The Activity and Cyclic Catalysis of Synthesized Iron-Supported Zr/Ti Solid Acid Catalysts in Methyl Benzoate Compounds

Chunjie Shi, Xiaofeng Yu *, Wei Wang, Ai Zhang and Shengjin Liu

Table of contents

Characterization of synthesized compounds

Methyl benzoate(1)[1] Clear liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01(d, *J* = 8.0 Hz, 2H), 7.50(t, *J* = 8.0 Hz, 1H), 7.48(t, *J* = 8.0 Hz, 2H), 3.84(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.69, 132.71, 130.11,129.42, 128.20, 51.73; HRMS(ESI-TOF) *m/z*: calcd for $C_8H_7INaO^{2+}$: 159.0419(M+Na)$^+$, found: 159.0417.

Methyl 2-Methylbenzoate (2)[1] Yellow liquid; ^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.82-7.80(m, 2H), 7.28-7.22(m, 2H), 3.82(s, 3H), 2.31(m, 3H); ^{13}C NMR(100 MHz, $CDCl_3$): δ = 166.80, 137.86, 133.43, 130.01, 129.94, 128.06, 126.56, 51.61, 20.91; HRMS(ESI-TOF) *m/z*: calcd for $C_9H_{10}NaO^{2+}$: 172.1745 (M+Na)$^+$, found: 172.1811.

Methyl 3-Methylbenzoate(3)[1] Clear liquid; ^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.88(dd, *J* = 8.2, 1.6 Hz, 1H), 7.33(td, *J* = 8.2, 1.6 Hz, 1H), 7.29-7.18(m, 2H), 3.81(s, 3H), 2.57(s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$):δ = 167.69, 140.12, 131.84, 131.59, 130.54, 129.45, 125.59, 51.49, 21.59; HRMS(ESI-TOF) *m/z*: calcd for $C_9H_{10}NaO^{2+}$: 172.1745 (M+Na)$^+$, found: 172.1521.

Methyl 4-Methylbenzoate(4)[1,2]White solid; mp 33-35 ℃; ^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.92(d, *J*=8.0Hz, 2H),7.20(d, *J* = 8.0 Hz, 2H), 3.87(s, 3H), 2.37(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.04, 143.46, 129.56, 129.02, 127.43, 51.80, 21.52;HRMS (ESI-TOF) *m/z*: 150.1745 calcd for $C_9H_{10}NaO^{2+}$: 172.1745 (M+Na)$^+$, found: 172.1701.

Methyl 2-chlorobenzoate(5)[3] Clear liquid; ^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.80(dd, *J* = 8.0, 1.0 Hz, 1H), 7.48-7.39(m, 2H), 7.35(td, *J* = 8.0 Hz, 1.2 Hz, 1H), 3.90(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.85, 133.46, 132.48, 131.29, 130.90, 129.92, 126.51, 52.21; HRMS(ESI-TOF) *m/z*: calcd for $C_8H_7ClNaO^{2+}$: 193.0028(M+Na)$^+$, found: 193.0027.

Methyl 3-chlorobenzoate(6)[1,3] Clear liquid; ^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.98(m, 1H), 7.88(m, 1H), 7.49(m, 1H), 7.36(t, *J* = 8.0 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$): δ = 168.17, 134.39, 132.80, 131.79, 129.60, 129.52, 127.60, 52.05; HRMS (ESI-TOF) *m/z*: calcd for $C_8H_7ClNaO^{2+}$:193.0026 (M+Na)$^+$, found: 193.0015.

Methyl 4-chlorobenzoate (7)[1,3] Clear liquid; ^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.92(d, *J* = 8.0 Hz, 2H), 7.20(d, *J* = 8.0 Hz, 2H), 3.87(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.04, 143.46, 129.56, 129.02, 127.44, 51.80; HRMS(ESI-TOF) *m/z*: calcd for $C_8H_7ClNaO^{2+}$: 193.0026 (M+Na)$^+$, found:193.0019.

Methyl 3-bromobenzoate(8)[1,3] White solid; mp 31-33 °C; ^{1}H NMR(400 MHz, $CDCl_3$):

δ =8.15(m, 1H), 7.92(m, 1H), 7.64(m, 1H), 7.29(t, *J*=8.0 Hz,1H), 3.90(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.52, 135.75, 132.48, 131.99, 129.88, 128.07, 122.38, 52.31; HRMS (ESI-TOF) *m/z*: calcd for $C_8H_7BrNaO^{2+}$: 236.9526 $(M+Na)^+$, found: 236.9517.

Methyl 4-bromobenzoate(9)[1,3] White solid; mp 77-80 ℃; ^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.88(m, 2H), 7.56(m, 2H), 3.90(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$):δ = 166.23, 131.66, 131.08, 129.01, 127.99, 52.24; HRMS(ESITOF) *m/z*: calcd for $C_8H_7BrNaO^{2+}$: 236.9526 $(M+Na)^+$, found: 236.9515.

Methyl 2-bromobenzoate(10)[3] Clear liquid; ^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.78(dd, *J* = 7.8, 1.0 Hz, 1H), 7.63(dd, *J* = 7.5, 1.0 Hz, 1H), 7.33-7.27(m, 2H), 3.91(s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$): δ = 166.44, 134.25, 132.55, 132.06, 131.25, 127.14, 121.55, 52.39; HRMS(ESI-TOF) *m/z*: calcd for $C_8H_7BrNaO^{2+}$: 236.9526 $(M+Na)^+$, found: 236.9514.

Methyl 4-fluorobenzoate(11)[1,3] Clear liquid; ^{1}H NMR(400 MHz, $CDCl_3$): δ = 8.03(dd, *J* = 8.4, 5.6 Hz, 2H), 7.08(t, *J* = 8.5 Hz ,2H),3.89(s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$): *δ* = 166.84, 165.76(d, $J_{C\text{-}F}$ = 253 Hz), 131.98(d, $J_{C\text{-}F}$ = 9.0 Hz), 115.36(d, $J_{C\text{-}F}$ = 3.0 Hz), 115.14 (d, $J_{C\text{-}F}$ = 21.9 Hz),51.82.;^{19}F NMR(376 MHz, $CDCl_3$): δ = 106.14; HRMS(ESI-TOF) *m/z*: calcd for $C_8H_7FNaO^{2+}$: 177.0325 $(M+Na)^+$, found:177.0320.

Methyl 2-fluorobenzoate(12)[1,3] Clear liquid ; ^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.92(td, *J* = 7.9, 1.64 Hz,1H), 7.47(m, 1H),7.19(t, *J* = 8.2 Hz,1H), 7.12(dd, *J* = 10.5, 9.0 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR(100 MHz, CDCl3): δ = 164.74(d, $J_{C\text{-}F}$ = 3.8 Hz), 160.54 (d, $J_{C\text{-}F}$ = 260 Hz), 134.47(d, $J_{C\text{-}F}$ = 9.2 Hz), 132.04, 123.86 (d, $J_{C\text{-}F}$ = 4.0 Hz), 118.60 (d, $J_{C\text{-}F}$ = 10 Hz), 116.97 (d, $J_{C\text{-}F}$ = 22.3 Hz), 52.13; ^{19}F NMR(376 MHz, $CDCl_3$): δ = 109.68; HRMS(ESI-TOF) *m/z*: calcd for $C_8H_7FNaO^{2+}$: 177.0321$(M+Na)^+$, found: 177.0324.

Methyl 3-fluorobenzoate(13)[3] Clear liquid; ^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 7.7 Hz, 1H), 7.39(d, *J* = 9.3 Hz, 1H), 7.25-7.23(m, 1H), 7.22(m, 1H), 3.91(s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$): δ =165.81 (d, $J_{C\text{-}F}$ = 3.2 Hz), 163.67 (d, $J_{C\text{-}F}$ = 245.0 Hz), 132.25 (d, $J_{C\text{-}F}$ = 7.2 Hz),129.96 (d, $J_{C\text{-}F}$ = 7.5 Hz), 125.23 (d, $J_{C\text{-}F}$ = 3.0 Hz), 119.72 (d, $J_{C\text{-}F}$ = 21 Hz), 116.40(d, $J_{C\text{-}F}$ = 25 Hz), 52.41; ^{19}F NMR(376 MHz, $CDCl_3$): δ = 112.56; HRMS(ESI-TOF) *m/z*: calcd for $C_8H_7FNaO^{2+}$: 177.0324 $(M+Na)^+$, found: 177.0317.

Methyl 4-nitrobenzoate(14)[2,3] Yellow solid; mp 94-97 ℃**;** ^{1}H NMR(400 MHz, $CDCl_3$): δ = 8.29(d, *J* = 8.0 Hz, 2H), 8.21(d, *J* = 8.5 Hz, 2H), 3.99(s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$): δ = 165.11, 150.48, 135.45, 130.66, 123.49, 52.79; HRMS(ESI-TOF) *m/z*: calcd for $C_8H_7NNaO^{4+}$: 204.0277 $(M+Na)^+$, found: 204.0267.

Methyl 2-nitrobenzoate(15)[2,3] Yellow liquid; ^{1}H NMR(400 MHz, $CDCl_3$):δ = 7.88(dd, *J* = 7.8, 0.9 Hz, 1H), 7.70-7.62(m, 3H), 3.91(s, 3H);^{13}C NMR(100 MHz, $CDCl_3$): δ = 165.52, 148.09, 132.94, 131.96,129.70, 126.97, 123.71, 52.91; HRMS(ESI-TOF) *m/z*: calcd for $C_8H_7NNaO^{4+}$: 204.0268 $(M+Na)^+$, found: 204.0271.

Methyl 3-nitrobenzoate(16)[2,3] Yellow solid; mp 76-80 ℃**;** ^{1}H NMR(400 MHz, $CDCl_3$): δ = 8.86(s, 1H), 8.42(dd, *J* = 8.0, 1.0 Hz, 1H), 8.37(d, *J* = 8.0 Hz, 1H), 7.68(t, *J* = 8.0 Hz, 1H), 4.00(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$):δ = 164.88, 148.20, 135.22, 131.81, 129.66, 127.33, 124.47, 52.75; HRMS(ESI-TOF)*m/z*: calcd for $C_8H_7NNaO^{4+}$: 204.0269 $(M+Na)^+$, found: 204.0257.

Methyl 2-methoxybenzoate(17)[3] Clear liquid; ^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.76(dd, *J* = 8.0, 1.6 Hz, 1H), 7.39(td, *J* = 8.2, 1.3Hz, 1H), 6.94-6.90(m, 2H), 3.82(s, 6H); ^{13}C NMR(100 MHz, $CDCl_3$): δ = 166.25, 158.75, 133.18, 131.19, 119.92, 119.76, 111.79, 55.41, 51.43; HRMS(ESI-TOF) *m/z*: calcd for $C_9H_{10}NaO^{3+}$: 189.0524 $(M+Na)^+$, found: 189.0527.

Methyl 3-methoxybenzoate(18)[1,3] Clear liquid; ^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.60(d, *J* = 7.9 Hz, 1H), 7.53(s, 1H), 7.28(t, *J* = 8.2 Hz, 1H), 7.04(dd, *J* = 7.6, 1.9 Hz, 1H), 3.86 (s, 3H), 3.76(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.52, 159.43, 131.31, 129.16, 121.68, 119.00, 113.93, 54.95, 51.74; HRMS(ESI-TOF) *m/z*: calcd for $C_9H_{10}NaO^{3+}$: 189.0524 $(M+Na)^+$, found:189.0521.

Methyl 4-methoxybenzoate(19)[1-3] White solid; mp 47-51 ºC; ^{1}H NMR(400 MHz, $CDCl_3$): δ = 8.0(d, *J* = 8.2 Hz, 2H), 6.89(d, *J* = 8.2 Hz, 2H), 3.85(s, 3H), 3.81(s, 3H);^{13}C NMR(100 MHz, $CDCl_3$): δ = 166.75, 163.3, 131.52, 122.54, 113.55, 55.30, 51.74; HRMS(ESI-TOF) *m/z*: calcd for $C_9H_{10}NaO^{3+}$:189.0525 $(M+Na)^+$, found: 189.0521.

Methyl 2-iodobenzoate(20)[3] Yellow liquid; ^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.96(d, *J* = 8.0 Hz, 1H), 7.77(dd, *J* = 8.0, 1.0 Hz, 1H), 7.34(t, *J* = 7.6 Hz, 1H), 7.12(td, *J* = 7.8, 1.5 Hz, 1H), 3.90(s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$):δ = 166.73, 141.23, 134.97, 132.68, 130.92, 127.92, 94.16, 52.50; HRMS(ESI-TOF) *m/z*: calcd for $C_8H_7INaO^{2+}$: 284.9385 $(M+Na)^+$, found: 284.9377.

Methyl 4-iodobenzoate(21)[3] White solid; mp 113-116 ºC; ^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.78(d, *J* = 8.0 Hz, 2H), 7.72(d, *J* = 8.0 Hz, 2H), 3.90(s, 3H);^{13}C NMR(100 MHz, CDCl3): δ = 166.46, 137.69, 131.02, 129.57,100.80, 52.30; HRMS(ESI-TOF) *m/z*: calcd for C8H7INaO^{2+}: 284.9386$(M+Na)^+$, found: 284.9378.

Methyl 3-iodobenzoate(22)[3] White solid; mp 112-115 ºC; ^{1}H NMR(400 MHz, $CDCl_3$):

δ = 8.36(m, 1H), 7.87(d, *J* = 7.8 Hz, 1H), 7.85(d, *J* =7.8 Hz, 1H), 7.17(t, *J* = 8.0 Hz, 1H), 3.91(s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$):δ = 165.51, 141.72, 138.44, 131.98, 130.06, 128.73, 93.87, 52.42; HRMS(ESI-TOF) *m/z*: calcd for $C_8H_7INaO^{2+}$: 284.9381 $(M+Na)^+$, found: 284.9371.

Methyl 3-trifluoromethylbenzoate(23)[1,3] Clear liquid; ^{1}H NMR(400 MHz, $CDCl_3$): δ = 8.28(s, 1H), 8.18(d, *J* = 8.0 Hz, 1H), 7.77(d, *J* = 8.0 Hz, 1H), 7.53(t, *J* = 8.0 Hz, 1H), 3.94(s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$): δ = 165.26, 132.50, 131.21 (q, J_{C-F} = 31 Hz), 130.87, 130.55 (q, J_{C-F} = 3.8 Hz), 129.07,128.78 (q, J_{C-F} = 4.0 Hz), 122.22 (q, J_{C-F} = 270.5 Hz), 51.90; ^{19}F NMR(376 MHz, $CDCl_3$): δ = 63.41; HRMS (ESI-TOF) *m/z*: calcd for $C_9H_7F_3NaO^{2+}$: 227.0291 $(M+Na)^+$, found: 227.0286.

Methyl 4-trifluoromethylbenzoate(24)[1,3] Clear liquid; ^{1}H NMR(400 MHz, $CDCl_3$): δ = 8.11(d, *J* = 8.0 Hz, 2H), 7.67(d, *J* = 8.0 Hz, 2H), 3.94(s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$): δ = 165.51, 134.33 (q, J_{C-F} = 32.5 Hz), 133.27, 129.76, 125.18 (q, J_{C-F} = 4.0 Hz), 124.92 (q, J_{C-F} = 272.5 Hz), 52.07; ^{19}F NMR (376 MHz, $CDCl_3$): δ = 63.60; HRMS (ESITOF) *m/z*: calcd for $C_9H_7F_3NaO^{2+}$: 227.0291 $(M+Na)^+$, found: 227.0294.

Methyl 2-trifluoromethylbenzoate(25)[2,3] Clear liquid; ^{1}H NMR(400 MHz, $CDCl_3$): δ=7.78-7.71(m, 2H), 7.59-7.57(m, 2H), 3.92(s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$): δ = 167.11, 131.67, 131.10, 130.99, 128.70 (q, J_{C-F} =31.3 Hz), 126.59 (q, J_{C-F} = 5.3 Hz), 126.43, 124.74, 52.51; ^{19}F NMR(376 MHz, $CDCl_3$): δ = 59.87; HRMS (ESI-TOF) *m/z*: calcd for $C_9H_7F_3NaO^{2+}$: 227.0292 $(M+Na)^+$, found: 227.0284.

Methyl 4-Tert-Butylbenzoate(26)[2,3] Clear liquid; ^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.98(d, *J* = 8.1 Hz, 2H), 7.42(d, *J* = 8.1 Hz, 2H), 3.90(s, 3H), 1.32(s, 9H); ^{13}C NMR(100 MHz, $CDCl_3$) δ = 166.73, 156.26, 129.44, 127.42, 125.19, 51.63, 34.87, 30.97; HRMS(ESI-TOF) *m/z*: calcd for $C_{12}H_{17}O_2$ 193.3 $(M+H)^+$, found 193.1.

Methyl 4-cyanobenzoate(27)[2] White solid; mp 58-61 ºC; ^{1}H NMR(400 MHz, $CDCl_3$): δ = 8.34-8.26(m, 2H), 7.84(dt, *J*= 8.0, 1.0 Hz, 1H), 7.60(dt, *J* = 8.0, 1.2 Hz, 1H), 3.97(s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$): δ = 165.04, 135.97, 133.63, 133.21, 131.39, 129.47, 117.85, 112.91,52.69; HRMS(ESITOF) *m/z*: calcd for $C_9H_7NNaO^{2+}$: 184.0366 $(M+Na)^+$, found: 184.0368.

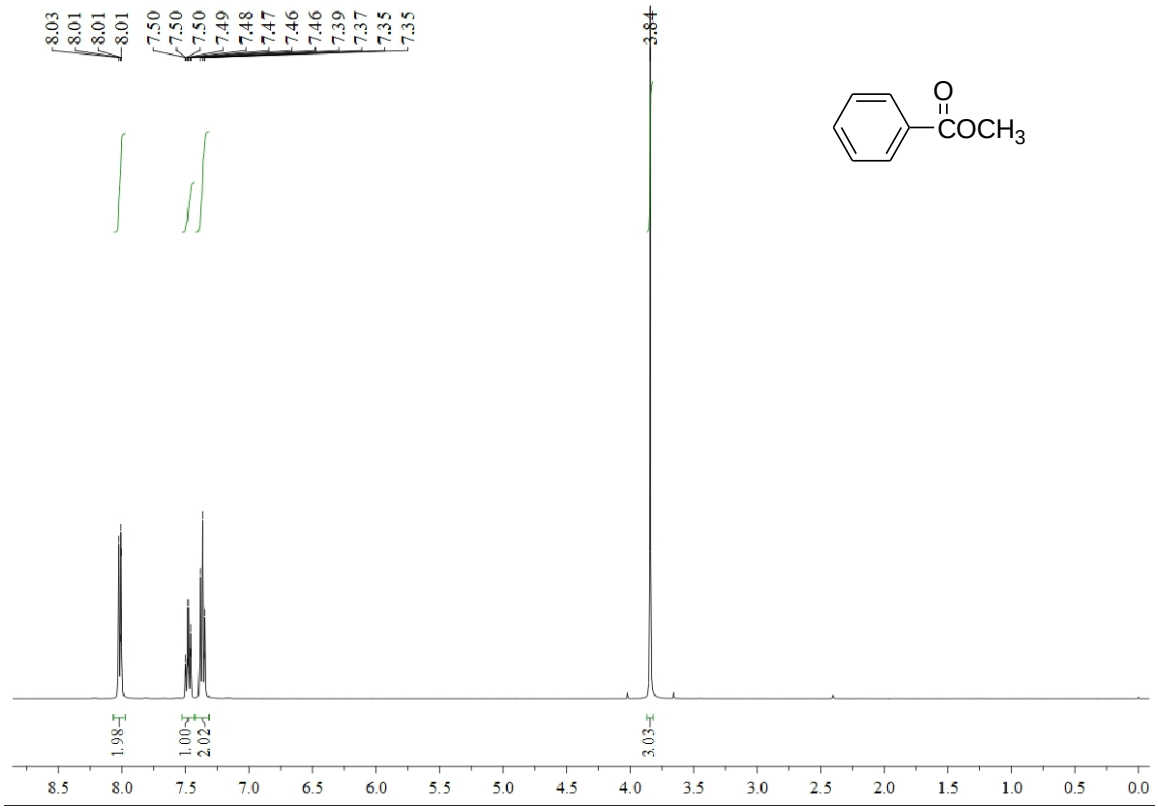
o-Dimethyl phthalate(28)[3] Clear liquid; ^{1}H NMR(400 MHz, $CDCl_3$):δ = 7.69(dd, *J* = 6.5, 4.0 Hz, 2H), 7.50(dd, *J* = 6.5, 4.0 Hz, 2H), 3.88(s, 6H); ^{13}C NMR(100 MHz, $CDCl_3$): δ = 167.70, 131.80, 130.97, 128.64, 52.29; HRMS(ESI-TOF)*m/z*: calcd for $C_{10}H_{10}NaO^{4+}$: 217.0472 $(M+Na)^+$, found: 217.0476.

p-Dimethyl terephthalate(29)[3] White solid; mp 141-143 ºC; ^{1}H NMR(400 MHz, $CDCl_3$): δ = 8.09(s, 4H), 3.94(s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.09, 133.81, 129.44, 52.30; HRMS (ESI-TOF) *m/z*: calcd for $C_{10}H_{10}NaO^{4+}$: 217.0472 $(M+Na)^+$, found: 217.0468.

m-Dimethyl terephthalate(30)[3] White solid; mp 65-68 °C; ^{1}H NMR(400 MHz, $CDCl_3$): δ = 8.68 (s, 1H), 8.21(d, *J* = 8.5 Hz, 2H), 7.53(t, *J* = 8.5 Hz, 1H), 3.95(s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.04, 133.66, 130.58, 128.53, 52.23; HRMS(ESI-TOF)*m/z*: calcd for $C_{10}H_{10}NaO^{4+}$: 217.0472 $(M+Na)^{+}$, found: 217.0488.

Methyl 3,4,5-trimethoxybenzoate(31)[2] White solid; mp 81-83 °C; ^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.30(s,2H),3.91(s,12H);^{13}C NMR(100 MHz,$CDCl_3$): δ = 166.50, 152.82,142.05, 125.04, 106.67, 60.72, 56.07, 52.05; HRMS (ESI-TOF)*m/z*: calcd for $C_{11}H_{15}O_5$ 227.3 $(M+H)^{+}$, found 227.1.

