

Supporting Information

Synthesis of Azines in Solid State: Reactivity of Solid Hydrazine with Aldehydes and Ketones

Byeongno Lee,[†] Kyu Hyung Lee,[†] Jaeheung Cho,[‡] Wonwoo Nam,[‡] and Nam Hwi Hur^{*,†}

[†]Department of Chemistry, Sogang University, Seoul 121-742, Korea. [‡]Department of Bioinspired Science, Department of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750, Korea,

* e-mail: nhhur@sogang.ac.kr

Table of Contents

1. Experimental details	S2
2. Instrumentation	S2
3. General procedure for the preparation of azines in the solid state reactions between 1 and carbonyl compounds.	S4
4. Analytical data of azines obtained from the solid state reactions between 1 and carbonyl compounds.	S6
5. References	S11
6. Table S1. Structural data for single crystal of 3a	S12
7. Table S2. Selected bond distances and bond angles (Å, °) of 3a	S13-14
8. Table S3. Check CIF/PLATON report for 3a	S15-17
9. NMR data for 3a-3j	S18-43

1. Experimental details

Materials. Hydrazine monohydrate ($\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$), 2-methoxycinnamaldehyde, 2 4-chlorobenzaldehyde, 4-bromobenzaldehyde, 4-hydroxybenzaldehyde, 4-hydroxy-3,5-dimethoxybenzaldehyde (syringaldehyde), 3-nitrobenzaldehyde, 4-nitrobenzaldehyde, 2-naphthaldehyde, 1-(3-nitrophenyl)ethanone, and 1-(4-methoxyphenyl)ethanone were purchased from Sigma-Aldrich, which were used without any further purification. Hydrazinium carboxylate (**1**) was prepared by the reaction of $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$ with supercritical carbon dioxide.

2. Instrumentation

General. Powder X-ray diffraction patterns were recorded with a Rigaku DMAX 2500 diffractometer ($\text{Cu K}\alpha$) operating at 40 kV and 150 mA. Nicolet 205 instrument was used to measure infrared spectra. Absorption spectra were recorded on an Agilent 8453 UV-visible spectrophotometer. Melting point was measured with a SMP10-BIBBY. GC/MS data were recorded on Agilent 5973N and elemental analyses were obtained using a Carlo Erba EA1180 at the Organic Chemistry Research Center in Sogang University. High resolution mass spectrum was collected on a JMS-700 (JEOL) using NBA (3-nitrobenzyl alcohol) as a matrix at the Korea Basic Science Institute. ^1H NMR and ^{13}C NMR spectra in solution were recorded on a Varian 400-MHz Gemini operating at 400 MHz for ^1H and 100 MHz for ^{13}C , respectively. All chemical shifts were referenced to tetramethylsilane.

X-ray crystallography. A single crystal of (2-OCH₃)C₆H₄CH=N-N=CHC₆H₄(2-OCH₃) was selected by a nylon loop (Hampton Research Co.) placed on a handmade cooper plate, which was placed inside a liquid N₂ Dewar vessel at approximately -40 °C and was mounted on a goniometer head in a N₂ cryostream. Data collections were carried out in a Bruker SMART AXS diffractometer equipped with a monochromator with a Mo K α (λ = 0.71073 Å) incident beam. The charge-coupled device data were integrated and scaled using the Bruker-SAINT software package, and the structure was solved and refined using SHELXTL V 6.12.^{S1} Hydrogen atoms were located in the calculated positions. There are two independent but virtually identical molecules in the asymmetric unit. The crystal data for (2-OCH₃)C₆H₄CH=CH-CH=N-N=CH-CH=CHC₆H₄(2-OCH₃): C₂₀H₂₀N₂O₂, Monoclinic, *P*2(1)/*n*, *Z* = 4, *a* = 19.0367(6), *b* = 4.9902(2), *c* = 19.2908(7) Å, β = 108.317(2) °, *V* = 1728.37(11) Å³, μ = 0.080 mm⁻¹, ρ_{calcd} = 1.223 g/cm³, *R*₁ = 0.0387, and *wR*₂ = 0.0971 for 3368 unique reflections and 220 variables. The crystallographic data for (2-OCH₃)C₆H₄CH=CH-CH=N-N=CH-CH=CHC₆H₄(2-OCH₃) are listed in Table S1, while Table S2 lists the selected bond distances and angles. CCDC-844336 for (2-OCH₃)C₆H₄CH=N-N=CHC₆H₄(2-OCH₃) contains the supplementary crystallographic data for this paper (see also Table S3, Check CIF/PLATON report). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Precaution. The solid hydrazine, hydrazinium carboxylate (**1**), could be harmful for health due to its sublimation character. The equipment of effective ventilation is highly recommended for handling the solid hydrazine to avoid vapor inhalation.

3. General procedure for the preparation of azines in the solid state reactions between **1** and carbonyl compounds.

A 10.0 mmol of carbonyl compound was mixed with 0.38 g of hydrazinium carboxylate (**1**, 5.0 mmole), which was then ground using a pestle and a mortar. After grinding at ambient temperature, the ground powder was stored in the closed vial. The ground mixture was heated at 60 °C until the reaction was complete. Complete conversion to azine was dependent upon the nature of carbonyl compounds. Typically aldehydes take about 5 h to complete the reactions while ketones take much longer (about 24 h). CO₂ and water were released from the reaction mixture. All azine derivatives obtained from the reactions of **1** with carbonyl compounds are characterized by ¹H and ¹³C NMR spectroscopy. The products have over 97 % of purity of reaction mixture based on ¹H NMR spectroscopy and their isolation yields are over 97 % based on **1**. The melting points of all azine products were measured after purification with appropriate solvent.

Crystal growth of 1,2-bis((E)-3-(2-methoxyphenyl)allylidene)hydrazine (**3a**).

Single crystals were grown by dissolving the azines in appropriate solvents. For the growth of **3a** crystals, a chloroform solvent was added into the solid powder of 0.1 g until the powder was completely dissolved at ambient temperature, followed by addition of the similar amount of ether without mixing in a 10 mL vial. The resulting solution was carefully stored in the refrigerator for a day. Yellow crystals were grown from the

solution, which were separated by filtering and washing with pentane (3×10 mL).

Synthesis of 1,2-bis((E)-3-(2-methoxyphenyl)allylidene)hydrazine (3a) by reaction of 2-methoxycinnamaldehyde with 1 at low and ambient temperature.

A 10.0 mmol of 2-methoxycinnamaldehyde (**2a**) was mixed with 0.38 g of hydrazinium carboxylate (**1**, 5.0 mmole), which was then ground using a pestle and a mortar. After grinding at ambient temperature, the ground powder was divided into two parts, which were stored in two separate vials. One vial with a slightly loosen cap was left in the lab table and the other was stored in the refrigerator set at 4 °C. No agitation was made until the reactions were complete. The reaction progress was carefully monitored by ^1H NMR spectroscopy (see Fig. S6).

Synthesis of 1,2-bis((E)-3-(2-methoxyphenyl)allylidene)hydrazine (3a) by reaction of 2-methoxycinnamaldehyde with hydrazine hydrate in solution.

A solution of hydrazine hydrate (0.267 g, 5.0 mmol) was slowly added for 10 min into a 10 mL of ether solution containing a 10.0 mmol (1.62 g) of 2-methoxycinnamaldehyde (**2a**), which was reacted for 5 h at room temperature. The azine (**3a**, ~75%) were obtained from the reaction along with about 12 % of unidentified compounds and about 13 % of un-reacted aldehyde, **2a**. The products were checked by ^1H NMR spectroscopy (see Fig. S7).

