

**CONVERSION OF OXAZOLINES TO CYANOMETHYL ESTERS WITH
PYRIDINIUM HYDROBROMIDE PERBROMIDE IN WATER**

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Supporting Information

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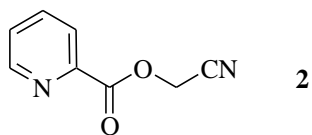
General Information

IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer.

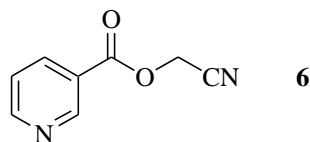
^1H and ^{13}C NMR spectra were recorded with a JEOL JNM-EX270 spectrometer at room temperature and the chemical shifts (δ) were given relative to internal standard SiMe_4 in CDCl_3 . Elemental analyses were performed on a Yanagimoto MT-6.

Typical procedure:

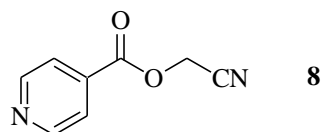
To a solution of 1,3-oxazolines (0.25 mmol) and pyridine (80 μL , 1.0 mmol) in H_2O (6mL), was added pyridinium hydrobromide perbromide (320 mg, 1.0 mmol) at room temperature. After stirring for 15-23 h at rt, the reaction mixture was treated with 0.5 M aq $\text{Na}_2\text{S}_2\text{O}_3$ (10 mL), 1.0 M NaHCO_3 (15mL) and extracted with EtOAc (60 mL). The organic layer was washed with 0.5 M $\text{Na}_2\text{S}_2\text{O}_3$ and successively washed with saturated aq NaCl , and dried over MgSO_4 . After removal of solvent in vacuo, the residue was purified by column chromatography on silica gel (Wako C-200 or Merck, Kieselgel 60, 230-400 mesh) with CCl_4 , $\text{CCl}_4\text{-CHCl}_3$ (2:1 v/v). Cyanomethyl esters **2-28** were respectively obtained in 59-94% yields.



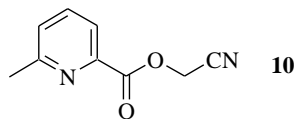
IR (neat, cm^{-1}) 2984, 2944, 2850, 2739, 1736, 1588, 1573, 1470, 1441, 1434, 1379, 1307, 1292, 1271, 1245, 1150, 1114, 1092, 1043, 999, 985, 916, 819, 750, 710, 699, 620. ^1H NMR(CDCl_3) δ 5.05 (2H, s), 7.57 (1H, t, $J = 8.1$ Hz), 7.92 (1H, t, $J = 8.1$ Hz), 8.19 (1H, d, $J = 8.1$ Hz), 8.80 (1H, d, $J = 8.1$ Hz). ^{13}C NMR (CDCl_3) δ 49.34, 113.99, 125.90, 127.91, 137.32, 145.99, 150.17, 163.65. *Anal.* Calcd for $\text{C}_8\text{H}_6\text{O}_2\text{N}_2$: C, 59.25; H, 3.72; N, 17.28. Found: C, 59.25; H, 3.83; N, 17.12.



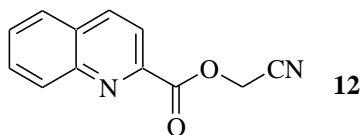
IR (neat, cm^{-1}) 3065, 3011, 2960, 1739, 1591, 1479, 1422, 1368, 1330, 1275, 1195, 1109, 1040, 1026, 986, 914, 832, 813, 739, 701. ^1H NMR (CDCl_3) δ 5.02 (2H, s), 7.46 (1H, t, $J = 8.1$ Hz), 8.33 (1H, d, $J = 8.1$ Hz), 8.85 (1H, d, $J = 5.4$ Hz), 9.26 (1H, brs). ^{13}C NMR(CDCl_3) δ 49.03, 113.97, 123.54, 124.01, 137.40, 151.14, 154.55, 163.76.



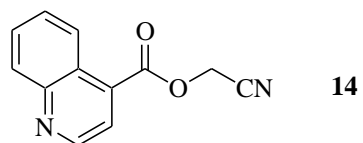
IR (neat, cm^{-1}) 2997, 2959, 1737, 1596, 1563, 1494, 1431, 1408, 1366, 1326, 1294, 1275, 1260, 1222, 1211, 1124, 1063, 993, 983, 955, 853, 759, 702, 676, 664. ^1H NMR (CDCl_3) δ 5.01 (2H, s), 7.87 (2H, d, $J = 8.1$ Hz), 8.85 (2H, d, $J = 8.1$ Hz), ^{13}C NMR (CDCl_3) δ 49.34, 113.75, 122.88, 135.33, 150.96, 163.76. *Anal.* Calcd for $\text{C}_8\text{H}_6\text{O}_2\text{N}_2$: C, 59.25; H, 3.72. Found: C, 58.89; H, 3.69.



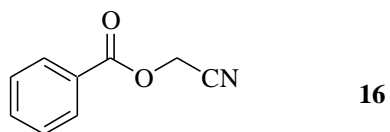
IR (neat, cm^{-1}) 2997, 2954, 1733, 1691, 1593, 1458, 1437, 1378, 1306, 1268, 1258, 1236, 1185, 1161, 1122, 1084, 1034, 1012, 994, 984, 916, 885, 830, 783, 762, 713, 669. ^1H NMR (CDCl_3) δ 2.68 (3H, s), 5.03 (2H, s), 7.42 (1H, d, $J = 8.1$ Hz), 7.78 (1H, t, $J = 8.1$ Hz), 8.00 (1H, d, $J = 8.1$ Hz). ^{13}C NMR (CDCl_3) δ 24.58, 49.31, 114.11, 123.19, 127.84, 137.32, 145.48, 159.52, 163.89. *Anal.* Calcd for $\text{C}_9\text{H}_8\text{O}_2\text{N}_2$: C, 61.35; H, 4.57; N, 15.90. Found: C, 61.16; H, 4.62; N, 15.73.



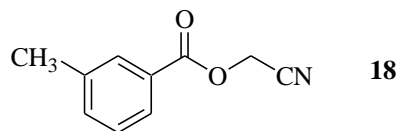
IR (neat, cm^{-1}) 2998, 2958, 1728, 1662, 1592, 1564, 1504, 1463, 1437, 1377, 1310, 1290, 1275, 1244, 1208, 1126, 1101, 983, 946, 916, 876, 845, 778, 767. ^1H NMR (CDCl_3) δ 5.12 (2H, s), 7.71 (1H, t, $J = 8.1$ Hz), 7.85 (1H, t, $J = 8.1$ Hz), 7.92 (1H, d, $J = 8.1$ Hz), 8.22 (1H, d, $J = 8.1$ Hz), 8.30 (1H, d, $J = 8.1$ Hz), 8.37 (1H, d, $J = 8.1$ Hz). ^{13}C NMR (CDCl_3) δ 49.57, 114.08, 121.15, 127.64, 129.28, 129.60, 130.65, 130.73, 137.64, 145.79, 147.54, 163.94.



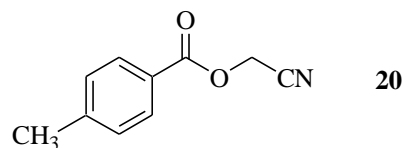
IR (neat, cm^{-1}) 2976, 1739, 1584, 1507, 1460, 1441, 1369, 1268, 1249, 1181, 1147, 1134, 1078, 1034, 1016, 969, 884, 860, 793, 774. ^1H NMR (CDCl_3) δ 5.09 (2H, s), 7.72 (1H, t, $J = 8.1$ Hz), 7.83 (1H, t, $J = 8.1$ Hz), 7.98 (1H, d, $J = 5.4$ Hz), 8.20 (1H, d, $J = 8.1$ Hz), 8.79 (1H, d, $J = 8.1$ Hz), 9.08 (1H, d, $J = 5.4$ Hz). ^{13}C NMR (CDCl_3) δ 49.25, 113.97, 122.73, 124.79, 125.08, 128.92, 130.14, 130.31, 131.80, 149.21, 149.67, 164.49. *Anal.* Calcd for $\text{C}_{12}\text{H}_8\text{O}_2\text{N}_2$: C, 67.91; H, 3.80; N, 13.20. Found: C, 67.53; H, 3.87; N, 12.99.



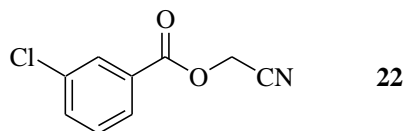
IR (neat, cm^{-1}) 3066, 2960, 1732, 1600, 1584, 1492, 1453, 1425, 1366, 1316, 1262, 1178, 1095, 1070, 1027, 990, 913, 803, 709. ^1H NMR (CDCl_3) δ 4.97 (2H, s), 7.49 (2H, t, $J = 8.1$ Hz), 7.64 (1H, t, $J = 8.1$ Hz), 8.07 (2H, d, $J = 8.1$ Hz). ^{13}C NMR (CDCl_3) δ 48.79, 114.43, 127.86, 128.67, 129.99, 134.11, 164.93.3. *Anal.* Calcd for $\text{C}_9\text{H}_7\text{O}_2\text{N}$: C, 67.07; H, 4.37; N, 8.69. Found: C, 67.24; H, 4.49; N, 8.55.



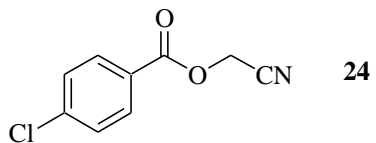
IR (neat, cm^{-1}) 2957, 1733, 1590, 1428, 1368, 1275, 1191, 1103, 1082, 1017, 915, 742. ^1H NMR (CDCl_3) δ 2.42 (3H, s), 4.95 (2H, s), 7.39 (2H, m), 7.85 (1H, d, $J = 8.1$ Hz), 7.87 (1H, brs). ^{13}C NMR (CDCl_3) δ 21.19, 48.73, 114.48, 127.14, 127.77, 128.55, 130.50, 134.89, 138.58, 165.09. *Anal.* Calcd for $\text{C}_{10}\text{H}_9\text{O}_2\text{N}$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.66; H, 5.03; N, 7.87.



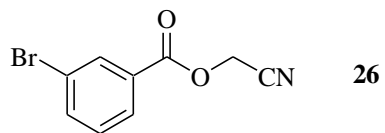
IR (neat, cm⁻¹) 2956, 1732, 1613, 1509, 1426, 1368, 1311, 1267, 1211, 1180, 1100, 1021, 995, 912, 840, 751, 690. ¹H NMR (CDCl₃) δ 2.43 (3H, s), 4.95 (2H, s), 7.28 (2H, d, *J* = 8.1 Hz), 7.95 (2H, d, *J* = 8.1 Hz). ¹³C NMR (CDCl₃) δ 21.76, 48.66, 114.55, 125.11, 129.41, 130.06, 145.13, 164.98.



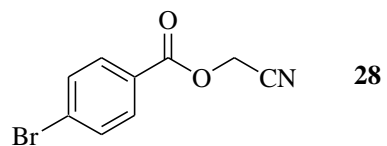
IR (neat, cm⁻¹) 3074, 3012, 2959, 1732, 1597, 1576, 1473, 1428, 1368, 1287, 1252, 1165, 1124, 1087, 1074, 1001, 915, 827, 810, 746, 673, 661. ¹H NMR (CDCl₃) δ 4.98 (2H, s), 7.43 (1H, t, *J* = 8.1 Hz), 7.60 (1H, dd, *J* = 8.1, 2.7 Hz), 7.94 (1H, dd, *J* = 8.1, 2.7), 8.03 (1H, brs). ¹³C NMR (CDCl₃) δ 49.05, 114.15, 128.06, 129.49, 129.95, 129.99, 134.13, 134.85, 163.78. *Anal.* Calcd for C₉H₆O₂NCl: C, 55.26; H, 3.09; N, 7.16. Found: C, 55.33; H, 3.26; N, 7.07.



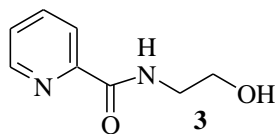
IR (neat, cm⁻¹) 3096, 2959, 1732, 1596, 1489, 1426, 1404, 1368, 1265, 1175, 1092, 1016, 990, 914, 850, 810, 757, 727, 685. ¹H NMR (CDCl₃) δ 4.97 (2H, s), 7.47 (2H, d, *J* = 8.1 Hz), 8.00 (2H, d, *J* = 8.1 Hz). ¹³C NMR (CDCl₃) δ 48.95, 114.24, 126.25, 129.10, 131.34, 140.78, 164.10. *Anal.* Calcd for C₉H₆O₂NCl: C, 55.26; H, 3.09; N, 7.16. Found: C, 55.43; H, 3.19; N, 7.13.



