	HCO_2Na (1.0)	LiBr (40)	83	50	2	1<
11	3.0	HCO_2Na (1.0)	LiI (40)	-	-	-	-
12	3.0	HCO_2Na (1.0)	$LiBF_4$ (40)	54	28	1<	1<
13	3.0	HCO_2Na (1.0)	LiOAc (40)	59	28	1<	1<
14	3.0	HCO_2Na (1.0)	LiO^{t}Bu (40)	96	56	2	1<
15	**2.25**	**HCO_2Na (1.0)**	**LiOH (40)**	**100**	**69**	**4**	**2**
16	1.875	HCO_2Na (1.0)	LiOH (40)	92	56	2	1
17	1.5	HCO_2Na (1.0)	LiOH (40)	97	56	7	4
18	2.25	HCO_2Na (1.0)	-	100	55	12	3
19	2.25	HCO_2Na (1.0)	NaOH (40)	100	64	5	3
20	2.25	HCO_2Na (1.0)	$Ca(OH)_2$ (20)	100	65	5	2
21	2.25	HCO_2Na (1.0)	KOH (40)	100	61	7	3
22	2.25	HCO_2H (1.0)	-	86	36	5	10
23	2.25	HCO_2H (1.0)	LiOH (100)	98	51	3	2
24	2.25	HCO_2H (1.0)	LiOH (140)	95	59	3	2
25	2.25	HCO_2Na (1.0)	H_2O (40)	100	55	10	3
26	2.25	$NaBH_4$ (0.25)	LiOH (40)	100	62	1<	1<
27	2.25	$NaBH_4$ (0.5)	LiOH (40)	100	47	1<	1<

[a] Reaction conditions: phenol (0.2 mmol, 1 equiv), N_2H_4 in THF solution (1 M) (x equiv), 10 mol% of 5 wt% Pd/C, various hydride sources, 4 Å molecular sieve (100 mg per 0.3 mmol N_2H_4 (THF) in 1,4-dioxane (0.2 M) with additives were stirred under argon for 12 h; Starting material conversion and NMR yields were given with 1,3,5-trimethoxylbenzene as the internal standard, and yields were calculated based on phenol.

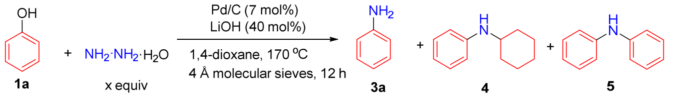
Table S10. Evaluation of temperature, Pd/C amount in N_2H_4 in THF solution (1M)[a]



entry	N_2H_4 in THF (x equiv)	Pd/C (y mol%)	T (°C)	conv. (%)	yield (%)		
					3a	4	5
1[b]	**2.25**	**10**	**150**	**100**	**69**	**4**	**2**
2	2.25	10	170	100	68	2	1
3	2.25	5	170	87	55	1	1<
4	2.25	6	170	97	65	3	1<
5[b]	**2.25**	**7**	**170**	**100**	**72**	**4**	**2**
6	2.25	9	170	100	69	3	2
7	2.25	12.5	170	100	67	3	1<
8	**2.5**	**7**	**170**	**100**	**72**	**2**	**1**
9	2.5	7	190	98	70	3	2
10	2.75	7	170	100	70	2	1
11	3.0	7	170	100	70	2	1
12	1.875	7	170	100	65	6	4
13	1.5	7	170	95	66	4	2

[a] Reaction conditions: phenol (0.4 mmol, 1 equiv), N_2H_4 in THF solution (1 M) (x equiv), y mol% of 5 wt% Pd/C, HCO_2Na (0.4 mmol, 1 equiv), 4 Å molecular sieve (100 mg per 0.3 mmol N_2H_4 (THF) in 1,4-dioxane (0.2 M) with LiOH (40 mol%) were stirred under argon for 12 h; Starting material conversion and NMR yields were given with 1,3,5-trimethoxylbenzene as the internal standard, and yields were calculated based on phenol; [b] 0.2 mmol phenol was used instead.

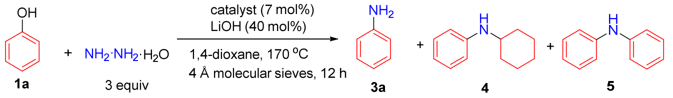
Table S11. Optimization of the hydrazine amount for the phenol with hydrazine acting both as *N* and *H* sources without extra hydride donor[a]



entry	$N_2H_4 \cdot H_2O$ (x equiv)	conv. (%)	**3a** (%)	**4 (%)**	**5 (%)**
1	$N_2H_4 \cdot H_2O$ 4.5 eq	100	69	1<	1<
2	$N_2H_4 \cdot H_2O$ 3.0 eq	100	72 (71)	1<	1<
3	$N_2H_4 \cdot H_2O$ 2.5 eq	84	64	1<	1<
4[b]	$N_2H_4 \cdot H_2O$ 4.5 eq	100	55	1<	1<

[a] Reaction conditions: phenol (0.4 mmol, 1 equiv), $N_2H_4 \cdot H_2O$ (x equiv), 7 mol% of 5 wt% Pd/C, LiOH (40 mol%), with 4 Å molecular sieve (100 mg per 0.3 mmol $N_2H_4 \cdot H_2O$) in 1,4-dioxane (2 mL) were stirred under argon for 12 h; Starting material conversion and NMR yields were given with 1,3,5-trimethoxylbenzene as the internal standard, isolated yield was given in parentheses, yields calculated based on phenol; [b] the reaction was run under 150 °C instead.

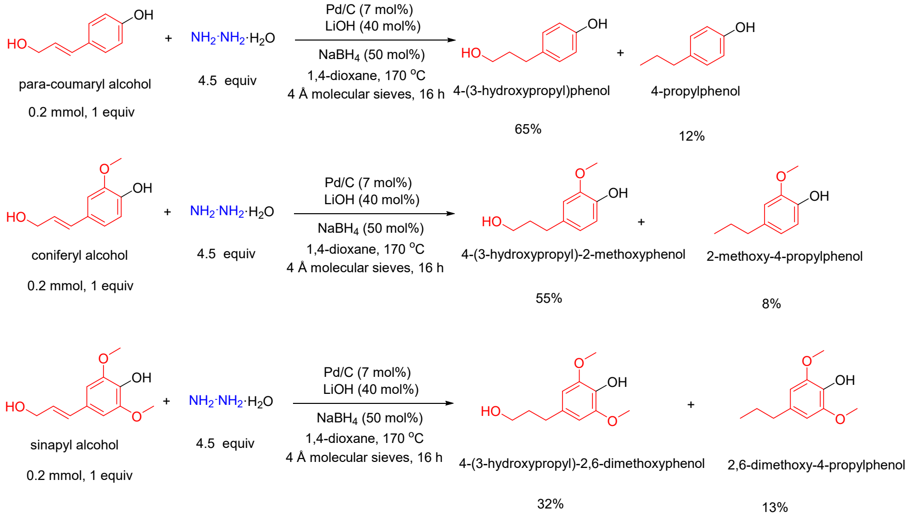
Table S12. Examination of other catalysts under standard conditions[a]



entry	catalyst	conv. (%)	**3a** (%)	**4 (%)**	**5 (%)**
1	Pd/C	100	72	1<	1<
2	Ru/C	4	-	-	-
3	Pt/C	6	-	-	-
4	Rh/C	6	-	-	-

[a] Reaction conditions: phenol (0.4 mmol, 1 equiv), $N_2H_4 \cdot H_2O$ (3 equiv), 7 mol% catalyst, LiOH (40 mol%), with 4 Å molecular sieve (100 mg per 0.3 mmol $N_2H_4 \cdot H_2O$) in 1,4-dioxane (2 mL) were stirred under argon for 12 h at 170 °C; Starting material conversion and NMR yields were given with 1,3,5-trimethoxylbenzene as the internal standard.

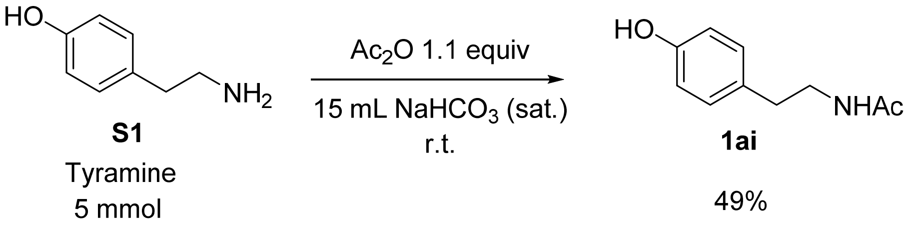
Scheme S1. The preliminary results of lignin monomers



The desired primary aniline products were not detected, instead 4-(3-hydroxypropyl)phenol type products and 4-propylphenol type products were observed.

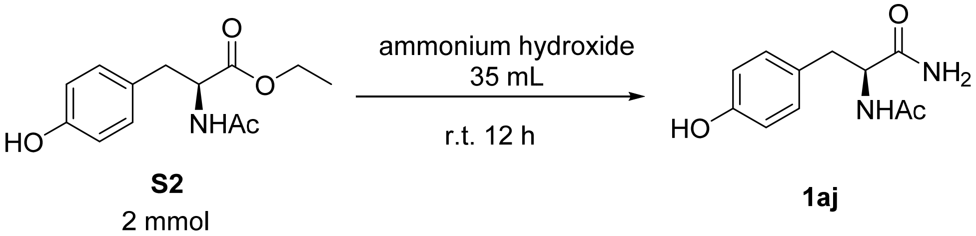
IV. Synthesis of Starting Phenol Materials

1. Synthesis of ***N*-(4-hydroxyphenethyl)acetamide (1ai):**



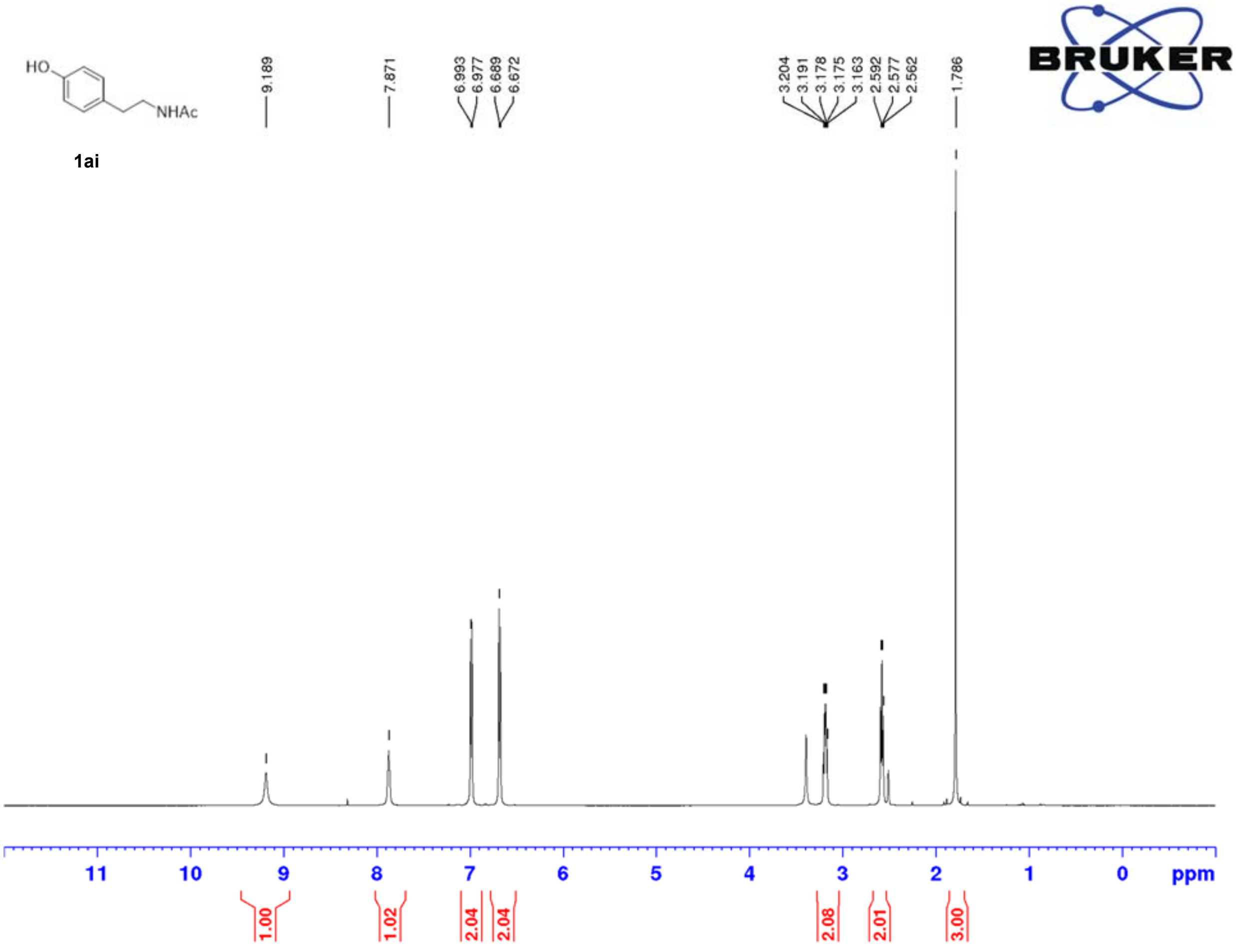
The synthesis of N-(4-hydroxyphenethyl)acetamide (**1ai**) was based on the reported literature.[30] Tyramine (**S1**) (5 mmol, 1 equiv) was dissolved into 15 mL NaHCO$_3$ saturated aq. solution. Then acetic anhydride (5.5 mmol, 1.1 equiv) was added slowly dropwise while the solution being stirred. The resulting suspension was allowed to stir at room temperature for one and half hour. Then aqueous solution was extracted with EtOAc (3x30 mL). The organic phases were collected, dried over Na$_2$SO$_4$ and the solvent was removed under vacuum. The product was then purified by the silica gel column chromatography (DCM: MeOH 30:1 to 10:1) to afford *N*-(4-hydroxyphenethyl)acetamide (**1ai**) as a white solid in 49% yield. ^{1}H NMR: (500 MHz, DMSO-d$_6$, ppm): δ 9.19 (br, 1H), 7.87 (br, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 8.4 Hz, 2H), 3.18 (dd, *J* = 13.3 Hz, 7.1 Hz, 2H), 2.58 (t, *J* = 7.5 Hz, 2H), 1.79 (s, 3H); ^{13}C NMR: (125 MHz, DMSO-d$_6$, ppm): δ 169.0, 155.6, 129.5, 115.1, 40.6, 34.4, 22.6; HRMS: (APCI, m/z) calcd for C$_{10}$H$_{14}$O$_2$N [M+H]$^+$ 180.1019, found: 180.1021

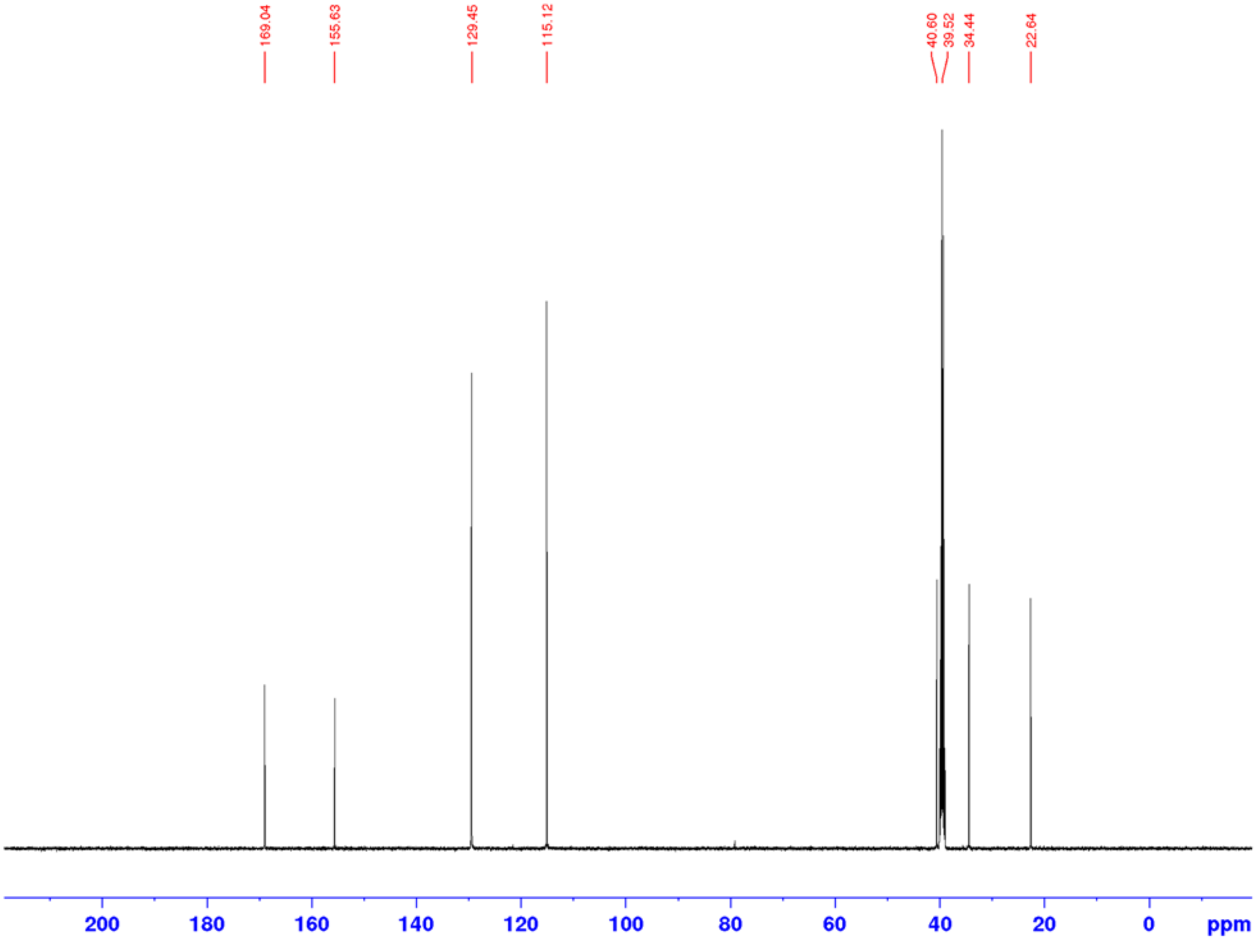
2. Synthesis of **Ac-Tyr-NH$_2$ (1ab):**

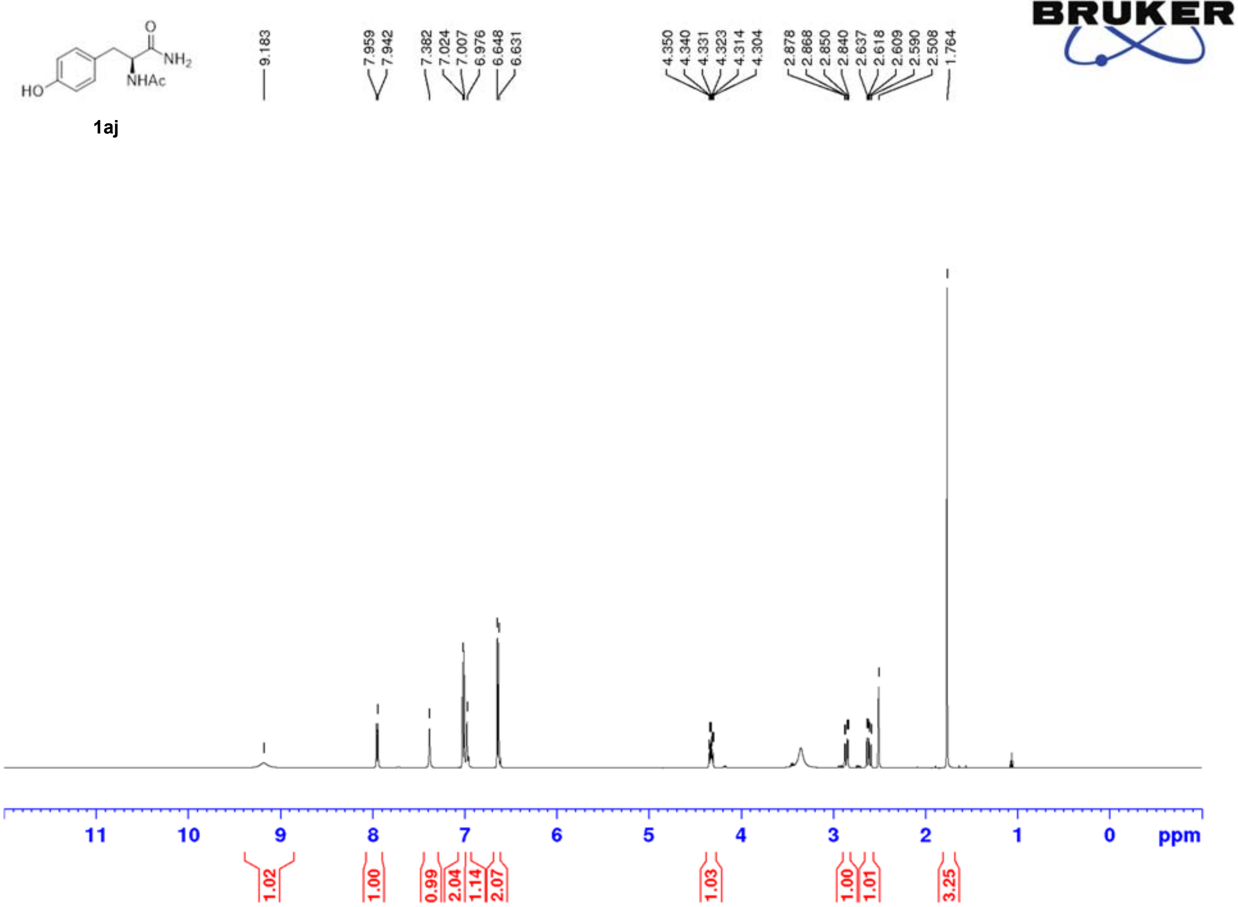


Ac-Tyr-OEt (**S2**) (2 mmol, 1 equiv) was dissolved into 35 mL ammonium hydroxide aq. solution. The resulting solution was allowed to stir at room temperature for 12 hours. Then water was removed with a rotary evaporator with the help of the ethanol (3x15 mL). After that, the crude compound was put under high vacuum for 4 hours to give the pure product as a white solid. This product was directly used without any further purification. ^{1}H NMR: (500 MHz, DMSO-d$_6$, ppm): δ 9.18 (br, 1H), 7.95 (dd, *J* = 8.4 Hz, 1H), 7.38 (br, 1H), 7.02 (d, *J* = 8.5 Hz, 2H), 6.98 (br, 1H), 6.64 (d, *J* = 8.5 Hz, 2H), 4.35 – 4.30 (m, 1H), 2.86 (dd, *J* = 13.8 Hz, 4.8 Hz, 1H), 2.61 (dd, *J* = 13.8 Hz, 9.6 Hz, 1H), 1.76 (s, 3H); ^{13}C NMR: (125 MHz, DMSO-d$_6$, ppm): δ 173.5, 169.0, 155.7, 130.0, 128.2, 114.8, 54.2, 36.9, 22.5; HRMS: (APCI, m/z) calcd for C$_{11}$H$_{13}$O$_3$N$_2$ [M-H]$^-$ 221.0932, found: 221.0923

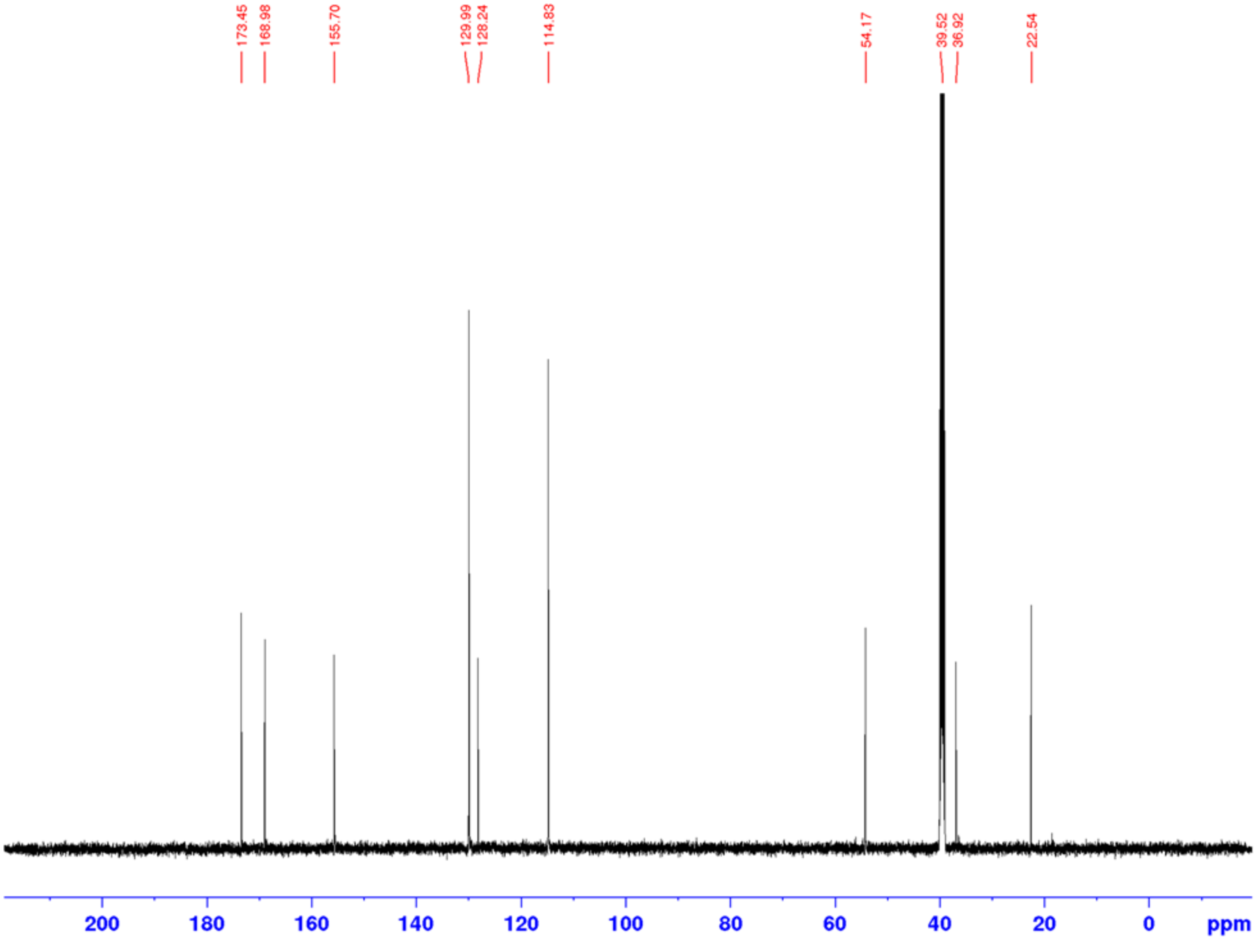
V. Spectroscopic Data of Synthesized Starting Phenol Materials



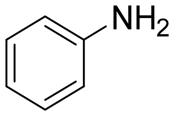

169.04
155.63
129.45
115.12
40.60
39.52
34.44
22.64
200
180
160
140
120
100
80
60
40
20
0
ppm


HO
O
NH2
NHAc
9.183
7.959
7.942
7.382
7.024
7.007
6.976
6.648
6.631
4.350
4.340
4.331
4.323
4.314
4.304
2.878
2.868
2.850
2.840
2.637
2.618
2.609
2.590
2.508
1.764
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.02
1.00
0.99
2.04
1.14
2.07
1.03
1.00
1.01
3.25

1aj

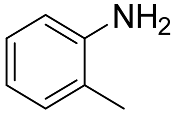

173.45
168.98
155.70
129.99
128.24
114.83
54.17
39.52
36.92
22.54
200
180
160
140
120
100
80
60
40
20
0
ppm

VI. Spectroscopic Data of Products



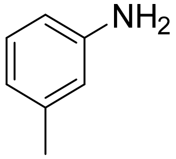
Aniline (3a) (CAS: 62-53-3):[1]

Following the general procedure, DCM was used to perform the extraction. After column chromatography on silica gel (eluent: DCM: pentane: 1:1 to 4:1), the product was isolated as a pale yellow oil (26.4 mg, 71% yield). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm): δ 7.19 (t, *J* = 7.9 Hz, 2H), 6.80 (t, *J* = 3.1 Hz, 1H), 6.79 (d, *J* = 4.1 Hz, 2H), 3.64 (br, 2H); ^{13}C NMR: (125 MHz, $CDCl_3$, ppm): δ 146.5, 129.4, 115.2; EI-MS (*m/z*): 93.0



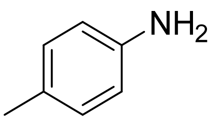
***o*-Toluidine (3b) (CAS: 95-53-4):[2]**

Following the general procedure, EtOAc was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 5:1), the product was isolated as a pale yellow oil (30.5 mg, 71% yield). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm): δ 7.07 – 7.04 (m, 2H), 6.74 – 6.68 (m, 2H), 3.60 (br, 2H), 2.18 (s, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$, ppm): δ 144.7, 130.6, 127.1, 122.4, 118.7, 115.0, 17.5; EI-MS (*m/z*): 107.0



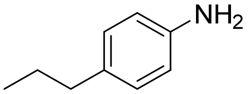
***m*-Toluidine (3c) (CAS: 108-44-1):[3]**

Following the general procedure, EtOAc was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 5:1), the product was isolated as a pale yellow oil (30.9 mg, 72% yield). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm): δ 7.06 (t, *J* = 7.7 Hz, 1H), 6.60 (d, *J* = 7.5 Hz, 1H), 6.53 – 6.50 (m, 2H), 3.60 (br, 2H), 2.28 (s, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$, ppm): δ 146.5, 139.2, 129.3, 119.6, 116.0, 112.4, 21.6; EI-MS (*m/z*):107.1



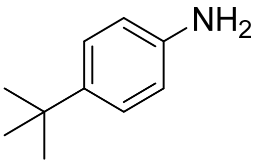
p-Toluidine (3d) (CAS: 106-49-0):[1]

Following the general procedure, EtOAc was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 5:1), the product was isolated as a pale yellow solid (31.0 mg, 72% yield). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm): δ 6.97 (d, J = 7.9 Hz, 2H), 6.62 (d, J = 8.4 Hz, 2H), 3.53 (br, 2H), 2.25 (s, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$, ppm): δ 143.9, 129.9, 127.9, 115.4, 20.6; EI-MS (*m/z*): 106.9



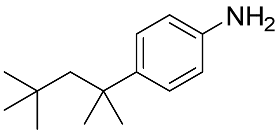
4-Propylaniline (3e) (CAS: 2696-84-6):[26]

Following the general procedure, EtOAc was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 5:1), the product was isolated as an orange oil (38.1 mg, 71% yield). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm): δ 6.99 (d, J = 8.4 Hz, 2H), 6.64 (d, J = 8.4 Hz, 2H), 3.54 (br, 2H), 2.50 (t, J = 7.6 Hz, 2H), 1.61 (sext, J = 7.5 Hz, 2H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$, ppm): δ 144.2, 133.0, 129.3, 115.3, 37.3, 25.0, 13.9; EI-MS (*m/z*): 135.1



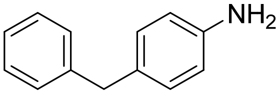
4-(*tert*-Butyl)aniline (3f) (CAS: 769-92-6):[4]

Following the general procedure, EtOAc was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 5:1), the product was isolated as a colorless oil (45.0 mg, 75% yield). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm): δ 7.19 (d, J = 8.6 Hz, 2H), 6.65 (d, J = 8.7 Hz, 2H), 3.55 (br, 2H), 1.29 (s, 9H); ^{13}C NMR: (125 MHz, $CDCl_3$, ppm): δ 143.9, 141.6, 126.2, 115.1, 34.0, 31.7; EI-MS (*m/z*): 149.1



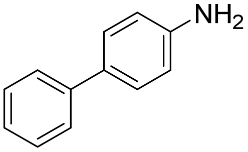
4-(2,4,4-Trimethylpentan-2-yl)aniline (3g) (CAS: 42265-56-5):[23]

Following the general procedure, EtOAc was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 3:1), the product was isolated as a colorless oil (42.8 mg, 52% yield). ^{1}H NMR: (500 MHz, CDCl$_3$, ppm): δ 7.16 (d, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 8.7 Hz, 2H), 3.54 (br, 2H), 1.69 (s, 2H), 1.33 (s, 6H), 0.74 (s, 9H); ^{13}C NMR: (125 MHz, CDCl$_3$, ppm): δ 143.7, 140.4, 127.0, 114.9, 57.1, 37.9, 32.4, 31.9, 31.8; HRMS: (APCI, m/z) calcd for $C_{14}H_{24}N$ [M+H]$^+$ 206.1903, found: 206.1903



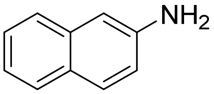
4-Benzylaniline (3h) (CAS: 1135-12-2):[23]

Following the general procedure, MeOH was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 3:1), the product was isolated as an orange oil (45.5 mg, 62% yield). ^{1}H NMR: (500 MHz, CDCl$_3$, ppm): δ 7.32 – 7.29 (m, 2H), 7.22-7.20 (m, 3H), 7.01 (d, *J* = 8.3 Hz, 2H), 6.65 (d, *J* = 8.3 Hz, 2H), 3.91 (s, 2H), 3.56 (br, 2H); ^{13}C NMR: (125 MHz, CDCl$_3$, ppm): δ 144.6, 142.0, 131.3, 129.9, 128.9, 128.5, 126.0, 115.4, 41.2; EI-MS (*m/z*): 183.1



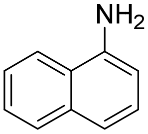
[1,1'-Biphenyl]-4-amine (3i) (CAS: 92-67-1):[9]

Following the general procedure, EtOAc was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 3:1), the product was isolated as a yellow solid (36.0 mg, 53% yield). ^{1}H NMR: (500 MHz, CDCl$_3$, ppm): δ 7.55 (dd, *J* = 8.1 Hz, 1.3 Hz, 2H), 7.44 – 7.39 (m, 4H), 7.28 (tt, *J* = 7.4 Hz, 1.1 Hz, 1H), 6.77 (d, *J* = 8.5 Hz, 2H), 3.73 (br, 2H); ^{13}C NMR: (125 MHz, CDCl$_3$, ppm): δ 146.0, 141.3, 131.7, 128.8, 128.1, 126.5, 126.4,115.4; EI-MS (*m/z*): 169.1



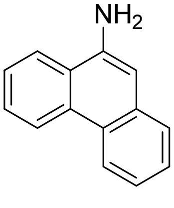
Naphthalen-2-amine (3j) (CAS: 91-59-8):[2]

Following the general procedure, EtOAc was used to perform the extraction. After column on silica gel isolation (eluent: hexanes: EtOAc = 5:1 to 3:1), the product was isolated as a white solid (49.1 mg, 86% yield). ^{1}H NMR: (500 MHz, CDCl$_3$, ppm): δ 7.72 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.27 – 7.24 (m, 1H), 7.00 (d, *J* = 2.2 Hz, 1H), 6.96 (dd, *J* = 8.7 Hz, 2.4 Hz, 1H), 3.84 (br, 2H); ^{13}C NMR: (125 MHz, CDCl$_3$, ppm): δ 144.2, 135.0, 129.3, 128.1, 127.8, 126.5, 125.9, 122.6, 118.3, 108.7; EI-MS (*m/z*): 143.1



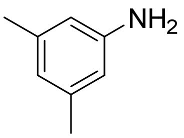
Naphthalen-1-amine (3k) (CAS: 134-32-7):[2]

Following the general procedure, EtOAc was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 5:1), the product was isolated as a white solid (41.5 mg, 73% yield). ^{1}H NMR: (500 MHz, CDCl$_3$, ppm): δ 7.84 – 7.81 (m, 2H), 7.49 – 7.45 (m, 2H), 7.35 – 7.29 (m, 2H), 6.79 (dd, *J* = 7.0 Hz, 1.3 Hz, 1H), 4.15 (br, 2H); ^{13}C NMR: (125 MHz, CDCl$_3$, ppm): δ 142.2, 134.5, 128.7, 126.5, 126.0, 125.0, 123.8, 120.9, 119.1, 109.8; EI-MS (*m/z*): 143.1



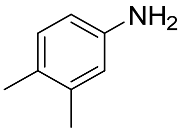
Phenanthren-9-amine (3l) (CAS: 947-73-9):[8]

Following the general procedure, EtOAc was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 3:1), the product was isolated as a pink solid (23.4 mg, 30% yield). ^{1}H NMR: (500 MHz, CDCl$_3$, ppm): δ 8.72 (d, *J* = 7.0 Hz, 1H), 8.60 (d, *J* = 8.2 Hz, 1H), 7.94 (dd, *J* = 3.1 Hz, 0.9 Hz, 1H), 7.77 – 7.63 (m, 3H), 7.52 – 7.49 (m, 1H), 7.46-7.42 (m, 1H), 4.16 (br, 2H); ^{13}C NMR: (125 MHz, CDCl$_3$, ppm): δ 140.0, 133.4, 131.3, 127.0, 126.8, 126.5, 126.4, 126.3, 125.6, 123.6, 123.5, 122.6, 121.4, 107.6; EI-MS (*m/z*): 193.1



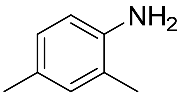
3,5-Dimethylaniline (3m) (CAS: 108-69-0):[10]

Following the general procedure, EtOAc was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 3:1), the product was isolated as a yellow solid (34.4 mg, 71% yield). ^{1}H NMR: (500 MHz, CDCl$_3$, ppm): δ 6.43 (s, 1H), 6.34 (s, 2H), 3.54 (br, 2H), 2.23 (s, 6H); ^{13}C NMR: (125 MHz, CDCl$_3$, ppm): δ 146.5, 139.1, 120.6, 113.2, 21.4; EI-MS (*m/z*): 121.1



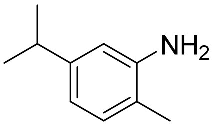
3,4-Dimethylaniline (3n) (CAS: 95-64-7):[24]

Following the general procedure, EtOAc was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 5:1), the product was isolated as a yellow solid (30.8 mg, 64% yield). ^{1}H NMR: (500 MHz, CDCl$_3$, ppm): δ 6.94 (d, *J* = 7.9 Hz, 1H), 6.54 (d, *J* = 2.3 Hz, 1H), 6.47 (dd, *J* = 7.9 Hz, 2.4 Hz, 1H), 3.47 (br, 2H), 2.20 (s, 3H), 2.17 (s, 3H); ^{13}C NMR: (125 MHz, CDCl$_3$, ppm): δ 144.3, 137.5, 130.4, 126.6, 117.0, 112.8, 20.0, 18.8; EI-MS (*m/z*): 121.1



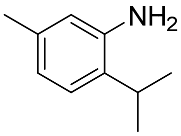
2,4-Dimethylaniline (3o) (CAS: 95-68-1):[25]

Following the general procedure, EtOAc was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 5:1), the product was isolated as a yellow solid (24.4 mg, 50% yield). ^{1}H NMR: (500 MHz, CDCl$_3$, ppm): δ 6.89 (s, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 6.61 (d, *J* = 7.9 Hz, 1H), 3.40 (br, 2H), 2.24 (s, 3H), 2.16 (s, 3H); ^{13}C NMR: (125 MHz, CDCl$_3$, ppm): δ 142.1, 131.2, 128.0, 127.4, 122.6, 115.2, 20.5, 17.4; EI-MS (*m/z*): 121.1



5-Isopropyl-2-methylaniline (3p) (CAS: 2051-53-8):[19]

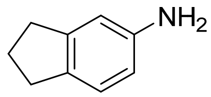
Following the general procedure, EtOAc was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 3:1), the product was isolated as a colorless oil (30.0 mg, 50% yield). ^{1}H NMR: (500 MHz, CDCl$_3$, ppm): δ 6.98 (d, *J* = 7.6 Hz, 1H), 6.60 (dd, *J* = 7.6 Hz, 1.7 Hz, 1H), 6.56 (d, *J* = 1.6 Hz, 1H), 3.57 (br, 2H), 2.80 (sept, *J* = 6.9 Hz, 1H), 2.14 (s, 3H), 1.22 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR: (125 MHz, CDCl$_3$, ppm): δ 148.1, 144.5, 130.5, 119.9, 116.9, 113.3, 33.9, 24.2, 17.1; EI-MS (*m/z*): 149.1



2-Isopropyl-5-methylaniline (3q) (CAS: 2437-39-0):[3]

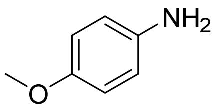
Following the general procedure, EtOAc was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 3:1), the product was isolated as a colorless oil (X mg, X% yield). ^{1}H NMR: (500 MHz, CDCl$_3$, ppm): δ 7.03 (d, *J* = 7.8 Hz, 1H), 6.61 (d, *J* = 7.8 Hz, 1H), 6.52 (d, *J* = 1.0 Hz, 1H), 3.60 (br, 2H), 2.87 (heptet, *J* = 6.9

Hz, 1H), 2.24 (s, 3H), 1.25 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR: (125 MHz, $CDCl_3$, ppm): δ 143.3, 136.3, 130.0, 125.5, 119.9, 116.7, 27.5, 22.6, 21.1; EI-MS (*m/z*): 149.1



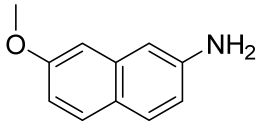
2,3-Dihydro-1*H*-inden-5-amine (3r) (CAS: 24425-40-9):[15]

Following the general procedure, EtOAc was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 3:1), the product was isolated as an orange solid (37.8 mg, 71% yield). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm): δ 7.02 (d, *J* = 7.9 Hz, 1H), 6.61 (s, 1H), 6.51 (dd, *J* = 7.6 Hz, 2.2 Hz, 1H), 3.44 (br, 2H), 2.84 – 2.80 (m, 4H), 2.05 (quint, *J* = 7.5 Hz, 2H); ^{13}C NMR: (125 MHz, $CDCl_3$, ppm): δ 145.6, 144.8, 134.5, 124.9, 113.5, 111.7, 33.1, 32.1, 25.8; EI-MS (*m/z*): 133.1



4-Methoxyaniline (3s) (CAS: 104-94-9):[10]

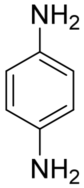
Following the general procedure, EtOAc was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 3:1), the product was isolated as a yellow solid (12.2 mg, 25% yield). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm): δ 6.75 (d, *J* = 8.8 Hz 2H), 6.65 (d, *J* = 8.9 Hz, 2H), 3.75 (s, 3H), 3.21 (br, 2H); ^{13}C NMR: (125 MHz, $CDCl_3$, ppm): δ 153.0, 140.0, 116.6, 115.0, 55.9; EI-MS (*m/z*): 123.1



7-Methoxynaphthalen-2-amine (3t) (CAS: 92287-46-2):[20]

Following the general procedure, EtOAc was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 1:1), the product was isolated as a pink solid (38.2 mg, 55% yield). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm): δ 7.60 – 7.57 (m, 2H), 6.92 – 6.89 (m, 3H), 6.79 (dd, *J* = 8.6 Hz, 2.3 Hz, 1H), 3.90 (s, 3H), 3.83 (br, 2H); ^{13}C

NMR: (125 MHz, $CDCl_3$, ppm): δ 158.3, 144.8, 136.3, 129.3, 129.1, 123.5, 115.9, 115.1, 108.0, 104.3, 55.3; EI-MS (*m/z*): 173.1

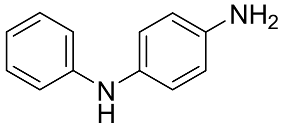


Benzene-1,4-diamine (3u) (CAS: 106-50-3):[11]

4-Aminophenol as staring material: following the general procedure, MeOH was used to perform the extraction. After preparative TLC isolation (eluent: DCM: MeOH = 10:1), the product was isolated as a grey solid (17.6 mg, 41% yield).

