

Intramolecular C–H Amination Reactions: Exploitation of the Rh₂(II)-Catalyzed Decomposition of Azidoacrylates

Benjamin J. Stokes, Huijun Dong, Brooke E. Leslie, Ashley L. Pumphrey, and Tom G. Driver*

*Department of Chemistry, University of Illinois at Chicago,
845 West Taylor Street, Chicago, Illinois, 60607-7061*

Supporting Information

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Contents

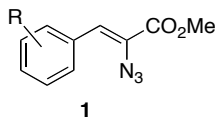
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General. ¹H NMR and ¹³C NMR spectra were recorded at ambient temperature using Bruker DRX 500 or Varian DRX 300 spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectra were acquired on a JEOL GCMate II or Thermo Finnigan LTQ FT spectrometer, and were obtained by peak matching. Microanalyses were performed by Atlantic Microlab, Atlanta, GA. Analytical thin layer chromatography was performed on Sorbent Technologies 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on Sorbent Technologies silica gel (SiO₂) 60Å (40 – 60 μm) mesh. All reactions were carried out under an atmosphere of nitrogen in glassware, which had been oven-dried. Unless otherwise noted, all reagents were commercially obtained and, where appropriate, purified prior to use. Acetonitrile, Methanol, Toluene, THF, Et₂O, and CH₂Cl₂ were dried by filtration through alumina according to the procedure of Grubbs.¹ Metal salts were stored in an MBraun labmaster nitrogen atmosphere dry box.

I. Preparation of vinyl azide reagents

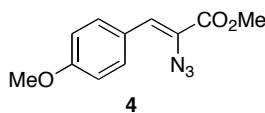
A. General Procedure for the preparation of vinyl azides

The requisite vinyl azides were prepared in one step from the condensation of methyl azidoacetate and aromatic or heteroaromatic aldehydes following the method reported by Moody and co-workers.² The yields were not optimized.

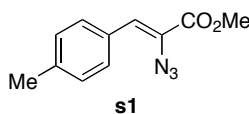


To a cooled ($-20\text{ }^{\circ}\text{C}$) solution of NaOMe (x.xxx g, xx.x mmol, 1.52 equiv) in MeOH was added a solution of aldehyde (x.xx mL, x.xx mmol, 1 equiv) and methyl azidoacetate (x.xx g, xx.xx mmol, 3 – 4 equiv) dropwise over 20 minutes. The resulting reaction mixture was warmed to $-10\text{ }^{\circ}\text{C}$. After four hours, the heterogeneous mixture was diluted with 20 mL of water and 20 mL of Et₂O. The phases were separated and the resulting aqueous phase was extracted with an additional $2 \times 20\text{ mL}$ of Et₂O. The combined organic phases were washed with $2 \times 20\text{ mL}$ of distilled water and $1 \times 20\text{ mL}$ of brine. The resulting organic phase was dried over MgSO₄ and the heterogeneous mixture was filtered. The filtrate was concentrated *in vacuo* to afford a light yellow oil. Purification by flash chromatography (x:xx EtOAc:hexanes) afforded the product.

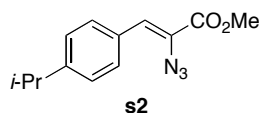
B. Vinyl azide syntheses



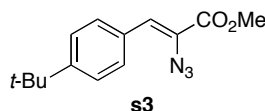
Vinyl Azide (3).³ The general procedure was followed using 0.976 g of sodium methoxide (18.0 mmol), 8 mL of methanol, 2.00 mL of *p*-methoxybenzaldehyde (16.4 mmol), and 5.70 g of methyl azidoacetate (49.4 mmol). Purification using flash chromatography (1:99 EtOAc:hexanes) afforded **4** as a light yellow solid (2.00 g, 49%). Vinyl azide **4** is available from Aldrich (L308463). The spectral data matched that reported by Luu and co-workers:³ ¹H NMR (CDCl₃, 500 MHz) δ 7.79 (d, $J = 9.0\text{ Hz}$, 2H), 6.91 (d, $J = 9.0\text{ Hz}$, 2H), 6.89 (s, 1H), 3.90 (s, 3H), 3.84 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 164.3, 160.5, 132.4, 125.9, 125.7, 123.0, 113.9, 55.3, 52.7; IR (thin film) 2953, 2119, 1712, 1601, 1253, 1175 cm⁻¹.



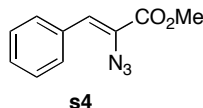
Vinyl Azide (s1).⁴ The general procedure was followed using 0.706 g of sodium methoxide (13.1 mmol), 4.0 mL of methanol, 1.1 mL of *p*-tolualdehyde (6.4 mmol), and 4.02 g of methyl azidoacetate (34.1 mmol). Purification using flash chromatography (1:99 EtOAc:hexanes) afforded **s1** as a white solid (0.940 g, 50%). The spectral data matched that reported by Knittel and co-workers:⁴ ¹H NMR (CDCl₃, 500 MHz) δ 7.72 (d, $J = 8.5\text{ Hz}$, 2H), 7.20 (d, $J = 8.5\text{ Hz}$, 2H), 6.91 (s, 1H), 3.91 (s, 3H), 2.38 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 164.1, 139.9, 130.6, 130.4, 129.2, 125.8, 124.4, 52.8, 21.5; IR (thin film) 2956, 2134, 1713, 1437, 1250, 1078 cm⁻¹.



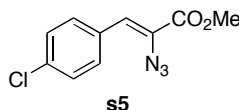
Vinyl azide (s2). The general procedure was followed using 0.547 g of sodium methoxide (10.1 mmol), 4.0 mL of methanol, 1.02 mL of 4-isopropylbenzaldehyde (6.75 mmol), and 2.33 g of methyl azidoacetate (20.24 mmol). Purification by flash chromatography (1:99 EtOAc:hexanes) afforded the product **s2** as a pale yellow low melting solid (0.449 g, 27%): ^1H NMR (CDCl_3 , 500 MHz) δ 7.77 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 6.93 (s, 1H), 3.91 (s, 3H), 2.94 (septet, J = 7.0 Hz, 1H), δ 1.28 (d, J = 7.0 Hz, 6H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 164.1, 150.7, 130.7 (2 \times C), 126.5, 125.8, 124.4, 52.7, 34.0, 23.7; IR (thin film) 2959, 2870, 2121, 1715, 1617, 1610, 1378 cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{N}_3\text{O}_2$: C, 63.66; H, 6.16; N, 17.13. Found: C, 63.79; H, 6.19; N, 17.06.



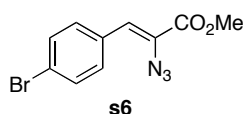
Vinyl azide (s3). The general procedure was followed using 0.557 g of sodium methoxide (10.32 mmol), 4.50 mL of methanol, 1.45 g of 4-*tert*-butylbenzaldehyde (8.97 mmol), and 4.13 g of methyl azidoacetate (35.88 mmol). Purification by flash chromatography (2:98 EtOAc:hexanes) and then recrystallization from hexanes afforded the product as a yellow solid (0.675 g, 29%): ^1H NMR (CDCl_3 , 500 MHz) δ 7.77 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 6.93 (s, 1H), 3.91 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 164.1, 153.0, 130.4, 130.3, 125.7, 125.5, 124.5, 52.8, 34.8, 31.1; IR (thin film): 2958, 2869, 2122, 1716, 1606, 1378, 1249, 1079 cm^{-1} . Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{N}_3\text{O}_2$: C, 64.85; H, 6.61; N, 16.20. Found: C, 65.30; H, 6.69; N, 16.17.



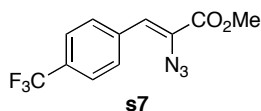
Vinyl azide (s4).⁵ The general procedure was followed using 0.601 g of sodium methoxide (11.1 mmol), 4.0 mL of methanol, 0.750 mL of benzaldehyde (7.4 mmol), and 2.53 g of methyl azidoacetate (22.3 mmol). Purification by flash chromatography (1:99 EtOAc:hexanes) afforded the product **s4** as a pale yellow low melting solid (0.622 g, 41%). The spectral data matched that reported by Ghosh and co-workers:⁵ ^1H NMR (CDCl_3 , 500 MHz) δ 7.83 (d, J = 8.0 Hz, 2H), 7.41 – 7.33 (m, 3H), 6.93 (s, 1H), 3.90 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 163.8, 133.0, 130.5, 129.3, 128.3, 125.4, 125.1, 52.7; IR (thin film) 2953, 2122, 1715, 1616, 1379, 1260, 1087 cm^{-1} .



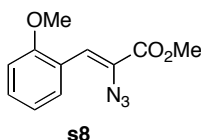
Vinyl azide (s5).⁴ The general procedure was followed using 0.405 g of sodium methoxide (7.5 mmol), 3.30 mL of methanol, 0.917 g of 4-chlorobenzaldehyde (6.52 mmol), and 3.00 g of methyl azidoacetate (26.10 mmol). Purification by flash chromatography (2:98 EtOAc:hexanes) yielded the product as a pale yellow solid (0.968 g, 63%): ^1H NMR (CDCl_3 , 500 MHz) δ 7.75 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 9.0 Hz, 2H), 6.85 (s, 1H), 3.92 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 163.8, 135.2, 131.8, 131.6, 128.7, 125.8, 124.0, 53.0; IR (thin film): 2952, 2336, 2123, 1716, 1487, 1253, 1080, 824 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{10}\text{H}_8\text{ClN}_3\text{O}_2$: 237.0305, found 237.0305. Anal. Calcd for $\text{C}_{10}\text{H}_8\text{ClN}_3\text{O}_2$: C, 50.54; H, 3.39; N, 17.68. Found: C, 50.61; H, 3.39; N, 17.45.



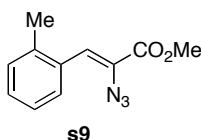
Vinyl azide (s6). The general procedure was followed using 0.289 g of sodium methoxide (5.35 mmol), 2.33 mL of methanol, 1.00 g of 4-bromobenzaldehyde (5.35 mmol), and 2.08 mL of methyl azidoacetate (21.4 mmol). Purification by flash chromatography (1:99 EtOAc:hexanes) afforded the product as a fluffy white solid (0.497 g, 33%): ^1H NMR (CDCl_3 , 500 MHz) δ 7.68 (d, J = 8.5 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H), 6.82 (s, 1H), 3.91 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 163.8, 132.1, 132.0, 131.7, 126.0, 124.0, 123.6, 53.1; IR (thin film): 2953, 2124, 1716, 1380, 1262, 1249, 1075, 819 cm^{-1} . Anal. Calcd for $\text{C}_{10}\text{H}_8\text{BrN}_3\text{O}_2$: C, 42.58; H, 2.86. Found: C, 42.95; H, 2.81.



Vinyl azide (s7). The general procedure was followed using 0.405 g of sodium methoxide (7.50 mmol), 3.30 mL of methanol, 1.14 g of 4-(trifluoromethyl)benzaldehyde (6.52 mmol), and 3.00 g of methyl azidoacetate (26.1 mmol). Purification by flash chromatography (2:98 EtOAc:hexanes) yielded the product as a pale yellow solid (0.566 g, 40%): ^1H NMR (CDCl_3 , 500 MHz) δ 7.90 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H), 6.89 (s, 1H), 3.93 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 163.6, 136.5, 130.6, 127.5, 125.33, 125.31, 123.9 (q, J_{CF} = 270 Hz), 123.2, 53.1; ^{19}F NMR (CDCl_3 , 282 MHz) δ -63.4; IR (thin film): 2127, 1710, 1611, 1439, 1321, 1269, 1104, 833 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_8\text{F}_3\text{N}_3\text{O}_2$: C, 48.72; H, 2.97; N, 15.49. Found: C, 48.89; H, 2.93; N, 15.29.

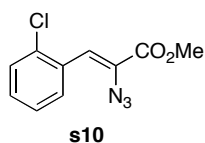


Vinyl azide (s8).³ The general procedure was followed using 0.870 g of sodium methoxide (16.1 mmol), 5.0 mL of methanol, 1.3 mL of *o*-methoxybenzaldehyde (10.7 mmol), and 4.90 g of methyl azidoacetate (42.8 mmol). Purification by flash chromatography (2:98 EtOAc:hexanes) yielded the product as a pale yellow solid (0.940 g, 38%). The spectral data for **s8** matched that reported by Luu and co-workers:³ ^1H NMR (CDCl_3 , 500 MHz) δ 8.20 (d, J = 7.5 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H), 7.40 (s, 1H), 7.00 (t, J = 7.5 Hz, 1H), 6.89 (d, J = 8.5 Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 164.2, 157.5, 130.8, 130.5, 125.0, 122.0, 120.3, 119.6, 110.4, 55.5, 52.8; IR (thin film): 2952, 2117, 2086, 1715, 1252, 1082 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}_3$: C, 56.65; H, 4.75; N, 18.02. Found: C, 56.91; H, 4.78; N, 17.90.

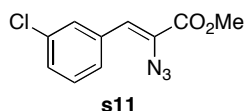


Vinyl azide (s9).⁶ The general procedure was followed using 0.472 g of sodium methoxide (8.74 mmol), 3.9 mL of methanol, 0.913 g of *o*-tolualdehyde (7.60 mmol), and 3.50 g of methyl azidoacetate (30.4 mmol). Purification by flash chromatography (2:98 EtOAc:hexanes) and then recrystallization from hexane yielded the product as a pale yellow solid (0.687 g, 42%). The spectral data matched that reported by Moody and co-workers:⁶ ^1H NMR (CDCl_3 , 500 MHz) δ 7.98 – 7.96 (m, 1H), 7.25 – 7.22 (m, 3H), 7.14 (s, 1H), 3.93 (s, 3H),

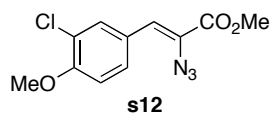
2.37 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 164.0, 137.6, 131.9, 130.3, 129.6, 129.2, 126.0, 125.8, 123.5, 53.0, 20.1; IR (thin film): 2115, 1713, 1611, 1440, 1247, 1078, 765 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}_2$: C, 60.82; H, 5.10; N, 19.34. Found: C, 61.00; H, 5.12; N, 19.10.



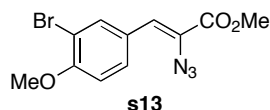
Vinyl azide (s10).⁷ The general procedure was followed using 0.475 g of sodium methoxide (8.80 mmol), 3.83 mL of methanol, 1.00 mL of 2-chlorobenzaldehyde (8.80 mmol), and 3.43 mL of methyl azidoacetate (35.2 mmol). Purification by flash chromatography (1:99 EtOAc:hexanes) afforded the product as a pale yellow solid (0.603 g, 29%). The spectral data matched that reported by Shim and co-workers:⁷ ^1H NMR (CDCl_3 , 500 MHz) δ 8.18 (d, J = 7.5 Hz, 1H), 7.41 (d, J = 8 Hz, 1H), 7.30 (s, 1H), 7.30 (t, J = 8 Hz, 1H), 7.26 (t, J = 7.5 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 163.8, 134.7, 131.2, 131.1, 130.2, 129.7, 127.2, 126.6, 120.8, 53.2; IR (thin film): 2132, 2115, 1717, 1608, 1435, 1385, 1244, 1082 cm^{-1} . Anal. Calcd for $\text{C}_{10}\text{H}_8\text{ClN}_3\text{O}_2$: C, 50.54; H, 3.39; N, 17.68. Found: C, 50.97; H, 3.45; N, 17.37.



Vinyl azide (s11). The general procedure was followed using 0.726 g of sodium methoxide (13.4 mmol), 6.0 mL of methanol, 1.00 mL of 3-chlorobenzaldehyde (8.79 mmol), and 4.04 g of methyl azidoacetate (35.2 mmol). Purification by flash chromatography (1:99 EtOAc:hexanes) yielded the product as a pale yellow solid (1.70 g, 81%): ^1H NMR (CDCl_3 , 500 MHz) δ 7.86 (s, 1H), 7.26 (m, 1H), 7.29 (m, 2H), 6.81 (s, 1H), 3.91 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 163.6, 134.8, 134.3, 130.0, 129.6, 129.2, 128.7, 126.5, 123.5, 53.0; IR (thin film) 2952, 2116, 1715, 1252, 1082 cm^{-1} . Anal. Calcd for $\text{C}_{10}\text{H}_8\text{ClN}_3\text{O}_2$: C, 50.54; H, 3.39. Found: C, 50.92; H, 3.38.

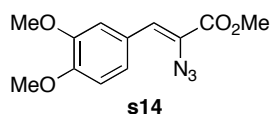


Vinyl azide (s12). The general procedure was followed using 0.220 g of sodium methoxide (4.04 mmol), 1.76 mL of methanol, 0.600 g of 3-chloro-4-methoxybenzaldehyde (3.52 mmol), and 1.62 g of methyl azidoacetate (14.1 mmol). Purification by flash chromatography (1:99 EtOAc:hexanes) yielded the product as a pale yellow solid (0.374 g, 40%): ^1H NMR (CDCl_3 , 500 MHz) δ 7.95 (s, 1H), 7.67 (d, J = 8.5 Hz, 1H), 6.93 (d, J = 8.5 Hz, 1H), 6.80 (s, 1H), 3.94 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 163.9, 155.6, 132.1, 130.7, 126.7, 124.3, 123.9, 122.5, 111.6, 56.2, 52.9; IR (thin film): 2359, 2120, 1708, 1378, 1256, 1061, 811 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{ClN}_3\text{O}_3$: C, 49.36; H, 3.77; N, 15.70. Found: C, 49.55; H, 3.79; N, 15.50.



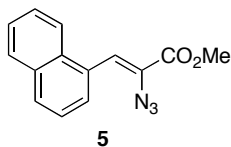
Vinyl azide (s13). The general procedure was followed using 0.246 g of sodium methoxide (4.56 mmol), 2.0 mL of methanol, 1.00 g of 3-bromo-4-methoxybenzaldehyde (4.56 mmol), and 1.33 mL of methyl azidoacetate (13.7 mmol). Purification by flash chromatography (5:95 EtOAc:hexanes) afforded the product as an off-white solid (0.336 g, 24%): ^1H NMR (CDCl_3 , 500 MHz) δ 8.10 (s, 1H), 7.73 (d, J = 8.5 Hz, 1H), 6.90 (d, J = 8.5 Hz,

1H), 6.79 (s, 1H), 3.93 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 164.0, 156.5, 135.3, 131.4, 127.3, 124.3, 123.8, 111.7, 111.4, 56.3, 52.9; IR (thin film): 2118, 1708, 1593, 1496, 1375, 1252, 1206, 1051 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{BrN}_3\text{O}_3$: C, 42.33; H, 3.23. Found: C, 42.66; H, 3.25.

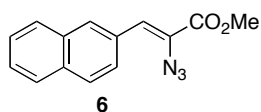


Vinyl azide (s14). The general procedure was followed using 3.30 mL of a 2.3 M solution of sodium methoxide in methanol, 1.28 g of 3,4-dimethoxybenzaldehyde (7.60 mmol), and 3.50 g of methyl azidoacetate (30.4 mmol). Purification by flash chromatography (5:95 EtOAc:hexanes) afforded the product as a yellow solid (0.490 g, 25%): ^1H NMR (CDCl_3 , 500 MHz) δ 7.51 (s, 1H), 7.34 (d, J = 8.5 Hz, 1H), 6.87 (s, 1H), 6.86 (d, J = 8 Hz, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 164.2, 150.2, 148.6, 126.2, 125.9, 125.0, 123.2, 112.9, 110.7, 55.9 (2 \times C), 52.8; IR (thin film): 2123, 1710, 1515, 1439, 1371, 1249, 1144, 1081, 1024 cm^{-1} . Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}_4$: C, 54.75; H, 4.98. Found: C, 54.85; H, 5.04.

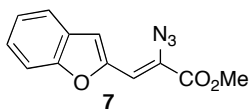
C. Construction of heteroaromatic vinyl azides



Vinyl azide 5. The general procedure was followed using 4.8 mL of a 2.3 M solution of sodium methoxide in methanol, 1.00 mL of 1-naphthaldehyde (7.36 mmol), and 2.54 g of methyl azidoacetate (2.21 mmol). Purification by flash chromatography (1:99 EtOAc:hexanes) yielded the product as a pale yellow solid (0.374 g, 40%): ^1H NMR (CDCl_3 , 500 MHz) δ 8.12 (d, J = 7.5 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.87 (t, J = 8 Hz, 2H), 7.70 (s, 1H), 7.60 – 7.50 (m, 3H), 3.99 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 163.9, 133.5, 131.6, 129.8, 129.4, 128.8, 128.2, 127.1, 126.7, 126.0, 125.2, 123.4, 122.4, 53.0; IR (thin film): 3087, 2127, 1709, 1432, 1256 1092 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_2$ (M) $^+$ 253.0851, found 253.0854.

