

SYNTHESIS AND STRUCTURAL STUDY OF DICHLORODIAZADIENES DERIVED FROM PARA-NITRO BENZALDEHYDE

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Abstract. N-substituted hydrazones of para-nitrobenzaldehyde were converted the corresponding dichlorodiazadienes. The structure of the prepared products was investigated by X-ray to demonstrate non-covalent Cl...Cl, Br...Cl interactions for synthesized compounds.

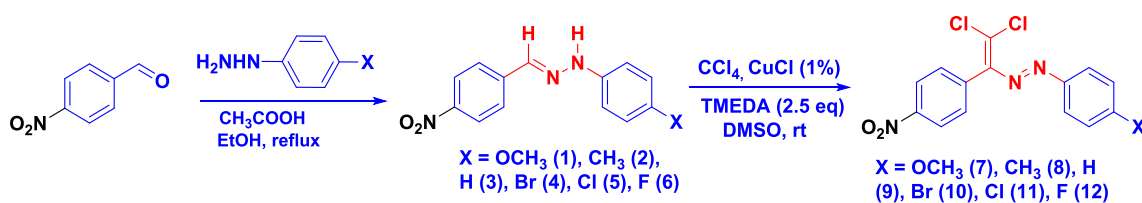
Keywords: dichlorodiazadiene, non-covalent interactions, catalytic olefination reaction.

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1. Introduction

Previously new synthesis of 1,1-dichlorodiazadienes based on derivatives of benzaldehyde in the condition of catalytic olefination reaction was demonstrated. Based on X-ray investigations, role of non-covalent interactions (N...Cl, Cl...O, π ... π , and weak F... π halogen, CH...F hydrogen bond) has been studied in the formation of monocrystals of these compounds (Nenajdenko *et al.*, 2017, Maharramov *et al.*, 2018, Maharramov *et al.*, 2018). The application of synthesized compounds has been investigated as dyes (Shikhaliyev *et al.*, 2018; Maharramov *et al.*, 2018; Shikhaliyev, 2019) as well as appropriate building blocks. Dichlorodiazadienes have been identified to have antimicrobial properties as physiologically active compounds (Shikhaliyev *et al.*, 2019). This study is devoted to conversion of hydrazones of para-nitrobenzaldehyde to the corresponding dichlorodiazadienes under the conditions of catalytic olefination reaction.



Scheme 1. Synthesis of compounds 1-12

The structures of the obtained compounds were approved by the X-ray and NMR methods. The crystallographic and structural data of compounds **8**, **9**, **10**, **11** and **12** are given in table 2.

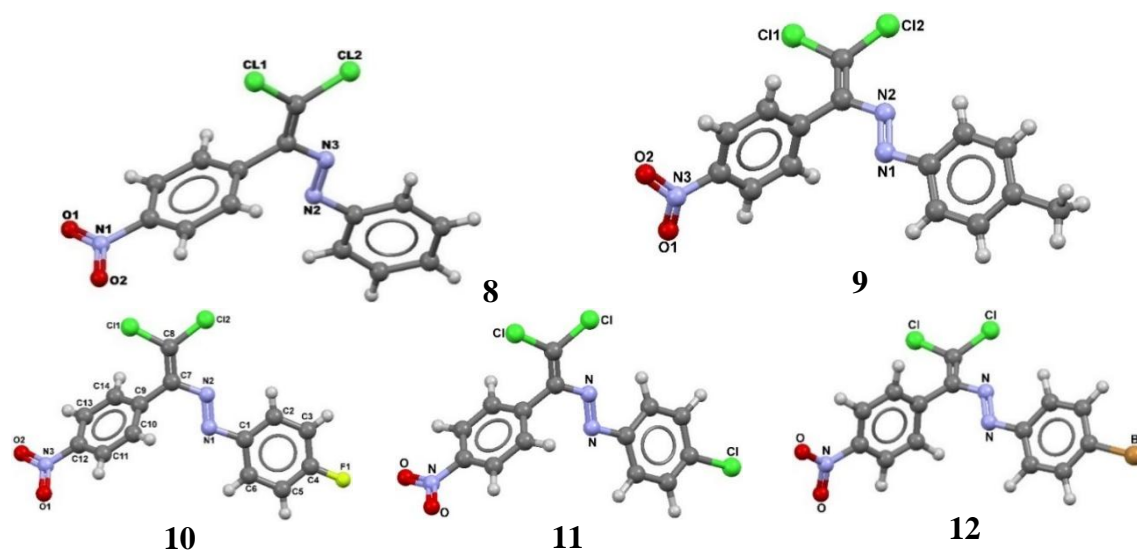
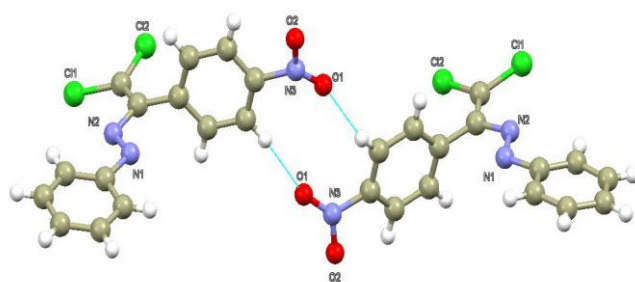


