Supporting Information for

Efficient and phosphine-free bidentate N-heterocyclic carbene/ruthenium catalytic systems for the dehydrogenative amidation of alcohols and amines

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1. Characterization data for L1-L16, [Ru]-1, [Ru-2] and amides 3a-3u

*3-Methyl-1-phenyl-1H-benzo[d]imidazol-3-ium iodide (**L1**).* White solid: m.p. 199.6-201.1 ℃. Isolated yield: 45% in two steps. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.16 (s, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 7.94 – 7.59 (m, 8H), 4.19 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 143.6, 133.6, 132.4, 131.3, 130.9, 127.9, 127.4, 125.6, 114.4, 113.8, 34.1. HR-MS (APCI): m/z calcd. for $C_{14}H_{13}N_2$ $[M-I]^+$: 209.1073; Found: 209.1072.

*3-Methyl-1-(p-tolyl)-1H-benzo[d]imidazol-3-ium iodide (**L2**).* White solid: m.p. 246.3-247.8 ℃. Isolated yield 47% in two steps. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.10 (s, 1H), 8.16 (d, *J* = 8.3 Hz, 1H), 7.86 – 7.76 (m, 2H), 7.75 – 7.70 (m, 3H), 7.57 (d, *J* = 8.1 Hz, 2H), 4.18 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 143.5, 140.8, 132.3, 131.4, 131.3, 131.1, 127.8, 127.3, 125.4, 114.4, 113.8, 34.0, 21.3. HR-MS (APCI): m/z calcd. for $C_{15}H_{15}N_2$ $[M-I]^+$: 223.1230; Found: 223.1227.

*3-Methyl-1-(m-tolyl)-1H-benzo[d]imidazol-3-ium iodide (**L3**).* White solid: m.p. 175.3-176.3 ℃. Isolated yield 43% in two steps. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.11 (s, 1H), 8.16 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.84 – 7.76 (m, 1H), 7.76 – 7.71 (m, 1H), 7.70 – 7.58 (m, 3H), 7.54 (d, *J* = 7.3 Hz, 1H), 4.18 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 143.5, 140.8, 133.6, 132.3, 131.5, 131.3, 130.7, 127.9, 127.4, 125.8, 122.5, 114.4, 113.9, 34.0, 21.3. HR-MS (APCI): m/z calcd. for $C_{15}H_{15}N_2$ $[M-I]^+$: 223.1230; Found: 223.1227.

*3-Methyl-1-(o-tolyl)-1H-benzo[d]imidazol-3-ium iodide (**L4**).* White solid: m.p. 201.8-203.2 ℃. Isolated yield 20% in two steps. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.02 (s, 1H), 8.18 (d, *J* = 8.3 Hz, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.72 – 7.61 (m, 4H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 4.19 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 144.0, 135.3, 132.4, 132.2, 132.1, 132.0, 131.7, 128.2, 128.1, 127.9, 127.3, 114.5, 113.8, 34.1, 17.4. HR-MS (APCI): m/z calcd. for $C_{15}H_{15}N_2$ $[M-I]^+$: 223.1230; Found: 223.1229.

*1-(4-Fluorophenyl)-3-methyl-1H-benzo[d]imidazol-3-ium iodide (**L5**).* White solid: m.p. 207.9-209.3 ℃. Isolated yield 41% in two steps. ^{1}H NMR (500 MHz, DMSO-d_6)

δ 10.13 (s, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 7.91 (dd, *J* = 8.8, 4.7 Hz, 2H), 7.84 – 7.77 (m, 2H), 7.74 (dd, *J* = 7.8, 7.6 Hz, 1H), 7.64 (dd, *J* = 8.8, 8.6 Hz, 2H), 4.19 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 163.2 (d, *J* = 248.5 Hz), 143.8, 132.2, 131.6, 129.9 (d, *J* = 2.7 Hz), 128.3 (d, *J* = 9.2 Hz), 127.9, 127.4, 117.9 (d, *J* = 23.5 Hz), 114.4, 113.7, 34.0. HR-MS (APCI): m/z calcd. for $C_{14}H_{12}N_2$ $[M-I]^+$: 227.0979; Found: 227.0978.

*1-(3-Fluorophenyl)-3-methyl-1H-benzo[d]imidazol-3-ium iodide (**L6**)*. White solid: m.p. 191.8-192.8 ℃. Isolated yield: 38% in two steps. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.19 (s, 1H), 8.17 (d, *J* = 8.3 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.87 – 7.78 (m, 3H), 7.78 – 7.69 (m, 2H), 7.62 – 7.58 (m, 1H), 4.19 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.7 (d, *J* = 246.7 Hz), 143.8, 134.8 (d, *J* = 10.7 Hz), 132.8 (d, *J* = 9.3 Hz), 132.3, 131.2, 128.0, 127.5, 122.0 (d, *J* = 3.3 Hz), 118.0 (d, *J* = 20.8 Hz), 114.5, 113.9, 113.5 (d, *J* = 25.5 Hz), 34.1. HR-MS (APCI): m/z calcd. for $C_{14}H_{12}FN_2$ $[M-I]^+$: 227.0979; Found: 227.0978.

*1-(2-Fluorophenyl)-3-methyl-1H-benzo[d]imidazol-3-ium iodide (**L7**)*. White solid: m.p. 234.5-236.0 ℃. Isolated yield 18% in two steps. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.15 (s, 1H), 8.24 (dd, *J* = 8.0, 1.3 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.94 – 7.63 (m, 4H), 7.60 – 7.45 (m, 2H), 4.26 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 144.0, 140.7, 135.8, 133.6, 131.9, 131.8, 130.6, 129.7, 128.2, 127.5, 114.6, 114.1, 98.2, 34.3. HR-MS (APCI): m/z calcd. for $C_{14}H_{12}FN_2$ $[M-I]^+$: 227.0979; Found: 227.0977.

*1-(4-Ethylphenyl)-3-methyl-1H-benzo[d]imidazol-3-ium iodide (**L8**)*. White solid: m.p. 262.2-263.6 ℃. Isolated yield: 46% in two steps. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.11 (s, 1H), 8.16 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.81 – 7.77 (m, 1H), 7.76 – 7.70 (m, 3H), 7.60 (d, *J* = 8.3 Hz, 2H), 4.18 (s, 3H), 2.77 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 146.9, 143.5, 132.3, 131.4, 131.3, 130.2, 127.8, 127.4, 125.4, 114.4, 113.8, 34.0, 28.3, 16.0. HR-MS (APCI): m/z calcd. for $C_{16}H_{17}N_2$ $[M-I]^+$: 237.1386; Found: 237.1386.

*1-(4-Methoxyphenyl)-3-methyl-1H-benzo[d]imidazol-3-ium iodide (**L9**)*. White solid: m.p. 247.5-248.8 ℃. Isolated yield: 44% in two steps. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.06 (s, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 7.82 – 7.69 (m, 5H), 7.33 – 7.25

(m, 2H), 4.17 (s, 3H), 3.89 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 160.9, 143.5, 132.2, 131.8, 127.8, 127.3, 127.2, 126.2, 115.9, 114.3, 113.7, 56.3, 33.9. HR-MS (APCI): m/z calcd. for $C_{15}H_{15}N_2O$ $[M-I]^+$: 239.1179; Found: 239.1176.

*1-(4-Chlorophenyl)-3-methyl-1H-benzo[d]imidazol-3-ium iodide (**L10**)*. White solid: m.p. 233.4-234.9 ℃. Isolated yield: 36% in two steps. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.18 (s, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 7.92 – 7.84 (m, 5H), 7.80 (dd, *J* = 7.8, 7.6 Hz, 1H), 7.74 (dd, *J* = 7.8, 7.6 Hz, 1H), 4.19 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 143.7, 135.5, 132.5, 132.3, 131.3, 130.9, 127.9, 127.6, 127.4, 114.5, 113.8, 34.1. HR-MS (APCI): m/z calcd. for $C_{14}H_{12}ClN_2$ $[M-I]^+$: 243.0684; Found: 243.0683.

*1-(4-(Ethoxycarbonyl)phenyl)-3-methyl-1H-benzo[d]imidazol-3-ium iodide (**L11**)*. White solid: m.p. 244.7-245.6 ℃. Isolated yield: 28% in two steps. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.25 (s, 1H), 8.31 (d, *J* = 8.4 Hz, 2H), 8.19 (d, *J* = 8.2 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 4.20 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 165.2, 143.8, 137.3, 132.4, 131.8, 131.7, 131.0, 128.0, 127.5, 125.8, 114.6, 113.8, 61.9, 34.1, 14.6. HR-MS (APCI): m/z calcd. for $C_{17}H_{17}N_2O_2$ $[M-I]^+$: 281.1285 ; Found: 281.1284.

*3-Methyl-1-(4-nitrophenyl)-1H-benzo[d]imidazol-3-ium iodide (**L12**)*. Yellow solid: m.p. 274.2-275.6℃. Isolated yield: 42% in two steps. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.30 (s, 1H), 8.61 (d, *J* = 8.6 Hz, 2H), 8.20 (d, *J* = 8.2 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.85 – 7.77 (m, 2H), 4.22 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 148.5, 144.0, 138.7, 132.4, 131.0, 128.2, 127.7, 126.9, 126.2, 114.6, 113.8, 34.2. HR-MS (APCI): m/z calcd. for $C_{14}H_{12}N_3O_2$ $[M-I]^+$: 254.0924; Found: 254.0923.

*3-Ethyl-1-(4-ethylphenyl)-1H-benzo[d]imidazol-3-ium iodide (**L13**)*. White solid: m.p. 244.6-245.4℃. Isolated yield: 46% in two steps. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.13 (s, 1H), 8.22 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.81 – 7.69 (m, 4H), 7.60 (d, *J* = 7.9 Hz, 2H), 4.61 (q, *J* = 7.1 Hz, 2H), 2.78 (q, *J* = 7.6 Hz, 2H), 1.63 (t, *J* = 7.2 Hz, 3H), 1.27 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 146.9, 142.7,

131.6, 131.5, 131.4, 130.1, 127.8, 127.3, 125.6, 114.4, 114.0, 42.9, 28.3, 16.0, 14.5. HR-MS (APCI): m/z calcd. for $C_{17}H_{19}N_2$ $[M-I]^+$: 251.1543; Found: 251.1542.

*1-(4-Ethylphenyl)-3-isopropyl-1H-benzo[d]imidazol-3-ium iodide (**L14**)*. White solid: m.p. 213.2-214.1℃. Isolated yield: 35% in two steps. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.98 (s, 1H), 7.99 – 7.82 (m, 3H), 7.80 – 7.63 (m, 3H), 7.52 (d, *J* = 8.0 Hz, 2H), 5.59 – 5.33 (m, 1H), 2.80 (q, *J* = 7.6 Hz, 2H), 2.00 (d, *J* = 6.8 Hz, 6H), 1.34 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 147.0, 141.4, 131.8, 131.4, 131.0, 130.0, 127.9, 127.3, 125.8, 114.7, 114.0, 51.5, 28.3, 22.0, 16.0. HR-MS (APCI): m/z calcd. for $C_{18}H_{21}N_2$ $[M-I]^+$: 265.1699; Found: 265.1698.

*1-(4-Ethylphenyl)-3-isopropyl-5,6-dimethyl-1H-benzo[d]imidazol-3-ium iodide (**L15**)*. White solid: m.p. 193.2-194.3℃. Isolated yield: 36% in two steps.^{1}H NMR (500 MHz, $CDCl_3$) δ 10.70 (s, 1H), 7.83 (d, *J* = 7.9 Hz, 2H), 7.63 (s, 1H), 7.53 – 7.45 (m, 3H), 5.42 – 5.35 (m, 1H), 2.78 (q, *J* = 7.6 Hz, 2H), 2.52 (s, 3H), 2.44 (s, 3H), 1.95 (d, *J* = 6.8 Hz, 6H), 1.32 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.2, 138.8, 138.0, 137.6, 130.5, 130.0, 128.9, 125.0, 113.8, 113.6, 52.9, 28.6, 22.1, 20.8, 20.7, 15.3. HR-MS (APCI): m/z calcd. for $C_{20}H_{25}N_2$ $[M-I]^+$: 293.2012; Found: 293.2010.

*5,6-Dichloro-1-(4-ethylphenyl)-3-isopropyl-1H-benzo[d]imidazol-3-ium iodide (**L16**)*. White solid: m.p. 258.8-260.1℃. Isolated yield: 12% in two steps. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.95 (s, 1H), 8.02 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.82 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 5.47 – 5.26 (m, 1H), 2.80 (d, *J* = 7.6 Hz, 2H), 1.96 (d, *J* = 6.8 Hz, 6H), 1.33 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.0, 141.8, 133.1, 132.7, 131.2, 130.2, 129.7, 129.5, 125.3, 115.6, 115.5, 53.9, 28.7, 21.9, 15.2. HR-MS (APCI): m/z calcd. for $C_{18}H_{19}Cl_2N_2^+$ $[M-I]^+$: 333.0920; Found: 333.0915.

*N-Benzylbenzamide (**3a**)*.[1] White solid. Isolated yield: 87%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.1 Hz, 2H), 7.53 – 7.46 (m, 1H), 7.44 – 7.38 (m, 2H), 7.37 – 7.32 (m, 4H), 7.31 – 7.26 (m, 1H), 6.53 (brs, 1H), 4.63 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 138.2, 134.4, 131.5, 128.7, 128.5, 127.9, 127.6, 126.9, 44.1.

*N-Hexylbenzamide (**3b**).* [2] White solid. Isolated yield: 88%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.71 (m, 2H), 7.53 – 7.44 (m, 1H), 7.45 – 7.36 (m, 2H), 6.24 (brs, 1H), 3.44 (td, *J* = 7.3, 5.7 Hz, 2H), 1.68 – 1.56 (m, 2H), 1.46 – 1.26 (m, 6H), 0.96 – 0.84 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 134.9, 131.2, 128.4, 127.0, 40.2, 31.5, 29.6, 26.7, 22.6, 14.0. ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 134.9, 131.2, 128.5, 126.8, 40.1, 31.5, 29.6, 26.6, 22.5, 14.0.

*N-(4-Methylbenzyl)benzamide (**3c**).* [2] White solid. Isolated yield: 90%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.75 (m, 2H), 7.57 – 7.48 (m, 1H), 7.44 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 6.47 (brs, 1H), 4.62 (d, *J* = 5.6 Hz, 2H), 2.37 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 137.3, 135.1, 134.4, 131.4, 129.4, 128.5, 127.9, 126.9, 43.9, 21.1.

*N-(4-Fluorobenzyl)benzamide (**3d**).* [2] White solid. Isolated yield: 81%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 6.9 Hz, 2H), 7.55 – 7.47 (m, 1H), 7.45 – 7.39 (m, 2H), 7.36 – 7.28 (m, 2H), 7.08 – 6.96 (m, 2H), 6.54 (brs, 1H), 4.60 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 162.3 (d, *J* = 246.0 Hz), 134.3, 134.0 (d, *J* = 2.5 Hz), 131.6, 129.6 (d, *J* = 8.1 Hz), 128.6, 126.9, 115.6 (d, *J* = 21.4 Hz), 43.4.

*N-(4-Trifluoromethylbenzyl)benzamide (**3e**).* [2] White solid. Isolated yield: 92%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.63 – 7.56 (m, 2H), 7.55 – 7.48 (m, 1H), 7.49 – 7.39 (m, 4H), 6.65 (brs, 1H), 4.74 – 4.63 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 142.4, 134.0, 131.8, 129.8 (q, *J* = 36.6 Hz), 128.7, 128.0, 127.0, 125.7, 124.1 (q, *J* = 272.1 Hz), 43.5.

*N-(Furan-2-ylmethyl)benzamide (**3f**).* [2] White solid. Isolated yield: 75%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.2, 1.7 Hz, 2H), 7.54 – 7.47 (m, 1H), 7.46 – 7.40 (m, 2H), 7.38 (d, *J* = 1.9 Hz, 1H), 6.43 (brs, 1H), 6.34 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.30 (dd, *J* = 3.2, 0.9 Hz, 1H), 4.65 (d, *J* = 5.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 151.1, 142.3, 134.2, 131.6, 128.6, 127.0, 110.5, 107.7, 37.0.

*N-Benzyl-N-methylbenzamide (**3g**).* [2] White solid. Isolated yield: 71%. ^{1}H NMR

(500 MHz, $CDCl_3$) δ 7.56 – 7.29 (m, 9H), 7.20 (s, 1H), 4.99 – 4.50 (m, 2H), 3.26 – 2.62 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 171.6, 137.0, 136.6, 136.2, 129.6, 128.7, 128.4, 128.2, 127.5, 127.0, 126.8, 55.2, 50.8, 37.0, 33.1.

N-Phenylbenzamide (***3h***).[2] White solid. Isolated yield: 31%. ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.4 Hz, 2H), 7.72 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.53 – 7.45 (m, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.36 – 7.28 (m, 2H), 7.13 – 7.05 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 137.9, 135.0, 131.9, 129.1, 128.8, 127.0, 124.6, 120.2.

*Piperidin-2-one (**3i**).*[2] Pale yellow oil. Isolated yield: 72%. ^1H NMR (500 MHz, $CDCl_3$) δ 6.80 (s, 1H), 3.30 (td, *J* = 5.9, 2.2 Hz, 2H), 2.35 (t, *J* = 6.5 Hz, 2H), 1.90 – 1.69 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.6, 42.2, 31.4, 22.2, 20.8.

*N-Benzyl-2-phenylacetamide (**3j**).*[2] White solid. Isolated yield: 76%. ^1H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.26 (m, 8H), 7.20 (dd, *J* = 6.8, 1.8 Hz, 2H), 5.74 (brs, 1H), 4.44 (d, *J* = 5.9 Hz, 2H), 3.65 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 138.1, 134.8, 129.4, 129.0, 128.6, 127.5, 127.41, 127.39, 43.8, 43.6.

*N-Benzylhexanamide (**3k**).*[2] White solid. Isolated yield: 75%. ^1H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.33 – 7.29 (m, 3H), 5.71 (brs, 1H), 4.47 (d, *J* = 5.6 Hz, 2H), 2.23 (t, *J* = 7.6 Hz, 2H), 1.74 – 1.65 (m, 2H), 1.41 – 1.30 (m, 4H), 0.92 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 138.4, 128.7, 127.8, 127.5, 43.6, 36.8, 31.5, 25.4, 22.4, 13.9.

*N-Benzylfuran-2-carboxamide (**3l**).*[2] White solid. Isolated yield: 77%. ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.38 – 7.27 (m, 5H), 7.14 (s, 1H), 6.70 (brs, 1H), 6.54 – 6.44 (m, 1H), 4.60 (dd, *J* = 5.8, 2.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 147.9, 143.9, 138.0, 128.7, 127.9, 127.6, 114.4, 112.1, 43.1.

*N-Benzyl-2-phenylpropanamide (**3m**).*[2] White solid. Isolated yield: 55%. ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.23 (m, 8H), 7.17 (d, *J* = 6.9 Hz, 2H), 5.69 (brs, 1H), 4.50 – 4.31 (m, 2H), 3.62 (q, *J* = 7.2 Hz, 1H), 1.59 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.0, 141.3, 138.3, 128.9, 128.6, 127.6, 127.4, 127.3, 127.2, 47.2,

43.6, 18.5.

*N-Benzyl-4-methylbenzamide (**3n**).* [1] White solid. Isolated yield: 91%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 4.3 Hz, 4H), 7.35 – 7.29 (m, 1H), 7.25 (d, *J* = 7.2 Hz, 2H), 6.41 (brs, 1H), 4.67 (dd, *J* = 5.7, 1.9 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 142.0, 138.3, 131.5, 129.2, 128.8, 127.9, 127.6, 126.9, 44.1, 21.4.

*N-Benzyl-4-trifluoromethylbenzamide (**3o**).* [1] White solid. Isolated yield: 73%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.45 – 7.31 (m, 5H), 6.51 (brs, 1H), 4.68 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 137.7, 137.6, 133.3 (q, *J* = 32.6 Hz), 128.9, 128.0, 127.8, 127.4, 125.7 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 272.5 Hz), 44.3.

*N-Benzyl-4-fluorobenzamide (**3p**).* [1] White solid. Isolated yield: 77%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.70 (m, 2H), 7.46 – 7.27 (m, 5H), 7.17 – 6.98 (m, 2H), 6.43 (brs, 1H), 4.63 – 4.58 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 164.8 (d, *J* = 252.0 Hz), 138.0, 130.6 (d, *J* = 3.3 Hz), 129.3 (d, *J* = 8.4 Hz), 128.8, 127.9, 127.7, 115.6 (d, *J* = 22.0 Hz), 44.3.

*N-Benzyl-3-fluorobenzamide (**3q**).* [1] White solid. Isolated yield: 78%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.51 (m, 2H), 7.48 – 7.30 (m, 6H), 7.26 – 7.15 (m, 1H), 6.52 (brs, 1H), 4.65 (dd, *J* = 5.8, 3.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 162.8 (d, *J* = 247.8 Hz), 137.9, 136.7 (d, *J* = 6.8 Hz), 130.2 (d, *J* = 8.0 Hz), 128.8, 127.9, 127.7, 122.4, 118.5 (d, *J* = 21.3 Hz), 114.4 (d, *J* = 22.8 Hz), 44.2.

*N-Benzyl-2-fluorobenzamide (**3r**).* [1] White solid. Isolated yield: 81%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 – 8.13 (m, 1H), 7.58 – 7.45 (m, 1H), 7.45 – 7.36 (m, 4H), 7.35 – 7.29 (m, 2H), 7.13 (dd, *J* = 12.1, 8.3 Hz, 1H), 7.06 (brs, 1H), 4.72 (d, *J* = 6.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2 (d, *J* = 3.2 Hz), 160.7 (d, *J* = 247.0 Hz), 138.1, 133.3 (d, *J* = 9.5 Hz), 132.2 (d, *J* = 2.3 Hz), 128.8, 127.7, 127.6, 124.8 (d, *J* = 3.2 Hz), 120.9 (d, *J* = 11.7 Hz), 116.0 (d, *J* = 24.8 Hz), 44.1.

*N-Benzyl-2-methylbenzamide (**3s**)*. White solid: m.p. 102.9-104.4 ºC. Isolated yield: 79%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.27 (m, 7H), 7.25 – 7.13 (m, 2H), 6.05 (brs, 1H), 4.62 (d, *J* = 5.8 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.9, 138.3, 136.3, 136.2, 131.0, 129.9, 128.8, 127.8, 127.6, 126.7, 125.7, 43.9, 19.8. HR-MS (ESI): m/z calcd. for $C_{15}H_{16}NO$ $[M+H]^+$: 226.1226; Found: 226.1225.

*N-Benzyl-2-(trifluoromethoxy)benzamide (**3t**)*. White solid: m.p. 82.3-83.6 ºC. Isolated yield: 70%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.58 – 7.48 (m, 1H), 7.46 – 7.26 (m, 7H), 6.79 (brs, 1H), 4.68 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.1, 146.0, 137.7, 132.3, 131.7, 128.8, 128.0, 127.8, 127.7, 127.4, 121.0, 120.3 (q, *J* = 259.80 Hz), 44.3. HR-MS (ESI): m/z calcd. for $C_{15}H_{13}F_3NO_2$ $[M+H]^+$: 296.0854; Found: 296.0890.

*N-Benzyl-2-(trifluoromethyl)benzamide (**3u**)*. White solid: m.p. 117.6-119.1 ºC. Isolated yield: 41%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.2 Hz, 1H), 7.65 – 7.50 (m, 3H), 7.40 – 7.28 (m, 5H), 6.07 (brs, 1H), 4.65 (d, *J* = 5.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 137.5, 135.8, 132.0, 129.8, 128.8, 128.6, 128.0, 127.8, 127.2 (t, *J* = 31.9 Hz), 126.4 (q, *J* = 5.0 Hz), 123.6 (d, *J* = 273.7 Hz), 44.4. HR-MS (ESI): m/z calcd. for $C_{15}H_{13}F_3NO$ $[M+H]^+$: 280.0944; Found: 280.0945.

[Ru]-1. Orange powder: m.p. 176.3 ℃ (decomp.). Purified by neutral alumina column chromatography with an eluent of petroleum ether and ethyl acetate (20: 1). Isolated yield: 29% (obtained by *in situ* catalyst generation for 0.5 h). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.66 (s, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.29 (s, 1H), 6.74 (d, *J* = 7.7 Hz, 1H), 5.86 – 5.64 (m, 1H), 5.50 (d, *J* = 6.1 Hz, 1H), 5.44 (d, *J* = 6.0 Hz, 1H), 5.36 (d, *J* = 6.1 Hz, 1H), 5.27 (d, *J* = 5.9 Hz, 1H), 2.73 – 2.49 (m, 2H), 2.34 (s, 3H), 2.32 (s, 3H), 2.32 – 2.27 (m, 1H), 2.16 (s, 3H), 1.84 (d, *J* = 7.2 Hz, 3H), 1.67 (d, *J* = 6.9 Hz, 3H), 1.24 (t, *J* = 7.7 Hz, 3H), 0.86 (d, *J* = 6.9 Hz, 3H), 0.72 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.4, 160.1, 143.7, 141.1, 137.7, 130.9, 130.4, 130.1, 129.2, 120.2, 111.3, 111.1, 110.9, 102.8, 101.9, 92.5, 90.4, 86.7, 83.9, 53.1, 30.4, 27.7, 21.8, 21.2, 20.9, 20.1, 19.6, 19.4, 19.3, 15.1. HR-MS (ESI): m/z calcd. for $C_{30}H_{37}IN_2Ru$ $[M]^+$: 654.1039; Found: 654.1060 (Ru was probably oxidized from +2 to +3 during the HR-MS measurement, leading to the observed charge of +1 of the

complex, and similar phenomenon was observed from Glorius and co-workers.[3]) The single crystal structure of this complex was deposited to CCDC with a CCDC deposition number of 1849029.

[Ru]-2. Orange powder: m.p. 182.5 ℃ (decomp.). Purified by neutral alumina column chromatography with an eluent of petroleum ether and ethyl acetate (10: 1). Isolated yield: 22% (obtained by *in situ* catalyst generation for 0.5 h). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.65 (s, 1H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.29 (s, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 5.83 – 5.64 (m, 1H), 5.60 – 5.31 (m, 4H), 4.96 (dd, *J* = 5.5 Hz, 1H), 2.85 – 2.48 (m, 2H), 2.34 (s, 3H), 2.32 (s, 3H), 2.21 (s, 3H), 1.83 (d, *J* = 7.1 Hz, 3H), 1.68 (d, *J* = 6.9 Hz, 3H), 1.24 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.4, 160.3, 145.1, 142.2, 138.8, 131.9, 131.4, 131.3, 130.4, 121.5, 112.3, 112.1, 112.0, 103.9, 92.4, 91.3, 89.5, 87.9, 82.0, 54.2, 28.8, 22.2, 21.1, 20.8, 20.43, 20.37, 16.1. HR-MS (ESI): m/z calcd. for $C_{27}H_{32}IN_2Ru$ $[M+H]^+$: 613.0648; Found: 613.0647. The single crystal structure of this complex was deposited to CCDC with a CCDC deposition number of 1854319.

References

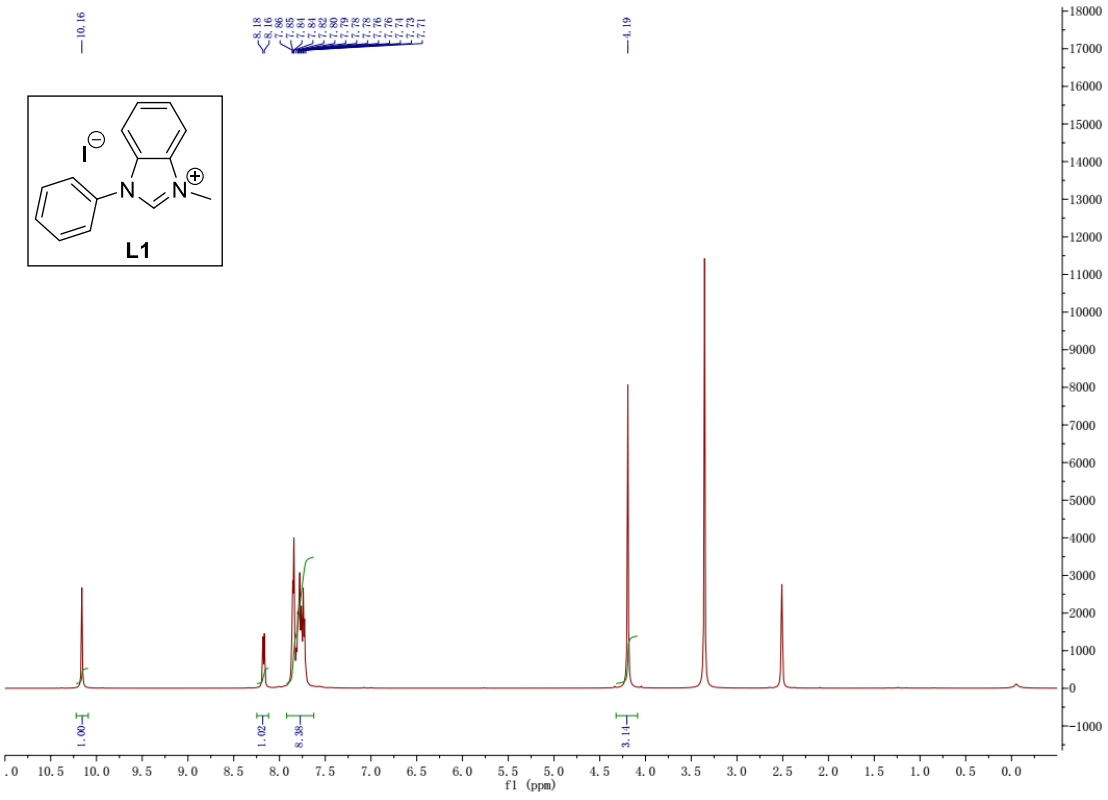
[1] H. Cheng, M. Q. Xiong, C. X. Cheng, H. J. Wang, Q. Lu, H. F. Liu, F. B. Yao, C. Chen, F. Verpoort, *Chem. Asian J.* **2018**, *13*, 440-448.