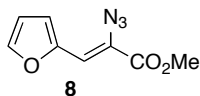


Vinyl azide 6. The general procedure was followed using 0.398 g of sodium methoxide (7.36 mmol), 3.0 mL of methanol, 1.00 g of 2-naphthaldehyde (6.40 mmol), and 2.95 g of methyl azidoacetate (25.6 mmol). Purification by flash chromatography (1:99 EtOAc:hexanes) and then recrystallization from hexanes yielded the product as a pale yellow solid: ^1H NMR (CDCl_3 , 500 MHz) δ 8.29 (s, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 6 Hz, 1H), 7.84–7.82 (m, 2H), 7.50 – 7.52 (m, 2H), 7.08 (s, 1H), 3.94 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 164.1, 133.5, 133.1, 131.0, 130.7, 128.7, 128.0, 127.6, 127.3, 127.2, 126.4, 125.6, 125.4, 52.9; IR (thin film): 3056, 2954, 2121, 1711, 1253, 1083, 746 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_2$: $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_2$ (M) $^+$ 253.0851, found 253.0863.

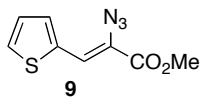


Vinyl azide 7.⁸ The general procedure was followed using 4.1 mL of a 2.3 M solution of sodium methoxide in methanol, 0.750 mL of 1-benzofuraldehyde (6.19 mmol), and 2.14 g of methyl azidoacetate (18.6 mmol). Purification by flash chromatography (1:99 EtOAc:hexanes) yielded the product as a pale yellow solid (0.450 g,

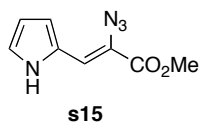
30%). The spectral data matched that reported by Krutošíková and co-workers:⁸ ¹H NMR (CDCl₃, 500 MHz) δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.47 (s, 1H), 7.47 (d, *J* = 8 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 6.95 (s, 1H), 3.93 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 163.2, 154.8, 150.7, 125.9, 123.3, 122.8, 121.8, 113.4, 112.7, 111.3, 111.2, 53.1; IR (thin film): 2954, 2118, 1715, 1289, 1227, 1081 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₂H₉N₃O₃ (M)⁺ 243.0644, found 243.0652.



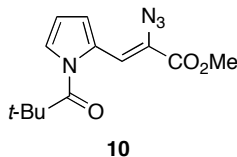
Vinyl azide 8.⁹ The representative procedure was followed using 0.844 g of sodium methoxide (15.6 mmol), 6.0 mL of methanol, 0.863 mL of 2-furaldehyde (10.4 mmol), and 3.59 g of methyl azidoacetate (31.2 mmol). Purification by flash chromatography (1:99 EtOAc:hexanes) afforded the product **8** as a pale yellow low melting solid (0.2714 g, 13%). The spectral data matched that reported by Krutosikova and co-workers:⁹ ¹H NMR (CDCl₃, 500 MHz) δ 7.48 (d, *J* = 2.0 Hz, 1H), 7.10 (d, *J* = 3.5 Hz, 1H), 6.85 (s, 1H), 6.52 (m, 1H), 3.88 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 163.6, 149.4, 143.9, 122.5, 115.3, 113.6, 112.5, 52.8; IR (thin film) 2955, 2130, 2116, 1714, 1618, 1364, 1282 cm⁻¹.



Vinyl azide 9.¹⁰ The general procedure was followed using 7.3 mL of a 2.3 M solution of sodium methoxide in methanol, 1.00 mL of 1-thiophenecarboxaldehyde (10.9 mmol), and 3.76 g of methyl azidoacetate (32.7 mmol). Purification by flash chromatography (1:99 EtOAc:hexanes) yielded the product as a pale orange oil (1.10 g, 48%). The spectral data matched that reported by Yarovenko and co-workers:¹⁰ ¹H NMR (CDCl₃, 500 MHz) δ 7.50 (d, *J* = 5.0 Hz, 1H), 7.32 (d, *J* = 3.5 Hz, 1H), 7.17 (s, 1H), 7.07 (dd, *J* = 5.0, 3.5 Hz, 1H), 3.90 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 163.6, 136.5, 132.1, 130.5, 127.0, 122.3, 119.5, 52.7; IR (thin film): 2952, 2124, 1711, 1611, 1272, 1209, 1082 cm⁻¹.

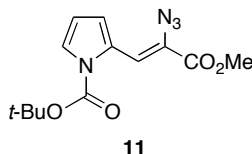


Vinyl azide s15. The general procedure was followed using 2.32 g of sodium methoxide, 12 mL of methanol, 2.00 g of 1-pyrrole-carboxaldehyde (21.0 mmol), and 7.26 g of methyl azidoacetate (63.1 mmol). Purification by flash chromatography (1:99 EtOAc:hexanes) yielded the product as a purple oil that rapidly decomposed (1.5 g, 48%): ¹H NMR (CDCl₃, 300 MHz) δ 9.80 (br s, 1H), 7.00 (br s, 1H), 6.87 (s, 1H), 6.48 (br s, 1H), 6.28 (m, 1H), 3.88 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 164.1, 126.8, 122.4, 118.1, 116.62, 116.58, 110.2, 52.5; IR (thin film): 3429, 2952, 2130, 1704, 1619, 1275, 1225 cm⁻¹.



Vinyl azide 10. To a cooled (−45 °C) solution of vinyl azide **s15** (0.165 g, 0.859 mmol) in 4.6 mL of THF was added dropwise 0.361 mL of a 2.5 M solution of BuLi in hexanes. Upon addition, the dark purple solution turned dark yellow/green. After 10 minutes, 0.127 mL of trimethylacetyl chloride (1.03 mmol) was added. The reaction mixture was warmed to room temperature. After 2 h, the reaction mixture was diluted with 30 mL of

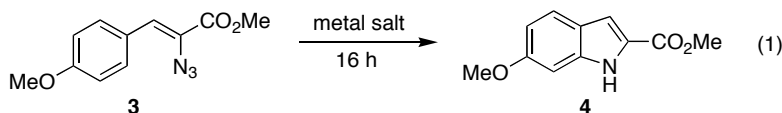
Et₂O and the resulting mixture was washed with 3 × 20 mL of distilled water and 1 × 20 mL of brine. The organic phase was dried over MgSO₄, and the resulting mixture was filtered. The filtrate was concentrated *in vacuo* to afford a light yellow oil. Purification by flash chromatography (1:99 EtOAc:hexanes) afforded the product as a light orange solid (0.227 g, 93%): ¹H NMR (CDCl₃, 500 MHz) δ 7.55 (s, 1H), 7.41 (dd, *J* = 3.0, 1.0 Hz, 1H), 7.27 (d, *J* = 3.5 Hz, 1H), 6.34 (t, *J* = 3.0 Hz, 1H), 3.88 (s, 3H), 1.46 (s, 9H); ¹³C NMR (CDCl₃, 125 MHz) δ 178.7, 164.2, 129.5, 123.4, 122.5, 119.0, 116.2, 112.0, 52.8, 42.1, 28.7; IR (thin film): 2953, 2120, 1708, 1603, 1278 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₃H₁₆N₄O₃Na (M + Na)⁺ 299.1115, found 299.1115. Anal. Calcd for C₁₃H₁₆N₄O₃: C, 56.51; H, 5.84; N, 20.28. Found: C, 56.72; H, 5.90; N, 20.03.



Vinyl azide 11. To a solution of vinyl azide **s15** (0.220 g, 1.15 mmol) and di-*tert*-butyldicarbonate (0.322 g, 1.47 mmol) in 1.5 mL of acetonitrile was added 0.015 g of 4-dimethylaminopyridine. After 16 h, the reaction mixture was diluted with 50 mL of CH₂Cl₂, and the resulting mixture was washed with 20 mL of a saturated aqueous solution of NaHCO₃. The resulting aqueous phase was extracted with 50 mL of CH₂Cl₂. The combined organic phases were washed with 20 mL of a saturated aqueous solution of NH₄Cl and 20 mL of brine. The resulting organic phase was dried over MgSO₄, and the mixture was filtered. The filtrate was concentrated *in vacuo* to afford a light yellow solid. Purification by flash chromatography (1:99 EtOAc:hexanes) afforded the product as a light yellow solid (0.270 g, 81%): ¹H NMR (CDCl₃, 500 MHz) δ 7.88 (s, 1H), 7.39 (m, 1H), 7.29 (m, 1H), 6.29 (t, *J* = 3.0 Hz, 1H), 3.88 (s, 3H), 1.63 (s, 9H); ¹³C NMR (CDCl₃, 125 MHz) δ 164.2, 149.1, 128.5, 124.5, 122.2, 120.0, 115.3, 111.7, 84.7, 52.7, 27.9; IR (thin film): 2980, 2122, 1742, 1710, 1331, 1310, 1250, 1127 cm⁻¹; HRMS (ESI) *m/z* calcd for C₁₃H₁₆N₄O₄Na (M + Na)⁺ 315.1064, found 315.1064.

II. General procedures for metal-catalyzed decomposition of vinyl azides

A. General Procedure for optimization of reaction conditions



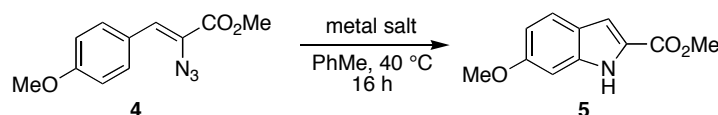
To a mixture of 0.010 g of vinyl azide **3** (0.043 mmol) and metal salt (x mol%) was added x.xx mL of solvent. The resulting mixture was heated to x °C. After 16h, the reaction mixture was cooled to room temperature and the heterogenous mixture was filtered through SiO₂. The filtrate was concentrated *in vacuo*. The resulting mixture was dissolved in 1.5 mL of CDCl₃ and 0.007 mL of dibromomethane (0.1 mmol) was added. The areas of the MeO peaks were compared with the area of the peak of dibromomethane to derive a ¹H NMR yield:

Table s1. Optimization of reaction conditions

entry	metal complex	mol %	temp (°C)	solvent	yield, % ^a
1	FeCl ₃	30	40	PhMe	10
2	Pd(OTf) ₂	10	40	PhMe	15
3	Rh ₂ (OAc) ₄	10	40	PhMe	9
4	Rh ₂ (O ₂ CCF ₃) ₄	5	30	PhMe	64
5	Rh ₂ (O ₂ CCF ₃) ₄	5	40	PhMe	>95
6	Rh ₂ (O ₂ CCF ₃) ₄	3	40	PhMe	40
7	Rh ₂ (pfb) ₄	3	40	PhMe	>95
8	Rh ₂ (pfb) ₄	5	30	PhMe	>95
9	Rh ₂ (pfb) ₄	3	40	CH ₂ Cl ₂	48
10	Rh ₂ (pfb) ₄	3	40	1,2-DCE	50
11	Rh ₂ (pfb) ₄	3	40	THF	14

^a As determined using ¹H NMR spectroscopy.**B. Metal complexes examined**

No indole formation was observed when the following metal complexes were employed as catalysts:

Table s2. Optimization of reaction conditions

entry	metal salt (mol %)	additive (mol %)	entry	metal salt	additive
1	Cu(CH ₃ CN) ₄ PF ₆	n.a.	19	Pd(PPh ₃) ₄ (10)	n.a.
2	Cu(CH ₃ CN) ₄ BF ₄	n.a.	20	(dba) ₃ Pd ₂ ·CHCl ₃ (10)	n.a.
3	CuCl	n.a.	21	Pd(OAc) ₂ (10)	n.a.
4	CuCl	DMF (20)	22	Pd(PhCN) ₂ Cl ₂ (10)	n.a.
5	(CuOTf) ₂ ·PhH ^a	n.a.	23	(dba) ₂ Pd ₂ (10)	n.a.
6	(CuOTf) ₂ ·PhMe ^a	n.a.	24	[(allyl)PdCl] ₂ (10)	n.a.
7	Cu(OTf) ₂ ^a	n.a.	25	(pyr) ^c PdCl ₂ (10)	n.a.
8	Cu(acac) ₂	n.a.	26	(4- <i>t</i> -Bu-pyr) ^e PdCl ₂ (10)	n.a.
9	Cu(pfac) ₂ ^b	n.a.	27	PdCl ₂ (10)	AgBF ₄ (15)
10	AgOTf (10)	n.a.	28	FeCl ₂ (30)	n.a.
11	AgOTf (10)	pyr ^c (10)	29	FeCl ₂ (30)	PPh ₃
12	AgClO ₄ (10)	n.a.	30	FeCl ₃ (30)	n.a.
13	AgOTf (10)	4- <i>t</i> -Bu-terpy ^d (15)	31	Fe(acac) ₃ (30)	n.a.
14	AgSbF ₆ (10)	4- <i>t</i> -Bu-terpy ^d (15)	32	FeBr ₃ (30)	n.a.
15	AgBF ₄ (10)	4- <i>t</i> -Bu-terpy ^d (15)	33	FeF ₃ (30)	n.a.
16	AgPF ₆ (10)	4- <i>t</i> -Bu-terpy ^d (15)	34	Fe(TPP)Cl ^f (10)	n.a.
17	AuCl (10)	AgOTf (15)	35	Co(salen) ^g (10)	n.a.
18	AgOTf (10)	n.a.	36	Co(TPP) ^f (10)	n.a.

^a Less than 10% of the indole product was observed at 60 °C; ^b pfac = CF₃C(O)CHC(O)CF₃; ^c pyr = pyridine; ^d 4-*t*-Bu-terpy = 4,4',4''-Tri-*tert*-Butyl-2,2':6',2''terpyridine; ^e 4-*t*-Bu-pyr = 4-*tert*-butylpyridine; ^f TPP = tetraphenylporphyrin; ^g salen = (1S,2S)-N,N'-Bis[3-oxo-2-(2,4,6-trimethylbenzoyl)butylidene]-1,2-diphenylethylenediamine.

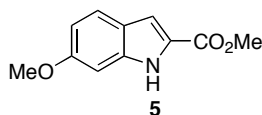
C. Optimized general procedure

To a mixture of x.xxx g of vinyl azide **4** (x.xx mmol) and $\text{Rh}_2(\text{pfb})_4$ (3 mol%) was added x.xx mL of solvent (1.0 M). The resulting mixture was heated to 40 °C. After 16h, the reaction mixture was cooled to room temperature and the heterogenous mixture was filtered through SiO_2 . The filtrate was concentrated *in vacuo*. Purification by flash chromatography provided the indole as a white solid.

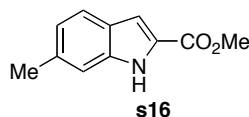
For more electron deficient arenes, increased catalyst loading and the temperature was required:

To a mixture of x.xxx g of vinyl azide **4** (x.xx mmol) and $\text{Rh}_2(\text{pfb})_4$ (5 mol%) was added x.xx mL of solvent (1.0 M). The resulting mixture was heated to 60 °C. After 16h, the reaction mixture was cooled to room temperature and the heterogenous mixture was filtered through SiO_2 . The filtrate was concentrated *in vacuo*. Purification by flash chromatography provided the indole as a white solid.

III. Characterization data for indoles



Indole 5.³ The general procedure was followed with 0.083 g of vinyl azide **4** (0.357 mmol), 0.011 g of $\text{Rh}_2(\text{pfb})_4$ (0.017 mmol), and 0.400 mL of toluene. Purification by flash chromatography (5:95 EtOAc:hexanes) afforded indole **5** as a white solid (0.072 g, 98%). Indole **5** is available from Aldrich (365572). The spectral data matched that reported by Luu and co-workers:³ ^1H NMR (CDCl_3 , 500 MHz) δ 8.88 (br s, 1H), 7.55 (d, J = 9 Hz, 1H), 7.17 (s, 1H), 6.83 (m, 2H), 3.93 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 162.4, 158.9, 137.9, 126.0, 123.4, 121.8, 112.3, 109.2, 93.6, 55.5, 51.8; IR (thin film): 3325, 2950, 1685, 1524, 1446, 1253, 1115, 827 cm^{-1} .



Indole s16.¹¹ The general procedure at 60 °C was followed using 0.049 g of vinyl azide **s1** (0.23 mmol), 0.0120 g of $\text{Rh}_2(\text{pfb})_4$ (0.011 mmol) and 0.150 mL of toluene. Purification by flash chromatography (20:80 EtOAc:hexanes) yielded the product as a white solid (0.038g, 88%) : ^1H NMR (CDCl_3 , 500 MHz) δ 8.88 (br s, 1H), 7.57 (d, J = 8.5 Hz, 1H), 7.20 (m, 2H), 7.00 (d, J = 8.0 Hz, 1H), 3.95 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (DMSO, 125 MHz) δ 161.3, 137.4, 133.7, 125.9, 124.2, 121.8, 121.2, 111.5, 107.3, 51.2, 21.1; IR (thin film): 3329, 2348, 1702, 1525, 1332, 1257, 1100 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{11}\text{NO}_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.89; H, 6.07; N, 7.03.

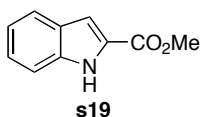


Indole s17.¹² The general procedure was followed with 0.071 g of vinyl azide **s2** (0.327 mmol), 0.016 g of $\text{Rh}_2(\text{pfb})_4$ (0.016 mmol), and 0.200 mL of toluene. Purification by flash chromatography (1:19 EtOAc:hexanes) afforded indole **s17** as a white solid (0.057 g, 91%): ^1H NMR (CDCl_3 , 500 MHz) δ 8.84 (br s, 1H), 7.61 (d, J = 8.5 Hz, 1H), 7.255 (s, 1H), 7.18 (d, J = 1.0 Hz, 1H), 7.07 (dd, J = 7.0, 1.5 Hz, 1H), 3.94 (s, 3H), 3.02 (septet, J

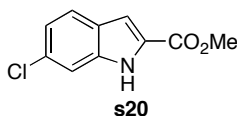
= 7.0 Hz, 1H), 1.33 (d, J = 7.0 Hz, 6H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 162.6, 146.9, 137.4, 126.7, 125.6, 122.3, 120.6, 108.77, 108.74, 53.4, 51.9, 34.4; IR (thin film): 3330, 3312, 1687, 1526, 1439, 1312, 1254 cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_2$: C, 71.87; H, 6.97; N, 6.45. Found: C, 71.98; H, 7.07; N, 6.39.



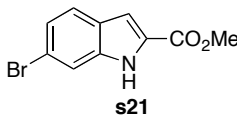
Indole s18. The general procedure at 60 °C was followed using 0.059 g of vinyl azide **s3** (0.23 mmol), 0.0120 g $\text{Rh}_2(\text{pfb})_4$ (0.011 mmol), and 0.150 mL of toluene. Purification by flash chromatography (15:85 EtOAc:hexanes) yielded the product as a white solid (0.037g, 71%): ^1H NMR (CDCl_3 , 500 MHz) δ 9.01 (br s, 1H), 7.63 (d, J = 8.5 Hz, 1H), 7.42 (s, 1H), 7.25 (d, J = 8.5 Hz, 1H), 7.19 (s, 1H), 3.96 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 162.6, 149.1, 137.2, 126.8, 125.2, 122.0, 119.6, 108.6, 107.8, 51.9, 35.0, 31.5; IR (thin film): 3304, 2964, 2361, 1695, 1441, 1232, 830, 654 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_2$: 231.1259, found 231.1262.



Indole s19.¹³ The general procedure was followed with 0.060 g of vinyl azide **s4** (0.300 mmol), 0.016 g of $\text{Rh}_2(\text{pfb})_4$ (0.015 mmol), and 0.200 mL of toluene. Purification by flash chromatography (1:19 EtOAc:hexanes) afforded indole **s19** as a white solid (0.0434 g, 84%). Indole **s19** is available from Aldrich (365572). The spectral data matched that reported by Sechi and co-workers:² ^1H NMR (CDCl_3 , 500 MHz) δ 9.01 (br s, 1H), 7.70 (d, J = 7.5 Hz, 1H), 7.43 (d, J = 7.5 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.24 (s, 1H), 7.16 (t, J = 7.5 Hz, 1H), 3.96 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 162.6, 136.9, 127.5, 127.1, 125.5, 122.7, 120.9, 111.9, 108.8, 52.1; IR (thin film): 3330, 3312, 1687, 1526, 1439, 1312, 1254 cm^{-1} .



Indole s20.¹¹ The general procedure at 60 °C was followed using 0.054 g of vinyl azide **s5** (0.23 mmol), 0.0120 g of $\text{Rh}_2(\text{pfb})_4$ (0.011 mmol) and 0.150 mL of toluene. Purification by flash chromatography (15:85 EtOAc:hexanes) yielded the product as a white solid (0.040g, 85%) : ^1H NMR (CDCl_3 , 500 MHz) δ 9.07 (br s, 1H), 7.60 (d, J = 8.7 Hz, 1H), 7.43 (s, 1H), 7.19 (s, 1H), 7.13 (d, J = 8.5 Hz, 1H), 3.96 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 162.2, 137.0, 131.4, 127.8, 126.0, 123.6, 121.9, 111.7, 108.8, 52.2; IR (thin film): 3317, 2361, 1697, 1520, 1319, 1240, 829 cm^{-1} . Anal. Calcd for $\text{C}_{10}\text{H}_8\text{ClNO}_2$: C, 57.30; H, 3.85; N, 6.68. Found: C, 57.13; H, 3.81; N, 6.54.