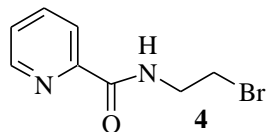
IR (neat, cm^{-1}) 3070, 3011, 2958, 1738, 1593, 1571, 1474, 1426, 1367, 1281, 1251, 1168, 1118, 1082, 1069, 998, 915, 818, 744, 724, 671, 652. ^1H NMR (CDCl_3) δ 4.97 (2H, s), 7.37 (1H, t, $J = 8.1$ Hz), 7.76 (1H, d, $J = 8.1$ Hz), 7.99 (1H, d, $J = 8.1$ Hz), 8.20 (1H, brs). ^{13}C NMR (CDCl_3) δ 49.06, 114.12, 122.73, 128.55, 129.71, 130.26, 132.93, 137.09, 163.66. *Anal.* Calcd for $\text{C}_9\text{H}_6\text{O}_2\text{NBr}$: C, 45.02; H, 2.51; N, 5.83. Found: C, 44.89; H, 2.53; N, 5.80.



IR (neat, cm^{-1}) 3101, 3067, 3019, 2968, 1731, 1589, 1508, 1420, 1398, 1363, 1311, 1288, 1276, 1177, 1119, 1106, 1070, 1011, 994, 907, 849, 830, 812, 752, 716. ^1H NMR (CDCl_3) δ 4.96 (2H, s), 7.64 (2H, d, $J = 8.1$ Hz), 7.92 (2H, d, $J = 8.1$ Hz), ^{13}C NMR (CDCl_3) δ 48.96, 114.22, 126.72, 129.54, 131.43, 132.12, 164.26. *Anal.* Calcd for $\text{C}_9\text{H}_6\text{O}_2\text{NBr}$: C, 45.02; H, 2.51. Found: C, 45.16; H, 2.68.

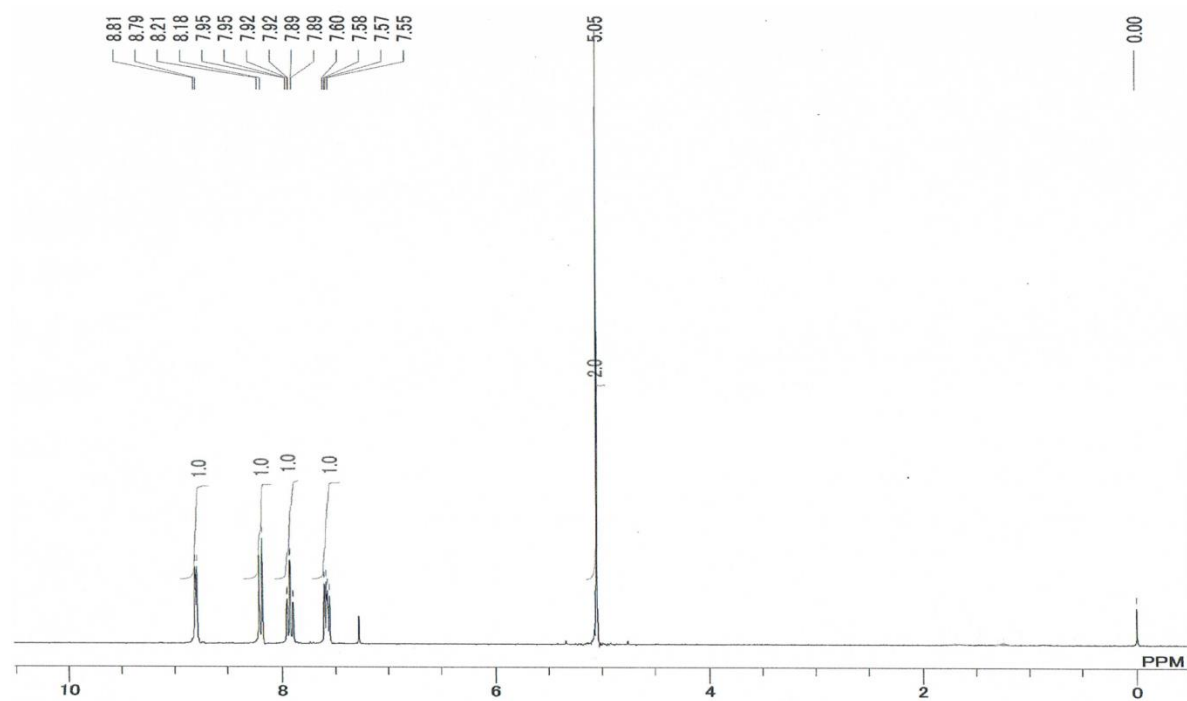
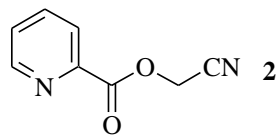


Brown oil. IR (neat, cm^{-1}) 3378, 3059, 2935, 2878, 1661, 1590, 1569, 1537, 1465, 1435, 1361, 1290, 1246, 1220, 1170, 1147, 1065, 997, 913, 820, 750, 693, 621. ^1H (CDCl_3) δ 3.66 (2H, t, $J = 5.4$ Hz), 3.86 (2H, t, $J = 5.4$ Hz), 7.44 (1H, m), 7.86 (1H, t, $J = 8.1$ Hz), 8.20 (1H, d, $J = 8.1$ Hz), 8.55 (1H, d, $J = 5.4$ Hz). ^{13}C NMR (CDCl_3) δ 42.53, 62.48, 122.29, 126.33, 137.44, 148.14, 149.71, 165.55. *Anal.* Calcd for $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_2$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.95; H, 6.04; N, 16.97.

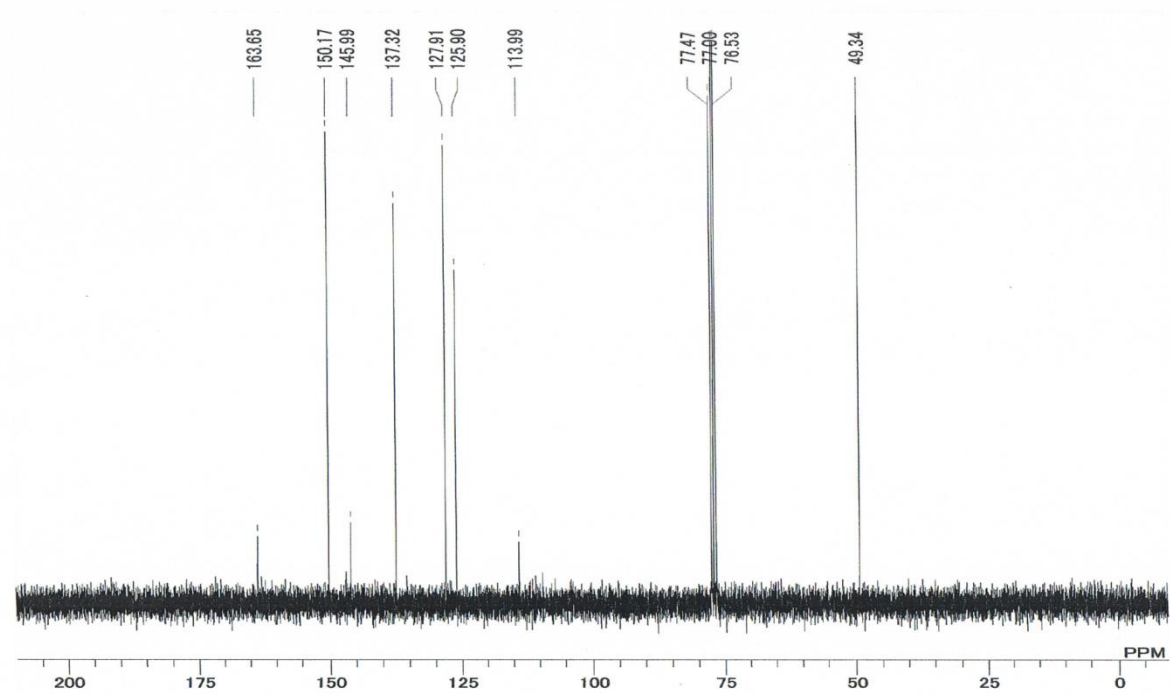
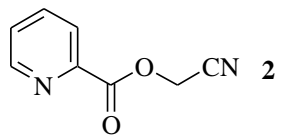


IR (KBr, cm^{-1}) 3338, 3069, 3057, 3037, 2977, 2948, 1663, 1627, 1591, 1570, 1532, 1522, 1467, 1439, 1431, 1404, 1353, 1303, 1294, 1284, 1225, 1183, 1163, 1140, 1085, 1072, 1042, 1002, 969, 952, 855, 820, 751, 679, 663, 621. ^1H (CDCl_3) δ 3.59 (2H, t, $J = 5.4$ Hz), 3.91 (2H, t, $J = 5.4$ Hz), 7.45 (1H, dd, $J = 8.1, 5.4$ Hz), 7.86 (1H, t, $J = 8.1$ Hz), 8.18 (1H, d, $J = 8.1$ Hz), 8.58 (1H, d, $J = 5.4$ Hz). ^{13}C NMR (CDCl_3) δ 31.86, 41.09, 122.24, 126.37, 137.35, 148.19, 149.39, 164.48. *Anal.* Calcd for $\text{C}_8\text{H}_9\text{ON}_2\text{Br}$: C, 41.94; H, 3.96; N, 12.23. Found: C, 42.04; H, 3.98; N, 12.20.

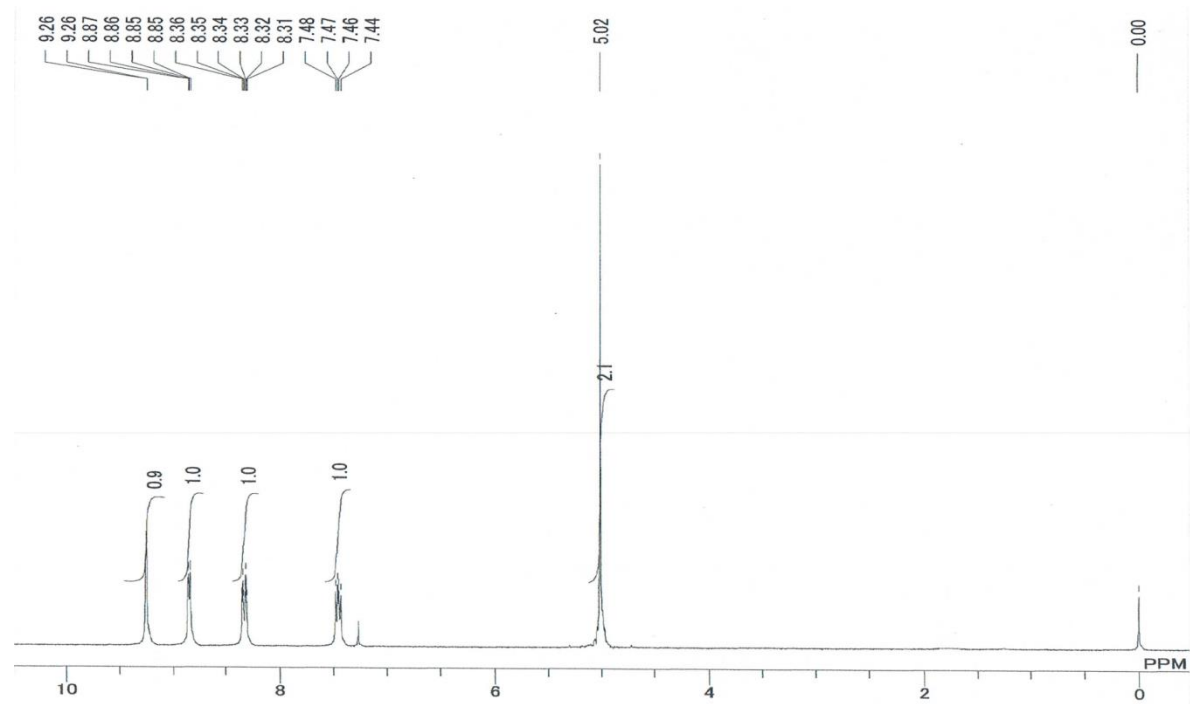
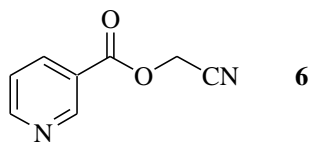
^1H NMR (CDCl_3 , 270.05 MHz)



