Electronic Supplementary Information (ESI)

N-Heterocyclic Carbene Catalyzed Esterification of Aromatic Aldehydes with Alcohols under Aerobic Condition

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1. General Information

Solvents were purified and dried by standard procedures before use. Optical rotations were measured using sodium D line on a JASCO-181 digital polarimeter. IR spectra were recorded on a Perkin-Elmer model 683 B and absorption is expressed in cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were recorded on Brucker AC-200 spectrometer unless mentioned

otherwise. Elemental analysis was carried out on a Carlo Erba CHNS-O analyzer. Purification was done using column chromatography (60-120 mesh).

2. Experimental section

2.1. General experimental procedure for esterification of aromatic aldehydes:

To a flame-dried round bottom flask equipped with a magnetic stir bar was added imidazolium salt **1a** (10 mol%), DBU (20 mol%) and THF (10 mL). The contents were evacuated and covered with molecular oxygen in balloon. The resultant reaction mixture was kept stirring at 25 °C for 45 min. To this mixture was added aromatic aldehydes (5 mmol) and alcohol (6 mmol) successively. It was allowed to stir at 25 °C. After completion of the reaction (monitored by TLC), THF was evaporated, H_2O (50 mL) added and the mixture extracted with EtOAc (3 x 50 ml). The combined organic layers were dried over anhyd. Na_2SO_4. concentrated to give crude ester, which was purified by silica gel-packed column chromatography to obtain pure esters.

3a: Methyl 3-methylbenzoate: Yield: 78%**,** colorless gum; **IR** ($CHCl_3$): 684, 815, 897, 976, 1043, 1166, 1239, 1381, 1607, 1682, 1722, 1873, 2496 cm^{-1}; ^{1}**H NMR** (200 MHz, $CDCl_3$): δ 2.41 (s, 3H), 3.91 (s, 3H), 7.30-7.34 (m, 2H), 7.81-7.85 (m, 2H); ^{13}C **NMR** (50 MHz, $CDCl_3$): δ 21.2, 51.8, 126.7, 128.1, 130.0, 133.5, 137.9, 166.9; **Analysis**: $C_9H_{10}O_2$ requires C 71.98, H 6.71found C 71.83, H 6.59 %.

3b: Methyl 4-methoxybenzoate: Yield: 72%**,** colorless solid; mp 49 – 51 ºC (lit.[13] m.p. 49 ºC); **IR** ($CHCl_3$): 770, 848, 1029, 1103, 1168, 1256, 1280, 1317, 1434, 1458, 1606, 1716, 2953 cm^{-1}; ^{1}**H NMR** (200 MHz, $CDCl_3$): δ 3.86 (s, 3H), 3.88 (s, 3H), 6.90 (d, J = 8.9 Hz, 2H), 7.98 (d, J = 8.9 Hz, 2H); ^{13}C **NMR** (50 MHz, $CDCl_3$): δ 51.7, 55.2, 113.5,

122.6, 131.5, 163.2, 166.5; **Analysis**: $C_9H_{10}O_3$ requires C 65.05, H 6.07 found C 64.91, H 5.93 %.

3c: Methyl 3,4-dimethoxybenzoate: Yield: 70%**,** colorless solid; mp 59 – 61 ºC (lit.[13] m.p. 60 ºC); **IR** ($CHCl_3$): 764, 1133, 1271, 1294, 1434, 1514, 1600, 1714 cm^{-1}; ^{1}**H NMR** (200 MHz, $CDCl_3$): δ 3.89 (s, 3H), 3.93 (s, 6H), 6.87 (d, *J* = 8.36 Hz, 1H), 7.53 (d, *J* = 1.9 Hz, 1H), 7.66 (dd, *J* = 1.9, 8.36 Hz, 1H); ^{13}C **NMR** (50 MHz, $CDCl_3$): δ 51.8, 55.8, 110.2, 111.9, 122.6, 123.5, 148.6, 152.9, 166.6; **Analysis**: $C_{10}H_{12}O_4$ requires C 61.22, H 6.16 found C 61.09, H 6.12 %.

3d: Methyl 3,4,5-trimethoxybenzoate: Yield: 65%**,** colorless solid; mp 82 – 85 ºC (lit.[13] m.p. 82 ºC); **IR** ($CHCl_3$): 761, 1132, 1229, 1342, 1413, 1465, 1591, 1719 cm^{-1}; ^{1}**H NMR** (200 MHz, $CDCl_3$): δ 3.90 (s, 3H), 3.91 (s, 9H), 7.28 (s, 2H); ^{13}C **NMR** (50 MHz, $CDCl_3$): δ 52.1, 56.1, 60.7, 106.7, 125.0, 142.1, 152.9, 166.4; **Analysis**: $C_{11}H_{14}O_5$ requires C 58.40, H 6.24 found C 58.31, H 6.12 %.

3e: Methyl 4-(methylthio)benzoate: Yield: 68%**,** colorless gum; **IR** ($CHCl_3$): 759, 1116, 1302, 1281, 1402, 1708 cm^{-1}; ^{1}**H NMR** (200 MHz, $CDCl_3$): δ 2.51 (s, 3H), 3.89 (s, 3H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.91 (d, *J* = 8.6 Hz, 2H); ^{13}C **NMR** (50 MHz, $CDCl_3$): δ 14.7, 51.8, 124.8, 126.3, 129.8, 145.3, 166.5; **Analysis**: $C_9H_{10}O_2S$ requires C 59.32, H 5.53 found C 59.18, H 5.41 %.

3f: Methyl 4-nitrobenzoate: Yield: 76%**,** colorless solid; mp 94 – 96 ºC (lit.[13] m.p. 96 ºC); **IR** ($CHCl_3$): 722, 818, 1076, 1104, 1136, 1262, 1298, 1338, 1536, 1618, 1719 cm^{-1}; ^{1}**H NMR** (200 MHz, $CDCl_3$): δ 3.98 (s, 3H), 8.21 (d, *J* = 8.6 Hz, 2H), 8.30 (d, *J* = 8.6 Hz, 2H); ^{13}C **NMR** (50 MHz, $CDCl_3$): δ 52.7, 123.5, 130.7, 135.4, 150.5, 165.0; **Analysis**: $C_8H_7NO_4$ requires C 53.04, H 3.89, N 7.73 found C 52.92, H 3.76, N 7.62 %.

3g: Methyl 3-nitrobenzoate: Yield: 82%**,** colorless solid; mp 78 – 80 ºC (lit.[13] m.p. 78 ºC); IR ($CHCl_3$): 719, 823, 1072, 1100, 1133, 1266, 1292, 1350, 1528, 1615, 1722 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.99 (s, 3H), 7.61-7.69 (m, 1H), 8.34-8.44 (m, 2H), 8.81-8.87 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 52.6, 124.4, 127.2, 129.5, 131.8, 135.1, 148.2, 164.6; **Analysis**: $C_8H_7NO_4$ requires C 53.04, H 3.89, N 7.73 found C 52.96, H 3.81, N 7.67 %.

3h: Methyl 4-bromobenzoate: Yield: 78%**,** colorless solid; mp 77 – 80 ºC (lit.[13] m.p. 79 ºC); **IR** ($CHCl_3$): 758, 847, 1157, 1276, 1397, 1590, 1716 cm^{-1}; ^{1}**H NMR** (200 MHz, $CDCl_3$): δ 3.92 (s, 3H), 7.57 (d, *J* = 10 Hz, 2H), 7.89 (d, *J* = 10 Hz, 2H); ^{13}C **NMR** (50 MHz, $CDCl_3$): δ 52.1, 127.9, 129.0, 131.0, 131.6, 166.0; **Analysis**: $C_8H_7BrO_2$ requires C 44.68, H 3.28 found C 44.59, H 3.12 %.

3i: Methyl 3-bromobenzoate: Yield: 72%**,** colorless gum; **IR** ($CHCl_3$): 718, 746, 1067, 1121, 1260, 1293, 1436, 1571, 1727 cm^{-1}; ^{1}**H NMR** (200 MHz, $CDCl_3$): δ 3.92 (s, 3H), 7.26-7.35 (m, 1H), 7.63-7.71 (m, 1H), 7.93-7.99 (m, 1H), 8.12-8.18 (m, 1H); ^{13}C **NMR**

(50 MHz, $CDCl_3$): δ 52.2, 122.4, 128.0, 129.8, 132.0, 132.6, 135.7, 165.4; **Analysis**: $C_8H_7BrO_2$ requires C 44.68, H 3.28 found C 44.53, H 3.11 %.

3j: Methyl 4-chlorobenzoate: Yield: 79%**,** colorless gum; **IR** ($CHCl_3$): 760, 1015, 1091, 1115, 1434, 1488, 1596, 1725 cm^{-1}; ^{1}**H NMR** (200 MHz, $CDCl_3$): δ 3.92 (s, 3H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.97 (d, *J* = 8.6 Hz, 2H); ^{13}C **NMR** (50 MHz, $CDCl_3$): δ 52.1, 128.6, 131.0, 139.3, 165.9; **Analysis**: $C_8H_7ClO_2$ requires C 56.32, H 4.14 found C 56.21, H 4.03 %.

3k: Methyl 3-chlorobenzoate: Yield: 70%**,** colorless gum; **IR** ($CHCl_3$): 748, 1126, 1259, 1283, 1295, 1437, 1728 cm^{-1}; ^{1}**H NMR** (200 MHz, $CDCl_3$): δ 3.92 (s, 3H), 7.32-7.40 (m, 1H), 7.48-7.54 (m, 1H), 7.88-7.94 (m, 1H), 7.97-8.02 (m, 1H); ^{13}C **NMR** (50 MHz, $CDCl_3$): δ 52.2, 127.6, 129.5, 131.8, 132.8, 134.5, 165.5; **Analysis**: $C_8H_7ClO_2$ requires C 56.32, H 4.14 found C 56.23, H 4.06 %.

3l: Methyl 4-flurobenzoate: Yield: 76%**,** colorlessgum; **IR** ($CHCl_3$): 607, 767, 854, 1092, 1113, 1154, 1280, 1436, 1508, 1601, 1727 cm^{-1}; ^{1}**H NMR** (200 MHz, $CDCl_3$): δ 3.90 (s, 3H), 7.04-7.13 (m, 2H), 7.99-8.09 (m, 2H); ^{13}C **NMR** (50 MHz, $CDCl_3$): δ 52.1, 115.4, 128.6, 131.0, 165.1, 166.1; **Analysis**: $C_8H_7FO_2$ requires C 62.34, H 4.58 found C 62.23, H 4.39 %.

3m: Methyl 4-(trifluromethyl)benzoate: Yield: 69%**,** pale yellow liquid; **IR** ($CHCl_3$): 775, 865, 1019, 1068, 1327, 1413, 1440, 1730, 2957 cm^{-1}; ^{1}**H NMR** (200 MHz, $CDCl_3$):

δ 3.92 (s, 3H), 7.70 (d, *J* = 8.2 Hz, 2H), 8.14 (d, *J* = 8.2 Hz, 2H); ^{13}C **NMR** (50 MHz, $CDCl_3$): δ 52.3, 120.9, 125.2-125.4 (m), 126.3, 128.1, 129.9, 132.5-135.7 (m), 165.5; $C_9H_7F_3O_2$ requires C 52.95, H 3.46 found C 52.76, H 3.33 %.

3n: Methyl 4-cyanobenzoate: Yield: 72%**,** colorless gum; **IR** ($CHCl_3$): 763, 866, 960, 1019, 1108, 1181, 1289, 1315, 1440, 1727, 2229 cm^{-1}; ^{1}**H NMR** (200 MHz, $CDCl_3$): δ 3.96 (s, 3H), 7.75 (d, *J* = 8.6 Hz, 2H), 8.14 (d, *J* = 8.6 Hz, 2H); ^{13}C **NMR** (50 MHz, $CDCl_3$): δ 52.6, 116.5, 117.7, 130.1, 132.1, 133.9, 165.1; **Analysis**: $C_9H_7NO_2$ requires C 67.07, H 4.38, N 8.69 found C 66.91, H 4.26, N 8.52 %.

3o: **Methyl Nicotinate : Yield**: 76%**,** colorless liquid; IR ($CHCl_3$): 824, 959, 1072, 1292, 1350, 1436, 1528, 1615, 1722, 3045 cm^{-1}; **^{1}H NMR** (200 MHz, $CDCl_3$): δ 3.93 (s, 3H), 7.33-7.40 (m, 1H), 8.23-8.29 (m, 1H), 8.71-8.76 (m,1H), 9.18 (m,1H); **^{13}C NMR** (50 MHz, $CDCl_3$): δ 52.3, 123.2, 126.0, 136.9, 150.8, 153.3, 165.5; **Analysis**: $C_7H_7NO_2$ requires C 61.31, H 5.14, N 10.21 found C 61.26, H 5.06, N 10.12 %.