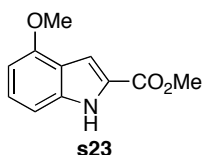


Indole s21. The general procedure at 60 °C was followed using 0.063 g of **s6** (0.22 mmol), 0.0122 g of $\text{Rh}_2(\text{pfb})_4$ (0.011 mmol), and 0.149 mL of toluene. Purification by flash chromatography (2:98 – 30:70 EtOAc:hexanes) afforded the product as a white solid (0.057 g, 83%): ^1H NMR (CDCl_3 , 500 MHz) δ 8.97 (br s, 1H), 7.59 (s, 1H), 7.55 (d, J = 8.5 Hz, 1H), 7.26 (d, J = 8.5 Hz, 1H), 7.19 (s, 1H), 3.96 (s, 3H); ^{13}C NMR (CDCl_3 , 500 MHz) δ 162.2, 137.5, 127.7, 126.3, 124.5, 123.9, 119.2, 114.8, 108.8, 52.2; IR (thin film): 3316,

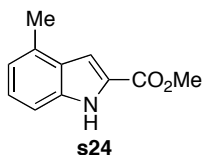
3302, 1701, 1522, 1440, 1319, 1241, 1220 cm^{-1} . Anal. Calcd for $\text{C}_{10}\text{H}_8\text{BrNO}_2$: C, 47.27; H, 3.17; N, 5.51. Found: C, 47.16; H, 3.21; N, 5.25.



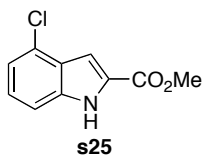
Indole s22. The general procedure at 60 °C was followed using 0.061 g of **s7** (0.23 mmol), 0.0120 g $\text{Rh}_2(\text{pfb})_4$ (0.011 mmol), and 0.150 mL of toluene. Purification by flash chromatography (20:80 EtOAc:hexanes) yielded the product as a white solid (0.055g, 88%) : ^1H NMR (CDCl_3 , 500 MHz) δ 9.35 (br s, 1H), 7.78 (d, J =8.5 Hz, 1H), 7.74 (s, 1H), 7.38 (d, J =8.5 Hz, 1H), 7.26 (m, 1H), 4.00 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 162.1, 135.6, 129.6, 127.4, 127.2, 124.7 (q, J_{CF} = 270 Hz), 123.3, 117.3, 109.6, 108.5, 52.4; ^{19}F NMR (CDCl_3 , 282 MHz) δ -62.0; IR (thin film): 3315, 2360, 1685, 1437, 1323, 1107, 828 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{11}\text{H}_8\text{F}_3\text{NO}_2$: 243.0507, found 243.0503.



Indole s23.³ The general procedure at 60 °C was followed using 0.053 g of vinyl azide **s8** (0.23 mmol), 0.0120 g of $\text{Rh}_2(\text{pfb})_4$ (0.011 mmol), and 0.150 mL of toluene. Purification by flash chromatography (20:80 EtOAc:hexanes) yielded the product as a white solid (0.043g, 91%). The spectral data matched that reported by Luu and co-workers:³ ^1H NMR (CDCl_3 , 500 MHz) δ 8.99 (br s, 1H), 7.36 (m, 1H), 7.27 (m, 1H), 7.04 (d, J =8.5 Hz, 1H), 6.53 (d, J =7.5 Hz, 1H), 3.98 (s, 3H), 3.96 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 162.4, 154.6, 138.2, 126.5, 125.8, 119.0, 106.5, 104.8, 99.8, 55.3, 52.0; IR (thin film): 3306, 2361, 1699, 1576, 1437, 1253, 1121, 754 cm^{-1} .

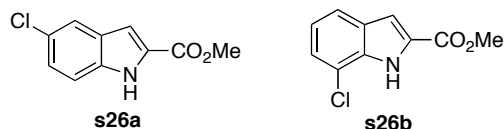


Indole s24.⁶ The general procedure at 60 °C was followed using 0.069 g of vinyl azide **s9** (0.23 mmol), 0.0100 g of $\text{Rh}_2(\text{pfb})_4$ (0.011 mmol), and 0.315 mL of toluene. Purification by flash chromatography (15:85 EtOAc:hexanes) yielded the product as a white solid (0.552 g, 93%). The spectral data matched that reported by Moody and co-workers:⁶ ^1H NMR (CDCl_3 , 500 MHz) δ 9.24 (br s, 1H), 7.30 – 7.23 (m, 3H), 6.96 (m, 1H), 3.98 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 162.6, 136.8, 132.3, 127.7, 126.4, 125.6, 120.7, 109.4, 107.4, 52.0, 18.6; IR (thin film): 3309, 2360, 1691, 1436, 1267, 936, 756, 692 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{11}\text{NO}_2$: C, 69.83; H, 5.86; N, 7.40, found C, 69.53; H, 5.84; N, 7.29.

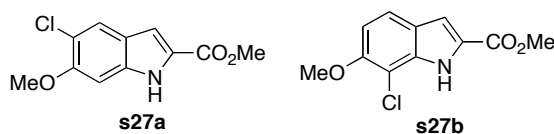


Indole s25.¹⁴ The general procedure at 60 °C was followed using 0.075 g of vinyl azide **s10** (0.32 mmol), 0.0170 g of $\text{Rh}_2(\text{pfb})_4$ (0.016 mmol), and 0.210 mL of toluene. Purification by flash chromatography (5:95 EtOAc:hexanes) yielded the product as a white solid (0.50 g, 76%): ^1H NMR (CDCl_3 , 500 MHz) δ 9.14 (br s,

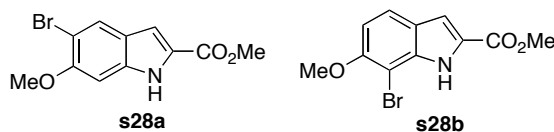
1H); 7.33 (s, 1H), 7.33 (t, $J = 8$ Hz, 1H), 7.23 (d, $J = 8$ Hz, 1H), 7.16 (d, $J = 8$ Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 162.2, 137.4, 127.9, 127.5, 126.7, 125.9, 120.5, 110.6, 107.2, 52.3; IR (thin film): 3310, 2980, 1738, 1689, 1442, 1369, 1359, 1313, 1232, 1149 cm^{-1} . Anal. Calcd for $\text{C}_{10}\text{H}_8\text{ClNO}_2$: C, 57.30; H, 3.85; N, 6.68. Found: C, 57.06; H, 3.89; N, 6.54.



Indoles s26.^{15,16} The general procedure at 60 °C was followed using 0.054 g of **s11** (0.23 mmol), 0.0120 g of $\text{Rh}_2(\text{pfb})_4$ (0.011 mmol) and 0.150 mL of toluene. Purification by flash chromatography (20:80 EtOAc:hexanes) yielded the indole product as a separable mixture of regioisomers (87:13; **s26a** : **s26b**). Major product **s27a** was obtained as a white solid (0.039g, 84%). The spectral data for **s26a** matched that reported by Frejd and co-workers:¹⁶ ^1H NMR (CDCl_3 , 500 MHz) δ 8.95 (br s, 1H), 7.67 (m, 1H), 7.35 (m, 1H), 7.29 (m, 1H), 7.15 (m, 1H), 3.95 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 163.9, 135.0, 128.4, 126.1, 125.9, 121.8, 113.0, 112.4, 108.1, 52.2. IR (thin film): 3324, 2361, 1697, 1558, 1438, 1257, 1061, 870, 766 cm^{-1} . Minor regioisomer **s26b** was obtained as a white solid (0.006 g, 13%): ^1H NMR (CDCl_3 , 500 MHz) δ 9.01 (br s, 1H), 7.60 (d, $J = 8.0$ Hz, 1H), 7.33 (d, $J = 7.5$ Hz, 1H), 7.10 (t, $J = 7.5$ Hz, 1H), 7.26 (s, 1H), 3.97 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 161.9, 134.2, 128.7, 127.9, 124.5, 121.6, 121.2, 117.2, 109.5, 52.2.

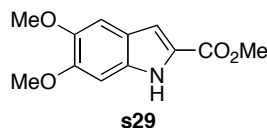


Indoles s27. The general procedure at 60 °C was followed using 0.067 g of vinyl azide **s12** (0.25 mmol), 0.0080 g of $\text{Rh}_2(\text{pfb})_4$ (0.008 mmol), and 0.256 mL of toluene. Purification by flash chromatography (15:85 EtOAc:hexanes) yielded the indole product as a separable mixture of regioisomers (79:21; **s27a** : **s27b**). Major product **s27a** was obtained as a white solid (0.044 g, 73%): ^1H NMR (CDCl_3 , 500 MHz) δ 8.97 (br s, 1H), 7.67 (s 1H), 7.10 (s, 1H), 6.89 (s, 1H), 3.94 (s, 6H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 162.2, 153.8, 136.2, 126.8, 123.3, 121.6, 118.1, 108.4, 94.1, 56.2, 52.0. Selected spectroscopic data for minor regioisomer **s27b** (0.012 g, 19%): ^1H NMR (CDCl_3 , 500 MHz) δ 8.5 (br s, 1H), 7.55 (d, $J = 9$ Hz, 1H), 7.20 (m, 1H), 6.93 (d, $J = 9$ Hz, 1H), 3.98 (s, 3H), 3.95 (s, 3H); IR (thin film): 3320, 2361, 1684, 1524, 1292, 1047, 817, 760 cm^{-1} . Mixture: Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{ClNO}_3$: C, 55.13; H, 4.21; N, 5.84. Found C, 55.05; H, 4.23; N, 5.81.



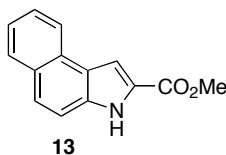
Indoles s28. The general procedure at 40 °C was followed using 0.025 g of vinyl azide **s13** (0.080 mmol), 0.0025 mg of $\text{Rh}_2(\text{pfb})_4$ (0.002 mmol), and 0.080 mL of toluene. Purification by flash chromatography (5:95 – 30:70 EtOAc:hexanes) afforded the indole product as a separable mixture of regioisomers (92:8; **s28a** : **s28b**). Major product **s28a** was obtained as a white solid (0.020 g, 90%): ^1H NMR (CDCl_3 , 500 MHz) δ 8.93 (br s, 1H), 7.86 (s, 1H), 7.09 (s, 1H), 6.87 (s, 1H), 3.93 (s, 6H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 162.0, 154.4, 136.8, 126.8, 126.6, 122.6, 108.3, 106.9, 94.0, 56.4, 52.0; IR (thin film): 3318, 1684, 1039, 866, 815, 759 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{BrNO}_3$: C, 46.50; H, 3.55; N, 4.93. Found: C, 46.79; H, 3.65; N, 4.90. Selected spectroscopic data for minor regioisomer **s28b** (0.002 g, 8%): ^1H NMR (CDCl_3 , 500 MHz) δ 8.81 (br s, 1H), 7.58 (d, $J = 8.5$ Hz, 1H), 7.24 (s, 1H), 6.90 (d, $J = 9.0$ Hz, 1H), 3.98 (s, 3H), 3.95 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 161.9,

154.3, 137.2, 127.3, 122.8, 122.2, 109.8, 108.2, 92.9, 57.2, 52.1; IR (thin film): 3327, 1704, 1629, 1505, 1259, 1201, 1172 cm^{-1} .

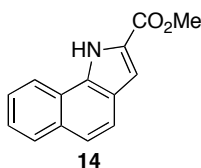


Indole s29.³ The general procedure at 40 °C was followed using 0.025 g of vinyl azide **s14** (0.095 mmol), 0.0031 mg of $\text{Rh}_2(\text{pfb})_4$ (0.003 mmol), and 0.095 mL of toluene. Purification by flash chromatography (5:95 – 30:70 EtOAc:hexanes) afforded the indole product as a white solid (0.020 g, 88%). The spectral data for **s30** matched that reported by Luu and co-workers:³ ^1H NMR (CDCl_3 , 500 MHz): δ 8.85 (br s, 1H), 7.11 (s, 1H), 7.04 (s, 1H), 6.85 (s, 1H), 3.92 (s, 3H), 3.91 (s, 6H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 162.3, 150.1, 146.2, 132.1, 125.6, 120.4, 108.8, 102.5, 93.8, 56.2, 56.1, 51.8; IR (thin film): 3329, 1685, 1525, 1252, 1218, 1148 cm^{-1} .

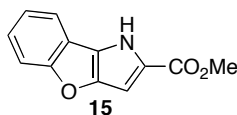
IV. Characterization data for *N*-heterocyclic compounds



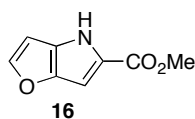
Benzindole 13.¹⁷ The general procedure at 40 °C was followed using 0.049 g of vinyl azide **6** (0.193 mmol), 0.0063 mg of $\text{Rh}_2(\text{pfb})_4$ (0.006 mmol), and 0.200 mL of toluene. Purification by flash chromatography (5:95 – 30:70 EtOAc:hexanes) afforded the indole product as a white solid (0.040 g, 90%). The temperature of this reaction could be lowered to 25 °C without a drop in conversion. The spectral data for **13** matched that reported by Babushkina and co-workers:¹⁷ ^1H NMR (CDCl_3 , 500 MHz): 9.64 (br s, 1H), 8.24 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.76 (s, 1H), 7.71 (d, J = 7.5 Hz, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.52 (d, J = 7.5 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 4.01 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz): 162.6, 134.4, 129.4, 128.8, 128.7, 127.1, 126.8, 125.3, 124.3, 123.0, 122.9, 113.1, 108.0, 52.06; IR (thin film): 3312, 1685, 1653, 1440, 754; HRMS (EI) m/z calcd for $\text{C}_{14}\text{H}_{11}\text{NO}_2$: 224.0717, found 224.0717.



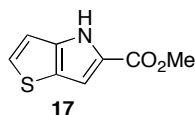
Benzindole 14.¹⁸ The general procedure at 60 °C was followed using 0.018 g of vinyl azide **7** (0.071 mmol), 0.0038 mg of $\text{Rh}_2(\text{pfb})_4$ (0.004 mmol), and 0.066 mL of toluene. Purification by flash chromatography (2:98 – 30:70 EtOAc:hexanes) afforded the product as a white solid (0.016 g, 98%). The spectral data for **14** matched that reported by Ohshiro and co-workers:¹⁸ ^1H NMR (CDCl_3 , 500 MHz): 9.71 (br s, 1H), 8.14 (d, J = 7.5 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.5 Hz, 1H), 7.58 (t, J = 6.5 MHz, 1H), 7.53 (d, J = 7.5 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.34 (s, 1H), 3.99 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz): 162.6, 132.8, 131.9, 129.0, 126.1, 125.7, 125.3, 124.8, 122.2, 121.8, 121.3, 120.4, 110.3, 52.1; IR (thin film): 3330, 1685, 1252, 1219, 1199, 1148, 1011, 846, 764 cm^{-1} .



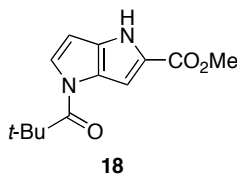
Benzo[4,5]furo[3,2-*b*]pyrrole 15.⁸ The general procedure at 40 °C was followed using 0.053 g of vinyl azide **8** (0.219 mmol), 0.0066 mg of Rh₂(pfb)₄ (0.006 mmol), and 0.200 mL of toluene. Purification by flash chromatography (5:95 EtOAc:hexanes) afforded the indole product as a white solid (0.043 g, 91%). The temperature of this reaction could be lowered to 25 °C without a drop in conversion. The spectral data for **15** matched that reported by Krutošiková and co-workers:⁸ ¹H NMR (CDCl₃, 500 MHz): ¹H NMR (CDCl₃, 500 MHz): 9.39 (br s, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 6.89 (s, 1H), 3.94 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz): 165.9, 164.6, 152.9, 129.1, 129.0, 128.1, 127.3, 123.2, 122.4, 116.7, 100.4, 55.6; IR (thin film): 3320, 1687, 1253, 1200, 827 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₂H₉NO₃: 214.05097, found 214.05095; Anal. Calcd for C₁₂H₉NO₃: C, 66.97; H, 4.22; N, 6.51. Found: C, 66.76; H, 4.20; N, 6.44.



Furo[3,2-*b*]pyrrole 16.⁹ The general procedure was followed with 0.025 g of vinyl azide **9** (0.129 mmol), 0.07 g of Rh₂(pfb)₄ (0.0064 mmol), and 0.087 mL of toluene. Purification by flash chromatography (1:19 EtOAc:hexanes) afforded pyrrole **16** as a white solid (0.017 g, 79%). The spectral data for **16** matched that reported by Krutosikova and co-workers:⁹ ¹H NMR (CDCl₃, 500 MHz) δ 8.87 (br s, 1H), 7.52 (s, 1H), 6.80 (s, 1H), 6.46 (s, 1H), 3.88 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 163.9, 148.7, 148.0, 128.8, 123.9, 98.9, 97.0, 51.6; IR (thin film): 3318, 3269, 3125, 1672, 1497, 1451, 1277 cm⁻¹.

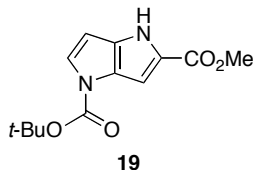


Thieno[3,2-*b*]pyrrole 17.¹⁰ The general procedure at 60 °C was followed using 0.048 g of vinyl azide **10** (0.231 mmol), 0.0126 mg of Rh₂(pfb)₄ (0.012 mmol), and 0.154 mL of toluene. Purification by flash chromatography (5:95 – 30:70 EtOAc:hexanes) afforded the product as a white solid (0.032 g, 77%). The spectral data for **17** matched that reported by Yarovenko and co-workers:¹⁰ ¹H NMR (CDCl₃, 500 MHz): 9.46 (br s, 1H), 7.10 (s, 1H), 7.00 (d, *J* = 5.5 Hz, 1H), 6.92 (d, *J* = 5.5 Hz, 1H), 3.91 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz): 161.9, 138.2, 131.8, 128.0, 120.8, 118.0, 107.6, 51.8; IR (thin film) 3286, 1697, 1516, 1455, 1443, 1372, 1252, 1202, 763, 651 cm⁻¹.



Pyrrollo[3,2-*b*]pyrrole 18. The general procedure at 60 °C was followed using 0.067 mg of vinyl azide **11** (0.242 mmol), 0.0125 mg of Rh₂(pfb)₄ (0.012 mmol), and 0.153 mL of toluene. Purification by flash chromatography (5:95 – 30:70 EtOAc:hexanes) afforded the product as an off-white solid (0.048 mg, 80%): ¹H NMR (CDCl₃, 500 MHz): 8.79 (br s, 1H), 7.55 (d, *J* = 3.5 Hz, 1H), 7.20 (s, 1H), 6.24 (d, *J* = 3.5 Hz, 1H), 3.88 (s, 3H), 1.49 (s, 9H); ¹³C NMR (CDCl₃, 125 MHz): 175.3, 162.6, 130.8, 128.2, 126.7, 124.4, 103.2, 98.6, 51.6, 40.2, 28.3; IR (thin film) 3325, 2955, 1685, 1441, 1335, 1309, 1206, 918, 729; Anal. Calcd for C₁₃H₁₆N₂O₃: C,

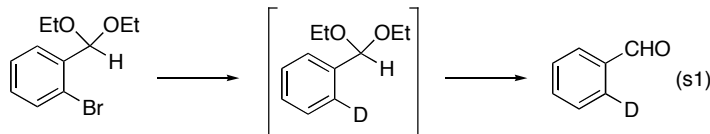
62.89; H, 6.50; N, 11.28. Found: C, 62.52; H, 6.51; N, 10.90.



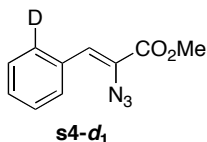
Pyrrolo[3,2-*b*]pyrrole 19. The general procedure at 60 °C was followed using 0.075 g of vinyl azide **12** (0.26 mmol), 0.0130 g of Rh₂(pfb)₄ (0.011 mmol), and 0.160 mL of toluene. Purification by flash chromatography (15:85 EtOAc:hexanes) yielded the product as a white solid (0.066 g, 93%): ¹H NMR (CDCl₃, 300 MHz) δ 9.09 (br s, 1H), 7.41 (br s, 1H), 6.91 (br s, 1H), 6.19 (s, 1H), 3.88 (s, 3H), 1.65 (s, 9H); ¹³C NMR (CDCl₃, 75.5 MHz) δ 162.4, 149.1, 131.4, 126.8, 126.3, 123.9, 100.8, 97.8, 83.4, 51.5, 28.1; IR (thin film): 3313, 2979, 1735, 1684, 1442, 1359, 1149, 731 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₃H₁₆N₂O₄: 264.1110, found 264.1118. Anal. Calcd for C₁₃H₁₆N₂O₄: C, 59.08; H, 6.10; N, 10.60. Found: C, 58.91; H, 6.07; N, 10.52.