[2] H. Cheng, M. Q. Xiong, N. Zhang, H. J. Wang, Y. Miao, W. Su, Y. Yuan, C. Chen, F. Verpoort, *ChemCatChem*, DOI: 10.1002/cctc.201800945.

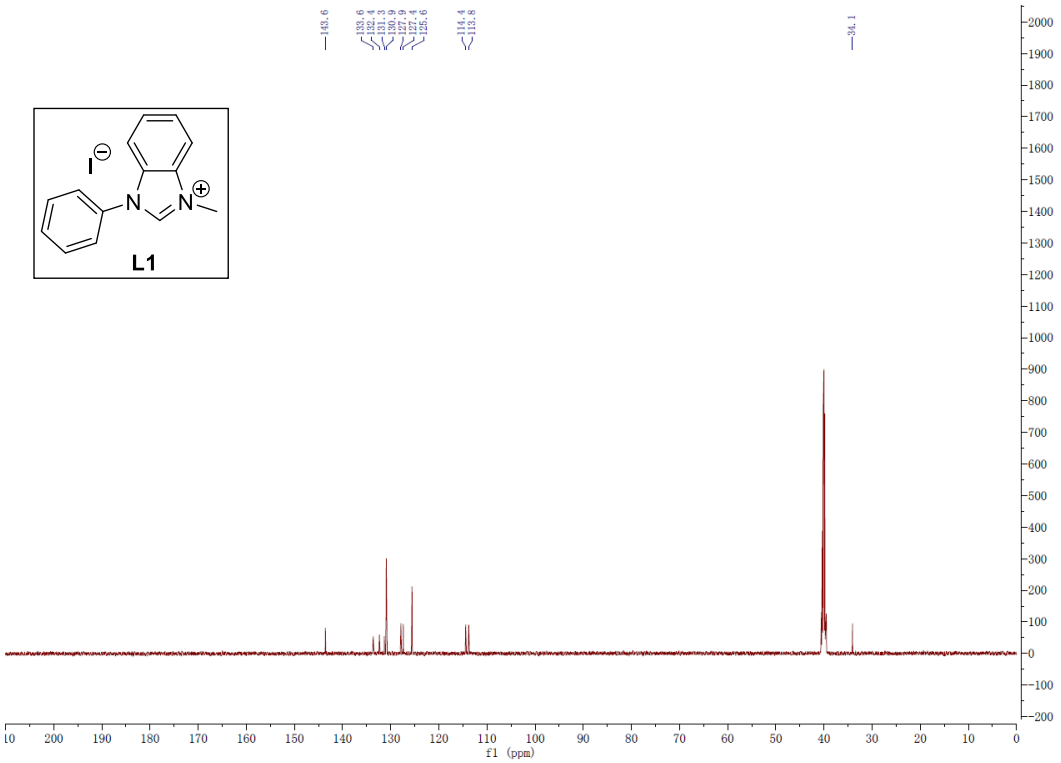
[3] N. Ortega, C. Richter, F. Glorius, *Org. Lett.* **2013**, *15*, 1776-1779.