Figure 1. Molecular structures of compounds **8**, **9**, **10**, **11** and **12**.

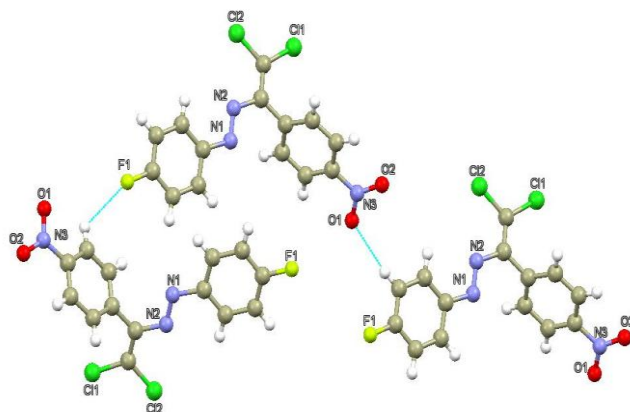
Table 2. The crystallographic and structural data of compounds **8**, **9**, **10**, **11** and **12**

	8	9	10	11	12
Empiric formula	C ₁₅ H ₁₁ Cl ₂ N ₃ O ₂	C ₁₄ H ₉ Cl ₂ N ₃ O ₂	C ₁₄ H ₈ BrCl ₂ N ₃ O ₂	C ₁₄ H ₈ Cl ₃ N ₃ O ₂	C ₁₄ H ₈ Cl ₂ FN ₃ O ₂
Fw	336.17	322.14	401.04	356.58	340.13
Cryst. Syst.	Orthorhombic	Tetragonal	Orthorhombic	Orthorhombic	Monoclinic
Spacegroup	Pna2 ₁	P-4c2	Pna2 ₁	Pna2 ₁	P2 ₁ /c
a (Å)	13.904(2)	15.0889(14)	13.9181(7)	13.8689(7)	15.8644(5)
b (Å)	13.443(2)	15.0889(14)	13.4336(6)	13.3674(7)	7.2242(2)
c (Å)	8.4016(17)	12.6584(12)	8.4080(4)	8.3620(5)	12.7595(4)
α, °	90	90	90	90	90
β, °	90	90	90	90	97.038(2) ^o .
γ, °	90	90	90	90	90
V, (Å ³)	1570.3(5)	2882.0(6)	1572.05(13)	1550.24(15)	1451.32(8)
ρ _{calc} (g cm ⁻³)	1.422	1.485	1.694	1.528	1.557
μ(MoKα) (mm ⁻¹)	0.423	0.457	2.963	0.600	0.468
Z	4	8	4	4	4

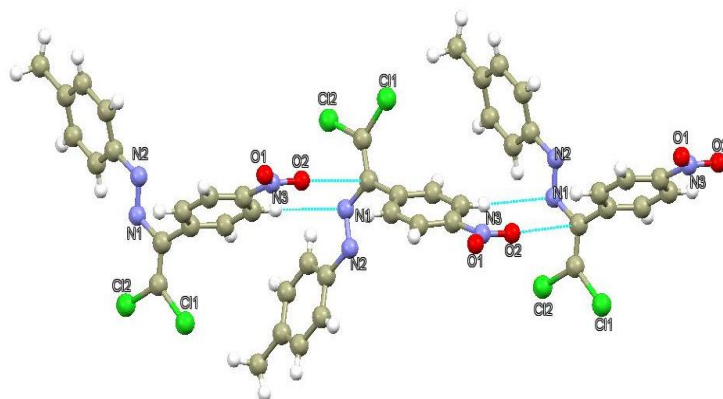
The presence of intermolecular and intramolecular non-covalent interactions were found in the corresponding dichlorodiazadienes by the X-ray method. While hydrazine fragment maintains the halogen atoms in para position, non-covalent interactions between the halogen atoms in the para position and Cl atoms in the vinyl group (Cl ••• Cl [3.488Å], Br ••• Cl [3.521Å]) were observed in crystal formation. The interaction of Br ••• π [4.411Å] was also determined in compound **12**. However, in the case of para CH₃, F, and H intermolecular hydrogen bond only was observed.



