SUPPORTING INFORMATION FOR

Bridging Amines with CO_2:

Organocatalyzed Reduction of CO_2 to Aminals

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1. Experimental details

1.1. General considerations

All reactions and manipulations were performed at 20 ºC in a recirculating mBraun LabMaster DP inert atmosphere (Ar) drybox and vacuum Schlenk lines. Glassware was dried overnight at 120 ºC before use. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker DPX 200 MHz spectrometer. Chemical shifts for ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced to solvent impurities. Mass spectrometer data were collected on a Shimadzu GCMS-QP2010 Ultra gas chromatograph mass spectrometer equipped with a Supelco SLB^{TM}-ms fused silica capillary column (30 m x 0.25 mm x 0.25 μm). Unless otherwise noted, reagents were purchased from commercial suppliers and dried over 4 Å molecular sieves prior to use. 4 Å molecular sieves (Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use. d_8-tetrahydrofuran (d_8-THF) and d_8-toluene were dried over a sodium(0)/benzophenone mixture and distilled before use. CD_3CN was dried over CaH_2 and distilled before use. Carbon dioxide was purchased from Messer in a 5.5 purity gas bottle.

Crystallography. The data were collected at 150(2) K with a Nonius Kappa-CCD area detector diffractometer[1] using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystals were introduced into glass capillaries with a protective coating of Paratone-N oil (Hampton Research). The unit cell parameters were determined from ten frames, then refined on all data. The data (combinations of φ- and ω-scans with a minimum redundancy of 4 for 90% of the reflections) were processed with HKL2000.[2] Absorption effects in **2h** were corrected empirically with the program SCALEPACK.[2] The structures were solved with SHELXT[3] and refined by full-matrix least-squares on F^2 with SHELXL-2014.[4] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at calculated positions and were treated as riding atoms with an isotropic

displacement parameter equal to 1.2 times that of the parent atom (1.5 for CH_3, with optimized geometry). Crystal data and structure refinement parameters are given in Table 1. The molecular plots were drawn with ORTEP-3.[5]

1.2. Screening of hydrosilanes

Table S1 presents a screening of hydrosilanes for the coupling of amine **1a** to aminal **2a** with **TBD** as catalyst (5 mol%).

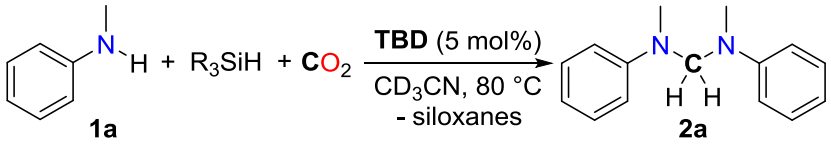
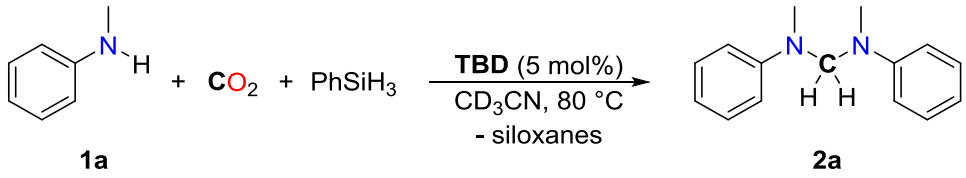


Table S1. Screening of hydrosilanes for the coupling of amines into aminals

Entry	Catalyst (mol%)	Reductant	Time (h)	Yield (%)
1	**TBD** (5)	$PhSiH_3$	3.0	91
2	**TBD** (5)	Ph_2SiH_2	5.5	80
3	**TBD** (5)	Et_3SiH	24	0
4	**TBD** (5)	$(EtO)_3SiH$	24	0
5	**TBD** (5)	PMHS	96	<5
6	**TBD** (5)	TMDS	96	0

Reaction conditions: NMR tube (2.5 mL), catalyst, amine (0.10 mmol), hydrosilane (6 eq. "Si-H"), CD_3CN (0.30 mL), CO_2 (1 bar). Yields determined by ^1H NMR with Ph_2CH_2 as internal standard.

1.3. Procedure for the TBD-catalyzed formation of symmetrical aminals



The procedure is detailed for the conversion of *N*-methylaniline (**1a)** to *N*,*N*-dimethyl-*N*,*N*-diphenylmethanediamine (**2a**), using **TBD** as catalyst. A 2.5 mL NMR tube equipped with a J. Young valve is charged successively with **TBD** (0.70 mg, 0.0050 mmol, 5 mol%), CD_3CN (0.30 mL), *N*-methylaniline (10.8 µL, 0.100 mmol, 1 eq), $PhSiH_3$ (24.7 µL, 0.200 mmol, 2 eq, 6 eq "Si-H") and Ph_2CH_2 as internal standard (16.7 µL, 0.100 mmol, 1 eq). The reaction mixture is frozen with liquid nitrogen, then degassed, exposed to a carbon dioxide atmosphere (1 bar) and warmed up to RT (under these conditions, CO_2 is introduced at

approximatively 1 eq). The flask is sealed and heated to 80 °C. The evolution of the formation of **2a** is monitored by ^{1}H NMR and the yield is determined using the internal standard.

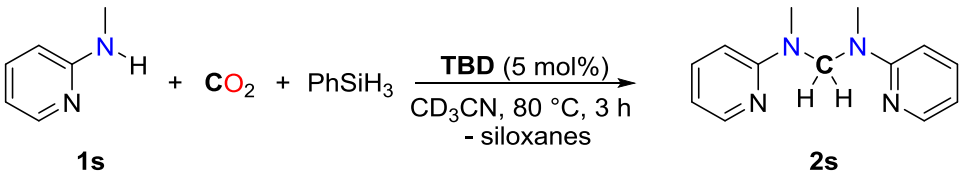
Procedure for the isolation of aminals: the volatiles were removed under *vacuum*. The crude mixture is then purified by flash chromatography over silica gel (*NB: the acidity of the silica gel was quenched by impregnation with 100 mL of the eluent + 10% NEt_3 for 1 h prior to the separation)* (eluent: AcOEt/*n*-pentane: 2/98).

2s: 88% isolated yield (white solid, 20 mg, yield over two runs).

2h: 84% isolated yield (beige solid, 24.1 mg, yield over two runs).

When an isolated yield was not performed, NMR data of the product were compared with the corresponding aminal samples (see section *1.8.*) and the yields determined by NMR with respect to the internal standard.

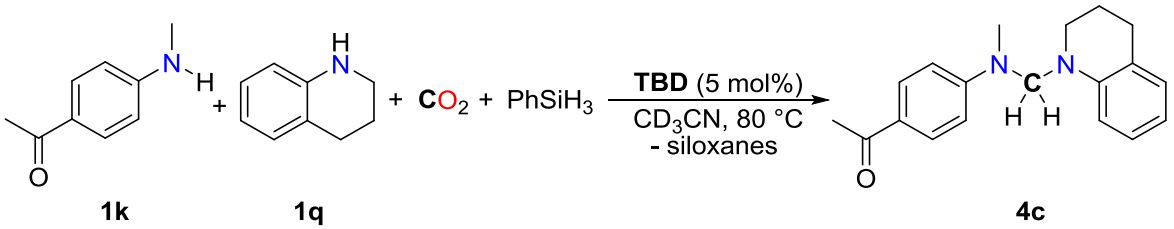
Scale-up reaction



1s **2s**

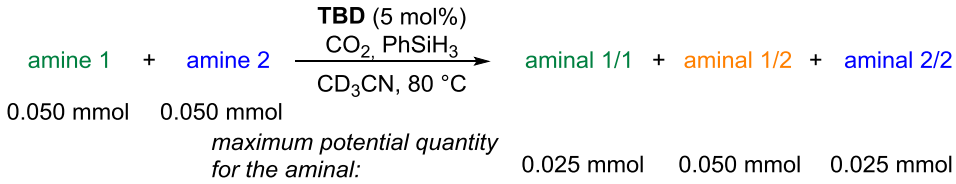
The procedure is detailed for the conversion of 2-aminomethylpyridine (**1s)** to *N*,*N*'-dimethyl-*N*,*N*'-di(pyridin-2-yl)methanediamine (**2s**), using **TBD** as catalyst. A 16 mL Schlenk flask equipped with a J. Young valve is charged successively with **TBD** (4.5 mg, 0.032 mmol, 5 mol%), CH_3CN (1.90 mL), **1s** (65.8 µL, 0.640 mmol, 1 eq), and $PhSiH_3$ (158 µL, 1.28 mmol, 2 eq, 6 eq ”Si-H”). The reaction mixture is frozen with liquid nitrogen, then degassed, exposed to a carbon dioxide atmosphere (1 bar) and warmed up to RT. The flask is sealed and heated to 80 °C. The procedure for the isolation of **2s** is described thereabove. **2s** was obtained as a white powder in 94% isolated yield (68.7 mg).

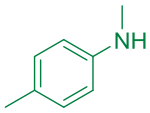
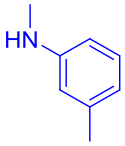
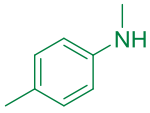
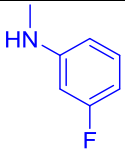
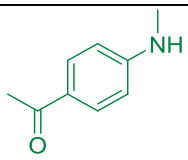
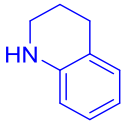
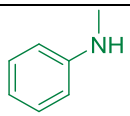
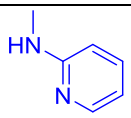
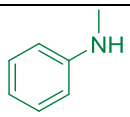
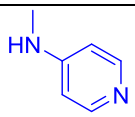
1.4. Procedure for the TBD-catalyzed formation of unsymmetrical aminals



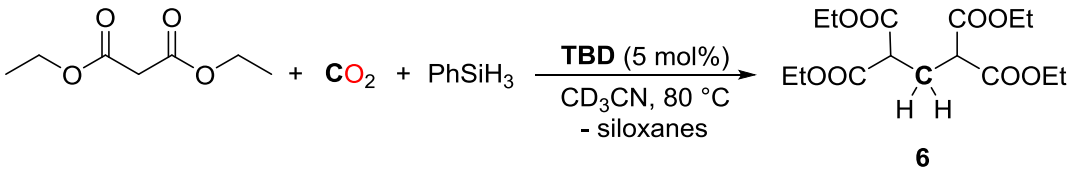
The procedure is detailed for the conversion of 4-acetyl-*N*-methylaniline (**1k)** and 1,2,3,4-tetrahydroquinoline (**1q**) to **4c**, using **TBD** as catalyst. A 2.5 mL NMR tube equipped with a J. Young valve is charged successively with **TBD** (0.70 mg, 0.0050 mmol, 5 mol%), CD_3CN (0.30 mL), 4-acetyl-*N*-methylaniline (7.5 mg, 0.050 mmol, 0.5 eq), 1,2,3,4-tetrahydroquinoline (6.3 µL, 0.050 mmol, 0.5 eq), $PhSiH_3$ (24.7 µL, 0.200 mmol, 2 eq, 6 eq "Si-H") and Ph_2CH_2 as internal standard (16.7 µL, 0.100 mmol, 1 eq). The reaction mixture is frozen with liquid nitrogen, then degassed, exposed to a carbon dioxide atmosphere (1 bar) and warmed up to RT. The flask is sealed and heated to 80 °C. The evolution of the formation of **4c** is monitored by ^{1}H NMR and the yield and products distribution are determined using the internal standard. See Table S2 below for details. ^{1}H NMR spectra of the reaction media are provided in section 3.2.

Table S2. Yield determination for unsymmetrical aminals



Entry	Amine 1	Consum-ption (mmol)	Conv.	Amine 2	Consum-ption (mmol)	Conv.	Aminal 1/1 formed (mmol)	Yield 1/1	Aminal 1/2 formed (mmol)	Yield 1/2	Aminal 2/2 formed (mmol)	Yield 2/2
1		0.044	**88%**		0.044	**88%**	0.011	**44%**	0.022	**44%**	0.011	**44%**
2		0.032	**64%**		0.030	**60%**	0.0060	**24%**	0.020	**40%**	0.0050	**20%**
3		0.045	**90%**		0.047	**94%**	0.0050	**20%**	0.035	**69%**	0.0060	**24%**
4		0.044	**88%**		0.050	**100%**	0.0015	**6%**	0.041	**82%**	0.0045	**18%**
5		0.042	**84%**		0.031	**62%**	0.0055	**22%**	0.031	**61%**	0.00	**0%**

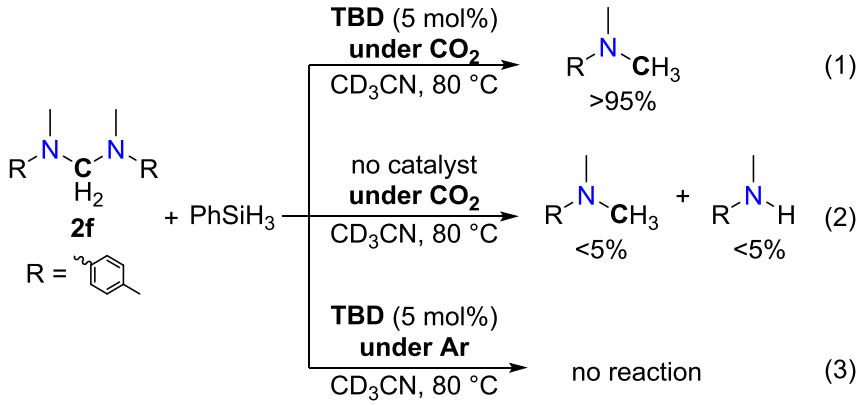
1.5. Procedure for the TBD-catalyzed coupling of diethyl malonate



6

A 2.5 mL NMR tube equipped with a J. Young valve is charged successively with **TBD** (0.70 mg, 0.0050 mmol, 5 mol%), CD_3CN (0.30 mL), diethyl malonate (15.2 µL, 0.100 mmol, 1 eq), $PhSiH_3$ (24.7 µL, 0.200 mmol, 2 eq, 6 eq "Si-H") and Ph_2CH_2 as internal standard (16.7 µL, 0.100 mmol, 1 eq). The reaction mixture is frozen with liquid nitrogen, then degassed, exposed to a carbon dioxide atmosphere (1 bar) and warmed up to RT (under these conditions, CO_2 is introduced at approximatively 1 eq). The tube is sealed and heated to 80 °C. The formation of **5** is monitored by ^{1}H NMR and the yield is determined using the internal standard. NMR data were compared with literature.[6]

1.6. Experiments for the reduction of aminals to methylamines



(1). A 2.5 mL NMR tube equipped with a J. Young valve is charged successively with **TBD** (0.70 mg, 0.0050 mmol, 5 mol%), CD_3CN (0.30 mL), **2f** (see *1.8.*) (12.7 mg, 0.050 mmol, 0.5 eq), $PhSiH_3$ (12.8 µL, 0.100 mmol, 2 eq, 3 eq "Si-H") and Ph_2CH_2 as internal standard (16.7 µL, 0.100 mmol, 1 eq). The reaction mixture is frozen with liquid nitrogen, degassed, exposed to a carbon dioxide atmosphere (1 bar) and warmed up to RT. The flask is then sealed and heated to 80 °C. The evolution of the formation of *N*,*N*-dimethyl-

p-toluidine and *N*-methyl-*p*-toluidine is followed by ^{1}H NMR and the yield is determined using the internal standard.

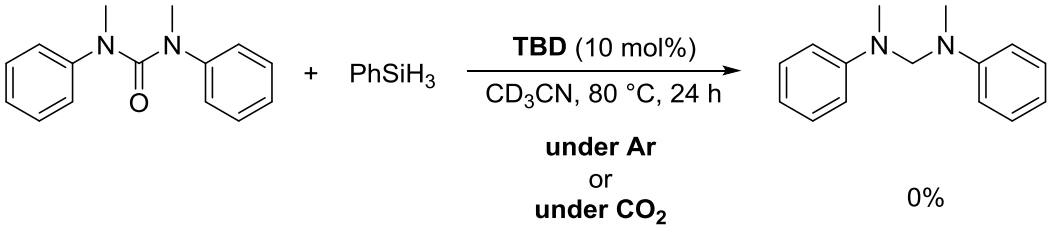
(2). The same procedure as for (1) is carried out in the absence of **TBD**.

(3). The same procedure as for (1) is carried out under an argon atmosphere.

Discussion:

To puzzle out the influence of the initial quantity of CO_2 in the formation of aminals, control experiments to establish the stability of aminal species toward an excess of CO_2 were carried out. Under these conditions, about 1 eq. of CO_2 with respect to the amine is sufficient to ensure the formation of the aminal and its stability towards reduction. However, when the later (**2f**) is put in reaction in the same conditions with fresh CO_2, its quantitative reduction to the methyl derivative takes place after 5 h (eq. 1). This reaction is catalyzed by **TBD** since most of the aminal remained untouched without it, and only small quantities (<5%) of the corresponding *N*-methylaniline and *N*,*N*-dimethylaniline were detected (eq. 2). Besides, no reaction occurred when **2f** is mixed with **TBD** and $PhSiH_3$ under Ar atmosphere (eq. 3).

1.7. Mechanistical investigations



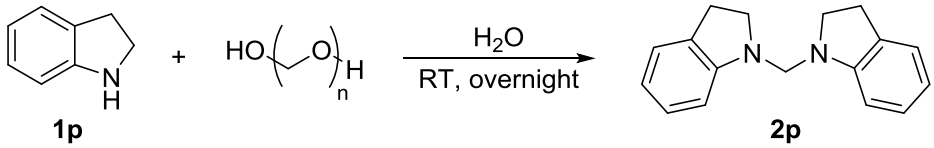
A 2.5 mL NMR tube equipped with a J. Young valve is charged successively with **TBD** (0.70 mg, 0.0050 mmol, 5 mol%), 1,3-dimethyl-1,3-diphenylurea (12 mg, 0.05 mmol) CD_3CN (0.30 mL), $PhSiH_3$ (24.7 µL, 0.200 mmol) and Ph_2CH_2 as internal standard (16.7 µL, 0.100 mmol, 1 eq). In a first case, the reaction mixture is frozen with liquid nitrogen, degassed, exposed to a carbon dioxide atmosphere (1 bar) and warmed up to RT. The flask is

sealed and heated to 80 °C. In a second case, the reaction was carried out under the glovebox atmosphere (Ar).