Copy of ^{1}H, ^{13}C NMR and ^{19}F NMR Spectra for desired products:



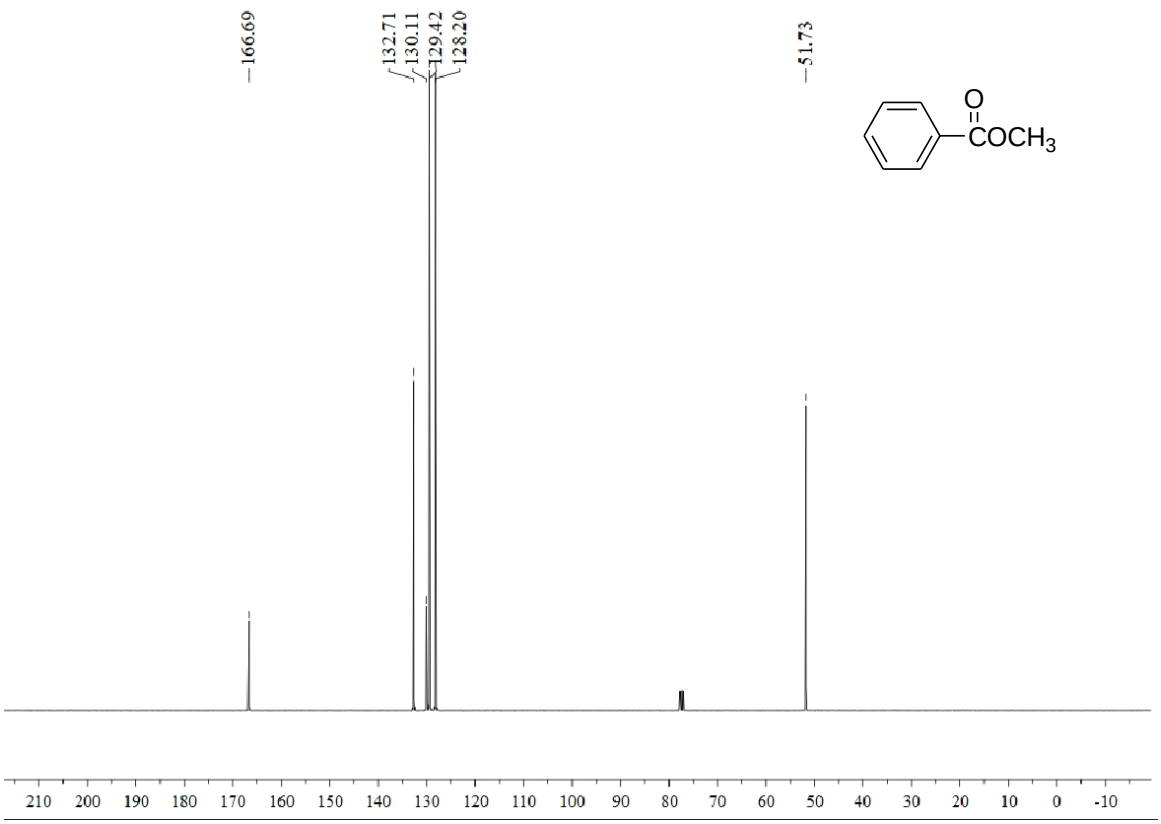
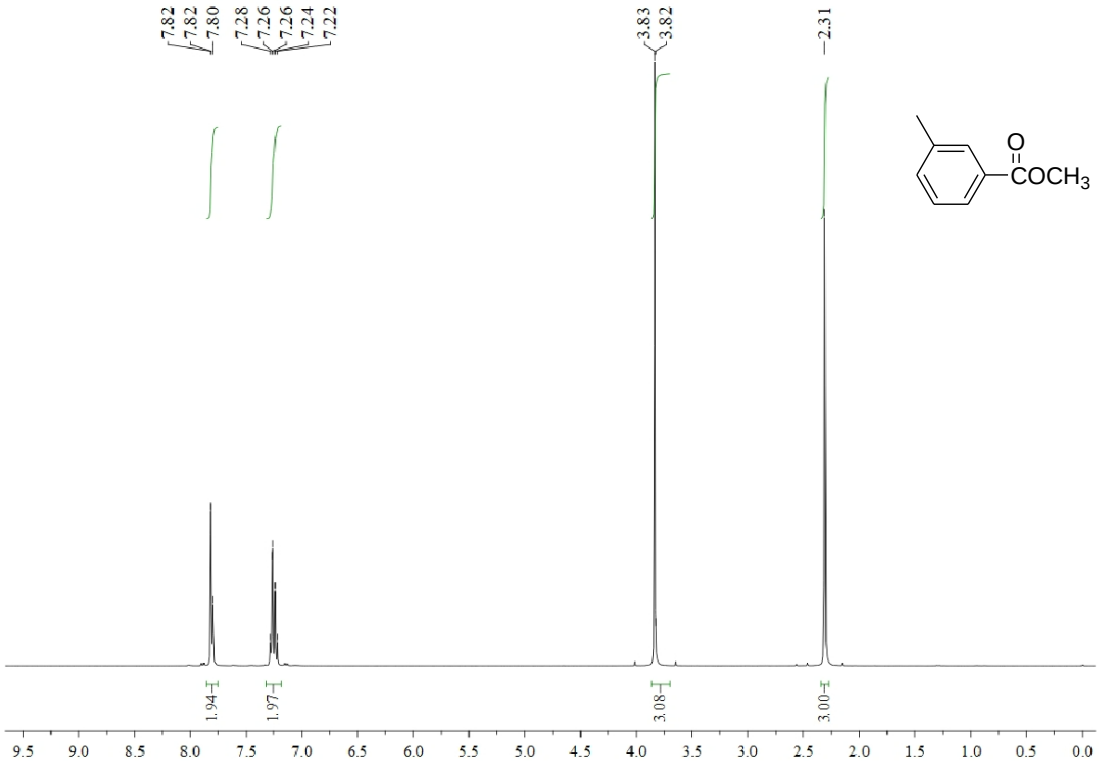


Figure S1 ^{1}H and ^{13}C NMR of Methyl benzoate



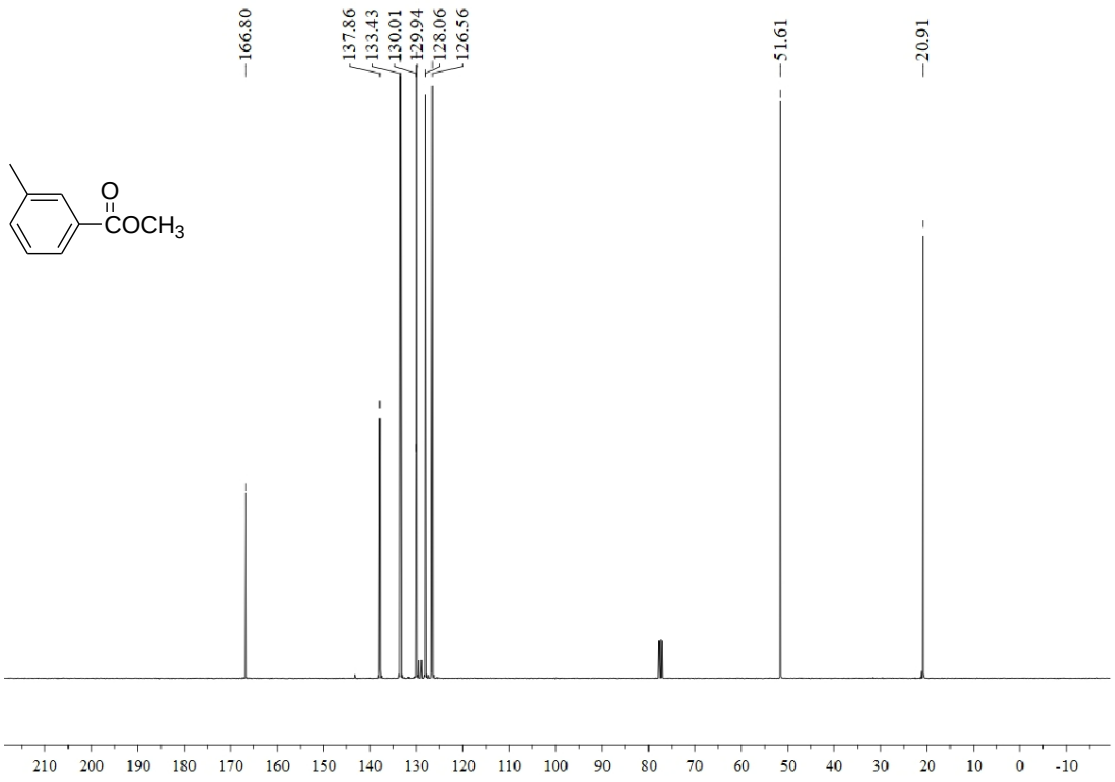
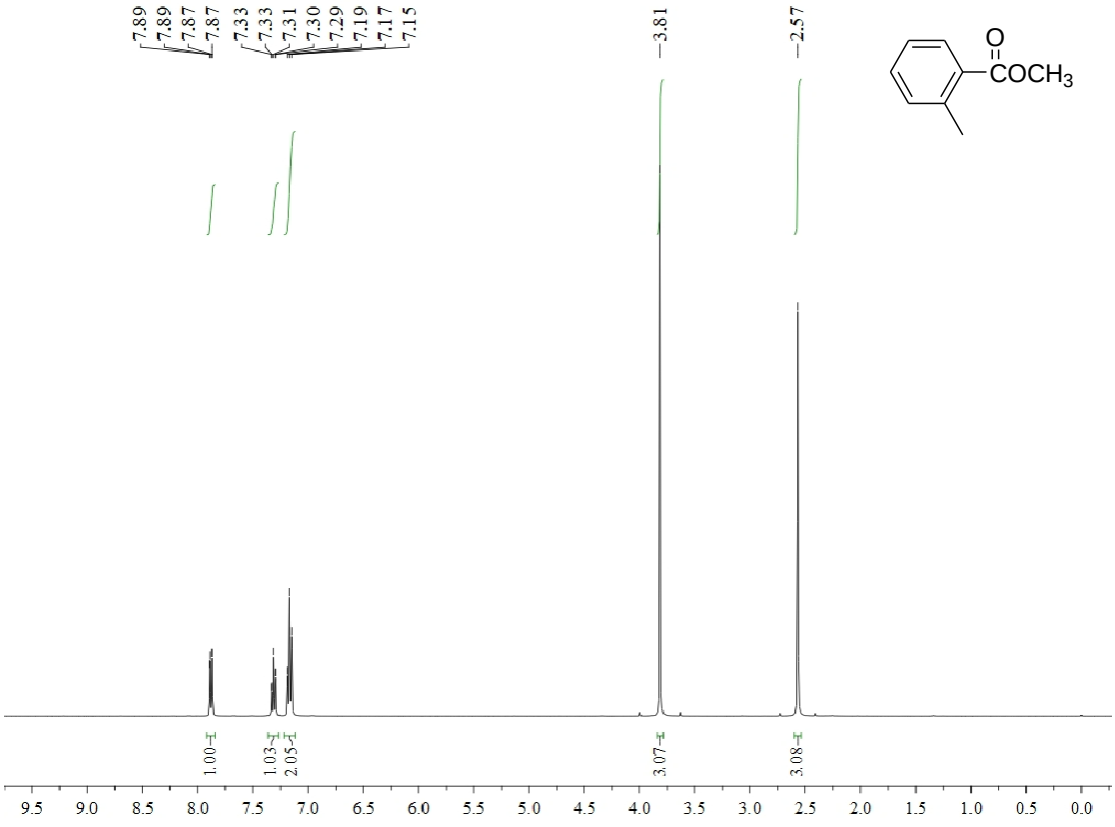


Figure S2 ^{1}H and ^{13}C NMR of Methyl 2-Methylbenzoate



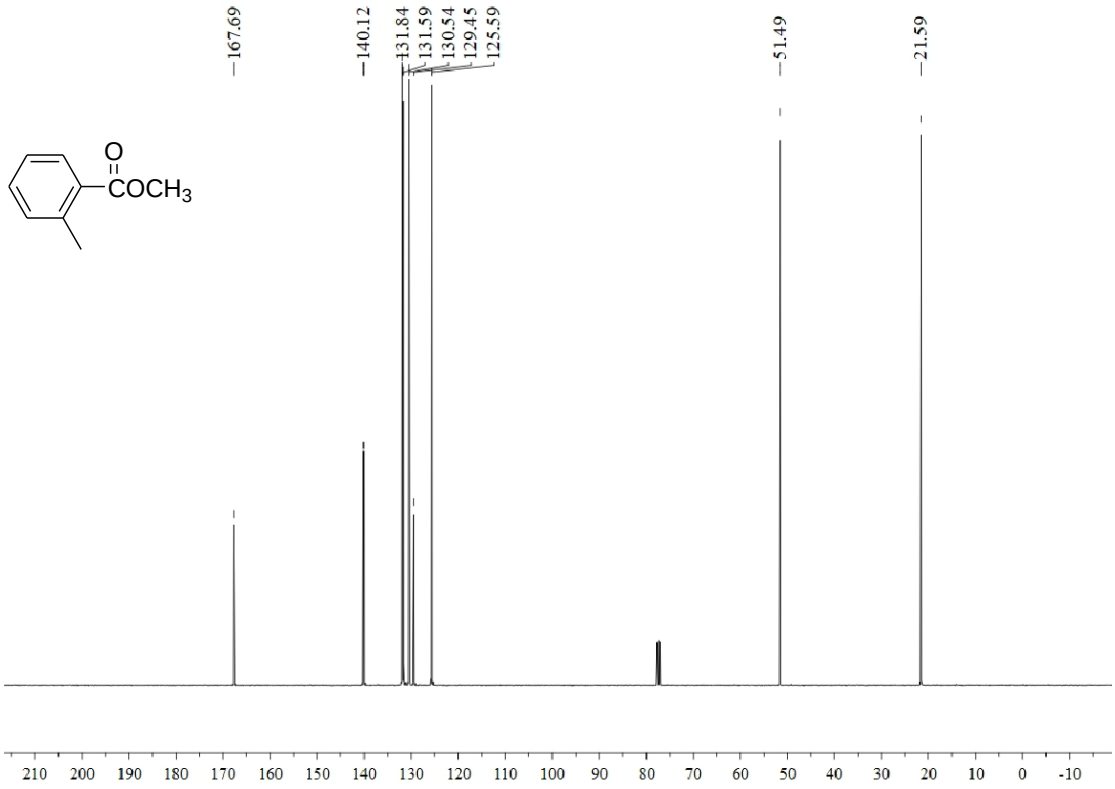
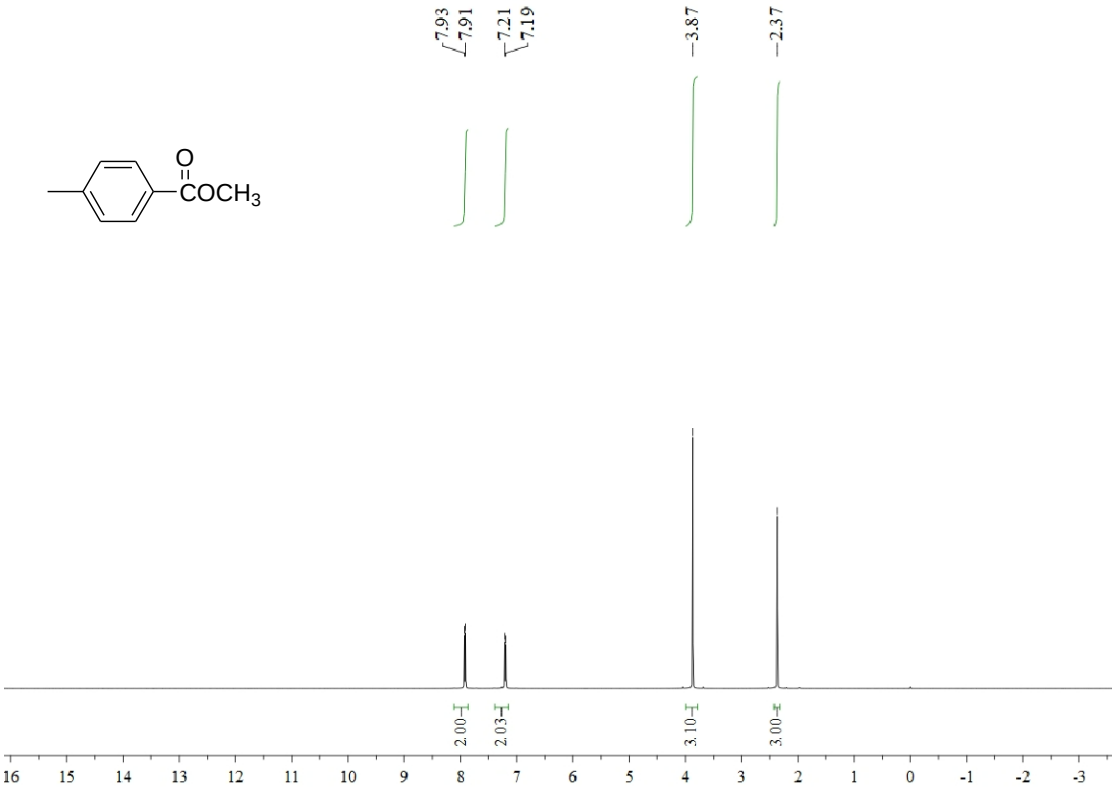


Figure S3 ^{1}H and ^{13}C NMR of Methyl 3-Methylbenzoate



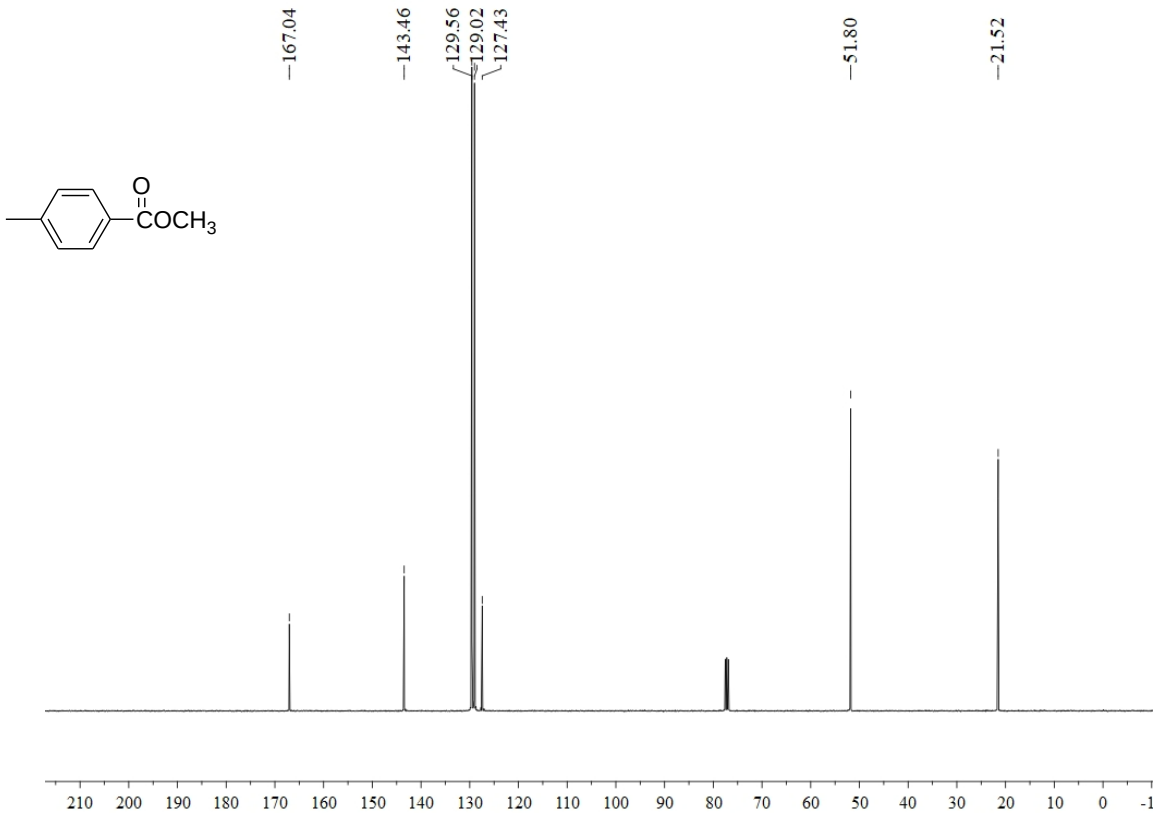
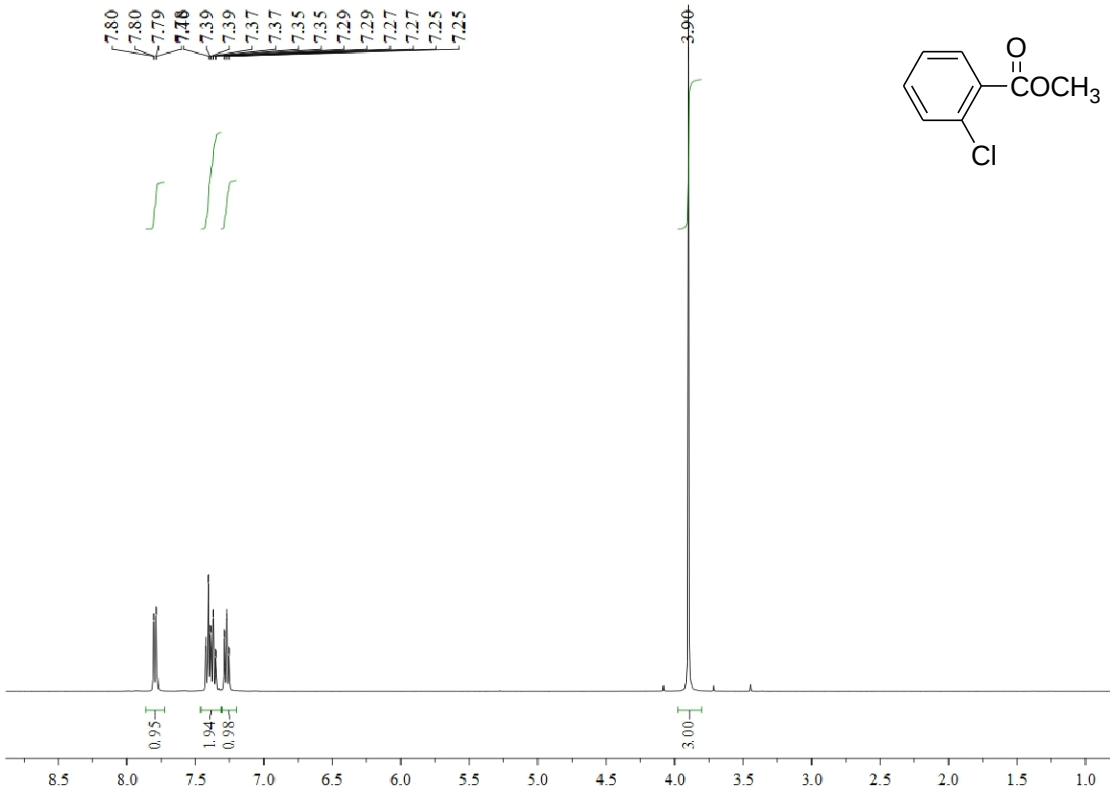


