Suzuki–Miyaura Coupling of Aryl Carbamates and Sulfamates: Experimental and Computational Studies

Kyle W. Quasdorf, Aurora Antoft-Finch, Peng Liu, Amanda L. Silberstein, Anna Komaromi, Tom Blackburn, Stephen D. Ramgren, K. N. Houk,* Victor Snieckus,* and Neil K. Garg*

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095

and

Department of Chemistry, Queen's University, Kingston, Ontario K7L 3N6, Canada

Supporting Information – Table of Contents

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). All commercially obtained reagents were used as received. $NiCl_2$ (anhydrous) and PCy_3 were obtained from Strem Chemicals. Finely powdered anhydrous K_3PO_4 was obtained from Acros.[1] Boronic acids were obtained from Oakwood Products, Inc., Frontier Scientific, Inc. and TCI. 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, and potassium permanganate staining. EMD silica gel 60 (particle size 0.040–0.063 mm) was used for flash column chromatography. ^{1}H NMR spectra were recorded on Bruker spectrometers (at 500 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. 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

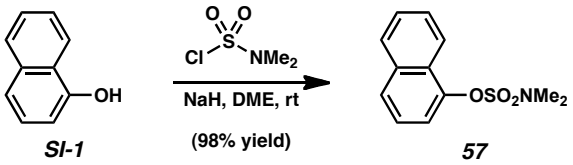
[1] Powdered potassium phosphate was found to be essential for reproducibility and high yields. Granular or pellet material from Sigma-Aldrich, Strem Chemicals, or Pfaltz & Bauer gave poor results, even after grinding with mortar and pestle.

Laboratory Devices Mel-Temp II instrument. High resolution mass spectra were obtained from the UC Irvine Mass Spectrometry Facility.

Experimental Procedures.

Note: Supporting information for aryl carbamates (synthesis and cross-couplings) and synthetic aplications have previously been reported.[2,3]

A. Synthesis of Aryl Sulfamate Substrates



SI-1 *57*

Representative Procedure (sulfamate 57 is used as an example). A round bottom flask was charged with NaH (0.60 g, 15.12 mmol, 1.2 equiv, 60% dispersion in oil). Then a solution of 1-naphthol (**SI-1**) (1.82 g, 12.60 mmol, 1 equiv) in DME (32 mL) was added dropwise via cannula to the NaH. A solution of dimethylsulfamoyl chloride (1.30 mL, 11.97 mmol, 0.95 equiv) in DME (10 mL) was then added dropwise via cannula to the reaction vessel. The reaction was allowed to stir for 17 h, and then quenched with H_2O (2 mL). The volatiles were removed under reduced pressure, and then Et_2O (20 mL) and H_2O (15 mL) were added. The layers were separated, and the organic layer was washed successively with a solution of 1 M KOH (10 mL) and H_2O (20 mL). The combined aqueous layers were extracted with Et_2O (3 x 15 mL). The combined organic layers were then washed with brine (15 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (4:1 Hexanes:EtOAc) to yield 1-naphthylsulfamate **57** as a white solid (2.97 g, 98% yield). R_f 0.29 (4:1 Hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (d, J = 8.5, 1H), 7.88 (d, J = 7.5, 1H), 7.77 (d, J = 8.0, 1H), 7.60-7.53 (m, 3H), 7.46 (t, J = 8.0, 1H), 3.07 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.0, 134.7, 127.8, 127.0, 126.7, 126.7, 126.6, 125.3, 121.4, 117.7, 38.8; IR (film): 3065, 2944, 195, 1456, 1357 cm^{-1}; HRMS-ESI (*m/z*) $[M + Na]^+$ calcd for $C_{12}H_{13}NO_3SNa$, 274.0514; found, 274.0511.

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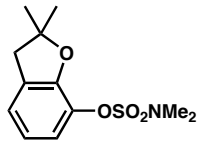
[2] Quasdorf, K. W.; Riener, M.; Petrova, K.; Garg, N. K. *J. Am. Chem. Soc.* **2009**, *131*, 17748–17749.

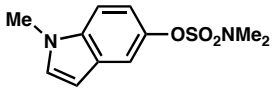
[3] Antoft-Finch, A.; Blackburn, T.; Snieckus, V. *J. Am. Chem. Soc.* **2009**, *131*, 17750–17752.

Note: Supporting information for the synthesis of the aryl sulfamates shown in Tables 6 and 7 have previously been reported.[2]



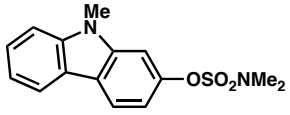
SI-2

SI-2 (Table 9, entry 1). Purification by flash chromatography (5:1 Benzene:Et_2O) afforded **SI-2** as a light yellow oil (66% yield). R_f 0.70 (5:1 Benzene:Et_2O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16 (dd, J = 8.2, 0.7, 1H), 7.03 (dd, J = 7.4, 1.1, 1H), 6.79 (dd, J = 8.0, 7.5 1H), 3.06 (s, 2H), 2.97 (s, 6H), 1.51 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.4, 134.3, 130.1, 123.5, 122.7, 120.4, 88.6, 43.2, 38.8, 28.4; IR (film): 2927, 1617, 1478, 1372, 1172, 1009 cm^{-1}; HRMS-ESI (*m/z*) $[M + Na]^+$ calcd for $C_{12}H_{17}NO_4SNa$, 294.0776; found, 294.0779.



SI-3

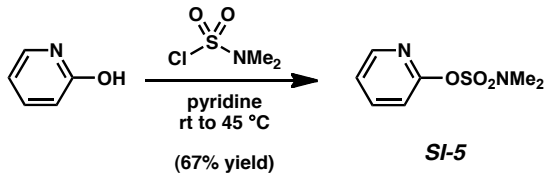
SI-3 (Table 9, entry 2). Supporting information for the synthesis of sulfamate **SI-3** has previously been reported.[2]



SI-4

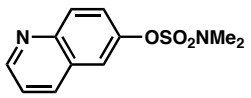
SI-4 (Table 9, entry 3). Purification by flash chromatography (2:1 Hexanes:EtOAc) afforded **SI-4** as a white solid (78% yield). R_f 0.70 (1:1 Hexanes:EtOAc); ^{1}HNMR (500 MHz, $CDCl_3$): δ 8.07-8.04 (m, 2H), 7.49 (t, J = 7.5, 1H), 7.39 (d, J = 8.0, 1H), 7.37 (s, 1H), 7.26 (t, J = 7.5, 1H), 7.13 (d, J = 8.0, 1H), 3.82 (s, 3H), 3.02 (s, 6H); ^{13}CNMR (125 MHz, $CDCl_3$): δ 148.5, 141.6, 141.2, 125.8, 122.1, 121.3,

210.8, 120.2, 119.4, 112.6, 108.6, 102.1, 38.7, 29.2; IR (film): 2935, 1599, 1452, 1359, 1179 cm^{-1}; HRMS-ESI (*m/z*) $[M + Na]^+$ calcd for $C_{15}H_{16}N_2O_3SNa$, 327.0779; found, 327.0774.



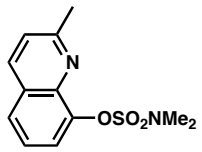
SI-5

SI-5 (Table 9, entry 4). To a solution of 2-hydroxypyridine (2.00 g, 21.05 mmol, 1 equiv) in pyridine (21.1 mL) was added dimethylsulfamoyl chloride (2.7 mL, 25.26 mmol, 1.2 equiv) dropwise via syringe. The resulting orange solution was heated to 45 °C and allowed to stir for 22 h. After cooling to 23 °C, the solution was diluted with Et_2O (60 mL) and 1 M KOH (15 mL), and the layers were separated. The aqueous layer was extracted with Et_2O (2 x 60 mL), followed by EtOAc (1 x 60 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 (3:2 Hexanes:EtOAc) to yield **SI-5** as a yellow oil (67% yield). R_f 0.29 (2:1 Hexanes: EtOAc); ^{1}HNMR (500 MHz, $CDCl_3$): δ 8.26-8.24 (m, 1H), 7.72-7.69 (m, 1H), 7.16 (m, 1H), 7.06 (d, *J* = 2.0, 1H), 2.92 (s, 6H); ^{13}CNMR (125 MHz, $CDCl_3$): δ 157.1, 147.9, 140.0, 122.1, 115.0, 38.3; IR (film): 2941, 1591, 1430, 1375, 1162 cm^{-1}; HRMS-ESI (*m/z*) $[M + Na]^+$ calcd for $C_7H_{10}N_2O_3SNa$, 225.0310; found, 225.0305.



12

12 (Table 9, entry 5). Purification by flash chromatography (100% Et_2O) afforded **12** as a white solid (84% yield). R_f 0.50 (4:1 Hexanes:EtOAc); ^{1}HNMR (500 MHz, $CDCl_3$): δ 8.91 (dd, *J* = 4.5, 2.0, 1H), 8.16-8.10 (m, 2H), 7.75 (d, *J* = 2.5, 1H), 7.60 (dd, *J* = 9.0, 2.5, 1H), 7.42-7.38 (m, 1H), 3.02 (s, 6H); ^{13}CNMR (125 MHz, $CDCl_3$): δ 150.7, 147.9, 146.5, 135.9, 131.6, 128.4, 124.2, 121.8, 118.7, 38.7; IR (film): 2979, 1498, 1174, 1113, 791 cm^{-1}; HRMS-ESI (*m/z*) $[M + Na]^+$ calcd for $C_{11}H_{12}N_2O_3SNa$, 275.0446; found, 275.0470.

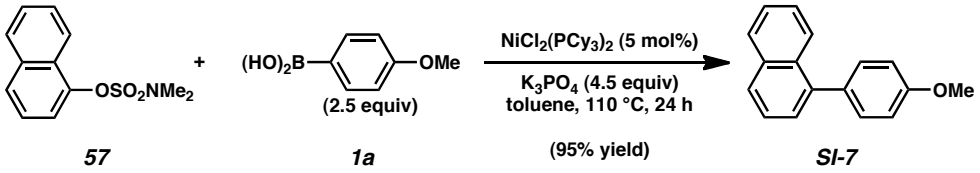


SI-6

SI-6 (Table 9, entry 6). Purification by flash chromatography (2:1 Hexanes:EtOAc) afforded **SI-6** as a white solid (78% yield). R_f 0.44 (2:1 Hexanes:EtOAc); ^{1}HNMR (500 MHz, $CDCl_3$): δ 8.05 (d, J = 8.5, 1H), 7.74 (d, J = 8.0, 1H), 7.69 (d, J = 8.0, 1H), 7.46 (t, J = 8.0, 1H), 7.33 (d, J = 8.5, 1H), 3.04 (s, 6H), 2.76 (s, 3H); ^{13}CNMR (125 MHz, $CDCl_3$): δ 159.6, 145.7, 136.0, 127.8, 126.1, 125.3, 122.7, 122.6, 38.9, 25.4; IR (film): 2922, 1426 1369, 1167, 1069 cm^{-1}; HRMS-ESI (*m/z*) $[M + Na]^+$ calcd for $C_{12}H_{14}N_2O_3SNa$, 289.0623; found, 289.0624.

B. Cross-Coupling Reactions of Aryl Sulfamates

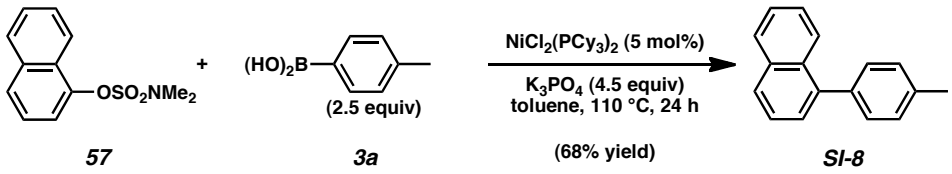
Note: Supporting information for the cross-coupling of the aryl sulfamates shown in Tables 6 and 7 have previously been reported.[2]



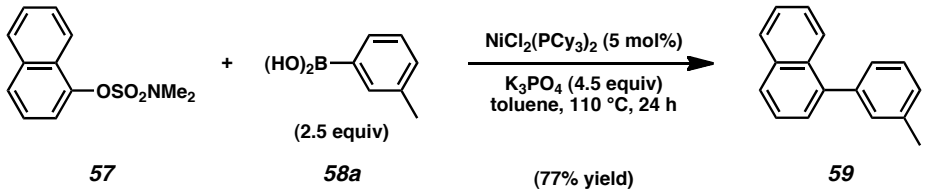
Representative Procedure (coupling of naphthyl sulfamate 57, Table 6, entry 1) is used as an example). SI-7. A 1-dram vial was charged with anhydrous powdered K_3PO_4 (382 mg, 1.80 mmol, 4.5 equiv, *obtained from Acros*) and a magnetic stir bar. The vial and contents were flame-dried under reduced pressure, then allowed to cool under N_2. Boronic acid **1a** (152 mg, 1.00 mmol, 2.5 equiv), $NiCl_2(PCy_3)_2$ (13.7 mg, 0.02 mmol, 5 mol%), and sulfamate substrate **57** (100 mg, 0.40 mmol, 1 equiv) were added. The vial was then evacuated and backfilled with N_2. Toluene (1.5 mL) was added and the vial was sealed with a Teflon-lined screw cap. The heterogeneous mixture was allowed to stir at 23 °C for 1 h, then heated to 110 °C for 24 h. The reaction vessel was cooled to 23 °C and then transferred to a round bottom flask containing CH_2Cl_2 (20 mL). Silica gel (3 mL) was added and the solvent was removed under reduced pressure to afford a free-flowing powder. This powder was then dry-loaded onto a silica gel column (4.5 x 5 cm) and purified by flash chromatography (2:1 Hexanes: Benzene) to yield biaryl product **SI-7** (89 mg, 95% yield) as a colorless solid. R_f 0.35 (2:1 Hexanes:Benzene); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, J = 8.5, 1H), 7.92 (d, J = 8.5, 1H), 7.86 (d, J = 8.5, 1H), 7.57-7.48 (m, 2H), 7.48-7.39 (m, 4H), 7.06 (d, J = 8.5, 2H), 3.92 (s, 3H). All spectral data are consistent with those previously reported.[4]

Any modifications of the conditions shown in this representative procedure are specified in the following schemes, which depict all of the results shown in Table 8–10 and Scheme 3.

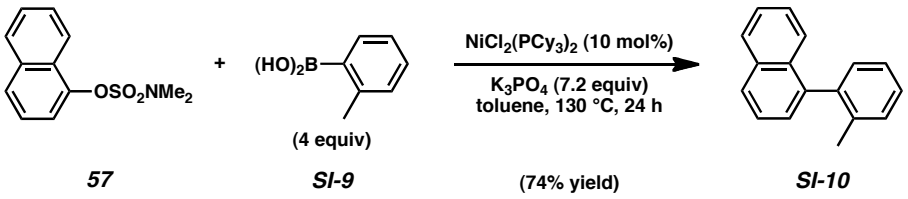
[4] Denmark, S. E.; Ober, M. H. *Org. Lett.* **2003**, *5*, 1357–1360.



SI-8 (Table 8, entry 1). Purification by flash chromatography (100% Hexanes) afforded a mixture (30.8 to 1) of biaryl product **SI-8** (68% yield) and 4,4'-dimethylbiphenyl. R_f 0.74 (9:1 Hexanes:EtOAc). All spectral data are consistent with those previously reported.[5]



59 (Table 8, entry 2). Purification by flash chromatography (100% Hexanes) afforded a mixture (15.8 to 1) of biaryl product **59** (77% yield) and 3,3'-dimethylbiphenyl. R_f 0.66 (9:1 Hexanes:EtOAc). All spectral data are consistent with those previously reported.[6]



SI-10 (Table 8, entry 3). Purification by flash chromatography (100% Hexanes) afforded a mixture (51.8 to 1) of biaryl product **SI-10** (74% yield) and 2,2'-dimethylbiphenyl. R_f 0.66 (9:1 Hexanes:EtOAc). All spectral data are consistent with those previously reported.[7]

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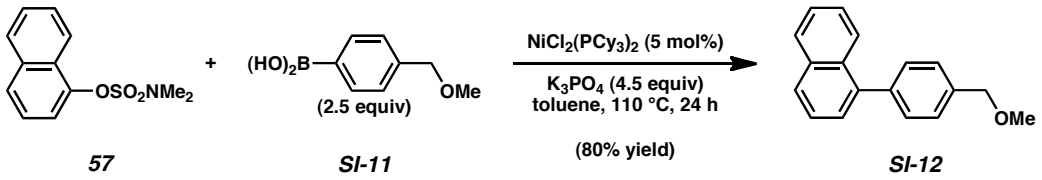
[5] Mino, T.; Shirae, Y.; Sakamoto, M.; Fujita, T. *J. Org. Chem.* **2005**, *70*, 2191–2194.

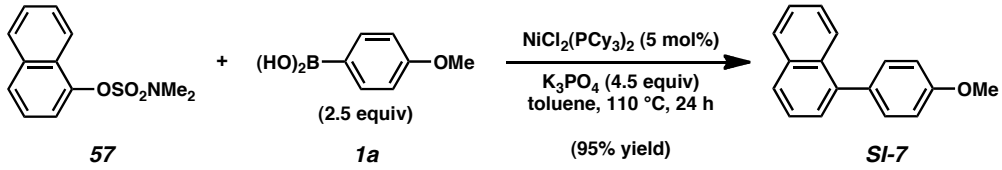
[6] Zhang, L.; Cheng, J.; Zhang, W.; Lin, B.; Pan, C.; Chen, J. *Synth. Commun.* **2007**, *37*, 3809–3814.

[7] Dalpozzo R.; Nino, A.; Maiuolo, L.; Oliverio, M.; Porcopio, A.; Russo, B.; Tocci, A. *Australian J. Chem.* **2007**, *60,* 75–79.



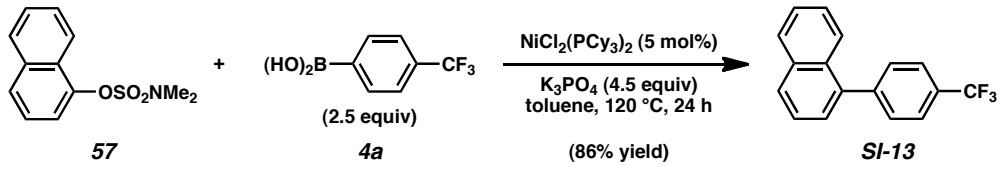
57 ***SI-11*** ***SI-12***

SI-12 (Table 8, entry 4). Purification by flash chromatography (9:1 Hexanes:EtOAc) afforded **SI-12** as a clear oil (80% yield). R_f 0.58 (9:1 Hexanes:EtOAc); ^{1}HNMR (500 MHz, C_6D_6): δ 8.02 (d, J = 8.4, 1H), 7.70 (d, J = 8.1, 1H), 7.65 (d, J = 7.9, 1H), 7.38 (d, J = 7.9, 2H), 7.35-7.25 (m, 5H), 7.22 (m, 1H) 4.31 (s, 2H), 3.18 (s, 3H); ^{13}CNMR (125 MHz, C_6D_6): δ 140.0, 139.8, 137.5, 133.8, 131.7, 129.7, 127.6, 127.4, 127.4, 127.2, 127.2, 126.7, 125.9, 125.7, 125.4, 125.1, 73.8, 57.3; IR (film): 2923, 1592, 1504, 1395, 1096 cm^{-1}; HRMS-ESI (*m/z*) $[M + NH_4]^+$ calcd for $C_{18}H_{16}ONH_4$, 266.1545; found, 266.1550.



57 ***1a*** ***SI-7***

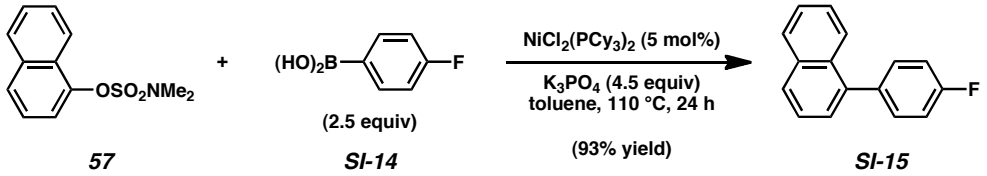
SI-7 (Table 8, entry 5). Purification by flash chromatography (2:1 Hexanes:Benzene) afforded **SI-7** as a white solid (95% yield). R_f 0.35 (2:1 Hexanes:Benzene). Spectral data match those reported above.



