Electronic Supplementary Material (ESI) for Green Chemistry.

Supported Nano-Gold-Catalyzed N-Formylation of Amines with Paraformaldehyde in Water under Ambient Conditions

Zhengang Ke, Yan Zhang, Xinjiang Cui, Feng Shi*

Supporting Information

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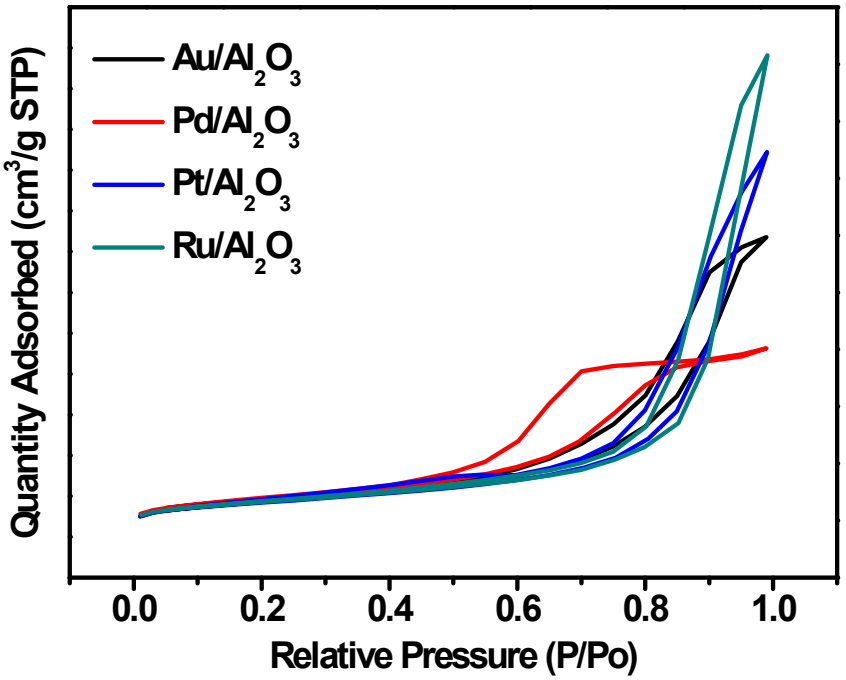
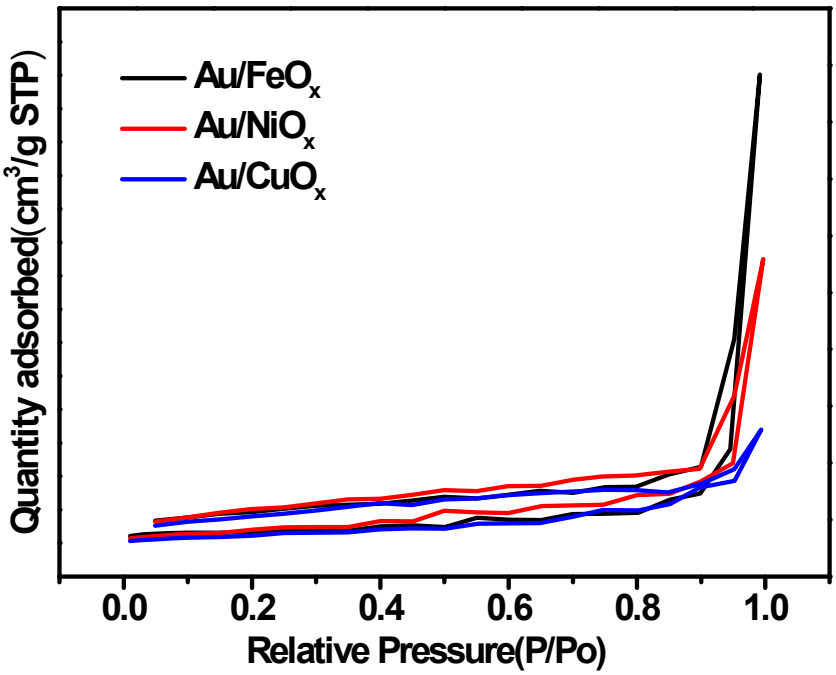
I. Characterization results of catalysts





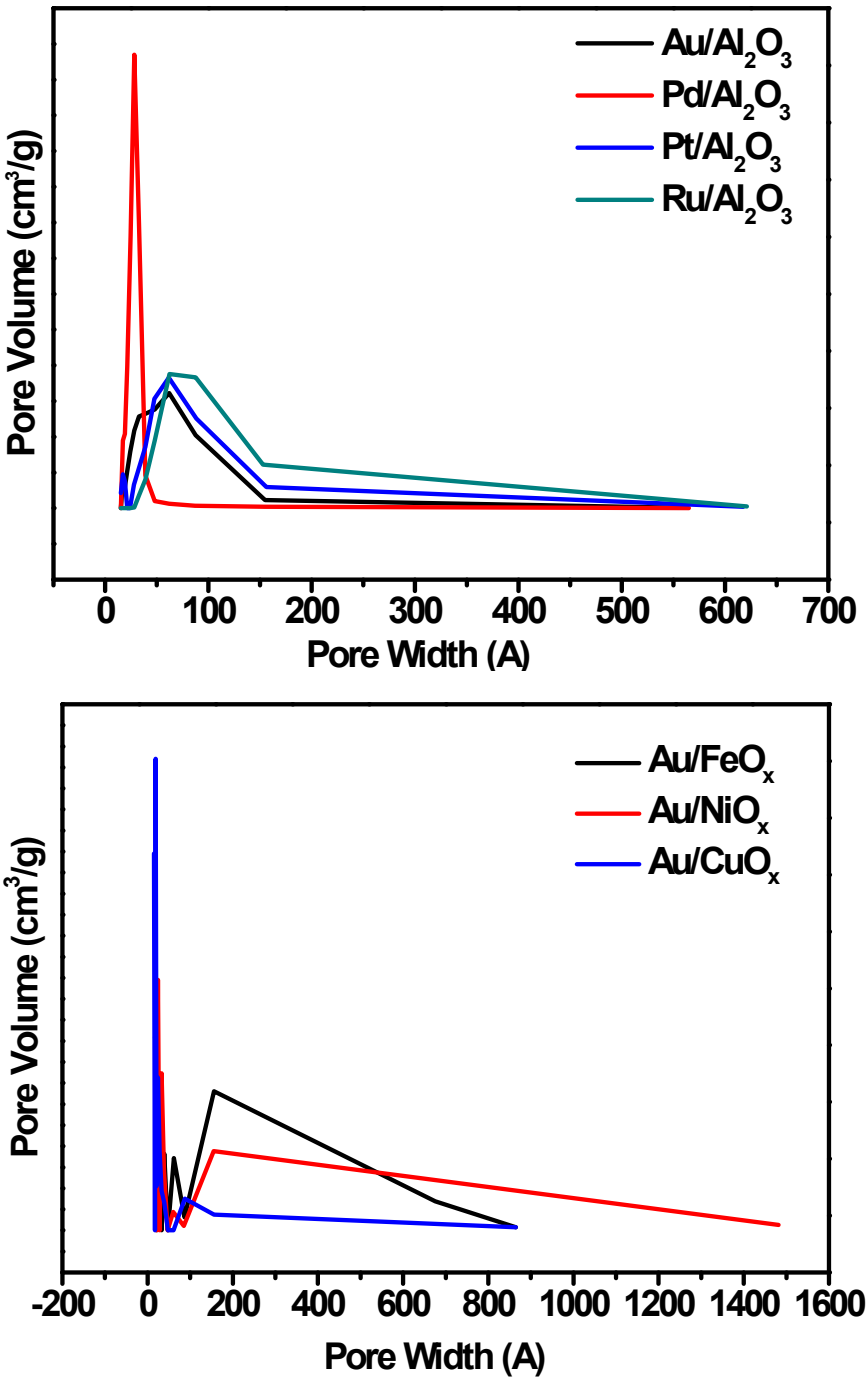


Figure S1. N_2 adsorption-desorption analysis of prepared various catalysts.

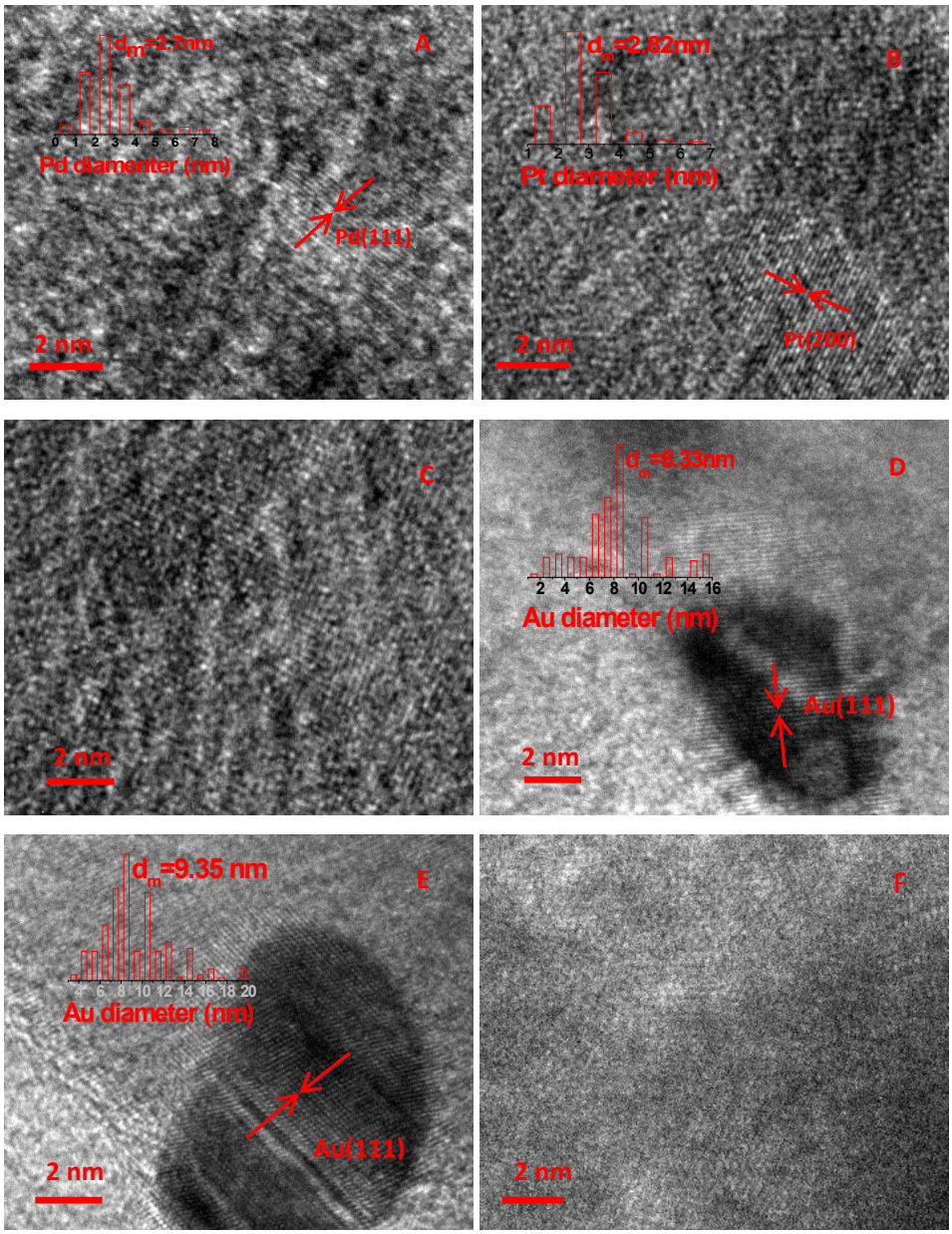
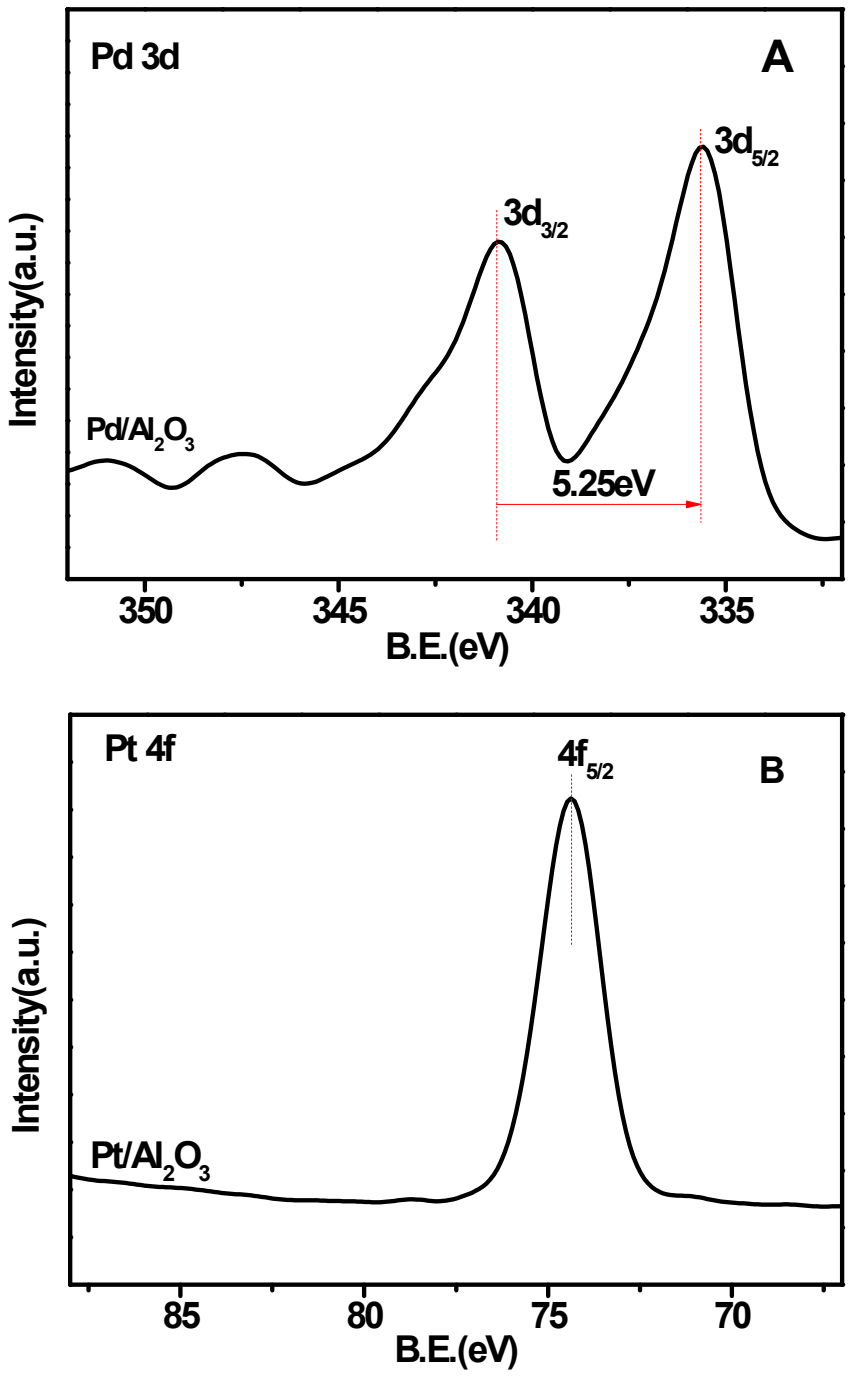
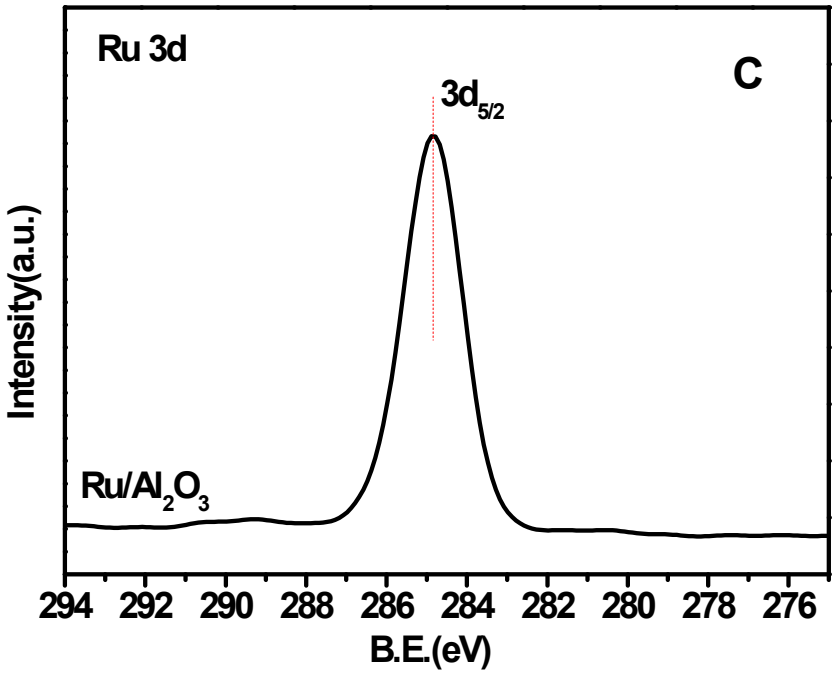
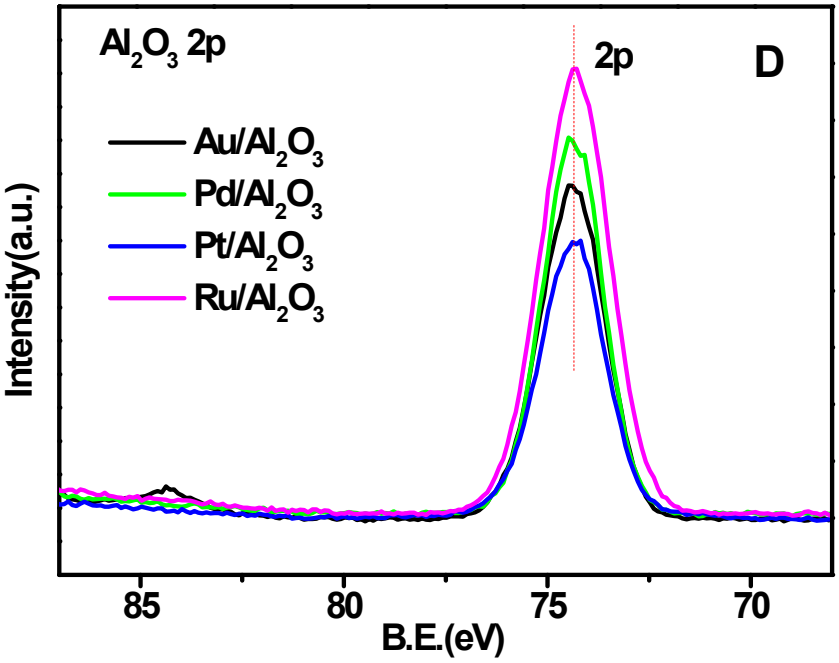
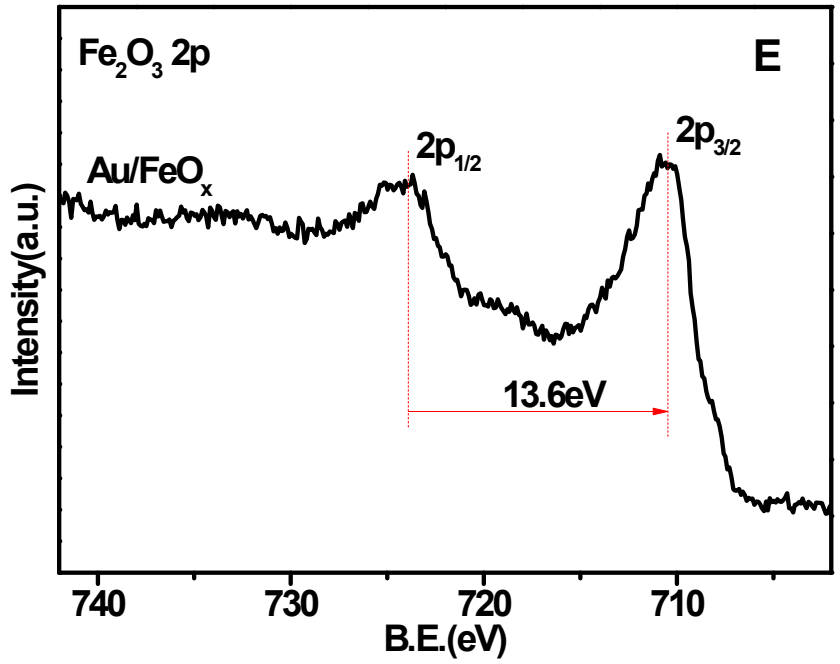


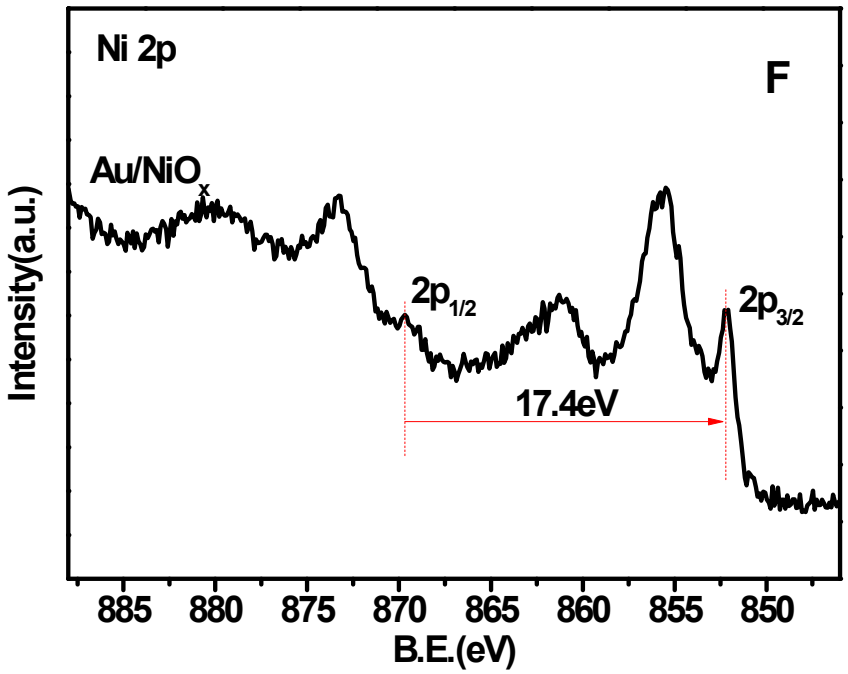
Figure S2. TEM images of catalyst samples synthesized with co-precipitation method. (A) Au/Al_2O_3, (B) Pd/Al_2O_3, (C) Pt/Al_2O_3, (D) Ru/Al_2O_3, (E) Au/FeO_x, (F) Au/NiO_x, (G) Au/CuO_x. Insets: SAED patterns of the corresponding samples.


Pd 3d
A
3d5/2
3d3/2
Pd/Al2O3
5.25eV
Intensity(a.u.)
350
345
340
335
B.E.(eV)
Pt 4f
4f5/2
B
Pt/Al2O3
Intensity(a.u.)
85
80
75
70
B.E.(eV)


Ru 3d
C
3d5/2
Intensity(a.u.)
Ru/Al2O3
294 292 290 288 286 284 282 280 278 276
B.E.(eV)


Al2O3 2p
2p
D
Au/Al2O3
Pd/Al2O3
Pt/Al2O3
Ru/Al2O3
Intensity(a.u.)
85 80 75 70
B.E.(eV)


Fe2O3 2p
E
Au/FeOx
2p1/2
2p3/2
13.6eV
Intensity(a.u.)
740
730
720
710
B.E.(eV)


Ni 2p
F
Au/NiOx
2p1/2
2p3/2
17.4eV
Intensity(a.u.)
885
880
875
870
865
860
855
850
B.E.(eV)

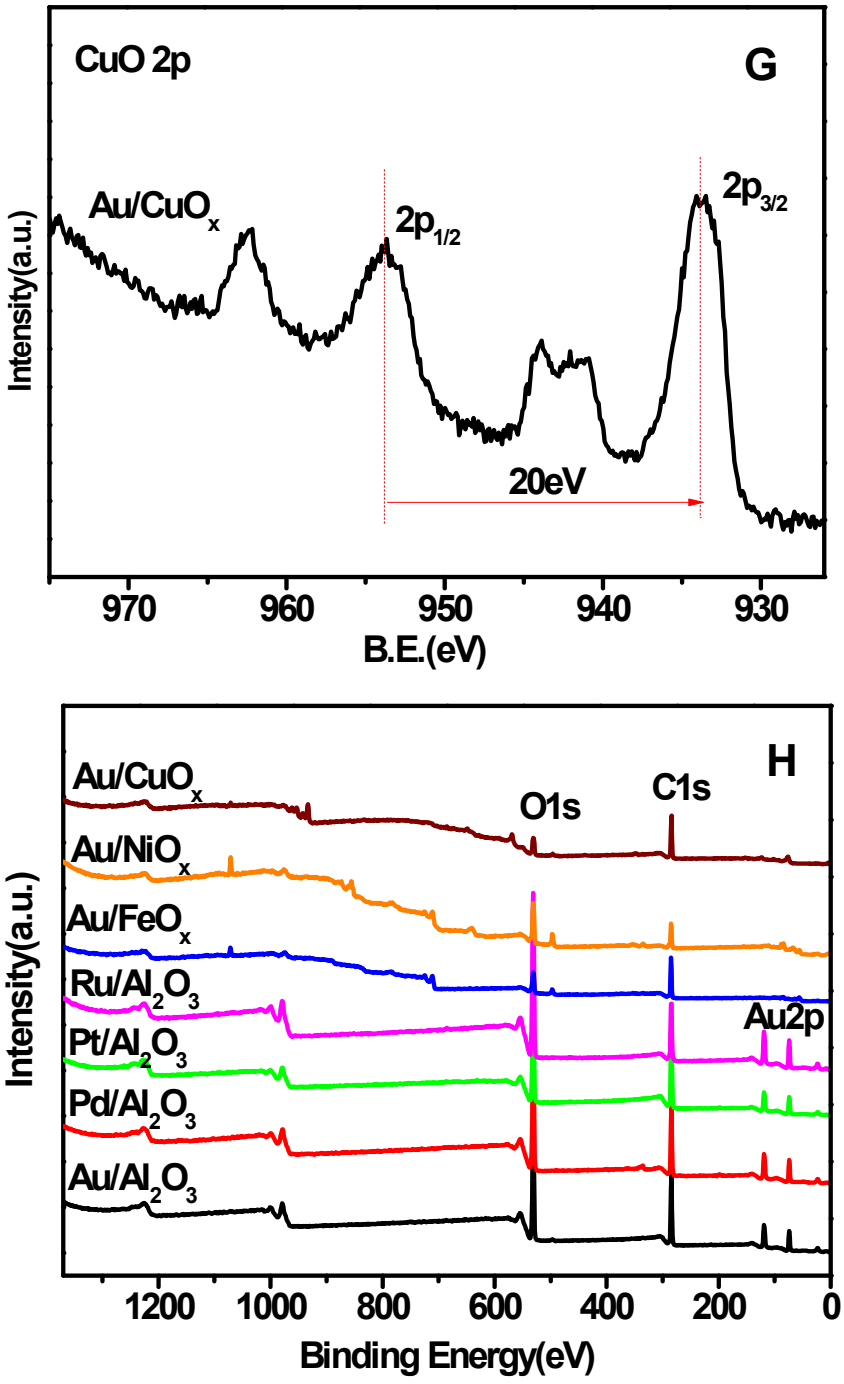
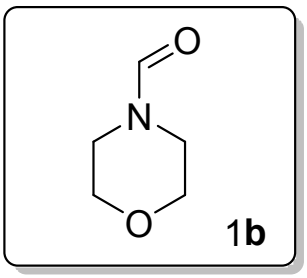


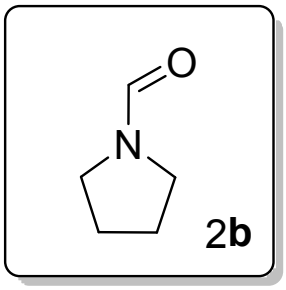
Figure S3. XPS spectra of catalyst samples

II. NMR characterizations of products

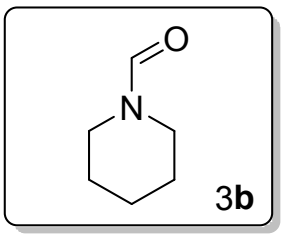
NMR peaks of products



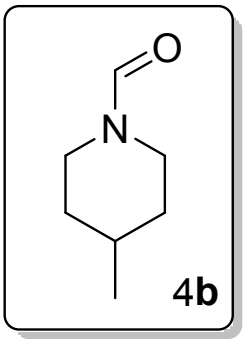
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 3.74 – 3.63 (m, 4H), 3.59 (q, *J* = 4.8 Hz, 2H), 3.45 – 3.35 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.82, 67.24, 66.45, 45.80, 40.63. This compound was obtained and purified by column chromatography using dichloromethane/methanol (10: 1, Rf = 0.77) to give a colorless oil.



