

An Efficient Diamine•Copper Complex-Catalyzed Coupling of Arylboronic Acids with Imidazoles

(Supporting Information)

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All reagents were used as supplied commercially without further purification except noted otherwise. ^1H NMR spectra were recorded on Varian XL-400 instruments. Mass spectra were measured by the Mass Spectrometry Facility at the University of California at San Francisco.

General Procedure for the N-Arylation of Imidazoles

A mixture of 2 mmol of arylboronic acid (**1**), 1 mmol of substituted imidazole (**3**) and 0.1 mmol of $[\text{Cu}(\text{OH})\cdot\text{TMEDA}]_2\text{Cl}_2$ (**2**) in 4 mL of dry dichloromethane was stirred under an atmosphere of O_2 at rt overnight. The reaction mixture was filtered and the filtrate was concentrated; and then the residue was subjected to preparative chromatography on a silica gel plate using CHCl_3 /hexanes (flushed with NH_3 gas) as the eluent to give N-arylimidazole (**4**).

N-phenylimidazole (4a): ^1H NMR (CDCl_3): δ 7.84 (s, 1H), 7.43-7.47 (m, 2H), 7.32-7.37 (m, 3H), 7.26 (s, 1H), 7.19 (s, 1H) ppm; MS (m/z): 144(M^+ , 100), 117, 90, 77, 69, 57; HRMS calcd. for $\text{C}_9\text{H}_8\text{N}_2$ (M^+) 144.069, found 144.069.

N-(4-methyl-1-phenyl)imidazole (4b): ^1H NMR (CDCl_3): δ 7.86 (s, 1H), 7.28 (s, 3H), 7.63 (s, 2H), 7.21 (s, 1H), 2.41 (s, 3H) ppm; ^1H NMR (CD_3CN): δ 8.44(s, 1H), 7.96 (s, 1H), 7.93 (d, $J=8.0$ Hz, 2H), 7.85 (d, $J=8.0$ Hz, 2H), 2.92 (s, 3H) ppm; MS (m/z): 158(M^+ ,100), 131, 104, 91, 77, 65, 57; HRMS calcd. for $\text{C}_{10}\text{H}_{10}\text{N}_2$ (M^+) 158.084, found 158.084.

N-(2-methyl-1-phenyl)imidazole (4c): ^1H NMR (CDCl_3): δ 7.61 (s, 1H), 7.21-7.36 (m, 5H), 7.07 (s, 1H), 2,19 (s, 3H) ppm; MS (m/z):158(M^+), 130, 107, 91, 83, 69(100); HRMS calcd. for $\text{C}_{10}\text{H}_{10}\text{N}_2$ (M^+) 158.084, found 158.084.

N-(4-fluoro-1-phenyl)imidazole (4d): $^1\text{H NMR}$ (CDCl_3): δ 7.79 (s, 1H), 7.33-7.36 (m, 2H), 7.14-7.21 (m, 4H) ppm; MS (m/z): 162 (M^+ , 100), 141, 135, 129, 108, 95, 83, 71, 57; HRMS calcd for $\text{C}_9\text{H}_7\text{FN}_2$ (M^+): 162.059; found: 162.059.

N-(4-methoxy-1-phenyl)imidazole (4e): $^1\text{H NMR}$ (CDCl_3): δ 7.78 (s, 1H), 7.31 (d, $J=8.0$ Hz, 2H), 7.20 (d, $J=8.0$ Hz, 2H), 7.00 (s, 1H), 6.98 (s, 1H), 3.85 (s, 3H) ppm; MS (m/z): 174 (M^+ , 100), 159, 147, 132, 120, 104, 92, 77, 63; HRMS calcd for $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}$ (M^+): 174.079; found: 174.079.

N-(2-methoxy-1-phenyl)imidazole (4f): $^1\text{H NMR}$ (CDCl_3): δ 7.82 (s, 1H), 7.37 (td, $J=7.7, 1.6$ Hz, 1H), 7.29 (dd, $J=7.7, 1.6$ Hz, 1H), 7.22 (s, 1H), 7.19 (s, 1H), 7.02-7.07 (m, 2H), 3.86 (s, 3H) ppm; MS (m/z): 174 (M^+), 159, 143, 107(100), 65, 43; HRMS calcd for $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}$ (M^+): 174.079; found: 174.079.

N-(4-methyl-1-phenyl)-2-methylimidazole (4g): $^1\text{H NMR}$ (CDCl_3): δ 7.27 (d, $J=7.9$ Hz, 2H), 7.17 (d, $J=7.9$ Hz, 2H), 7.02 (s, 1H), 6.98 (s, 1H), 2.42 (s, 3H), 2.35 (s, 3H) ppm; MS (m/z): 172 (M^+), 144, 131, 119, 104, 97, 91, 83, 69(100), 57; HRMS calcd for $\text{C}_{11}\text{H}_{12}\text{N}_2$ (M^+): 172.100; found: 172.100.

Mixture of N-(2-methyl-1-phenyl)-4(5)-methylimidazole (4h+4h'): $^1\text{H NMR}$ (CDCl_3): δ 7.48 and 7.45 (s, 1H), 7.16-7.38 (m, 4H), 6.93 and 6.77 (s, s, 1H), 2.32 and 2.05 (s, s, 3H), 2.20 and 1.99 (s, s, 3H) ppm; MS (m/z): 172 (M^+), 111, 97, 83, 69, 57(100); HRMS calcd for $\text{C}_{11}\text{H}_{12}\text{N}_2$ (M^+): 172.100; found: 172.100.

Mixture of N-(2-methyl-1-phenyl)-4(5)-phenylimidazole (4i+4i'): $^1\text{H NMR}$ (CDCl_3): δ 7.84-7.86 (m, 2H), 7.62 and 7.65 (s, s, 1H), 7.09-7.43 (m, 8H), 2.26 and 1.93 (s, s, 3H) ppm; MS (m/z): 235 (M^++1), 234 (M^+), 233 (M^+-1), 206, 130(100), 117, 104, 91, 77, 65; HRMS calcd for $\text{C}_{16}\text{H}_{14}\text{N}_2$ (M^+): 234.116; found: 234.116.