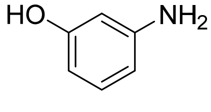
Hydroquinone as staring material: following the general procedure, MeOH was used to perform the extraction. After preparative TLC isolation (eluent: DCM: MeOH = 10:1), the product was isolated as a grey solid (21.7 mg, 50% yield).

^{1}H NMR: (500 MHz, $CDCl_3$, ppm): δ 6.57 (s, 4H), 3.33 (br, 4H); ^{13}C NMR: (125 MHz, $CDCl_3$, ppm): δ 138.7, 116.8; EI-MS (*m/z*): 108.0



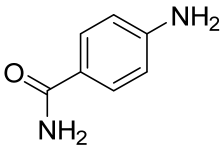
***N*^{1}-phenylbenzene-1,4-diamine (3v) (CAS: 101-54-2):[12]**

Following the general procedure, EtOAc was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 1:1), the product was isolated as a red solid (33.3 mg, 45% yield). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm): δ 7.19 (t, J = 6.5 Hz, 2H), 7.00 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 6.79 (t, J = 7.4 Hz, 1H), 6.67 (d, J = 8.6 Hz, 2H), 5.41 (br, 1H), 3.55 (br, 2H); ^{13}C NMR: (125 MHz, $CDCl_3$, ppm): δ 146.0, 142.2, 134.0, 129.4, 123.5, 119.1, 116.3, 115.2; EI-MS (*m/z*): 184.1



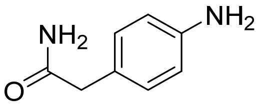
3-Aminophenol (3w) (CAS: 591-27-5):[22]

Following the general procedure, MeOH was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 1:1), the product was isolated as a light yellow solid (19.2 mg, 44% yield). ^{1}H NMR: (500 MHz, DMSO-d$_6$, ppm): δ 8.84 (br, 1H), 6.77 (t, *J* = 8.1 Hz, 1H), 6.00 – 5.99 (m, 2H), 5.94 – 5.91 (m, 1H), 4.87 (br, 2H); ^{13}C NMR: (125 MHz, DMSO-d$_6$, ppm): δ 158.1, 149.8, 129.4, 105.4, 103.3, 100.9; EI-MS (*m/z*): 109.0



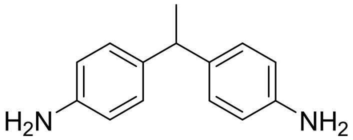
4-Aminobenzamide (3x) (CAS: 2835-68-9):[16]

Following the general procedure, MeOH was used to perform the extraction. After preparative TLC isolation (eluent: DCM: MeOH = 10:1), the product was isolated as a light yellow solid (25.0 mg, 46% yield). ^{1}H NMR: (500 MHz, DMSO-d$_6$, ppm): δ 7.59 (d, *J* = 8.6 Hz, 2H), 7.52 (br, 1H), 6.84 (br, 1H), 6.53 (d, *J* = 8.7 Hz, 2H), 5.60 (br, 2H); ^{13}C NMR: (125 MHz, DMSO-d$_6$, ppm): δ 168.1, 151.7, 129.1, 120.9, 112.5; EI-MS (*m/z*): 136.1



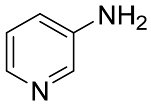
2-(4-Aminophenyl)acetamide (3y) (CAS: 6633-76-7):[21]

Following the general procedure, MeOH was used to perform the extraction. After preparative TLC isolation (eluent: DCM: MeOH = 10:1), the product was isolated as a white solid (42.0 mg, 70% yield). ^{1}H NMR: (500 MHz, DMSO-d$_6$, ppm): δ 7.25 (br, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.74 (br, 1H), 6.49 (d, *J* = 8.4 Hz, 2H), 4.89 (br, 2H), 3.15 (s, 2H); ^{13}C NMR: (125 MHz, DMSO-d$_6$, ppm): δ 173.1, 147.0, 129.4, 123.4, 113.7, 41.6; EI-MS (*m/z*): 150.1



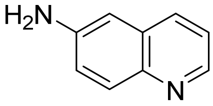
4,4'-(Ethane-1,1-diyl)dianiline (3z) (CAS: 14755-35-2):[29]

Following the general procedure, MeOH was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 2:3), the product was isolated as a white solid (12.0 mg, 14% yield). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm): δ 6.99 (d, *J* = 8.2 Hz, 4H), 6.61 (d, 2H), 3.95 (q, *J* = 7.2 Hz, 1H), 3.54 (br, 4H), 1.54 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$, ppm): δ 144.3, 137.5, 128.4, 115.3, 43.2, 22.4; EI-MS (*m/z*): 212.1



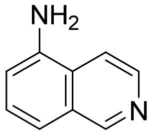
Pyridin-3-amine (3aa) (CAS: 462-08-8):[6]

Following the general procedure, MeOH was used to perform the extraction. After preparative TLC isolation (eluent: EtOAc: MeOH = 2:1), the product was isolated as a yellow solid (16.8 mg, 45% yield). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm): δ 8.09 (d, *J* = 2.7 Hz, 1H), 8.01 (d, *J* = 5.8 Hz, 1H), 7.05 (dd, *J* = 8.1 Hz, 4.1 Hz, 1H), 6.97 (ddd, *J* = 8.2 Hz, 2.8 Hz, 1.4 Hz, 1H), 3.71 (br, 2H); ^{13}C NMR: (125 MHz, $CDCl_3$, ppm): δ 142.6, 140.2, 123.8, 121.6; EI-MS (*m/z*): 94.0



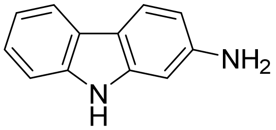
Quinolin-6-amine (3ab) (CAS: 580-15-4):[14]

Following the general procedure, EtOAc was used to perform the extraction. After preparative TLC isolation (eluent: EtOAc), the product was isolated as a brown solid (41.6 mg, 72% yield). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm): δ 8.65 (t, *J* = 4.2 Hz, 1.6 Hz, 1H), 7.90 (t, *J* = 8.5 Hz, 2H), 7.26 (dd, *J* = 8.3 Hz, 4.2 Hz, 1H), 7.15 (dd, *J* = 8.9 Hz, 2.6 Hz, 1H), 6.89 (d, *J* = 2.5 Hz, 1H), 3.94 (br, 2H); ^{13}C NMR: (125 MHz, $CDCl_3$, ppm): δ 146.9, 144.8, 143.5, 133.9 130.6, 129.9, 121.7, 121.5, 107.5; EI-MS (*m/z*): 144.0



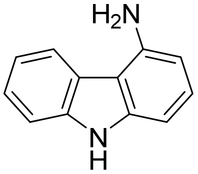
Isoquinolin-5-amine (3ac) (CAS: 1125-60-6):[4]

Following the general procedure, MeOH was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 1:2), the product was isolated as a yellow solid (17.5 mg, 30% yield). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm): δ 9.18 (d, *J* = 0.7 Hz, 1H), 8.49 (d, *J* = 6.0 Hz, 1H), 7.58 (d, *J* = 6.0 Hz, 1H), 7.42 – 7.41 (m, 2H), 6.97 – 6.95 (m, 1H), 4.21 (br, 2H); ^{13}C NMR: (125 MHz, $CDCl_3$, ppm): δ 153.1, 142.2, 141.4, 129.6, 127.9, 126.1, 118.2, 114.2, 113.2; EI-MS (*m/z*): 144.1



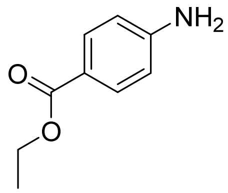
9*H*-carbazol-2-amine (3ad) (CAS: 4539-51-9):[18]

Following the general procedure, MeOH was used to perform the extraction. After preparative TLC isolation (eluent: acetone: EtOAc: hexanes = 1: 2: 2), the product was isolated as a yellow solid (47.8 mg, 66% yield). ^{1}H NMR: (500 MHz, acetone-d6, ppm): δ 9.84 (br, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.0 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 1.8 Hz, 1H), 6.57 (dd, *J* = 8.3 Hz, 2.0 Hz, 1H), 4.68 (br, 2H); ^{13}C NMR: (125 MHz, acetone-d6, ppm): δ 148.7, 143.2, 140.8, 125.2, 124.1, 121.5, 119.4, 119.3, 115.5, 111.0, 109.5, 96.0; EI-MS (*m/z*): 182.1



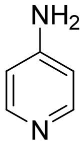
9*H*-carbazol-4-amine (3ae) (CAS: 18992-64-8):[17]

Following the general procedure, MeOH was used to perform the extraction. After preparative TLC isolation (eluent: DCM: hexanes = 10:1), the product was isolated as a yellow solid (22.0 mg, 30% yield). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm): δ 8.04 (br, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.25 – 7.22 (m, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.55 (d, *J* = 7.7, 1H), 4.34 (br, 2H); ^{13}C NMR: (125 MHz, $CDCl_3$, ppm): δ 142.8, 141.0, 139.1, 127.1, 124.7, 123.1, 121.1, 119.6, 111.0, 110.3, 106.2, 101.3; EI-MS (*m/z*): 182.1



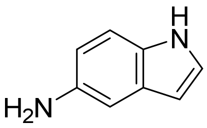
Ethyl 4-aminobenzoate (3af) (CAS: 94-09-7):[5]

Following the general procedure, EtOAc was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 5:1), the product was isolated as a white solid (21.1 mg, 32% yield). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm): δ 7.86 – 7.85 (m, 2H), 6.64 – 6.63 (m, 2H), 4.31 (q, J = 7.1 Hz, 2H), 4.05 (br, 2H), 1.36 (t, J = 7.1 Hz, 3H); ^{13}C NMR: (125 MHz, $CDCl_3$, ppm): δ 166.8, 150.8, 131.7, 120.2, 113.9, 60.4, 14.6; EI-MS (*m/z*): 165.2



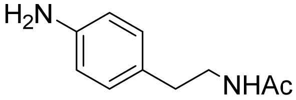
Pyridin-4-amine (3ag) (CAS: 504-24-5):[7]

Following the general procedure, MeOH was used to perform the extraction. After preparative TLC isolation (eluent: DCM: MeOH = 5:1), the product was isolated as a white solid (19.5 mg, 52% yield). ^{1}H NMR: (500 MHz, DMSO-d_6, ppm): δ 7.95 (dd, J = 4.8 Hz, 1.6 Hz, 2H), 6.44 (dd, J = 4.7 Hz, 1.6 Hz, 2H), 5.95 (br, 2H); ^{13}C NMR: (125 MHz, DMSO-d_6, ppm): δ 154.2, 149.5, 108.8; EI-MS (*m/z*): 94.0



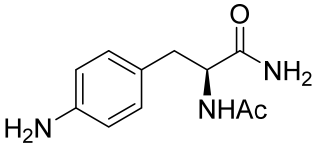
1*H*-indol-5-amine (3ah) (CAS: 5192-03-0):[16]

Following the general procedure, MeOH was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 1:1), the product was isolated as a yellow solid (47.3 mg, 90% yield). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm): δ 7.99 (br, 1H), 7.19 (d, J = 8.5 Hz, 1H), 7.12 (t, J = 2.8 Hz, 1H), 6.96 (d, J = 2.2 Hz, 1H), 6.67 (dd, J = 8.5 Hz, 2.2 Hz, 1H), 6.39 – 6.37 (m, 1H), 3.39 (br, 2H); ^{13}C NMR: (125 MHz, CDCl$_3$, ppm): δ 139.6, 130.8, 128.9, 124.8, 113.1, 111.6, 105.7, 101.7; EI-MS (*m/z*): 132.0



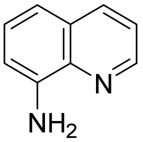
N-(4-aminophenethyl)acetamide (3ai) (CAS: 40377-41-1):[27]

Following the general procedure, MeOH was used to perform the extraction. After preparative TLC isolation (eluent: DCM: MeOH = 10:1), the product was isolated as a grey solid (45.0 mg, 63% yield). ^{1}H NMR: (500 MHz, CDCl$_3$, ppm): δ 6.95 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 2H), 5.68 (br, 1H), 3.62 (br, 2H), 3.42 (q, *J* = 6.6 Hz, 2H), 2.67 (t, *J* = 7.0 Hz, 2H), 1.90 (s, 3H); ^{13}C NMR: (125 MHz, CDCl$_3$, ppm): δ 170.2, 145.0, 129.6, 128.7, 115.4, 40.9, 34.7, 23.4; EI-MS (*m/z*): 178.1



(*S*)-2-acetamido-3-(4-aminophenyl)propanamide (3aj) (CAS: 115094-27-4):[28]

Following the general procedure, MeOH was used to perform the extraction. After preparative TLC isolation (eluent: EtOAc: MeOH = 5:1), the product was isolated as a pale yellow solid (28.8 mg, 33% yield). ^{1}H NMR: (500 MHz, DMSO-d$_6$, ppm): δ 7.90 (d, *J* = 8.5 Hz, 1H), 7.35 (s, 1H), 6.88 (s, 1H), 6.87 (d, *J* = 8.3 Hz, 2H), 6.44 (d, *J* = 8.3 Hz, 2H), 4.83 (s, 2H), 4.30 – 4.25 (m, 1H), 2.78 (dd, *J* = 13.8 Hz, 4.8 Hz, 1H), 2.54 (dd, *J* = 13.8 Hz, 9.5 Hz, 1H), 1.76 (s, 3H); ^{13}C NMR: (125 MHz, DMSO-d$_6$, ppm): δ 173.6, 168.9, 146.8, 129.5, 113.7, 54.3, 37.0, 22.6; HRMS: (ESI, m/z) calcd for $C_{11}H_{15}N_3O_2Na$ $[M+Na]^+$ 244.1062, found: 244.1057



Quinolin-8-amine (3ak) (CAS: 578-66-5):[13]

Following the general procedure, EtOAc was used to perform the extraction. After preparative TLC isolation (eluent: hexanes: EtOAc = 1:1), the product was isolated as a yellow solid (14.1 mg, 24% yield). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm): δ 8.76 (dd, *J* = 4.2 Hz, 1.7 Hz, 1H), 8.07 (dd, *J* = 8.3 Hz, 1.7 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.16 (dd, *J* = 8.1 Hz, 1.1 Hz, 1H), 6.93 (dd, *J* = 7.5 Hz, 1.2 Hz, 1H), 5.00 (br, 2H); ^{13}C NMR: (125 MHz, $CDCl_3$, ppm): δ 147.6, 144.1, 138.6, 136.1, 129.0, 127.5, 121.5, 116.2, 110.2; EI-MS (*m/z*): 144.0

VII. References

[1] M. Huang, J. Hou, R. Yang, L. Zhang, X. Zhu, Y. Wan, *Synthesis* **2014**, *46*, 3356.
[2] R. Green, J.F. Hartwig, *Angew. Chem., Int. Ed.* **2015,** *54*, 3768.
[3] X. Jin, Y. Koizumi, K. Yamaguchi, K. Nozaki, N. Mizuno, *J. Am. Chem. Soc.* **2017**, *139*, 13821.
[4] Q. Shen, J. Hartwig, *J. Am. Chem. Soc.* **2006**, *128*, 10028.
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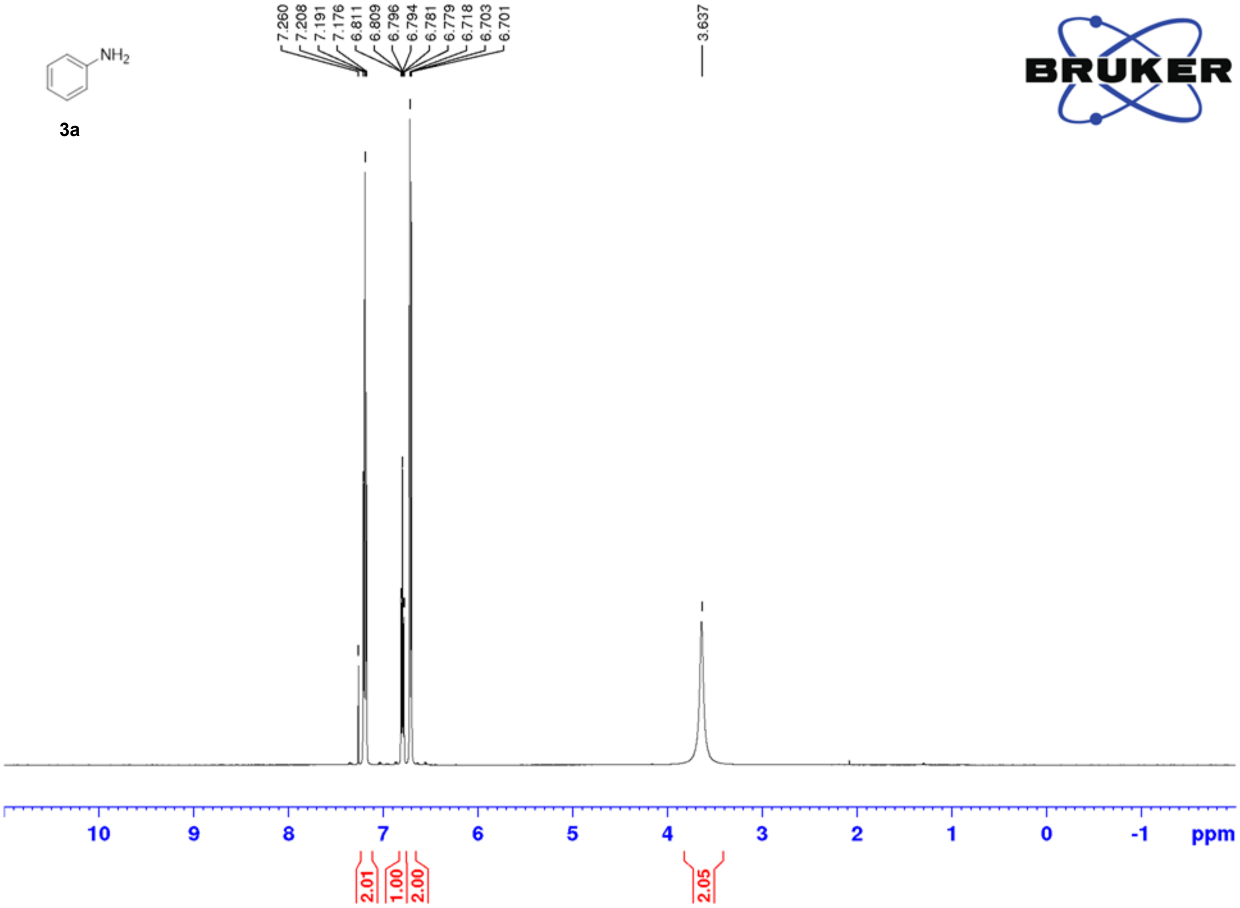
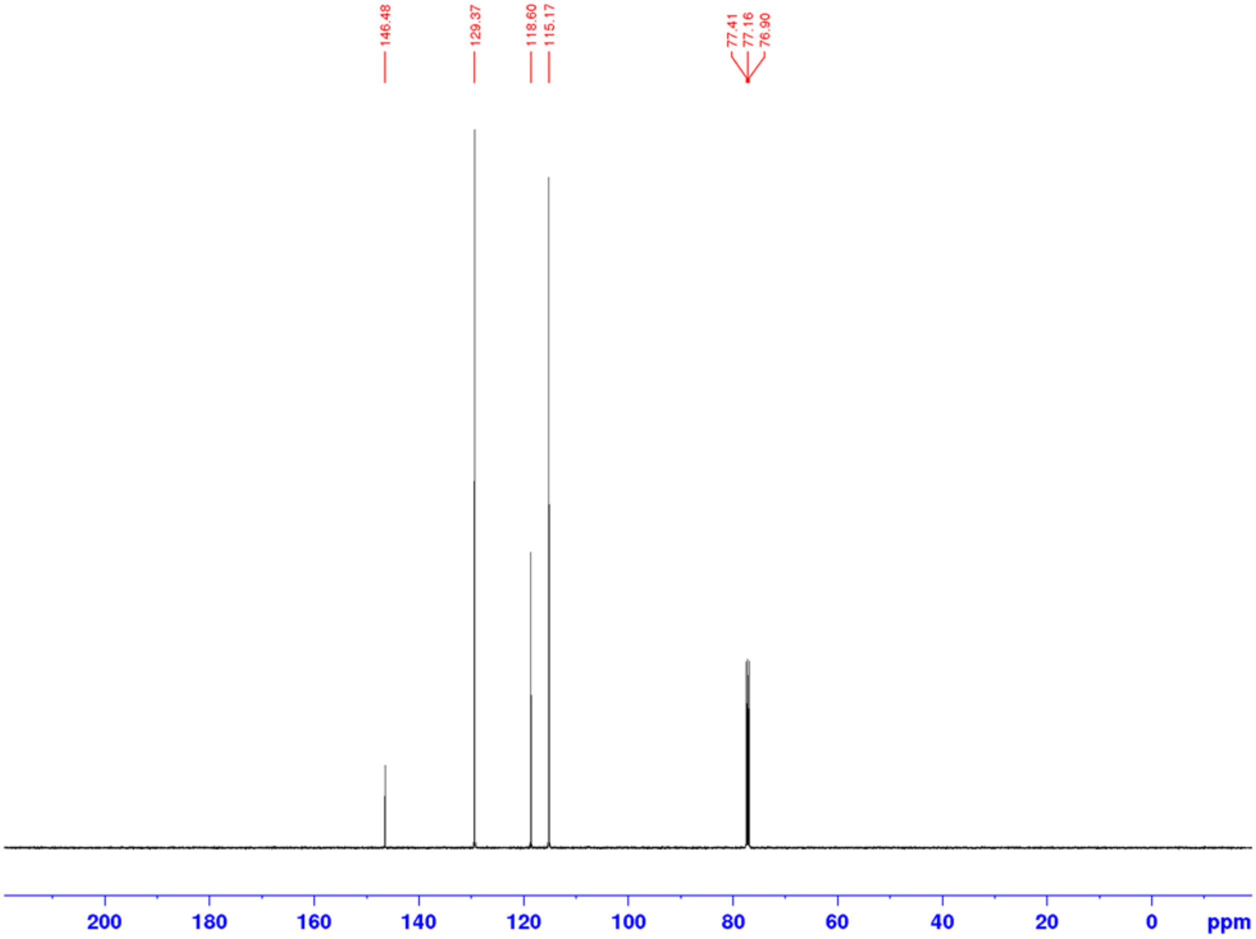
VIII. NMR Spectra of Products

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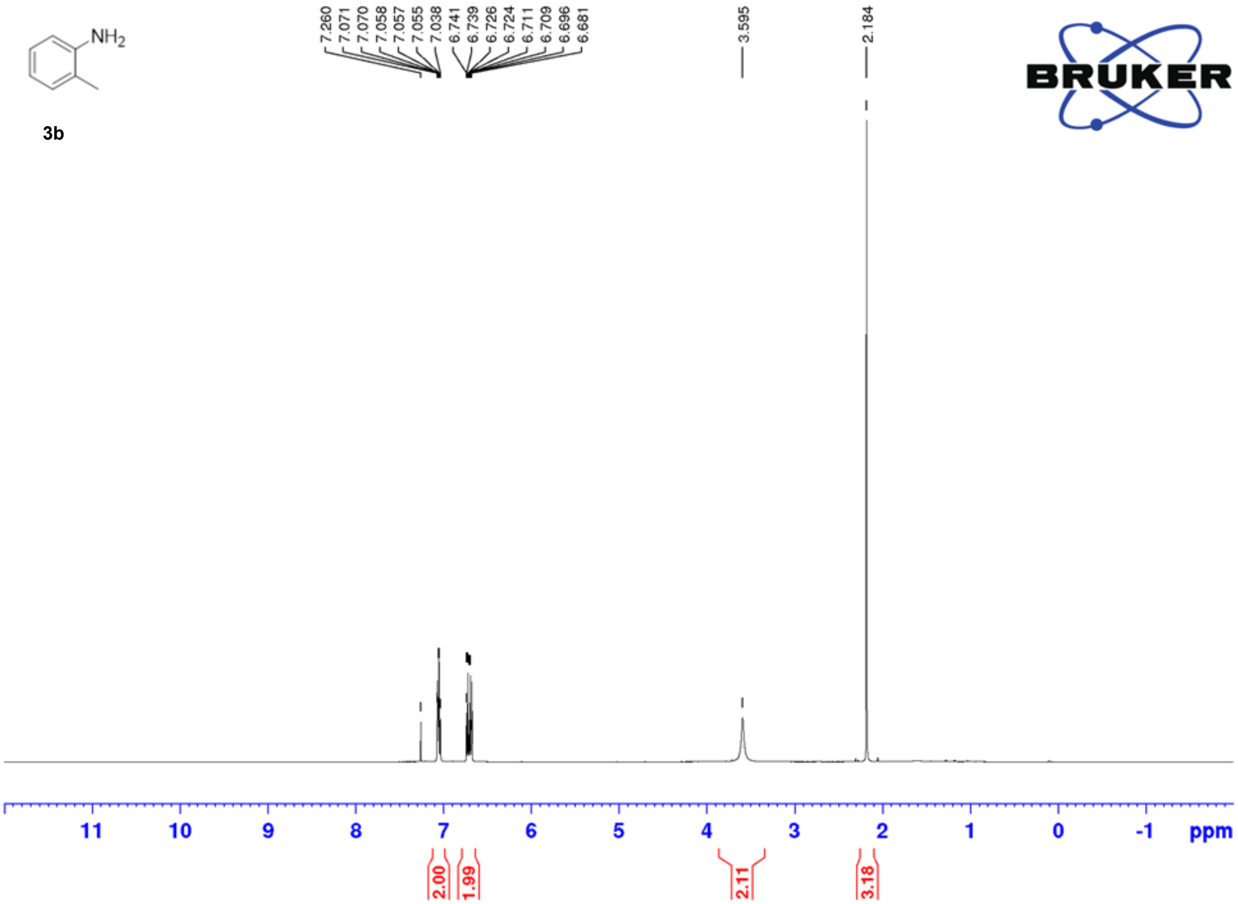

3b

NH2
7.260
7.071
7.070
7.058
7.057
7.055
7.038
6.741
6.739
6.726
6.724
6.711
6.709
6.696
6.681
3.595
2.184
11
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6
5
4
3
2
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-1
ppm
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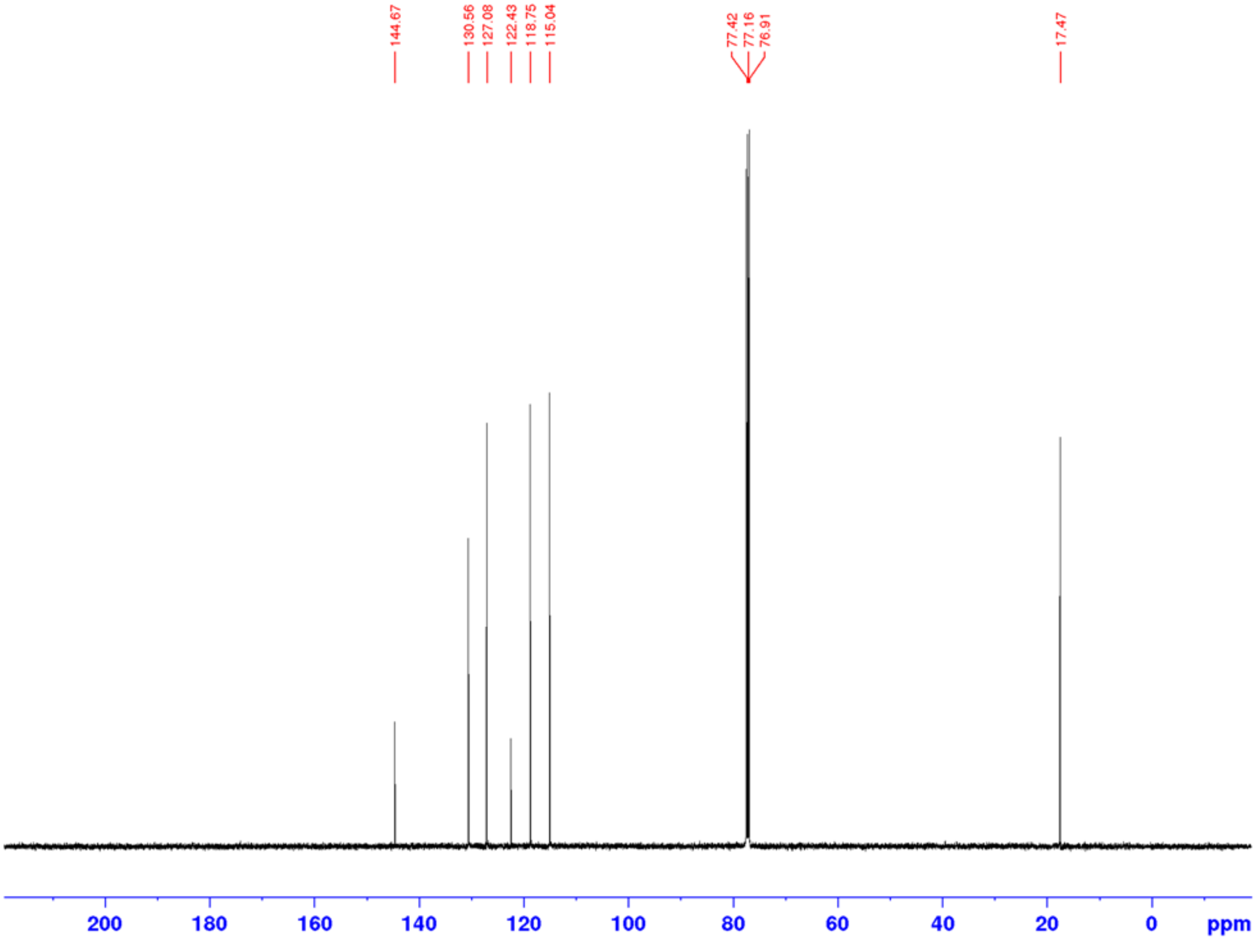
1.99
2.11
3.18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118.75
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120
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0
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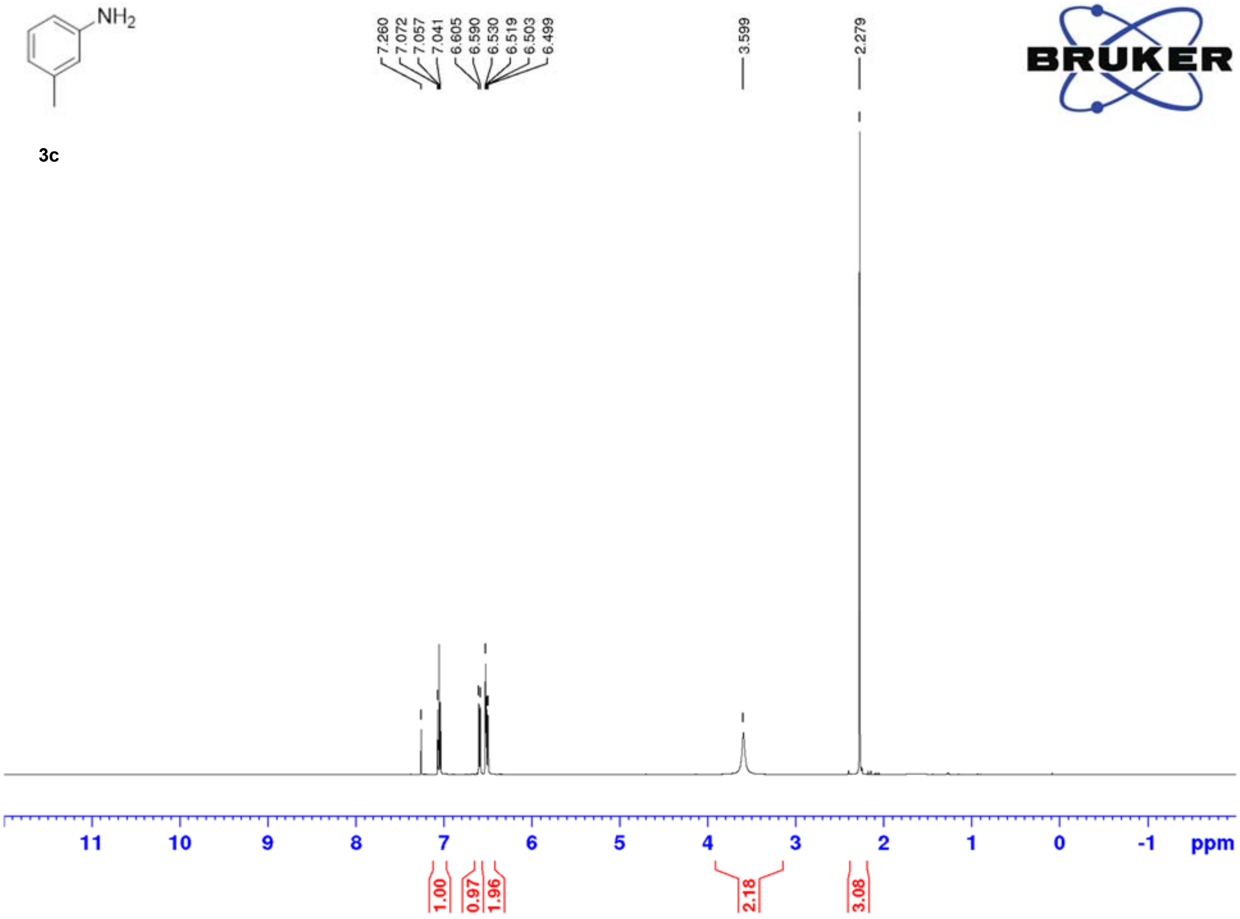
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6.499
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2.279
11
10
9
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0.97
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2.18
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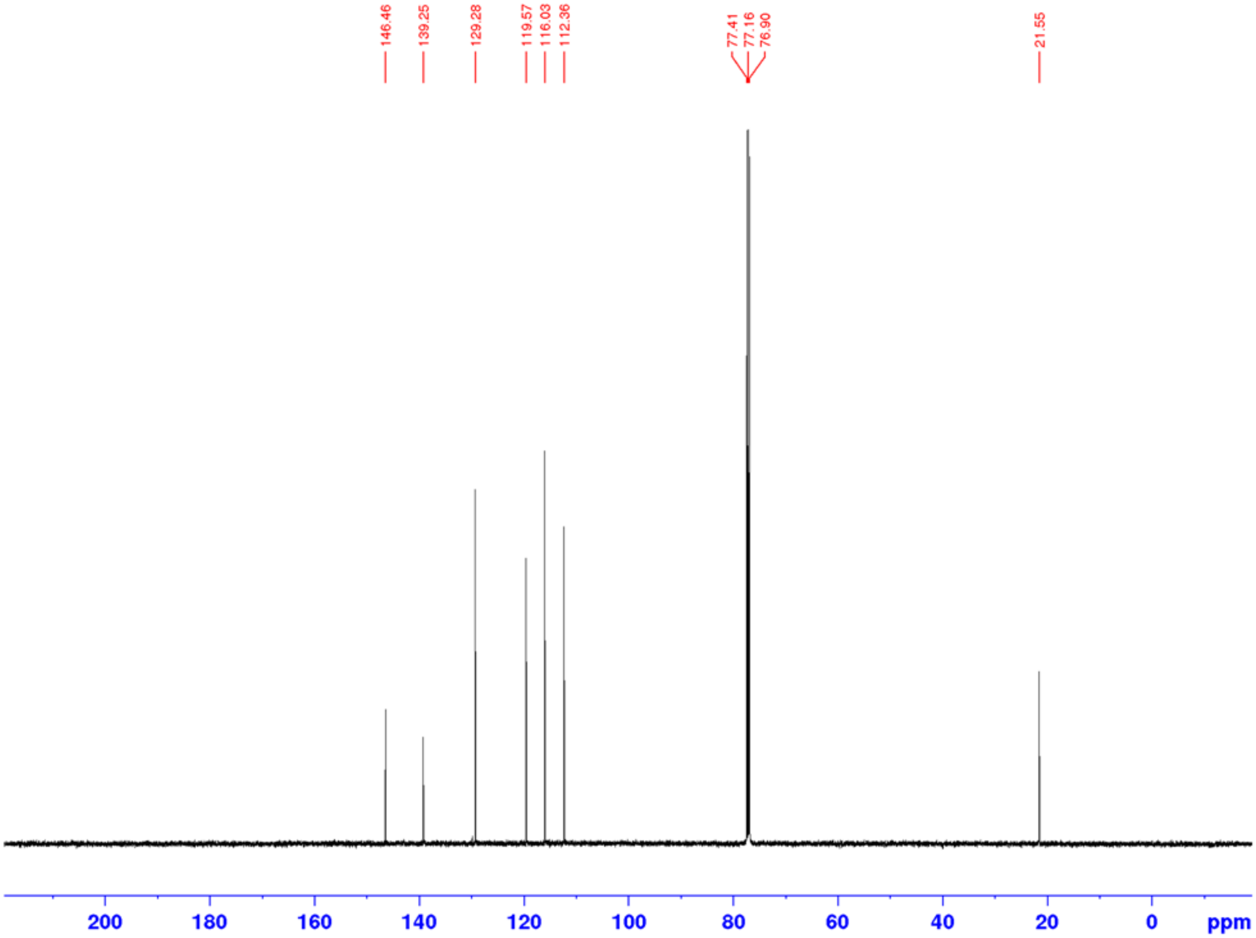
3c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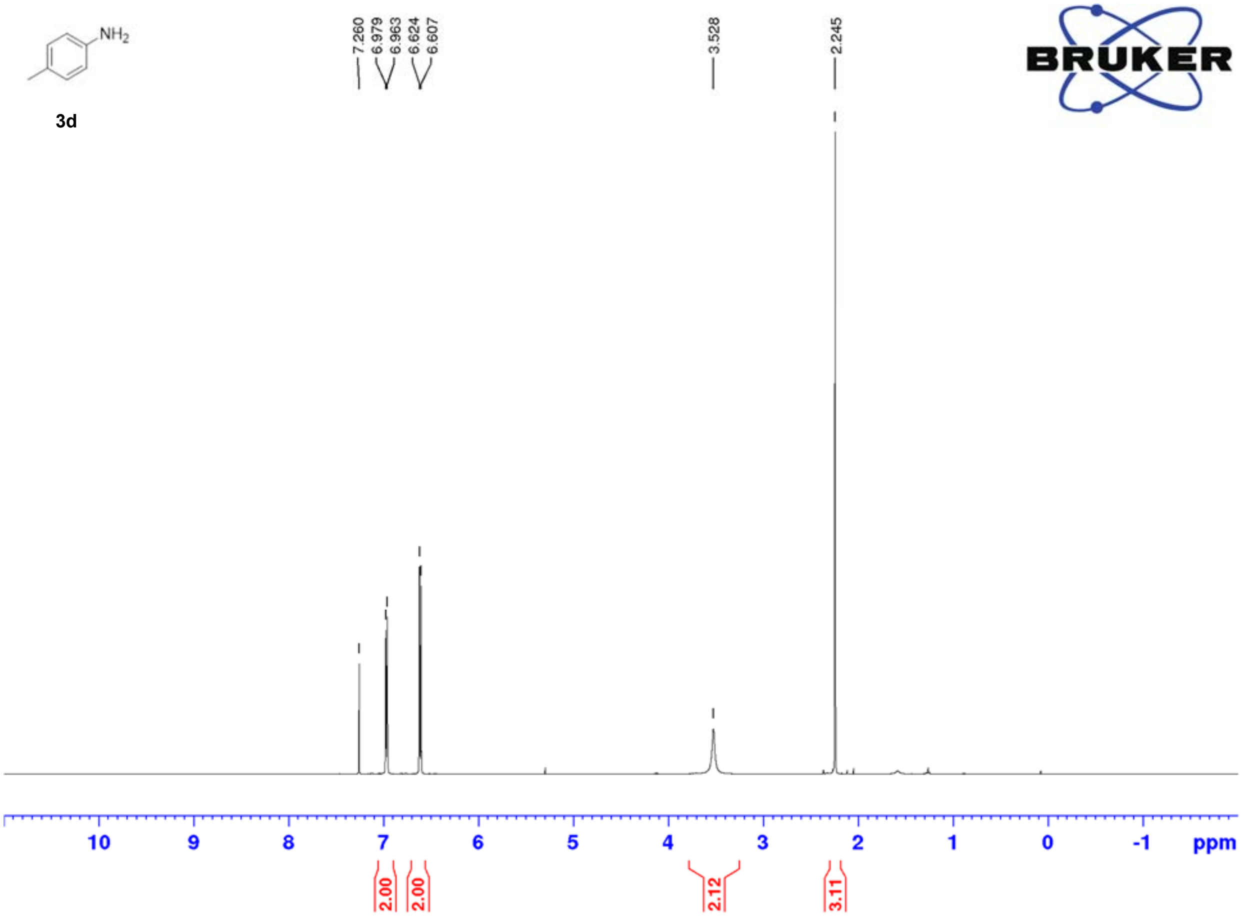

