Nickel-Catalyzed Amination of Aryl Carbamates and Sequential Site-Selective Cross-Couplings

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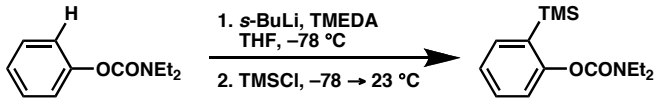
Supporting Information – Table of Contents

Experimental Materials and Methods. Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of nitrogen using anhydrous solvents (either freshly distilled or passed through activated alumina columns). Unless otherwise stated, commercially obtained reagents were used as received. Amines were purified by filtration over basic Brockman Grade I 58 Å Al_2O_3 (Activity 1), followed by distillation over calcium hydride, prior to use. $Ni(cod)_2$ was obtained from Strem Chemicals and SIPr•HCl was obtained from Sigma Aldrich. Dioxane was purified by distillation over sodium benzophenone ketyl radical and degassed by the freeze-pump-thaw method. Reaction temperatures were controlled using an IKAmag temperature modulator, and unless stated otherwise, reactions were performed at room temperature (rt, approximately 23 °C). Thin-layer chromatography (TLC) was conducted with EMD gel 60 F254 pre-coated plates (0.25 mm) and visualized using a combination of UV, anisaldehyde, ceric ammonium molybdate, iodine, vanillin, and potassium permanganate staining. Silicycle Siliaflash P60 (particle size 0.040–0.063 mm) was used for flash column chromatography. ^{1}H NMR spectra were recorded on Bruker spectrometers (at 300, 400, 500, 600 MHz) and are reported relative to deuterated solvent signals. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C NMR spectra were recorded on Bruker Spectrometers (at 125 MHz). Data for ^{13}C NMR spectra are reported in terms of chemical shift. ^{19}F NMR (at 300, 400 MHz) spectra are reported in terms of chemical shift. IR spectra were recorded on a Perkin-Elmer 100 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Melting points are uncorrected and were obtained on a Laboratory Devices Mel-Temp II instrument. High resolution mass spectra were obtained from the UC Irvine Mass Spectrometry Facility.

Experimental Procedures.

A. Synthesis of Aryl Carbamate Substrates

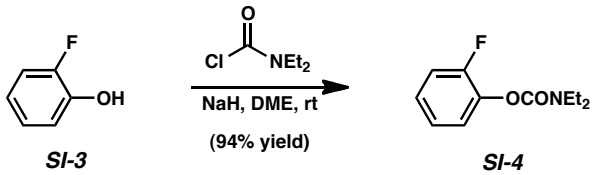
Note: Supporting information for the synthesis of the aryl carbamates shown in Tables 1–3 have previously been reported,[1] with the exception of the carbamate **SI-2**, carbamate **SI-4**, and carbamate **SI-6**.



SI-1 ***SI-2***

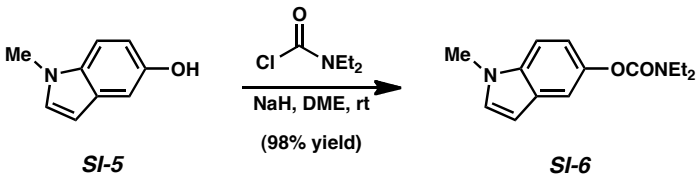
SI-2 (Table 2, Entry 3). To a solution of phenyl carbamate (**SI-1**) (1.0 g, 4.82 mmol, 1 equiv) in THF (24 mL) was added TMEDA (0.79 mL, 5.31 mmol, 1.1 equiv) at 0 °C. The solution was cooled to –78 °C and *s*-BuLi (1.04 M in Hexanes, 5.11 mL, 5.31 mmol, 1.1 equiv) was added dropwise over 15 min. The mixture was stirred at –78 °C for 1 h and then TMSCl (0.80 ml, 6.3 mmol, 1.3 equiv) was added dropwise over 10 min. The resulting mixture was stirred at –78 °C for 45 min and then allowed to warm to 23 °C. The reaction was quenched with saturated aqueous NH_4Cl (10 mL). The layers were separated and the aqueous layer was extracted with Et_2O (5 x 25 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, and then evaporated to dryness. The crude residue was purified by flash chromatography (5:1 Hexanes:EtOAc) to furnish 2-(trimethylsilyl)phenyl carbamate **SI-2** as a colorless solid (1.17 g, 85% yield). R_f 0.41 (5:1 Hexanes:EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (dd, J = 7.5, 1.5 Hz, 1H), 7.37 (ddd, J = 7.5, 1.5, 1.0 Hz, 1H), 7.18 (td, J = 7.0, 1.0 Hz, 1H), 7.04 (dd, J = 8.0, 0.5 Hz, 1H), 3.49 (q, J = 7.5 Hz, 2H), 3.49 (q, J = 7.5 Hz, 2H), 3.40 (q, J = 7.5 Hz, 2H), 1.26 (t, J = 7.5 Hz, 3H), 1.20 (t, J = 7.5 Hz, 3H), 0.29 (s, 9H); ^{13}CNMR (125 MHz, $CDCl_3$): δ 156.5, 154.6, 135.0, 131.7, 130.5, 124.9, 122.4, 42.1, 41.7, 14.3, 13.4, –0.7; IR (film): 2972, 1714, 1412, 1258, 1152 cm^{-1}; HRMS-ESI (*m/z*) $[M + Na]^+$ calcd for $C_{14}H_{23}NO_2SiNa$, 288.1396; found, 288.1393.

[1] a) Yamazaki, K.; Kawamorita, S.; Ohmiya, H.; Sawamura, M. *Org. Lett.* **2010**, *12*, 3978–3981. b) Quasdorf, K. W.; Riener, M.; Petrova, K.; Garg, N. K. *J. Am. Chem. Soc.* **2009**, *131*, 17748–17749. c) Sengupta, S.; Leite, M.; Raslan, D. S.; Quenelle, C.; Snieckus, V. *J. Org. Chem.* **1992**, *57*, 4066–4068. d) Zhao, Z.; Snieckus, V. *Org. Lett.* **2005**, *7*, 2523–2526. e) Kamila, S.; Mukherjee, C.; Mondal, S. S.; De, A. *Tetrahedron* **2003**, *59* 1339–1348. f) Bedford, R. B.; Webster, R. L.; Mitchell, C. J. *Org. Biomol. Chem.* **2009**, *7*, 4853–4857. g) Azzena, U.; Pisano, L.; Pittalis, M. *Appl. Organolmetal. Chem.* **2008**, *22*, 523–528.



SI-3 *SI-4*

SI-4 (Table 2, entry 5). To a round bottom flask containing NaH (0.85 g, 21.4 mmol, 1.2 equiv, 60% dispersion in oil) was added a solution of 2-flurophenol (**SI-3**) (2.0 g, 17.8 mmol, 1 equiv) in DME (71 mL) via cannula transfer. A solution of diethylcarbamoyl chloride (2.15 mL, 16.9 mmol, 0.95 equiv) in DME (10 mL) was then added dropwise via cannula to the reaction vessel. The reaction mixture was allowed to stir for 15 h and was then quenched with H_2O (10 mL). The volatiles were removed under reduced pressure, and Et_2O (50 mL) and H_2O (20 mL) were added. The layers were separated, and the organic layer was washed successively with 1 M KOH (20 mL) and H_2O (20 mL). The combined aqueous layers were extracted with Et_2O (3 x 25 mL). The combined organic layers were then washed with brine (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (5:1 Hexanes:EtOAc) to yield 2-flurophenylsulfamate **SI-4** as a clear oil (3.35 g, 94% yield). R_f 0.27 (5:1 Hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21–7.09 (m, 4H), 3.46 (q, J = 6.5, 2H), 3.39 (q, J = 6.5, 2H), 1.27 (t, J = 6.5, 3H) 1.21 (t, J = 7.0, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.6 (d, J = 246.5), 153.2, 139.0 (d, J = 12.1), 126.2 (d, J = 7.0), 124.2, 124.1 (d, J = 3.9), 116.3 (d, J = 18.4), 42.4, 42.0, 13.9, 13.2; IR (film): 2977, 1720, 1600, 1502, 1417, 1255 cm^{-1}; HRMS-ESI (*m/z*) $[M + Na]^+$ calcd for $C_{11}H_{14}FNO_2Na$, 234.0906; found, 234.0912.

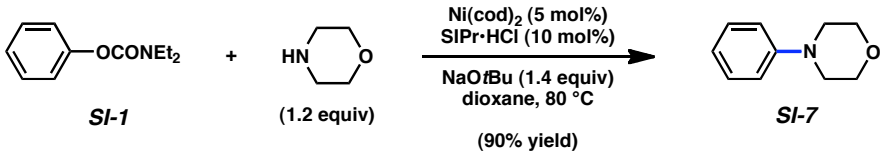


SI-5 *SI-6*

SI-6 (Table 2, entry 6). To a round bottom flask containing NaH (0.33 g, 8.15 mmol, 1.2 equiv, 60% dispersion in oil) was added a solution of *N*-methyl-5-hydroxyindole (**SI-5**) (1.0 g, 6.79 mmol, 1 equiv) in DME (27 mL) via cannula transfer. A solution of diethylcarbamoyl chloride (0.875 mL, 6.45 mmol, 0.95 equiv) in DME (15 mL) was then added dropwise via cannula to the reaction vessel. The reaction was allowed to stir for 3.5 d, and then quenched with H_2O (10 mL). The volatiles were

removed under reduced pressure, and then Et_2O (50 mL) and H_2O (15 mL) were added. The layers were separated, and the organic layer was washed successively with 1 M KOH (20 mL) and H_2O (20 mL). The combined aqueous layers were extracted with Et_2O (3 x 20 mL). The combined organic layers were then washed with brine (20 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (9:1 Benzene:Et_2O) to yield carbamate **SI-6** as a white solid (1.55g, 98% yield). R_f 0.44 (9:1 Benzene:Et_2O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (d, J = 2.5, 1H), 7.26 (d, J = 9.0, 1H), 7.05 (d, J = 3.0, 1H), 6.98 (dd, J = 8.5, 2.3, 1H), 6.43 (dd, J = 3.0, 0.5, 1H), 3.78 (s, 3H), 3.47 (bs, 2H), 3.41 (bs, 2H), 1.27 (bs, 3H), 1.21 (bs, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.4, 145.1, 134.5, 129.8, 128.7, 116.3, 113.2, 109.4, 101.1, 42.3, 41.9, 33.1, 14.4, 13.6; IR (film): 2972, 1708, 1467, 1418, 1218, 1159 cm^{-1}; HRMS-ESI (*m/z*) $[M + Na]^+$ calcd for $C_{14}H_{18}N_2O_2Na$, 269.1266; found, 269.1267.

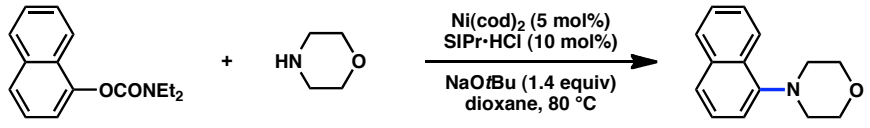
B. Aminations of Aryl Carbamates



SI-1 (1.2 equiv) (90% yield) ***SI-7***

Representative Procedure (coupling of phenylcarbamate SI-1, Table 1, entry 3) is used as an example). SI-7. A 20 mL reaction vial was charged with $Ni(cod)_2$ (6.8 mg, 0.025 mmol, 5 mol%), SIPr•HCl (21.2 mg, 0.05 mmol, 10 mol%), anhydrous powdered NaO*t*Bu (67.2 mg, 0.7 mmol, 1.4 equiv), and a magnetic stir bar, all in a glove box. Subsequently, a solution of carbamate substrate **SI-1** (96.6 mg, 0.50 mmol, 1 equiv) and morpholine (52.4 μL, 0.60 mmol, 1.2 equiv) in dioxane (2.5 mL) was added. The vessel was removed from the glove box, and then heated to 80 °C for 3 h. After cooling the reaction vessel to 23 °C and concentrating under reduced pressure, the crude residue was loaded onto a silica gel column (2.5 x 10 cm) and purified by flash chromatography (9:1 Hexanes: EtOAc) to yield aminated product **SI-7** (73.4 mg, 90% yield) as a white solid. R_f 0.29 (9:1 Hexanes:EtOAc). Spectral data match those previously reported.[2]

Any modifications of the conditions shown in this representative procedure are specified in the following schemes, which depict all of the results shown in Tables 1, 2, and 3.



SI-8 (1.2 equiv) (91% yield) ***SI-9***

SI-9 (Table 1, entry 1). Purification by flash chromatography (9:1 Hexanes:EtOAc) afforded aminated product **SI-9** (91% yield) as a white solid. R_f 0.38 (9:1 Hexanes:EtOAc). Spectral data match those previously reported.[3]

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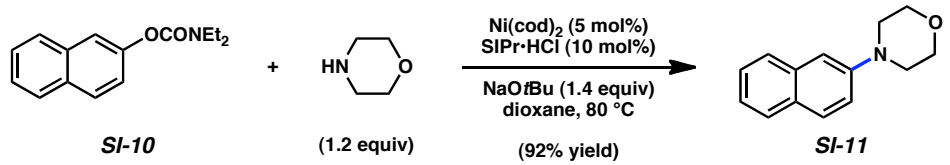
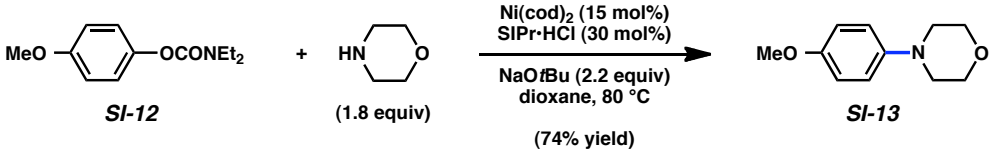
[2] Barker, T. J.; Jarvo, E. R. *J. Am. Chem. Soc.* **2009**, *131*, 15598–15599.

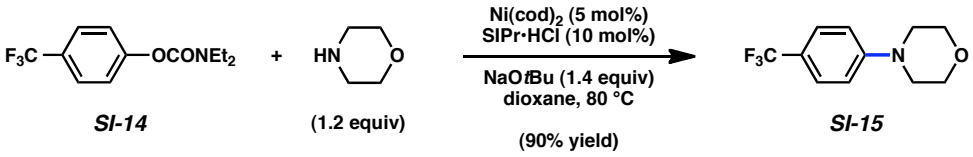
[3] Desmarets, C.; Champagne, B.; Walcarius, A.; Bellouard, C.; Omar-Amrani, R.; Ahajji, A.; Fort, Y.; Schneider, R. *J. Org. Chem*. **2006**, *71*, 1351–1361.



SI-11 (Table 1, entry 2). Purification by flash chromatography (9:1 Hexanes:EtOAc) afforded aminated product **SI-11** (92% yield) as a white solid. R_f 0.32 (9:1 Hexanes:EtOAc). Spectral data match those previously reported.[4]



SI-13 (Table 1, entry 4). Purification by flash chromatography (10:1:1 Benzene:Et_2O:CH_2Cl_2) afforded aminated product **SI-13** (74% yield) as a white solid. R_f 0.18 (10:1:1 Benzene:Et_2O:CH_2Cl_2). Spectral data match those previously reported.[5]

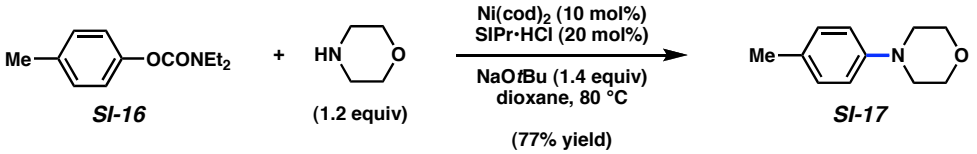


SI-15 (Table 1, entry 5). Purification by flash chromatography (30:1 Benzene:Et_2O) afforded aminated product **SI-15** (90% yield) as a white solid. R_f 0.30 (30:1 Benzene:Et_2O). Spectral data match those previously reported.[6]

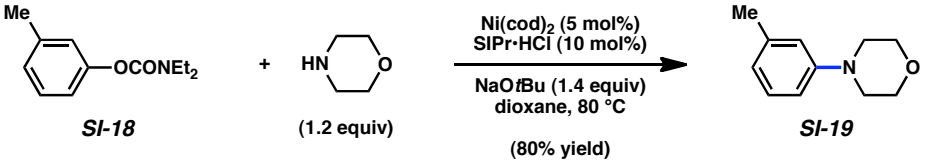
[4] Gao, C.; Yang, L. *J. Org. Chem.* **2008**, *73*, 1624–1627.

[5] Wolfe, J. P.; Buchwald, S. L. *J. Org. Chem.* **1996**, *61*, 1133–1135.

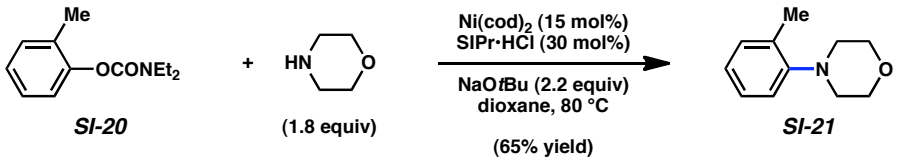
[6] Guo, D.; Huang, H.; Xu, J.; Jiang, H.; Liu, H. *Org. Lett.* **2008**, *10*, 4513–4516.



SI-17 (Table 1, entry 6). Purification by flash chromatography (19:1 Benzene:Et_2O) afforded aminated product **SI-17** (77% yield) as a white solid. R_f 0.53 (19:1 Benzene:Et_2O). Spectral data match those previously reported.[7]

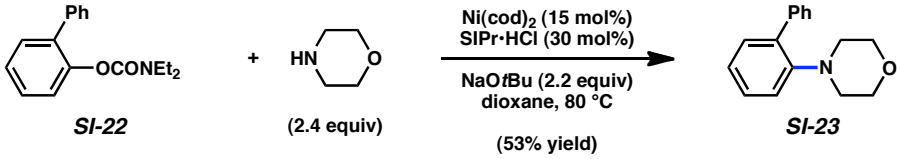


SI-19 (Table 1, entry 7). Purification by flash chromatography (19:1 Benzene:Et_2O) afforded aminated product **SI-19** (80% yield) as a yellow oil. R_f 0.49 (19:1 Benzene:Et_2O). Spectral data match those previously reported.[7]

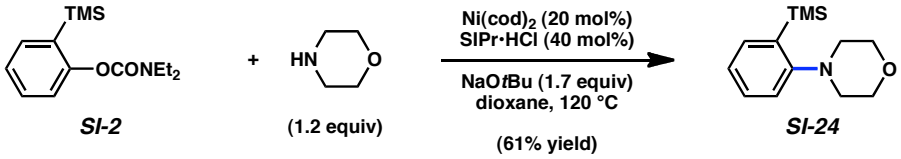


SI-21 (Table 2, entry 1). Purification by flash chromatography (19:1 Hexanes:EtOAc) afforded aminated product **SI-21** (65% yield) as a yellow oil. R_f 0.37 (19:1 Hexanes:EtOAc). Spectral data match those previously reported.[7]

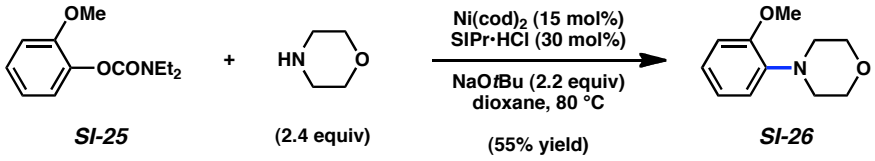
[7] Desmarets, C.; Schneider, R.; Fort, Y. *J. Org. Chem.* **2002**, *67*, 3029–3036.



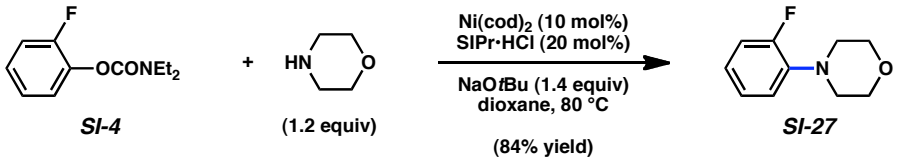
SI-23 (Table 2, entry 2). Purification by flash chromatography (100% Benzene) afforded aminated product **SI-23** (53% yield) as an off-white solid. R_f 0.53 (100% Benzene); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (dd, J = 8.2, 1.2, 2H), 7.42 (t, J = 7.6, 2H), 7.35–7.30 (m, 2H), 7.28 (dd, J = 7.6, 1.6, 1H), 7.12 (td, J = 7.5, 1.1, 1H), 7.05 (dd, J = 8.1, 0.8, 1H), 3.62 (t, J = 4.6, 4H), 2.84 (t, J = 4.6, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.1, 141.1, 135.1, 131.7, 128.9, 128.5, 128.3, 127.0, 123.0, 118.1, 67.1, 51.6; IR (film): 2950, 2815, 1593, 1480, 1439, 1221, 1110 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{16}H_{17}NOH$, 240.1388; found, 240.1394.



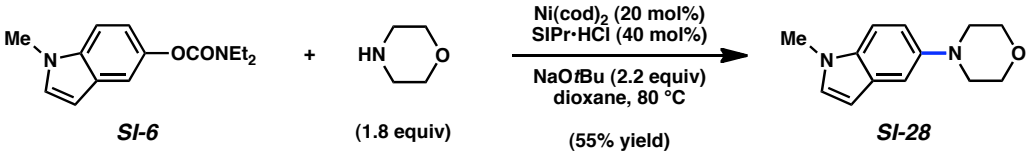
SI-24 (Table 2, entry 3). Purification by flash chromatography (5:1 Benzene:Hexanes) afforded aminated product **SI-24** (61% yield) as a white solid. R_f 0.31 (100% Benzene); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (d, J = 7.3, 1H), 7.41 (t, J = 7.1, 1H), 7.33 (d, J = 7.9, 1H), 7.22 (t, J = 7.2, 1H), 3.85 (t, J = 4.3, 4H), 2.89 (bs, 4H), 0.31 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.5, 138.8, 135.6, 130.5, 125.9, 122.8, 67.4, 54.5, 0.2; IR (film): 2852, 1583, 1473, 1258, 1109 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{13}H_{21}NOSiH$, 236.1471; found, 236.1466.



SI-26 (Table 2, entry 4). Purification by flash chromatography (9:1 Benzene:Et_2O) afforded aminated product **SI-26** (55% yield) as a yellow oil. R_f 0.23 (9:1 Benzene:Et_2O). Spectral data match those previously reported.[8]



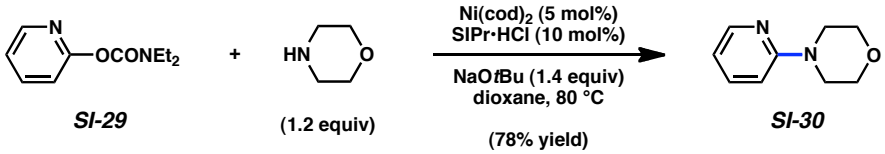
SI-27 (Table 2, entry 5). Purification by flash chromatography (40:1 Benzene:Et_2O) afforded aminated product **SI-27** (84% yield) as an off-white solid. R_f 0.22 (40:1 Benzene:Et_2O). Spectral data match those previously reported.[9]



SI-28 (Table 2, entry 6). Purification by flash chromatography (6:1:1 Benzene:Et_2O:CH_2Cl_2) afforded aminated product **SI-28** (55% yield) as a off-white solid. R_f 0.21 (10:1:1 Benzene:Et_2O:CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 (d, J = 8.8, 1H), 7.16 (d, J = 2.2, 1H), 7.03–6.97 (m, 2H), 6.41 (d, J = 3.0, 1H), 3.91 (t, J = 4.7, 4H), 3.76 (s, 3H), 3.13 (t, J = 4.7, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.9, 132.9, 129.5, 129.2, 115.2, 110.1, 108.0, 100.8, 67.6, 52.4, 33.2; IR (film): 3093, 2968, 1616, 1490, 1231, 1115 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{13}H_{16}N_2OH$, 217.1341; found, 217.1342.

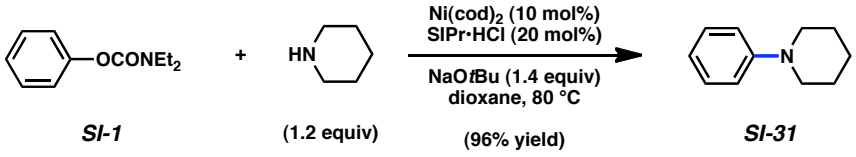
[8] Li, J.; Cui, M.; Yu, A.; Wu, Y. *J. Organomet. Chem.* **2007**, *692*, 3732–3742.

[9] Fasani, E.; Tilocca, F.; Protti, S.; Merli, D.; Albini, A. *Org. Biomol. Chem.* **2008**, *6*, 4634–4642.



