Supporting Information

Indy-N-Heterocyclic Carbene Complexes of Rhodium, Palladium and Gold: Synthesis, Characterizations, and Hydration of alkynes

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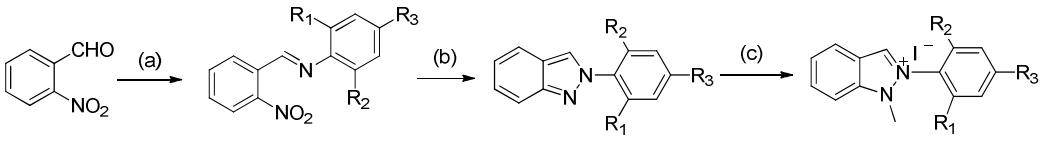
Contents:

1. General considerations:

Solvents for reactions were distilled according to general practice prior to use. All reagents were purchased and used without further purification unless specified otherwise. Solvents for chro-matography were technical grade and distilled prior to use. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed using Huanghai silica gel plates with HSGF 254. Qingdao Haiyang Chemical HG/T2354-92 silica gel was used for silica gel flash chro-matography. Visualization of the developed chromatogram was performed by UV absorbance (254 nm) or appropriate stains. ^{1}H NMR and ^{13}C NMR data were recorded on Bruker 400MHz nuclear resonance spectrometers unless otherwise specified, respectively. Gas chromatograph was recorded on a SHIMADZU GC-2014 spectrometer. HRMS (ESI) analysis was performed by The Analytical Instrumentation Center at Peking University; Shenzhen Graduate School and (HRMS) data were reported with ion mass/charge (m/z) ratios as values in atomic mass units.

2. Ligand Synthesis and Characterization:



	R_1	R_2	R_3
1a:	H	H,	H
1b:	CH_3	H	H
1c:	CH_3	CH_3	H
1d:	CH_3	CH_3	CH_3
1e:	CH_3	CH_3	Cl
1f:	CH_3	CH_3	Br
1g:	*i*Pr	*i*Pr	H
1h:	Ph	H	H

	R_1	R_2	R_3
2a:	H	H,	H
2b:	CH_3	H	H
2c:	CH_3	CH_3	H
2d:	CH_3	CH_3	CH_3
2e:	CH_3	CH_3	Cl
2f:	CH_3	CH_3	Br
2g:	*i*Pr	*i*Pr	H
2h:	Ph	H	H

	R_1	R_2	R_3
3a:	H	H,	H
3b:	CH_3	H	H
3c:	CH_3	CH_3	H
3d:	CH_3	CH_3	CH_3
3e:	CH_3	CH_3	Cl
3f:	CH_3	CH_3	Br
3g:	*i*Pr	*i*Pr	H
3h:	Ph	H	H

General Procedure for the Synthesis Schiff bases (1)

A mixture of 2-nitrobenzaldenhyde (2.30 g, 15.2 mmol) and aniline (1.2 equiv.) was stirred at 90 ^{o}C for 3 h, and then cooled to room temperature. Ethanol (10 ml) was added into the reaction mixture, and the solution was set in refrigerator overnight for recrystallization. After the mixture was filtered and the resulting solid was washed with 4 mL cold ethanol three times and then the solid was dried to obtain the crude products.

(E)-N-(2-nitrobenzylidene)aniline (1a): yield 89%, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.30 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.06 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.73 (t, *J* = 7.4 Hz, 1H), 7.60 (m, 1H), 7.43 (m, 2H), 7.29 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.86, 151.09, 149.34, 133.61, 131.23, 131.11, 129.76, 129.32, 126.96, 124.55, 121.23. HRMS (ESI^+): 227.0817, calcd mass for $[C_{13}H_{11}N_2O_2]^+$: 227.0821.

(E)-2-methyl-N-(2-nitrobenzylidene)aniline(1b): yield 92%, yellow solid. ^{1}H NMR (400 MHz, CDCl3) δ 8.84 (s, 1H), 8.33 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.63 (m, 1H), 7.26 (dd, *J* = 9.5, 4.2 Hz, 2H), 7.19 (m, 1H), 7.04 (d, *J* = 7.4 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.06, 150.18, 149.30, 133.54, 132.36, 131.28, 131.13, 130.49, 129.90, 126.94, 126.67, 124.51, 117.85, 17.93. HRMS (ESI^+): 241.0973, calcd mass for $[C_{14}H_{13}N_2O_2]^+$: 241.0977.

(E)-2,6-dimethyl-N-(2-nitrobenzylidene)aniline (1c): yield 90%, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) :δ 8.67 (s, 1H), 8.34 (dd, *J* = 7.8, 1.0 Hz, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.71 – 7.58 (m, 1H), 7.11 (d, *J* = 7.5 Hz, 2H), 7.06 – 6.90 (m, 1H), 2.23 (s, 6H). ^{13}C

NMR (100 MHz, $CDCl_3$): δ 158.89, 150.40, 149.17, 133.77, 131.36, 131.24, 129.66, 128.19, 127.03, 124.55, 124.32, 18.29. HRMS (ESI^+): 255.1128, calcd mass for $[C_{15}H_{15}N_2O_2]^+$: 255.1134.

(E)-2,4,6-trimethyl-N-(2-nitrobenzylidene)aniline (1d): yield 92%, yellow solid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.66 (s, 1H), 8.35 (d, *J* = 7.7 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.70 – 7.63 (m, 1H), 6.93 (s, 2H), 2.32 (s, 3H), 2.21 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.81, 149.16, 147.99, 133.73, 133.71, 131.35, 131.24, 129.64, 128.89, 127.03, 124.52, 20.76, 18.24. HRMS (ESI^+): 269.1288, calcd mass for $[C_{16}H_{17}N_2O_2]^+$: 269.1290.

(E)-4-chloro-2,6-dimethyl-N-(2-nitrobenzylidene)aniline (1e): yield: 87%, yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.31 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.13 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.80 (t, *J* = 7.4 Hz, 1H), 7.68 (m, 1H), 7.08 (s, 2H), 2.19 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.51, 149.16, 148.88, 133.81, 131.56, 130.99, 129.60, 129.13, 128.90, 127.88, 124.61, 18.19. HRMS (ESI^+): 289.0733, calcd mass for $[C_{15}H_{14}N_2O_2Cl]^+$: 289.0744.

(E)-4-bromo-2,6-dimethyl-N-(2-nitrobenzylidene)aniline (1f): yield 88%, yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.30 (dd, *J* = 7.7, 1.2 Hz, 1H), 8.13 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.68 (m, 1H), 7.23 (s, 2H), 2.18 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.47, 149.41, 149.13, 133.84, 131.59, 130.99, 130.78, 129.62, 129.28, 124.63, 117.02, 18.12. HRMS (ESI^+): 333.0230, calcd mass for $[C_{15}H_{14}N_2O_2Br]^+$: 333.0239.

(E)-2,6-diisopropyl-N-(2-nitrobenzylidene)aniline (1g): yield 93%, yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.34 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.13 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.80 (m, 1H), 7.68 (m, 1H), 7.17 (m, 3H), 3.03 (m, 2H), 1.22 (d, *J* = 6.9 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.22, 149.34, 148.31, 137.52, 133.77, 131.35, 131.04, 129.70, 124.77, 124.59, 123.14, 27.95, 23.50. HRMS (ESI^+): 311.1755 calcd mass for $[C_{19}H_{23}N_2O_2]^+$: 311.1760.

(E)-N-(2-nitrobenzylidene)biphenyl-2-amine (1h): yield 88%, yellow oil. ^1H NMR (400 MHz, DMSO) δ 8.88 (s, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.93 (t, *J* = 7.8 Hz, 1H), 7.80 (t, *J* = 7.3 Hz, 1H), 7.73 (dd, *J* = 10.5, 4.7 Hz, 1H), 7.39 (m, 8H), 7.18 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (100 MHz, DMSO) δ 157.76, 149.58, 149.20, 139.40, 135.51, 134.34, 132.21, 130.96, 130.58, 130.37, 129.79, 129.21, 128.27, 127.48, 127.22, 125.02, 119.54. HRMS (ESI^+): 303.1122, calcd mass for $[C_{19}H_{15}N_2O_2]^+$: 303.1134.

General Procedure for the Synthesis 2H-indazoles (2)

A mixture of compound **1** (10 mmol) and triethyl phosphate (10 equiv.) was stirred at 160 ^{o}C for 12 h in the 100 ml sealed tube. The solvent was removed by rotary evaporation, and then the crude product was purified by column chromatography on SiO_2.

2-phenyl-2H-indazole (2a): yield 65%, yellow solid. ^{1}H NMR (400 MHz, CDCl3) δ 8.41 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.34 (m, 1H), 7.13 (m, 1H). ^{13}C NMR (100MHz, $CDCl_3$) δ 149.84, 140.57, 129.59, 127.92, 126.86, 122.81, 122.49, 121.02, 120.43, 117.99. HRMS (ESI^+):195.0920, calcd mass for $[C_{13}H_{11}N_2]^+$: 195.0922.

2-o-tolyl-2H-indazole (2b): yield 68%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.82 (dd, *J* = 8.8, 0.7 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.38 (m, 5H), 7.16 (m, 1H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.26, 140.34, 133.95, 131.28, 129.19, 126.64, 126.60, 126.42, 124.36, 122.17, 121.97, 120.33, 117.94, 17.90. HRMS (ESI^+): 209.1073, calcd mass for $[C_{14}H_{13}N_2]^+$: 209.1079.

2-(2,6-dimethylphenyl)-2H-indazole (2c): yield 68%, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 0.6 Hz, 1H), 7.83 (dd, *J* = 8.8, 0.7 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.36 (m, 2H), 7.18 (m, 3H), 2.01 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.18, 139.74, 135.58, 129.39, 128.17, 126.20, 124.49, 122.06, 121.87, 120.40, 118.09, 17.21. HRMS (ESI^+): 223.1212, calcd mass for $[C_{15}H_{15}N_2]^+$: 223.1235.

2-mesityl-2H-indazole (2d): yield 63%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.79 (dd, *J* = 22.1, 8.6 Hz, 2H), 7.35 (m, 1H), 7.15 (m, 1H), 7.00 (s, 2H), 2.37 (s, 3H), 1.96 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ149.15, 139.23, 137.33, 135.19, 128.78, 126.08, 124.64, 121.95, 121.84, 120.35, 118.07, 21.12, 17.11. HRMS (ESI^+):237.1352, calcd mass for $[C_{16}H_{17}N_2]^+$: 237.1392.

2-(4-chloro-2,6-dimethylphenyl)-2H-indazole (2e): yield 65%, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.78 (dd, *J* = 17.9, 8.6 Hz, 2H), 7.36 (m, 1H), 7.17 (m, 3H), 1.98 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ149.38, 138.30, 137.47, 134.86, 128.04, 126.41, 124.54, 122.28, 121.95, 120.37, 118.09, 17.18. HRMS (ESI^+): 257.0845, calcd mass for $[C_{15}H_{14}N_2Cl]^+$: 257.0846.

2-(4-bromo-2,6-dimethylphenyl)-2H-indazole (2f): yield 61%, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.78 (dd, *J* = 20.2, 8.6 Hz, 2H), 7.37 (m, 3H), 7.17 (m, 1H), 1.98 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.39, 138.82, 137.73, 131.02, 126.43, 124.48, 123.14, 122.29, 121.95, 120.36, 118.09, 17.09. HRMS (ESI^+): 301.0369, calcd mass for $[C_{15}H_{13}N_2Br]^+$: 301.0340.

2-(2,6-diisopropylphenyl)-2H-indazole (2g): yield 68%, white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.38 (dd, *J* = 11.6, 3.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.19 (m, 1H), 2.18 (m, 2H), 1.16 (d, *J* = 6.8 Hz, 6H), 1.11 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.88, 146.15, 137.13, 130.17, 126.12, 125.67, 123.51, 122.09, 121.64, 120.38, 118.21, 28.20, 24.65, 24.02. HRMS (ESI^+): 279.1837, calcd mass for $[C_{19}H_{23}N_2]^+$: 279.1861.

2-(biphenyl-2-yl)-2H-indazole (2h): yield 60%, white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (m, 2H), 7.61 (s, 1H), 7.54 (m, 3H), 7.51 (m, 1H), 7.31 (m, 1H), 7.22 (m, 3H), 7.11 (m, 2H), 7.04 (dd, *J* = 8.0, 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.15, 138.83, 138.08, 137.03, 131.12, 129.08, 128.61, 128.41, 127.63, 127.36, 126.48, 125.41, 122.02, 121.89, 120.48, 117.87. HRMS (ESI^+): 271.1245, calcd mass for $[C_{19}H_{15}N_2]^+$: 271.1235.

General Procedure for the Synthesis compounds 3

To a suspension of compound **2** (1 mmol) in CH_3CN was added CH_3I (5 equiv.). The reaction mixture was stirred at 80 ^oC for 5 h and then the solvent was evaporated under reduced pressure. The reaction mixture was subsequently washed with diethyl ether (3 x 2 mL) to obtain a yellow solid.

1-methyl-2-phenyl-1H-indazol-2-ium iodide (3a): yield 82%, yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 9.35 (s, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 7.4 Hz, 2H), 7.85 (m, 2H), 7.73 (m, 3H), 7.50 (m, 1H), 4.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.78, 134.78, 134.30, 132.99, 132.07, 130.74, 127.70, 126.10, 123.86, 119.91, 111.59, 36.41. HRMS (ESI^+): 209.1073, calcd mass for $[C_{14}H_{13}N_2]^+$: 209.1073.

1-methyl-2-o-tolyl-1H-indazol-2-ium iodide (3b): yield 90%, yellow solid. 1H NMR (400 MHz, CDCl3) δ 9.45 (s, 1H), 8.30 (d, *J* = 8.5 Hz, 1H), 7.89 (m, 3H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.51 (q, *J* = 6.6 Hz, 3H), 4.12 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.23, 135.99, 134.94, 134.60, 133.49, 132.23, 131.28, 129.03, 128.40, 126.24, 124.12, 119.97, 111.72, 35.63, 17.61. HRMS (ESI^+): 223.1230, calcd mass for $[C_{15}H_{15}N_2]^+$: 223.1230.

2-(2,6-dimethylphenyl)-1-methyl-1H-indazol-2-ium iodide (3c): yield 89%, yellow solid. ^1H

NMR (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 8.37 (d, *J* = 8.5 Hz, 1H), 8.06 (d, *J* = 8.8 Hz, 1H), 7.91 – 7.79 (m, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 4.06 (s, 3H), 1.98 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.71, 136.50, 135.03, 134.98, 133.25, 130.62, 129.78, 126.23, 124.40, 119.99, 111.89, 35.14, 17.93. HRMS (ESI^+): 237.1308, calcd mass for $[C_{16}H_{17}N_2]^+$: 237.1386.

2-mesityl-1-methyl-1H-indazol-2-ium iodide (3d): yield 90%, yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 1H), 8.39 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 7.89 (t, *J* = 7.9 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.11 (s, 2H), 4.08 (s, 3H), 2.39 (s, 3H), 1.98 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.85, 140.63, 136.01, 134.99, 134.91, 130.36, 128.05, 126.12, 124.30, 119.91, 111.85, 34.99, 21.35, 17.76. HRMS (ESI^+): 251.1422, calcd mass for $[C_{17}H_{19}N_2]^+$:251.1543.

2-(4-chloro-2,6-dimethylphenyl)-1-methyl-1H-indazol-2-ium iodide (3e): yield 87%, yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 8.37 (d, *J* = 8.5 Hz, 1H), 8.06 (d, *J* = 8.9 Hz, 1H), 7.94 (m, 1H), 7.57 (m, 1H), 7.34 (s, 2H), 4.12 (s, 3H), 2.06 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.88, 139.12, 138.54, 135.54, 135.24, 129.70, 129.09, 126.36, 124.27, 119.94, 111.92, 35.31, 18.13. HRMS (ESI^+): 271.0954, calcd mass for $[C_{16}H_{16}ClN_2]^+$:.271.0997.

2-(4-bromo-2,6-dimethylphenyl)-1-methyl-1H-indazol-2-ium iodide (3f): yield 89%, yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 8.36 (d, *J* = 8.5 Hz, 1H), 8.06 (d, *J* = 8.8 Hz, 1H), 7.92 (m, 1H), 7.55 (m, 1H), 7.33 (s, 2H), 4.11 (s, 3H), 2.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.92, 139.29, 138.55, 135.54, 135.32, 129.79, 129.08, 126.44, 124.36, 120.02, 111.86, 35.20, 18.15. HRMS (ESI^+): 315.0468, calcd mass for $[C_{16}H_{16}BrN_2]^+$:315.0491.

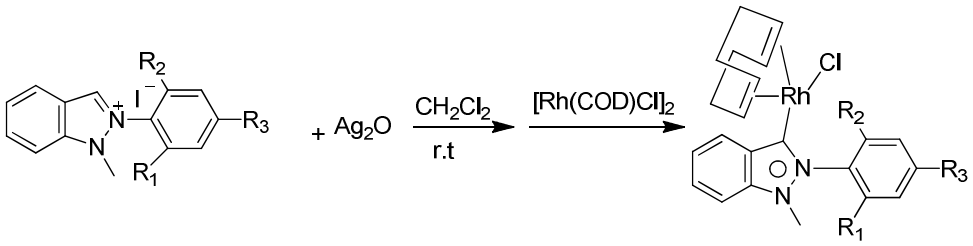
2-(2,6-diisopropylphenyl)-1-methyl-1H-indazol-2-ium iodide (3g): yield 90%, yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 8.50 (d, *J* = 8.5 Hz, 1H), 8.25 (d, *J* = 8.8 Hz, 1H), 7.94 (m, 1H), 7.71 (t, *J* = 7.9 Hz, 1H), 7.56 (m, 1H), 7.43 (d, *J* = 7.9 Hz, 2H), 4.11 (s, 3H), 1.92 (dd, *J* = 13.6, 6.8 Hz, 2H), 1.18 (dd, *J* = 6.6, 5.4 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.00, 140.76, 135.66, 135.27, 134.16, 127.55, 126.45, 125.55, 124.62, 119.88, 112.13, 35.32, 29.09, 25.33, 23.04. HRMS (ESI^+): 293..2025, calcd mass for $[C_{20}H_{25}N_2]^+$:293.2012.