3d

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6.624
6.607
3.528
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BRUKER
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6
5
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ppm
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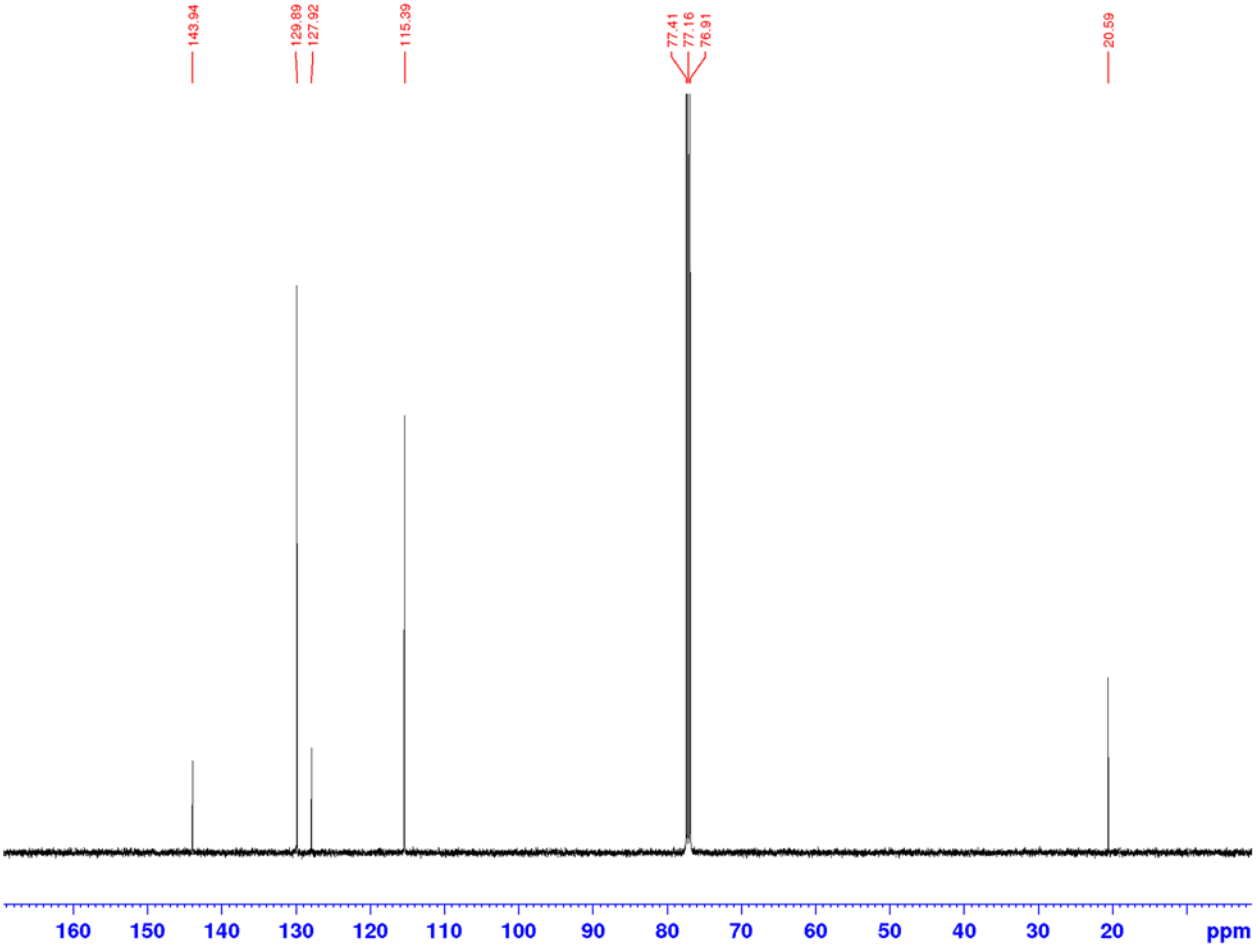
2.00
2.12
3.11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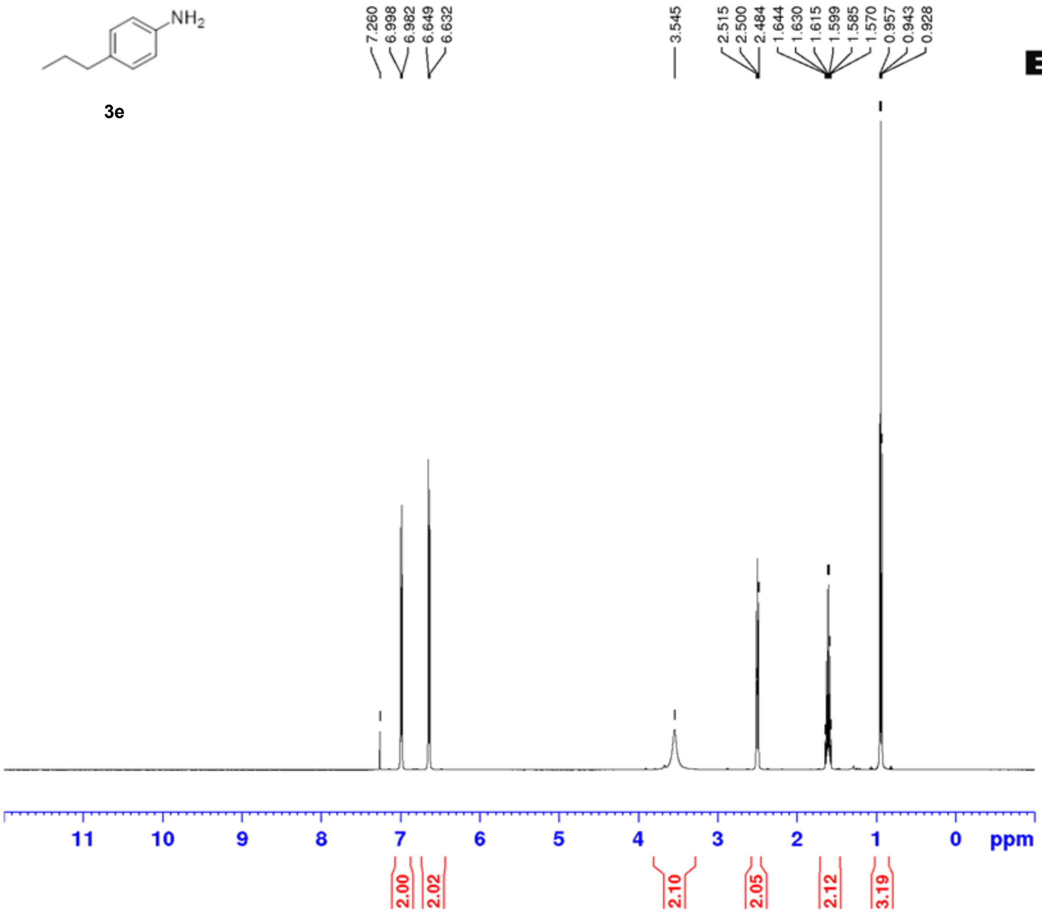
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2.500
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1.630
1.615
1.599
1.585
1.570
0.957
0.943
0.928
11
10
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4
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2.02
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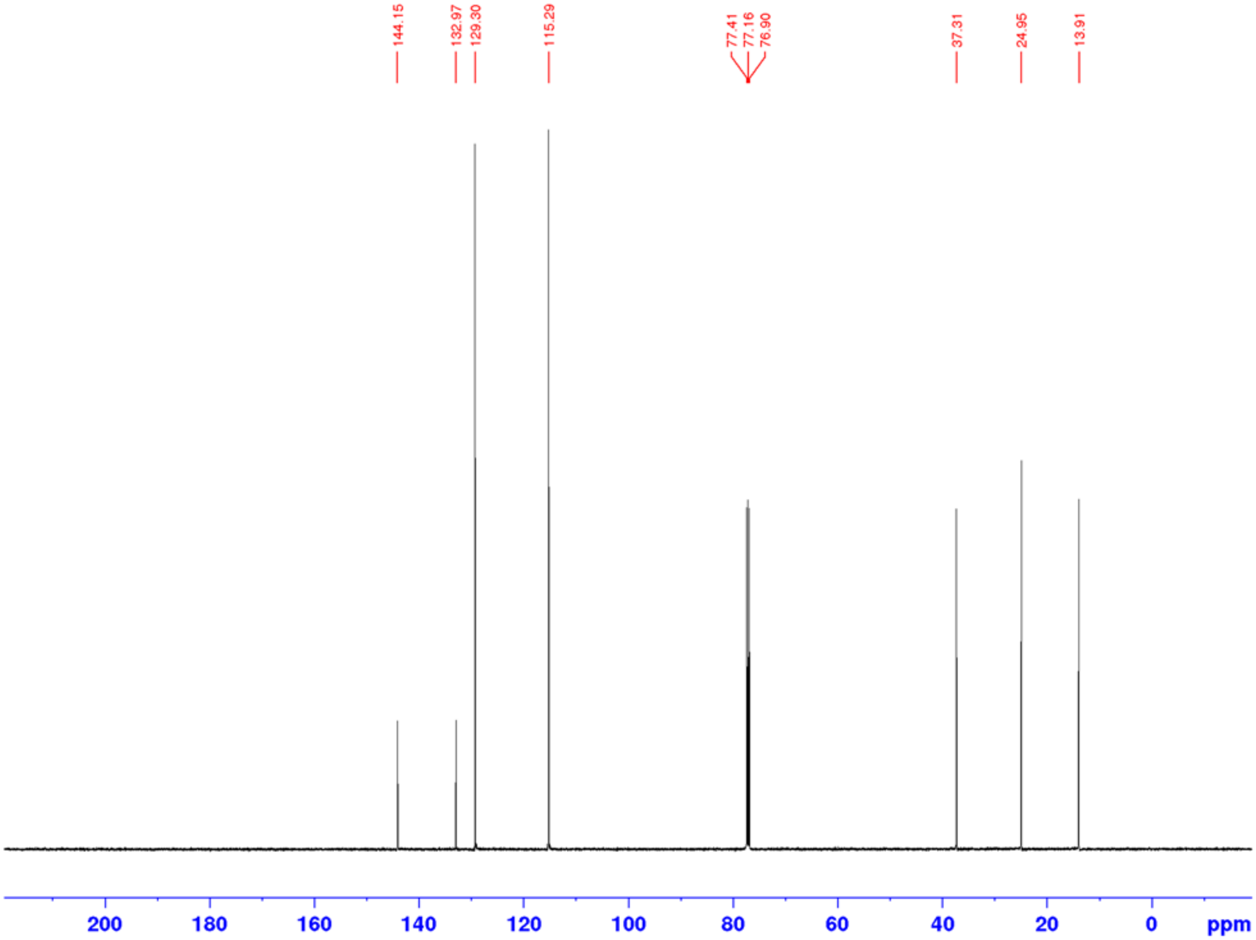
2.12
3.19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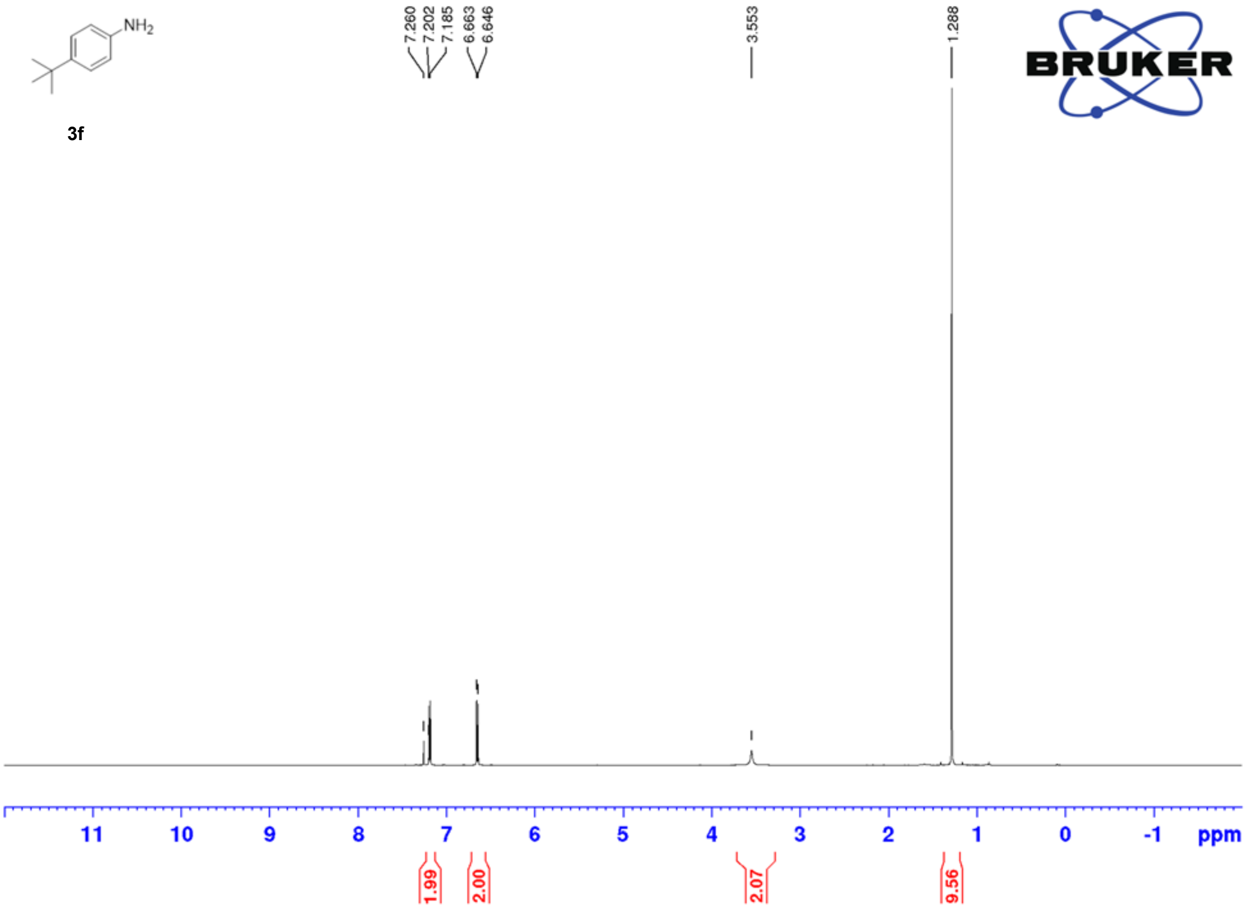
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1.288
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11
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5
4
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ppm
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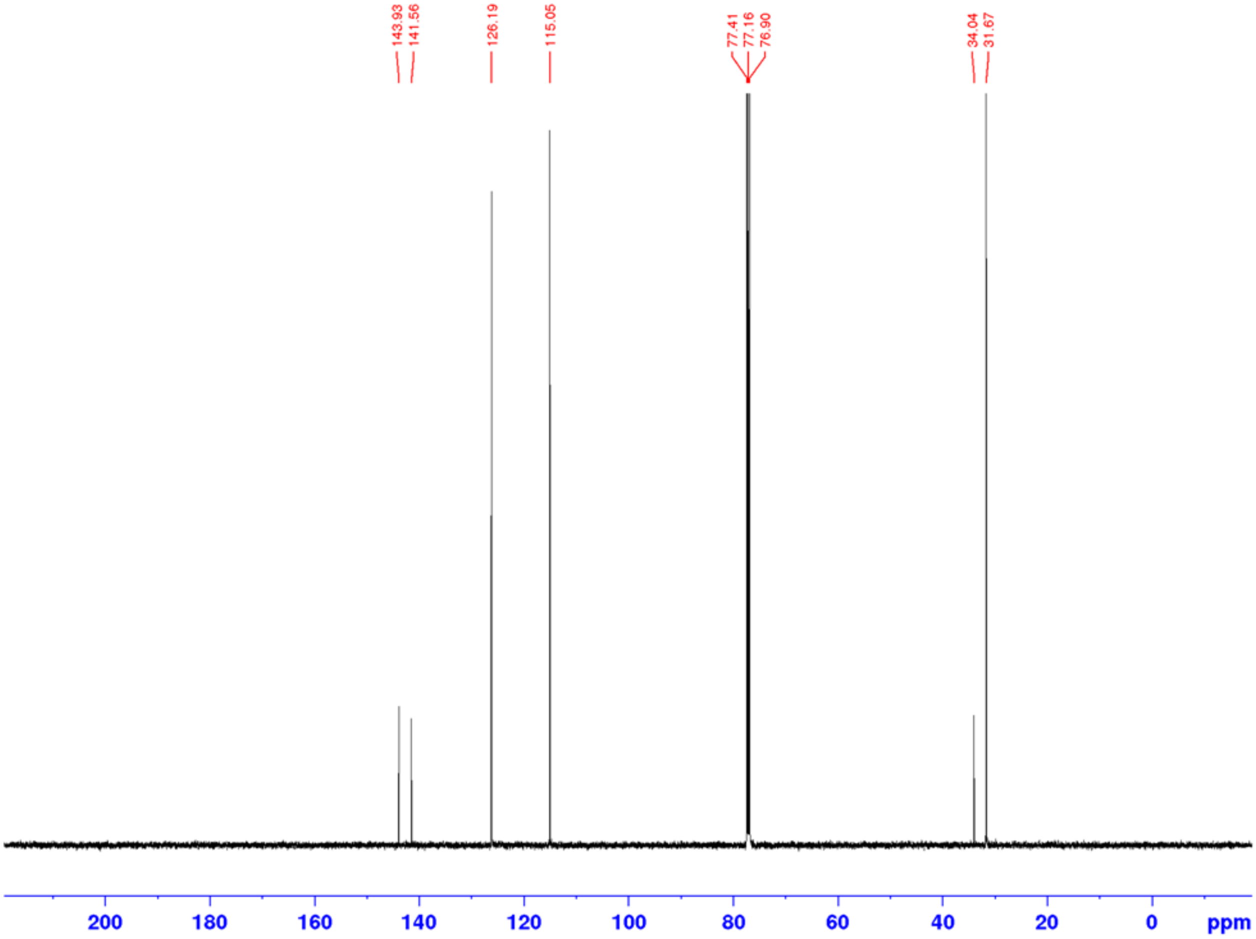
2.07
9.56

3f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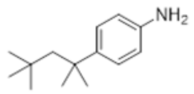
NH2

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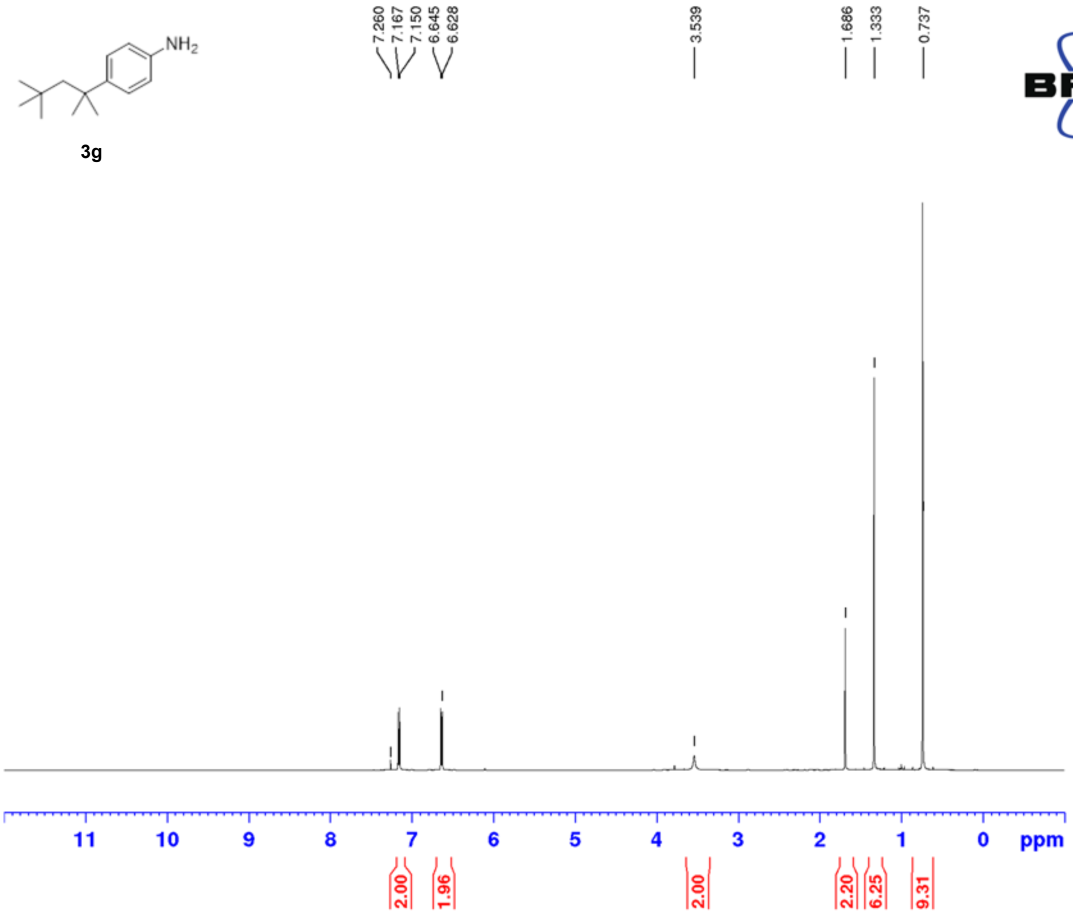
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4
3
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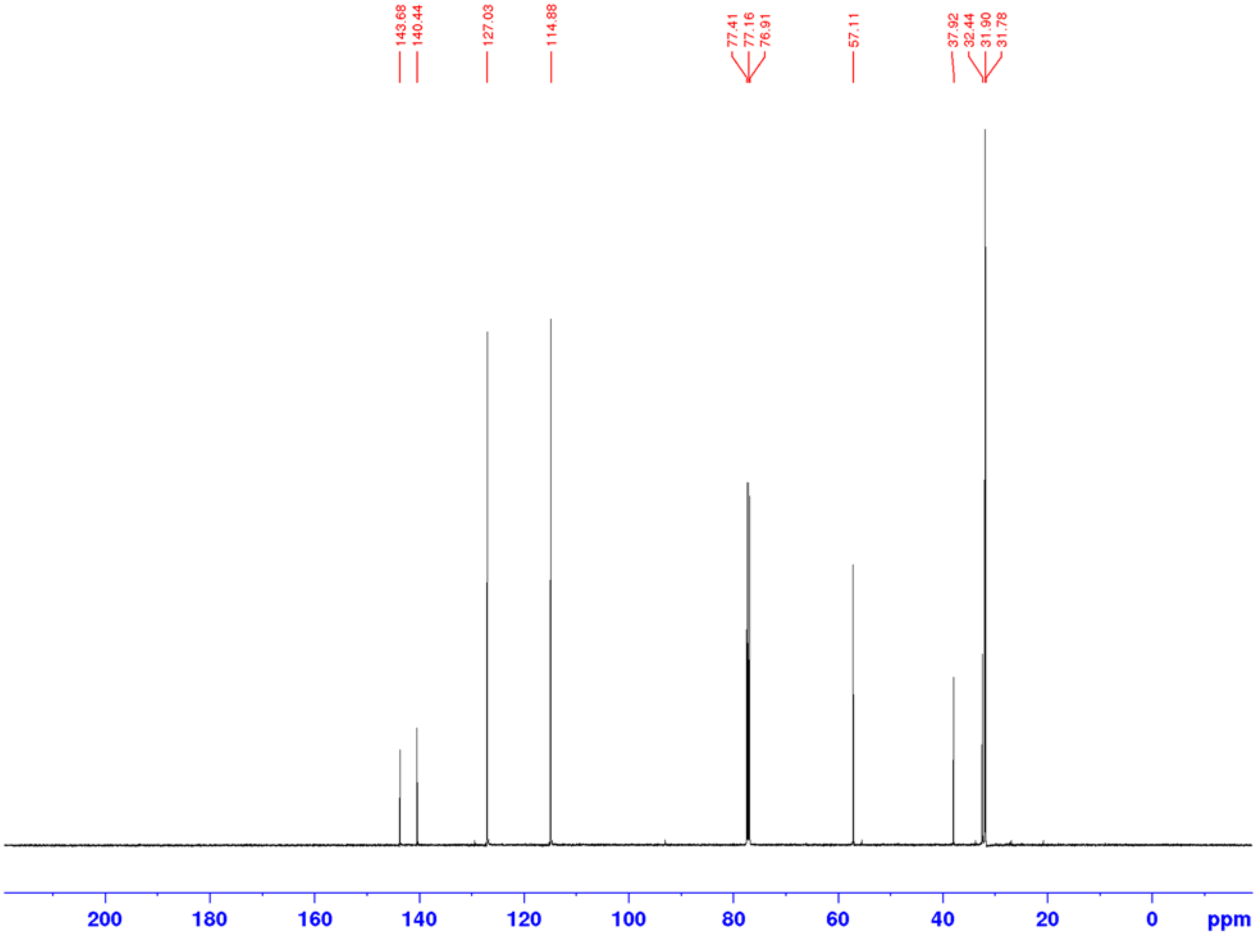
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40
20
0
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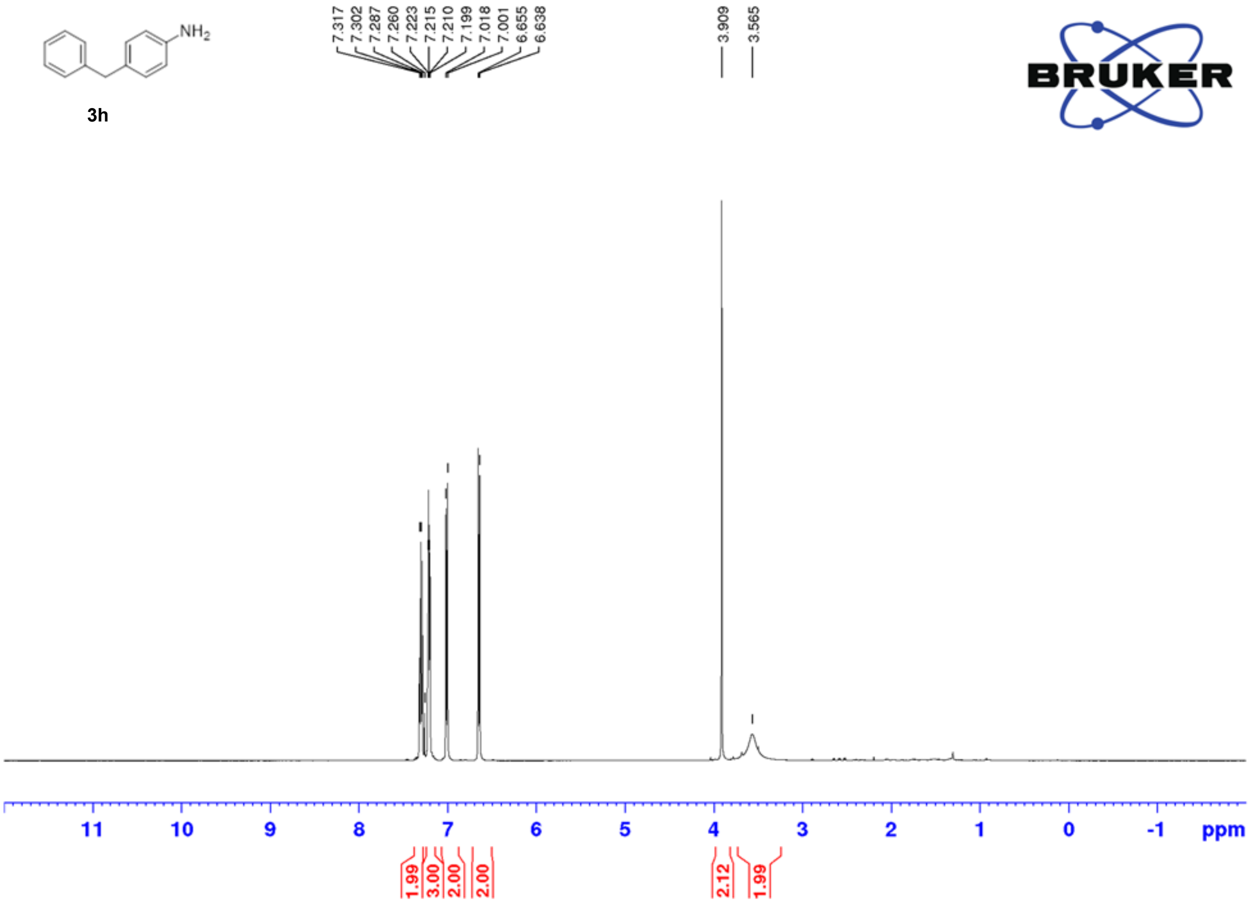
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6.655
6.638
3.909
3.565
11
10
9
8
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2
1
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-1
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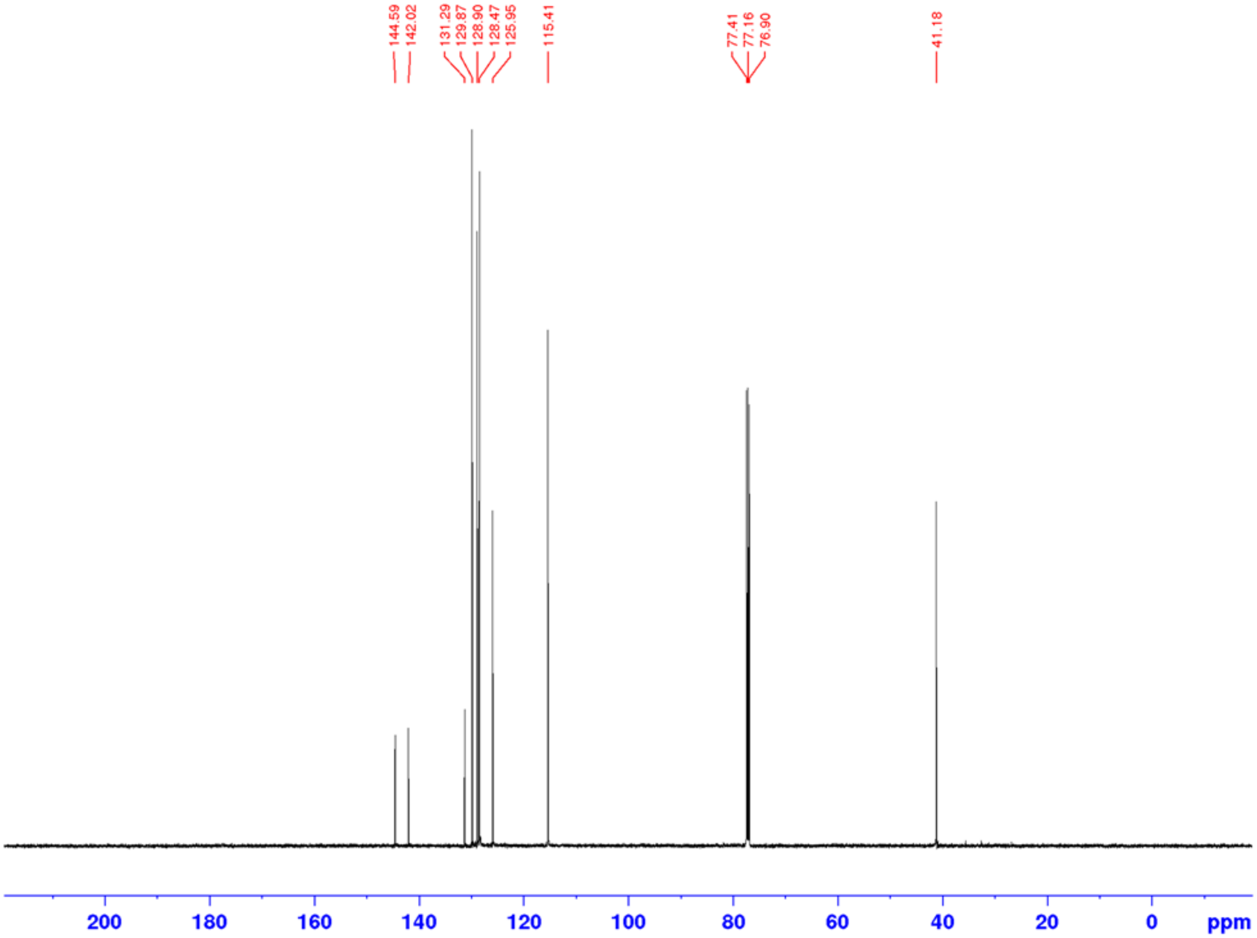
3.00
2.00
2.00
2.12
1.99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120
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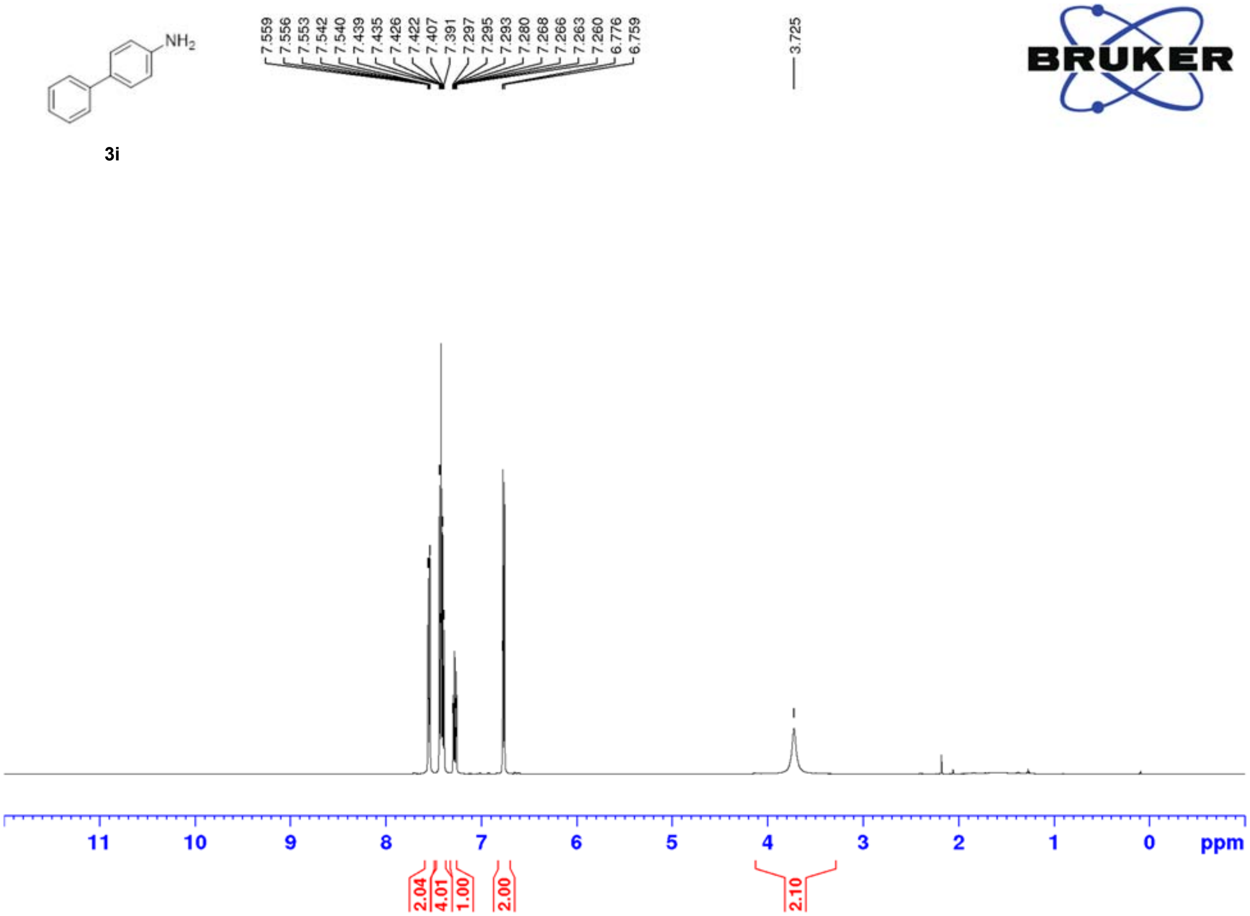

