A conjugated ketone as a catalyst in alcohol amination reactions under transition-metal and hetero-atom free conditions

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Supporting Information

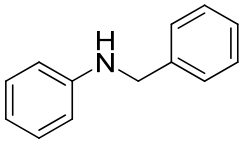
General

NMR spectra were measured using a Varian NMR system at 400.1 MHz (^{1}H) and 100.6 MHz (^{13}C). All spectra were recorded in $CDCl_3$ and chemical shifts (δ) are reported in ppm relative to tetramethylsilane referenced to the residual solvent peaks.

Typical procedure for benzyl alcohol amination with aniline

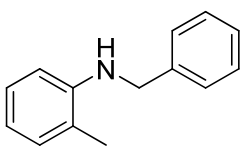
All of the reactions were performed in a pressure tube. Aniline (1 mmol), 1.5 mmol alcohol, 50 mg of catalyst, 0.5 mmol KOH and 2 mL of toluene were added to a pressure tube followed by exchange with Ar. The tube was sealed and maintained at 150°C for 4-8 h. After completion of the reaction, the tube was cooled to room temperature, and 10 mL of EtOH were added for quantitative analysis with a GC-FID (Agilent 7890A). The crude mixture was purified by column chromatography.

Synthesis of N-benzylaniline[1]



Benzyl alcohol (162 mg, 1.5 mmol), aniline (93 mg, 1 mmol), 50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted at 150 ^{o}C under Argon atmosphere for 4 h. The crude mixture was purified by column chromatograph (ethyl acetate / petroleum ether = 1/100, v/v; Silica Gel: 200-300 mesh; Rf = 0.15). Following the procedure above, N-benzylaniline (light yellow solid, m.p. 35-36 ^{o}C) was obtained (174 mg, Isolated yield = 95%). ^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.30 (m, 5H), 7.17 (m, 2H), 6.72 (m, 1H), 6.64 (m, 2H), 4.33 (s, 2H), 4.03 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$):δ = 148.18, 139.47, 129.29, 128.66, 127.54, 127.26, 117.60, 112.88, 48.37.

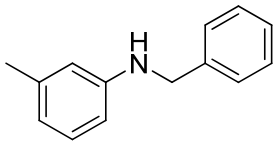
Synthesis ofN-benzyl-2-methylaniline[2]



Benzyl alcohol (162 mg, 1.5 mmol), 2-methylaniline (107 mg, 1 mmol), 50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted at 150 ^{o}C under Argon atmosphere for 8 h. The crude mixture was purified by column

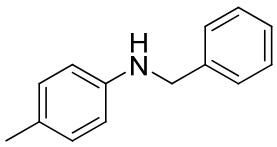
chromatograph (ethyl acetate / petroleum ether = 1/100, v/v; Silica Gel: 200-300 mesh; Rf = 0.18). Following the procedure above, N-benzyl-2-methylaniline (light yellow solid, m.p. 57-59 ^{o}C) was obtained (120 mg, Isolated yield = 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (m, 4H), 7.28 (t, 1H), 7.09 (dd, 2H), 6.65 (m, 2H), 4.37 (s, 2H), 3.89 (s, 1H), 2.17 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$):δ = 146.05, 139.50, 130.10, 128.69, 127.59, 127.29, 127.19, 117.25, 110.06, 48.37, 17.58.

Synthesis ofN-benzyl-3-methylaniline[2]



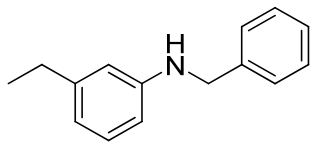
Benzyl alcohol (162 mg, 1.5 mmol), 3-methylaniline (107 mg, 1 mmol), 50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted at 150 ^{o}C under Argon atmosphere for 4 h. The crude mixture was purified by column chromatograph (ethyl acetate / petroleum ether = 1/100, v/v; Silica Gel: 200-300 mesh; Rf = 0.15). Following the procedure above, N-benzyl-3-methylaniline (yellow liquid) was obtained (191 mg, Isolated yield = 97%). ^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.31 (m, 5H), 7.06 (m, 1H), 6.50 (m, 3H), 4.32 (s, 2H), 3.95 (s, 1H), 2.27 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$):δ = 148.29, 139.63, 139.09, 129.20, 128.66, 127.58, 127.24, 118.58, 113.68, 110.02, 48.41, 21.68.

Synthesis of N-benzyl-4-methylaniline[1]



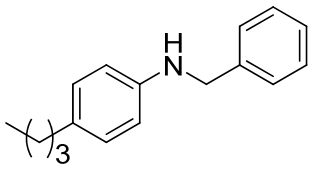
Benzyl alcohol (162 mg, 1.5 mmol), 4-methylaniline (107 mg, 1 mmol), 50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted at 150 ^{o}C under Argon atmosphere for 4 h. The crude mixture was purified by column chromatograph (ethyl acetate / petroleum ether = 1/100, v/v; Silica Gel: 200-300 mesh; Rf = 0.15). Following the procedure above, N-benzyl-4-methylaniline (yellow liquid) was obtained (183 mg, Isolated yield = 93%). ^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.29 (m, 5H), 6.98 (d, 2H), 6.56 (d, 2H), 4.30 (s, 2H), 4.01 (s, 1H), 2.23 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$):δ = 145.89, 139.66, 129.78, 128.63, 127.55, 127.19, 126.85, 113.09, 48.72, 20.43.

Synthesis ofN-benzyl-3-ethylaniline[3]



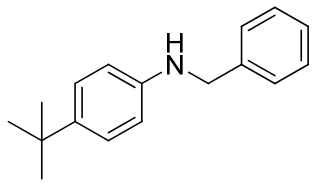
Benzyl alcohol (162 mg, 1.5 mmol), 3-ethylaniline (121 mg, 1 mmol), 50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted at 150 ^{o}C under Argon atmosphere for 8 h. The crude mixture was purified by column chromatograph (ethyl acetate / petroleum ether = 1/100, v/v; Silica Gel: 200-300 mesh; Rf = 0.10). Following the procedure above, N-benzyl-4-methylaniline (light yellow liquid) was obtained (177 mg, Isolated yield = 84%).^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.30 (m, 5H), 7.09 (m, 1H), 6.51 (m, 3H), 4.30 (s, 1H), 3.95 (s, 1H), 2.56 (q, 2H), 1.20 (t, 3H).^{13}C NMR (101 MHz, $CDCl_3$):δ = 148.35, 145.51, 139.64, 129.27, 128.67, 127.65, 127.26, 117.40, 112.63, 110.22, 48.50, 29.09, 15.59.

Synthesis ofN-benzyl-4-butylaniline[4]



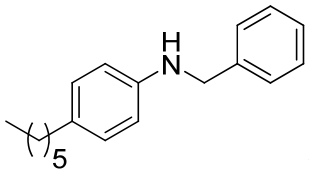
Benzyl alcohol (162 mg, 1.5 mmol), 4-butylaniline (149 mg, 1 mmol), 50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted at 150 ^{o}C under Argon atmosphere for 8 h. The crude mixture was purified by column chromatograph (ethyl acetate / petroleum ether = 1/100, v/v; Silica Gel: 200-300 mesh; Rf = 0.10). Following the procedure above, N-benzyl-4-methylaniline (yellow liquid) was obtained (203 mg, Isolated yield = 85%).^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 (m, 5H), 6.98 (d, 2H), 6.57 (d, 2H), 4.29 (s, 2H), 3.89 (s, 1H), 2.49 (t, 2H), 1.55 (m, 2H), 1.32 (m, 2H), 0.91 (t,3H).^{13}C NMR (101 MHz, $CDCl_3$):δ = 146.16, 139.73, 132.10, 129.17, 128.63, 127.60, 127.20, 112.94, 48.72, 34.77, 34.05, 22.39, 14.04.

Synthesis of N-benzyl-4-(tert-butyl)aniline[5]



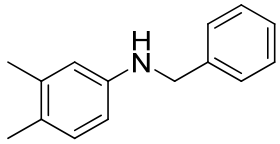
Benzyl alcohol (162 mg, 1.5 mmol), 4-(tert-butyl)aniline (149 mg, 1 mmol), 50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted at 150 ^{o}C under Argon atmosphere for 8 h. The crude mixture was purified by column chromatograph (ethyl acetate / petroleum ether = 1/100, v/v; Silica Gel: 200-300 mesh; Rf = 0.10). Following the procedure above, N-benzyl-4-methylaniline (yellow liquid) was obtained (221 mg, Isolated yield = 92%).^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.28 (m, 7H), 6.60 (m, 2H), 4.30 (s, 2H), 3.93 (s, 1H), 1.28 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$):δ = 145.92, 140.39, 139.76, 128.64, 127.61, 127.22, 126.07, 112.62, 48.69, 33.91, 31.60.

Synthesis ofN-benzyl-4-hexylaniline



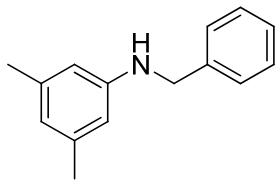
Benzyl alcohol (162 mg, 1.5 mmol), 4-hexylaniline (177 mg, 1 mmol), 50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted at 150 ^{o}C under Argon atmosphere for 8 h. The crude mixture was purified by column chromatograph (ethyl acetate / petroleum ether = 1/100, v/v; Silica Gel: 200-300 mesh; Rf = 0.10). Following the procedure above, N-benzyl-4-methylaniline (light yellow liquid) was obtained (234 mg, Isolated yield = 88%).^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.31 (m, 5H), 6.98 (d, 2H), 6.57 (d, 2H), 4.29 (s, 2H), 3.89 (s, 1H), 2.48 (t, 2H), 1.53 (m, 2H), 1.28 (m, 6H), 0.87 (t, 3H).^{13}C NMR (101 MHz, $CDCl_3$):δ = 146.16, 139.73, 132.15, 129.15, 128.63, 127.60, 127.20, 112.94, 48.72, 35.10, 31.86, 31.84, 29.05, 22.69, 14.17. HR-MS calculated for 268.2065, found 268.2060 (C19H26N).

Synthesis ofN-benzyl-3,4-dimethylaniline[6]



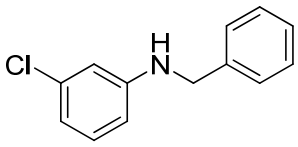
Benzyl alcohol (162 mg, 1.5 mmol), 3, 4-dimethylaniline (121 mg, 1 mmol), 50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted at 150 ^{o}C under Argon atmosphere for 8 h. The crude mixture was purified by column chromatograph (ethyl acetate / petroleum ether = 1/100, v/v; Silica Gel: 200-300 mesh; Rf = 0.10). Following the procedure above, N-benzyl-4-methylaniline (yellow liquid) was obtained (206 mg, Isolated yield = 98%).^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.30 (m, 5H), 6.92 (d, 1H), 6.46 (s, 1H), 6.39 (d, 1H), 4.28 (s, 2H), 3.81 (s, 1H), 2.18 (s, 3H), 2.14 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$):δ = 146.46, 139.87, 137.37, 130.36, 128.64, 127.57, 127.18, 125.61, 114.80, 110.32, 48.71, 20.11, 18.76.

Synthesis ofN-benzyl-3,5-dimethylaniline[2]



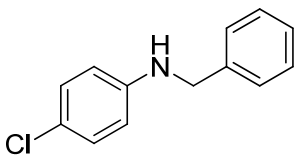
Benzyl alcohol (162 mg, 1.5 mmol), 3, 5-dimethylaniline (121 mg, 1 mmol), 50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted at 150 ^{o}C under Argon atmosphere for 8 h. The crude mixture was purified by column chromatograph (ethyl acetate / petroleum ether = 1/100, v/v; Silica Gel: 200-300 mesh; Rf = 0.10). Following the procedure above, N-benzyl-4-methylaniline(light yellow liquid) was obtained (182 mg, Isolated yield = 86%).^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.30 (m, 5H), 6.39 (s, 1H), 6.28 (s, 2H), 4.29 (s, 2H), 3.97 (s, 1H), 2.22 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$):δ = 148.28, 139.65, 138.97, 128.64, 127.62, 127.22, 119.73, 110.88, 48.48, 21.54.

Synthesis ofN-benzyl-3-chloroaniline[2]



Benzyl alcohol (162 mg, 1.5 mmol), 3-chloroaniline (127 mg, 1 mmol), 50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted at 150 ^{o}C under Argon atmosphere for 8 h. The crude mixture was purified by column chromatograph (ethyl acetate / petroleum ether = 1/100, v/v; Silica Gel: 200-300 mesh; Rf = 0.18). Following the procedure above, N-benzyl-3-chloroaniline(light yellow solid, m.p. 93-94 ^{o}C) was obtained (212 mg, Isolated yield = 98%). ^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.31(m, 5H), 7.06 (t, 1H), 6.64 (m, 2H), 6.48 (dd, 1H), 4.29 (s, 2H), 4.12 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$):δ = 149.22, 138.76, 135.06, 130.23, 128.76, 127.50, 127.47, 117.47, 112.55, 111.18, 48.15.

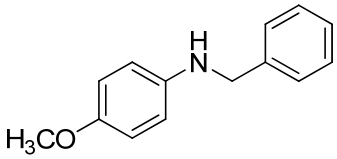
Synthesis of N-benzyl-4-chloroaniline[1]



Benzyl alcohol (162 mg, 1.5 mmol), 4-chloroaniline (127 mg, 1 mmol), 50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted

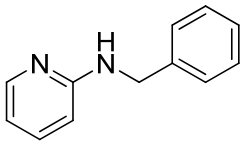
at 150 °C under Argon atmosphere for 4 h. The crude mixture was purified by column chromatograph (ethyl acetate / petroleum ether = 1/100, v/v; Silica Gel: 200-300 mesh; Rf = 0.15). Following the procedure above, N-benzyl-4-chloroaniline(yellow liquid) was obtained (200 mg, Isolated yield = 92%). ^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.30 (m, 5H), 7.10 (d, 2H), 6.54 (m, 2H), 4.29 (s, 2H), 4.15 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$):δ = 146.58, 138.90, 129.10, 128.73, 127.47, 127.42, 122.23, 114.03, 48.43.

Synthesis of N-benzyl-4-methoxyaniline[5]



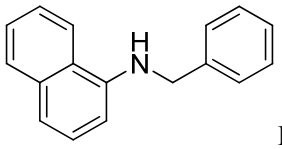
Benzyl alcohol (162 mg, 1.5 mmol), 4-methoxyaniline (123 mg, 1 mmol), 50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted at 150 °C under Argon atmosphere for 4 h. The crude mixture was purified by column chromatograph (ethyl acetate / petroleum ether = 1/100, v/v; Silica Gel: 200-300 mesh; Rf = 0.08). Following the procedure above, N-benzyl-4-methoxyaniline(yellow solid, m.p. 47-49 °C) was obtained (170 mg, Isolated yield = 80%).^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.32 (m, 5H), 6.77 (d, 2H), 6.60 (d, 2H), 4.28 (s, 2H), 3.79 (s, 1H), 3.73 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$):δ = 152.24, 142.47, 139.71, 128.62, 127.57, 127.19, 114.94, 114.14, 55.84, 49.29.

Synthesis of N-benzylpyridin-2-amine[1]



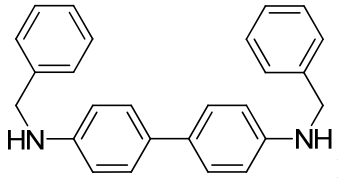
Benzyl alcohol (162 mg, 1.5 mmol), pyridin-2-amine (94 mg, 1 mmol), 50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted at 150 °C under Argon atmosphere for 8 h. The crude mixture was purified by column chromatograph (ethyl acetate / petroleum ether = 1/3, v/v; Silica Gel: 200-300 mesh; Rf = 0.22). Following the procedure above, N-benzylpyridin-2-amine(light yellow solid, m.p. 94-95 °C) was obtained (180 mg, Isolated yield = 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ =8.10 (d, 1H), 7.33 (m, 6H), 6.59 (m, 1H), 6.37 (d, 1H), 4.94 (s, 1H), 4.51 (d, 2H).^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.63, 148.16, 139.18, 137.52, 128.66, 127.42, 127.26, 113.18, 106.85, 46.35.

Synthesis of N-benzylnaphthalen-2-amine[1]



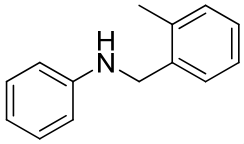
Benzyl alcohol (162 mg, 1.5 mmol), naphthalen-1-amine (143 mg, 1 mmol), 50 mg cat-9 and 1 mmol KOH were added into a 15 mL reaction tube and reacted at 150 °C under Argon atmosphere for 4 h. The crude mixture was purified by column chromatograph (ethyl acetate / petroleum ether = 1/80, v/v; Silica Gel: 200-300 mesh; Rf = 0.15). Following the procedure above, N-benzylnaphthalen-1-amine (light yellow solid, m.p. 65-68 °C) was obtained (221 mg, Isolated yield = 95%). ^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.81 (t, 2H), 7.35 (m, 9H), 6.63 (d, 1H), 4.72 (s, 1H), 4.49 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$):δ = 139.08, 134.33, 128.76, 128.74, 127.80, 127.45, 126.63, 125.78, 124.81, 123.43, 119.93, 117.74, 104.87, 48.69.

Synthesis ofN^4,$N^{4'}$-dibenzyl-[1,1'-biphenyl]-4,4'-diamine[2]



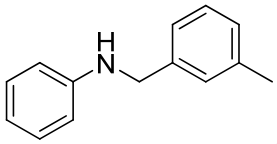
Benzyl alcohol (162 mg, 1.5 mmol), benzidine (92 mg, 0.5 mmol), 50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted at 150 ^{o}C under Argon atmosphere for 8 h. The crude mixture was purifiedby filtration and removing the toluene on a Rot-Vap. Following the procedure above, N^{4},$N^{4'}$-dibenzyl-[1,1'-biphenyl]-4,4'-diamine(light yellow solid, m.p. 178-179 ^{o}C) was obtained (159 mg, Isolated yield = 87%).^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.32 (m, 14H), 6.67 (d, 4H), 4.35 (s, 4H), 4.04 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$):δ = 146.74, 139.53, 130.92, 128.67, 127.54, 127.26, 127.21, 113.20, 48.51.

Synthesis ofN-(2-methylbenzyl)aniline[2]



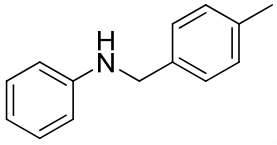
Aniline (93 mg, 1 mmol), 2-methylbenzyl alcohol (183 mg, 1.5 mmol), 50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted at 150 ^{o}C under Argon atmosphere for 4 h. The crude mixture was purified by column chromatograph (ethyl acetate / petroleum ether = 1/100, v/v; Silica Gel: 200-300 mesh; Rf = 0.20). Following the procedure above, N-(2-methylbenzyl)aniline (light yellow solid, m.p. 29-31 ^{o}C) was obtained (190 mg, Isolated yield = 96%). ^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.35 (dd, 1H), 7.19 (m, 5H), 6.73 (m, 1H), 6.64 (d, 2H), 4.27 (s, 2H), 3.85 (s, 1H), 2.37 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$):δ = 148.31, 137.02, 136.38, 130.44, 129.30, 128.29, 127.45, 126.18, 117.50, 112.73, 46.42, 18.95.

Synthesis ofN-(3-methylbenzyl)aniline[1]



Aniline (93 mg, 1 mmol), 3-methylbenzyl alcohol (183 mg, 1.5 mmol), 50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted at 150 ^{o}C under Argon atmosphere for 4 h. The crude mixture was purified by column chromatograph (ethyl acetate / petroleum ether = 1/100, v/v; Silica Gel: 200-300 mesh; Rf = 0.16). Following the procedure above, N-(3-methylbenzyl)aniline (yellow liquid) was obtained (190 mg, Isolated yield = 96%). ^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.17 (m, 6H), 6.68 (m, 3H), 4.27 (s, 2H), 4.03 (s, 1H), 2.34 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$):δ = 148.24, 139.38, 138.34, 129.29, 128.57, 128.34, 128.04, 124.64, 117.59, 112.90, 48.42, 21.46.

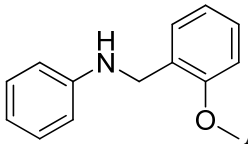
Synthesis ofN-(4-methylbenzyl)aniline[2]



Aniline (93 mg, 1 mmol), 4-methylbenzyl alcohol (183 mg, 1.5 mmol),

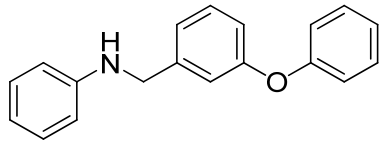
50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted at 150 ^{o}C under Argon atmosphere for 4 h. The crude mixture was purified by column chromatograph (ethyl acetate / petroleum ether = 1/100, v/v; Silica Gel: 200-300 mesh; Rf = 0.15). Following the procedure above, N-(4-methylbenzyl)aniline (light yellow solid, m.p. 62-64 ^{o}C) was obtained (155 mg, Isolated yield = 84%). ^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.19 (m, 6H), 6.68 (m, 3H), 4.27 (s, 2H), 3.97 (s, 1H), 2.34 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ = 148.24, 136.90, 136.38, 129.33, 129.27, 127.55, 117.52, 112.87, 48.12, 21.12.

