Supplementary Information

A comparison between KBH_4 and $NaBH_4$ in their reduction of pyridinium salts

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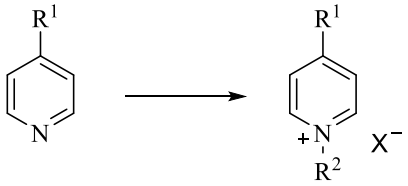


2a-h **3a-h**

General procedure for the synthesis of pyridinium salts.

All reactions were run on the multi-gram scale, using the following general procedure.

1-Benzyl-4-(3-nitrophenyl)-pyridinium bromide (3a). Benzyl bromide (1.6 g, 9.4 mmol) was added to a solution of 4-(3-nitrophenyl)-pyridine **2a** (1.6 g, 8.0 mmol) in acetone (20 mL). The resulting mixture was stirred at 60 °C for 10 h. The mixture was then cooled to 0 °C, and stirred for 20 minutes after petroleum ether (10 mL) was added. The mixture was filtrated to give white solid product **3a** (2.5 g, 84%), which was ove1-dried and pure enough to use in the next step. mp 266–268 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.36 (d, J = 6.8 Hz, 2H), 8.83 (s, 1H), 8.69 (d, J = 6.8 Hz, 2H), 8.50 – 8.47 (m, 2H), 7.94 (t, J = 8.0 Hz, 1H), 7.61 – 7.59 (m, 2H), 7.48 – 7.44 (m, 3H), 5.91 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 152.9, 148.5, 145.1, 135.3, 134.7, 134.4, 131.1, 129.3, 129.2, 128.8, 126.2, 125.9, 123.0, 62.5; HRMS (ESI): *m/z* calcd. for $C_{18}H_{15}BrN_2O_2$ $[M - Br]^+$: 291.1128; found: 291.1137; IR (ATR): 2975, 1636, 1511, 1349, 1162 cm^{-1}.

1-Benzyl-pyridinium bromide (3b).[1] General procedure was followed, but pyridine **2b** (40.4

mmol scale) was used as the starting material. The product **3b** was a white solid (8.6 g, 85%), but it was highly hydroscopic. Thus, it was difficult for us to determine its melting point. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.57 (d, *J* = 6.0 Hz, 2H), 8.42 (t, *J* = 7.8 Hz, 1H), 8.02 (t, *J* = 7.1 Hz, 2H), 7.69 – 7.67 (m, 2H), 7.36 – 7.35 (m, 3H), 6.31 (s, 2H); LRMS (ESI) *m/z* (%): 170 (100) $[M - Br]^+$.

1-Benzyl-4-methyl-pyridinium bromide (3c). General procedure was followed, but 4-methyl-pyridine **2c** (21.5 mmol scale) was used as the starting material. The product **3c** was obtained as a white solid (5.2 g, 92%). mp 158–159 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.42 (d, *J* = 6.2 Hz, 2H), 7.75 (d, *J* = 6.2 Hz, 2H), 7.67 – 7.66 (m, 2H), 7.35 – 7.34 (m, 3H), 6.23 (s, 2H), 2.57 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 144.2, 133.4, 129.8, 129.6, 129.5, 128.8, 63.1, 22.3; HRMS (ESI): *m/z* calcd. for $C_{13}H_{14}BrN$ $[M - Br]^+$: 184.1121; found: 184.1134; IR (ATR): 2782, 1586, 1498, 1330, 1093 cm^{-1}.

1-(4-Nitrobenzyl)-4-methyl-pyridinium bromide (3d). General procedure was followed, but 4-methyl-pyridine **2d** (8.6 mmol scale) was used as the starting material, 4-nitrobenzyl bromide (1.9 g, 8.8 mmol) was used as the another starting material. The product **3d** was obtained as a white solid (2.4 g, 91%). mp 101–103 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.10 (d, *J* = 6.6 Hz, 2H), 8.30 (d, *J* = 8.7 Hz, 2H), 8.06 (d, *J* = 6.4 Hz, 2H), 7.76 (d, *J* = 8.7 Hz, 2H), 5.08 (s, 2H), 2.63 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 159.9, 147.8, 144.1, 141.5, 130.0, 128.9, 124.1, 61.2, 21.6; HRMS (ESI): *m/z* calcd. for $C_{13}H_{13}BrN_2O_2$ $[M - Br]^+$: 229.0972; found: 229.0977; IR (ATR): 3356, 3019, 1636, 1523, 1343, 1156 cm^{-1}.

1-(4-Nitrobenzyl)-4-(3-nitrophenyl)-pyridinium bromide (3e). General procedure was followed, but 4-(3-nitrophenyl)-pyridine **2e** (9.0 mmol scale) was used as the starting material,

4-nitrobenzyl bromide (1.9 g, 8.8 mmol) was used as the another starting material. The product **3e** was obtained as a yellow solid (3.0 g, 80%). mp 194–195 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.39 (d, J = 7.0 Hz, 2H), 8.86 (t, J = 1.9 Hz, 1H), 8.75 (d, J = 7.0 Hz, 2H), 8.53 – 8.49 (m, 2H), 8.32 (d, J = 8.8 Hz, 2H), 7.96 (t, J = 8.1 Hz, 1H), 7.84 (d, J = 8.8 Hz, 2H), 6.08 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 153.3, 148.6, 147.9, 145.4, 141.3, 135.2, 134.7, 131.2, 130.1, 126.3, 126.0, 124.1, 123.1, 61.4; HRMS (ESI): *m/z* calcd. for $C_{18}H_{14}BrN_3O_4$ $[M - Br]^+$: 336.0979; found: 336.0988; IR (ATR): 3343, 3019, 1642, 1511, 1349, 1168 cm^{-1}.

1-Benzyl-4-(4-cyanophenyl)-pyridinium bromide (3f). General procedure was followed, but 4-(4-cyanophenyl)-pyridine **2f** (5.0 mmol scale) was used as the starting material. The product **3f** was obtained as a white solid (1.4 g, 80%). mp 238–239 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.56 (d, J = 6.9 Hz, 2H), 8.25 (d, J = 6.9 Hz, 2H), 7.89 (d, J = 8.5 Hz, 2H), 7.82 (d, J = 8.5 Hz, 2H), 7.67 – 7.65 (m, 2H), 7.37 – 7.36 (m, 3H), 6.27 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 153.3, 145.1, 137.9, 134.4, 133.3, 129.3, 129.2, 129.1, 128.9, 125.8, 118.1, 114.1, 62.5; HRMS (ESI): *m/z* calcd. for $C_{19}H_{15}BrN_2$ $[M - Br]^+$: 271.1230; found: 271.1245; IR (ATR): 3343, 3031, 2227, 1629, 1449, 1156 cm^{-1}.

1-Allyl-4-(4-nitrophenyl)-pyridinium bromide (3g). General procedure was followed, but 4-(4-nitrophenyl)-pyridine **2g** (5.0 mmol scale) was used as the starting material, allyl bromide (0.7 g, 5.8 mmol) was used as the starting material. The product **3g** was obtained as a yellow solid (1.4 g, 88%). The compound was highly hydroscopic, so its melting point was not determined. ^{1}H NMR (500 MHz, CD_3CN) δ 9.19 (d, J = 6.2 Hz, 2H), 8.47 (d, J = 6.0 Hz, 2H), 8.41 (d, J = 8.5 Hz, 2H), 8.19 (d, J = 8.6 Hz, 2H), 6.27 – 6.19 (m, 1H), 5.63 – 5.52 (m,

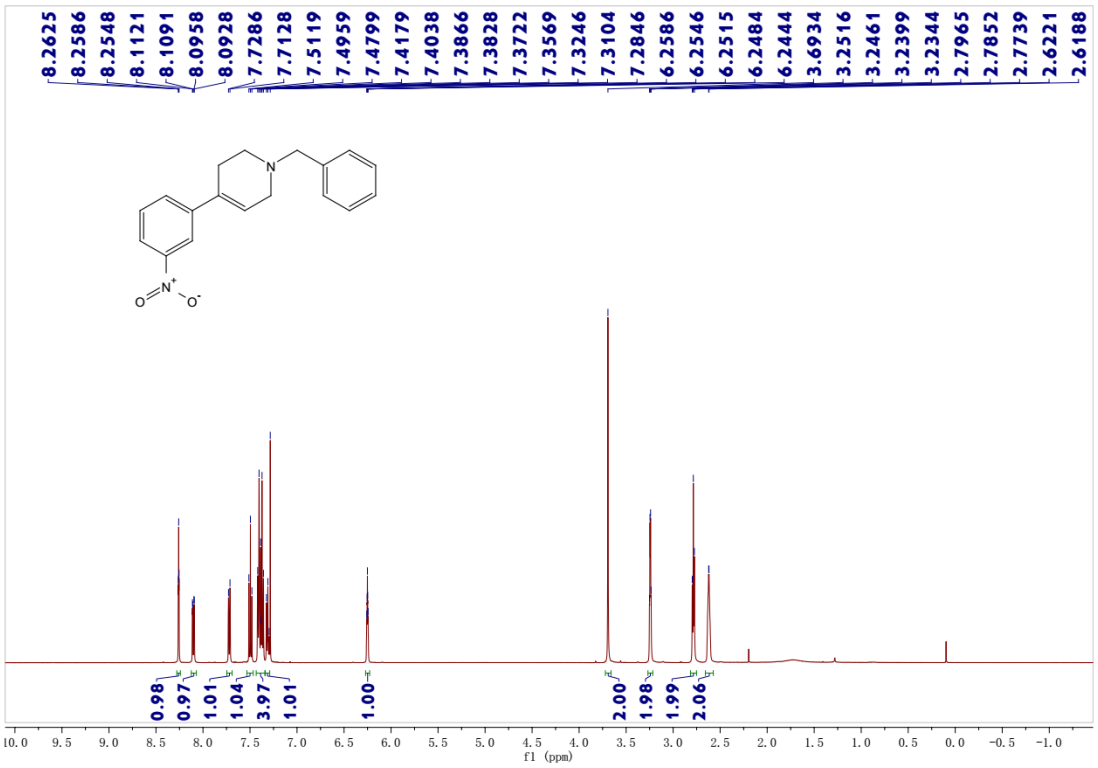
2H), 5.46 (d, J = 6.2 Hz, 2H); ^{13}C NMR (125 MHz, CD_3CN) δ 155.5, 151.1, 146.5, 141.2, 132.2, 131.1, 127.6, 125.9, 124.0, 63.8; HRMS (ESI): *m/z* calcd. for $C_{14}H_{13}BrN_2O_2$ $[M - Br]^+$: 241.0972; found: 241.0971; IR (ATR): 3417, 3006, 1636, 1523, 1343 cm^{-1}.

1-Methyl-4-(4-nitrophenyl)-pyridinium iodide (3h). General procedure was followed, but 4-(4-nitrophenyl)-pyridine **2h** (4.0 mmol scale) was used as the starting material, methyl iodide (0.7 g, 4.9 mmol) was used as the starting material. The product **3h** was obtained as a yellow solid (1.2 g, 88%). mp 218–219 °C (lit.[2] 216-219 °C); ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.13 (d, J = 6.6 Hz, 2H), 8.61 (d, J = 6.7 Hz, 2H), 8.45 (d, J = 8.8 Hz, 2H), 8.32 (d, J = 8.8 Hz, 2H), 4.39 (s, 3H); LRMS (ESI) *m/z* (%): 215 (100) $[M - I]^+$.