3i

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7.391
7.297
7.295
7.293
7.280
7.268
7.266
7.263
7.260
6.776
6.759
3.725
11
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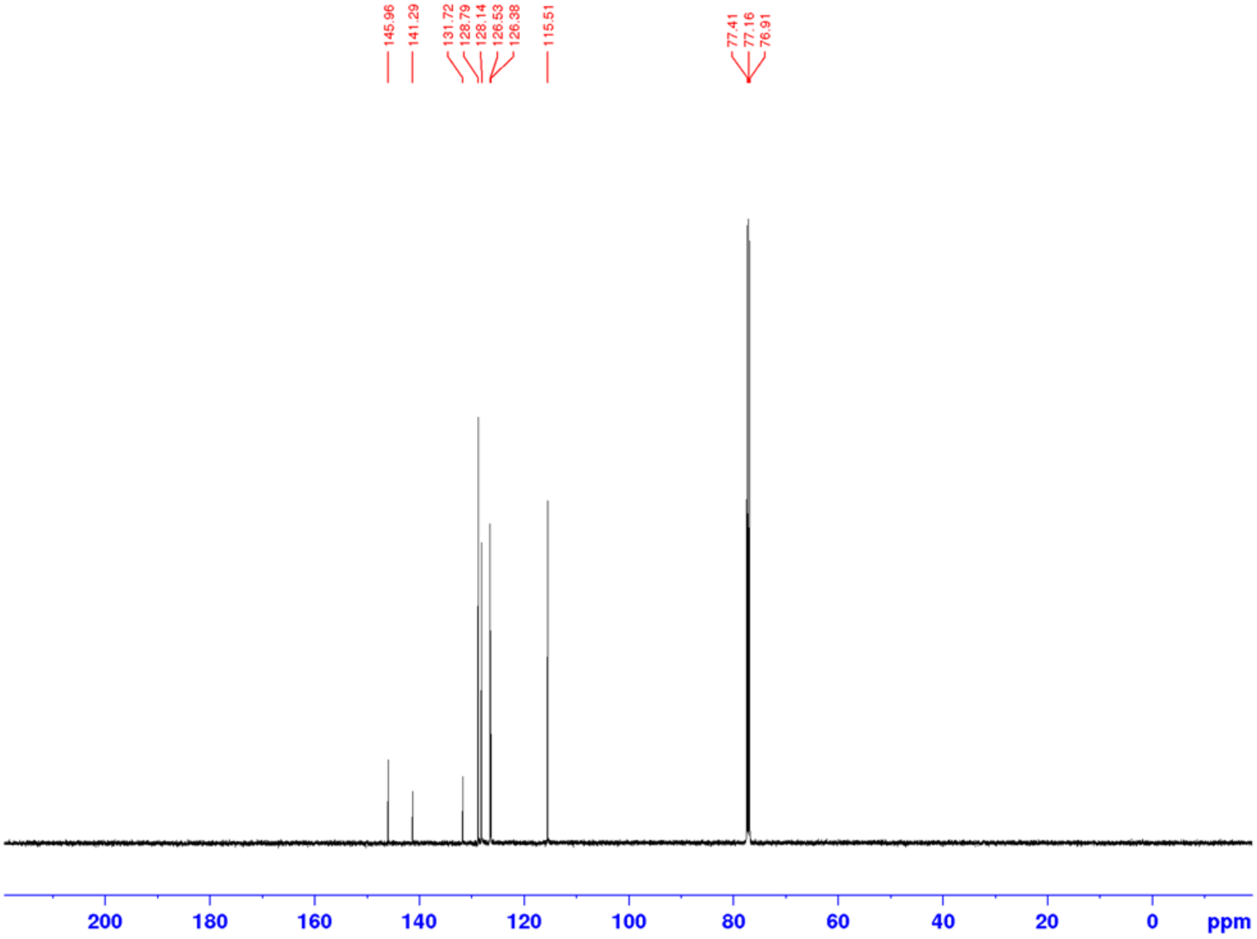
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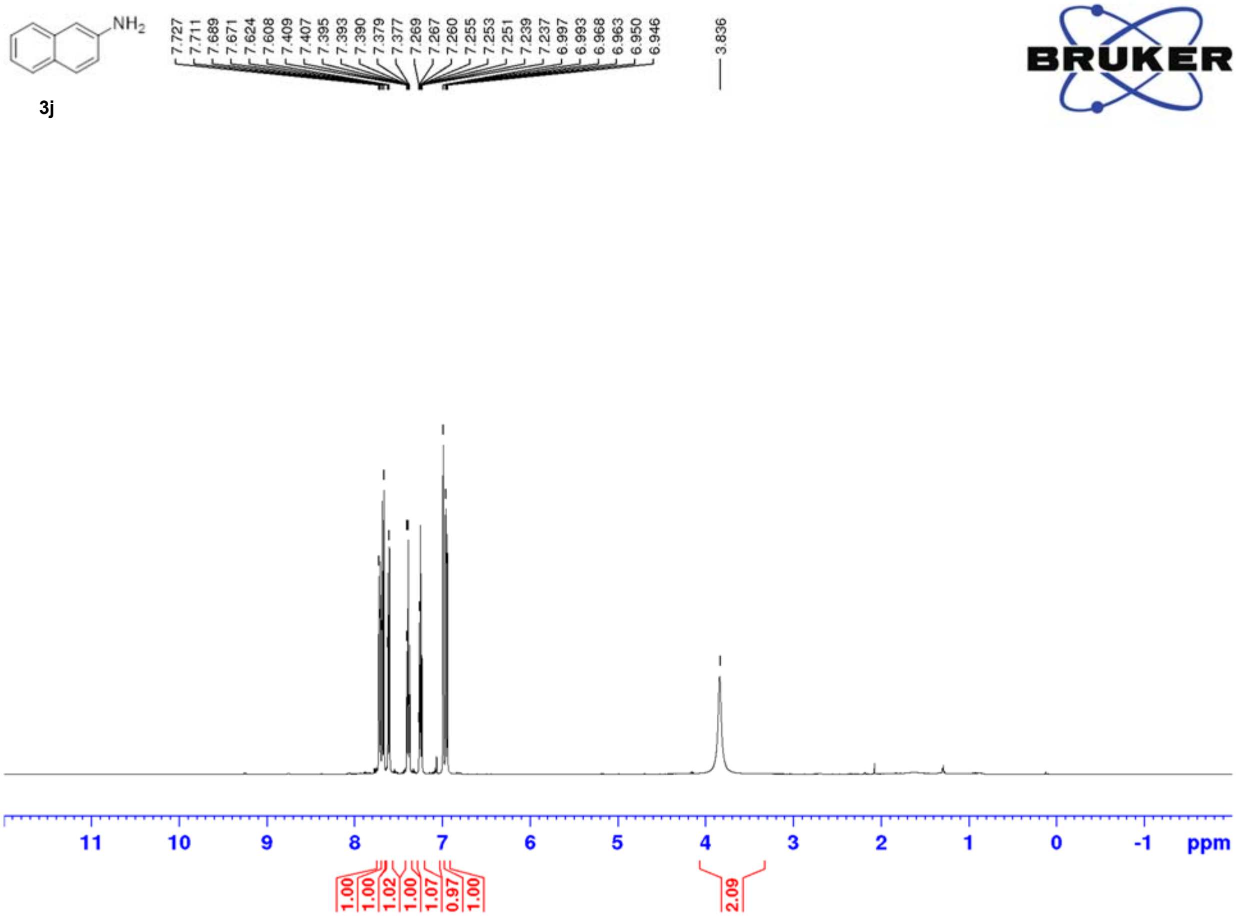
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7.379
7.377
7.269
7.267
7.260
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7.253
7.251
7.239
7.237
6.997
6.993
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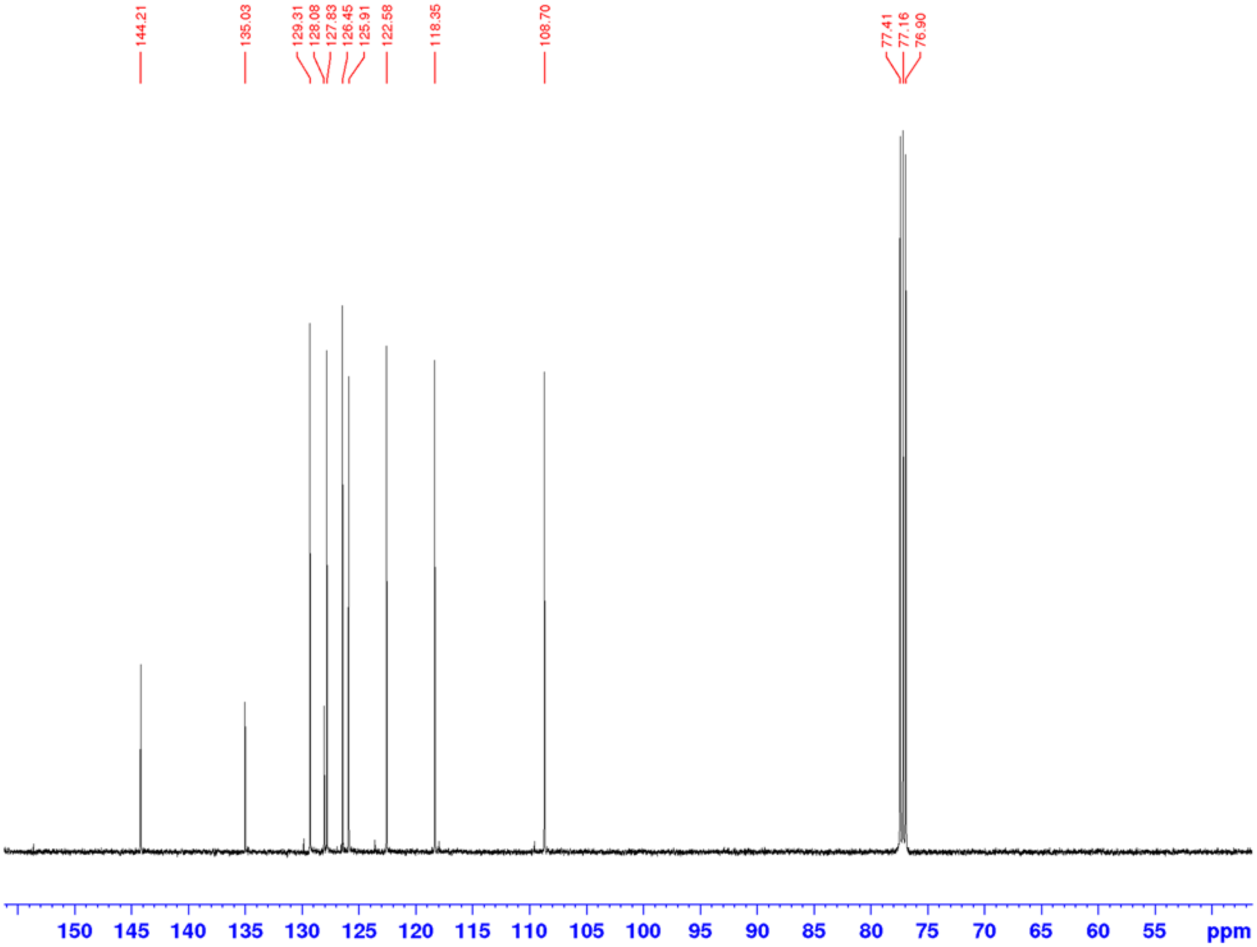
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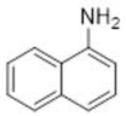
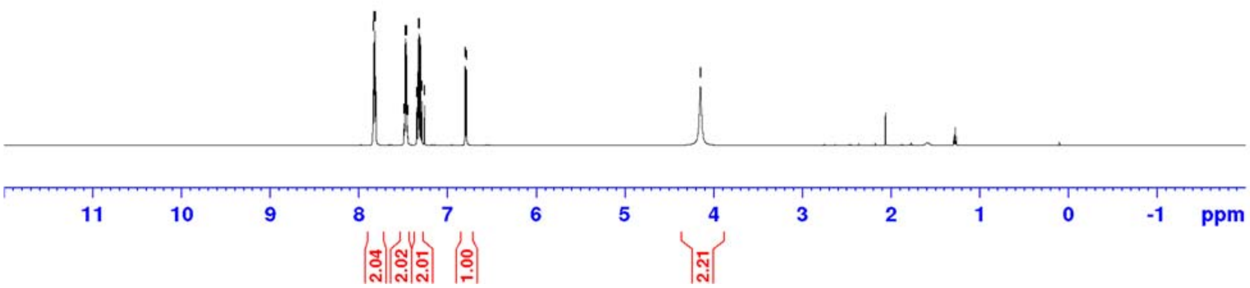


3k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6.803
6.800
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6.786
4.148
11
10
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4
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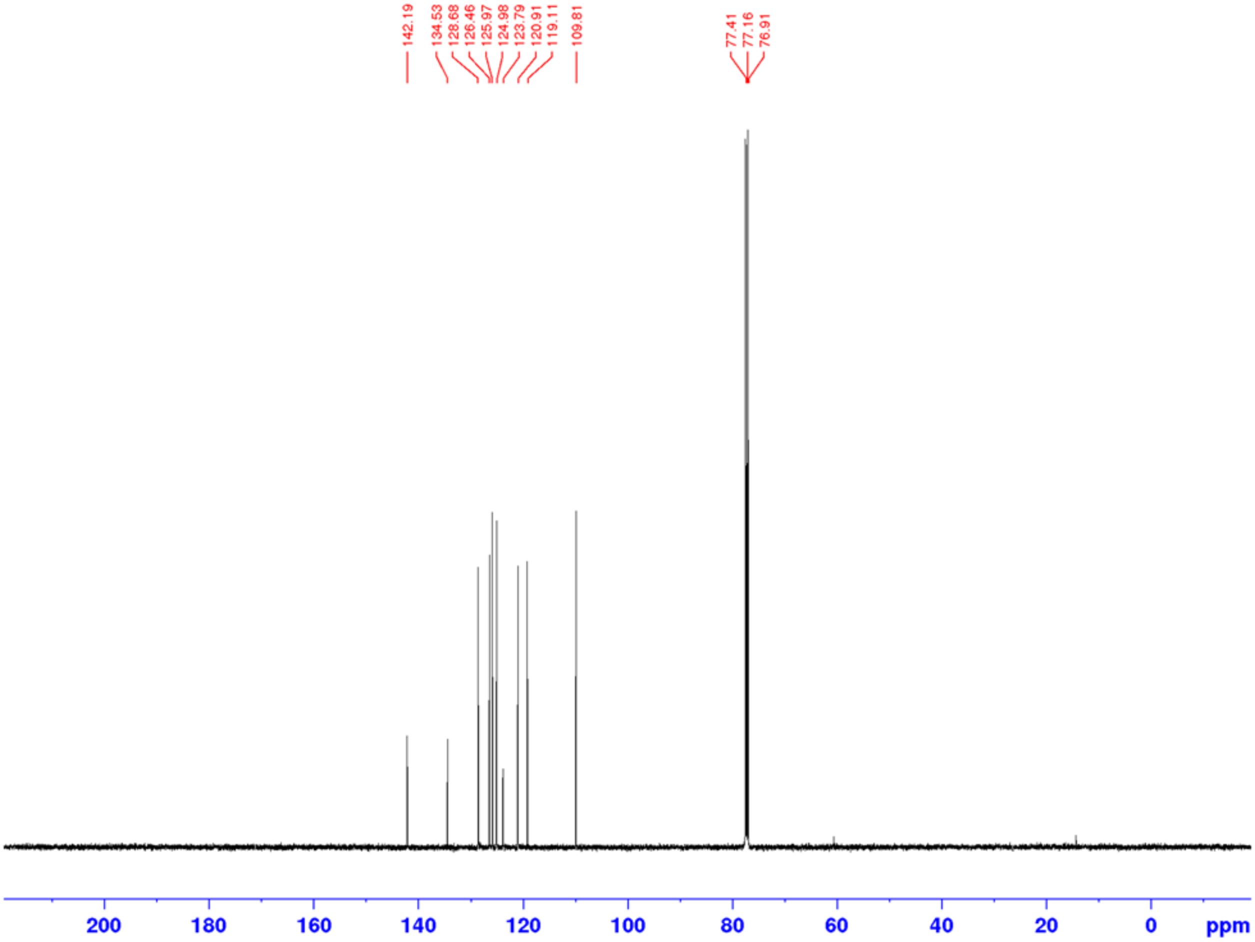
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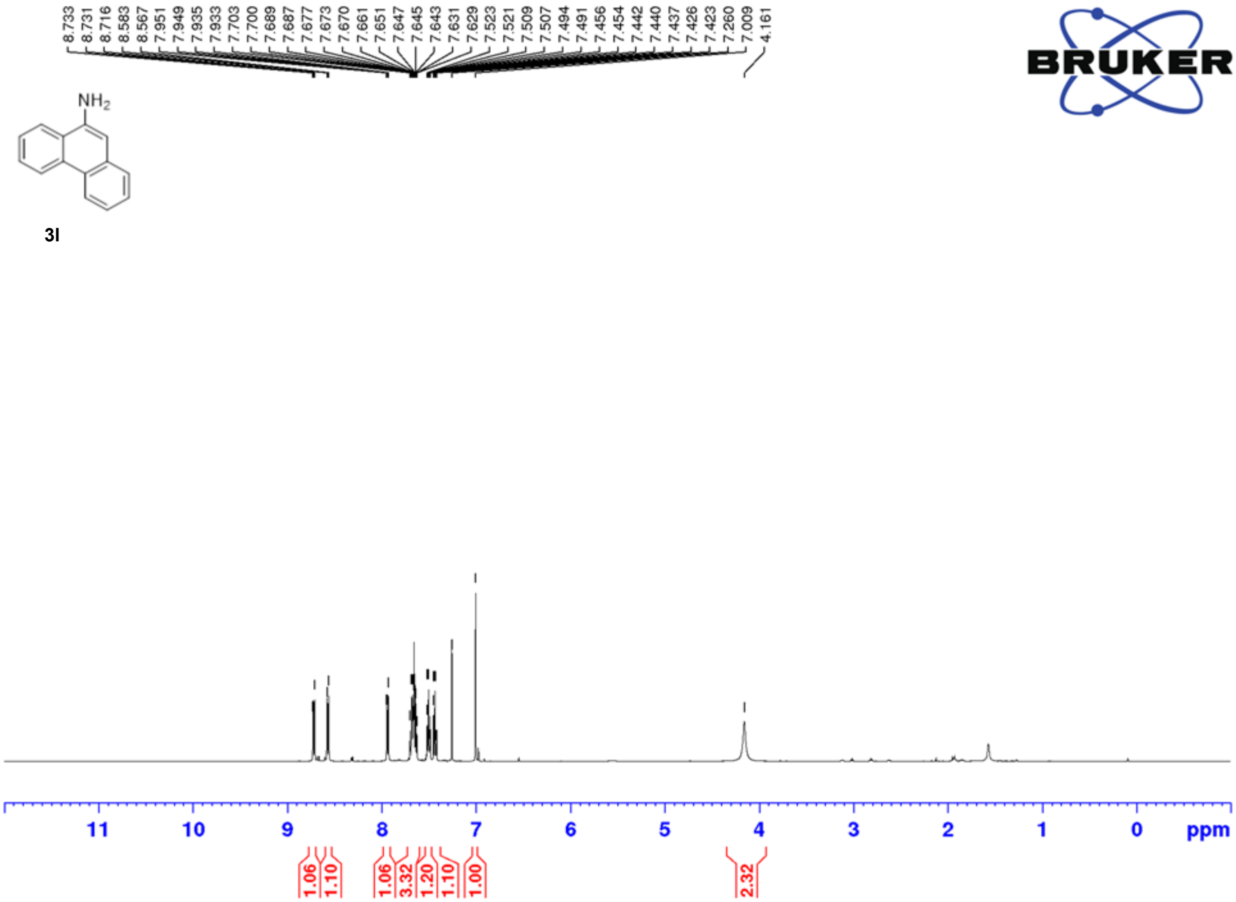
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7.437
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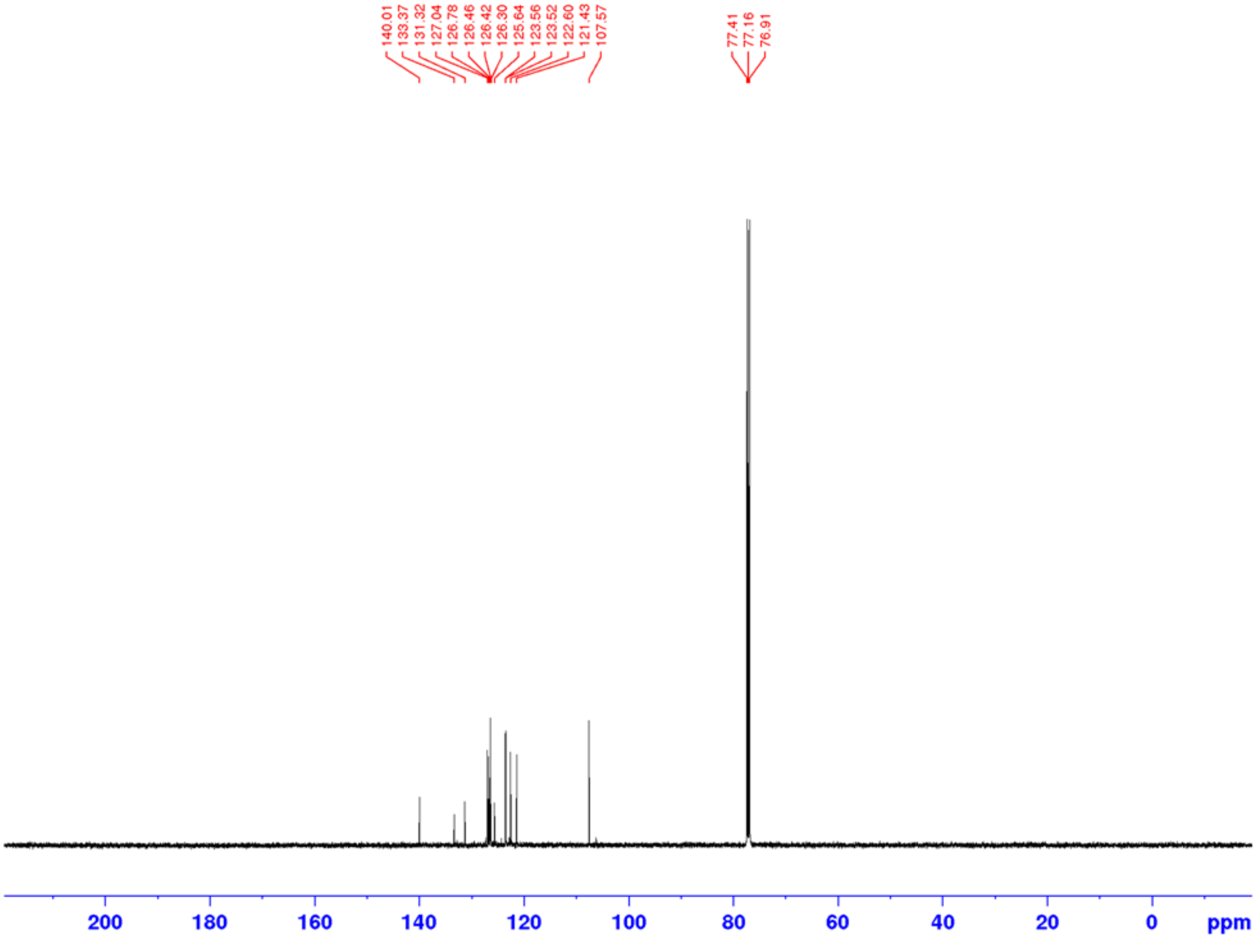
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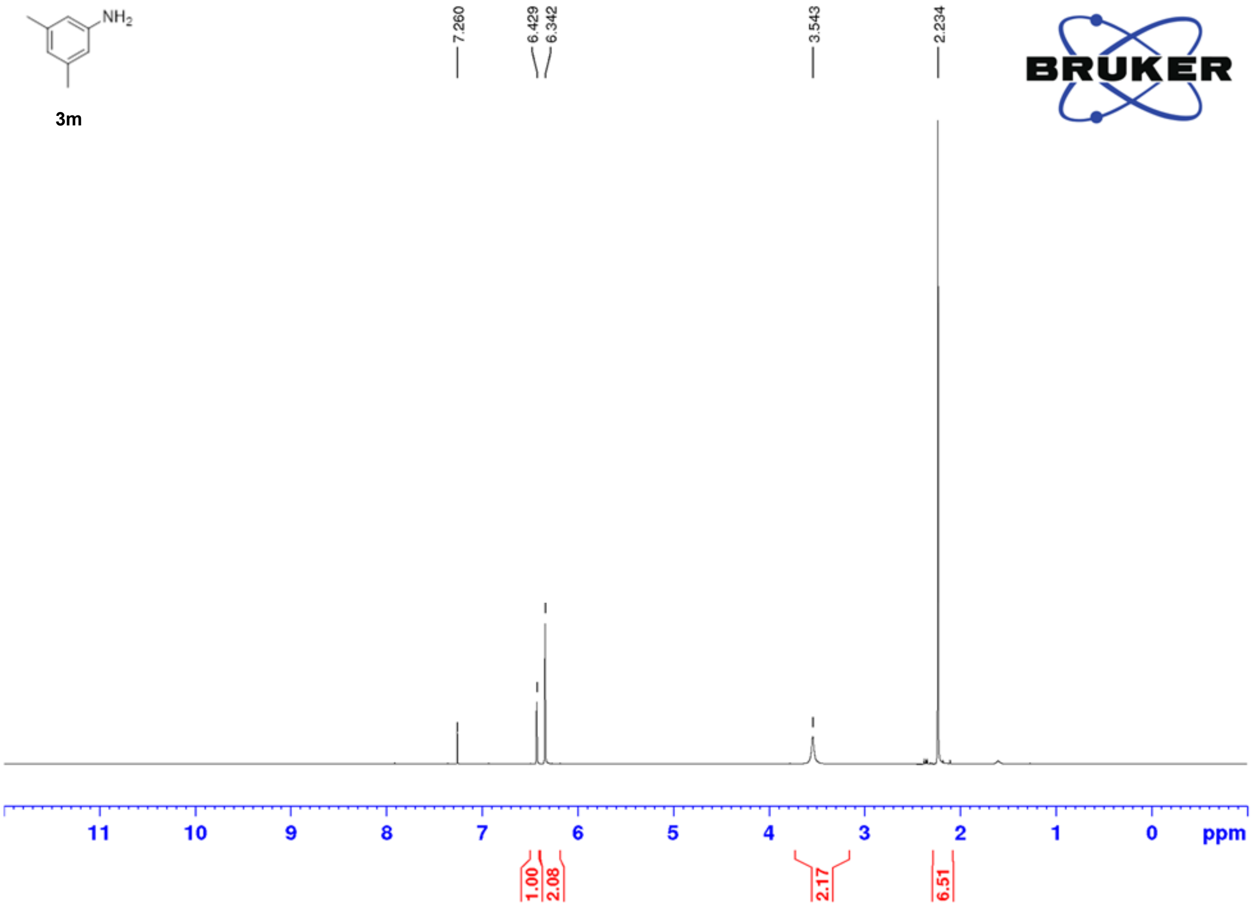
3m

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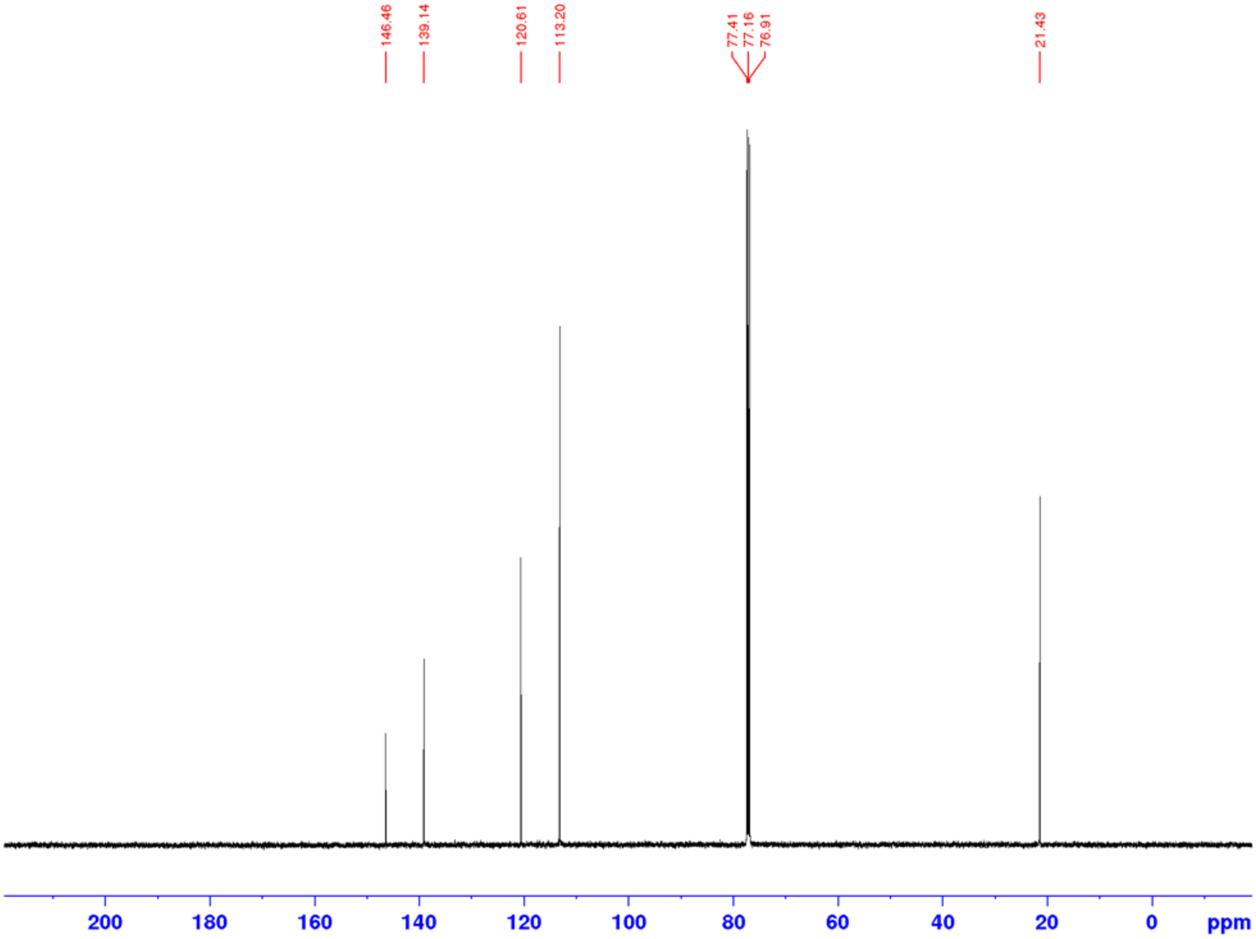
6.51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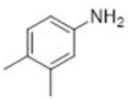
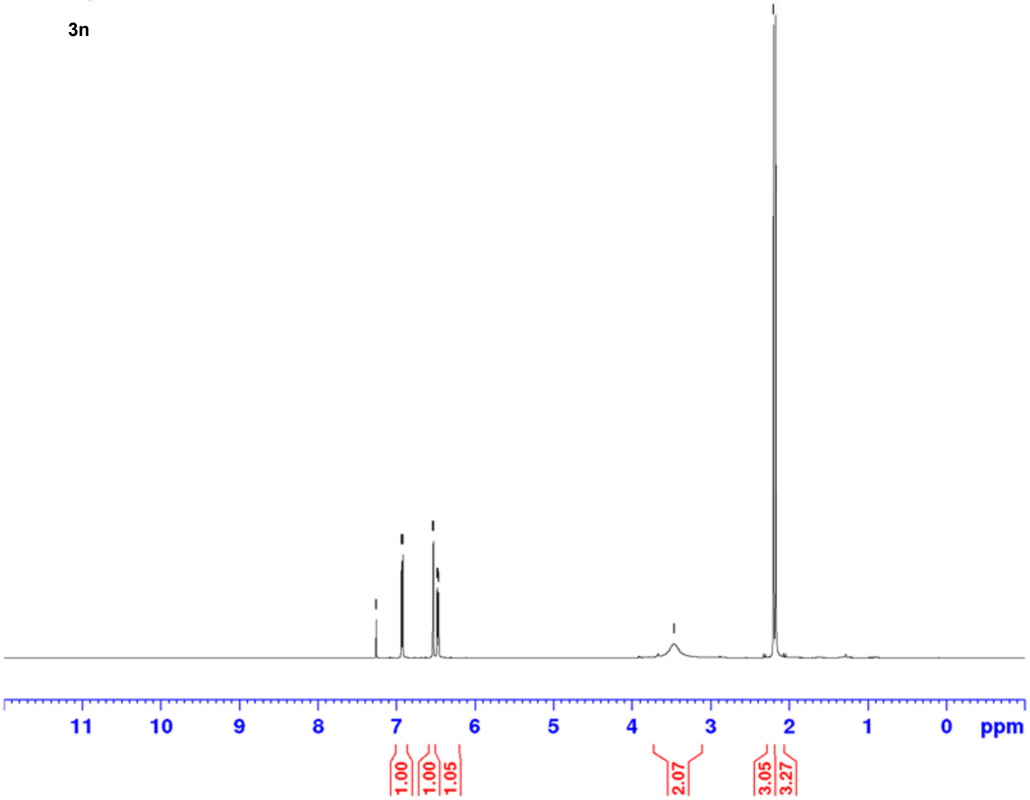

NH2

3n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11
10
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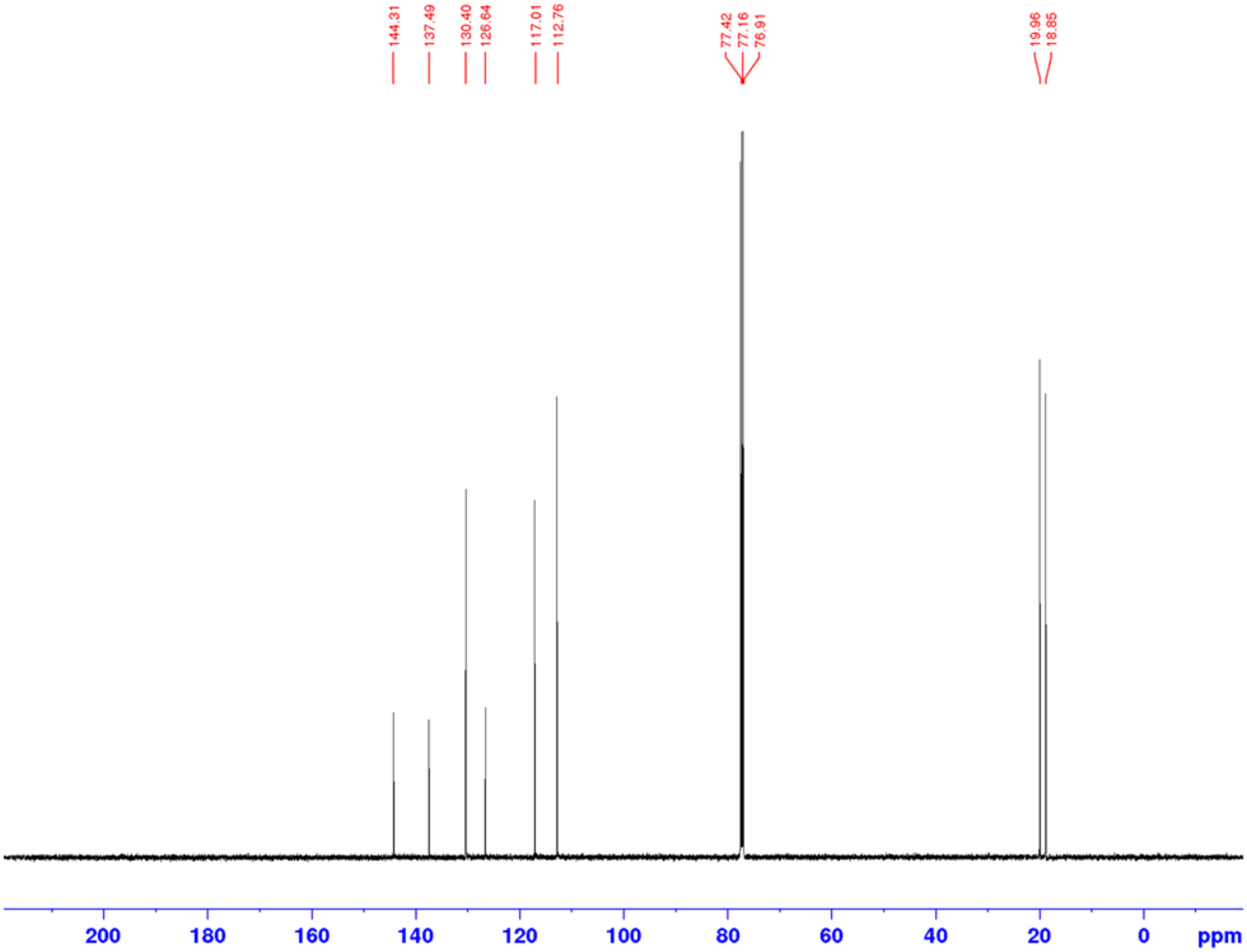
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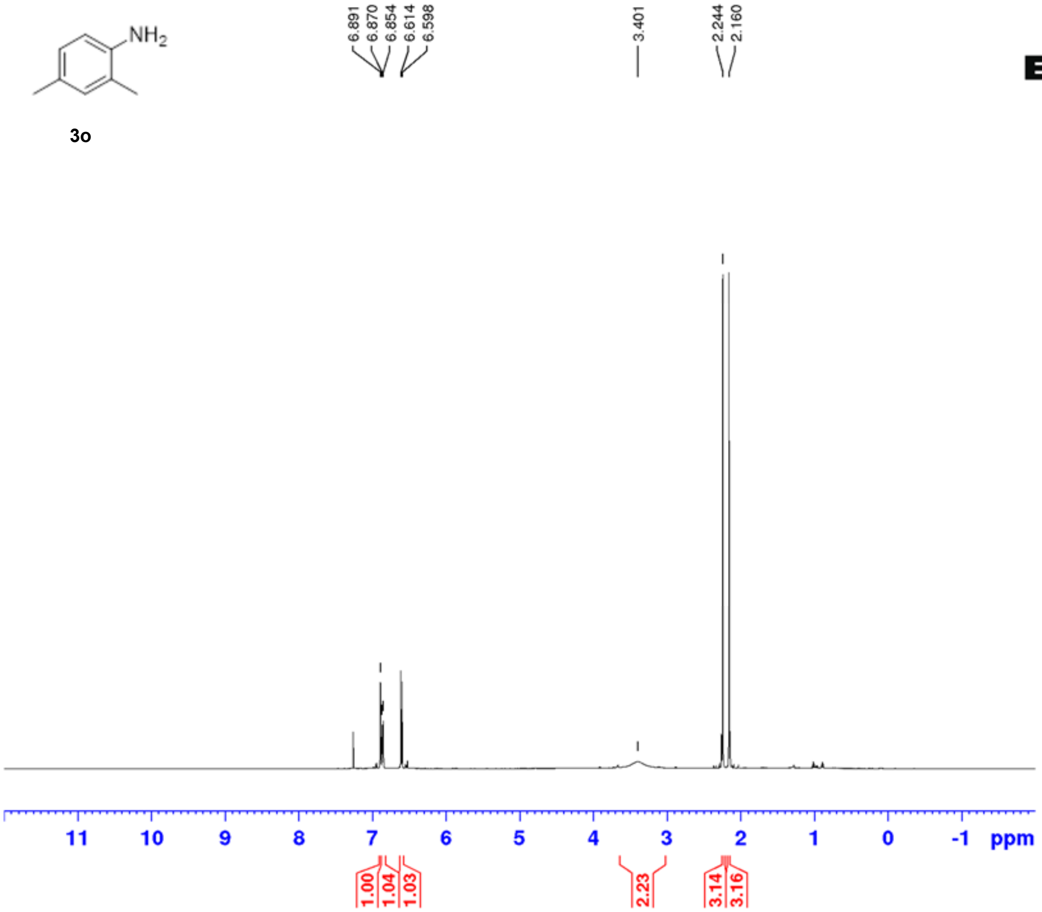
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10
9
8
7
6
5
4
3
2
1
0
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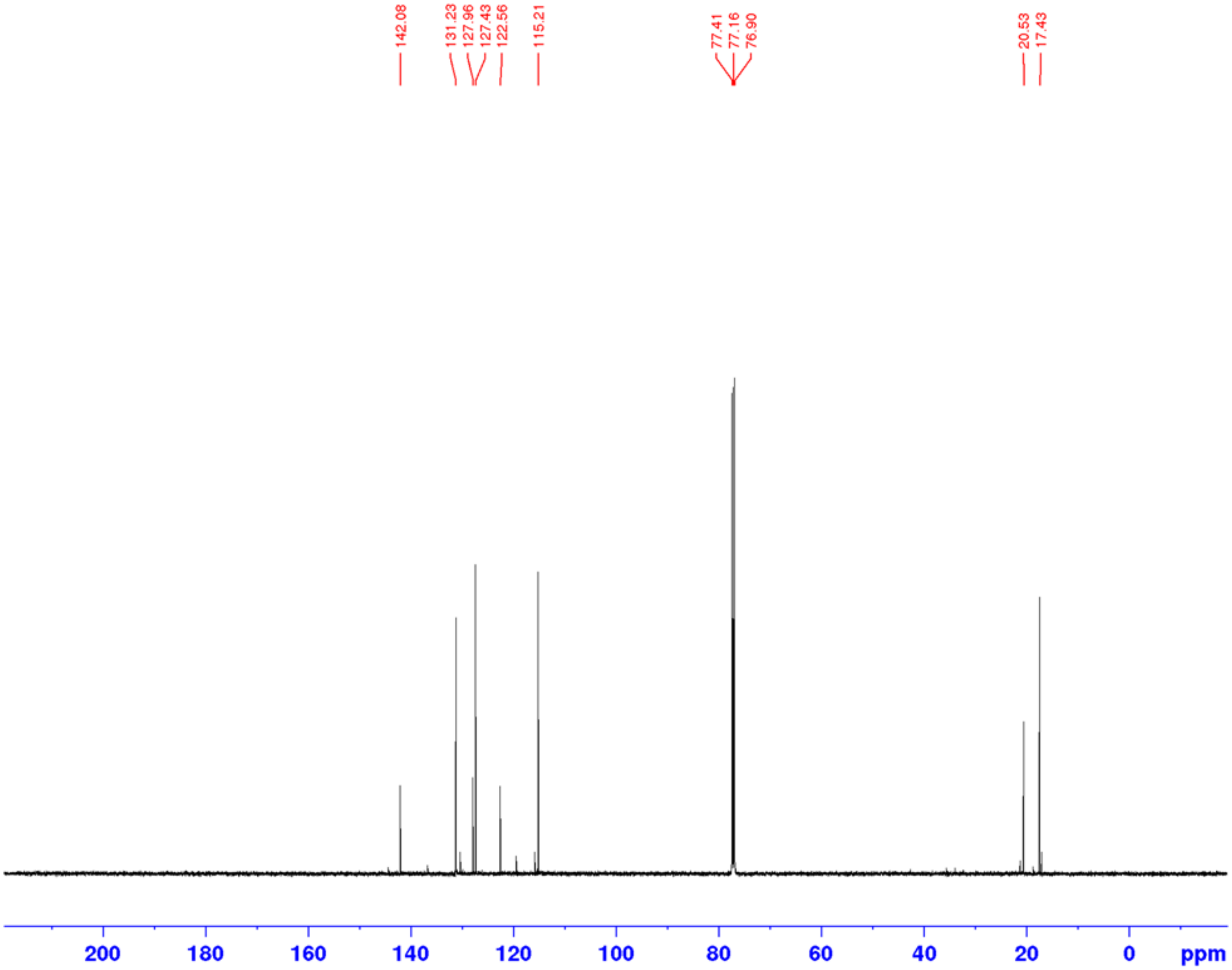
ppm
1.00
1.04
1.03
2.23
3.14
3.16