3p: Methyl furan-2-carboxylate: Yield: 63%**,** colorless liquid; **IR** ($CHCl_3$): 797, 1121, 1177, 1197, 1306, 1479, 1731, 3127, 3144 cm^{-1}; ^{1}**H NMR** (200 MHz, $CDCl_3$): δ 3.90 (s, 3H), 6.50 (d, *J* = 3.8 HZ, 1H), 7.17 (d, *J* = 3.8 Hz, 1H), 7.57 (S, 1H); ^{13}C **NMR** (50 MHz, $CDCl_3$): δ 52.0, 111.9, 118.0, 144.8, 146. 5, 159.2; **Analysis**: $C_6H_6O_3$ requires C 57.14, H 4.80 found C 57.02.59, H 4.69 %.

3q: Ethyl 4-nitrobenzoate: Yield: 80%**,** colorless solid; mp 97 – 99 ºC (lit.[19a] m.p. 97-98 ºC); **IR** ($CHCl_3$): 757, 872, 1103, 1277, 1320, 1352, 1528, 1724 cm^{-1}; ^{1}**H NMR** (200 MHz, $CDCl_3$): δ 1.44 (t, *J* = 7.4 HZ, 3H), 4.43 (q, *J* = 7.3, 14.6 Hz, 2H), 8.21 (d, *J* = 8.9 Hz, 2H), 8.30 (d, *J* = 8.9 Hz, 2H); ^{13}C **NMR** (50 MHz, $CDCl_3$): δ 14.2, 61.9, 123.5, 130.6, 135.8, 150.5, 164.4; **Analysis**: $C_9H_9NO_4$ requires C 55.39, H 4.65, N 7.18 found C 55.21, H 4.52, N 7.01 %.

3r: Isopropyl 4-nitrobenzoate: Yield: 76%**,** colorless solid; mp 105 – 108 ºC (lit.[19a] m.p. 105-106 ºC); **IR** ($CHCl_3$): 717, 874, 1103, 1287, 1322, 1349, 1375, 1525, 1607, 1713 cm^{-1}; ^{1}**H NMR** (200 MHz, $CDCl_3$): δ 1.39 (d, *J* = 6.4 HZ, 6H), 5.24-5.31 (m, 1H), 8.19 (d, *J* = 8.4 Hz, 2H), 8.27 (d, *J* = 8.4 Hz, 2H); ^{13}C **NMR** (50 MHz, $CDCl_3$): δ 21.8, 69.7, 123.4, 130.6, 136.2, 150.4, 164.1; **Analysis**: $C_{10}H_{11}NO_4$ requires C 57.41, H 5.30, N 6.70 found C 57.30, H 5.19, N 6.54 %.

3s: Benzyl 4-nitrobenzoate: Yield: 80%**,** colorless solid; mp 82 – 84 ºC (lit.[19a] m.p. 81-82 ºC); **IR** ($CHCl_3$): 743, 1103, 1286, 1348, 1523, 1713 cm^{-1}; ^{1}**H NMR** (200 MHz, $CDCl_3$): δ 5.40 (s, 2H), 7.37-7.46 (m, 5H), 8.21-8.31 (m, 4H); ^{13}C **NMR** (50 MHz, $CDCl_3$): δ 67.5, 123.5, 128.4, 128.6, 128.7, 130.7, 135.2, 135.4, 150.5, 164.3; **Analysis**: $C_{14}H_{11}NO_4$ requires C 65.37, H 4.31, N 5.44 found C 65.23, H 4.21, N 5.31 %.

3t: Allyl 4-nitrobenzoate: Yield: 76%**,** colorless oil; **IR** ($CHCl_3$): 720, 855, 933, 995, 1014, 1048, 1102, 1271, 1319, 1348, 1526, 1608, 1727 cm^{-1}; ^{1}**H NMR** (200 MHz, $CDCl_3$): δ 4.84-4.87 (m, 2H), 5.34 (dd, *J* = 1.3, 10.4 Hz, 1H), 5.31-5.46 (m, 1H), 5.94-

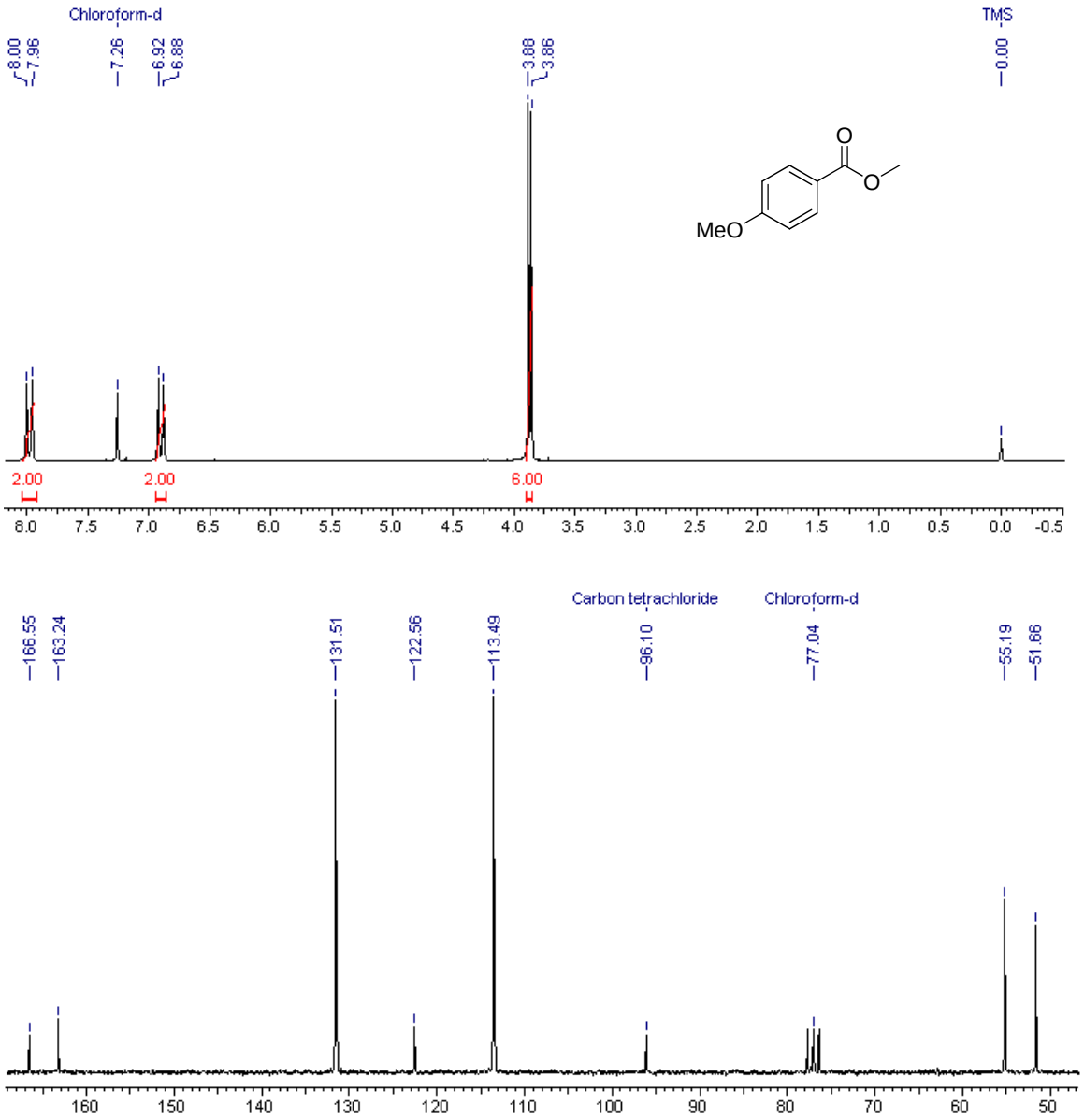
6.13 (m, 1H), 8.21 (d, *J* = 8.9 Hz, 2H), 8.29 (d, *J* = 8.9 Hz, 2H) ; ^{13}C **NMR** (50 MHz, $CDCl_3$): δ 66.3, 119.0, 123.5, 130.7, 131.6, 135.5, 150.6, 164.1; **Analysis**: $C_{10}H_9NO_4$ requires C 57.97, H 4.38, N 6.76 found C 57.78, H 4.19, N 6.59 %.

3u: Prop-2-ynyl 4-nitrobenzoate: Yield: 82%**,** yellow gum; **IR** ($CHCl_3$): 715, 875, 1124, 1286, 1322, 1350, 1527, 1608, 1728, 3290 cm^{-1}; ^{1}**H NMR** (200 MHz, $CDCl_3$): δ 2.55 (t, *J* =2.53, 1H), 4.94 (d, *J* = 2.6, 2H), 8.24 (d, *J* = 8.4 Hz, 2H), 8.32 (d, *J* = 8.4 Hz, 2H) ; ^{13}C **NMR** (50 MHz, $CDCl_3$): δ 53.2, 75.8, 123.6, 130.9, 134.7, 150.8, 163.8; **Analysis**: $C_{10}H_7NO_4$ requires C 58.54, H 3.44, N 6.83 found C 58.42, H 3.29, N 6.74 %.

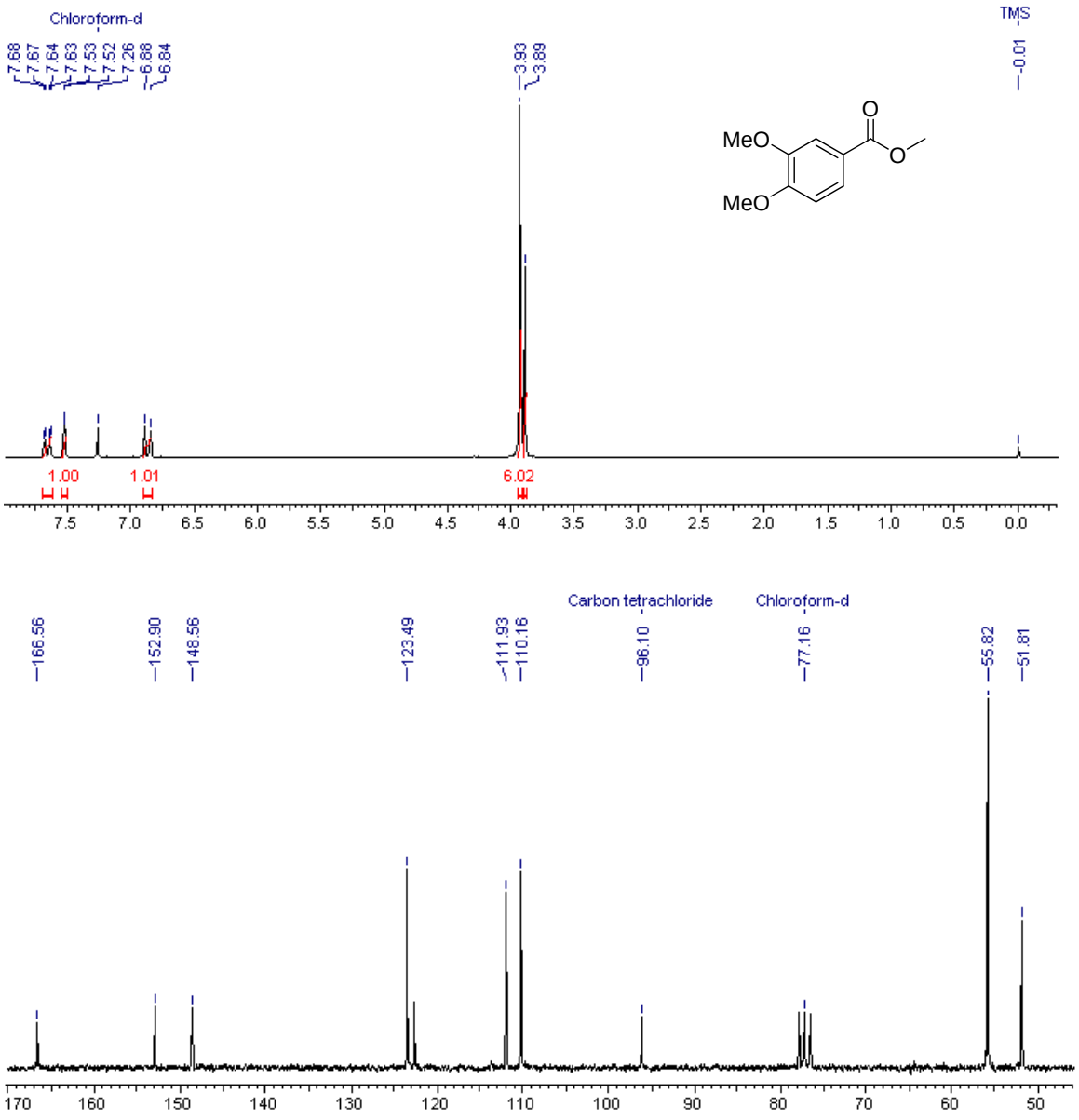
3v: (*S*)-tetrahydrofuran-3-yl 4-nitrobenzoate: Yield: 66%**,** colorless gum; $[\alpha]^D_{25}$ −31.24 (c 1.2, CH_2Cl_2); lit[19a] $[\alpha]^D_{25}$ +31.26 (c 1.0, CH_2Cl_2) for corresponding (*R*)-enantiomer; IR ($CHCl_3$): 720, 878, 1086, 1106, 1120, 1529, 1604, 1718, 2877, 2933, 3076 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.14-2.21 (m, 1H), 2.29-2.43 (m, 1H), 3.91-4.07 (m, 4H), 5.57-5.60 (m, 1H), 8.21 (d, *J* = 8.8 Hz, 2H), 8.30 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 32.8, 66.9, 72.9, 76.4, 123.5, 130.7, 135.2, 150.7, 164.1; Analysis: $C_{11}H_{11}NO_5$ requires C 55.70, H 4.67, N 5.90 found C 55.62, H 4.51, N 5.79 %.

