

Pd(CH₃CN)₂Cl₂/Pipicolinic Acid as a Highly Efficient Catalytic System for Suzuki-Miyaura Cross-coupling Reaction of Bromoaryl Carboxylic Acids in Water

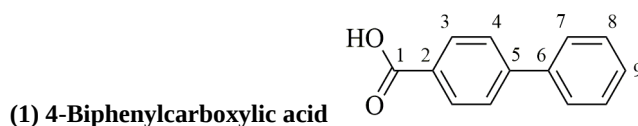
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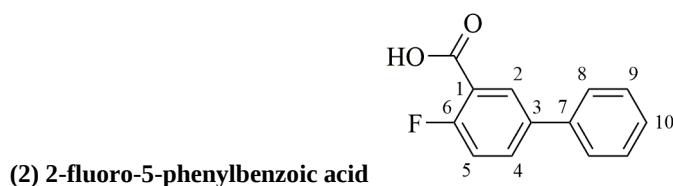
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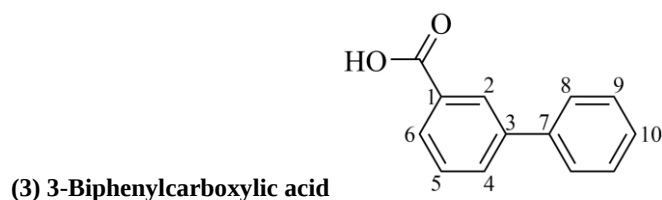
(A) Analytical data for products



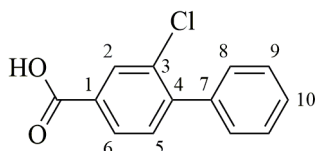
White solid: ¹H NMR (400 MHz, DMSO-*d*₆): δ 13.02 (s, 1H, COOH-H), 8.04 (d, *J*=8.0Hz, 2H, C3-H), 7.79 (d, *J*=8.0Hz, 2H, C4-H), 7.71-7.73 (m, 2H, C7-H), 7.51-7.47 (m, 2H, C8-H), 7.41 (t, *J*=8Hz, 1H, C9-H). ¹³C NMR (100MHz, DMSO-*d*₆): δ 167.6 (COOH), 144.8 (C5), 139.5 (C6), 130.4 (C3), 130.1(C2), 129.5(C4), 128.7(C9), 127.4(C7), 127.3(C8).



White solid: ¹H NMR (400 MHz, DMSO-*d*₆): δ 13.42 (s, 1H, COOH-H), 8.07-8.10 (m, 1H, C2-H), 7.88-7.99 (m, 1H, C4-H), 7.64-7.70 (m, 2H, C5-H, C10-H), 7.46-7.50 (m, 2H, C8-H), 7.37-7.42 (m, 2H, C9-H); ¹³C NMR (100MHz, DMSO-*d*₆): δ 165.4 (d, *J*=3.0 Hz, COOH), 161.1(d, *J*=260Hz, C6), 138.7(C7), 136.9 (d, *J*=4.0Hz, C3), 133.2 (d, *J*=9.0Hz, C4), 130.2(C2), 129.5(C8), 128.3(C9), 127.1 (C10), 120.2 (d, *J*=11.0Hz, C1), 118.1 (d, *J*=23.0Hz, C5)

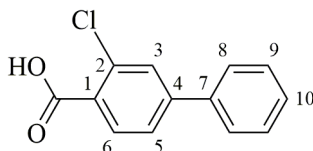


White solid: ¹H NMR (400 MHz, DMSO-*d*₆): δ 13.15 (s, 1H, COOH-H), 8.18(s, 1H, C2-H), 7.88-7.99 (m, 2H, C4-H, C5-H), 7.66-7.71 (m, 2H, C6-H), 7.58-7.62 (m, 1H, C8-H), 7.45-7.51 (m, 2H, C9-H), 7.38-7.42 (m, 1H, C10-H). ¹³C NMR (100MHz, DMSO-*d*₆): δ 167.1(COOH), 141.0(C-3), 139.7(C-7), 132.0(C-4), 131.6(C-1), 129.8(C-2), 129.6(C-8), 128.7(C-6), 128.3(C-10), 127.8(C-5), 127.3(C-8).



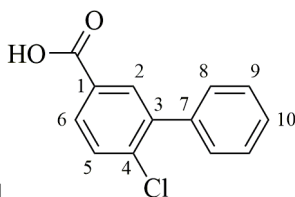
(4)3-chloro-4-phenylbenzoic acid

White solid: ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 13.37 (s, 1H, COOH-H), 8.02 (d, $J=1.2\text{Hz}$, 1H, C2-H), 7.94 (dd, $J_1=1.2\text{ Hz}$, $J_2=6.4\text{Hz}$, 1H, C6-H), 7.752(d, $J=6.4$, 1H, C5-H), 7.44-7.48(m, 5H, C8-H, C9-H, C10-H). ^{13}C NMR (100MHz, $\text{DMSO}-d_6$): δ 166.39 (COOH), 144.30 (C4), 138.32 (C7), 132.26 (C3), 132.01 (C2), 130.83 (C1), 129.51 (C8), 128.76 (C9), 128.73 (C5), 128.62 (C6).



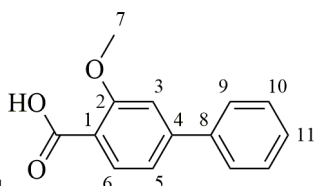
(5) 2-chloro-4-phenylbenzoic acid

White solid: ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 13.42(s, 1H, COOH-H), 7.90(d, $J=8.0\text{Hz}$, 1H, C6-H), 7.80(d, $J=1.6\text{Hz}$, 1H, C3-H), 7.72-7.73(m, 1H, C5-H), 7.69-7.71(m, 2H, C8-H), 7.46-7.50(m, 2H, C9-H), 7.40-7.44(m, 1H, C10-H); ^{13}C NMR (100MHz, $\text{DMSO}-d_6$): δ 166.87(COOH), 144.76(C4), 138.04(C7), 133.14(C2), 132.13(C6), 130.13(C3), 129.54(C1), 129.13(C9), 128.99(C5), 127.44(C8), 125.73(C10).



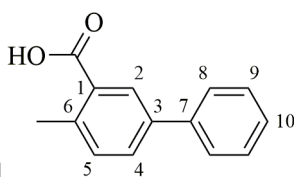
(6) 4-chloro-3-phenylbenzoic acid

White solid: ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 13.24 (s, 1H, COOH-H), 7.92-7.94 (m, 1H, C6-H), 7.89(d, $J=1.6\text{Hz}$, C2-H), 7.68 (d, $J = 8.3\text{ Hz}$, 1H, C5-H), 7.41-7.50 (m, 5H, C8-H, C9-H, C10-H). ^{13}C NMR (100MHz, $\text{DMSO}-d_6$): δ 166.81(COOH), 140.45(C4), 138.40(C3), 136.45(C7), 132.43(C2), 130.73(C6), 130.49 (C5), 130.16(C1), 129.56(C9), 128.79(C8), 128.55(C10).



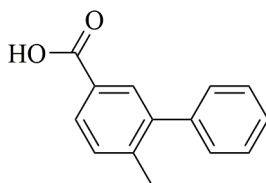
(7) 2-methoxy-4-phenylbenzoic acid

White solid: ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 12.66(s, 1H, COOH-H), 7.75-7.77(m, 1H, C6-H), 7.72-7.74(m, 2H, C9-H), 7.47-7.52(m, 2H, C8-H), 7.40-7.44(m, 1H, C5-H), 7.34(s, 1H, C3-H), 7.26-7.30(m, 1H, C11-H), 3.92(s, 3H, OCH_3 -H); ^{13}C NMR (100MHz, $\text{DMSO}-d_6$): δ 167.54(COOH), 159.20(C2), 145.52(C4), 139.73(C8), 132.03(C10), 129.43(C6), 128.73(C9), 127.53(C11), 120.19(C5), 118.80(C3), 111.16(C1), 56.26(OCH_3).



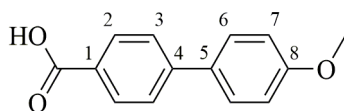
(8) 2-methyl-5-phenylbenzoic acid

White solid: ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 13.01 (s, 1H, COOH-H), 8.03 (s, 1H, C2-H), 7.71-7.75 (m, 1H, C4-H), 7.65-7.67 (m, 2H, C8-H), 7.45-7.49 (m, 2H, C9-H), 7.39-7.40 (m, 1H, C5-H), 7.35-7.38 (m, 1H, C10-H), 2.56 (s, 3H, CH_3 -H). ^{13}C NMR (100MHz, $\text{DMSO}-d_6$): δ 169.1 (COOH), 139.6(C7), 138.6(C3), 138.2(C6), 132.7(C4), 131.5(C2), 130.2(C1), 129.5(C9), 128.62(C5), 128.0(C10), 126.9(C8), 21.3(CH_3).



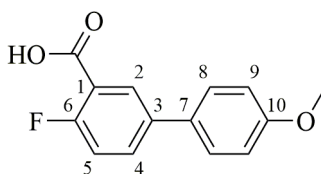
(9) 4-methyl-3-phenylbenzoic acid

White solid: ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 12.93 (s, 1H, COOH-H), 7.85 (dd, $J_1=1.6\text{Hz}$, $J_2=7.6\text{Hz}$, C6-H), 7.76 (d, $J=1.6\text{Hz}$, 1H, C2-H), 7.429-7.47 (m, 2H, C8-H), 7.37-7.41 (m, 2H, C9-H), 7.34-7.36 (m, 1H, C5-H), 7.32-7.33 (m, 1H, C10-H), 2.29 (s, 3H, CH_3 -H); ^{13}C NMR (100MHz, $\text{DMSO}-d_6$): δ 167.62(COOH), 141.89 (C4), 140.81 (C7), 140.76 (C3), 131.16 (C2), 130.76 (C5), 129.34 (C9), 129.00 (C6), 128.85 (C8), 128.60 (C1), 127.78 (C10), 20.80(CH_3).



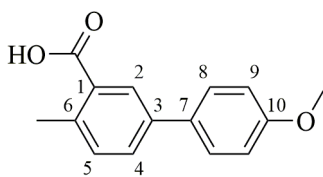
(10) 4-(4-methoxyphenyl)benzoic acid

White solid: ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 12.94, (s, 1H, COOH-H), 8.00(d, $J=8.4$, 2H, C2-H), 7.75(d, $J=8.4$, 2H, C3-H), 7.69(d, $J=8.8$, 2H, C6-H), 7.06(d, $J=8.8$, 2H, C7-H), 3.82(s, 3H, OCH_3 -H). ^{13}C NMR (100MHz, $\text{DMSO}-d_6$): δ 167.65 (COOH), 160.02 (C8), 144.41 (C4), 131.69 (C5), 130.41 (C6), 129.31 (C1), 128.58 (C3), 126.56 (C2), 114.96 (C7), 55.68 (OCH_3).



(11) 2-fluoro-5-(4-methoxyphenyl)benzoic acid

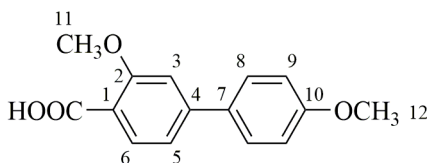
White solid: ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 13.36(s, 1H, COOH-H), 8.03-8.06 (m, 1H, C2-H), 7.84-7.88 (m, 1H, C4-H), 7.59-7.63 (m, 2H, C9-H), 7.33-7.40 (m, 1H, C5-H), 7.01-7.06 (m, 2H, C8-H), 3.81(s, 3H, OCH_3 -H); ^{13}C NMR (100MHz, $\text{DMSO}-d_6$): δ 165.50(d, $J=3.0\text{ Hz}$, COOH), 160.675(d, $J=255.0\text{Hz}$, C6), 159.61 (C10), 132.62(d, $J=8.7\text{Hz}$, C2), 131.08 (C3), 129.56 (C7), 128.27 (C8), 127.67 (C4), 120.08 (d, $J=8.0\text{Hz}$, C1), 117.92(d, $J=22.5$, C5), 114.94(C9), 55.65(OCH_3).