V. Mechanistic experiments

A. Synthesis of labeled vinyl azide



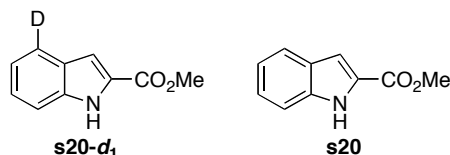
2-Deuteriobenzaldehyde. A similar procedure as reported by Wills and co-workers was employed for the synthesis of 2-deuteriobenzaldehyde.¹⁹ To a cooled (−74 °C) solution of 2-bromobenzaldehyde diethyl acetal (5.00 mL, 24.7 mmol) in 38.0 mL of Et₂O was added 12.0 mL of a 2.5 M solution of BuLi in hexanes by syringe pump (9.5 mL/h). After 90 minutes, 2.1 mL of methanol-*d*₃ (49.4 mmol) was added to the white heterogeneous mixture. After addition, the reaction mixture was allowed to warm to 0 °C. The mixture was diluted with 50 mL of distilled water and 50 mL of Et₂O. The phases were separated, and 70 mL of a 4% solution of HCl in distilled water was added to the organic phase. The resulting mixture was vigorously stirred. After 16 h, the phases were separated, and the resulting organic phase was washed 60 mL of brine. The organic phase was dried over MgSO₄, and the resulting heterogeneous mixture was filtered. The filtrate was carefully concentrated *in vacuo* (~150 mm Hg, 15 °C) to afford a clear oil. Purification by distillation afforded 2 mL of 2-deuteriobenzaldehyde. The spectral data of the labeled compound matched that reported by Imhof and co-workers:²⁰ ¹H NMR (CDCl₃, 500 MHz) δ, 9.99 (s, 1H), 7.85 (d, *J* = 7.0 Hz, 1H), 7.60 (t, *J* = 7.0 Hz, 1H), 7.50 (m, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 192.2, 136.2, 134.3, 129.6, 129.3 (*J*_{CD} = 25 Hz), 128.8, 128.7.



Vinyl azide s4-*d*₁. The general procedure for the synthesis of vinyl azides was followed using 0.456 g of sodium methoxide (8.44 mmol), 4.00 mL of methanol, 0.757 mL of 2-deuteriobenzaldehyde (7.00 mmol), and 2.42 g of methyl azidoacetate (21.00 mmol). Purification by flash chromatography (2:98 EtOAc:hexanes) yielded the product as a light yellow solid (0.705 g, 48%): ¹H NMR (CDCl₃, 500 MHz) δ 7.80 (m, 1H), 7.30 –

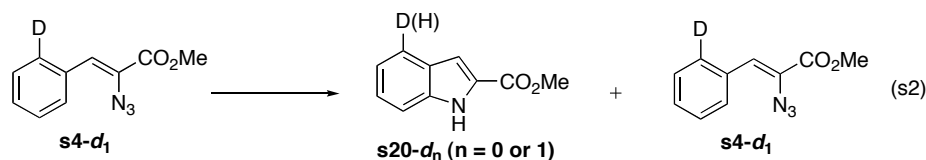
7.44 (m, 3H), 6.92 (s, 1H), 3.91 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 163.9, 133.0, 130.5, 130.2 ($J_{\text{CD}} = 25$ Hz), 129.4, 128.4, 128.3, 125.4, 125.2, 52.8; IR (thin film): 2951, 2338, 2125, 1716, 1437, 1249, 1078 cm^{-1} . Anal. calcd for $\text{C}_{10}\text{H}_8\text{DN}_3\text{O}_2$: C, 58.82; H+D as H, 4.44; N, 20.58. Found: C, 58.82; H+D as H, 4.48; N, 20.58.

B. Rhodium(II)-mediated indole formation



Indole s-20-*d*₁ and s-20. The general procedure at 60 °C was followed using 0.015 g of vinyl azide **s4-*d*₁** (0.75 mmol), 0.0069 g of $\text{Rh}_2(\text{pfb})_4$ (0.0065 mmol), and 0.100 mL of toluene. Analysis of the crude ^1H NMR spectrum revealed a 50:50 mixture of **s-20-*d*₁** and **s-20** based on comparison of the integration of the C-4 substituent of the indole. Purification by flash chromatography (3:97 EtOAc:hexanes) yielded the product as a white solid (0.012 g, 87%): ^1H NMR (CDCl_3 , 500 MHz) δ 8.96 (br s, 1H), 7.70 (d, $J = 8.0$ Hz, 0.5 H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.33 (t, $J = 8.0$ Hz, 1H), 7.23 (s, 1H), 7.16 (m, 1H), 3.95 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 162.5, 136.9, 127.4, 127.1, 125.4, 122.3 ($J_{\text{CD}} = 25$ Hz) 120.8, 111.9, 108.8, 52.0; IR (thin film): 3331, 2359, 1699, 1558, 1457, 1253, 771 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{10}\text{H}_8\text{DNO}_2$: 176.0696, found 176.0692.

C. Partial indole formation

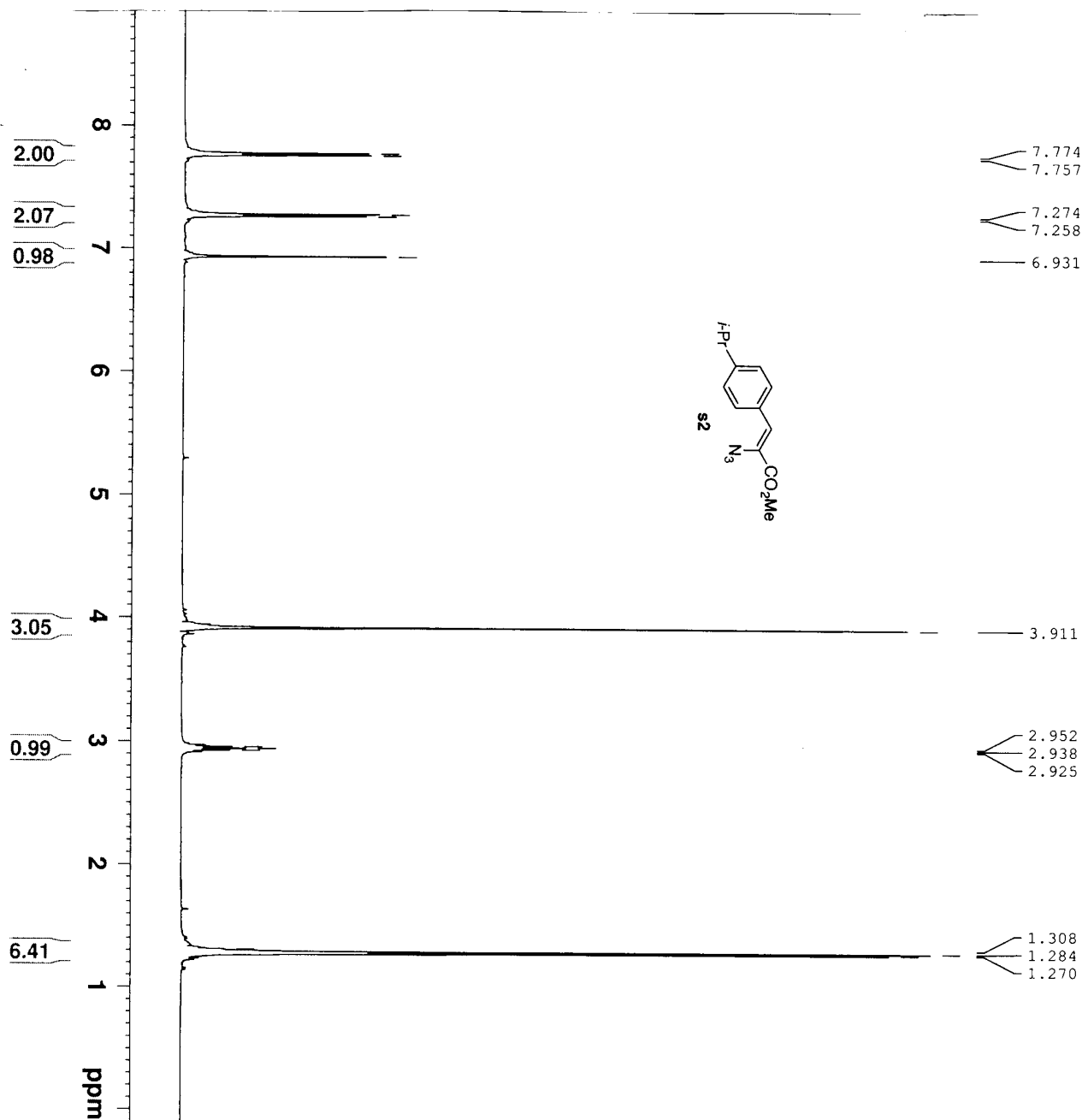


The general procedure at 60 °C was followed using 0.029 g of vinyl azide **s4-*d*₁** (0.14 mmol), 0.0075 g of $\text{Rh}_2(\text{pfb})_4$ (0.0071 mmol), and 0.200 mL of toluene. After 2.5 h, the reaction mixture was cooled to room temperature. Analysis of the crude ^1H NMR spectrum revealed approximately a 75:25 mixture of **s-20-*d*_n** and **s-4-*d*₁** based on comparison of the integration of methoxy substituents. Purification by flash chromatography (1:99 EtOAc:hexanes) afforded the vinyl azide **s4-*d*₁** as a white solid (0.071 g, 25%). Comparison of the aryl protons revealed no change in their relative integrations.

VI. References

- (1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.
- (2) Henn, L.; Hickey, D. M. B.; Moody, C. J.; Rees, C. W. *J. Chem. Soc., Perkin Trans. I* **1984**, 2189-2196.
- (3) Coowar, D.; Bouissac, J.; Hanbali, M.; Paschaki, M.; Mohier, E.; Luu, B. *J. Med. Chem.* **2004**, *47*, 6270-6282.
- (4) Knittel, D. *Monatsh. Chem.* **1985**, *116*, 1133-1140.
- (5) Ghosh, S. K.; Verma, R.; Ghosh, U.; Mamdapur, V. R. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1705-1711.
- (6) Bentley, D. J.; Fairhurst, J.; Gallagher, P. T.; Manteuffel, A. K.; Moody, C. J.; Pinder, J. L. *Org. Biomol. Chem.* **2004**, *2*, 701-708.
- (7) Shim, S. C.; Yeo, Y. K.; Choi, K. N.; Lee, H.-K. *J. Korean Chem. Soc.* **1988**, *32*, 156-158.
- (8) Krutošiková, A.; Dandarova, M.; Bobosik, V. *Collect. Czech. Chem. Commun.* **1994**, *59*, 473-481.
- (9) Krutosikova, A.; Dandarova, M.; Chylova, J.; Vegh, D. *Monatsh. Chem.* **1992**, *123*, 807-815.
- (10) Yarovenko, V. N.; Semenov, S. L.; Zavarzin, I. V.; Ignatenko, A. V.; Krayushkin, M. M. *Russ. Chem. Bull.* **2003**, *52*, 451-456.
- (11) Knittel, D. *Synthesis* **1985**, 186-188.
- (12) Holzapfel, C. W.; Dwyer, C. *Heterocycles* **1998**, *48*, 1513-1518.
- (13) Sechi, M.; Derudas, M.; Dallochio, R.; Dessi, A.; Bacchi, A.; Sannia, L.; Carta, F.; Palomba, M.; Ragab, O.; Chan, C.; Shoemaker, R.; Sei, S.; Dayam, R.; Neamati, N. *J. Med. Chem.* **2004**, *47*, 5298-5310.
- (14) Uhle, F. C. *J. Am. Chem. Soc.* **1949**, *71*, 761-766.
- (15) Nazaré, M.; Will, D. W.; Matter, H.; Schreuder, H.; Ritter, K.; Urmann, M.; Essrich, M.; Bauer, A.; Wagner, M.; Czech, J.; Lorenz, M.; Laux, V.; Wehner, V. *J. Med. Chem.* **2005**, *48*, 4511-4525.
- (16) Tullberg, E.; Schacher, F.; Peters, D.; Frejd, T. *Synthesis* **2006**, 1183-1189.
- (17) Babushkina, T. A.; Vasil'ev, A. M.; Shagalov, L. B.; Eraksina, V. N.; Tkachenko, T. A.; Suvorov, N. N. *J. Org. Chem. USSR (Engl. Transl.)* **1975**, *11*, 864-871.
- (18) Itoh, S.; Fukui, Y.; Ogino, M.; Haranou, S.; Komatsu, M.; Ohshiro, Y. *J. Org. Chem.* **1992**, *57*, 2788-2793.
- (19) Matharu, D. S.; Morris, D. J.; Kawamoto, A. M.; Clarkson, G. J.; Wills, M. *Org. Lett.* **2005**, *7*, 5489-5491.
- (20) Imhof, W.; Göbel, A.; Ohlmann, D.; Flemming, J.; Fritzsche, H. *J. Organomet. Chem.* **1999**, *584*, 33-43.

VII. ¹H NMR Spectra of new vinyl azides



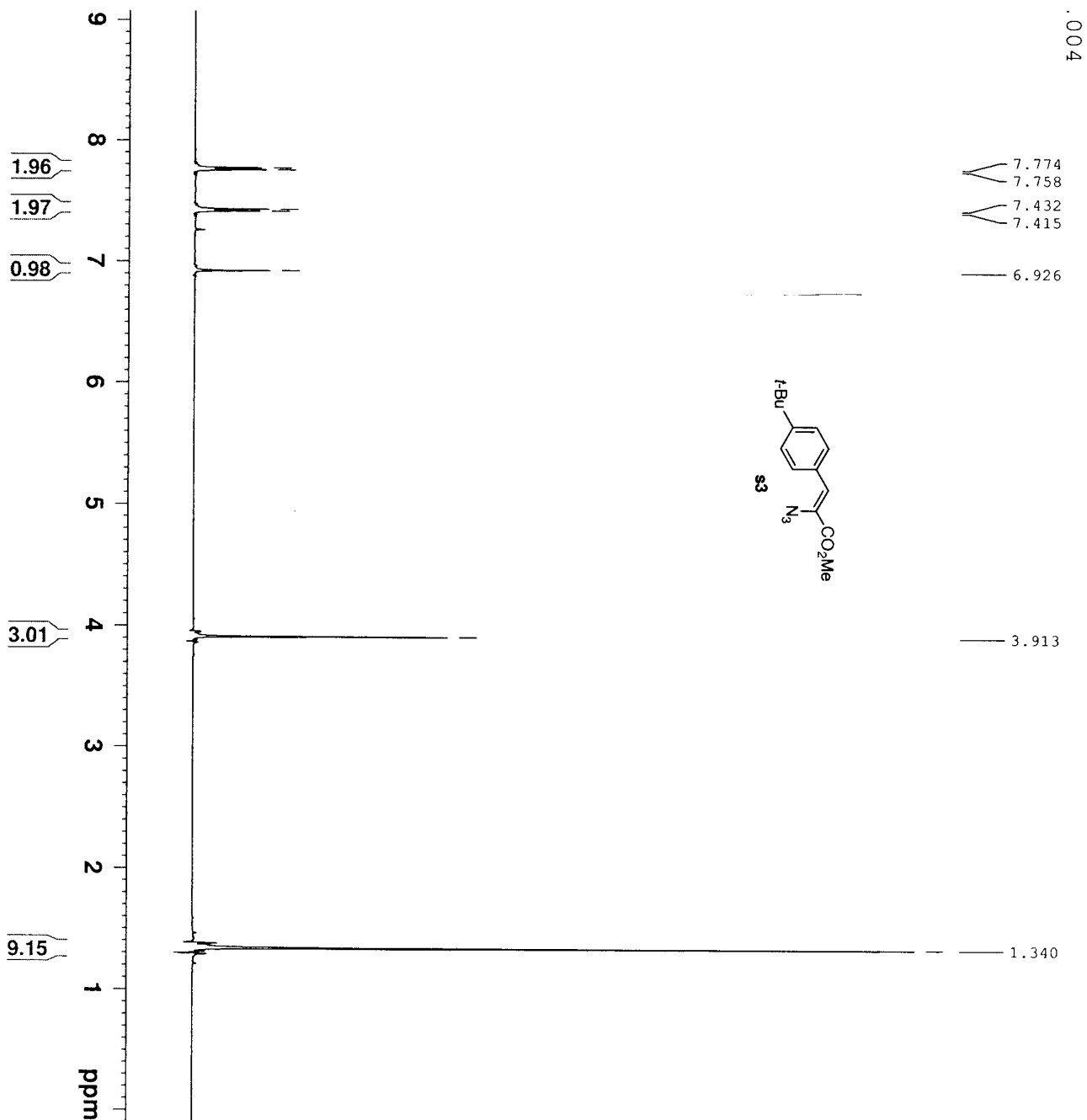
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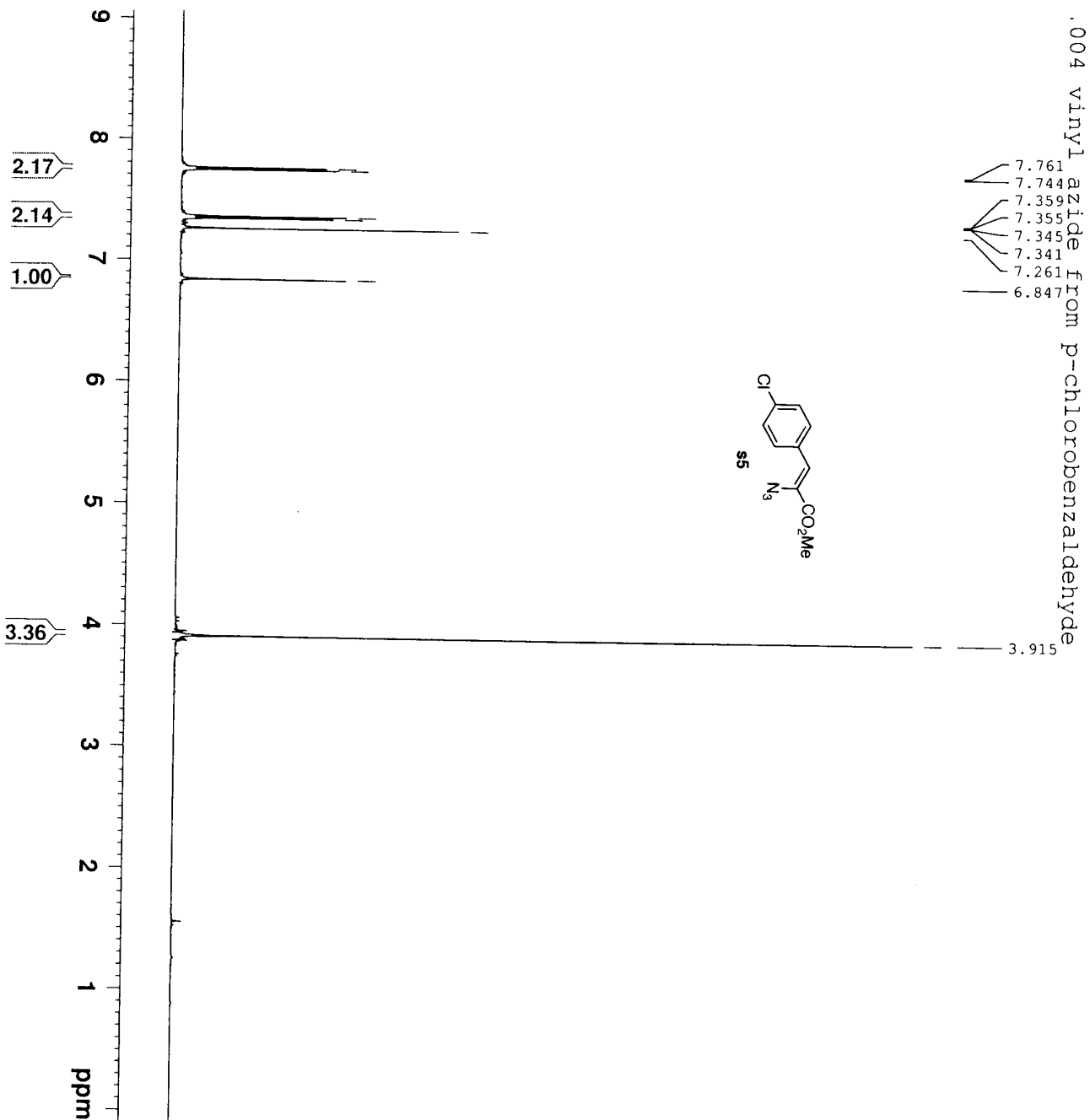