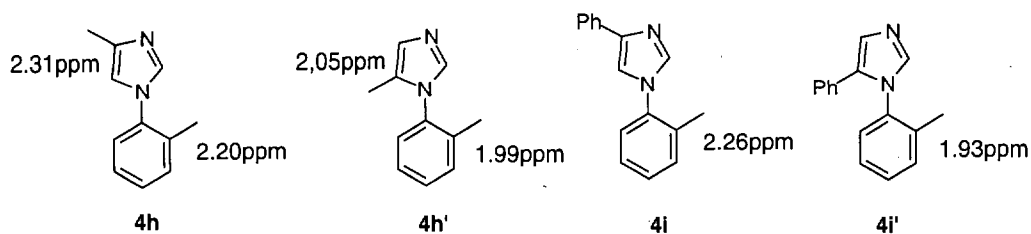
N-(4-methyl-1-phenyl)benzimidazole (4j): $^1\text{H NMR}$ (CDCl_3): δ 8.10 (s, 1H), 7.87-7.89 (m, 1H), 7.50-7.53 (m, 1H), 7.32-7.41 (m, 6H), 2.46 (s, 3H) ppm; MS (m/z): 209 (M^++1), 208 (M^+), 207 (M^+-1), 192, 180, 166, 152, 104, 91(100), 77, 65; HRMS calcd for $\text{C}_{14}\text{H}_{12}\text{N}_2$ (M^+): 208.100; found: 208.100.

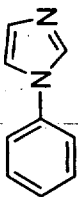
N-(4-methoxy-1-phenyl)benzimidazole (4k): $^1\text{H NMR}$ (CDCl_3): δ 8.06 (s, 1H), 7.86-7.88 (m, 1H), 7.45-7.47 (m, 1H), 7.41 (d, $J=9.0$ Hz, 2H), 7.30-7.33 (m, 2H), 7.06 (d, $J=9.0$ Hz, 2H), 3.88

(s, 3H) ppm; MS (m/z): 224(M⁺, 100), 209, 192, 181, 154, 128, 112, 102, 92, 77, 64; HRMS calcd for C₁₄H₁₂N₂O(M⁺): 224.095; found: 224.095.

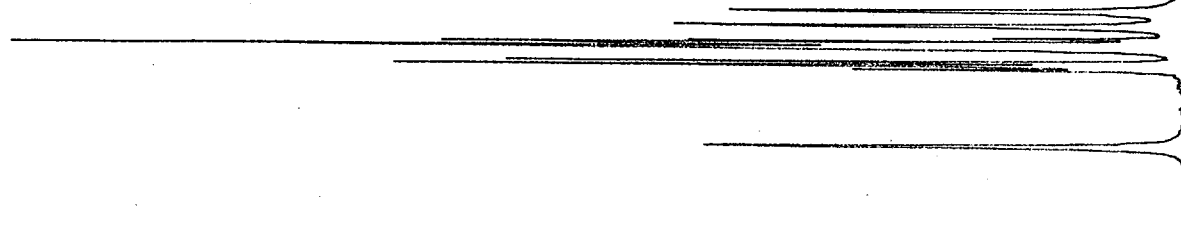
Ratio-Determination of the two pairs of isomers of N-(2-methyl-1-phenyl)-4(5)-phenylimidazole and N-(2-methyl-1-phenyl)-4(5)-methylimidazole

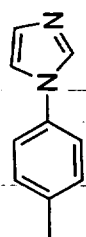
Ratios of the two pairs of N-arylimidazole isomers can be easily determined by the comparison of the respective methyl peaks in their ¹H NMR spectra using CDCl₃ as the solvent. Chemical shifts of methyl groups of these isomers are listed as follows.



