

Supporting Information

Efficient Pd(II)-Catalyzed Regioselective Ortho-halogenation of Arylcyanamide

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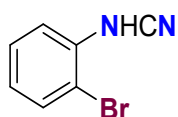
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	Contents	Page
1	General Information	S1
2	Preparation of Deuterated bromocyanamide	S2
3	Characterization Data of the Products and References	S2-S11
4	Scans of ¹ H and ¹³ C NMR Spectra	S12-S76

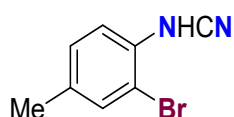
General Information: PdCl₂(98%), CuCl₂(98%), Pd(OAc)₂(98%), NBS, CH₃CN, Toluene, THF, DME, DCE, BHT, CH₃COOAg, TFA, 4-*t*-BuPhenol, PTSA, were procured from Aldrich and utilized with no further purification. The solvents were dried according to the standard processes before use. Varian (400 MHz) spectrometer was employed to record ¹H and ¹³C NMR spectra. Infrared (IR) spectra recorded on a Perkin Elmer Spectrum One FT-IR spectrometer. In the experimental procedure, a VKSI Medico Centrifuge machine was used for the synthesis of substituted 2-halo arylcyanamide

Preparation of Deuterated bromocyanamide:

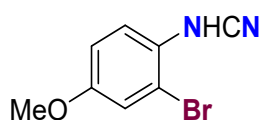
Duetero Phenylcyanamide was completely dissolved in DCE (3 mL) at room temperature. To the reaction mixture Pd(OAc)₂ (5 mol %, 11.2 mg), NBS (1 mmol), BHT (3 mmol, 660 mg) were added consecutively at room temperature and stirring was continued for 0.5 h. Then the reaction temperature rises to 80 °C and stirred for 8 h. After completion of the reaction (monitored by TLC), to separate the organic layer the reaction mixture was washed with water (3 X 5 mL) and brine solution (3 X 5 mL). A Rotary evaporator was used to concentrate the clear organic layer and the crude mixture was purified by silica gel (60-120 mesh) column chromatography using ethylacetate in hexane as eluent to afford the brominated cyanamide as solid.



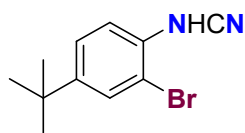
2-Bromophenylcyanamide 2a:^{1,3}White solid;Analytical TLC on silica gel, 1:10 ethyl acetate/hexane $R_f = 0.8$; yield 91%;mp 144-145 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.33 (m, 2H), 6.81 (d, $J = 8.4$ Hz, 1H), 6.72-6.67 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 139.6, 137.9, 130.3, 128.6, 121.0, 118.9, 114.7;FT-IR (KBr) 3423, 3048, 2217, 1656, 1578, 1490, 1438, 1409, 1288, 1261, 1078, 1023, 823. Anal. Calcd. for C₇H₅BrN₂: C, 42.67; H, 2.56; Br, 40.55; N, 14.22. Found: C, 42.90; H, 2.54; N, 14.14.



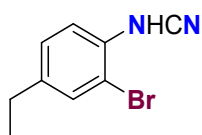
2-Bromo-4-methylphenylcyanamide 2b:White solid;Analytical TLC on silica gel, 1:19 ethyl acetate/hexane $R_f = 0.8$; yield 94%;mp 147-148 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.33 (s, 1H), 7.14-7.05 (m, 2H), 5.33 (br s, 1H, 1NH), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 139.4, 137.4, 133.6, 133.1, 123.4, 121.4, 115.5, 20.6; FT-IR (KBr) 3368, 3077, 2951, 2212, 1599, 1533, 1441, 1287, 1205, 823 cm⁻¹. Anal. Calcd. for C₈H₇BrN₂: C, 45.53; H, 3.34; Br, 37.86; N, 13.27. Found: C, 45.85; H, 3.30; N, 13.16.



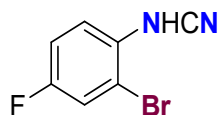
2-Bromo-4-methoxyphenylcyanamide 2c: White solid; Analytical TLC on silica gel, 1:10 ethyl acetate/hexane $R_f = 0.7$; yield 95%; mp 151-152 °C; ^1H NMR (400 MHz, DMSO) δ 7.17 (d, $J = 10.4$ Hz, 1H), 7.15-6.83 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.6, 138.4, 136.7, 132.7, 116.4, 115.6, 115.0, 55.5; FT-IR (KBr) 3412, 3033, 2898, 2225, 1602, 1583, 1491, 1287, 1146, 1027, 826 cm^{-1} . Anal. Calcd. for $\text{C}_8\text{H}_7\text{BrN}_2\text{O}$: C, 42.32; H, 3.11; Br, 35.19; N, 12.34; O, 7.05. Found: C, 42.60; H, 3.08; N, 12.25.



4-tert-Butyl-2-bromophenylcyanamide 2d: White solid; Analytical TLC on silica gel, 1:10 ethyl acetate/hexane $R_f = 0.8$; yield 87%; mp 144-145 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.30 (s, 1H), 7.03 (d, $J = 8.0$ Hz, 1H), 6.91 (d, $J = 8.4$ Hz, 1H), 6.74 (br s, 1H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.4, 137.8, 132.4, 128.7, 124.9, 117.5, 110.6, 21.4; FT-IR (KBr) 3405, 3201, 2922, 2858, 2222, 1654, 1607, 1581, 1453, 1410, 1389, 1268, 1155, 1018 cm^{-1} . Anal. Calcd. for $\text{C}_{11}\text{H}_{13}\text{BrN}_2$: C, 52.19; H, 5.18; Br, 31.57; N, 11.07. Found: C, 52.50; H, 5.16; N, 11.00.

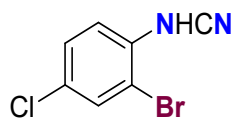


2-Bromo-4-ethylphenylcyanamide 2e: White solid; Analytical TLC on silica gel, 1:10 ethyl acetate/hexane $R_f = 0.8$; yield 91%; mp 139-140 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.42 (d, $J = 8.4$ Hz, 1H), 7.37-7.35 (m, 1H), 7.15 (d, $J = 8.0$ Hz, 1H), 6.00 (br s, 1H), 2.62-2.56 (q, 2H), 1.20 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.5, 135.8, 132.4, 128.3, 126.4, 122.8, 117.1, 26.3, 14.3; FT-IR (KBr) 3250, 3090, 2928, 2218, 1672, 1610, 1574, 1496, 1449, 1309, 1246, 1125, 1096 cm^{-1} . Anal. Calcd. for $\text{C}_9\text{H}_9\text{BrN}_2$: C, 48.02; H, 4.03; Br, 35.50; N, 12.45. Found: C, 48.36; H, 4.00; N, 12.37.

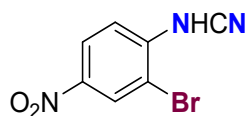


2-Bromo-4-fluorophenylcyanamide 2f: White solid; Analytical TLC on silica gel, 1:10 ethyl acetate/hexane $R_f = 0.7$; yield 89%; mp 144-145 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.49 (s, 1H), 7.36 (d, $J = 7.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.1, 141.3, 133.5, 128.9, 128.4, 124.5, 115.8; FT-IR (KBr) 3423, 3017, 2205, 1601, 1491, 1287, 1027, 808 cm^{-1} . Anal.

Calcd. for $C_7H_4BrFN_2$: C, 39.10; H, 1.88; Br, 37.16; F, 8.84; N, 13.03. Found: C, 39.40; H, 1.86; N, 12.92.



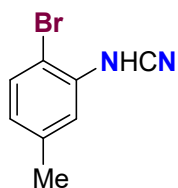
2-Bromo-4-chlorophenylcyanamide 2g: White solid; Analytical TLC on silica gel, 1:10 ethyl acetate/hexane $R_f = 0.7$; yield 90%; mp 142-143 °C; 1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.31 (m, 3H), 5.55 (br s, 1H, 1NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 137.2, 130.8, 130.0, 124.1, 122.2, 115.2; FT-IR (KBr) 3323, 3046, 3007, 2207, 1621, 1491, 1287, 1146, 1027, 828 cm^{-1} . Anal. Calcd. for $C_7H_4BrClN_2$: C, 36.32; H, 1.74; Br, 34.52; Cl, 15.32; N, 12.10. Found: C, 36.62; H, 1.72; N, 12.09.



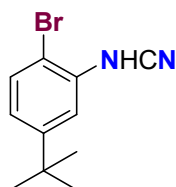
2-Bromo-4-nitrophenylcyanamide 2h: White solid; Analytical TLC on silica gel, 1:4 ethyl acetate/hexane $R_f = 0.6$; yield 75%; mp 154-155 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, $J = 9.6$ Hz, 1H), 7.38-7.33 (m, 1H), 6.81 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 138.4, 137.7, 136.9, 125.6, 122.2, 116.8; FT-IR (KBr) 3426, 3082, 3005, 2234, 1657, 1504, 1438, 1325, 1216, 1099, 829 cm^{-1} . Anal. Calcd. for $C_7H_4BrN_3O_2$: C, 34.74; H, 1.67; Br, 33.01; N, 17.36; O, 13.22; Found: C, 34.99; H, 1.65; N, 17.29.



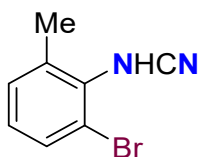
2-Bromo-4-(trifluoromethyl)phenylcyanamide 2i: White solid; Analytical TLC on silica gel, 1:5 ethyl acetate/hexane $R_f = 0.6$; yield 78%; mp 155-157 °C; 1H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1 H), 7.38-7.33 (m, 1H), 6.72-6.68 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 136.7, 134.0, 132.7, 132.1, 115.6, 115.0, 90.1; FT-IR (KBr) 3426, 3007, 2238, 2219, 2036, 1631, 1567, 1491, 1287, 1250, 1146, 1027, 896 cm^{-1} . Anal. Calcd. for $C_8H_4BrF_3N_2$: C, 36.25; H, 1.52; Br, 30.15; F, 21.51; N, 10.57. Found: C, 36.55; H, 1.49; N, 10.48.



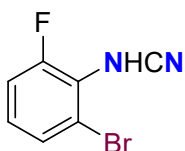
2-Bromo-5-methylphenylcyanamide 2j: White solid; Analytical TLC on silica gel, 1:10 ethyl acetate/hexane $R_f = 0.8$; yield 93%; mp 139-140 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.33 (s, 1H), 7.14-7.05 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.4, 137.4, 134.8, 133.6, 133.1, 130.5, 115.5, 20.6; FT-IR (KBr) 3250, 3090, 2928, 1672, 1610, 1574, 1496, 1449, 1309, 1246, 1125, 1096 cm^{-1} . Anal. Calcd. for $\text{C}_8\text{H}_7\text{BrN}_2$: C, 45.53; H, 3.34; Br, 37.86; N, 13.27. Found: C, 45.80; H, 3.31; N, 13.20.



5-tert-Butyl-2-bromophenylcyanamide 2k: White solid; Analytical TLC on silica gel, 1:10 ethyl acetate/hexane $R_f = 0.8$; yield 85%; mp 141-142 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.33 (m, 2H), 6.81 (d, $J = 8.4$ Hz, 1H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.8, 135.2, 134.4, 130.0, 129.5, 128.7, 92.5, 34.5, 30.4; FT-IR (KBr) 3250, 3090, 2928, 1672, 1610, 1574, 1496, 1449, 1309, 1246, 1125, 1096 cm^{-1} . Anal. Calcd. for $\text{C}_{11}\text{H}_{13}\text{BrN}_2$: C, 52.19; H, 5.18; Br, 31.57; N, 11.07. Found: C, 52.39; H, 5.16; N, 11.00.

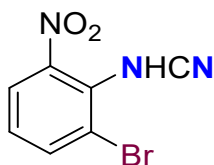


2-bromo-6-methylphenylcyanamide 2l: Gummy, Analytical TLC on silica gel, 1:19 ethyl acetate/hexane $R_f = 0.8$; yield 82%; ^1H NMR (400 MHz, CDCl_3) δ 7.27-7.21 (m, 1H), 7.17-7.12 (m, 2H), 6.09 (br s, 1NH), 2.14 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.0, 139.6, 137.8, 134.5, 130.9, 129.9, 117.0, 20.6; FT-IR (KBr) 3412, 3074, 2867, 2223, 1690, 1435, 1379, 1229, 1125, 1036, 941, 875 cm^{-1} . Anal. Calcd. for $\text{C}_8\text{H}_7\text{BrN}_2$: C, 45.53; H, 3.34; Br, 37.86; N, 13.27. Found: C, 45.73; H, 3.32; N, 13.20.

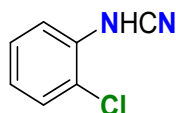


2-bromo-6-fluorophenylcyanamide 2m: Gummy, Analytical TLC on silica gel, 1:19 ethyl acetate/hexane $R_f = 0.8$; yield 72%; ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.33 (m, 1H), 6.81 (d, $J = 7.6$ Hz, 1H), 6.72-6.68 (m, 1H), 6.07 (br s, 1NH); ^{13}C NMR (100 MHz, CDCl_3) δ 149.6, 141.6, 136.7, 134.0, 132.1, 126.1, 122.2; FT-IR (KBr) 3412, 3074, 2867, 2223, 1690,

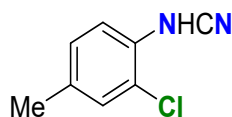
1435, 1379, 1229, 1125, 1036, 941, 875 cm^{-1} . Anal. Calcd. for $\text{C}_7\text{H}_4\text{BrFN}_2$: C, 39.10; H, 1.88; Br, 37.16; F, 8.84; N, 13.03. Found: C, 39.40; H, 1.85; N, 12.94.



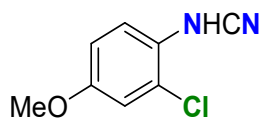
2-bromo-6-nitrophenylcyanamide 2n: White solid, Analytical TLC on silica gel, 1:4 ethyl acetate/hexane $R_f = 0.5$; yield 64%; mp 141-142 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.40 (d, $J = 9.2$ Hz, 2 H), 7.65 (d, $J = 8.8$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.6, 141.6, 136.7, 134.0, 132.1, 120.9, 115.1; FT-IR (KBr) 3375, 3065, 2215, 1656, 1564, 1490, 1379, 1229, 1125, 1036, 941, 832 cm^{-1} . Anal. Calcd. for $\text{C}_7\text{H}_4\text{BrN}_3\text{O}_2$: C, 34.74; H, 1.67; Br, 33.01; N, 17.36; O, 13.22. Found: C, 34.98; H, 1.64; N, 17.30.



2-Chlorophenylcyanamide 3a:^{1,2,4} Analytical TLC on silica gel, 1:19 ethyl acetate/hexane $R_f = 0.8$; white solid; yield 95%; ^1H NMR (400 MHz, CDCl_3) δ 7.42-7.38 (m, 2H), 7.36-7.31 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.8, 135.8, 130.9, 130.6, 130.1, 128.9, 94.0; FT-IR (KBr) 3265, 3064, 2263, 1693, 1489, 1070, 927, 909, 769 cm^{-1} . Anal. Calcd. for $\text{C}_7\text{H}_5\text{ClN}_2$: C, 55.10; H, 3.30; Cl, 23.24; N, 18.36. Found: C, 55.37; H, 3.27; N, 18.30.

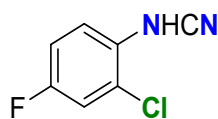


2-Chloro-4-methylphenylcyanamide 3b: Analytical TLC on silica gel, 1:19 ethyl acetate/hexane $R_f = 0.8$; colorless liquid; yield 96%; ^1H NMR (400 MHz, CDCl_3) δ 7.63 (s, 1H), 7.10-7.15 (m, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.3, 134.6, 132.4, 127.5, 124.6, 120.0, 93.3, 21.3; FT-IR (KBr) 3208, 3087, 2899, 2222, 2036, 1587, 1496, 1458, 1265, 1212, 1104, 941, 808, 678 cm^{-1} . Anal. Calcd. for $\text{C}_8\text{H}_7\text{ClN}_2$: C, 57.67; H, 4.23; Cl, 21.28; N, 16.81. Found: C, 57.93; H, 4.20; N, 16.70.

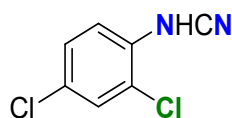


2-Chloro-4-methoxyphenylcyanamide 3c: Analytical TLC on silica gel, 1:19 ethyl acetate/hexane $R_f = 0.8$; colorless solid; yield 97%; ^1H NMR (400 MHz, CDCl_3) δ 7.15 (s, 1H), 7.13-7.10 (m, 2H), 3.30 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.7, 138.6, 133.8,

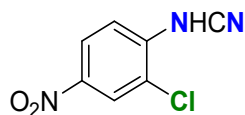
131.9, 127.8, 114.7, 91.8, 55.4; FT-IR (KBr) 3296, 3000, 2896, 2835, 2549, 2216, 2098, 1601, 1580, 1503, 1292, 1252, 1179, 1156, 1028, 927 cm^{-1} . Anal. Calcd. for $\text{C}_8\text{H}_7\text{ClN}_2\text{O}$: C, 52.62; H, 3.86; Cl, 19.41; N, 15.34; O, 8.76. Found: C, 52.95; H, 3.83; N, 15.24.



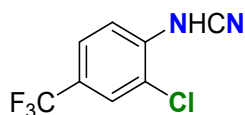
2-Chloro-4-fluorophenylcyanamide 3d: Analytical TLC on silica gel, 1:5 ethyl acetate/hexane $R_f = 0.7$; oily liquid; yield 89%; ^1H NMR (400 MHz, CDCl_3) δ 7.63 (s, 1H), 6.83-6.80 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.8 (d, $J = 11$ Hz), 138.2, 136.5, 134.0, 133.7, 115.8 (d, $J = 9$ Hz), 88.1; FT-IR (KBr) 3208, 3056, 2218, 2071, 1554, 1140, 909, 822, 770 cm^{-1} . Anal. Calcd. for $\text{C}_7\text{H}_4\text{ClFN}_2$: C, 49.29; H, 2.36; Cl, 20.78; F, 11.14; N, 16.42. Found: C, 49.60; H, 2.31; N, 16.31.



2,4-Dichlorophenylcyanamide 3e: Analytical TLC on silica gel, 1:4 ethyl acetate/hexane $R_f = 0.7$; colorless liquid; yield 91%; ^1H NMR (400 MHz, CDCl_3) δ 7.93 (s, 1H), 6.93-6.90 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.1, 137.1, 134.2, 132.5, 130.6, 129.1, 92.5; FT-IR (KBr) 3297, 3076, 2222, 2094, 1505, 1114, 929, 802, 790 cm^{-1} . Anal. Calcd. for $\text{C}_7\text{H}_4\text{Cl}_2\text{N}_2$: C, 44.95; H, 2.16; Cl, 37.91; N, 14.98. Found: C, 45.25; H, 2.12; N, 14.88.

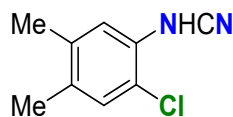


2-Chloro-4-nitrophenylcyanamide 3f: Analytical TLC on silica gel, 1:4 ethyl acetate/hexane $R_f = 0.6$; white solid; yield 78%; ^1H NMR (400 MHz, CDCl_3) δ 8.11 (d, $J = 12$ Hz, 1H), 7.38-7.33 (m, 1H), 6.72-6.68 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.6, 138.4, 136.7, 134.0, 132.1, 120.1, 90.9; FT-IR (KBr) 3082, 2705, 2232, 2034, 1607, 1504, 1459, 1438, 1305, 1261, 1216, 1145, 1099, 970, 926 cm^{-1} . Anal. Calcd. for $\text{C}_7\text{H}_4\text{ClN}_3\text{O}_2$: C, 42.55; H, 2.04; Cl, 17.94; N, 21.27; O, 16.20. Found: C, 42.80; H, 2.00; N, 21.17.

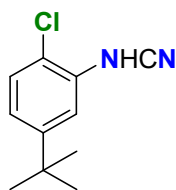


2-Chloro-4-(trifluoromethyl)phenylcyanamide 3g: Analytical TLC on silica gel, 1:5 ethyl acetate/hexane $R_f = 0.6$; white solid; yield 82%; ^1H NMR (400 MHz, CDCl_3) δ 7.84 (s, 1H), 7.38-7.33 (m, 1H), 6.72-6.68 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.4, 136.7, 134.0, 132.7, 132.1, 115.6, 115.0, 90.9; FT-IR (KBr) 3074, 2217, 2083, 1526, 1348, 1093, 973, 892,

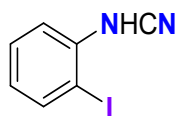
850, 809, 736 cm^{-1} . Anal. Calcd. for $\text{C}_8\text{H}_4\text{ClF}_3\text{N}_2$: C, 43.56; H, 1.83; Cl, 16.07; F, 25.84; N, 12.70. Found: C, 43.86; H, 1.80; N, 12.62.



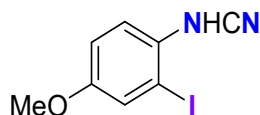
2-Chloro-4,5-dimethylphenylcyanamide 3h: Analytical TLC on silica gel, 1:19 ethyl acetate/hexane $R_f = 0.9$; white solid; yield 98%; ^1H NMR (400 MHz, CDCl_3) δ 7.46 (s, 1H), 7.01 (s, 1H), 2.34 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.6, 137.8, 134.5, 133.3., 130.9, 129.9, 90.6, 20.6, 18.2; FT-IR (KBr) 3265, 3065, 2920, 2857, 2234, 2085, 1490, 1435, 1379, 1229, 1125, 1036, 941, 901, 875 cm^{-1} . Anal. Calcd. for $\text{C}_9\text{H}_9\text{ClN}_2$: C, 59.84; H, 5.02; Cl, 19.63; N, 15.51. Found: C, 60.18; H, 5.00; N, 15.41.



5-Tert-butyl-2-chlorophenylcyanamide 3i: Analytical TLC on silica gel, 1:19 ethyl acetate/hexane $R_f = 0.9$; colorless solid; yield 88%; ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.33 (m, 2H), 6.81(d, $J = 8.4$ Hz, 1H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.8, 135.2, 134.4, 130.0, 129.5, 128.7, 92.5, 34.5, 30.4; FT-IR (KBr) 3351, 3065, 3035, 2920, 2867, 2085, 1490, 1435, 1379, 1229, 1204, 1125, 1036, 941, 901, 875 cm^{-1} . Anal. Calcd. for $\text{C}_{11}\text{H}_{13}\text{ClN}_2$: C, 63.31; H, 6.28; Cl, 16.99; N, 13.42. Found: C, 63.61; H, 6.26; N, 13.32.

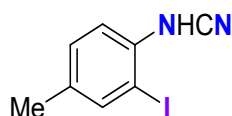


2-Iodophenylcyanamide 4a: Analytical TLC on silica gel, 1:19 ethyl acetate/hexane $R_f = 0.8$; yield 91%; ^1H NMR (400 MHz, CDCl_3) δ 7.42-7.38 (m, 2H), 7.36-7.31 (m, 2H), 5.82 (br s, 1H, NH); ^{13}C NMR (100 MHz, CDCl_3) δ 140.8, 137.8, 130.9, 130.6, 130.1, 128.9, 94.0; FT-IR (KBr) 3350, 3064, 2222, 1693, 1489, 1250, 1070, 909, 569 cm^{-1} . Anal. Calcd. for $\text{C}_7\text{H}_5\text{IN}_2$: C, 34.45; H, 2.07; N, 11.48. Found: C, 34.59; H, 2.05; N, 11.42.

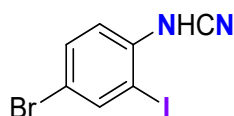


2-Iodo-4-methoxyphenylcyanamide 4b: Analytical TLC on silica gel, 1:19 ethyl acetate/hexane $R_f = 0.8$; yield 92%; ^1H NMR (400 MHz, CDCl_3) δ 7.15 (s, 1H), 7.13-7.10 (m, 2H), 5.37 (br s, 1H, 1NH), 3.30 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.1, 138.6, 133.8,

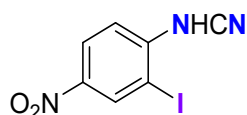
131.9, 127.8, 121.7, 91.8, 55.4; FT-IR (KBr) 3318, 3097, 2896, 2835, 2298, 1601, 1580, 1503, 1292, 1252, 1179, 1028, 927, 566 cm^{-1} . Anal. Calcd. for $\text{C}_8\text{H}_7\text{IN}_2\text{O}$: C, 35.06; H, 2.57; N, 10.22. Found: C, 35.22; H, 2.54; N, 10.16.



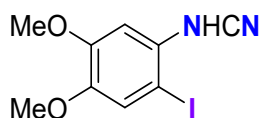
2-Iodo-4-methylphenylcyanamide 4c: Analytical TLC on silica gel, 1:19 ethyl acetate/hexane $R_f = 0.8$; yield 89%; ^1H NMR (400 MHz, CDCl_3) δ 7.63 (s, 1H), 7.10-7.15 (m, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.3, 135.6, 132.4, 128.5, 124.6, 120.0, 94.3, 21.3; FT-IR (KBr) 3322, 3087, 2899, 2236, 1587, 1496, 1265, 1212, 1104, 941, 808, 578 cm^{-1} . Anal. Calcd. for $\text{C}_8\text{H}_7\text{IN}_2$: C, 37.23; H, 2.73; N, 10.86. Found: C, 37.36; H, 2.71; N, 10.81.



4-Bromo-2-iodophenylcyanamide 4d: Analytical TLC on silica gel, 1:24 ethyl acetate/hexane $R_f = 0.7$; yield 90%; ^1H NMR (400 MHz, CDCl_3) δ 7.93 (s, 1H), 6.93-6.90 (m, 2H), 5.82 (br s, 1H, 1NH); ^{13}C NMR (100 MHz, CDCl_3) δ 139.1, 137.1, 134.2, 132.5, 130.6, 129.1, 92.5; FT-IR (KBr) 3399, 3076, 2214, 1670, 1505, 1250, 1114, 929, 802, 590 cm^{-1} . Anal. Calcd. for $\text{C}_7\text{H}_4\text{BrIN}_2$: C, 30.19; H, 1.45; N, 10.06. Found: C, 30.32; H, 1.43; N, 10.00.

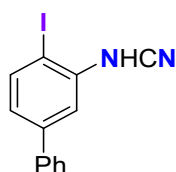


2-Iodo-4-nitrophenylcyanamide 4e: Analytical TLC on silica gel, 1:4 ethyl acetate/hexane $R_f = 0.5$; yield 71%; ^1H NMR (400 MHz, CDCl_3) δ 7.84 (s, 1H), 7.38-7.33 (m, 1H), 6.72-6.68 (m, 1H), 5.24 (s br, 1NH); ^{13}C NMR (100 MHz, CDCl_3) δ 149.6, 141.6, 136.7, 134.0, 132.1, 115.1, 90.9; FT-IR (KBr) 3415, 3082, 2234, 1675, 1607, 1504, 1459, 1438, 1345, 1261, 1145, 1099, 870, 526 cm^{-1} . Anal. Calcd. for $\text{C}_7\text{H}_4\text{IN}_3\text{O}_2$: C, 29.09; H, 1.39; N, 14.54. Found: C, 29.24; H, 1.36; N, 14.48.

