# Convenient synthesis of electron-donating substituted benzonitriles by photolysis of phenyl halides and esters.

Valentina Dichiarante, Maurizio Fagnoni*, Angelo Albini.

*Department of Organic Chemistry, The University, V. Taramelli 10, 27100 Pavia, Italy*

E-mail: fagnoni@unipv.it

**SUPPLEMENTARY INFORMATION**

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**Experimental section. General:** NMR spectra were recorded on a 300 MHz spectrometer. The attributions were made by comparison of the spectral characteristics, in particular with those of authentic sample. The photochemical reactions were performed in quartz tubes by using nitrogen-purged solution and a multilamp reactor fitted with six 15-W phosphor-coated lamps (maximum of emission 310 nm) for the irradiation. The reaction course was followed by TLC (cyclohexane-ethyl acetate) and HPLC (SUPELCO DISCOVERY HS C18 250x4.66 mm) column (MeCN/water (from 40:60 to 50:50, flux 1 mL $min^{-1}$) with UV detection at $\lambda$ = 270 nm. All of the starting aromatic halides were of commercial origin and purified just before use. Esters **4b-c** and **5b-c** were obtained from the corresponding phenols.[1]

## Preparative photocyanations

**4-aminobenzonitrile (9):** From 191 mg (0.05 M) of 4-chloroaniline, 586 mg of KCN (0.3 M) in 30 ml of MeCN/water 1:1 irradiated for 15h. Separation by column chromatography afforded the title compound (110 mg, 62% yield) as a light yellow solid. m.p. 87-88°C (lit.[2] 86°C). A small amount of aniline was detected by GC. Anal. Calcd. for $C_7H_6N_2$: C 71.17, H 5.12. Found: C 71.0, H 5.3. Spectroscopical data in accordance with literature.[2]

**2-aminobenzonitrile (10):** From 38 mg (0.01 M) of 2-chloroaniline, 586 mg of KCN (0.3 M) in 30 ml of MeCN/water 1:1 irradiated for 40h (90% of consumption of **2a**). Separation by column chromatography afforded the title compound (15 mg, 53% yield based on consumed **2a**) as a light yellow solid. m.p. 48-50°C (lit.[3] 50-51°C). Anal. Calcd. for $C_7H_6N_2$: C 71.17, H 5.12. Found: C 70.9, H 5.2. Spectroscopical data in accordance with literature.[4]

2-Aminobenzonitrile was also obtained in 22% yield from a solution of 33 mg (0.01 M) of 2-fluoroaniline, 195 mg of KCN (0.1 M) in 30 ml of MeCN/water 1:3 irradiated for 18h.

**3-aminobenzonitrile (11):** From 38 mg (0.01 M) of 3-chloroaniline, 586 mg of KCN (0.3 M) in 30 ml of MeCN/water 1:1 irradiated for 30h (90% of consumption of **3**). Separation by column chromatography afforded the title compound (6 mg, 19% yield based on consumed **3**) as a light yellow solid. m.p. 50-51°C (lit.[5] 51-53°C) Spectroscopical data in accordance with literature.[6]

**4-*N*,*N*-dimethylaminobenzonitrile (12):** From 162 mg (0.025 M) of 4-chloro-*N*,*N*-dimethylaniline, 586 mg of KCN (0.3 M) in 30 ml of MeCN/water 1:1 irradiated for 16h. Separation by column chromatography afforded the title compound (58 mg, 53% yield) as a light yellow solid. m.p. 77-79°C (lit.[7] 80-81°C). Anal. Calcd. for $C_9H_{10}N_2$: C 73.94, H 6.89. Found: C 74.0, H 6.7. Spectroscopical data in accordance with literature.[8]