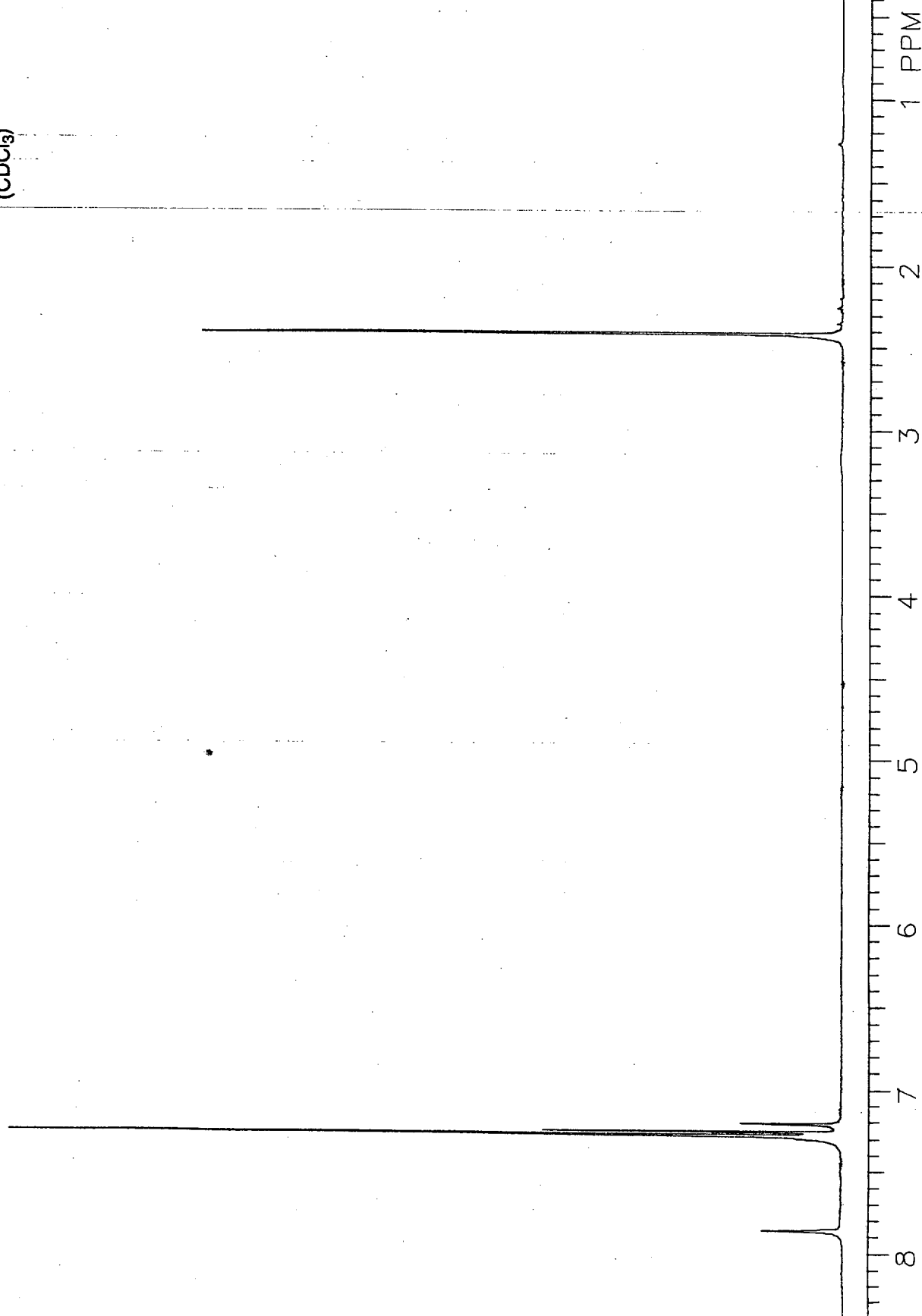


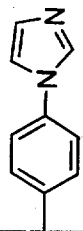
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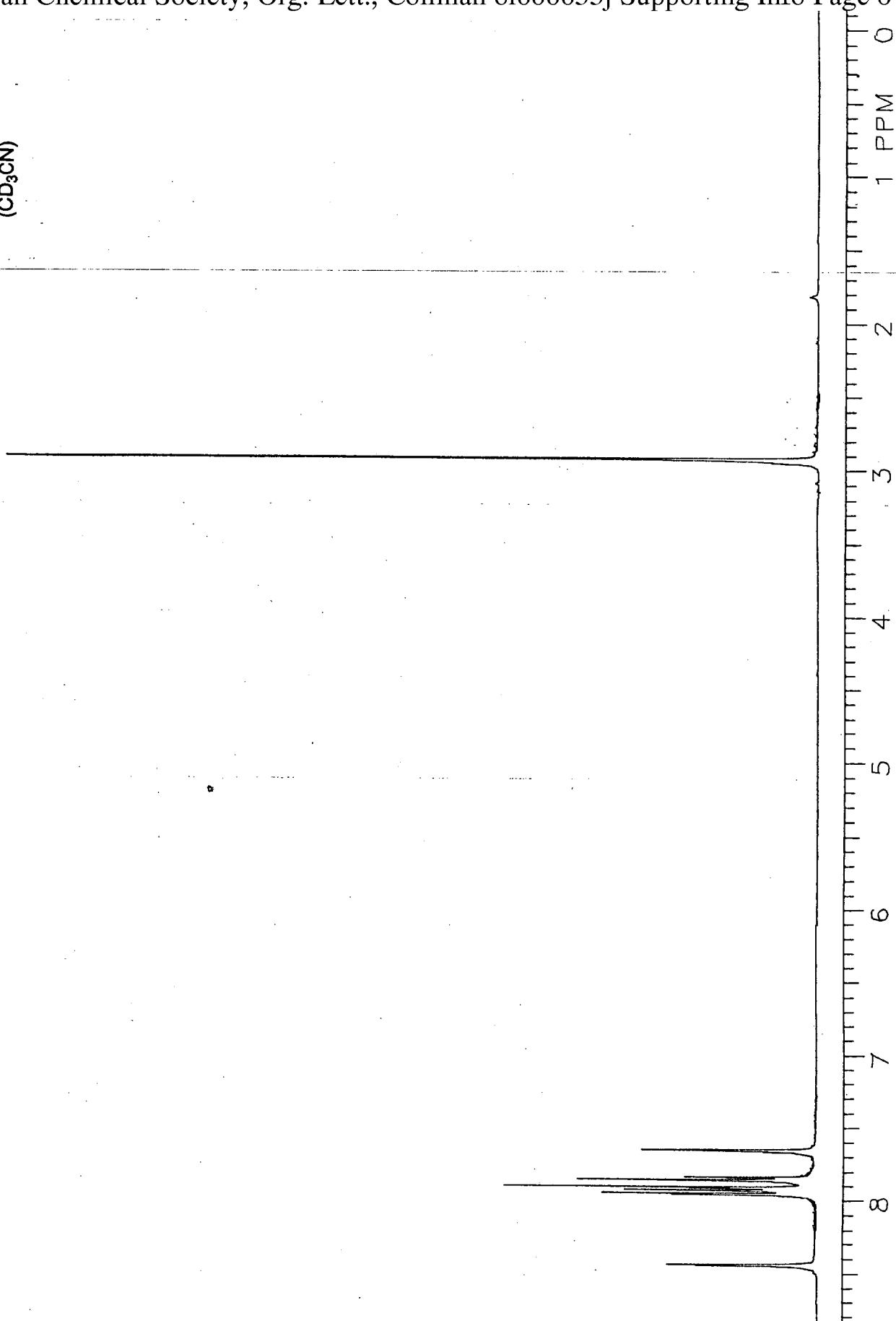