Figure S4 ^{1}H and ^{13}C NMR of Methyl 4-methylbenzoate



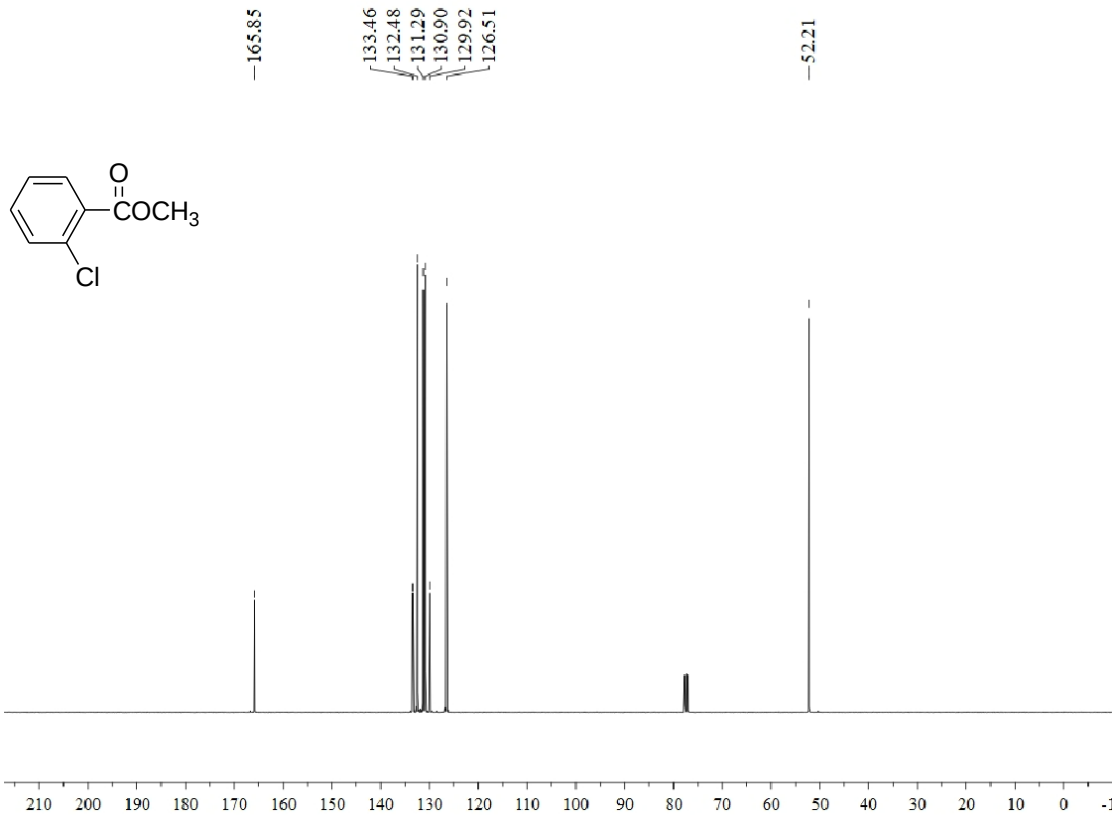


Figure S5 ^{1}H and ^{13}C NMR of Methyl 2-chlorobenzoate

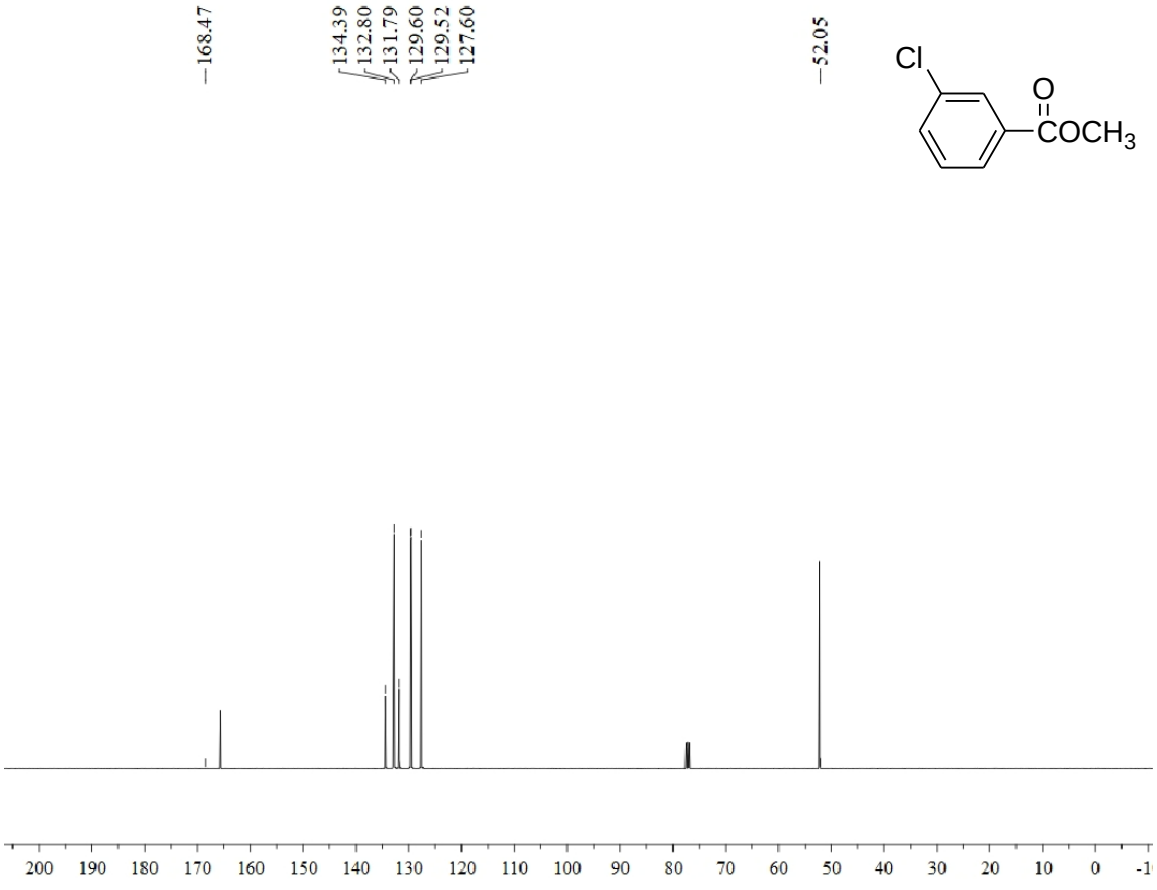
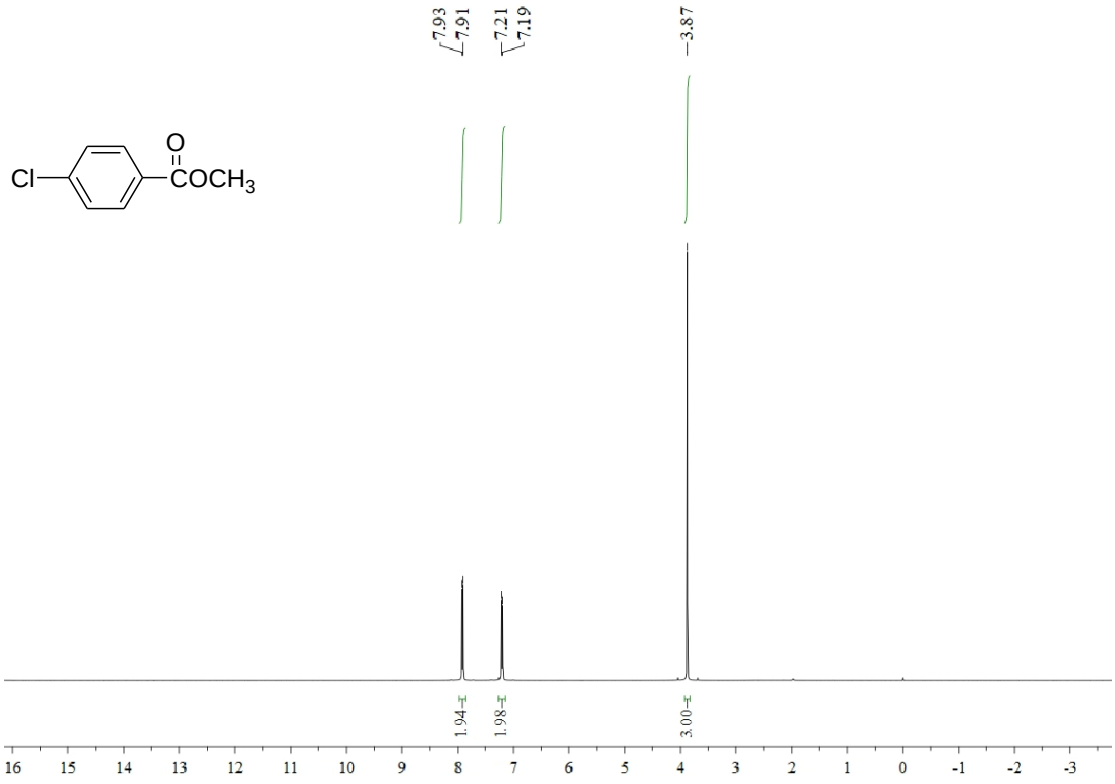


Figure S6 ^{1}H and ^{13}C NMR of Methyl 3-chlorobenzoate



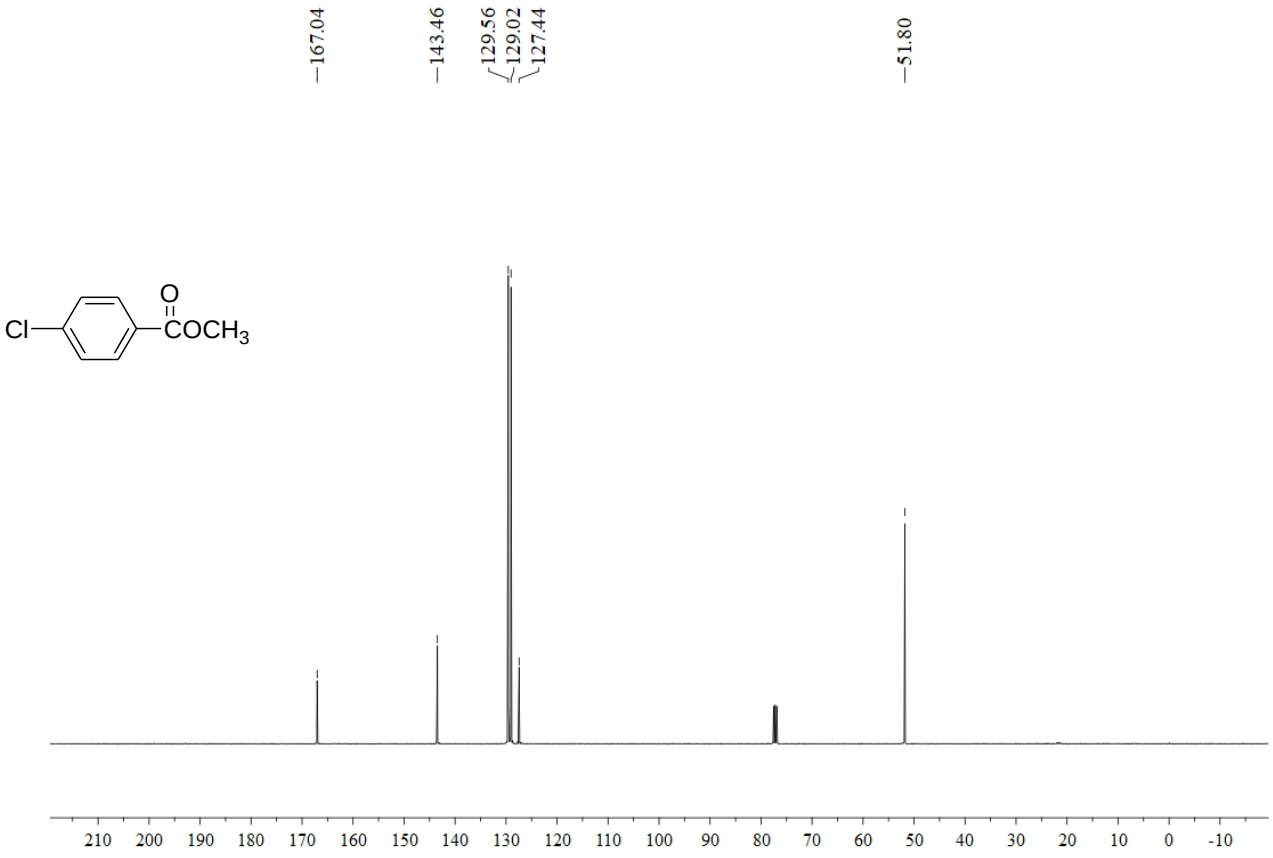
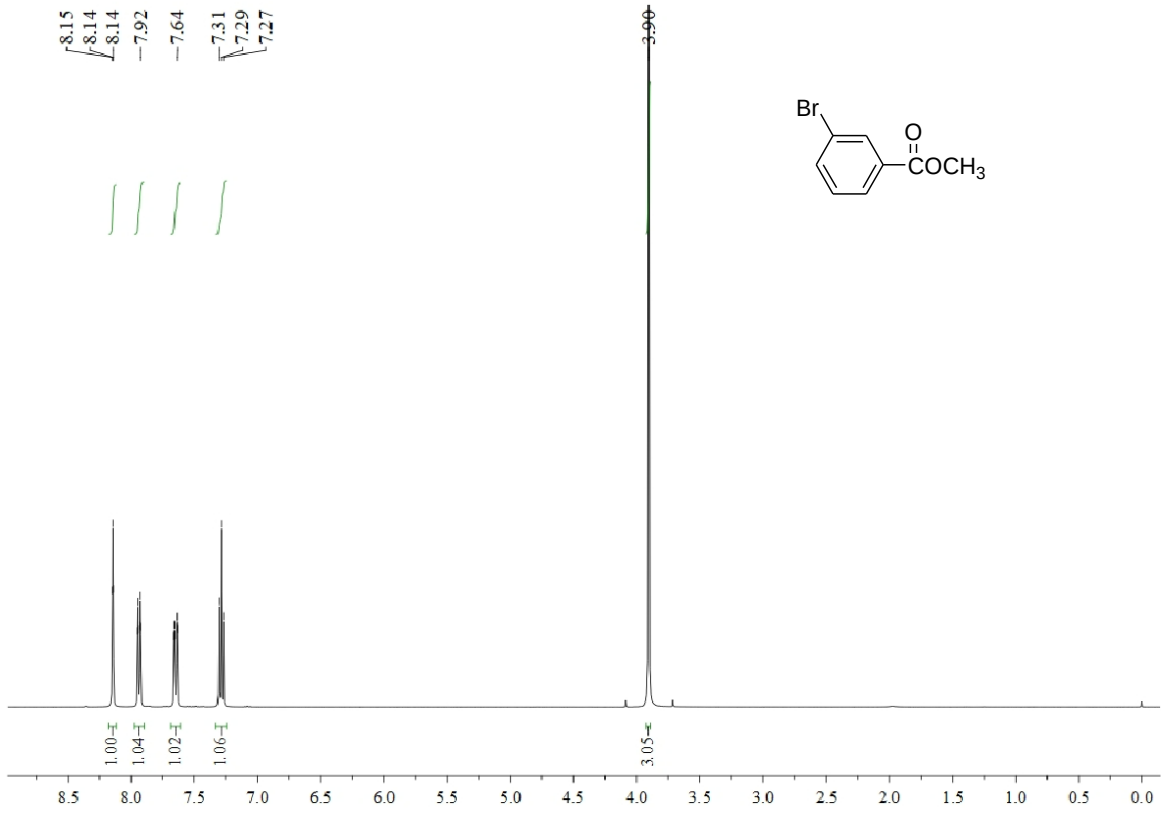


Figure S7 ^{1}H and ^{13}C NMR of Methyl 4-chlorobenzoate



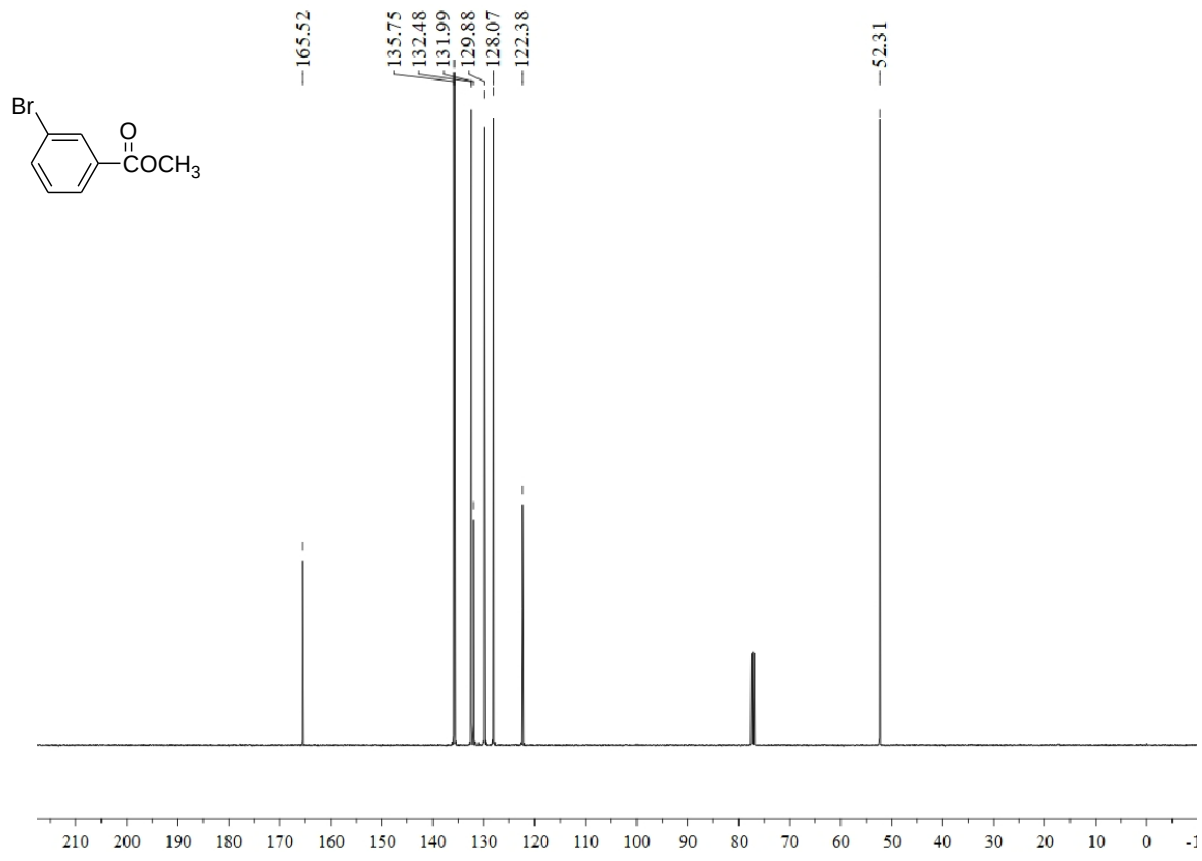
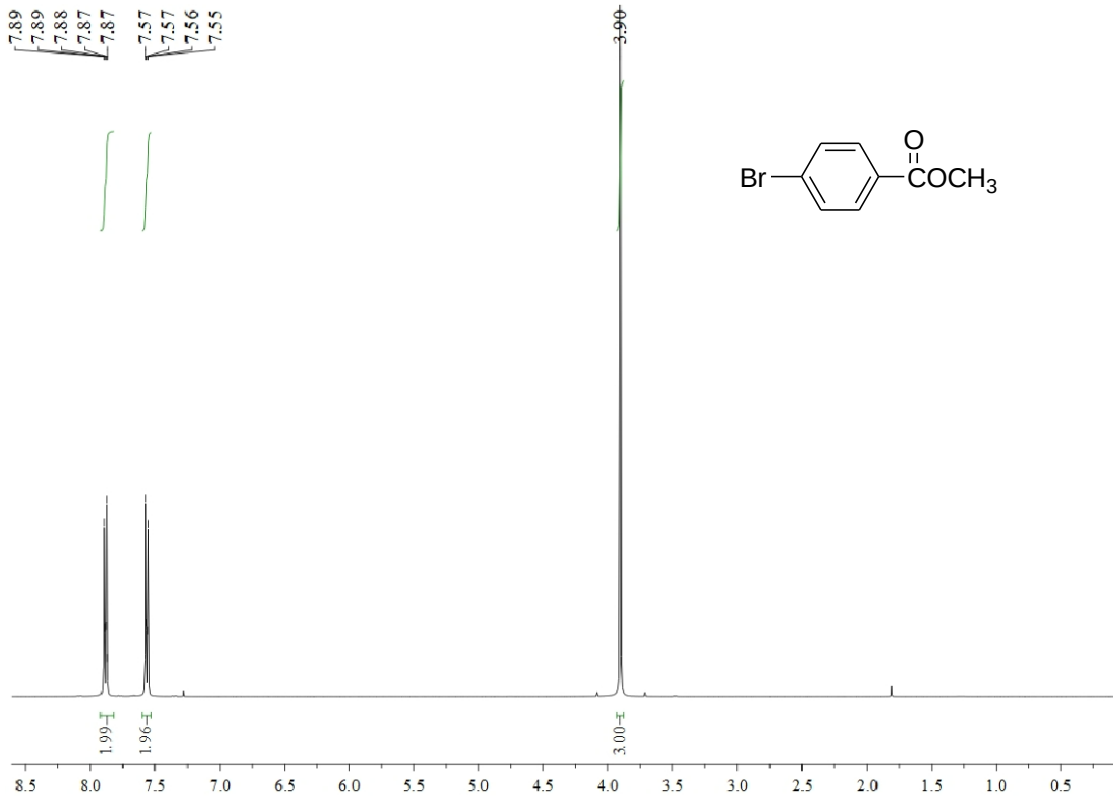


Figure S8 ^{1}H and ^{13}C NMR of Methyl 3-bromobenzoate



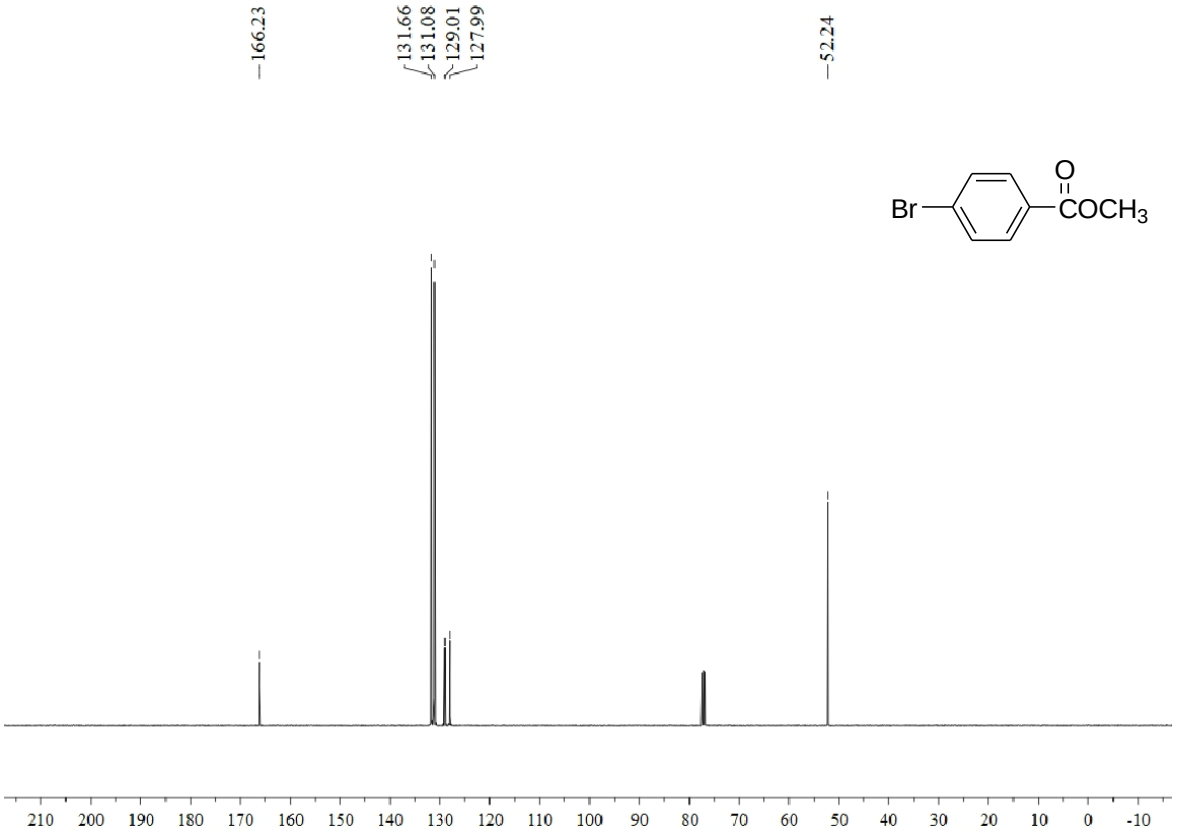
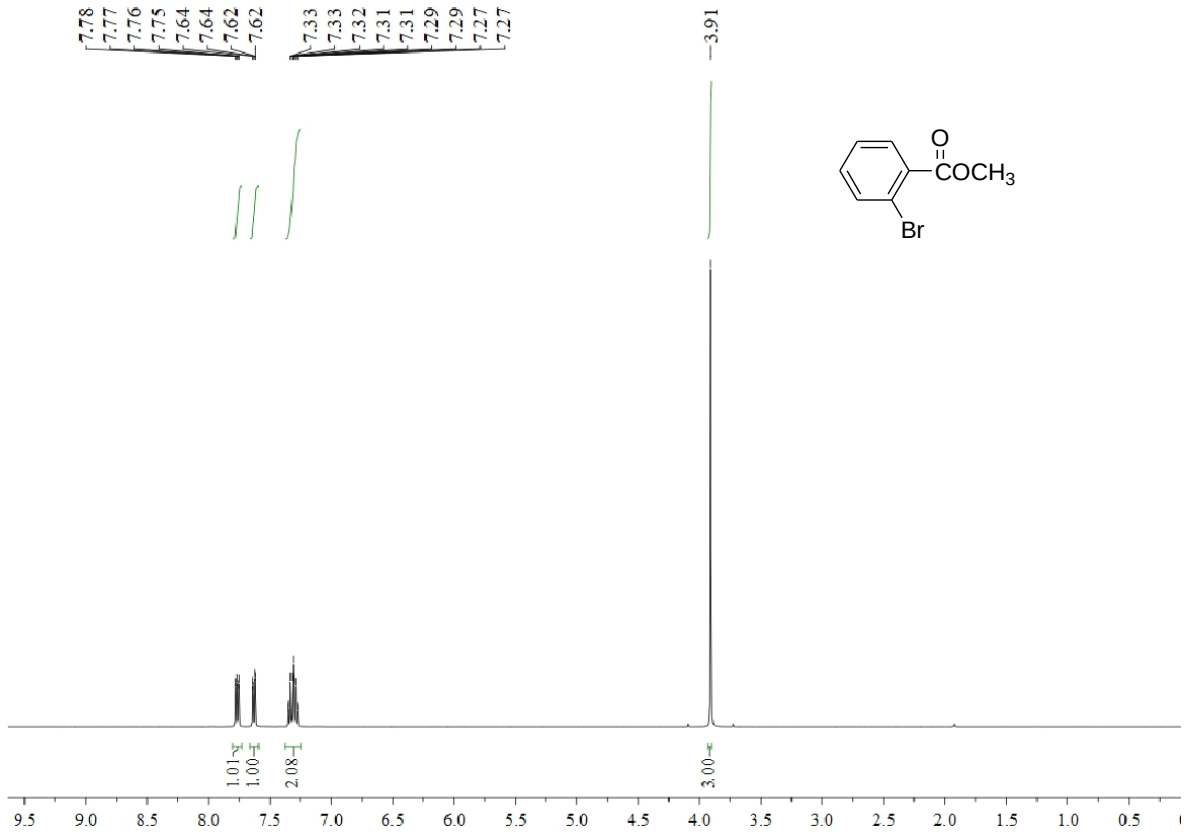