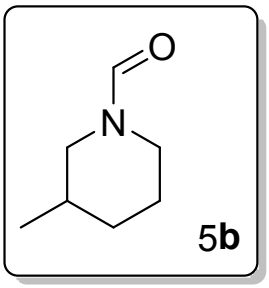
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 3.77 – 3.17 (m, 4H), 2.09 – 1.64 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.87, 46.00, 43.10, 24.89, 24.22. This compound was obtained and purified by column chromatography using dichloromethane/methanol (10: 1, Rf = 0.33) to give colorless oil.



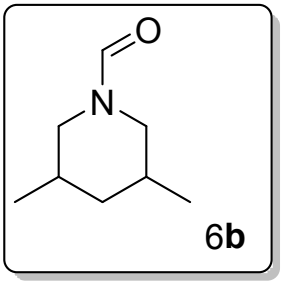
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 3.54 – 3.43 (m, 2H), 3.30 (dd, *J* = 13.7, 8.2 Hz, 2H), 1.75 – 1.65 (m, 2H), 1.56 (qd, *J* = 11.2, 5.7 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.80, 46.83, 40.63, 26.60, 25.09, 24.74. This compound was obtained and purified by column chromatography using dichloromethane/methanol (10:1, Rf = 0.6) to give a colorless oil.



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 4.40 – 4.29 (m, 1H), 3.67 – 3.50 (m, 1H), 3.04 (tt, *J* = 11.8, 5.8 Hz, 1H), 2.62 (td, *J* = 12.8, 2.9 Hz, 1H), 1.79 – 1.58 (m, 3H), 1.18 – 1.03 (m, 2H), 0.98 (t, *J* = 7.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.75, 46.15, 39.94, 34.73, 33.28, 31.37, 21.70. This compound was obtained and purified by column chromatography using dichloromethane/methanol (10:1, Rf = 0.6) to give a colorless oil.

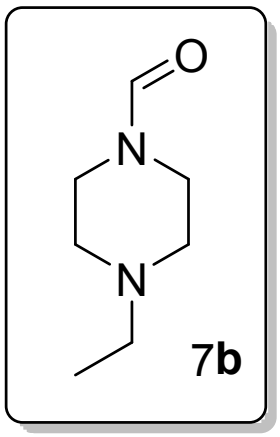


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 5.6 Hz, 1H), 4.22 (dd, *J* = 16.5, 8.1 Hz, 1H), 3.48 (dd, *J* = 22.4, 9.4 Hz, 1H), 3.07 – 2.96 (m, 1H), 2.74 – 2.64 (m, 1H), 2.32 (dd, *J* = 12.8, 10.8 Hz, 1H), 1.86 (dd, *J* = 9.4, 3.8 Hz, 1H), 1.79 – 1.65 (m, 1H), 1.63 – 1.36 (m, 2H), 1.31 – 1.13 (m, 2H), 0.98 – 0.86 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.80, 160.72, 56.97, 53.30, 47.02, 46.37, 40.17, 34.65, 33.23, 33.16, 31.92, 31.55, 30.64, 29.59, 28.98, 25.98, 24.27, 18.86, 18.60, 18.54. This compound was obtained and purified by column chromatography using dichloromethane/methanol (10:1, Rf = 0.64) to give a pale yellow oil.

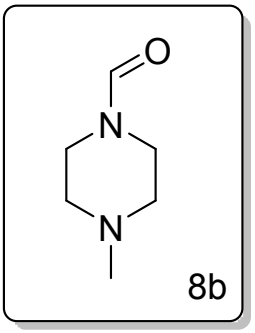


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 4.41 – 3.58 (m, 1H), 3.54 – 3.26 (m, 1H), 3.04 – 1.39 (m, 6H), 0.92 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.30, 160.59, 53.02, 52.51, 46.67, 46.44, 42.55, 39.51, 32.38, 30.83, 27.45, 26.10, 18.96, 18.78, 18.08, 17.57. This compound was obtained and purified by column

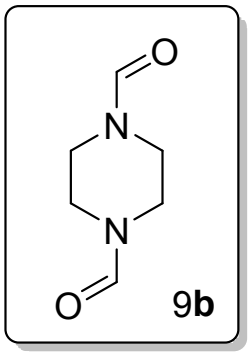
chromatography using dichloromethane/methanol (100:1, Rf = 0.84) to give a pale yellow oil.



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 3.64 – 3.54 (m, 2H), 3.43 (dd, *J* = 19.2, 14.2 Hz, 2H), 2.45 (ddd, *J* = 10.2, 7.6, 4.5 Hz, 6H), 1.10 (t, *J* = 7.2 Hz, 3H).^{3}C NMR (101 MHz, $CDCl_3$) δ 160.69, 53.19, 52.27, 51.97, 45.60, 39.93, 11.87. This compound was obtained and purified by column chromatography using dichloromethane/methanol (10:1, Rf = 0.41) to give a pale yellow oil.

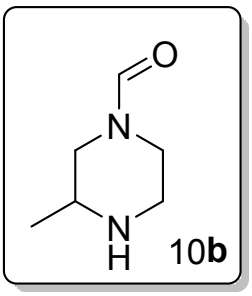


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 3.58 (s, 2H), 3.45 – 3.35 (m, 2H), 2.46 – 2.35 (m, 4H), 2.33 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.71, 55.40, 54.22, 46.13, 45.52, 39.85. This compound was obtained and purified by column chromatography using dichloromethane/methanol (10:1, Rf = 0.6) to give a pale yellow oil.

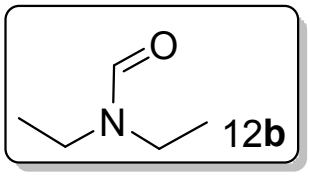


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 3.60 (dd, *J* = 15.1, 9.6 Hz, 2H), 3.41 (dd, *J* = 14.5, 8.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.95, 160.78, 46.09, 44.97, 40.54,

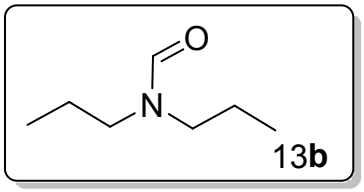
39.50. This compound was obtained and purified by column chromatography using dichloromethane/methanol (10:1, Rf = 0.5) to give a white solid.



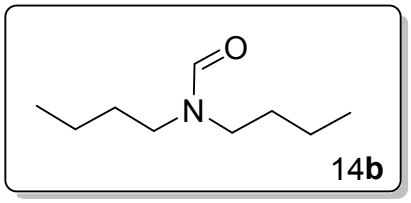
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (t, *J* = 11.7 Hz, 1H), 4.31 – 4.18 (m, 1H), 3.46 (dd, *J* = 15.7, 6.1 Hz, 1H), 3.21 – 2.99 (m, 2H), 2.84 – 2.66 (m, 3H), 2.36 (dd, *J* = 12.7, 10.5 Hz, 1H), 1.85 (s, 2H), 1.09 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.82, 160.76, 52.94, 51.58, 50.42, 47.18, 46.49, 46.16, 45.19, 40.51, 19.32, 19.13. This compound was obtained and purified by column chromatography using dichloromethane/ methanol (10:1, Rf = 0.43) to give a yellow oil.



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 3.37 (q, *J* = 7.2 Hz, 2H), 3.29 (q, *J* = 7.2 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.17, 41.82, 36.57, 14.86, 12.74. This compound was obtained and purified by column chromatography using dichloromethane/methanol (10:1, Rf = 0.77) to give a colorless oil.

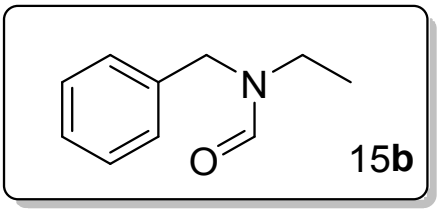


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 3.30 – 3.22 (m, 2H), 3.17 (t, *J* = 7.1 Hz, 2H), 1.63 – 1.50 (m, 4H), 0.90 (td, *J* = 7.4, 3.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.80, 49.18, 43.78, 21.85, 20.55, 11.31, 10.92. This compound was obtained and purified by column chromatography using dichloromethane/methanol (10:1, Rf = 0.67) to give a colorless oil.

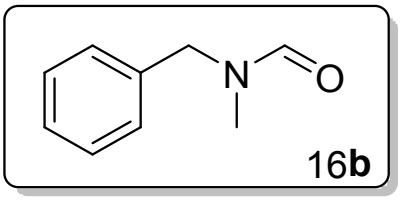


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 3.35 – 3.25 (m, 2H), 3.19 (t, *J* = 7.2 Hz, 2H), 1.61 – 1.43 (m, 4H), 1.32 (dp, *J* = 14.3, 7.2 Hz, 4H), 0.94 (td, *J* = 7.3, 2.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.66, 47.16, 41.89, 30.77, 29.41, 20.15, 19.64, 13.76,

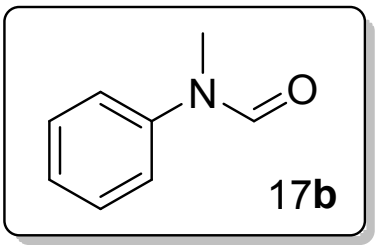
13.60. This compound was obtained and purified by column chromatography using dichloromethane/methanol (20:1, Rf = 0.75) to give a colorless oil.



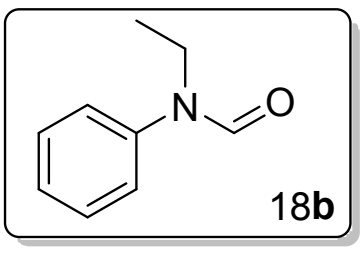
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 9.9 Hz, 1H), 7.40 – 7.14 (m, 5H), 4.47 (d, *J* = 63.4 Hz, 2H), 3.25 (dq, *J* = 34.8, 7.2 Hz, 2H), 1.11 (dt, *J* = 34.3, 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.58, 136.60, 136.29, 128.86, 128.65, 128.15, 128.05, 127.53, 127.48, 50.88, 44.87, 41.50, 36.84, 14.36, 12.21. This compound was obtained and purified by column chromatography using petroleum ether(b.p.30-60^{o}C)/ethyl acetate (50:1, Rf = 0.63) to give a brown oil.



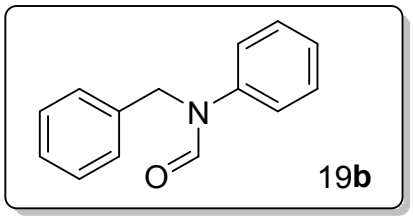
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 67.7, 30.9 Hz, 1H), 7.41 – 7.13 (m, 5H), 4.54 – 4.47 (m, 1H), 4.41 (d, *J* = 12.4 Hz, 1H), 2.81 (d, *J* = 24.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.73, 162.56, 136.07, 135.81, 128.91, 128.76, 128.70, 128.26, 128.11, 127.82, 127.64, 127.40, 53.49, 47.79, 34.02, 29.46. This compound was obtained and purified by column chromatography using petroleum ether(b.p.30-60^{o}C)/ethyl acetate (50:1, Rf = 0.74) to give a brown oil.



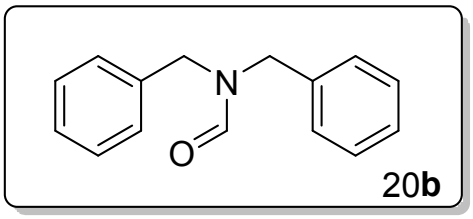
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 – 8.39 (m, 1H), 7.45 – 7.09 (m, 5H), 3.34 – 3.28 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.34, 142.23, 129.64, 129.08, 126.41, 123.64, 122.84, 122.41, 32.06. This compound was obtained and purified by column chromatography using petroleum ether(b.p.30-60^{o}C)/ethyl acetate (6:1, Rf = 0.51) to give a brown oil.



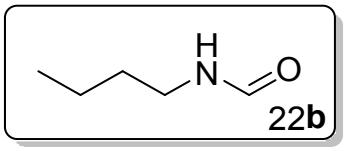
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.46 – 7.14 (m, 5H), 3.80 (dq, *J* = 56.1, 7.2 Hz, 2H), 1.22 – 1.13 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.02, 140.87, 129.63, 129.25, 127.01, 126.85, 126.09, 124.28, 40.09, 13.04. This compound was obtained and purified by column chromatography using petroleum ether(b.p.30-60^{o}C)/ethyl acetate (6:1, Rf = 0.58) to give a brown oil.



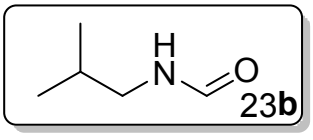
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.45 – 6.95 (m, 10H), 4.92 (d, *J* = 65.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.38, 141.05, 136.69, 129.58, 129.09, 128.87, 128.60, 127.88, 127.46, 126.90, 125.44, 124.12, 48.89. This compound was obtained and purified by column chromatography using petroleum ether(b.p.30-60^{o}C)/ethyl acetate (100:1, Rf = 0.31) to give a pale yellow solid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.42 – 7.11 (m, 10H), 4.41 (s, 2H), 4.26 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.82, 136.07, 135.69, 128.93, 128.70, 128.54, 128.15, 127.72, 127.67, 50.28, 44.71. This compound was obtained and purified by column chromatography using petroleum ether(b.p.30-60^{o}C)/ethyl acetate (100 : 1, Rf = 0.42) to give a pale yellow solid.

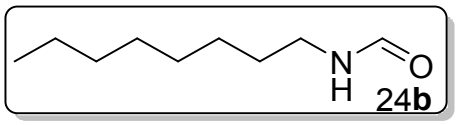


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 7.91 (m, 1H), 5.78 (s, 1H), 3.44 – 3.07 (m, 2H), 1.59 – 1.45 (m, 2H), 1.43 – 1.28 (m, 2H), 0.94 (td, *J* = 7.3, 2.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.77, 46.17, 39.94, 34.71, 33.27, 31.36, 21.72. This compound was obtained and purified by column chromatography using dichloromethane/methanol (50:1, Rf = 0.29) to give a colorless oil.

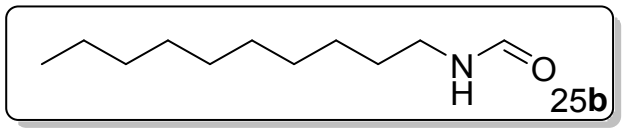


Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 7.97 (m, 1H), 6.24 – 5.26 (m, 1H), 3.20 – 2.91 (m, 2H), 2.16 – 1.66 (m, 1H), 0.99 – 0.84 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.86, 164.32, 161.26, 53.95, 49.29, 45.45, 29.63, 28.43, 26.46, 19.99, 19.77, 19.73, 19.57. This compound was obtained and purified by column

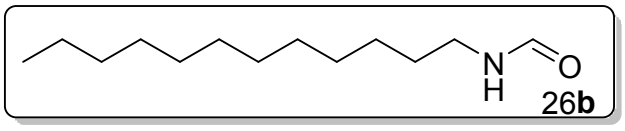
chromatography using dichloromethane/methanol (50:1, Rf = 0.25) to give a colorless oil.



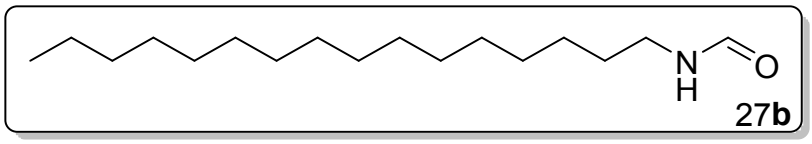
1H NMR (400 MHz, CDCl3) δ 8.30 – 7.91 (m, 1H), 5.53 (d, J = 149.5 Hz, 1H), 3.25 (ddd, J = 32.5, 13.6, 6.8 Hz, 2H), 1.49 (dt, J = 47.9, 23.9 Hz, 2H), 1.29 (d, J = 10.8 Hz, 9H), 0.88 (t, J = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.57, 161.13, 77.35, 77.03, 76.71, 41.75, 38.20, 31.70, 31.65, 31.24, 29.52, 28.88, 28.78, 26.79, 26.34, 22.54, 14.01. This compound was obtained and purified by column chromatography using dichloromethane/methanol (100:1, Rf = 0.6) to give a colorless solid.



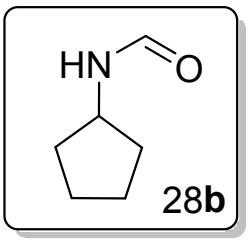
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 7.98 (m, 1H), 5.62 (s, 1H), 3.25 (ddd, *J* = 33.4, 13.5, 6.8 Hz, 2H), 1.59 – 0.81 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.56, 161.12, 41.76, 38.21, 31.87, 31.25, 29.53, 29.51, 29.48, 29.28, 29.23, 29.13, 26.84, 26.38, 22.66, 14.09. This compound was obtained and purified by column chromatography using dichloromethane/methanol (150:1, Rf = 0.35) to give a white solid.



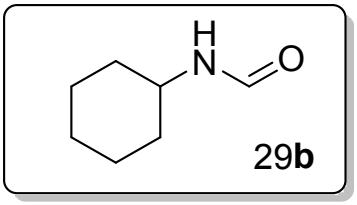
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 7.98 (m, 1H), 5.46 (d, *J* = 90.1 Hz, 1H), 3.39 – 3.04 (m, 2H), 1.51 (dd, *J* = 13.9, 6.8 Hz, 2H), 1.28 (d, *J* = 16.7 Hz, 19H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.51, 161.07, 41.73, 38.22, 31.90, 31.26, 29.62, 29.61, 29.54, 29.52, 29.47, 29.33, 29.23, 29.13, 26.84, 26.39, 22.67, 14.09. This compound was obtained and purified by column chromatography using dichloromethane/methanol (150:1, Rf = 0.36) to give a white solid.



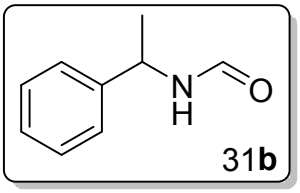
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 7.98 (m, 1H), 5.57 (s, 1H), 3.25 (ddd, *J* = 34.1, 13.5, 6.7 Hz, 2H), 3.25 (ddd, *J* = 34.1, 13.5, 6.7 Hz, 2H), 1.57 – 1.47 (m, 2H), 1.28 (d, *J* = 17.2 Hz, 29H), 0.88 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.50, 161.07, 41.73, 38.22, 36.01, 31.92, 31.27, 29.68, 29.65, 29.56, 29.55, 29.52, 29.48, 29.35, 29.23, 29.14, 26.84, 26.39, 22.68, 14.10. This compound was obtained and purified by column chromatography using dichloromethane/methanol (150:1, Rf = 0.41) to give a white solid.



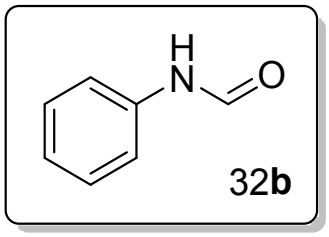
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 11.5 Hz, 1H), 5.51 (d, *J* = 127.9 Hz, 1H), 4.45 – 3.72 (m, 1H), 1.99 (qd, *J* = 11.7, 6.6 Hz, 2H), 1.79 – 1.55 (m, 4H), 1.42 (qt, *J* = 38.4, 19.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.95, 160.82, 53.58, 49.96, 34.10, 33.06, 23.66, 23.39. This compound was obtained and purified by column chromatography using dichloromethane/methanol (20:1, Rf = 0.64) to give a colorless oil.



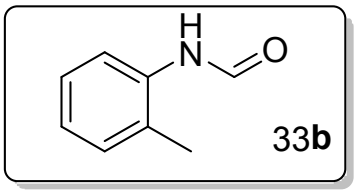
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 13.7 Hz, 1H), 5.89 – 5.29 (m, 1H), 3.96 – 2.75 (m, 1H), 1.99 – 1.85 (m, 2H), 1.80 – 1.57 (m, 3H), 1.44 – 1.25 (m, 3H), 1.24 – 1.09 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.50, 160.26, 50.93, 47.09, 34.71, 33.05, 25.43, 25.04, 24.73. This compound was obtained and purified by column chromatography using dichloromethane/methanol (20:1, Rf = 0.73) to give a colorless oil.



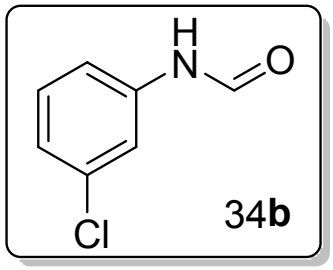
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.43 – 7.19 (m, 5H), 6.04 (s, 1H), 5.21 (p, *J* = 7.0 Hz, 1H), 1.61 – 1.41 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.10, 160.27, 160.24, 142.82, 142.61, 128.94, 128.75, 127.78, 127.55, 126.15, 125.78, 51.67, 47.62, 23.58, 21.72. This compound was obtained and purified by column chromatography using dichloromethane/methanol (50:1, Rf = 0.62) to give a brown oil.



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 – 8.43 (m, 1H), 8.32 (d, *J* = 42.3 Hz, 1H), 7.58 (t, *J* = 22.3 Hz, 1H), 7.43 – 7.24 (m, 2H), 7.23 – 7.01 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.77, 159.16, 136.93, 136.77, 129.77, 129.11, 125.30, 124.83, 120.04, 118.85. This compound was obtained and purified by column chromatography using petroleum ether(b.p.30-60^{o}C)/ethyl acetate (50:1, Rf = 0.75) to give a brown oil.



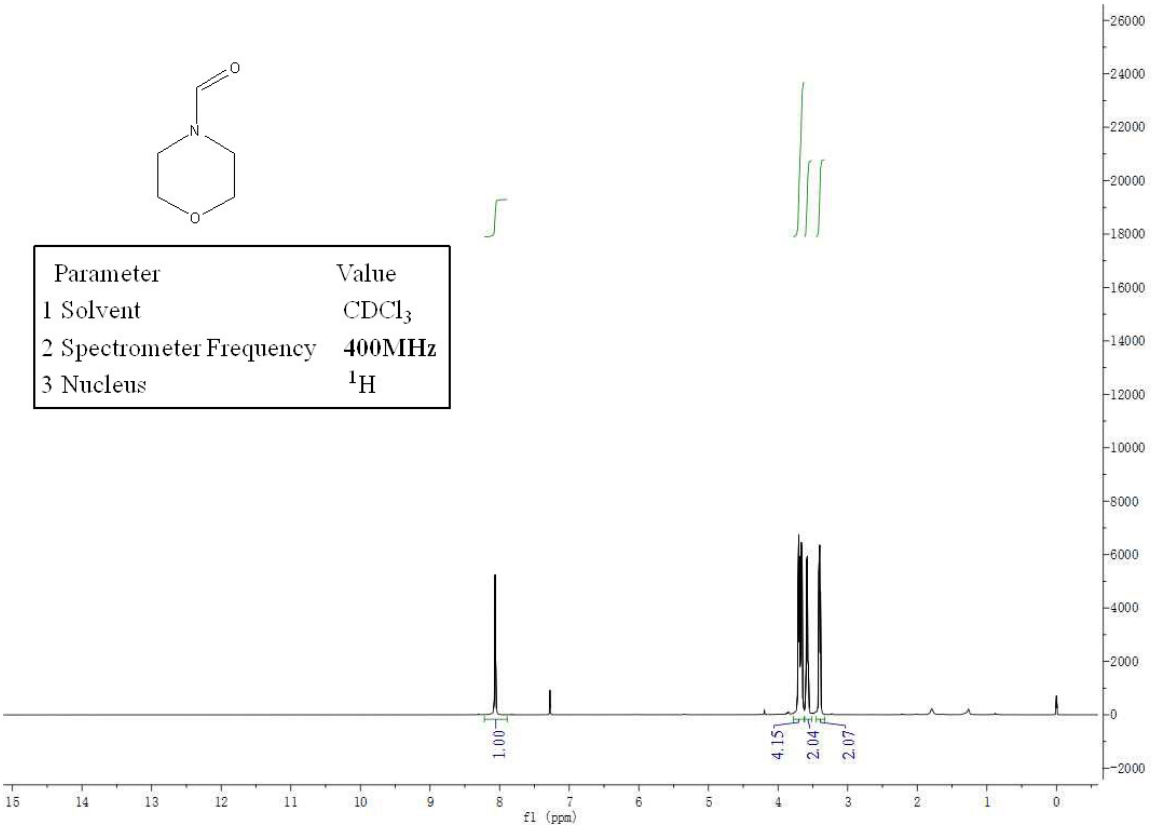
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (dd, *J* = 34.8, 23.5 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.27 – 7.07 (m, 4H), 2.29 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.00, 134.65, 131.26, 130.57, 129.64, 128.50, 127.16, 126.88, 126.05, 125.52, 123.04, 120.67, 17.71, 17.69. This compound was obtained and purified by column chromatography using dichloromethane/methanol (50:1, Rf = 0.53) to give a yellow solid.

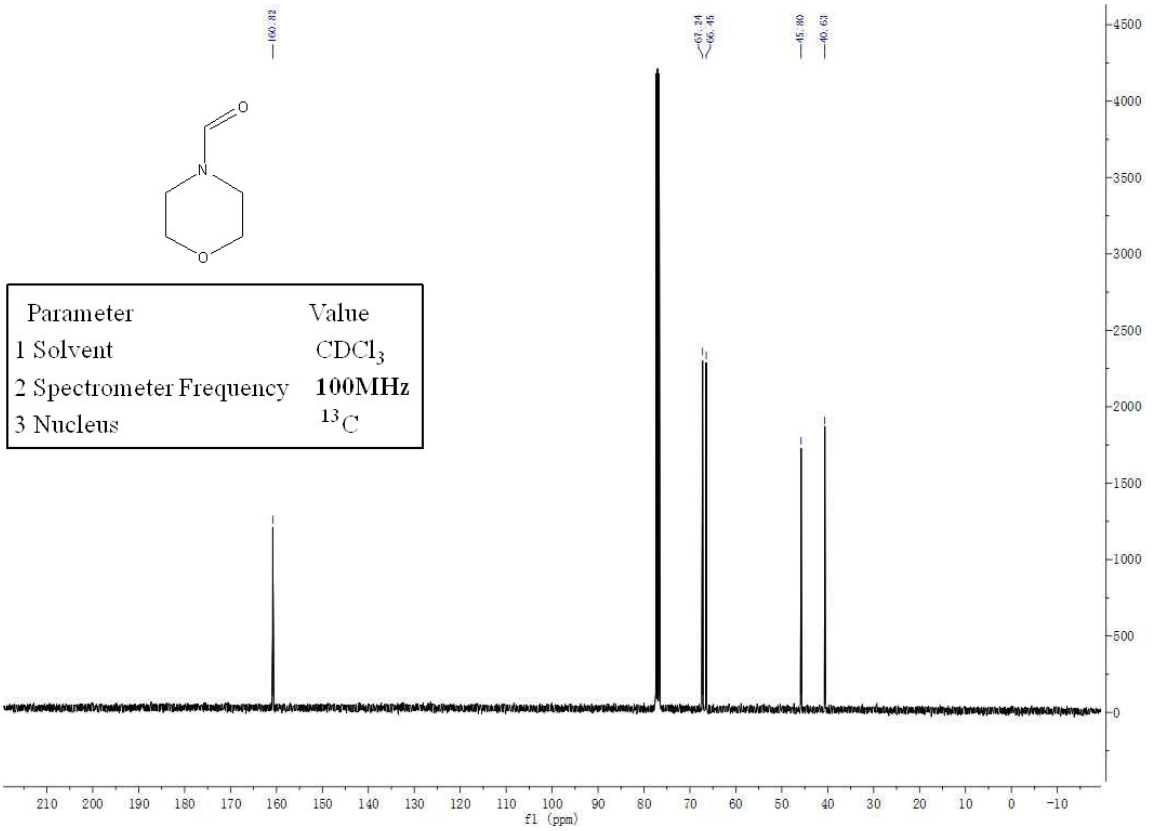


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 11.2 Hz, 1H), 8.54 (s, 1H), 8.37 (t, *J* = 5.3 Hz, 1H), 7.65 (dd, *J* = 18.6, 16.7 Hz, 2H), 7.39 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.27 (dt, *J* = 13.0, 8.1 Hz, 3H), 7.20 – 7.08 (m, 3H), 6.99 (dd, *J* = 8.0, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.35, 159.06, 138.00, 137.95, 135.50, 134.78, 130.84, 130.13, 125.36, 124.94, 120.14, 118.80, 117.93, 116.72. This compound was obtained and purified by column chromatography using dichloromethane/methanol (50:1, Rf = 0.63) to give a yellow solid.