Synthesis of 1,2-bis((E)-3-(2-methoxyphenyl)allylidene)hydrazine (3a) by reaction of 2-methoxycinnamaldehyde in the absence of a solvent.

A solution of hydrazine hydrate (0.267 g, 5.0 mmol) was slowly added for 10 min into a

10.0 mmol (1.62 g) of 2-methoxycinnamaldehyde (**2a**) without a solvent, which was reacted for 2 h at room temperature. The azine (**3a**, ~40%) were obtained from the reaction along with about 12 % of unidentified compounds and about 48 % of un-reacted aldehyde, **2a**. The products were checked by ^1H NMR spectroscopy (see Fig. S8)..

4. Analytical data of azines obtained from the solid state reactions between **1** and carbonyl compounds.

Analytical data are obtained from the purified samples. The purity is based on the ^1H NMR spectrum.

1,2-bis((E)-3-(2-methoxyphenyl)allylidene)hydrazine (3a). Yield/purity (1.56 g, 97 />98%). mp 175 °C (CHCl_3 /ether). Elemental analysis (Found: C, 75.13; H, 5.99; N, 8.53. Calc. For $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_2$: C, 74.98; H, 6.29; N, 8.74 %). $\lambda_{\text{max}}(\text{CHCl}_3)/\text{nm}$ 370 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; 5.75×10^4). $\nu_{\text{max}}(\text{powder})/\text{cm}^{-1}$ 1653w and 1558m, $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$. δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 3.90 (6H, s, OCH_3), 6.92 (d, $J = 8.4$ Hz, 2H, C-*H*, phenyl), 6.98 (t, $J = 7.6$ Hz, 2H, C-*H*, phenyl), 7.16 (dd, $J_{a,b} = 10.0$ Hz, $J_{b,c} = 16.4$ Hz, 2H, $\text{CH}_c=\text{CH}_b\text{CH}_a=\text{N}$), 7.32 (dd, $J = 8.4$ Hz, $J = 7.6$ Hz, 2H, C-*H*, phenyl), 7.42 (d, $J_{b,c} = 16.4$ Hz, 2H, - $\text{CH}_c=\text{CH}_b$ -), 7.56 (d, $J = 7.6$ Hz, 2H, C-*H*, phenyl), 8.38 (d, $J_{a,b} = 10.0$ Hz, 2H, $\text{CH}_a=\text{N}$). δ_{C} (100 MHz; CDCl_3 ; Me_4Si) 55.5 (OCH_3), 111.1 (CH-C=N), 120.8 (CH, phenyl), 124.8 ($\text{C}_{\text{quart}}-1$, phenyl), 125.9, 127.8, 130.67 (CHs, phenyl), 138.5 (Ph-CH=CH), 157.5 ($\text{C}_{\text{quart}}-2$ phenyl), 164.3 (C=N) (see Fig. S1 – S5). MS (EI+) $m/z = 320$ (100), 289 (75), 187 (97), 131 (33), 91 (22), 77 (14). HRMS (ES+) Calc. For $\text{C}_{20}\text{H}_{21}\text{N}_2\text{O}_2$ ($\text{M}+\text{H}$) $^+$ m/z 321.1603 (M^+), Obsd. 321.1603.

1,2-bis(4-chlorobenzylidene)hydrazine (3b).

Yield/purity (1.35g, 97/>98%). mp 208-210 °C (CH₂Cl₂/ether), lit. 209-210 °C.^{S2}

Elemental analysis (Found: C, 60.38; H, 3.50; N, 10.07. Calc. For C₁₄H₁₀Cl₂N₂: C, 60.67; H, 3.64; Cl, 25.58; N, 10.11 %). $\lambda_{\max}(\text{CHCl}_3)/\text{nm}$ 313 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; 4.77×10^4). δ_{H} (400 MHz; CDCl₃; Me₄Si) 7.44 (d, $J = 8.4$ Hz, 4H, C3-*H* and C5-*H*, phenyl), 7.79 (d, $J = 8.4$ Hz, 4H, C2-*H* and C6-*H*, phenyl), 8.61 (s, 2H, CH=N). δ_{C} (100 MHz; CDCl₃; Me₄Si) 129.1 (CH-2 and C-6, phenyl), 129.7 (CH-3 and CH-5, phenyl), 132.4 (C_{quart}-1, phenyl), 137.3 (C_{quart}-4, phenyl), 161.1 (C=N) (see Fig. S9 and S10).

1,2-bis(4-bromobenzylidene)hydrazine (3c).

Yield/purity (1.78 g, 97/>98%). mp 223 °C (CH₂Cl₂/ether), lit. 223.5-224.5 °C.^{S3}

Elemental analysis (Found: C, 46.21; H, 2.54; N, 7.90. Calc. For C₁₄H₁₀Br₂N₂: C, 45.94; H, 2.75; Br, 43.66; N, 7.65 %). $\lambda_{\max}(\text{CHCl}_3)/\text{nm}$ 316 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; 4.30×10^4). δ_{H} (400 MHz; CDCl₃; Me₄Si) 7.59 (d, $J = 8.0$ Hz, 4H, C3-*H* and C5-*H*, phenyl), 7.71 (d, $J = 8.0$ Hz, 4H, C2-*H* and C6-*H*, phenyl), 8.60 (s, 2H, CH=N). δ_{C} (100 MHz; CDCl₃; Me₄Si) 125.8 (C_{quart}-4, phenyl), 129.9 (CH-2 and C-6, phenyl), 132.1 (CH-3 and CH-5, phenyl), 132.9 (C_{quart}-1, phenyl), 161.2 (C=N) (see Fig. S11 and S12).

1,2-Bis(4-hydroxybenzylidene)hydrazine (3d).

Yield/purity (1.18 g, 98/>98%). mp 267 °C (CHCl₃), lit. 265-268 °C.^{S4}

Elemental analysis (Found: C, 69.87; H, 5.06; N, 11.49. Calc. For C₁₄H₁₂N₂O₂: C, 69.99; H, 5.03; N, 11.66 %). $\lambda_{\max}(\text{CH}_3\text{OH})/\text{nm}$ 333 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; 4.32×10^4). δ_{H} (400 MHz; CD₃OD/DMSO-d₆, 10/1; Me₄Si): 4.87 (s, 2H, OH, exchangeable signal), 6.86 (d, $J = 8.4$

Hz, 4H, *CH*-3 and *CH*-5), 7.69 (d, $J = 8.4$ Hz, 4H, *CH*-2 and *CH*-6), 8.52 (s, 2H, *CH*=N); δ_C (100 MHz; CD₃OD/DMSO-*d*₆, 10/1; Me₄Si) 115.7 (*CH*-3 and *CH*-5), 125.6 (*C*_{quart}-1), 130.3 (*CH*-2 and *CH*-6), 160.6 (*CH* = N), 160.9 (*C*_{quart}-4) (see Fig. S13 and S14).

4,4'-hydrazine-1,2-diylidenebis(methan-1-yl-1-ylidene)bis(2,6-dimethoxyphenol)

(3e).^{S5,S6}

Yield/purity (1.75 g, 97/>98%). mp 214-215 °C (CHCl₃/ether). Elemental analysis (Found: C, 60.13; H, 5.75; N, 7.61. Calc. For C₁₈H₂₀N₂O₆: C, 59.99; H, 5.59; N, 7.77 %). λ_{\max} (CHCl₃)/nm 349 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; 5.64×10^4). δ_H (400 MHz; CDCl₃; Me₄Si) 3.97 (s, 6H, OCH₃), 5.83 (br s, 2H, OH, exchangeable signal), 7.10 (s, 4H, C2-*H* and C6-*H*, phenyl), 8.56 (s, 2H, *CH*=N). δ_C (100 MHz; CDCl₃; Me₄Si) 56.4 (OCH₃), 105.3 (*CH*-2 and C-6, phenyl), 125.6 (*C*_{quart}-1, phenyl), 137.7 (*C*_{quart}-OH-4, phenyl), 147.2 (*C*_{quart}-OMe-3 and *C*_{quart}-OMe-5, phenyl), 161.4 (*C*=N) (see Fig. S15 and S16).