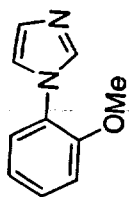
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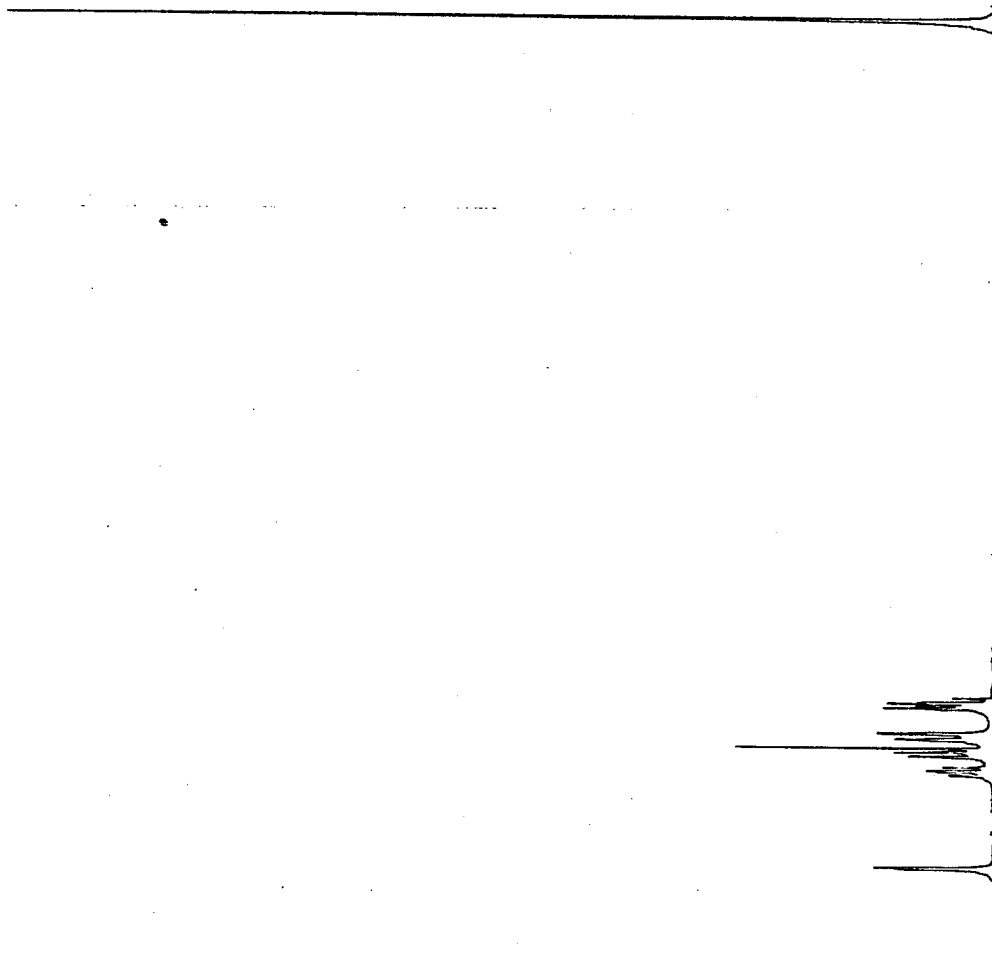


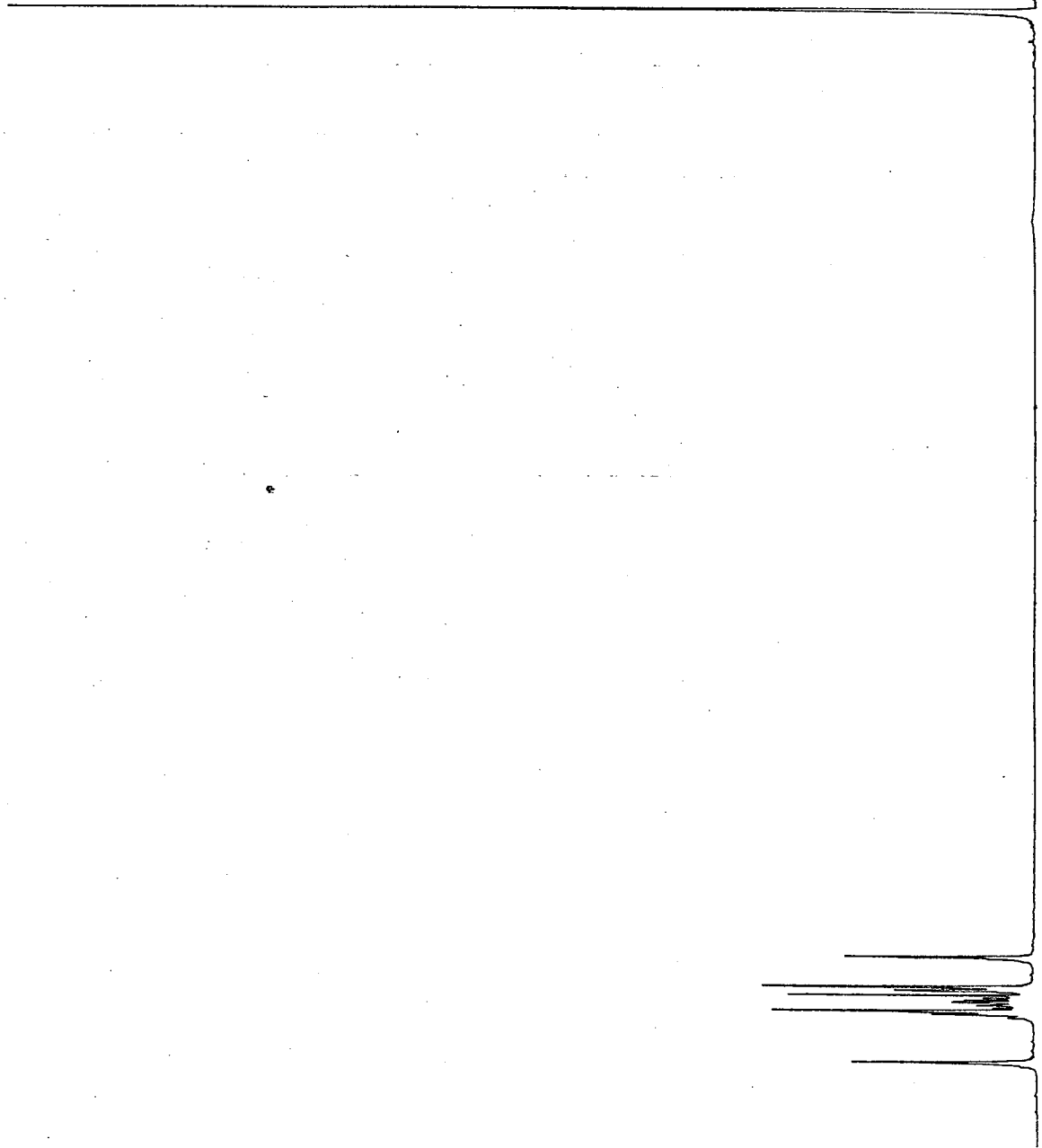
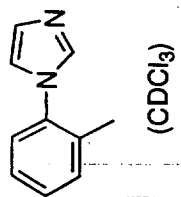
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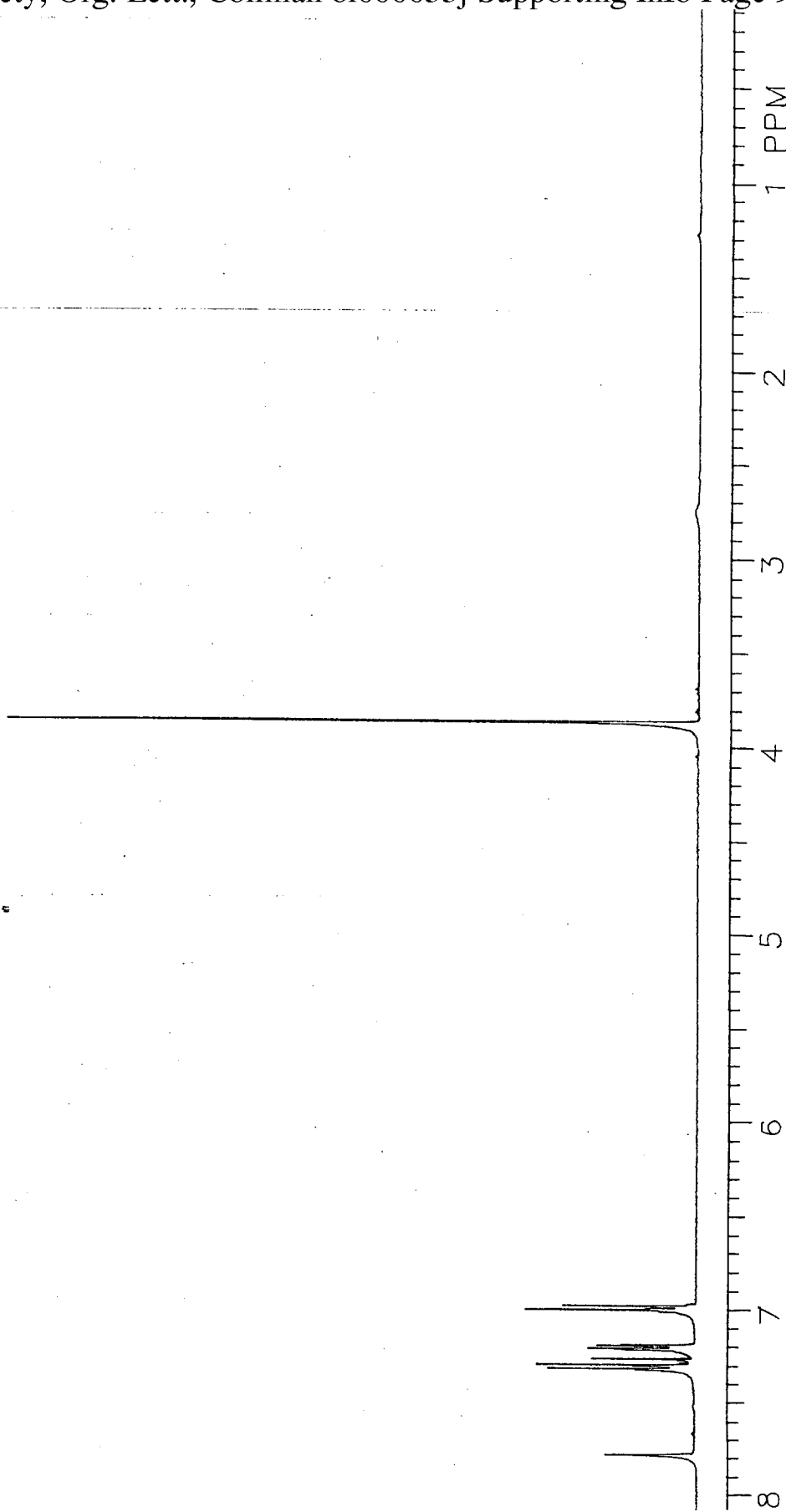
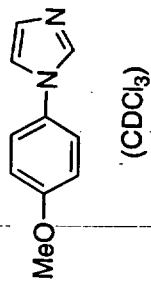