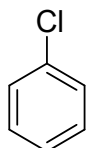


2-iodo-4,5-dimethoxyphenylcyanamide 4f: Analytical TLC on silica gel, 1:20 ethyl acetate/hexane $R_f = 0.9$; yield 95%; ^1H NMR (400 MHz, CDCl_3) δ 7.46 (s, 1H), 7.01 (s, 1H), 3.34 (s, 3H), 3.30 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.6, 137.8, 134.5, 130.9, 129.9,

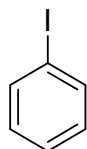
113.9, 90.6, 56.6, 54.6; FT-IR (KBr) 3375, 3065, 2920, 2215, 1656, 1490, 1379, 1229, 1125, 1036, 941, 901, 675 cm^{-1} . Anal. Calcd. for $\text{C}_9\text{H}_9\text{IN}_2\text{O}_2$: C, 35.55; H, 2.98; I, 41.73; N, 9.21; O, 10.52. Found: C, 35.95; H, 2.96; N, 9.14.



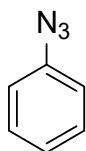
6-Iodo-3-phenyl phenylcyanamide 4g: Analytical TLC on silica gel, 1:20 ethyl acetate/hexane $R_f = 0.9$; White solid; yield 88%; ^1H NMR (400 MHz, CDCl_3) δ 7.40 (s, 1H), 7.30-7.19 (m, 5H), 7.04-7.01 (m, 2H), 6.81 (br s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.0, 137.4, 135.3, 134.1, 132.7, 129.6, 127.0, 126.7, 124.6, 115.3, 110.3; FT-IR (KBr) 3210, 2224, 1605, 1580, 1497, 1439, 1405, 1388, 1286, 1154, 1025 cm^{-1} . Anal. Calcd. for $\text{C}_{13}\text{H}_9\text{IN}_2$: C, 48.77; H, 2.83; I, 39.64; N, 8.75. Found: C, 49.07; H, 2.80; N, 8.60.



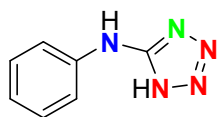
Chloro benzene: Analytical TLC on silica gel, 1:49 ethyl acetate/hexane $R_f = 0.9$; Colorless liquid; yield 98%; ^1H -NMR (400 MHz, CDCl_3) δ 7.37-7.33 (m, 2H), 7.29-7.25 (m, 3H); FT-IR (KBr) 3064, 2364, 2063, 1693, 1489, 1070, 927, 909, 769 cm^{-1} .



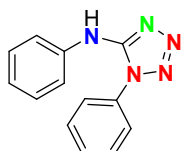
Iodobenzene: Analytical TLC on silica gel, Hexane $R_f = 0.9$; colorless liquid; yield 92%; ^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, $J = 8.4$ Hz, 2H), 7.28 (d, $J = 9.6$ Hz, 2H); FT-IR (KBr) 3166, 2954, 2234, 1600, 1494, 1399, 1251, 1091, 1011, 820 cm^{-1} .



Phenyl azide: Analytical TLC on silica gel, Hexane $R_f = 0.9$; colorless liquid; yield 90%; ^1H NMR (400 MHz, CDCl_3) δ 8.11 (d, $J = 9.2$ Hz, 2H), 7.61-7.43 (m, 3H); FT-IR (KBr) 3166, 2954, 2234, 1600, 1494, 1399, 1251, 1091, 1011, 820 cm^{-1} .



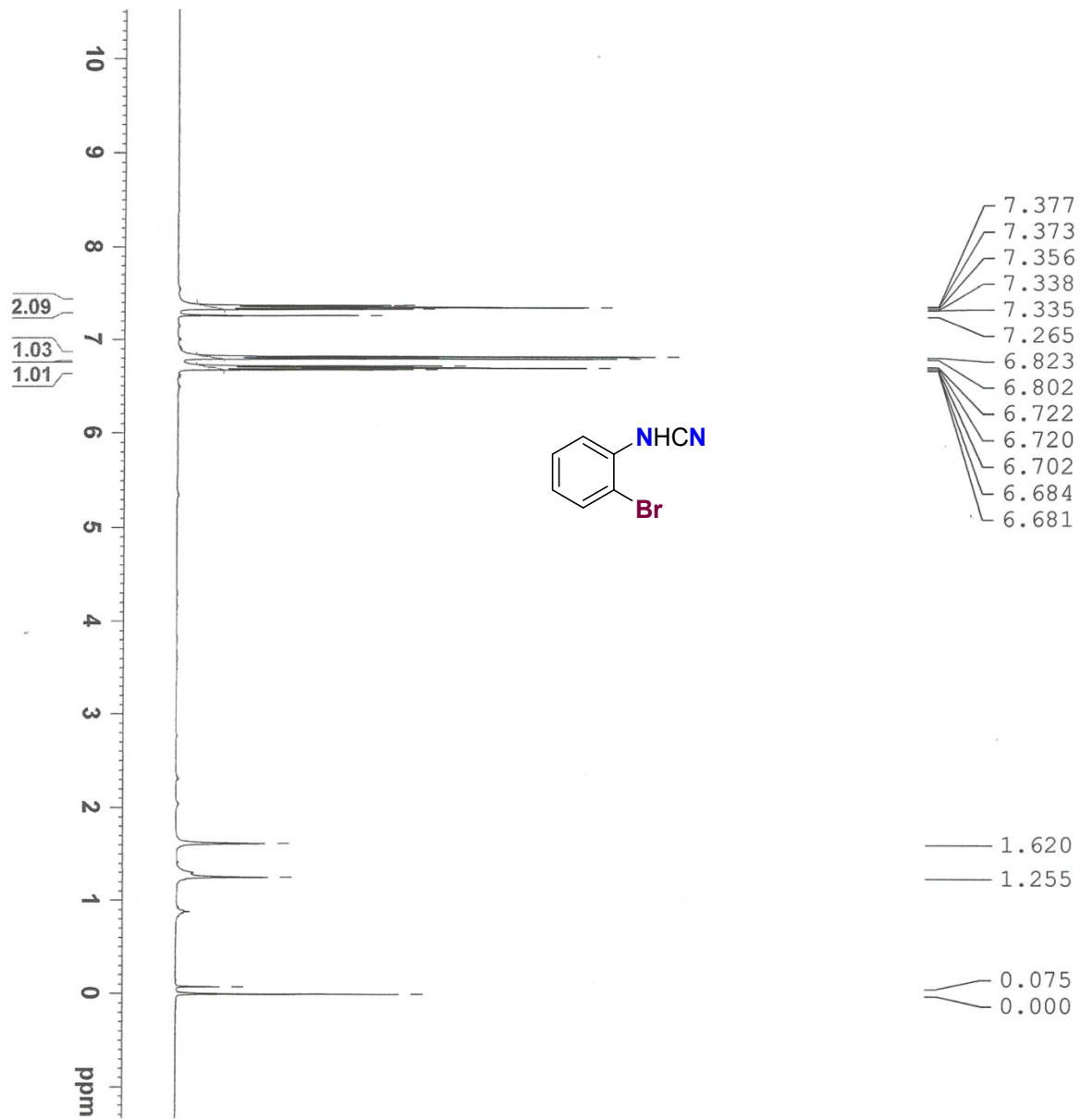
N-Phenyl-1H-tetrazol-5-amine (8a): Yield (90%), white solid, mp 167–168°C (mp 162–163°C³⁴). R_f 0.6 (EtOAc–hexane, 3:7). IR spectrum, ν , cm^{-1} : 3987, 3350, 3064, 1693, 1587, 1250, 1148, 1070, 909, 764. ^1H NMR spectrum, δ , ppm: 7.97 (2H, br. s, NH_2); 7.61–7.57 (2H, m, H Ar); 7.40–7.28 (2H, m, H Ar); 7.21–7.17 (1H, m, H Ar).

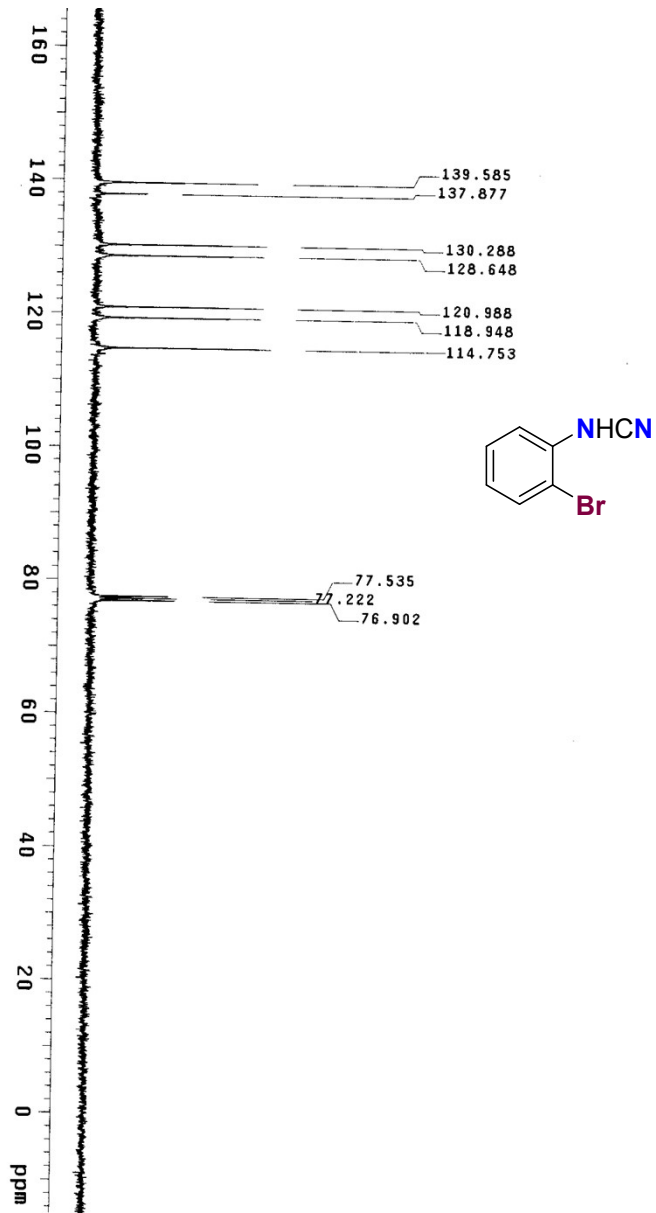


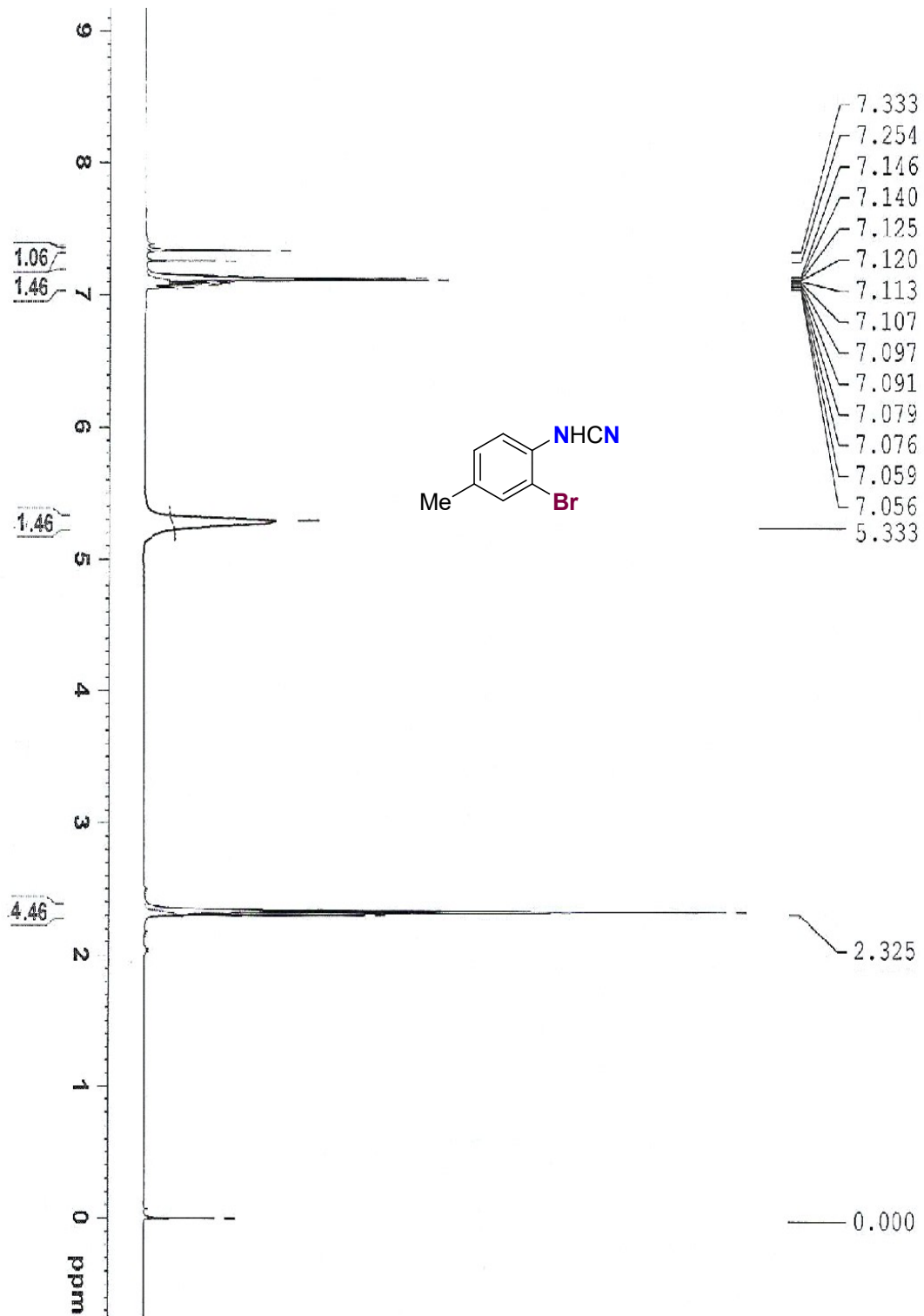
N,1-Diphenyl-1H-tetrazol-5-amine (8b): Yield 208 mg (88%), white solid, mp 198–199°C. R_f 0.7 (EtOAc–hexane, 3:7). IR spectrum, ν , cm^{-1} : 3426, 3097, 1645, 1631, 1567, 1512, 1491, 1287, 1250, 1146, 1027, 896. ^1H NMR spectrum, δ , ppm (J , Hz): 7.54–7.41 (7H, m, H Ar); 6.85 (3H, d, $J = 8.8$, H Ar); 6.02 (1H, br. s, NH).

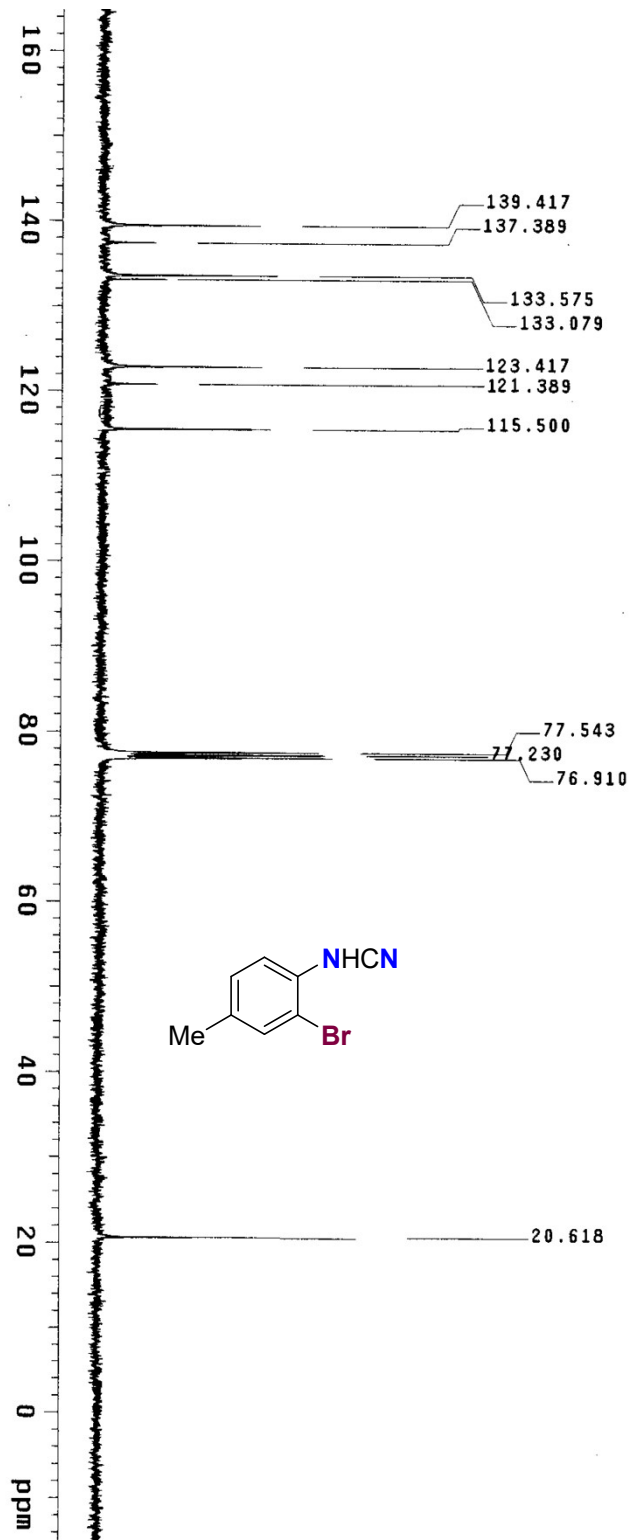
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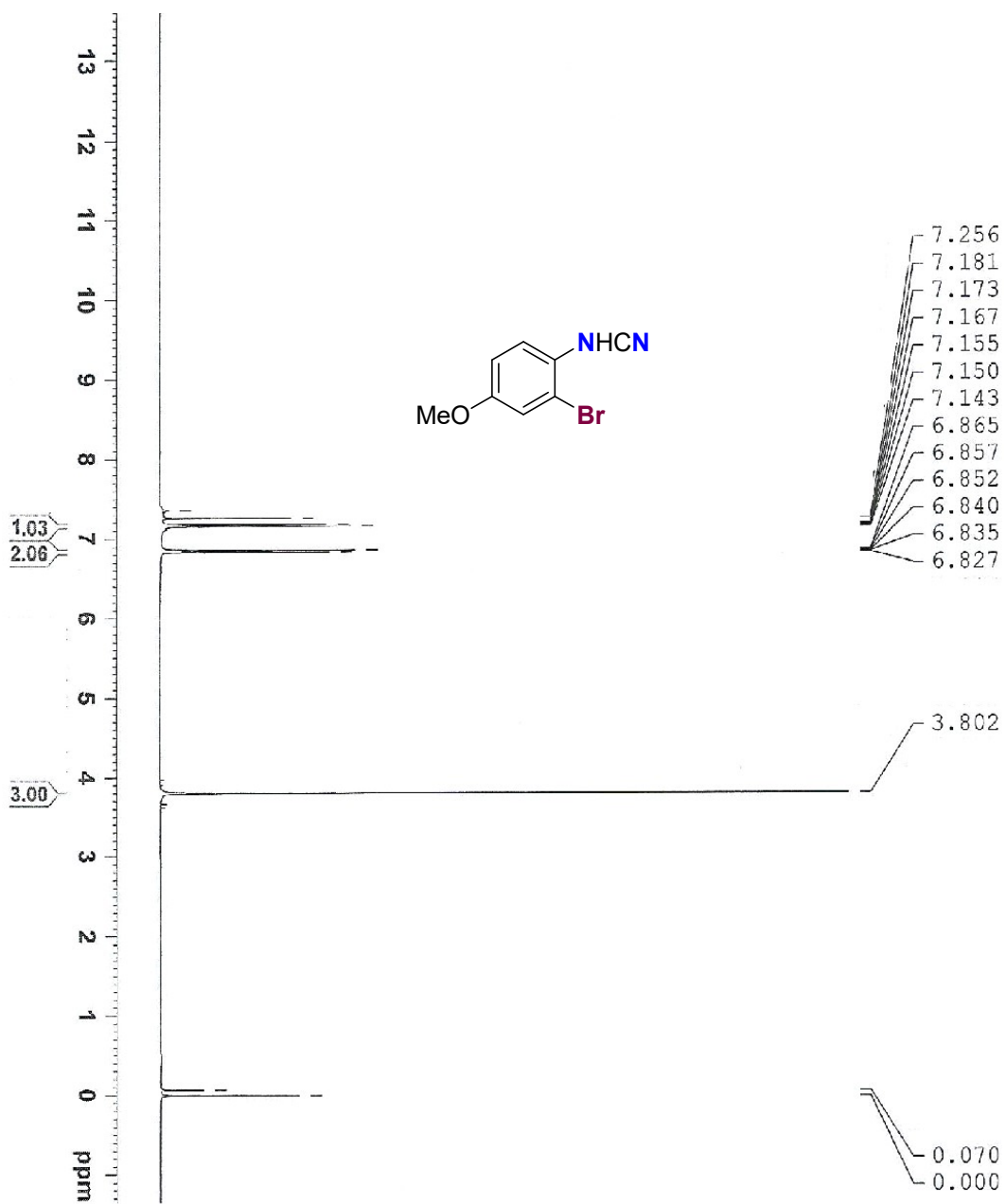
1. Ghosh, H.; Yella, R.; Ali, A. R.; Sahoo, S. K.; Patel, B. K. *Tetrahedron Lett.* **2009**, *50*, 2407-2410.
2. Pierron, P. *Bull. Soc. Chim. Fr.* **1907**, *35*, 1197-1204
3. T. Ramana, P. Saha, M. Das and T. Punniyamurthy, *Org. Lett.* 2010, **12**, 84.
4. Chun-Yen Chen, Fung Fuh Wonga, Jiann-Jyh Huang, Shao-Kai Lin, Mou-Yung Yeh *Tetrahedron Lett.* **2008**, *49*, 6505–6507