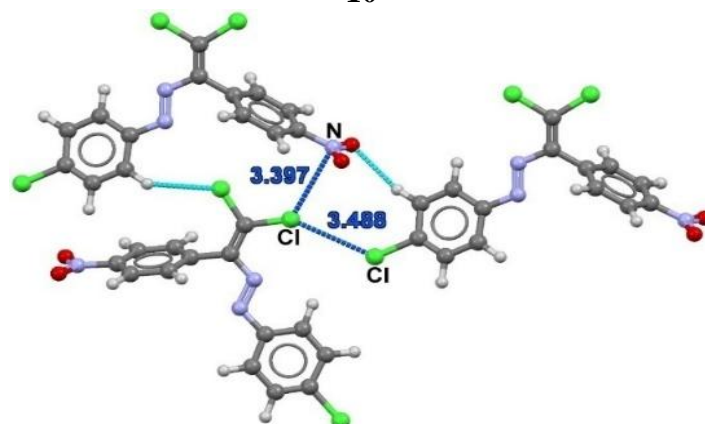
8



9



10



11

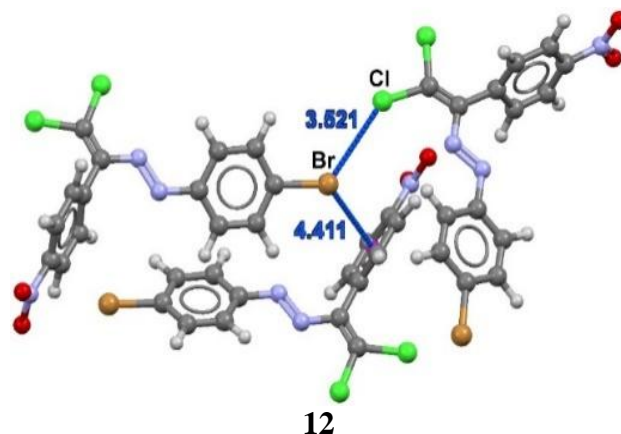


Figure 2. Intermolecular and intramolecular interactions of compounds **8**, **9**, **10**, **11** and **12** are presented in dash lines

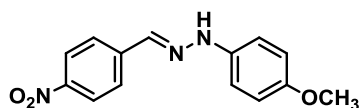
Thus, the influence of the nature of halogen atoms on the crystal design was determined. Thus, in comparison with chlorine and bromine, the effect of intermolecular non-covalent interactions in the presence of fluorine atom has not been established, which is due to the fact that the fluorine atom enters to this type of bond weakly.

2. Materials and instrumentation

The X-ray analysis of the compounds **8**, **9**, **10**, **11** and **12** were carried out using the Bruker APEX II CCD ($T = 296$ K, λ MoK α - radiation, graphite monochromator, φ - and ω -scan) diffractometer. NMR ^1H and ^{13}C spectra were recorded at Bruker Avance 300 (working frequency is 300 MHz, CDCl_3 and DMSO respectively). SiMe_4 has been used as an internal standard. Thin chromatography was performed on silhouette plate UB-254 and acidified KMnO_4 solution and UB lamp rays were used to make spots visible. Column chromatography was performed on silica gel of Merck firm (63-200). Synthesis of substances was carried out at Chemistry Department of Baku State University (Azerbaijan).

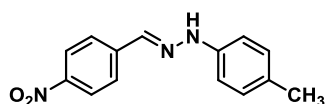
Synthesis of phenylhydrazones

Hydrazones **1-6** were synthesized according to the reported method. A mixture of (2-nitrophenyl)hydrazine (10.2 mmol), CH_3COONa (0.82 g), ethanol (50 mL) and corresponding 4-substituted aldehyde (10 mmol) was refluxed at 80°C with stirring for 2 h. The reaction mixture was cooled to room temperature and water (50 mL) was added to give a precipitate of crude product, which filtered off, washed with diluted ethanol (1:1 with water) and dried in vacuum of rotary evaporator.