(12) 2-methyl-5-(4-methoxyphenyl)benzoic acid

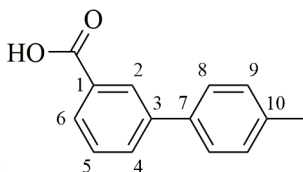
White solid: ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 12.91(s, 1H, COOH-H), 8.04(s, 1H, C2-H), 7.61-7.69 (m, 1H, C4-H), 7.57-7.60 (m, 2H, C8-H), 7.34(d, $J=8.0\text{ Hz}$, 1H, C5-H), 7.00-7.04 (m, 2H,

C9-H), 3.79(s, 3H, OCH₃-H), 2.54(s, 3H, CH₃-H); ¹³C NMR (100MHz, DMSO-*d*₆): δ 169.10 (COOH), 159.45(C10), 137.86 (C3), 137.63 (C6), 132.62 (C7), 131.95 (C4), 131.47 (C1), 129.66 (C2), 128.07 (C8), 128.02 (C5), 114.89 (C9), 55.61(OCH₃), 21.27(CH₃).



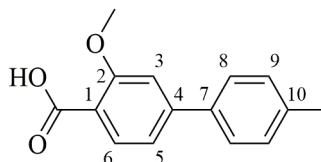
(13) 2-methoxy-4-(4'-methoxyphenyl)-benzoic acid

White solid: ¹H NMR (400 MHz, DMSO-*d*₆): δ 12.50(s, 1H, COOH-H), 7.71-7.73(m, 2H, C8-H), 7.70(s, 1H, C3-H), 7.29-7.23(m, 2H, C5-H, C6-H), 7.03-7.07 (m, 2H, C9), 3.91(s, 3H,OCH₃-H), 3.61(s, 3H, OCH₃-H). ¹³C NMR (100MHz, DMSO-*d*₆): δ 167.44 (COOH), 160.02 (C2), 159.31 (C10), 145.22 (C4), 132.05 (C7), 131.98 (C6), 128.70 (C8), 119.42 (C5), 118.26 (C3), 114.85 (C9), 110.60 (C1), 55.29 (C11), 55.73(C12).



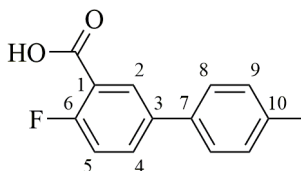
(14) 3-(4-methylphenyl)benzoic acid

White solid: ¹H NMR (400 MHz, DMSO-*d*₆): δ 13.06 (s, 1H, COOH-H), 8.17 (s, 1H, C2-H), 7.88-7.93 (m, 2H, C8-H), 7.58-7.60 (m, 3H, C4-H, C5-H, C6-H), 7.29-7.34 (m, 2H, C9-H), 2.36 (s, 3H, CH₃-H); ¹³C NMR (100MHz, DMSO-*d*₆): δ 167.71 (COOH), 140.88 (C3), 137.73 (C7), 136.84 (C4), 131.92 (C1), 131.29 (C10), 130.14 (C9), 129.73 (C2), 128.41 (C6), 127.49 (C5), 127.06 (C8), 21.14 (CH₃) .



(15) 2-methoxy-4-(4-methoxyphenyl)benzoic acid

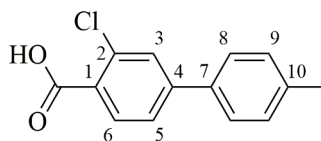
White solid: ¹H NMR (400 MHz, DMSO-*d*₆): δ 12.58(s, 1H, COOH-H), 7.75(d, *J*=8.0 Hz, 1H, Ar-H), 7.31(d, *J*=1.2Hz, 1H, C3-H), 7.28 (d, *J*=8.0Hz, 2H, C9-H), 7.24-7.26 (m, 1H, C5-H), 3.92(s, 3H, OCH₃-H), 2.34(s, 3H, CH₃-H); ¹³C NMR (100MHz, DMSO-*d*₆): δ 167.48 (COOH), 159.27 (C2), 145.47 (C4), 138.20 (C7), 136.80 (C6), 132.04 (C10), 129.89 (C9), 127.30 (C8), 119.89 (C5), 118.53 (C1), 110.84 (C3), 56.25 (OCH₃), 21.15(CH₃).



(16) 2-fluoro-5-(4-methylphenyl)-benzoic acid

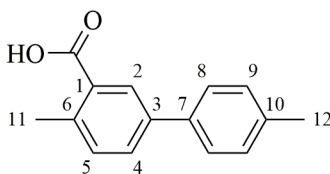
White solid: ¹H NMR (400 MHz, DMSO-*d*₆): δ 13.28(s, 1H, COOH-H), 8.07-8.03 (m, 1H, C5-H), 7.88 (s, 1H, C2-H), 7.56-7.58(m, 2H, C8-H), 7.42-7.37 (m, 1H, C4-H) 7.29(s, 2H, C9-H), 2.34 (s, 3H, CH₃-H); ¹³C NMR (100MHz, DMSO-*d*₆): δ 165.46, (d, *J*=2.8Hz, COOH), 160.911(d, *J*=255.4,

C6), 137.68 (C6), 136.86(d, $J = 3.6$, C3), 135.84 (C10), 132.86(d, $J = 8.6$ Hz, C4), 130.13 (C9), 129.84 (C1), 126.95 (C8), 120.13(d, $J = 10.9$ Hz, C2), 117.99(d, $J = 22.5$ Hz, C5), 21.10 (CH₃).



(17) 2-chloro-4-(4-methylphenyl)benzoic acid

White solid: ¹H NMR (400 MHz, DMSO-*d*₆): δ 13.35(s, 1H, COOH-H), 7.88(d, $J = 8.4$ Hz, 1H, C6-H), 7.78(d, $J = 1.6$ Hz, 1H, C3-H), 7.68(dd, $J_1 = 1.2$ Hz, $J_2 = 8.4$ Hz, 1H, C5-H), 7.61(d, $J = 8.0$ Hz, 2H, C8-H), 7.28(d, $J = 8.0$ Hz, C9-H), 2.34(s, 3H, CH₃-H); ¹³C NMR (100MHz, DMSO-*d*₆): δ 166.84 (COOH), 144.71(C4), 138.75 (C7), 135.10 (C2), 133.16 (C6), 132.15 (C1), 130.15 (C9), 129.71 (C10), 128.66 (C3), 127.26 (C5), 125.40 (C8), 21.15 (CH₃).

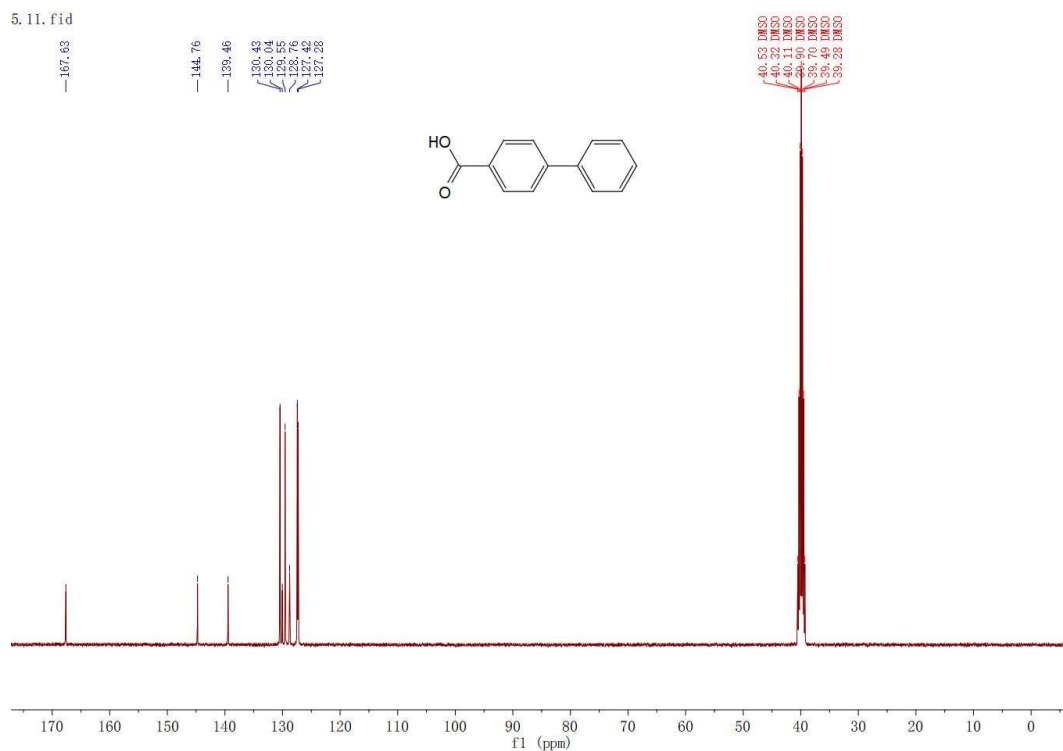
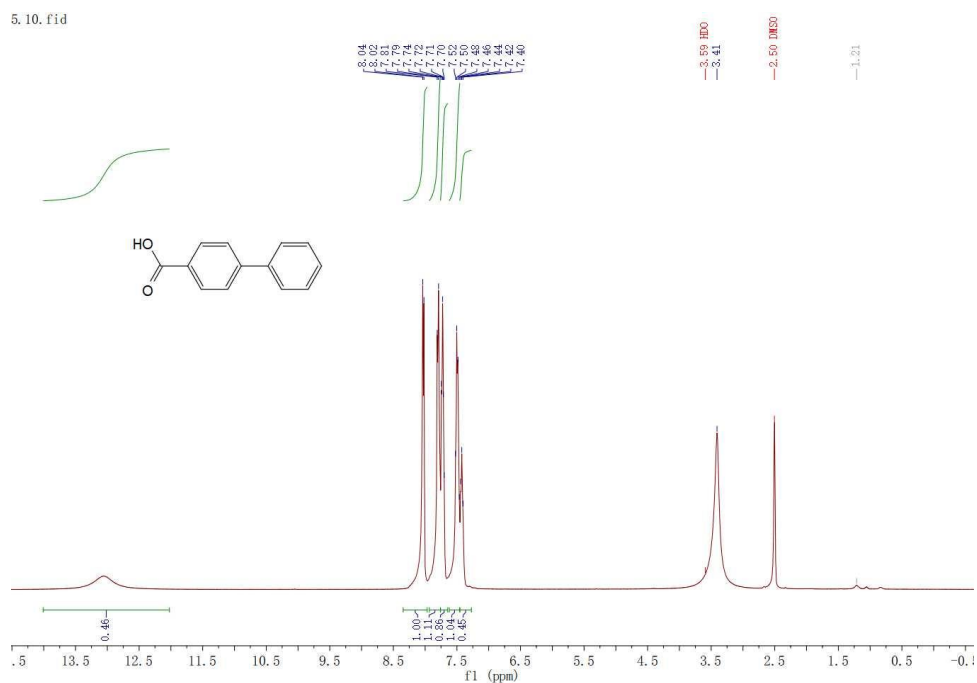