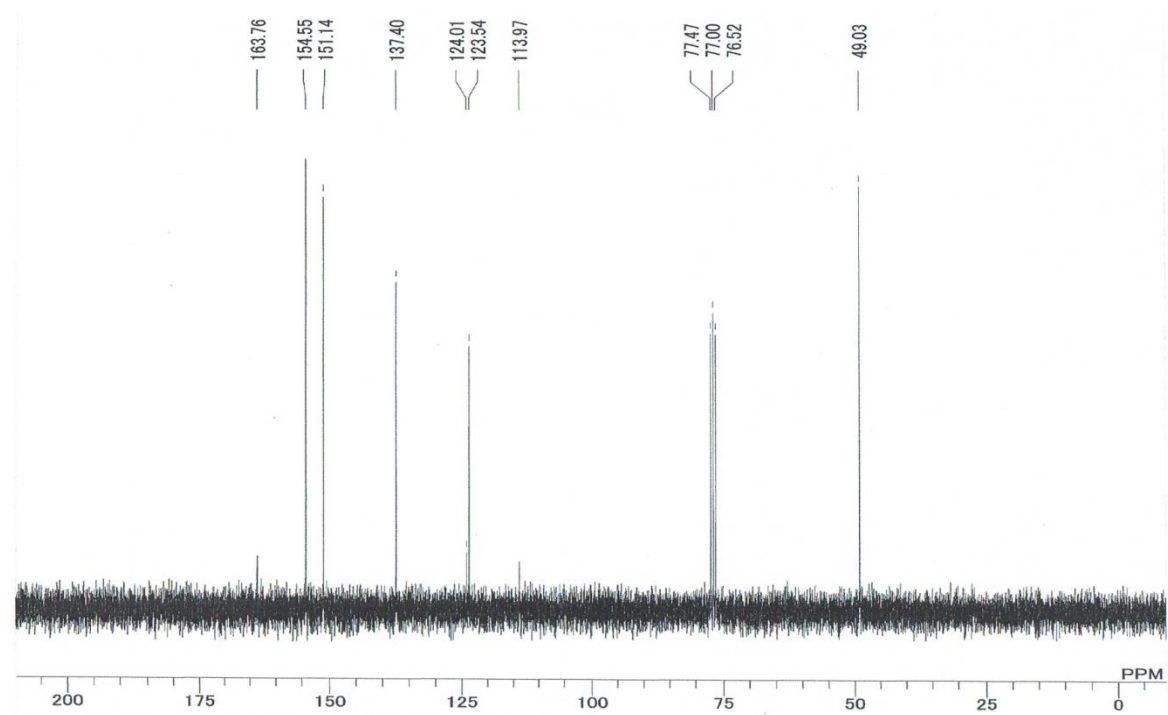
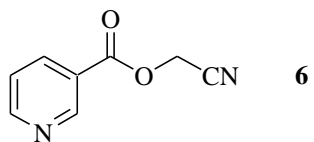
^{13}C NMR (CDCl_3 , 67.80 MHz)



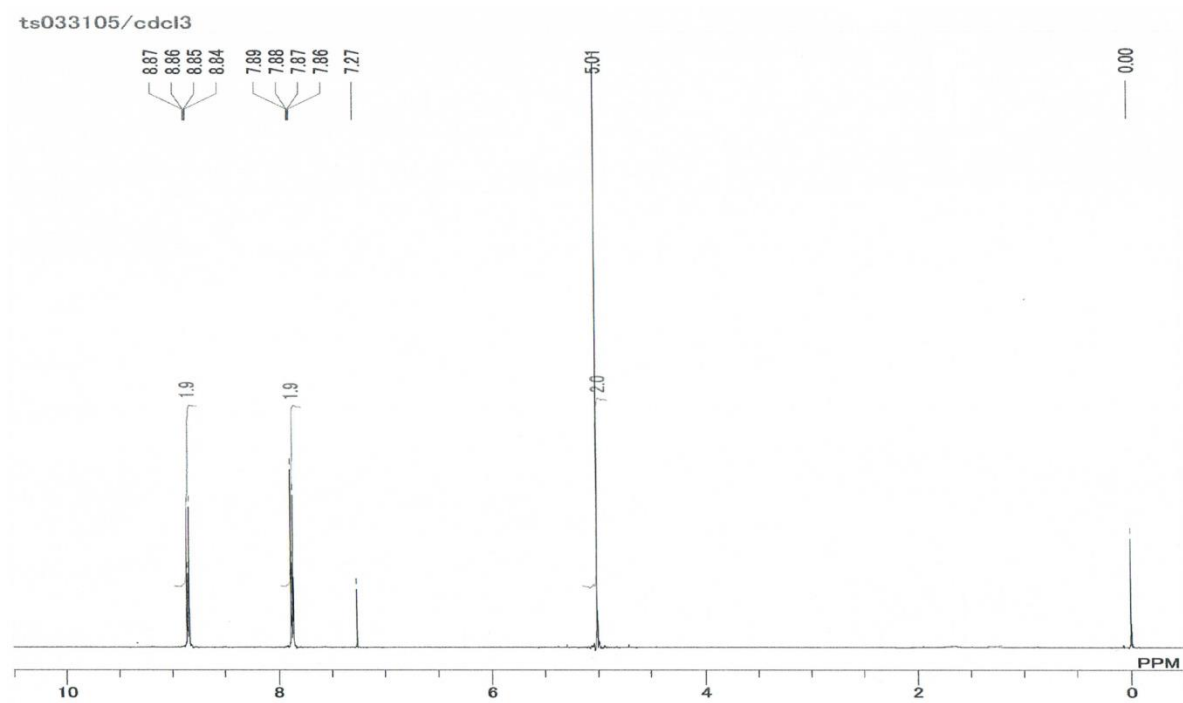
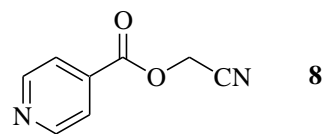
^1H NMR (CDCl_3 , 270.05 MHz)



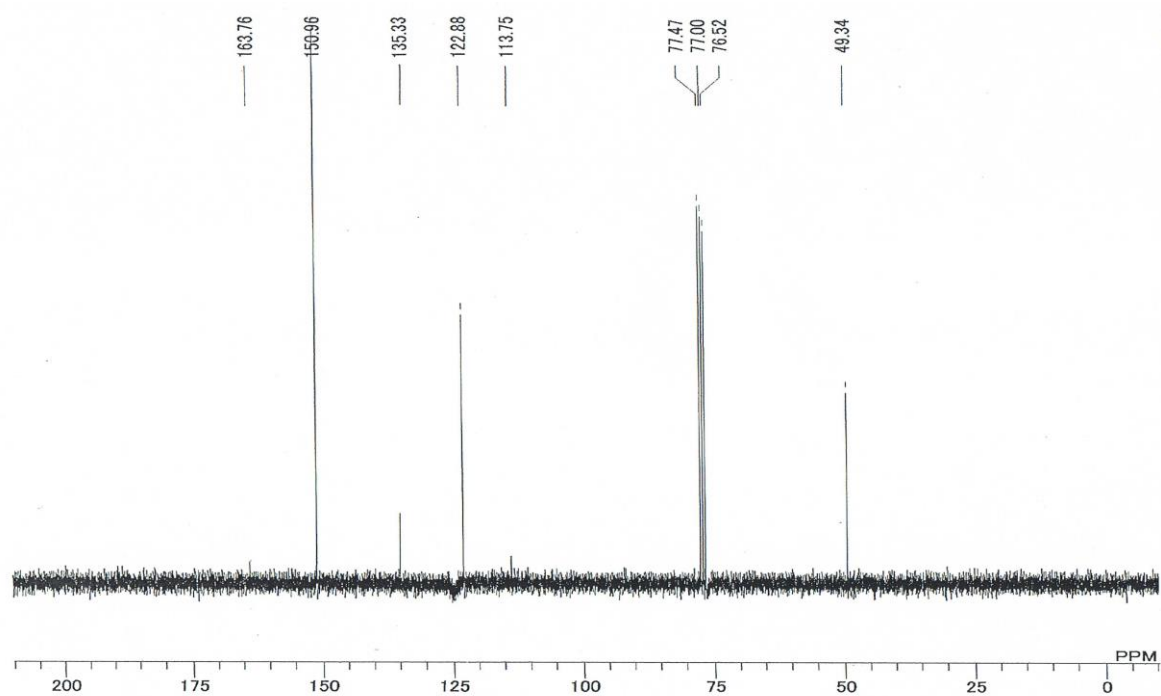
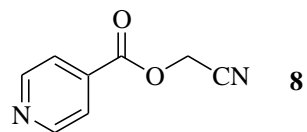
^{13}C NMR (CDCl_3 , 67.80 MHz)



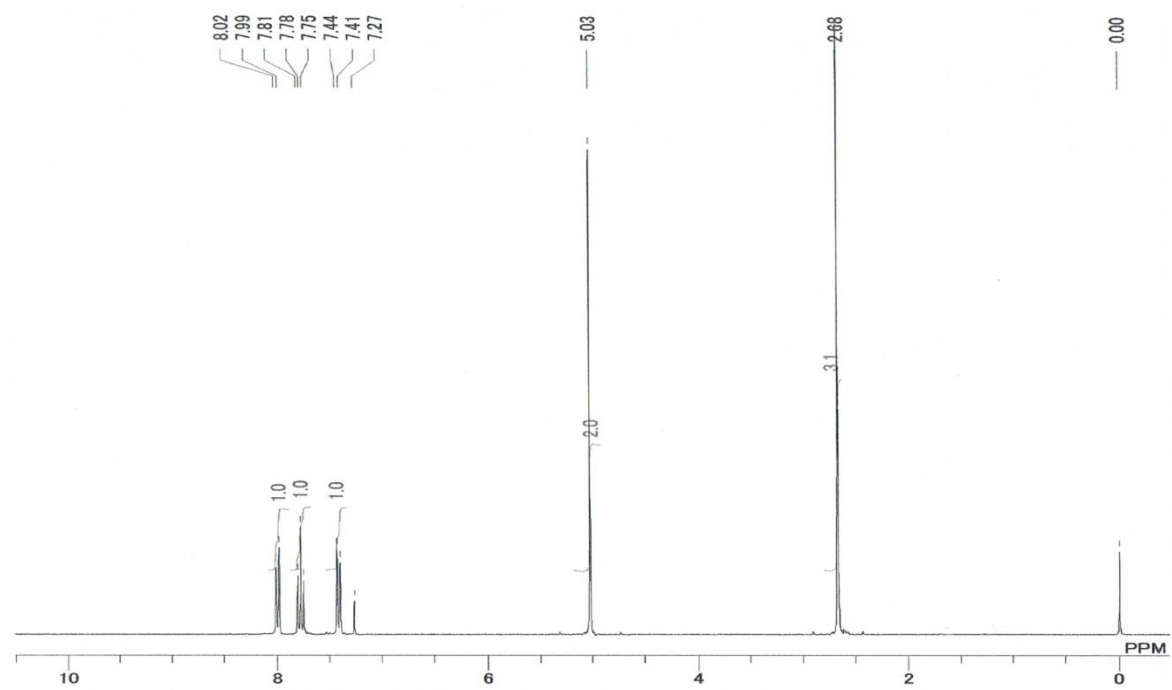
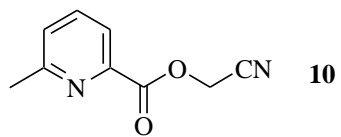
^1H NMR (CDCl_3 , 270.05 MHz)