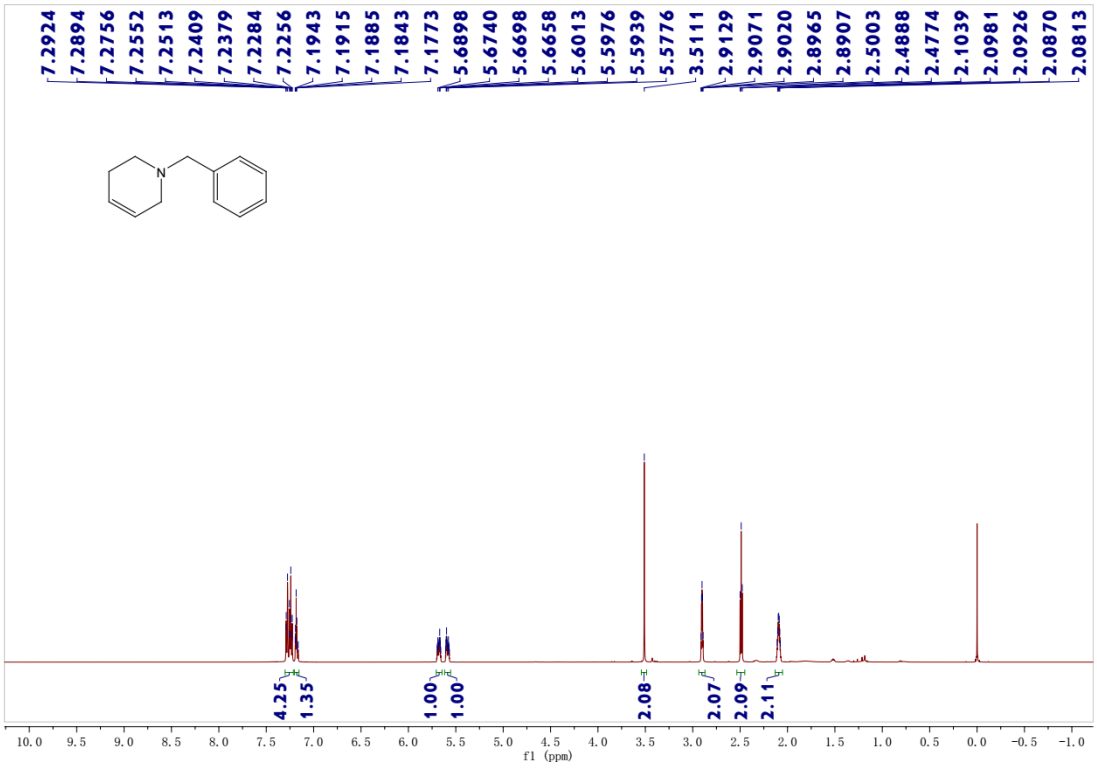
References

1. E. Anders, J.G. Tropsch, E. Irmer, and G.M. Sheldrick, *Chem. Ber.*, 1990, **123**, 321.
2. Y. Zhang, T.Y. Zhou, K.D. Zhang, J.L. Dai, Y.Y. Zhu, and X. Zhao, *Chem. Asian. J.*, 2014, **9**, 1530.

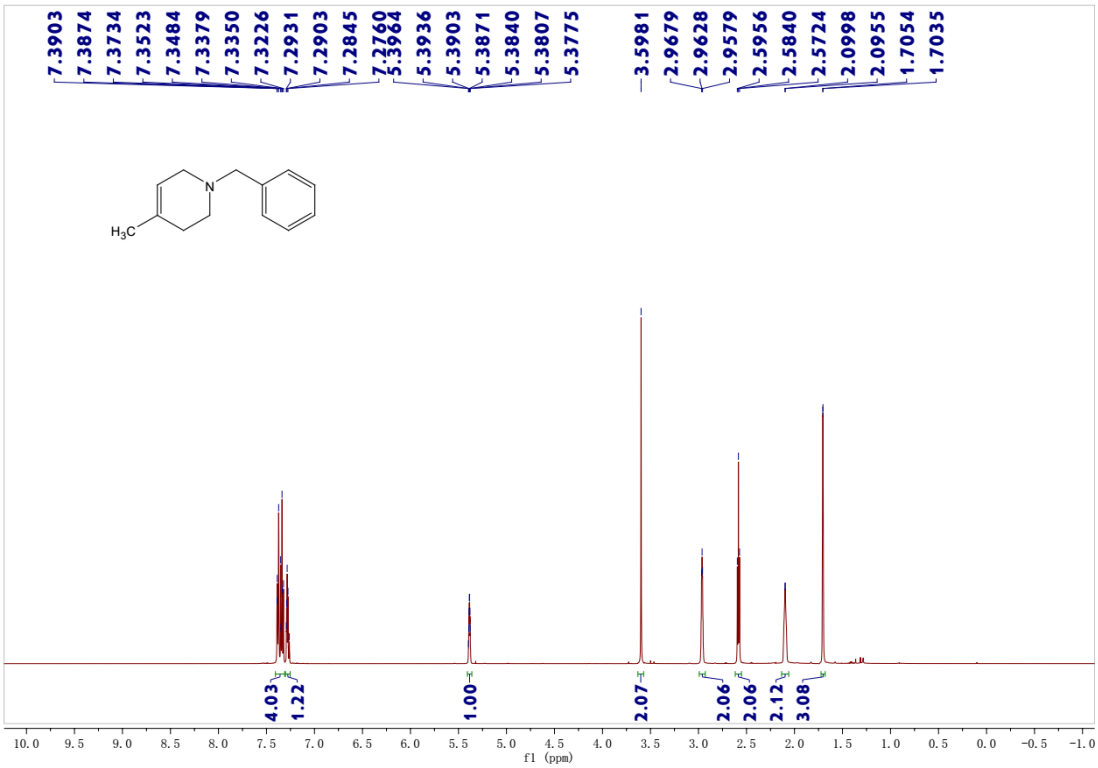
^{1}H NMR of 1-benzyl-4-(3-nitro-phenyl)-1,2,3,6-tetrahydro-pyridine (**1a**)



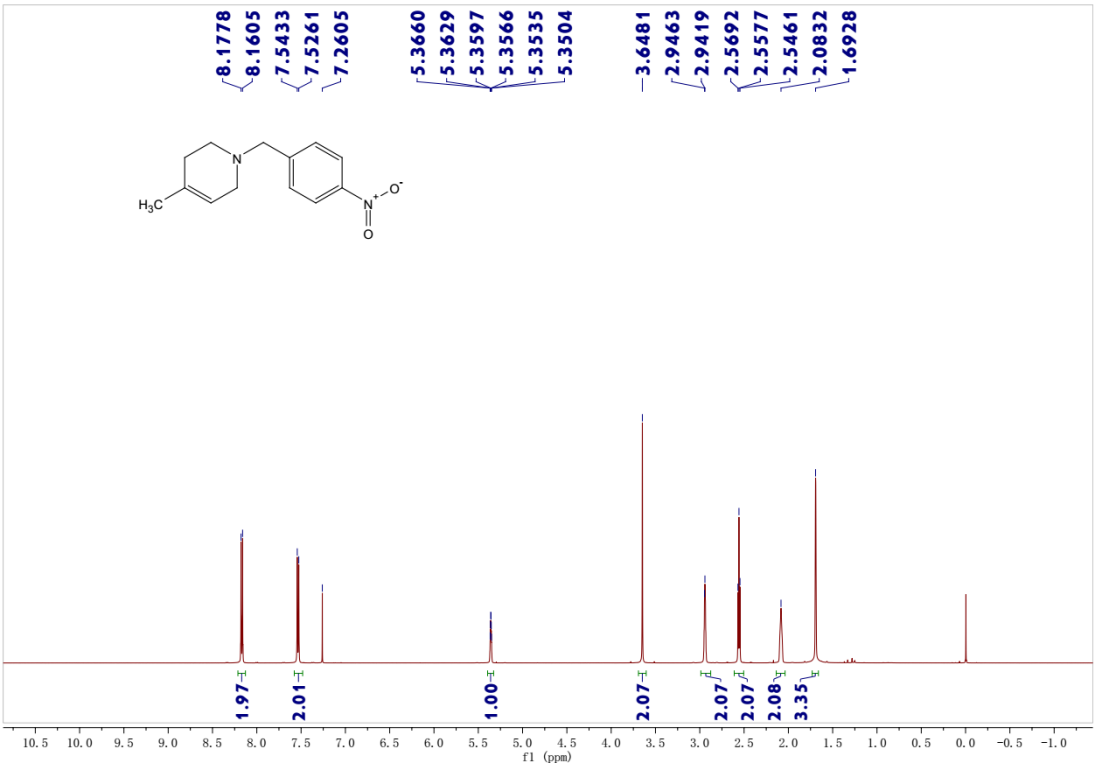
^{1}H NMR of 1-benzyl-1,2,3,6-tetrahydro-pyridine (**1b**)



^{1}H NMR of 1-benzyl-4-methyl-1,2,3,6-tetrahydro-pyridine (**1c**)



^{1}H NMR of 1-(4-nitro-benzyl)-4-methyl-1,2,3,6-tetrahydro-pyridine (**1d**)



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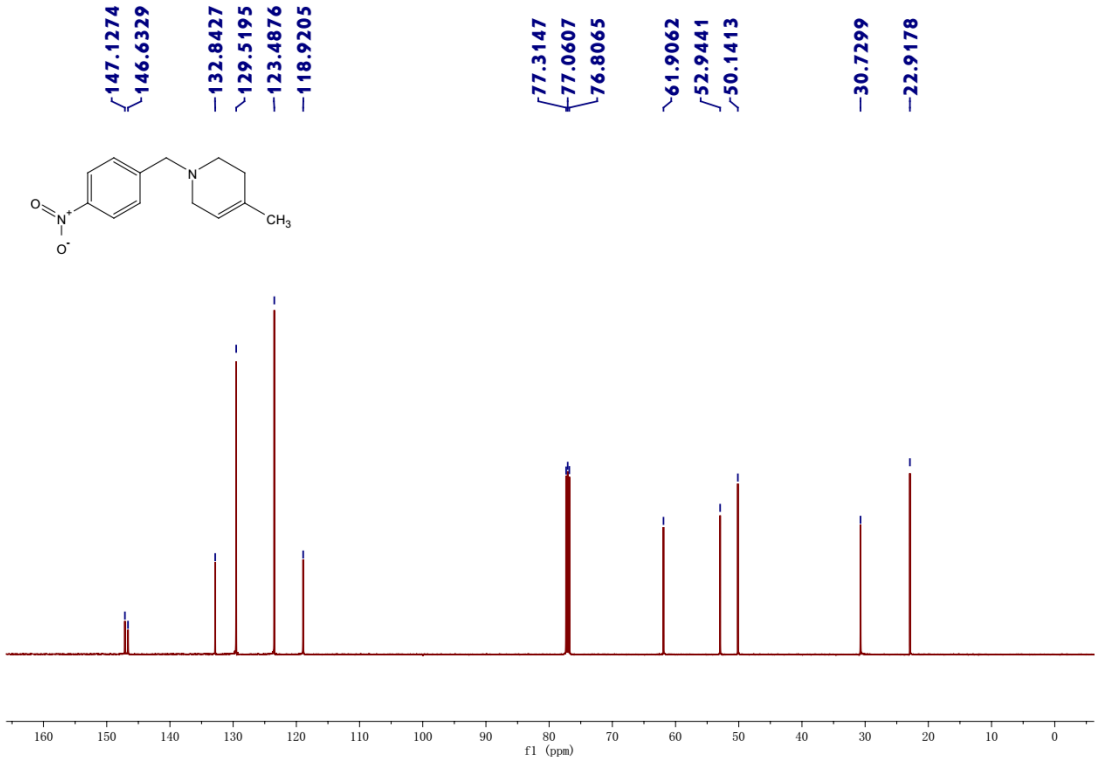

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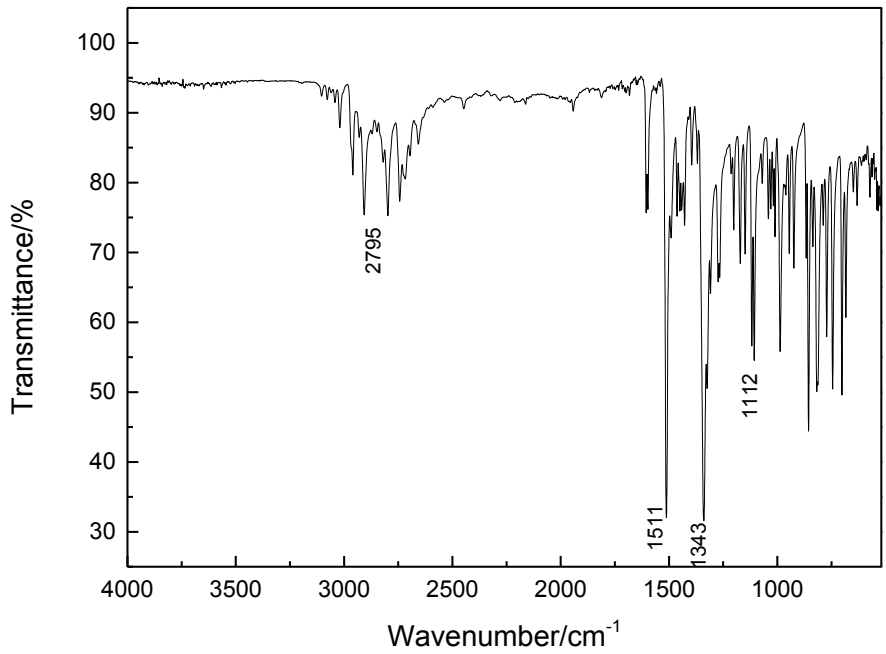