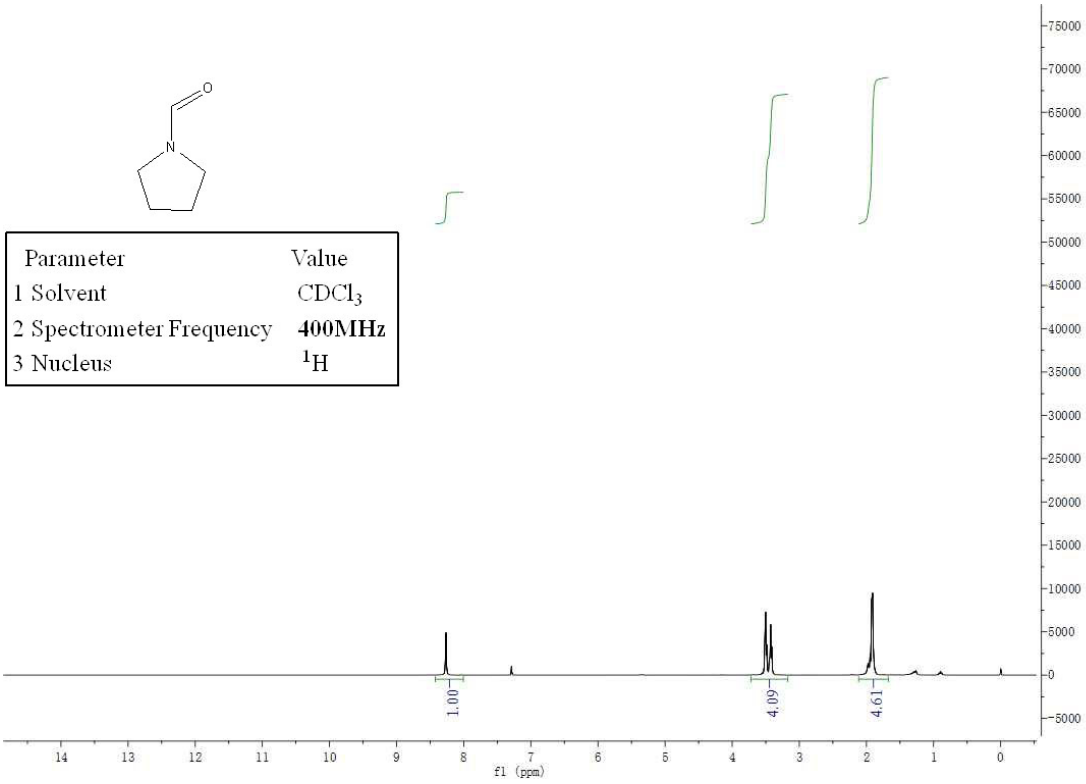
III. NMR spectra of products

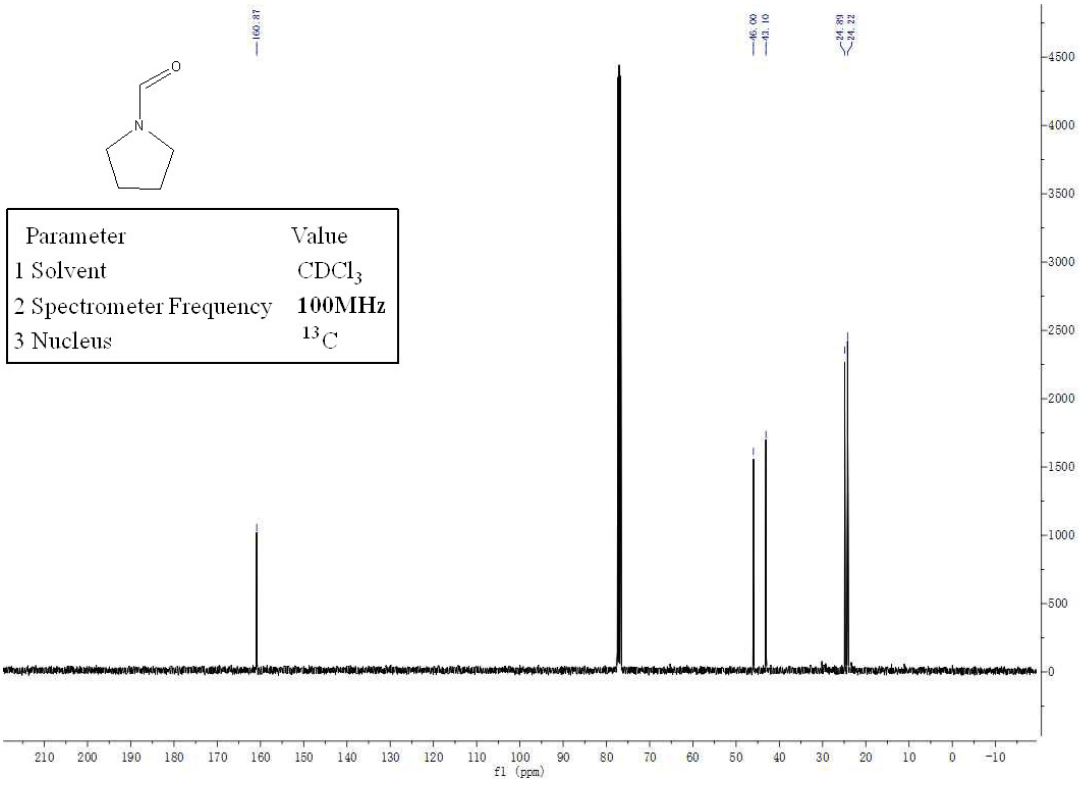
NMR Spectra of compound 1**b**



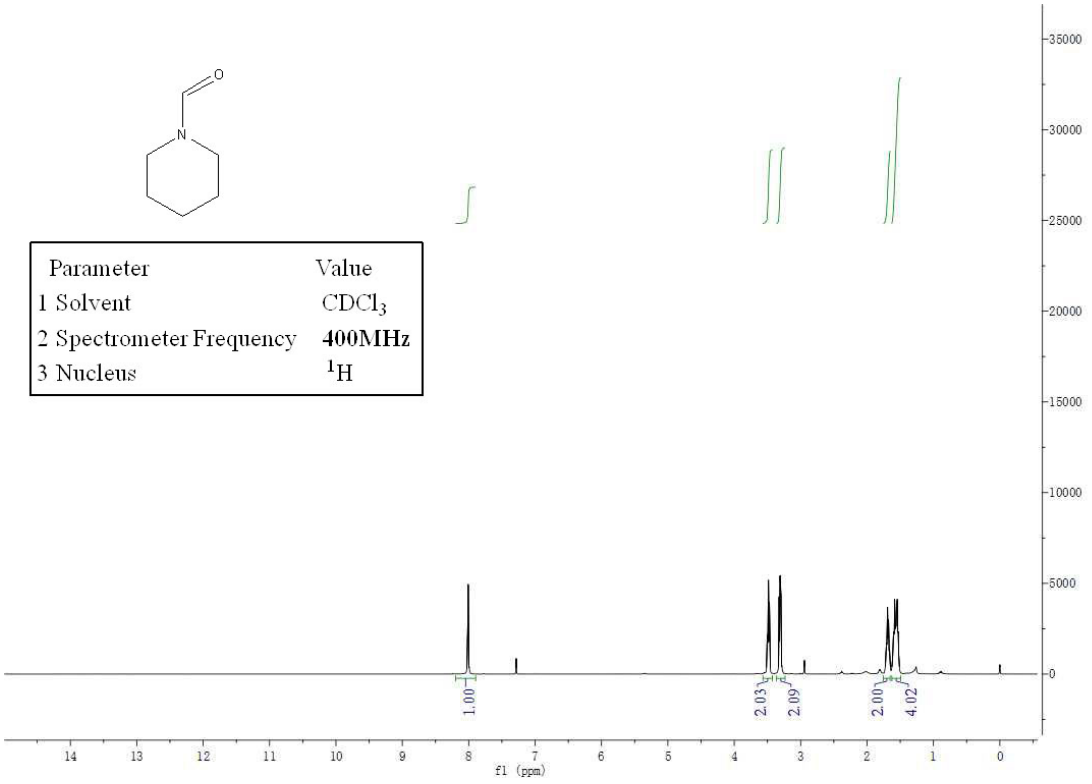


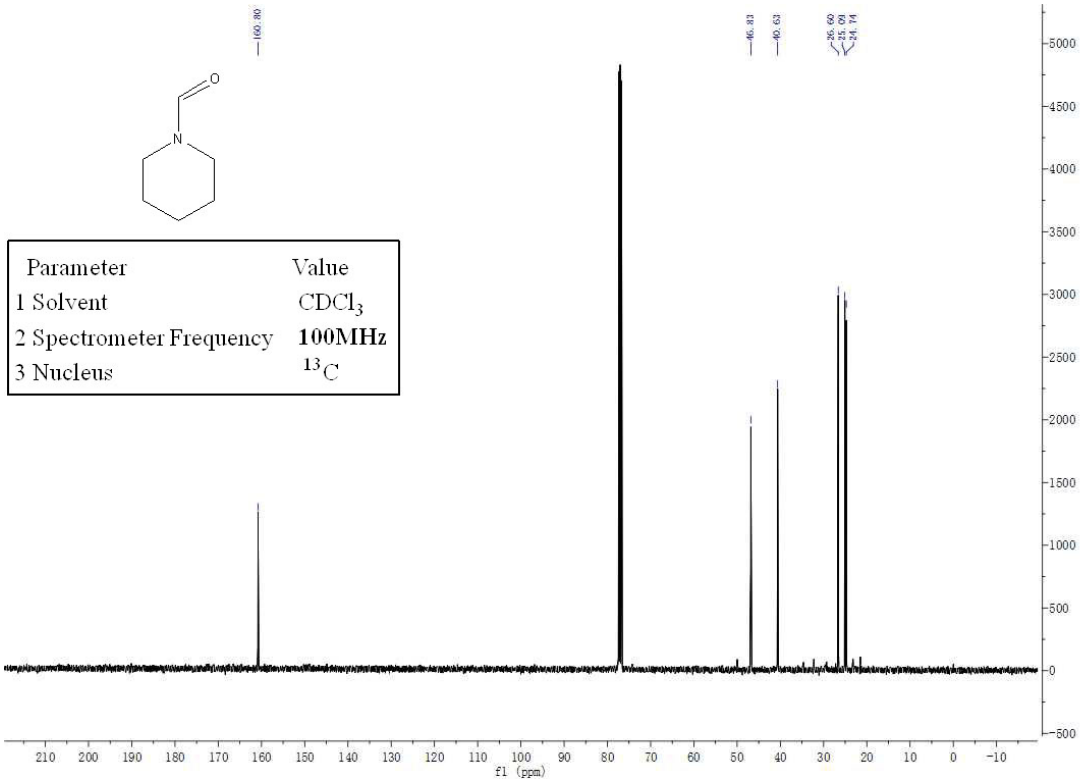
NMR Spectra of compound 2**b**



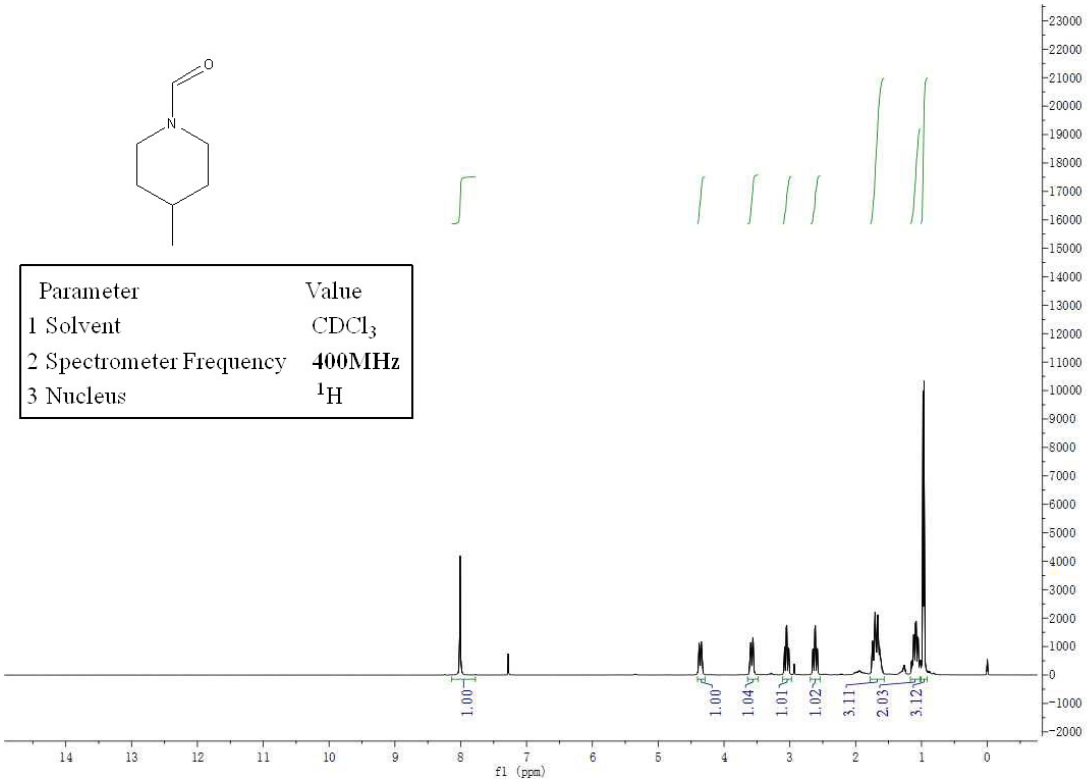


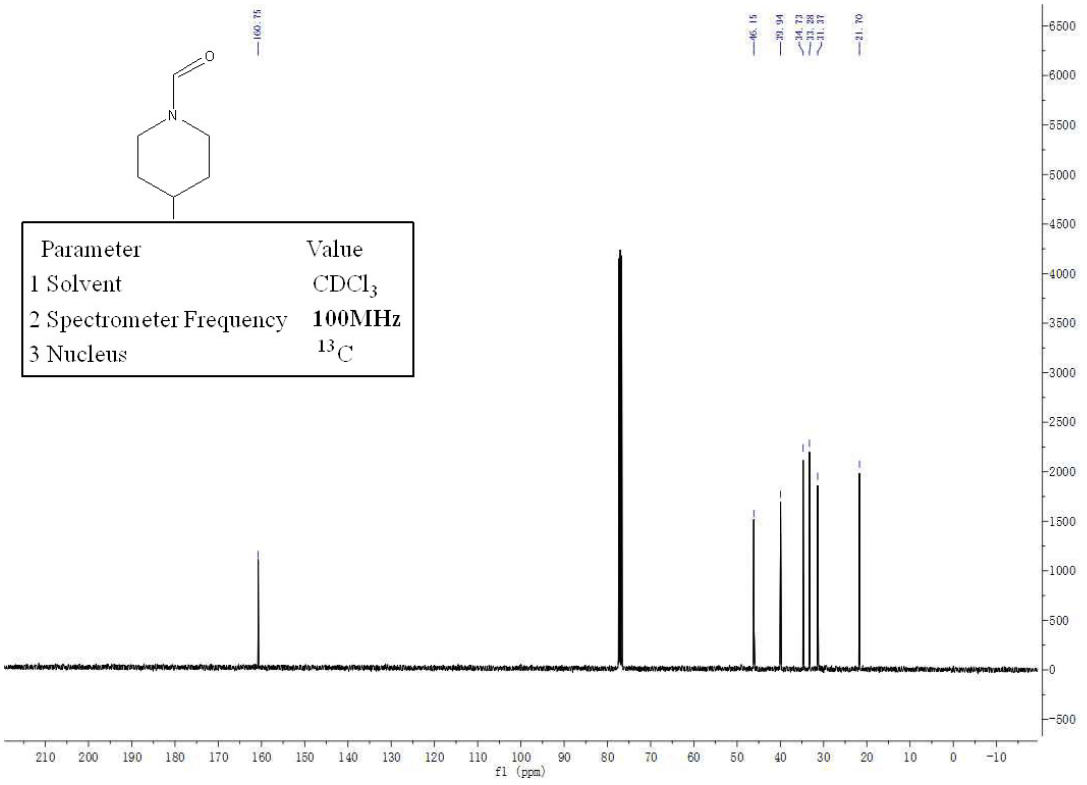
NMR Spectra of compound 3**b**



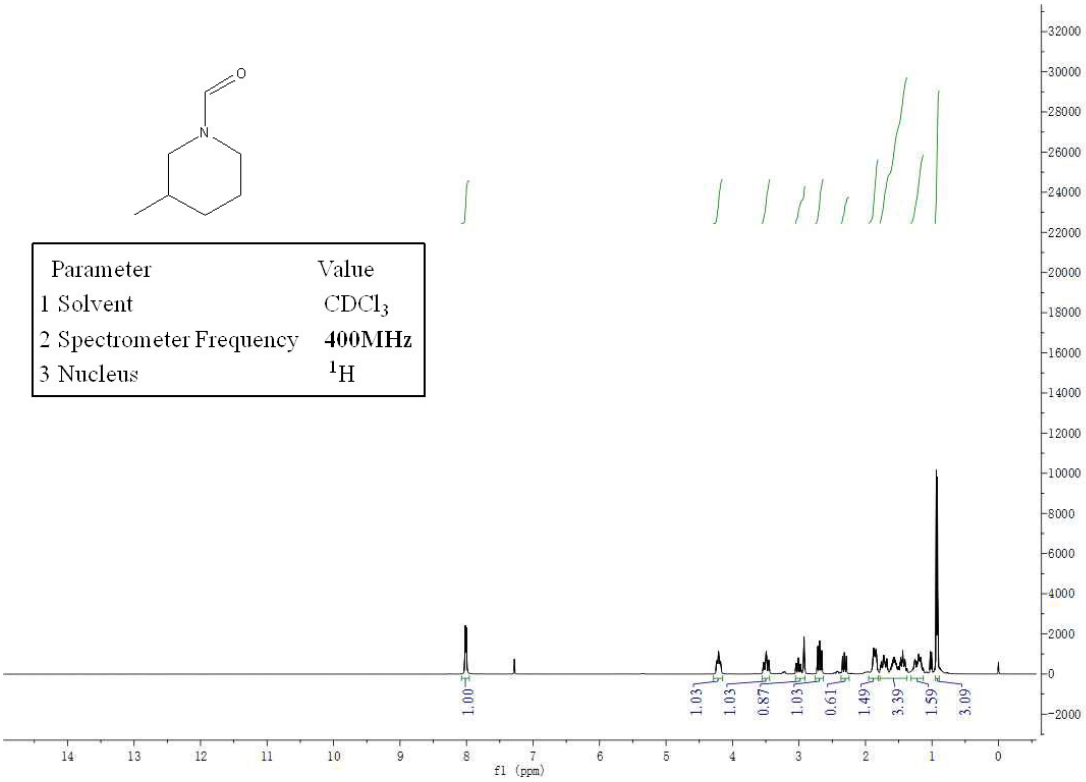


NMR Spectra of 4**b**

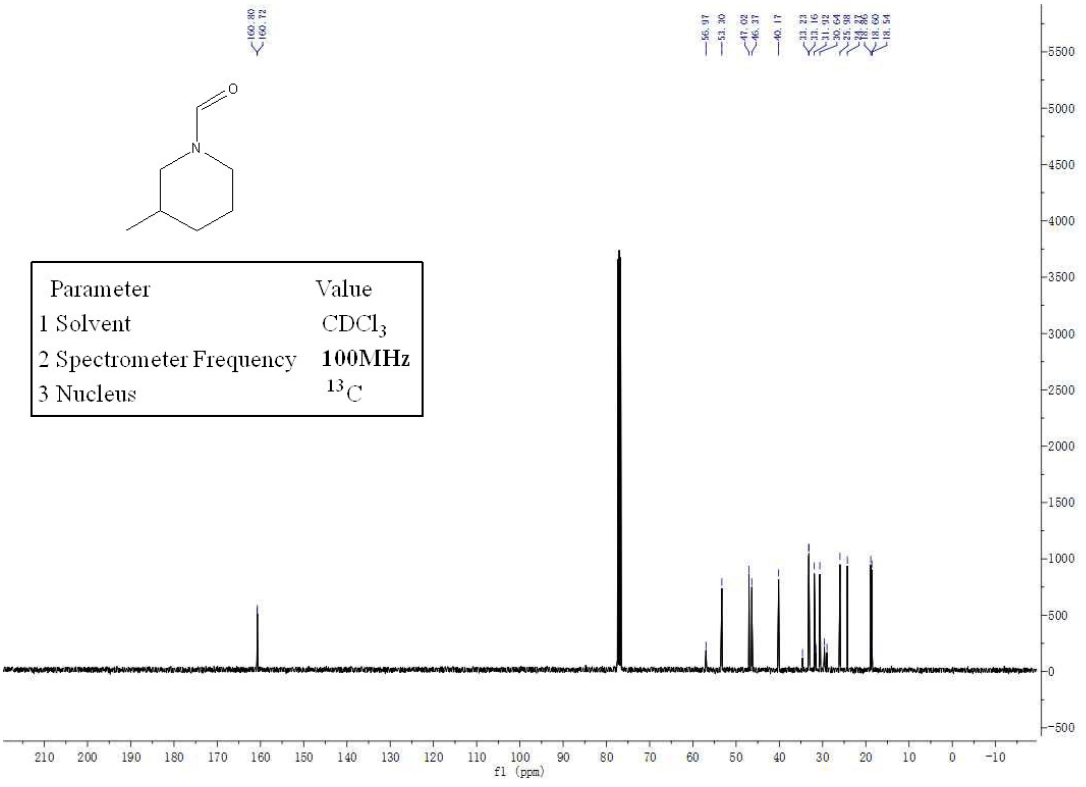




NMR Spectra of 5**b**

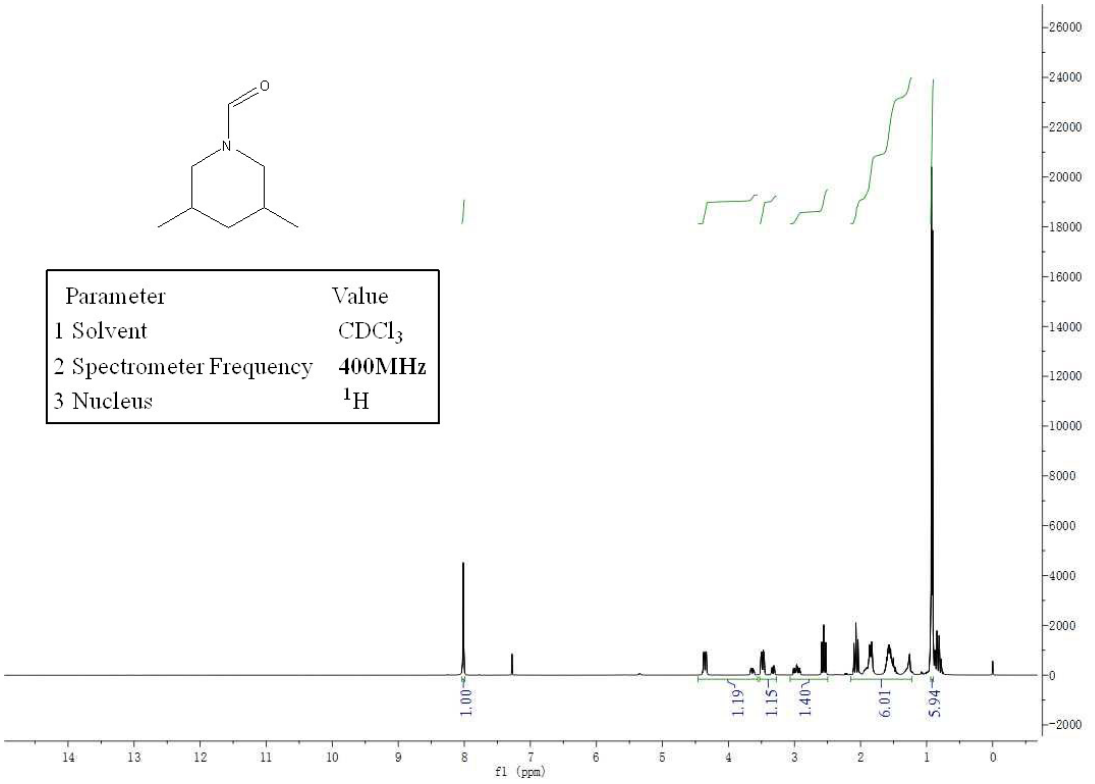


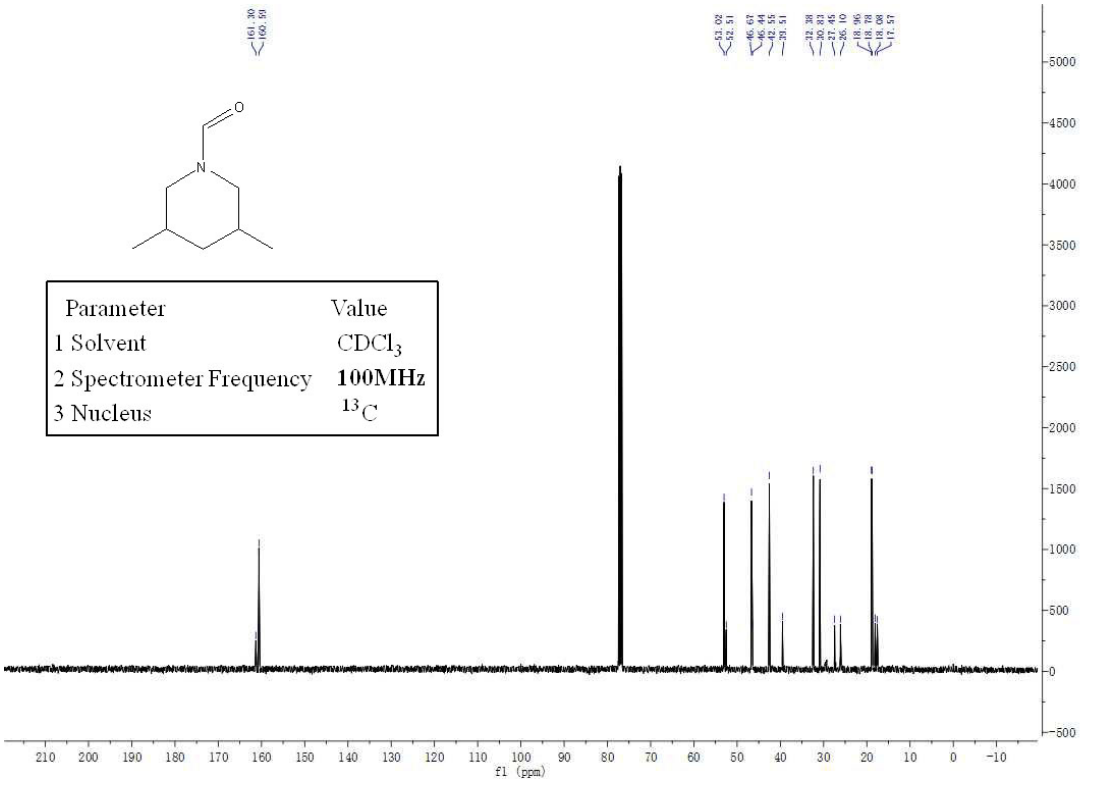
Parameter	Value
1 Solvent	$CDCl_3$
2 Spectrometer Frequency	**400MHz**
3 Nucleus	^{1}H