2-([1,1'-biphenyl]-2-yl)-1-methyl-1H-indazol-2-ium iodide (3h): yield 79%, yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 7.82 (m, 2H), 7.68 (m, 3H), 7.47 (dd, *J* = 8.0, 7.4 Hz,, 1H), 7.23 (m, 3H), 7.09 (m, 2H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.91, 140.01, 135.32, 135.22, 134.85, 133.69, 131.77, 129.99,

129.35, 129.08, 127.94, 126.12, 123.98, 119.69, 111.19, 35.44. HRMS (ESI^+): 285.1333, calcd mass for $[C_{20}H_{25}N_2]^+$: 285.1386.

The chloride analogue of 5h was obtained by chloride exchange between 5h and Dowex-21K chloride exchange resin in methanol for 12 h. ^1H NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 7.82 (m, 2H), 7.68 (m, 3H), 7.47 (dd, *J* = 8.0, 7.4 Hz, 1H), 7.23 (m, 3H), 7.09 (m, 2H), 3.92 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 140.91, 140.01, 135.32, 135.22, 134.85, 133.69, 131.77, 129.99, 129.96, 129.93, 129.35, 129.08, 127.94, 126.12, 123.98, 119.69, 111.19, 35.44.

3. Synthesis and Characterization of Rhodium Complexes 4



3c:	$R_1 = CH_3$	$R_2 = CH_3$	$R_3 = H$
3d:	$R_1 = CH_3$	$R_2 = CH_3$	$R_3 = CH_3$
3e:	$R_1 = CH_3$	$R_2 = CH_3$	$R_3 = Cl$
3f:	$R_1 = CH_3$	$R_2 = CH_3$	$R_3 = Br$
3g:	$R_1 = i$Pr	$R_2 = i$Pr	$R_3 = H$
3h:	$R_1 = Ph$	$R_2 = H$	$R_3 = H$

4c:	$R_1 = CH_3$	$R_2 = CH_3$	$R_3 = H$
4d:	$R_1 = CH_3$	$R_2 = CH_3$	$R_3 = CH_3$
4e:	$R_1 = CH_3$	$R_2 = CH_3$	$R_3 = Cl$
4f:	$R_1 = CH_3$	$R_2 = CH_3$	$R_3 = Br$
4g:	$R_1 = i$Pr	$R_2 = i$Pr	$R_3 = H$
4h:	$R_1 = Ph$	$R_2 = H$	$R_3 = H$

A mixture of 1H-indazol salts and Ag_2O in anhydrous CH_2Cl_2 was stirred at room temperature in dark under argon atmosphere. Then $[Rh(COD)Cl]_2$was added into the mixture and stirred for another 3 h. The reaction mixture was subsequently filtered through a short pad of Celite and the solvent of the filtrate was concentrated by rotary evaporation, the resulting solid was washed with hexane or ether to obtain the crude purified product.

Synthesis of Complex 4c: A solution of Ag_2O (0.06 mmol, 14 mg) and complex **3c** (45 mg, 0.12 mmol) in anhydrous CH_2Cl_2 (4 mL)was stirred at room temperature in dark for 60 min under argon atmosphere. Then $[Rh(COD)Cl]_2$ (0.06 mmol, 29 mg) was added into the mixture and stirred for another 3 h to obtain a yellow solid as purified product, yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 8.1 Hz, 1H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.40 (s, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 5.08 (s, 1H, COD_{vinyl}), 4.86 (s, 1H, COD_{vinyl}), 3.59 (s, 1H, COD_{vinyl}), 3.44 (s, 3H,NCH_3), 2.94 (s, 1H, COD_{vinyl}), 2.52 (d, *J* = 26.1 Hz, 4H, COD_{allyl}), 1.93 (m, 10H, 4H of COD_{allyl} and 6H of o-$ArCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.49 (d, *J*(Rh-C)= 46 Hz, $C_{carbene}$), 140.01, 138.65, 136.25, 136.07, 132.04, 131.81, 131.32, 130.41, 129.47, 127.87, 121.83, 108.74, 97.71 (CH of COD), 97.31 (CH of COD), 68.91 (CH of COD), 66.96 (CH of COD), 33.85 (CH_2 of COD), 32.8 (NCH_3), 32.00 (CH_2 of COD), 29.19 (CH_2 of COD), 28.21 (CH_2 of COD), 20.05 ($ArCH_3$), 17.53. ($ArCH_3$).

Synthesis of Complex 4d: A solution of Ag_2O (0.06 mmol, 14 mg) and complex **3d** (45 mg,0.12 mmol) in anhydrous CH_2Cl_2 (4 mL)was stirred at room temperature in dark for 60 min under argon atmosphere. Then $[Rh(COD)Cl]_2$ (0.06 mmol, 29 mg) was added into the mixture and

stirred for another 3 h to obtain a yellow solid as purified product, yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 8.1 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.01 (s, 1H), 5.08 (s, 1H, COD_{vinyl}), 4.84 (s, 1H, COD_{vinyl}), 3.57 (s, 1H, COD_{vinyl}), 3.42 (s, 3H, NCH_3), 3.00 (s, 1H, COD_{vinyl}), 2.47 (d, *J* = 17.8 Hz, 7H, 4H of COD_{allyl} and 3H of *p*-$ArCH_3$), 1.86 (m, 10H, 4H of COD_{allyl} and 6H of o-$ArCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.18 (d, *J*(Rh-C)= 45Hz, $C_{carbene}$), 140.41, 139.93, 138.20, 135.83, 133.54, 131.99, 131.68, 131.28, 130.07, 128.53, 121.70, 108.70, 97.61 (CH of COD), 97.06 (CH of COD), 68.82 (CH of COD), 66.98 (CH of COD), 33.76 (CH_2 of COD), 32.71(NCH_3), 32.11 (CH_2 of COD), 29.14 (CH_2 of COD), 28.33 (CH_2 of COD), 21.27 (*p*-$ArCH_3$), 19.91 (o-$ArCH_3$), 17.45 (*o*-$ArCH_3$).

Synthesis of Complex 4e: A solution of Ag_2O (0.06 mmol, 14 mg) and complex **3e** (48 mg, 0.12 mmol) in anhydrous CH_2Cl_2 (4 mL) was stirred at room temperature in dark for 20 min under argon atmosphere. Then $[Rh(COD)Cl]_2$ (0.06 mmol, 29 mg) was added into the mixture and stirred for another 3 h to obtain a yellow solid as purified product, yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 8.1 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.37 (s, 1H), 7.30 (dd, *J* = 15.5, 7.9 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 1H), 5.07 (s, 1H, COD_{vinyl}), 4.84 (s, 1H, COD_{vinyl}), 3.56 (s, 1H, COD_{vinyl}), 3.41 (s, 3H, NCH3), 2.93 (s, 1H, COD_{vinyl}), 2.50 (s, 4H, COD_{allyl}), 1.99 (m, 10H, 4H of COD_{allyl} and 6H of *o*-ArCH3). ^{13}C NMR (100MHz, $CDCl_3$) δ 198.13 (d, *J*(Rh-C)= 45Hz, $C_{carbene}$), 140.69, 140.22, 138.13, 135.97, 134.71, 132.11, 131.38, 129.32, 127.77, 122.10, 108.80, 104.99, 98.32 (CH of COD), 97.80 (CH of COD), 69.30 (CH of COD), 66.90 (CH of COD), 33.77 (CH_2 of COD), 32.95 (NCH_3), 32.07 (CH_2 of COD), 29.21 (CH_2 of COD), 28.23 (CH_2 of COD), 20.10 (*o*-$ArCH_3$), 17.52 (*o*-$ArCH_3$).

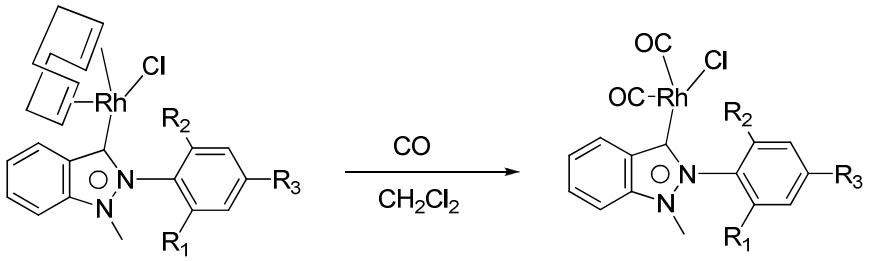
Synthesis of Complex 4f: A solution of Ag_2O (0.06 mmol, 14 mg) and complex **3f** (53 mg, 0.12 mmol) in anhydrous CH_2Cl_2 (4 mL) was stirred at room temperature for 20 min in dark under argon atmosphere. Then $[Rh(COD)Cl]_2$ (0.06 mmol, 29 mg) was added into the mixture and stirred for another 3 h to obtain a yellow solid as purified product, yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 8.1 Hz, 1H), 7.64 (m, 1H), 7.57 (s, 1H), 7.39 (s, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 5.11 (s, 1H, COD_{vinyl}), 4.88 (s, 1H, COD_{vinyl}), 3.58 (s, 1H, COD_{vinyl}), 3.43 (s, 3H, NCH_3), 2.93 (s, 1H, COD_{vinyl}), 2.54 (s, 4H, COD_{allyl}), 2.30 (m, 2H), 1.90 (m, 10H, 4H of COD_{allyl} and 6H of *o*-$ArCH_3$).^{13}C NMR (100 MHz, $CDCl_3$) δ 198.12(d, *J*(Rh-C)= 46Hz, $C_{carbene}$), 140.23, 135.97, 135.25, 134.71, 132.12, 131.38, 130.74, 129.31, 127.78, 124.30, 122.12,

108.80, 98.34 (CH of COD), 97.82 (CH of COD), 69.31 (CH of COD), 67.07 (CH of COD), 33.77 (CH_2 of COD), 32.98 (NCH_3), 32.08 (CH_2 of COD), 29.21 (CH_2 of COD), 28.23 (CH_2 of COD), 20.09 (*o*-$ArCH_3$), 17.51 (*o*-$ArCH_3$).

Synthesis of Complex 4g: A solution of Ag_2O (0.06 mmol,14 mg) and complex **3g** (50 mg,0.12 mmol) in anhydrous CH_2Cl_2 (4 mL) was stirred at room temperature for 90 min in dark under argon atmosphere. Then $[Rh(COD)Cl]_2$ (0.06 mmol, 29 mg) was added into the mixture and stirred for another 3 h to obtain a yellow solid as purified product, yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 8.1 Hz, 1H), 7.62 (m, 2H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.24 (m, 3H), 5.15 (s, 1H, COD_{vinyl}), 4.90 (s, 1H, COD_{vinyl}), 3.59 (s, 1H, COD_{vinyl}), 3.41 (s, 3H), 2.86 (s, 1H, COD_{vinyl}), 2.39 (d, *J* = 37.2 Hz, 2H), 2.08 (s, 2H), 1.72 (m, 6H), 1.14 (m, 12H).^{13}C NMR (100 MHz, $CDCl_3$) δ 200.64 (d, *J*(Rh-C)= 45Hz, $C_{carbene}$),148.68, 146.88, 141.38, 132.83, 132.00, 131.89, 131.10, 125.45, 123.80, 122.29, 109.23, 98.29 (CH of COD), 97.05 (CH of COD), 67.71 (CH of COD), 34.49 (NCH_3), 33.79 (CH of COD), 32.06 (CH of COD), 29.05 (CH_2 of COD)., 28.321 ($C(CH_3)_2$), 28.21 (CH_2 of COD),26.34 (CH_2 of COD), 25.18 (CH_3), 24.64 (CH_3), 23.60 (CH_2 of COD).

Synthesis of Complex 4h: A solution of Ag_2O (0.06 mmol, 14 mg) and complex **3h** (38 mg,0.12 mmol) in anhydrous CH_2Cl_2 (4 mL) was stirred at room temperature for 40 min in dark under argon atmosphere. Then $[Rh(COD)Cl]_2$ (0.06 mmol, 29 mg) was added into the mixture and stirred for another 3 h to obtain a yellow solid as purified product, yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (m, 1H), 8.67 (d, *J* = 8.1 Hz, 1H), 7.74 (m, 2H), 7.61 (m, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.29 (m, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.81 (d, *J* = 7.5 Hz, 2H), 5.08 (m, 2H, COD_{vinyl}), 3.70 (t, *J* = 7.2 Hz, 1H, COD_{vinyl}), 3.11 (s, 3H, NCH_3), 3.02 (d, *J* = 5.8 Hz, 1H, COD_{vinyl}), 2.57 (m,1H, COD_{allyl}), 2.41 (m, 1H, COD_{allyl}), 2.09 (m, 1H, COD_{allyl}), 1.89 (m, 3H, COD_{allyl}), 1.57 (m, 2H, COD_{allyl}). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.06 (d, *J*(Rh-C)= 44Hz, $C_{carbene}$), 141.13, 137.34, 136.90, 135.70, 131.87, 131.59, 131.30, 130.59, 130.45, 128.54, 128.10, 127.41, 122.05, 109.00, 97.84, 97.78, 97.73, 68.21 (CH of COD), 68.06 (CH of COD), 67.44 (CH of COD), 67.29 (CH of COD), 34.11 (CH_2 of COD), 33.59 (CH_2 of COD, 32.20 (NCH_3), 28.98 (CH_2 of COD), 28.57 (CH_2 of COD).

4. Synthesis and Characterization of Rh-CO Complexes 5



4c:	$R_1 = CH_3$	$R_2 = CH_3$	$R_3 = H$
4d:	$R_1 = CH_3$	$R_2 = CH_3$	$R_3 = CH_3$
4e:	$R_1 = CH_3$	$R_2 = CH_3$	$R_3 = Cl$
4f:	$R_1 = CH_3$	$R_2 = CH_3$	$R_3 = Br$
4g:	$R_1 = i$Pr	$R_2 = i$Pr	$R_3 = H$
4h:	$R_1 = Ph$	$R_2 = H$	$R_3 = H$

5c:	$R_1 = CH_3$	$R_2 = CH_3$	$R_3 = H$
5d:	$R_1 = CH_3$	$R_2 = CH_3$	$R_3 = CH_3$
5e:	$R_1 = CH_3$	$R_2 = CH_3$	$R_3 = Cl$
5f:	$R_1 = CH_3$	$R_2 = CH_3$	$R_3 = Br$
5g:	$R_1 = i$Pr	$R_2 = i$Pr	$R_3 = H$
5h:	$R_1 = Ph$	$R_2 = H$	$R_3 = H$

A solution of complex **4** (20 mg) in CH_2Cl_2 (2 mL) was stirred at room temperature and then carbon monoxide was bubble into the mixture for 10 min. The solvent was subsequently removed under reduced pressure and the resulting residue was washed with hexane or ether. The residue was dried under vacuum to obtain a yellow solid complex.

Complex 5c: yellow solid, yield 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.3 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.32 (m, 4H), 3.62 (s, 3H), 2.14 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.68 (d, *J*(Rh, C_{co}) = 52 Hz, CO), 183.63 (d, *J*(Rh, C_{co}) = 23 Hz, CO), 183.06 (d, *J*(Rh, C) = 13 Hz, $C_{carbene}$), 139.78, 136.96, 135.71, 132.53, 131.24, 131.08, 130.59, 129.07, 122.55, 108.66, 32.75 (NCH_3), 18.44 (*o*-ArCH_3). FT-IR(CH_2Cl_2): ν(CO_{sym}) 2064 cm^{-1} (s) and ν(CO_{asym}) 1987 cm^{-1} (s).

Complex 5d: yellow solid, yield 96%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.10 (s, 2H), 3.61 (s, 3H), 2.43 (s, 3H), 2.09 (s, 6H). ^{13}C NMR (100MHz, $CDCl_3$) δ 185.77 (d, *J*(Rh, C_{co}) = 52 Hz, CO), 183.57 (d, *J*(Rh, C_{co}) = 45 Hz, CO), 183.00 (d, *J*(Rh, C) = 9 Hz, $C_{carbene}$), 141.44, 139.73, 136.50, 133.18, 132.42, 131.03, 130.52, 129.76, 122.46, 108.64, 32.66, 21.33, 18.34. FT-IR(CH_2Cl_2): ν(CO_{sym}) 2068 cm^{-1} (s) and ν(CO_{asym}) 1987 cm^{-1} (s).