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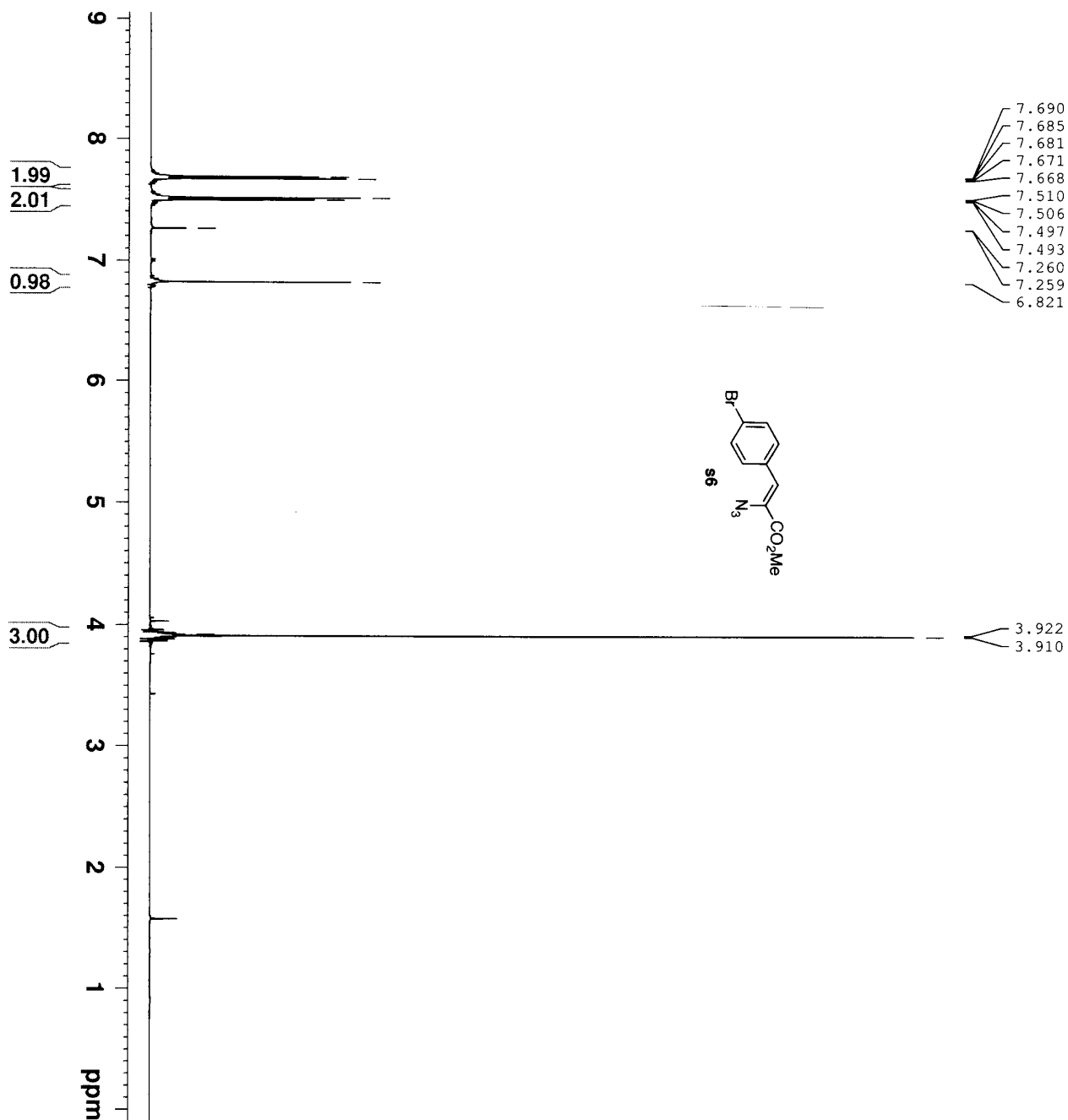
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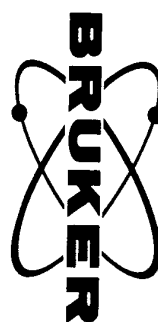
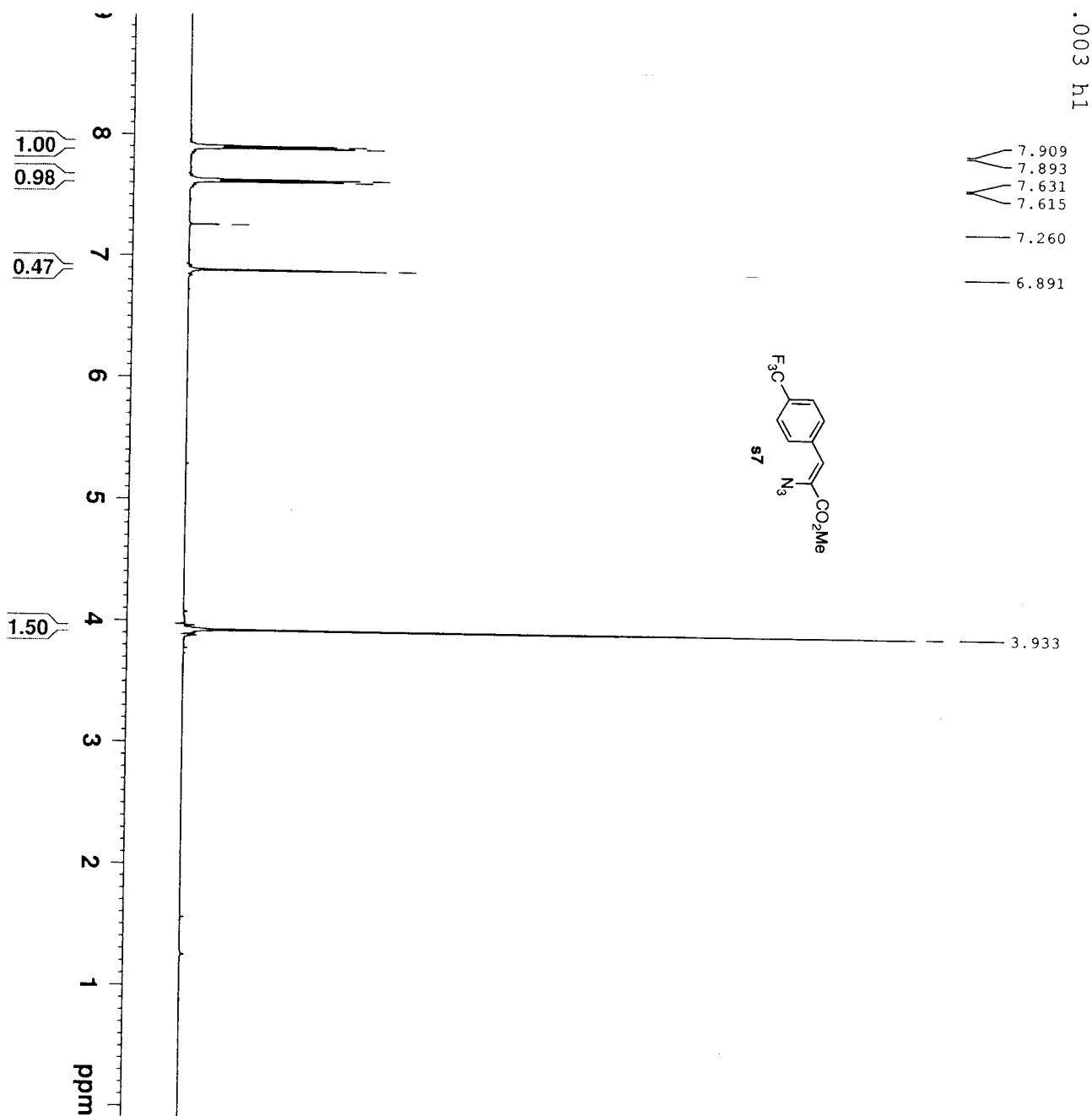
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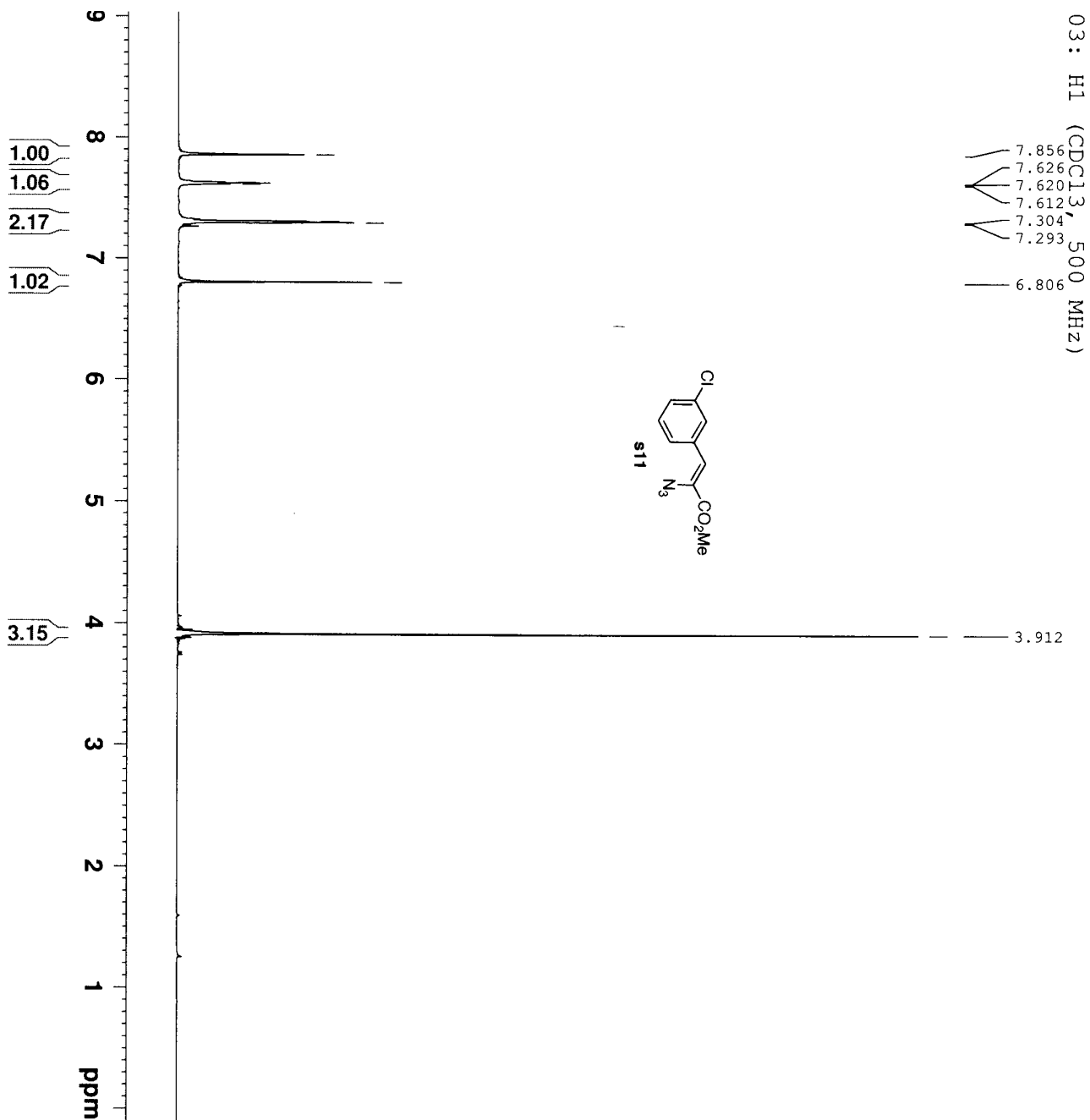


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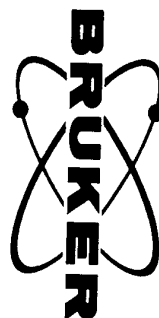
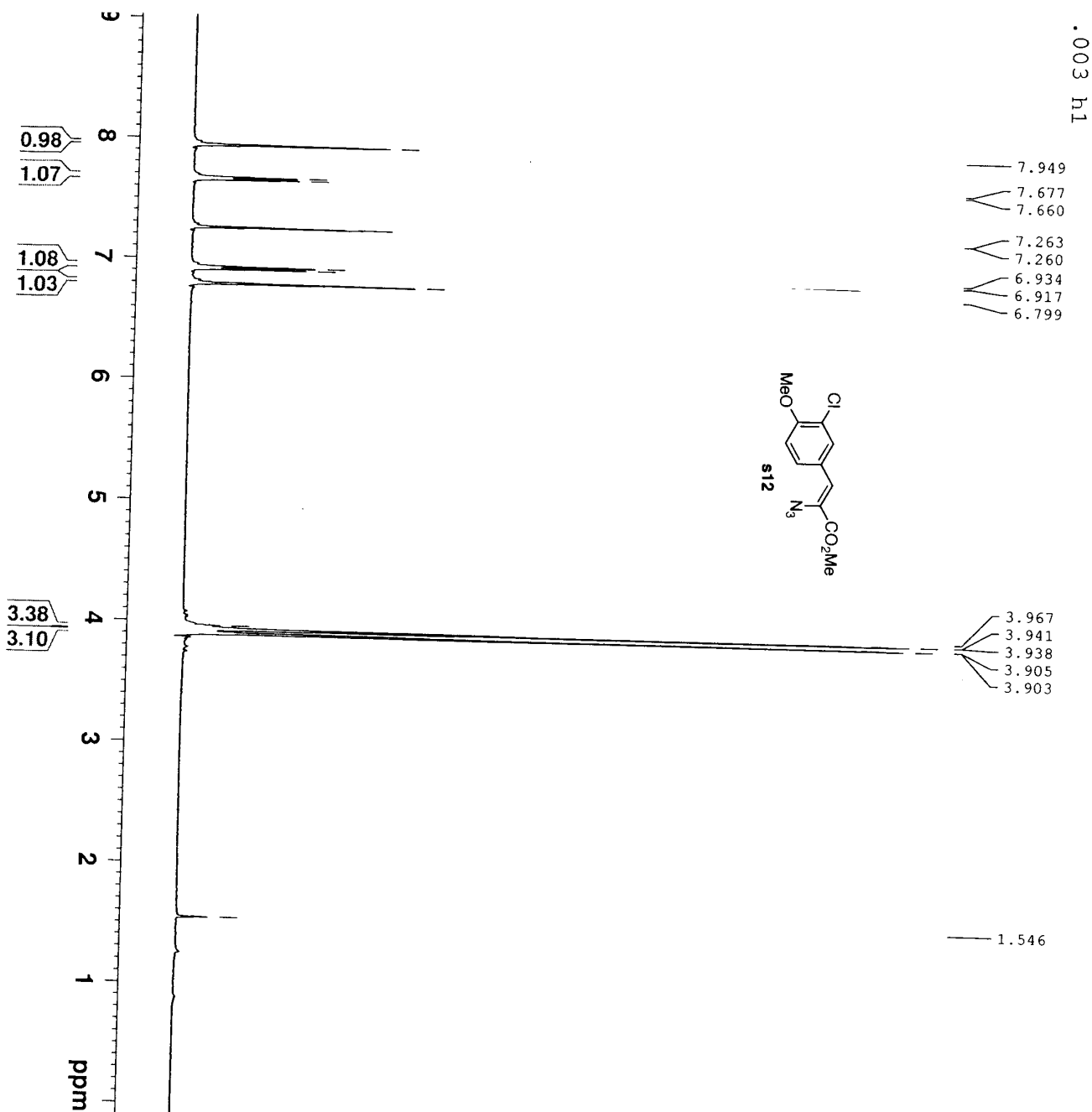