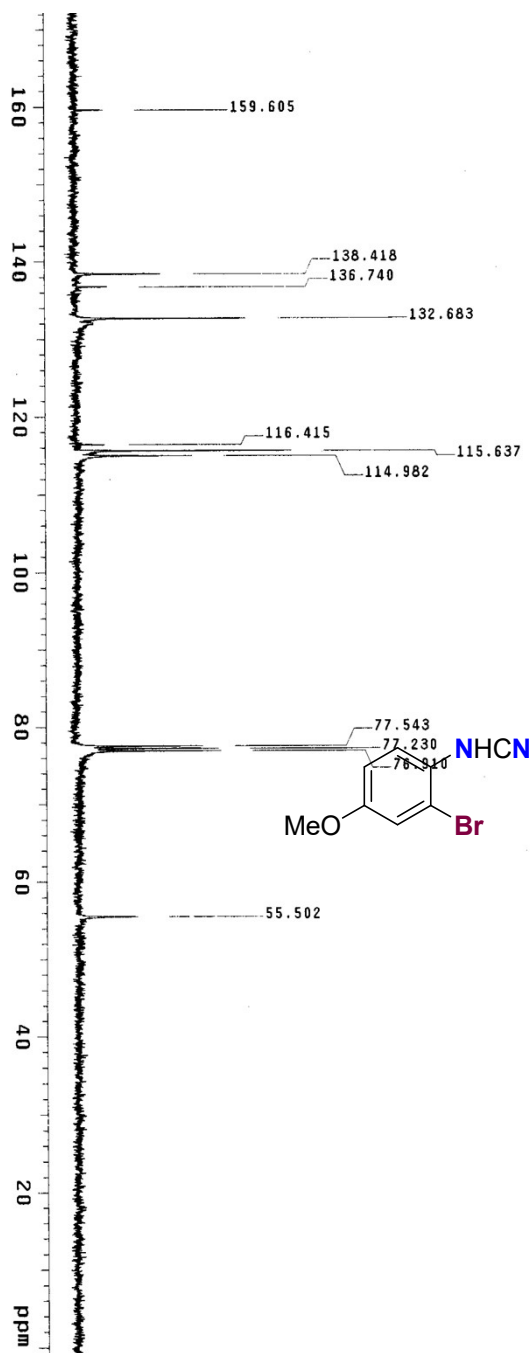


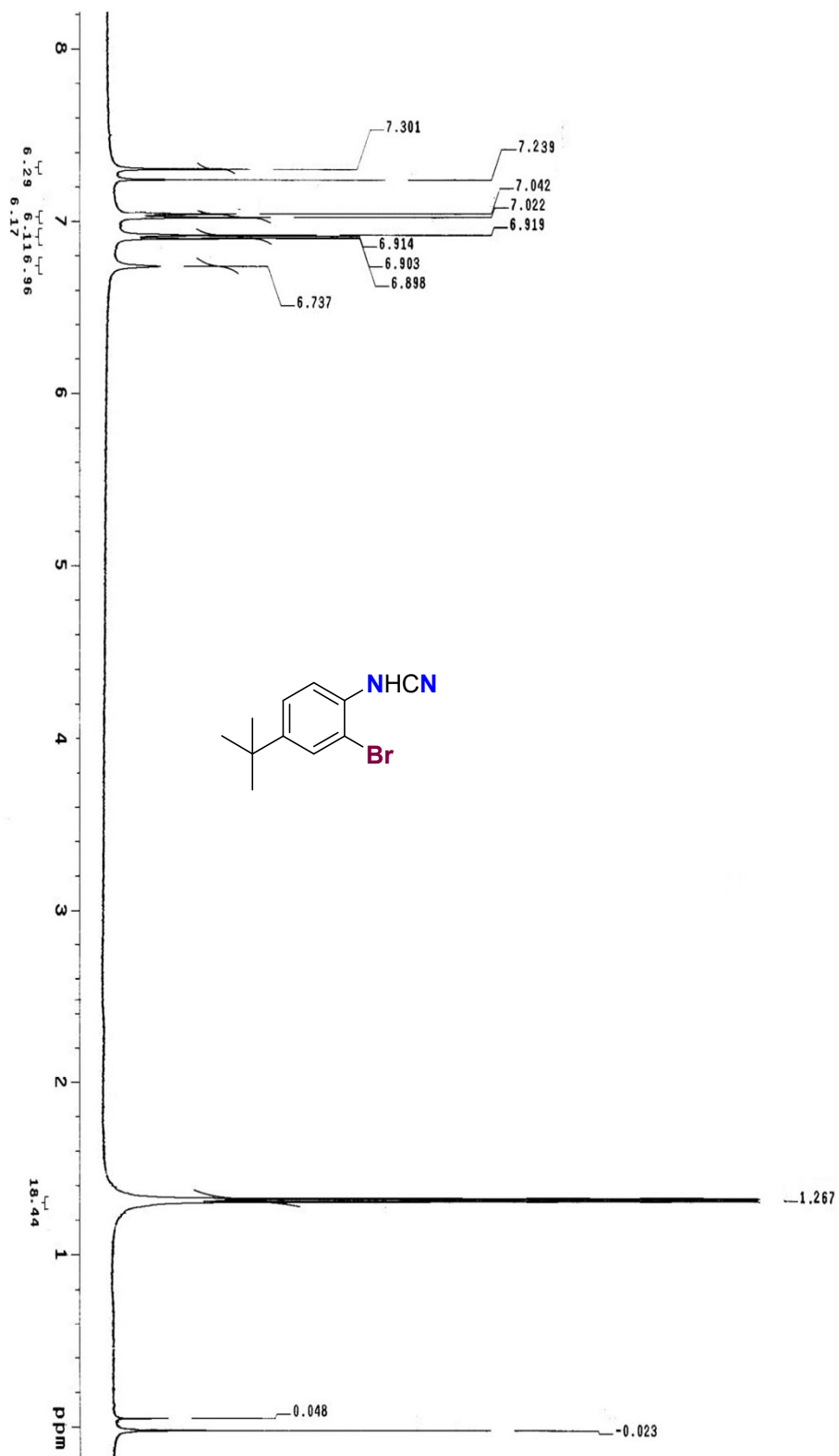


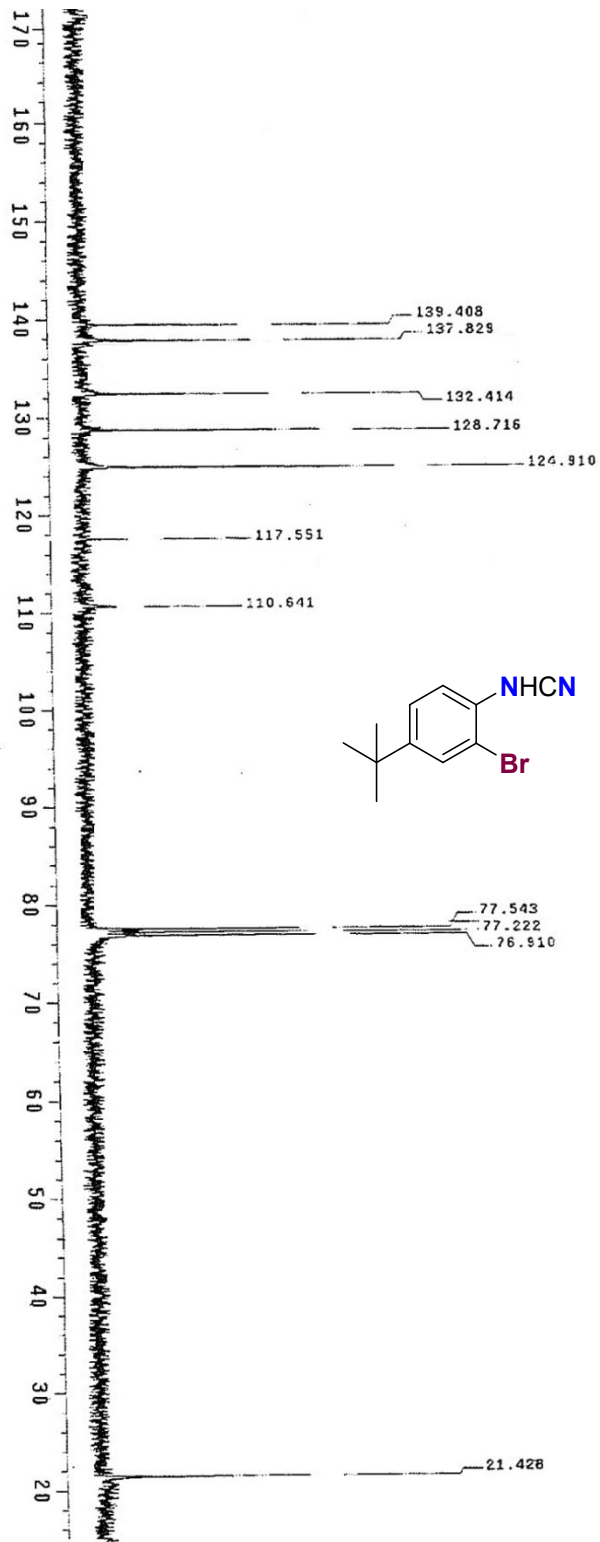


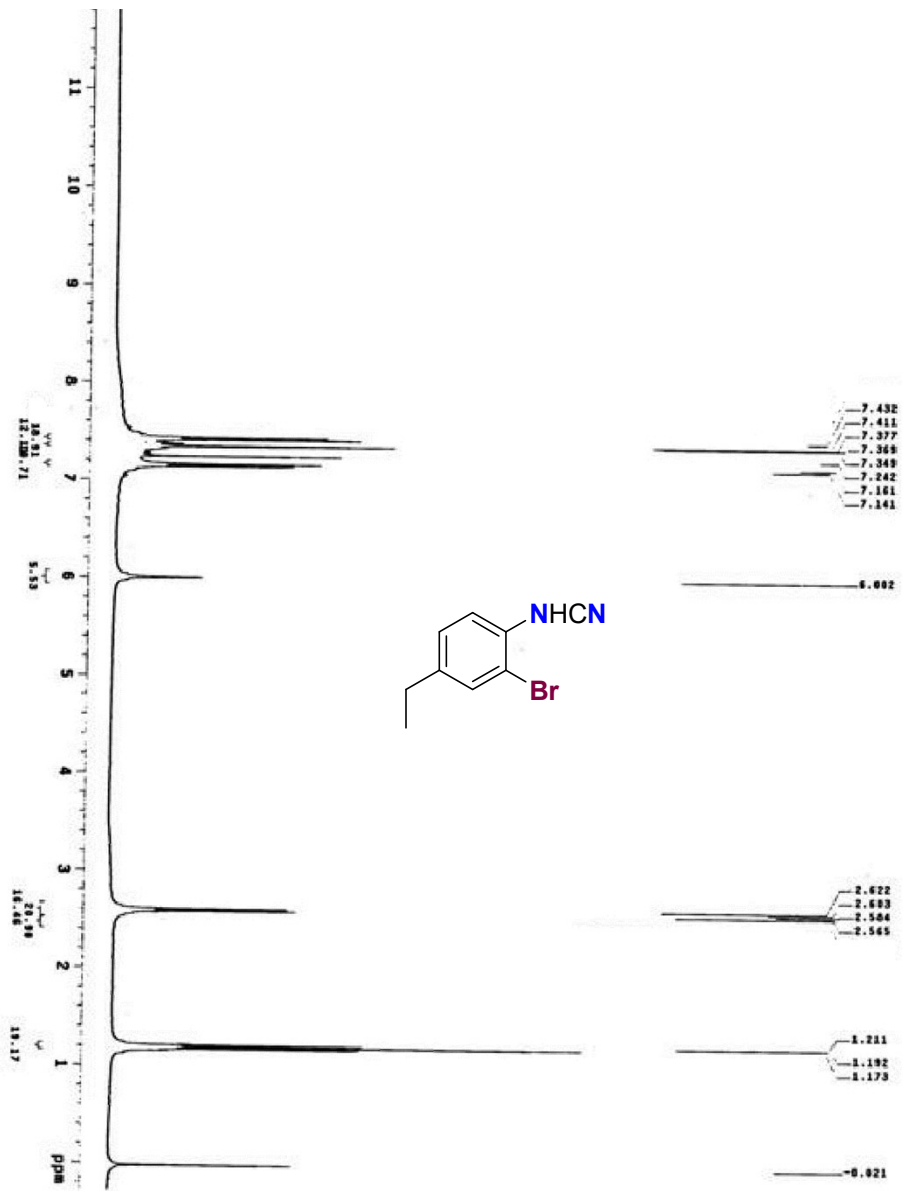


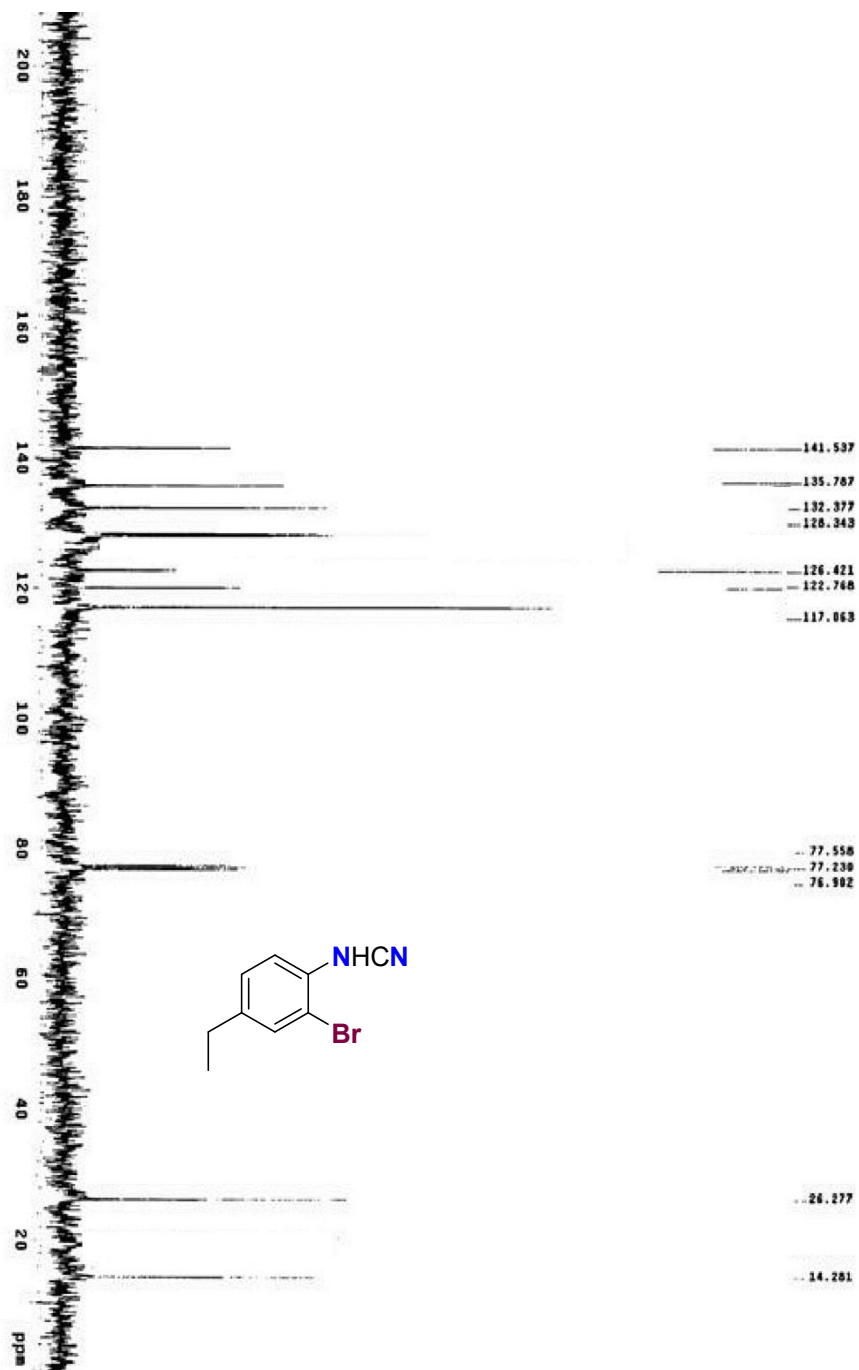


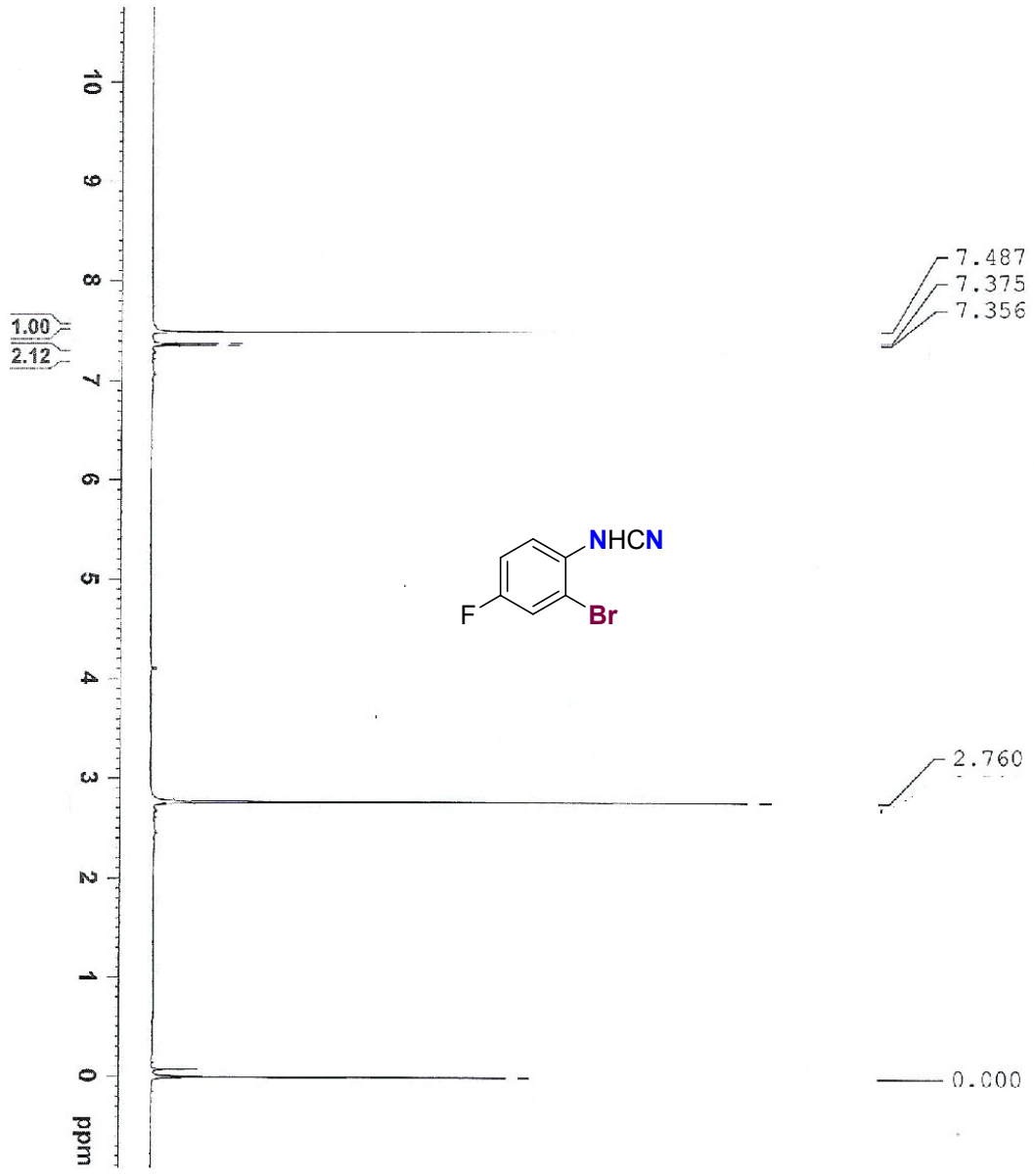


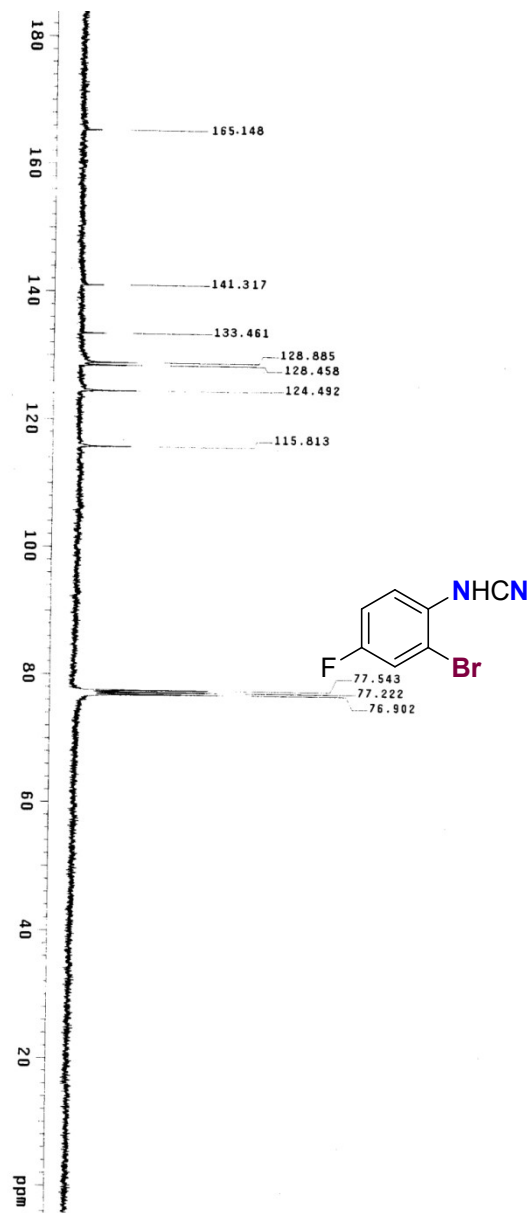


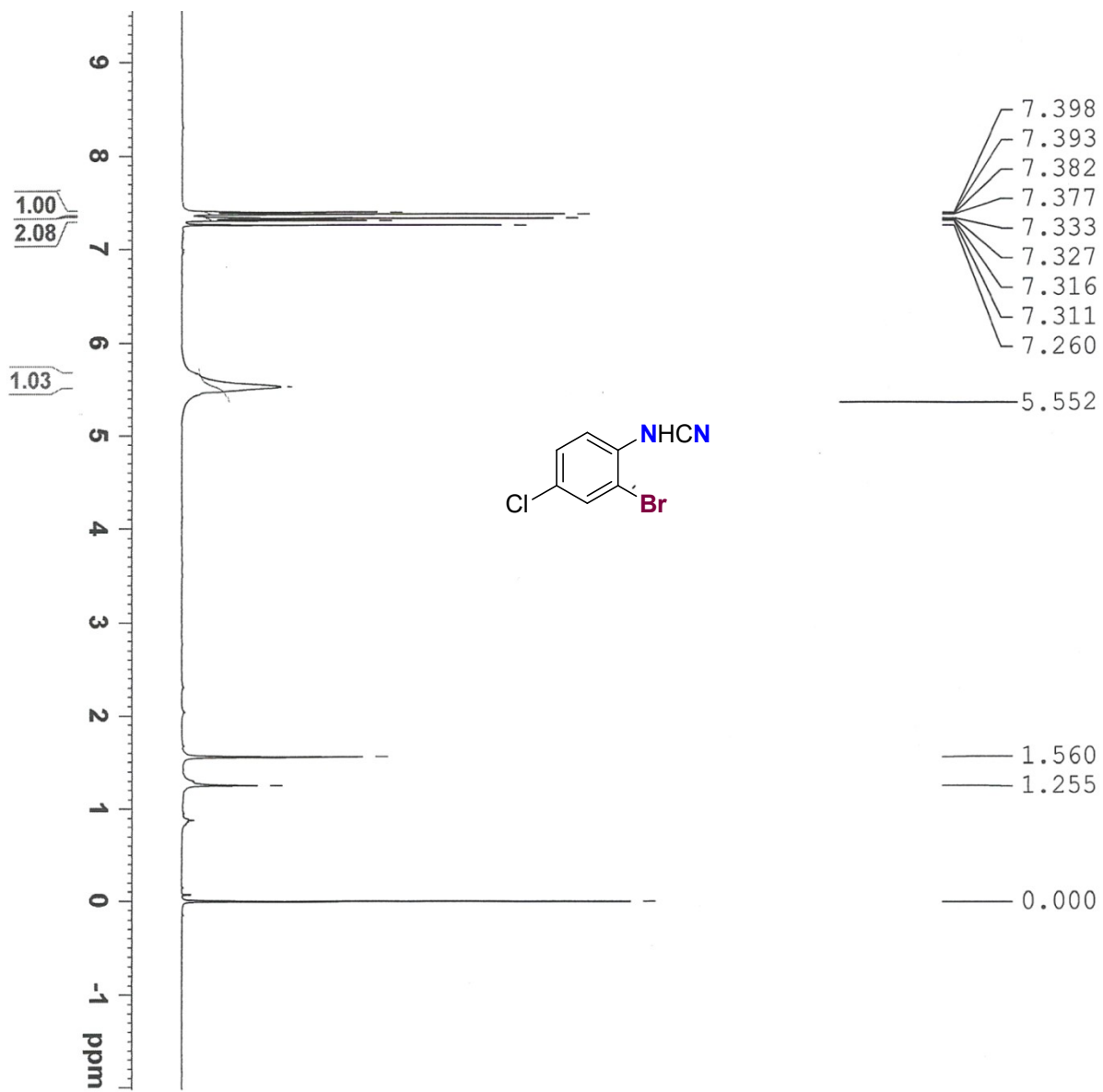


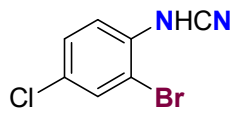
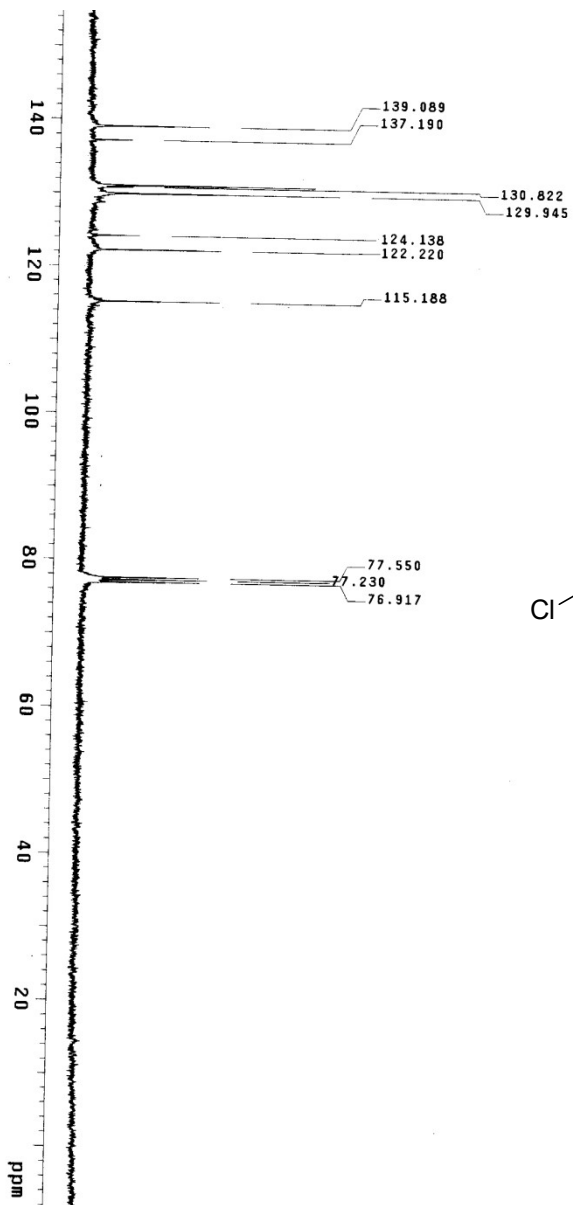