3o


142.08
131.23
127.96
127.43
122.56
115.21
77.41
77.16
76.90
20.53
17.43
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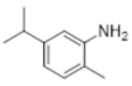
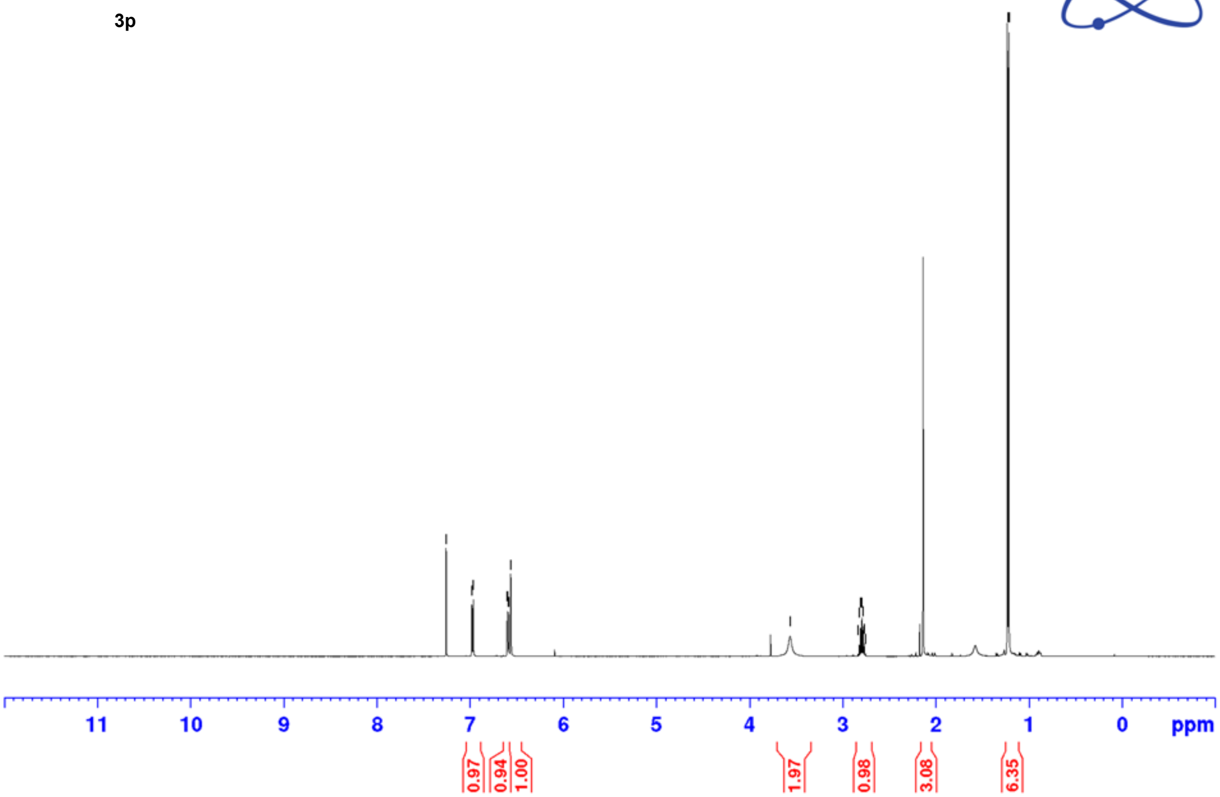
180
160
140
120
100
80
60
40
20
0
ppm


NH2

3p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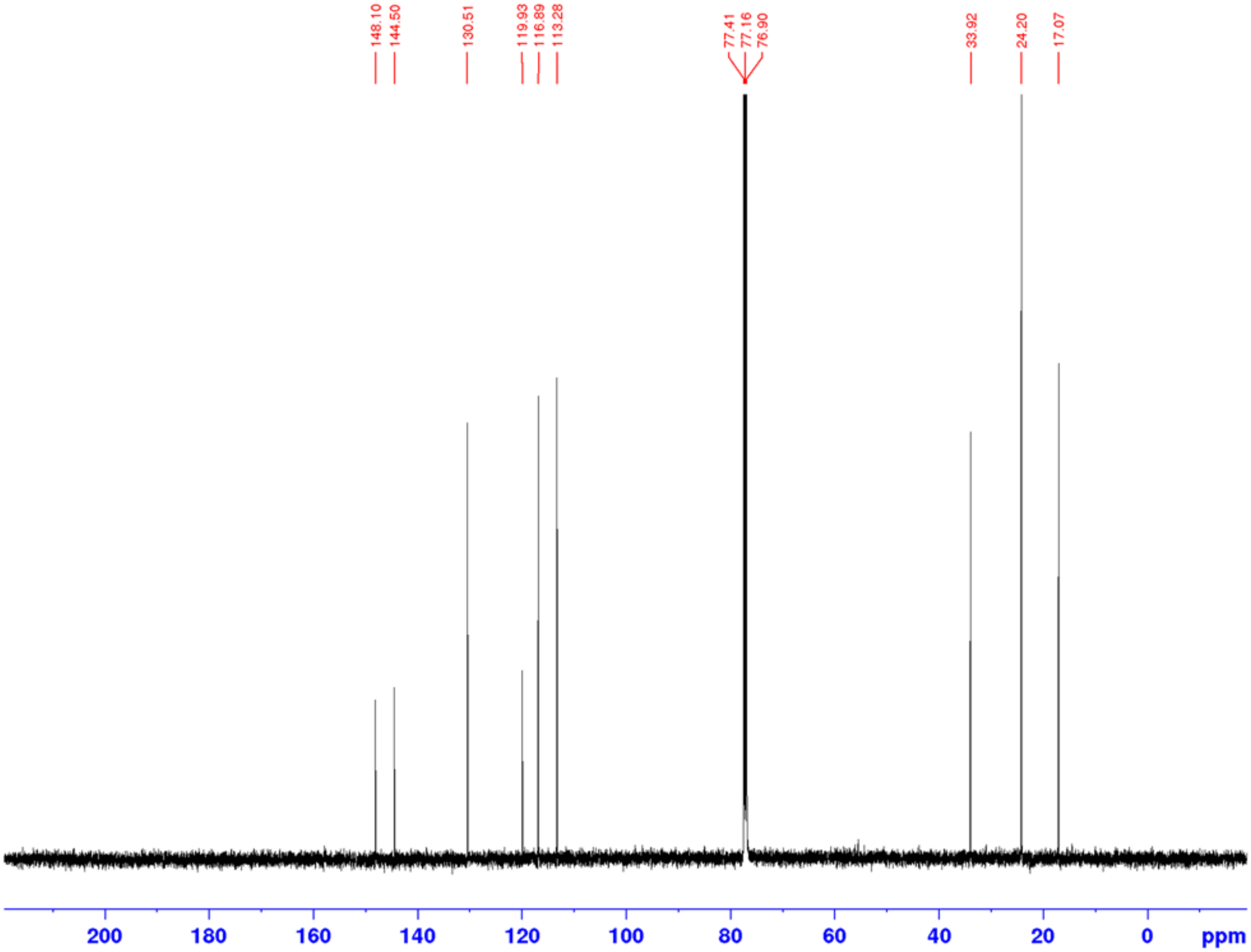
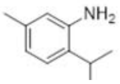
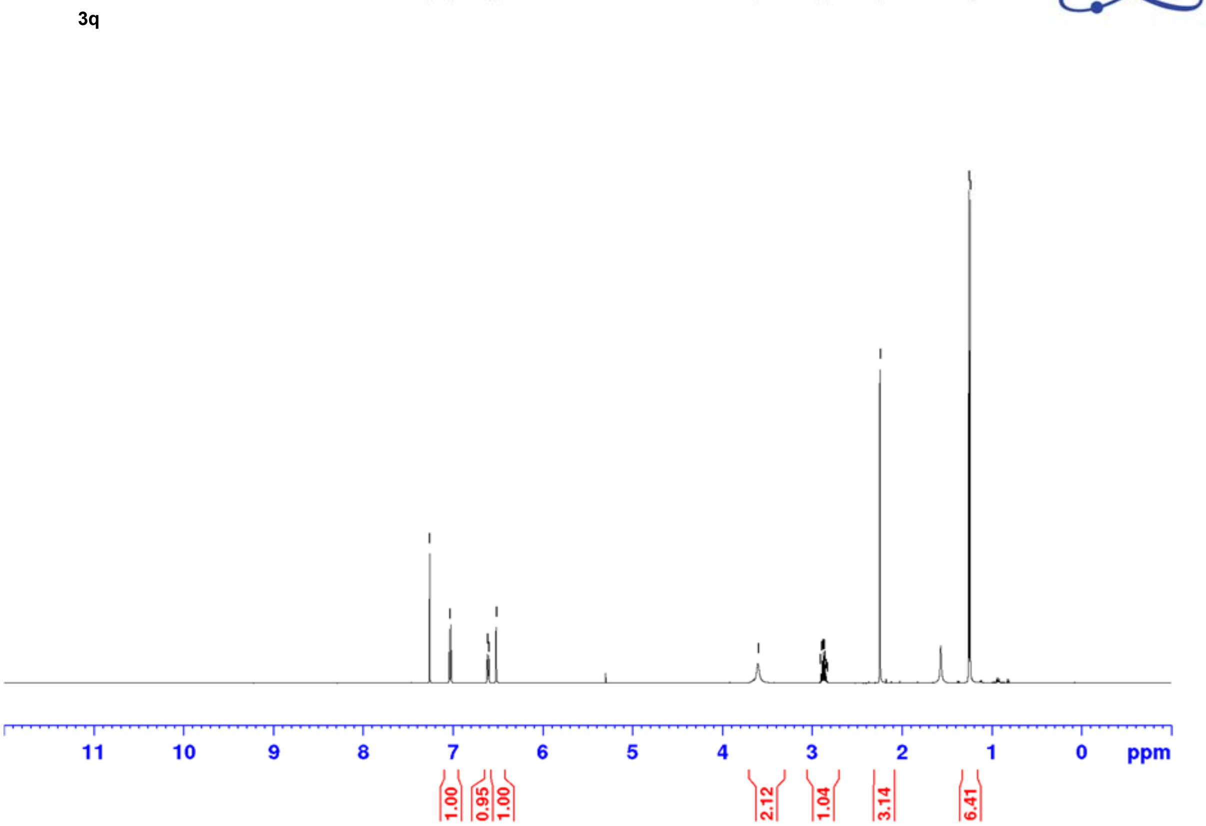
6.984
6.969
6.605
6.601
6.590
6.586
6.566
6.563
3.568
2.837
2.823
2.809
2.796
2.782
2.768
2.754
2.139
1.225
1.212
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.97
0.94
1.00
1.97
0.98
3.08
6.35


148.10
144.50
130.51
119.93
116.89
113.28
77.41
77.16
76.90
33.92
24.20
17.07
200
180
160
140
120
100
80
60
40
20
0
ppm



3q



7.260
7.038
7.022
6.617
6.601
6.520
6.518
3.602
2.913
2.899
2.886
2.879
2.872
2.858
2.845
2.831
2.244
1.254
1.240
11
10
9
8
7
6
5
4
3
2
1
0
ppm
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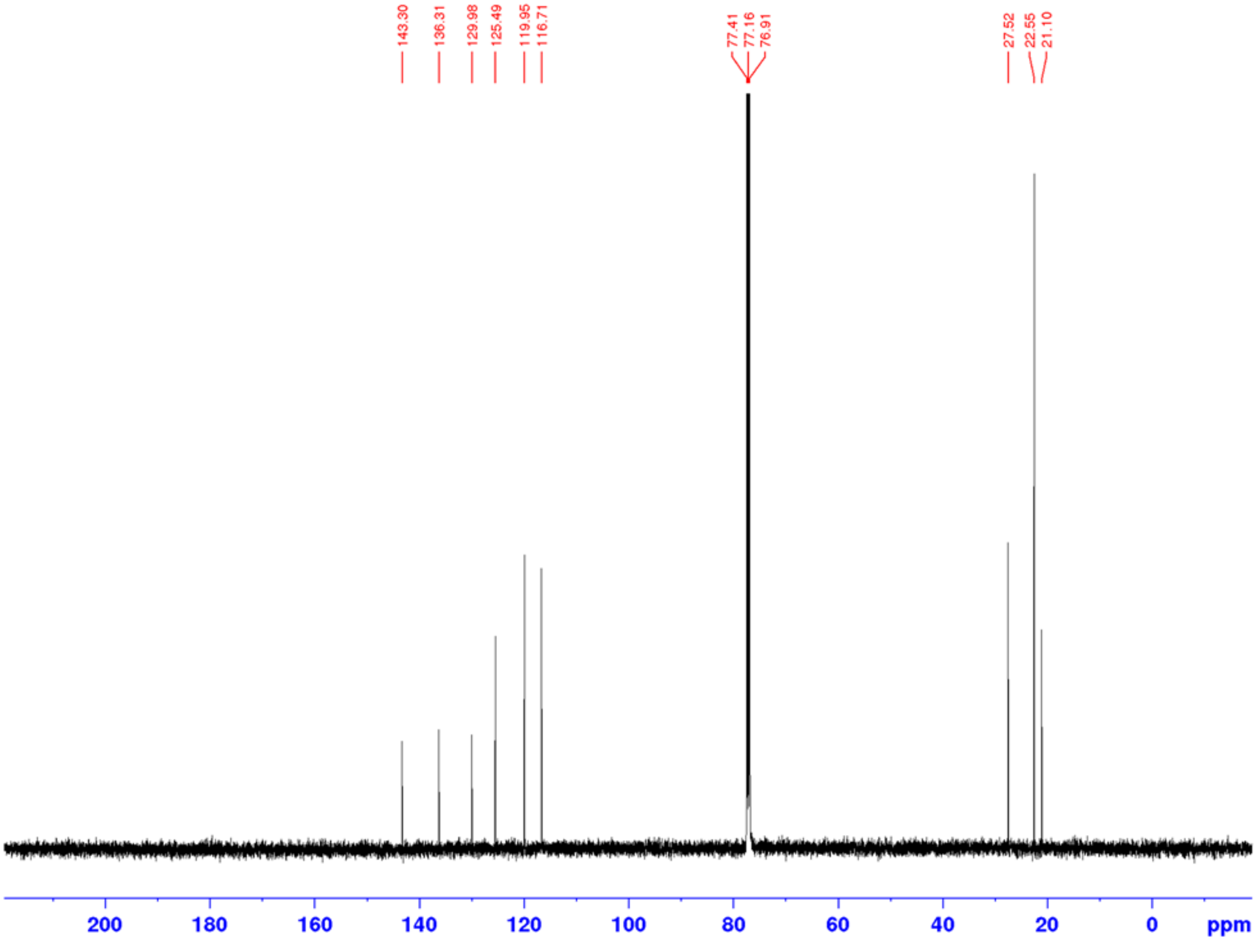
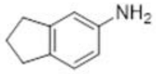
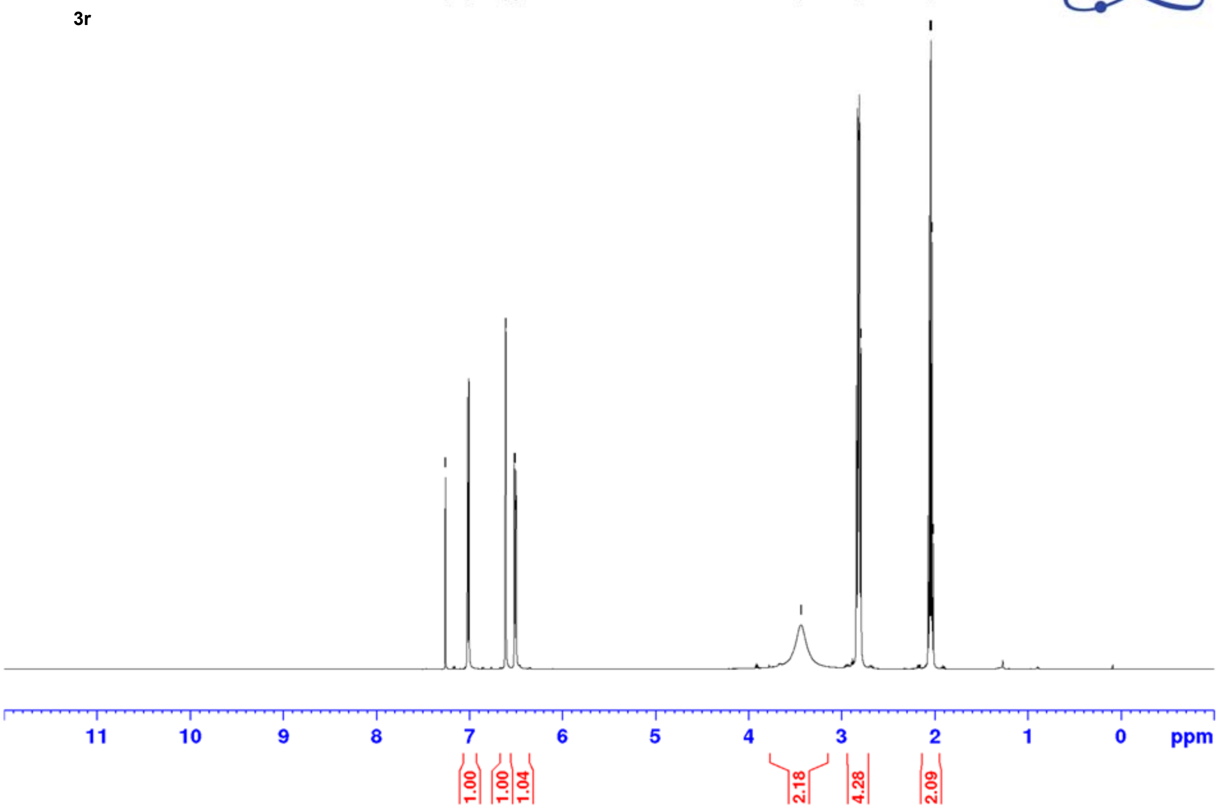
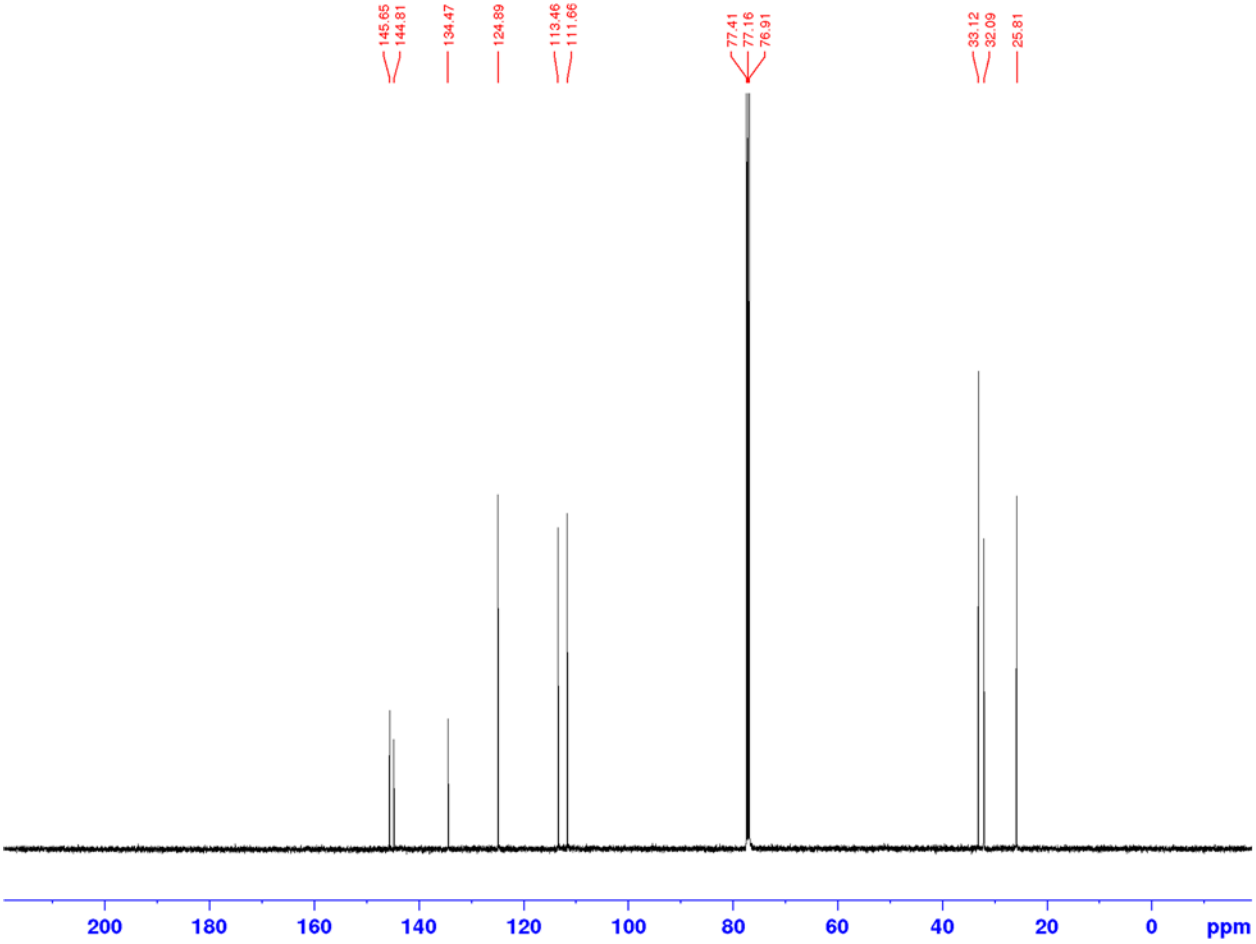
0.95
1.00
2.12
1.04
3.14
6.41

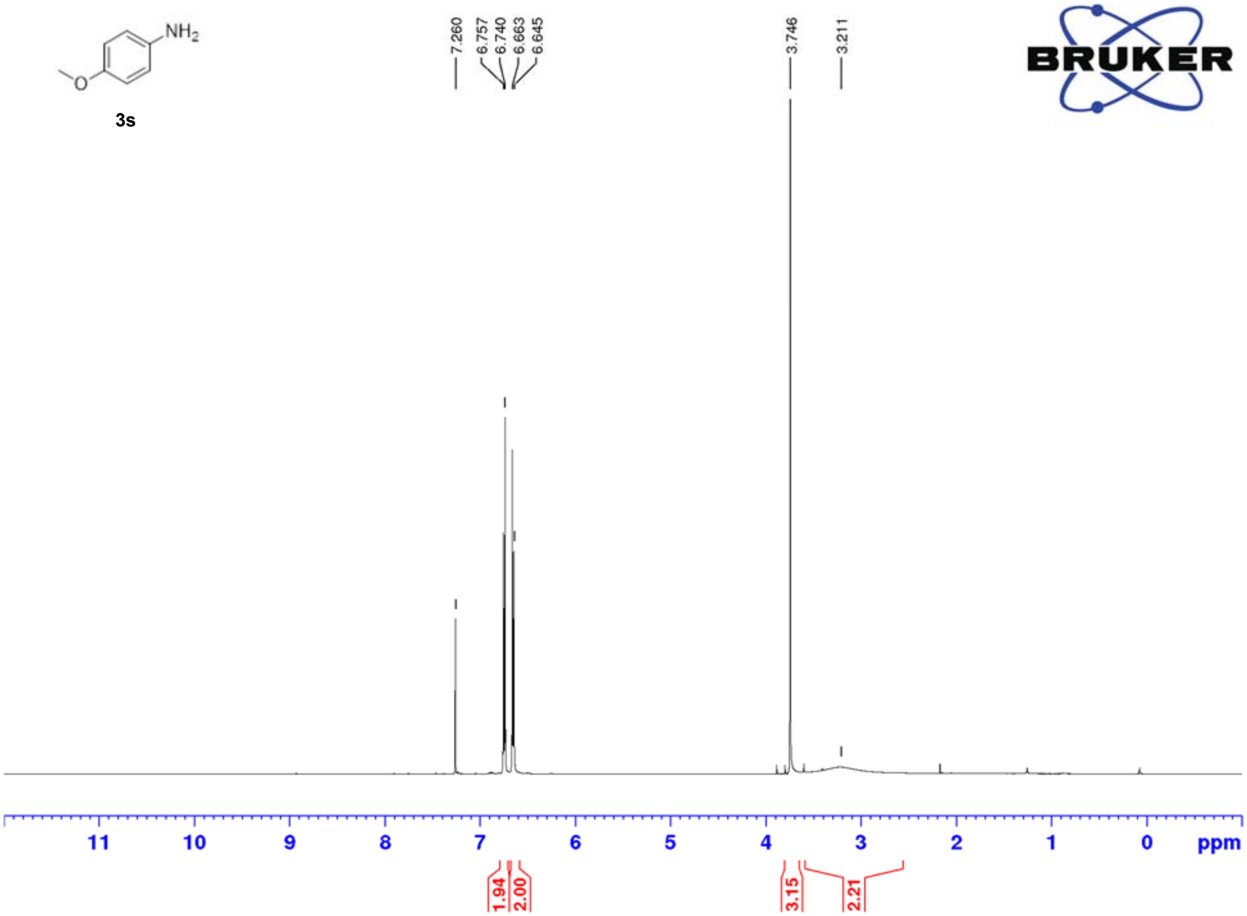

143.30
136.31
129.98
125.49
119.95
116.71
77.41
77.16
76.91
27.52
22.55
21.10
200
180
160
140
120
100
80
60
40
20
0
ppm

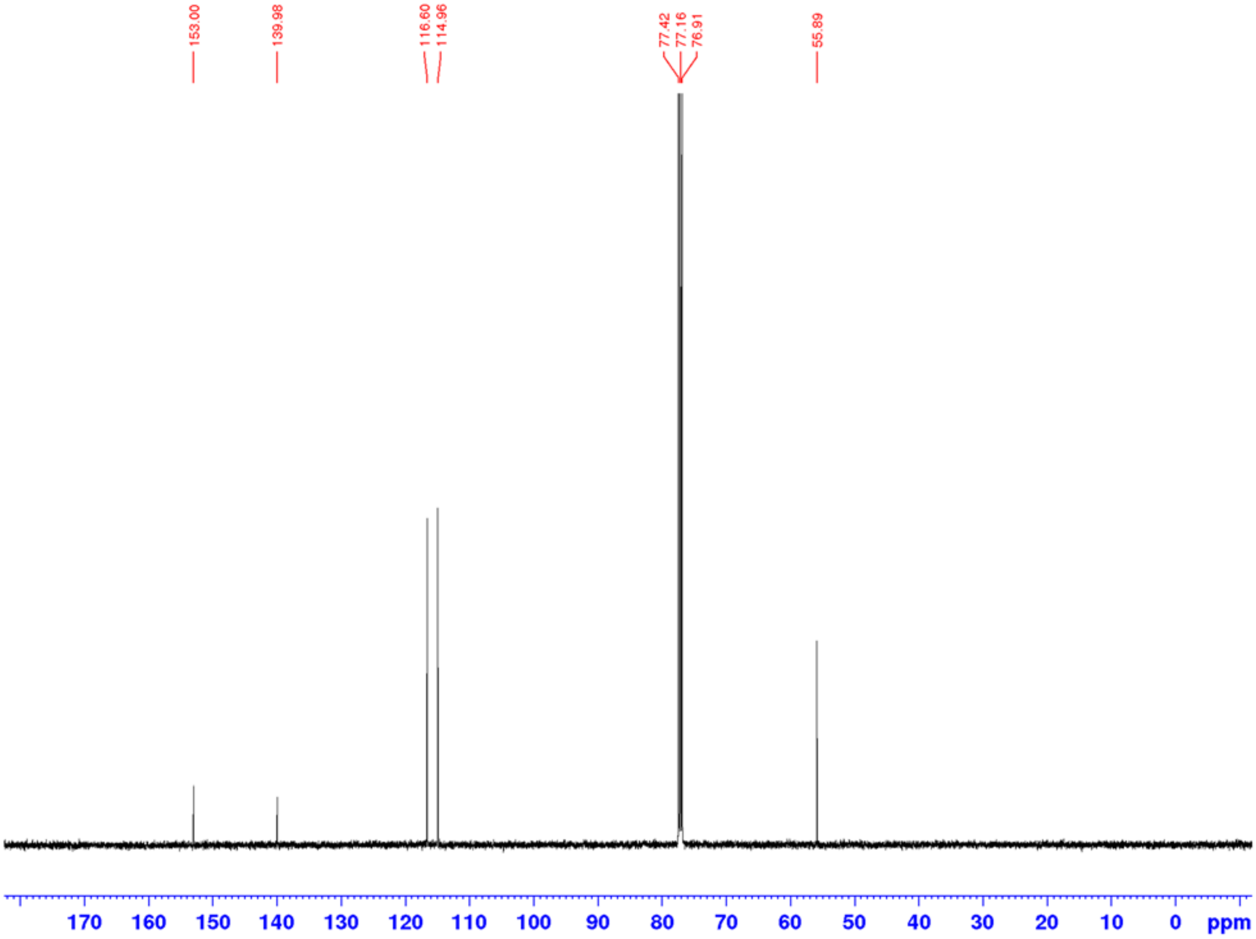

NH2

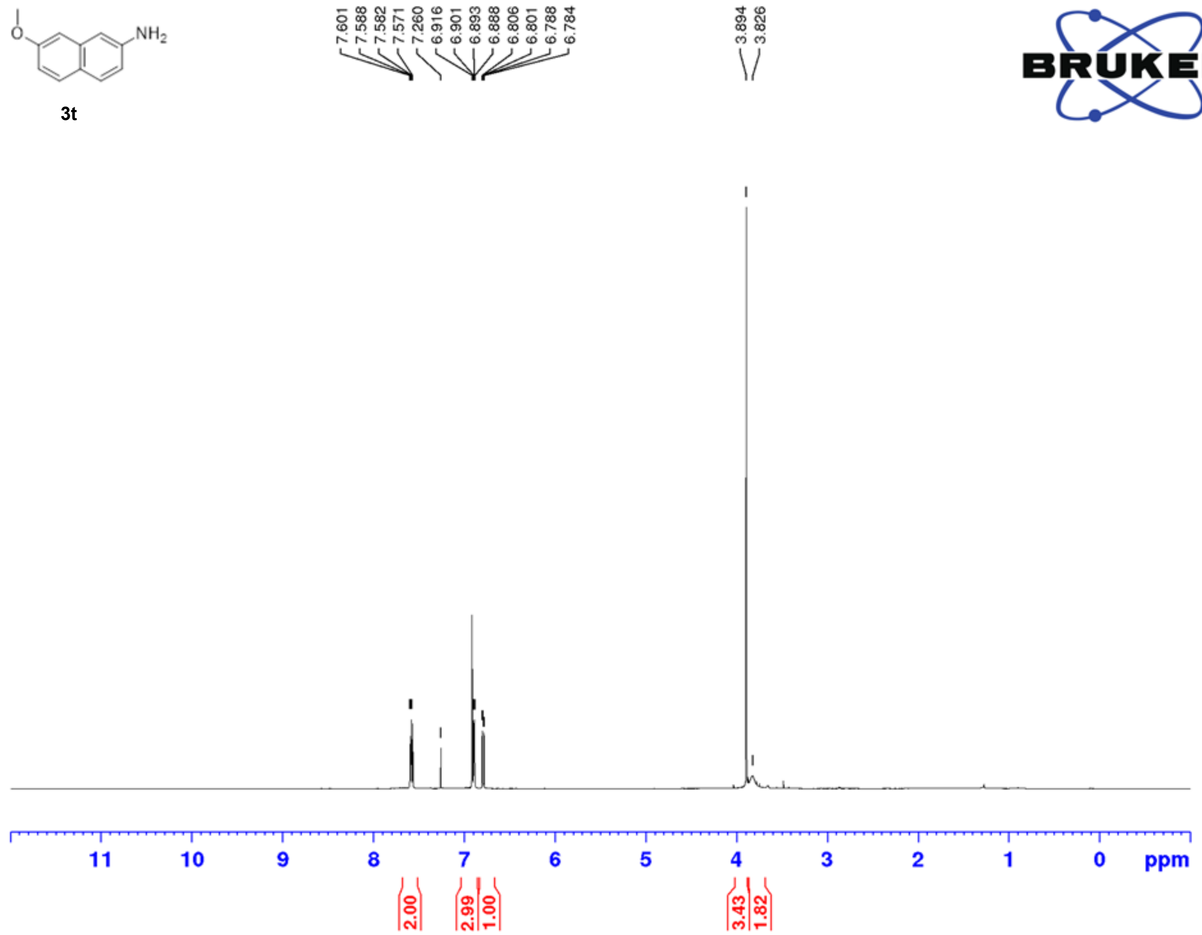
3r


7.260
7.023
7.007
6.612
6.519
6.514
6.503
6.498
3.440
2.845
2.830
2.814
2.810
2.795
2.075
2.060
2.054
2.046
2.039
2.031
2.016
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.04
2.18
4.28
2.09


145.65
144.81
134.47
124.89
113.46
111.66
77.41
77.16
76.91
33.12
32.09
25.81
200
180
160
140
120
100
80
60
40
20
0
ppm

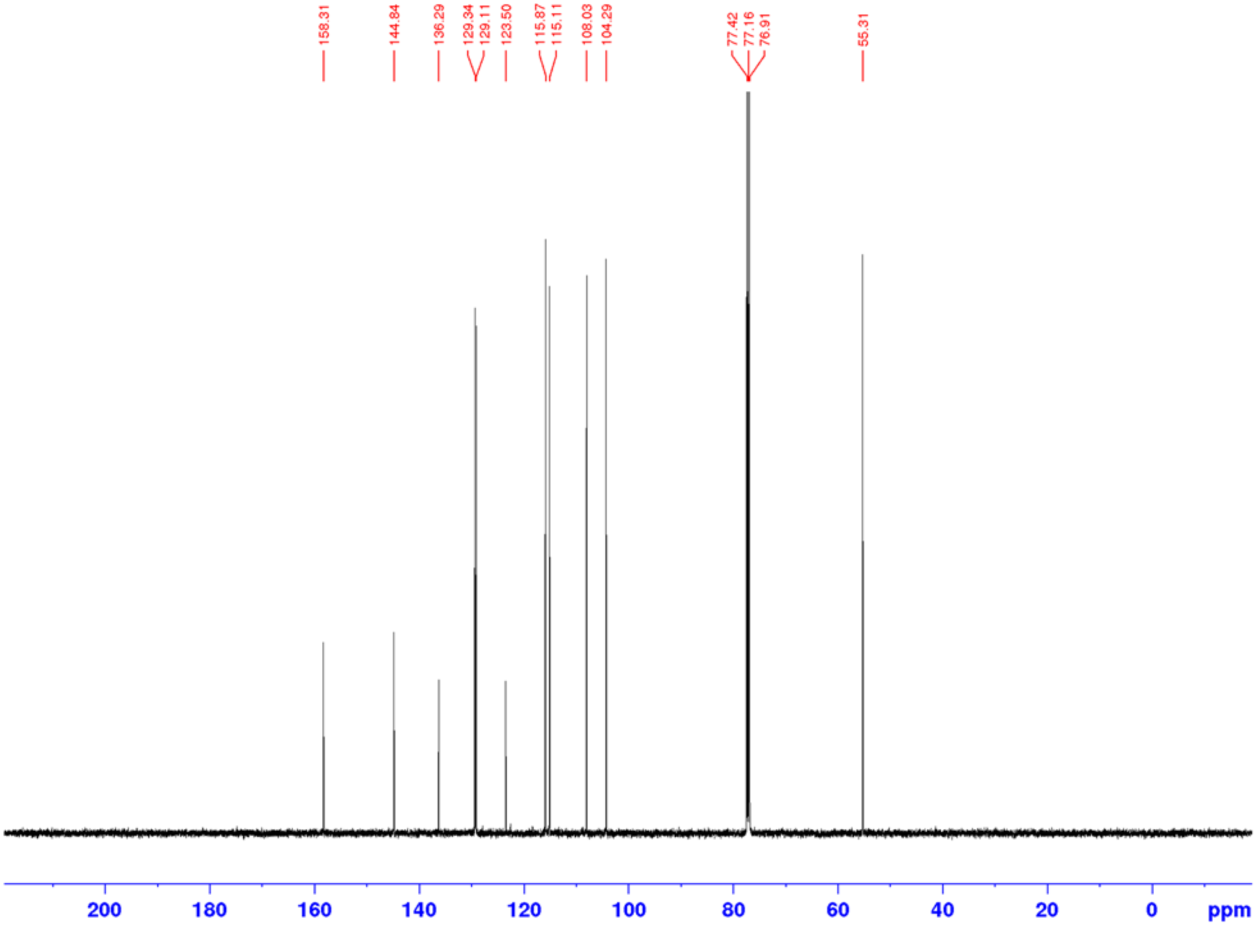

NH2
O
3s
7.260
6.757
6.740
6.663
6.645
3.746
3.211
BRUKER
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.94
2.00
3.15
2.21

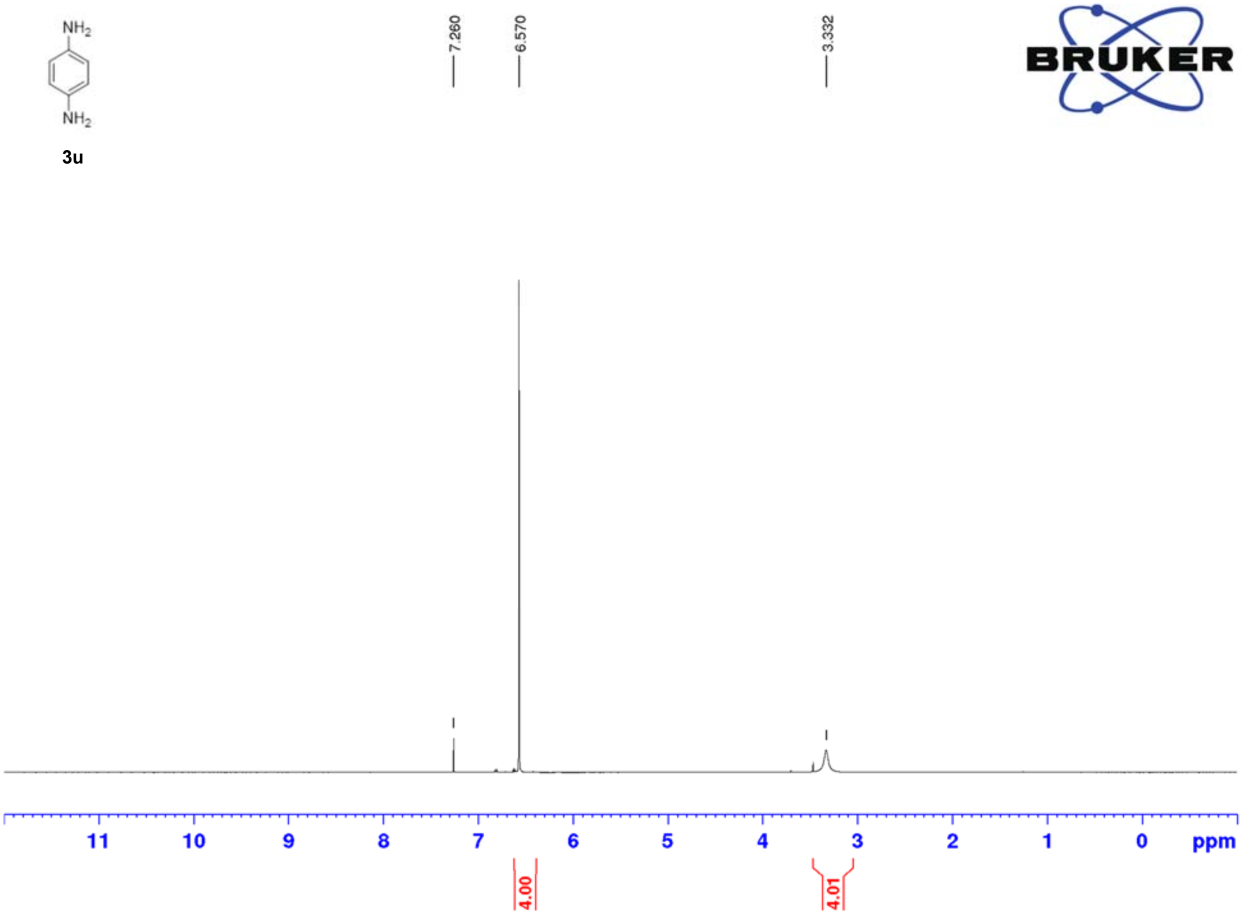

153.00
139.98
116.60
114.96
77.42
77.16
76.91
55.89
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