Complex 5e: yellow solid, yield 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.3 Hz, 1H), 7.72 (t, *J* = 7.7 Hz, 1H), 7.36 (dd, *J* = 12.0, 7.4 Hz, 2H), 7.31 (s, 2H), 3.63 (s, 3H), 2.13 (s, 6H). ^{13}C NMR (100MHz, $CDCl_3$) δ 185.47 (d, *J*(Rh, C_{co}) = 53 Hz, CO), 184.19 (d, *J*(Rh, C_{co}) = 40 Hz, CO), 183.32 (d, *J*(Rh, C) = 75 Hz, $C_{carbene}$), 139.88, 138.84, 137.00, 134.16, 132.82, 131.08,

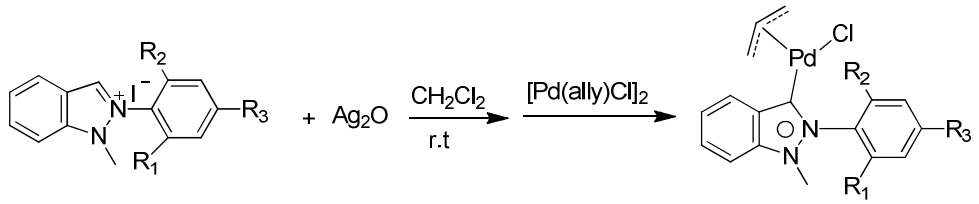
130.55, 129.05, 122.75, 108.68, 32.81, 18.43. FT-IR(CH_2Cl_2): ν(CO_{sym}) 2068 cm^{-1} (s) and ν(CO_{asym}) 1987 cm^{-1} (s)

Complex 5f: yellow solid, yield 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.2 Hz, 1H), 7.72 (t, *J* = 7.8 Hz, 1H), 7.48 (s, 1H), 7.35 (m, 3H), 3.63 (s, 3H), 2.13 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.65(d, *J*(Rh, C_{co}) = 52 Hz, CO), 185.61(d, *J*(Rh, C_{co}) = 13 Hz, CO), 183.05(d, *J*(Rh, C) = 23 Hz, $C_{carbene}$)183.16, 182.93, 139.85, 139.04, 134.73, 132.85, 132.03, 130.96, 130.26, 125.42, 122.72, 109.04, 33.01, 18.37. FT-IR(CH_2Cl_2): ν(CO_{sym}) 2066 cm^{-1} (s) and ν(CO_{asym}) 1985 cm^{-1} (s)

Complex 5g: yellow solid, yield 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 7.8 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.38 (m, 3H), 3.58 (s, 3H), 2.48 (m, 2H), 1.36 (d, *J* = 6.3 Hz, 6H), 1.11 (d, *J* = 6.5 Hz, 6H). ^{13}C NMR (100MHz, $CDCl_3$) δ 187.51(d, *J*(Rh, C_{co}) = 39 Hz, CO), 185.64(d, *J*(Rh, C_{co}) = 52 Hz, CO), 183.35(d, *J*(Rh, C) = 75 Hz, $C_{carbene}$), 147.41, 140.83, 132.83, 132.65, 131.95, 131.63, 131.20, 125.05, 122.79, 109.04, 34.44, 28.41, 24.85, 24.50. FT-IR(CH_2Cl_2): ν(CO_{sym}) 2066 cm^{-1} (s) and ν(CO_{asym}) 1991 cm^{-1} (s)

Complex 5h: yellow solid, yield 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.1 Hz, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 7.74 (t, *J* = 7.4 Hz, 1H), 7.62 (m, 4H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.20 (m, 5H), 7.08 (d, *J* = 8.5 Hz, 1H), 3.35 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 185.81(d, *J*(Rh, C_{co}) = 53 Hz, CO), 183.87(d, *J*(Rh, C_{co}) = 7 Hz, CO), 183.30(d, *J*(Rh, C) = 43 Hz, $C_{carbene}$), 140.45, 138.83, 136.83, 134.96, 132.56, 131.65, 131.40, 131.11, 130.96, 130.17, 128.75, 128.67, 128.29, 128.06, 122.64, 108.72, 33.90. FT-IR(CH_2Cl_2): ν(CO_{sym}) 2066 cm^{-1} (s) and ν(CO_{asym}) 1996 cm^{-1} (s)

5. Synthesis and Characterization of Palladium Complexes 6



3c: $R_1 = CH_3$ $R_2 = CH_3$ $R_3 = H$
3d: $R_1 = CH_3$ $R_2 = CH_3$ $R_3 = CH_3$
3e: $R_1 = CH_3$ $R_2 = CH_3$ $R_3 = Cl$
3f: $R_1 = CH_3$ $R_2 = CH_3$ $R_3 = Br$
3g: $R_1 = i$Pr $R_2 = i$Pr $R_3 = H$

6c: $R_1 = CH_3$ $R_2 = CH_3$ $R_3 = H$
6d: $R_1 = CH_3$ $R_2 = CH_3$ $R_3 = CH_3$
6e: $R_1 = CH_3$ $R_2 = CH_3$ $R_3 = Cl$
6f: $R_1 = CH_3$ $R_2 = CH_3$ $R_3 = Br$
6g: $R_1 = i$Pr $R_2 = i$Pr $R_3 = H$

A mixture of 1H-indazol salts and Ag_2O in anhydrous CH_2Cl_2 was stirred at room temperature in dark under argon atmosphere. Then $[Pd(ally)Cl]_2$ was added into mixture and stirred for another 3 h. The reaction mixture was subsequently filtered through a short pad of Celite and the solvent of the filtrate was removed by rotary evaporation. The resulting solid was washed with hexane or ether to get the crude purified product.

Synthesis of Complex 6c: A solution of Ag_2O (0.06 mmol, 14 mg) and complex **3c** (45 mg,0.12 mmol) in anhydrous CH_2Cl_2 (4 mL) was stirred at room temperature for 60 min in dark under argon atmosphere. Then $[Pd(ally)Cl]_2$ (0.06 mmol, 22 mg) was added into the mixture and stirred for another 3 h to obtain a yellow solid complex **6c**, yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.2 Hz, 1H), 7.66 (m, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.31 (dd, *J* = 8.4, 5.7 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 5.11 (m, 1H), 4.16 (d, *J* = 7.6 Hz, 1H), 3.59 (s, 3H), 3.14 (d, *J* = 13.6 Hz, 1H), 3.06 (s, 1H), 2.23 (s, 3H), 2.09 (s, 3H), 1.88 (d, *J* = 11.4 Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$) δ 187.80, 139.93, 137.08, 136.91, 136.50, 132.03, 131.71, 130.68, 128.72, 121.91, 114.90, 108.72, 73.14, 48.02, 32.95, 18.16.

Synthesis of Complex 6d: A solution of Ag_2O (0.06 mmol, 14 mg) and complex **3d** (45 mg, 0.12 mmol) in anhydrous CH_2Cl_2 (4 mL) was stirred at room temperature for 90 min in dark under argon atmosphere. Then $[Pd(ally)Cl]_2$ (0.06 mmol, 22 mg) was added into the mixture and stirred for another 3 h to obtain a gray solid as purified product, yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.3 Hz, 1H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.30 (dd, *J* = 7.9, 3.2 Hz, 2H), 7.04 (d, *J* = 10.0 Hz, 2H), 5.13 (m, 1H), 4.16 (d, *J* = 7.5 Hz, 1H), 3.58 (s, 3H), 3.15 (d, *J* = 13.6 Hz, 1H), 3.07 (d, *J* = 6.4 Hz, 1H), 2.39 (s, 3H), 2.17 (s, 3H), 2.04 (s, 3H), 1.91 (d, *J* = 11.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.52, 140.70, 139.86, 136.73, 133.95, 131.90, 131.65, 130.57, 129.30, 121.78,

114.87, 108.73, 73.00, 48.00, 32.87, 21.28, 18.01.

Synthesis of Complex 6e: A solution of Ag_2O (0.06 mmol, 14 mg) and complex **3e** (48 mg, 0.12 mmol) in anhydrous CH_2Cl_2 (4 mL) was stirred at room temperature for 30 min in dark under argon atmosphere. Then $[Pd(ally)Cl]_2$ (0.06 mmol, 22 mg) was added into the mixture and stirred for another 3 h to obtain a gray solid as purified product, yield: 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.2 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.31 (m, 2H), 7.25 (s,2H), 5.17 (m, 1H), 4.19 (d, *J* = 7.5 Hz, 1H), 3.58 (s, 3H), 3.19 (d, *J* = 13.7 Hz, 1H), 3.10 (d, *J* = 6.1 Hz, 1H), 2.20 (s, 3H), 2.08 (s, 3H), 2.00 (d, *J* = 11.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.65, 139.97, 139.05, 138.84, 136.20, 134.95, 132.30, 131.68, 130.47, 128.73, 128.58, 122.06, 115.02, 108.92, 73.30, 48.13, 33.07, 18.45, 18.13.

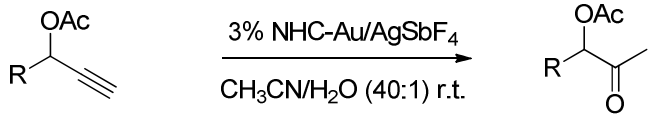
Synthesis of Complex 6f: A solution of Ag_2O (0.06 mmol, 14 mg) and complex **3f** (53 mg, 0.12 mmol) in anhydrous CH_2Cl_2 (4 mL) was stirred at room temperature for 15 min in dark under argon atmosphere. Then $[Pd(ally)Cl]_2$ (0.06 mmol, 22 mg) was added into the mixture and stirred for another 3 h to obtain a yellow solid as purified product, yield:83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.1 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.27 (m, 1H), 7.22 (s, 2H), 5.13 (m, 1H), 4.14 (d, *J* = 7.5 Hz, 1H), 3.56 (s, 3H), 3.12 (t, *J* = 14.9 Hz, 2H), 2.09 (dd, *J* = 43.7, 9.1 Hz, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.03, 140.02, 138.97, 136.27, 134.96, 132.34, 131.78, 130.63, 128.70, 122.14, 115.05, 108.78, 73.49, 48.09, 33.01, 18.44.

Synthesis of Complex 6g: A solution of Ag_2O (0.06 mmol, 14 mg) and complex **3g** (50 mg, 0.12 mmol) in anhydrous CH_2Cl_2 (4 mL) was stirred at room temperature for 90 min in dark under argon atmosphere. Then $[Pd(ally)Cl]_2$ (0.06 mmol, 22 mg) was added into the mixture and stirred for another 3 h to obtain a yellow solid as purified product, yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.2 Hz, 1H), 7.67 (m, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.34 (m, 4H), 5.08 (m, 1H), 4.22 (dd, *J* = 7.6, 1.4 Hz, 1H), 3.56 (s, 3H), 3.18 (d, *J* = 13.7 Hz, 1H), 2.85 (d, *J* = 6.5 Hz, 1H), 2.69 (m, 1H), 2.39 (m, 1H), 1.74 (d, *J* = 11.8 Hz, 1H), 1.38 (d, *J* = 6.7 Hz, 3H), 1.29 (d, *J* = 6.7 Hz, 3H), 1.12 (dd, *J* = 11.4, 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.85, 147.43, 140.95, 133.83, 132.12, 131.46, 131.42, 124.68, 122.12, 114.77, 109.00, 73.52, 48.53, 34.40, 28.25, 24.73, 24.42, 24.10.

6. Synthesis and Characterization of Gold Complex 7

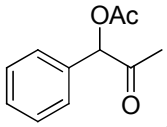
A solution of Ag_2O (0.06 mmol, 14 mg) and complex **3g** (50 mg, 0.12 mmol) in anhydrous CH_2Cl_2 (4 mL) was stirred at room temperature in dark for 90 min under argon atmosphere. Then [$AuCl(SMe_2)$] (0.12 mmol, 36 mg) was added into the mixture and stirred for another 3 h to obtain a yellow solid complex **7**, yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.2 Hz, 1H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.37 (dd, *J* = 14.7, 7.8 Hz, 3H), 3.65 (s, 3H), 2.13 (m, 2H), 1.31 (d, *J* = 6.7 Hz, 3H), 1.14 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.72, 146.72, 139.65, 133.05, 132.32, 132.06, 129.93, 128.87, 124.93, 123.00, 109.18, 33.36, 28.67, 24.96, 23.20.

7. Catalytic Protocols and Product Characterization

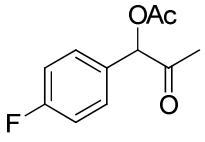


8 **9**

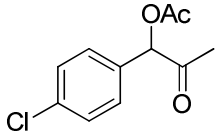
A mixture of NHC-Au (7.8 mg, 0.015 mmol) and $AgSbF_6$ (5.1 mg, 0.015 mmol) in CH_3CN (1 mL) was stirred at room temperature for 10 min under an argon atmosphere. 0.5 mmol complex **8** and 25 μL deionized water was subsequently added into the reaction mixture and stirred at room temperature for another 3 h. Then the reaction mixture was filtered through Celite, the filtrate was evaporated under reduced pressure and the crude product was purified by column chromatography on SiO_2.



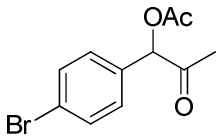
2-oxo-1-phenylpropyl acetate. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, J = 4.3 Hz, 5H), 5.98 (s, 1H), 2.20 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.68, 170.24, 133.07, 129.35, 129.04, 128.03, 80.89, 26.08, 20.66.



1-(4-fluorophenyl)-2-oxopropyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (m, 2H), 7.07 (dd, J = 11.9, 5.3 Hz, 2H), 5.94 (s, 1H), 2.16 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.54, 170.10, 161.95, 129.85, 116.18, 115.96, 80.00, 26.02, 20.57.

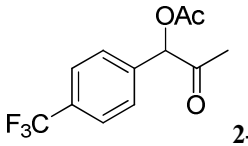


1-(4-chlorophenyl)-2-oxopropyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 4H), 5.92 (s, 1H), 2.16 (d, J = 1.3 Hz, 3H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.31, 169.98, 135.34, 131.72, 129.26, 129.21, 80.01, 25.97, 20.55.

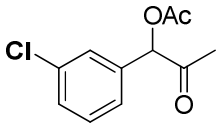


1-(4-bromophenyl)-2-oxopropyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (m, 2H), 7.28 (m, 2H), 5.91 (s, 1H), 2.17 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$)

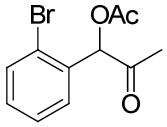
δ 201.24, 169.99, 132.20, 129.53, 123.57, 80.08, 26.00, 20.58.



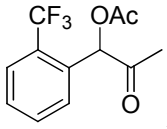
2-oxo-1-(4-(trifluoromethyl)phenyl)propyl acetate. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 6.03 (s, 1H), 2.21 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.16, 169.93, 137.11, 131.57, 128.15, 125.94, 125.89, 80.08, 25.98, 20.52.



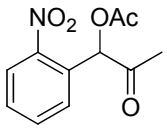
1-(3-chlorophenyl)-2-oxopropyl acetate. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 0.4 Hz, 1H), 7.37 (m, 2H), 7.30 (m, 1H), 5.94 (s, 1H), 2.21 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.18, 169.99, 135.04, 134.93, 130.27, 129.48, 127.91, 126.05, 80.03, 26.05, 20.60.



1-(2-bromophenyl)-2-oxopropyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (m, 2H), 7.08 (m, 2H), 5.94 (s, 1H), 2.16 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.54, 170.10, 164.42, 161.95, 129.94, 129.07, 116.18, 80.00, 26.02, 20.57.

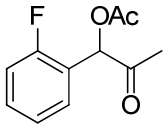


2-oxo-1-(2-(trifluoromethyl)phenyl)propyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.51 (dd, *J* = 17.0, 7.9 Hz, 2H), 6.41 (s, 1H), 2.16 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.64, 169.73, 132.46, 130.28, 129.54, 126.46, 126.41, 126.35, 126.30, 75.68, 26.54, 20.38.

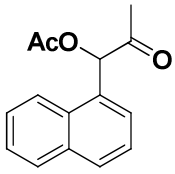


1-(2-nitrophenyl)-2-oxopropyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 1H), 7.65 (m, 1H), 7.52 (dd, *J* = 12.4, 4.4 Hz, 2H), 6.72 (s, 1H), 2.28 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.70, 169.49, 148.06, 133.72, 130.02, 129.86, 129.61,

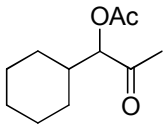
125.10, 75.58, 26.98, 20.53.



1-(2-fluorophenyl)-2-oxopropyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 2H), 7.11 (m, 2H), 6.30 (s, 1H), 2.14 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.73, 169.88, 131.20, 129.59, 124.75, 121.00, 120.86, 115.77, 73.98, 26.05, 20.45.