Figure S9 ^{1}H and ^{13}C NMR of Methyl 4-bromobenzoate



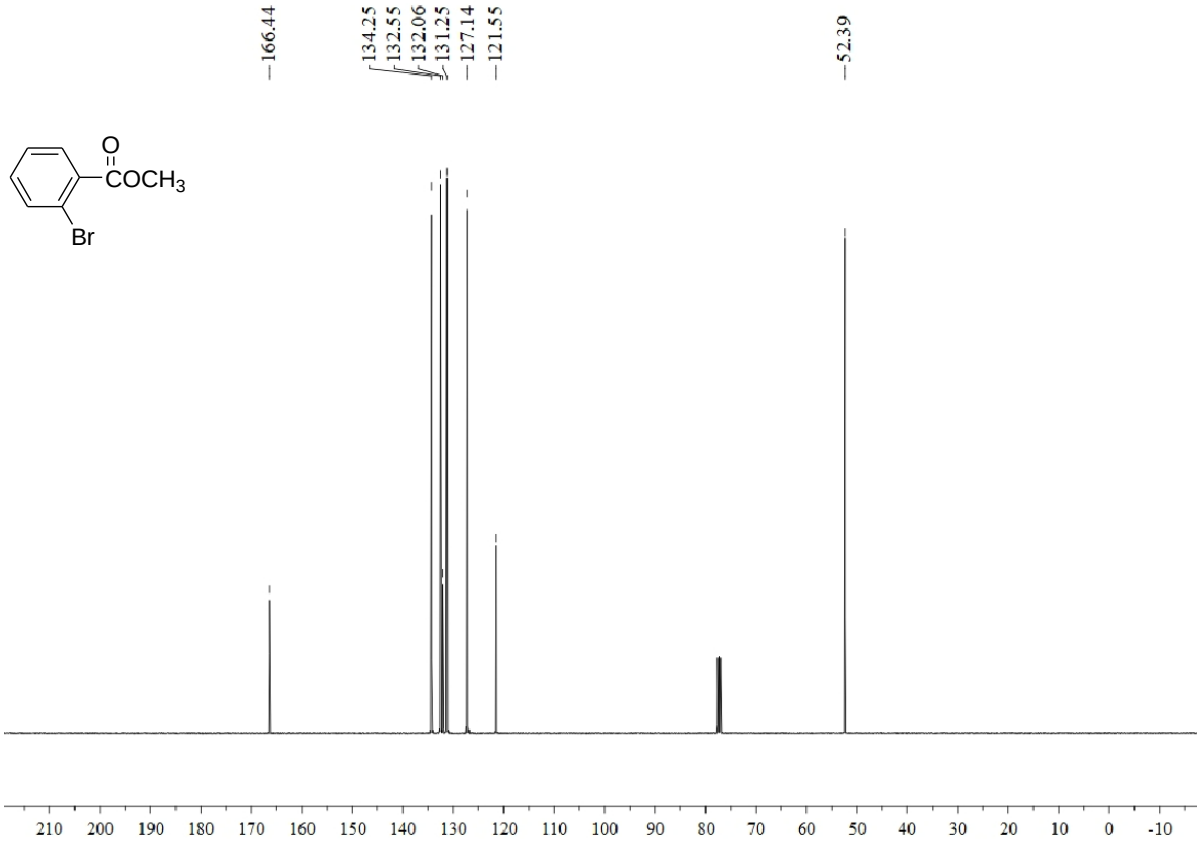
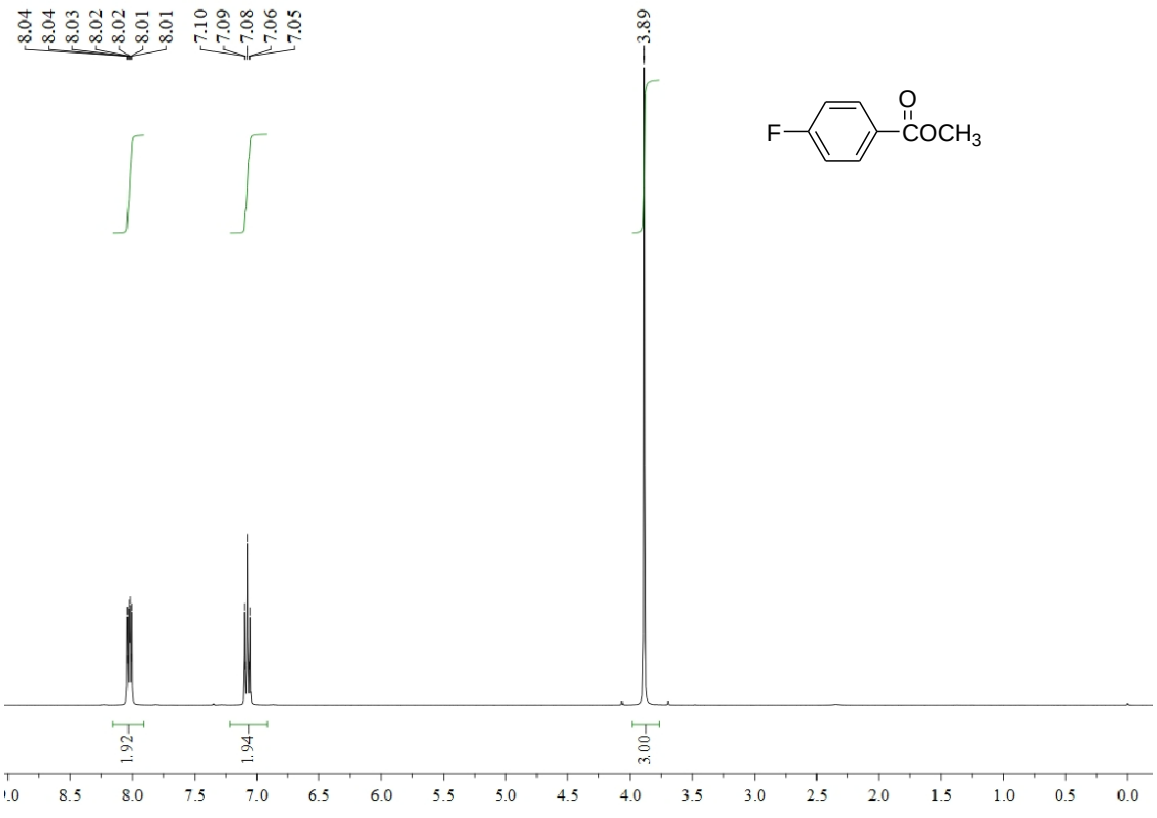


Figure S10 ^{1}H and ^{13}C NMR of Methyl 2-bromobenzoate



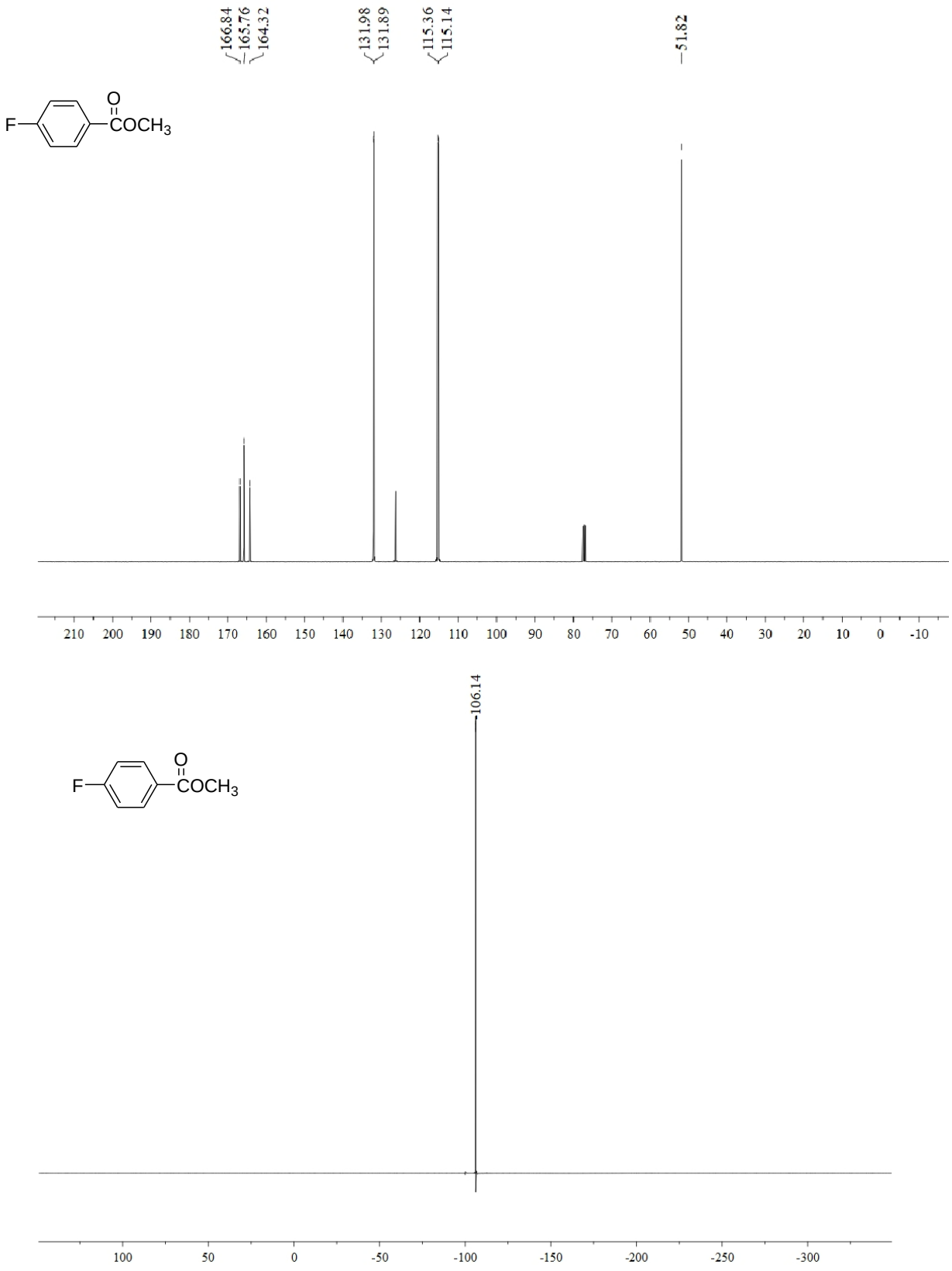
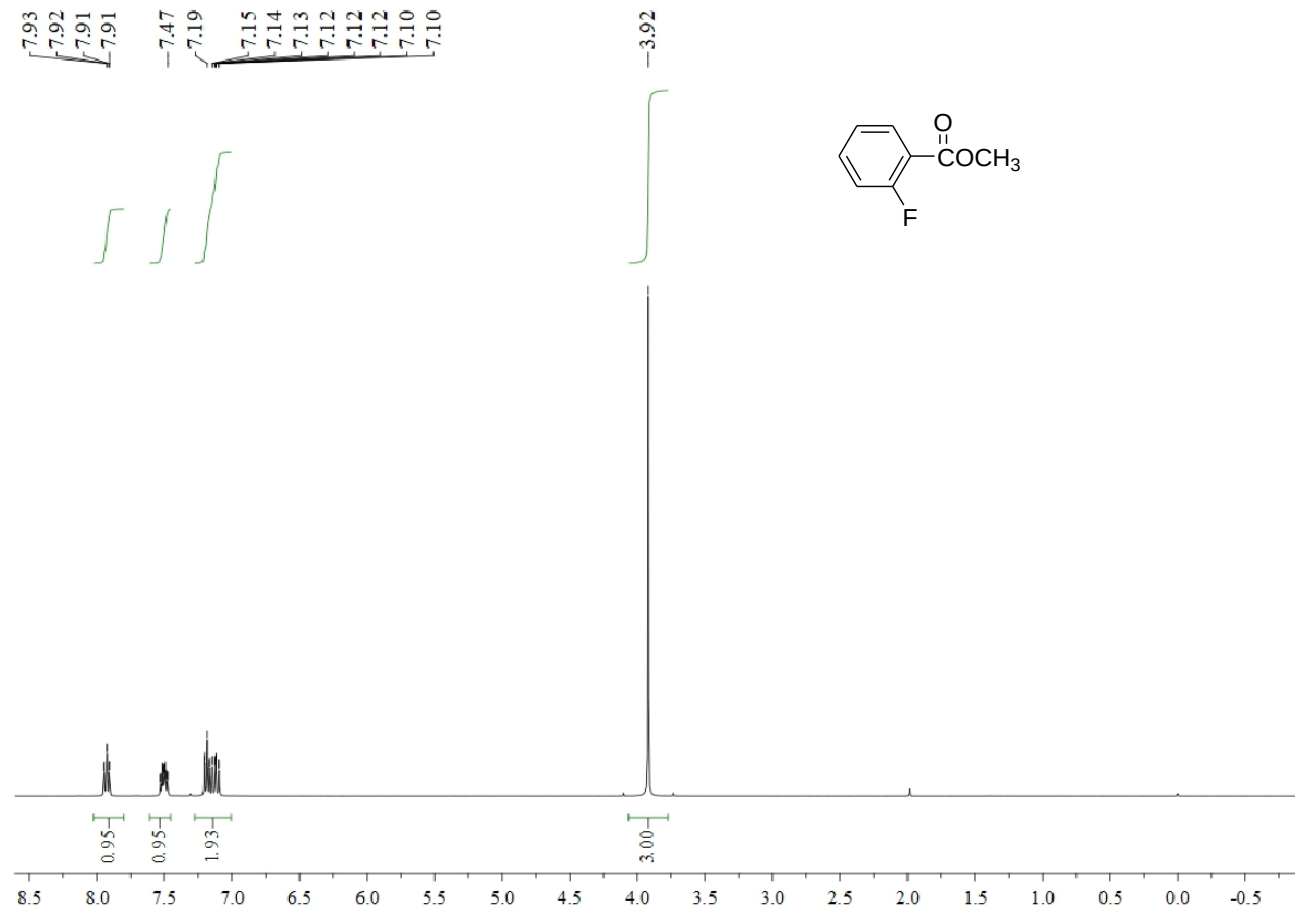
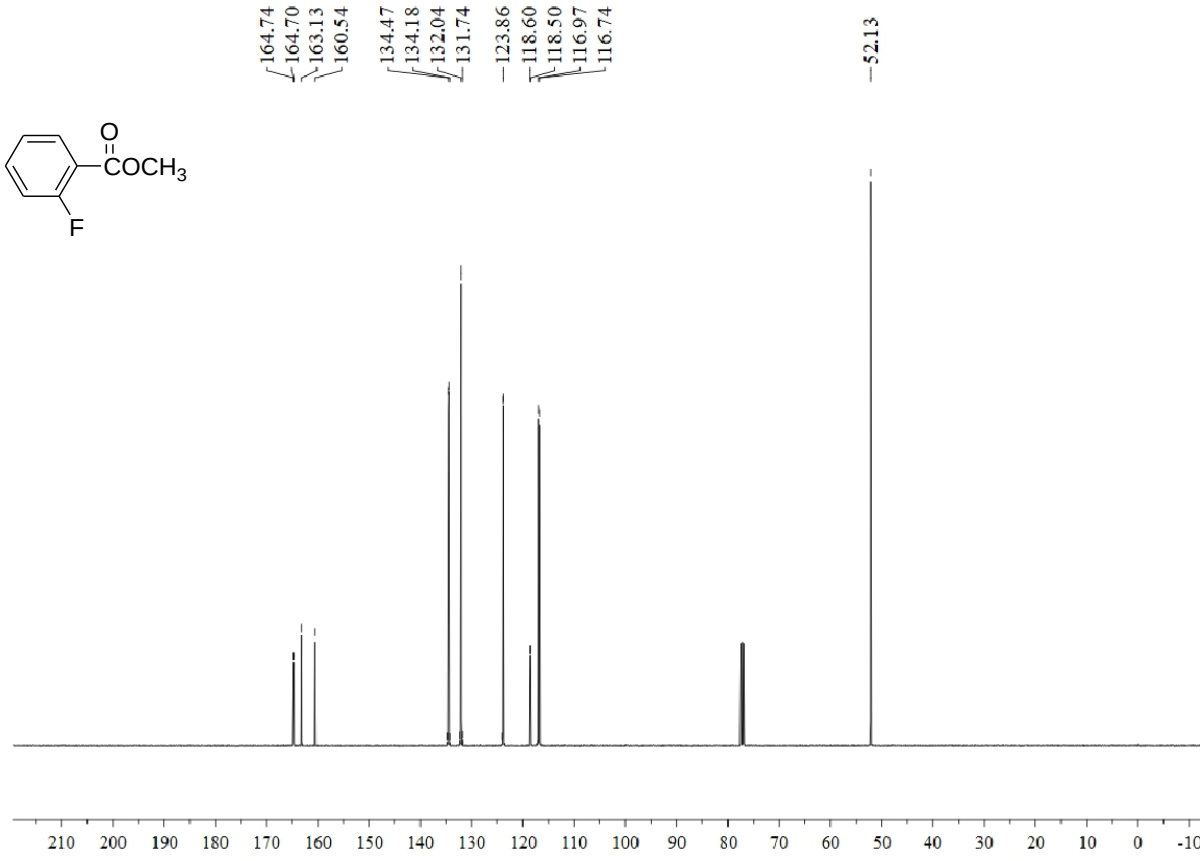


Figure S11 ^{1}H, ^{13}C and ^{19}F NMR of Methyl 4-fluorobenzoate


7.93
7.92
7.91
7.91
7.47
7.19
7.15
7.14
7.13
7.12
7.12
7.12
7.10
7.10
3.92
O
COCH3
F
0.95
0.95
1.93
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


164.74
164.70
163.13
160.54
134.47
134.18
132.04
131.74
123.86
118.60
118.50
116.97
116.74
52.13
O
COCH3
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

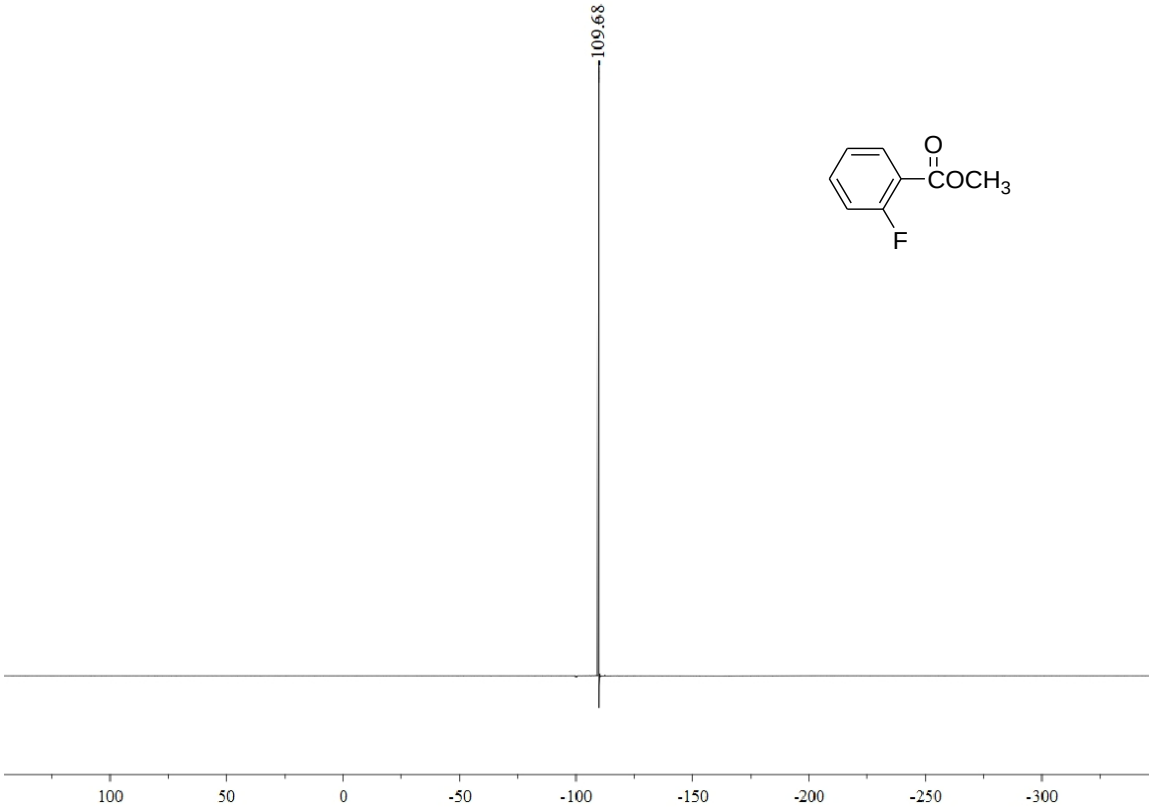
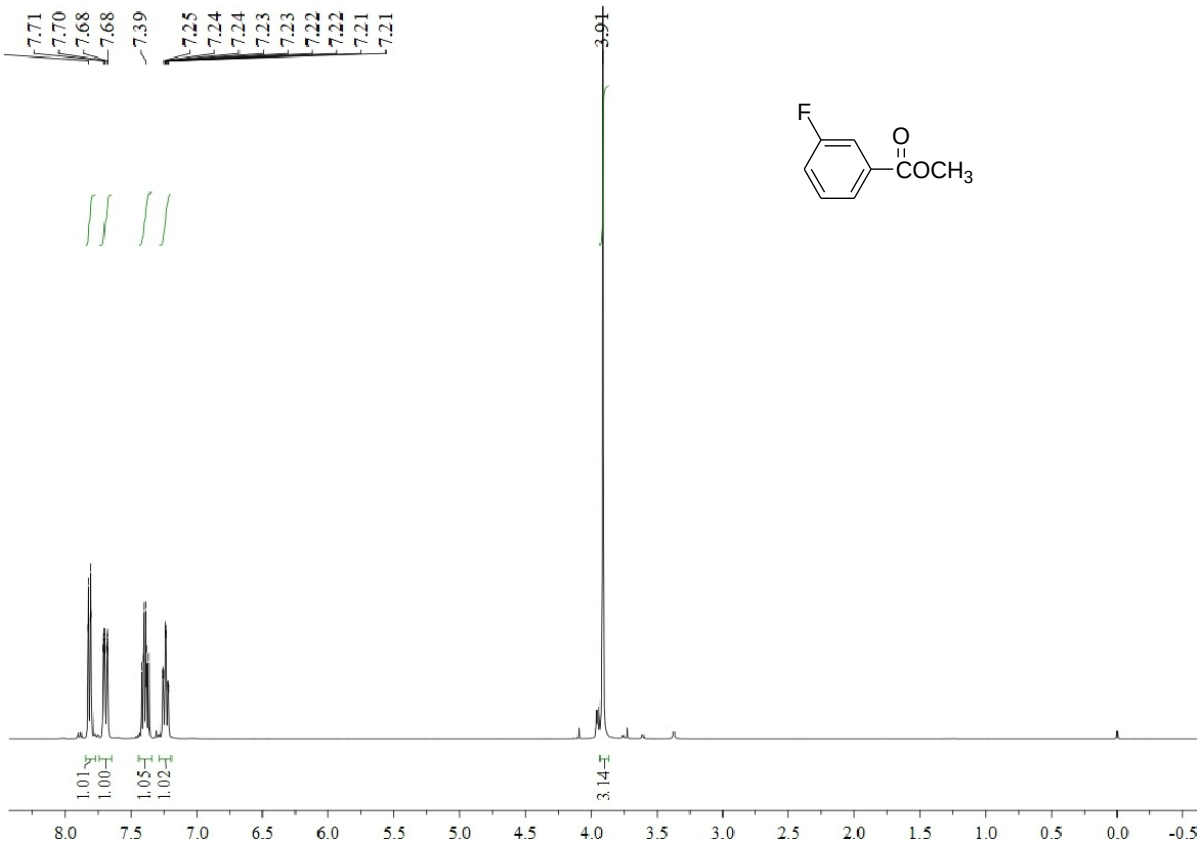
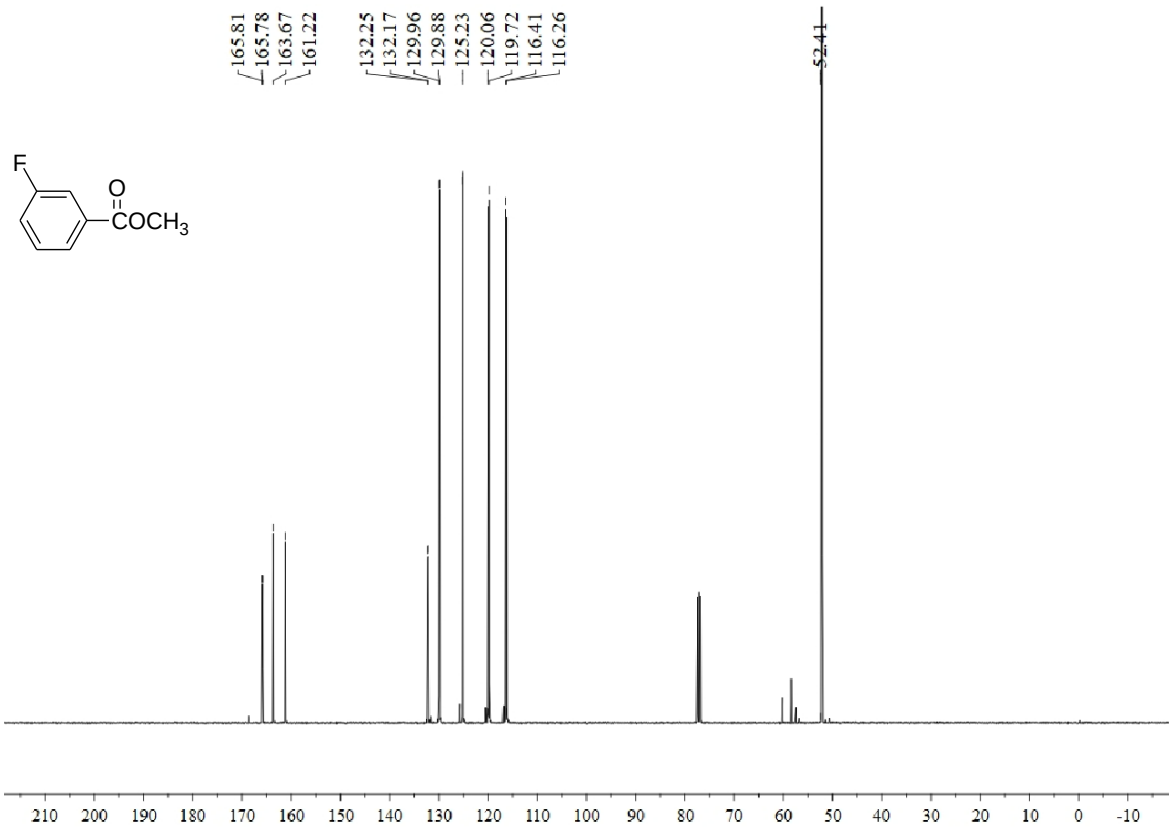