(18) 2-methyl-5-(4-methylphenyl)benzoic acid

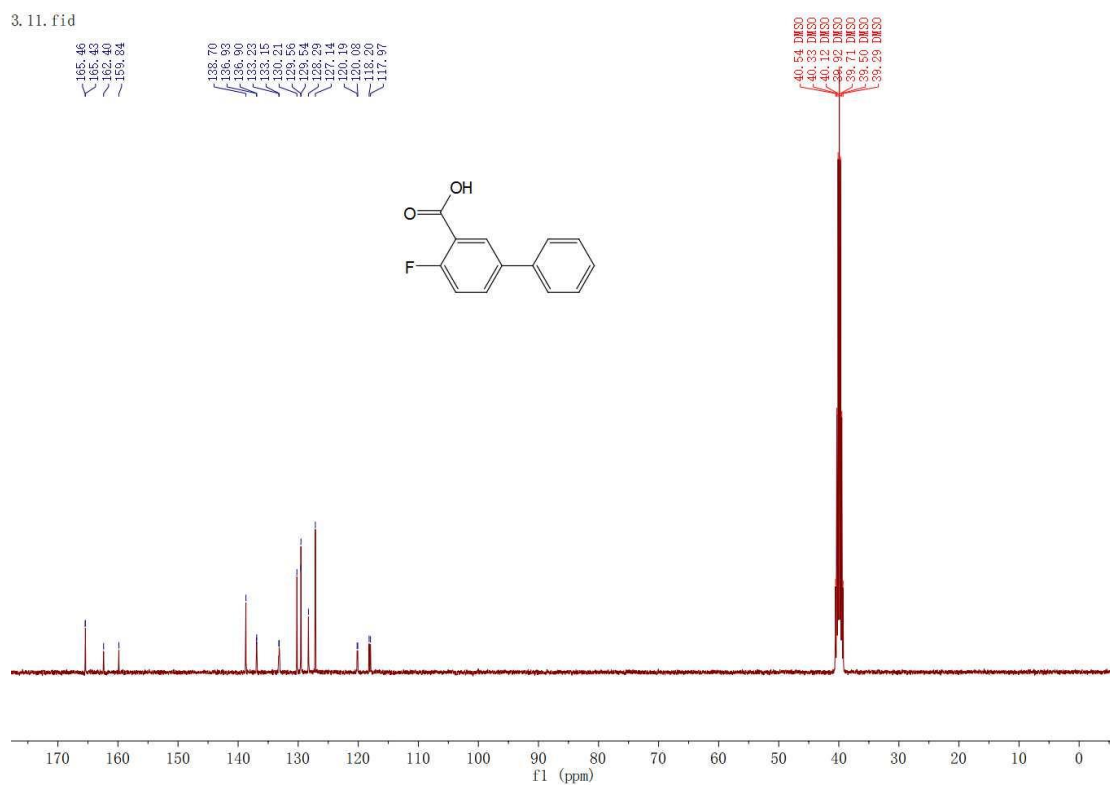
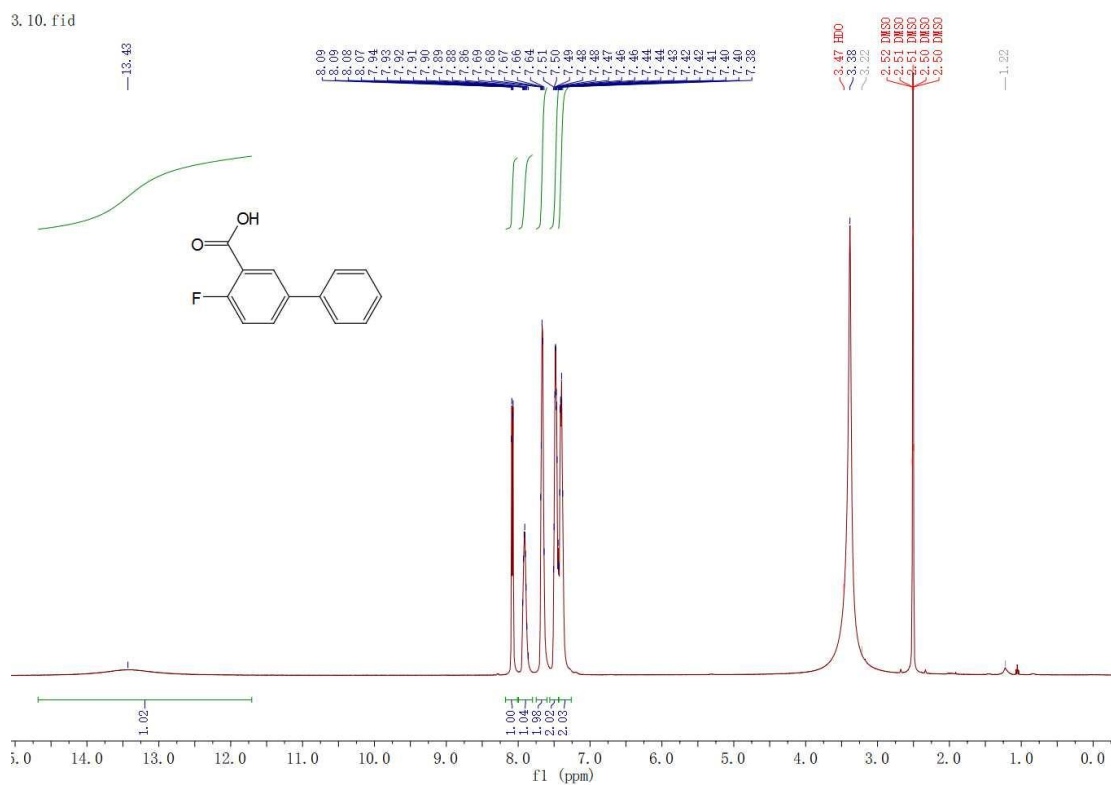
White solid: ¹H NMR (400 MHz, DMSO-*d*₆): δ 12.91 (s, 1H, COOH-H), 8.04 (s, 1H, C2-H), 7.72 (s, 1H, C5-H), 7.56 (s, 2H, C8-H), 7.37 (s, 1H, C4-H), 7.28 (s, 2H, C9-H), 2.54 (s, 2H, C11-H), 2.34 (s, 2H, C12-H). ¹³C NMR (100MHz, DMSO-*d*₆): δ 169.08 (COOH), 138.21 (C3), 138.09 (C6), 137.37 (C7), 136.72 (C4), 132.67 (C1), 131.50 (C2), 130.08 (C9), 129.92 (C10), 128.31 (C5), 126.76 (C8), 21.30 (C11), 21.13 (C12).