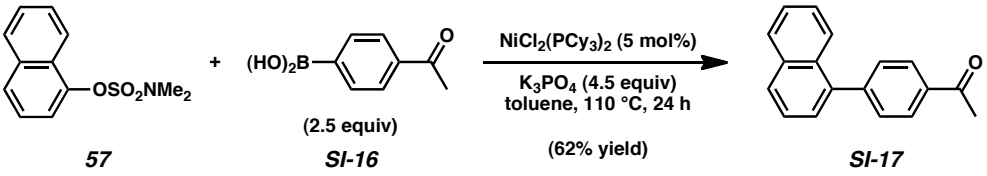
57 ***4a*** ***SI-13***

SI-13 (Table 8, entry 6). Purification by flash chromatography (2:1 Hexanes:Benzene) afforded a mixture (25.0 to 1) of biaryl product **SI-13** (86% yield) and 4,4'-bis(trifluoromethyl)biphenyl. R_f 0.76 (2:1 Hexanes:Benzene). All spectral data are consistent with those previously reported.[8]

[8] Song, C.; Ma, Y.; Chai, Q.; Ma, C.; Jiang, W.; Andrus, M. B. *Tetrahedron* **2005**, *61*, 7438–7446.



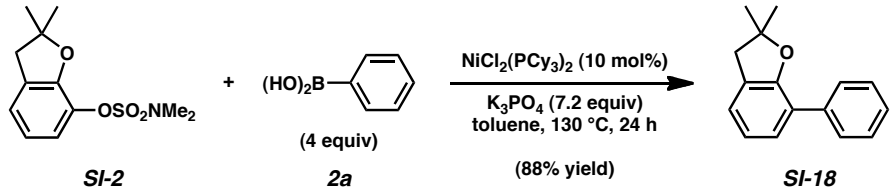
SI-15 (Table 8, entry 7). Purification by flash chromatography (20:1 Hexanes:EtOAc) afforded **SI-15** as a white solid (93% yield). R_f 0.61 (9:1 Hexanes:EtOAc); ^{1}HNMR (500 MHz, $CDCl_3$): δ 7.91 (d, J = 7.6, 1H), 7.87 (d, J = 8.4, 1H), 7.85 (d, J = 8.4, 1H), 7.55-7.48 (m, 2H), 7.48-7.42 (m, 3H), 7.40 (d, J = 7.0, 1H) 7.19 (t, J = 8.6, 2H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 139.3, 136.8 (d), 134.0, 131.8, 131.8, 131.7, 128.5, 128.0, 127.2, 126.3, 126.0, 125.9, 125.5, 115.4, 115.3; IR (film): 3043, 1604, 1503, 1395, 1219, 1157 cm^{-1}; HRMS-ESI (*m/z*) $[M + NH_4]^+$ calcd for $C_{16}H_{11}FNH_4$, 240.1189; found, 240.1198. All spectral data are consistent with those previously reported.[9]



SI-17 (Table 8, entry 8). Purification by flash chromatography (9:1 Hexanes:EtOAc) afforded **SI-17** as a white solid (62% yield). R_f 0.52 (4:1 Hexanes:EtOAc); ^{1}HNMR (500 MHz, $CDCl_3$): δ 8.10 (d, J = 8.3, 2H), 7.92 (dd, J = 13.0, 8.2, 2H), 7.86 (d, J = 8.4, 1H), 7.61 (d, J = 8.3, 2H), 7.57-7.50 (m, 2H), 7.49-7.41 (m, 2H), 2.69 (s, 3H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 197.7, 145.7, 138.9, 135.9, 133.7, 131.1, 130.2, 128.3, 128.3, 128.3, 126.8, 126.3, 125.9, 125.5, 125.2, 26.6; IR (film): 3054, 1682, 1605, 1503, 1403, 1268 cm^{-1}; HRMS-ESI (*m/z*) $[M + NH_4]^+$ calcd for $C_{18}H_{14}ONH_4$, 264.1388; found, 264.1394. All spectral data are consistent with those previously reported.[10]

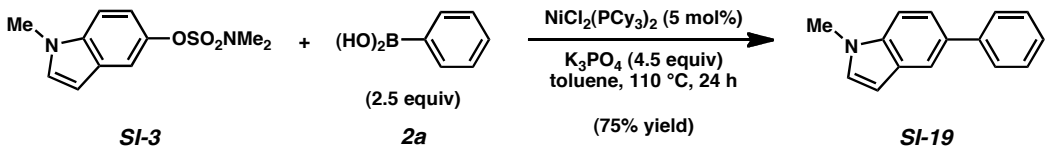
[9] Okamoto, H.; Satake, K.; Kimura, M. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3557–3562.

[10] Adjabeng, G.; Brenstrum, T.; Frampton, C. S.; Robertson, A. J.; Hillhouse, J.; McNulty, J.; Capretta, A. *J. Org. Chem.* **2004**, *69*, 5082–5086.



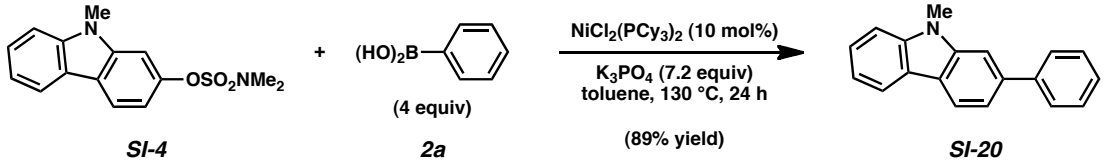
SI-2 ***2a*** ***SI-18***

SI-18 (Table 9, entry 1). Purification by flash chromatography (1:1 Benzene:Hexanes) afforded **SI-18** as a light yellow oil (88% yield). R_f 0.52 (1:1 Benzene:Hexanes); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.7, 2H), 7.45 (t, *J* = 7.7, 2H), 7.34-7.31 (m, 2H), 7.14 (dd *J* = 7.2, 0.9, 1H), 6.93 (t, *J* = 7.5, 1H), 3.09 (s, 2H), 1.54 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.3, 137.7, 128.4, 128.4, 128.2, 127.9, 127.0, 124.3, 123.4, 120.0, 86.5, 43.0, 28.4; IR (film): 2972, 1597, 1459, 1425, 1139 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{16}H_{17}O$, 225.1279; found, 225.1274.



SI-3 ***2a*** ***SI-19***

SI-19 (Table 9, entry 2). Purification by flash chromatography (2:1 Hexanes:Benzene) afforded **SI-19** as a white solid (75% yield). R_f 0.42 (2:1 Hexanes:Benzene). All spectral data are consistent with those previously reported.[11]



SI-4 ***2a*** ***SI-20***

SI-20 (Table 9, entry 3). Purification by flash chromatography (4:1 Hexanes:EtOAc) afforded **SI-20** as a white solid (89% yield). R_f 0.74 (4:1 Hexanes:EtOAc). All spectral data are consistent with those previously reported.[12]

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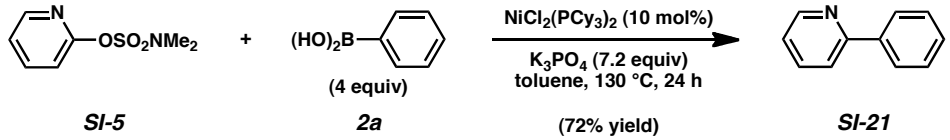
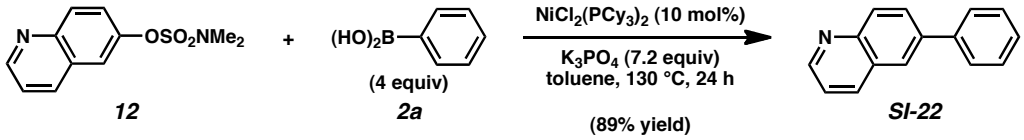
[11] Quasdorf, K. W.; Riener, M.; Petrova, K. V.; Garg, N. K. *J. Am. Chem. Soc.* **2009**, *131*, 17748–17749.

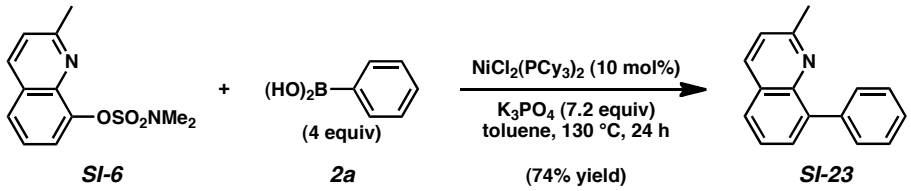
[12] Kong, W.; Fu, C.; Ma, S. *Chem. Commun.* **2009**, 4572–4574.



SI-21 (Table 9, entry 4). Purification by flash chromatography (4:1 Hexanes:EtOAc) afforded **SI-21** as a white solid (72% yield). R_f 0.52 (2:1 Hexanes:EtOAc). All spectral data are consistent with those previously reported.[13]



SI-22 (Table 9, entry 5). Purification by flash chromatography (1:1 Hexanes:Benzene) afforded **SI-22** as a white solid (89% yield). R_f 0.35 (1:1 Hexanes:EtOAc). All spectral data are consistent with those previously reported.[14]



SI-23 (Table 9, entry 6). Purification by flash chromatography (4:1 Hexanes:EtOAc) afforded **SI-23** as a white solid (74% yield). R_f 0.62 (4:1 Hexanes:EtOAc); ^{1}HNMR (500 MHz, $CDCl_3$): δ 8.09 (d, J = 8.0, 1H), 7.87-7.84 (m, 2H), 7.82-7.76 (m, 2H), 7.58-7.52 (m, 3H), 7.48-7.43 (m, 1H), 7.31 (d, J = 8.0, 1H), 2.79 (s,3H); ^{13}CNMR (125MHz, $CDCl_3$): δ 158.5, 145.3, 139.7, 139.5, 136.0, 130.9, 130.1, 127.6, 127.1, 126.9, 126.7, 125.2, 121.6, 25.5; IR (film): 3050, 1612, 1600, 1496, 1326, 1238 cm^{-1}; HRMS-ESI (*m/z*) $[M + Na]^+$ calcd for $C_{16}H_{14}N$, 220.1126; found, 220.1126.

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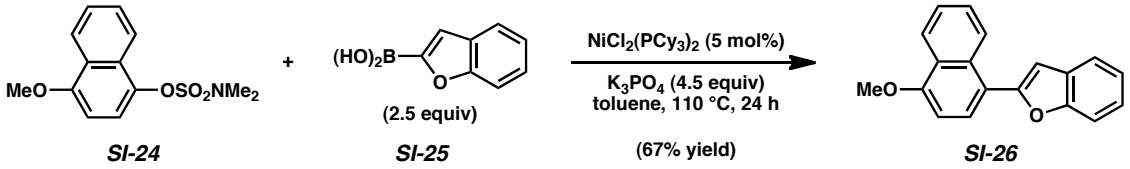
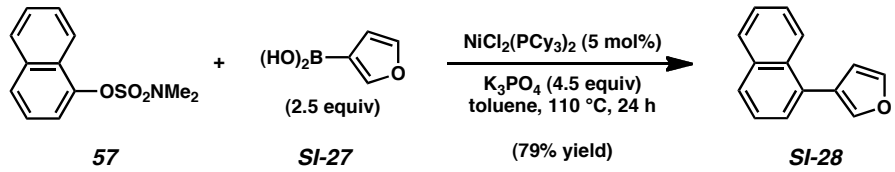
[13] Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 6647–6653.

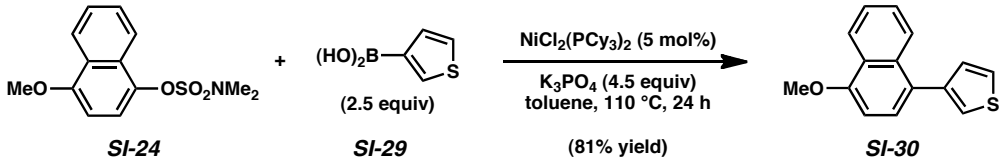
[14] So, C. M.; Lau, C. P.; Kwong, F. Y. *Angew. Chem. Int. Ed.* **2008**, *47*, 8059–8063.



SI-26 (Table 10, entry 1). Purification by flash chromatography (4:1 Hexanes:EtOAc) afforded **SI-26** as a yellow oil (67% yield). R_f 0.58 (4:1 Hexanes:EtOAc); ^{1}HNMR (400 MHz, $CDCl_3$): δ 8.42 (d, *J* =8.5, 1H), 8.38 (d, *J* =8.3, 1H), 7.82 (d, *J* = 8.1, 1H), 7.66 (d, *J* = 7.5, 1H), 7.61-7.53 (m, 3H), 7.35-7.25 (m, 2H), 7.00 (s, 3H), 6.91 (d, *J* = 8.1, 1H), 4.07 (s, 3H); ^{13}CNMR (125MHz, $CDCl_3$): δ 156.3, 156.0, 154.8, 131.7, 129.2, 127.9, 127.3, 125.7, 125.4, 125.2, 123.9, 122.8, 122.4, 120.8, 120.7, 111.1, 104.7, 103.4, 55.6; IR (film): 2934, 1584, 1448, 1246, 1080 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{19}H_{15}O_2$, 275.1072; found, 275.1078.



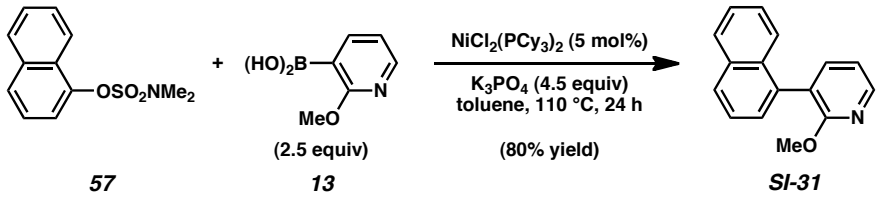
SI-28 (Table 10, entry 2). Purification by flash chromatography (100% Hexanes) afforded **SI-28** as a white solid (79% yield). R_f 0.62 (100% Hexanes). All spectral data are consistent with those previously reported.[15]



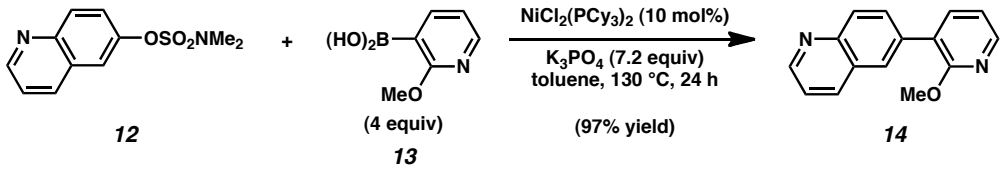
SI-30 (Table 10, entry 3). Purification by flash chromatography (2:1 Hexanes:EtOAc) afforded **SI-30** as a yellow oil (81% yield). R_f 0.55 (1:1 Hexanes:EtOAc); ^{1}HNMR (400 MHz, $CDCl_3$): δ 8.35-8.33 (m, 1H), 8.00-7.97 (m, 1H), 7.52-7.43 (m, 3H), 7.40 (d, *J* = 7.9, 1H), 7.34 (dd, *J* = 3.0, *J* = 1.3, 1H), 7.28 (dd, *J* = 4.9, 1.3,1H), 6.85, (d, *J* = 8.7, 1H), 4.05 (s, 3H); ^{13}CNMR (125MHz, $CDCl_3$): δ 155.0,

[15] Molander, G. A.; Biolatto, B. *J. Org. Chem.* **2003**, *68*, 4302–4314.

141.2, 132.6, 129.7, 127.3, 126.8, 126.6, 125.6, 125.5, 125.1, 125.0, 122.9, 122.2, 103.3, 55.5; IR (film): 2933, 1578, 1458, 1232, 1101 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{15}H_{12}OS$, 241.0687; found, 241.0693.

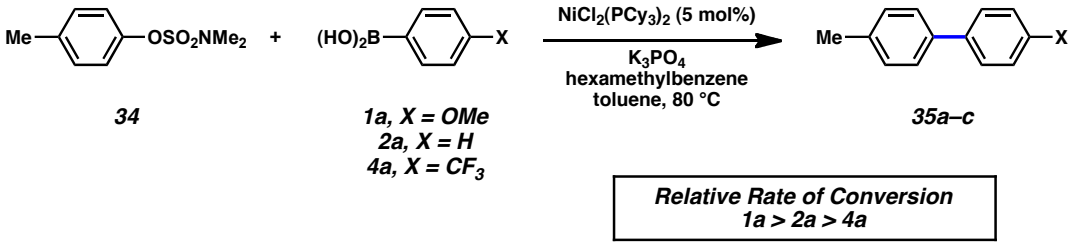


SI-31 (Table 10, entry 4). Purification by flash chromatography (10:1 Hexanes:EtOAc) afforded **SI-31** as a white solid (80% yield). R_f 0.70 (10:1 Hexanes:EtOAc); ^{1}HNMR (500 MHz, $CDCl_3$): δ 8.32 (d, *J* = 5.0, 1.9, 1H), 7.93-7.90 (m, 2H), 7.61-7.42 (m, 6H), 7.06-7.03 (m, 1H), 3.98 (s, 3H); ^{13}CNMR (125 MHz, $CDCl_3$): δ 161.6, 146.3, 140.1, 134.9, 133.5, 131.7, 128.2, 128.2, 127.4, 125.9, 125.8, 125.7, 125.3, 123.5, 116.6, 53.4; IR (film): 2945, 1578, 1459, 1362, 1174 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{16}H_{13}NO$, 236.1075; found, 236.1082.

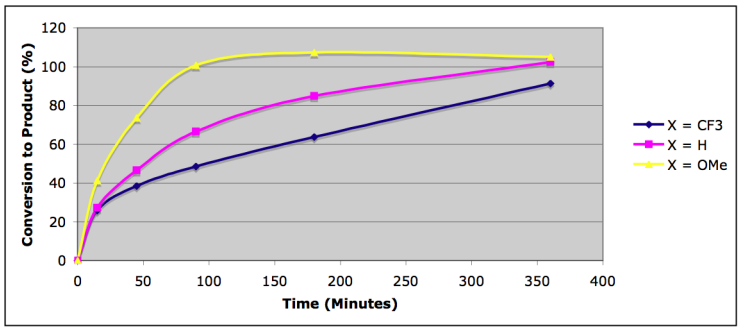


Biaryl 14. Purification by flash chromatography (10:1 Hexanes:EtOAc) afforded **14** as a white solid (97% yield). R_f 0.70 (10:1 Hexanes:EtOAc); ^{1}HNMR (500 MHz, $CDCl_3$): δ 8.85 (dd, *J* = 4.0, 1.4, 1H), 8.15 (dd, *J* = 5.0, 1.8, 1H), 8.11-8.07 (m, 2H), 7.88-7.86 (m, 2H), 7.62 (dd, *J* = 7.3, 1.8, 1H), 7.31 (q, *J*=4.2, 1H), 6.95-6.92 (dd, *J* = 7.3, 5.0, 1H), 3.95 (s, 3H); ^{13}CNMR (125 MHz, $CDCl_3$); δ 160.8, 150.4, 147.5, 146.1, 138.7, 136.0, 135.0, 130.8, 128.9, 128.0, 127.7, 123.6, 121.2, 117.1, 53.5; IR (film): 3046, 2945, 1578, 1461, 1403, 1018 cm^{-1}; HRMS-ESI (*m/z*) $[M + H]^+$ calcd for $C_{15}H_{13}NO$, 237.1028; found, 237.1025.

C. Mechanistic and Competition Experiments

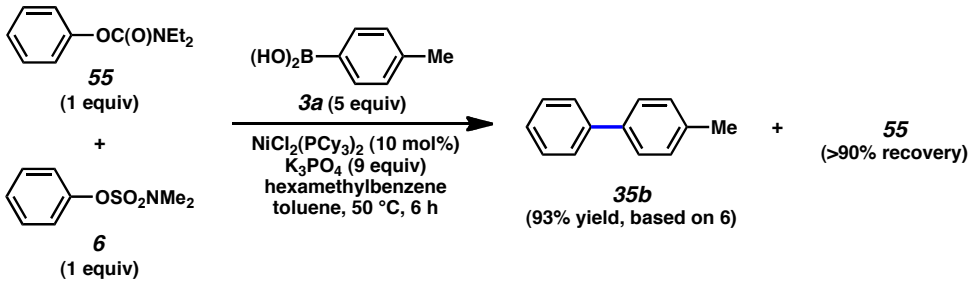


Influence of boronic acid on the reaction rate. To determine the influence of boronic acid identity on reaction rate, sulfamate **34** was allowed to react independently with boronic acids **1a**, **2a**, and **4a**. To monitor progress over time, in each case, five reactions were setup simultaneously under identical reaction conditions. These reactions were removed from heat at varying time points (15 min, 45 min, 90 min, 3 h, 6 h) and the percentage conversions were determined by ^{1}H NMR analysis with hexamethylbenzene as internal standard. The results shown below indicate that the relative rate of cross-coupling is dependent on the identity of the boronic acid, with a direct correlation between electron-richness of the boronic acid and reaction rate (i.e., rate of conversion: **1a**>**2a**>**4a**).