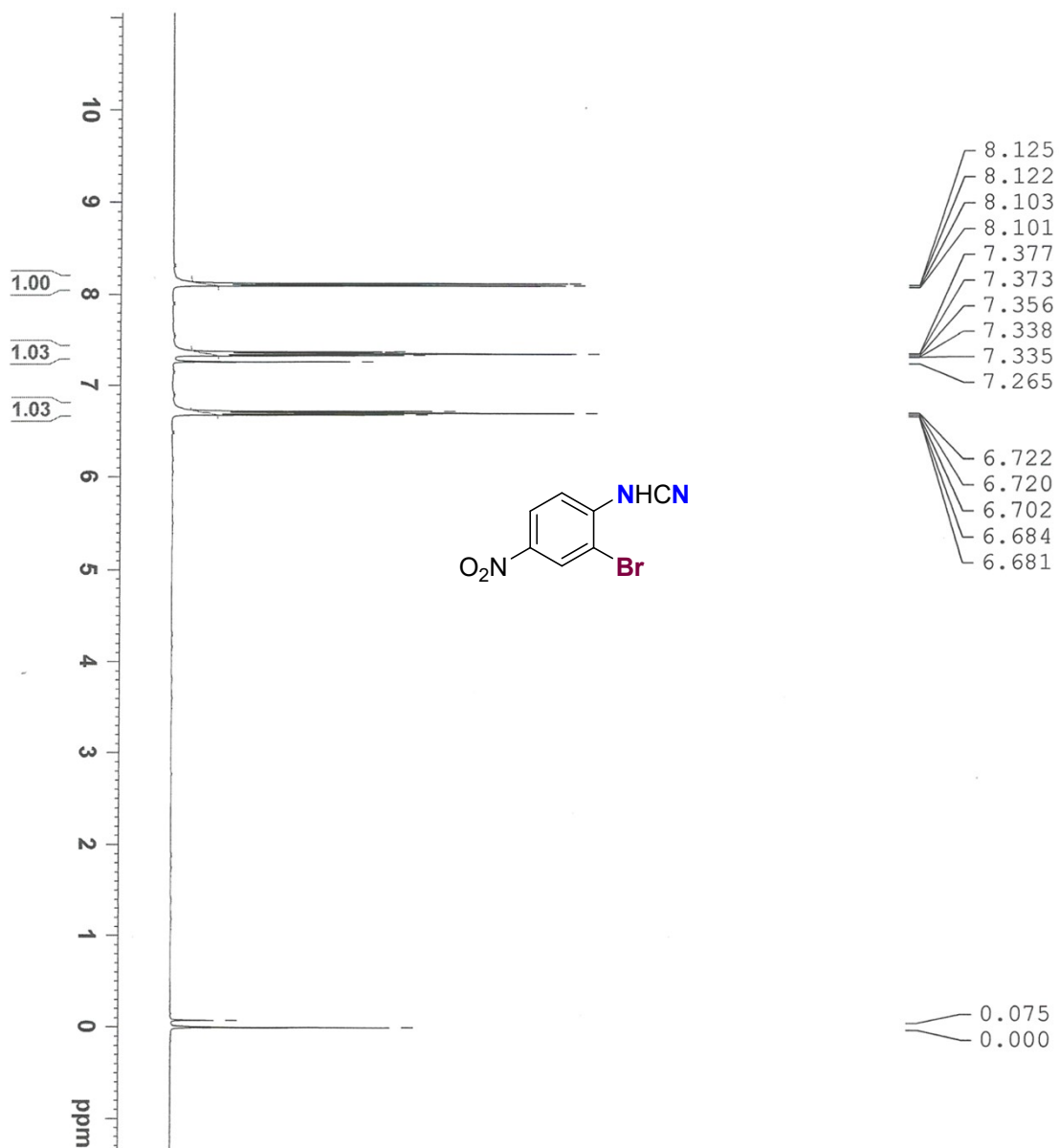


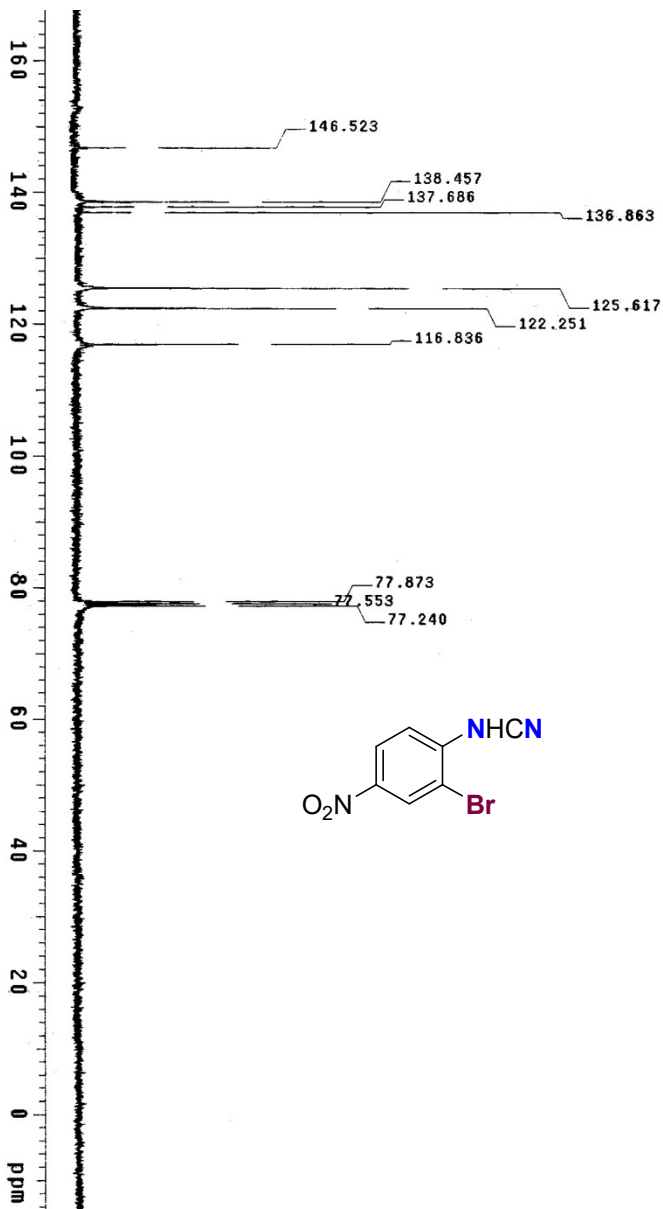


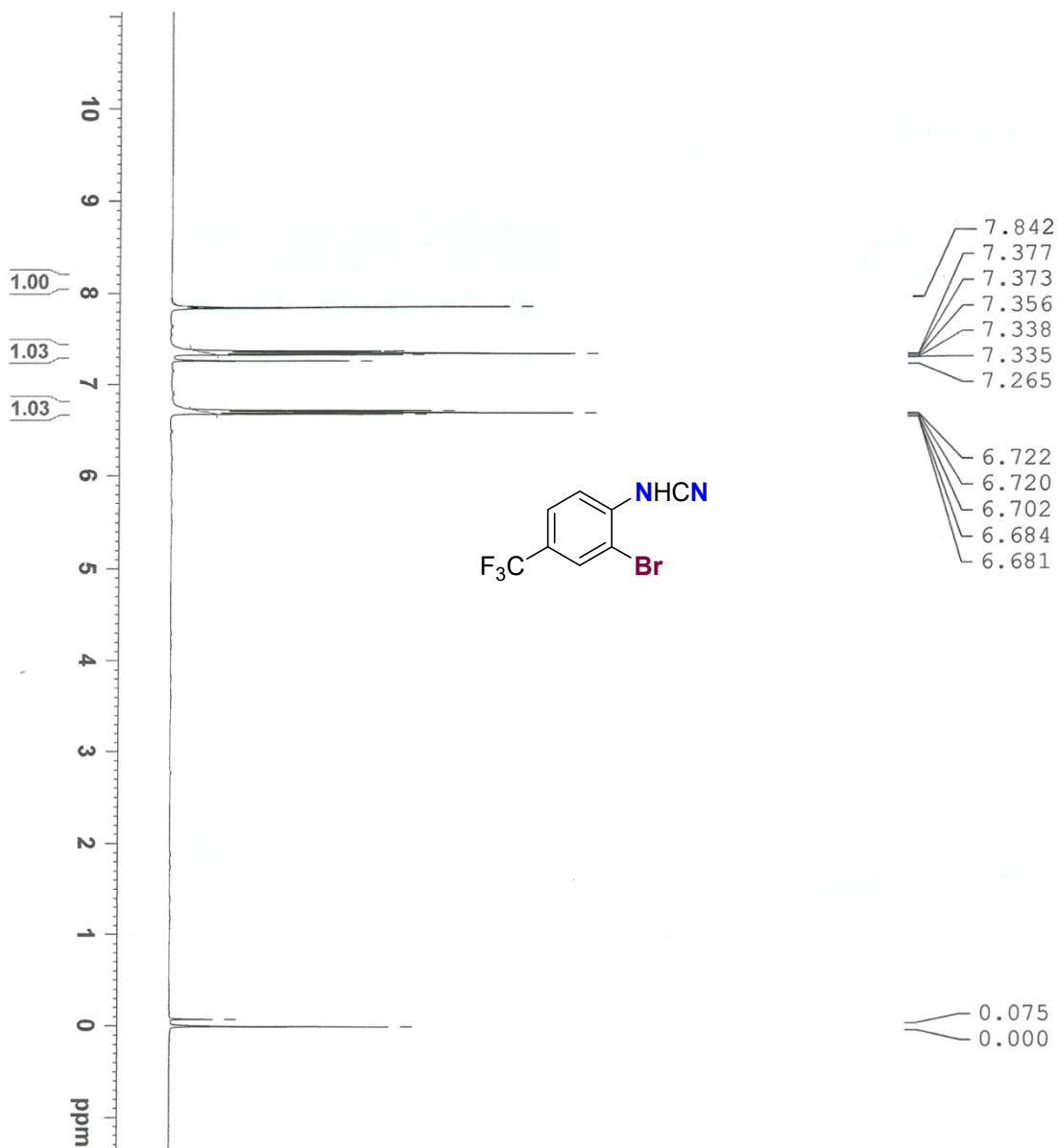


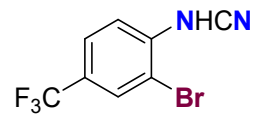
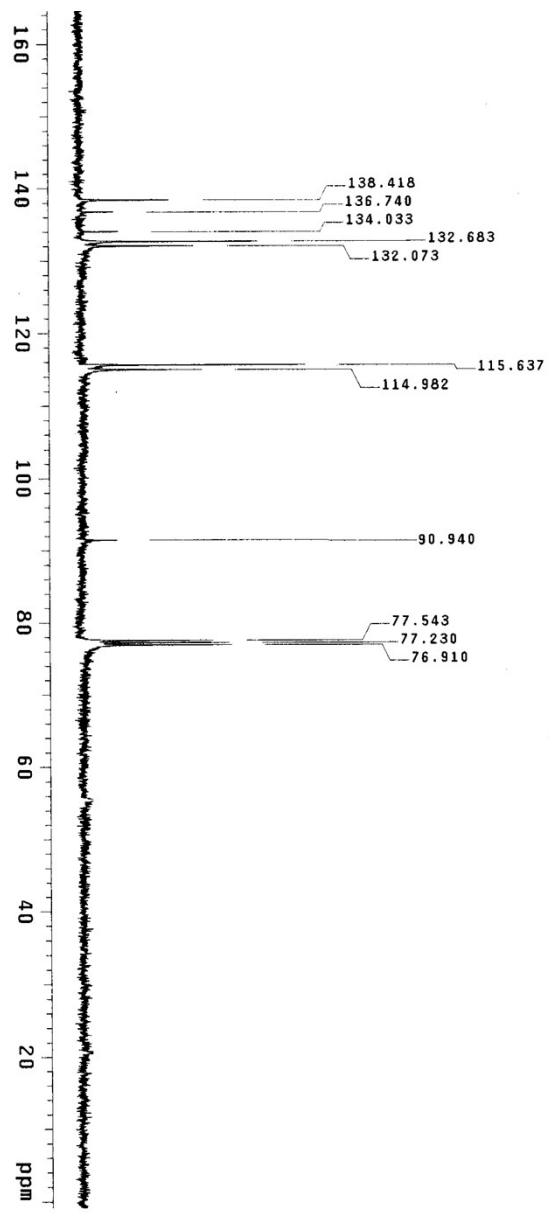


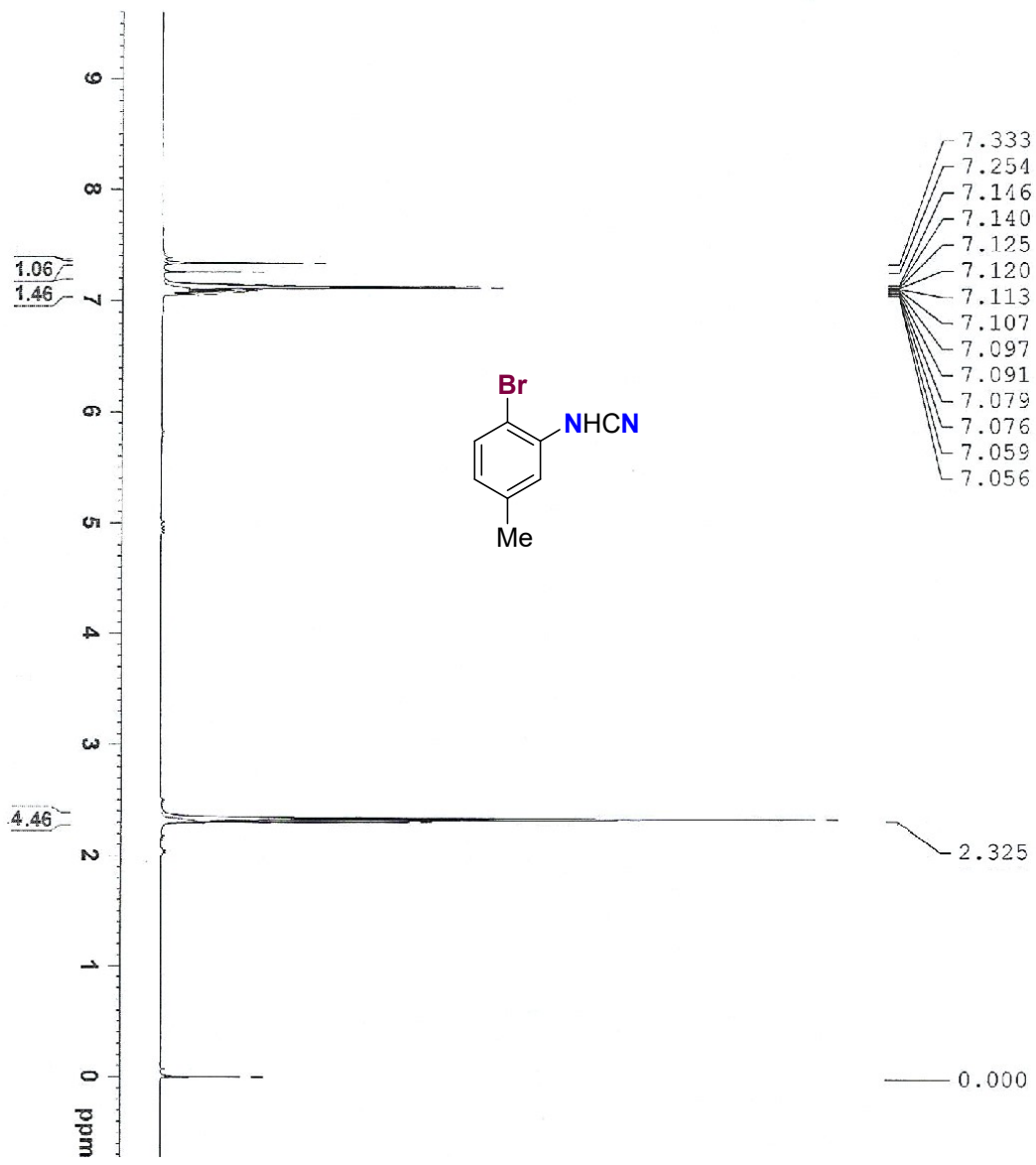


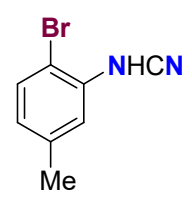
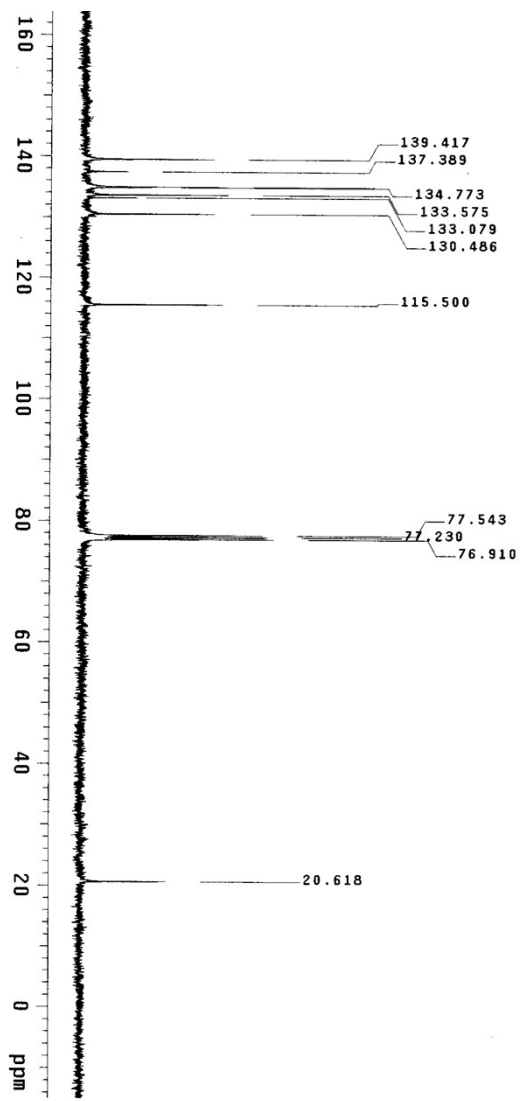


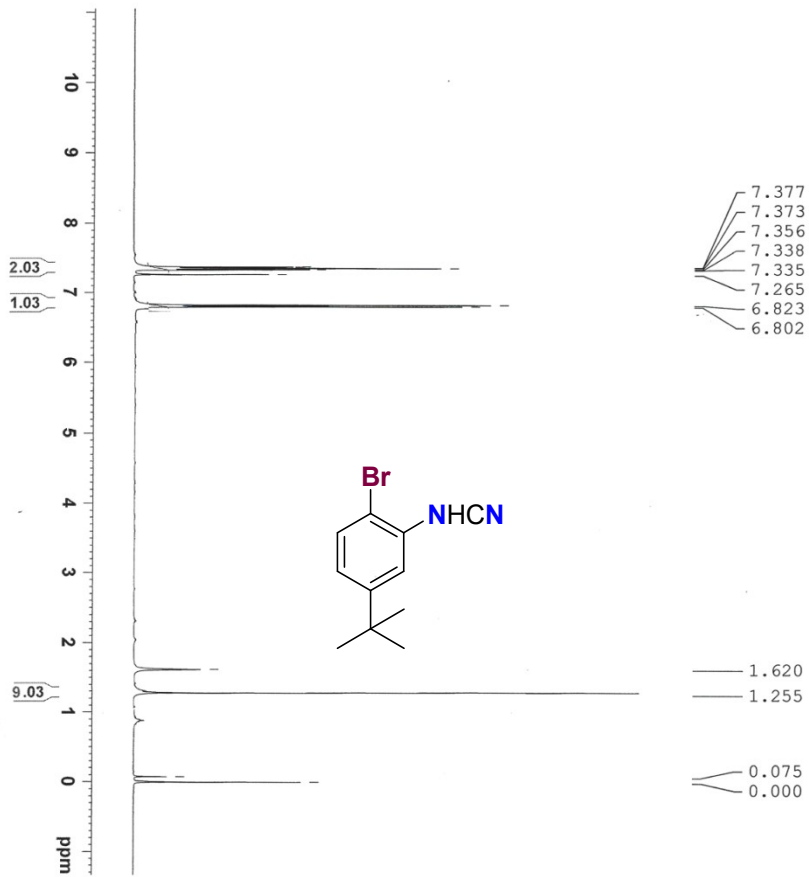




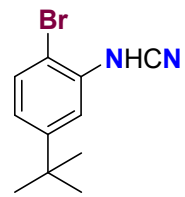
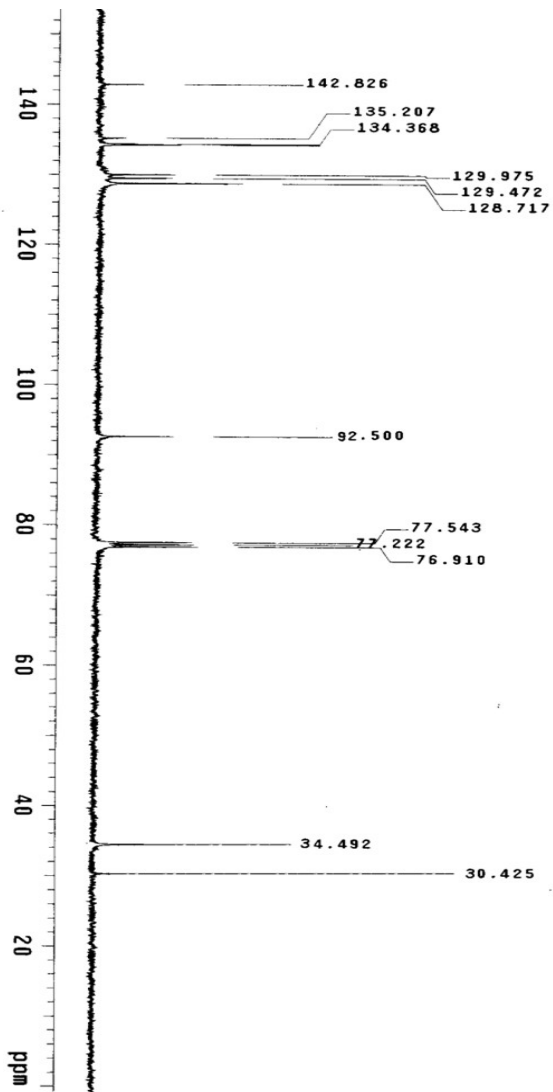