2. Original ^{1}H and ^{13}C NMR spectra for L1-L16, 3a-3u, [Ru]-1 and [Ru-2]:

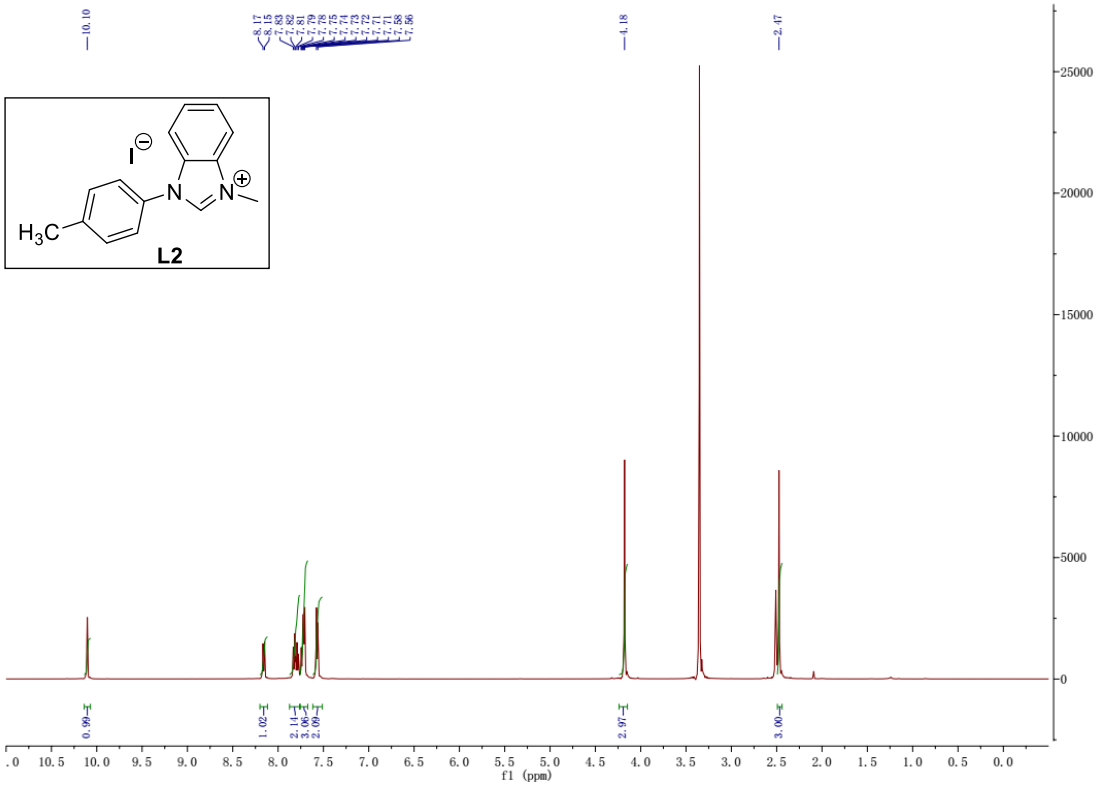
- ^{1}H NMR spectrum for **L1**



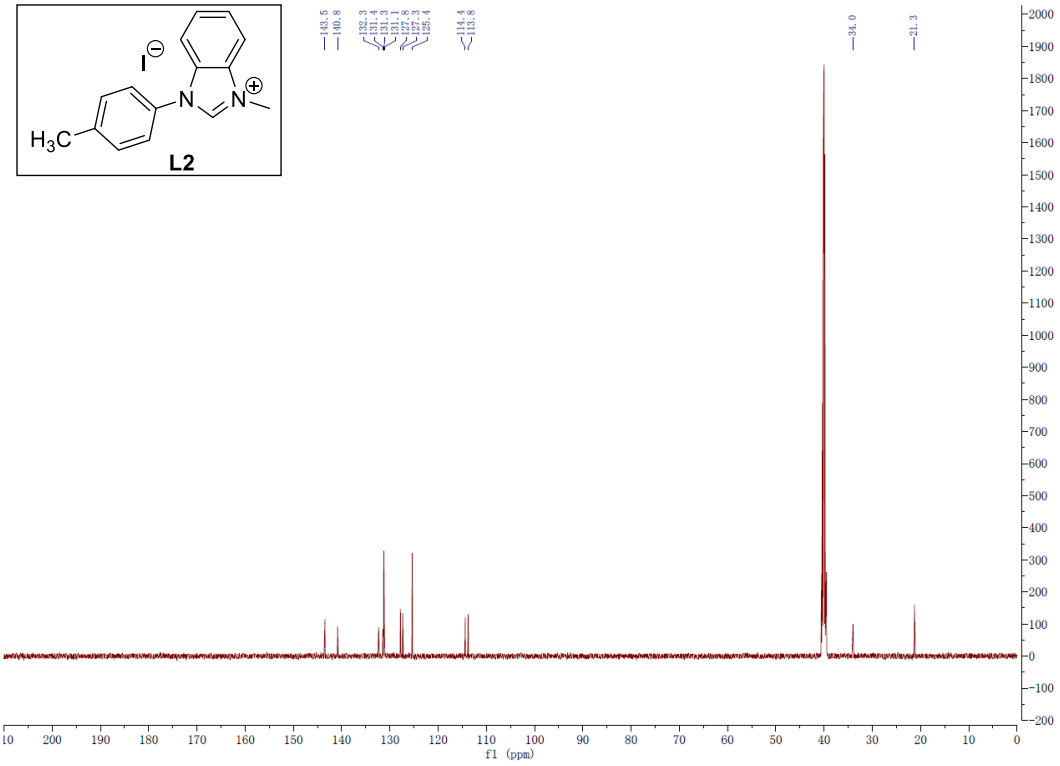
- ^{13}C NMR spectrum for **L1**



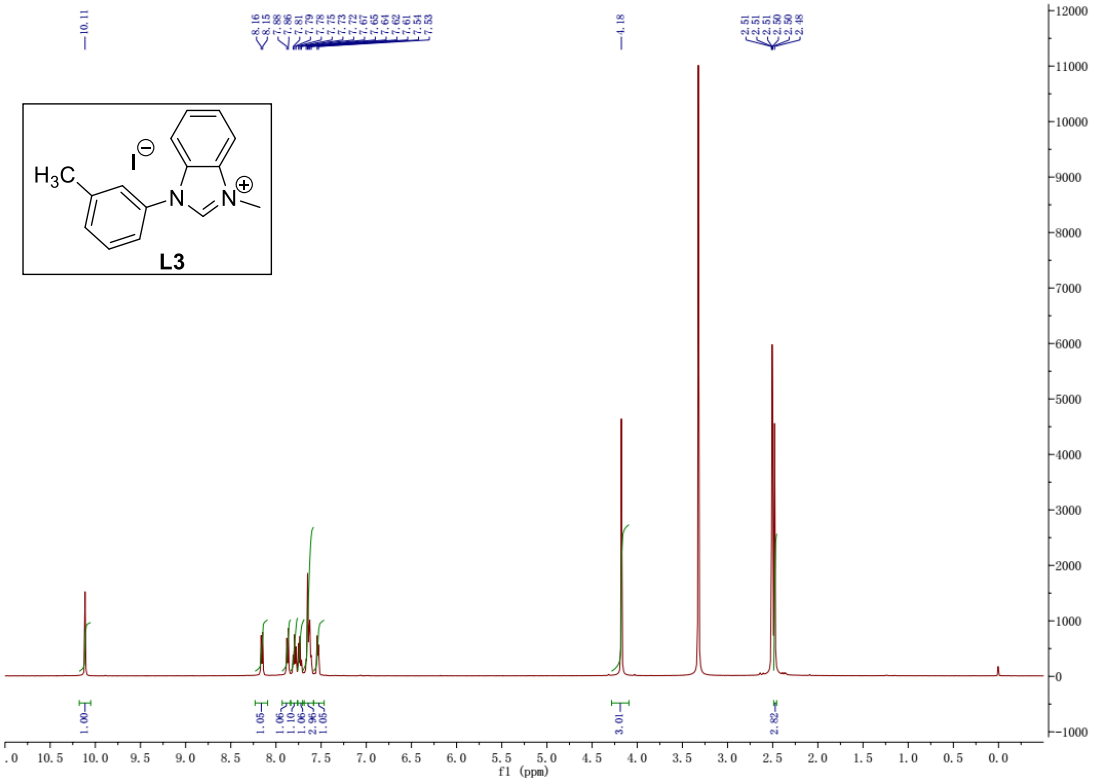
➢ ^{1}H NMR spectrum for **L2**



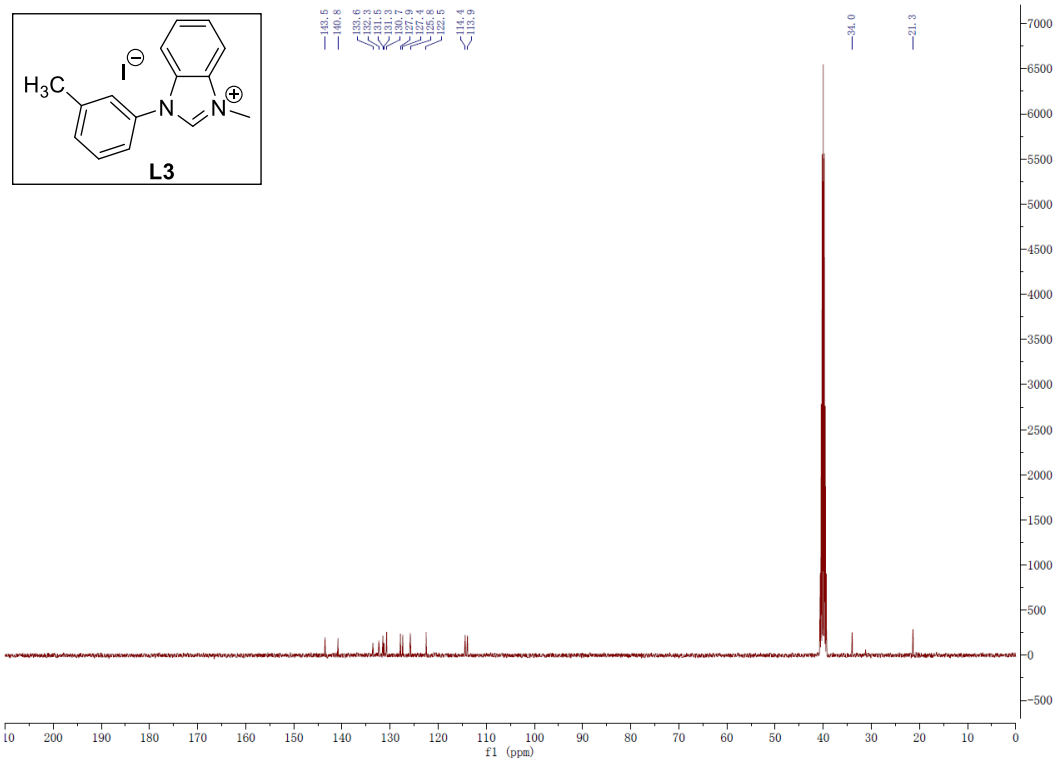
➢ ^{13}C NMR spectrum for **L2**



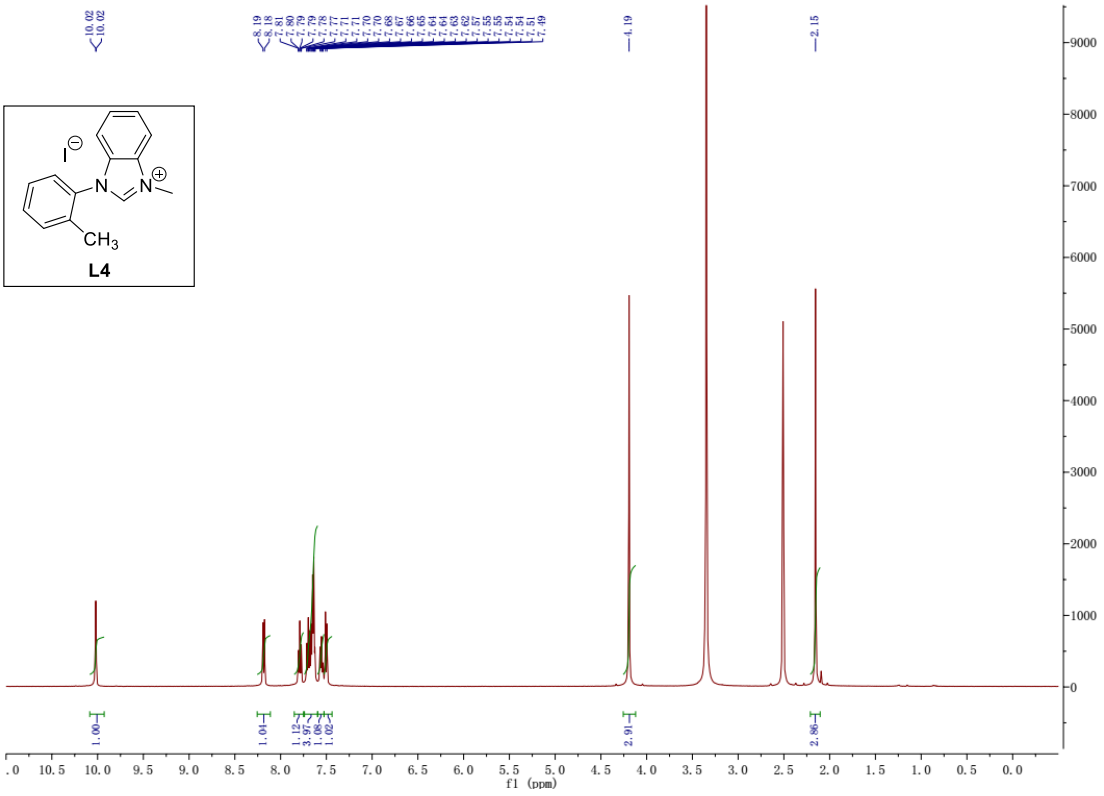
➢ ^{1}H NMR spectrum for **L3**



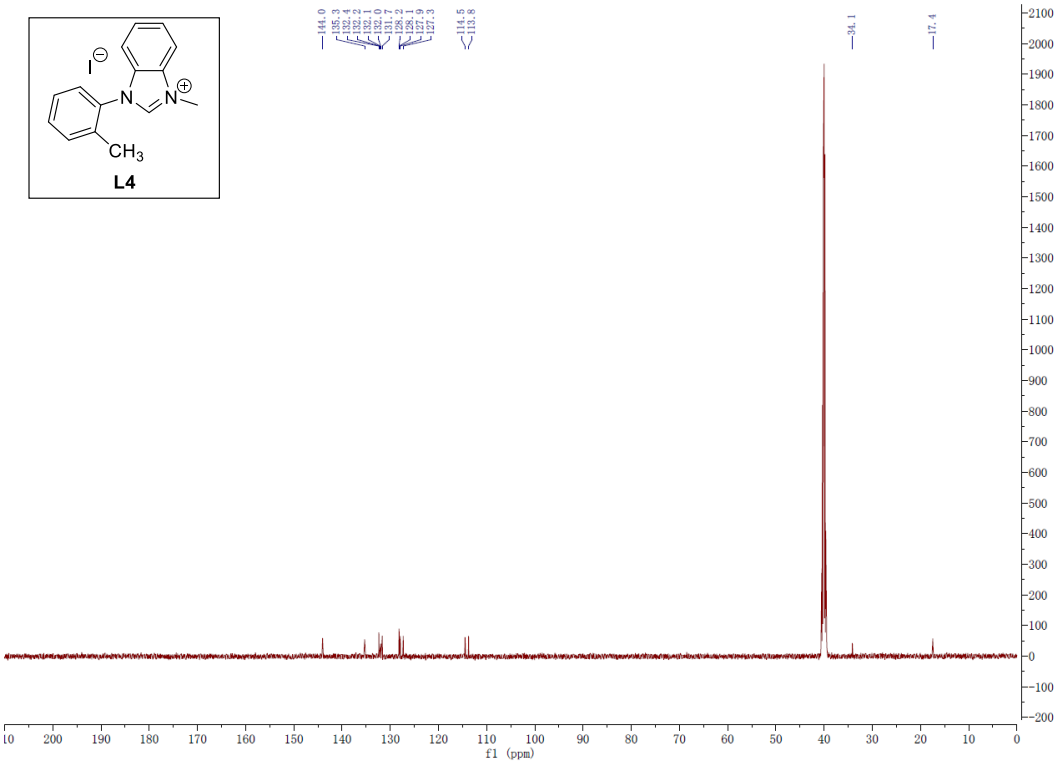
➢ ^{13}C NMR spectrum for **L3**



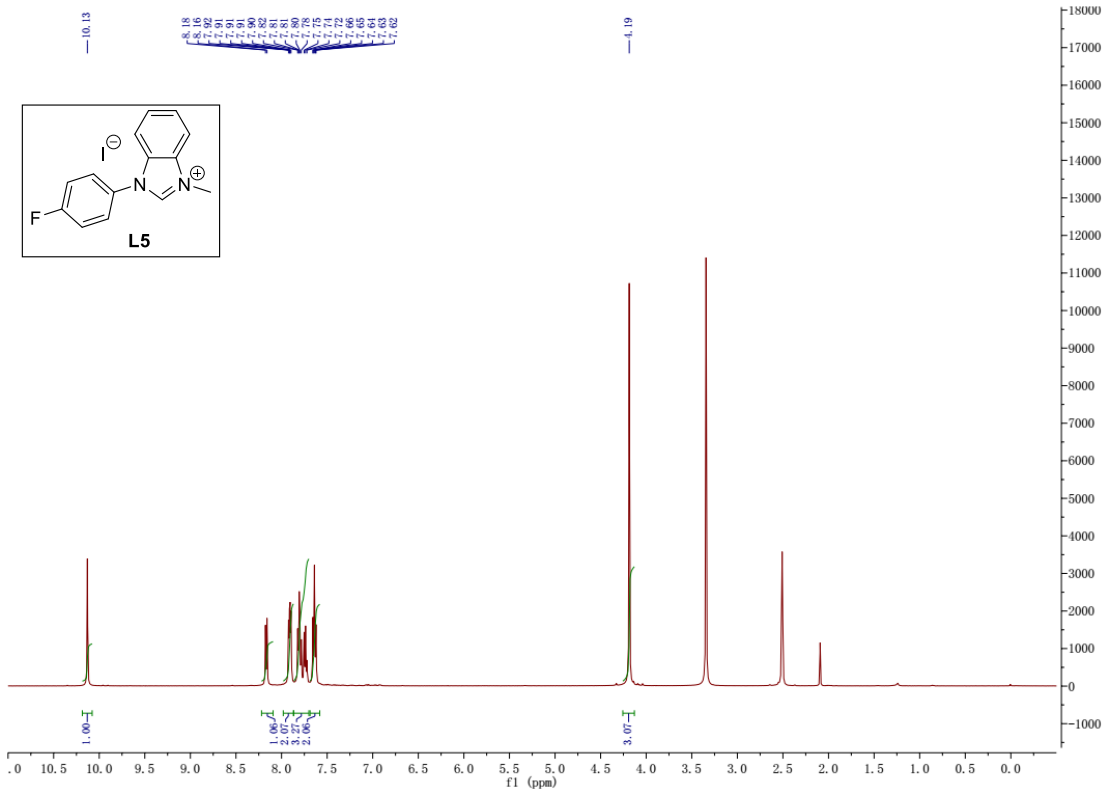
➢ ^{1}H NMR spectrum for **L4**



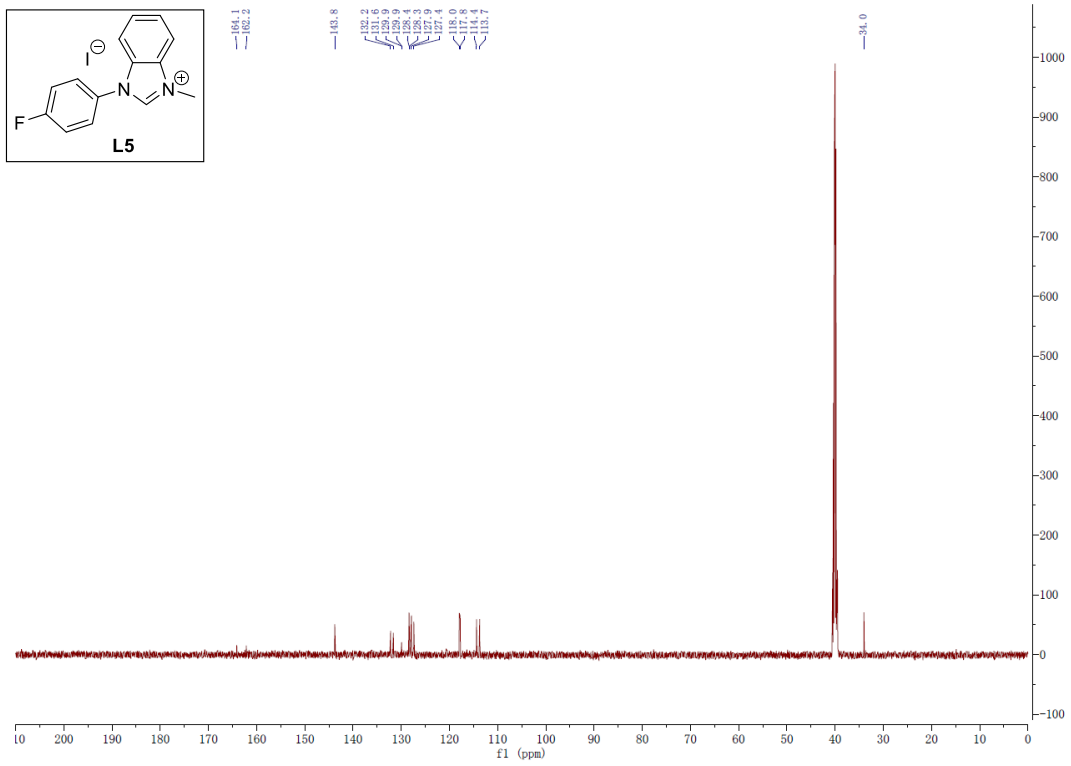
➢ ^{13}C NMR spectrum for **L4**



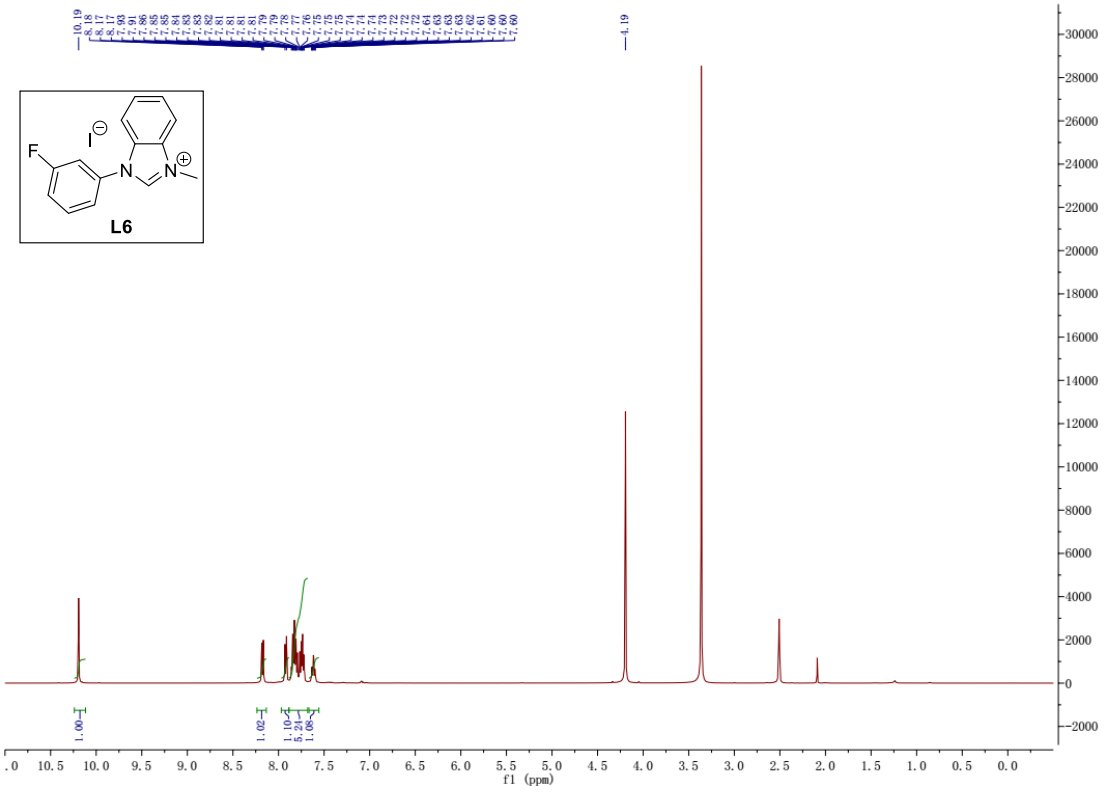
➢ ^{1}H NMR spectrum for **L5**



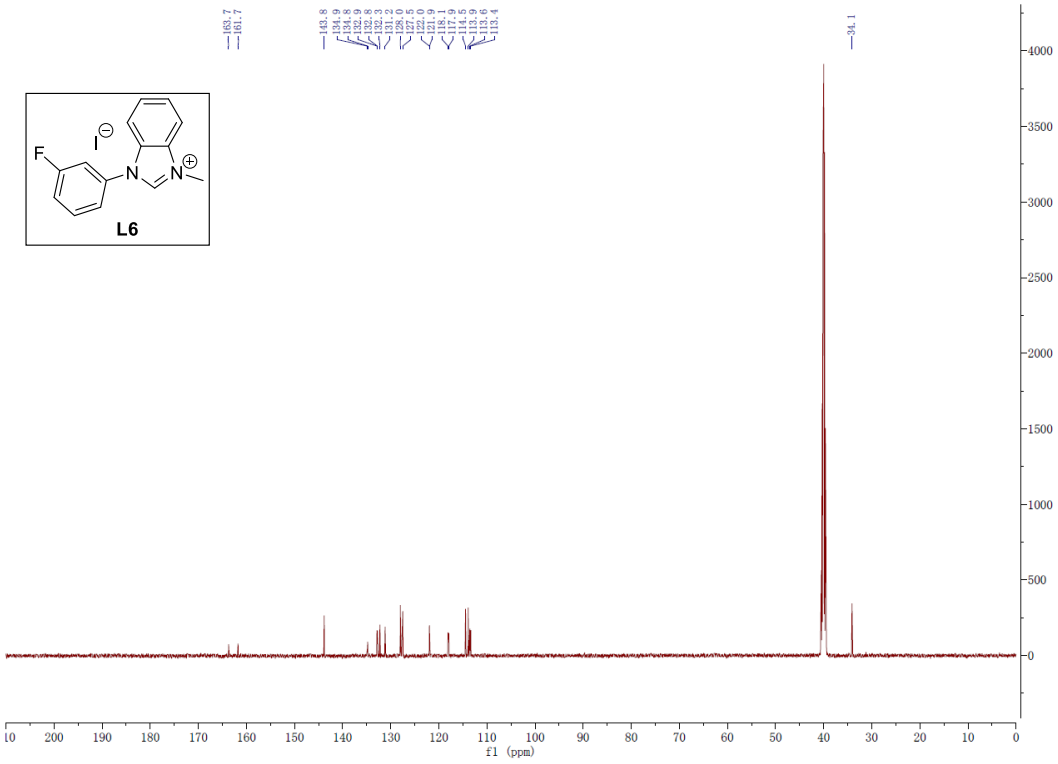
➢ ^{13}C NMR spectrum for **L5**



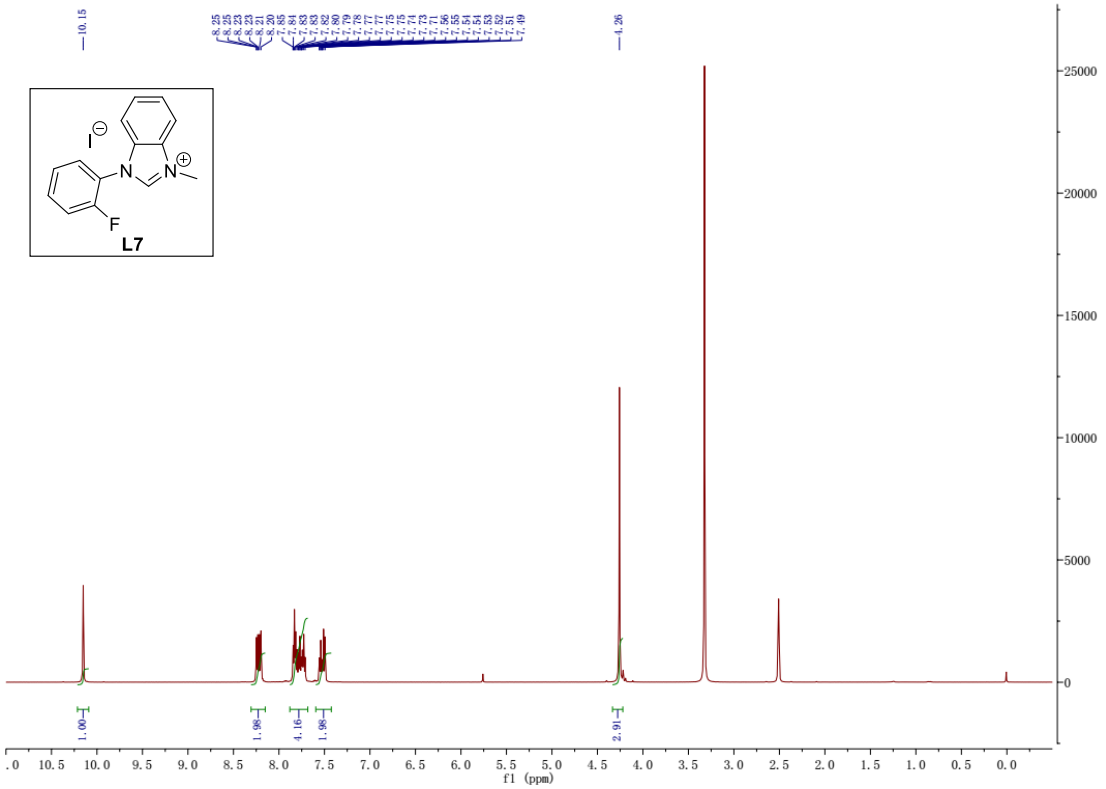
➢ ^{1}H NMR spectrum for **L6**



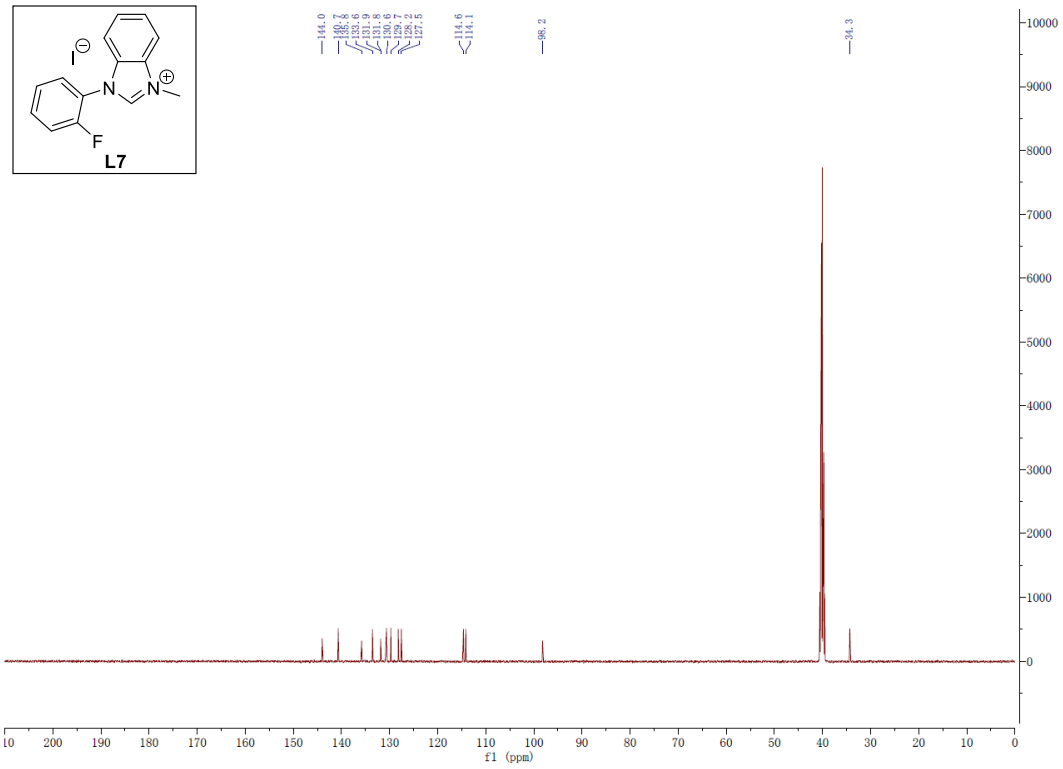
➢ ^{13}C NMR spectrum for **L6**



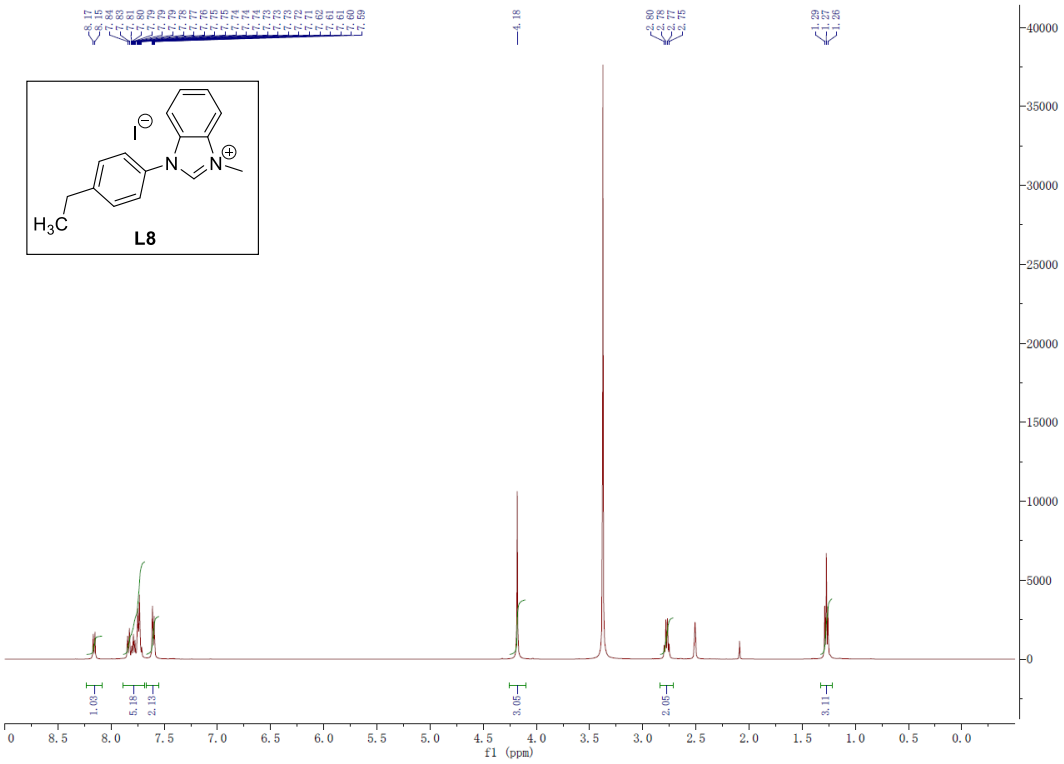
➢ ^{1}H NMR spectrum for **L7**



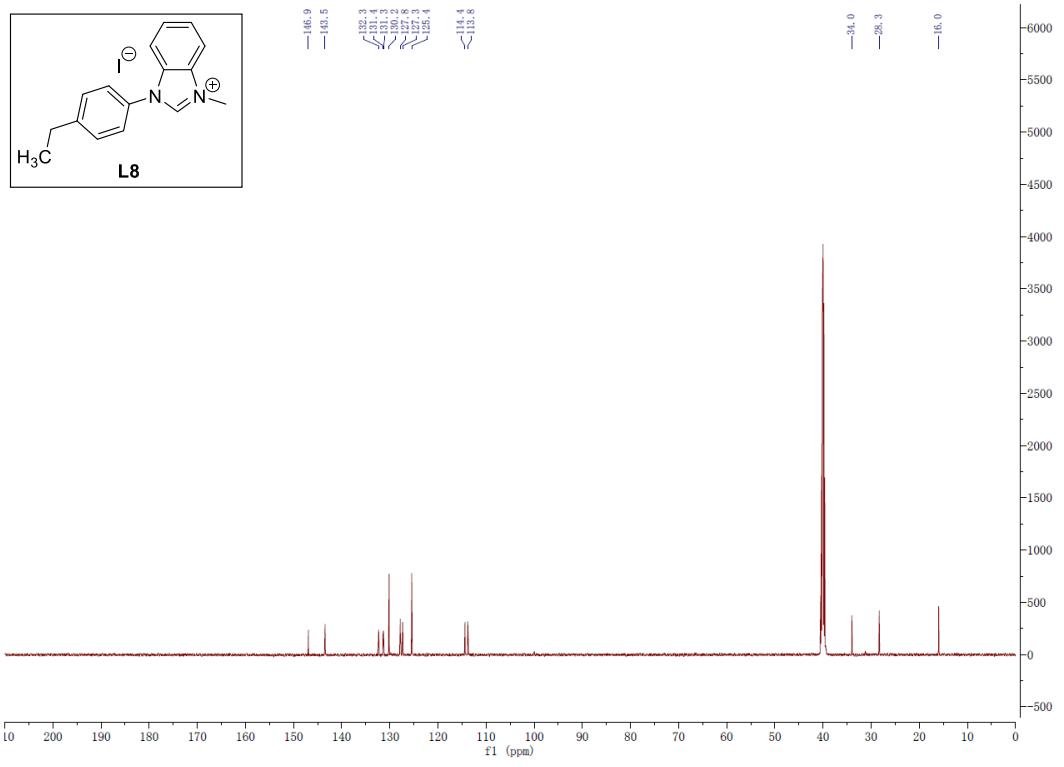
