Synthesis of a series of methyl benzoates by esterification with a Zr/Ti solid acid catalyst

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Characterization of ^{1}H, ^{19}F and ^{13}C NMR spectra of esterification products

Methyl 2-Methylbenzoate(1)[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(2)[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(3)[1] White solid; mp 33-35 °C; ^{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-fluorobenzoate(4)[2] 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(5)[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-fluorobenzoate(6)[2,4] 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-chlorobenzoate(7)[1,5] 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(8)[1,5] 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 (9)[1,5,6] 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 2-bromobenzoate(10)[7] 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 3-bromobenzoate(11)[7] 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(12)[8] White solid; mp 77-80 °C ; ^{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-iodobenzoate(13)[9] 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 3-iodobenzoate(14)[10] 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 4-iodobenzoate(15)[11] 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 benzoate(16)[6] 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 4-Tert-Butylbenzoate(17)[8]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(18)[12] 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.

Methyl 2-nitrobenzoate(19)[5] 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(20)[5] Yellow solid; mp 76-80 °C**;** ^{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 4-nitrobenzoate(21)[5,6] Yellow solid; mp 94-97 °C**;** ^{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-methoxybenzoate(22)[1] 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(23)[1] 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(24)[1,6] 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-trifluoromethylbenzoate(25)[13] Clear liquid; ^1H 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 3-trifluoromethylbenzoate(26)[13] Clear liquid; ^1H 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(27)[13] Clear liquid; ^1H 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.

o-Dimethyl phthalate(28)[14] Clear liquid; ^1H 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.

m-Dimethyl terephthalate(29)[14] White solid; mp 65-68 ºC; ^1H 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.

p-Dimethyl terephthalate(30)[14] White solid; mp 141-143 ºC; ^1H 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.

Methyl 3,4,5-trimethoxybenzoate(31)[5] White solid; mp 81-83 ºC; ^1H 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.

Methyl 2,3,4,5,6-pentafluorobenzoate(32)[15,16] Clear liquid; ^1H NMR(400 MHz, $CDCl_3$):δ = 4.01(s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$): δ = 259.13, 146.64, 144.29-144.10(m), 141.93-141.62(m),138.82-138.67(m), 136.46-136.18(m), 108.09-107.73(m), 52.78; ^{19}F NMR (376 MHz, $CDCl_3$): δ =112.56; HRMS(ESI-TOF)*m/z*: calcd for $C8H3F5O2^{4+}$: 217.0472 $(M+H)^+$, found: 217.0476.

Copy of ^{1}H, ^{19}F and ^{13}C NMR spectra of esterification products

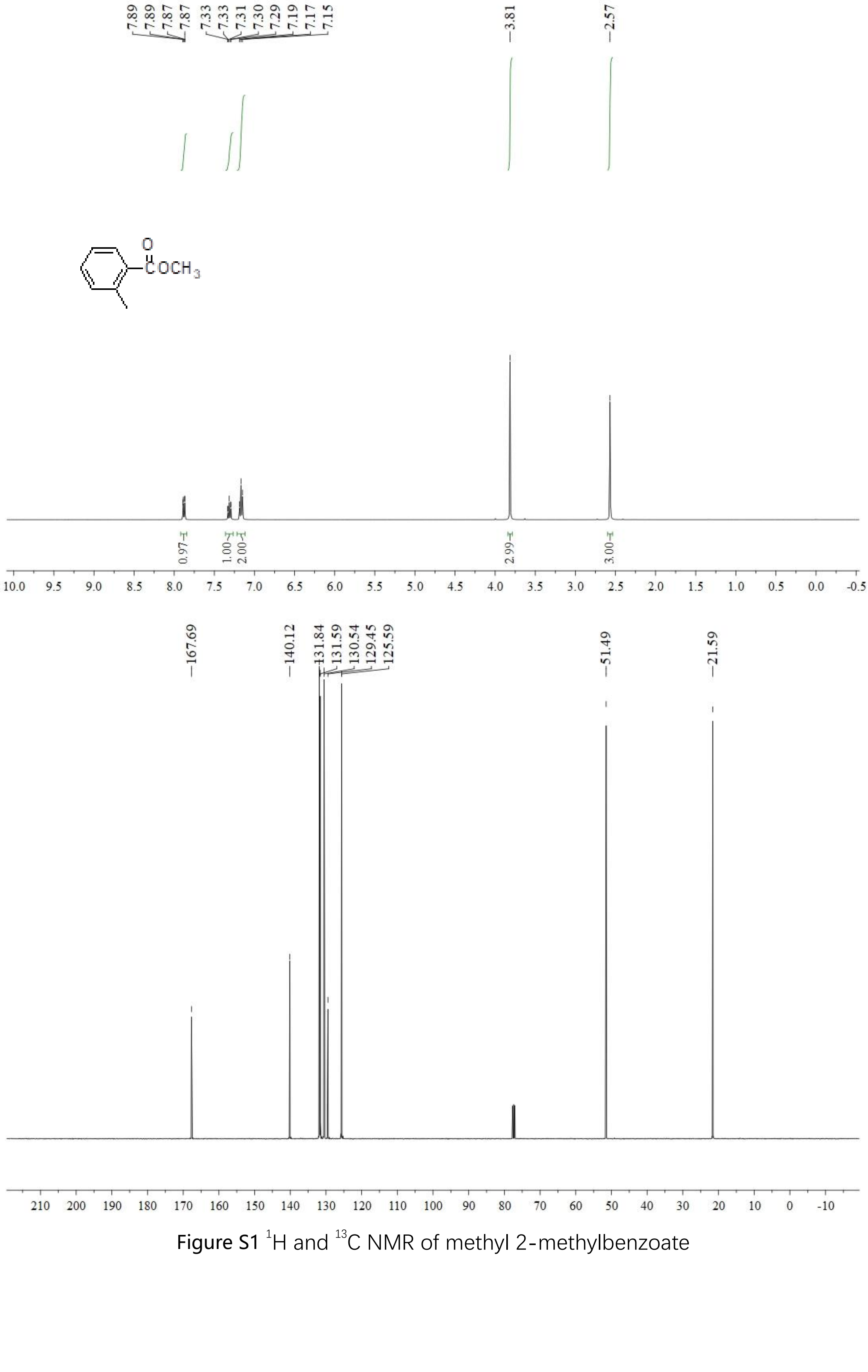


Figure S1 ^{1}H and ^{13}C NMR of methyl 2-methylbenzoate

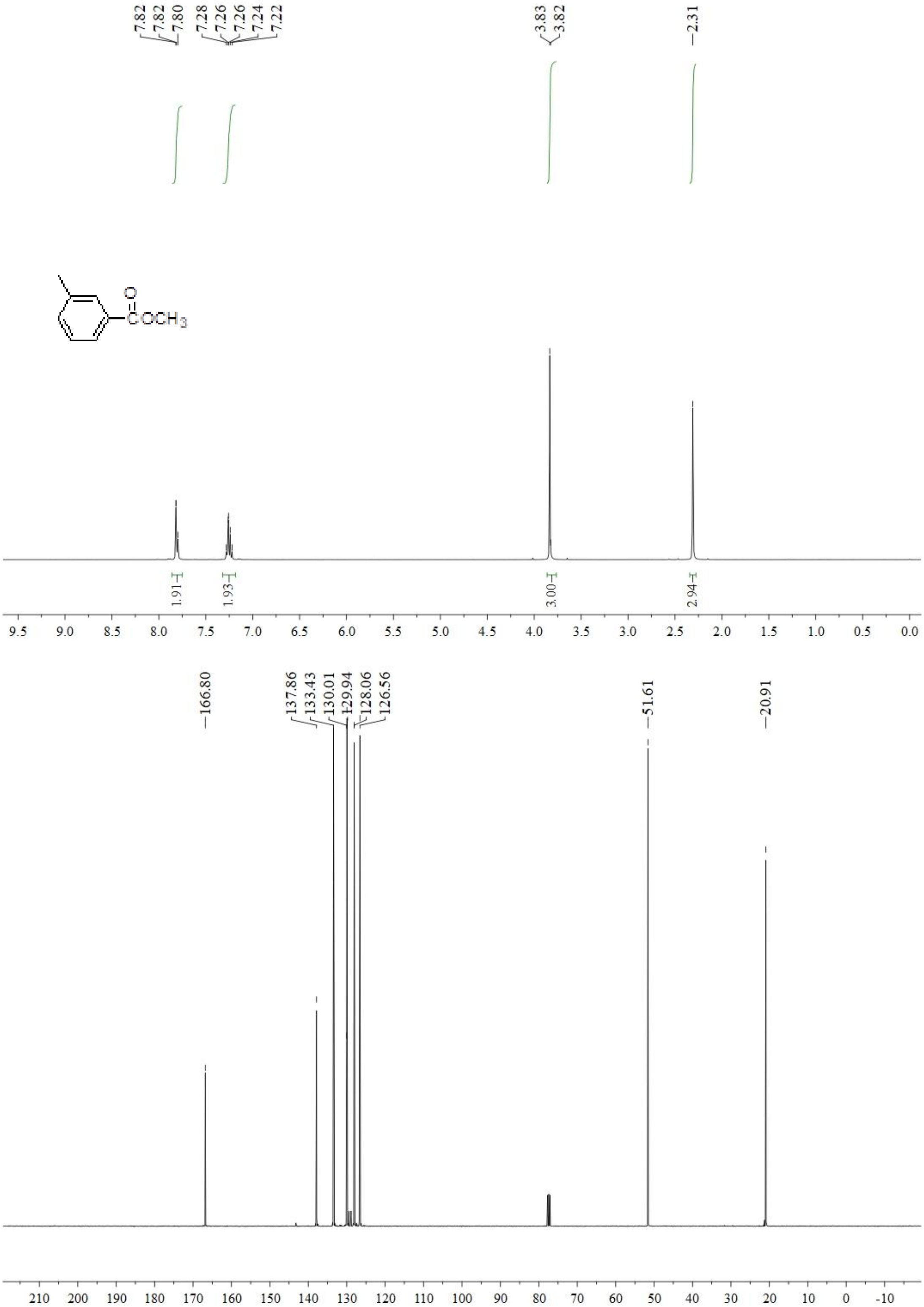


Figure S2 ^{1}H and ^{13}C NMR of methyl 3-methylbenzoate

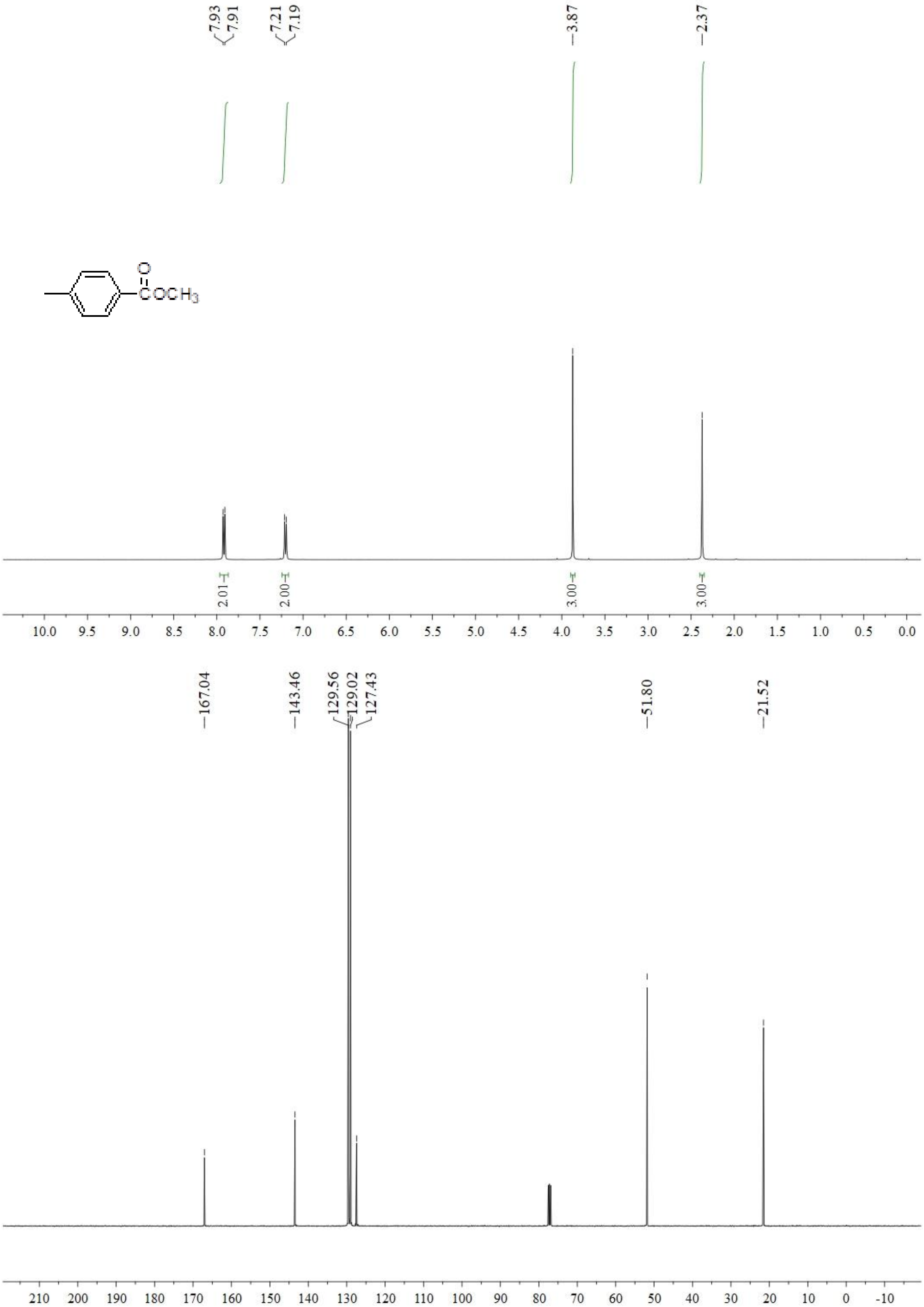
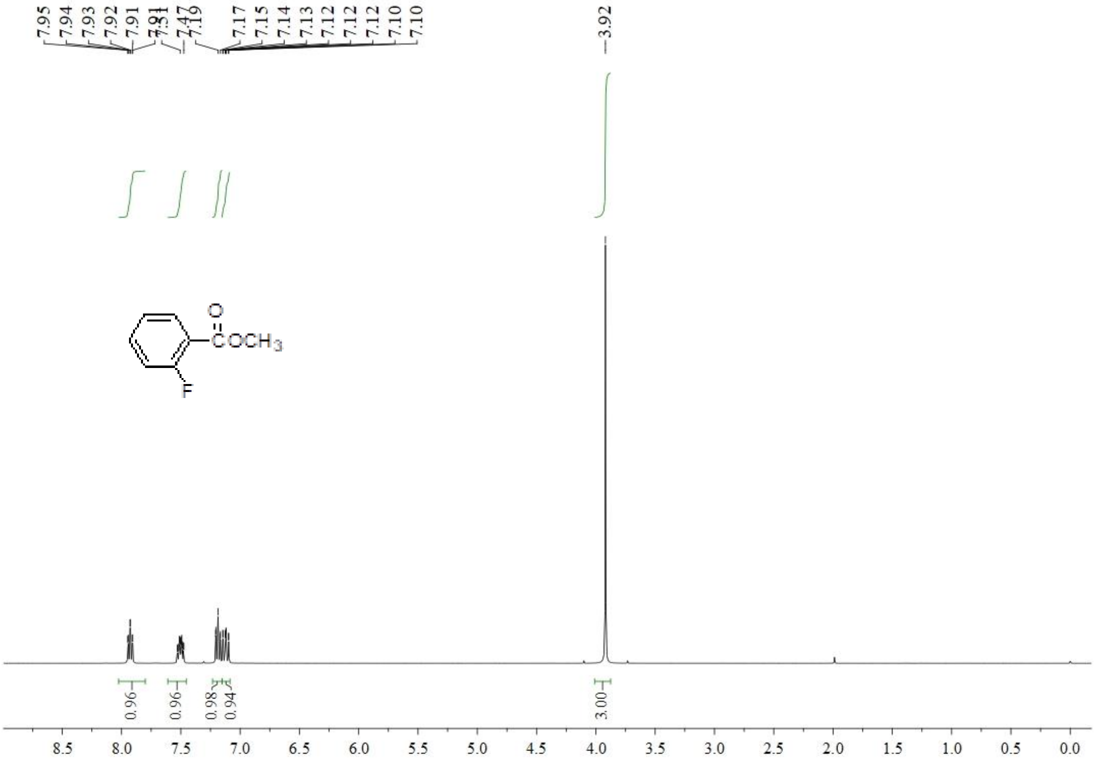


Figure S3 ^{1}H and ^{13}C NMR of methyl 4-methylbenzoate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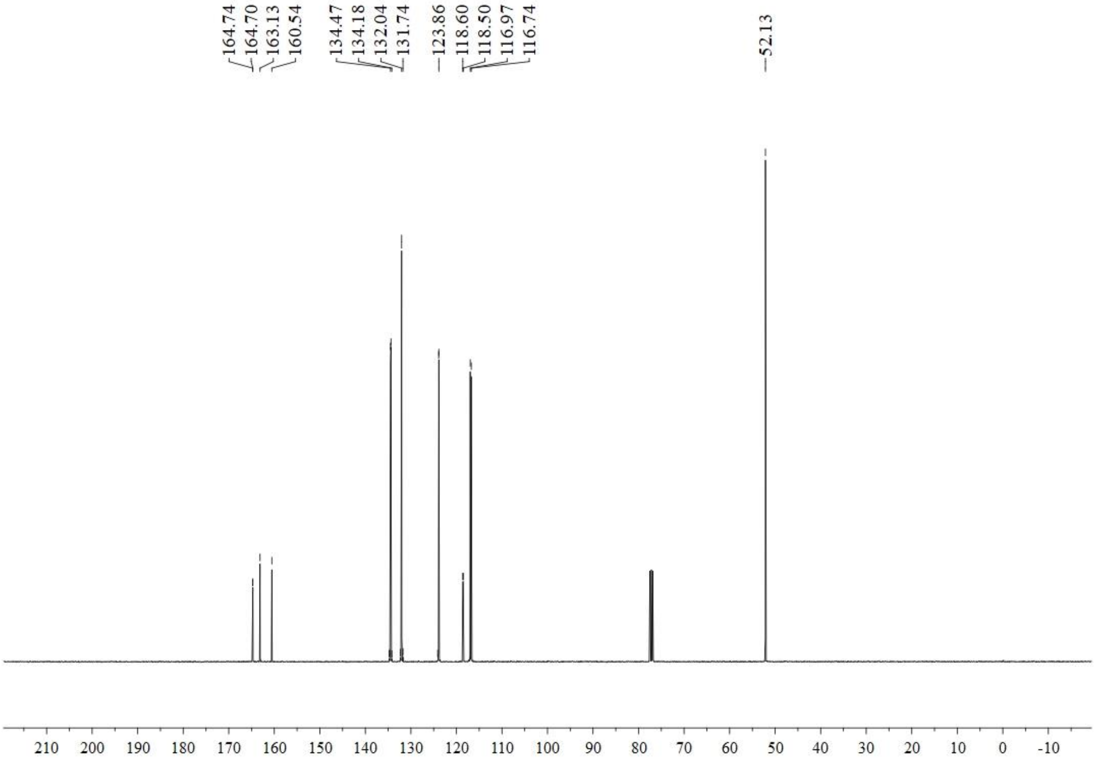
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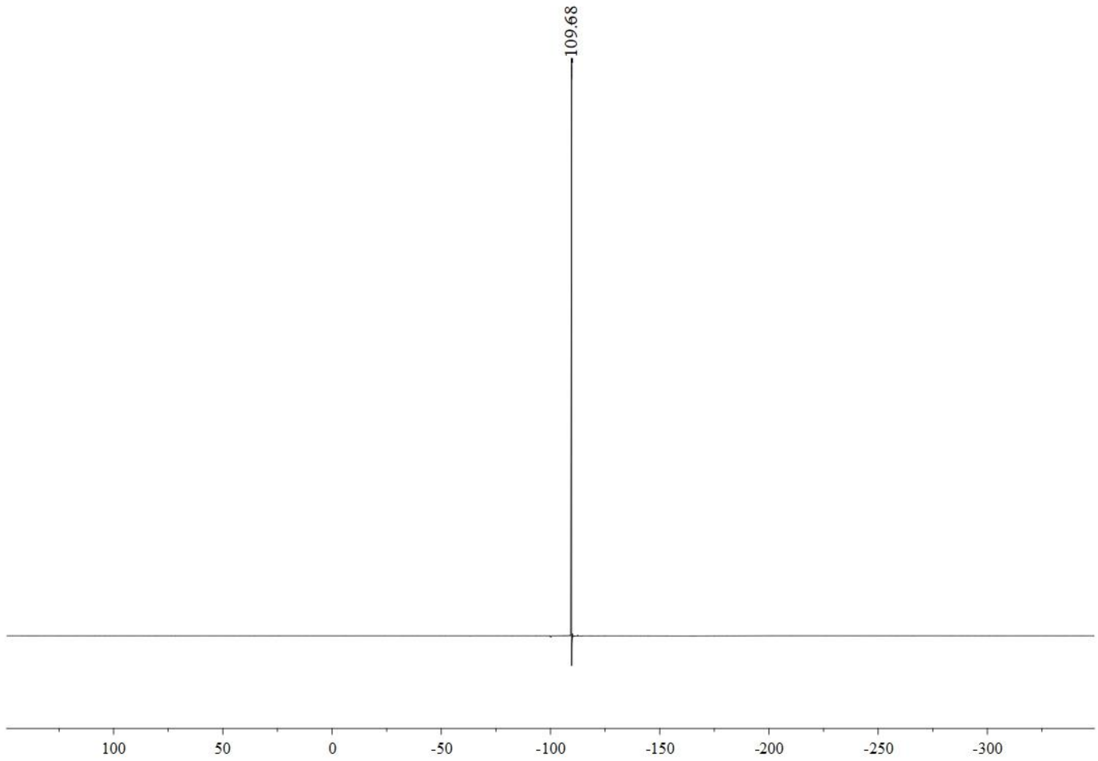
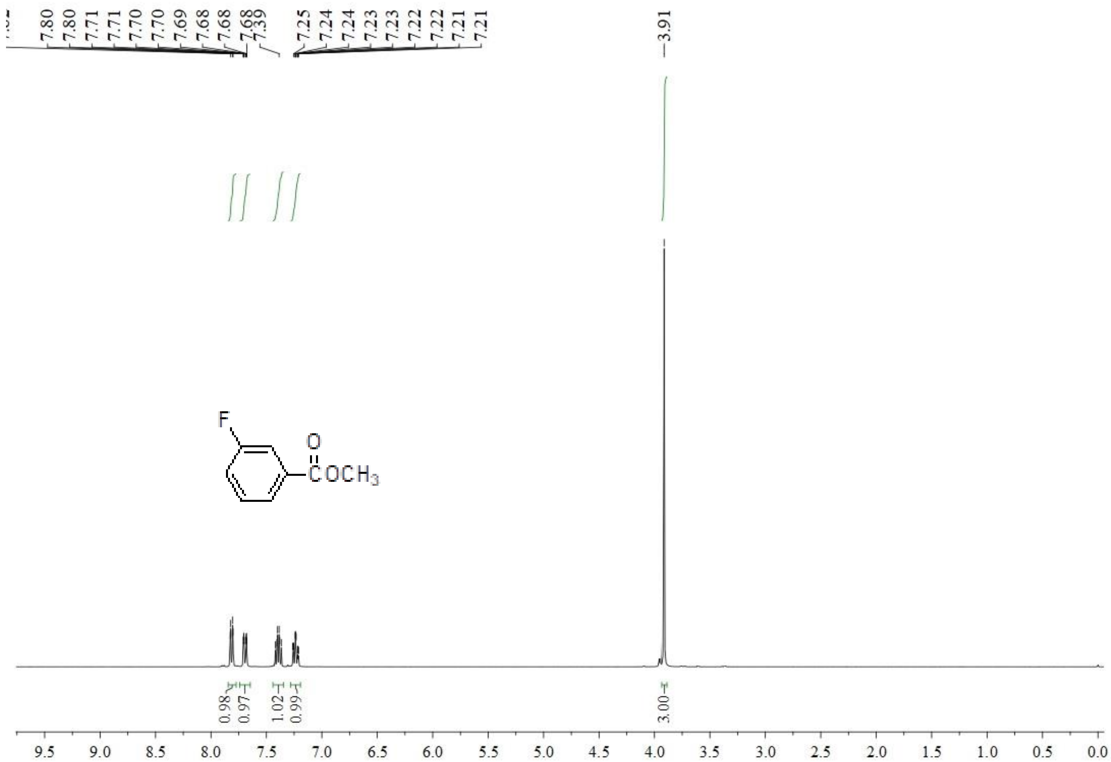
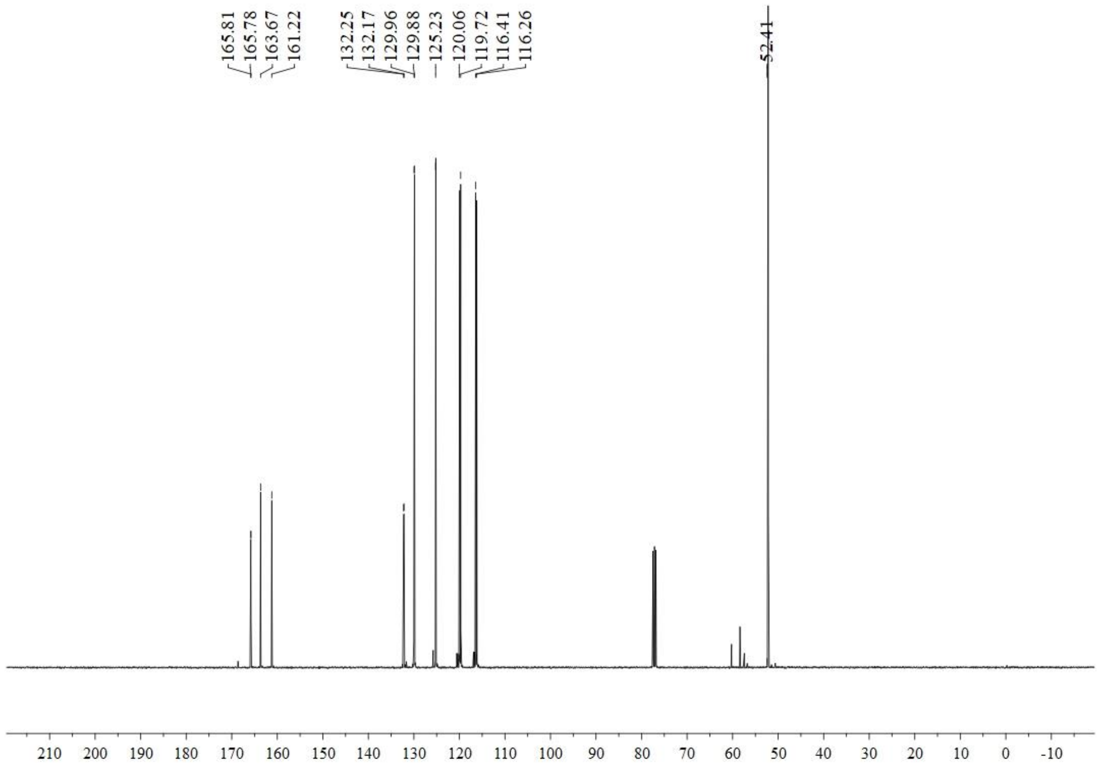


