Precipitation-driven self-sorting of imines

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Supporting Information

General Methods

All reactions were performed at 21 ºC in oven-dried glassware. Reagents and solvents were purchased from commercial suppliers and used without further purification.

Mass spectral measurements were performed by the Mass Spectrometry Facility of the Department of Chemistry and Biochemistry at the University of Texas at Austin. NMR spectra were obtained on JEOL ECX-400 and ECA-500 spectrometers, with working frequencies (for ^{1}H nuclei) of 400 and 500 MHz, respectively. All ^{13}C NMR spectra were recorded with simultaneous decoupling of ^{1}H nuclei. ^{1}H NMR chemical shifts are reported in ppm units relative to the residual signal of the solvent ($CDCl_3$: 7.25 ppm). All NMR spectra were recorded at 21 °C in $CDCl_3$. Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrophotometer using Pike MIRacle Micrometer pressure clamp. Microanalyses were conducted by Intertek USA, Inc. Melting points measurements were performed in open capillary tubes using Mel-Temp Thermo Scientific apparatus, and are uncorrected.

Imine solubilities quoted in the manuscript were measured in the following fashion. An imine sample (20 mg) was suspended in either EtOH (3 mL) or EtOH/H_2O mixture (1:2.4 v/v, 5 mL). The suspension was sonicated for 2 h at 21 °C and filtered. The residual solid (if any) was weighed and dried. The solubility of a corresponding imine was obtained by subtracting the weight of the precipitate from the original 20 mg sample. For imines that were fully soluble, only the lower limit of solubility was established.

Experiments are presented in the order following the discussion in the manuscript.
Compound designators are identical to those in the main text of the manuscript.

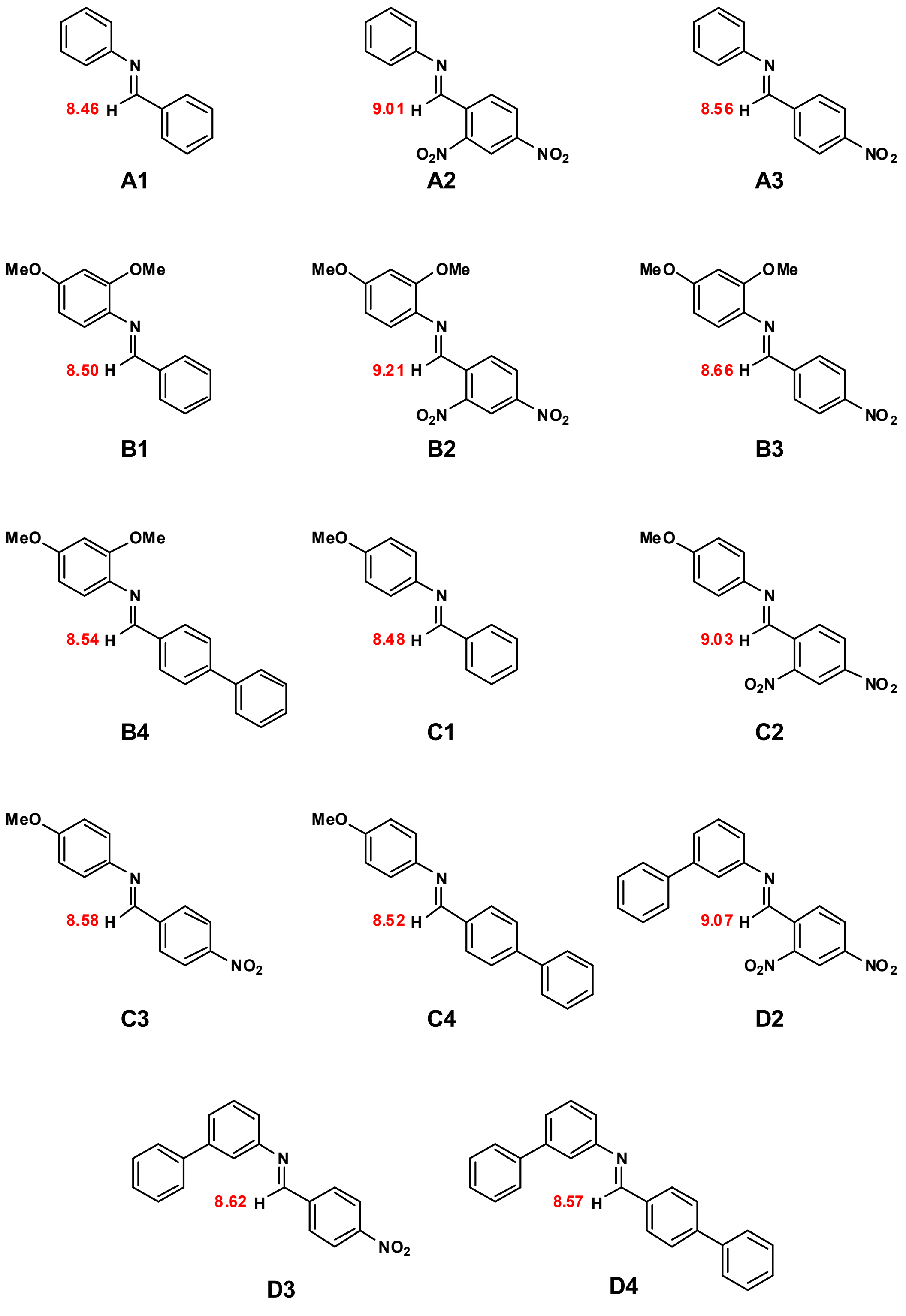
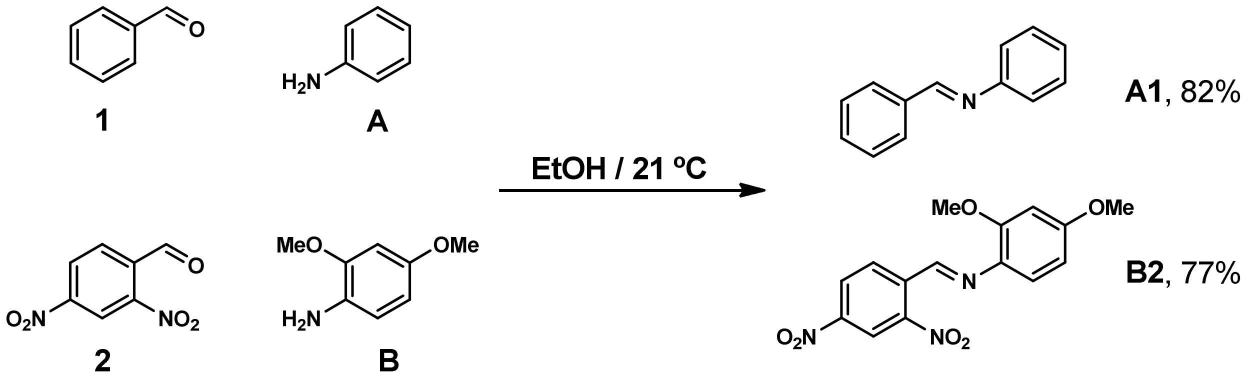


Figure S1. Structures of imines investigated in this study. Characteristic ^{1}H NMR chemical shifts of azomethine protons are shown in red.

Self-Sorting of [2×2] Imine Mixtures through Precipitation

Experiment #1:

N-benzylideneaniline (**A1**) and *N*-(2,4-dinitro-benzylidene)-2,4-dimethoxyaniline (**B2**)



Benzaldehyde (**1**, 130 μL, 1.25 mmol) and 2,4-dinitrobenzaldehyde (**2**, 250 mg, 1.25 mmol) were dissolved in 50 mL of EtOH with sonication. Then, aniline (**A**, 115 μL, 1.25 mmol) and 2,4-dimethoxyaniline (**B**, 195 mg, 1.25 mmol) were added into the solution. The mixture became cloudy. After overnight stirring, orange precipitate was filtered and dried. ^{1}H NMR spectroscopic analysis of the precipitate indicated formation of pure *N*-(2,4-dinitro-benzylidene)-2,4-dimethoxyaniline (**B2**, 80 mg, 19%). The filtrate was clear at the beginning but forms orange precipitate within minutes. Solvent was removed from the filtrate using a rotary evaporator, and 50 mL of EtOH was added to the orange solid. The mixture was stirred for 2 h and the formed precipitate was filtered using Whatman 40 filter paper. The precipitate was dried in vacuo (3 mmHg) at 21 ºC for 60 min, resulting in 248 mg of an orange solid, while the filtrate was evaporated to dryness, resulting in 249 mg of an orange solid.

^{1}H NMR spectroscopic analysis of the second precipitate shows the presence of **B2** (58%), **A2** (2%), and **A1** (1%). Analogous analysis of the filtrate revealed the presence of **A1** (82%), **B1** (11%), **A2** (7%), and **B2** (2%).

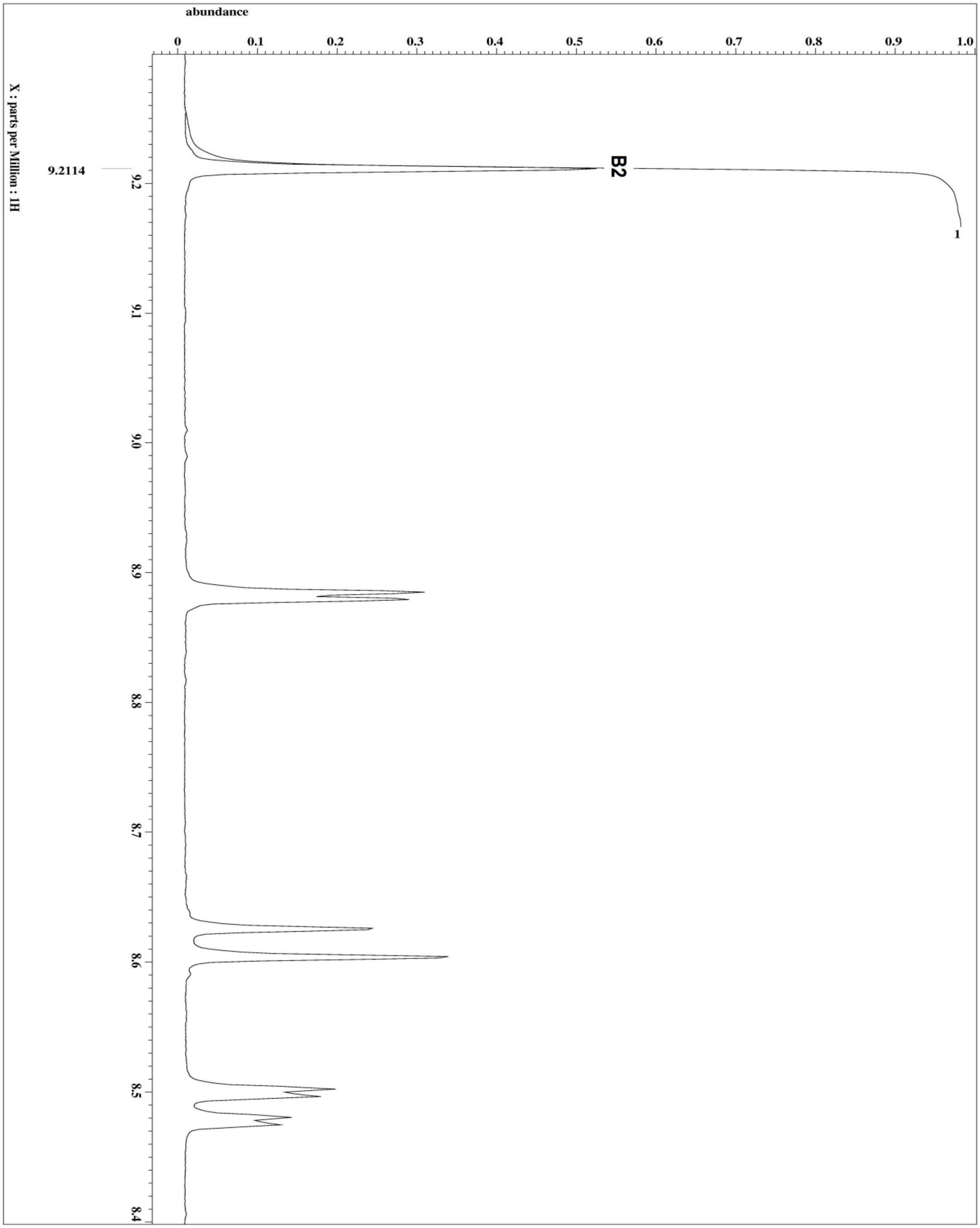


Figure S2. Imine region of the ^{1}H NMR spectrum of the first precipitate in Experiment #1, showing exclusive formation of imine **B2** (σ=9.21 ppm).

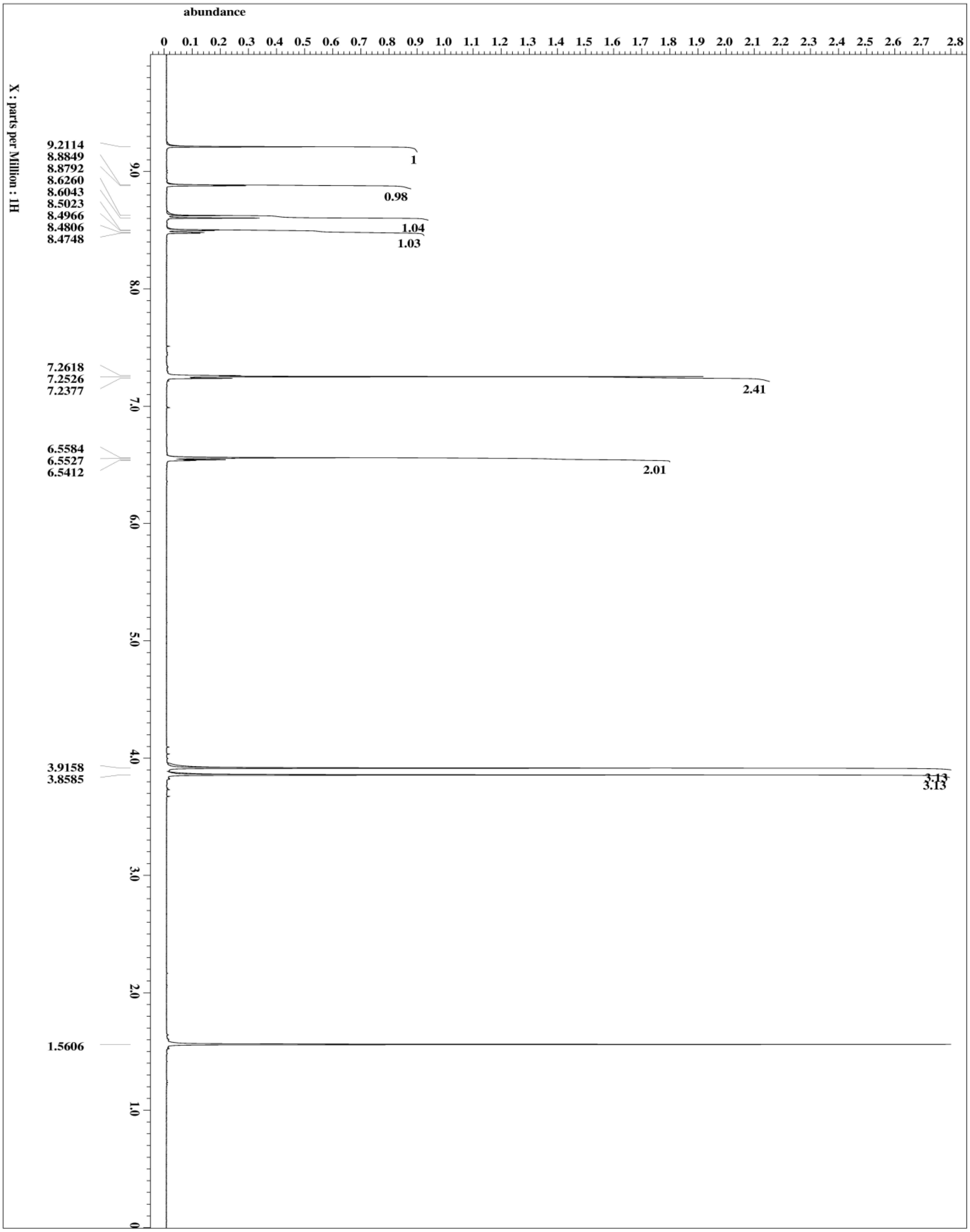


Figure S3. Complete ^{1}H NMR spectrum of the first precipitate in Experiment #1.

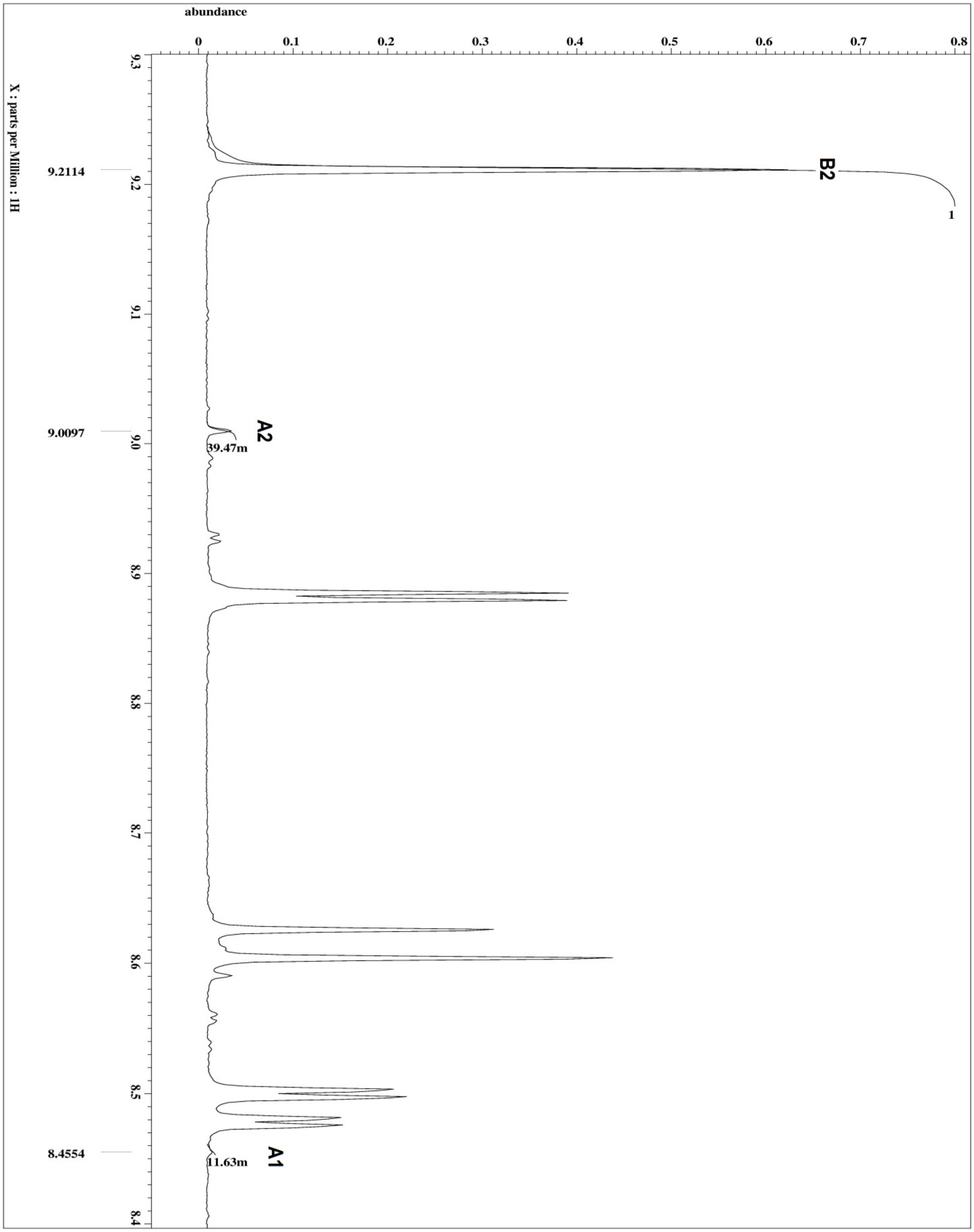


Figure S4. Imine region of the ^{1}H NMR spectrum of the second precipitate in Experiment #1 shows the presence of **B2** (σ=9.21 ppm), and minor amounts of **A2** (σ=9.01 ppm) and **A1** (σ=8.46 ppm).

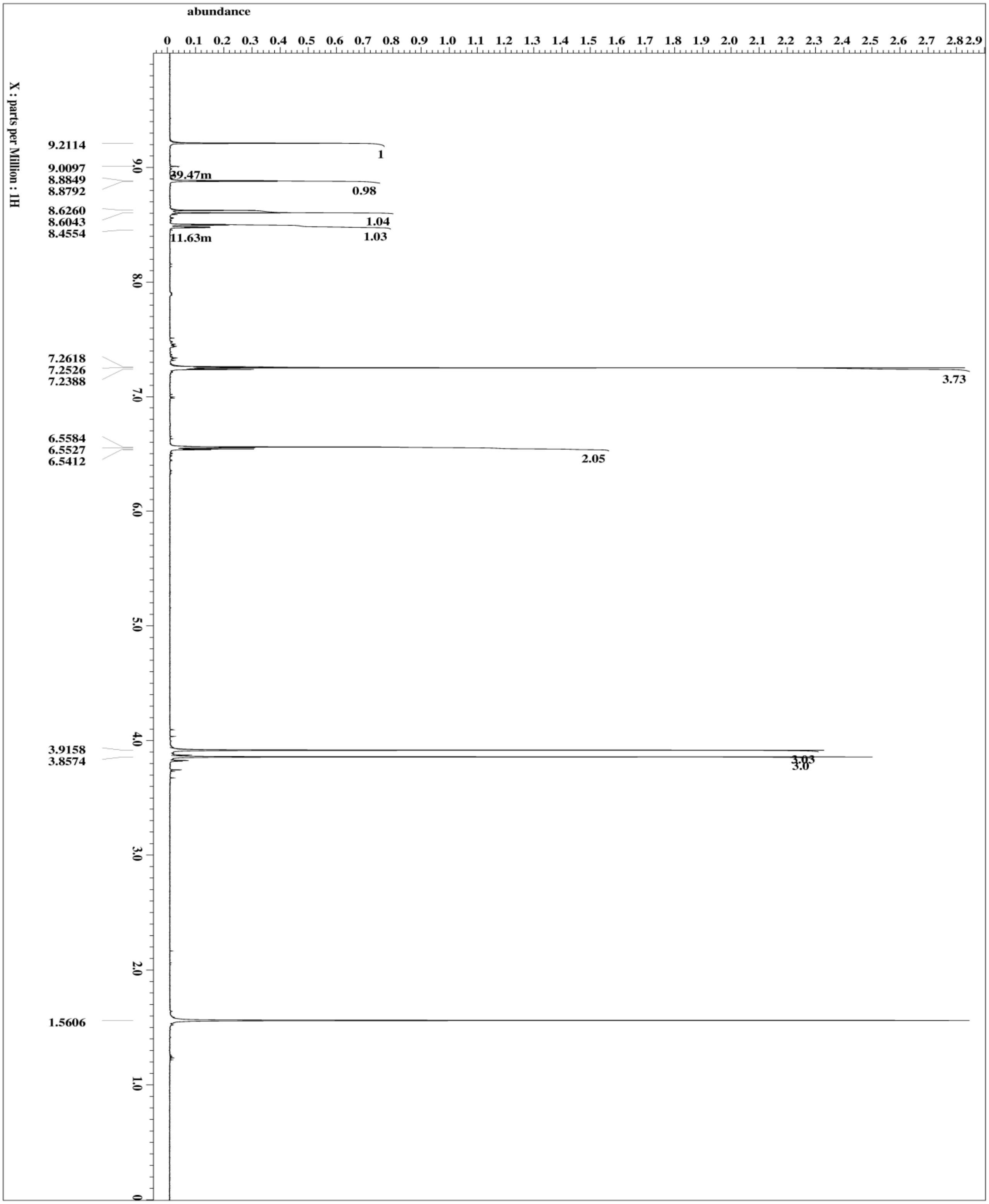


Figure S5. Complete ^{1}H NMR spectrum of the second precipitate in Experiment #1.