➢ ^{13}C NMR spectrum for **L7**



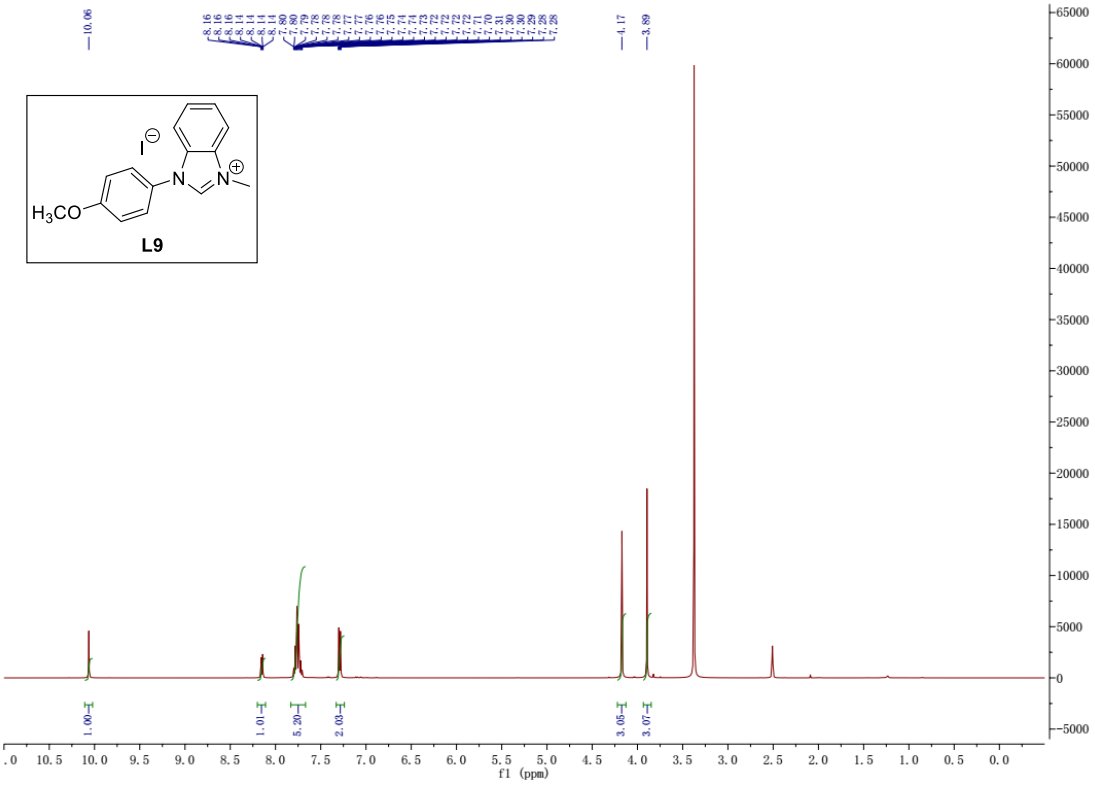
➢ ^{1}H NMR spectrum for **L8**



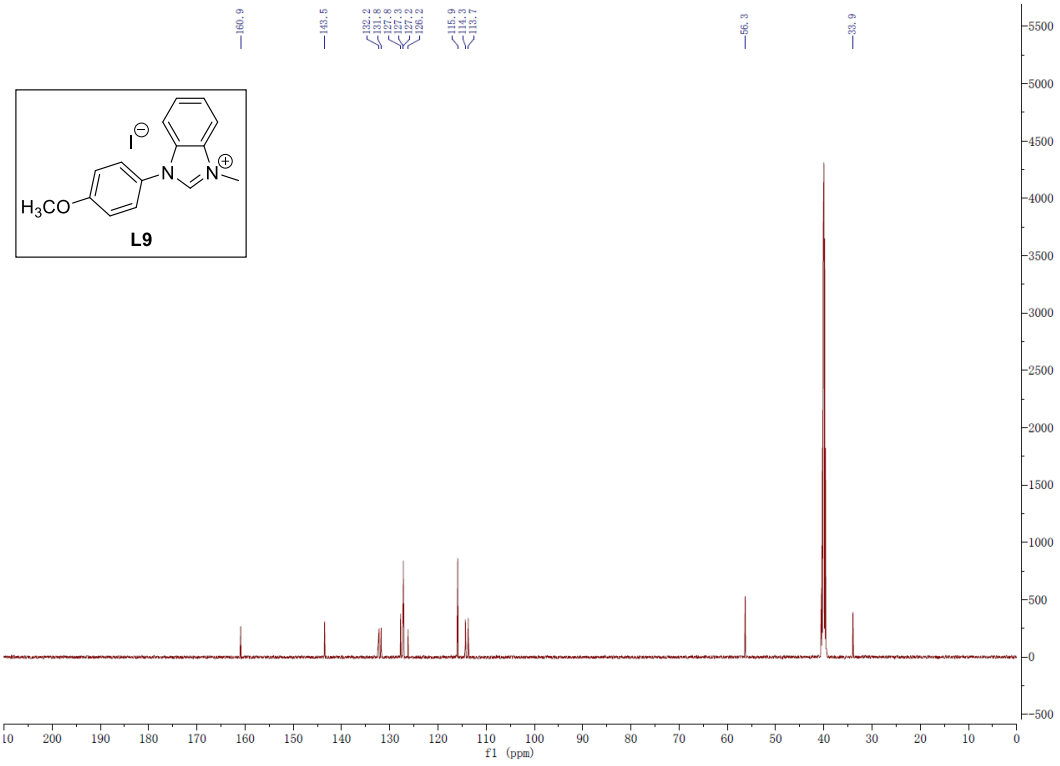
➢ ^{13}C NMR spectrum for **L8**



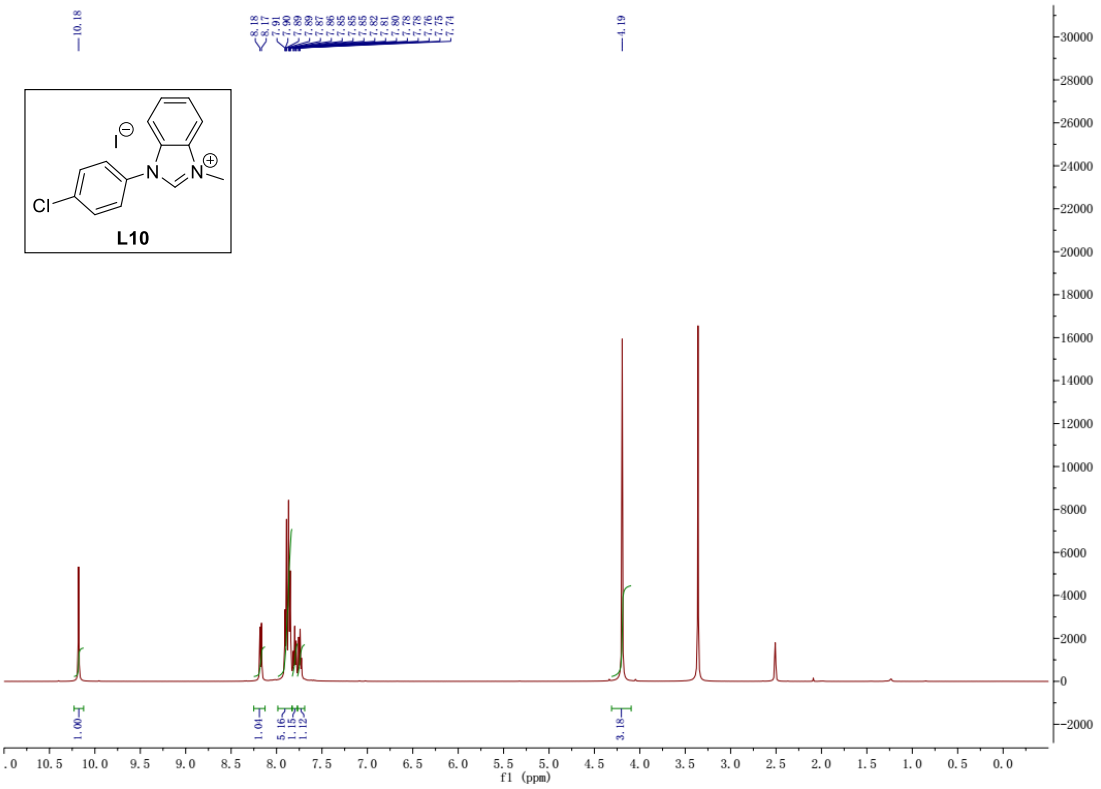
➢ ^{1}H NMR spectrum for **L9**



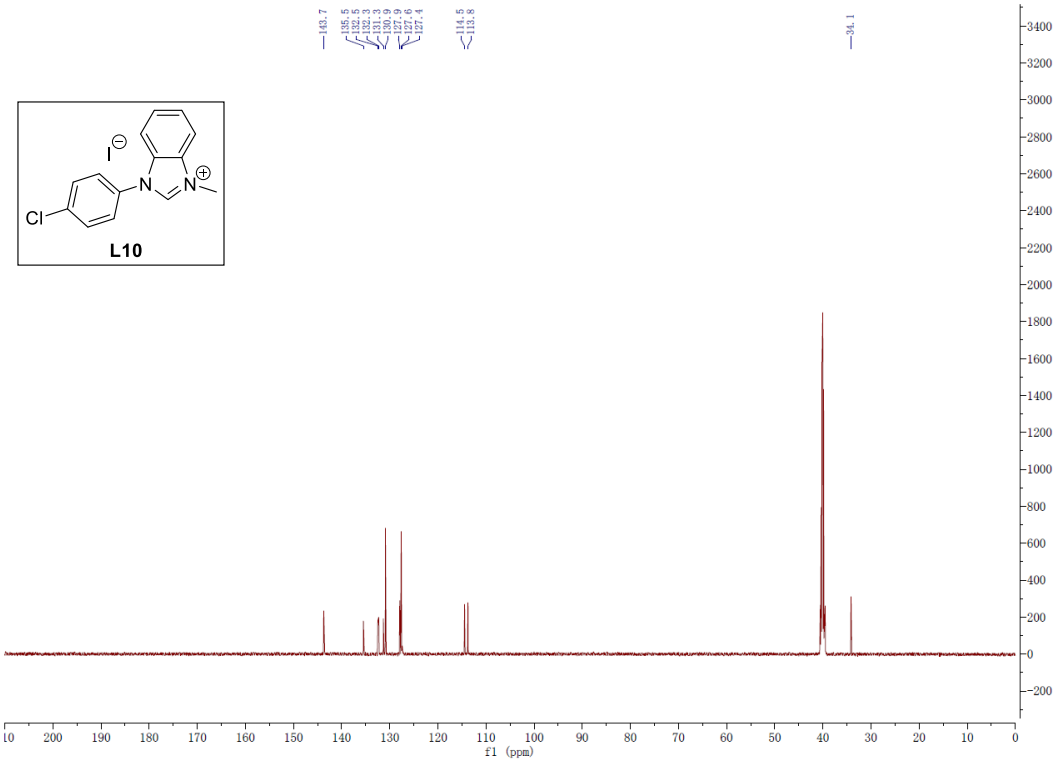
➢ ^{13}C NMR spectrum for **L9**



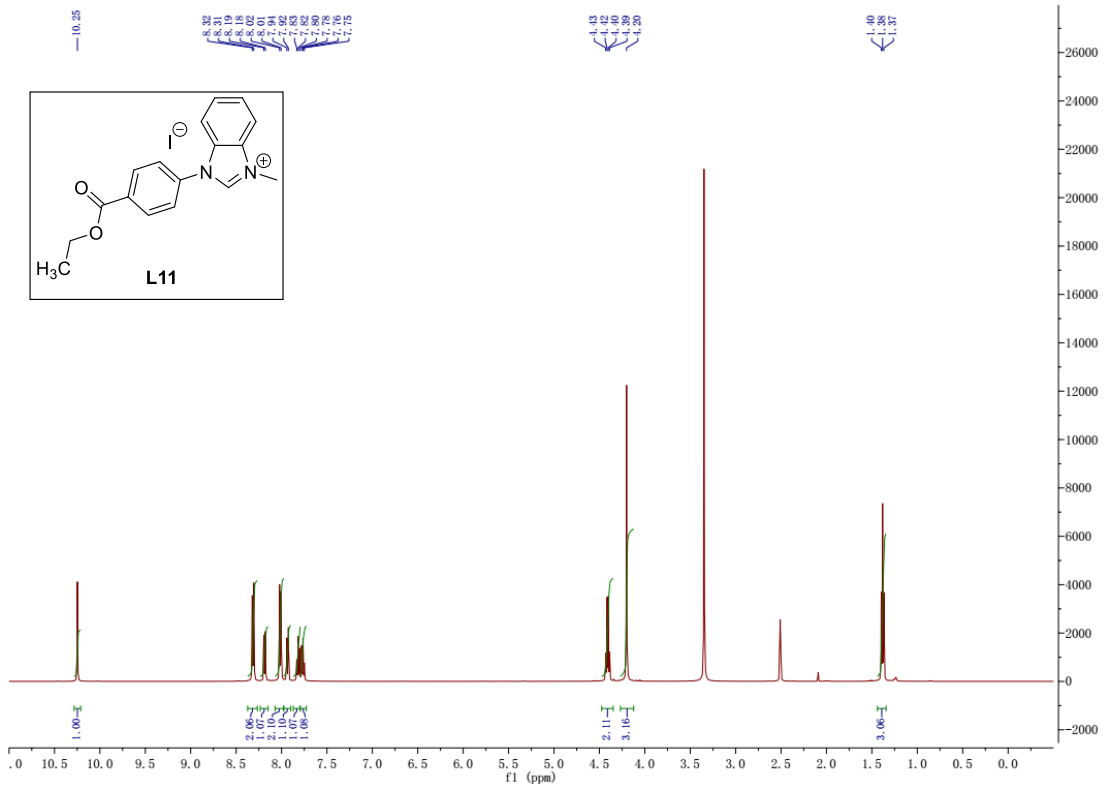
➢ ^{1}H NMR spectrum for **L10**



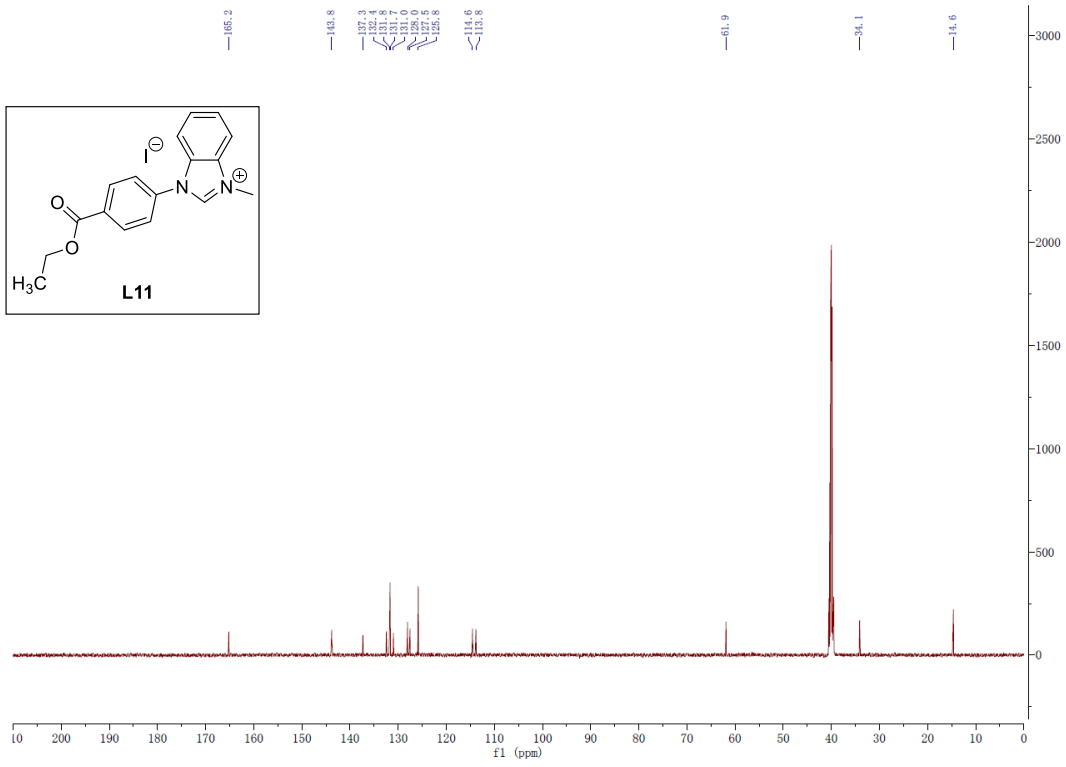
➢ ^{13}C NMR spectrum for **L10**



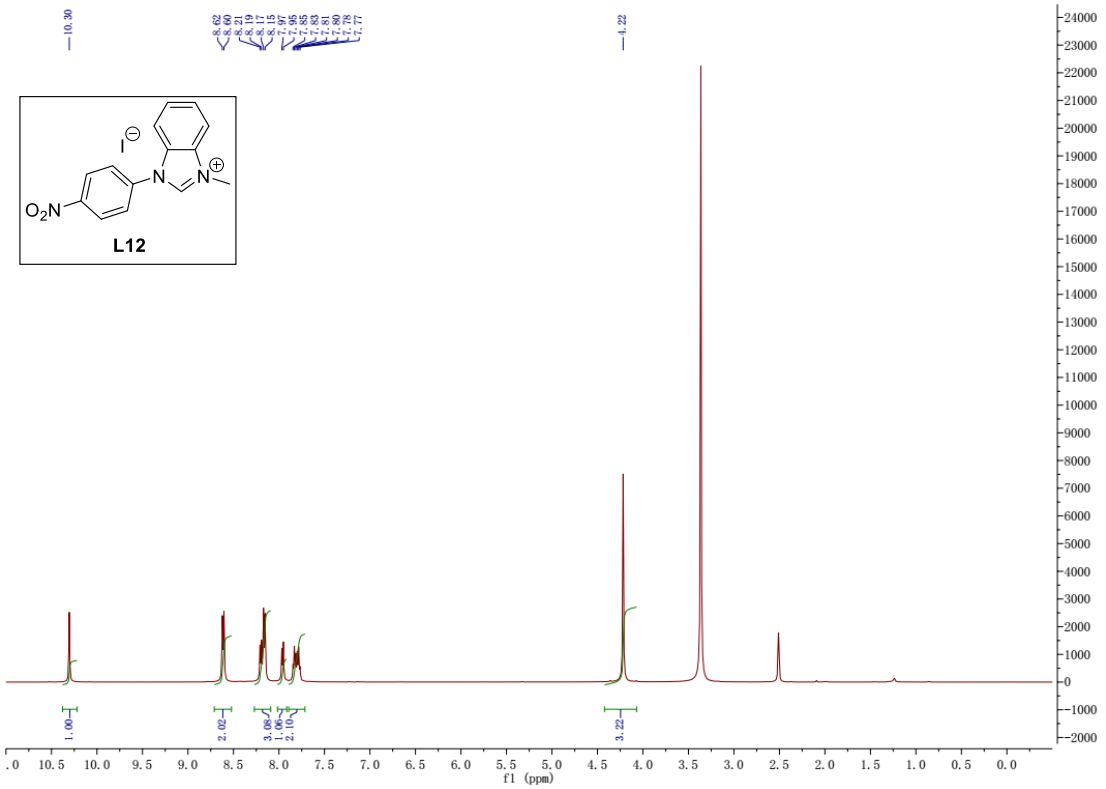
➢ ^{1}H NMR spectrum for **L11**



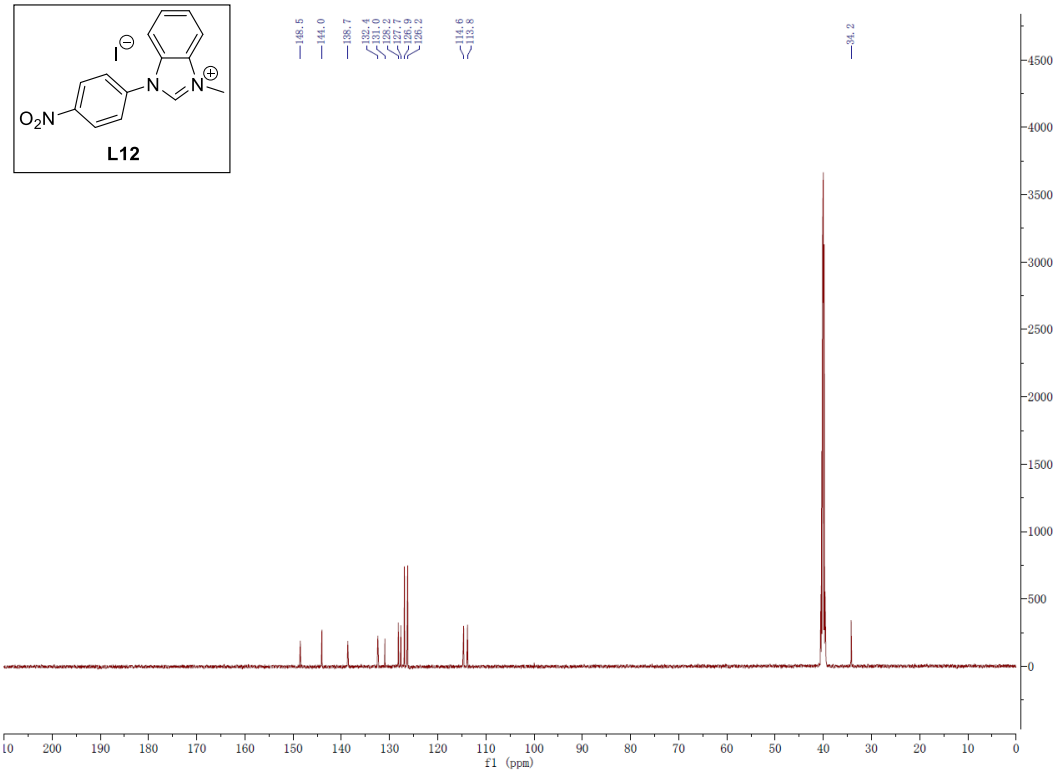
➢ ^{13}C NMR spectrum for **L11**



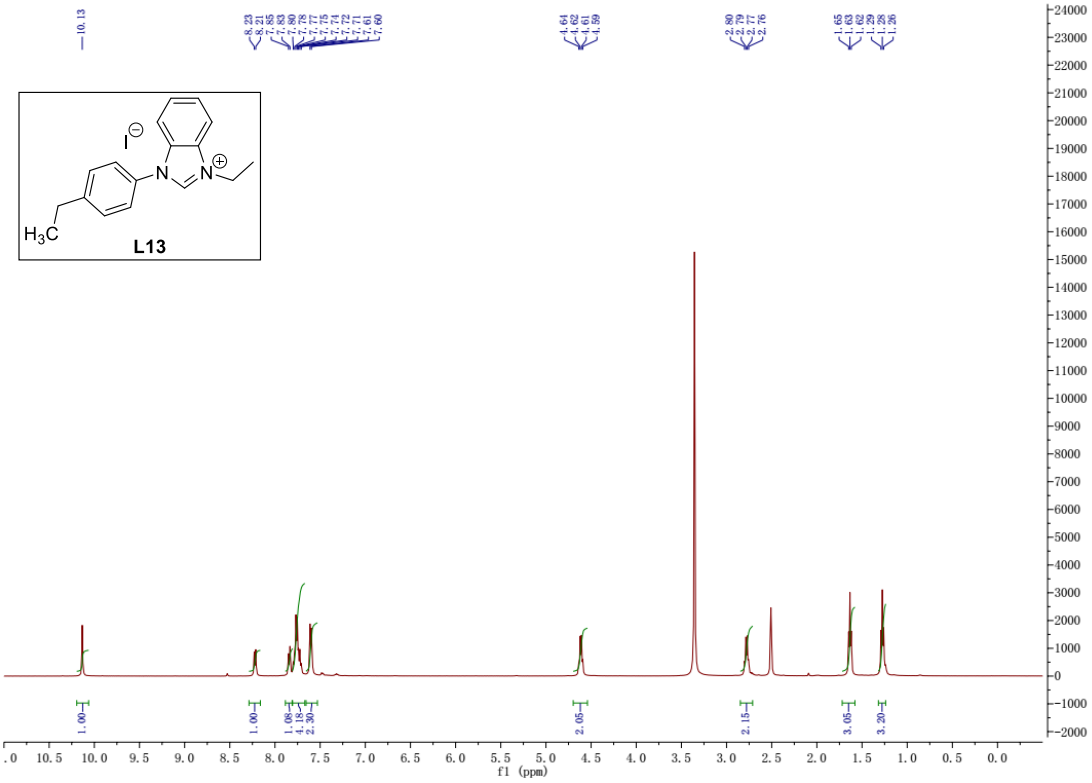
➢ ^{1}H NMR spectrum for **L12**



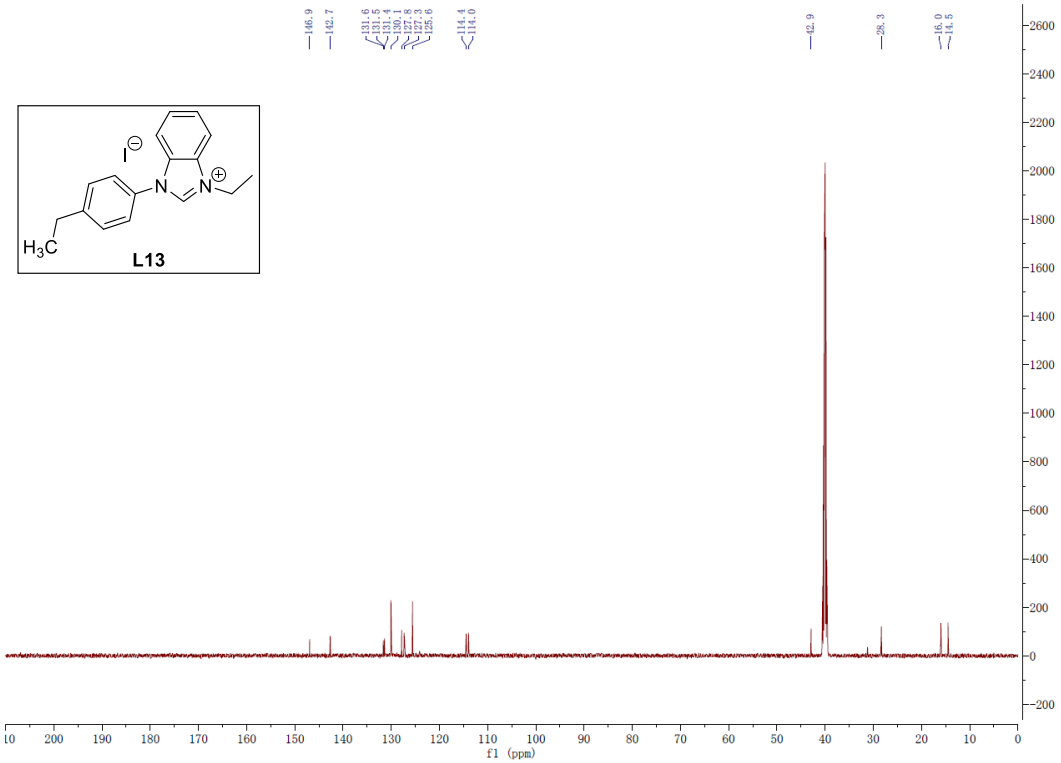
➢ ^{13}C NMR spectrum for **L12**



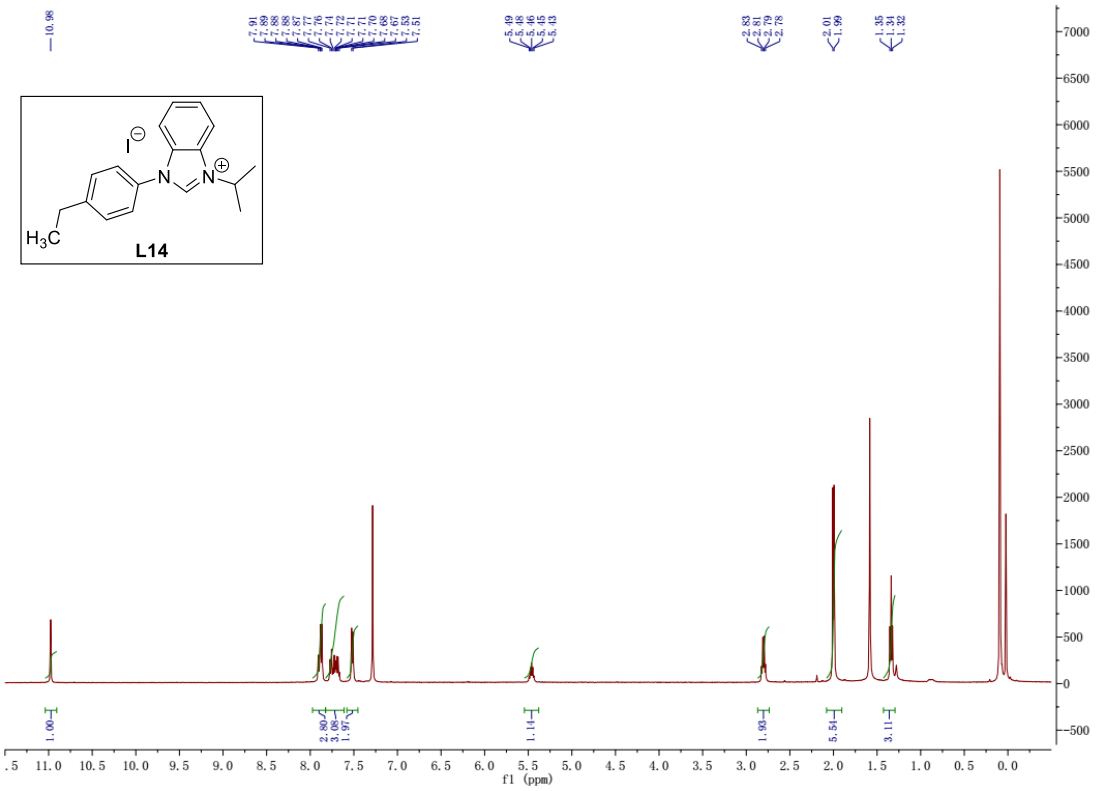
➢ ^{1}H NMR spectrum for **L13**



➢ ^{13}C NMR spectrum for **L13**



➢ ^{1}H NMR spectrum for **L14**



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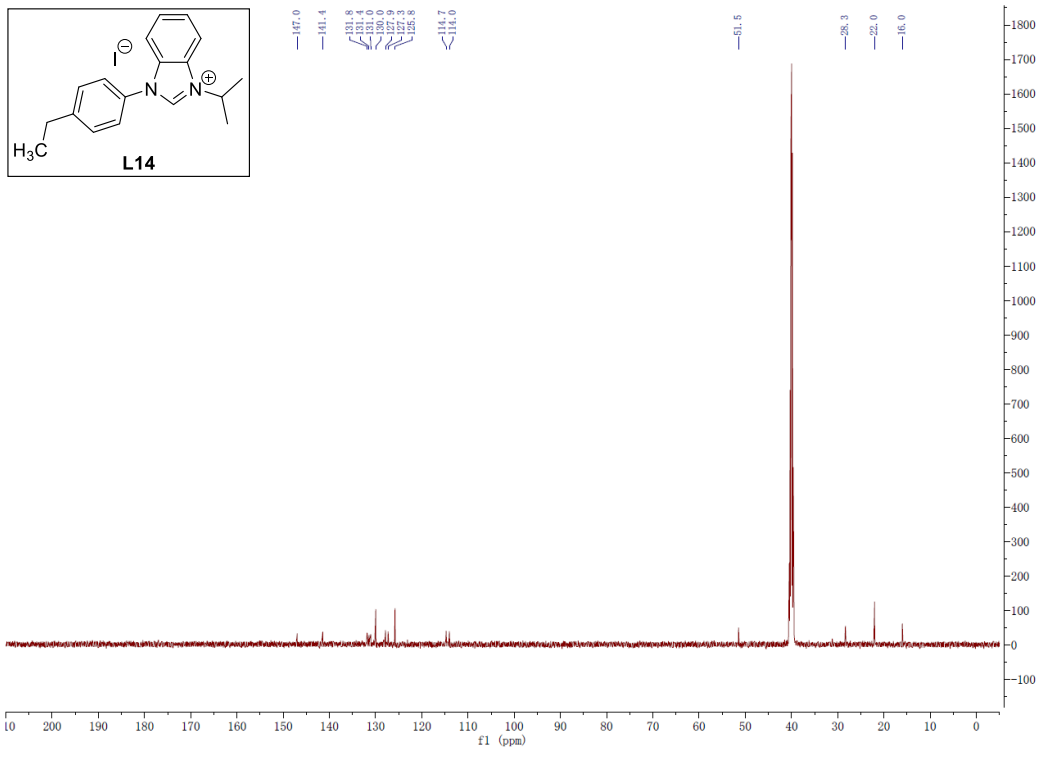
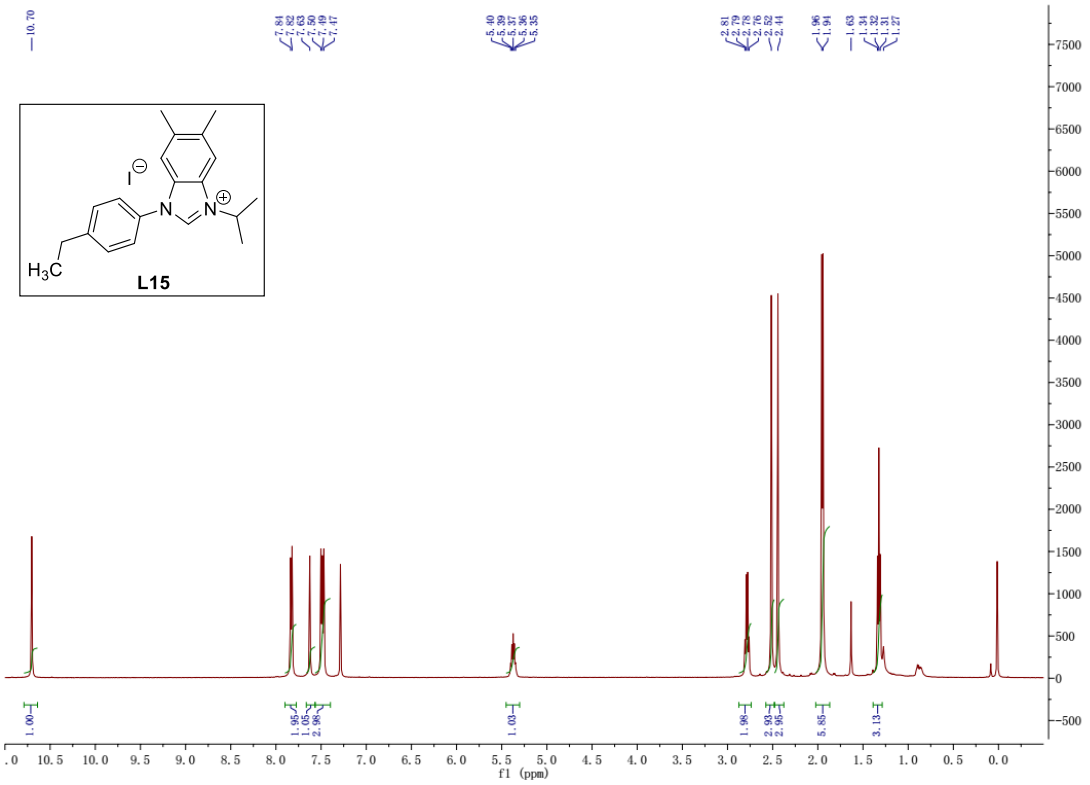
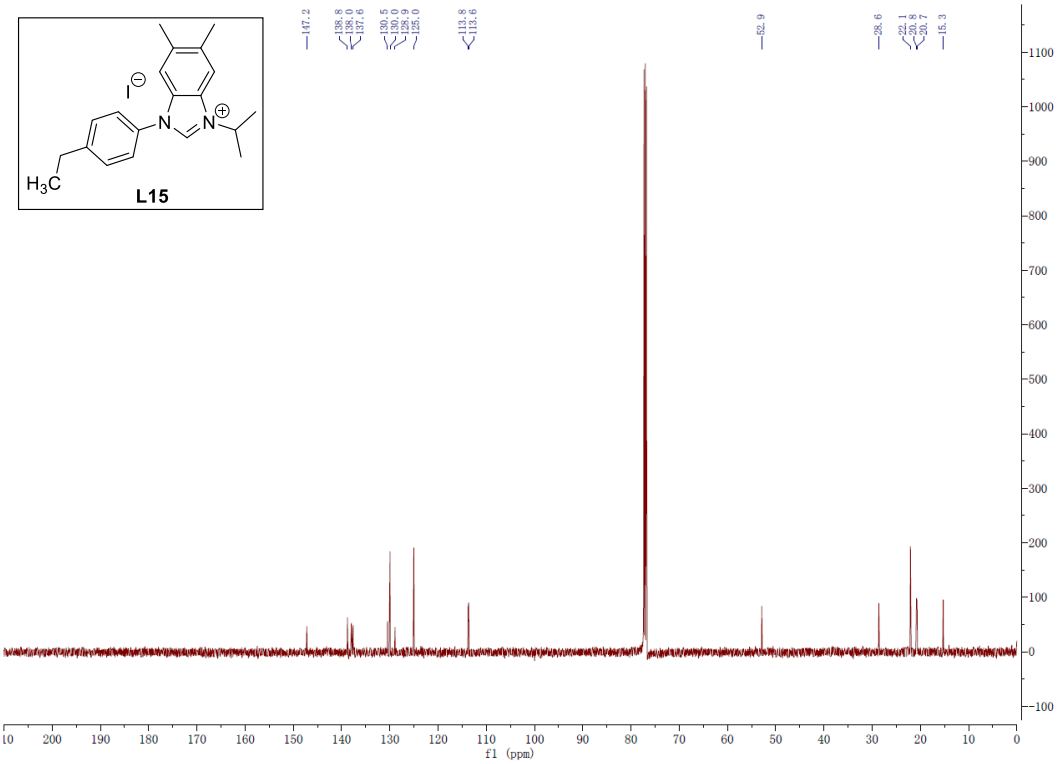