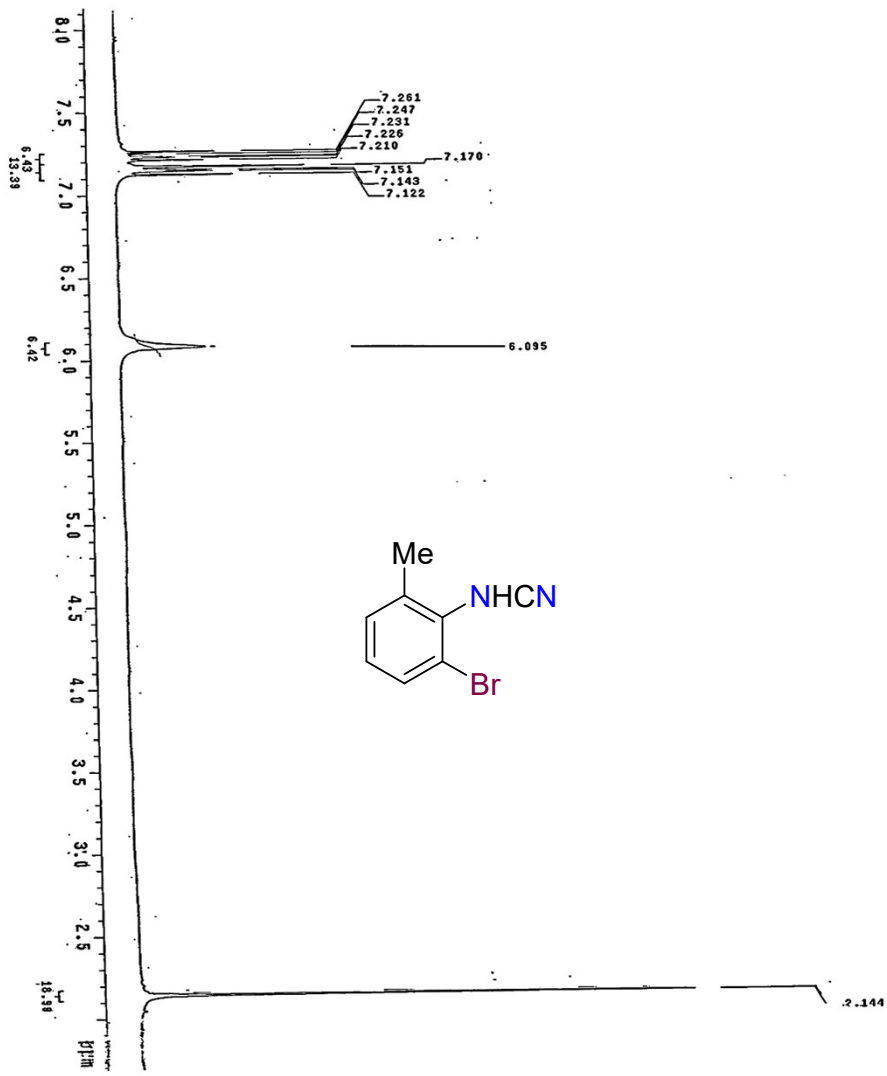


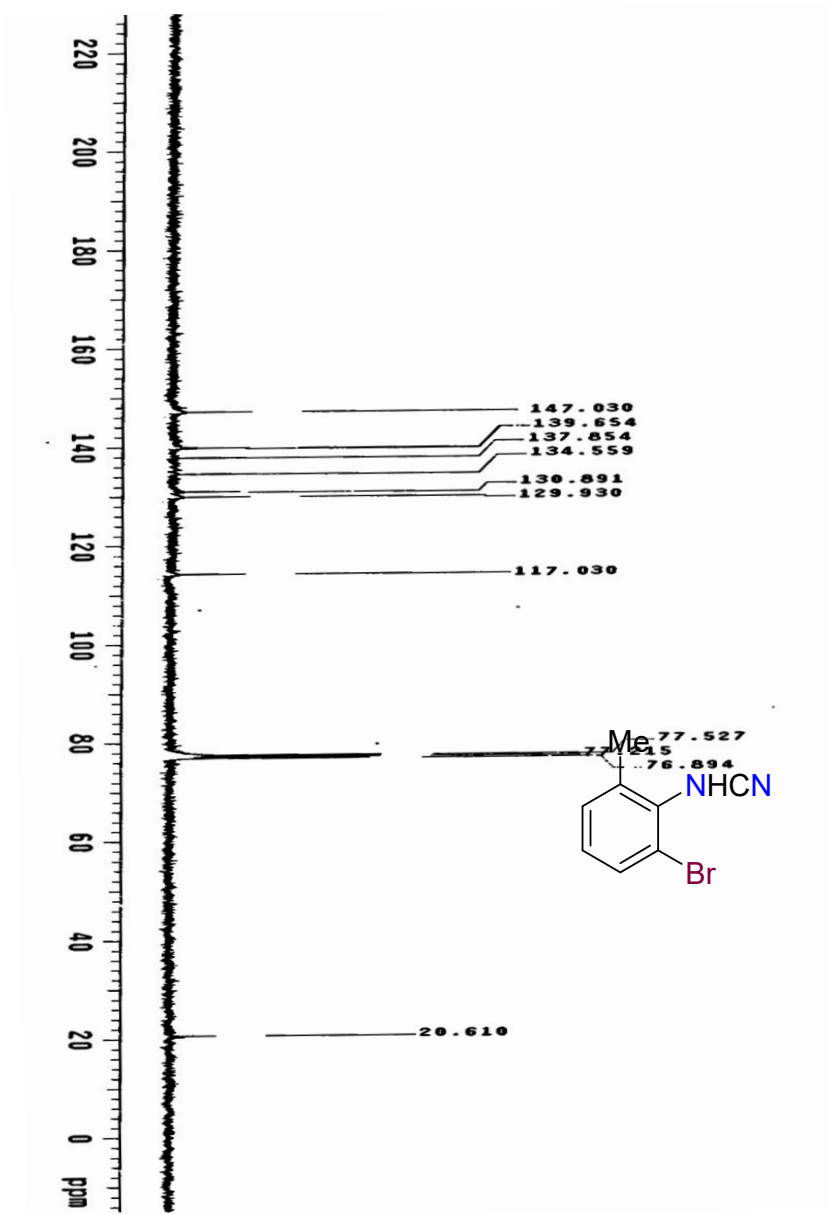


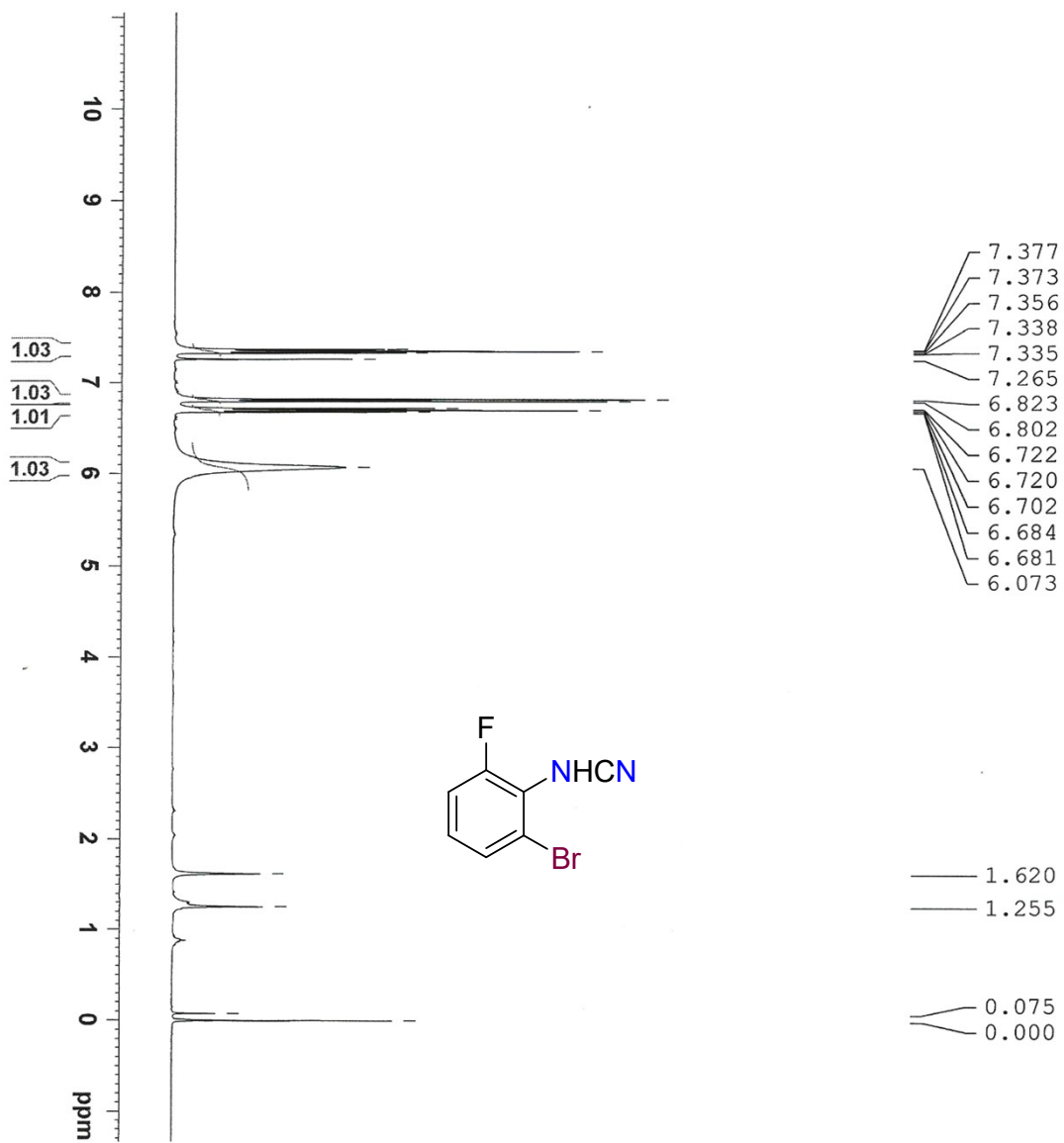


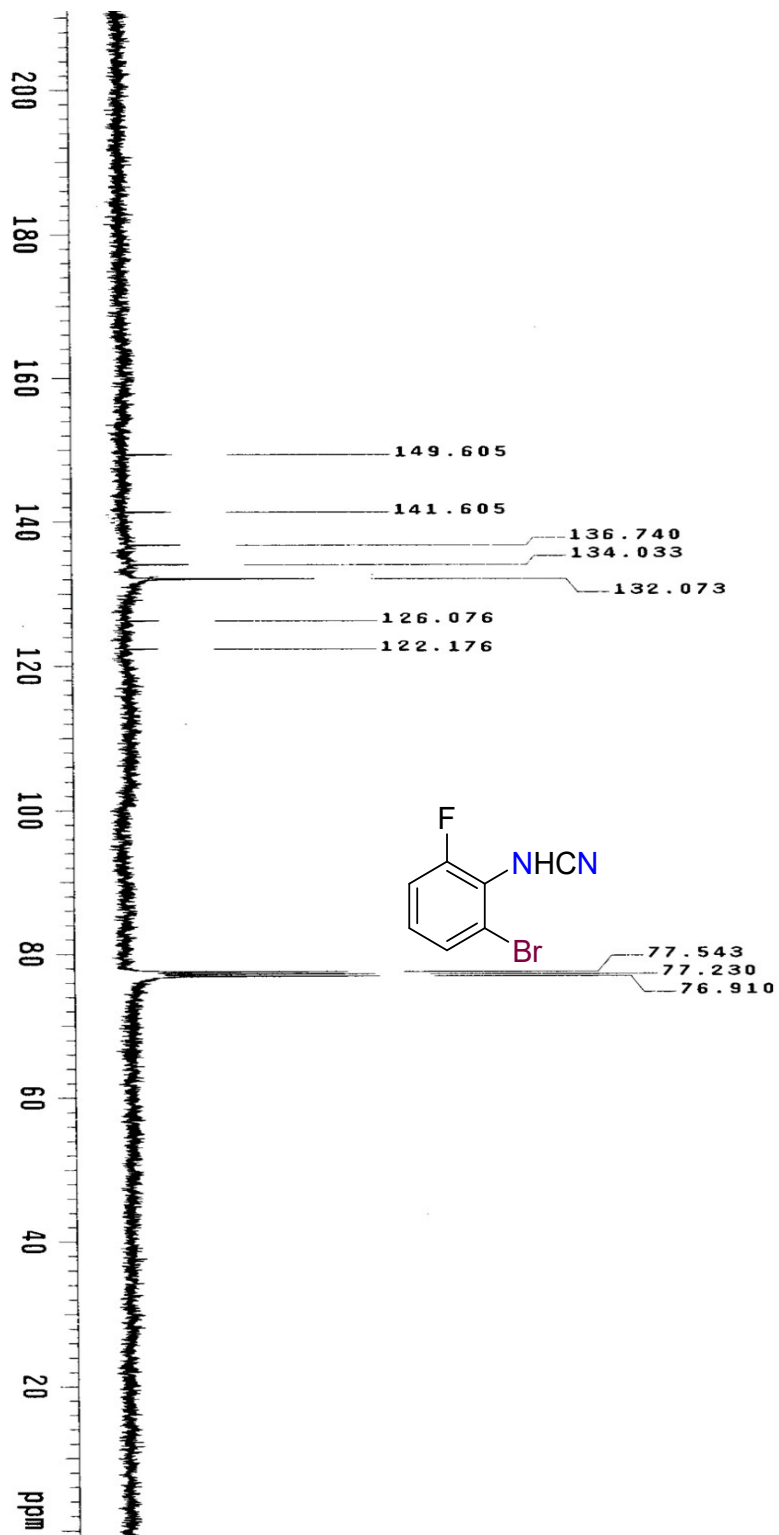
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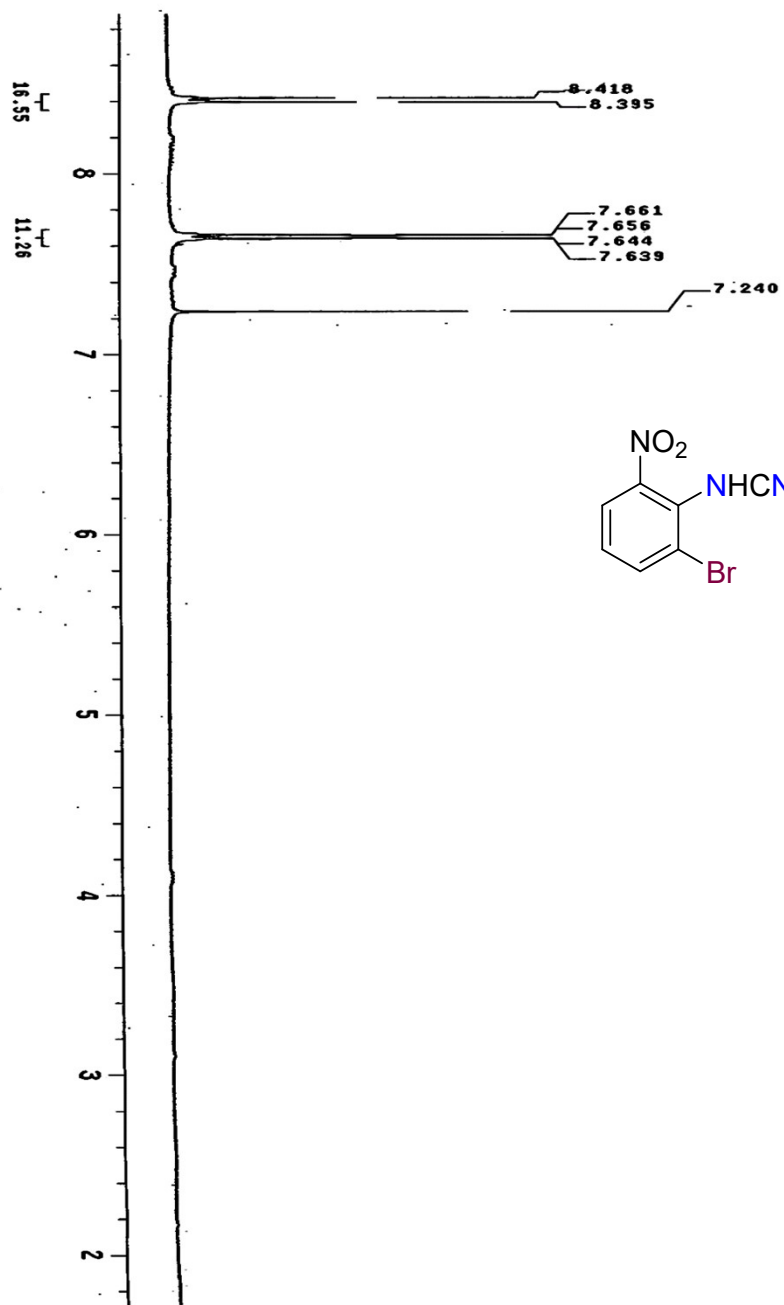