(B) NMR spectra

(1) 4-Biphenylcarboxylic acid

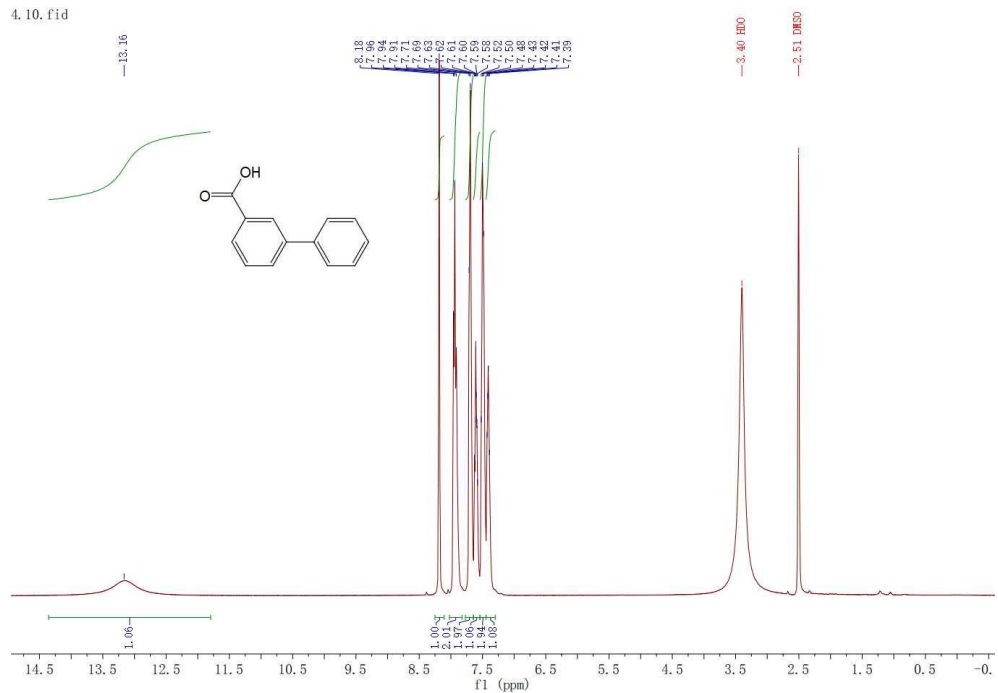


(2) 2-fluoro-5-phenylbenzoic acid

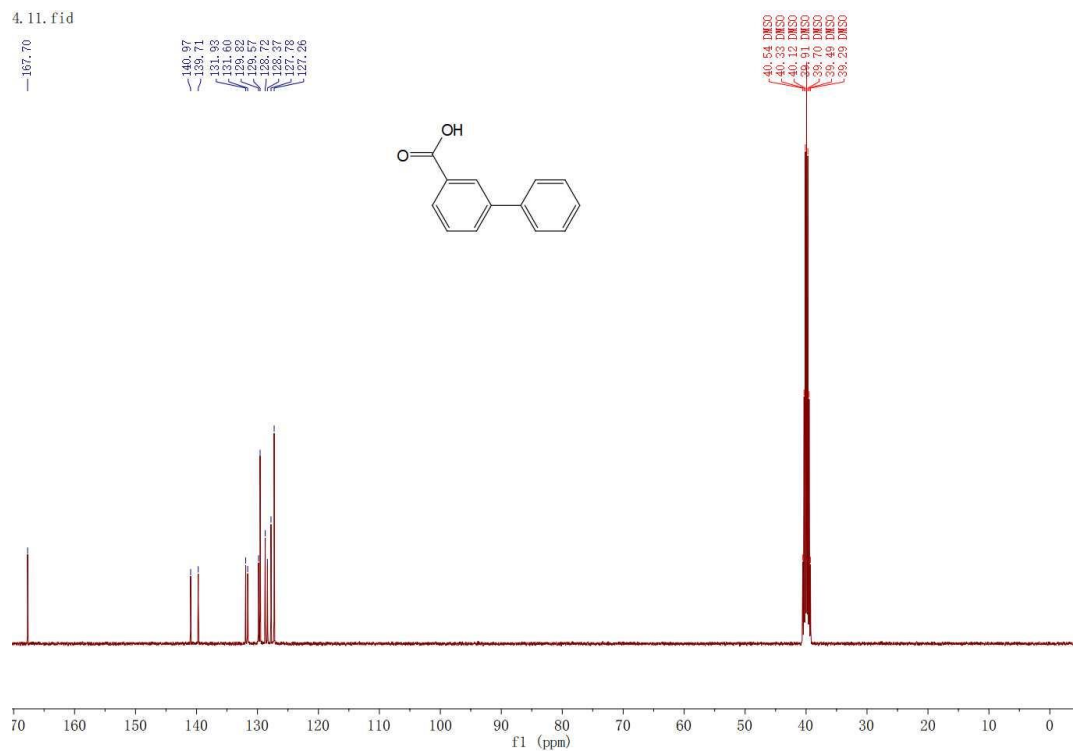


(3) 3-Biphenylcarboxylic acid

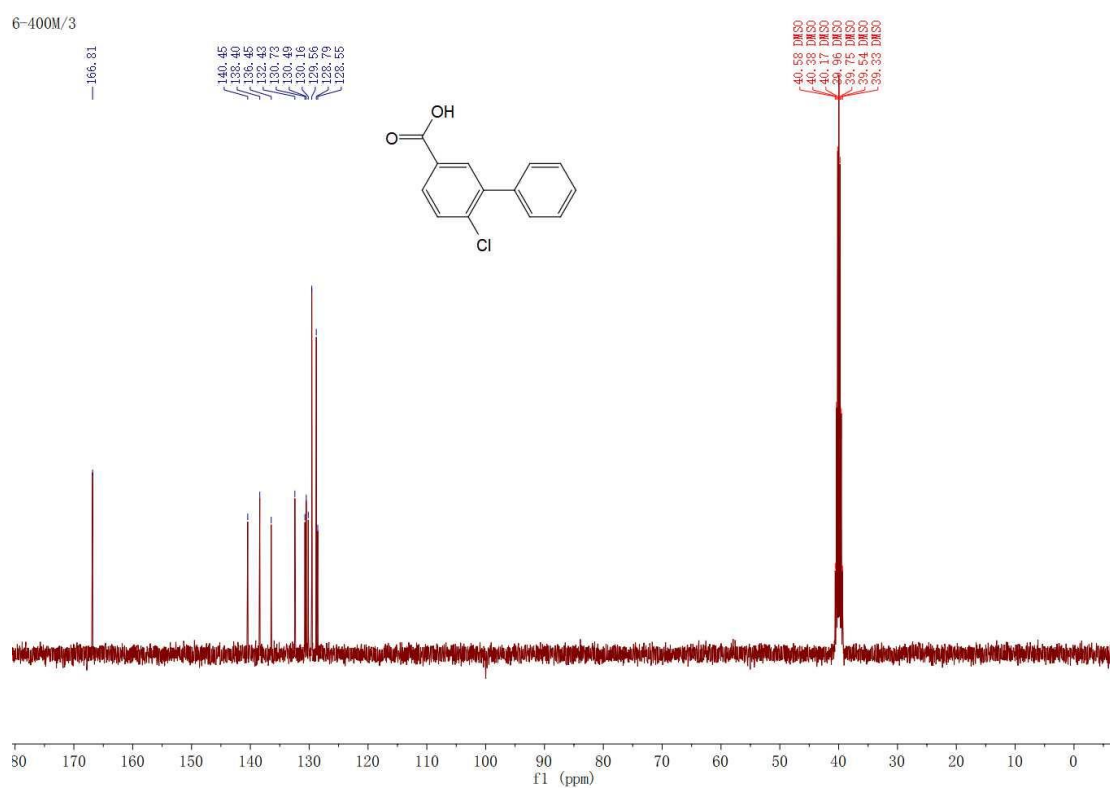
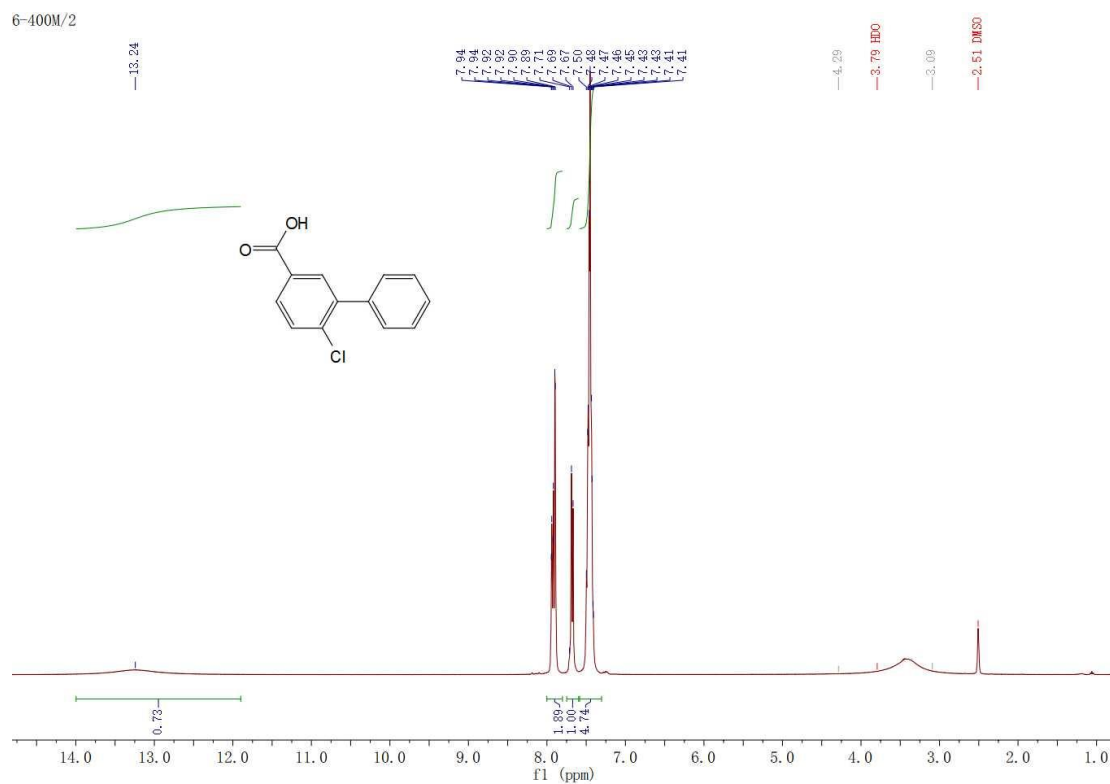
4.10. fid