Discussion:

The formation of urea was considered as a possible pathway since its reduction could afford an aminal product. However, control experiments show that **TBD** is not able to promote the hydrosilylation of the tested urea. Under an Ar or CO_2 atmosphere, 1,3-dimethyl-1,3-diphenylurea was found unreacted after 24 h at 80 °C.

1.8. Procedure for the synthesis of aminals samples



1p **2p**

The procedure is detailed for the conversion of indoline (**1p)** to the corresponding aminal **2p**. A 4 mL vial equipped with a magnetic stir bar is charged successively with paraformaldehyde (150.2 mg, 5.00 mmol, 1 eq), indoline (1.120 mL, 10.00 mmol, 2 eq) and distillated water (3 mL). The reaction mixture is sealed and stirred overnight at RT. Distillated water (10 mL) is added and the solution is extracted with AcOEt (2x10 mL). (*NB: Most described aminals are sensitive to acidic media: a simple work-up with HCl (1 M) is very likely to give the initial amine.).* Organic layers are combined, washed with brine (2x10 mL) and dried with $MgSO_4$. The solvents were removed under reduced pressure, affording the aminal **2o** as an orange solid.

- With this method, good conversions to the aminals **2b**, **2d**, **2e**, **2g**, **2h**, **2i, 2j**, **2k**, **2l**, **2m**, **2p**, and **2q** were obtained and their NMR data were collected without any further purification.
- **2f** was successfully purified by a flash chromatography on silica gel (eluent: AcOEt/petroleum ether 10/90) without any degradation. **2s** has been isolated by

stirring the silica gel with 10% of Et_3N in the eluent (AcOEt/petroleum ether: 2/98) for 1 h before the preparation of the column.

- For aminals **2g**, **2n** and **2t**, conversions from 20% to 85% were obtained and purification attempts on silica gel were unsuccessful (the starting amine was recovered instead of the desired aminal). Selected ^{1}H NMR data corresponding to the desired compounds were collected (see *3.2.*).
- The procedure was inefficient (yield <10%) for **2c**.
- **^{1}H NMR** and **^{13}C NMR** of the following products are identical to reported data: **2a**,[7] **2o**,[8] **2r**[9] and **2u**.[10]

1.9. Crystallization of aminals

Satisfactory crystals for XRD analysis of **kj** grew in the reaction medium at RT (Figure S4). Crystals of **2f** (Figure S1), **2h** (Figure S2), **2j** (Figure S3), **2l** (Figure S5) and **2q** (Figure S6) were obtained by cooling a saturated CH_3CN solution of the corresponding aminal from 80 °C to 20 °C. Table S3 gathers the associated data to the corresponding structures.

Table S3. Crystal Data and Structure Refinement Details

	2f	**2h**	**2j**	**2k**	**2l**	**2q**
Chemical formula	$C_{17}H_{22}N_2$	$C_{15}H_{16}Cl_2N_2$	$C_{17}H_{16}N_4$	$C_{19}H_{22}N_2O_2$	$C_{17}H_{22}N_2$	$C_{19}H_{22}N_2$
M (g mol^{-1})	254.36	295.20	276.34	310.38	254.36	278.38
cryst syst	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	6.6390(6)	9.5965(6)	9.0980(8)	7.6950(3)	8.2662(8)	7.4891(4)
b (Å)	10.1221(7)	9.7098(8)	9.2750(5)	10.8336(4)	9.3707(9)	10.2554(9)
c (Å)	11.8800(12)	9.8586(8)	9.9433(7)	11.3346(5)	9.7747(7)	10.7397(9)
α (deg)	67.098(5)	118.511(4)	88.510(4)	115.666(3)	93.736(5)	76.374(4)
β (deg)	87.102(4)	106.751(5)	71.674(3)	91.615(3)	107.585(4)	70.139(5)
γ (deg)	75.801(5)	102.281(4)	66.442(4)	107.985(2)	92.110(4)	88.479(5)
V (Å^3)	712.04(11)	702.81(11)	725.31(10)	795.48(6)	718.96(11)	752.66(10)
Z	2	2	2	2	2	2
D_{calcd} (g cm^{-3})	1.186	1.395	1.265	1.296	1.175	1.228
μ(Mo Kα) (mm^{-1})	0.070	0.449	0.078	0.085	0.069	0.072
F(000)	276	308	292	332	276	300
reflns collcd	31690	33874	39255	35475	41173	42158
indep reflns	2672	2656	2730	3017	2705	2845
obsd reflns [$I > 2\sigma(I)$]	1734	1962	2192	2117	2215	2392
R_{int}	0.026	0.054	0.050	0.040	0.044	0.031
params refined	176	174	192	212	174	190
$R1$	0.064	0.037	0.041	0.040	0.041	0.038
$wR2$	0.189	0.103	0.119	0.108	0.114	0.107
S	1.055	1.049	1.046	1.049	1.064	1.068
$\Delta\rho_{min}$ (e Å^{-3})	–0.17	–0.23	–0.16	–0.17	–0.15	–0.19
$\Delta\rho_{max}$ (e Å^{-3})	0.15	0.27	0.17	0.16	0.13	0.19

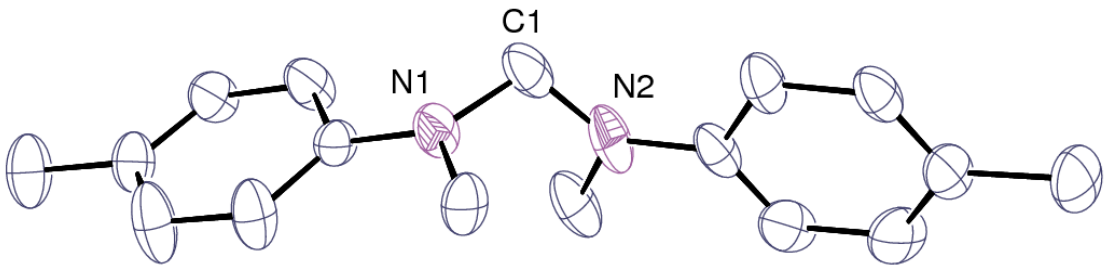


Figure S1. View of compound **2f**. Hydrogen atoms are omitted. Displacement ellipsoids are drawn at the 30% probability level.

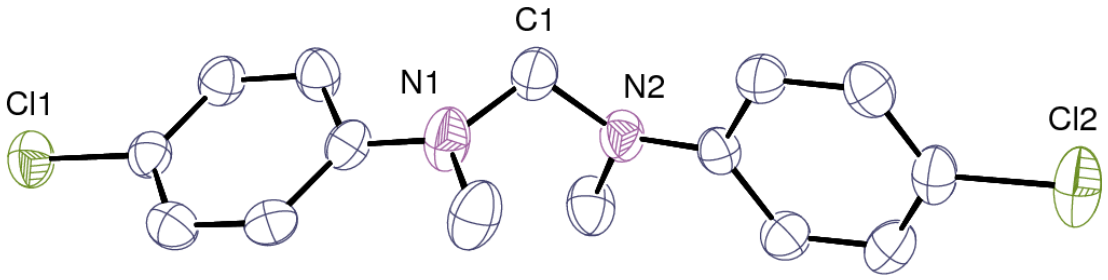


Figure S2. View of compound **2h**. Hydrogen atoms are omitted. Displacement ellipsoids are drawn at the 50% probability level.

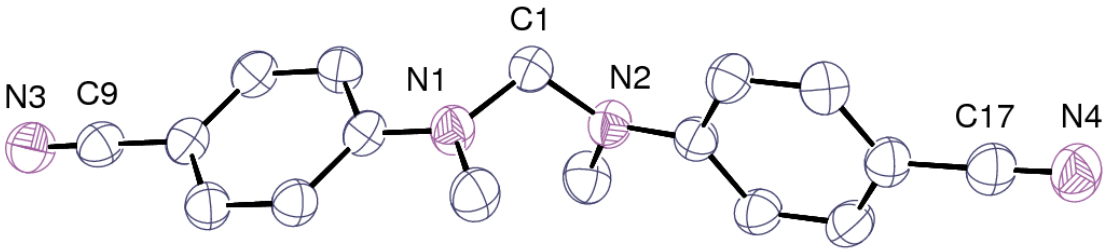


Figure S3. View of compound **2j**. Hydrogen atoms are omitted. Displacement ellipsoids are drawn at the 50% probability level.

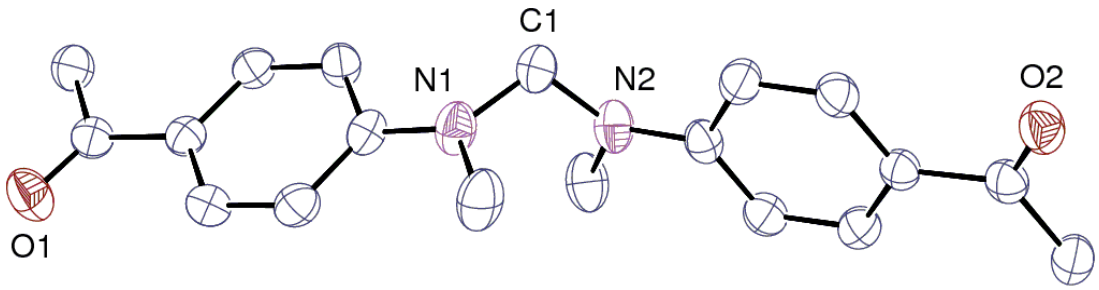


Figure S4. View of compound **2k**. Hydrogen atoms are omitted. Displacement ellipsoids are drawn at the 50% probability level.

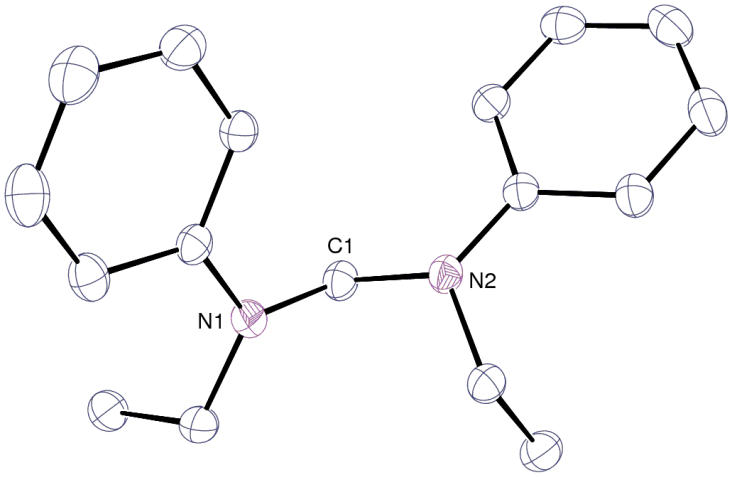


Figure S5. View of compound **2l**. Hydrogen atoms are omitted. Displacement ellipsoids are drawn at the 30% probability level.

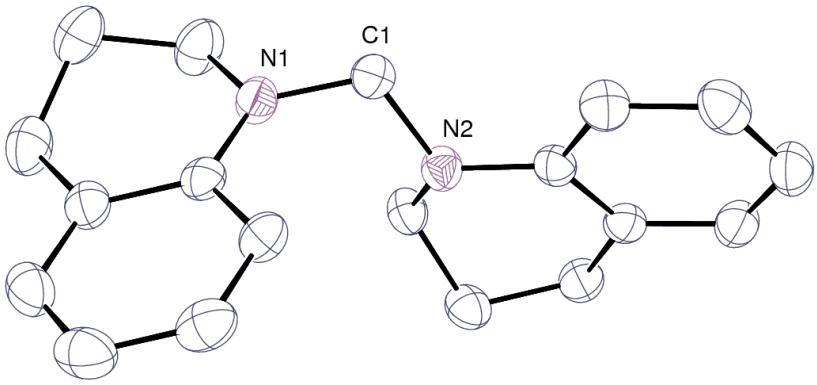


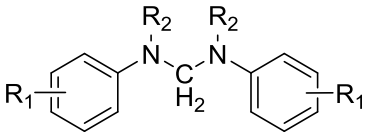
Figure S6. View of compound **2q**. Hydrogen atoms are omitted. Displacement ellipsoids are drawn at the 50% probability level.

2. Characterization of aminals

2.1. In situ NMR data

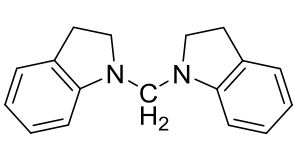
The following tables 4-6 present the *in situ* ^{1}**H NMR** data for the N–CH_2–N group of the aminals in CD_3CN.

Table S4. Symmetrical aminals **2a-2o**

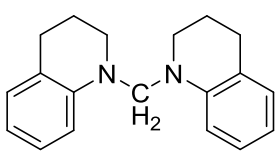


Aminal	R_1	R_2	δ N–CH_2–N in CD_3CN (ppm)
2a	H	Me	4.77
2b	3–Me	Me	4.76
2c	3–OMe	Me	4.79
2d	3–Cl	Me	4.73
2e	3–F	Me	4.78
2f	4–Me	Me	4.68
2g	4–OMe	Me	4.54
2h	4–Cl	Me	4.69
2i	4–F	Me	4.63
2j	4–CN	Me	4.89
2k	4–Ac	Me	4.95
2l	H	Et	4.73
2m	H	Allyl	4.86
2n	H	Ph	5.50
2o	H	Bn	5.13

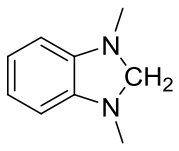
Table S5. Symmetrical aminals **2p-2u**



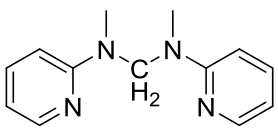
2p



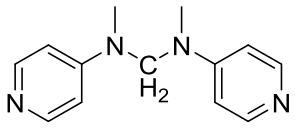
2q



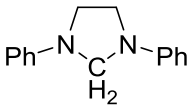
2r



2s



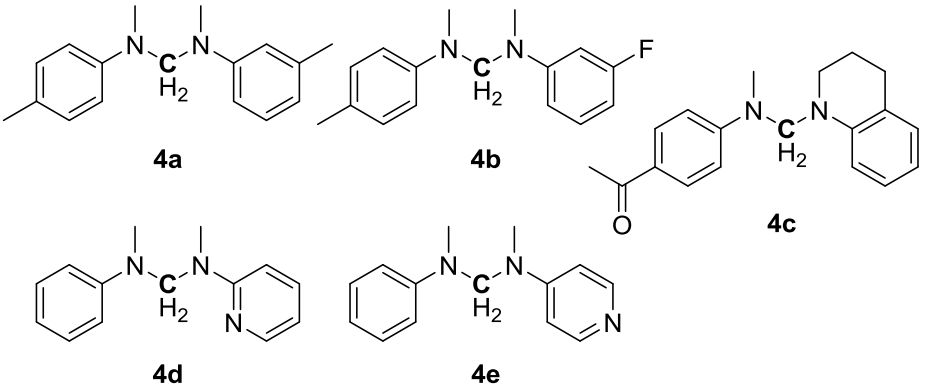
2t



2u

Aminal	δ N–CH_2–N in CD_3CN (ppm)
2p	4.52
2q	4.67
2r	4.21
2s	5.56
2t	4.90
2u	4.62

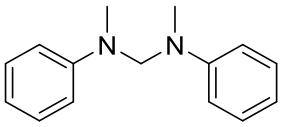
Table S6: Mixed aminals **4a-4e**



Aminal	δ N–CH_2–N in CD_3CN. (ppm)
4a	4.71
4b	4.71
4c	4.81
4d	5.22
4e	4.83

2.2. NMR characterization

- **2a:** *N*,*N*'-dimethyl-*N*,*N*'-diphenylmethanediamine

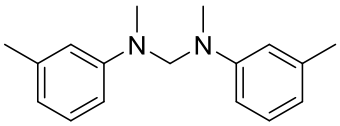


NMR data for **2a** are reported from literature.[7]

^{1}H NMR ($CDCl_3$, 298 K): δ 2.85 (s, 6H, NCH_3); 4.70 (s, 2H, NCH_2N); 6.60–7.45 (m, 10H, Ar).

^{13}C NMR ($CDCl_3$, 298 K): δ 36.06 (NCH$_3$); 70.11 (NCH$_2$N); 113.56 (Ar–C2, Ar–C6); 117.68 (Ar–C4); 129.10 (Ar–C3, Ar–C5); 149.11 (Ar–C1).

- **2b:** *N*,*N*'-dimethyl-*N*,*N*'-di-m-tolylmethanediamine



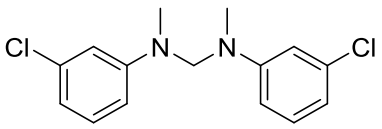
Appearance: pale oil

^{1}H NMR ($CDCl_3$, 298 K): δ 2.38 (s, 6H, NCH_3); 2.93 (s, 6H, PhCH_3); 4.81 (s, 2H, NCH_2N); 6.66–6.71 (m, 6H, Ar); 7.17–7.25 (m, 2H, Ar).

^{13}C NMR ($CDCl_3$, 298 K): δ 22.00 (PhCH$_3$); 36.29 (NCH$_3$); 70.49 (NCH$_2$N); 110.95 (Ar); 114.53 (Ar); 118.75 (Ar); 129.15 (Ar); 138.97 (Ar); 149.47 (Ar).

Anal. Calc. for $C_{17}H_{22}N_2$ (mol. wt. 254.38): C 80.27; H 8.72; N 11.01. Found: C 79.09; H 8.84; N 11.07.

- **2d:** *N*,*N*'-bis(3-chlorophenyl)-*N*,*N*'-dimethylmethanediamine



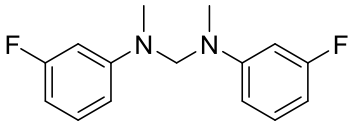
Appearance: white solid

^{1}H NMR ($CDCl_3$, 298 K): δ 2.87 (s, 6H, NCH_3); 4.75 (s, 2H, NCH_2N); 6.68–6.80 (m, 6H, Ar); 7.13–7.22 (m, 2H, Ar).

^{13}C NMR ($CDCl_3$, 298 K): δ 36.29 (NCH$_3$); 69.53 (NCH$_2$N); 111.73 (Ar); 113.50 (Ar); 117.84 (Ar); 130.27 (Ar); 135.17 (Ar); 150.10 (Ar).