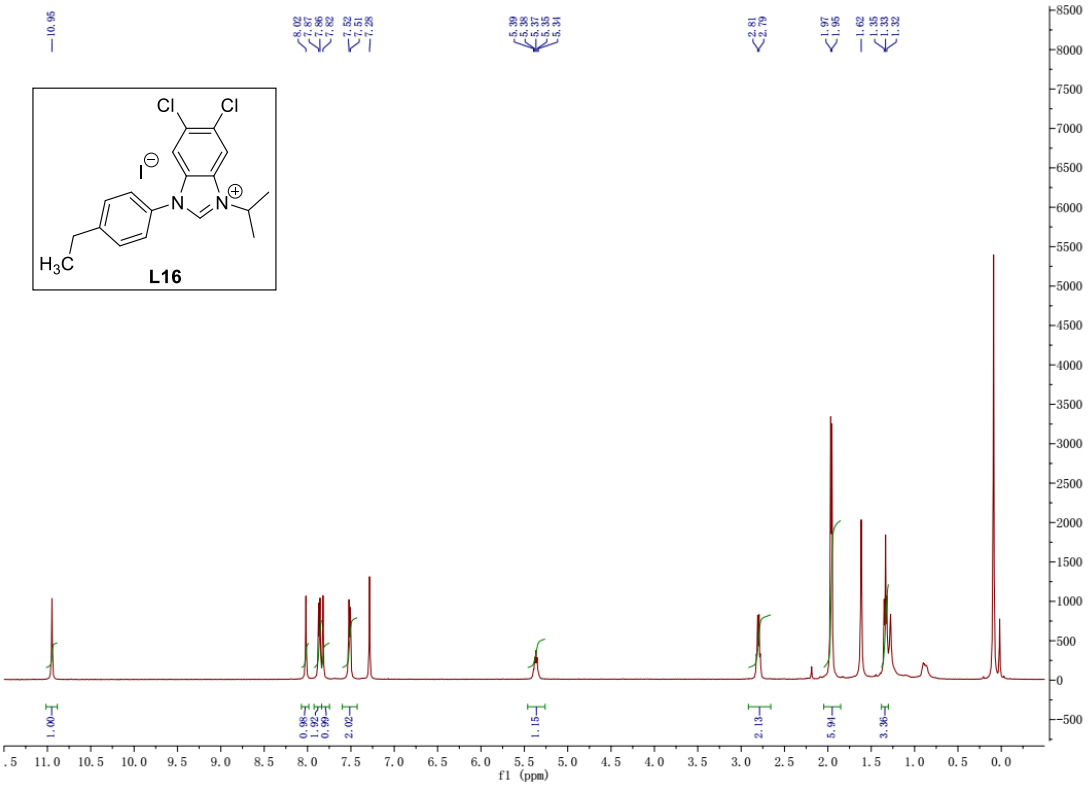
➢ ^{1}H NMR spectrum for **L15**



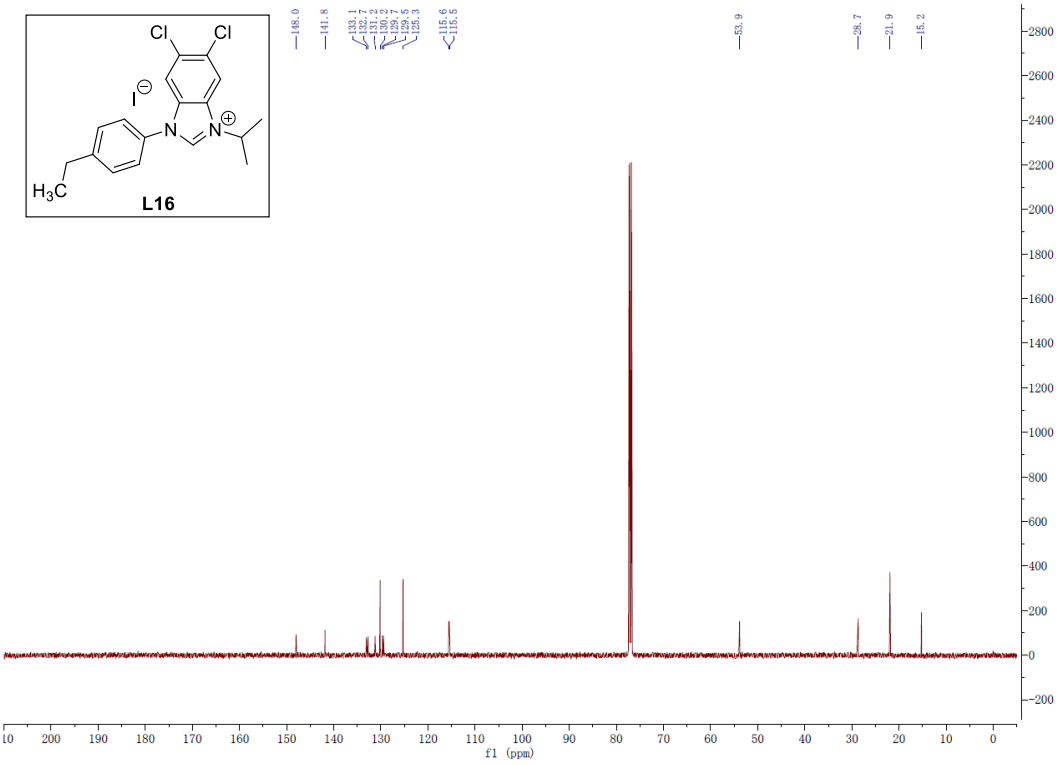
➢ ^{13}C NMR spectrum for **L15**



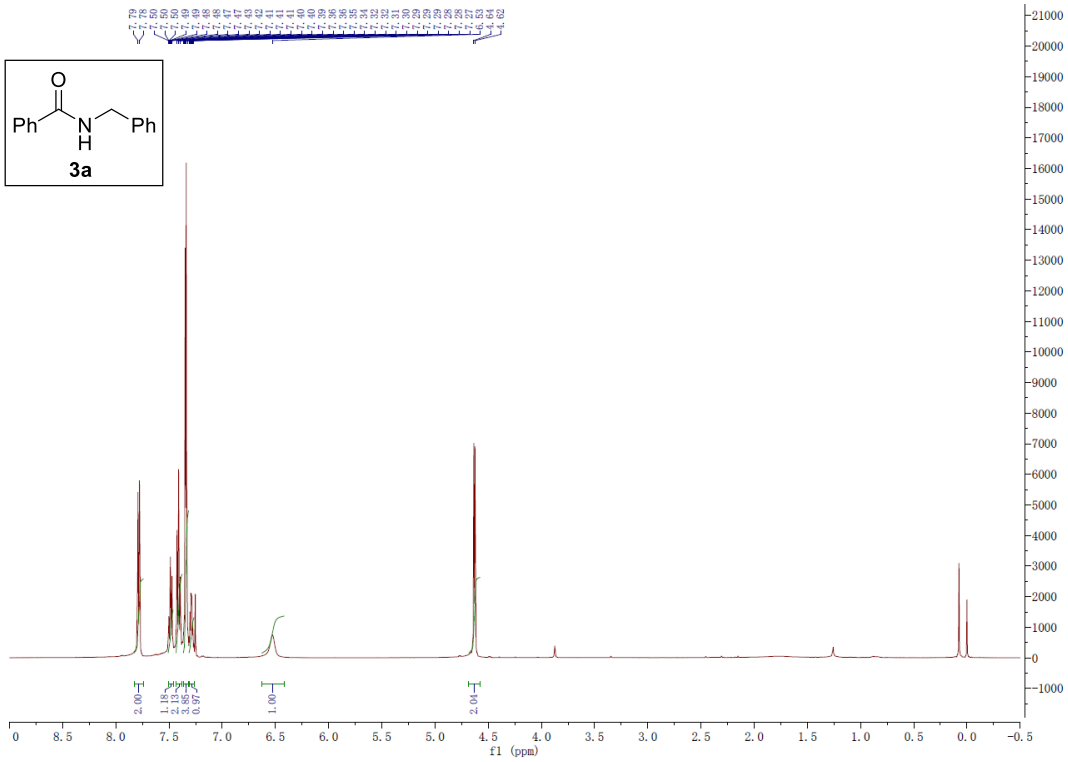
➢ ^{1}H NMR spectrum for **L16**



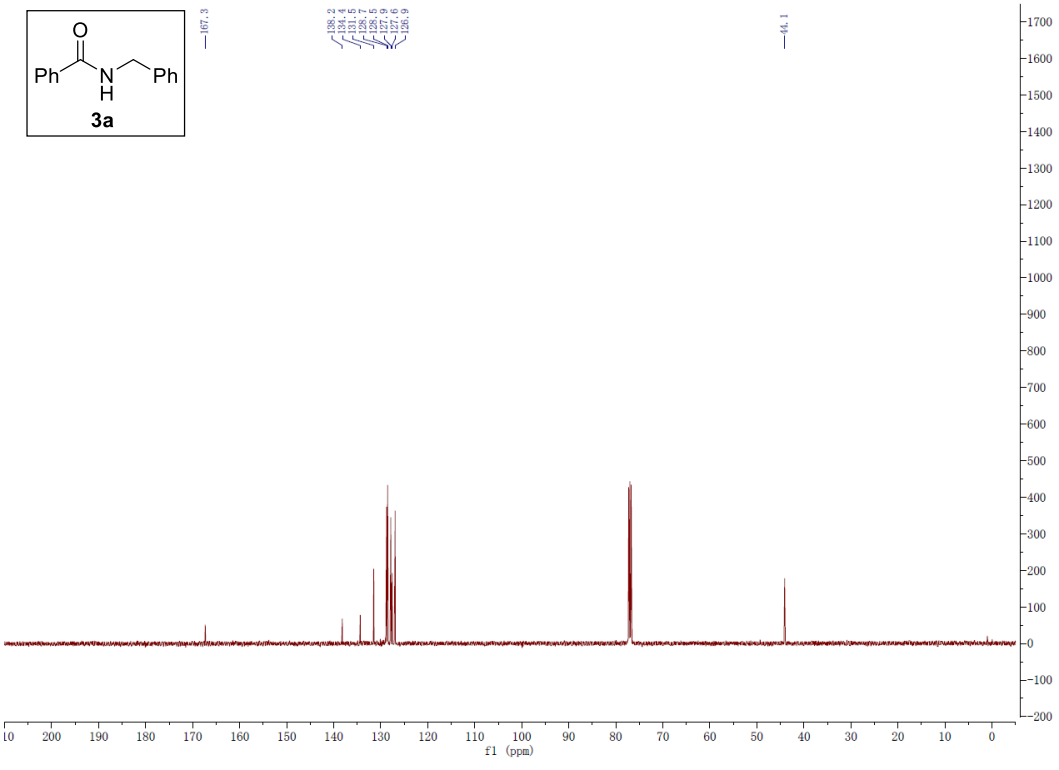
➢ ^{13}C NMR spectrum for **L16**



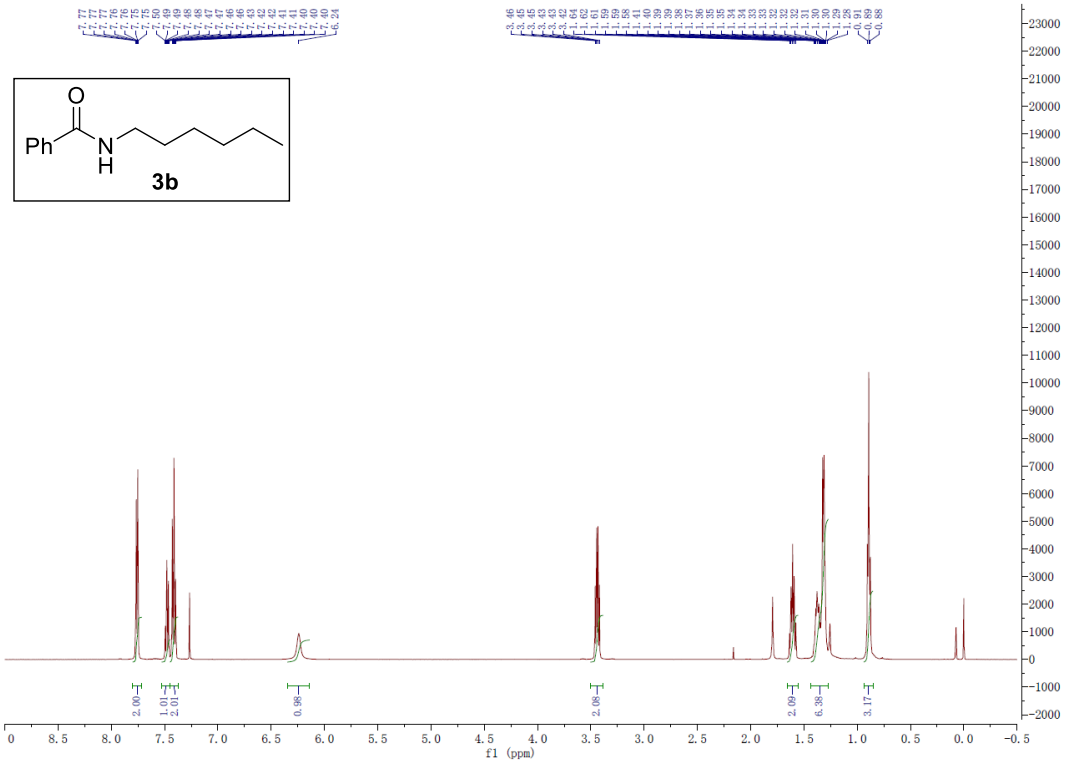
➢ ^{1}H NMR spectrum for **3a**



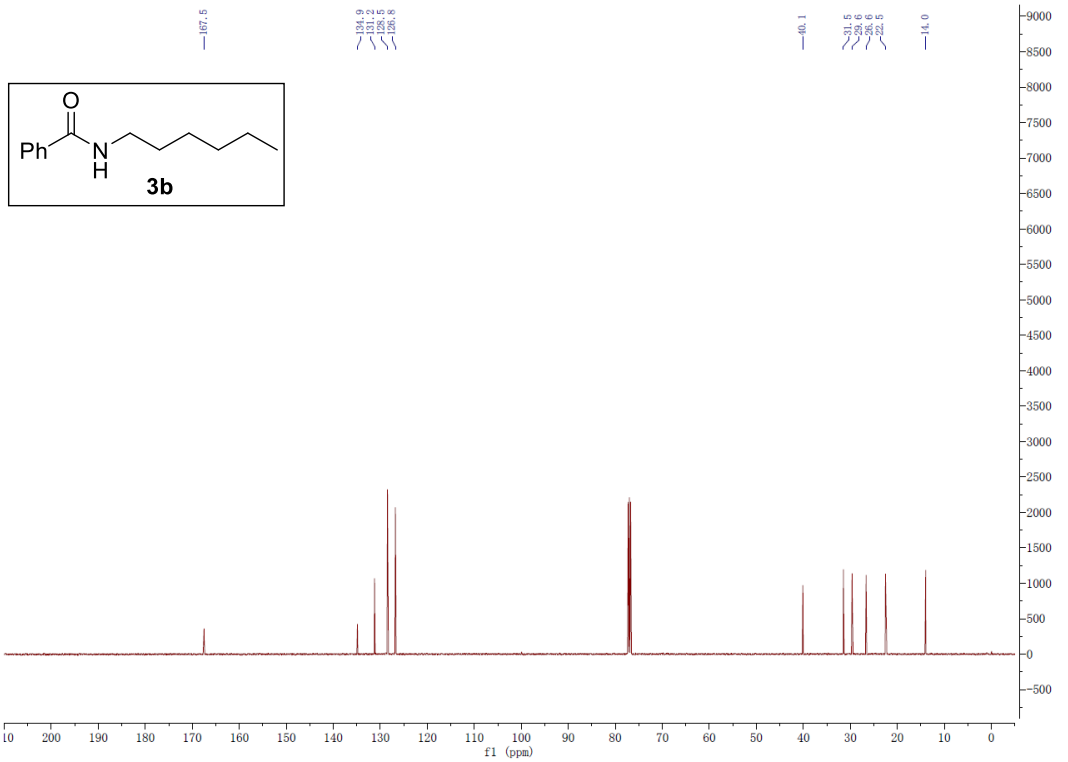
➢ ^{13}C NMR spectrum for **3a**



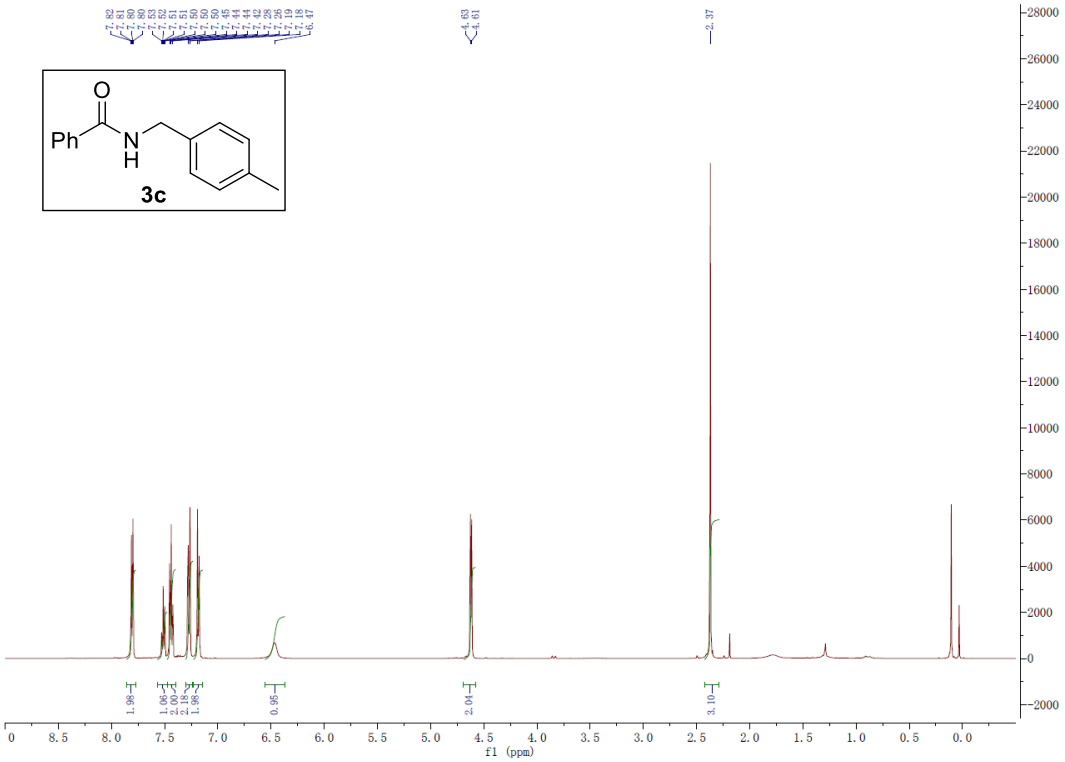
➢ ^{1}H NMR spectrum for **3b**



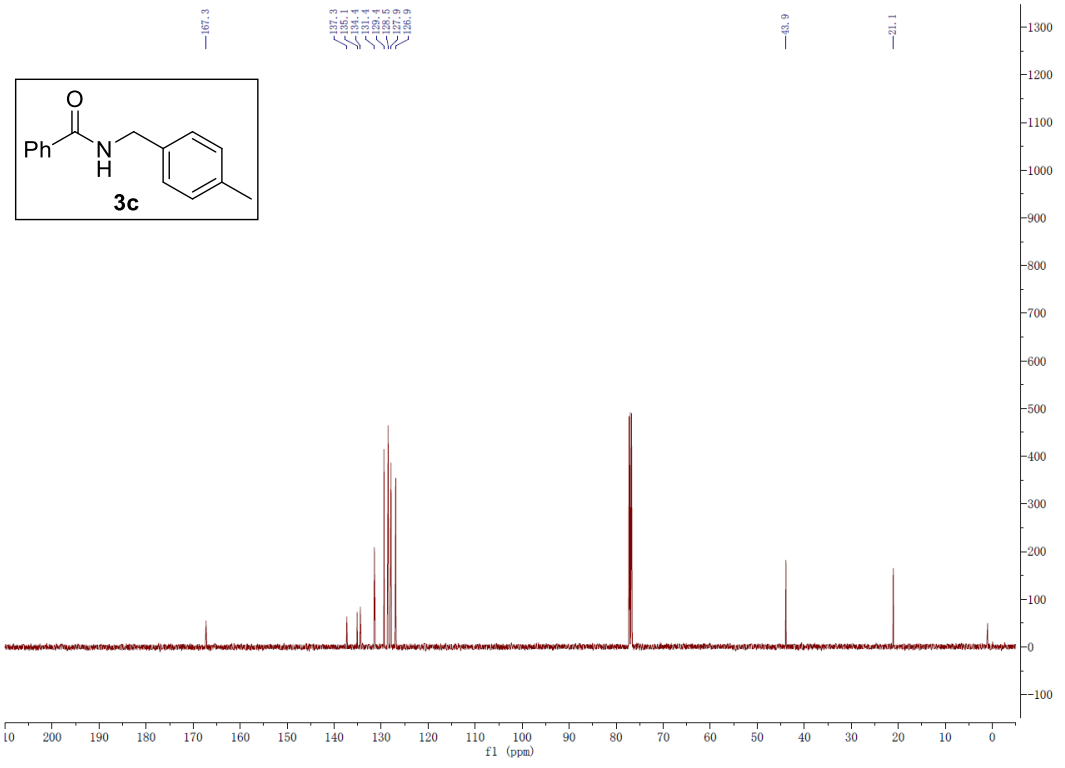
➢ ^{13}C NMR spectrum for **3b**



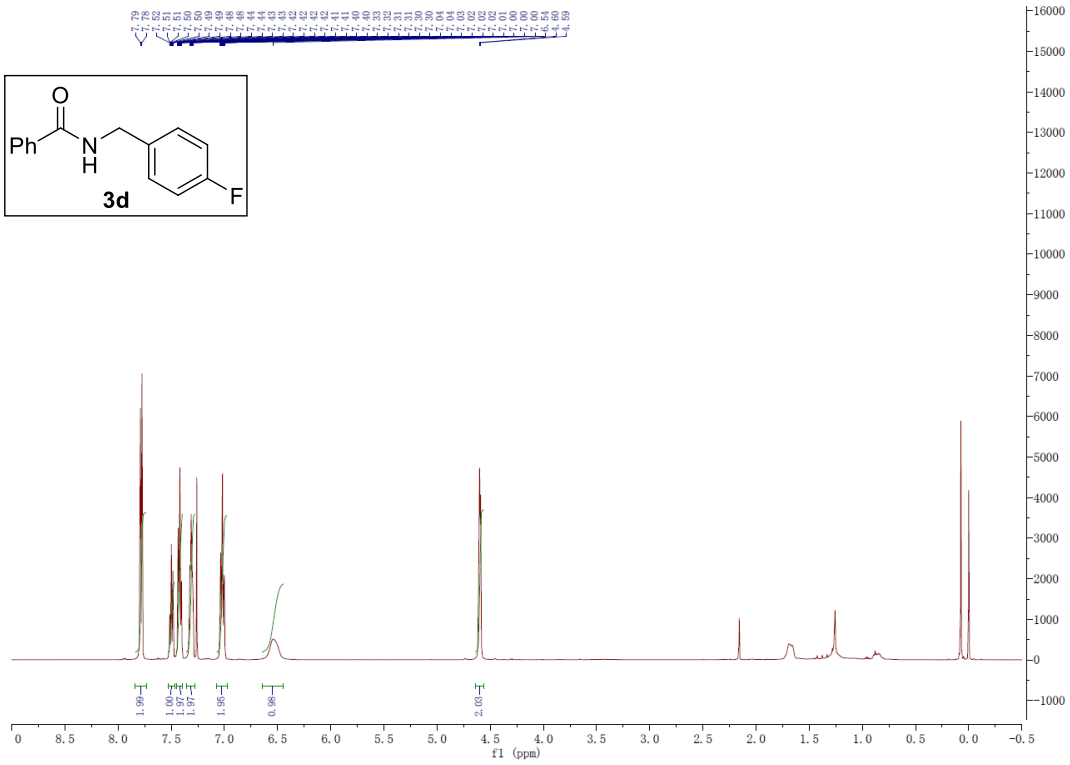
➢ ^{1}H NMR spectrum for **3c**



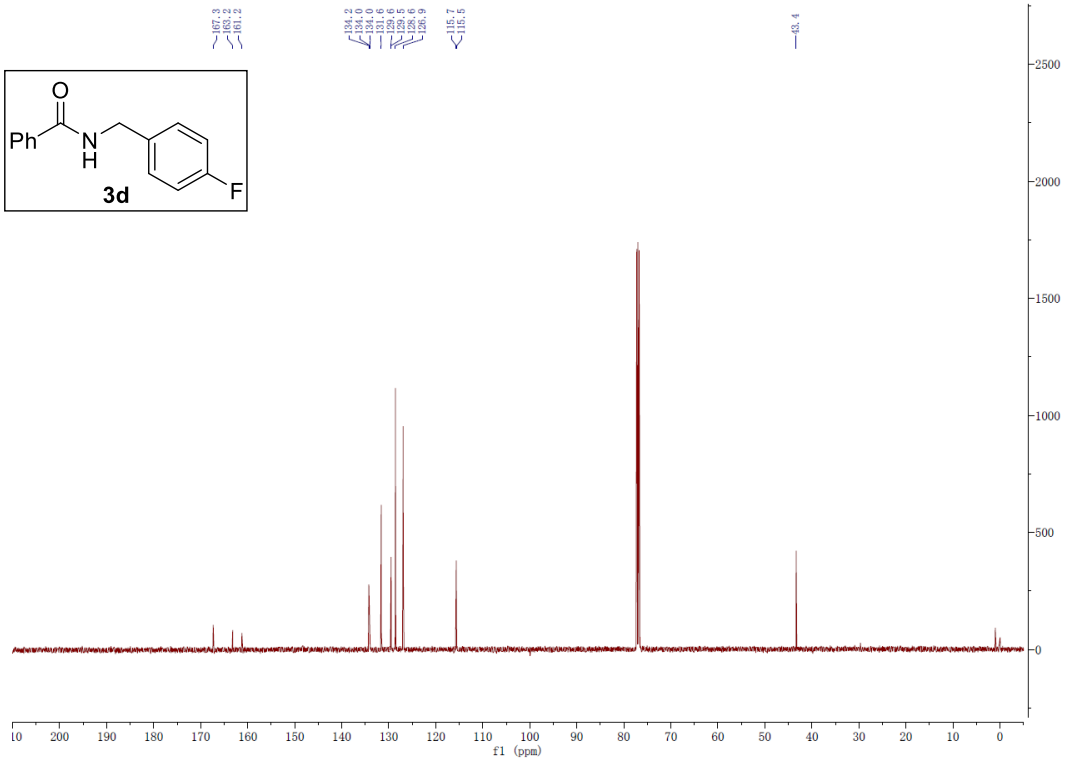
➢ ^{13}C NMR spectrum for **3c**



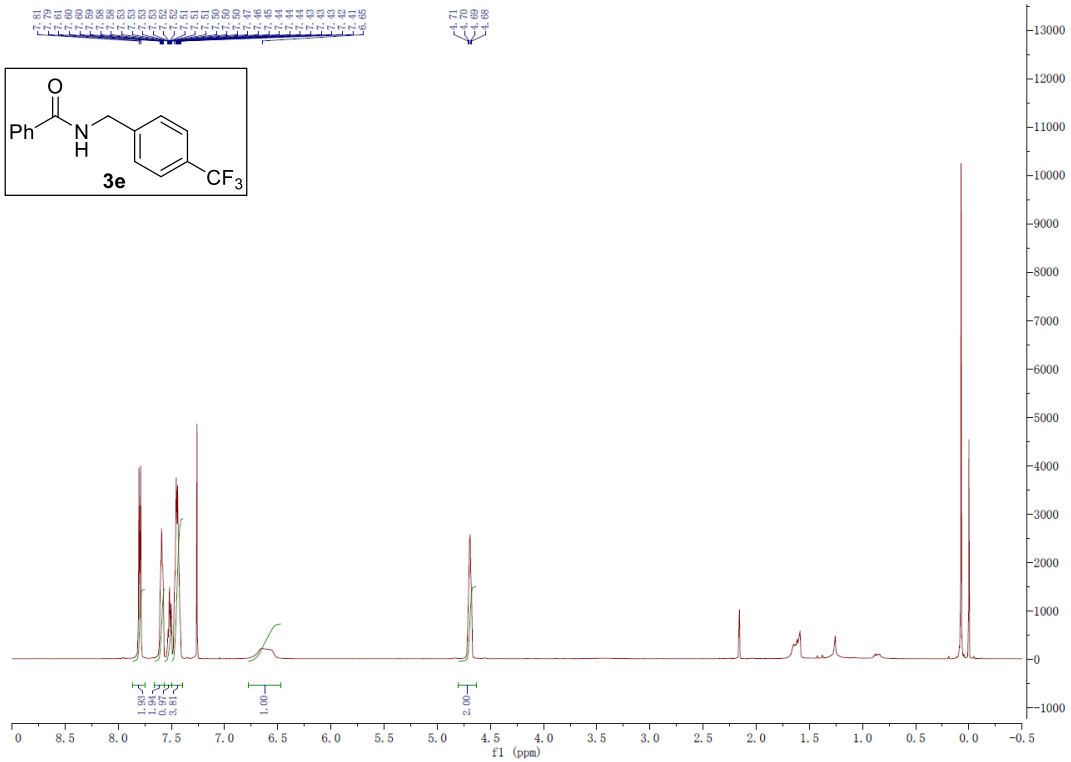
➢ ^{1}H NMR spectrum for **3d**



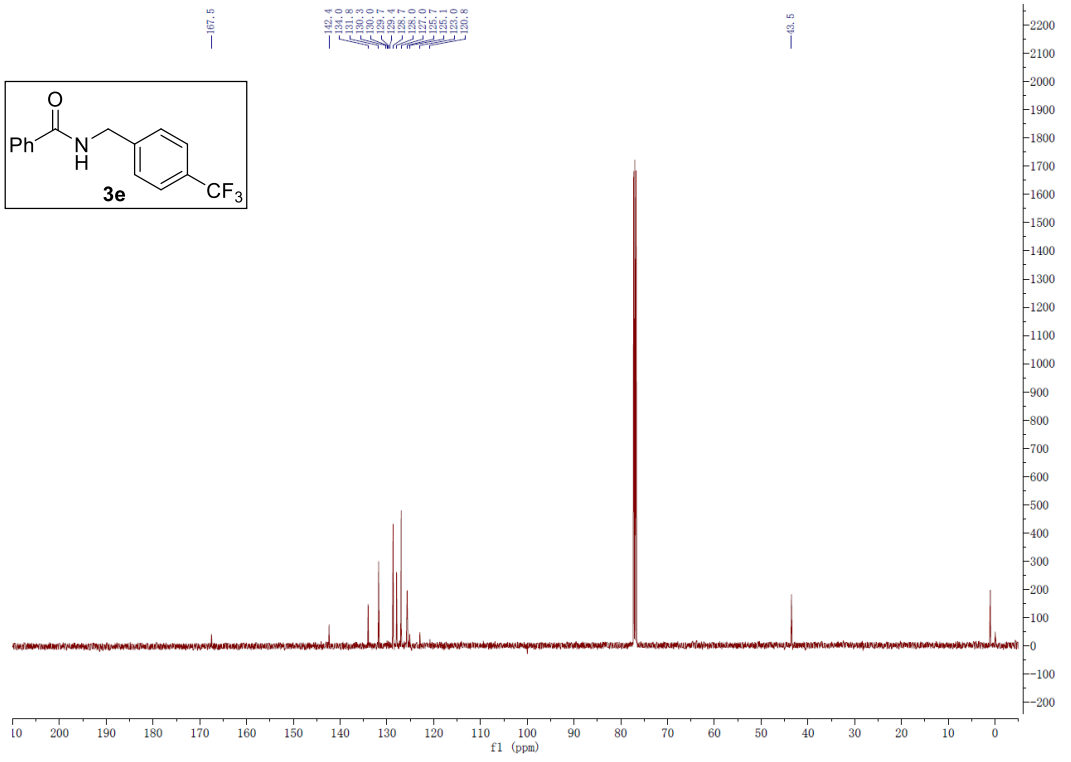
➢ ^{13}C NMR spectrum for **3d**