Figure S12 ^{1}H, ^{13}C and ^{19}F NMR of Methyl 2-fluorobenzoate





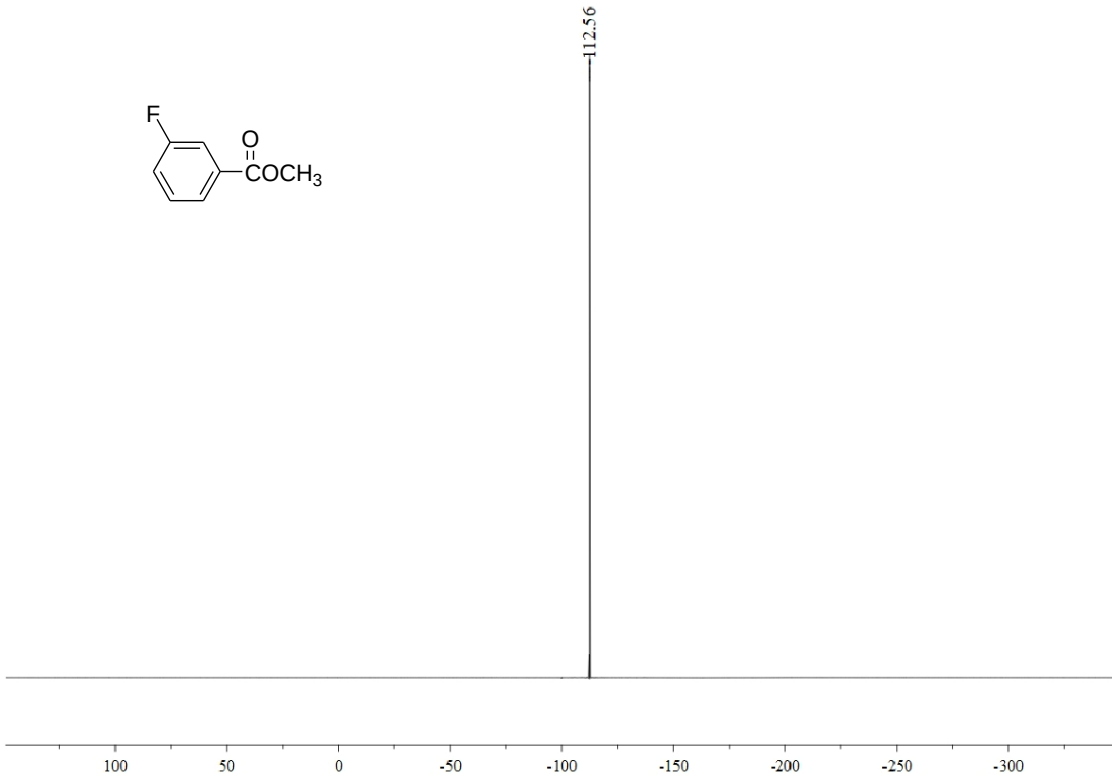


Figure S13 ^{1}H, ^{13}C and ^{19}F NMR of Methyl 3-fluorobenzoate

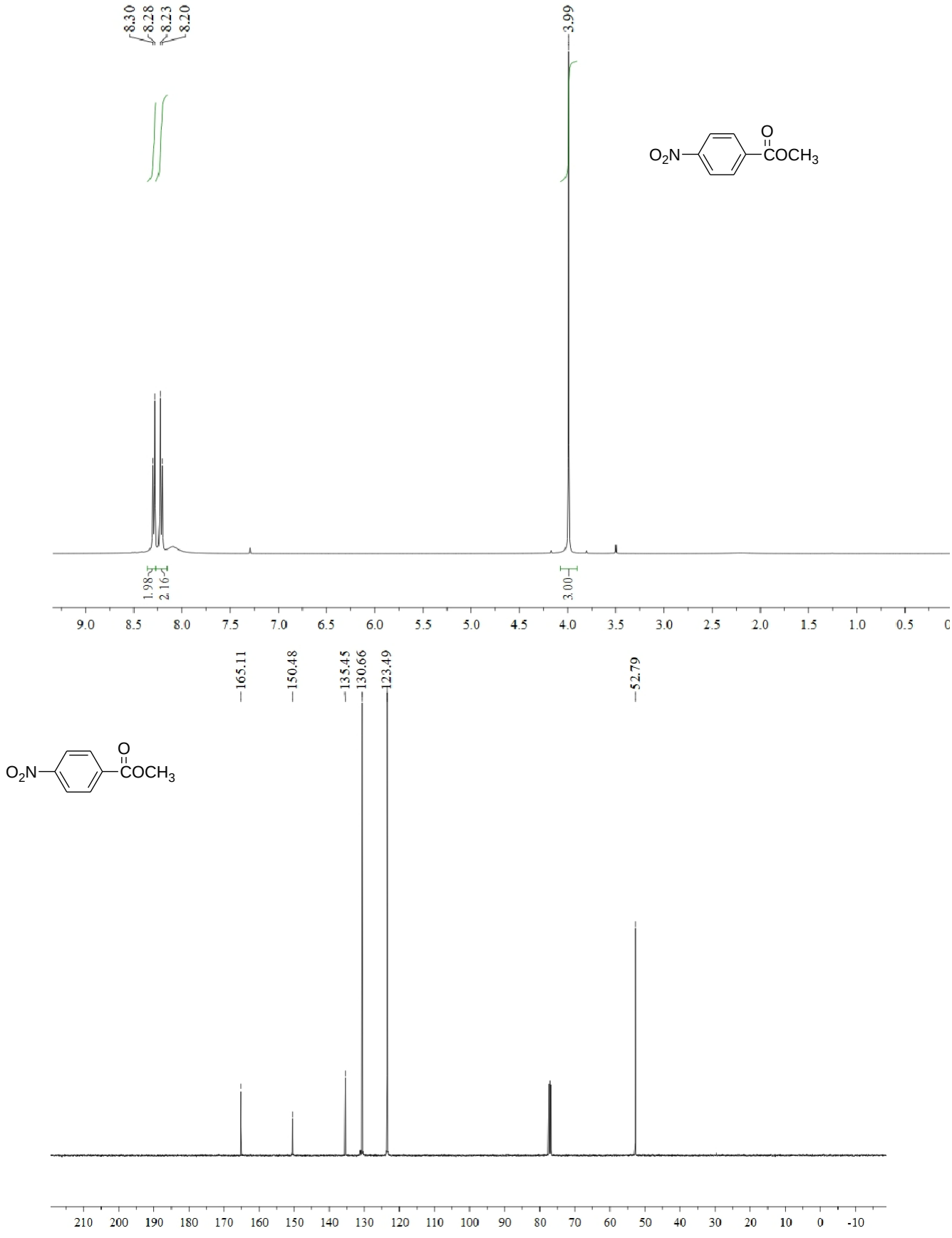


Figure S14 ^{1}H and ^{13}C NMR of Methyl 4-nitrobenzoate

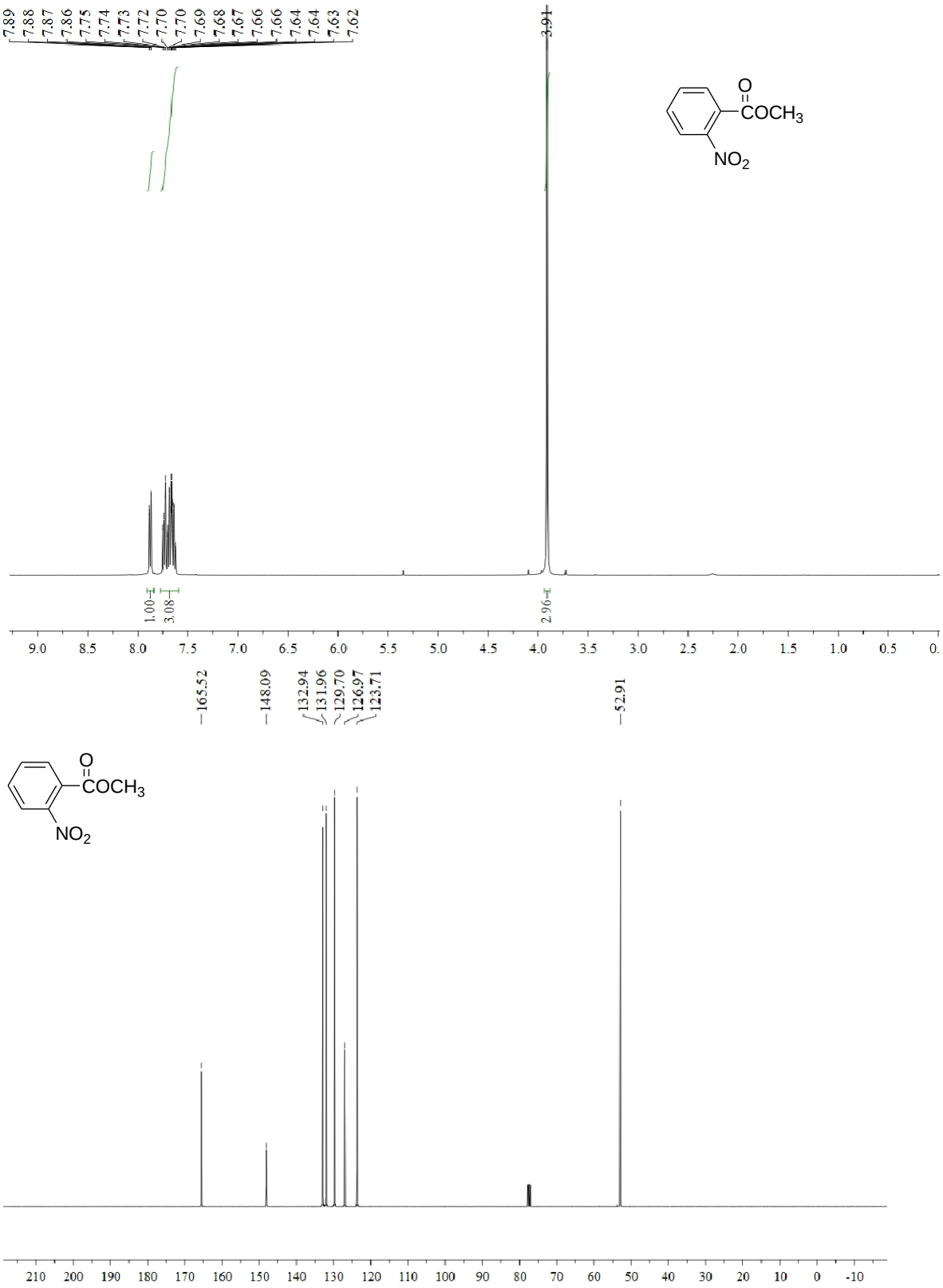


Figure S15 ^{1}H and ^{13}C NMR of Methyl 2-nitrobenzoate

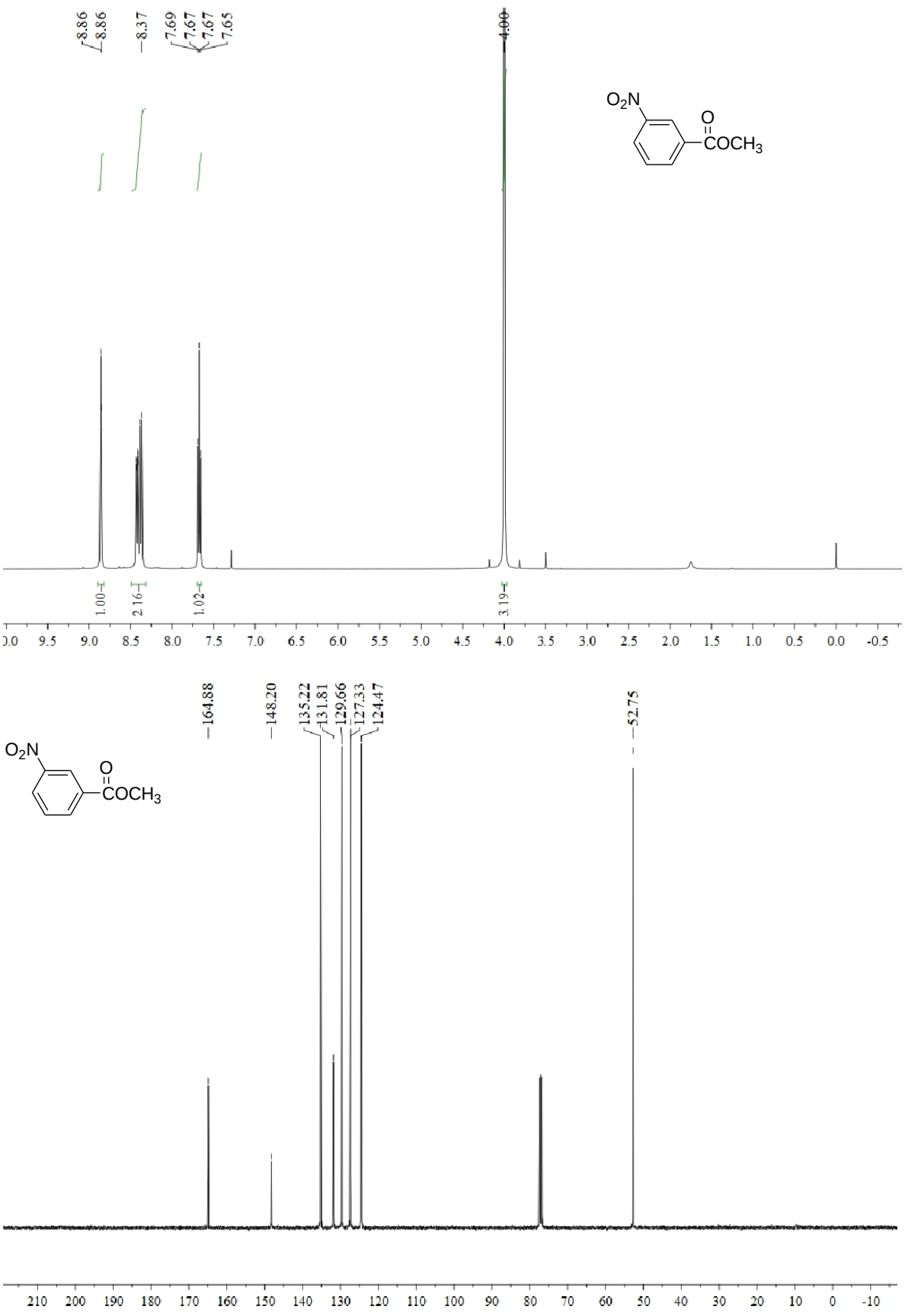


Figure S16 ^{1}H and ^{13}C NMR of Methyl 3-nitrobenzoate

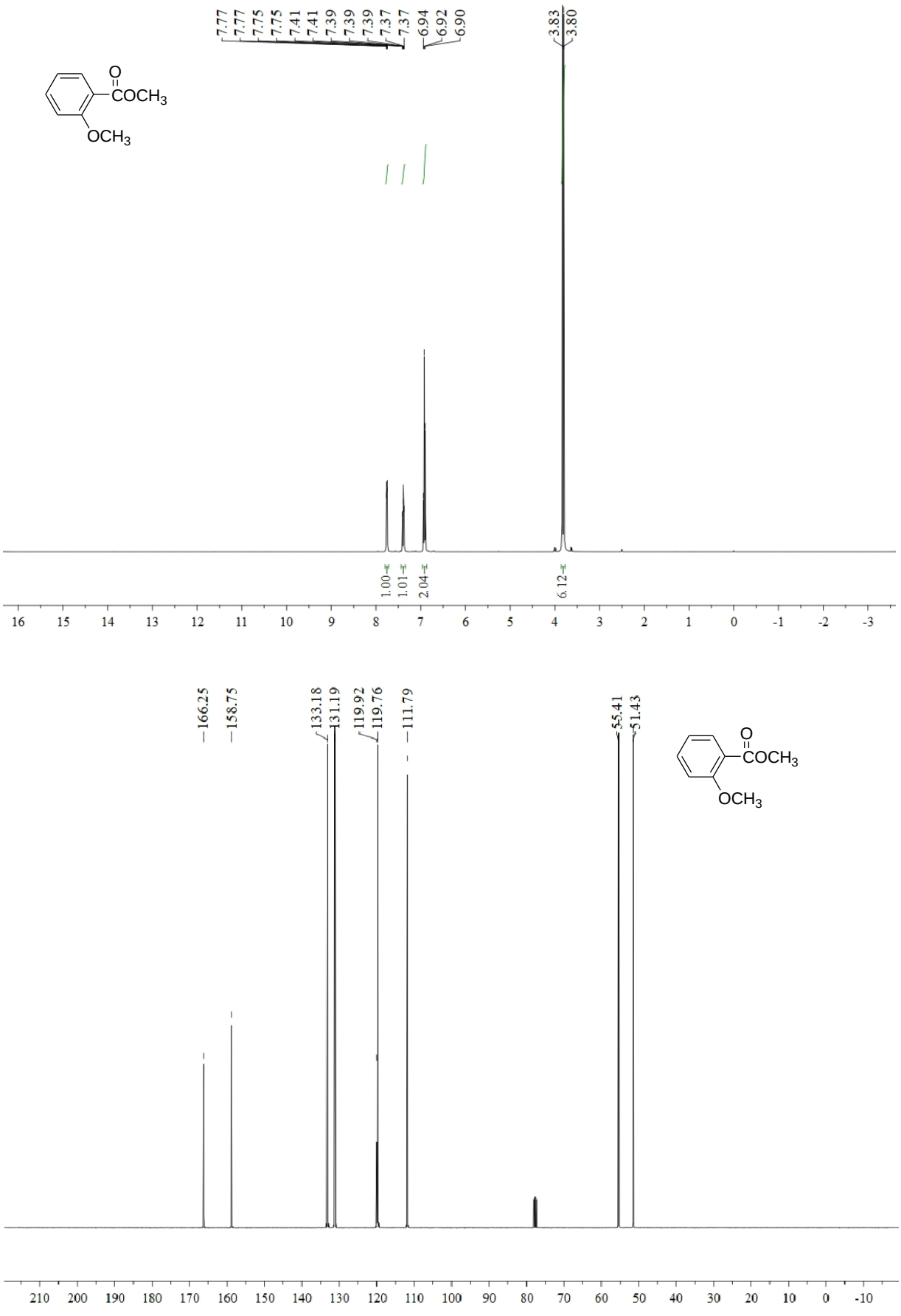


Figure S17 ^{1}H and ^{13}C NMR of Methyl 2-methoxybenzoate

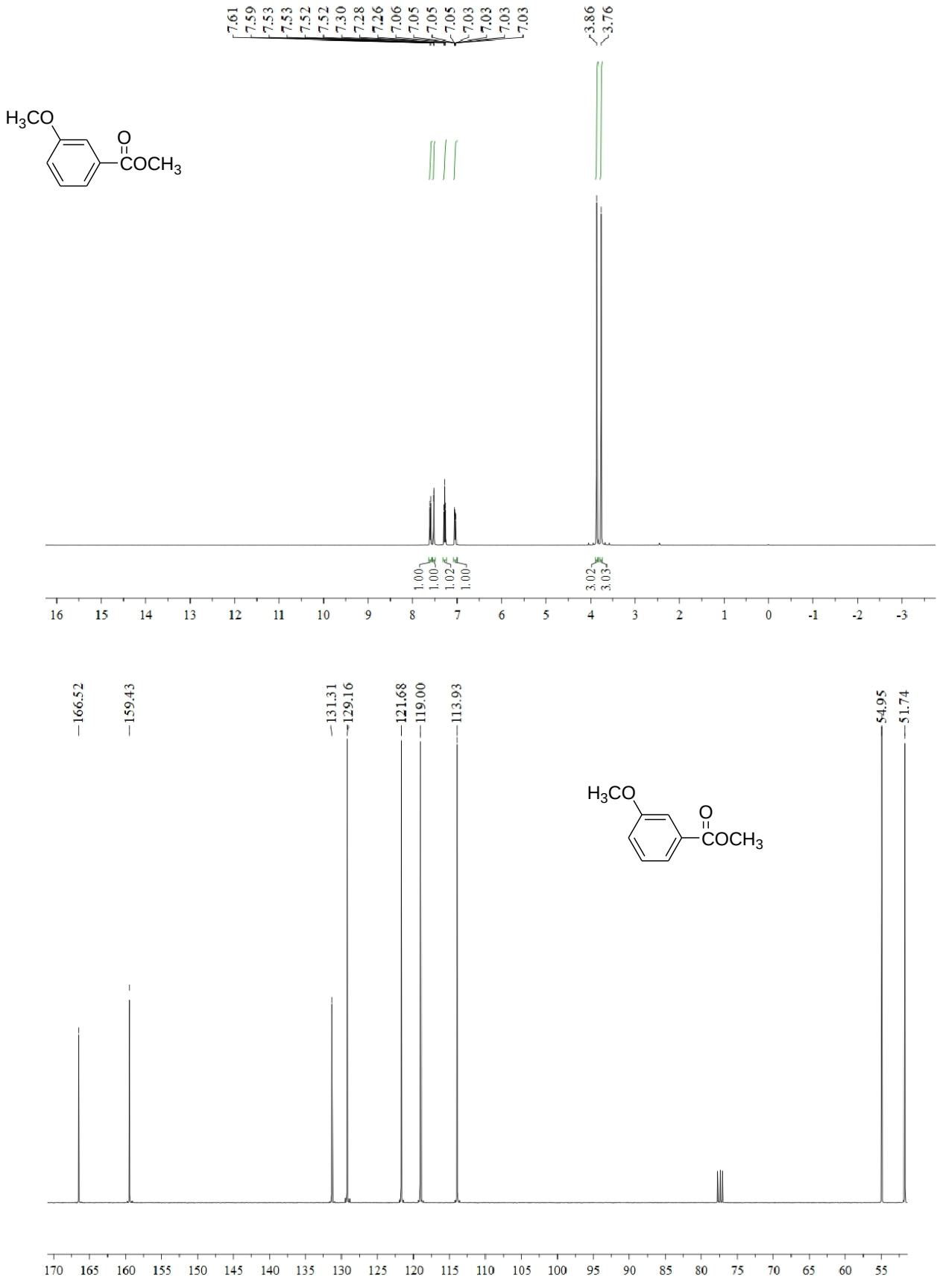


Figure S18 ^{1}H and ^{13}C NMR of Methyl 3-methoxybenzoate

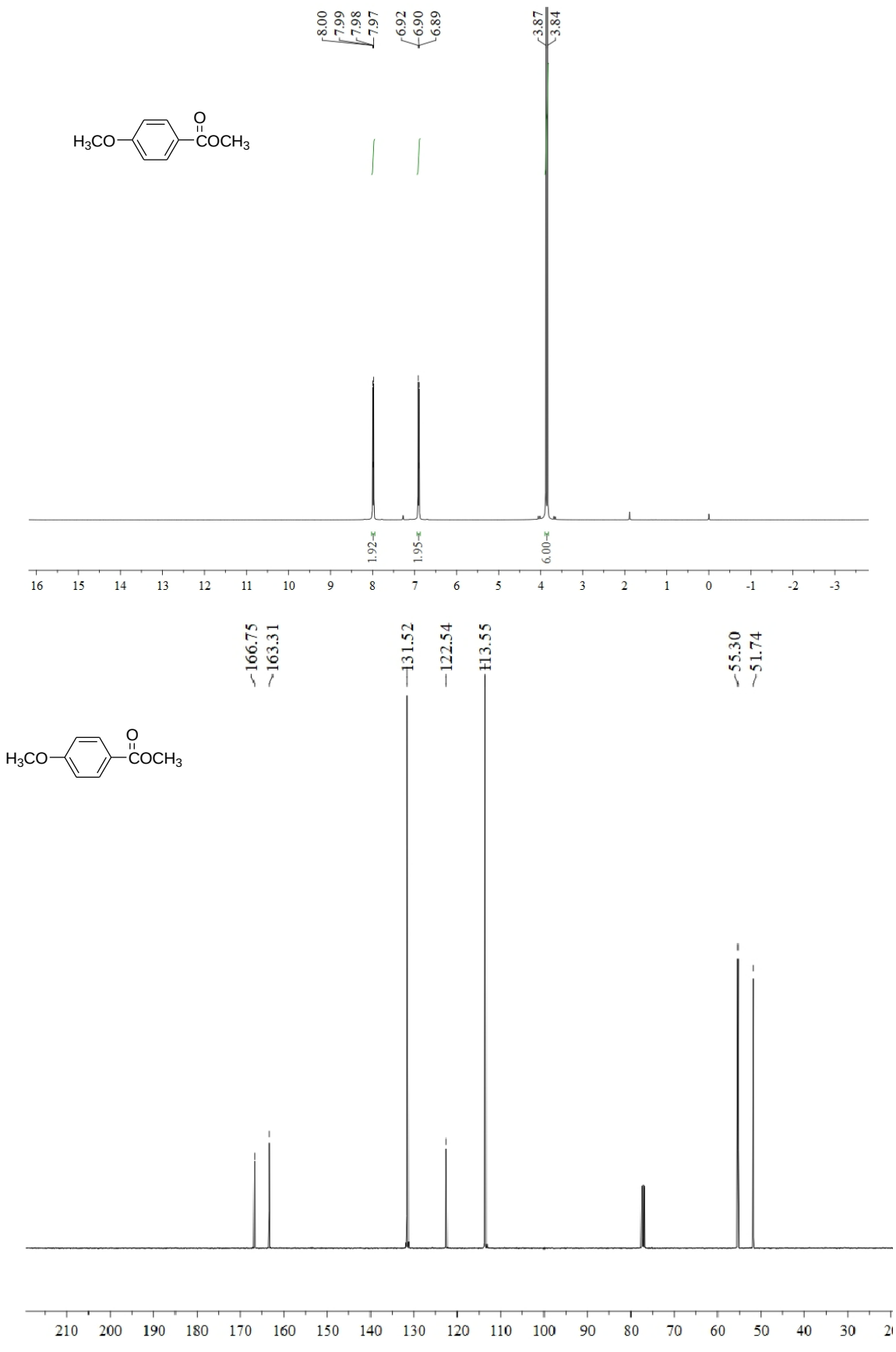


Figure S19 ^{1}H and ^{13}C NMR of Methyl 4-methoxybenzoate