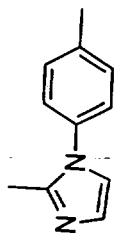
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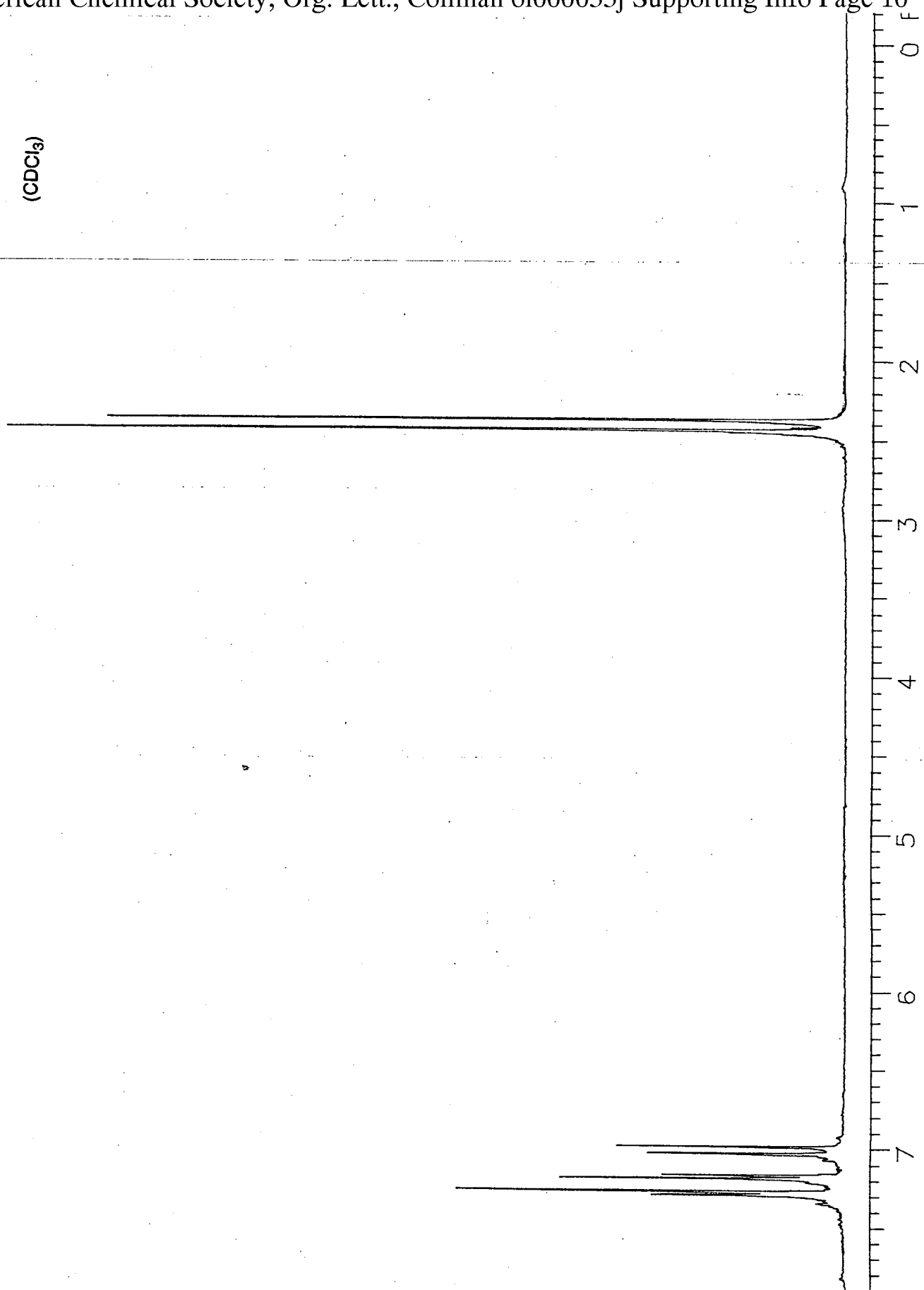


