Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information

Room Temperature N-Alkylation of Amines with Alcohols under UV Irradiation Catalyzed by Cu-Mo/TiO_2

Lina Zhang[ab], Yan Zhang[a], Youquan Deng[a], Feng Shi*[a]

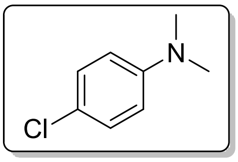
[a] *State Key Laboratory for Oxo Synthesis and Selective Oxidation, Centre for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, No.18, Tianshui Middle Road, Lanzhou, 730000, China.*

[b] *University of Chinese Academy of Sciences, Beijing, 100049, China*

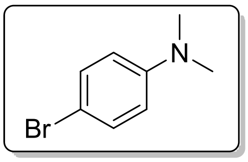
Typical procedure for catalyst preparation: MoO_3 (12 mg) was dissolved with stirring in 1 M NaOH (1 mL) at room temperature until the complete dissolution of MoO_3, then deionized water (30 mL) was added. Following, TiO_2 (0.5 g, P25, J&K Scientific, anatase/rutile =80/20, BET surface, 35-65 m^2/g) was dispersed in the solution and $CuCl_2$ aqueous solution (14 mg/ 5 mL) were added into the solution under vigorous stirring. After the addition of $CuCl_2$ was completed, the solution was stirred for another 3 h at room temperature. Then $NaBH_4$ (20 mg) was added to the solution in ice water bath and stirred for 2 h. The solid sample was recovered by centrifugation and washed with water. The obtained solid was dried at 80 ^oC.

Typical procedure of photocatalytic reaction: amine (0.2 mmol), catalyst (20 mg) and alcohol (5 mL) were added into a glass tube (35 mL). Argon was bubbled through the solution for 5 min. Then the tube was sealed with a rubber cap and photoirradiated by a LED light (λ = 365 nm) with magnetic stirring at room temperature for 21 h. Subsequently, 10 mg biphenyl and 5 mL ethanol were added for quantitative analysis by GC-FID (Agilent 6890A) and some products were purified by vacuum distillation after removing the catalyst by filtration or flash column chromatography.

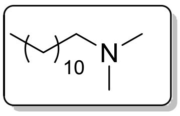
Characterization data of isolated products



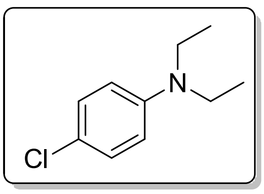
4-chloro-N,N-dimethylaniline[1], brown solid (95%, Entry 3, Table 3) Mp 32-37 ^{o}C. The product was separated by vacuum distillation after remove the catalyst by filtration. ^{1}H NMR (400MHz, $CDCl_3$,): δ=2.92(s, 6H), 6.62-6.64(d, 2H), 7.15-7.17(d, 2H). ^{13}C NMR (100MHz, $CDCl_3$,): 149.2, 128.8, 121.5, 113.7, 40.7; MS (E.I., 70 eV) m/z (rel. int.): 156(36), 155(71), 154(100), 141(20), 140(26), 118(11), 111(11), 77(14).



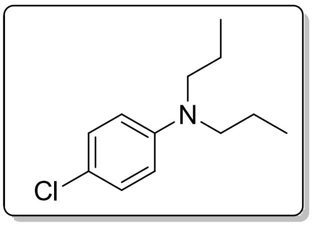
4-bromo-N,N-dimethylaniline[2], brown solid (80%, Entry 4, Table 3). Mp 53-55 ^{o}C. The product was separated by column chromatography (petroleum ether (b.p. 60-90ºC)/EtOAc = 24/1). ^{1}H NMR (400MHz, $CDCl_3$,): δ=2.92(s, 6H), 6.60-6.62(d, 2H), 7.29-7.31(d, 2H); ^{13}C NMR (100MHz, $CDCl_3$,): 149.5, 131.7, 114.2, 108.6, 40.6; MS (E.I., 70 eV) m/z (rel. int.): 201(90), 200(100), 199(95), 198(99), 185(12), 184(12), 183(13), 118(25), 104(13), 77(15), 50(10), 44(13).



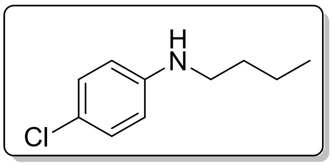
N,N-Dimethyldodecylamine[3], colorless liquid (94% yield, Entry 7, Table 3). The product was separated by vacuum distillation after remove the catalyst by filtration. ^{1}H NMR (400MHz, $CDCl_3$,): δ=0.87-0.91(t, 3H), 1.27-1.29(m, 20H), 2.22(s, 6H), 2.25-2.27(t, 2H); ^{13}C NMR (100MHz, $CDCl_3$,): 65.6, 52.2, 46.8, 31.9, 30.6, 29.6, 29.3, 27.3, 22.7, 19.2, 14.1, 13.7, 10.2; MS (E.I., 70 eV) m/z (rel. int.): 213(6), 212(1), 198(0.5), 184(0.2), 170(0.2), 156(0.2), 142(0.2), 128(0.4), 114(0.6), 100(0.4), 84(1.4), 72(5.2), 69(9.5), 58(100), 59(4.2), 41(4.4), 29(1.8).



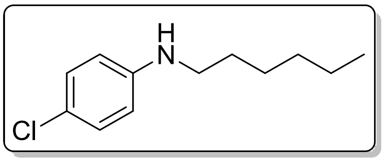
4-chloro-N,N-diethylaniline[4], brown liquid (80%, Entry 1, Table 4). The product was separated by column chromatography (petroleum ether (b.p. 60-90ºC)/EtOAc = 24/1). ^{1}H NMR (400MHz, $CDCl_3$,): δ=1.12-1.15(t, 6H), 3.29-3.34(q, 4H), 6.57-6.59(d, 2H), 7.12-7.14(d, 2H); ^{13}C NMR (100MHz, $CDCl_3$,): 146.4, 129.0, 120.1, 113.0, 44.5, 12.4; MS (E.I., 70 eV) m/z (rel. int.): 185(10), 184(4), 183(30), 170(33), 169(11), 168(100), 142(12), 141(5), 140(40), 138(11), 111(13), 77(7), 75(8).



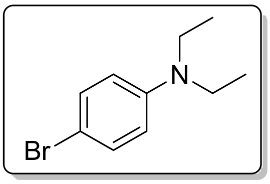
4-chloro-N,N-dipropylaniline[5], brown liquid (83%, Entry 2, Table 4). The product was separated by column chromatography (petroleum ether (b.p. 60-90ºC)/EtOAc = 24/1). ^{1}H NMR (400MHz, $CDCl_3$,): δ=0.89-0.93(t, 6H), 1.53-1.62(m, 4H), 3.17-3.21(t, 4H), 6.52-6.54(d, 2H), 7.10-7.12(d, 2H); ^{13}C NMR (100MHz, $CDCl_3$,): 146.8, 128.9, 119.8, 112.9, 53.0, 20.3, 11.4; MS (E.I., 70 eV) m/z (rel. int.): 213(7), 211(23), 184(34), 183(13), 182(100), 154(9), 142(17), 141(6), 140(55), 111(10), 77(5), 75(5), 43(12).



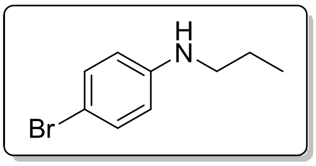
N-butyl-4-chloroaniline[6], yellow liquid (90%, Entry 3, Table 4). The product was separated by column chromatography (petroleum ether (b.p. 60-90ºC)/EtOAc = 35/1). ^{1}H NMR (400MHz, $CDCl_3$,): δ=0.93-0.97(t, 3H), 1.37-1.44(m, 2H), 1.56-1.62(m, 2H), 3.05-3.09(t, 2H), 6.52-6.54(d, 2H), 7.10-7.12(d, 2H); ^{13}C NMR (100MHz, $CDCl_3$,): 146.8, 129.0, 121.9, 113.9, 44.0, 31.5, 20.3, 13.9; MS (E.I., 70 eV) m/z (rel. int.): 185(7), 183(22), 142(33), 141(9), 140(100), 111(5), 105(4), 77(4), 75(5).



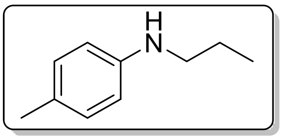
4-chloro-N-hexylaniline[7], yellow liquid (93%, Entry 4, Table 4). The product was separated by column chromatography (petroleum ether (b.p. 60-90ºC)/EtOAc = 35/1). ^{1}H NMR (400MHz, $CDCl_3$,): δ=0.88-0.91(t, 3H), 1.29-1.49(m, 6H), 1.56-1.64(m, 2H), 3.05-3.08(t, 2H), 3.81(s, 1H), 6.53-6.55(d, 2H), 7.10-7.12(d, 2H); ^{13}C NMR (100MHz, $CDCl_3$,): 146.7, 129.1, 122.0, 114.0, 44.4, 31.6, 29.3, 26.8, 22.6, 14.0; MS (E.I., 70 eV) m/z (rel. int.): 213(6), 212(3), 211(20), 142(33), 141(9), 140(100), 127(3), 111(4), 105(4), 77(3), 75(3).



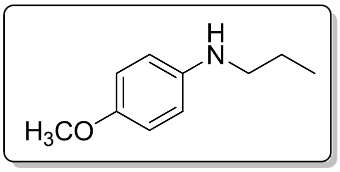
4-bromo-N,N-diethylaniline[8], brown liquid (95%，Entry 5, Table 4) The product was separated by vacuum distillation after remove the catalyst by filtration. ^{1}H NMR (400MHz, $CDCl_3$,): δ=1.12-1.15(t, 6H), 3.28-3.33(q, 4H), 6.52-6.54(d, 2H), 7.24-7.27(d, 2H); ^{13}C NMR (100MHz, $CDCl_3$,): 146.8, 131.9, 113.5, 107.0, 44.5, 12.4; MS (E.I., 70 eV) m/z (rel. int.): 229(32), 228(6), 227(32), 215(10), 214(98), 213(11), 212(100), 186(26), 184(36), 182(10), 157(11), 155(11), 133(11), 118(15), 105(17), 104(10), 76(8).



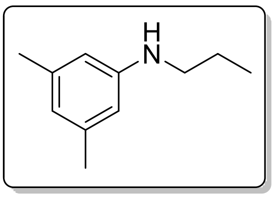
4-bromo-N-propylaniline[9], brown liquid (65%, Entry 6, Table 4). The product was separated by column chromatography (petroleum ether (b.p. 60-90ºC)/EtOAc = 24/1). ^{1}H NMR (400MHz, $CDCl_3$,): δ=0.97-1.01(t, 3H), 1.59-1.66(m, 2H), 3.02-3.06(t, 2H), 6.47-6.49(d, 2H), 7.25-7.26(d, 2H); ^{13}C NMR (100MHz, $CDCl_3$,): 147.3, 131.9, 114.3, 108.7, 45.9, 22.5, 11.6; MS (E.I., 70 eV) m/z (rel. int.): 215(4), 213(4), 186(15), 177(26), 135(11), 134(100), 119(19), 105(8), 91(6), 77(7).



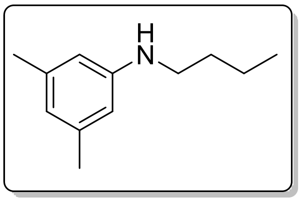
4-methyl-N-propylaniline[10], yellow liquid (60%, Entry 7, Table 4). The product was separated by column chromatography (petroleum ether (b.p. 60-90ºC)/EtOAc = 24/1). ^{1}H NMR (400MHz, $CDCl_3$,): δ=0.97-1.00(t, 3H), 1.60-1.65(m, 2H), 2.23(s, 3H), 3.04-3.07(t, 2H), 6.53-6.55(d, 2H), 6.97-6.99(d, 2H); ^{13}C NMR (100MHz, $CDCl_3$,): 146.2, 129.7, 126.5, 113.1, 46.3, 22.7, 20.4, 11.6; MS (E.I., 70 eV) m/z (rel. int.): 149(29), 121(9), 120(100), 106(3), 91(13), 77(5), 65(5).



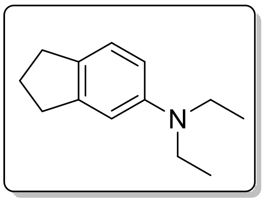
4-methoxy-N-propylaniline[11], brown liquid (70%, Entry 8, Table 4). The product was separated by column chromatography (petroleum ether (b.p. 60-90ºC)/EtOAc = 24/1). ^{1}H NMR (400MHz, $CDCl_3$,): δ=0.97-1.01(t, 3H), 1.60-1.66(m, 2H), 3.02-3.06(t, 2H), 3.74(s, 3H), 6.59-6.61(d, 2H), 6.77-6.79(d, 2H); ^{13}C NMR (100MHz, $CDCl_3$,): 152.4, 142.0, 114.9, 114.6, 55.8, 41.3, 22.6, 11.6; MS (E.I., 70 eV) m/z (rel. int.): 165(34), 150(6), 137(9), 136(100), 121(8), 108(12), 92(4), 77(4).



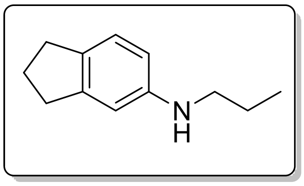
3,5-dimethyl-N-propylaniline[12], colorless liquid (94%, Entry 9, Table 4). The product was separated by column chromatography (petroleum ether (b.p. 60-90ºC)/EtOAc = 35/1). ^{1}H NMR (400MHz, $CDCl_3$,): δ=0.96-1.00(t, 3H), 1.57-1.63(m, 2H), 2.23(s, 6H), 3.04-3.07(t, 2H), 3.49(s, 1H), 6.24(s, 2H), 6.35(s, 1H). ^{13}C NMR (100MHz, $CDCl_3$,): 148.7, 138.9, 119.1, 110.7, 45.9, 22.8, 21.5, 11.7; MS (E.I., 70 eV) m/z (rel. int.): 164(3), 163(26), 135(11), 134(100), 119(2), 105(6), 91(6), 77(8).



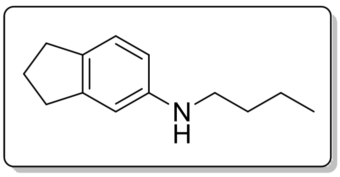
N-butyl-3,5-dimethylaniline[13], colorless liquid (91%, Entry 10, Table 4). The product was separated by column chromatography (petroleum ether (b.p. 60-90ºC)/EtOAc = 35/1). ^{1}H NMR (400MHz, $CDCl_3$,): δ=0.93-0.97(t, 3H), 1.39-1.56(m, 4H), 2.23(s, 6H), 3.06-3.09(t, 2H), 3.46(s, 1H), 6.24(s, 2H), 6.35(s, 1H). ^{13}C NMR (100MHz, $CDCl_3$,): 148.7, 138.9, 119.2, 110.7, 43.8, 31.8, 21.5, 20.4, 13.9; MS (E.I., 70 eV) m/z (rel. int.): 178(3), 177(26), 135(11), 134(100), 105(5), 91(5), 77(6).



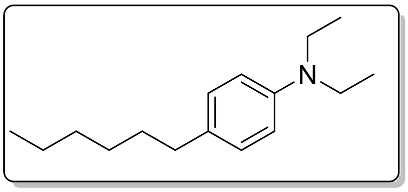
N,N-diethyl-2,3-dihydro-1H-inden-5-amine, colorless liquid (80%, Entry 11, Table 4). The product was separated by column chromatography (petroleum ether (b.p. 60-90ºC)/EtOAc = 24/1). ^{1}H NMR (400MHz, $CDCl_3$,): δ=1.13-1.16(t, 6H), 2.01-2.06(m, 2H), 2.80-2.86(m, 4H), 3.30-3.35(q, 4H), 6.57-6.68(d, 2H), 7.07-7.09(d, 1H); ^{13}C NMR (100MHz, $CDCl_3$,): 145.6, 130.9, 128.8, 124.8, 111.2, 109.1, 33.4, 31.9, 25.7, 12.5; MS (E.I., 70 eV) m/z (rel. int.): 190(4), 189(31), 188(4), 175(14), 174(100), 146(13), 117(11), 116(6), 115(12), 91(5).



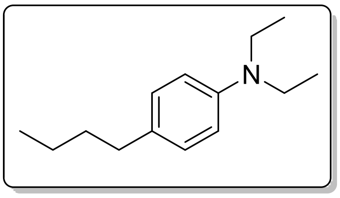
N-propyl-2,3-dihydro-1H-inden-5-amine[14], colorless liquid (78%, Entry 12, Table 4). The product was separated by column chromatography (petroleum ether (b.p. 60-90ºC)/EtOAc = 24/1). ^{1}H NMR (400MHz, $CDCl_3$,): δ=0.97-1.00(t, 3H), 1.58-1.63(m, 2H), 1.99-2.03(m, 2H), 2.77-2.84(m, 4H), 3.04-3.08(t, 2H), 6.41-6.42(d, 1H), 6.53(s, 1H), 7.01-7.02(d, 1H); ^{13}C NMR (100MHz, $CDCl_3$,): 147.3, 145.4, 132.9, 124.7, 111.3, 109.0, 46.5, 33.2, 31.9, 25.7, 22.8, 11.7; MS (E.I., 70 eV) m/z (rel. int.): 175(26), 147(12), 146(100), 117(7), 115(11), 91(6).