Figure S4 ^{1}H, ^{13}C and ^{19}F NMR of methyl methyl 2-fluorobenzoate





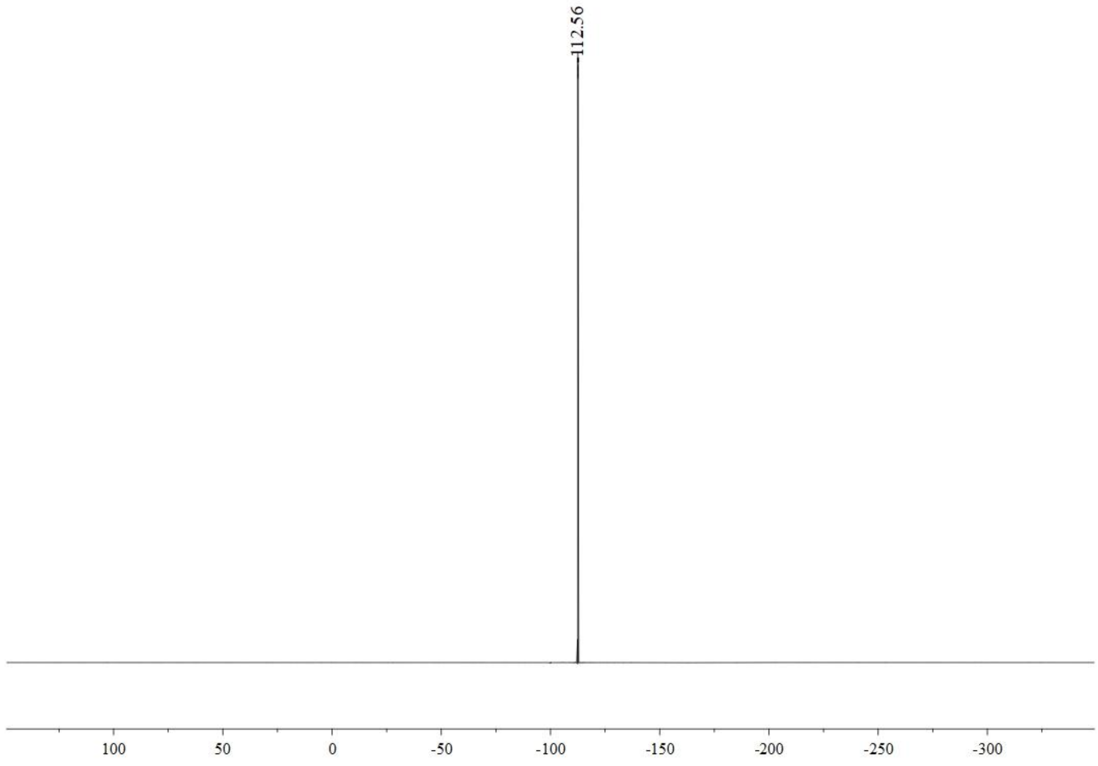
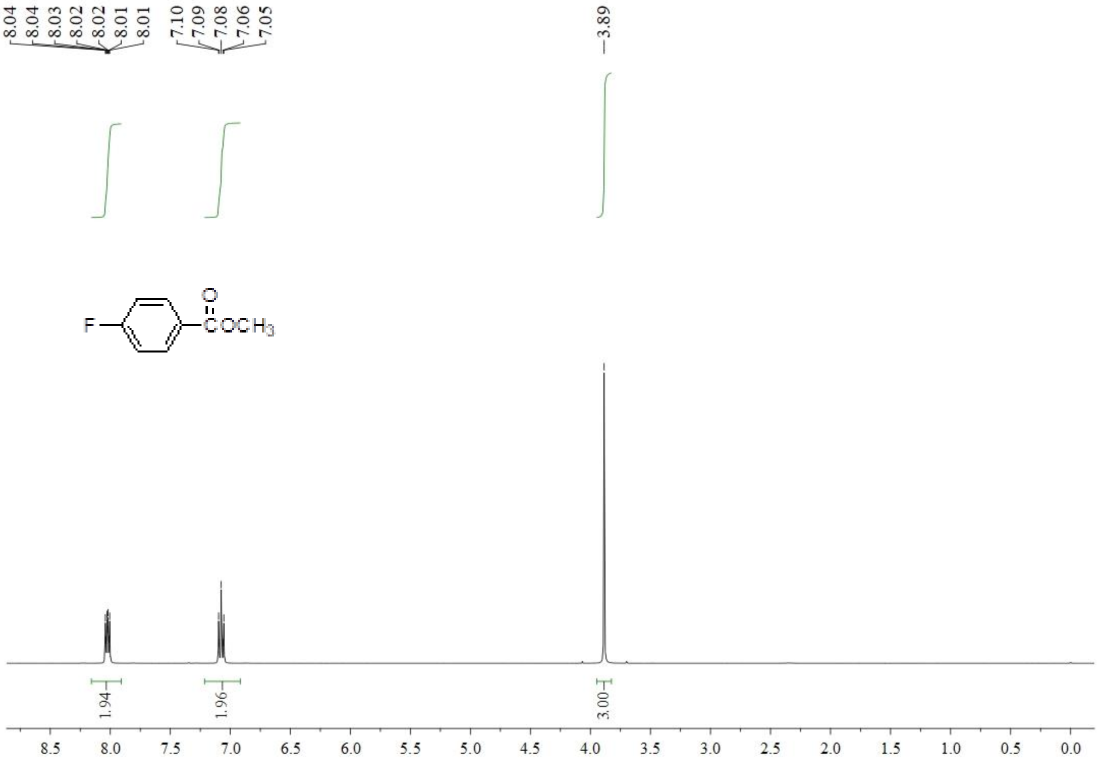
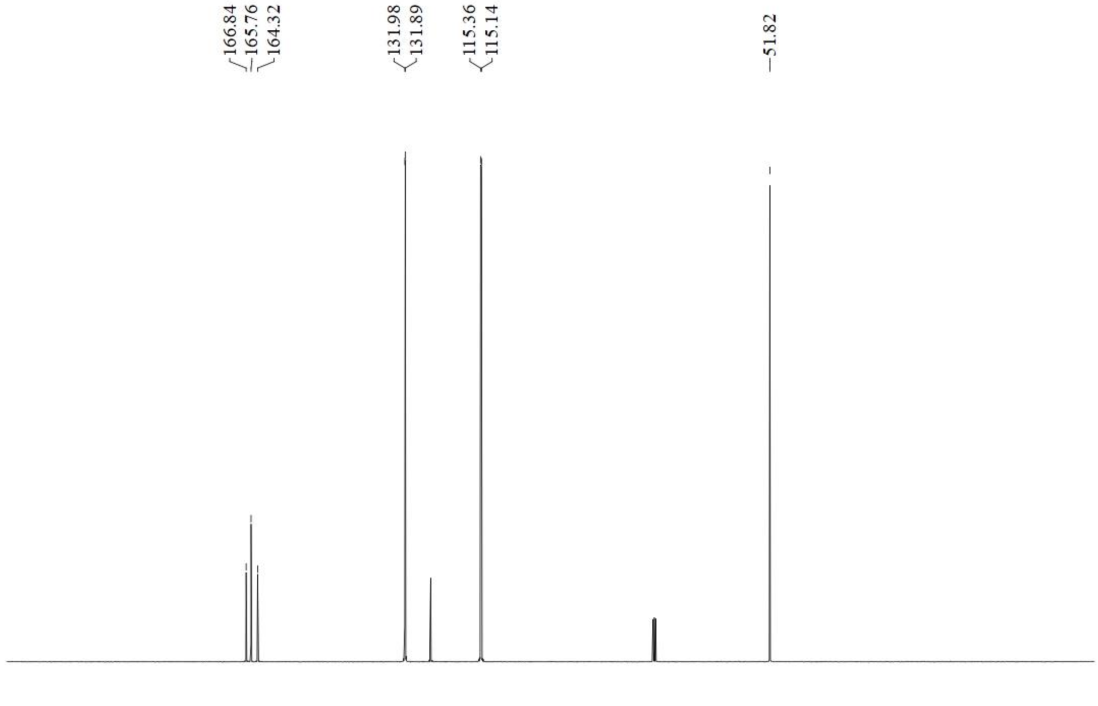


Figure S5 ^{1}H, ^{13}C and ^{19}F NMR of methyl methyl 3-fluorobenzoate


8.04
8.04
8.03
8.02
8.02
8.01
8.01
7.10
7.09
7.08
7.06
7.05
3.89
F
COCH3
O
1.94
1.96
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


166.84
165.76
164.32
131.98
131.89
115.36
115.14
51.82
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

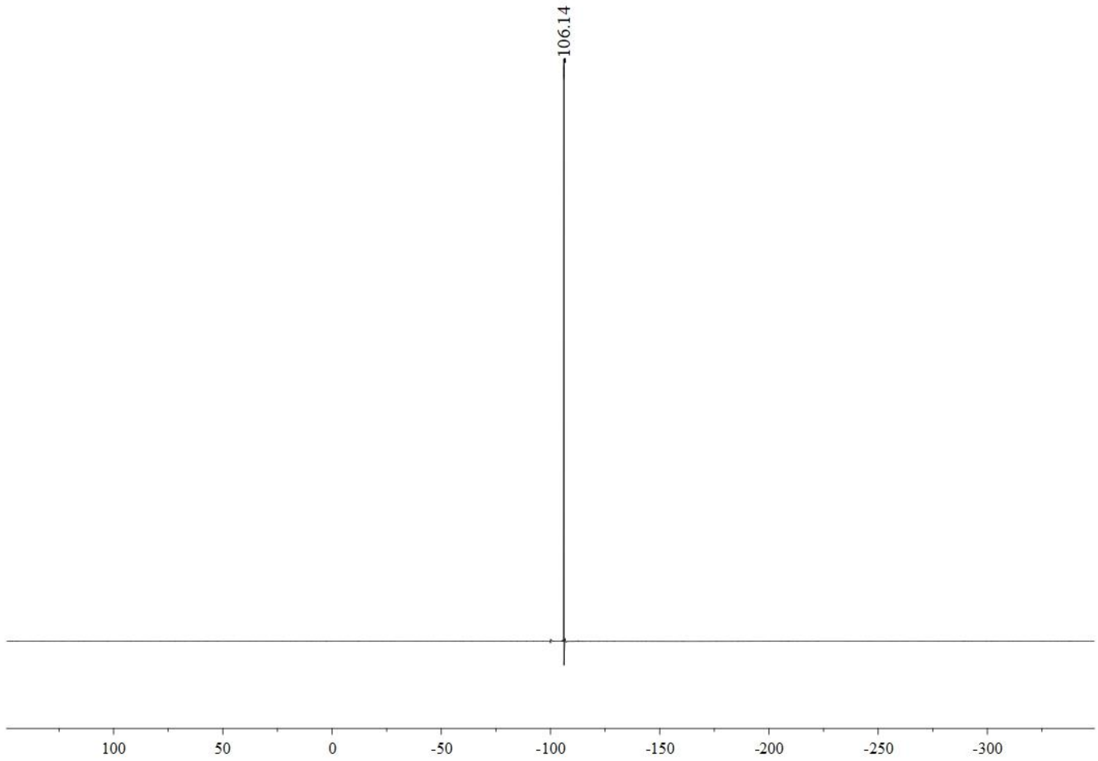
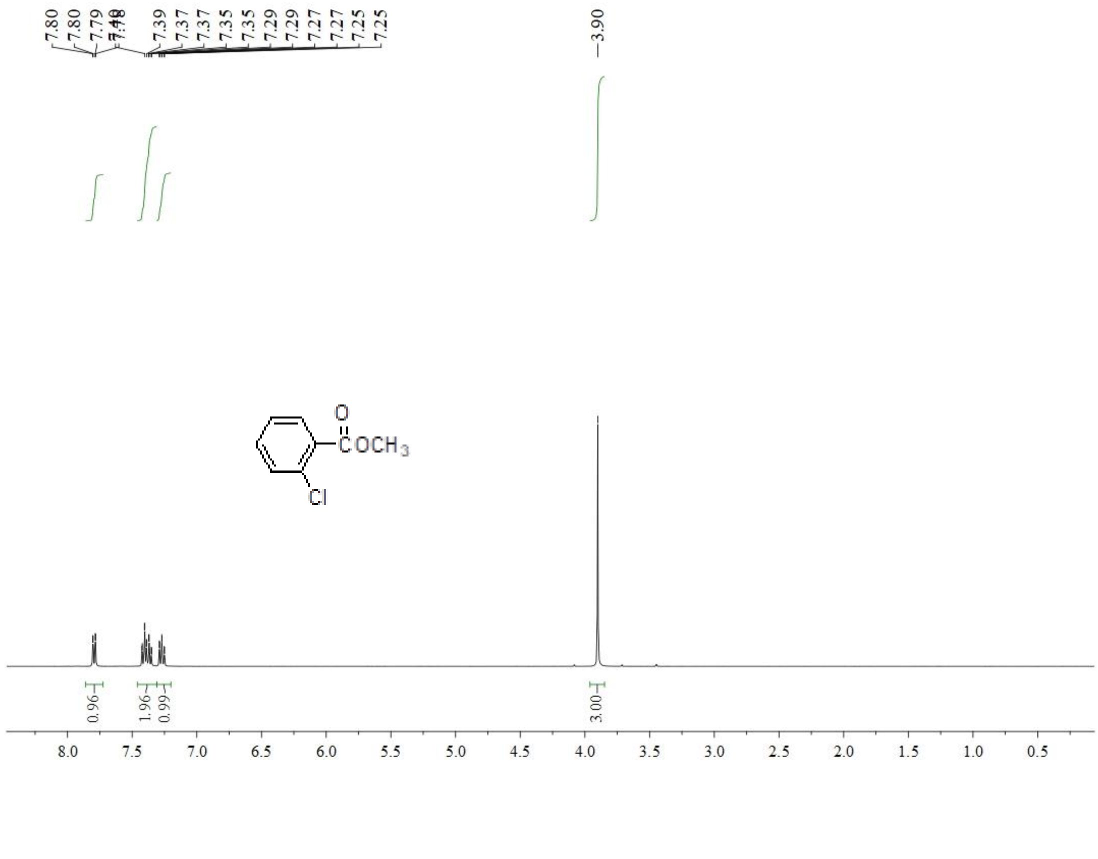


Figure S6 ^{1}H, ^{13}C and ^{19}F NMR of methyl methyl 4-fluorobenzoate



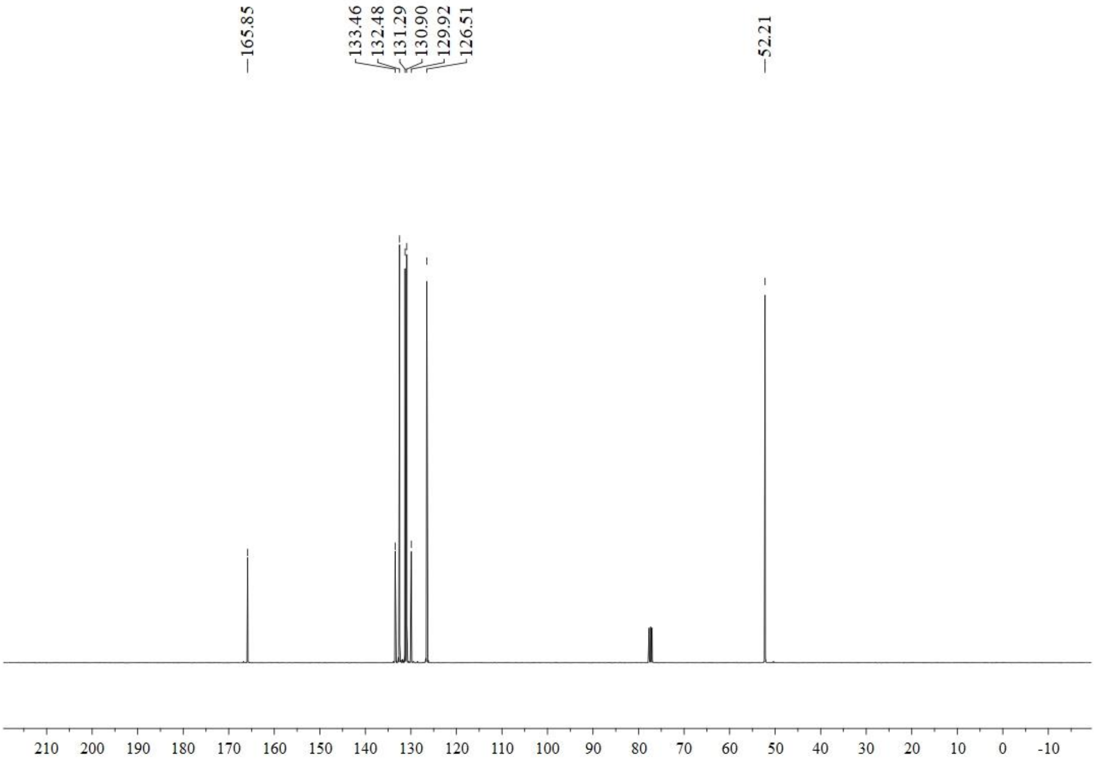
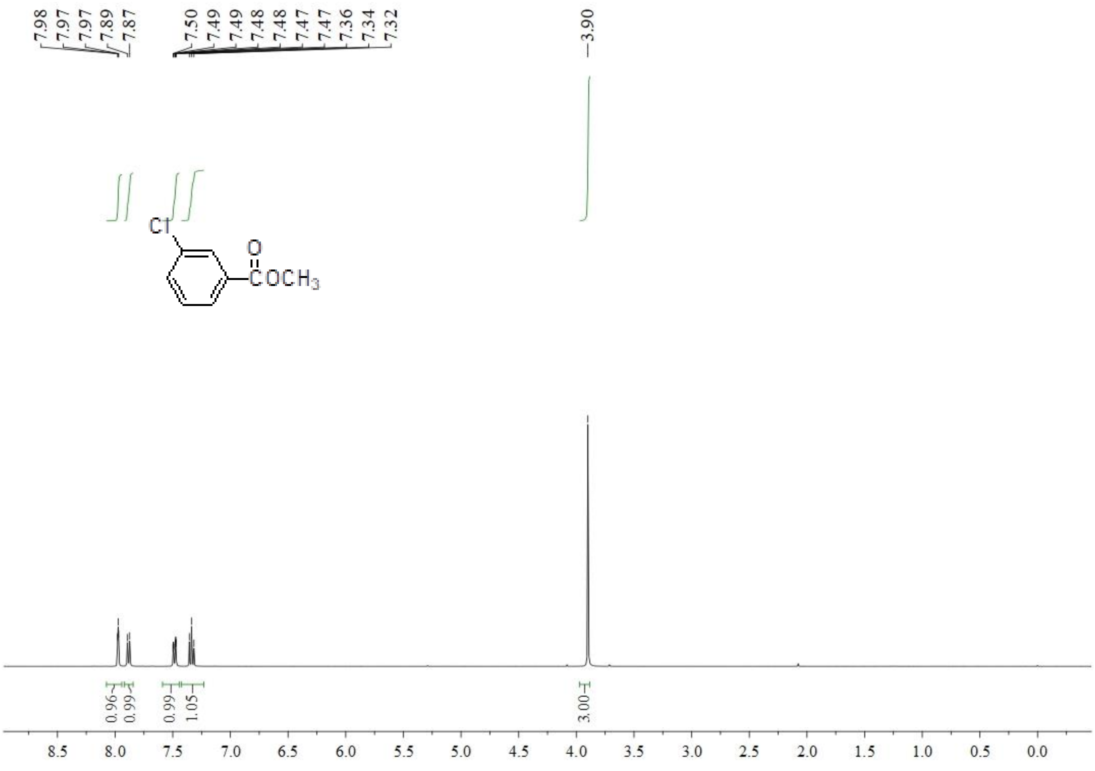