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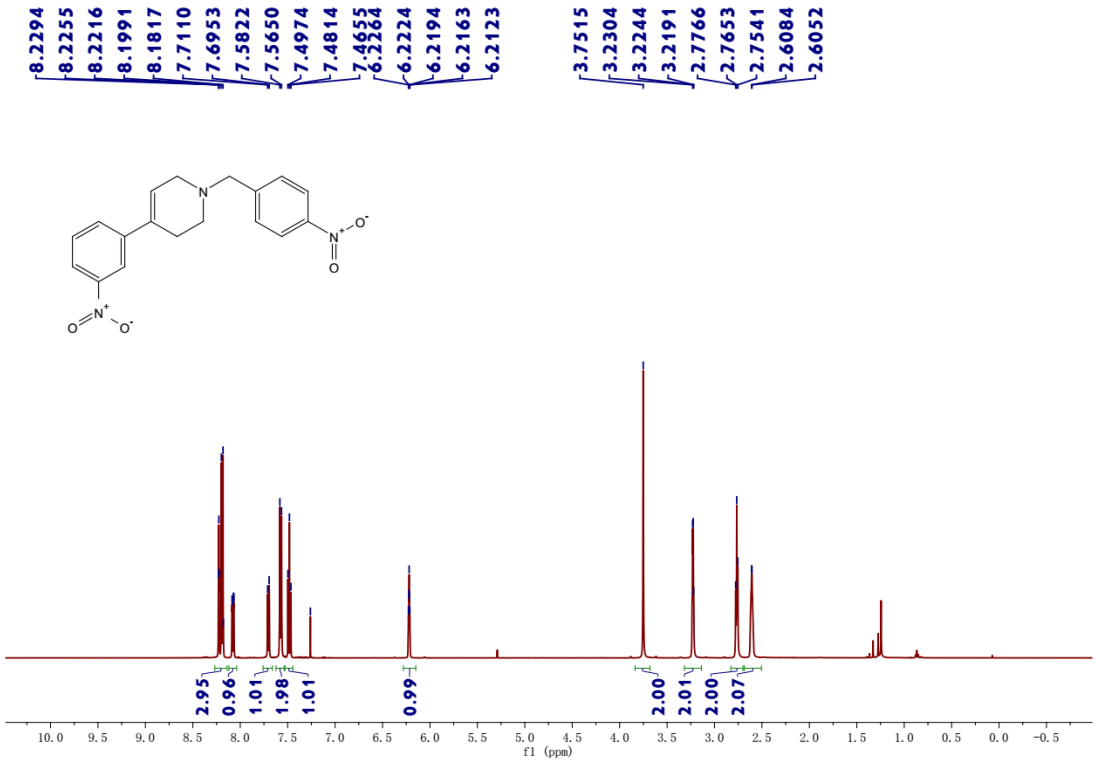

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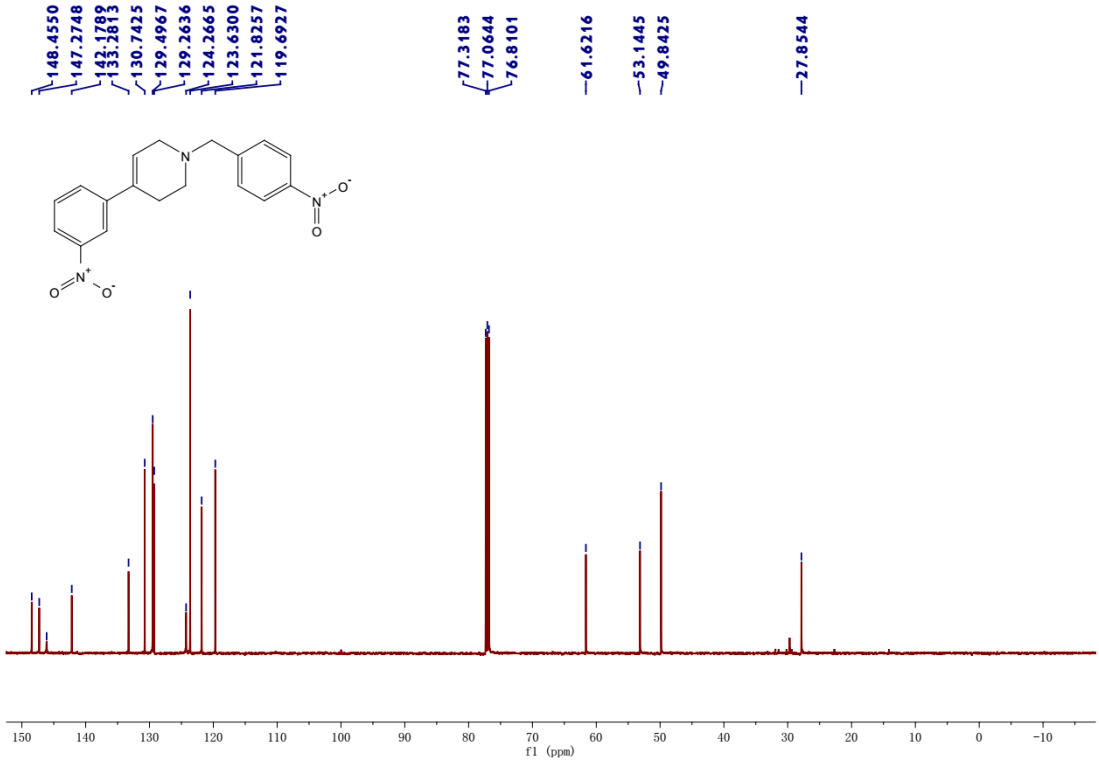

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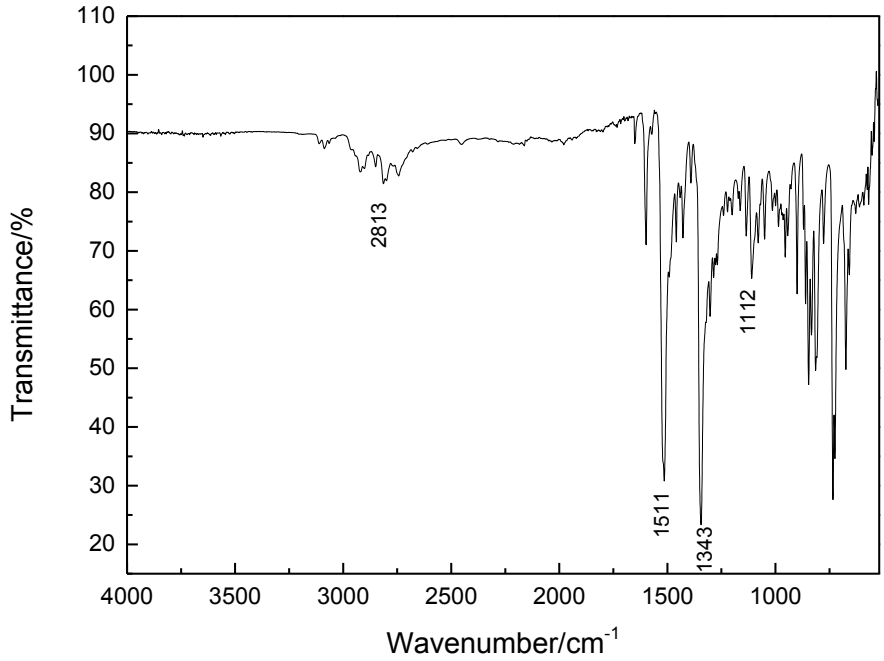

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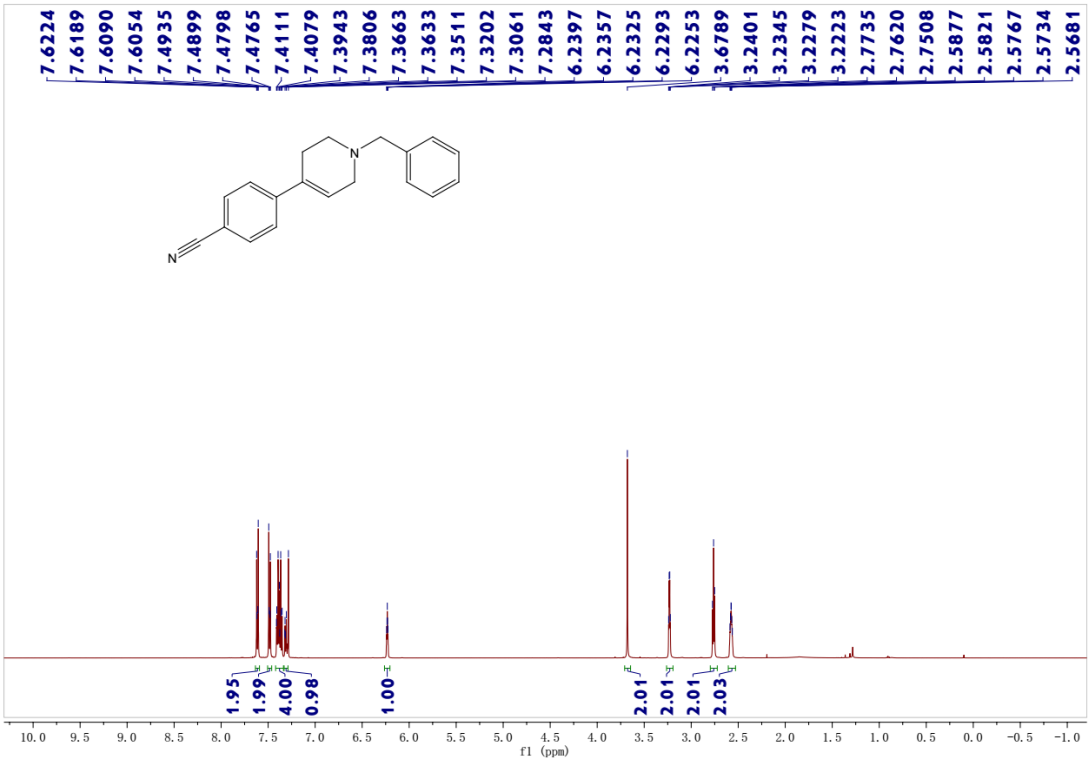

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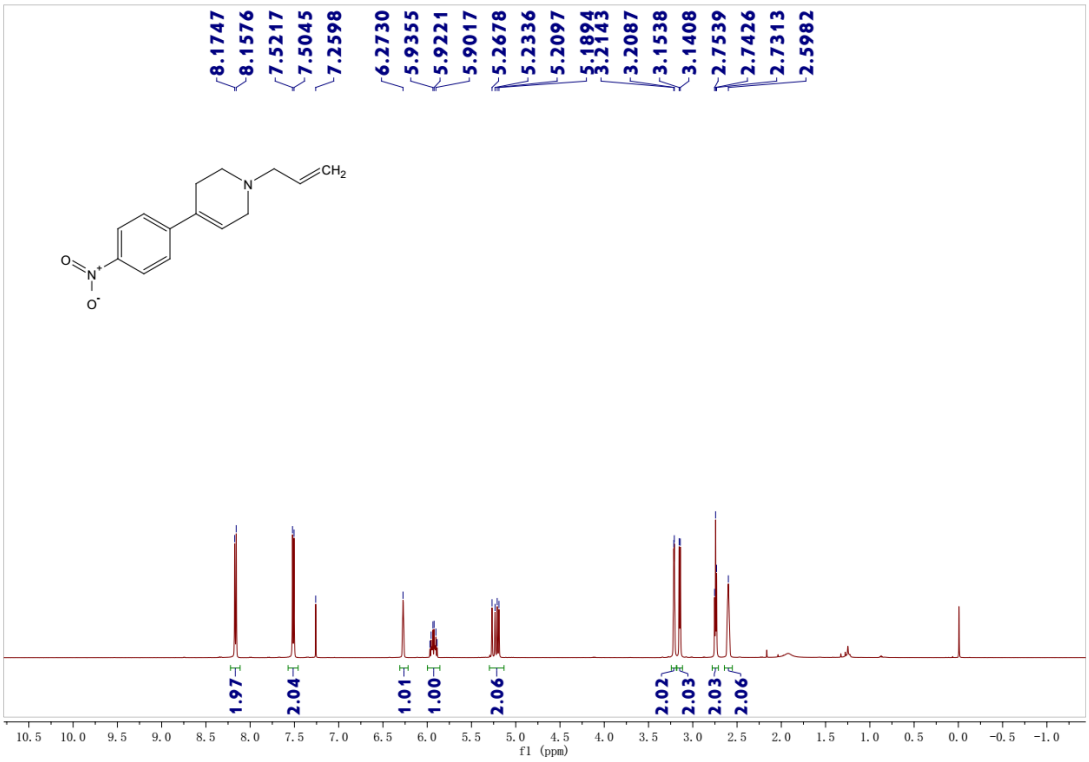