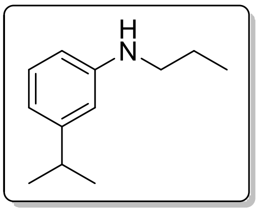
N-butyl-2,3-dihydro-1H-inden-5-amine[15], colorless liquid (87%, Entry 13, Table 4). The product was separated by column chromatography (petroleum ether (b.p. 60-90ºC)/EtOAc = 24/1). ^{1}H NMR (400MHz, $CDCl_3$,): δ=0.93-0.96(t, 3H), 1.37-1.43(m, 2H), 1.95-1.99(m, 2H), 2.00-2.04(m, 2H), 2.77-2.83(m, 4H), 3.05-3.09(t, 2H), 3.39(s, 1H), 6.41-6.43(m, 1H), 6.53(s, 1H), 7.01-7.02(d, 1H); ^{13}C NMR (100MHz, $CDCl_3$,): 147.3, 145.4, 132.9, 124.7, 111.3, 109.0, 44.3, 33.2, 32.0, 31.8, 25.7, 20.4, 13.9; MS (E.I., 70 eV) m/z (rel. int.): 190(3), 189(22), 147(12), 146(100), 144(5), 117(6), 115(10), 91(6).



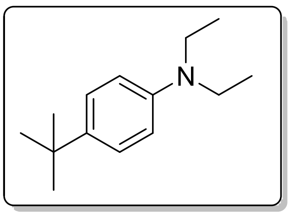
N,N-diethyl-4-hexylaniline, pale yellow liquid (95%, Entry 14, Table 4). The product was separated by column chromatography (petroleum ether (b.p. 60-90ºC)/EtOAc = 30/1). ^{1}H NMR (400MHz, $CDCl_3$,): δ=0.86-0.88(t, 3H), 1.12-1.15(t, 6H), 1.26-1.32(m, 6H), 1.52-1.58(m, 2H), 2.47-2.51(t, 2H), 3.29-3.34(q, 4H), 6.62-6.64(d, 2H), 7.01-7.03(d, 2H); ^{13}C NMR (100MHz, $CDCl_3$,): 146.0, 129.1, 117.9, 112.4, 44.6, 38.8, 35.0, 31.9, 29.2, 22.7, 14.2, 12.7; MS (E.I., 70 eV) m/z (rel. int.): 233(27), 219(15), 218(100), 207(9), 190(5), 163(6), 162(48), 147(6), 132(8), 118(16), 114(33), 86(8), 73(5), 43(8).



4-butyl-N,N-diethylaniline[16], pale yellow liquid (83%, Entry 15, Table 4). The product was separated by column chromatography (petroleum ether (b.p. 60-90ºC)/EtOAc = 30/1). ^{1}H NMR (400MHz, $CDCl_3$,): δ=0.90-0.94(t, 3H), 1.13-1.17(t, 6H), 1.32-1.36(m, 2H), 1.53-1.56(m, 2H), 2.49-2.53(t, 2H), 3.31-3.36(q, 4H), 6.73-6.75(s, 2H), 7.03-7.05(d, 2H). ^{13}C NMR (100MHz, $CDCl_3$,): 145.9, 129.7, 129.1, 112.4, 44.6, 34.6, 34.0, 22.4, 14.0, 12.6; MS (E.I., 70 eV) m/z (rel. int.): 205(32), 191(15), 190(100), 162(45), 132(8), 118(14), 106(4), 91(4), 77(3).

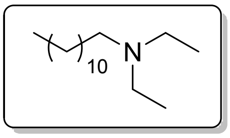


3-isopropyl-N-propylaniline, pale yellow liquid (88%, Entry 16, Table 4). The product was separated by column chromatography (petroleum ether (b.p. 60-90ºC)/EtOAc = 40/1). ^{1}H NMR (400MHz, $CDCl_3$,): δ=0.98-1.02(t, 3H), 1.19-1.24(d, 6H), 1.61-1.67(m, 2H), 2.77-2.83(m, 1H), 3.06-3.10(t, 2H), 6.43-6.45(d, 1H), 6.48(s, 1H), 5.57-6.59(d, 1H), 7.08-7.12(t, 1H). ^{13}C NMR (100MHz, $CDCl_3$,): 150.1, 148.6, 129.2, 115.5, 111.2, 110.1, 45.9, 34.3, 24.0, 22.8, 11.7; MS (E.I., 70 eV) m/z (rel. int.): 178(3), 177(24), 149(12), 148(100), 133(8), 132(8), 106(5), 91(4), 77(4).

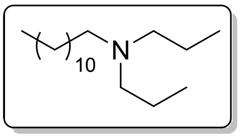


4-(tert-butyl)-N,N-diethylaniline[17], colorless liquid (85%, Entry 17, Table 4). The product was separated by column chromatography (petroleum ether (b.p. 60-90ºC)/EtOAc = 24/1). ^{1}H NMR

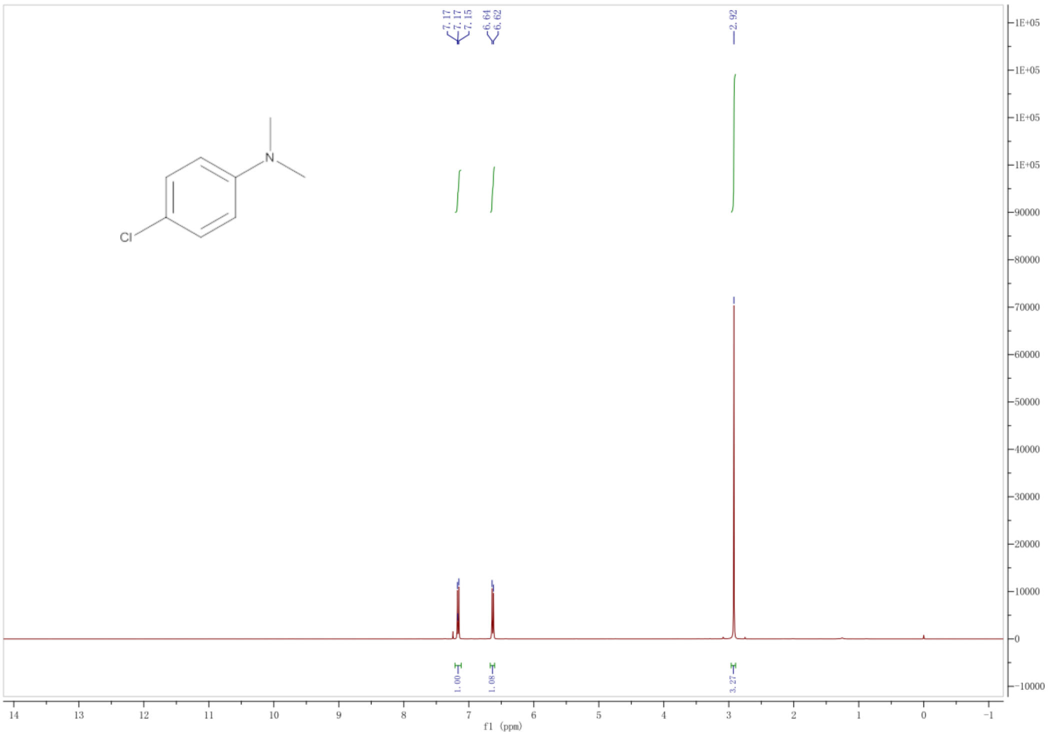
(400MHz, $CDCl_3$,): δ=1.13-1.17(t, 6H), 1.29(s, 9H), 3.30-3.35(q, 4H), 6.66-6.68(d, 2H), 7.23-7.26(d, 2H); ^{13}C NMR (100MHz, $CDCl_3$,): 145.2, 138.3, 126.1, 111.9, 44.5, 33.7, 31.6, 12.6; MS (E.I., 70 eV) m/z (rel. int.): 206(4), 205(23), 191(15), 190(100), 174(3), 160(6), 146(8), 118(4), 91(3).

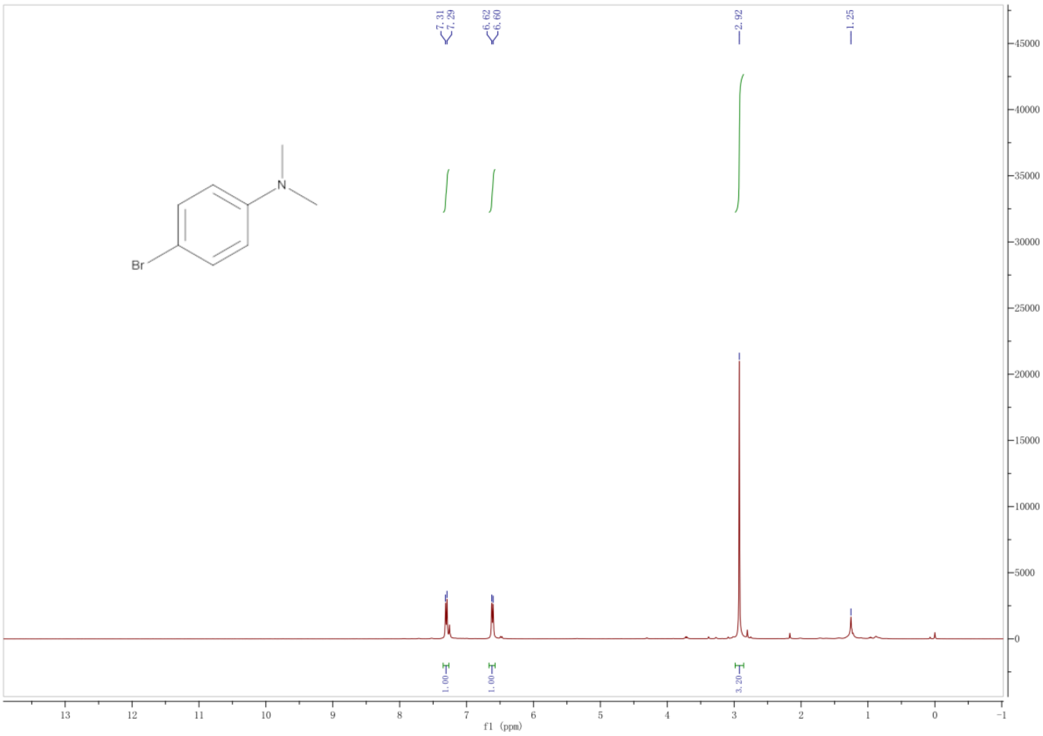


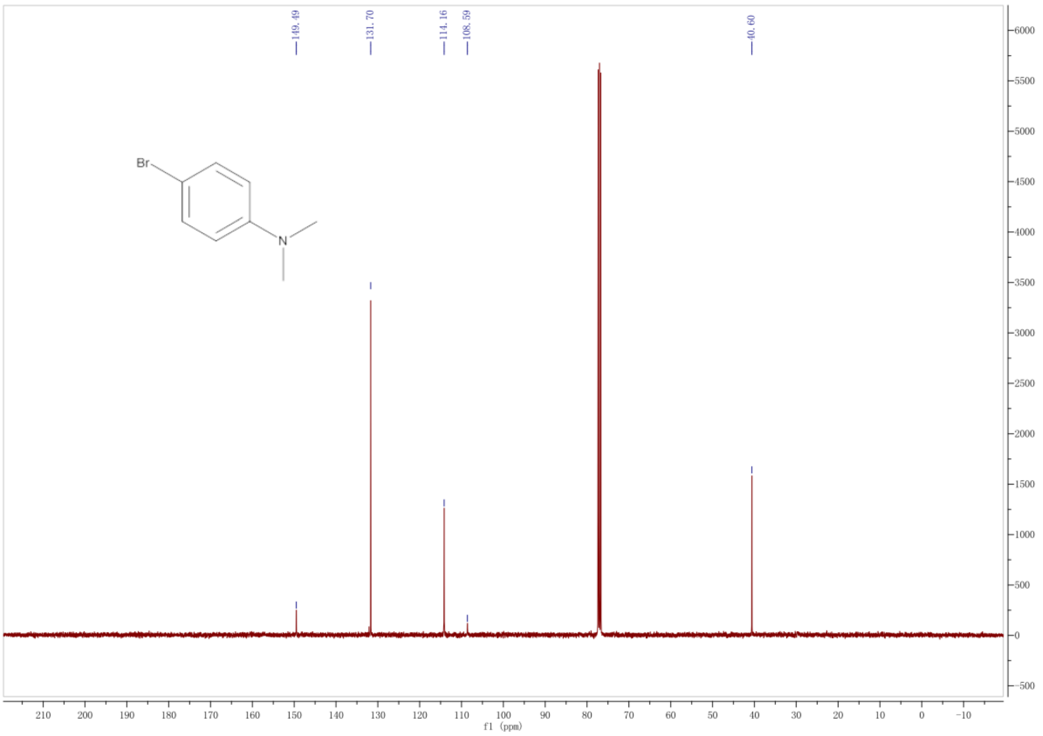
N,N-diethyldodecan-1-amine[18], colorless liquid (90%, Entry 18, Table 4). The product was separated by column chromatography (petroleum ether (b.p. 60-90ºC)/EtOAc = 24/1). ^{1}H NMR (400MHz, $CDCl_3$,): δ=0.86-0.90(t, 3H), 1.17-1.21(t, 6H), 1.30-1.72(m, 22H), 2.63-2.66(m, 2H), 2.74-2.80(m, 2H); ^{13}C NMR (100MHz, $CDCl_3$,): 65.6, 52.1, 46.8, 31.9, 29.6, 29.3, 27.3, 22.7, 19.2, 14.1; MS (E.I., 70 eV) m/z (rel. int.): 241(3), 240(1), 226(5), 212(0.5), 198(0.1), 184(0.1), 170(0.1), 156(0.2), 142(0.3), 128(0.2), 114(0.04), 100(0.2), 86(100), 72(4).

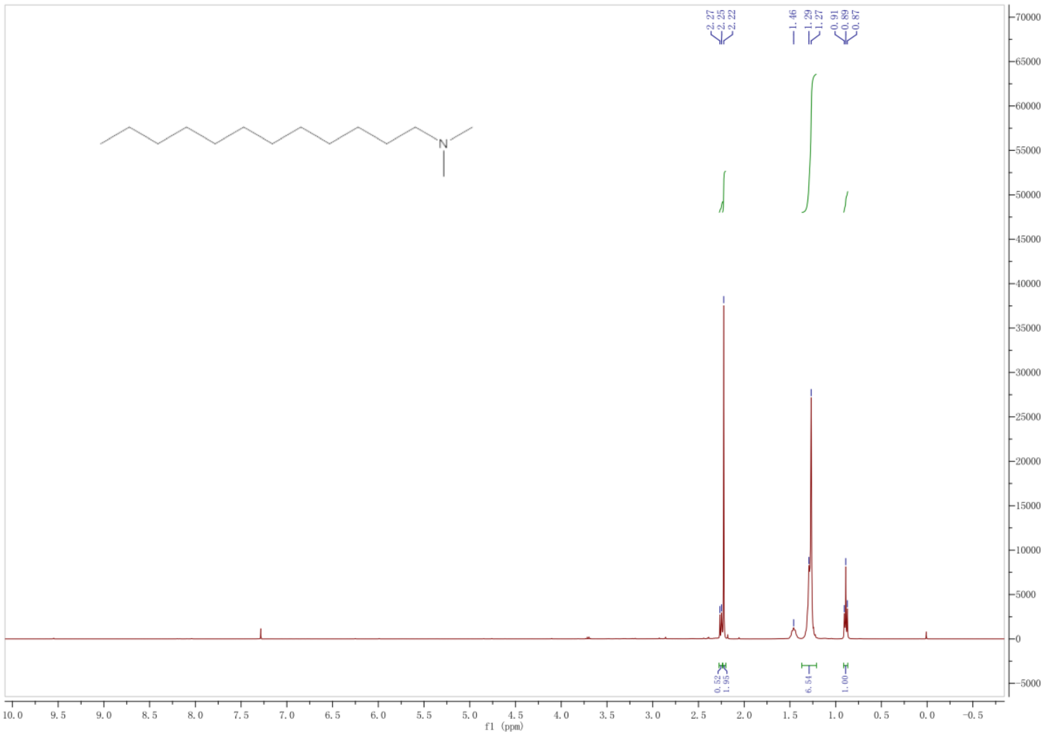


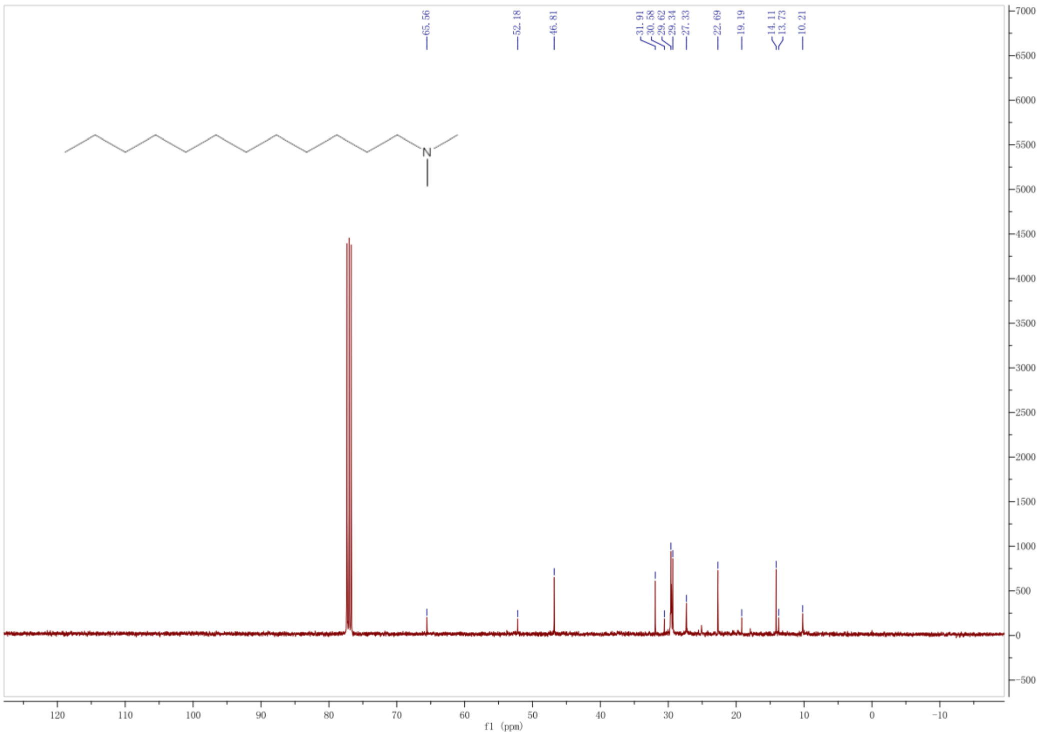
N,N-dipropyldodecan-1-amine[19], colorless liquid (81%, Entry 19, Table 4). The product was separated by column chromatography (petroleum ether (b.p. 60-90ºC)/EtOAc = 24/1). ^{1}H NMR (400MHz, $CDCl_3$,): δ= 0.85-0.90(m, 9H), 1.26-1.30(m, 20H), 1.32-1.40(m, 6H), 2.36-2.41(m, 4H); ^{13}C NMR (100MHz, $CDCl_3$,): 56.3, 54.3, 31.9, 29.6, 29.4, 27.7, 27.0, 22.7, 20.2, 14.1, 12.0; MS (E.I., 70 eV) m/z (rel. int.): 269(4), 268(3), 254(1), 240(94), 226(1), 212(0.4), 198(0.4), 184(0.2), 170(0.3), 168(2), 154(1), 140(2), 126(1), 115(9), 114(100), 86(25), 72(7), 43(12).