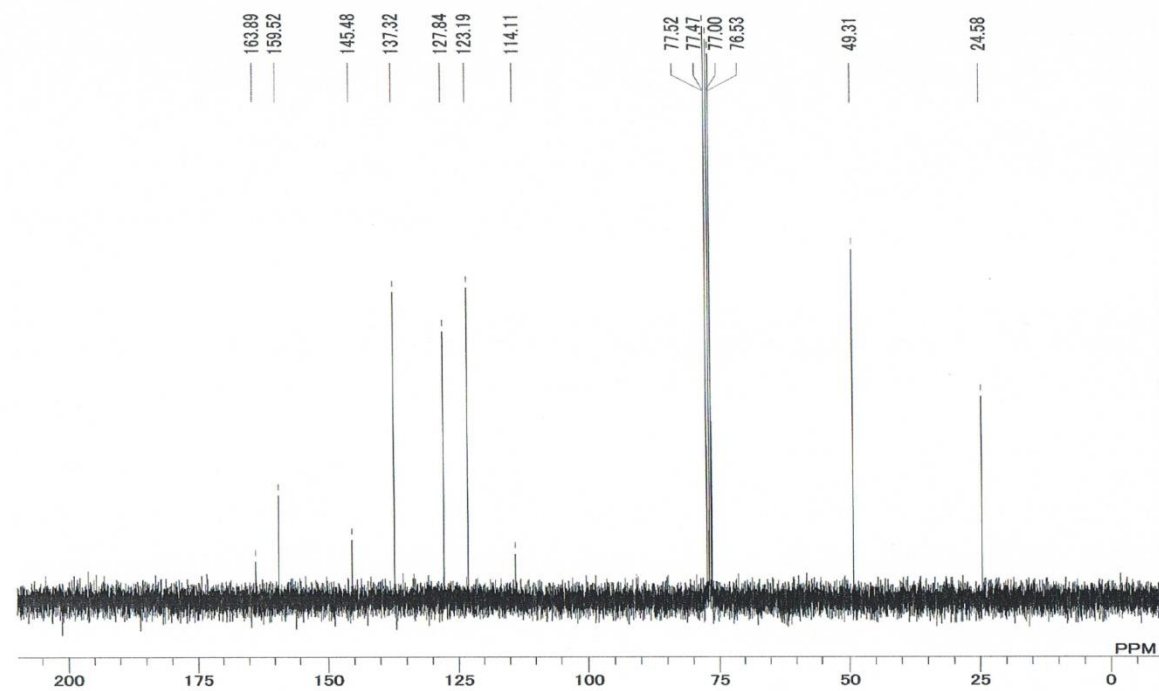
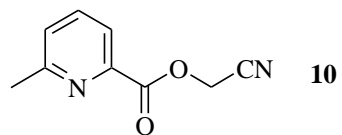
^{13}C NMR (CDCl_3 , 67.80 MHz)



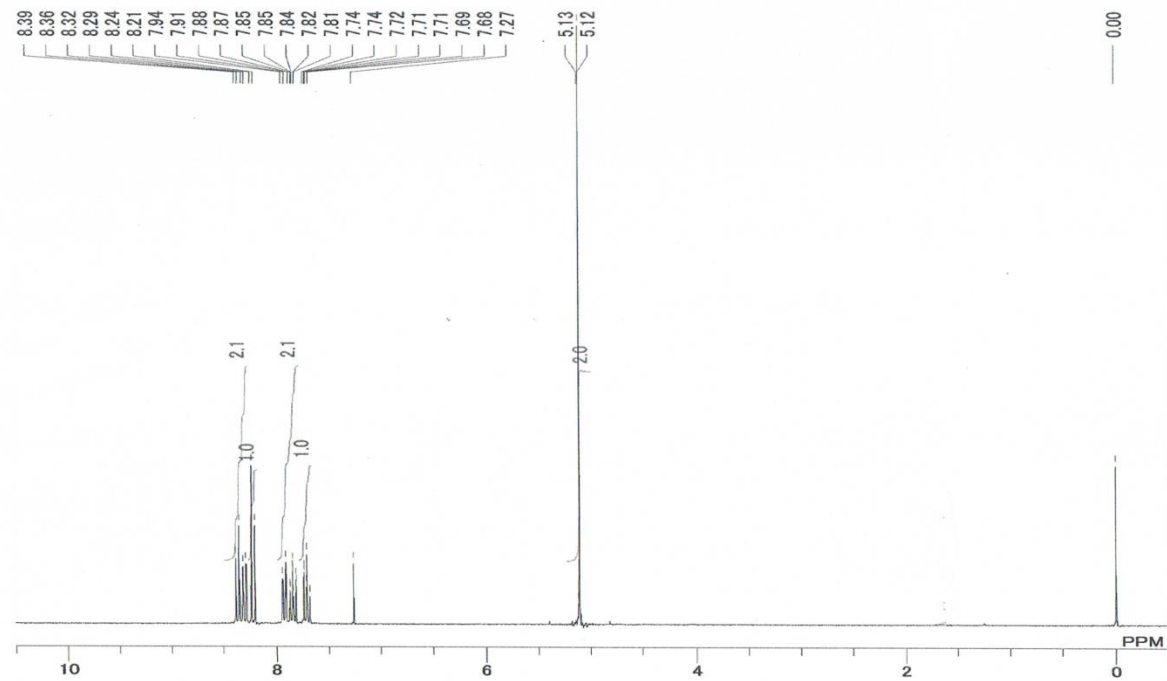
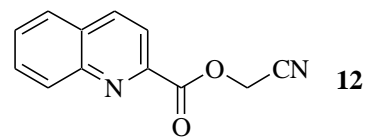
^1H NMR (CDCl_3 , 270.05 MHz)



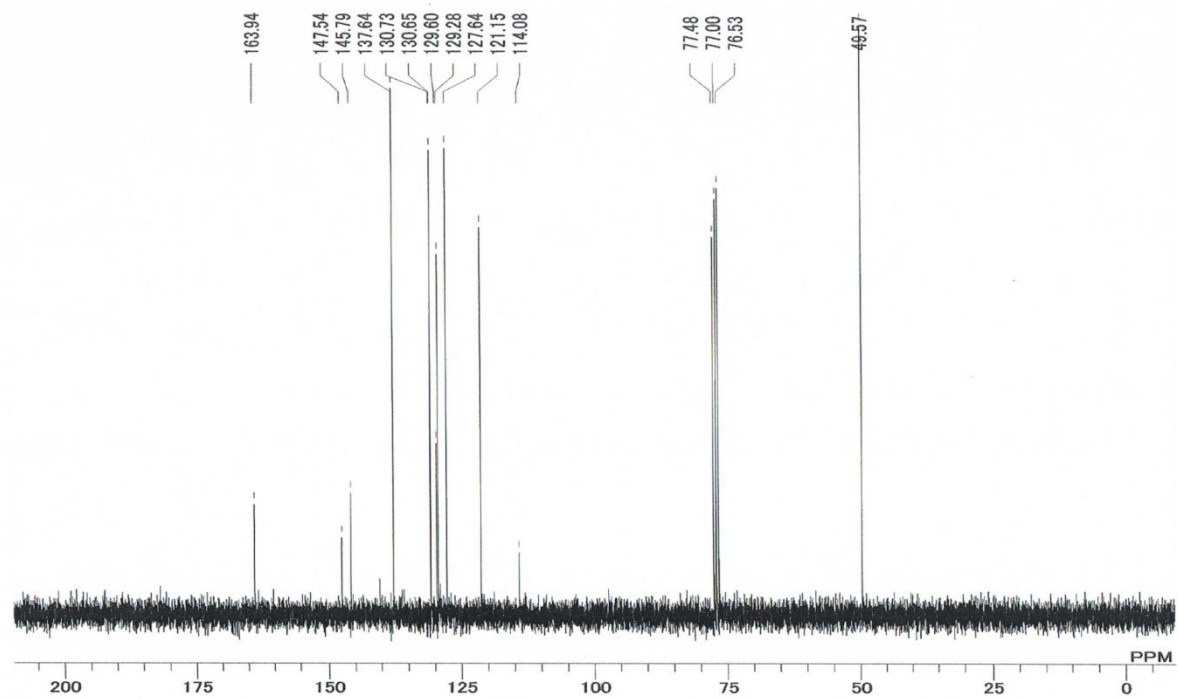
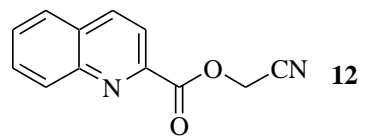
^{13}C NMR (CDCl_3 , 67.80 MHz)



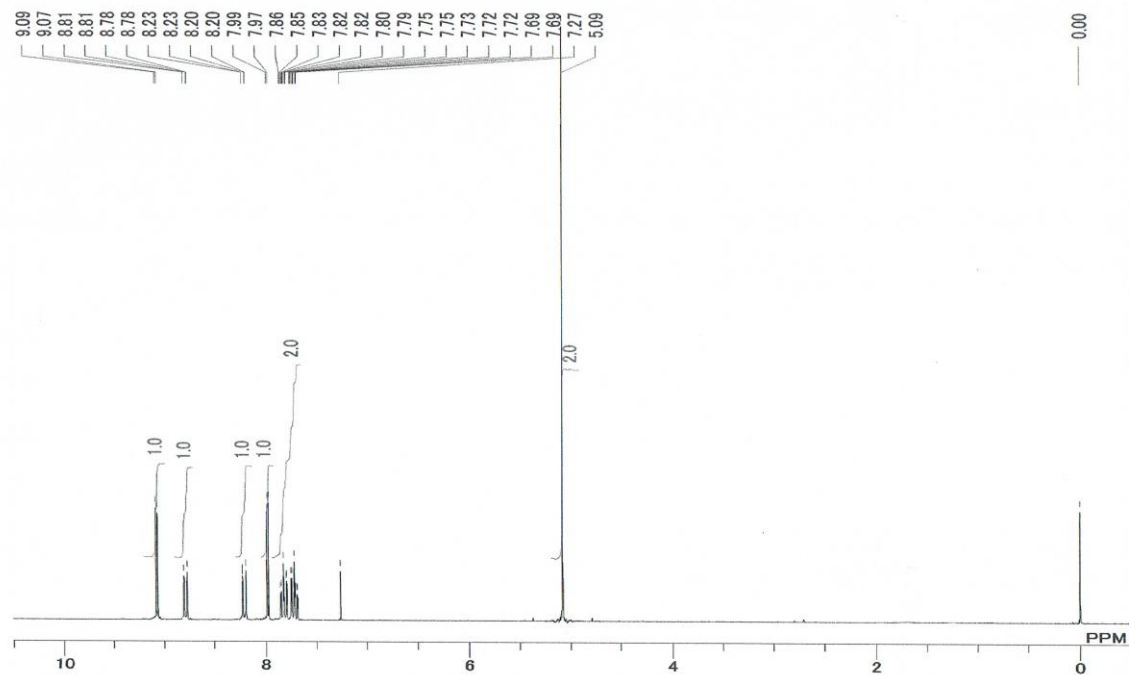
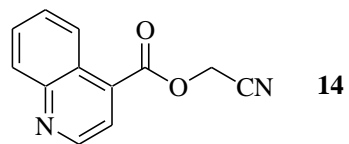
^1H NMR (CDCl_3 , 270.05 MHz)



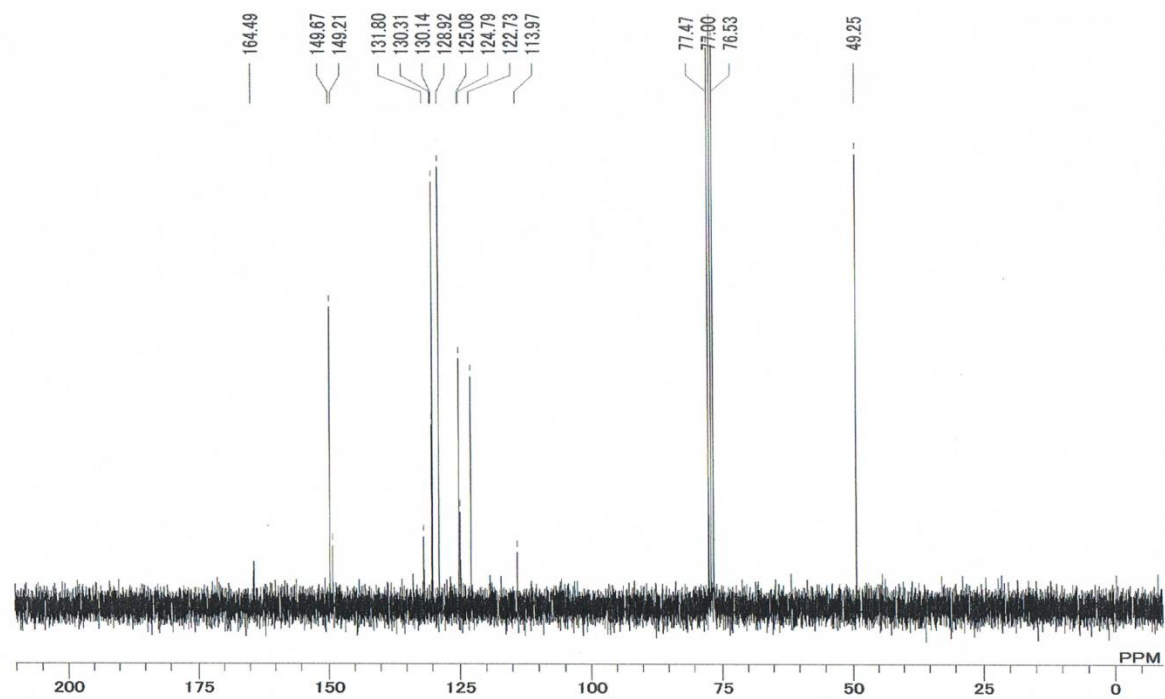
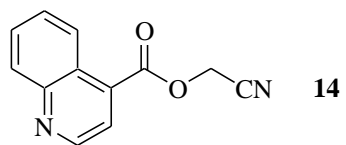
^{13}C NMR (CDCl_3 , 67.80 MHz)