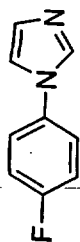
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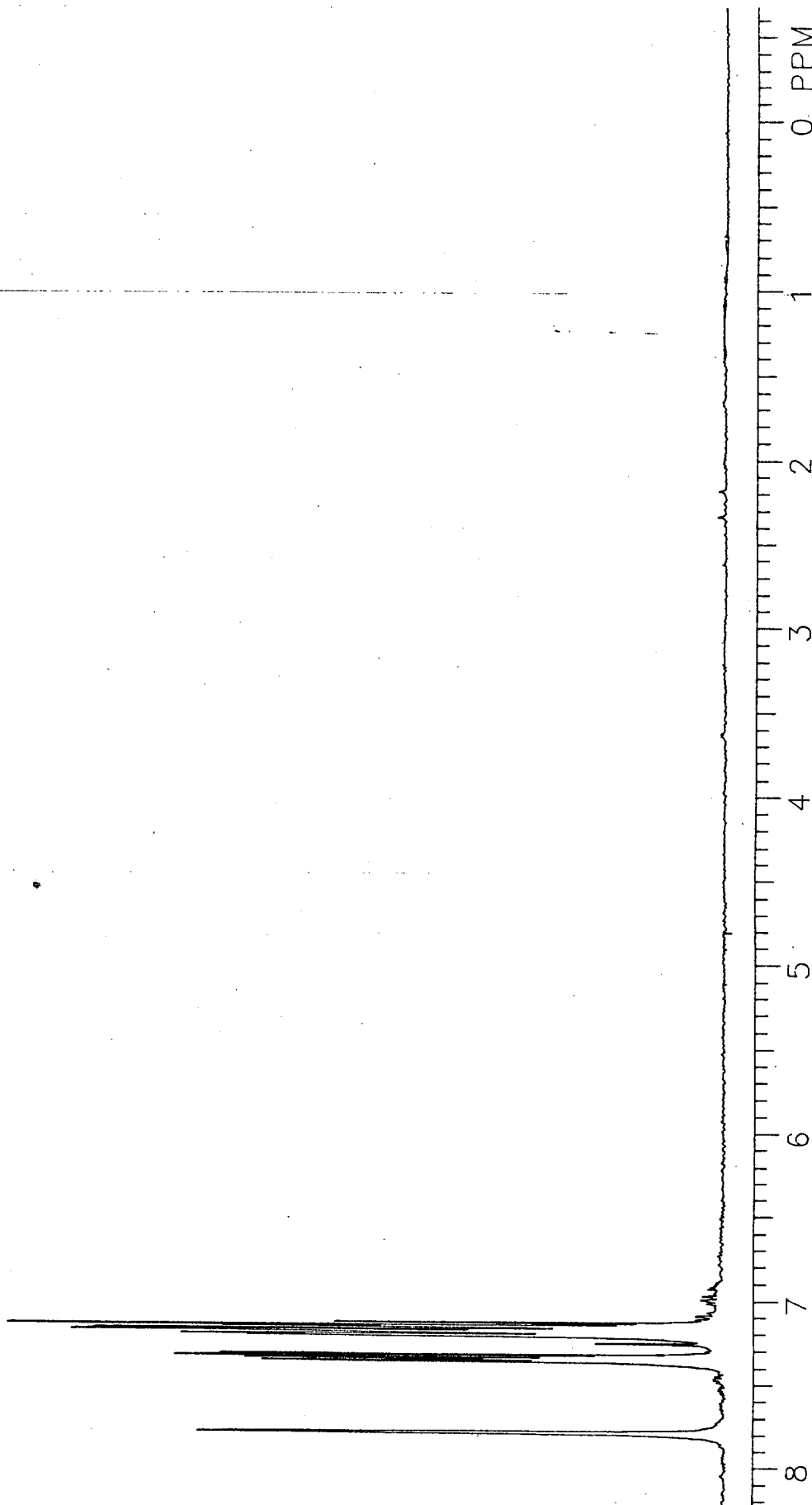