Anal. Calc. for $C_{15}H_{16}Cl_2N_2$ (mol. wt. 295.21): C 61.03; H 5.46; Cl 24.02; N 9.49. Found: C 60.89; H 5.48; Cl not measured; N 9.48.

- **2e:** *N*,*N*'-bis(3-fluorophenyl)-*N*,*N*'-dimethylmethanediamine

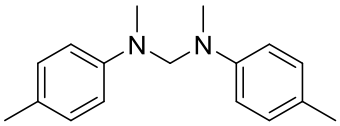


Appearance: pale orange solid

^{1}H NMR ($CDCl_3$, 298 K): δ 2.88 (s, 6H, NCH_3); 4.75 (s, 2H, NCH_2N); 6.50–6.61 (m, 6H, Ar); 7.14–7.23 (m, 2H, Ar).

^{13}C NMR ($CDCl_3$, 298 K): δ 36.26 (N*C*H_3); 69.50 (N*C*H_2N); 100.54 (Ar, $^2J_{CF}$ = 25.6 Hz); 100.36 (Ar, $^2J_{CF}$ = 22.2 Hz); 109.04 (Ar, $^4J_{CF}$ = 2.2 Hz); 130.38 (Ar, $^3J_{CF}$ = 10.2 Hz); 150.75 (Ar, $^3J_{CF}$ = 10.8 Hz); 164.09 (Ar, $^1J_{CF}$ = 242 Hz).

- **2f:** *N*,*N*'-dimethyl-*N*,*N*'-di-p-tolylmethanediamine



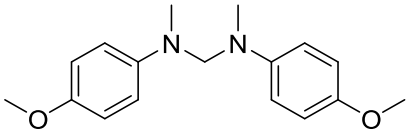
Appearance: pale brownish solid

^{1}H NMR ($CDCl_3$, 298 K): δ 2.29 (s, 6H, PhCH_3); 2.86 (s, 6H, NCH_3); 4.70 (s, 2H, NCH_2N); 6.80 (d, 4H, Ar, $^3J_{HH}$ = 8.0 Hz); 7.08 (d, 4H, Ar, $^3J_{HH}$ = 8.0 Hz).

^{13}C NMR ($CDCl_3$, 298 K): δ 20.42 (6H, Ph*C*H_3); 36.62 (6H, N*C*H_3); 71.42 (2H, NCH_2N); 114.13 (Ar); 127.07 (Ar); 129.77 (Ar); 147.30 (Ar).

Anal. Calc. for $C_{17}H_{22}N_2$ (mol. wt. 254.38): C 80.27; H 8.72; N 11.01. Found: C 80.35; H 8.98; N 11.20.

- **2g:** *N*,*N*'-bis(4-methoxyphenyl)-*N*,*N*'-dimethylmethanediamine

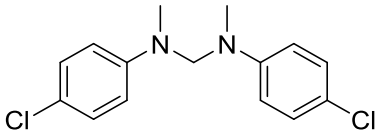


Selected ^{1}H NMR data (see *1.8.*).

^{1}H NMR ($CDCl_3$, 298 K): δ 2.85 (s, 6H, NCH_3); 3.79 (s, 6H, OCH_3); 4.57 (s, 2H, NCH_2N); 6.61 (d, 4H, Ar, $^3J_{HH}$ = 8.8 Hz); 6.83 (d, 4H, Ar, $^3J_{HH}$ = 8.8 Hz).

^{13}C NMR ($CDCl_3$, 298 K): δ 37.55 (N*C*H_3); 55.77 (O*C*H_3); 73.89 (N*C*H_2N); 113.68 (Ar); 114.84 (Ar); 116.18 (Ar); 144.00 (Ar).

- **2h:** *N*,*N*'-bis(4-chlorophenyl)-*N*,*N*'-dimethylmethanediamine



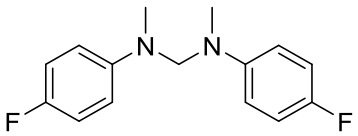
Appearance: beige solid

^{1}H NMR ($CDCl_3$, 298 K): δ 2.86 (s, 6H, NCH_3); 4.71 (s, 2H, NCH_2N); 6.73 (d, 4H, Ar, $^{3}J_{HH}$ = 8.8 Hz); 7.20 (d, 4H, Ar, $^{3}J_{HH}$ = 8.8 Hz).

^{13}C NMR ($CDCl_3$, 298 K): δ 36.68 (N*C*H_3); 70.51 (N*C*H_2N); 114.96 (Ar); 122.93 (Ar); 129.14 (Ar); 147.69 (Ar).

Anal. Calc. for $C_{15}H_{16}Cl_2N_2$ (mol. wt. 295.21): C 61.03; H 5.46; Cl 24.02; N 9.49. Found: C 60.91; H 5.47; Cl not measured; N 9.54.

- **2i:** *N*,*N*'-bis(4-fluorophenyl)-*N*,*N*'-dimethylmethanediamine

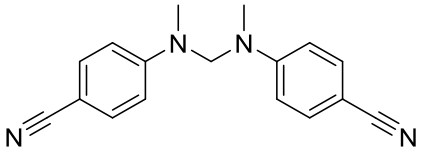


Appearance: beige solid

^{1}H NMR ($CDCl_3$, 298 K): δ 2.87 (s, 6H, NCH_3); 4.63 (s, 2H, NCH_2N); 6.71-6.89 (m, 4H, Ar); 6.90-7.10 (m, 4H, Ar).

^{13}C NMR ($CDCl_3$, 298 K): δ 37.33 (N*C*H_3); 72.75 (N*C*H_2N); 115.53 (Ar, $^{3}J_{CF}$ = 8.3 Hz); 115.66 (Ar, $^{2}J_{CF}$ = 21.8 Hz); 145.94 (Ar, $^{4}J_{CF}$ = 1.4 Hz); 156.32 (Ar, $^{1}J_{CF}$ = 242 Hz).

- **2j:** *4*,*4*'-(methylenebis(methylazanediyl))dibenzonitrile



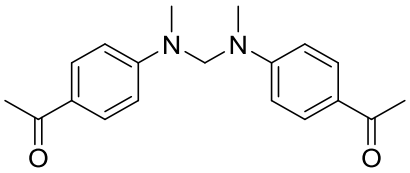
Appearance: white solid

^{1}H NMR ($CDCl_3$, 298 K): δ 2.87 (s, 6H, NCH_3); 4.84 (s, 2H, NCH_2N); 6.66 (d, 4H, Ar, $^{3}J_{HH}$ = 8.8 Hz); 7.38 (d, 4H, Ar, $^{3}J_{HH}$ = 8.8 Hz).

^{13}C NMR ($CDCl_3$, 298 K): δ 35.96 (N*C*H_3); 67.41 (N*C*H_2N); 99.51 (Ar); 112.56 (Ar); 120.07 (*C*N); 133.59 (Ar); 151.12 (Ar).

Anal. Calc. for $C_{17}H_{16}N_4$ (mol. wt. 276.34): C 73.89; H 5.84; N 20.27. Found: C 73.56; H 5.81; N 20.49.

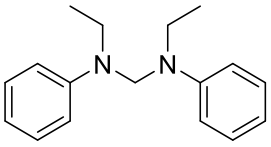
- **2k:** 1,1'-((methylenebis(methylazanediyl))bis(4,1-phenylene))bis(ethan-1-one)



Appearance: mustard yellow solid

^{1}H NMR ($CDCl_3$, 298 K): δ 2.50 (s, 6H, COCH_3); 2.95 (s, 6H, NCH_3); 4.96 (s, 2H, NCH_2N); 6.74 (d, 4H, Ar, $^3J_{HH}$ = 8.5 Hz); 7.87 (d, 4H, Ar, $^3J_{HH}$ = 8.5 Hz).
^{13}C NMR ($CDCl_3$, 298 K): δ 26.16 (CO*C*H_3); 36.02 (N*C*H_3); 67.60 (N*C*H_2N); 111.76 (Ar); 126.98 (Ar); 130.66 (Ar); 152.08 (Ar); 196.54 (*C*OCH_3).
Anal. Calc. for $C_{19}H_{22}N_2O_2$ (mol. wt. 310.40): C 73.52; H 7.14; N 9.03; O 10.31. Found: C 73.06; H 7.20; N 9.12; O not measured.

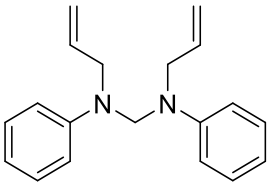
- **2l:** *N*,*N*'-diethyl-*N*,*N*'-diphenylmethanediamine



Appearance: peach solid

^{1}H NMR ($CDCl_3$, 298 K): δ 1.13 (t, 6H, NCH$_2$CH_3, $^3J_{HH}$ = 6.9 Hz); 3.42 (q, 4H, NCH_2CH$_3$, $^3J_{HH}$ = 6.9 Hz); 4.72 (s, 2H, NCH_2N); 6.76–7.86 (m, 6H, Ar); 7.21–7.28 (m, 4H, Ar).
^{13}C NMR ($CDCl_3$, 298 K): δ 11.98 (NCH$_2$*C*H$_3$); 42.20 (N*C*H$_2$CH$_3$); 65.66 (N*C*H_2N); 113.94 (Ar); 117.43 (Ar); 129.37 (Ar); 147.81 (Ar).
Anal. Calc. for $C_{17}H_{22}N_2$ (mol. wt. 254.38): C 80.27; H 8.72; N 11.01. Found: C 80.27; H 8.90; N 11.20.

- **2m:** *N*,*N*'-diallyl-*N*,*N*'-diphenylmethanediamine



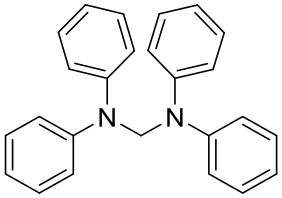
Appearance: brown oil

^{1}H NMR ($CDCl_3$, 298 K): δ 4.36 (s, 4H, NC*H*$_2$CHCH$_2$, $^3J_{HH}$ = 4.0 Hz); 4.87 (s, 2H, NC*H*$_2$N); 5.13–5.22 (m, 4H, NCH$_2$CHC*H*$_2$); 5.79–5.97 (m, 2H, NCH$_2$C*H*CH$_2$); 6.80–6.96 (m, 4H, Ar); 7.23–7.30 (m, 6H, Ar).

^{13}C NMR ($CDCl_3$, 298 K): δ 50.06 (N*C*H$_2$CHCH$_2$); 65.83 (N*C*H$_2$N); 100.08 (Ar); 113.87 (Ar); 116.47 (NCH$_2$CH*C*H$_2$); 117.80 (NCH$_2$CH*C*H$_2$); 129.32 (Ar); 134.06 (NCH$_2$*C*HCH$_2$); 148.22 (Ar).

Anal. Calc. for $C_{19}H_{22}N_2$ (mol. wt. 278.40): C 81.97; H 7.97; N 10.06. Found: C 81.24; H 7.97; N 10.08.

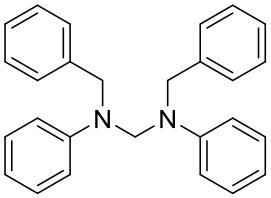
- **2n:** *N*,*N*,*N*',*N*'-tetraphenylmethanediamine



Selected ^{1}H NMR data (see *1.8.*).

^{1}H NMR ($CDCl_3$, 298 K): δ 5.56 (s, 2H, NC*H*$_2$N); 6.93–7.38 (m, 20H, Ar).

- **2o:** *N*,*N*'-dibenzyl-*N*,*N*'-diphenylmethanediamine

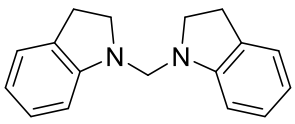


NMR data for **2o** are reported from literature.[8]

^{1}H NMR ($CDCl_3$, 298 K): δ 2.21 (s, 4H, NC*H*$_2$); 4.37 (s, 2H, NC*H*$_2$N); 6-71–7.43 (m, 20H, Ar).

^{13}C NMR ($CDCl_3$, 298 K): δ 60.42 (N*C*H$_2$); 77.35 (N*C*H$_2$N); 113.40 (Ar); 118.10 (Ar); 127.34 (Ar); 127.70 (Ar); 128.66 (Ar); 129.30 (Ar); 139.05 (Ar); 147.57 (Ar).

- **2p:** di(indolin-1-yl)methane



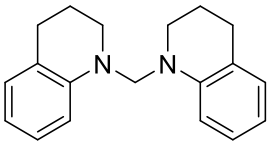
Appearance: persian orange solid

^{1}H NMR ($CDCl_3$, 298 K): δ 3.10 (t, 4H, CH_2, $^3J_{HH}$ = 8.4 Hz); 3.59 (t, 4H, CH_2, $^3J_{HH}$ = 8.4 Hz); 4.63 (s, 2H, NCH_2N); 6.78–6.88 (m, 4H, Ar); 7.19–7.26 (m, 4H, Ar).

^{13}C NMR ($CDCl_3$, 298 K): δ 28.63 (NCH_2CH_2); 52.71 (NCH_3CH_2); 63.97 (NCH_2N); 107.30 (Ar); 118.06 (Ar); 124.81 (Ar); 127.39 (Ar); 130.02 (Ar); 151.61 (Ar).

Anal. Calc. for $C_{17}H_{18}N_2$ (mol. wt. 250.36): C 81.56; H 7.25; N 11.19. Found: C 81.40; H 7.19; N 11.34.

- **2q:** bis(3,4-dihydroquinolin-1(2H)-yl)methane



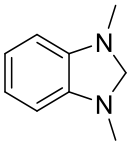
Appearance: persian orange solid

^{1}H NMR ($CDCl_3$, 298 K): δ 1.96 (tt, 4H, CH_2, $^3J_{HH}$ = 6.2 Hz, $^3J_{HH}$ = 5.5 Hz); 2.80 (t, 4H, CH_2, $^3J_{HH}$ = 6.2 Hz); 3.31 (tt, 4H, CH_2, $^3J_{HH}$ = 5.5 Hz); 4.73 (s, 2H, NCH_2N); 6.63–6.77 (m, 4H, Ar); 7.01–7.12 (m, 4H, Ar).

^{13}C NMR ($CDCl_3$, 298 K): δ 22.18 ($NCH_2CH_2CH_2$); 28.26 ($NCH_2CH_2CH_2$); 47.01 ($NCH_2CH_2CH_2$); 67.53 (NCH_2N); 111.53 (Ar); 116.74 (Ar); 123.24 (Ar); 127.22 (Ar); 129.32 (Ar); 145.00 (Ar).

Anal. Calc. for $C_{19}H_{22}N_2$ (mol. wt. 278.40): C 81.97; H 7.97; N 10.06. Found: C 81.46; H 8.14; N 10.35.

- **2r:** 1,3-dimethyl-2,3-dihydro-1H-benzo[d]imidazole

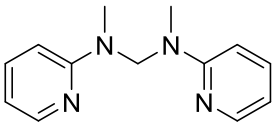


NMR data for **2r** are reported from literature.[9]

^{1}H NMR ($CDCl_3$, 298 K): δ 2.74 (s, 6H, NCH_3); 4.33 (s, 2H, NCH_2N); 6.43 (dd, 2H, Ar); 6.69 (dd, 2H, Ar).

^{13}C NMR ($CDCl_3$, 298 K): δ 34.29 (NCH_3); 80.19 (NCH_2N); 105.97 (Ar); 119.05 (Ar); 143.12 (Ar).

- **2s:** *N*,*N*'-dimethyl-*N*,*N*'-di(pyridin-2-yl)methanediamine



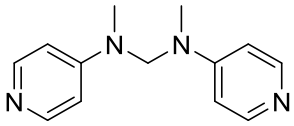
Appearance: white solid

^{1}H NMR ($CDCl_3$, 298 K): δ 2.99 (s, 6H, NCH_3); 5.61 (s, 2H, NCH_2N); 6.54–6.62 (m, 4H, Ar); 7.46–7.50 (m, 2H, Ar); 8.17–8.19 (m, 2H, Ar).

^{13}C NMR ($CDCl_3$, 298 K): δ 34.76 (N*C*H_3); 61.59 (N*C*H_2N); 105.95 (Ar); 112.46 (Ar); 137.57 (Ar); 147.78 (Ar); 159.00 (Ar).

Anal. Calc. for $C_{13}H_{16}N_4$ (mol. wt. 228.30): C 68.39; H 7.06; N 24.54. Found: C 68.13; H 7.04; N 24.69.

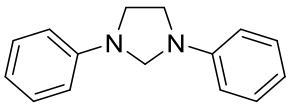
- **2t:** *N*,*N*'-dimethyl-*N*,*N*'-di(pyridin-4-yl)methanediamine



Selected ^{1}H NMR data (see *1.8.*).

^{1}H NMR ($CDCl_3$, 298 K): δ 2.84 (s, 6H, NCH_3); 4.97 (s, 2H, NCH_2N); 6.41 (d, 4H, Ar, $^{3}J_{HH}$ = 6.1 Hz); 8.15 (d, 4H, Ar, $^{3}J_{HH}$ = 6.1 Hz).

- **2u:** 1,3-diphenylimidazolidine



NMR data for **2u** are reported from literature.[10]

Appearance: colorless plates

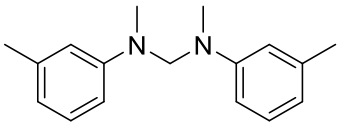
^{1}H NMR ($CDCl_3$, 298 K): δ 3.66 (s, 4H, NCH_2CH_2N); 4.67 (s, 2H, NCH_2N); 6.68 (d, 4H, Ar, $^{3}J_{HH}$ = 8.1 Hz); 6.80 (t, 2H, Ar, $^{3}J_{HH}$ = 7.3 Hz); 7.30 (d, 4H, Ar, $^{3}J_{HH}$ = 7.7 Hz).