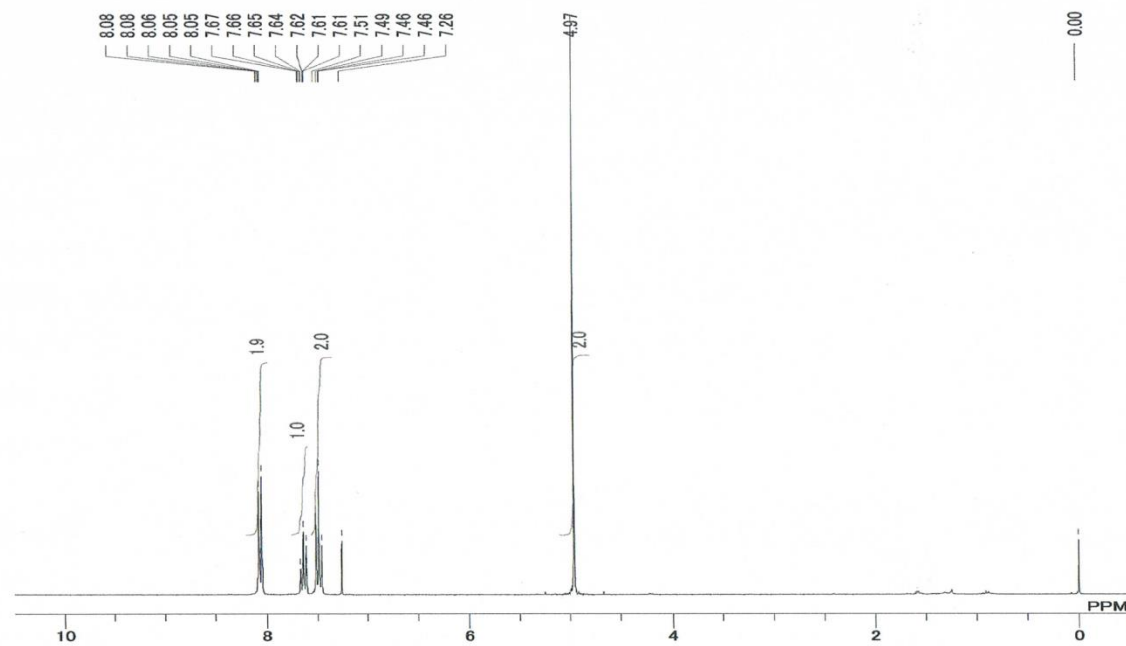
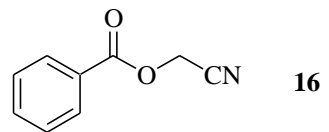
^1H NMR (CDCl_3 , 270.05 MHz)



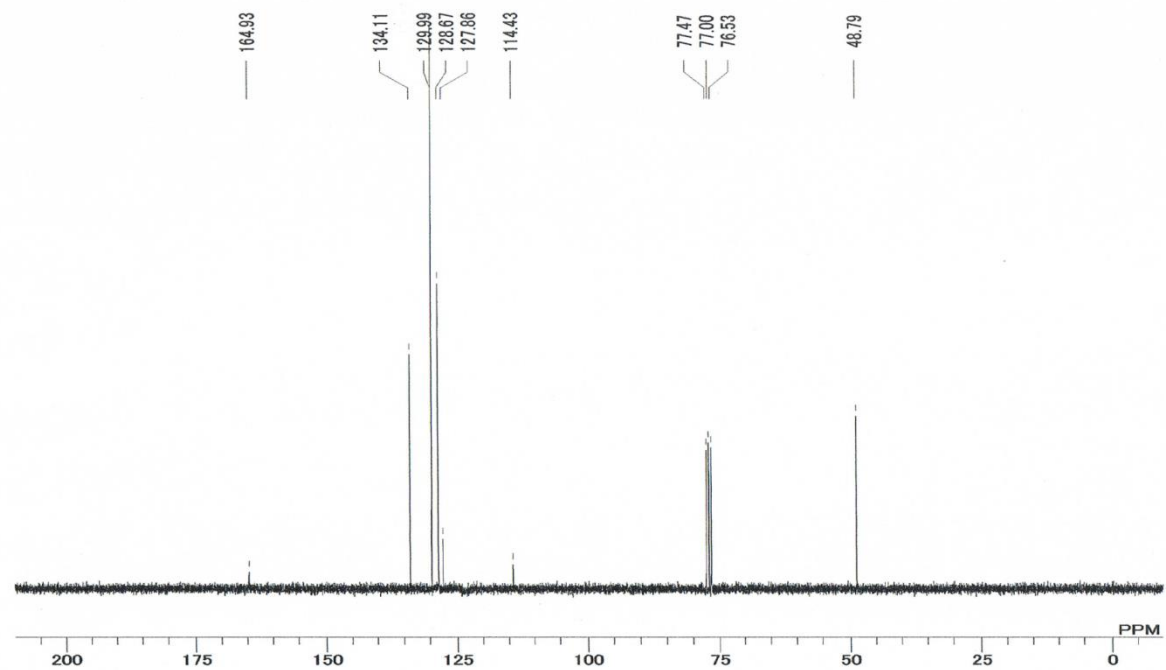
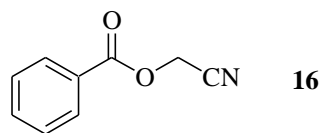
^{13}C NMR (CDCl_3 , 67.80 MHz)



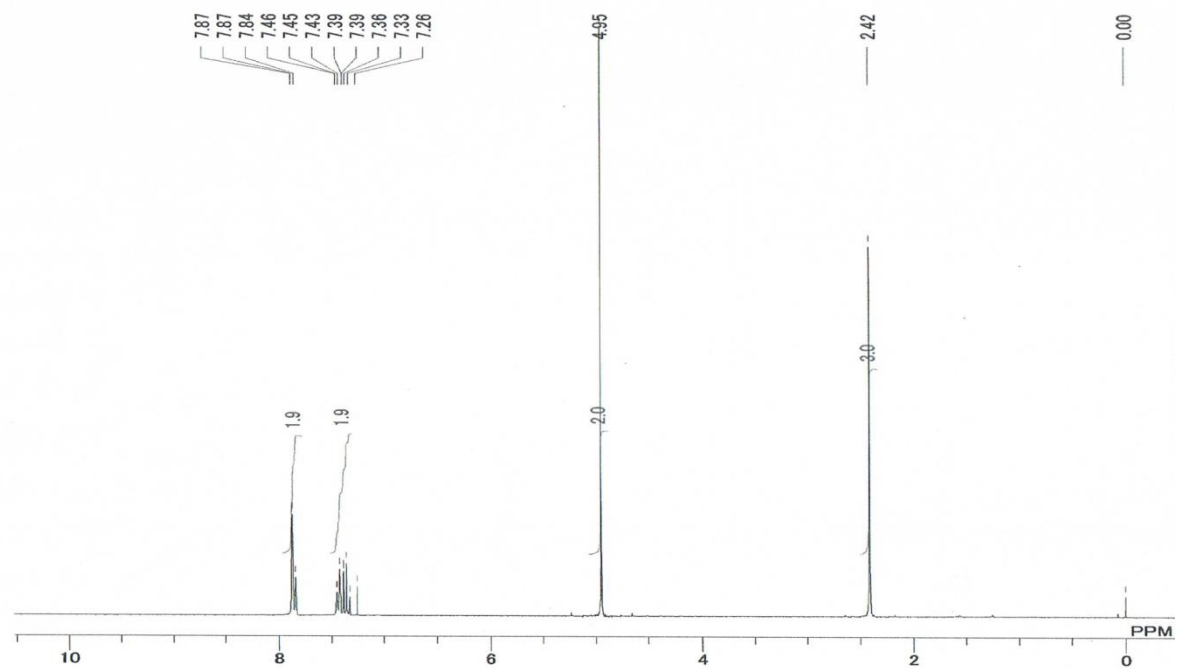
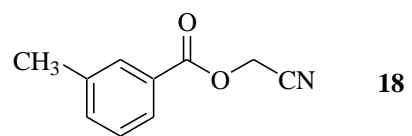
^1H NMR (CDCl_3 , 270.05 MHz)



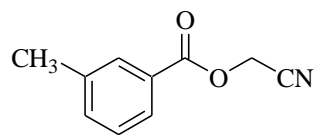
^{13}C NMR (CDCl_3 , 67.80 MHz)



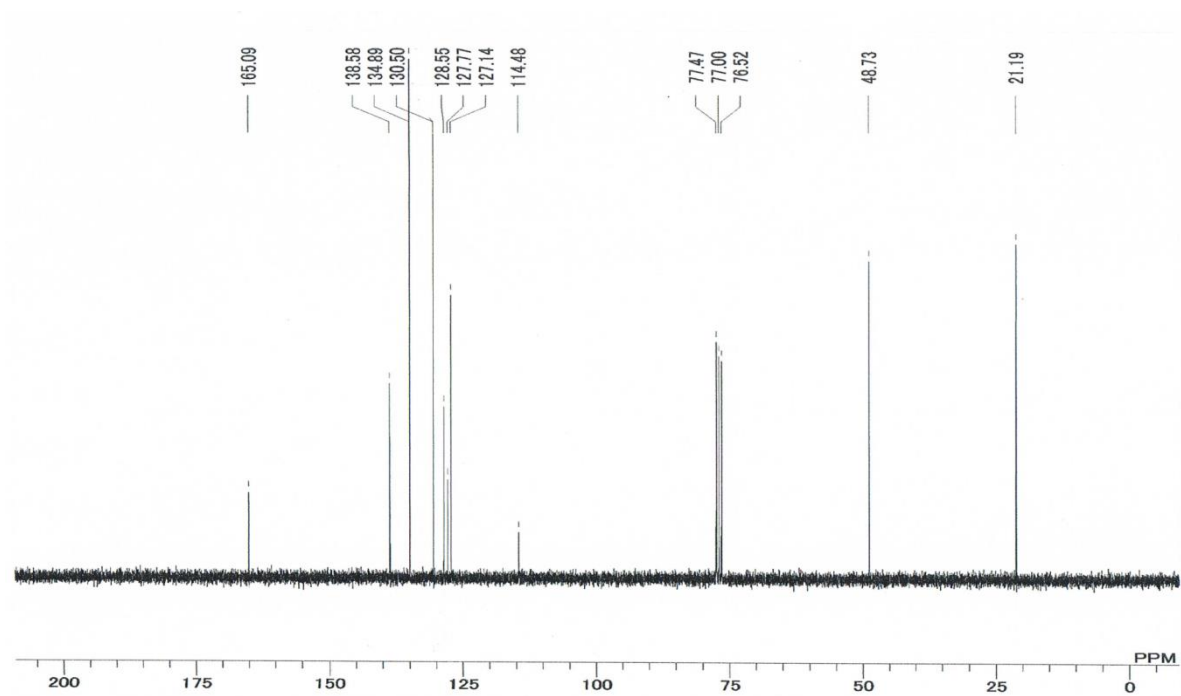
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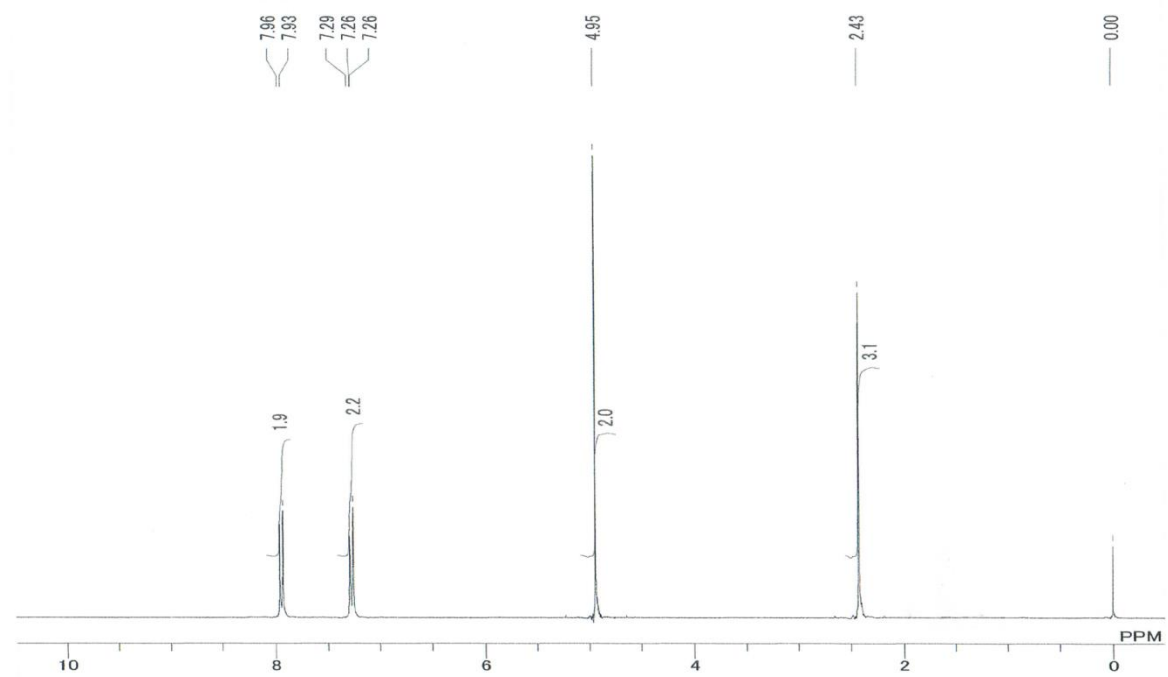
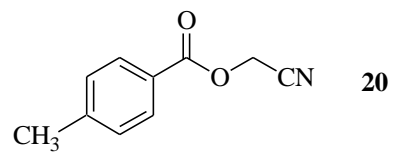
^{13}C NMR (CDCl_3 , 67.80 MHz)