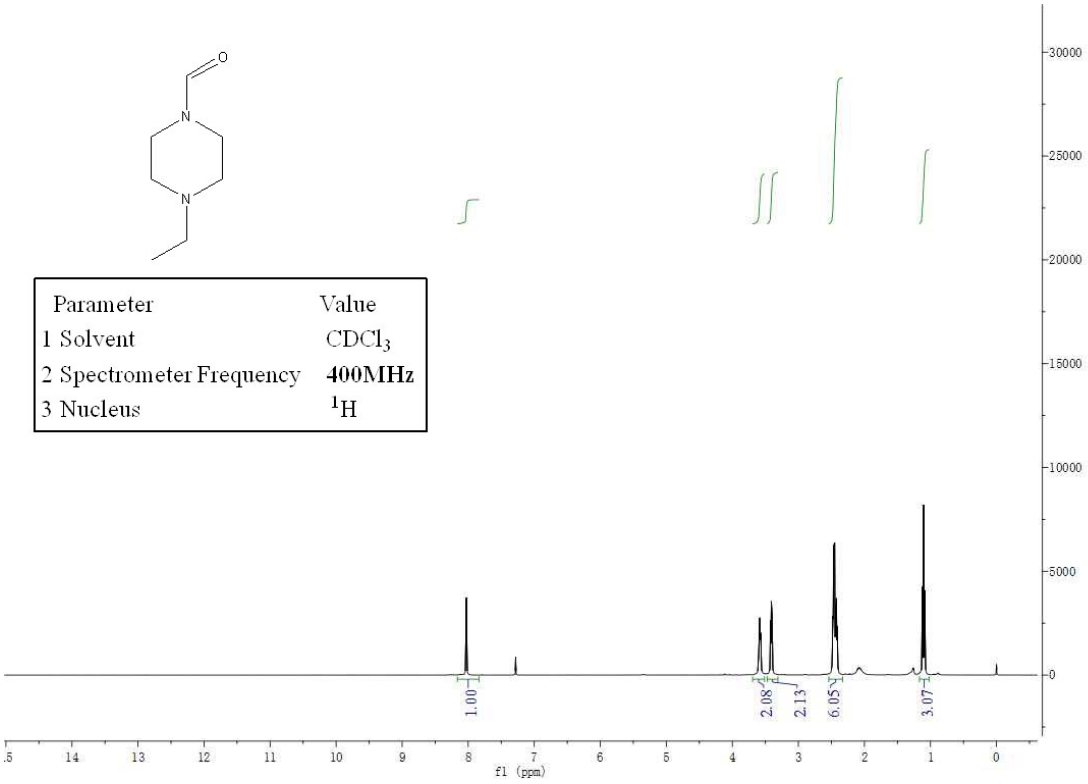
Parameter	Value
1 Solvent	$CDCl_3$
2 Spectrometer Frequency	**100MHz**
3 Nucleus	^{13}C