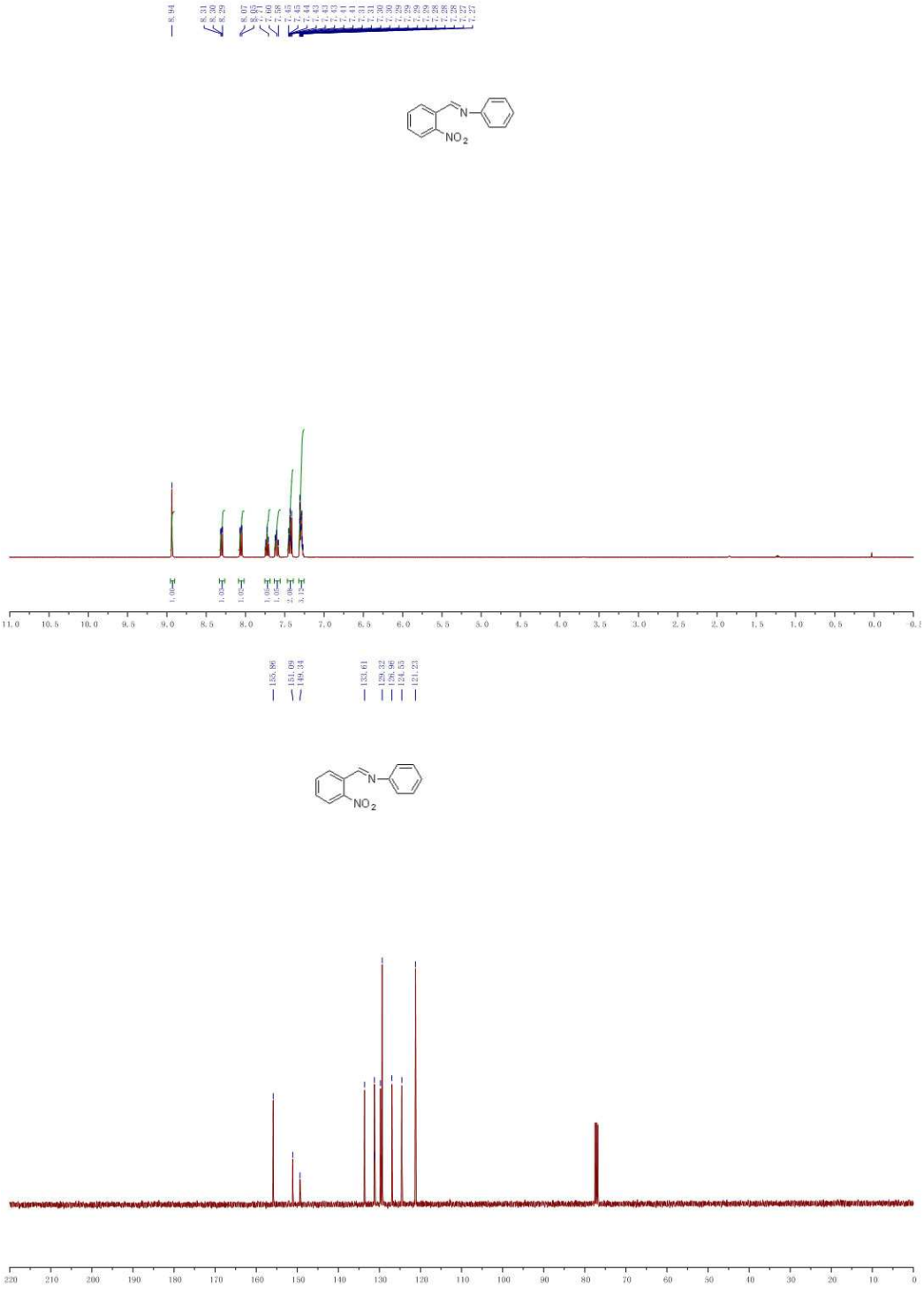


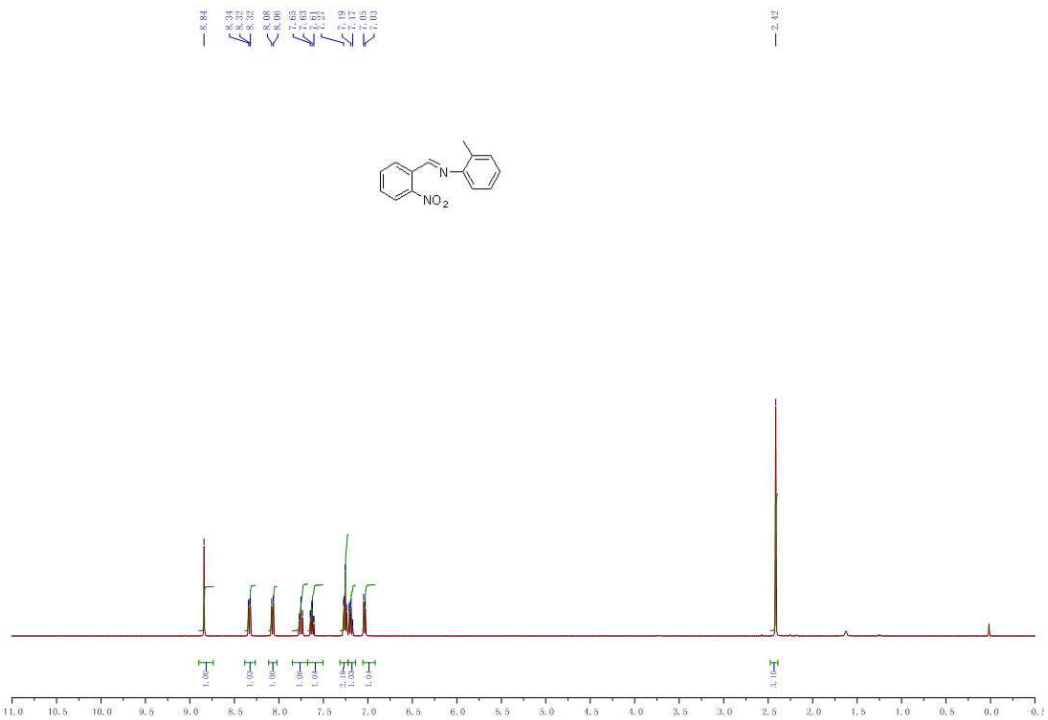
1-(naphthalen-1-yl)-2-oxopropyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.4 Hz, 1H), 7.91 (m, 2H), 7.55 (m, 4H), 6.69 (s, 1H), 2.21 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.77, 170.18, 134.13, 131.23, 130.29, 129.43, 128.91, 128.23, 127.15, 126.26, 125.31, 123.82, 79.38, 26.26, 20.72.



1-cyclohexyl-2-oxopropyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.81 (d, *J* = 4.6 Hz, 1H), 2.13 (s, 6H), 1.86 (m, 1H), 1.75 (dd, *J* = 12.0, 3.1 Hz, 2H), 1.59 (m, 3H), 1.19 (m,5H). ^{13}C NMR (100MHz, $CDCl_3$) δ 205.52, 170.70, 82.58, 39.01, 29.27, 27.20, 27.10, 26.02, 25.85, 25.80, 20.56.