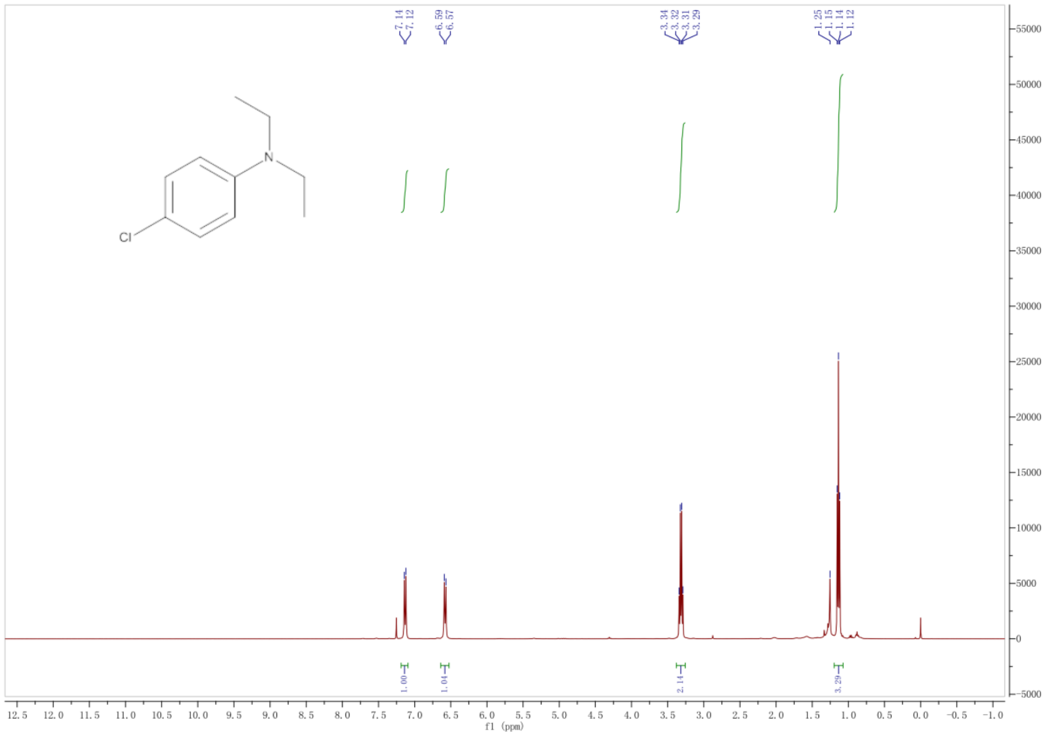


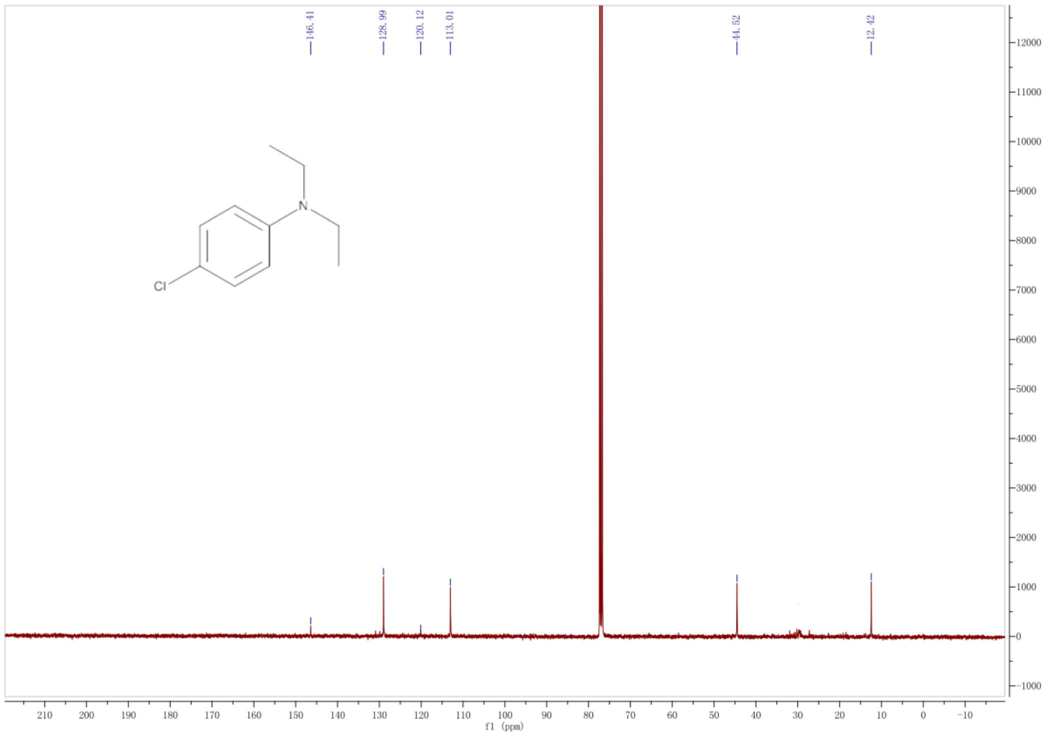

7.31
7.29
6.62
6.60
2.92
1.25
Br
N
1.00
1.00
3.20
f1 (ppm)

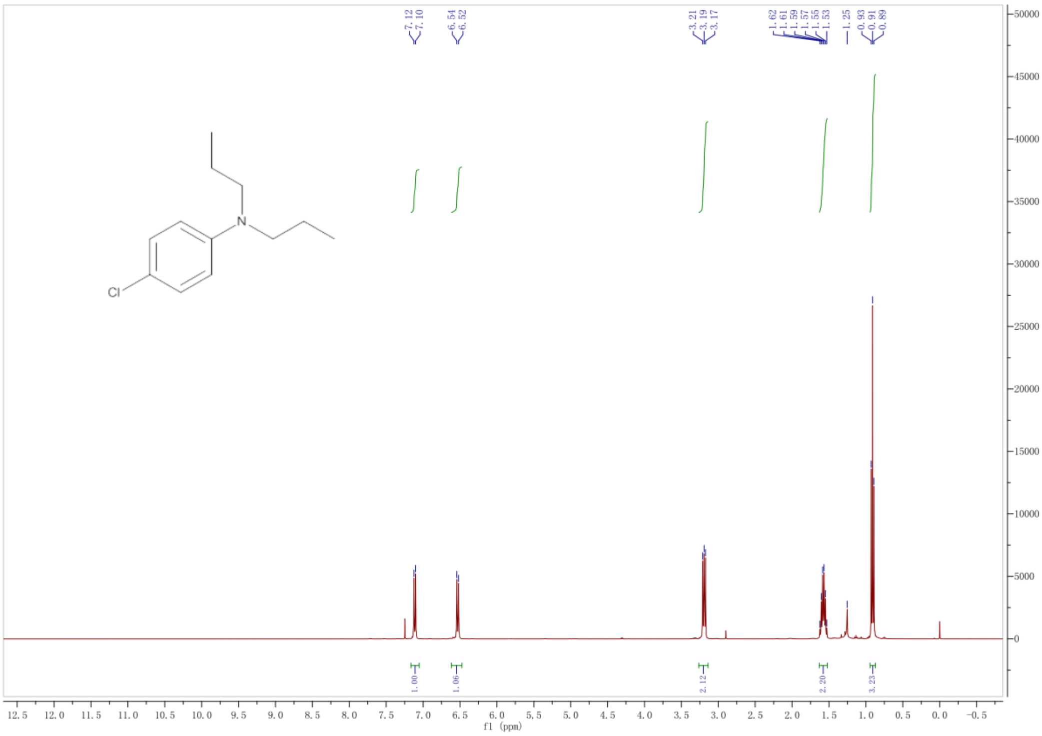

149.49
131.70
114.16
108.59
40.60
Br
N
f1 (ppm)

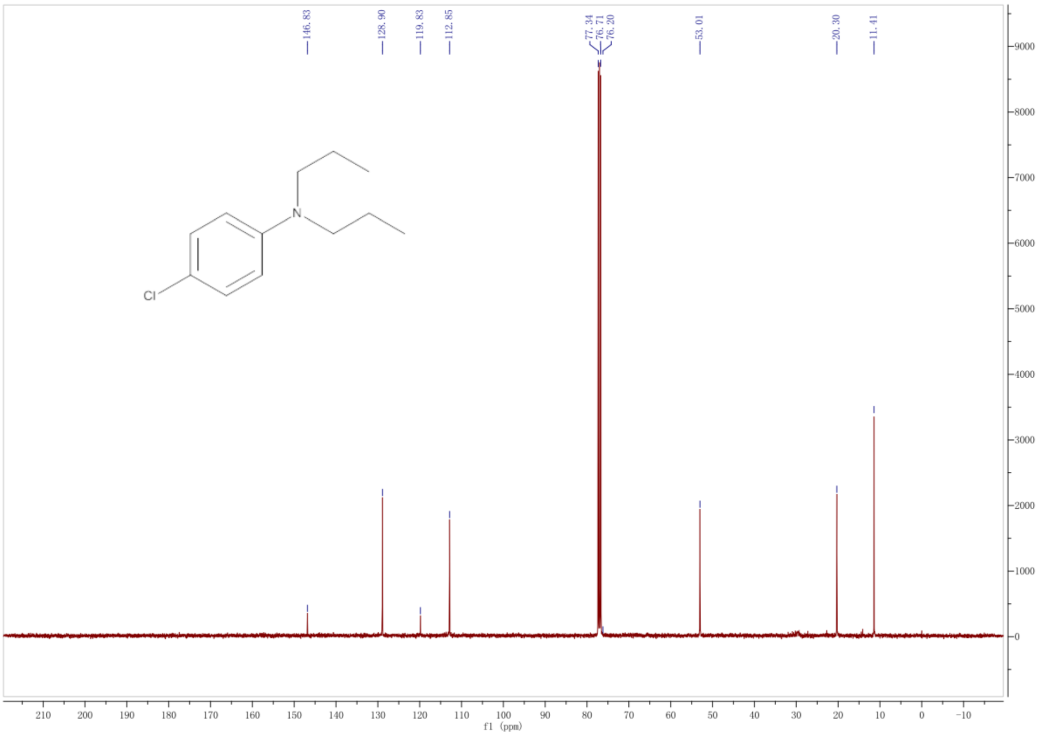


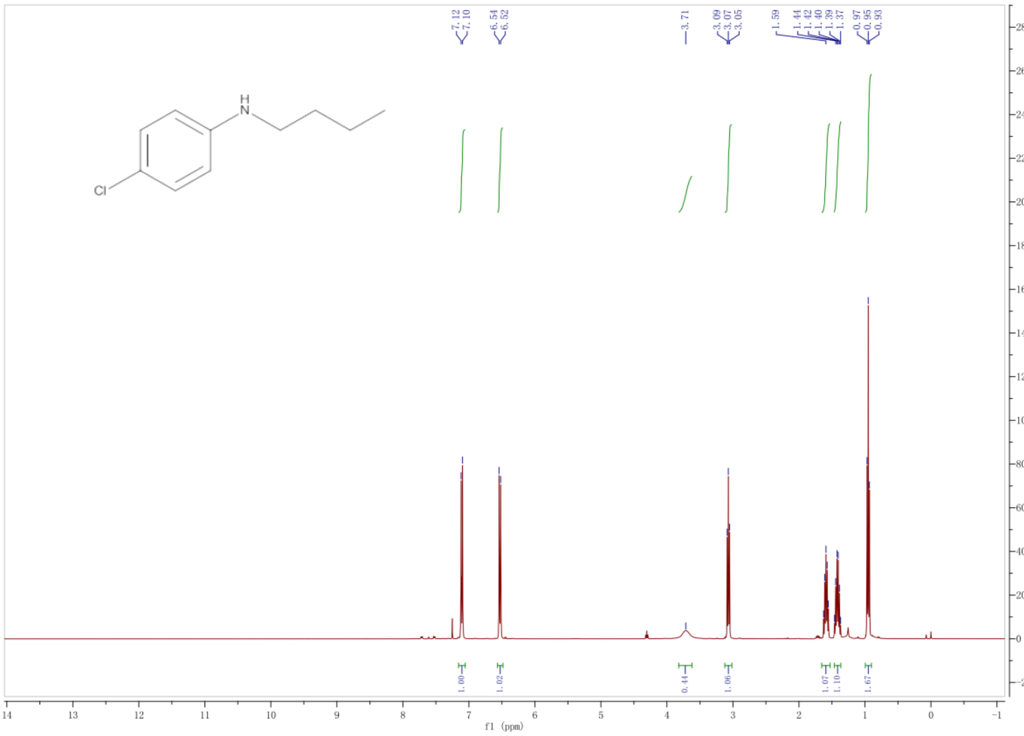


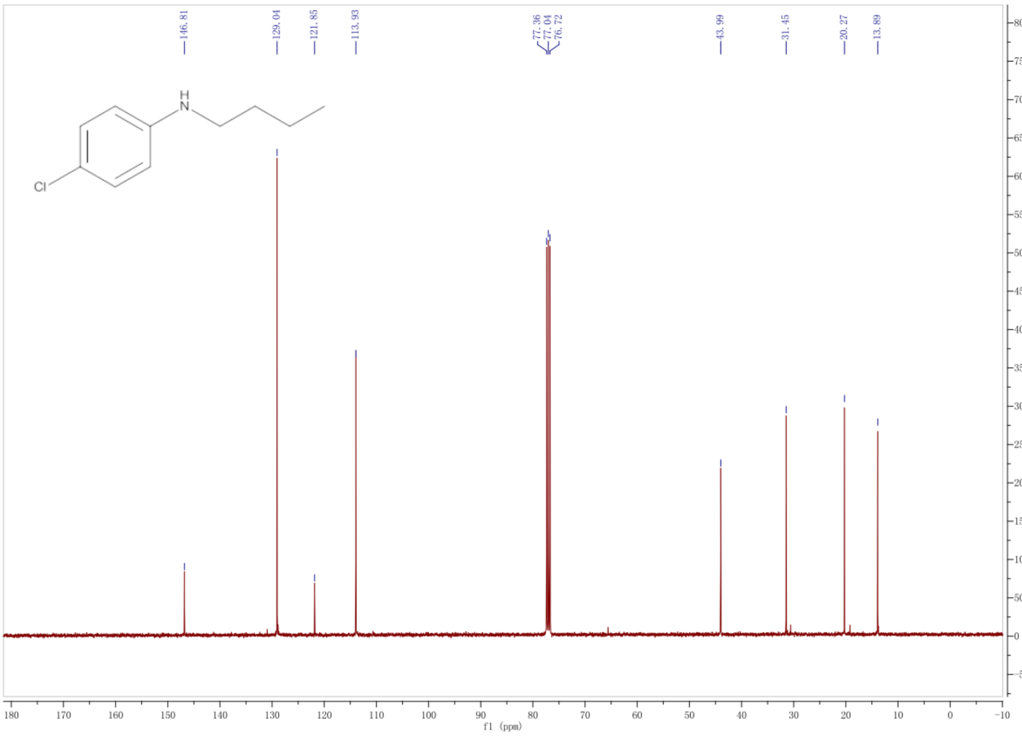

7.14
7.12
6.59
6.57
3.34
3.32
3.31
3.29
1.25
1.15
1.14
1.12
Cl
N
1.00
1.04
2.14
3.29
f1 (ppm)