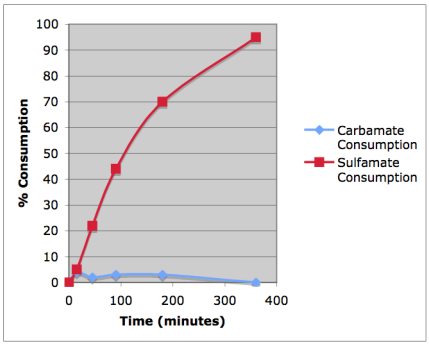


Representative procedure (coupling of sulfamate 34 with boronic acid 2a is used as an example). A 1-dram vial was charged with anhydrous powdered K_3PO_4 (419 mg, 1.98 mmol, 4.5 equiv, *obtained from Acros*) and a magnetic stir bar. The vial and contents were flame-dried under reduced pressure, and then allowed to cool under N_2. Boronic acid **2a** (134 mg, 1.10 mmol, 2.5 equiv), $NiCl_2(PCy_3)_2$ (15 mg, 0.0219 mmol, 5 mol%), and the sulfamate substrate **34** (94 mg, 0.439 mmol, 1 equiv) were added. The vial was then evacuated and backfilled with N_2. 1.5 mL of a 4.6 mg/mL solution of hexamethylbenzene in toluene was added and the vial was sealed with a Teflon-lined screw cap. The heterogeneous mixture was allowed to stir at 23 °C for 1 h, and then heated to 80 °C for the desired time indicated above. The reaction vessel was then immediately opened and the contents transferred to a test tube containing 1 M HCl (5 mL) and Et_2O (5 mL). Et_2O (1 mL) and H_2O (1 mL) were used to

dissolve and transfer residual solids to the test tube. The layers were separated and the aqueous layer was extracted with Et_2O (3x5 mL). The combined organic layers were dried over $MgSO_4$. A sample (1.5 mL) was taken, and the solvent was removed under reduced pressure. The residue was dissolved in $CDCl_3$; the resulting solution was subjected to filtration through a cotton plug and analyzed by ^1H NMR.

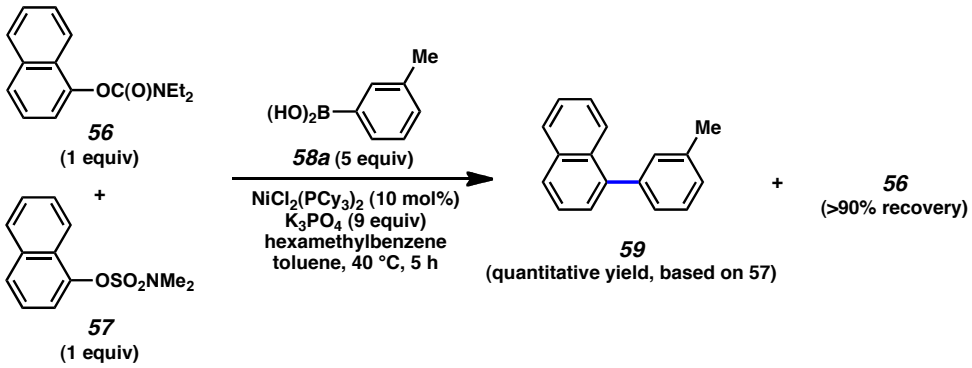


Sulfamate-selective coupling using aryl substrates. Experiments were carried out to effect the selective cross-coupling of aryl sulfamate **6** without effecting reaction of aryl carbamate **55**. To monitor progress over time, five reactions were setup simultaneously under identical reaction conditions. These reactions were removed from heat at varying time points (15 min, 45 min, 90 min, 3 h, 6 h) and the percentage conversions were determined by ^1H NMR analysis with hexamethylbenzene internal standard. The results shown below indicate that selective sulfamate coupling was readily achieved at 50 °C reaction temperature.

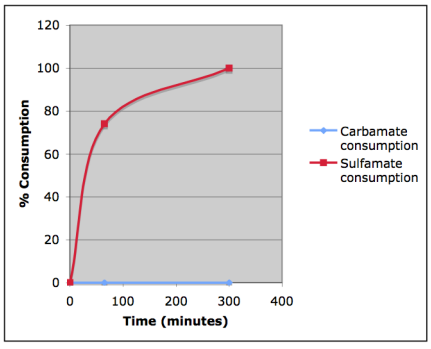


Procedure: A 1-dram vial was charged with anhydrous powdered K_3PO_4 (380 mg, 1.79 mmol, 9 equiv, *obtained from Acros*) and a magnetic stir bar. The vial and contents were flame-dried under reduced pressure, then allowed to cool under N_2. Boronic acid **3a** (135 mg, 1.00 mmol, 5 equiv), $NiCl_2(PCy_3)_2$ (13.8 mg, 0.02 mmol, 10 mol%) were added. The vial was then evacuated and backfilled with N_2. A solution containing sulfamate **6** (40 mg, 0.20 mmol, 1 equiv), carbamate **55** (38 mg, 0.20

mmol, 1 equiv) and hexamethylbenzene (4.9 mg, 0.03 mmol, 15 mol%) in toluene (1.5 mL) was added and the vial was sealed with a Teflon-lined screw cap. The heterogeneous mixture was stirred at 23 °C for 1 h, then heated to 50 °C for the desired time indicated above. The reaction vessel was then immediately opened and the contents transferred to a test tube containing 1 M HCl (5 mL) and ethyl acetate (5 mL). Ethyl acetate (1 mL) and H_2O (1 mL) were used to dissolve and transfer residual solids to the test tube. The layers were separated and the aqueous layer was extracted with ethyl acetate (3x5 mL). The combined organic layers were dried over $MgSO_4$. A sample (1.5 mL) was evaporated to dryness under reduced pressure. The residue was dissolved in $CDCl_3$ and analyzed by ^1H NMR.

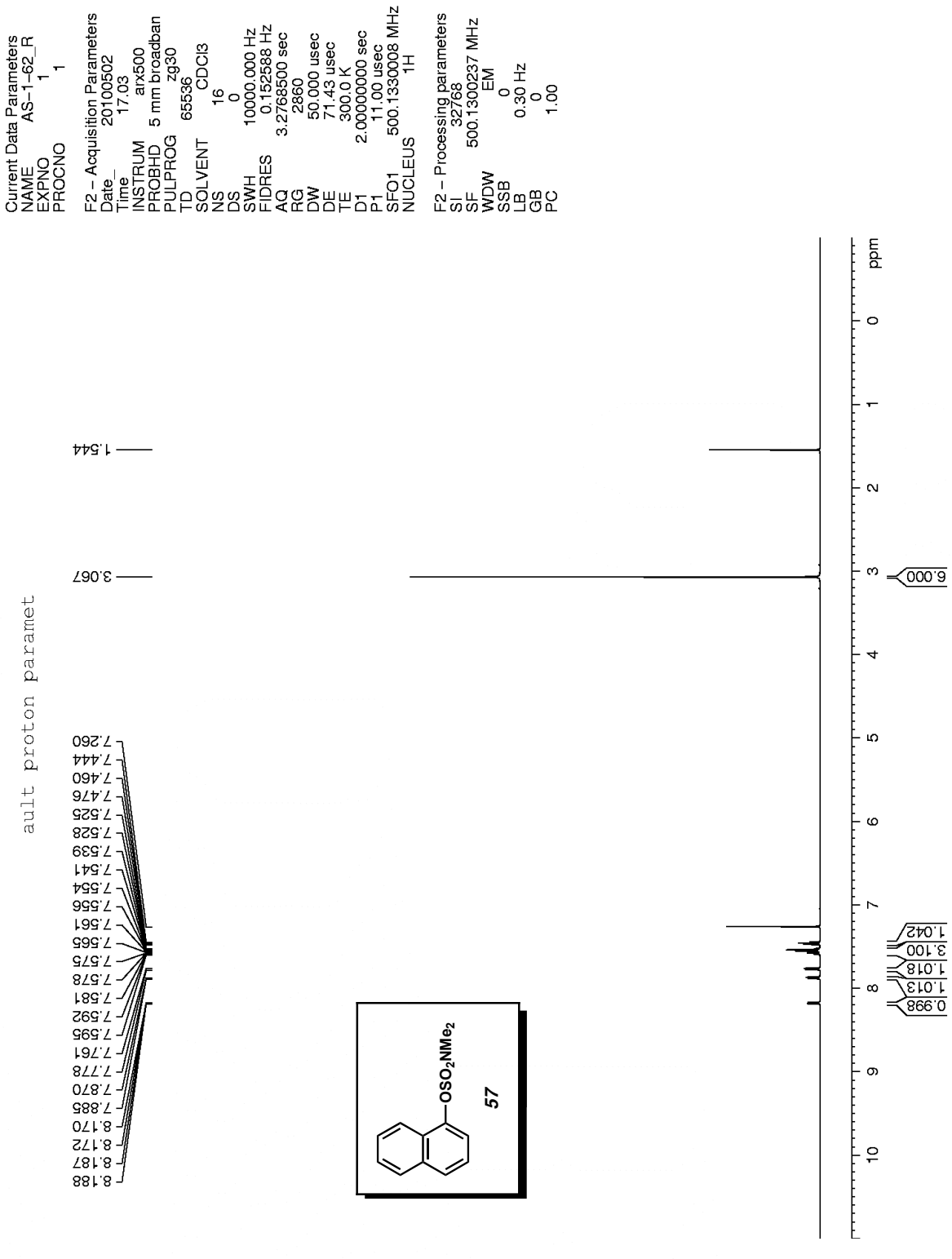


Sulfamate-selective coupling using fused aromatic substrates. Experiments were carried out to effect the selective cross-coupling of aryl sulfamate **57** without disturbing aryl carbamate **56**. To monitor progress over time, two reactions were setup simultaneously under identical reaction conditions. These reactions were stopped at varying time points (65 min and 5 h) and the percentage conversions were determined by ^1H NMR analysis with hexamethylbenzene internal standard. The results shown below indicate that selective sulfamate coupling was readily achieved at 40 °C reaction temperature.



Procedure: A 1-dram vial was charged with anhydrous powdered K_3PO_4 (119 mg, 0.90 mmol, 9 equiv, *obtained from Acros*) and a magnetic stir bar. The vial and contents were flame-dried under reduced pressure, then allowed to cool under N_2. Boronic acid **58a** (68 mg, 0.50 mmol, 0.5 equiv), $NiCl_2(PCy_3)_2$ (6.9 mg, 0.01 mmol, 10 mol%) were added. The vial was then evacuated and backfilled with N_2. A solution containing sulfamate **57** (25 mg, 0.10 mmol, 1 equiv), carbamate **56** (24 mg, 0.10 mmol, 1 equiv), and hexamethylbenzene (2.4 mg, 0.02 mmol, 15 mol%) in toluene (0.7 mL) was added and the vial was sealed with a Teflon-lined screw cap. The heterogeneous mixture was allowed to stir at 23 °C for 1 h, then heated to 40 °C for the desired time indicated above. The reaction vessel was then cooled, immediately opened and the contents transferred to a test tube containing 1 M HCl (5 mL) and ethyl acetate (5 mL). Ethyl acetate (1 mL) and H_2O (1 mL) were used to dissolve and transfer residual solids to the test tube. The layers were separated and the aqueous layer was extracted with ethyl acetate (3x5 mL). The combined organic layers were dried over $MgSO_4$. A sample (1.5 mL) was evaporated to dryness under reduced pressure. The residue was dissolved in $CDCl_3$ and analyzed by ^1H NMR.

