

The Reaction of Azides with Dichloroindium Hydride: Very Mild Production of Amines and Pyrrolidin-2-imines through Possible Indium-Aminyl Radicals

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SUPPORTING INFORMATION

- Page S2: General Procedure for the Reactions of Azides with Dichloroindium Hydride.
- Page S3: Preparation and Characterization Data for Azides **1**, **3**, **5**, and **7**.
- Page S6: Characterization Data for All the Reaction Products.
- Page S9: Copies of NMR spectra.

General Procedure for the Reactions of Azides with Dichloroindium Hydride.

The starting azide (1 equiv.) was added at 0 °C to an acetonitrile solution of dichloroindium hydride (1.1 equiv.), generated in situ by stirring under argon anhydrous indium trichloride (1.1 equiv., previously dried by heating at 130 °C under argon for 1 h) and triethylsilane (1.1 equiv.) in acetonitrile (4 mL) for 5 min at 0 °C (Hayashi, N.; Shibata, I.; Baba, A. *Org. Lett.* **2004**, *6*, 4981). When used, triethylborane was added immediately after the azide. The resulting mixture was stirred at 0 °C until disappearance of the starting material. The final crude was quenched with an acid aqueous solution and extracted with diethyl ether to remove the silane residues. The aqueous phase was neutralized and extracted with diethyl ether to give the amine, which was in a few cases eventually purified by column chromatography. Yields and reaction times are reported in Table 1.

Analogous results can be obtained by dissolving the azide into the solution of dry indium trichloride and then adding triethylsilane (and, when it is the case, triethylborane).

Preparation and Characterization Data for Azides 1, 3, 5, and 7.

Aromatic azides **1a-h** were prepared by standard diazotization of the corresponding anilines followed by treatment with sodium azide, and were identified by comparison with literature data.

1a: Huber, M. L.; Pinhey, J. T. *J. Chem. Soc., Perkin Trans. 1* **1990**, 721.

1b: Nicolaides, A.; Enyo, T.; Miura, D.; Tomioka, H. *J. Am. Chem. Soc.* **2001**, 123, 2628.

1c: Butler, R. N.; Collier, S.; Fleming, A. F. M. *J. Chem. Soc., Perkin Trans. 2* **1996**, 801.

1d: Tomioka, H.; Sawai, S. *Org. Biomol. Chem.* **2003**, 4441.

1f: Hassan, S. S. M.; Tadros, F. S. *Anal. Chem.* **1985**, 57, 162.

1g: Klump, S. P.; Shechter, H. *Tetrahedron Lett.* **2002**, 43, 8421.

1h: Liu, Q.; Tor, Y. *Org. Lett.* **2003**, 5, 2571.

4-Azidobenzoic acid methyl ester **1e** was previously reported (Logue, M. W.; Han, B. H. *J. Org. Chem.* **1981**, 46, 1638) but characterized as a mixture of products; IR (μ_{max} , CHCl₃) 2118 (N₃) and 1718 (CO) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.89 (3 H, s), 7.03 (2 H, A part of AA'BB', *J* = 8.9 Hz), 8.00 (2 H, B part of AA'BB', *J* = 8.9 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 52.6 (CH₃), 119.3 (CH), 127.3 (CH), 131.9 (CH), 145.2 (C), 166.7 (C).

Sulfonyl and acyl azides **1i,j** were synthesized by treatment of the corresponding acid chlorides with sodium azide in DMSO (Regitz, M.; Hocker, J.; Liedhegener, A. *Org. Synth. Coll. Vol. V*, **1973**, 179).

1i: Dang, H. -S.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1493.

1j: Bose, D. S.; Reddy, A. V. N. *Tetrahedron Lett.* **2003**, 44, 3543.

Alkyl azides **1k,l** were prepared by treatment of the corresponding alkyl bromide and iodide, respectively, with sodium azide in DMSO (L'abbé, G.; Sannen, I.; Dehaen, W. *J. Chem. Soc., Perkin Trans. 1* **1993**, 27). 3-Phenylpropyl azide (**1k**) (Moriarty, R. M.; Reardon, R. C. *Tetrahedron* **1970**, 26, 1379): IR (μ_{max} , CHCl₃) 2096 (N₃) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.91 (2 H, dt, *J_d* = 7.5, *J_t* = 6.7 Hz), 2.70 (2 H, t, *J* = 7.5 Hz), 3.27 (2 H, t, *J* = 6.7 Hz), 7.16-7.24 (3 H, m), 7.26-7.32 (2 H, m); ¹³C

NMR (100 MHz, CDCl₃) δ 30.4 (CH₂), 32.7 (CH₂), 50.6 (CH₂), 126.1 (CH), 128.4 (CH), 128.5 (CH), 140.8 (C). 2-Phenylethyl azide (**1l**) (Kratzky, A. R.; Liso, G.; Lunt, E.; Patel, R. C.; Thind, S. S.; Zia, A. J. *Chem. Soc., Perkin Trans. I* **1980**, 849): IR (μ_{max}, CHCl₃) 2097 (N₃) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.89 (2 H, t, *J* = 7.3 Hz), 3.49 (2 H, t, *J* = 7.3 Hz), 7.18-7.23 (2 H, m), 7.23-7.27 (1 H, m), 7.29-7.35 (2 H, m); ¹³C NMR (100 MHz, CDCl₃) δ 35.3 (CH₂), 52.4 (CH₂), 126.7 (CH), 128.6 (CH), 128.7 (CH), 138.0 (C).

Azide **3a**: L'abbé, G.; Sannen, I.; Dehaen, W. *J. Chem. Soc., Perkin Trans. I* **1993**, 27; mp = 46 °C; spectral data not reported. IR (μ_{max}, CHCl₃) 2103 (N₃) and 2238 (CN) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.62-2.72 (2 H, m), 3.32-3.43 (2 H, m), 7.27-7.42 (10 H, m); ¹³C NMR (75 MHz, CDCl₃) δ 38.1 (CH₂), 47.8 (CH₂), 49.3 (C), 121.3 (C), 126.5 (CH), 128.2 (CH), 129.1 (CH), 139.0 (C); MS *m/z* (70 eV) 234 (M⁺ – 28, 19%), 192 (36%), 105 (100%).

Azides **3b-d**, **5**: Benati, L.; Bencivenni, G.; Leardini, R.; Minozzi, M.; Nanni, D.; Scialpi, R.; Spagnolo, P.; Zanardi, G.; Rizzoli, C. *Org. Lett.* **2004**, 6, 417.

2-(2-Azidoethyl)-5-phenyl-2-(phenylsulfonyl)-4-pentenenitrile (3e). 5-Phenyl-2-(phenylsulfonyl)-4-pentenenitrile was prepared in 70% yield from phenylsulfonylacetonitrile and cinnamyl bromide following a general method reported in the literature for the synthesis of 2-alkyl-2-aryl(phenylsulfonyl)acetonitriles (Abd-El-Aziz, A. S.; de Denus, C. R.; Hutton, H. M. *Can. J. Chem.* **1995**, 73, 289); ¹H NMR (300 MHz, CDCl₃) δ 2.80 (1 H, dddd, *J*₁ = 14.1, *J*₂ = 10.4, *J*₃ = 7.4, *J*₄ = 1.4 Hz), 3.10 (1 H, dddd, *J*₁ = 14.1, *J*₂ = 7.4, *J*₃ = 4.5, *J*₄ = 1.4 Hz), 4.03 (1 H, dd, *J*₁ = 10.4, *J*₂ = 4.5 Hz), 6.08 (1 H, dt, *J*_d = 15.7, *J*_t = 7.4 Hz), 6.59 (1 H, dt, *J*_d = 15.7, *J*_t = 1.1 Hz), 7.23-7.34 (5 H, m), 7.59-7.66 (2 H, m), 7.72-7.78 (1 H, m), 8.01-8.05 (2 H, m) (a ¹H NMR spectrum is reported in: Lu, X.; Jiang, X.; Tao, X. *J. Organomet. Chem.* **1988**, 344, 109); ¹³C NMR (75 MHz, CDCl₃) δ 30.8 (CH₂), 57.8 (CH), 114.1 (C), 121.0 (CH), 126.9 (CH), 128.6 (C), 129.0 (CH), 130.0 (CH), 130.1 (CH), 135.8 (CH), 135.9 (C), 136.3 (CH).

5-Phenyl-2-(phenylsulfonyl)-4-pentenenitrile was alkylated with 1,2-dibromoethane according to a reported general alkylation procedure (Diez-Barra, E.; De La Hoz, A.; Moreno, A.; Sanchez-Verdù, P. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2589) to give 2-(2-bromoethyl)-5-phenyl-2-(phenylsulfonyl)-4-pentenenitrile (92%); IR (μ_{max} , CHCl₃) 2237 (CN) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.51-2.77 (2 H, m), 2.81 (2 H, dd, J_1 = 7.6, J_2 = 1.4 Hz), 3.53-3.69 (2 H, m), 6.06 (1 H, dt, J_d = 15.6, J_t = 7.5 Hz), 6.57 (1 H, dt, J_d = 15.6, J_t = 1.3 Hz), 7.24-7.38 (5 H, m), 7.62-7.72 (2 H, m), 7.75-7.84 (1 H, m), 8.00-8.09 (2 H, m); ¹³C NMR (75 MHz, CDCl₃) δ 25.5 (CH₂), 35.0 (CH₂), 37.1 (CH₂), 65.9 (C), 115.8 (C), 119.6 (CH), 126.9 (CH), 128.8 (CH), 129.1 (CH), 130.0 (CH), 131.2 (CH), 134.2 (C), 136.0 (CH), 136.1 (C), 137.7 (CH); MS *m/z* (70 eV) 405 (M⁺ + 2, <1%), 403 (M⁺, <1%), 263 (99%), 261 (100%).

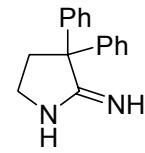
Treatment of 2-(2-bromoethyl)-5-phenyl-2-(phenylsulfonyl)-4-pentenenitrile with sodium azide in DMSO gave azide **3e** (85%); IR (μ_{max} , CHCl₃) 1152 (SO₂Ph), 2102 (N₃), and 2254 (CN) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.28 (1 H, ddd, J_1 = 14.7, J_2 = 8.5, J_3 = 6.5 Hz), 2.40 (1 H, ddd, J_1 = 14.7, J_2 = 8.5, J_3 = 6.5 Hz), 2.88 (2 H, dd, J_1 = 7.4, J_2 = 1.1 Hz), 3.57-3.77 (2 H, m), 6.07 (1 H, dt, J_d = 15.7, J_t = 7.4 Hz), 6.55 (1 H, dt, J_d = 15.7, J_t = 1.2 Hz), 7.21-7.39 (5 H, m), 7.60-7.71 (2 H, m), 7.73-7.83 (1 H, m), 8.00-8.10 (2 H, m); ¹³C NMR (75 MHz, CDCl₃) δ 31.1 (CH₂), 37.4 (CH₂), 47.6 (CH₂), 64.4 (C), 116.2 (C), 119.8 (CH), 126.9 (CH), 128.7 (CH), 129.1 (CH), 130.0 (CH), 131.2 (CH), 134.2 (C), 135.9 (CH), 136.1 (C), 137.6 (CH); MS ESI 389 (M⁺ + Na, 100%), 367 (M⁺ + 1, 10%).

(2-Azidophenyl)acetonitrile (7). (2-Aminophenyl)acetonitrile (commercially available) (5 mmol) was diazotized according to a standard procedure and treated dropwise in 45 min at 0-5 °C with an aqueous (10 mL) solution of sodium azide (10 mmol). The reaction crude was extracted with diethyl ether (3 × 25 mL), the organic phase was dried over magnesium sulfate, and the solvent evaporated to give azide **7** (3.1 mmol, 60%) as a solid, mp = 57.5-58.7 °C; IR (μ_{max} , CHCl₃) 2132 (N₃), and 2255 (CN) cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.67 (2 H, s), 7.13-7.22 (2 H, m), 7.35-7.46 (2 H, m); ¹³C NMR (75 MHz, CDCl₃) δ 19.1 (CH₂), 117.1 (C), 117.9 (CH), 120.1 (C), 124.9 (CH), 129.3 (CH), 129.4 (CH), 137.7 (C); MS *m/z* 158 (M⁺, 20%), 103 (100%).

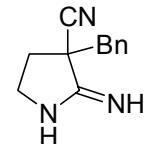
Characterization Data for All the Reaction Products.

All the amines obtained from azides **1** (Table 1) are commercially available compounds and their identification was based on spectral comparison with authentic samples.

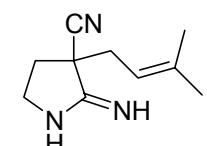
3,3-Diphenyl-2-pyrrolidinimine (4a). mp = 209.3-210 °C; IR (μ_{max} , CHCl_3) 3504 (NH), 3403 (NH), 1650 (C=N) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.85 (2 H, t, J = 6.4 Hz), 3.58 (2 H, t, J = 6.4 Hz), 9.12 (2 H, br s), 7.21-7.28 (5 H, m), 7.30-7.40 (5 H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 39.8 (CH_2), 44.5 (CH_2), 61.1 (C), 127.8 (CH), 128.1 (CH), 128.9 (CH), 139.0 (C), 173.7 (C); MS ESI 237 ($\text{M}^+ + 1$). Anal. calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2$: C, 81.33; H, 6.82; N, 11.85. Found: C, 81.46; H, 6.81; N, 11.73.



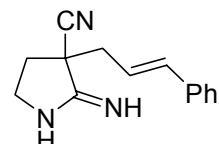
3-Benzyl-2-imino-3-pyrrolidinecarbonitrile (4b). Benati, L.; Bencivenni, G.; Leardini, R.; Minozzi, M.; Nanni, D.; Scialpi, R.; Spagnolo, P.; Zanardi, G.; Rizzoli, C. *Org. Lett.* **2004**, 6, 417.



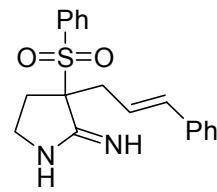
2-Imino-3-(3-methyl-2-butenyl)-3-pyrrolidinecarbonitrile (4c). Benati, L.; Bencivenni, G.; Leardini, R.; Minozzi, M.; Nanni, D.; Scialpi, R.; Spagnolo, P.; Zanardi, G.; Rizzoli, C. *Org. Lett.* **2004**, 6, 417.



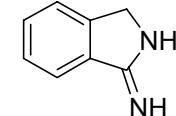
2-Imino-3-(3-phenyl-2-propenyl)-3-pyrrolidinecarbonitrile (4d). Benati, L.; Bencivenni, G.; Leardini, R.; Minozzi, M.; Nanni, D.; Scialpi, R.; Spagnolo, P.; Zanardi, G.; Rizzoli, C. *Org. Lett.* **2004**, 6, 417. ^{13}C NMR not reported. ^{13}C NMR (100 MHz, CDCl_3) δ 35.8 (CH_2), 39.2 (CH_2), 47.9 (C), 53.1 (CH_2), 120.4 (CN), 121.8 (CH), 126.4 (CH), 128.0 (CH), 128.6 (CH), 135.9 (CH), 136.2 (C), 162.0 (C).



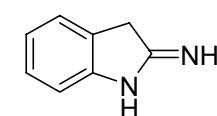
3-(3-Phenyl-2-propenyl)-3-(phenylsulfonyl)-2-pyrrolidinimine (**4e**). mp = 180.1-182.5 °C; IR (μ_{max} , CHCl₃) 3491 (NH), 3395 (NH), 1661 (C=N) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.17 (1 H, ddd, J_1 = 14.6, J_2 = 8.9, J_3 = 5.7 Hz), 2.39 (1 H, ddd, J_1 = 14.6, J_2 = 8.6, J_3 = 4.4 Hz), 2.79 (1 H, ddd, J_1 = 14.1, J_2 = 8.7, J_3 = 5.7 Hz), 2.88 (1 H, ddd, J_1 = 13.9, J_2 = 9.0, J_3 = 0.8 Hz), 3.25 (1 H, ddd, J_1 = 13.9, J_2 = 5.7, J_3 = 1.7 Hz), 3.30 (1 H, ddd, J_1 = 13.9, J_2 = 9.0, J_3 = 4.4 Hz), 5.03 (2 H, br s), 6.05 (1 H, ddd, J_1 = 15.6, J_2 = 9.3, J_3 = 5.5 Hz), 6.56 (1 H, d, J = 15.7 Hz), 7.18-7.37 (5 H, m), 7.53-7.63 (2 H, m), 7.65-7.74 (1 H, m), 7.92-8.00 (2 H, m); ¹³C NMR (100 MHz, CDCl₃) δ 30.6 (CH₂), 34.2 (CH₂), 52.7 (CH₂), 77.2 (C), 121.7 (CH), 126.3 (CH), 127.7 (CH), 128.5 (CH), 129.1 (CH), 130.0 (CH), 134.3 (CH), 135.3 (C), 135.8 (CH), 136.5 (C), 159.9 (C); MS *m/z* (70 eV) 340 (M⁺, 1%), 199 (100%); MS ESI 363 (M⁺ + Na, 90%), 341 (M⁺ + 1, 100%). Anal. calcd for C₁₉H₂₀N₂O₂S: C, 67.03; H, 5.29; N, 8.23. Found: C, 67.16; H, 5.28; N, 8.32.



1-Isoindolinimine (**6**). Benati, L.; Bencivenni, G.; Leardini, R.; Minozzi, M.; Nanni, D.; Scialpi, R.; Spagnolo, P.; Zanardi, G.; Rizzoli, C. *Org. Lett.* **2004**, 6, 417. Sawanischi, H.; Sashida, H.; Tsuchiya, T. *Chem. Pharm. Bull.* **1985**, 33, 4564. The trifluoroacetate was also obtained and characterized, since it seems less susceptible to tautomerism with respect to the free base. ¹H NMR (300 MHz, DMSO-d₆/TFA) δ 4.83 (2 H, s), 7.60-7.70 (1 H, m), 7.75-7.85 (2 H, m), 8.30-8.37 (1 H, m), 9.45 (1 H, s, NH), 9.85 (1 H, s, NH), 10.59 (1 H, s, NH); ¹³C NMR (75 MHz, DMSO-d₆/TFA) δ 51.4 (CH₂), 115.4 (CF₃), 124.0 (CH), 124.2 (CH), 128.4 (C), 128.6 (CH), 133.7 (CH), 144.5 (C), 158.9 (CO, TFA), 164.0 (C).



1,3-Dihydro-2*H*-indol-2-imine (**8**). This compound is not stable and readily decomposed after the reaction mixture was quenched with water (a deep violet color developed after few minutes). Therefore, it was characterized as trifluoroacetate, as previously reported



(Diana, P.; Barraja, P.; Lauria, A.; Almerico, A. M.; Dattolo, G. Cirrincione, G. *Tetrahedron* **2000**, *56*, 5177). The trifluoroacetate was obtained by quenching the reaction mixture directly with TFA, evaporating acetonitrile and excess TFA, and dissolving the residue in DMSO-d₆/TFA. ¹H NMR (400 MHz, DMSO-d₆/TFA) δ 4.12 (2 H, s), 7.18 (2 H, m), 7.33 (1 H, m), 7.39 (1 H, m), 9.39 (1 H, s, NH), 9.59 (1 H, s, NH), 11.95 (1 H, s, NH) [above lit. ¹H NMR (200 MHz, DMSO-d₆/TFA) δ 4.17 (2 H, s), 7.12 (1 H, dt), 7.18 (1 H, dt), 7.27 (1 H, dd), 7.39 (1 H, dd), 9.86 (1 H, s), 10.02 (1 H, s), 12.41 (1 H, s)]; ¹³C NMR (100 MHz, DMSO-d₆/TFA) δ 37.7 (CH₂), 113.9 (CH), 117.3 (CF₃), 126.4 (CH), 126.6 (CH), 128.1 (C), 130.4 (CH), 144.5 (C), 161.2 (CO, TFA), 173.9 (C).