3w: (*R*)-tetrahydrofuran-3-yl 4-nitrobenzoate: Yield: 64%**,** colorless gum; $[\alpha]^D_{25}$ +31.24 (c 1.2, CH_2Cl_2); lit[19a] $[\alpha]^D_{25}$ +31.26 (c 1.0, CH_2Cl_2); IR ($CHCl_3$): 721, 879, 1084, 1105, 1122, 1528, 1604, 1718, 2877, 2933, 3076 cm^{-1}; ^{1}**H NMR** (200 MHz, $CDCl_3$): δ 2.14-2.20 (m, 1H), 2.30-2.35 (m, 1H), 3.91-3.93(m, 1H), 3.98-4.03 (m, 3H), 5.55-5.58 (m, 1H), 8.20 (d, *J* = 8.8 Hz, 2H), 8.29 (d, *J* = 8.8 Hz, 2H); ^{13}C **NMR** (50 MHz, $CDCl_3$):

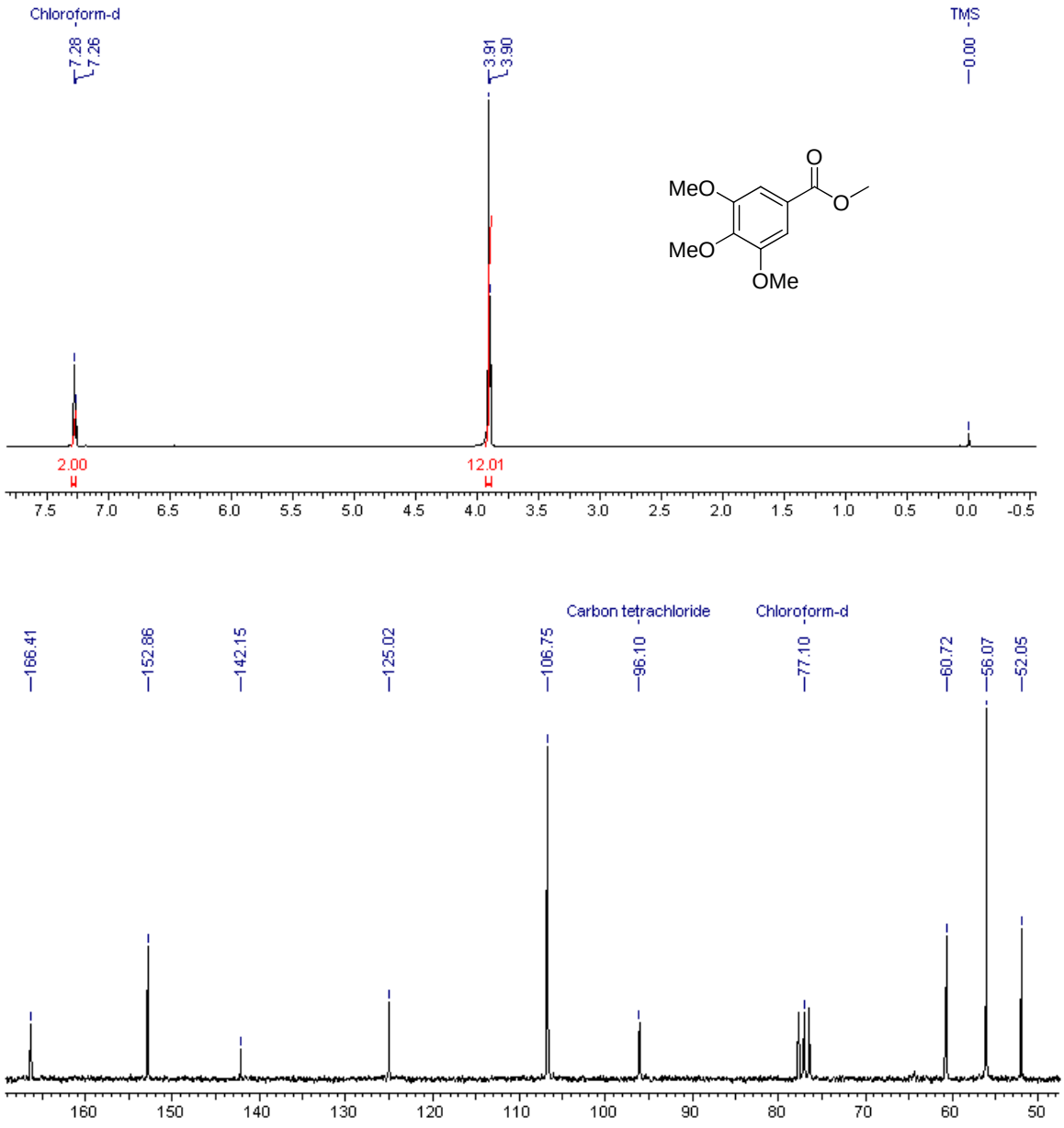
δ 32.8, 66.9, 72.9, 76.4, 123.5, 130.7, 135.2, 150.7, 164.1; Analysis: $C_{11}H_{11}NO_5$ requires C 55.70, H 4.67, N 5.90 found C 55.60, H 4.49, N 5.76 %.



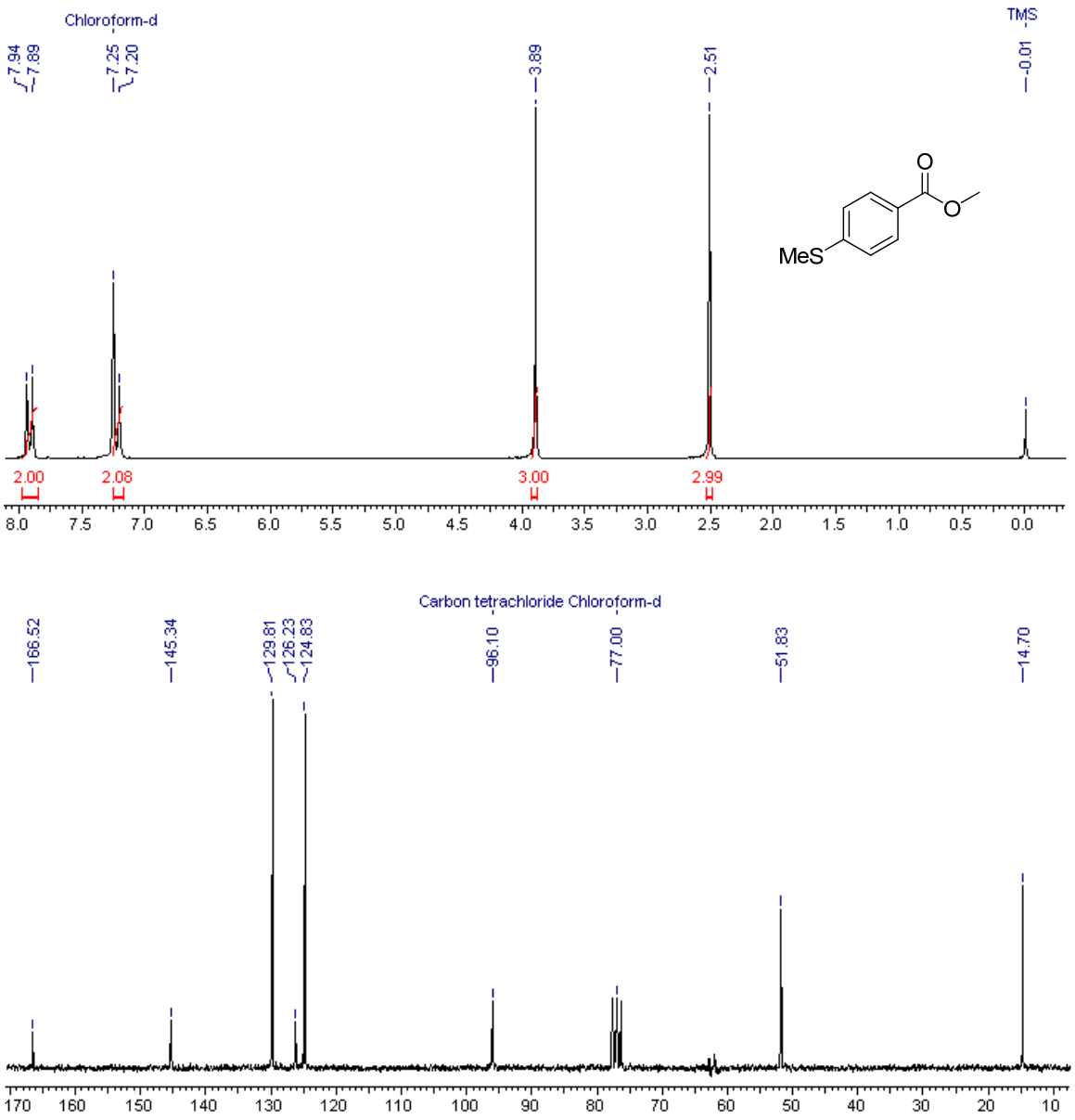
^{1}H and ^{13}C NMR spectra of Methyl 4-methoxybenzoate



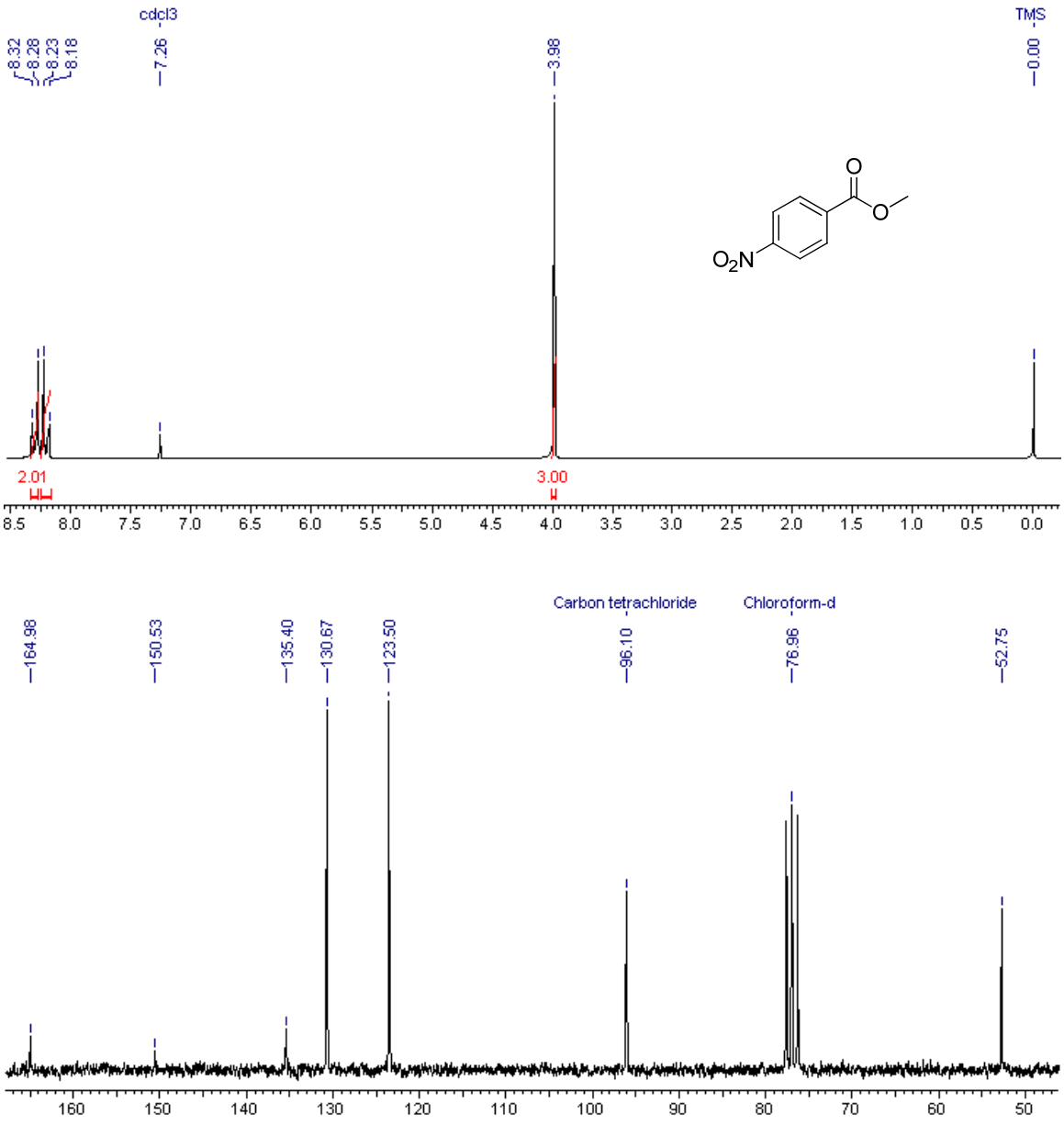
^{1}H and ^{13}C NMR spectra of Methyl 3,4-dimethoxybenzoate