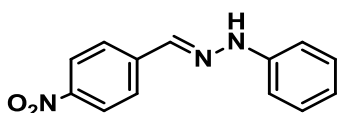


Compound 1.
(E)-1-(4-methoxyphenyl)-2-(4-nitrobenzylidene)-hydrazine.

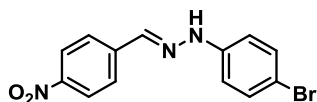
It is obtained from the reaction of 4-nitrobenzaldehyde with 4-methoxyphenyl hydrazine. Red solid substance, yield 80%, $\text{Mp} = 175^\circ\text{C}$. ^1H NMR (300 MHz, DMSO) δ 11.0 (s, 1H, NH), 8.30 – 8.24 (m, 2H, arom.), 7.90 – 7.84 (m, 2H, arom.), 7.64 (s, 1H, CH), 7.13 – 7.02 (m, 4H, arom.), 3.80 (s, 3H, OCH_3). ^1H NMR (75 MHz, DMSO) δ 150.9, 148.5, 145.6, 140.7, 139.8, 125.9, 125.5, 117.4, 114.5, 55.3.

**Compound 2.****(E)-1-(4-nitrobenzylidene)-2-(p-tolyl)hydrazine.**

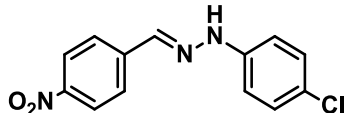
It is obtained from the reaction of 4-nitrobenzaldehyde with 4-toluenefenylhydrazine. Orange solid substance, yield 87%, $M_p=152^\circ\text{C}$, $^1\text{H NMR}$ (300 MHz, DMSO) δ 10.82(s,1H, NH), 8.22-8.20(d, 2H, $J=6.15\text{Hz}$, arom., CH), 7.89- 7.84(t,3H, $J=6.25\text{Hz}$, arom.), 7.06(s,4H, arom.), 2.23(s,3H, CH_3). $^{13}\text{C NMR}$ (75 MHz, DMSO) δ 162.3, 146.2, 143.2, 142.5, 133.3, 130.1, 129.1, 126.2, 124.53, 113.0, 20.7.

**Compound 3.****(E)-1-(4-nitrobenzylidene)-2-phenylhydrazine.**

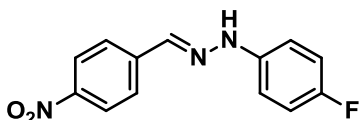
It is obtained from the reaction of 4-nitrobenzaldehyde with phenylhydrazine. Orange solid substance, yield 88%, $M_p=130^\circ\text{C}$. $^1\text{H NMR}$ (300 MHz, DMSO) δ 10.90 (s,1H, NH), 8.23-8.21 (d, 2H, $J=6.12\text{Hz}$, arom.), 7.93-7.86(t, 3H, $J=9.02\text{Hz}$, arom.), 7.29- 7.24 (t, 3H, $J=9.15\text{ Hz}$, arom.), 7.16-7.13(d,1H, $J=9.26\text{Hz}$), 6.86- 6.81 (t,1H, $J=9.15\text{Hz}$), $^{13}\text{C NMR}$ (75 MHz, DMSO) δ 162.3, 146.4, 144.8, 143.0, 134.0, 129.7, 126.4, 124.5, 120.3, 112.9.

Compound 4.**(E)-1-(4-bromophenyl)-2-(4-nitrobenzylidene)hydrazine.**

It is obtained from the reaction of 4-nitrobenzaldehyde with 4-bromophenyl hydrazine. Red solid substance, yield 92%, $M_p=142^\circ\text{C}$. $^1\text{H NMR}$ (300 MHz, DMSO) δ 11.00 (s, 1H, NH), 8.24-8.21 (d,2H, $J=9.24\text{ Hz}$, arom.), 7.94(s, 1H, CH), 7.90-7.87(d,2H, $J=9\text{Hz}$, arom.), 7.43-7.40(d, 2H, $J=9.12\text{Hz}$, arom.), 7.11-7.08(d, 2H, $J=9.05\text{ Hz}$, arom.). $^{13}\text{C NMR}$ (75 MHz, DMSO) δ 162.3, 146.6, 144.2, 142.7, 135.0, 132.3, 126.7, 124.5, 114.9, 111.3.