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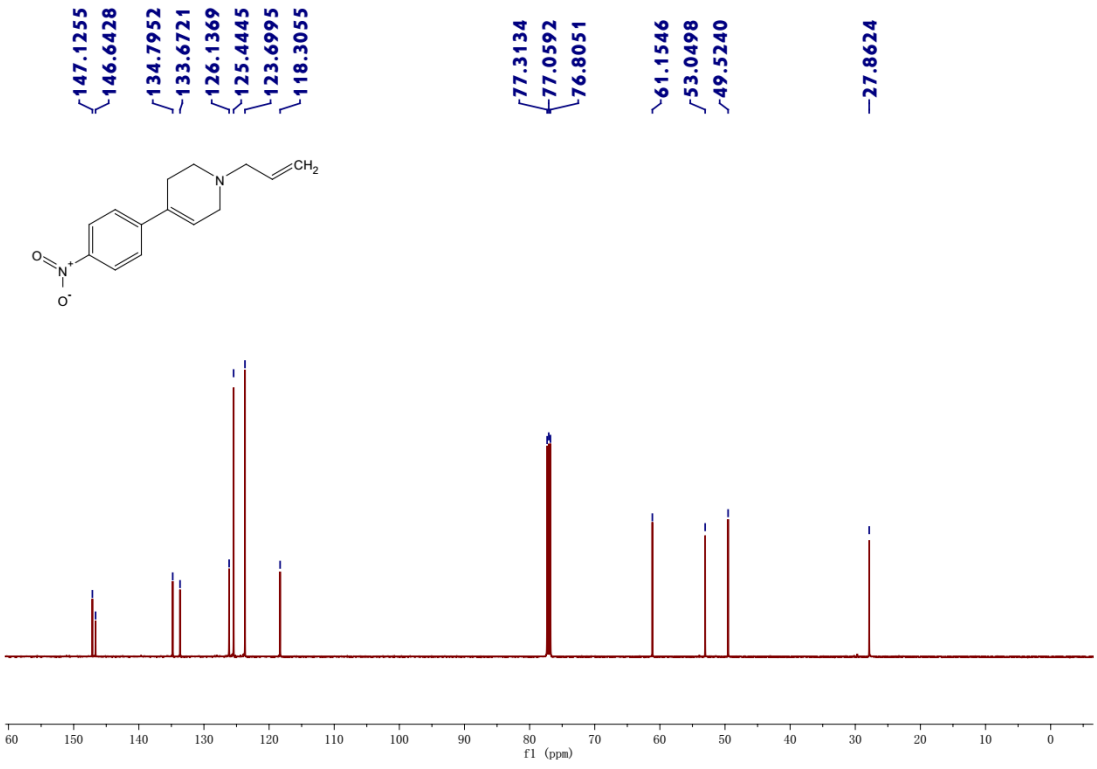
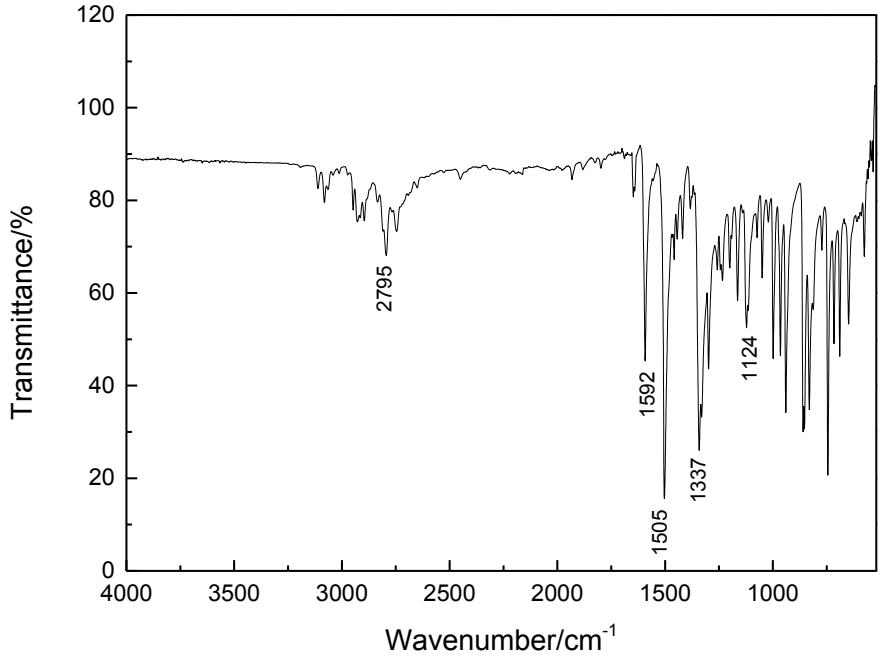


IR of 1-allyl-4-(4-nitro-phenyl)-1,2,3,6-tetrahydro-pyridine (**1g**)



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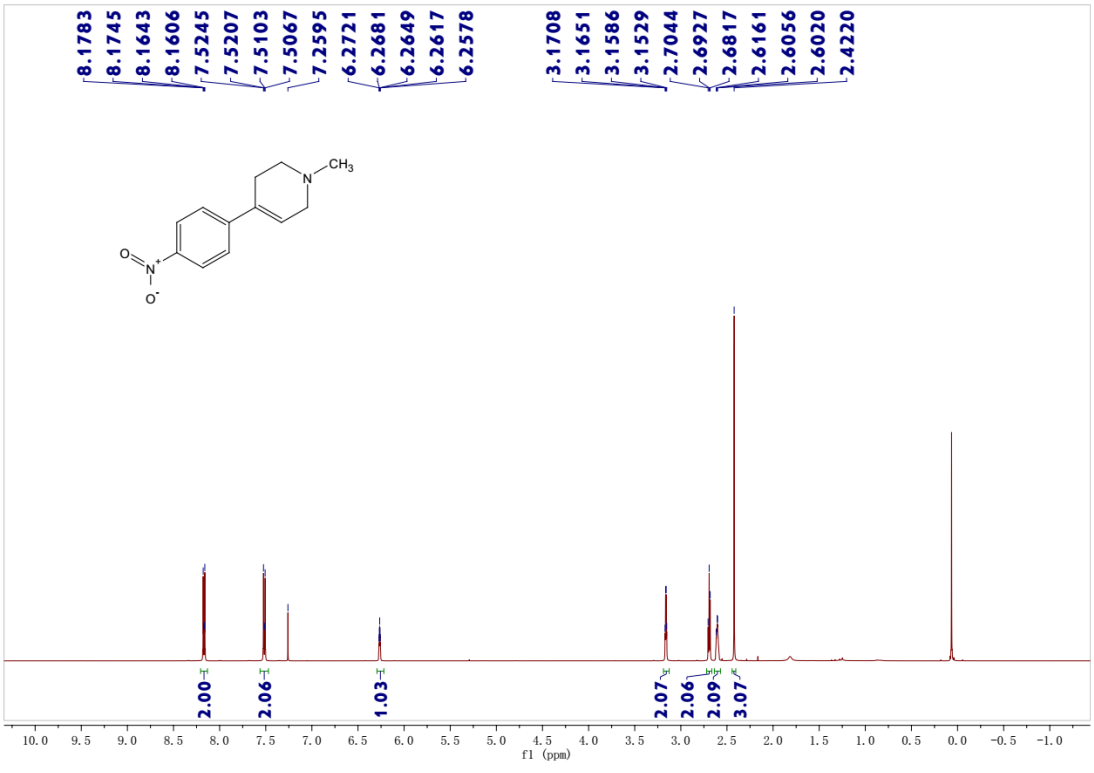