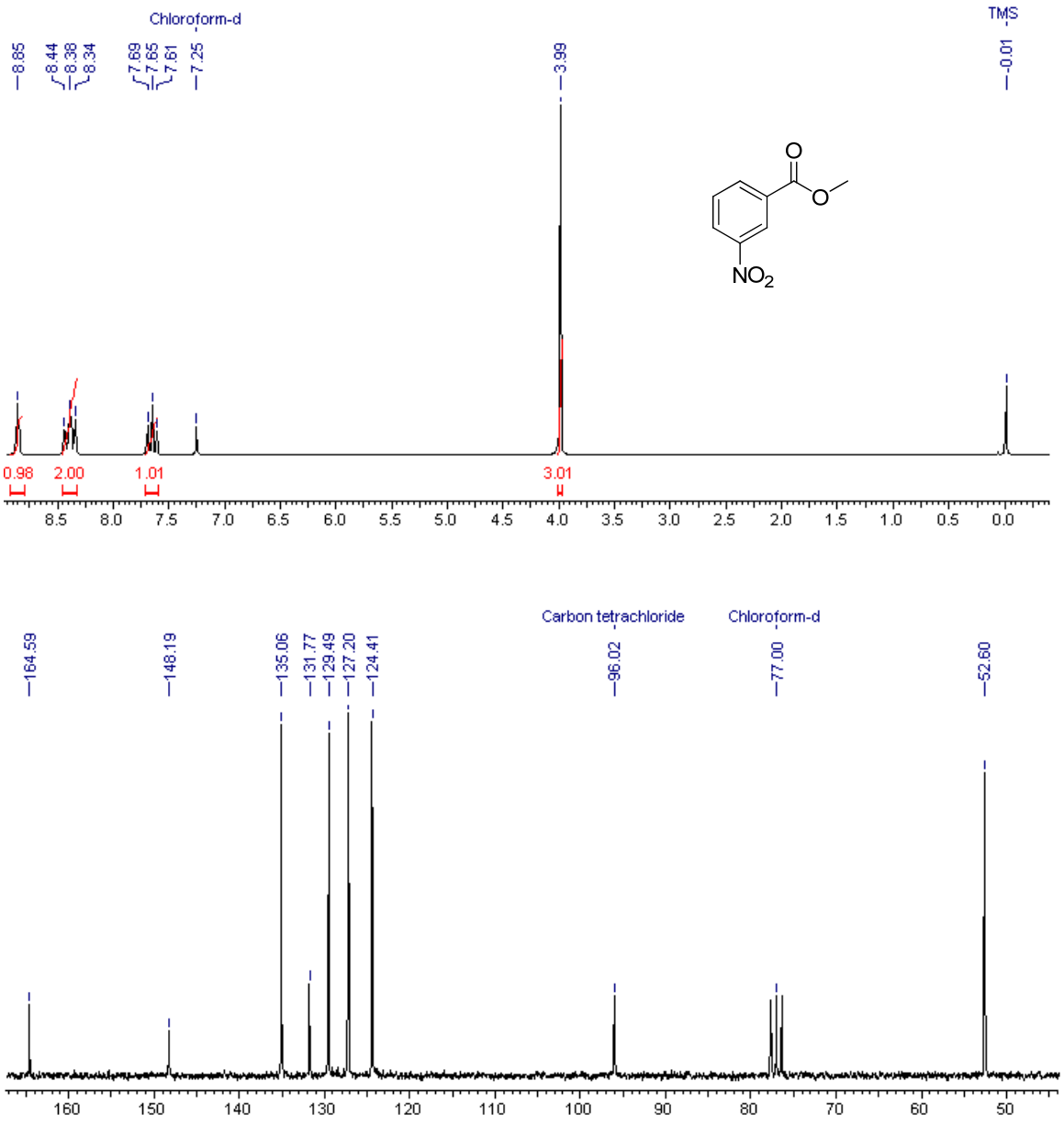
^{1}H and ^{13}C NMR spectra of Methyl 3,4,5-trimethoxybenzoate



^{1}H and ^{13}C NMR spectra of Methyl 4-(methylthio)benzoate



^{1}H and ^{13}C NMR spectra of Methyl 4-nitrobenzoate



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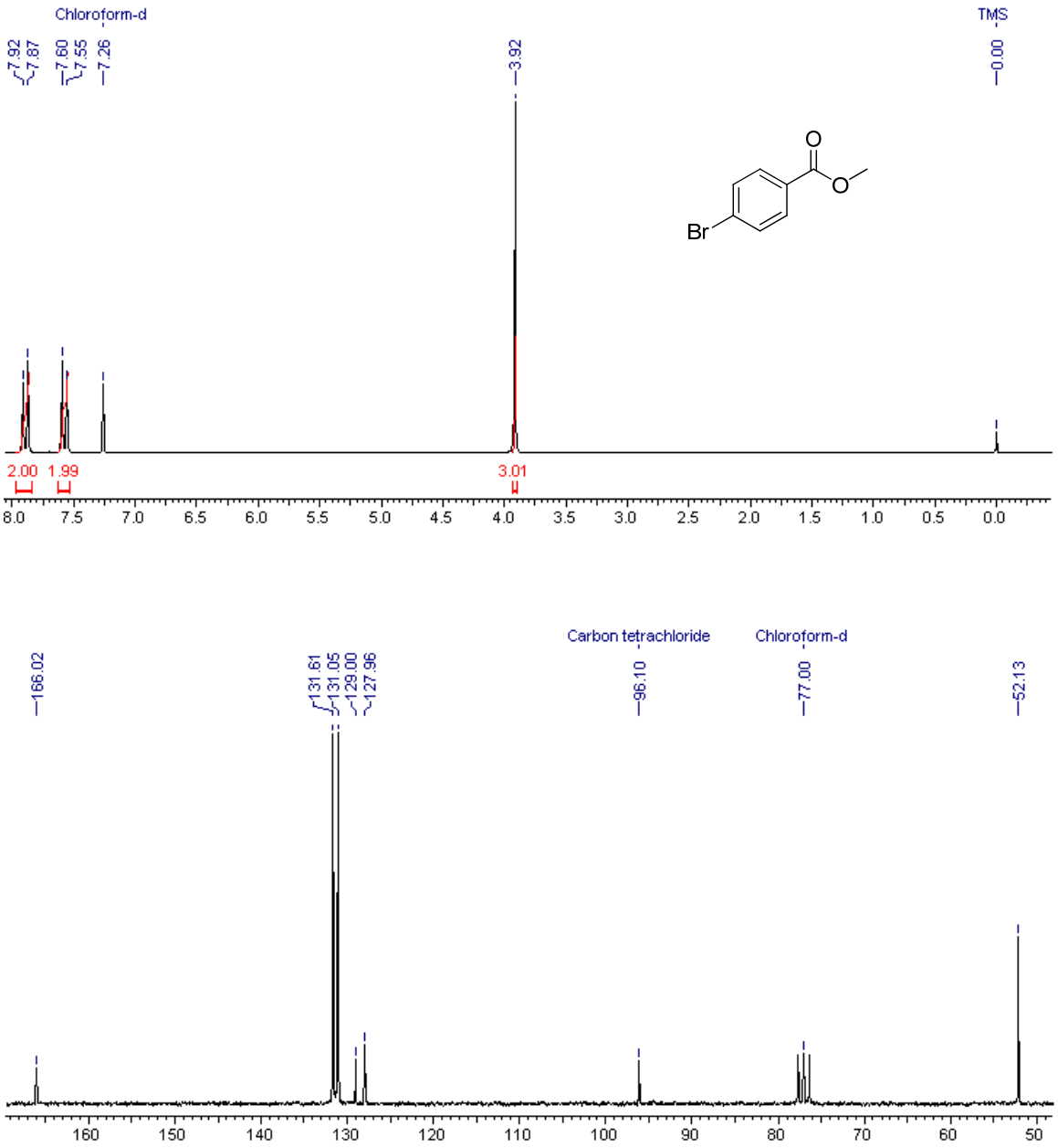
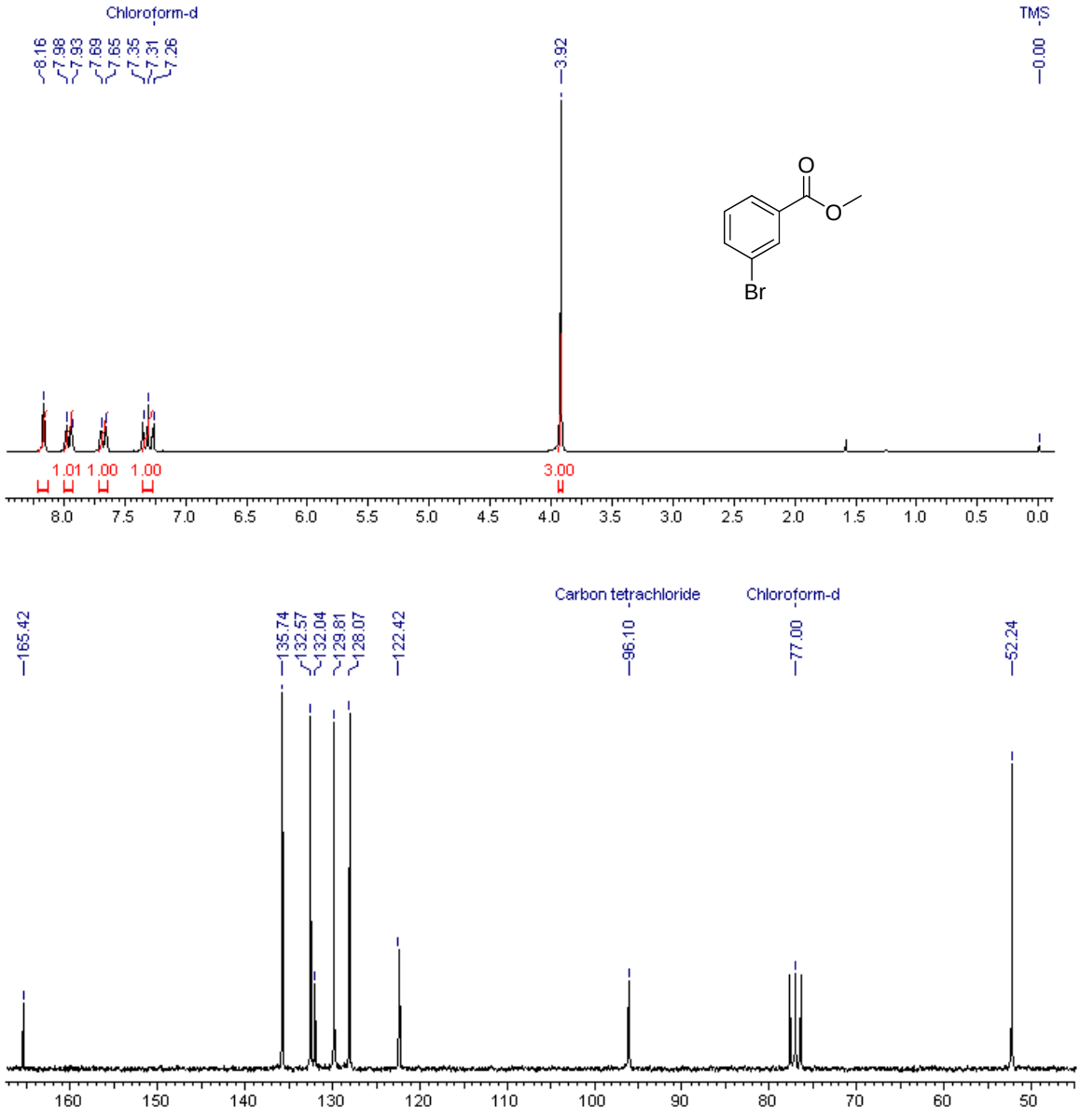
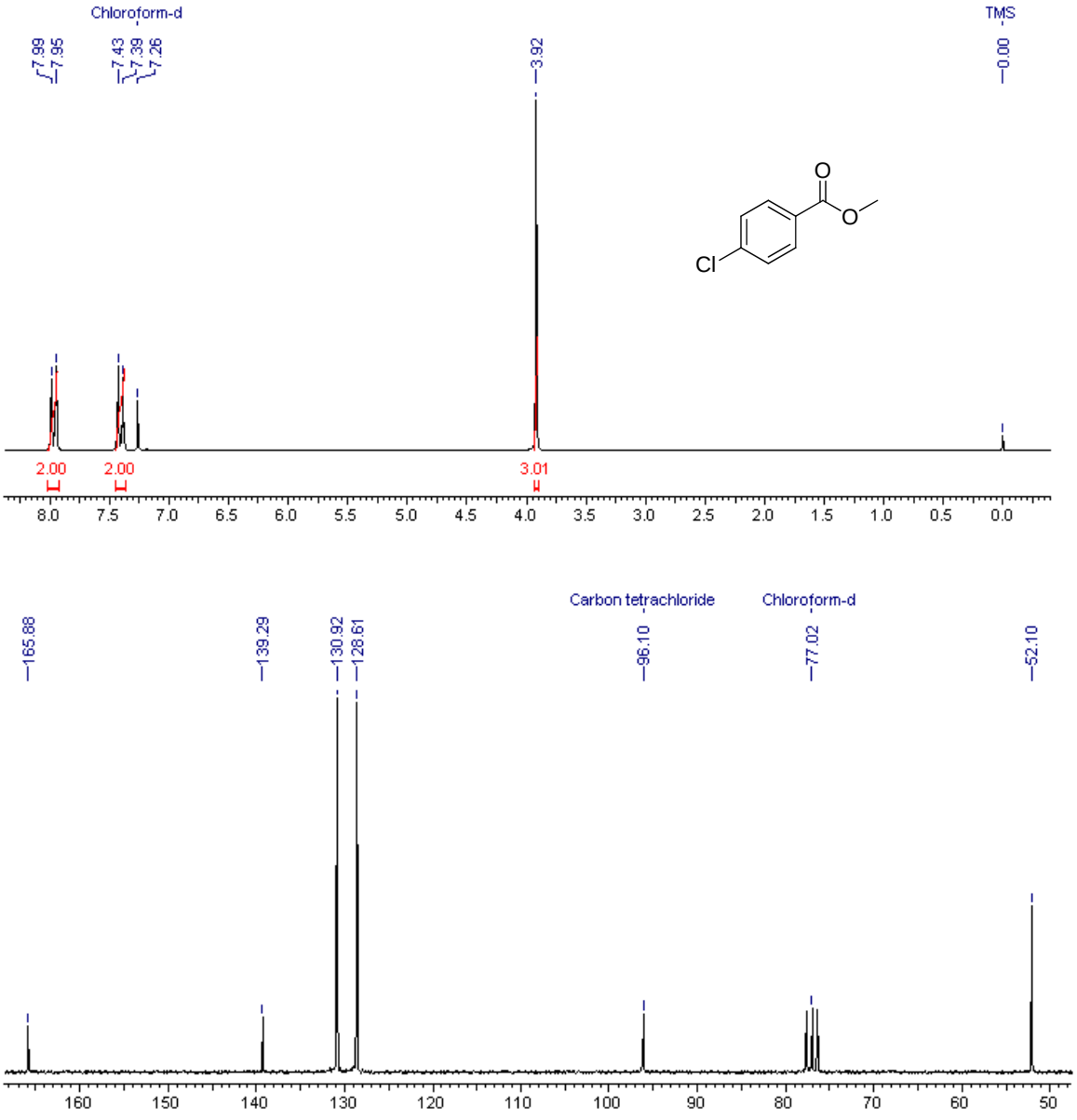