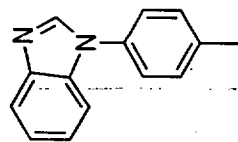
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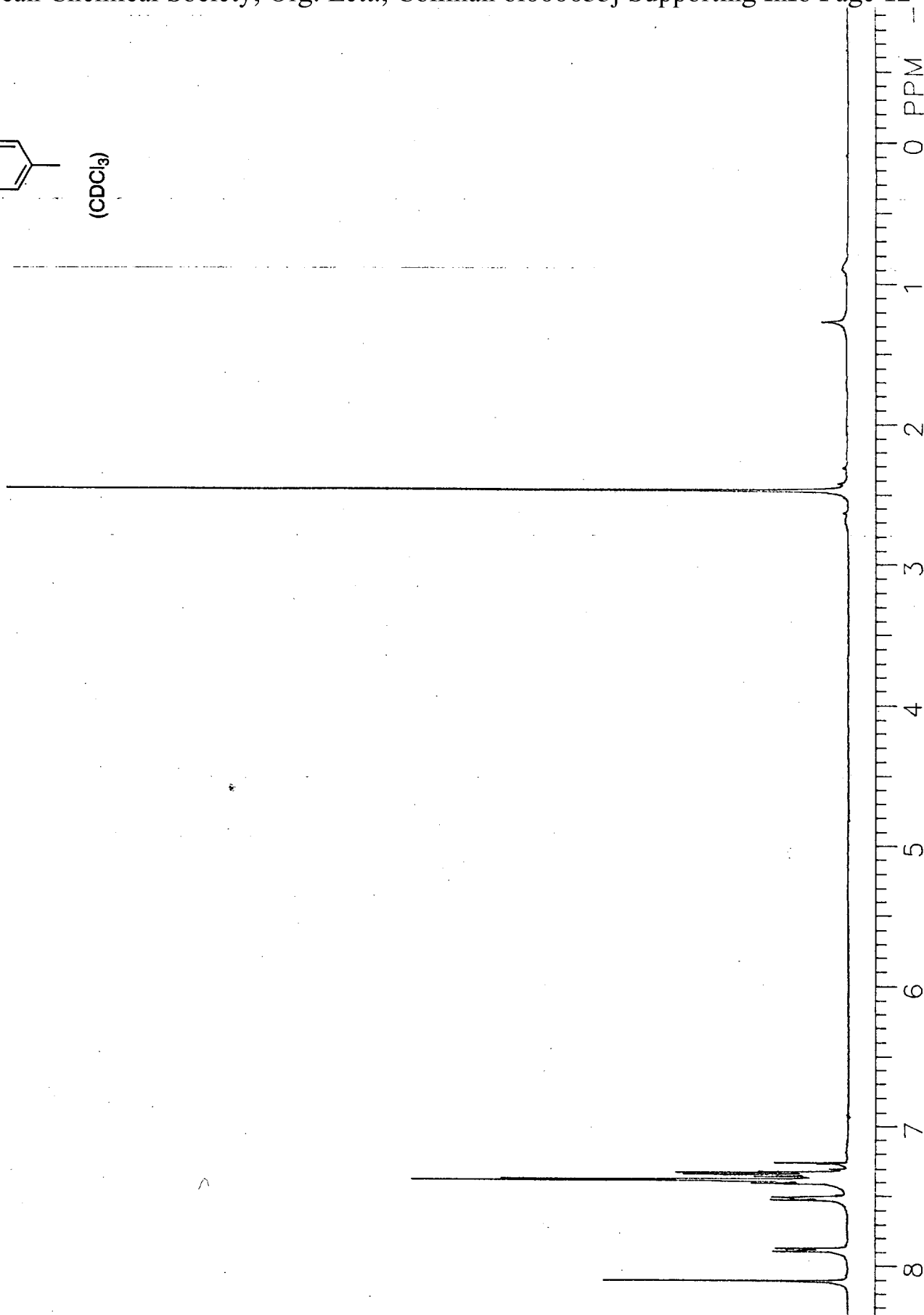


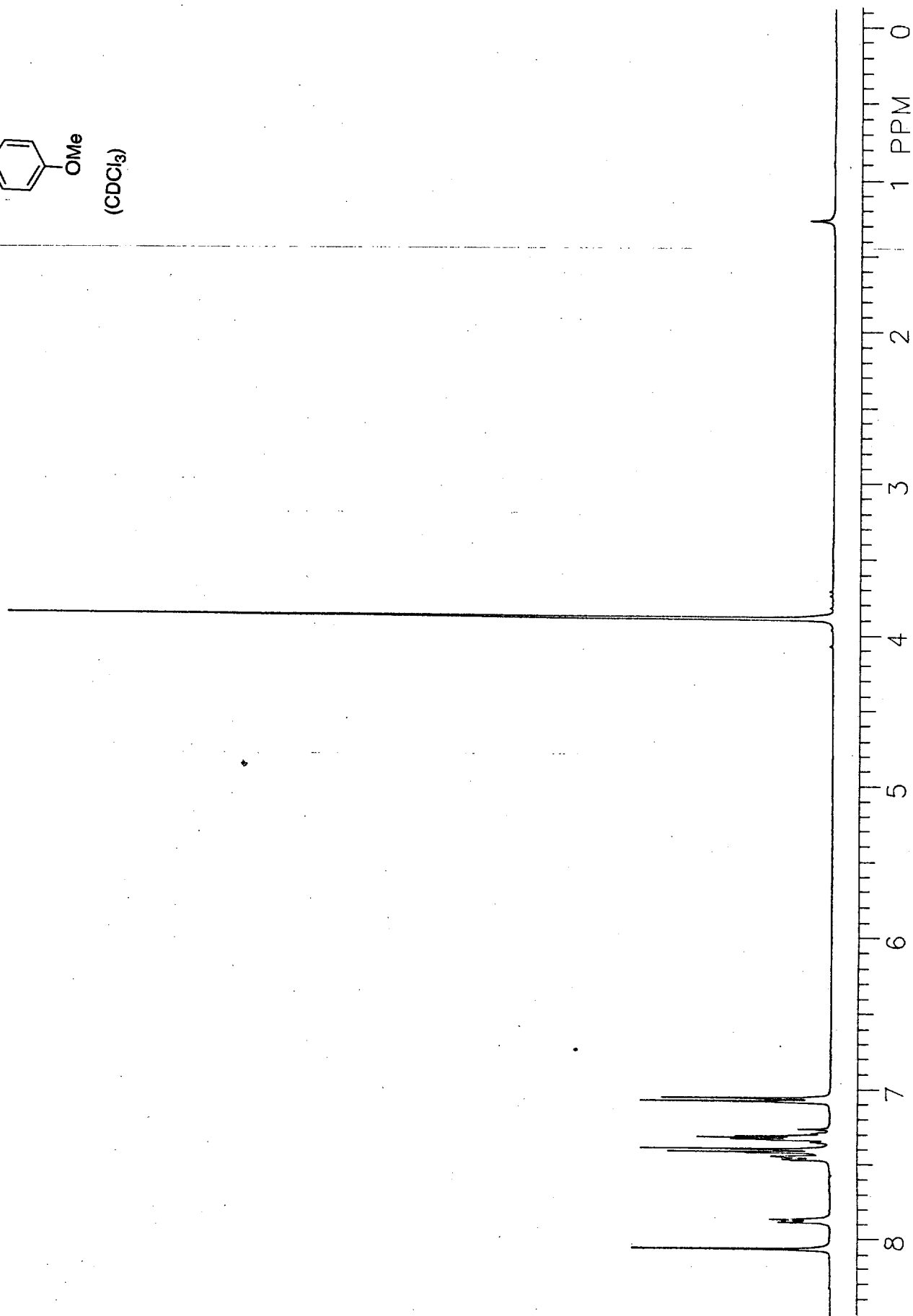
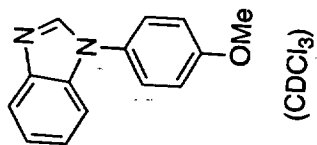
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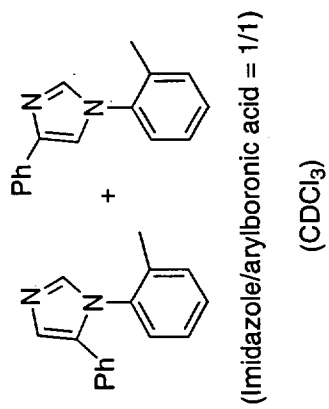