8. NMR spectra

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NO2
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1.03
1.00
1.00
1.01
2.02
1.03
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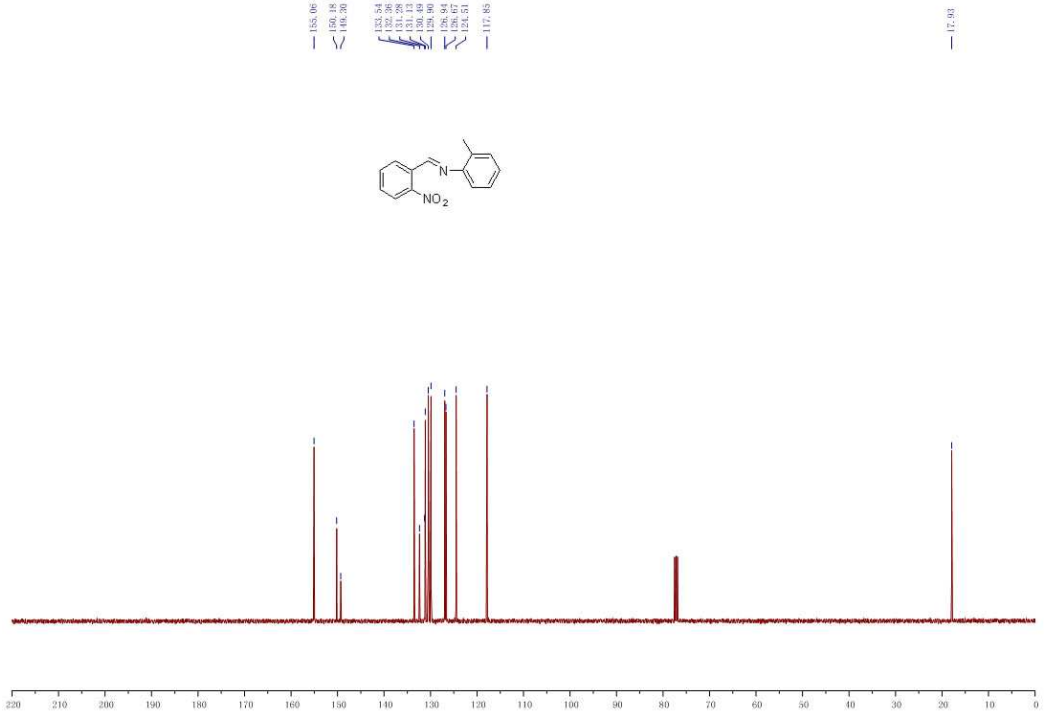
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NO2
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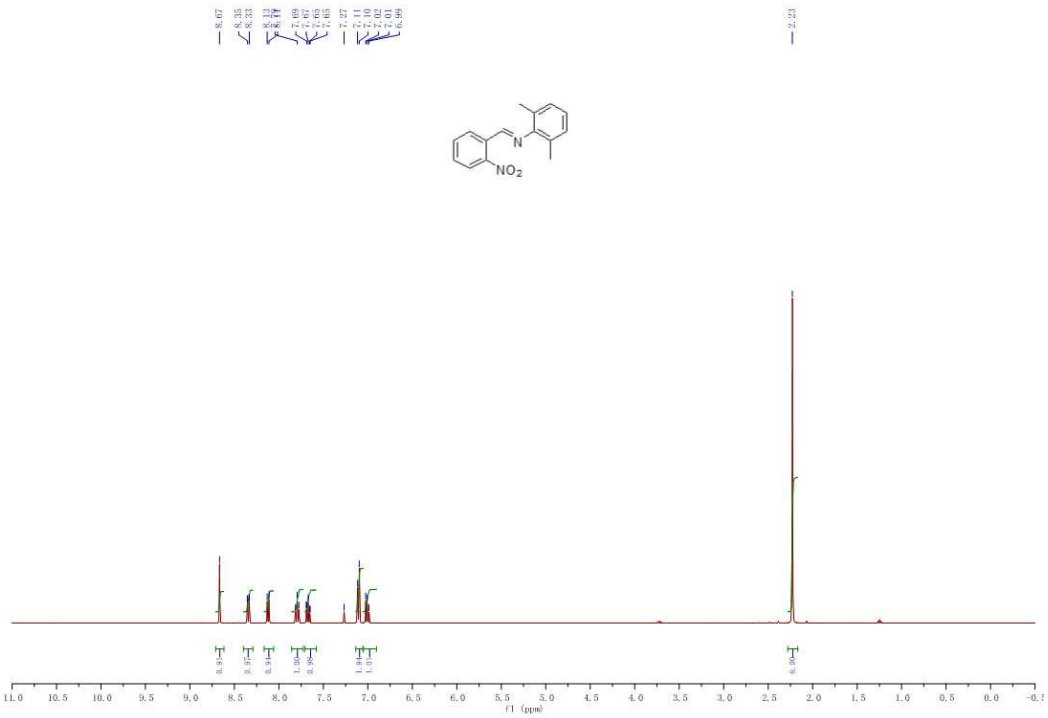
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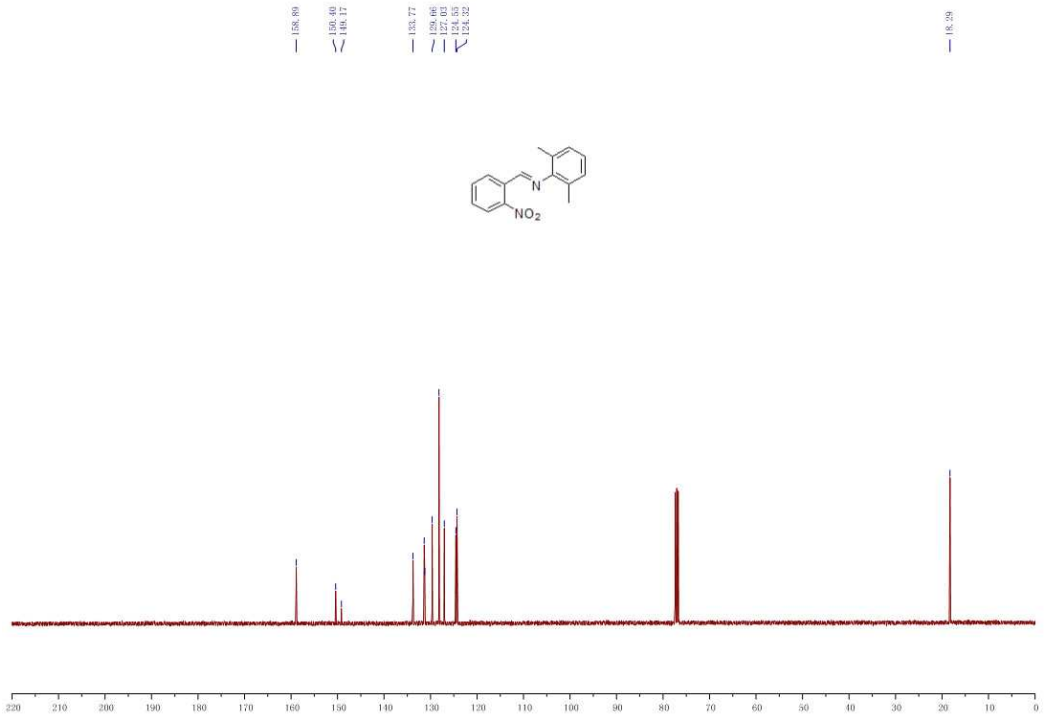
NO2
f1 (ppm)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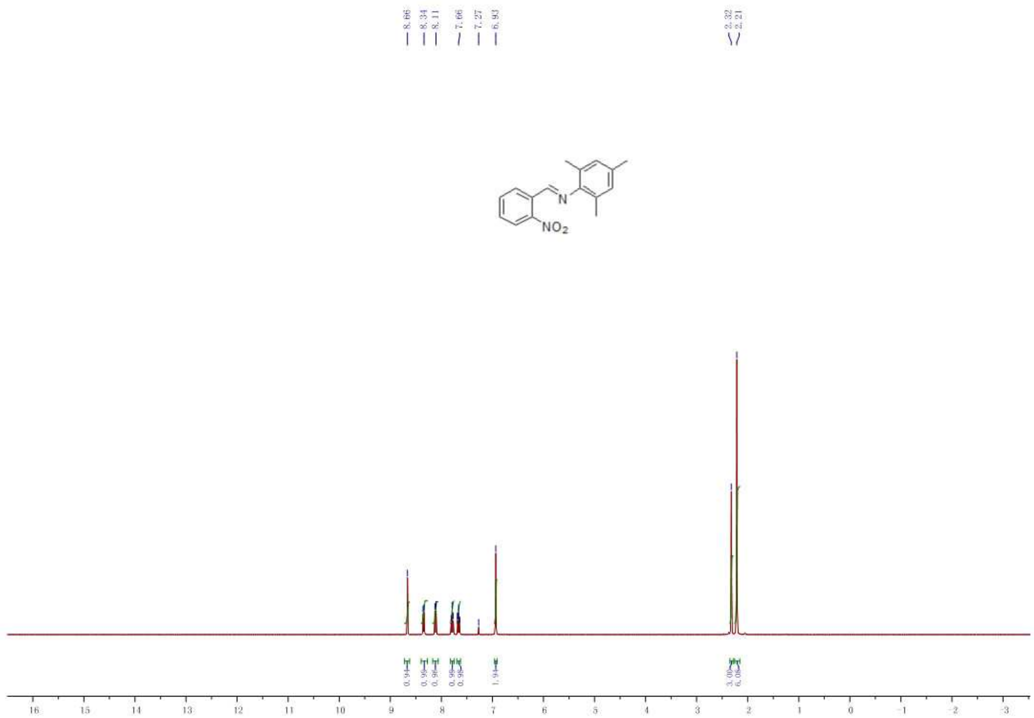
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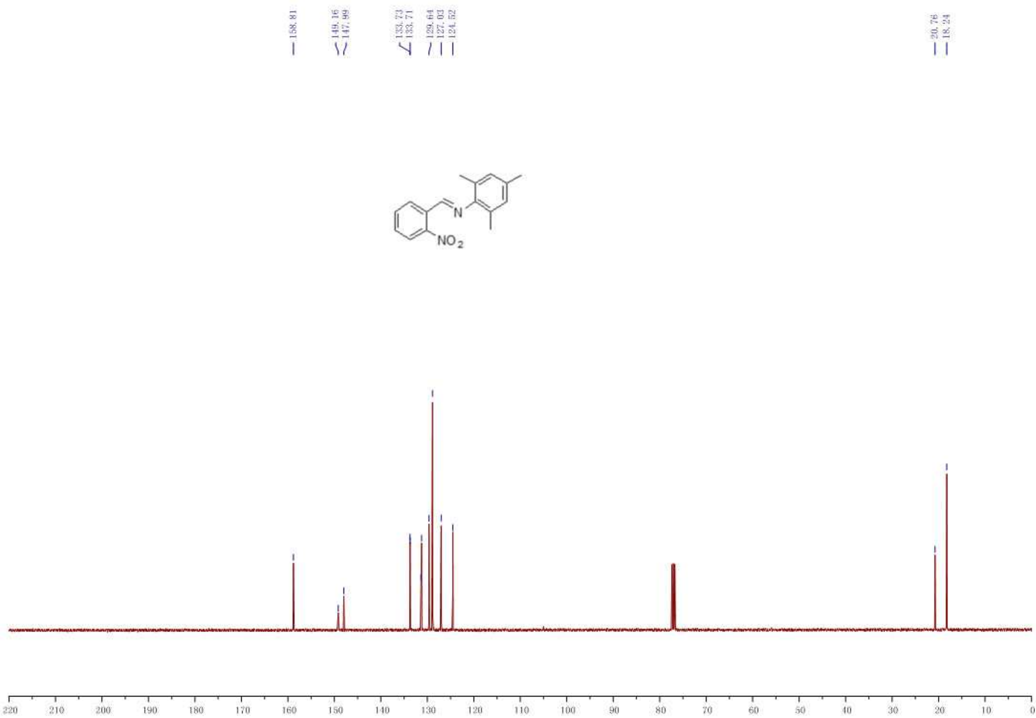
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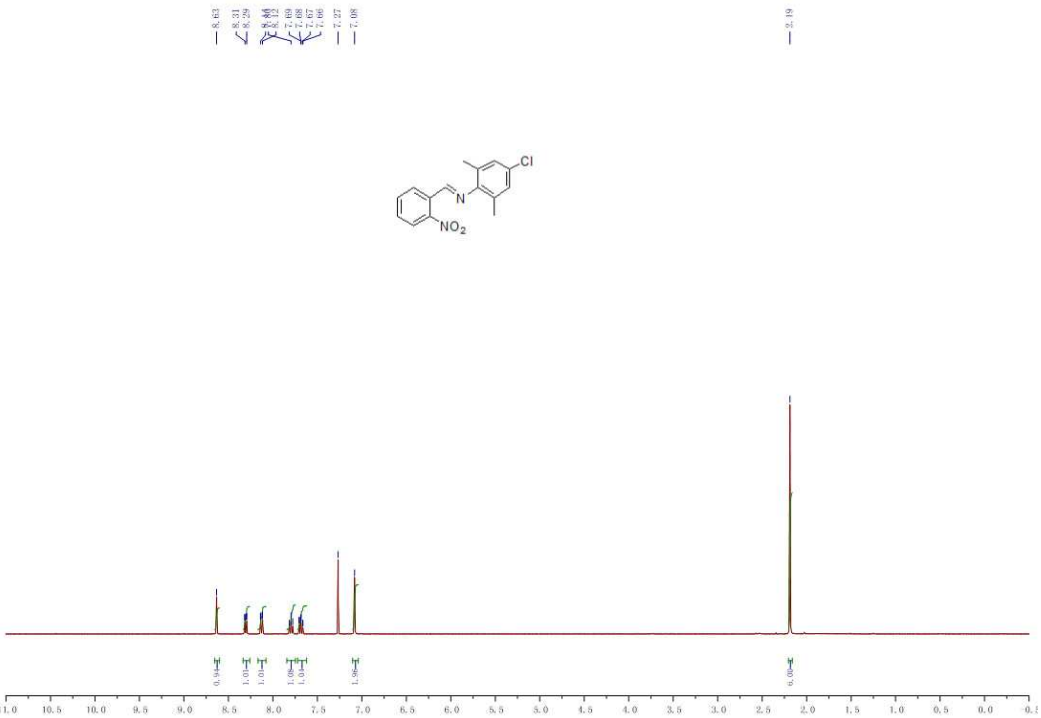
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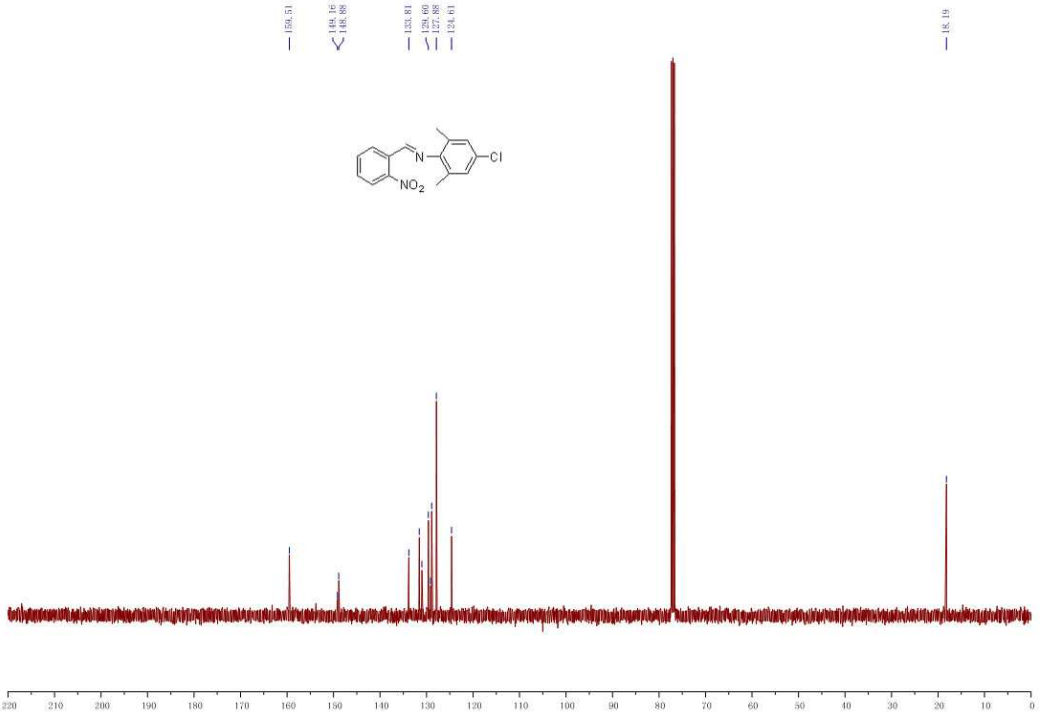
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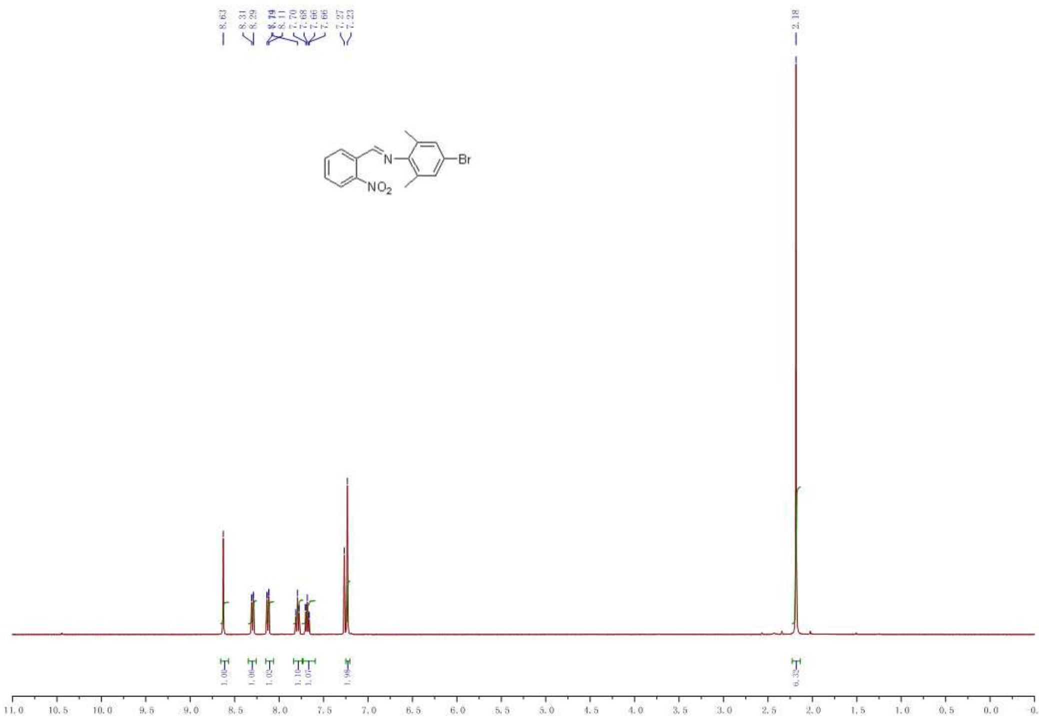
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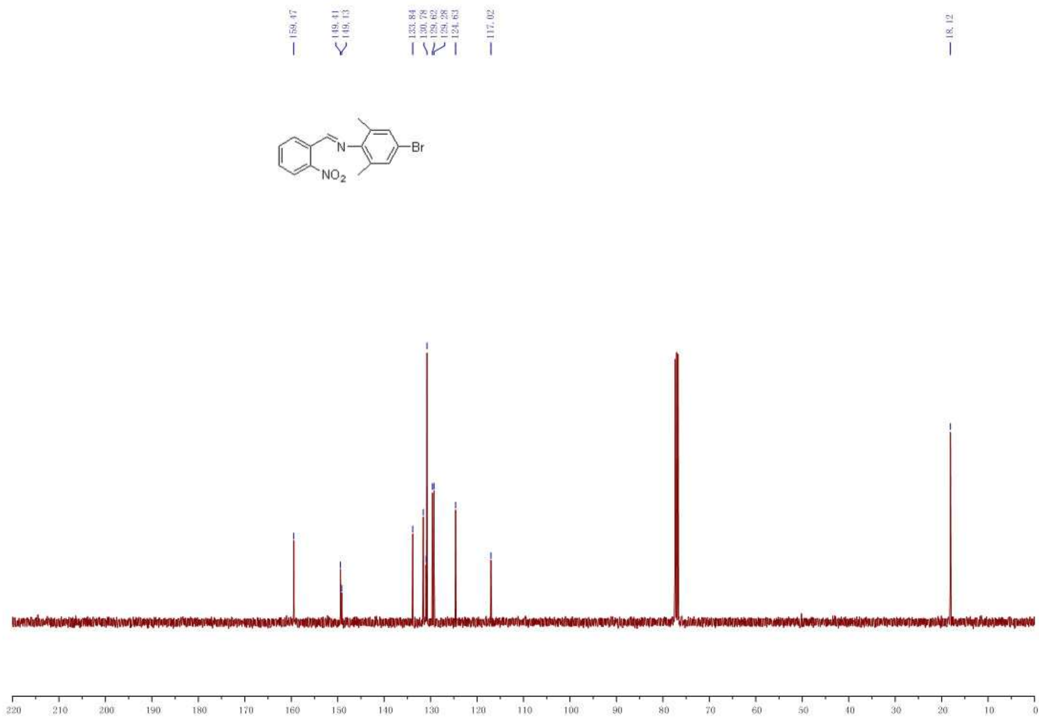
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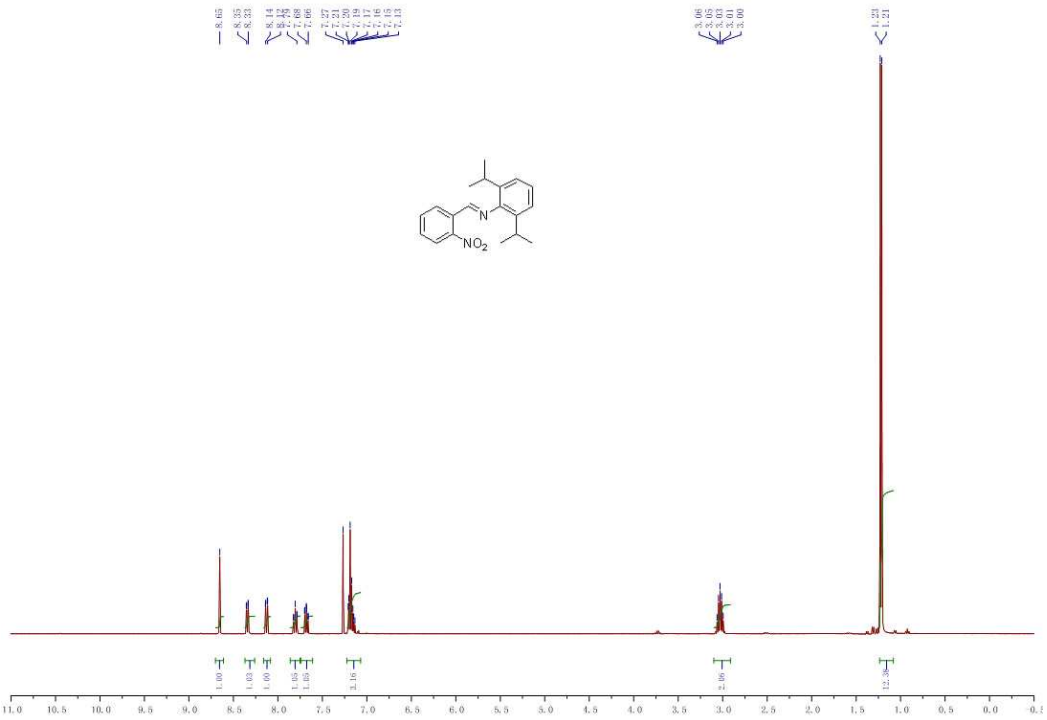
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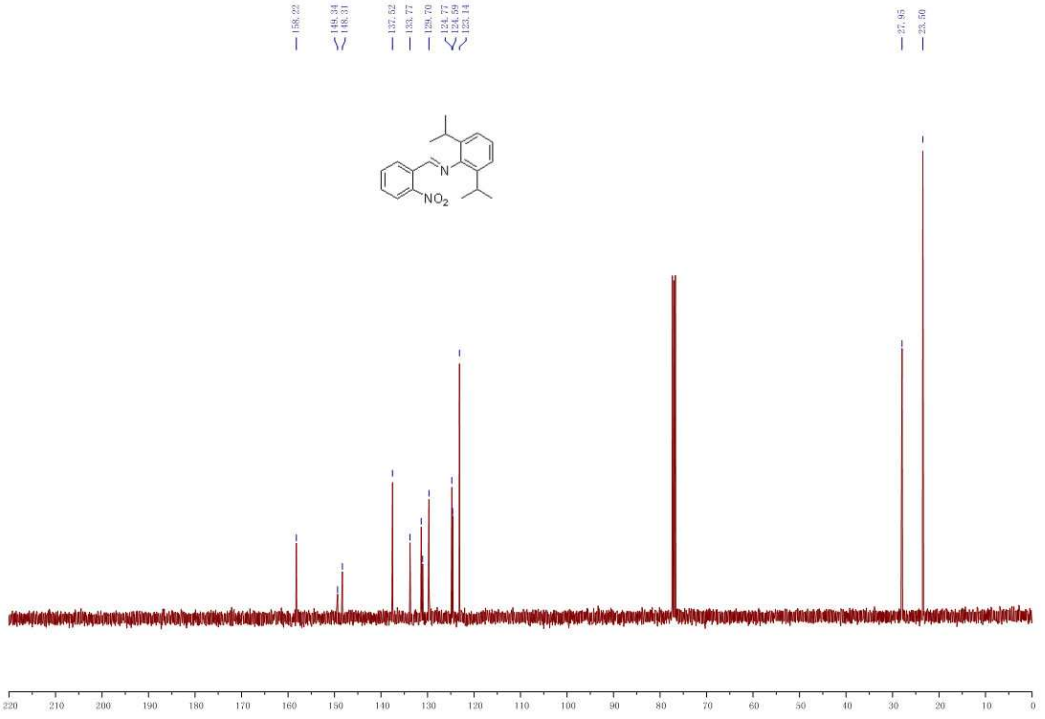
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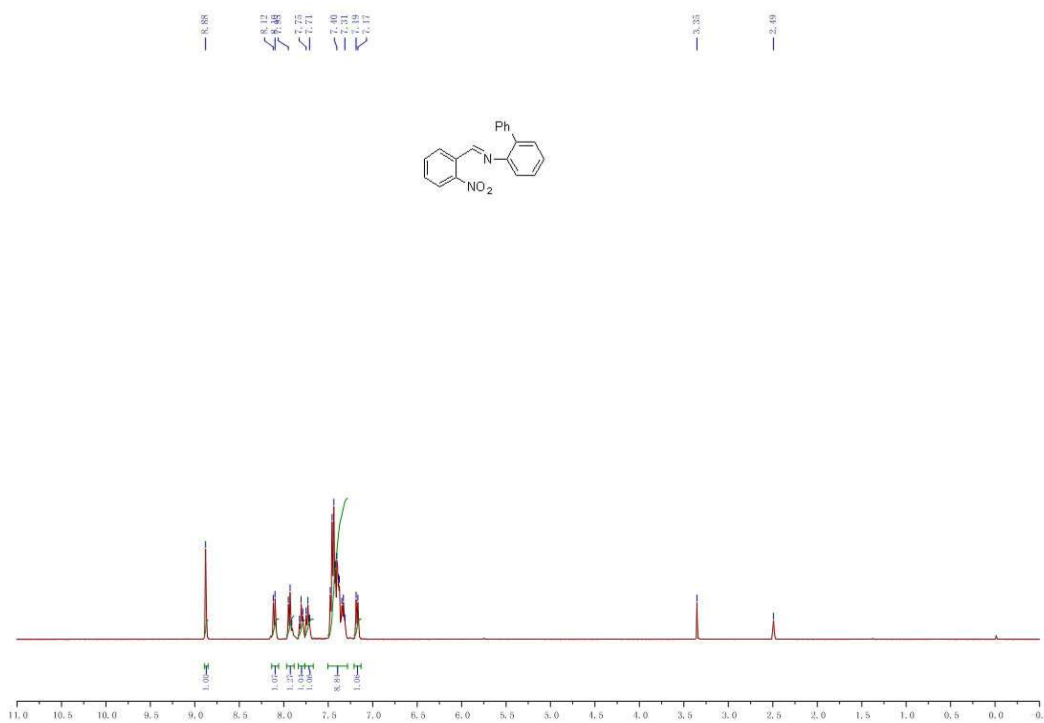
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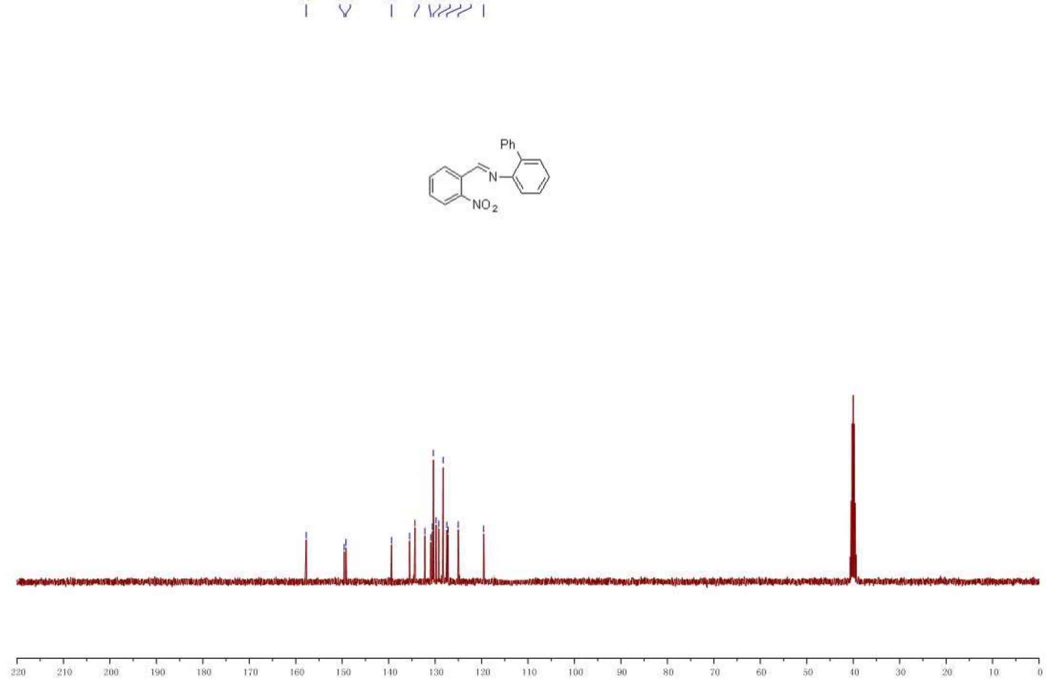
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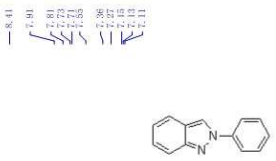