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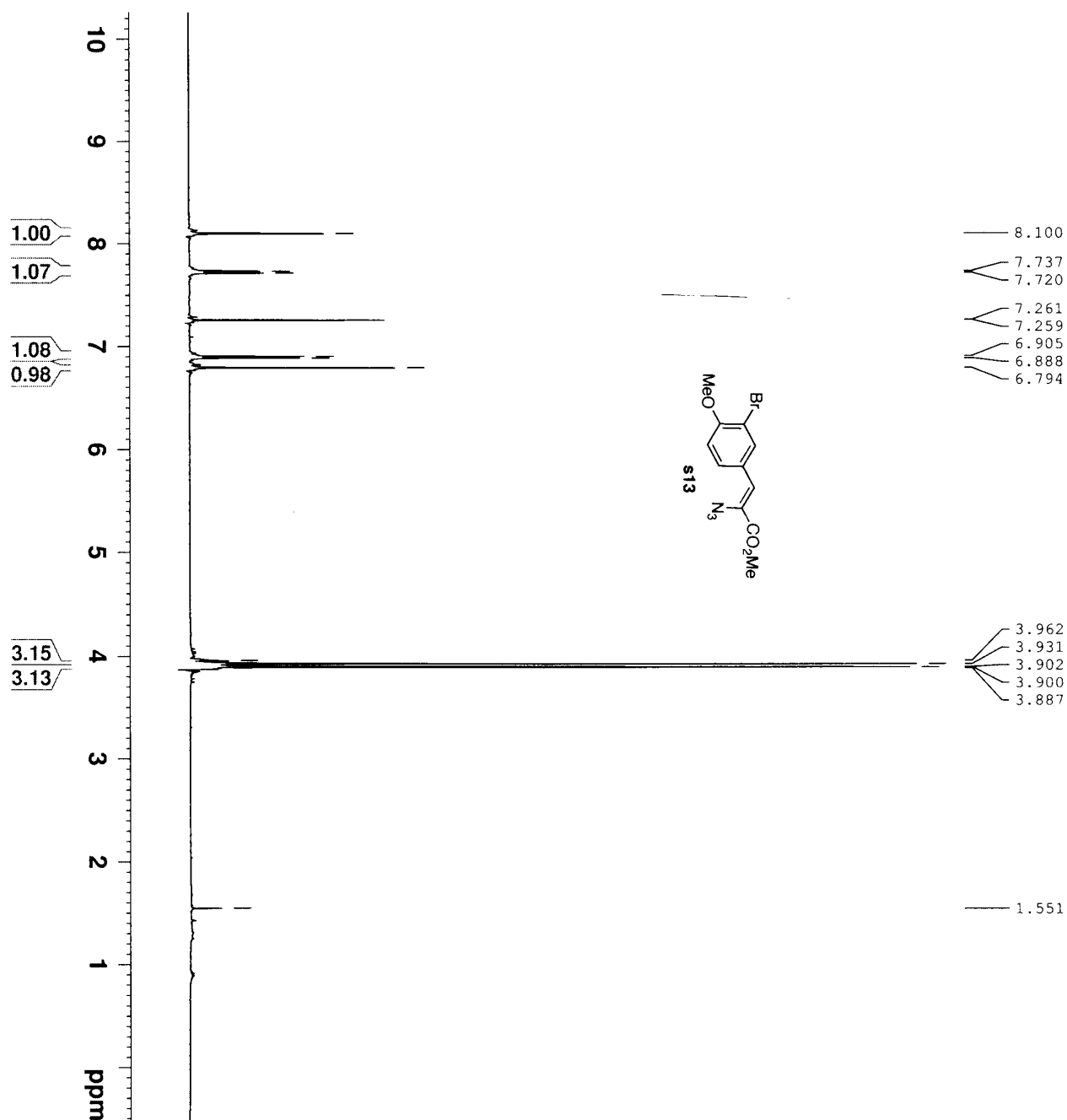
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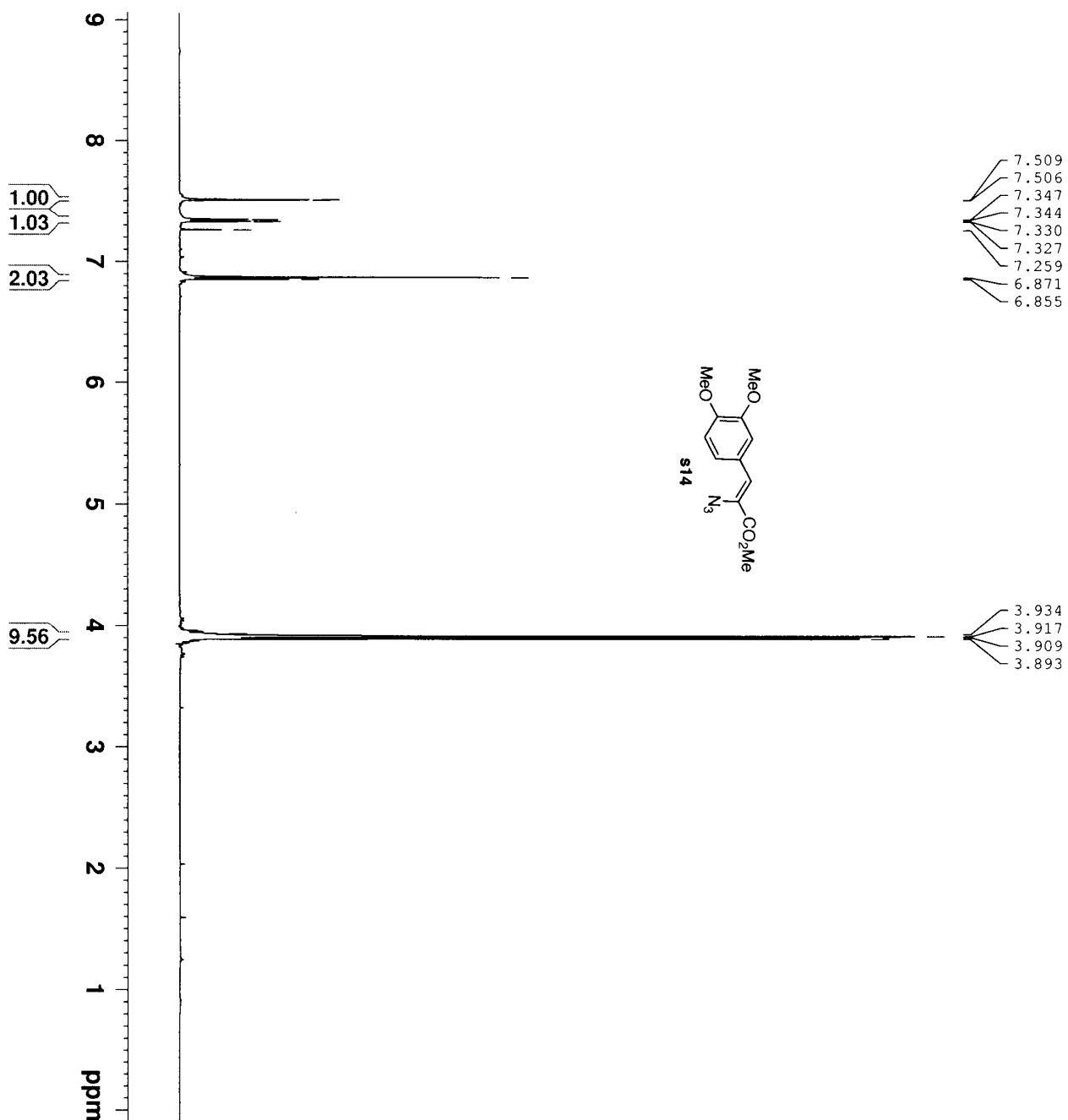
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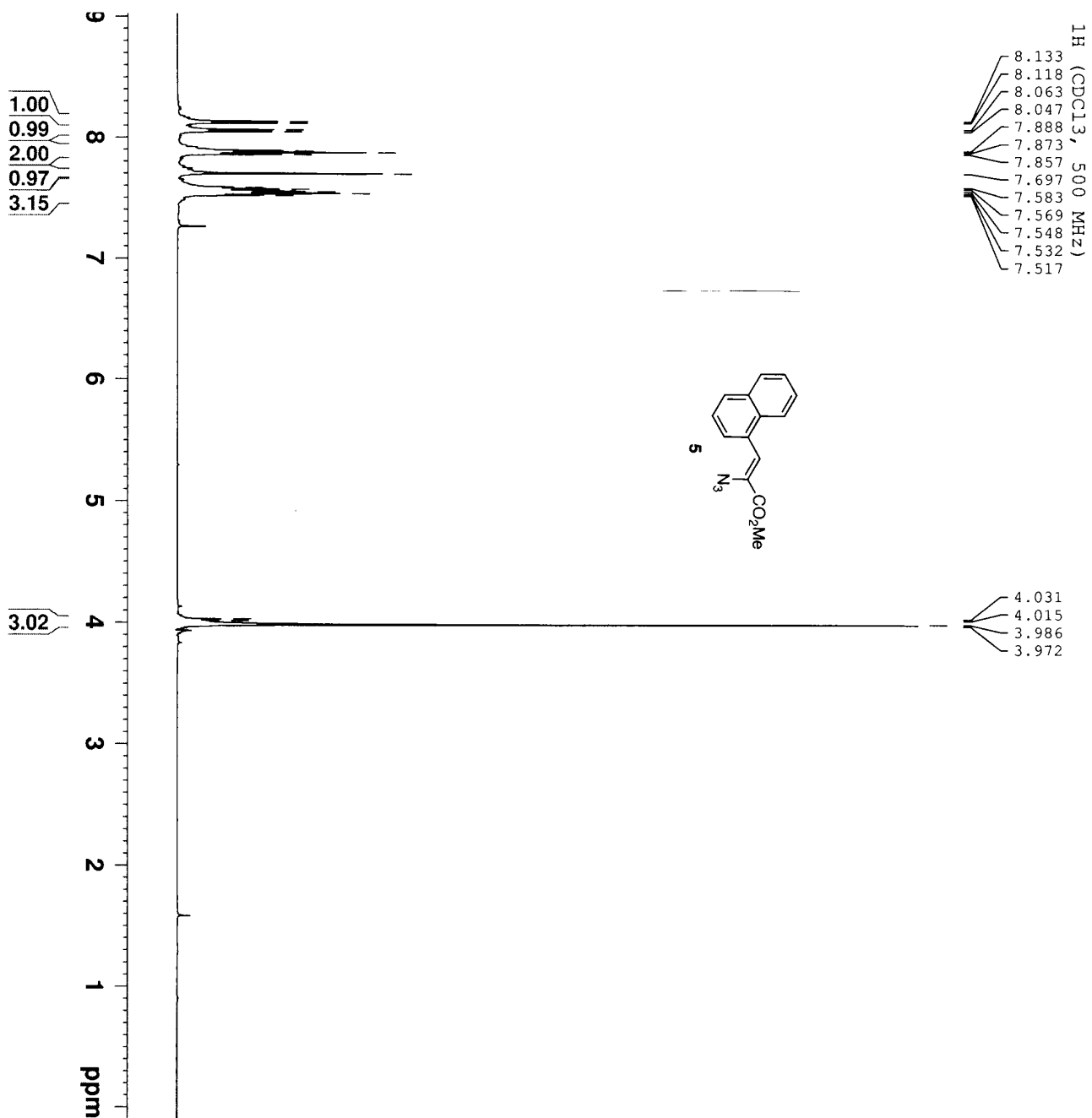
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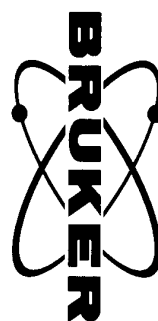
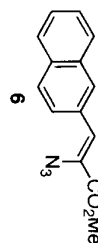
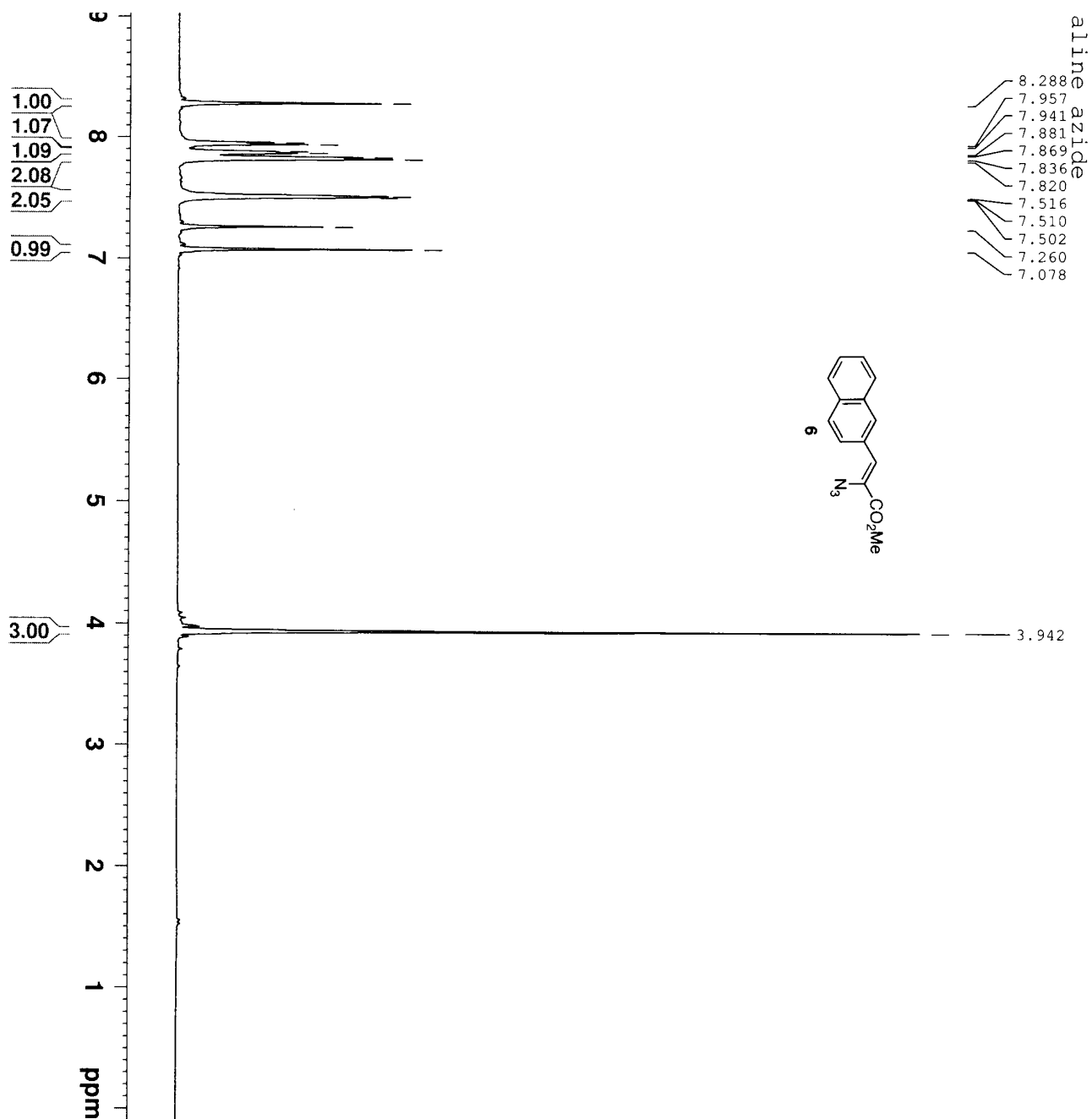


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 NS 8
 DS 2
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 FIDRES 0.183399 Hz
 AQ 2.7264309 sec
 RG 143.7
 DW 83.200 use
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F2 - Processing parameters
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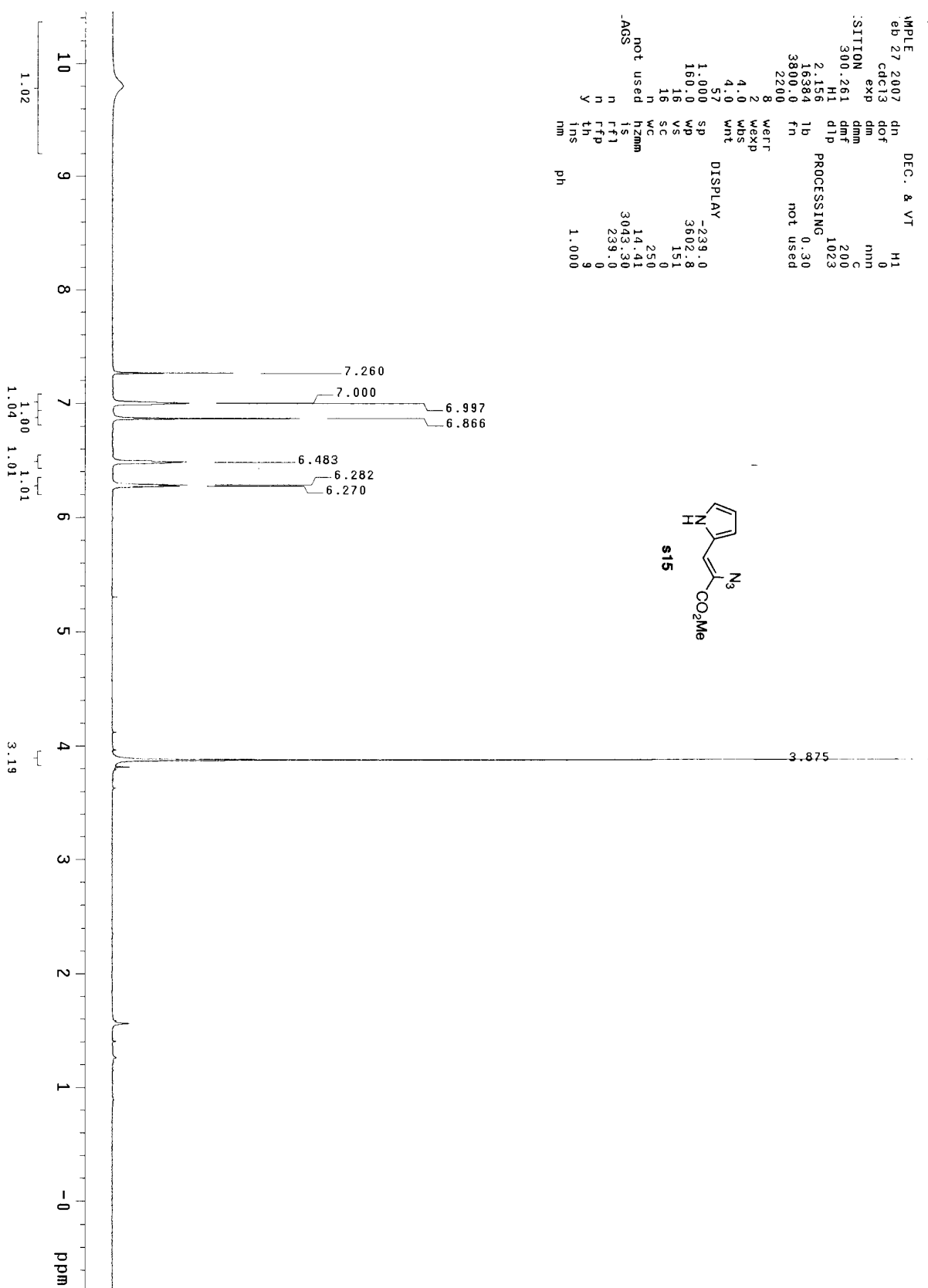
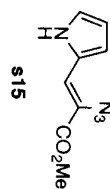
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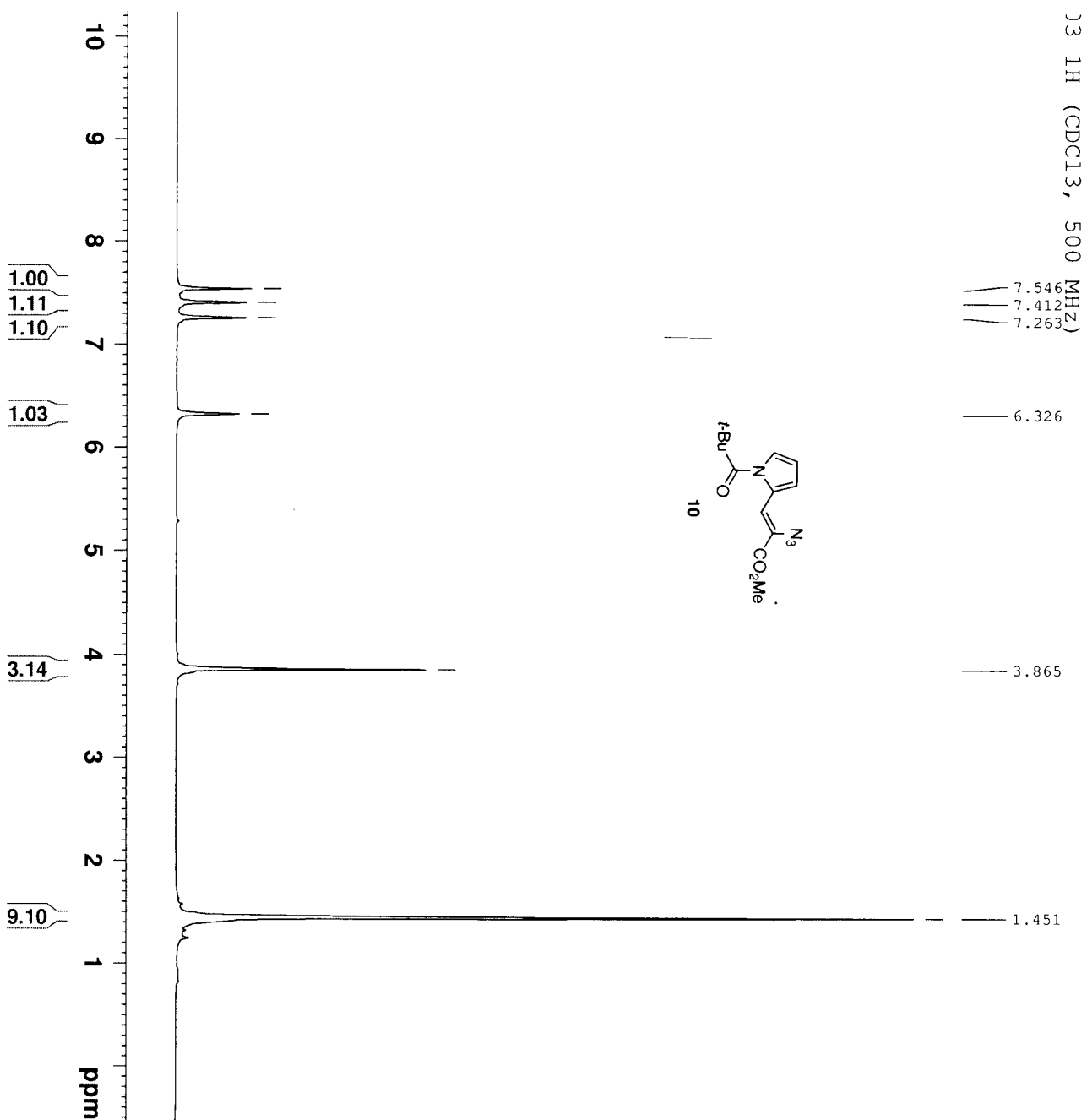
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104: second column on pyrrole-2-carbaldehyde

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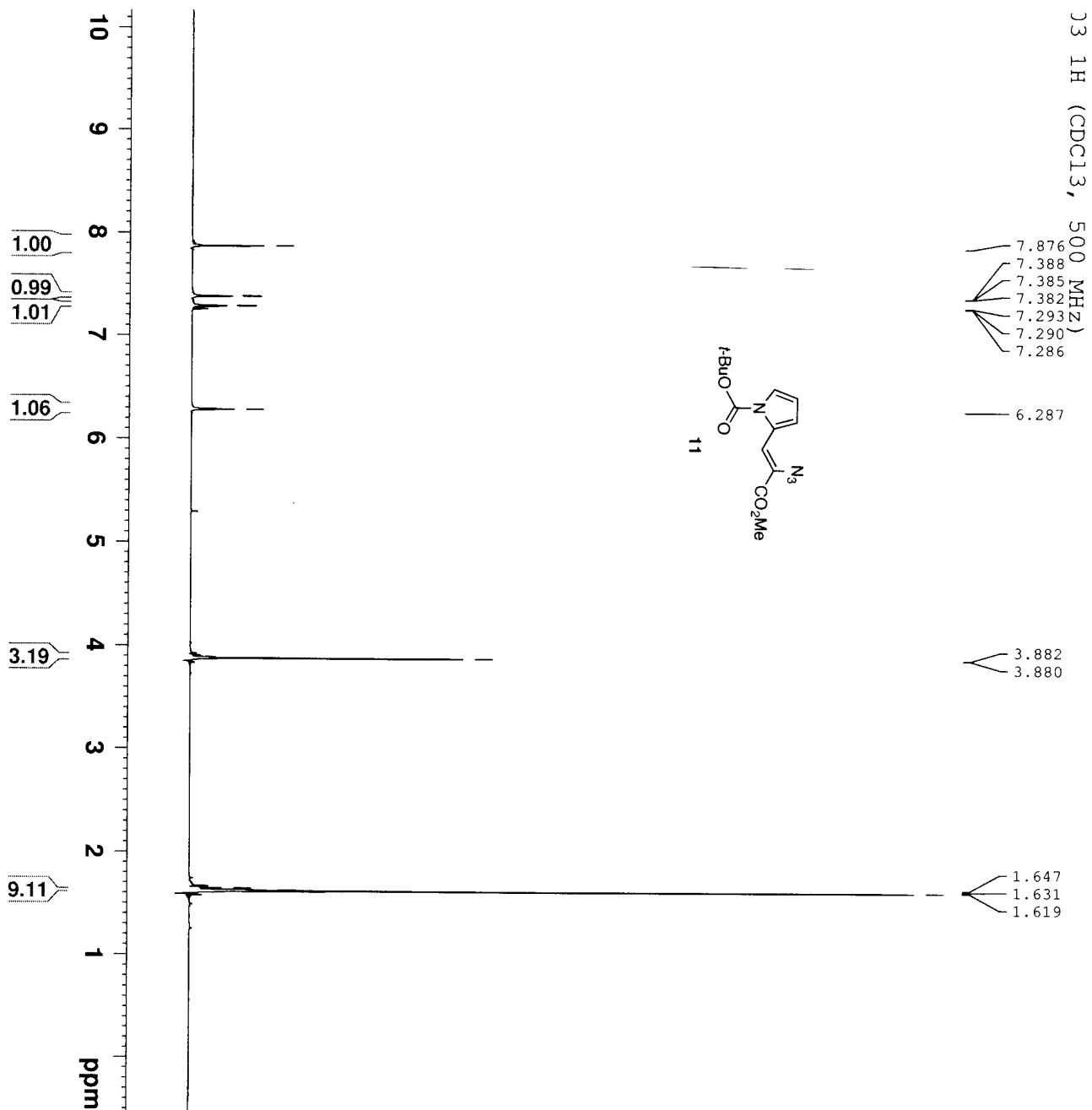