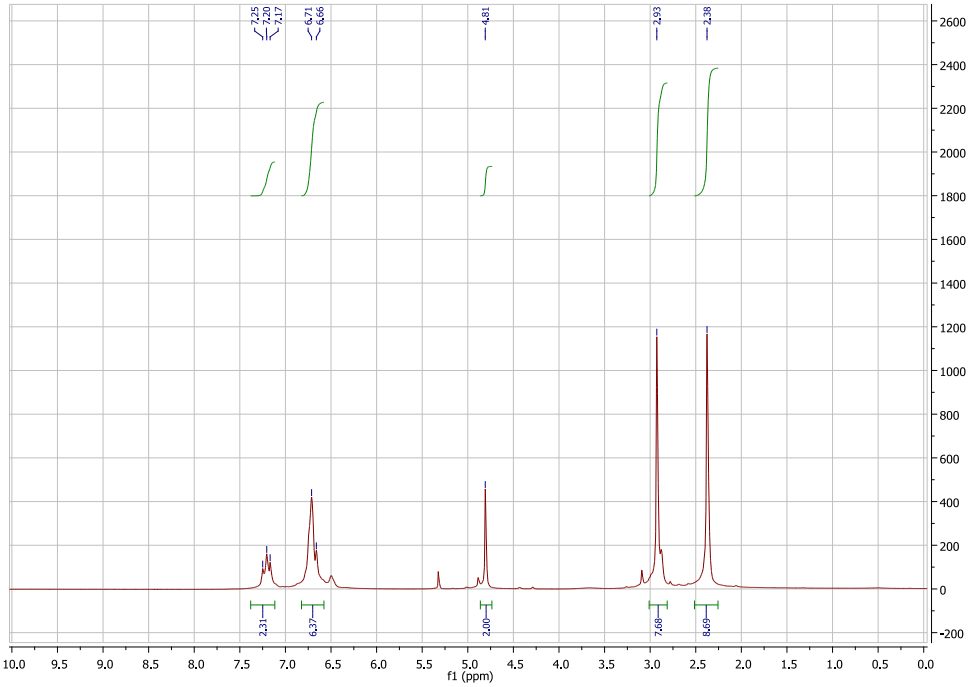
^{13}C NMR (C_6D_6, 298 K): δ 46.47 (N*C*H_2*C*H_2N); 65.85 (N*C*H_2N); 112.44 (Ar); 117.64 (Ar); 129.36 (Ar); 146.41 (Ar).

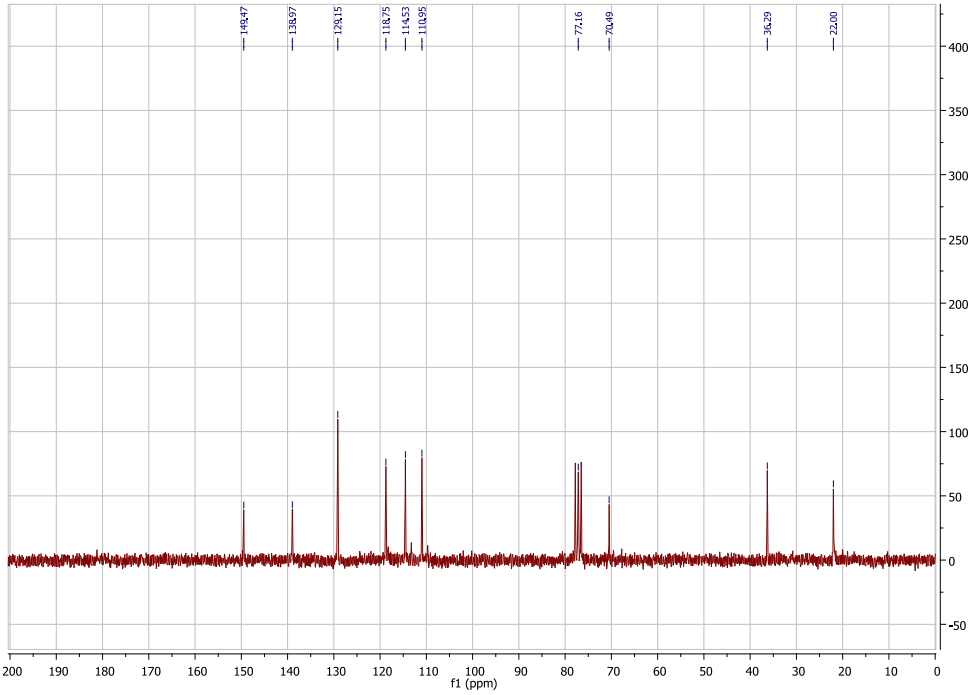
3. NMR spectra

3.1. ^{1}H and ^{13}C NMR spectra of aminals

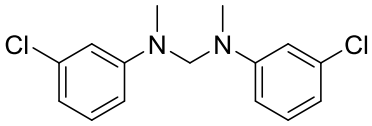
- **2b:** *N*,*N*'-dimethyl-*N*,*N*'-di-m-tolylmethanediamine

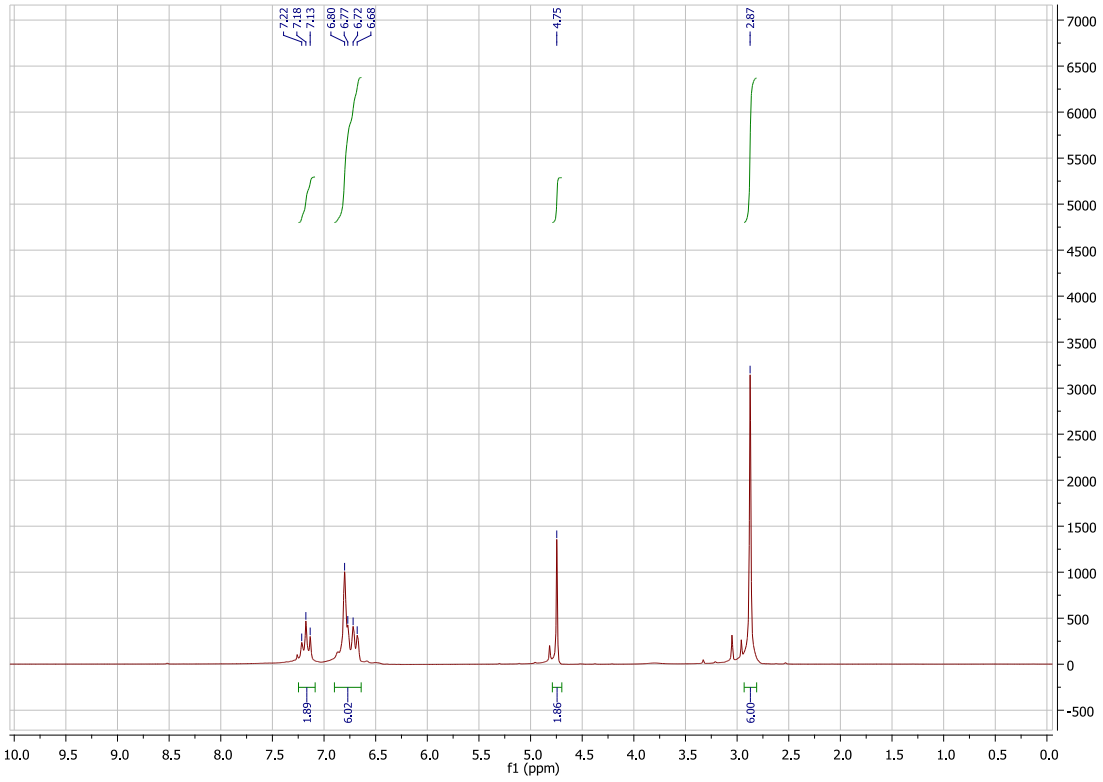


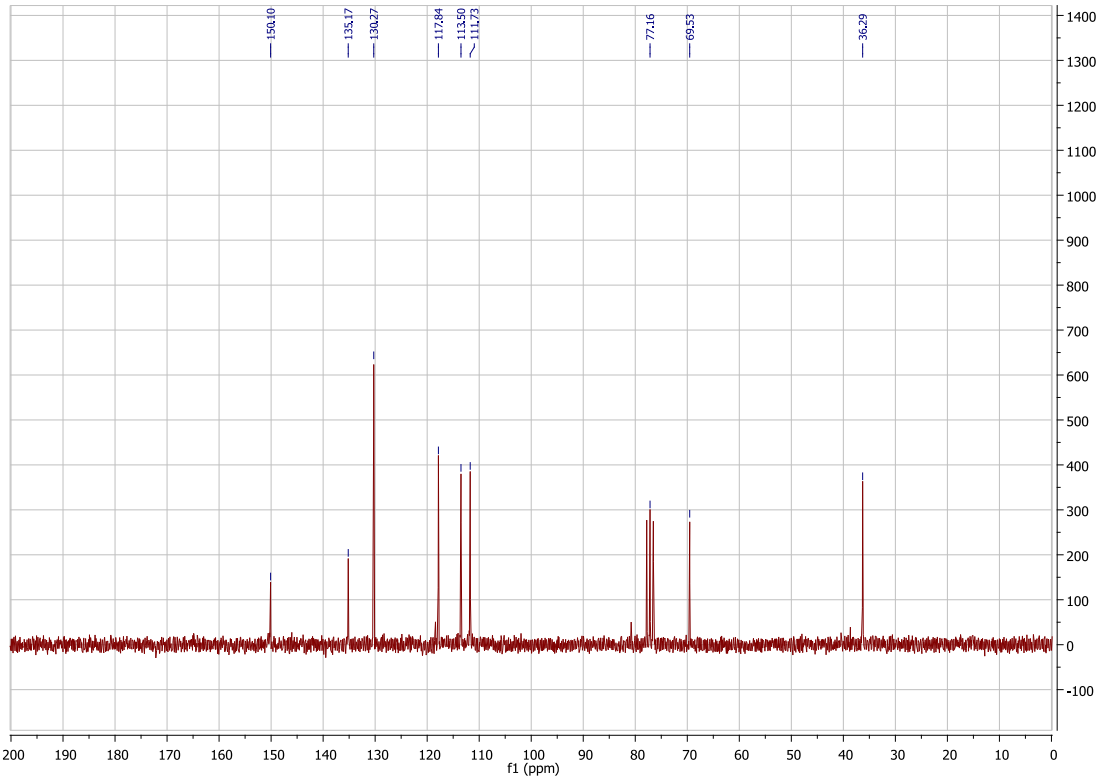




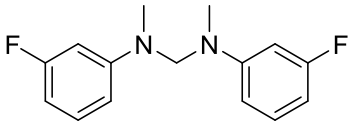
- **2d:** *N*,*N*'-bis(3-chlorophenyl)-*N*,*N*'-dimethylmethanediamine

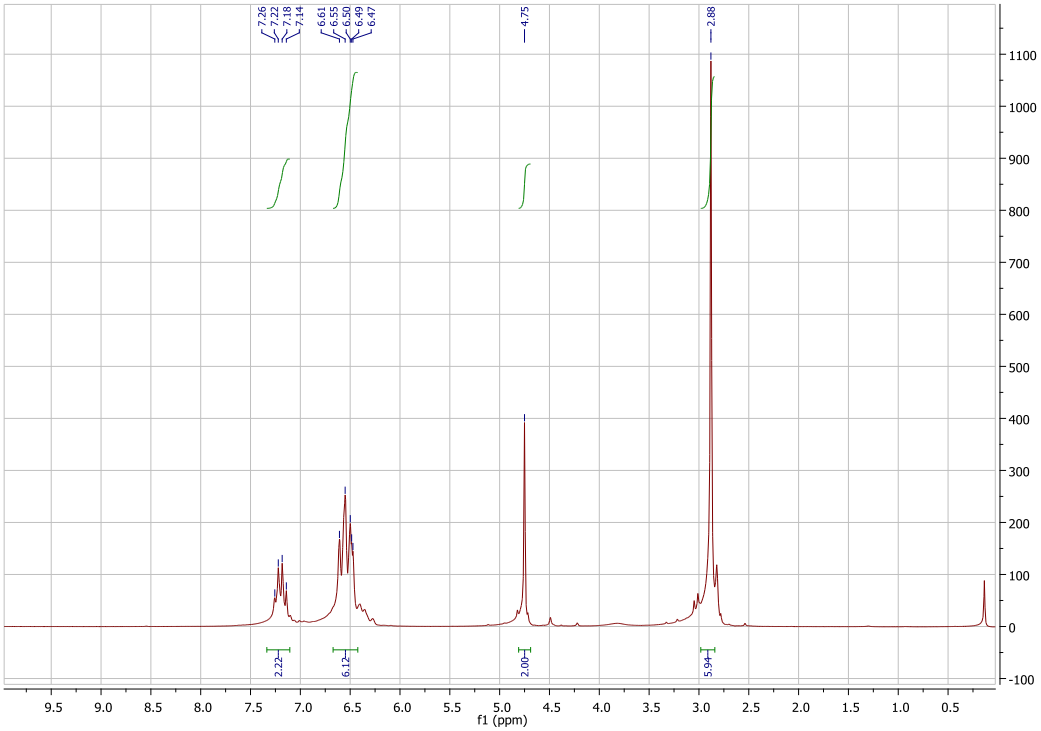


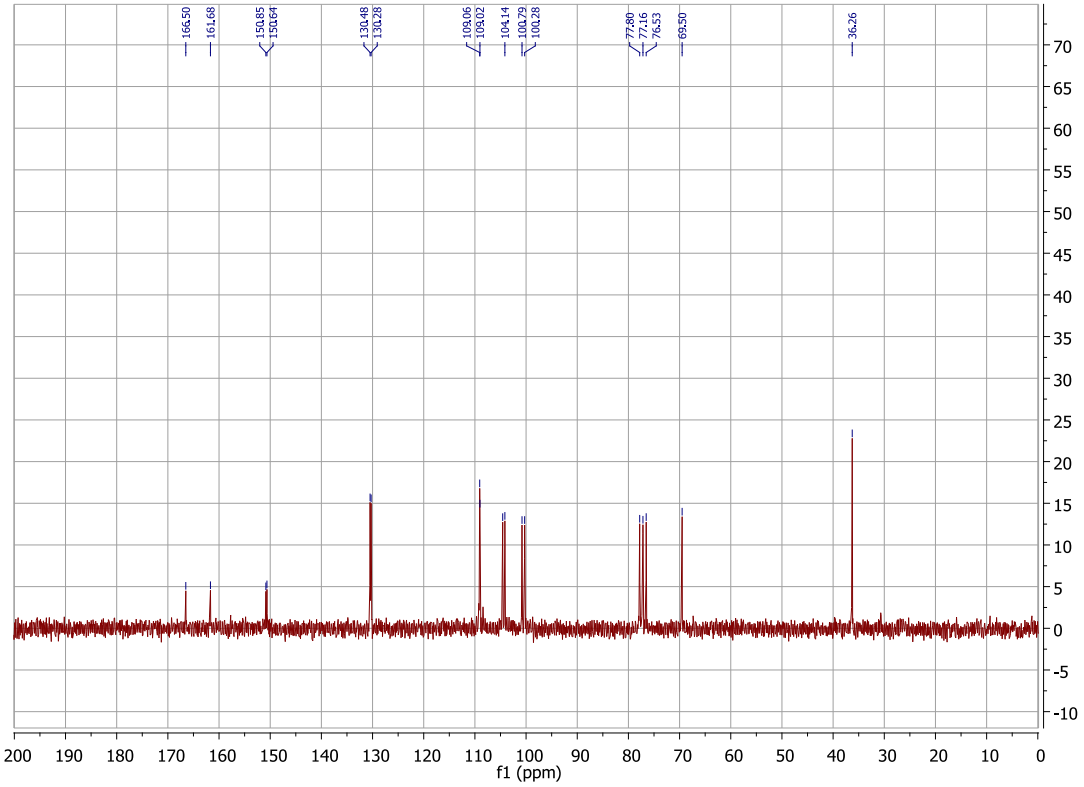




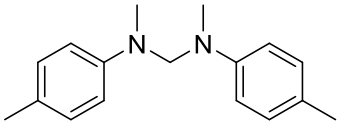
- **2e:** *N*,*N*'-bis(3-fluorophenyl)-*N*,*N*'-dimethylmethanediamine