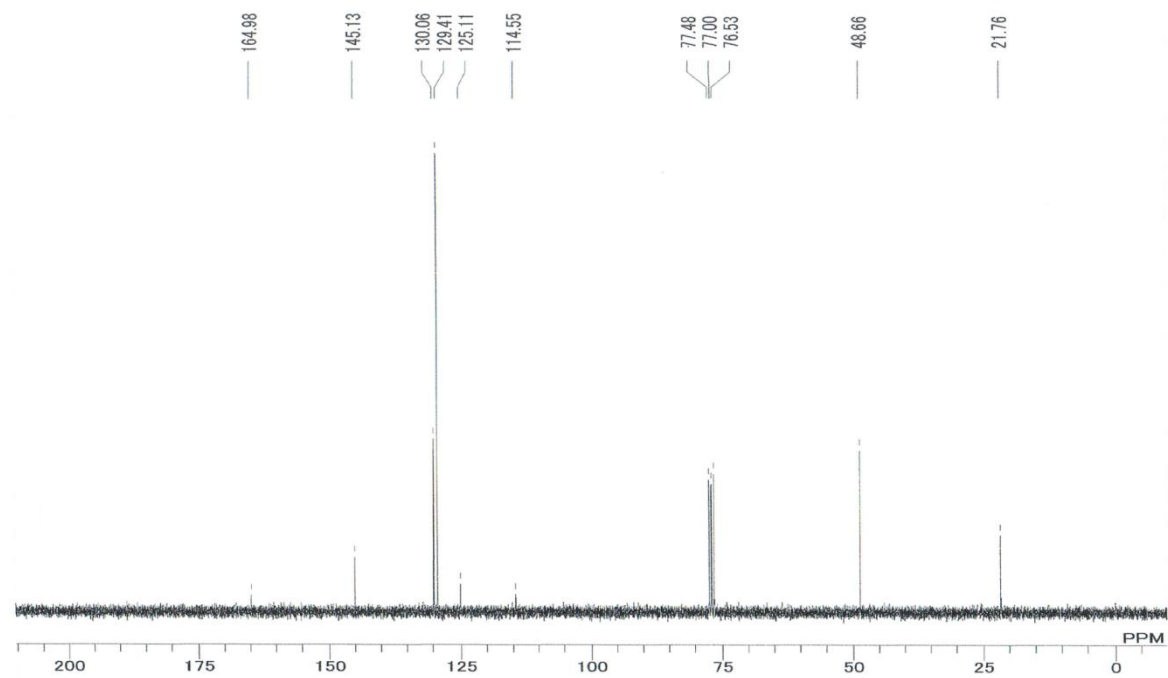
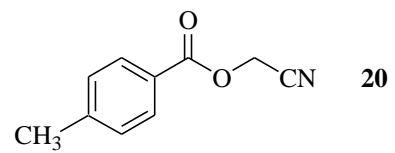
18



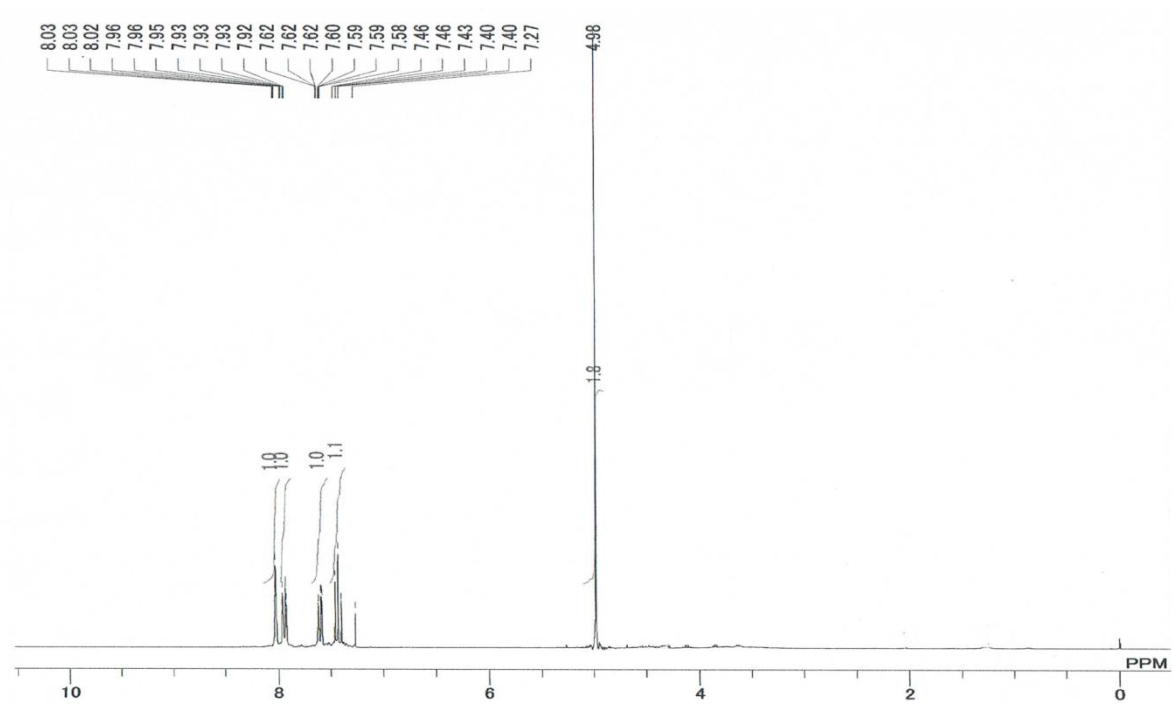
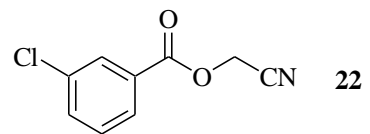
^1H NMR (CDCl_3 , 270.05 MHz)



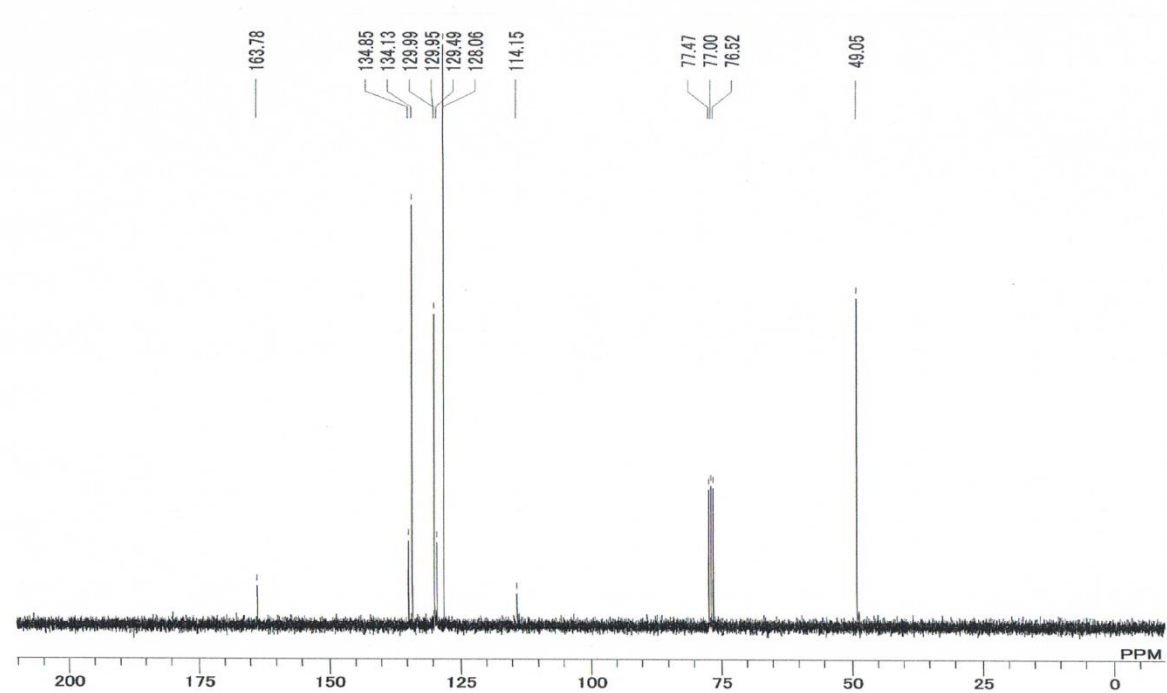
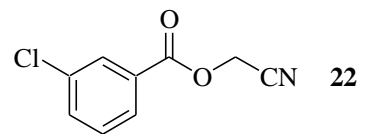
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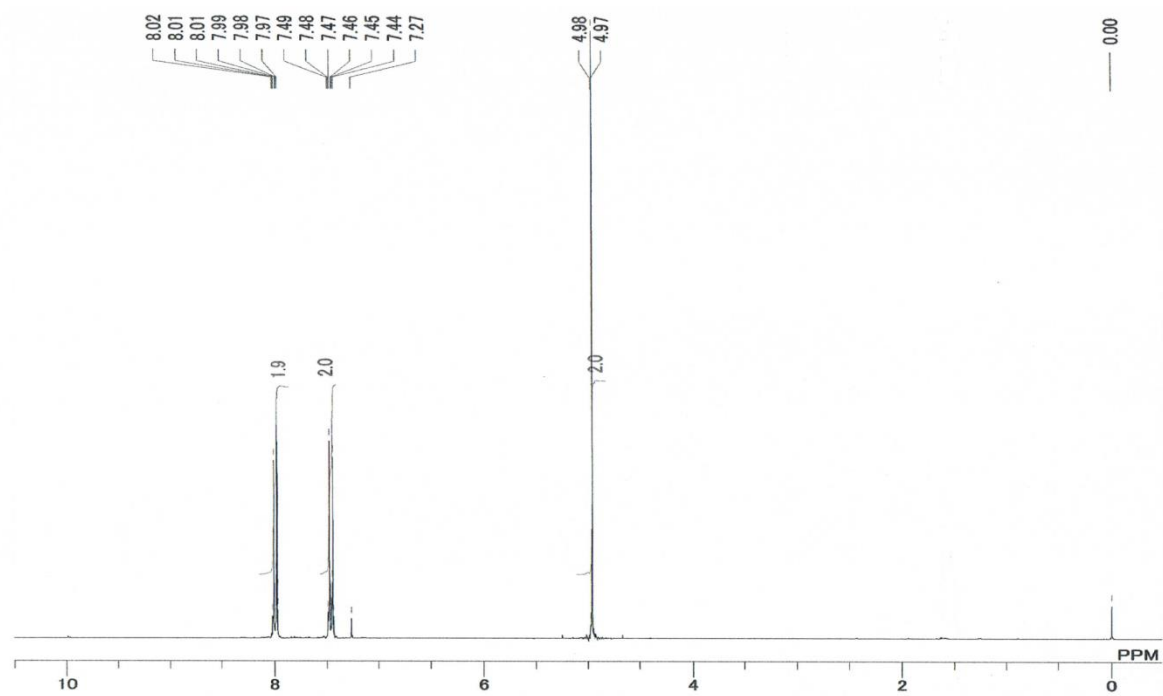
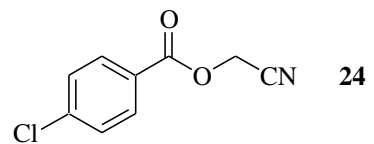
^1H NMR (CDCl_3 , 270.05 MHz)