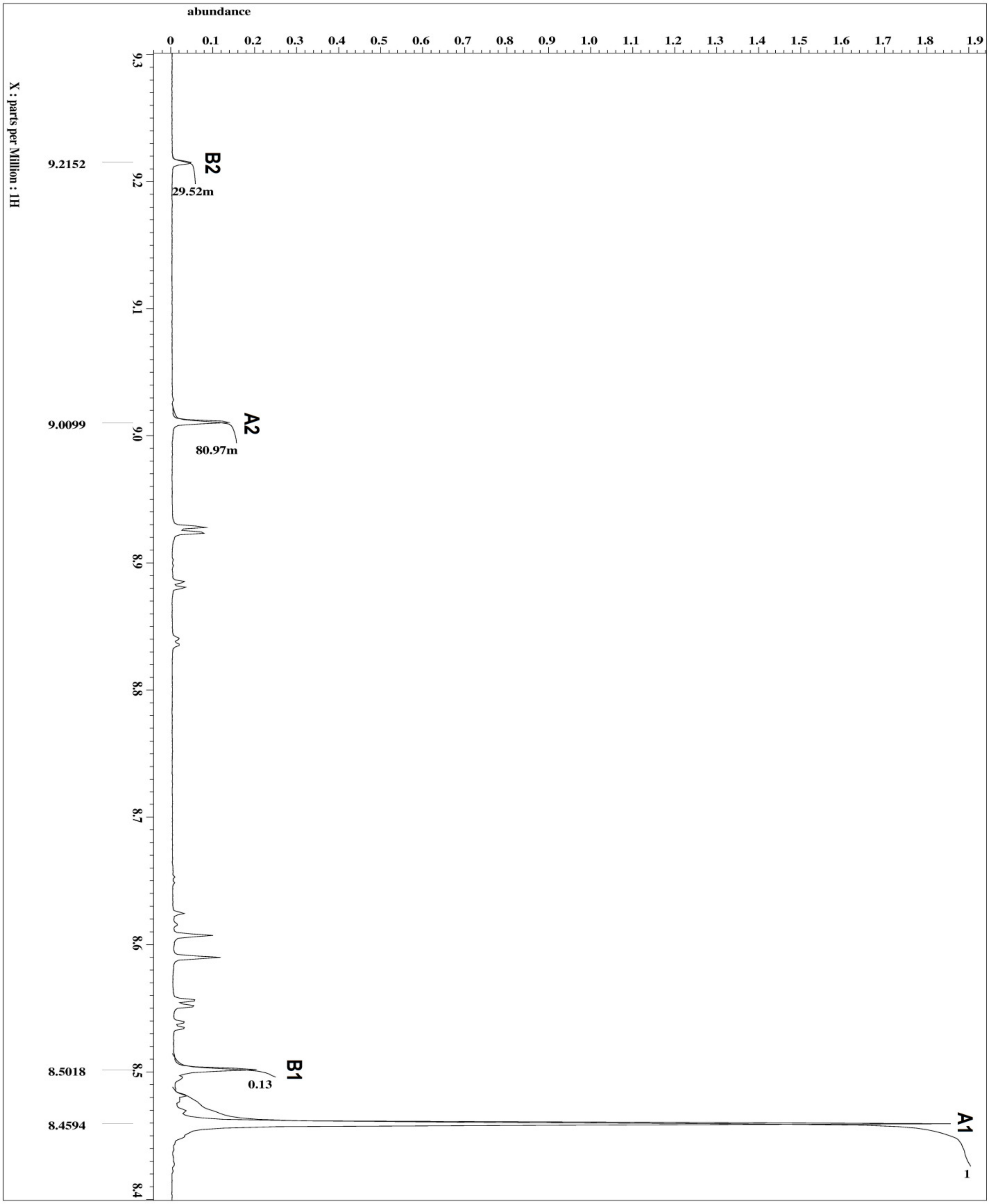


Figure S6. Imine region of the ^{1}H NMR spectrum of the filtrate in Experiment #1 indicates the presence of **A1** (σ=8.46 ppm), and minor amounts of **B2** (9.21 ppm), **A2** (9.01 ppm), and **B1** (8.50 ppm).

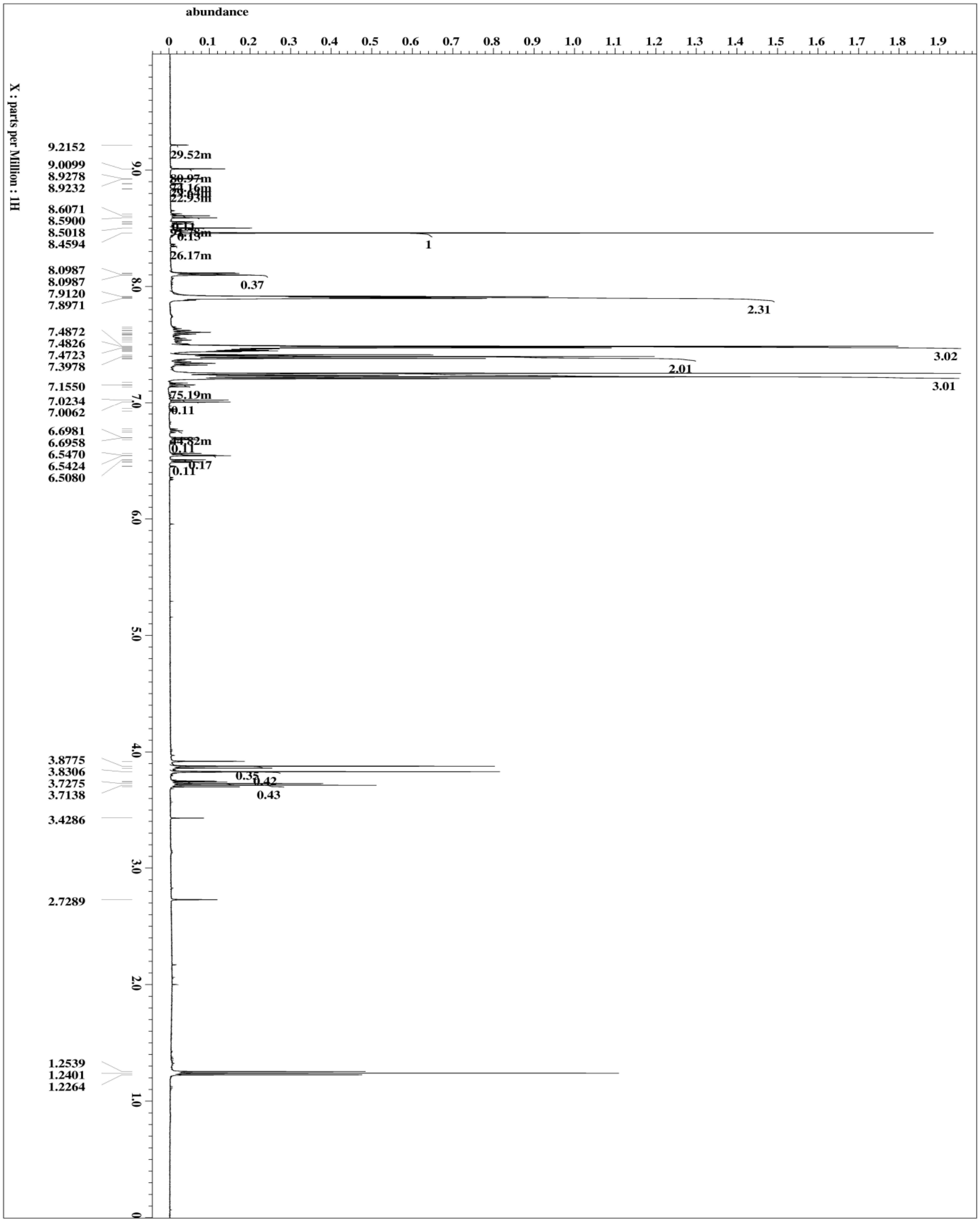
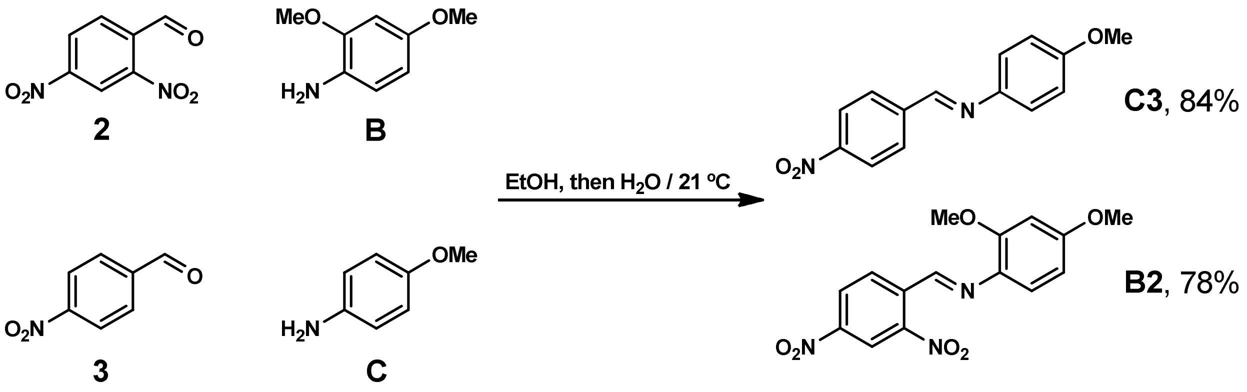


Figure S7. Complete ^{1}H NMR spectrum of the filtrate in Experiment #1.

Experiment #2:
N-(2,4-dinitro-benzylidene)-2,4-dimethoxyaniline (**B2**) and 4-methoxy-*N*-(4-nitrobenzylidene)aniline (**C3**)



Compounds 2,4-dinitrobenzaldehyde (**2**, 150 mg, 0.75 mmol) and 4-nitrobenzaldehyde (**3**, 114 mg, 0.75 mmol) were dissolved in absolute EtOH (18 mL) with sonication. Once dissolved, 2,4-dimethoxyaniline (**B**, 117 mg, 0.75 mmol) and 4-methoxyaniline (**C**, 93 mg, 0.75 mmol) were added into the solution. The mixture was stirred for 4 h and the formation of precipitate was observed after 1 h of stirring. After 4 h, H_2O (24 mL) was injected via a syringe pump at a rate of 3 mL h^{-1}. The orange precipitate was vacuum filtered using Whatman 40 filter paper and dried in vacuo (3 mmHg) at 21 ºC overnight, resulting in 400 mg of orange solid.

^{1}H NMR analysis of the precipitate showed the formation of imines **C3** (84%), **B2** (78%), **C2** (11%), and **B3** (10%).

The same procedure was repeated twice giving similar yields for all four imines: in the second trial (Figures S10 and S11), the yields were 78% for **B2**, 10% of **C2**, 8% of **B3**, and 86% of **C3**. In the third trial (Figures S12 and S13), the yields were 77% for **B2**, 15% for **C2**, 10% for **B3**, and 83% for **C3**.

This experiment was performed at both higher and lower concentrations of starting materials. Running the experiment at ten times lower concentration (4.17mM) still formed an orange precipitate (Figures S14 and S15) by the end of H_2O addition consisting of imines **C3** (39%), **B2** (17%), **C2** (9%), and **B3** (3%), while the filtrate (Figures S16 and S17) is a mixture of imines **C3** (28%), **B2** (45%), **C2** (18%), and **B3** (30%). No precipitation occurred prior to H_2O addition.

Increasing the concentration of the starting materials resulted to faster formation of precipitate (within 5 minutes), composed primarily of imines **B2** and **C3**. At two times higher concentration (83.4 mM, Figures S18 and S19) the yields were **B2** (77%), **C2** (18%), **B3** (9%) and **C3** (77%). At three times concentrated (125 mM, Figures S20 and S21) the yields were **B2** (83%), **C2** (12%), **B3** (5%) and **C3** (73%). At five times concentrated (209 mM, Figures S22 and S23) the yields were **B2** (51%), **C2** (42%), **B3** (4%) and **C3** (34%). The formation of 4-nitrobenzaldehyde diethyl acetal (singlet at σ = 5.57 ppm), was detected at this concentration.

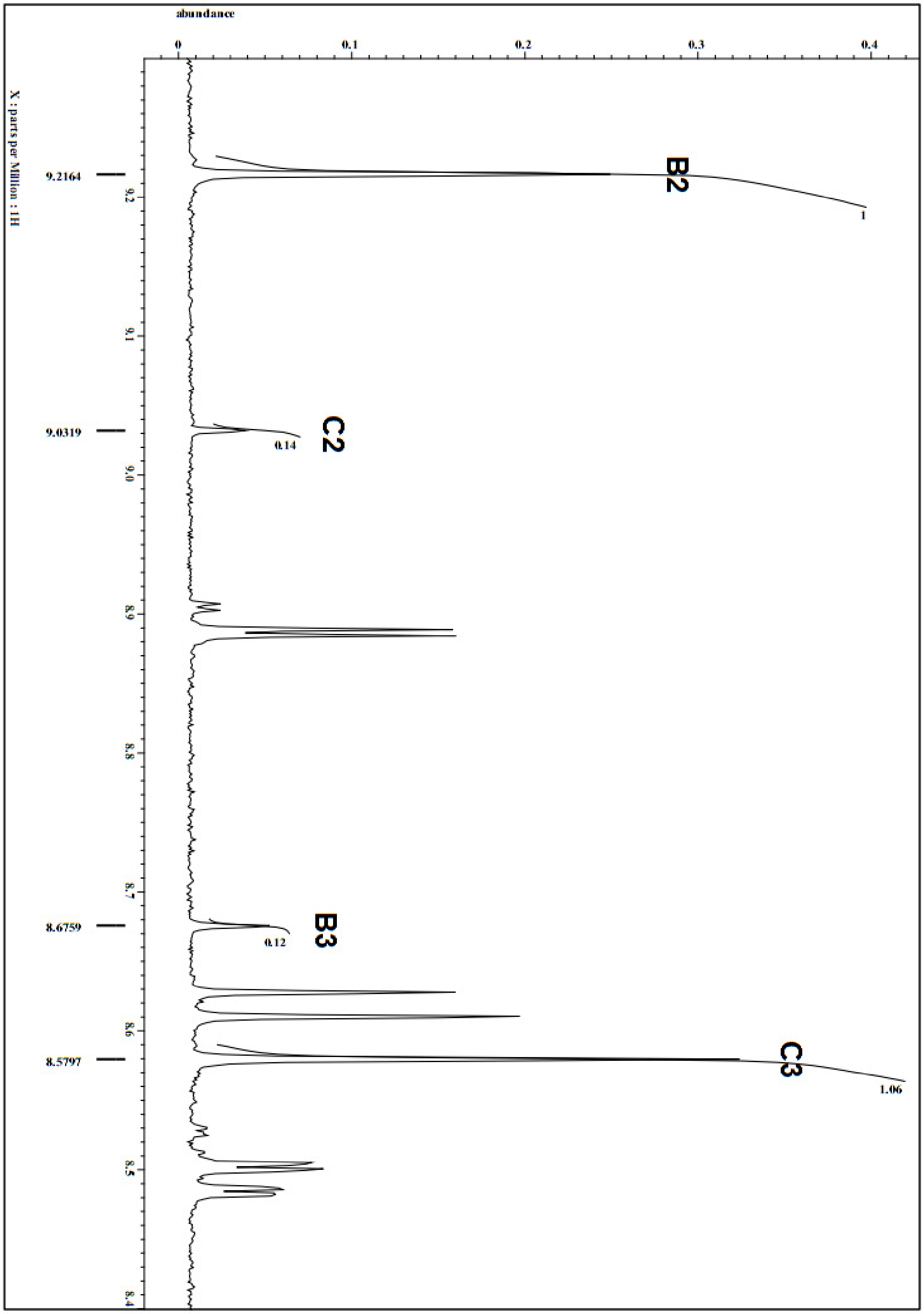


Figure S8. Imine region of the ^{1}H NMR spectrum of the precipitate in Experiment #2, with imines **B2** (σ=9.22 ppm) and **C3** (σ=8.58 ppm) as major products. Trial 1.

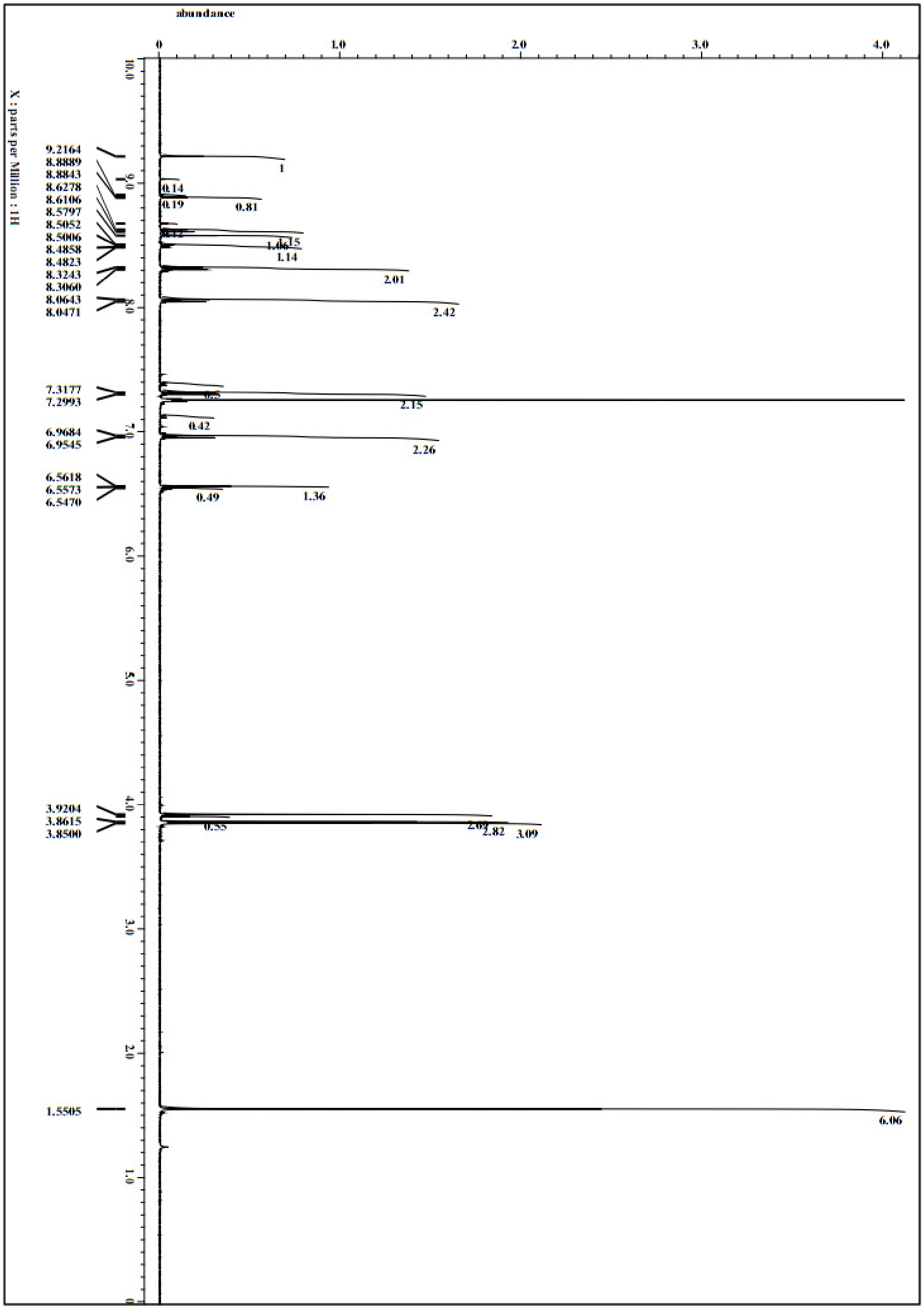


Figure S9. Complete ^{1}H NMR spectrum of the precipitate in Experiment #2, trial 1.

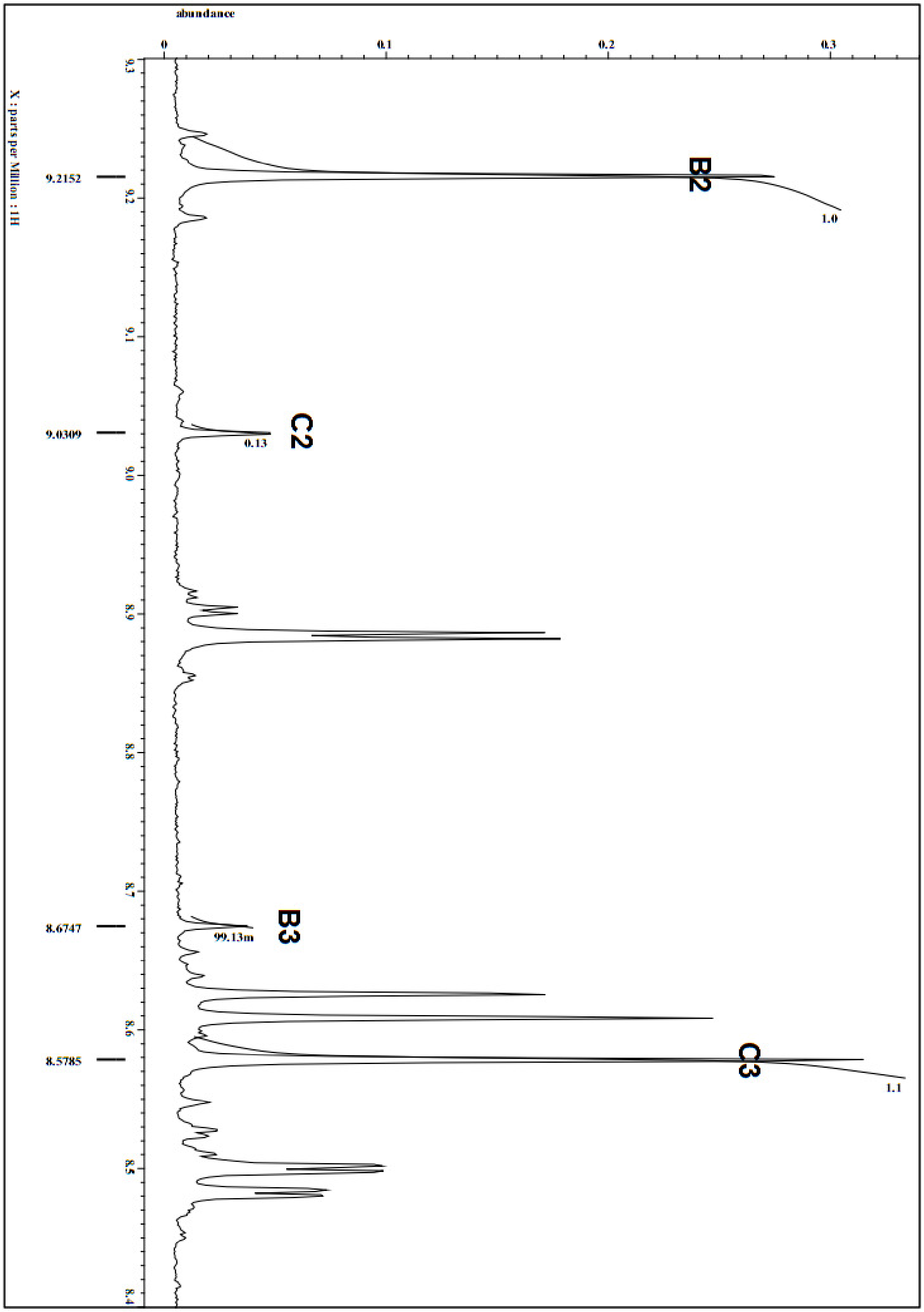


Figure S10. Imine region of the ^{1}H NMR spectrum of the precipitate in Experiment #2, trial 2.

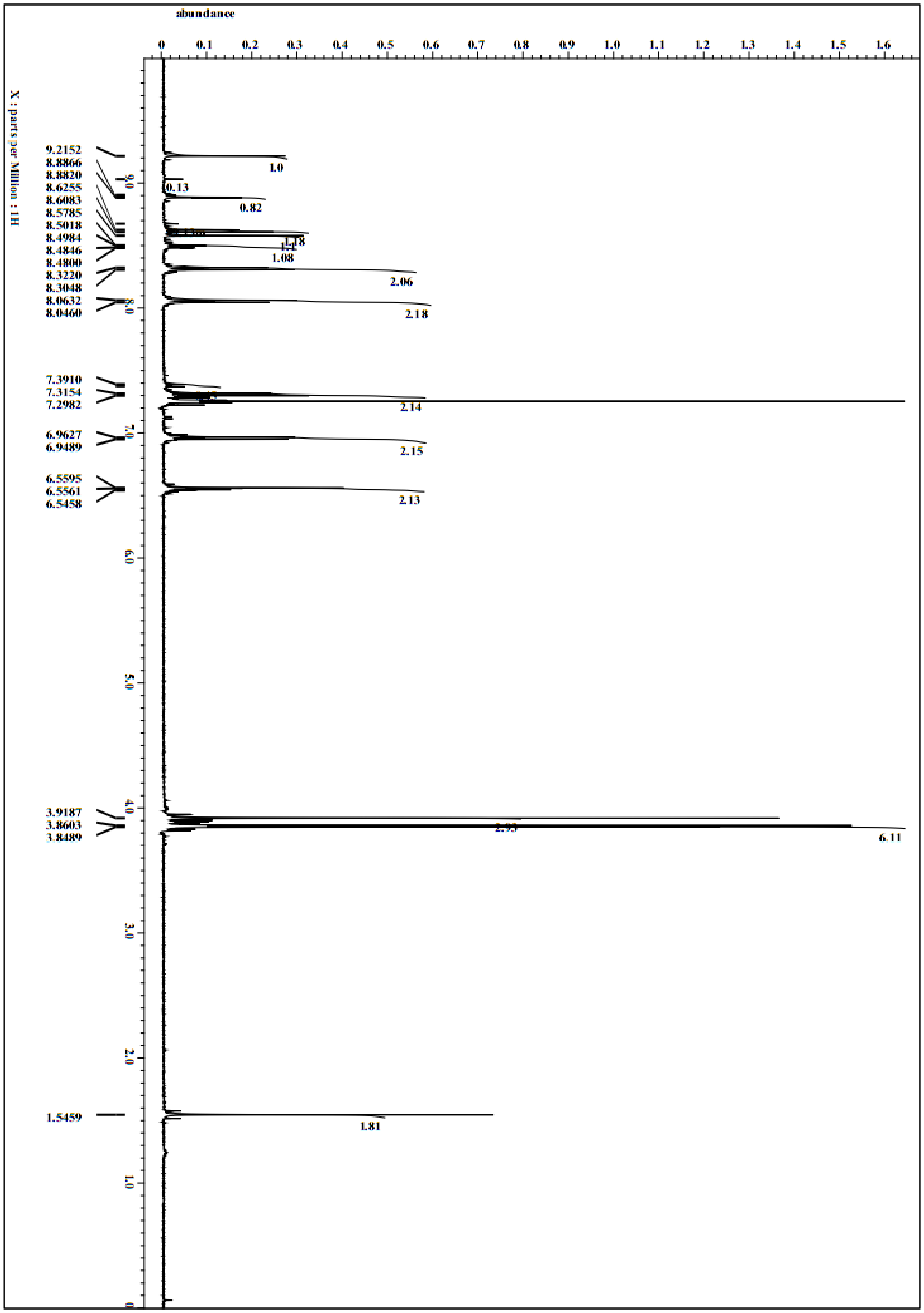


Figure S11. Complete ^{1}H NMR spectrum of the precipitate in Experiment #2, trial 2.