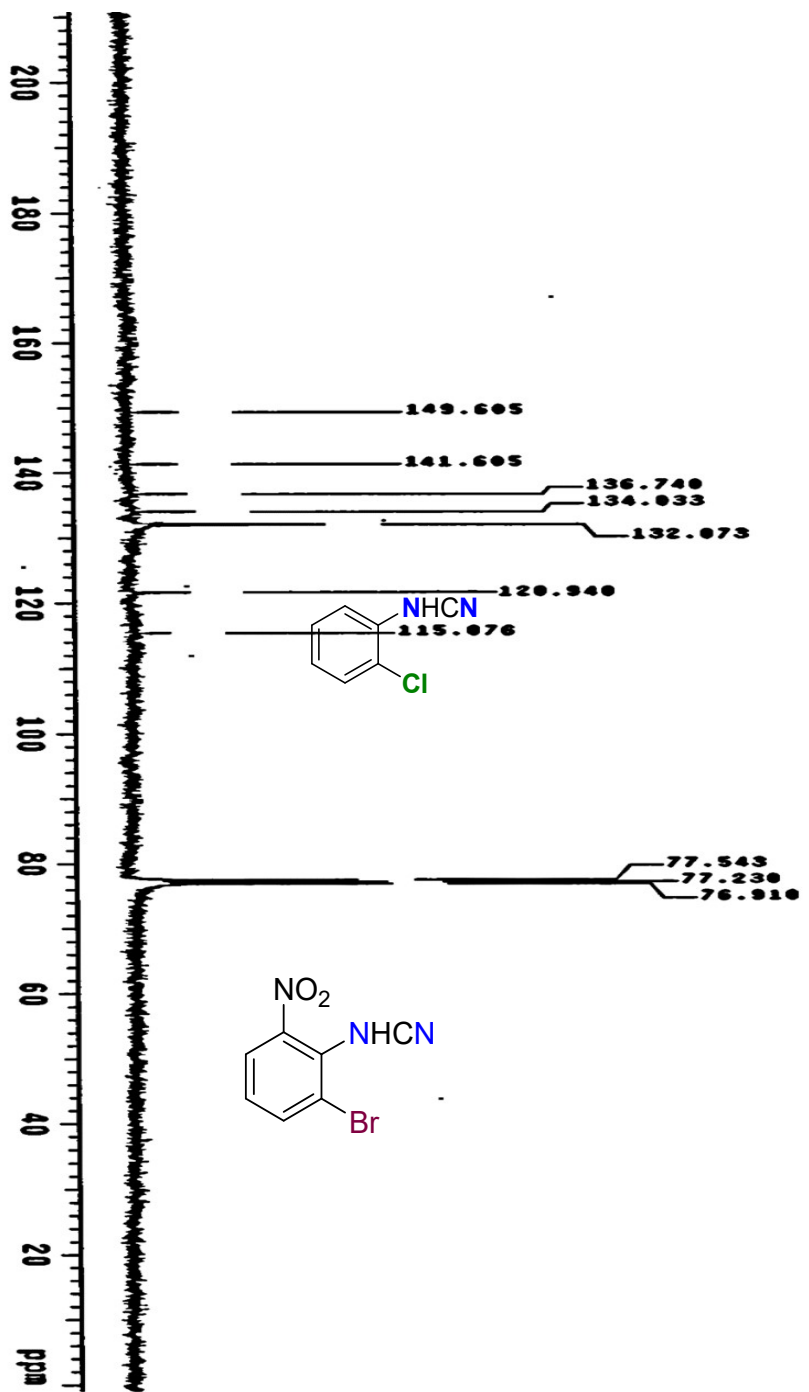


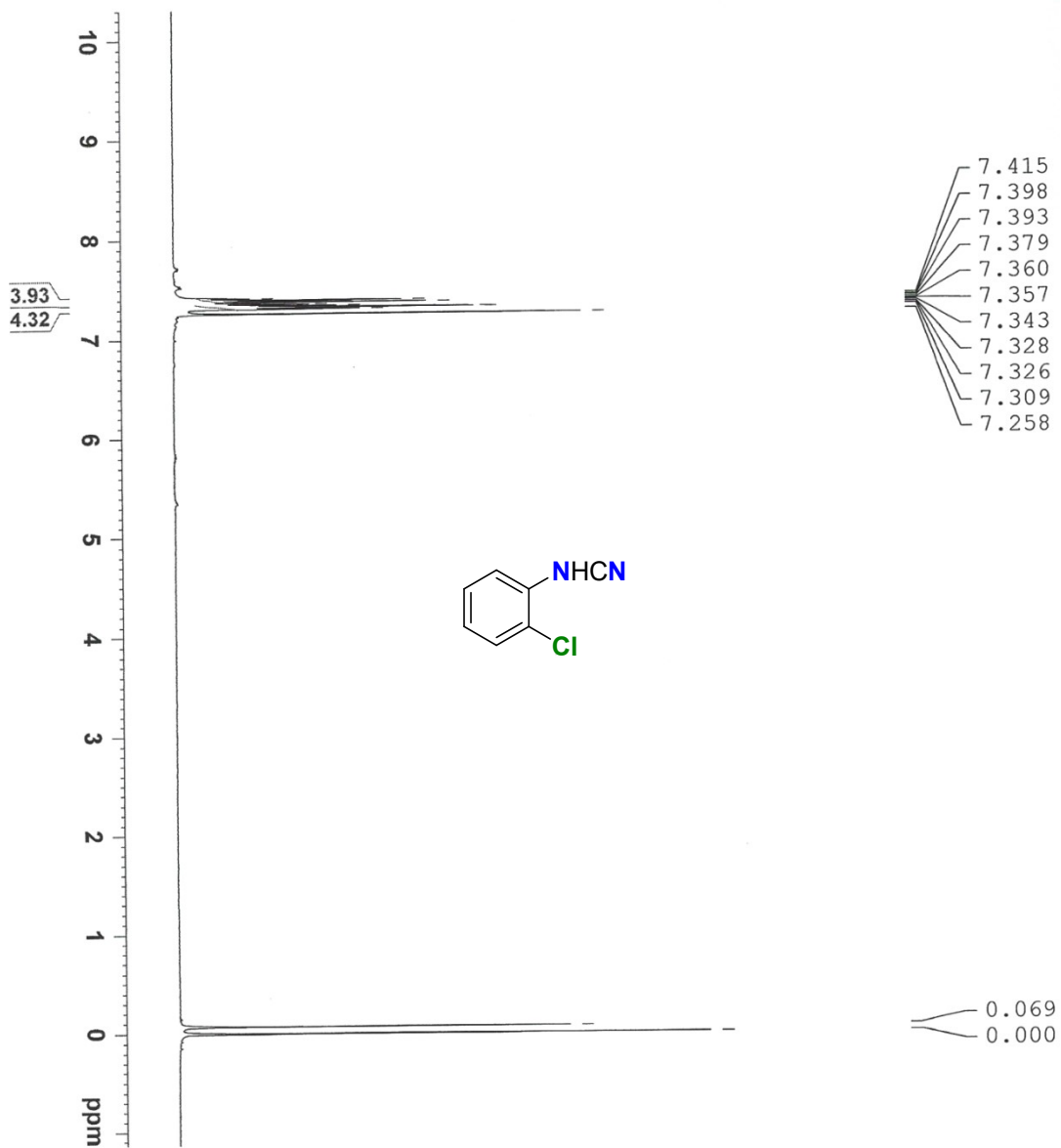


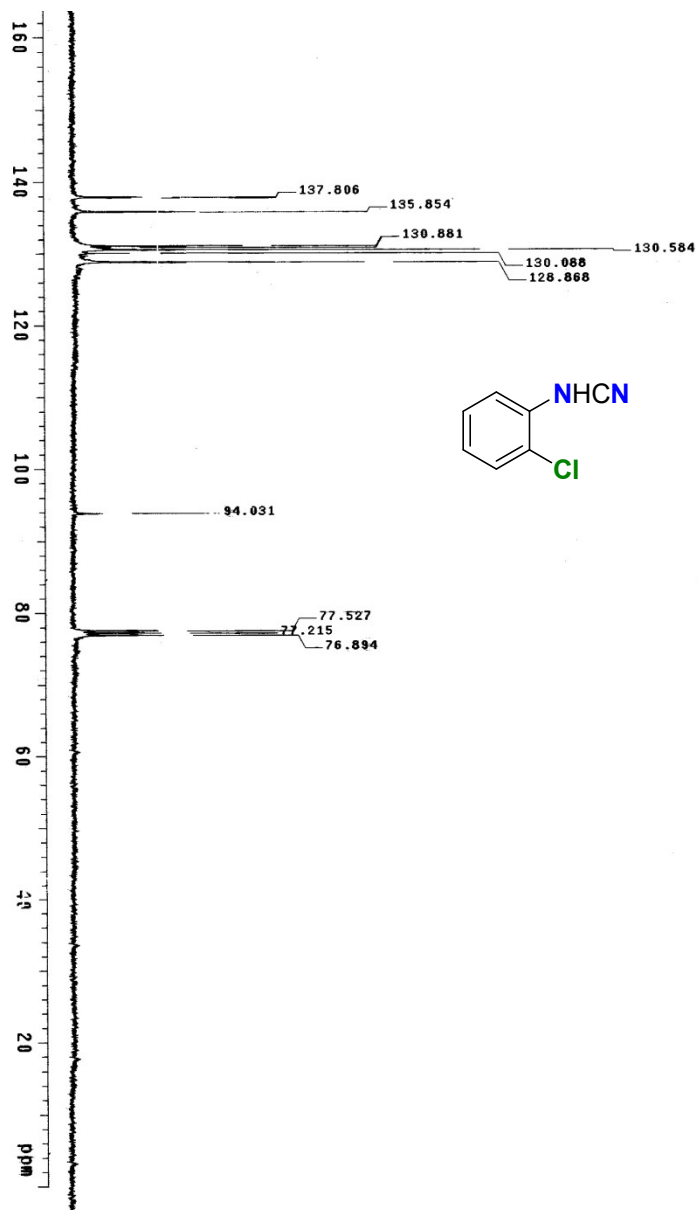


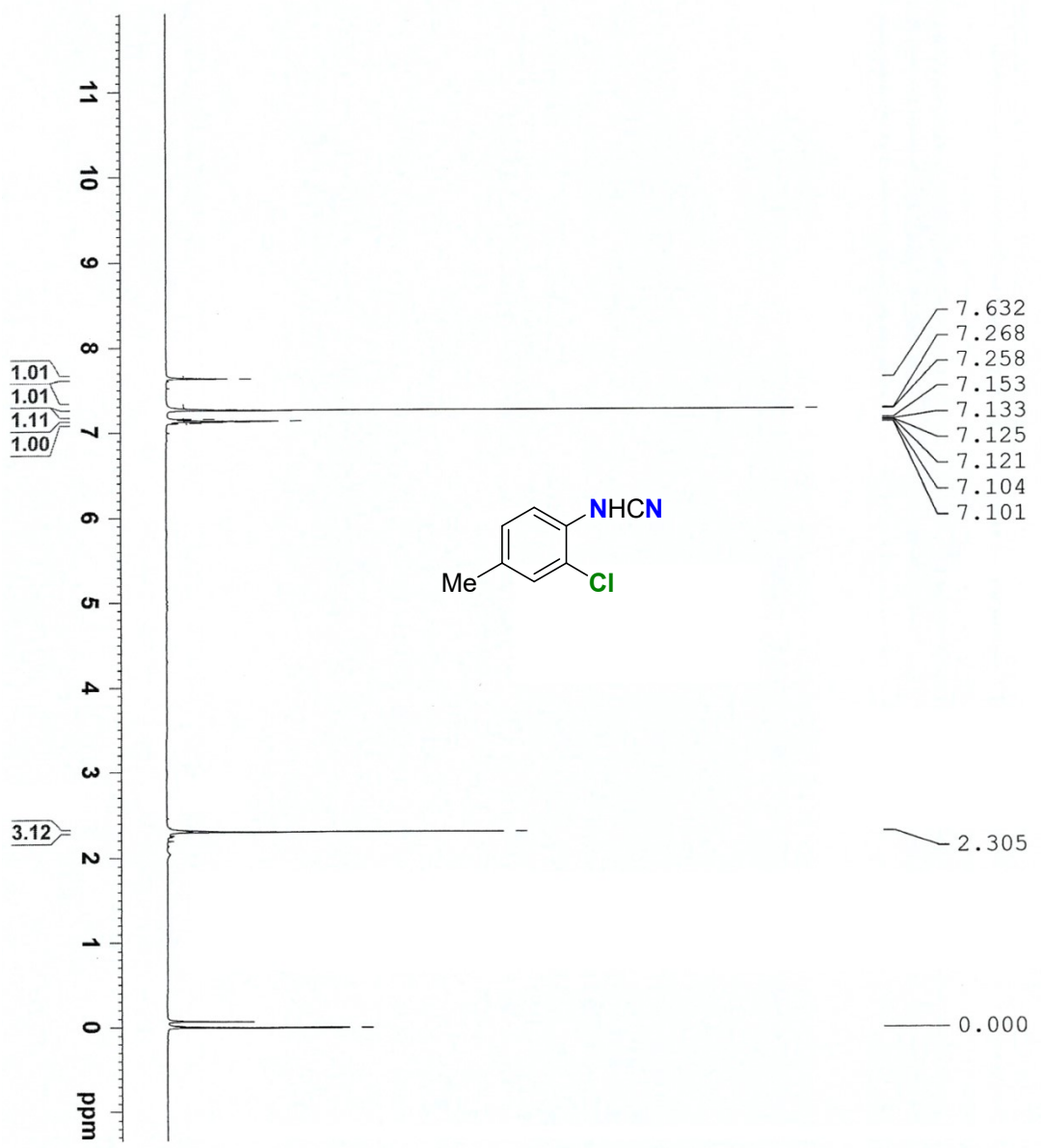


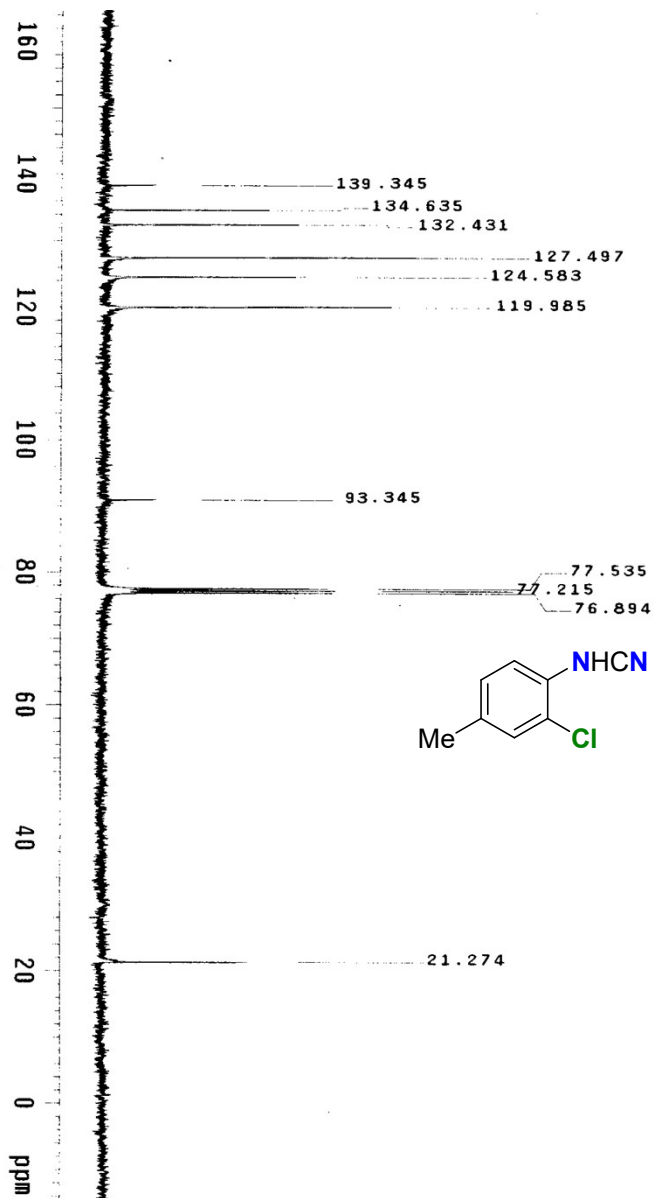


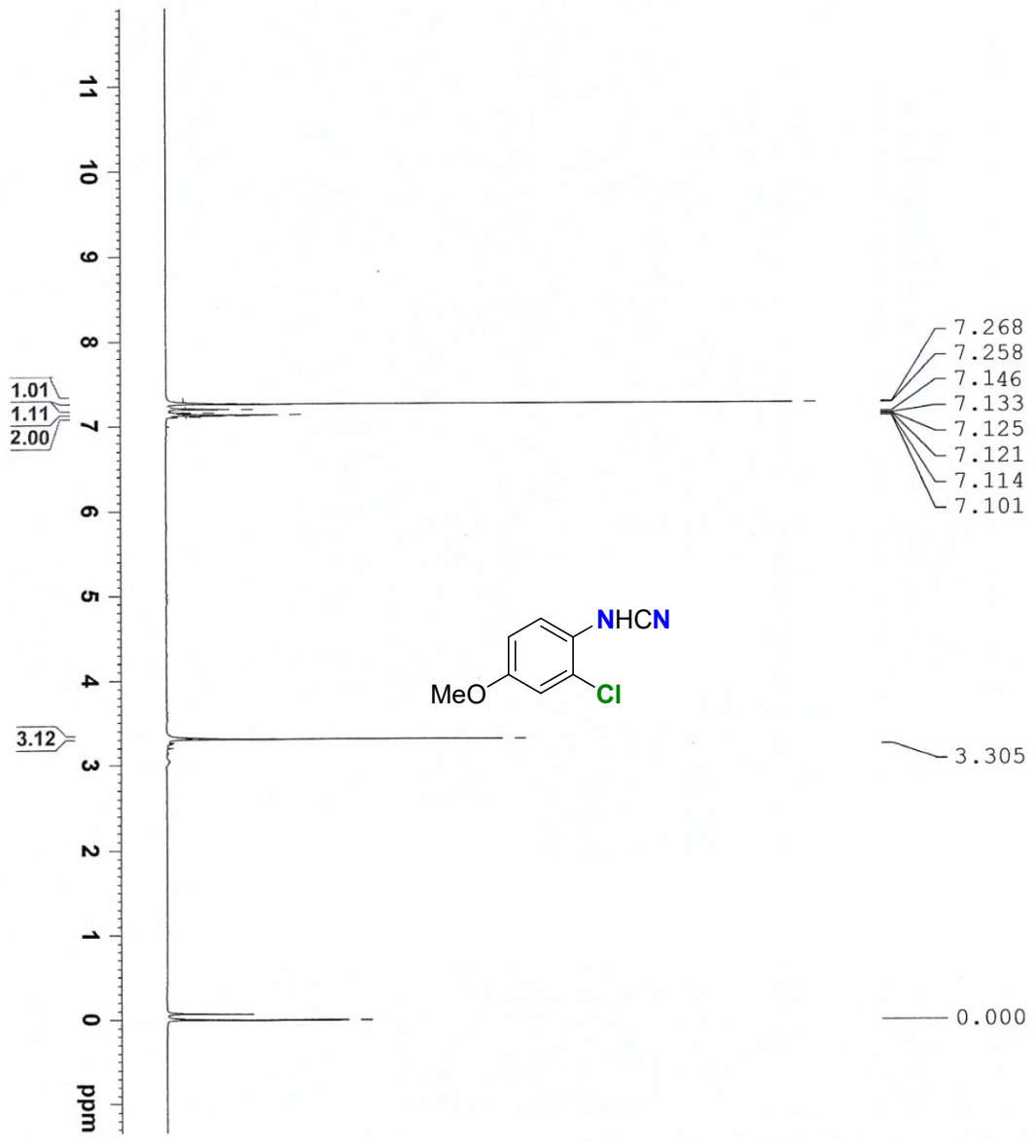


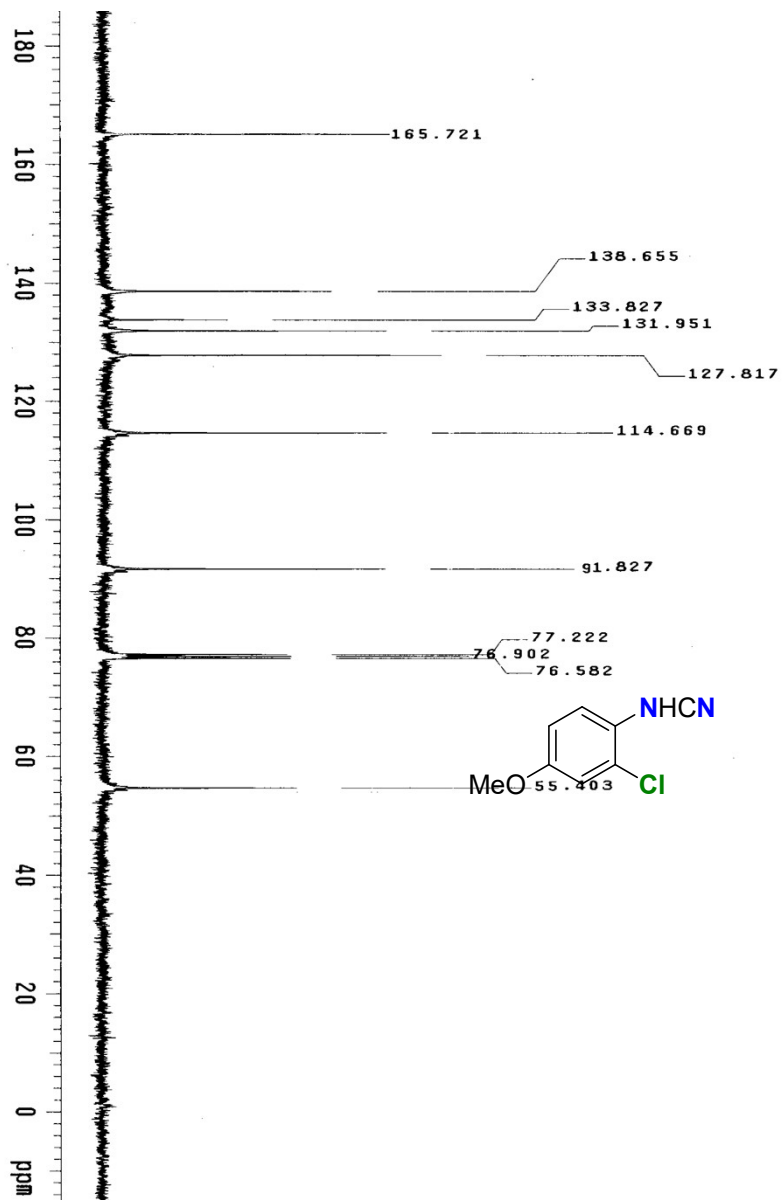


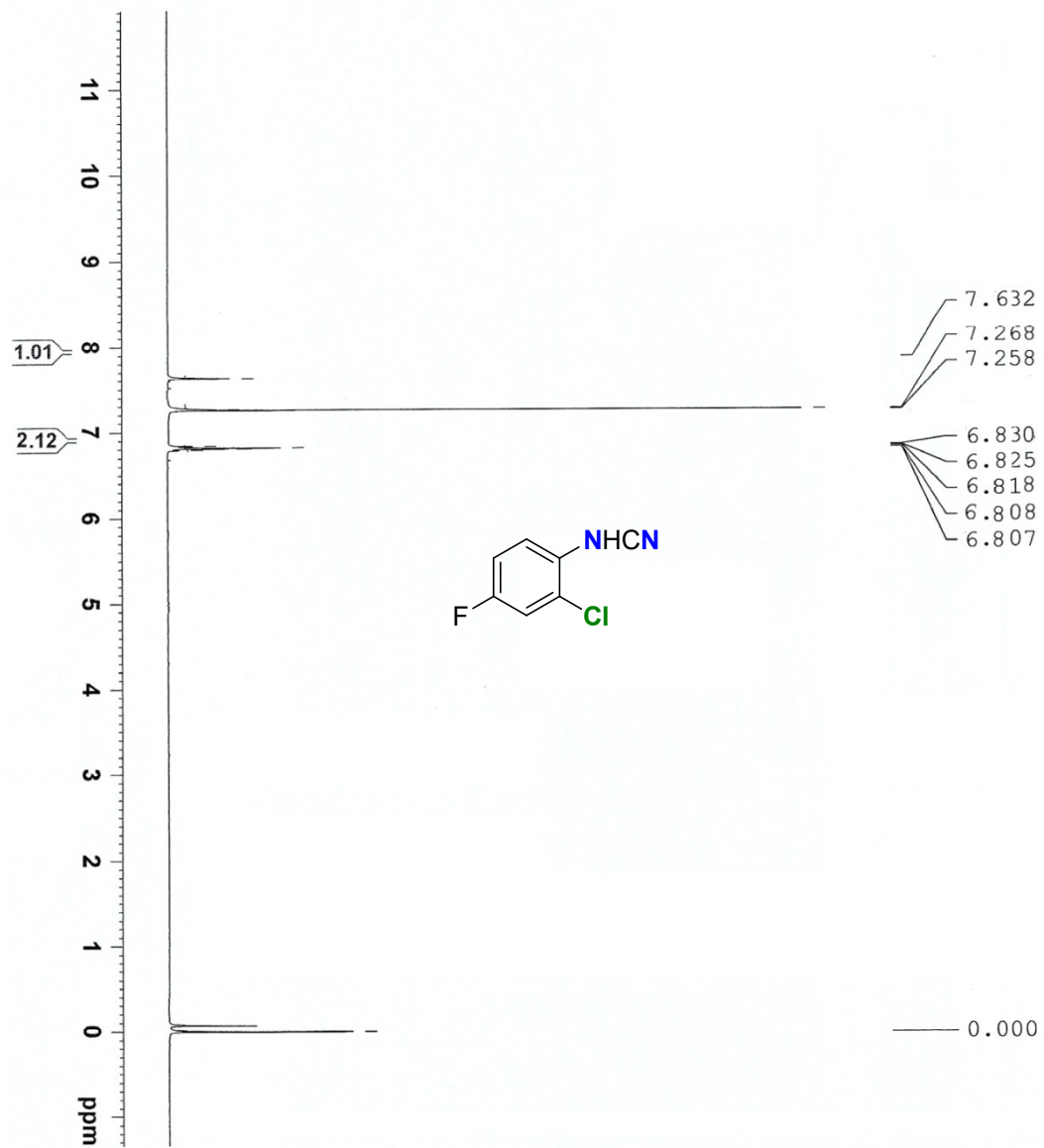


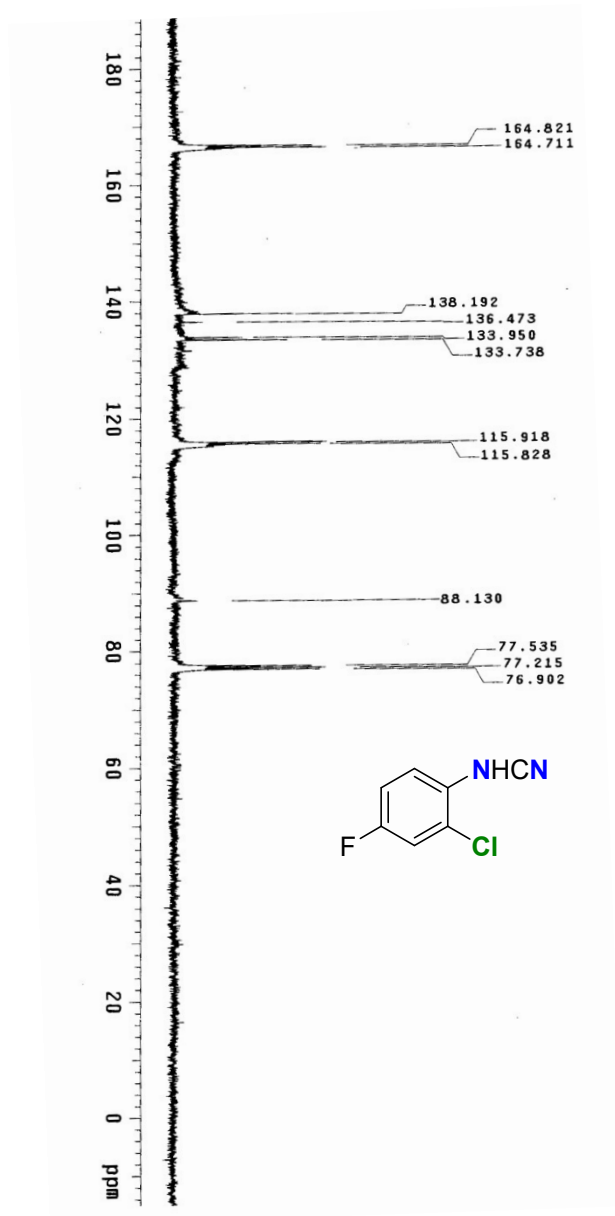


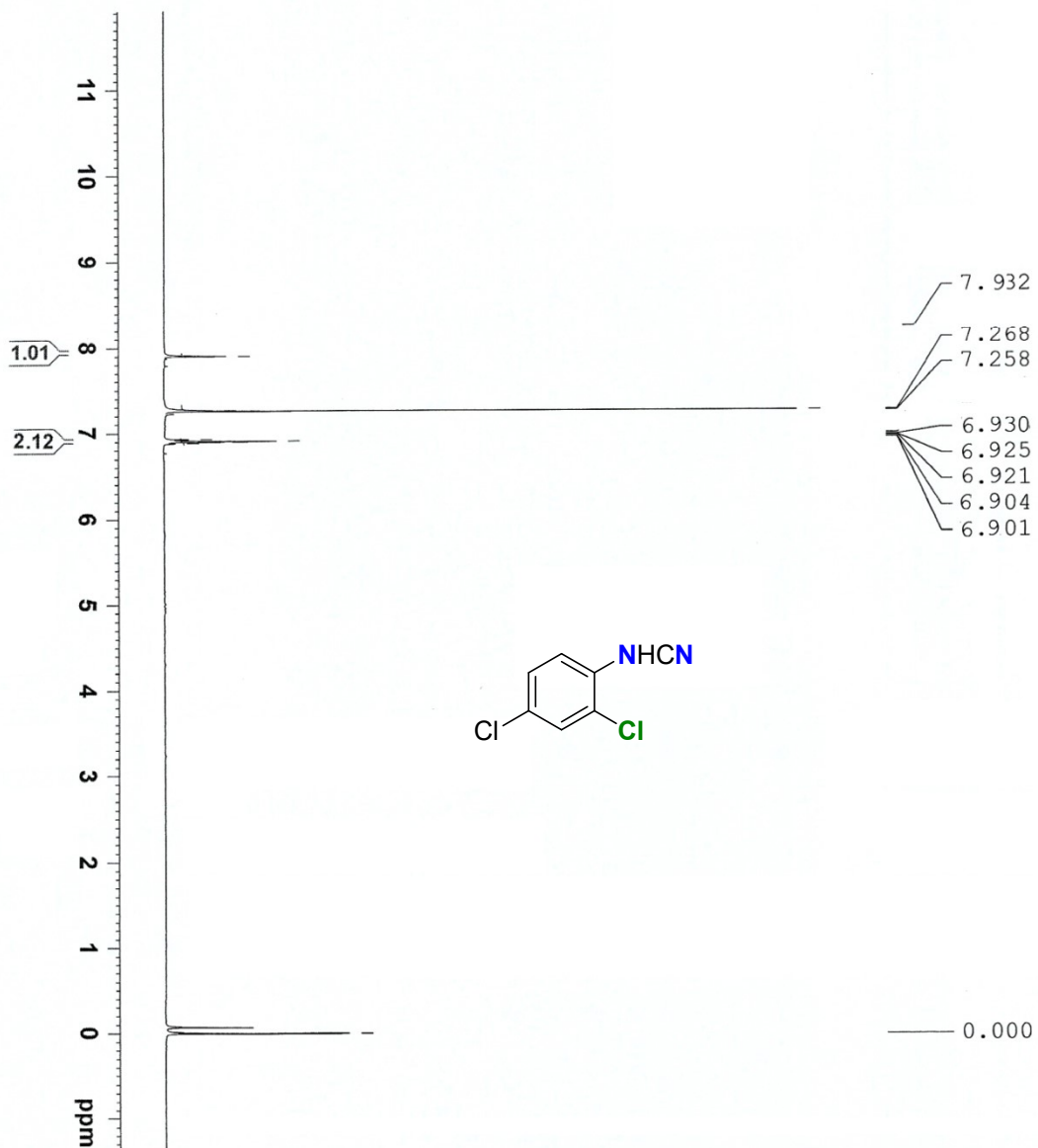


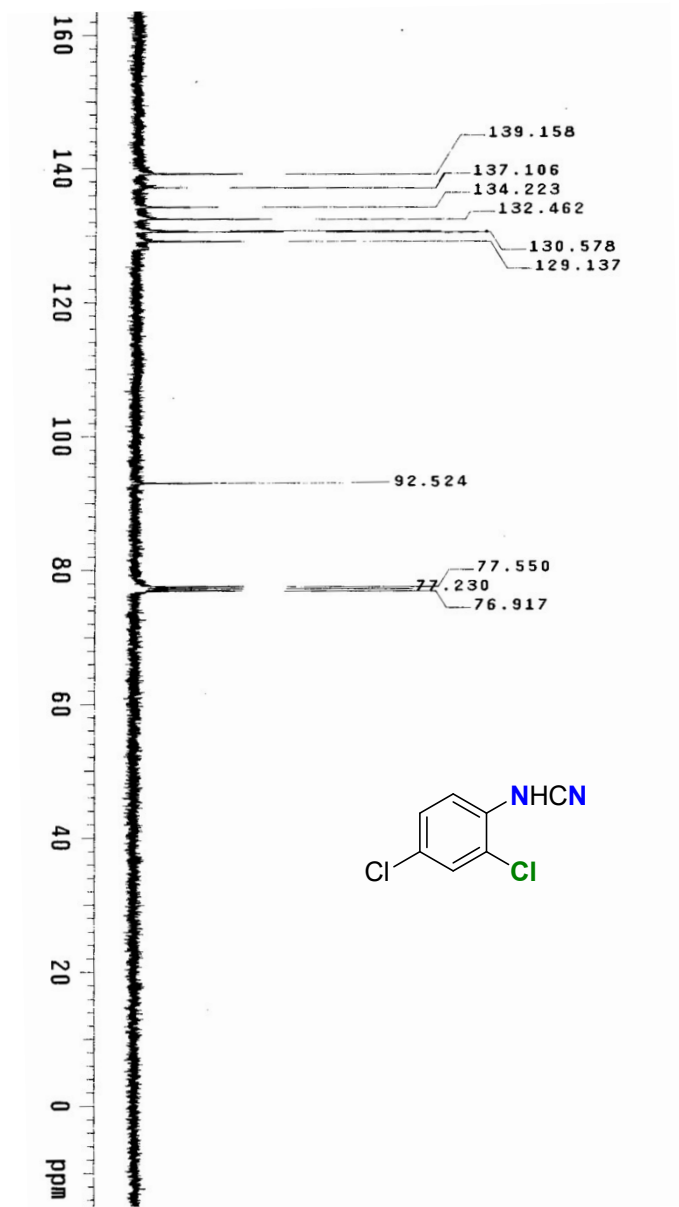


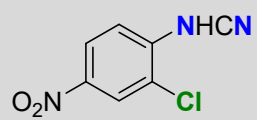


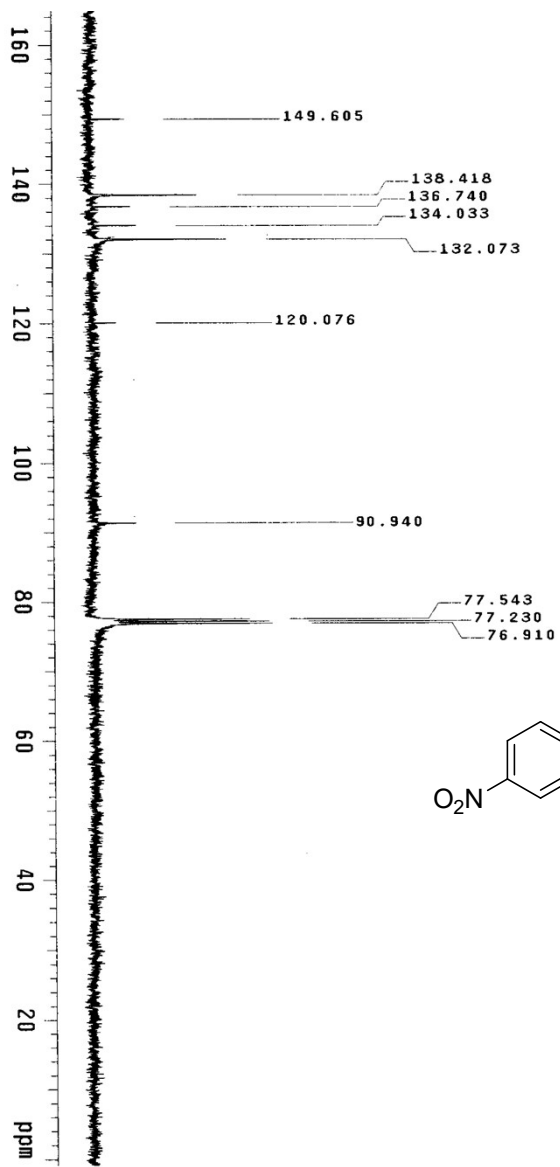