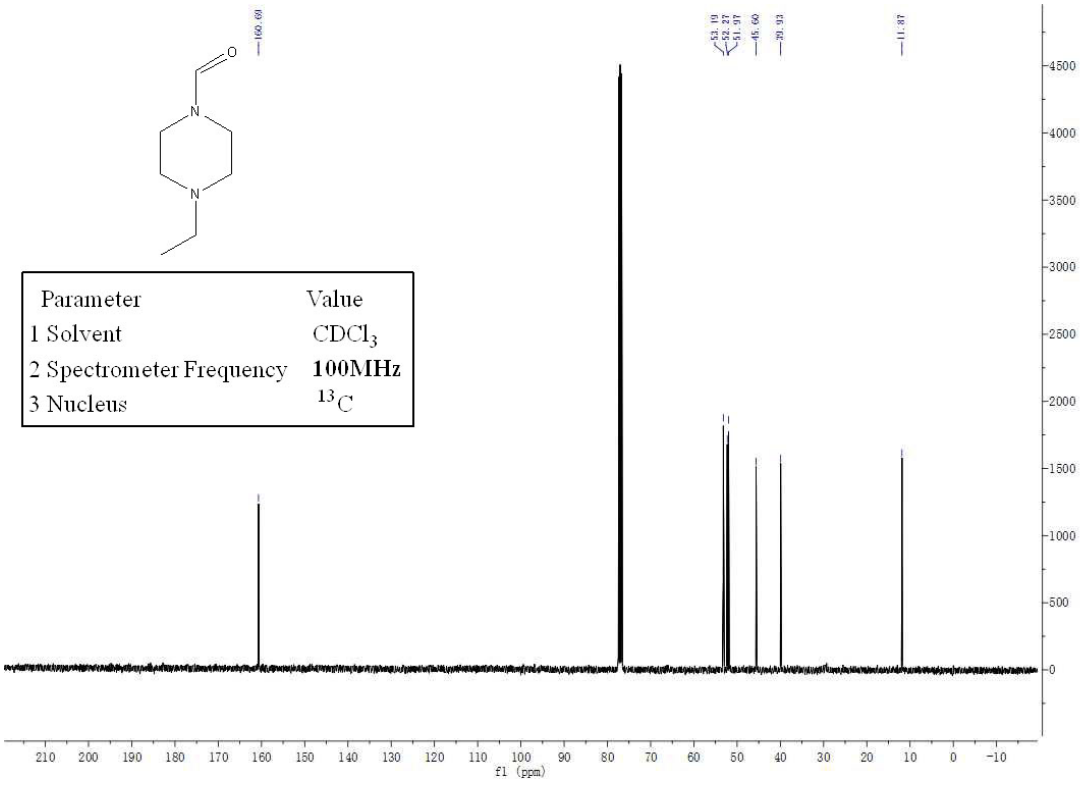
NMR Spectra of 6**b**



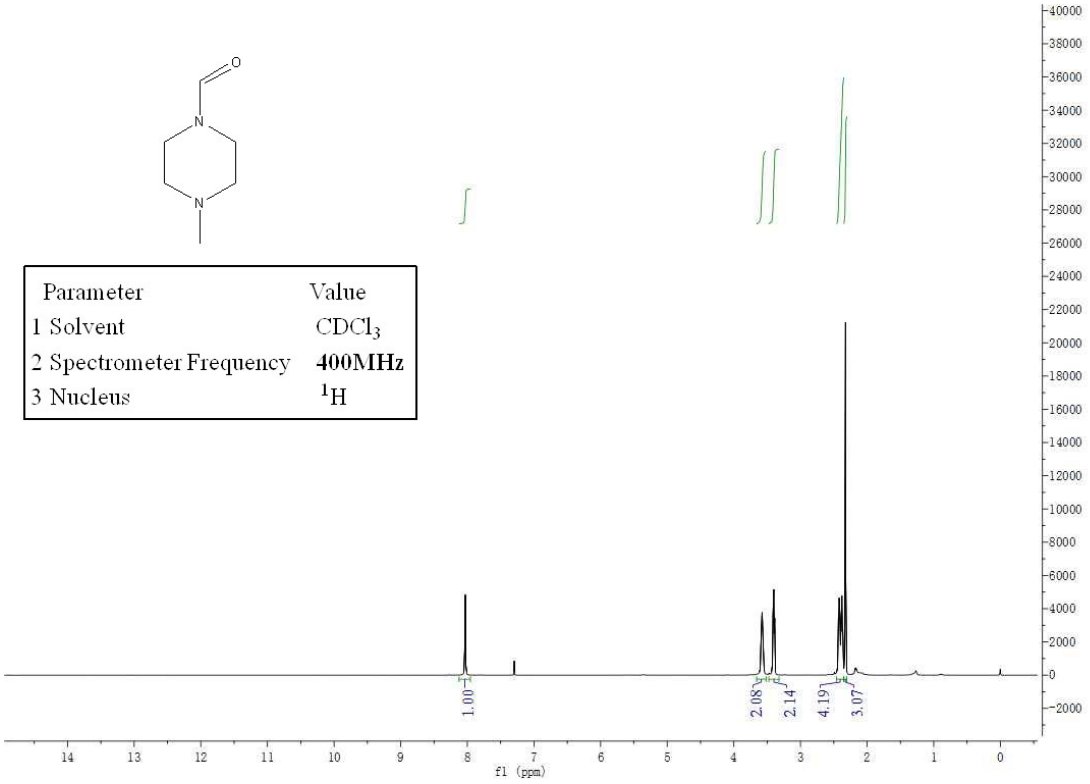


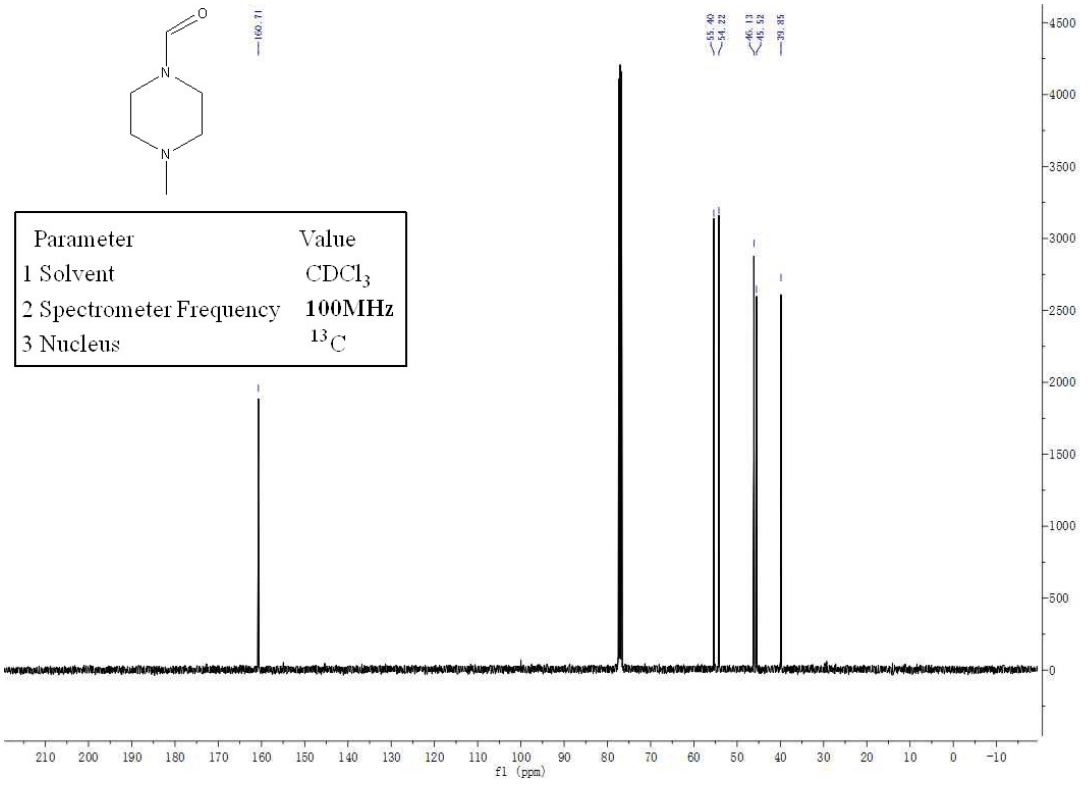
NMR Spectra of 7**b**



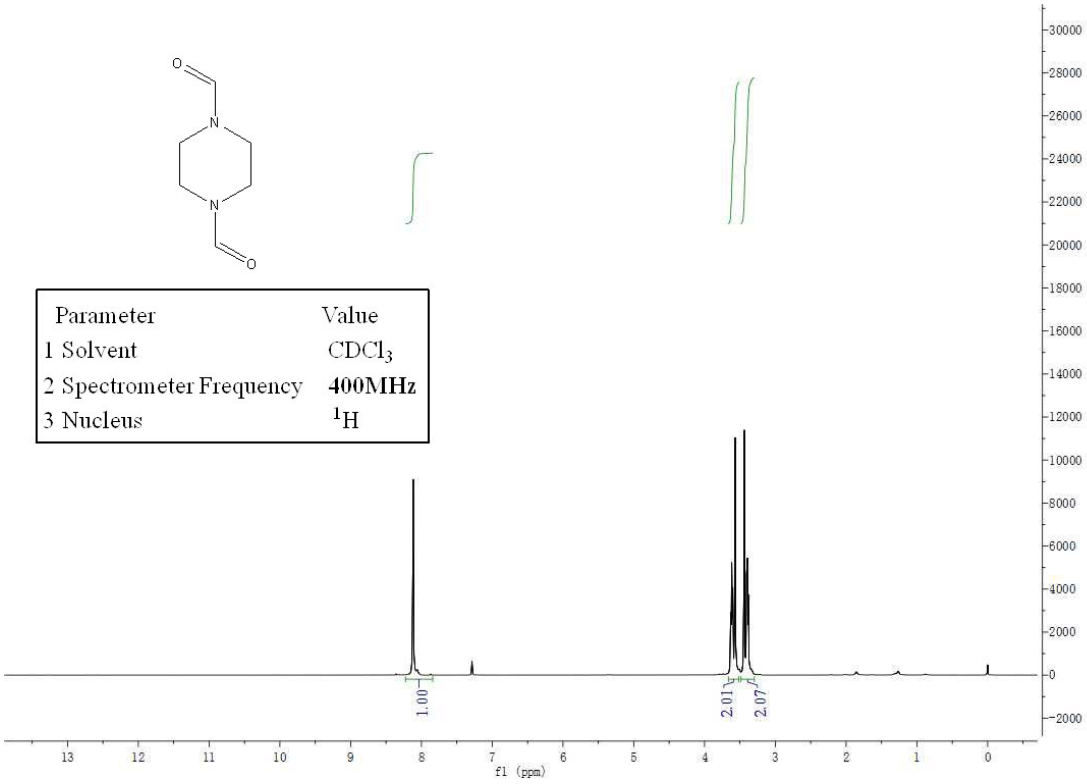


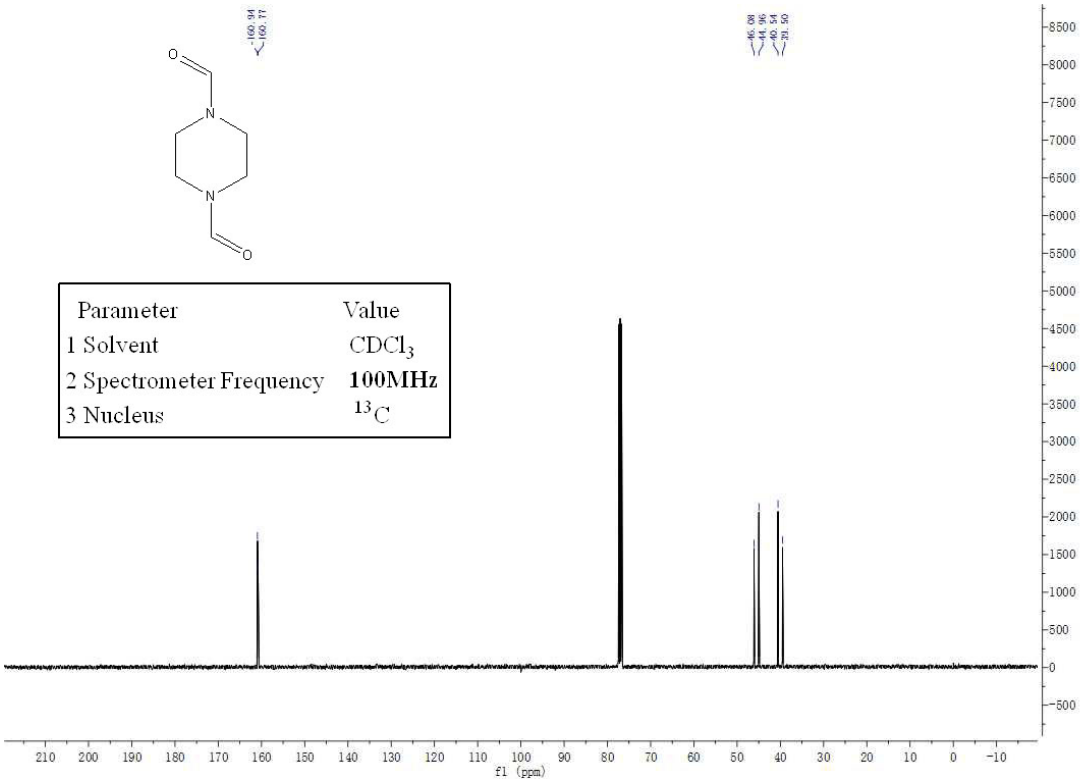
NMR Spectra of 8**b**



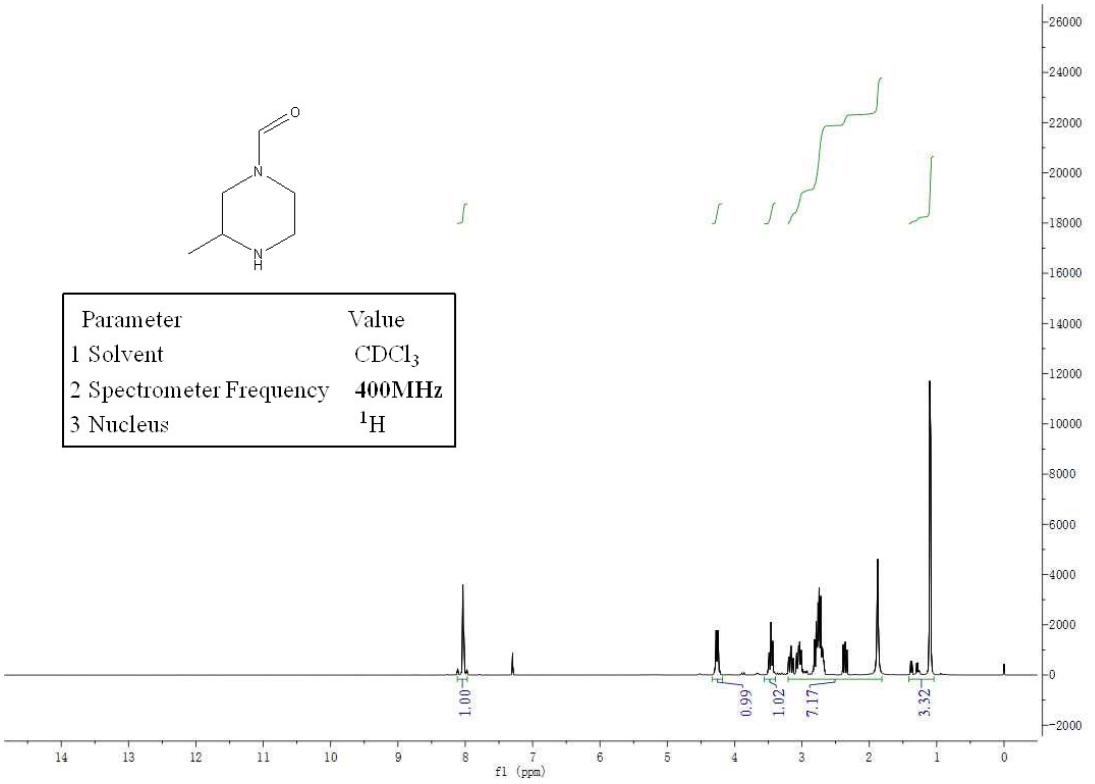


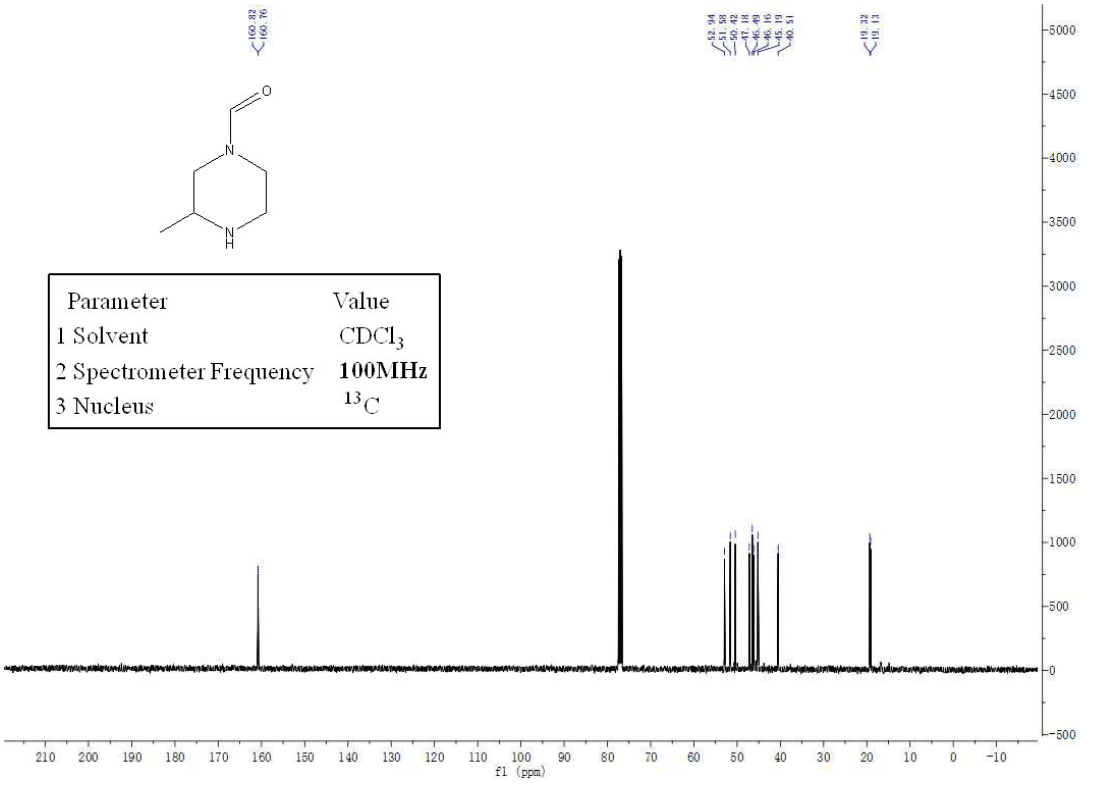
NMR Spectra of 9**b**



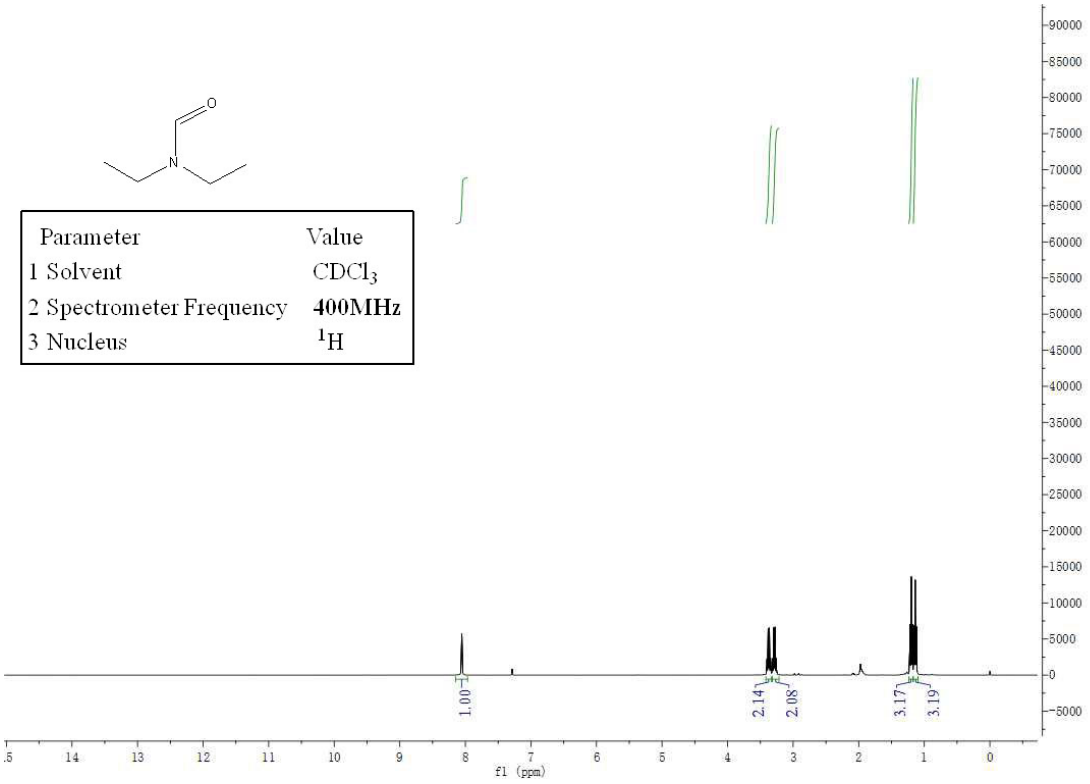


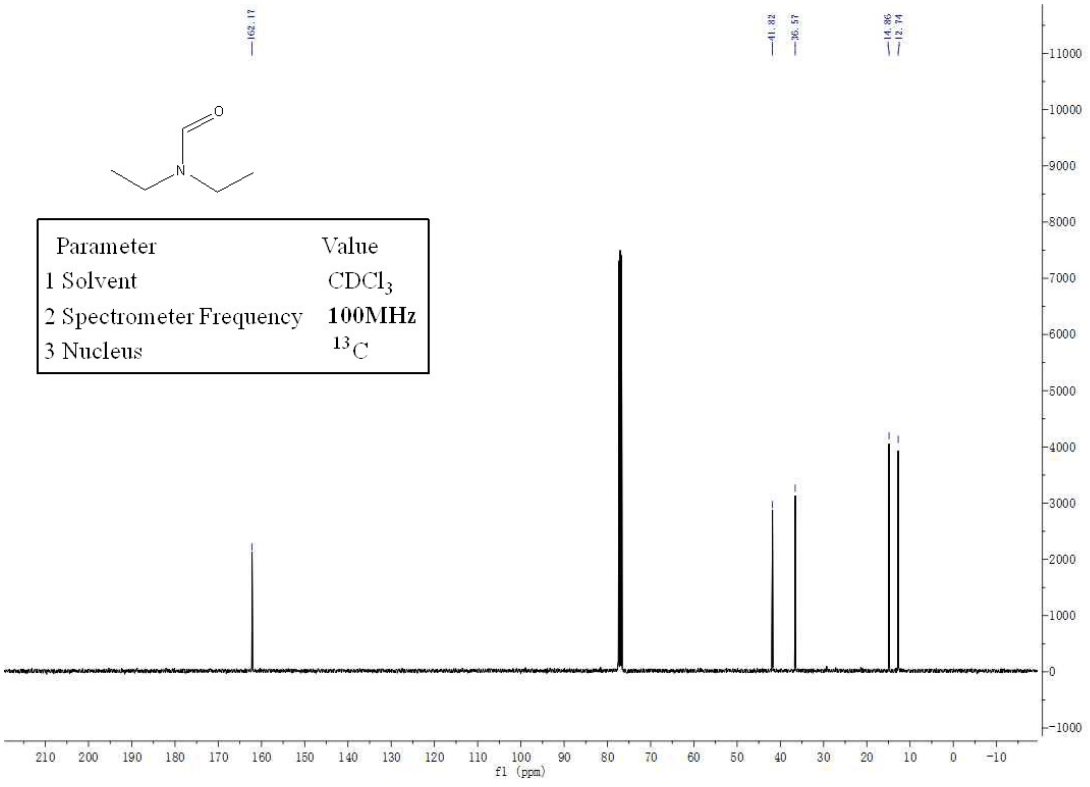
NMR Spectra of 10**b**



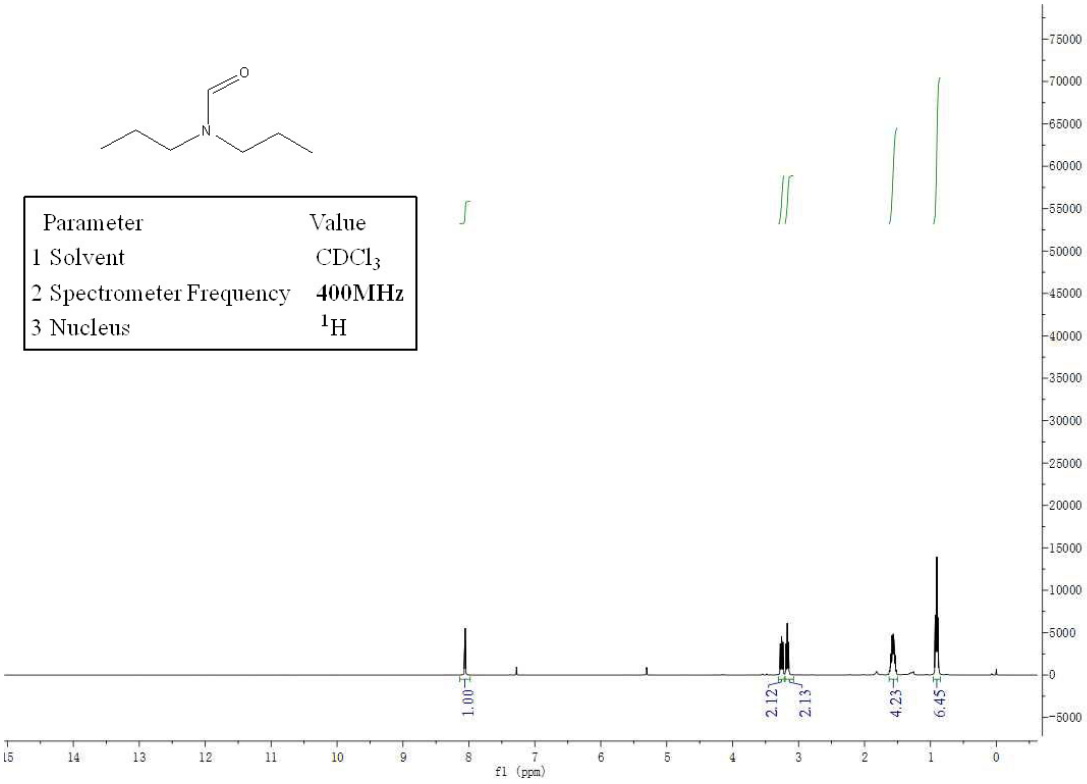


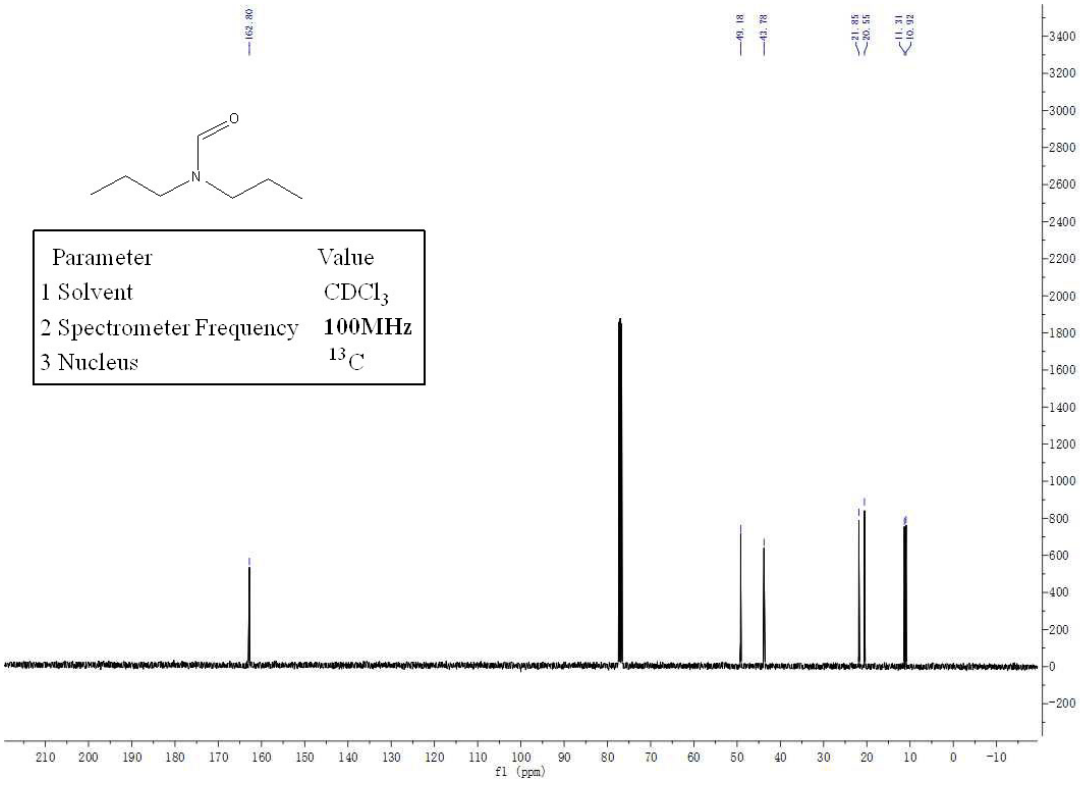
NMR Spectra of 11**b**



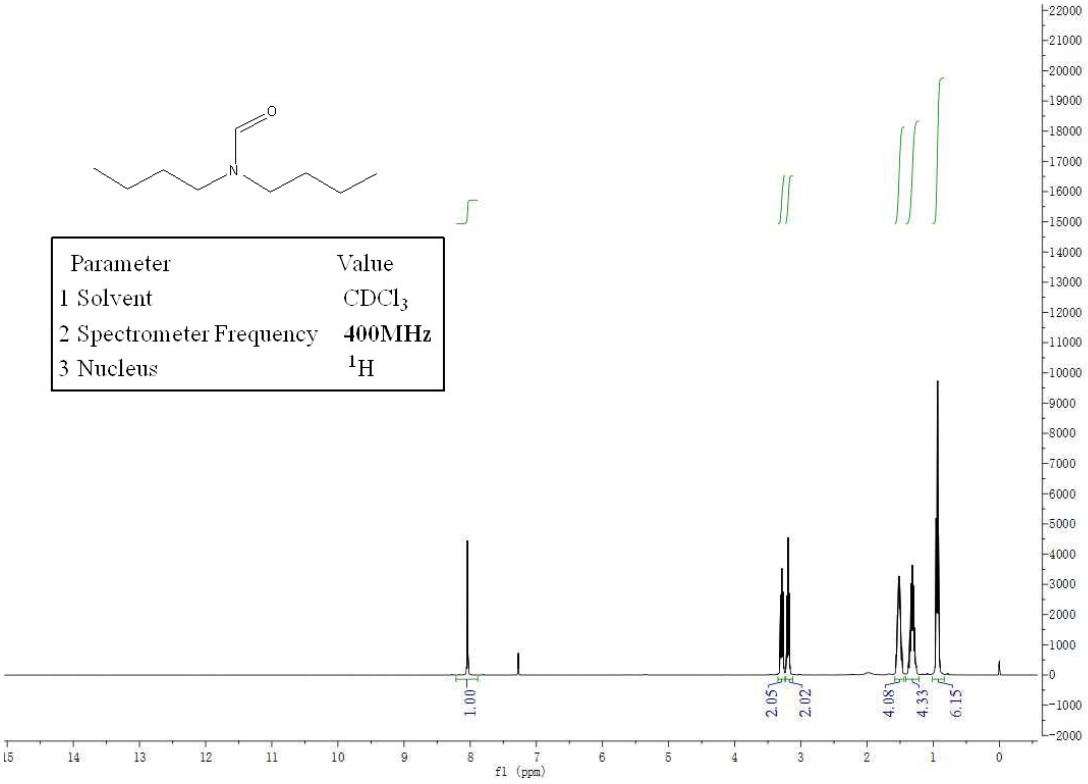


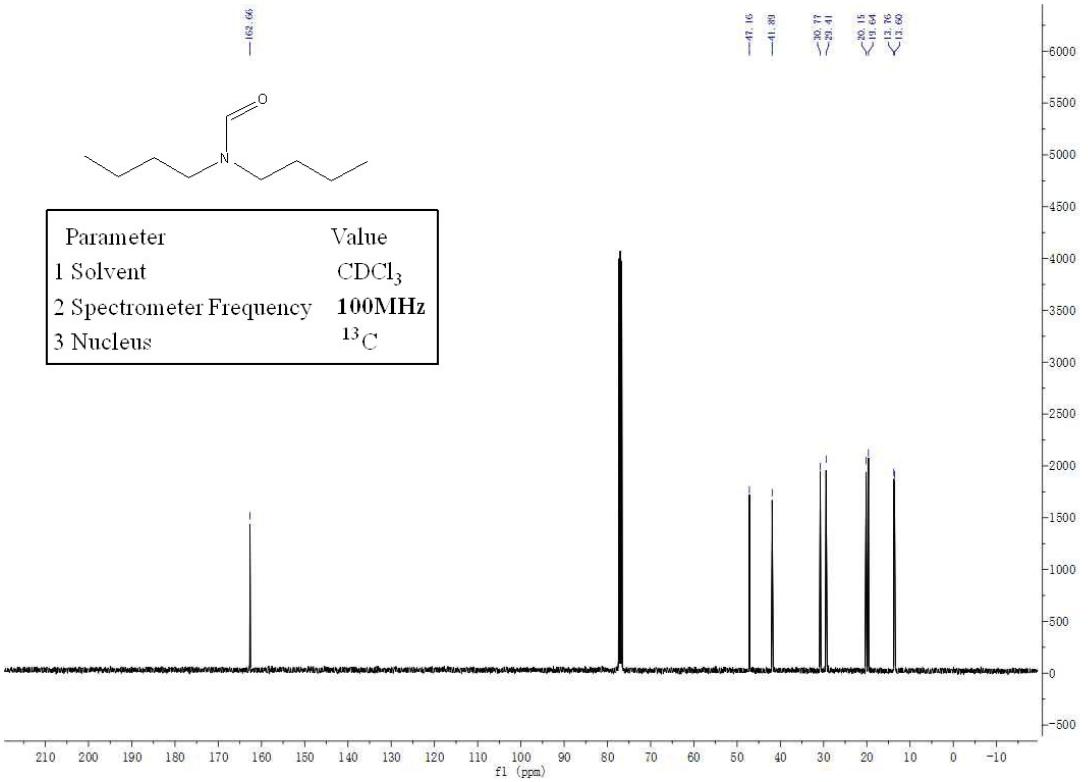
NMR Spectra of 12**b**



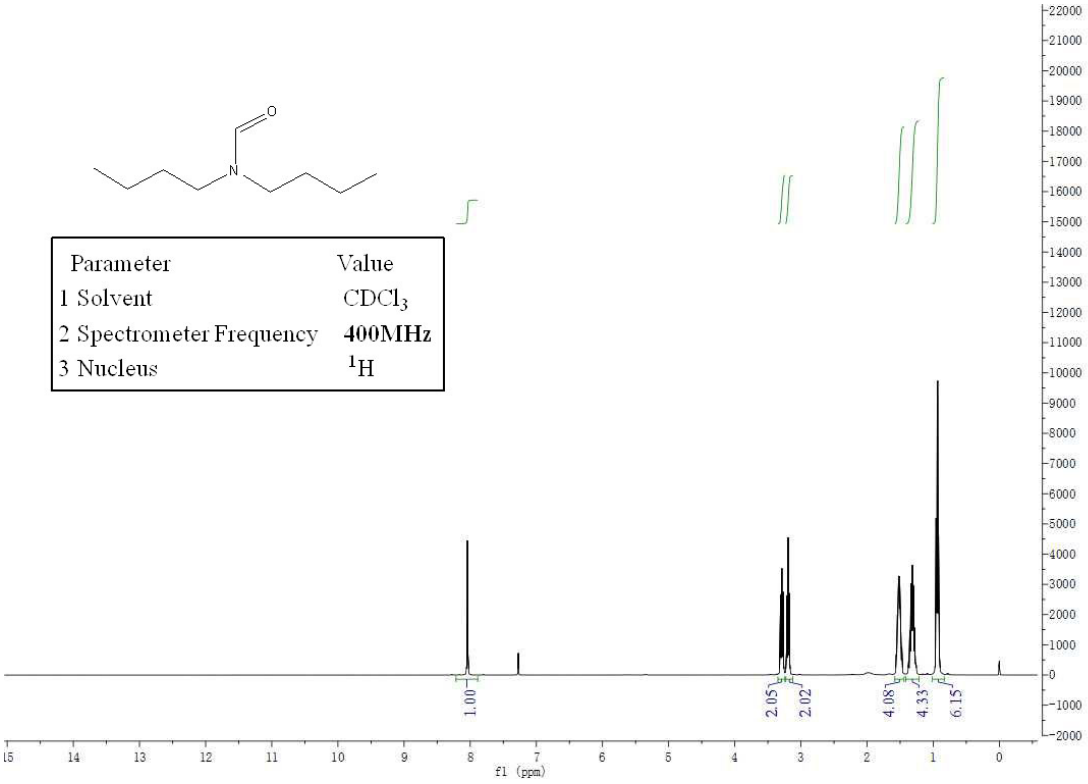


NMR Spectra of 13**b**

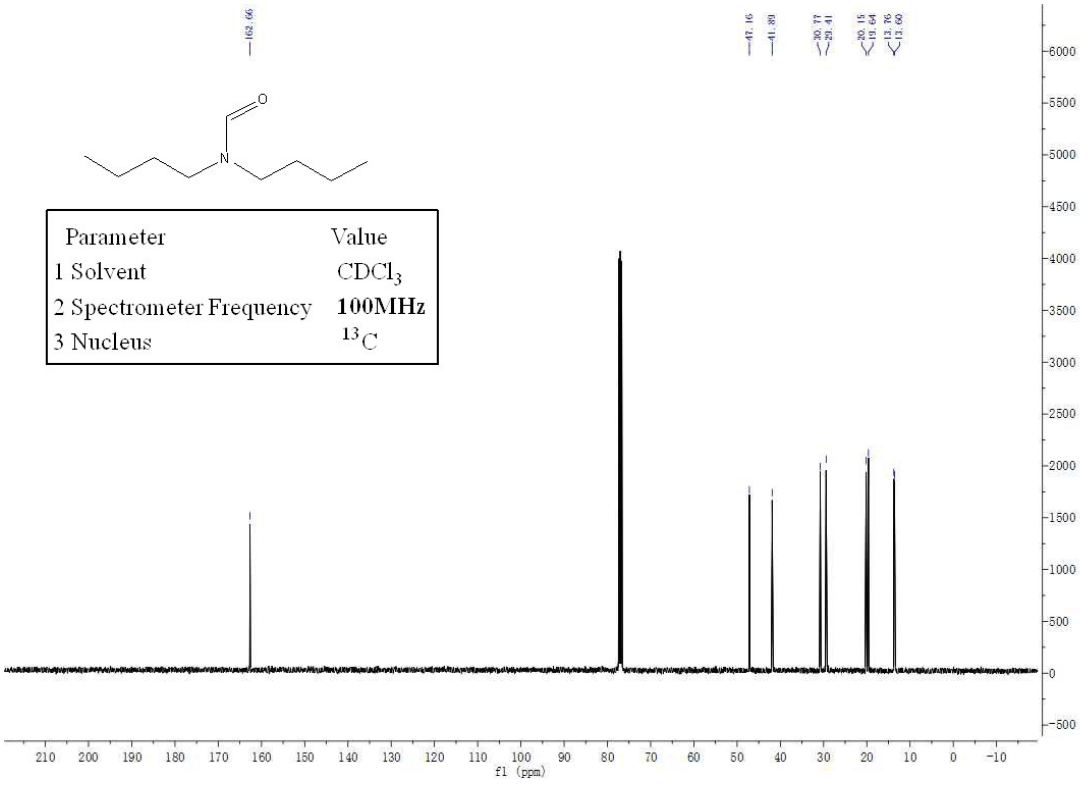




NMR Spectra of 14**b**

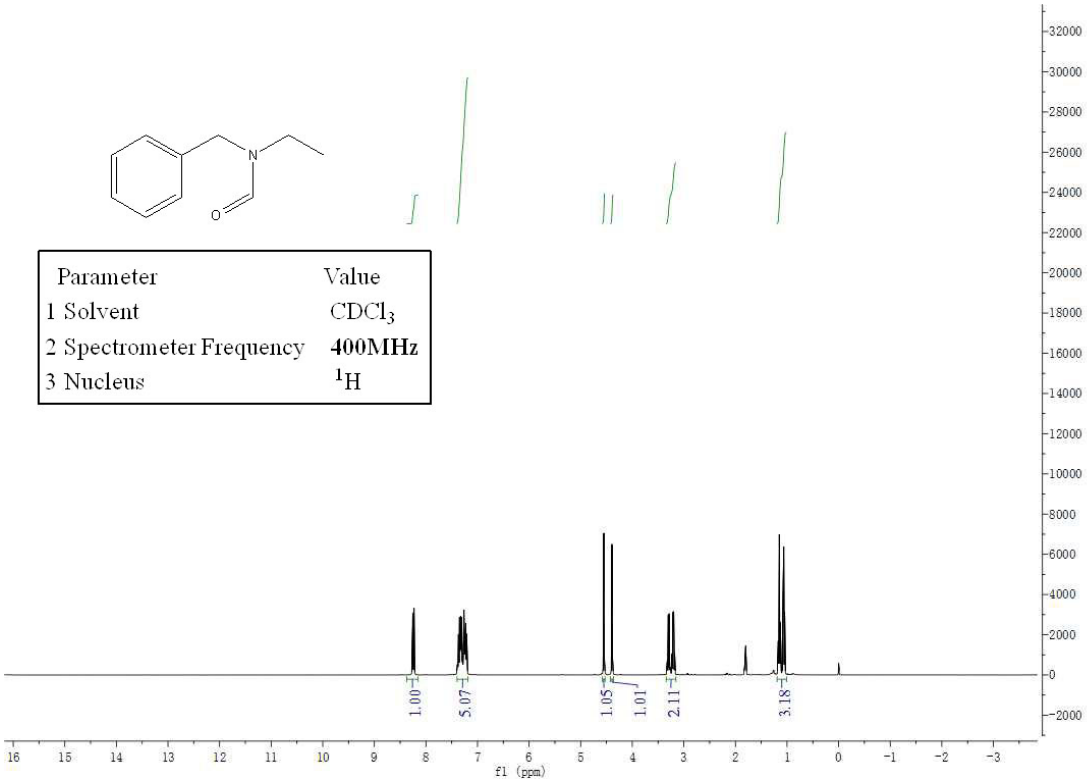


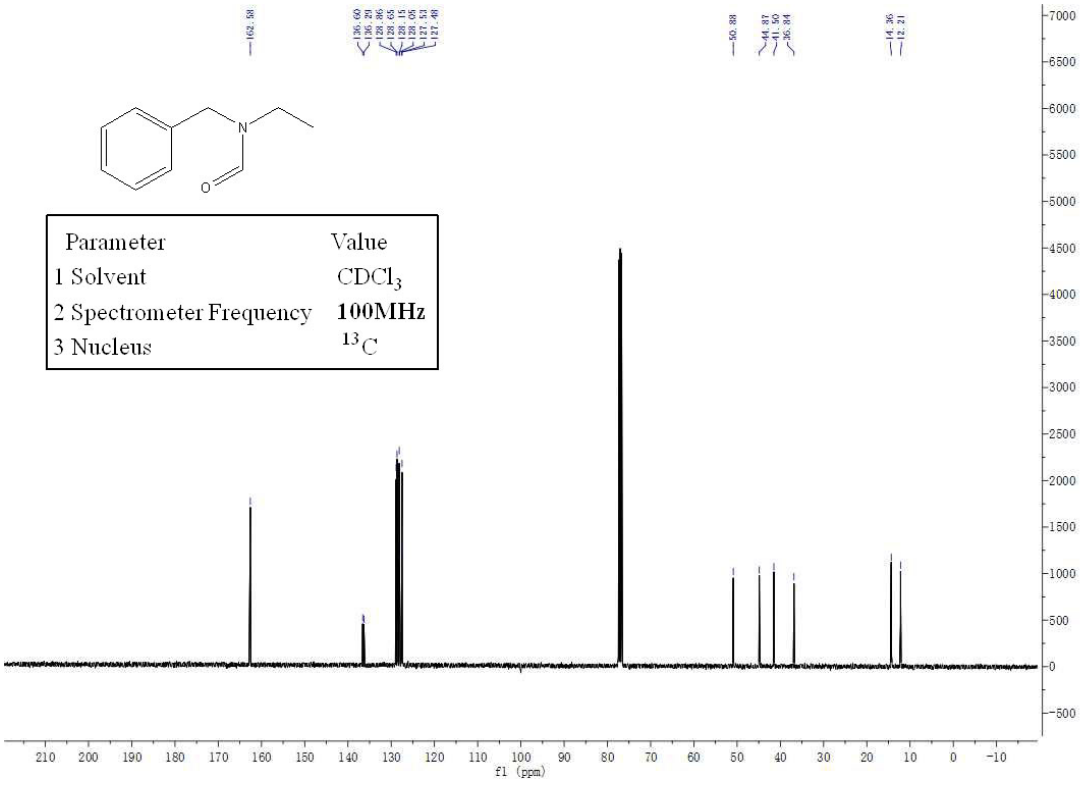
Parameter	Value
1 Solvent	$CDCl_3$
2 Spectrometer Frequency	**400MHz**
3 Nucleus	^{1}H



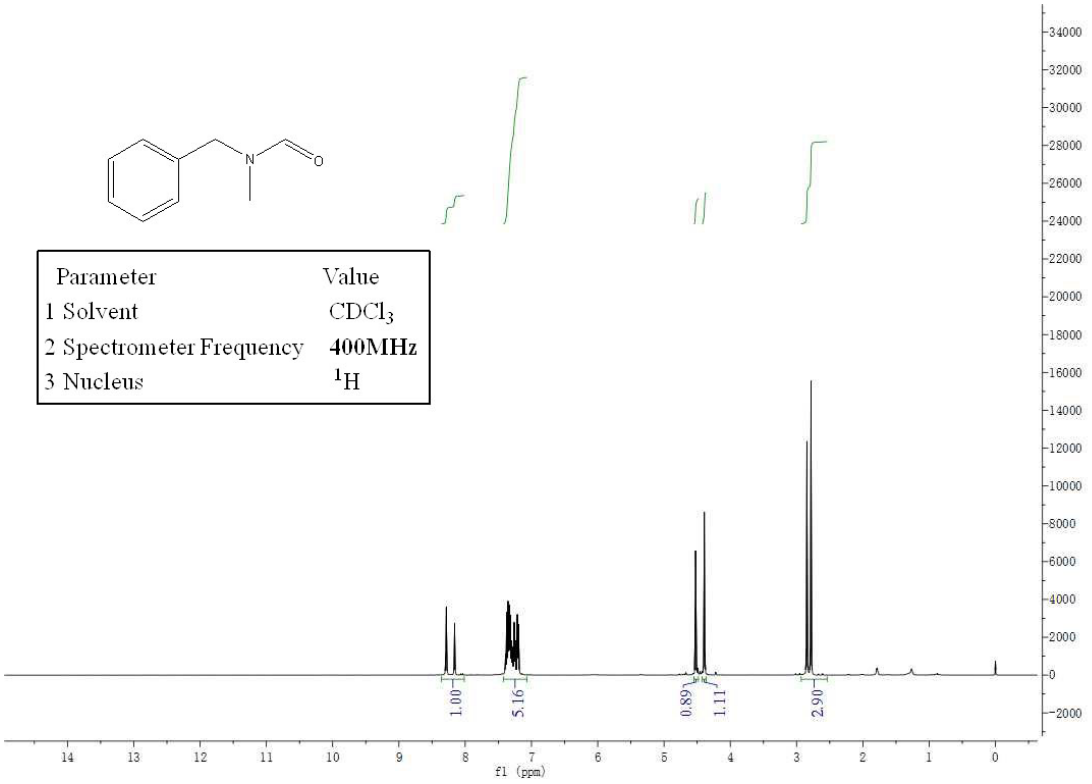
Parameter	Value
1 Solvent	$CDCl_3$
2 Spectrometer Frequency	**100MHz**
3 Nucleus	^{13}C