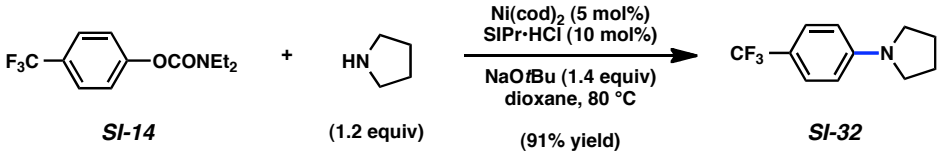
SI-29 (1.2 equiv) (78% yield) ***SI-30***

SI-30 (Table 2, entry 7). Purification by flash chromatography (2:1 Hexanes:EtOAc) afforded aminated product **SI-30** (78% yield) as a pale yellow oil. R_f 0.28 (9:1 Benzene:Et_2O). Spectral data match those previously reported.[10]



SI-1 (1.2 equiv) (96% yield) ***SI-31***

SI-31 (Table 3, entry 1). Purification by flash chromatography (50:1 Hexanes:EtOAc) afforded aminated product **SI-31** (96% yield) as a clear oil. R_f 0.29 (50:1 Hexanes:EtOAc). Spectral data match those previously reported.[11]



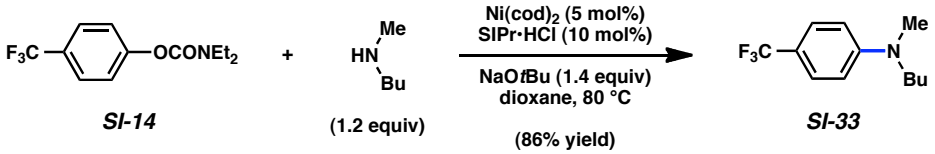
SI-14 (1.2 equiv) (91% yield) ***SI-32***

SI-32 (Table 3, entry 2). Purification by flash chromatography (50:1 Hexanes:Et_2O) afforded aminated product **SI-32** (91% yield) as a white solid. R_f 0.28 (50:1 Hexanes:Et_2O). Spectral data match those previously reported.[12]

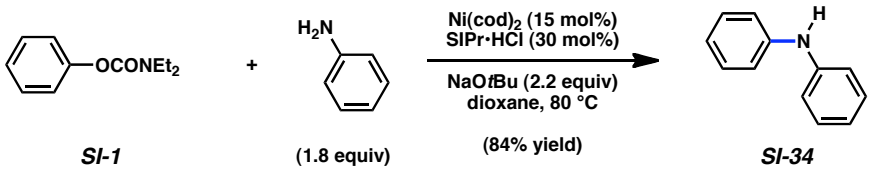
[10] Wagaw, S.; Buchwald, S. L. *J. Org. Chem*. **1996**, *61*, 7240–7241.

[11] Shimasaki, T.; Tobisu, M.; Chatani, N. *Angew. Chem. Int. Ed.* **2010**, *49*, 2929–2932.

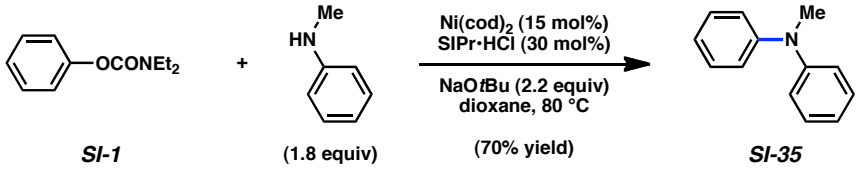
[12] Brenner, E.; Schneider, R.; Fort, Y. *Tetrahedron* **1999**, *55*, 12829–12842.



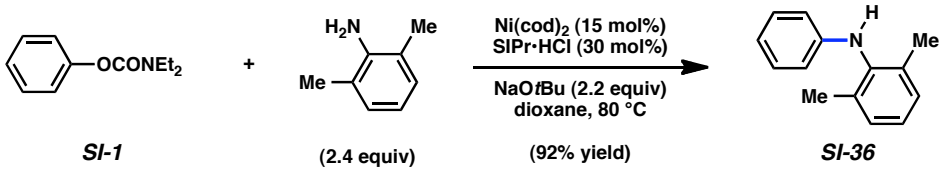
SI-33 (Table 3, entry 3). Purification by flash chromatography (50:1 Hexanes:Et_2O) afforded aminated product **SI-33** (86% yield) as a clear oil. R_f 0.32 (50:1 Hexanes:Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42 (d, J = 9.0, 2H), 6.66 (d, J = 8.7, 2H), 3.35 (t, J = 7.3, 2H), 2.97 (s, 3H), 1.62–1.52 (m, 2H), 1.35 (sextet, J = 7.2, 2H), 0.95 (t, J = 7.4, 3H), ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.4, 126.6 (q, J = 3.8), 125.4 (q, J = 268.3), 117.0 (q, J = 32.0), 110.9, 52.9, 38.4, 28.9, 20.4, 14.0; ^{19}F NMR (300 MHz, $CDCl_3$): δ –60.8; IR (film): 2960, 2933, 2876, 1616, 1533, 1322, 1197, 1100, 1068 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{12}H_{16}F_3H$, 232.1313; found 232.1307.



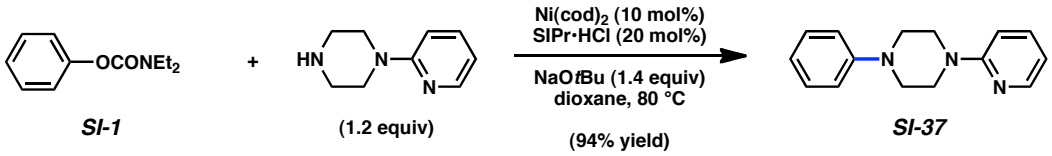
SI-34 (Table 3, entry 4). Purification by flash chromatography (4:1 Hexanes:CH_2Cl_2) afforded aminated product **SI-34** (84% yield) as a yellow solid. R_f 0.28 (4:1 Hexanes:CH_2Cl_2). Spectral data match those previously reported.[7]



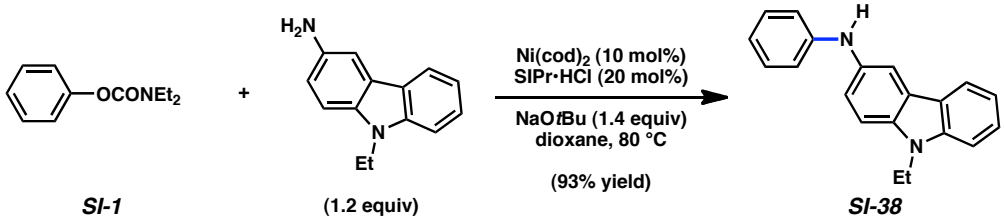
SI-35 (Table 3, entry 5). Purification by flash chromatography (100:1 Hexanes:Et_2O) afforded aminated product **SI-35** (70% yield) as a yellow oil. R_f 0.12 (100:1 Hexanes:Et_2O). Spectral data match those previously reported.[7]



SI-36 (Table 3, entry 6). Purification by flash chromatography (20:1 Hexanes:Et_2O) afforded aminated product **SI-36** (92% yield) as a clear oil. R_f 0.41 (20:1 Hexanes:Et_2O). Spectral data match those previously reported.[7]

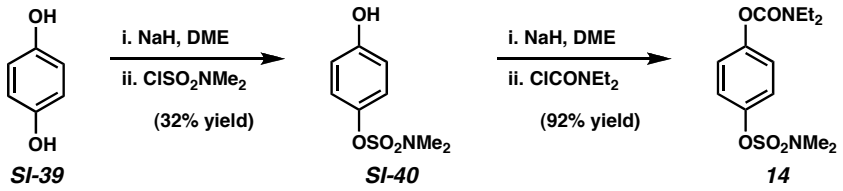


SI-37 (Table 3, entry 7). Purification by flash chromatography (8:1 Hexanes:EtOAc) afforded aminated product **SI-37** (94% yield) as a white solid. R_f 0.30 (8:1 Hexanes:EtOAc). Spectral data match those previously reported.[11]



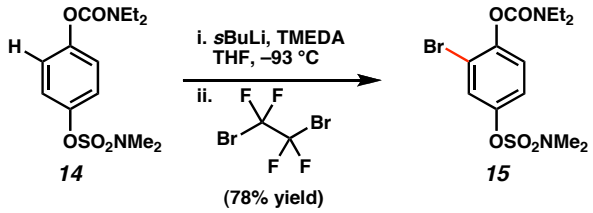
SI-38 (Table 3, entry 8). Purification by flash chromatography (300:150:1 Hexanes:CH_2Cl_2:Et_3N) afforded aminated product **SI-38** (93% yield) as a white solid. R_f 0.30 (2:1 Hexanes:CH_2Cl_2); ^{1}H NMR (500 MHz, C_6D_6): δ 7.94 (d, J = 6.7, 1H), 7.74 (d, J = 1.7, 1H), 7.39 (t, J = 7.6, 1H), 7.21–7.16 (m, 4H), 7.07 (d, J = 8.2, 1H), 6.95 (d, J = 8.5, 1H), 6.91 (d, J = 8.4, 2H), 6.82, (td, J = 7.4, 0.8, 1H), 5.15 (s, 1H), 3.69 (q, J = 7.2, 2H), 0.92 (t, J = 7.3, 3H); ^{13}C NMR (125 MHz, C_6D_6): δ 147.0, 140.9, 137.0, 134.9, 129.7, 126.0, 124.2, 123.3, 121.9, 121.0, 119.4, 119.1, 115.6, 114.4, 109.2, 108.8, 37.4, 13.6; IR (film): 3383, 3048, 2974, 1598, 1504, 1489, 1470, 1299, 1229, 1150 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{20}H_{18}N_2H$, 287.1548; found 287.1551.

C. Experiments Involving Carbamate and Sulfamate Substrates

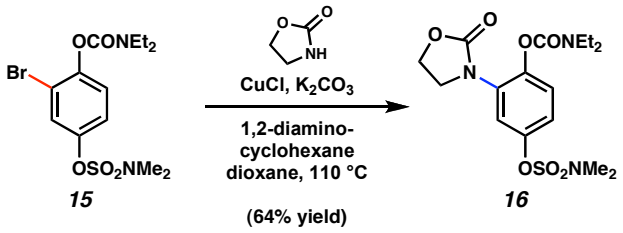


Carbamate Sulfamate 14. To a round bottom flask containing NaH (0.308 g, 25.9 mmol, 1.2 equiv, 60% dispersion in oil) was added a solution of hydroquinone (**SI-39**) (3.0 g, 27.3 mmol, 1 equiv) in DME (60 mL) via cannula transfer. A solution of dimethylsulfamoyl chloride (2.76 mL, 25.9 mmol, 1.2 equiv) in DME (60 mL) was then added immediately via cannula transfer. The reaction was allowed to stir for 12 h and the reaction was quenched with deionized H_2O (20 mL). The volatiles were removed under reduced pressure, and then Et_2O (50 mL) and H_2O (20 mL) were added. The layers were separated and the organic phase was washed with H_2O (3 x 30 mL). The combined aqueous layers were extracted with Et_2O (3 x 50 mL). The combined organic layers were then washed with brine (20 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (7:1:1 Benzene:CH_2Cl_2:Et_2O) to yield sulfamate **SI-40** as a white solid (1.77 g, 32% yield).

To a round bottom flask containing NaH (0.560 g, 14.0 mmol, 1.2 equiv, 60% dispersion in oil) was added a solution of **SI-40** (2.53 g, 11.7 mmol, 1 equiv) in DME (23 mL). A solution of diethylcarbamoyl chloride (1.45 mL, 11.0 mmol, 0.95 equiv) in DME (23 mL) was then added dropwise to the reaction vessel. After stirring for 12 h, the reaction mixture was quenched with deionized H_2O (9 mL). The solvent was removed under reduced pressure and then Et_2O (22 mL) was added. The organic layer was washed with H_2O (3 x 9 mL). The combined aqueous layers were back-extracted with Et_2O (3 x 22 mL). The combined organic layers were washed with brine (9 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (1:1 Hexanes:EtOAc) to yield carbamate sulfamate **14** as a white solid (3.39 g, 92% yield). R_f 0.54 (7:1:1 Benzene:Et_2O:CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (d, J = 8.5, 2H), 7.14 (d, J = 9, 2H), 3.41 (m, 4H), 2.69 (s, 6H), 1.25 (t, J = 7, 3H), 1.20 (t, J = 7, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.9, 149.9, 147.1, 123.1, 122.7, 42.5, 42.1, 38.9, 14.4, 13.5; IR (film): 2983, 2939, 1721, 1474, 1357, 1273, 1156 cm^{-1}; HRMS-ESI (*m/z*) [M + Na]$^+$ calcd for $C_{13}H_{20}N_2O_5SNa$, 339.0991; found 339.0988.

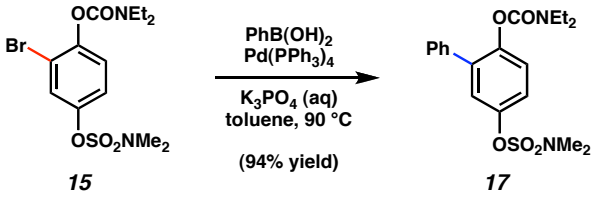


Bromide 15. To a solution of carbamate **14** (280.7 mg, 0.887 mmol, 1.0 equiv) and TMEDA (0.145 mL, 0.976 mmol, 1.1 equiv) in THF (4.4 mL) at –93 °C was added *s*-BuLi (0.720 mL, 0.976 mmol, 1.1 equiv) dropwise. After stirring for 45 min, 1,2-dibromotetrafluoroethane (0.148 mL, 1.242 mmol, 1.4 equiv) was added dropwise and the reaction was allowed to warm to 23 °C over 15 min. The reaction mixture was quenched with saturated aqueous NH_4Cl (3 mL) and stirred at 23 °C for 60 min. The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 3 mL). The combined organic layers were washed with brine (1 x 5 mL), dried by passage over a plug of silica gel, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (3:1:1 Hexanes:CH_2Cl_2:Et_2O) to yield brominated product **15** (272.0 mg, 78% yield) as an off-white solid. R_f 0.17 (3:1:1 Hexanes:CH_2Cl_2:Et_2O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (t, J = 1.5, 1H), 7.26 (d, J = 1.5, 2H), 3.50 (q, J = 7.0, 2H), 3.40 (q, J = 7.0, 2H), 2.99 (s, 6H), 1.31 (t, J = 7.0, 3H), 1.23 (t, J = 7.0, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.9, 147.6, 147.3, 126.5, 124.8, 121.7, 116.9, 42.6, 42.3, 38.9, 14.4, 13.4; IR (film): 2977, 1724, 1592, 1472, 1372, 1148 cm^{-1}; HRMS-ESI (*m/z*) $[M + Na]^+$ calcd for $C_{13}H_{19}BrN_2O_5SNa$, 417.0096; found 417.0107.

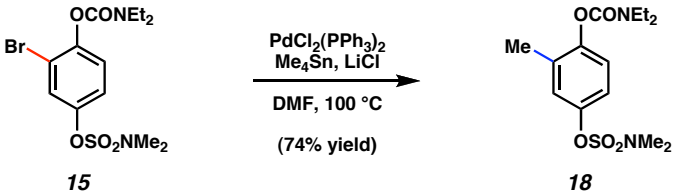


Oxazolidinone 16. A 1 mL vial was charged with K_2CO_3 (55.7 mg, 0.404 mmol, 2 equiv) and a magnetic stir bar. The vial and contents were flame-dried under reduced pressure, and then allowed to cool under N_2. Bromide **15** (80.0 mg, 0.202 mmol, 1 equiv) and 2-oxazolidinone (17.6 mg, 0.202 mmol, 1 equiv) were added. The vial was then evacuated and backfilled with N_2 three times and brought into a glove box. CuCl (2.0 mg, 0.020 mmol, 10 mol%) was added and the reaction vessel was removed from the glove box and placed under an atmosphere of N_2. (±)-trans-1,2-diaminocyclohexane (4.8 μL, 0.040mmol, 20 mol%) was then added, followed by anhydrous dioxane (110 μL). The

reaction vessel was shielded from light, sealed with a Teflon-coated cap, and heated to 110 °C. After 13 h, the reaction was allowed to cool to 23 °C. The residue was diluted in EtOAc (1 mL) and filtered over a pad of celite (EtOAc eluent, 7 mL). Concentration under reduced pressure afforded the crude product, which was further purified by flash chromatography (1:1 Benzene:EtOAc) to yield oxazolidinone **16** as a yellow oil (51.9 mg, 64% yield). R_f 0.28 (1:1 Benzene:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (dd, J = 2.0, 1.0, 1H), 7.23 (d, J = 2.0, 2H), 4.44 (t, J = 8.0, 2H), 3.98 (t, J = 7.8, 2H), 3.44 (q, J = 7.2, 2H), 3.36 (q, J = 7.0, 2H), 2.96 (s, 6H), 1.23 (t, J = 7.0, 3H), 1.19 (t, J = 7.3, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.1, 153.2, 147.2, 145.4, 131.1, 124.9, 121.9, 120.7, 62.8, 47.2, 42.5, 42.2, 38.9, 14.2, 13.4; IR (film): 2977, 1753, 1717, 1611, 1504, 1367, 1146 cm^{-1}; HRMS-ESI (*m/z*) $[M + Na]^+$ calcd for $C_{16}H_{23}N_3O_7SNa$, 424.1154; found 424.1150.

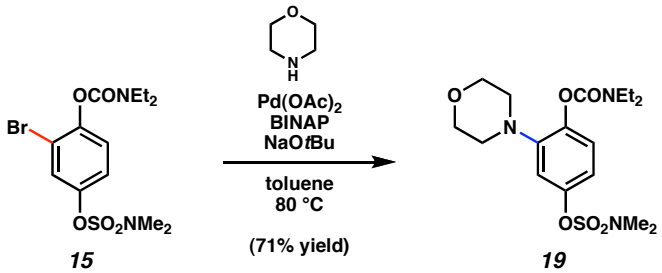


Biaryl 17. A 20 mL scintillation vial was charged with a magnetic stir bar, K_3PO_4 (1 mL, 2 M aqueous) and toluene (1.7 mL), and the resulting biphasic mixture was sparged with N_2 for 1 h. To the solution were added bromide **15** (150 mg, 0.379 mmol, 1 equiv), phenylboronic acid (56 mg, 0.455 mmol, 1.2 equiv) and $Pd(PPh_3)_4$ (66 mg, 0.057 mmol, 15 mol%). The resulting mixture was sparged with N_2 for 10 min. The vial was sealed with a Teflon-coated screw-cap and heated at 90 °C for 14 h. After cooling to 23 °C, dichloromethane (10 mL) and Na_2SO_4 were added and the mixture was allowed to stand for 30 min. The crude mixture was then filtered over silica gel and concentrated under reduced pressure. The crude residue was purified by flash chromatography (3:1:1 Hexanes:CH_2Cl_2:Et_2O) to yield biaryl **17** as a yellow oil (140 mg, 94% yield). R_f 0.22 3:1:1 Hexanes:CH_2Cl_2:Et_2O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40–7.22 (m, 8H), 3.23 (m, 4H), 2.99 (s, 6H), 1.04 (t, J = 6.8, 3H), 0.99 (t, J = 6.8, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.8, 147.2, 146.9, 137.0, 136.7, 129.1, 128.3, 127.8, 124.6, 123.8, 121.5, 42.2, 41.8, 38.9, 14.0, 13.2; IR (film): 2976, 1714, 1471, 1367, 1141 cm^{-1}; HRMS-ESI (*m/z*) $[M + Na]^+$ calcd for $C_{19}H_{24}N_2O_5SNa$, 415.1304; found 415.1297.



15 ***18***

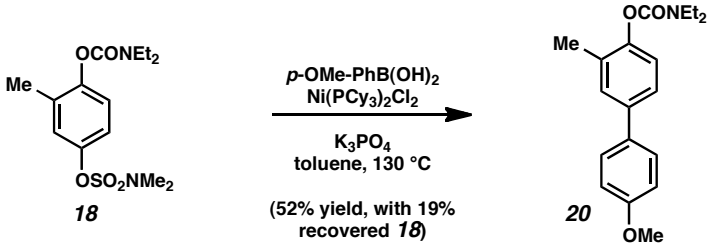
Sulfamate 18. To a 4 mL vial charged with anhydrous lithium chloride (53.6 mg, 1.265 mmol, 5 equiv) was added a solution of bromide **15** (100.0 mg, 0.253 mmol, 1 equiv) in *N,N*-dimethylformamide (2.5 mL) that had been rigorously sparged with N_2, all in a glove box. Next, $PdCl_2(PPh_3)_2$ (4.2 mg, 0.006 mmol, 2.5 mol%) was added and the mixture was stirred until a yellow solution formed. To this solution was added neat tetramethyltin (87.7 μL, 0.633 mmol, 2.5 equiv) dropwise. The reaction vial was sealed, removed from the glove box, and heated to 100 °C for 16 h. The reaction was allowed to cool to 23 °C and was then quenched by the addition of H_2O (2.5 mL). The aqueous layer was extracted with EtOAc (5 x 6 mL). The combined organic layers were washed with brine (2 x 15 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The crude oil was redissolved in EtOAc (5 mL) and then washed sequentially with aqueous 1 M KF (3 x 5 mL), saturated aqueous NH_4Cl (1 x 5 mL), and H_2O (1 x 5 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure to yield sulfamate **18** as a white solid (62.1 mg, 74% yield). R_f 0.39 (5:1 Benzene:Et_2O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14 (bs, 1H), 7.10–7.05 (m, 2H), 3.45 (q, J = 7.0, 2H), 3.37 (q, J = 6.5, 2H), 2.94 (s, 6H), 2.21 (s, 3H), 1.26 (t, J = 6.5, 3H), 1.19 (t, J = 6.8, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.7, 148.4, 147.0, 132.4, 124.0, 123.3, 119.9, 42.4, 42.0, 38.8, 16.5, 14.3, 13.4; IR (film): 2976, 1714, 1416, 1367, 1273, 1134 cm^{-1}; HRMS-ESI (*m/z*) [M + Na]$^+$ calcd for $C_{14}H_{22}N_2O_5SNa$, 353.1147; found 353.1142.



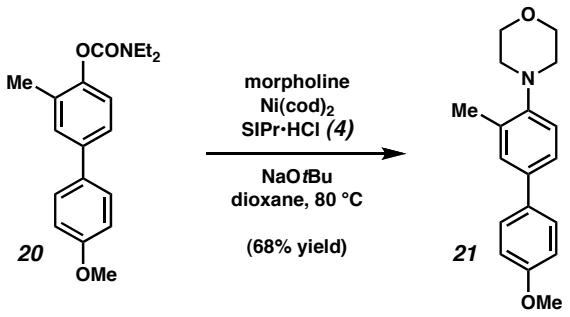
15 ***19***

Amine 19. A 4 mL reaction vial was charged with $Pd(OAc)_2$ (5.7 mg, 0.025 mmol, 10 mol%), BINAP (17.4 mg, 0.028 mmol, 11 mol%), anhydrous powdered NaO*t*Bu (34.0 mg, 0.354 mmol, 1.4 equiv), bromide **15** (100.0 mg, 0.253 mmol, 1 equiv), morpholine (26.6 μL, 0.304 mmol, 1.2 equiv) and a

magnetic stir bar, all in a glove box. Subsequently, toluene (1.0 mL) that had been rigorously sparged with N_2, was added. The vessel was sealed under an atmosphere of argon, and then heated to 80 °C for 16 h. After cooling to 23 °C, the crude mixture was diluted with Et_2O, filtered over a plug of celite with additional Et_2O (10 mL), and concentrated under reduced pressure. The crude residue was purified by flash chromatography (1:1 Benzene:Et_2O) to furnish aminated product **19** (72.1 mg, 71% yield) as a yellow oil. R_f 0.33 (1:1 Benzene:Et_2O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.06 (d, J = 8.0, 1H), 6.96–6.92 (m, 2H), 3.79 (t, J = 4.8, 4H), 3.45 (q, J = 7.0, 2H), 3.38 (q, J = 7.0, 2H), 3.00 (t, J = 4.5, 4H), 2.95 (s, 6H), 1.25 (t, J = 7.0, 3H), 1.21 (t, J = 7.0, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.6, 147.8, 145.9, 143.5, 124.5, 116.2, 113.7, 67.2, 51.6, 42.3, 41.8, 38.9, 14.4, 13.5; IR (film): 2972, 1716, 1608, 1584, 1498, 1413, 1367, 1139 cm^{-1}; HRMS-ESI (*m/z*) [M + Na]$^+$ calcd for $C_{17}H_{27}N_3O_6SNa$, 424.1518; found 424.1508.

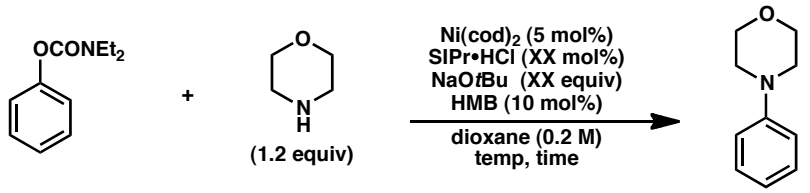


Carbamate 20. A 4 mL vial containing K_3PO_4 (0.324 g, 1.53 mmol, 7.2 equiv) was flame-dried and cooled to 23 °C. The $Ni(PCy_3)_2Cl_2$ (25.3 mg, 0.042 mmol, 20 mol%), boronic acid (0.161 g, 1.06 mmol, 5 equiv) and sulfamate **18** (70 mg, 0.212 mmol, 1 equiv) were added to the vial. Toluene (0.7 mL) was added, and the resulting mixture was stirred at 23 °C for 1 h. The reaction was then heated at 130 °C for 8 h. The reaction was then cooled to 23 °C and purified by flash chromatography (9:1 Benzene:CH_2Cl_2 → 8:1:1 Hexanes:EtOAc:CH_2Cl_2) to produce carbamate **20** (34.7 mg, 52% yield) as a white solid, along with recovered sulfamate **18** (13.3 mg, 19% yield). R_f 0.24 (8:1:1 Hexanes:EtOAc:CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.48 (d, J = 9, 2H), 7.37 (s, 1H), 7.35 (d, J = 9.6, 1H), 7.10 (d, J = 8.4, 1H) 6.95 (d, J = 8.4, 2H), 3.85 (s, 3H), 3.49 (m, 2H), 3.41 (m, 2H), 2.27 (s, 3H), 1.25 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 154.1, 149.2, 138.2, 133.5, 130.7, 129.4, 128.2, 125.2, 122.5, 114.2, 55.4, 42.4, 42.0, 16.6, 14.4, 13.5; IR (film): 2973, 2931, 1711, 1608, 1416, 1213, 1153 cm^{-1}; HRMS-ESI (*m/z*) [M + Na]$^+$ calcd for $C_{19}H_{23}NO_3Na$, 336.1576; found 336.1567.