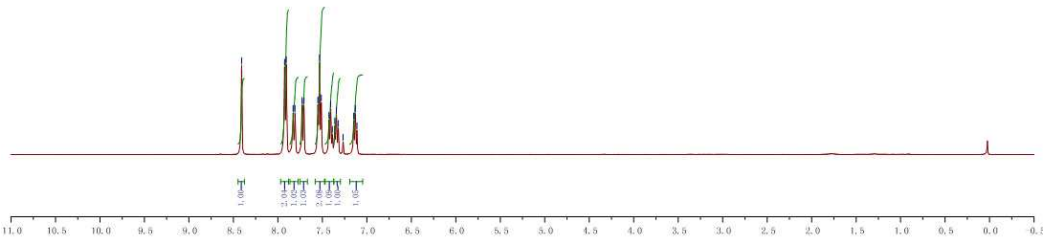

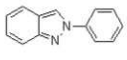

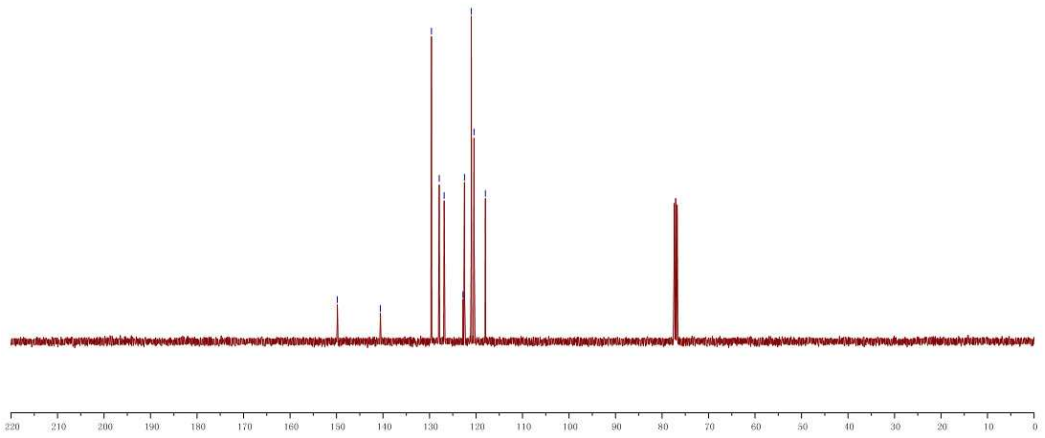


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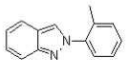

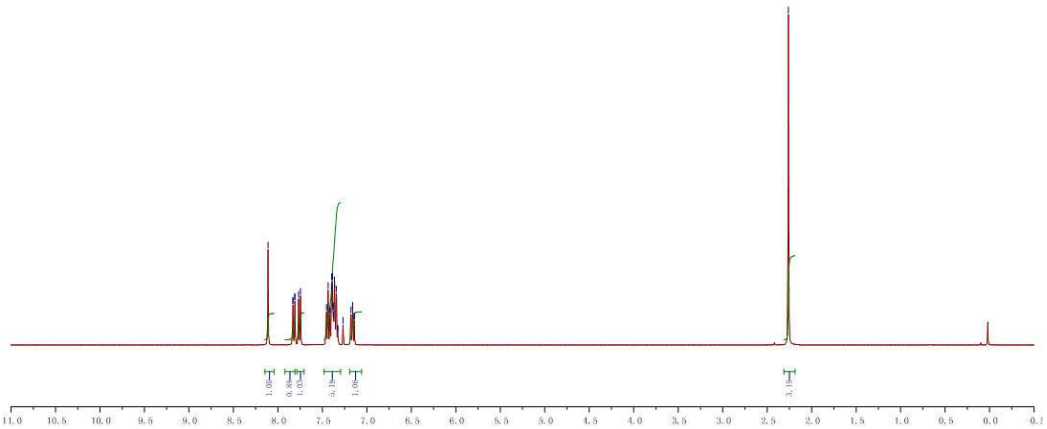
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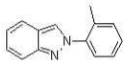