Synthesis of N-(2-methoxybenzyl)aniline[7]



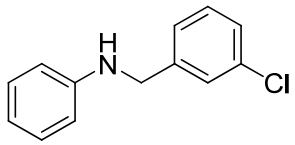
Aniline (93 mg, 1 mmol), 2-methoxybenzyl alcohol (207 mg, 1.5 mmol), 50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted at 150 ^{o}C under Argon atmosphere for 8 h. The crude mixture was purified by column chromatograph (ethyl acetate / petroleum ether = 1/150, v/v; Silica Gel: 200-300 mesh; Rf = 0.08). Following the procedure above, N-(2-methoxybenzyl)aniline (white solid, m.p. 93-94 ^{o}C) was obtained (177 mg, Isolated yield = 83%).^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.21 (m, 4H), 6.90 (dd, 2H), 6.67 (dd, 3H), 4.33 (s, 2H), 4.12 (s, 1H), 3.85 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$):δ = 157.43, 148.45, 129.19, 128.93, 128.32, 127.38, 120.55, 117.36, 113.09, 110.28, 55.33, 43.49.

Synthesis ofN-(3-phenoxybenzyl)aniline[8]



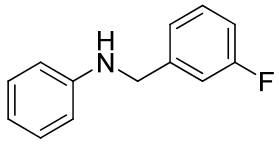
Aniline (93 mg, 1 mmol), (3-phenoxyphenyl)methanol (300 mg, 1.5 mmol), 50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted at 150 ^{o}C under Argon atmosphere for 8 h. The crude mixture was purified by column chromatograph (ethyl acetate / petroleum ether = 1/150, v/v; Silica Gel: 200-300 mesh; Rf= 0.08). Following the procedure above, N-(3-chlorobenzyl) aniline (light yellow solid, m.p. 58-60 ^{o}C) was obtained (266 mg, Isolated yield = 97%).^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.31 (m, 3H), 7.14 (m, 4H), 7.01 (dd, 3H), 6.90 (d, 1H), 6.72 (t, 1H), 6.61 (d, 2H), 4.30 (s, 2H), 4.05 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$):δ = 157.62, 157.08, 147.96, 141.68, 129.94, 129.78, 129.28, 123.33, 122.17, 118.96, 117.80, 117.70, 117.51, 112.93, 48.08.

Synthesis ofN-(3-chlorobenzyl)aniline[2]



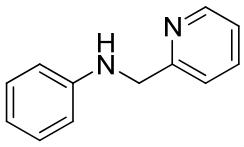
Aniline (93 mg, 1 mmol), (3-chlorophenyl)methanol (213 mg, 1.5 mmol), 50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted at 150 ^{o}C under Argon atmosphere for 8 h. The crude mixture was purified by column chromatograph (ethyl acetate / petroleum ether = 1/100, v/v; Silica Gel: 200-300 mesh; Rf = 0.08). Following the procedure above, N-(3-chlorobenzyl) aniline (light yellow liquid) was obtained (206 mg, Isolated yield = 95%).^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.23 (m, 6H), 6.67 (m, 3H), 4.30 (s, 2H), 4.06 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$):δ = 147.81, 141.77, 134.56, 129.92, 129.34, 127.45, 127.40, 125.44, 117.90, 112.93, 47.81.

Synthesis ofN-(3-fluorobenzyl)aniline[9]



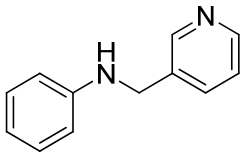
Aniline (93 mg, 1 mmol), (3-fluorophenyl)methanol (189 mg, 1.5 mmol), 50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted at 150 ^{o}C under Argon atmosphere for 8 h. The crude mixture was purified by column chromatograph (ethyl acetate / petroleum ether = 1/150, v/v; Silica Gel: 200-300 mesh; Rf = 0.13). Following the procedure above, N-(3-fluorobenzyl) aniline (light yellow liquid) was obtained (129 mg, Isolated yield = 64%).^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.20 (m, 5H), 6.94 (td, J = 8.4, 2.2 Hz, 1H), 6.72 (t, J = 7.3 Hz, 1H), 6.60 (d, J = 7.7 Hz, 2H), 4.32 (s, 2H), 4.08 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$):δ = 164.41, 161.96, 147.84, 142.41, 142.34, 130.18, 130.10, 129.34, 122.82, 122.80, 117.87, 114.30, 114.18, 114.09, 113.97, 112.93, 47.82.

Synthesis of N-(pyridin-2-ylmethyl)aniline[2]



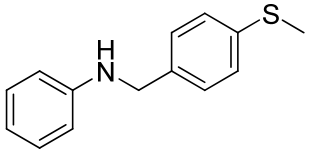
Aniline (93 mg, 1 mmol), pyridin-2-ylmethanol (164 mg, 1.5 mmol), 50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted at 150 ^{o}C under Argon atmosphere for 8 h. The crude mixture was purified by column chromatograph (ethyl acetate / petroleum ether = 1/2, v/v; Silica Gel: 200-300 mesh; Rf = 0.28). Following the procedure above, N-(pyridin-2-ylmethyl)aniline (yellow solid, m.p. 50-51 ^{o}C) was obtained (180 mg, Isolated yield = 98%).^{1}H NMR (400 MHz, $CDCl_3$):δ = 8.59 (d, 1H), 7.64 (t, 1H), 7.35 (t, 1H), 7.18 (t, 3H), 6.72 (t, 1H), 6.67 (d, 2H), 4.63 (s, 1H), 4.47 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$):δ = 158.55, 149.21, 147.91, 136.68, 129.27, 122.12, 121.63, 117.63, 113.08, 49.31.

Synthesis of N-(pyridin-3-ylmethyl)aniline[2]



Aniline (93 mg, 1 mmol), pyridin-3-ylmethanol (164 mg, 1.5 mmol), 50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted at 150 ^{o}C under Argon atmosphere for 8 h. The crude mixture was purified by column chromatograph (ethyl acetate / petroleum ether = 1/2, v/v; Silica Gel: 200-300 mesh; Rf = 0.15). Following the procedure above, N-(pyridin-3-ylmethyl)aniline (light yellow solid, m.p. 93-95 ^{o}C) was obtained (140 mg, Isolated yield = 76%). ^{1}H NMR (400 MHz, $CDCl_3$):δ = 8.56 (m, 2H), 7.70 (d, 1H), 7.22 (m, 3H), 6.70 (m, 3H), 4.36 (s, 2H), 4.05 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$):δ = 149.19, 148.74, 147.64, 135.13, 134.94, 129.37, 123.57, 118.08, 112.98, 45.84.

Synthesis ofN-(4-methylthiobenzyl) .aniline[10]



Aniline (93 mg, 1 mmol), 4-methylthiobenzyl alcohol (231 mg, 1.5

mmol), 50 mg cat-9, 0.5 mmol KOH and 2 ml toluene were added into a 15 mL reaction tube and reacted at 150 ^{o}C under Argon atmosphere for 8 h. The crude mixture was purified by column chromatograph (ethyl acetate / petroleum ether = 1/150, v/v; Silica Gel: 200-300 mesh; Rf = 0.07). Following the procedure above,N-(4-methylthiobenzyl)aniline (light brown solid, m.p. 34-36 ^{o}C) was obtained (218 mg, Isolated yield = 95%).^{1}H NMR (400 MHz, $CDCl_3$):δ = 7.21 (m, 6H), 6.68 (m, 3H), 4.28 (s, 2H), 4.05 (s, 1H), 2.47 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$):δ = 148.03, 137.21, 136.42, 129.30, 128.06, 127.04, 117.70, 112.93, 47.91, 16.07.

Supplementary References

(1). Cui, X.; Zhang, Y.; Shi, F.; Deng, Y. *Chem. Eur. J.***2011**, *17*, 1021-1028.