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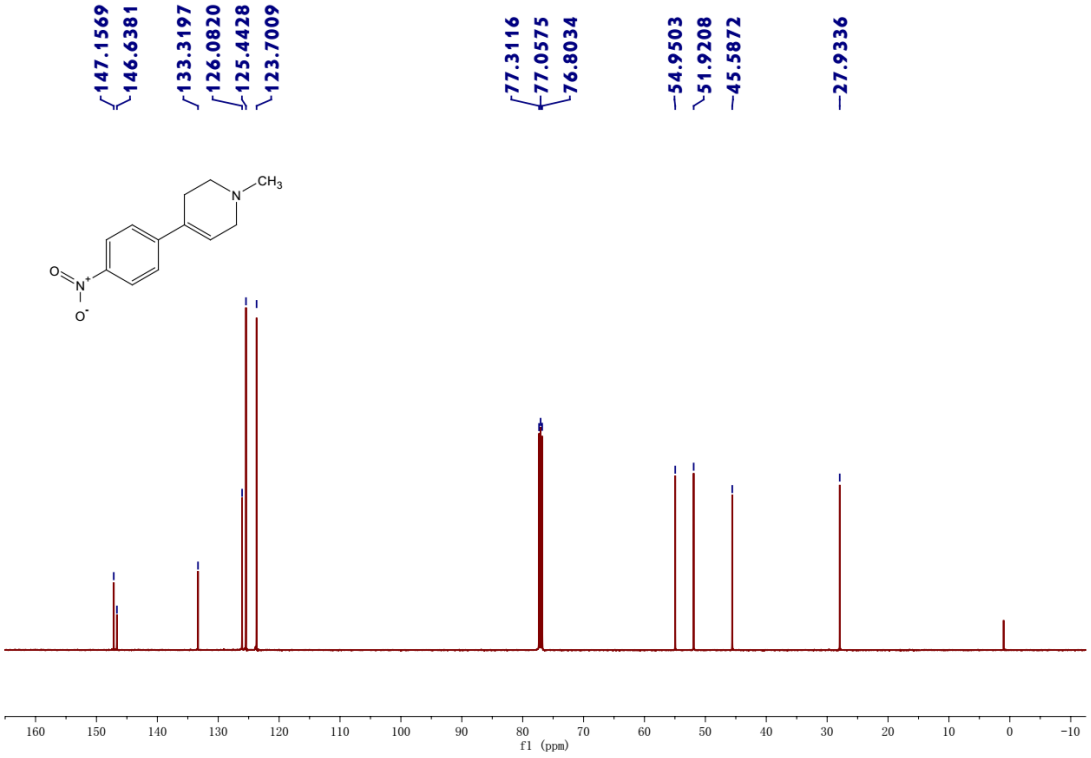
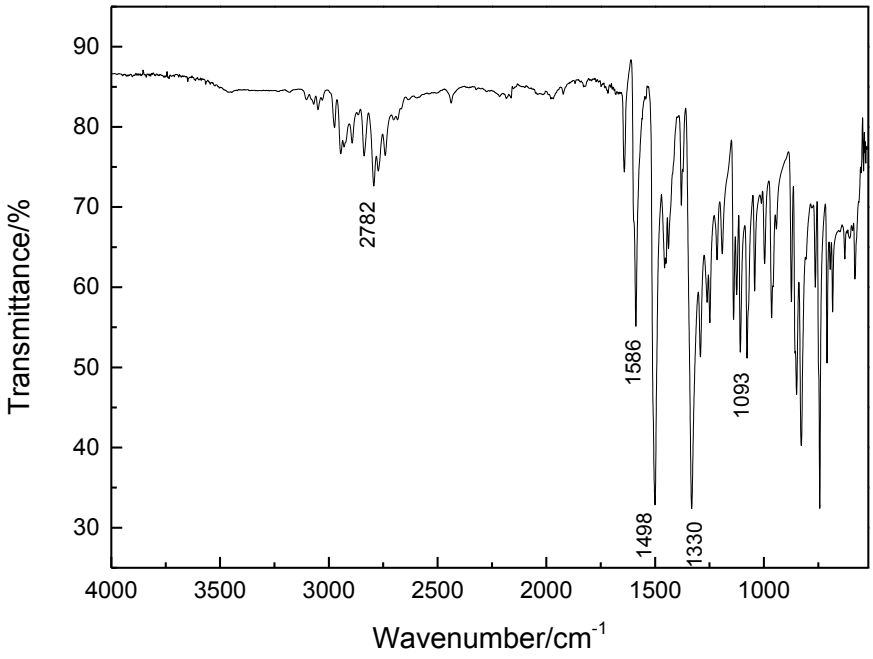
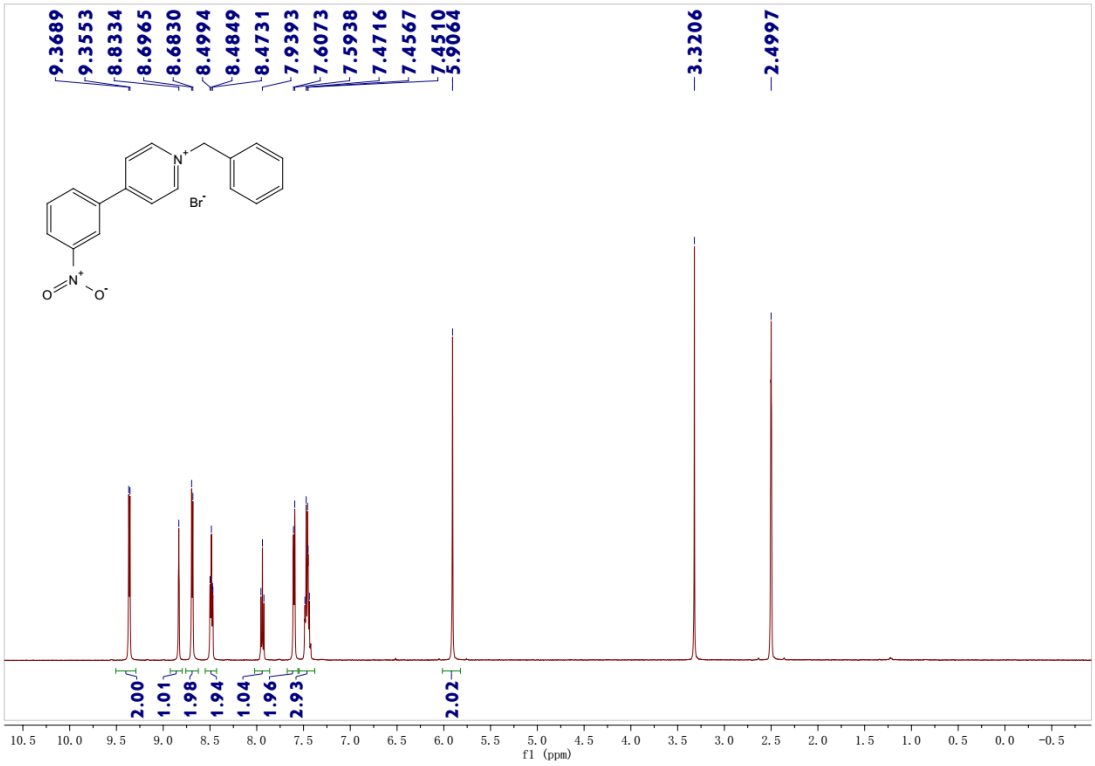


IR of 1-methyl-4-(4-nitro-phenyl)-1,2,3,6-tetrahydro-pyridine (**1h**)



^{1}H NMR of 1-benzyl-4-(3-nitro-phenyl)-pyridinium bromide (**3a**)



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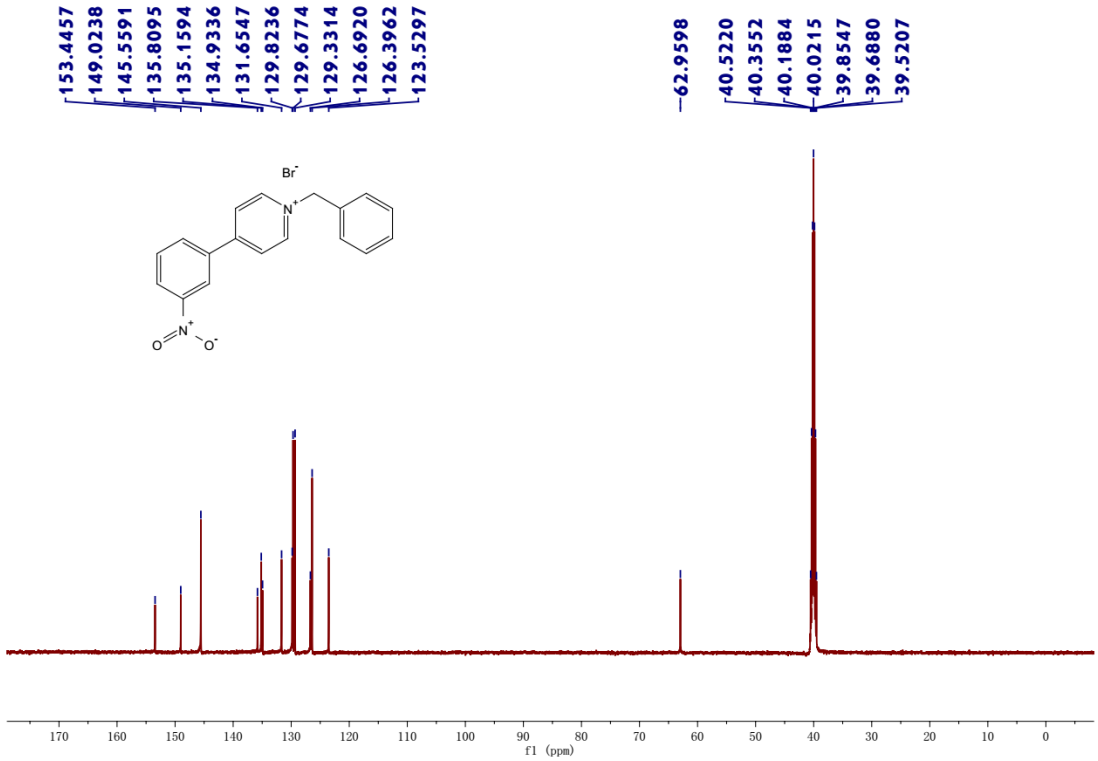

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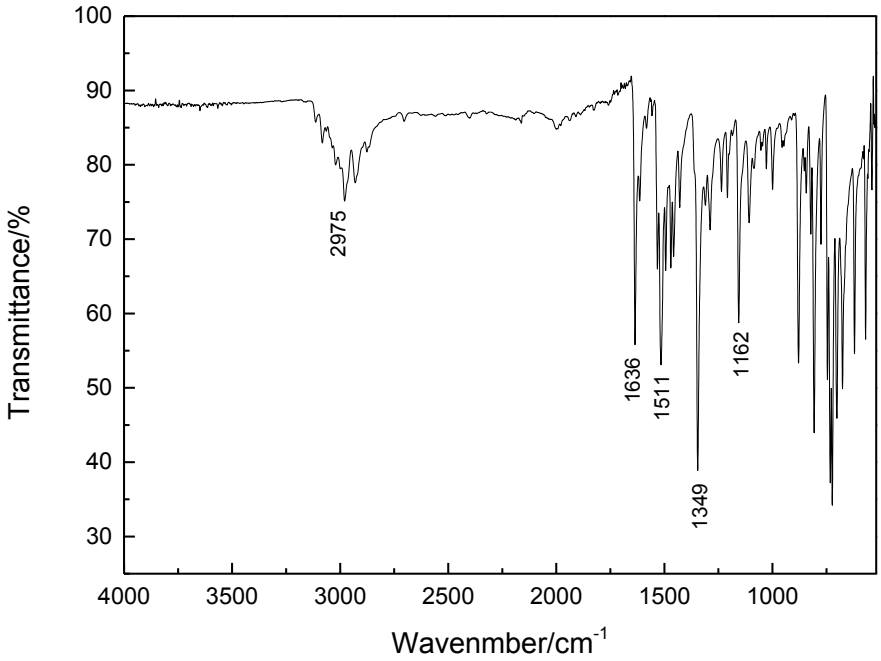
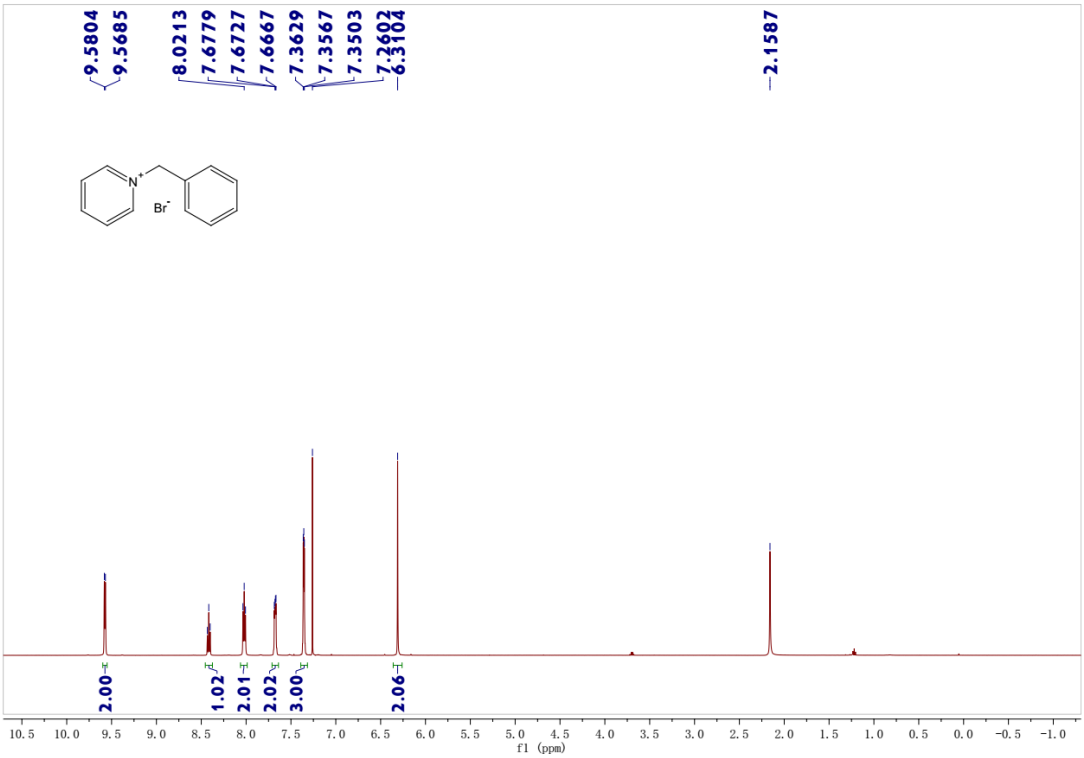


^{1}H NMR of 1-benzyl-pyridinium bromide (**3b**)