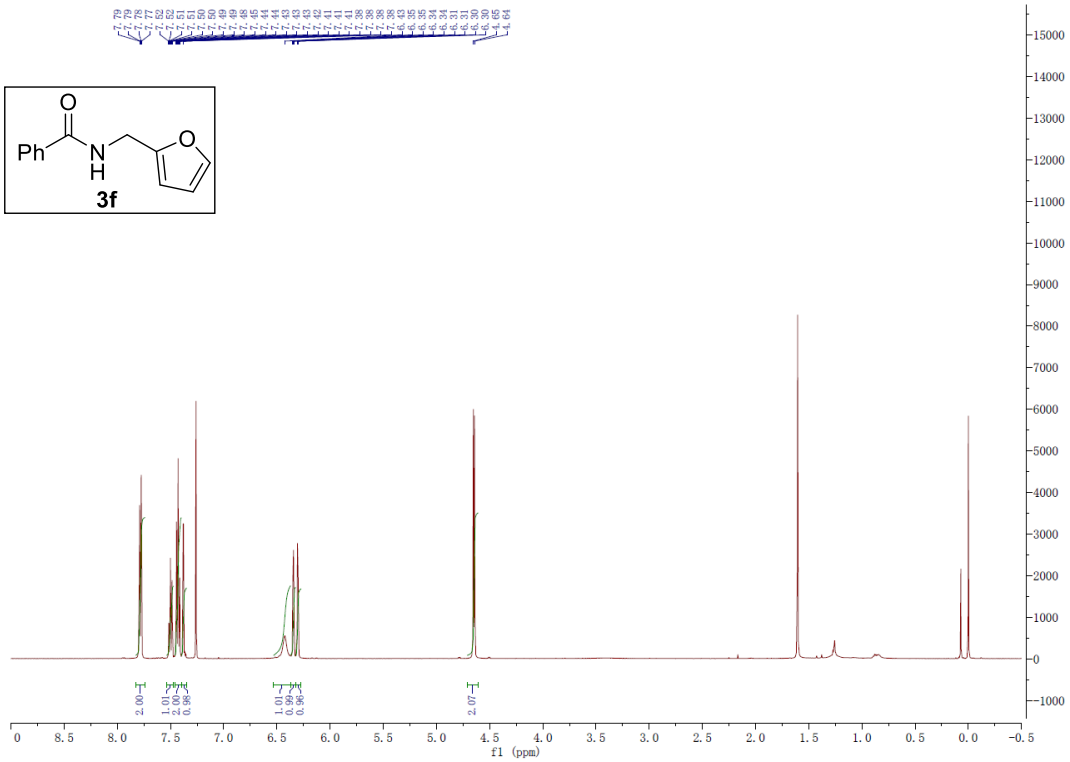
➢ ^{1}H NMR spectrum for **3e**



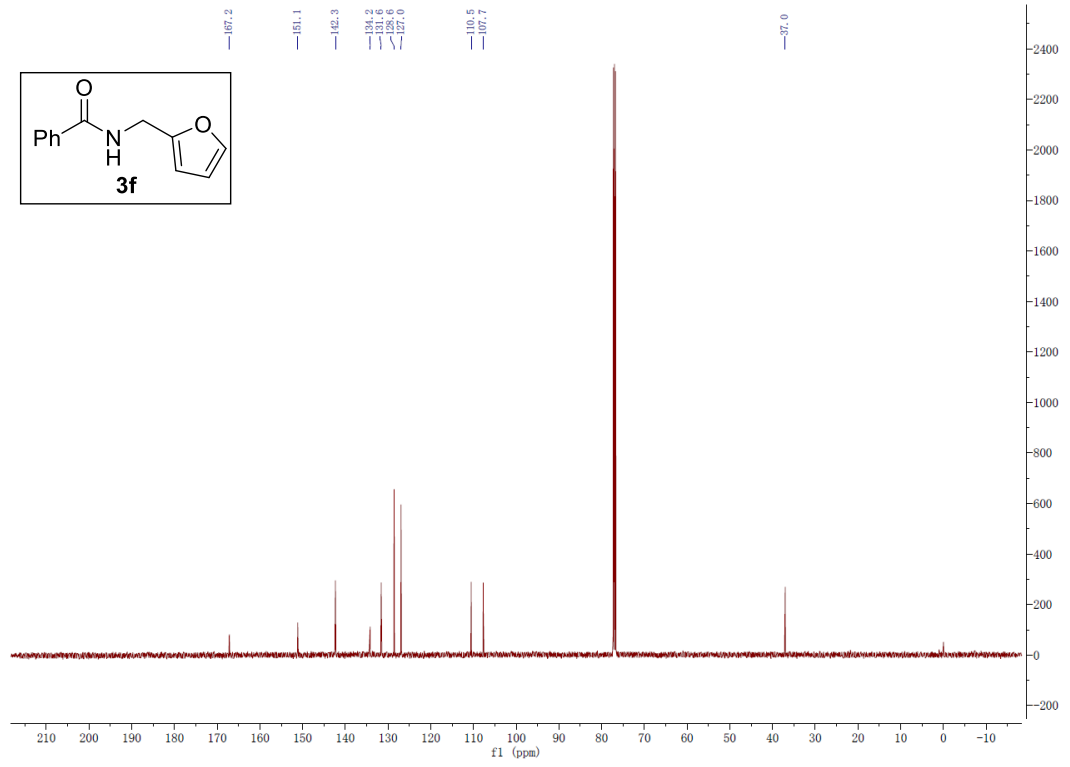
➢ ^{13}C NMR spectrum for **3e**



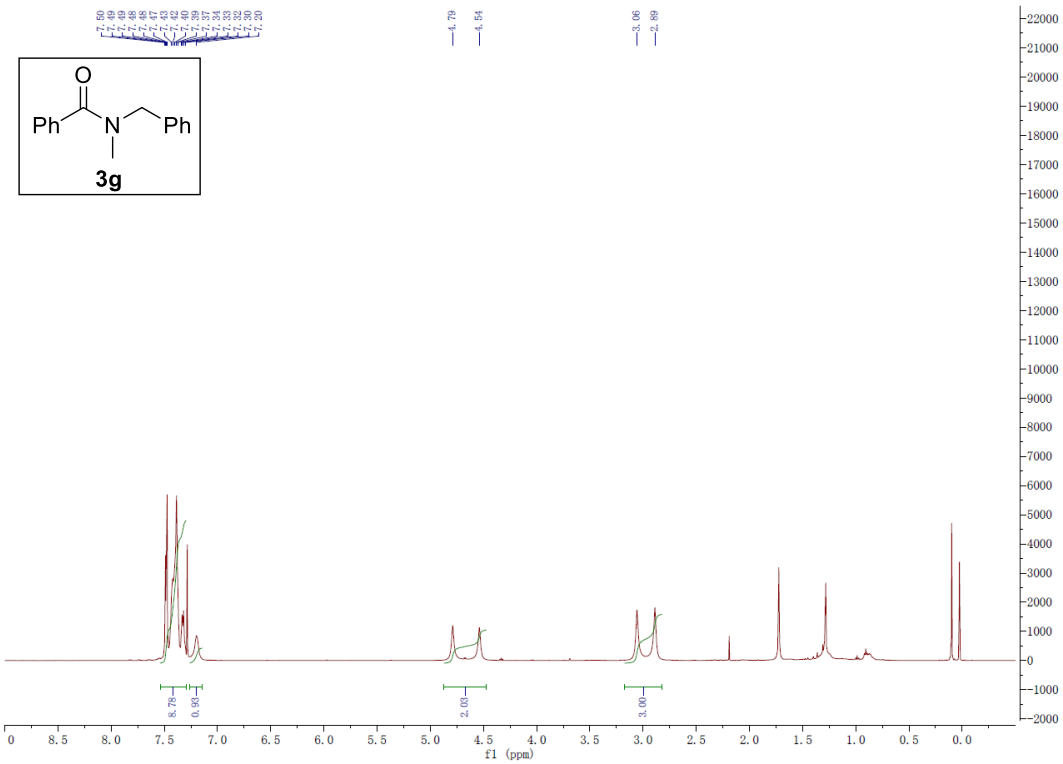
➢ ^{1}H NMR spectrum for **3f**



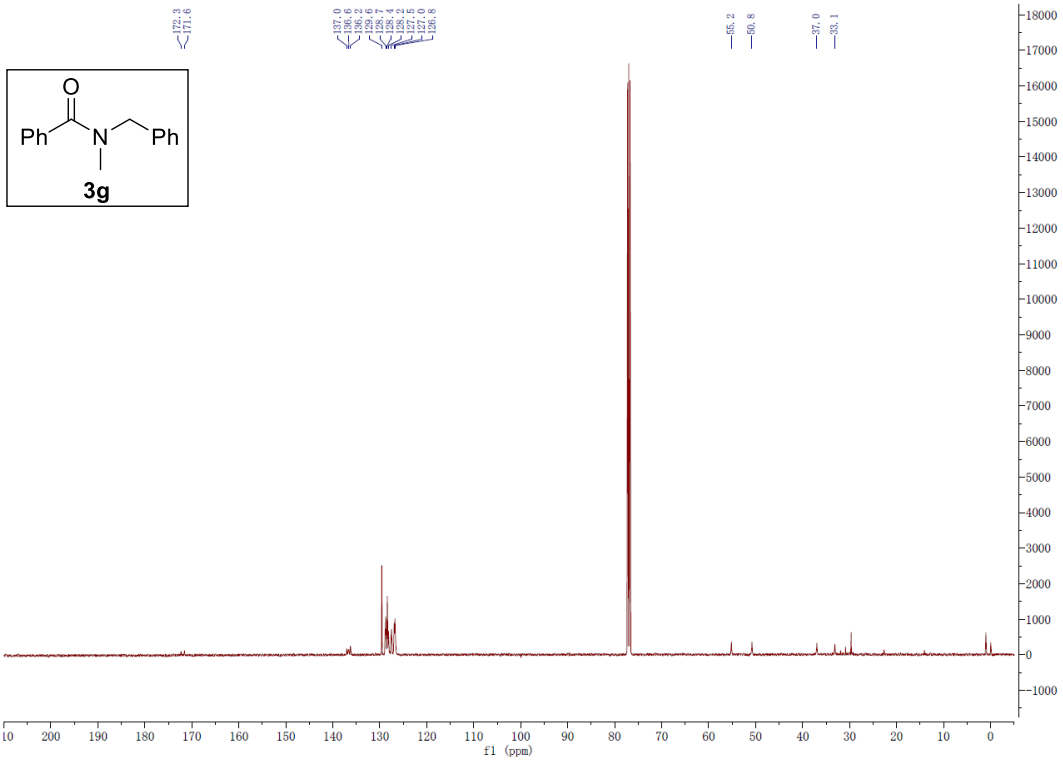
➢ ^{13}C NMR spectrum for **3f**



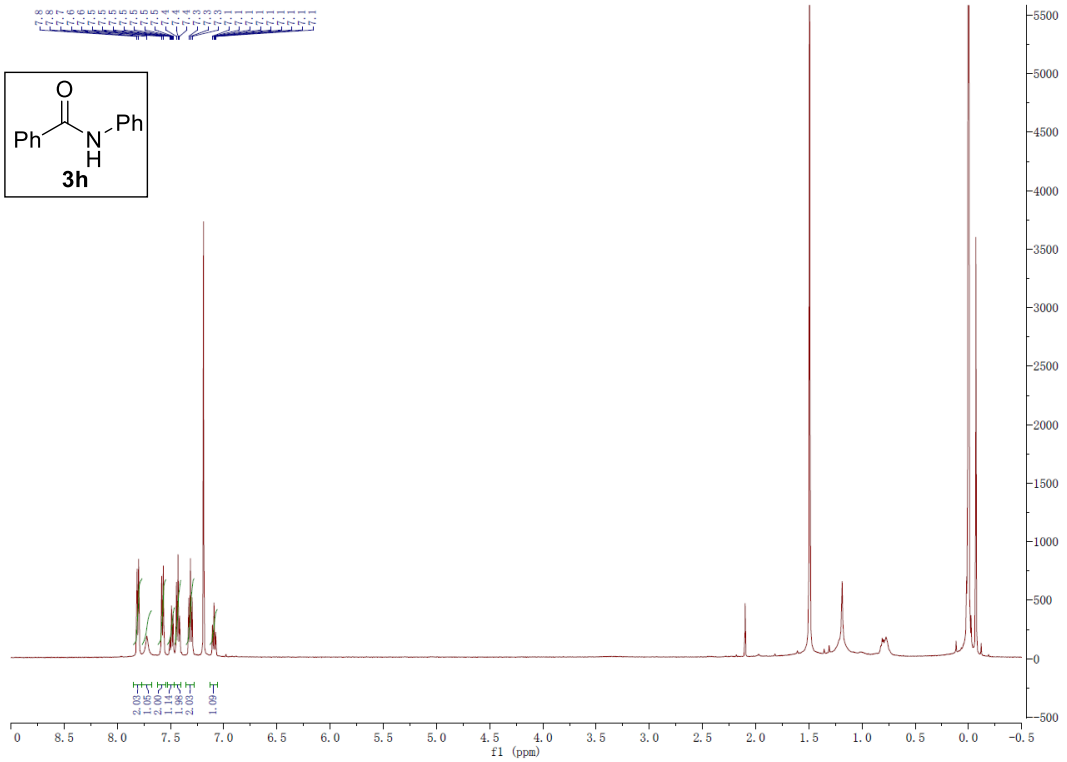
➢ ^{1}H NMR spectrum for **3g**



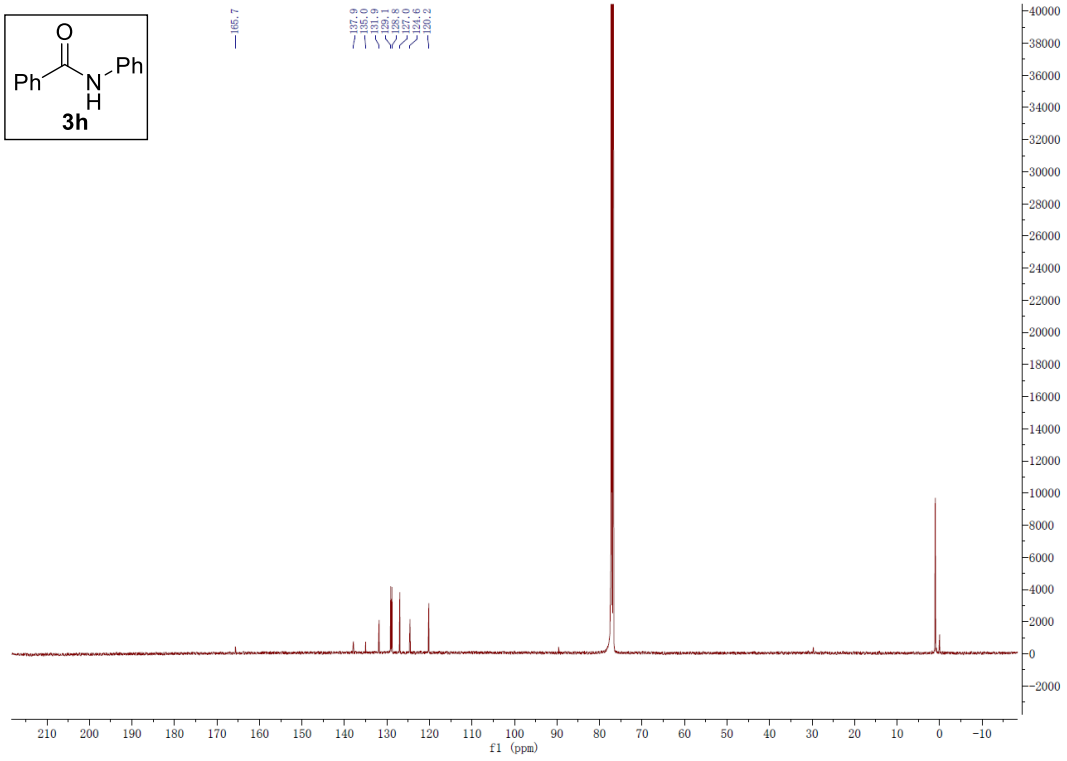
➢ ^{13}C NMR spectrum for **3g**



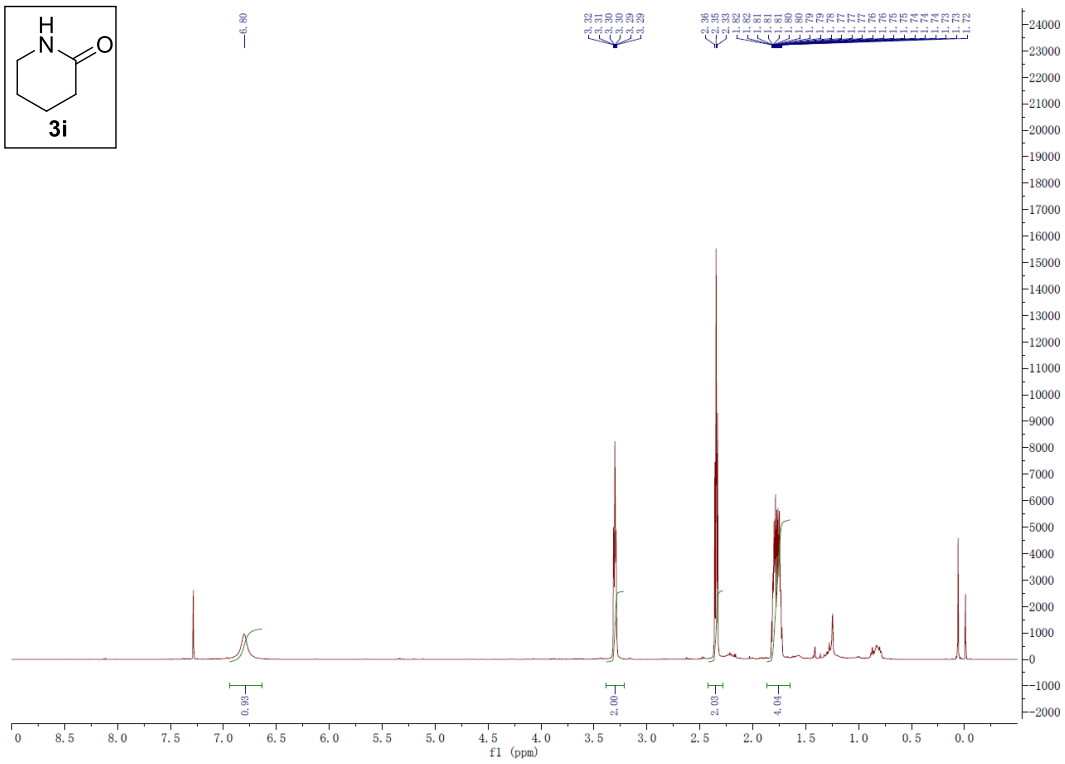
➢ ^{1}H NMR spectrum for **3h**



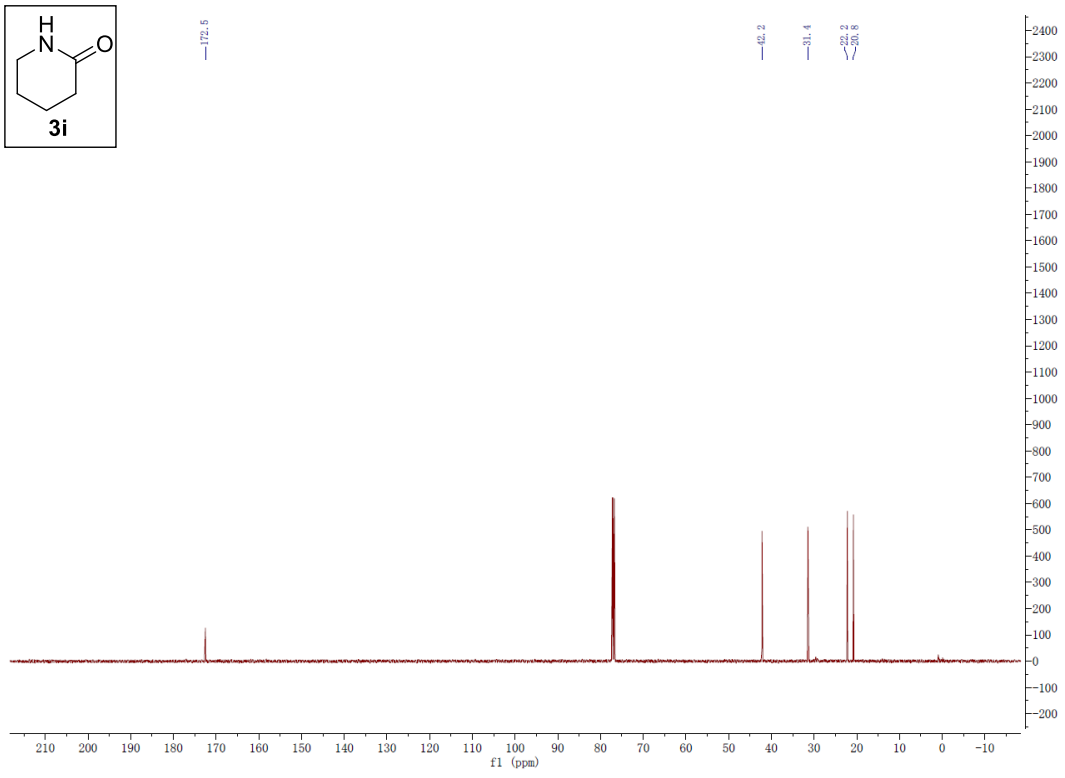
➢ ^{13}C NMR spectrum for **3h**



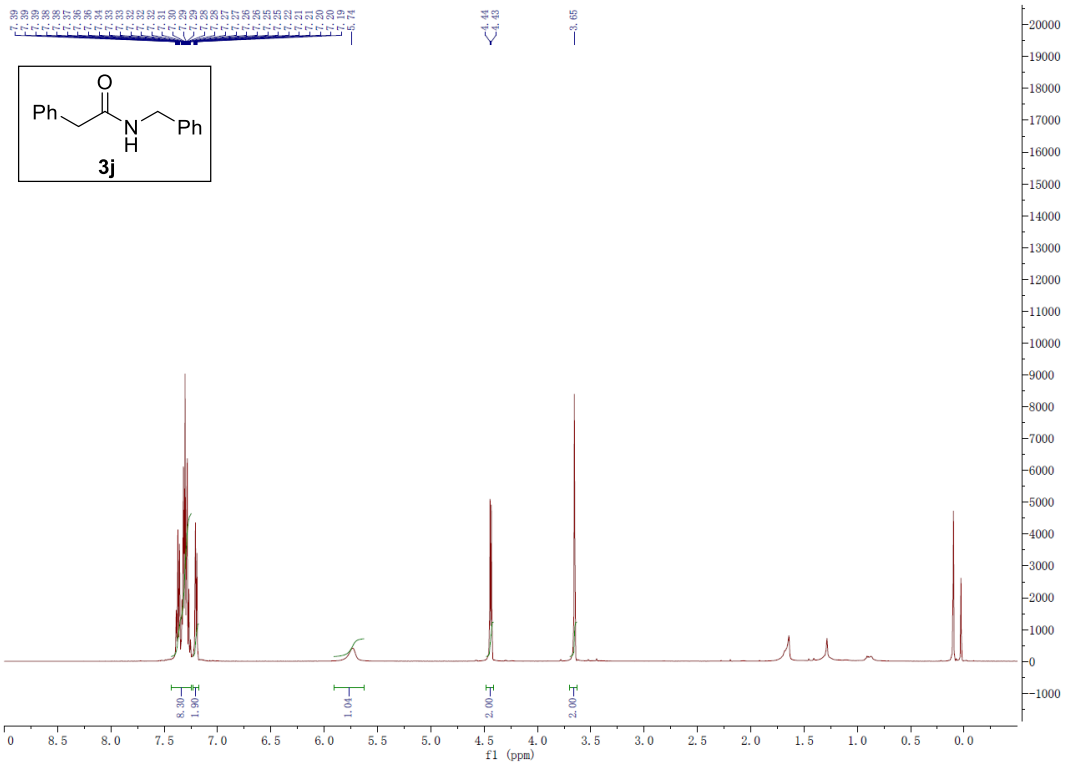
➢ ^{1}H NMR spectrum for **3i**



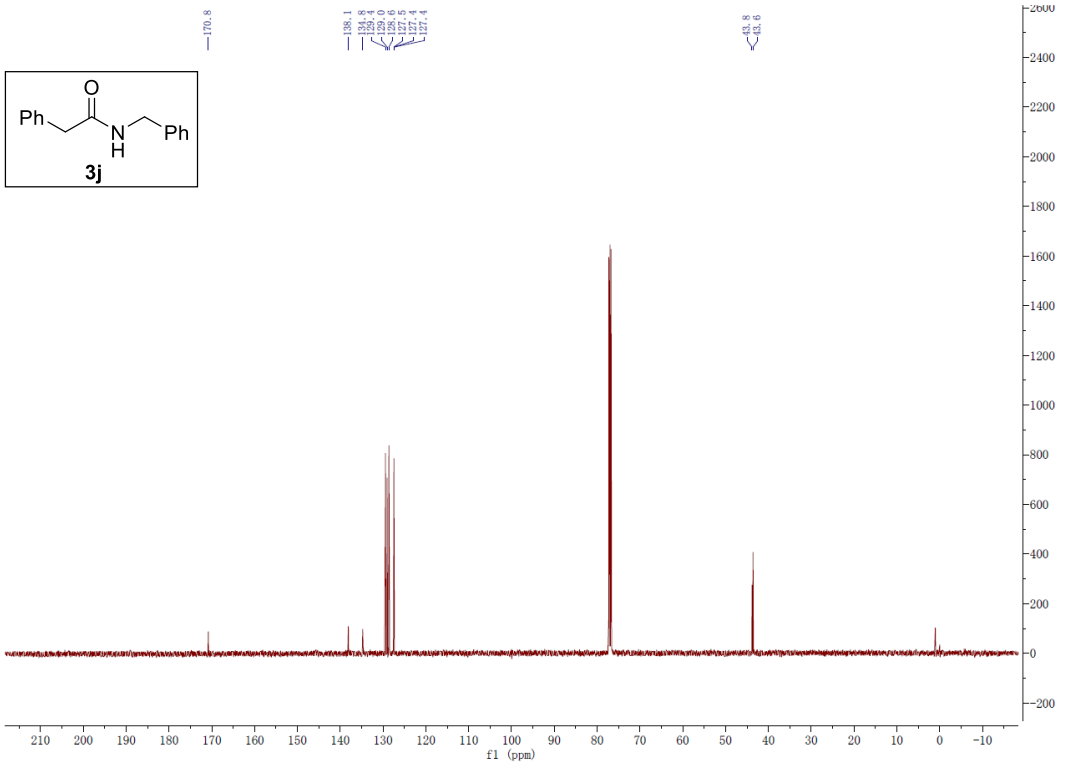
➢ ^{13}C NMR spectrum for **3i**



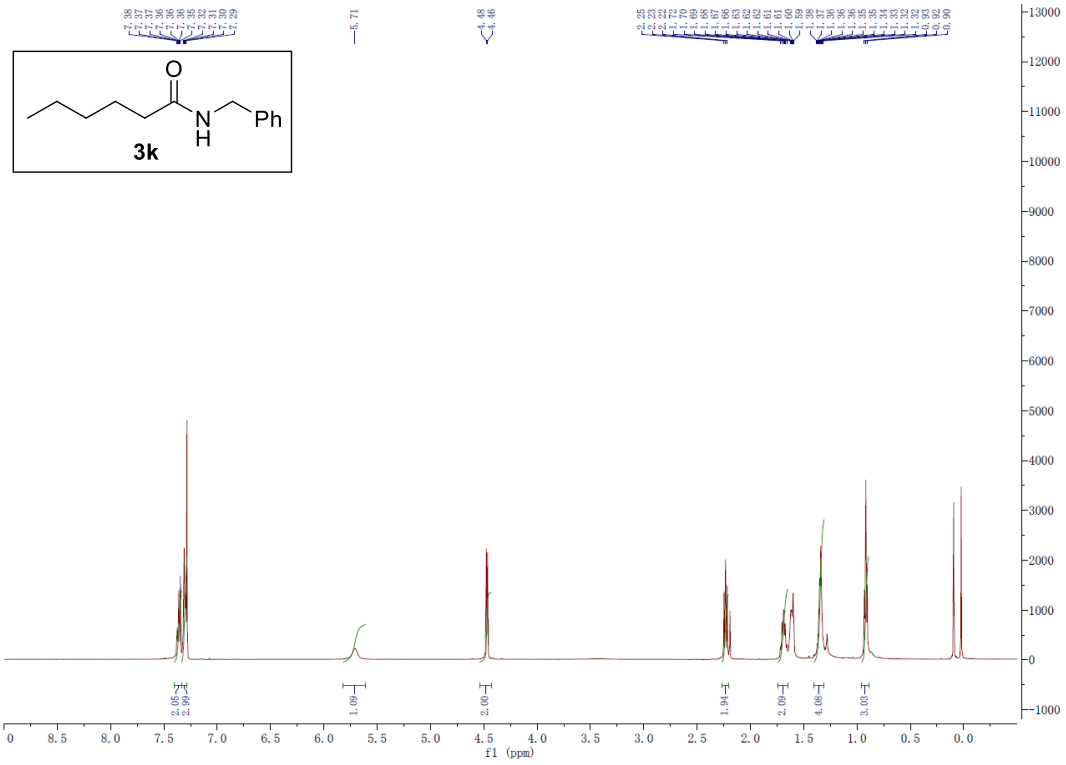
➢ ^{1}H NMR spectrum for **3j**



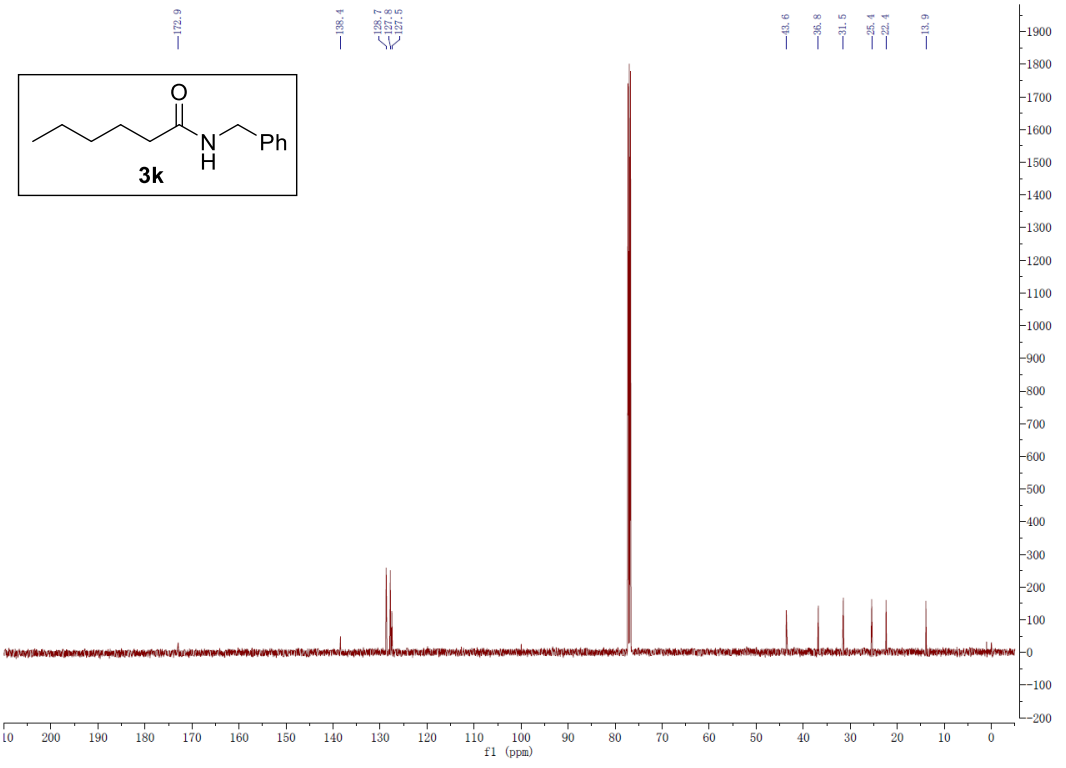
➢ ^{13}C NMR spectrum for **3j**