Amine 21. A 4 mL vial was charged with carbamate **20** (45.5 mg, 0.145 mmol, 1 equiv), $Ni(cod)_2$ (4.1 mg, 0.015 mmol, 10 mol%), SIPr•HCl (12.8 mg, 0.03 mmol, 20 mol%), anhydrous powdered NaO*t*Bu (30.6 mg, 0.319 mmol, 2.2 equiv), and a magnetic stir bar, all in a glove box. Subsequently, morpholine (30.5 μL, 0.348 mmol, 2.4 equiv) and dioxane (0.73 mL) were added. The vessel was sealed and removed from the glove box, and then heated to 80 °C for 3 h. After cooling the reaction vessel to 23 °C, the reaction mixture was filtered over a pad of silica, washed with EtOAc (10 mL) and evaporated to dryness. The crude residue was dissolved in CH_2Cl_2 (0.5 mL), and the resulting solution was layered with benzene (0.1 mL) and hexanes (1.5 mL). The hexane and benzene layers mixed upon standing, and the resulting mixture was placed in a freezer (ca. –10 °C) overnight. After 12 h, the crystals that were formed were collected by filtration and washed with cold hexanes (4 mL) to yield amine **21** (27.8 mg, 68% yield) as a yellow solid. R_f 0.39 (8:1:1 Hexanes:EtOAc:CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49 (d, J = 7.8, 2H), 7.39 (s, 1H), 7.36 (d, J = 7.8, 1H), 7.07 (d, J = 7.8, 1H) 6.96 (d, J = 7.8, 2H), 3.87 (bs, 4H), 3.85 (bs, 3H), 2.95 (bs, 4H), 2.37 (bs, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.9, 150.3, 136.0, 133.7, 133.0, 130.0, 128.0, 125.0, 119.3, 114.3, 67.6, 55.5, 52.4, 18.2; IR (film): 2990, 2963, 2854, 2836, 1718, 1605, 1581, 1496, 1224, 1116, 1023 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{18}H_{21}NO_2H$, 284.1650; found 284.1648.

D. Key Optimization Studies



Entry	SIPr•HCl (mol%)	NaO*t*Bu (equiv)	temp	time	Conversion (%)
1	2.5	1.313	rt	24 h	59
2	5	1.325	rt	24 h	73
3	10	1.4	rt	24 h	92
4	30	1.6	rt	24 h	>95%
5	10	1.4	80 °C	3 h	>95%

Computational Methods

N,*N*-dimethyl phenylcarbamate and dimethyl amine are used as representatives of experimental substrates. *N,N'*-bis(2,6-dimethylphenyl)4,5-dihydroimidazol-2-ylidene is used as model for the experimental ligand, *N,N'*-bis(2,6-diisopropylphenyl)4,5-dihydroimidazol-2-ylidene (SIPr). Geometry optimizations and frequency calculations were performed using B3LYP and a mixed basis set employing SDD for metal and 6-31G(d) for other atoms. Single point energies were calculated with B3LYP and a mixed basis set of SDD for metal and 6-311+G(2d,p) basis set for other atoms. Energies reported are Gibbs free energies in solution, which involve zero-point vibrational energy corrections, thermal corrections to Gibbs free energy at 298 K, and solvation free energy corrections computed by singlet point CPCM calculations with B3LYP/SDD–6-311+G(2d,p) on gas-phase optimized geometries. In CPCM calculations, 1,4-dioxane was used as solvent. The molecular cavities were built up using the United Atom Topological Model (UAHF). Vibrational frequencies were calculated for all optimized structures to confirm the nature of the stationary points. All calculations were performed using Gaussian 09 package.

A. Complete Reference of Gaussian 09

Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2010**.

B. Single Point Calculations using Other DFT Methods and Basis Sets

We performed single point calculations for the energy profiles shown in Figures 2 in the manuscript using other DFT methods and basis sets. The geometries were optimized using B3LYP and a mixed basis set of SDD for metal and 6-31G(d) for other atoms. Different DFT methods (B3LYP, B3P86, B3PW91) and basis sets (6-31G(d), 6-311+G(2d,p)) were used to calculate the single point energies and solvation energy corrections for all species (shown in Figure S1 and Table S1).

Figure S1. Energy diagrams of nickel-catalyzed amination between *N,N*-dimethylphenylcarbamate and dimethylamine calculated using different DFT methods and basis sets (Energies are Gibbs free energies in kcal/mol).

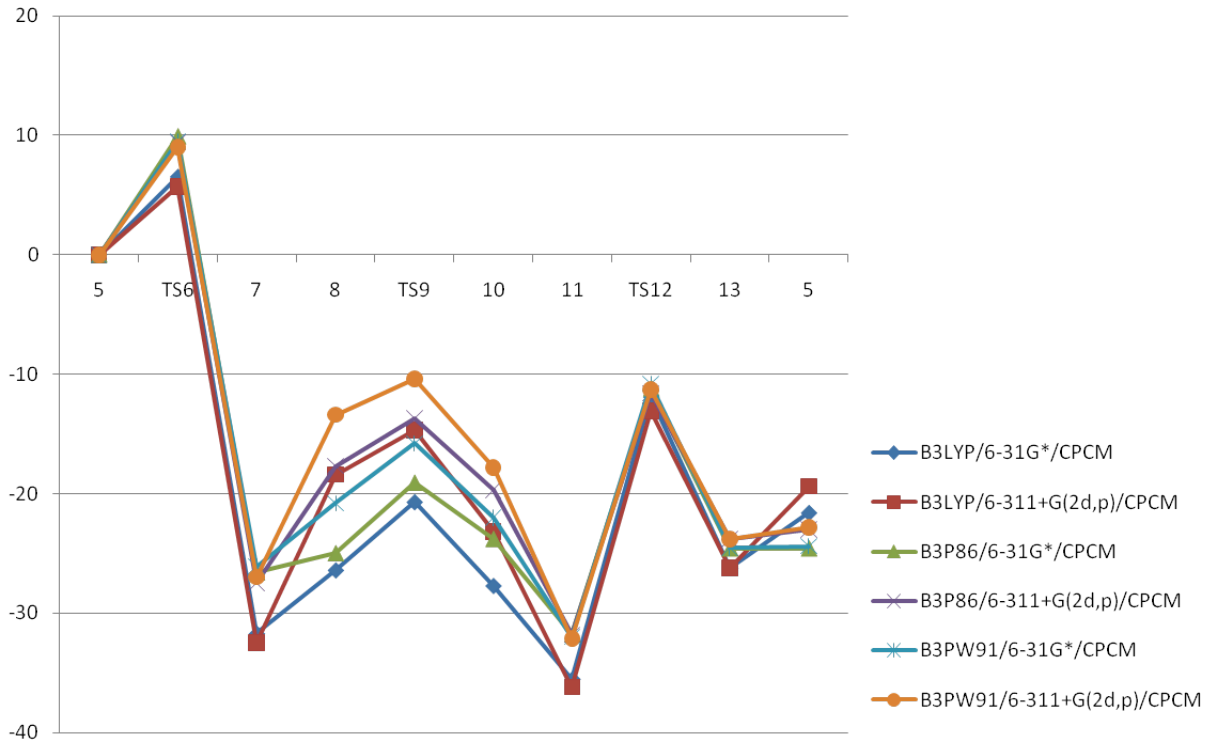


Table S1. Energies of nickel-catalyzed amination between *N,N*-dimethyl phenylcarbamate and dimethylamine calculated using different DFT methods and basis sets (Energies are Gibbs free energies in kcal/mol).

	5	**TS6**	**7**	**8**	**TS9**	**10**	**11**	**TS12**	**13**	**5**
B3LYP /6-31G*/CPCM	0.0	6.5	-31.7	-26.4	-20.7	-27.7	-35.5	-11.9	-26.2	-21.6
B3LYP /6-311+G(2d,p)/CPCM	0.0	5.7	-32.5	-18.4	-14.7	-23.2	-36.2	-13.1	-26.2	-19.4
B3P86 /6-31G*/CPCM	0.0	9.9	-26.6	-25.0	-19.1	-23.8	-31.8	-11.2	-24.6	-24.6
B3P86 /6-311+G(2d,p)/CPCM	0.0	9.4	-27.5	-17.7	-13.7	-19.7	-31.8	-11.6	-23.8	-23.0
B3PW91 /6-31G*/CPCM	0.0	9.5	-26.1	-20.8	-15.8	-22.0	-32.0	-10.8	-24.5	-24.4
B3PW91 /6-311+G(2d,p)/CPCM	0.0	9.0	-27.0	-13.4	-10.4	-17.8	-32.1	-11.3	-23.8	-22.8

C. The Cartesian coordinates (Å), and Gibbs free energies at 298K for the optimized structures.

For transition state structures, one imaginary frequency was observed and given below. For all minimum structures, no imaginary frequencies were observed.

5

Total SCF energy: -1572.50113709 a.u.

Enthalpy at 298K: -1571.908190 a.u.

Gibbs free energy at 298K: -1572.014494 a.u.

Free energy in solution at 298K: -1572.458643 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.41142000	1.91417000	1.53913500
C	1.36290900	1.90276200	3.21553400
C	-0.34955500	0.18778100	3.29867800
C	-0.96022300	0.70565600	2.11292100
H	-0.82116900	-0.65607900	3.79884900
C	0.78955400	0.75491200	3.82842700
H	1.24276900	0.34141700	4.72575200
H	-1.99320100	0.43162600	1.90213400
C	0.76238300	2.49168300	2.12454600
O	-1.30555300	2.88485100	0.90518900
C	-1.28374900	2.85234600	-0.43397100
O	-0.64872200	1.99267700	-1.07397200
H	1.15635000	3.41149500	1.69846600
H	2.26775500	2.34008300	3.63061600
Ni	-0.05263000	0.48757700	0.31068100
N	-2.01780300	3.82997300	-1.02560300
C	-2.76058200	4.83706800	-0.28136100
H	-3.83666900	4.74226800	-0.47975500

H	-2.58251500	4.71639100	0.78455100
H	-2.44192300	5.84153500	-0.58927000
C	-2.11353900	3.88690400	-2.47556300
H	-1.51984200	3.08153800	-2.90424900
H	-3.15899000	3.77869000	-2.79366700
H	-1.73884400	4.85079700	-2.84407900
C	0.40258700	-1.19786900	-0.38592500
N	-0.40520000	-2.28207800	-0.57864200
N	1.64334200	-1.57458500	-0.81013800
C	0.26193900	-3.42676000	-1.22639800
C	-1.81633400	-2.29835100	-0.33880200
C	1.73366000	-2.97584900	-1.25828500
C	2.80724400	-0.74023700	-0.76200500
H	0.11600700	-4.34818300	-0.65202800
C	-2.29648900	-2.89450700	0.84315700
C	-2.69477000	-1.75941500	-1.29883900
H	2.17445100	-3.03963700	-2.25957100
C	3.11754200	0.05914000	-1.87859700
C	3.63140400	-0.76363700	0.37936500
C	-3.67951500	-2.94280900	1.05274700
C	-1.34203400	-3.44511200	1.87614600
C	-4.07132900	-1.82782800	-1.05132000
C	-2.17594400	-1.09540700	-2.55220700
C	4.28327100	0.83278700	-1.83989400
C	2.19888300	0.11189400	-3.07641200
C	4.78987000	0.02180900	0.37648300
C	3.25895600	-1.57730400	1.59599600
C	-4.56316200	-2.41502300	0.11295900

H	-4.06191000	-3.39558600	1.96442800
H	-1.88344600	-3.76286400	2.77290500
H	-0.78777100	-4.31586100	1.50226200
H	-0.60267700	-2.69112600	2.16593600
H	-4.76108300	-1.41626900	-1.78446600
H	-1.43403100	-1.71486600	-3.06915400
H	-2.99525000	-0.89857800	-3.25148600
H	-1.68797200	-0.14281800	-2.31428400
C	5.11731200	0.81232100	-0.72365600
H	4.53383500	1.45638700	-2.69471100
H	2.63333000	0.72839000	-3.86989000
H	2.00644700	-0.88420800	-3.49321800
H	1.22808600	0.54038100	-2.80150400
H	5.43468600	0.01563600	1.25191600
H	2.32052900	-1.21522300	2.03122800
H	3.12156100	-2.63939200	1.35918400
H	4.03932800	-1.50626800	2.36025300
H	-5.63496400	-2.46119500	0.28809400
H	6.02127700	1.41590200	-0.70932200
H	-0.14612200	-3.59282000	-2.23246800
H	2.36419500	-3.56385400	-0.57873200

TS6

Total SCF energy:	-1572.48623239 a.u.
Enthalpy at 298K:	-1571.894822 a.u.
Gibbs free energy at 298K:	-1572.000684 a.u.
Free energy in solution at 298K:	-1572.449576 a.u.

Imaginary frequency: -194.54 cm^{-1}

Cartesian coordinates

ATOM	X	Y	Z
C	-0.12043700	1.77464900	1.67640100
C	1.26056900	2.19695900	3.61631800
C	-0.57945300	0.63003600	3.79176800
C	-0.91030600	0.86527400	2.43475600
H	-1.20510300	-0.03327100	4.38652400
C	0.49865700	1.27720400	4.37283100
H	0.74818100	1.09999700	5.41573100
H	-1.85157000	0.48556800	2.04185000
C	0.94530300	2.47470000	2.29733300
O	-1.07140700	3.10013900	0.62737000
C	-0.85726400	2.83253300	-0.60327400
O	-0.33887000	1.73576700	-1.03050600
H	1.52136400	3.19686400	1.72573600
H	2.11048400	2.69546200	4.07817000
Ni	0.01019700	0.48424400	0.43212300
C	0.25028700	-1.25728000	-0.39694400
N	-0.70811100	-2.17445900	-0.66715200
N	1.42305000	-1.76630600	-0.83825400
C	-0.20727400	-3.38309100	-1.35458800
C	1.30543400	-3.10384000	-1.45552100
H	-0.68346400	-3.49120100	-2.33603800
H	-0.43329000	-4.28330900	-0.77241200
H	1.66361500	-3.08266800	-2.49089600
H	1.90846700	-3.83735700	-0.90809000
N	-1.19085900	3.78784000	-1.53427400

C	-1.91513400	4.98533000	-1.14279900
H	-1.51117700	5.85319700	-1.67937100
H	-2.98729900	4.90570200	-1.38090400
H	-1.80221900	5.13595100	-0.07099000
C	-1.12780100	3.50534600	-2.95675900
H	-0.44104300	2.67965100	-3.13224600
H	-2.11615600	3.23979200	-3.36451000
H	-0.76952300	4.39386700	-3.49147200
C	-2.10205600	-2.01870200	-0.36474400
C	-2.60278300	-2.55157000	0.83863800
C	-2.93826200	-1.36663000	-1.29043900
C	-3.97201800	-2.42539200	1.10037700
C	-4.30172600	-1.26236500	-0.98928900
C	-4.81720000	-1.78806400	0.19356900
H	-4.37326300	-2.82826700	2.02700100
H	-4.96083000	-0.75963400	-1.69257100
H	-5.87831200	-1.69871900	0.41073200
C	2.69333100	-1.10583900	-0.73859300
C	3.10981200	-0.26133800	-1.78435300
C	3.50210100	-1.34687900	0.38756000
C	4.37362700	0.33301500	-1.68861500
C	4.75837800	-0.73274700	0.44363100
C	5.19435000	0.09775500	-0.58728900
H	4.71085200	0.98958200	-2.48681900
H	5.39385600	-0.90548900	1.30858000
H	6.17343200	0.56616500	-0.52978400
C	2.20615700	0.03743700	-2.95696400
H	1.82552600	-0.87538200	-3.43087500

H	1.33803000	0.62335000	-2.63238400
H	2.74283400	0.61030500	-3.71975300
C	3.01832800	-2.21246800	1.52715400
H	2.11328500	-1.79166200	1.98031000
H	2.77474200	-3.23154600	1.20156000
H	3.78312000	-2.28782100	2.30598600
C	-2.38167300	-0.75594500	-2.55442200
H	-1.74183200	0.10270800	-2.31803900
H	-1.77369600	-1.46873200	-3.12439300
H	-3.19236000	-0.41354200	-3.20547400
C	-1.68656700	-3.20909600	1.84383500
H	-1.15349400	-4.06931800	1.42048800
H	-0.92822900	-2.50348200	2.20232700
H	-2.25507200	-3.56631200	2.70795000

7

Total SCF energy: -1572.55602277 a.u.

Enthalpy at 298K: -1571.894822 a.u.

Gibbs free energy at 298K: -1572.065526 a.u.

Free energy in solution at 298K: -1572.510379 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ni	0.12795100	0.64169300	0.52753200
C	-0.10170700	-0.88518000	-0.54790800
C	-0.99135300	-2.38729000	-2.13656400
C	0.35171400	-2.93531600	-1.62950300
H	-1.81278500	-3.09651800	-2.00801000
H	0.23858800	-3.86534400	-1.05977300

N	0.82620100	-1.85203100	-0.74034300
N	-1.19064900	-1.19082600	-1.28997700
H	1.07219100	-3.11649700	-2.43225500
H	-0.95807200	-2.09293400	-3.19291600
C	-1.11658800	0.09956900	1.85787900
C	-1.79684400	1.14094700	2.52191100
C	-1.38352300	-1.20797100	2.30086300
C	-2.68754600	0.88692600	3.56904200
H	-1.61417200	2.17060400	2.22903300
C	-2.25810900	-1.47029600	3.36341000
H	-0.90603400	-2.05228100	1.81270900
C	-2.91876600	-0.42104400	4.00158200
H	-3.19546000	1.71763600	4.05578700
H	-2.42533400	-2.49712300	3.68481400
H	-3.60275100	-0.61810400	4.82386600
O	0.61706400	2.36438200	1.34744500
C	1.39645400	2.59490100	0.35613000
O	1.45507400	1.70759000	-0.57451400
N	2.13008300	3.73935100	0.28961200
C	2.09150600	4.71487400	1.36505500
H	3.07983500	4.81269200	1.83566800
H	1.79645200	5.69968200	0.97837200
H	1.36958700	4.39001200	2.11279000
C	3.03127000	3.99417200	-0.81805000
H	2.78995100	4.95367700	-1.29538000
H	4.07382300	4.03712200	-0.47213300
H	2.93101200	3.19391700	-1.54973400
C	2.20423200	-1.83852200	-0.31307200

C	3.15782100	-1.24022400	-1.16462800
C	2.58838300	-2.49690700	0.87018000
C	4.50304300	-1.27647300	-0.78360900
C	3.94756100	-2.50737200	1.21117500
C	4.89837700	-1.89787800	0.39894700
H	5.24547800	-0.81324100	-1.42843900
H	4.25492200	-3.00785000	2.12590100
H	5.94825200	-1.91880000	0.67912900
C	-2.32449600	-0.33469800	-1.53087900
C	-3.58524900	-0.70726800	-1.02307000
C	-2.16581800	0.80531600	-2.34582600
C	-4.67961500	0.12096100	-1.29745300
C	-3.28954200	1.60452500	-2.58955900
C	-4.53554600	1.27425500	-2.06402200
H	-5.65392500	-0.14707500	-0.89726100
H	-3.17884500	2.49047500	-3.20973300
H	-5.39616500	1.90753300	-2.26256400
C	2.76230200	-0.55789800	-2.45205400
H	2.13641900	-1.19510400	-3.08862300
H	2.20506400	0.35930400	-2.24061400
H	3.65330600	-0.29304900	-3.03001000
C	1.59815600	-3.17414400	1.78609000
H	1.13862000	-2.45353200	2.47129900
H	0.78478700	-3.65846000	1.23691500
H	2.09805900	-3.93771400	2.39061000
C	-3.78536000	-1.96323300	-0.21009900
H	-4.78694800	-1.97618300	0.22974500
H	-3.69160100	-2.86819100	-0.82608000

H	-3.06039700	-2.03168800	0.60450700
C	-0.84017500	1.17619300	-2.96863300
H	-0.14819000	1.60618100	-2.23613600
H	-0.33718900	0.30673000	-3.40789400
H	-0.99114500	1.90994900	-3.76698100

8

Total SCF energy: -1617.61569826 a.u.

Enthalpy at 298K: -1616.892203 a.u.

Gibbs free energy at 298K: -1617.003548 a.u.

Free energy in solution at 298K: -1617.459161 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ni	0.27367100	0.23273500	0.85607000
C	0.57760900	-0.00948900	-3.32150100
C	-0.94925500	-0.10216200	-3.22909200
H	1.02281100	-0.84450100	-3.86991100
H	-1.33970000	-1.06007200	-3.59216400
C	-0.14393900	-1.58750800	1.26533300
C	0.72561900	-2.69193100	1.19603700
C	-1.40315900	-1.81986800	1.85867600
C	0.36411400	-3.95630200	1.68104800
H	1.71599800	-2.56841800	0.76395300
C	-1.77193500	-3.07568000	2.35240100
H	-2.11954200	-1.00325200	1.93850200
C	-0.88874200	-4.15523400	2.26222900
H	1.06702800	-4.78463700	1.60713000
H	-2.75181600	-3.21103500	2.80741900

H	-1.17242800	-5.13405700	2.64175400
N	1.16730500	0.41760100	2.67440900
H	1.28210900	1.42124000	2.51342900
O	0.61150300	2.16516000	0.77827600
C	-0.13047300	3.25950100	1.26408500
C	-1.57764000	2.87528100	1.63919500
C	0.55664800	3.85553100	2.52274000
C	-0.14894100	4.37171900	0.18909900
H	-2.10593700	2.45345600	0.78086200
H	-1.58001500	2.11696200	2.43172100
H	-2.14706700	3.74113400	2.00374400
H	1.61055800	4.06549800	2.30577700
H	0.08058700	4.79067600	2.84564100
H	0.51096300	3.16165700	3.37253300
H	-0.72546600	5.24883400	0.51211500
H	0.87477300	4.69895500	-0.02688300
H	-0.58319000	4.00091300	-0.74371300
C	2.50410600	-0.20269400	2.70240200
H	2.39927000	-1.28941400	2.74080300
H	3.04780800	0.06904400	1.79412500
H	3.07797100	0.13047800	3.58039600
C	0.42766900	0.17510300	3.92237300
H	-0.51423700	0.72846200	3.90234400
H	0.19985500	-0.88958100	4.00836500
H	1.00980300	0.49127500	4.80075900
C	-0.05775100	0.03944600	-1.03351700
N	-1.19379000	0.02551100	-1.77586900
N	0.98397100	-0.03952700	-1.90167600

H	-1.45778900	0.69979300	-3.77245900
H	0.91694400	0.92266100	-3.78835200
C	-2.55647600	-0.05760800	-1.32168800
C	-3.34331100	1.11042900	-1.30450300
C	-3.11539400	-1.32285300	-1.04264500
C	-4.67459900	1.01130800	-0.88076300
C	-4.45012900	-1.37495100	-0.62426300
C	-5.22139900	-0.21856200	-0.52539100
H	-5.28429500	1.91071400	-0.84208200
H	-4.88731800	-2.34079700	-0.38456600
H	-6.25387300	-0.27975000	-0.19138700
C	2.37796900	-0.20568000	-1.58248100
C	3.19629400	0.92722600	-1.39795700
C	2.91466600	-1.51089700	-1.58302200
C	4.55004100	0.71747900	-1.10132400
C	4.27271700	-1.67106300	-1.28166400
C	5.08335300	-0.56723700	-1.02593800
H	5.19022600	1.58136300	-0.94150100
H	4.69444500	-2.67299200	-1.26087600
H	6.13550100	-0.70746500	-0.79152500
C	2.65092300	2.32541200	-1.52161700
H	2.15159000	2.47632800	-2.48756800
H	1.91420900	2.51671200	-0.72813400
H	3.46149100	3.05824800	-1.45022100
C	2.08783800	-2.71875100	-1.96220800
H	2.00544100	-2.80979100	-3.05460900
H	2.55802300	-3.63842700	-1.60080700
H	1.07629900	-2.67766900	-1.55381700

C	-2.34830900	-2.60655900	-1.25584700
H	-1.33241300	-2.55447100	-0.86223700
H	-2.85013800	-3.44054500	-0.75812200
H	-2.29050300	-2.85058300	-2.32625600
C	-2.81155200	2.43211100	-1.80450900
H	-3.01199000	2.54536400	-2.87968100
H	-3.29768600	3.27146200	-1.29823200
H	-1.73490200	2.52020200	-1.65462900

TS9

Total SCF energy: -1617.59749836 a.u.

Enthalpy at 298K: -1616.880462 a.u.

Gibbs free energy at 298K: -1616.995999 a.u.

Free energy in solution at 298K: -1617.453272 a.u.