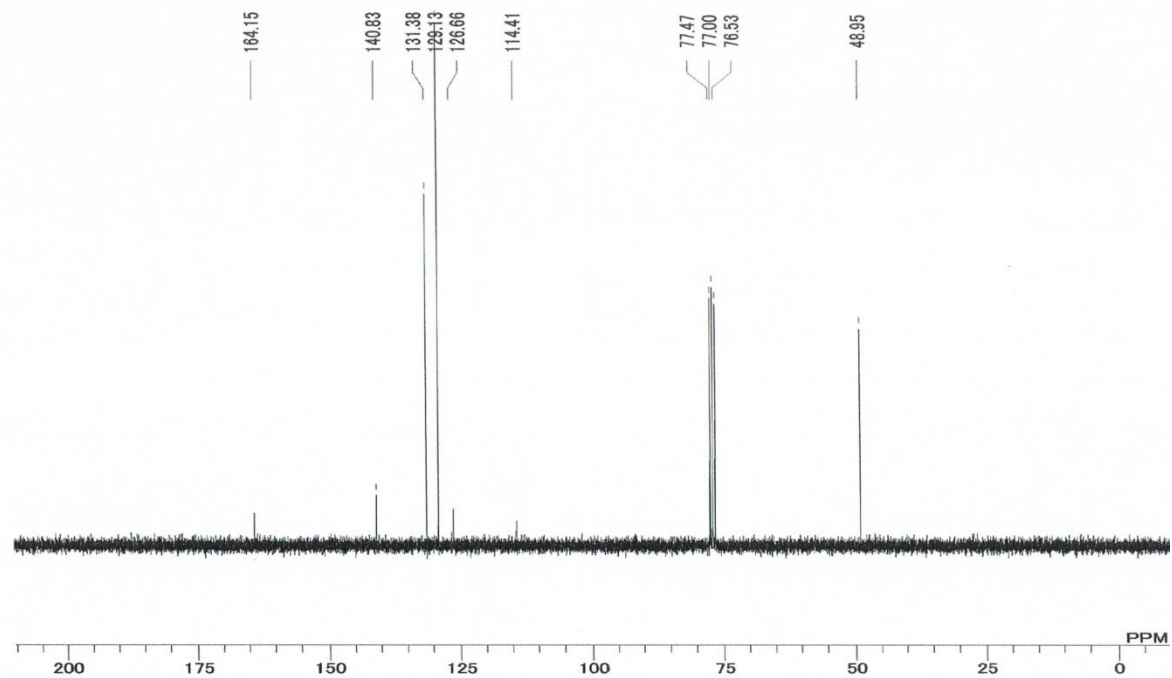
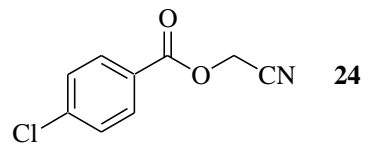
^{13}C NMR (CDCl_3 , 67.80 MHz)



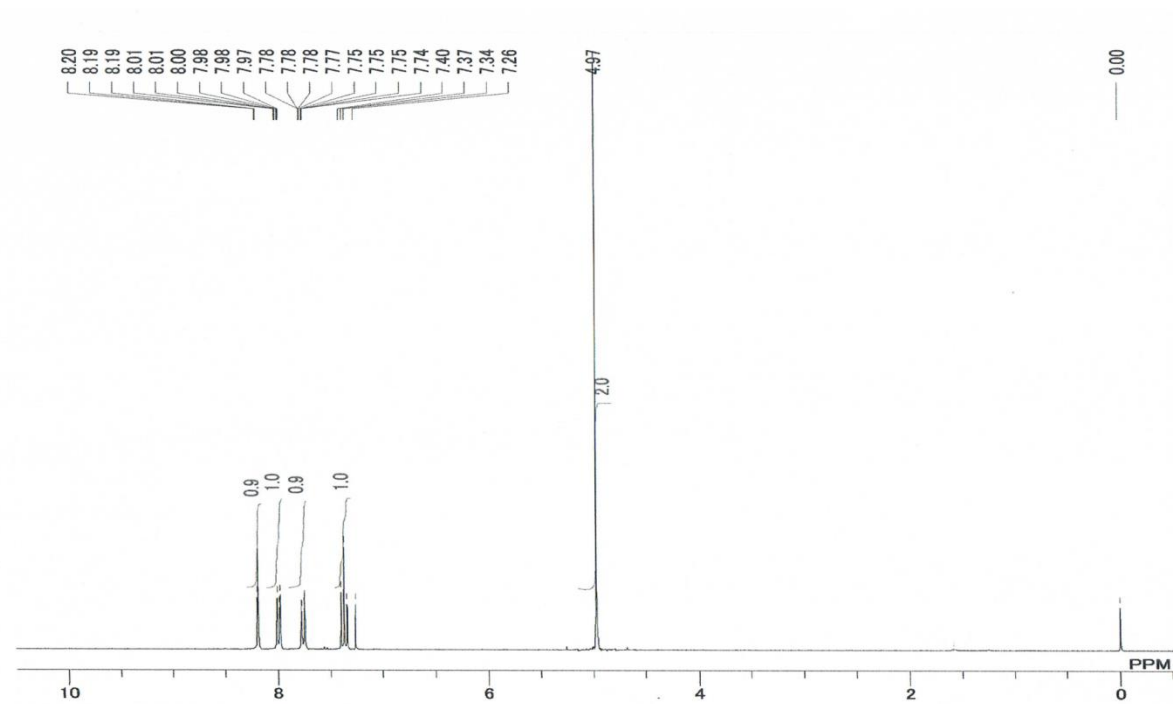
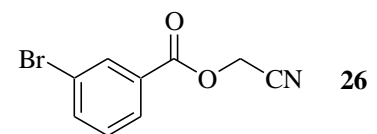
$^1\text{H NMR}$ (CDCl_3 , 270.05 MHz)



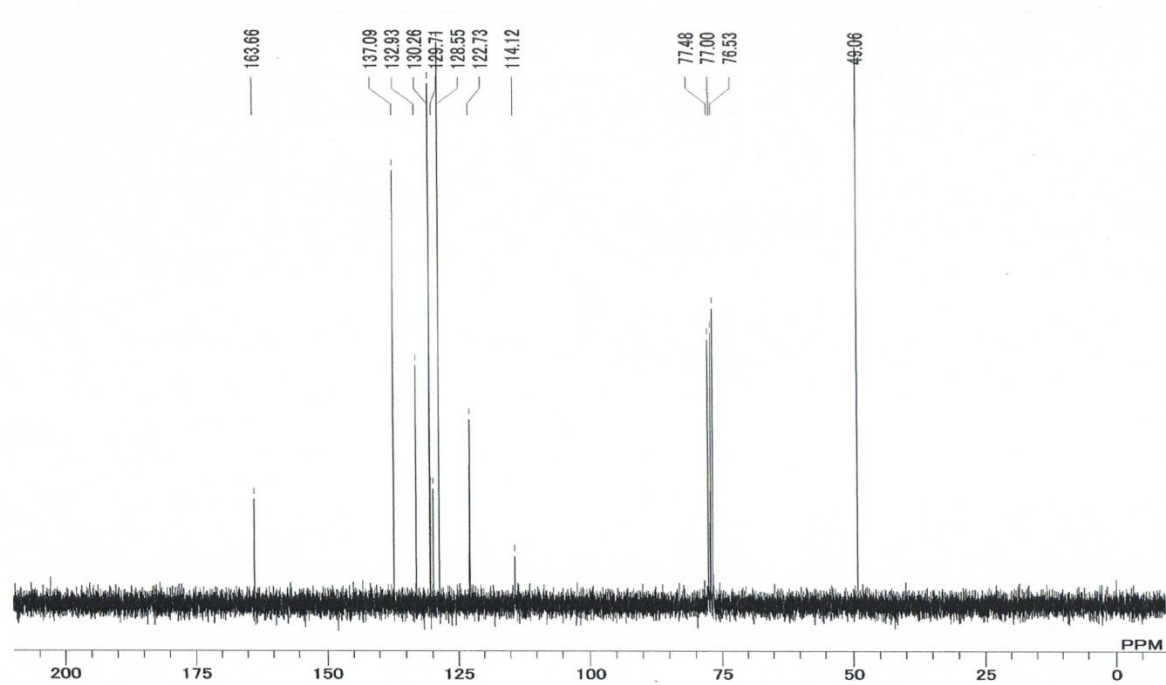
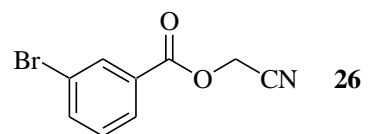
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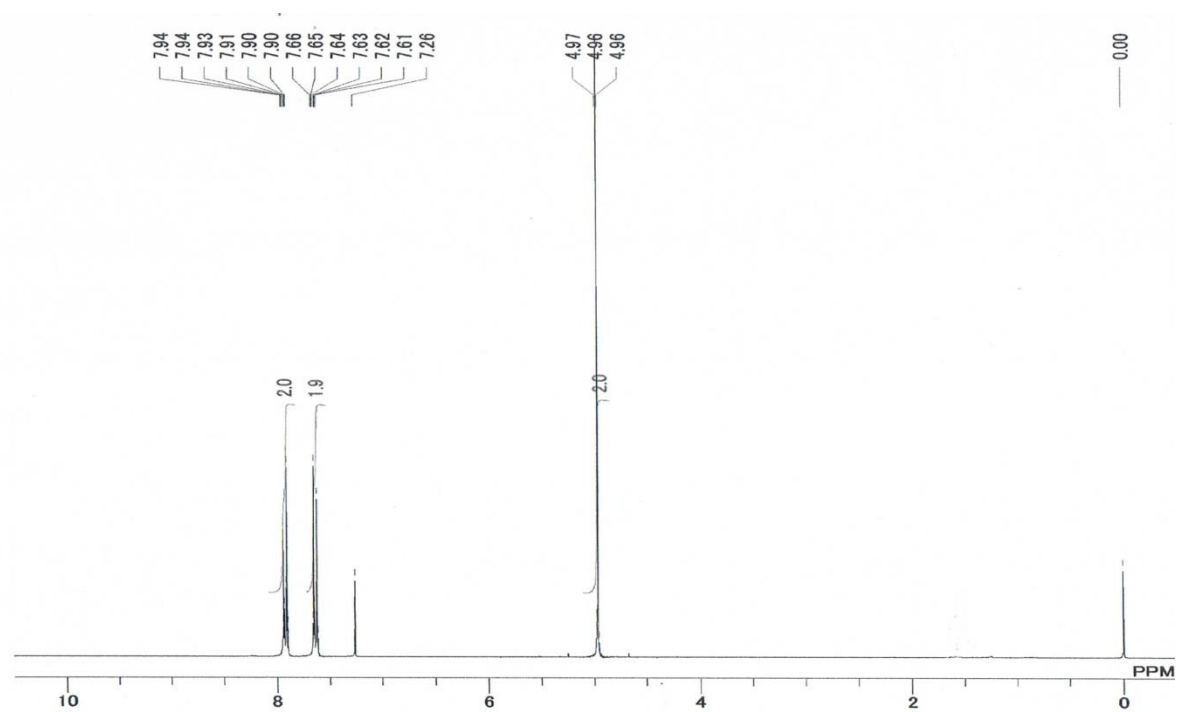
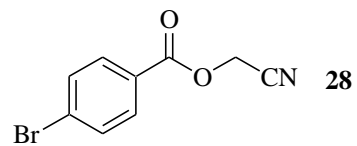
^1H NMR (CDCl_3 , 270.05 MHz)