4.11. fid

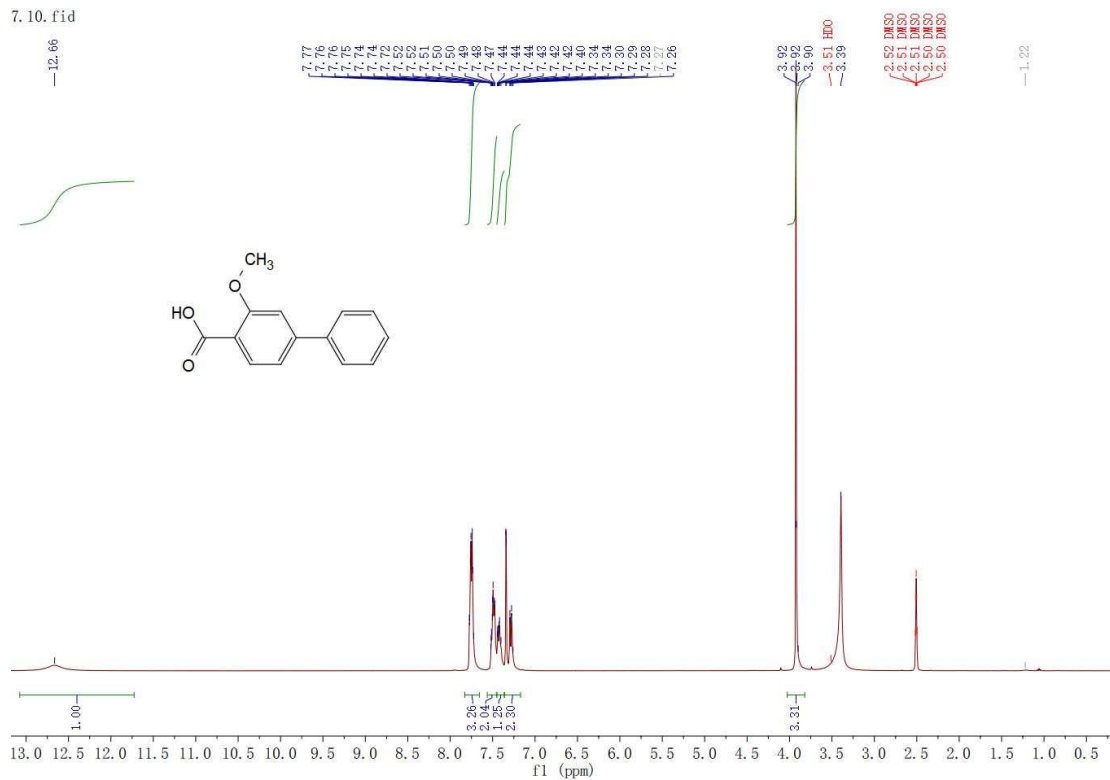


(4)3-chloro-4-phenylbenzoic acid

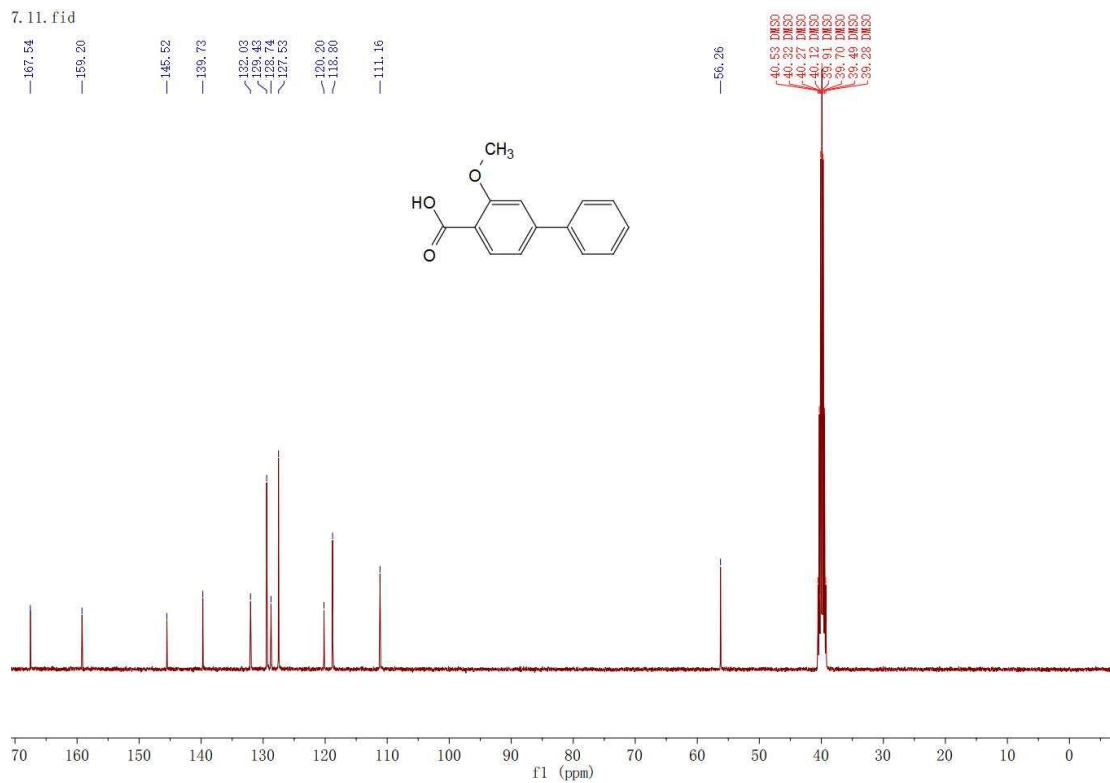


(7)2-methyl-4-phenylbenzoic acid

7.10. fid

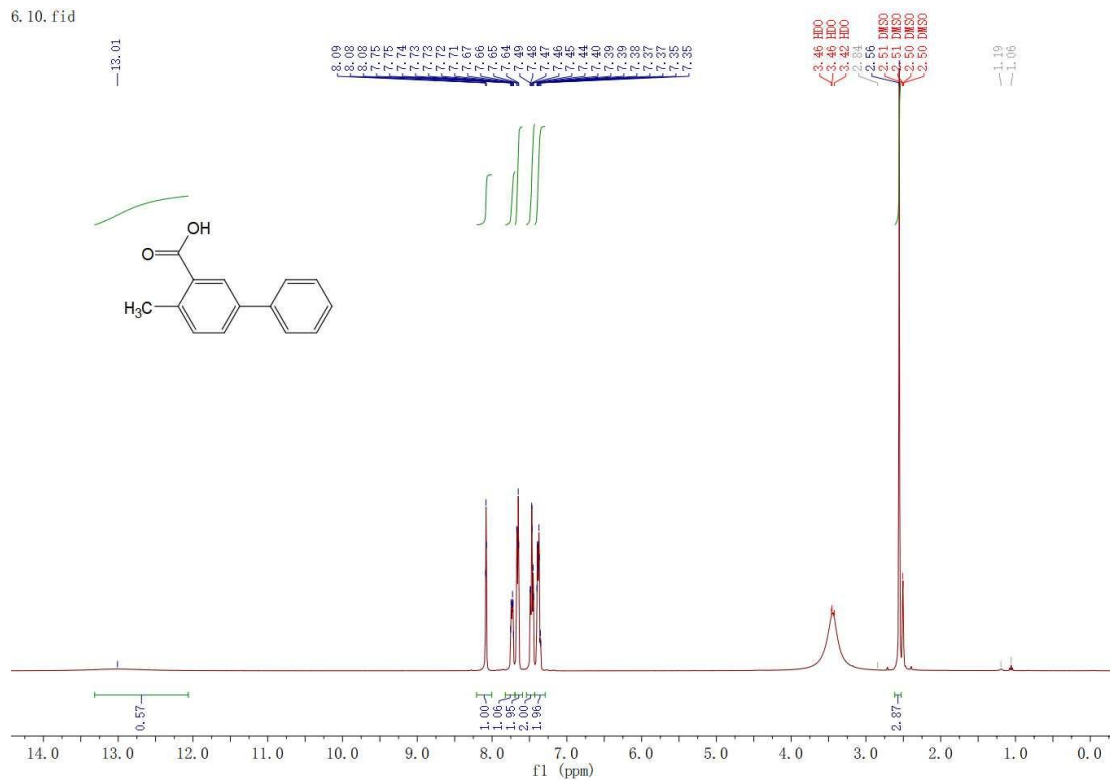


7.11. fid

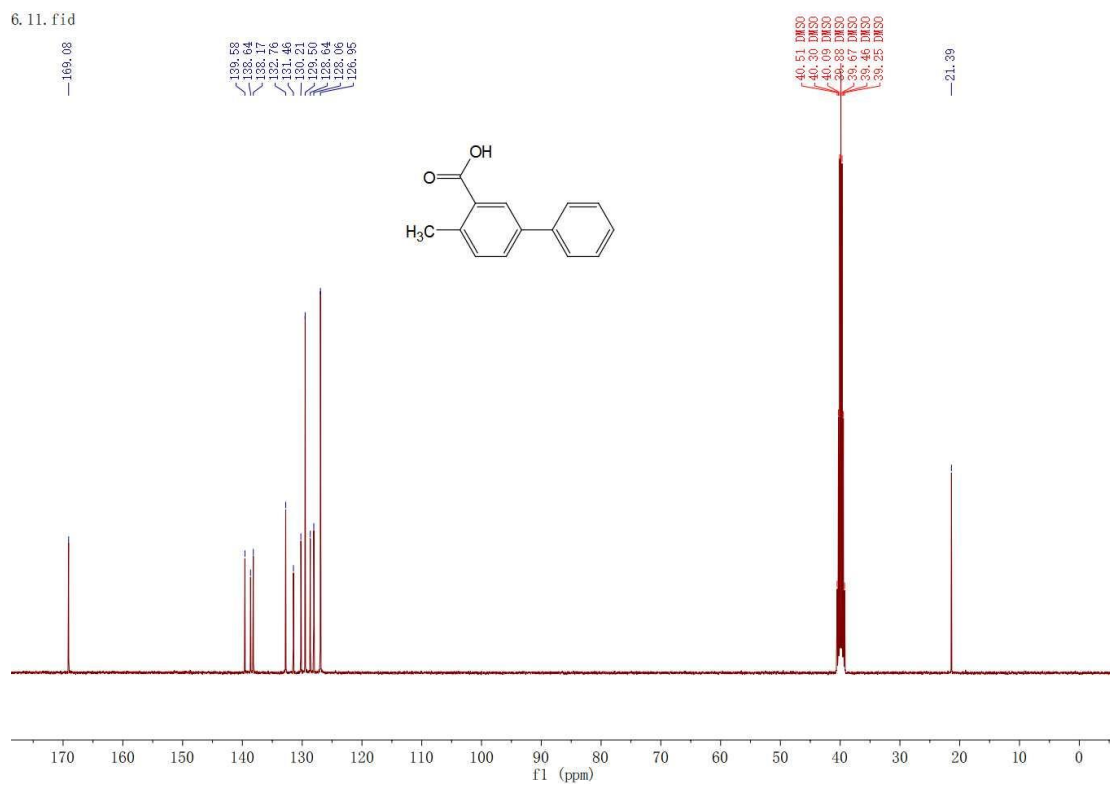


(8)2-methyl-5-phenylbenzoic acid

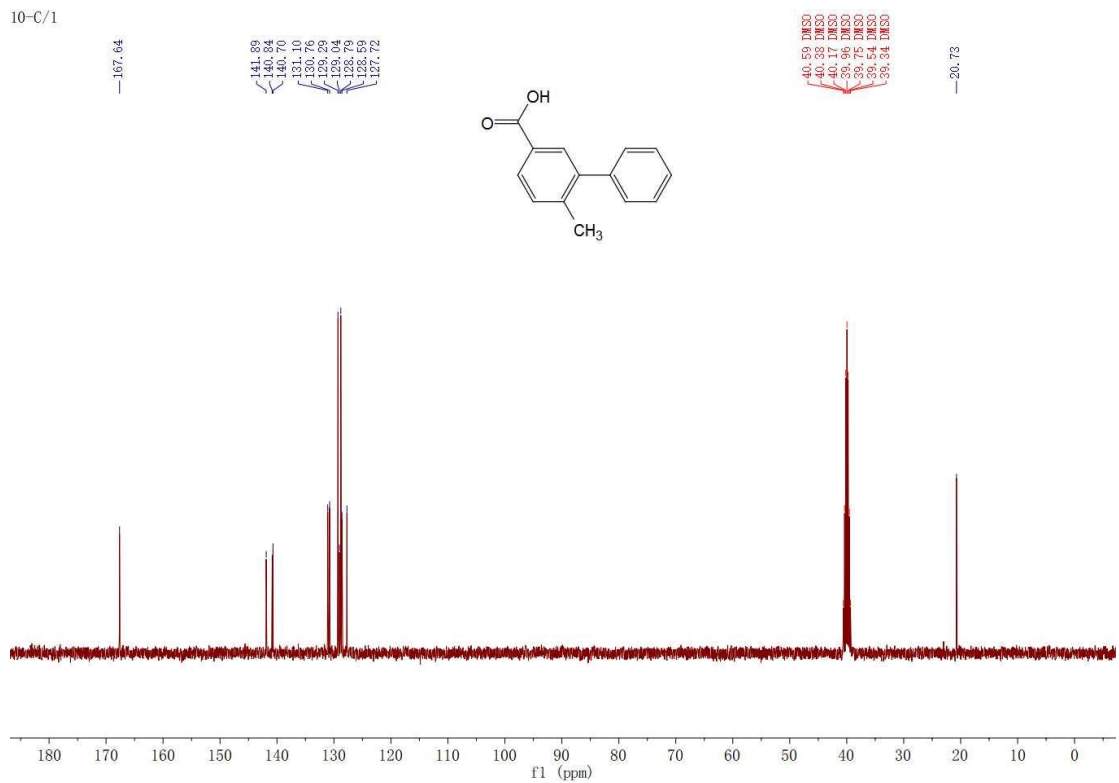
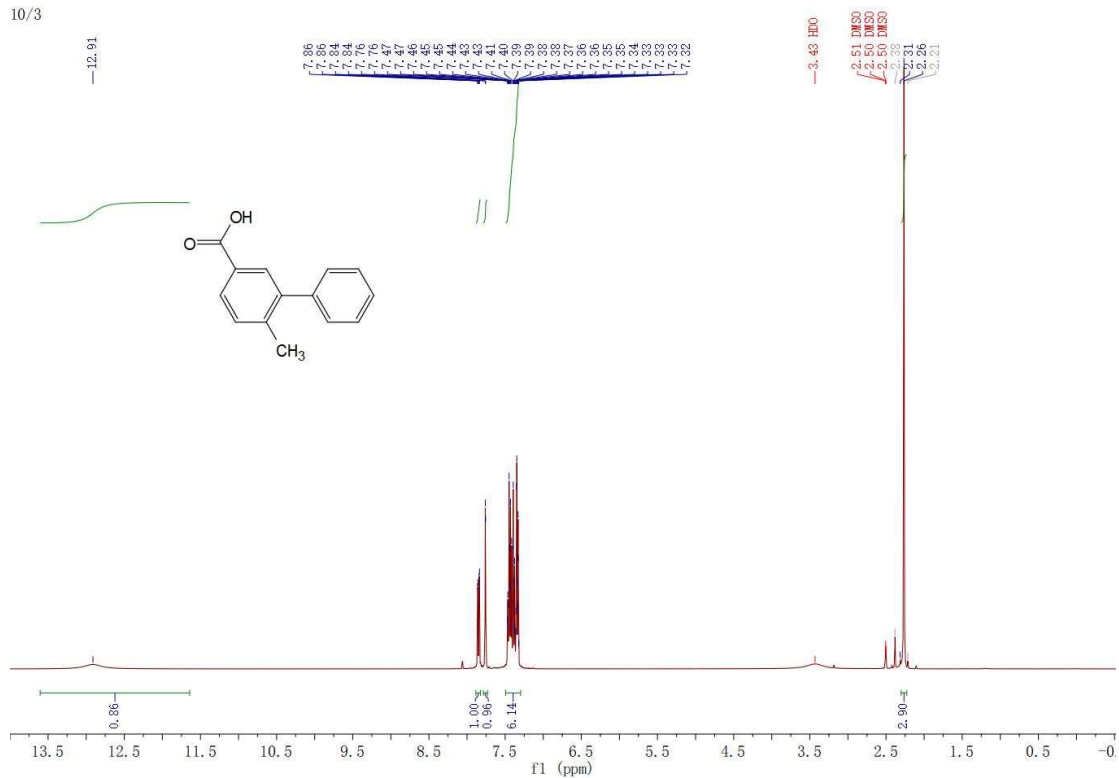
6. 10. fid



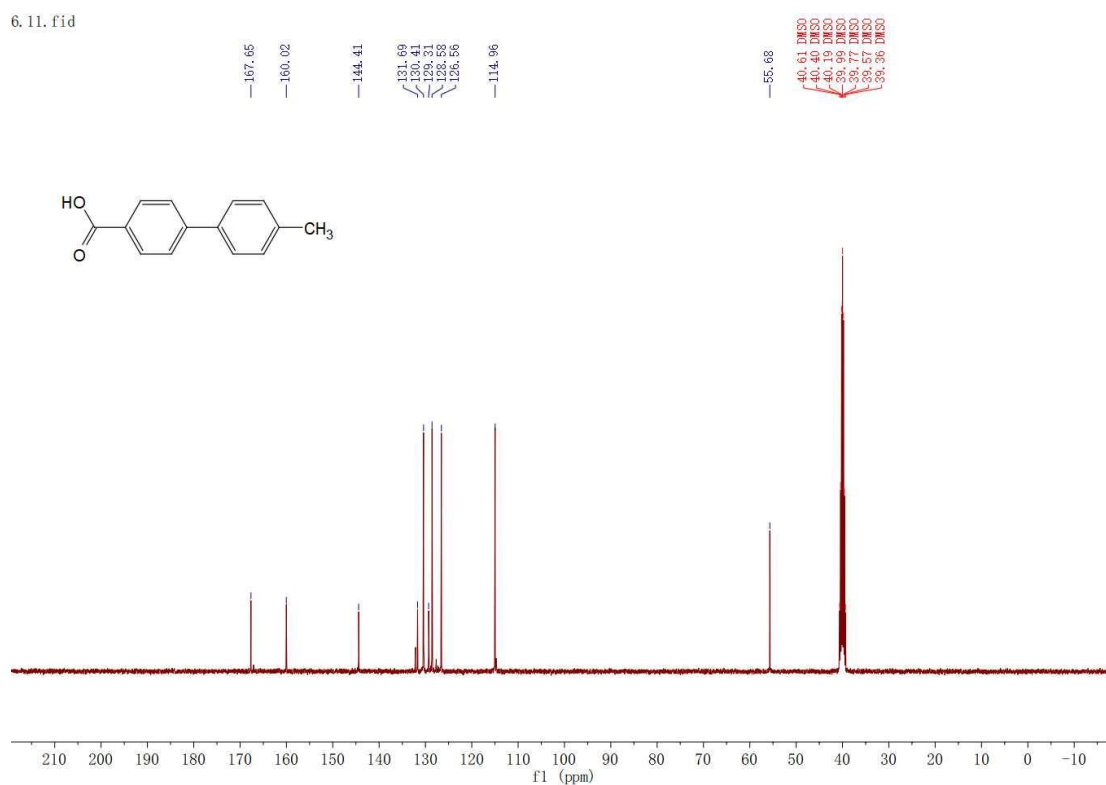
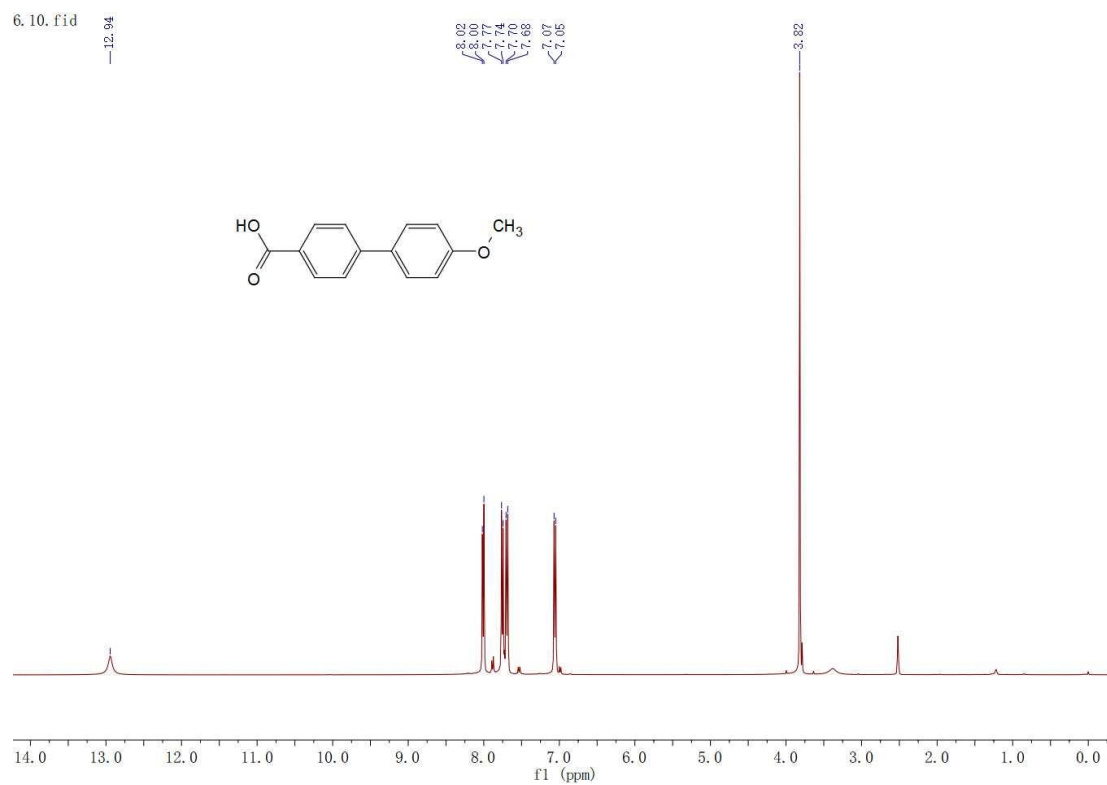
6. 11. fid