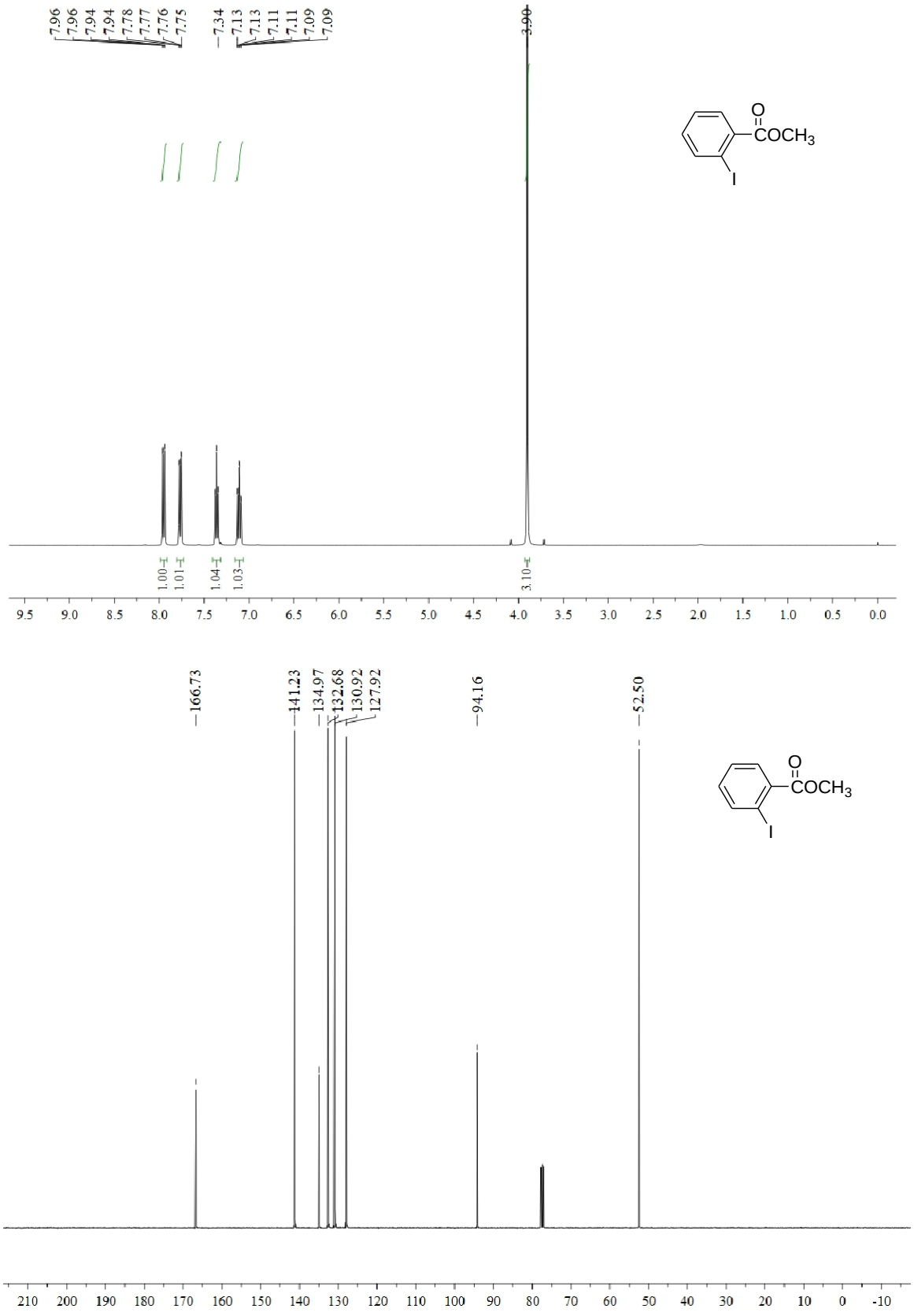


Figure S20 ^{1}H and ^{13}C NMR of Methyl 2-iodobenzoate

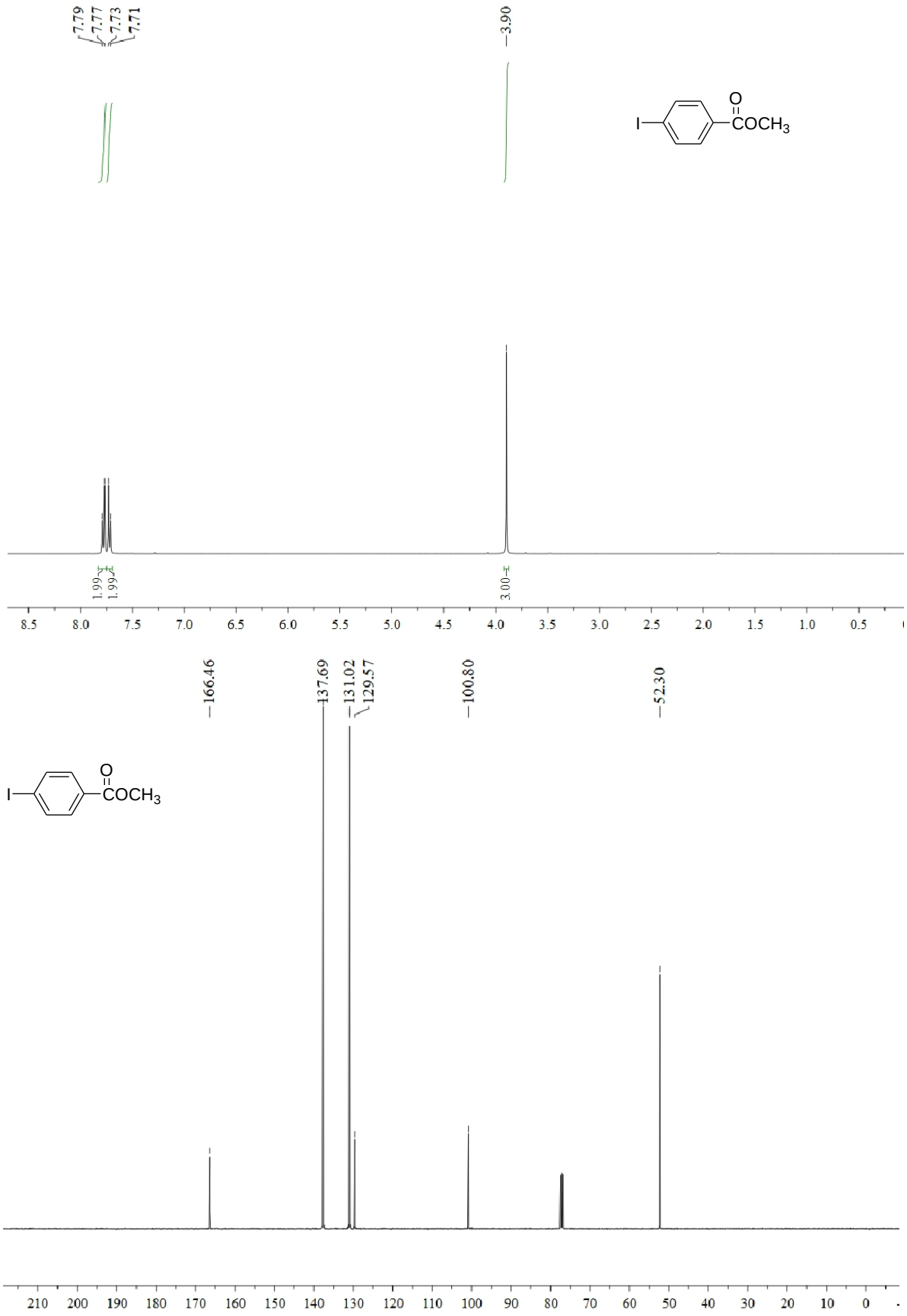


Figure S21 ^{1}H and ^{13}C NMR of Methyl 4-iodobenzoate

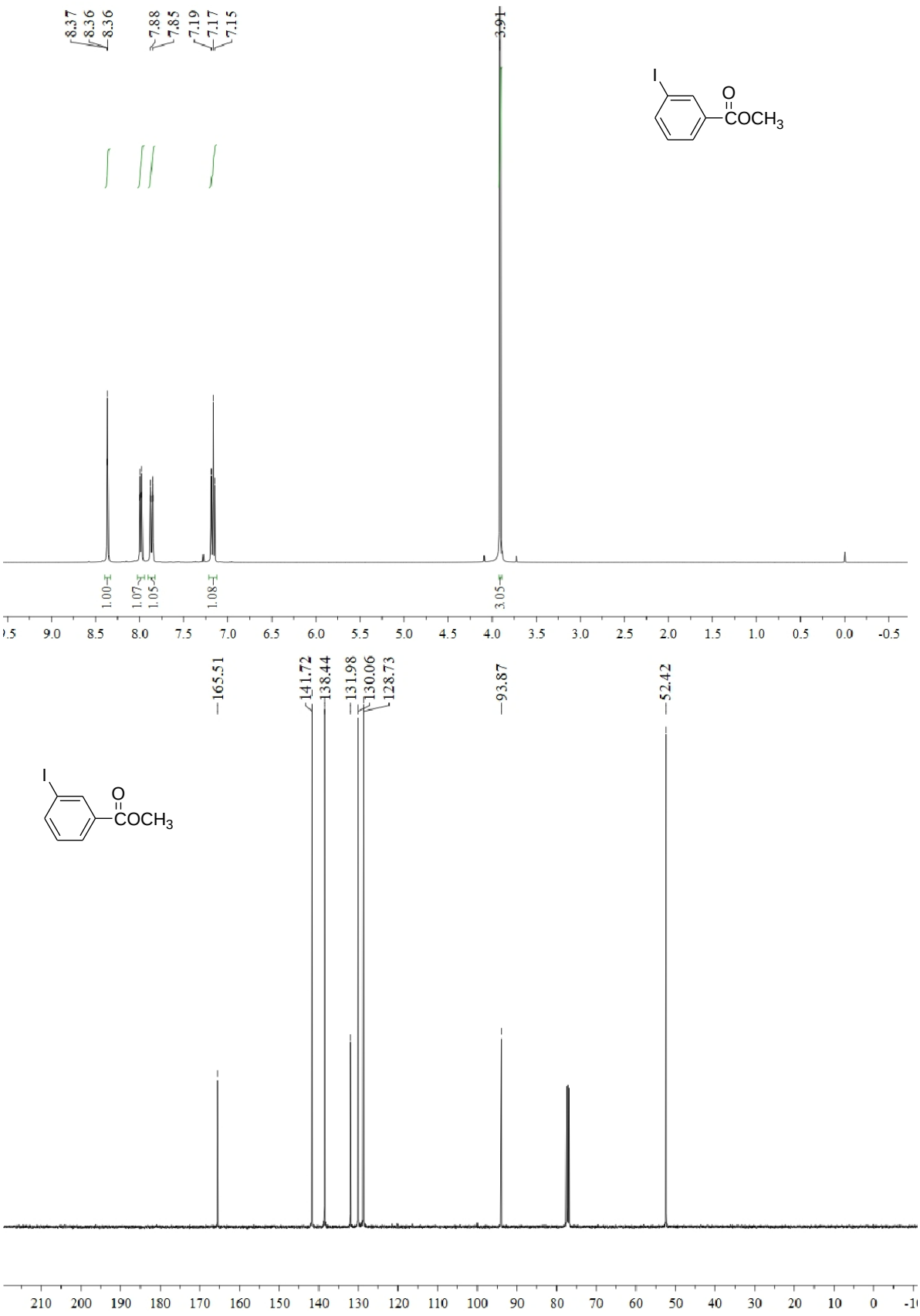
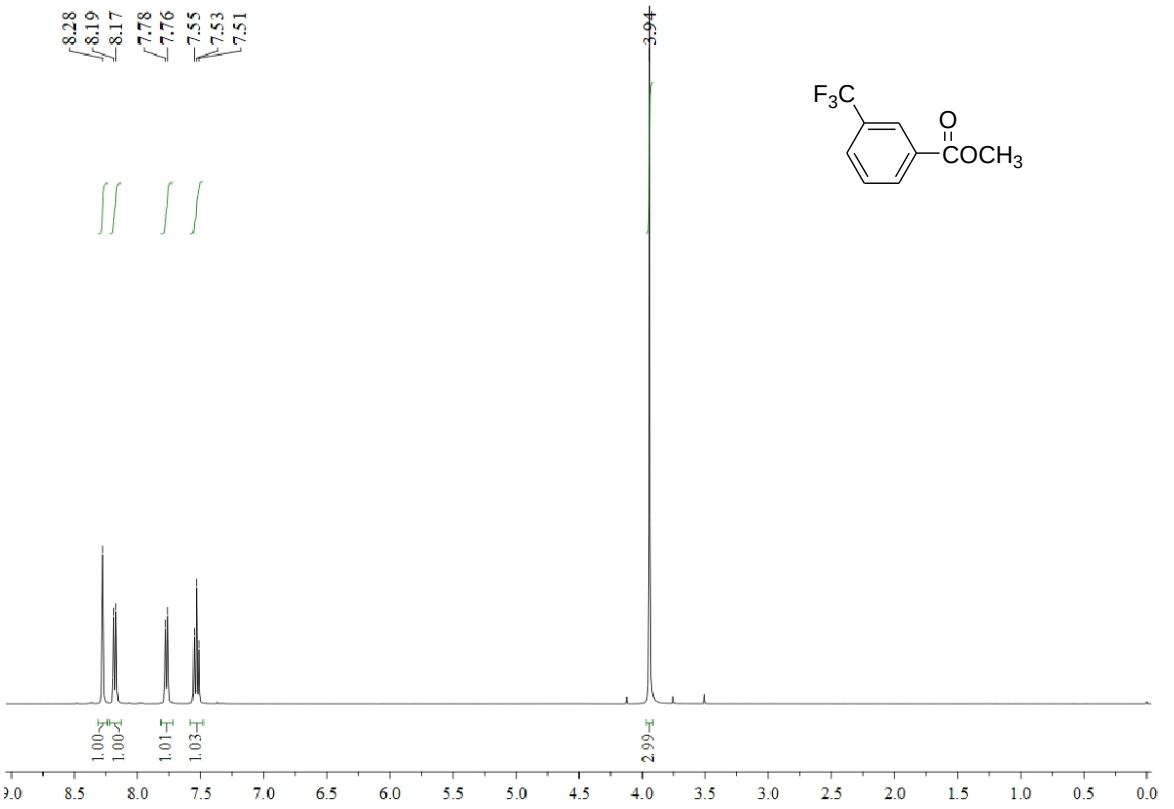
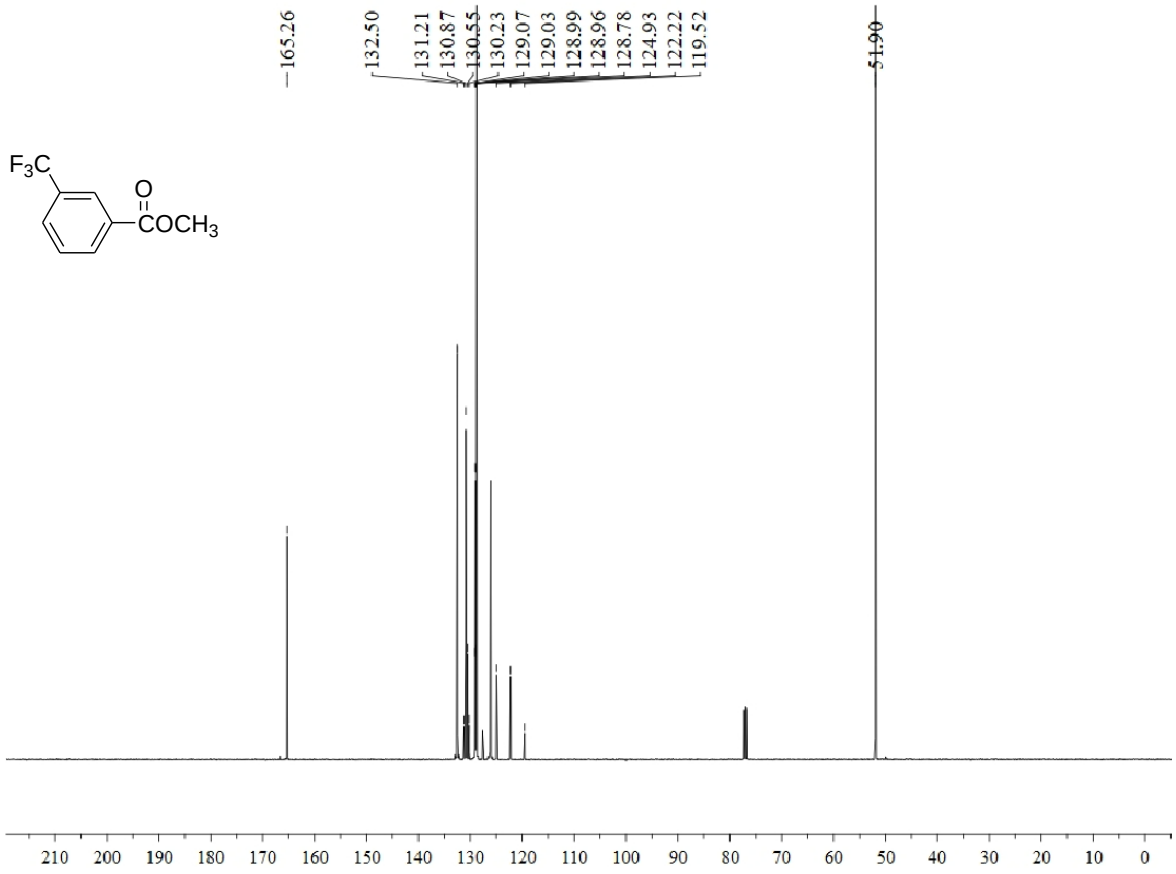


Figure S22 ^{1}H and ^{13}C NMR of Methyl 3-iodobenzoate


8.28
8.19
8.17
7.78
7.76
7.55
7.53
7.51
3.94
F3C
O
COCH3
1.00
1.00
1.01
1.03
2.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


165.26
132.50
131.21
130.87
130.55
130.23
129.07
129.03
128.99
128.96
128.78
124.93
122.22
119.52
51.90
F3C
O
COCH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

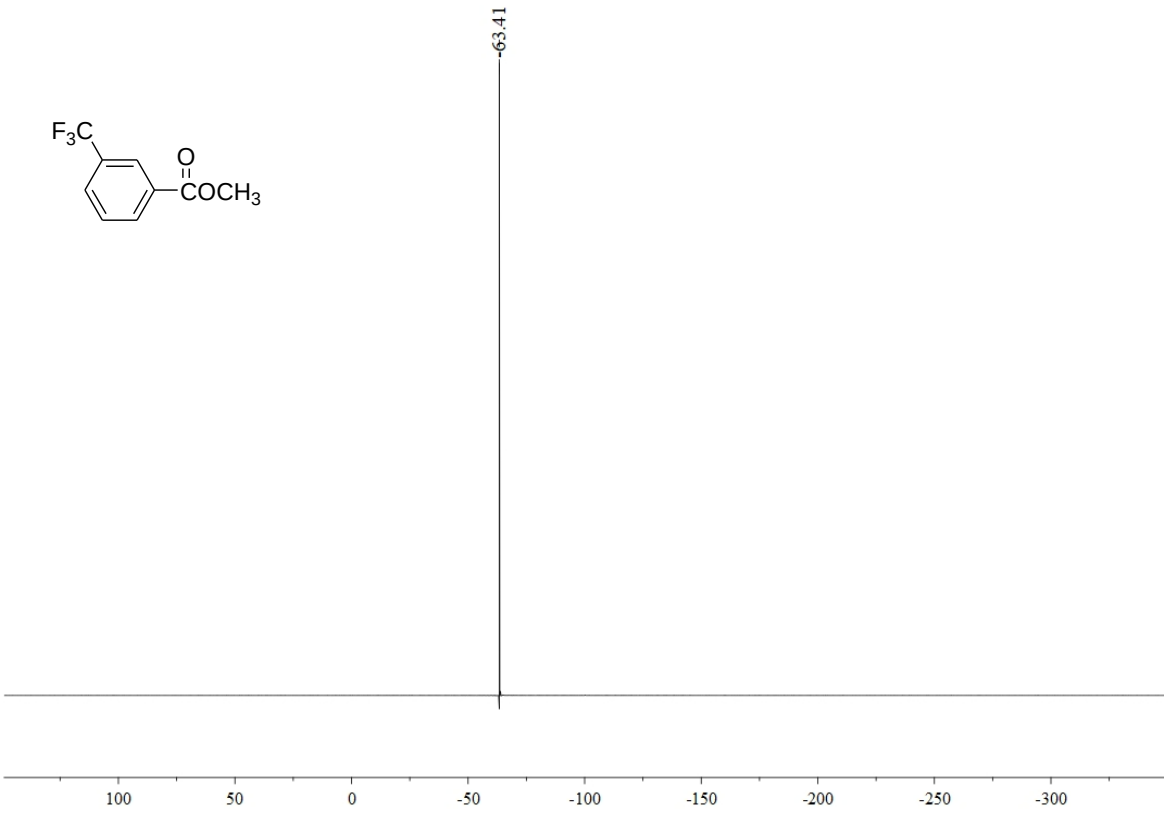
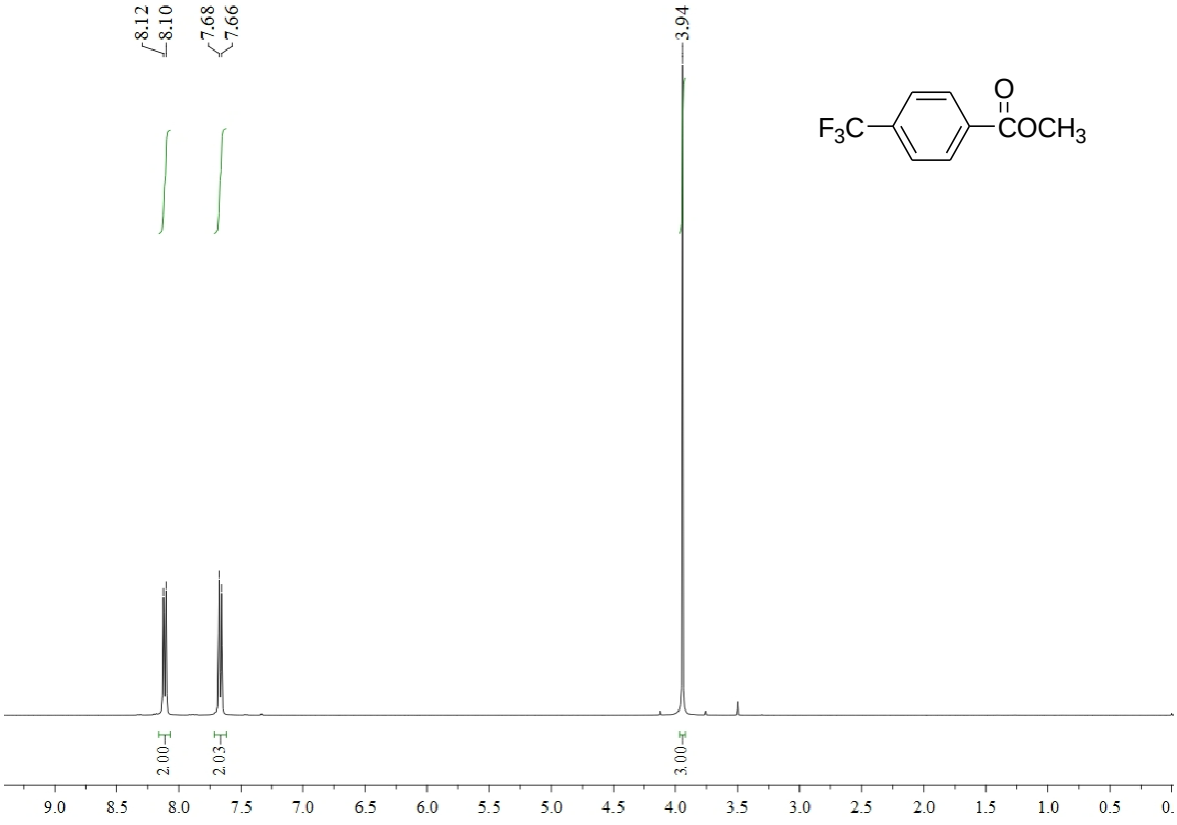