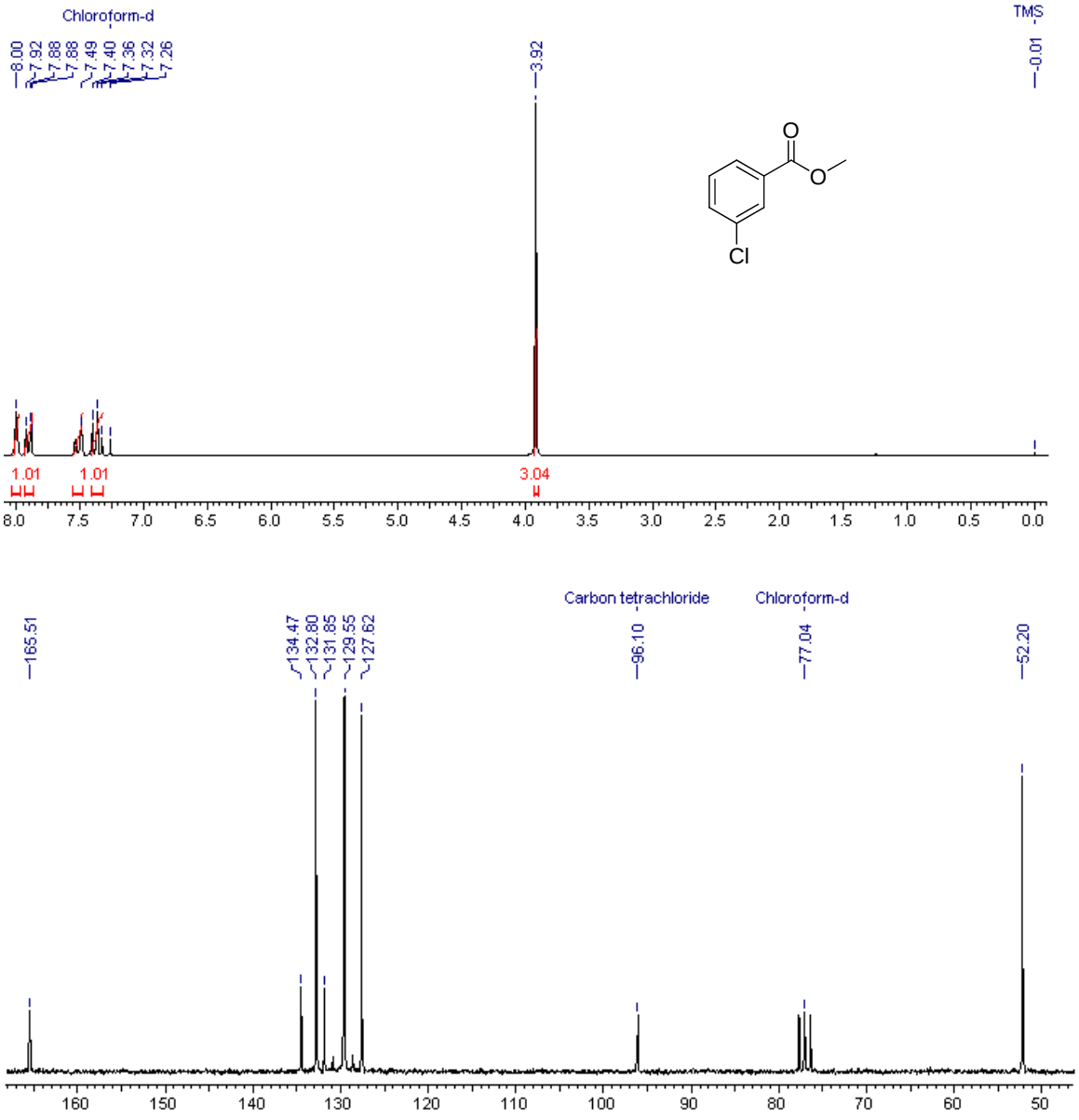
^{1}H and ^{13}C NMR spectra of Methyl 4-bromobenzoate



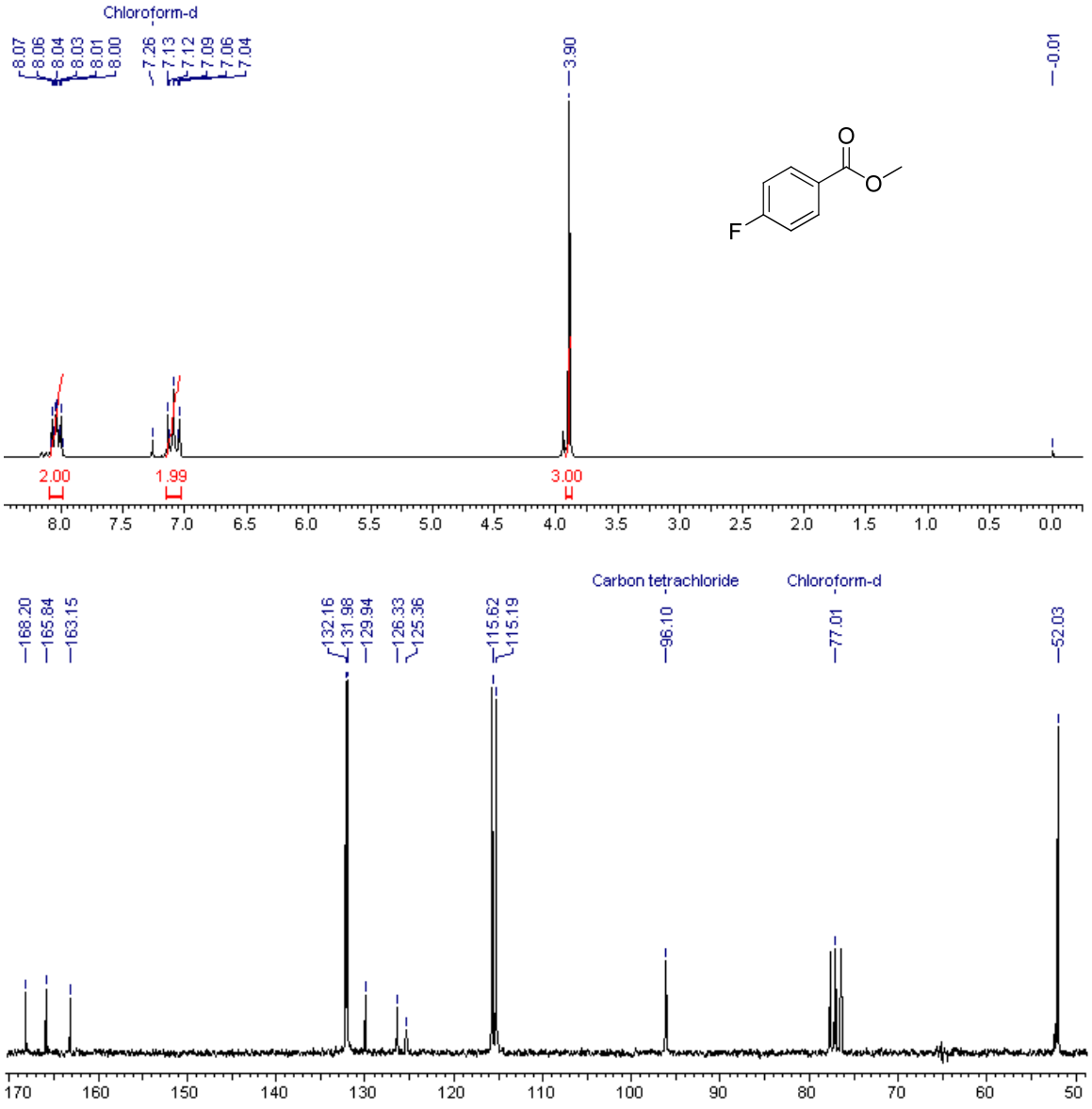
^{1}H and ^{13}C NMR spectra of Methyl 3-bromobenzoate