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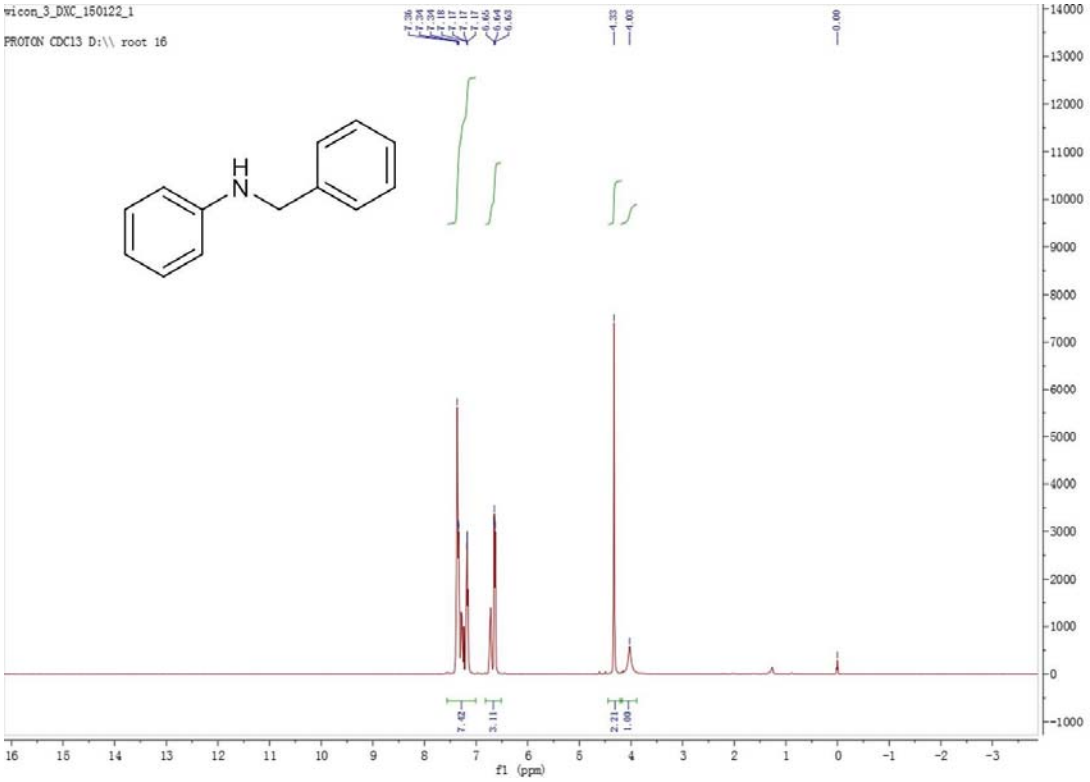
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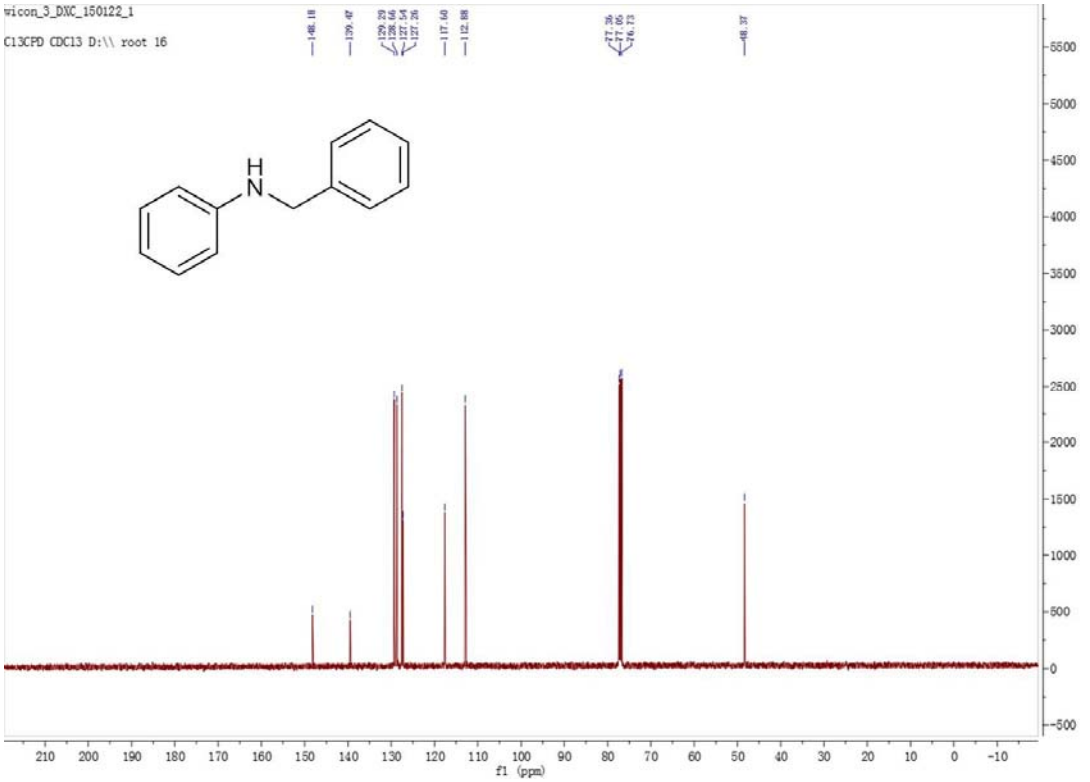
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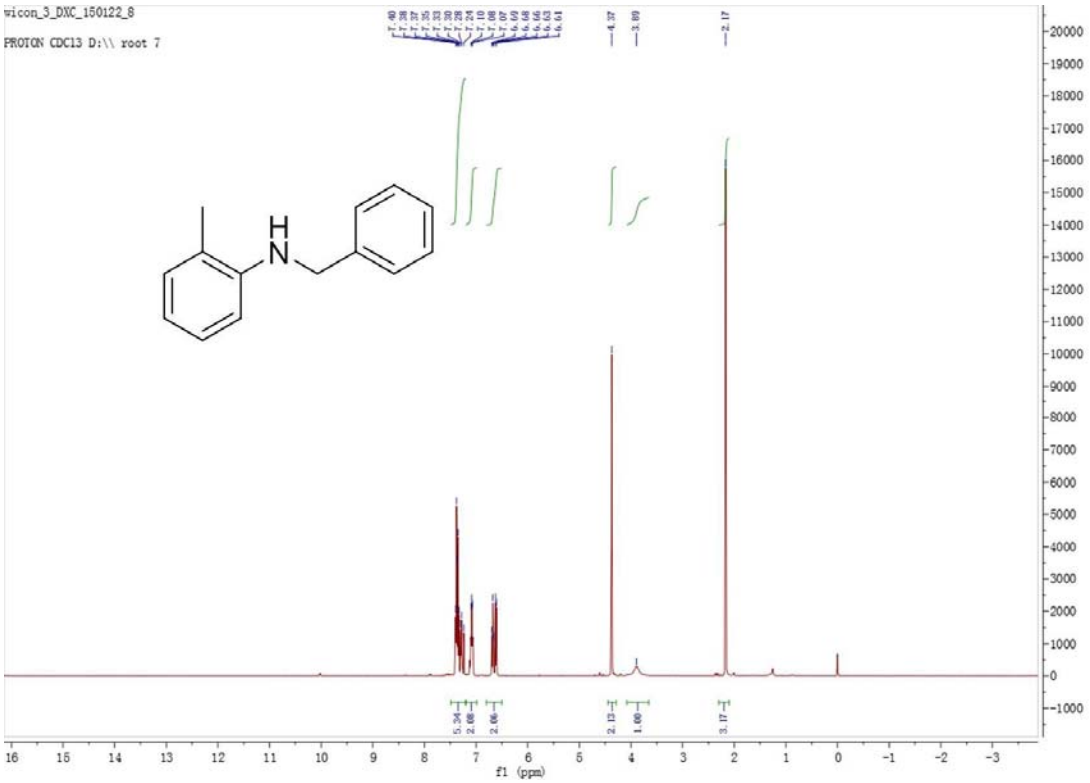
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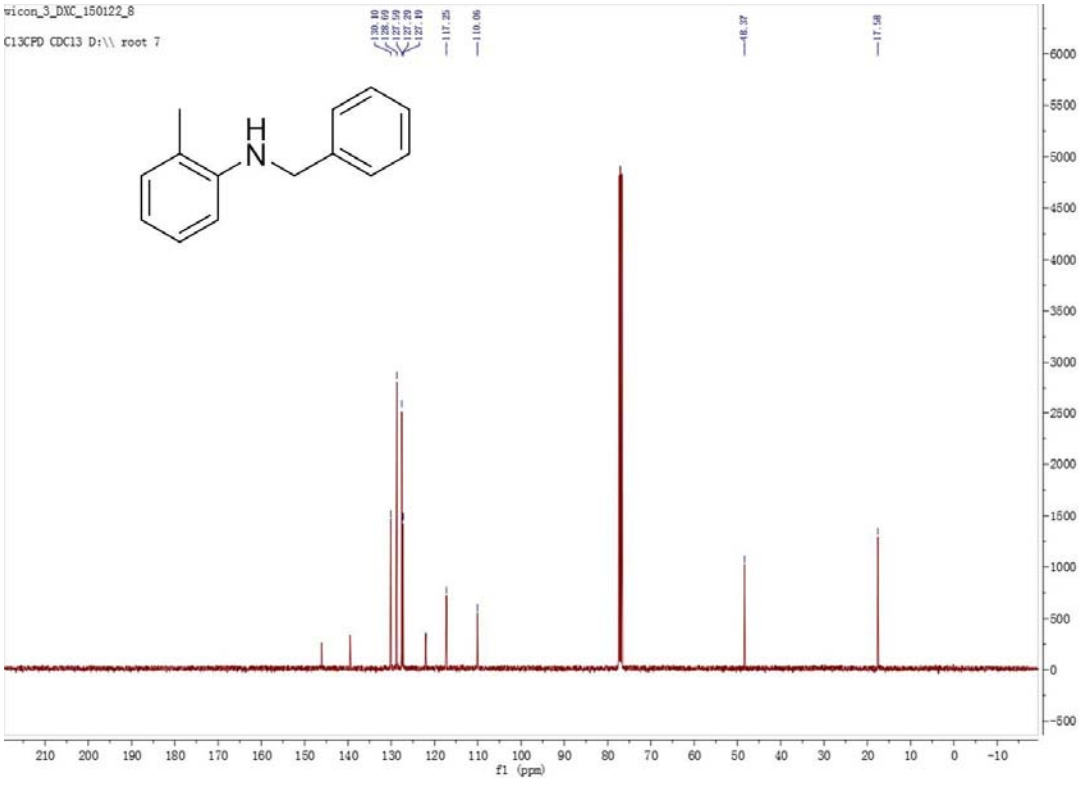
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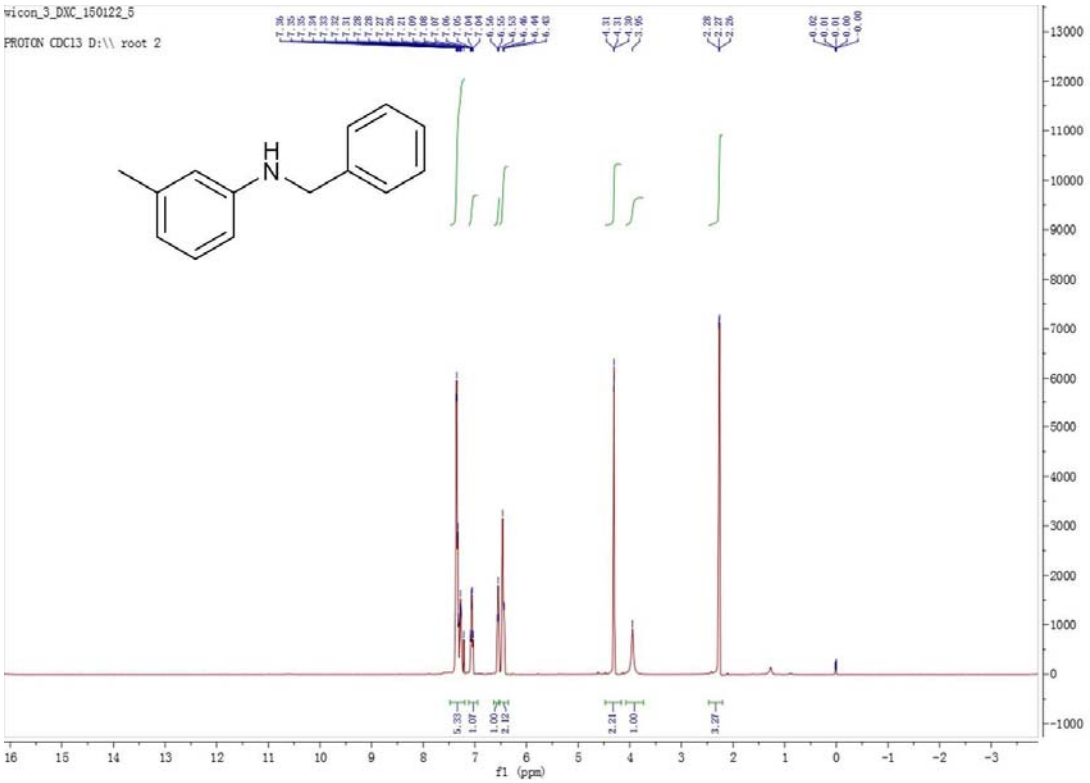
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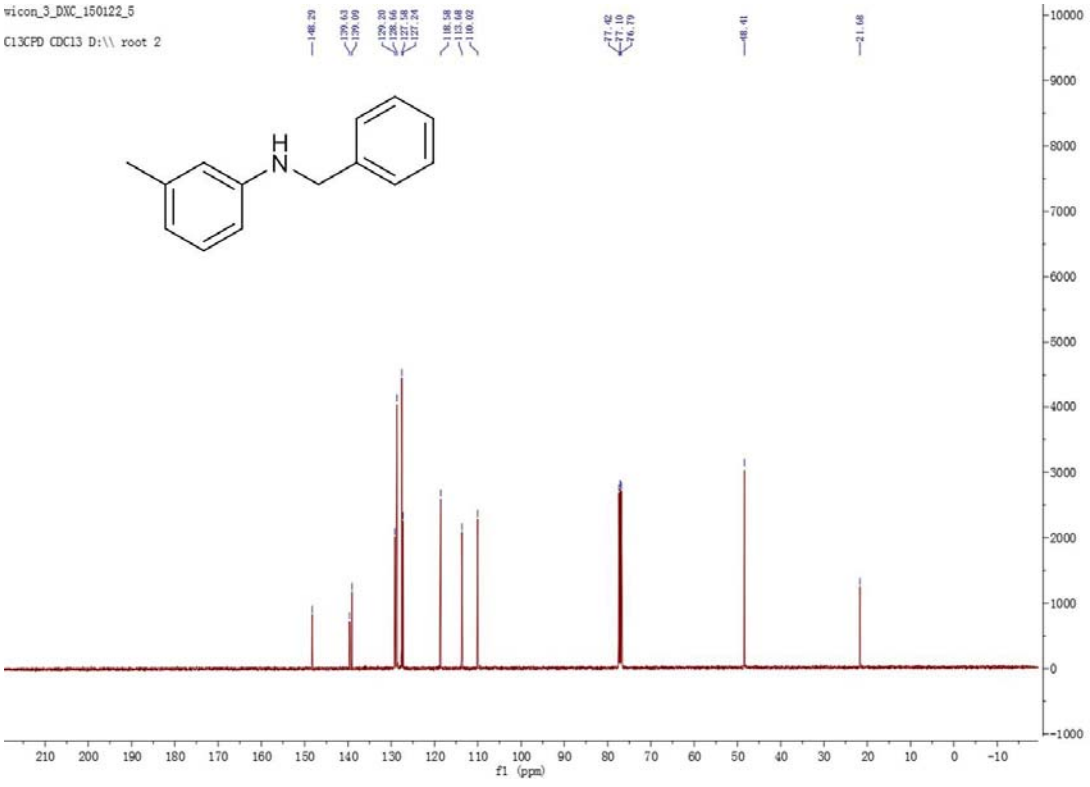
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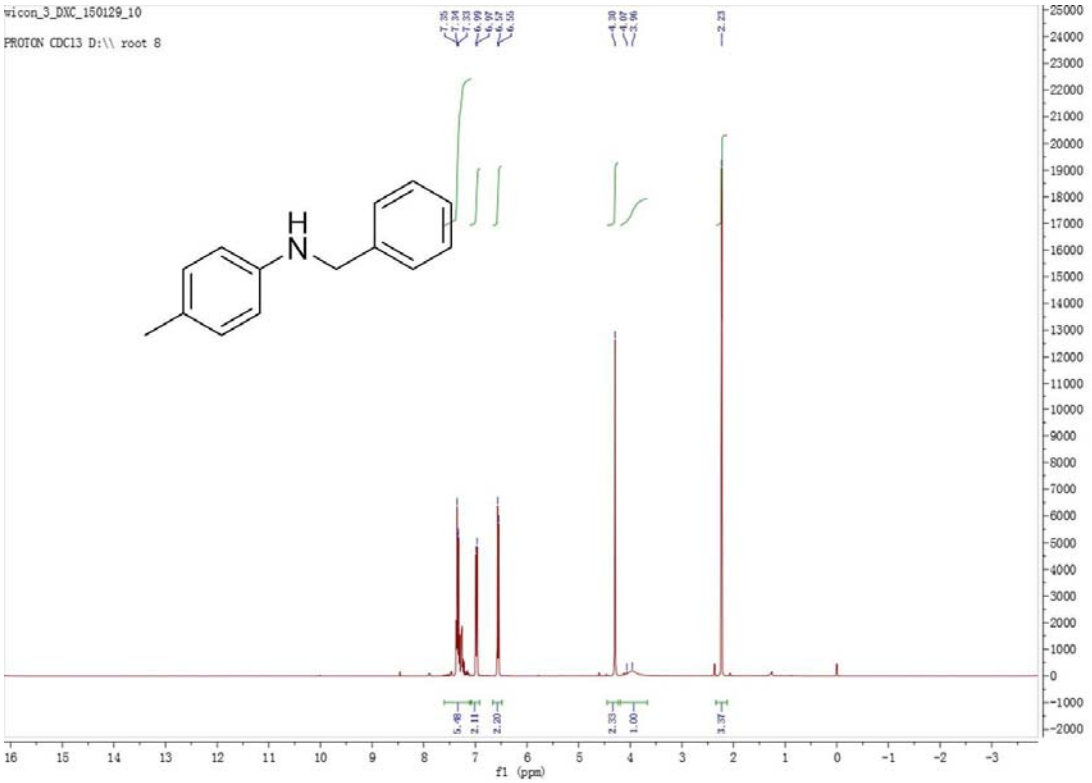
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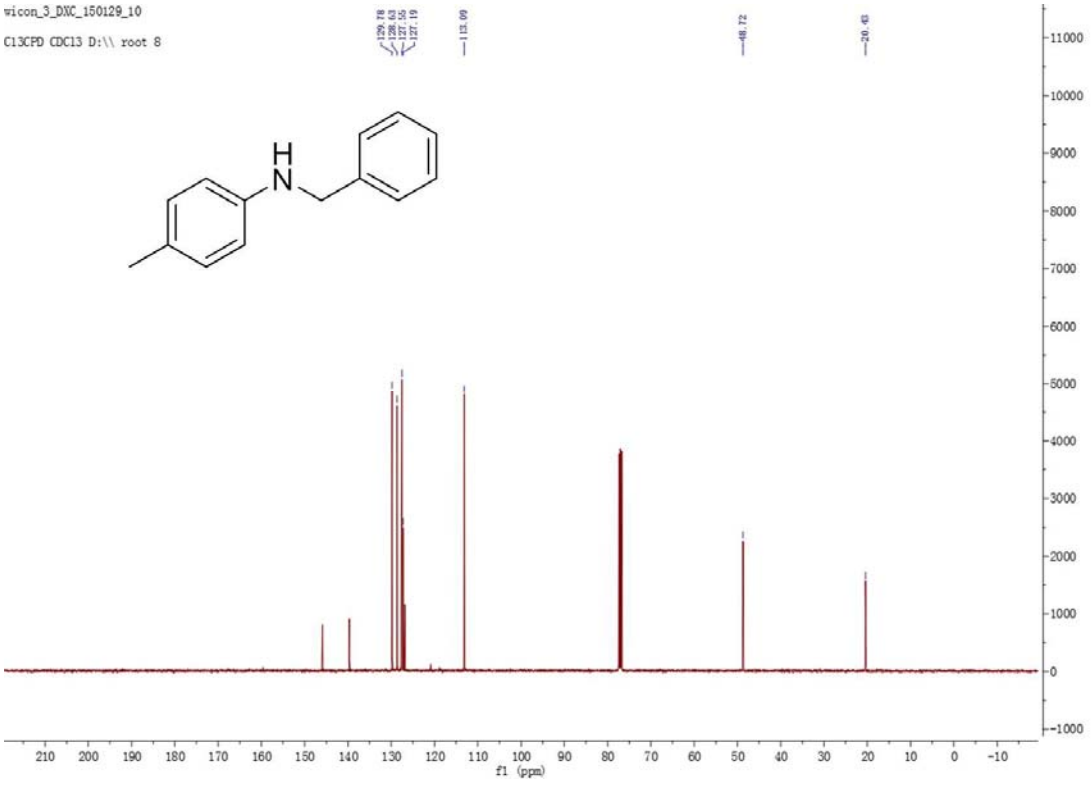
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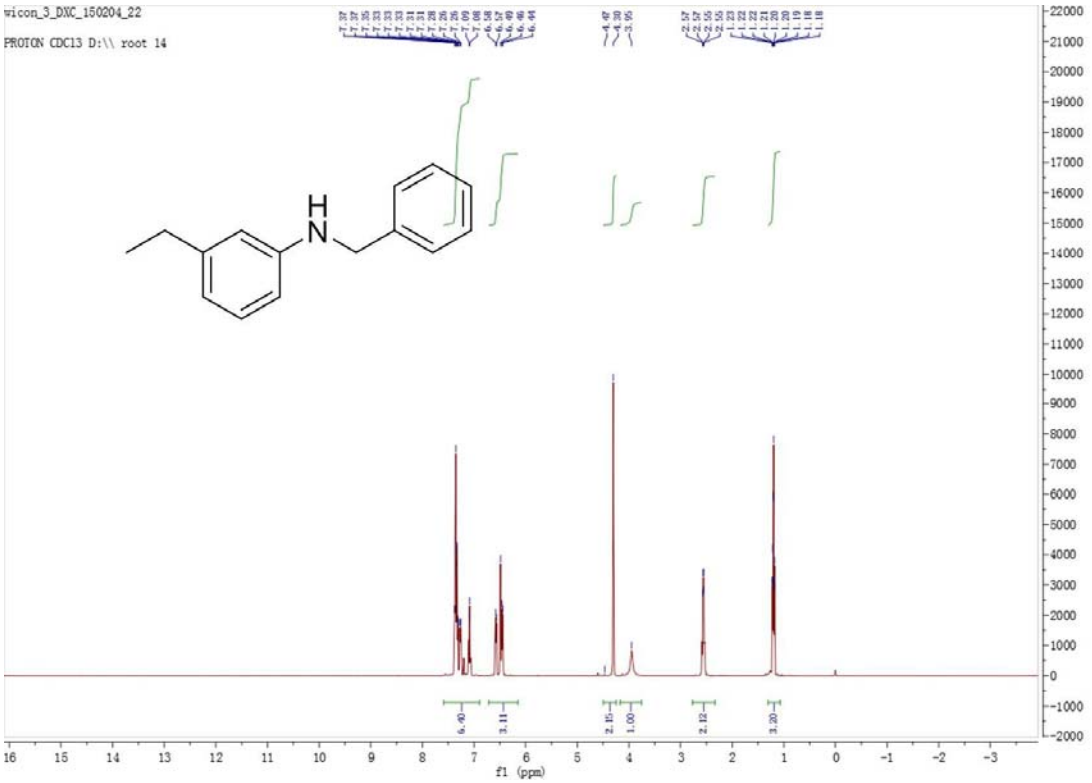
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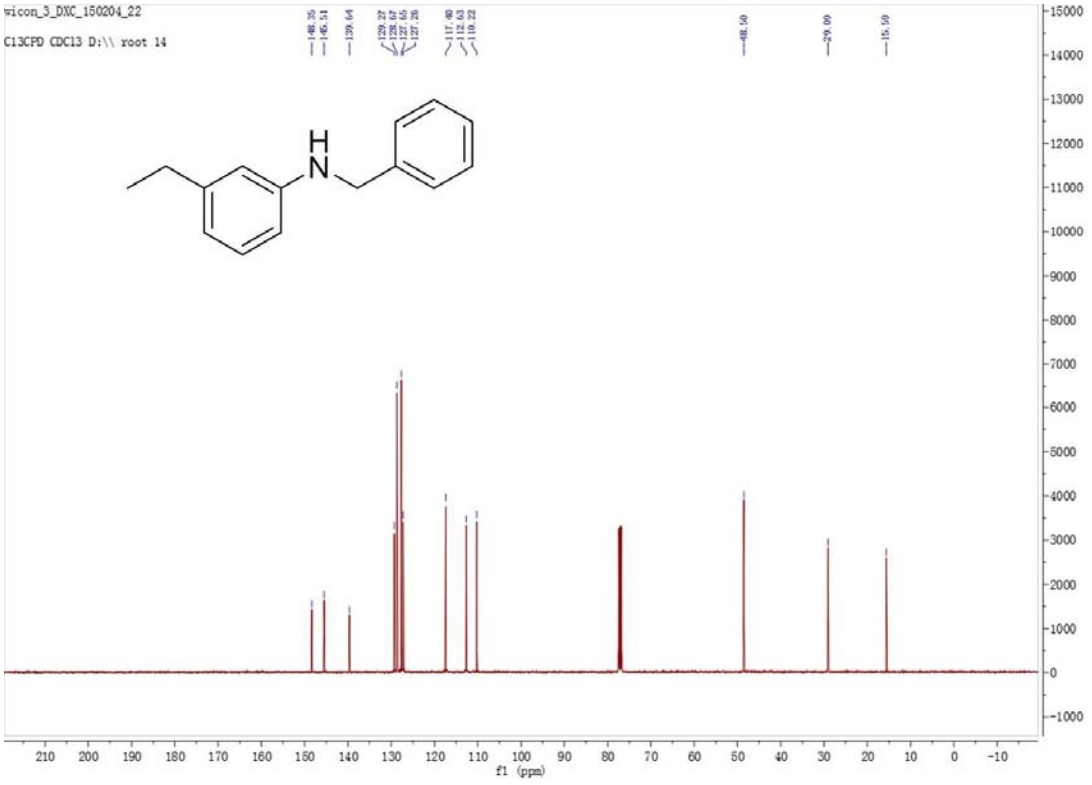
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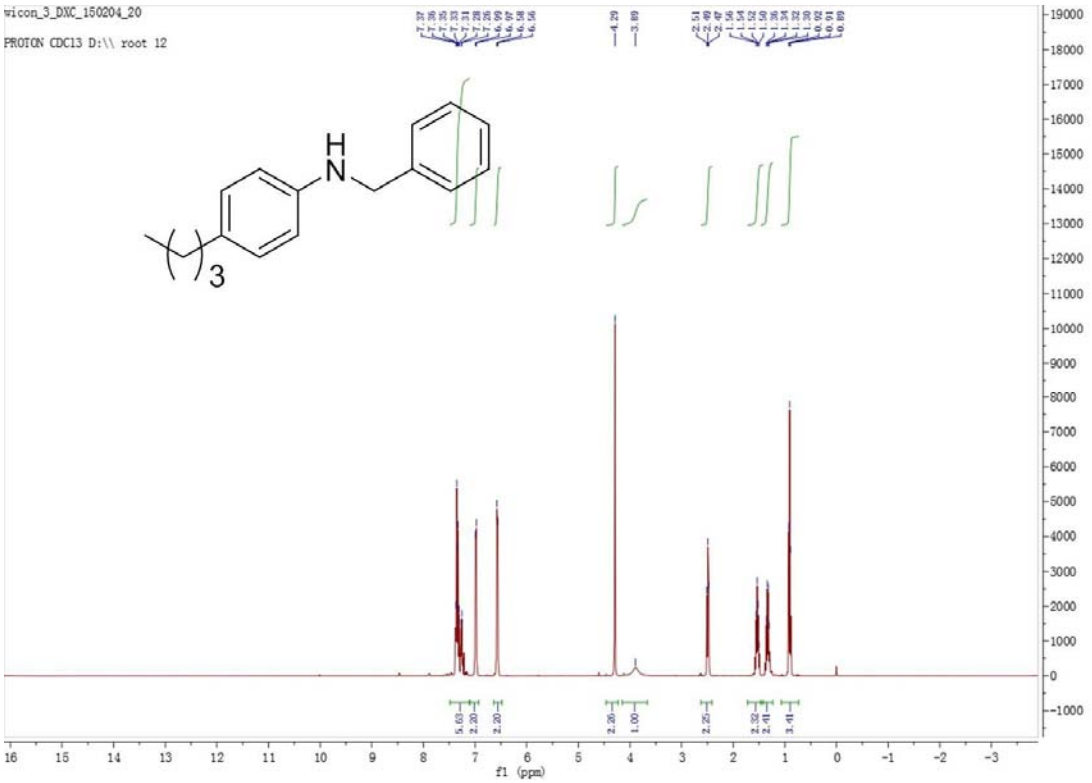
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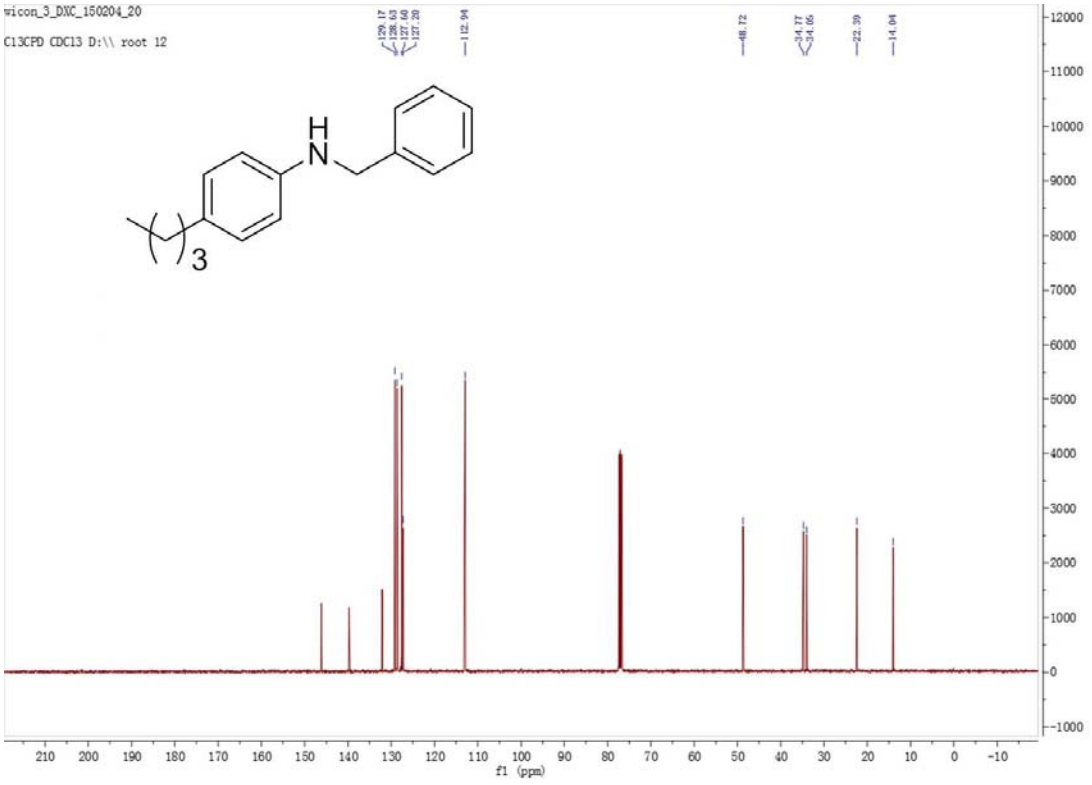
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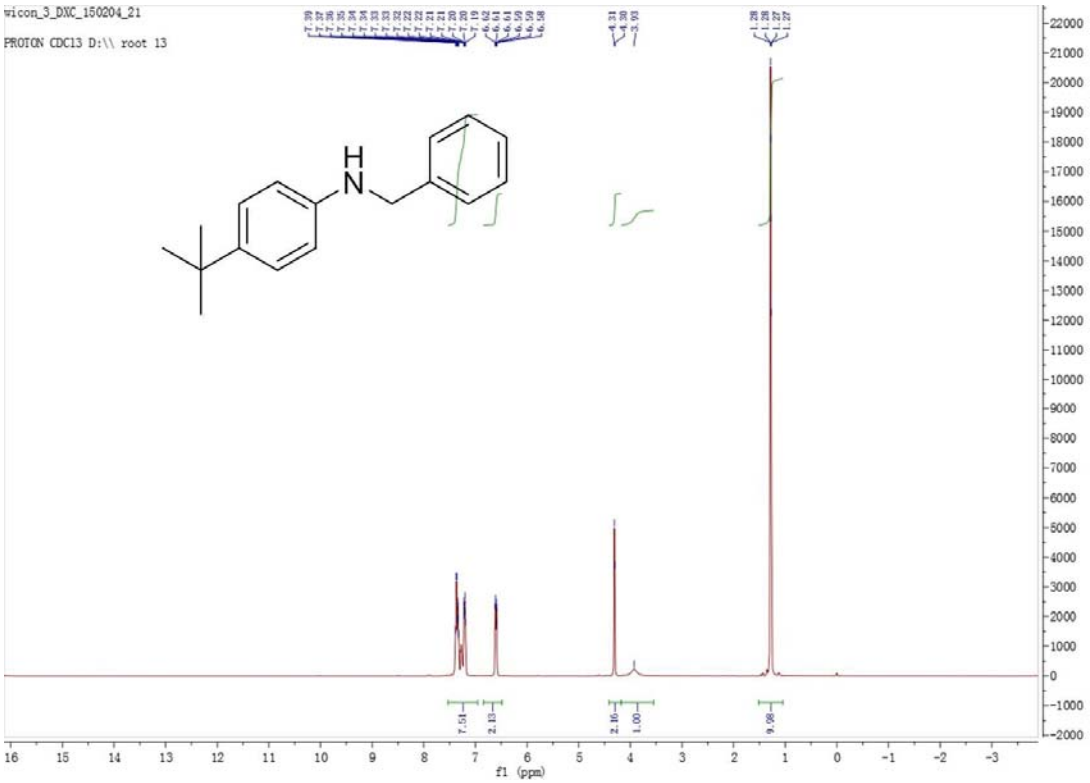
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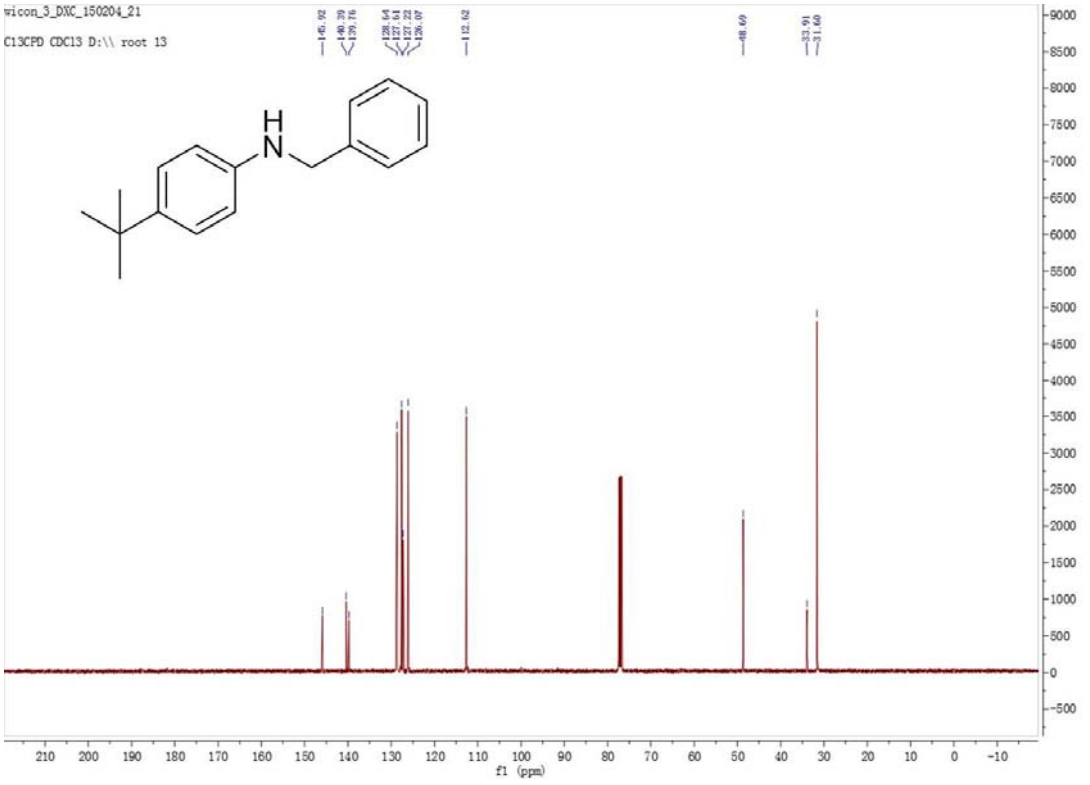
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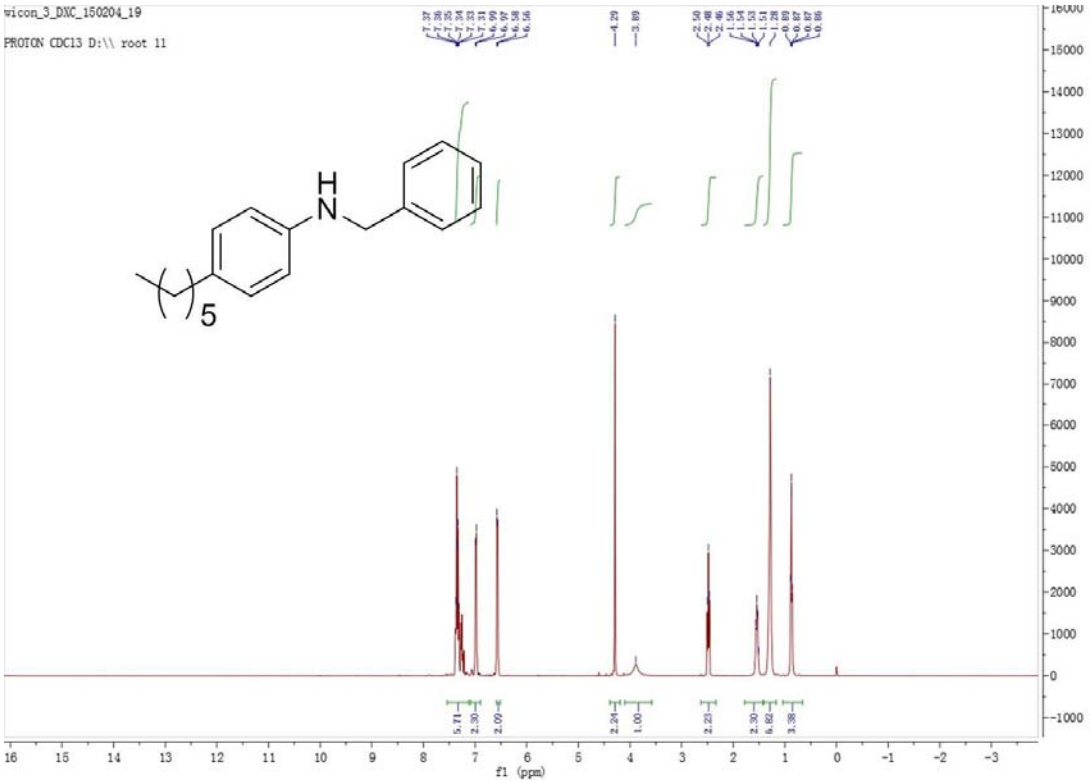
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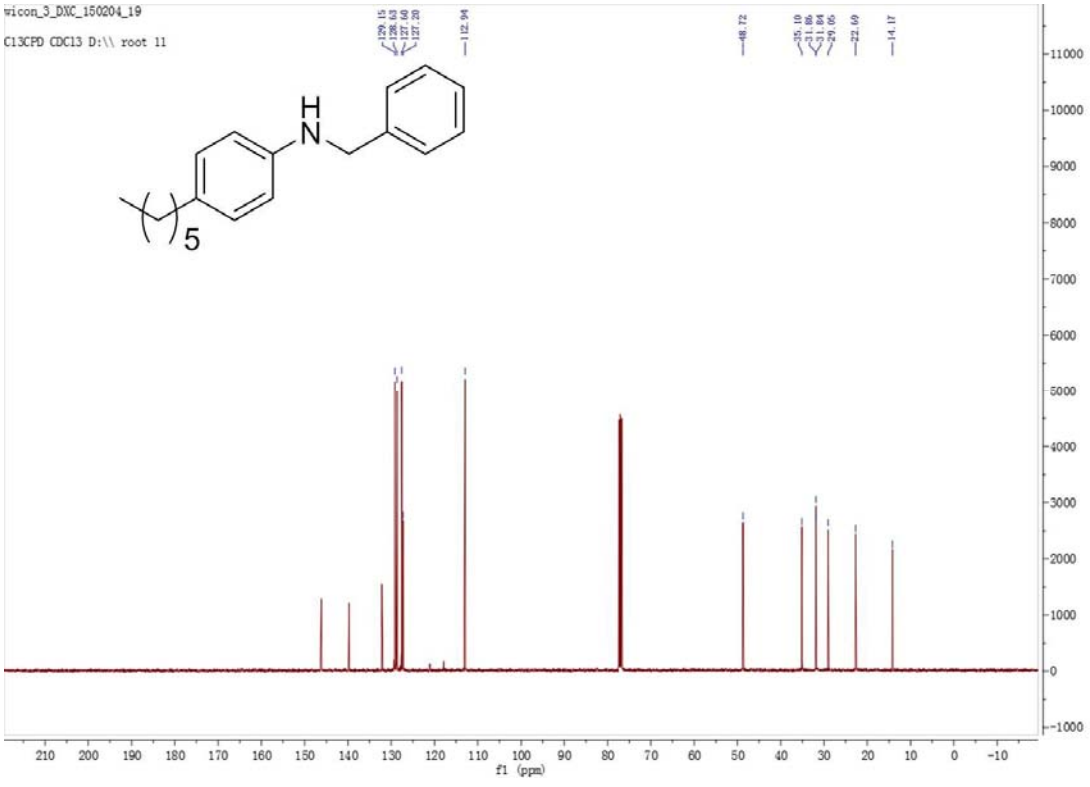
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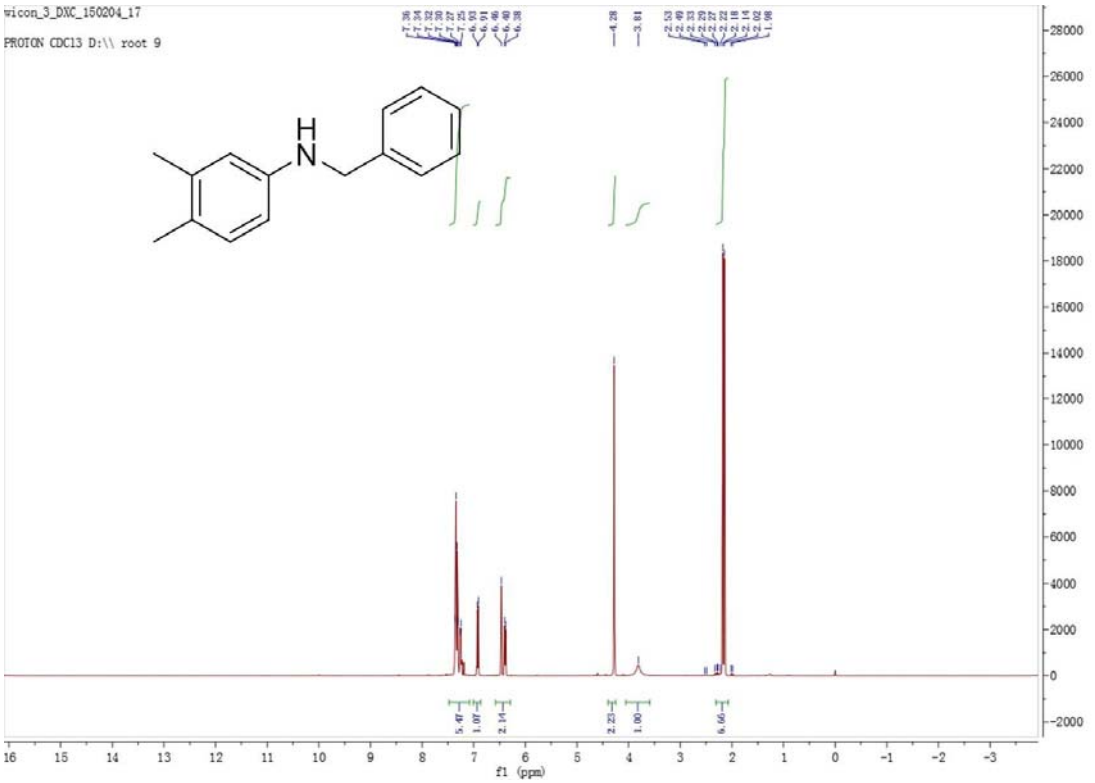
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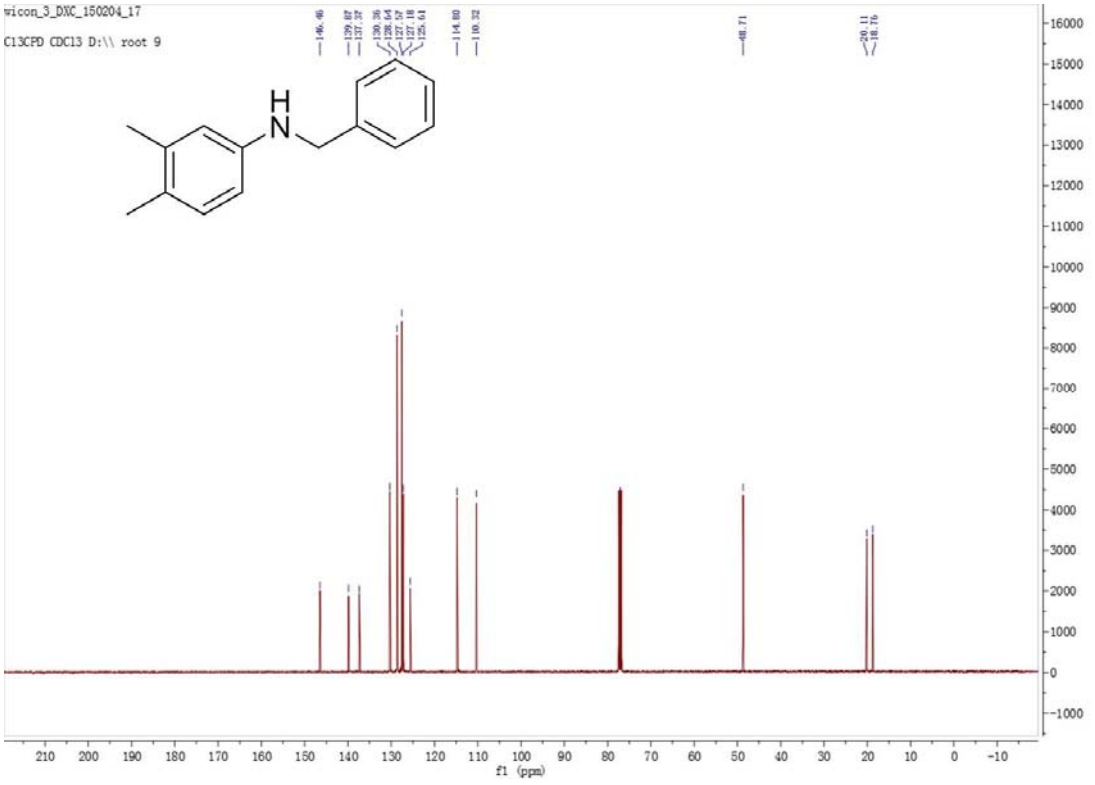
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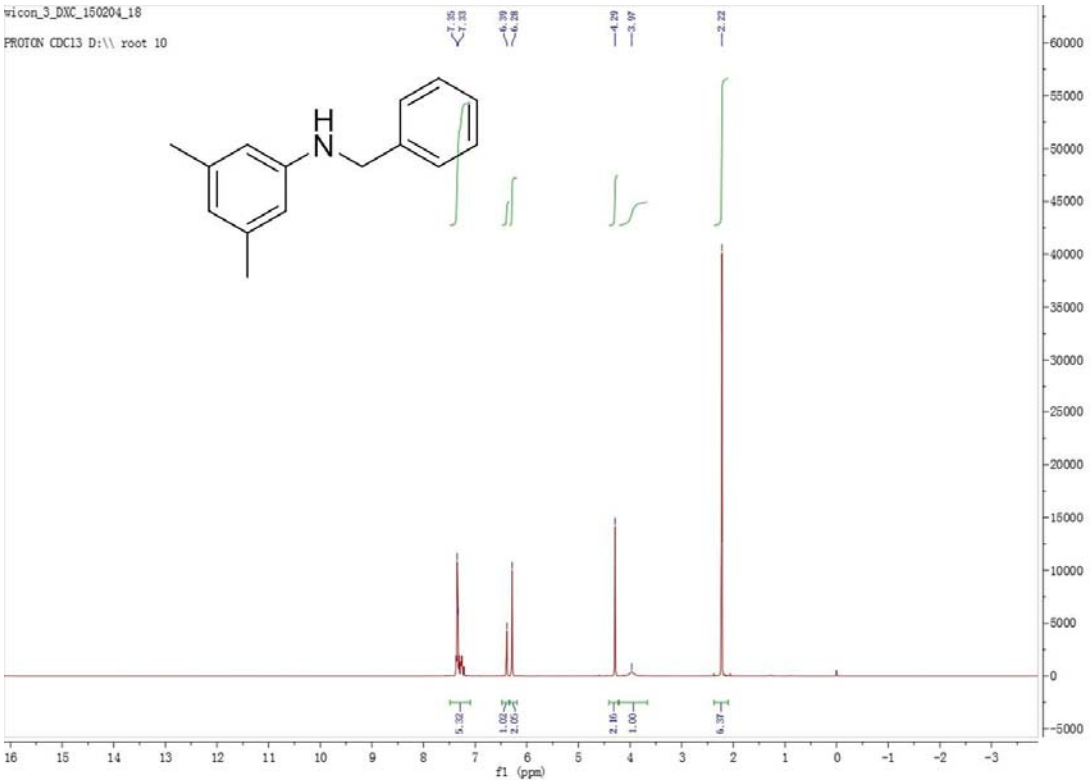
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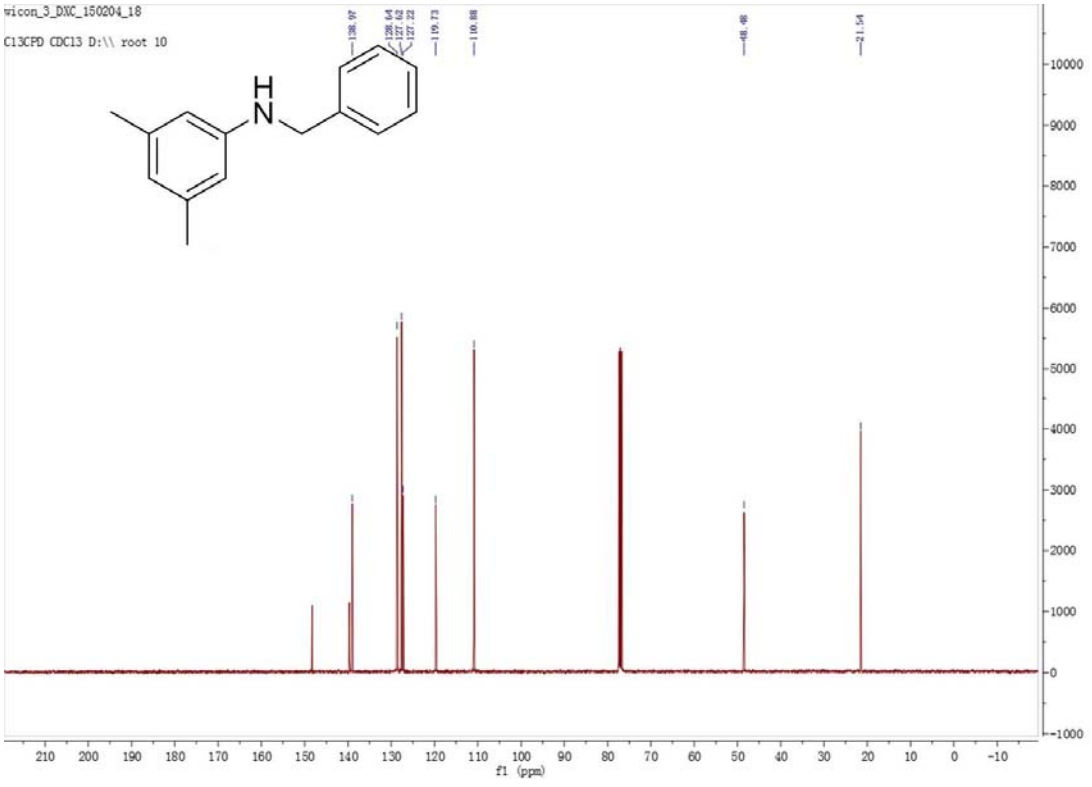
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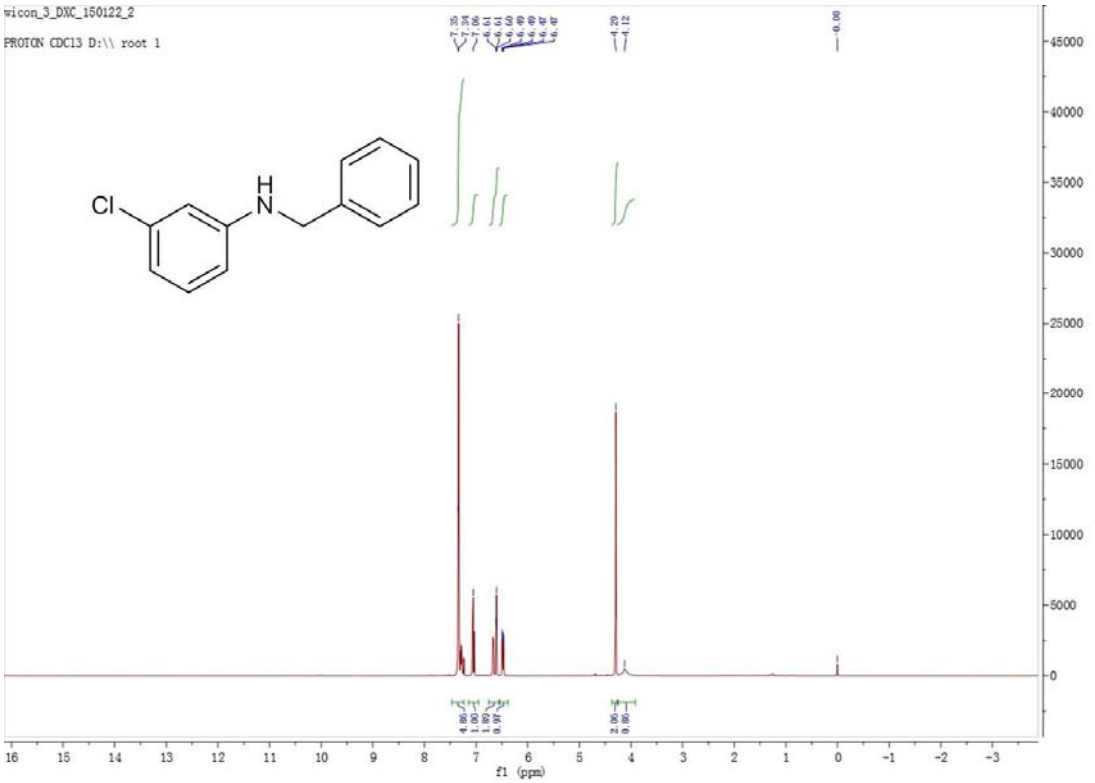
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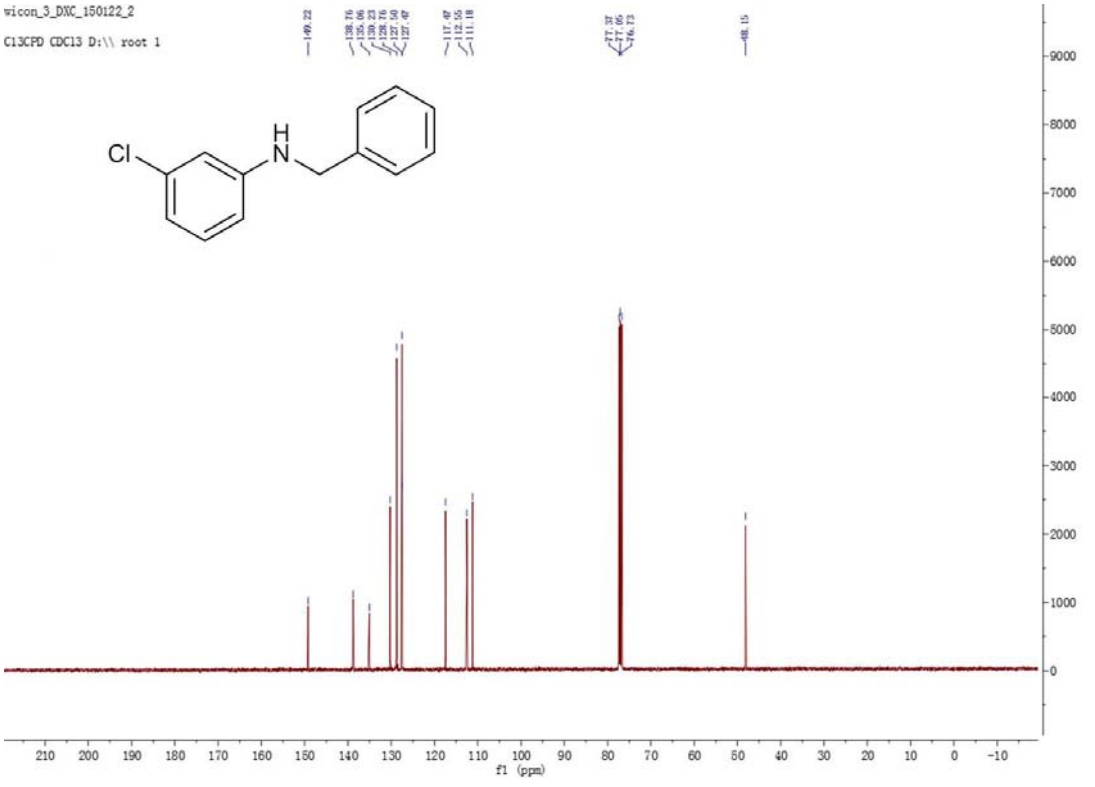
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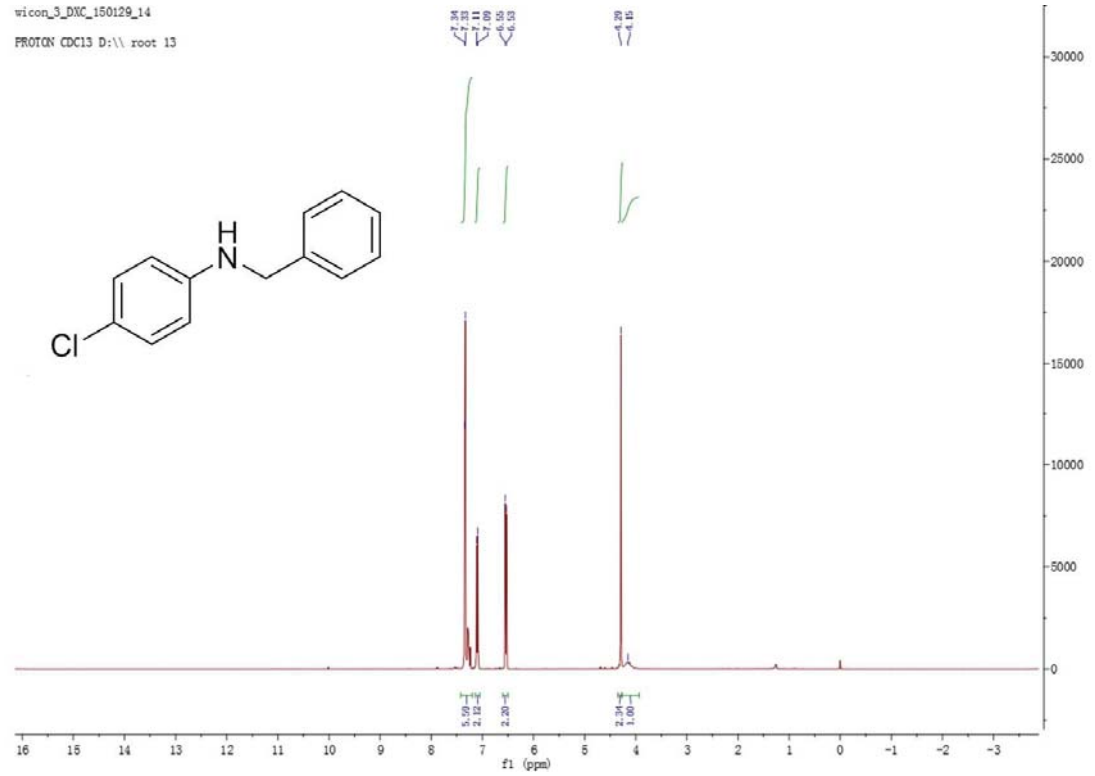
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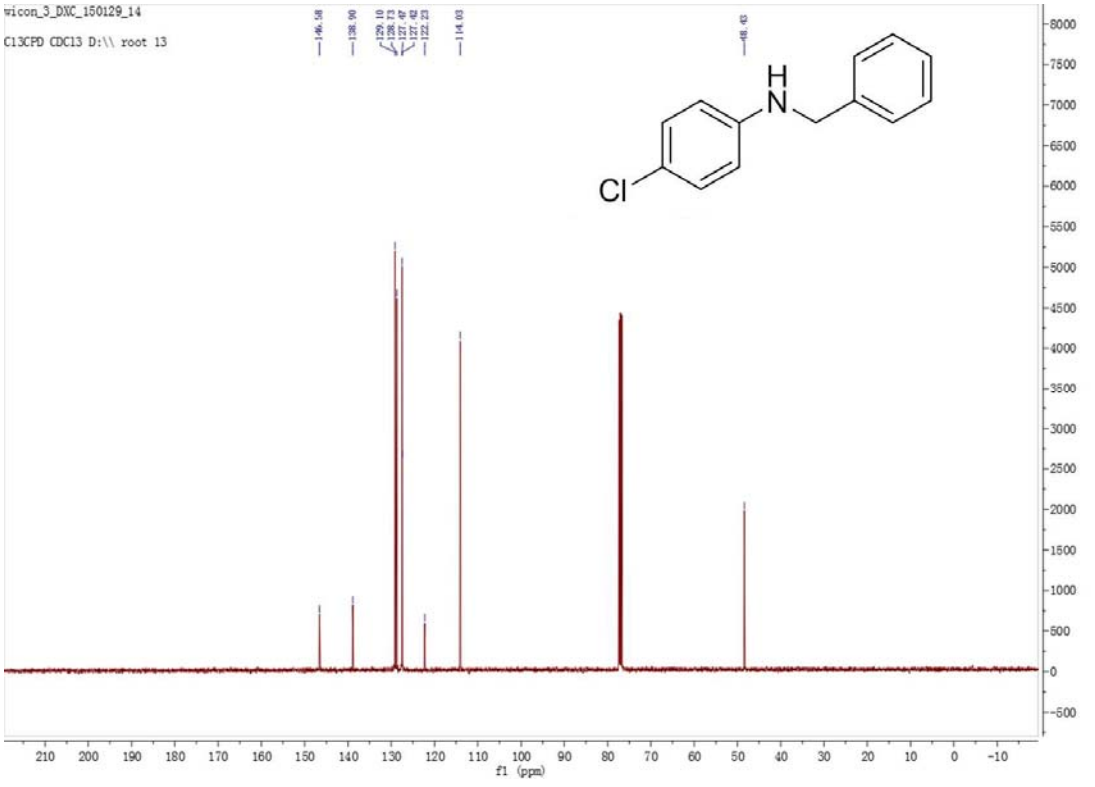
2.00
1.00
f1 (ppm)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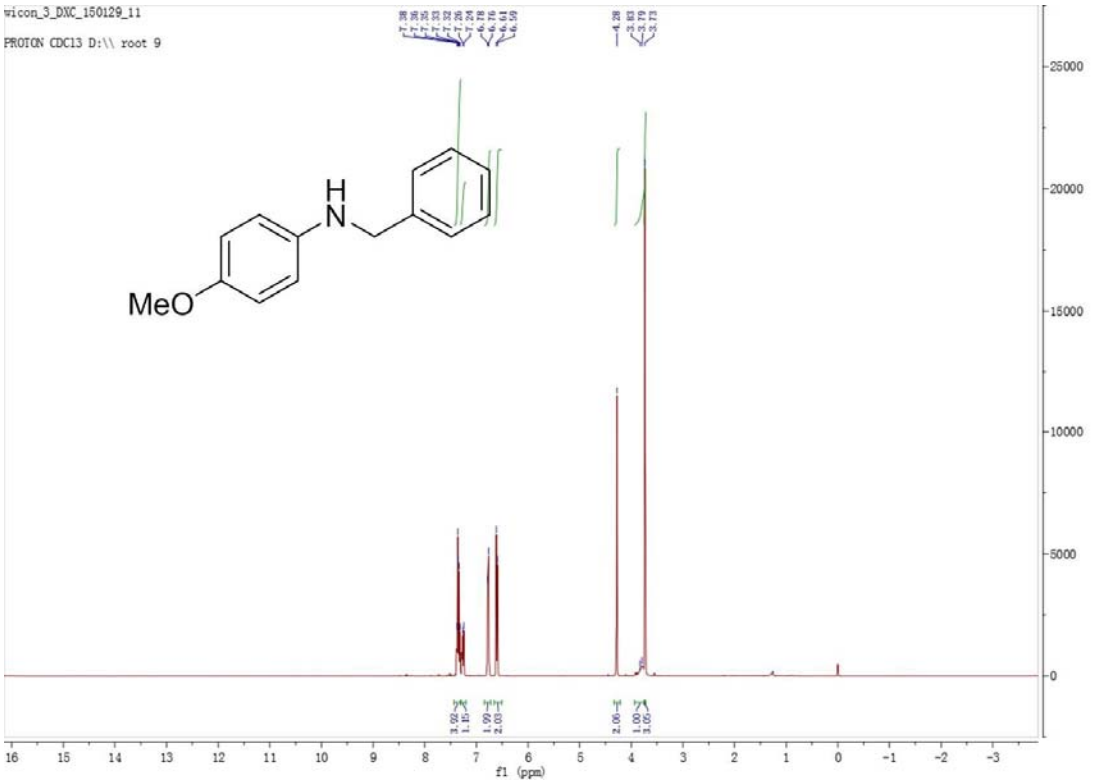
C13CPD CDCl3 D:\\ root 13
146.58
138.90
129.10
128.73
127.47
127.42
122.23
114.03
48.45
H
N
Cl
f1 (ppm)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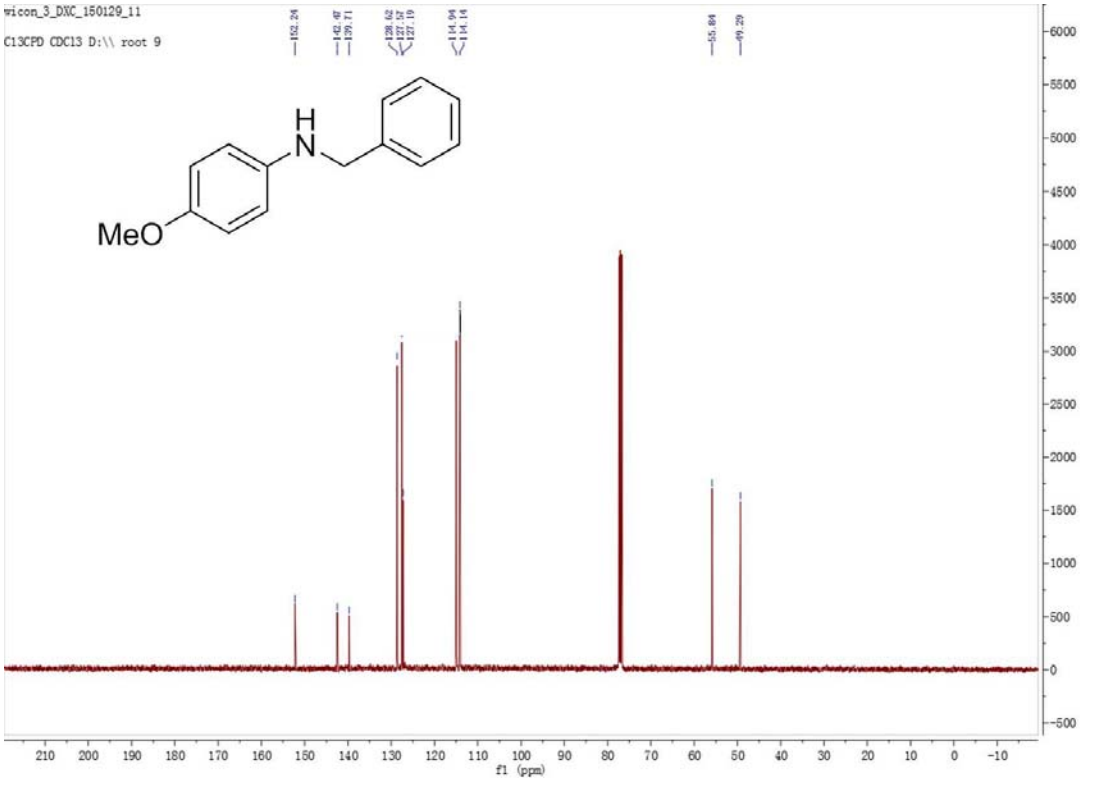
MeO
H
N
f1 (ppm)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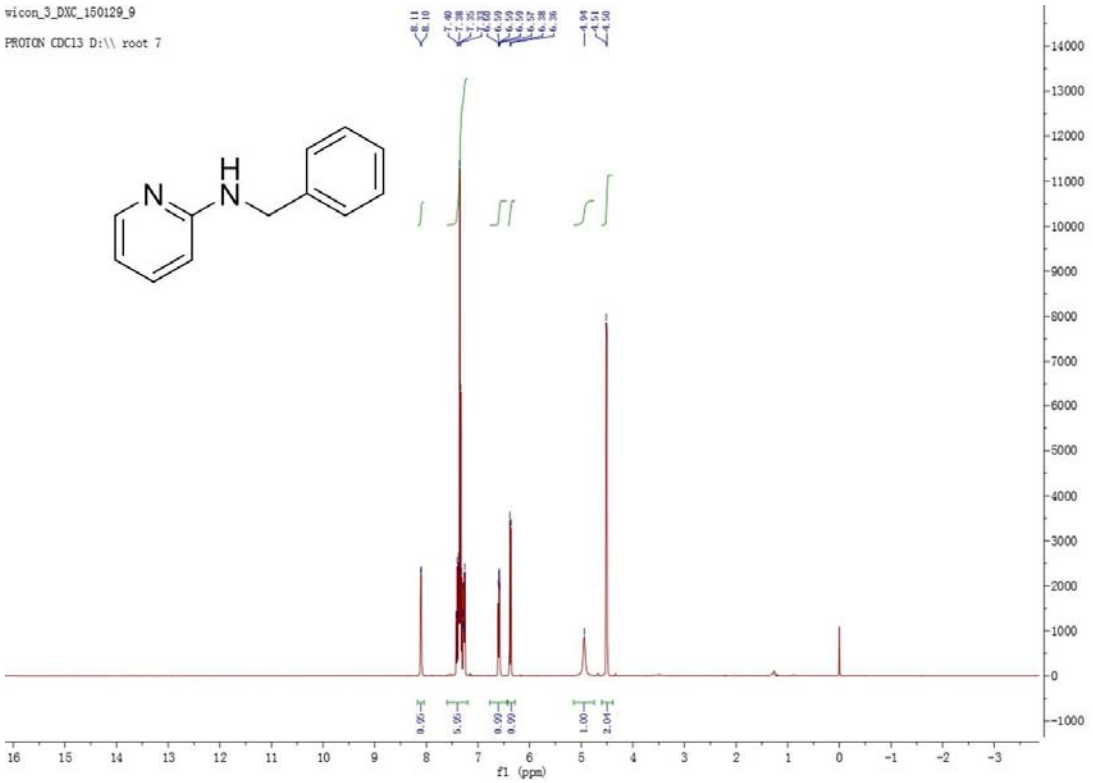
MeO
H
N
f1 (ppm)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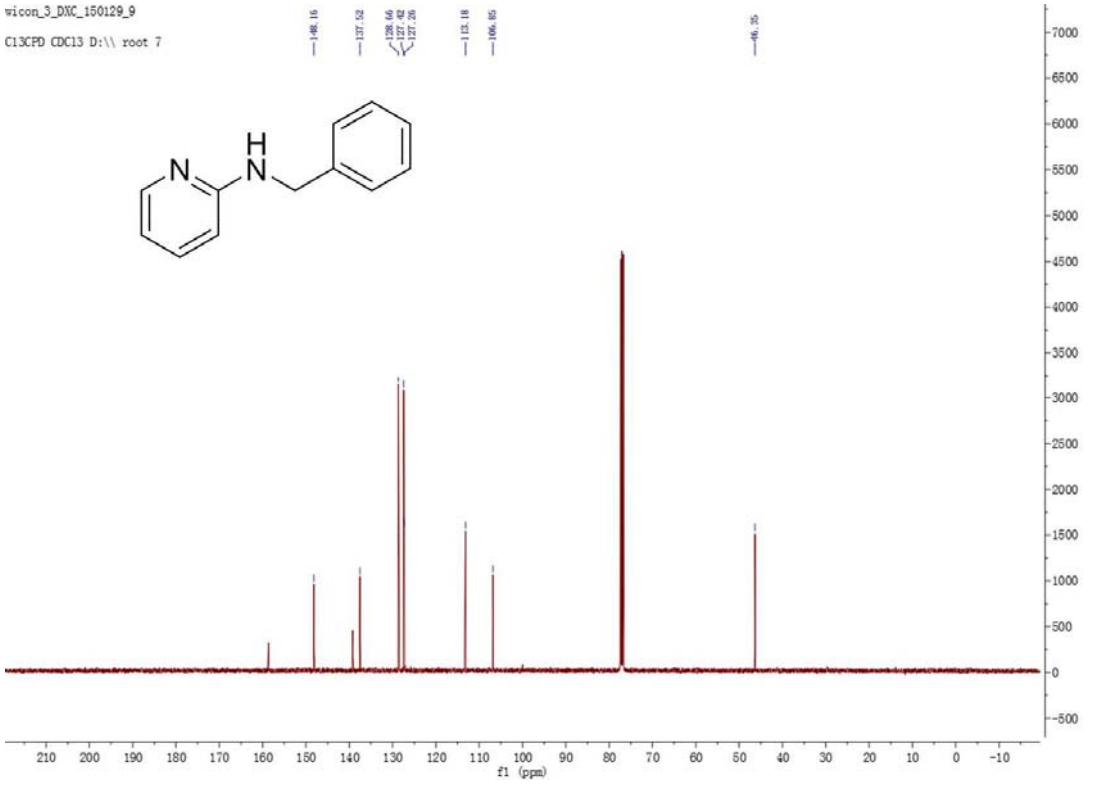
f1 (ppm)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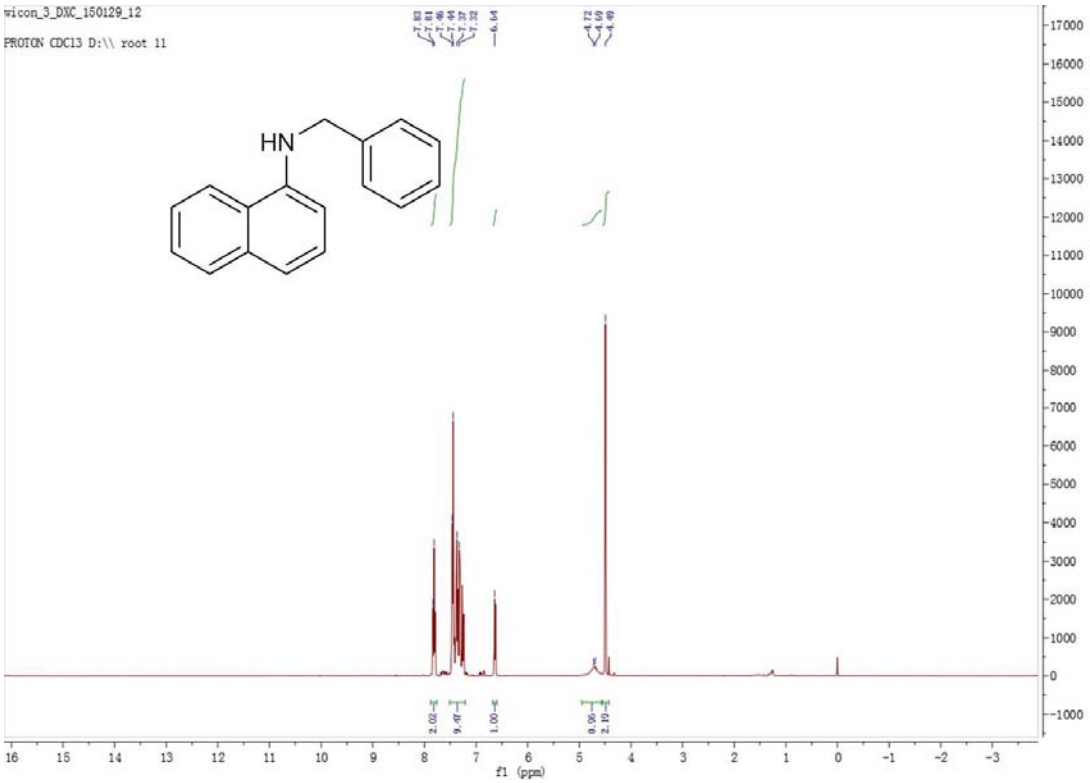
f1 (ppm)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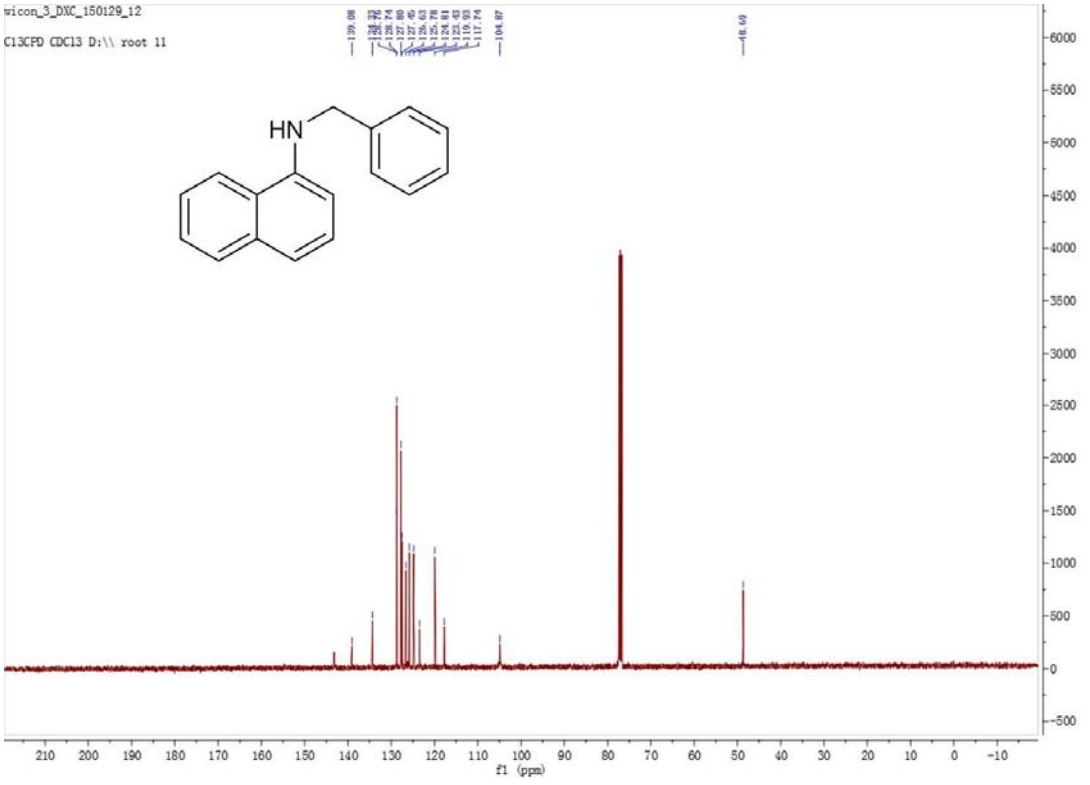
PROTON CDC13 D:\\ root 11
HN
f1 (ppm)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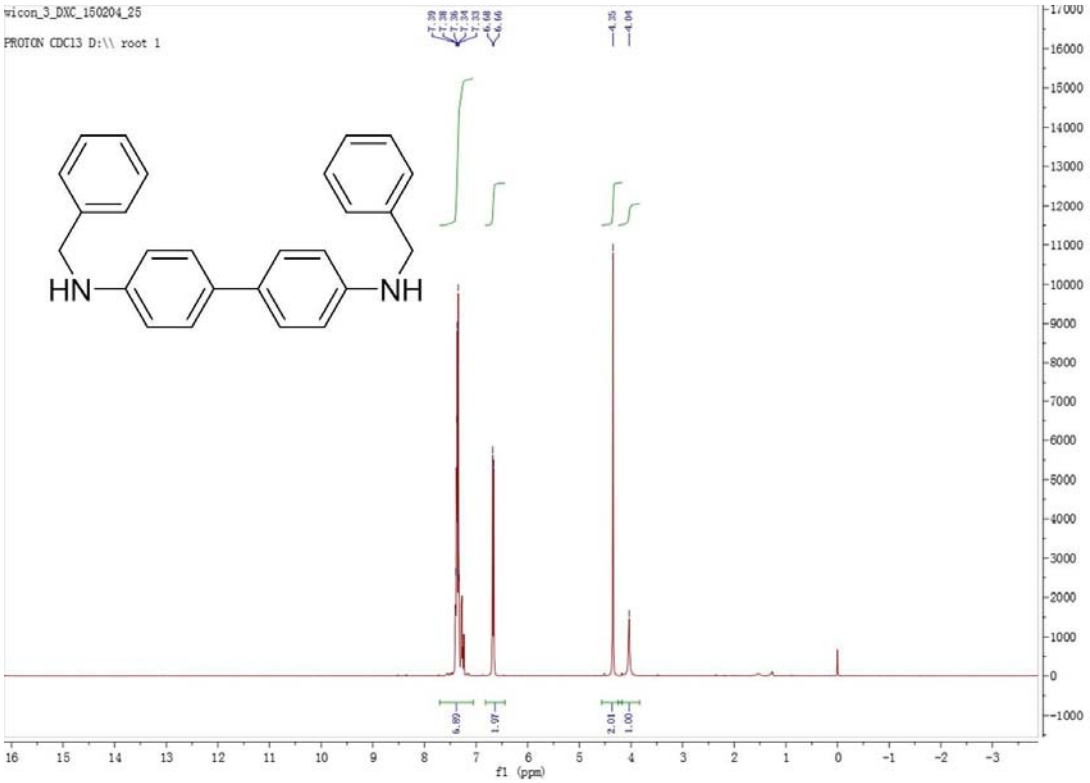
C13CPD CDC13 D:\\ root 11
HN
f1 (ppm)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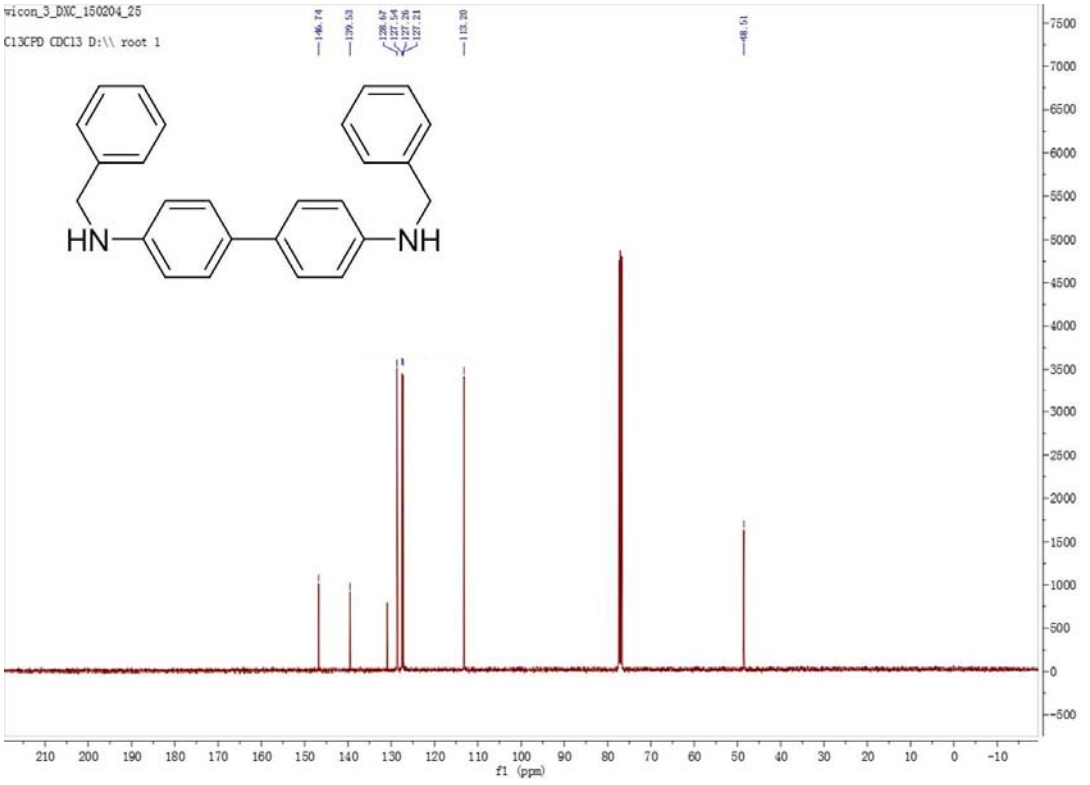
HN
NH
f1 (ppm)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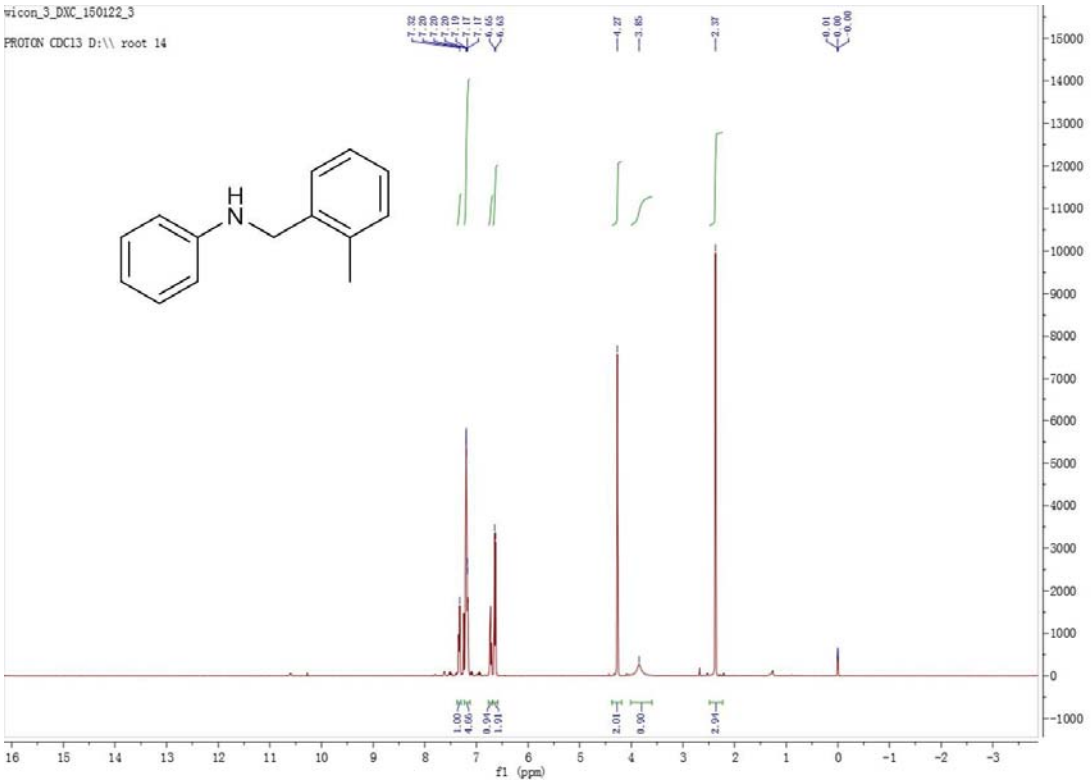
HN
NH
f1 (ppm)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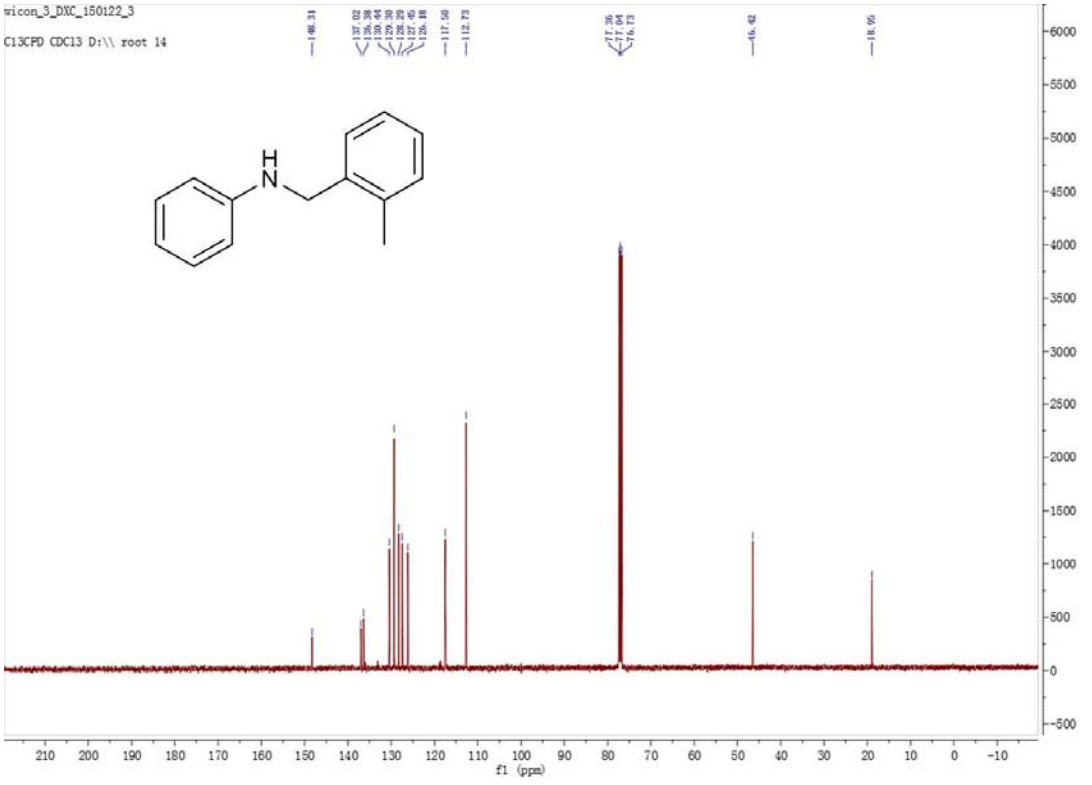
PROTON CDC13 D:\\ root 14
f1 (ppm)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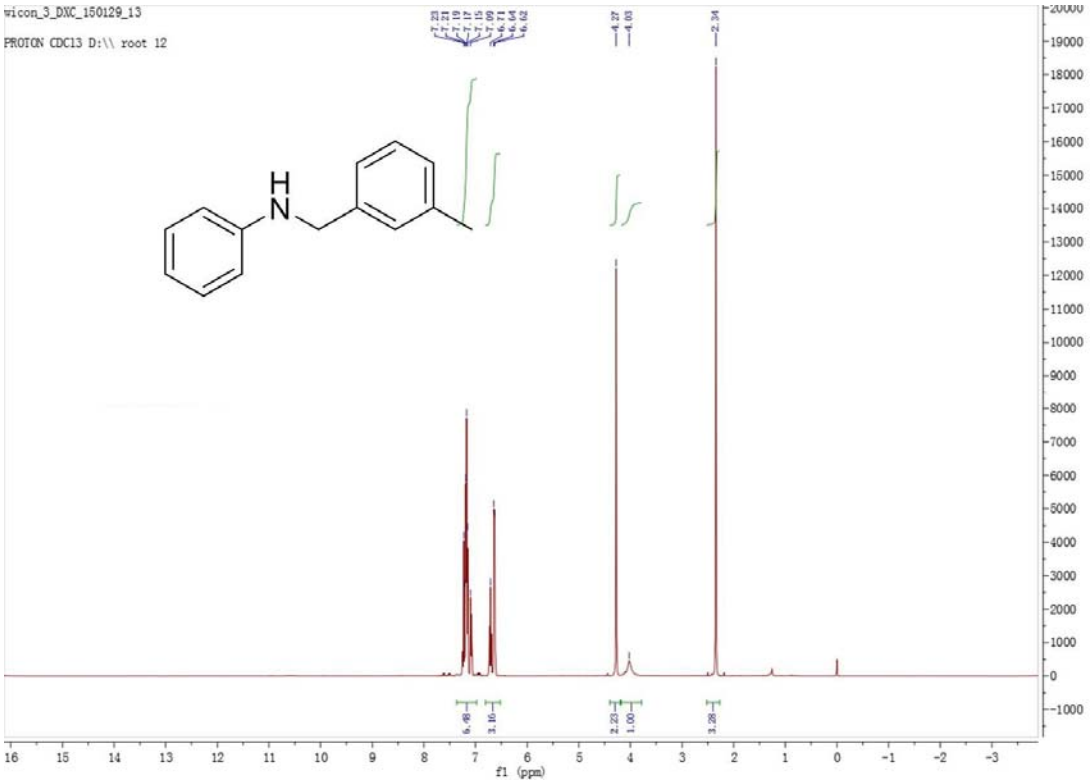
f1 (ppm)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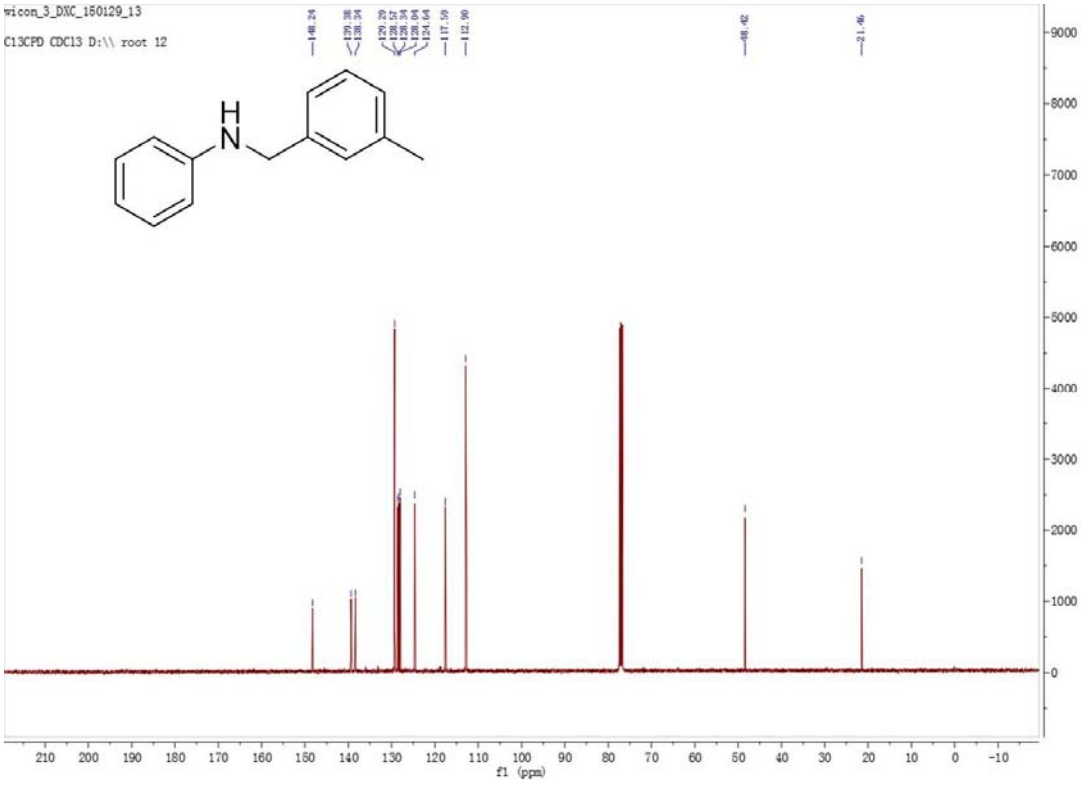
PROTON CDC13 D:\\ root 12
f1 (ppm)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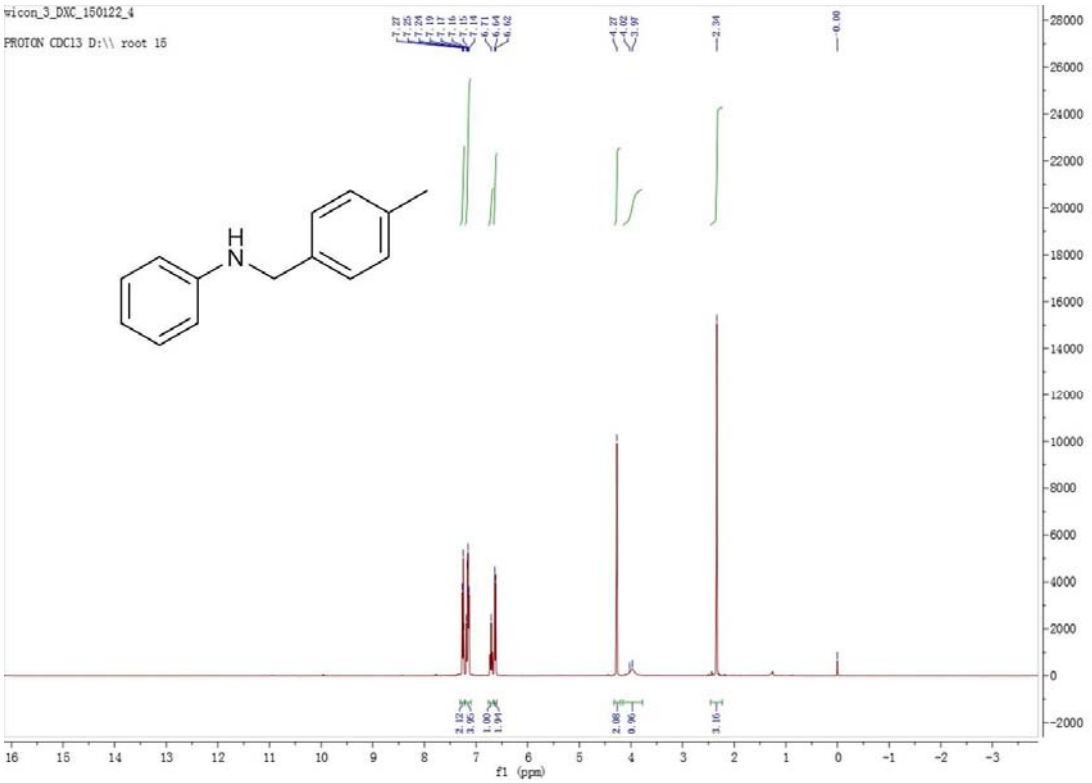
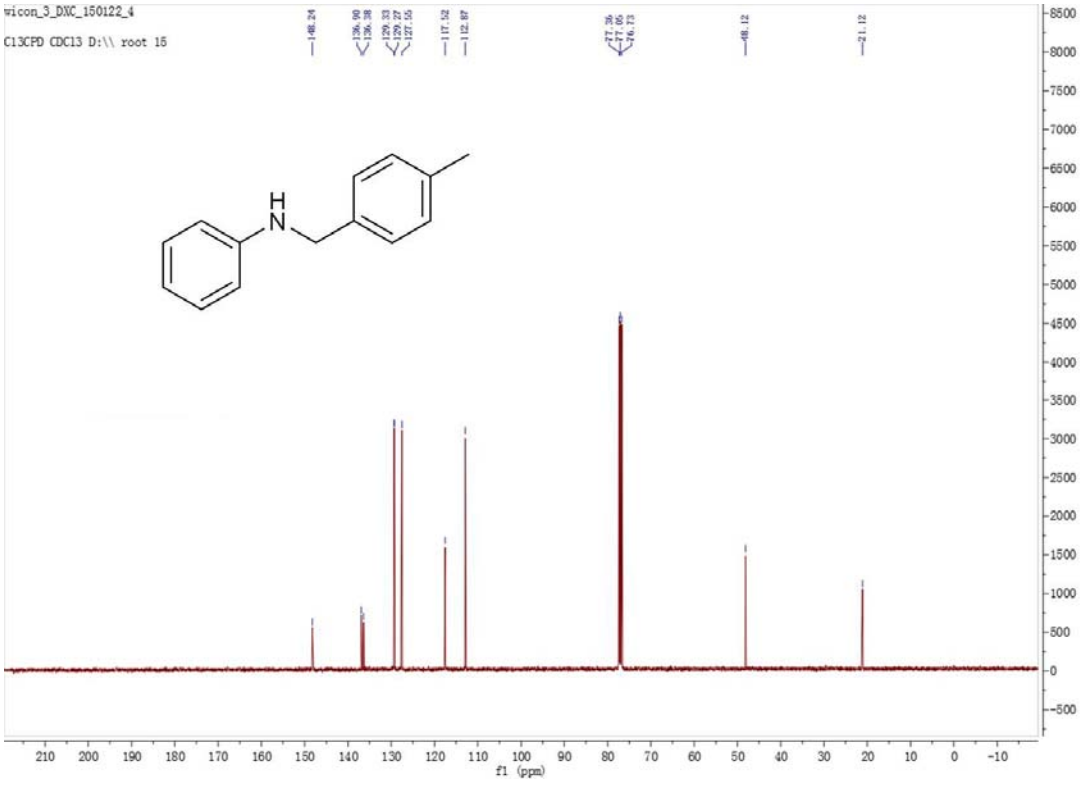
f1 (ppm)