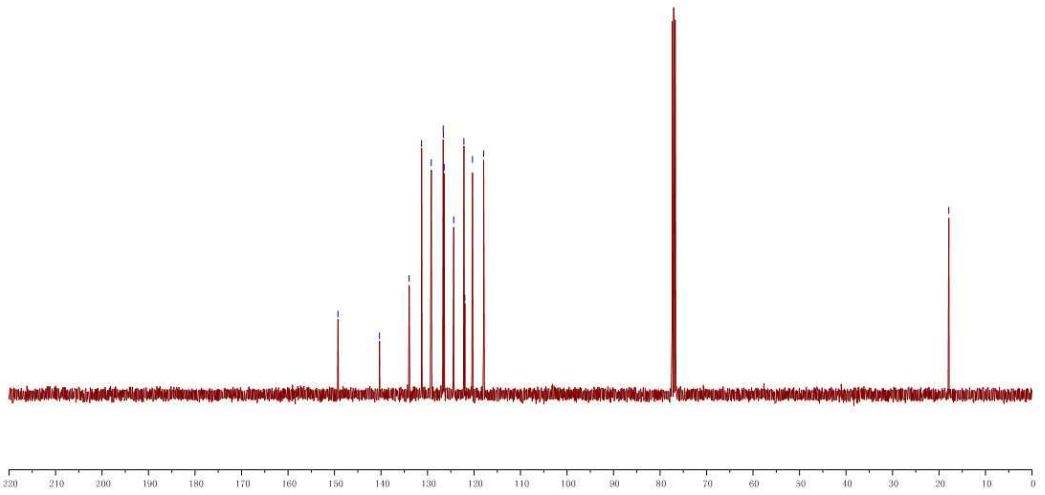
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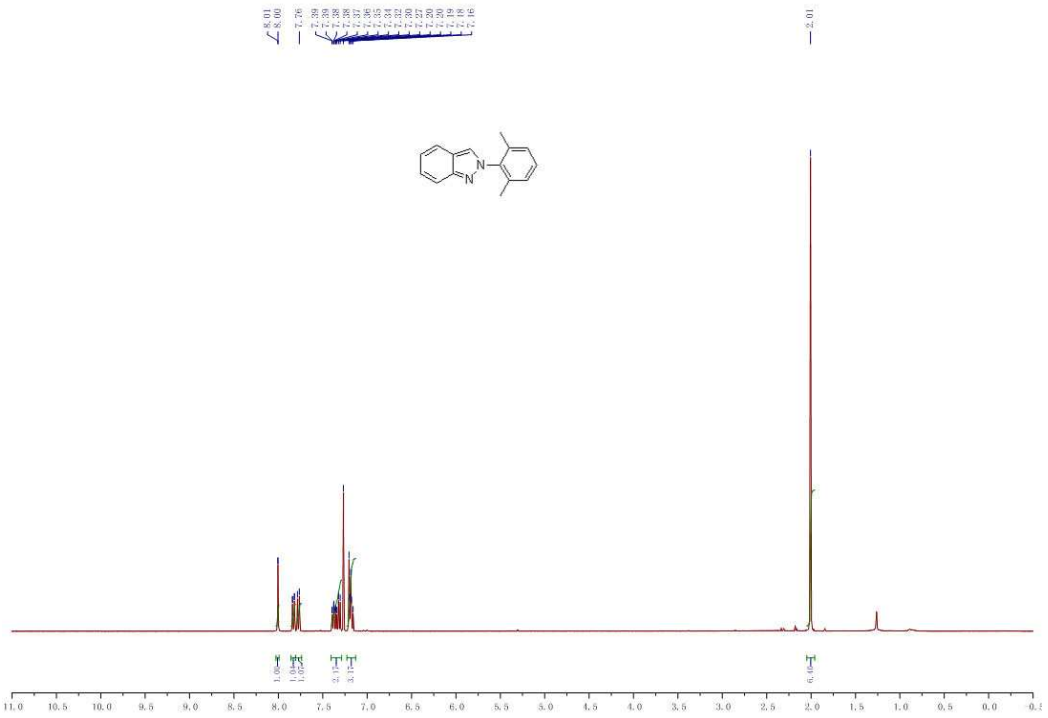
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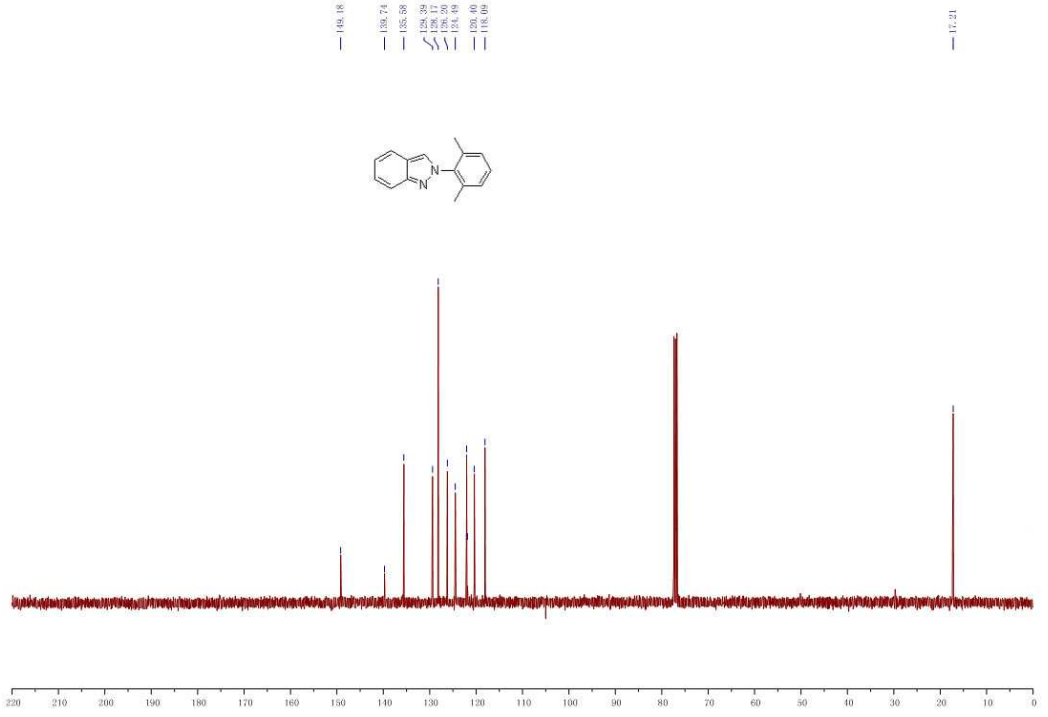
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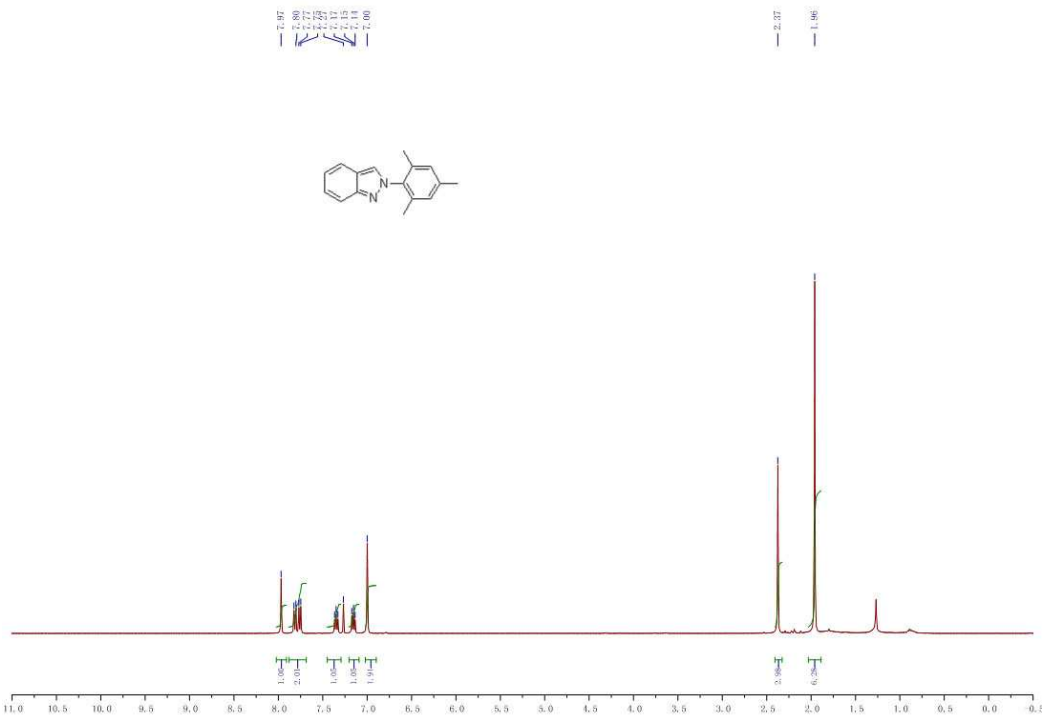
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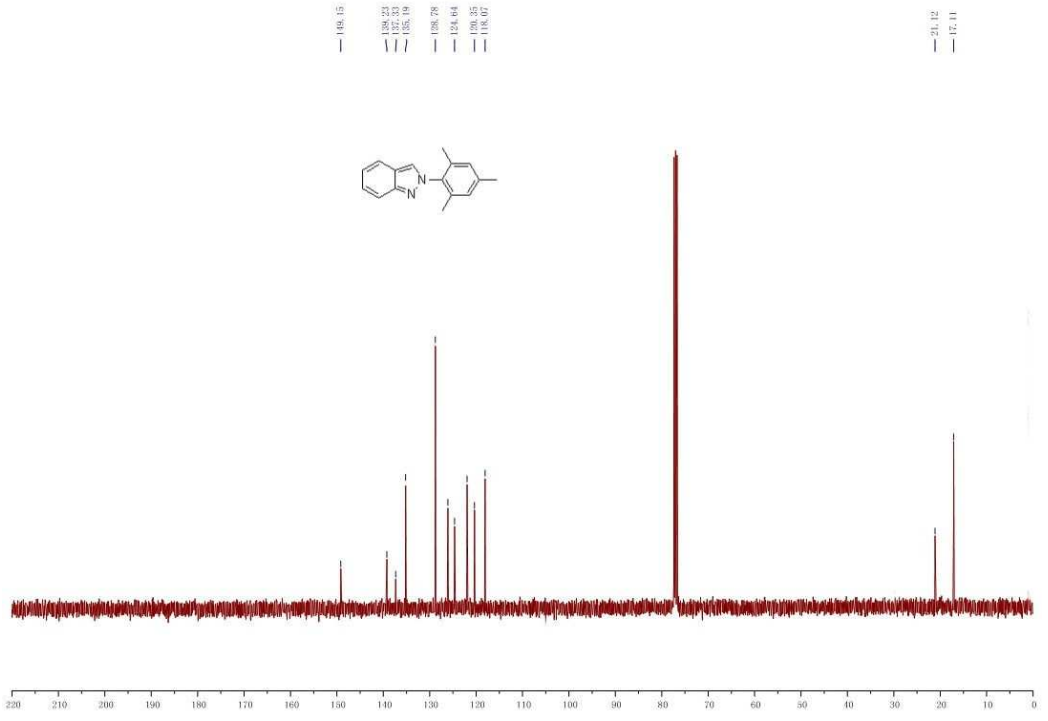
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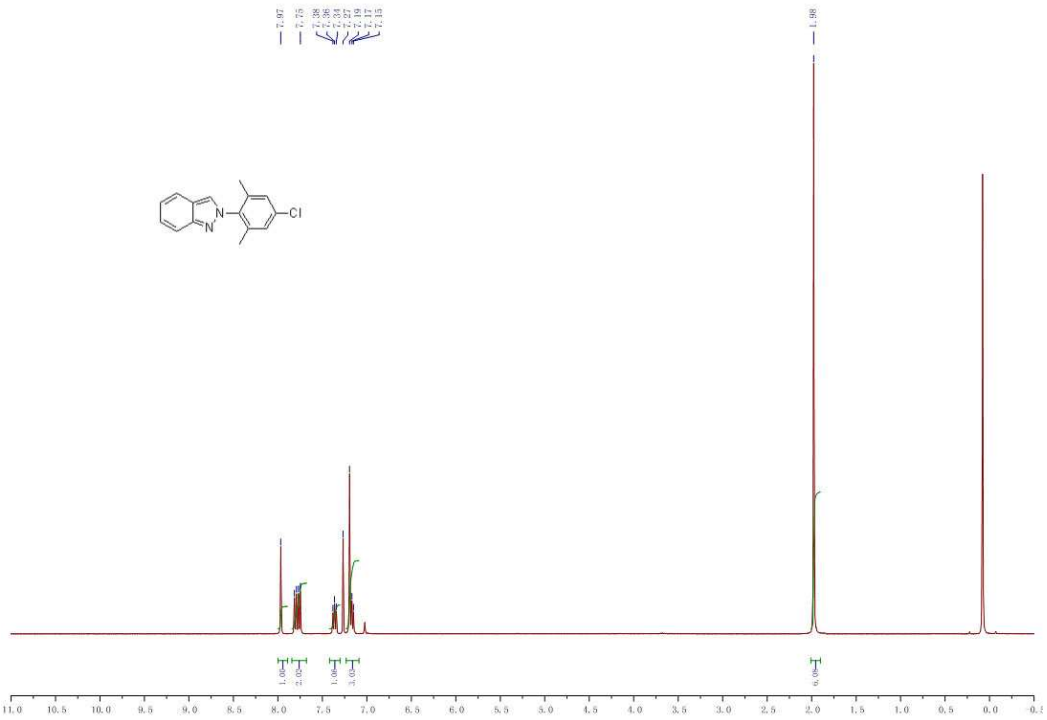
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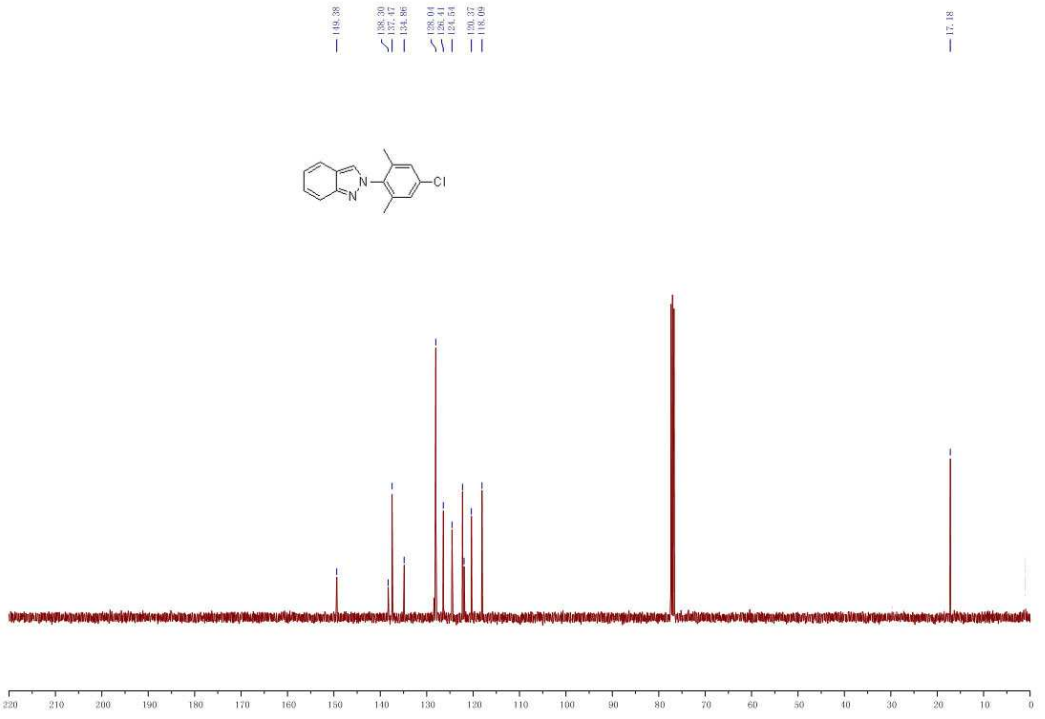
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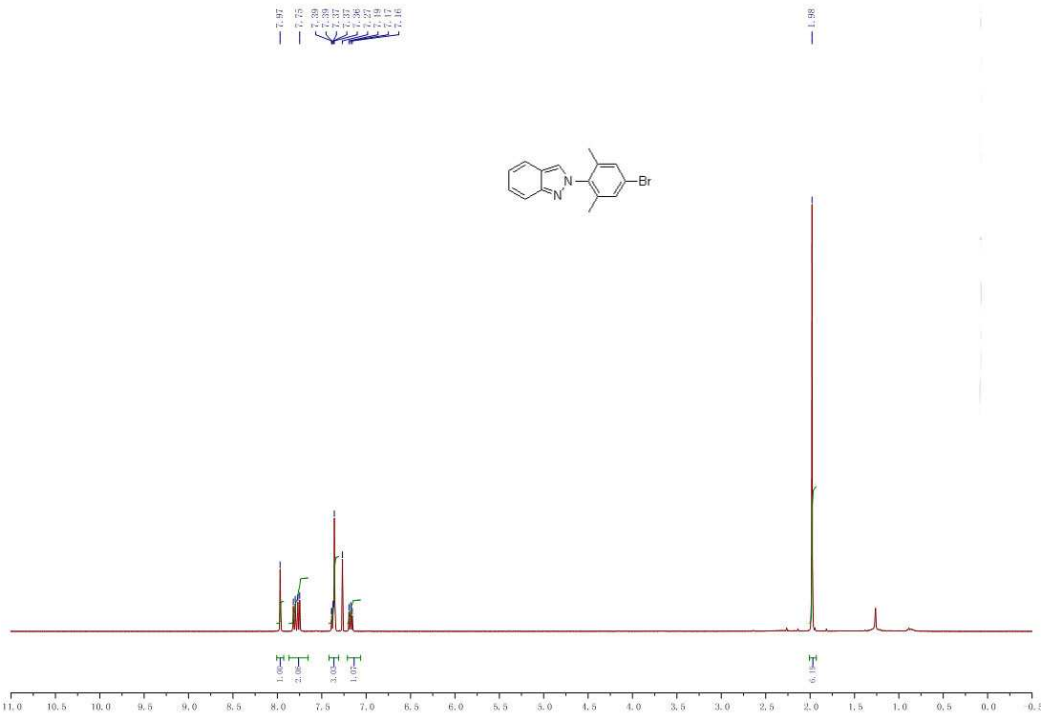
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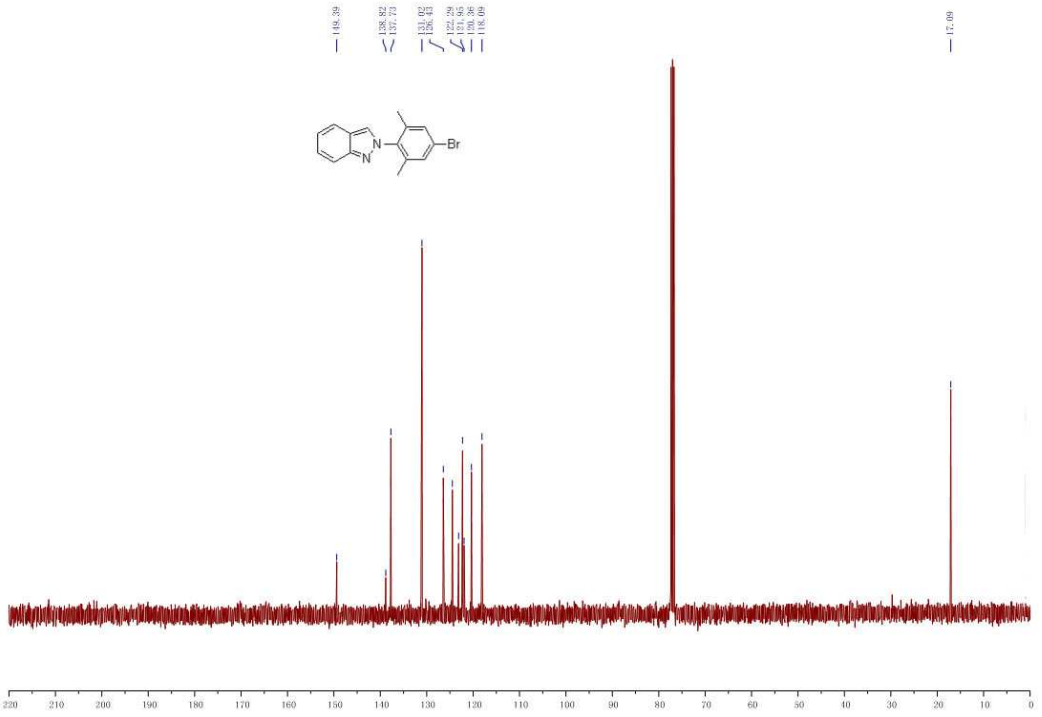
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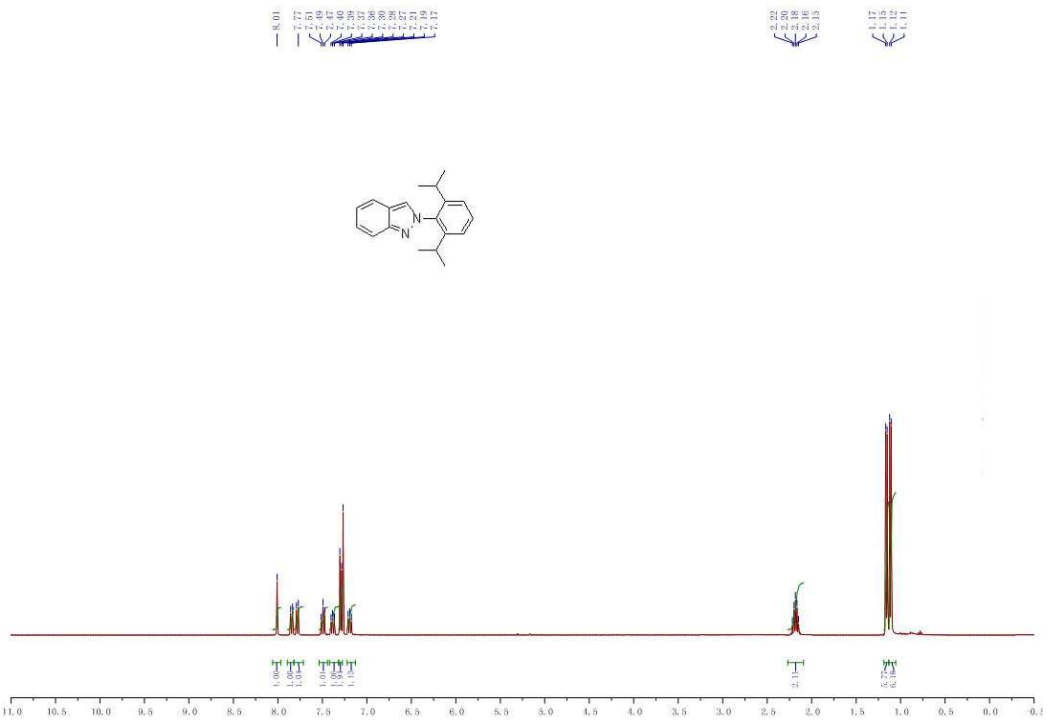