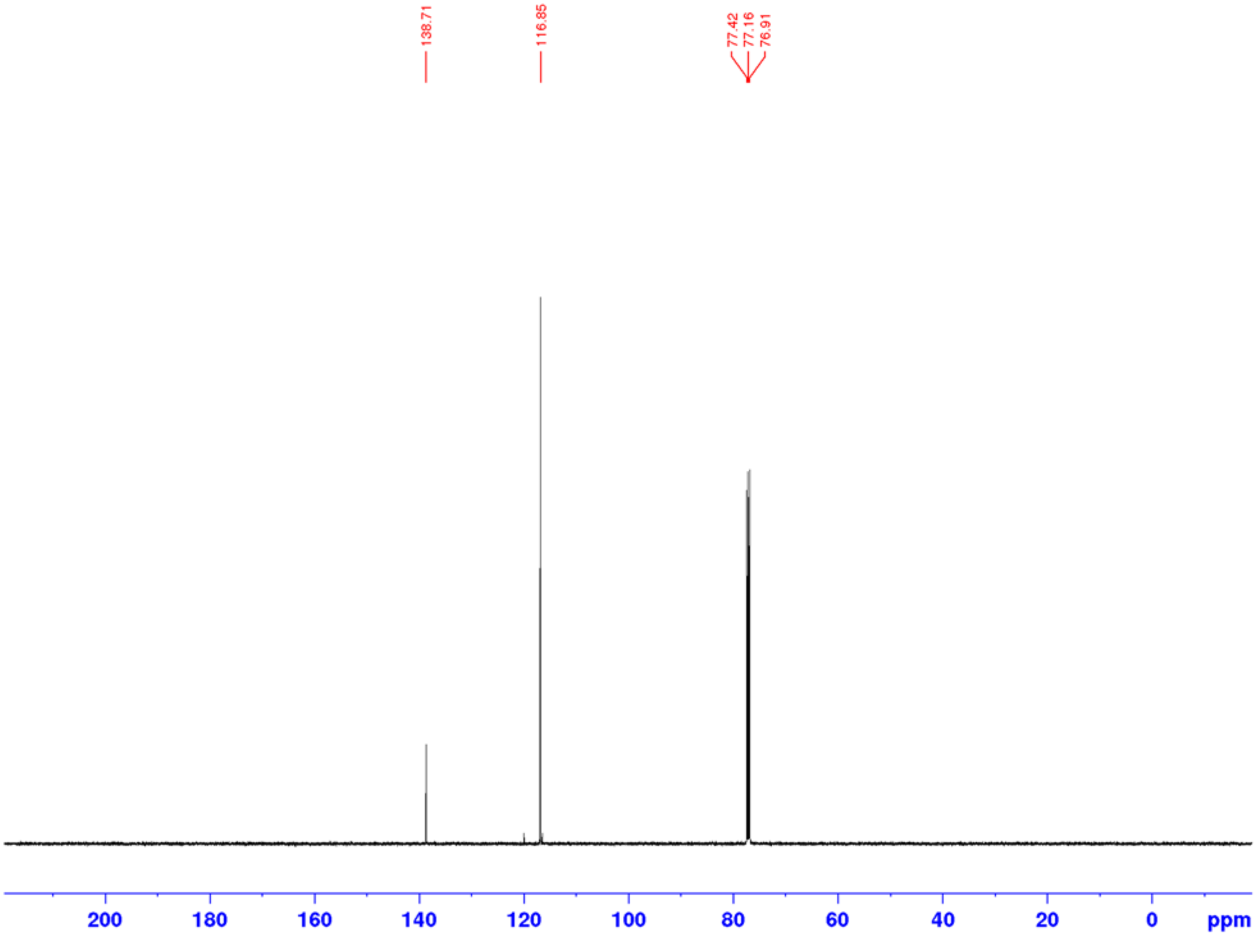
3t

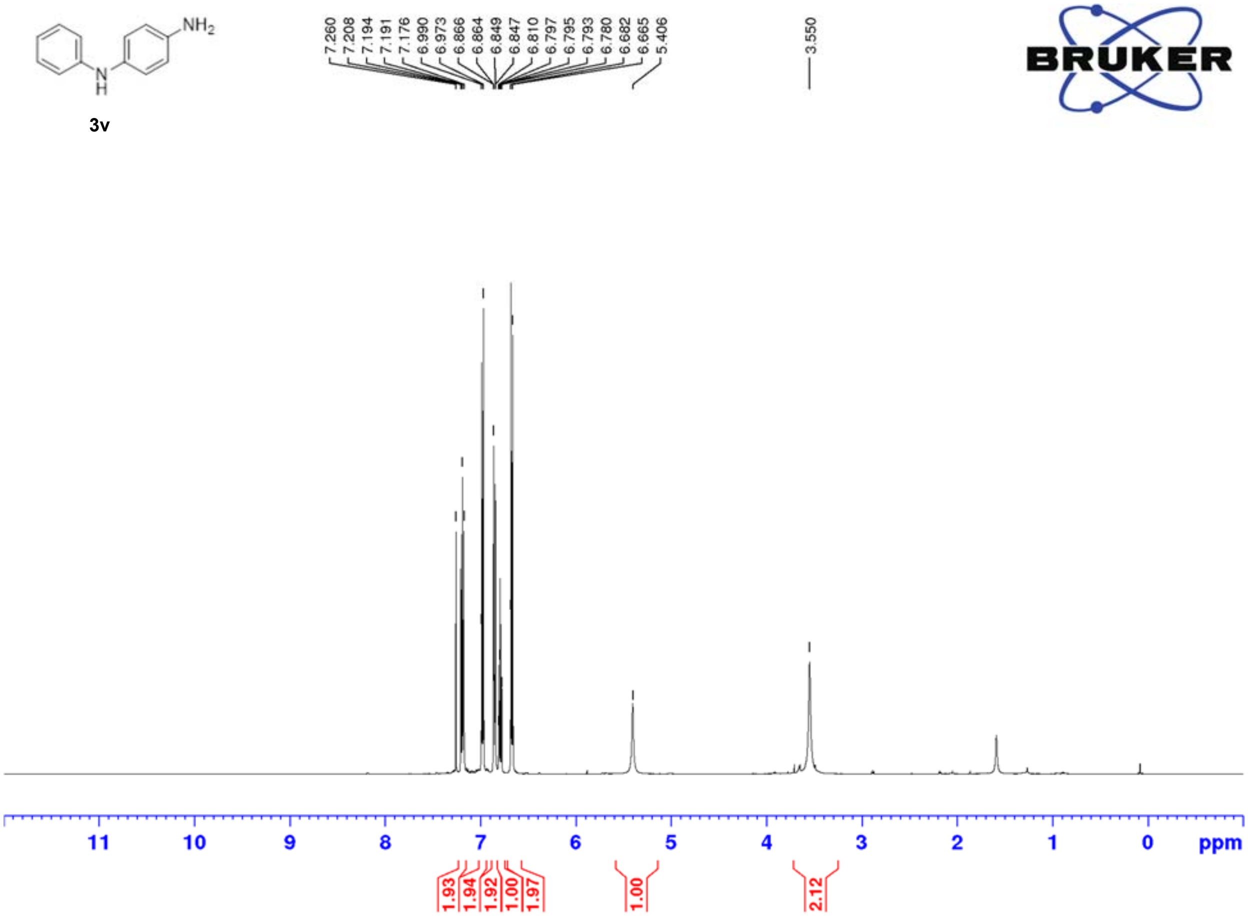
NH2
O
7.601
7.588
7.582
7.571
7.260
6.916
6.901
6.893
6.888
6.806
6.801
6.788
6.784
3.894
3.826
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.99
1.00
3.43
1.82


158.31
144.84
136.29
129.34
129.11
123.50
115.87
115.11
108.03
104.29
77.42
77.16
76.91
55.31
200
180
160
140
120
100
80
60
40
20
0
ppm

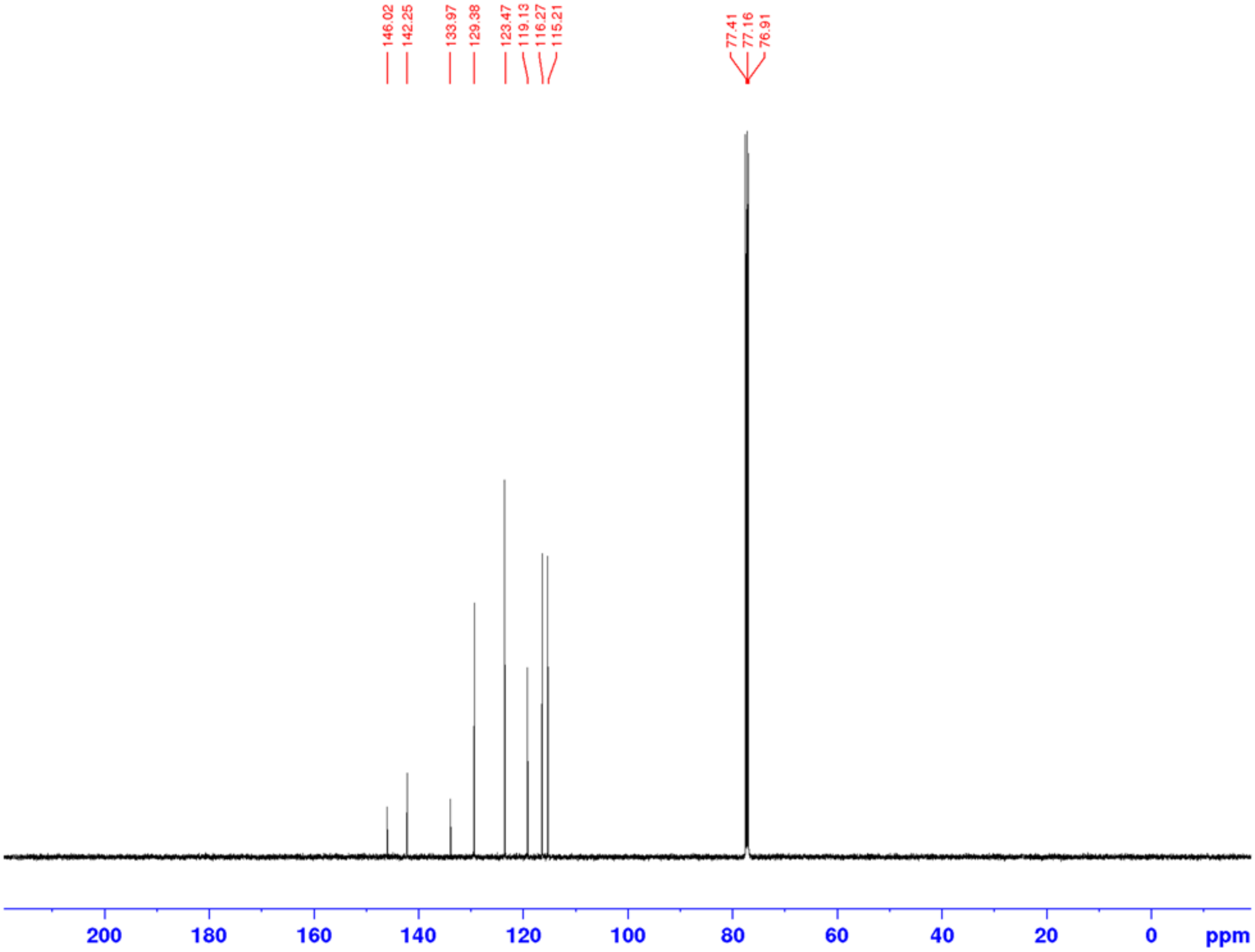


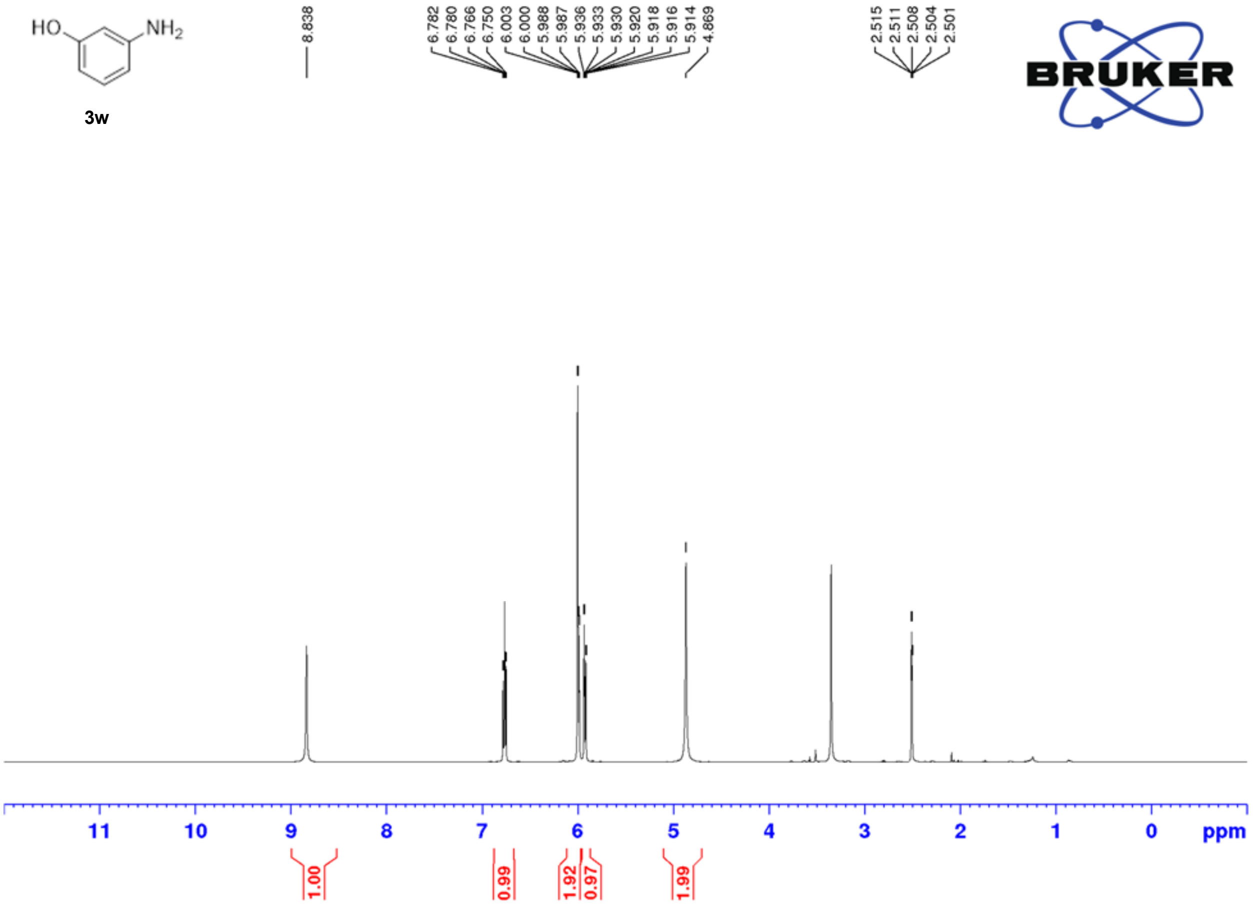
3u


138.71
116.85
77.42
77.16
76.91
200
180
160
140
120
100
80
60
40
20
0
ppm


NH2
H
N
7.260
7.208
7.194
7.191
7.176
6.990
6.973
6.866
6.864
6.849
6.847
6.810
6.797
6.795
6.793
6.780
6.682
6.665
5.406
3.550
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.93
1.94
1.92
1.00
1.97
1.00
2.12

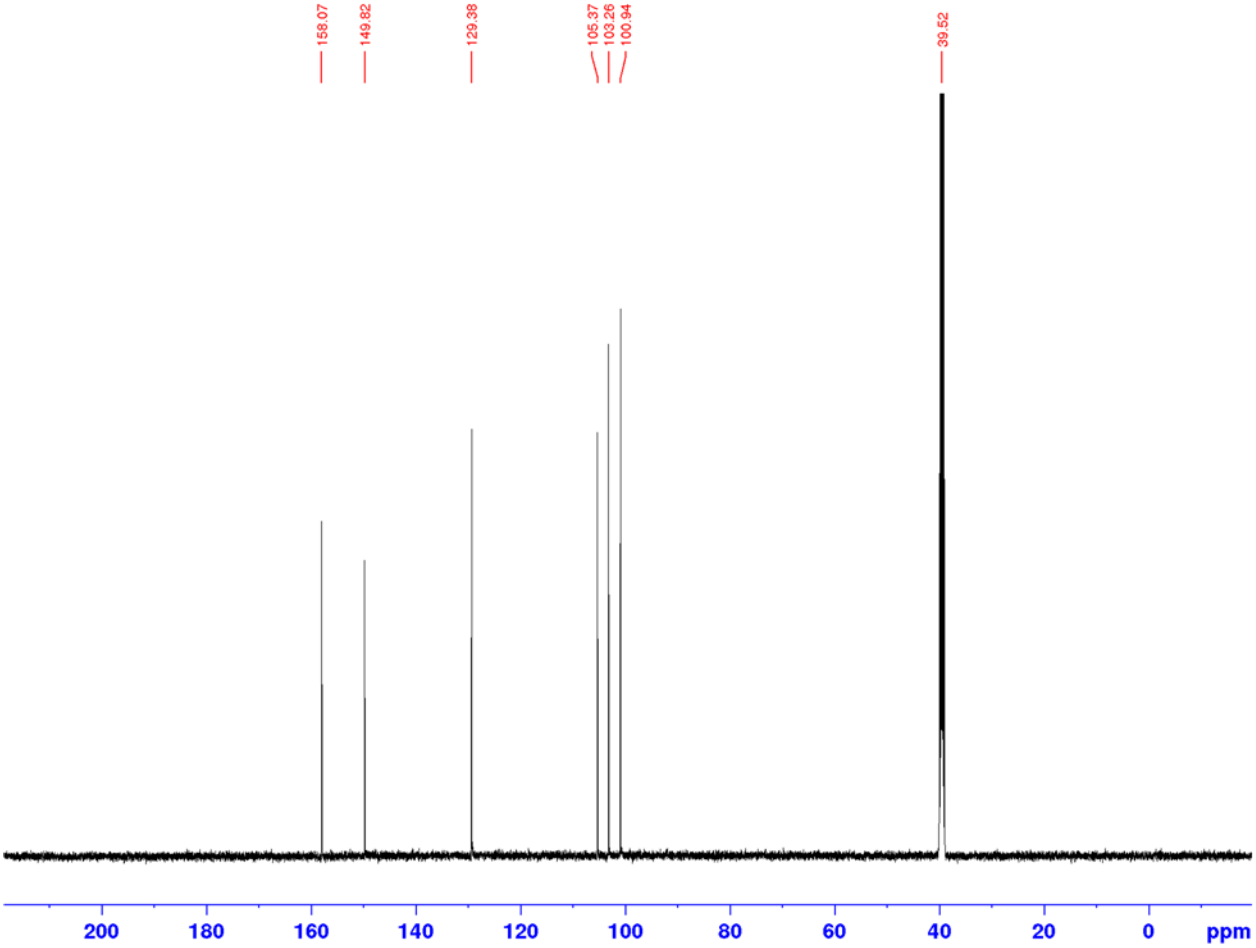
3v

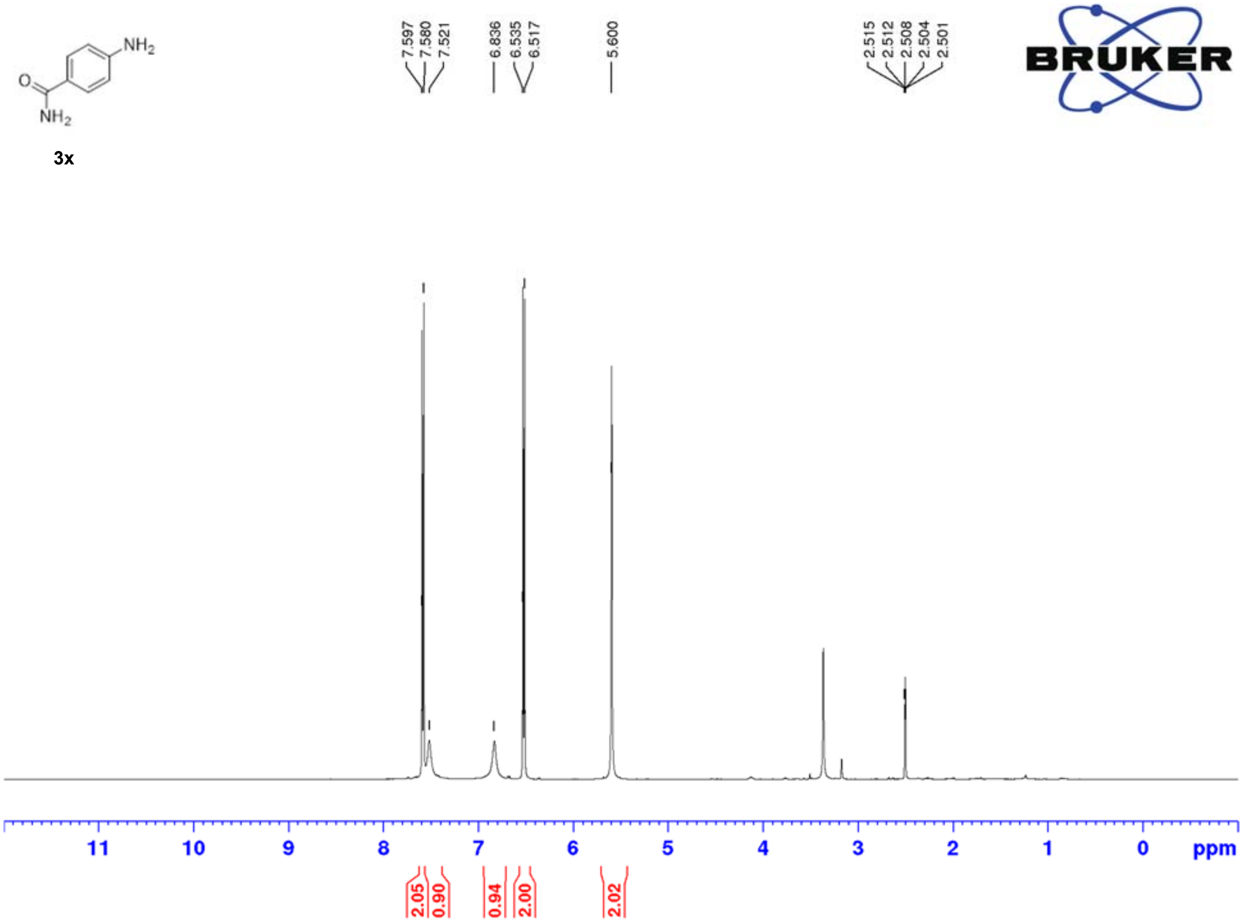

146.02
142.25
133.97
129.38
123.47
119.13
116.27
115.21
77.41
77.16
76.91
200
180
160
140
120
100
80
60
40
20
0
ppm


HO
NH2

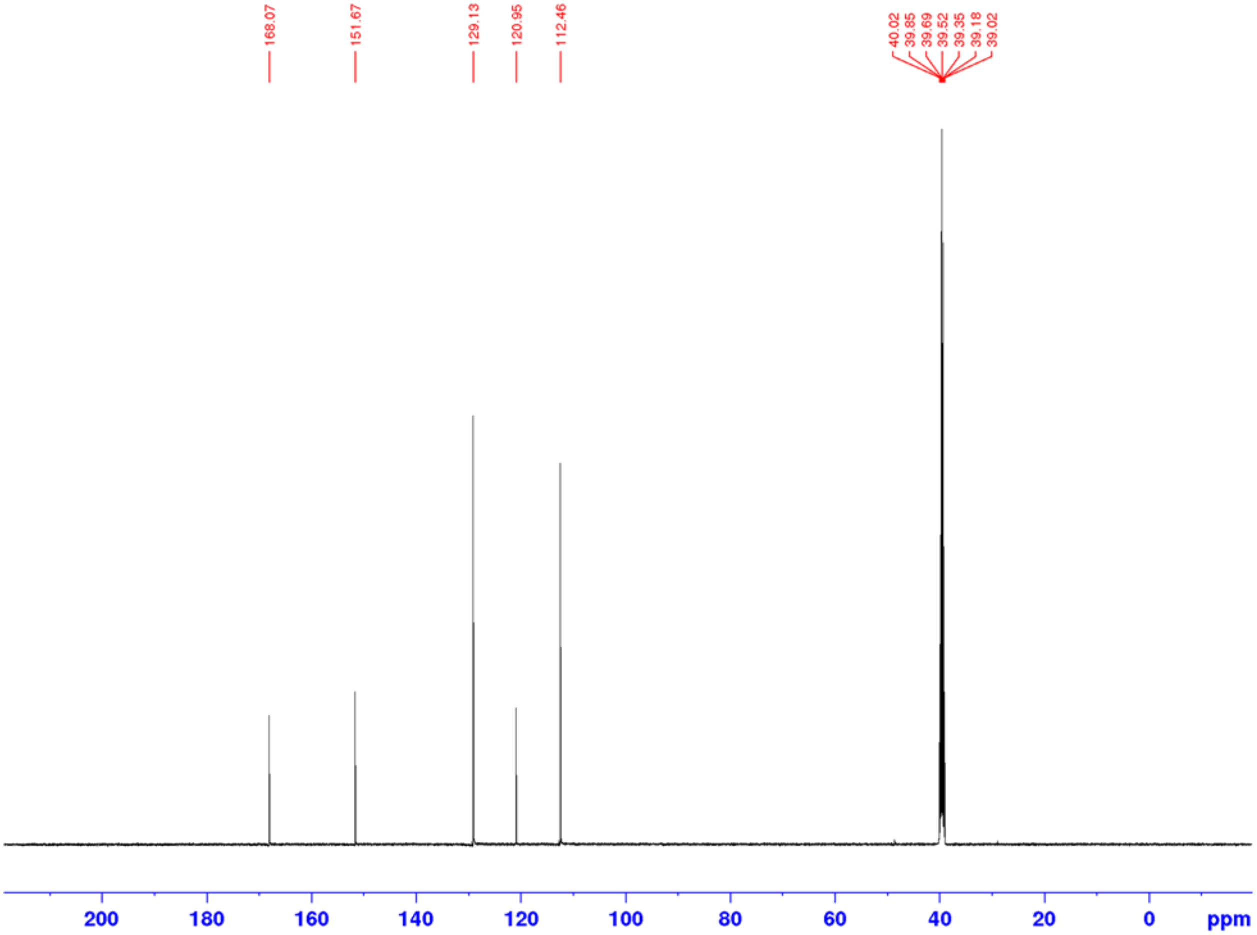
3w

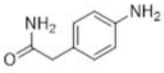
8.838
6.782
6.780
6.766
6.750
6.003
6.000
5.988
5.987
5.936
5.933
5.930
5.920
5.918
5.916
5.914
4.869
2.515
2.511
2.508
2.504
2.501
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.99
1.92
0.97
1.99


158.07
149.82
129.38
105.37
103.26
100.94
39.52
200
180
160
140
120
100
80
60
40
20
0
ppm

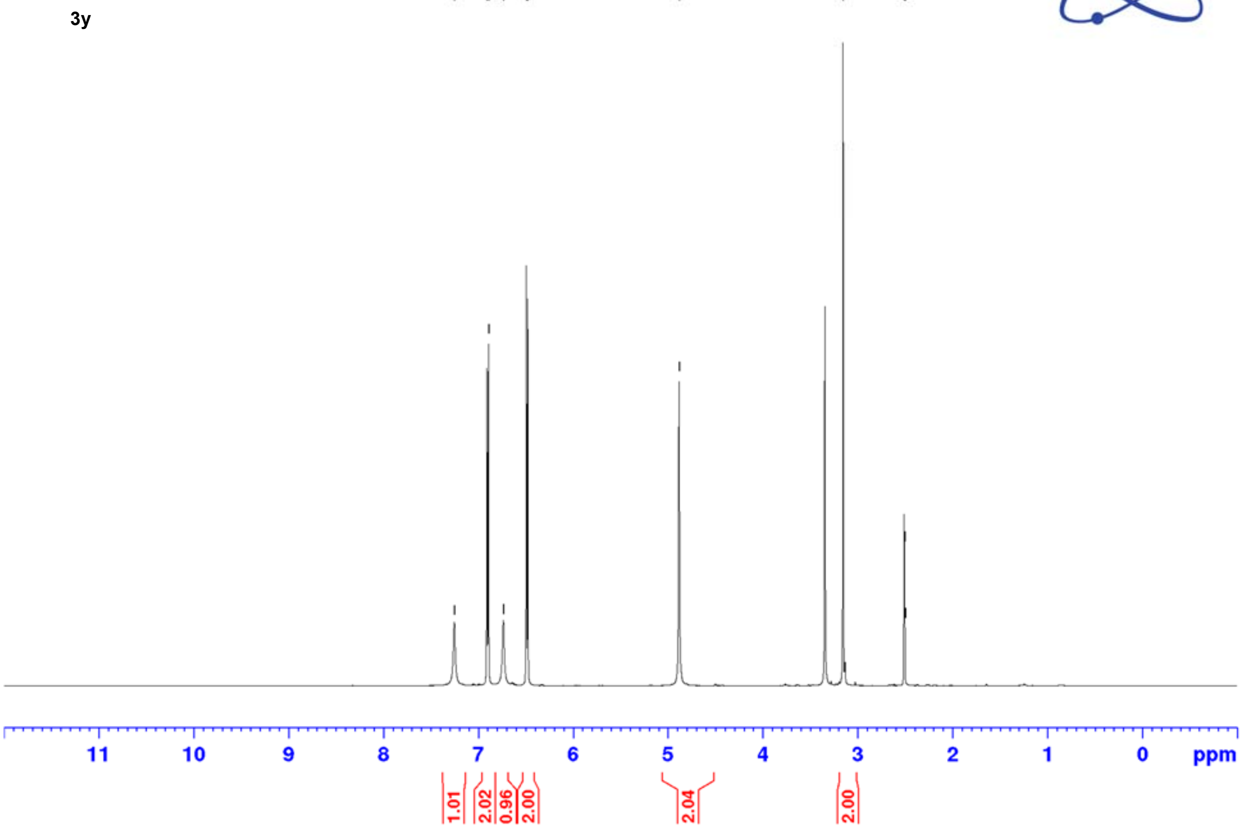

3x

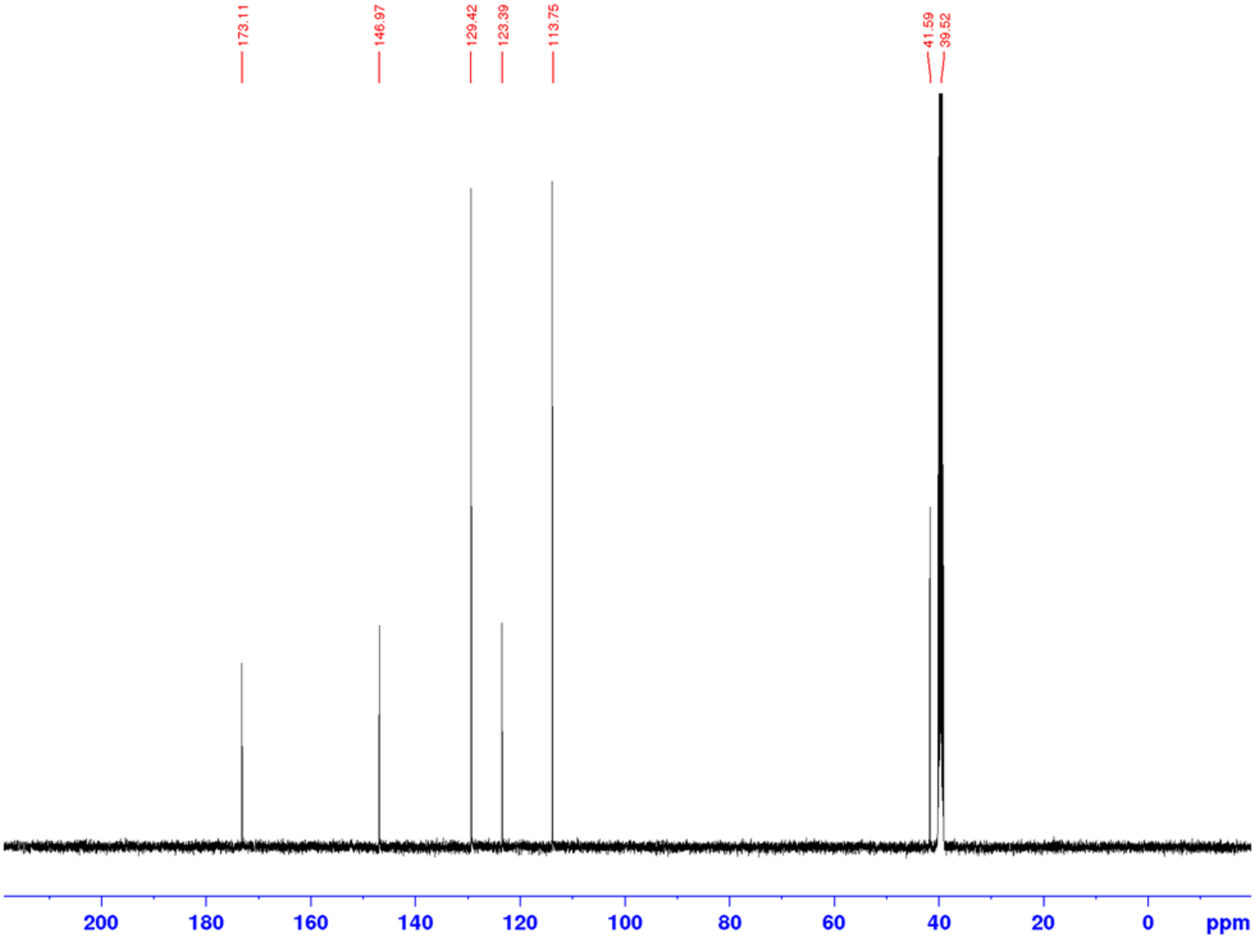
NH2
O
NH2
7.597
7.580
7.521
6.836
6.535
6.517
5.600
2.515
2.512
2.508
2.504
2.501
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.05
0.90
0.94
2.00
2.02

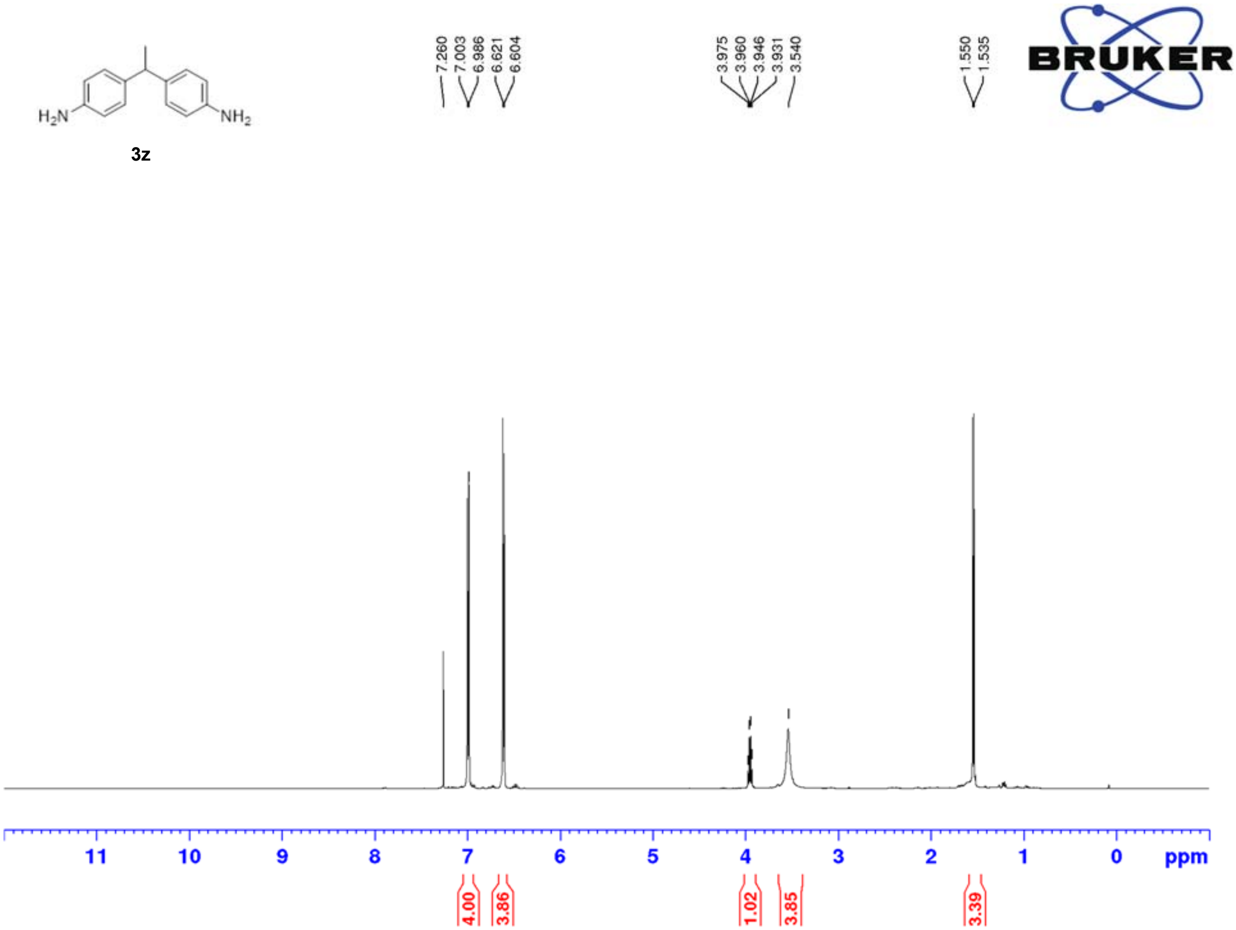

168.07
151.67
129.13
120.95
112.46
40.02
39.85
39.69
39.52
39.35
39.18
39.02
200
180
160
140
120
100
80
60
40
20
0
ppm


NH2
NH2
O

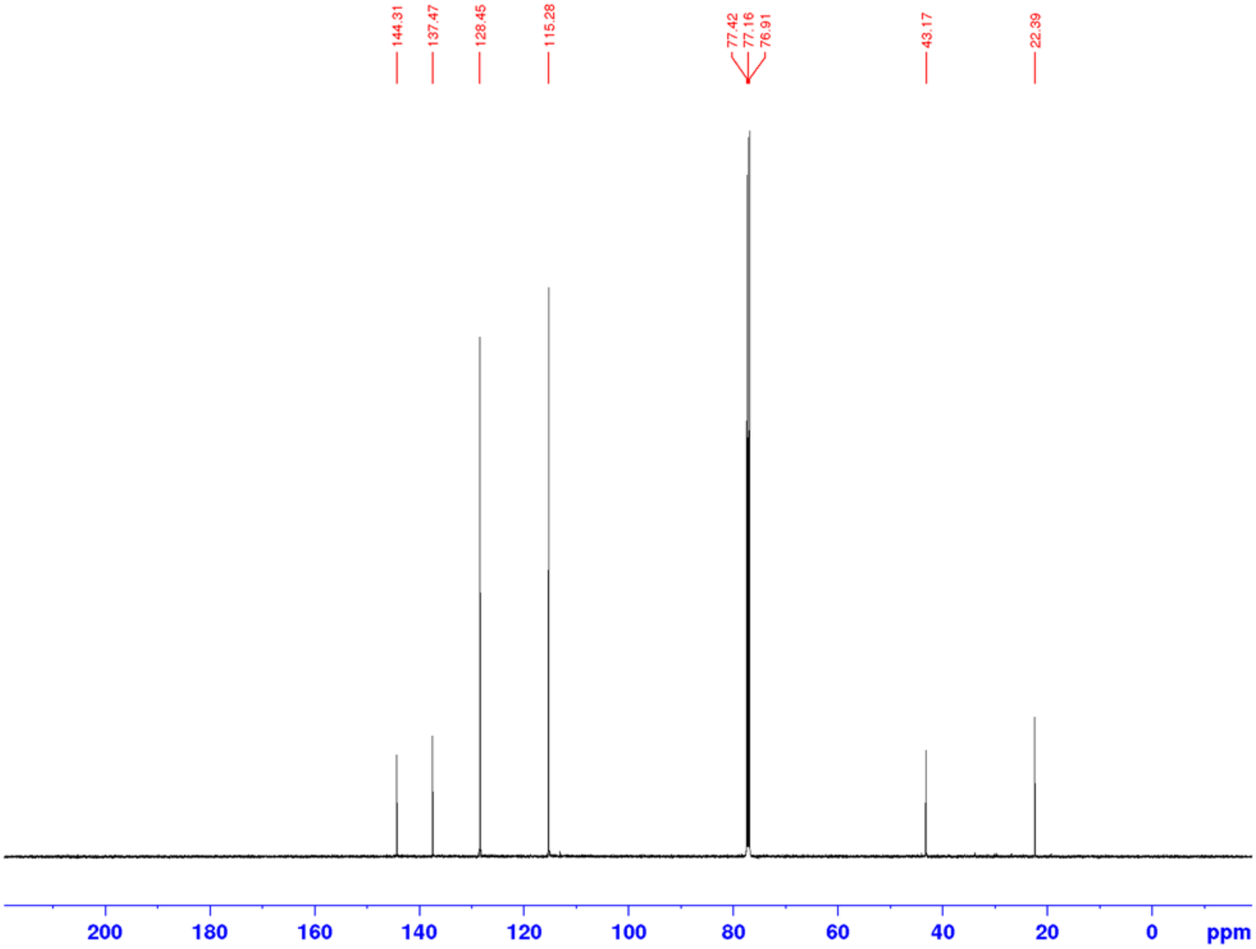
3y

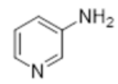

7.253
6.910
6.893
6.736
6.495
6.478
4.883
3.154
2.515
2.511
2.508
2.504
2.501
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
2.02
0.96
2.00
2.04
2.00


173.11
146.97
129.42
123.39
113.75
41.59
39.52
200
180
160
140
120
100
80
60
40
20
0
ppm