^{1}H NMR Spectra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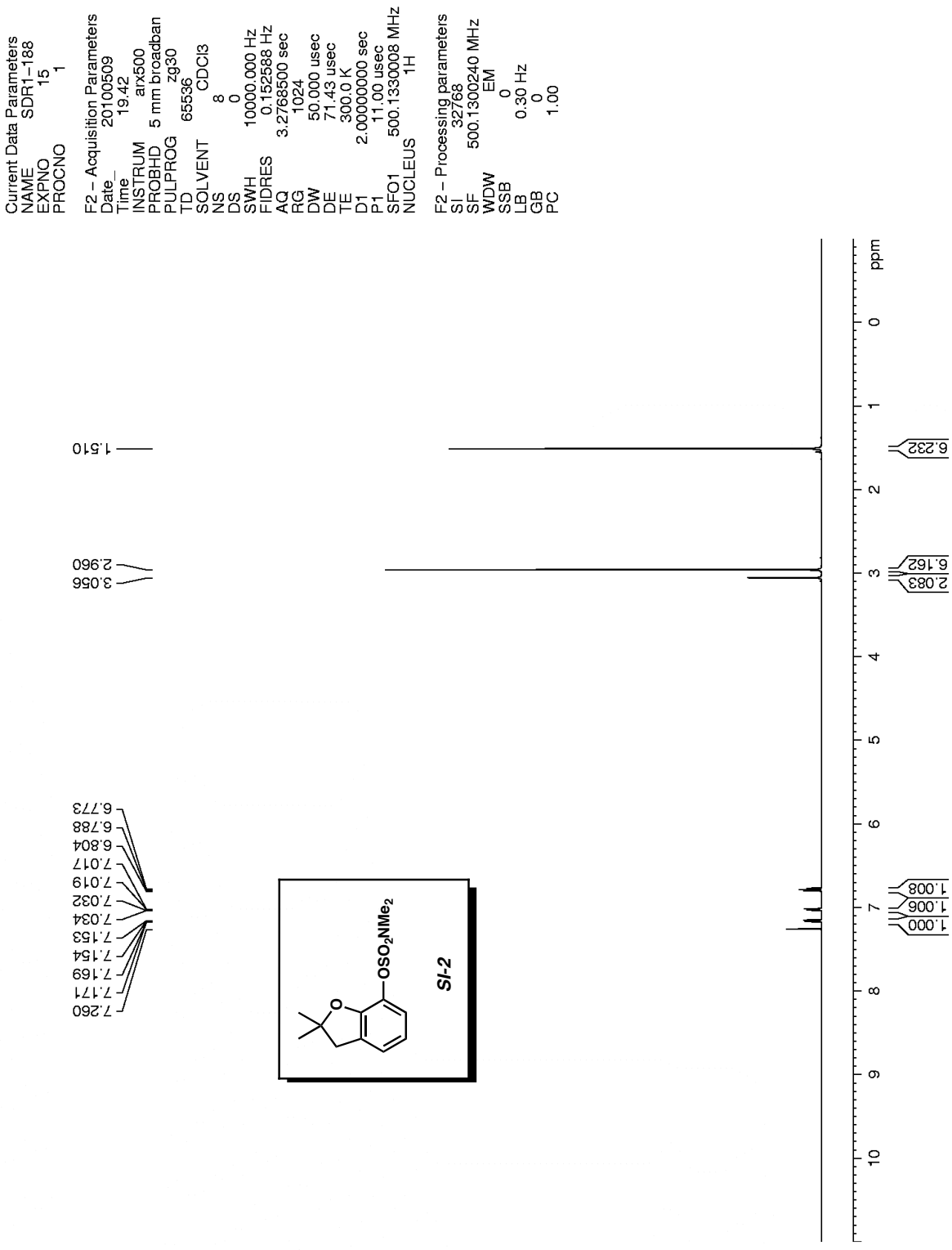
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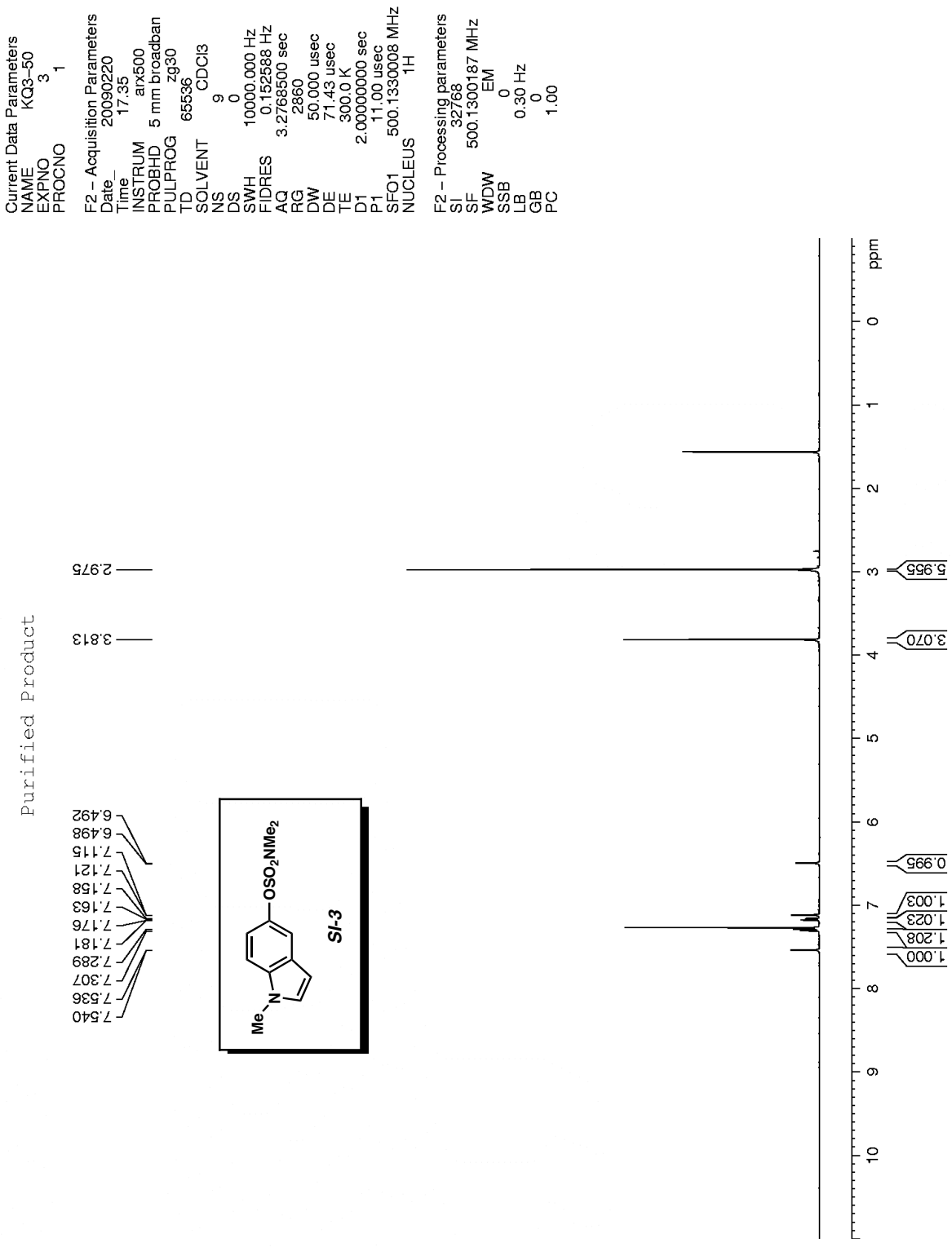
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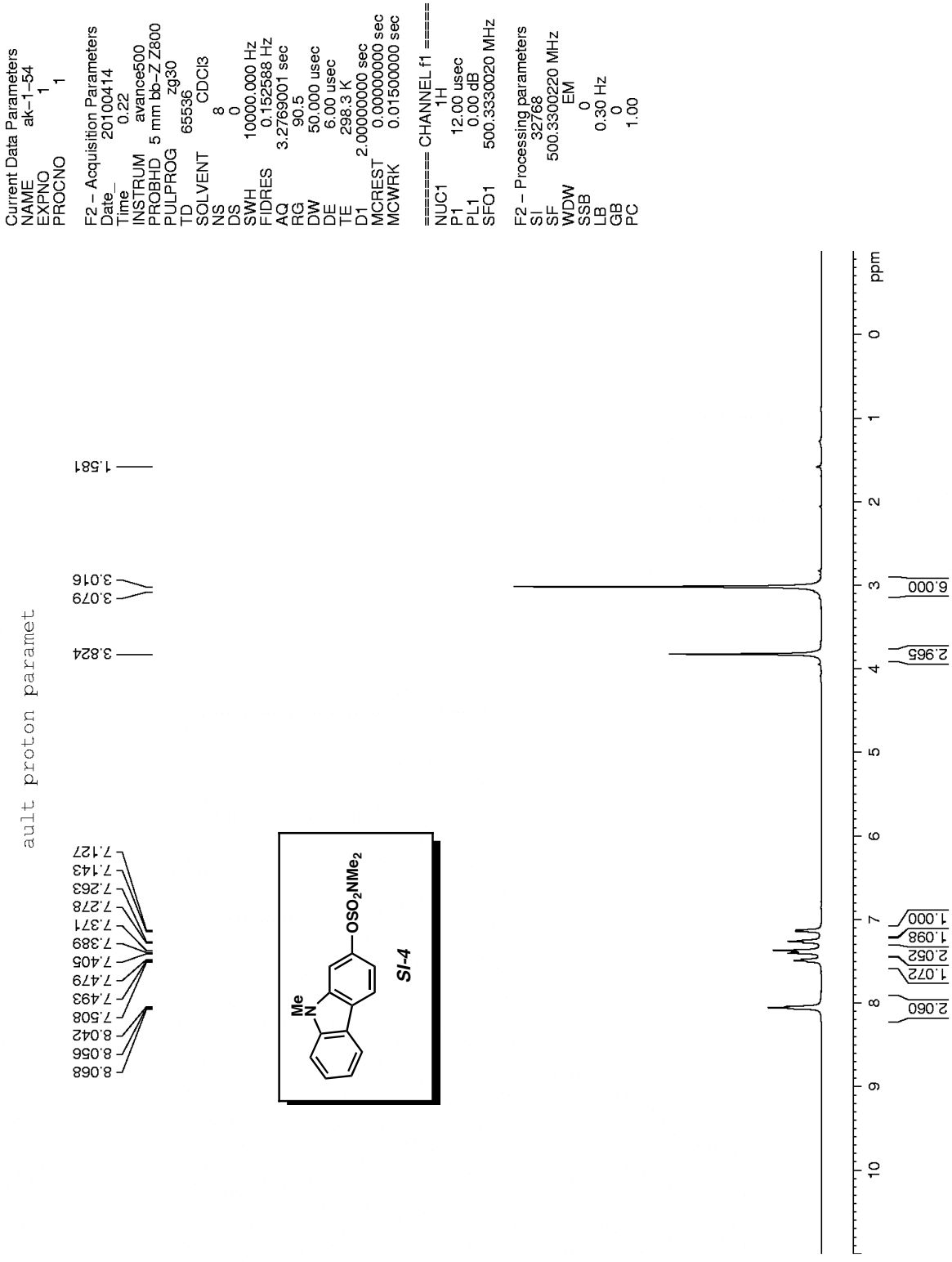
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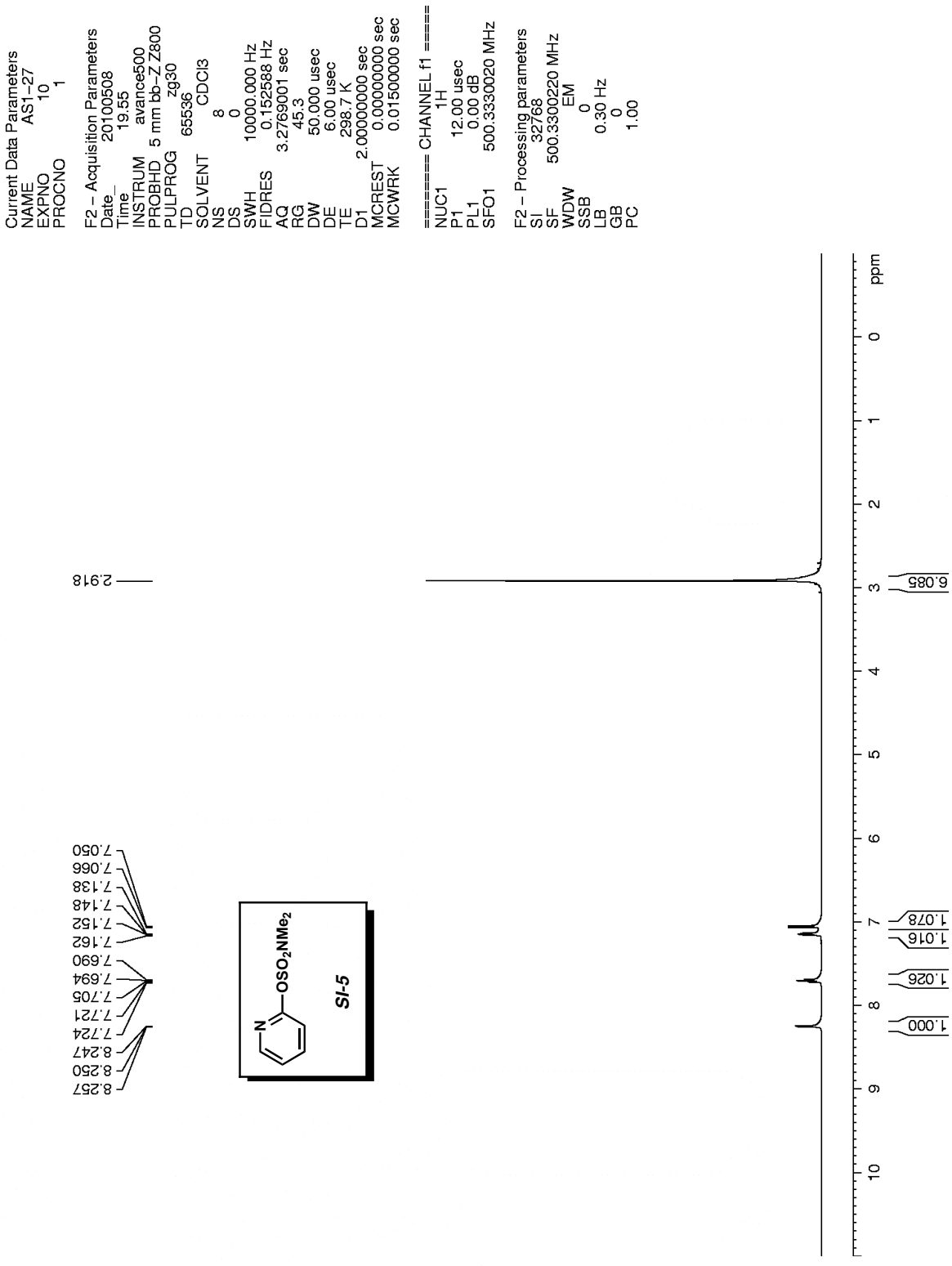
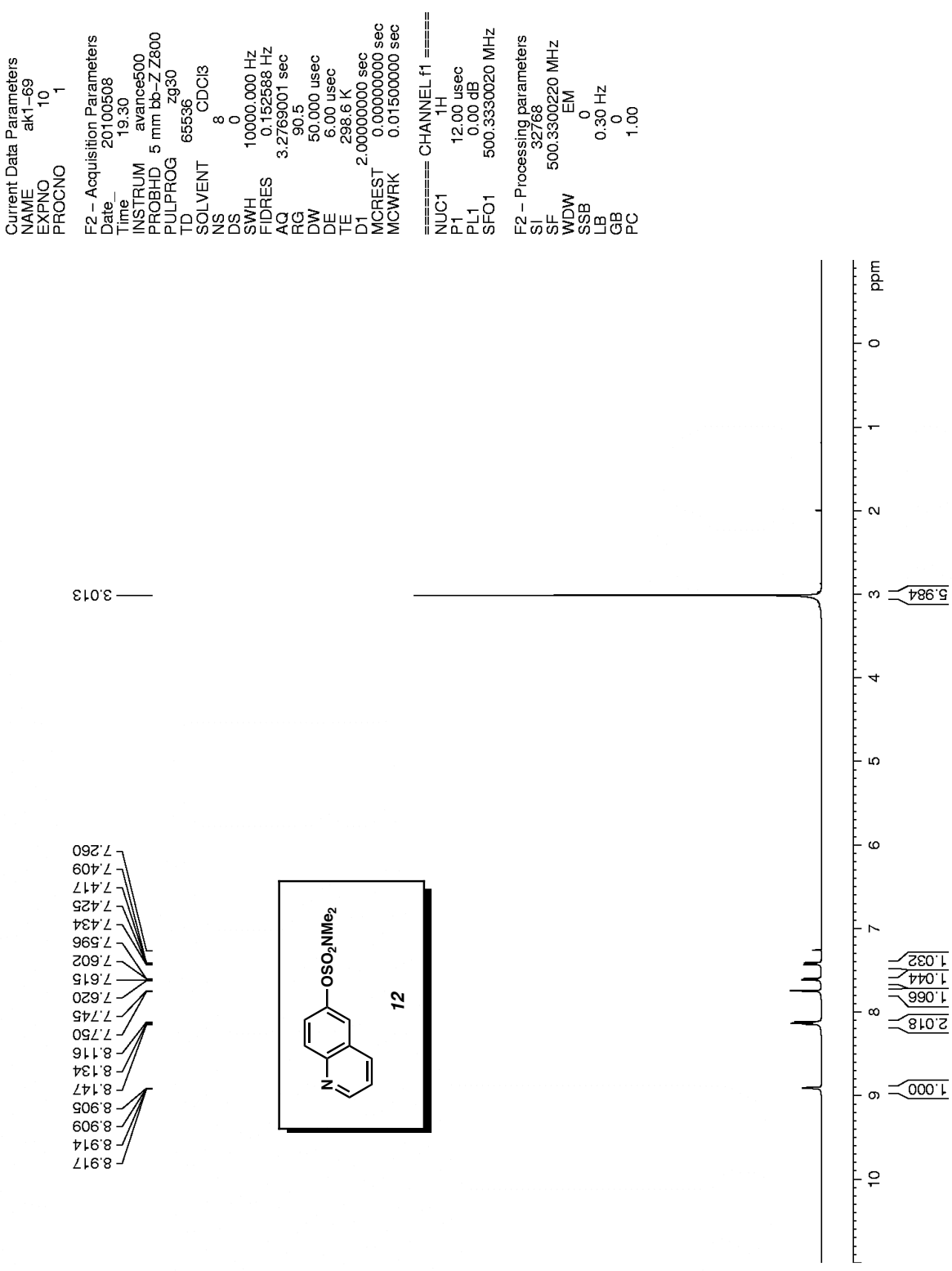
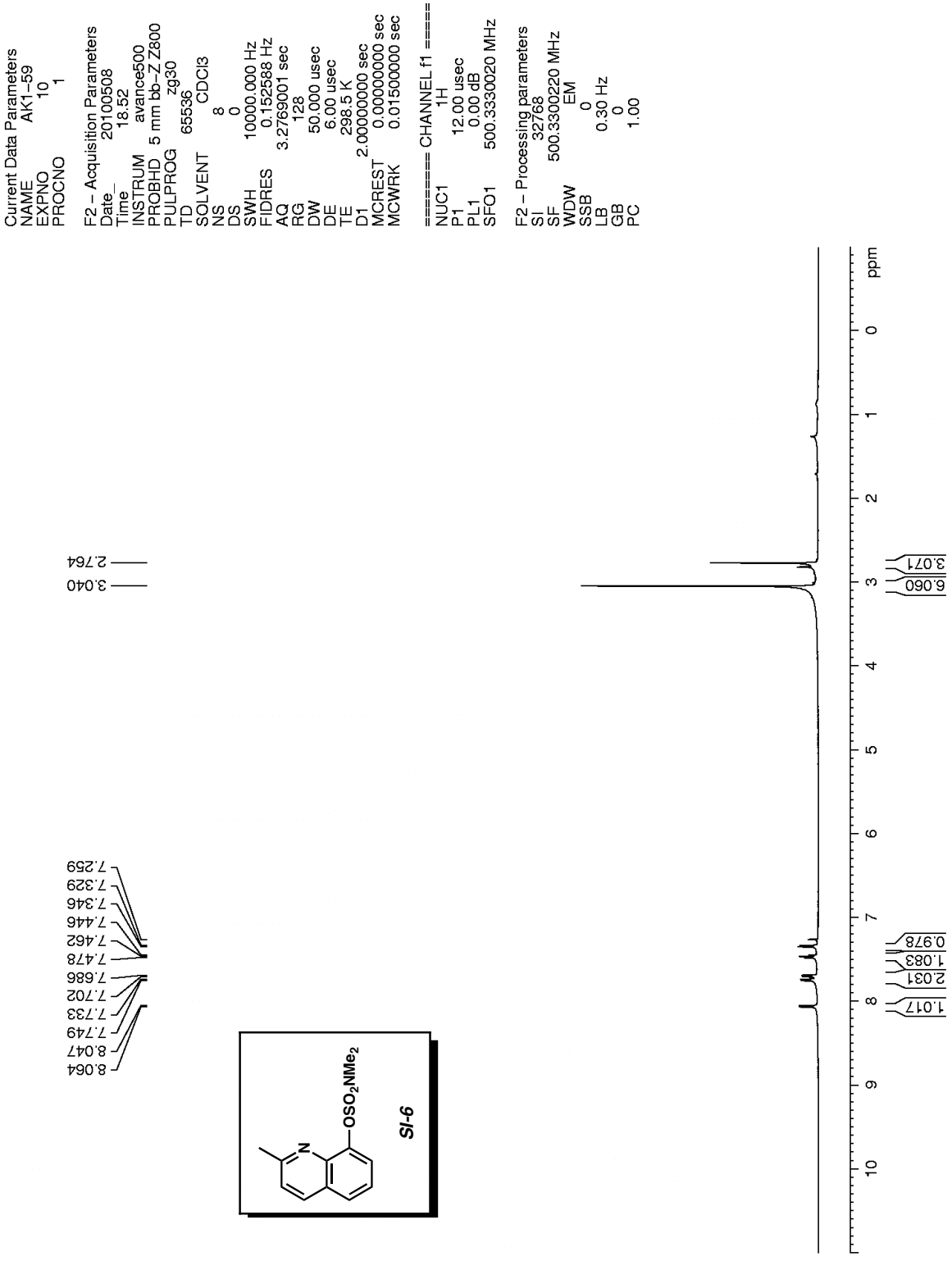
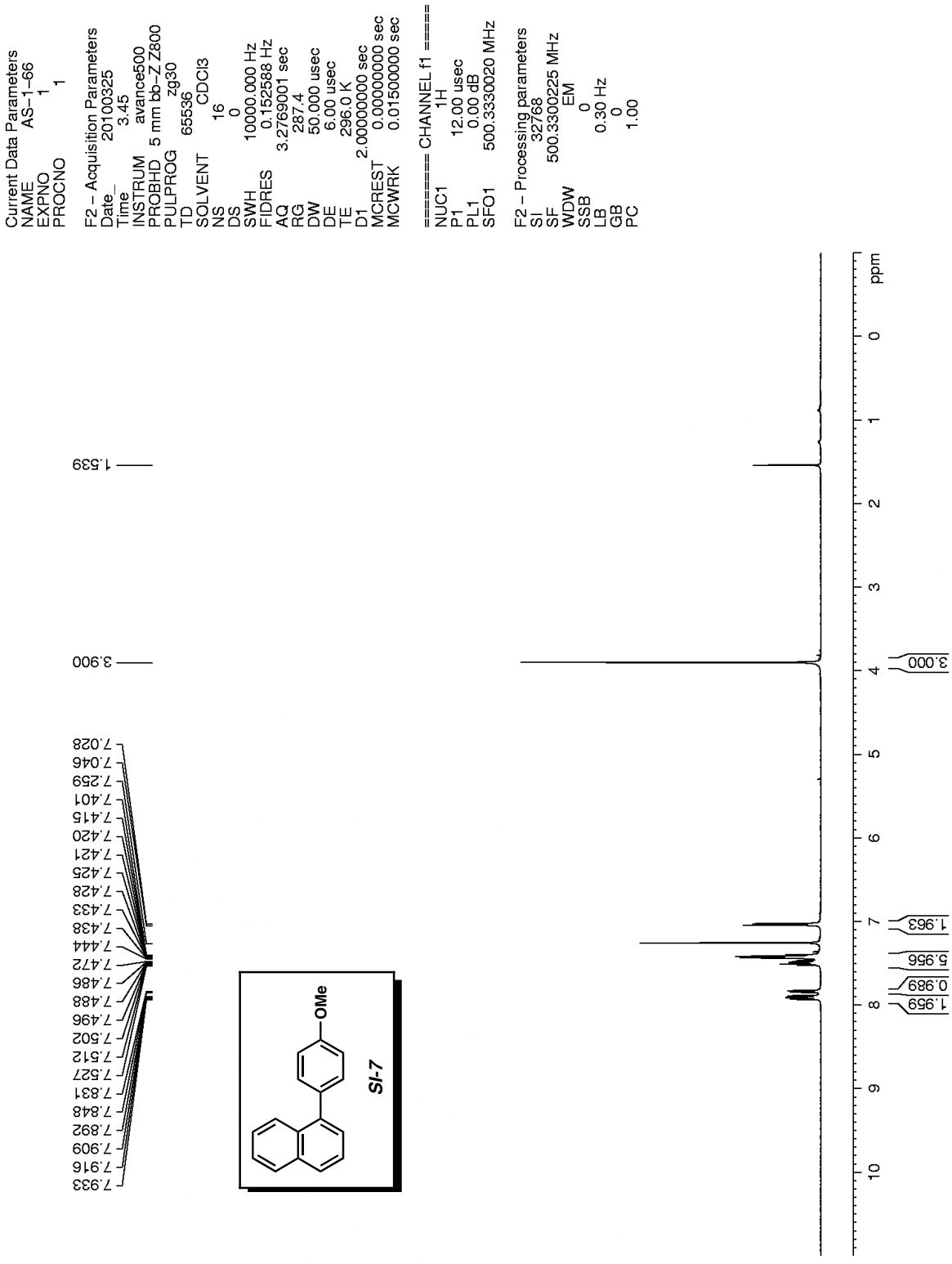
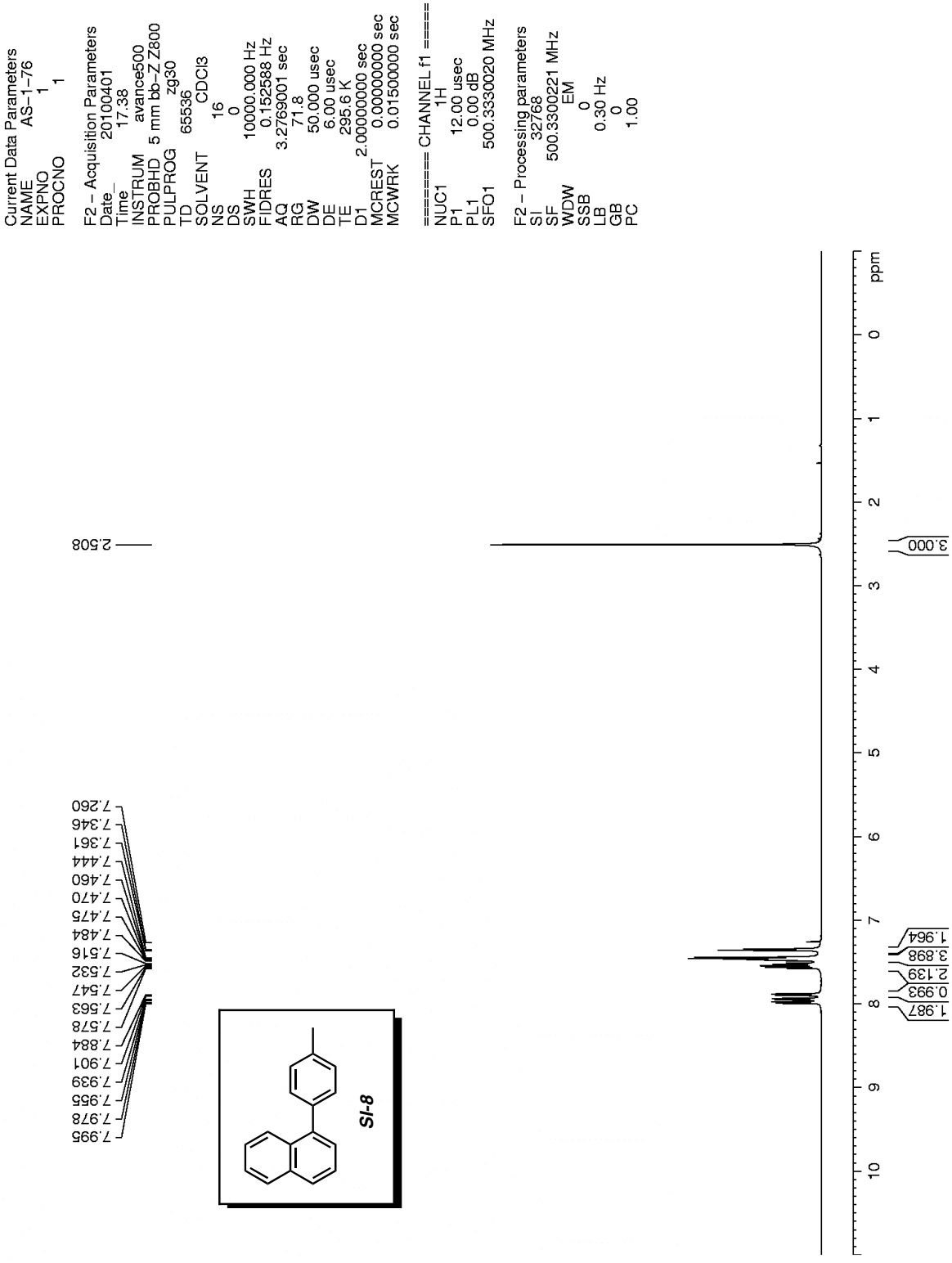
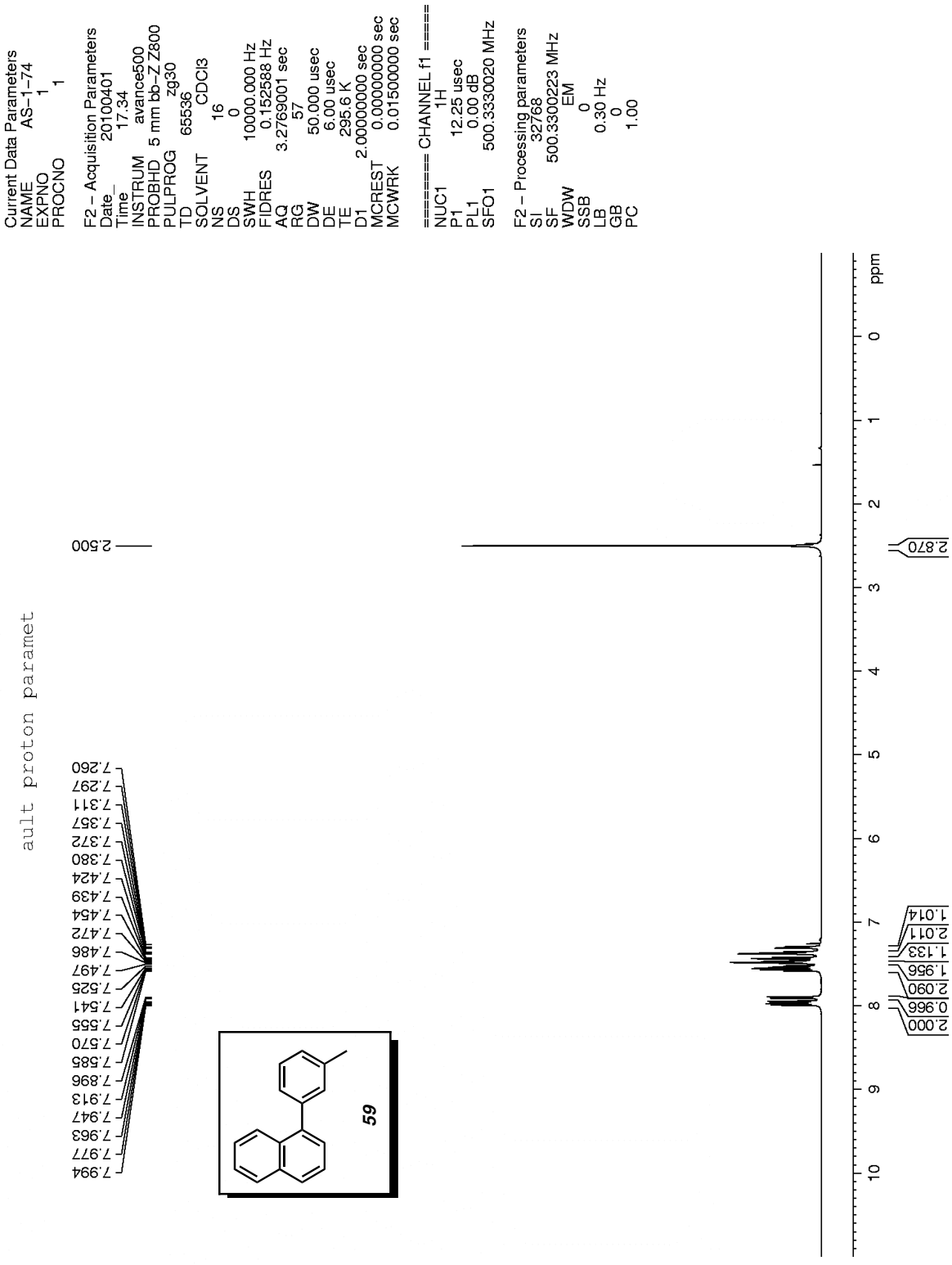