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 FIDRES 0.183399 Hz
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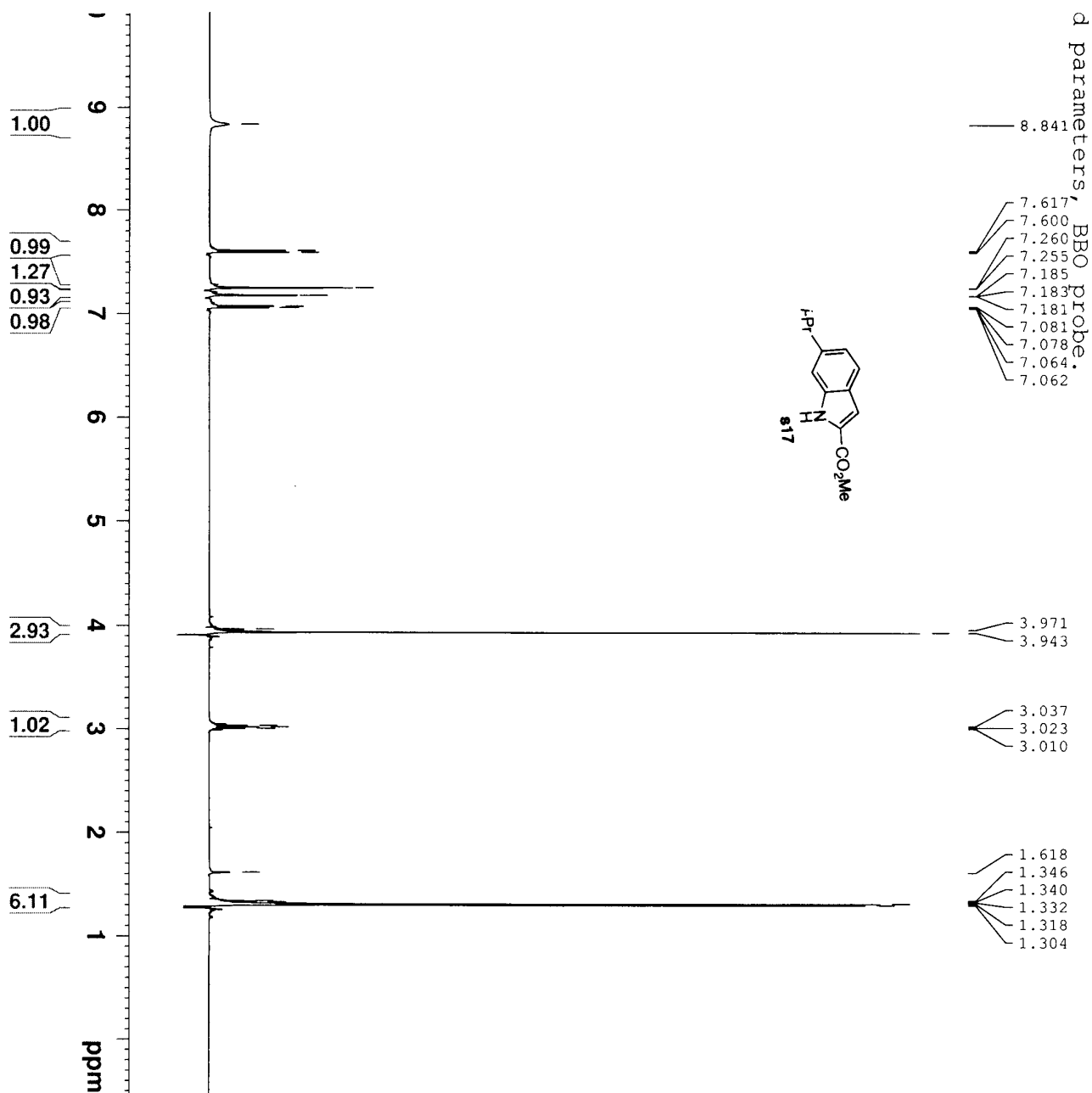


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VIII. ¹H NMR Spectra of new indoles



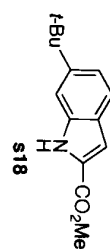
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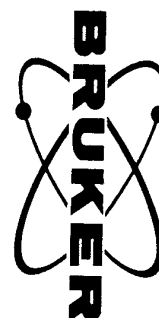
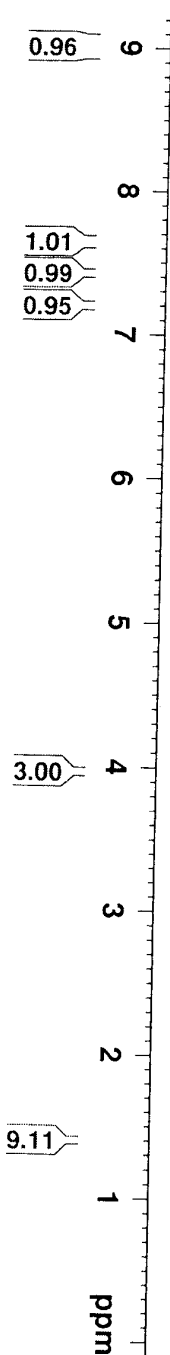
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7.190



3.960

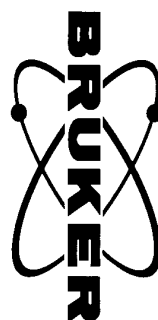
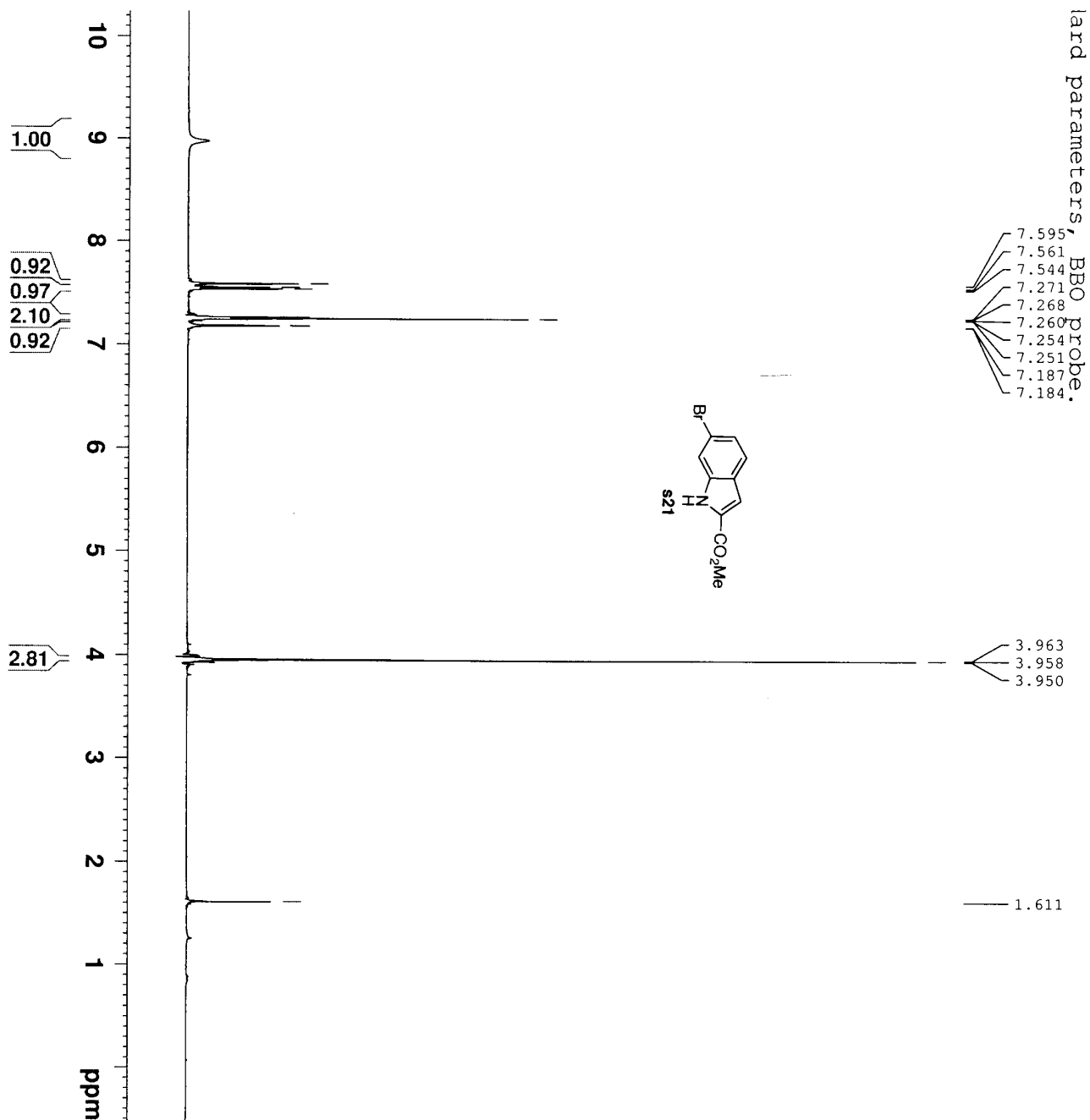
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RG 128
DW 83.200 use
DE 6.00 use
TE 300.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 3.50 use
PL1 -2.00 dB
SFO1 500.6427535 MHz
F2 - Processing parameters
SI 32768
SF 500.6400128 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

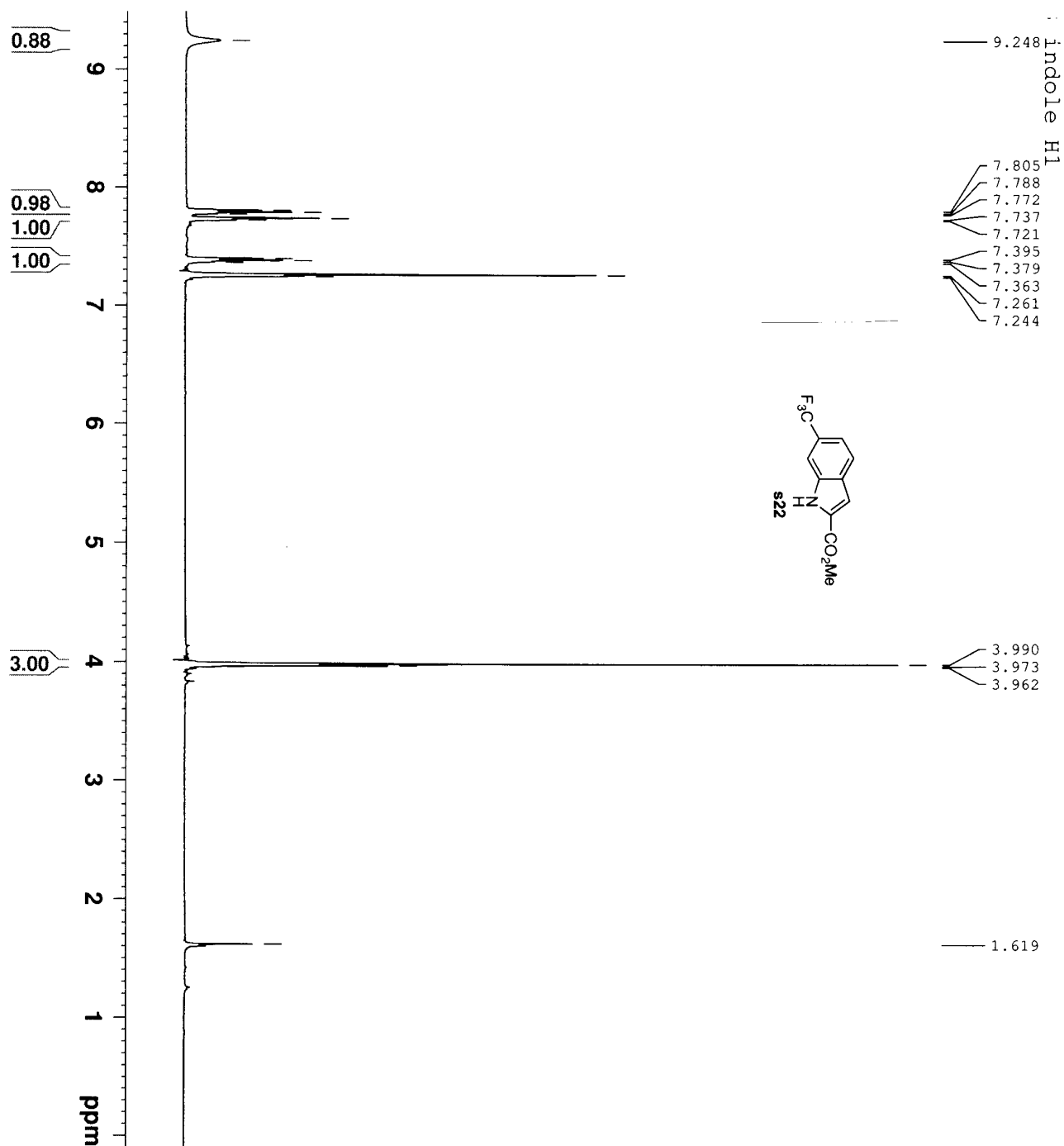


Current Data Parameters
 NAME BJS ii013.2F1
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20070322
 Time 13.38
 INSTRUM spect
 PROBD 5 mm BBO BB-1H
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 6009.615 Hz
 FIDRES 0.183399 Hz
 AQ 2.7264309 sec
 RG 406.4
 DW 83.200 use
 DE 6.00 use
 TE 300.0 K
 D1 1.00000000 sec
 MCREST 0.00000000 sec
 MCWRR 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 3.50 use
 PL1 -2.00 dB
 SFO1 500.6427535 MHz

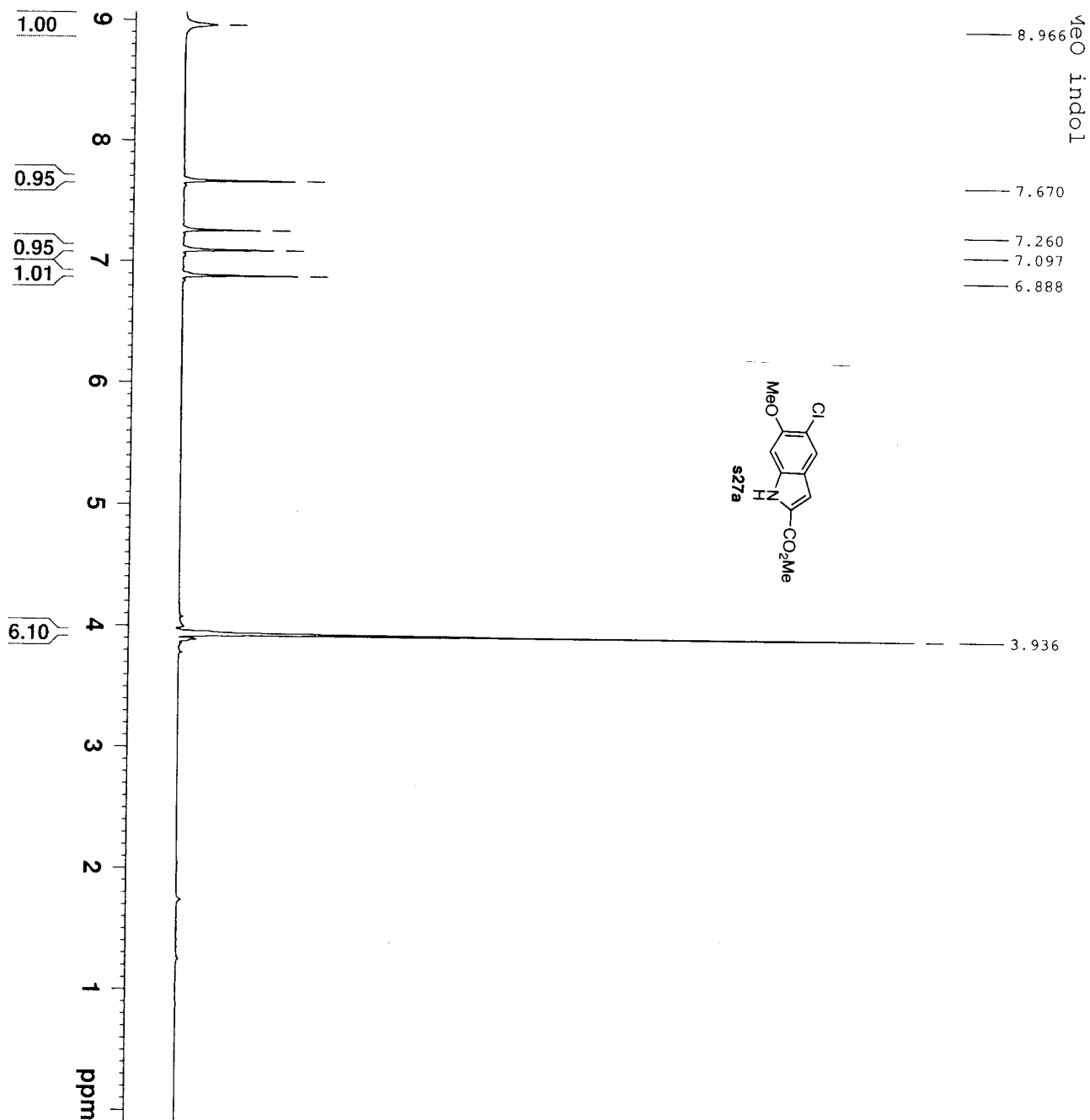
F2 - Processing parameters
 SI 32768
 SF 500.6400128 MHz
 WDM EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



Current Data Parameters
 NAME hjd1070.a.0
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20070321
 Time 14.23
 INSTRUM spect
 PROBD 5 mm BBO BB-1H
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 6009.615 Hz
 FIDRES 0.183399 Hz
 AQ 2.7264309 sec
 RG 362
 DW 83.200 use
 DE 6.00 use
 TE 300.0 K
 D1 1.00000000 sec
 MCREST 0.00000000 sec
 MCWRR 0.01500000 sec