Figure S23 ^{1}H, ^{13}C and ^{19}F NMR of Methyl 3-trifluoromethylbenzoate



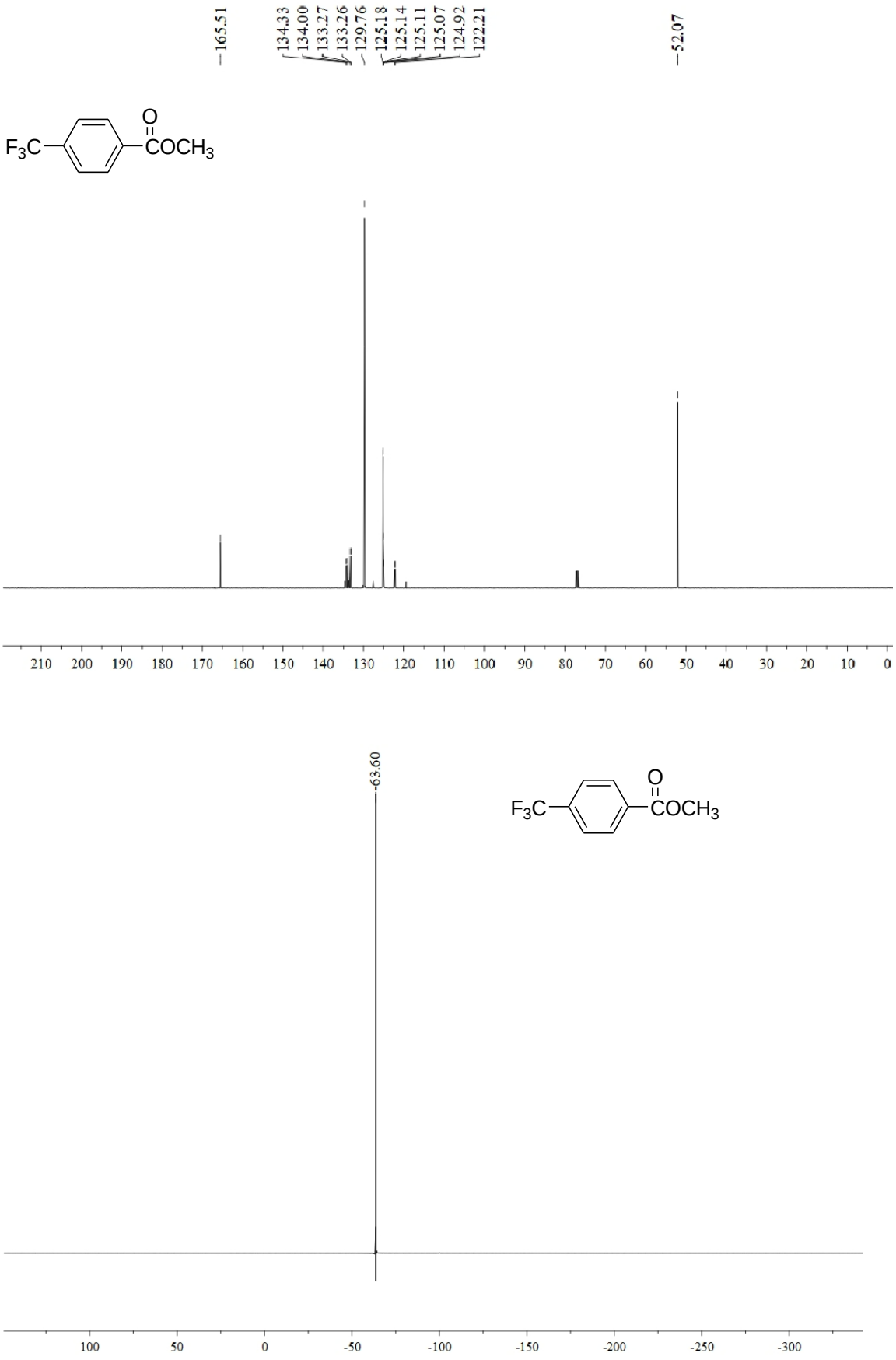
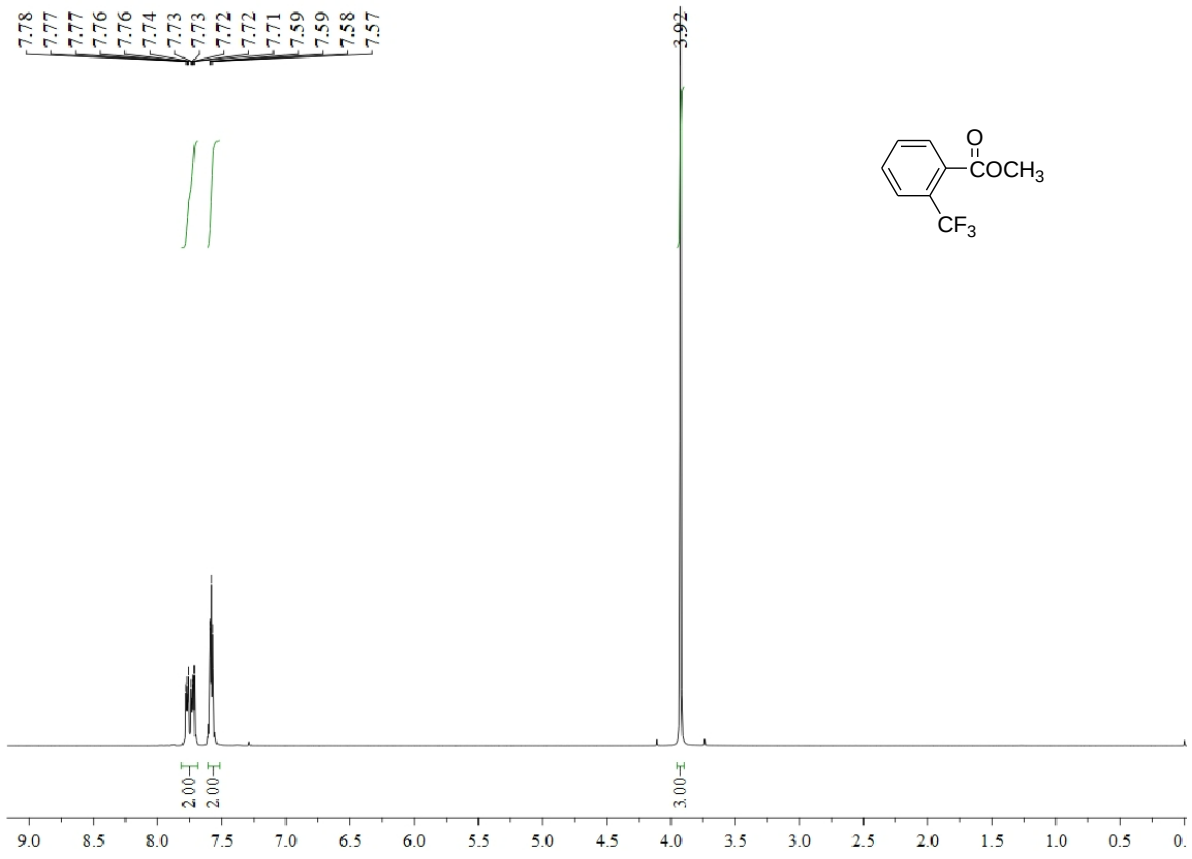
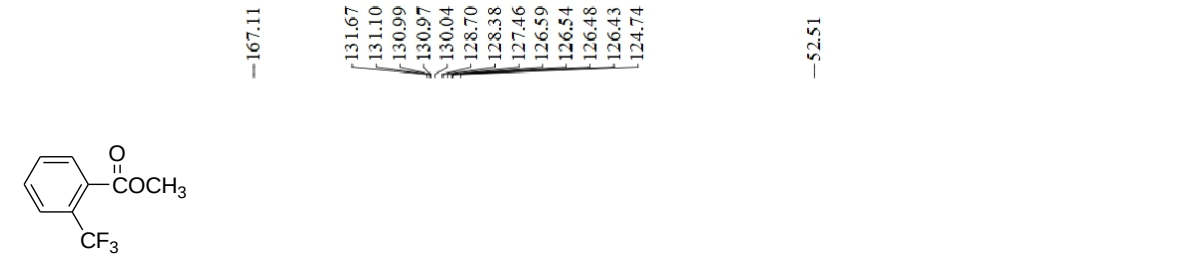
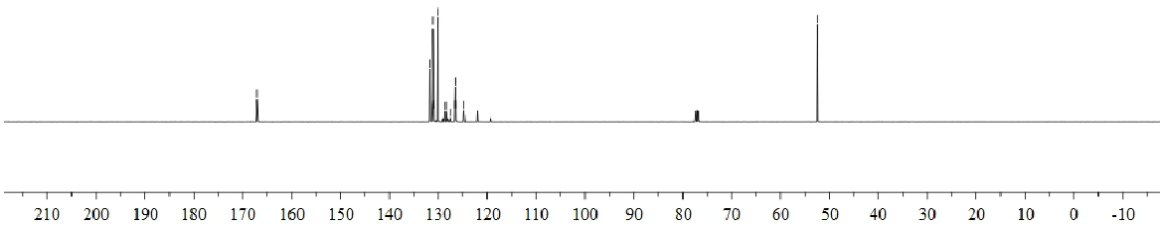


Figure S24 ^{1}H, ^{13}C and ^{19}F NMR of Methyl 4-trifluoromethylbenzoate


7.78
7.77
7.77
7.76
7.76
7.74
7.73
7.73
7.72
7.72
7.71
7.59
7.59
7.58
7.57
3.92
O
COCH3
CF3
2.00
2.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


167.11
131.67
131.10
130.99
130.97
130.04
128.70
128.38
127.46
126.59
126.54
126.48
126.43
124.74
52.51

O
COCH3
CF3


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

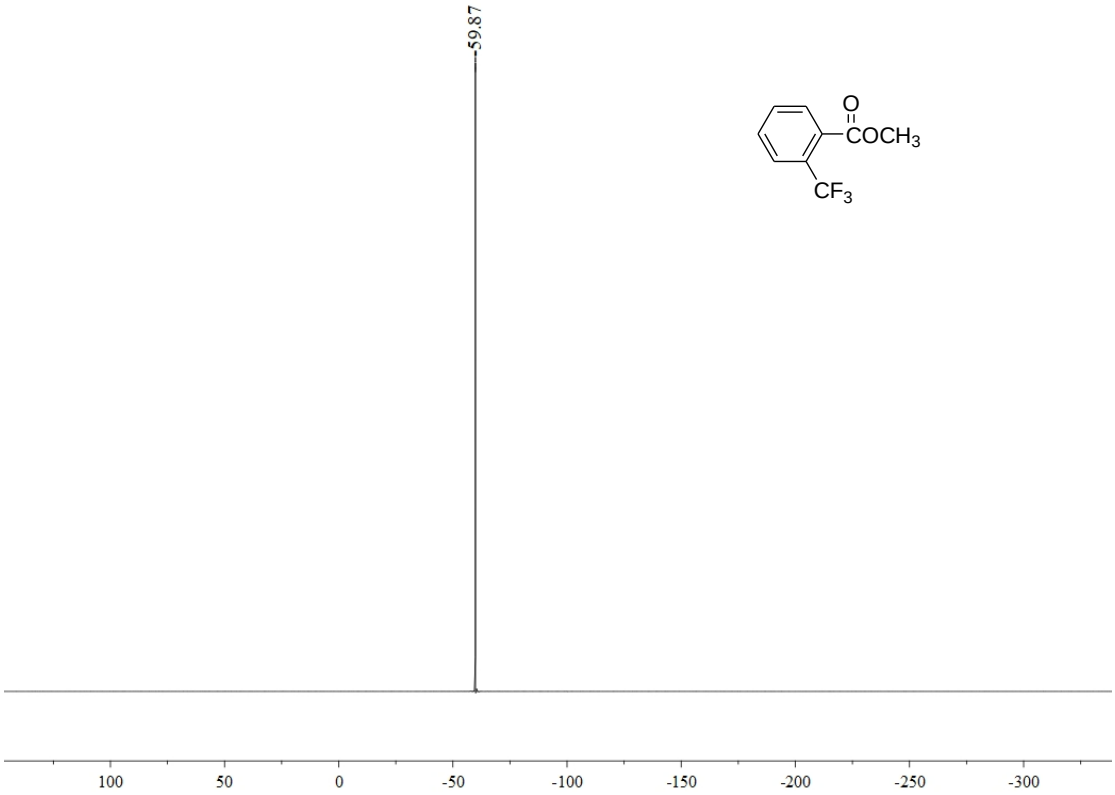
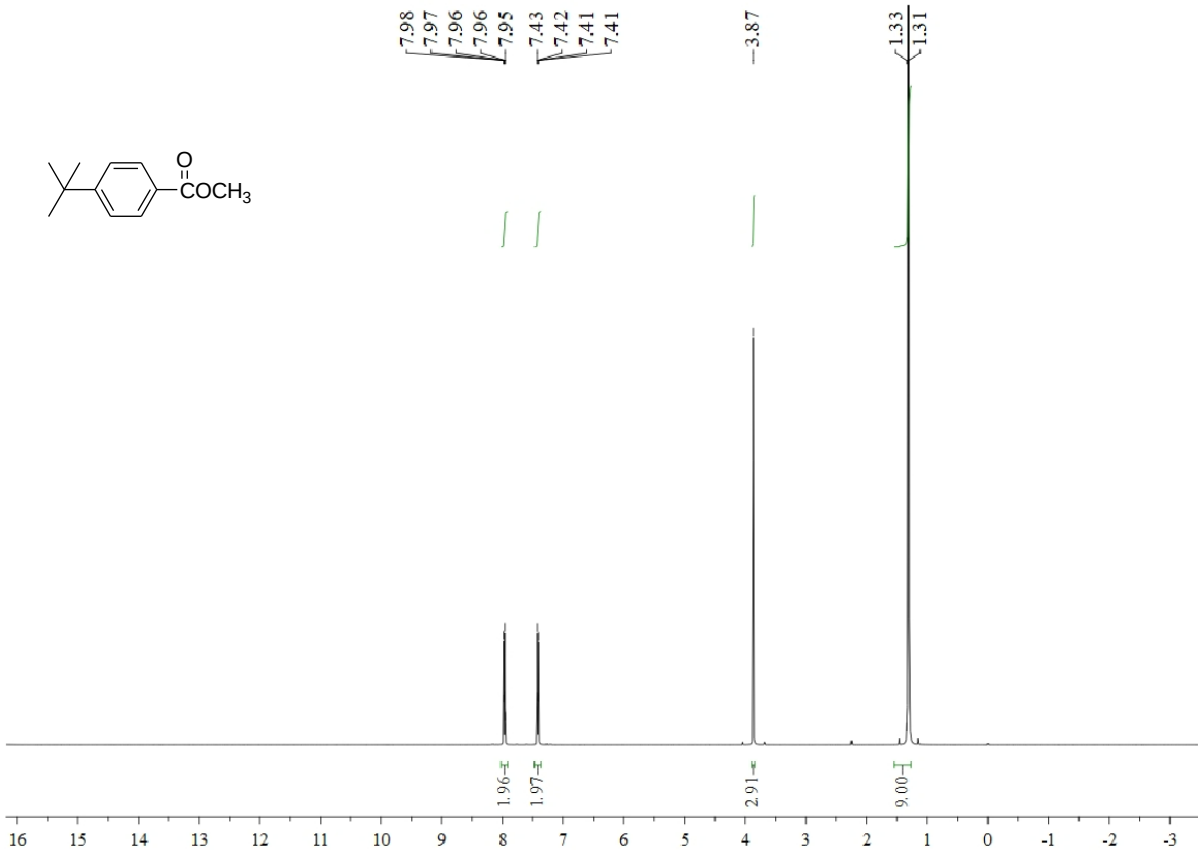


Figure S25 ^{1}H, ^{13}C and ^{19}F NMR of Methyl 2-trifluoromethylbenzoate



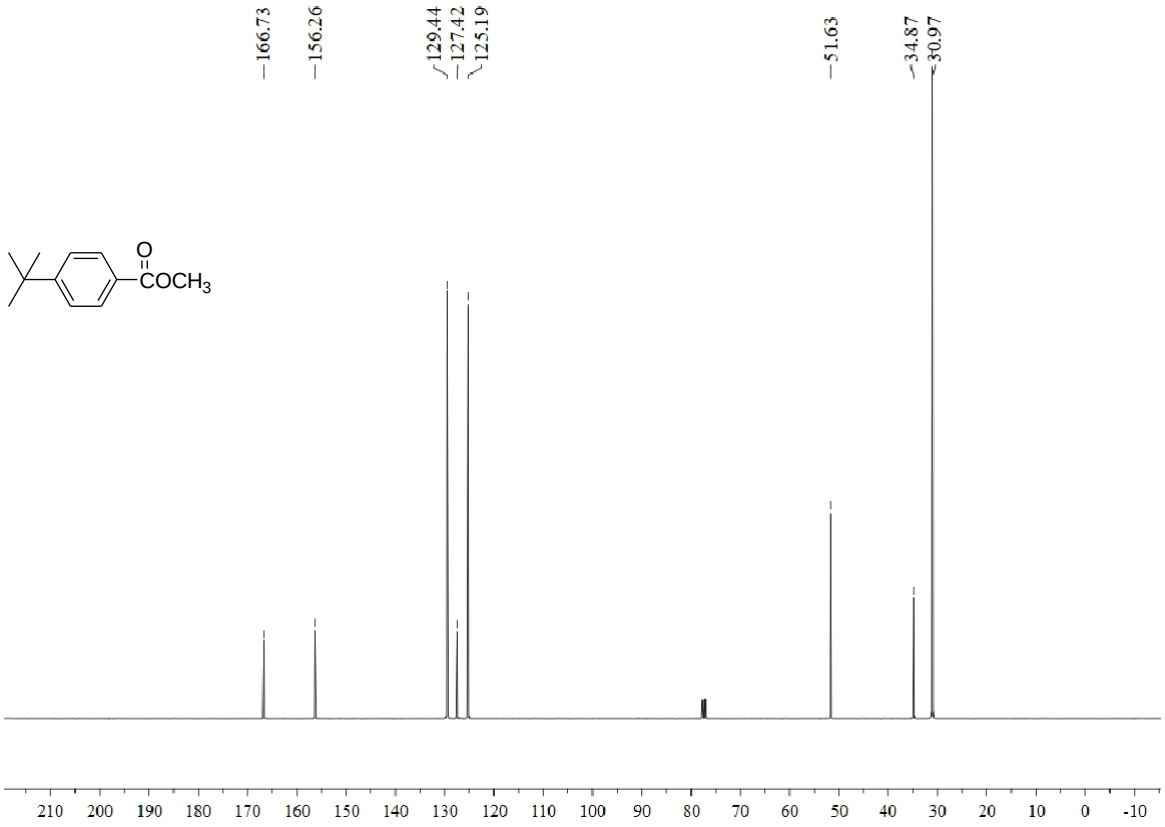
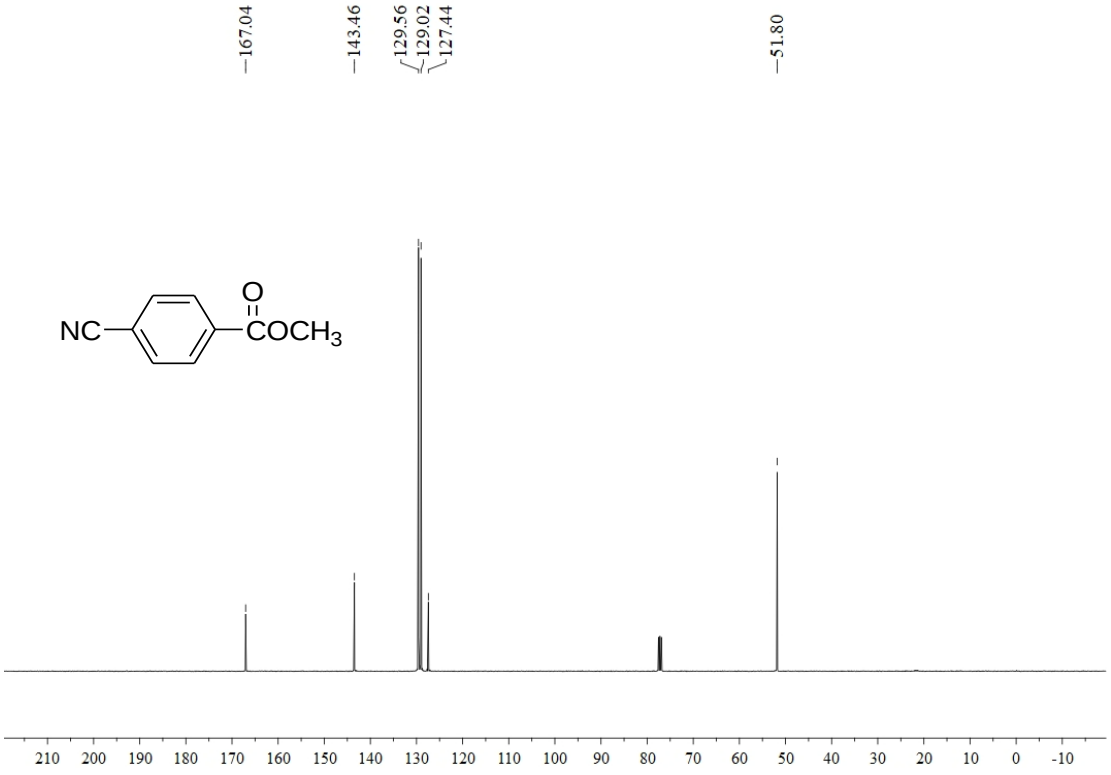


Figure S26 ^{1}H and ^{13}C NMR of Methyl 4-tert-butylbenzoate



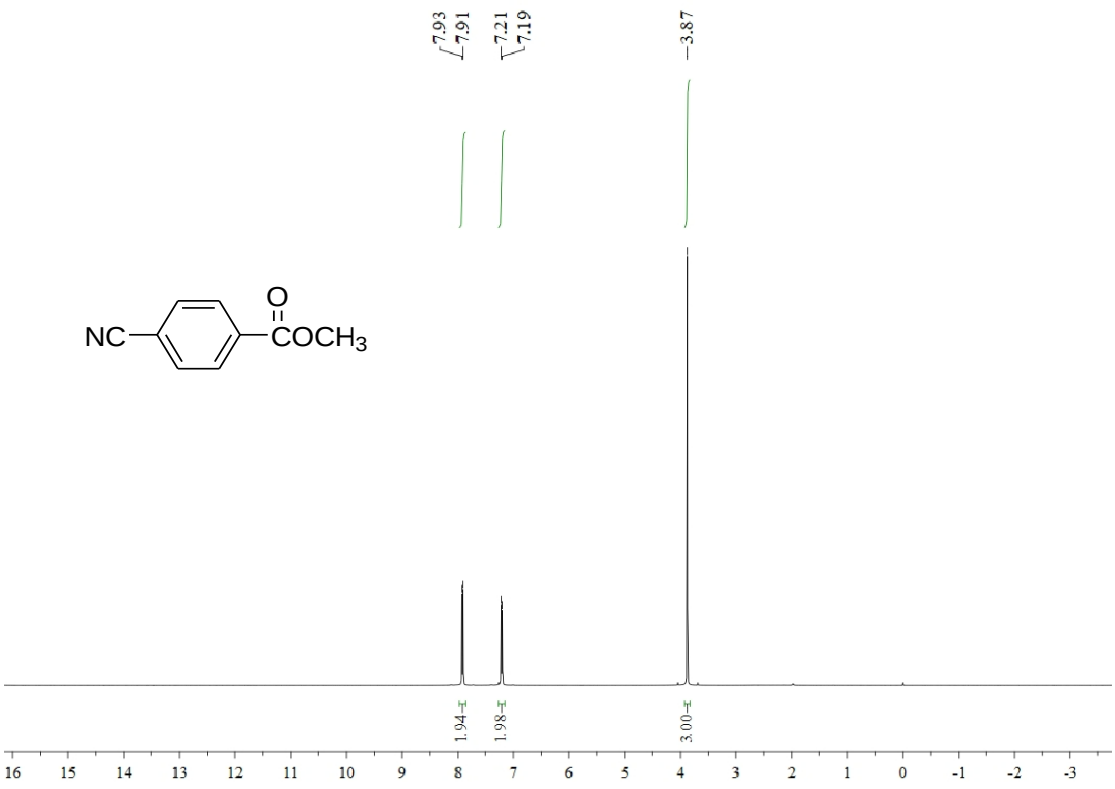
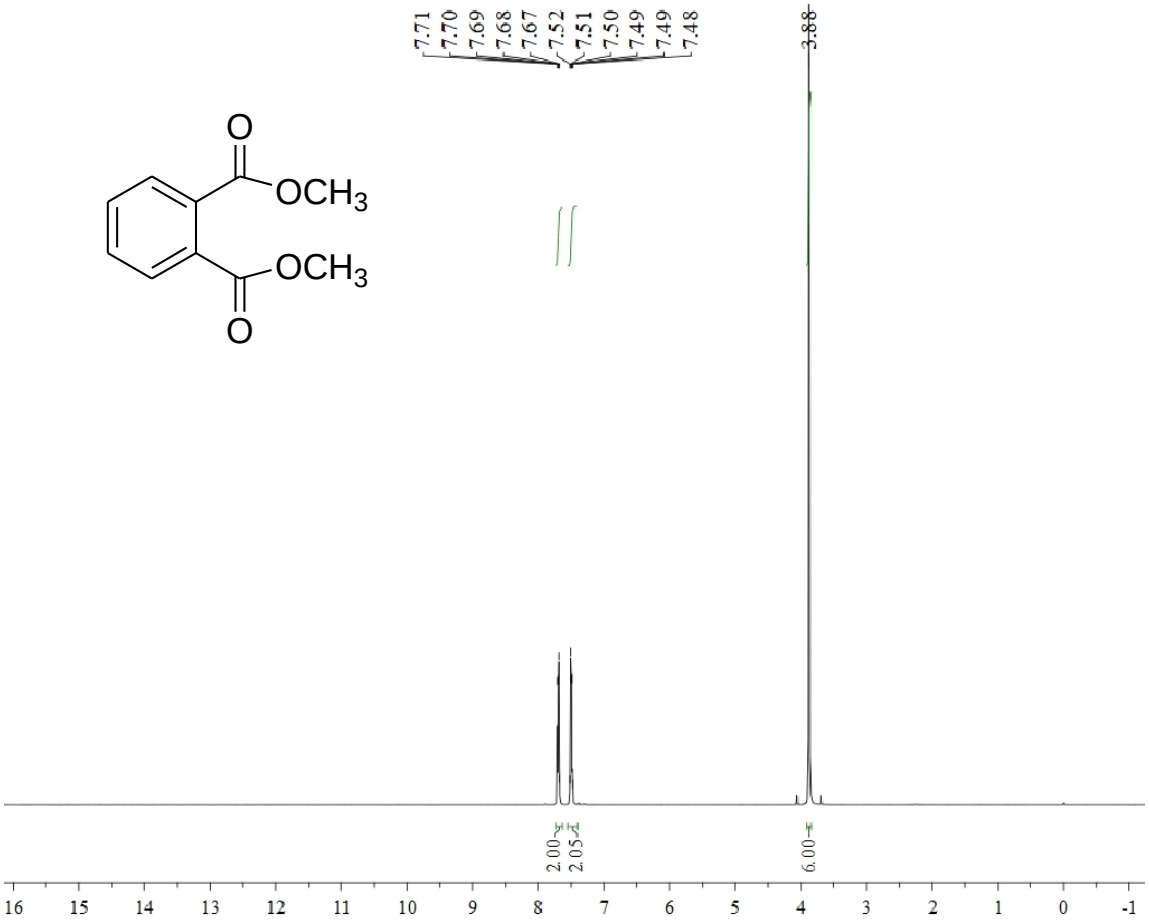