Figure S7 ^{1}H and ^{13}C NMR of methyl 2-chlorobenzoate



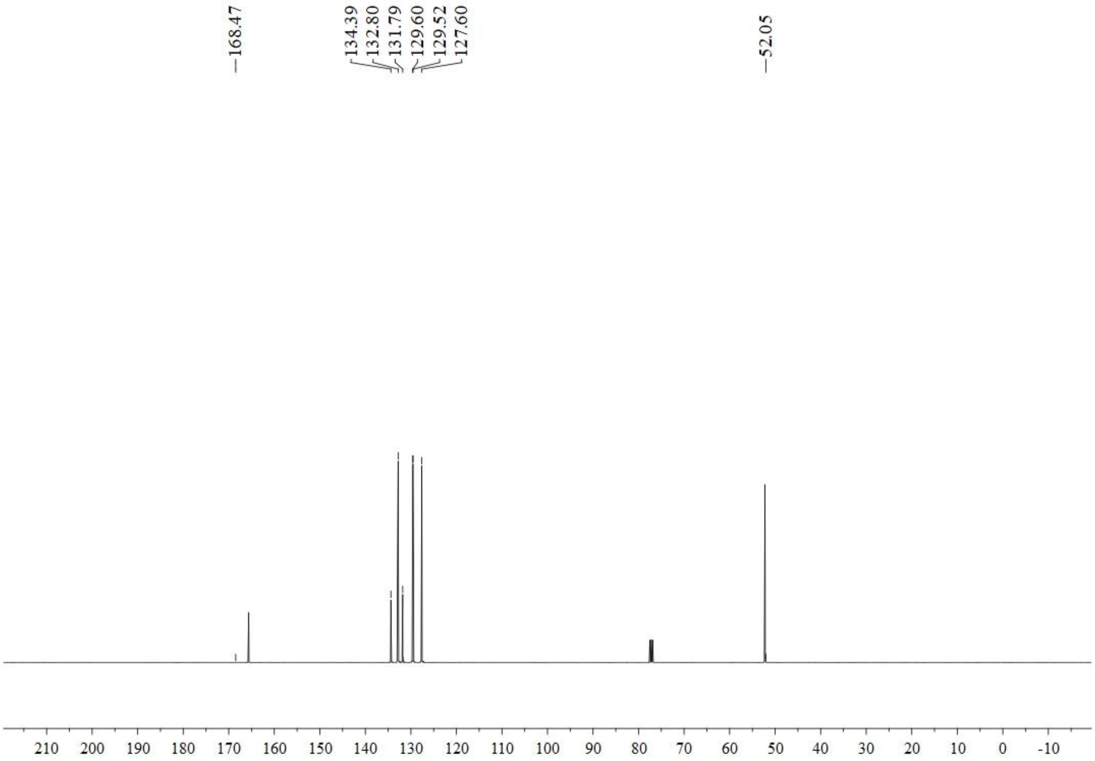


Figure S8 ^{1}H and ^{13}C NMR of methyl 3-chlorobenzoate

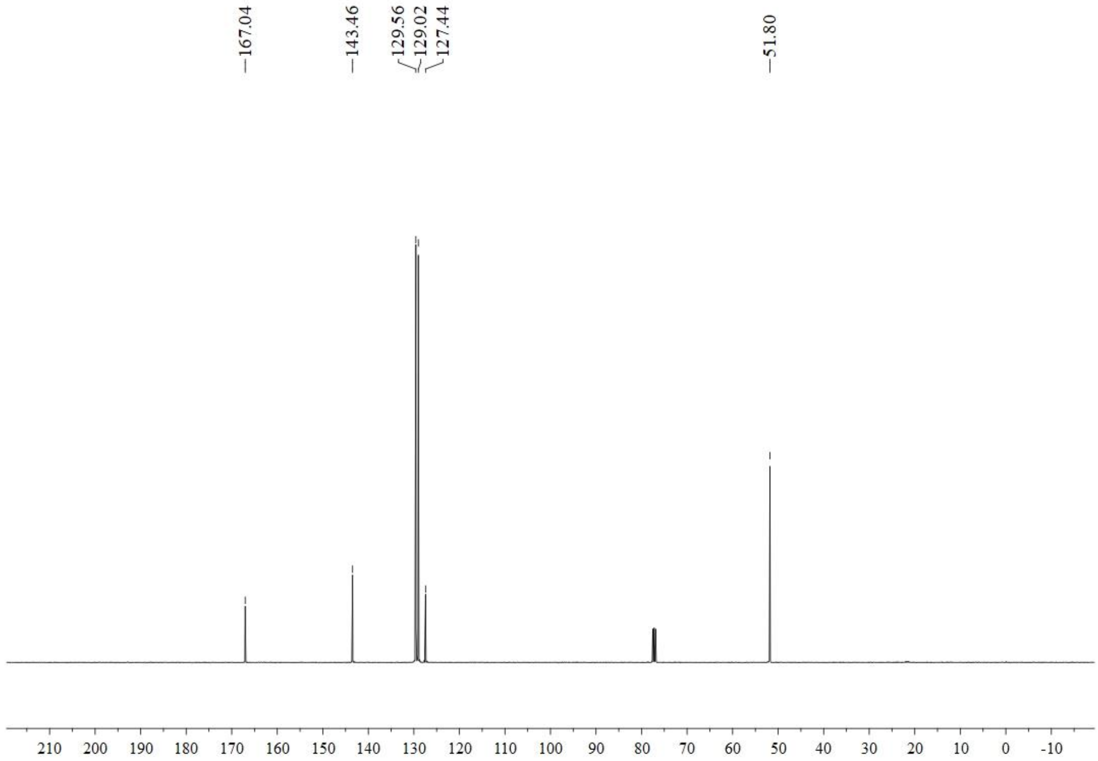
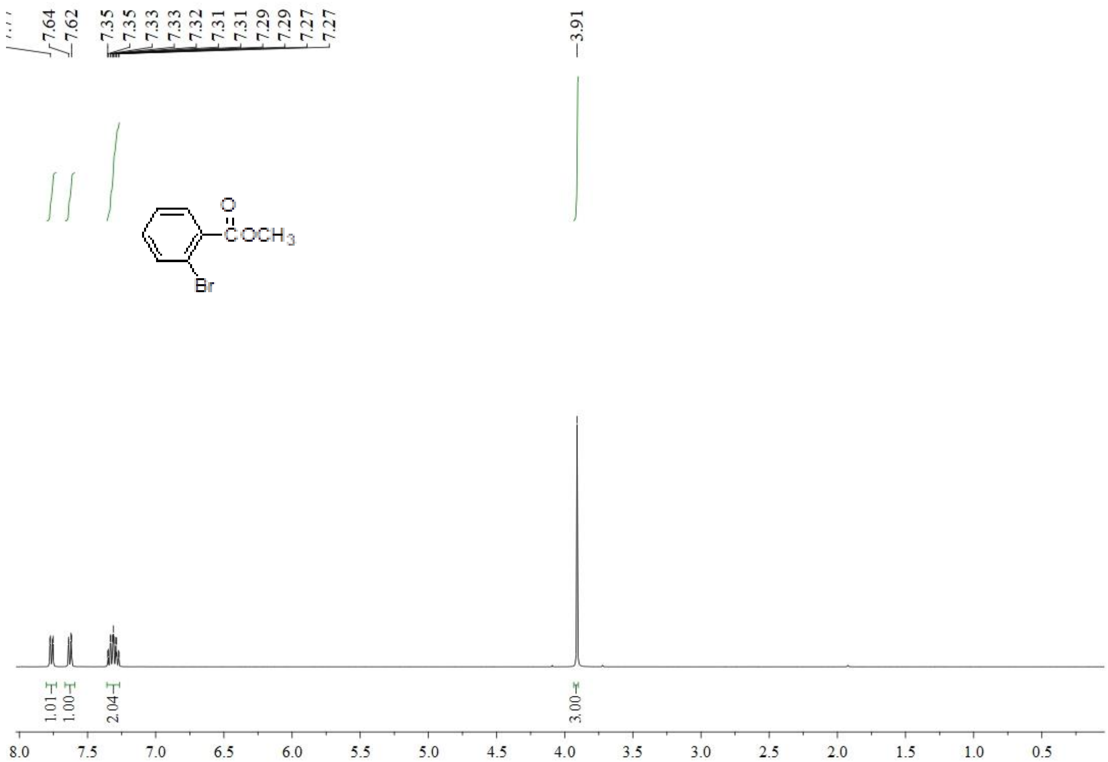


Figure S9 ^{1}H and ^{13}C NMR of methyl 4-chlorobenzoate



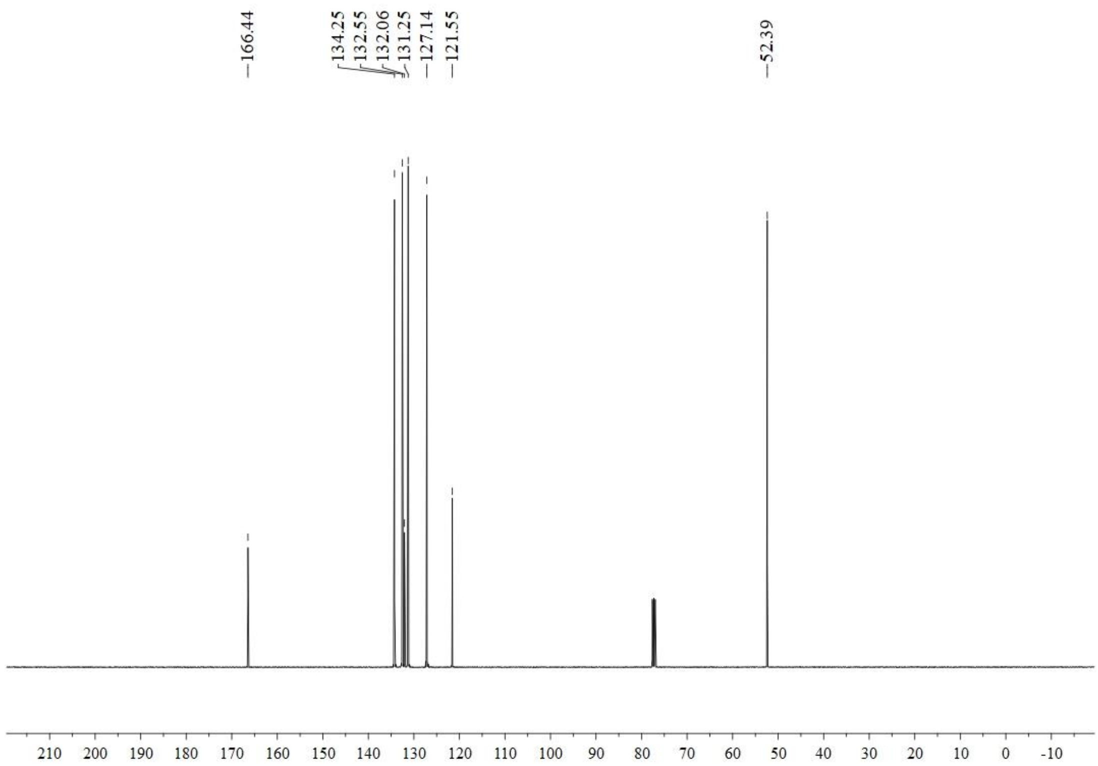
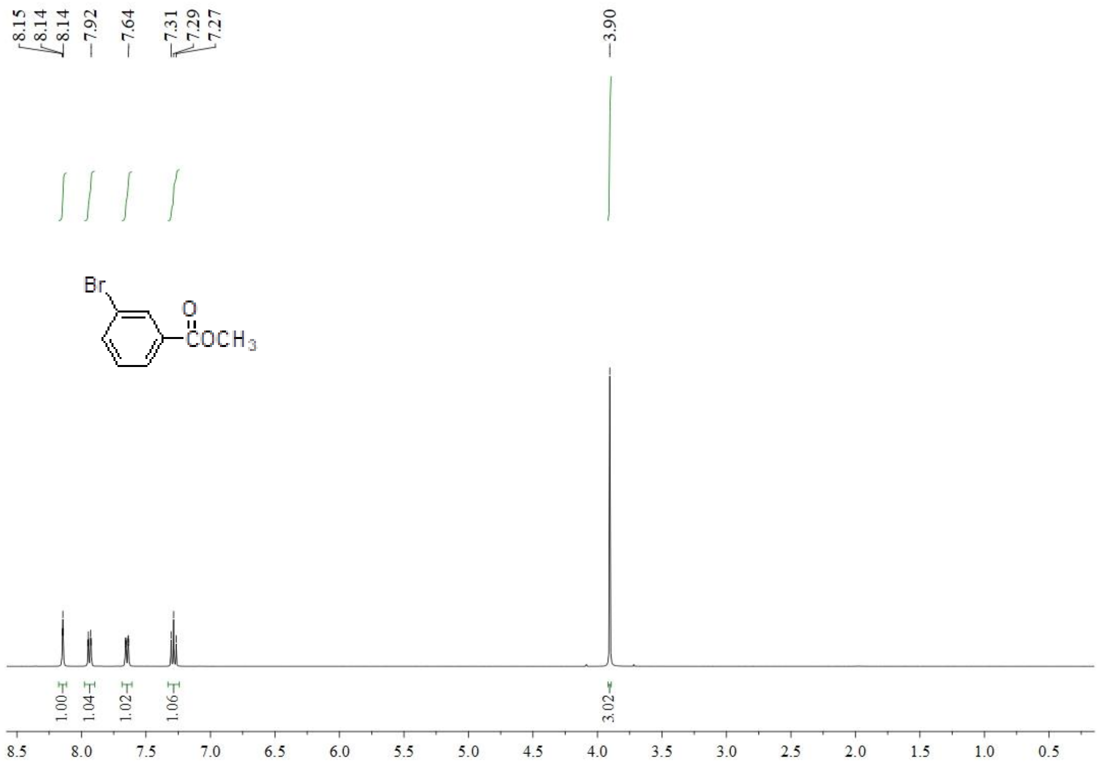


Figure S10 ^{1}H and ^{13}C NMR of methyl 2-bromobenzoate



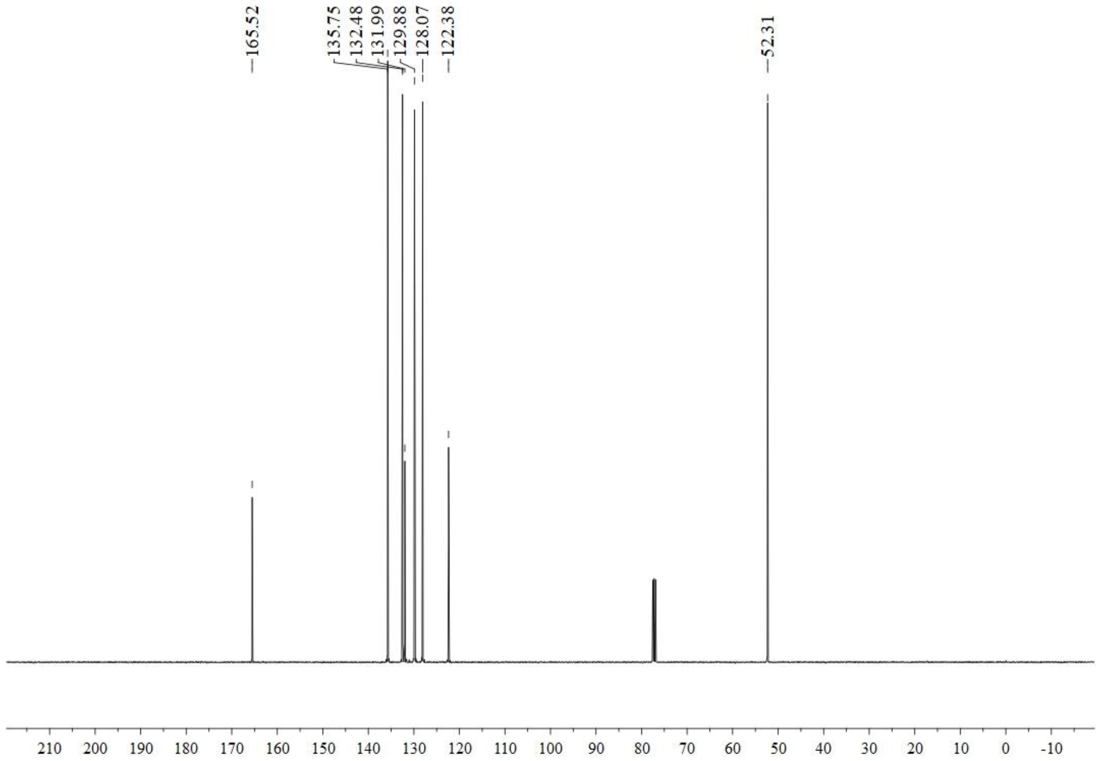
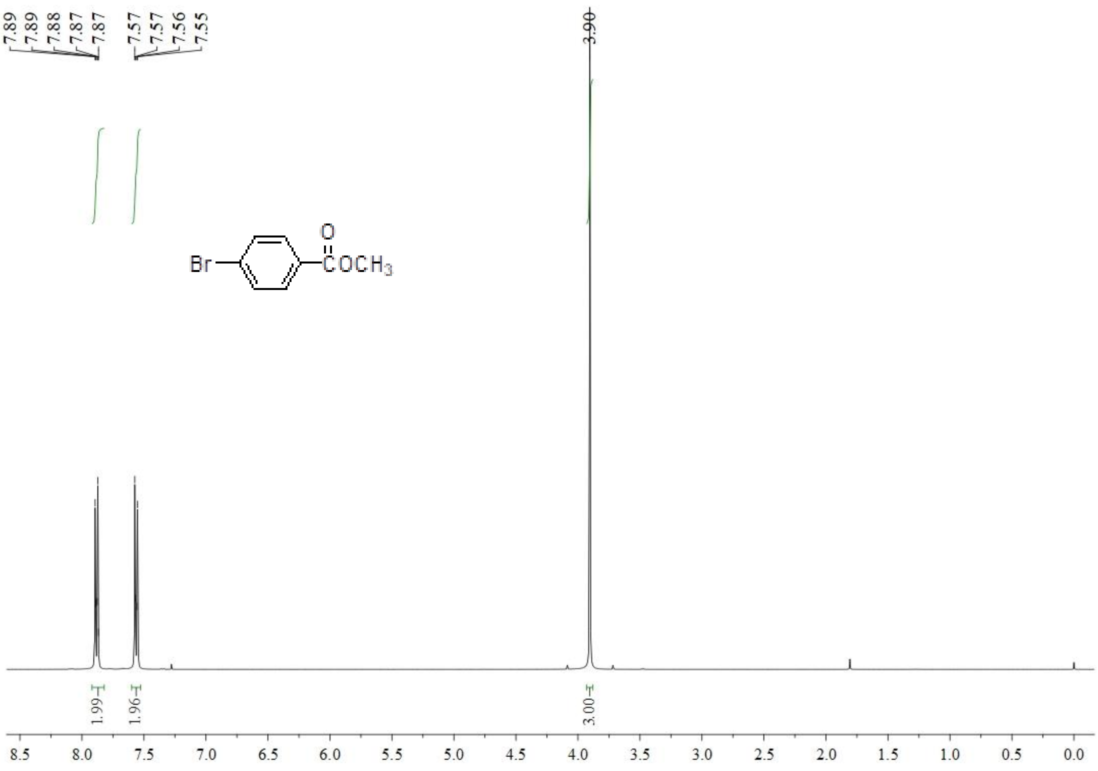