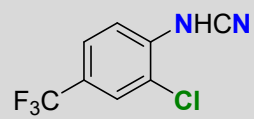


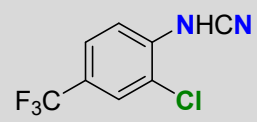


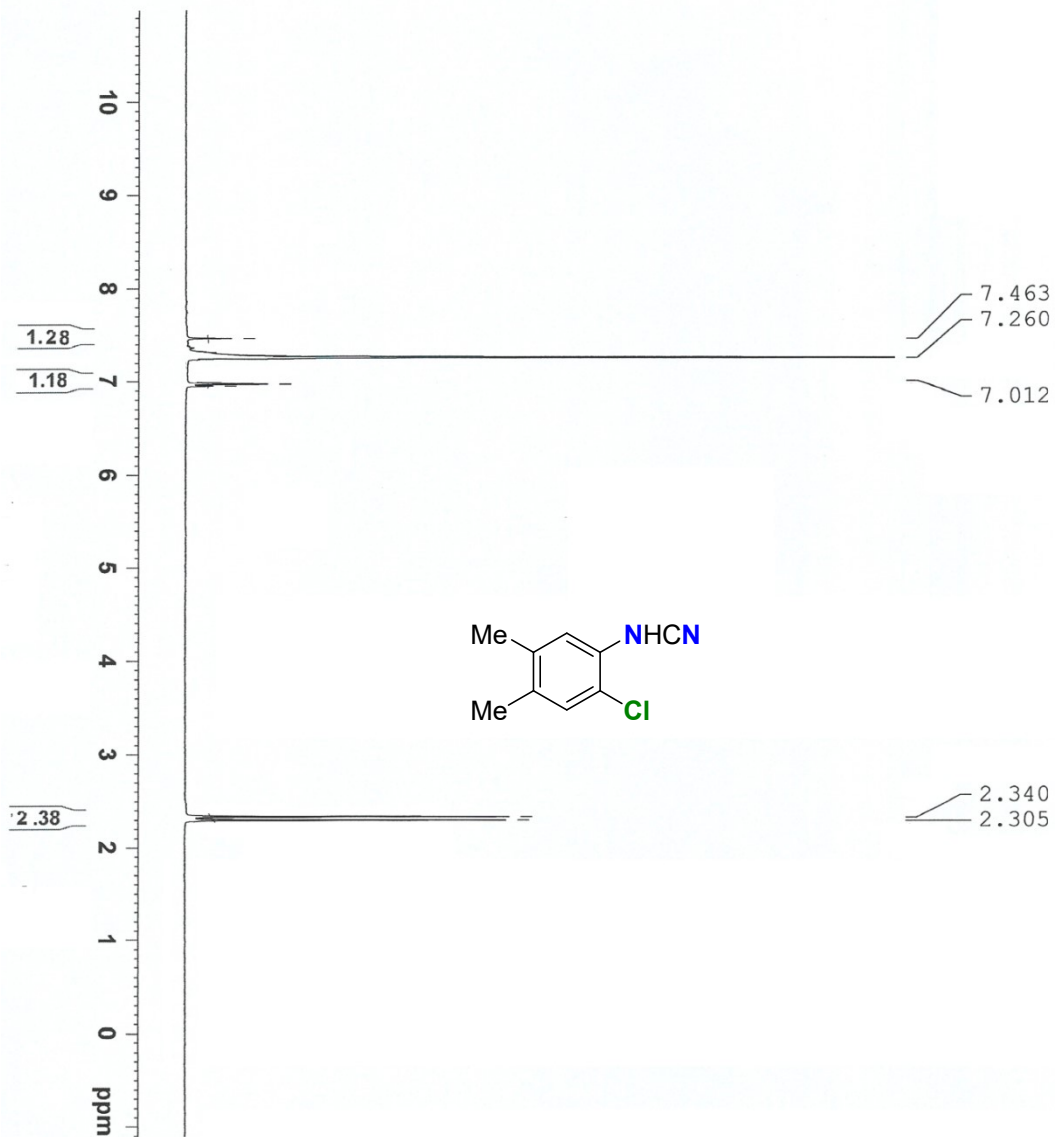


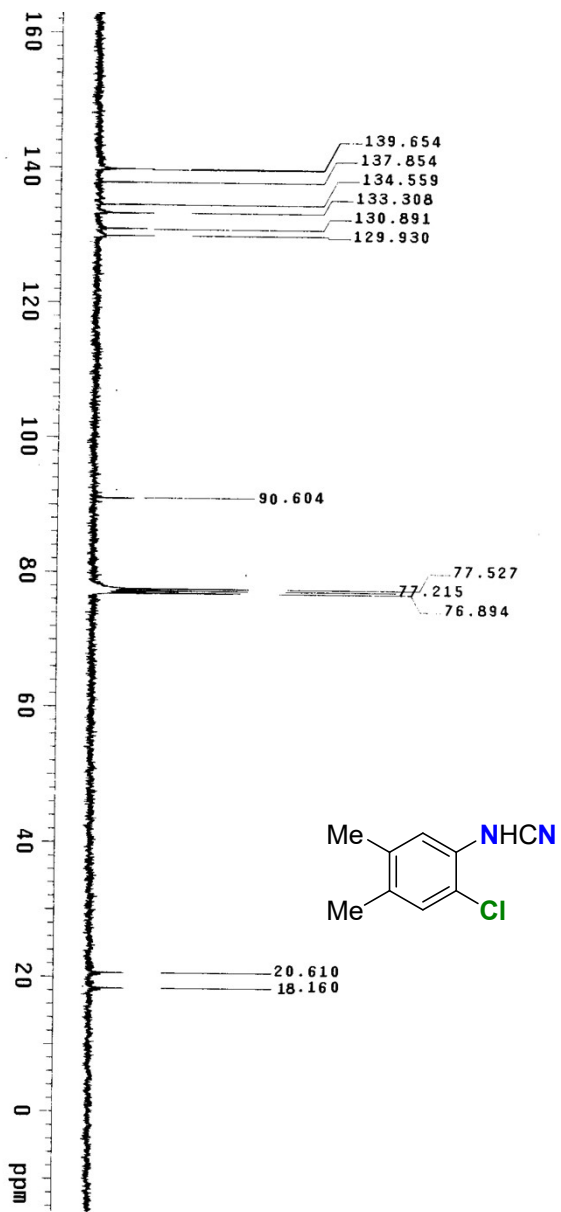


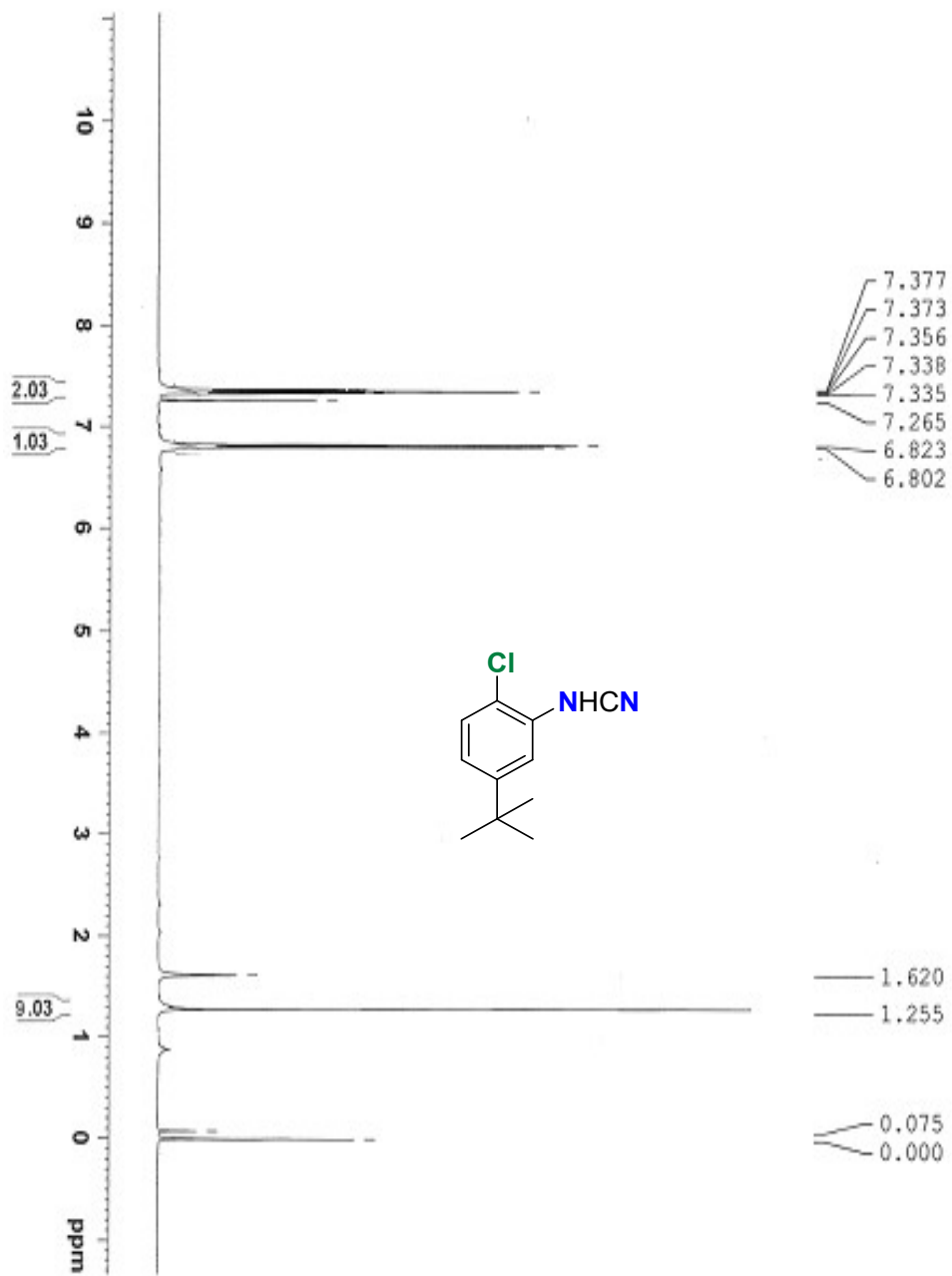


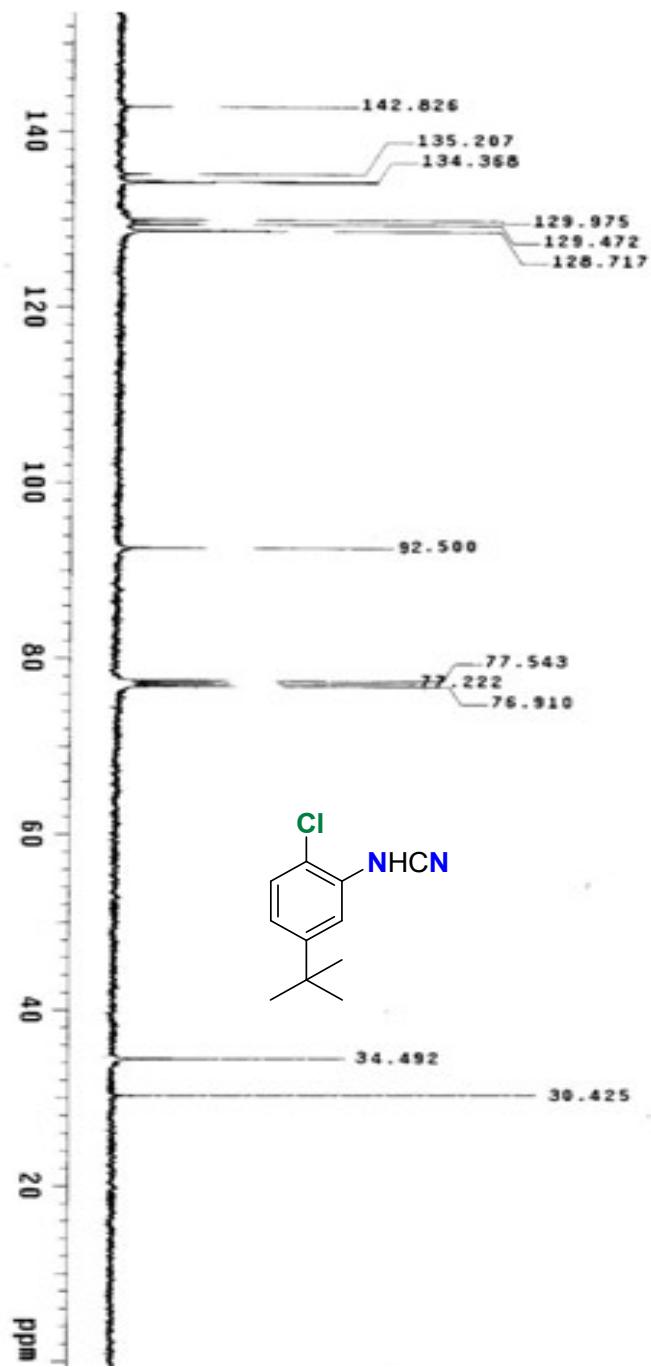


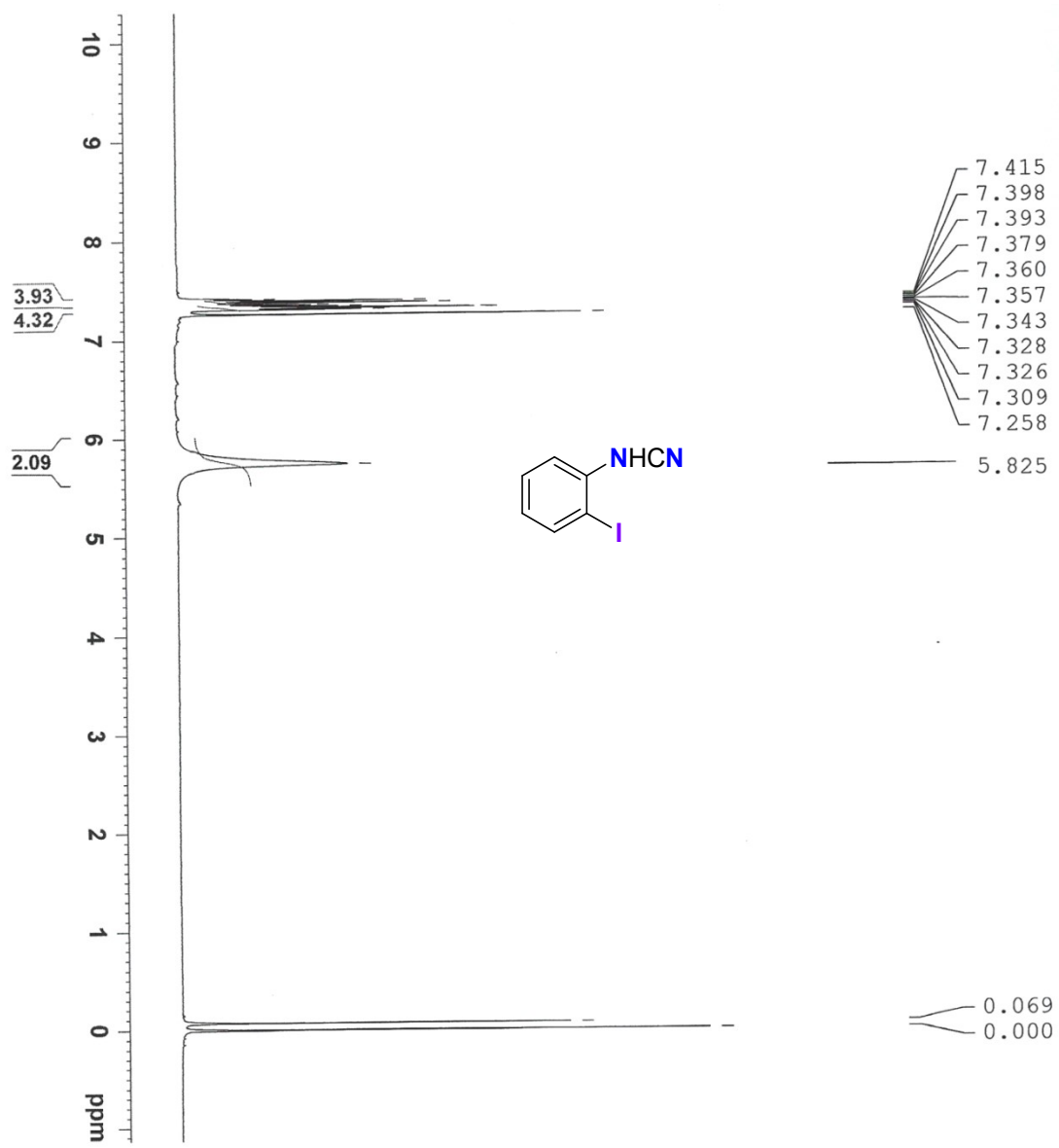


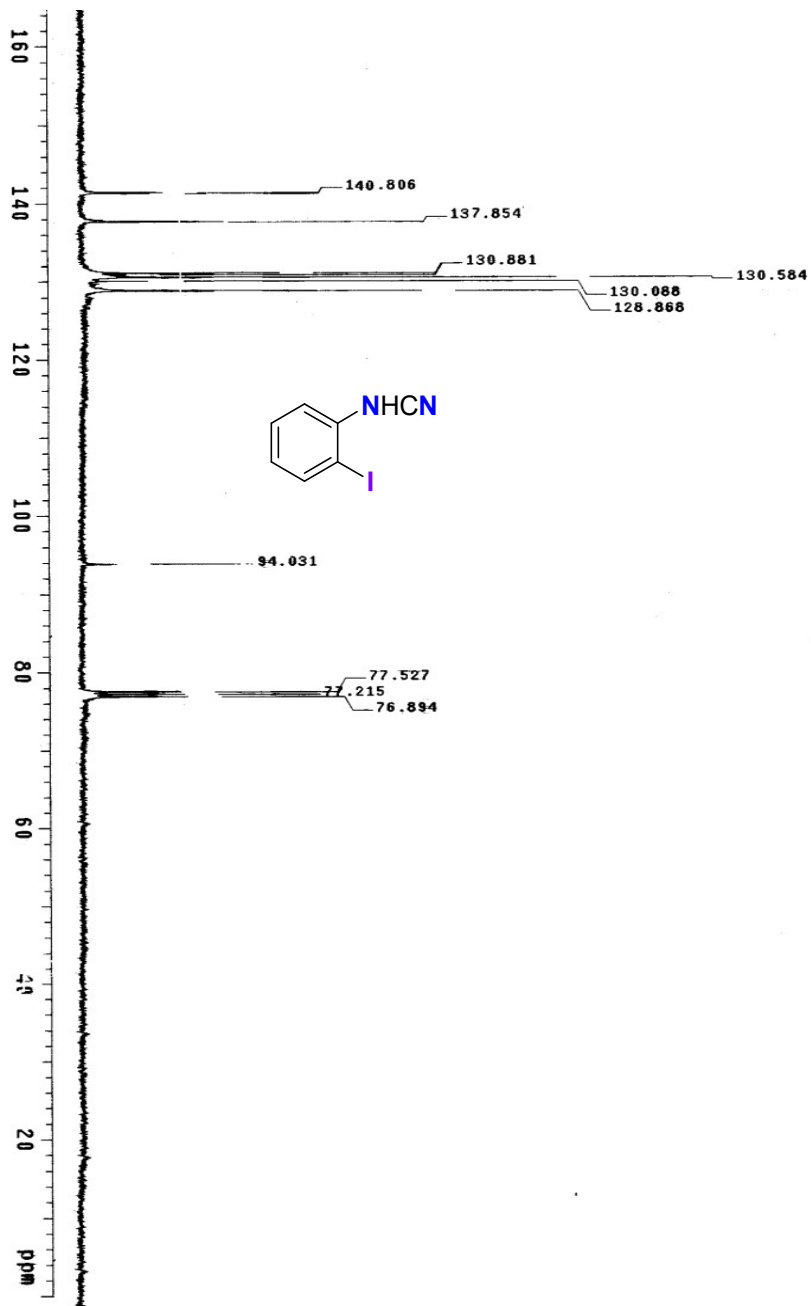


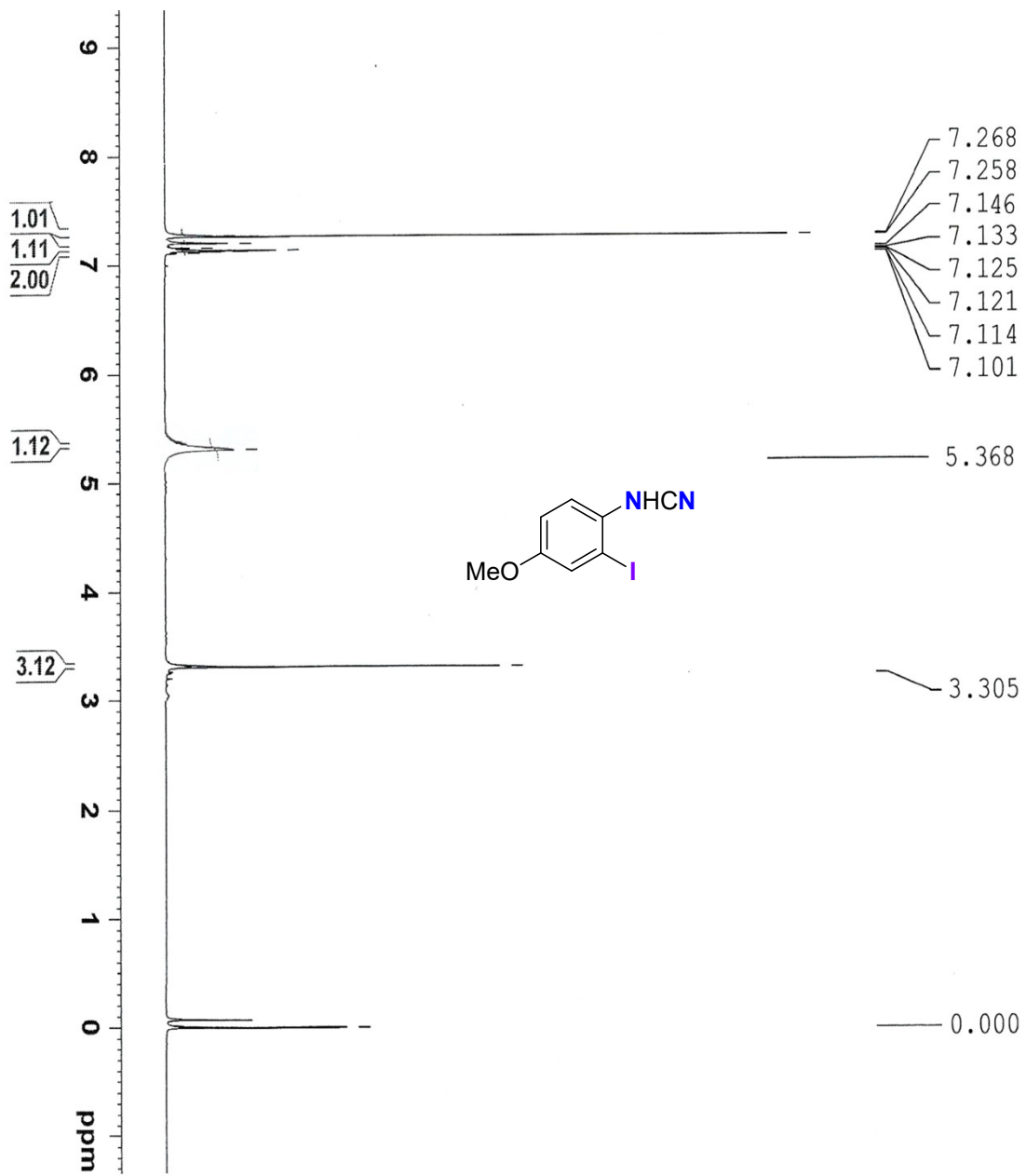


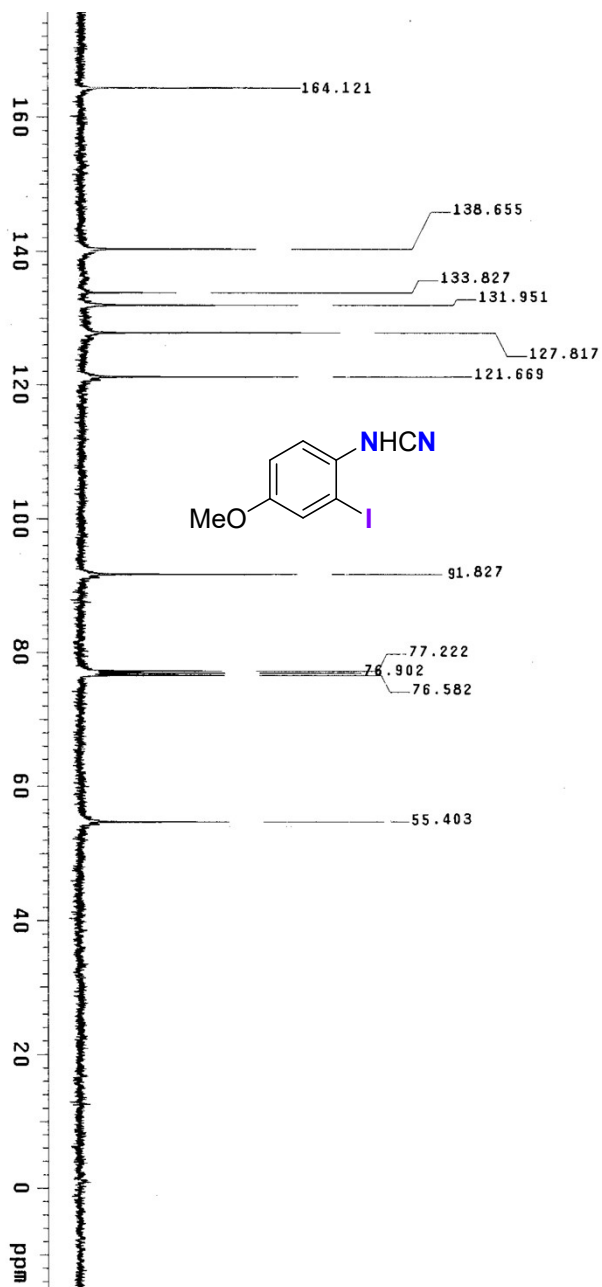


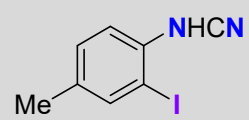


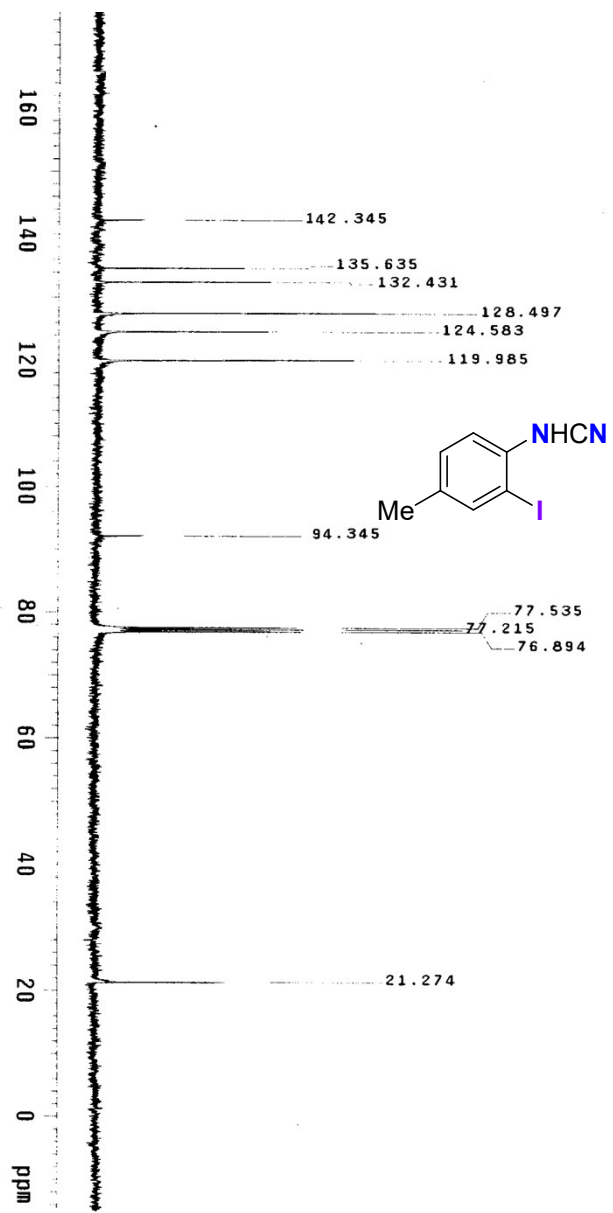


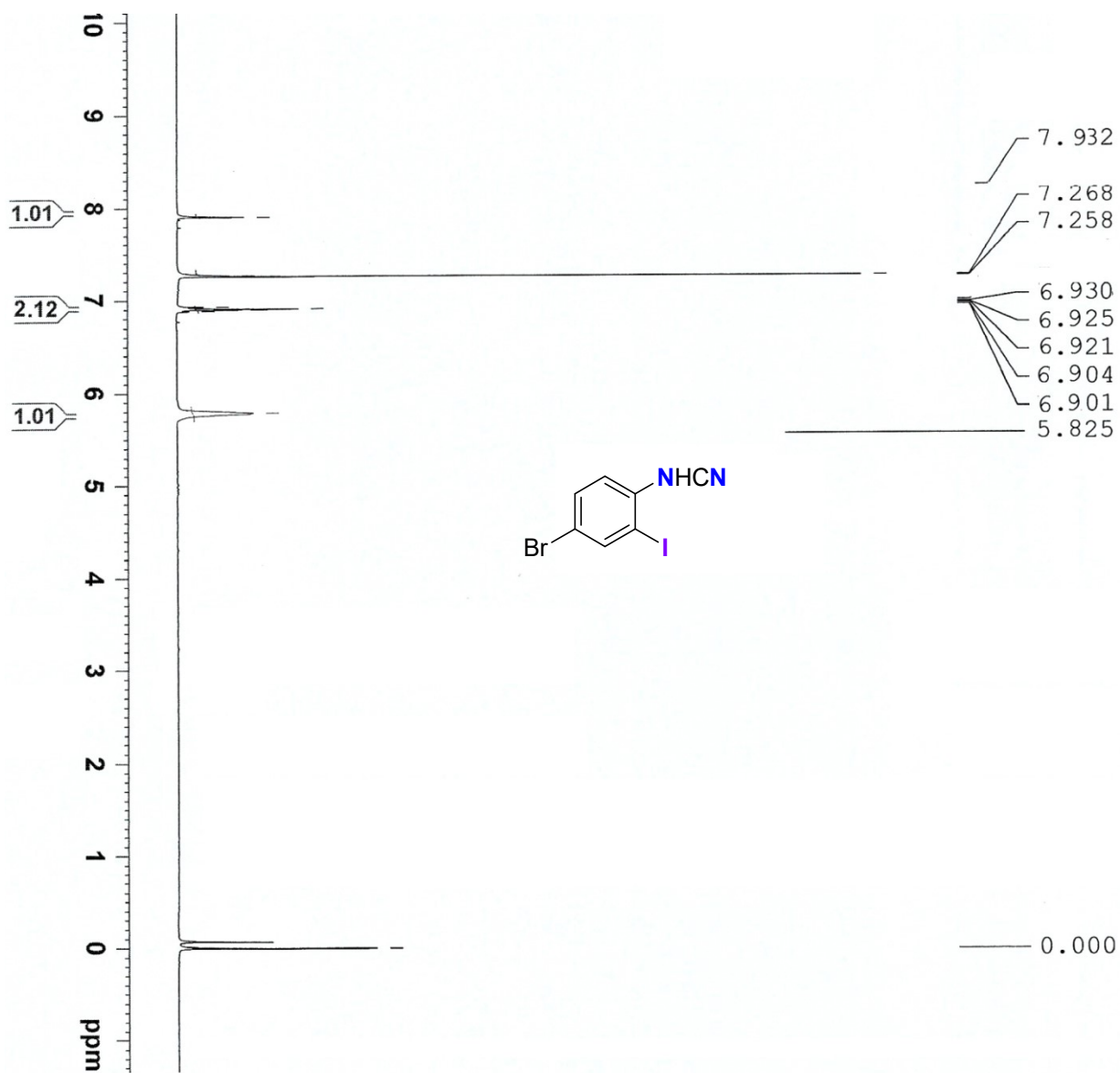


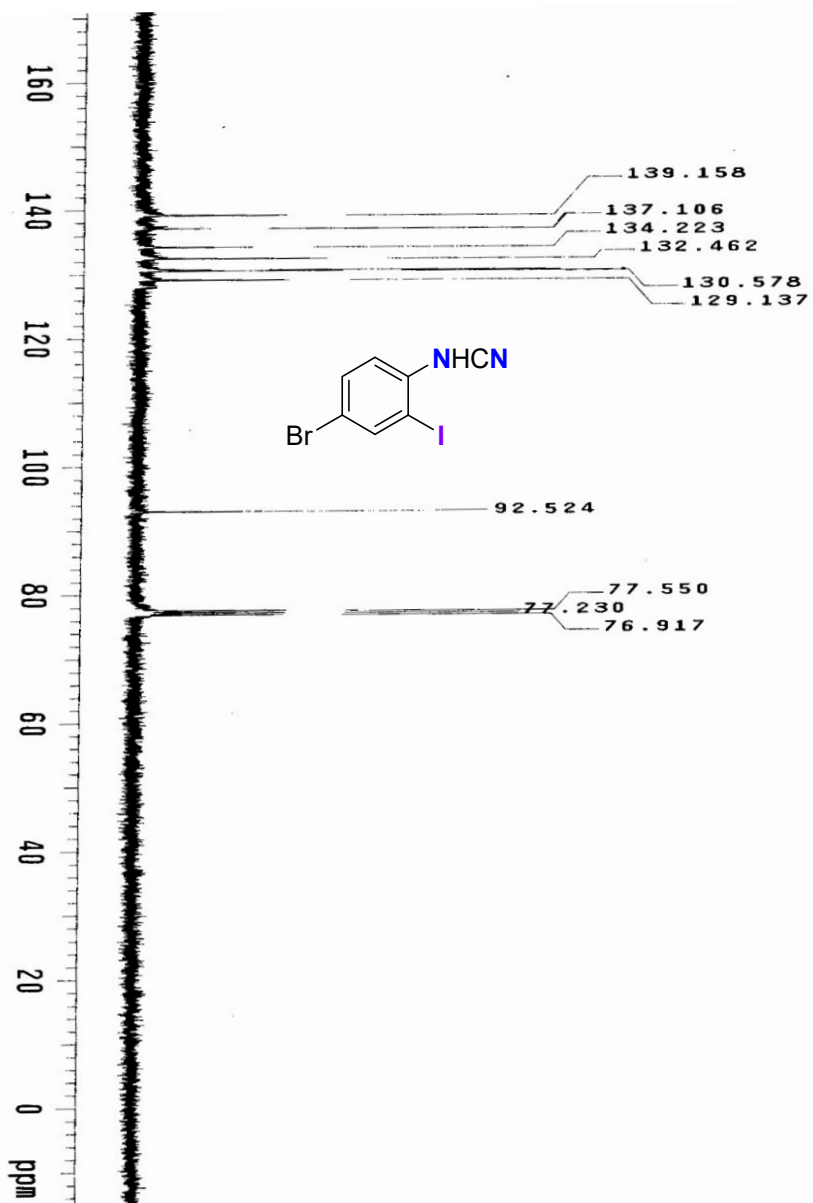