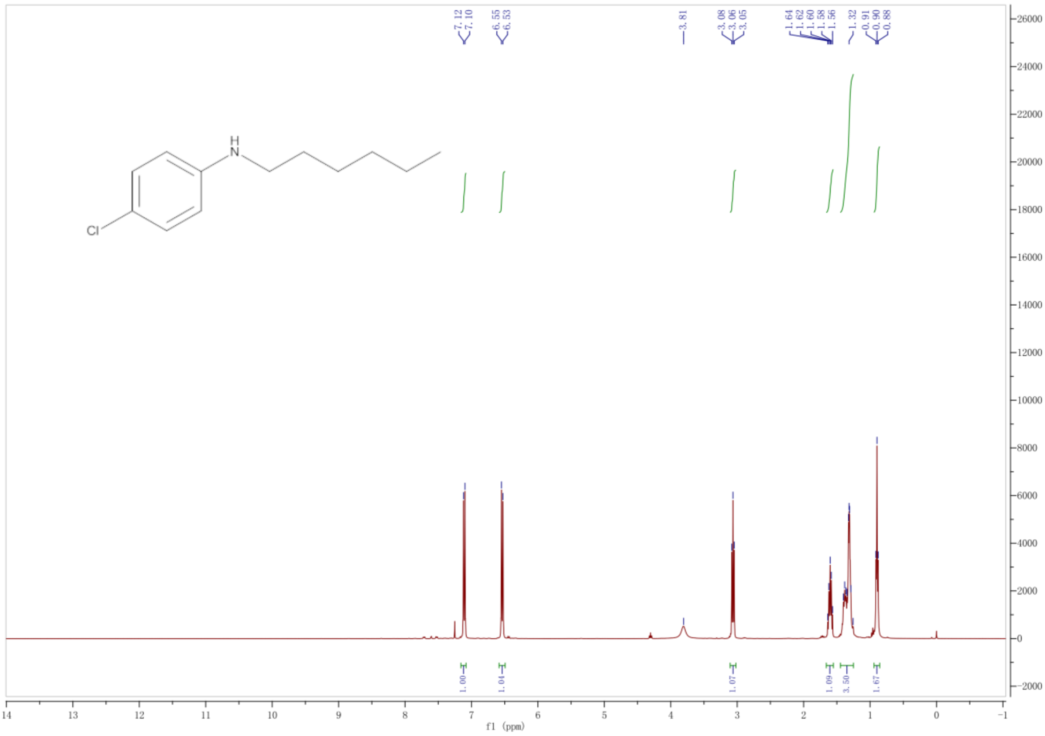

146.41
128.99
120.12
113.01
44.52
12.42
Cl
N
f1 (ppm)

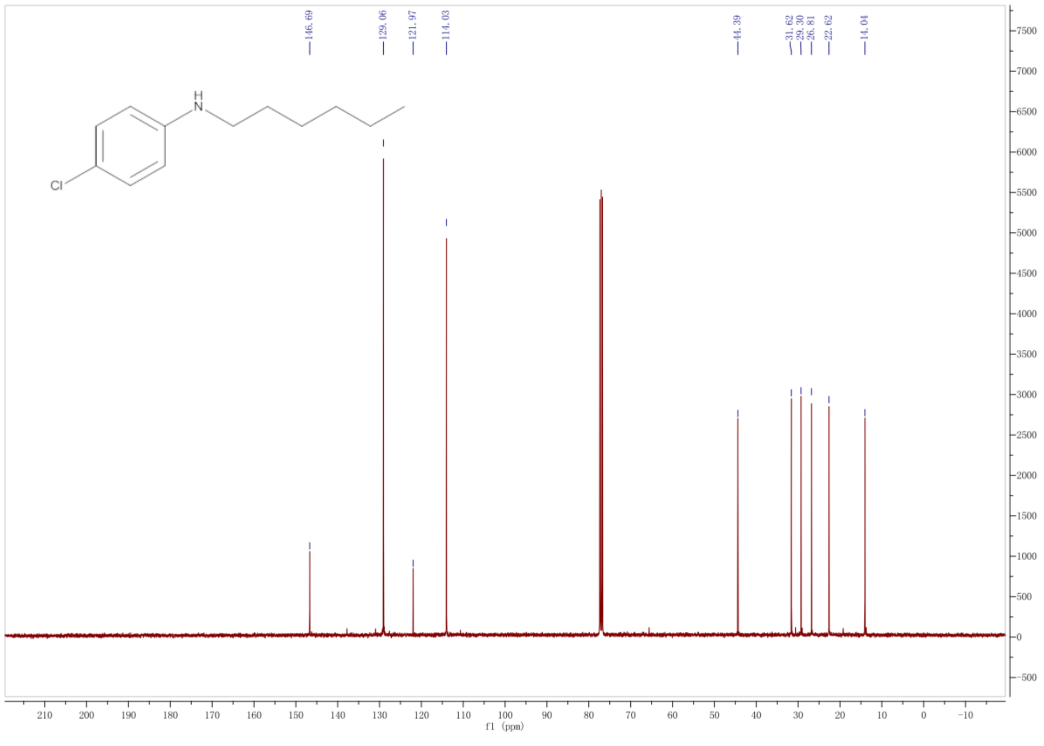

7.12
7.10
6.54
6.52
3.21
3.19
3.17
1.62
1.61
1.59
1.57
1.55
1.53
1.25
0.93
0.91
0.89
Cl
N
1.00
1.06
2.12
2.20
3.23
f1 (ppm)

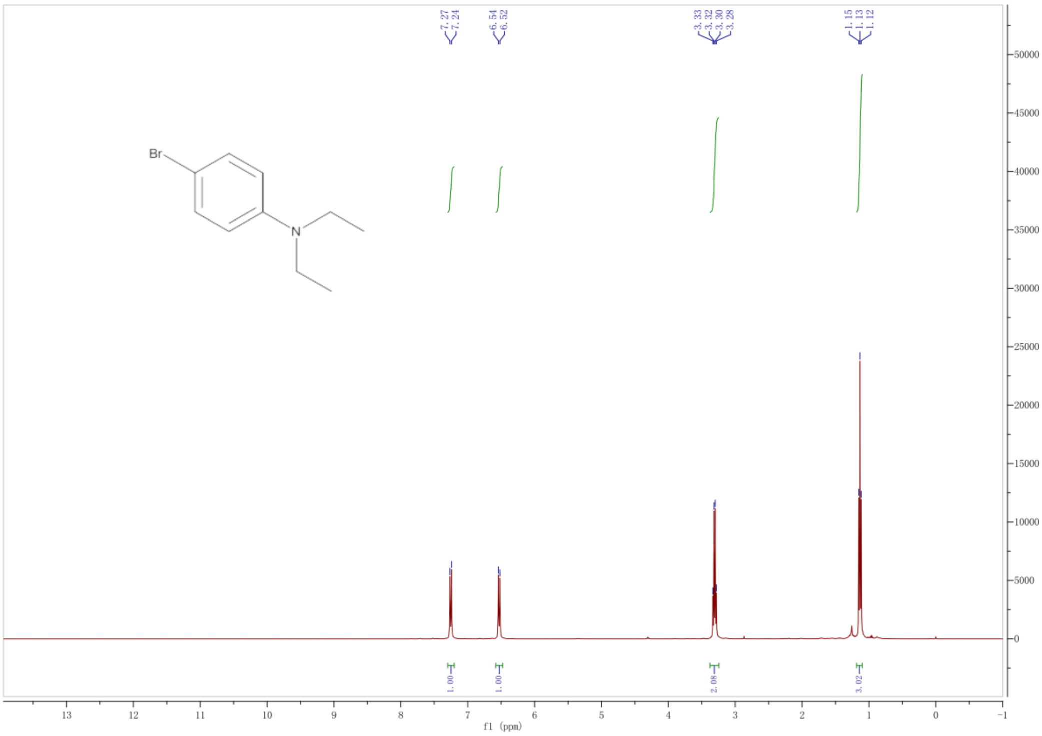

146.83
128.90
119.83
112.85
77.34
76.71
76.20
53.01
20.30
11.41
Cl
N
f1 (ppm)

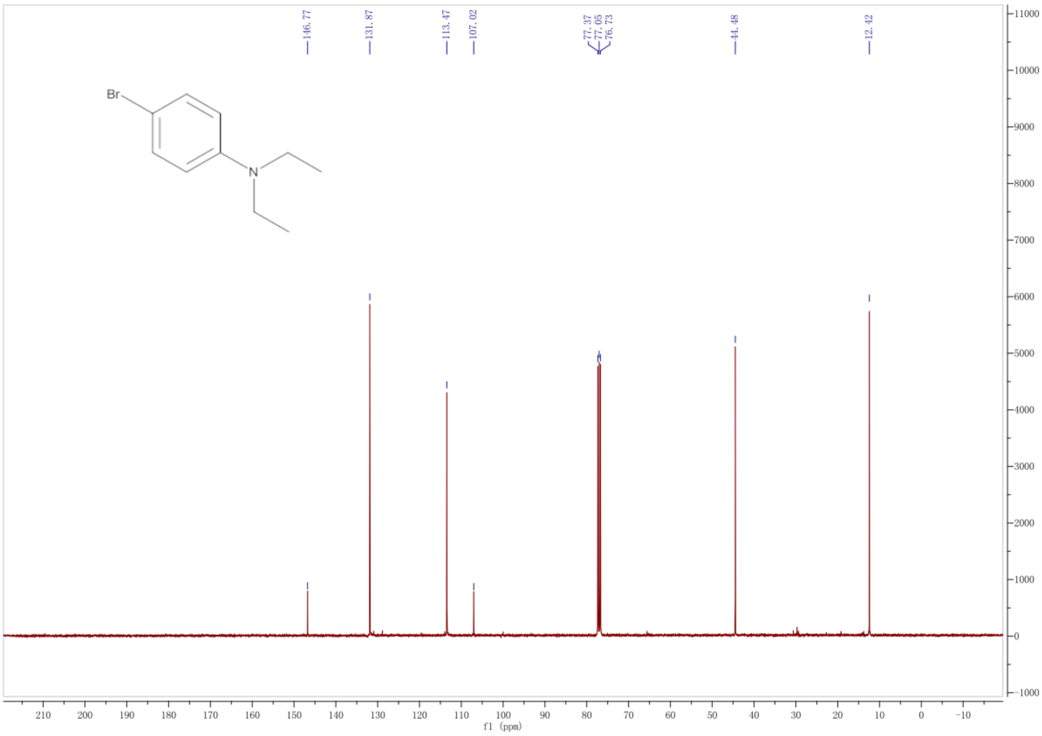

7.12
7.10
6.54
6.52
3.71
3.09
3.07
3.05
1.59
1.44
1.42
1.40
1.39
1.37
0.97
0.95
0.93
H
N
Cl
1.00
1.02
0.44
1.06
1.07
1.10
1.67
f1 (ppm)

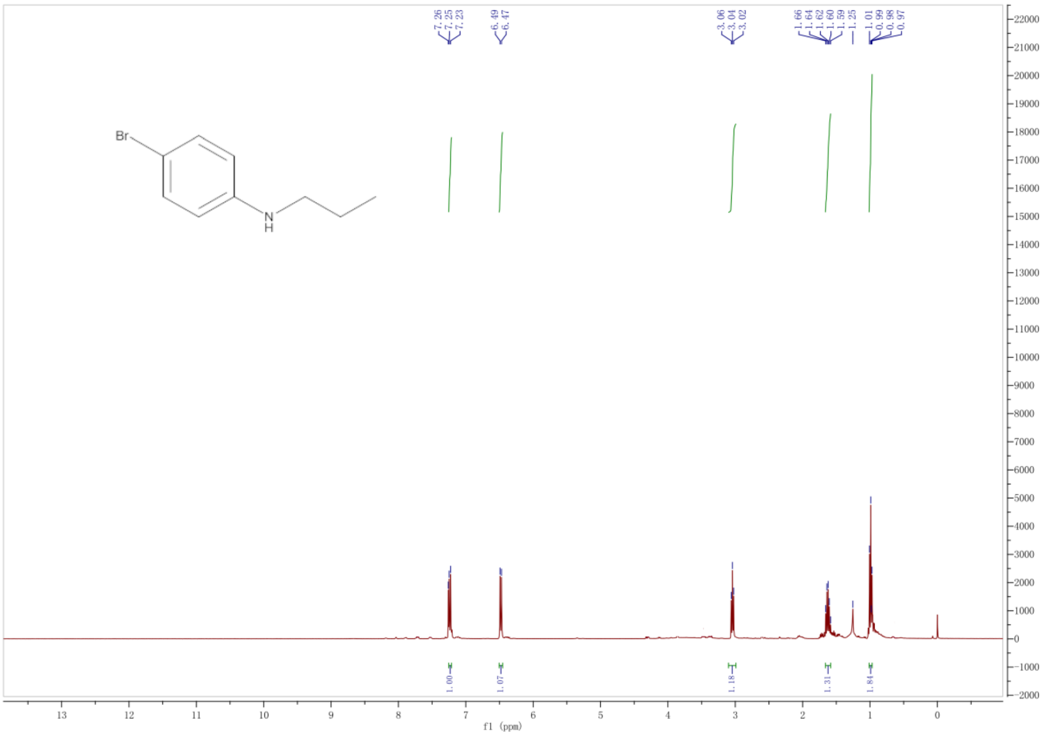

146.81
129.04
121.85
113.93
77.36
77.04
76.72
43.99
31.45
20.27
13.89
H
N
Cl
f1 (ppm)