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: 020505_carbometossiN3

GEMINI-300BB "g300"

Relax. delay 2.000 sec

Pulse 25.3 degrees

Acq. time 2.666 sec

Width 4500.5 Hz

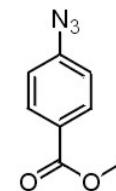
16 repetitions

OBSERVE H1, 300.0315602 MHz

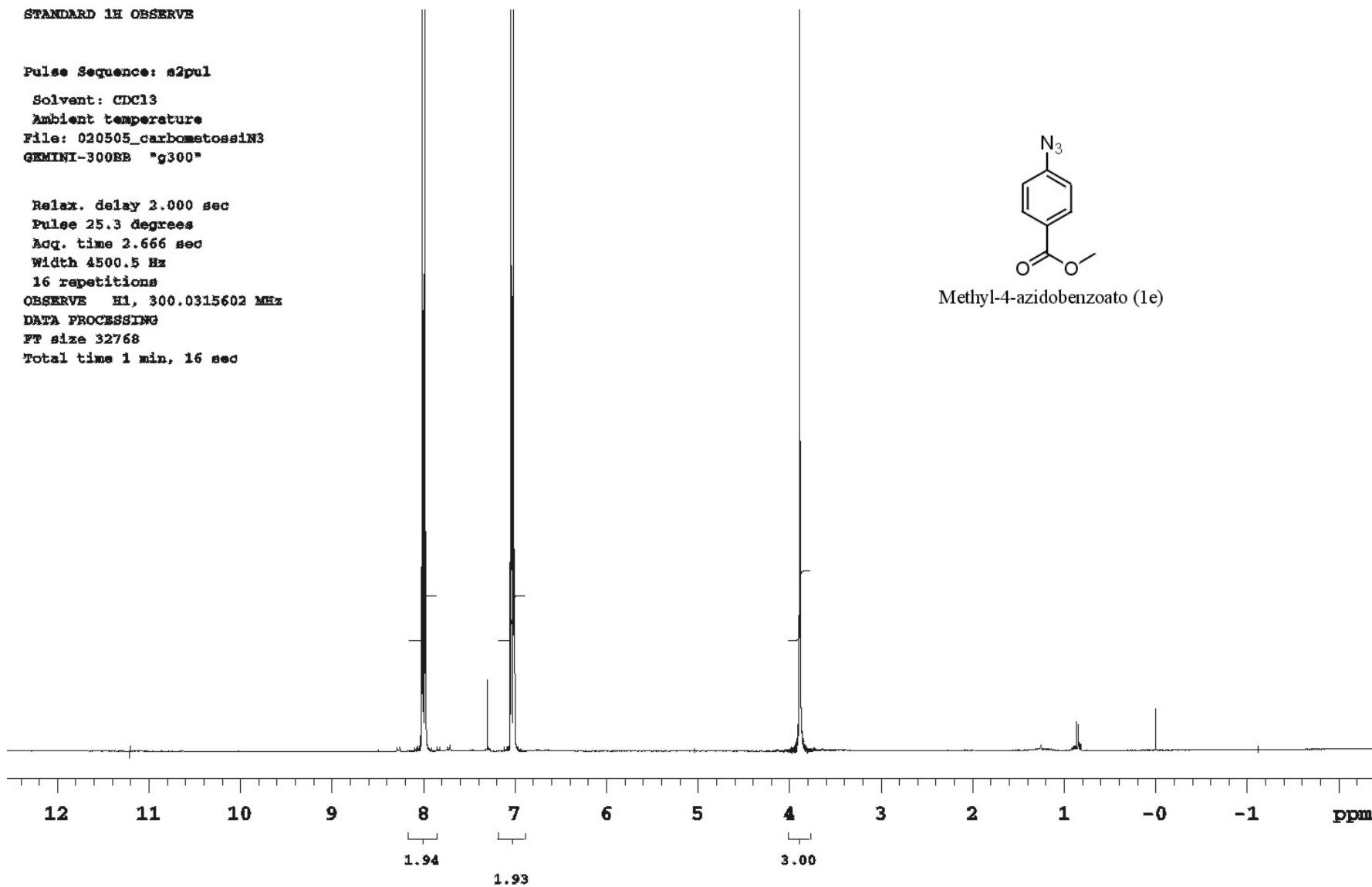
DATA PROCESSING

FT size 32768

Total time 1 min, 16 sec



Methyl-4-azidobenzoato (1e)



¹³C RESOLUTION
DECOUPLED DICKANE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: 020505_carbometossiN3_13C
GEMINI-300BB "g300"

Relax. delay 2.000 sec

Pulse 60.0 degrees

Acq. time 0.750 sec

Width 20000.0 Hz

32 repetitions

OBSERVE C13, 75.4429558 MHz

DECOPLE H1, 300.0325732 MHz

Power 43 dB

on during acquisition

off during delay

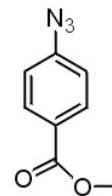
WALTZ-16 modulated

DATA PROCESSING

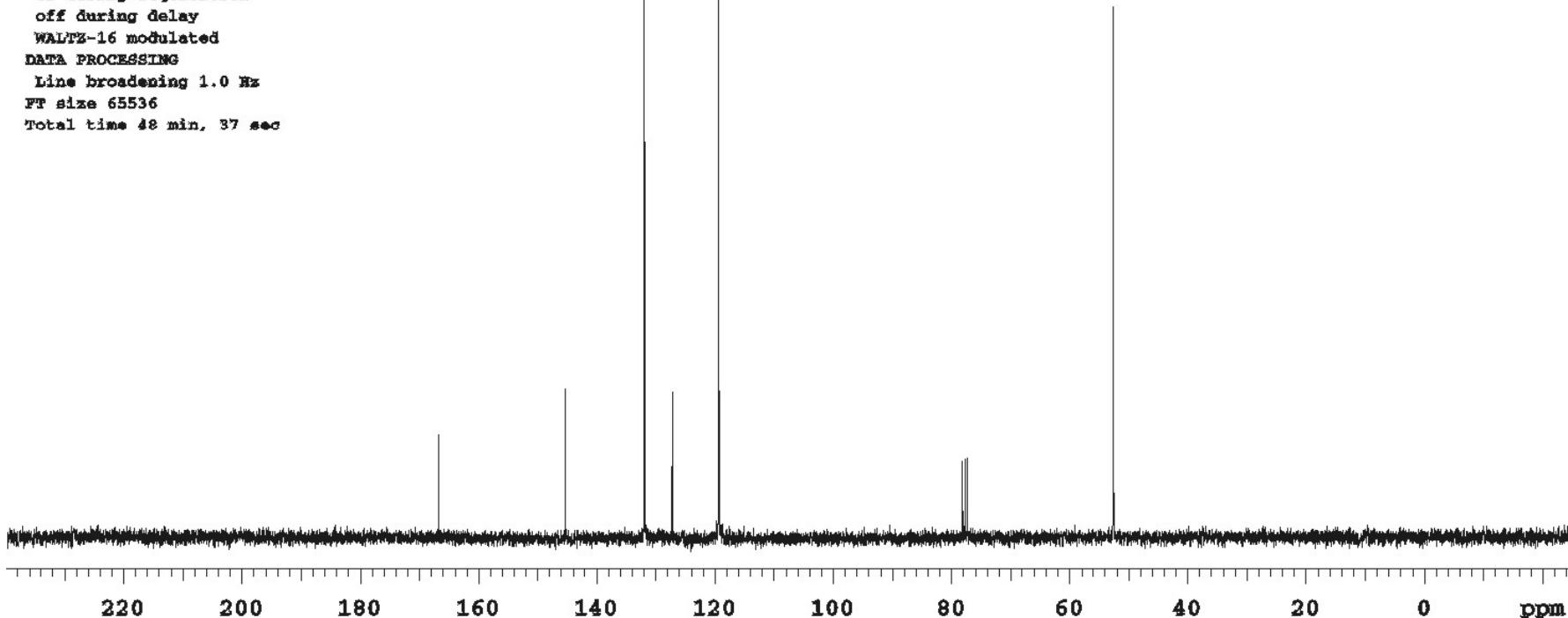
Line broadening 1.0 Hz

FT size 65536

Total time 48 min, 37 sec



Methyl-4-azidobenzoate (1e)



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 25.0 C / 298.1 K

File: phenylpropN3_1h

Mercury-400BB "m400"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 2.731 sec

Width 5998.8 Hz

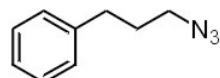
4 repetitions

OBSERVE H1, 399.9245859 MHz

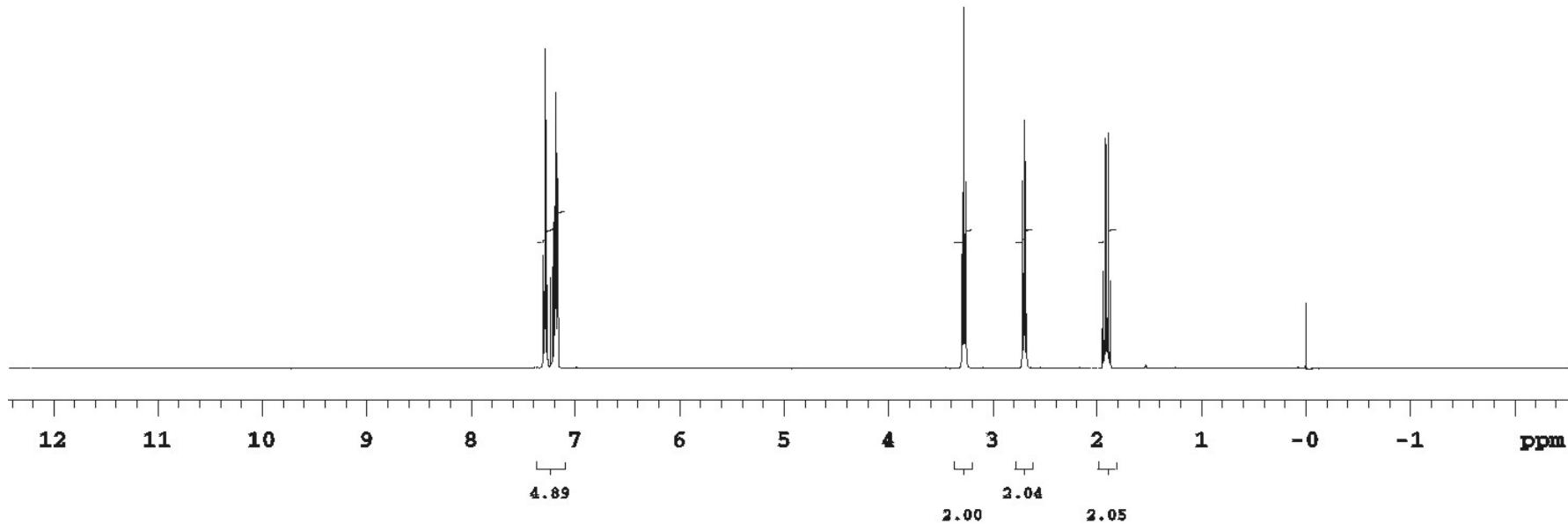
DATA PROCESSING

FT size 65536

Total time 0 min, 17 sec



3-Phenylpropyl azide (1K)



¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 25.0 C / 298.1 K

File: phenylpropn3_13C

Mercury-400BB "m400"

Relax. delay 3.000 sec

Pulse 59.4 degrees

Acq. time 1.000 sec

Width 26525.2 Hz

68 repetitions

OBSERVE C13, 100.5611186 MHz

DECOUPLE H1, 399.9265569 MHz

Power 40 dB

continuously on

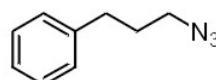
WALTZ-16 modulated

DATA PROCESSING

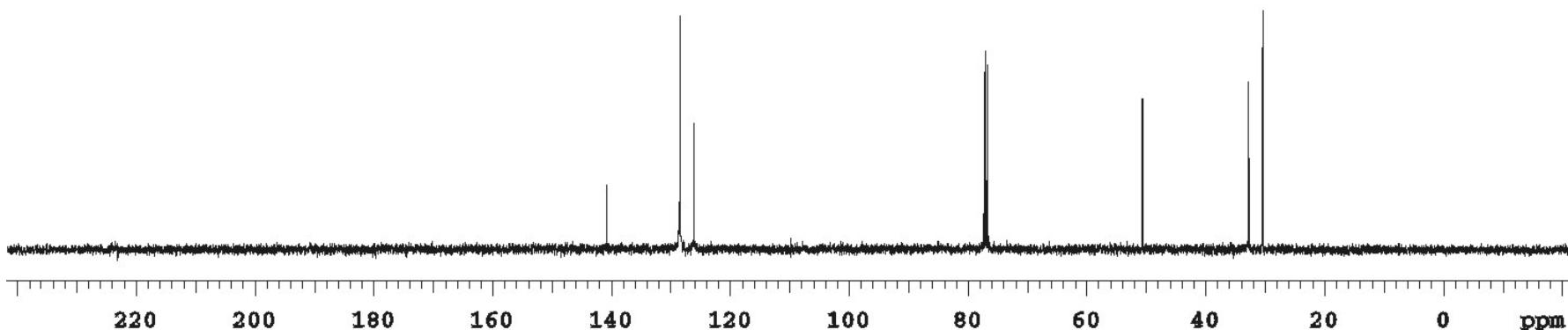
Line broadening 1.0 Hz

PT size 65536

Total time 1 hr, 10 min, 42 sec



3-Phenylpropyl azide (1K)



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 25.0 C / 298.1 K

File: phenylethylN3_1h

Mercury-400BB "m400"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 2.731 sec

Width 5998.8 Hz

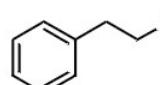
4 repetitions

OBSERVE H1, 399.9245860 MHz

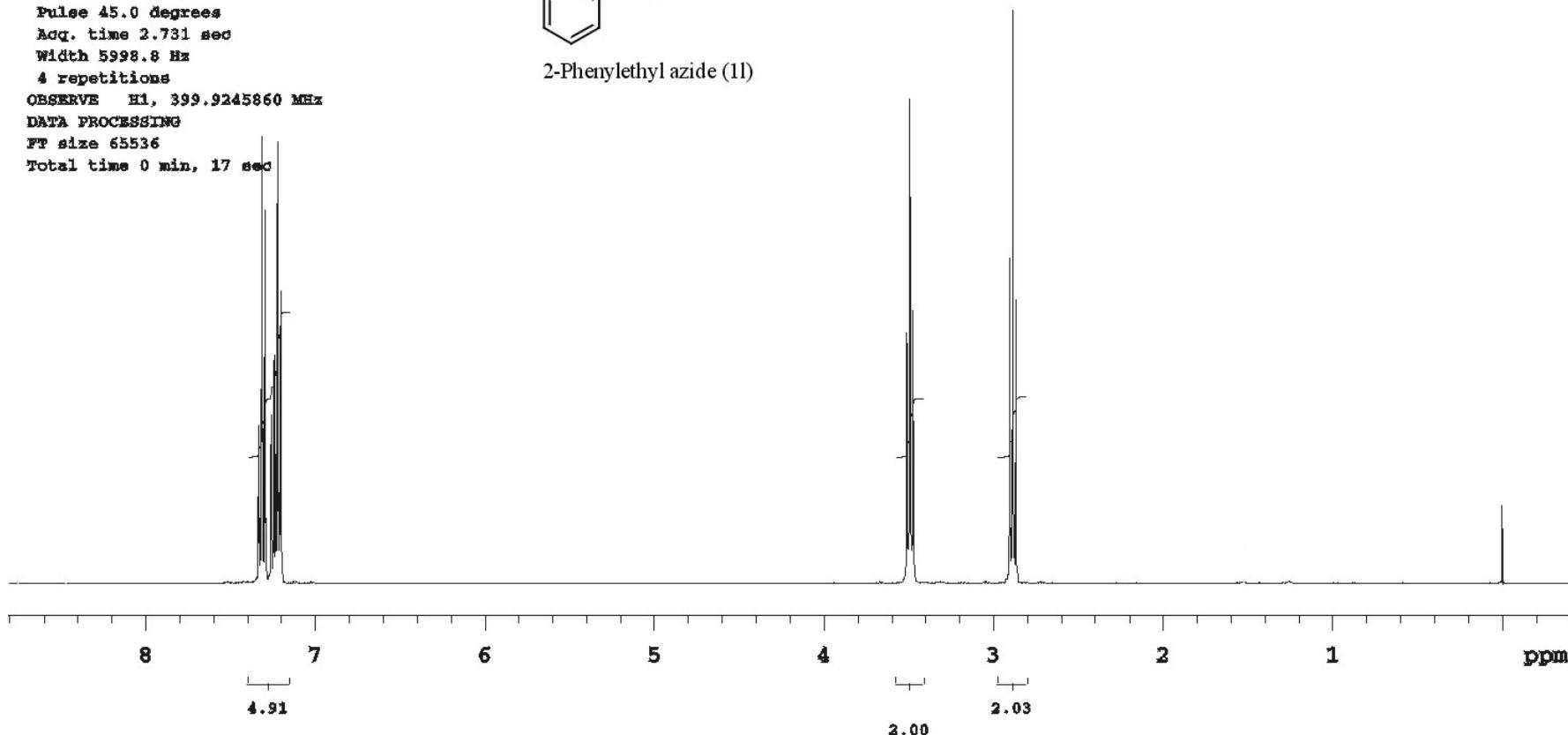
DATA PROCESSING

FT size 65536

Total time 0 min, 17 sec



2-Phenylethyl azide (1l)



¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 25.0 C / 298.1 K

File: PhenylethylN3_13C

Mercury-400BB "m400"

Relax. delay 3.000 sec

Pulse 59.4 degrees

Acq. time 1.000 sec

Width 26525.2 Hz

18 repetitions

OBSERVE C13, 100.5611186 MHz

DECOUPLE H1, 399.9265569 MHz

Power 40 dB

continuously on

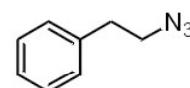
WALTZ-16 modulated

DATA PROCESSING

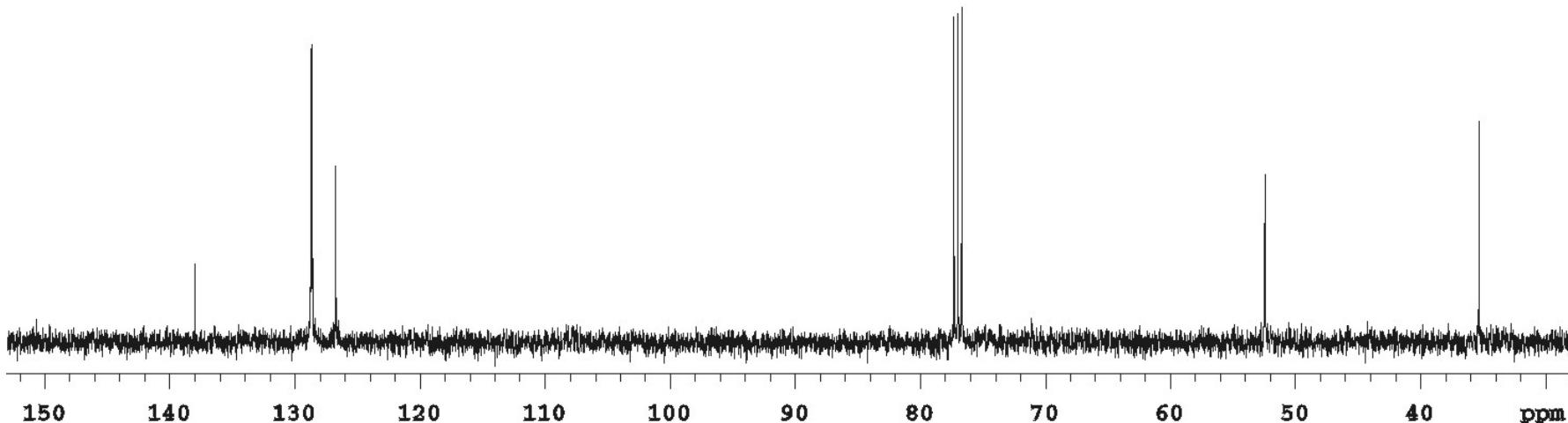
Line broadening 1.0 Hz

PT size 65536

Total time 1 hr, 10 min, 42 sec



2-Phenylethyl azide (1l)



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: R57_1h

GEMINI-300BB "g300"

Relax. delay 1.000 sec

Pulse 50.5 degrees

Acq. time 2.666 sec

Width 4500.5 Hz

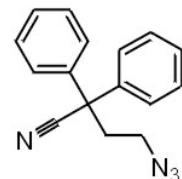
16 repetitions

OBSERVE H1, 300.0315764 MHz

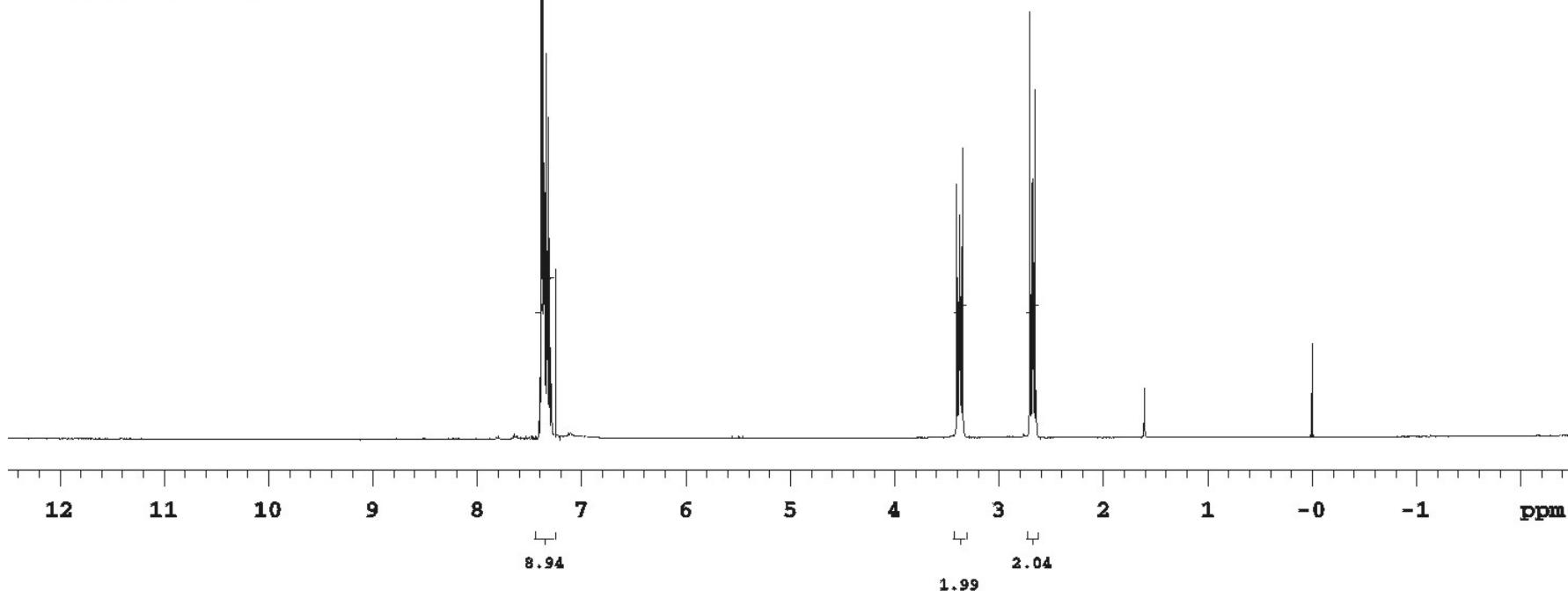
DATA PROCESSING

FT size 32768

Total time 1 min, 0 sec



4-azido-2,2-diphenylbutanenitrile (3a)