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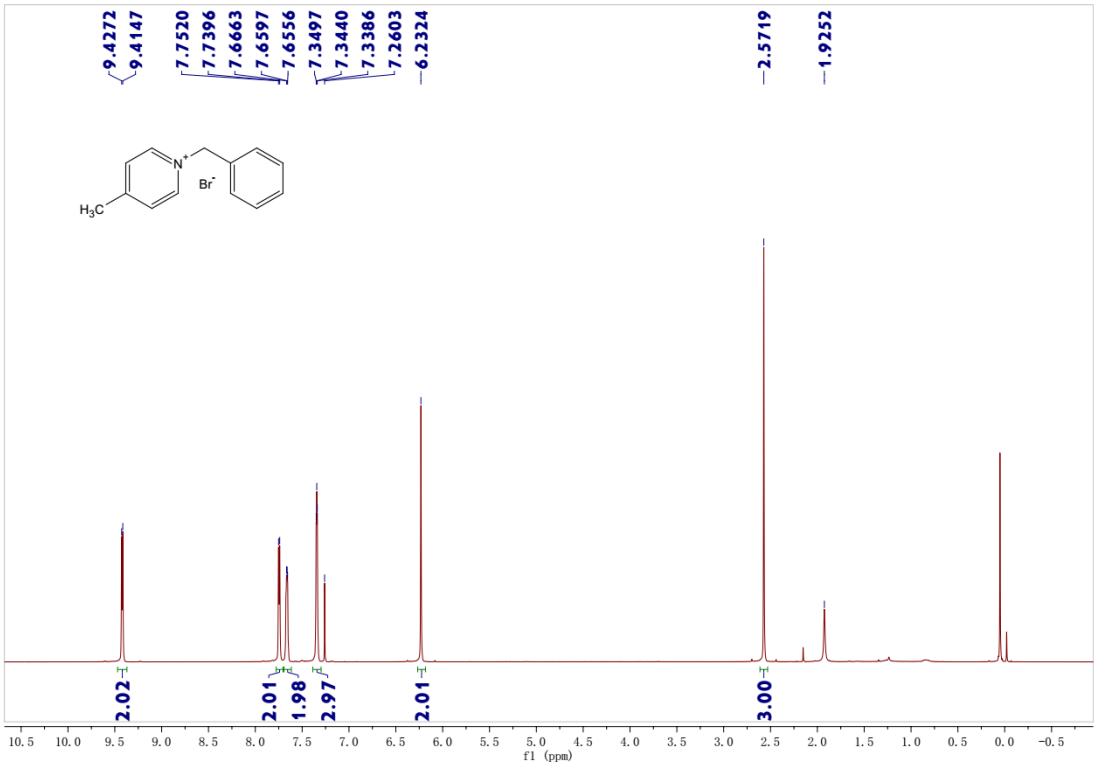

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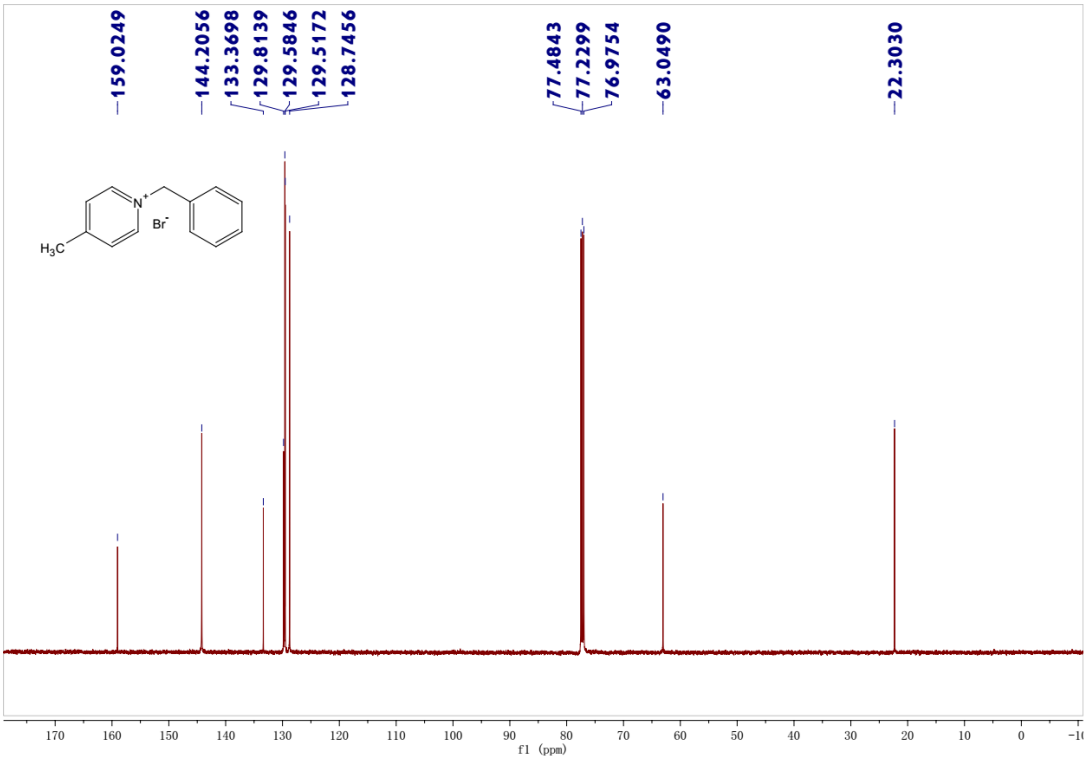

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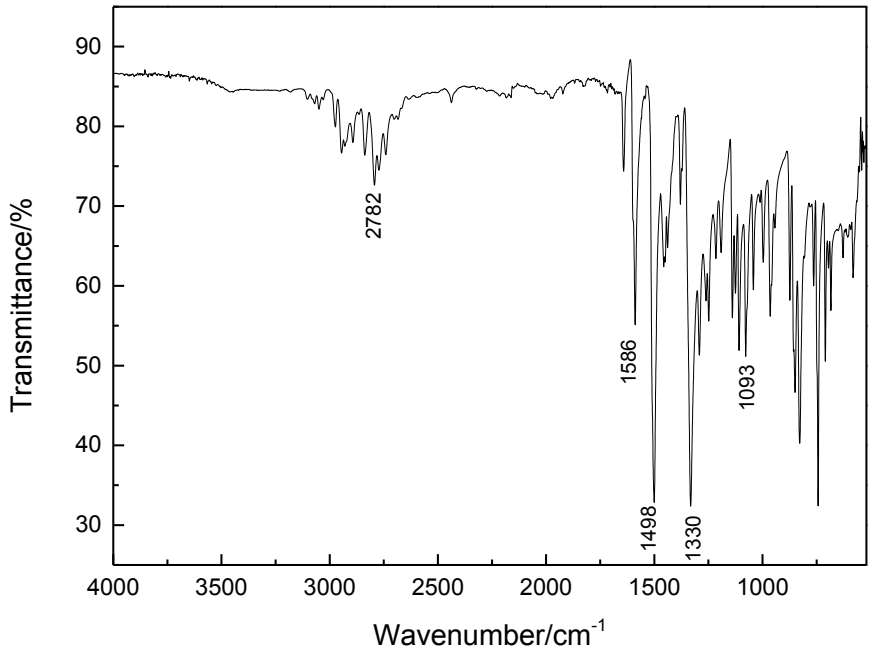

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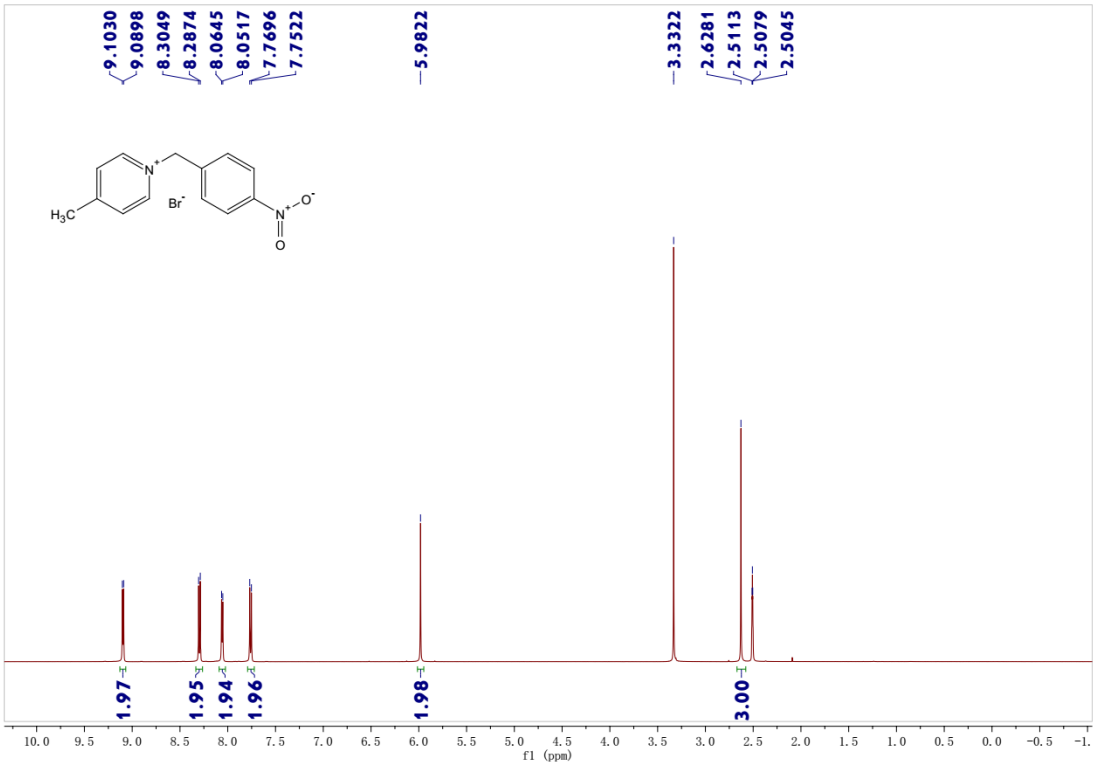

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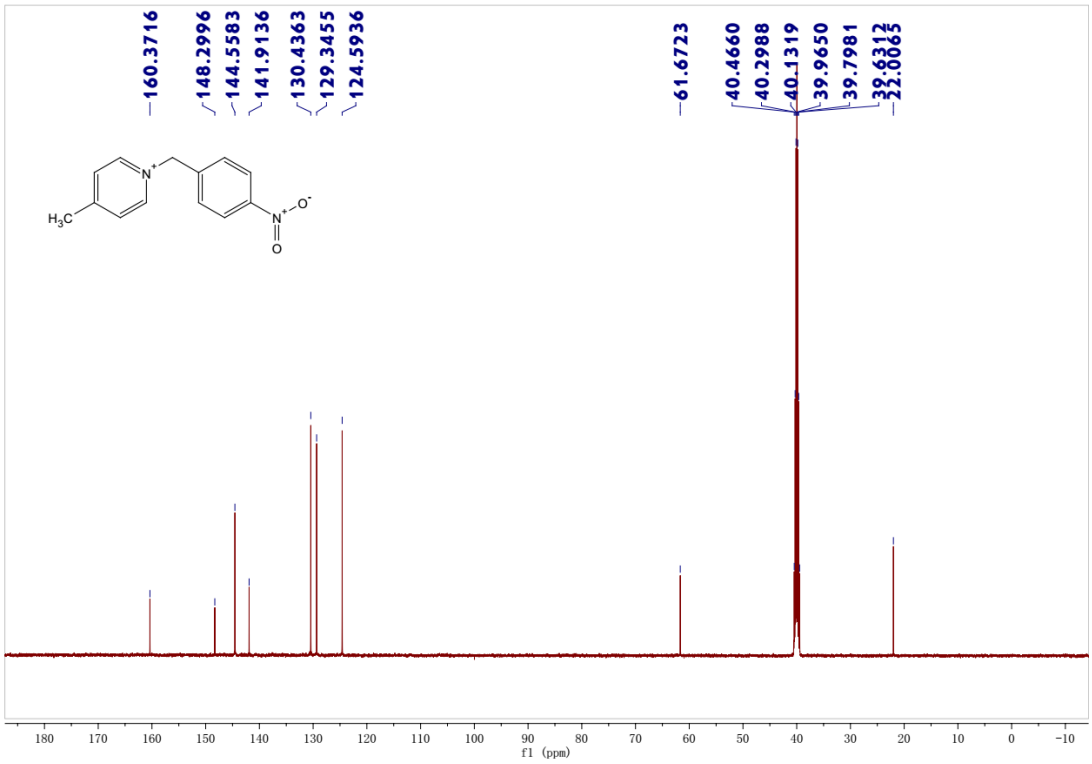
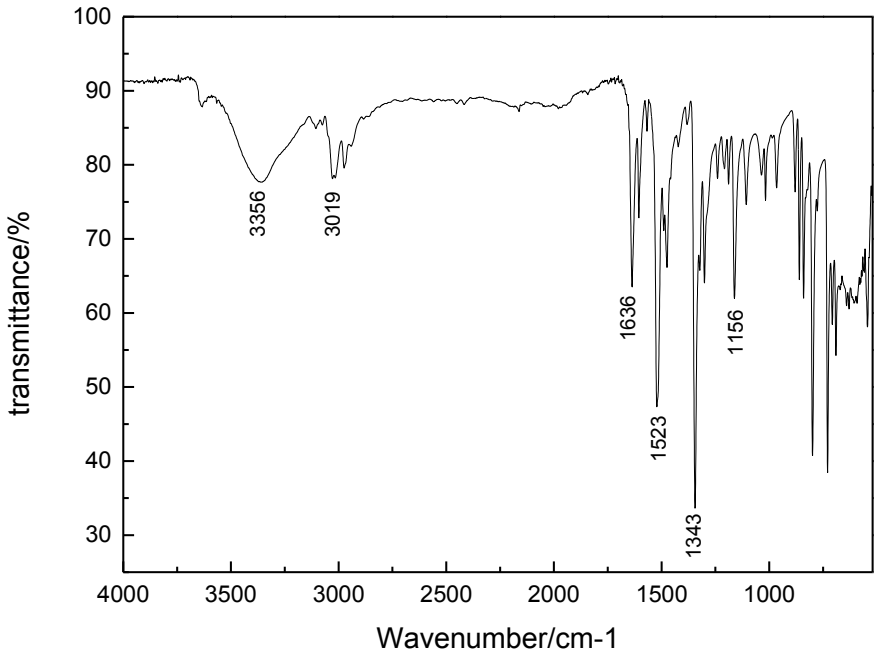