wicon_3_DXC_150122_4
PROTON CDC13 D:\\ root 15
f1 (ppm)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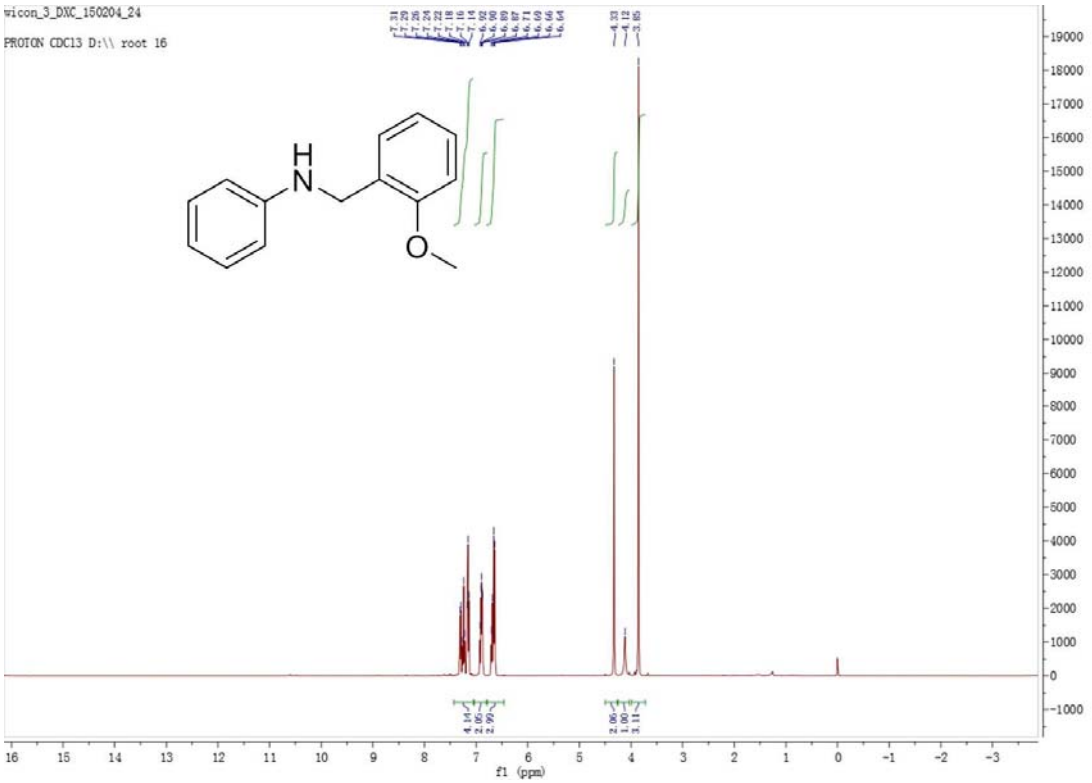
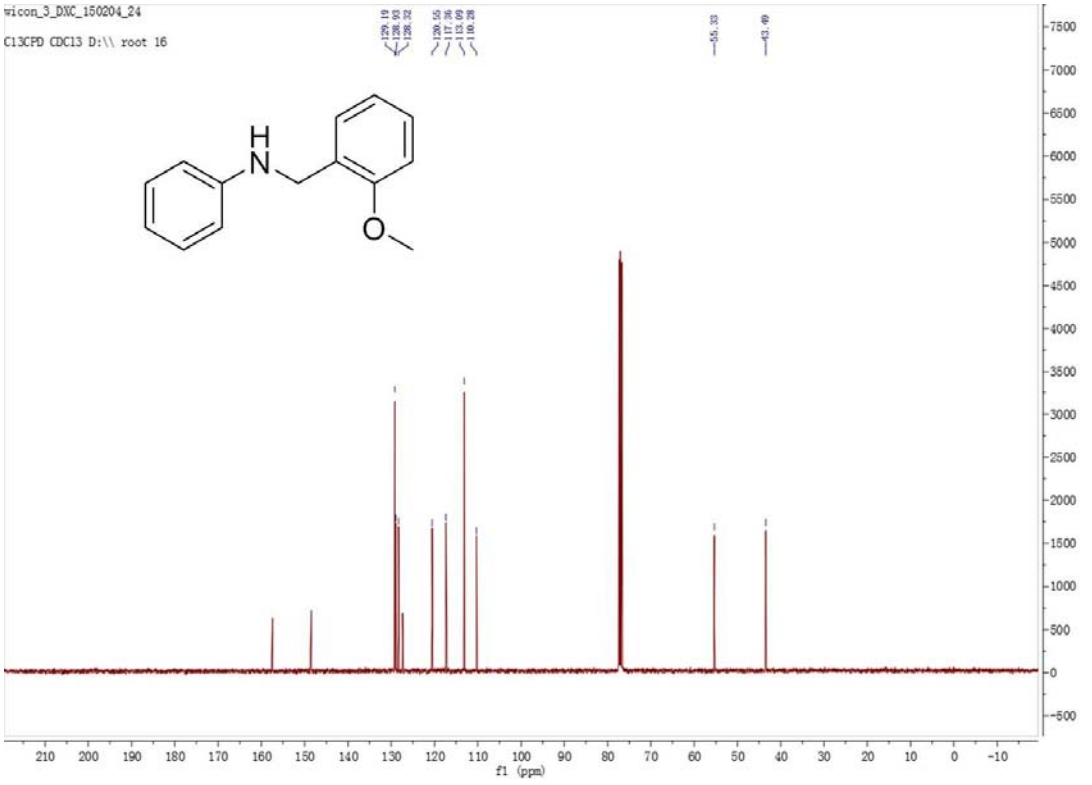
f1 (ppm)