Imaginary frequency: -915.73 cm^{-1}

Cartesian coordinates

ATOM	X	Y	Z
Ni	0.06798100	0.25408800	0.74762500
C	0.63890500	-1.24424600	-3.16919900
C	-0.88397600	-1.03503700	-3.18180100
H	0.92388700	-2.28618200	-3.34539600
H	-1.43689000	-1.94965900	-3.41565100
C	-0.21754800	-1.39231300	1.60651700
C	0.85086800	-2.22614700	1.97978200
C	-1.51132400	-1.77583200	2.00272600
C	0.63570800	-3.39724700	2.71639800
H	1.86902800	-1.96248800	1.70368100
C	-1.72832600	-2.94604000	2.73980800

H	-2.36694900	-1.15775700	1.74128500
C	-0.65552100	-3.76391200	3.10008400
H	1.48387100	-4.02026900	2.99469400
H	-2.74086300	-3.21392200	3.03634900
H	-0.82294700	-4.67146800	3.67499200
N	0.30201900	1.19808400	2.39771200
H	0.44824400	2.17268200	1.54043500
O	0.49876100	2.64993400	0.44943900
C	0.44829700	4.07271600	0.43913800
C	-0.89721400	4.55965400	1.01643400
C	1.60718600	4.61565700	1.30148600
C	0.60936500	4.58726500	-1.00175600
H	-1.73259000	4.17194400	0.42331800
H	-1.02380600	4.20779600	2.04687100
H	-0.96153100	5.65540800	1.02372400
H	2.56571700	4.25127100	0.91536400
H	1.63109500	5.71302800	1.30738200
H	1.50852600	4.27415200	2.33879400
H	0.55896100	5.68292600	-1.03570500
H	1.57567800	4.28071900	-1.41565600
H	-0.17968700	4.19266500	-1.64989500
C	1.51082700	0.91243600	3.16627000
H	1.44547000	-0.04834100	3.69708500
H	2.37687400	0.87500000	2.49685900
H	1.69312300	1.70025200	3.91600600
C	-0.86123500	1.35035600	3.26678200
H	-1.73242300	1.65038800	2.67433000
H	-1.10972500	0.41590200	3.79009100

H	-0.68330700	2.12644700	4.02996400
C	-0.04665400	-0.45100500	-1.04400700
N	-1.16039400	-0.59680200	-1.79648600
N	1.00928600	-0.83117600	-1.79823100
H	-1.19859600	-0.25906300	-3.88860700
H	1.16033600	-0.62093000	-3.90316600
C	-2.51744600	-0.35942100	-1.38485600
C	-3.02682300	0.95228400	-1.42000700
C	-3.32540700	-1.46017100	-1.03637900
C	-4.36206600	1.15277400	-1.04954400
C	-4.65621900	-1.21314300	-0.67817600
C	-5.17108100	0.08141800	-0.67691400
H	-4.76728900	2.16128700	-1.06406500
H	-5.28948500	-2.05015200	-0.39533900
H	-6.20555900	0.25463400	-0.39238500
C	2.38129800	-0.92410600	-1.37507900
C	3.19374700	0.22482100	-1.42304100
C	2.89775600	-2.18297900	-1.00543400
C	4.53398800	0.10094000	-1.03592100
C	4.24397600	-2.25882300	-0.62816800
C	5.05574600	-1.12652600	-0.63445800
H	5.17126600	0.98115900	-1.05964100
H	4.65327300	-3.21987400	-0.32698600
H	6.09793200	-1.20330400	-0.33587000
C	2.64772500	1.55623700	-1.87179900
H	2.10025700	1.47226500	-2.81884900
H	1.95596600	1.97204600	-1.12838500
H	3.46336100	2.27132000	-2.02041200

C	2.05084400	-3.43443700	-1.02349200
H	1.93689200	-3.82951000	-2.04257300
H	2.51810600	-4.22228200	-0.42534700
H	1.05280900	-3.25683100	-0.61542500
C	-2.79487300	-2.87468400	-1.04605700
H	-1.82663000	-2.94501000	-0.54353100
H	-3.48710800	-3.54672000	-0.53057000
H	-2.67488800	-3.25695700	-2.06899600
C	-2.16432100	2.11278500	-1.84786400
H	-1.72871300	1.94801300	-2.84183600
H	-2.75512400	3.03293700	-1.89413500
H	-1.33372000	2.27215700	-1.15161300

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Total SCF energy: -1617.60755966 a.u.

Enthalpy at 298K: -1616.886029 a.u.

Gibbs free energy at 298K: -1617.005198 a.u.

Free energy in solution at 298K: -1618.06911822 a.u.

ATOM	X	Y	Z
Ni	0.01811400	-0.00789400	0.73710000
C	-1.46147700	-0.65556900	-3.17658300
C	-1.36713800	0.88052500	-3.16521300
H	-2.47123400	-1.01615700	-3.39540700
H	-2.33843500	1.36219300	-3.31909900
C	-1.59029000	0.13341800	1.69822200
C	-2.28243500	-1.01246600	2.12834700
C	-2.07867400	1.38458100	2.11371200
C	-3.42461400	-0.91112100	2.93171100

H	-1.92911400	-2.00112600	1.84335600
C	-3.22052600	1.48756500	2.91712700
H	-1.56350600	2.29548400	1.81695100
C	-3.90078400	0.33985000	3.32929300
H	-3.93859100	-1.81591700	3.25153000
H	-3.57392300	2.46996000	3.22567800
H	-4.78625800	0.41894100	3.95542100
N	1.17413500	-0.09719100	2.13350200
H	2.67683600	-0.23504700	0.91238700
O	3.27783200	-0.30710800	0.12449300
C	4.65312400	-0.37342700	0.51945100
C	5.04658500	0.91428800	1.26296500
C	4.88367800	-1.60527000	1.41097300
C	5.44908300	-0.50255800	-0.78415700
H	4.85866200	1.78916500	0.63106600
H	4.45936000	1.02661400	2.18186100
H	6.10792300	0.90863500	1.53986100
H	4.56843900	-2.51488100	0.88824400
H	5.94115400	-1.71040700	1.68263000
H	4.30464700	-1.52887400	2.33887100
H	6.52542300	-0.55634300	-0.58511400
H	5.15086300	-1.40772100	-1.32444200
H	5.25904000	0.35947700	-1.43289200
C	1.19092800	-1.29158100	2.97149400
H	0.40146200	-1.26826600	3.74184000
H	1.04419900	-2.18898900	2.36180500
H	2.15529100	-1.39465500	3.49893200
C	1.38718900	1.09362400	2.94908400

H	1.39258400	1.99087200	2.32173700
H	0.60298700	1.21668400	3.71523800
H	2.35419500	1.04547800	3.47984200
C	-0.69728100	0.05232200	-1.04722700
N	-0.85847900	1.16043000	-1.80578100
N	-1.06625400	-1.01121300	-1.79693500
H	-0.67331400	1.27045600	-3.91768200
H	-0.77501600	-1.11746700	-3.89558400
C	-0.53896600	2.50409000	-1.40966500
C	0.79324300	2.94986400	-1.51596600
C	-1.57756500	3.35886300	-0.98838500
C	1.07627500	4.27000000	-1.14123800
C	-1.24697200	4.66934000	-0.62523100
C	0.06967100	5.12150900	-0.69230700
H	2.09963600	4.62969600	-1.21338800
H	-2.03451600	5.33789500	-0.28689200
H	0.30894000	6.14207900	-0.40521400
C	-0.99116200	-2.38922300	-1.39660400
C	0.23987500	-3.06784700	-1.48814900
C	-2.17161400	-3.04149900	-0.98705900
C	0.27405000	-4.41787500	-1.11416800
C	-2.08872500	-4.39051100	-0.62448000
C	-0.87514200	-5.07377200	-0.68007600
H	1.21622100	-4.95670700	-1.17542600
H	-2.98806800	-4.90533900	-0.29620600
H	-0.82803900	-6.12141700	-0.39474800
C	1.49768200	-2.38825500	-1.97666400
H	1.30501400	-1.74316600	-2.84115900

H	1.96557600	-1.76118100	-1.20737300
H	2.23639000	-3.13746700	-2.28018100
C	-3.49628900	-2.31717300	-0.93158500
H	-3.84949900	-2.03336400	-1.93170800
H	-4.26429000	-2.95690400	-0.48661100
H	-3.42836600	-1.40563600	-0.33036400
C	-3.01369900	2.89355000	-0.92818300
H	-3.10563500	1.93495300	-0.41006300
H	-3.63036200	3.62276000	-0.39452900
H	-3.44513200	2.77789800	-1.93167800
C	1.89909200	2.05525700	-2.02481900
H	1.57534300	1.45447900	-2.88222800
H	2.75429700	2.65914900	-2.34595100
H	2.26039500	1.35487600	-1.26127800

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Total SCF energy: -1383.92420628 a.u.

Enthalpy at 298K: -1383.349281 a.u.

Gibbs free energy at 298K: -1383.451204 a.u.

Free energy in solution at 298K: -1383.82905792 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ni	-0.00651200	0.32201300	1.11357500
C	-0.75425200	-2.29259400	-2.09268600
C	0.78083500	-2.36467000	-2.01544700
H	-1.23527300	-3.26116800	-1.92012100
H	1.14046100	-3.34407100	-1.67621900
C	-0.00458600	1.95291700	0.16508500

C	-1.20620000	2.61324000	-0.15162300
C	1.19795100	2.61813900	-0.13850700
C	-1.20690400	3.87909100	-0.74934800
H	-2.16075200	2.14219700	0.07476900
C	1.19996100	3.88403300	-0.73671100
H	2.15210200	2.15168100	0.09927500
C	-0.00320600	4.52125400	-1.04668700
H	-2.15371800	4.36587400	-0.97751400
H	2.14722700	4.37441600	-0.95500500
H	-0.00271400	5.50534800	-1.50935100
C	0.00387800	-0.81407000	-0.40013500
N	-1.08459400	-1.35294800	-1.00105000
N	1.09907100	-1.33216300	-1.00751300
H	-1.10541000	-1.90641800	-3.05552700
H	1.26406500	-2.14247500	-2.97131200
N	-0.01767300	0.65911300	2.86413400
C	-1.21923200	1.05233400	3.58131600
H	-1.26678700	0.57098100	4.57424300
H	-1.25903900	2.14372000	3.75062100
H	-2.11378600	0.76185800	3.02175400
C	1.17190100	1.06156700	3.59595900
H	1.20083600	2.15315600	3.76611300
H	1.21145400	0.58017600	4.58922800
H	2.07552100	0.77888500	3.04701600
C	-2.45148700	-1.09223600	-0.64742600
C	-3.00804500	-1.75180400	0.46637100
C	-3.21936000	-0.22910900	-1.45452200
C	-4.35244000	-1.51288900	0.77443000

C	-4.56118900	-0.02319500	-1.11127500
C	-5.12548800	-0.65557800	-0.00560200
H	-4.79347700	-2.01209400	1.63352200
H	-5.16331100	0.64754500	-1.71889200
H	-6.16807300	-0.48178300	0.24699500
C	2.46354600	-1.07937800	-0.63768300
C	3.23939400	-0.23092400	-1.45228500
C	3.01041000	-1.72844700	0.48654500
C	4.58071400	-0.02798700	-1.10695500
C	4.35518200	-1.49234000	0.79724900
C	5.13620100	-0.64930000	0.00984000
H	5.18975400	0.63011600	-1.72137600
H	4.78988900	-1.98307100	1.66446600
H	6.17892900	-0.47921400	0.26441700
C	2.64762900	0.46793100	-2.65355300
H	1.78116900	1.07378100	-2.36922000
H	3.38673500	1.13122900	-3.11285000
H	2.32055300	-0.23988300	-3.42577900
C	2.18311900	-2.64717000	1.35480800
H	1.44582300	-2.08260500	1.93878300
H	1.62858000	-3.38543800	0.76371100
H	2.82299300	-3.19144400	2.05609300
C	-2.18927100	-2.68801200	1.32359300
H	-1.44973200	-2.13717100	1.91774600
H	-2.83440300	-3.23862100	2.01500500
H	-1.63776200	-3.41937500	0.72113900
C	-2.62754800	0.47447500	-2.65323100
H	-2.48094100	-0.21074400	-3.49898100

H	-3.29407100	1.27102100	-2.99707300
H	-1.66121200	0.92756500	-2.41389500

TS12

Total SCF energy: -1383.89159731 a.u.

Enthalpy at 298K: -1383.317527 a.u.

Gibbs free energy at 298K: -1383.349281 a.u.

Free energy in solution at 298K: -1383.792104 a.u.

Imaginary frequency: -386.75 cm^{-1}

Cartesian coordinates

ATOM	X	Y	Z
Ni	-0.00109900	0.42569300	0.99488900
C	-0.77285500	-2.85314000	-1.50021200
C	0.76795800	-2.85430100	-1.50007500
H	-1.19523000	-3.76552100	-1.06242200
H	1.18888800	-3.76744200	-1.06248000
C	0.00349100	2.21436800	0.27025900
C	-1.20317200	2.74160100	-0.25975400
C	1.21485400	2.73773400	-0.25287500
C	-1.19111200	3.70148900	-1.27155600
H	-2.15939100	2.37462000	0.10075100
C	1.21158900	3.69772500	-1.26465300
H	2.16785400	2.36746200	0.11276000
C	0.01249800	4.19377000	-1.78507700
H	-2.13869900	4.06672900	-1.66376900
H	2.16255500	4.05998800	-1.65141000
H	0.01592200	4.94761100	-2.56747400

C	-0.00122400	-1.03168800	-0.17677200
N	-1.09240900	-1.68136000	-0.66215900
N	1.08912300	-1.68322900	-0.66160100
H	-1.19369900	-2.74077400	-2.50575200
H	1.18919100	-2.74223200	-2.50549200
N	-0.00240000	1.88059300	2.10566600
C	-1.21022900	2.44382700	2.69724600
H	-1.19619700	2.28049100	3.78385100
H	-1.29784000	3.52832100	2.51183200
H	-2.09863500	1.94849700	2.30130200
C	1.20261600	2.44200000	2.70468900
H	1.29310800	3.52632100	2.51965400
H	1.18149900	2.27889300	3.79121200
H	2.09275200	1.94522300	2.31444800
C	-2.45535100	-1.32936200	-0.38659100
C	-3.07366400	-1.83157800	0.77468500
C	-3.15761300	-0.53358900	-1.31204000
C	-4.41786300	-1.51424800	1.00134500
C	-4.50178500	-0.24306600	-1.04899700
C	-5.12930800	-0.72753500	0.09718100
H	-4.90738600	-1.89172500	1.89575500
H	-5.05622200	0.37305500	-1.75252400
H	-6.17377600	-0.49302800	0.28535500
C	2.45257900	-1.33382600	-0.38507800
C	3.15689000	-0.53907800	-1.30983900
C	3.06908300	-1.83738200	0.77658400
C	4.50139100	-0.25102000	-1.04572000
C	4.41366500	-1.52250700	1.00432000

C	5.12719000	-0.73689100	0.10082700
H	5.05745500	0.36427400	-1.74869200
H	4.90186500	-1.90102200	1.89901600
H	6.17194500	-0.50430000	0.28981900
C	-2.47914700	0.02623300	-2.53979000
H	-1.66824000	0.70771000	-2.26052900
H	-2.04785000	-0.75954600	-3.17162900
H	-3.19336800	0.58571300	-3.15175400
C	-2.30462300	-2.66685000	1.76990600
H	-1.81371300	-3.52543500	1.29637400
H	-1.51685200	-2.07273100	2.24964900
H	-2.96839300	-3.04863400	2.55181000
C	2.48016300	0.02250600	-2.53772400
H	3.19579300	0.58071300	-3.14919200
H	2.04747600	-0.76218700	-3.16996500
H	1.67059100	0.70557300	-2.25849000
C	2.29775800	-2.67154300	1.77095800
H	1.51117900	-2.07591500	2.25079000
H	1.80499700	-3.52862100	1.29662300
H	2.96032600	-3.05542400	2.55285300

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Total SCF energy:	-1383.91740982 a.u.
Enthalpy at 298K:	-1383.341905 a.u.
Gibbs free energy at 298K:	-1383.437013 a.u.
Free energy in solution at 298K:	-1383.813068 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Ni	-0.00066800	0.37762900	0.70290000
C	-0.75518700	-3.15373300	-1.29347900
C	0.78662100	-3.15961400	-1.27005700
H	-1.18458600	-4.03027400	-0.79273000
H	1.19219300	-4.02007800	-0.72236100
C	-0.01519200	3.07540800	0.58505300
C	-1.23292300	3.53284900	0.04866200
C	1.17841800	3.56747300	0.02576900
C	-1.24993300	4.43044700	-1.01803000
H	-2.17683800	3.17885500	0.44210100
C	1.14922400	4.46472200	-1.04138400
H	2.13963400	3.24244900	0.40187200
C	-0.06211100	4.90537200	-1.57422600
H	-2.20790800	4.75942400	-1.41243100
H	2.08971800	4.82096200	-1.45390700
H	-0.08007600	5.60695500	-2.40325400
C	0.00598800	-1.18726600	-0.16772200
N	-1.08346500	-1.91682200	-0.56705100
N	1.10277000	-1.89876900	-0.58023500
H	-1.15648900	-3.12769600	-2.31477200
H	1.22042100	-3.17637500	-2.27761600
N	0.00698200	2.12767900	1.68903000
C	-1.18930600	2.20936700	2.56519500
H	-1.05518000	1.50847000	3.39001100
H	-1.32029200	3.22856300	2.96241000
H	-2.08276100	1.90525500	2.02204300

C	1.22853500	2.21967900	2.52765400
H	1.35783400	3.23763000	2.92892200
H	1.13012600	1.51042600	3.35025300
H	2.10849000	1.93247400	1.95390700
C	-2.44561000	-1.53130500	-0.35759400
C	-3.12118800	-1.98932000	0.78993300
C	-3.10043100	-0.75223600	-1.33137900
C	-4.47031000	-1.65303800	0.94922300
C	-4.45054400	-0.43839500	-1.13672300
C	-5.13432700	-0.88616400	-0.00715500
H	-5.00121100	-1.99673500	1.83396400
H	-4.96624400	0.16521800	-1.88003100
H	-6.18391700	-0.63702000	0.12783900
C	2.46129200	-1.50389300	-0.36480500
C	3.11747900	-0.73335600	-1.34448100
C	3.13349900	-1.94409200	0.79217000
C	4.46437300	-0.40853000	-1.14599100
C	4.47967200	-1.59720500	0.95467900
C	5.14422600	-0.83779500	-0.00715400
H	4.98055000	0.18888400	-1.89388800
H	5.00740400	-1.92712800	1.84652200
H	6.19126600	-0.58017700	0.13100500
C	-2.35328600	-0.23043500	-2.53455000
H	-1.52350400	0.41385000	-2.21950400
H	-1.92179000	-1.03923600	-3.13705100
H	-3.01697600	0.35048600	-3.18297900
C	-2.39661300	-2.78938500	1.84499100
H	-2.01405500	-3.74068200	1.45401000