1,2-bis(3-nitrobenzylidene)hydrazine (3f)

Yield/purity (1.46 g, 97/>98%). mp 192-194 °C (CHCl₃), lit. 195-196 °C.^{S2} Elemental analysis (Found: C, 56.64; H, 3.09; N, 18.59. Calc. For C₁₄H₁₀N₄O₄: C, 56.38; H, 3.38; N, 18.78 %). λ_{\max} (CHCl₃)/nm 279 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; 4.78×10^4). δ_H (400 MHz; CDCl₃; Me₄Si) 7.68 (t, $J = J' = 8.0$ Hz, 2H, C5-*H*, phenyl), 8.18 (d, $J = 8.0$ Hz, 2H, C4-*H*, phenyl), 8.36 (d, $J' = 8.0$ Hz, 2H, C6-*H*), 8.73 (s, 4H, C2-*H*, phenyl and *CH*=N). δ_C (100 MHz; CDCl₃; Me₄Si) 123.2 (*CH*-2, phenyl), 125.8 (*CH*-4, phenyl), 129.9 (*CH*-5, phenyl), 134.2 (*CH*-6, phenyl), 135.5 (*C*_{quart}-1, phenyl), 148.7 (*C*_{quart}-3 phenyl), 160.6 (*C*=N) (see Fig. S17 and S18).

1,2-bis(4-nitrobenzylidene)hydrazine (3g)

Yield/purity (1.45 g, 97/>97%). mp >300 °C, slightly dec. (CHCl₃), lit. 299-302 °C.^{S4} (Found: C, 56.33; H, 3.27; N, 18.92. Calc. For C₁₄H₁₀N₄O₄: C, 56.38; H, 3.38; N, 18.78 %). $\lambda_{\max}(\text{CHCl}_3)/\text{nm}$ 328 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; 3.51×10^4). δ_{H} (400 MHz; CDCl₃/acetone-d₆ (2/1); Me₄Si) 6.64 (d, J = 8.4 Hz, 4H, C2-*H* and C6-*H*, phenyl), 7.42 (d, J = 8.4 Hz, 4H, C3-*H* and C5-*H*, phenyl), 8.28 (s, 2H, CH=N), δ_{C} (100 MHz; CDCl₃/acetone-d₆ (2/1); Me₄Si) 115.7 (CH-3 and CH-5, phenyl), 126.1 (*C*_{quart}-1, phenyl), 130.1 (CH-2 and CH-6, phenyl), 159.8 (*C*_{quart}-4, phenyl), 160.8 (C=N) (see Fig. S19 and S20).

1,2-Bis(naphthalen-2-ylmethylene)hydrazine (3h).

Yield/purity (1.49 g, 97/>98%). mp 233 °C (CHCl₃), lit. 232-232.5 °C.^{S7} Elemental analysis (Found: C, 85.63; H, 5.24; N, 8.98. Calc. For C₂₂H₁₆N₂: C, 85.69; H, 5.23; N, 9.08 %). $\lambda_{\max}(\text{CHCl}_3)/\text{nm}$ 330 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; 4.95×10^4). δ_{H} NMR (400 MHz, CDCl₃, Me₄Si) 7.54-7.57 (m, 4H, naphthyl CHs), 7.87-7.95 (m, 6H, naphthyl CHs), 8.13-8.17 (m, 4H, naphthyl CHs), 8.88 (s, 2H, CH=N); δ_{C} 123.7, 126.7, 127.5, 127.9, 128.69, 128.71, 131.0 (CH, naphthyl), 131.8 (*C*_{quart}-5), 133.2 (*C*_{quart}-10), 134.9 (*C*_{quart}-2), 162.4 (CH = N) (see Fig. S21 and S22).

1,2-bis(1-(3-nitrophenyl)ethylidene)hydrazine (3i)

Yield/purity (1.58 g, 97/>98%). mp 201-203 °C (CHCl₃), lit. 202-203 °C.^{S2} Elemental analysis (Found: C, 58.77; H, 4.16; N, 17.43. Calc. For C₁₆H₁₄N₄O₄: C, 58.89; H, 4.32; N, 17.17 %). $\lambda_{\max}(\text{CHCl}_3)/\text{nm}$ 271 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; 7.74×10^4). δ_{H} (400 MHz; CDCl₃;

Me₄Si) 2.41 (s, 6H, CH₃), 7.63 (t, *J* = 8.0 Hz, 2H, C5-*H*, phenyl), 8.27-8.31 (m, 6H, C2-*H*, C4-*H* and C6-*H*, phenyl), 8.76 (s, 2H, CH=N). δ_C (100 MHz; CDCl₃; Me₄Si) 15.2 (CH₃), 121.6 (CH-2, phenyl), 124.5 (CH-4, phenyl), 129.4 (CH-5, phenyl), 132.4 (CH-6, phenyl), 139.6 (C_{quart}-1, phenyl), 148.5 (C_{quart}-3 phenyl), 156.7 (C=N) (see Fig. S23 and S24).

1,2-bis(1-(4-methoxyphenyl)ethylidene)hydrazine (3j)

Yield/purity (1.44 g, >97/>98 %). mp 200-202 °C (CHCl₃/pentane). lit. 134-136 °C.^{S8} Elemental analysis (Found: C, 73.06; H, 6.69; N, 9.71. Calc. For C₁₈H₂₀N₂O₂: C, 72.95; H, 6.80; N, 9.45 %). λ_{max}(CHCl₃)/nm 249 (ε/dm³ mol⁻¹ cm⁻¹; 1.15x10⁵). δ_H (400 MHz; CDCl₃; Me₄Si) 2.32 (s, 6H, N=CCH₃), 3.85 (s, 6H, OCH₃), 6.94 (d, *J* = 8.8 Hz, 4H, C3-*H* and C5-*H*, phenyl), 7.88 (d, *J* = 8.8 Hz, 4H, C2-*H* and C6-*H*, phenyl); δ_C (100 MHz; CDCl₃; Me₄Si) 14.8 (N=CCH₃), 55.4 (OCH₃), 113.6 (CH-3 and CH-5, phenyl), 128.1 (CH-2 and CH-6, phenyl), 131.3 (C_{quart}-1, phenyl), 157.80 (C_{quart}-4, phenyl), 160.79 (C=N) (see Fig. S25 and S26).