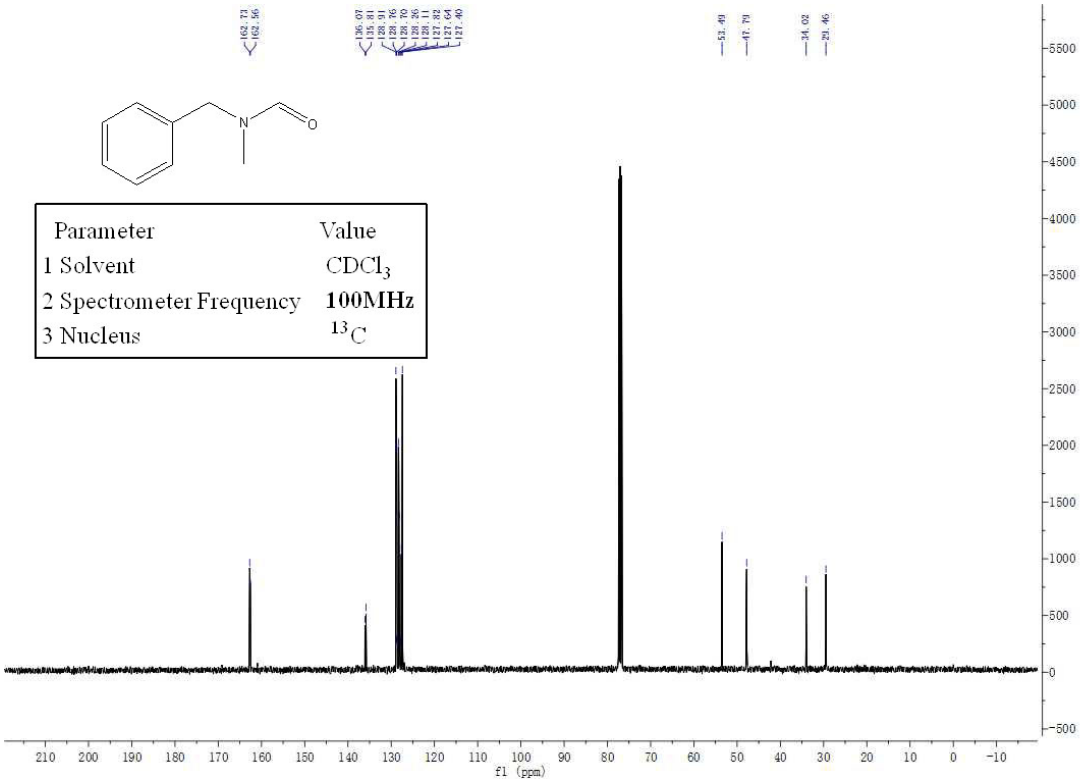
NMR Spectra of 15**b**



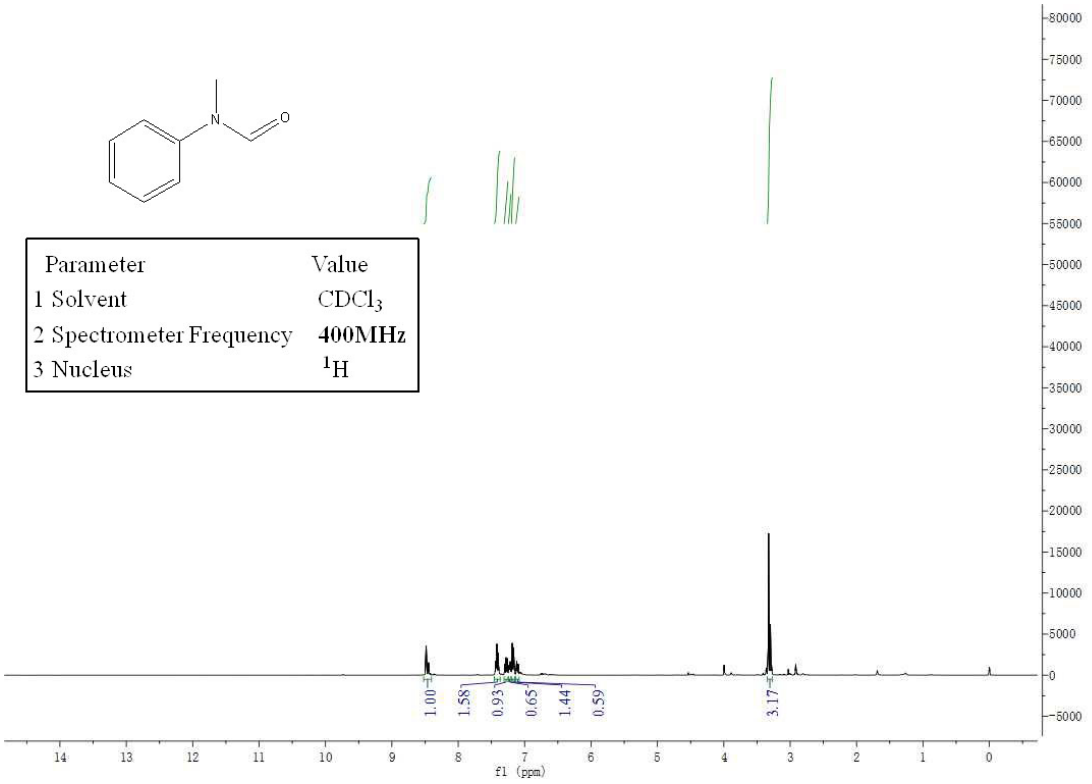


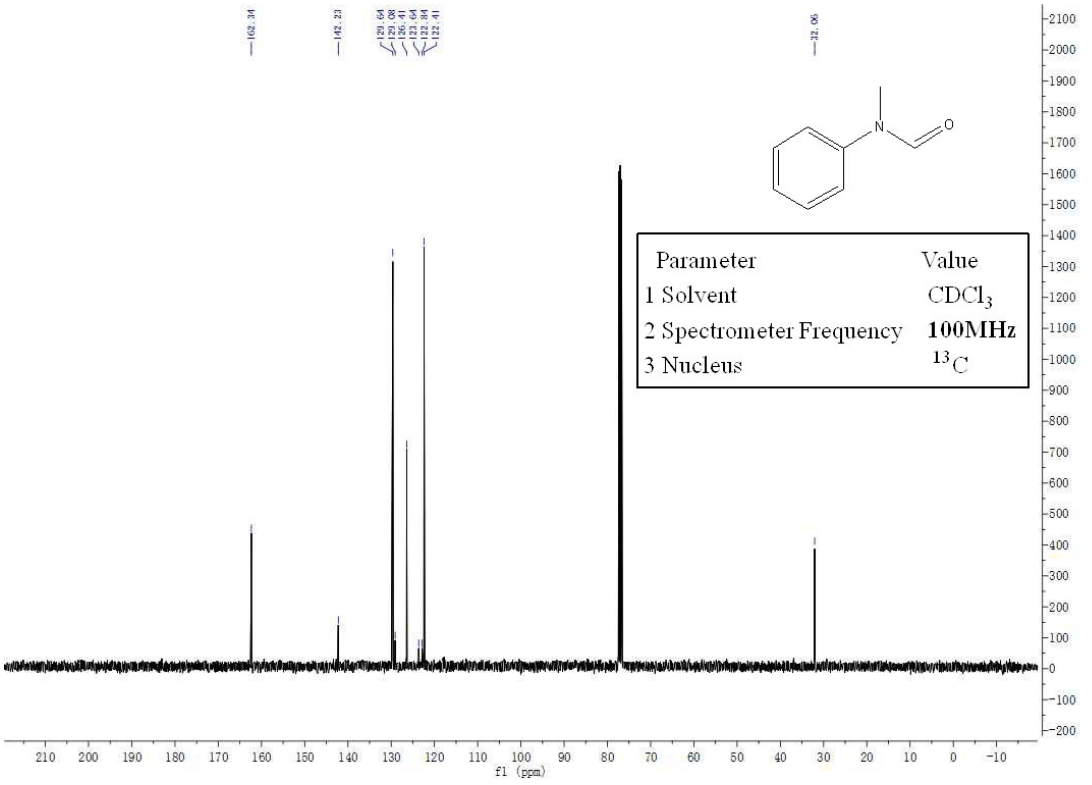
NMR Spectra of 16**b**



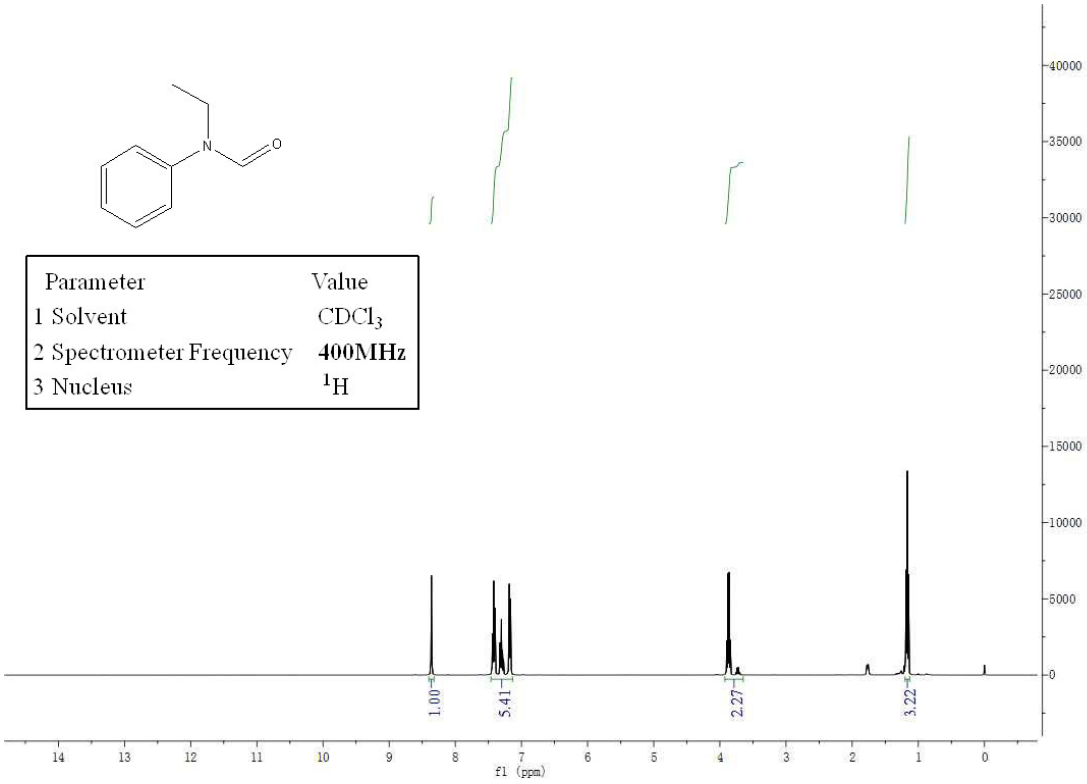


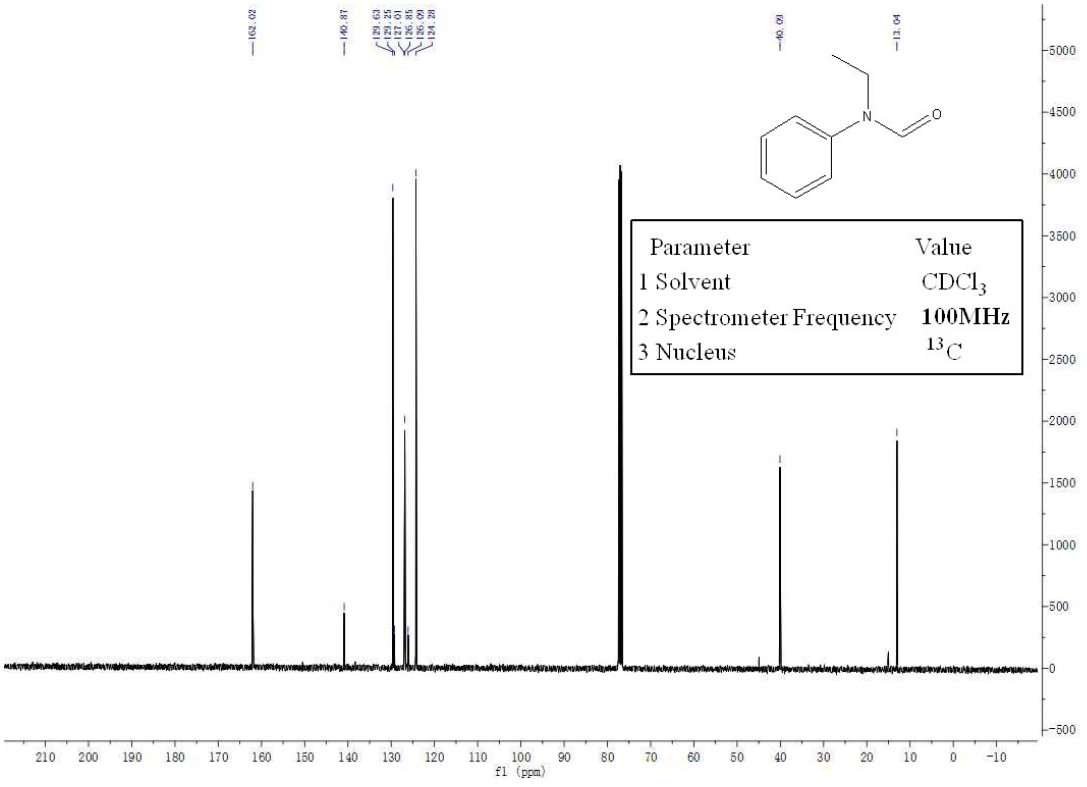
NMR Spectra of 17**b**



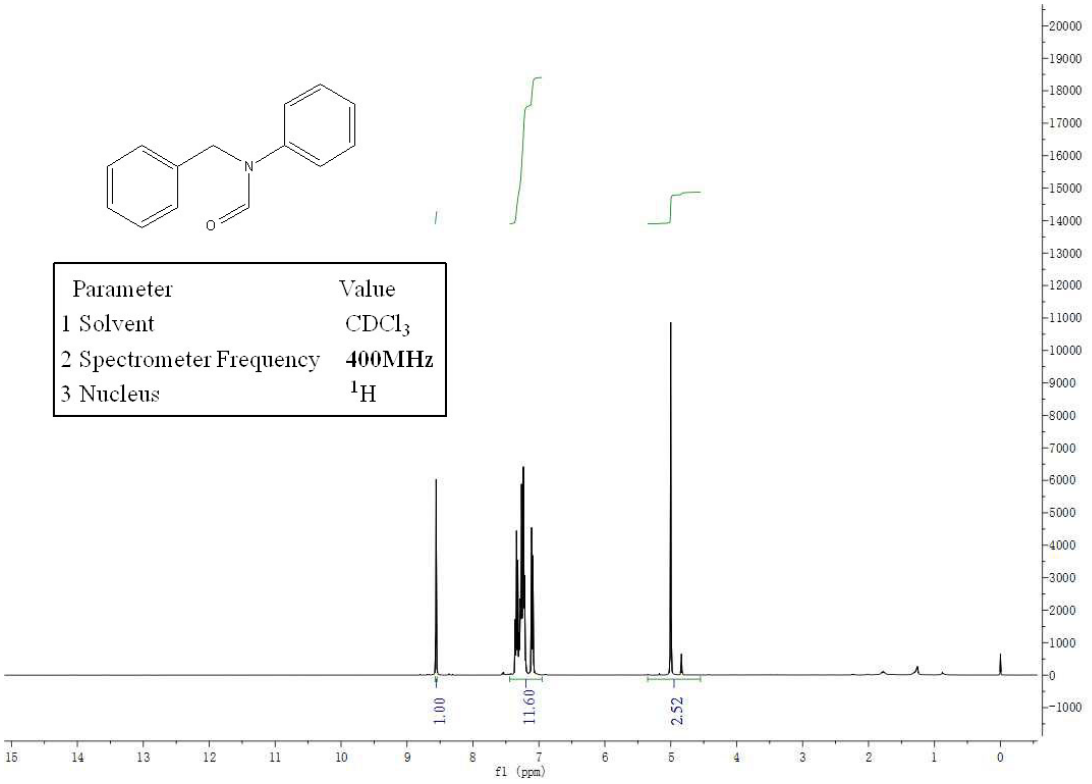


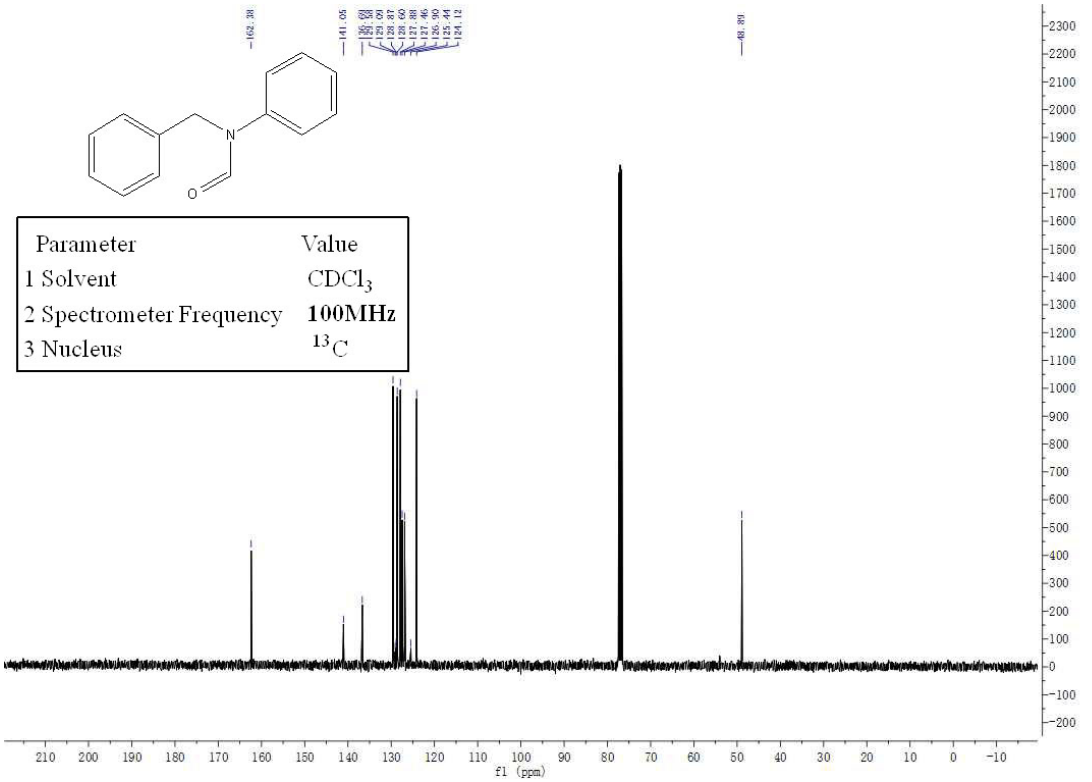
NMR Spectra of 18**b**



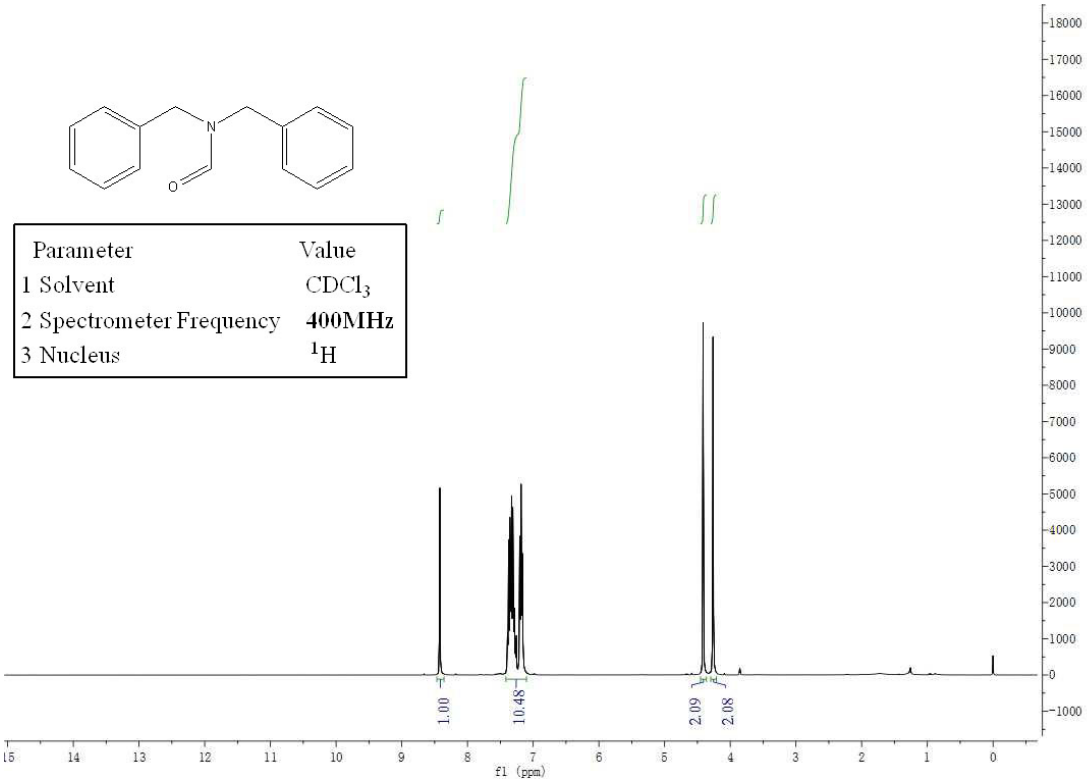


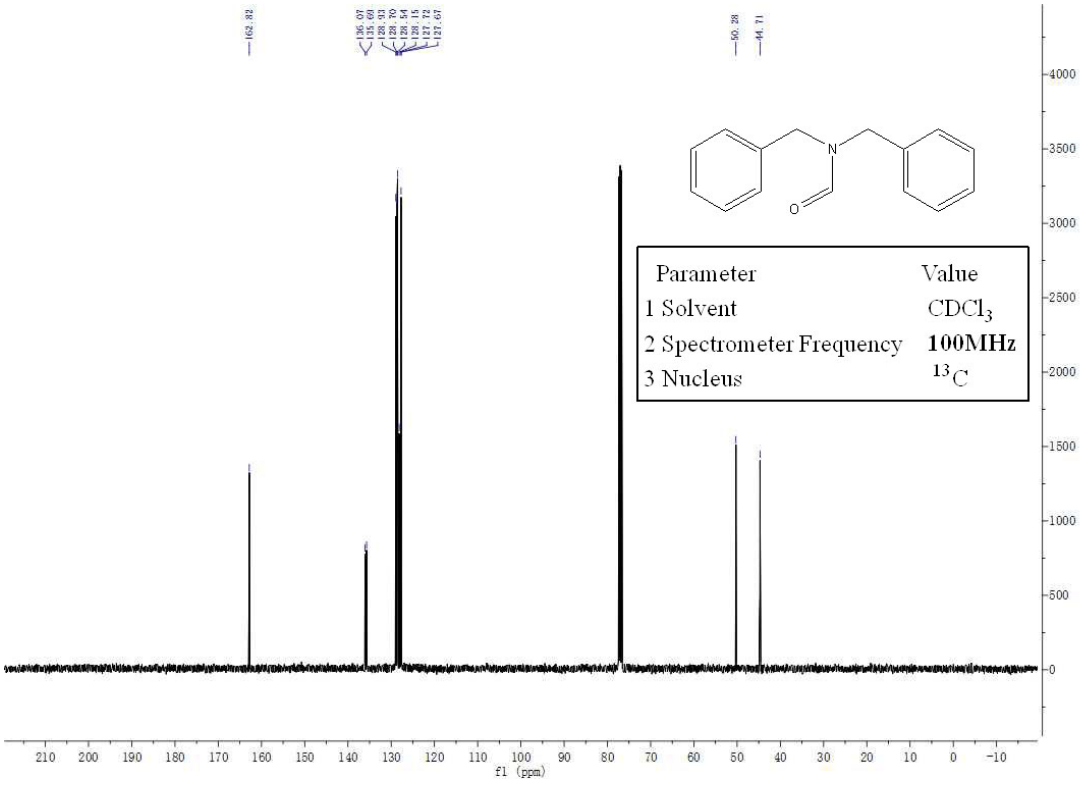
NMR Spectra of 19**b**



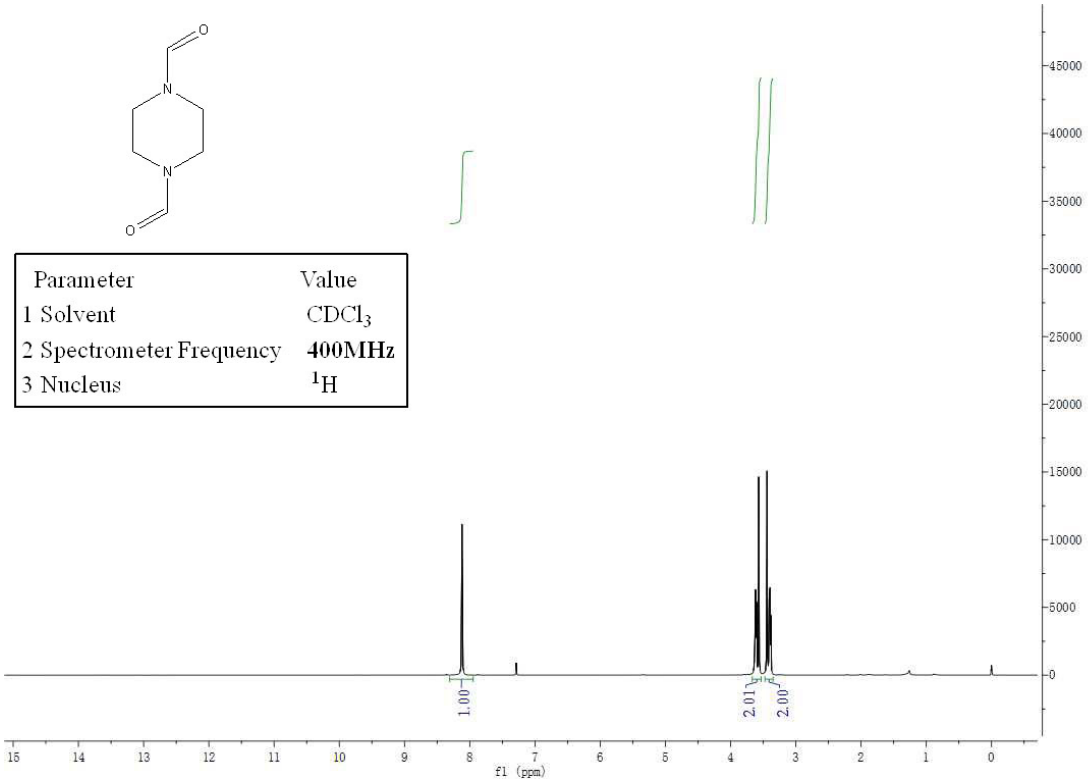


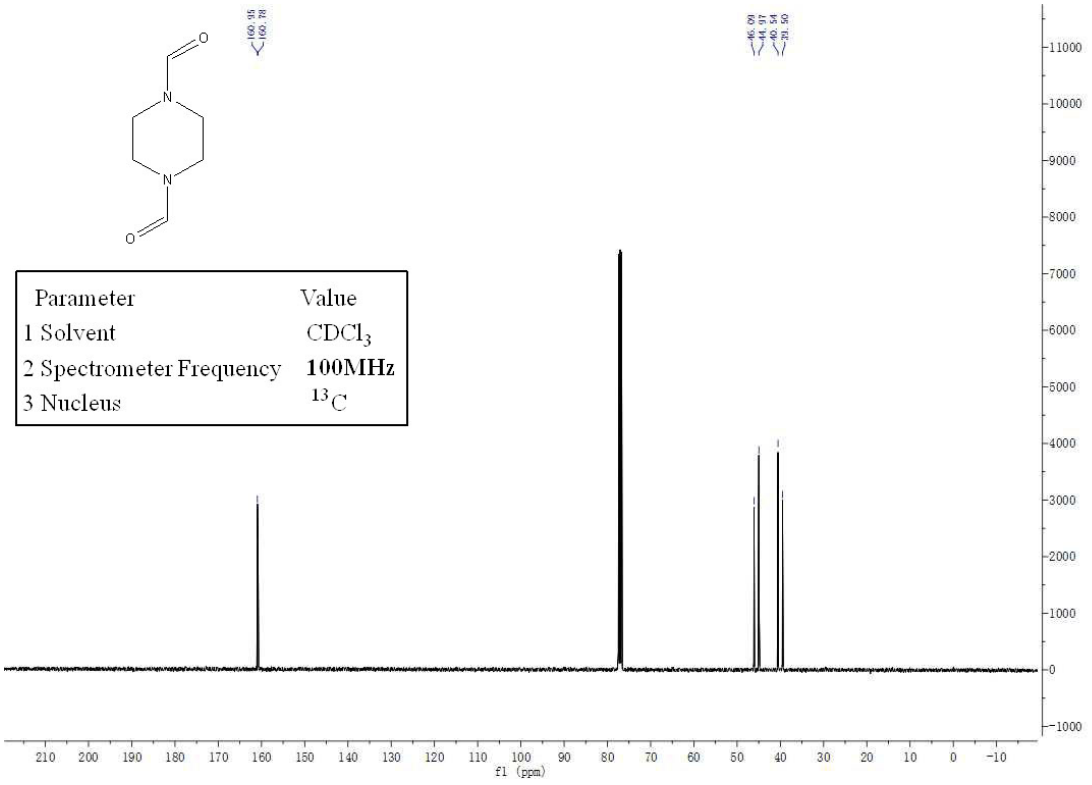
NMR Spectra of 20**b**