Figure S11 ^{1}H and ^{13}C NMR of methyl 3-bromobenzoate



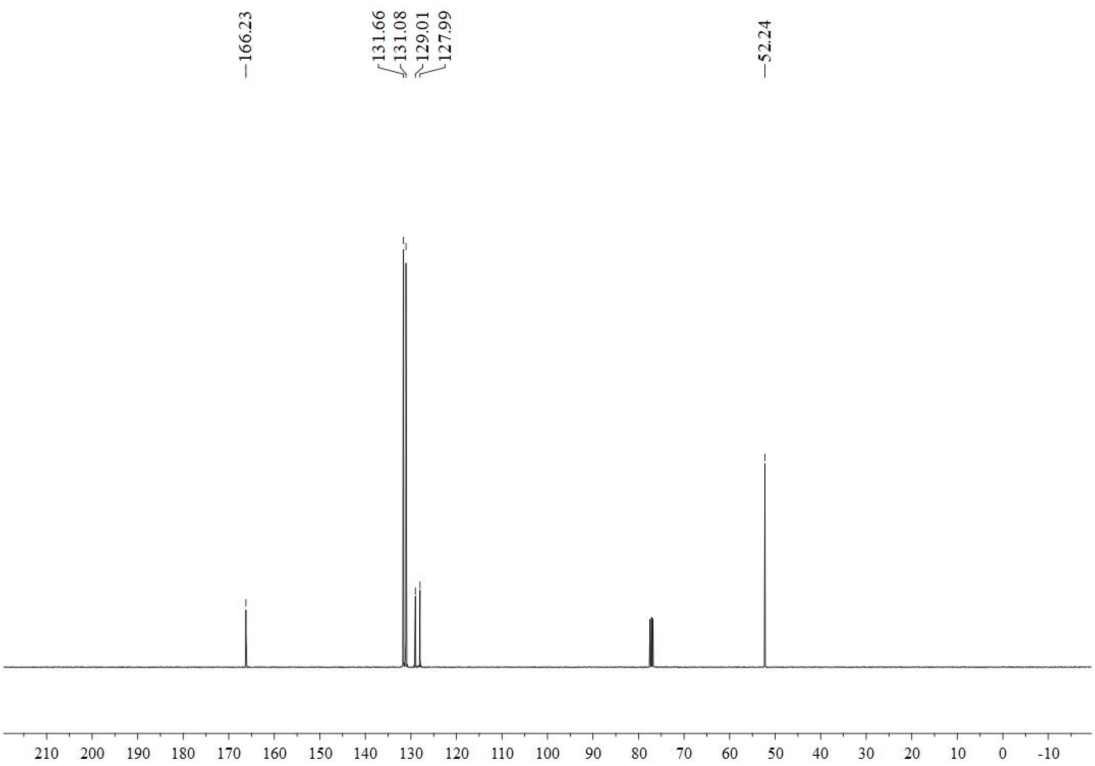
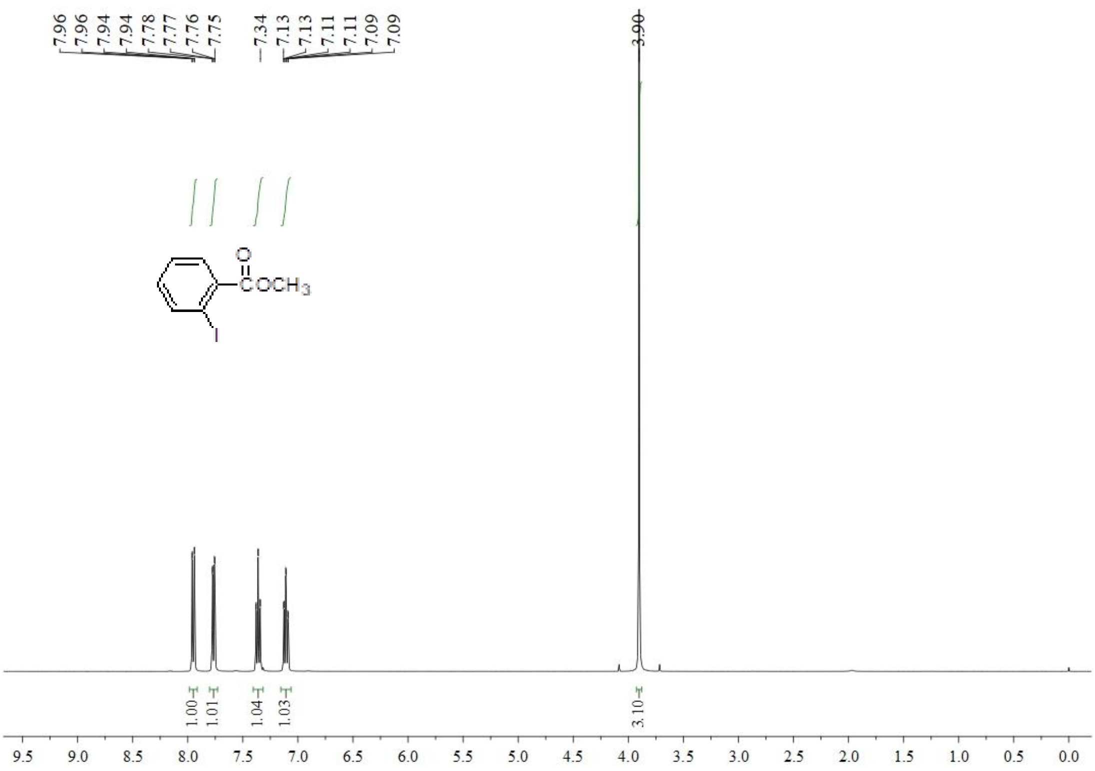


Figure S12 ^{1}H and ^{13}C NMR of methyl 4-bromobenzoate



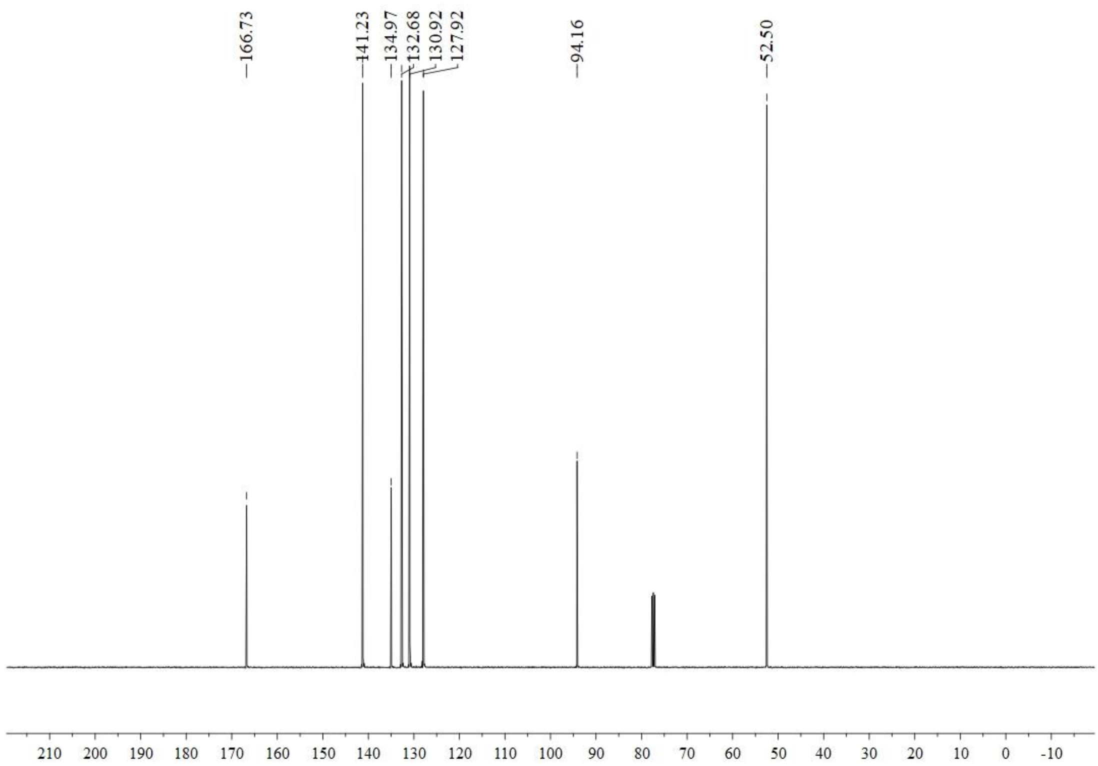
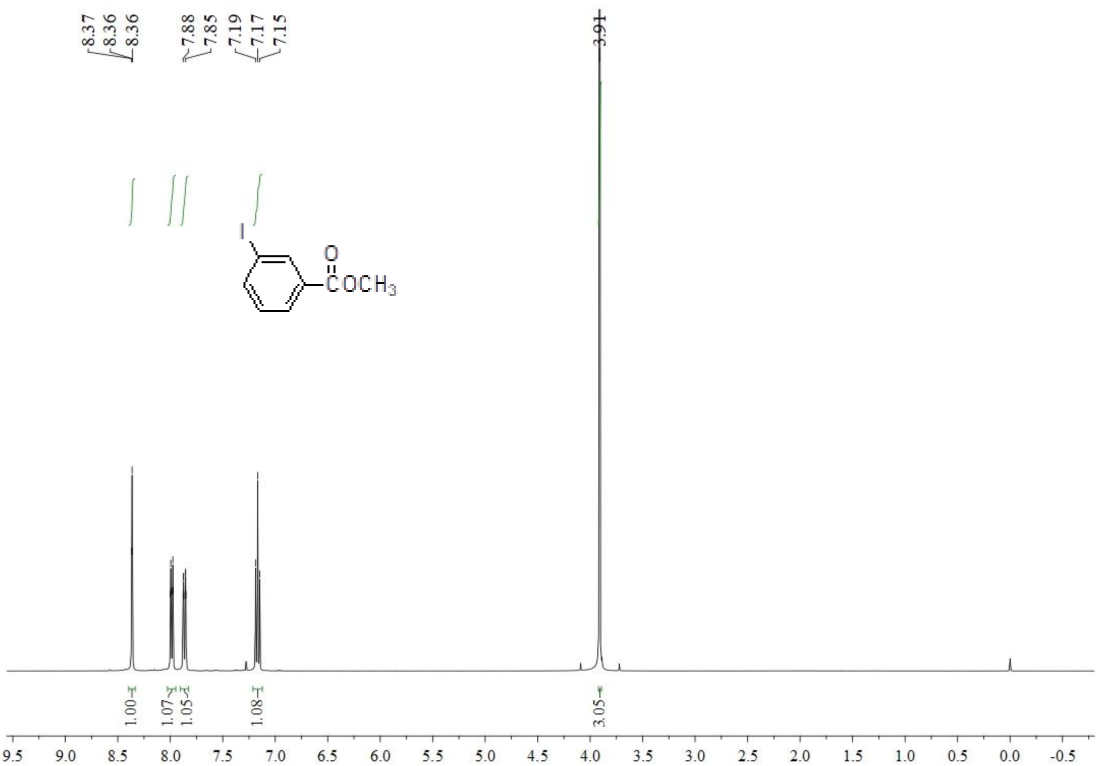


Figure S13 ^{1}H and ^{13}C NMR of methyl 2-iodobenzoate



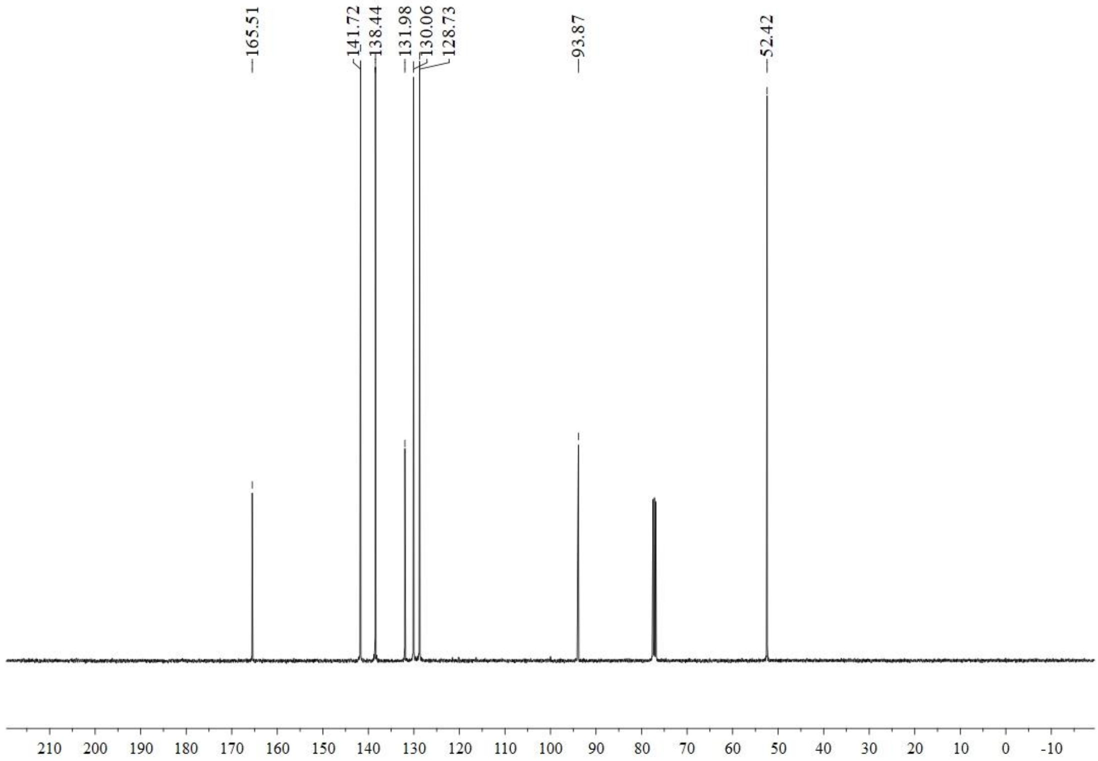
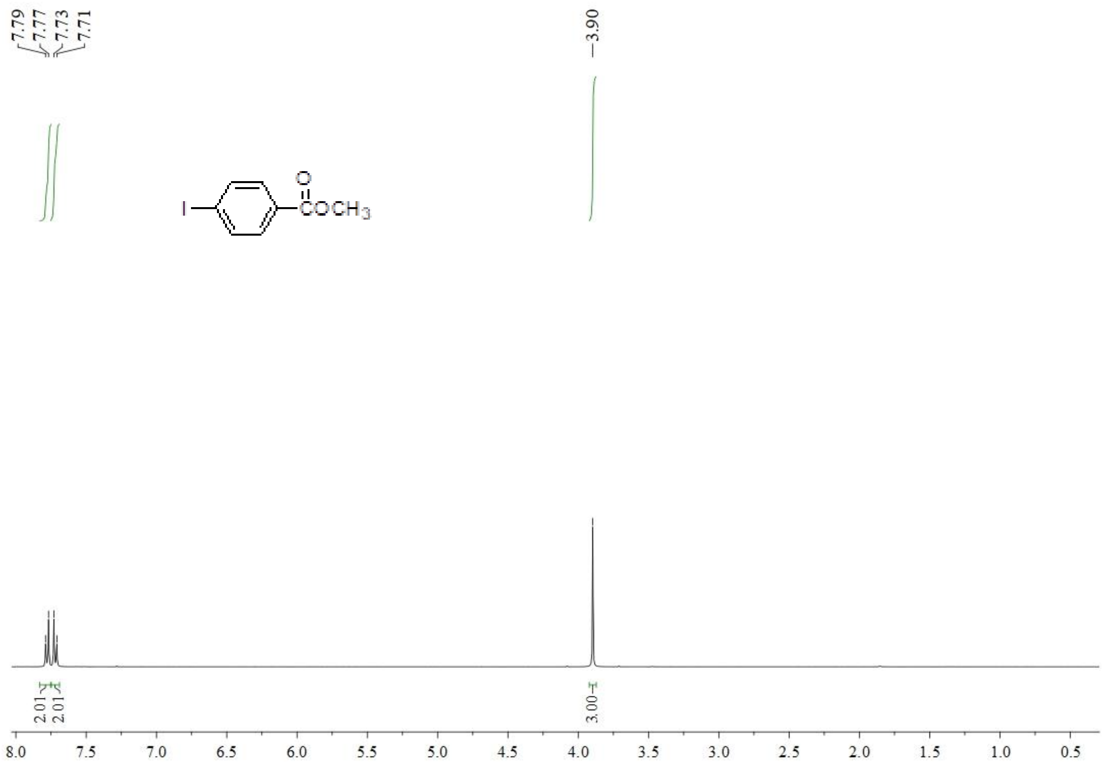


Figure S14 ^{1}H and ^{13}C NMR of methyl 3-iodobenzoate



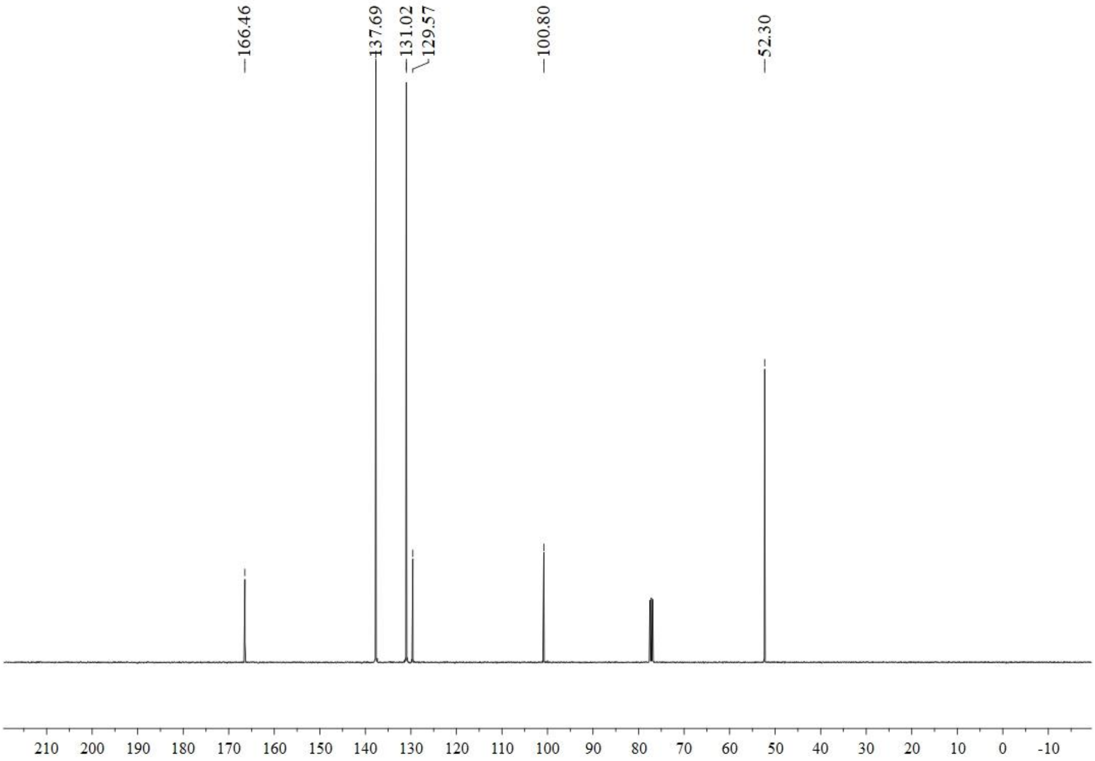
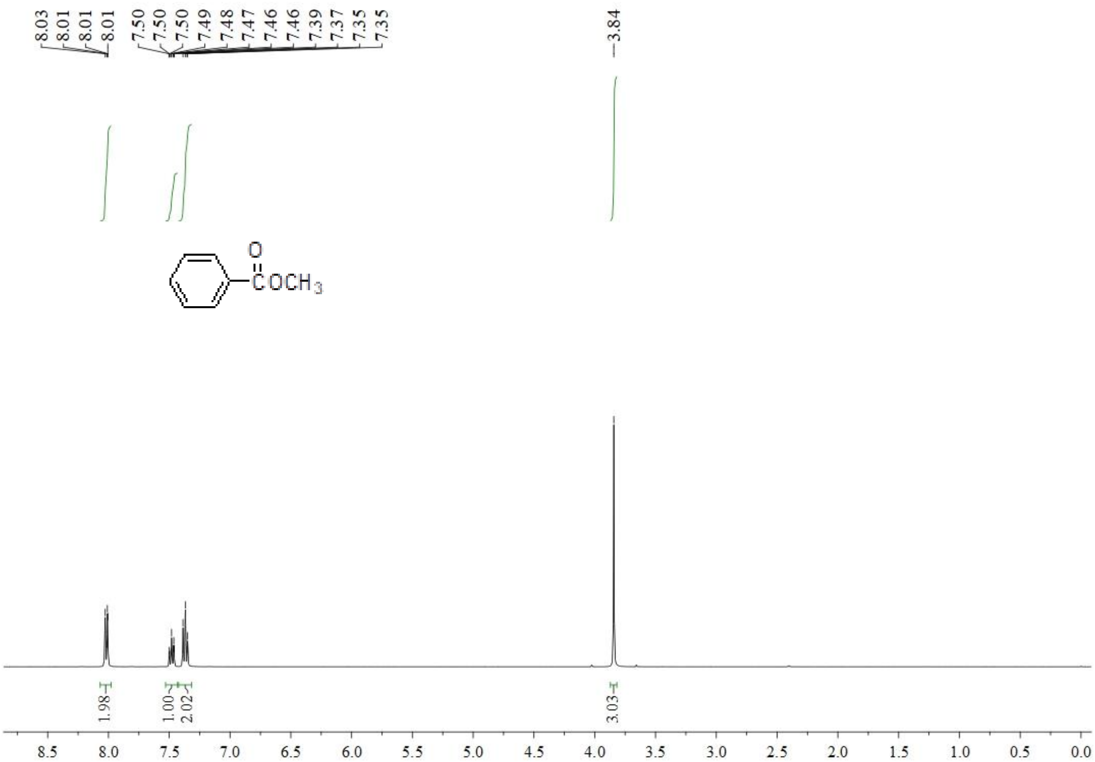