5. References

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Table S1. Structural data for 1,2-bis((E)-3-(2-methoxyphenyl)allylidene)hydrazine (3a)

Formula sum	C ₂₀ H ₂₀ N ₂ O ₂
Formula weight	320.38
Crystal system	monoclinic
Space group	<i>P</i> 1 21/n 1 (no. 14)
Unit cell dimensions	$a = 19.0000(6) \text{ \AA}$ $b = 4.9688(2) \text{ \AA}$ $c = 19.2500(7) \text{ \AA}$ $\beta = 108.0()^\circ$
Cell volume	1728.37(11) \AA^3
Z	4
Density, calculated	1.231 g/cm ³
R _{All}	0.048
Pearson code	mP176
Formula type	NOP10Q10
Wyckoff sequence	e ⁴⁴

Table S2. Selected bond distances and bond angles (Å , °)

O1—C2	1.359(2)	C3—H3	0.950
O1—C1	1.422(2)	C1—H1A	0.980
O2—C12	1.359(2)	C1—H1B	0.980
O2—C11	1.422(2)	C1—H1C	0.980
N1—C10	1.281(2)	C14—C15	1.375(2)
N1—N1 ⁱ	1.398(2)	C14—C13	1.383(2)
N2—C20	1.281(2)	C14—H14	0.950
N2—N2 ⁱⁱ	1.398(3)	C15—C16	1.375(3)
C4—C3	1.367(2)	C15—H15	0.950
C4—C5	1.375(2)	C16—C17	1.391(2)
C4—H4	0.950	C16—H16	0.950
C5—C6	1.375(2)	C17—C12	1.406(2)
C5—H5	0.950	C17—C18	1.453(2)
C6—C7	1.391(2)	C18—C19	1.336(2)
C6—H6	0.950	C18—H18	0.950
C7—C2	1.406(2)	C19—C20	1.422(2)
C7—C8	1.453(2)	C19—H19	0.950
C8—C9	1.336(2)	C20—H20	0.950
C8—H8	0.950	C12—C13	1.383(2)
C9—C10	1.430(2)	C11—H11A	0.980
C9—H9	0.950	C11—H11B	0.980
C10—H10	0.950	C11—H11C	0.980
C2—C3	1.383(2)	C13—H13	0.950
C2—O1—C1	117.00(11)	H1A—C1—H1C	109.50
C12—O2—C11	117.5(1)	H1B—C1—H1C	109.50
C10—N1—N1 ⁱ	111.50(17)	C15—C14—C13	120.50(16)
C20—N2—N2 ⁱⁱ	111.50(17)	C15—C14—H14	119.60
C3—C4—C5	120.00(14)	C13—C14—H14	119.60
C3—C4—H4	119.80	C16—C15—C14	119.50(14)
C5—C4—H4	119.80	C16—C15—H15	120.20
C6—C5—C4	119.50(16)	C14—C15—H15	120.20
C6—C5—H5	120.20	C15—C16—C17	121.50(15)
C4—C5—H5	120.20	C15—C16—H16	119.20
C5—C6—C7	121.50(14)	C17—C16—H16	119.20

C5—C6—H6	119.10	C16—C17—C12	117.50(14)
C7—C6—H6	119.10	C16—C17—C18	122.00(13)
C6—C7—C2	117.50(13)	C12—C17—C18	119.50(13)
C6—C7—C8	122.00(13)	C19—C18—C17	126.50(15)
C2—C7—C8	120.00(13)	C19—C18—H18	116.60
C9—C8—C7	126.00(15)	C17—C18—H18	116.60
C9—C8—H8	116.80	C18—C19—C20	121.50(16)
C7—C8—H8	116.80	C18—C19—H19	119.00
C8—C9—C10	122.00(16)	C20—C19—H19	119.00
C8—C9—H9	118.80	N2—C20—C19	121.00(16)
C10—C9—H9	118.80	N2—C20—H20	119.30
N1—C10—C9	120.50(16)	C19—C20—H20	119.30
N1—C10—H10	119.50	O2—C12—C13	124.00(12)
C9—C10—H10	119.50	O2—C12—C17	115.00(12)
O1—C2—C3	124.00(13)	C13—C12—C17	120.50(13)
O1—C2—C7	115.00(12)	O2—C11—H11A	109.50
C3—C2—C7	120.00(14)	O2—C11—H11B	109.50
C4—C3—C2	120.00(14)	H11A—C11—H11B	109.50
C4—C3—H3	119.80	O2—C11—H11C	109.50
C2—C3—H3	119.80	H11A—C11—H11C	109.50
O1—C1—H1A	109.50	H11B—C11—H11C	109.50
O1—C1—H1B	109.50	C12—C13—C14	119.50(14)
H1A—C1—H1B	109.50	C12—C13—H13	120.20
O1—C1—H1C	109.50	C14—C13—H13	120.20

Symmetry codes:

(i) 0.5-x, 1.5+y, 1.5-z; (ii) 0.5-x, 1.5+y, 0.5-z.

Table S3. CheckCIF/PLATON report

Structure factors have been supplied for datablock(s) chem158

No syntax errors found. CIF dictionary Interpreting this report

Datablock: chem158

Bond precision:	C-C = 0.0021 Å	Wavelength=0.71073
Cell:	a=19.0367(6) b=4.9902(2) c=19.2908(7)	
	alpha=90 beta=108.317(2) gamma=90	
Temperature:	170 K	
	Calculated	Reported
Volume	1739.72(11)	
	1739.71(11) Space group	P 21/n
	P2(1)/n	
Hall group	-P 2yn	? Moiety formula C20 H20 N2 O2
Sum formula	C20 H20 N2 O2	C20 H20 N2 O2
Mr	320.38	320.38
Dx, g cm ⁻³	1.223	1.223
Z	4	4
Mu (mm ⁻¹)	0.080	0.080
F000	680.0	680.0
F000'	680.28	
h, k, lmax	23, 6, 23	23, 6, 23
Nref	3420	3368
Tmin, Tmax	0.976, 0.984	0.976, 0.984
Tmin'	0.976	

Correction method= NONE

Data completeness= 0.985 Theta(max)= 26.000

R(reflections)= 0.0387(2766) wR2(reflections)=

0.1075(3368) S = 0.835 Npar= 220

The following ALERTS were generated. Each ALERT has the format

test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

Alert level C

ABSTY03_ALERT_1_C The _exptl_absorpt_correction_type has been given as none. However values have been given for Tmin and Tmax. Remove these if an absorption correction has not been applied.

(cont.d)

```

From the CIF: _exptl_absorpt_correction_T_min      0.976
From the CIF: _exptl_absorpt_correction_T_max      0.984
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.600      50
PLAT912_ALERT_4_C Missing # of FCF Reflections Above STh/L= 0.600      2

```

Alert level G

```

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF .... ?
PLAT128_ALERT_4_G Alternate Setting of Space-group P21/c .....
P21/n