IR of 1-(4-nitro-benzyl)-4-methyl-pyridinium bromide (**3d**)



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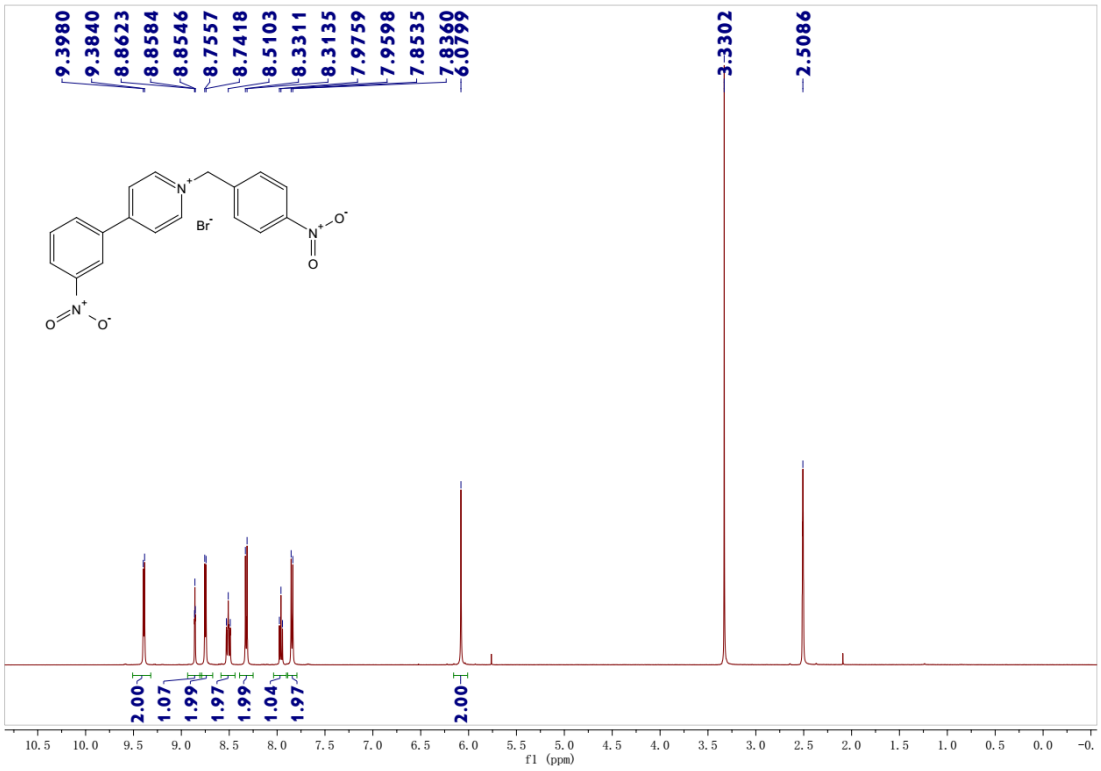

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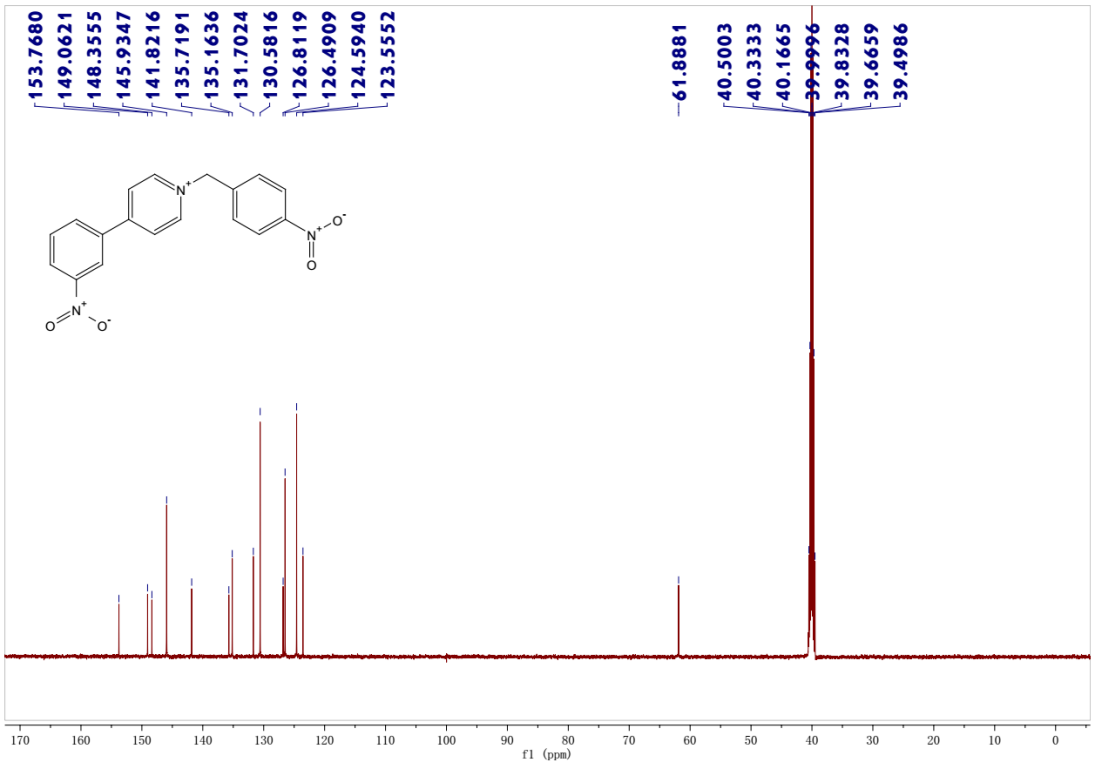
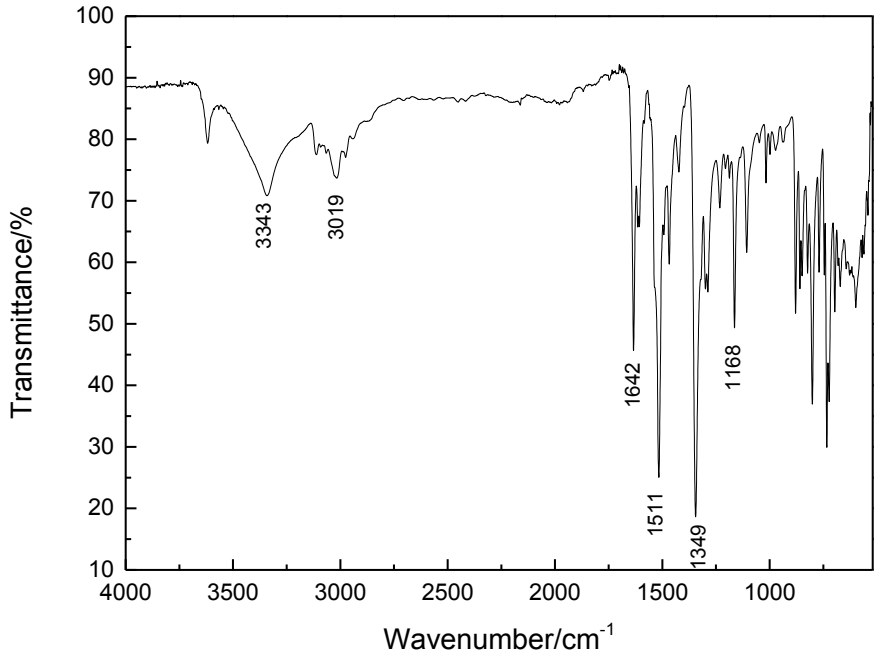


IR of 1-(4-nitro-benzyl)-4-(3-nitro-phenyl)-pyridinium bromide (**3e**)



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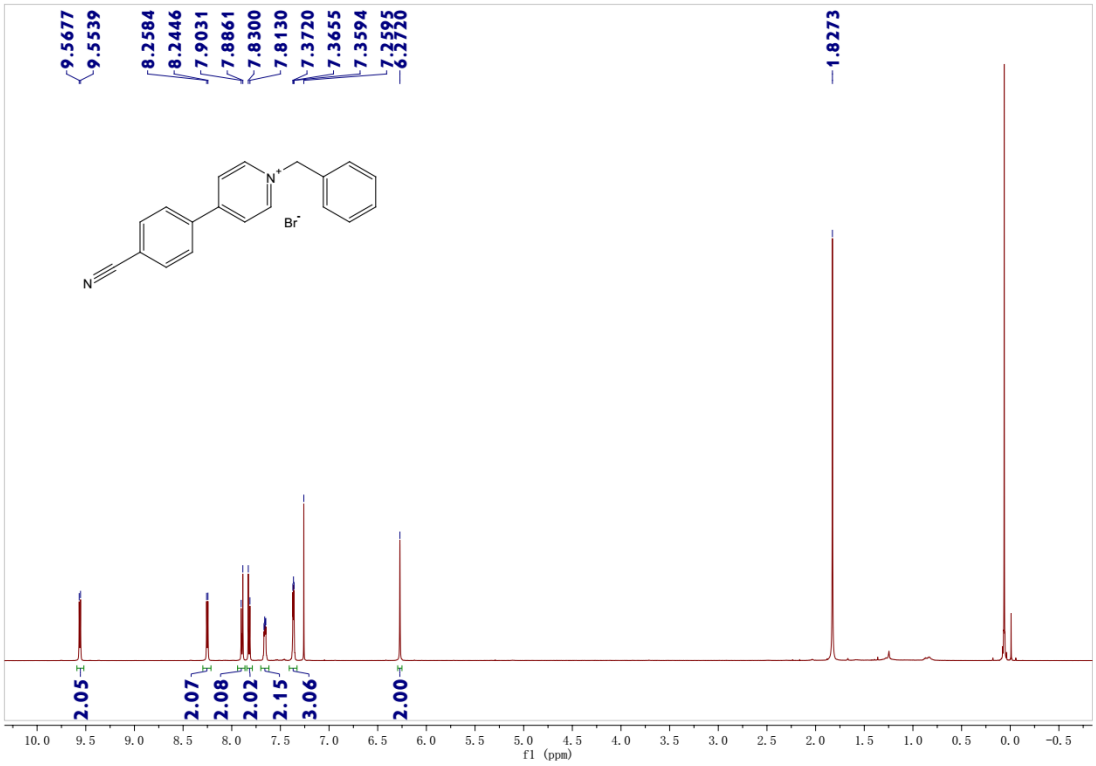