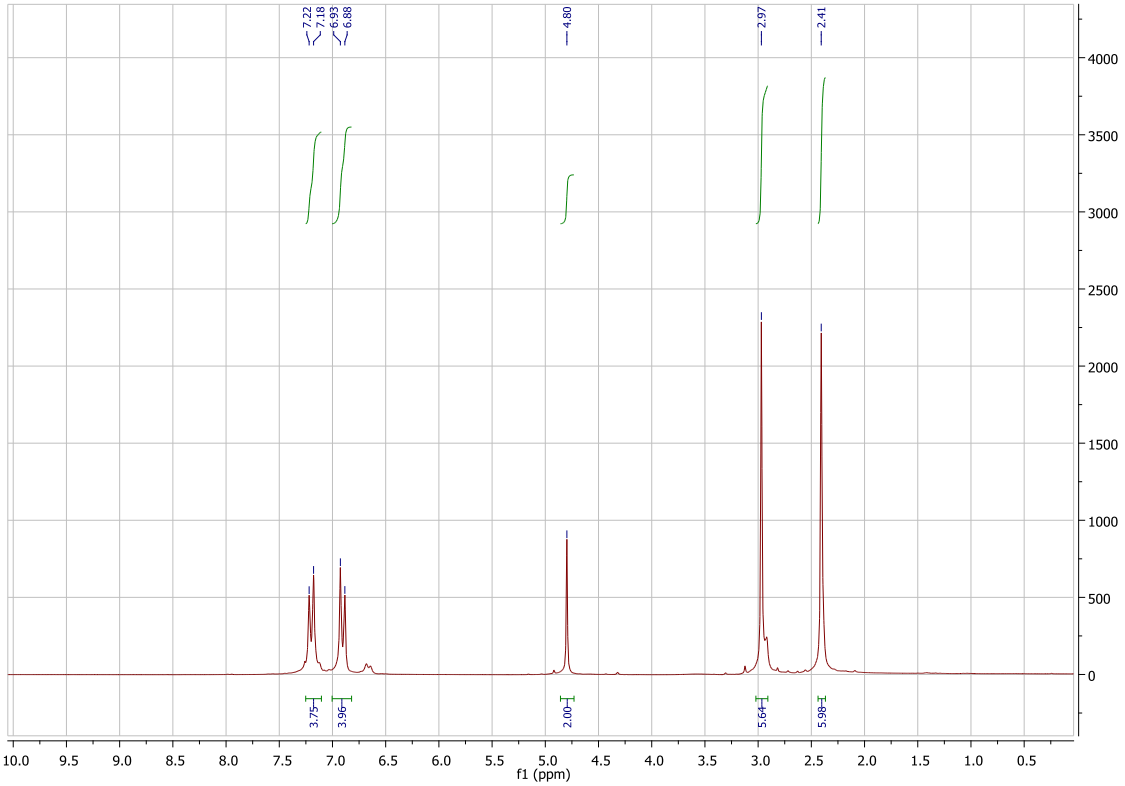


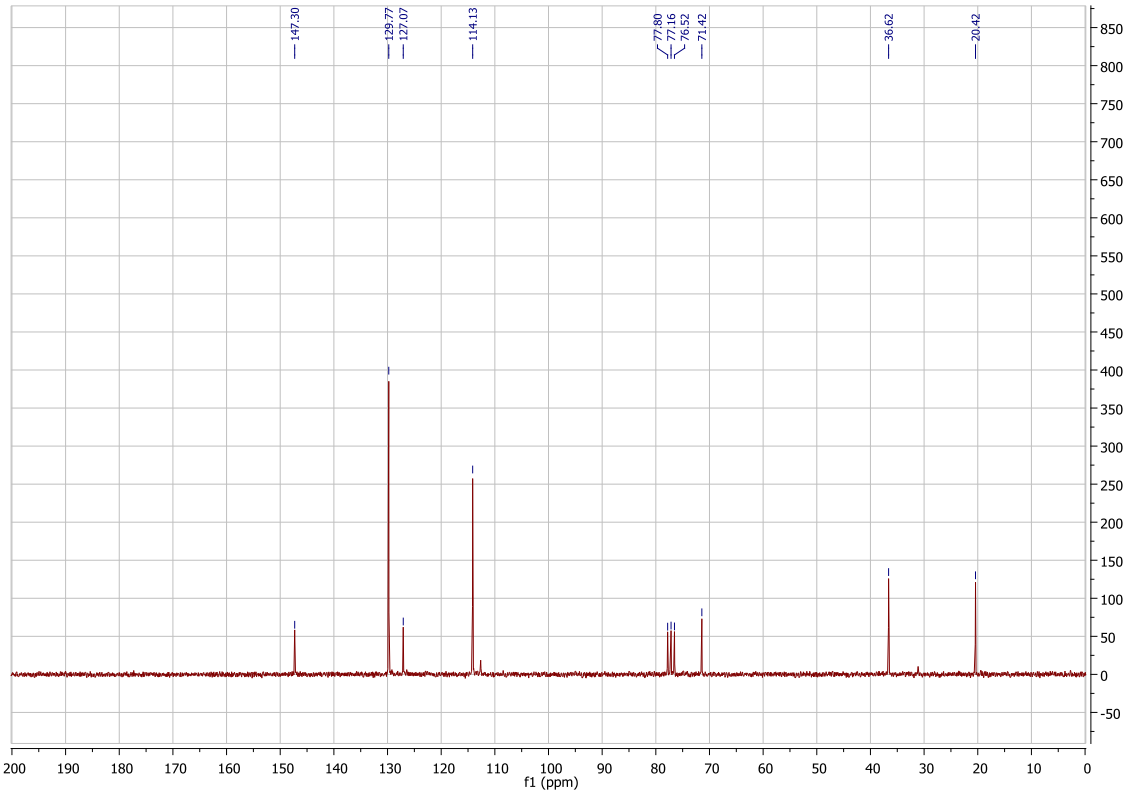




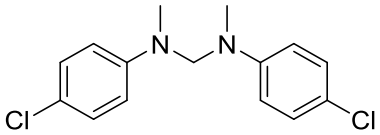
- **2f:** *N*,*N*'-dimethyl-*N*,*N*'-di-p-tolylmethanediamine

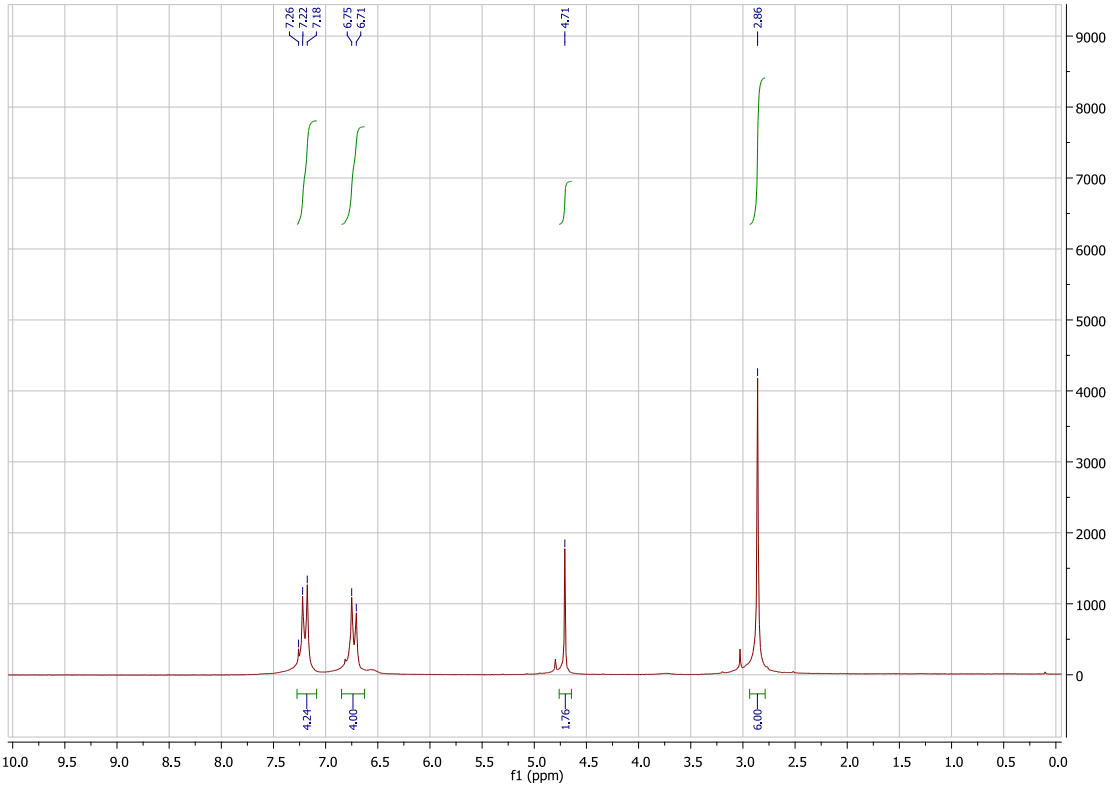


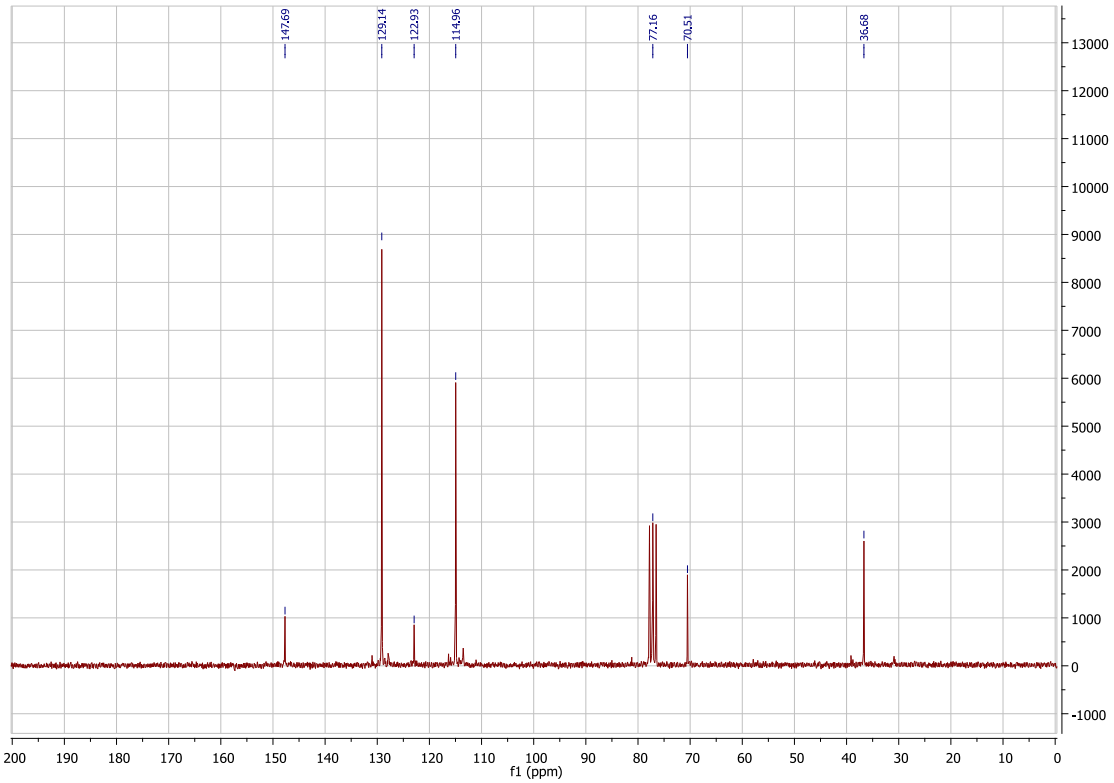




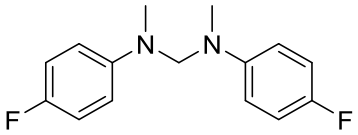
- **2h:** *N*,*N*'-bis(4-chlorophenyl)-*N*,*N*'-dimethylmethanediamine

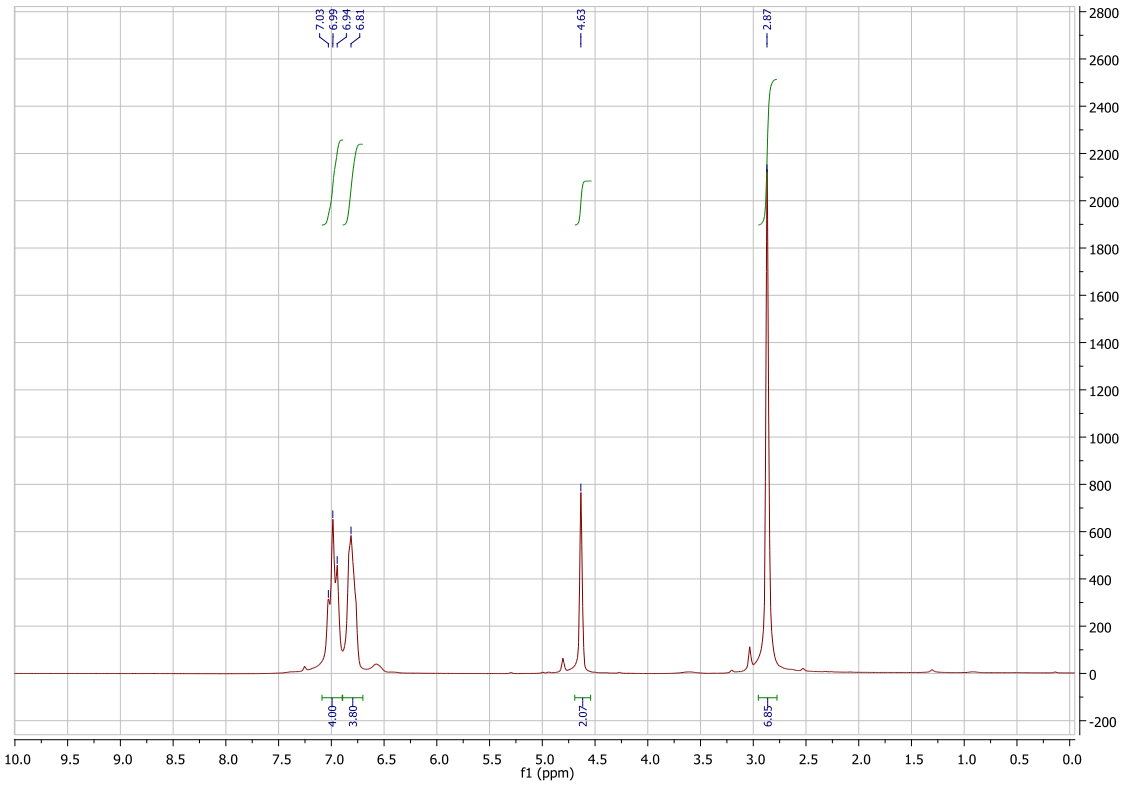


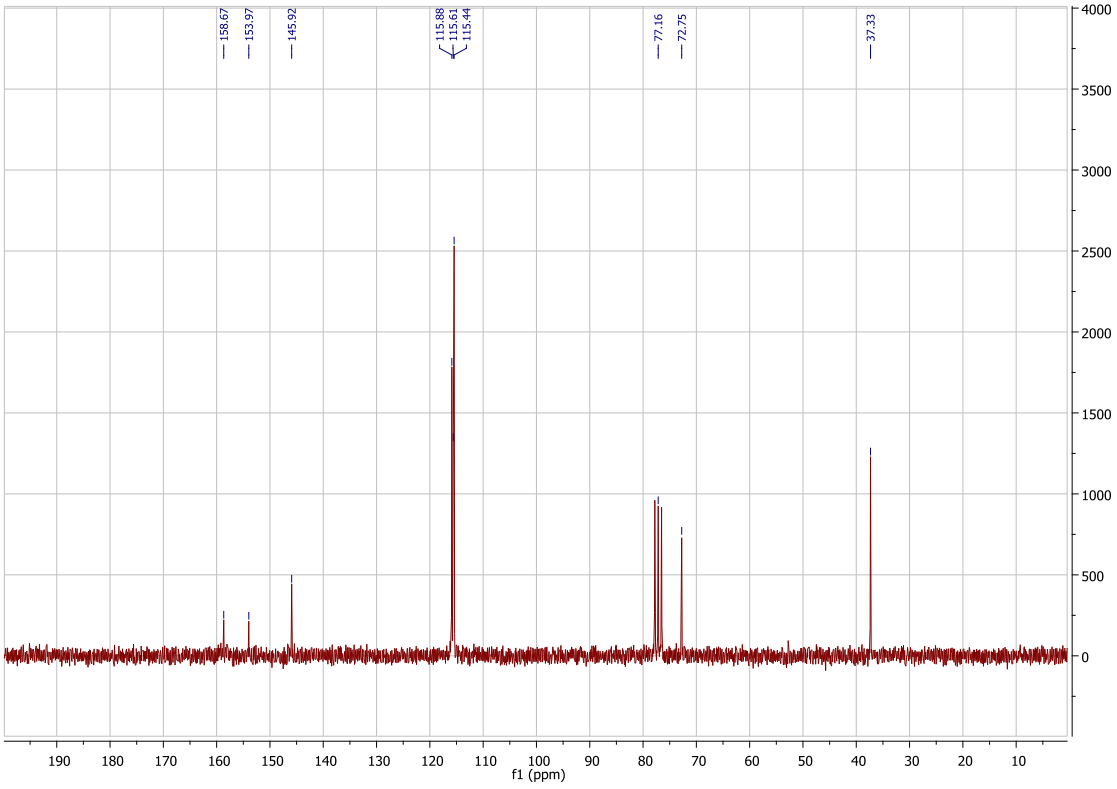




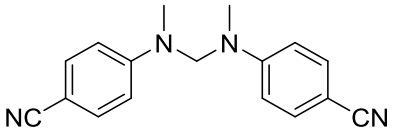
- **2i:** *N*,*N*'-bis(4-fluorophenyl)-*N*,*N*'-dimethylmethanediamine