Figure S15 ^{1}H and ^{13}C NMR of methyl 4-iodobenzoate



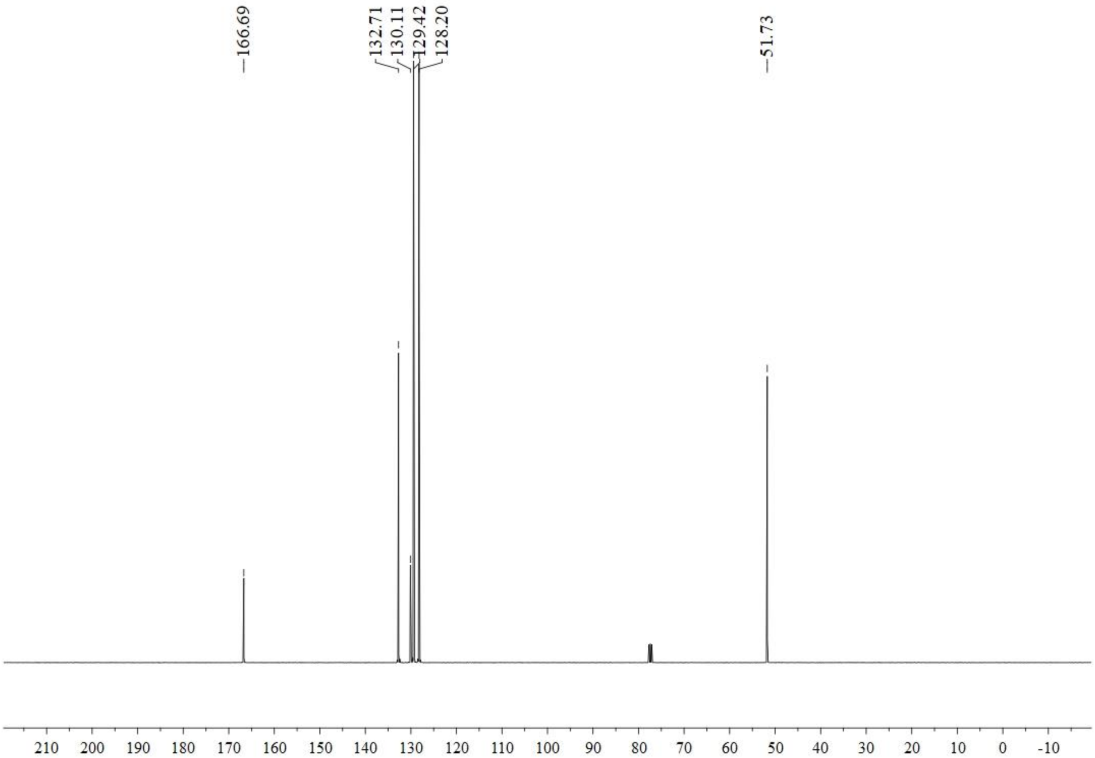
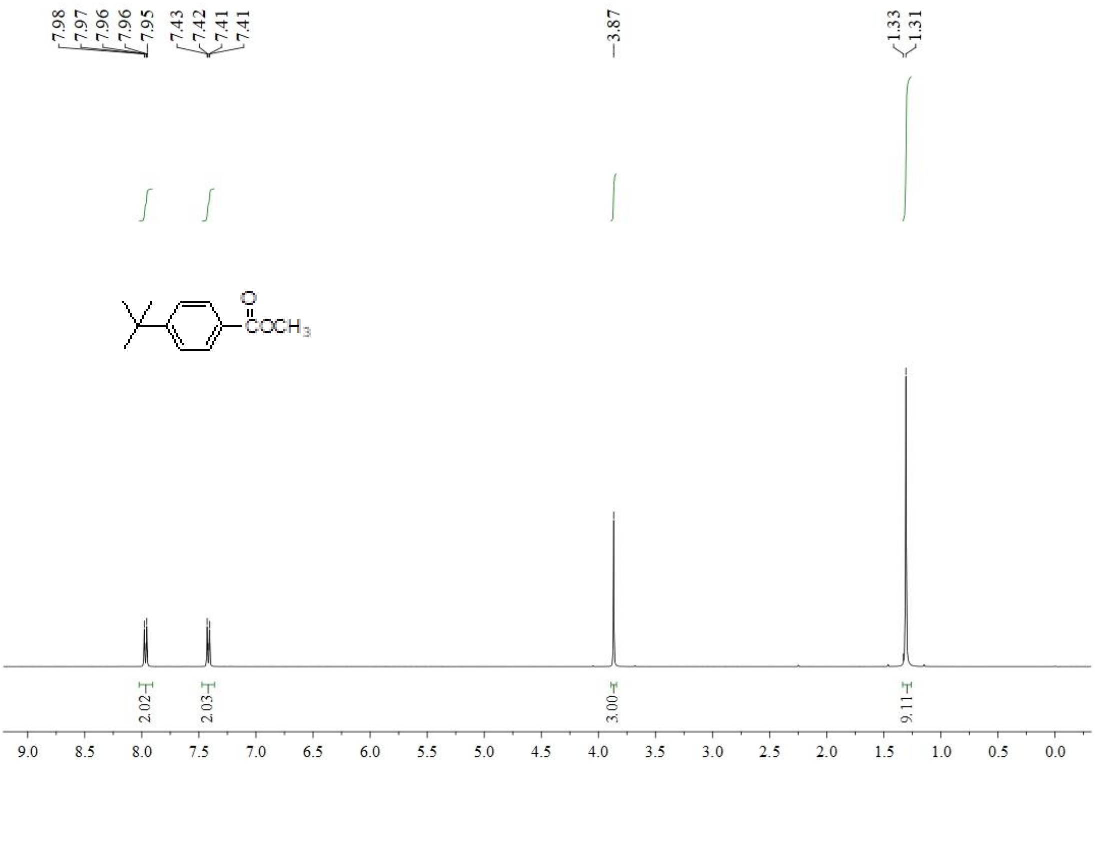


Figure S16 [1]H and [13]C NMR of methyl benzoate



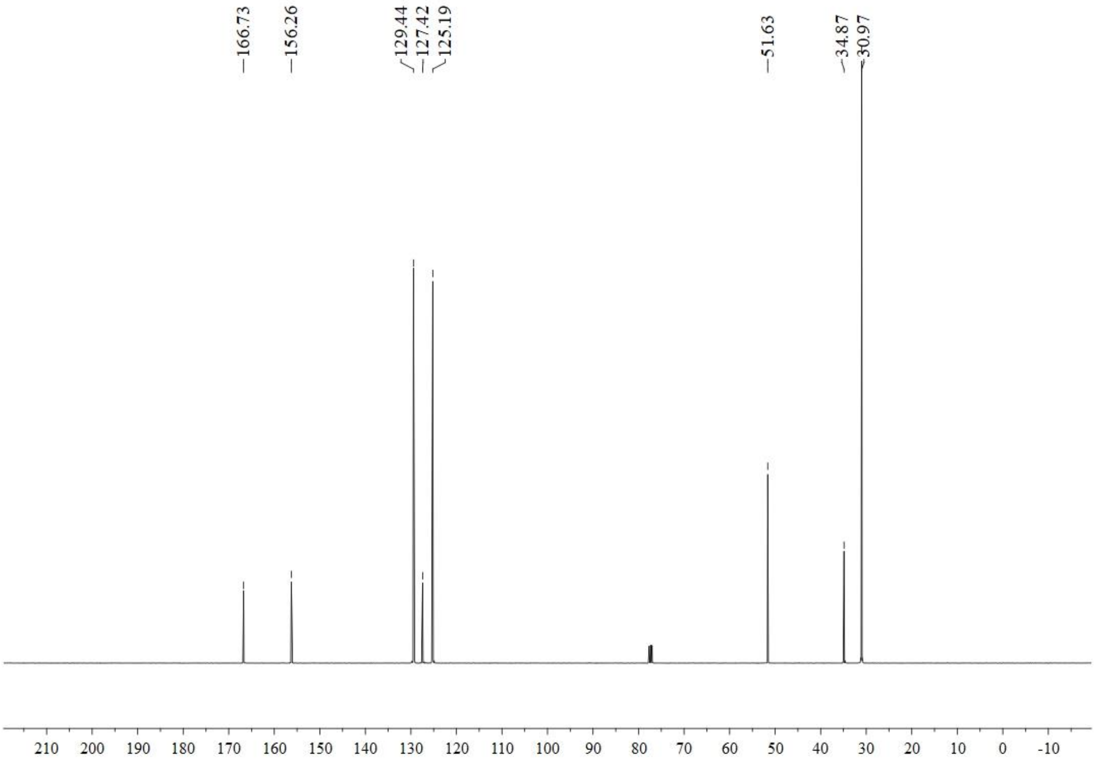
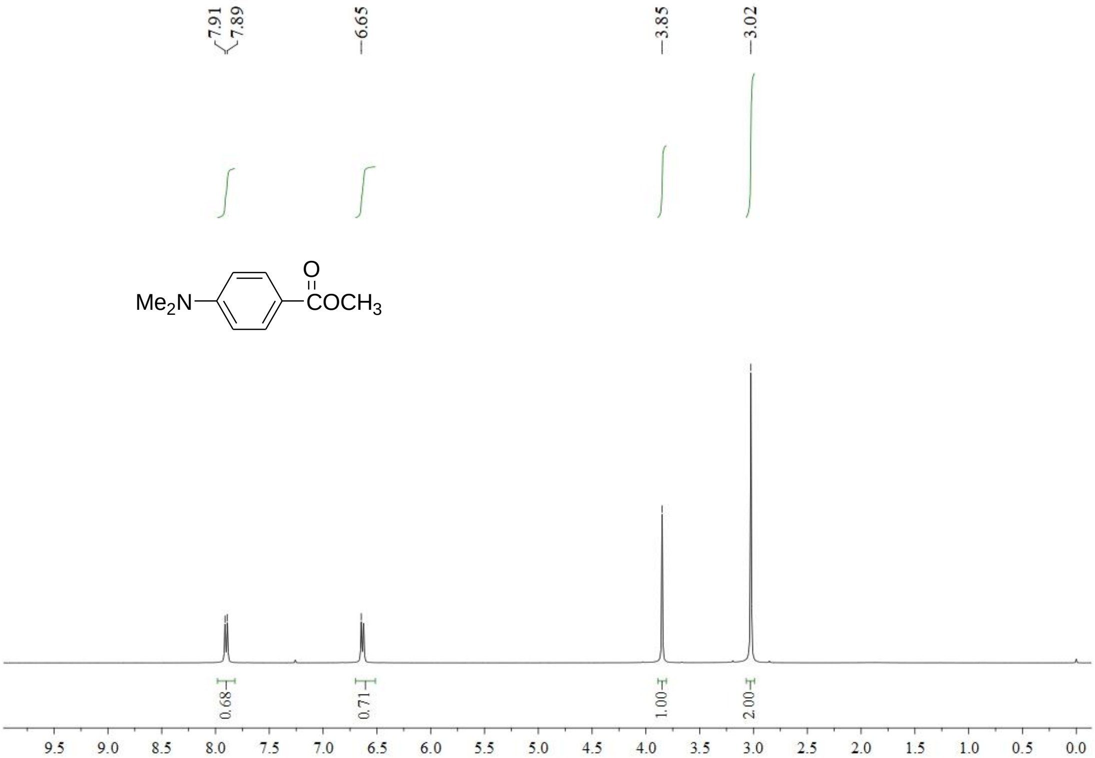


Figure S17 ^{1}H and ^{13}C NMR of methyl 4-Tert-Butylbenzoate



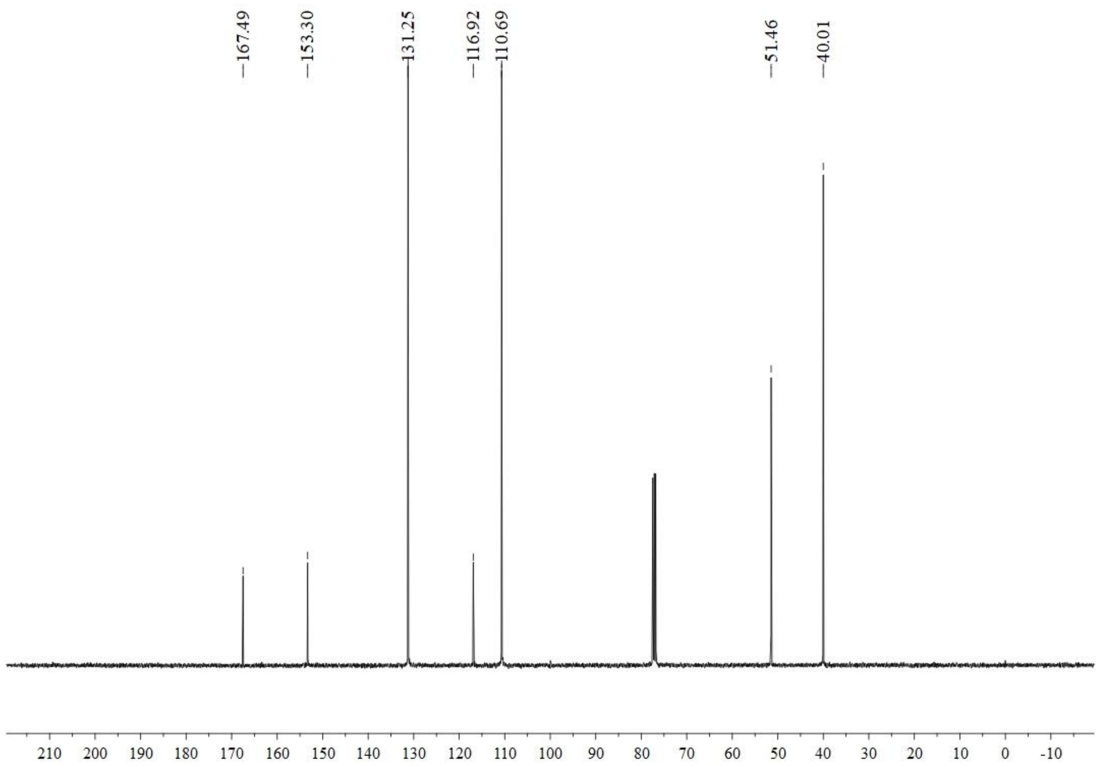
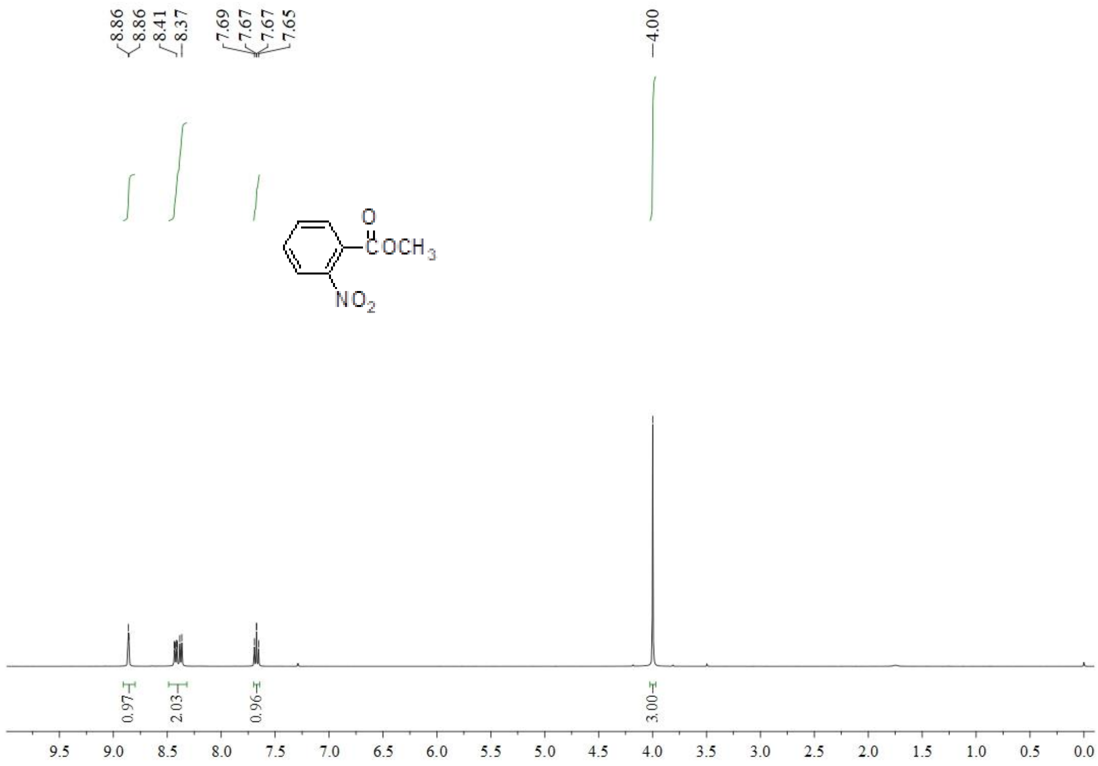


Figure S18 ^{1}H and ^{13}C NMR of methyl 4-cyanobenzoate



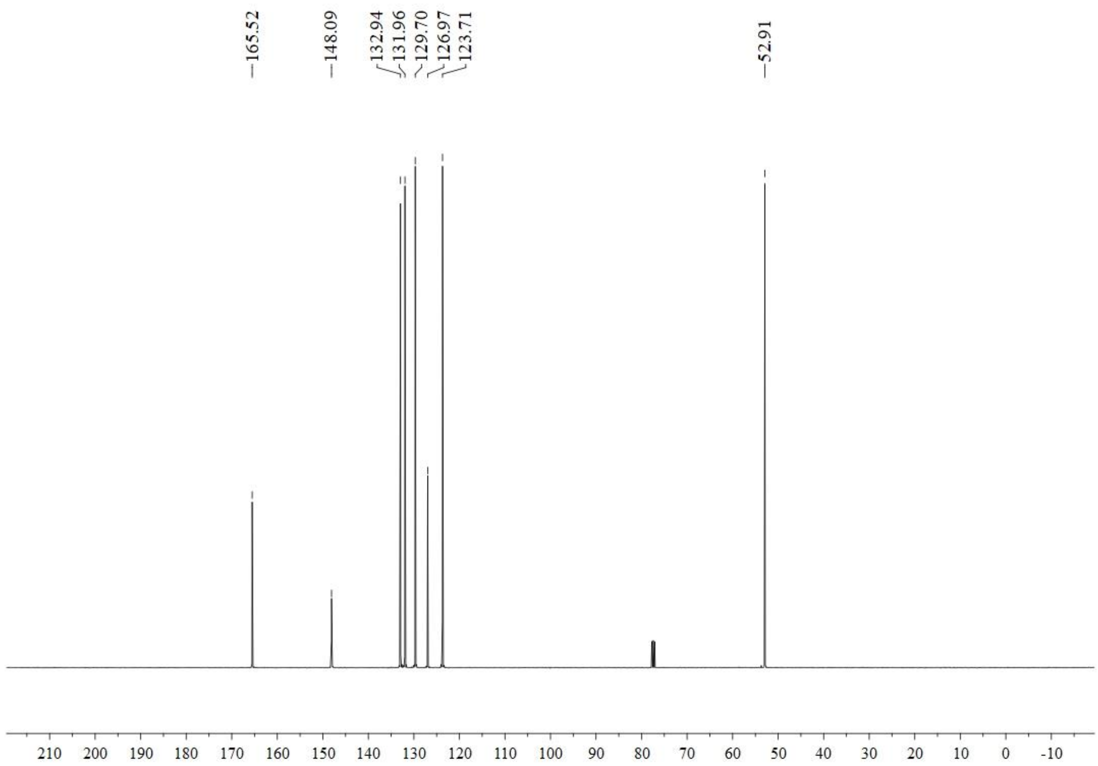
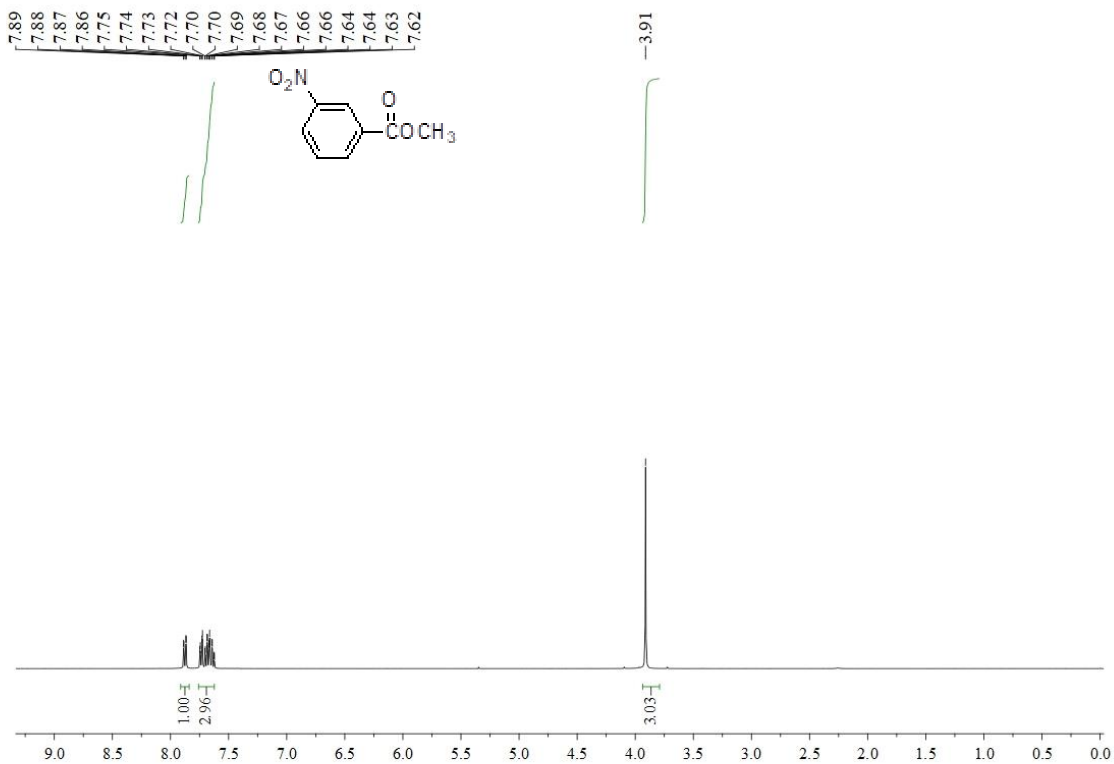