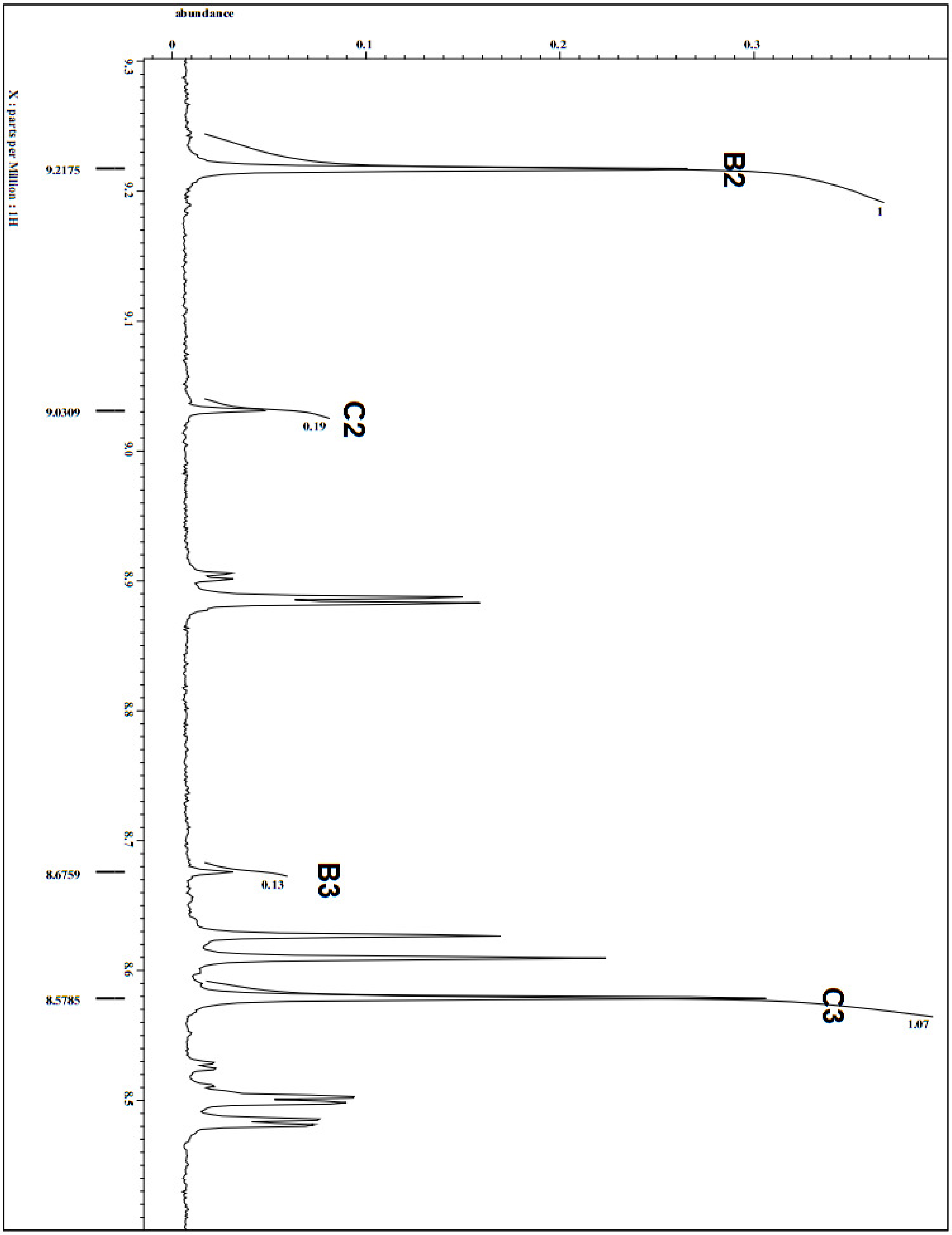


Figure S12. Imine region of the ^{1}H NMR spectrum of the precipitate in Experiment #2, trial 3.

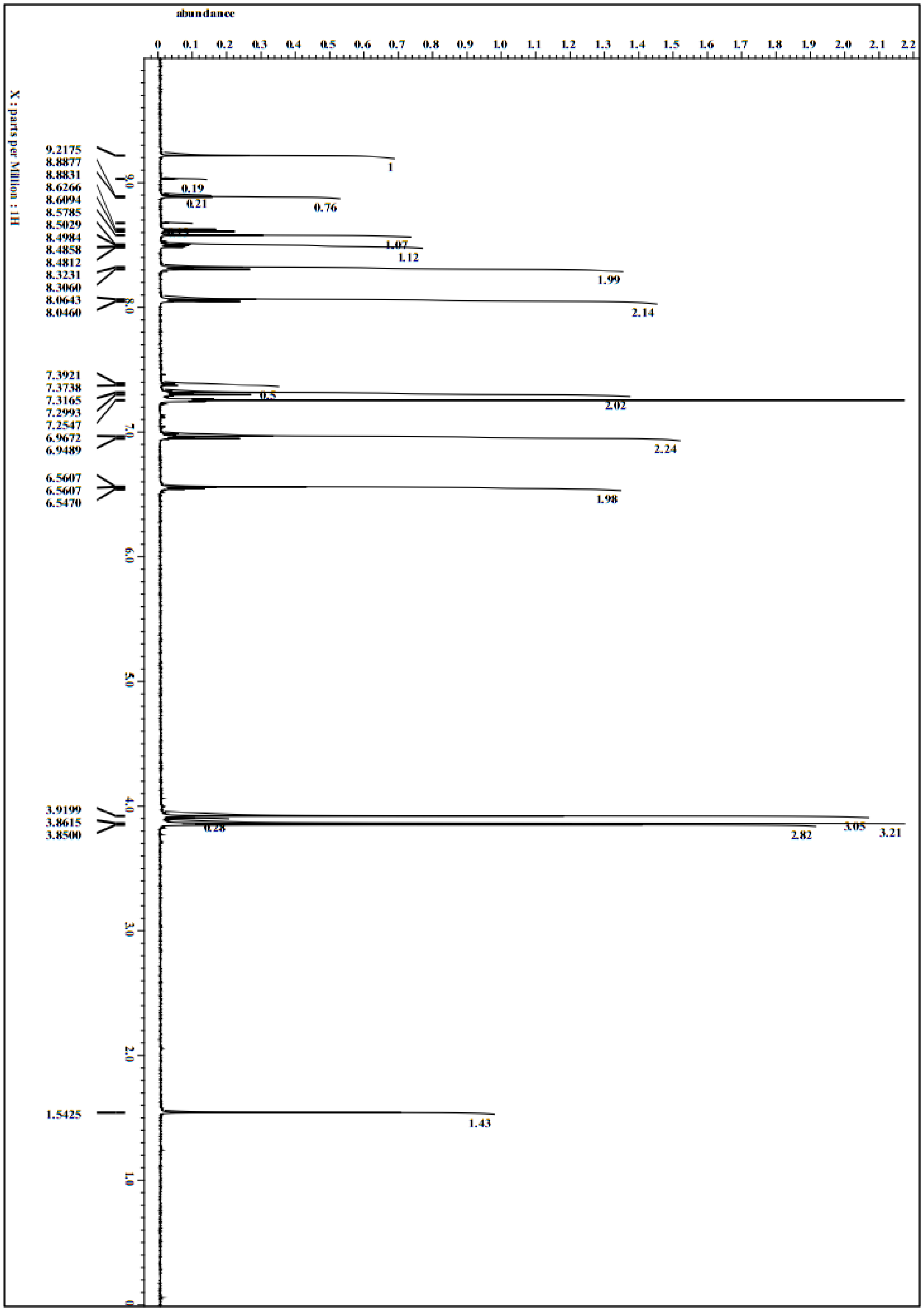


Figure S13. Complete ^{1}H NMR spectrum of the precipitate in Experiment #2, trial 3.

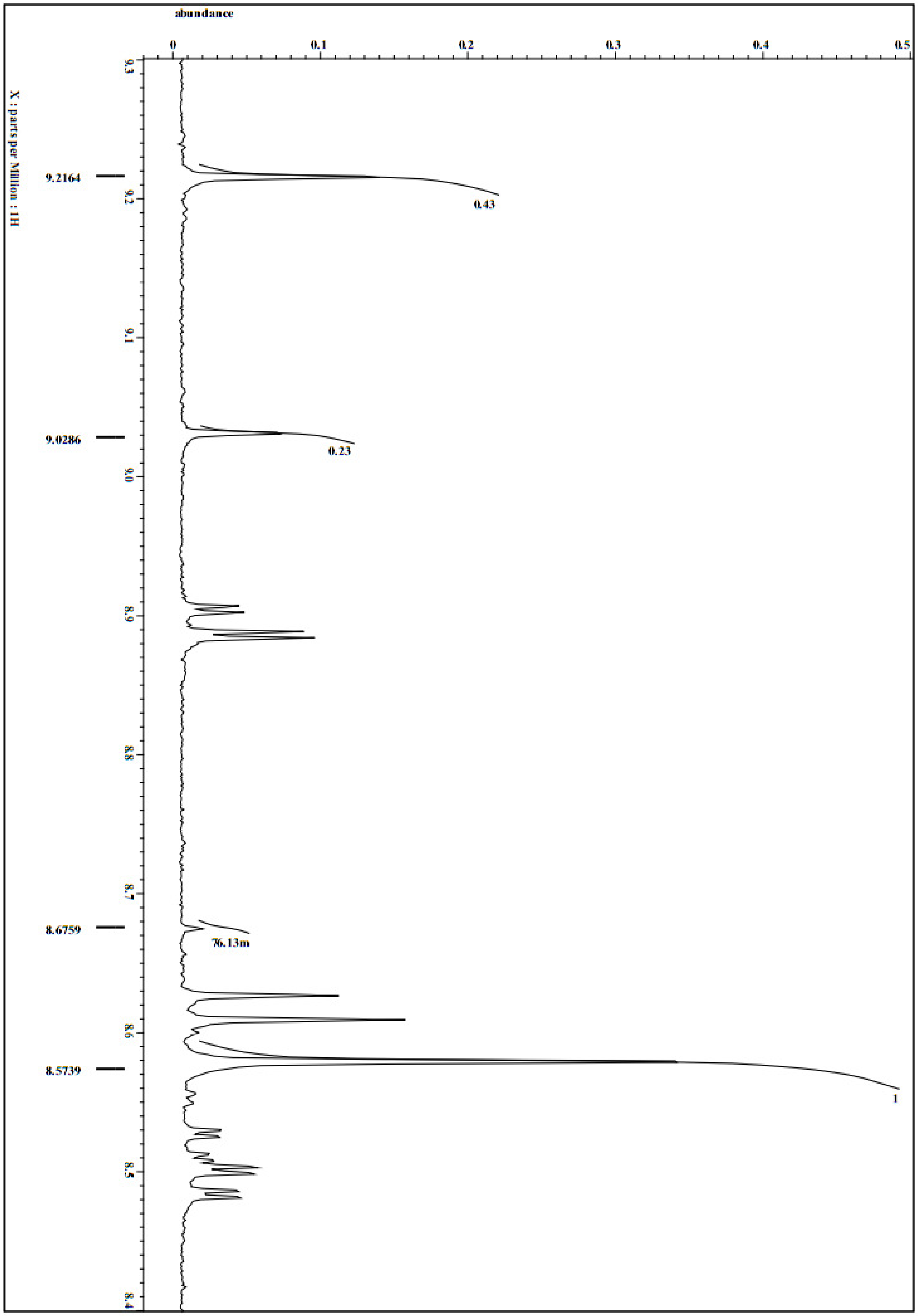


Figure S14. Imine region of the ^{1}H NMR spectrum of the precipitate in the variant of Experiment #2 performed with 4.17 mM solutions of starting materials.

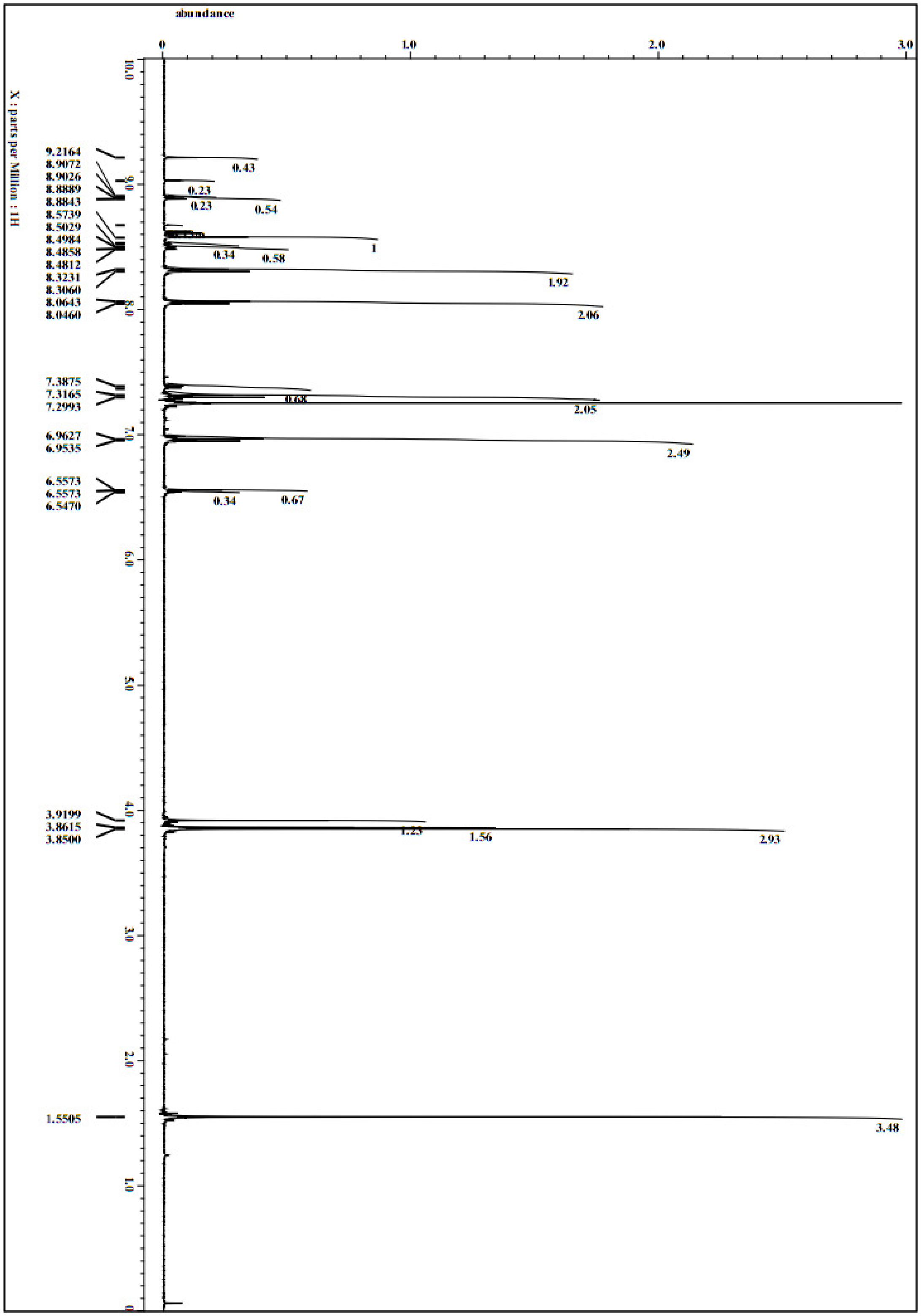


Figure S15. Complete ^{1}H NMR spectrum of the precipitate in the variant of Experiment #2 performed with 4.17 mM solutions of starting materials.

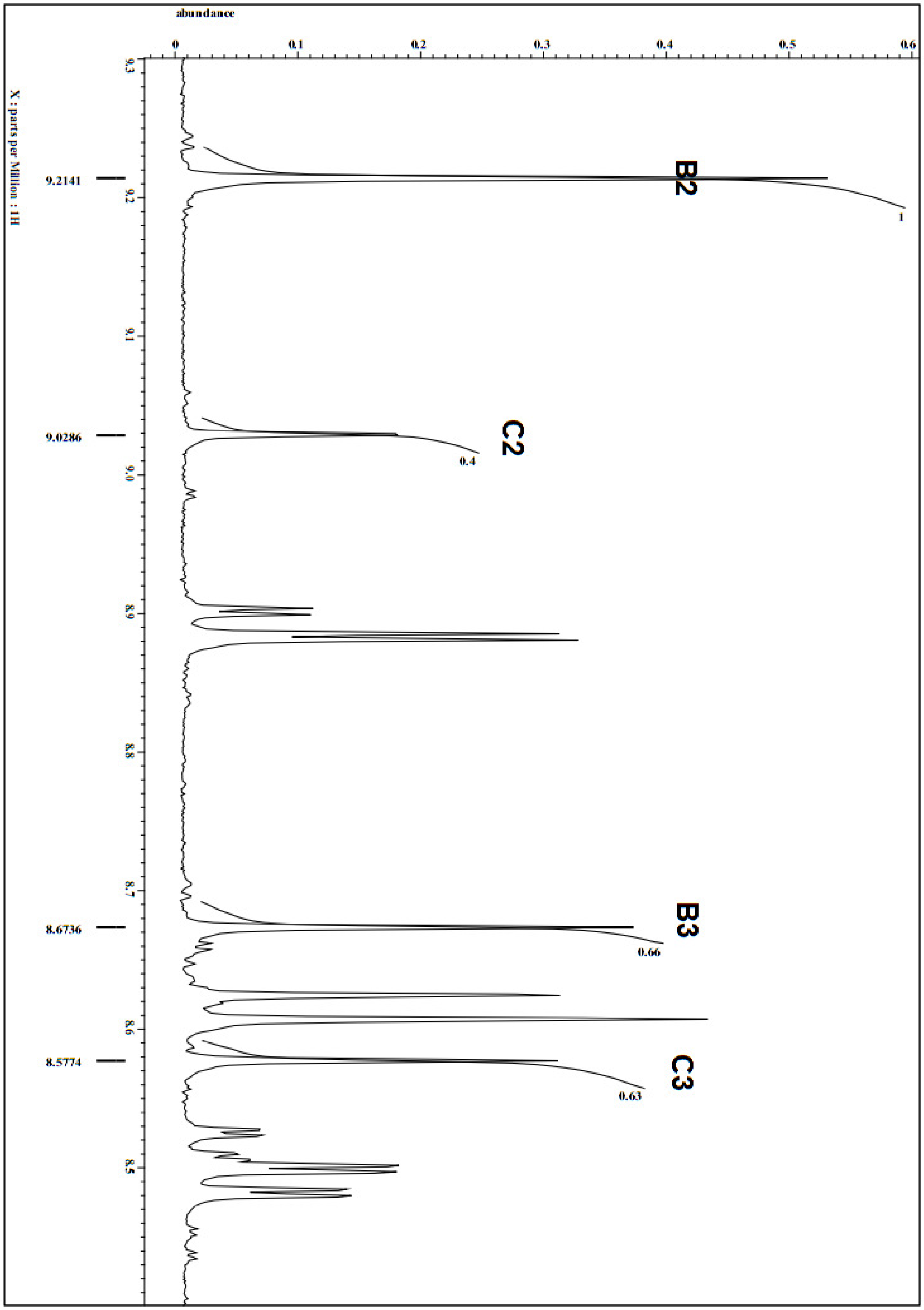


Figure S16. Imine region of the ^{1}H NMR spectrum of the filtrate in the variant of Experiment #2 performed with 4.17 mM solutions of starting materials.

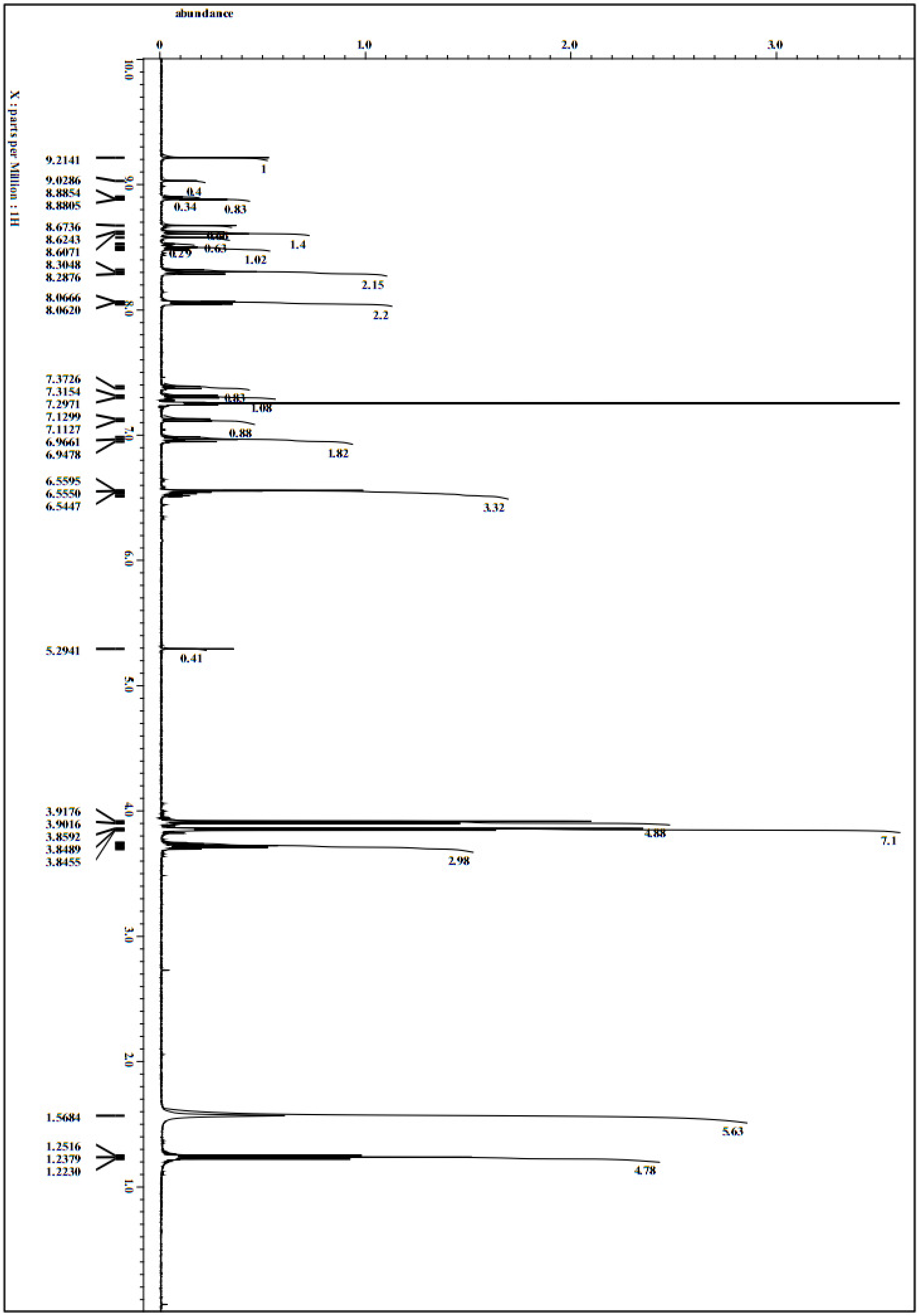


Figure S17. Complete ^{1}H NMR spectrum of the filtrate in the variant of Experiment #2 performed with 4.17 mM solutions of starting materials.

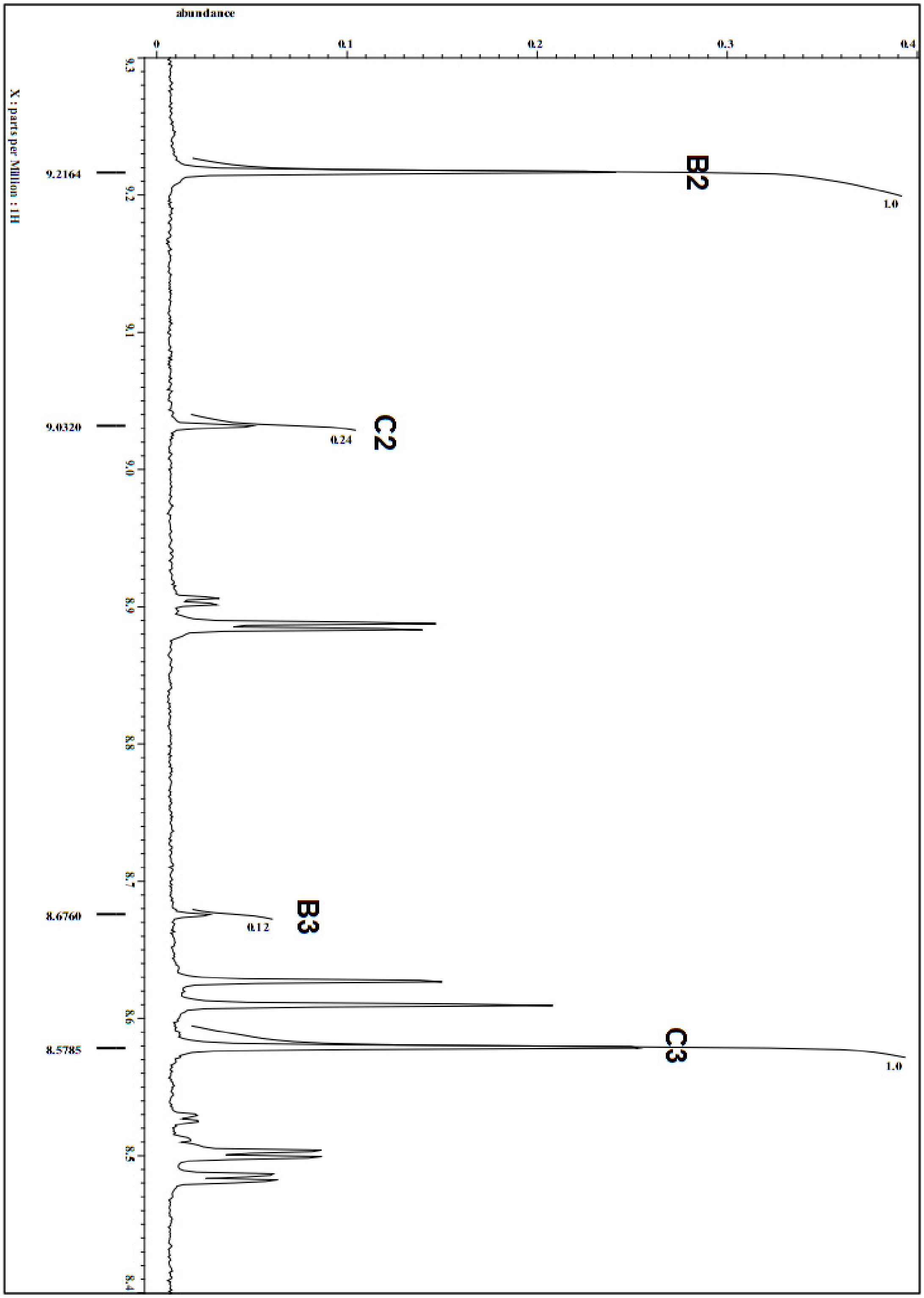


Figure S18. Imine region of the ^1H NMR spectrum of the precipitate in the variant of Experiment #2 performed with 83.4 mM solutions of starting materials.