Current Data Parameters
NAME AS1–27
EXPNO 10
PROCNO 1
F2 – Acquisition Parameters
Date_ 20100508
Time 19.55
INSTRUM avance500
PROBHD 5 mm bb–Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2769001 sec
RG 45.3
DW 50.000 usec
DE 6.00 usec
TE 298.7 K
D1 2.00000000 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 500.3300220 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.918
7.050
7.066
7.138
7.148
7.152
7.162
7.690
7.694
7.705
7.721
7.724
8.247
8.250
8.257
SI-5
6.085
1.000
1.026
1.016
1.078
ppm

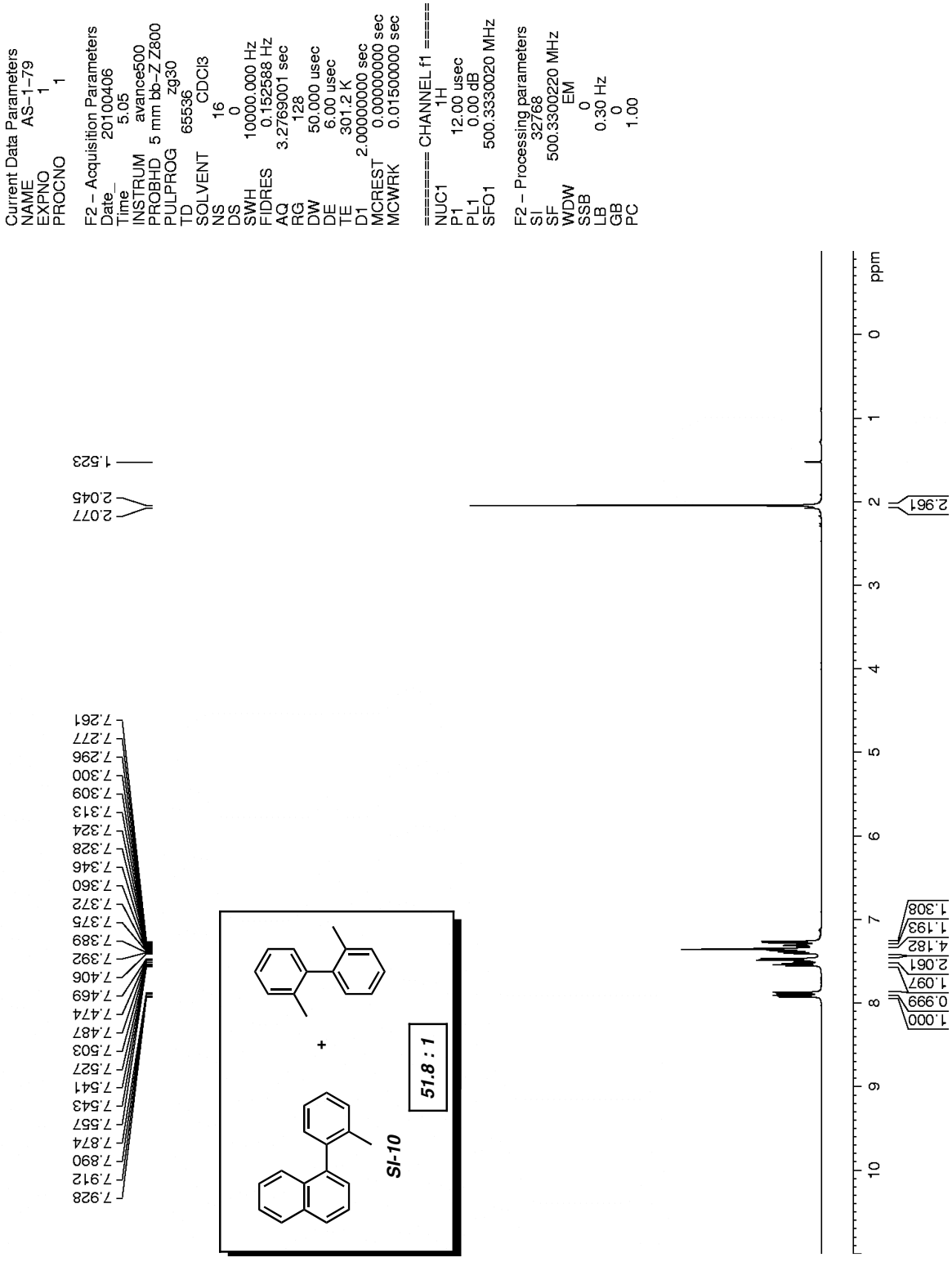

Current Data Parameters
NAME ak1-69
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100508
Time 19.30
INSTRUM avance500
PROBHD 5 mm bb-Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2769001 sec
RG 90.5
DW 50.000 usec
DE 6.00 usec
TE 298.6 K
D1 2.00000000 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 500.3300220 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.917
8.914
8.909
8.905
8.147
8.134
8.116
7.750
7.745
7.620
7.615
7.602
7.596
7.434
7.425
7.417
7.409
7.260
3.013
OSO2NMe2
N
12
1.000
2.018
1.066
1.044
1.032
5.984
10
9
8
7
6
5
4
3
2
1
0
ppm

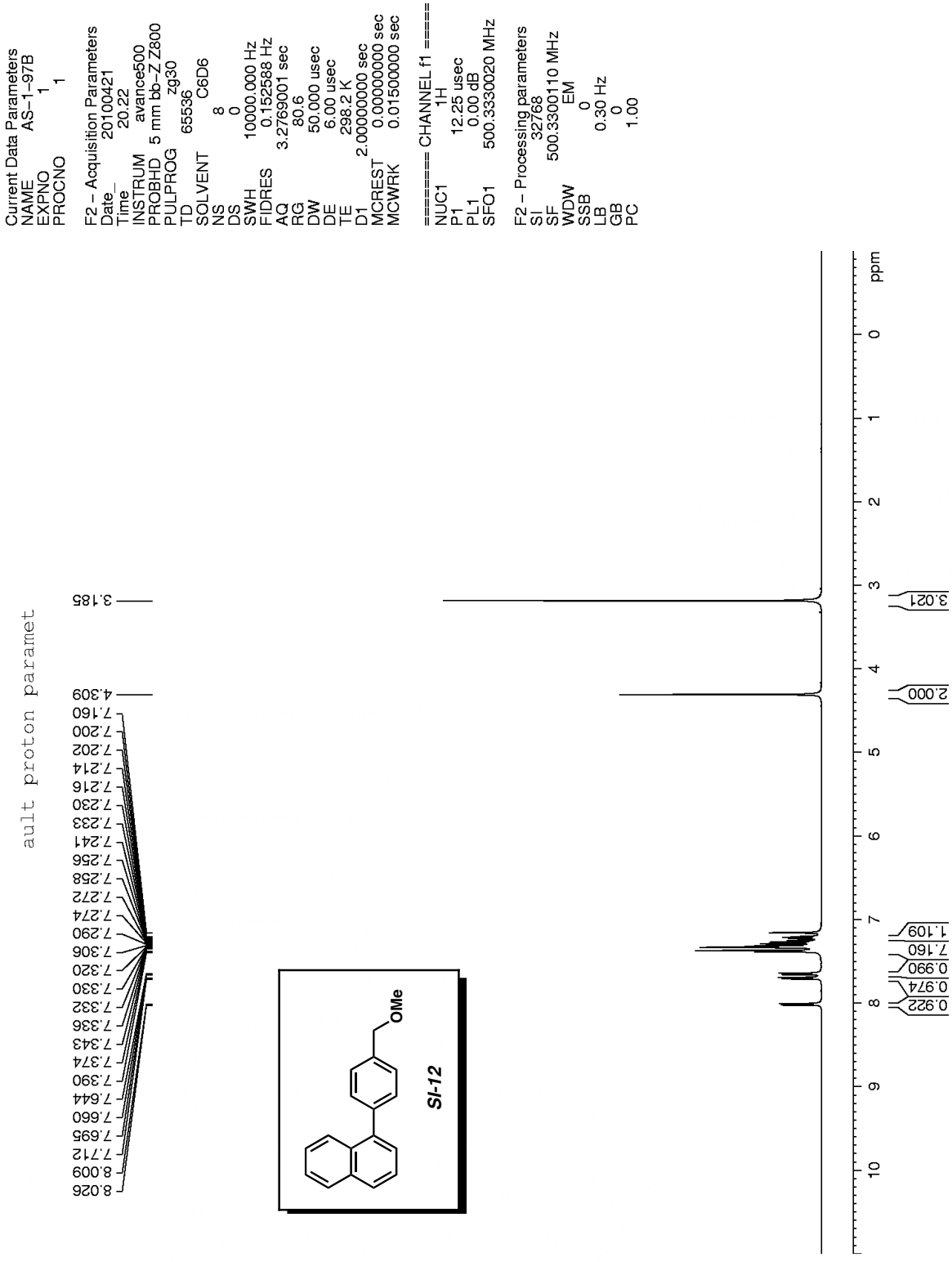

Current Data Parameters
NAME AK1–59
EXPNO 10
PROCNO 1
F2 – Acquisition Parameters
Date_ 20100508
Time 18.52
INSTRUM avance500
PROBHD 5 mm bb–Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2769001 sec
RG 128
DW 50.000 usec
DE 6.00 usec
TE 298.5 K
D1 2.00000000 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 500.3300220 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.064
8.047
7.749
7.733
7.702
7.686
7.478
7.462
7.446
7.346
7.329
7.259
3.040
2.764
OSO2NMe2
N
SI-6
6.060
3.071
2.031
1.083
1.017
0.978
ppm

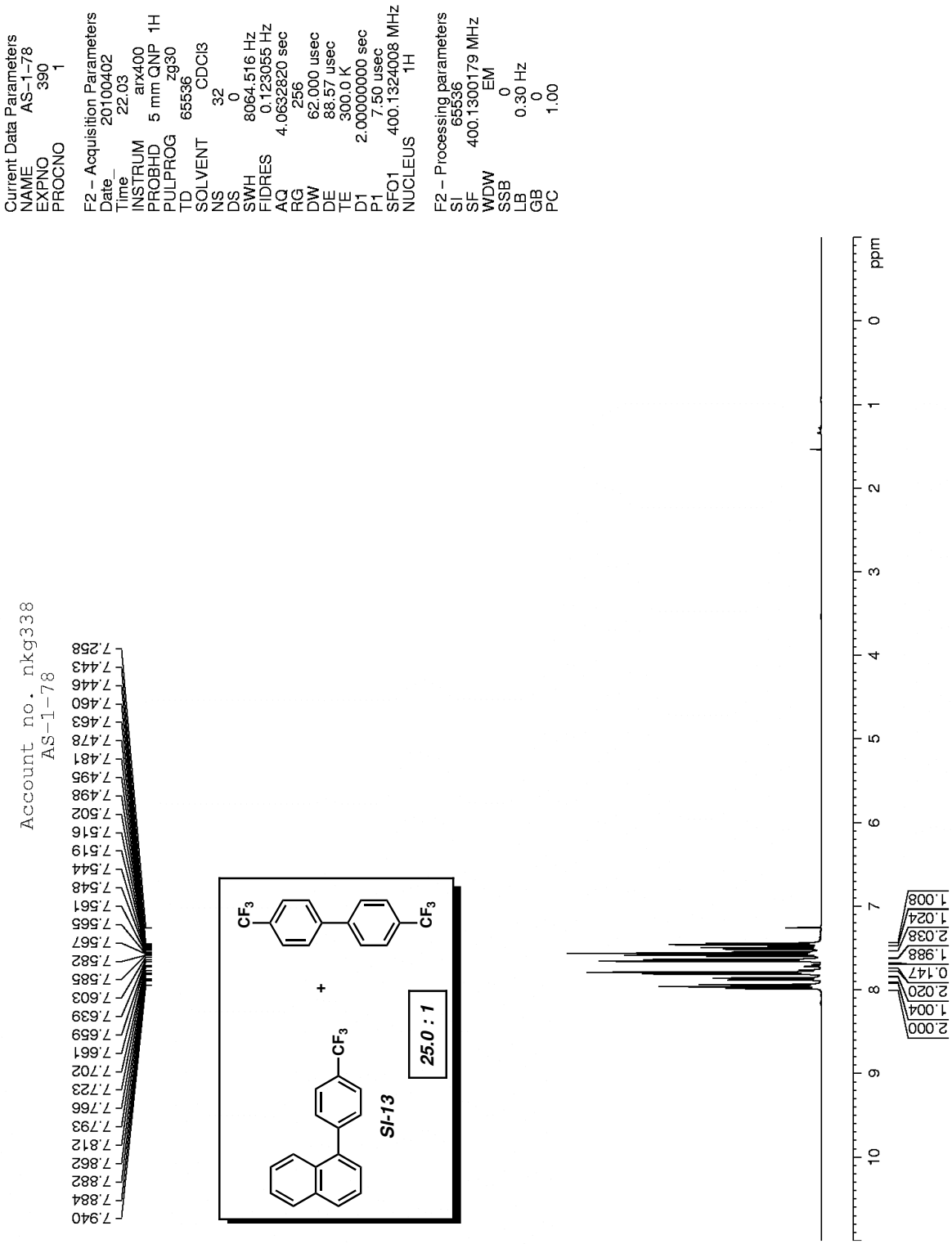

Current Data Parameters
NAME AS–1–66
EXPNO 1
PROCNO 1
F2 – Acquisition Parameters
Date_ 20100325
Time 3.45
INSTRUM avance500
PROBHD 5 mm bb–Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2769001 sec
RG 287.4
DW 50.000 usec
DE 6.00 usec
TE 296.0 K
D1 2.00000000 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 500.3300225 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.933
7.916
7.909
7.892
7.848
7.831
7.527
7.512
7.502
7.496
7.488
7.486
7.472
7.444
7.438
7.433
7.428
7.425
7.421
7.420
7.415
7.401
7.259
7.046
7.028
1.539
3.900
OMe
SI-7
ppm
3.000
1.963
5.956
0.989
1.959