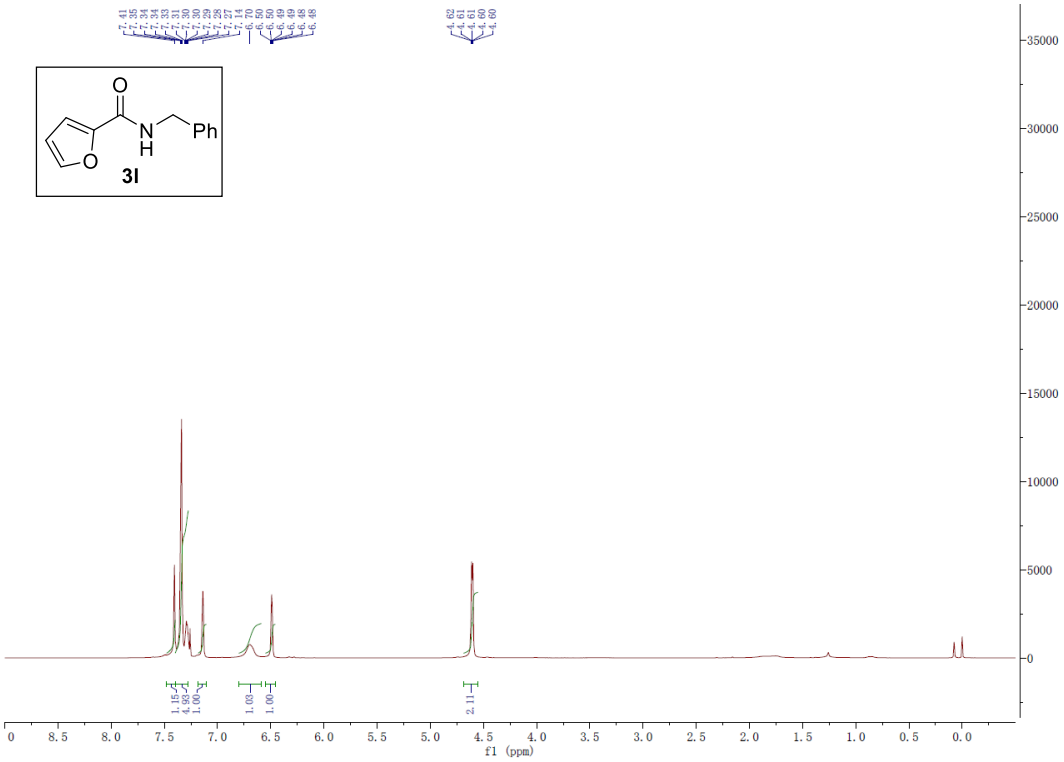
➢ ^{1}H NMR spectrum for **3k**



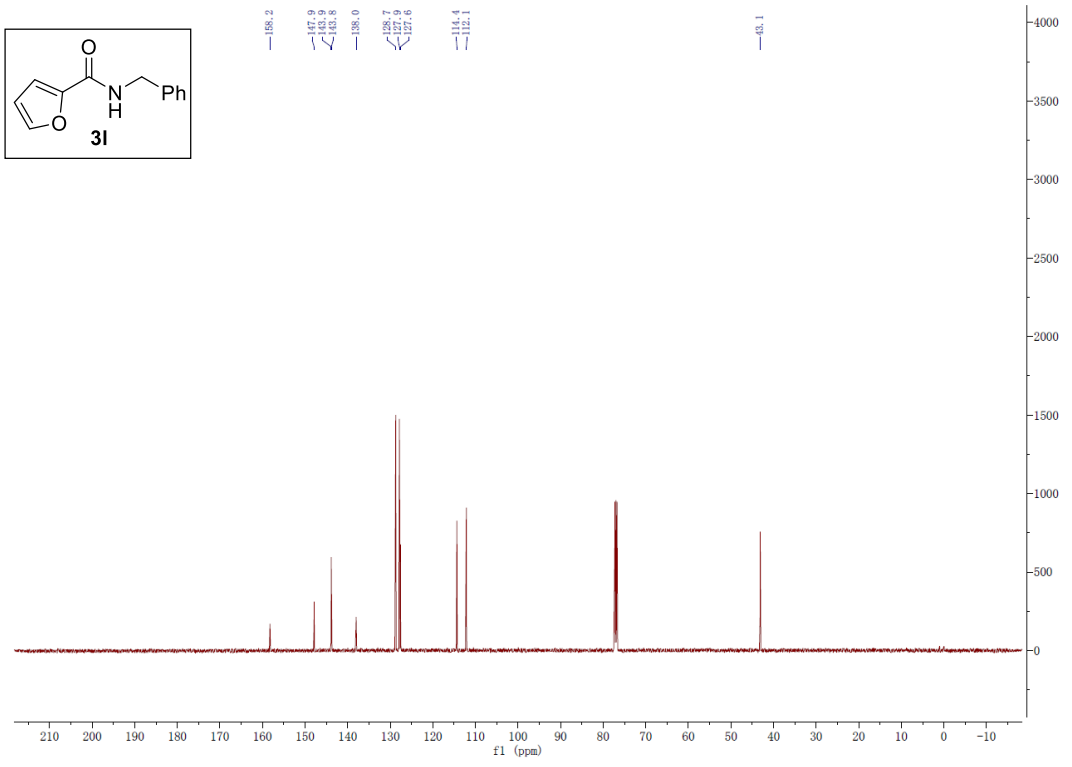
➢ ^{13}C NMR spectrum for **3k**



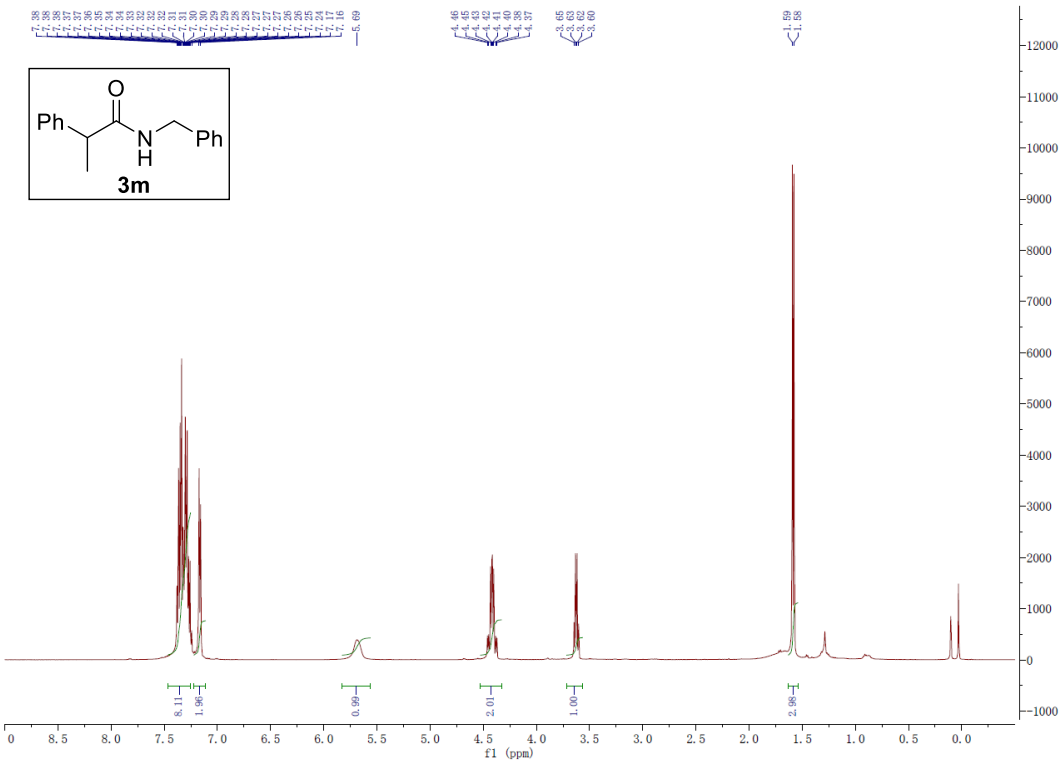
➢ ^{1}H NMR spectrum for **3l**



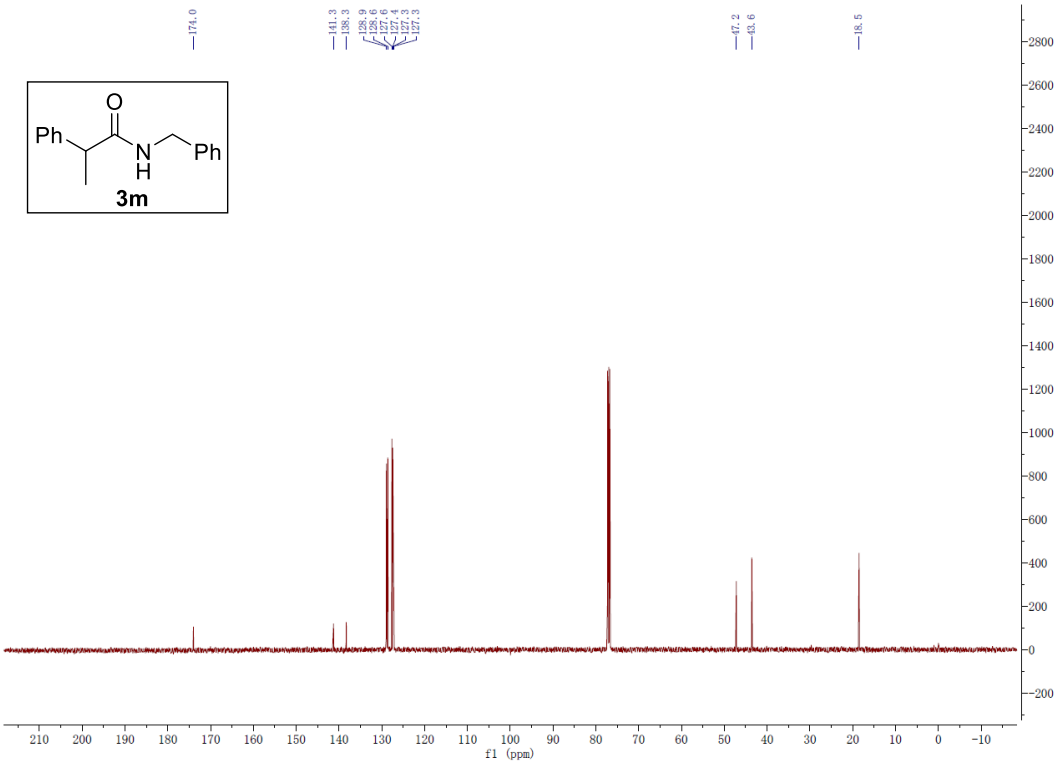
➢ ^{13}C NMR spectrum for **3l**



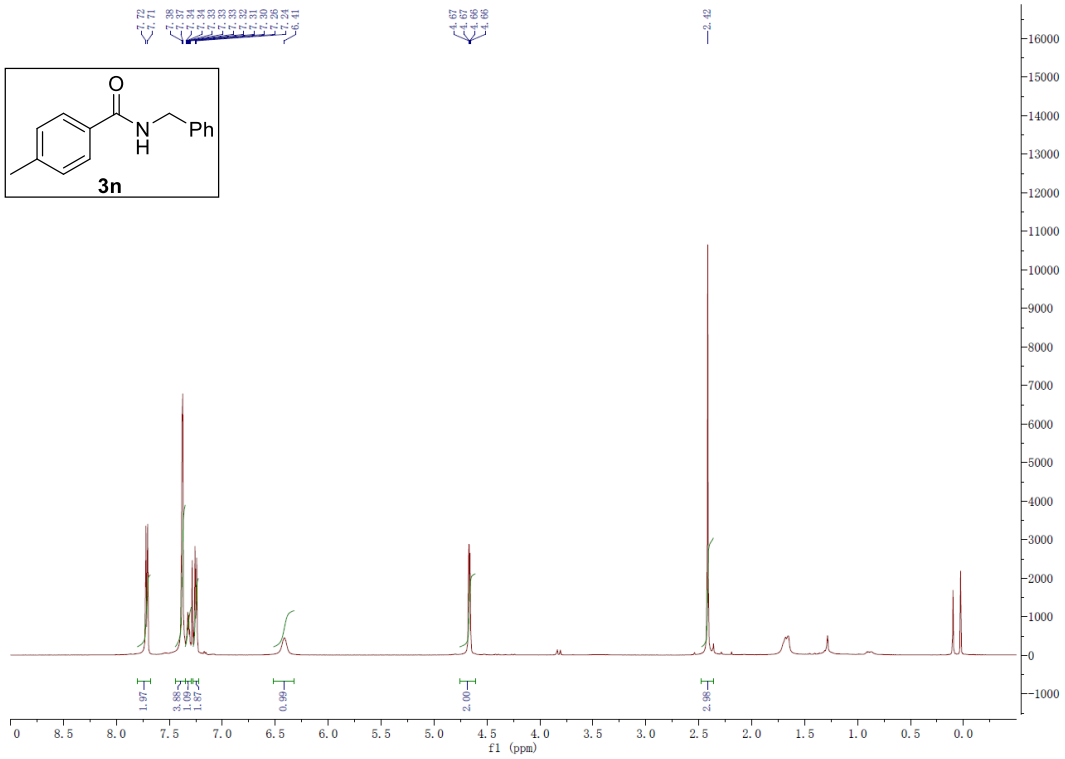
➢ ^{1}H NMR spectrum for **3m**



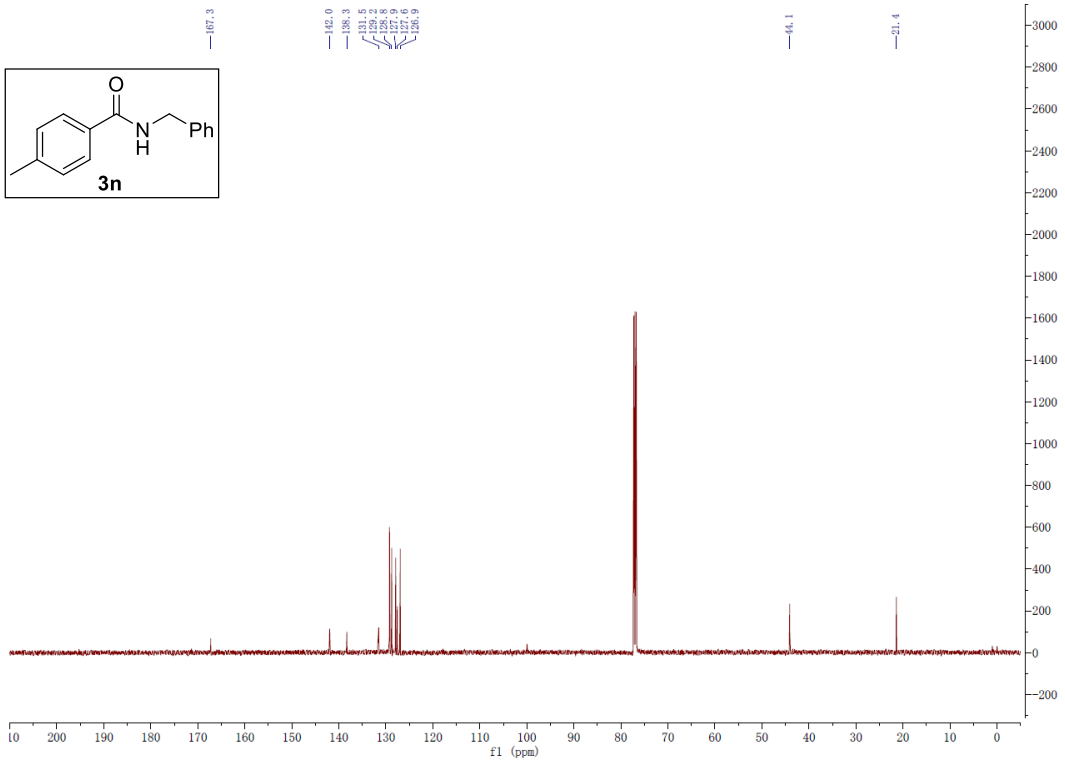
➢ ^{13}C NMR spectrum for **3m**



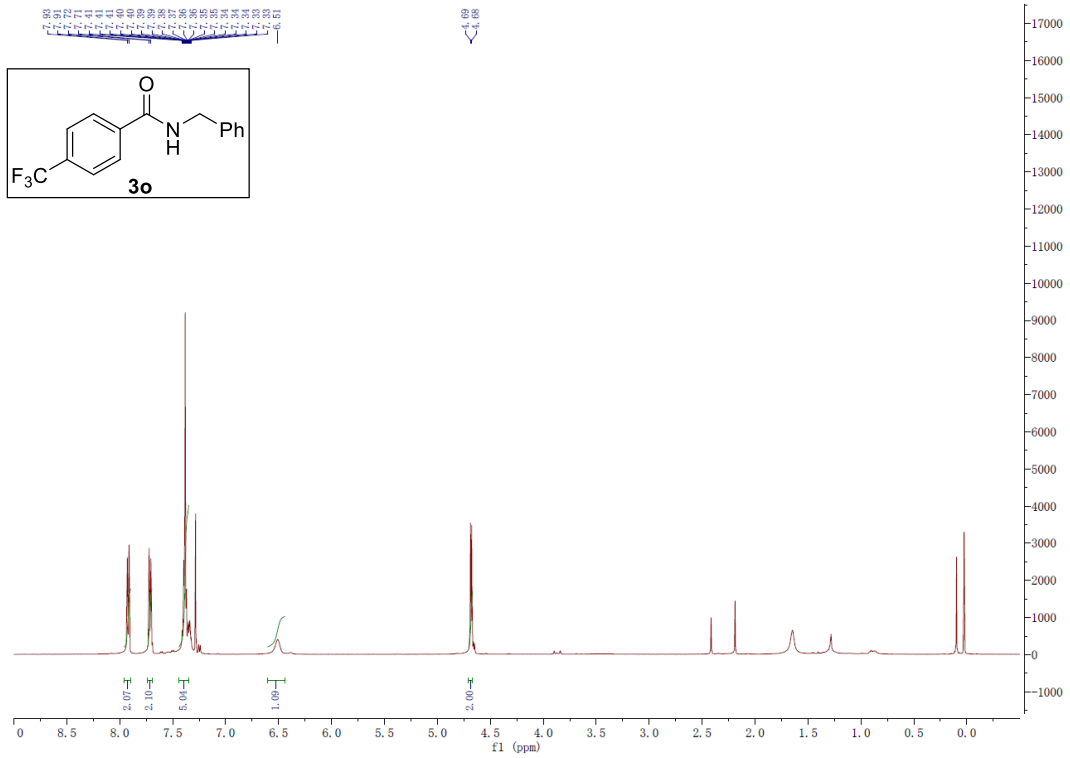
➢ ^{1}H NMR spectrum for **3n**



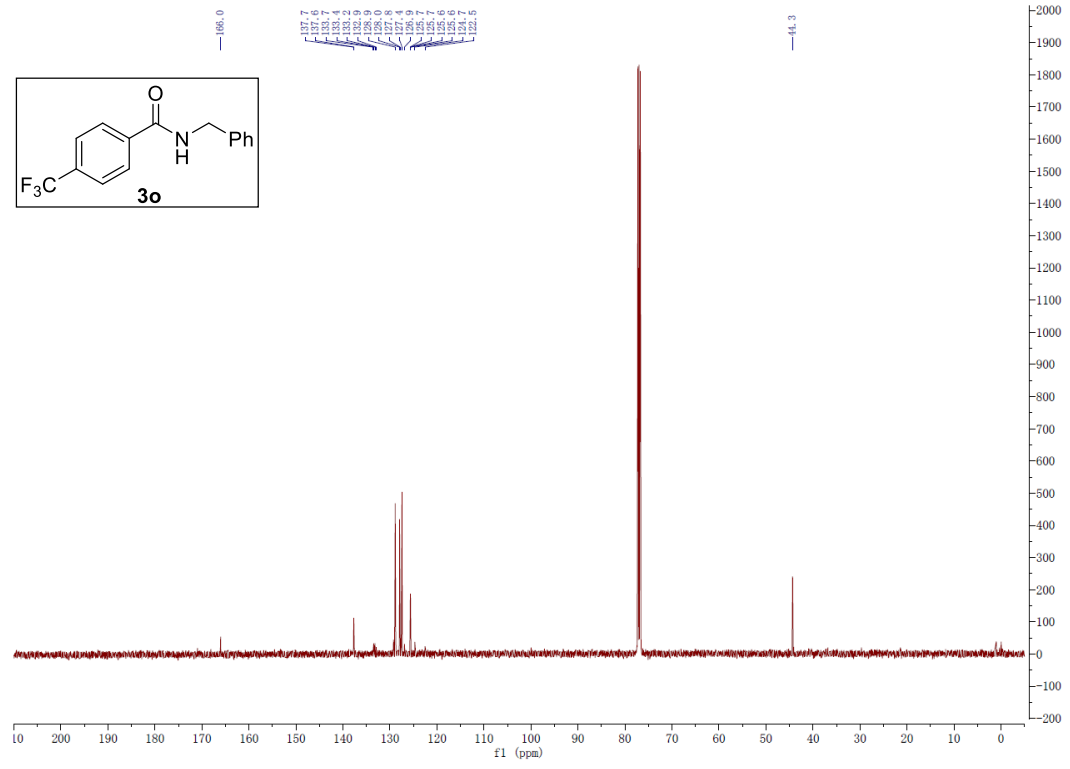
➢ ^{13}C NMR spectrum for **3n**



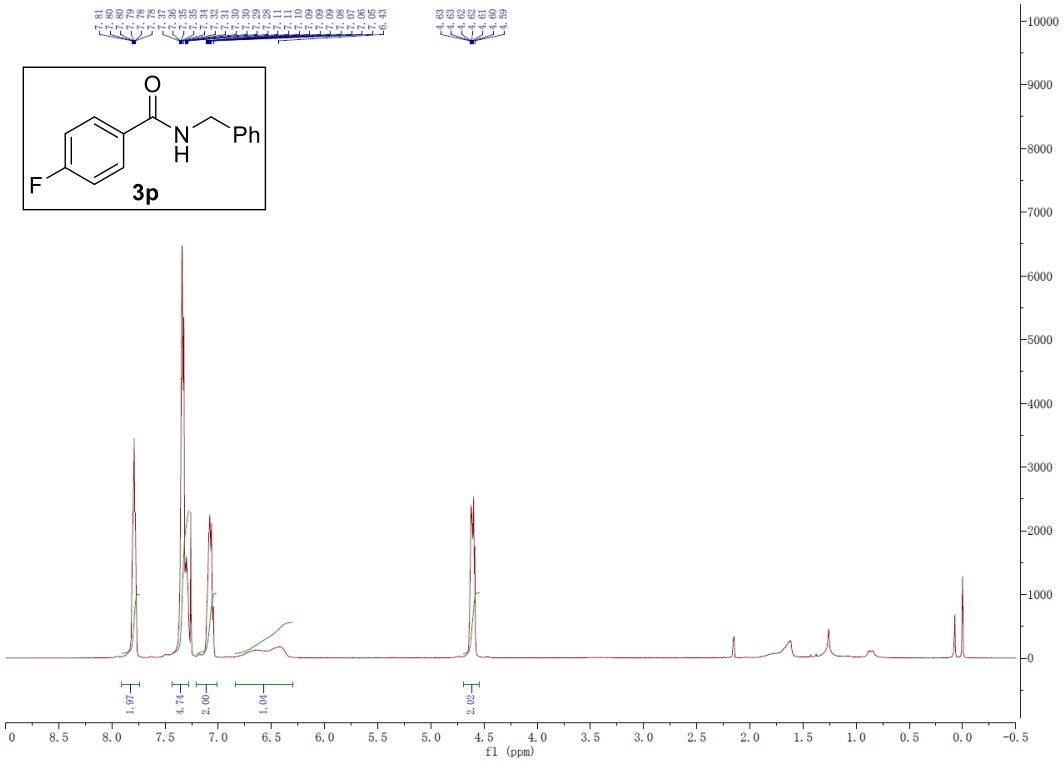
➢ ^{1}H NMR spectrum for **3o**



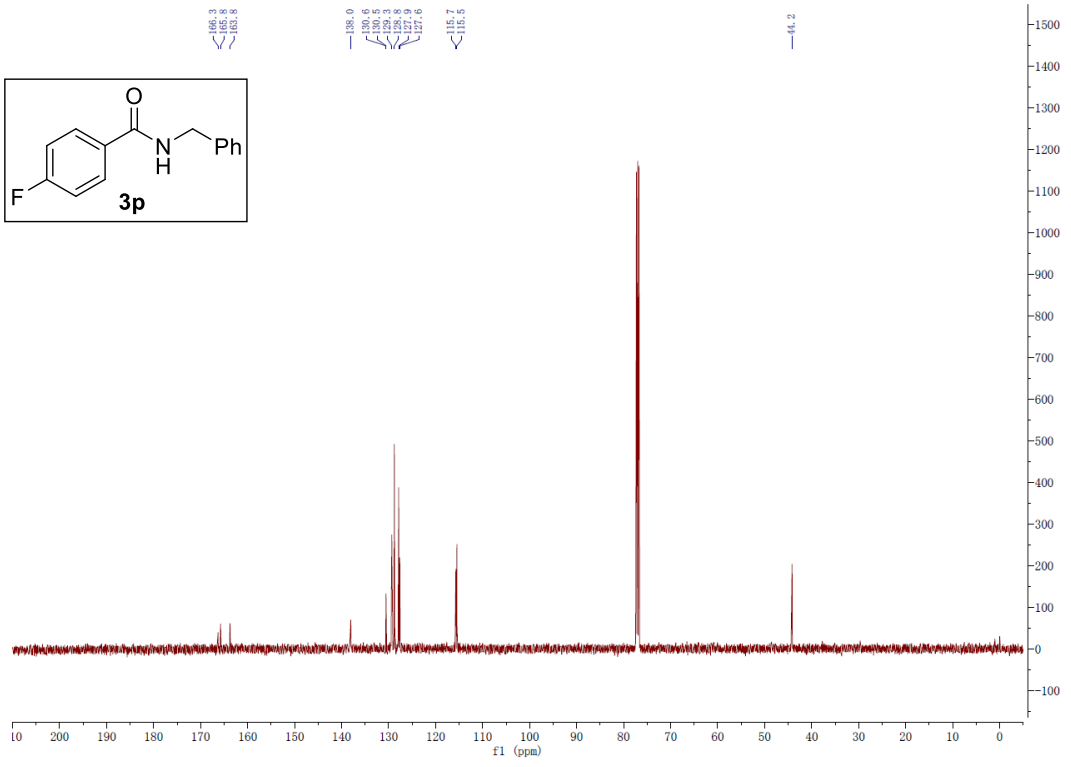
➢ ^{13}C NMR spectrum for **3o**



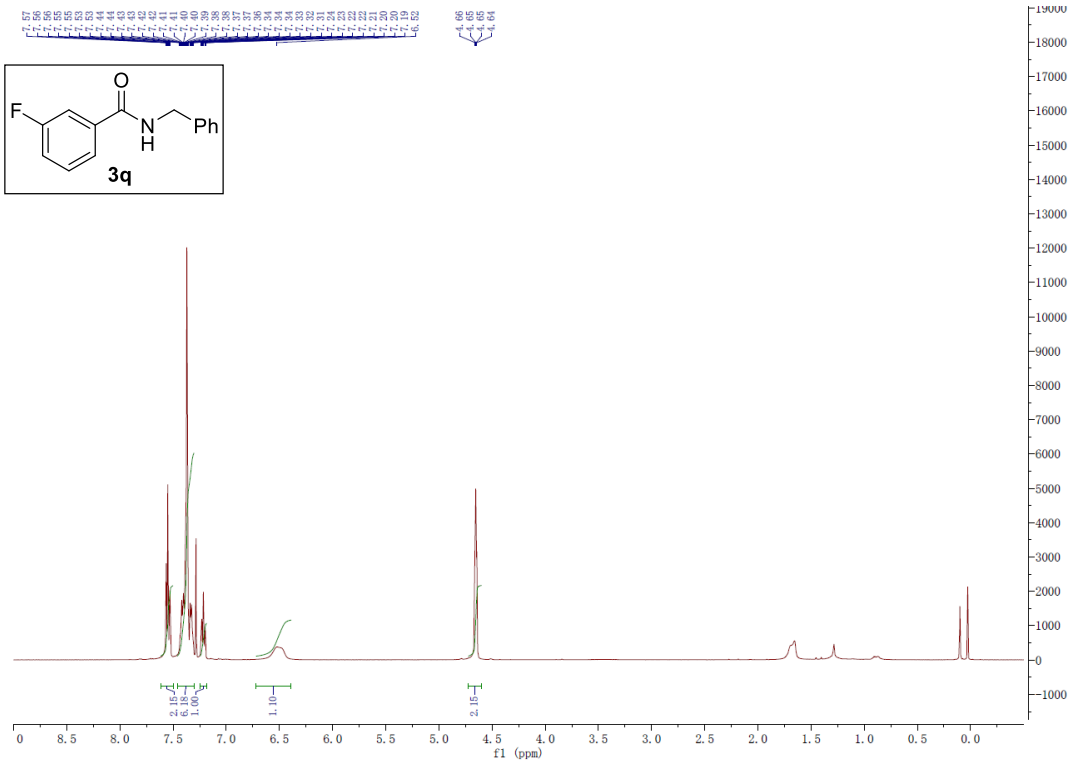
➢ ^{1}H NMR spectrum for **3p**



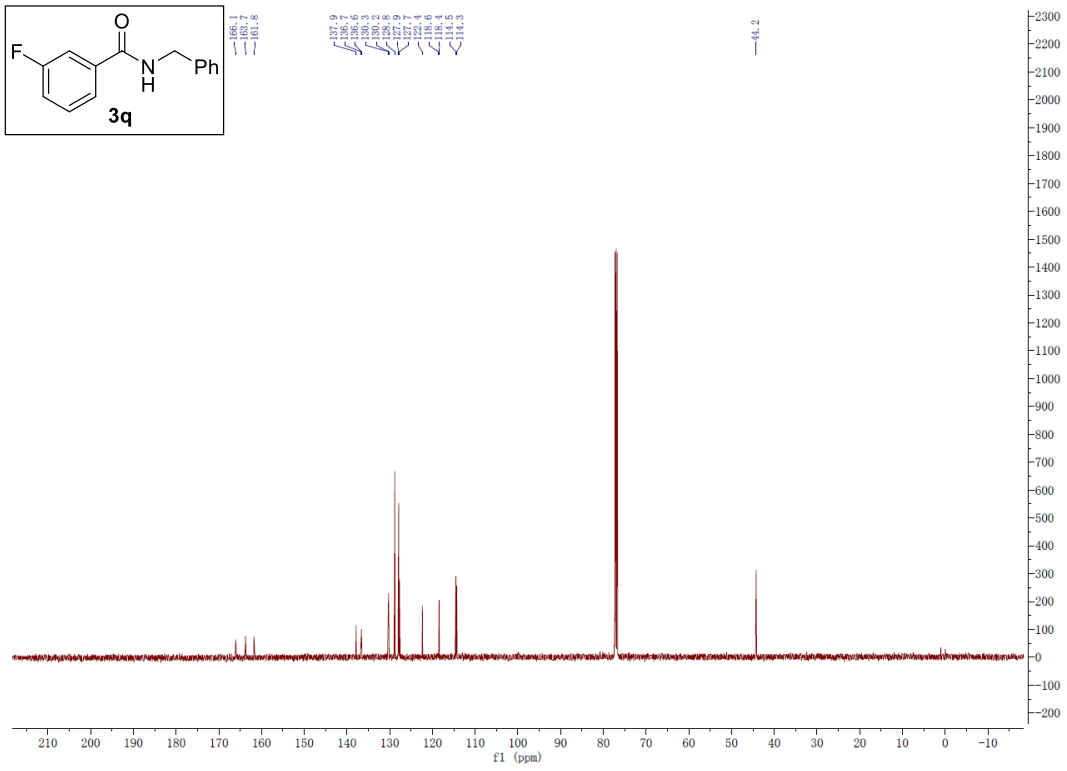
➢ ^{13}C NMR spectrum for **3p**



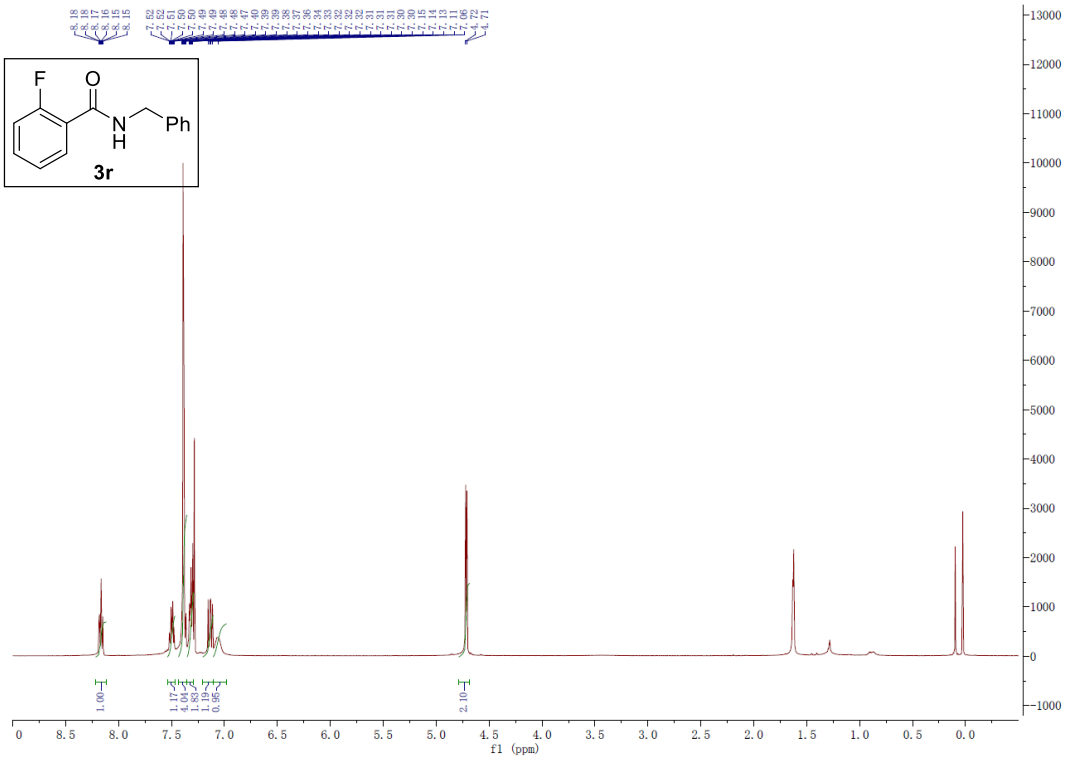