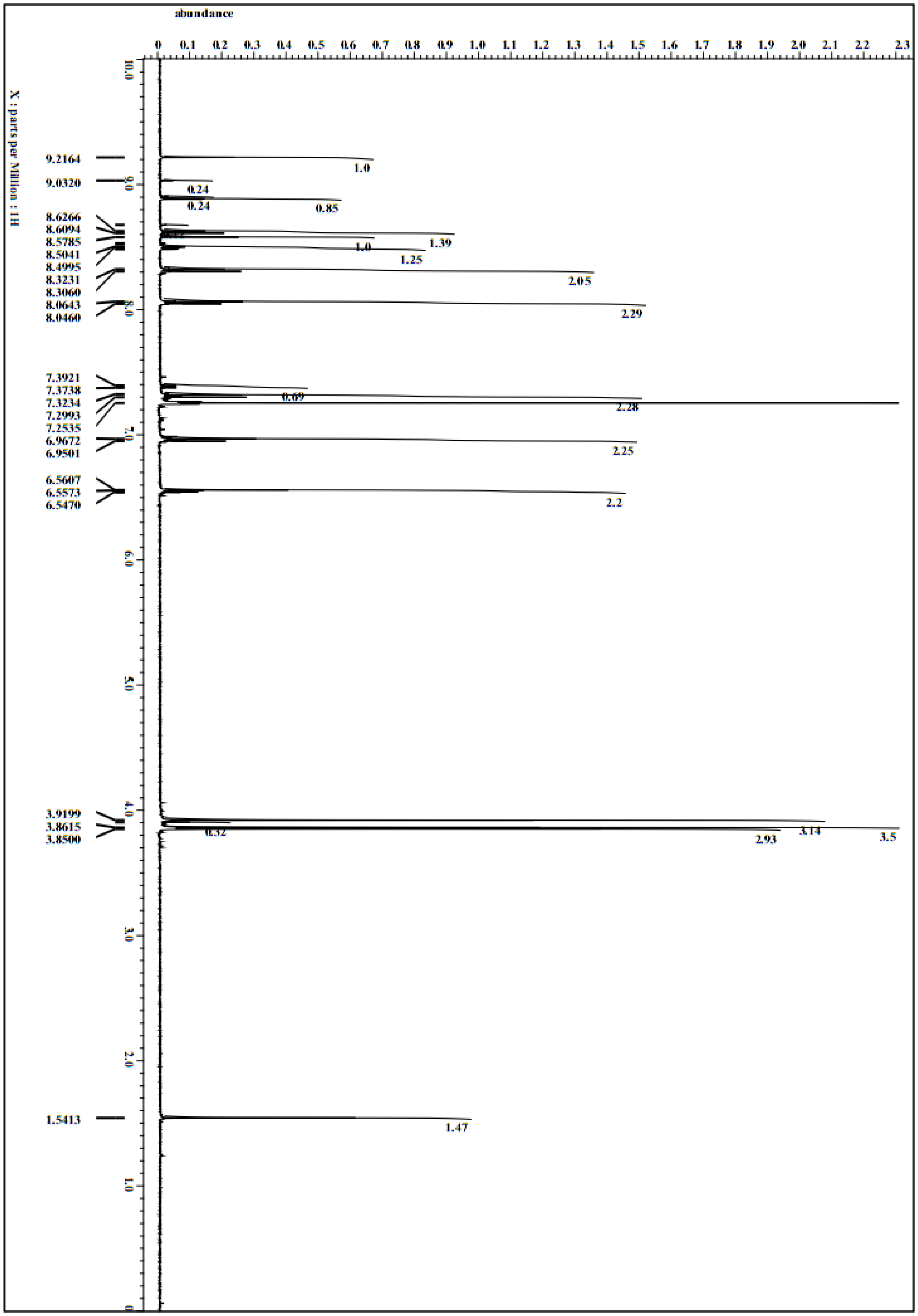


Figure S19. Complete ^{1}H NMR spectrum of the precipitate in the variant of Experiment #2 performed with 83.4 mM solutions of starting materials.

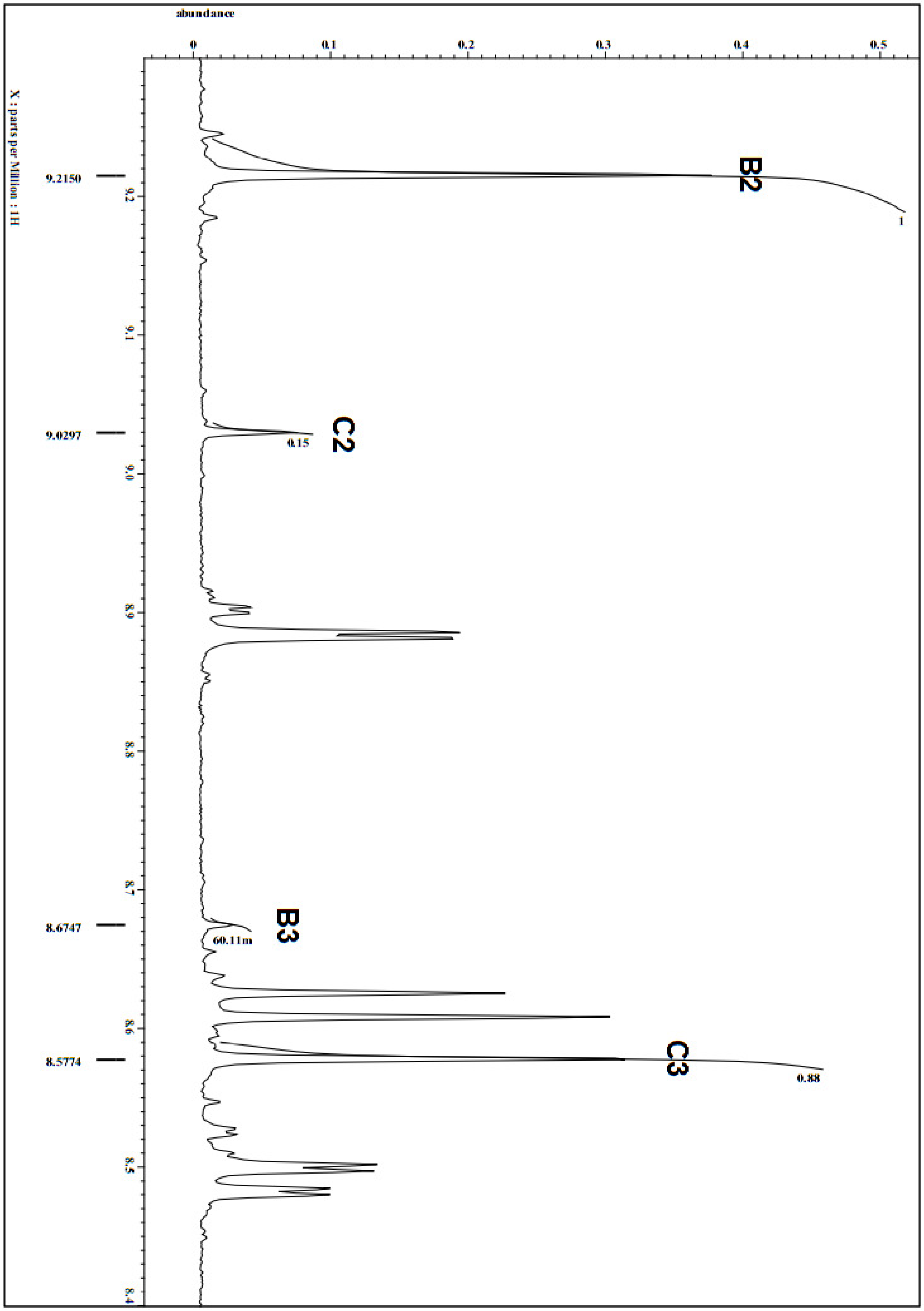


Figure S20. Imine region of the ^{1}H NMR spectrum of the precipitate in the variant of Experiment #2 performed with 125 mM solutions of starting materials.

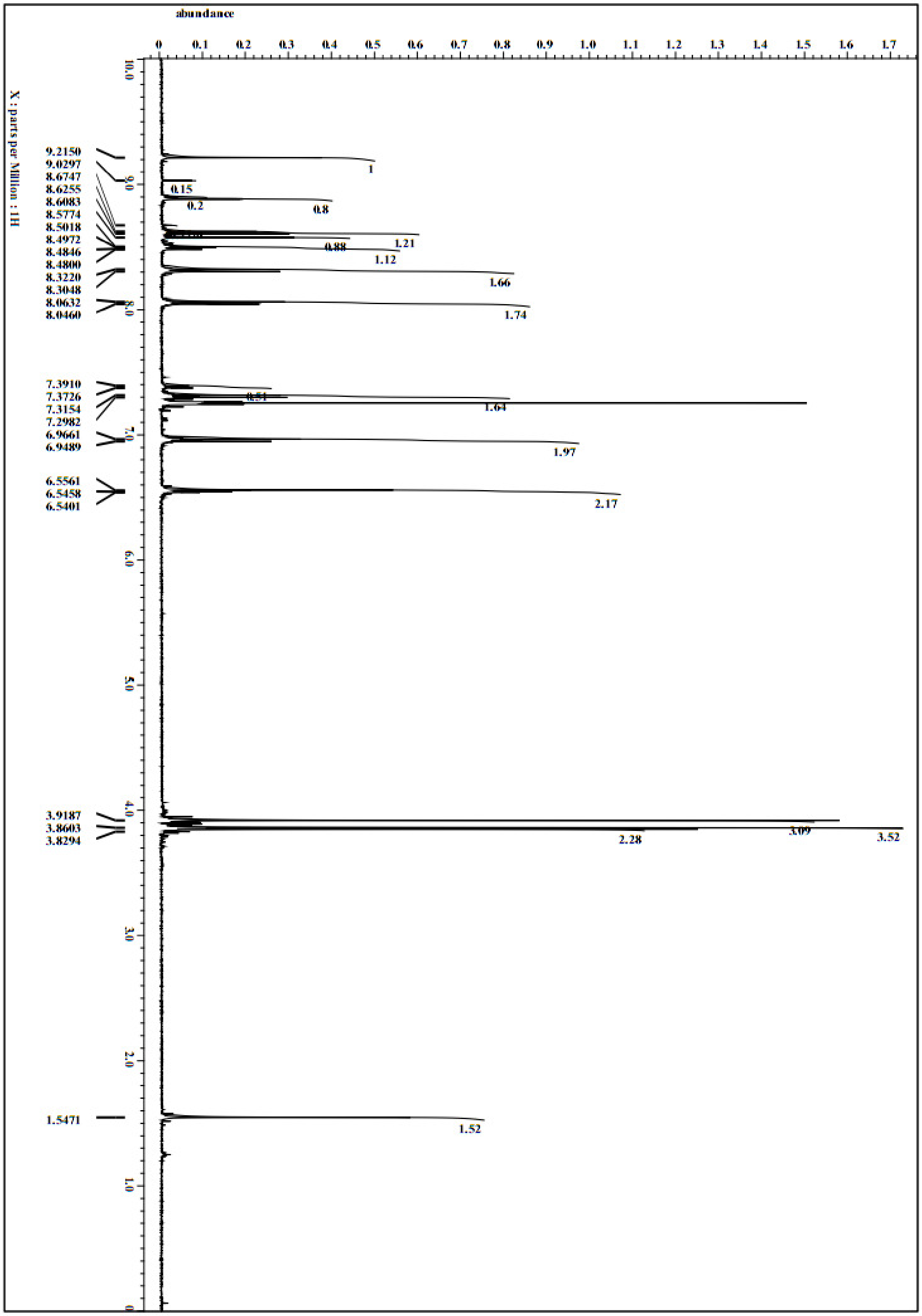


Figure S21. Complete ^{1}H NMR spectrum of the precipitate in the variant of Experiment #2 performed with 125 mM solutions of starting materials.

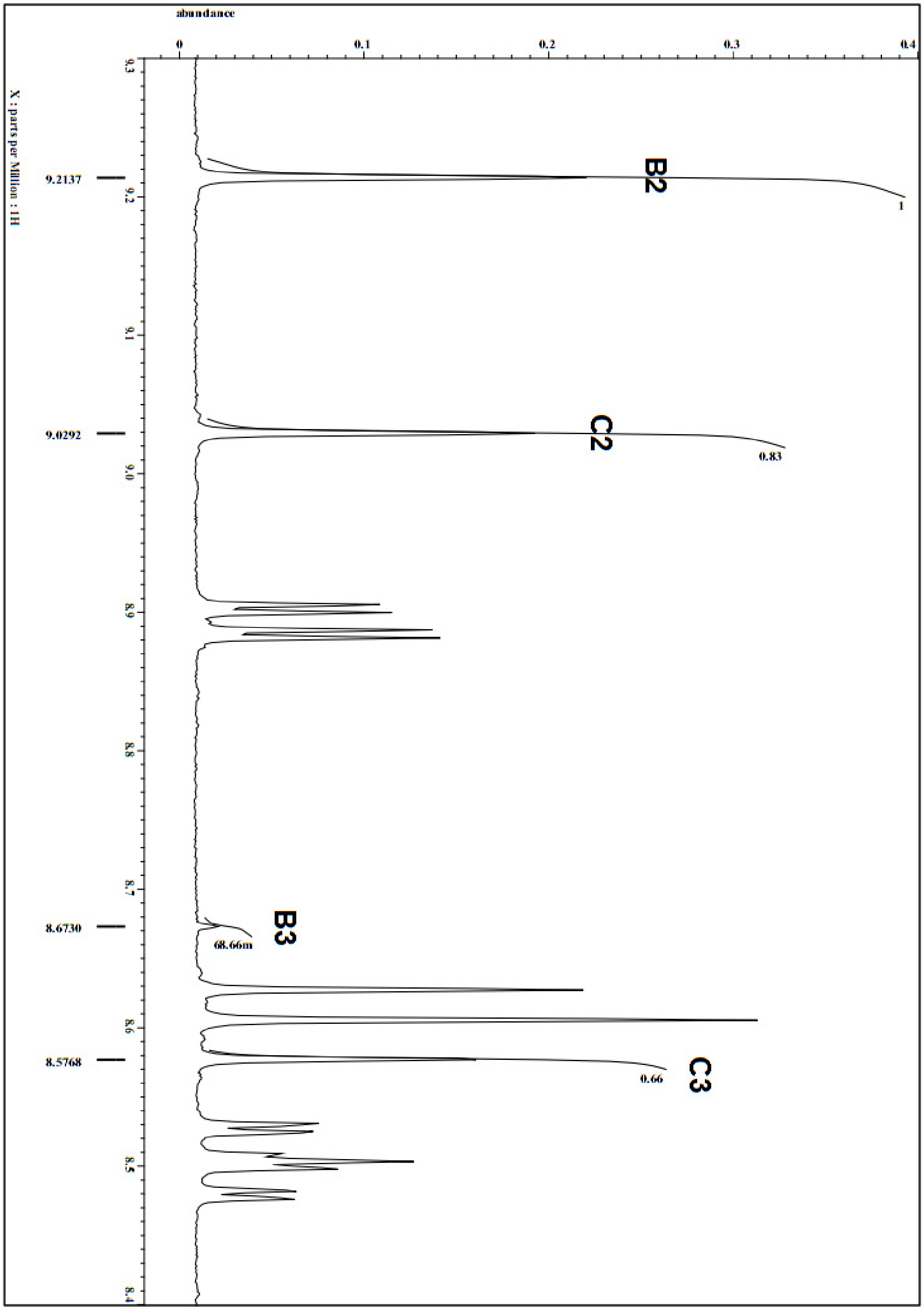


Figure S22. Imine region of the ^{1}H NMR spectrum of the precipitate in the variant of Experiment #2 performed with 209 mM solutions of starting materials.

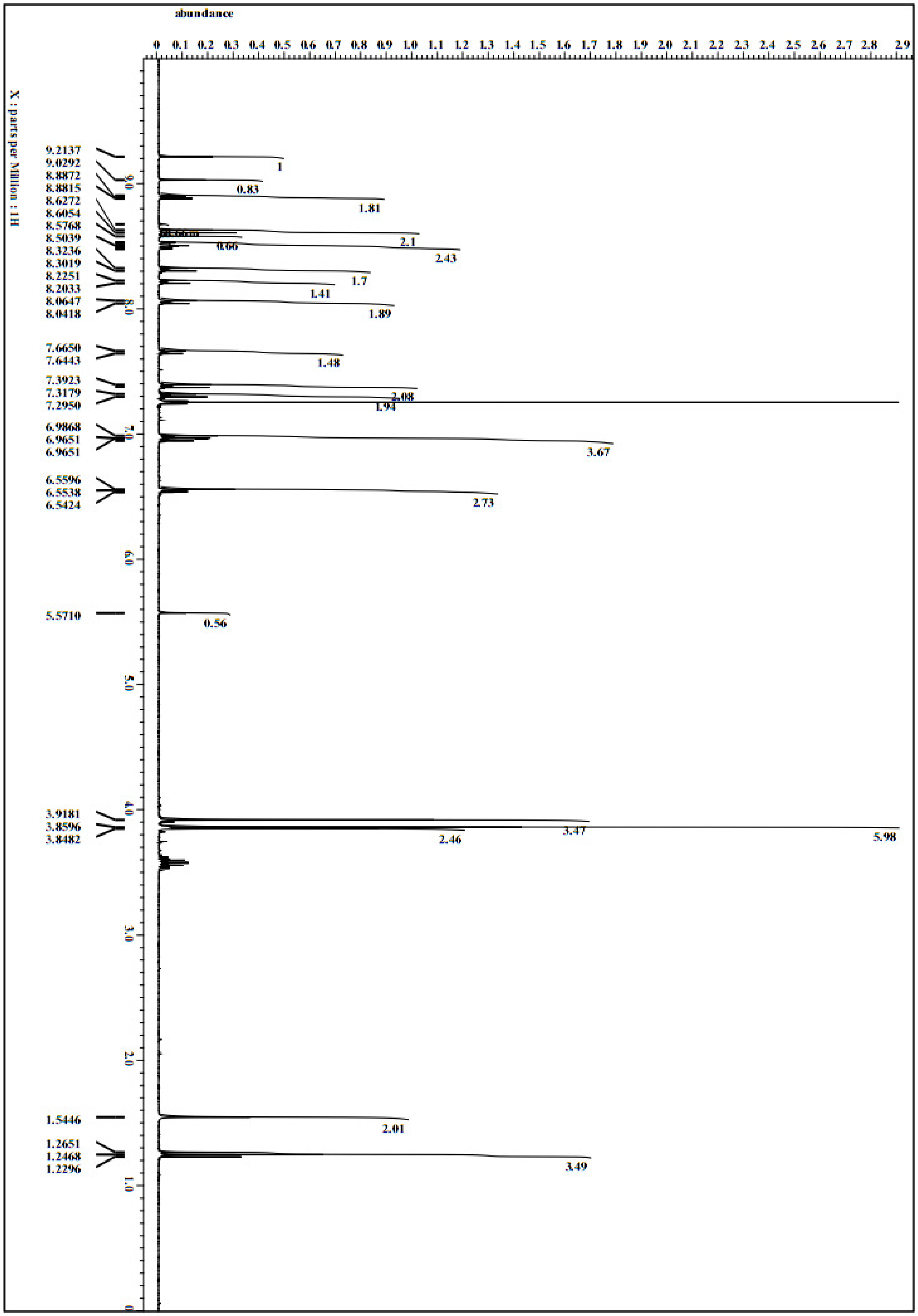
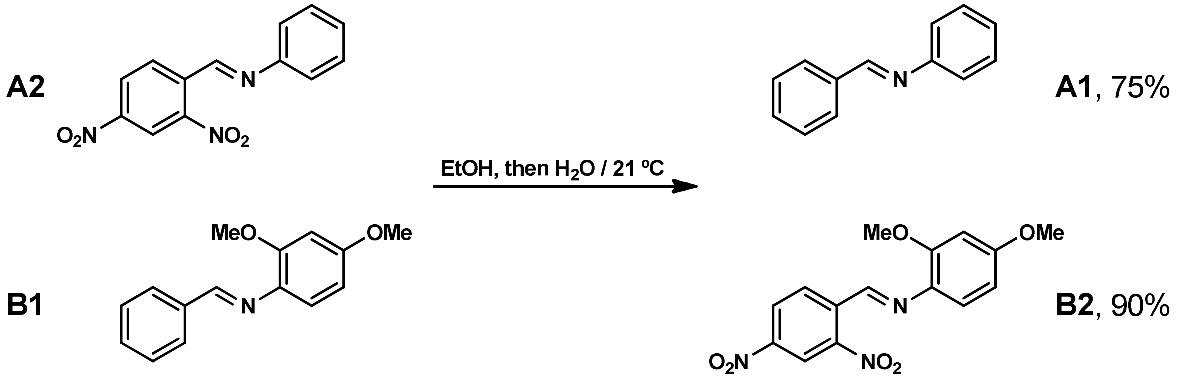


Figure S23. Complete ^{1}H NMR spectrum of the precipitate in the variant of Experiment #2 performed with 209 mM solutions of starting materials. Singlet at σ = 5.57 ppm is assigned to 4-nitrobenzaldehyde diethyl acetal.

Experiment #3

Precipitation-Driven Imine Transmutation



Compounds *N*-(2,4-dinitrobenzylidene)aniline, **A2** (100 mg, 0.37 mmol) and *N*-benzylidene-2,4-dimethoxyaniline, **B1** (89 mg, 0.37 mmol) were completely dissolved in absolute EtOH (50 mL). Precipitation starts after overnight stirring. Then, H_2O (96 mL) was added via a syringe pump at a rate of 1 mL h^{-1}. The orange precipitate was filtered out and identified as *N*-(2,4-dinitrobenzylidene)-2.4-dimethoxyaniline, **B2** (112 mg, 90%), with only a minor amount of starting imine **A2** left. Water fraction was extracted with CH_2Cl_2 and filtered through 5-cm silica gel plug. After solvent removal, off-white solid was obtained and identified as pure *N*-benzylideneaniline, **A1** (50 mg, 75%).

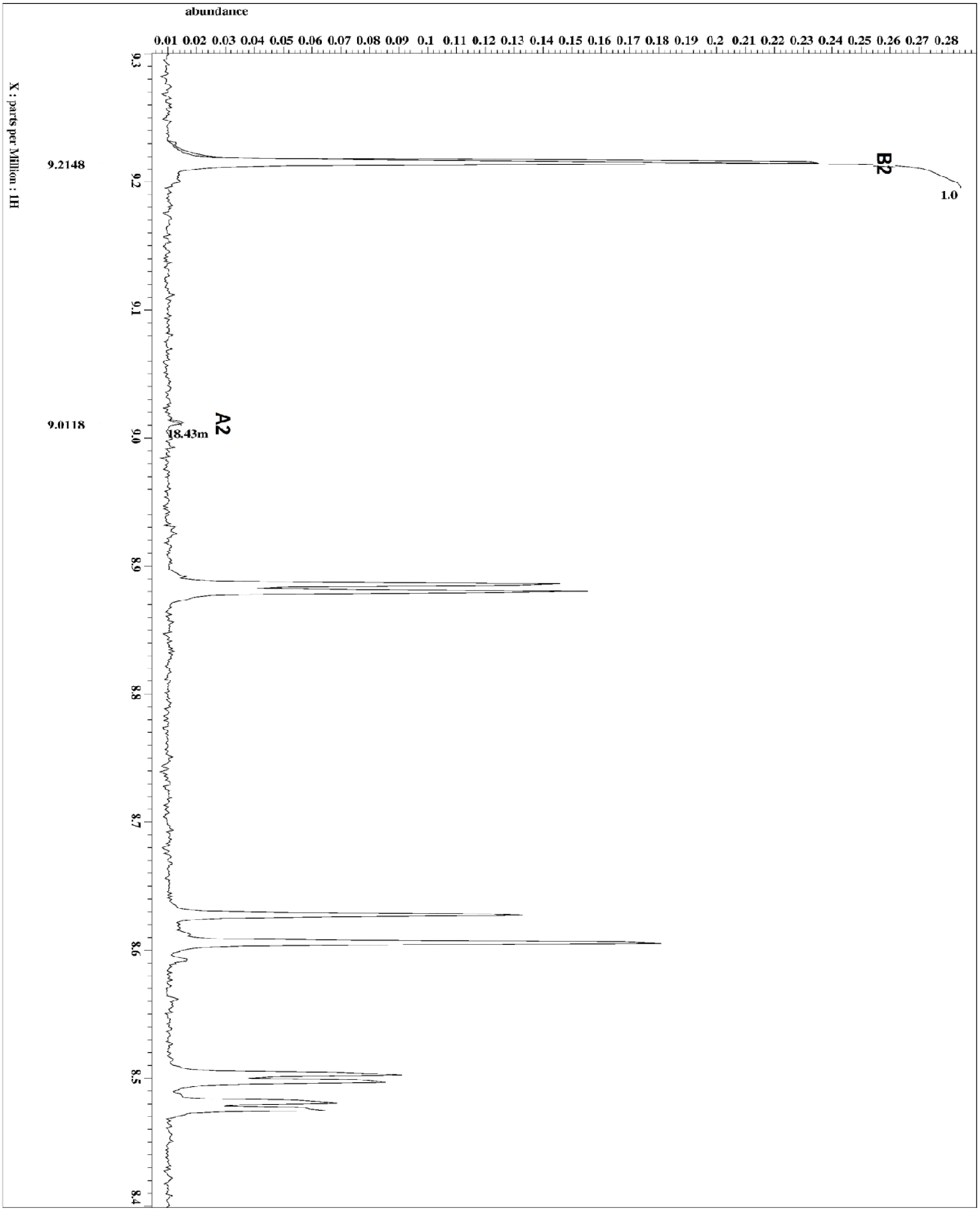


Figure S24. Imine region of the ^{1}H NMR spectrum of the precipitate in Experiment #3, with imine **B2** (σ=9.21 ppm) as the major product.