```

```

0 ALERT level A = Most likely a serious problem - resolve or explain
0 ALERT level B = A potentially serious problem, consider carefully
3 ALERT level C = Check. Ensure it is not caused by an omission or oversight
2 ALERT level G = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
0 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more

serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 27/06/2011; check.def file version of 27/06/2011
(cont.d)

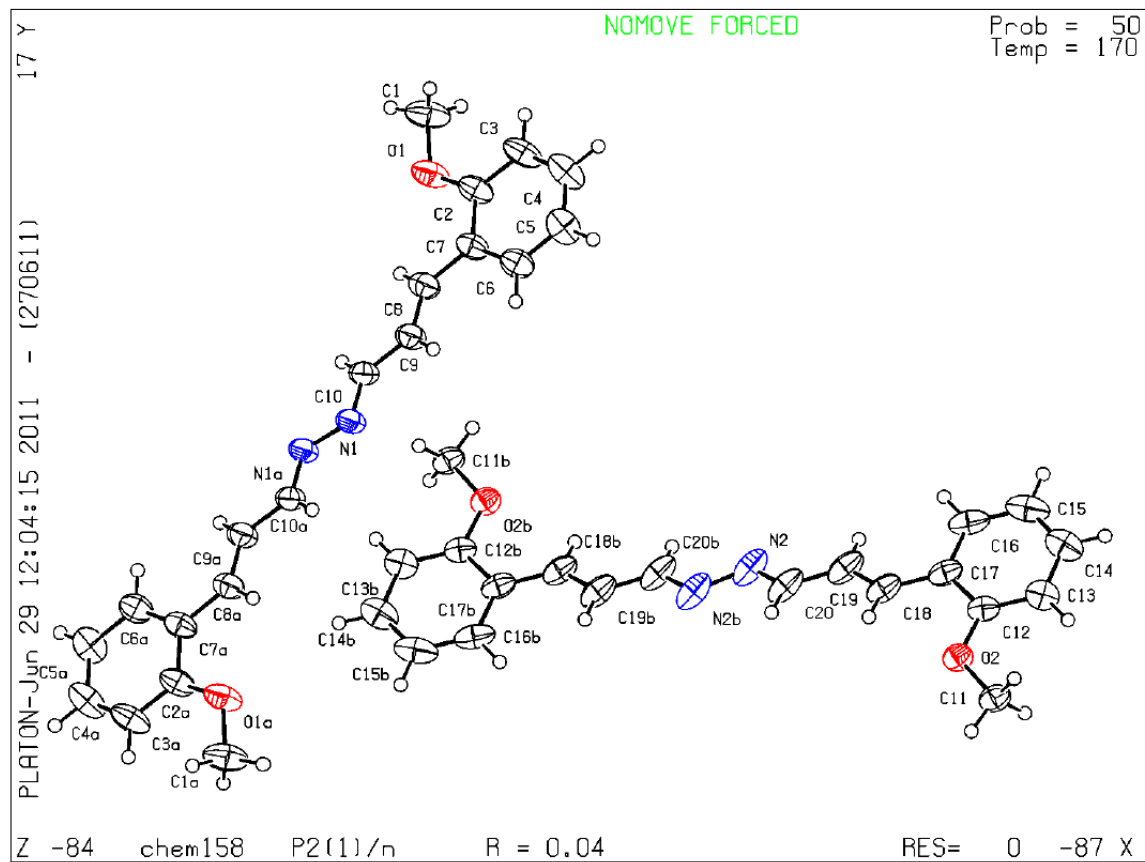


Fig. S1 ^1H NMR Spectrum of **3a**

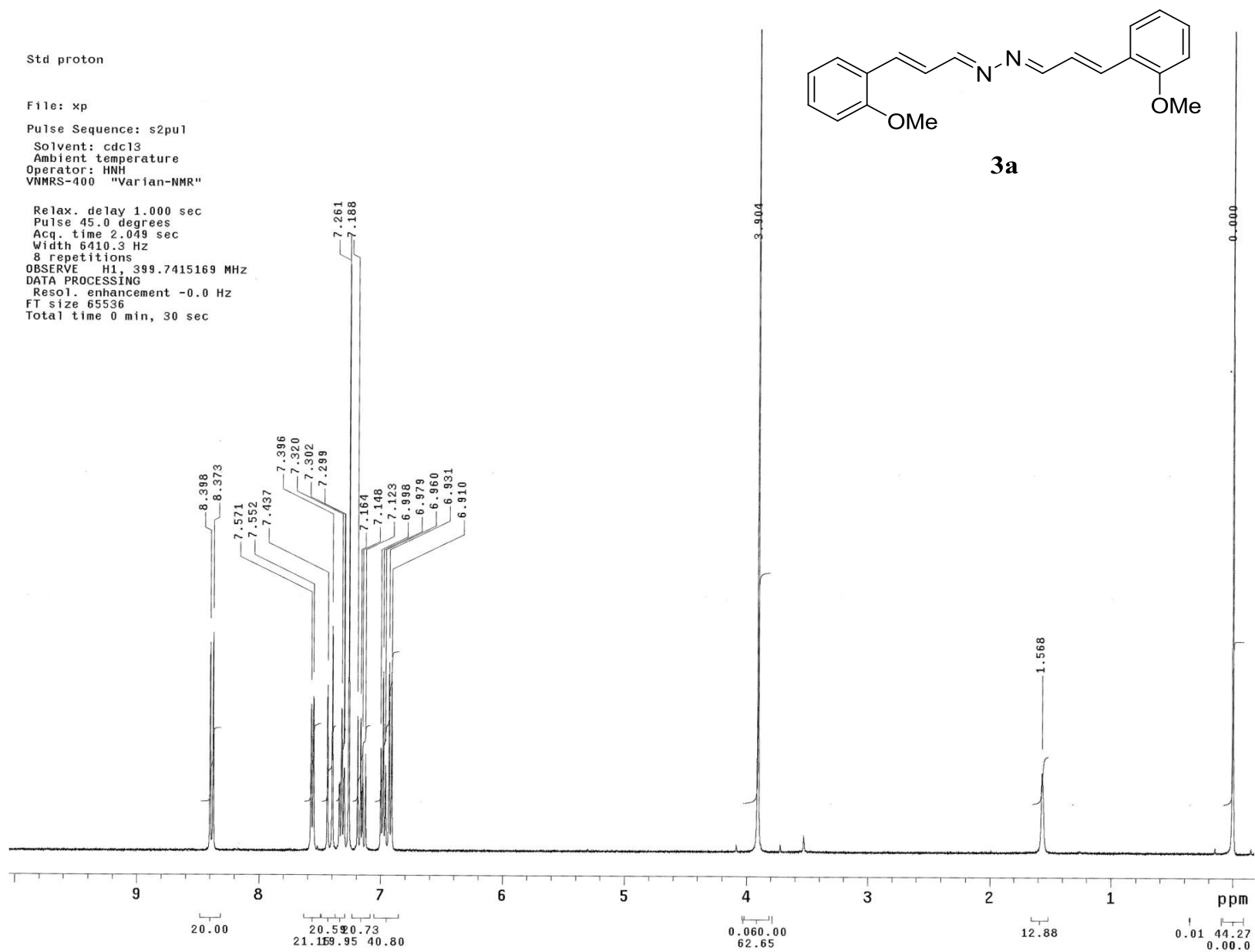


Fig. S2 Enhanced ^1H NMR Spectrum of **3a**

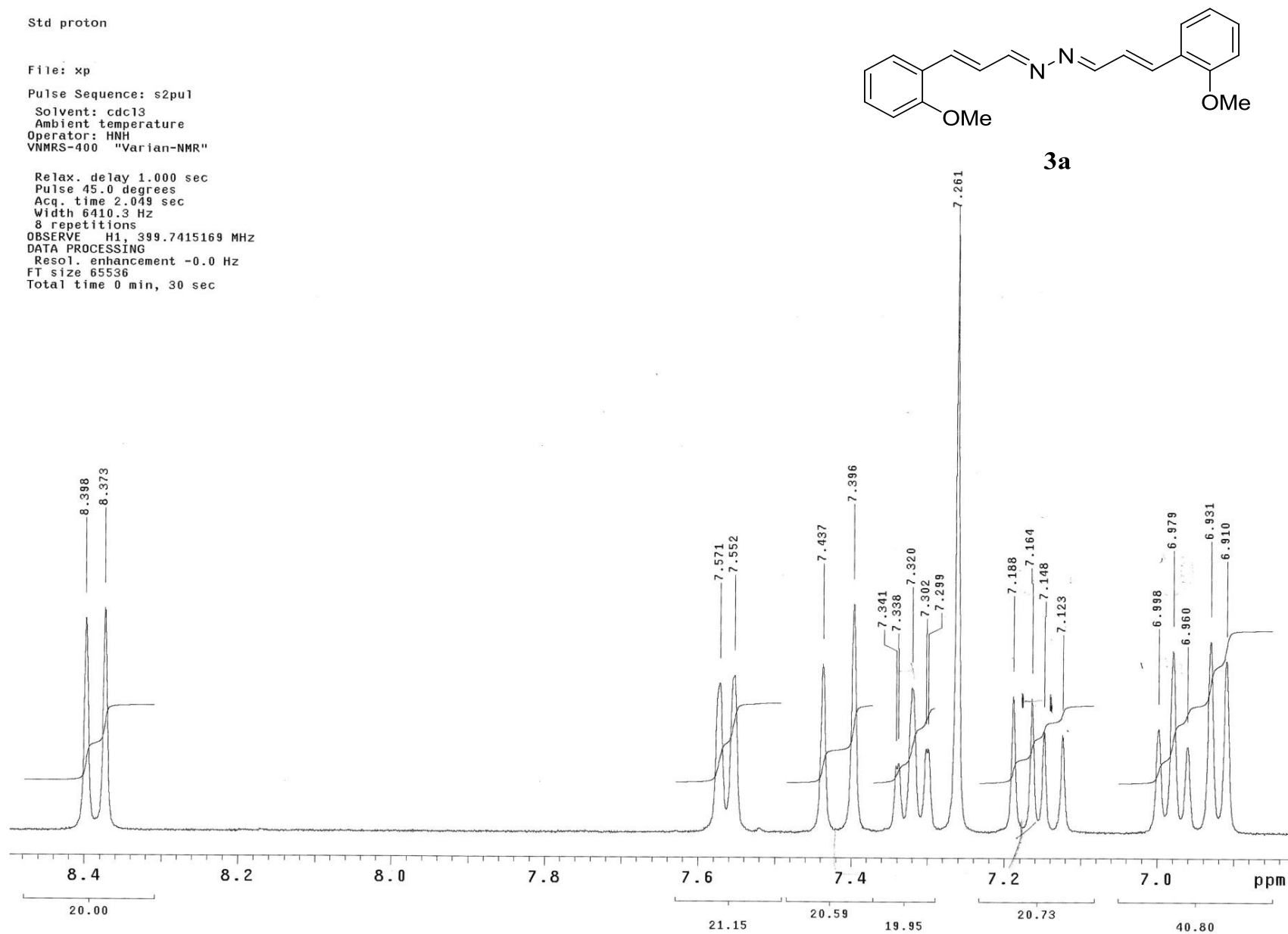


Fig. S3 ^{13}C NMR Spectrum of **3a**