**4-(methylthio)benzonitrile (15):** From 143 mg (0.03 M) of 4-chlorothioanisole, 195 mg of KCN (0.1 M) in 30 ml of MeCN/water 1:3 irradiated for 30h. Separation by column chromatography afforded the title compound (76 mg, 57% yield) as a colorless solid. m.p. 61-63°C (lit.[9] 62.5-64.5°C) accompanied by 9 mg of thioanisole (8% yield). Anal. Calcd. for $C_8H_7NS$: C 64.39, H 4.73. Found: C 64.5, H 4.6. Spectroscopical data in accordance with literature.[10]

**5-cyano-benzo[1,3]dioxole (16):** From 235 mg (0.05M) of chlorobenzodioxole, 195 mg of KCN (0.1 M) in 30 ml of MeCN/water 1:3. Separation by column chromatography afforded the title compound (170 mg, 77% yield) as a colorless solid. m.p. 91-94°C (lit.[11] 90-92°C). Spectroscopical data in accordance with the literature.[11] Anal. Calcd. for $C_8H_5NO_2$: C 65.31, H 3.4. Found: C 65.4, H 3.2.

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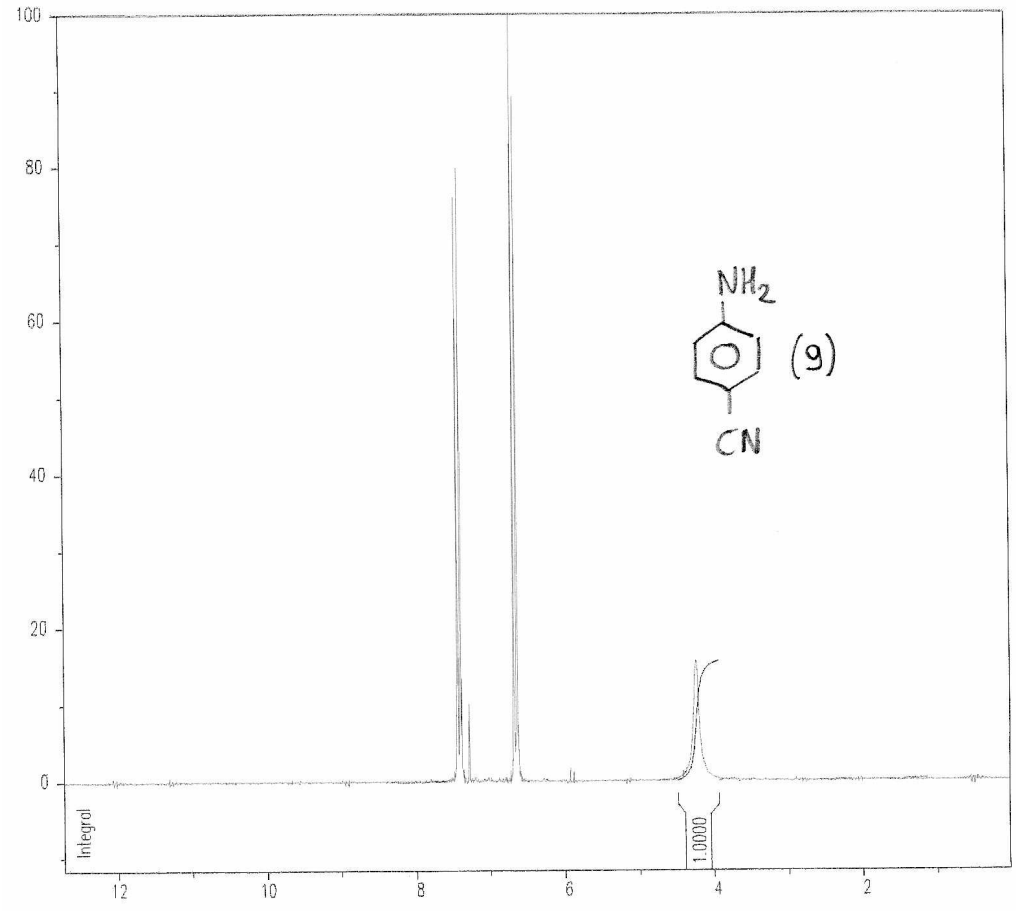