Compound 5.**(E)-1-(4-chlorophenyl)-2-(4-nitrobenzylidene) hydrazine.**

It is obtained from the reaction of 4-nitrobenzaldehyde with 4-bromophenyl hydrazine. Red solid substance, yield 91%, $M_p=148^\circ\text{C}$. $^1\text{H NMR}$ (300 MHz, DMSO) δ 11.00(s,1H, NH), 8.24-8.21(d,2H, $J=9.32\text{Hz}$, arom.), 7.94(s, 1H, CH), 7.90-7.87(d, 2H, 9.14Hz, arom.), 7.31-7.28(d,2H, $J=9.03\text{Hz}$, arom.), 7.16-7.13(d,2H, $J=9.12\text{Hz}$, arom.). $^{13}\text{C NMR}$ (75 MHz, DMSO) δ 146.6, 143.8, 142.7, 134.9, 129.5, 126.6, 124.5, 123.6, 114.4

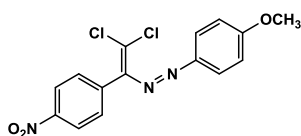
Compound 6.**(E)-1-(4-fluorophenyl)-2-(4-nitrobenzylidene)hydrazine.**

It is obtained from the reaction of 4-nitrobenzaldehyde with 4-bromophenyl hydrazine. Red solid substance, yield 95%, $M_p=155^\circ\text{C}$. $^1\text{H NMR}$ (300 MHz, DMSO) δ 10.90(s, 1H, NH), 8.23-8.20(d,2H, $J=9.12\text{Hz}$, arom.), 7.91(s,1H, CH) 7.88- 7.86(d, 2H, $J=6.14\text{Hz}$, arom.), 7.14-7.08(m, 4H, arom.). $^{13}\text{C NMR}$ (75 MHz, DMSO) δ 146.4, 143.0 141.5, 134.0, 126.4, 124.5, 116.4, 116.1, 114.0.

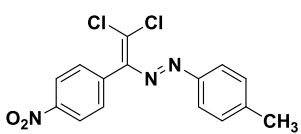
Synthesis of dichlorodiazadiens

Diazenes **7-12** were synthesized according to the reported method. A 20 mL screw neck vial was charged with DMSO (10 mL), **1-6** (1mmol), tetramethylethylenediamine (TMEDA) (295 mg, 2.5mmol), CuCl (2 mg, 0.02 mmol) and CCl_4 (20 mmol, 10 equiv.). After 1-3 hours (until TLC analysis showed complete consumption of corresponding hydrazones) reaction mixture was poured into ~0.01 M solution of HCl (100 mL, ~pH=2-3), and extracted with dichloromethane (3x20 mL).

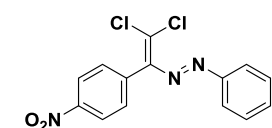
The combined organic phase was washed with water (3x50 mL), brine (30 mL), dried over anhydrous Na₂SO₄ and concentrated in vacuo of the rotary evaporator. The residue was purified by column chromatography on silica gel using appropriate mixtures of hexane and dichloromethane (3/1-1/1), and corresponding diazenes were obtained.



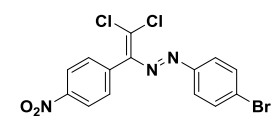
Compound 7. 1-(2,2-dichloro-1-(4-nitrophenyl)vinyl)-2-(4-methoxy-phenyl)diazene. It is obtained from the reaction (E)-1-(4-methoxyphenyl)-2-(4-nitrobenzylidene) hydrazine with CCl₄. Yellow crystals, yield 40 %, Mp= 120-123⁰. ¹H NMR (300 MHz, CDCl₃) δ 8.29(d, 2H, J=9.32Hz, arom.), 7.76(d, 2H, J=9.21Hz, arom.), 7.37(d, 2H, J=9.15Hz, arom.), 6.95(d, 2H, J=9.04Hz, arom.), 3.88(s, 3H, OCH₃), ¹³C NMR (75 MHz, CDCl₃) δ 163.0, 150.4, 147.8, 147.0, 139.9, 133.9, 131.2, 125.4, 123.3, 114.3, 55.6.