Std carbon

File: xp

Pulse Sequence: s2pu1

Solvent: cdc13

Ambient temperature

Operator: HNH

VNMR-400 "Varian-NMR"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.300 sec

Width 24509.8 Hz

32 repetitions

OBSERVE C13, 100.5150857 MHz

DECOUPLE H1, 399.7435210 MHz

Power 37 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 9 min, 49 sec

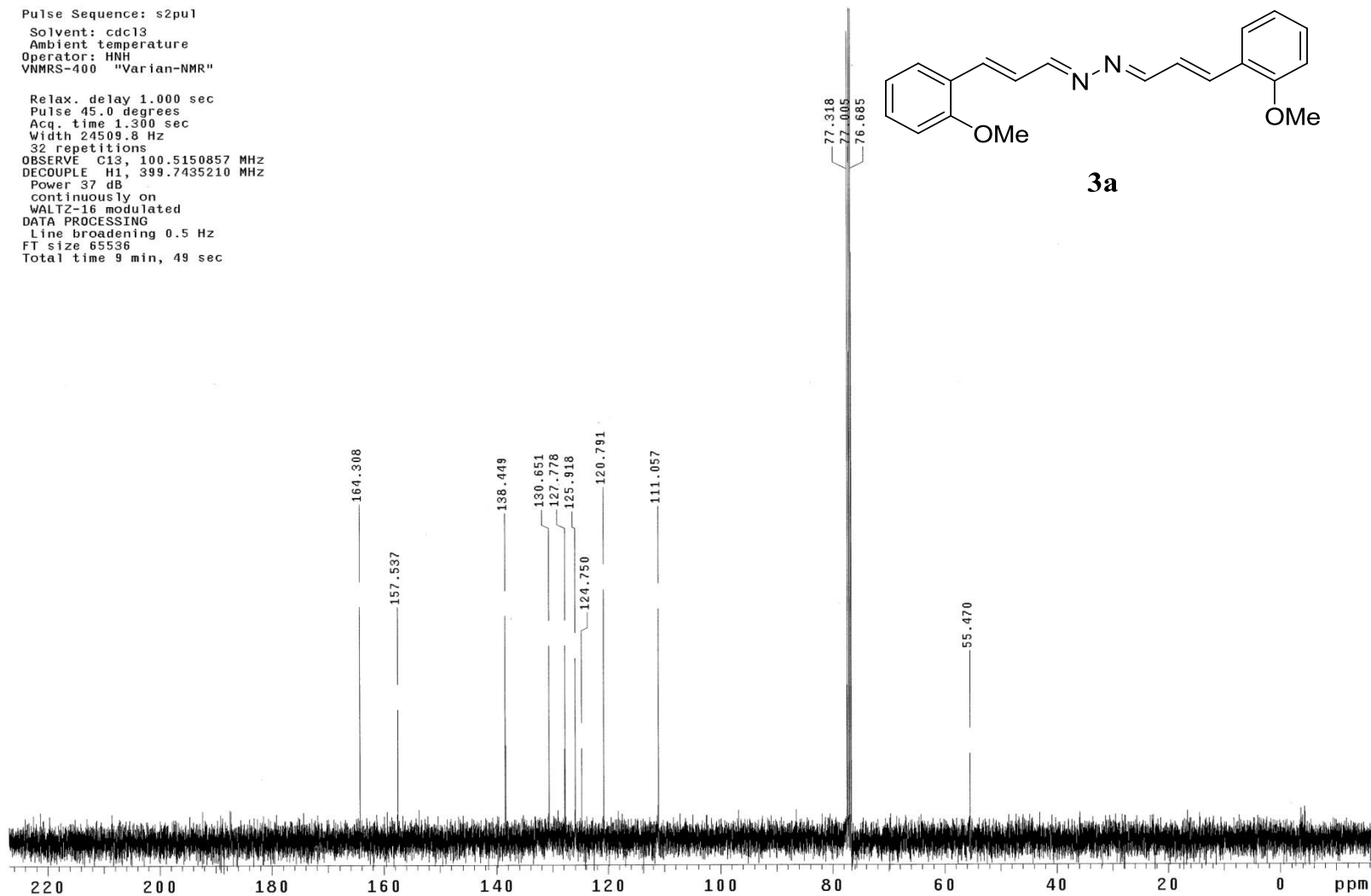


Fig. S4 COSY NMR Spectrum of **3a**

Std proton

File: home/vnmr1/vnmrsys/data/HNH/LKH/2011/10/1001-methoxy-cinnam-new-compound-gcosy.fid

Pulse Sequence: gCOSY

Solvent: cdcl3

Ambient temperature

Operator: HNH

File: 1001-methoxy-cinnam-new-compound-gcosy

VNMR-400 "Varian-NMR2"

Relax. delay 1.000 sec