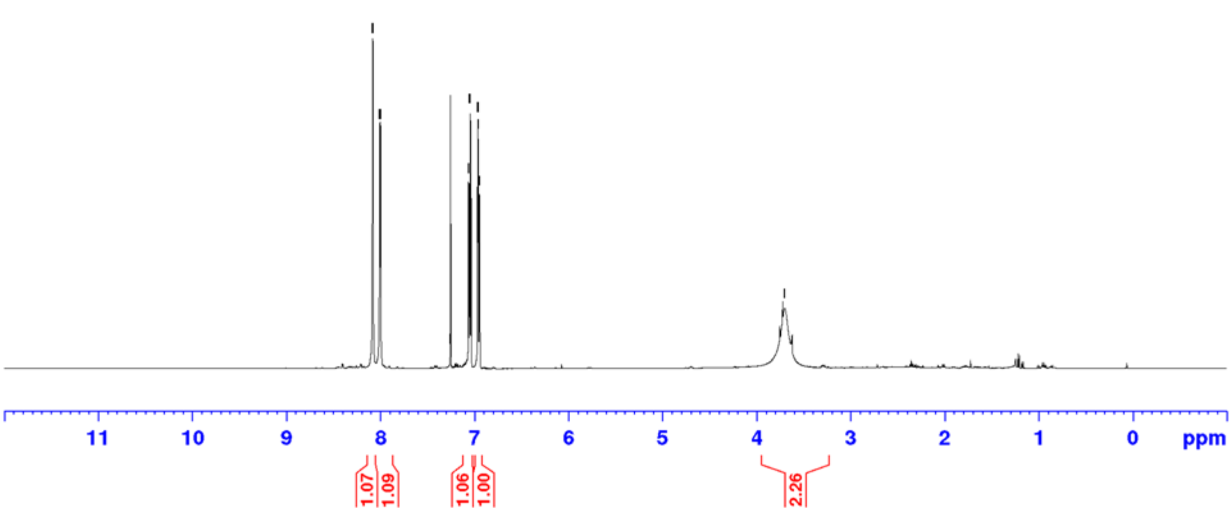

H2N
NH2
7.260
7.003
6.986
6.621
6.604
3.975
3.960
3.946
3.931
3.540
1.550
1.535
11
10
9
8
7
6
5
4
3
2
1
0
ppm
4.00
3.86
1.02
3.85
3.39

3z


144.31
137.47
128.45
115.28
77.42
77.16
76.91
43.17
22.39
200
180
160
140
120
100
80
60
40
20
0
ppm


NH2
N

3aa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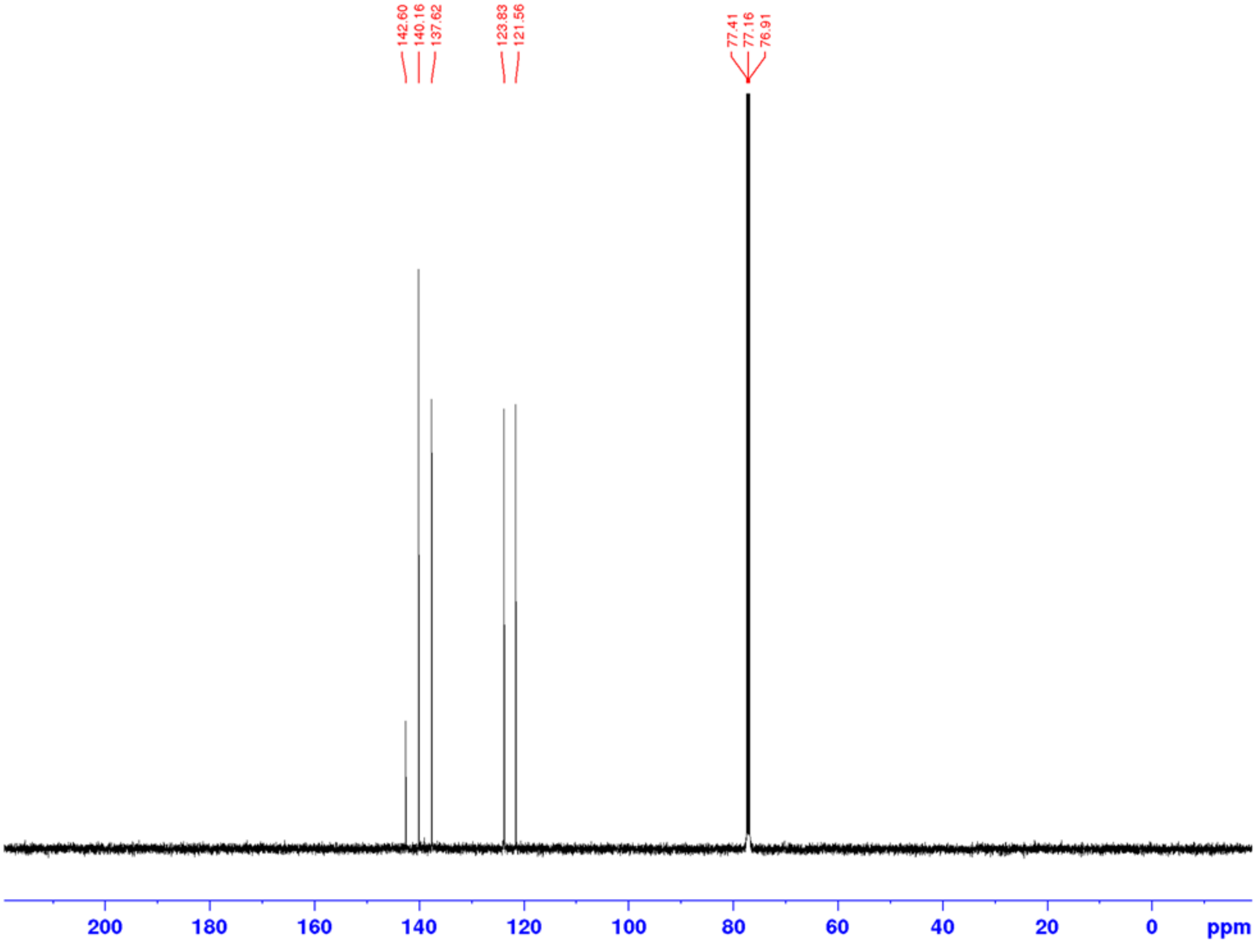
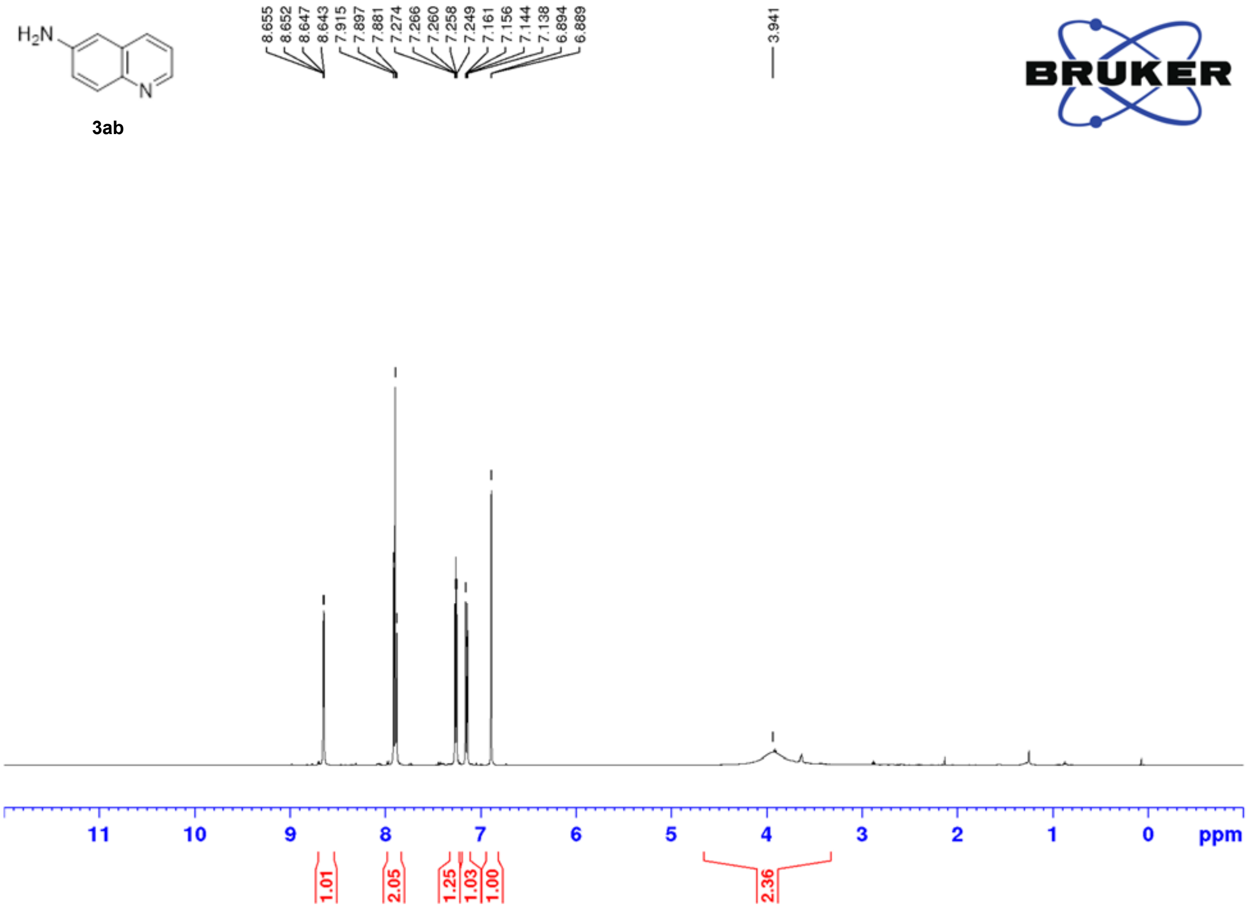
8.084
8.014
8.012
8.005
8.003
7.260
7.068
7.067
7.059
7.058
7.052
7.051
7.043
7.042
6.972
6.969
6.966
6.963
6.955
6.952
6.950
6.947
3.708
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.07
1.09
1.06
1.00
2.26


142.60
140.16
137.62
123.83
121.56
77.41
77.16
76.91
200
180
160
140
120
100
80
60
40
20
0
ppm


H2N
N
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8.652
8.647
8.643
7.915
7.897
7.881
7.274
7.266
7.260
7.258
7.249
7.161
7.156
7.144
7.138
6.894
6.889
3.941
11
10
9
8
7
6
5
4
3
2
1
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ppm
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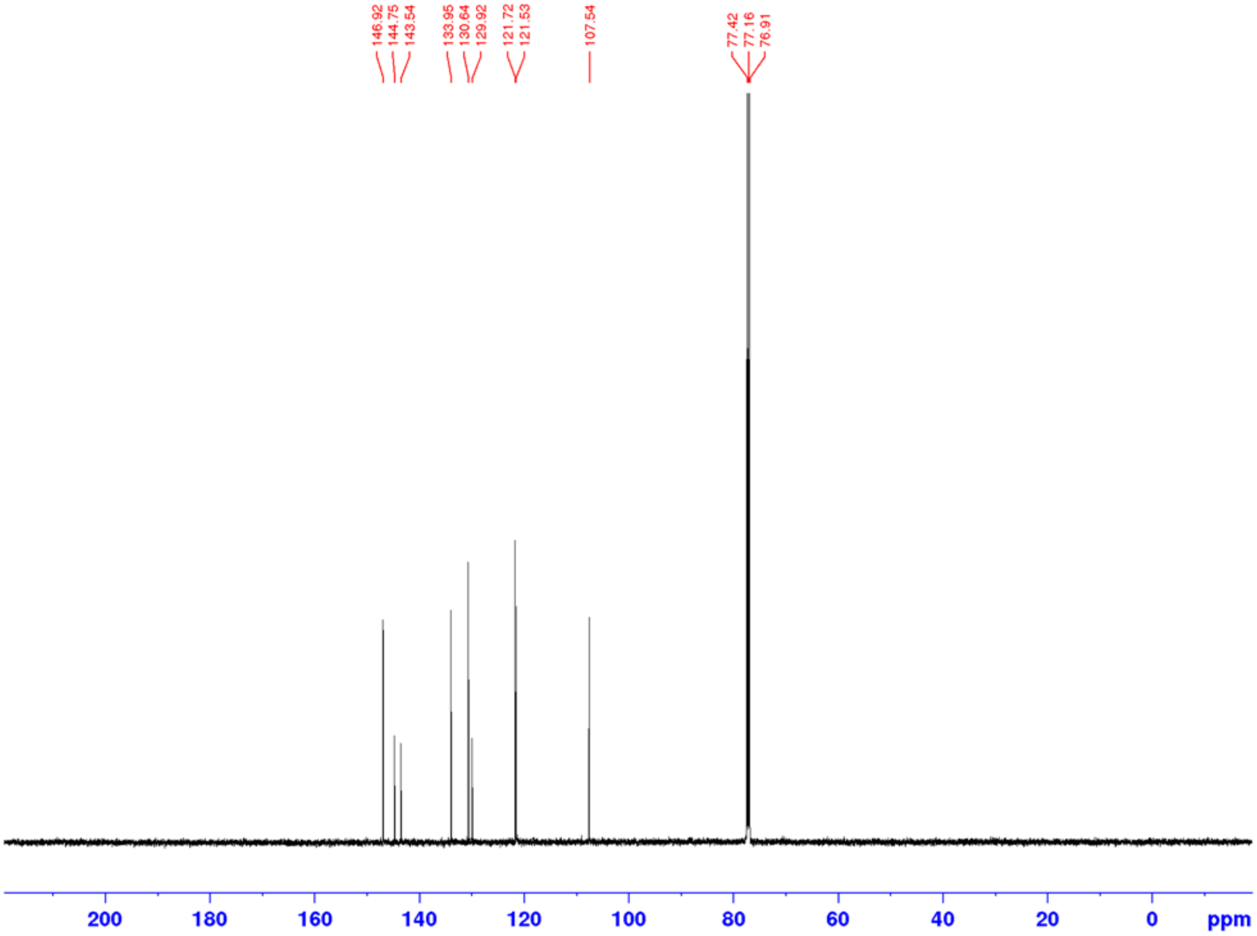
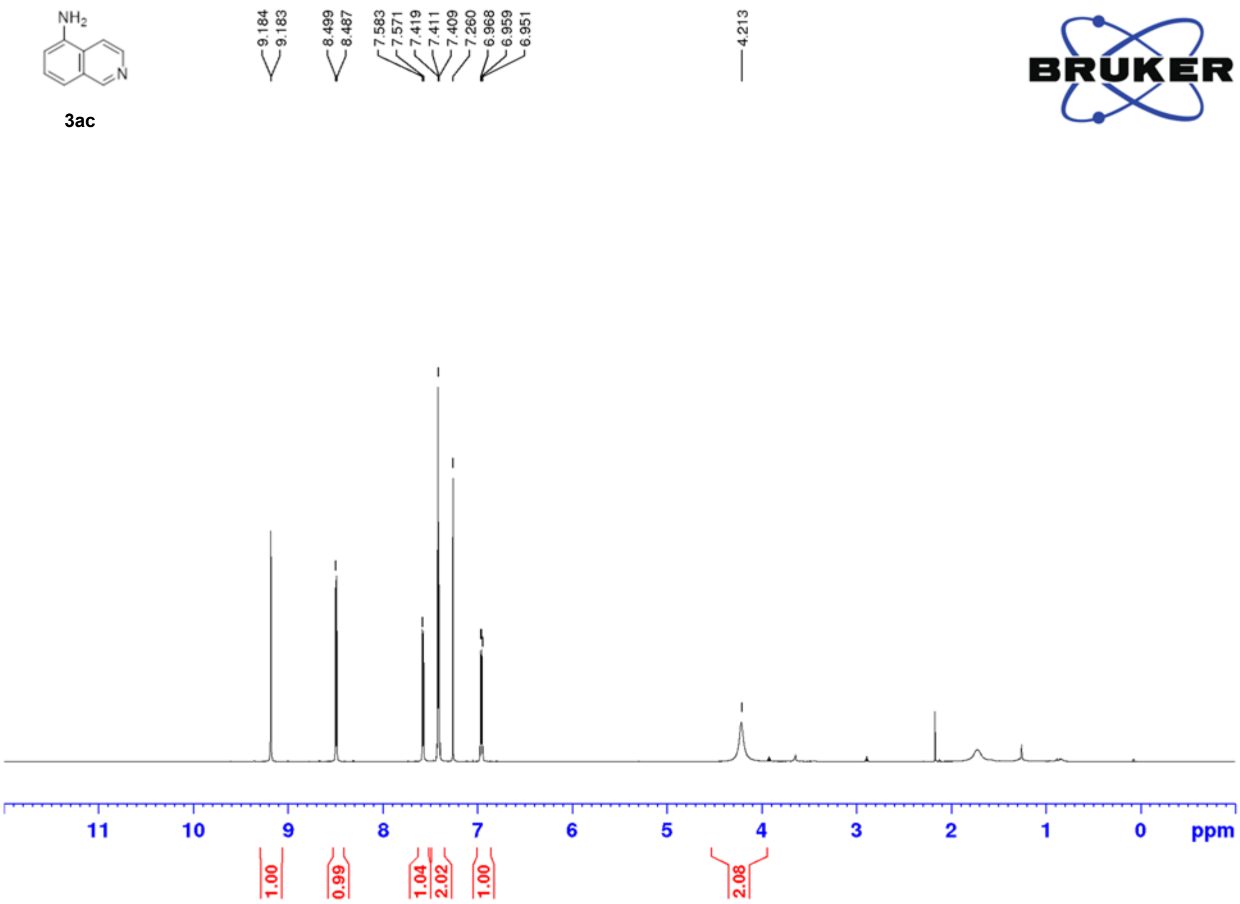
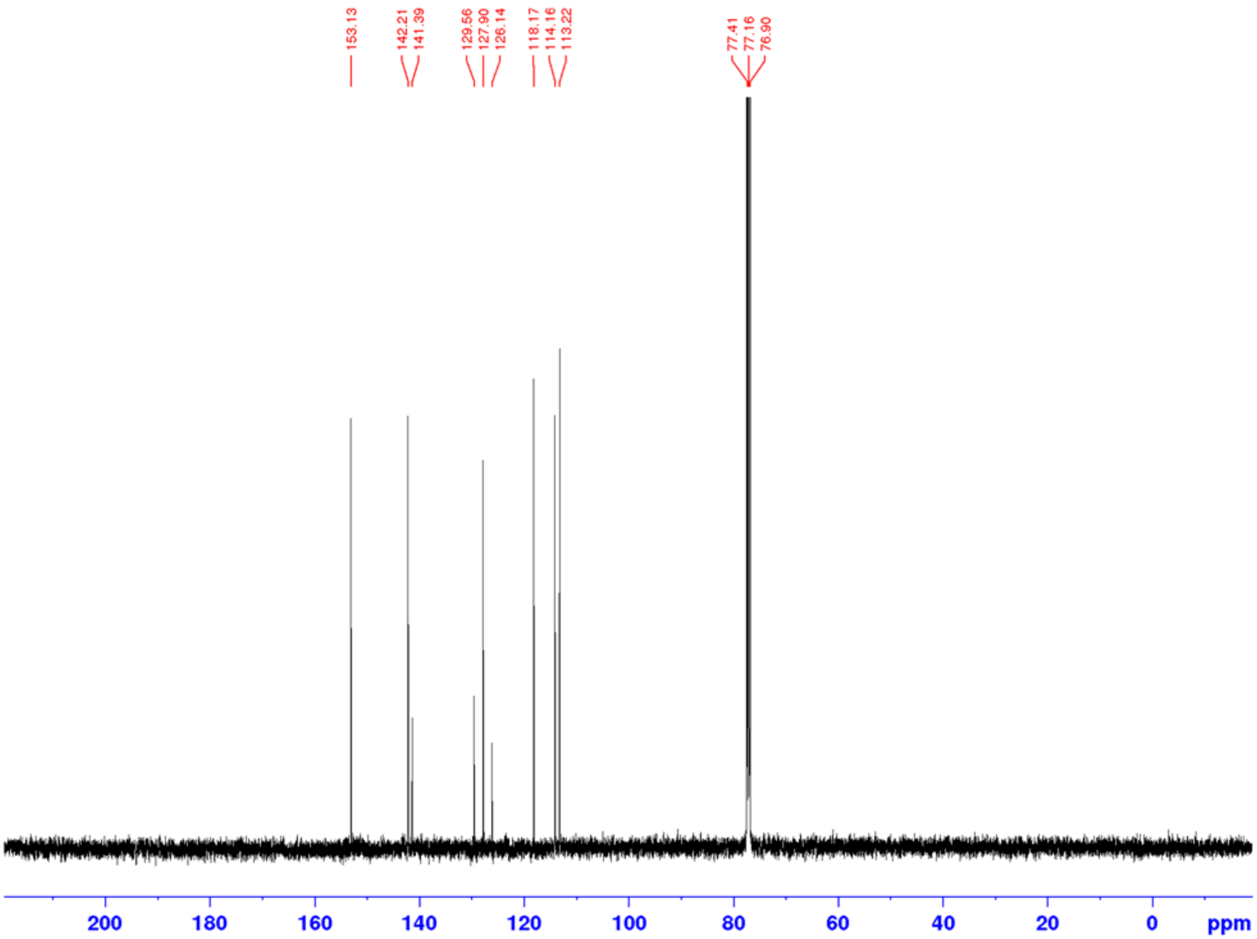
2.05
1.25
1.03
1.00
2.36

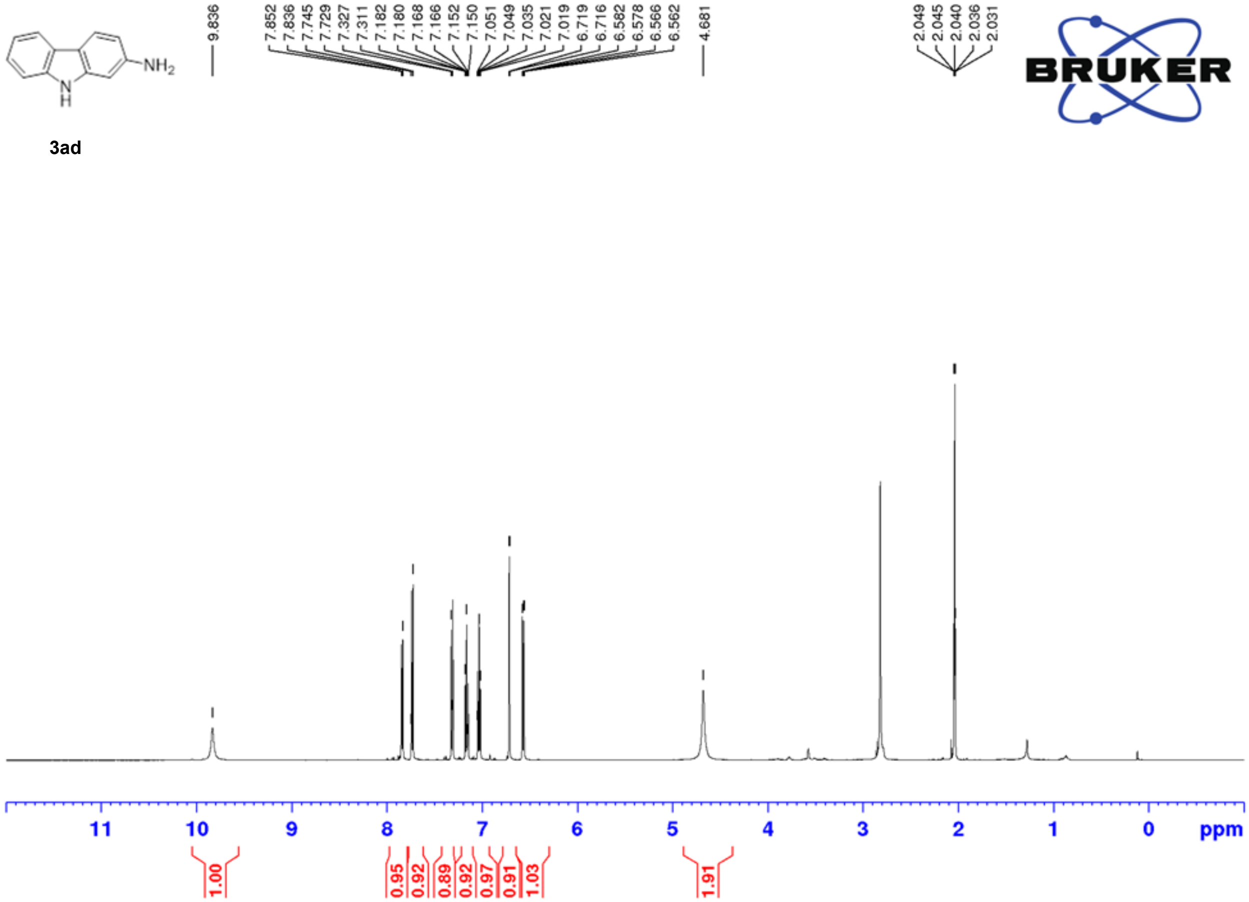
3ab


146.92
144.75
143.54
133.95
130.64
129.92
121.72
121.53
107.54
77.42
77.16
76.91
200
180
160
140
120
100
80
60
40
20
0
ppm


3ac

NH2
N
9.184
9.183
8.499
8.487
7.583
7.571
7.419
7.411
7.409
7.260
6.968
6.959
6.951
4.213
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.99
1.04
2.02
1.00
2.08


153.13
142.21
141.39
129.56
127.90
126.14
118.17
114.16
113.22
77.41
77.16
76.90
200
180
160
140
120
100
80
60
40
20
0
ppm



3ad

NH2
N
H
9.836
7.852
7.836
7.745
7.729
7.327
7.311
7.182
7.180
7.168
7.166
7.152
7.150
7.051
7.049
7.035
7.021
7.019
6.719
6.716
6.582
6.578
6.566
6.562
4.681
2.049
2.045
2.040
2.036
2.031
11
10
9
8
7
6
5
4
3
2
1
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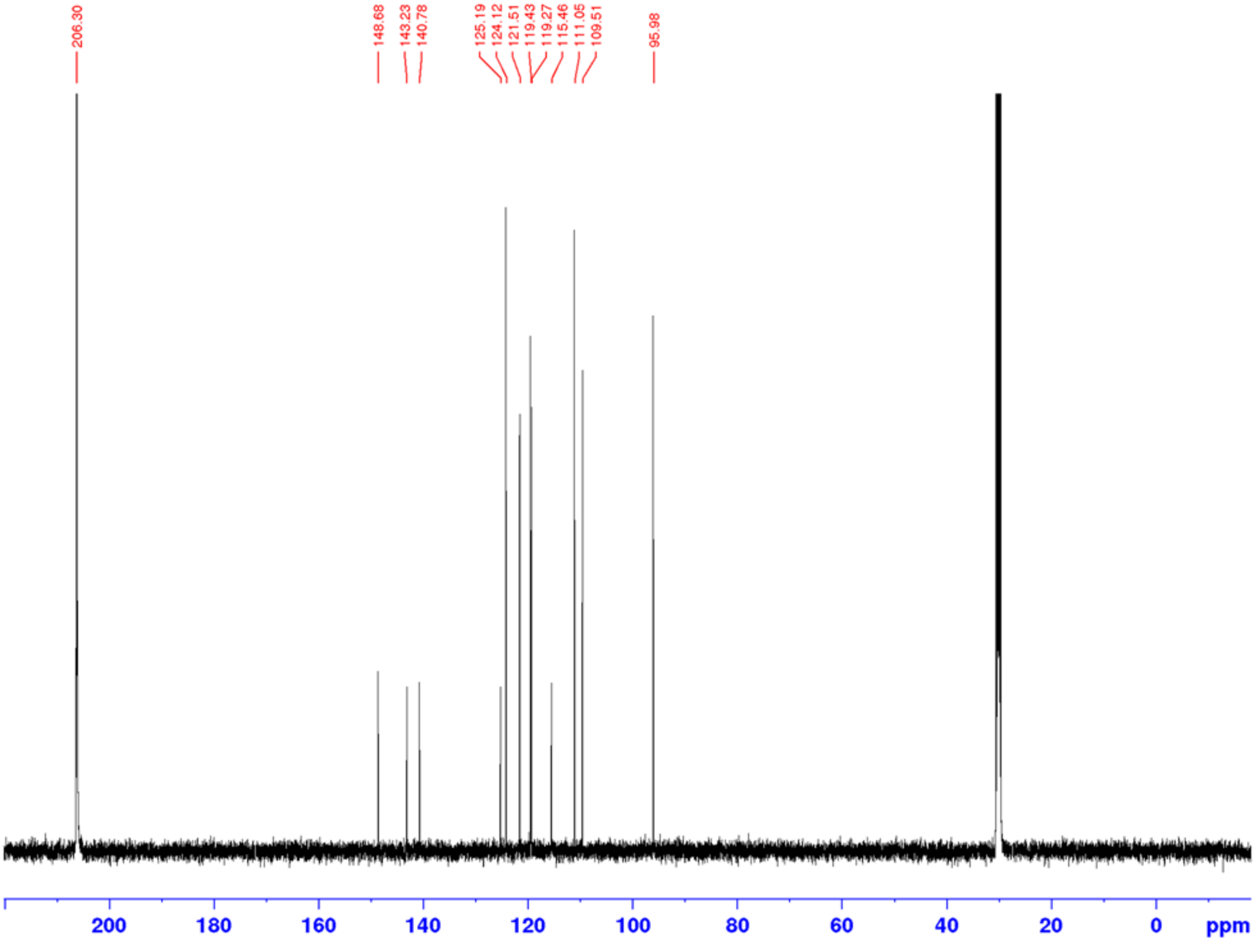
ppm
1.00
0.95
0.92
0.89
0.92
0.97
0.91
1.03
1.91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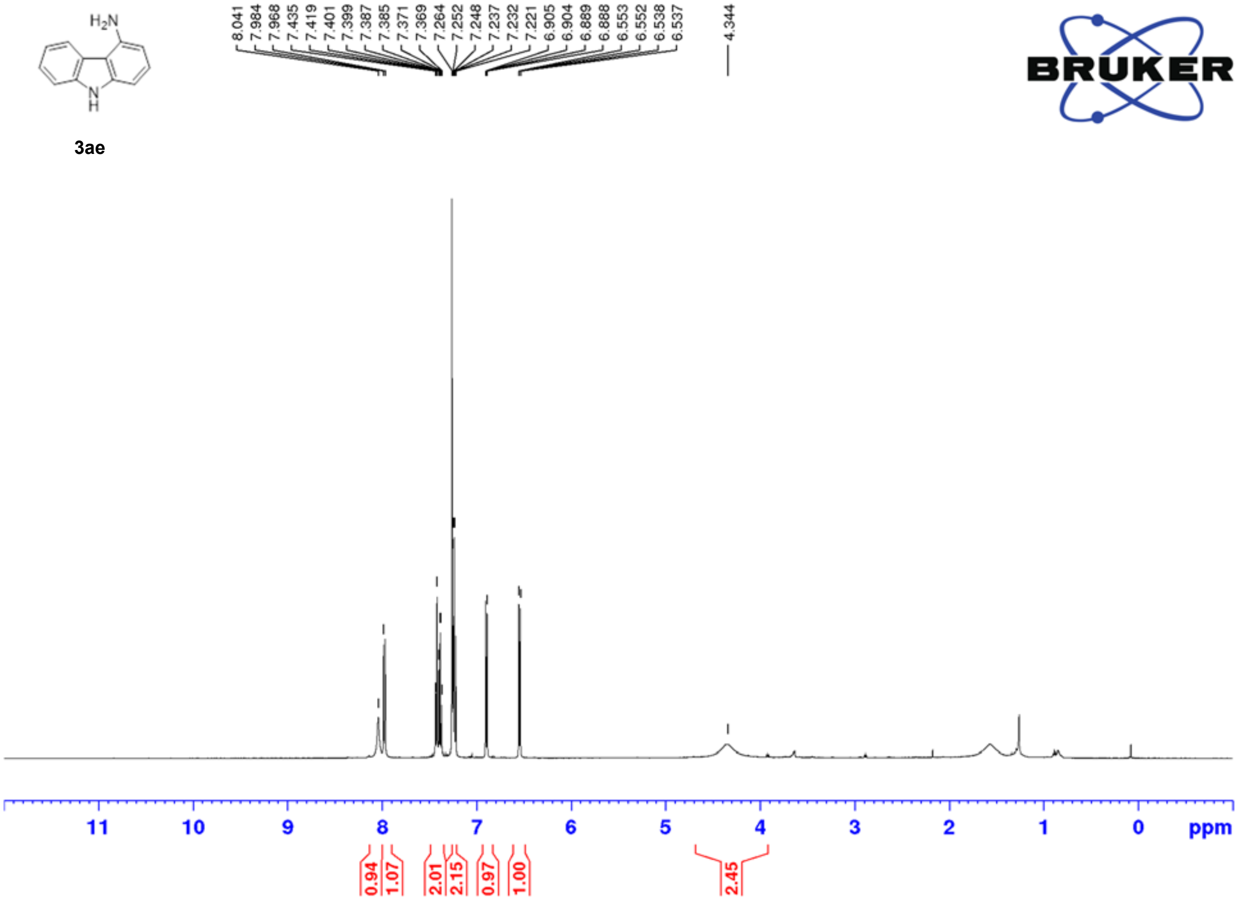
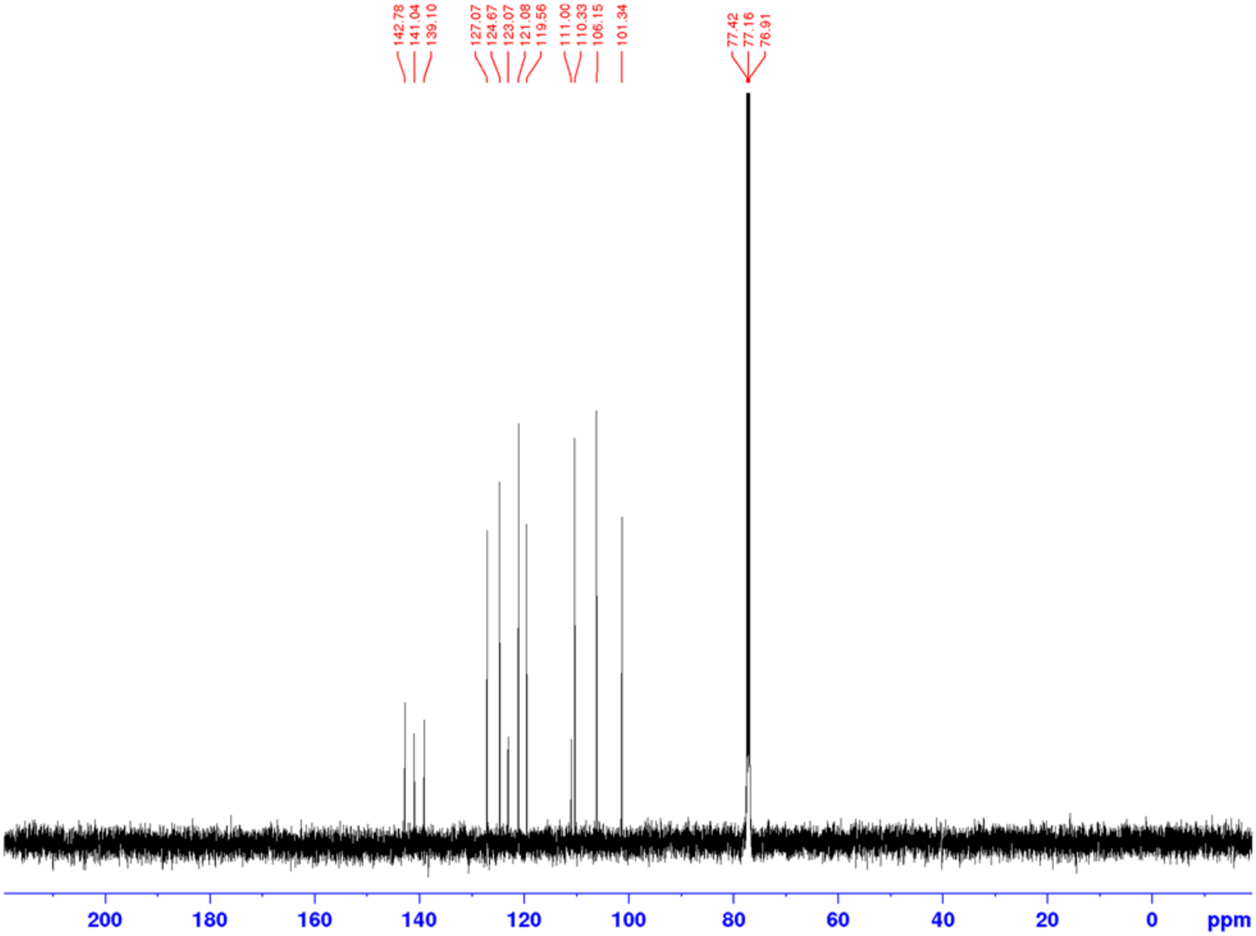
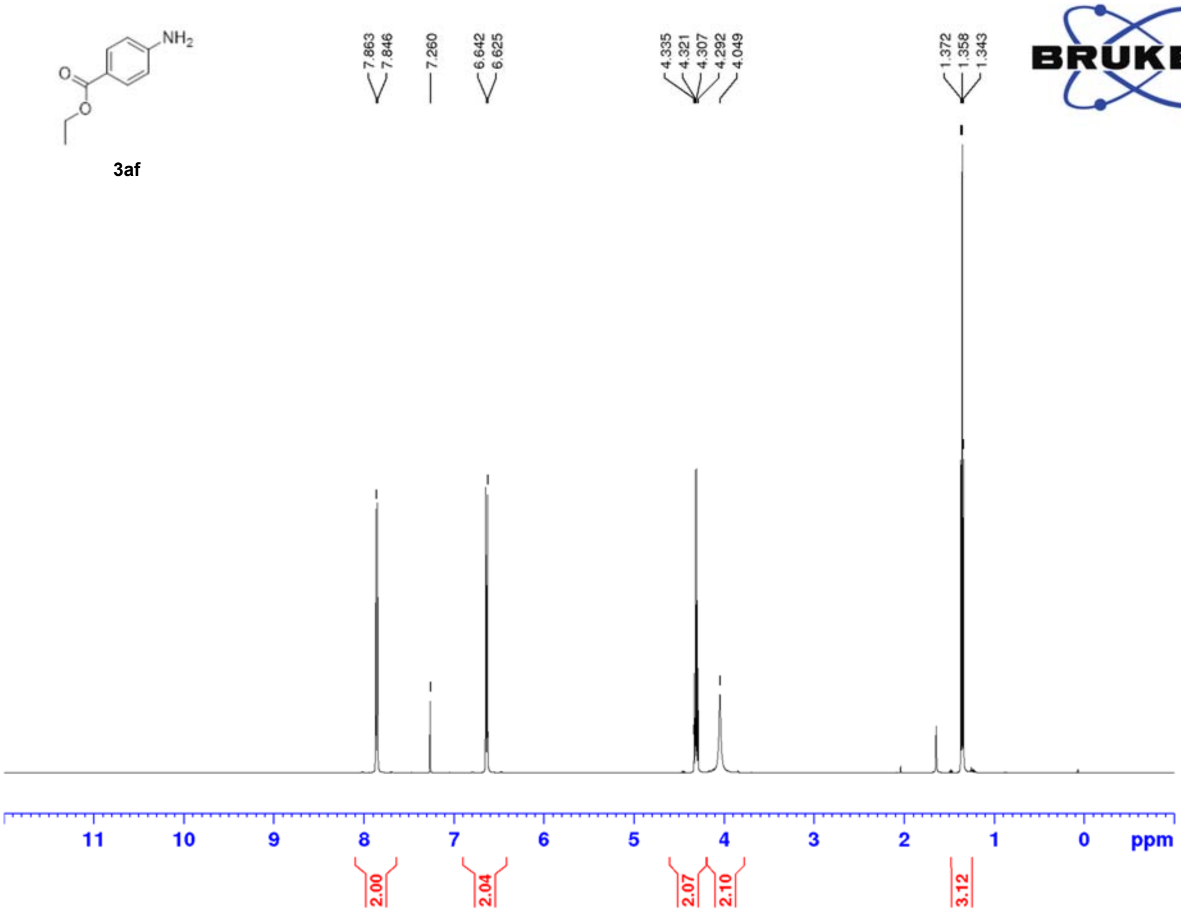
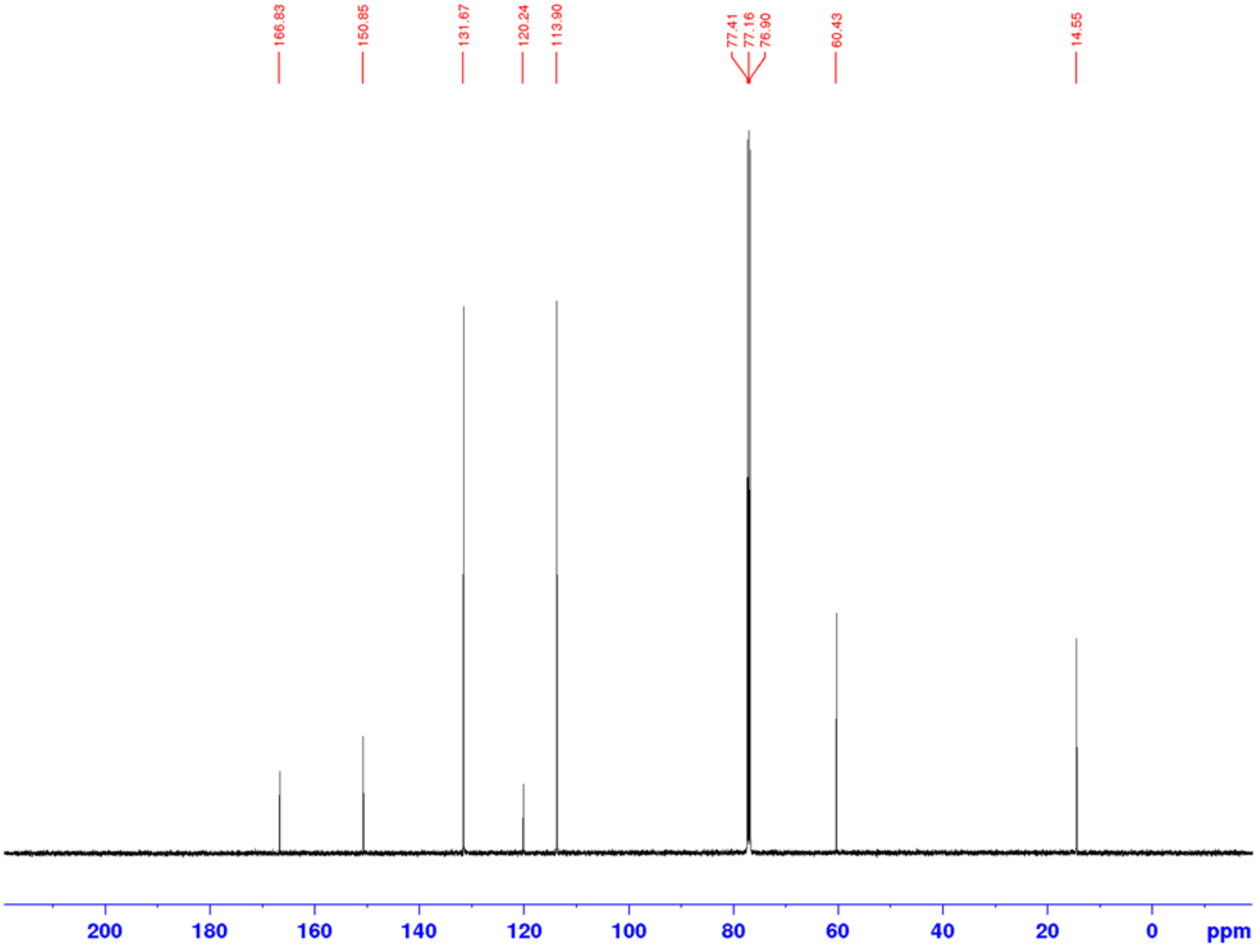
148.68
143.23
140.78
125.19
124.12
121.51
119.43
119.27
115.46
111.05
109.51
95.98
200
180
160
140
120
100
80
60
40
20
0
ppm