H	-1.53424800	-2.22891400	2.22579300
H	-3.06137800	-3.01914200	2.68391100
C	2.37422200	-0.23332800	-2.55929600
H	3.03780500	0.34331100	-3.21163200
H	1.95237700	-1.05384700	-3.15288800
H	1.53761600	0.40914900	-2.25912300
C	2.40858000	-2.73626900	1.85310900
H	1.53979900	-2.17726000	2.22151000
H	2.03570100	-3.69523500	1.47163100
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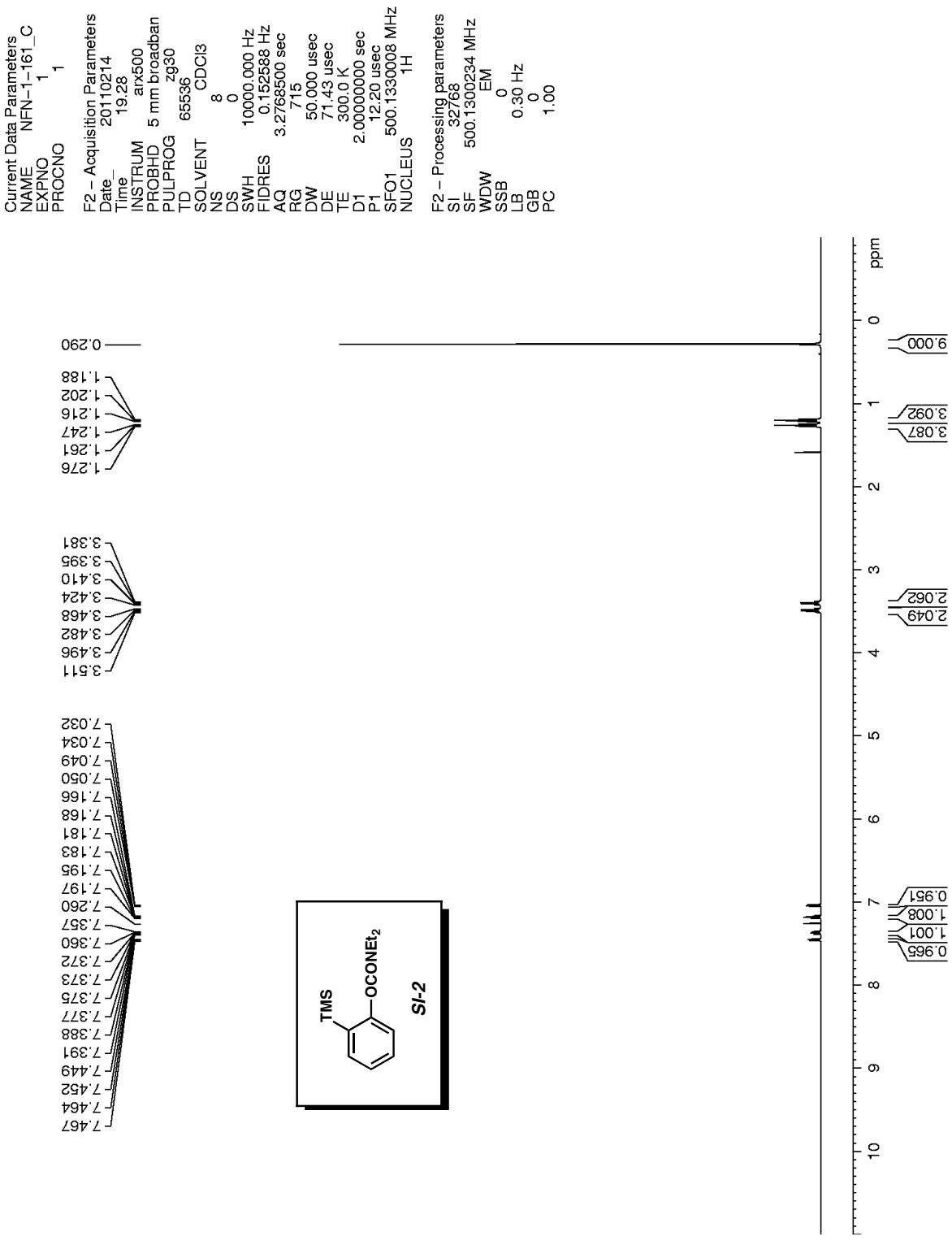
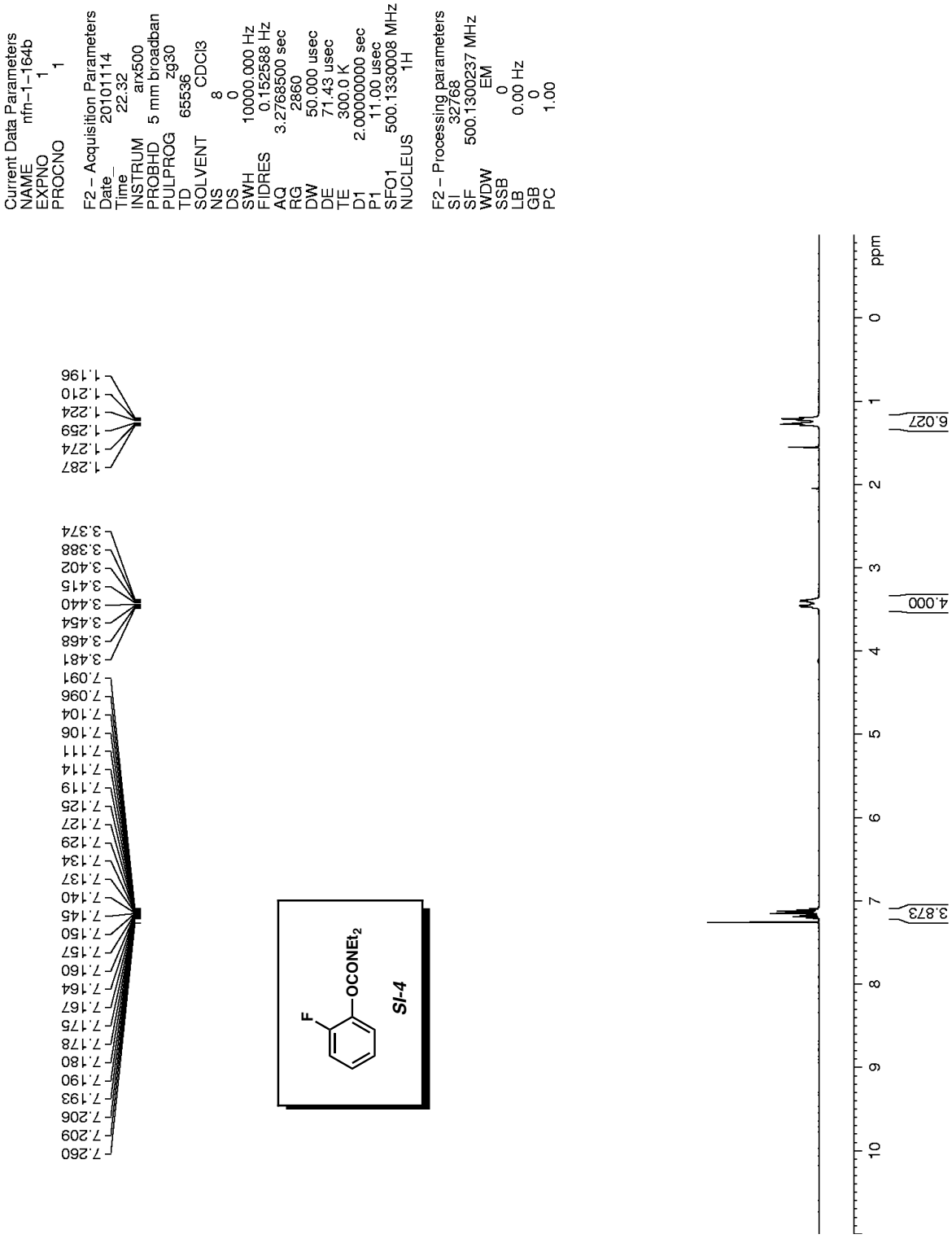
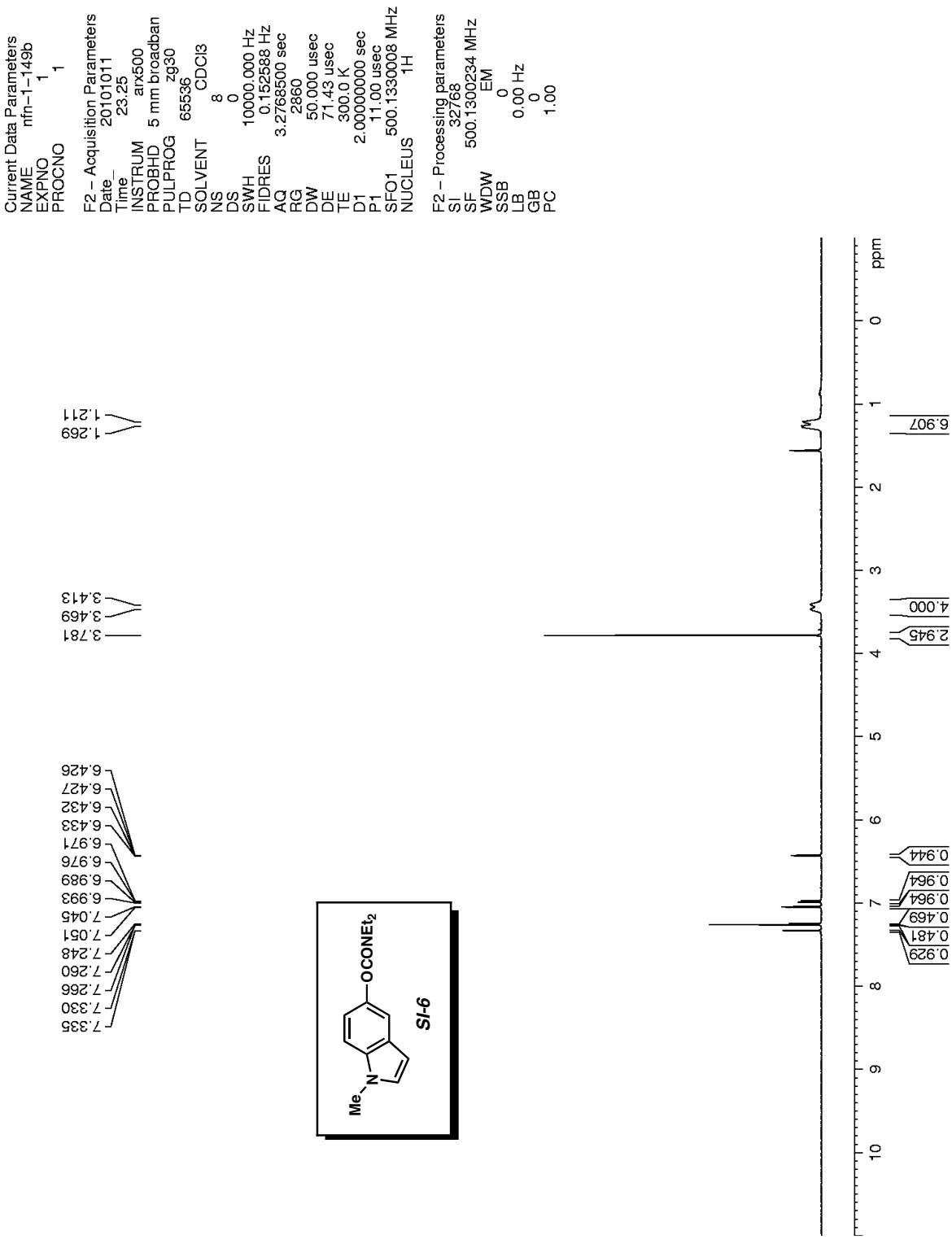
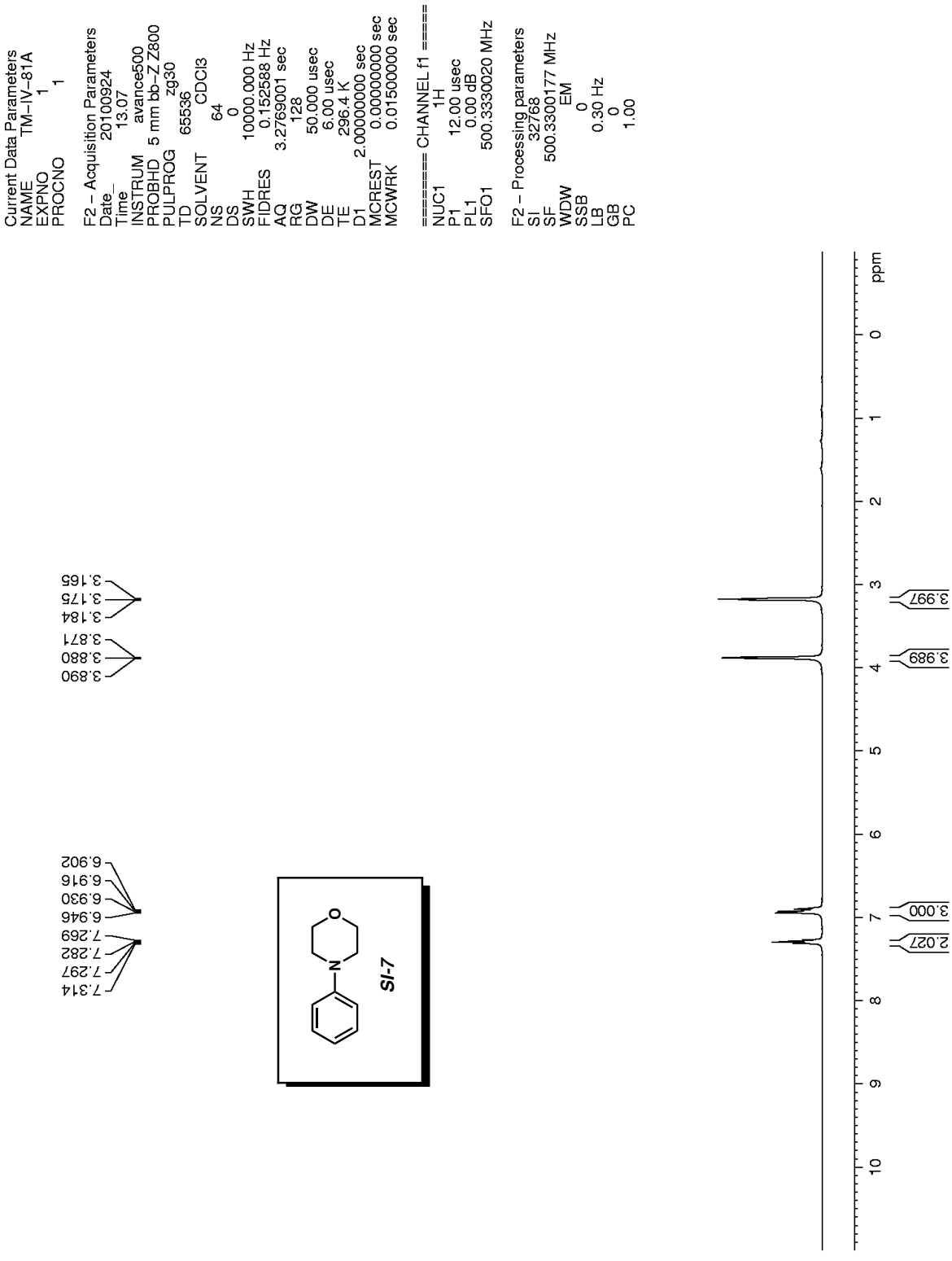
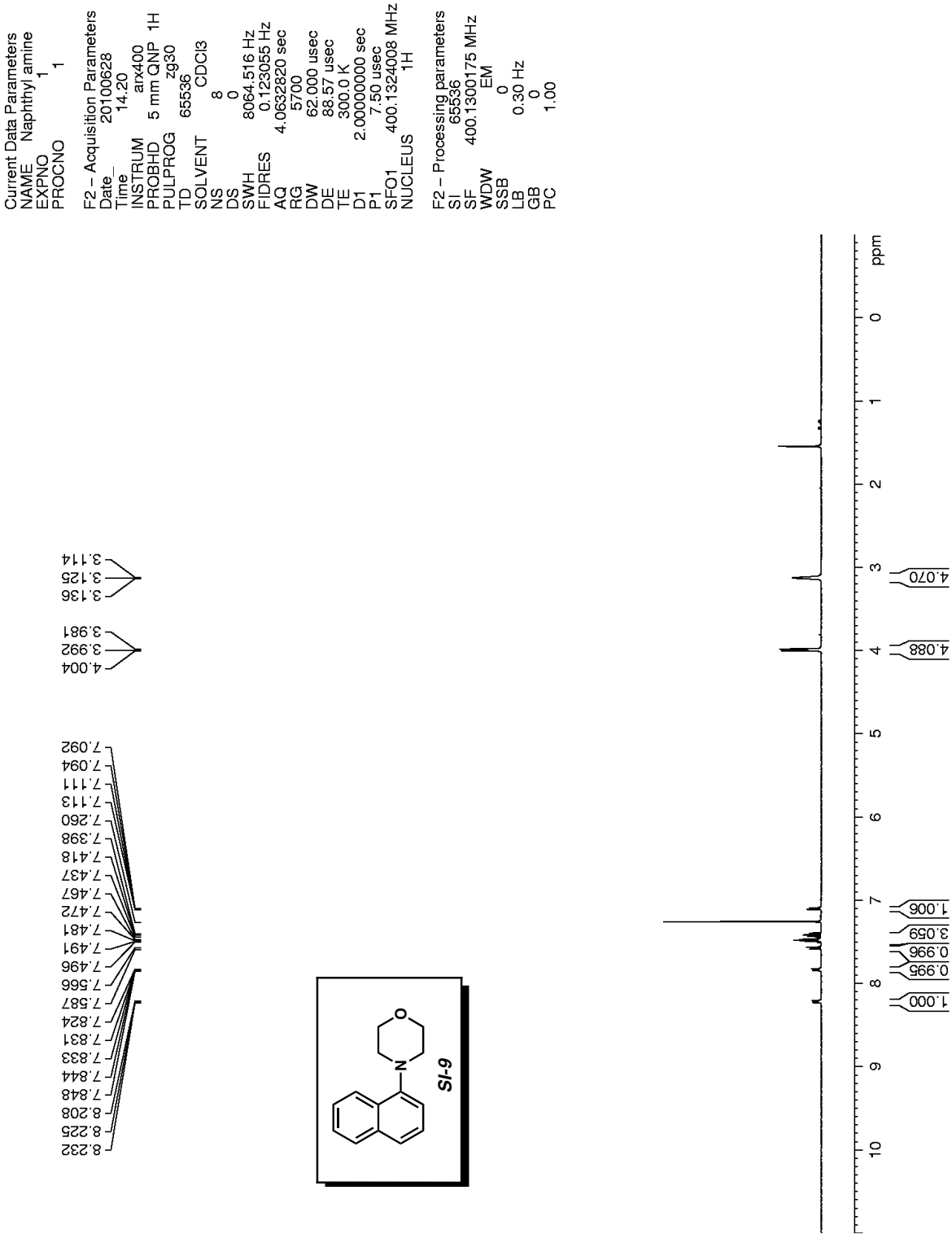
^{1}H NMR Spectra