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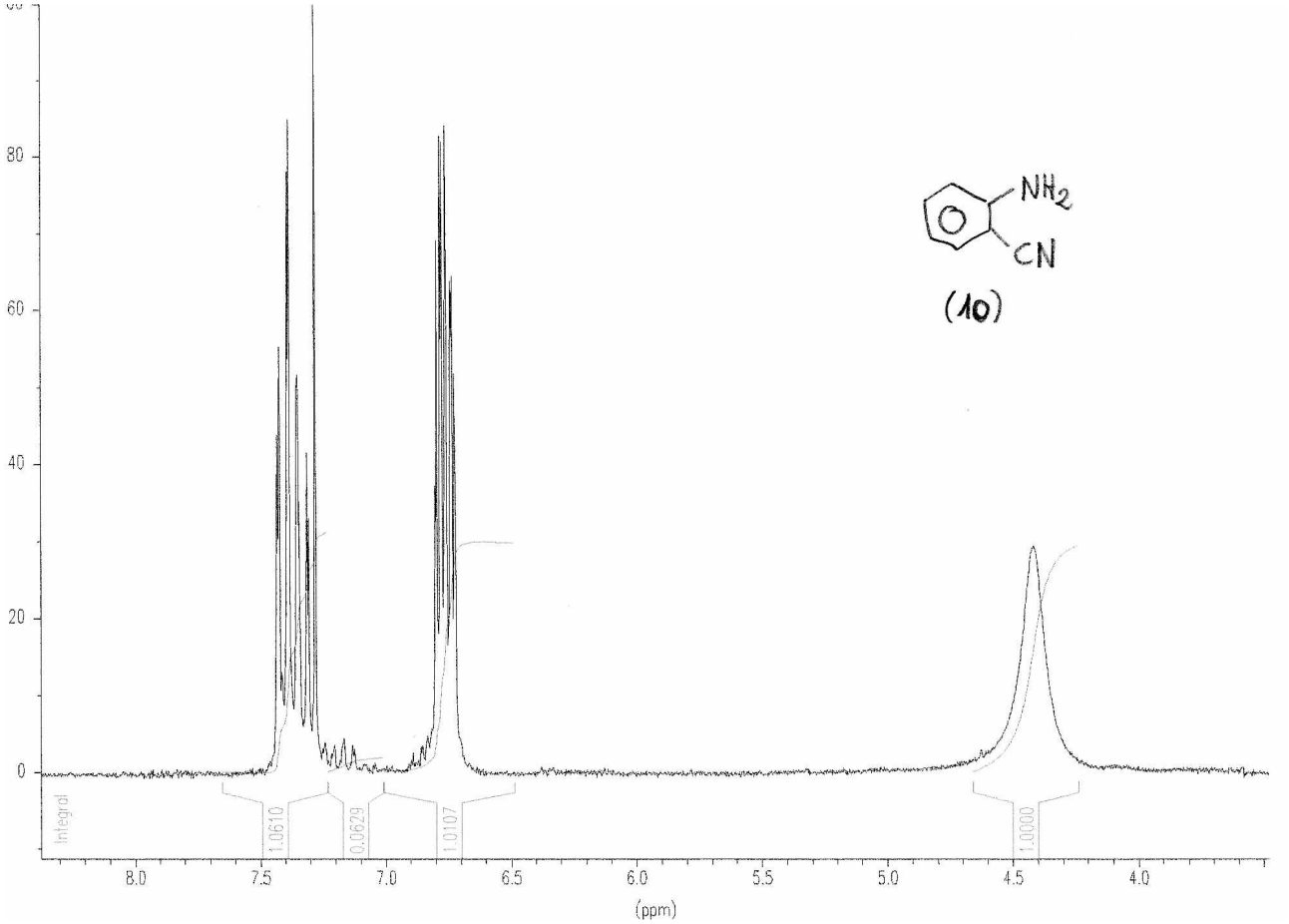