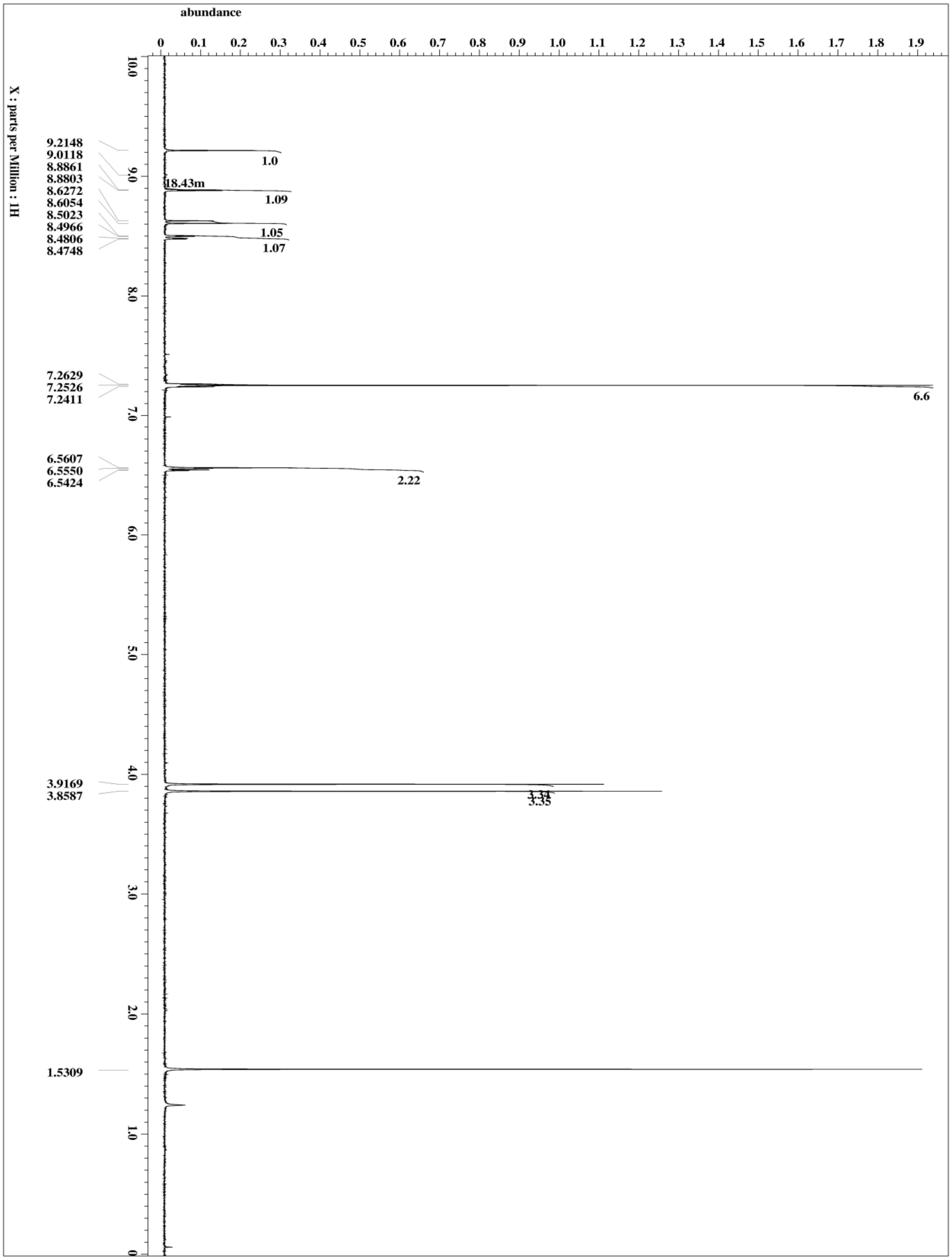


Figure S25. Complete ^{1}H NMR spectrum of the precipitate in Experiment #3.

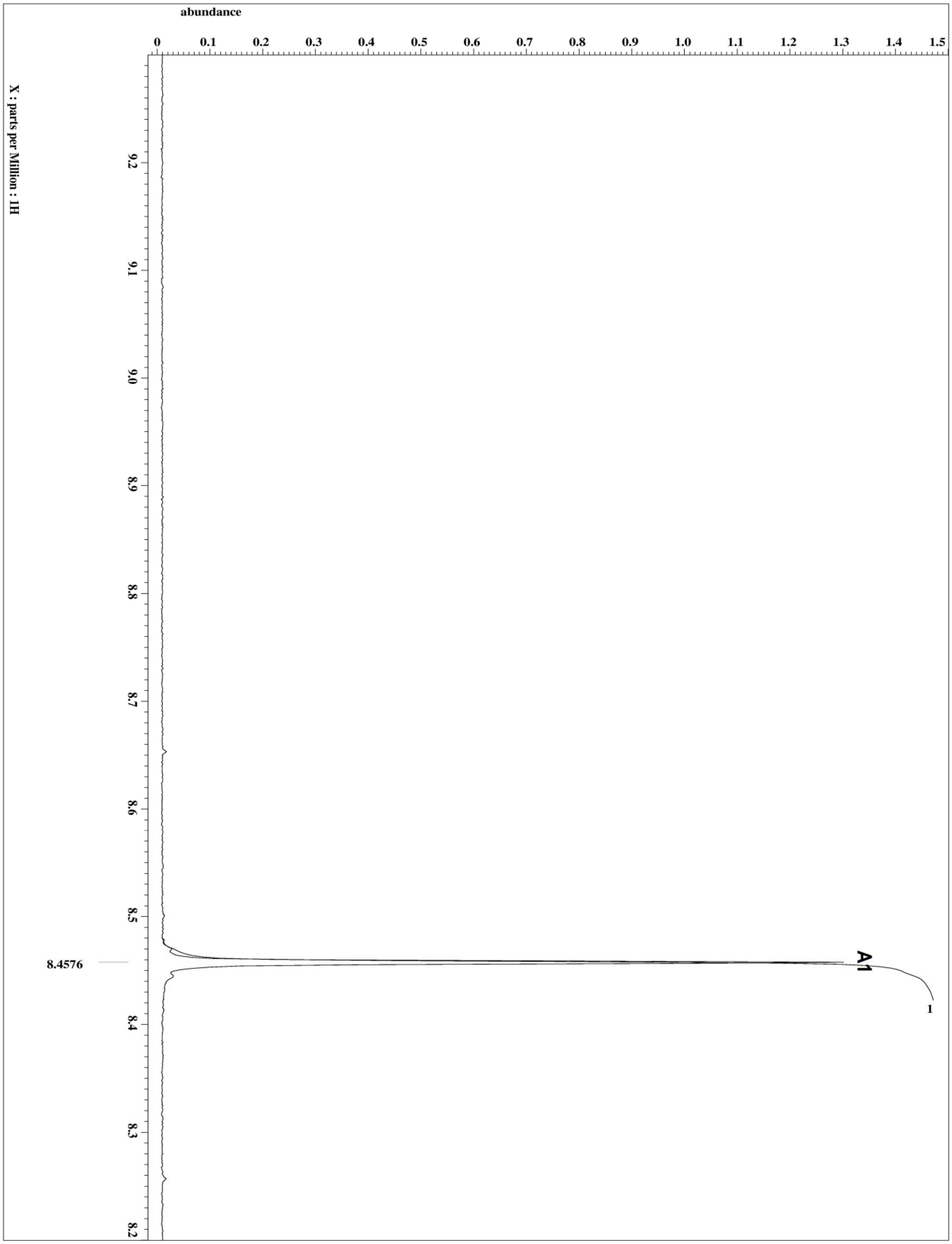


Figure S26. Imine region of the ^{1}H NMR spectrum of the filtrate in Experiment #3, with pure imine **A1** (σ=8.46 ppm) as the only product.

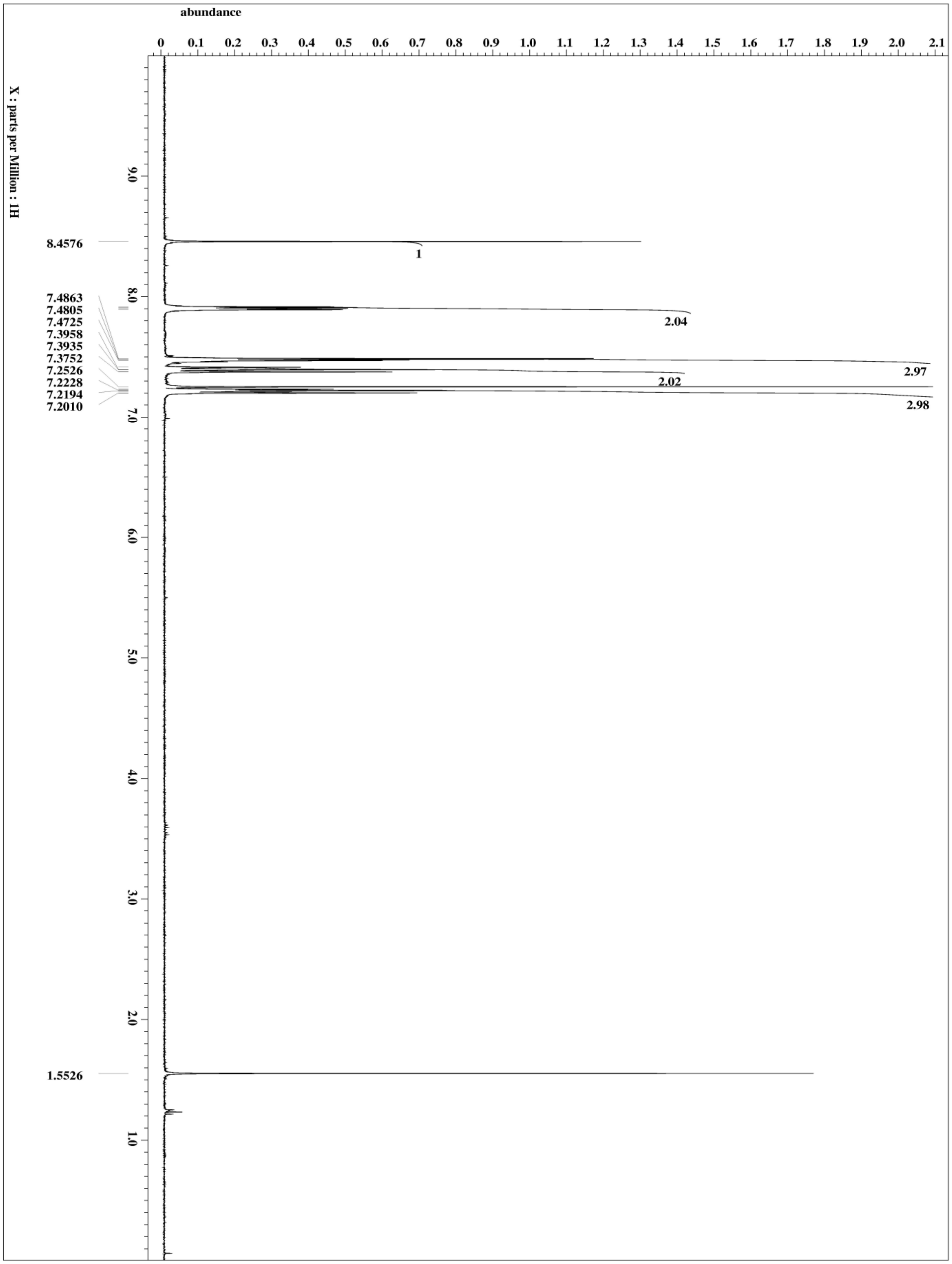
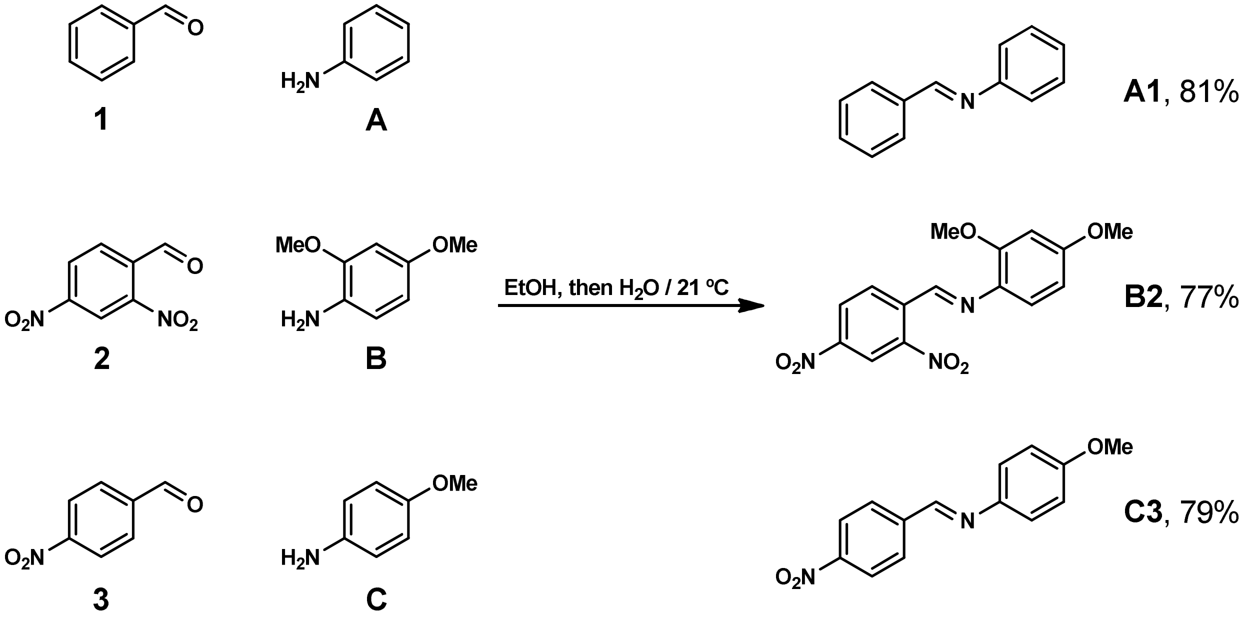


Figure S27. Complete ^{1}H NMR spectrum of the filtrate in Experiment #3.

Self-Sorting of [3×3] Imine Mixtures through Precipitation

Experiment #4:
N-benzylideneaniline (**A1**), *N*-(2,4-dinitro-benzylidene)-2,4-dimethoxyaniline (**B2**),
and 4-methoxy-*N*-(4-nitrobenzylidene)aniline (**C3**)



Benzaldehyde (**1,** 130 µL, 1.25 mmol), 2,4-dinitrobenzaldehyde (**2**, 250 mg, 1.25 mmol), and 4-nitrobenzaldehyde (**3**, 190 mg, 1.25 mmol) were dissolved in absolute EtOH (50 mL), with sonication. Once dissolved, aniline (**A**, 115 µL, 1.25 mmol), 2,4-dimethoxyaniline (**B**, 195 mg, 1.25 mmol), and 4-methoxyaniline (**C**, 155 mg, 1.25 mmol) were added into the solution. The mixture was stirred for 4 h. Then, H_2O (120 mL) was injected via a syringe pump, at a rate of 5 mL h^{-1}. After H_2O addition was complete, mixture was left to stir for 2 h, and the orange precipitate was filtered using Whatman 40 filter paper. The precipitate was dried in vacuo (3 mmHg) at 21 ^{o}C overnight, to give 679 mg of an orange precipitate. The yellow filtrate was collected and extracted with CH_2Cl_2 (170 mL) After solvent evaporation, 270 mg of a red-orange oil was obtained.

^{1}H NMR analysis of the precipitate showed the formation of imines **C3** (79%), **B2** (77%), **C2** (15%), **B3** (7%), **A3** (4%), **B1** (4%), and **A2** (1%). Analogous analysis of the filtrate revealed the presence of **A1** (81%), **B1** (9%), **C1** (9%), **A3** (8%), **B3** (1%), **C3** (1%), **A2** (0.8%), **B2** (0.3%), and **C2** (0.2%).

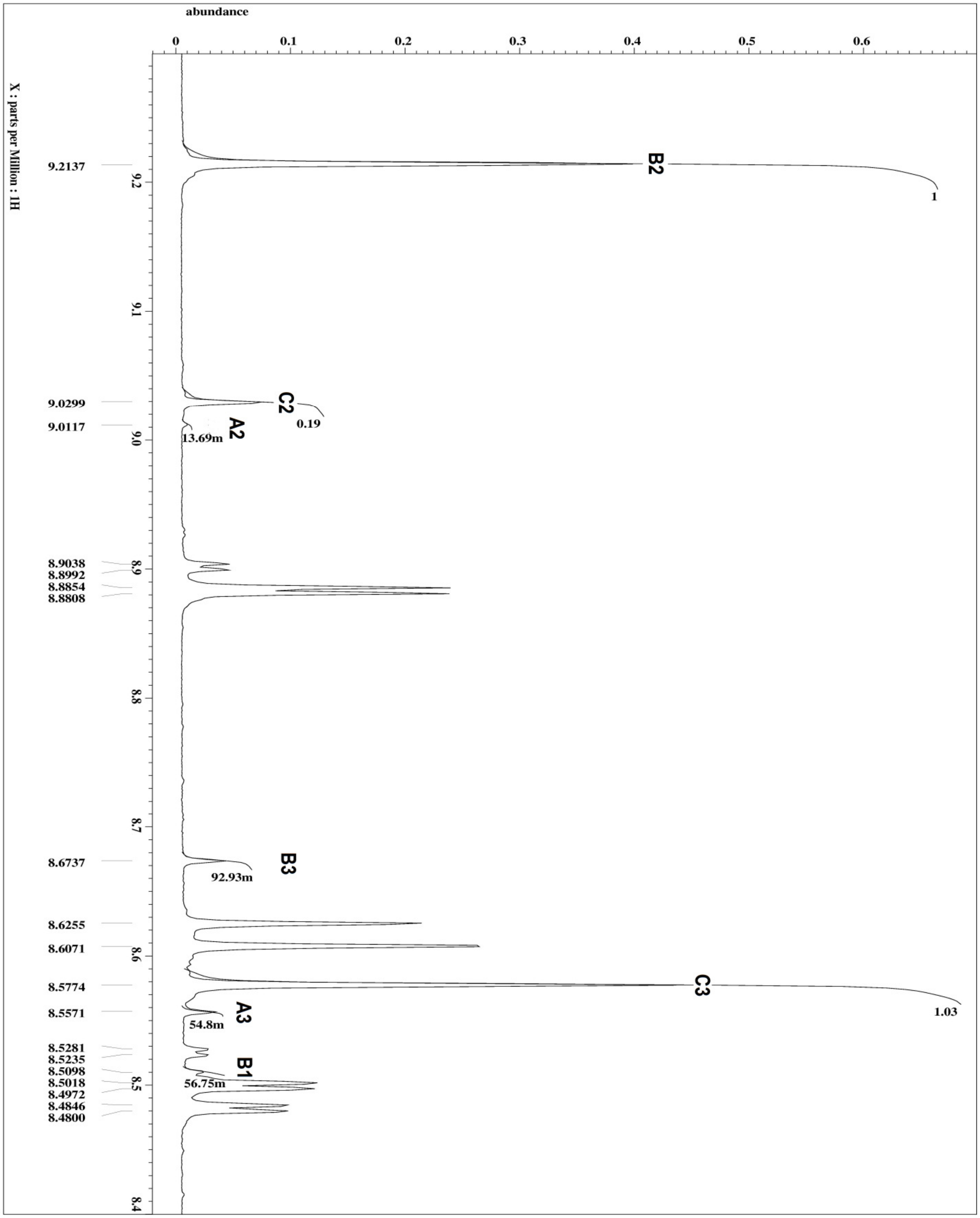


Figure S28. Imine region of the ^{1}H NMR spectrum of the precipitate in Experiment #4 with **C3** (σ=8.58 ppm) and **B2** (σ=9.21 ppm) as the major imine products.

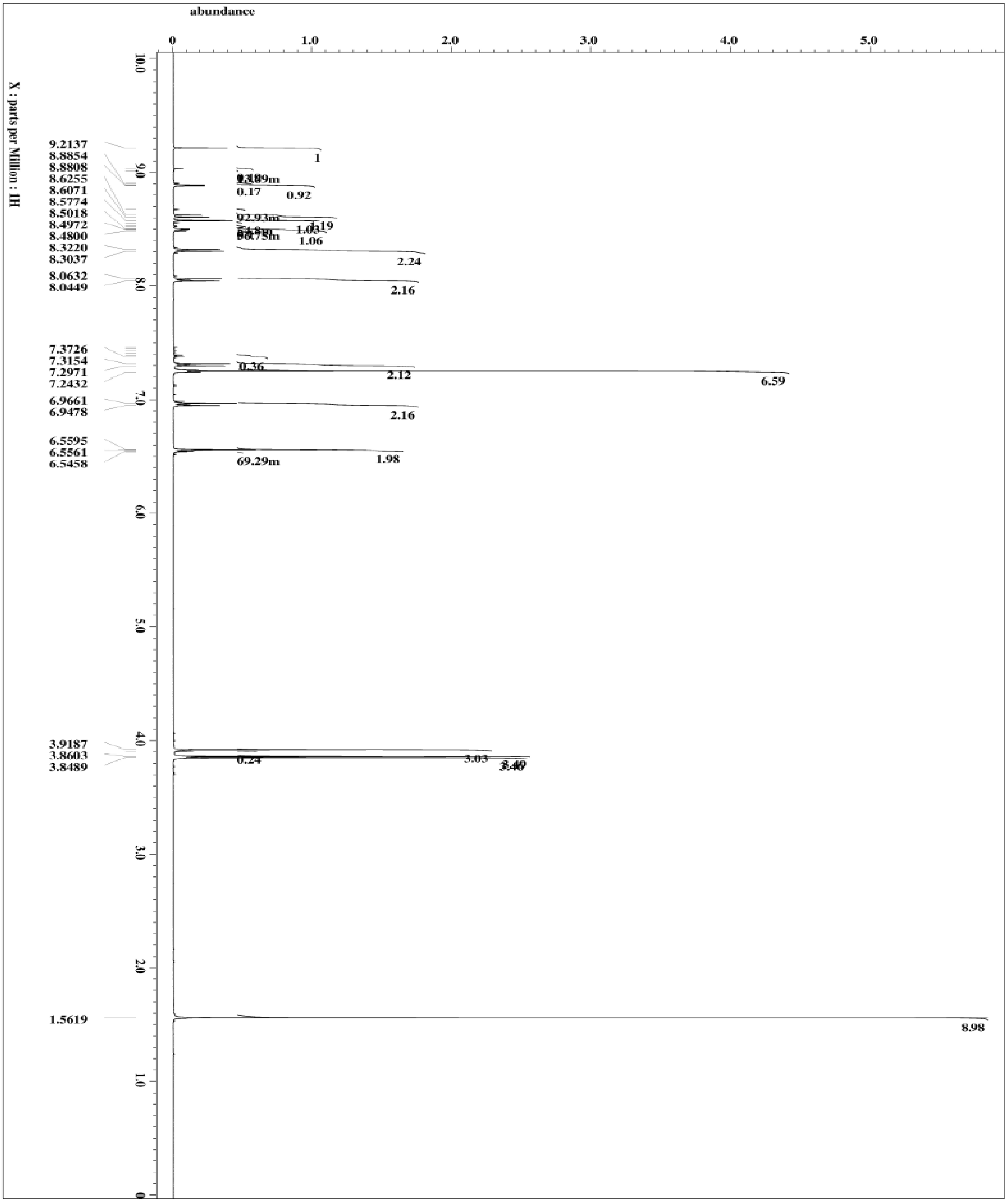


Figure S29. Complete ^{1}H NMR spectrum of the precipitate in Experiment #4.