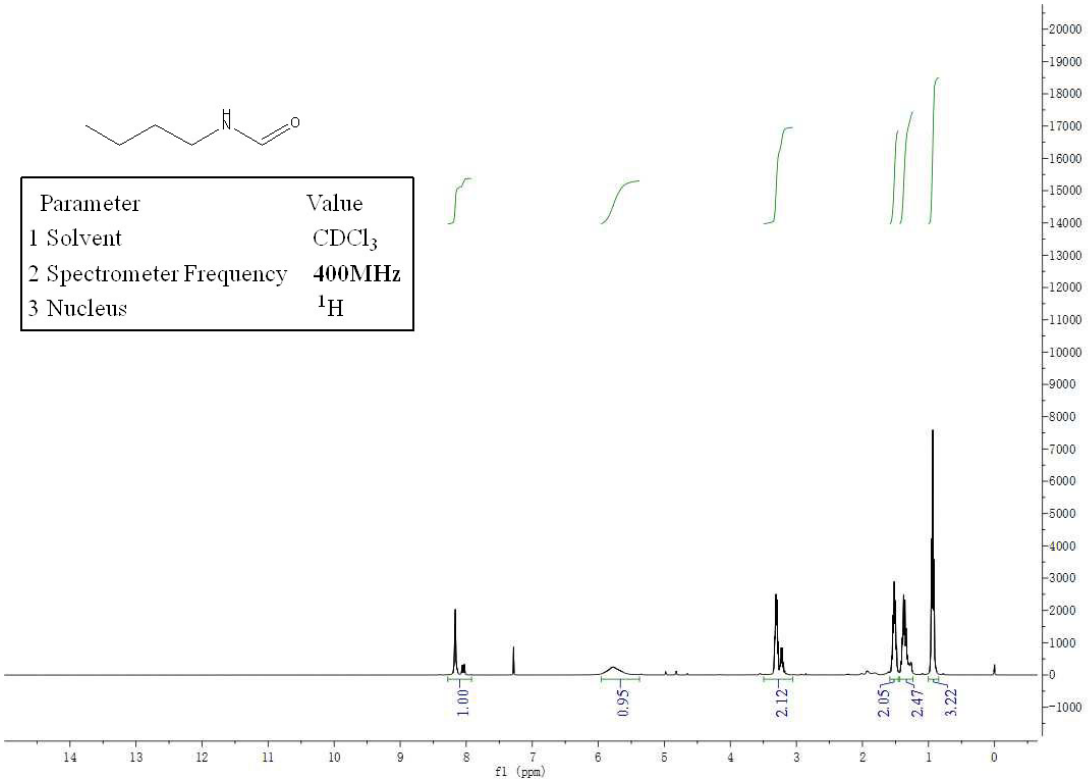


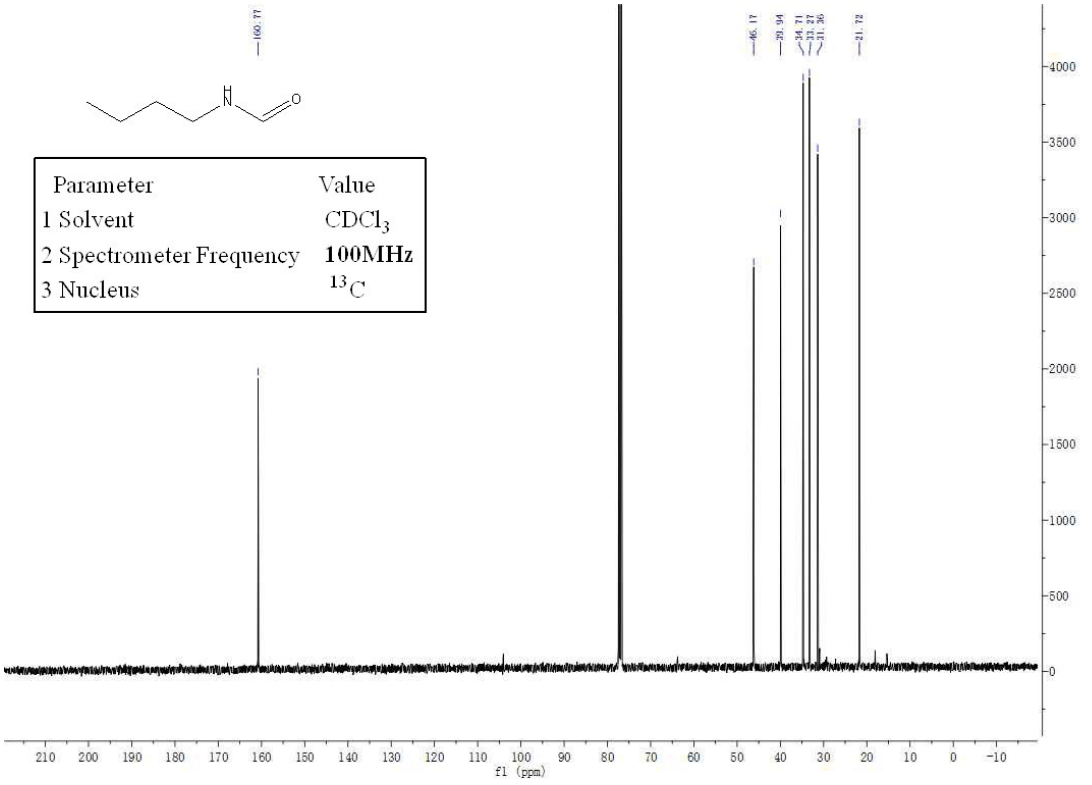
NMR Spectra of 21**b**



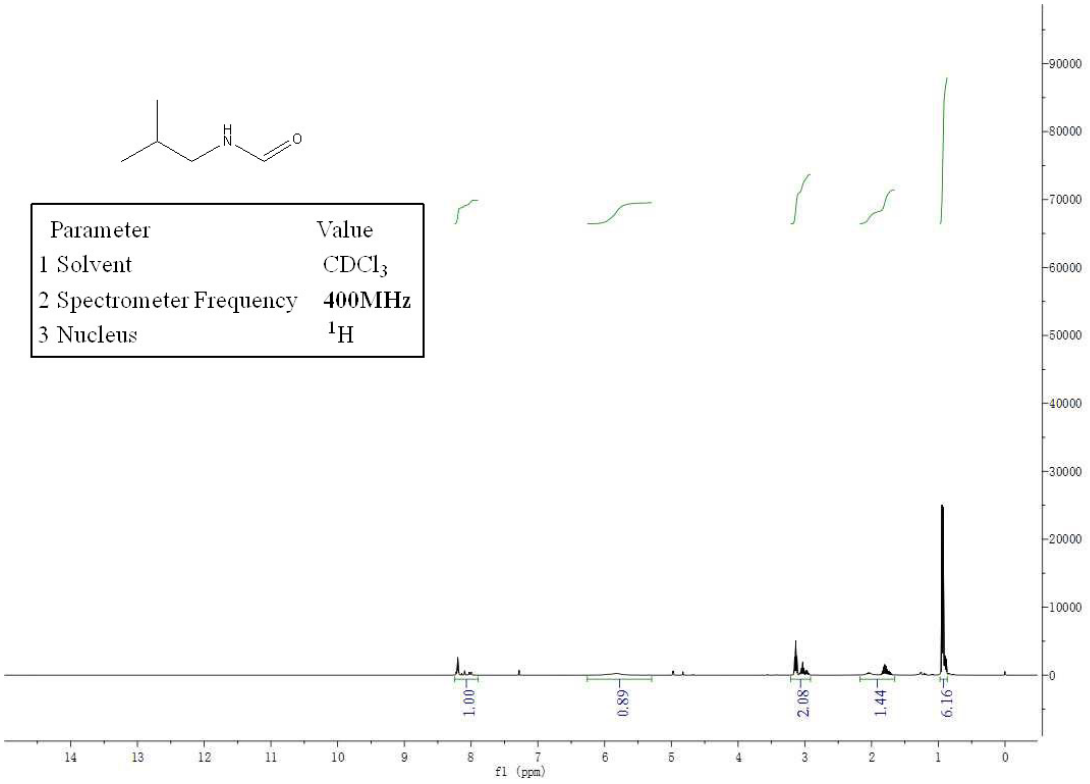


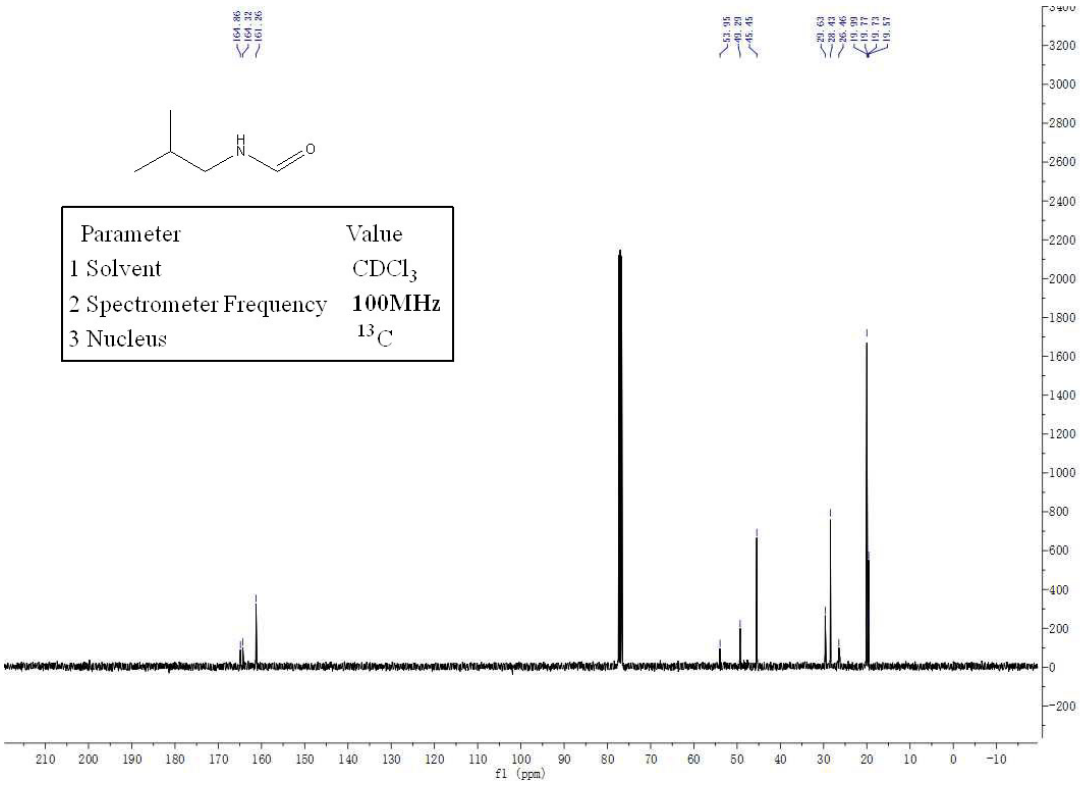
NMR Spectra of 22**b**





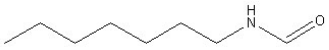
NMR Spectraof 23**b**





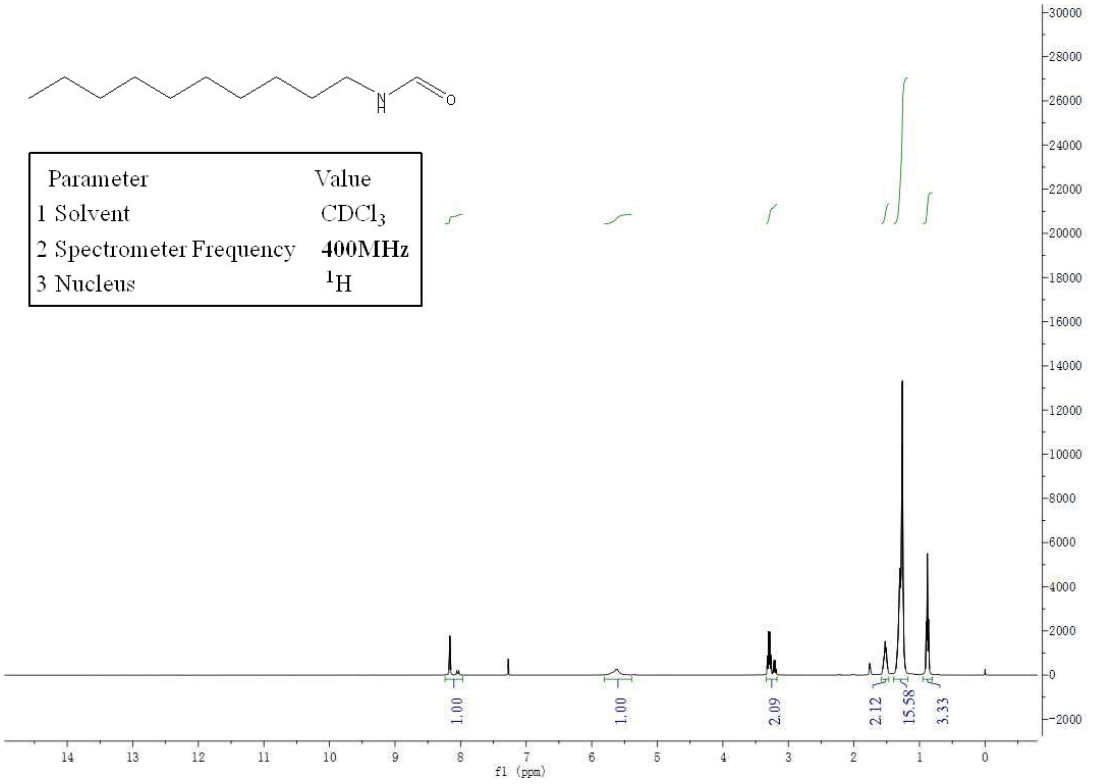
NMR Spectra of 24**b**

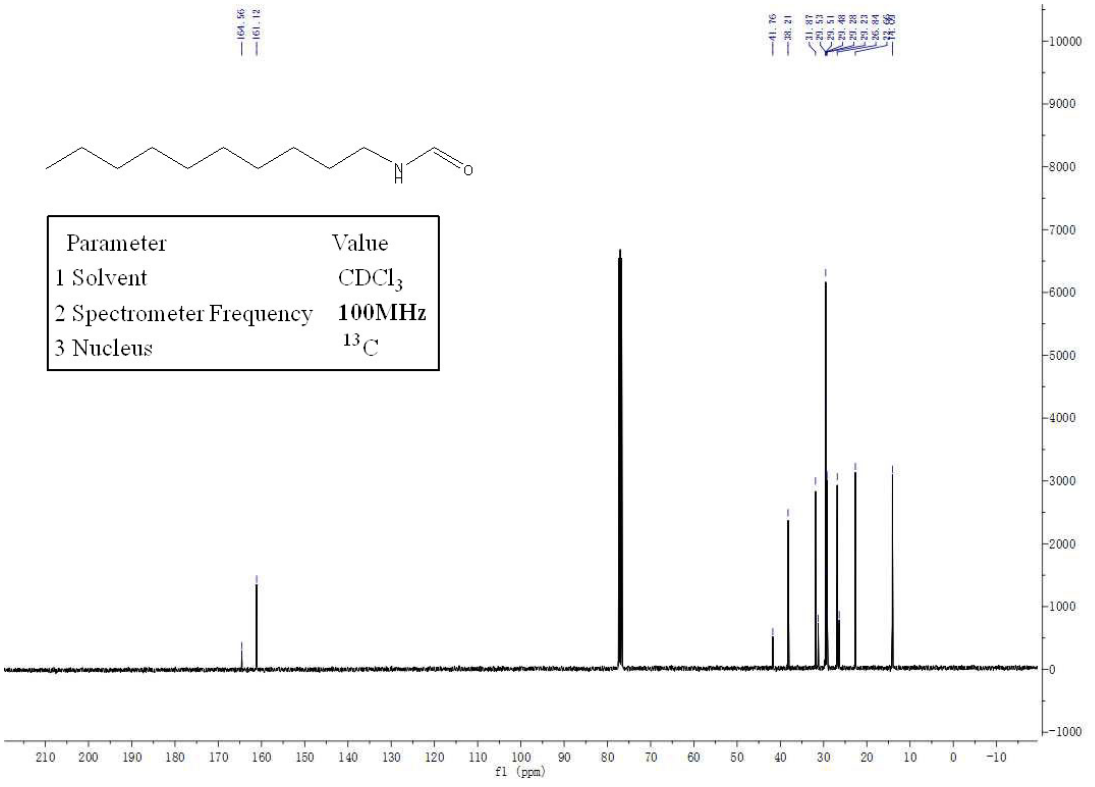
Parameter	Value
1 Solvent	$CDCl_3$
2 Spectrometer Frequency	**400MHz**
3 Nucleus	^{1}H



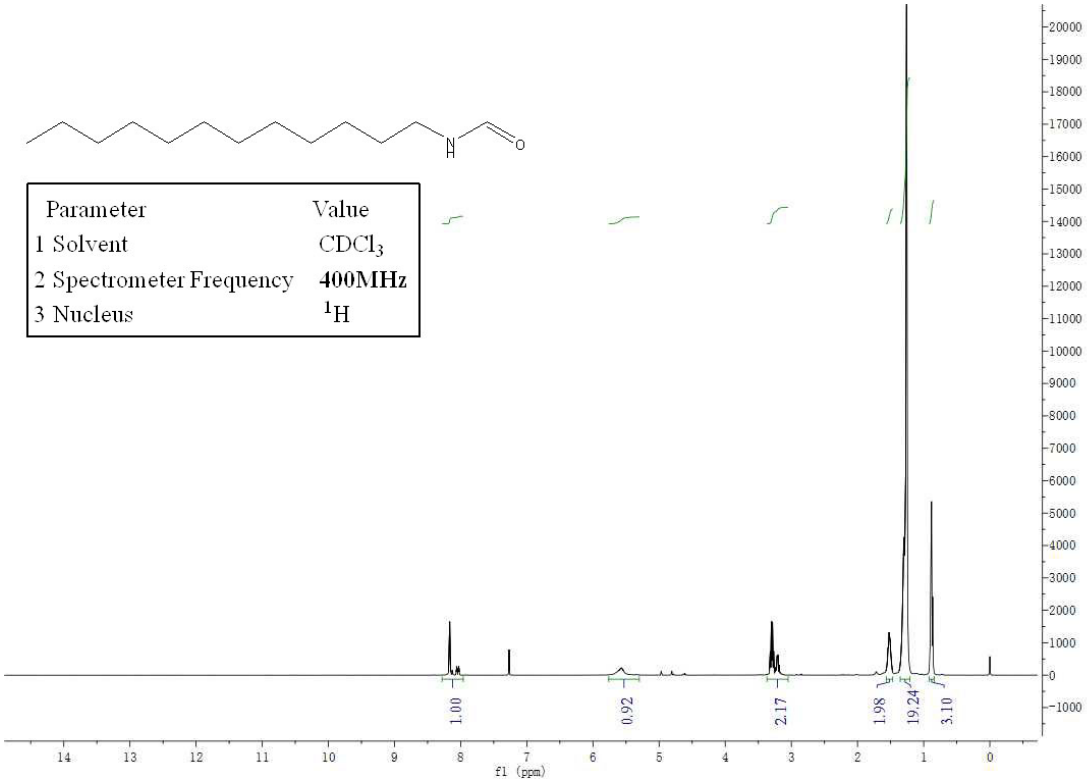
Parameter	Value
1 Solvent	$CDCl_3$
2 Spectrometer Frequency	**100MHz**
3 Nucleus	^{13}C