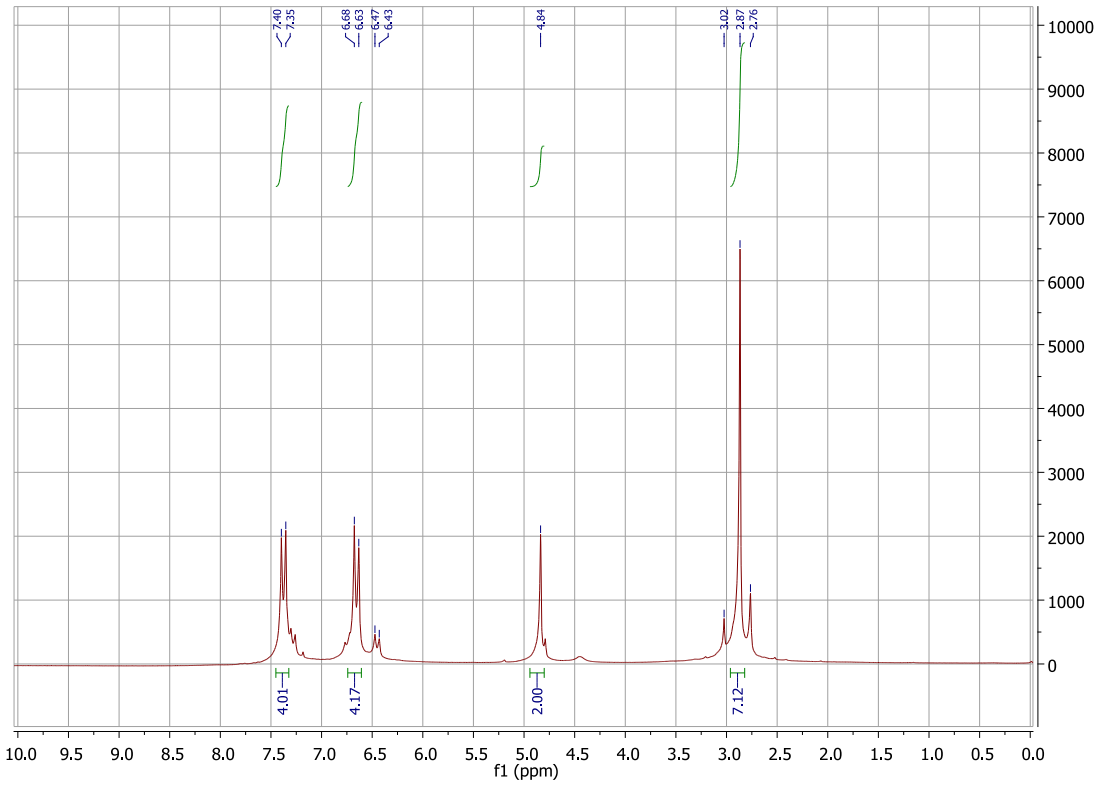


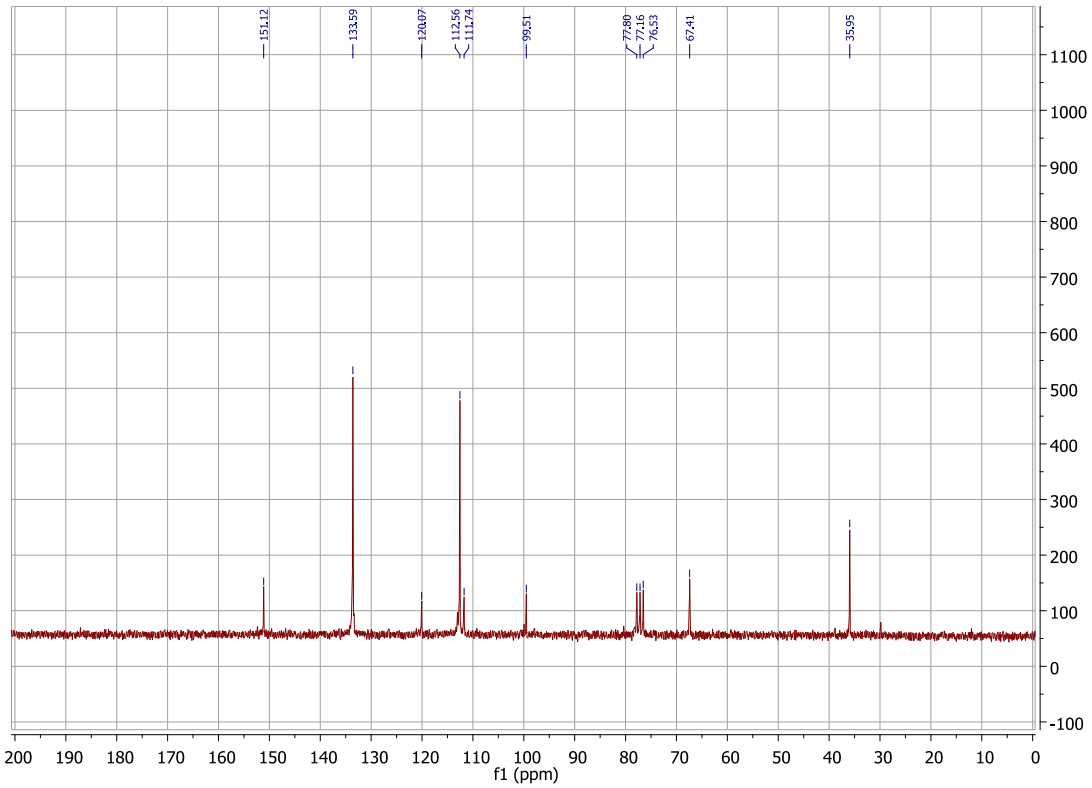




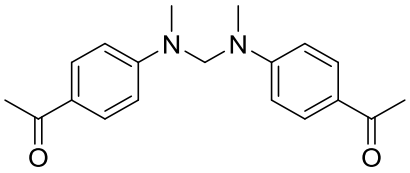
- **2j:** *4,4'*-(methylenebis(methylazanediyl))dibenzonitrile

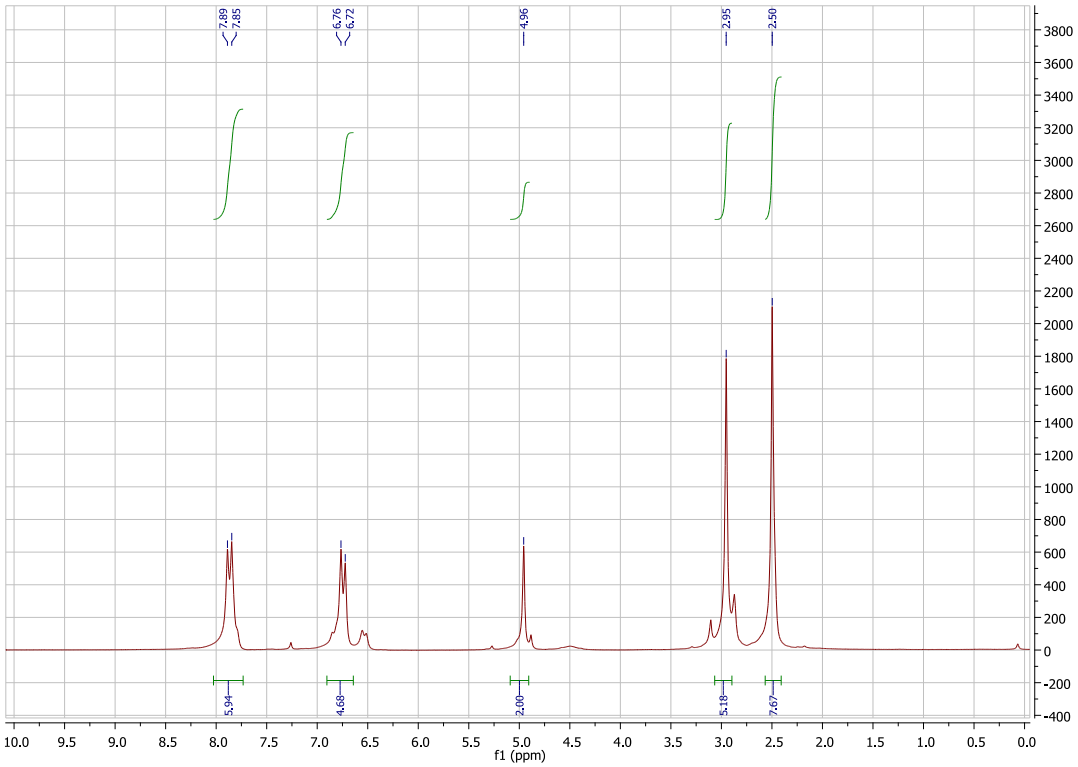


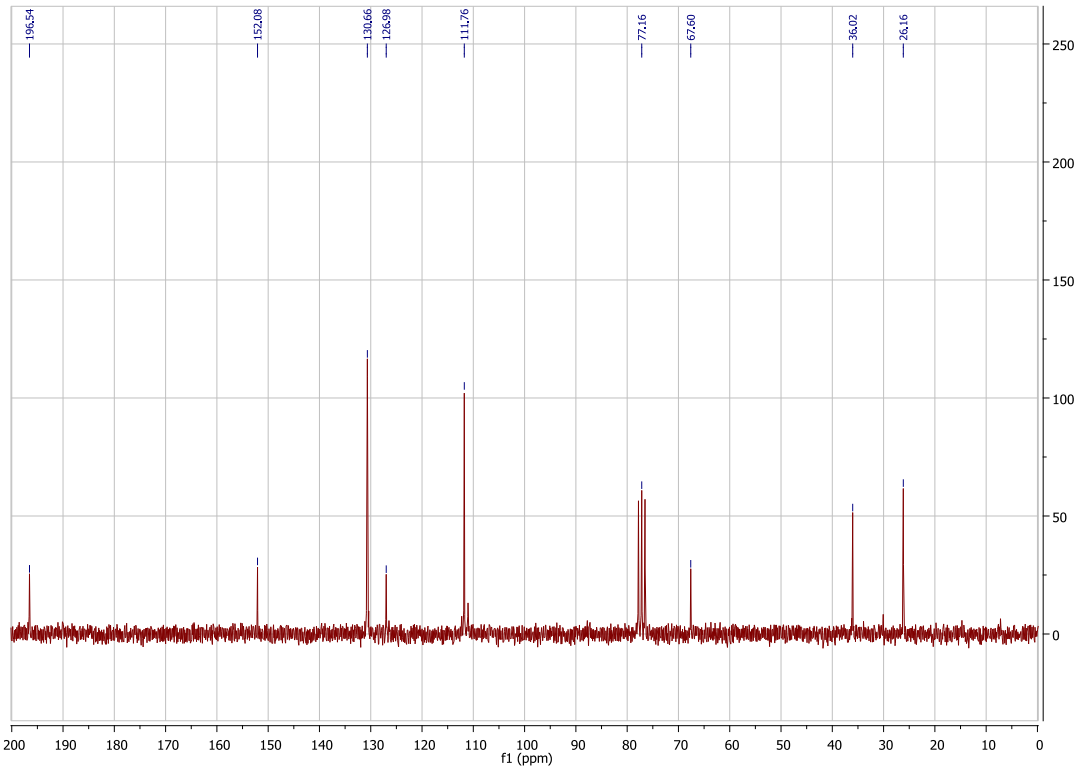




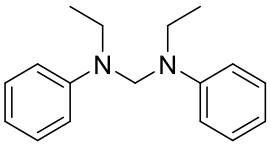
- **2k:** 1,1'-((methylenebis(methylazanediyl))bis(4,1-phenylene))bis(ethan-1-one)

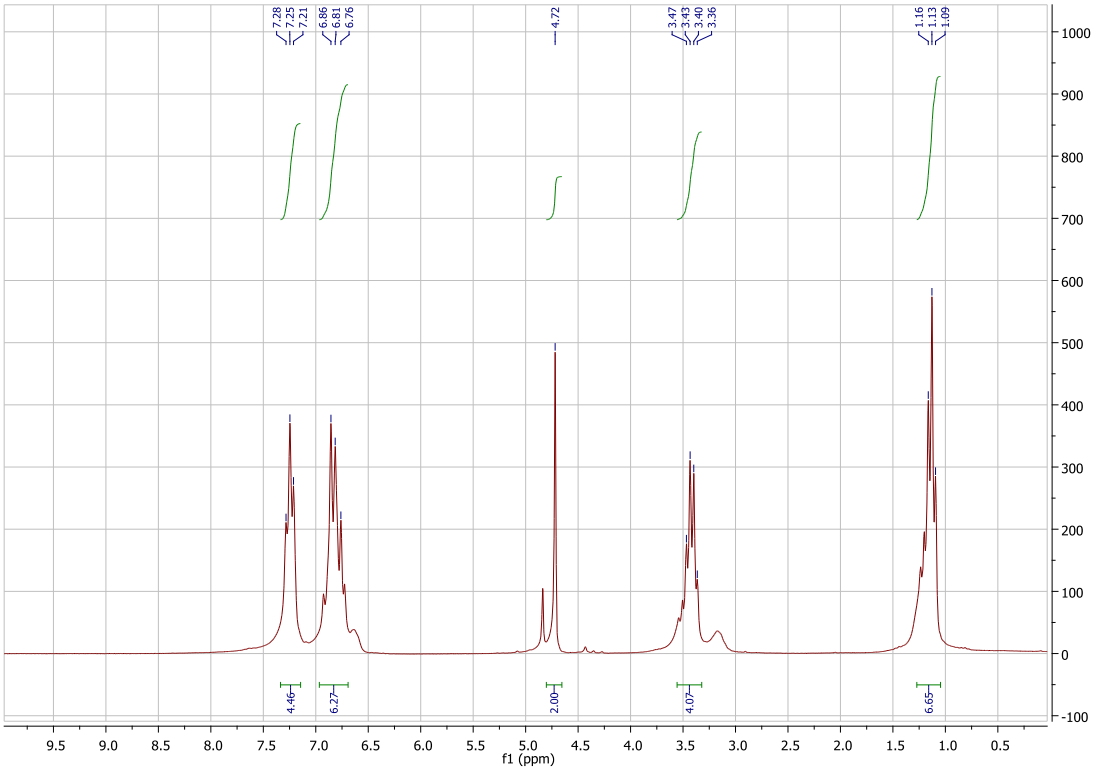


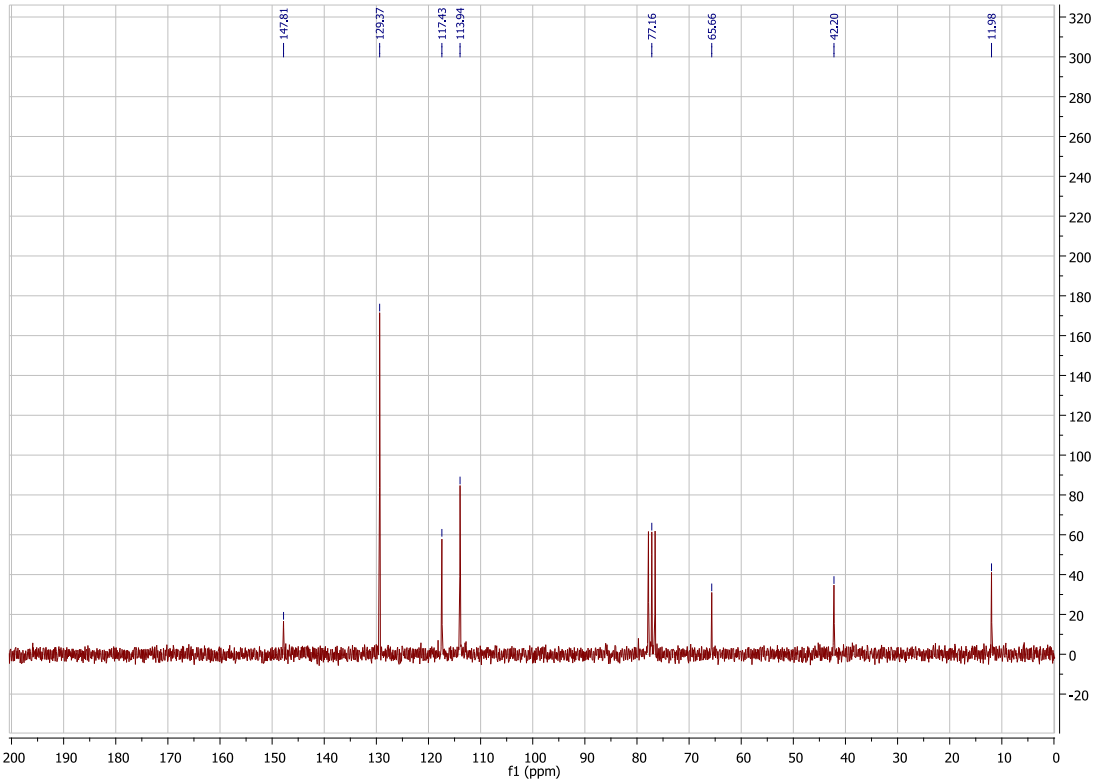




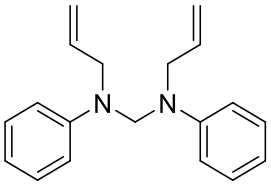
- **2l:** *N*,*N*'-diethyl-*N*,*N*'-diphenylmethanediamine

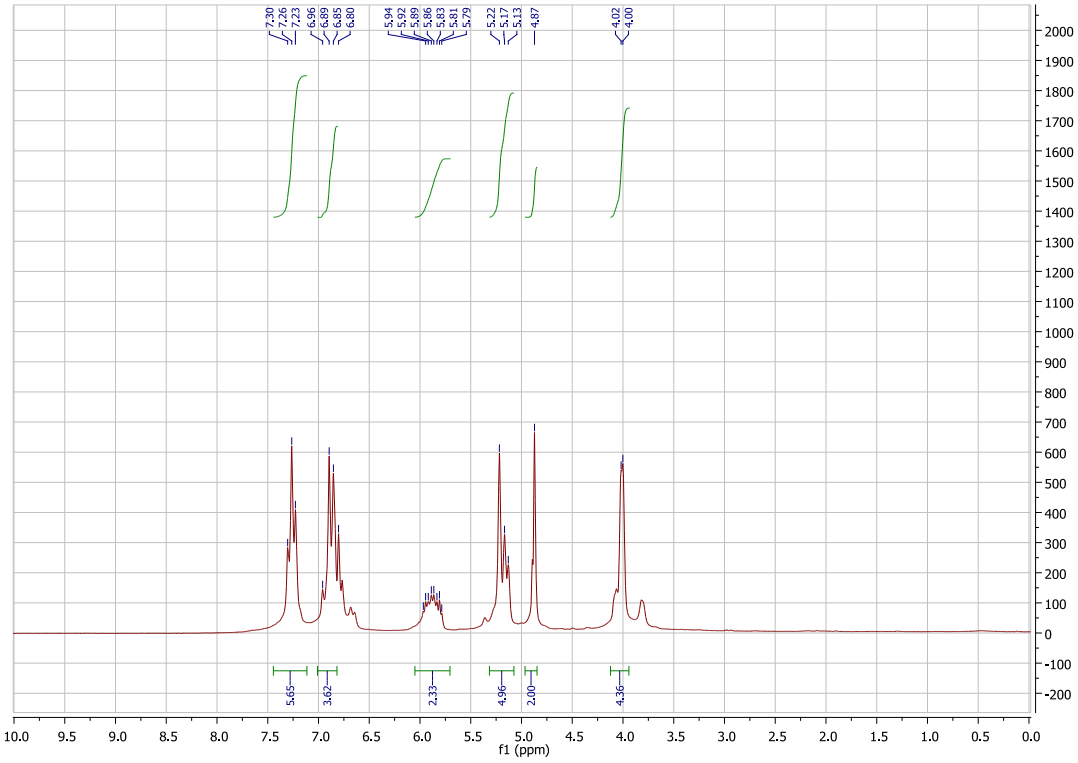


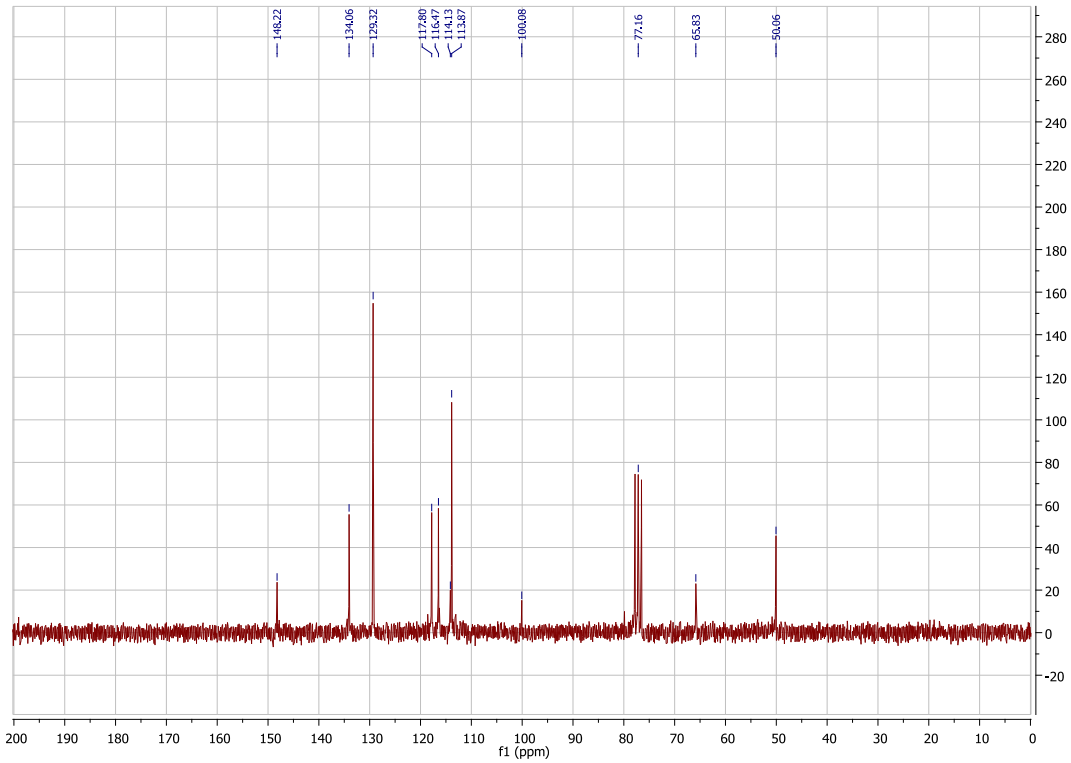




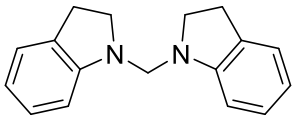
- **2m:** *N*,*N*'-diallyl-*N*,*N*'-diphenylmethanediamine