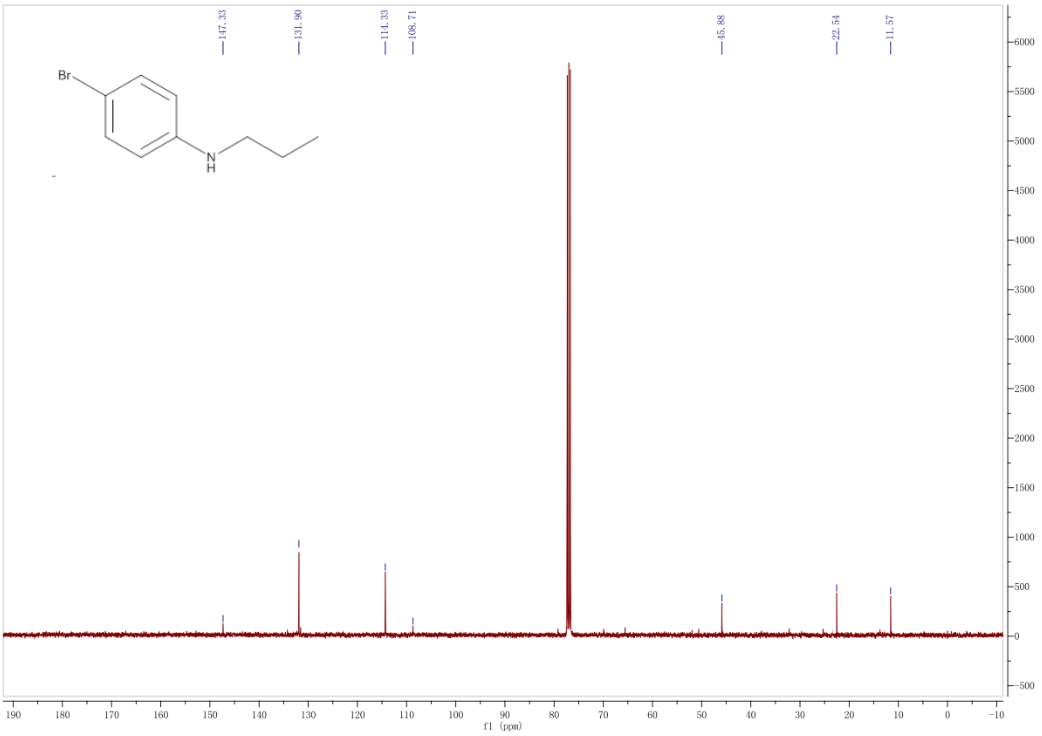


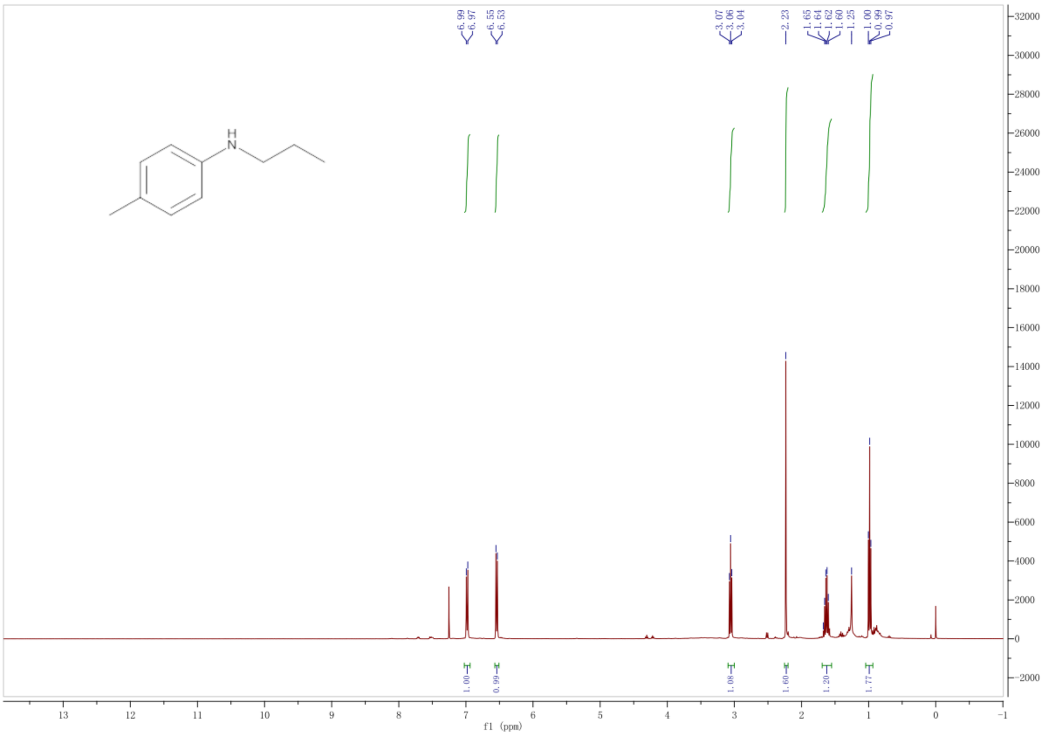


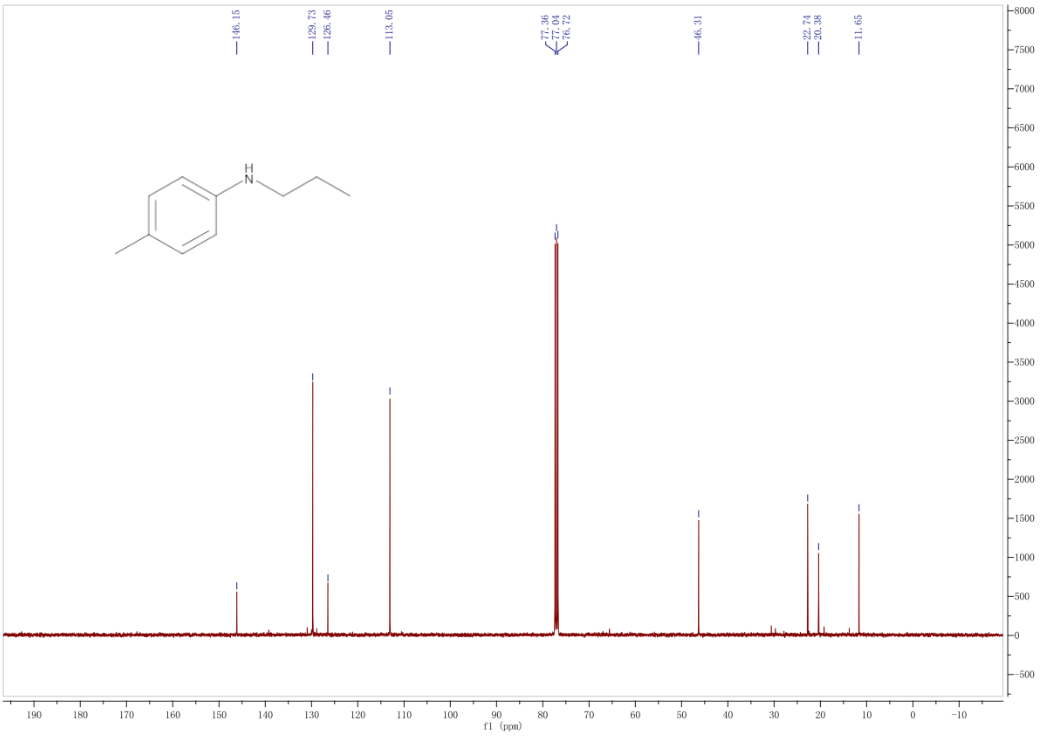

7.27
7.24
6.54
6.52
3.33
3.32
3.30
3.28
1.15
1.13
1.12
Br
N
1.00
1.00
2.08
3.02
f1 (ppm)

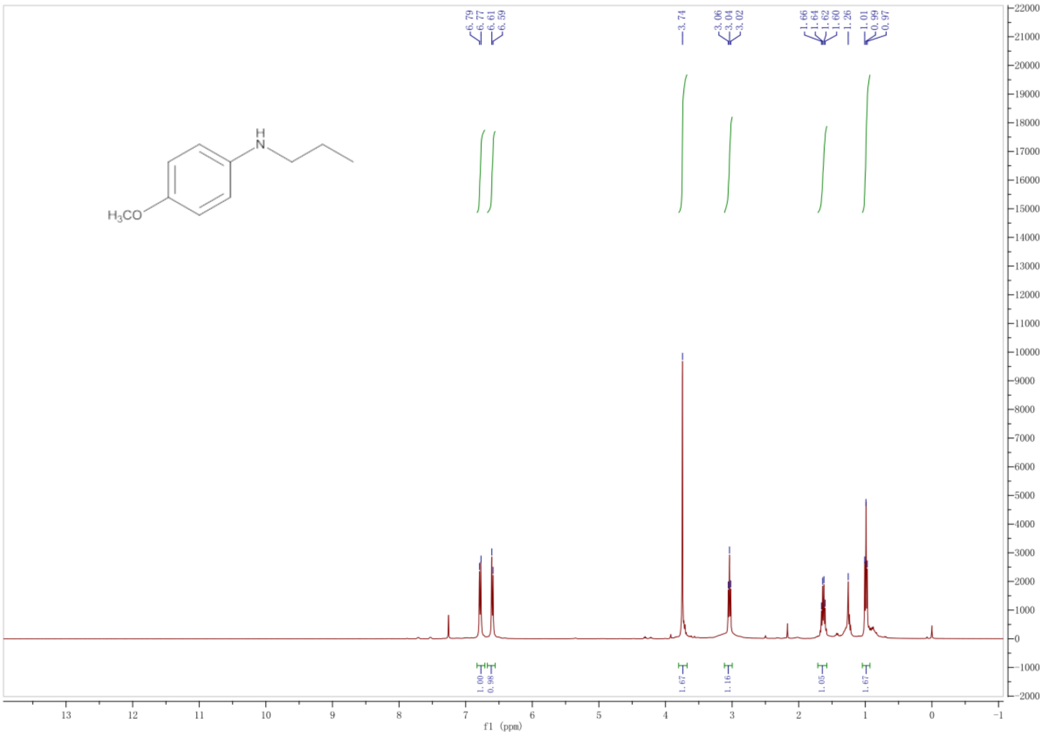

146.77
131.87
113.47
107.02
77.37
77.05
76.73
44.48
12.42
Br
N
f1 (ppm)

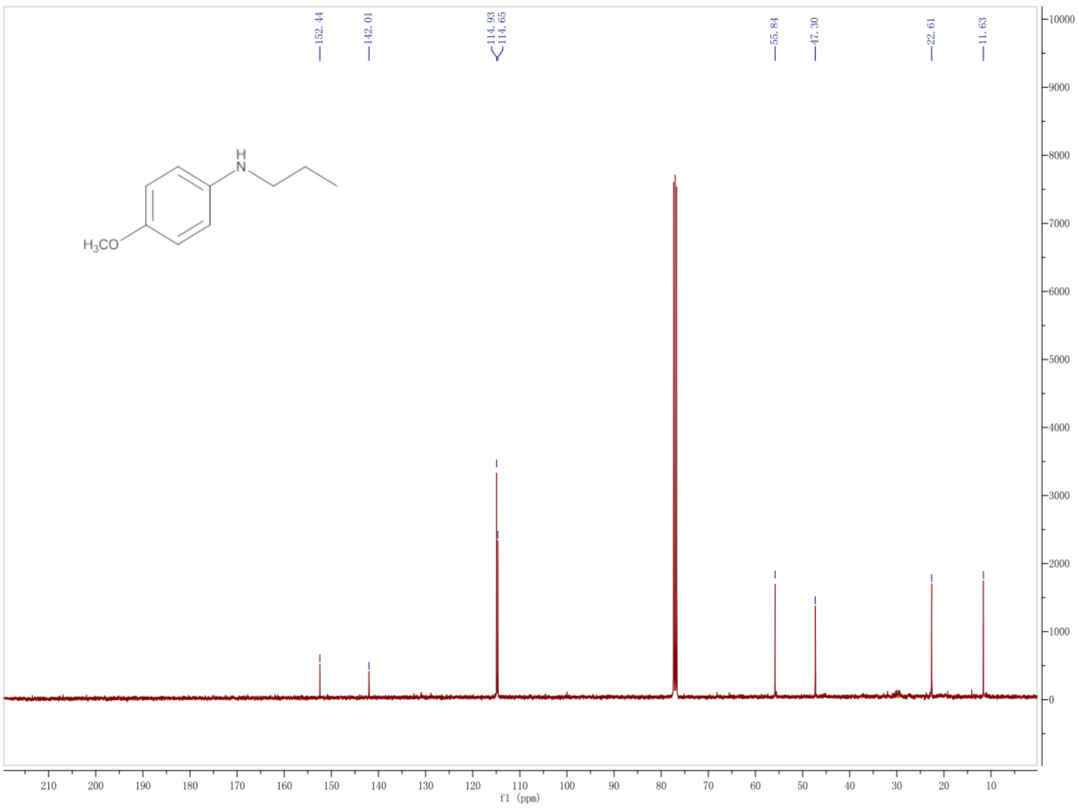


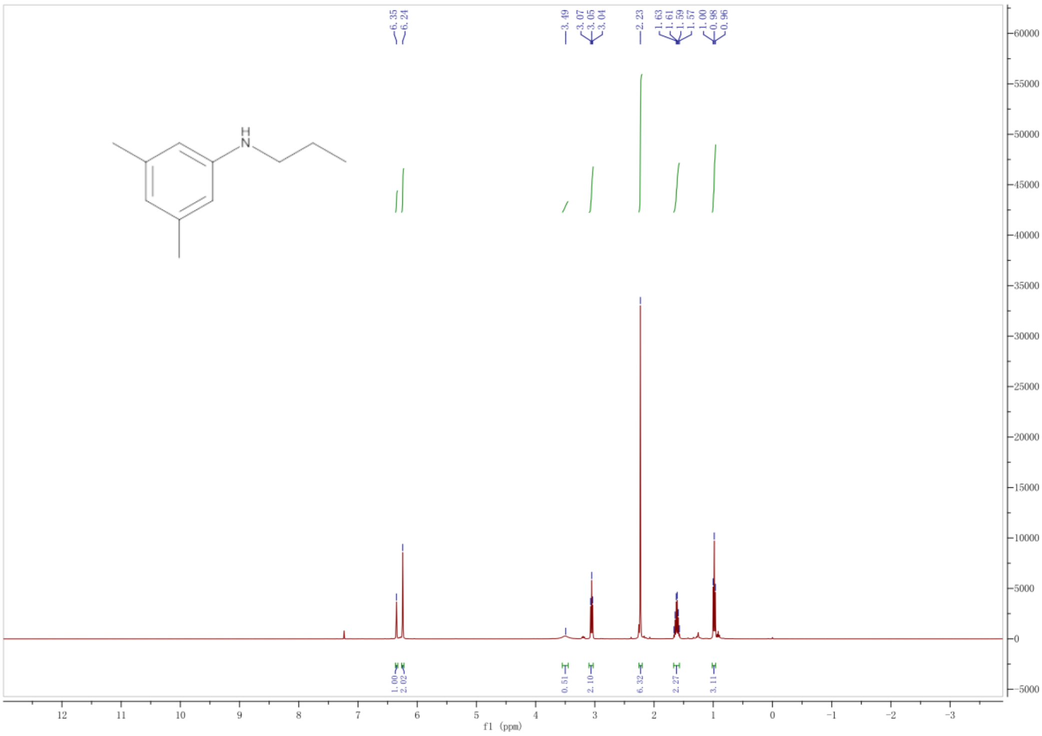


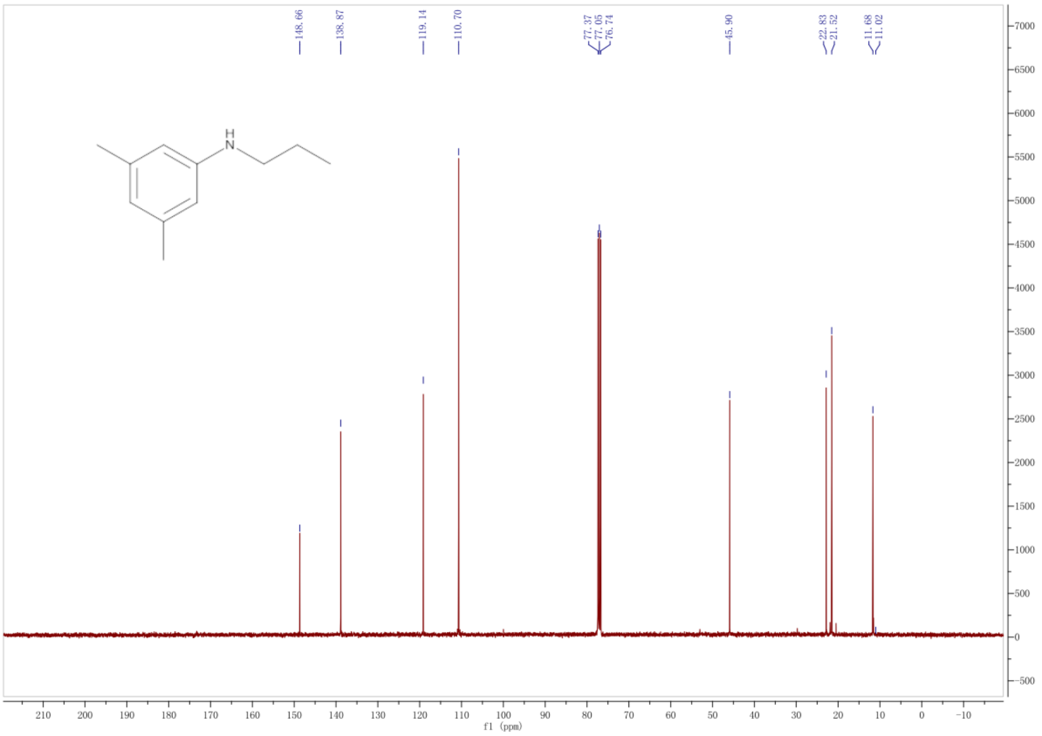

6.99
6.97
6.55
6.53
3.07
3.06
3.04
2.23
1.65
1.64
1.62
1.60
1.25
1.00
0.99
0.97
1.00
0.99
1.08
1.60
1.20
1.77
f1 (ppm)

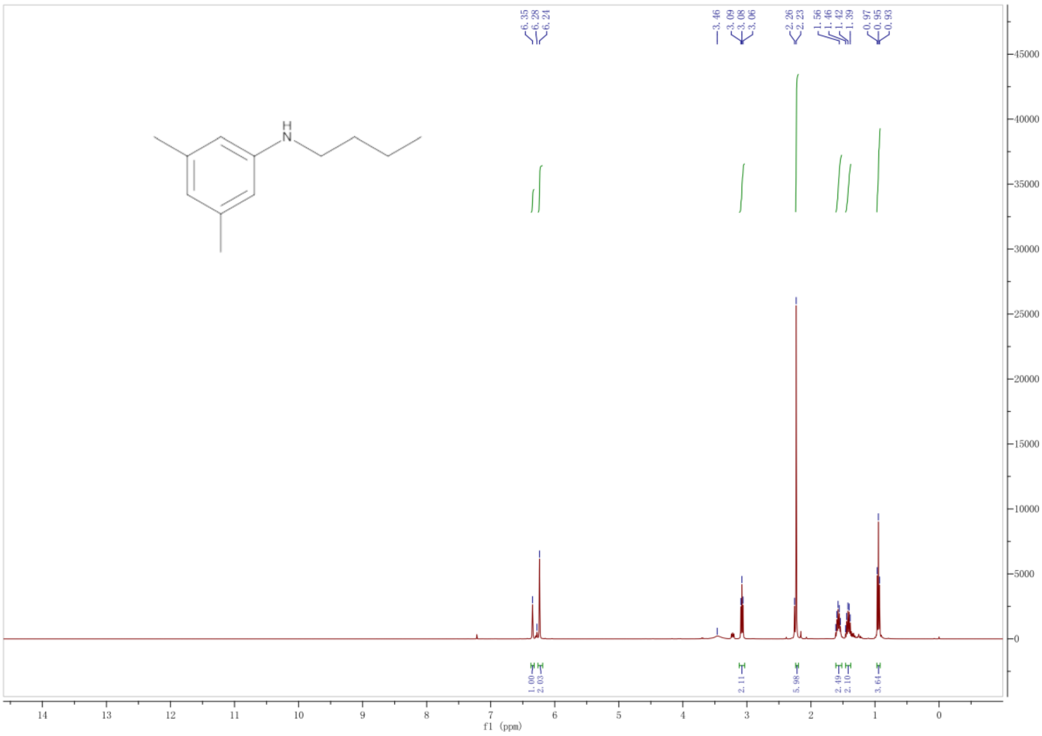

146.15
129.73
126.46
113.05
77.36
77.04
76.72
46.31
22.74
20.38
11.65
f1 (ppm)