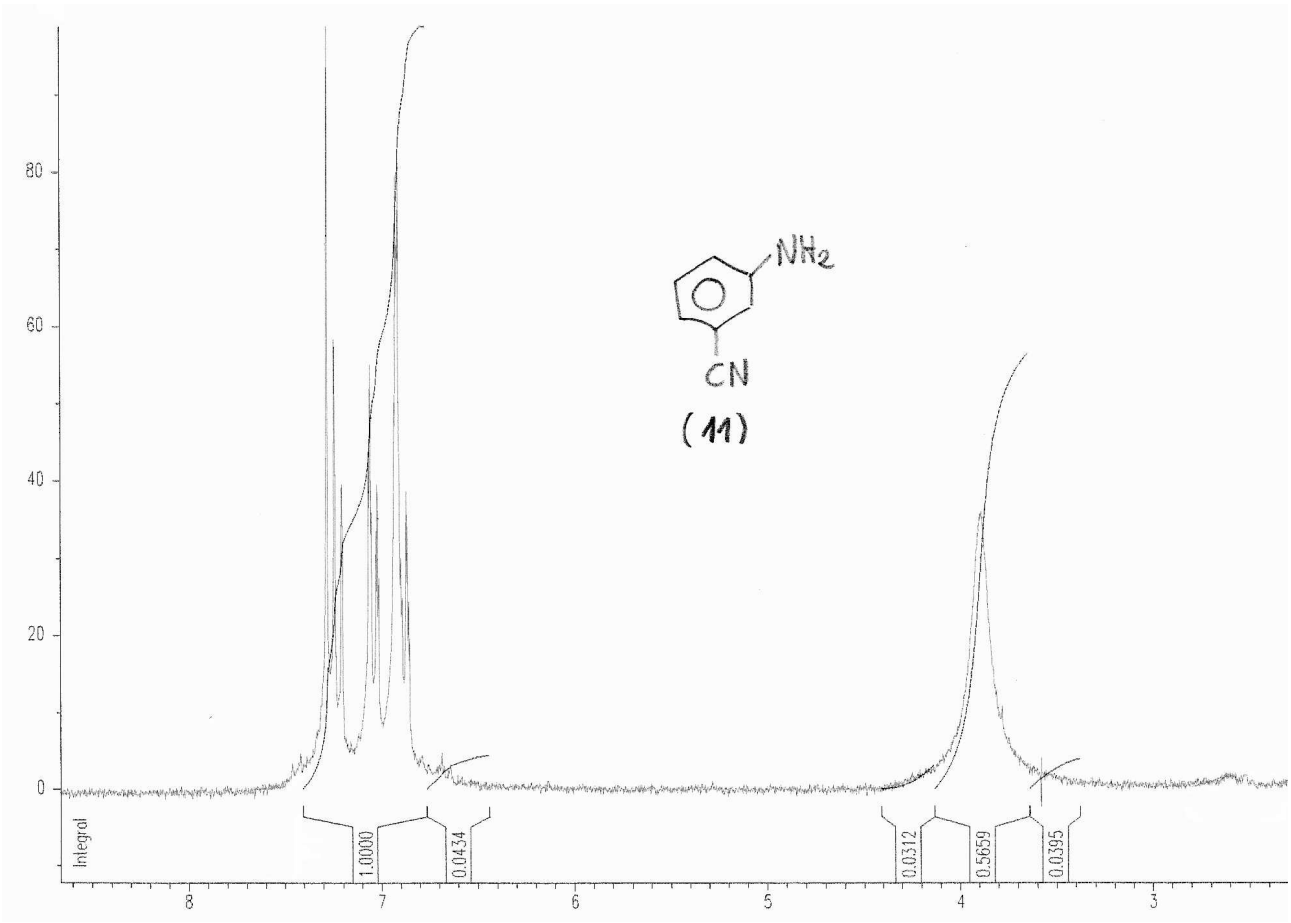

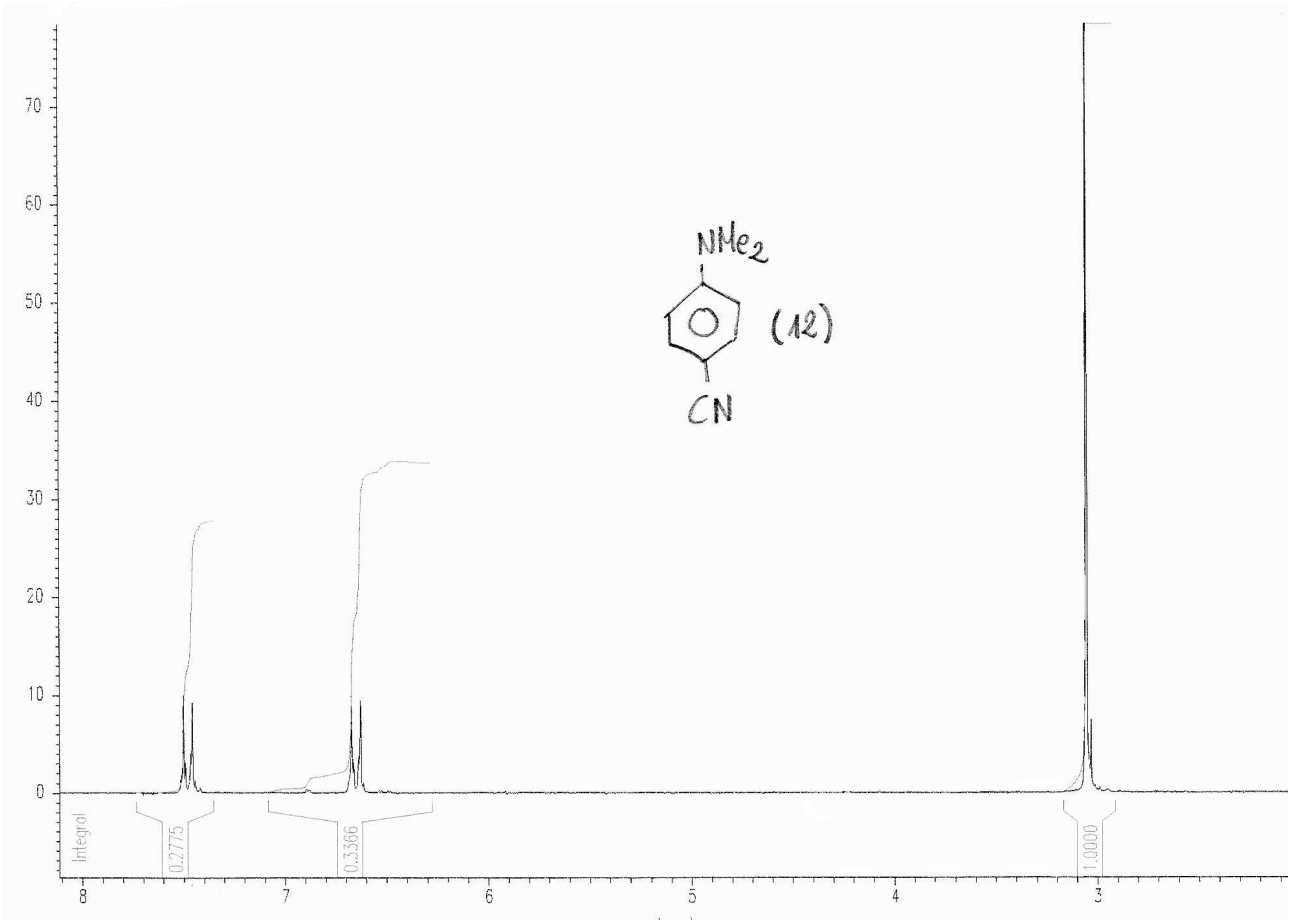

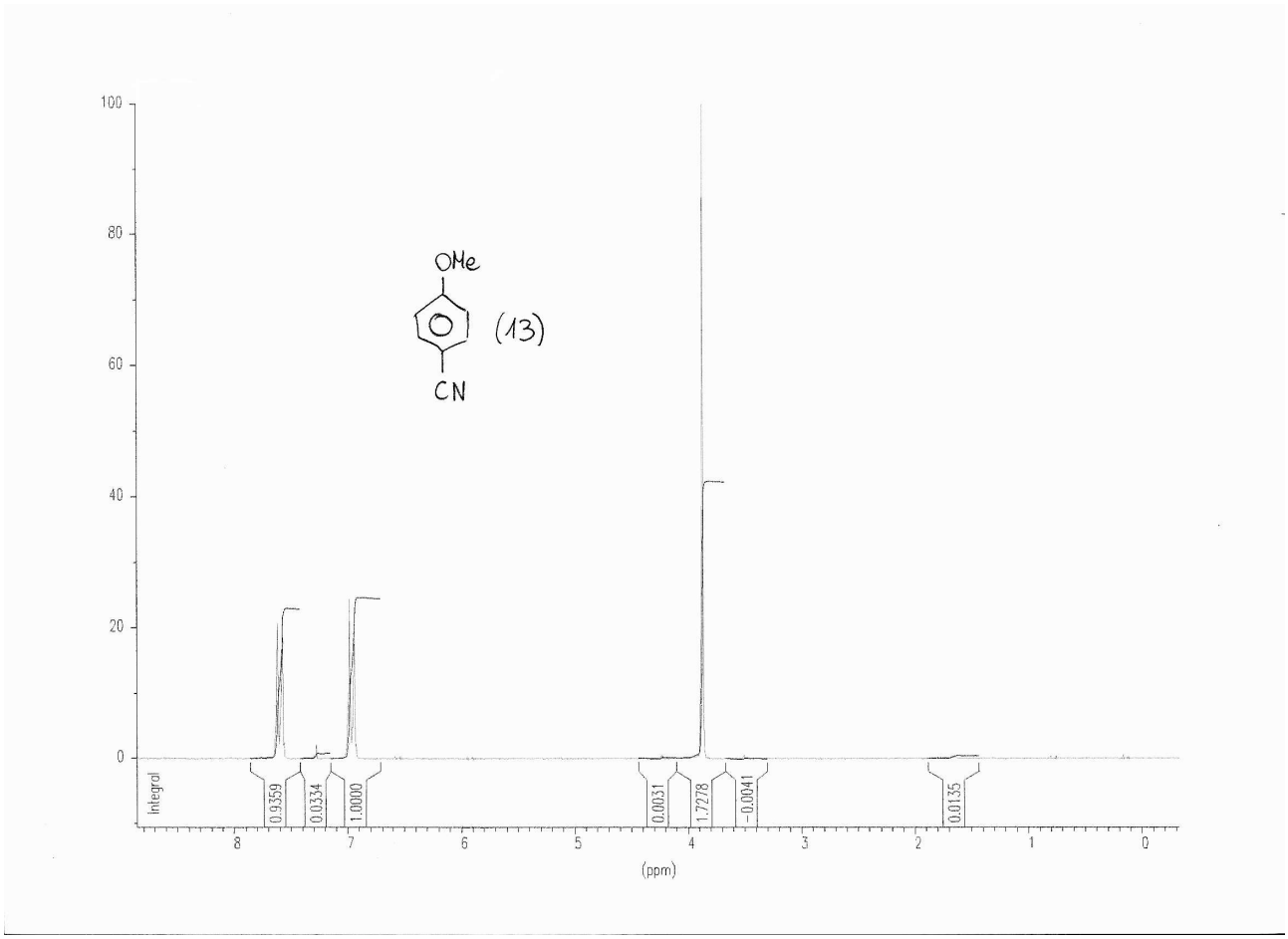

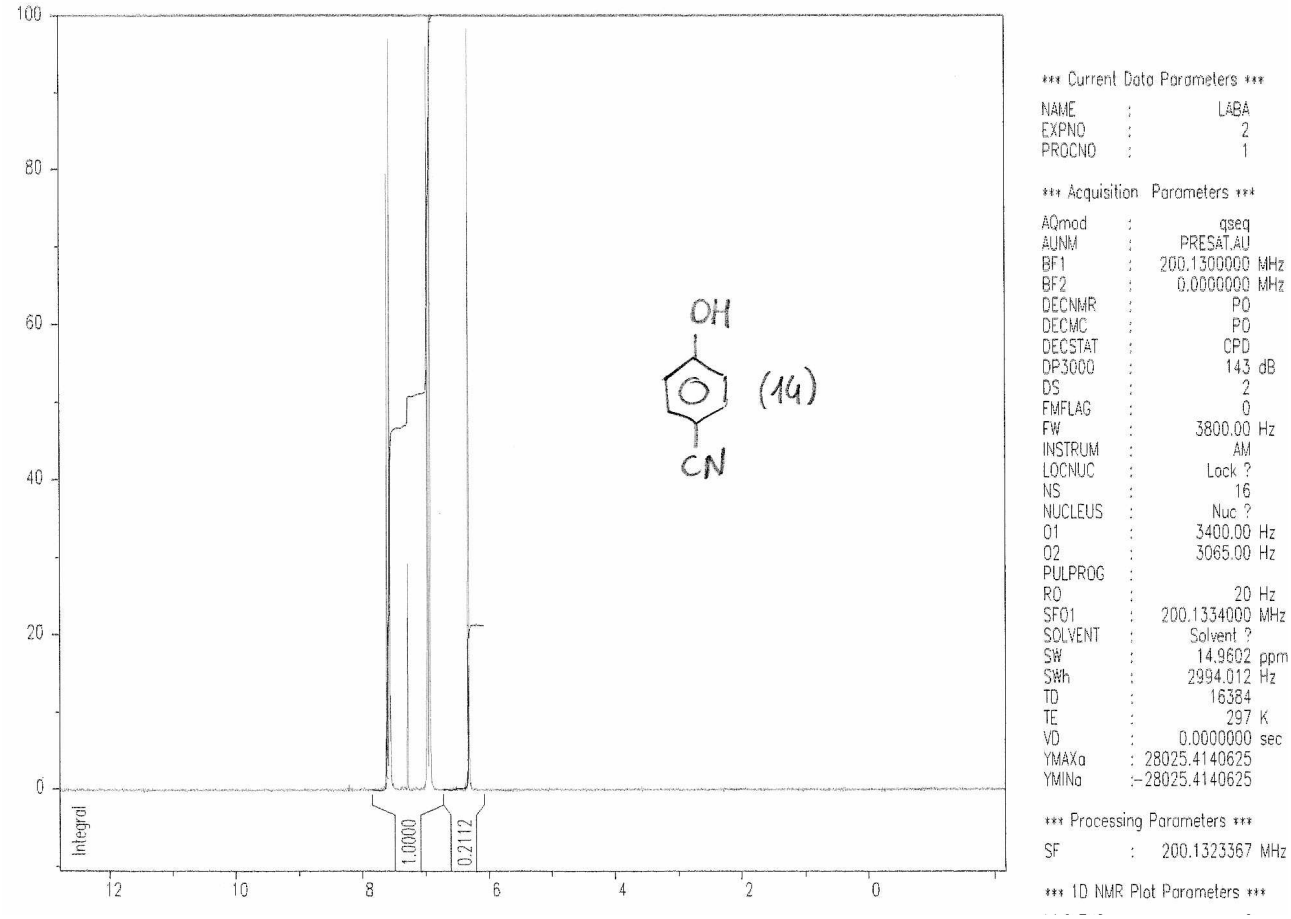


*** Current Data Parameters ***

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*** Acquisition Parameters ***

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| O1 | : | 3400.00 Hz |
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| PULPROG | : | |
| RO | : | 20 Hz |
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*** Processing Parameters ***

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*** 1D NMR Plot Parameters ***