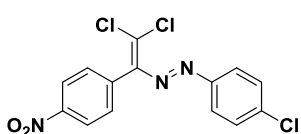
Compound 8. (E)-1-(2,2-dichloro-1-(4-nitrophenyl)vinyl)-2-(p-tolyl)diazene. It is obtained from the reaction (E)-1-(4-toluolphenyl)-2-(4-nitrobenzylidene) hydrazine with CCl₄. Red crystals, yield 82%, Mp=140°C. ¹H NMR (300 MHz, CDCl₃) δ 8.28(d, 2H, J=9.15Hz, arom.), 7.70(d, 2H, J=9.12Hz, arom.), 7.37(d, 2H, J=9.02Hz, arom.), 7.26(d, 2H, J=9.14Hz, arom.), 2.42(s, 3H, CH₃). ¹³C NMR (75 MHz, CDCl₃) δ 150.8, 150.5, 147.8, 143.1, 139.6, 135.3, 131.3, 129.9, 123.3, 123.3, 21.6.



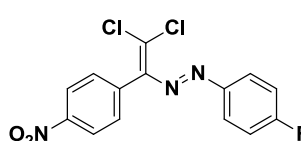
Compound 9. (E)-1-(2,2-dichloro-1-(4-nitrophenyl)vinyl)-2-phenyl-diazene. It is obtained from the reaction (E)-1-(4-nitrobenzylidene)-2-phenylhydrazine with CCl₄. Red crystals, yield 70 %, Mp=125°C. ¹H NMR (300 MHz, CDCl₃) δ 8.30 (d, 2H, J=9.12, arom.), 7.78(m, 2H, arom.), 7.48(d, 2H, J=6.18Hz, arom.), 7.39(d, 2H, J=6.12Hz, arom.). ¹³C NMR (75 MHz, CDCl₃) δ 152.5, 150.5, 147.9, 139.5, 136.3, 132.1, 131.2, 129.1, 123.3, 123.3.



Compound 10. (E)-1-(4-bromophenyl)-2-(2,2-dichloro-1-(4-nitrophenyl)-vinyl)diazene. It is obtained from the reaction (E)-1-(4-bromophenyl)-2-(4-nitrobenzylidene) hydrazine with CCl₄. Red crystals, yield 88%, Mp=145°C. ¹H NMR (300 MHz, CDCl₃) δ 8.31-8.28(d, 2H, J=9.02Hz, arom.), 7.65-7.56(m, 4H, arom.), 7.39-7.36(d, 2H, J=9.24Hz, arom.). ¹³C NMR (75 MHz, CDCl₃) δ 151.2, 150.6, 147.9, 139.2, 137.1, 132.4, 131.2, 126.8, 124.7, 123.4.



Compound 11. (E)-1-(4-chlorophenyl)-2-(2,2-dichloro-1-(4-nitro-phenyl)vinyl)diazene. It is obtained from the reaction (E)-1-(4-chlorophenyl)-2-(4-nitrobenzylidene) hydrazine with CCl₄. Red crystals, yield 64% ,Mp=175°C. ¹H NMR (300 MHz, CDCl₃) δ 8.31(d, 2H, J=6.15, arom.) , 7.72(d, 2H, J=9.21. arom.), 7.44(d, 2H, J=9.05Hz, arom.), 7.39- 7.37(d, 2H, J=6.13Hz. arom.). ¹³C NMR (75 MHz, CDCl₃) δ 150.9, 150.5, 147.9, 139.2, 138.2, 137.02, 131.2, 129.4, 124.5, 123.4.



Compound 12. (E)-1-(4-chlorophenyl)-2-(2,2-dichloro-1-(4-nitro-phenyl)vinyl)diazene. It is obtained from the reaction (E)-1-(4-chlorophenyl)-2-(4-nitrobenzylidene) hydrazine with CCl₄. Red crystals, yield 62 %, Mp=148°C. ¹H NMR (300 MHz, CDCl₃) δ 8.30(d, 2H, J=9.21Hz), 7.81-7.77(m 2H, arom.), 7.39(d, 2H, J=9.02Hz. arom.), 7.15(t, 2H, J=9.22Hz, arom.). ¹³C NMR (75 MHz, CDCl₃) δ 166.6, 163.3, 150.4, 149.1, 147.9, 139.4, 131.2, 125.5, 125.3, 123.4, 116.4, 116.1.

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