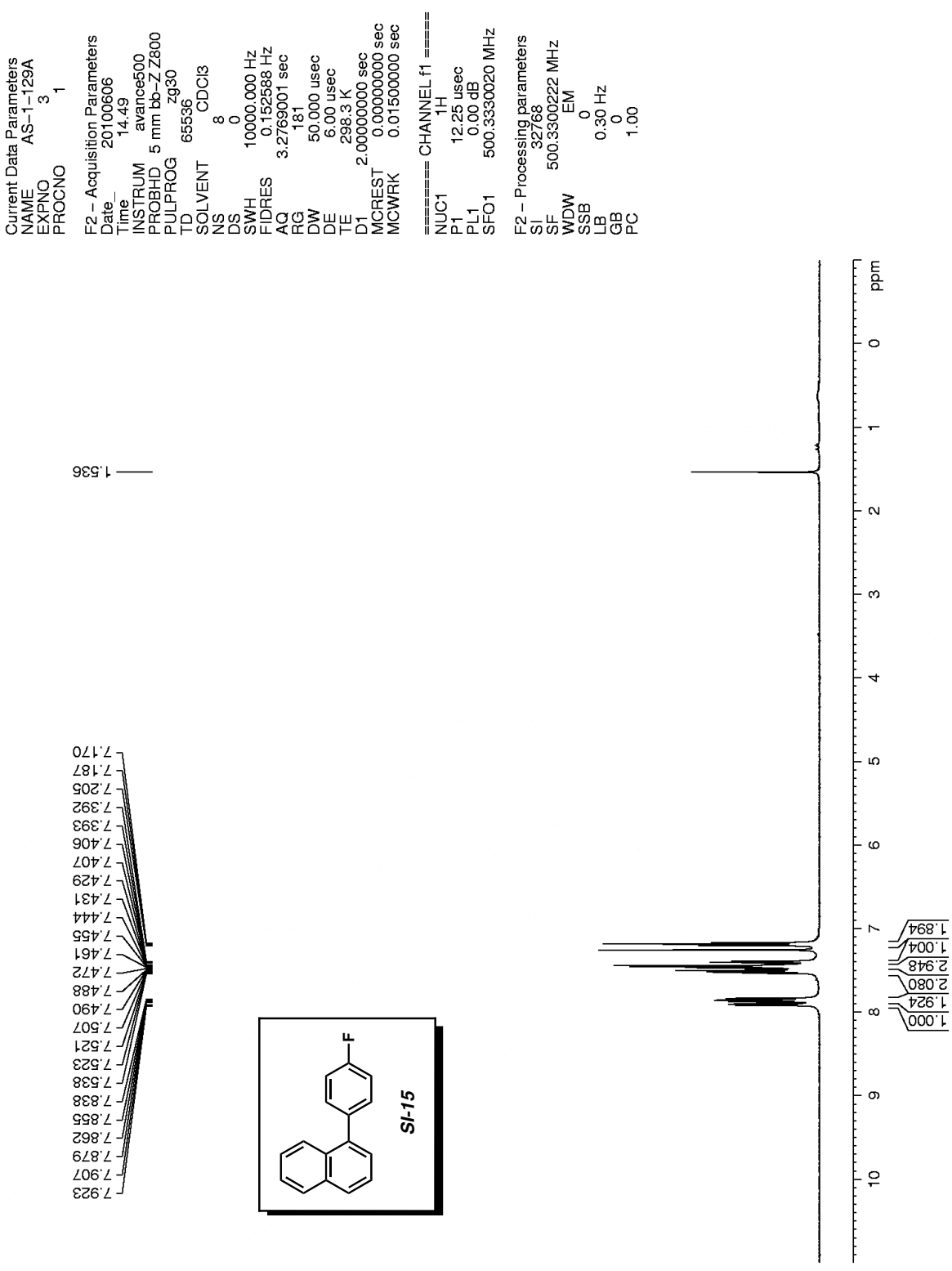

Current Data Parameters
NAME AS–1–76
EXPNO 1
PROCNO 1
F2 – Acquisition Parameters
Date_ 20100401
Time 17.38
INSTRUM avance500
PROBHD 5 mm bb–Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2769001 sec
RG 71.8
DW 50.000 usec
DE 6.00 usec
TE 295.6 K
D1 2.00000000 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 500.3300221 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2.508
7.995
7.978
7.955
7.939
7.901
7.884
7.578
7.563
7.547
7.532
7.516
7.484
7.475
7.470
7.460
7.444
7.361
7.346
7.260
SI-8
3.000
1.987
0.993
2.139
3.898
1.964
ppm

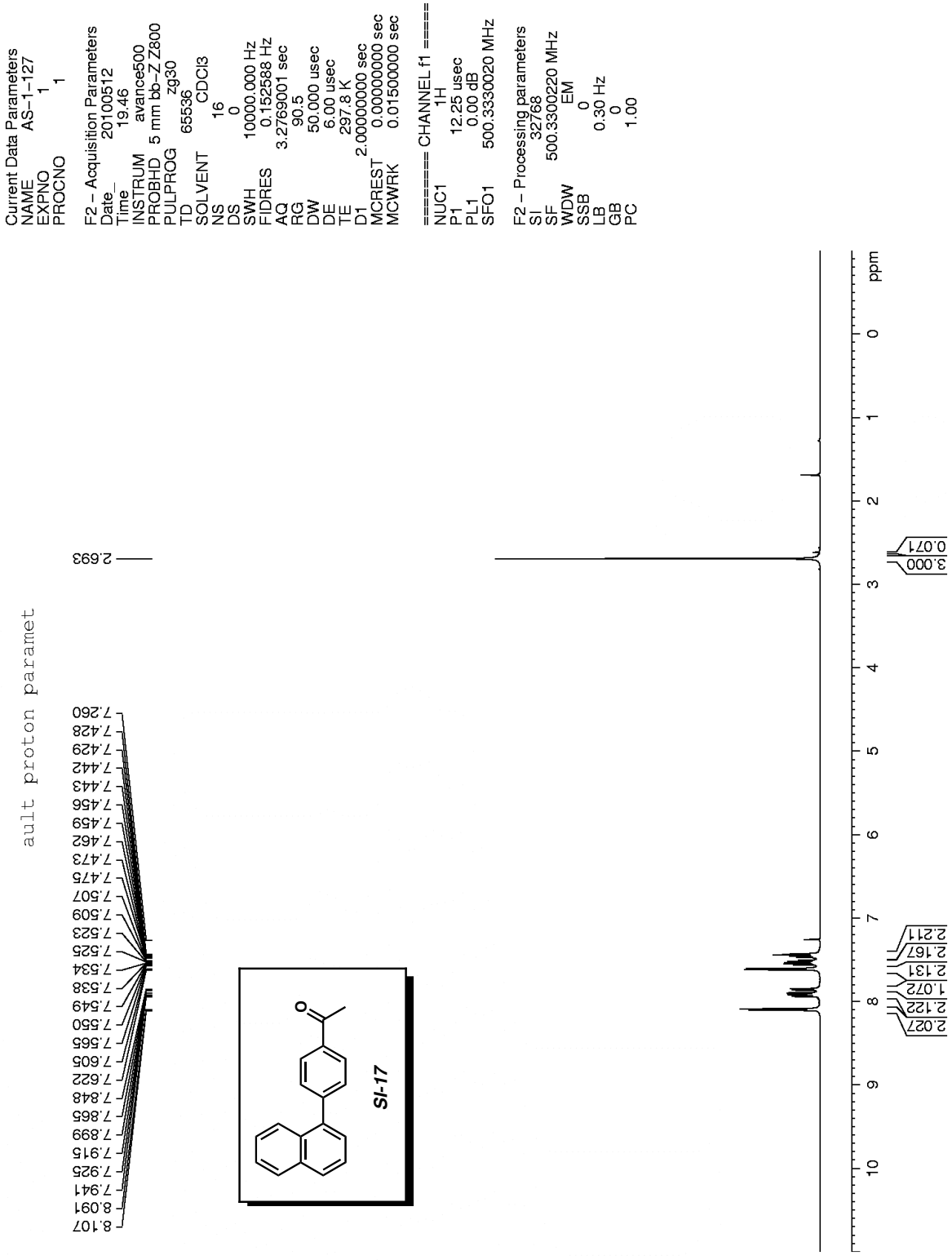

Current Data Parameters
NAME AS–1–74
EXPNO 1
PROCNO 1
F2 – Acquisition Parameters
Date_ 20100401
Time 17.34
INSTRUM avance500
PROBHD 5 mm bb–Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2769001 sec
RG 57
DW 50.000 usec
DE 6.00 usec
TE 295.6 K
D1 2.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ======
NUC1 1H
P1 12.25 usec
PL1 0.00 dB
SFO1 500.3330020 MHz
F2 – Processing parameters
SI 32768
SF 500.3300223 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ault proton paramet
7.994
7.977
7.963
7.947
7.913
7.896
7.585
7.570
7.555
7.541
7.525
7.497
7.486
7.472
7.454
7.439
7.424
7.380
7.372
7.357
7.311
7.297
7.260
2.500
59
2.870
2.000
0.966
2.090
1.956
1.133
2.011
1.014
ppm

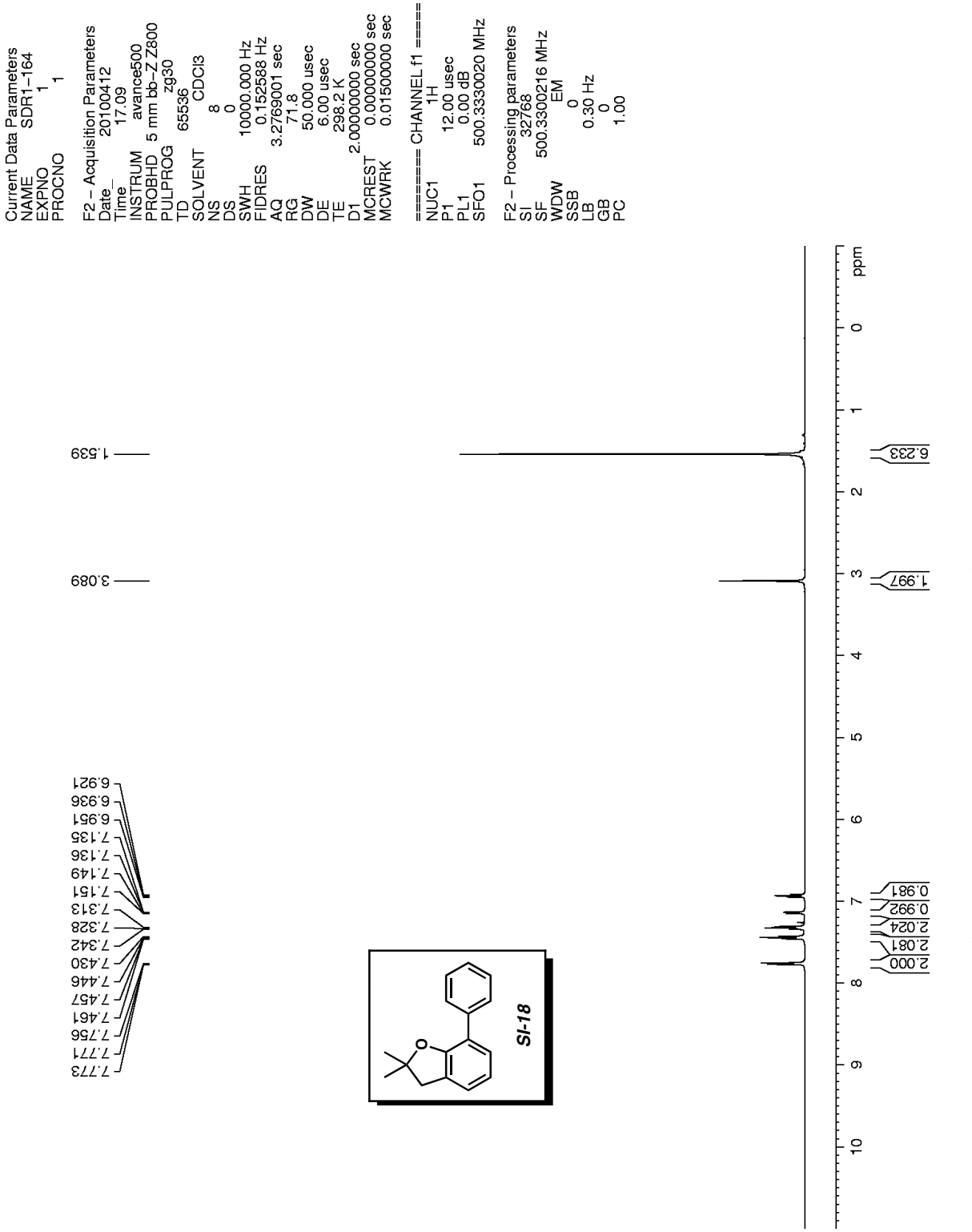

Current Data Parameters
NAME AS–1–79
EXPNO 1
PROCNO 1
F2 – Acquisition Parameters
Date_ 20100406
Time 5.05
INSTRUM avance500
PROBHD 5 mm bb–Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2769001 sec
RG 128
DW 50.000 usec
DE 6.00 usec
TE 301.2 K
D1 2.00000000 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 500.3300220 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.928
7.912
7.890
7.874
7.557
7.543
7.541
7.527
7.503
7.487
7.474
7.469
7.406
7.392
7.389
7.375
7.372
7.360
7.346
7.328
7.324
7.313
7.309
7.300
7.296
7.277
7.261
2.077
2.045
1.523
SI-10
51.8 : 1
2.961
1.000
0.999
1.097
2.061
4.182
1.193
1.308
ppm

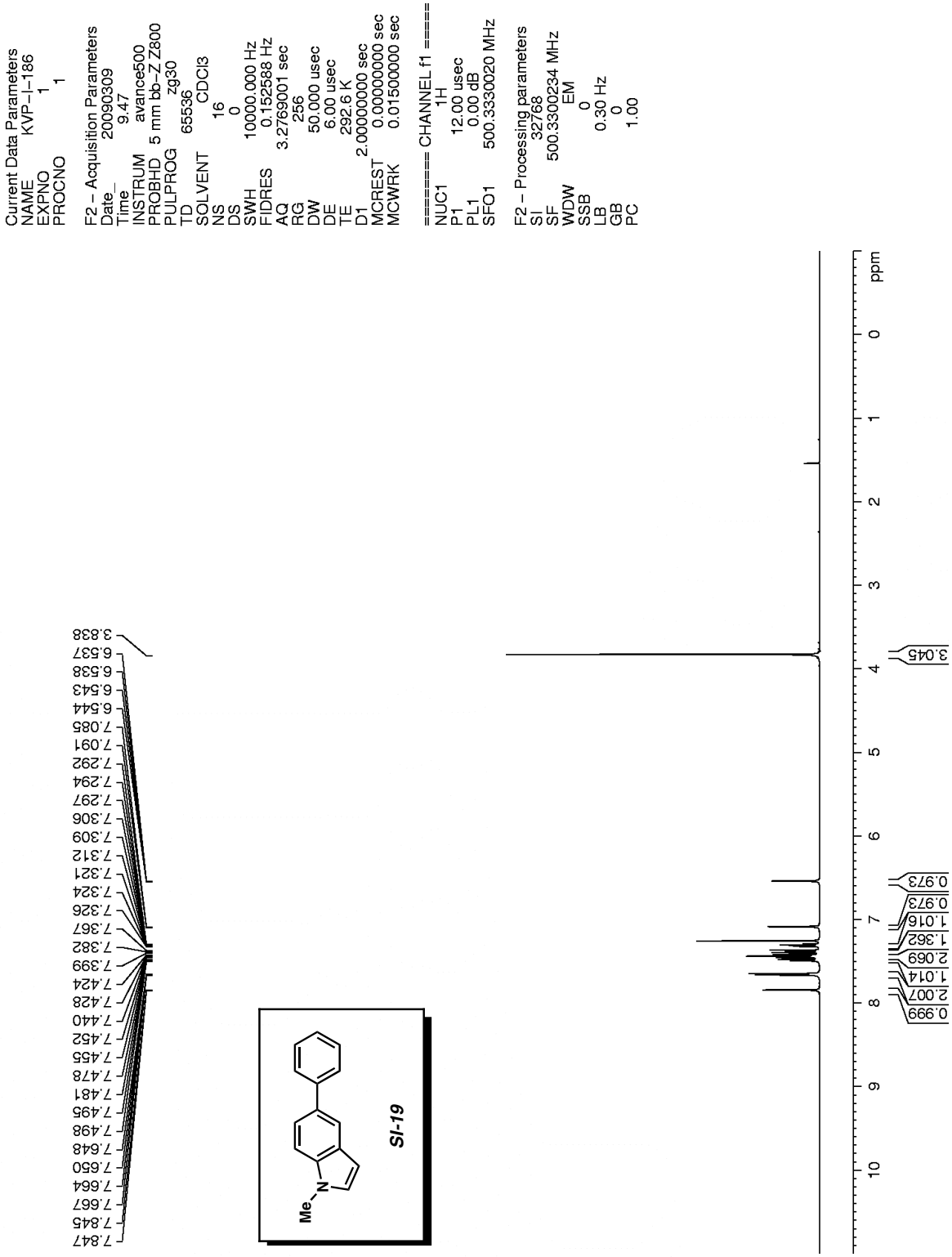

Current Data Parameters
NAME AS–1–97B
EXPNO 1
PROCNO 1
F2 – Acquisition Parameters
Date_ 20100421
Time 20.22
INSTRUM avance500
PROBHD 5 mm bb–Z Z800
PULPROG zg30
TD 65536
SOLVENT C6D6
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2769001 sec
RG 80.6
DW 50.000 usec
DE 6.00 usec
TE 298.2 K
D1 2.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ======
NUC1 1H
P1 12.25 usec
PL1 0.00 dB
SFO1 500.3330020 MHz
F2 – Processing parameters
SI 32768
SF 500.3300110 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ault proton paramet
3.185
4.309
7.160
7.200
7.202
7.214
7.216
7.230
7.233
7.241
7.256
7.258
7.272
7.274
7.290
7.306
7.320
7.330
7.332
7.336
7.343
7.374
7.390
7.644
7.660
7.695
7.712
8.009
8.026
OMe
SI-12
3.021
2.000
1.109
7.160
0.990
0.974
0.922
ppm

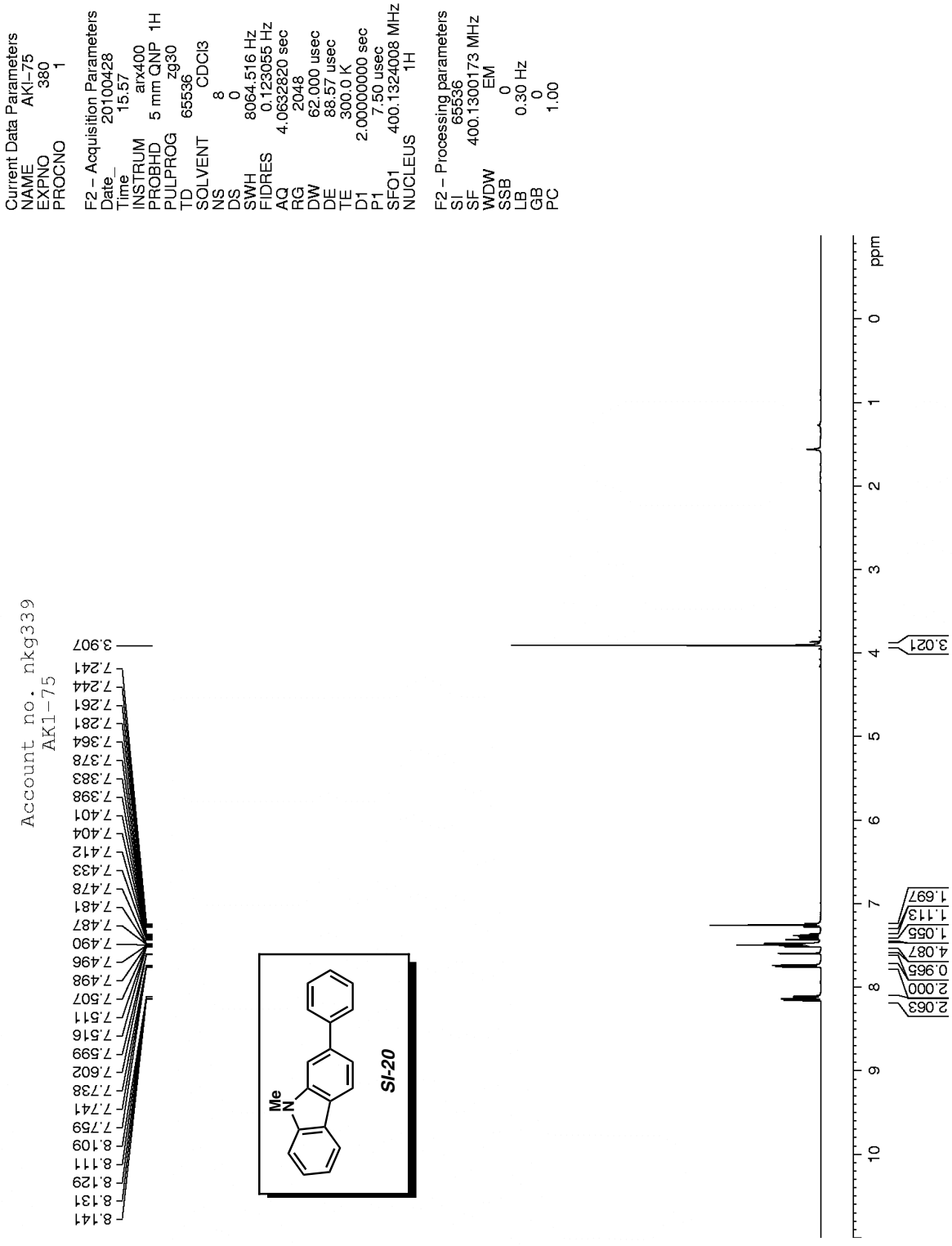

Current Data Parameters
NAME AS-1-78
EXPNO 390
PROCNO 1
F2 – Acquisition Parameters
Date_ 20100402
Time_ 22.03
INSTRUM arx400
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 0
SWH 8064.516 Hz
FIDRES 0.123055 Hz
AQ 4.0632820 sec
RG 256
DW 62.000 usec
DE 88.57 usec
TE 300.0 K
D1 2.00000000 sec
P1 7.50 usec
SFO1 400.1324008 MHz
NUCLEUS 1H
F2 – Processing parameters
SI 65536
SF 400.1300179 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Account no. nkg338
AS-1-78
7.940
7.884
7.882
7.862
7.812
7.793
7.766
7.723
7.702
7.661
7.659
7.639
7.603
7.585
7.582
7.567
7.565
7.561
7.548
7.544
7.519
7.516
7.502
7.498
7.495
7.481
7.478
7.463
7.460
7.446
7.443
7.258
CF3
CF3
+
CF3
SI-13
25.0 : 1
ppm
2.000
1.004
2.020
0.147
1.988
2.038
1.024
1.008