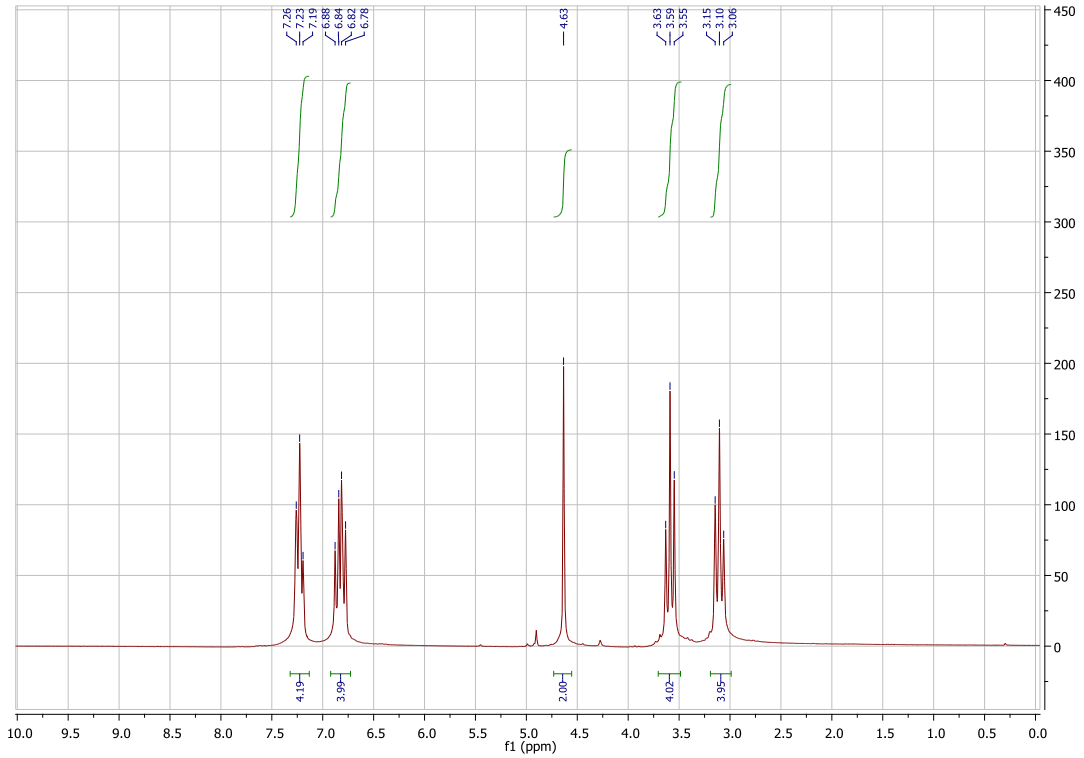


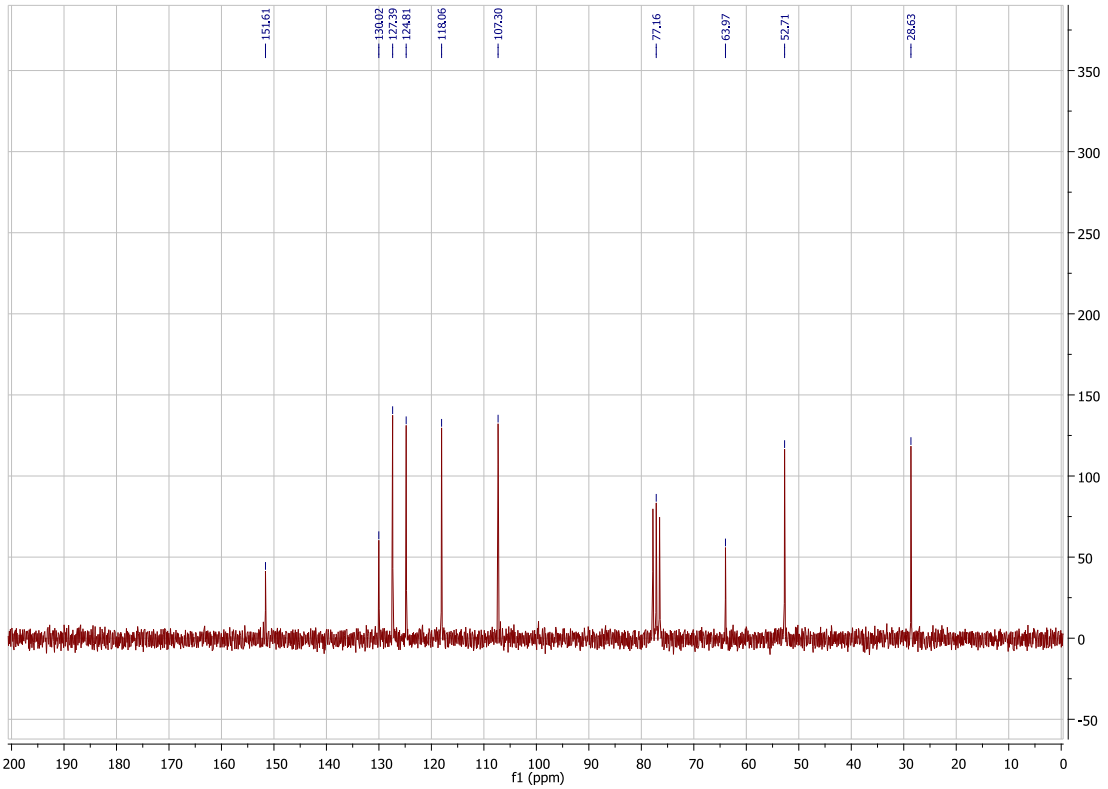




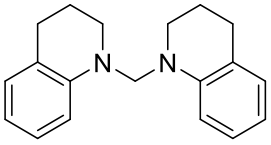
- **2p:** di(indolin-1-yl)methane

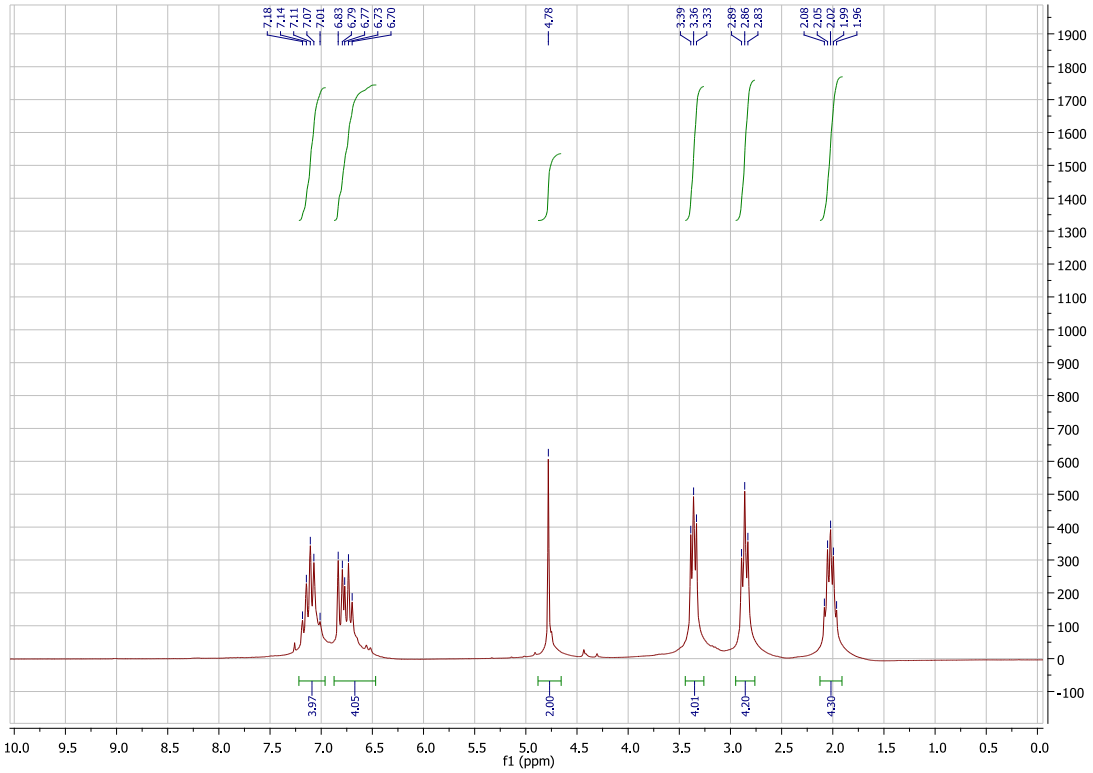


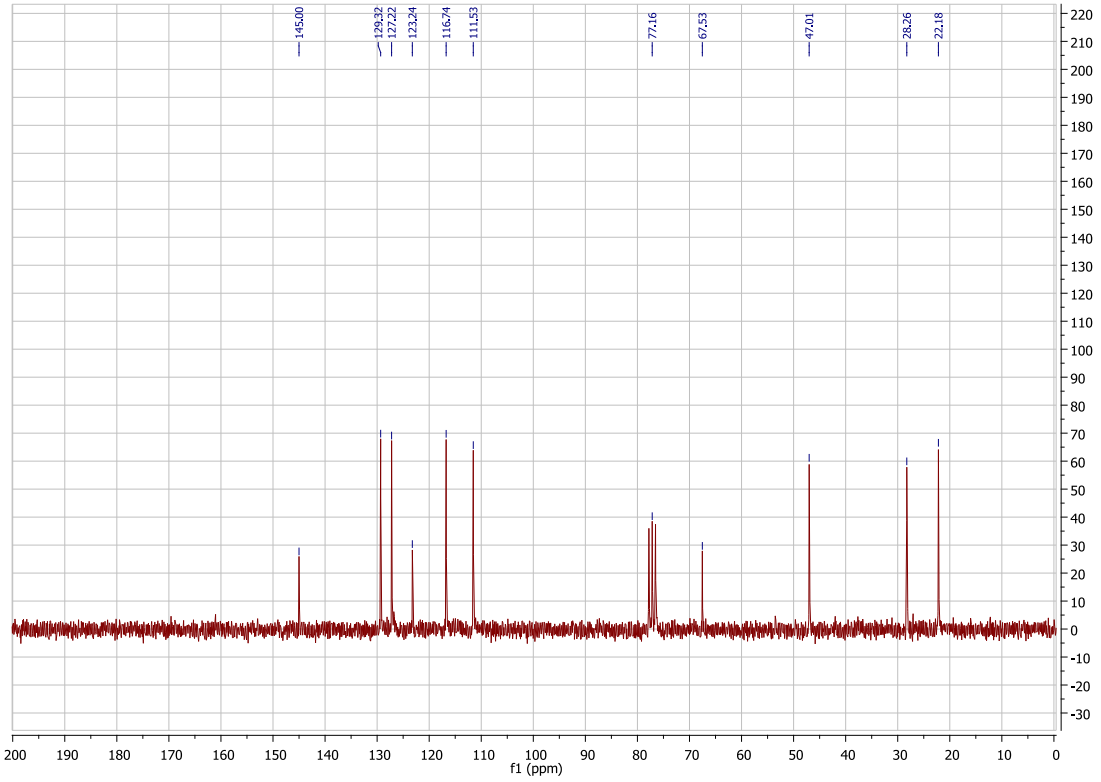




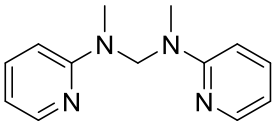
- **2q:** bis(3,4-dihydroquinolin-1(2H)-yl)methane