Figure S19 ^{1}H and ^{13}C NMR of Methyl 2-nitrobenzoate



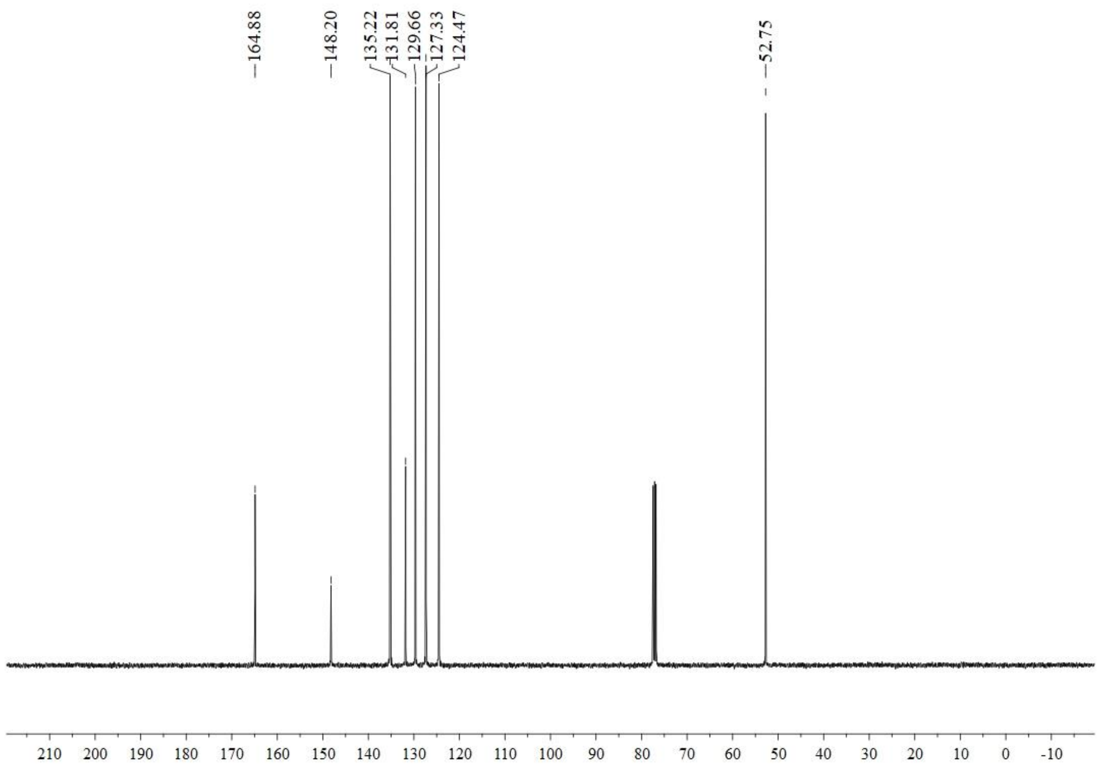
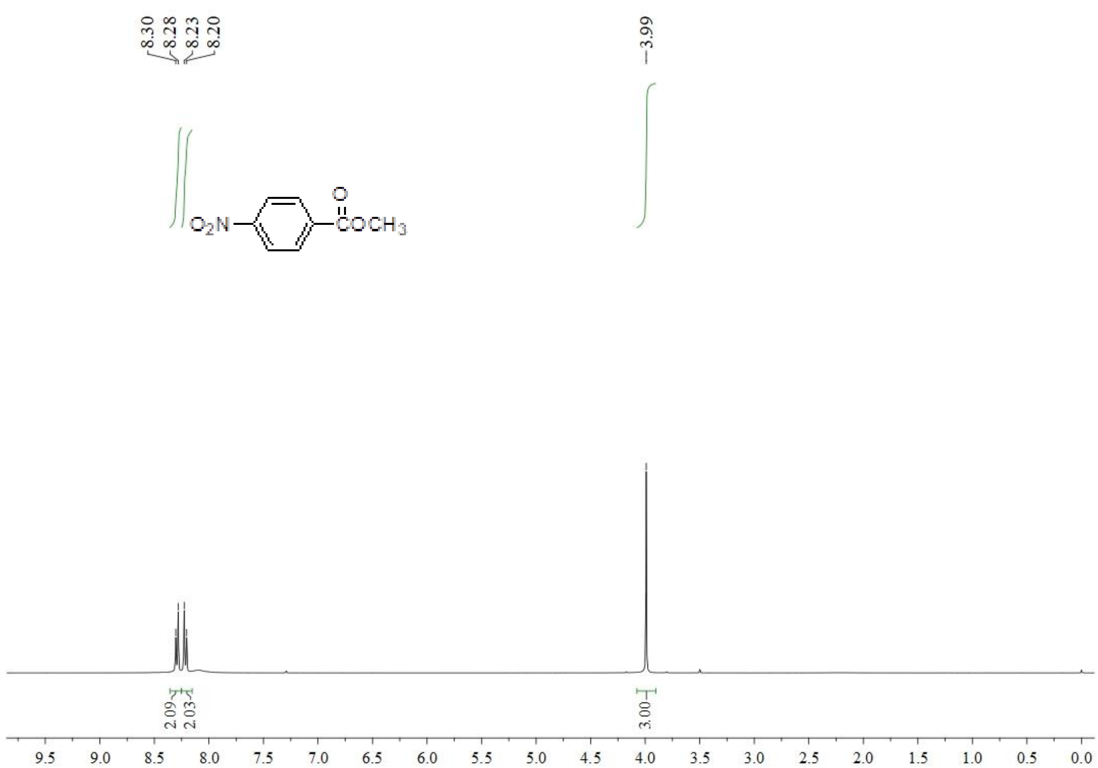


Figure S20 ^{1}H and ^{13}C NMR of Methyl 3-nitrobenzoate



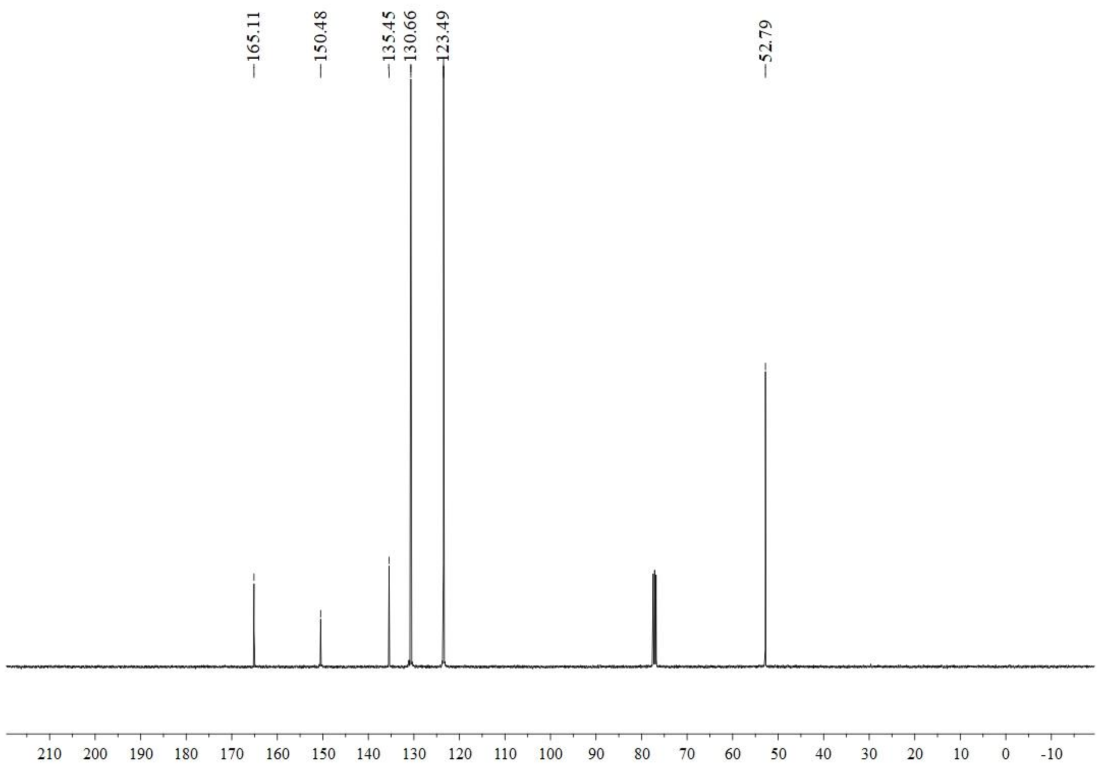
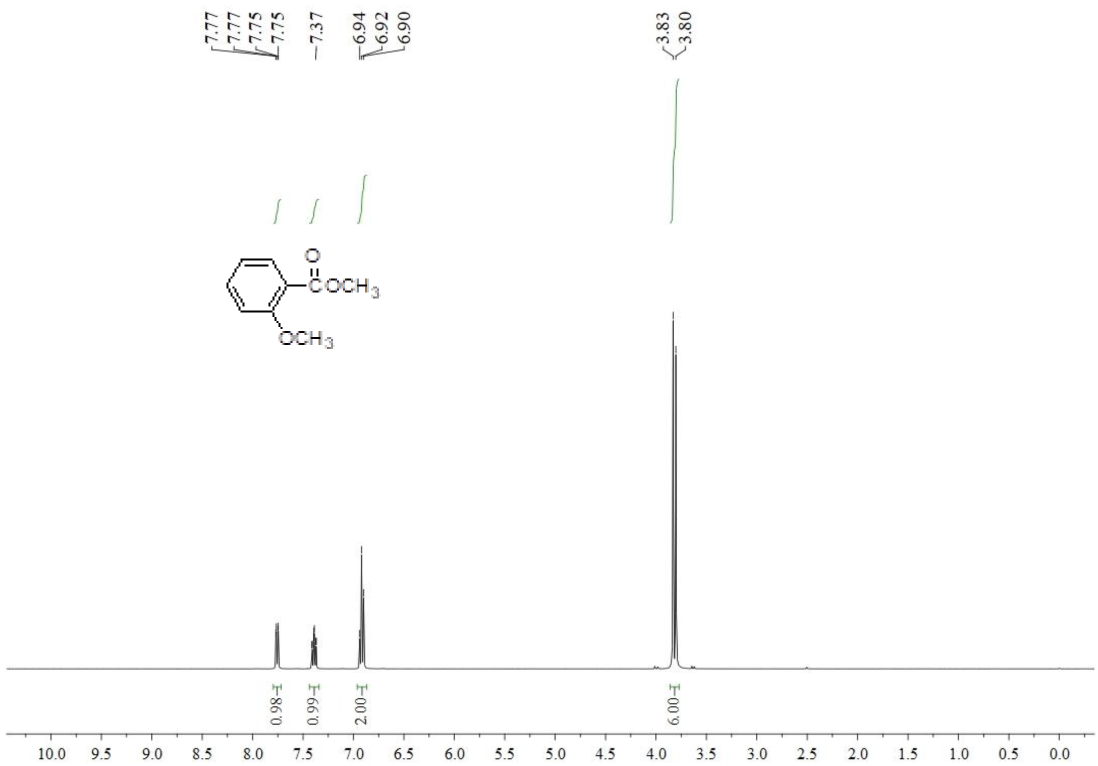


Figure S21 ^{1}H and ^{13}C NMR of Methyl 4-nitrobenzoate



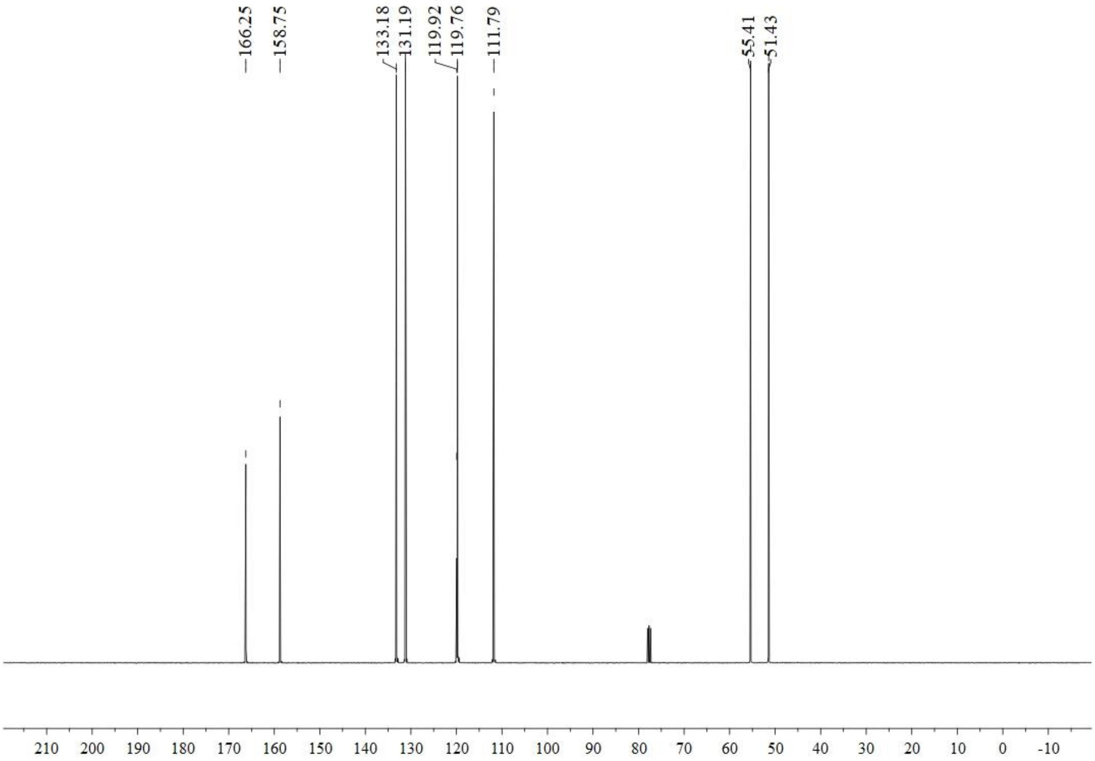
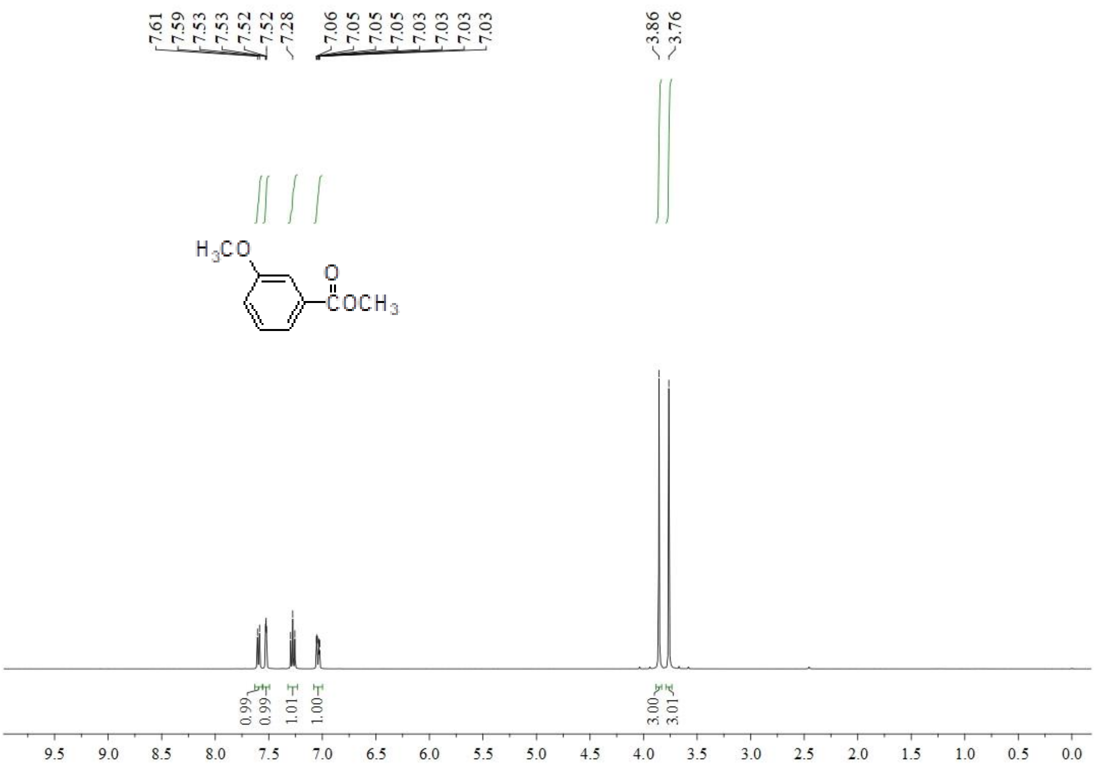


Figure S22 ^{1}H and ^{13}C NMR of Methyl 2-methoxybenzoate



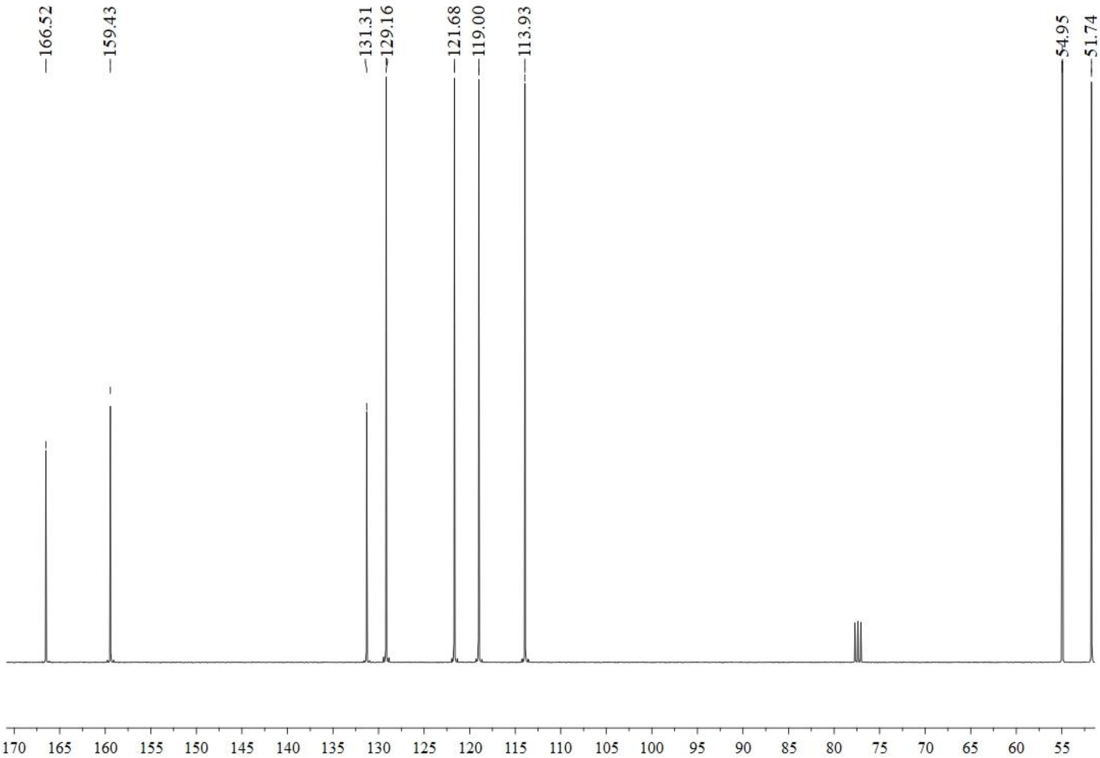
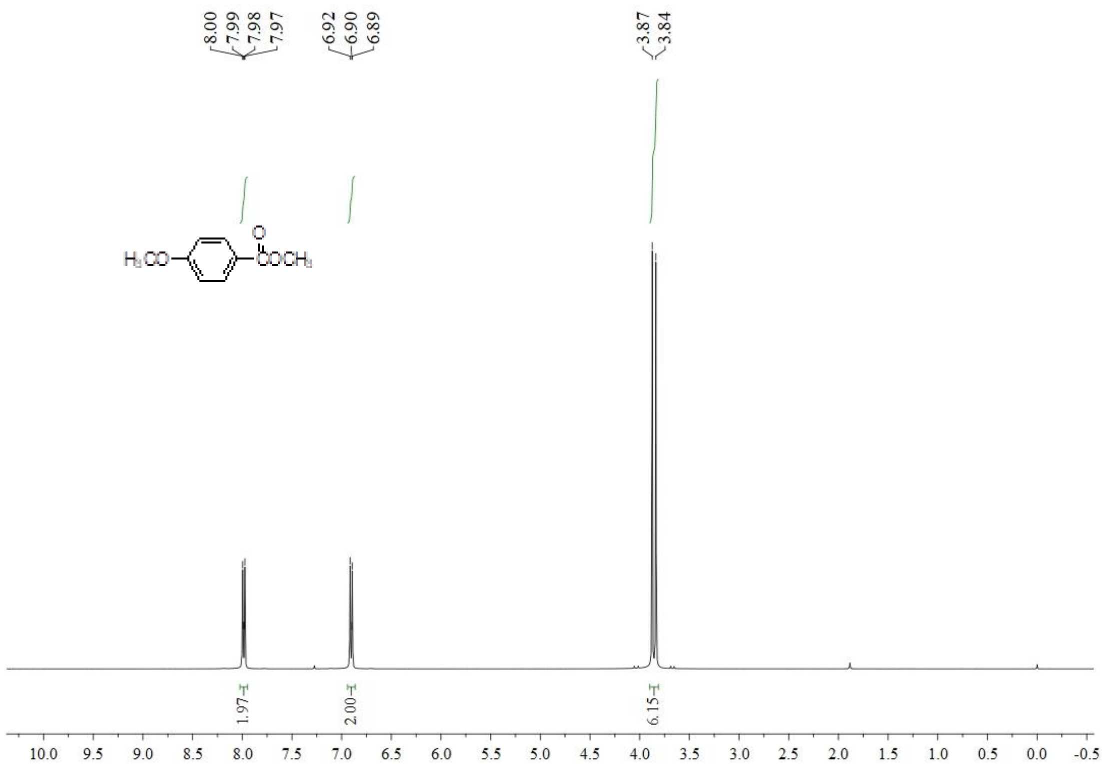