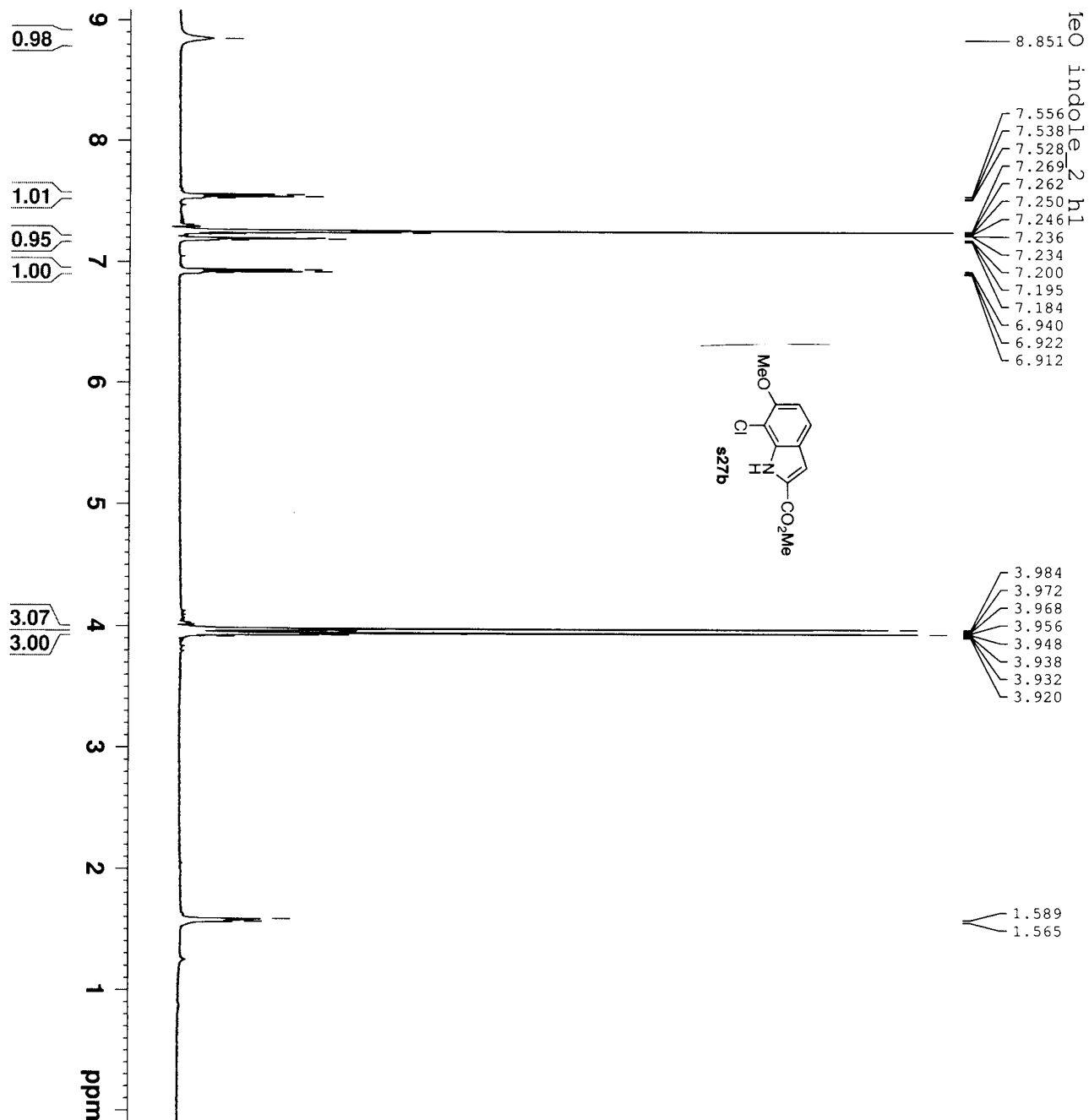
===== CHANNEL f1 =====
 NUC1 1H
 P1 3.50 use
 PL1 -2.00 dB
 SFO1 500.6427535 MHz
 F2 - Processing parameters
 SI 32768
 SF 500.6400129 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



Current Data Parameters
 NAME hjd1071b
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20070316
 Time 13.11
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 6009.615 Hz
 FIDRES 0.183399 Hz
 AQ 2.7264309 sec
 RG 256
 DW 83.200 use
 DE 6.00 use
 TE 300.0 K
 D1 1.00000000 sec
 MCREST 0.00000000 sec
 MCWRK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 3.50 use
 PL1 -2.00 dB
 SFO1 500.6427535 MHz
 F2 - Processing parameters
 SI 32768
 SF 500.6400126 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



Current Data Parameters
 NAME hdi071.b_2.0
 EXPNO 1
 PROCNO 1

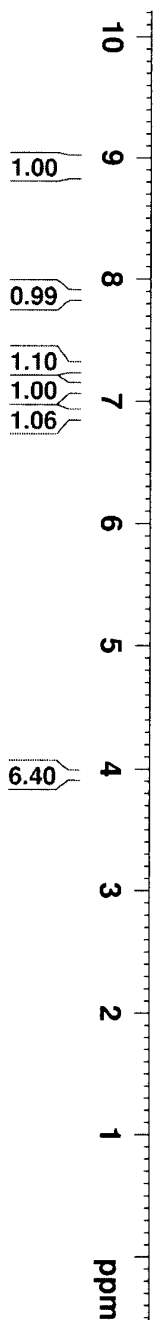
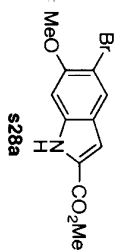
F2 - Acquisition Parameters
 Date_ 20070321
 Time 14.47
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zg
 TD 32768
 SOLVENT CDCl₃
 NS 8
 DS 2
 SWH 6009.615 Hz
 FIDRES 0.18339 Hz
 AQ 2.7264309 sec
 RG 512
 DW 83.200 use
 DE 6.00 use
 TE 300.0 K
 D1 1.00000000 sec
 MCREST 0.00000000 sec
 MCWRK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 ¹H
 P1 3.50 use
 PL1 -2.00 dB
 SFO1 500.6427535 MHz

F2 - Processing parameters
 SI 32768
 SF 500.6400128 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

ard parameters, BBO probe.

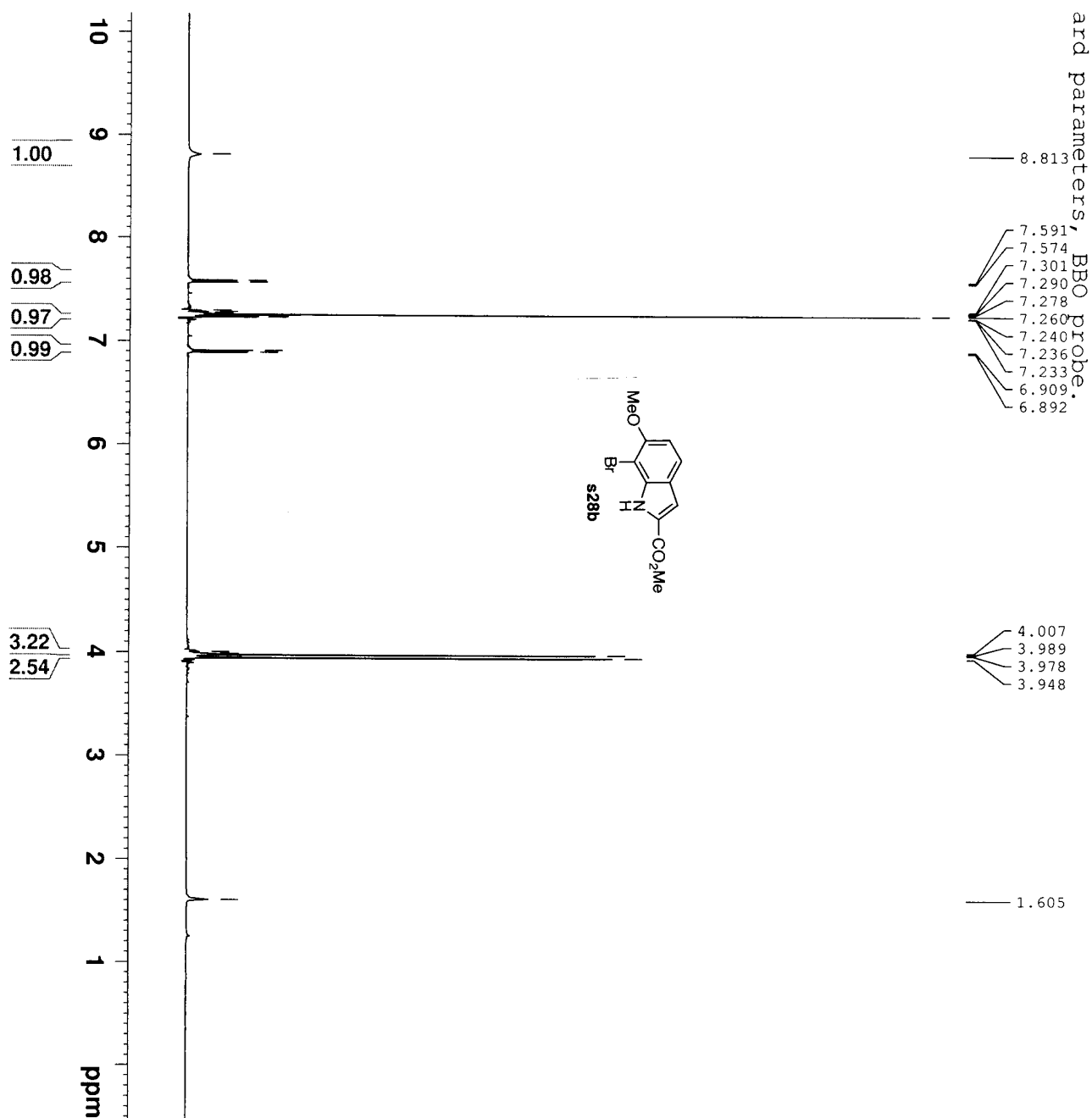
7.855
7.260
7.096
7.092
6.874
3.934
3.931



Current Data Parameters
NAME BJS ii013.2A1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070322
Time 11.46
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 2
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7264309 sec
RG 287.4
DW 83.200 use
DE 6.00 use
TE 300.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

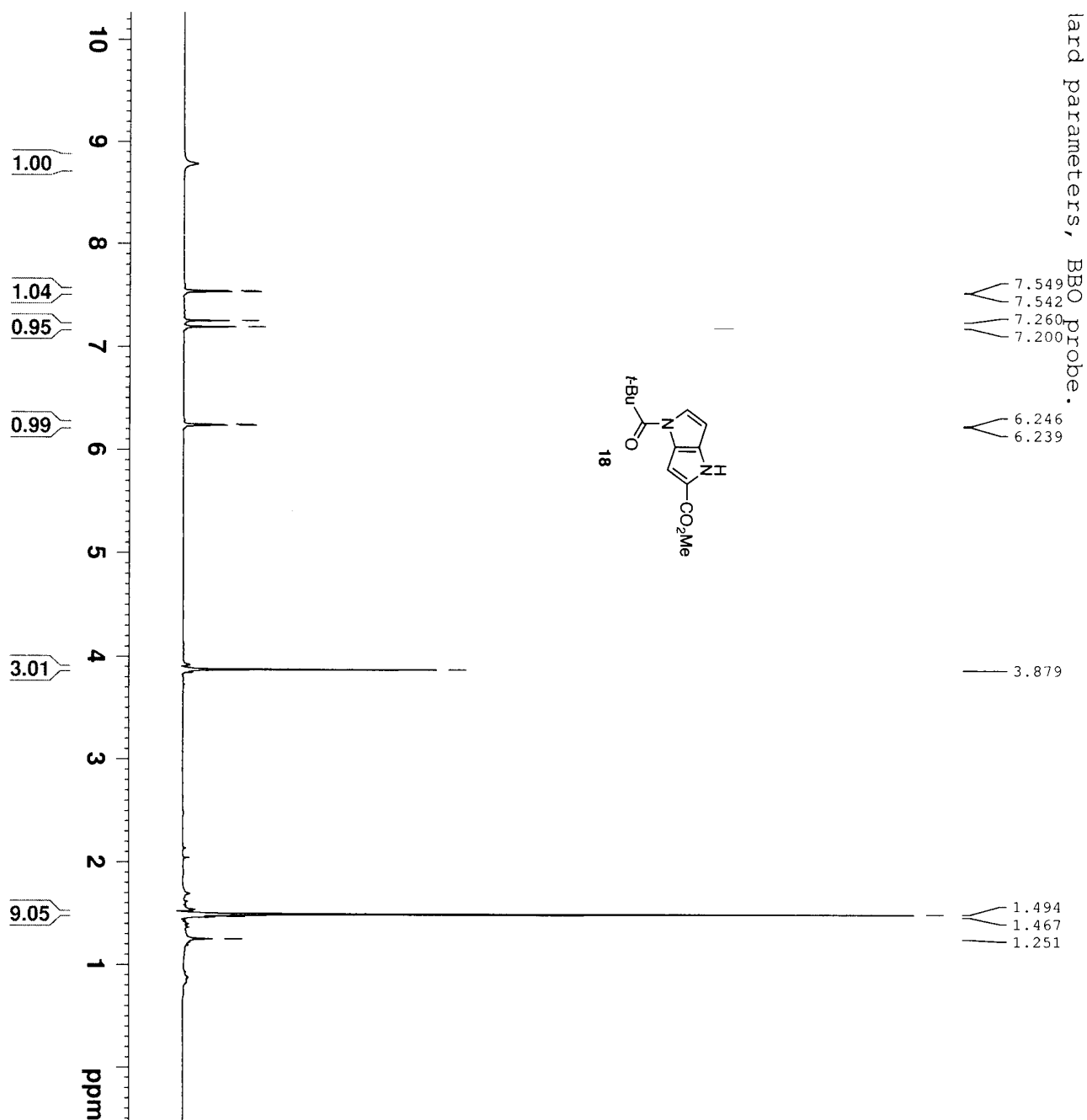
===== CHANNEL f1 =====
NUC1 1H
P1 3.50 use
PL1 -2.00 dB
SFO1 500.6427535 MHz
F2 - Processing parameters
SI 32768
SF 500.6400128 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME BJS 11013A.F21
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070329
Time 14.35
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 2
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7264309 sec
RG 256
DW 83.200 use
DE 6.00 use
TE 300.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

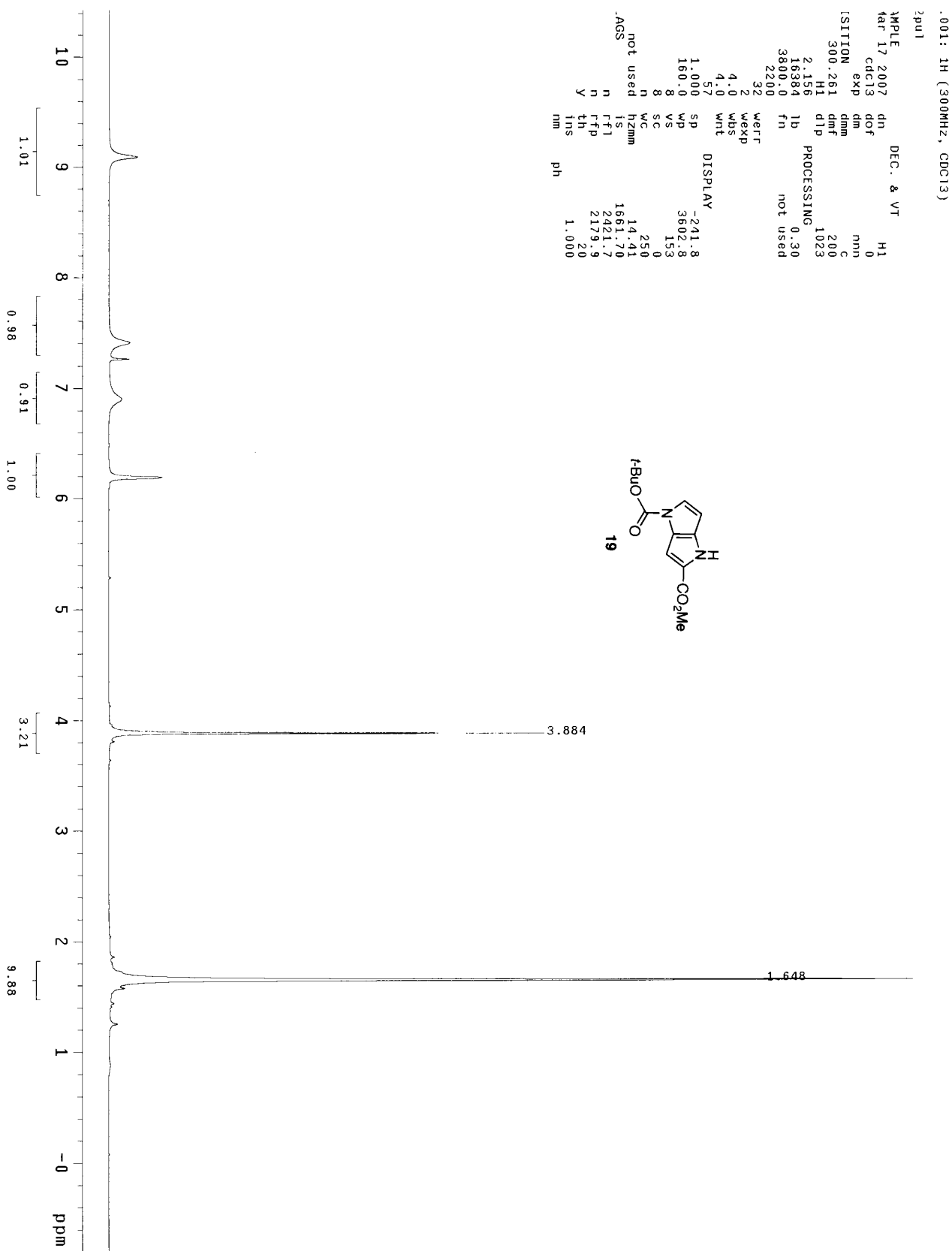
===== CHANNEL f1 =====
NUC1 1H
P1 3.50 use
PL1 -2.00 dB
SFO1 500.6427535 MHz
F2 - Processing parameters
SI 32768
SF 500.6400128 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



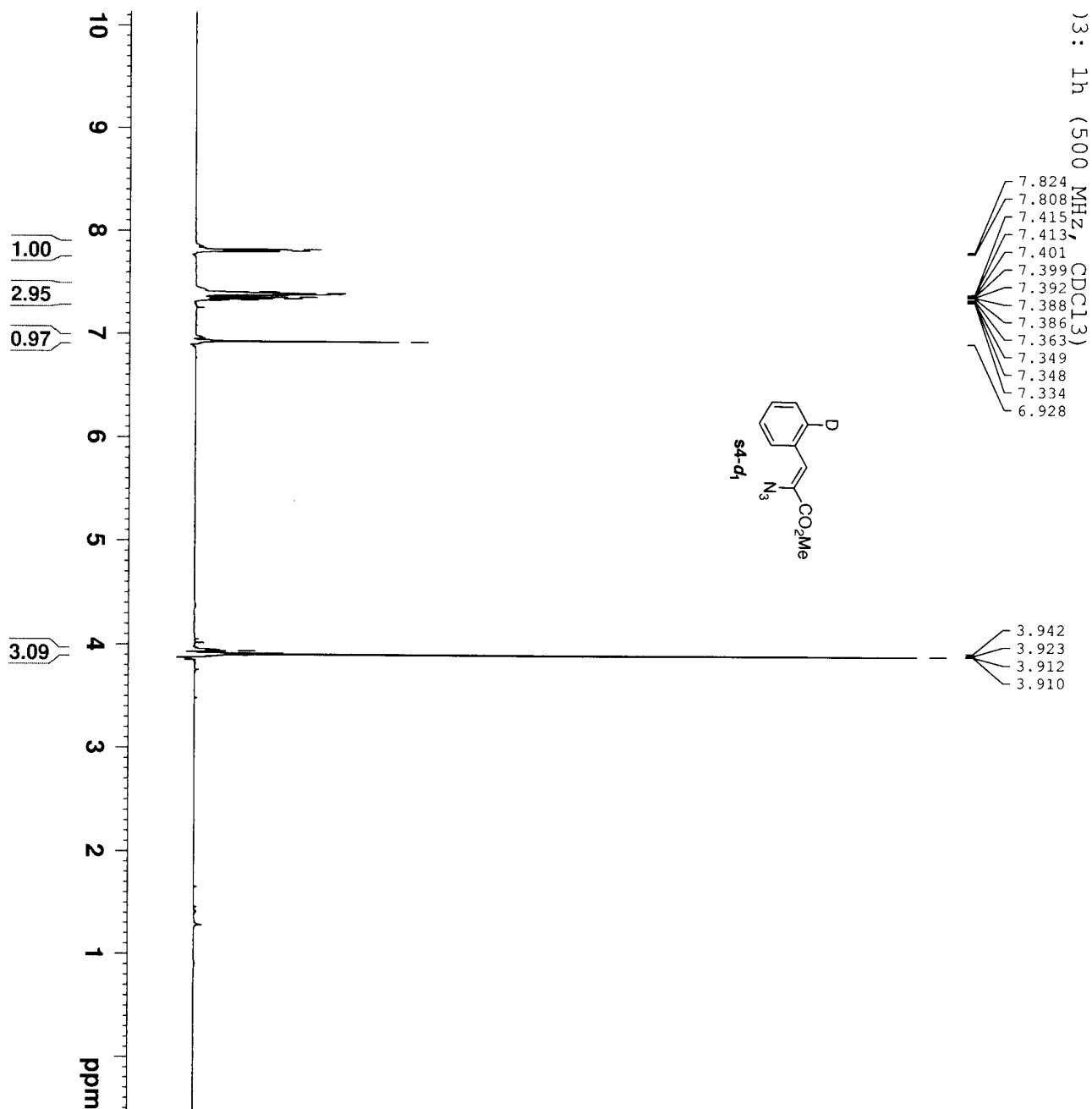
Current Data Parameters
NAME BJS i1011.2b1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070317
Time 11.36
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 8
DS 2
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7264309 sec
RG 256
DW 83.200 use
DE 6.00 use
TE 300.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 3.50 use
PL1 -2.00 dB
SFO1 500.6427535 MHz
F2 - Processing parameters
SI 32768
SF 500.6400128 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



XI. ¹H NMR Spectra of mechanistic experiments



Current Data Parameters
NAME tdi145.003
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070310
Time 17.08
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT CDCl₃
NS 8
DS 2
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7264309 sec
RG 57
DE 83.200 use
TE 300.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 3.50 use
PL1 -2.00 dB
SFO1 500.6427535 MHz
F2 - Processing parameters
SI 32768
SF 500.6400118 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