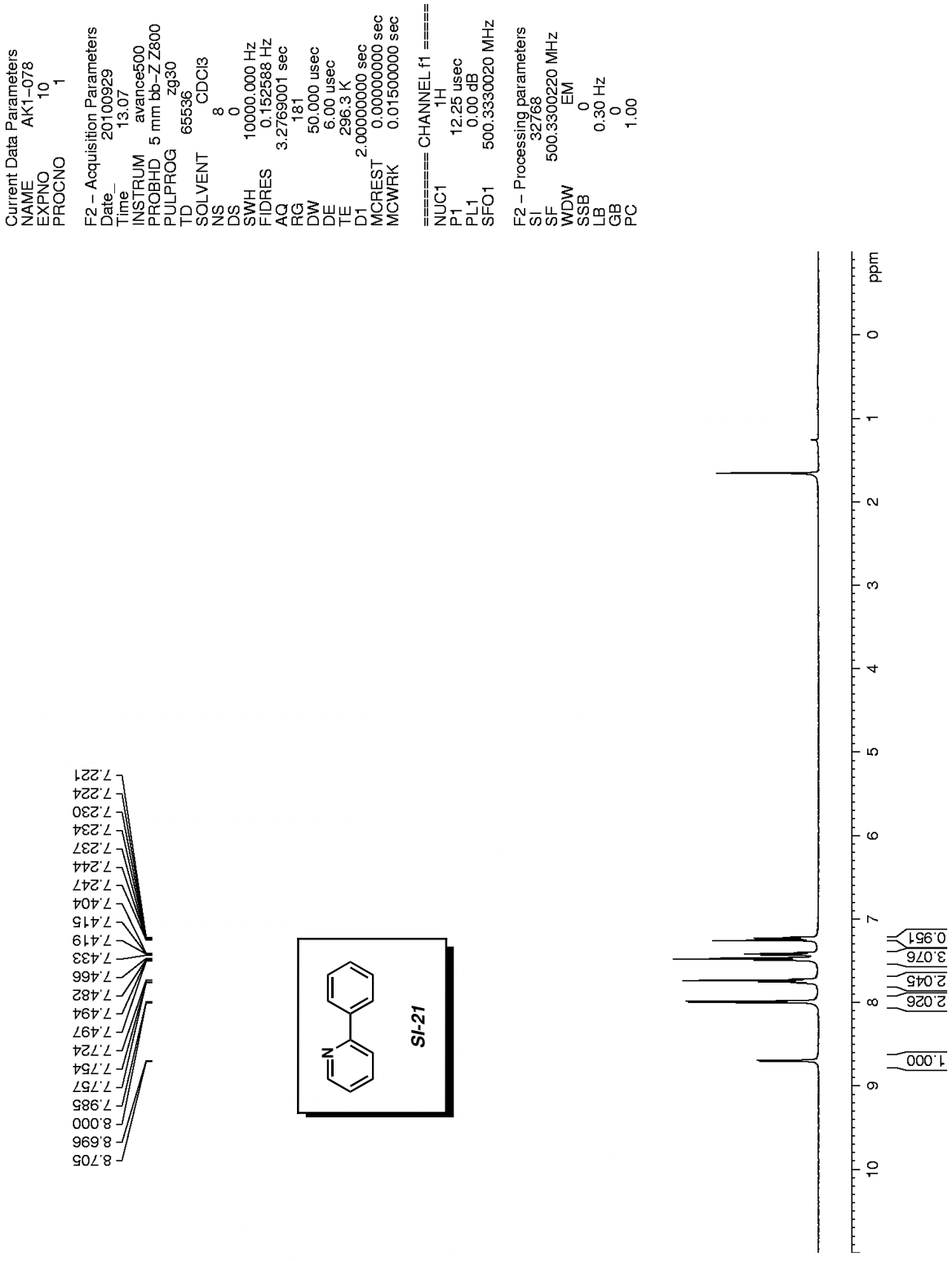

Current Data Parameters
NAME AS-1-129A
EXPNO 3
PROCNO 1
F2 – Acquisition Parameters
Date_ 20100606
Time 14.49
INSTRUM avance500
PROBHD 5 mm bb-Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2769001 sec
RG 181
DW 50.000 usec
DE 6.00 usec
TE 298.3 K
D1 2.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ======
NUC1 1H
P1 12.25 usec
PL1 0.00 dB
SFO1 500.3330020 MHz
F2 – Processing parameters
SI 32768
SF 500.3300222 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.536
7.923
7.907
7.879
7.862
7.855
7.838
7.538
7.523
7.521
7.507
7.490
7.488
7.472
7.461
7.455
7.444
7.431
7.429
7.407
7.406
7.393
7.392
7.205
7.187
7.170
F
SI-15
1.000
1.924
2.080
2.948
1.004
1.894
ppm


Current Data Parameters
NAME AS–1–127
EXPNO 1
PROCNO 1
F2 – Acquisition Parameters
Date_ 20100512
Time 19.46
INSTRUM avance500
PROBHD 5 mm bb–Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2769001 sec
RG 90.5
DW 50.000 usec
DE 6.00 usec
TE 297.8 K
D1 2.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ======
NUC1 1H
P1 12.25 usec
PL1 0.00 dB
SFO1 500.3330020 MHz
F2 – Processing parameters
SI 32768
SF 500.3300220 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ault proton paramet
8.107
8.091
7.941
7.925
7.915
7.899
7.865
7.848
7.622
7.605
7.565
7.550
7.549
7.538
7.534
7.525
7.523
7.509
7.507
7.475
7.473
7.462
7.459
7.456
7.443
7.442
7.429
7.428
7.260
2.693
SI-17
3.000
0.071
2.211
2.167
2.131
1.072
2.122
2.027
ppm


Current Data Parameters
NAME SDR1–164
EXPNO 1
PROCNO 1
F2 – Acquisition Parameters
Date_ 20100412
Time 17.09
INSTRUM avance500
PROBHD 5 mm bb–Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2769001 sec
RG 71.8
DW 50.000 usec
DE 6.00 usec
TE 298.2 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 500.3300216 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.773
7.771
7.756
7.461
7.457
7.446
7.430
7.342
7.328
7.313
7.151
7.149
7.136
7.135
6.936
6.921
3.089
1.539
SI-18
2.000
2.081
2.024
0.992
0.981
1.997
6.233
ppm

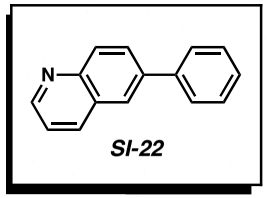

Current Data Parameters
NAME KVP–I–186
EXPNO 1
PROCNO 1
F2 – Acquisition Parameters
Date_ 20090309
Time 9.47
INSTRUM avance500
PROBHD 5 mm bb–Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2769001 sec
RG 256
DW 50.000 usec
DE 6.00 usec
TE 292.6 K
D1 2.00000000 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 500.3300234 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.847
7.845
7.667
7.664
7.650
7.648
7.498
7.495
7.481
7.478
7.455
7.452
7.440
7.428
7.424
7.399
7.382
7.367
7.326
7.324
7.321
7.312
7.309
7.306
7.297
7.294
7.292
7.091
7.085
6.544
6.543
6.538
6.537
3.838
Me
N
SI-19
3.045
0.999
2.007
1.014
2.069
1.362
1.016
0.973
0.973
0.973
10
9
8
7
6
5
4
3
2
1
0
ppm

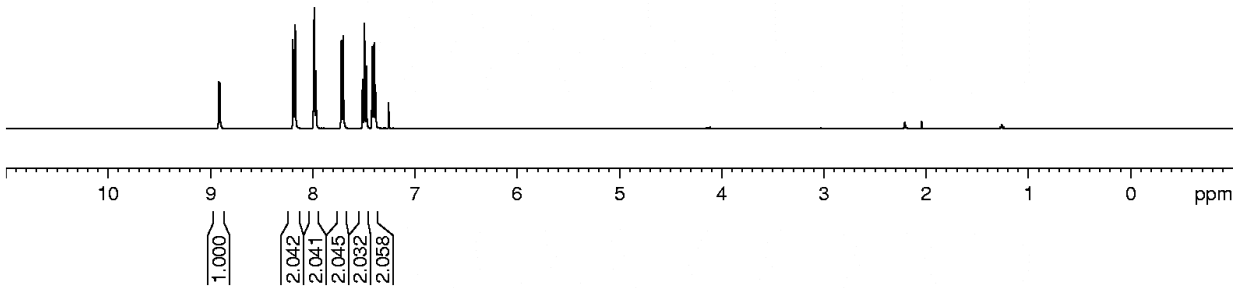

Current Data Parameters
NAME AK1-75
EXPNO 380
PROCNO 1
F2 – Acquisition Parameters
Date_ 20100428
Time 15.57
INSTRUM arx400
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8064.516 Hz
FIDRES 0.123055 Hz
AQ 4.0632820 sec
RG 2048
DW 62.000 usec
DE 88.57 usec
TE 300.0 K
D1 2.00000000 sec
P1 7.50 usec
SFO1 400.1324008 MHz
NUCLEUS 1H
F2 – Processing parameters
SI 65536
SF 400.1300173 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Account no. nkg339
AK1-75
8.141
8.131
8.129
8.111
8.109
7.759
7.741
7.738
7.602
7.599
7.516
7.511
7.507
7.498
7.496
7.490
7.487
7.481
7.478
7.433
7.412
7.404
7.401
7.398
7.383
7.378
7.364
7.281
7.261
7.244
7.241
3.907
Me
N
SI-20
3.021
2.063
2.000
0.965
4.087
1.055
1.113
1.697
ppm


Current Data Parameters
NAME AK1–078
EXPNO 10
PROCNO 1
F2 – Acquisition Parameters
Date_ 20100929
Time 13.07
INSTRUM avance500
PROBHD 5 mm bb–Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2769001 sec
RG 181
DW 50.000 usec
DE 6.00 usec
TE 296.3 K
D1 2.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ======
NUC1 1H
P1 12.25 usec
PL1 0.00 dB
SFO1 500.3330020 MHz
F2 – Processing parameters
SI 32768
SF 500.3300220 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.705
8.696
8.000
7.985
7.757
7.754
7.724
7.497
7.494
7.482
7.466
7.433
7.419
7.415
7.404
7.247
7.244
7.237
7.234
7.230
7.224
7.221
SI-21
1.000
2.026
2.045
3.076
0.951
ppm

Account no. nkg339
AK1-77

8.180
8.174
8.172
7.996
7.990
7.988
7.983
7.973
7.968
7.726
7.722
7.717
7.707
7.704
7.703
7.702
7.697
7.516
7.514
7.510
7.496
7.493
7.481
7.477
7.421
7.418
7.411
7.408
7.401
7.390
7.384
7.381
7.261