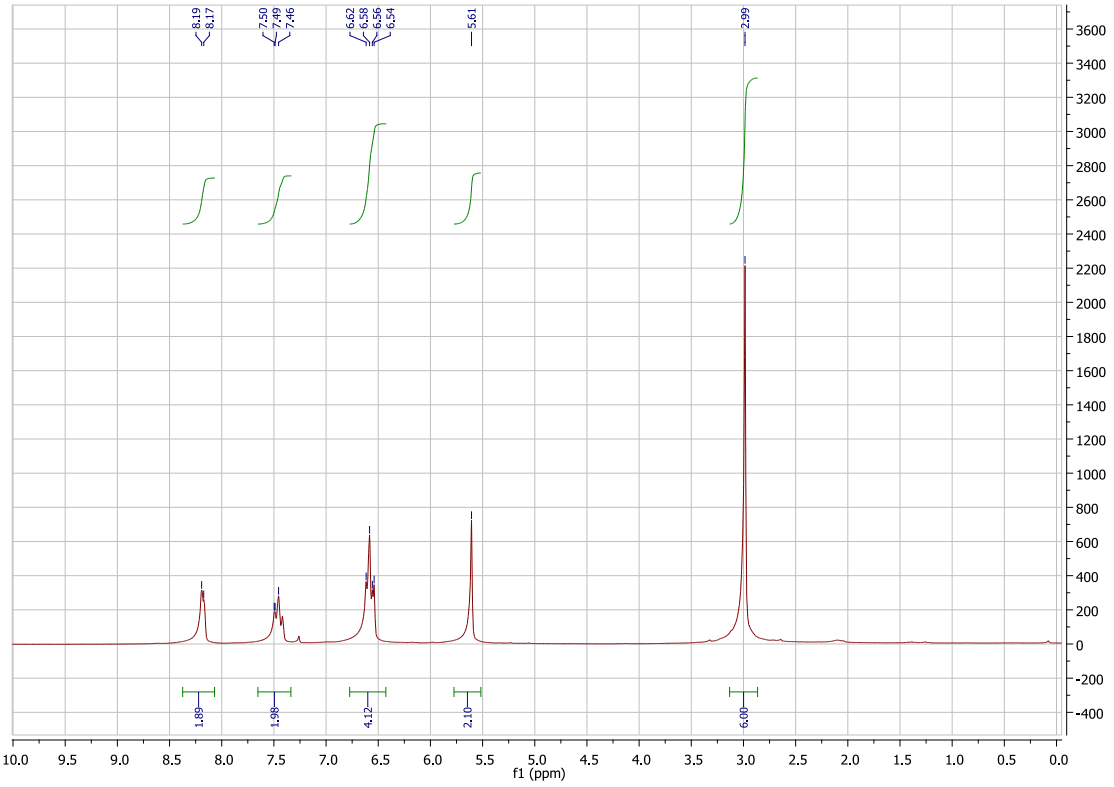


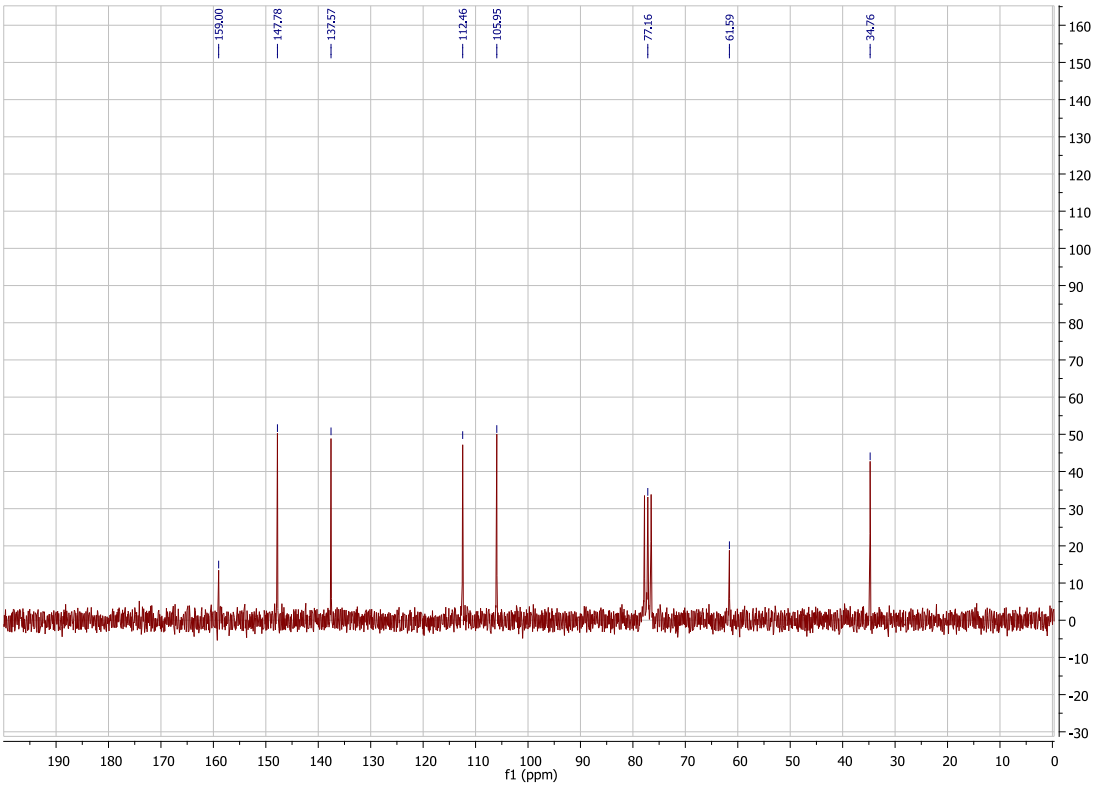




- **2s:** *N*,*N*'-dimethyl-*N*,*N*'-di(pyridin-2-yl)methanediamine



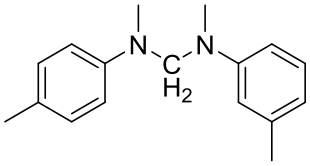


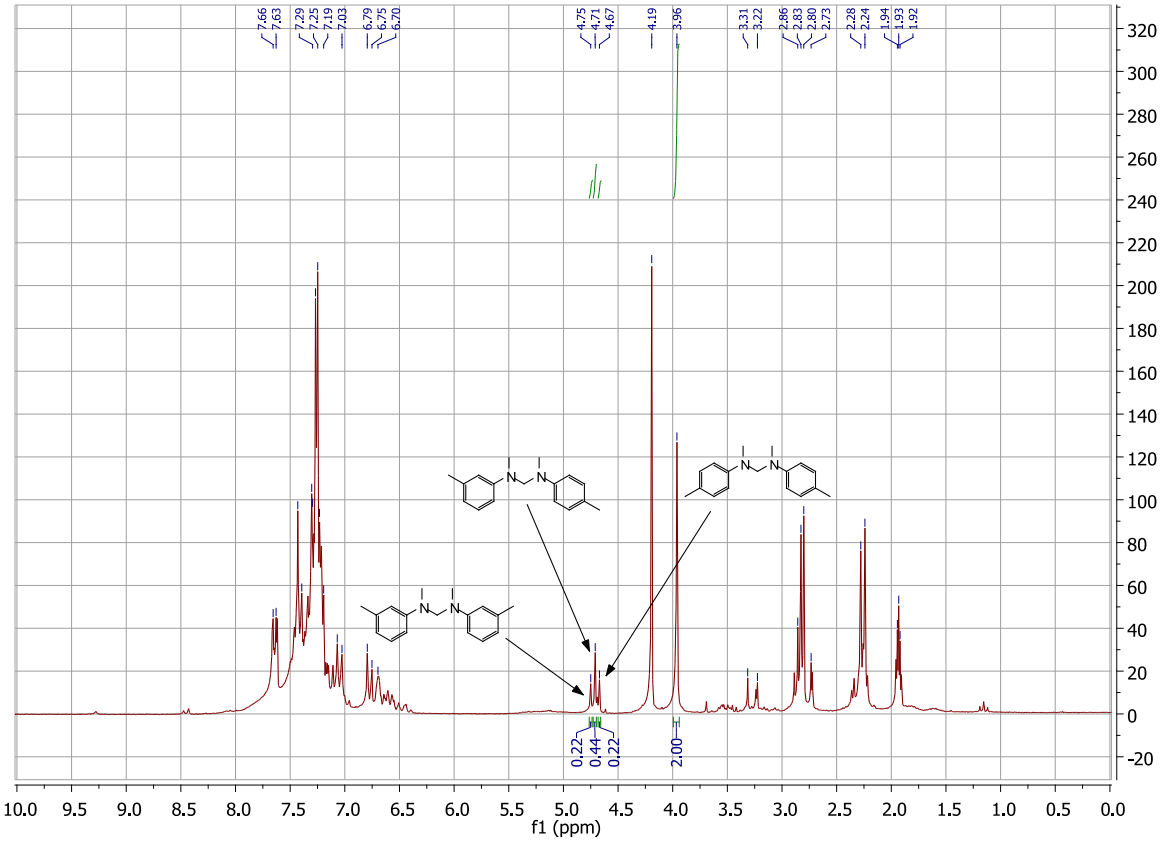


3.2. ^{1}H NMR spectra of crude mixture for mixed aminals

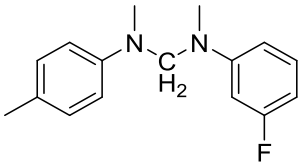
The following spectra present the NMR data of the aminals **4a**, **4b**, **4c**, **4d** and **4e,** from the crude mixture.

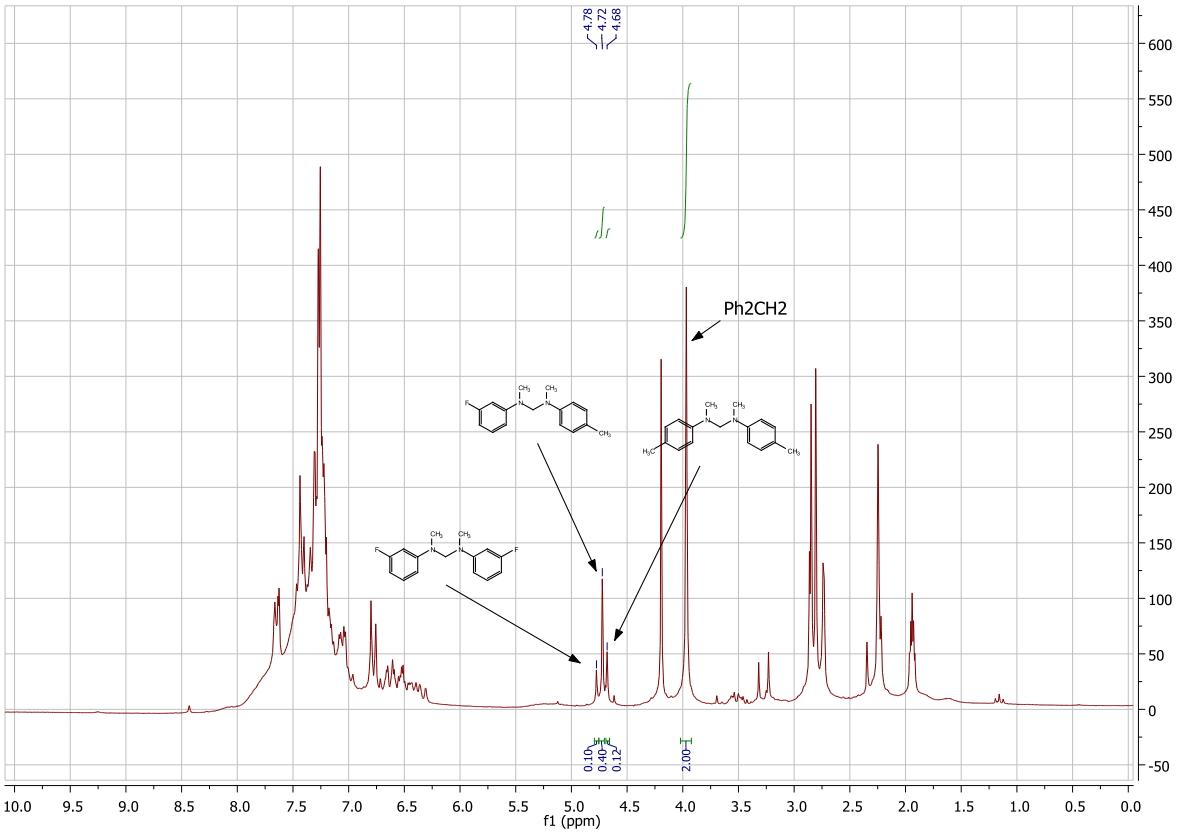
- **4a:** *N*,*N*'-dimethyl-*N*'-(m-tolyl)-*N*-(p-tolyl)methanediamine



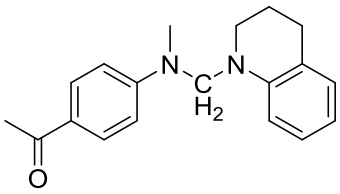


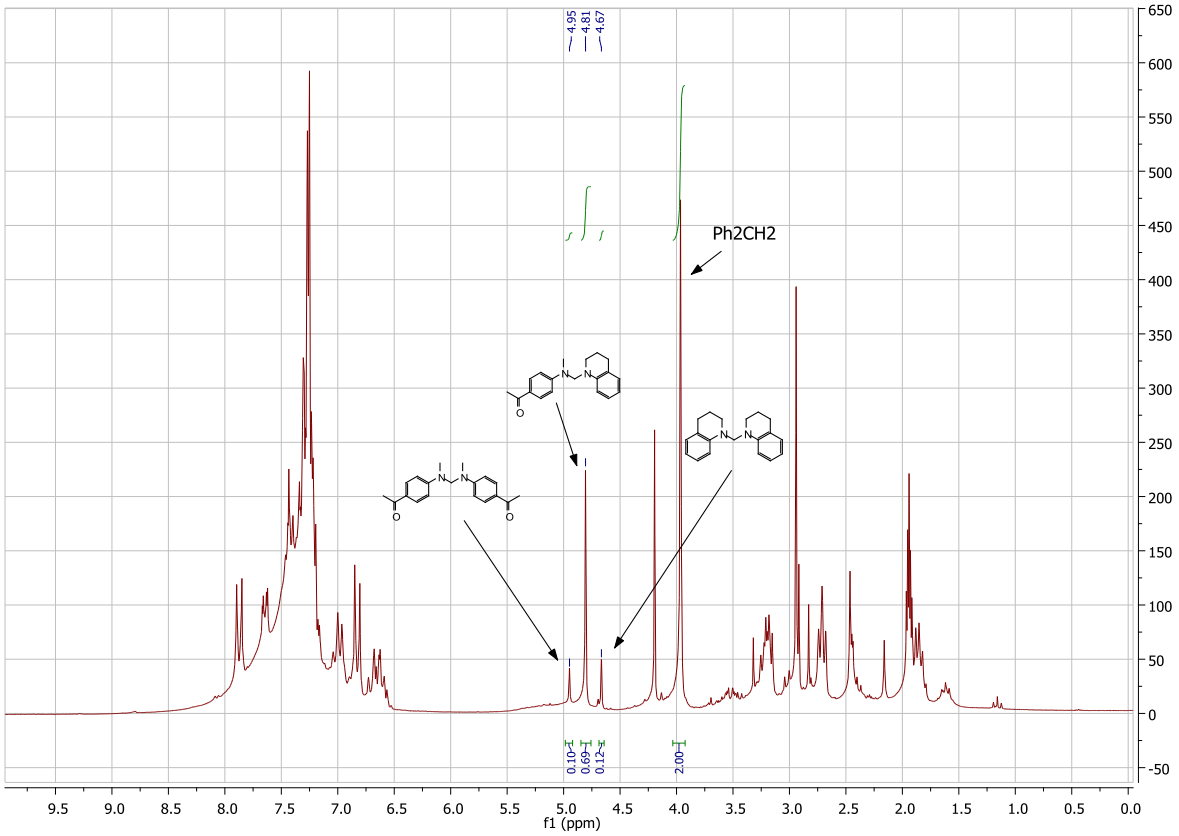
- **4b:** N-(3-fluorophenyl)-N,N'-dimethyl-N'-(p-tolyl)methanediamine



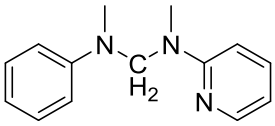


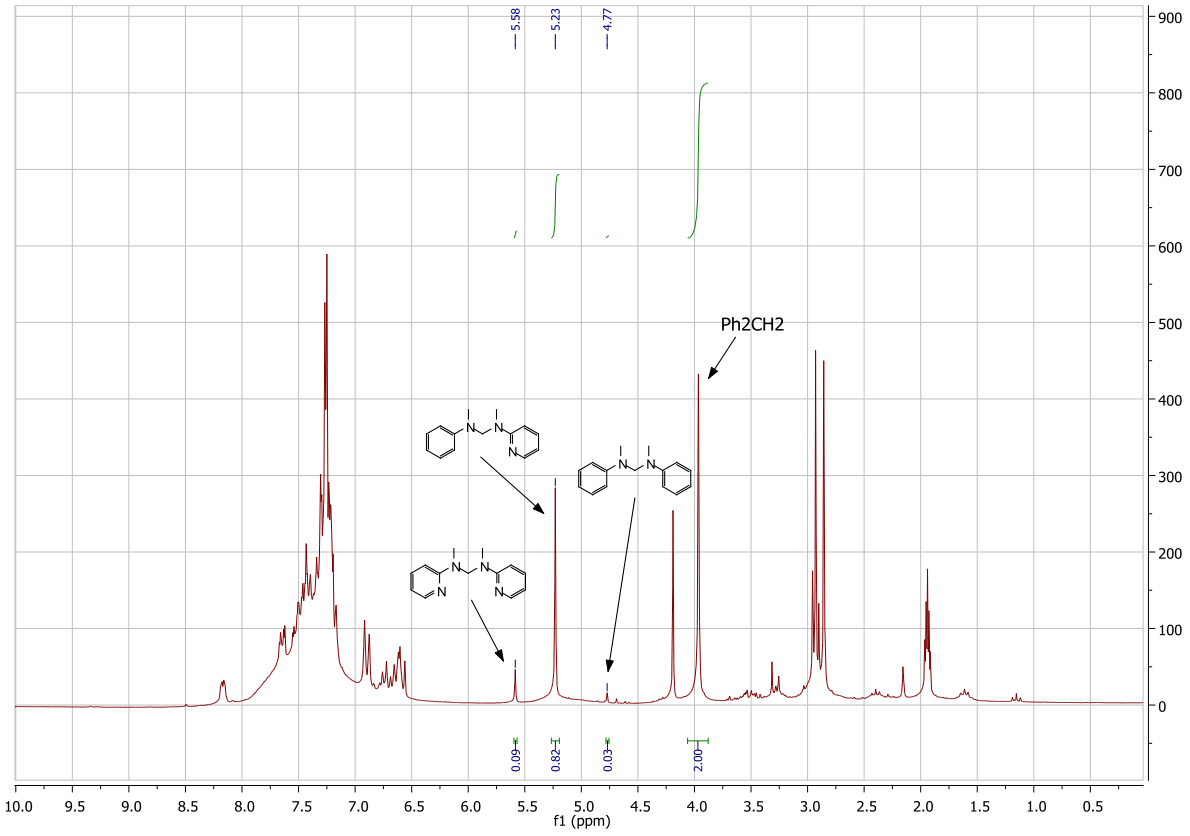
- **4c:** 1-(4-(((3,4-dihydroquinolin-1(2H)-yl)methyl)(methyl)amino)phenyl)ethan-1-one



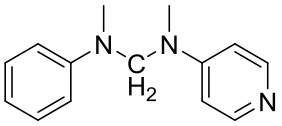


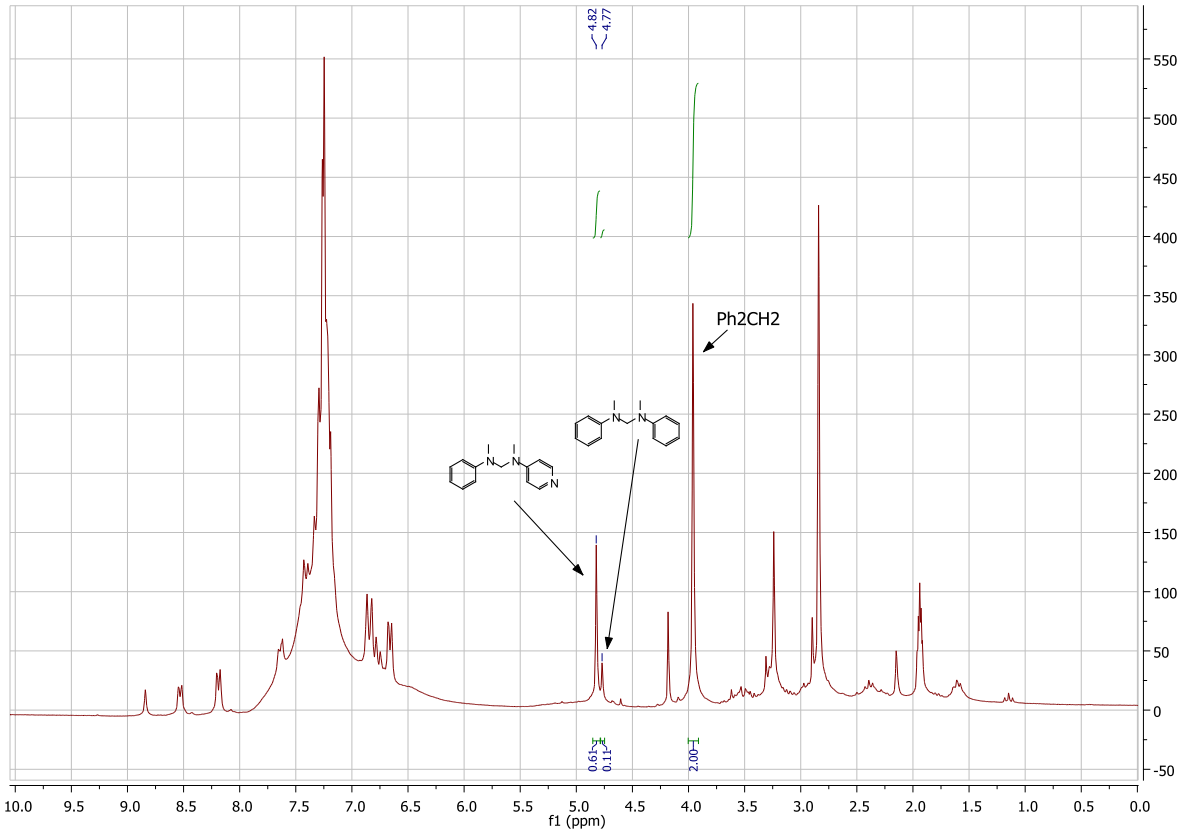
- **4d:** N,N'-dimethyl-N-phenyl-N'-(pyridin-2-yl)methanediamine





- **4e:** N,N'-dimethyl-N-phenyl-N'-(pyridin-4-yl)methanediamine





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