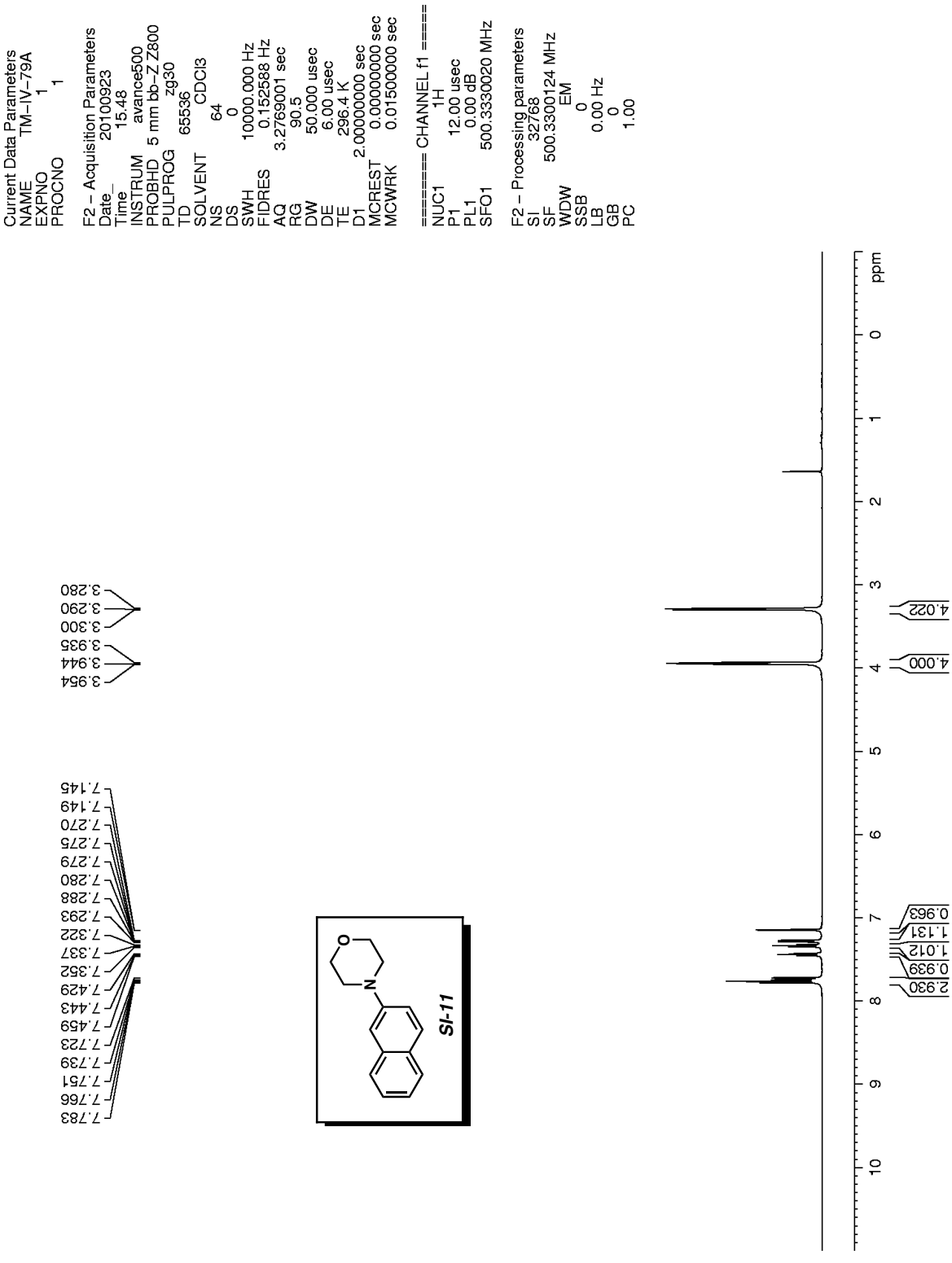


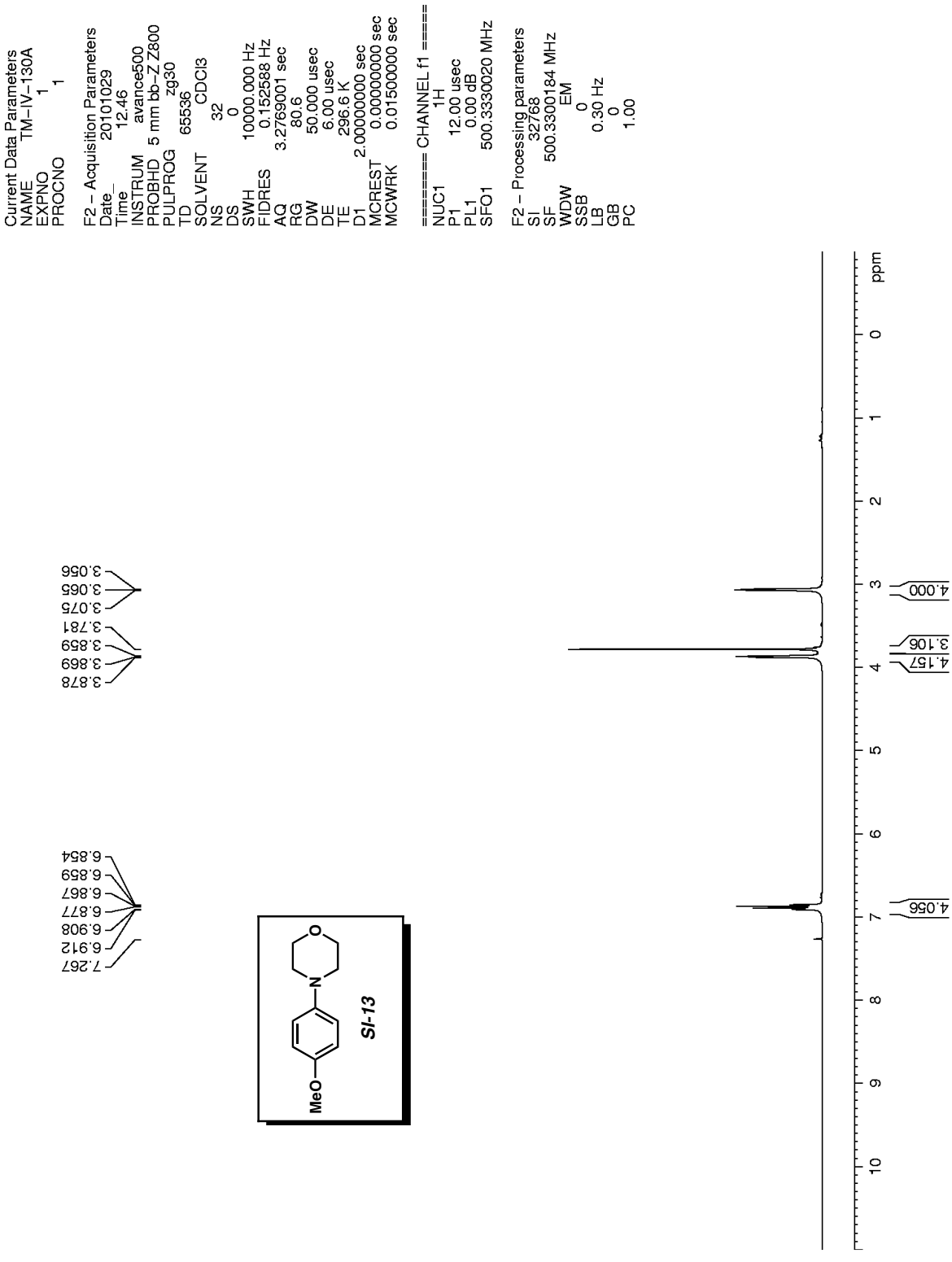


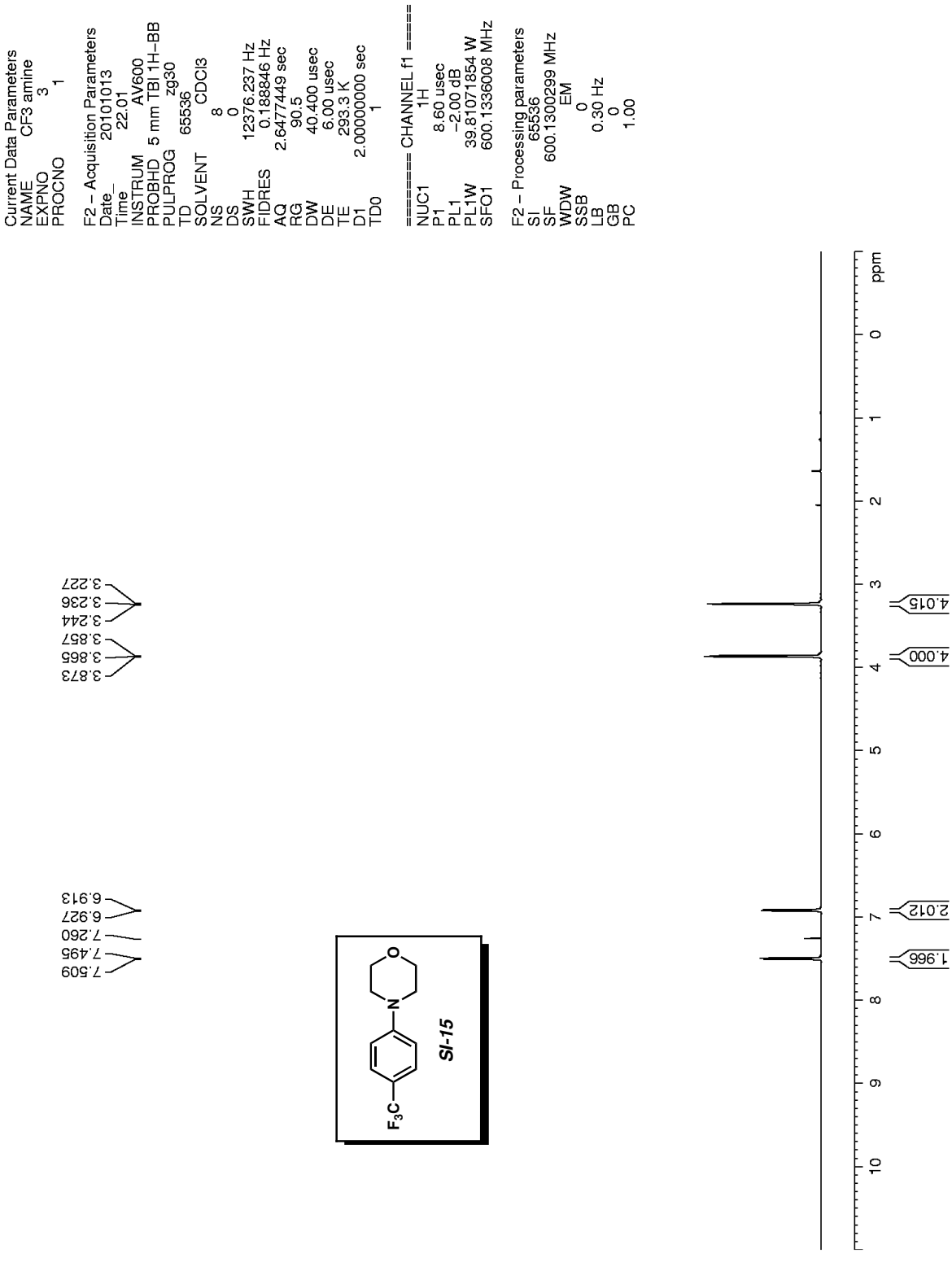


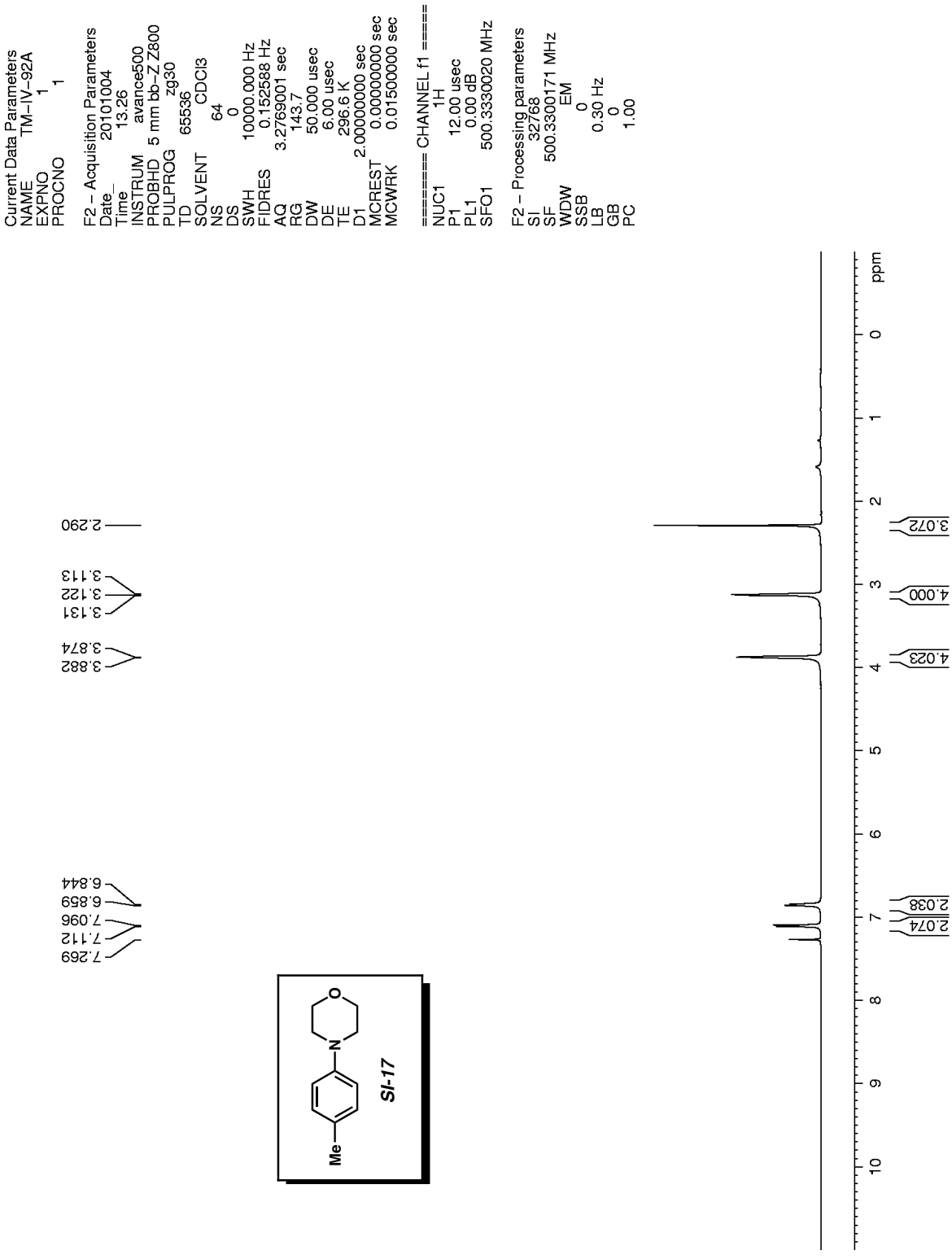








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EXPNO 1
PROCNO 1
F2 – Acquisition Parameters
Date_ 20101004
Time 13.26
INSTRUM avance500
PROBHD 5 mm bb-Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2769001 sec
RG 143.7
DW 50.000 usec
DE 6.00 usec
TE 296.6 K
D1 2.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
SFO1 500.3330020 MHz
F2 – Processing parameters
SI 32768
SF 500.3300171 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.290
3.113
3.122
3.131
3.874
3.882
6.844
6.859
7.096
7.112
7.269
Me
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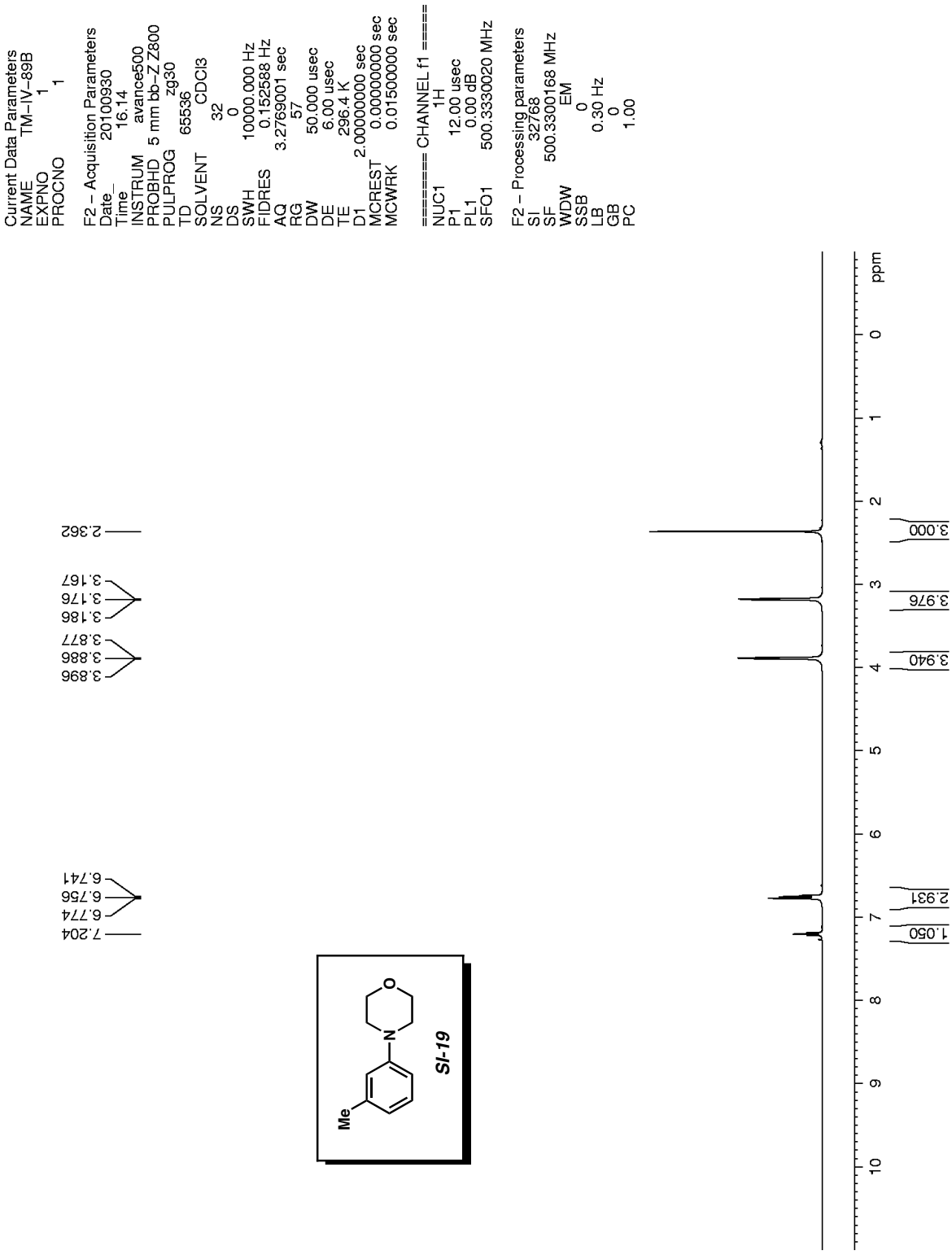
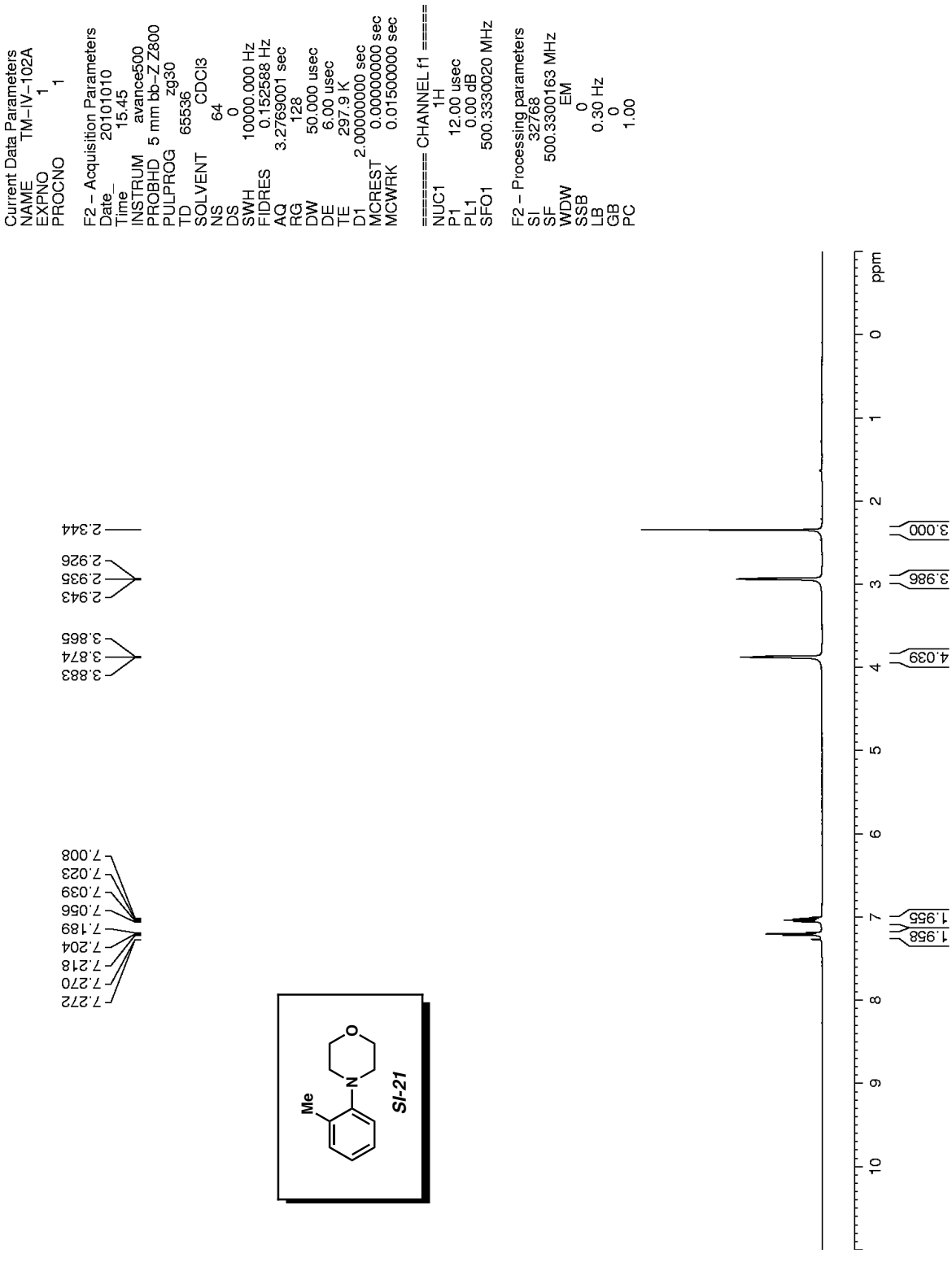
4.000
4.023
2.038
2.074
ppm




Current Data Parameters
NAME TM–IV–102A
EXPNO 1
PROCNO 1
F2 – Acquisition Parameters
Date_ 20101010
Time 15.45
INSTRUM avance500
PROBHD 5 mm bb–Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 64
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2769001 sec
RG 128
DW 50.000 usec
DE 6.00 usec
TE 297.9 K
D1 2.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
SFO1 500.3330020 MHz
F2 – Processing parameters
SI 32768
SF 500.3300163 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.344
2.926
2.935
2.943
3.865
3.874
3.883
7.008
7.023
7.039
7.056
7.189
7.204
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7.272
Me
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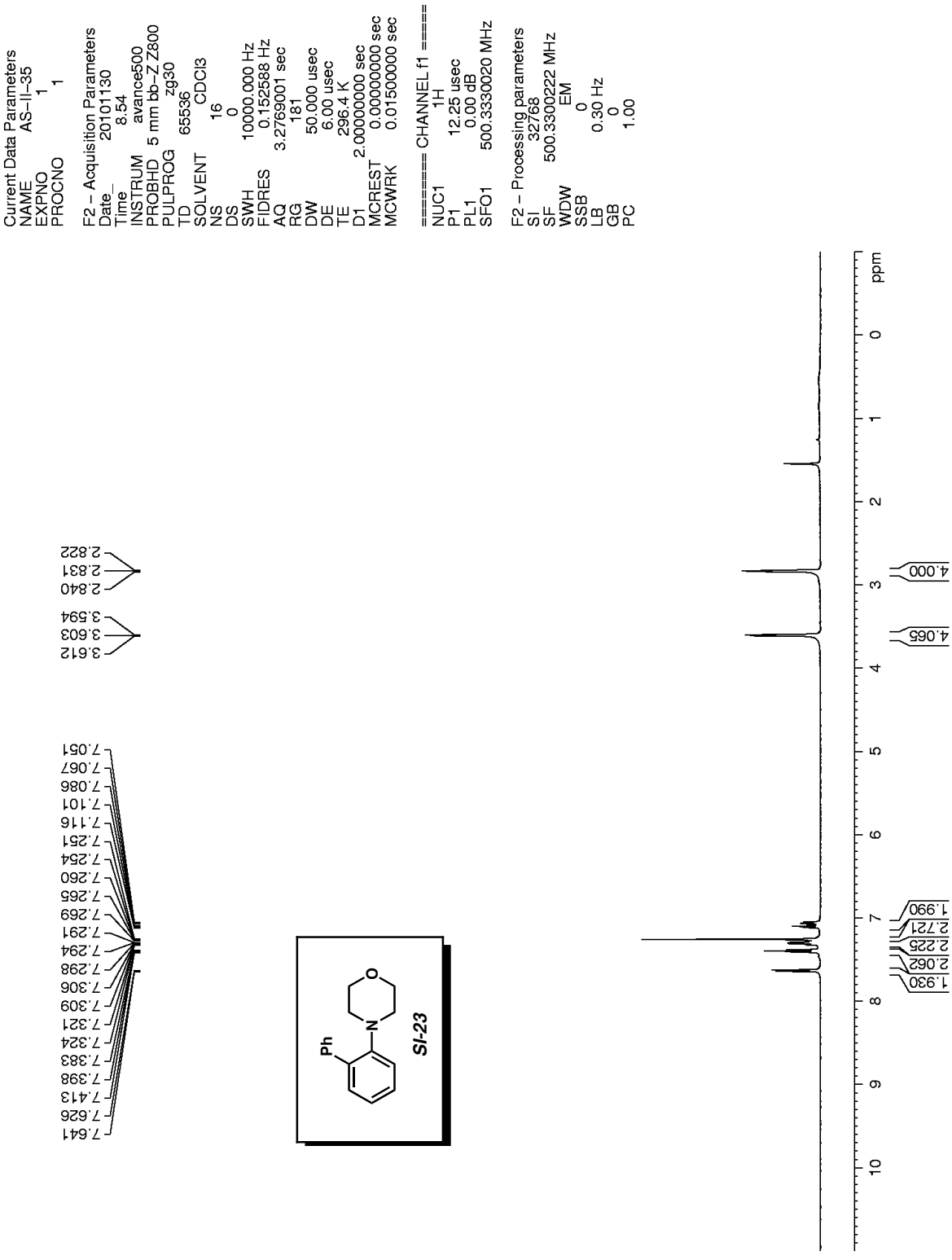
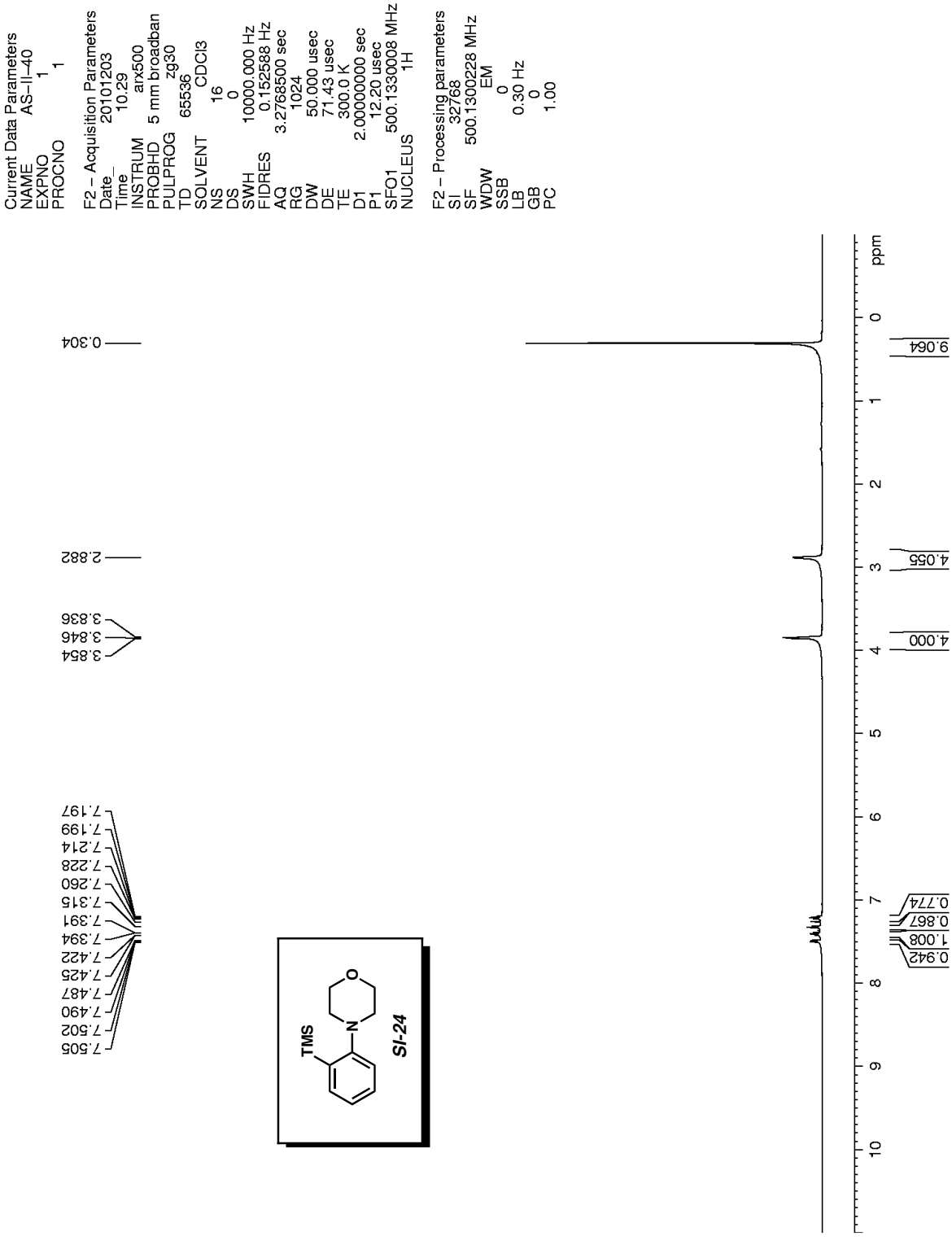
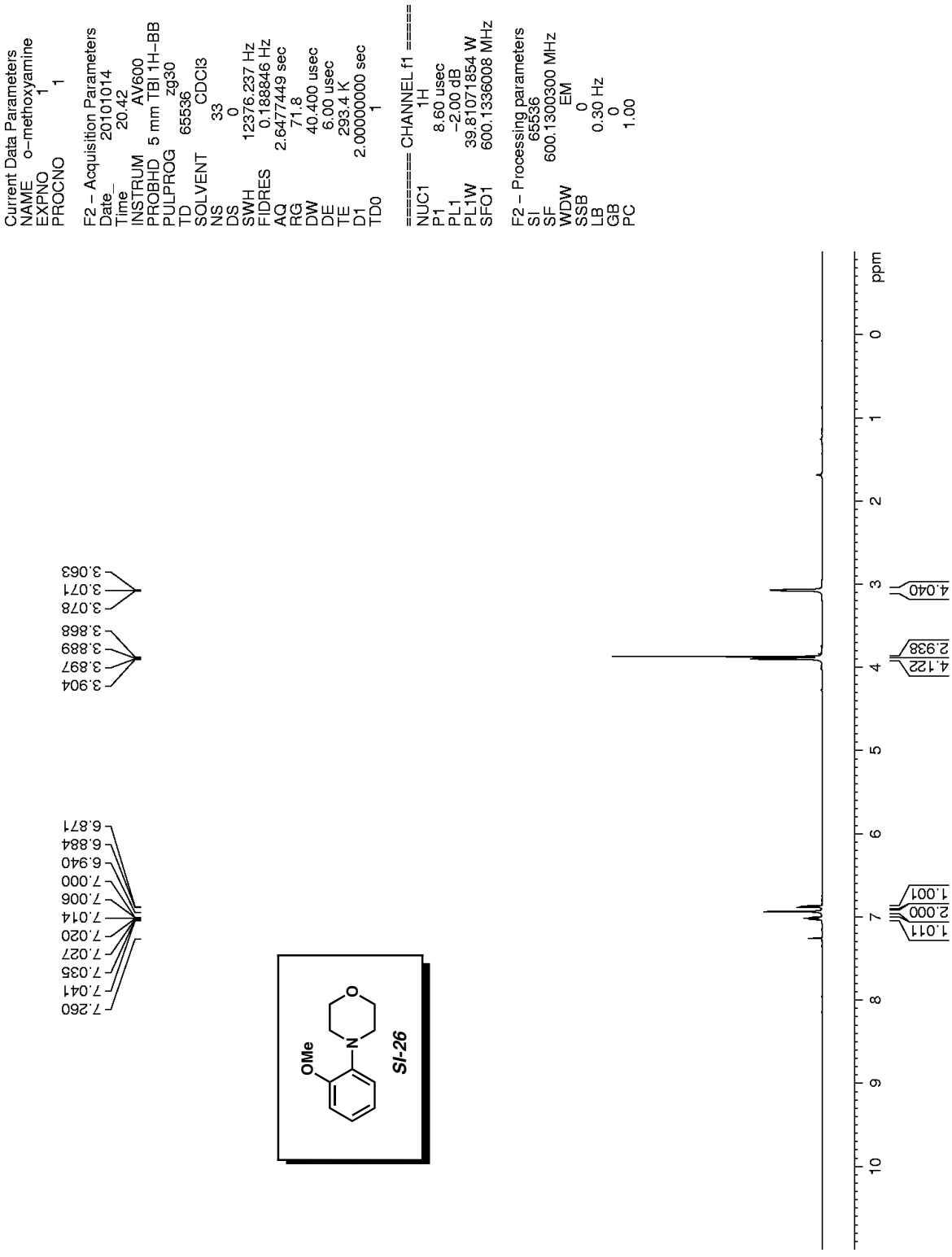
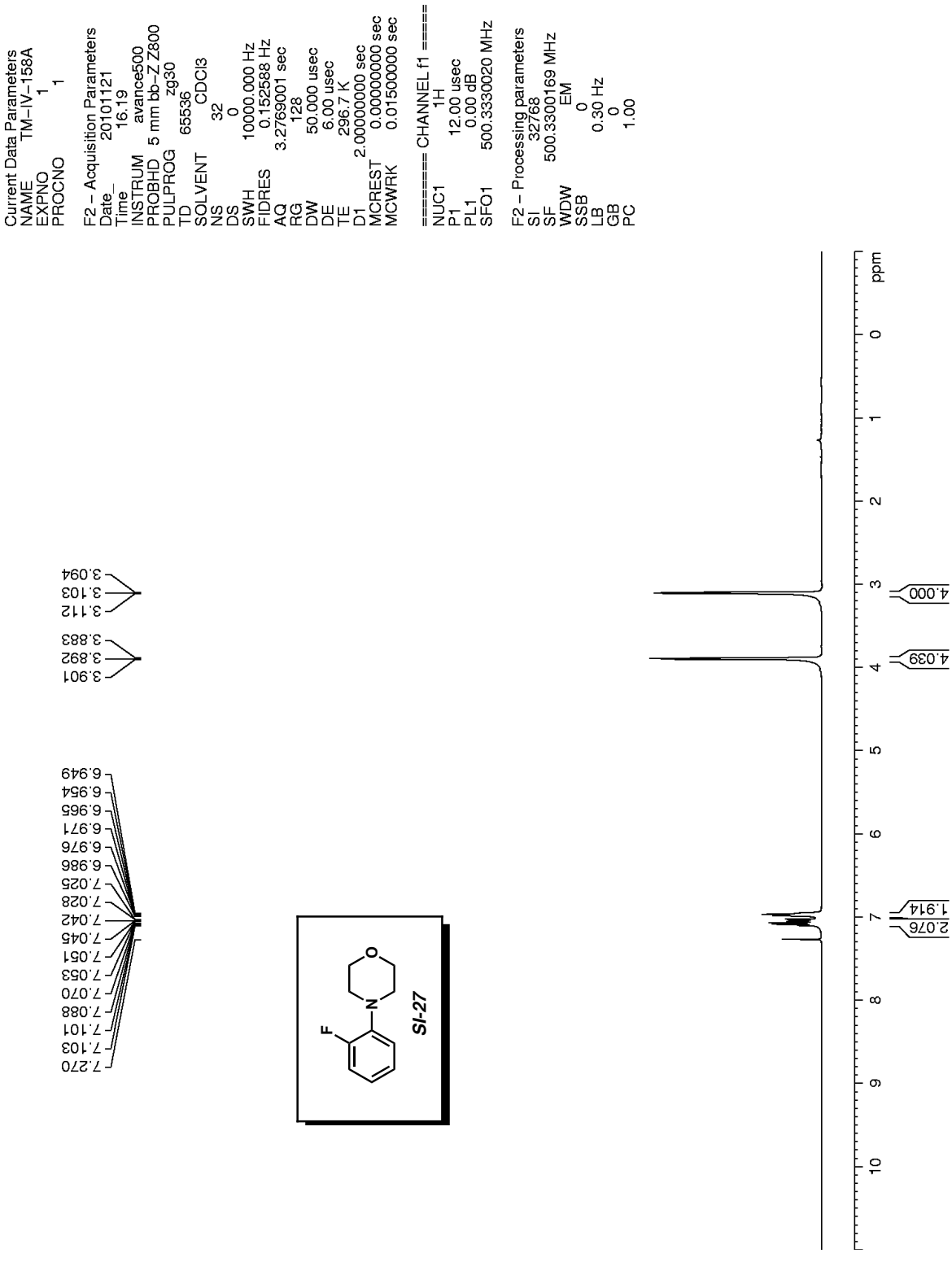
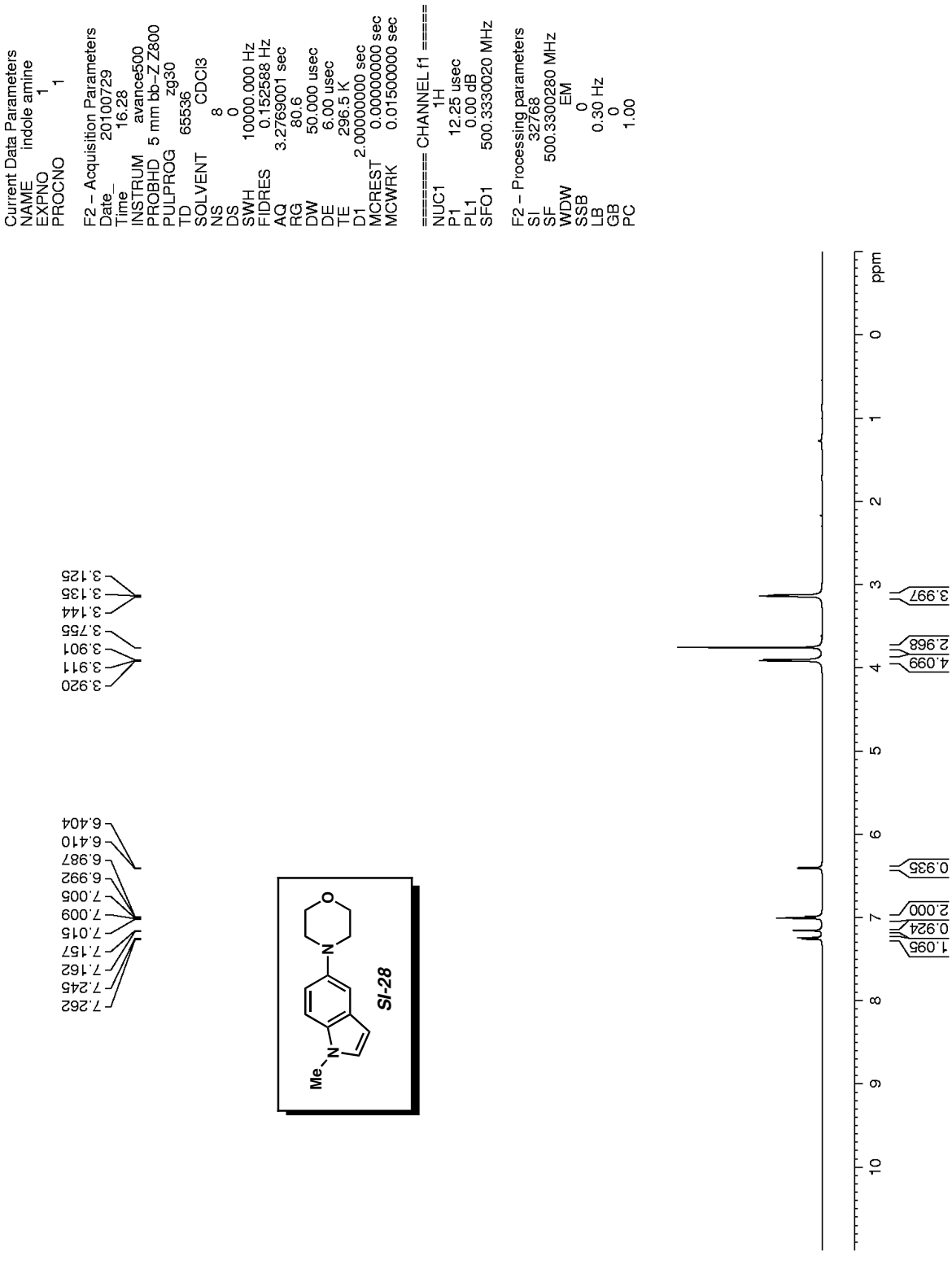
ppm