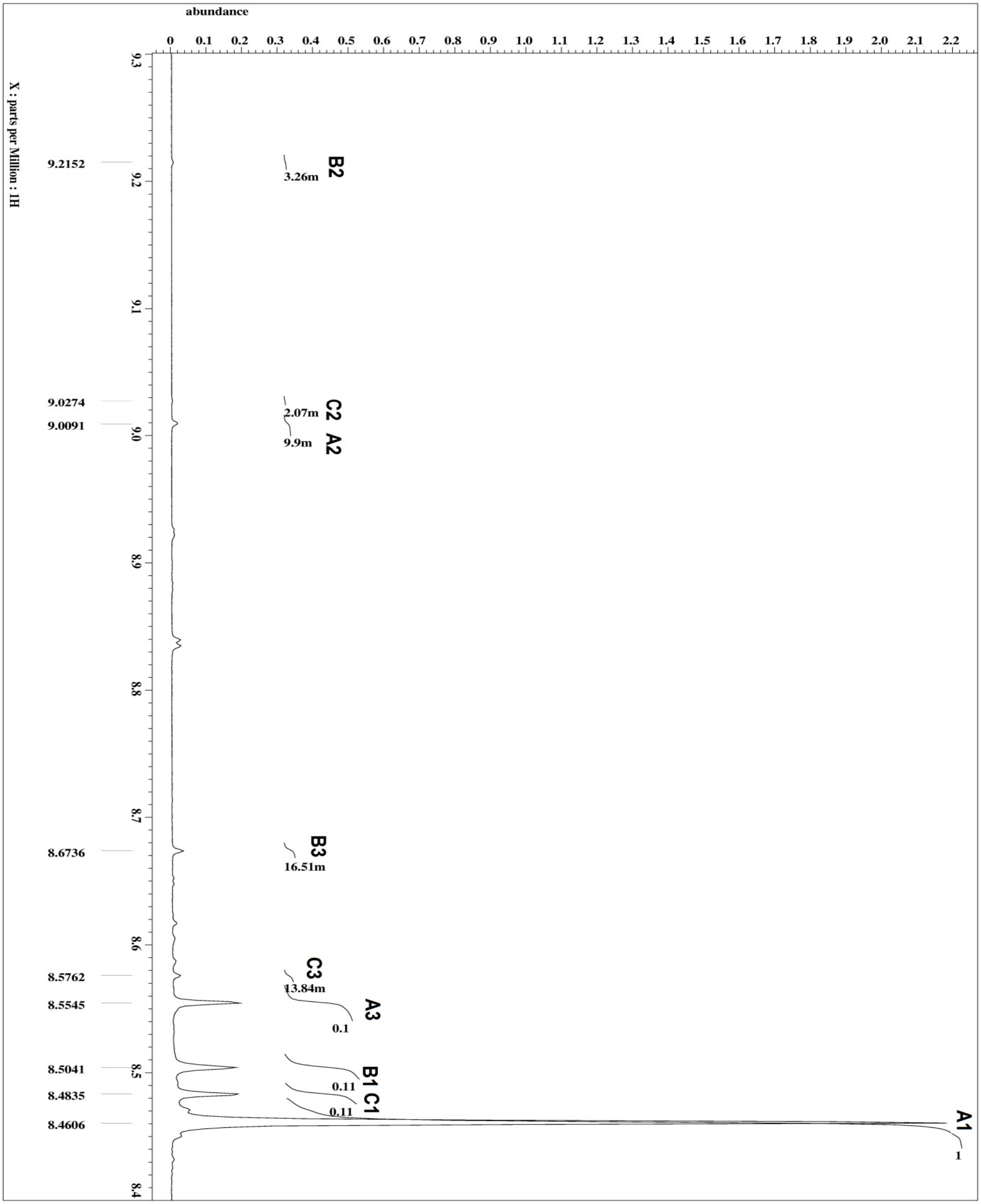


Figure S30. Imine region of the ^{1}H NMR spectrum of the filtrate in Experiment #4 with **A1** (σ=8.46 ppm) as the major imine product.

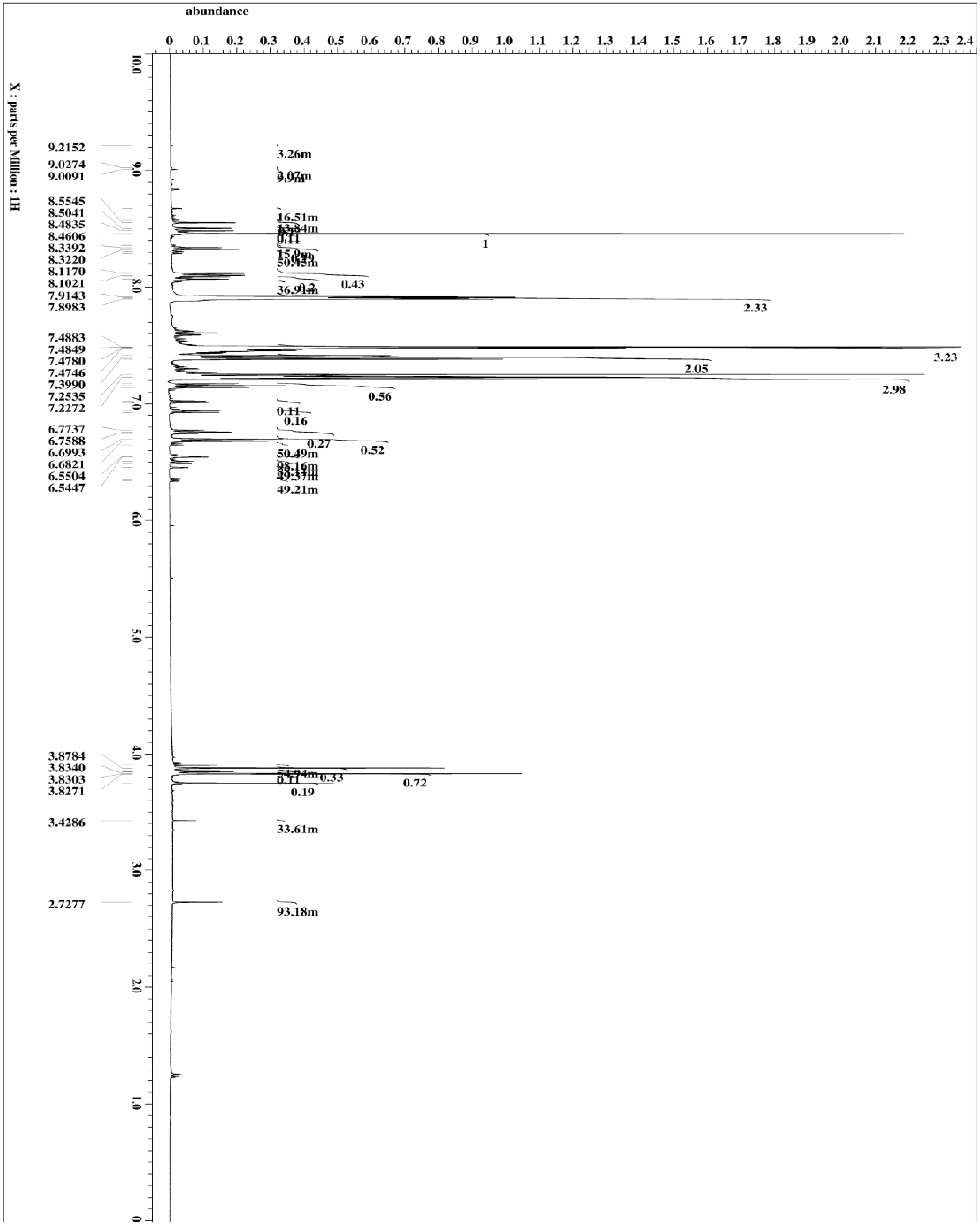
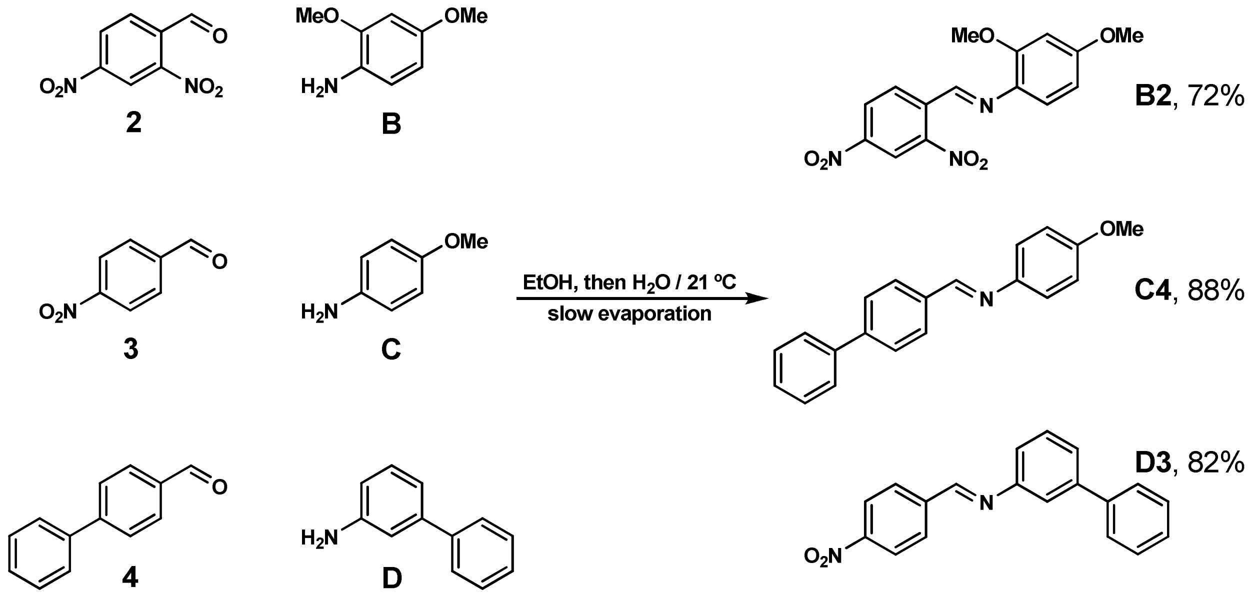


Figure S31. Complete ^{1}H NMR spectrum of the filtrate in Experiment #4.

Experiment #5:

N-(2,4-dinitro-benzylidene)-2,4-dimethoxyaniline (**B2**), *N*-(4-nitrobenzylidene)-[1,1'-biphenyl]-3-amine (**D3**), and *N*-([1,1'-biphenyl]-4-ylmethylene)-4-methoxyaniline (**C4**)



Compounds 2,4-dinitrobenzaldehyde (**2**, 50 mg, 0.25 mmol), 4-nitrobenzaldehyde (**3**, 38 mg, 0.25 mmol), and 4-phenylbenzaldehyde (**4,** 46 mg, 0.25 mmol), were dissolved in absolute EtOH (35 mL), with sonication. Once dissolved, 2,4-dimethoxyaniline (**B**, 39 mg, 0.25 mmol), 4-methoxyaniline (**C**, 31 mg, 0.25 mmol), and 3-aminobiphenyl (**D**, 43 mg, 0.25 mmol) were added into the solution. The mixture was stirred for 12 h, during which the formation of bright yellow precipitate was observed. After 12 h, H_2O (40 mL) was injected via a syringe pump, at a rate of 1 mL h^{-1}. The yellow precipitate gradually changed into orange. After H_2O addition was complete, the mixture was stirred for 7 d in an open flask. The solution was then exposed to a low pressure N_2 stream for 3 d to remove the solvent, resulting in 200 mg of an orange solid.

^{1}H NMR analysis of the solid, orange residue indicated the dominant formation of imines **B2** (72%), **C4** (88%), and **D3** (82%), with only traces of imines **C2** (5%), **C3** (5%), **D4** (5%), **B3** (3%), and **D2** (2%). Two additional trials were performed which confirmed the same preferences. The yields for the second trial (Figures S34 and S35) were **B2** (67%), **C4** (84%), **D3** (81%), **D2** (2%), **C2** (9%), **B3** (7%), **C3** (6%), and **D4** (7%). The yields for the third trial (Figures S36 and S37) were **B2** (73%), **C4** (82%), **D3** (84%), **D2** (1%), **C2** (7%), **B3** (2%), **C3** (4%), and **D4** (7%).

A 30 mg aliquot of this imine mixture was dissolved in 20 mL of MeCN and stirred at 21 ºC for 7 d. ^{1}H NMR spectroscopic analysis of the solution during this period showed that the ratio of the imines to each other remained the same. However, heating the same solution to 110 ºC for 24 h caused the system to form all possible imines.

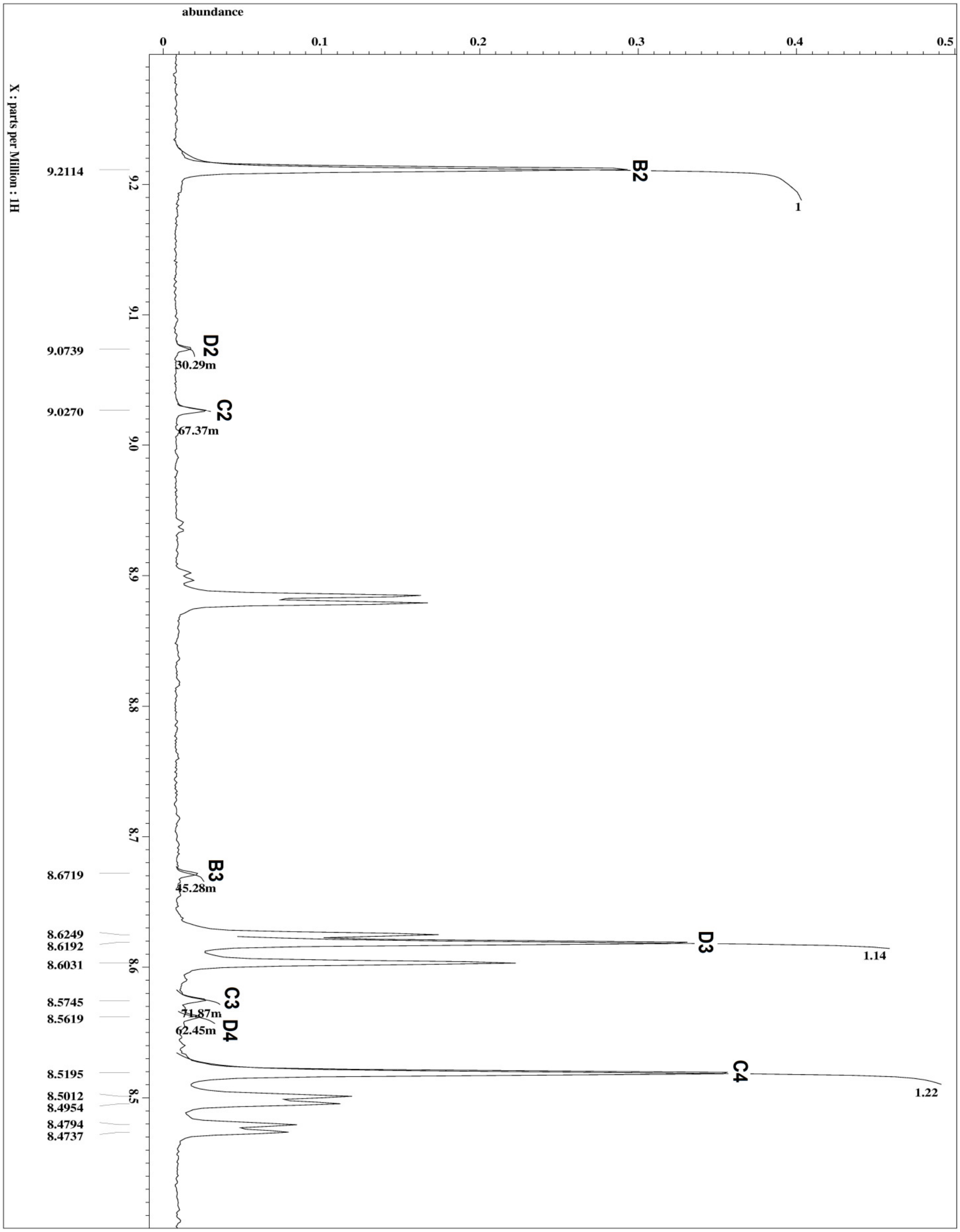


Figure S32. Imine region of the ^{1}H NMR spectrum of the solid obtained in Experiment #5, with **B2** (σ=9.21 ppm), **D3** (σ=8.62 ppm), and **C4** (σ=8.52 ppm) as the major imine products, trial 1.

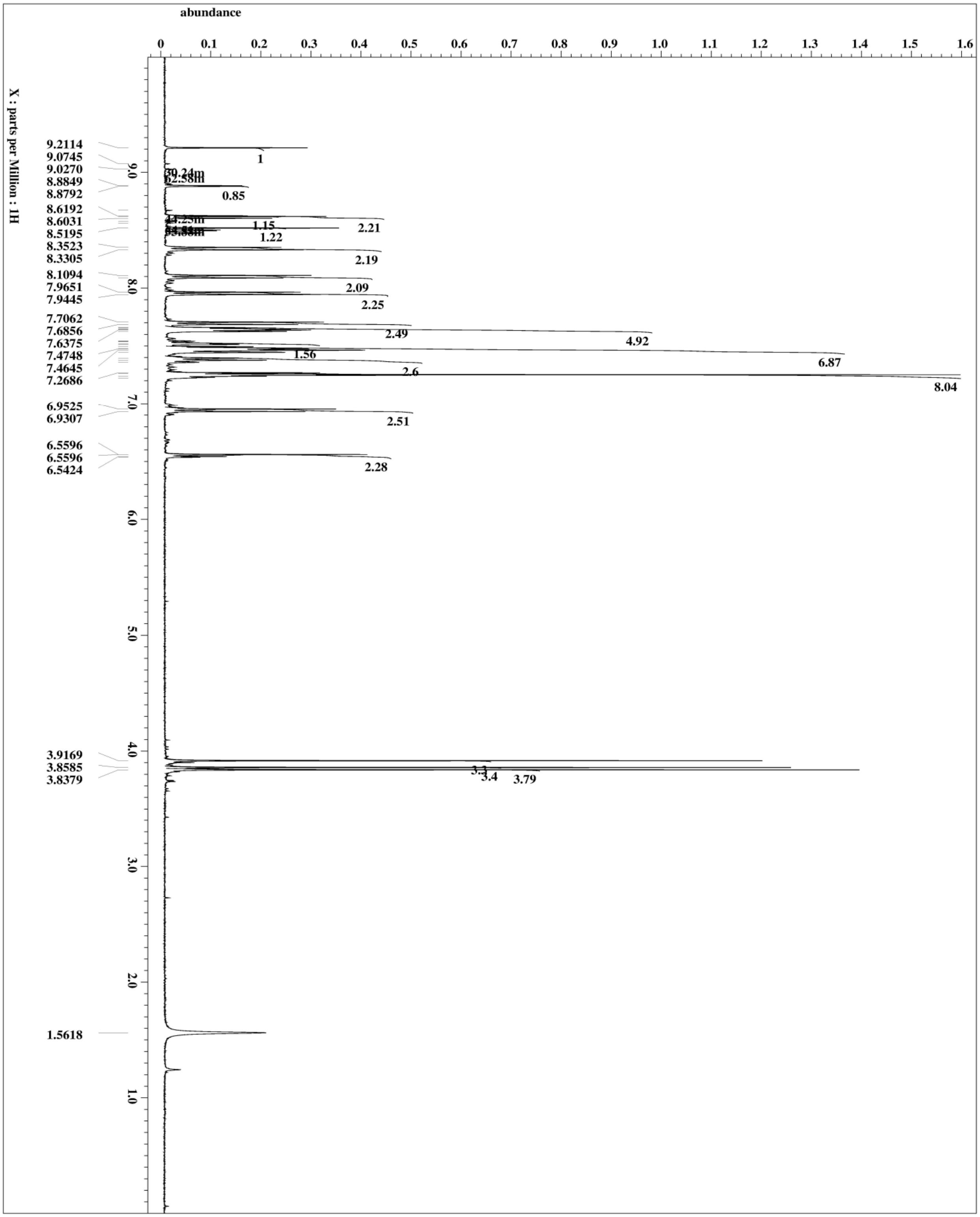


Figure S33. Complete ^{1}H NMR spectrum of the solid obtained in Experiment #5, trial 1.

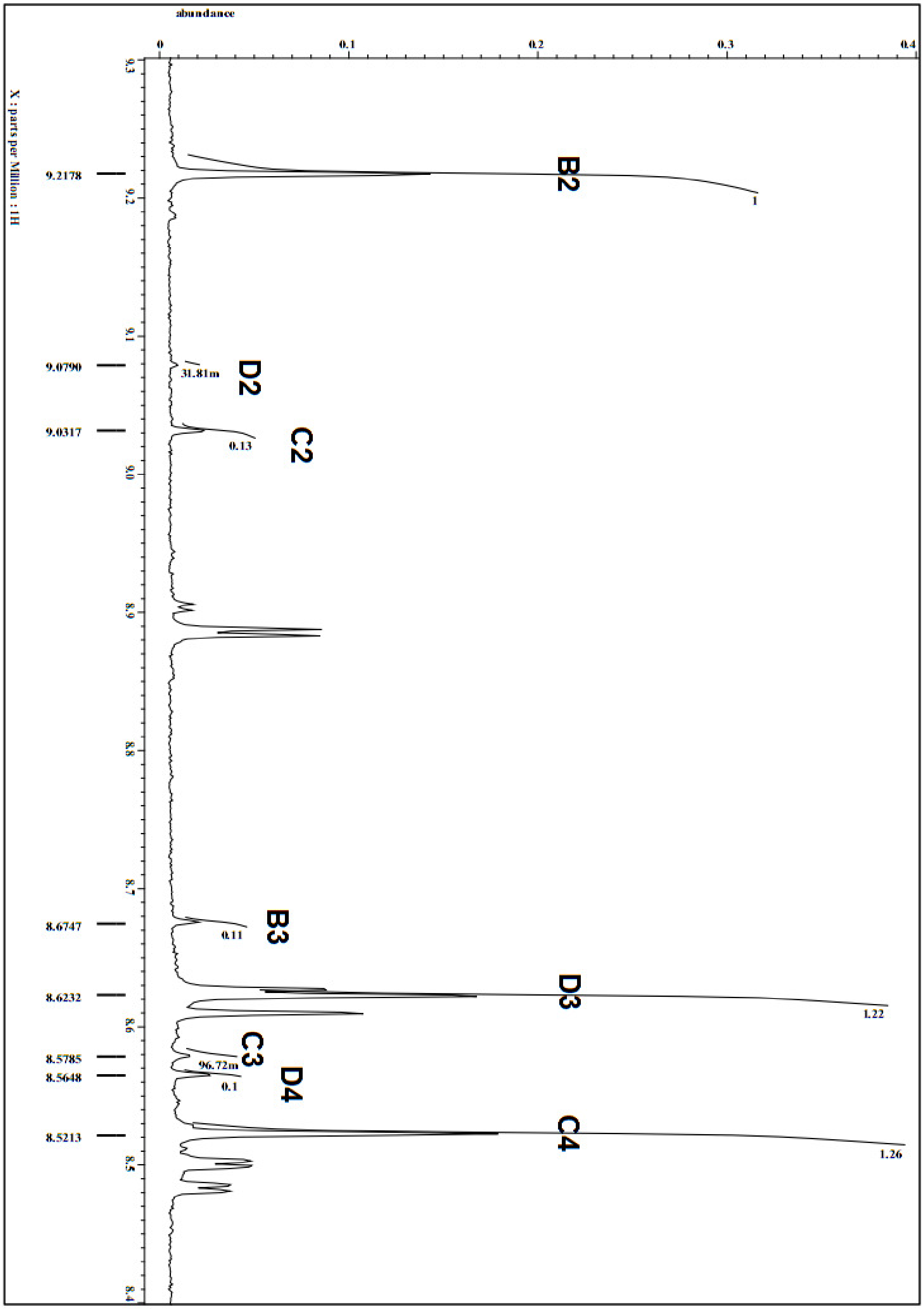


Figure S34. Imine region of the ^{1}H NMR spectrum of the solid obtained in Experiment #5, with **B2** (σ=9.22 ppm), **D3** (σ=8.62 ppm), and **C4** (σ=8.52 ppm) as the major imine products, trial 2.

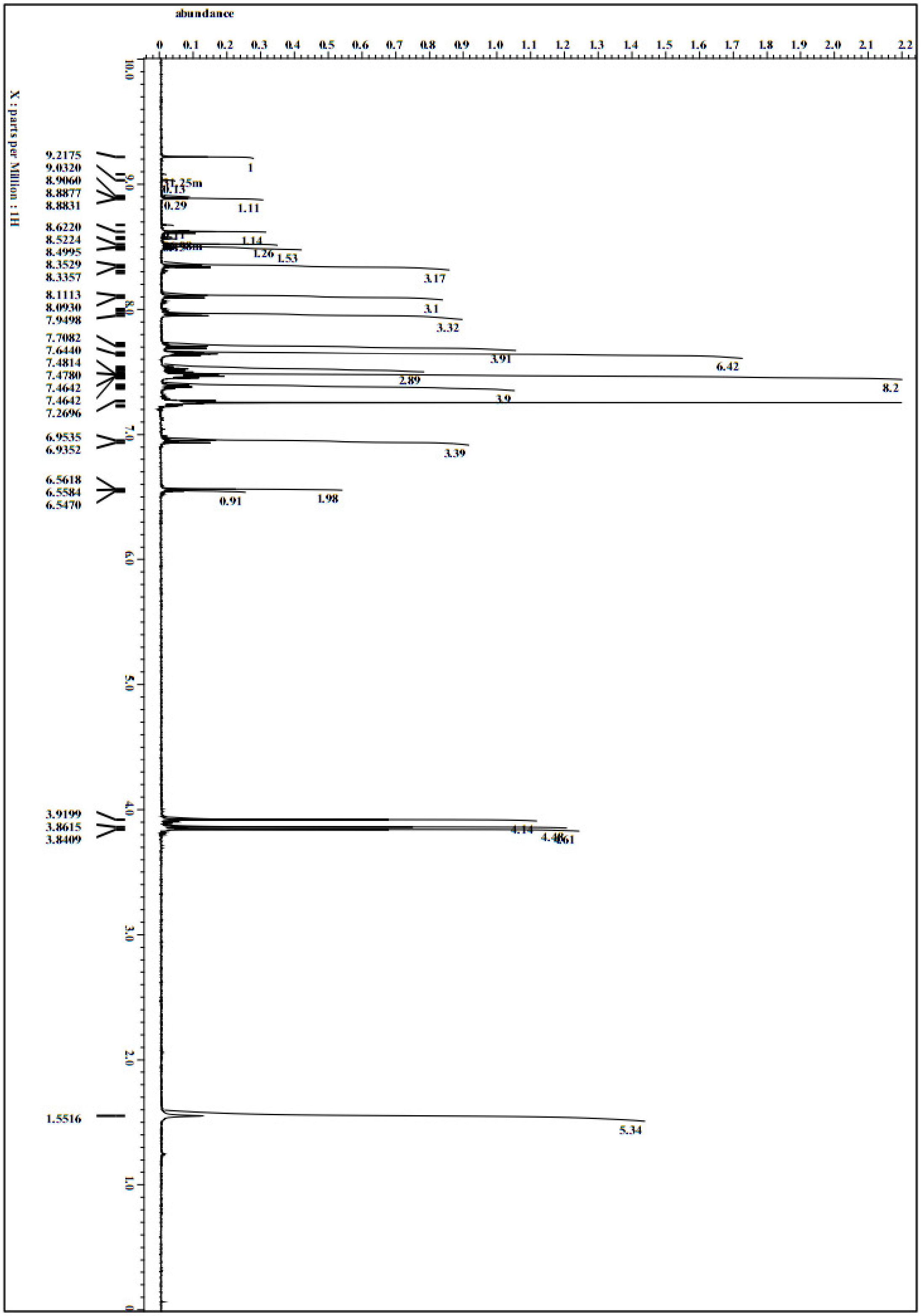


Figure S35. Complete ^{1}H NMR spectrum of the solid obtained in Experiment #5, trial 2.