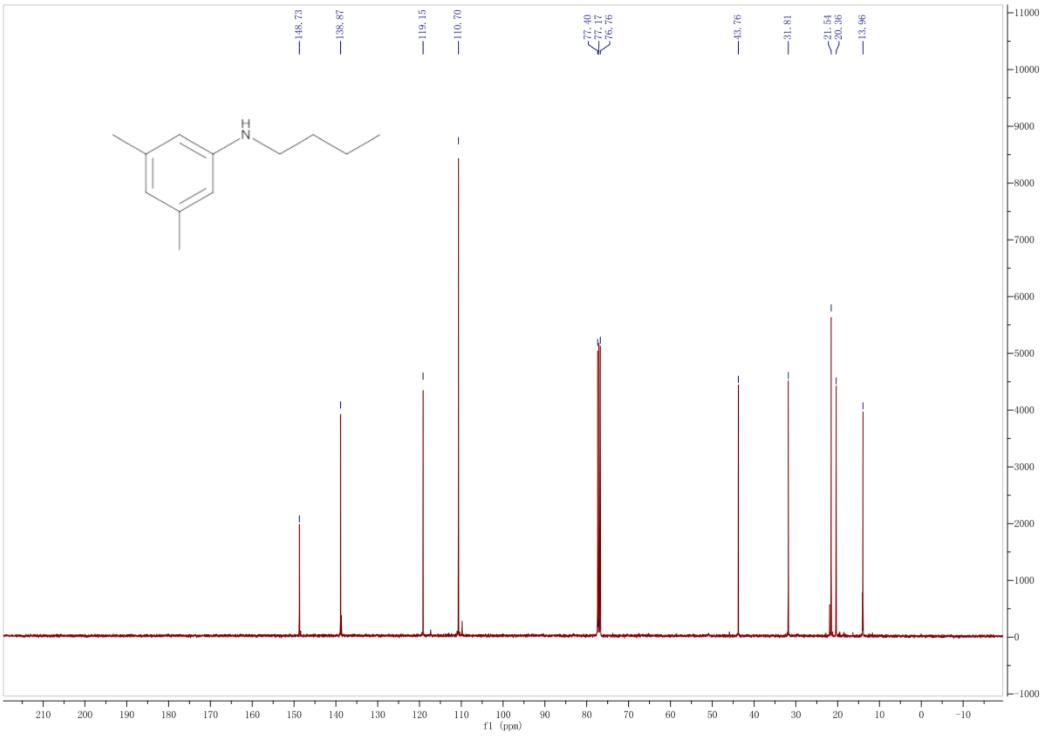


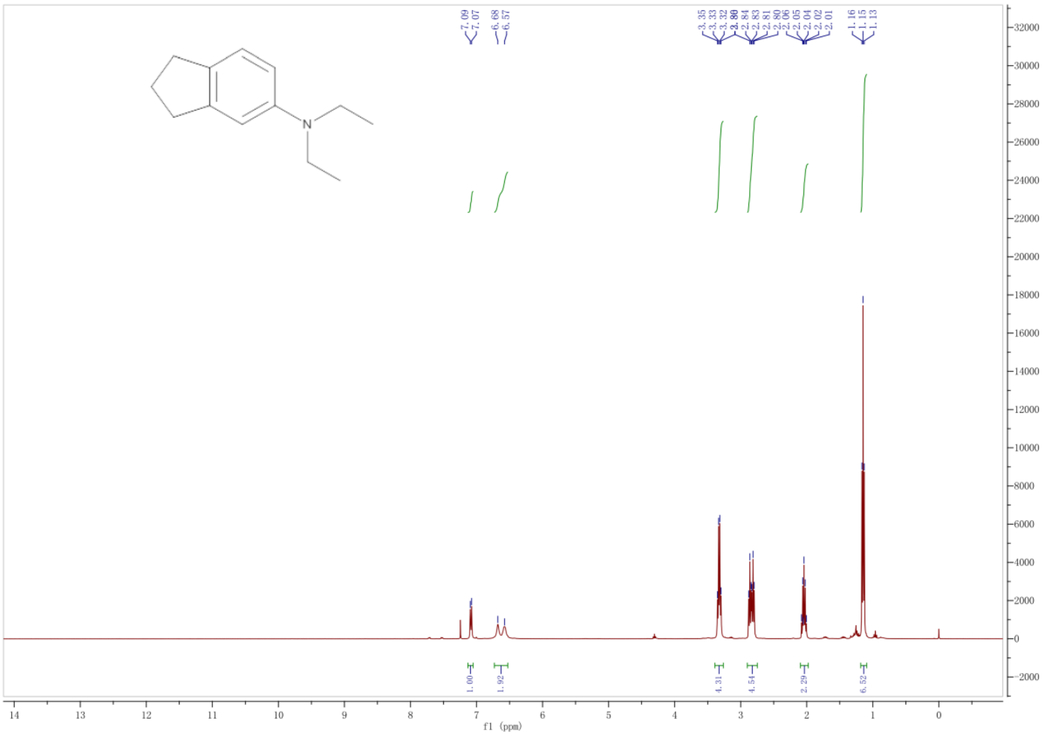


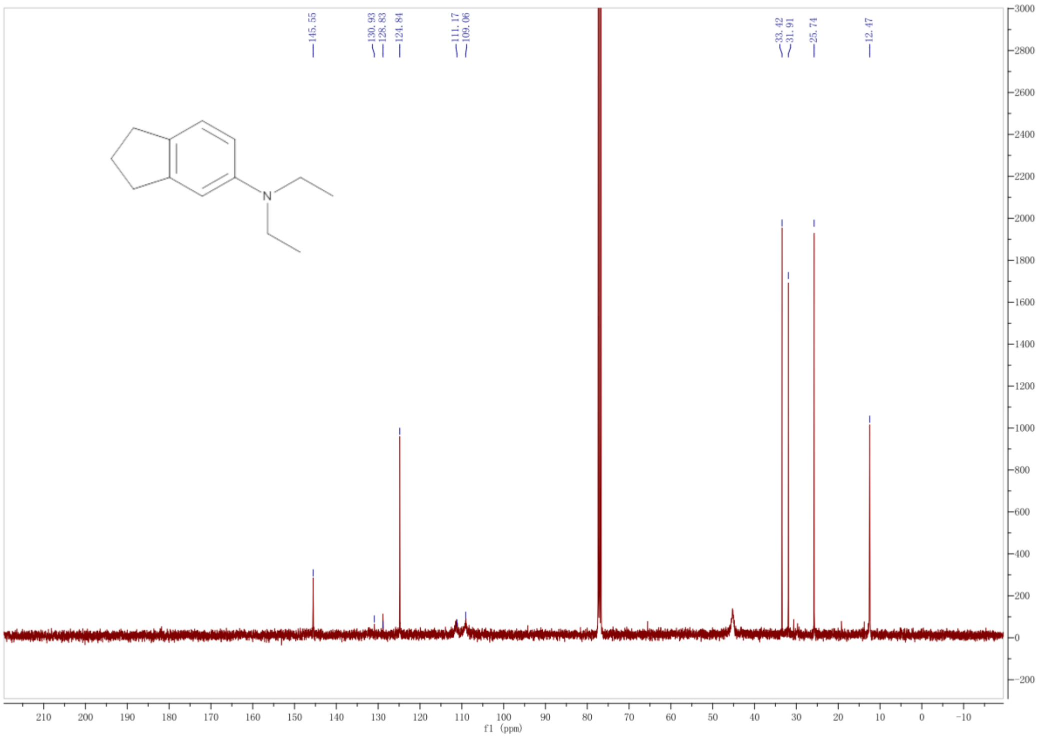

6.35
6.24
3.49
3.07
3.05
3.04
2.23
1.63
1.61
1.59
1.57
1.00
0.98
0.96
1.00
2.02
0.51
2.10
6.32
2.27
3.11
f1 (ppm)

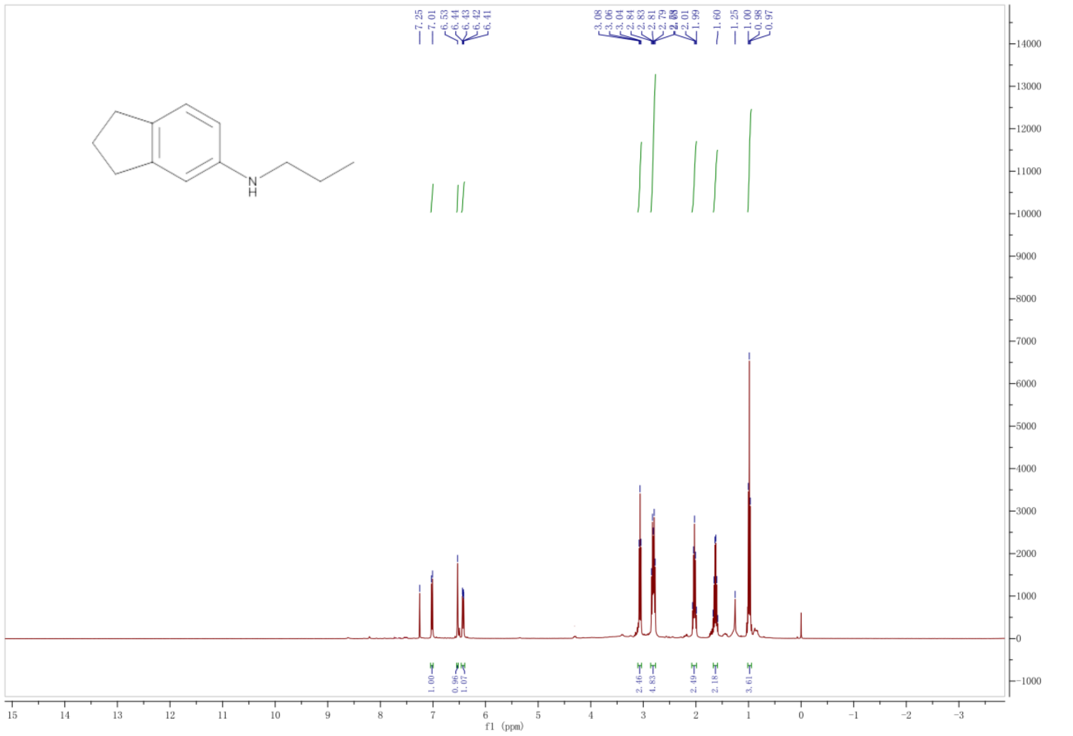

148.66
138.87
119.14
110.70
77.37
77.05
76.74
45.90
22.83
21.52
11.68
11.02
f1 (ppm)