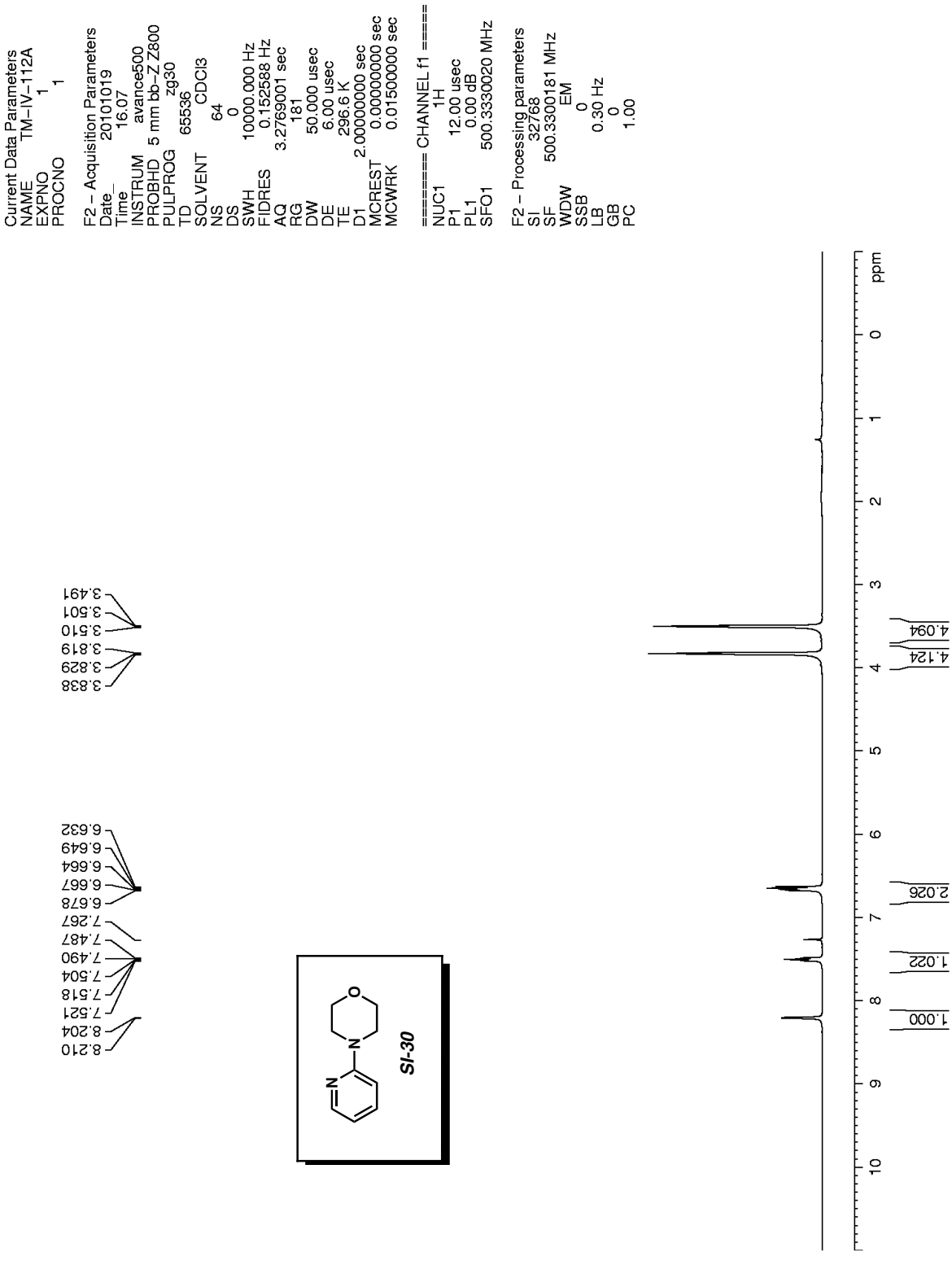


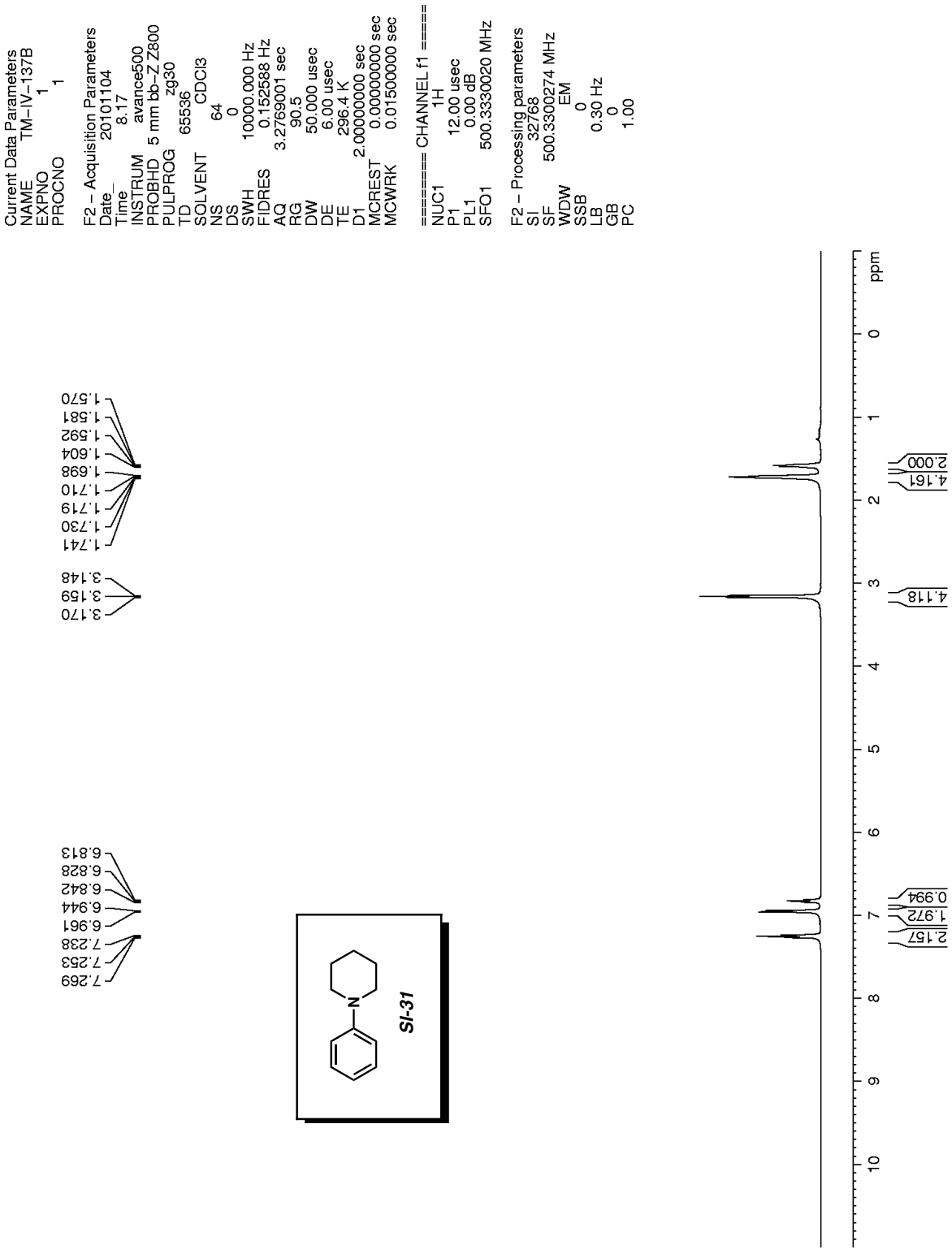


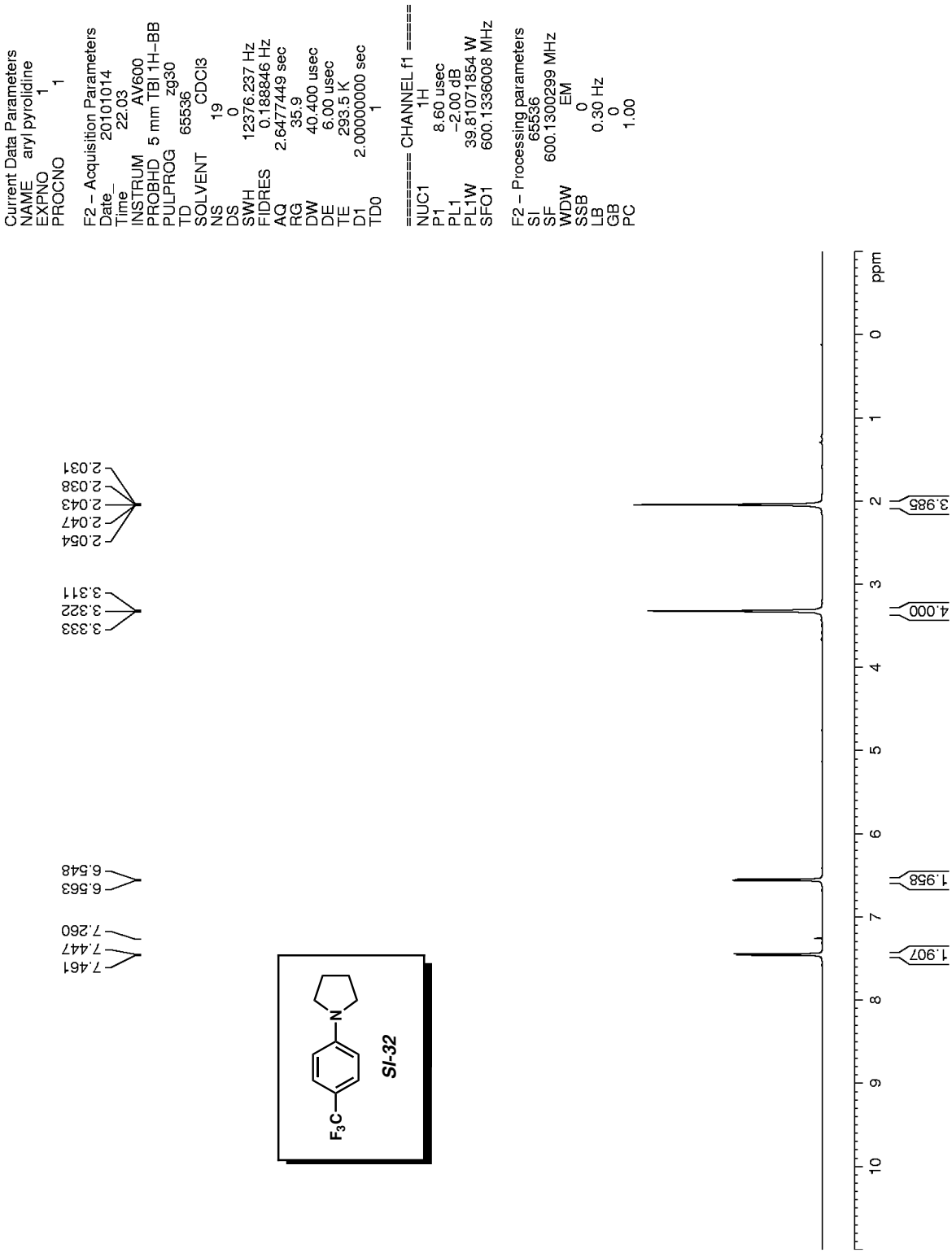


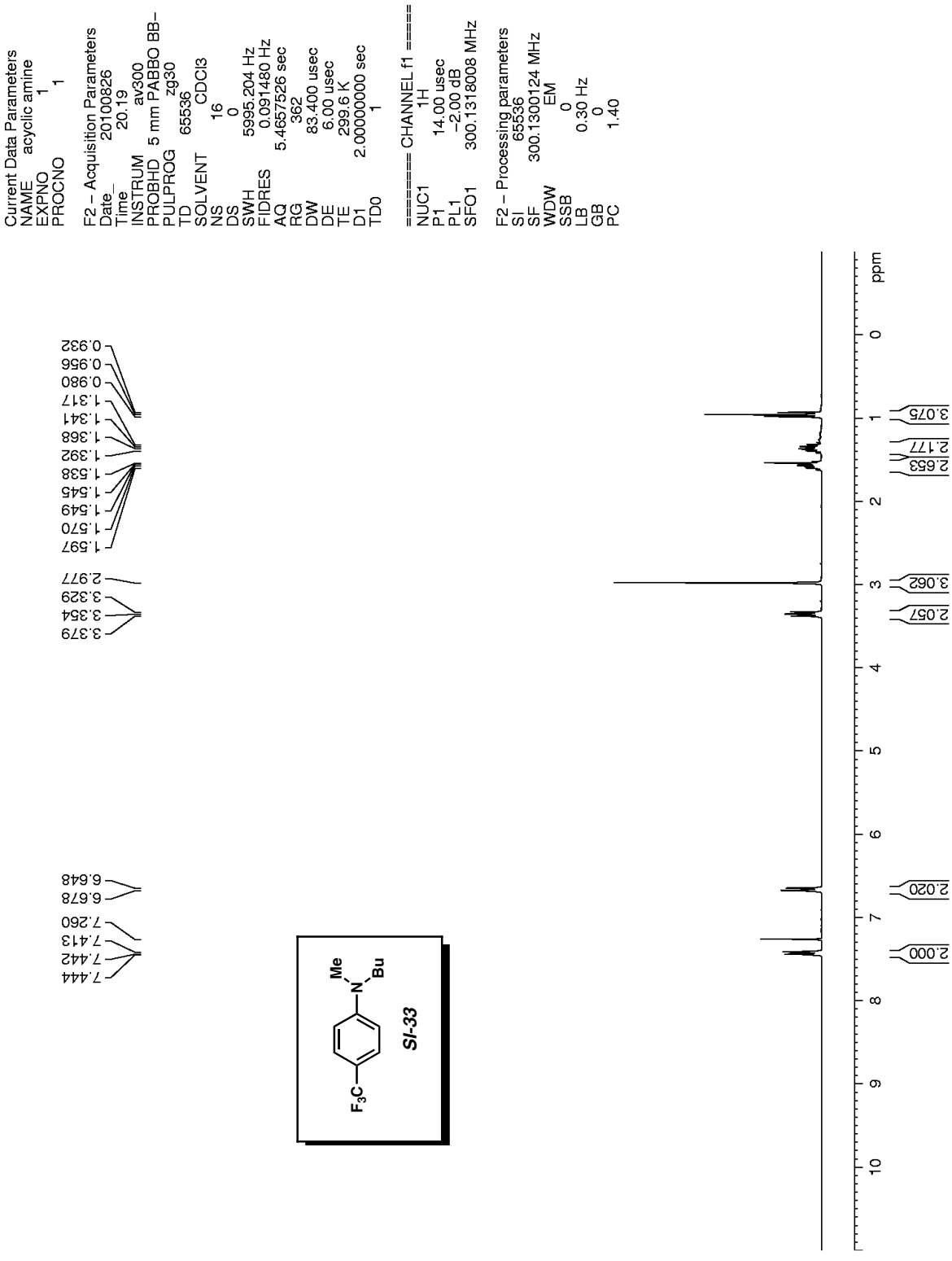


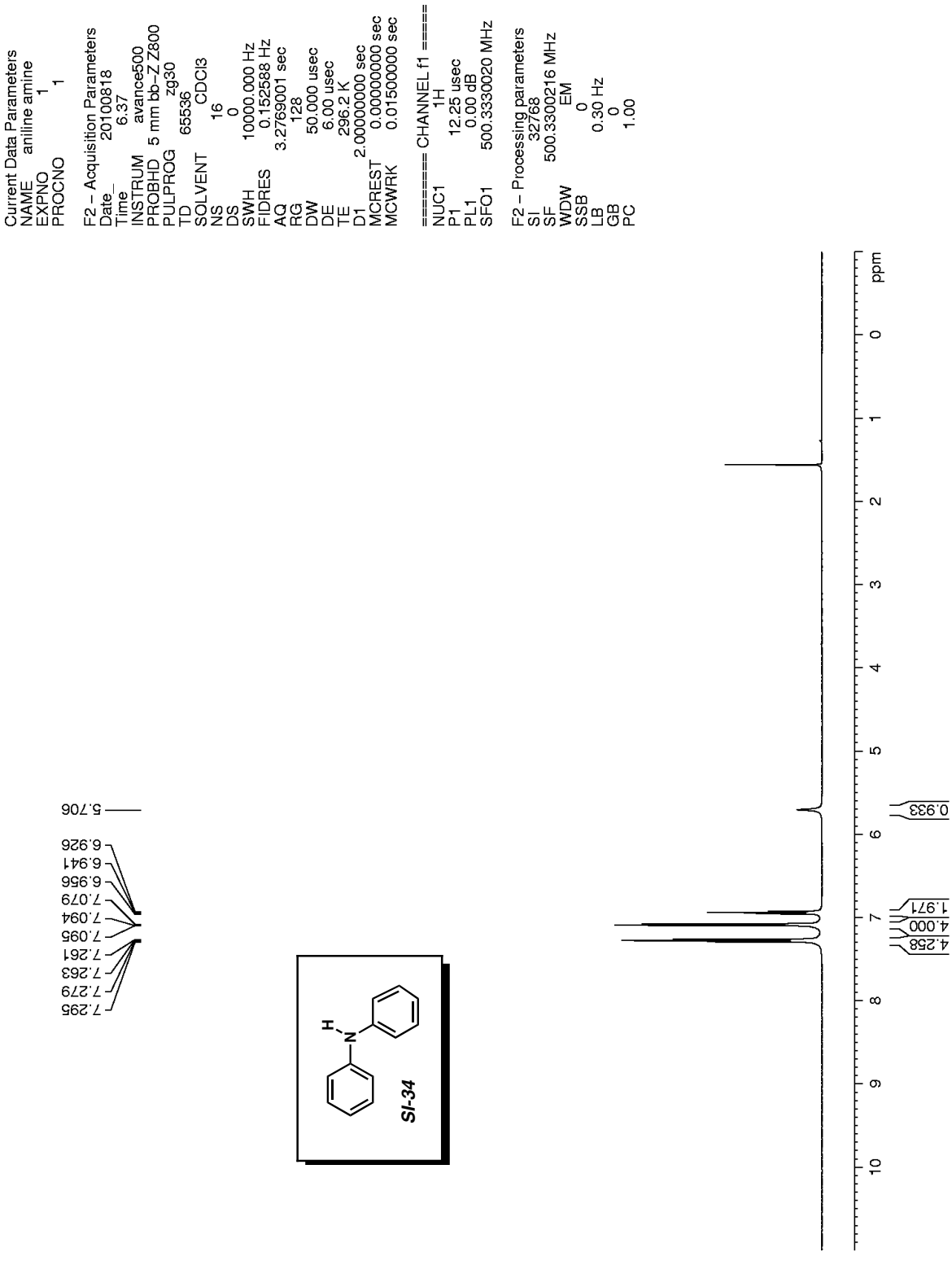


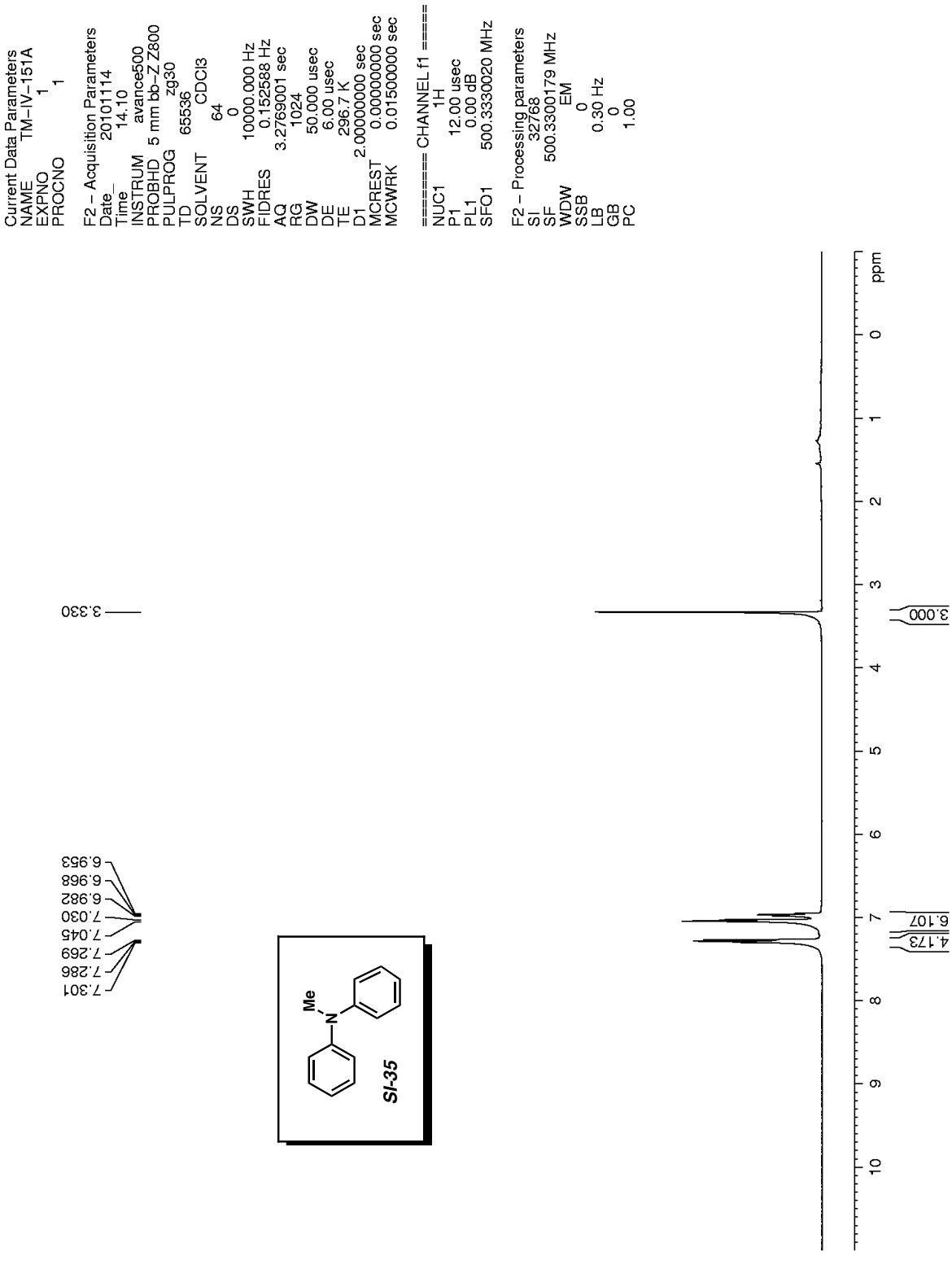


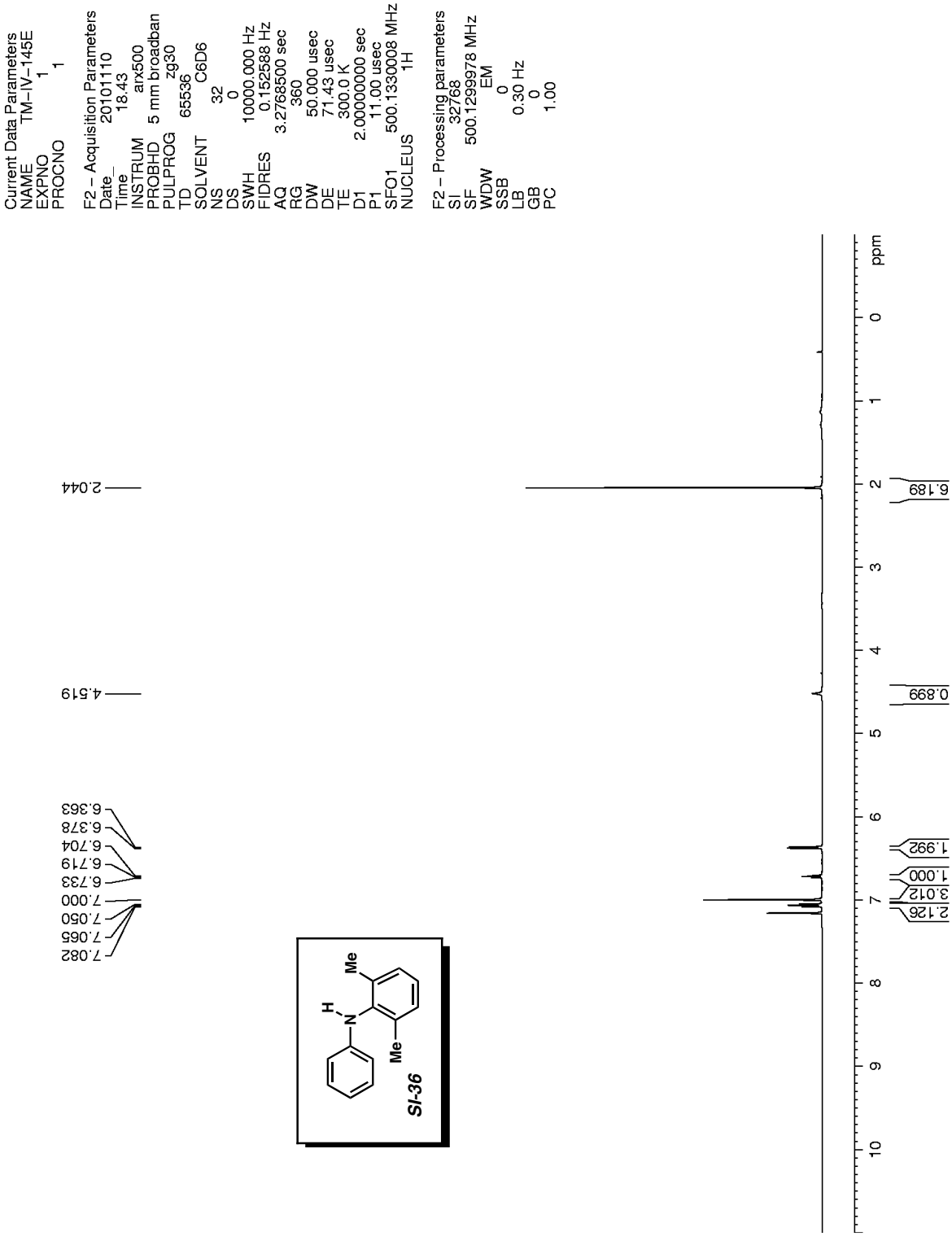


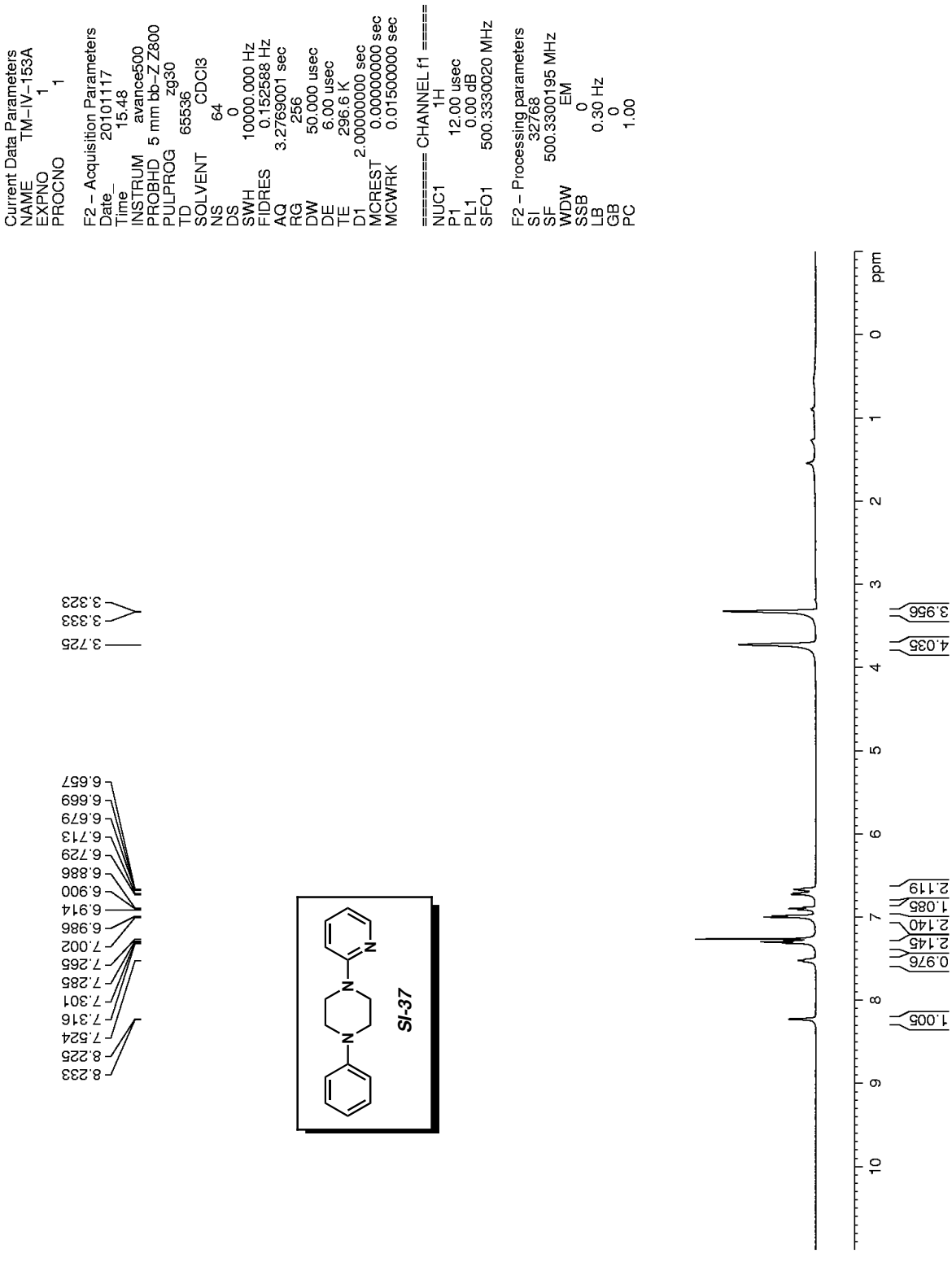


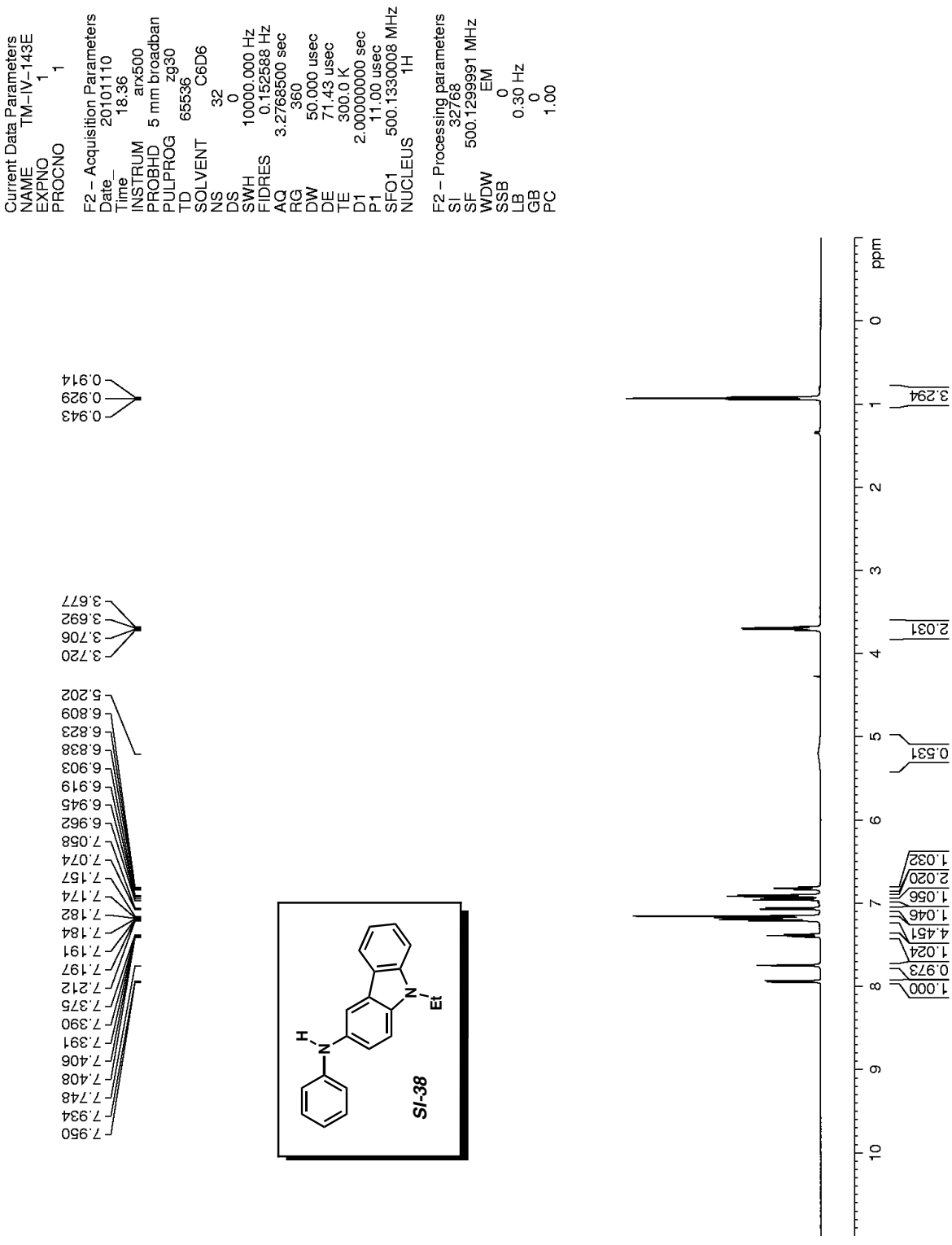


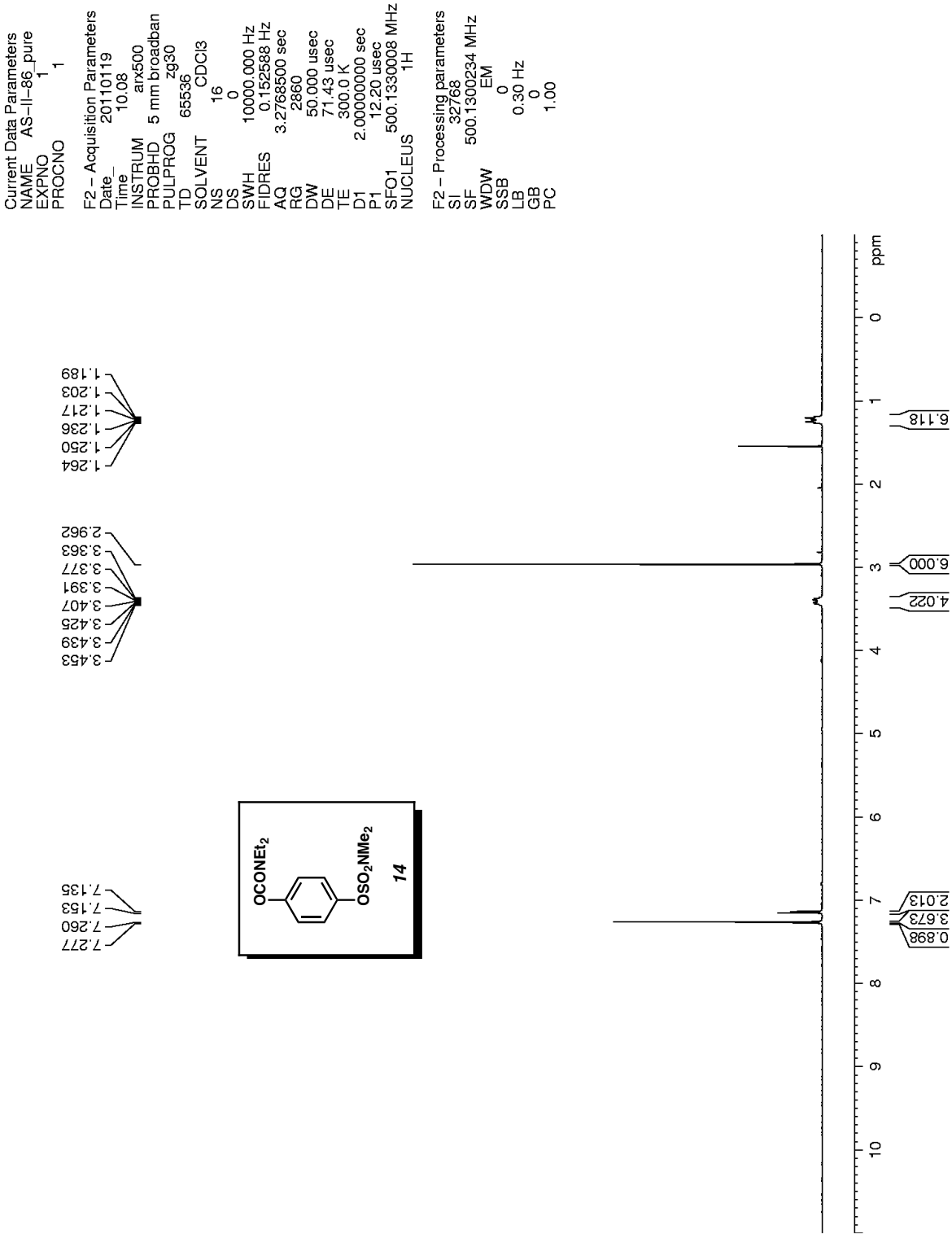








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NAME AS–II–86_pure
EXPNO 1
PROCNO 1
F2 – Acquisition Parameters
Date_ 20110119
Time_ 10.08
INSTRUM arx500
PROBHD 5 mm broadban
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2768500 sec
RG 2860
DW 50.000 usec
DE 71.43 usec
TE 300.0 K
D1 2.00000000 sec
P1 12.20 usec
SFO1 500.1330008 MHz
NUCLEUS 1H
F2 – Processing parameters
SI 32768
SF 500.1300234 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.189