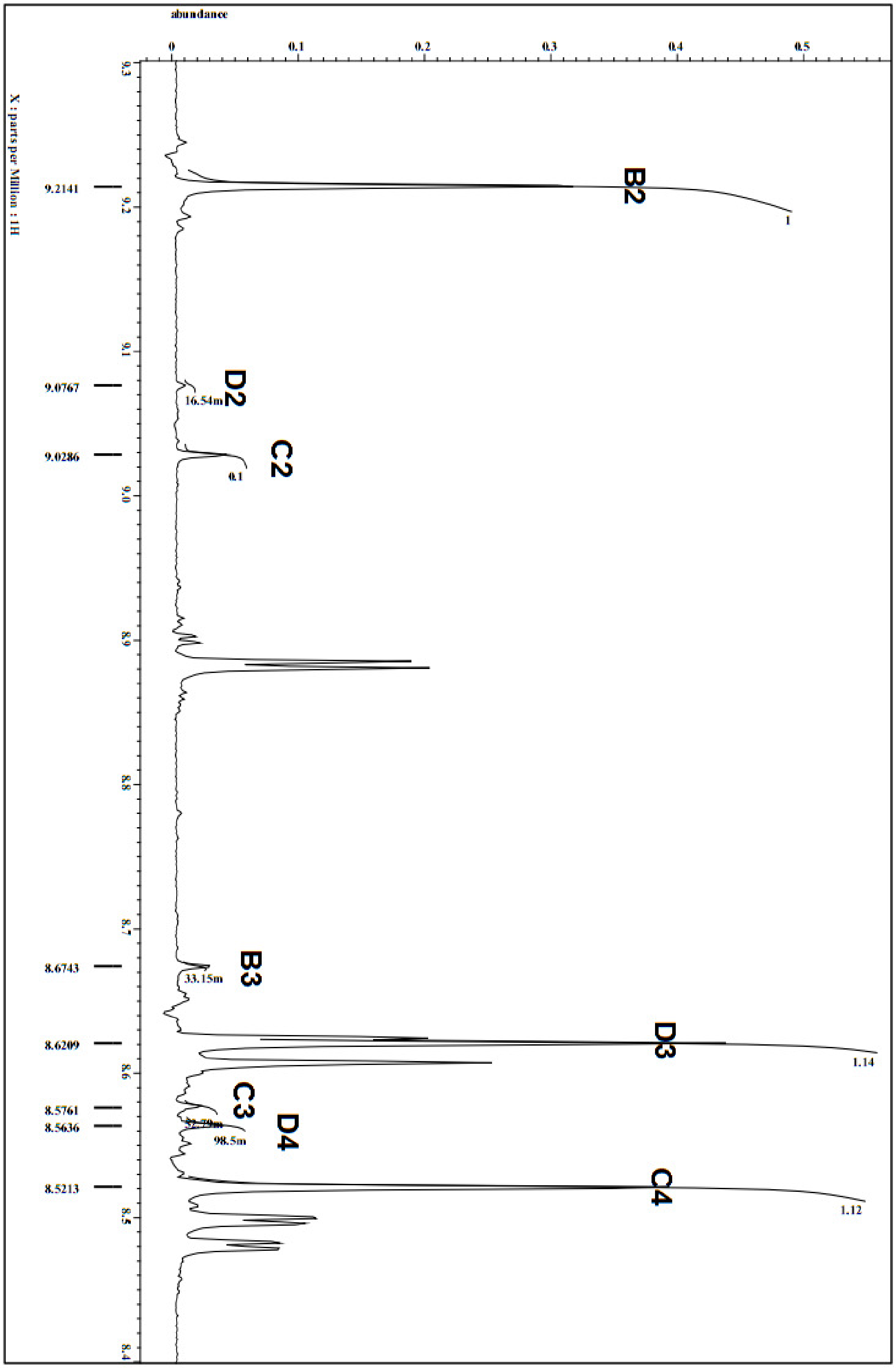


Figure S36. Imine region of the ^{1}H NMR spectrum of the solid obtained in Experiment #5, with **B2** (σ=9.21 ppm), **D3** (σ=8.62 ppm), and **C4** (σ=8.52 ppm) as the major imine products, trial 3.

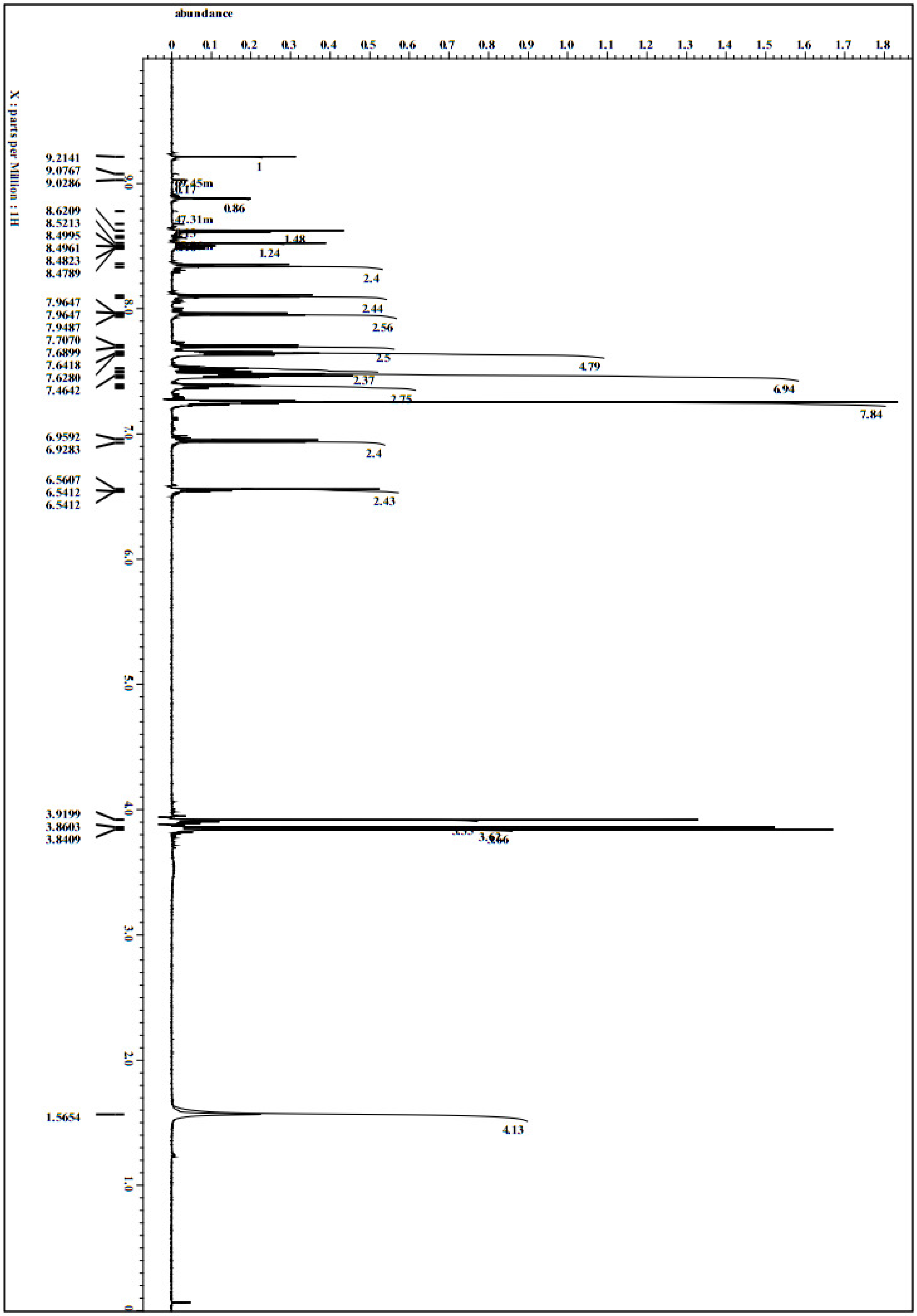


Figure S37. Complete ^{1}H NMR spectrum of the solid obtained in Experiment #5, trial 3.

Spectroscopic Characterization Data for New Compounds

The azomethine peaks of the imines obtained in [2×2] and [3×3] precipitation experiments were assigned to appropriate imines by comparison to the spectral data of the following published reports:

A1 P. Nongkunsarn and C. A. Ramsden, *Tetrahedron*, 1997, **53**, 3805–3830.
A2 H. B. Singh and W. R. McWhinnie, *J. Chem. Soc., Dalton Trans.*, 1985, 821–825.
A3 R. Torregrosa, I. M. Pastor and M. Yus, *Tetrahedron*, 2005, **61**, 11148–11155.
B1 S. Saito, K. Hatanaka and H. Yamamoto, *Org. Lett.*, 2000, **2**, 1891–1894.
B2 K. Osowska and O. Š. Miljanić, *Angew. Chem. Int. Ed.*, 2011, **50**, 8345–8349.
C1 T. Nakajima, T. Inada, T. Igarashi, T. Sekioka and I. Shimizu, *Bull. Chem. Soc. Jpn.*, 2006, **79**, 1941–1949.
C2 K. Osowska and O. Š. Miljanić, *J. Am. Chem. Soc.*, 2011, **133**, 724–727.
C3 J. S. Bennett, K. L. Charles, M. R. Miner, C. F. Heuberger, E. J. Spina, M. F. Bartels and T. Foreman, *Green Chem.*, 2009, **11**, 166–168.
C4 D. Miyazaki, K. Nomura, T. Yamashita, I. Iwakura, T. Ikeno and T. Yamada, *Org. Lett.*, 2003, **5**, 3555–3558.

Five new imines (**B3**, **B4**, **D2**, **D3**, **D4**) were synthesized for comparison purposes using the following general procedure: aldehyde (0.50 mmol) and aniline (0.50 mmol) were dissolved in PhMe (8 mL), and 4Å molecular sieves were added to remove H_2O. These mixtures were stirred for 12–24 h at 80 ºC. Reaction completion was monitored by ^{1}H NMR spectroscopy. Spectroscopic data for these new imines is given below:

B3: brown powder, mp 96 °C. IR (neat): 3002, 1602, 1584, 1516, 1342, 1308, 1295, 848, 831, 795 cm^{-1}. ^{1}H NMR (400 MHz): δ 8.66 (s, 1H), 8.27 (d, $^3J_{H-H}$ = 8.7 Hz, 1H), 8.03 (d, $^3J_{H-H}$ = 8.7 Hz, 1H), 7.11 (d, $^3J_{H-H}$ = 8.2 Hz, 1H), 6.55–6.50 (m, 2H), 3.89 (s, 3H), 3.83 (s, 3H) ppm. ^{13}C NMR (100 MHz): δ 160.23, 155.94, 154.36, 148.96, 142.41, 133.48, 129.19, 124.00, 121.67, 104.70, 99.60, 50.04, 55.66 ppm. HRMS (ESI): Calcd for $C_{15}H_{15}N_2O_4^+$: 287.1026. Found: 287.1026. Anal. calcd for $C_{19}H_{13}N_3O_4$: C,62.93; H, 4.93; N, 9.79. Found: C, 62.14; H, 4.56; N, 9.87.

B4: yellow-green powder, mp 124 °C. IR (neat): 3026, 1623, 1605, 1593, 1307, 1206, 1031, 828, 767 cm^{-1}. ^{1}H NMR (400 MHz): δ 8.54 (s, 1H), 7.97 (d, $^3J_{H-H}$ = 8.2 Hz, 2H), 7.68 (d, $^3J_{H-H}$ = 8.2 Hz, 2H), 7.65–7.62 (m, 2H), 7.48–7.44 (m, 2H), 7.39–7.35 (m, 1H), 7.02 (d, $^3J_{H-H}$ = 8.2 Hz, 2H), 6.55 (d, $^3J_{H-H}$ = 2.7 Hz, 1H), 6.50 (dd, $^3J_{H-H}$ = 8.2 Hz, $^4J_{H-H}$ = 2.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz): δ 159.22, 159.10, 153.89, 143.70, 140.47, 135.68, 135.19, 129.27, 128.96, 127.89, 127.41, 127.26, 120.54, 104.40, 99.59, 56.06, 55.64 ppm. HRMS (ESI): Calcd for $C_{21}H_{20}NO_2^+$:

318.1488. Found: 318.1487. Anal. calcd for $C_{21}H_{19}NO_2$: C,79.45; H, 6.03.; N, 4.41. Found: C, 78.21; H, 5.69; N, 4.26.

D2: light-brown powder, mp 118 °C. IR (neat): 1597, 1523, 1476, 1343, 1147, 1059, 906, 833, 762, 697 cm^{-1}. ^1H NMR (400 MHz): δ 9.07 (s, 1H), 8.92 (d, $^4J_{H–H}$ = 2.3 Hz, 1H), 8.62–8.54 (m, 2H), 7.64–7.45 (m, 7H), 7.40–7.29 (m, 2H) ppm. ^{13}C NMR (100 MHz): δ 153.58, 150.69, 149.20, 148.69, 142.78, 140.36, 136.06, 131.59, 129.98, 129.02, 127.90, 127.66, 127.27, 126.89, 120.50, 120.48, 119.96 ppm. HRMS (CI): Calcd for $C_{19}H_{14}N_3O_4^+$: 348.0984. Found: 348.0980.

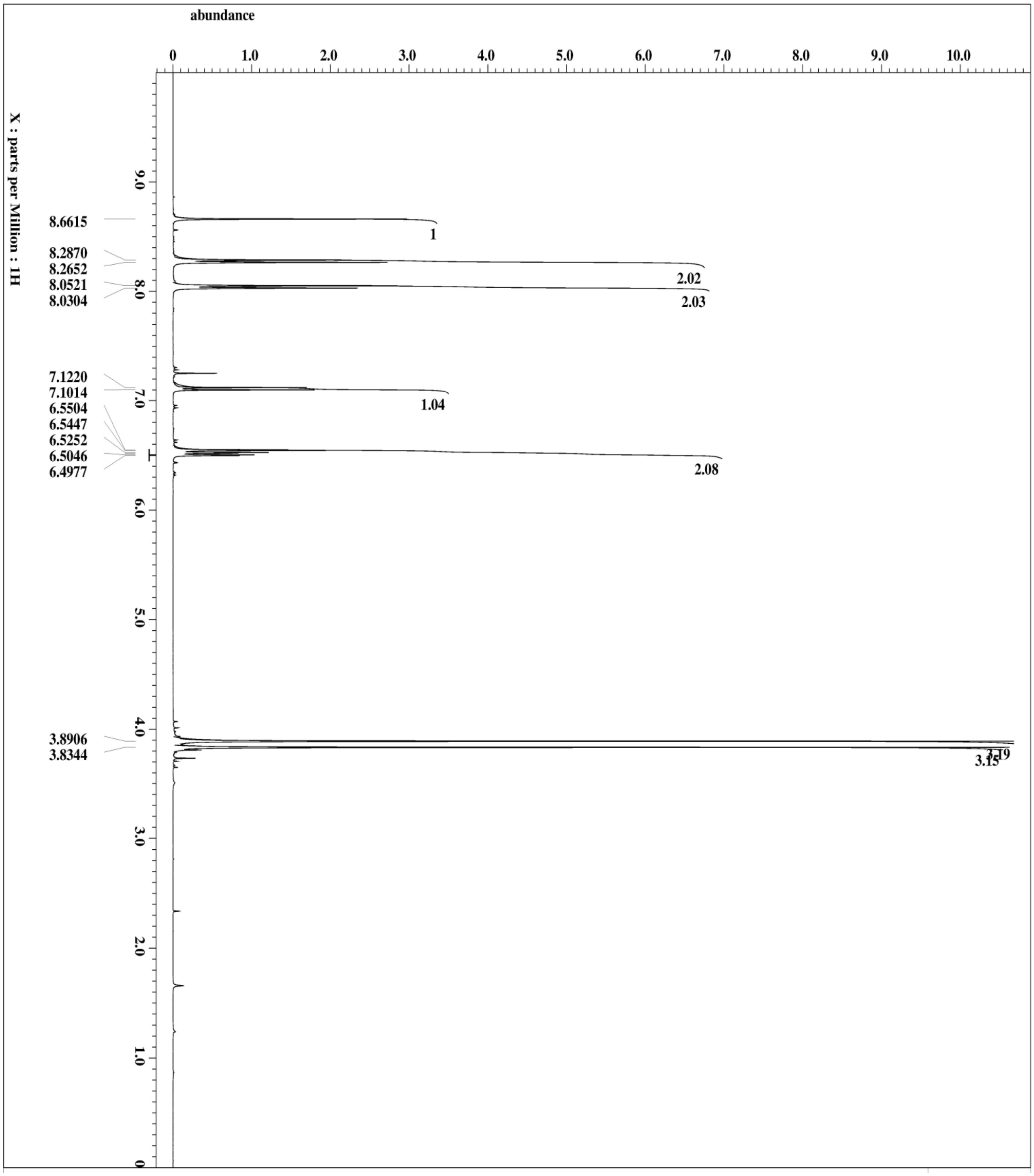
D3: yellow-green powder, mp 112 °C. IR (neat): 1595, 1517, 1476, 1347, 1315, 857, 841, 760, 702 cm^{-1}. ^1H NMR (400 MHz): δ 8.62 (s, 1H), 8.34 (d, $^3J_{H–H}$ = 8.7 Hz, 2H), 8.10 (d, $^3J_{H–H}$ = 8.7 Hz, 2H), 7.65–7.63 (m, 2H), 7.54–7.44 (m, 5H), 7.39–7.35 (m, 1H), 7.25–7.23 (m, 1H) ppm. ^{13}C NMR (100 MHz): δ 157.77, 151.53, 149.42, 142.62, 141.61, 140.63, 129.83, 129.56, 128.97, 127.77, 127.27, 125.93, 124.15, 119.98, 119.72 ppm. HRMS (ESI): Calcd for $C_{19}H_{15}N_2O_2^+$: 303.1128. Found: 303.1128. Anal. calcd for $C_{19}H_{14}N_2O_2$: C,75.48; H, 4.67; N, 9.27 Found: C, 74.58; H, 4.20; N, 9.08.

D4: yellow powder, mp 127 °C. IR (neat): 1627, 1593, 1475, 1408, 1176, 1007, 890, 763, 699 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.57 (s, 1H), 8.00 (d, $^3J_{H–H}$ = 8.2 Hz, 2H), 7.73 (d, $^3J_{H–H}$ = 8.7 Hz, 2H), 7.68–7.64 (m, 4H), 7.50–7.44 (m, 7H), 7.42–7.35 (m, 2H), 7.24–7.21 (m, 1H) ppm. ^{13}C NMR (125 MHz): δ 160.34, 152.71, 144.22, 142.41, 140.97, 140.35, 135.22, 129.68, 129.45, 129.03, 128.91, 128.05, 127.59, 127.31, 124.88, 119.95, 119.75 ppm. HRMS (CI): Calcd for $C_{25}H_{21}N^{2+}$: 335.1674. Found: 335.1670. Anal. calcd for $C_{25}H_{19}N$: C, 90.05; H, 5.74; N, 4.20 Found: C, 89.25; H, 5.23; N, 4.16.

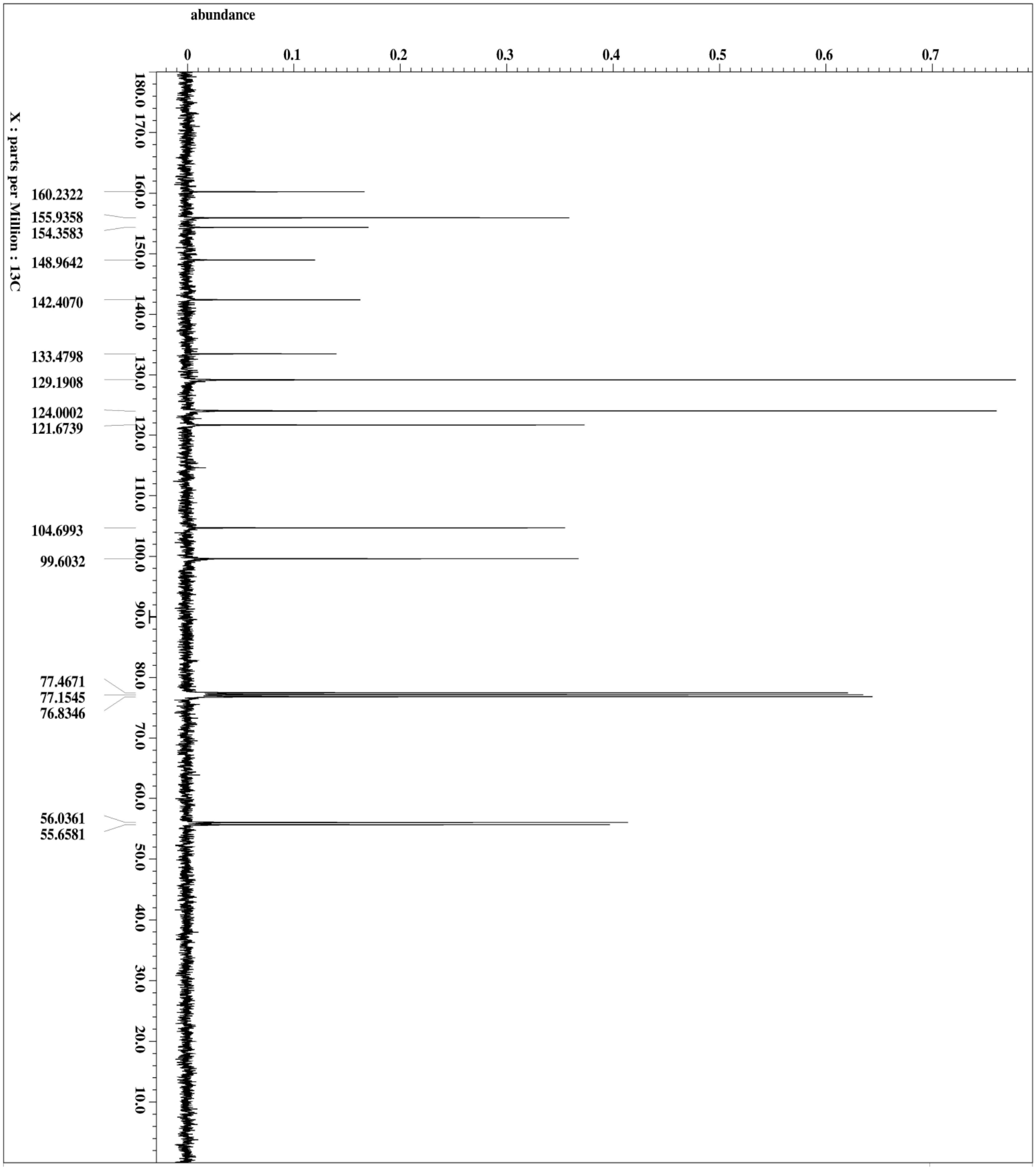
NMR Spectral Data for New Compounds

^{1}H NMR ($CDCl_3$, 400 MHz)

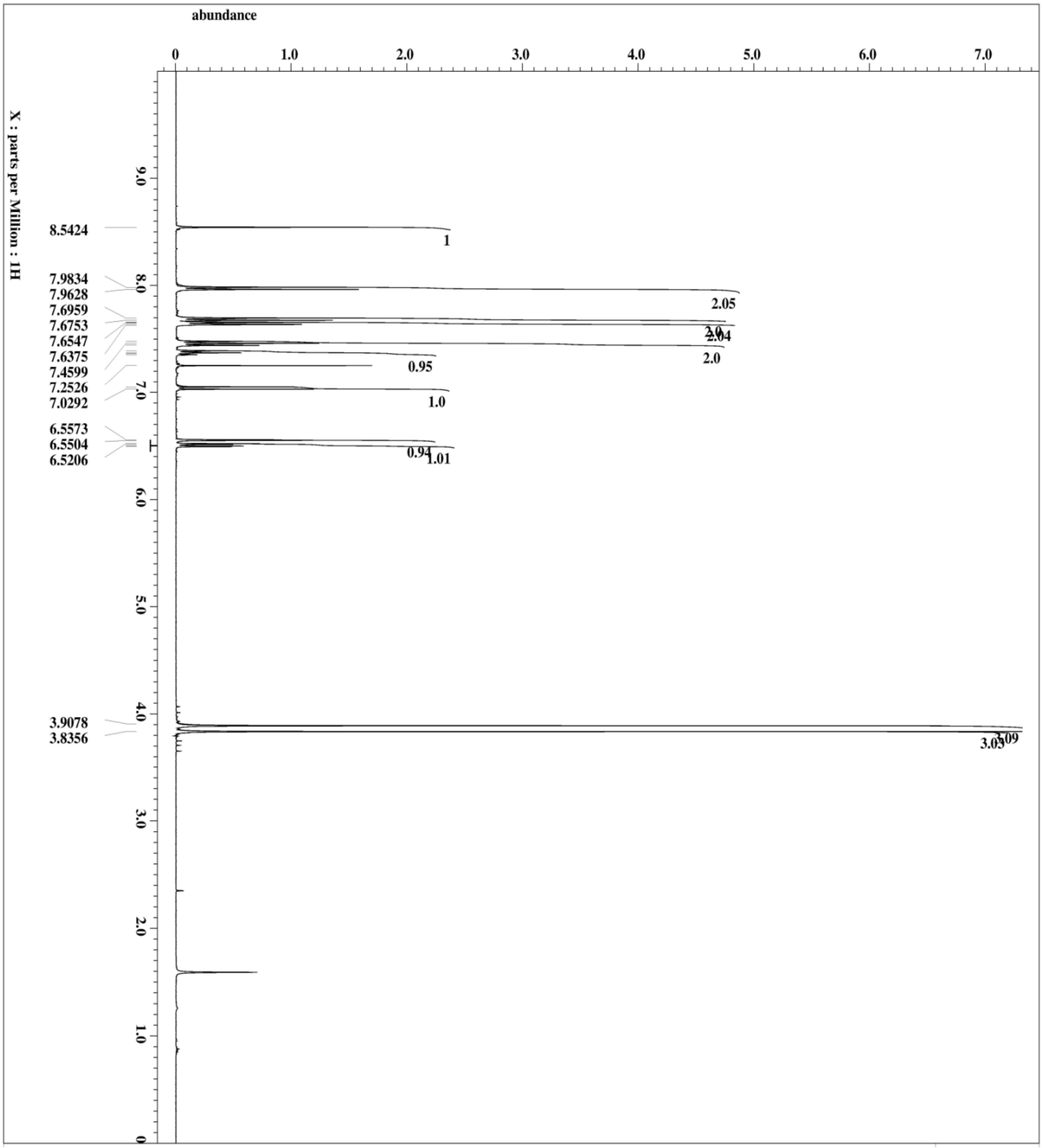
N-(4-nitrobenzylidene)-2,4-dimethoxyaniline (**B3**)