¹³C RESOLUTION
DECOUPLED DICKANE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: R57_13C

GEMINI-300BB "g300"

Relax. delay 2.000 sec

Pulse 56.9 degrees

Acq. time 0.750 sec

Width 20000.0 Hz

64 repetitions

OBSERVE C13, 75.4430086 MHz

DECOUPLE H1, 300.0325732 MHz

Power 43 dB

on during acquisition

off during delay

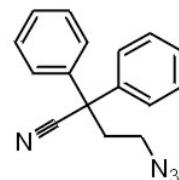
WALTZ-16 modulated

DATA PROCESSING

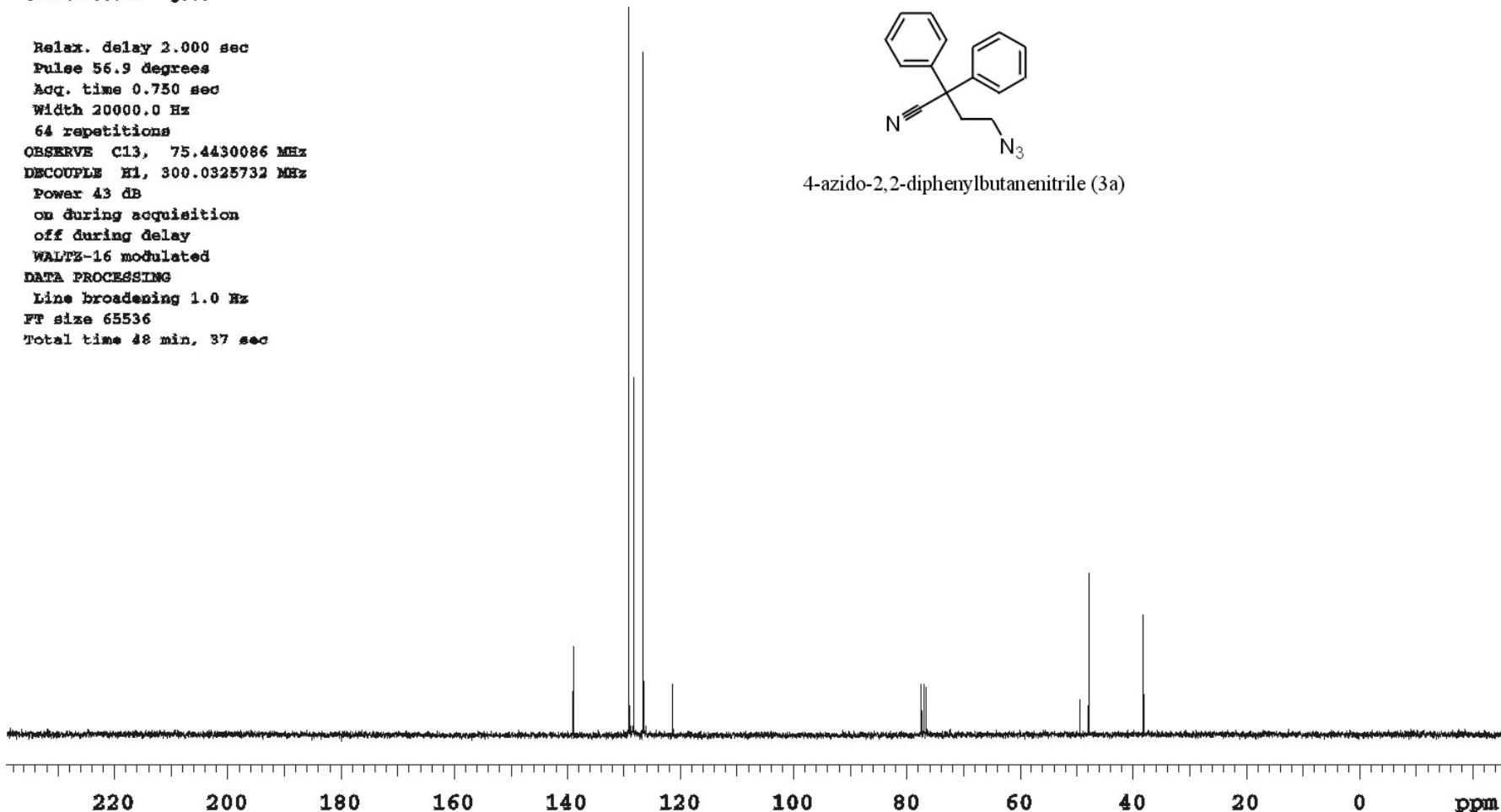
Line broadening 1.0 Hz

FT size 65536

Total time 48 min, 37 sec



4-azido-2,2-diphenylbutanenitrile (3a)



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: 2207056h

GEMINI-300BB "g300"

Pulse 50.5 degrees

Acq. time 2.666 sec

Width 4500.5 Hz

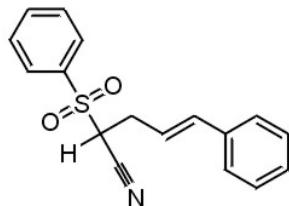
8 repetitions

OBSERVE H1, 300.0315775 MHz

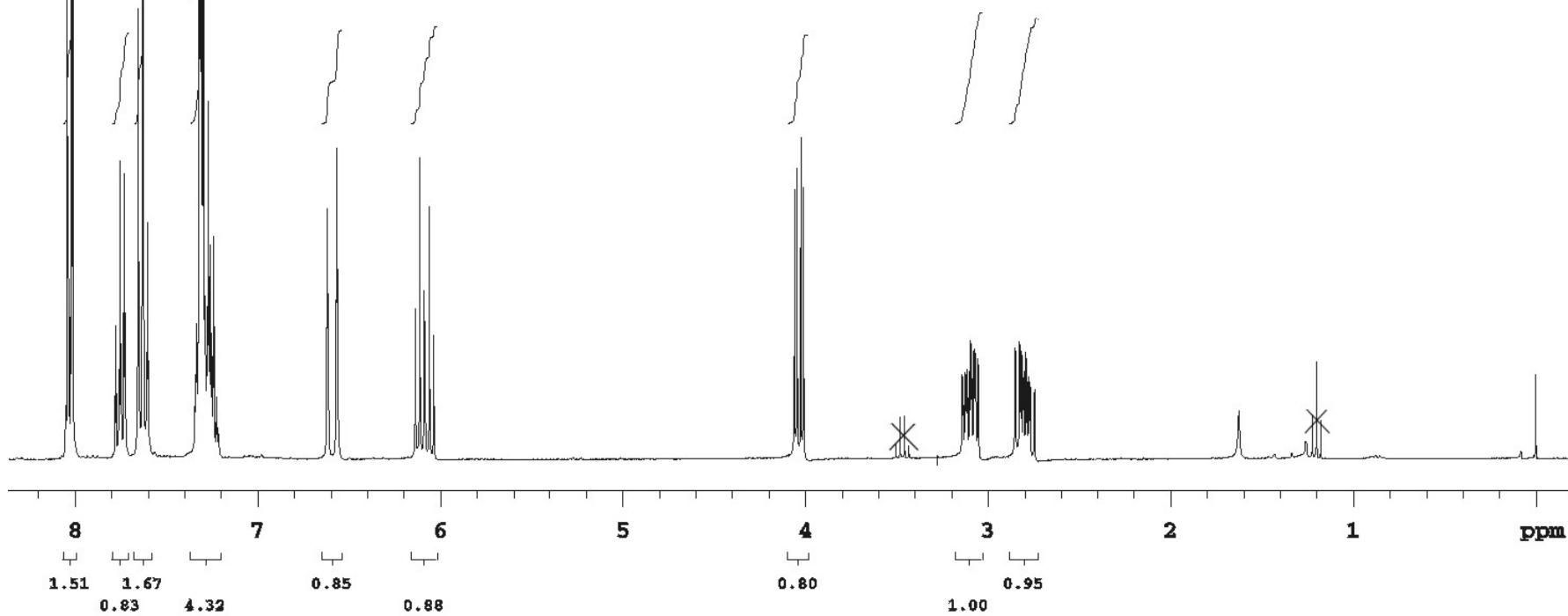
DATA PROCESSING

PP size 32768

Total time 6 min, 23 sec



5-Phenyl-2-(phenylsulfonyl)-4-pentenenitrile



¹³C RESOLUTION
DECOUPLED DICKANE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: 2207056c

GEMINI-300BB "g300"

Relax. delay 1.500 sec

Pulse 60.0 degrees

Acq. time 0.750 sec

Width 20000.0 Hz

48 repetitions

OBSERVE C13, 75.4429723 MHz

DECOPLE H1, 300.0325732 MHz

Power 43 dB

on during acquisition

off during delay

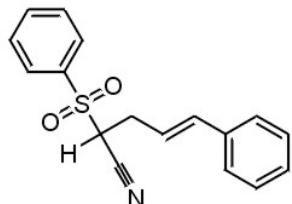
WALTZ-16 modulated

DATA PROCESSING

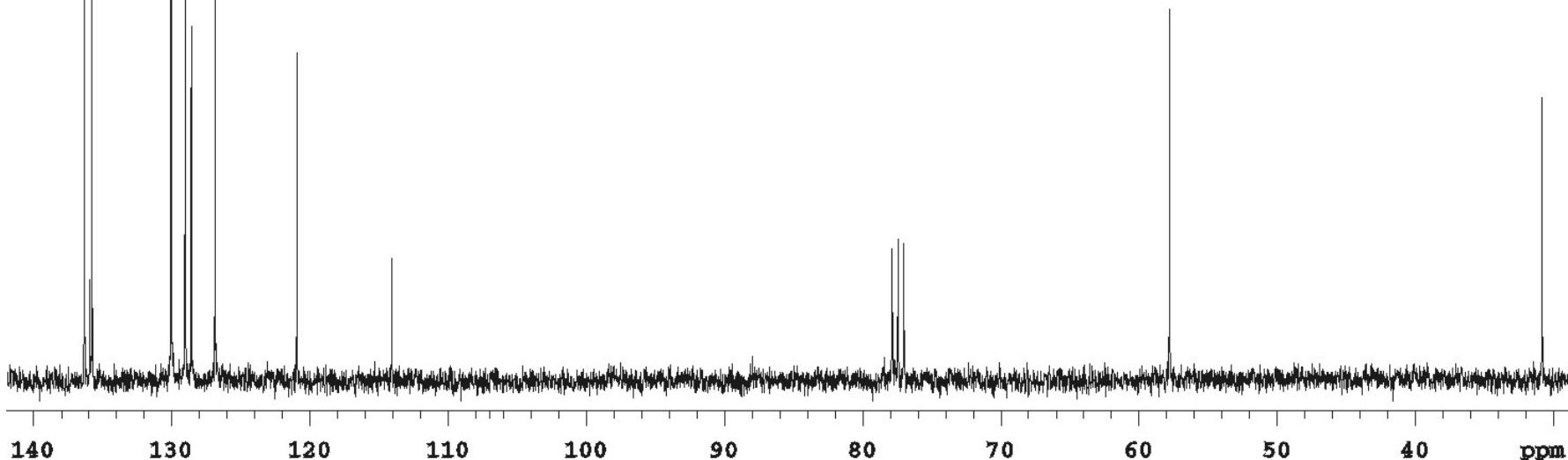
Line broadening 1.0 Hz

FT size 65536

Total time 40 min, 16 sec



5-Phenyl-2-(phenylsulfonyl)-4-pentenenitrile



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: 070905H

GEMINI-300BB "g300"

Pulse 50.5 degrees

Acq. time 2.666 sec

Width 4500.5 Hz

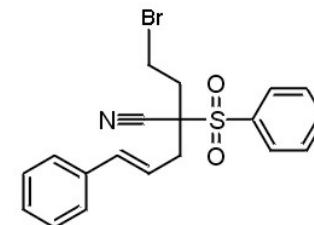
8 repetitions

OBSERVE H1, 300.0315740 MHz

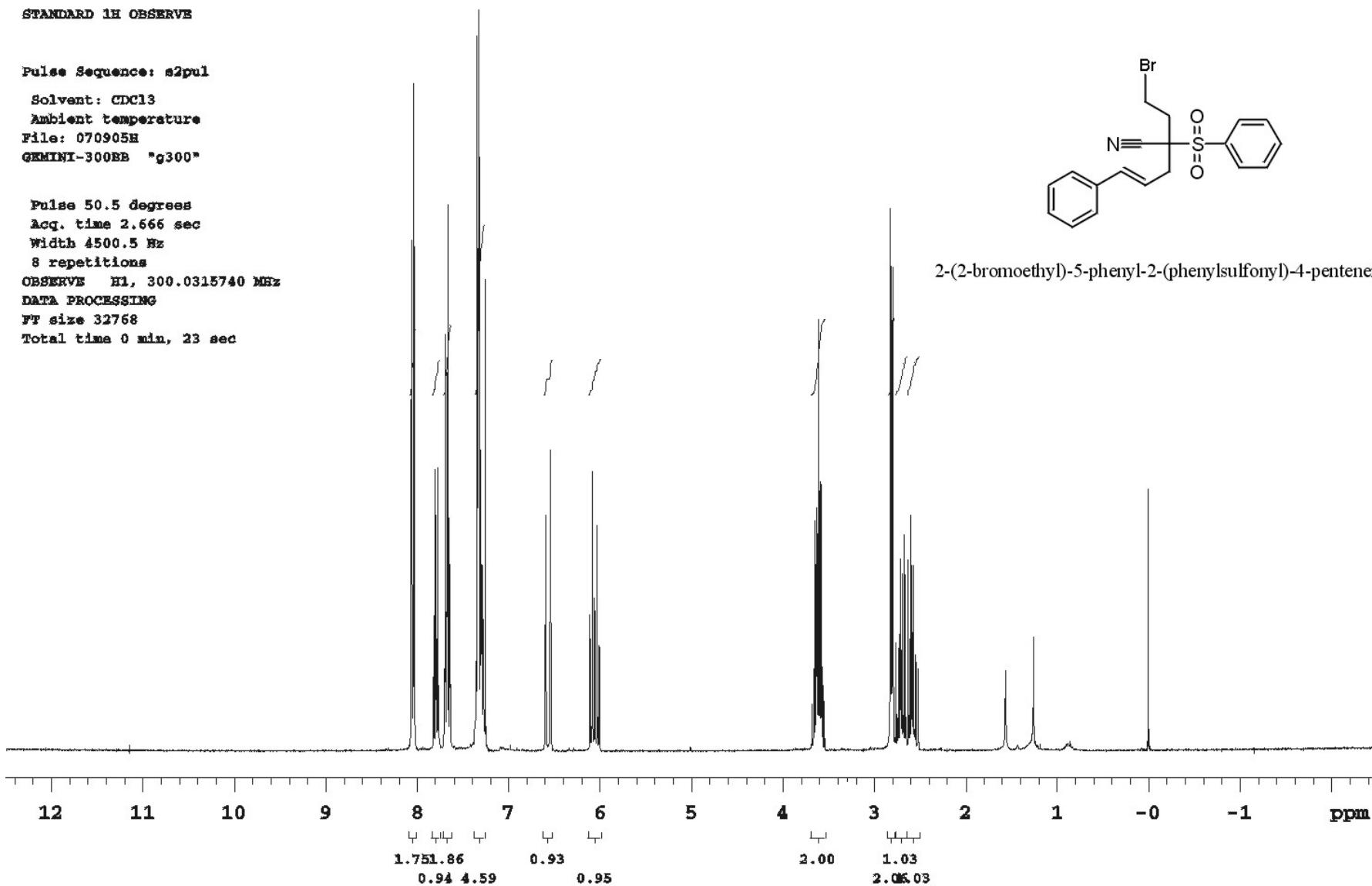
DATA PROCESSING

PP size 32768

Total time 0 min, 23 sec



2-(2-bromoethyl)-5-phenyl-2-(phenylsulfonyl)-4-pentenenitrile



¹³C RESOLUTION
DECOUPLED DICKANE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: 070905C

GEMINI-300BB "g300"

Relax. delay 1.500 sec

Pulse 60.0 degrees

Acq. time 0.750 sec

Width 20000.0 Hz

160 repetitions

OBSERVE C13, 75.4429723 MHz

DECOPLE H1, 300.0325732 MHz

Power 43 dB

on during acquisition

off during delay

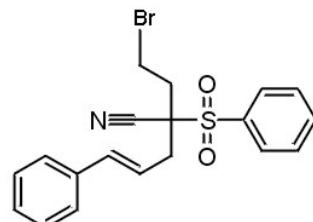
WALTZ-16 modulated

DATA PROCESSING

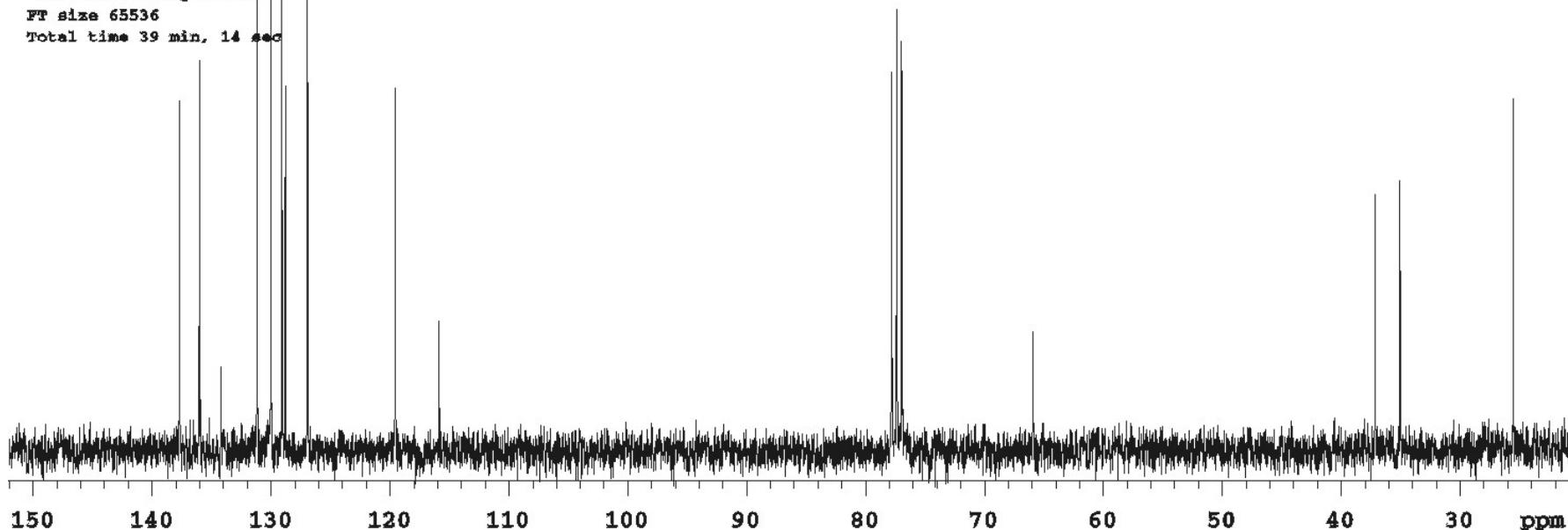
Line broadening 1.0 Hz

FT size 65536

Total time 39 min, 14 sec



2-(2-bromoethyl)-5-phenyl-2-(phenylsulfonyl)-4-pentenenitrile



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: 190905H

GEMINI-300BB "g300"