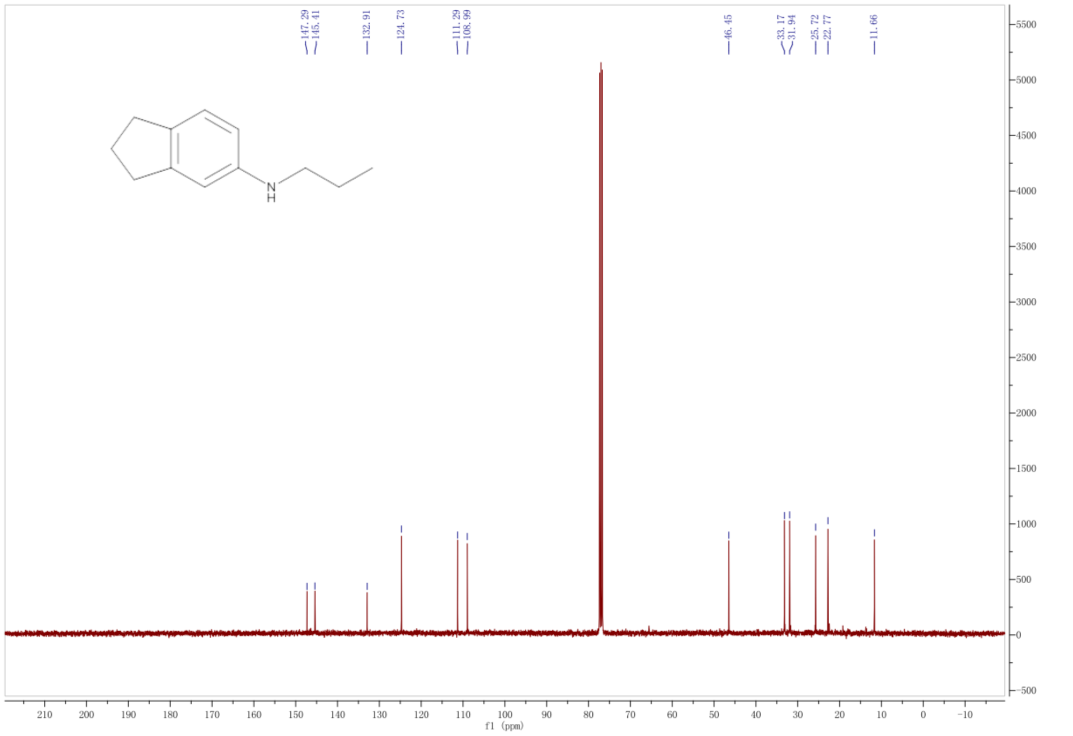


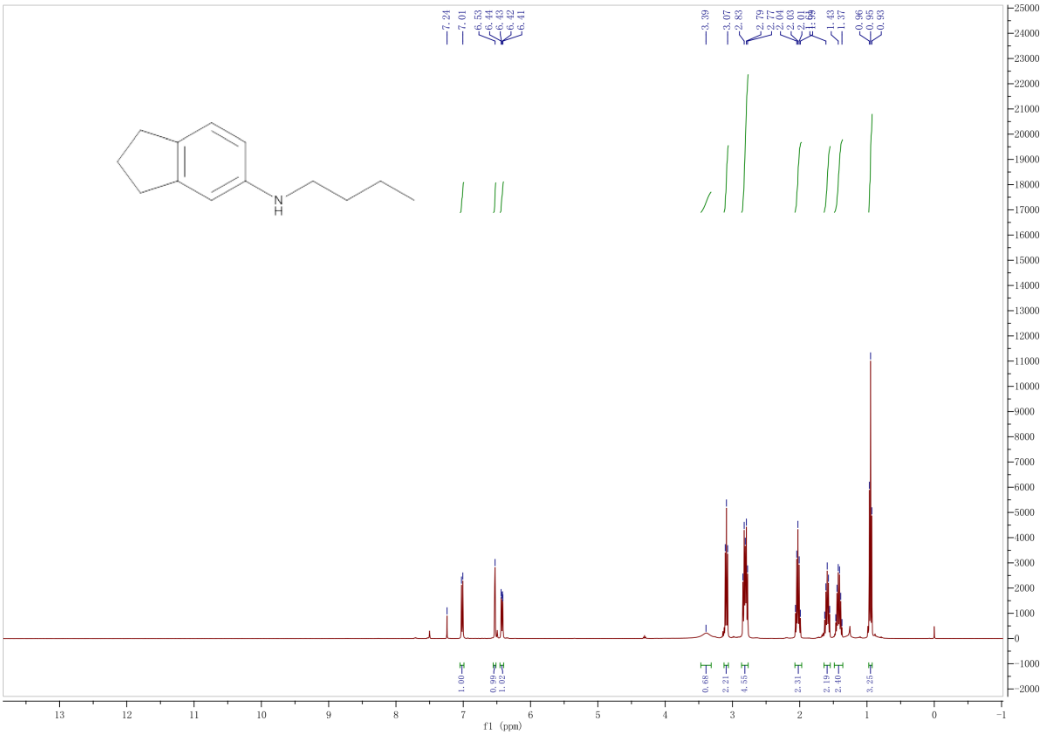


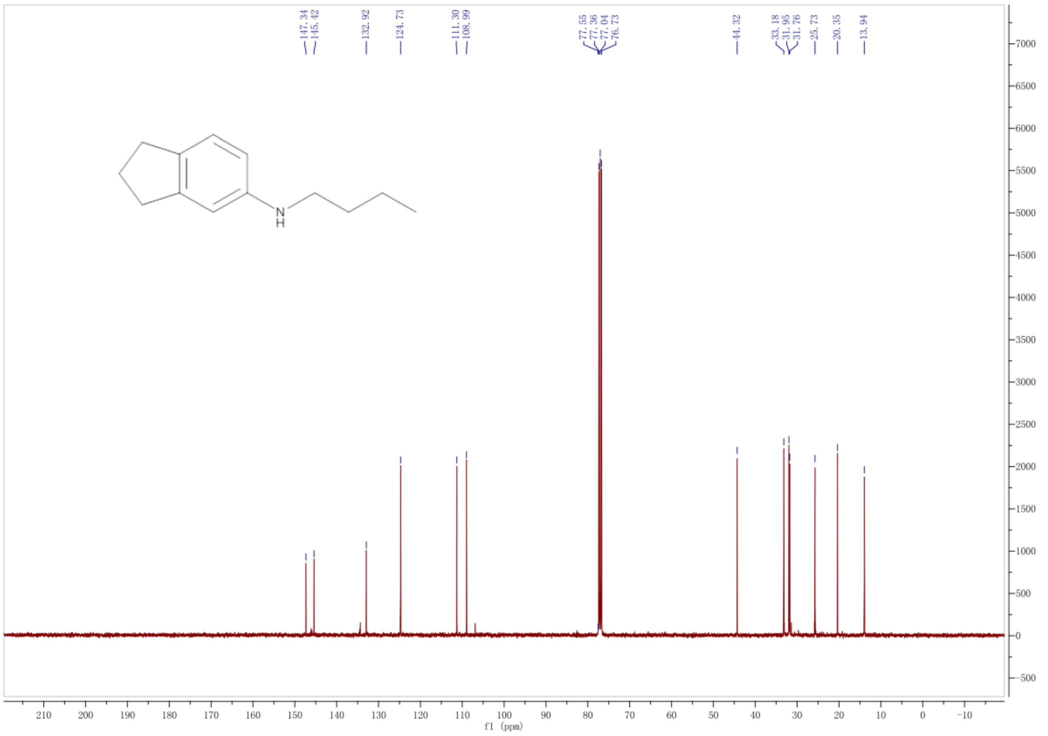


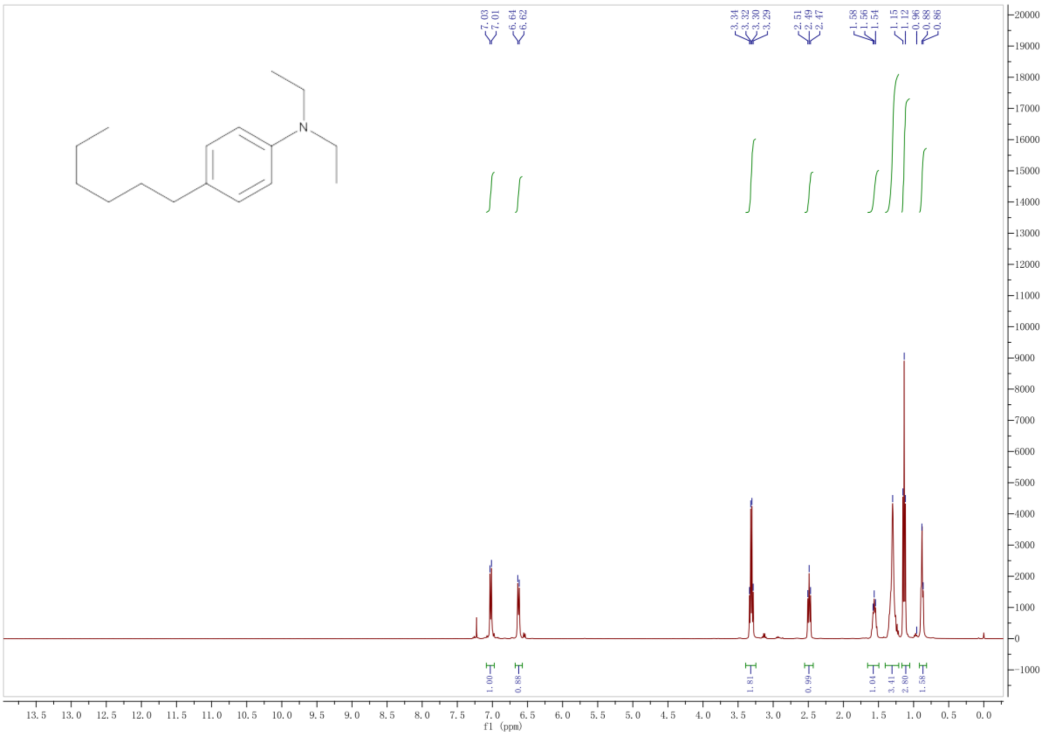


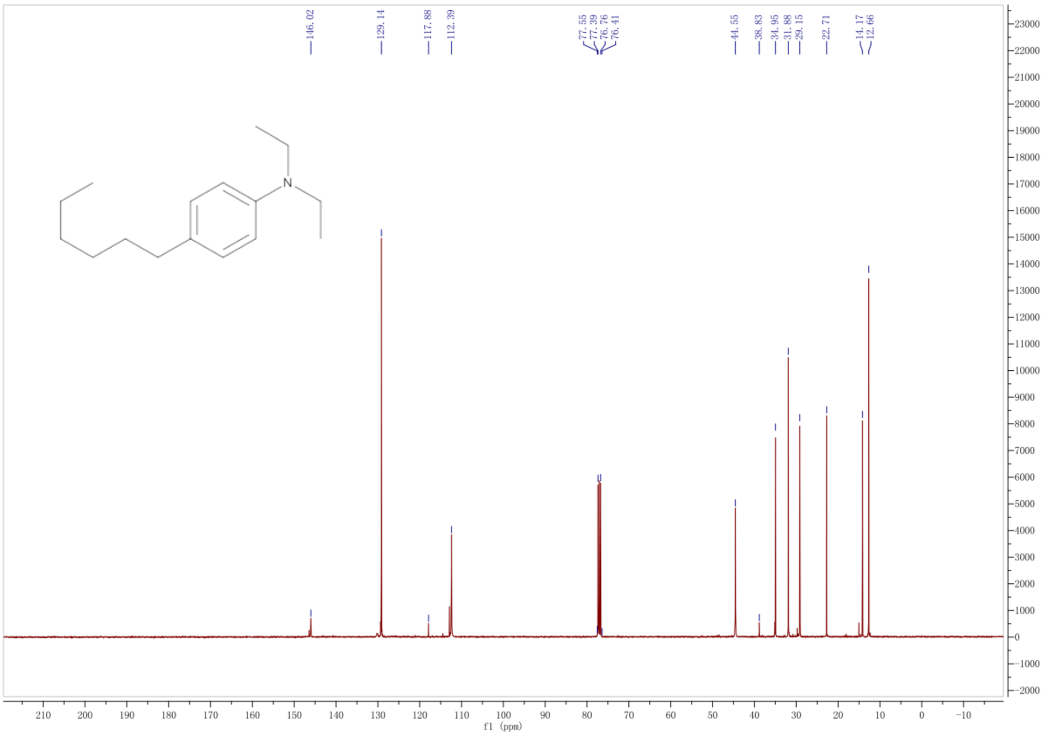


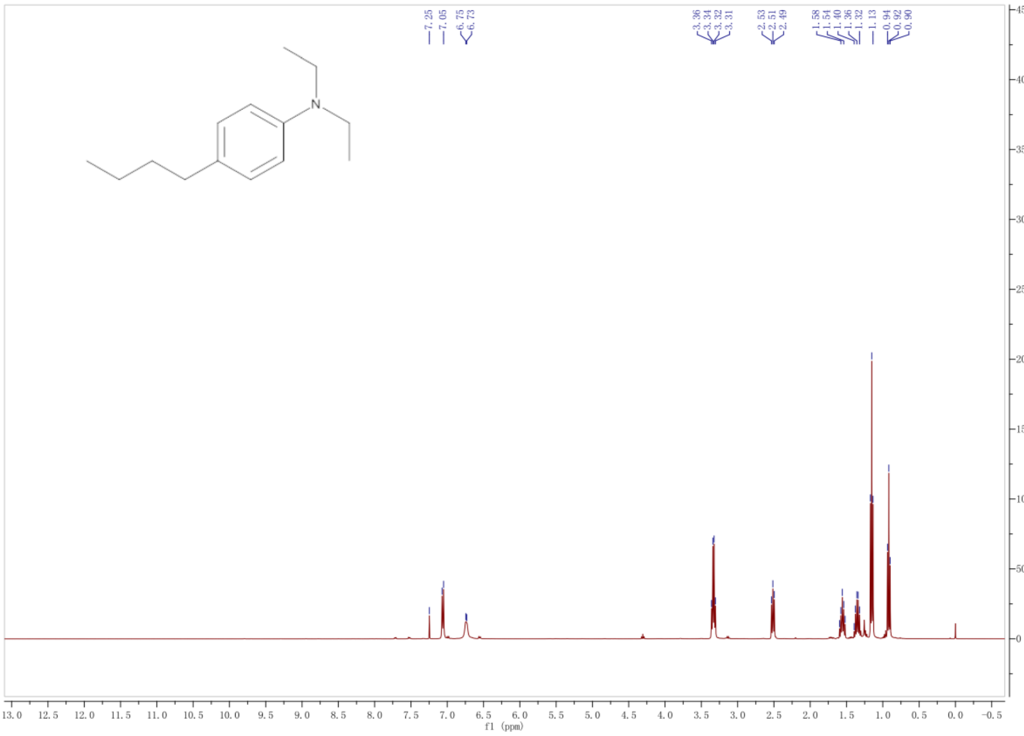


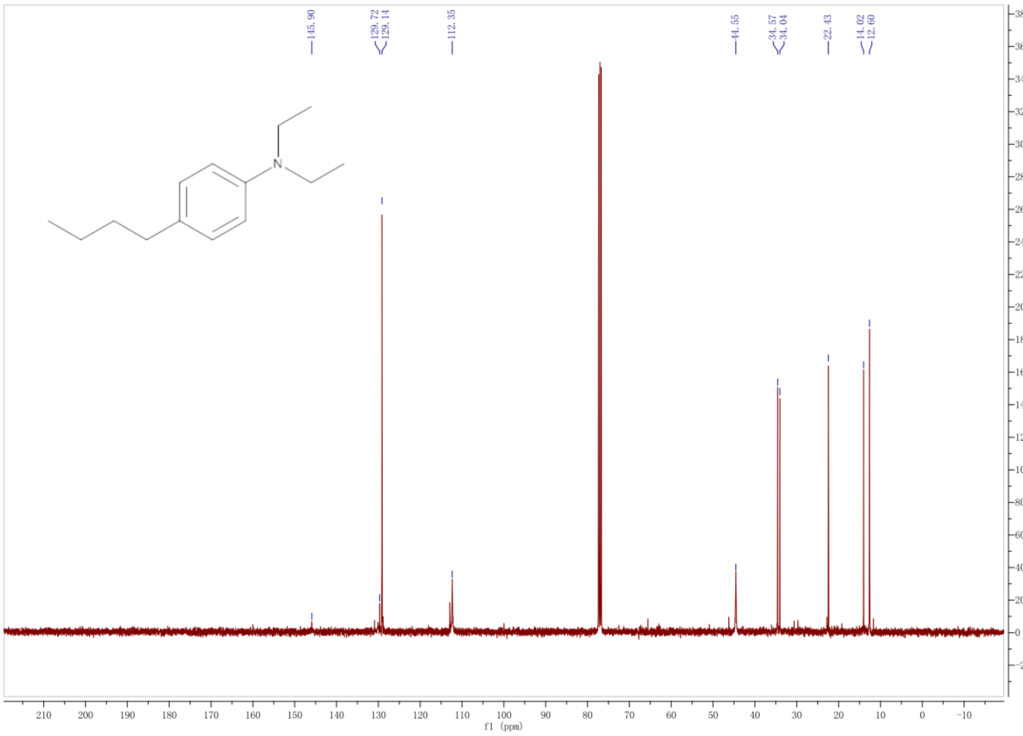


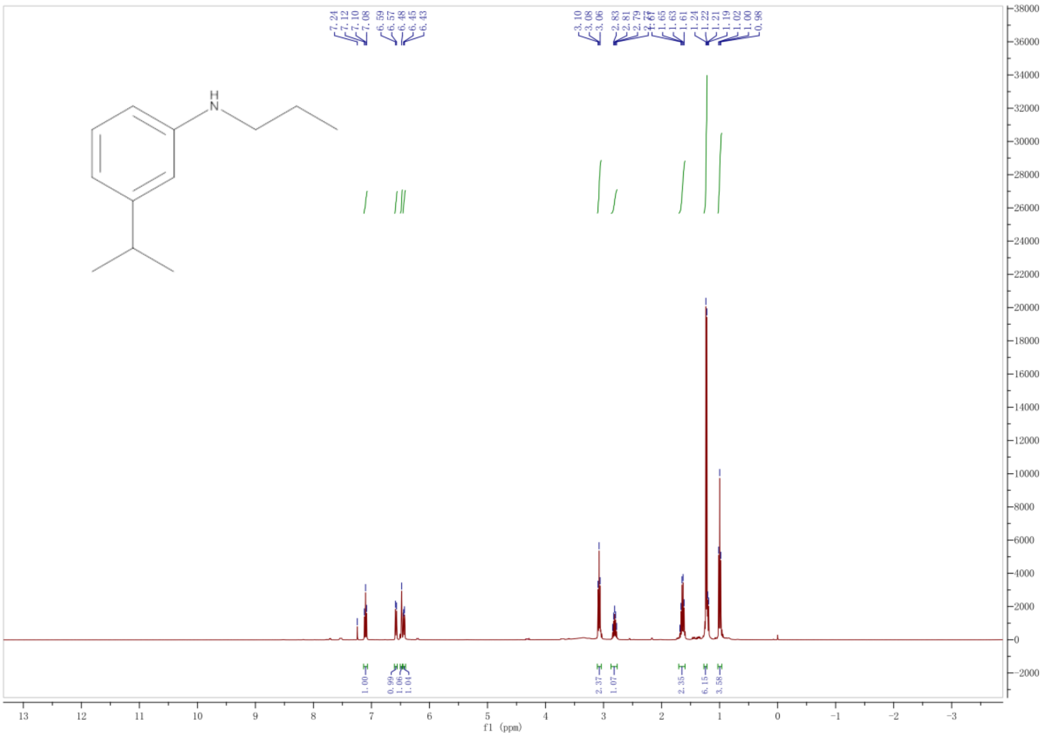


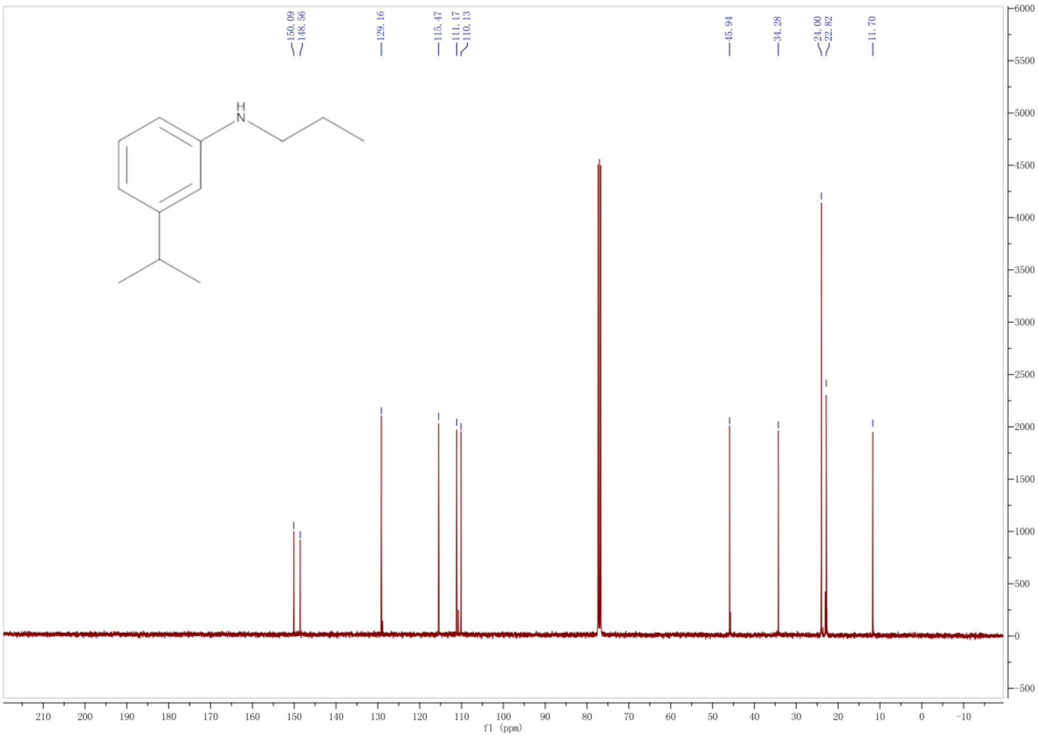


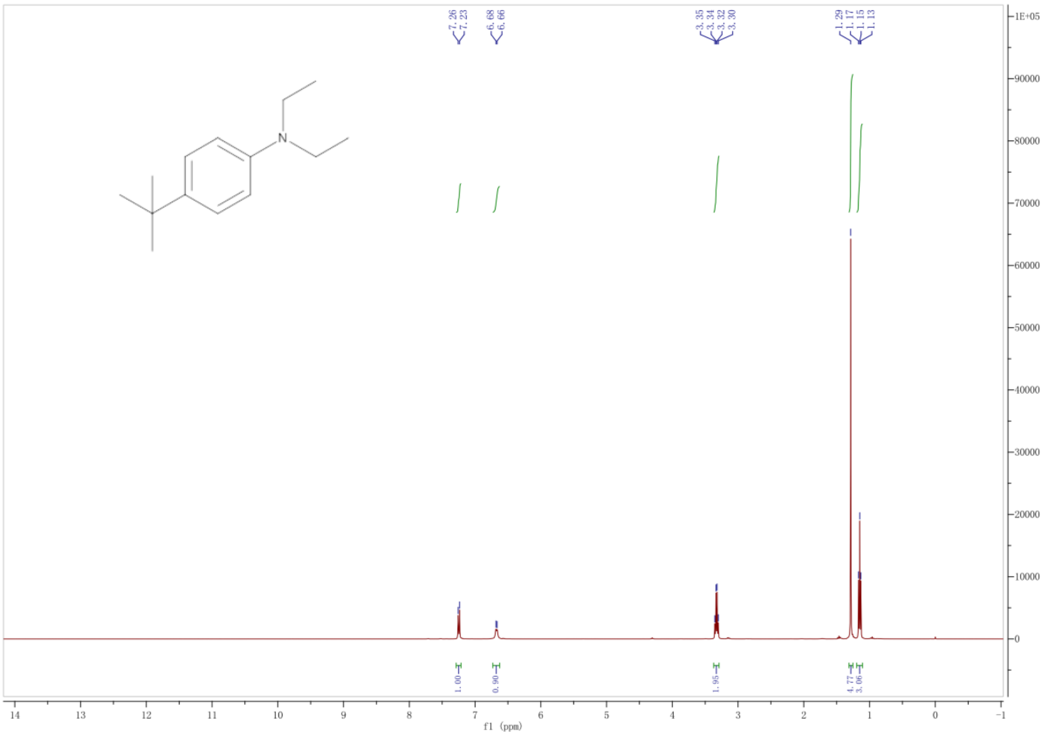


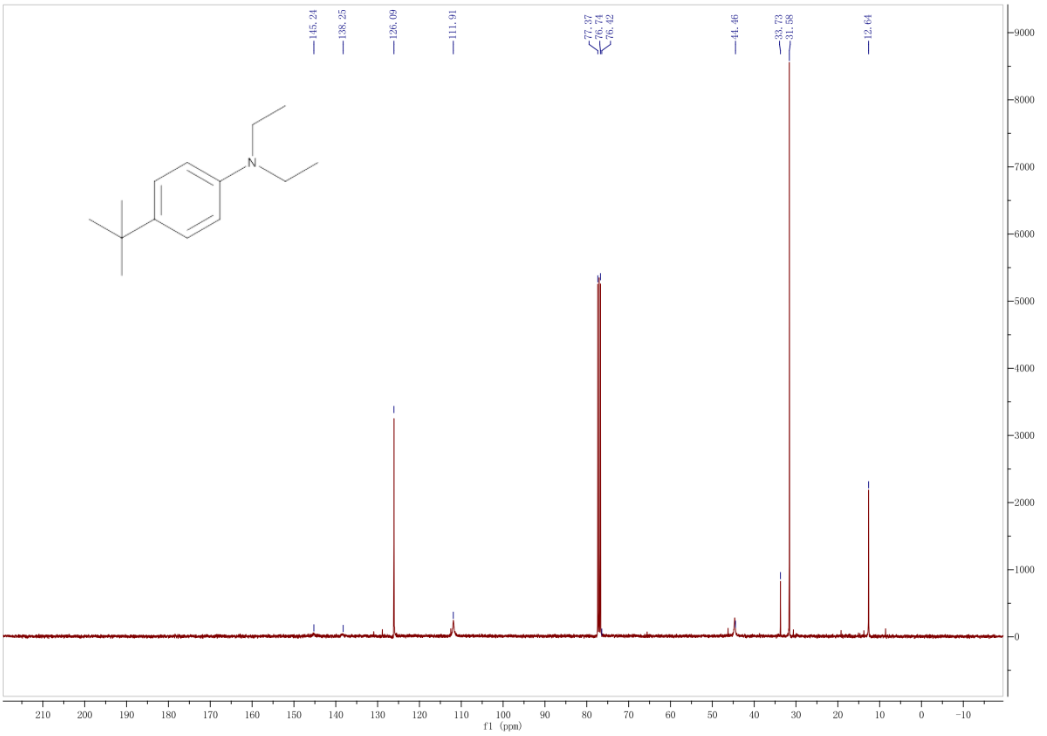


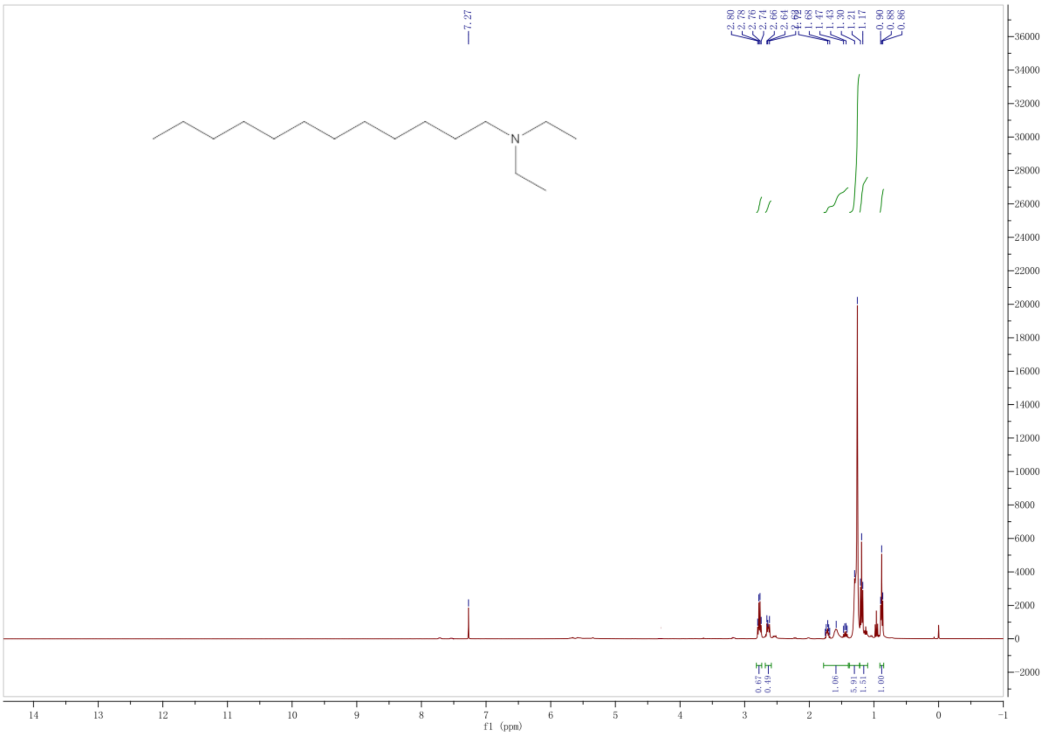


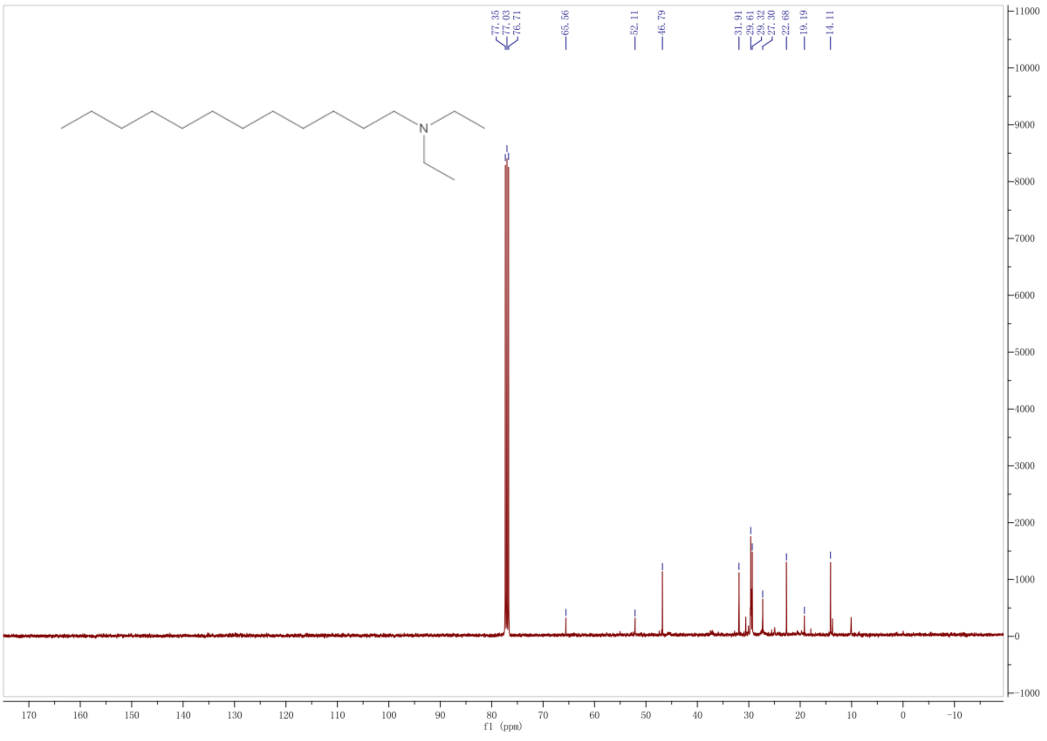


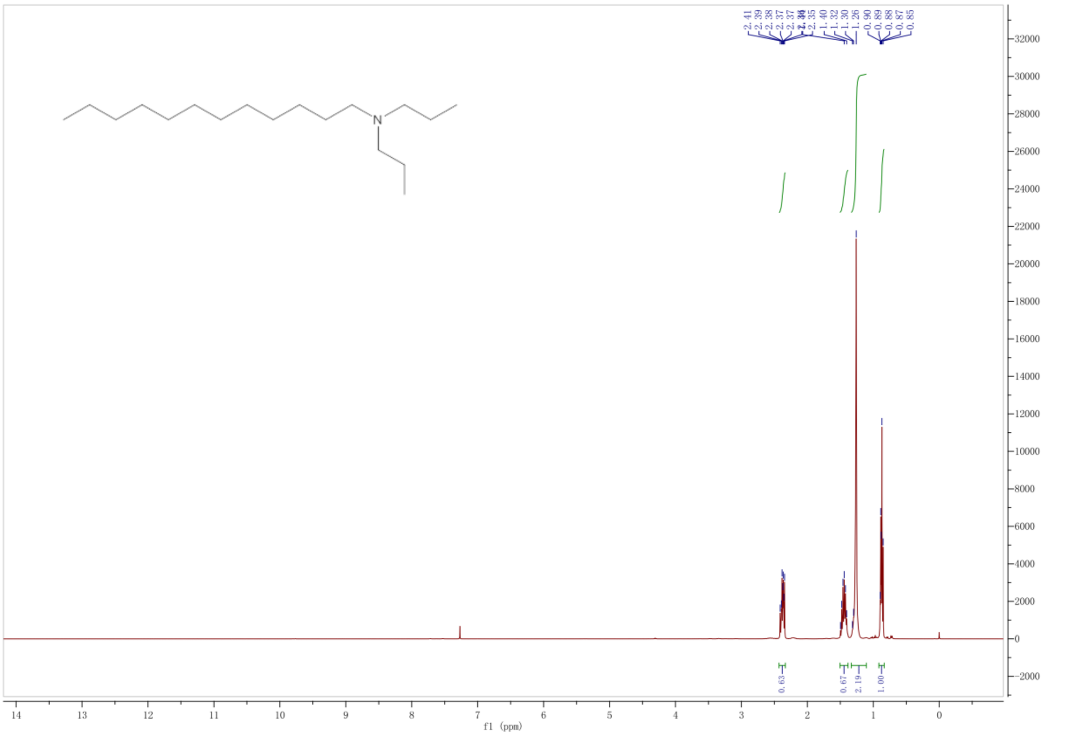


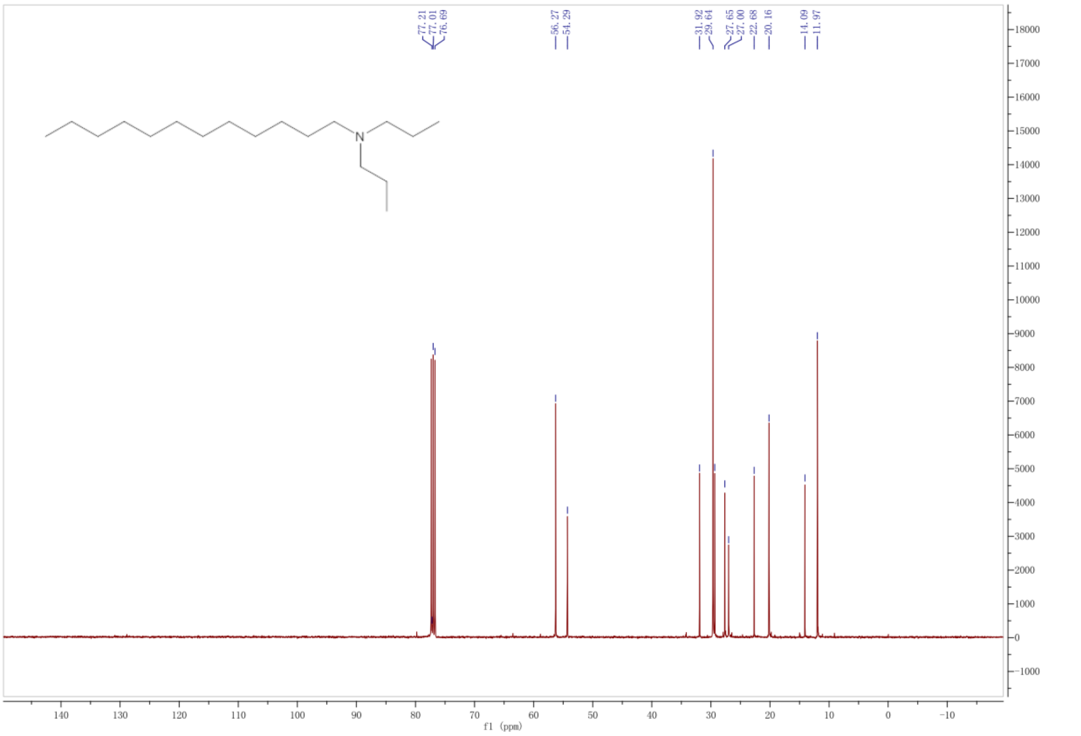

7.26
7.23
6.68
6.66
3.35
3.34
3.32
3.30
1.29
1.17
1.15
1.13
N
1.00
0.90
1.95
4.77
3.06
f1 (ppm)


145.24
138.25
126.09
111.91
77.37
76.74
76.42
44.46
33.73
31.58
12.64
N
f1 (ppm)









1. R. A. da Silva, I. H. S. Estevam and L. W. Bieber, *Tetrahedron Lett.*, 2007, **48**, 7680.
2. B. Das, K. Venkateswarlu, M. Krishnaiah and H. Holla, *Tetrahedron Lett.*, 2006, **47**, 8693.
3. X. Cui, X. Dai, Y. Deng and F. Shi, *Chem. Eur. J.*, 2013, **19**, 3665.
4. T. Saitoh and J. Ichikawa, *J. Am. Chem. Soc.*, 2005, **127**, 9696.
5. R. Fielden, O. Meth-Cohn and H. Suschitzky, *J. Chem. Soc., Perkin Trans. 1*, 1973, 696.