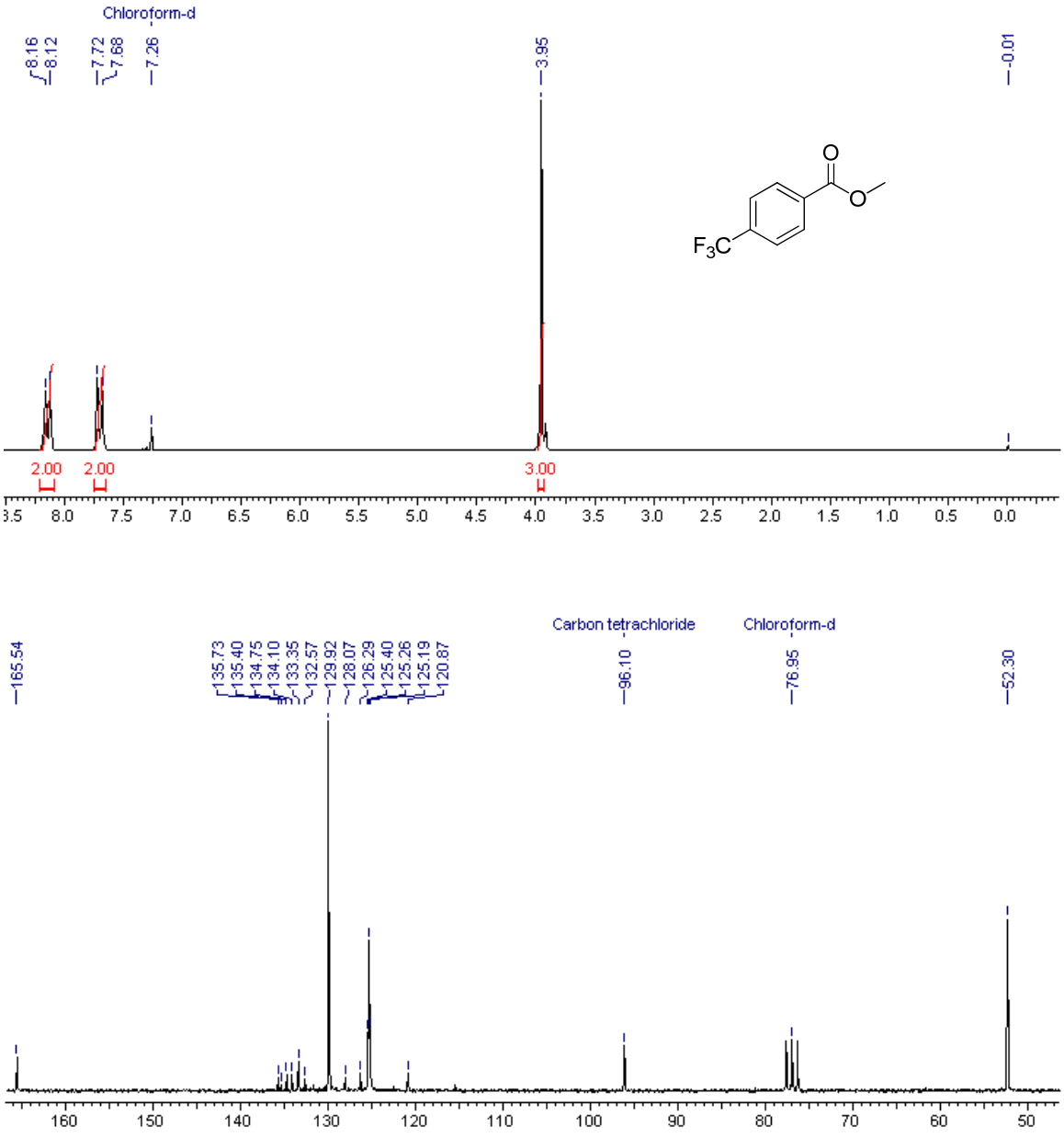
^{1}H and ^{13}C NMR spectra of Methyl 4-chlorobenzoate



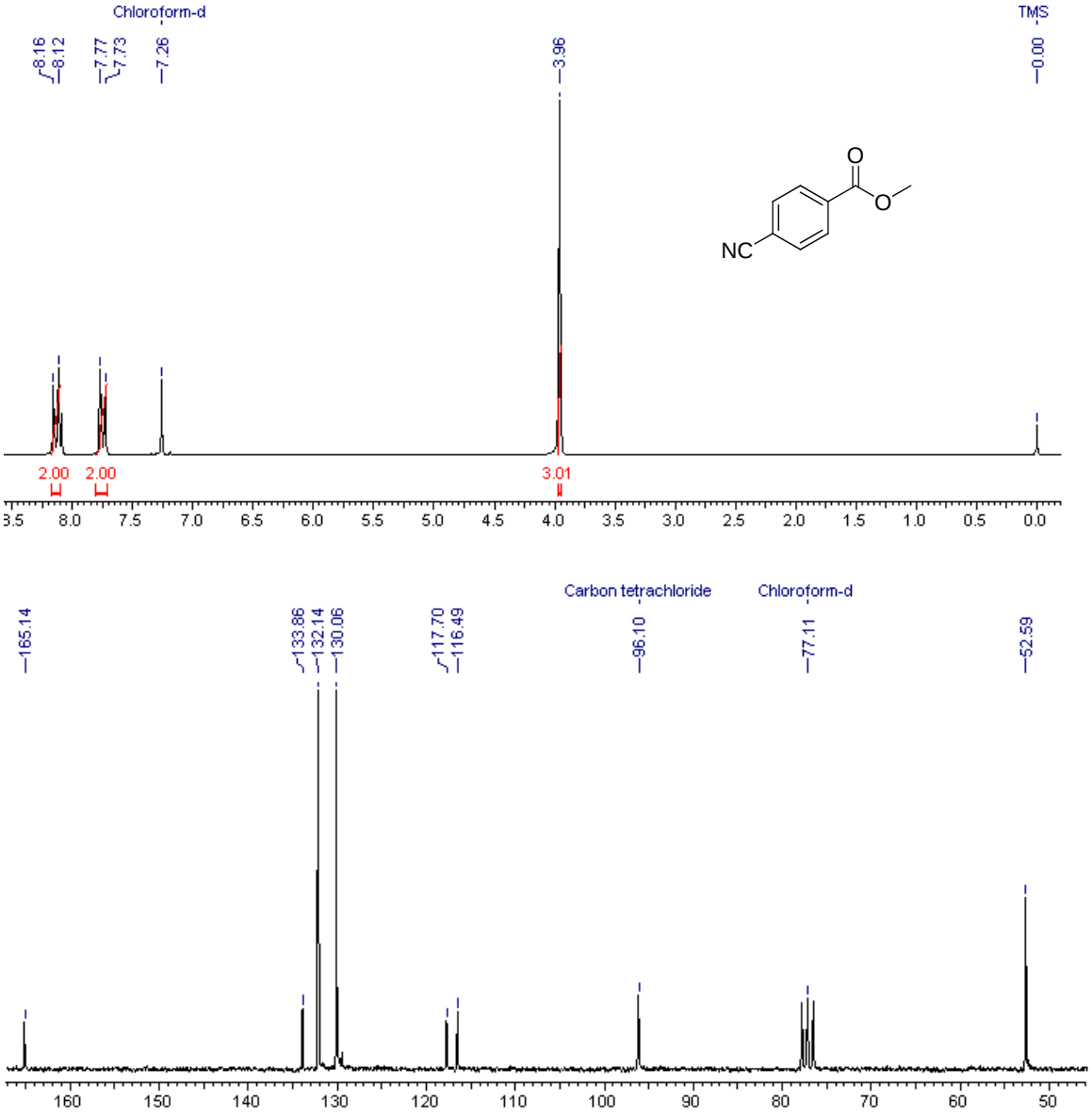
^{1}H and ^{13}C NMR spectra of Methyl 3-chlorobenzoate



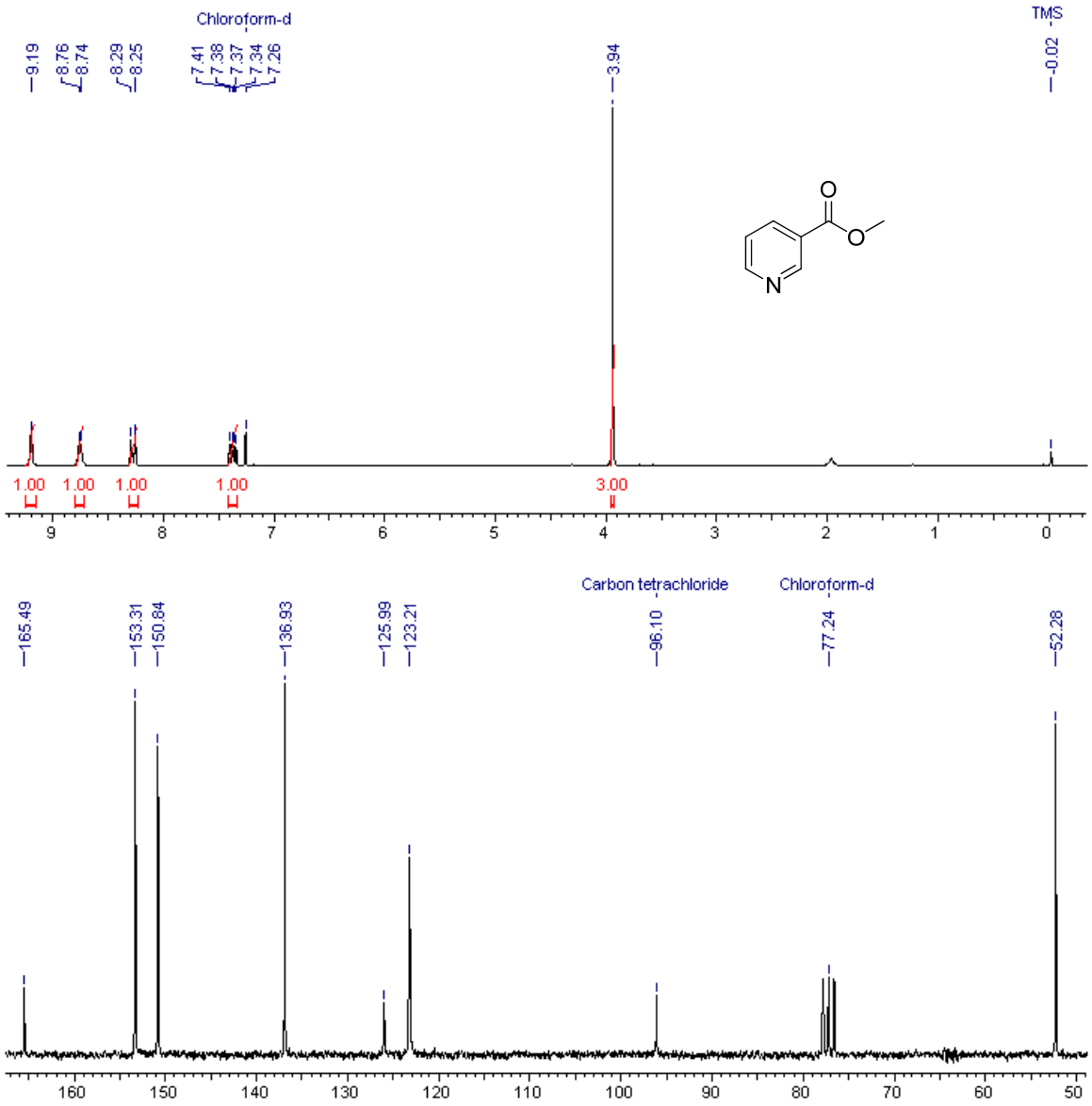
^{1}H and ^{13}C NMR spectra of Methyl 4-flurobenzoate



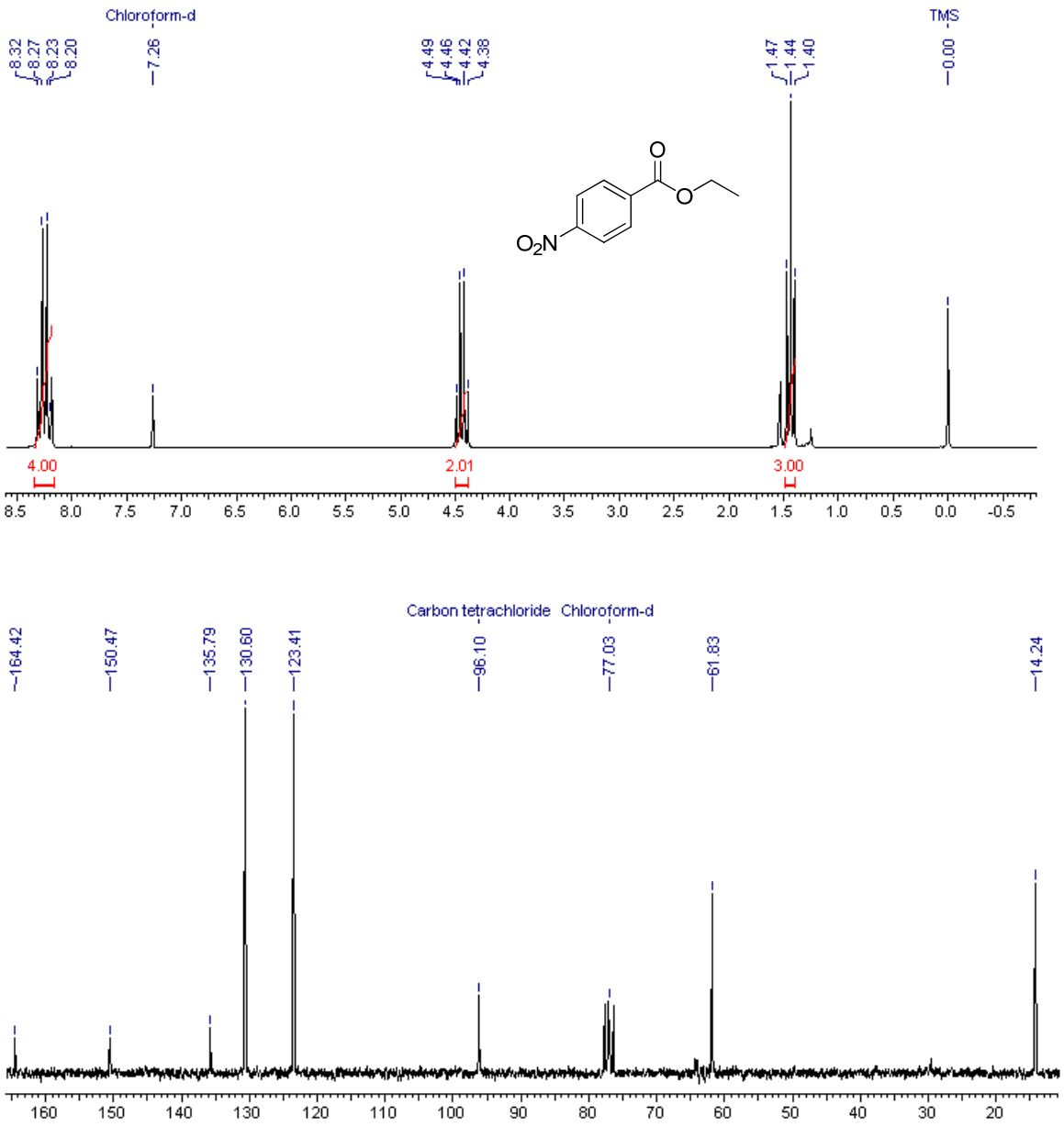
^{1}H and ^{13}C NMR spectra of Methyl 4-(trifluromethyl)benzoate