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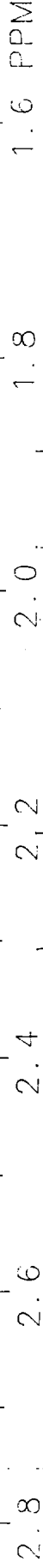


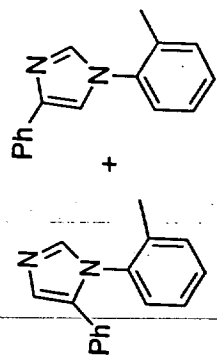




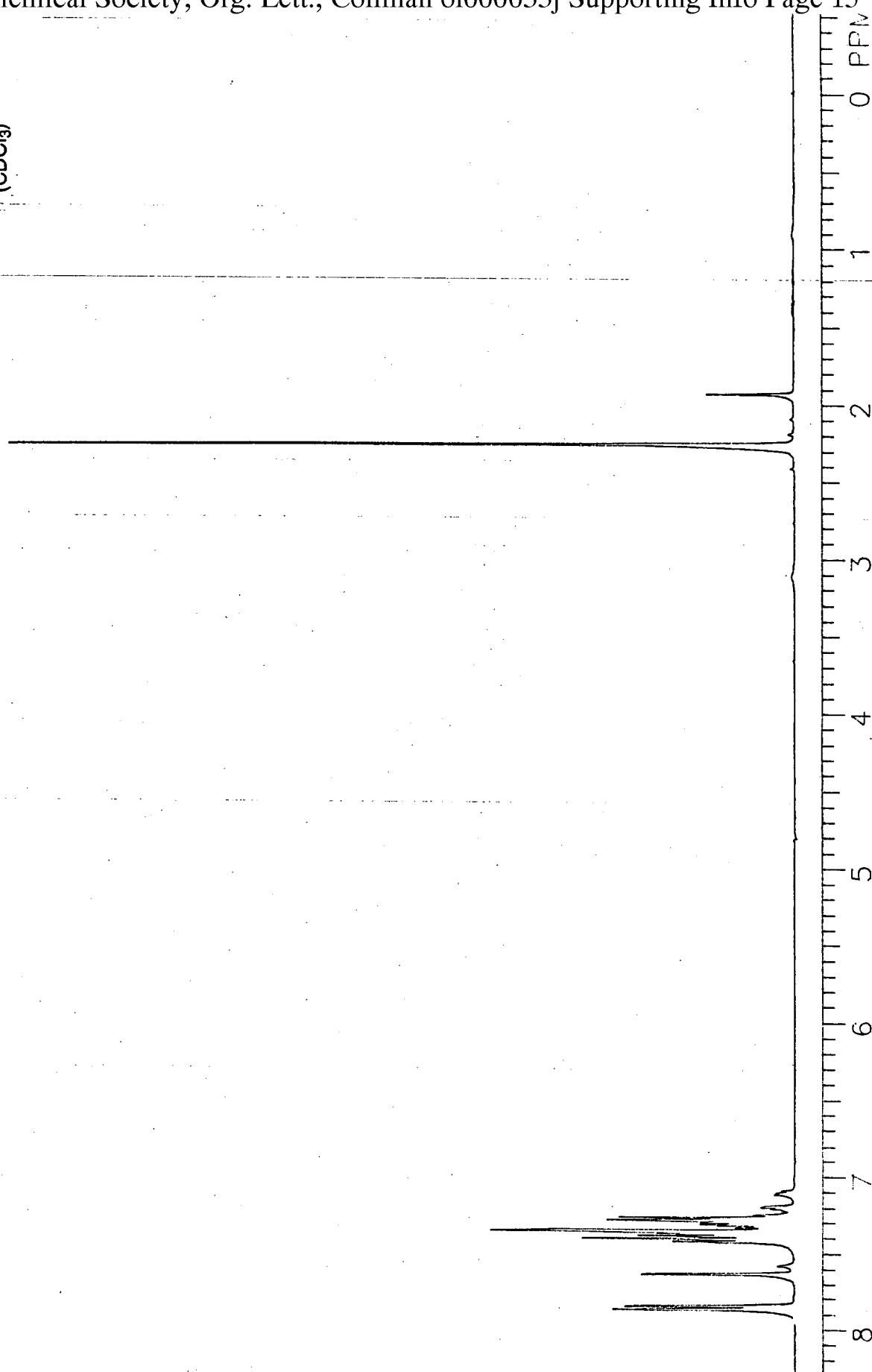
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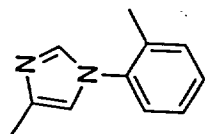
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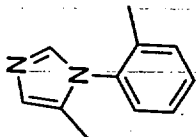


(CDCl₃)





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(CDCl₃)