wicon_3_DXC_150204_24
PROTON CDC13 D:\\ root 16
f1 (ppm)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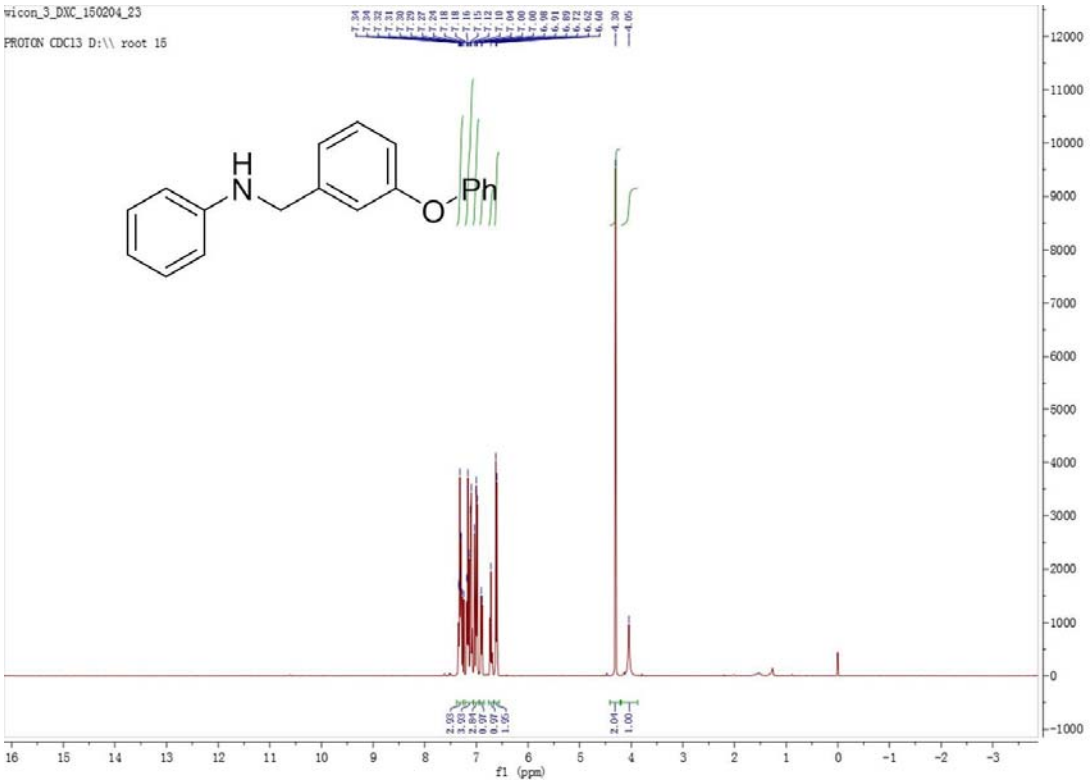
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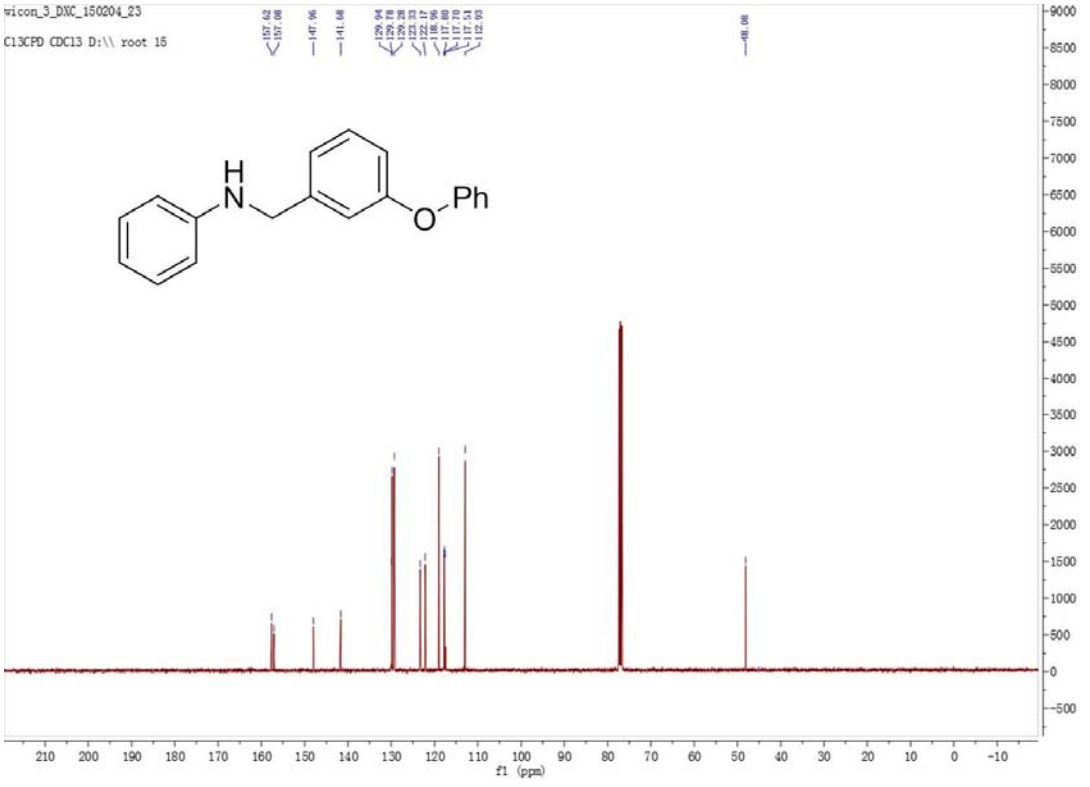
PROTON CDCl3 D:\\ root 15
H
N
O
Ph
f1 (ppm)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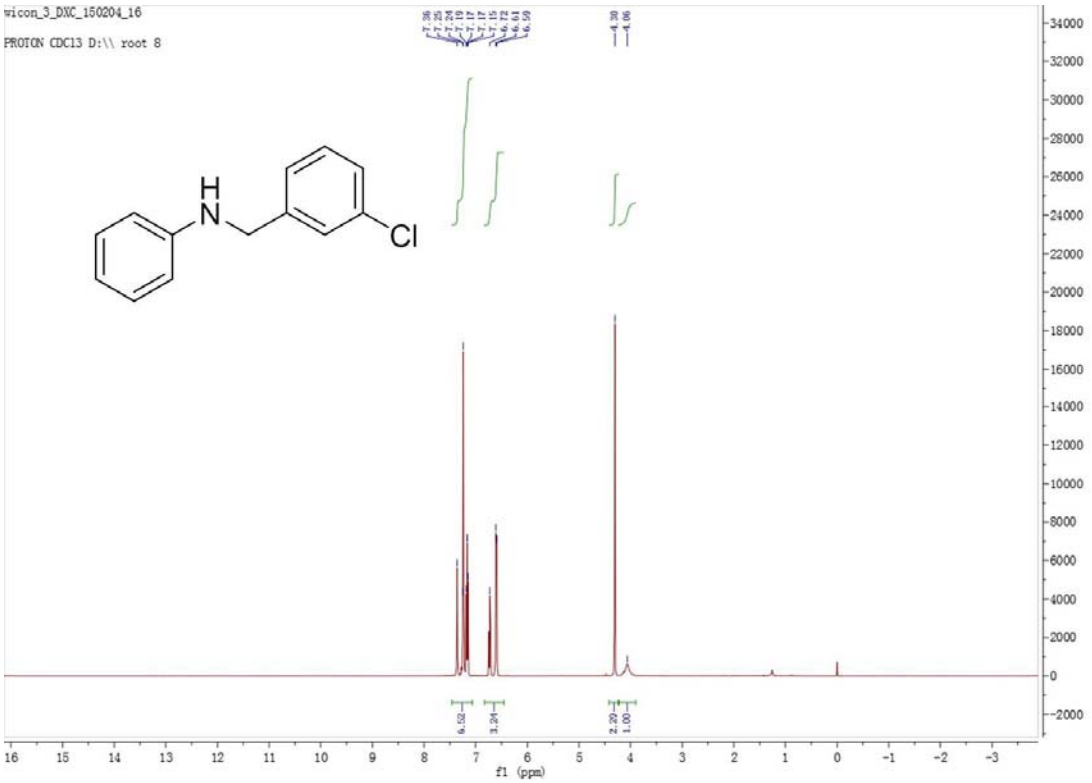
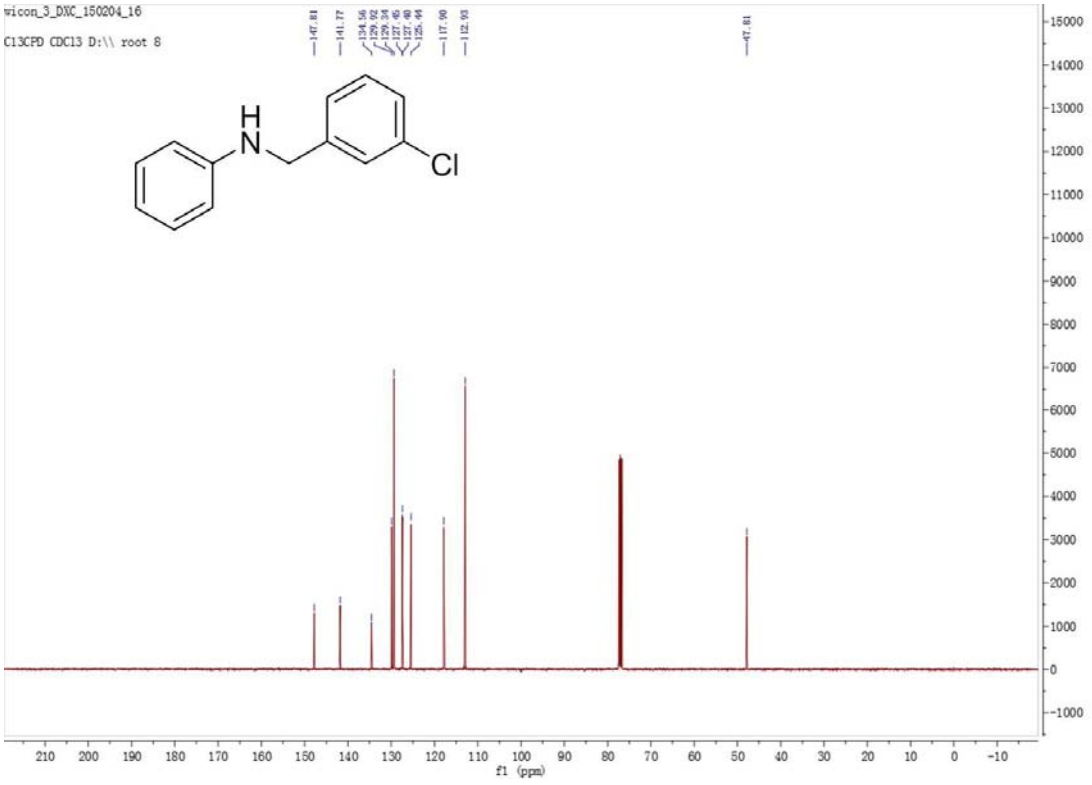
N
O
Ph
f1 (ppm)