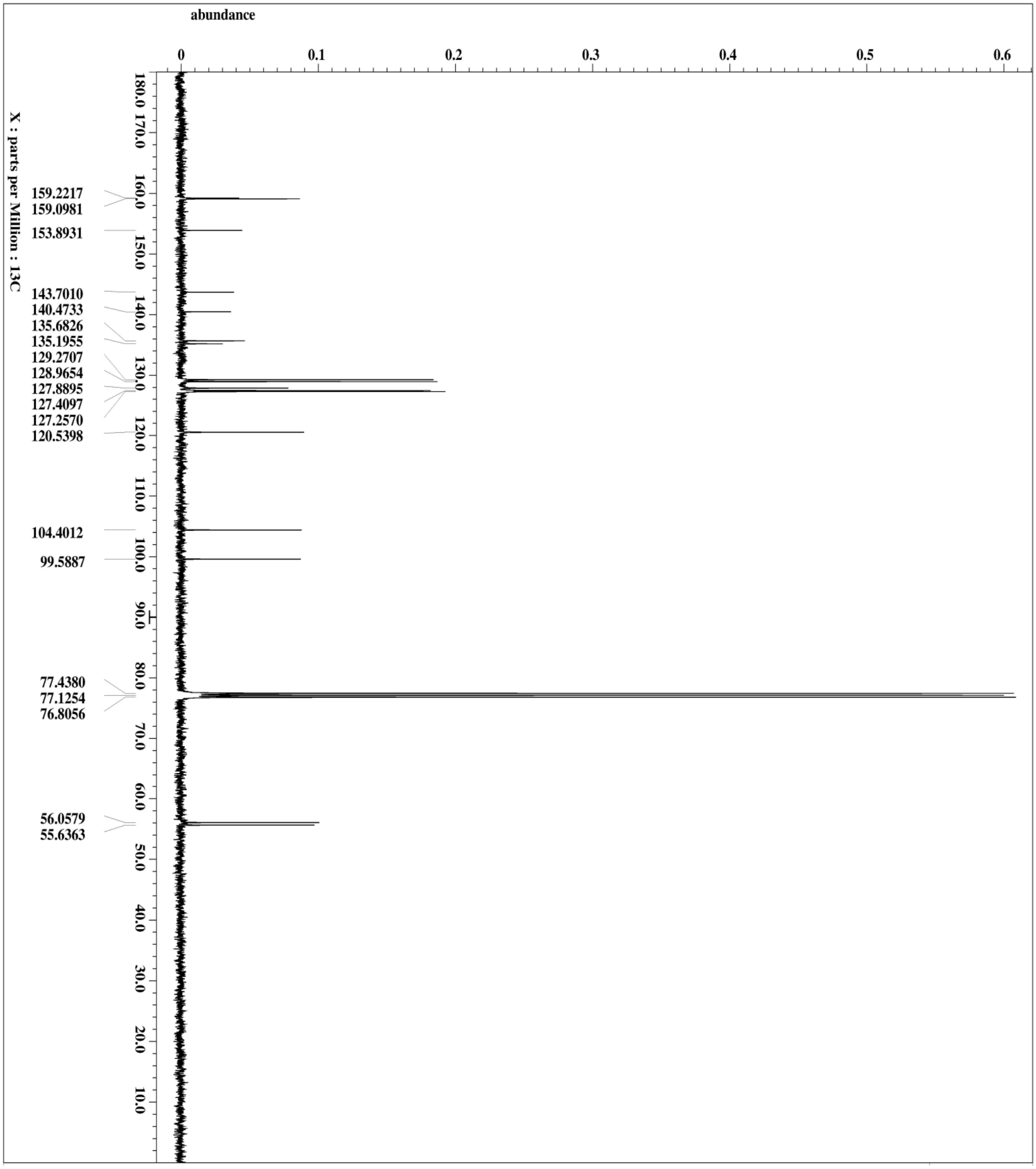
^{13}C NMR (CDCl$_3$, 125 MHz)
N-(4-nitrobenzylidene)-2,4-dimethoxyaniline (**B3**)



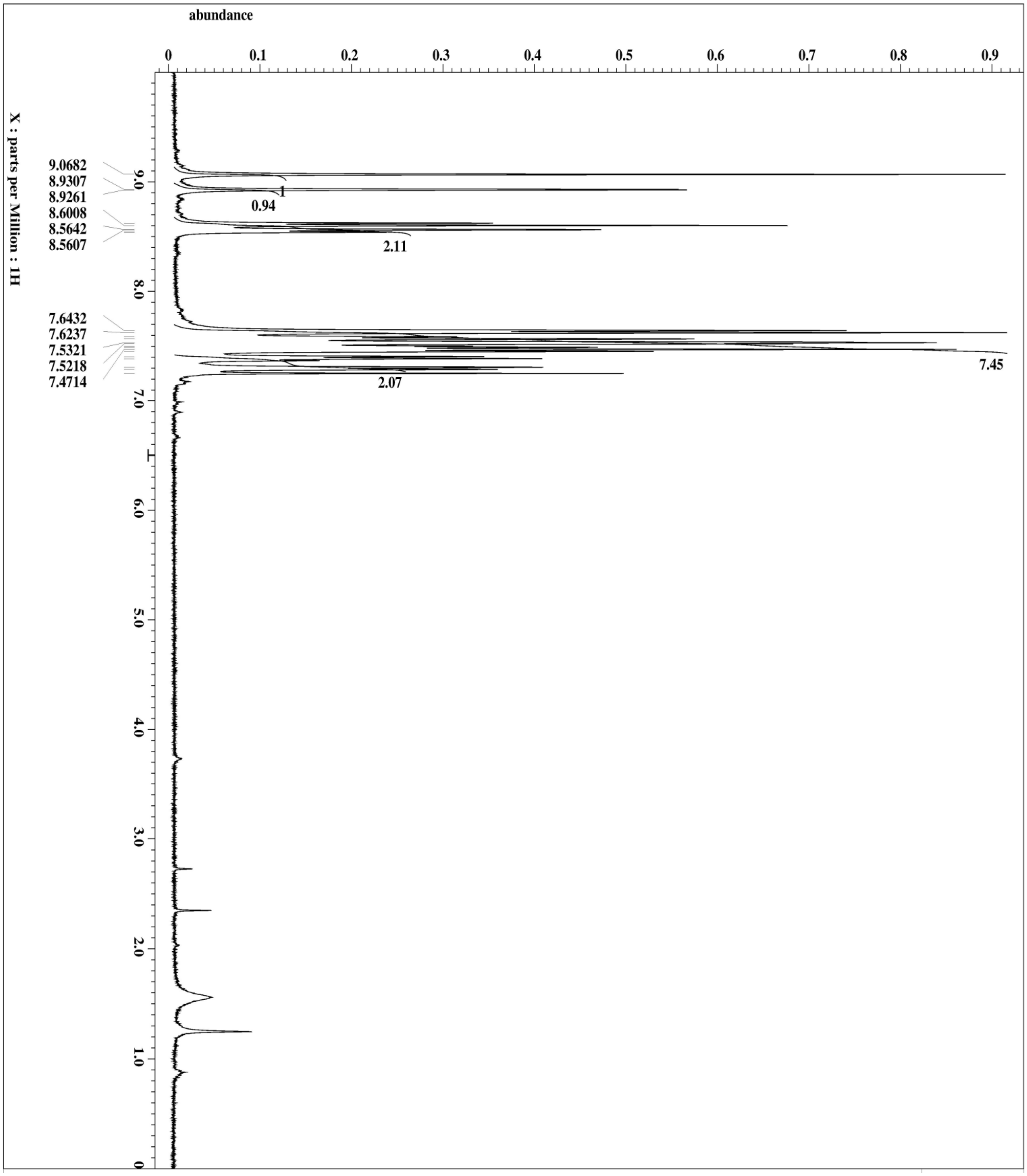
^{1}H NMR (CDCl3, 400 MHz)
N-([1,1'-biphenyl]-4-ylmethylene)-2,4-dimethoxyaniline (**B4)**



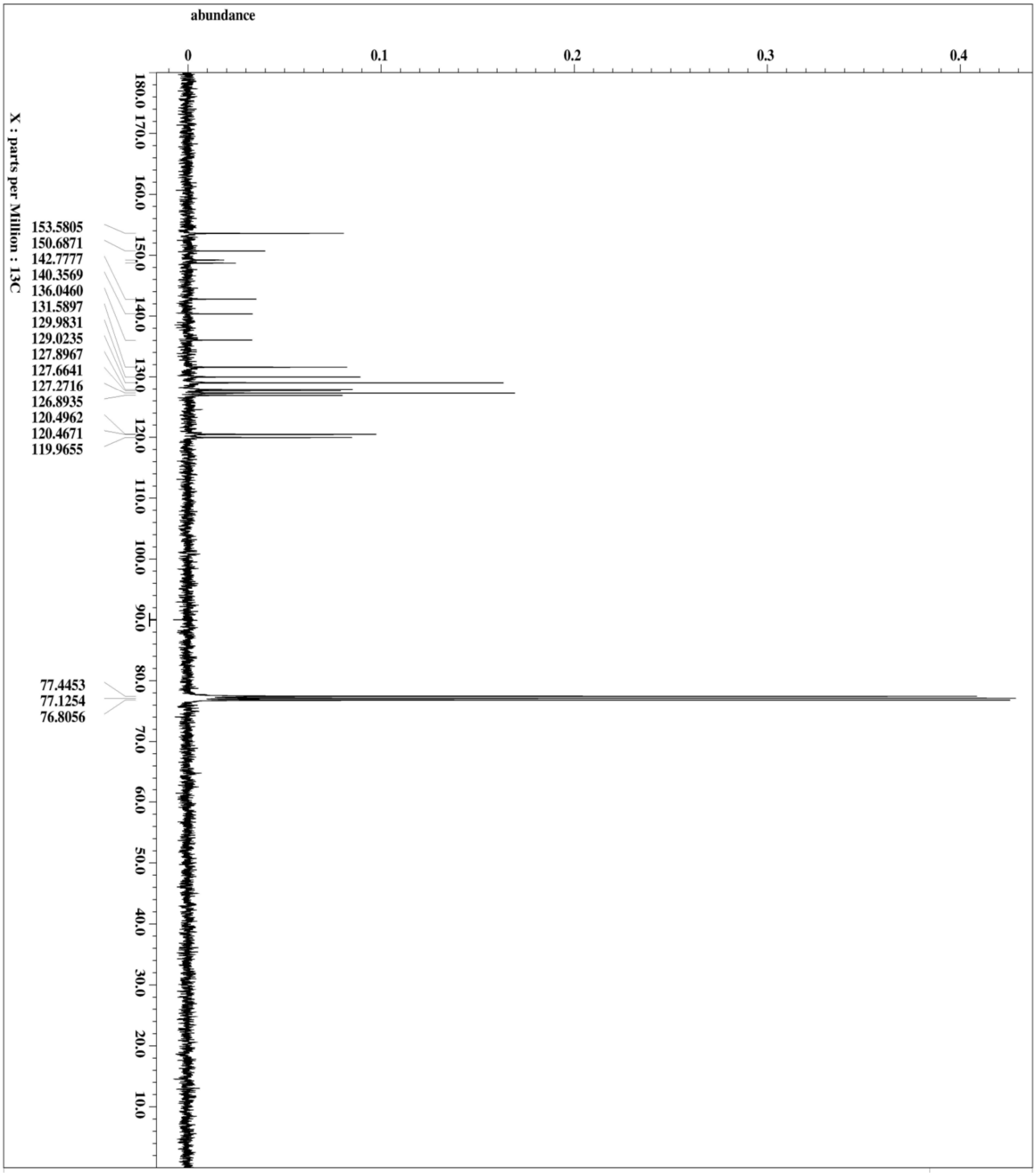
^{13}C NMR ($CDCl_3$, 125 MHz)
N-([1,1'-biphenyl]-4-ylmethylene)-2,4-dimethoxyaniline (**B4)**



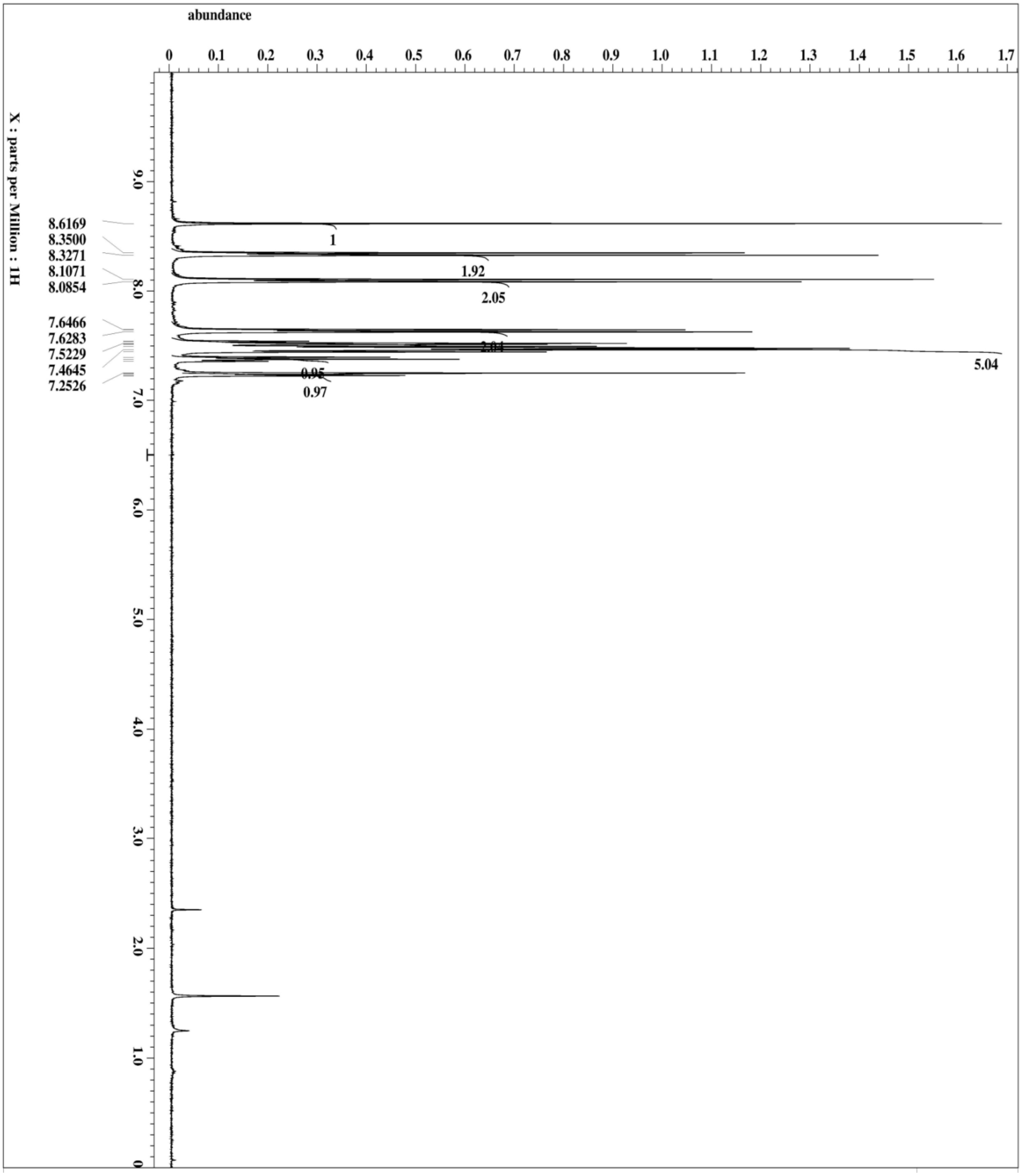
^{1}H NMR (CDCl$_3$, 400 MHz)
N-(2,4-Dinitro-benzylidene)-[1,1'-biphenyl]-3-amine (**D2**)



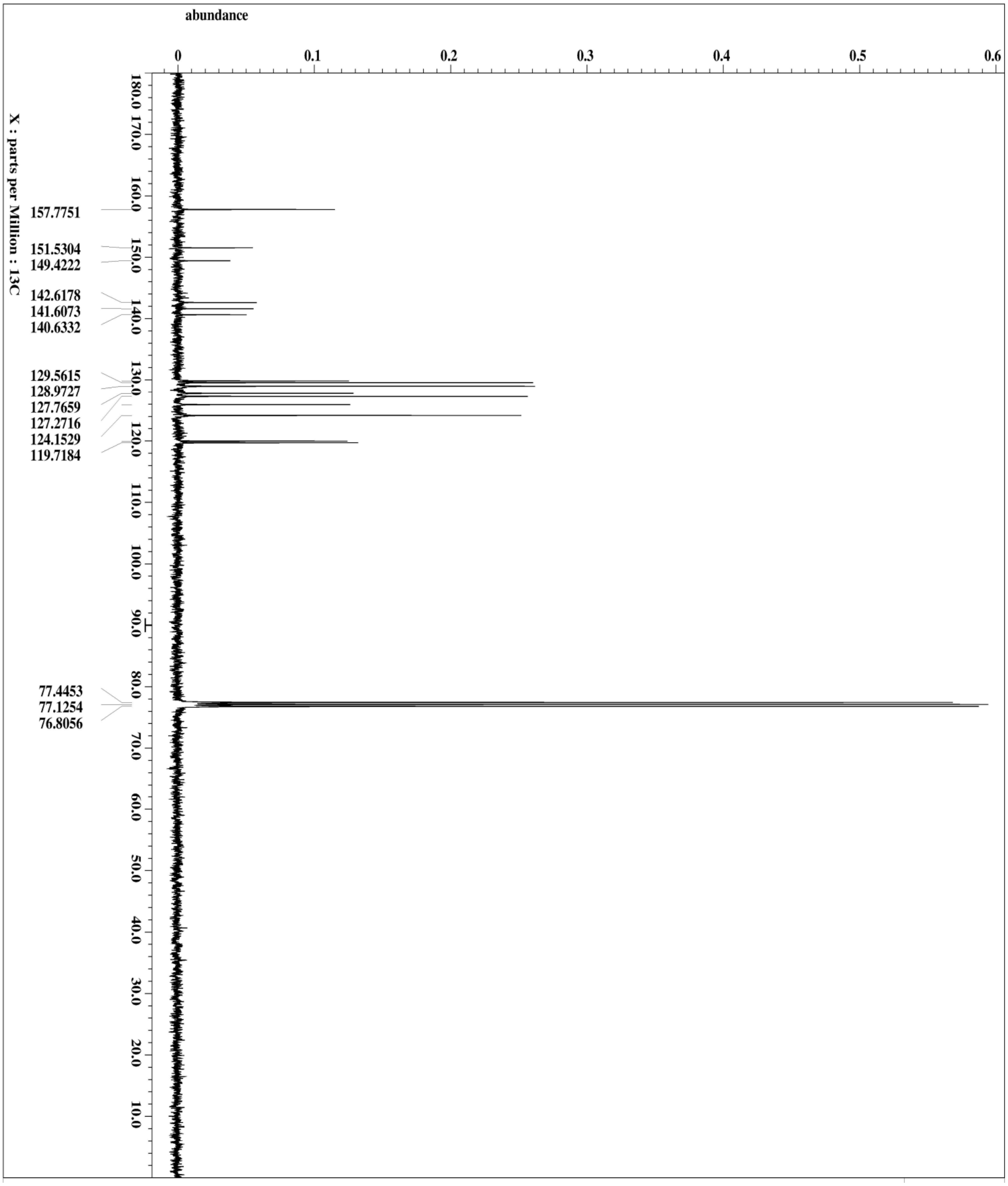
^{13}C NMR (CDCl$_3$, 125 MHz)
N-(2,4-Dinitro-benzylidene)-[1,1'-biphenyl]-3-amine (**D2**)



^{1}H NMR (CDCl$_3$, 400 MHz)
N-(4-nitrobenzylidene)-[1,1'-biphenyl]-3-amine (**D3**)

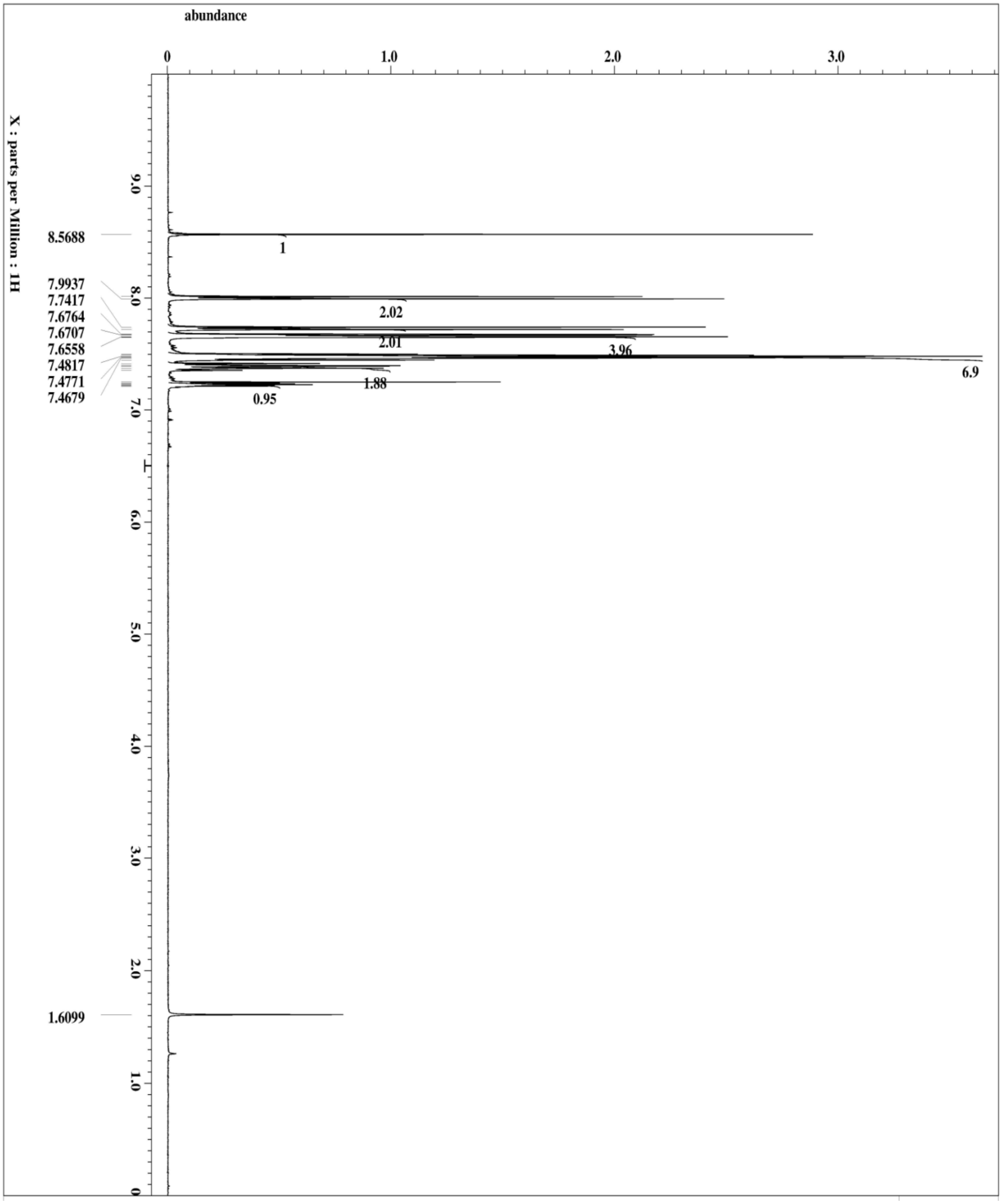


^{13}C NMR ($CDCl_3$, 125 MHz)
N-(4-nitrobenzylidene)-[1,1'-biphenyl]-3-amine (**D3**)



^{1}H NMR ($CDCl_3$, 400 MHz)

N-([1,1'-biphenyl]-4-ylmethylene)-4-[1,1'-biphenyl]-3-amine (**D4**)



^{13}C NMR ($CDCl_3$, 125 MHz)
N-([1,1'-biphenyl]-4-ylmethylene)-4-[1,1'-biphenyl]-3-amine (**D4**)