Pulse 50.5 degrees

Acq. time 2.666 sec

Width 4500.5 Hz

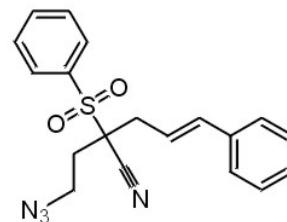
8 repetitions

OBSERVE H1, 300.0315752 MHz

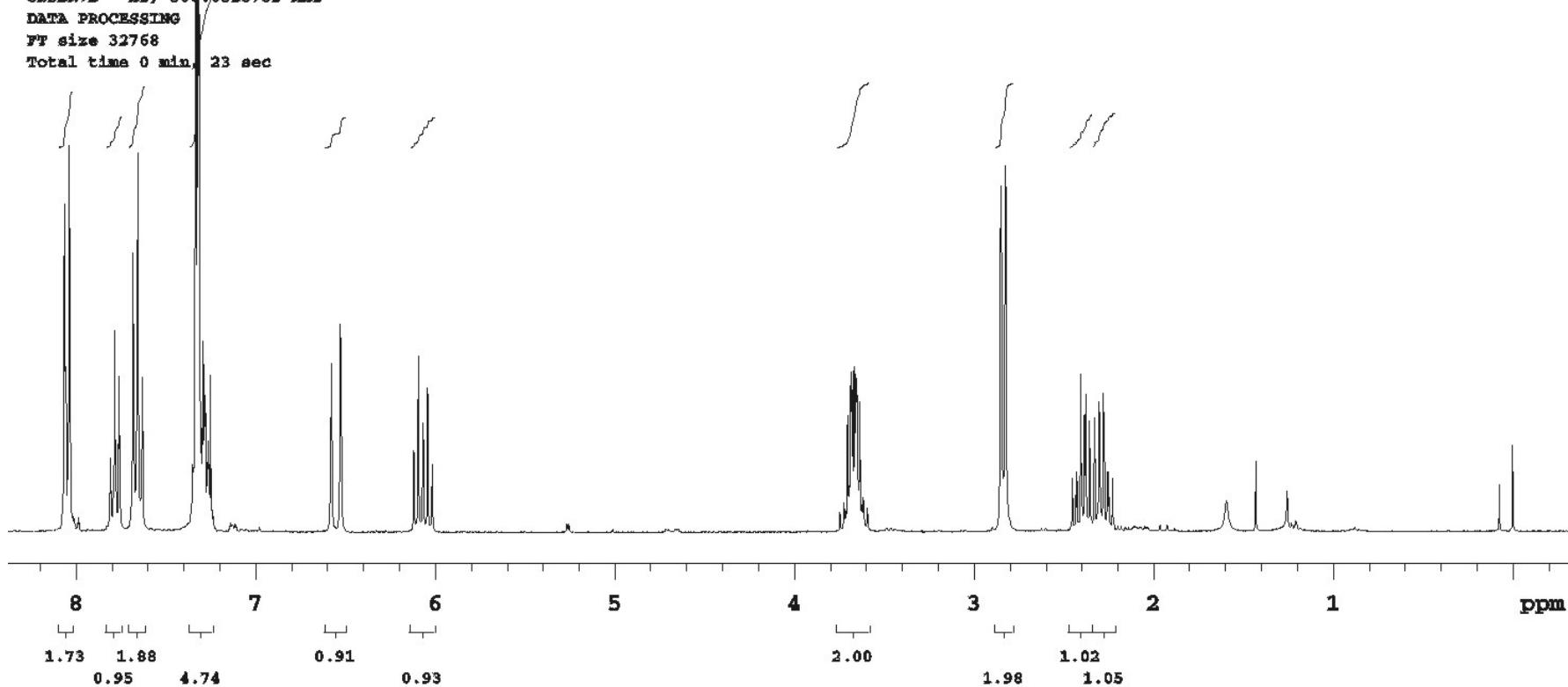
DATA PROCESSING

PP size 32768

Total time 0 min, 23 sec



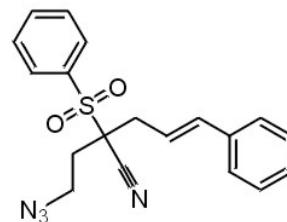
2-(2-Azidoethyl)-5-phenyl-2-(phenylsulfonyl)-4-pentenenitrile (3e)



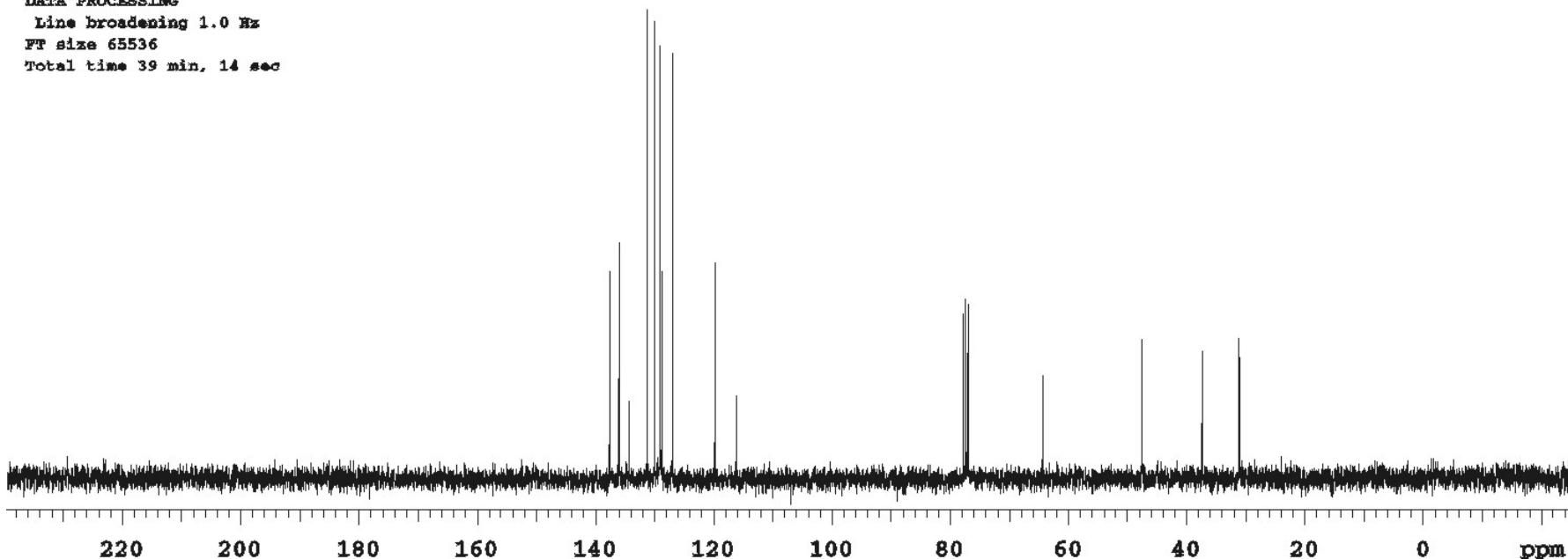
¹³C RESOLUTION
DECOUPLED DICHEM

Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: 190905C
GEMINI-300BB "g300"

Relax. delay 1.500 sec
Pulse 60.0 degrees
Acq. time 0.750 sec
Width 20000.0 Hz
96 repetitions
OBSERVE C13, 75.4429723 MHz
DECOUPLE H1, 300.0325732 MHz
Power 43 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 39 min, 14 sec



2-(2-Azidoethyl)-5-phenyl-2-(phenylsulfonyl)-4-pentenenitrile (3e)



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: 190106_R67_1h

GEMINI-300BB "g300"

Relax. delay 2.000 sec

Pulse 50.5 degrees

Acq. time 2.666 sec

Width 4500.5 Hz

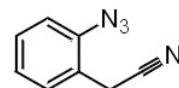
8 repetitions

OBSERVE H1, 300.0315720 MHz

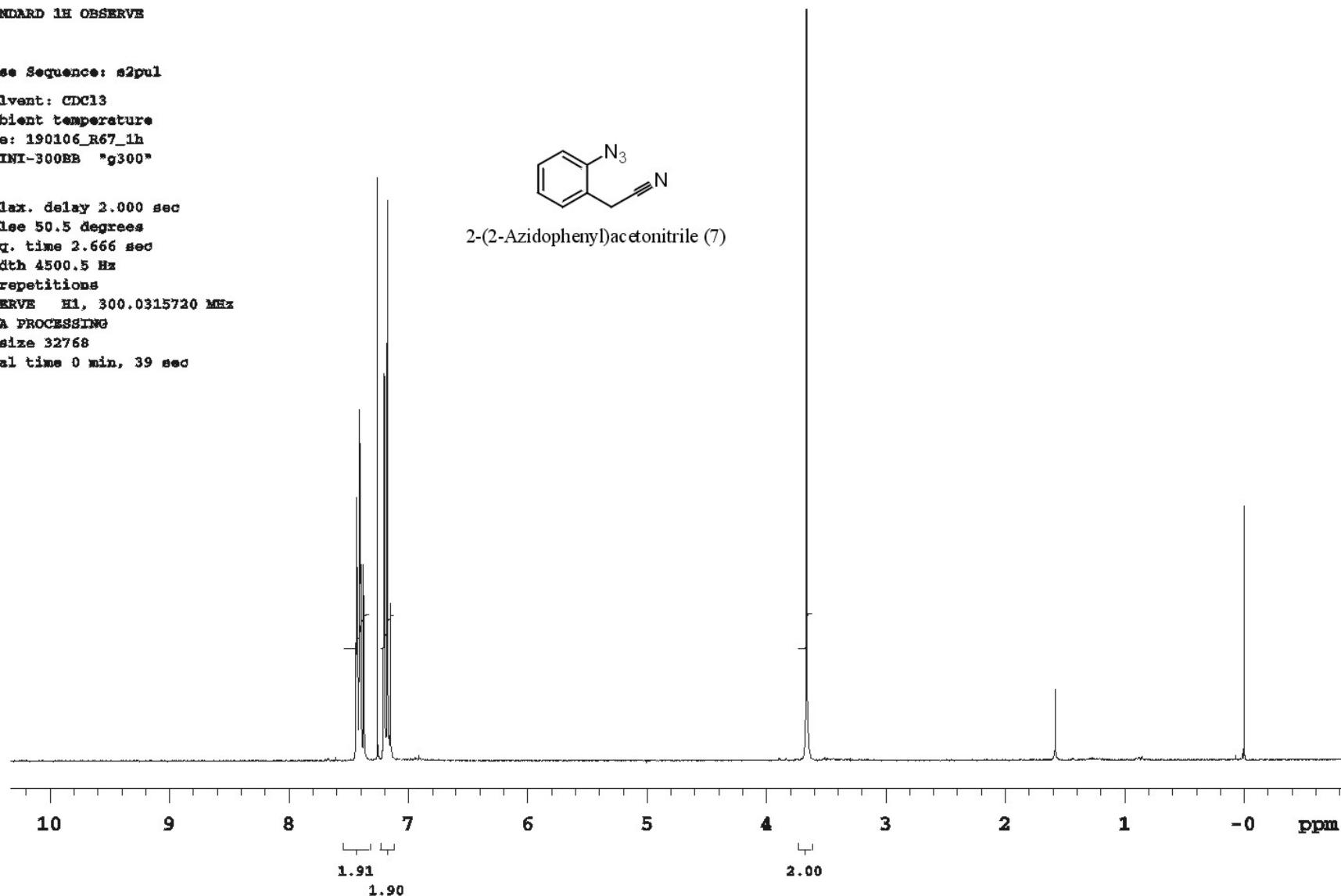
DATA PROCESSING

FT size 32768

Total time 0 min, 39 sec



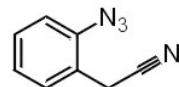
2-(2-Azidophenyl)acetonitrile (7)



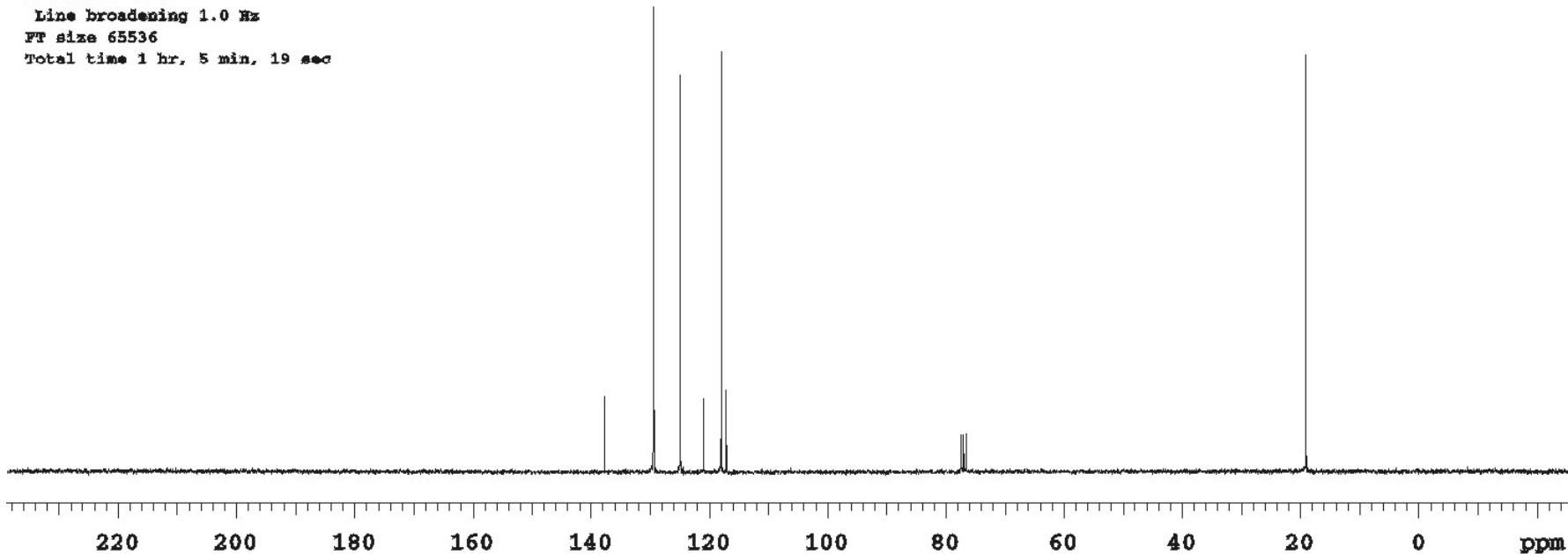
¹³C RESOLUTION
DECOUPLED DICHEM

Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
File: 190106_R67_13C
GEMINI-300BB "g300"

Relax. delay 3.000 sec
Pulse 56.9 degrees
Acq. time 0.750 sec
Width 20000.0 Hz
64 repetitions
OBSERVE C13, 75.4430272 MHz
DECOUPLE H1, 300.0325732 MHz
Power 43 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 5 min, 19 sec



2-(2-Azidophenyl)acetonitrile (7)



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: 310305_pMeONH2

GEMINI-300BB "g300"

Pulse 50.5 degrees

Acq. time 2.666 sec

Width 4500.5 Hz

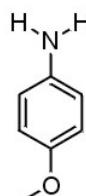
8 repetitions

OBSERVE H1, 300.0315742 MHz

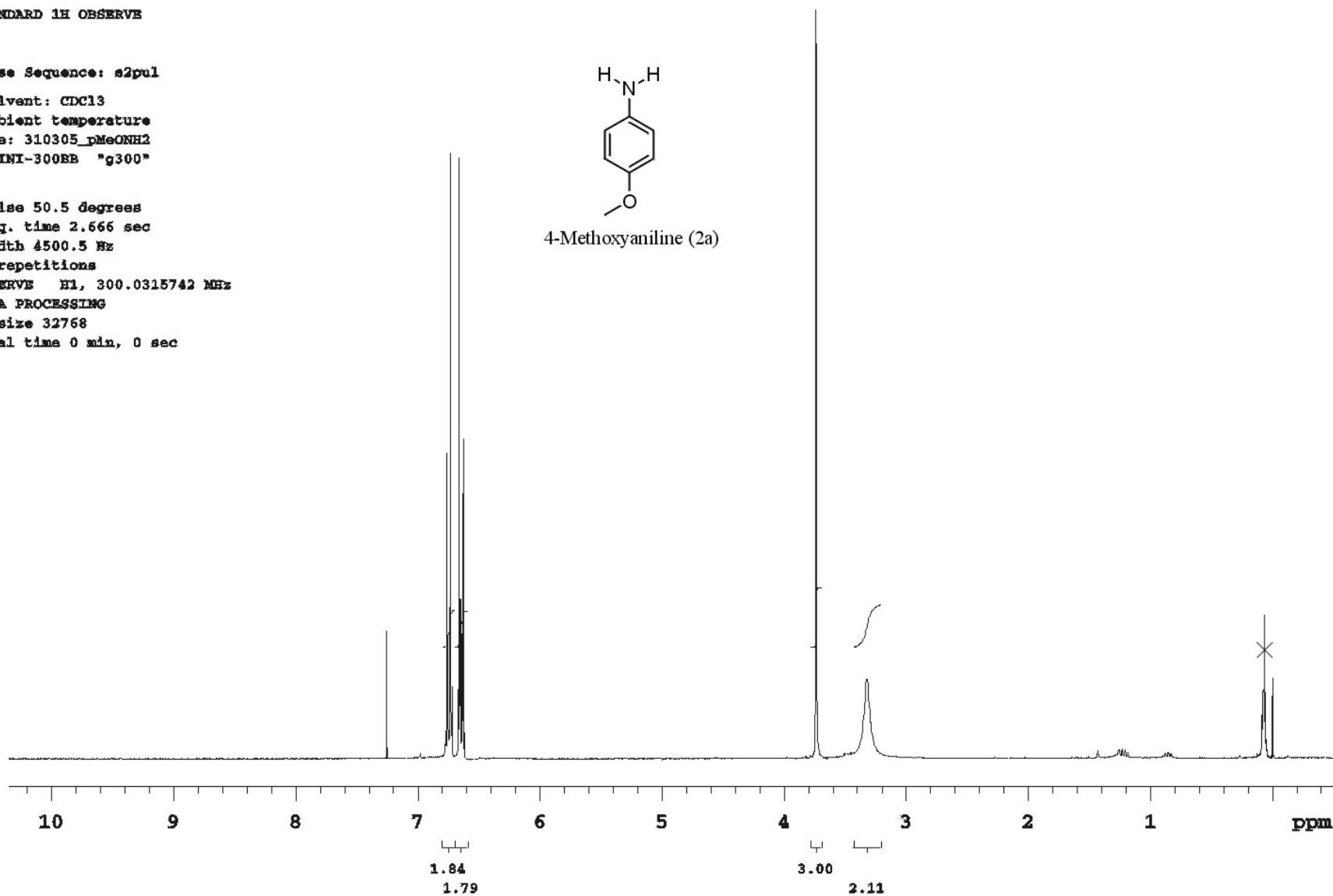
DATA PROCESSING

PP size 32768

Total time 0 min, 0 sec



4-Methoxyaniline (2a)



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 25.0 C / 298.1 K

File: 23mar06_1H_4CN-Ph-NH2

Mercury-400BB "m400"

Pulse 45.0 degrees

Acq. time 2.731 sec

Width 5998.8 Hz

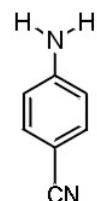
8 repetitions

OBSERVE H1, 399.9245716 MHz

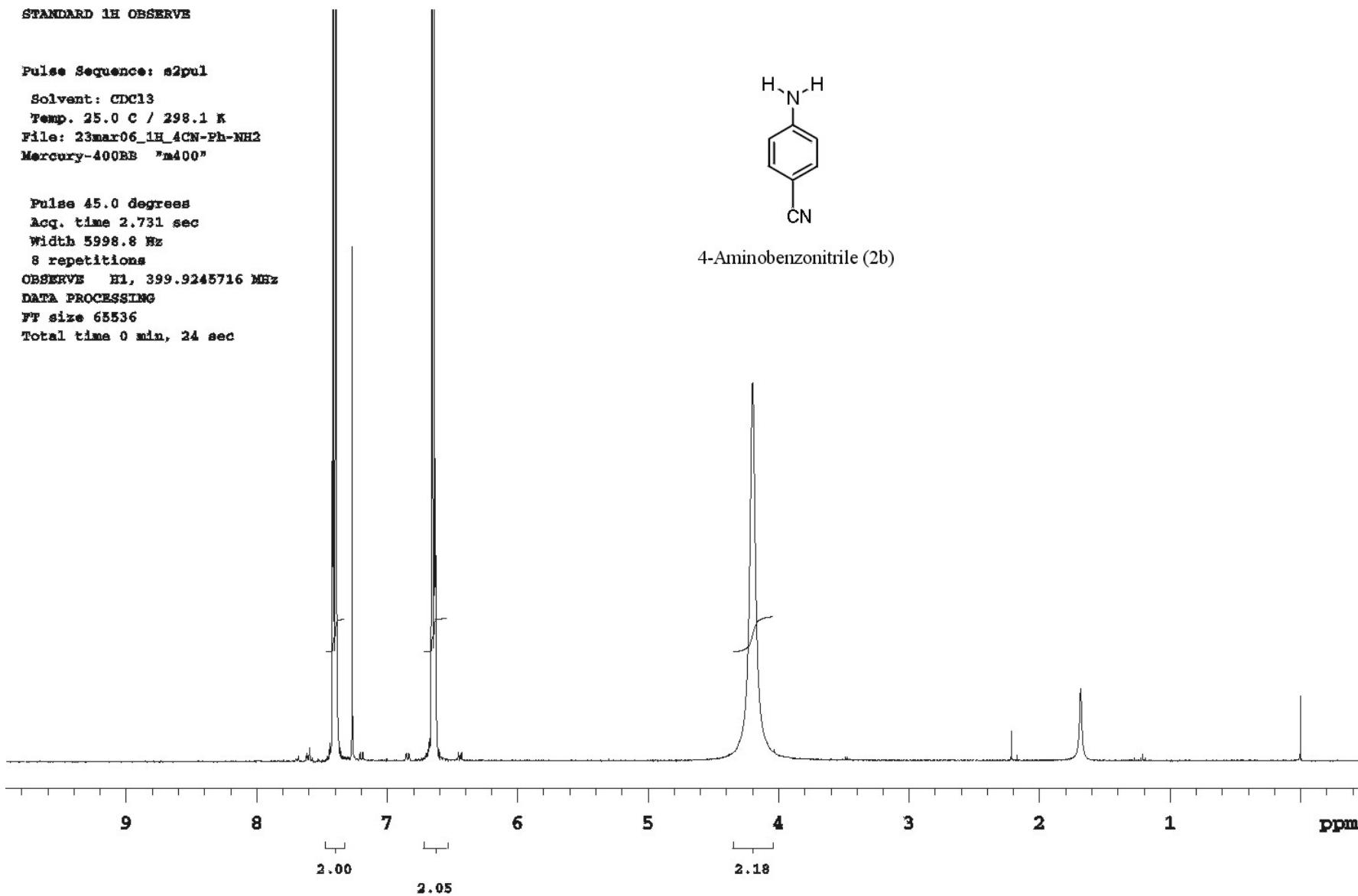
DATA PROCESSING

PP size 65536

Total time 0 min, 24 sec



4-Aminobenzonitrile (2b)



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: 100205_pCLPBMH2_dopocolonna.