wicon_3_DXC_150204_16
PROTON CDC13 D:\\ root 8
H
N
Cl
f1 (ppm)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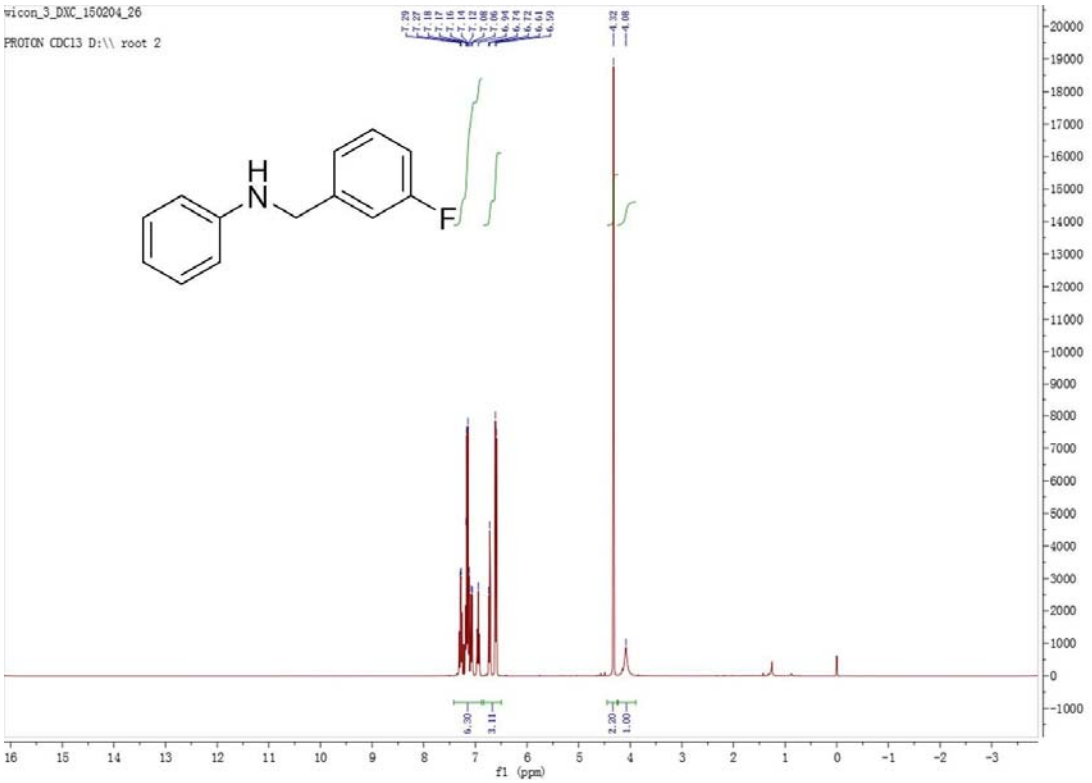
N
Cl
f1 (ppm)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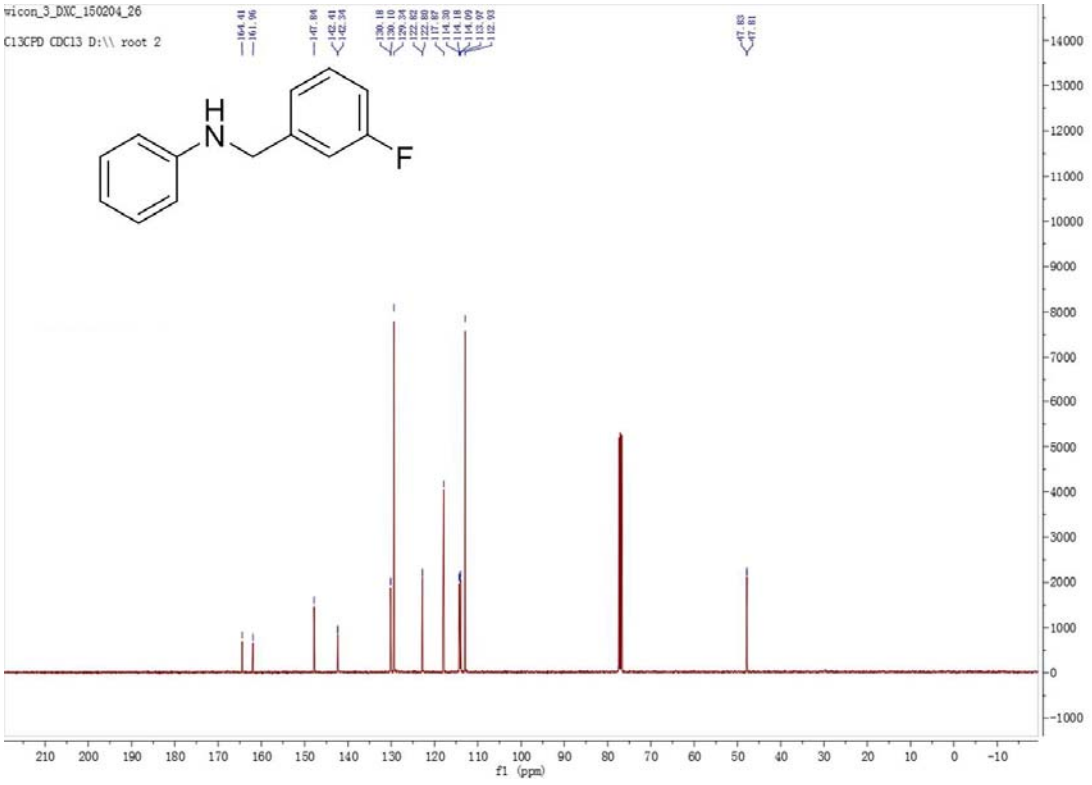
f1 (ppm)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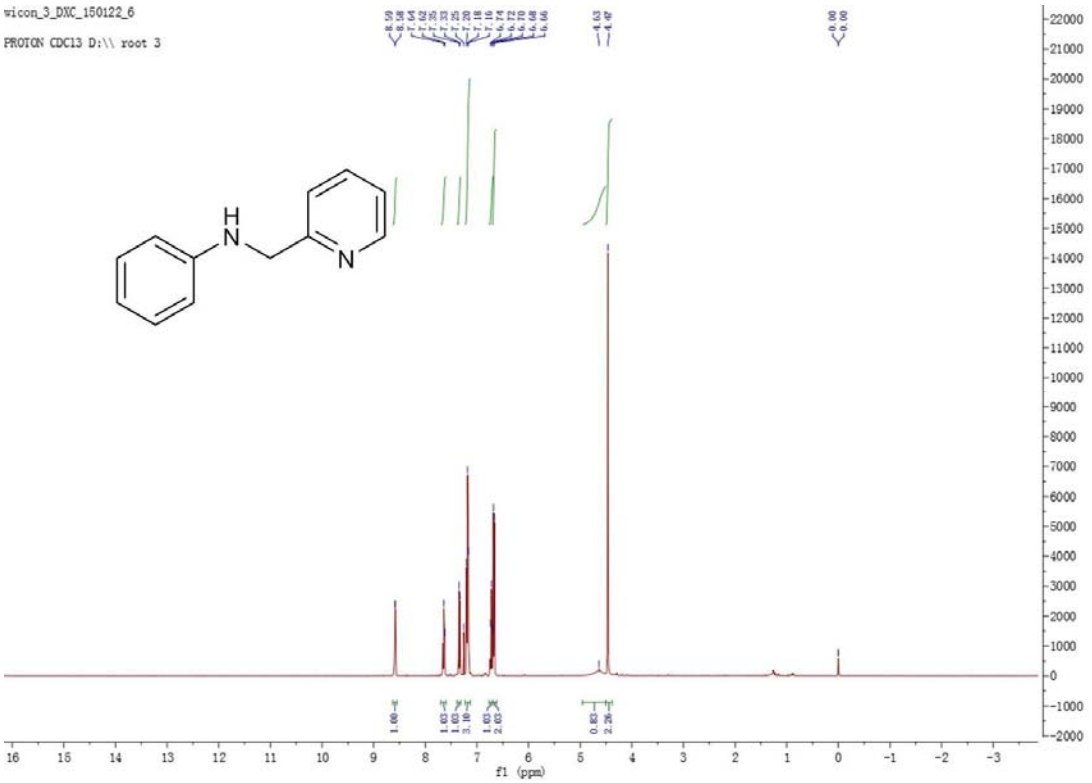
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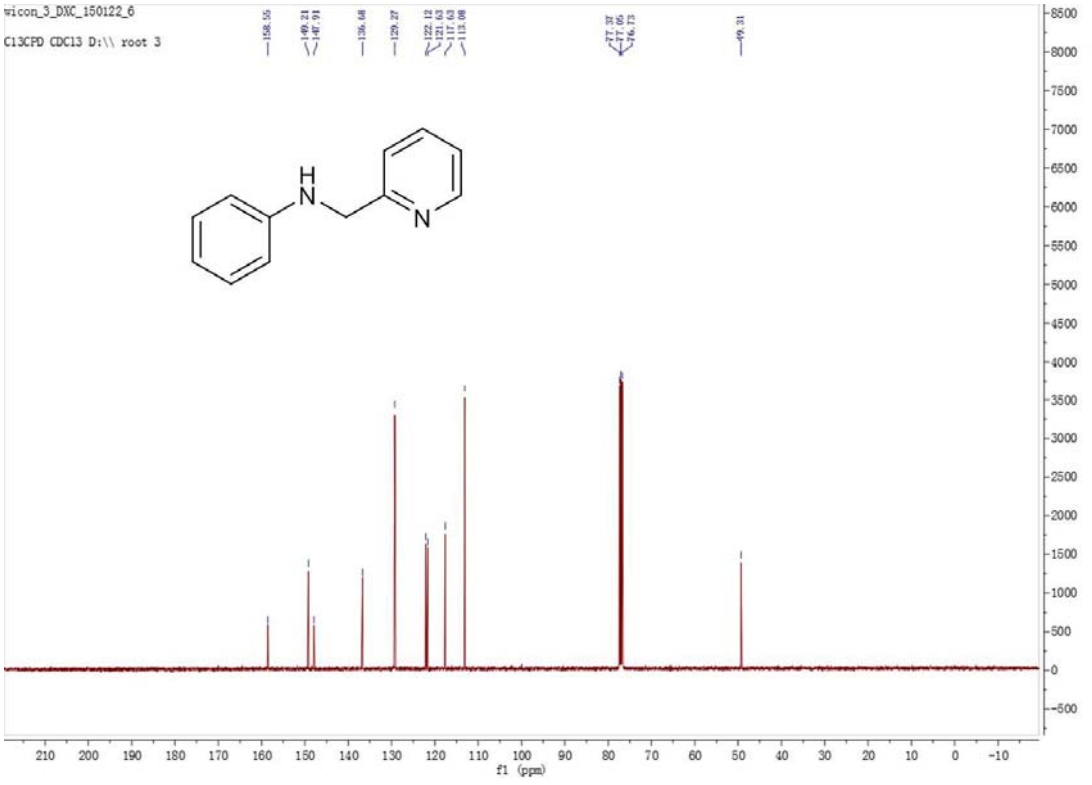
PROTON CDCl3 D:\\ root 3
f1 (ppm)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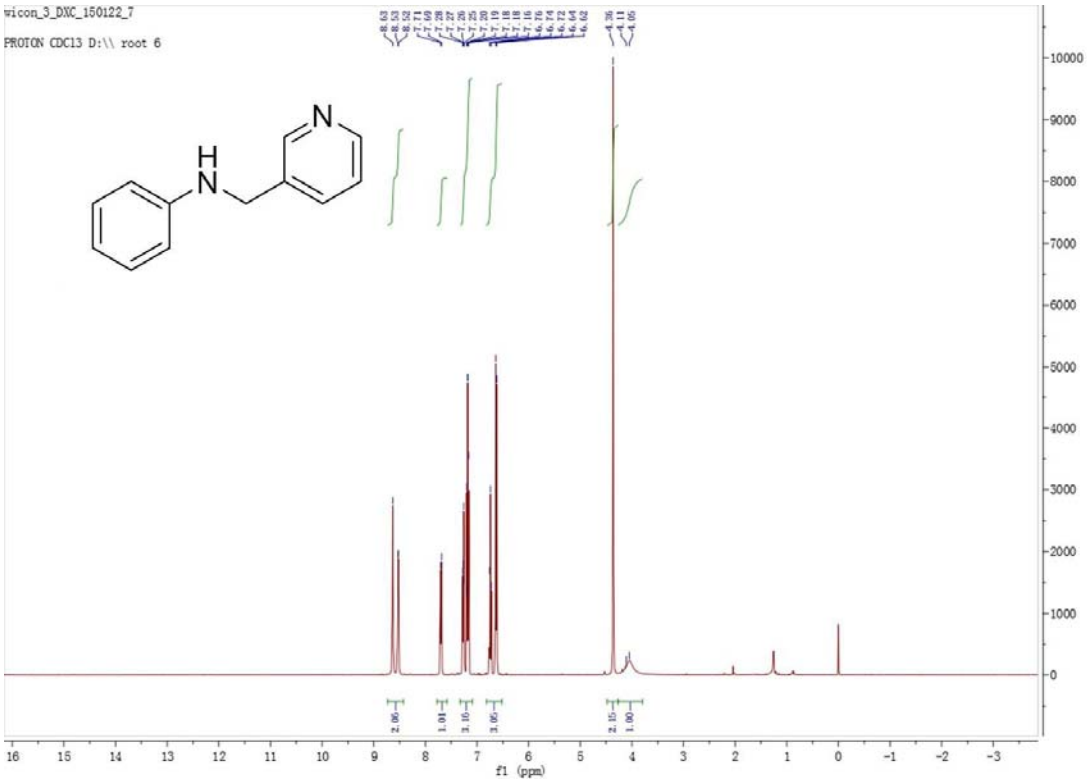
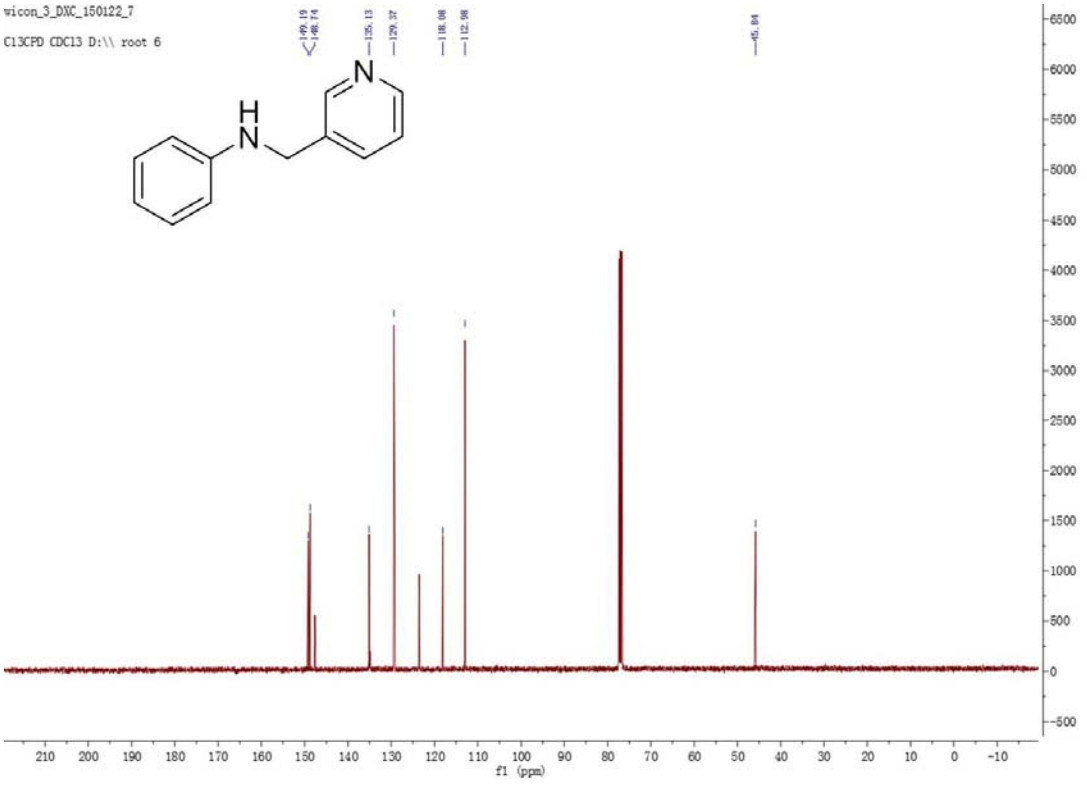
f1 (ppm)