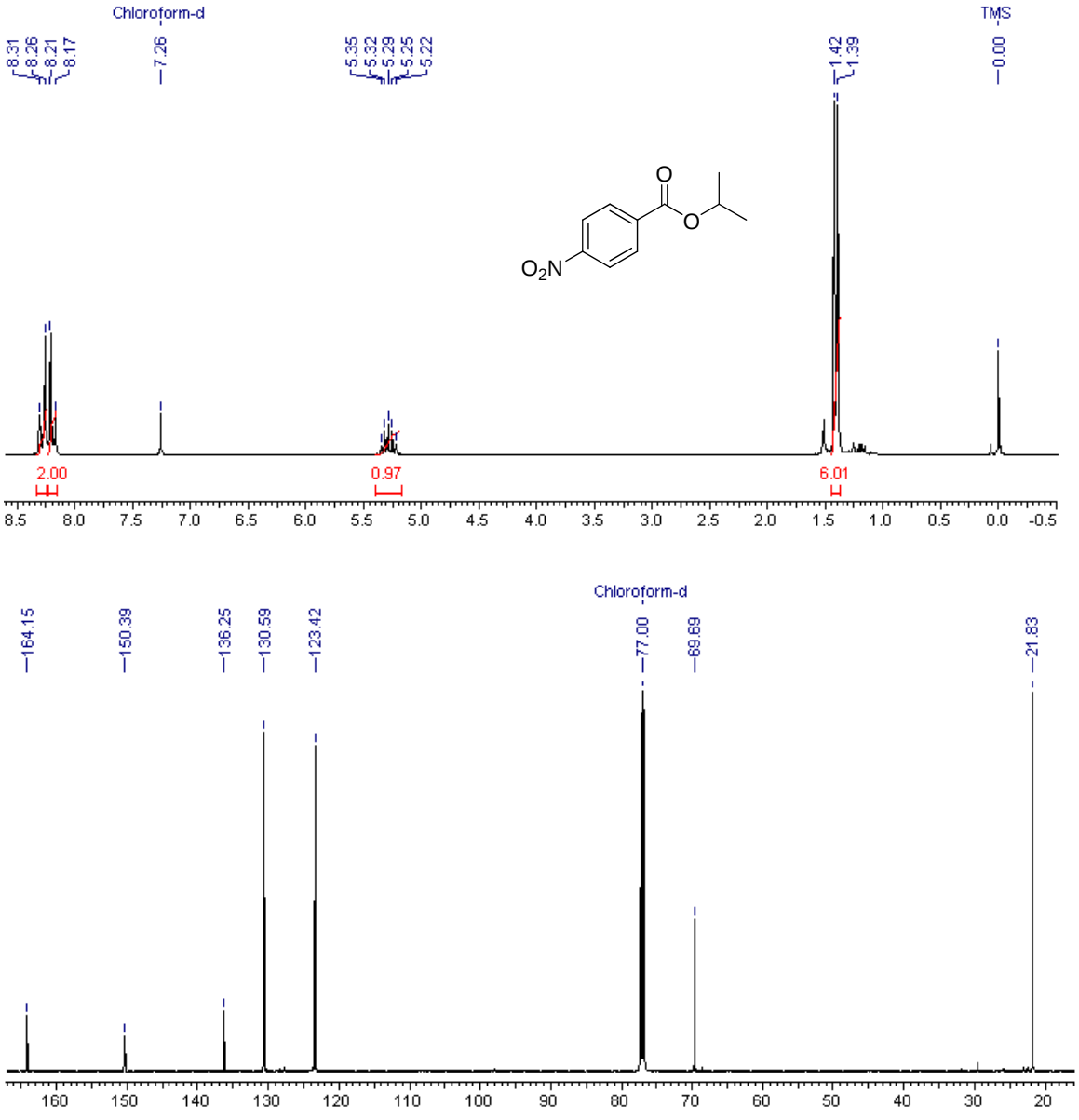
^{1}H and ^{13}C NMR spectra of Methyl 4-cyanobenzoate



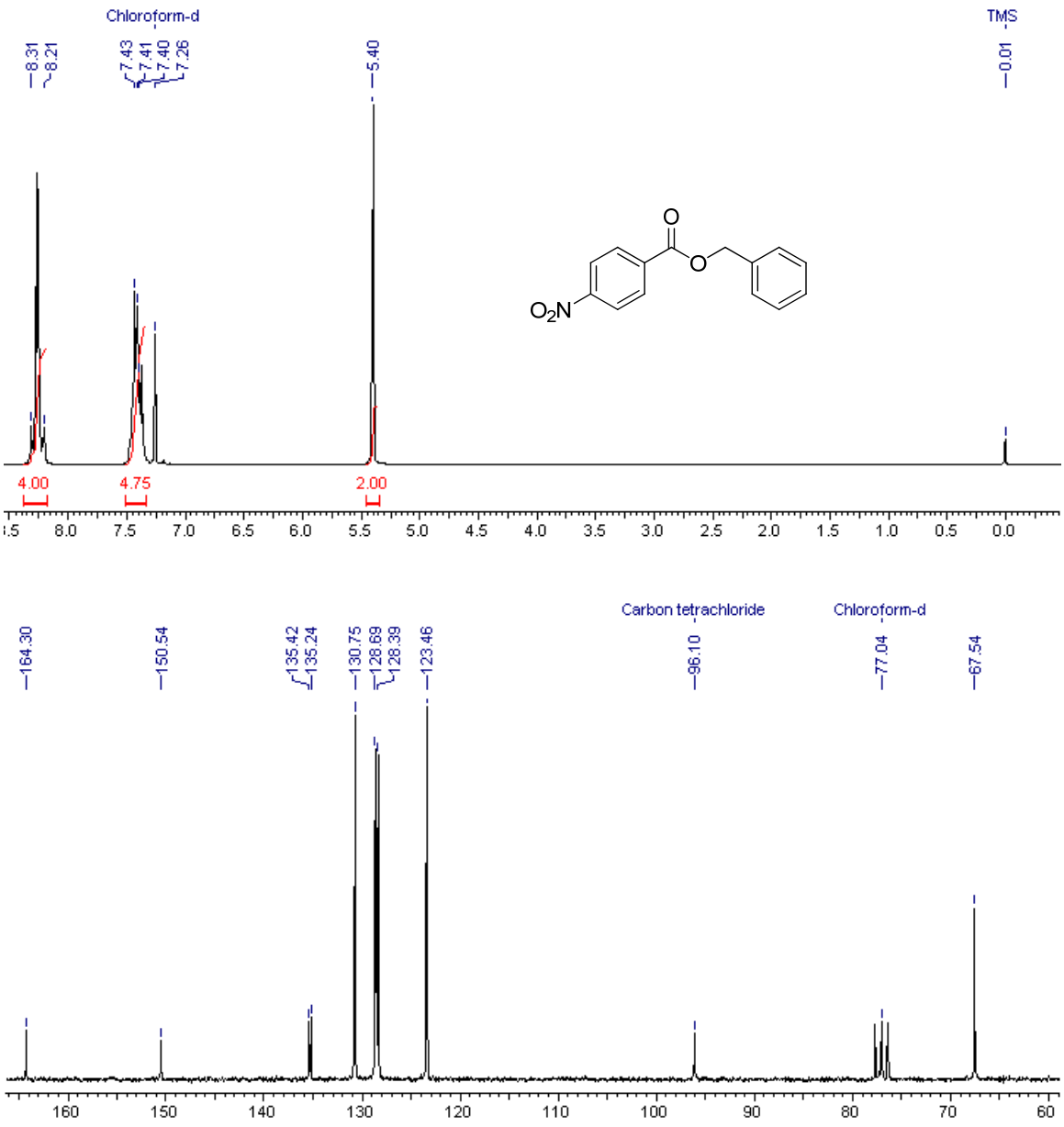
^{1}H and ^{13}C NMR spectra of Methyl Nicotinate



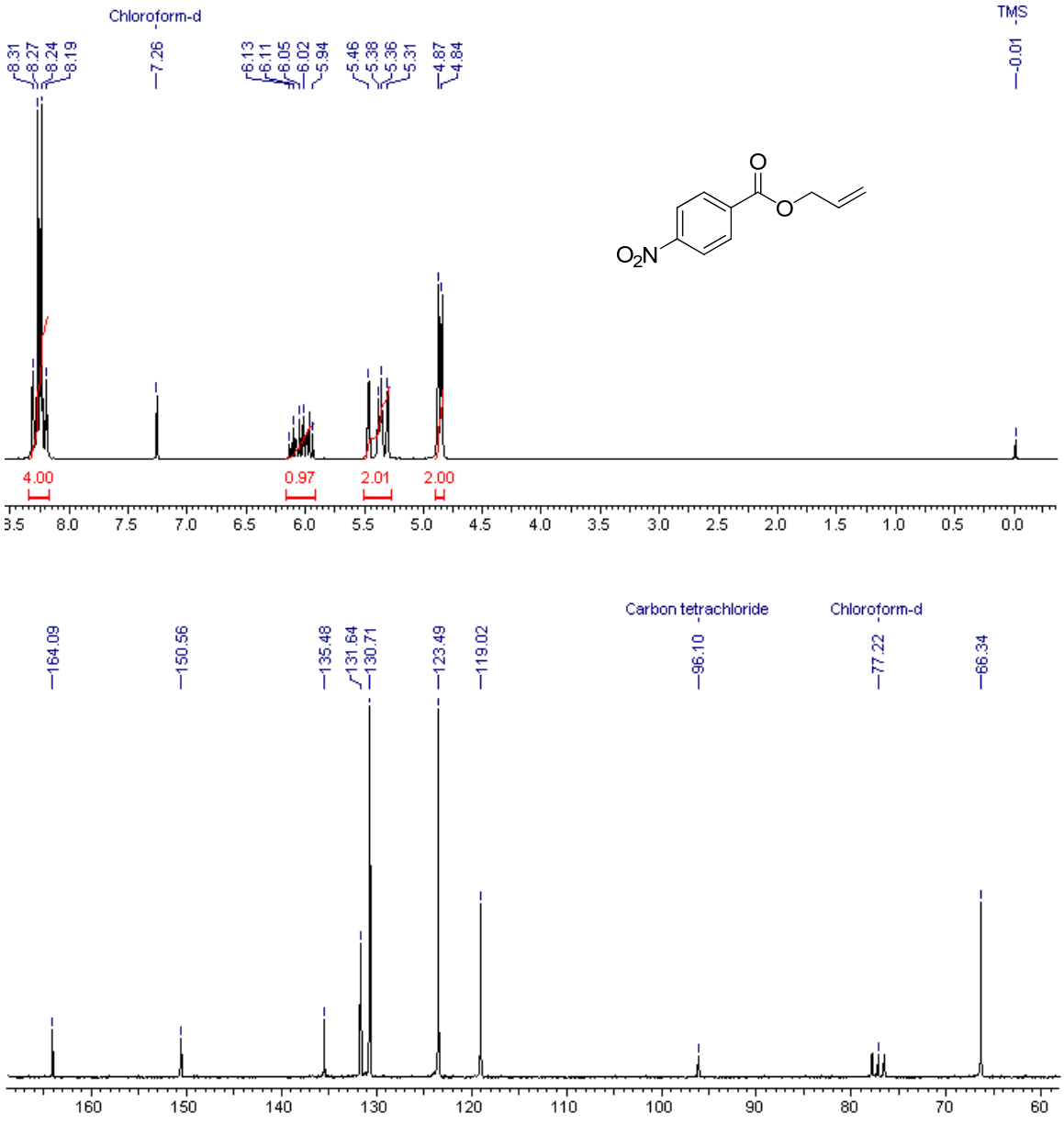
^{1}H and ^{13}C NMR spectra of Ethyl 4-nitrobenzoate