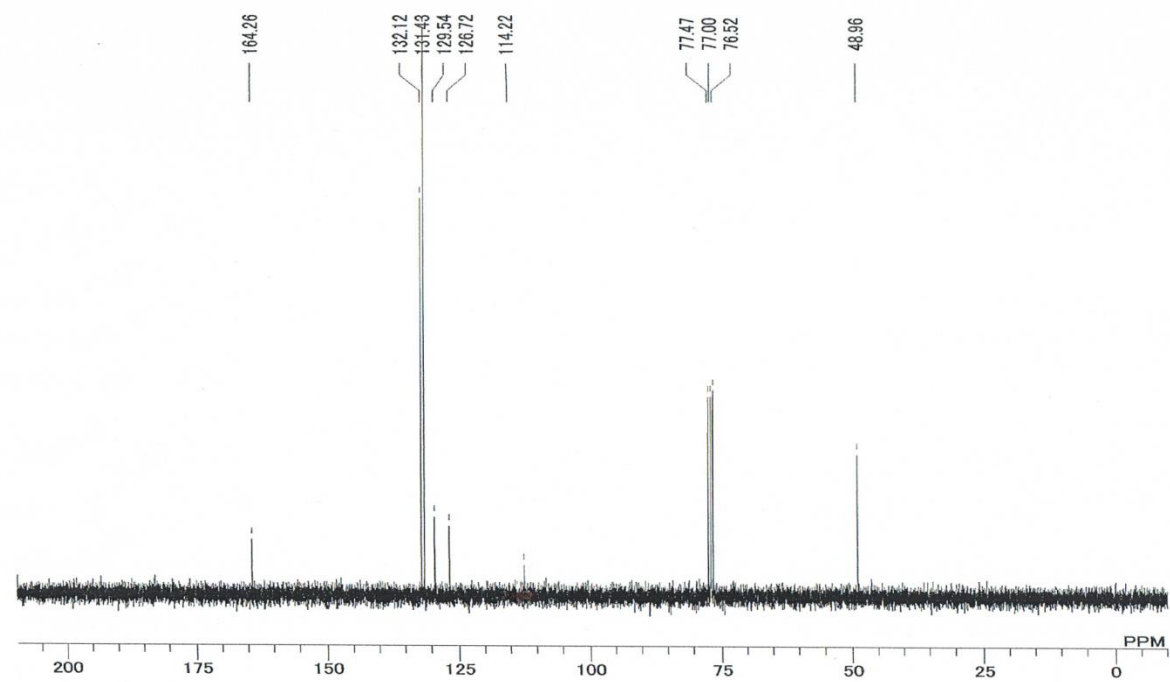
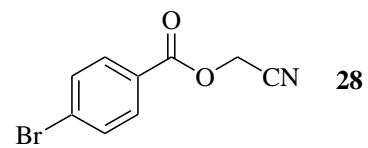
^{13}C NMR (CDCl_3 , 67.80 MHz)



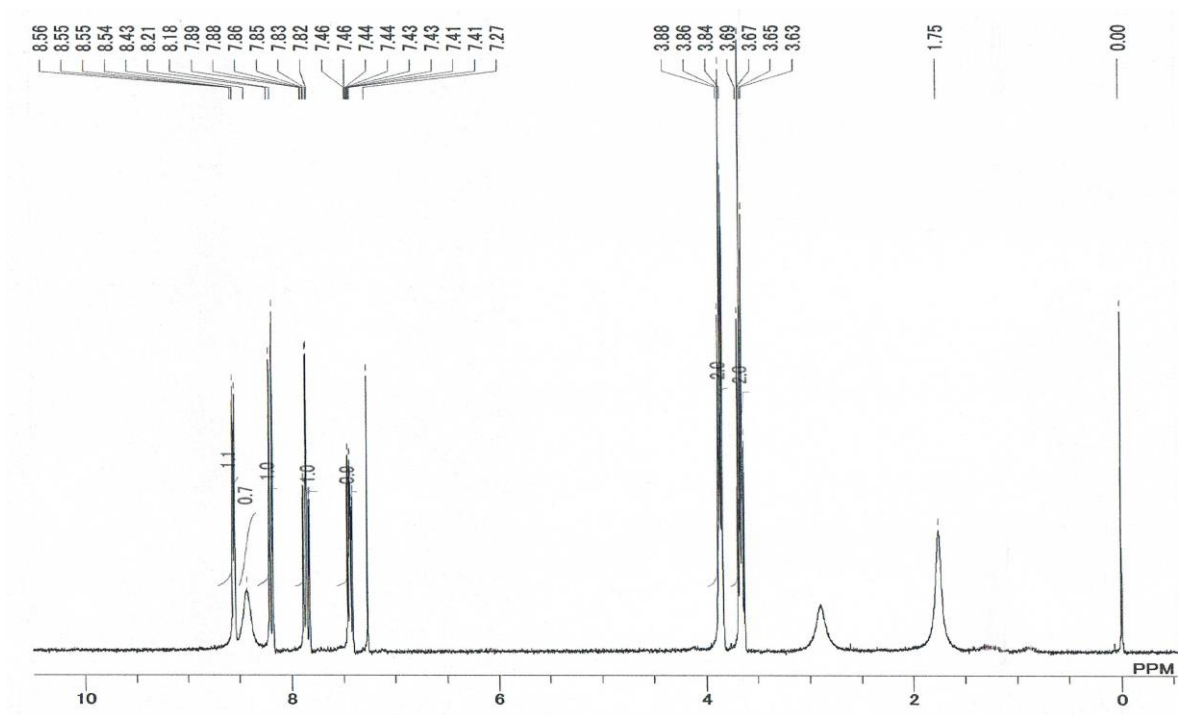
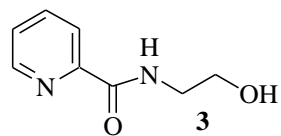
^1H NMR (CDCl_3 , 270.05 MHz)



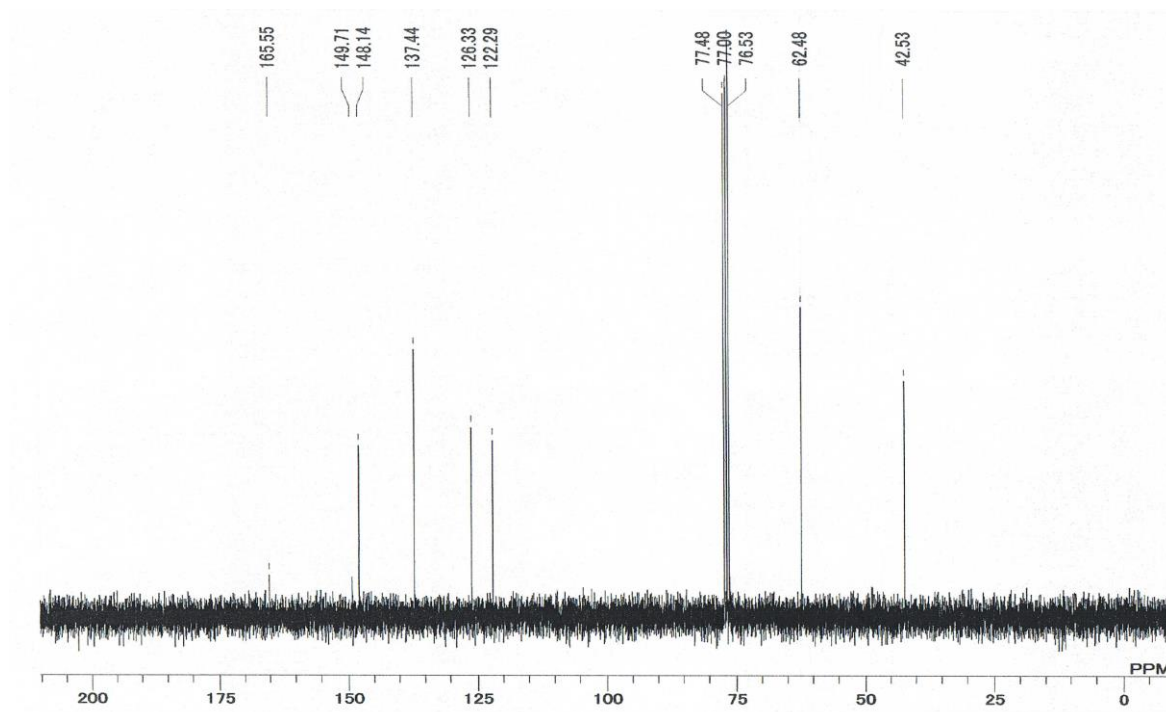
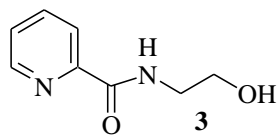
^{13}C NMR (CDCl_3 , 67.80 MHz)



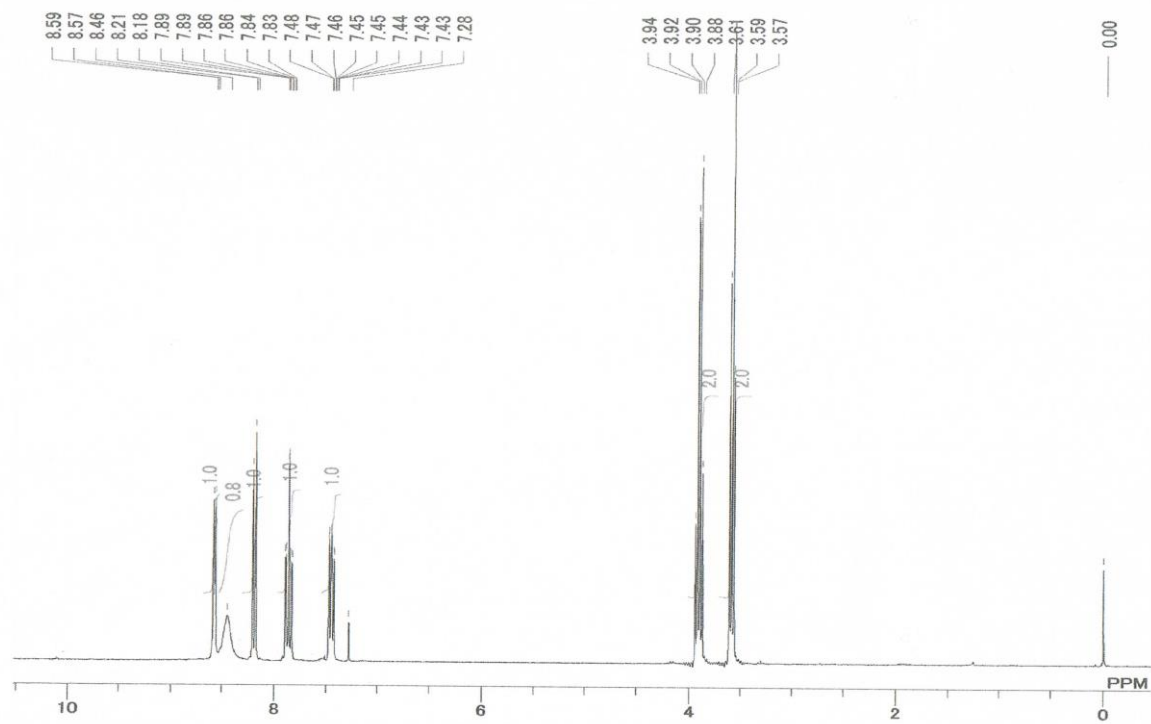
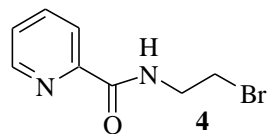
^1H NMR (CDCl_3 , 270.05 MHz)



^{13}C NMR (CDCl_3 , 67.80 MHz)



^1H NMR (CDCl_3 , 270.05 MHz)



^{13}C NMR (CDCl_3 , 67.80 MHz)