6. H. Yang, C. Xi, Z. Miao and R. Chen, *Eur. J. Org. Chem.*, 2011, **2011**, 3353.
7. A. Shafir and S. L. Buchwald, *J. Am. Chem. Soc.*, 2006, **128**, 8742.
8. M. Kirchgessner, K. Sreenath and K. R. Gopidas, *J. Org. Chem.*, 2006, **71**, 9849.
9. X. Li, D. Yang, Y. Jiang and H. Fu, *Green Chem.*, 2010, **12**, 1097.
10. R. Nacario, S. Kotakonda, D. M. D. Fouchard, L. M. V. Tillekeratne and R. A. Hudson, *Org. Lett.*, 2005, **7**, 471.
11. H. Xu and C. Wolf, *Chem. Commun.*, 2009, 1715.
12. K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji and H. Tanida, *Tetrahedron Lett.*, 1966, **7**, 9.
13. X. Qian, Z. Yu, A. Auffrant and C. Gosmini, *Chem. Eur. J.*, 2013, **19**, 6225.
14. O. Saidi, A. J. Blacker, M. M. Farah, S. P. Marsden and J. M. J. Williams, *Chem. Commun.*, 2010, **46**, 1541.
15. F. Chatel, G. Boyer and J.-P. Galy, *Synth. Commun.*, 2002, **32**, 2893.
16. J. Louie and J. F. Hartwig, *Tetrahedron Lett.*, 1995, **36**, 3609.
17. K. Kamikawa, S. Sugimoto and M. Uemura, *J. Org. Chem.*, 1998, **63**, 8407.
18. G. B. Fisher, J. C. Fuller, J. Harrison, S. G. Alvarez, E. R. Burkhardt, C. T. Goralski and B. Singaram, *J. Org. Chem.*, 1994, **59**, 6378.
19. V. E. Limanov, S. B. Ivanov, T. B. Kruchenok and I. M. Tsvirova, *Pharm. Chem. J.*, 1984, **18**, 416.