Acq. time 0.160 sec

Width 6410.3 Hz

2D Width 6410.3 Hz

2 repetitions

128 increments

OBSERVE H1, 399.7324022 MHz

DATA PROCESSING

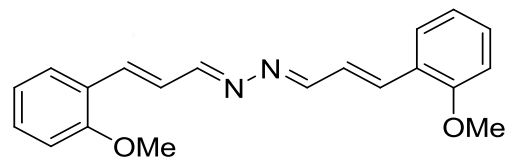
Sine bell 0.080 sec

F1 DATA PROCESSING

Sine bell 0.040 sec

FT size 2048 x 2048

Total time 5 min, 20 sec



3a

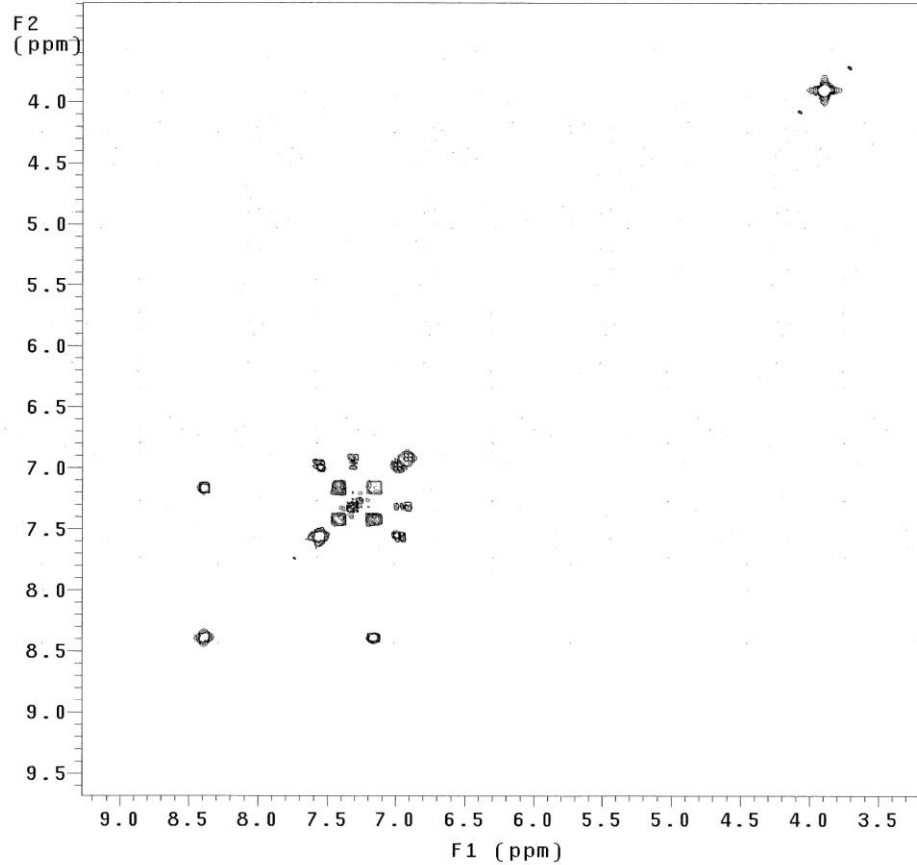
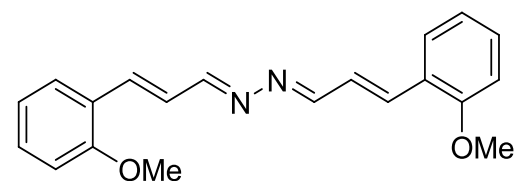


Fig. S5 Hetero COSY NMR Spectrum of 3a

Std proton

Sample: 1006_GHSQC
File: home/vnmr1/vnmrsys/data/HNH/1006_GHSQC.fid
Pulse Sequence: gHSQC
Solvent: cdcl3
Ambient temperature
Operator: HNH
File: 1006_GHSQC
VNMR-400 "Varian-NMR2"

Relax. delay 1.000 sec
Acq. time 0.199 sec
Width 6410.3 Hz
2D Width 20100.5 Hz
4 repetitions