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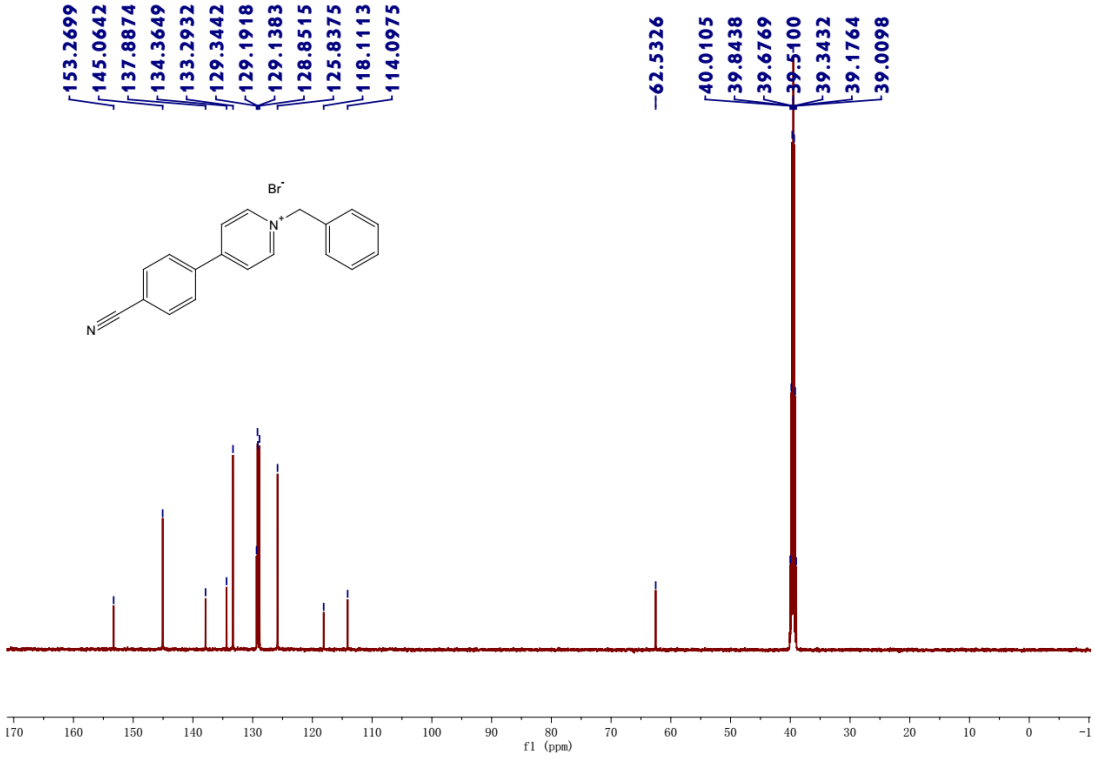
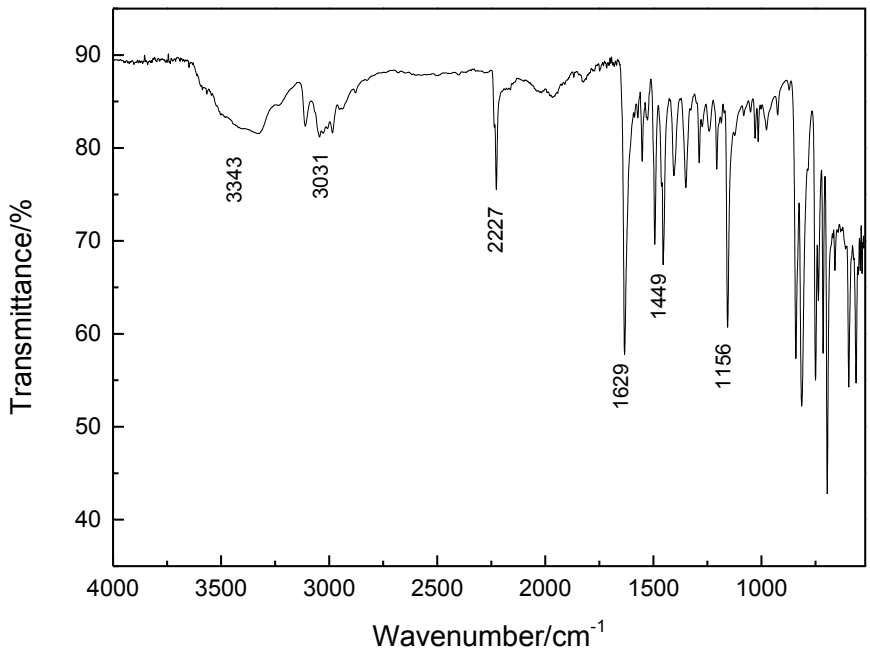
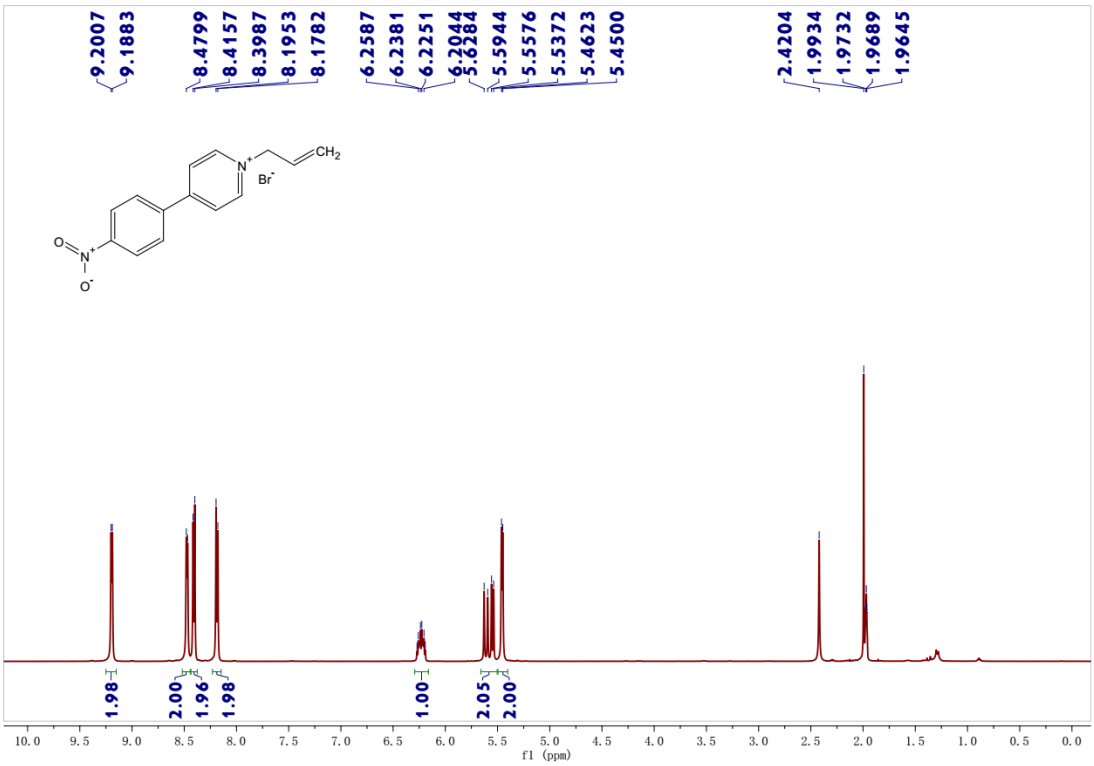


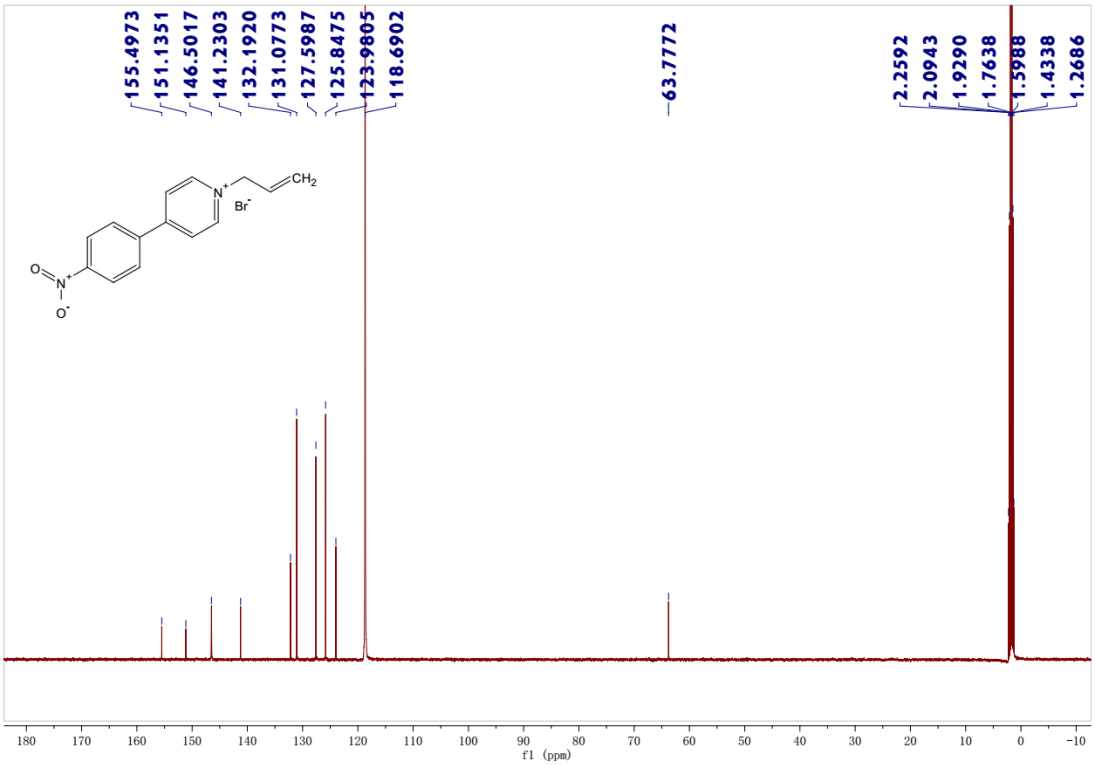
IR of 1-benzyl-4-(4-cyano-phenyl)-pyridinium bromide (**3f**)



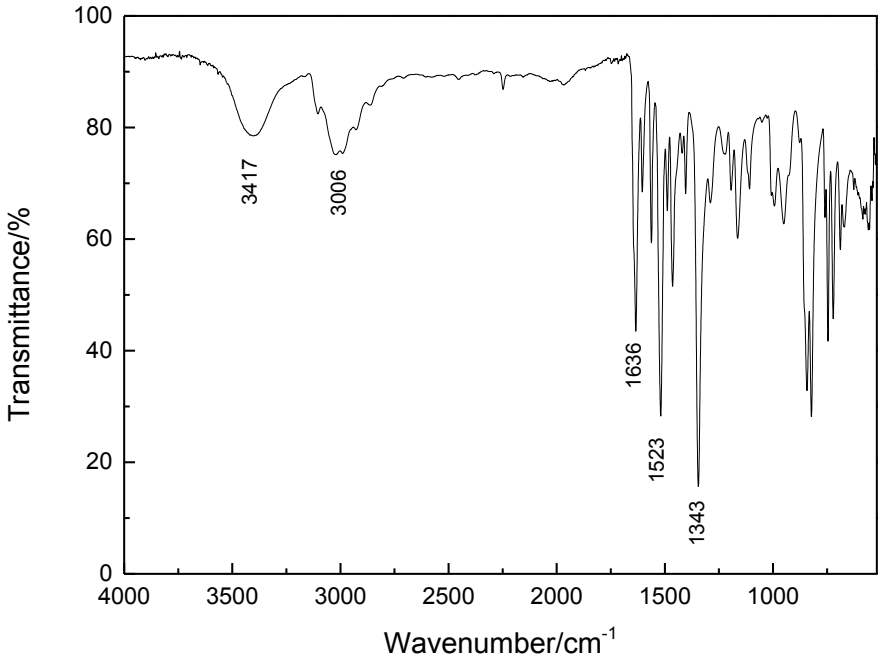
^{1}H NMR of 1-allyl-4-(4-nitro-phenyl)-pyridinium bromide (**3g**)



^{13}C NMR of 1-allyl-4-(4-nitro-phenyl)-pyridinium bromide (**3g**)



IR of 1-allyl-4-(4-nitro-phenyl)-pyridinium bromide (**3g**)



^{1}H NMR of 1-methyl-4-(4-nitro-phenyl)-pyridinium iodide (**3h**)