(9)4-methyl-3-phenylbenzoic acid

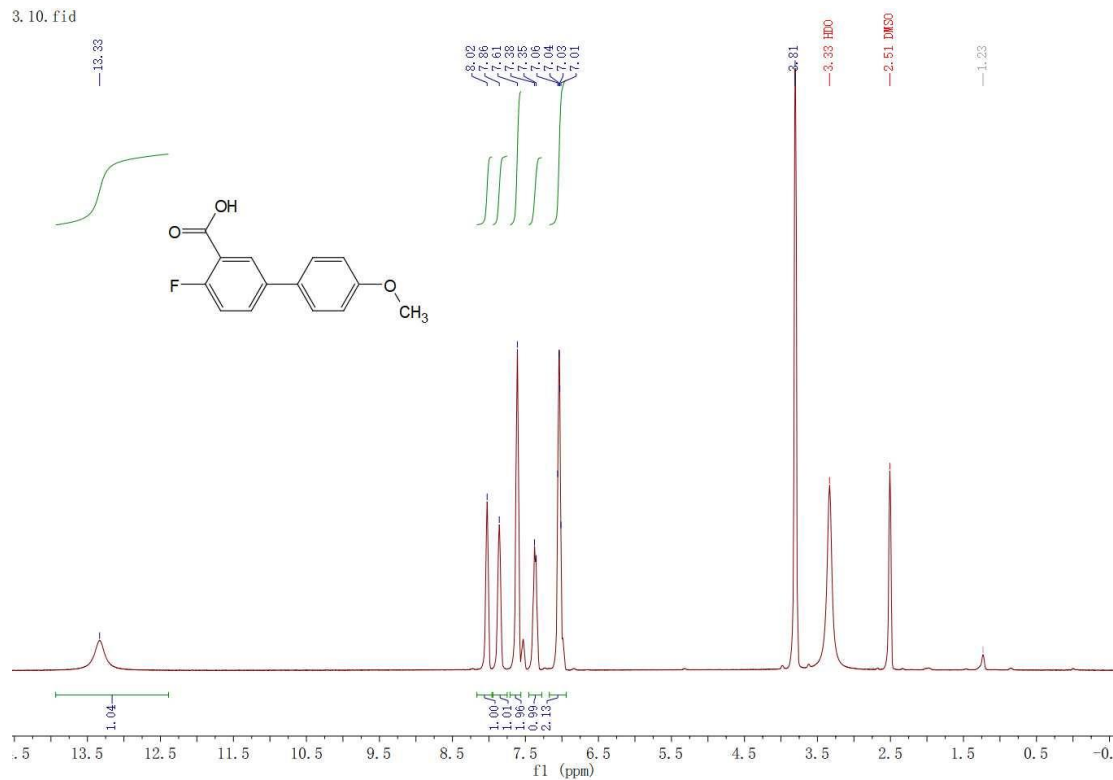


(10)4-(4-methoxyphenyl)-benzoic acid

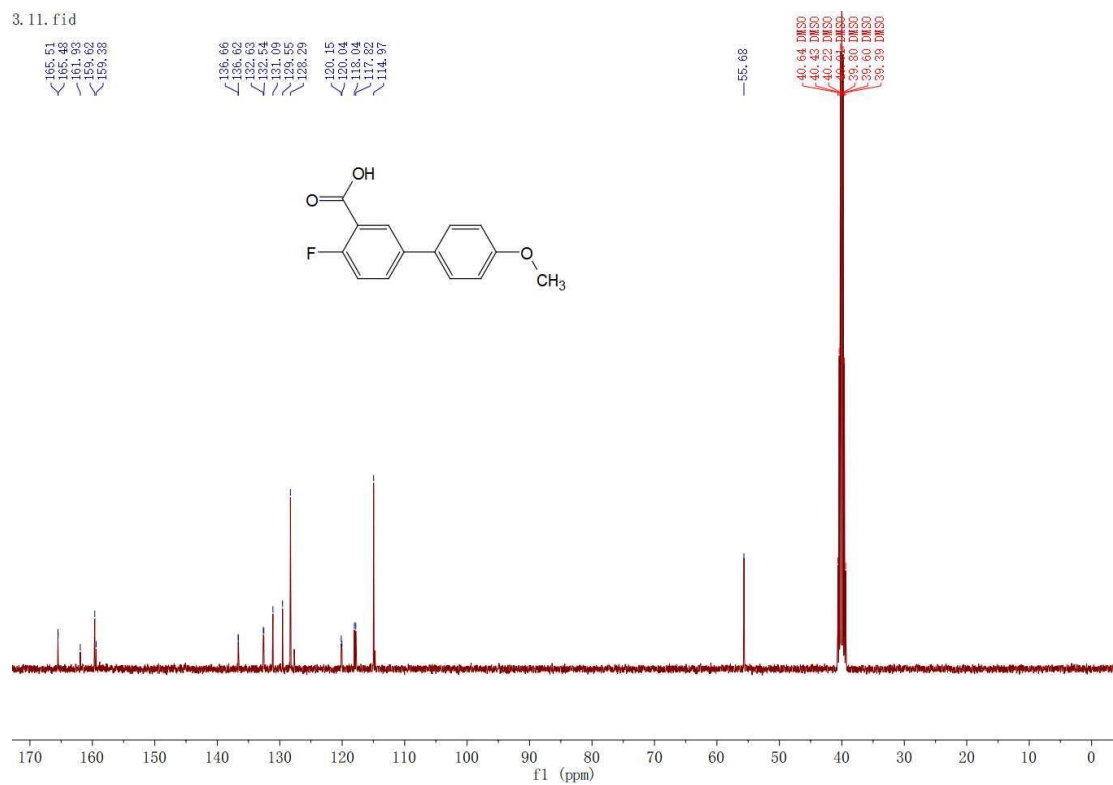


(11)2-fluoro-5-(4-methoxyphenyl)benzoic acid

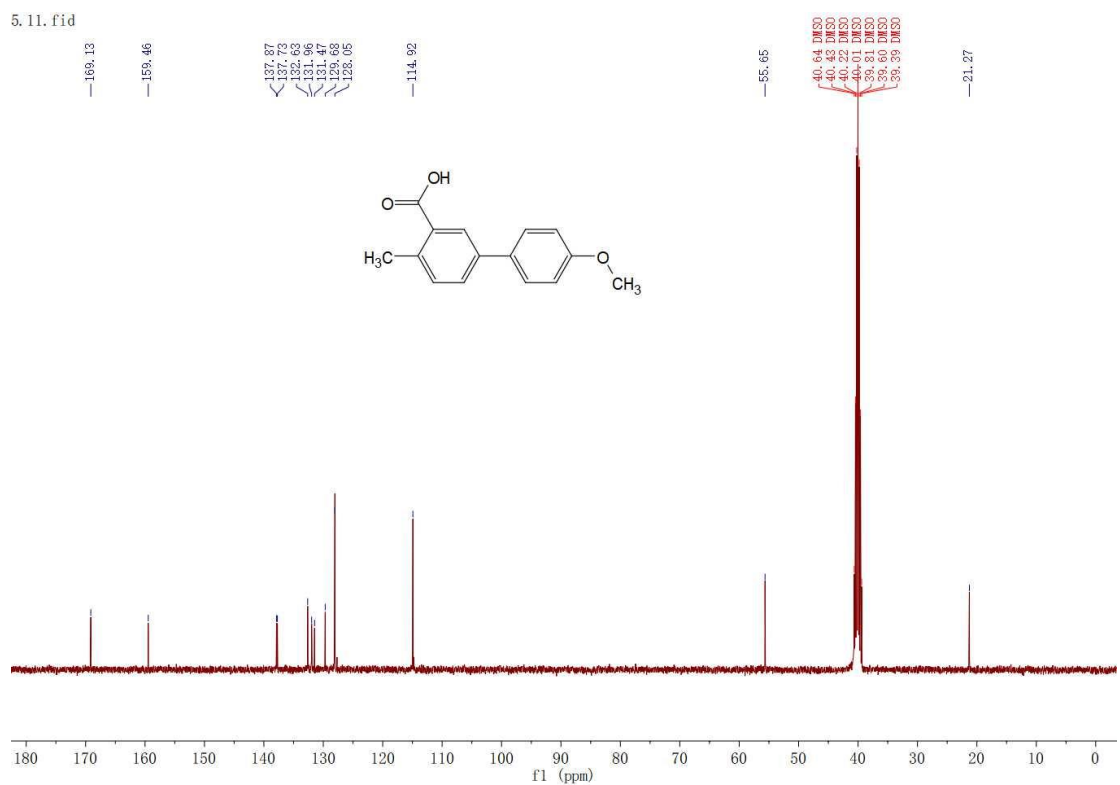
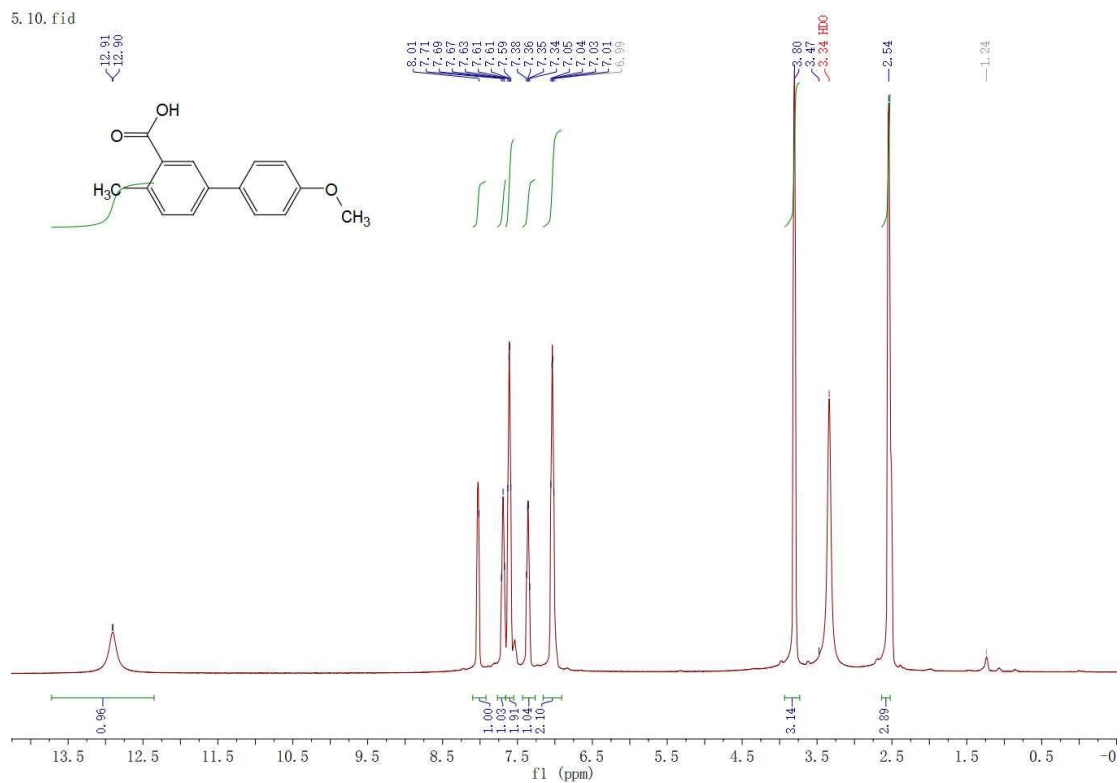
3.10. fid