Figure S23 ^{1}H and ^{13}C NMR of Methyl 3-methoxybenzoate



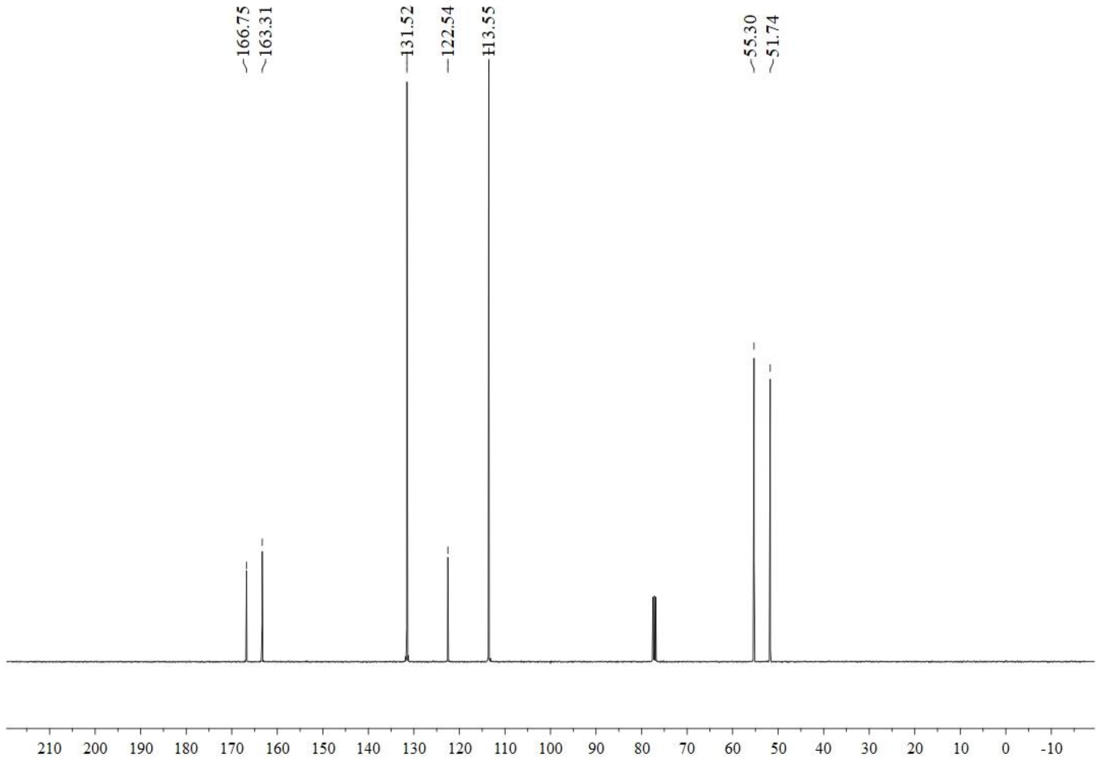


Figure S24 ^{1}H and ^{13}C NMR of Methyl 4-methoxybenzoate

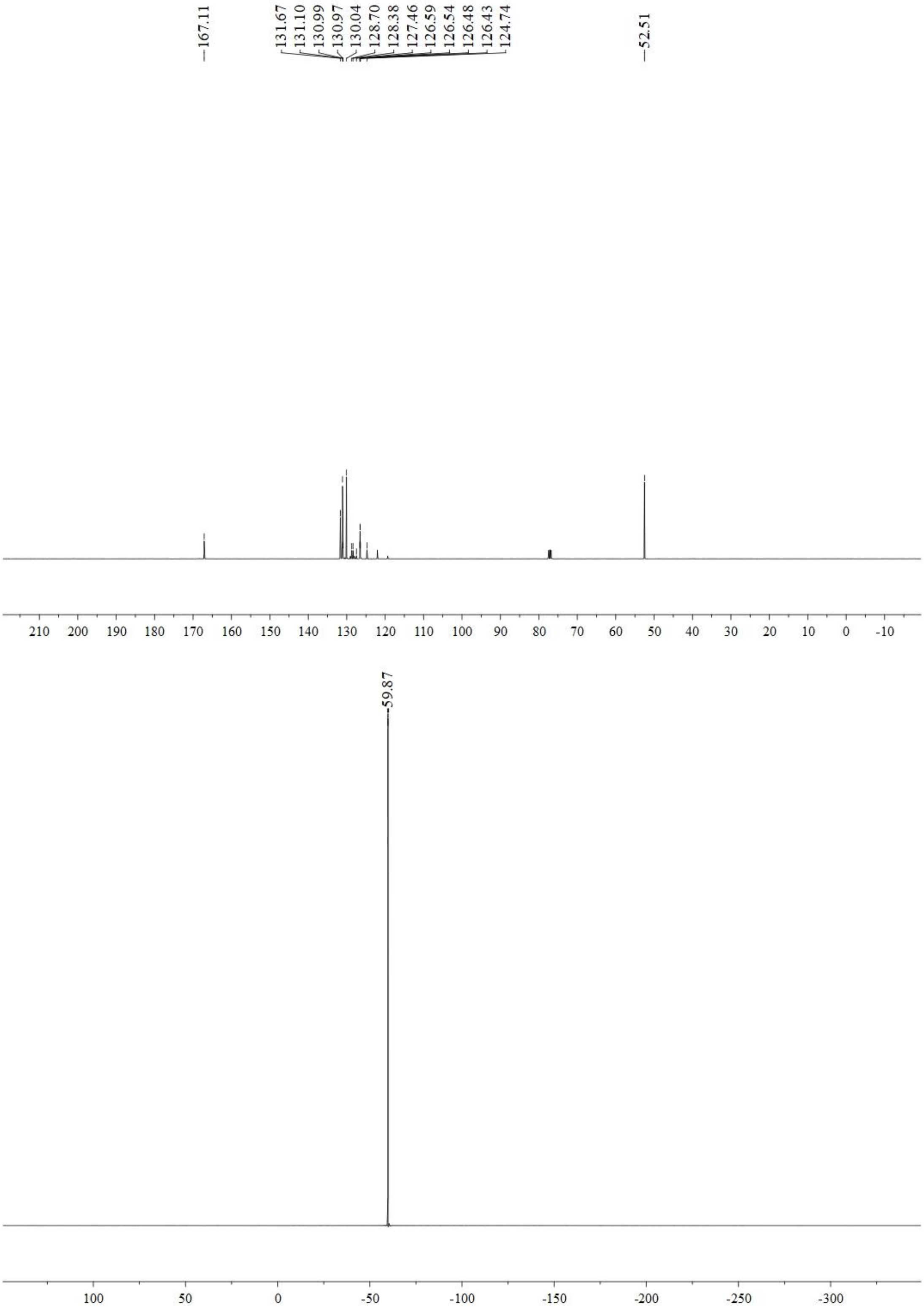
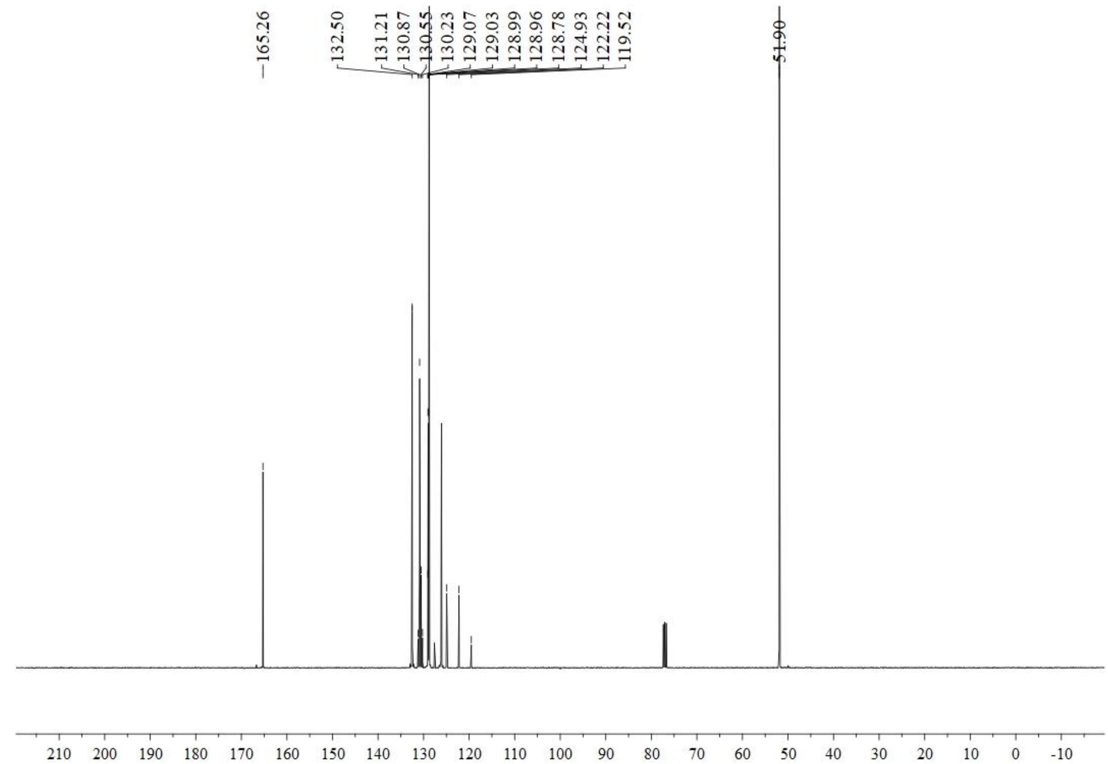


Figure S25 ^{1}H, ^{13}C and ^{19}F NMR of Methyl 2-trifluoromethylbenzoate


8.28
8.19
8.17
7.76
7.55
7.53
7.51
3.94
F3C
O
COCH3
1.00
1.00
1.00
1.02
3.10
9.5 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
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

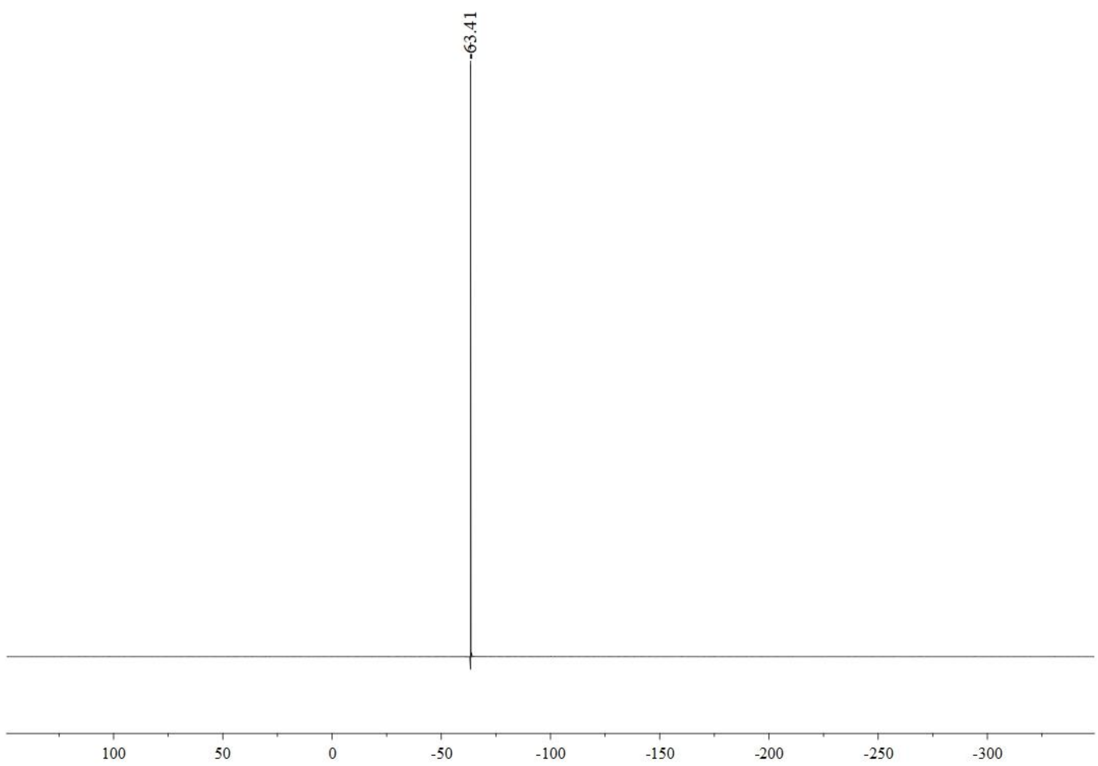
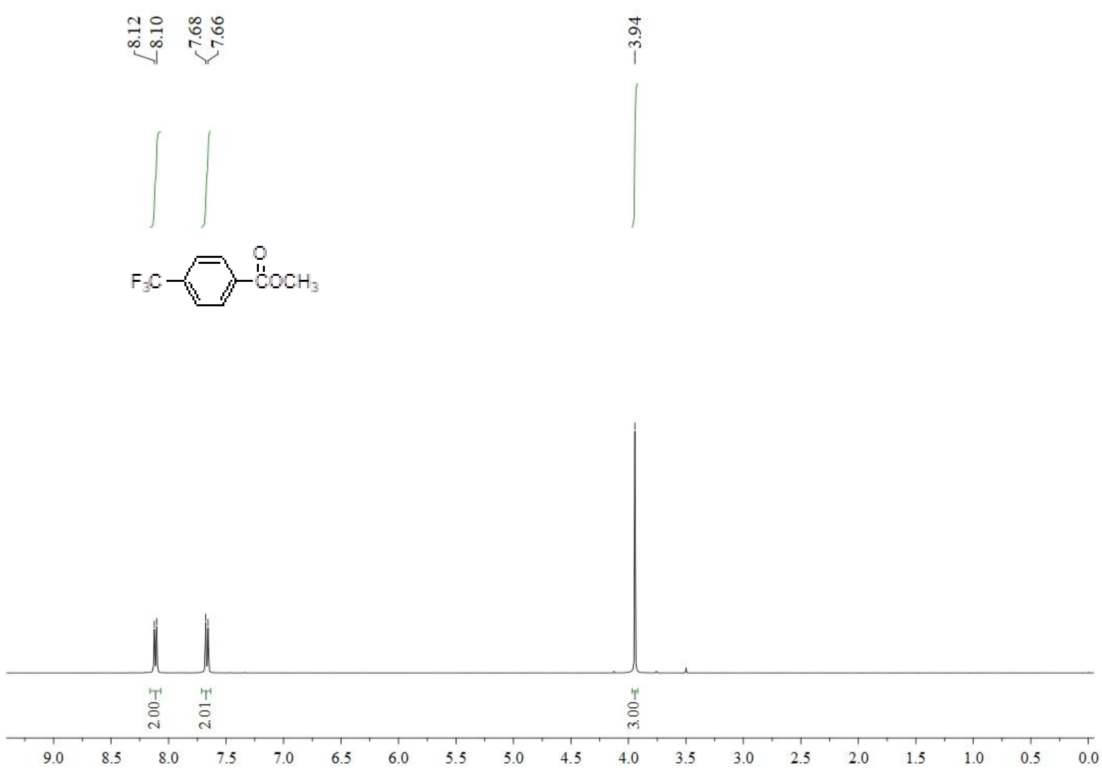
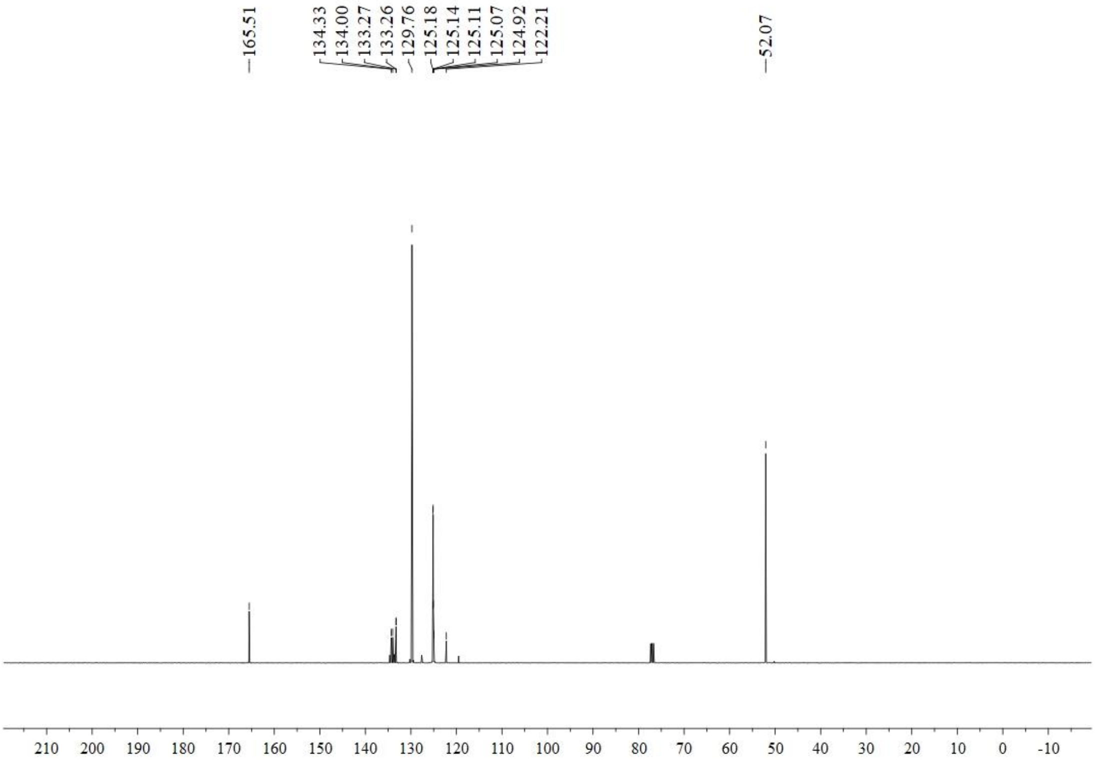