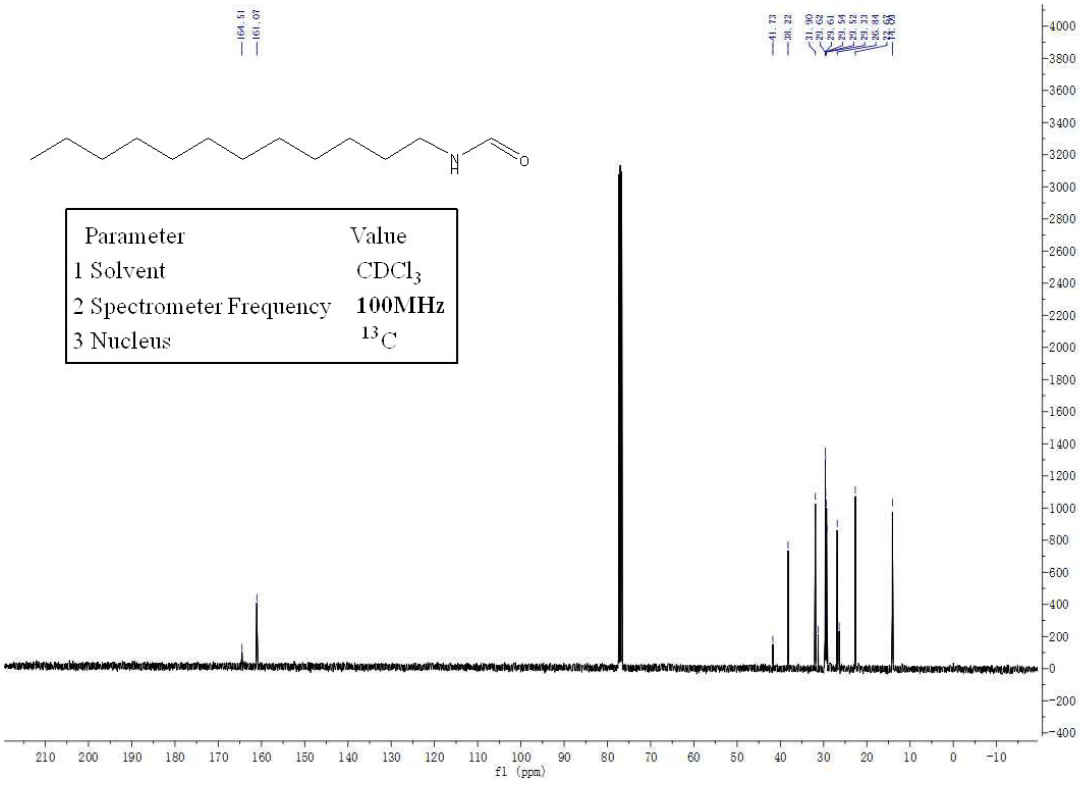
NMR Spectra of 25**b**



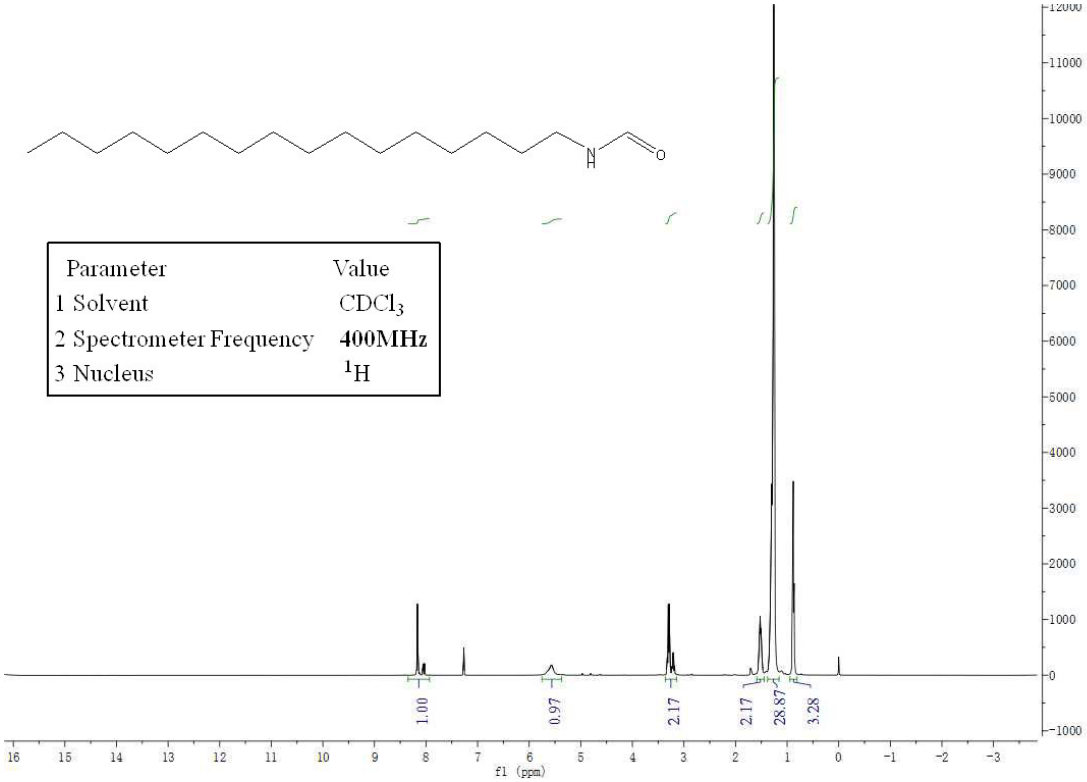


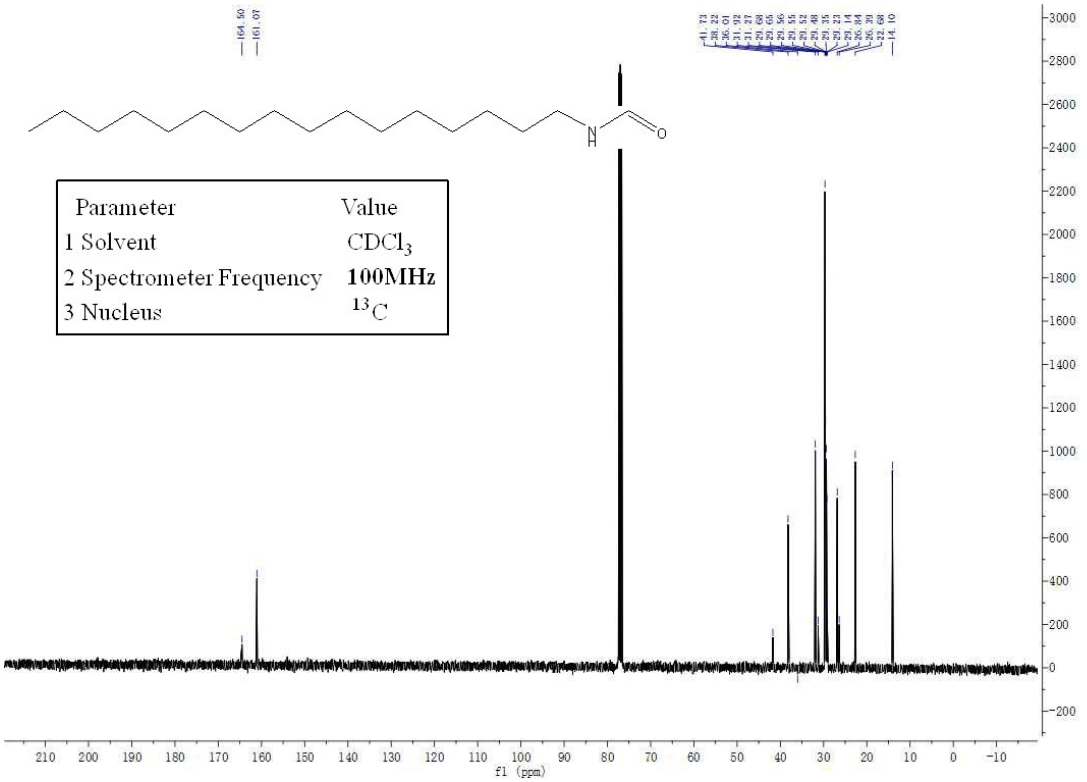
NMR Spectra of 26**b**



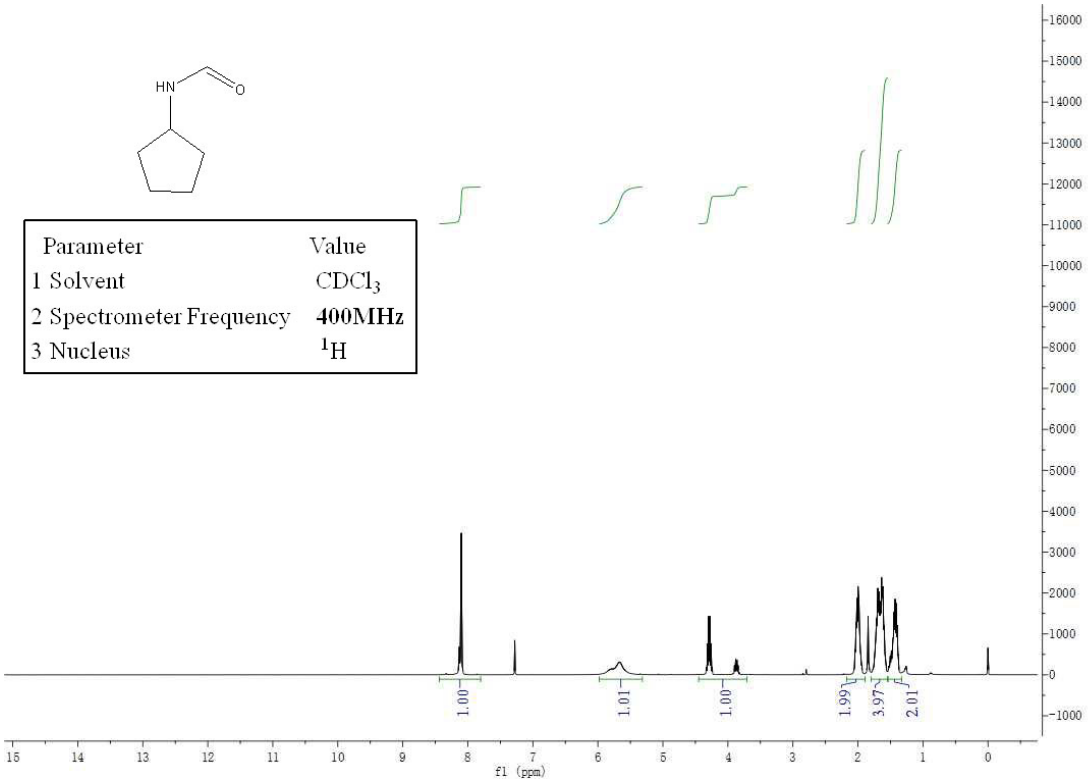


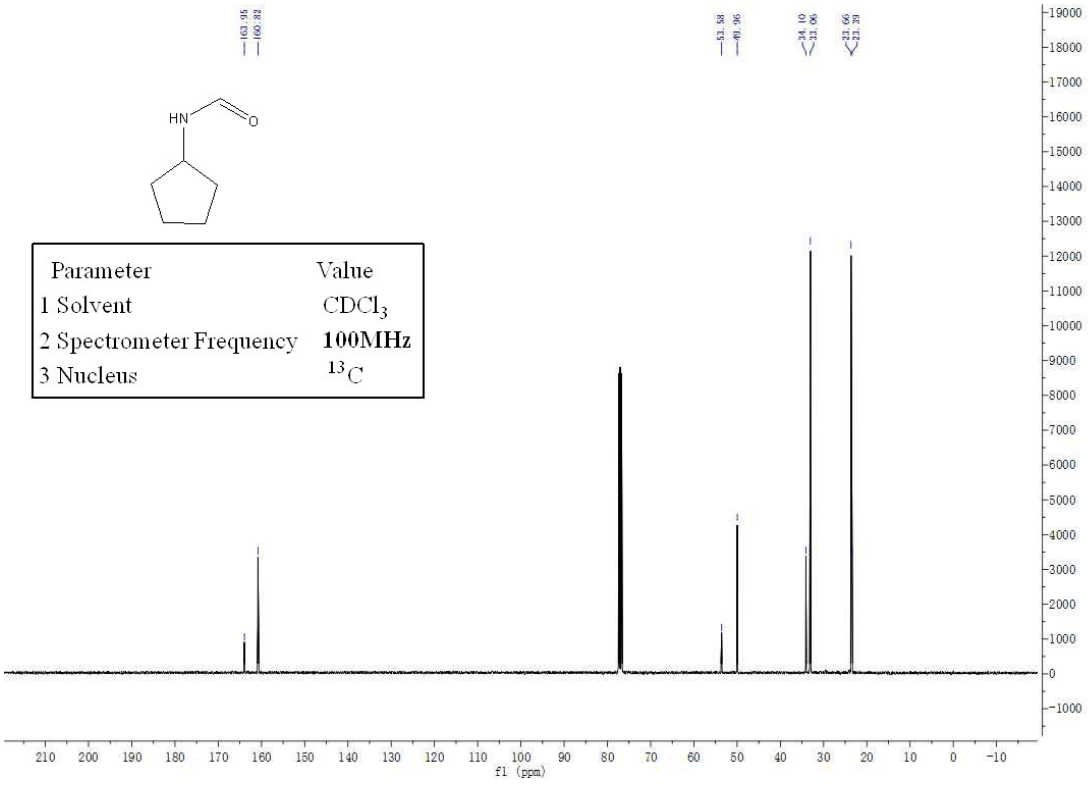
NMR Spectra of 27**b**



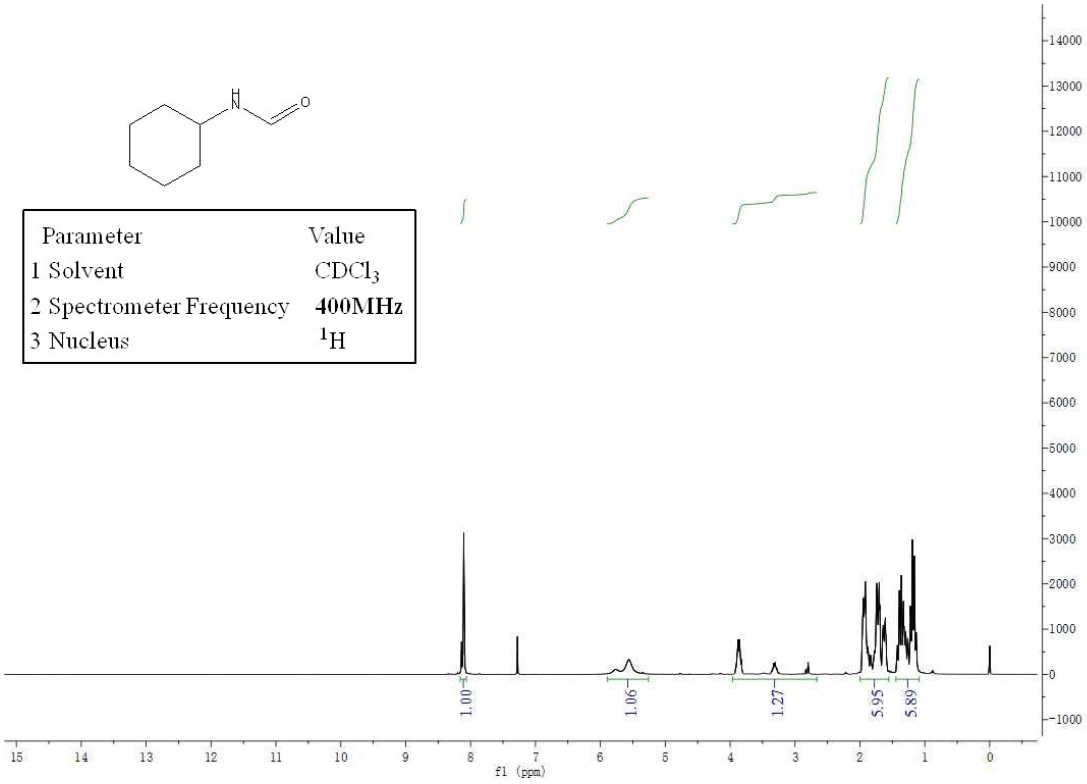


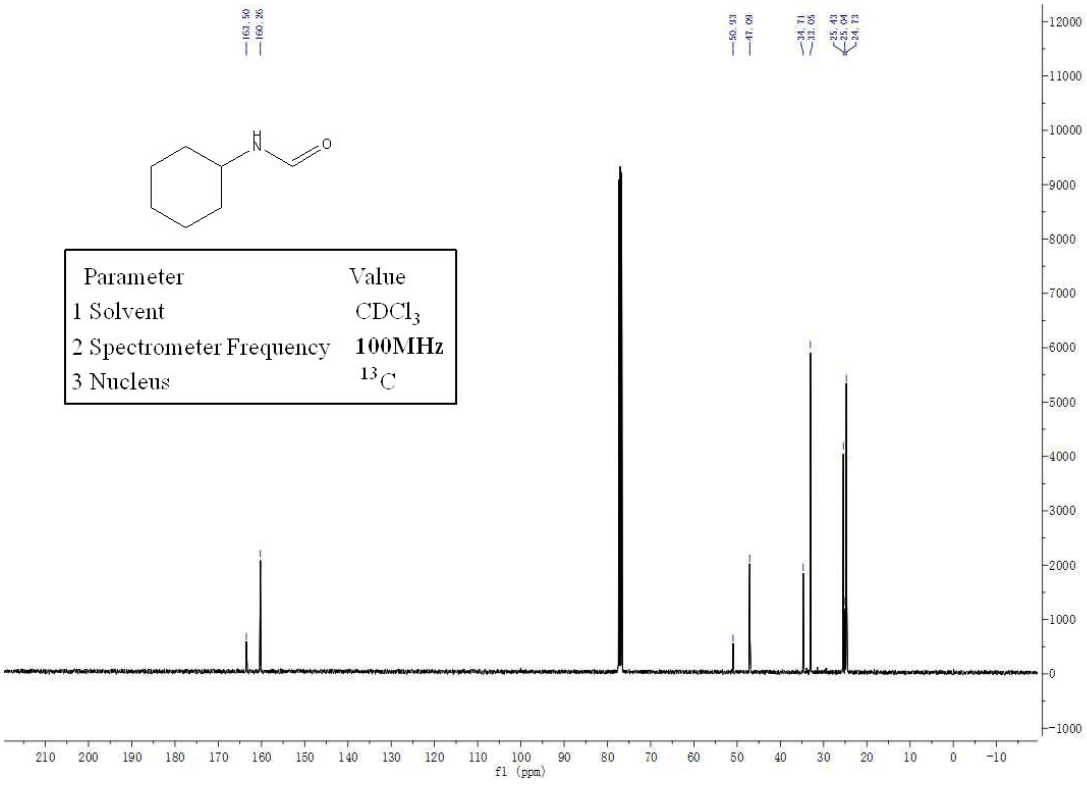
NMR Spectra of 28**b**



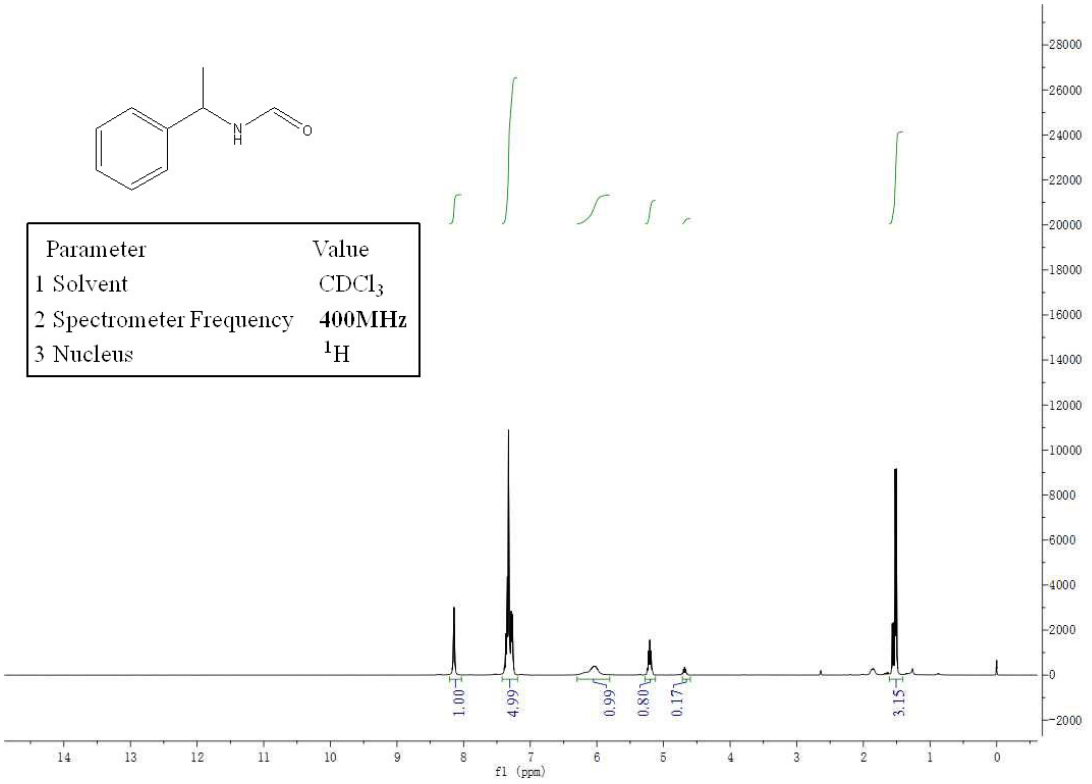


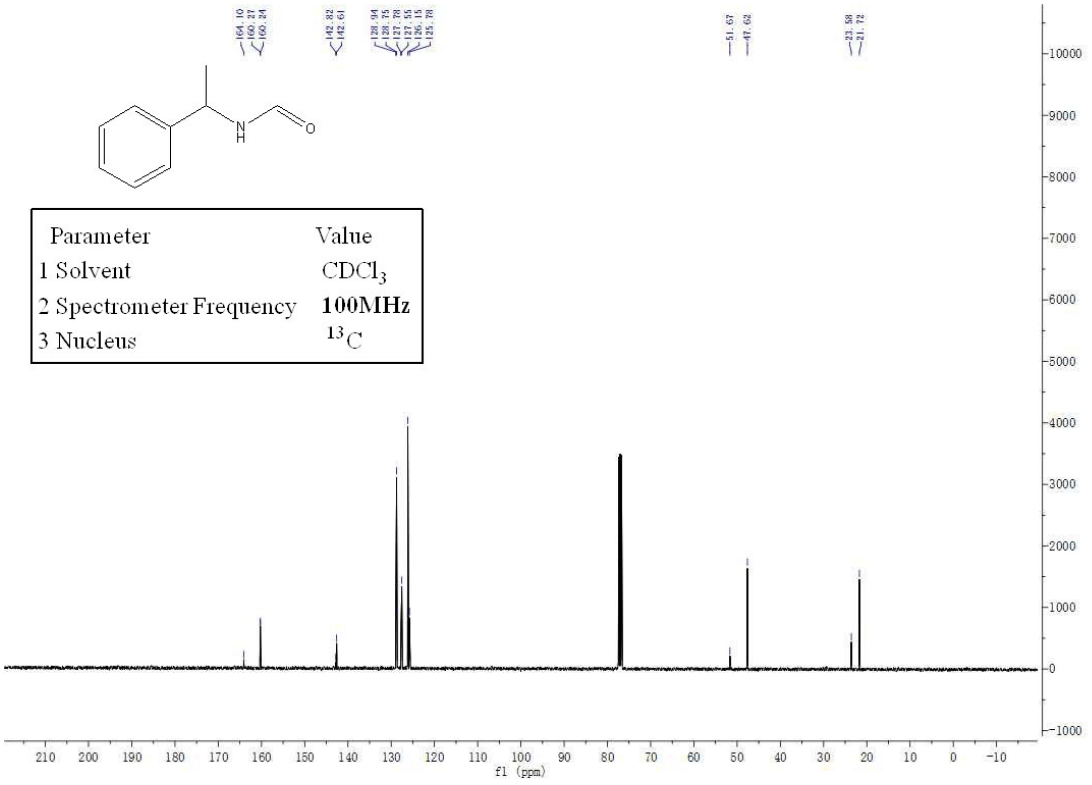
NMR Spectra of 29**b**



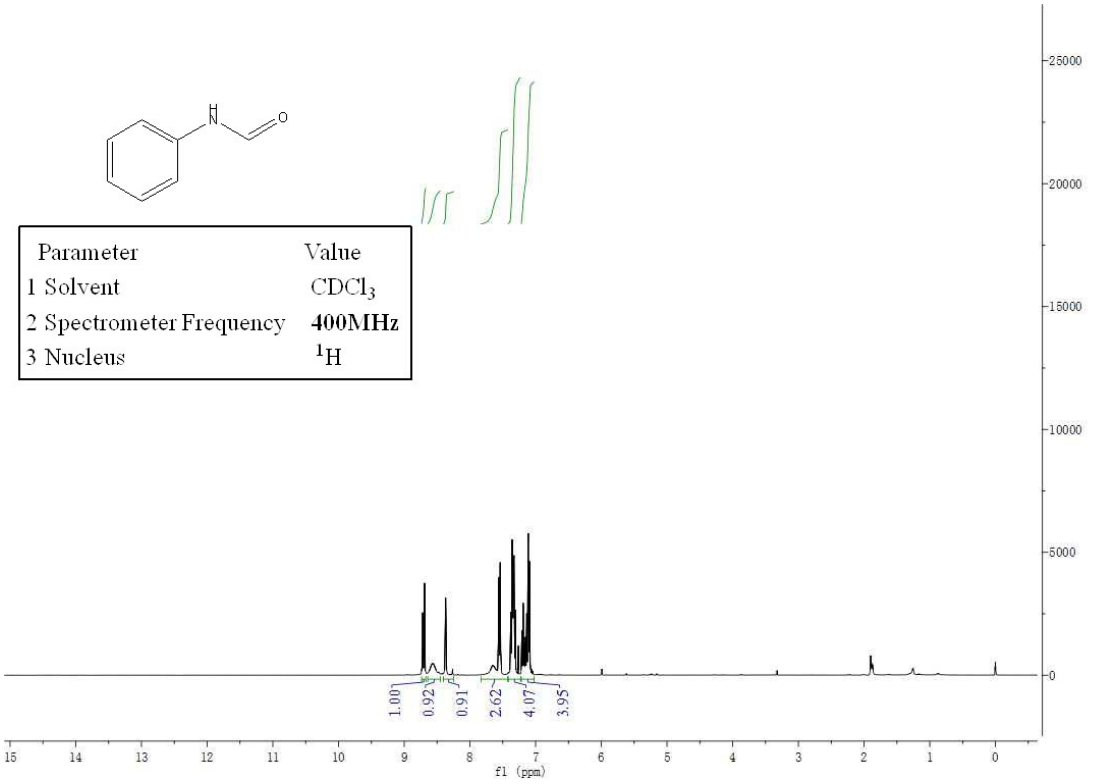


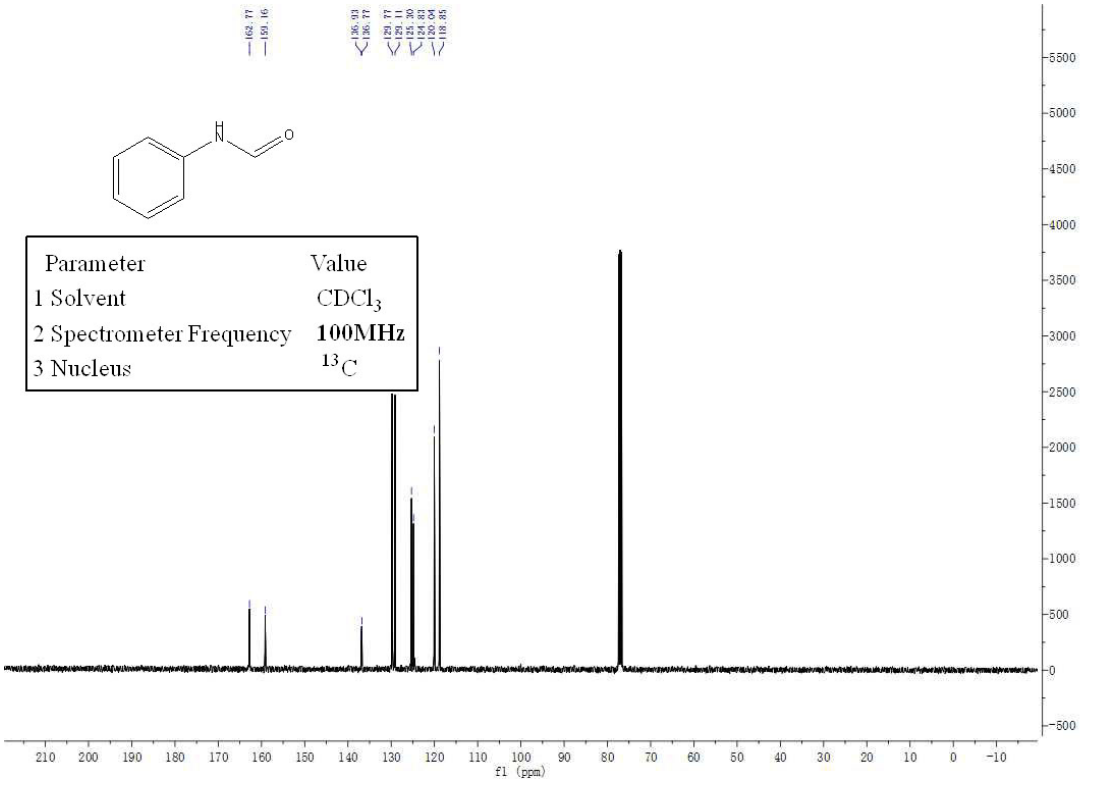
NMR Spectra of 31**b**



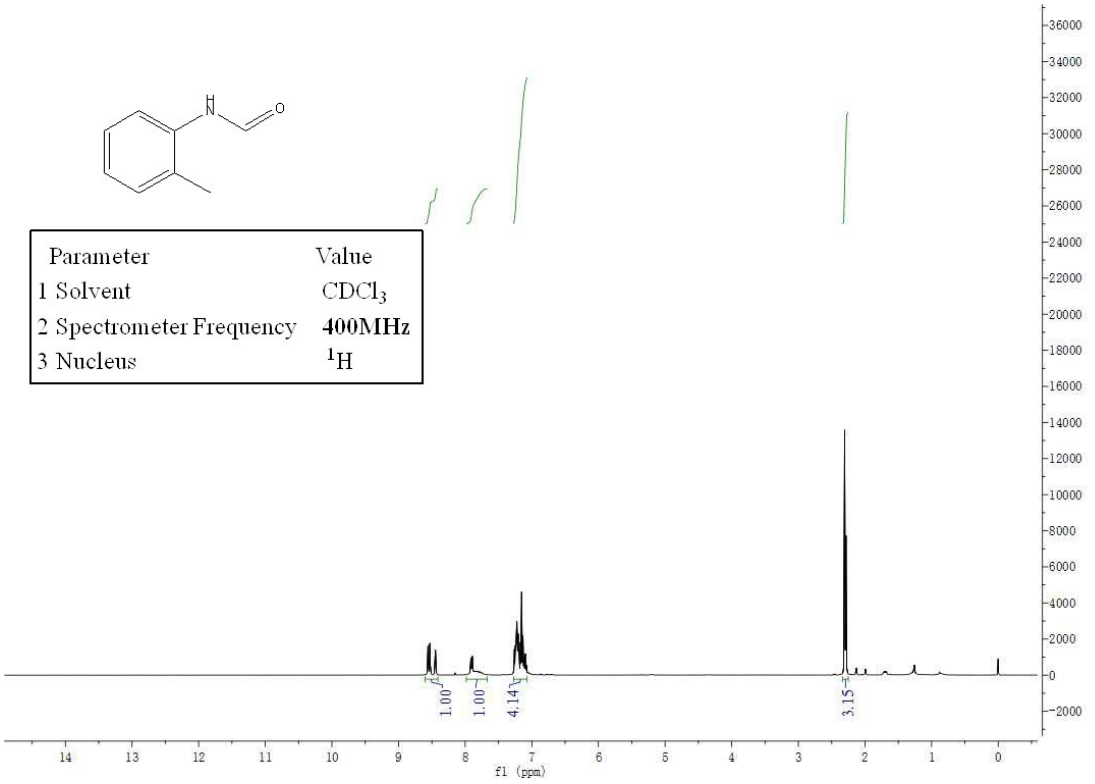


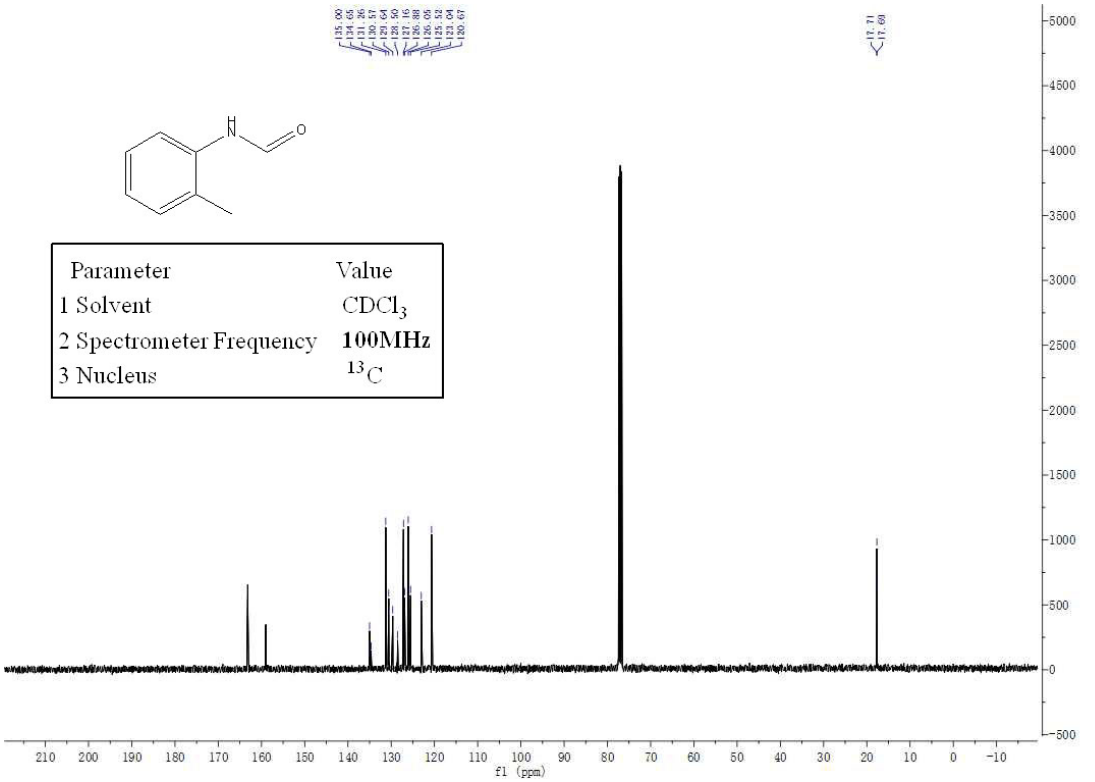
NMR Spectra of 32**b**



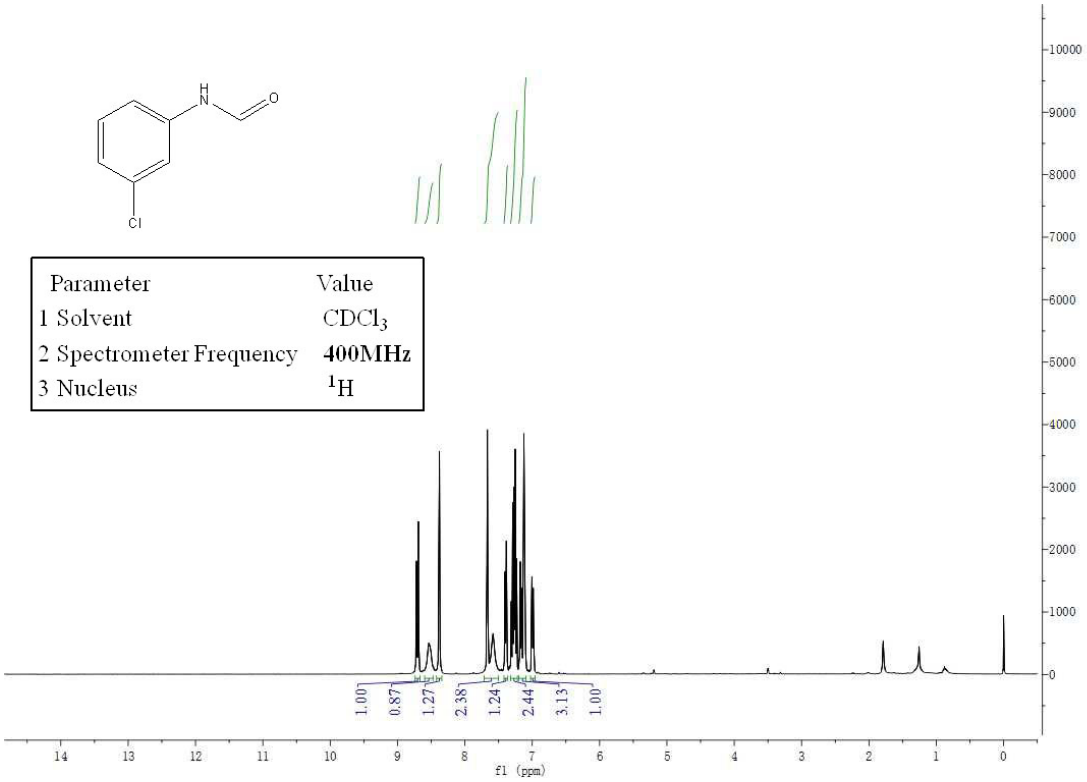


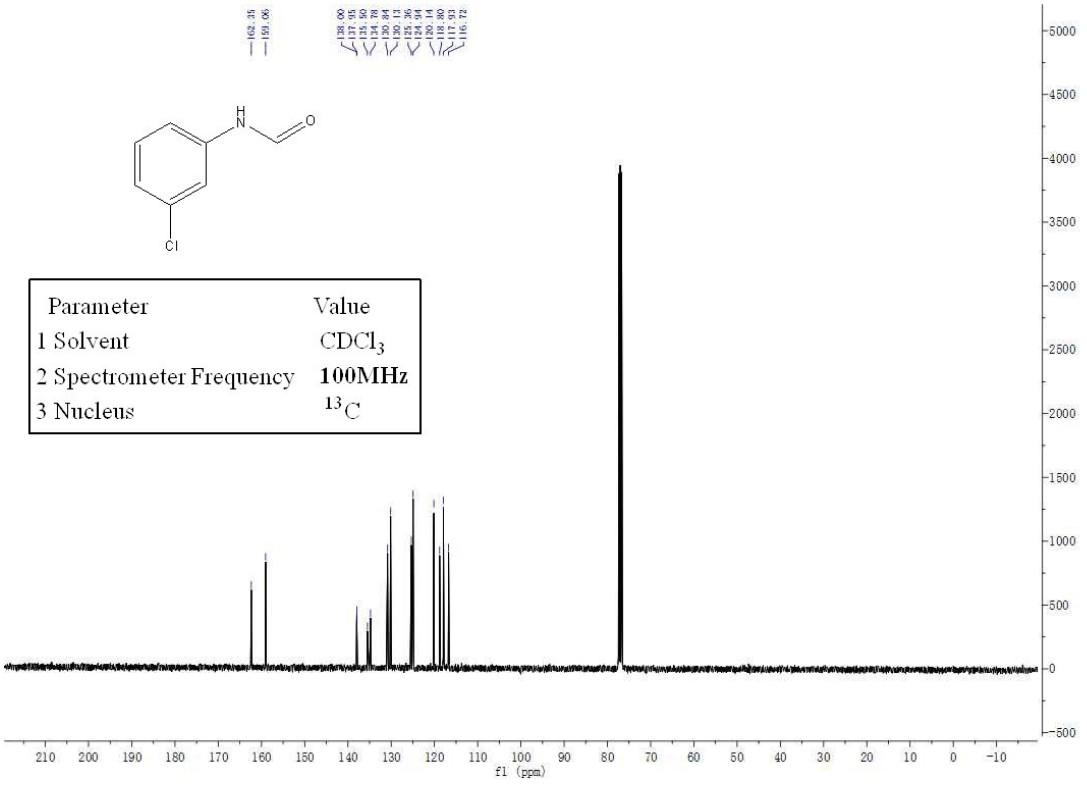
NMR Spectra of 33**b**





NMR Spectra of 34**b**





IV Reference

1. X. Cui, Y. Zhang, Y. Deng and F. Shi, Chem. Commun., 2014, 50, 189-191.
2. B. Karami, M. Farahi and F. Pam, Tetrahedron Let., 2014, 55, 6292-6296.
3. T. Lebleu, H. Kotsuki, J. Maddaluno and J. Legros, Tetrahedron Lett., 2014, 55, 362-364.
4. M. Lei, L. Ma and L. Hu, Tetrahedron Lett., 2010, 51, 4186-4188.
5. N. Ortega, C. Richter and F. Glorius, Organic Lett., 2013, 15, 1776-1779.
6. A. Romanens and G. Bélanger, Org. Lett., 2015, 17, 322-325.
7. C. Zhang, Z. Xu, T. Shen, G. Wu, L. Zhang and N. Jiao, Org. Lett., 2012, 14, 2362-2365.
8. Y. Zhao, S. Cai, J. Li and D. Z. Wang, Tetrahedron, 2013, 69, 8129-8131.