➢ ^{1}H NMR spectrum for **3q**



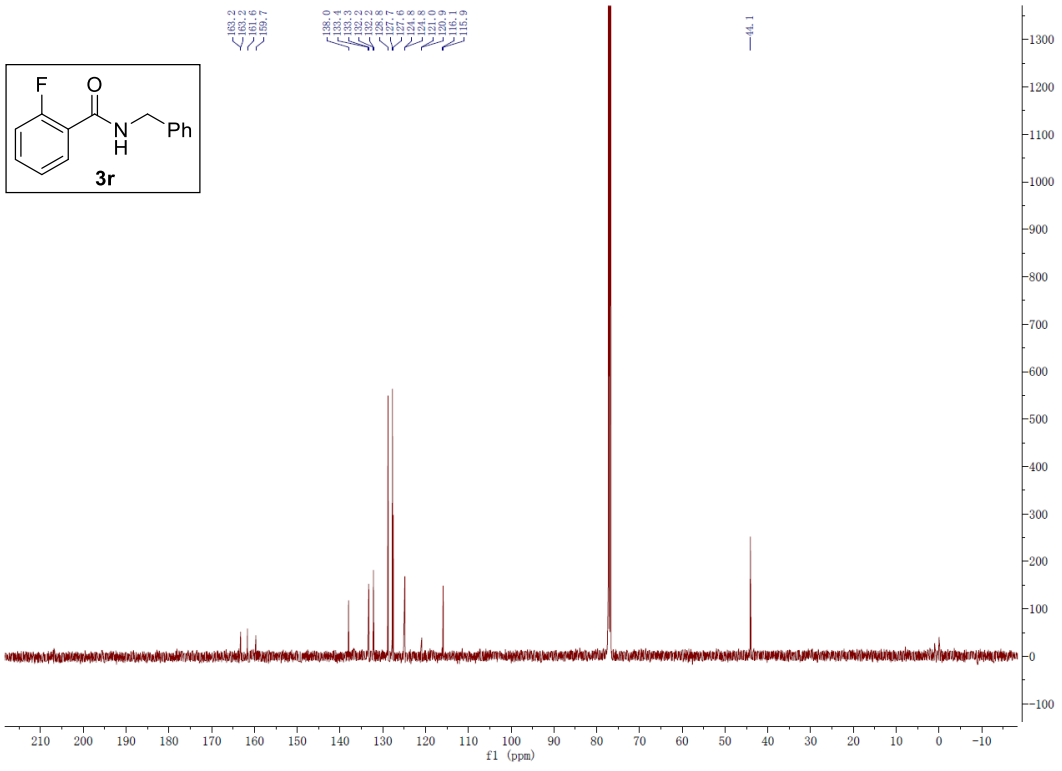
➢ ^{13}C NMR spectrum for **3q**



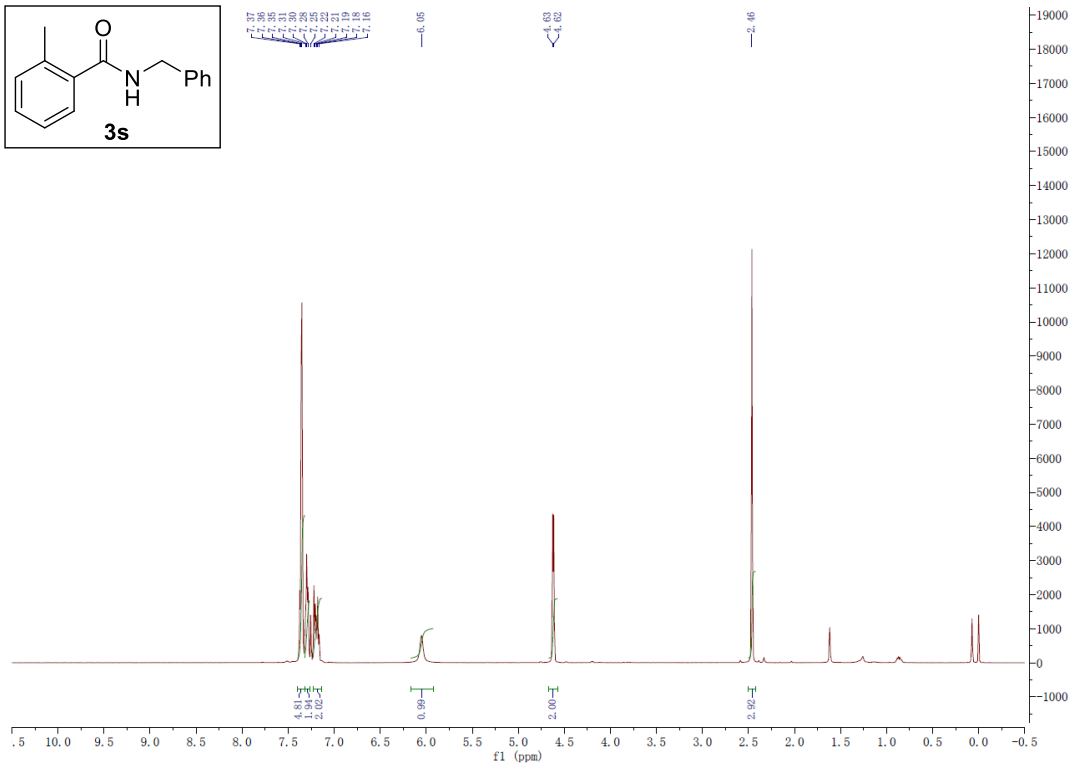
➢ ^{1}H NMR spectrum for **3r**



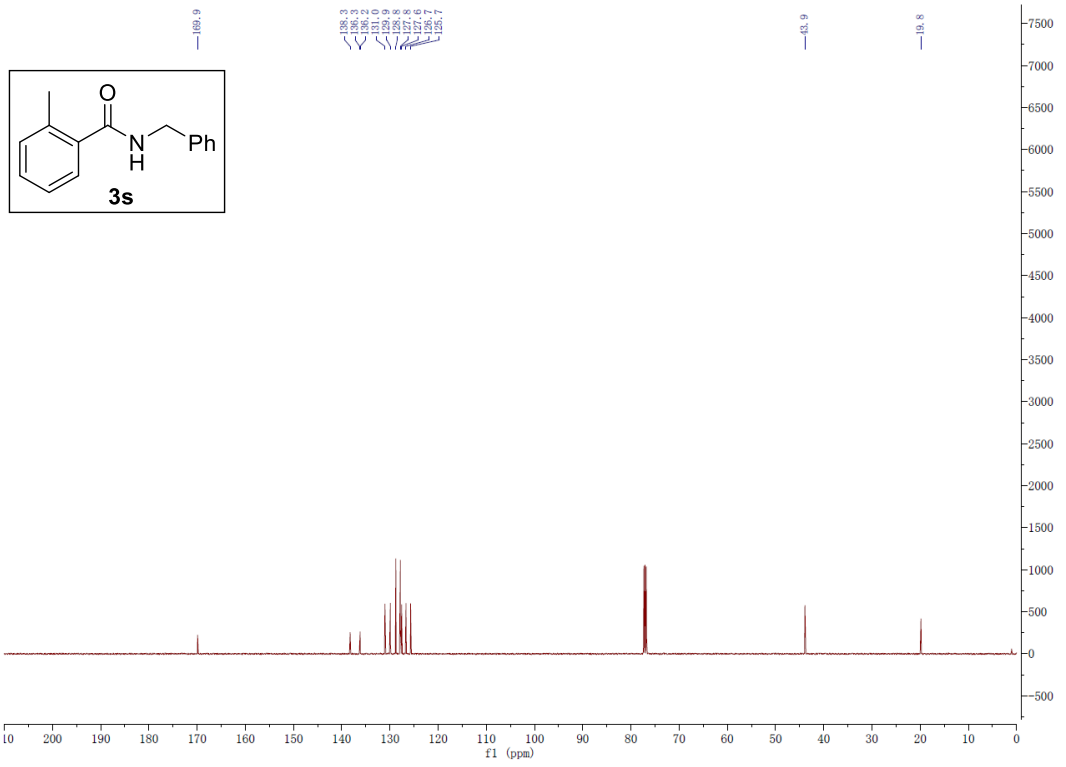
➢ ^{13}C NMR spectrum for **3r**



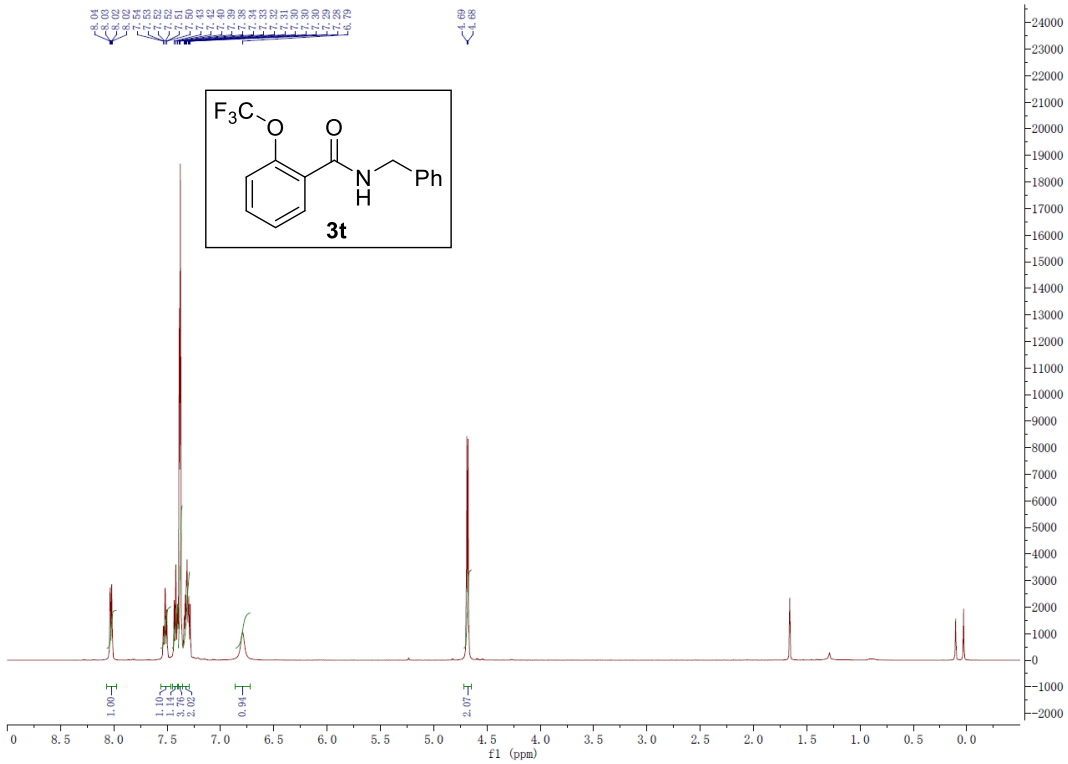
➢ ^{1}H NMR spectrum for **3s**



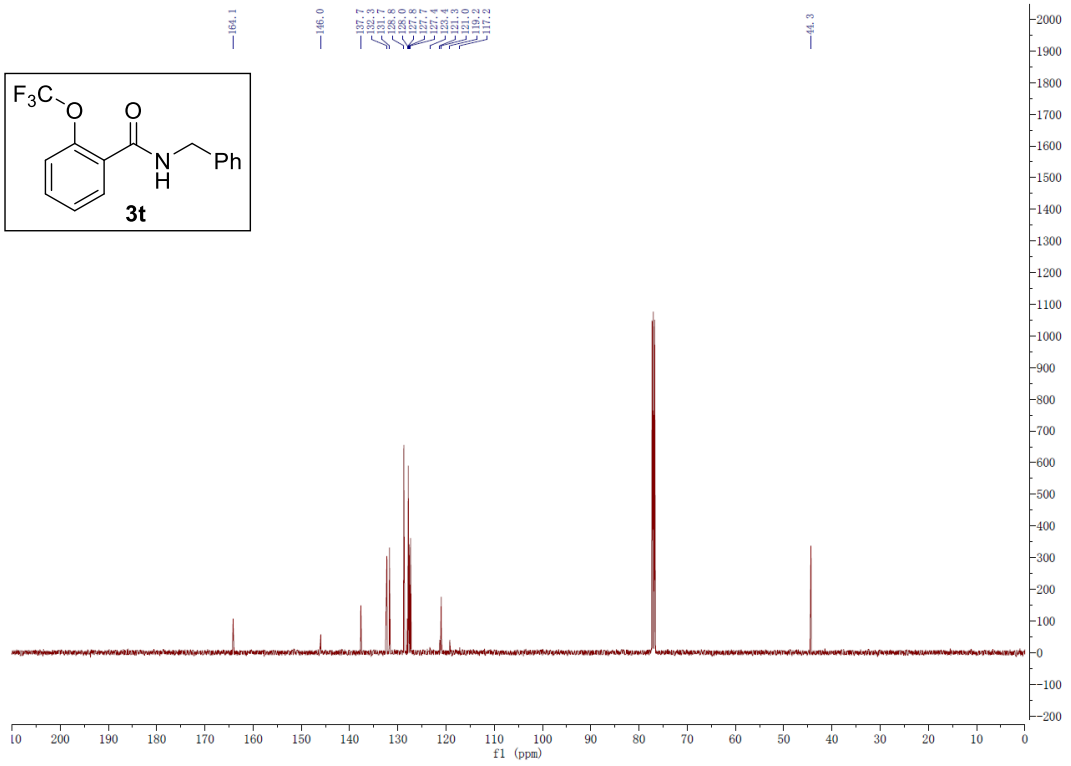
➢ ^{13}C NMR spectrum for **3s**



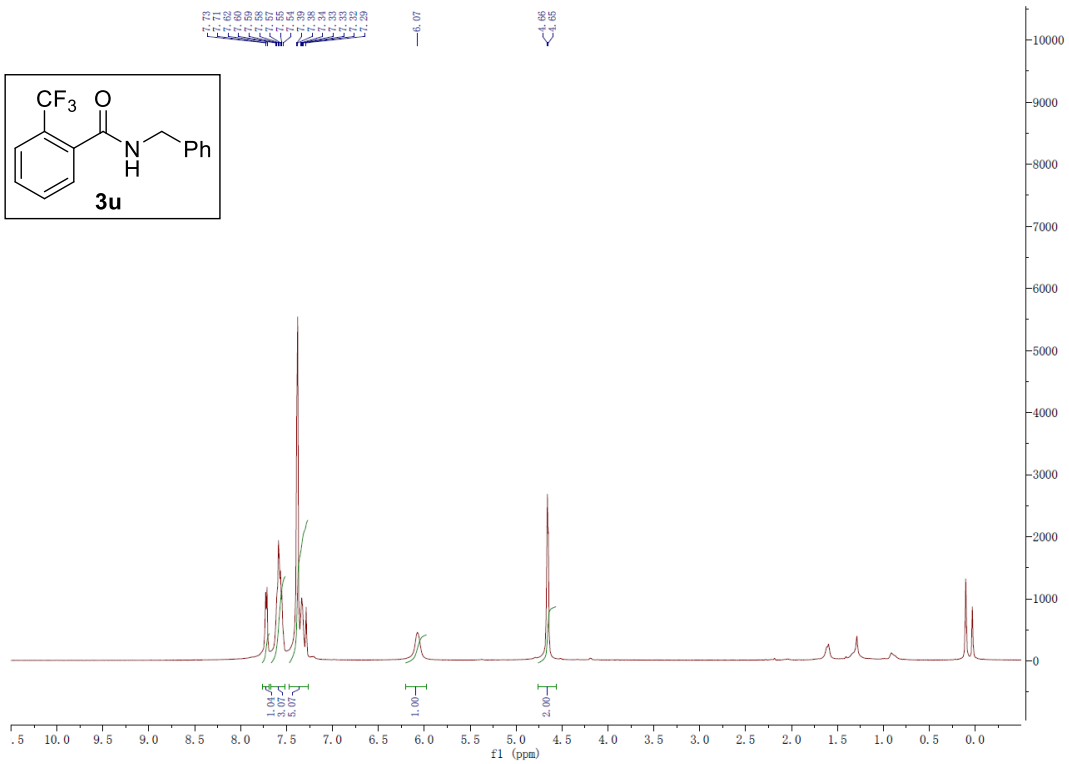
➢ ^{1}H NMR spectrum for **3t**



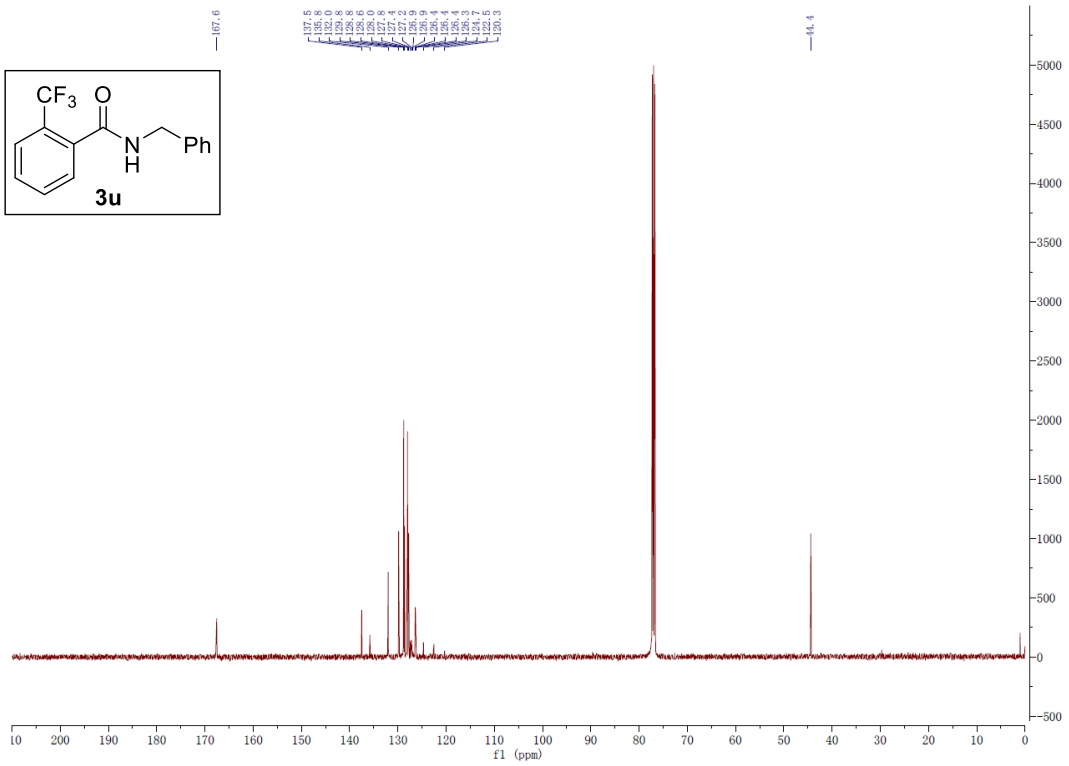
➢ ^{13}C NMR spectrum for **3t**



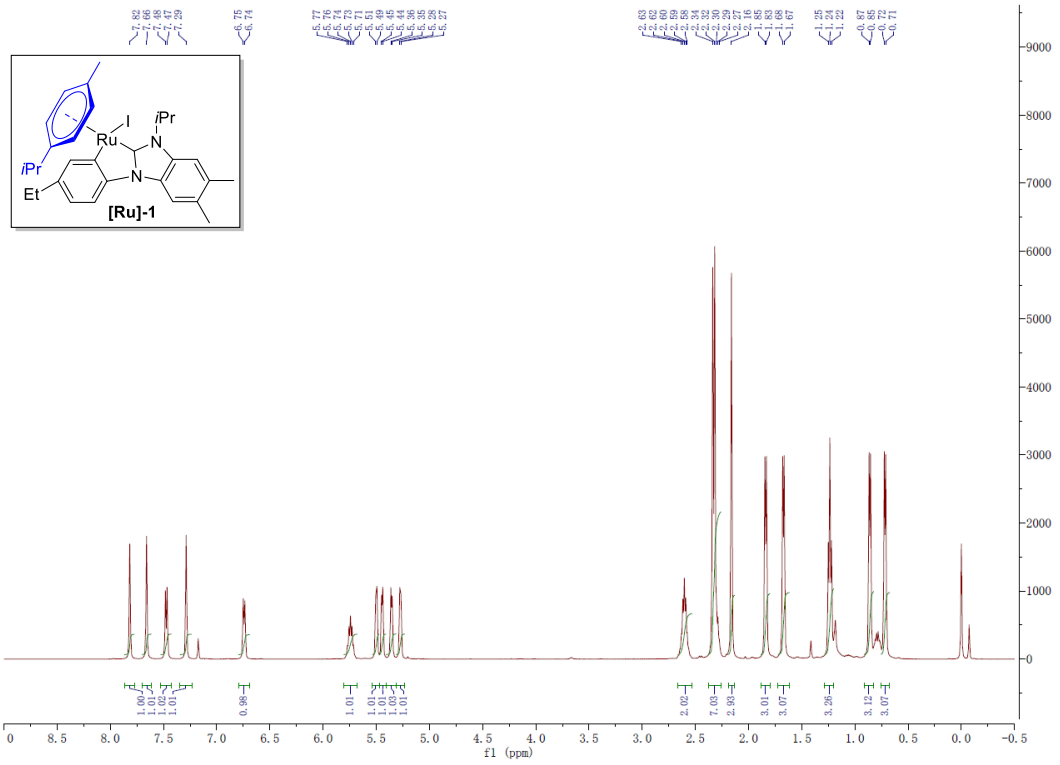
➢ ^{1}H NMR spectrum for **3u**



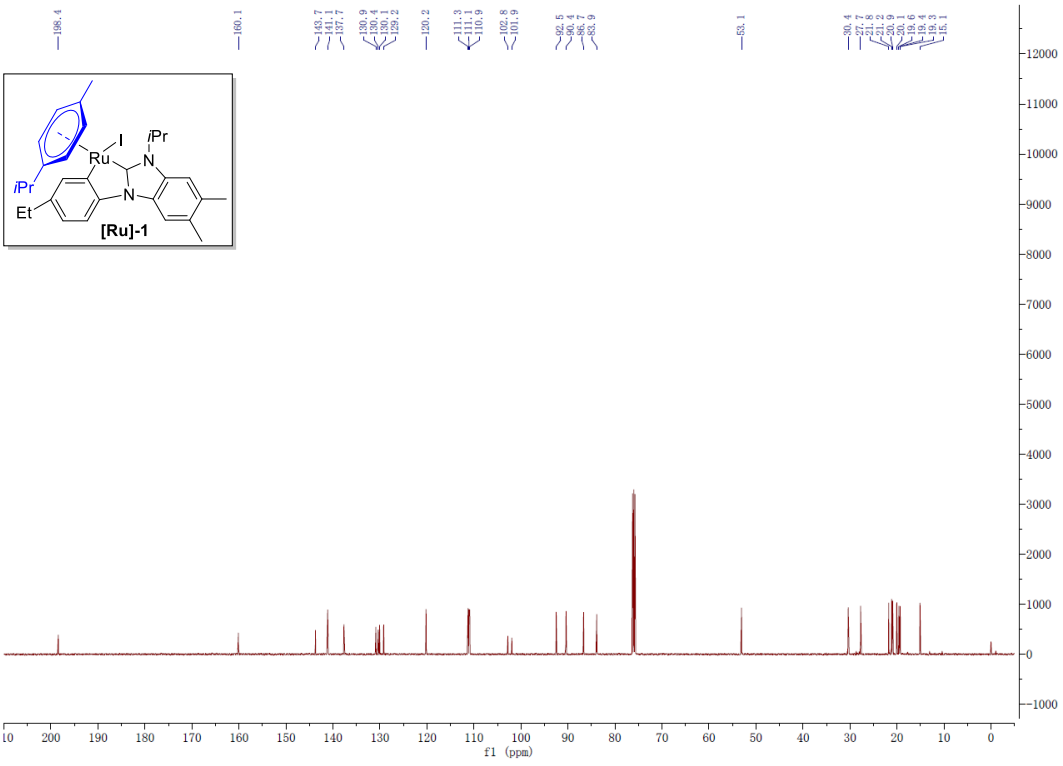
➢ ^{13}C NMR spectrum for **3u**



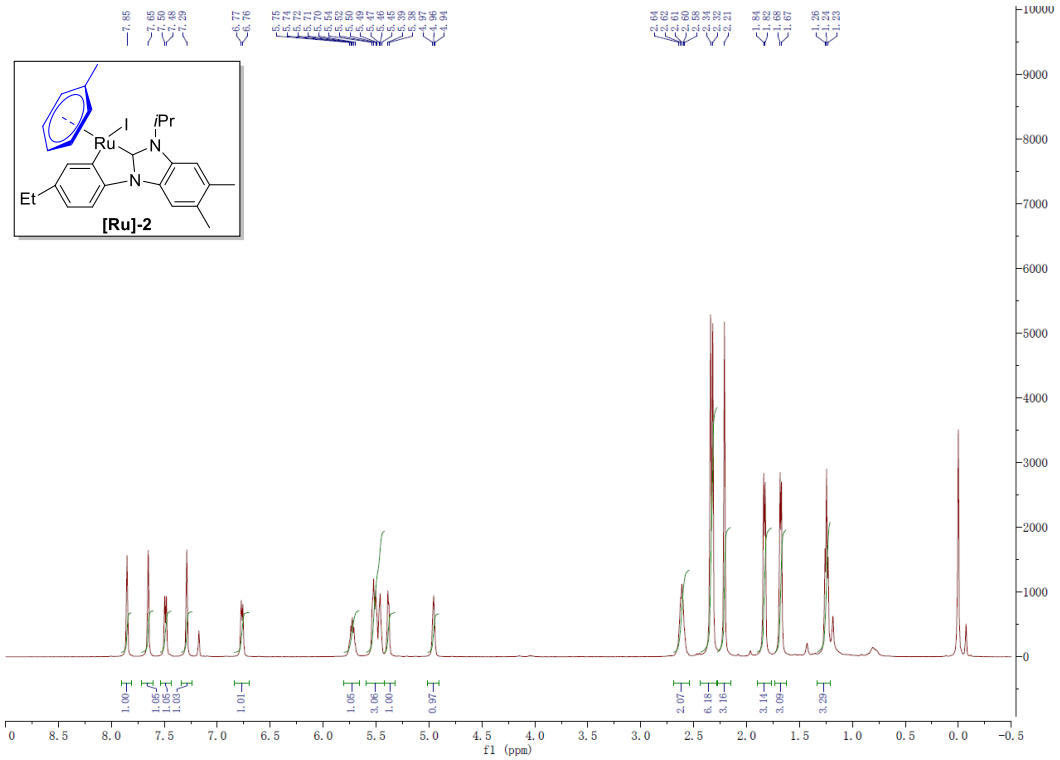
➢ ^{1}H NMR spectrum for **[Ru]-1**



➢ ^{13}C NMR spectrum for **[Ru]-1**



➢ ^{1}H NMR spectrum for **[Ru]-2**



➢ ^{13}C NMR spectrum for **[Ru]-2**