1.203
1.217
1.236
1.250
1.264
2.962
3.363
3.377
3.391
3.407
3.425
3.439
3.453
7.135
7.153
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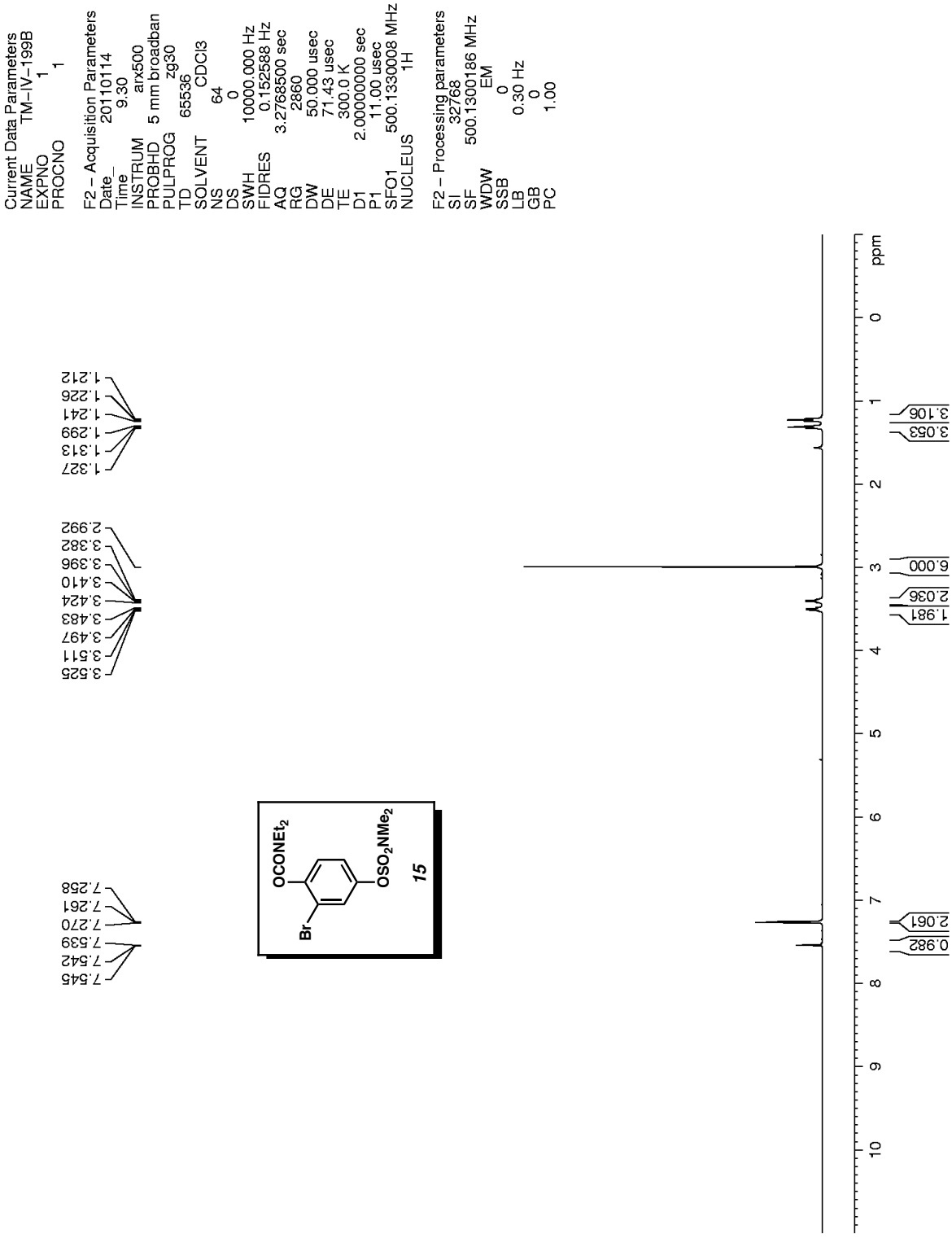

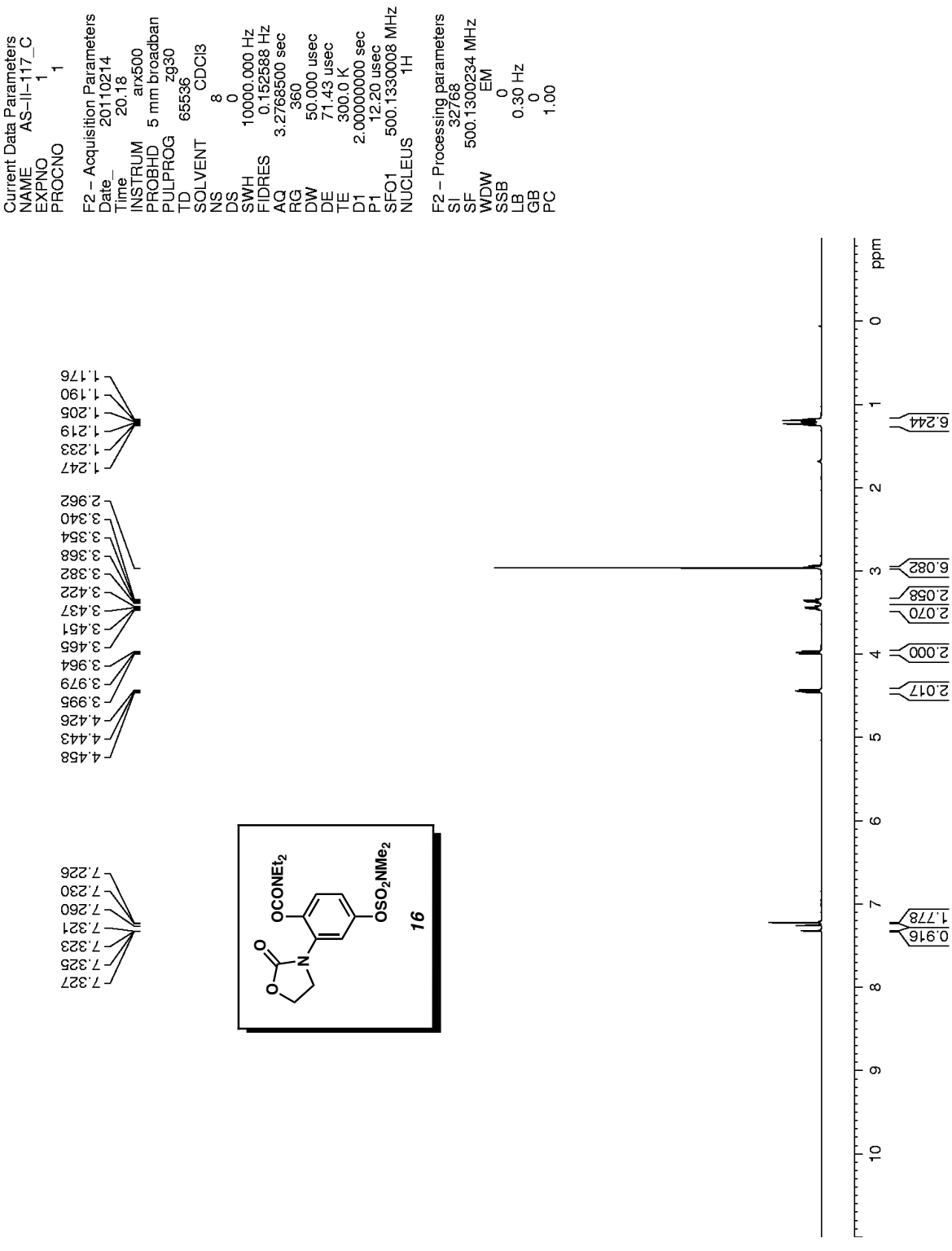

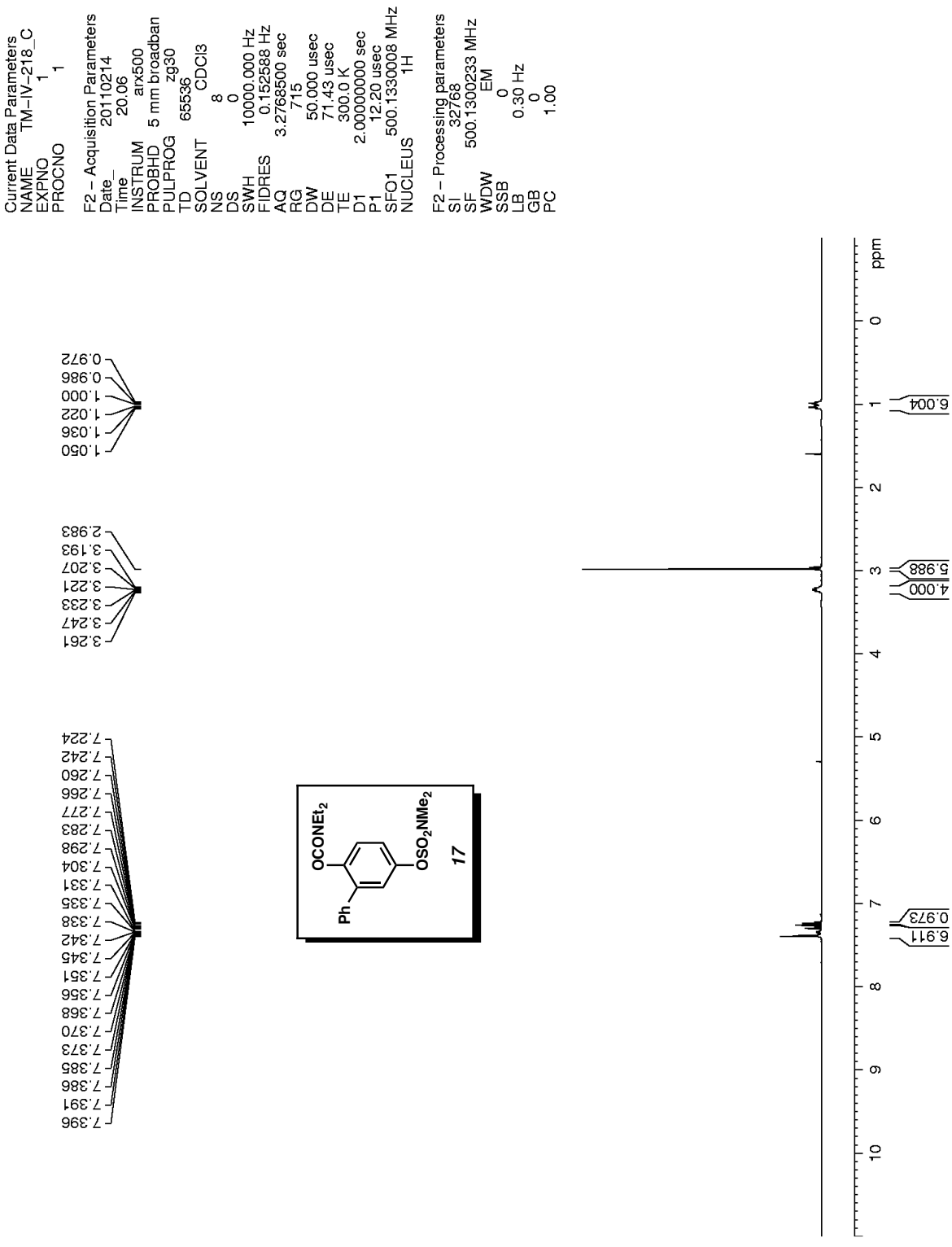
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EXPNO 1
PROCNO 1
F2 – Acquisition Parameters
Date_ 20110214
Time_ 20.06
INSTRUM arx500
PROBHD 5 mm broadban
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2768500 sec
RG 715
DW 50.000 usec
DE 71.43 usec
TE 300.0 K
D1 2.00000000 sec
P1 12.20 usec
SFO1 500.1330008 MHz
NUCLEUS 1H
F2 – Processing parameters
SI 32768
SF 500.1300233 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OCONEt2
OSO2NMe2
Ph
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ppm
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