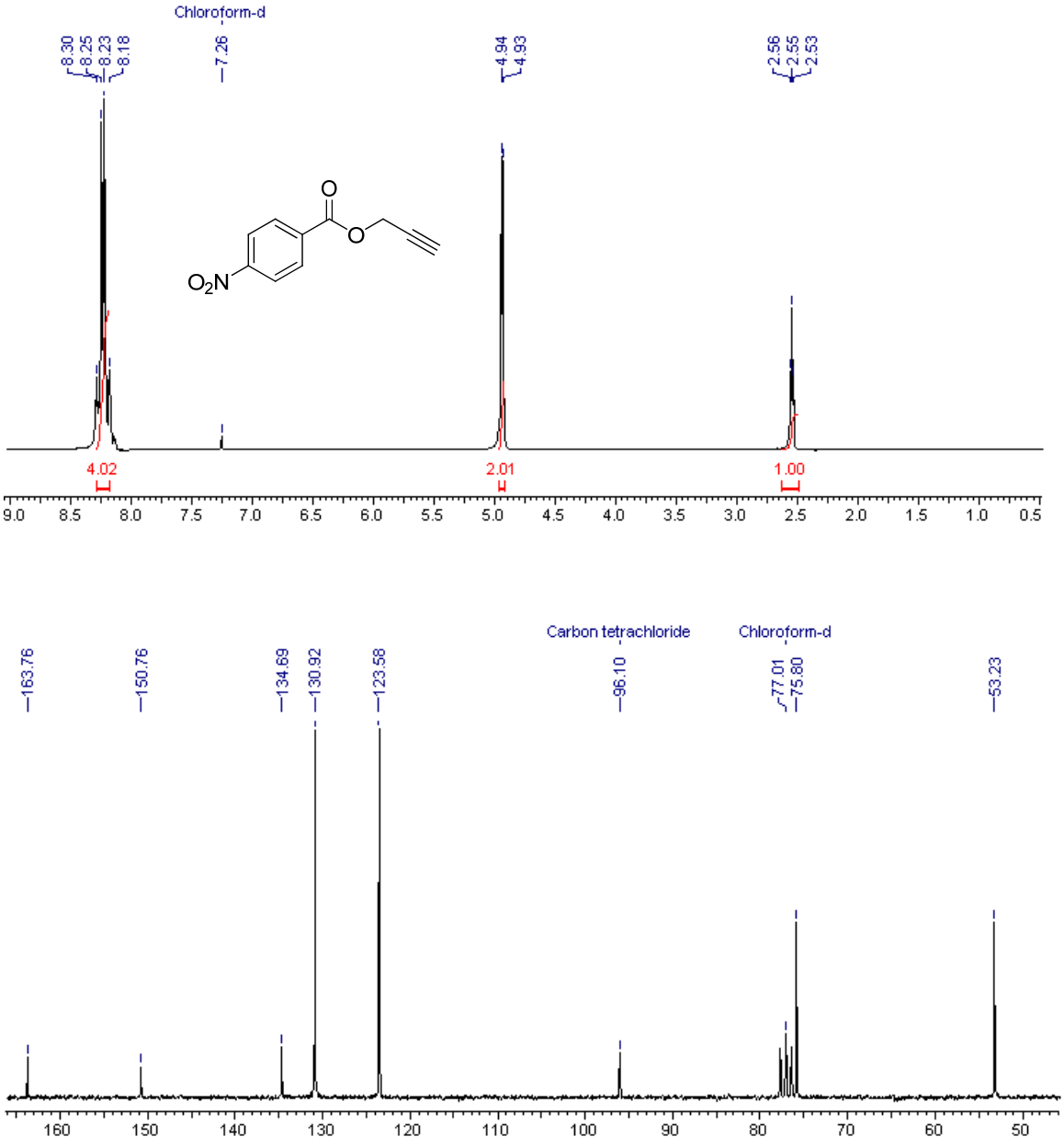
^{1}H and ^{13}C NMR spectra of Isopropyl 4-nitrobenzoate



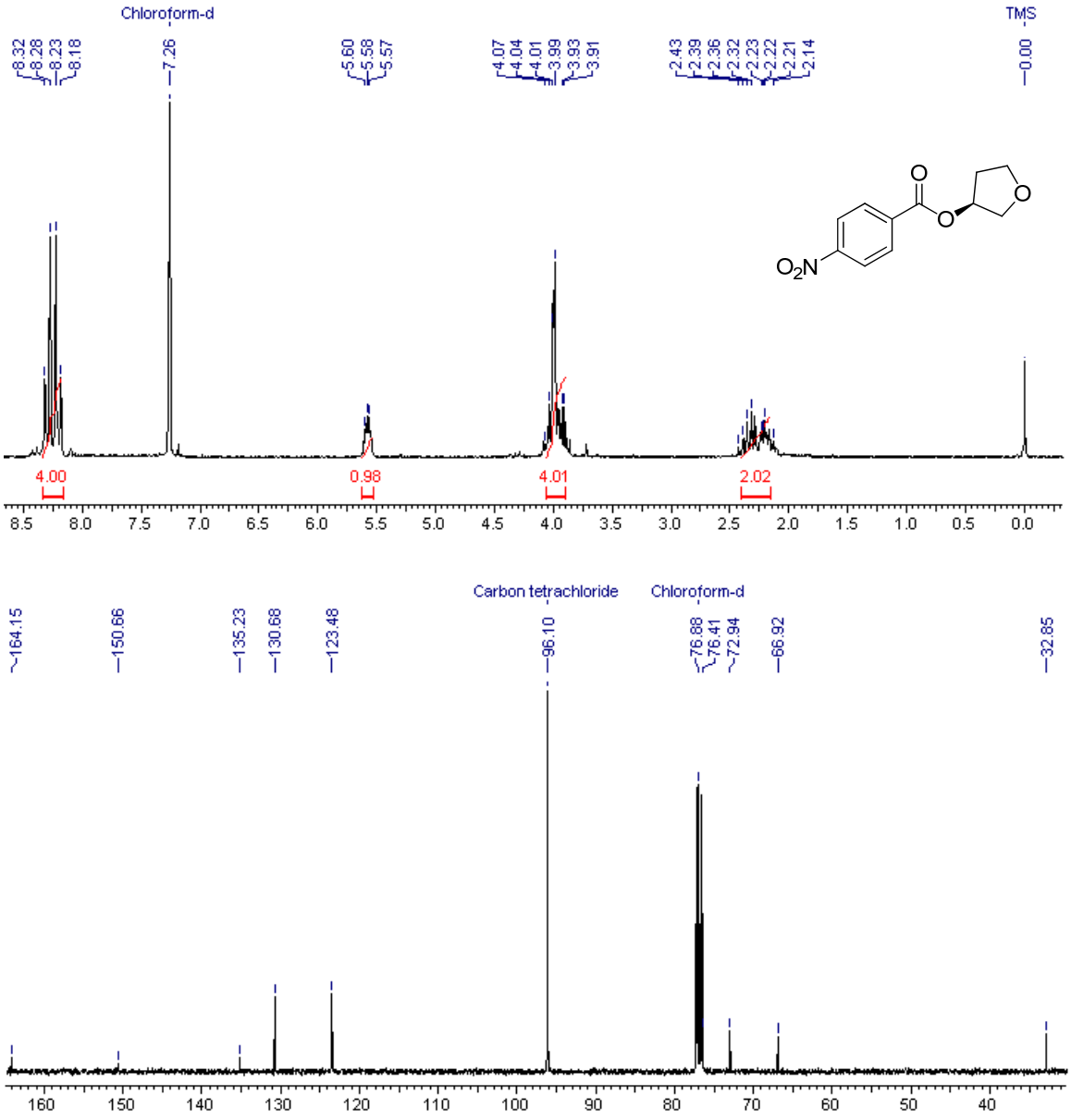
^{1}H and ^{13}C NMR spectra of Benzyl 4-nitrobenzoate



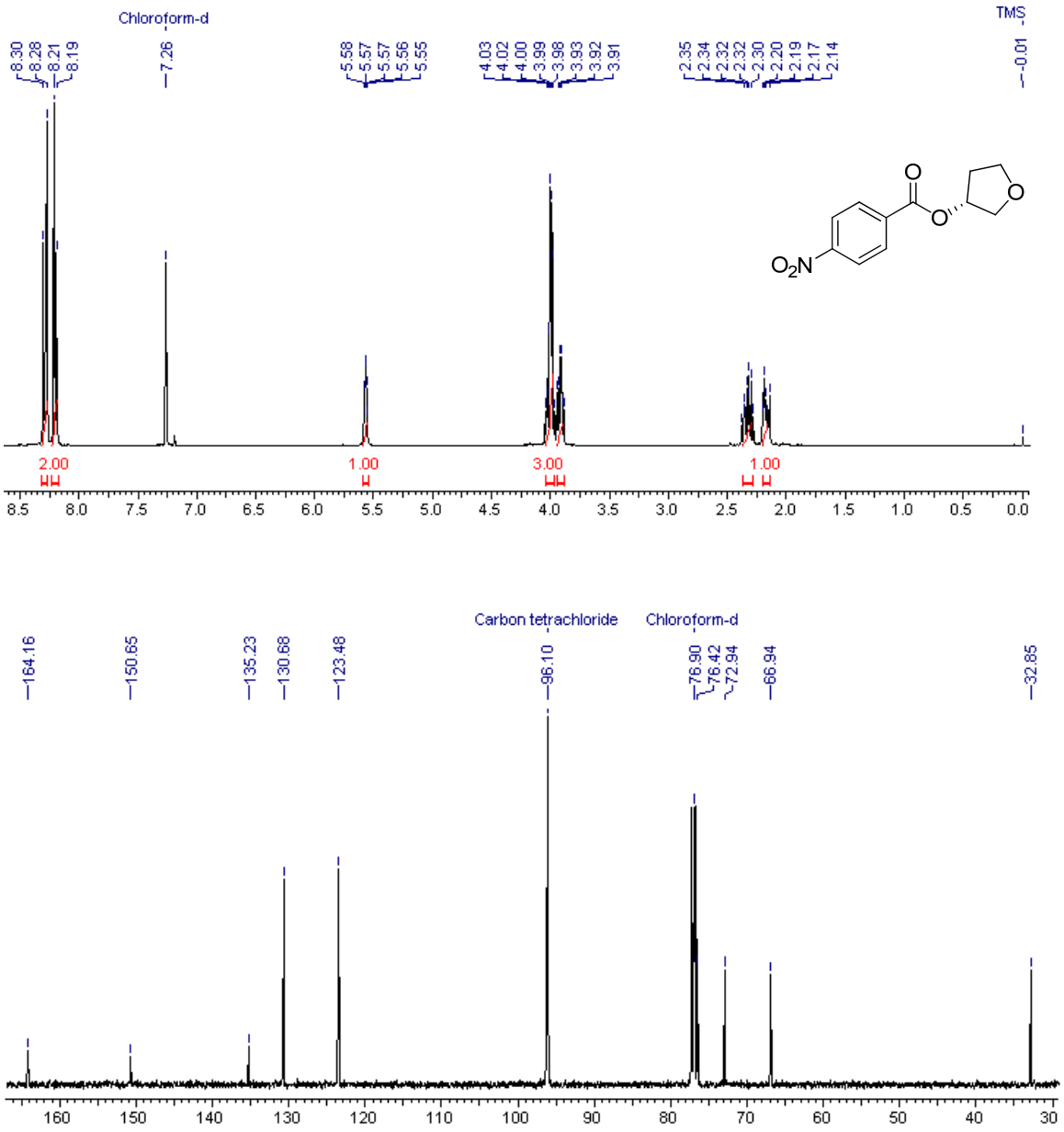
^{1}H and ^{13}C NMR spectra of Allyl 4-nitrobenzoate



^{1}H and ^{13}C NMR spectra of Prop-2-ynyl 4-nitrobenzoate



^{1}H and ^{13}C NMR spectra of (*S*)-tetrahydrofuran-3-yl 4-nitrobenzoate



^{1}H and ^{13}C NMR spectra of (*R*)-tetrahydrofuran-3-yl 4-nitrobenzoate