wicon_3_DXC_150122_7
PROTON CDC13 D:\\ root 6
f1 (ppm)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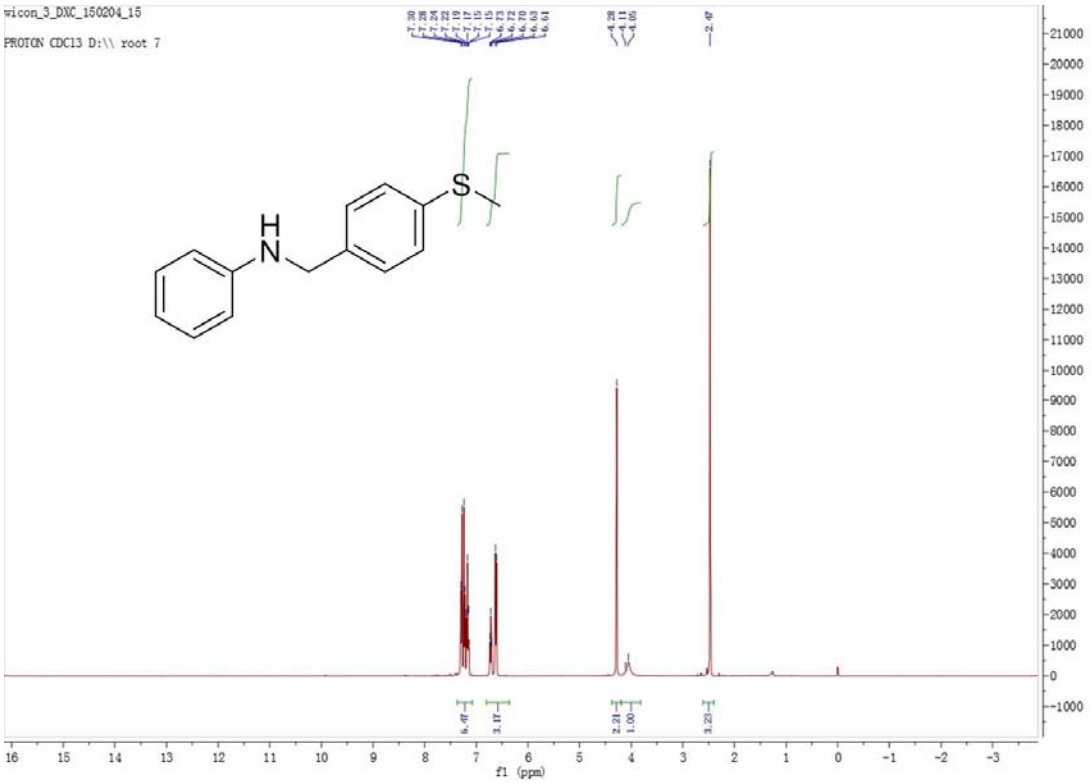
f1 (ppm)