3.11. fid

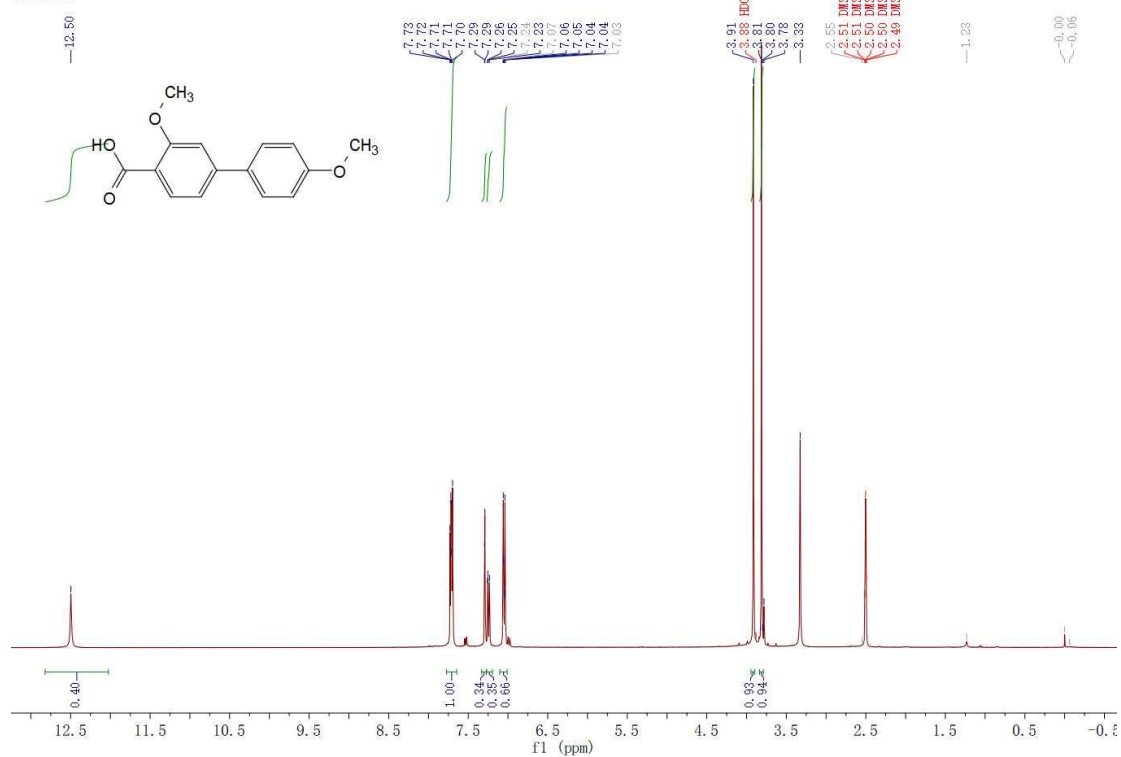


(12)2-methyl-5-(4-methoxyphenyl)benzoic acid

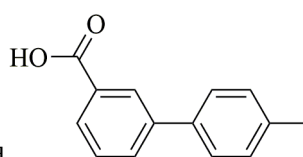
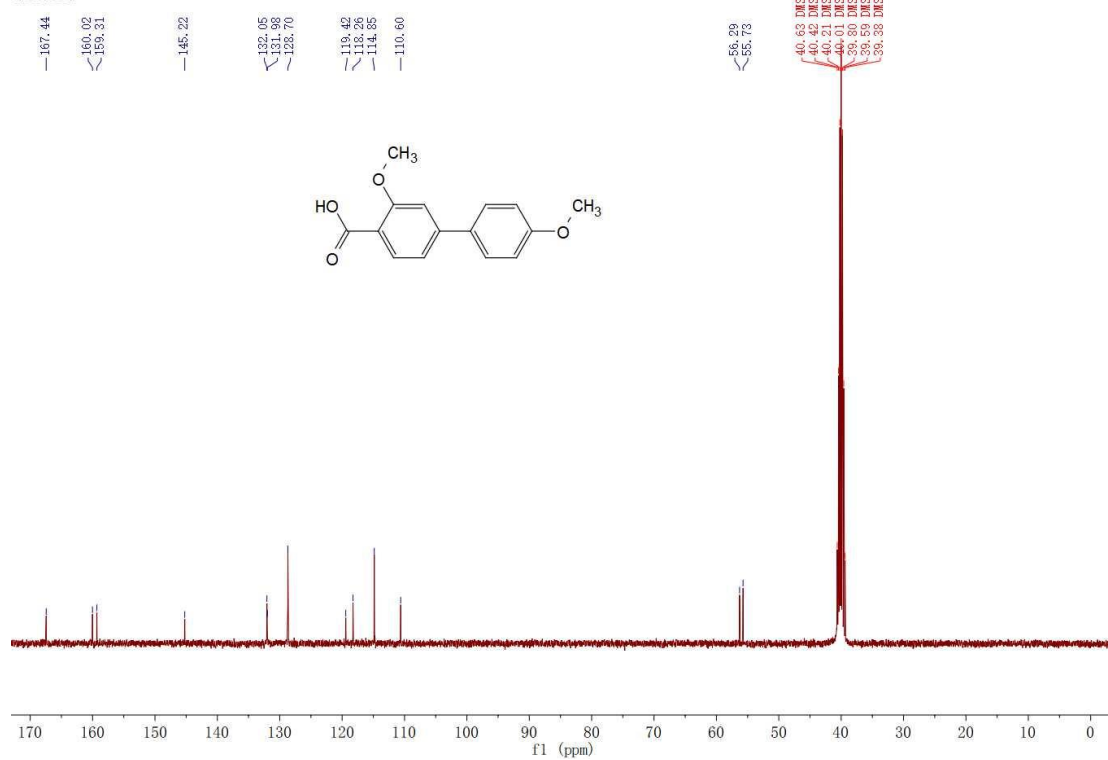