Figure S27 ^{1}H and ^{13}C NMR of Methyl 4-cyanobenzoate



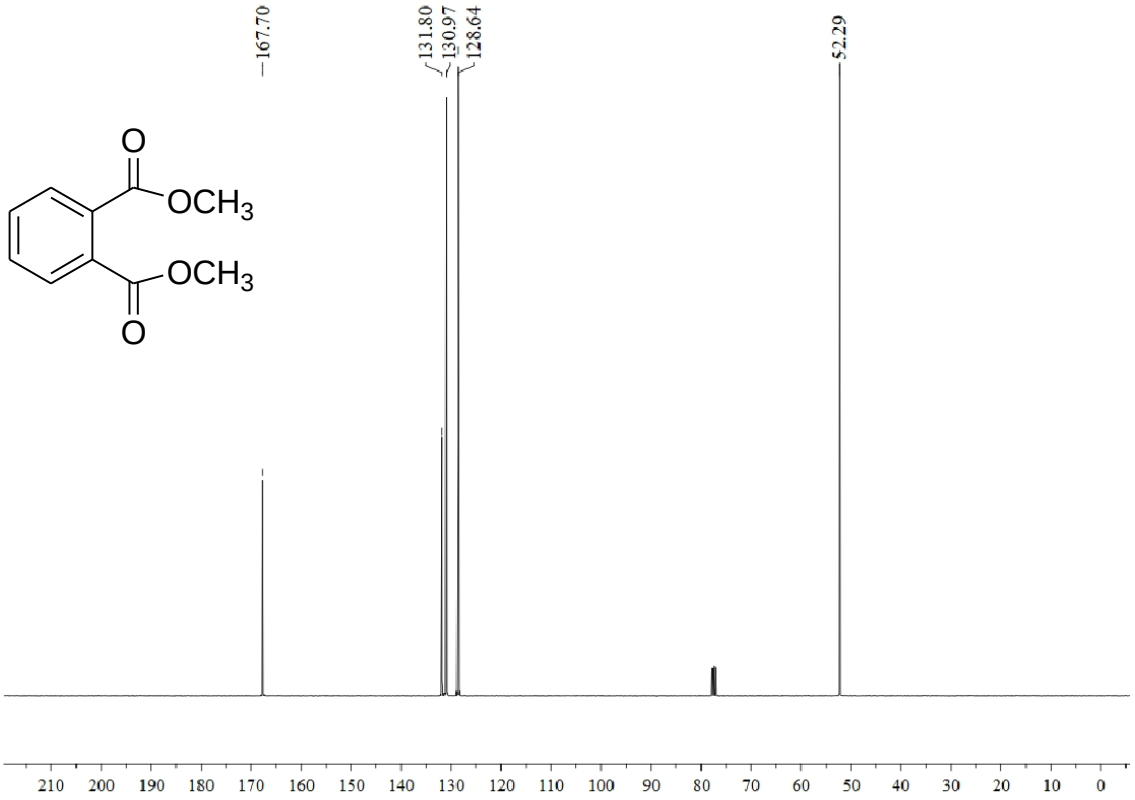
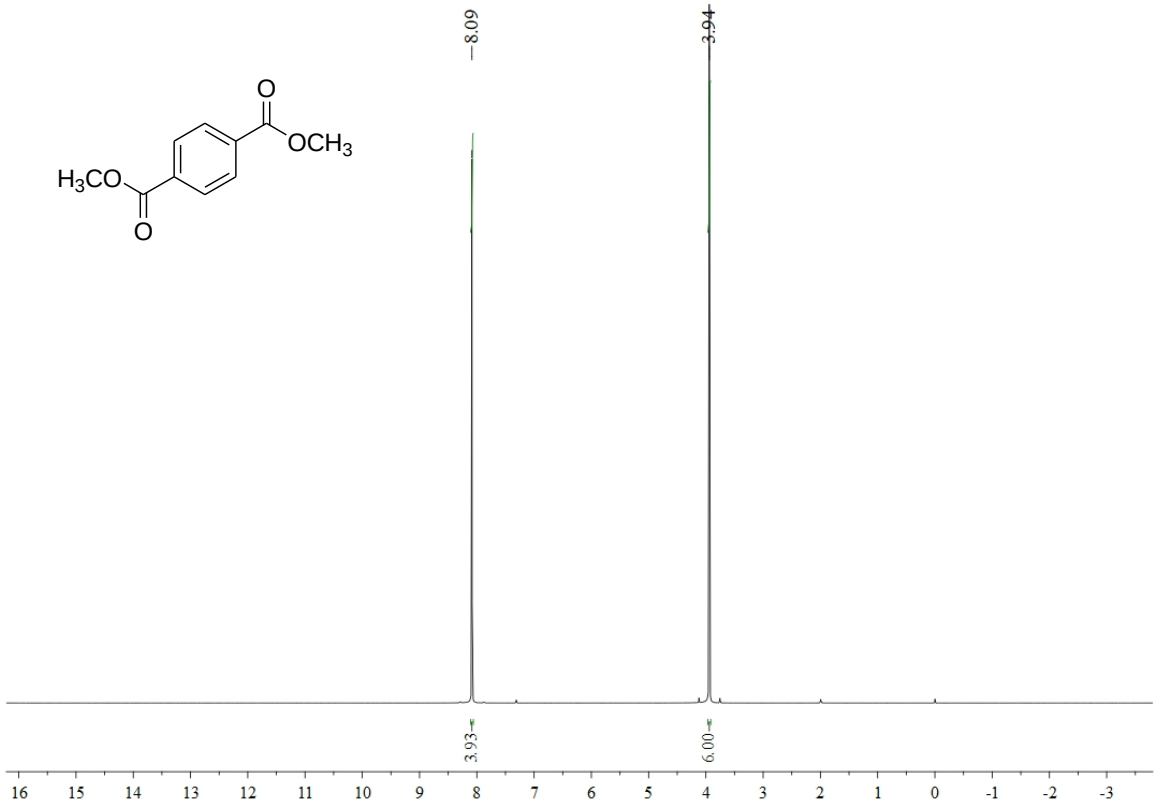


Figure S28 ^{1}H and ^{13}C NMR of o-Dimethyl phthalate



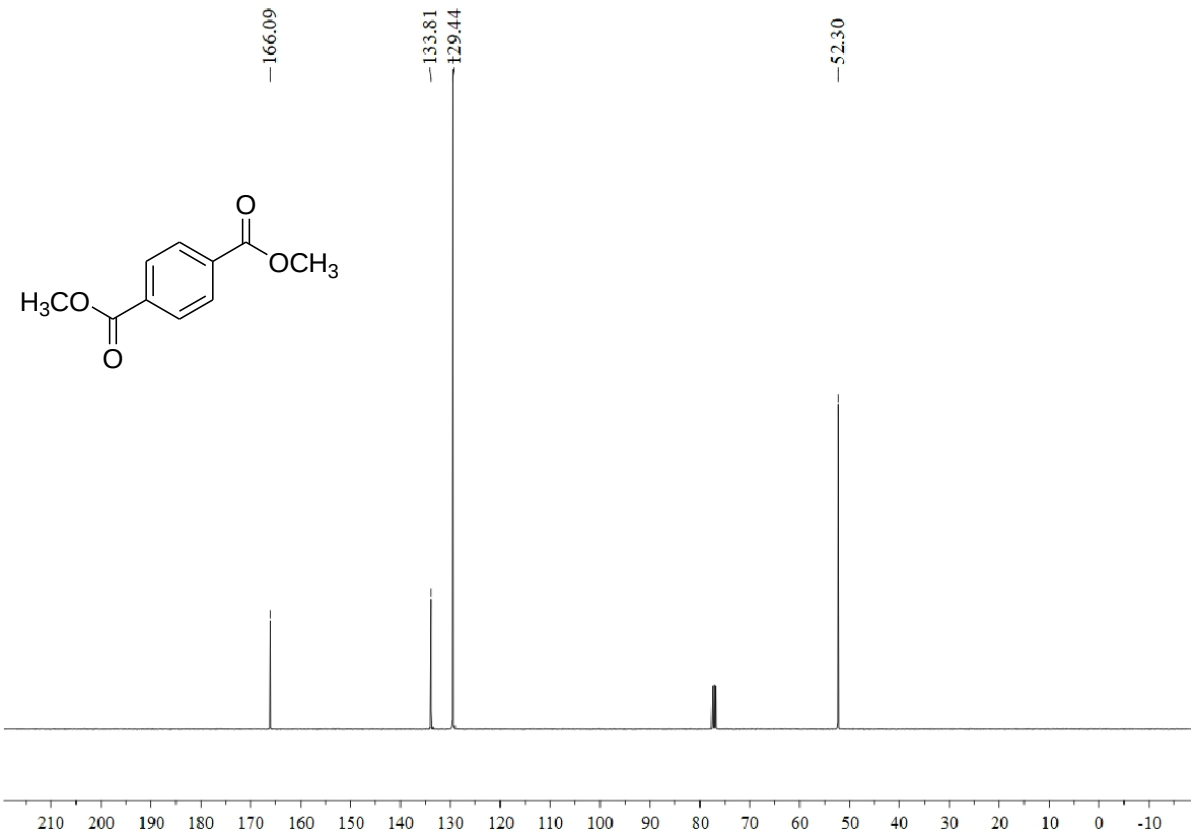
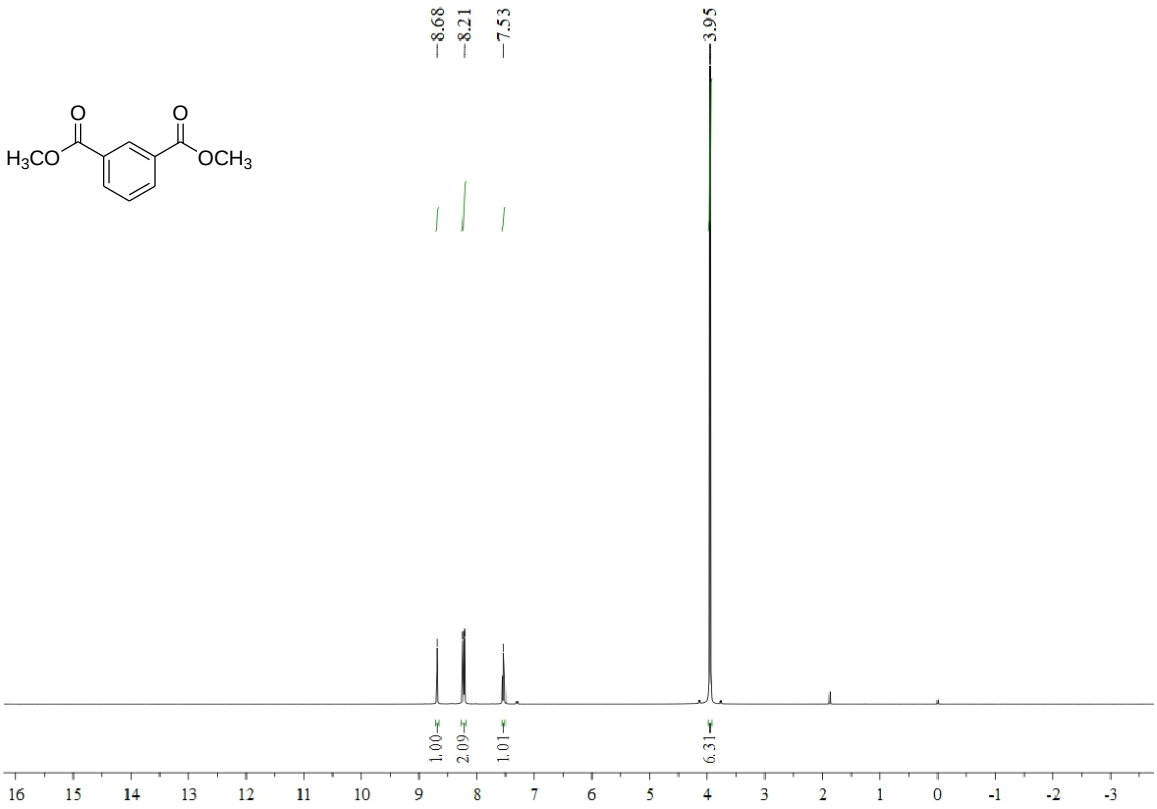


Figure S29 ^{1}H and ^{13}C NMR of p-Dimethyl terephthalate



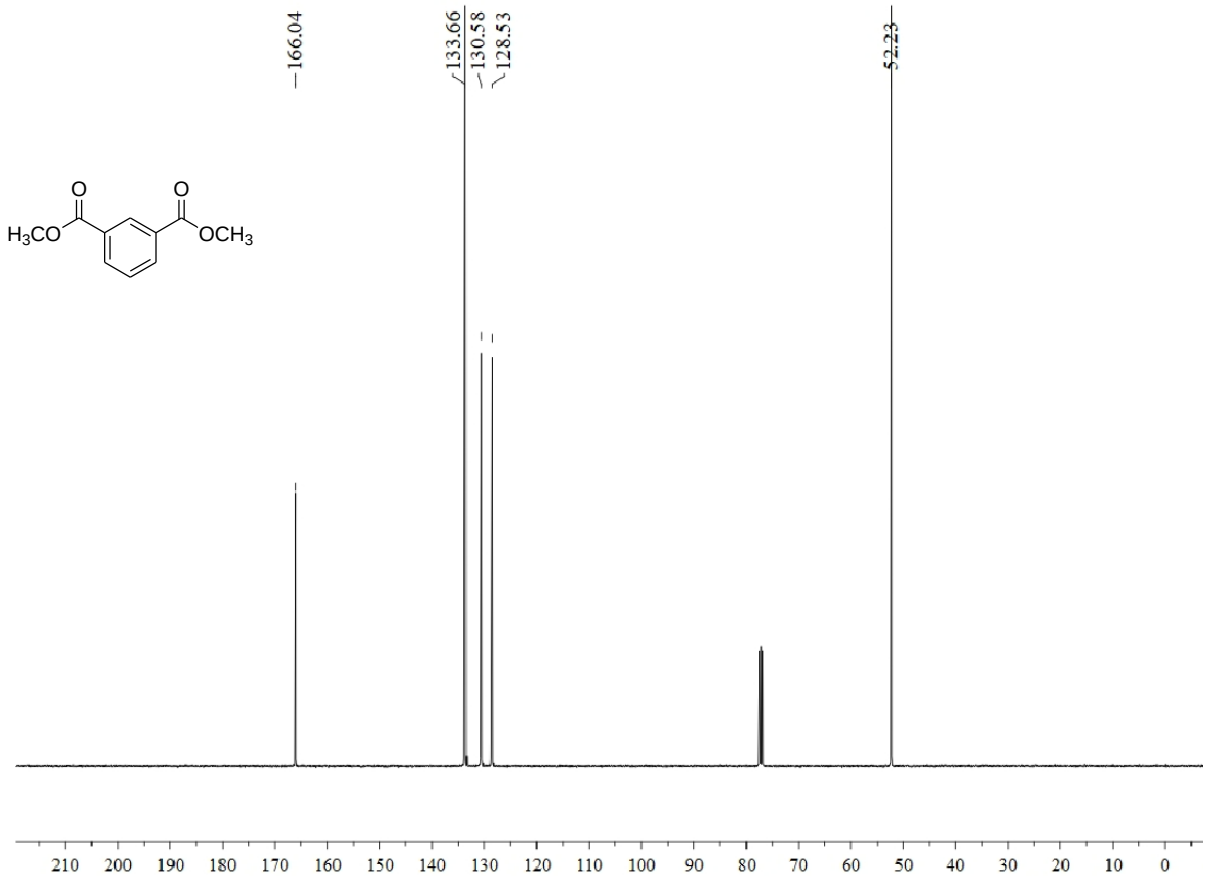
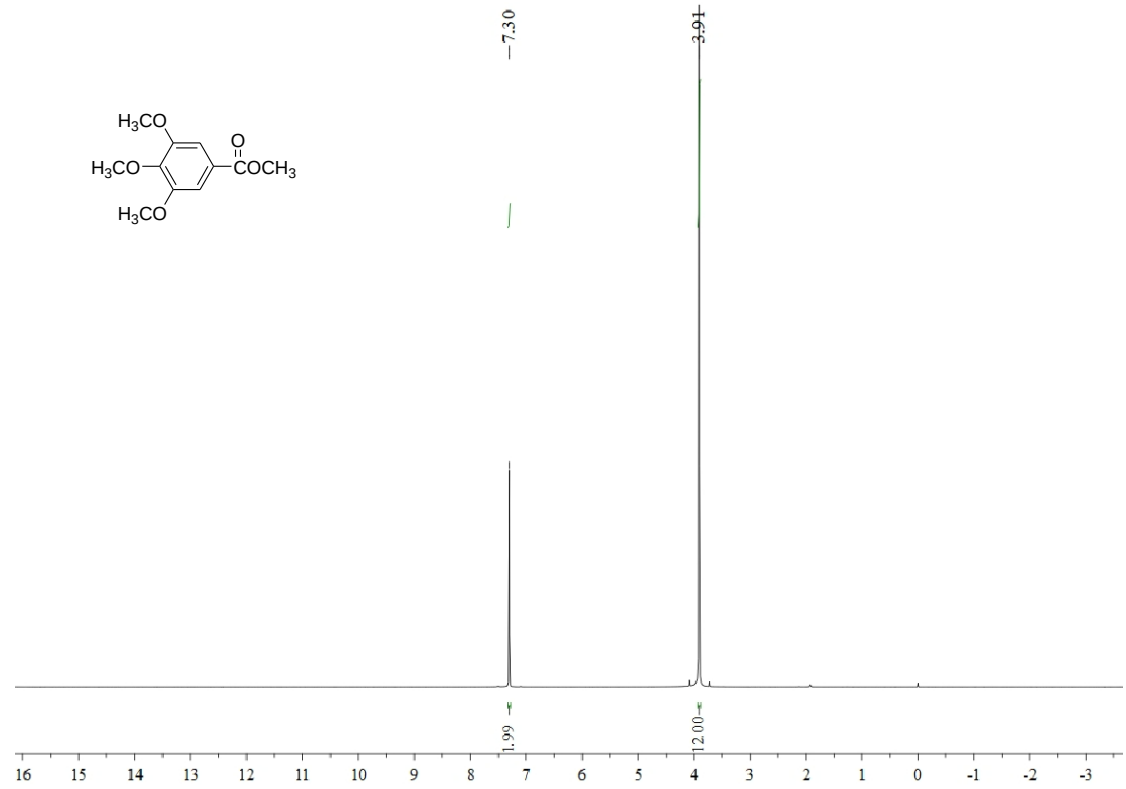


Figure S30 ^{1}H and ^{13}C NMR of m-Dimethyl terephthalate



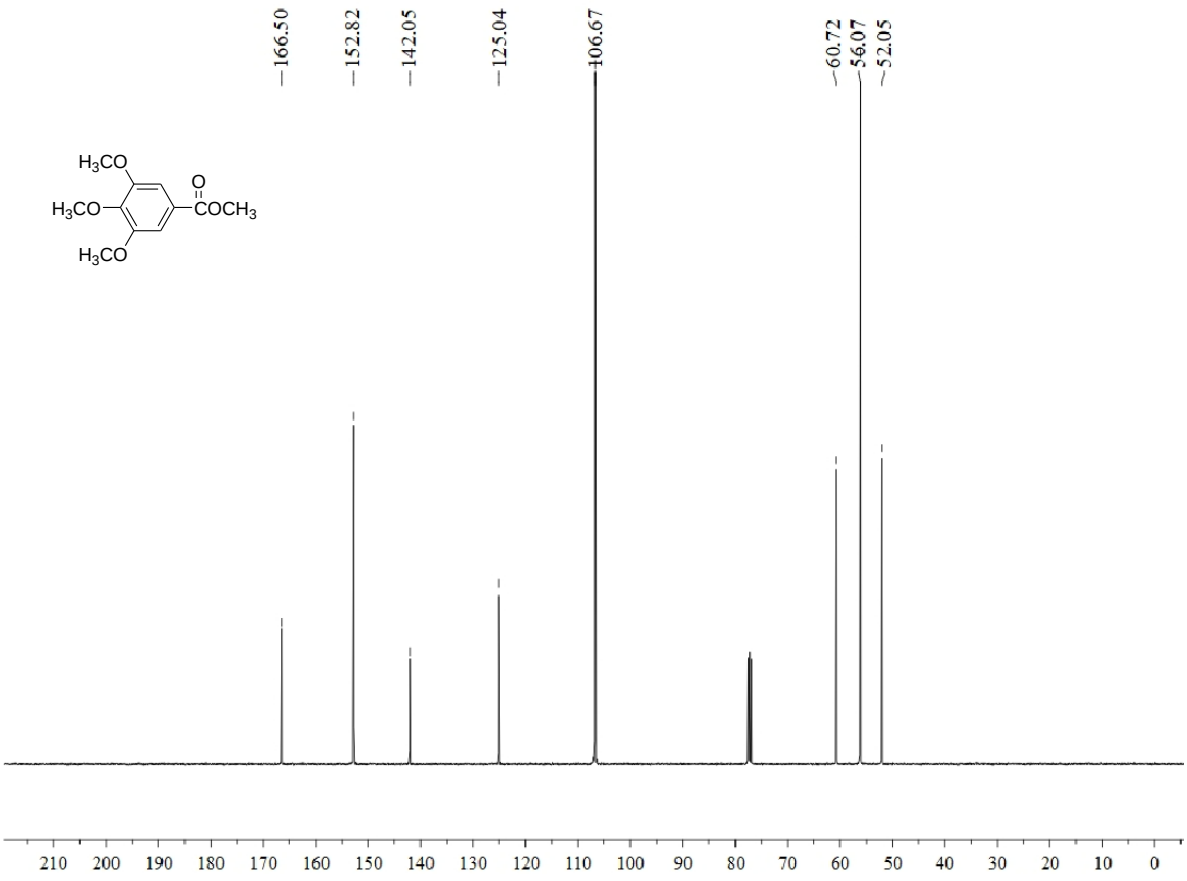


Figure S31 ^{1}H and ^{13}C NMR of Methyl 3,4,5-trimethoxybenzoate

References:

1. Cao, Y.-F.; Li, L.-J.; Liu, M.; Xu, H.; Dai, H.-X. Palladium-Catalyzed, Copper(I)-Promoted Methoxycarbonylation of Arylboronic Acids with O-Methyl S-Aryl Thiocarbonates. *The Journal of Organic Chemistry* **2020**, *85*, 4475-4481, doi:10.1021/acs.joc.0c00198.
2. Zhu, Y.; Yan, H.; Lu, L.; Liu, D.; Rong, G.; Mao, J. Copper-Catalyzed Methyl Esterification Reactions via C–C Bond Cleavage. *The Journal of Organic Chemistry* **2013**, *78*, 9898-9905, doi:10.1021/jo4016387.
3. Jiang, Y.; Pan, S.; Zhang, Y.; Yu, J.; Liu, H. Copper-Catalyzed Decarboxylative Methylation of Aromatic Carboxylic Acids with PhI(OAc)2. *European Journal of Organic Chemistry* **2014**, *2014*, 2027-2031, doi:https://doi.org/10.1002/ejoc.201301815.