GEMINI-300BB "g300"

Pulse 50.5 degrees

Acq. time 2.666 sec

Width 4500.5 Hz

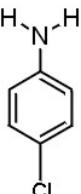
8 repetitions

OBSERVE H1, 300.0315764 MHz

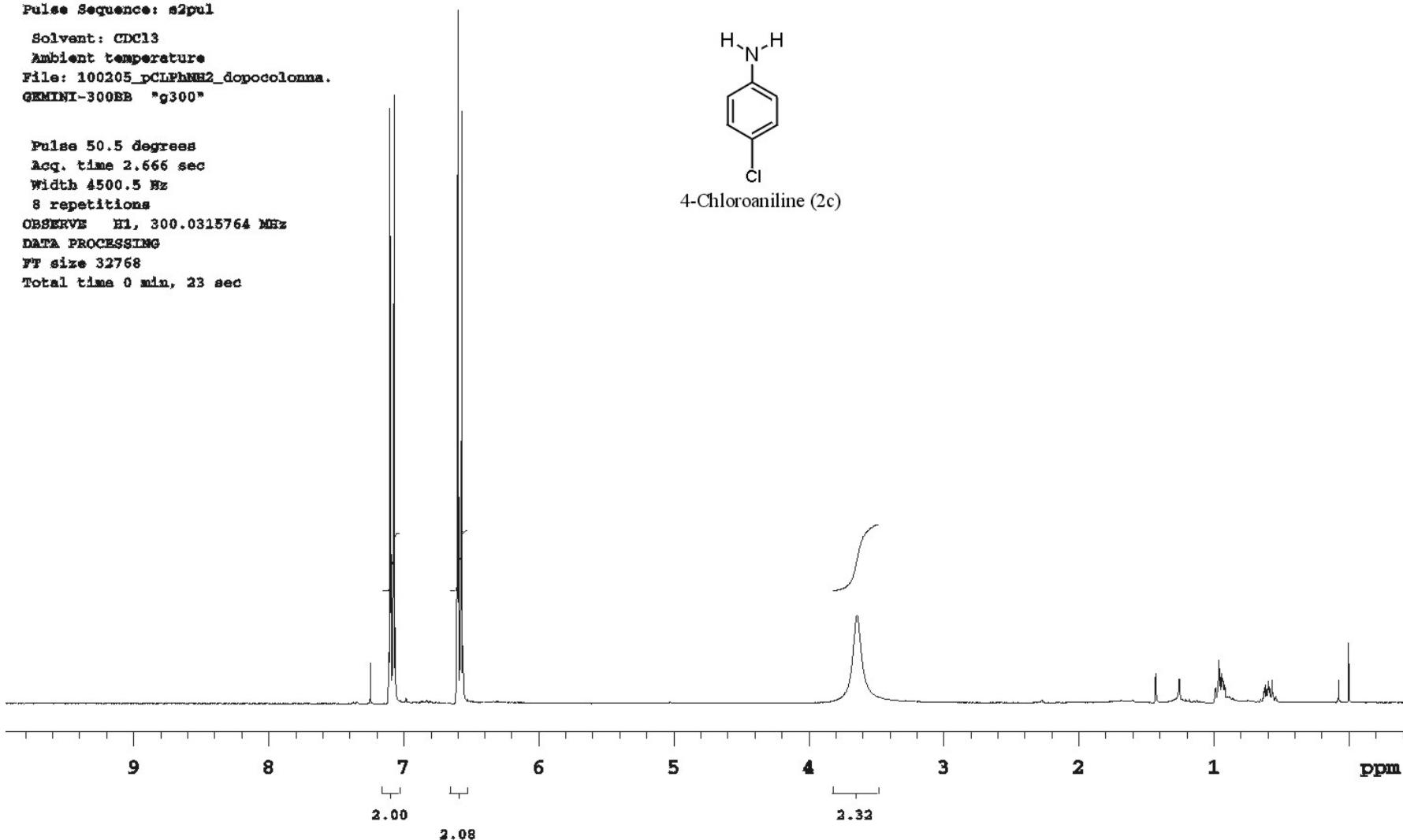
DATA PROCESSING

PP size 32768

Total time 0 min, 23 sec



4-Chloroaniline (2c)



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 25.0 C / 298.1 K

File: PINE2

Mercury-400BB "m400"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 2.731 sec

Width 5998.8 Hz

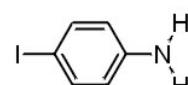
8 repetitions

OBSERVE H1, 399.9245809 MHz

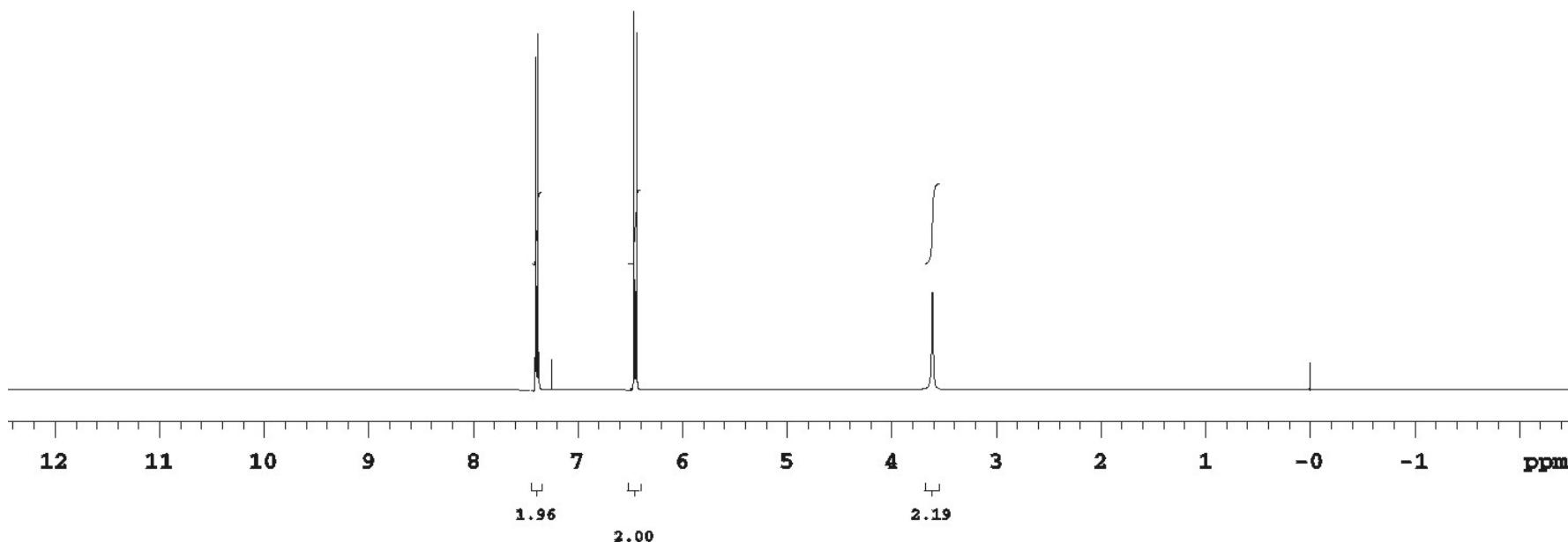
DATA PROCESSING

FT size 65536

Total time 0 min, 32 sec



4-Iodoaniline (2d)



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 25.0 C / 298.1 K

File: pCarbometossi_1h

Mercury-400BB "m400"

Pulse 45.0 degrees

Acq. time 2.731 sec

Width 5998.8 Hz

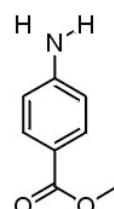
8 repetitions

OBSERVE H1, 399.9245745 MHz

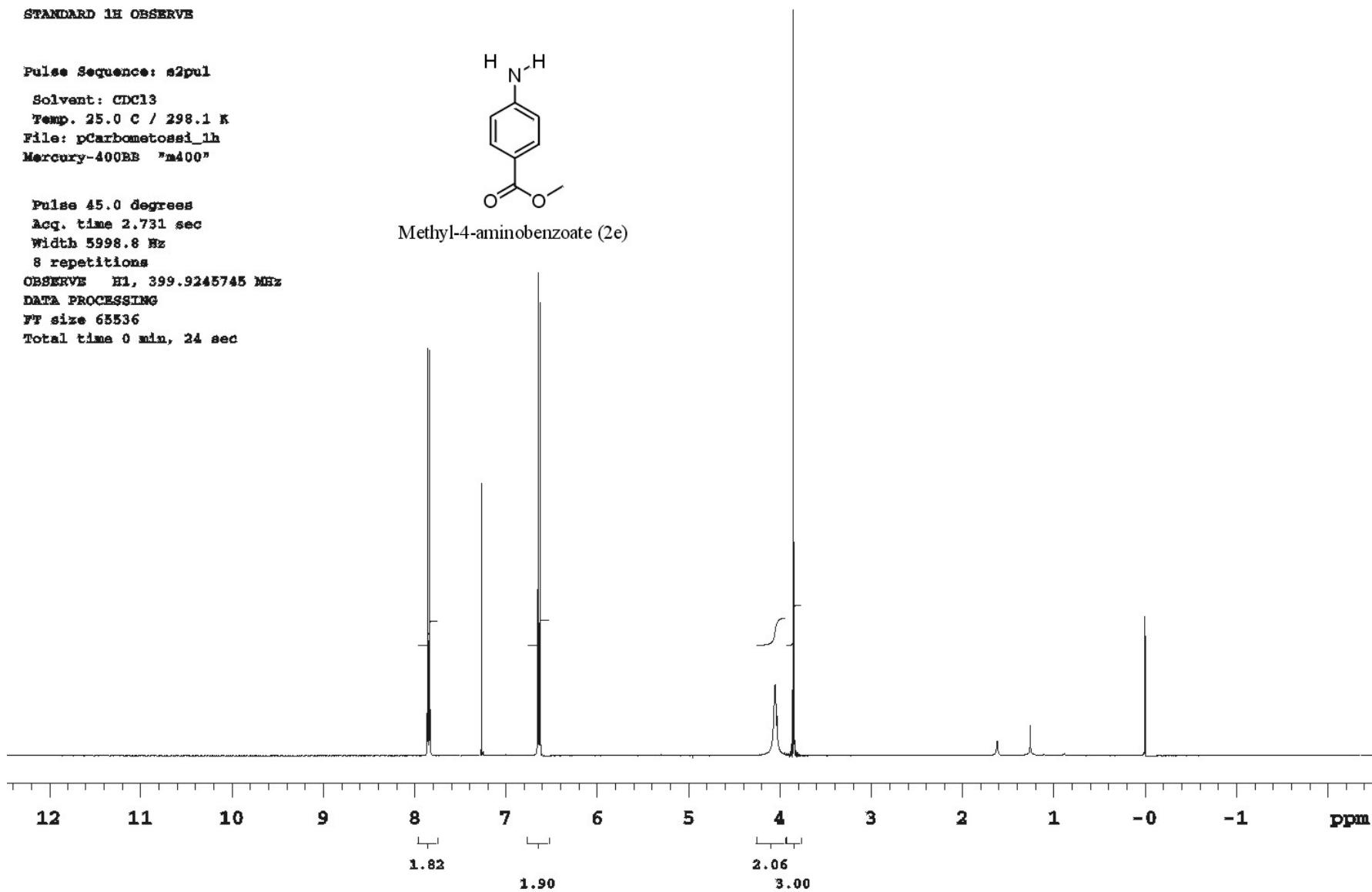
DATA PROCESSING

PP size 65536

Total time 0 min, 24 sec



Methyl-4-aminobenzoate (2e)



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 25.0 C / 298.1 K

File: pNO2NH2_1h

Mercury-400BB "m400"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 2.731 sec

Width 5998.8 Hz

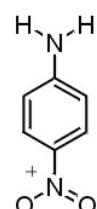
8 repetitions

OBSERVE H1, 399.9245740 MHz

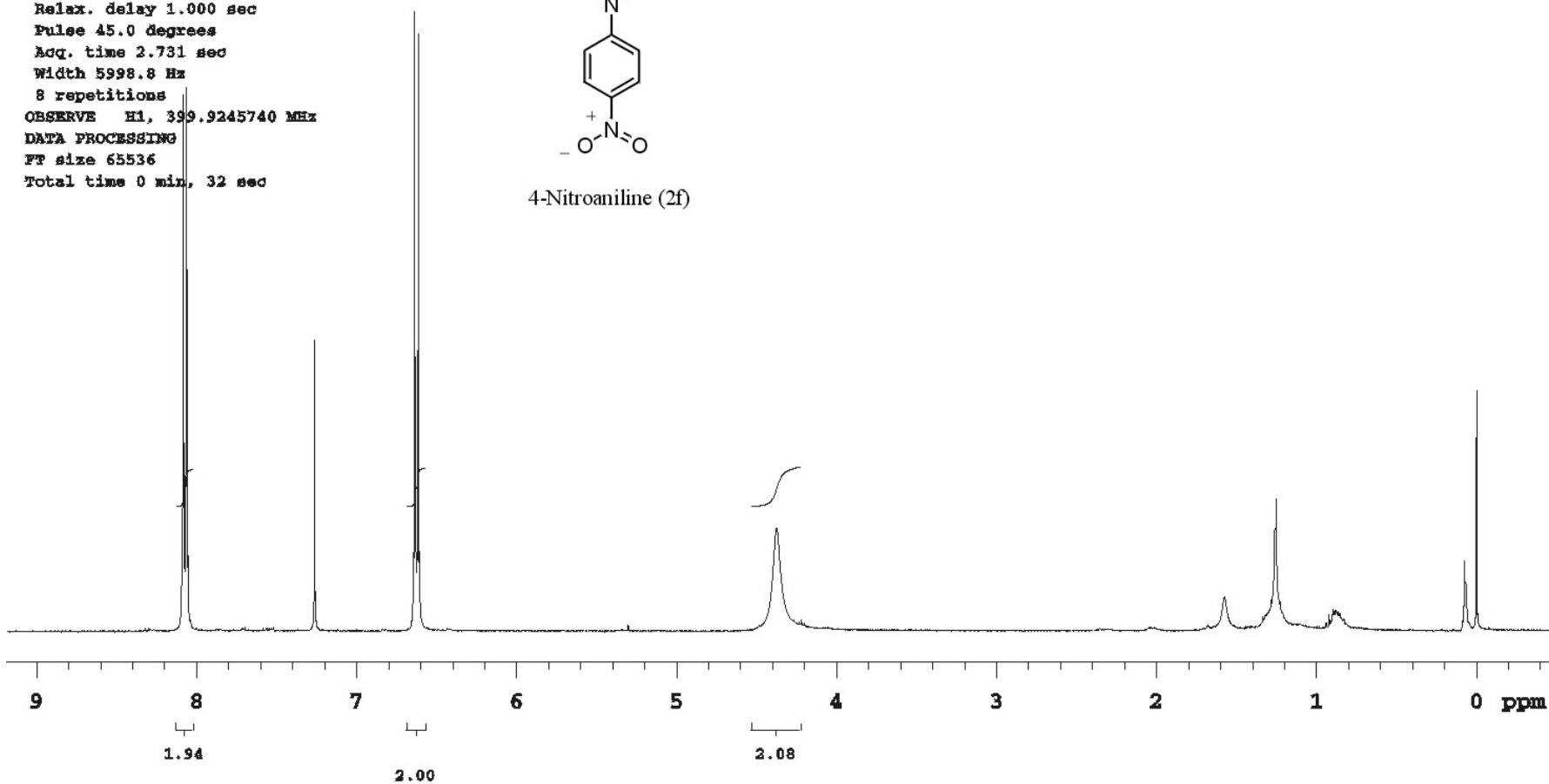
DATA PROCESSING

FT size 65536

Total time 0 min, 32 sec



4-Nitroaniline (2f)



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 25.0 C / 298.1 K

File: 150605_NaftN1_OH-

Mercury-400BB "m400"

Relax. delay 2.000 sec

Pulse 45.0 degrees

Acq. time 2.733 sec

Width 5995.2 Hz

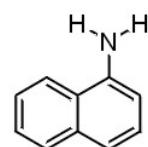
16 repetitions

OBSERVE H1, 399.9245955 MHz

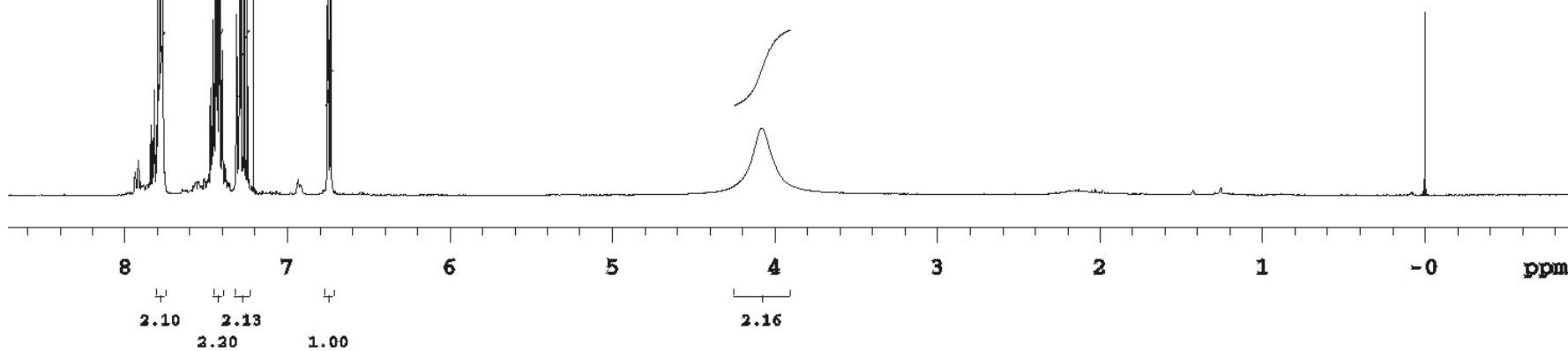
DATA PROCESSING

FT size 65536

Total time 1 min, 18 sec



1-naphthalenamine (2g)



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 25.0 C / 298.1 K

File: pAcN3-20_sacracCOH-
Mercury-400BB "m400"

Relax. delay 2.000 sec

Pulse 45.0 degrees

Acq. time 2.733 sec

Width 5995.2 Hz

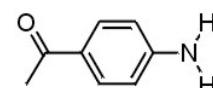
16 repetitions

OBSERVE H1, 399.9245720 MHz

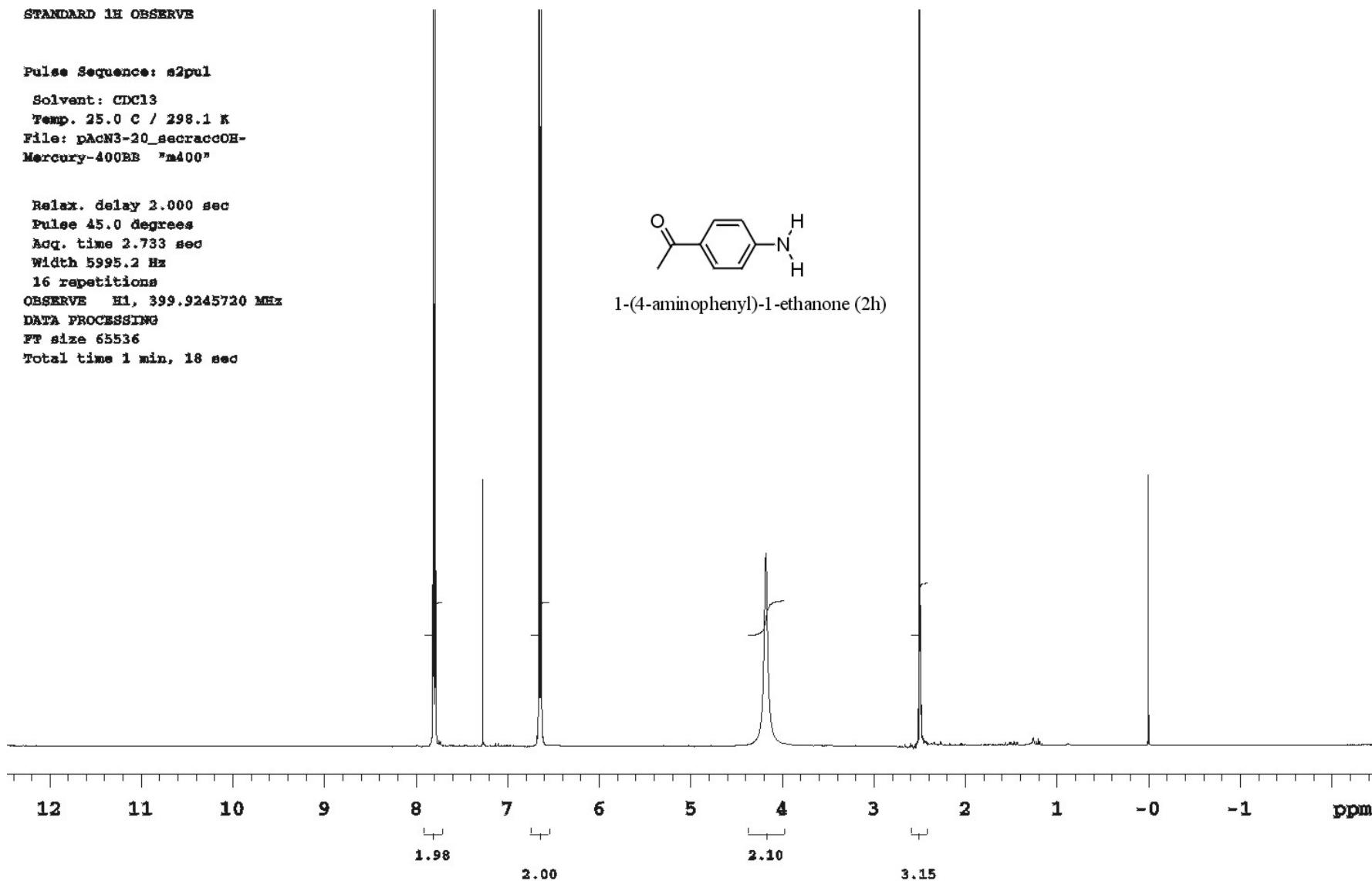
DATA PROCESSING

FT size 65536

Total time 1 min, 18 sec



1-(4-aminophenyl)-1-ethanone (2h)