Figure S26 ^{1}H, ^{13}C and ^{19}F NMR of Methyl 3-trifluoromethylbenzoate





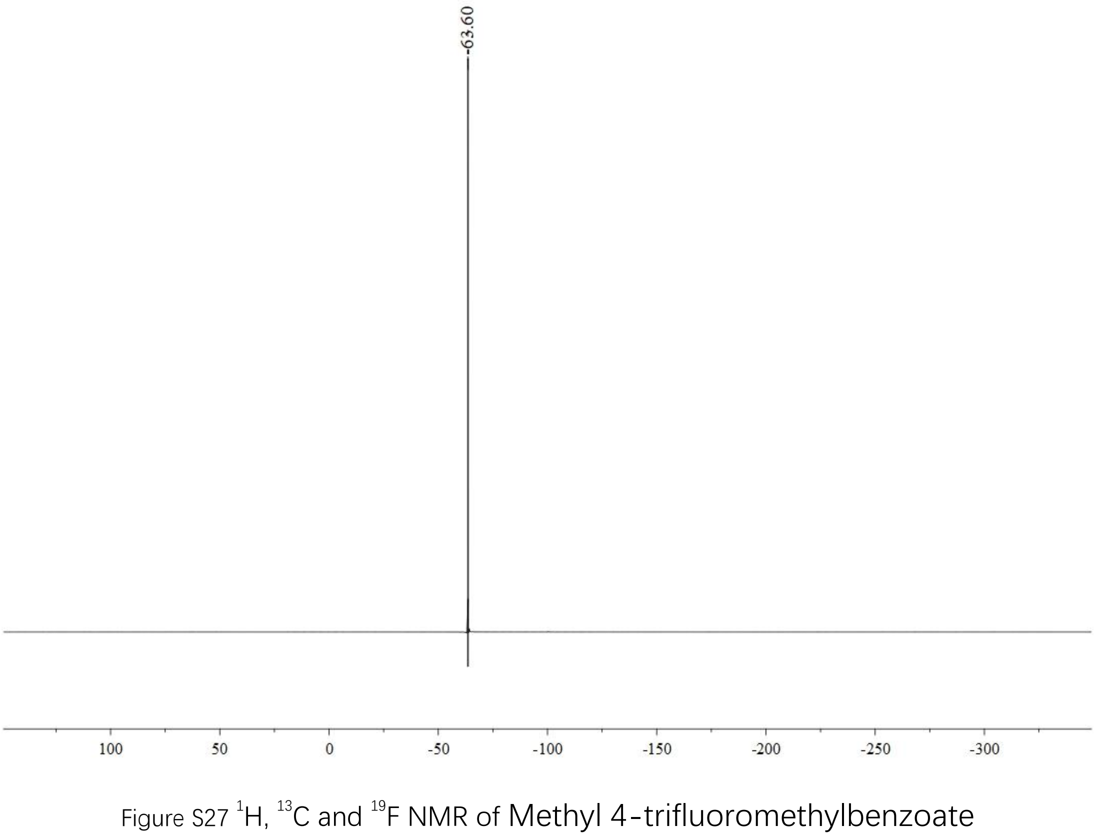


Figure S27 ^{1}H, ^{13}C and ^{19}F NMR of Methyl 4-trifluoromethylbenzoate

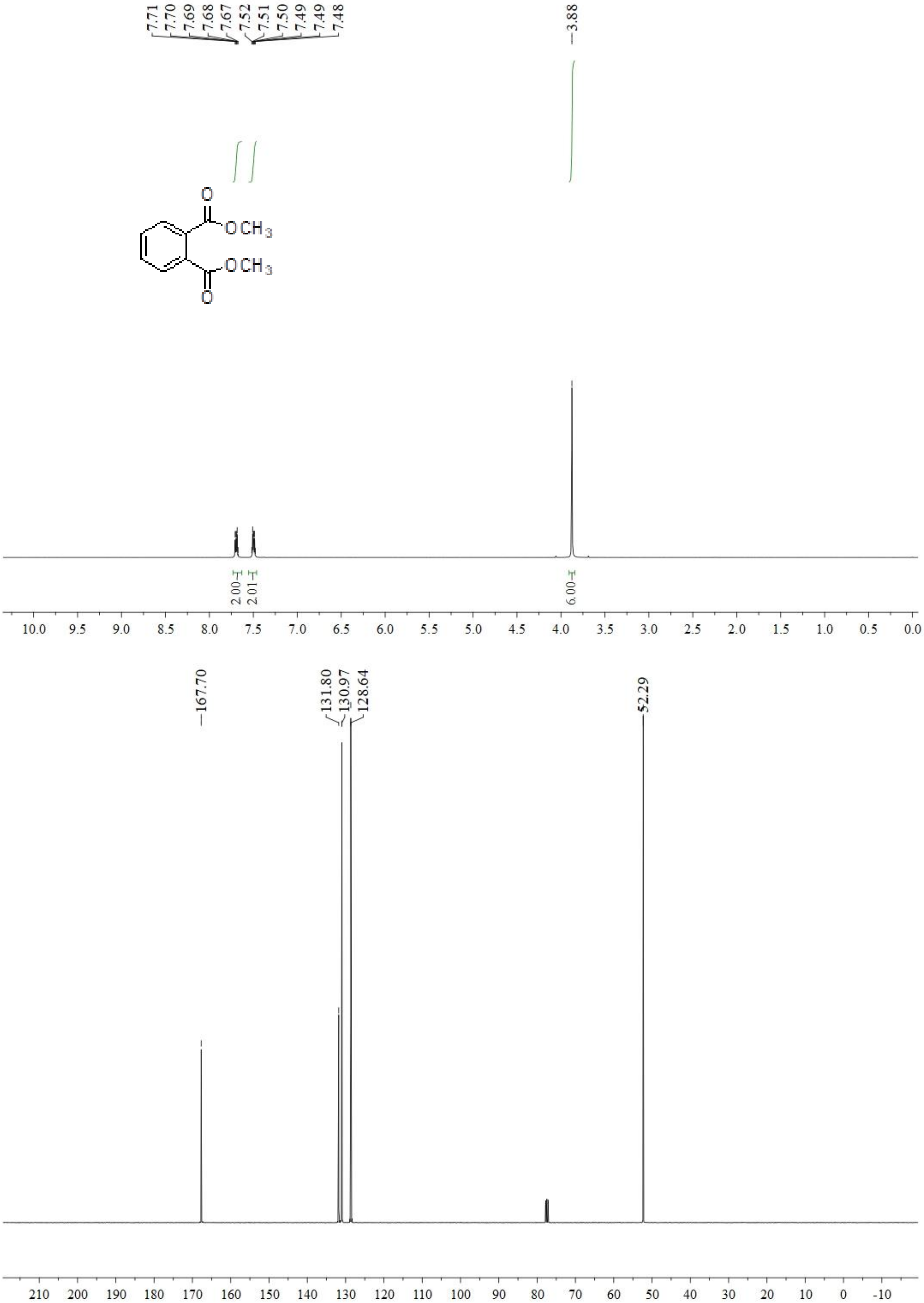


Figure S28 ^{1}H and ^{13}C NMR of *o*-Dimethyl phthalate

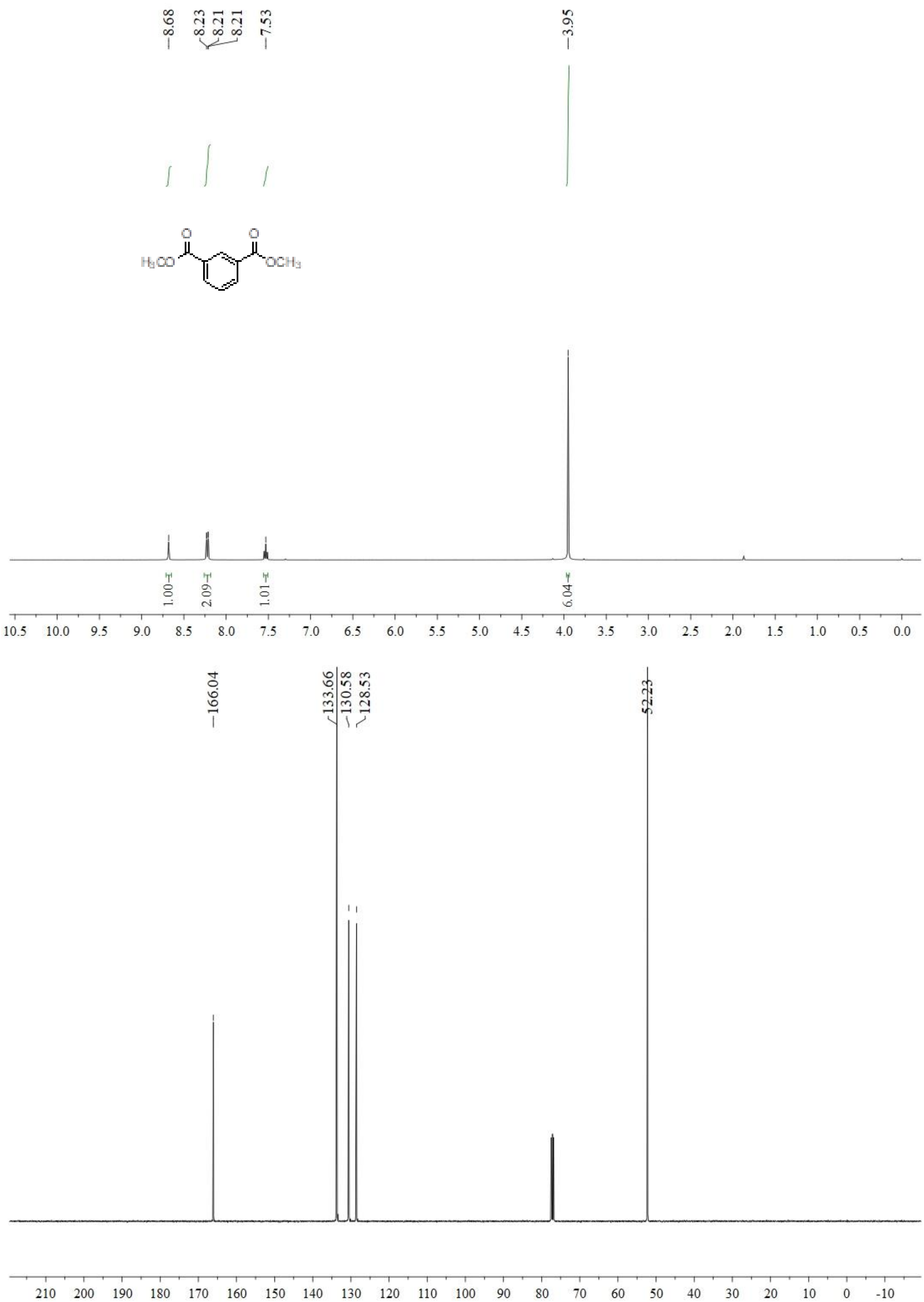


Figure S29 ^{1}H and ^{13}C NMR of *m*-Dimethyl terephthalate

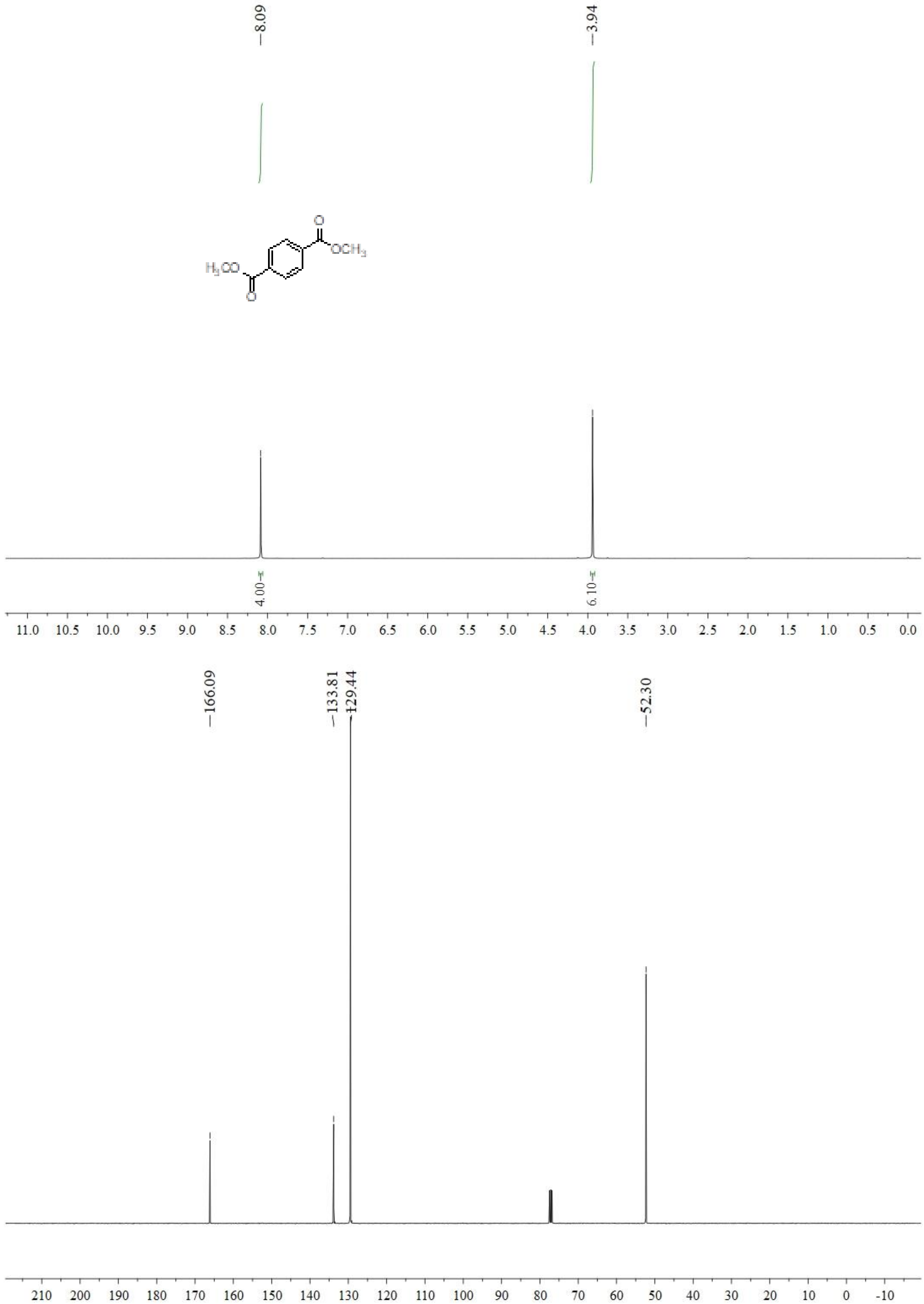


Figure S30 ^{1}H and ^{13}C NMR of *p*-Dimethyl terephthalate

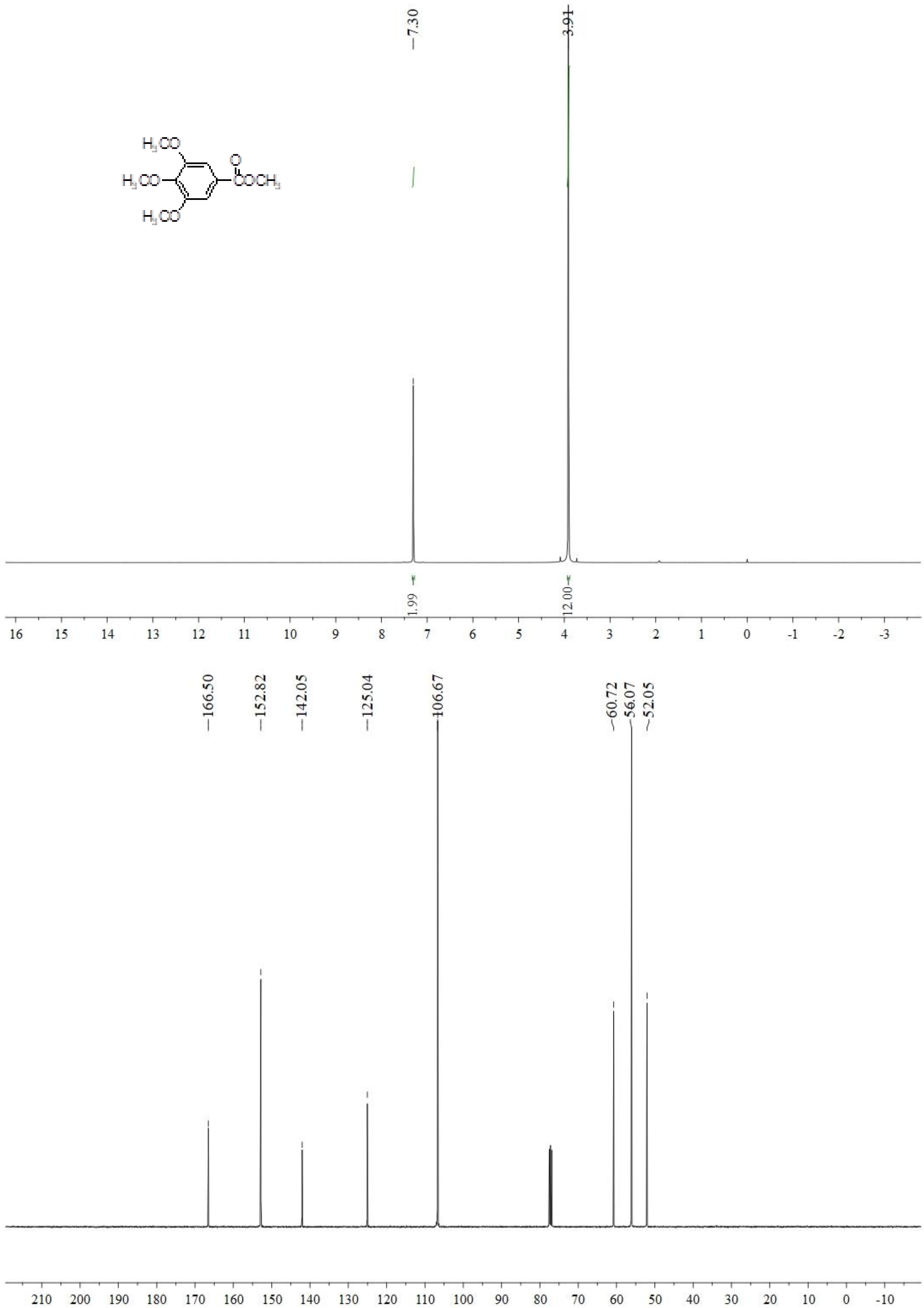
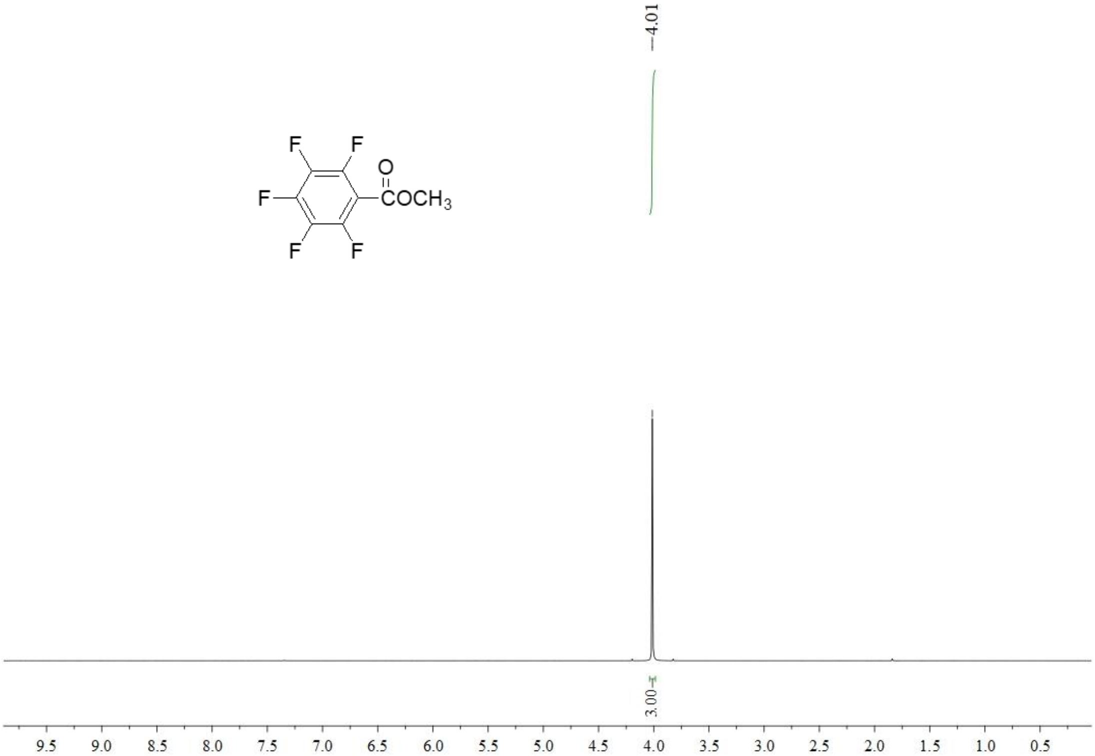
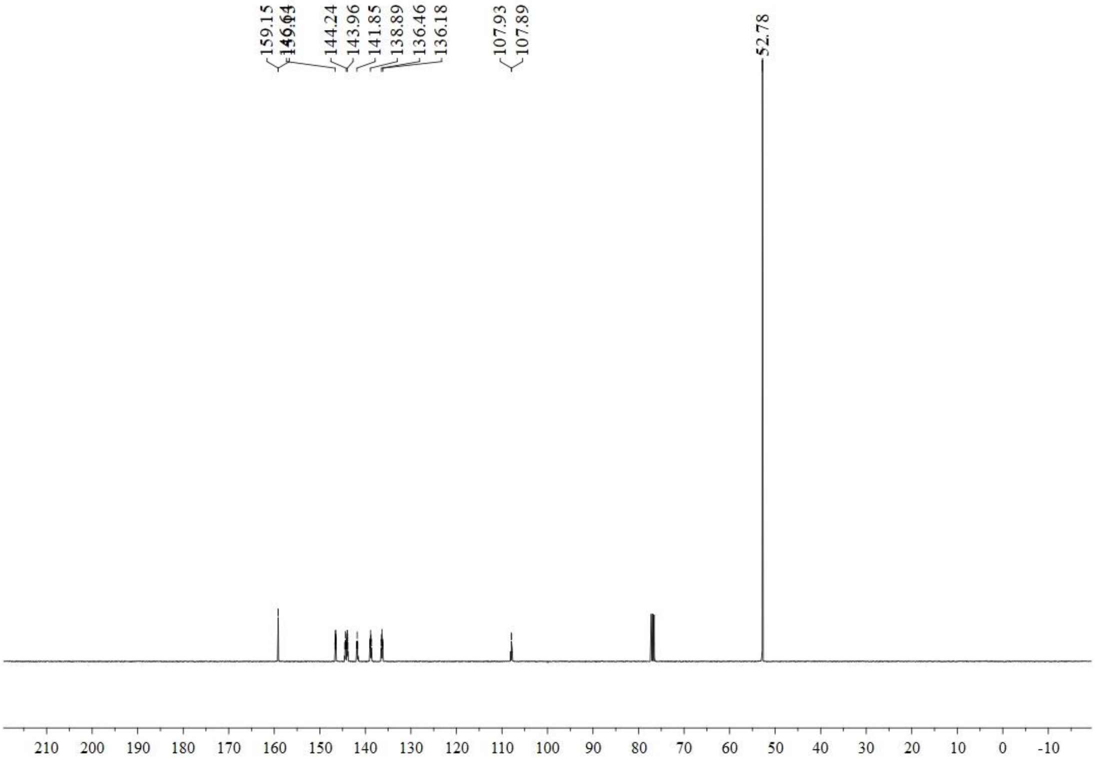


Figure S31 1H and 13C NMR of methyl 3,4,5-trimethoxybenzoate



F
F
F
F
F
O
COCH3
4.01
3.00
9.5 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



159.15
144.24
143.96
141.85
138.89
136.46
136.18
107.93
107.89
52.78
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

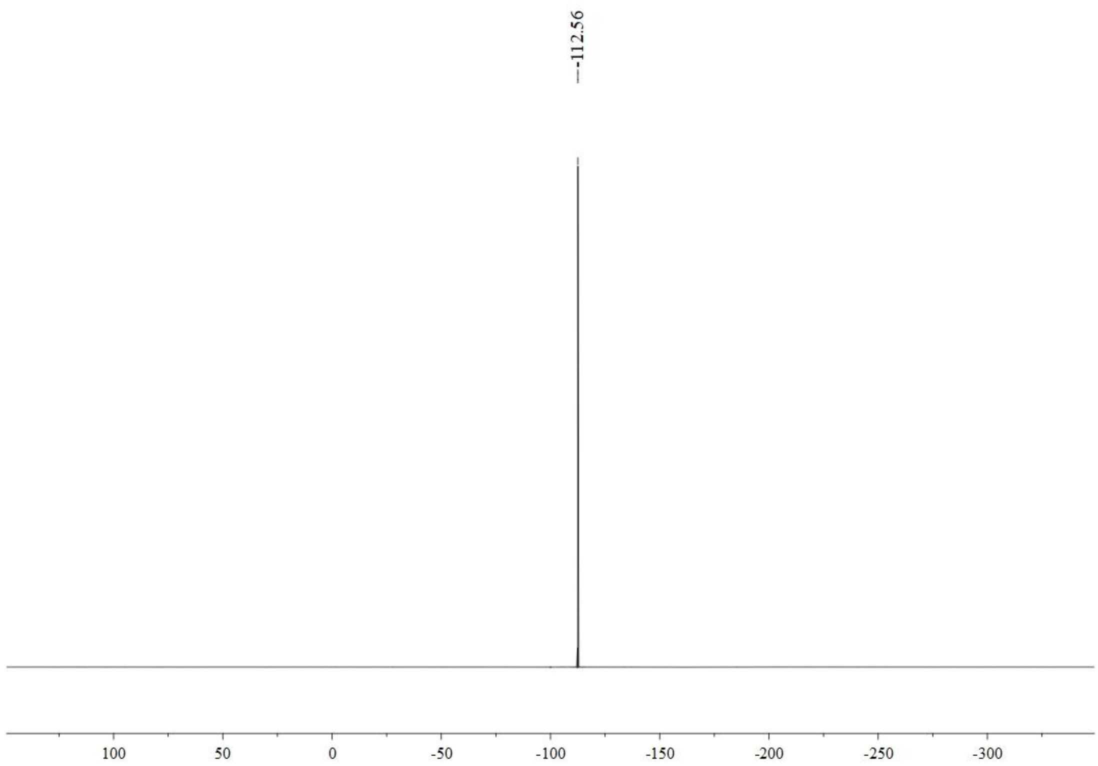


Figure S32 ^{1}H, ^{13}C and ^{19}F NMR of Methyl 2,3,4,5,6-pentafluorobenzoate

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