(13)2-methoxy-4-(4'-methoxyphenyl)-benzoic acid

4.10. fid

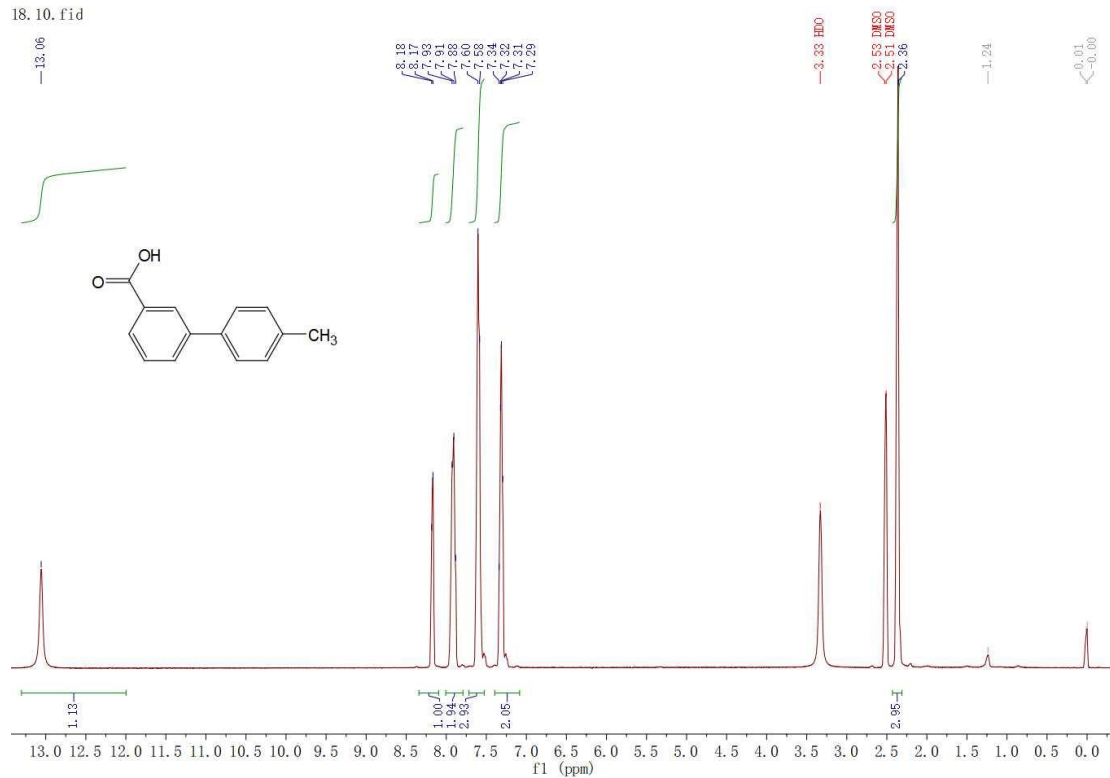


4.11. fid

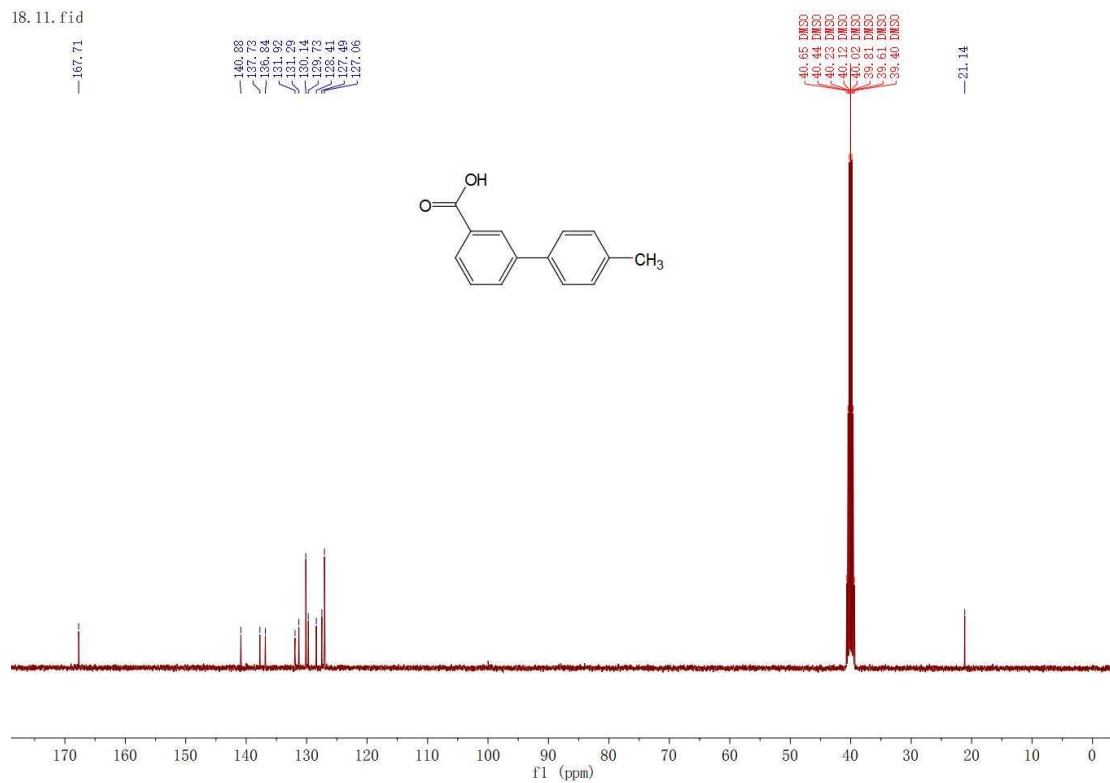


(14)3-(4-methylphenyl)benzoic acid

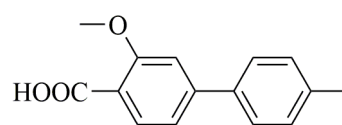
18. 10. fid



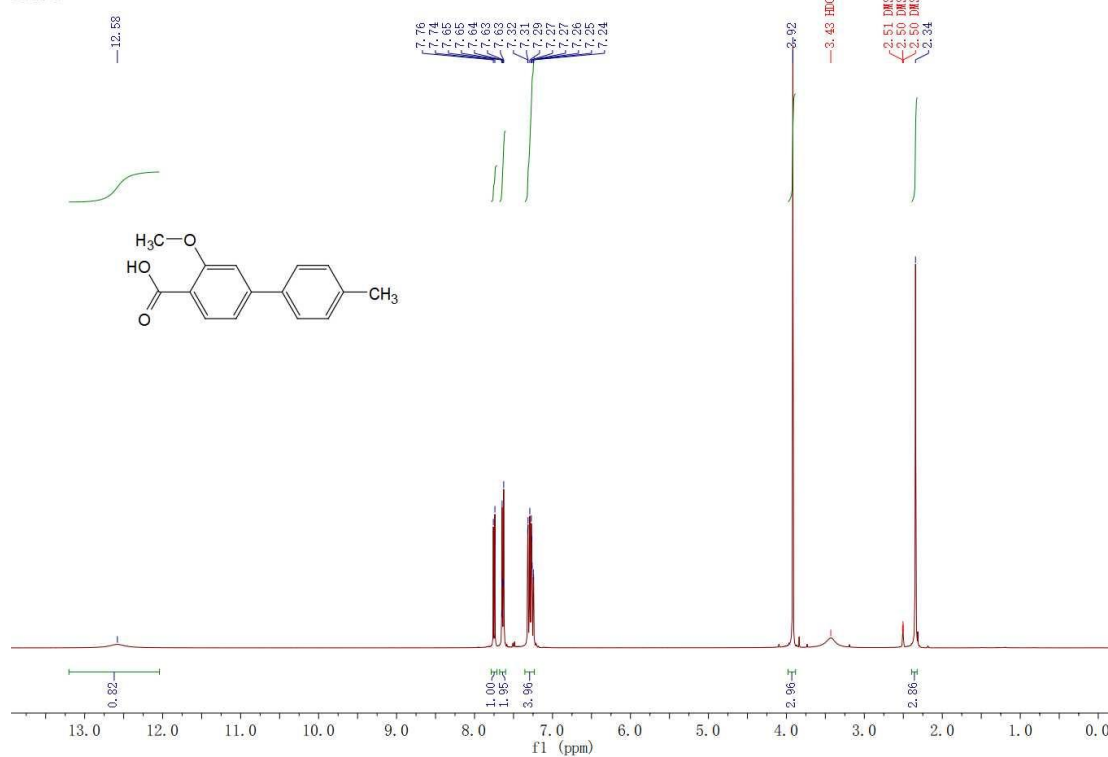
18. 11. fid



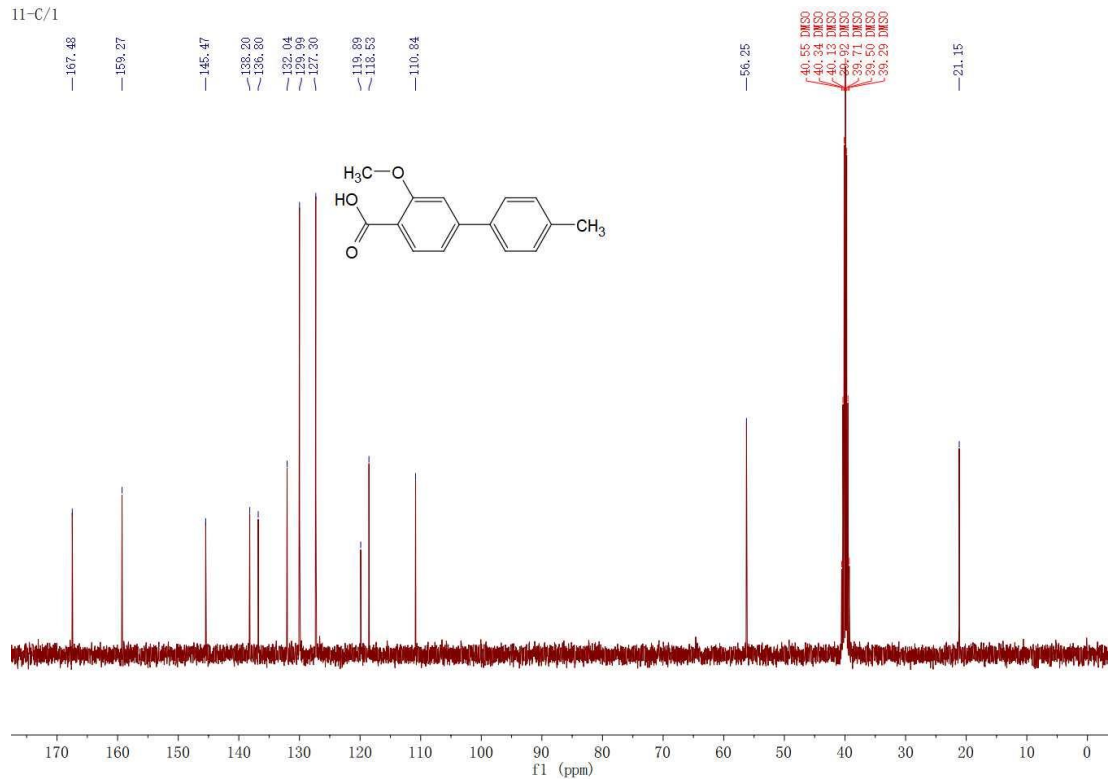
(15)2-methoxy-4-(4-methylphenyl)benzoic acid



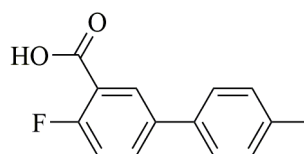
11-H/1



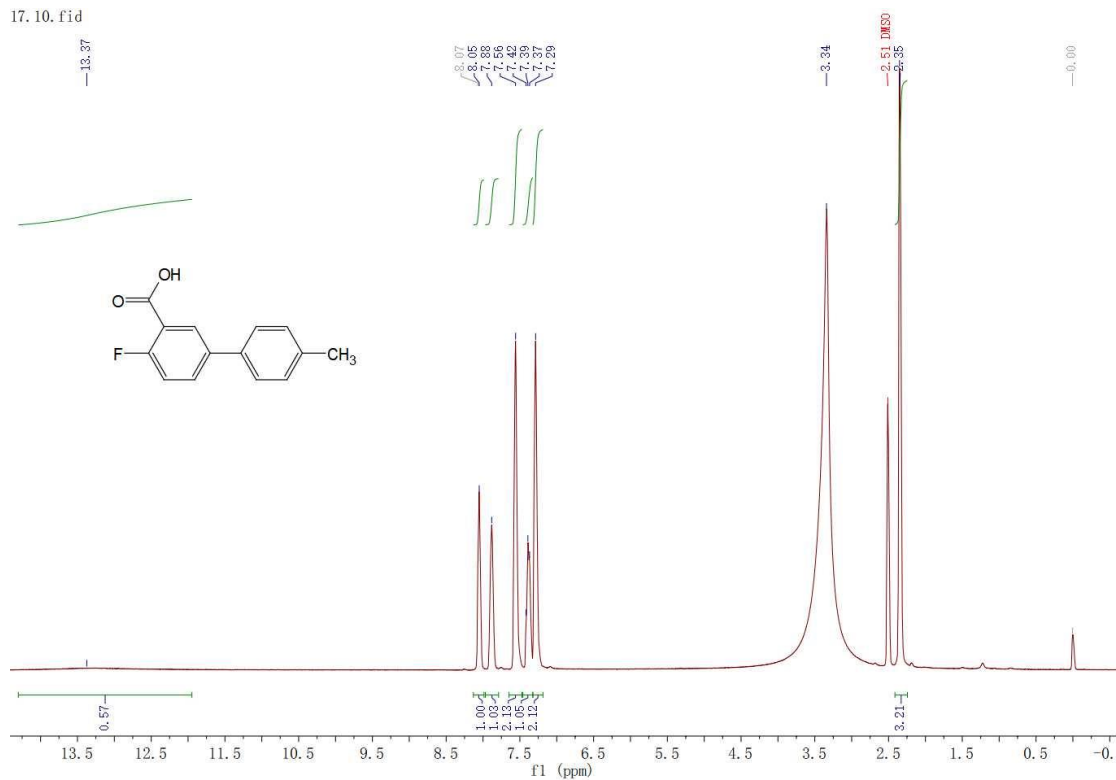
11-C/1



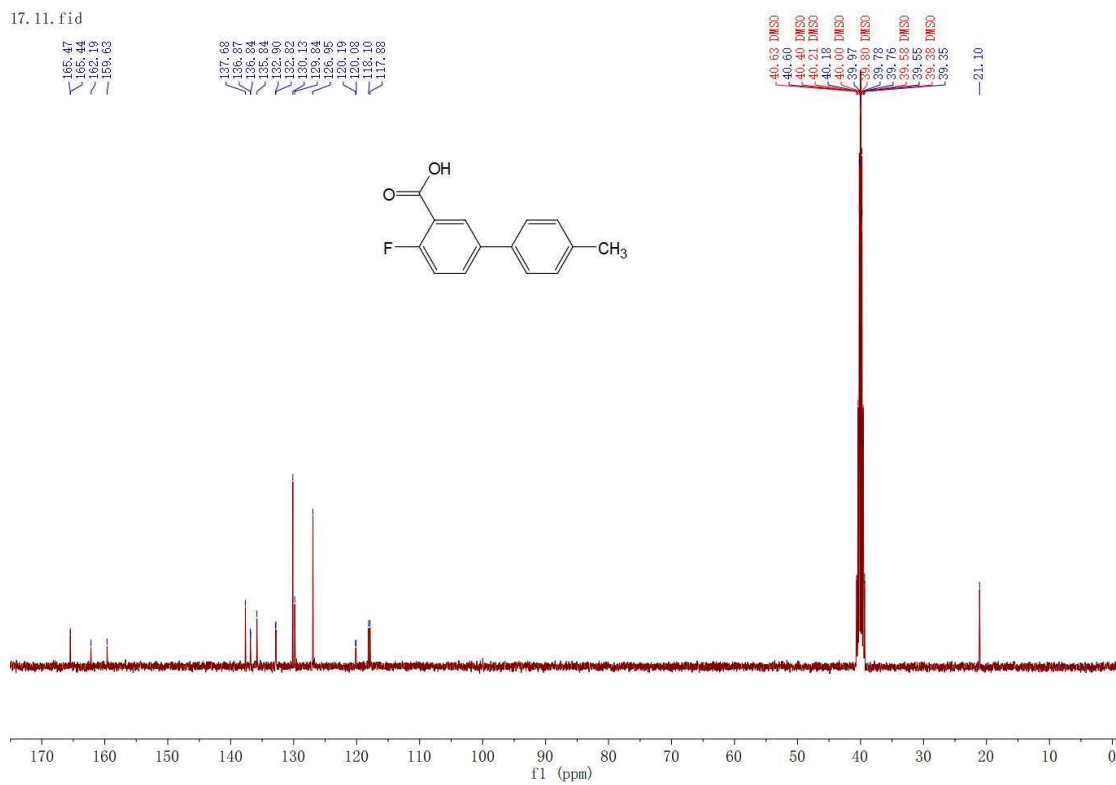
(16) 2-fluoro-5-(4'-methylphenyl)-benzoic acid



17. 10. fid



17. 11. fid



(18) 2-methyl-5-(4-methylphenyl)benzoic acid