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 25.0 C / 298.1 K

File: SO2NH2_1h

Mercury-400BB "m400"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 2.731 sec

Width 5998.8 Hz

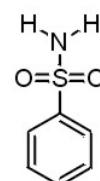
8 repetitions

OBSERVE H1, 399.9245745 MHz

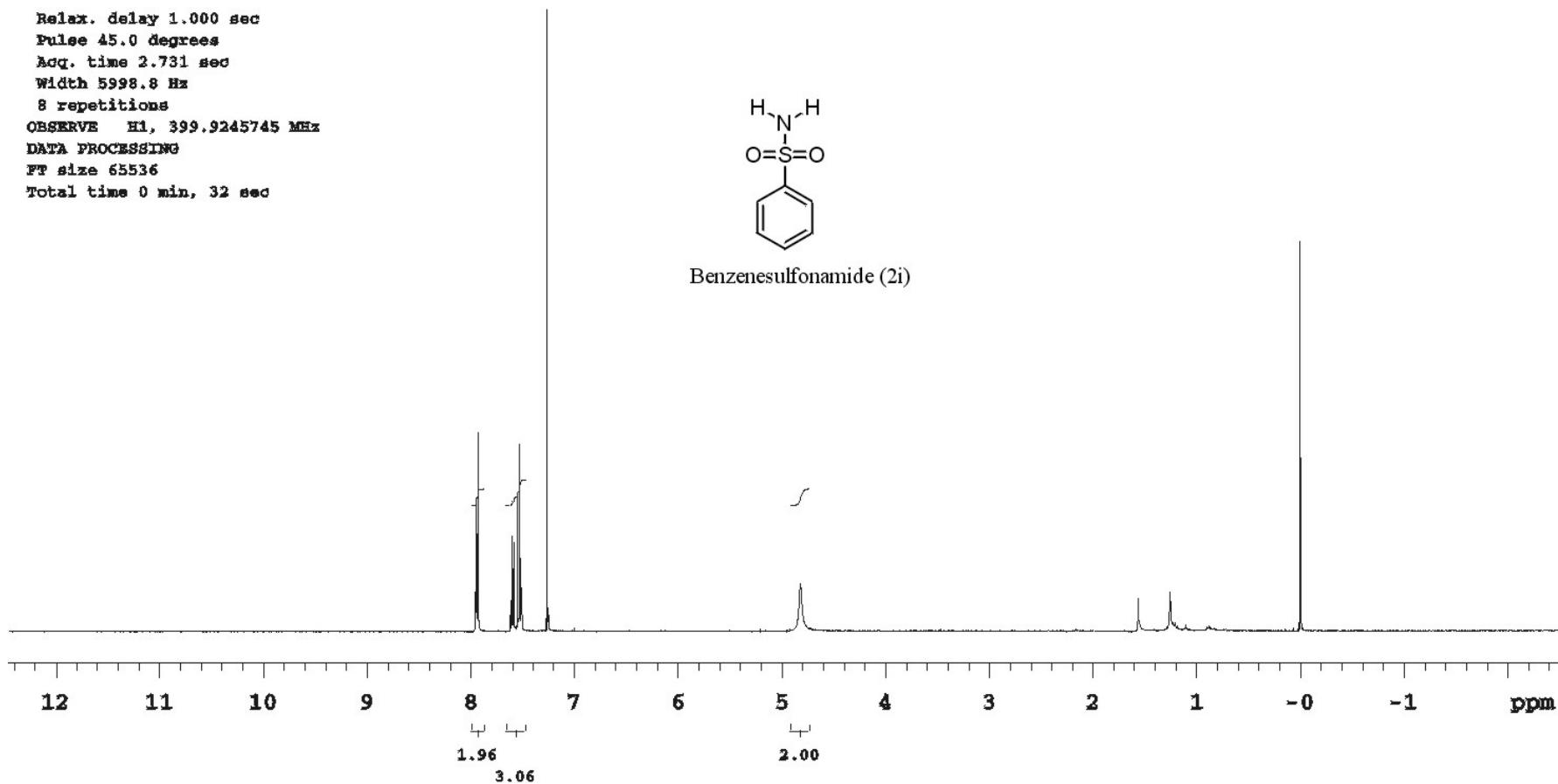
DATA PROCESSING

FT size 65536

Total time 0 min, 32 sec



Benzenesulfonamide (2i)



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 25.0 C / 298.1 K

File: 200506_R5_benzamide

Mercury-400BB "m400"

Relax. delay 2.000 sec

Pulse 45.0 degrees

Acq. time 2.733 sec

Width 5995.2 Hz

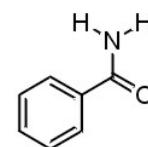
16 repetitions

OBSERVE H1, 399.9245726 MHz

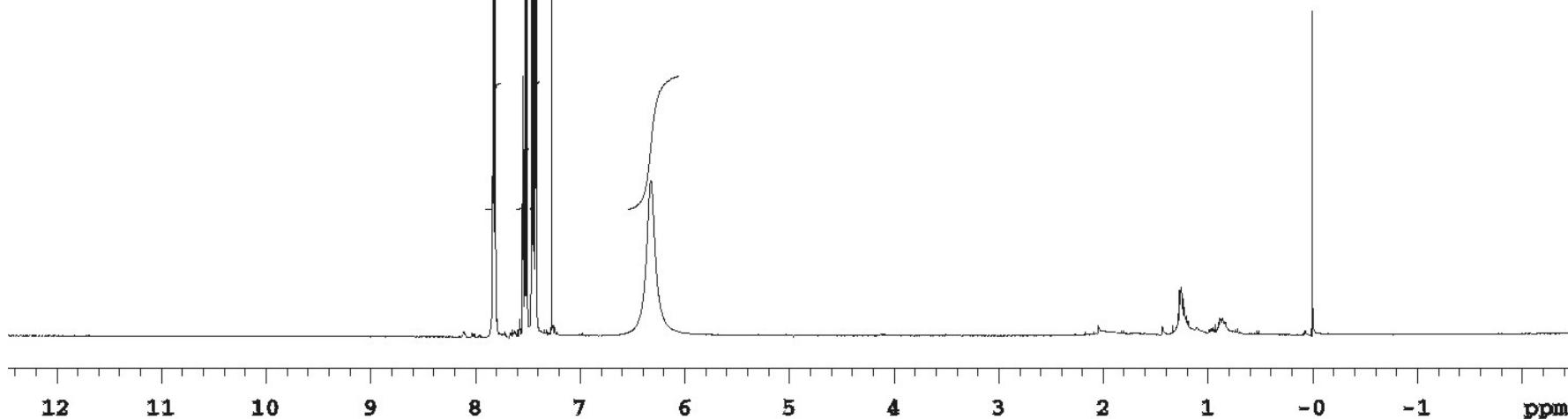
DATA PROCESSING

FT size 65536

Total time 1 min, 18 sec



Benzamide (2j)



STANDARD 1H OBSERVE

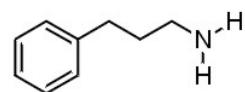
Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: 040205_1h_propylammina

GEMINI-300BB "g300"



3-Phenyl-1-propanamine (2k)

Pulse 50.5 degrees

Acq. time 2.666 sec

Width 4500.5 Hz

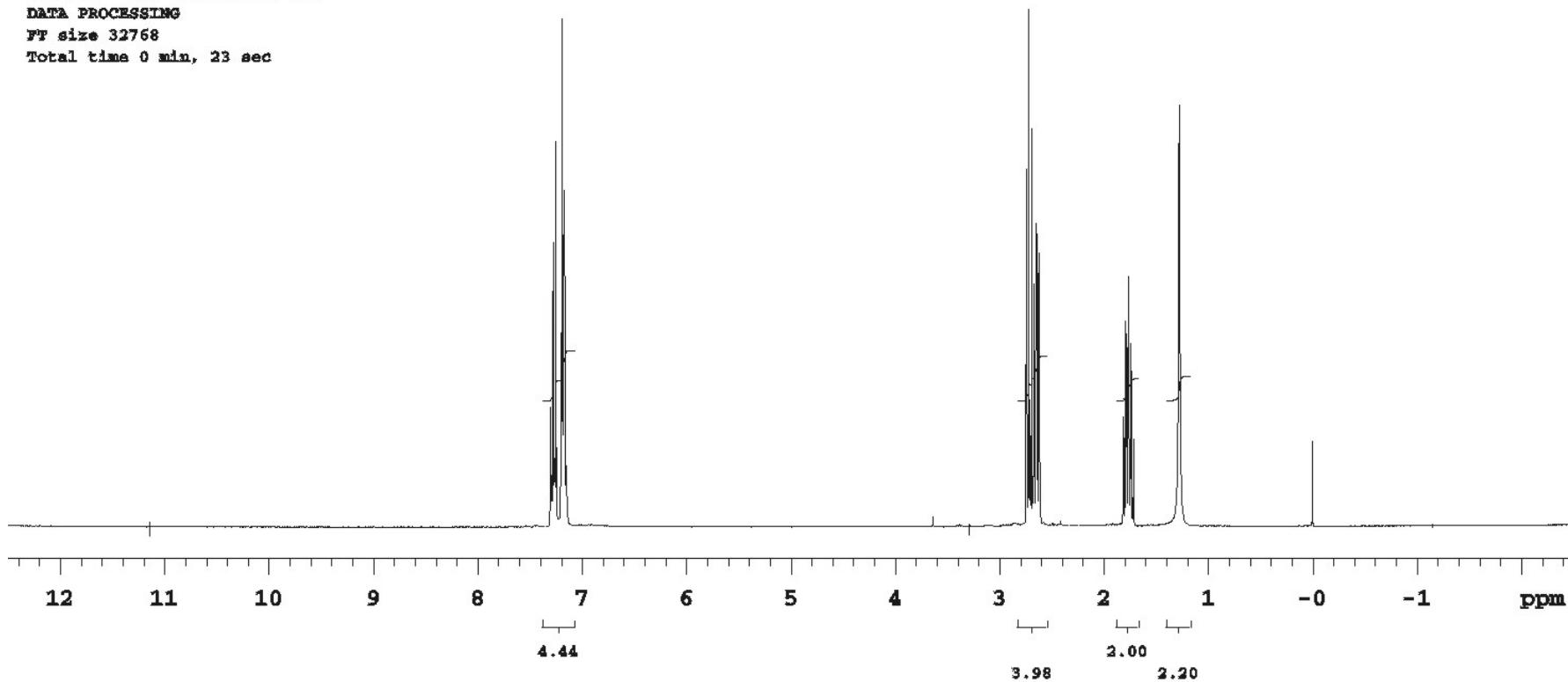
8 repetitions

OBSERVE H1, 300.0315745 MHz

DATA PROCESSING

PP size 32768

Total time 0 min, 23 sec



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

File: 240205_phethylamine_rif_1h

GEMINI-300BB "g300"

Pulse 25.3 degrees

Acq. time 2.666 sec

Width 4500.5 Hz

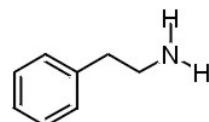
8 repetitions

OBSERVE H1, 300.0315736 MHz

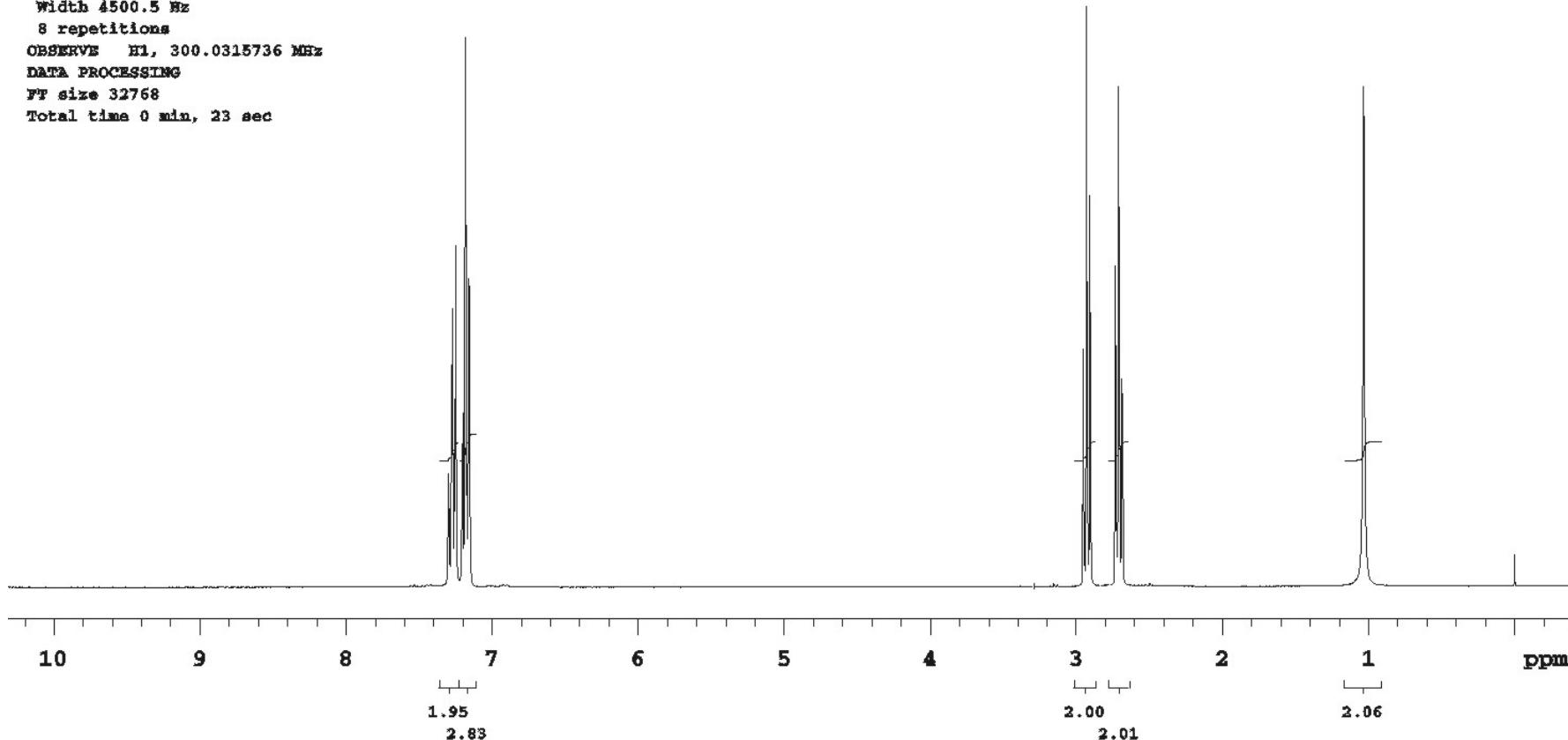
DATA PROCESSING

PP size 32768

Total time 0 min, 23 sec



2-Phenyl-1-ethanamine (2l)



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 25.0 C / 298.1 K

Mercury-400BB "m400"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 2.731 sec

Width 5998.8 Hz

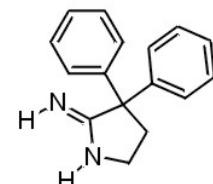
16 repetitions

OBSERVE H1, 399.9245527 MHz

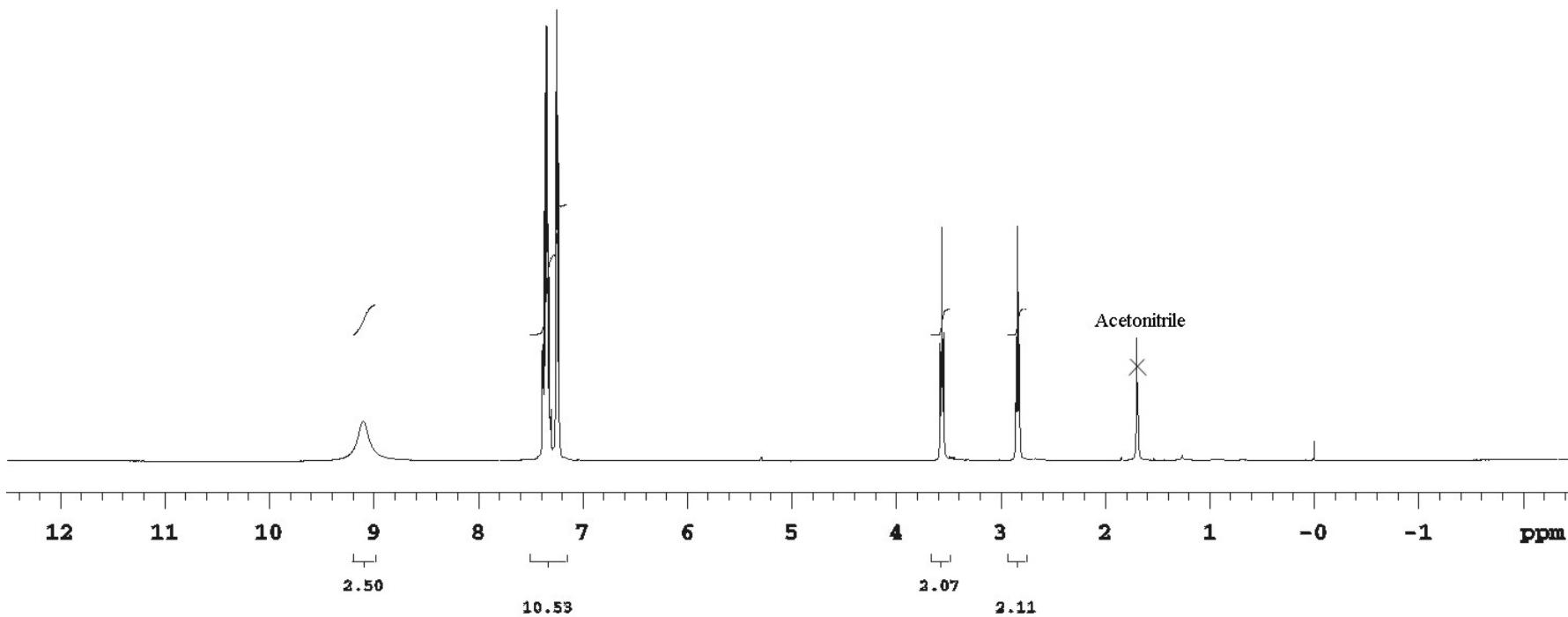
DATA PROCESSING

PP size 65536

Total time 1 min, 2 sec



3,3-Diphenyl-2-pyrrolidinimine (4a)



¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 25.0 C / 298.1 K
Mercury-400BB "m400"