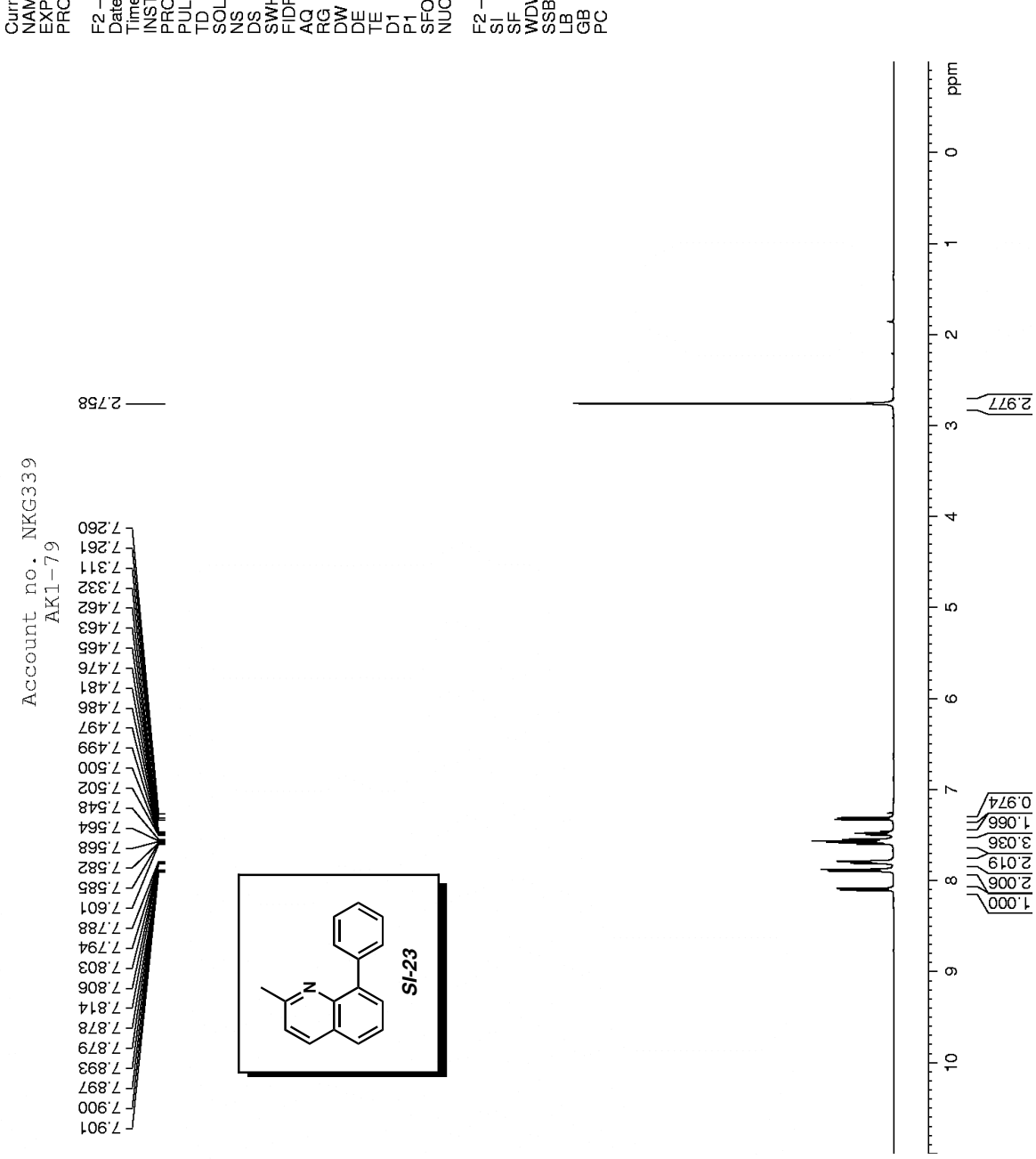


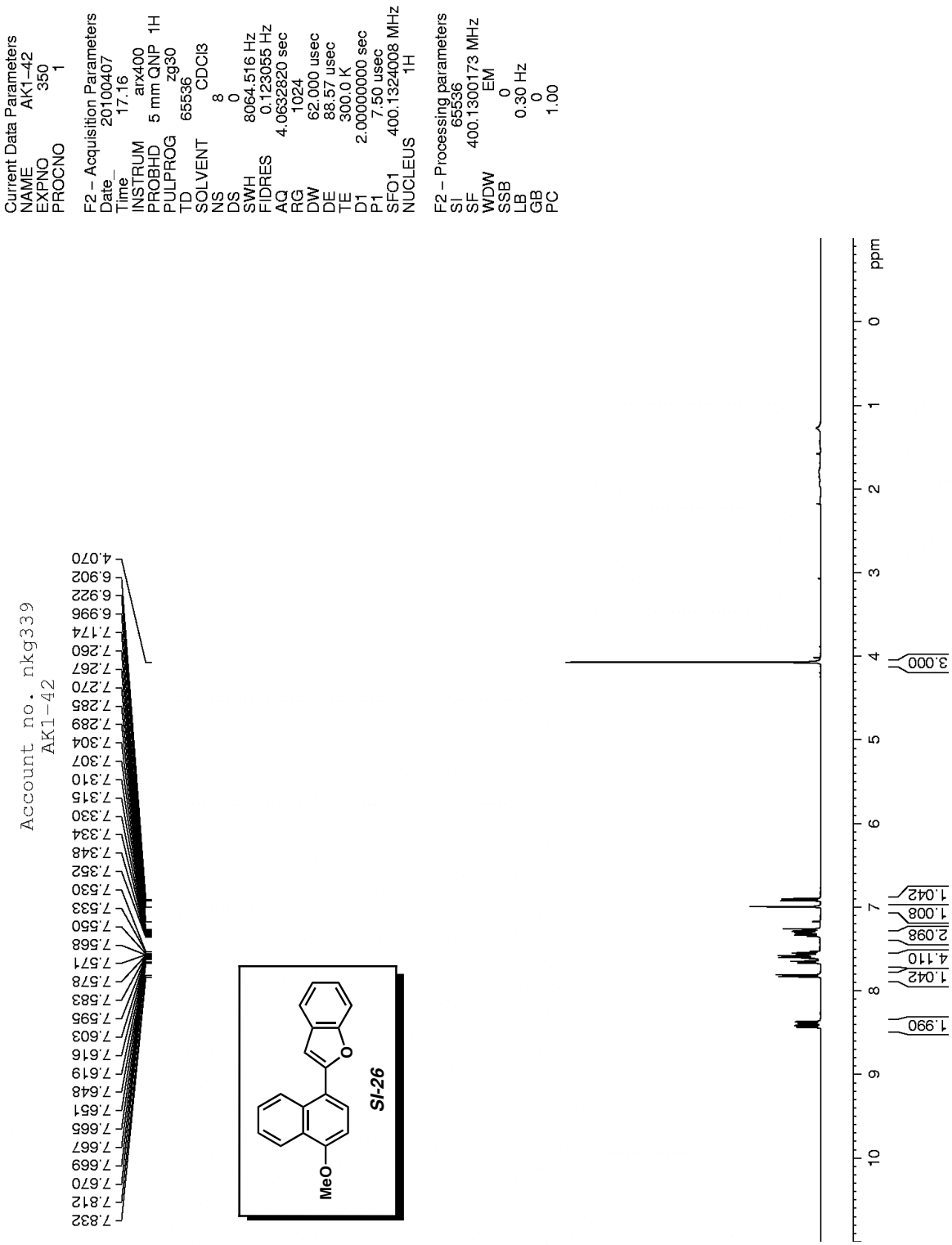


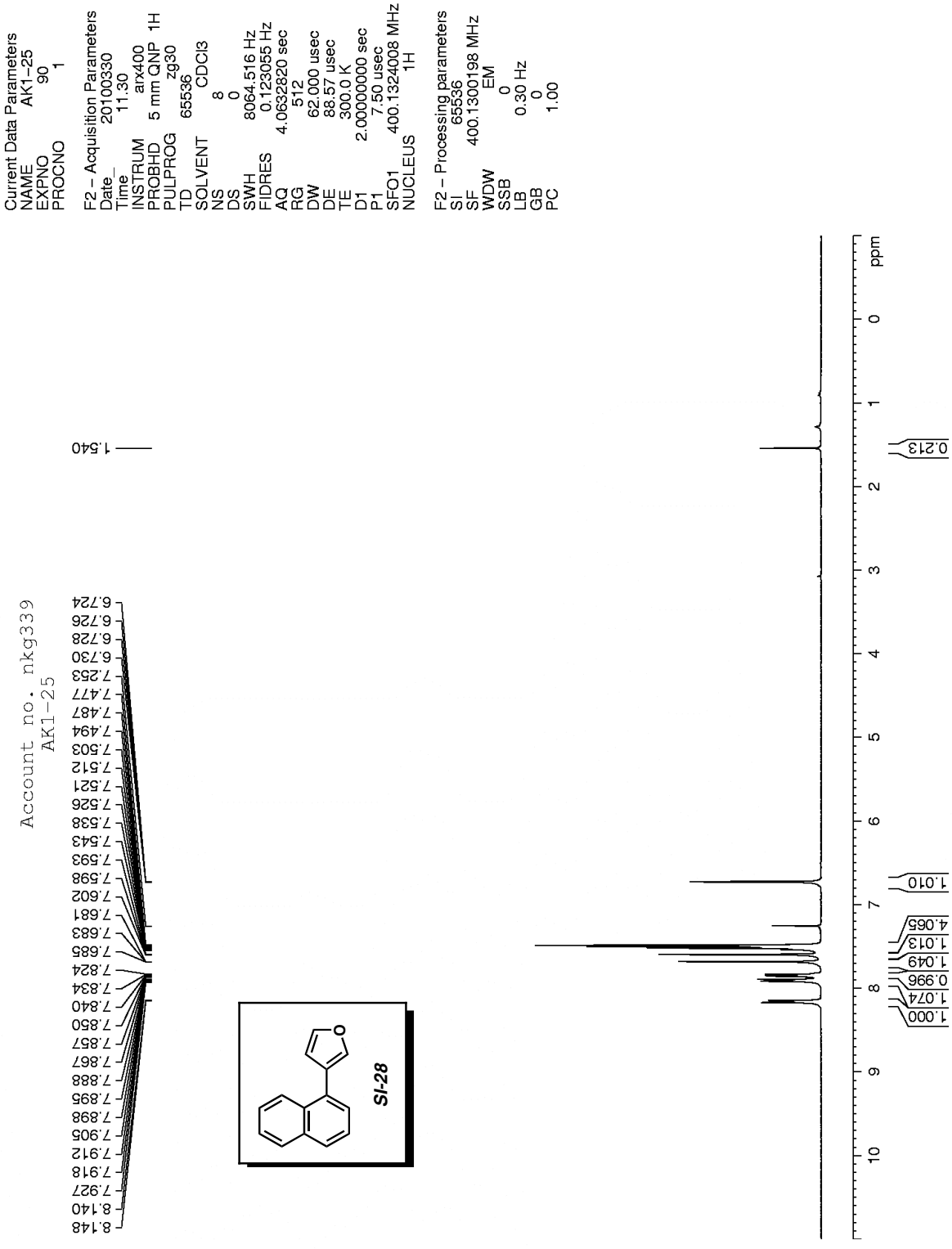
Current Data Parameters
NAME AK1-77
EXPNO 550
PROCNO 1

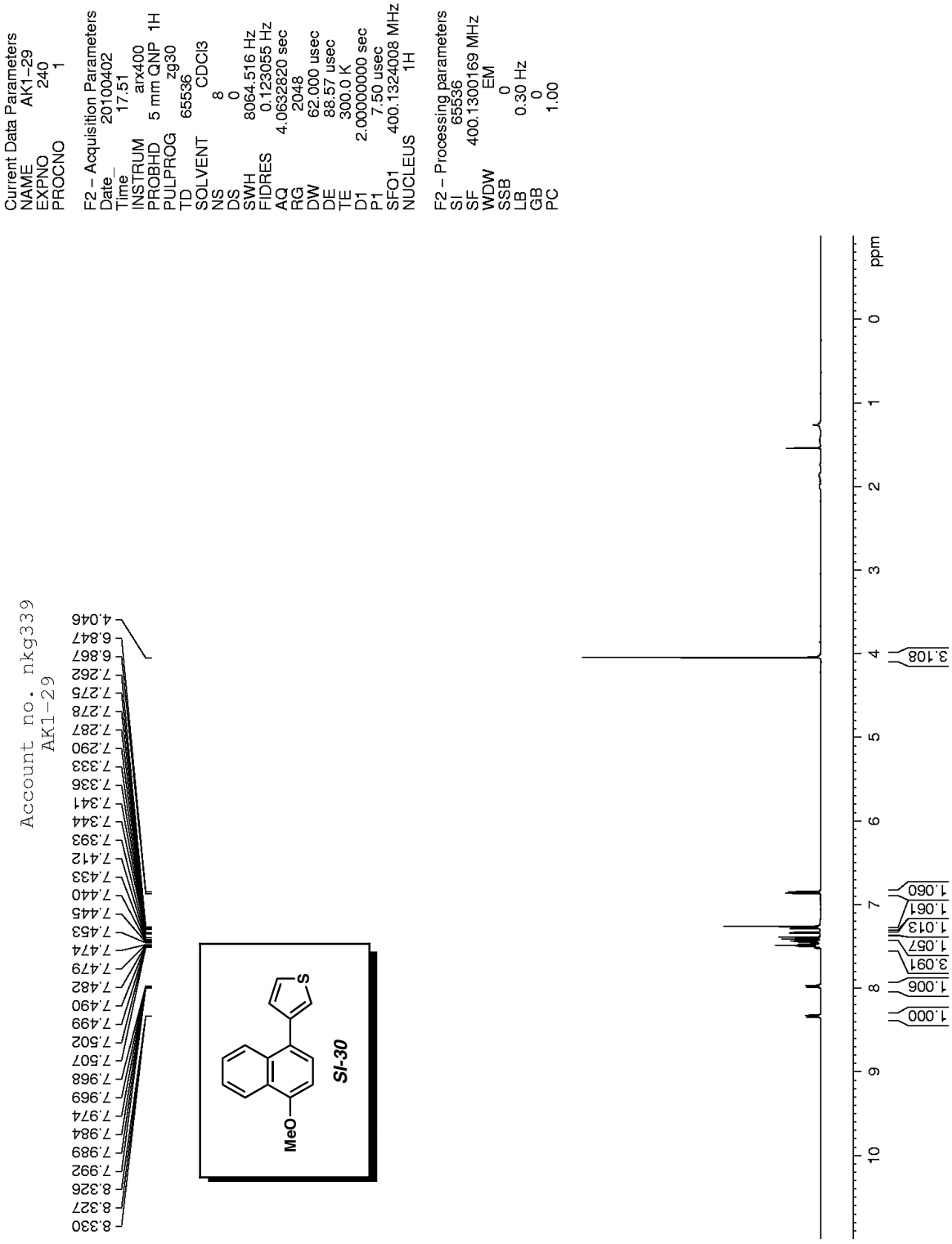
F2 – Acquisition Parameters
Date_ 20100428
Time 20.26
INSTRUM arx400
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8064.516 Hz
FIDRES 0.123055 Hz
AQ 4.0632820 sec
RG 360
DW 62.000 usec
DE 88.57 usec
TE 300.0 K
D1 2.00000000 sec
P1 7.50 usec
SFO1 400.1324008 MHz
NUCLEUS 1H

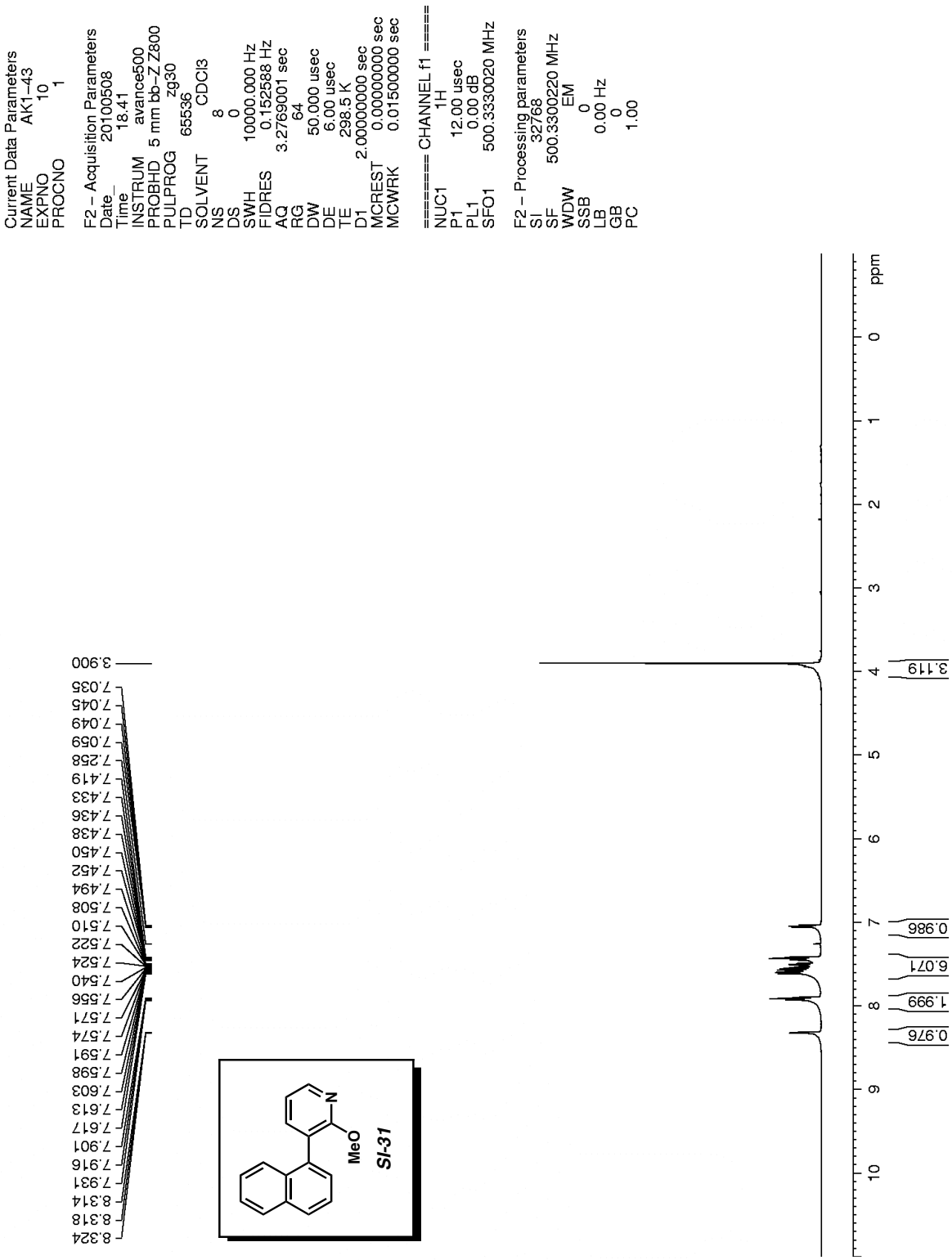
F2 – Processing parameters
SI 65536
SF 400.1300173 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

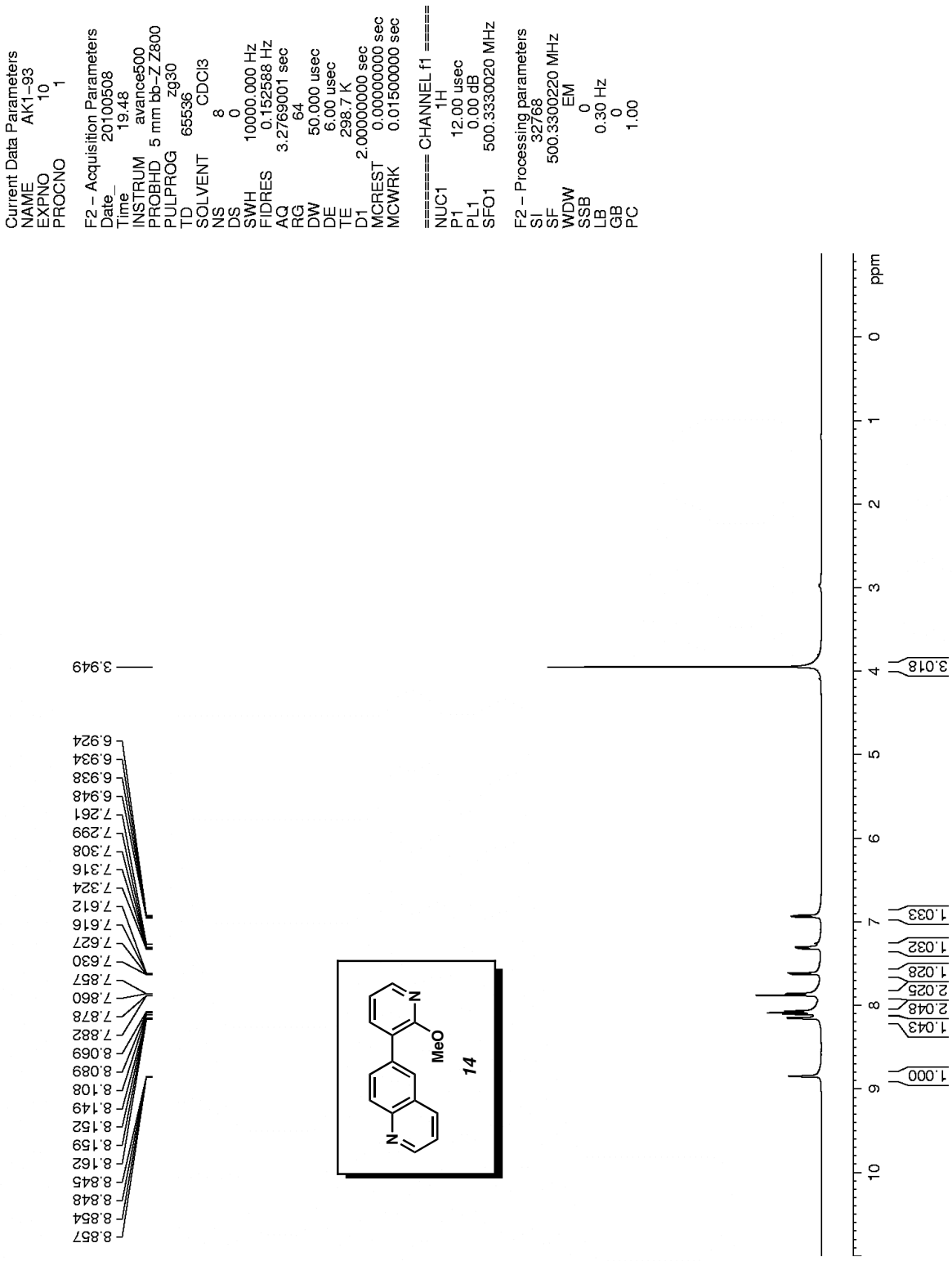

Current Data Parameters
NAME AK1-79
EXPNO 500
PROCNO 1
F2 – Acquisition Parameters
Date_ 20100429
Time_ 19.49
INSTRUM arx400
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8064.516 Hz
FIDRES 0.123055 Hz
AQ 4.0632820 sec
RG 180
DW 62.000 usec
DE 88.57 usec
TE 300.0 K
D1 2.00000000 sec
P1 7.50 usec
SFO1 400.1324008 MHz
NUCLEUS 1H
F2 – Processing parameters
SI 65536
SF 400.1300173 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Account no. NKG339
AK1-79
7.260
7.261
7.311
7.332
7.462
7.463
7.465
7.476
7.481
7.486
7.497
7.499
7.500
7.502
7.548
7.564
7.568
7.582
7.585
7.601
7.788
7.794
7.803
7.806
7.814
7.878
7.879
7.893
7.897
7.900
7.901
2.758
SI-23
2.977
1.000
2.006
2.019
3.036
1.066
0.974
ppm


Current Data Parameters
NAME AK1-42
EXPNO 350
PROCNO 1
F2 – Acquisition Parameters
Date_ 20100407
Time_ 17.16
INSTRUM arx400
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8064.516 Hz
FIDRES 0.123055 Hz
AQ 4.0632820 sec
RG 1024
DW 62.000 usec
DE 88.57 usec
TE 300.0 K
D1 2.00000000 sec
P1 7.50 usec
SFO1 400.1324008 MHz
NUCLEUS 1H
F2 – Processing parameters
SI 65536
SF 400.1300173 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Account no. nkg339
AK1-42
7.832
7.812
7.670
7.669
7.667
7.665
7.651
7.648
7.619
7.616
7.603
7.595
7.583
7.578
7.571
7.568
7.550
7.533
7.530
7.352
7.348
7.334
7.330
7.315
7.310
7.307
7.304
7.289
7.285
7.270
7.267
7.260
7.174
6.996
6.922
6.902
4.070
MeO
SI-26
3.000
1.990
1.042
4.110
2.098
1.008
1.042
ppm


Current Data Parameters
NAME AK1-25
EXPNO 90
PROCNO 1
F2 – Acquisition Parameters
Date_ 20100330
Time 11.30
INSTRUM arx400
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8064.516 Hz
FIDRES 0.123055 Hz
AQ 4.0632820 sec
RG 512
DW 62.000 usec
DE 88.57 usec
TE 300.0 K
D1 2.00000000 sec
P1 7.50 usec
SFO1 400.1324008 MHz
NUCLEUS 1H
F2 – Processing parameters
SI 65536
SF 400.1300198 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Account no. nkg339
AK1-25
SI-28
ppm
1.000
1.074
0.996
1.049
1.013
4.065
1.010
0.213


Current Data Parameters
NAME AK1-29
EXPNO 240
PROCNO 1
F2 – Acquisition Parameters
Date_ 20100402
Time_ 17.51
INSTRUM arx400
PROBHD 5 mm QNP 1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8064.516 Hz
FIDRES 0.123055 Hz
AQ 4.0632820 sec
RG 2048
DW 62.000 usec
DE 88.57 usec
TE 300.0 K
D1 2.00000000 sec
P1 7.50 usec
SFO1 400.1324008 MHz
NUCLEUS 1H
F2 – Processing parameters
SI 65536
SF 400.1300169 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Account no. nkg339
AK1-29
8.330
8.327
8.326
7.992
7.989
7.984
7.974
7.969
7.968
7.507
7.502
7.499
7.490
7.482
7.479
7.474
7.453
7.445
7.440
7.433
7.412
7.393
7.344
7.341
7.336
7.333
7.290
7.287
7.278
7.275
7.262
6.867
6.847
4.046
MeO
S
SI-30
1.000
1.006
3.091
1.057
1.013
1.061
1.060
3.108
10
9
8
7
6
5
4
3
2
1
0
ppm


Current Data Parameters
NAME AK1-43
EXPNO 10
PROCNO 1
F2 – Acquisition Parameters
Date_ 20100508
Time_ 18.41
INSTRUM avance500
PROBHD 5 mm bb-Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2769001 sec
RG 64
DW 50.000 usec
DE 6.00 usec
TE 298.5 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 500.3300220 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
3.900
7.035
7.045
7.049
7.059
7.258
7.419
7.433
7.436
7.438
7.450
7.452
7.494
7.508
7.510
7.522
7.524
7.540
7.556
7.571
7.574
7.591
7.598
7.603
7.613
7.617
7.901
7.916
7.931
8.314
8.318
8.324
N
MeO
SI-31
3.119
0.976
1.999
6.071
0.986
ppm


Current Data Parameters
NAME AK1-93
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100508
Time 19.48
INSTRUM avance500
PROBHD 5 mm bb-Z Z800
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2769001 sec
RG 64
DW 50.000 usec
DE 6.00 usec
TE 298.7 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 500.3300220 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.857
8.854
8.848
8.845
8.162
8.159
8.152
8.149
8.108
8.089
8.069
7.882
7.878
7.860
7.857
7.630
7.627
7.616
7.612
7.324
7.316
7.308
7.299
7.261
6.948
6.938
6.934
6.924
3.949
MeO
14
1.000
1.043
2.048
2.025
1.028
1.032
1.033
3.018
10
9
8
7
6
5
4
3
2
1
0
ppm