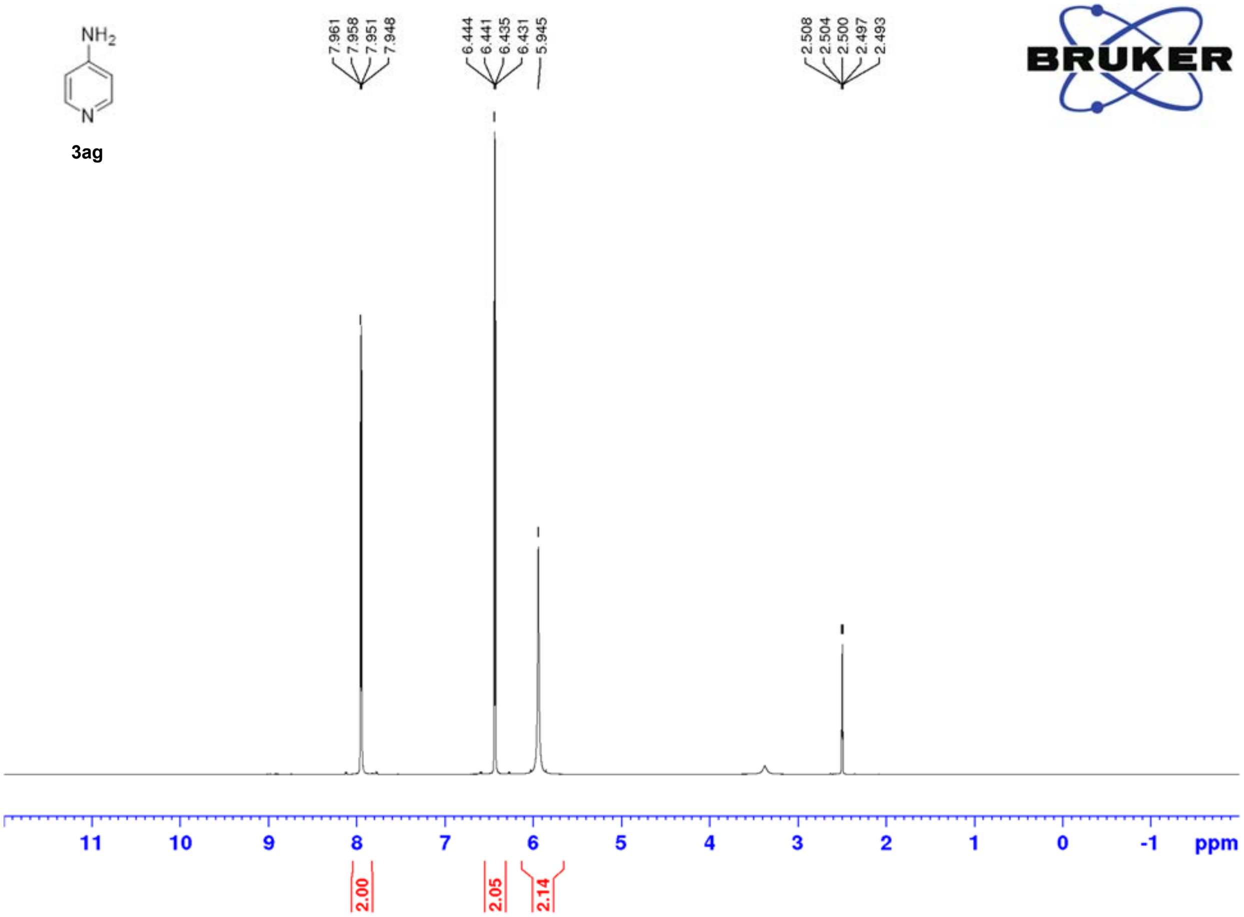

H$_2$N
N
H
3ae
8.041
7.984
7.968
7.435
7.419
7.401
7.399
7.387
7.385
7.371
7.369
7.264
7.252
7.248
7.237
7.232
7.221
6.905
6.904
6.889
6.888
6.553
6.552
6.538
6.537
4.344
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.94
1.07
2.01
2.15
0.97
1.00
2.45

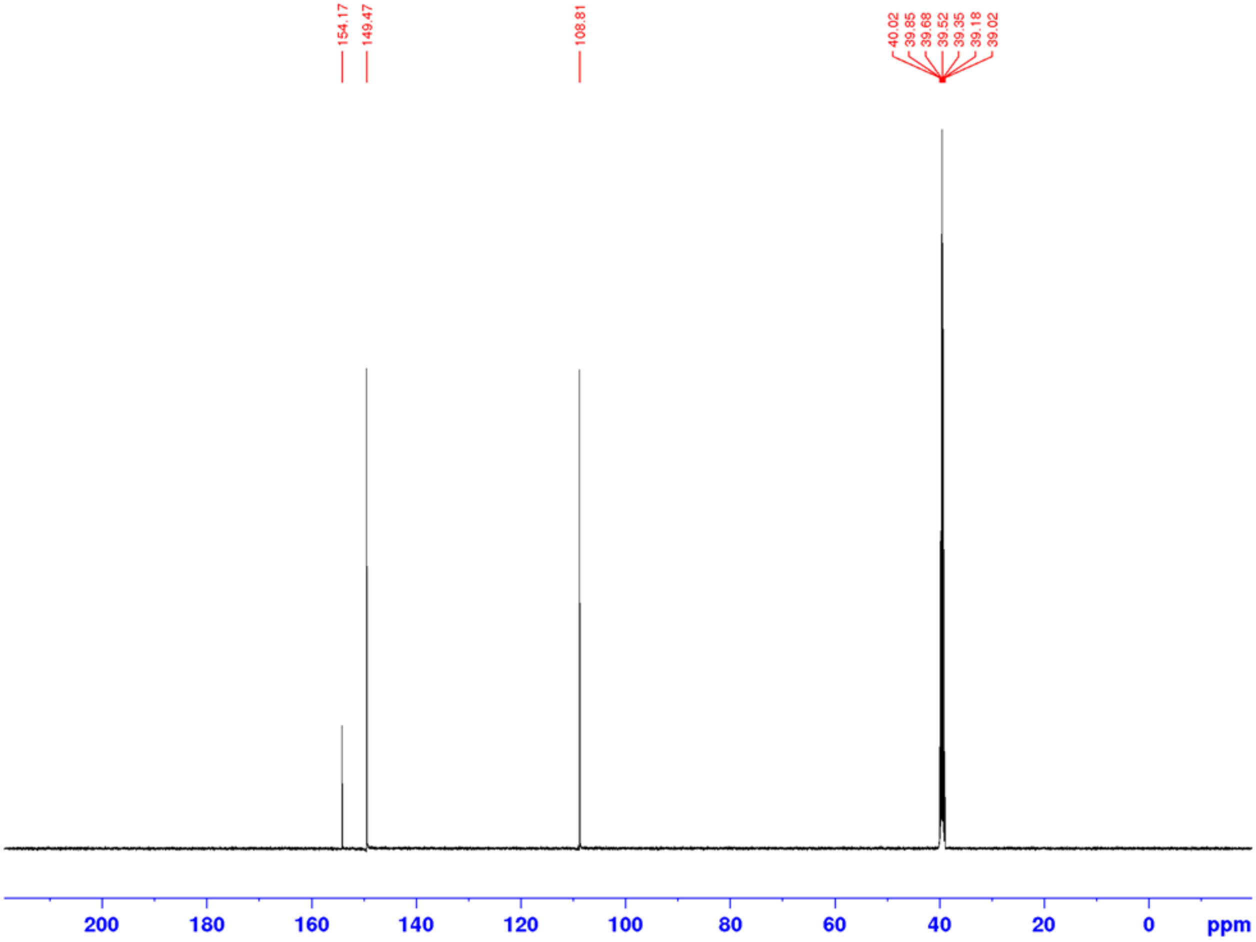

142.78
141.04
139.10
127.07
124.67
123.07
121.08
119.56
111.00
110.33
106.15
101.34
77.42
77.16
76.91
200
180
160
140
120
100
80
60
40
20
0
ppm

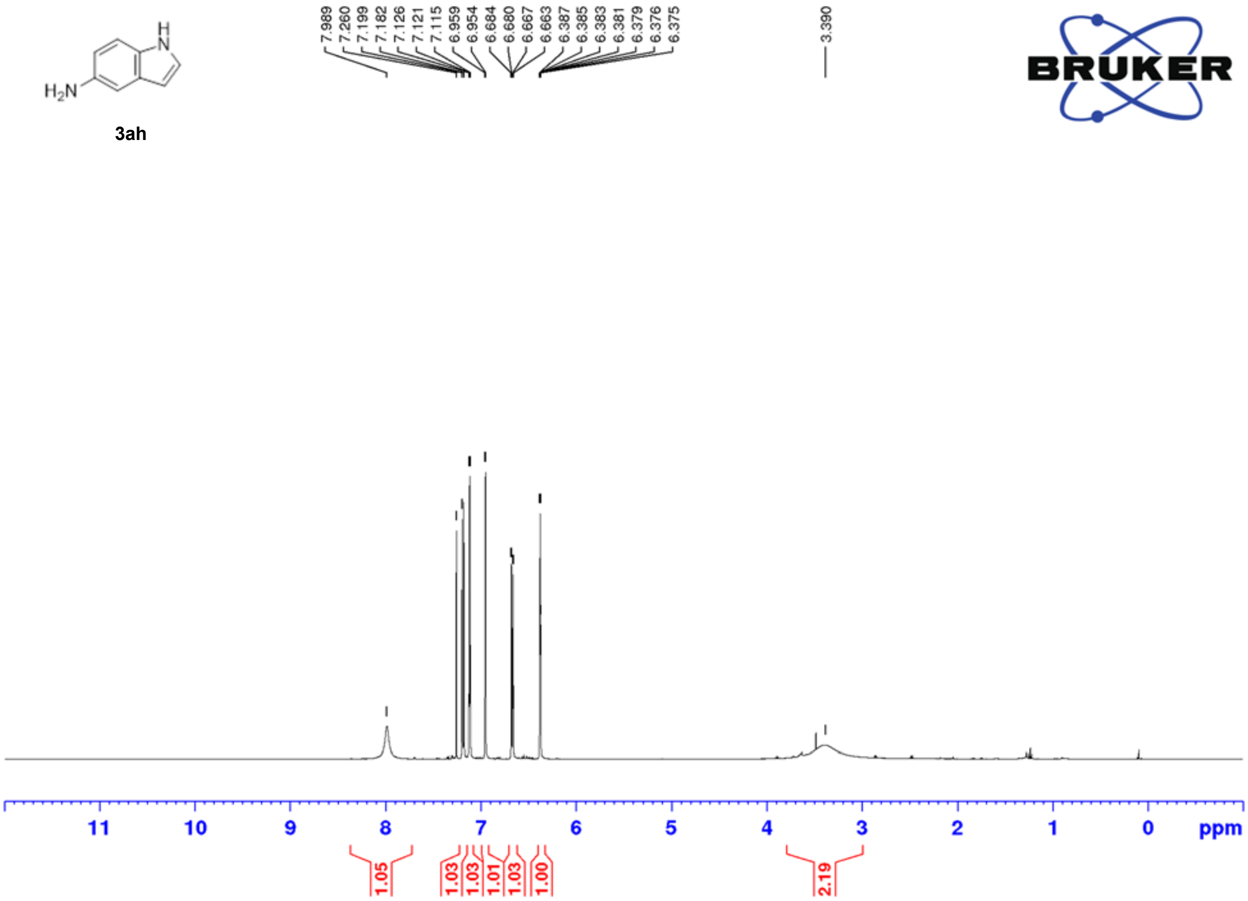

3af

NH2
O
O
7.863
7.846
7.260
6.642
6.625
4.335
4.321
4.307
4.292
4.049
1.372
1.358
1.343
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.04
2.07
2.10
3.12

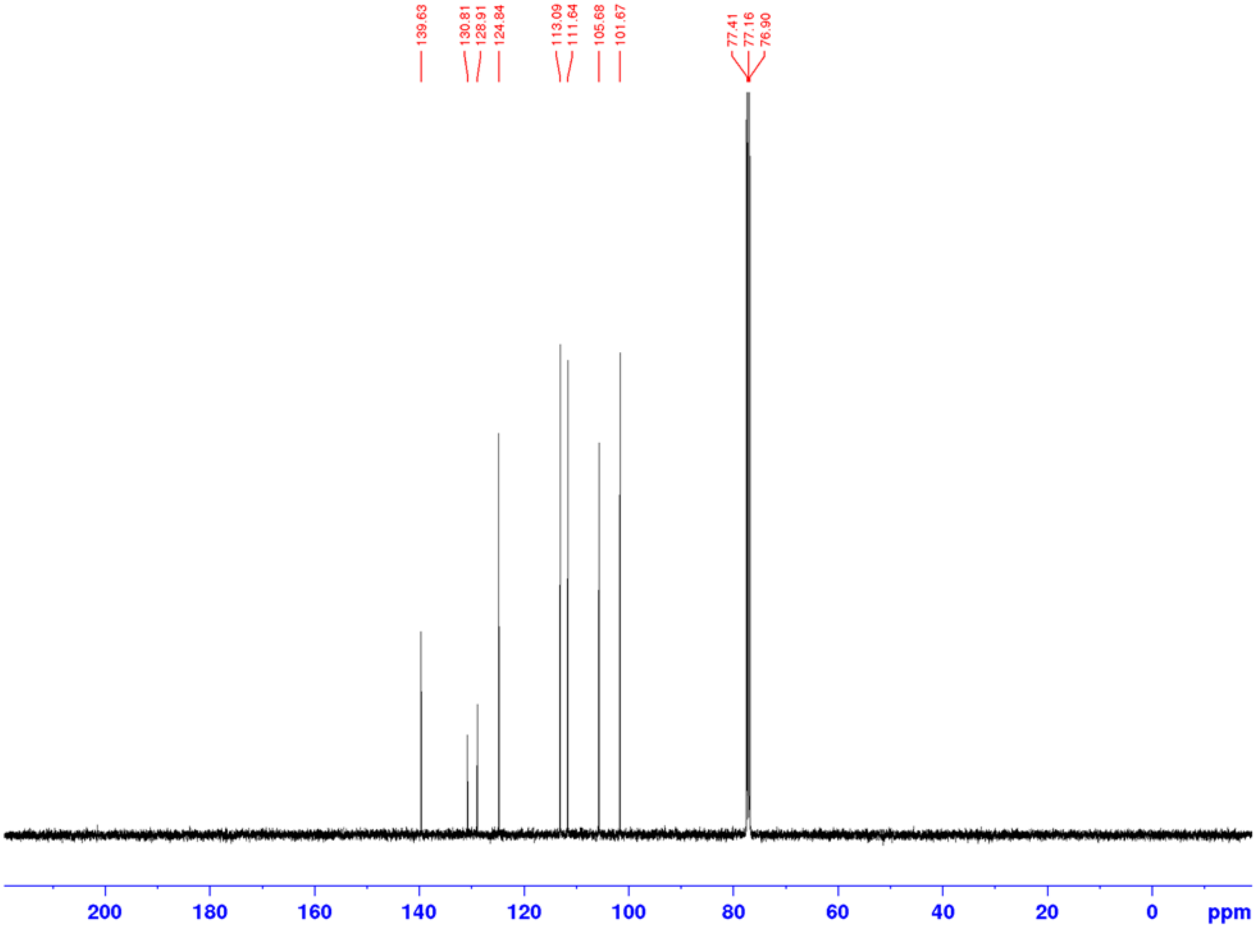

166.83
150.85
131.67
120.24
113.90
77.41
77.16
76.90
60.43
14.55
200
180
160
140
120
100
80
60
40
20
0
ppm

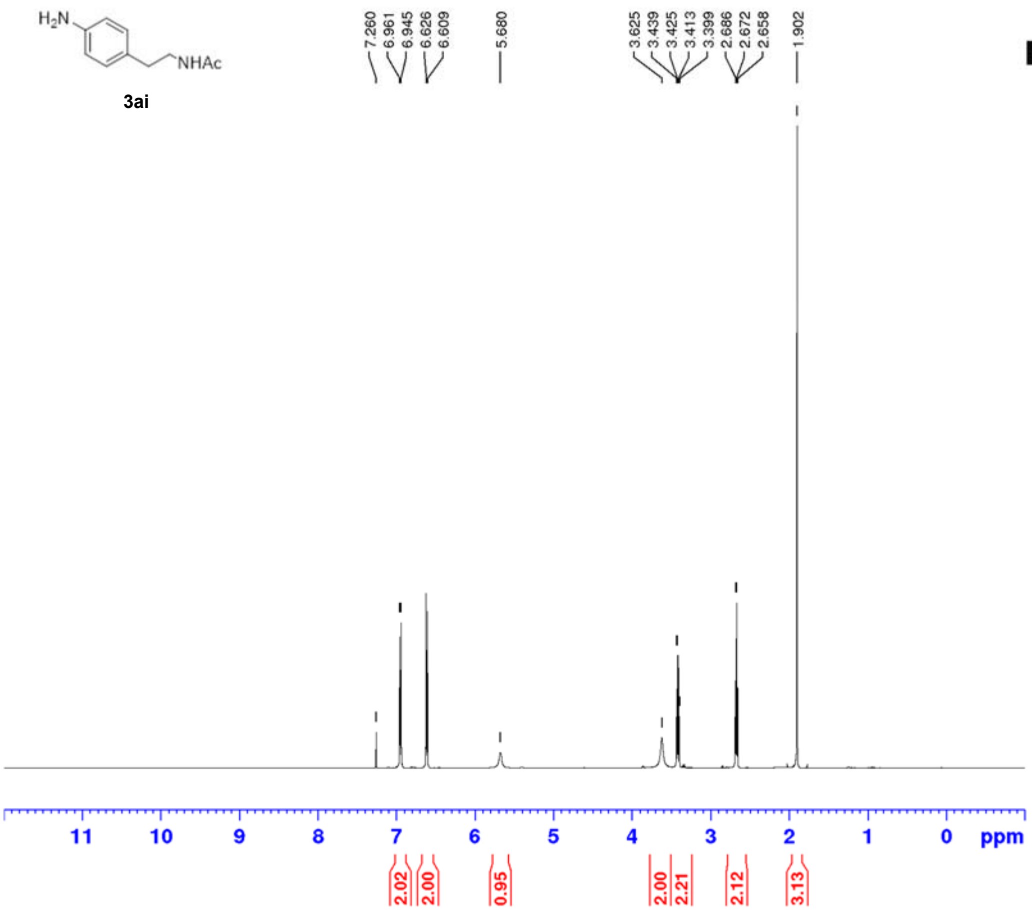

3ag
NH2
N
7.961
7.958
7.951
7.948
6.444
6.441
6.435
6.431
5.945
2.508
2.504
2.500
2.497
2.493
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
2.00
2.05
2.14


154.17
149.47
108.81
40.02
39.85
39.68
39.52
39.35
39.18
39.02
200
180
160
140
120
100
80
60
40
20
0
ppm


7.989
7.260
7.199
7.182
7.126
7.121
7.115
6.959
6.954
6.684
6.680
6.667
6.663
6.387
6.385
6.383
6.381
6.379
6.376
6.375
3.390
H
N
H₂N
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.05
1.03
1.03
1.01
1.03
1.00
2.19

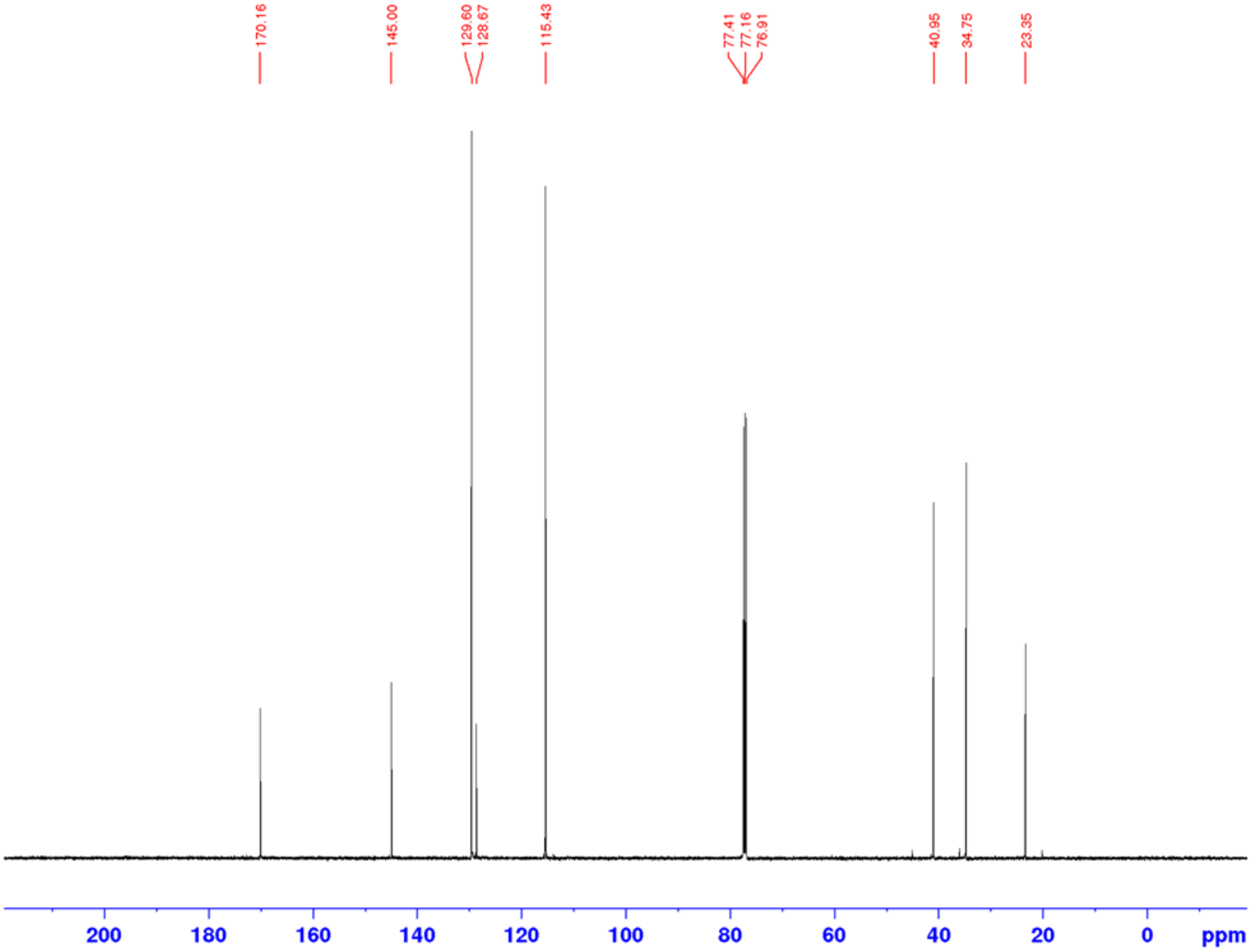
3ah

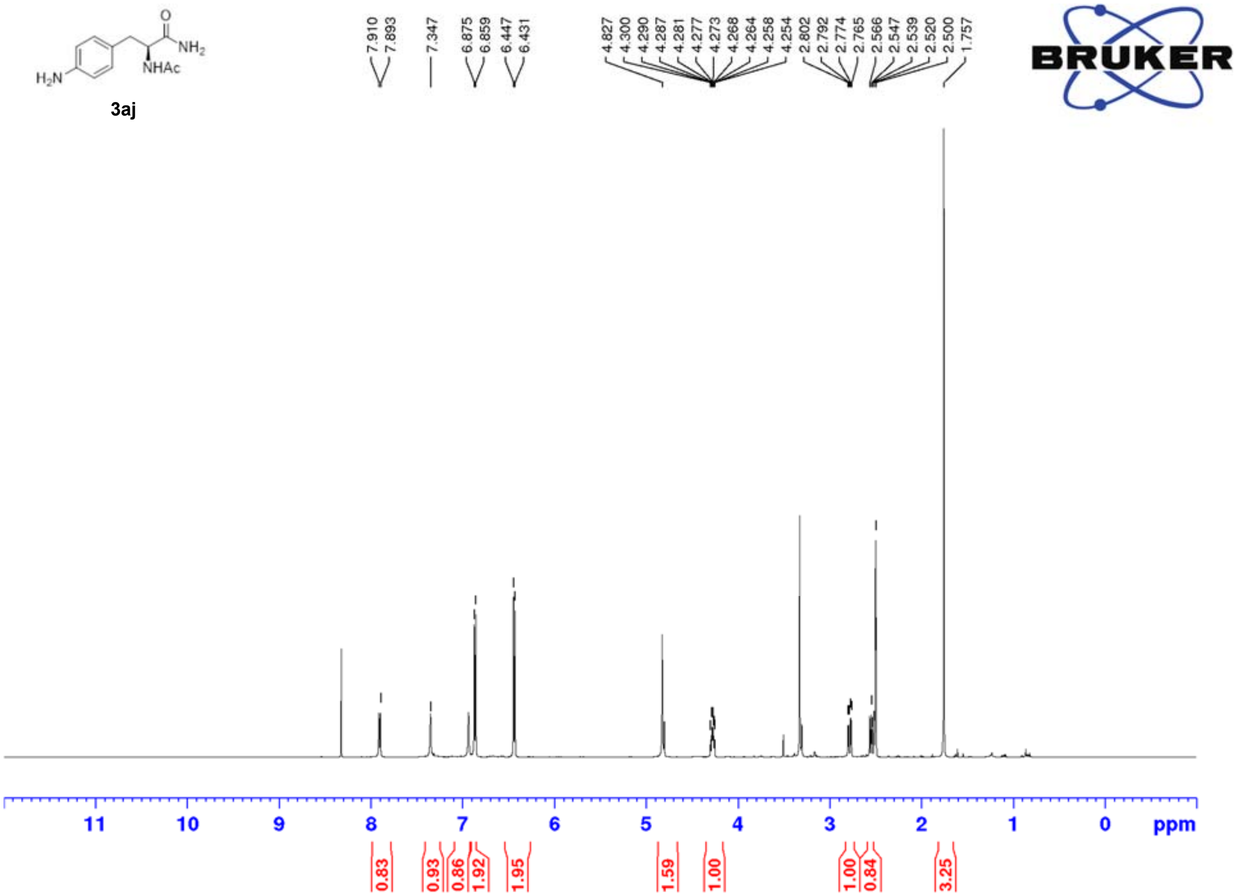

139.63
130.81
128.91
124.84
113.09
111.64
105.68
101.67
77.41
77.16
76.90
200
180
160
140
120
100
80
60
40
20
0
ppm



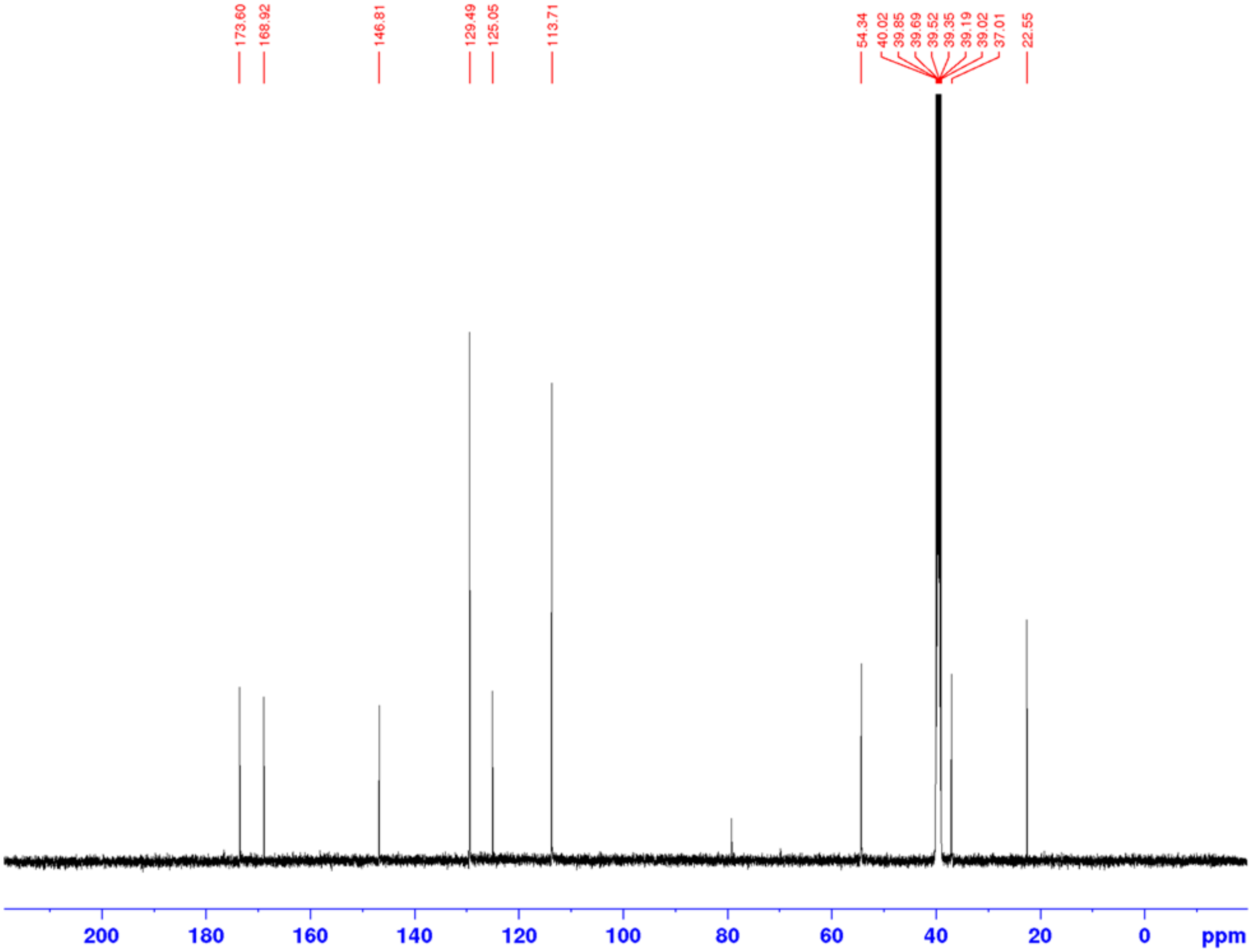
3ai

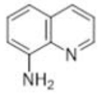
H2N
NHAc
7.260
6.961
6.945
6.626
6.609
5.680
3.625
3.439
3.425
3.413
3.399
2.686
2.672
2.658
1.902
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.02
2.00
0.95
2.00
2.21
2.12
3.13


170.16
145.00
129.60
128.67
115.43
77.41
77.16
76.91
40.95
34.75
23.35
200
180
160
140
120
100
80
60
40
20
0
ppm

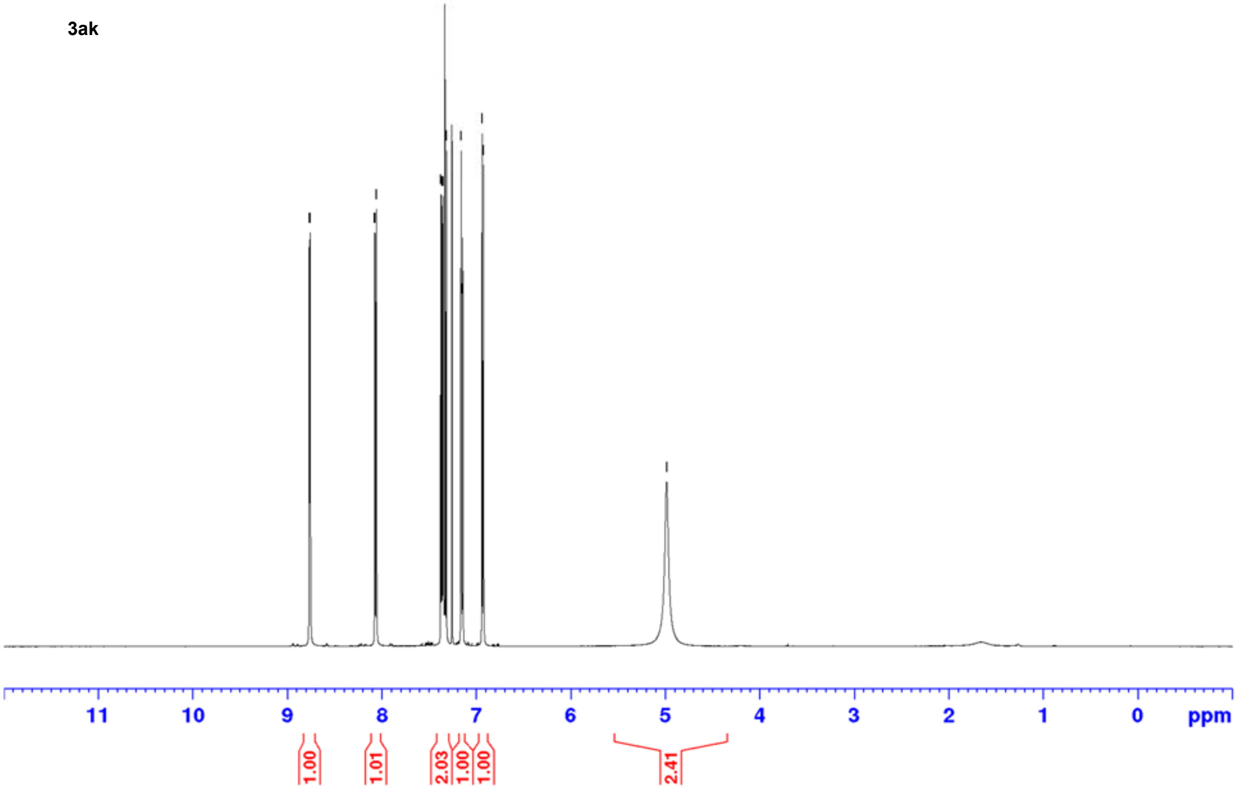

H2N
O
NH2
NHAc
7.910
7.893
7.347
6.875
6.859
6.447
6.431
4.827
4.300
4.290
4.287
4.281
4.277
4.273
4.268
4.264
4.258
4.254
2.802
2.792
2.774
2.765
2.566
2.547
2.539
2.520
2.500
1.757
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.83
0.93
0.86
1.92
1.95
1.59
1.00
1.00
0.84
3.25

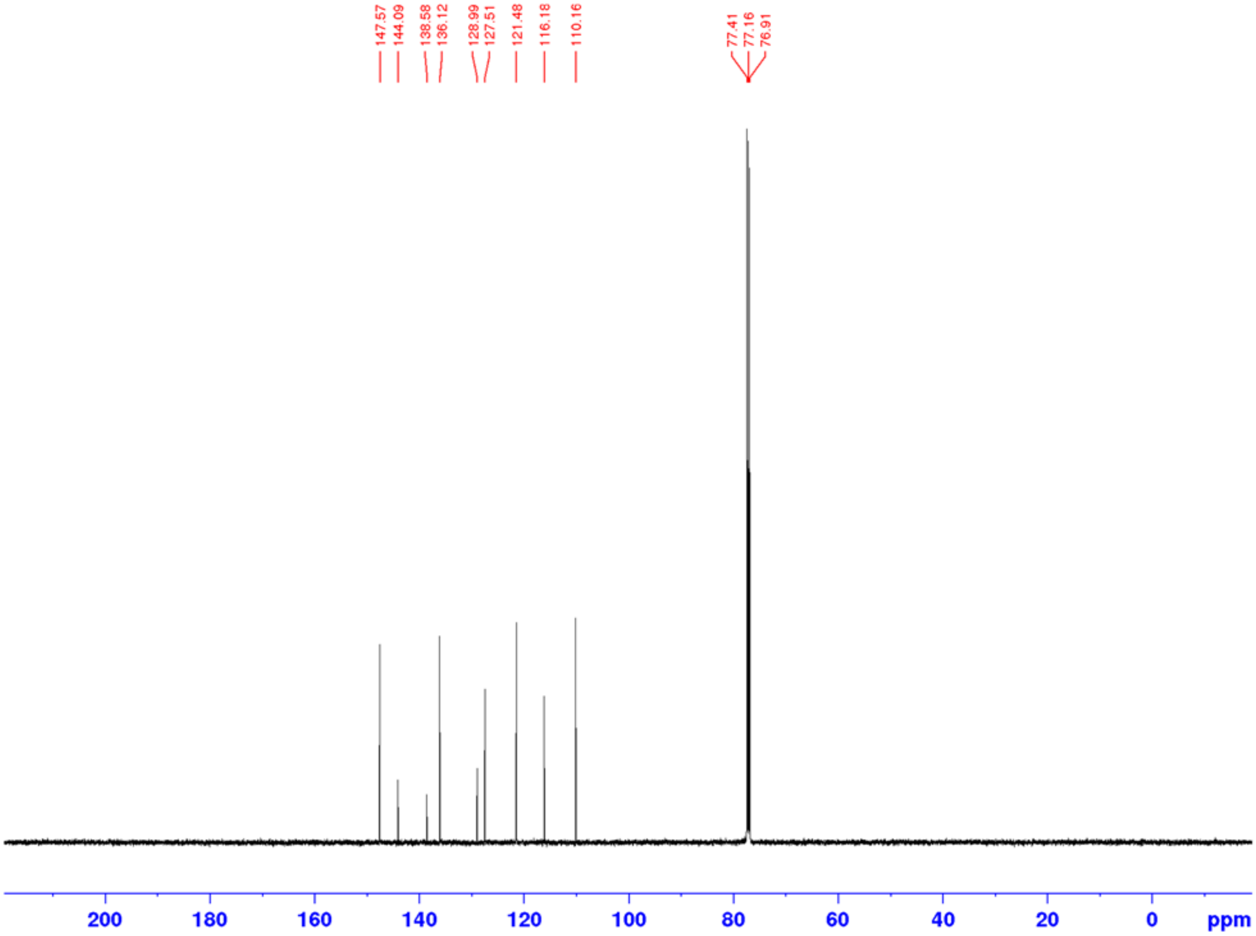
3aj


173.60
168.92
146.81
129.49
125.05
113.71
54.34
40.02
39.85
39.69
39.52
39.35
39.19
39.02
37.01
22.55
200
180
160
140
120
100
80
60
40
20
0
ppm


N
NH2

3ak


8.771
8.767
8.762
8.759
8.078
8.075
8.062
8.058
7.379
7.371
7.362
7.354
7.351
7.335
7.319
7.260
7.164
7.162
7.148
7.146
6.942
6.940
6.927
6.925
4.988
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
2.03
1.00
1.00
2.41


147.57
144.09
138.58
136.12
128.99
127.51
121.48
116.18
110.16
77.41
77.16
76.91
200
180
160
140
120
100
80
60
40
20
0
ppm