Relax. delay 3.000 sec

Pulse 59.4 degrees

Acq. time 1.000 sec

Width 26525.2 Hz

32 repetitions

OBSERVE C13, 100.5611291 MHz

DECOUPLE H1, 399.9265569 MHz

Power 40 dB

continuously on

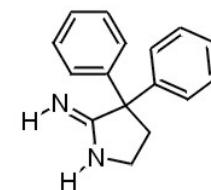
WALTZ-16 modulated

DATA PROCESSING

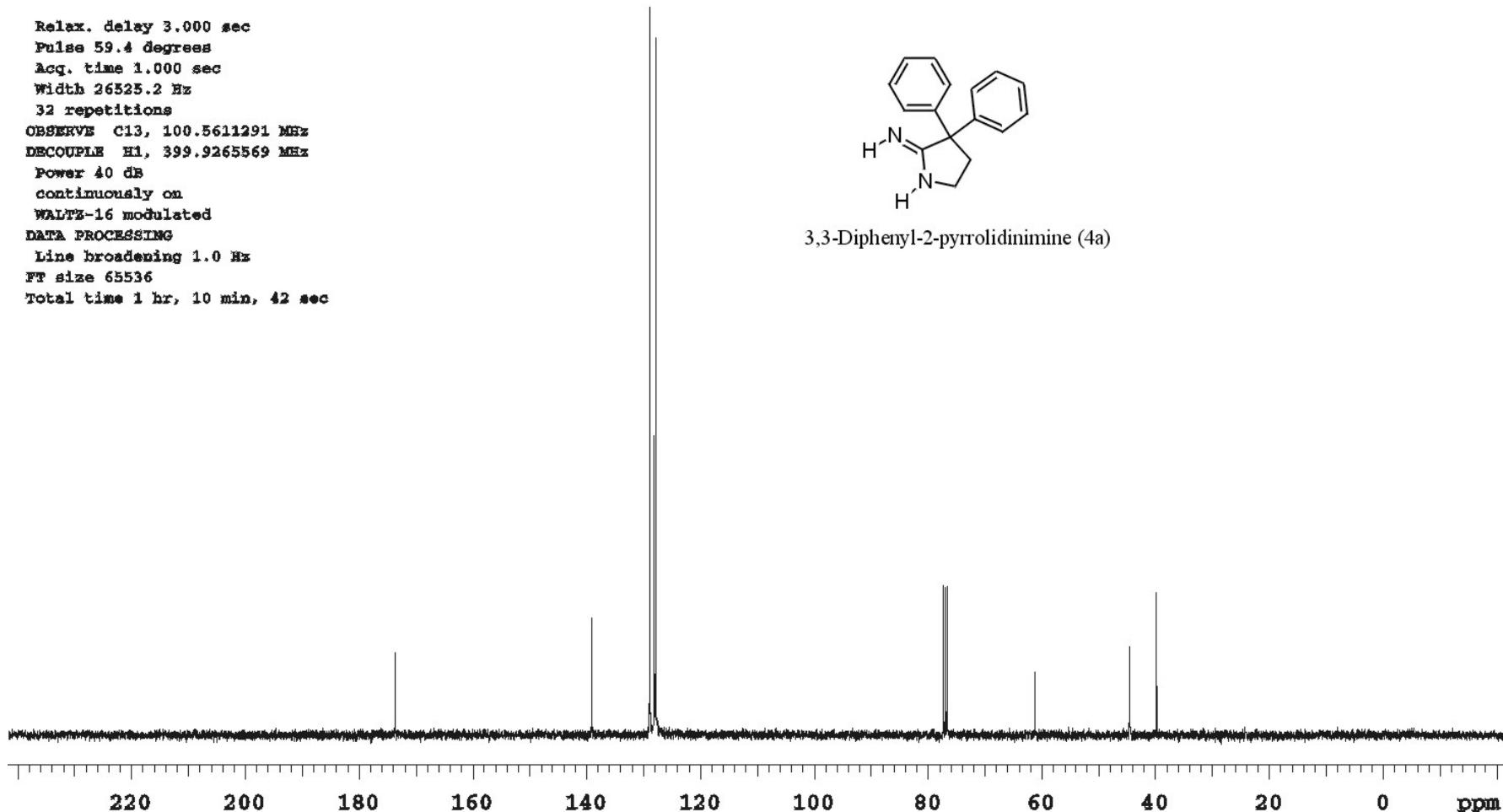
Line broadening 1.0 Hz

FT size 65536

Total time 1 hr, 10 min, 42 sec



3,3-Diphenyl-2-pyrrolidinimine (4a)



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 25.0 C / 298.1 K

Mercury-400BB "m400"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 2.731 sec

Width 5998.8 Hz

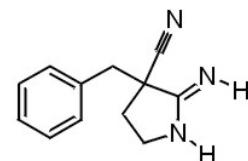
16 repetitions

OBSERVE H1, 399.9245732 MHz

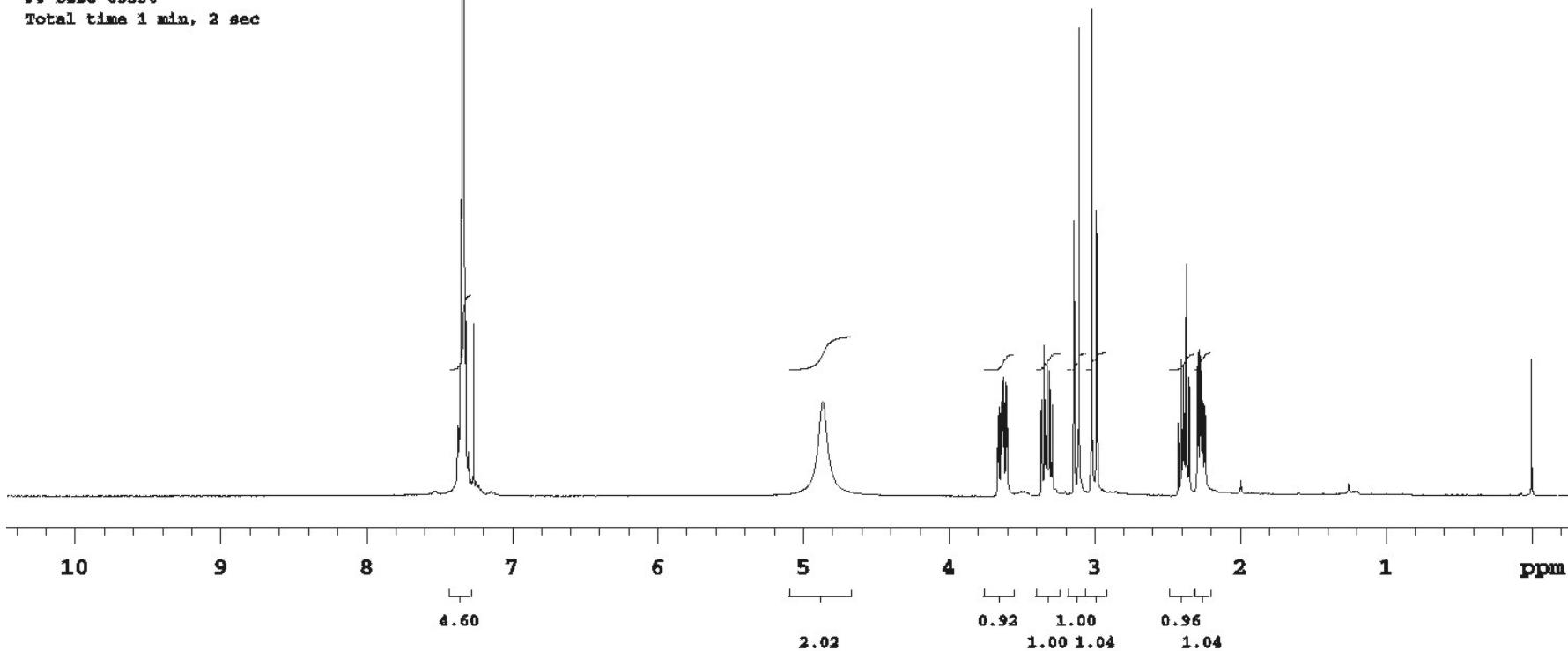
DATA PROCESSING

PP size 65536

Total time 1 min, 2 sec



3-Benzyl-2-imino-3-pyrrolidinecarbonitrile (4b)



¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 25.0 C / 298.1 K

Mercury-400BB "m400"

Relax. delay 3.000 sec

Pulse 59.4 degrees

Acq. time 1.000 sec

Width 26525.2 Hz

34 repetitions

OBSERVE C13, 100.5611178 MHz

DECOUPLE H1, 399.9265569 MHz

Power 40 dB

continuously on

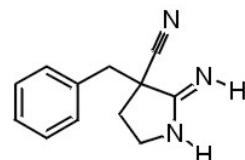
WALTZ-16 modulated

DATA PROCESSING

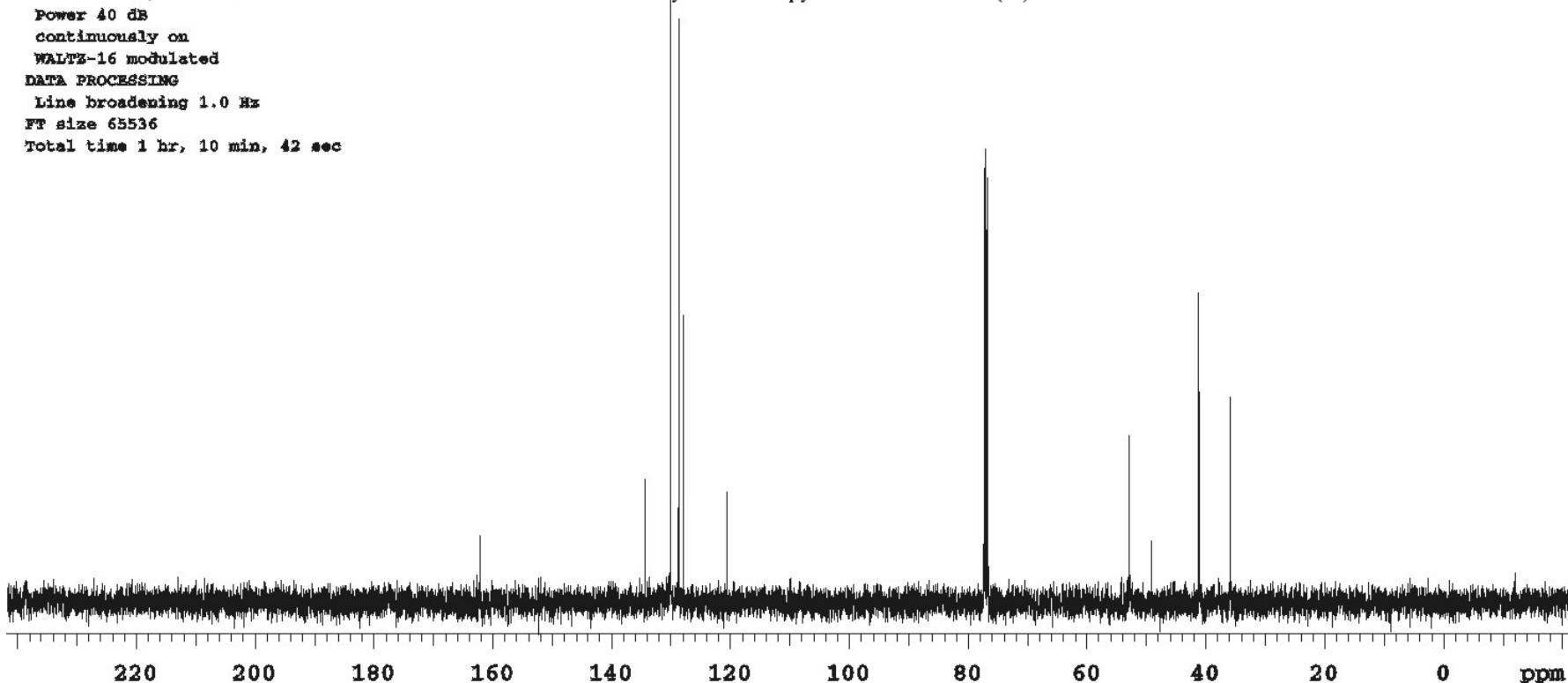
Line broadening 1.0 Hz

FT size 65536

Total time 1 hr, 10 min, 42 sec



3-Benzyl-2-imino-3-pyrrolidinecarbonitrile (4b)



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 25.0 C / 298.1 K

File: crotol_1h

Mercury-400BB "m400"

Relax. delay 2.000 sec

Pulse 45.0 degrees

Acq. time 2.731 sec

Width 5998.8 Hz

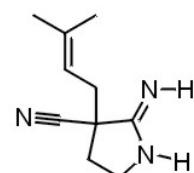
8 repetitions

OBSERVE H1, 399.9245663 MHz

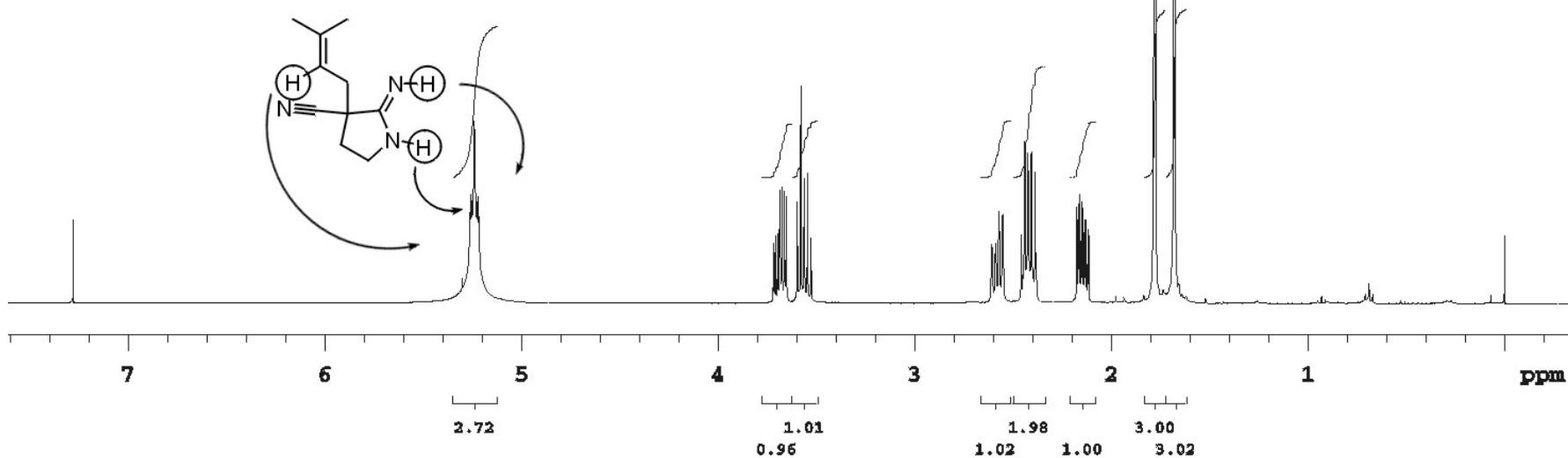
DATA PROCESSING

FT size 65536

Total time 0 min, 40 sec



2-Imino-3-(3-methyl-2-butenyl)-3-pyrrolidinecarbonitrile (4c)



¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 25.0 C / 298.1 K

File: crotol_13C

Mercury-400BB "m400"

Relax. delay 3.000 sec

Pulse 59.4 degrees

Acq. time 1.000 sec

Width 26525.2 Hz

50 repetitions

OBSERVE C13, 100.5611194 MHz

DECOUPLE H1, 399.9265569 MHz

Power 40 dB

continuously on

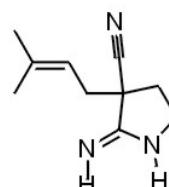
WALTZ-16 modulated

DATA PROCESSING

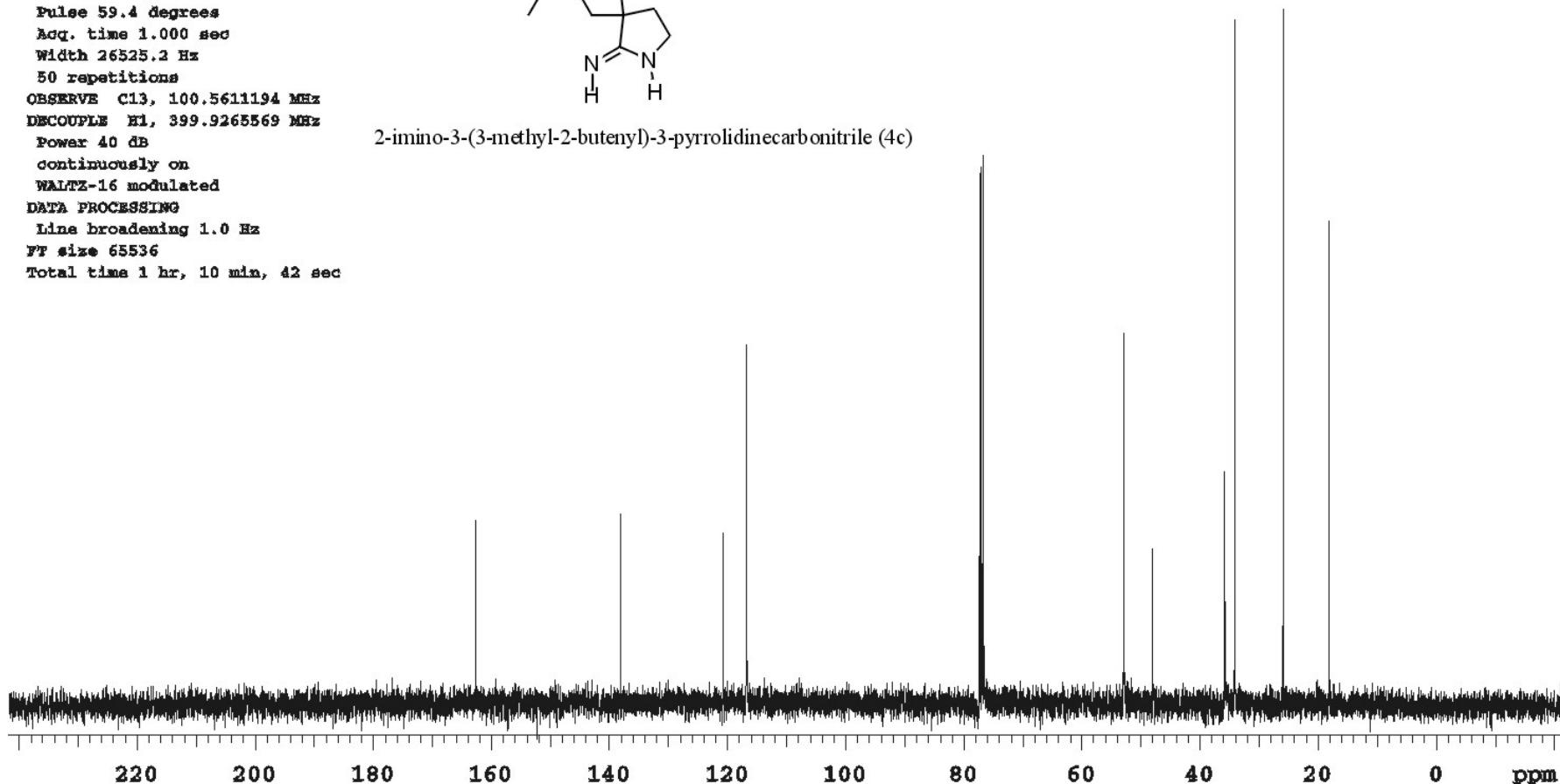
Line broadening 1.0 Hz

PT size 65536

Total time 1 hr, 10 min, 42 sec



2-imino-3-(3-methyl-2-butenyl)-3-pyrrolidinecarbonitrile (4c)



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 25.0 C / 298.1 K

Mercury-400BB "m400"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 2.731 sec

Width 5998.8 Hz

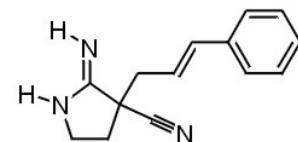
16 repetitions

OBSERVE H1, 399.9245751 MHz

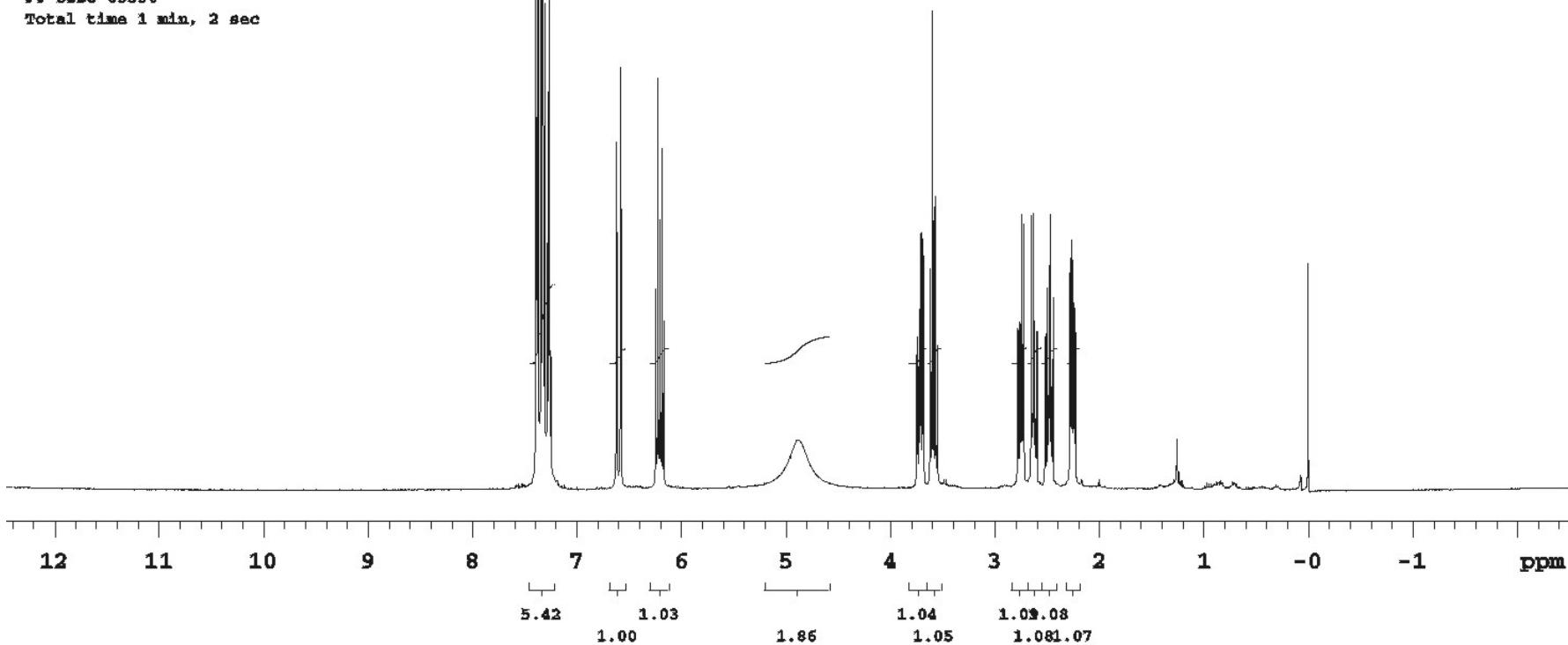
DATA PROCESSING

PP size 65536

Total time 1 min, 2 sec



2-Imino-3-(3-phenyl-2-propenyl)-3-pyrrolidinecarbonitrile (4d)



¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 25.0 C / 298.1 K

Mercury-400BB "m400"

Relax. delay 3.000 sec

Pulse 59.4 degrees

Acq. time 1.000 sec

Width 26525.2 Hz

37 repetitions

OBSERVE C13, 100.5611178 MHz

DECOUPLE H1, 399.9265569 MHz

Power 40 dB

continuously on

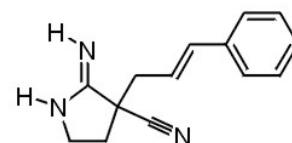
WALTZ-16 modulated

DATA PROCESSING

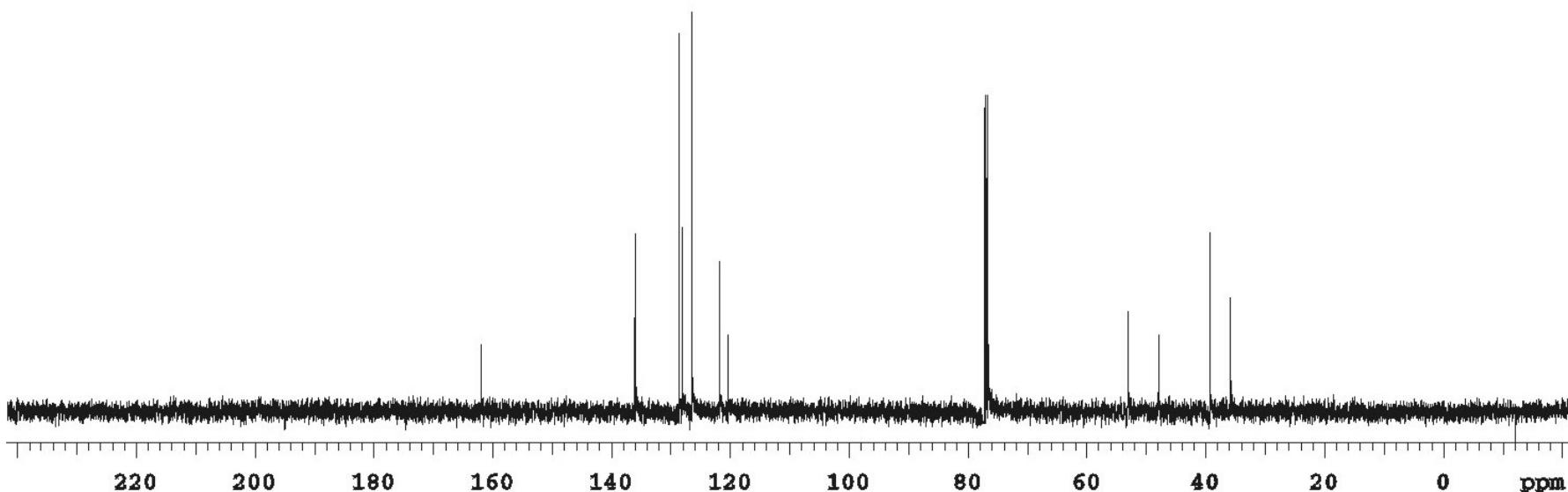
Line broadening 1.0 Hz

FT size 65536

Total time 1 hr, 10 min, 42 sec



2-Imino-3-(3-phenyl-2-propenyl)-3-pyrrolidinecarbonitrile (4d)

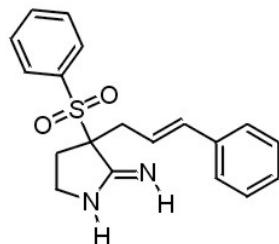


STANDARD 1H OBSERVE

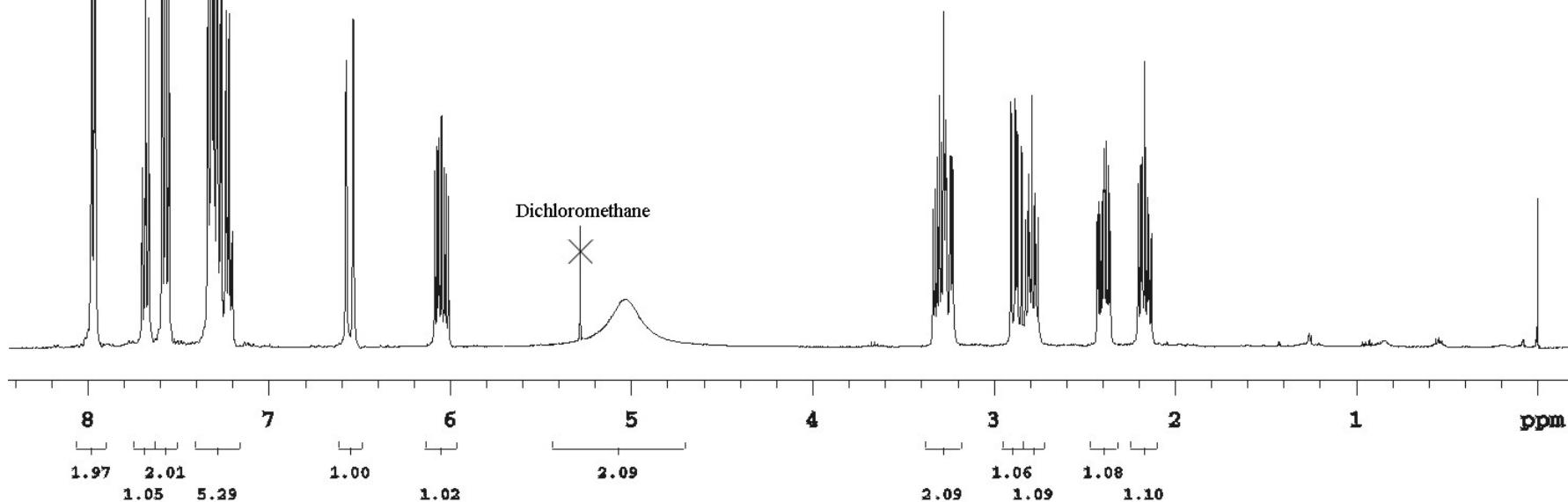
Pulse Sequence: s2pul
Solvent: CDCl₃
Temp. 25.0 C / 298.1 K
File: 011205_B50_runitipipt_1h
Mercury-400BB "m400"

Pulse 45.0 degrees
Acq. time 2.731 sec
Width 5998.8 Hz
16 repetitions
OBSERVE: H1, 399.9245739 MHz

DATA PROCESSING
PP size 65536
Total time 0 min, 46 sec



3-(3-Phenyl-2-propenyl)-3-(phenylsulfonyl)-2-pyrrolidinimine (4e)



¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 25.0 C / 298.1 K

File: 011205_R50_13C_pytriuniti

Mercury-400BB "m400"

Relax. delay 3.000 sec

Pulse 59.4 degrees

Acq. time 1.000 sec

Width 26525.2 Hz

112 repetitions

OBSERVE C13, 100.5611219 MHz

DECOUPLE H1, 399.9265569 MHz

Power 40 dB

continuously on

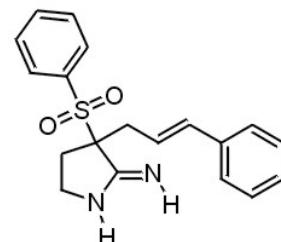
WALTZ-16 modulated

DATA PROCESSING

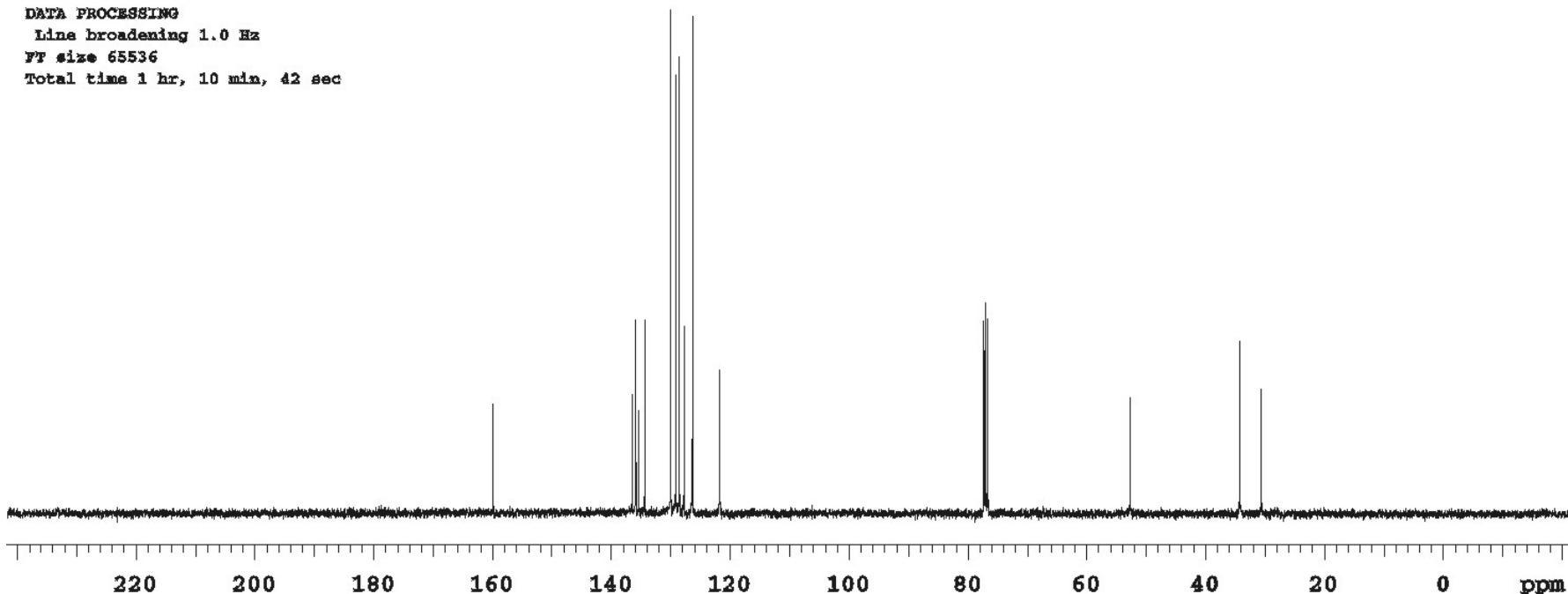
Line broadening 1.0 Hz

PT size 65536

Total time 1 hr, 10 min, 42 sec



3-(3-Phenyl-2-propenyl)-3-(phenylsulfonyl)-2-pyrrolidinimine (4e)



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: DMSO

Temp. 25.0 C / 298.1 K

File: R73_1h_DMSO_STD

Mercury-400BB "m400"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 2.731 sec

Width 5998.8 Hz

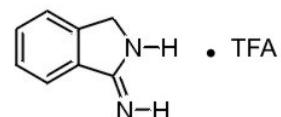
8 repetitions

OBSERVE H1, 399.9264694 MHz

DATA PROCESSING

FT size 65536

Total time 0 min, 32 sec

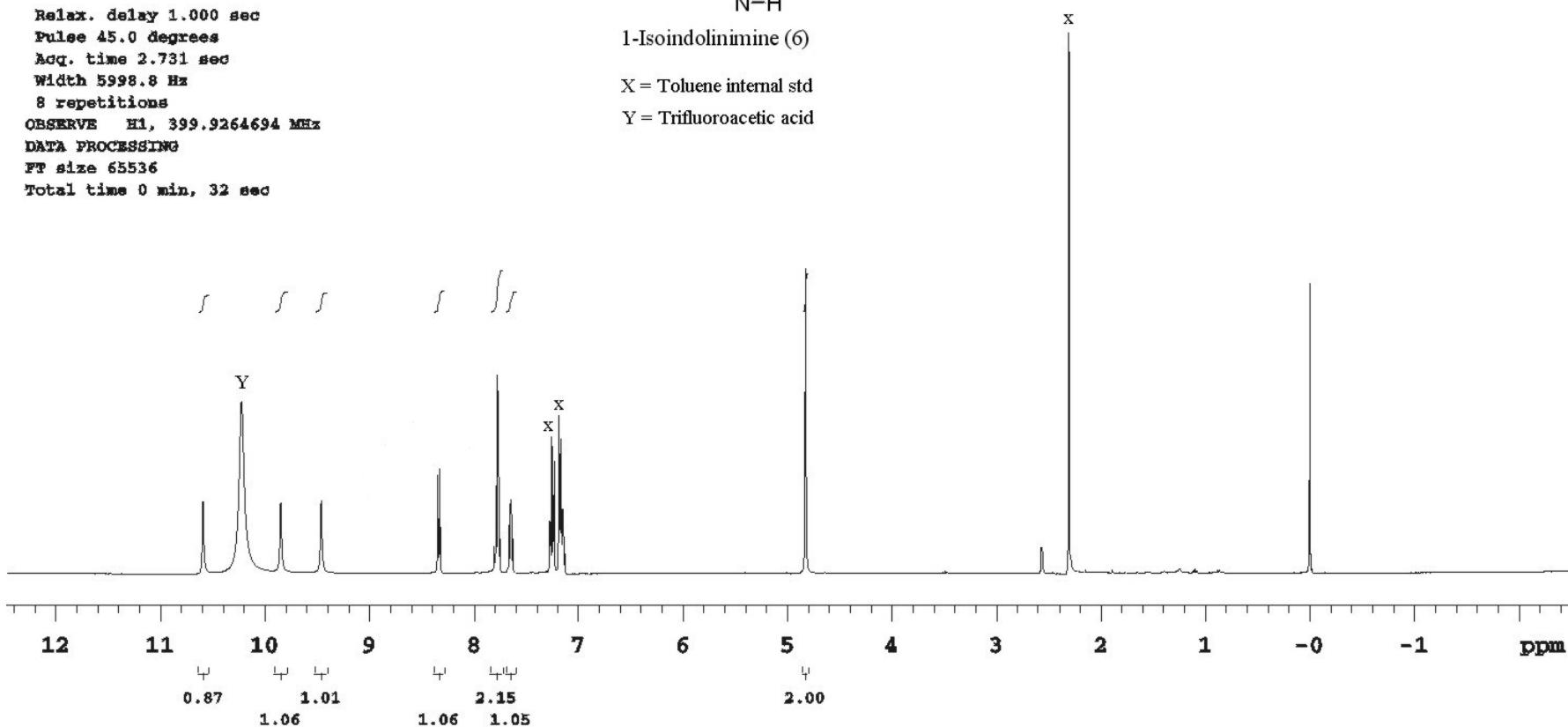


1-Isoindolinimine (6)

X

X = Toluene internal std

Y = Trifluoroacetic acid



¹³C RESOLUTION
DECOUPLED DICHEM

Pulse Sequence: s2pul

Solvent: DMSO

Ambient temperature

File: 090206_R73_13C_DMSO
GEMINI-300BB "g300"

Relax. delay 3.000 sec

Pulse 56.9 degrees

Acq. time 0.750 sec

Width 20000.0 Hz

128 repetitions

OBSERVE C13, 75.4433613 MHz

DECOPLE H1, 300.0339983 MHz

Power 43 dB

on during acquisition

off during delay

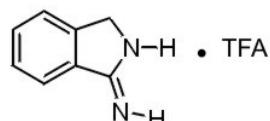
WALTZ-16 modulated

DATA PROCESSING

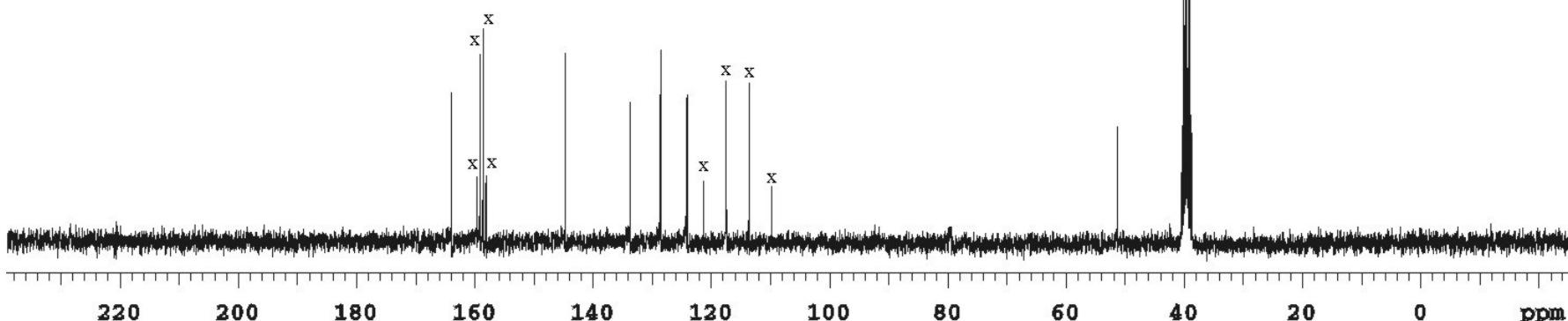
Line broadening 1.0 Hz

FT size 65536

Total time 0 min, 0 sec



DMSO



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: DMSO

Temp. 25.0 C / 298.1 K

File: 310106_R70_1h_buono

Mercury-400BB "m400"

Relax. delay 2.000 sec

Pulse 45.0 degrees

Acq. time 2.731 sec

Width 5998.8 Hz

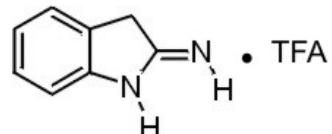
16 repetitions

OBSERVE H1, 399.9263824 MHz

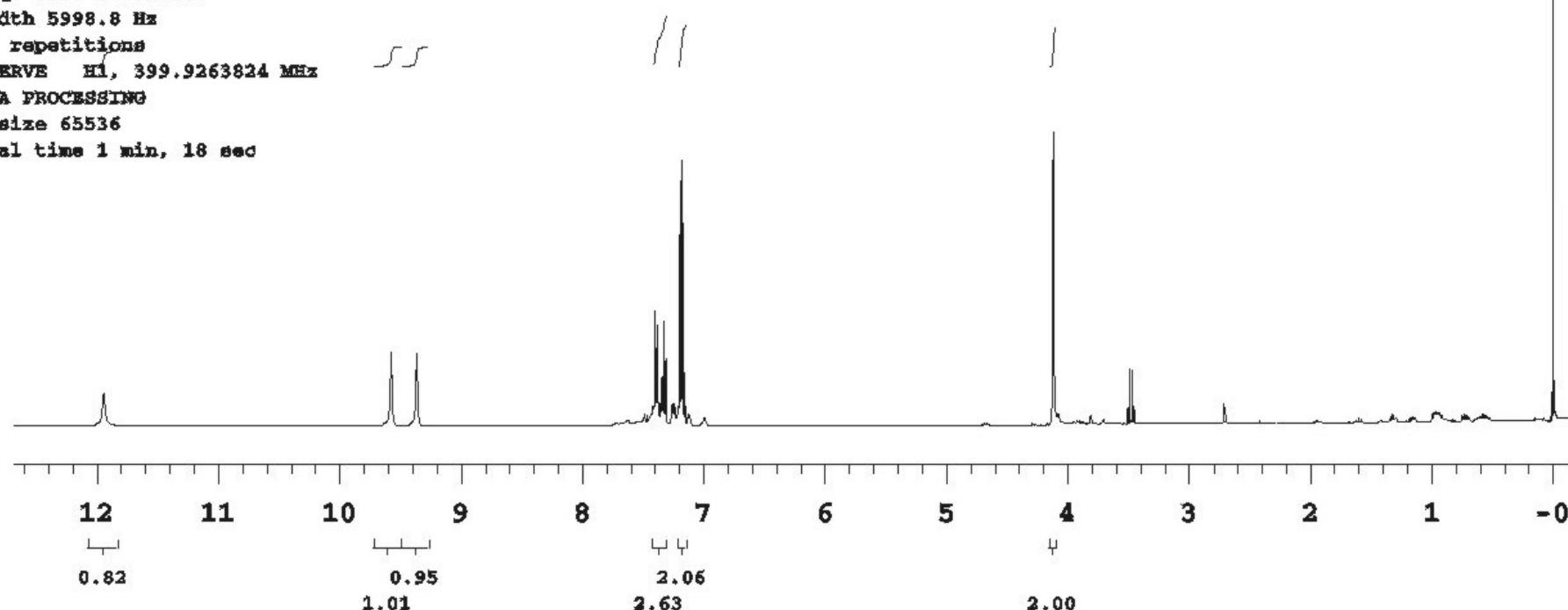
DATA PROCESSING

PP size 65536

Total time 1 min, 18 sec



1,3-dihydro-2H-indol-2-imine (8)



¹³C OBSERVE

Pulse Sequence: s2pul

Solvent: DMSO

Temp. 25.0 C / 298.1 K

File: 310106_R70_13C_buomo

Mercury-400BB "m400"

Relax. delay 2.000 sec

Pulse 59.4 degrees

Acq. time 1.000 sec

Width 26525.2 Hz

112 repetitions

OBSERVE C13, 100.5613625 MHz

DECOUPLE H1, 399.9284566 MHz

Power 40 dB

continuously on

WALTZ-16 modulated

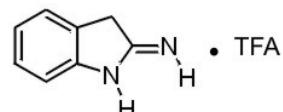
DATA PROCESSING

Line broadening 1.0 Hz

PT size 65536

Total time 54 min, 2 sec

X



1,3-dihydro-2H-indol-2-imine (8)

X = Trifluoroacetic acid

DMSO