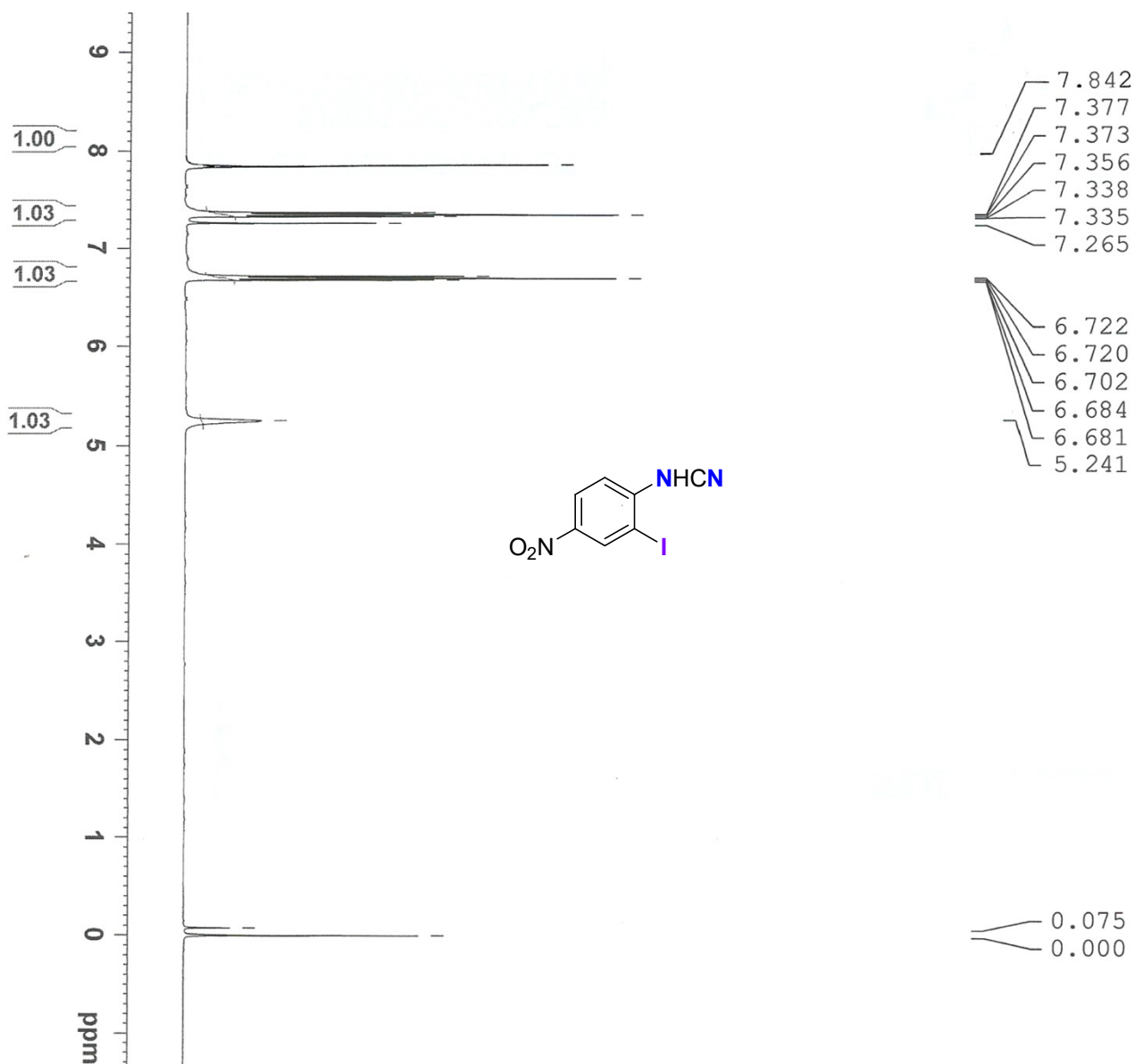


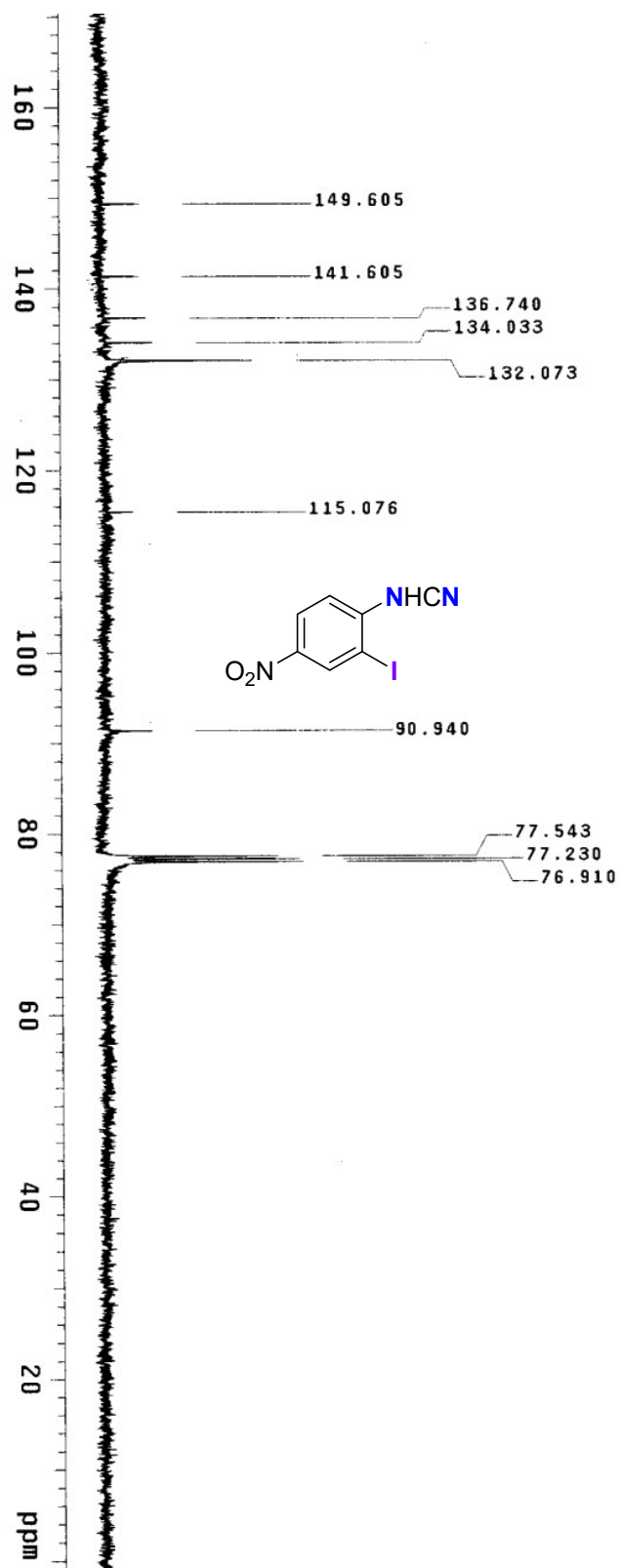


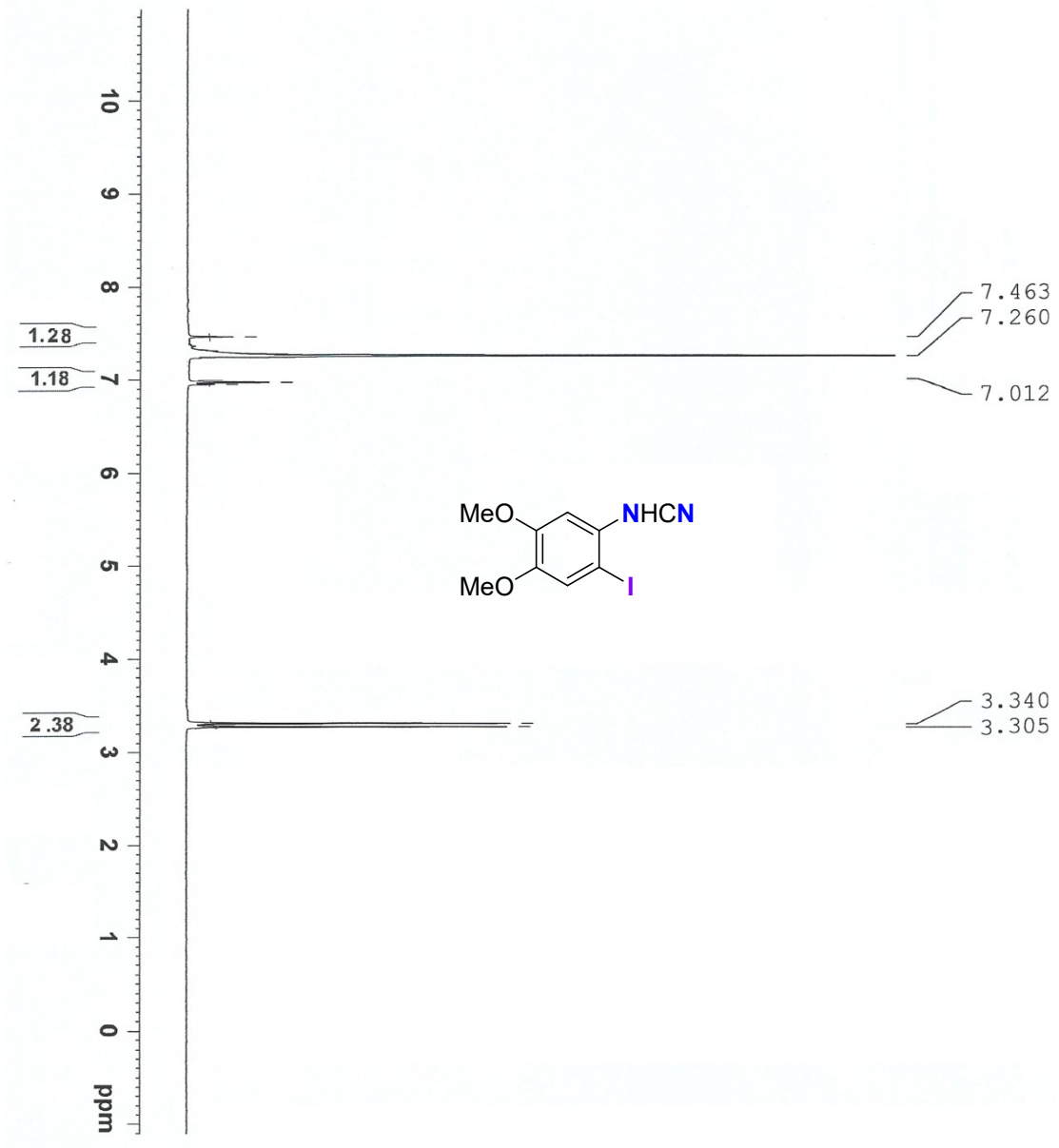


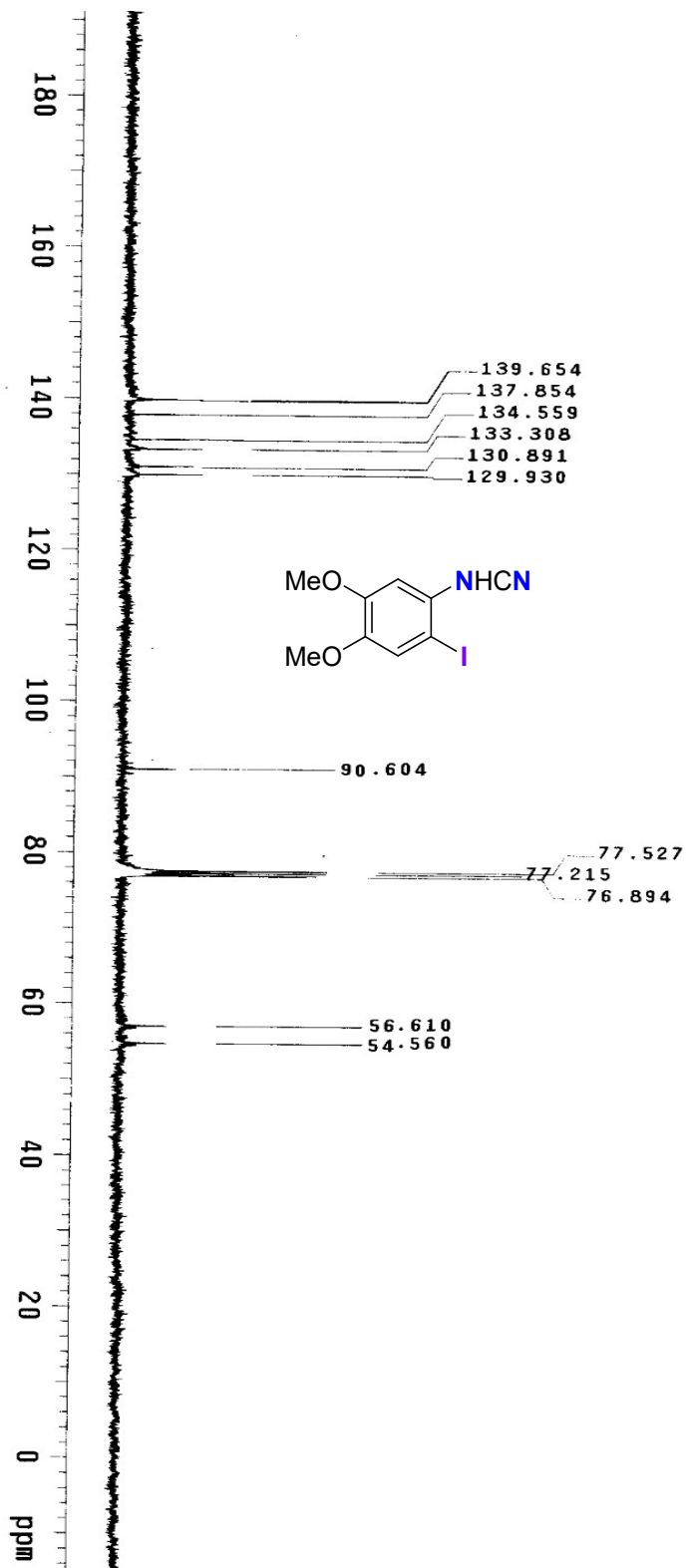


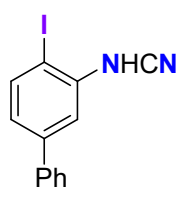
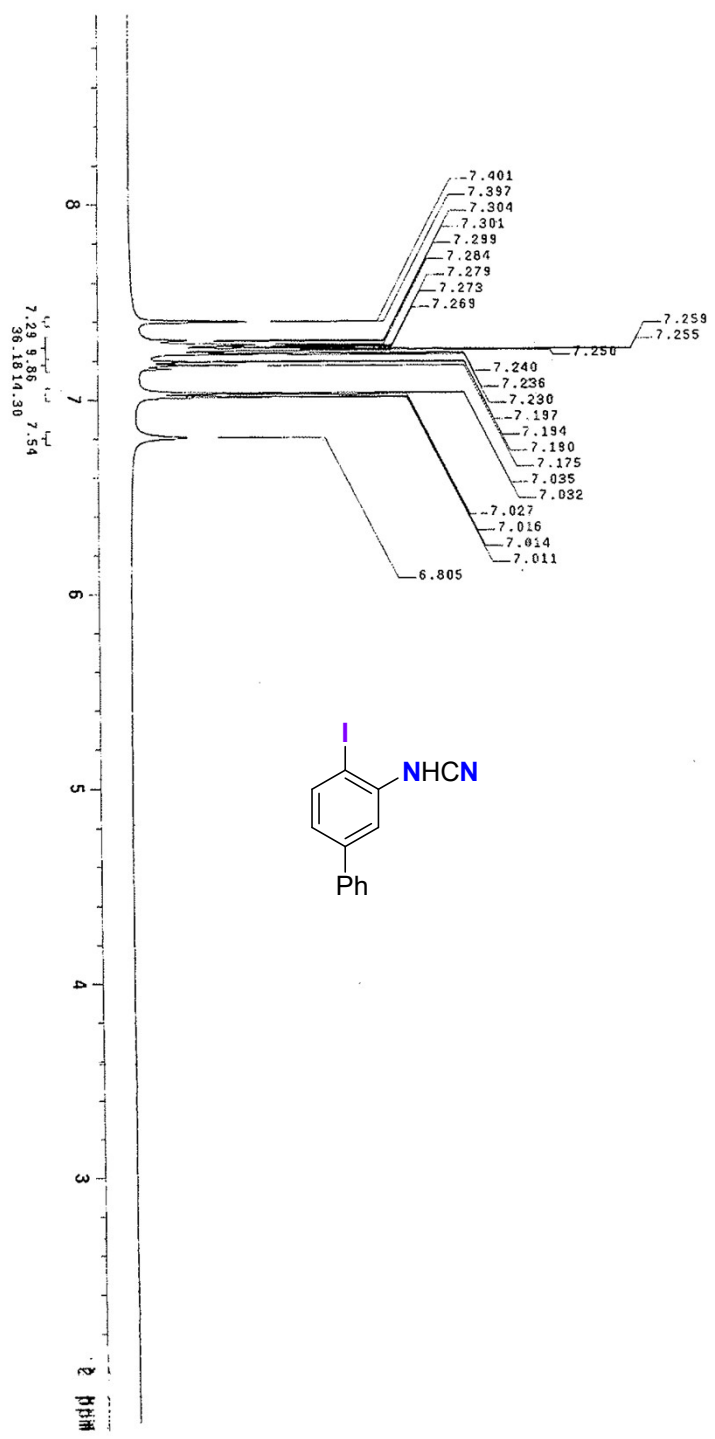


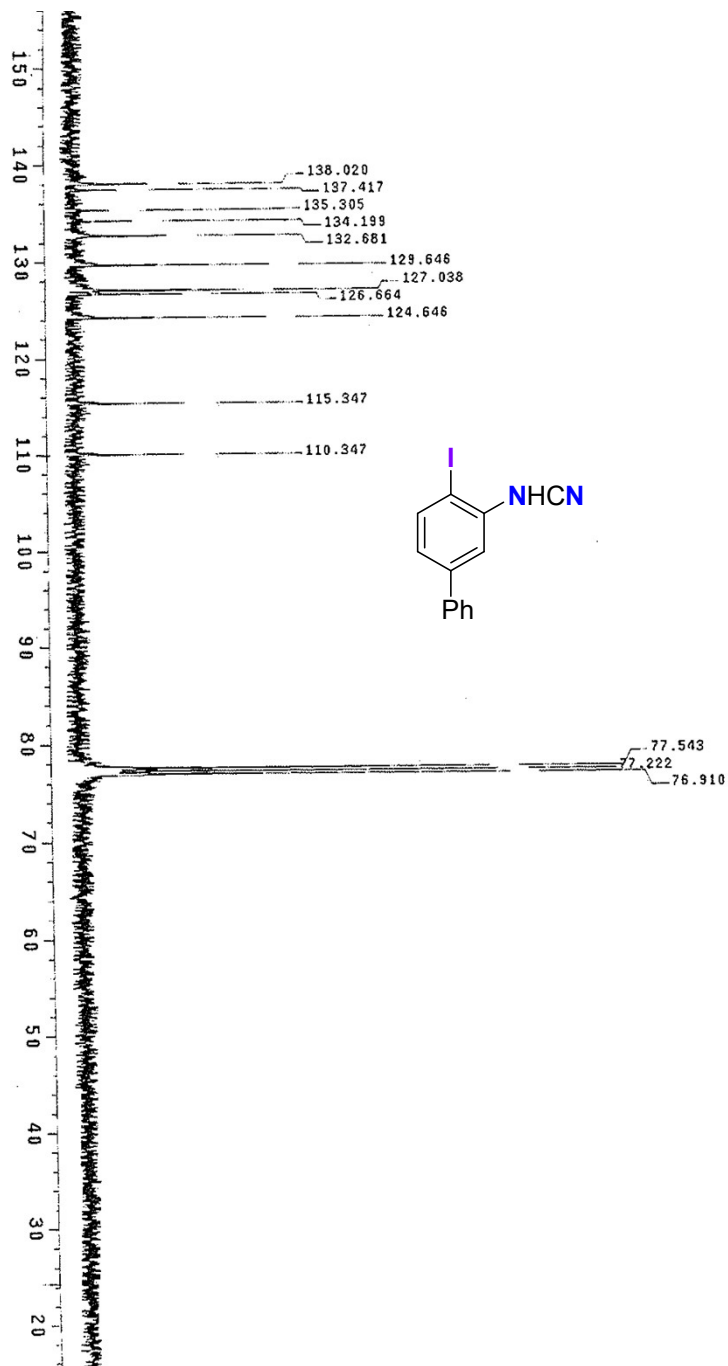


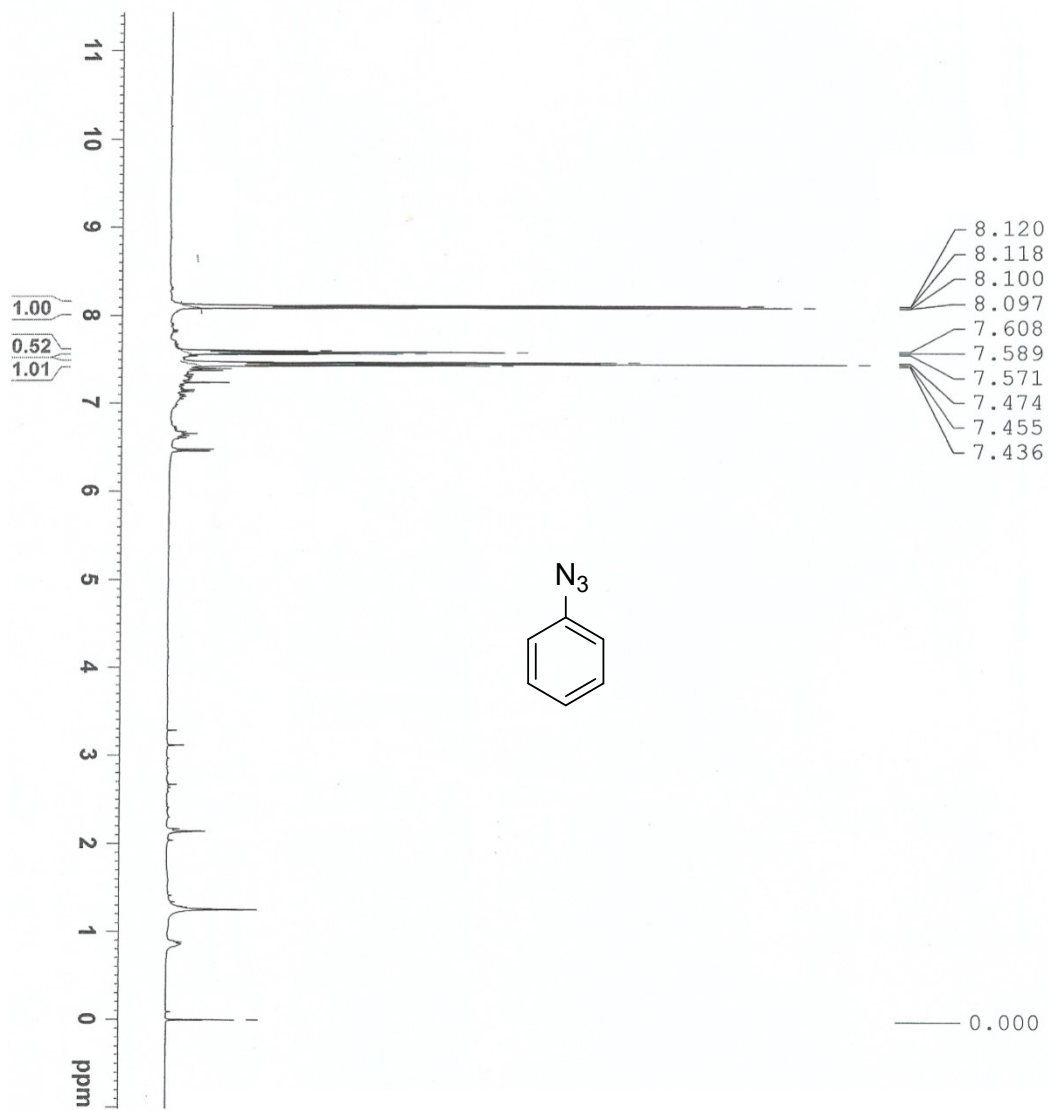


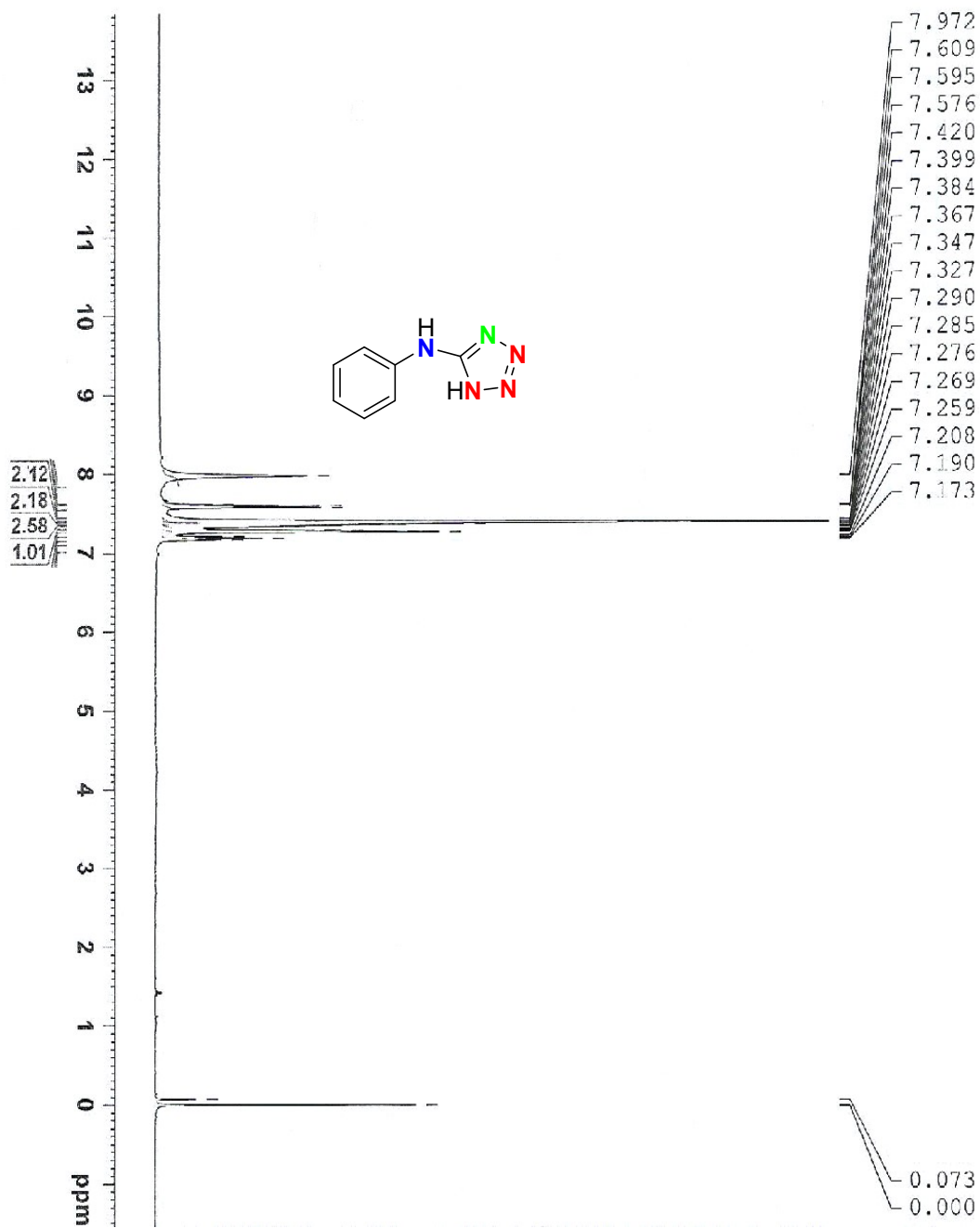


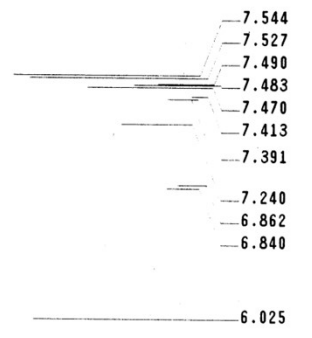
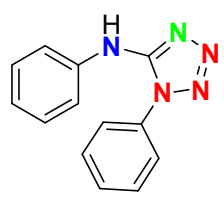
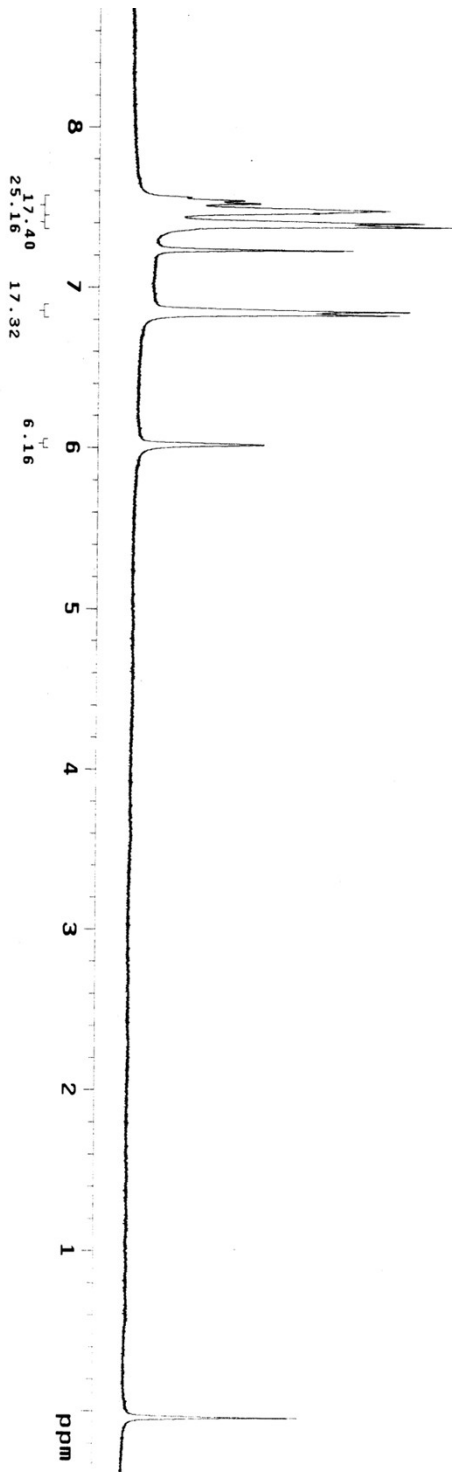












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