2 x 128 increments
OBSERVE H1, 399.7324022 MHz
DECOUPLE C13, 100.5218386 MHz
Power 36 dB
on during acquisition
off during delay
W40_oneprobe modulated
DATA PROCESSING
Gauss apodization 0.092 sec
F1 DATA PROCESSING
Gauss apodization 0.012 sec
FT size 4096 x 2048
Total time 21 min, 48 sec



3a

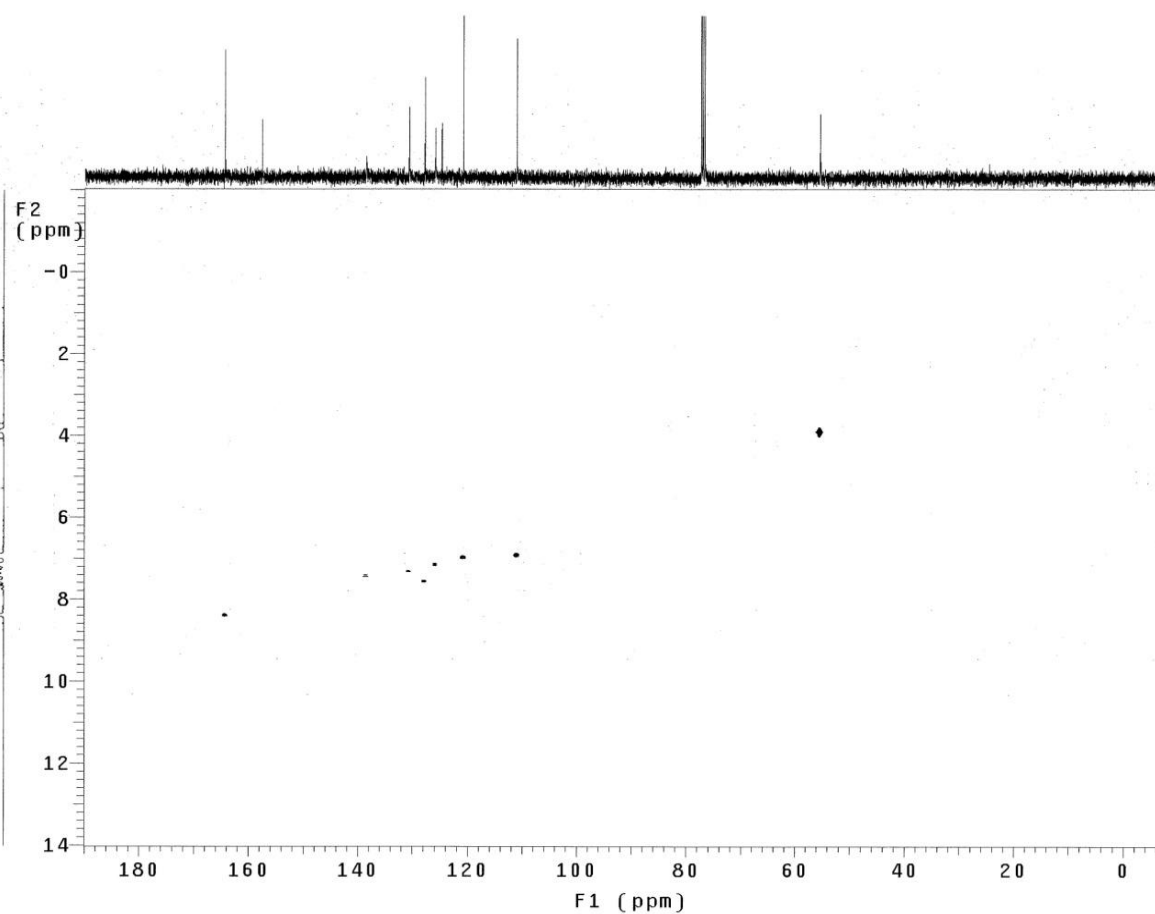


Fig. S6 ^1H NMR spectra for the change of **2a** with **1** to **3a**

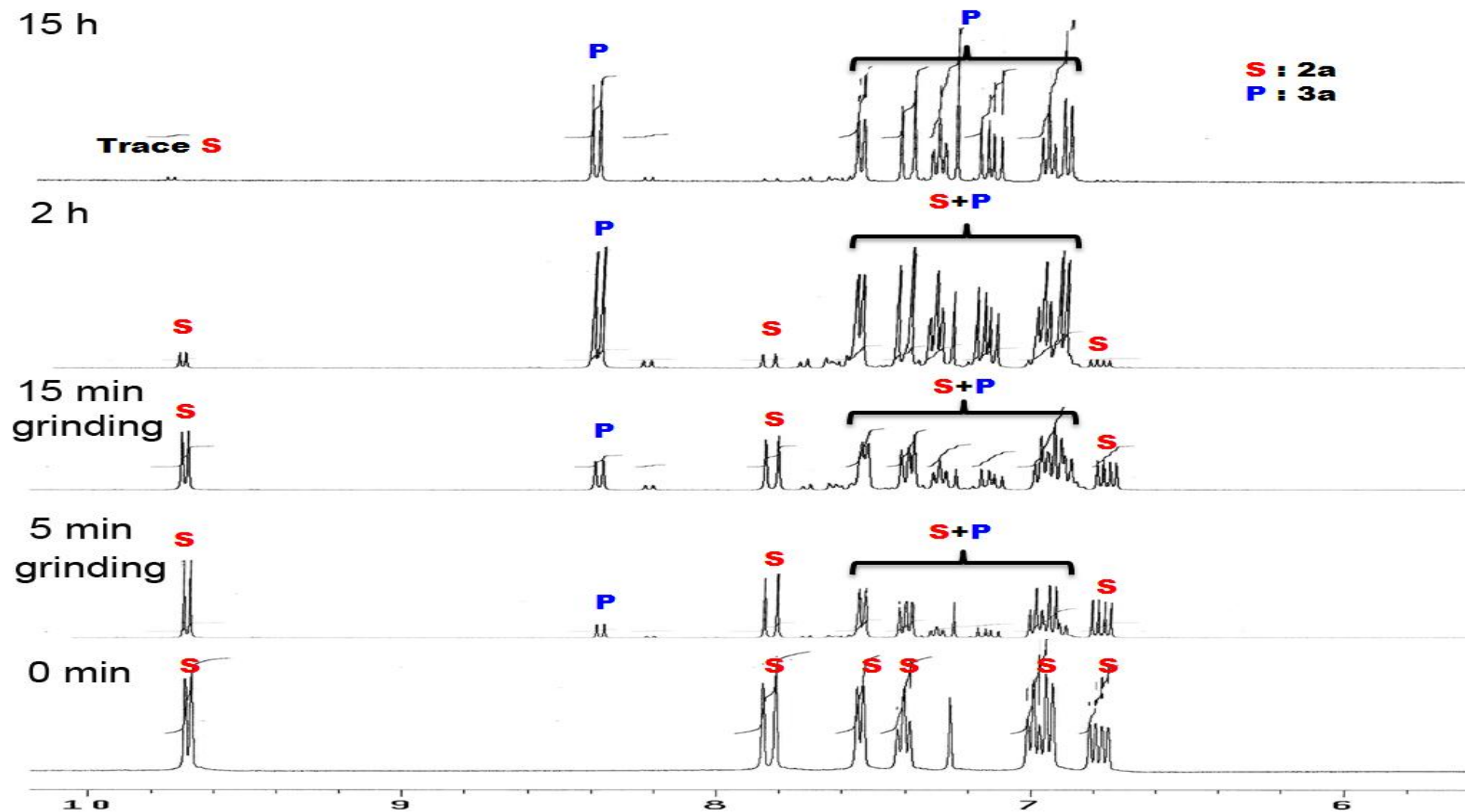


Fig. S7 The ^1H NMR spectrum for the reaction of **2a** with hydrazine hydrate in ether solvent.

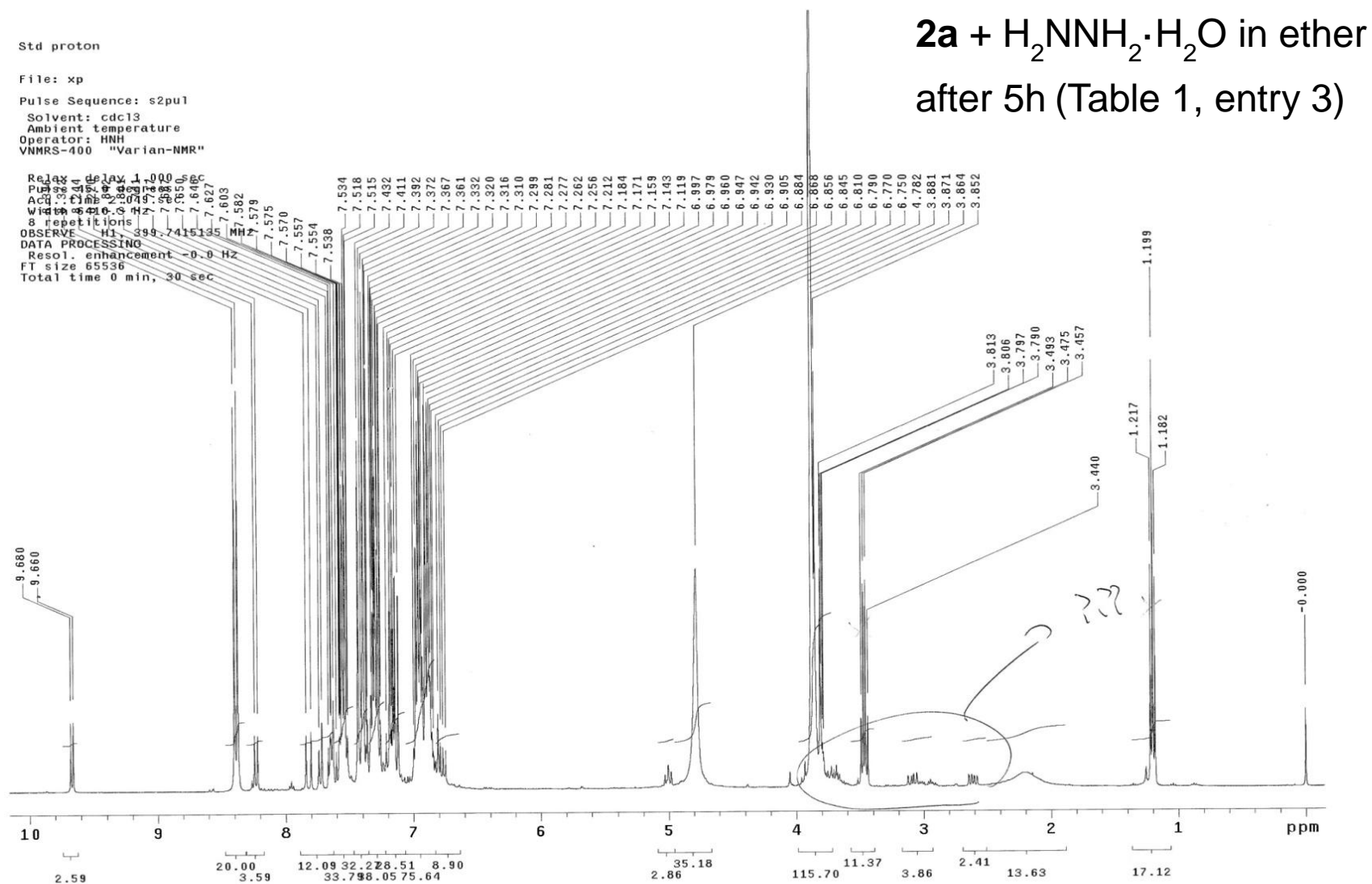


Fig. S8 The ^1H NMR spectrum for the reaction of **2a** with hydrazine hydrate in the absence of a solvent.