wicon_3_DXC_150204_15
PROTON CDC13 D:\\ root 7
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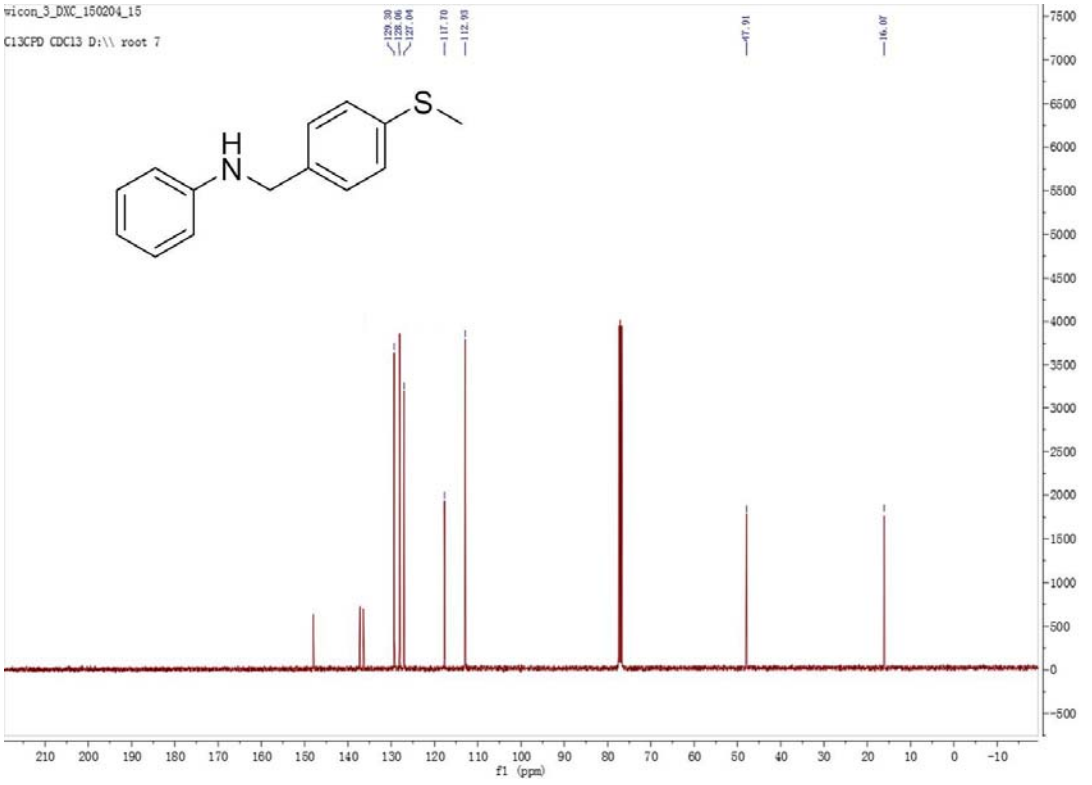
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f1 (ppm)