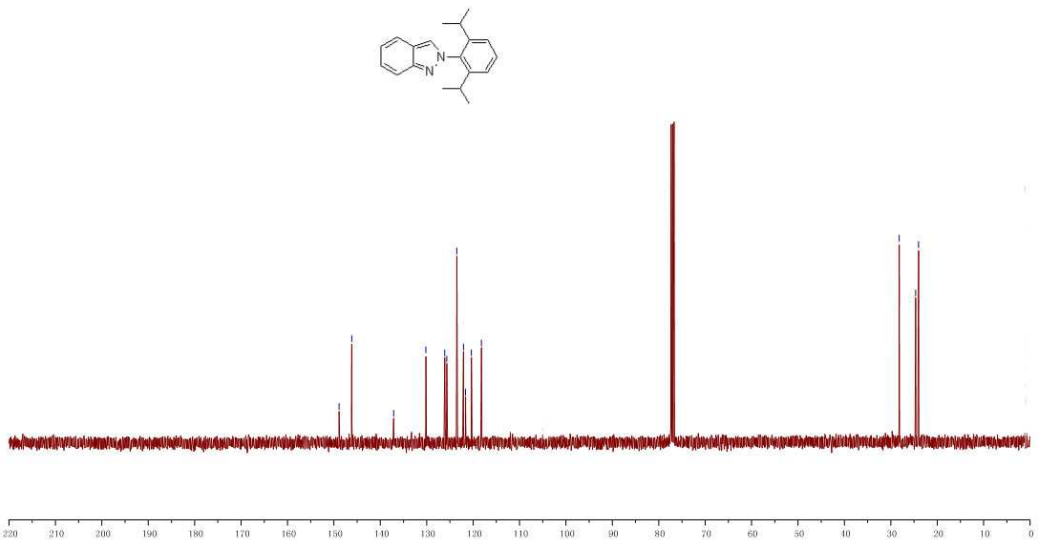

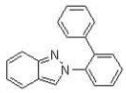

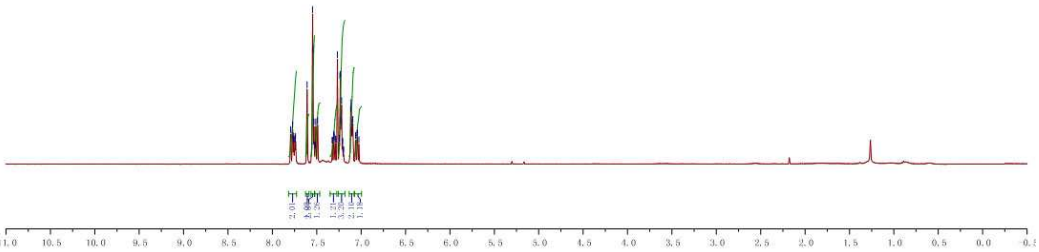

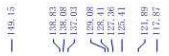

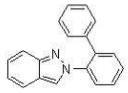

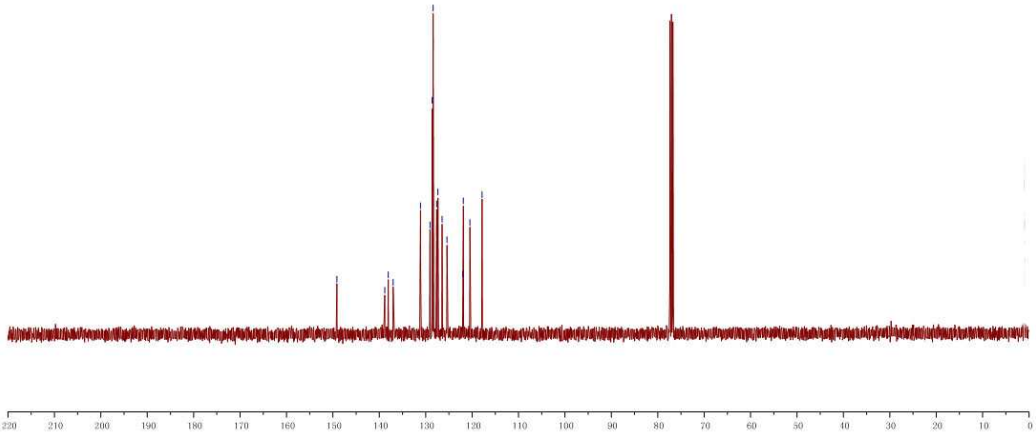

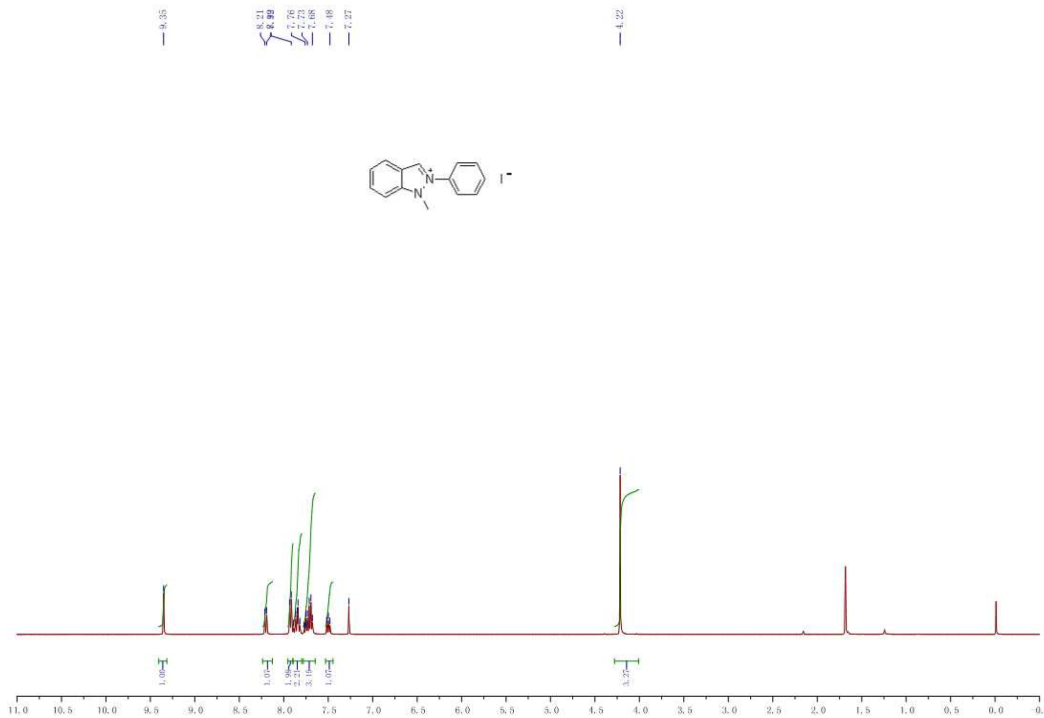
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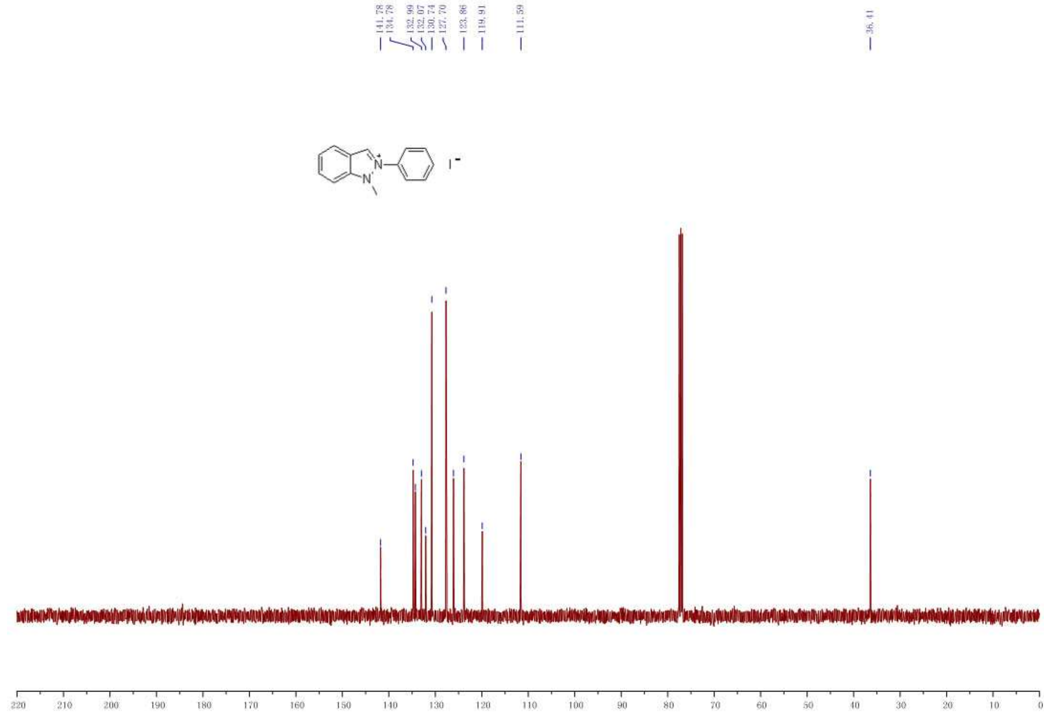
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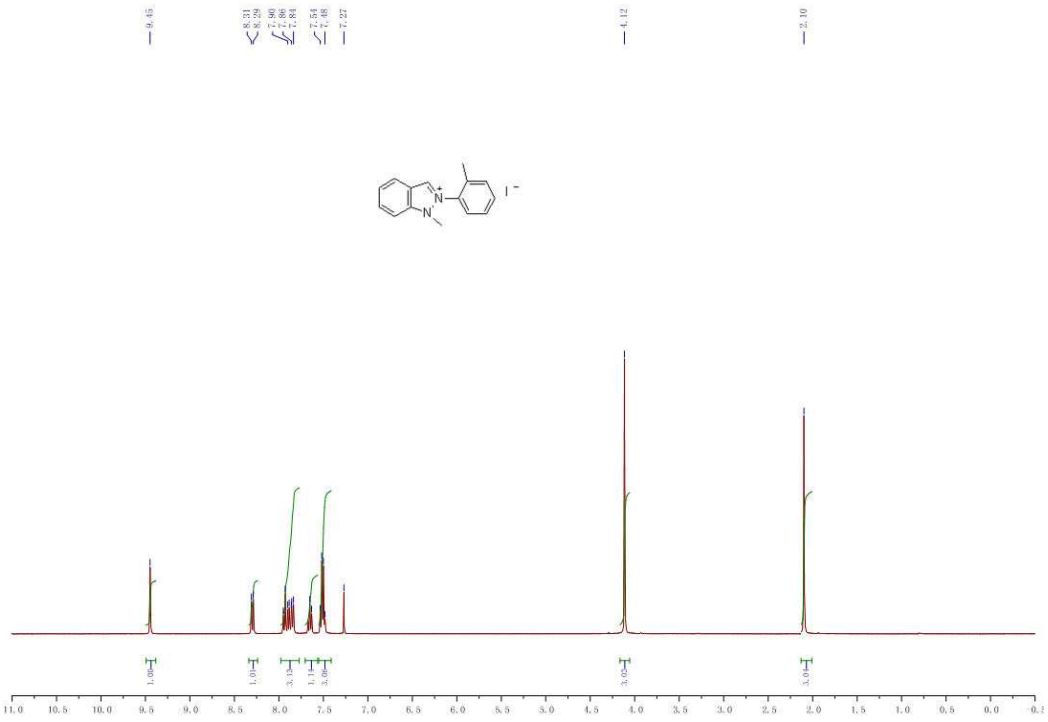
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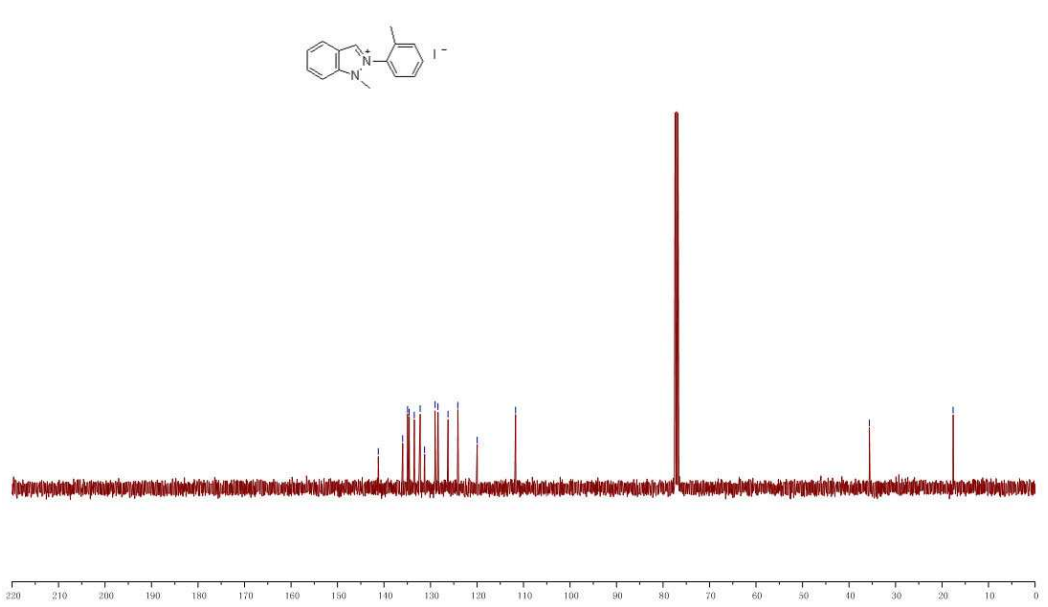
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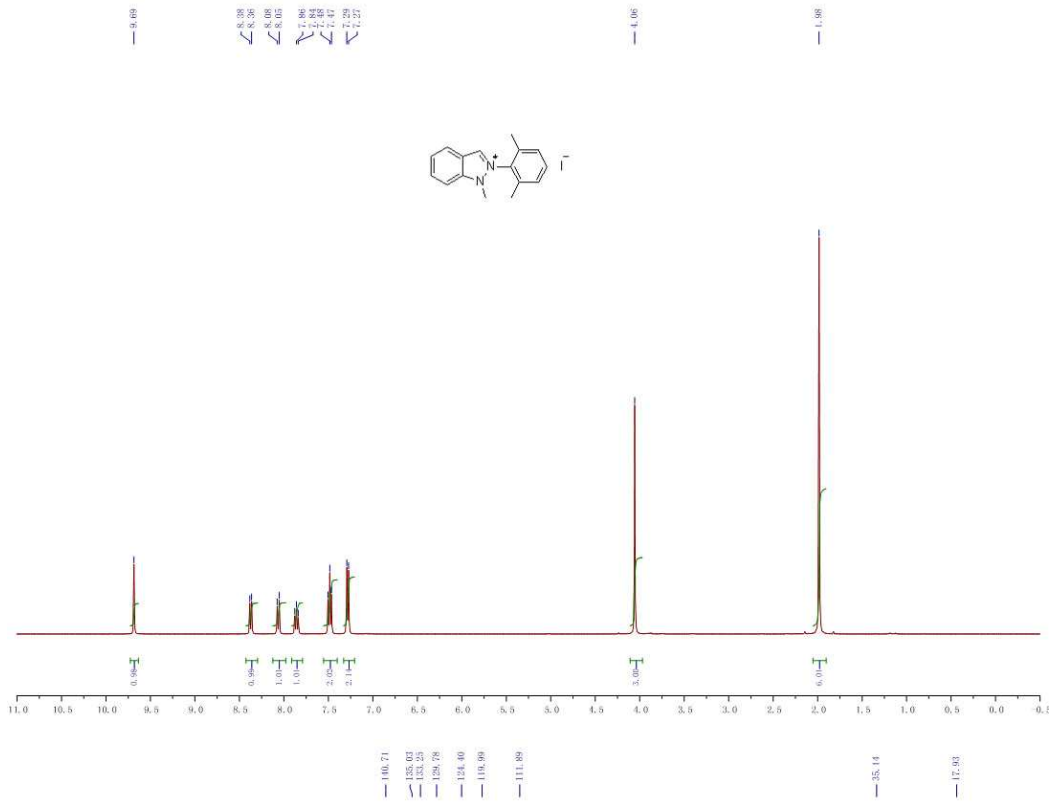
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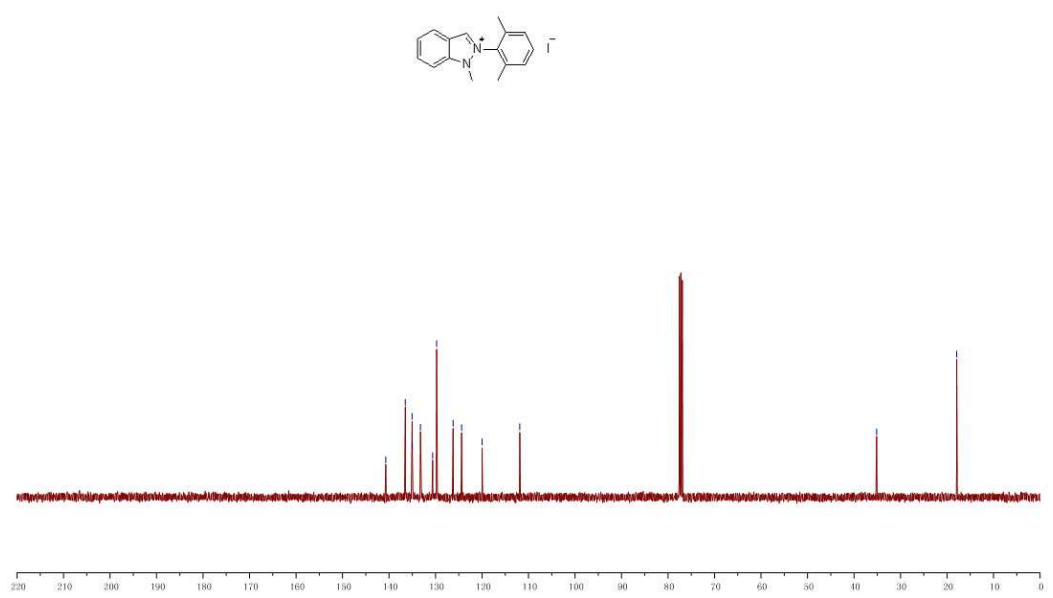
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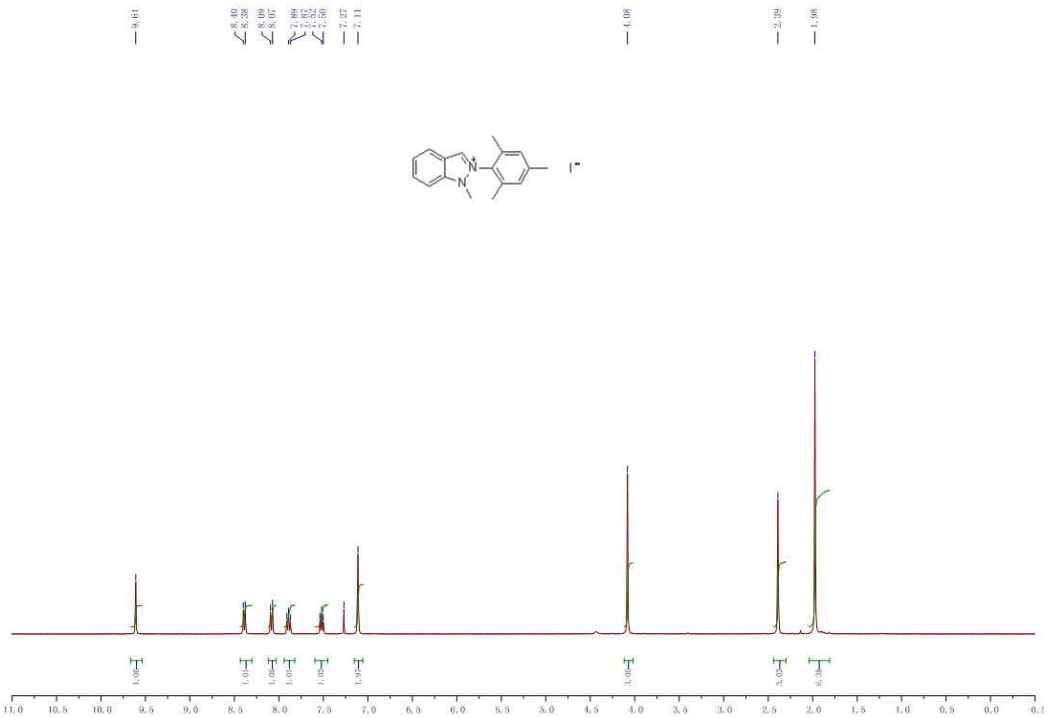
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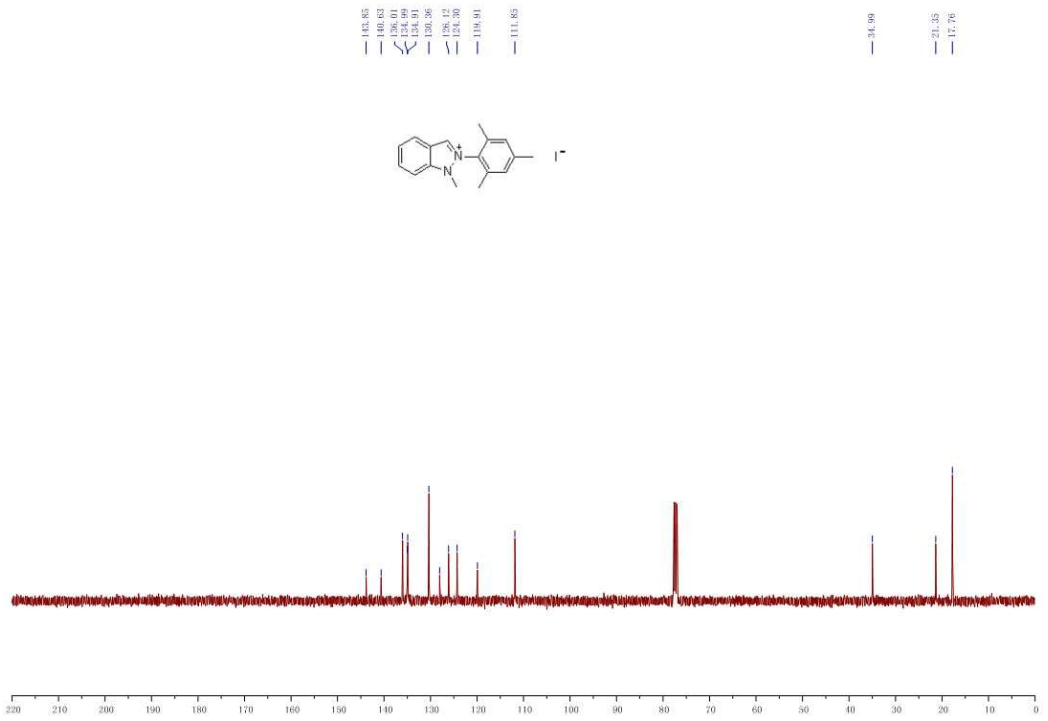
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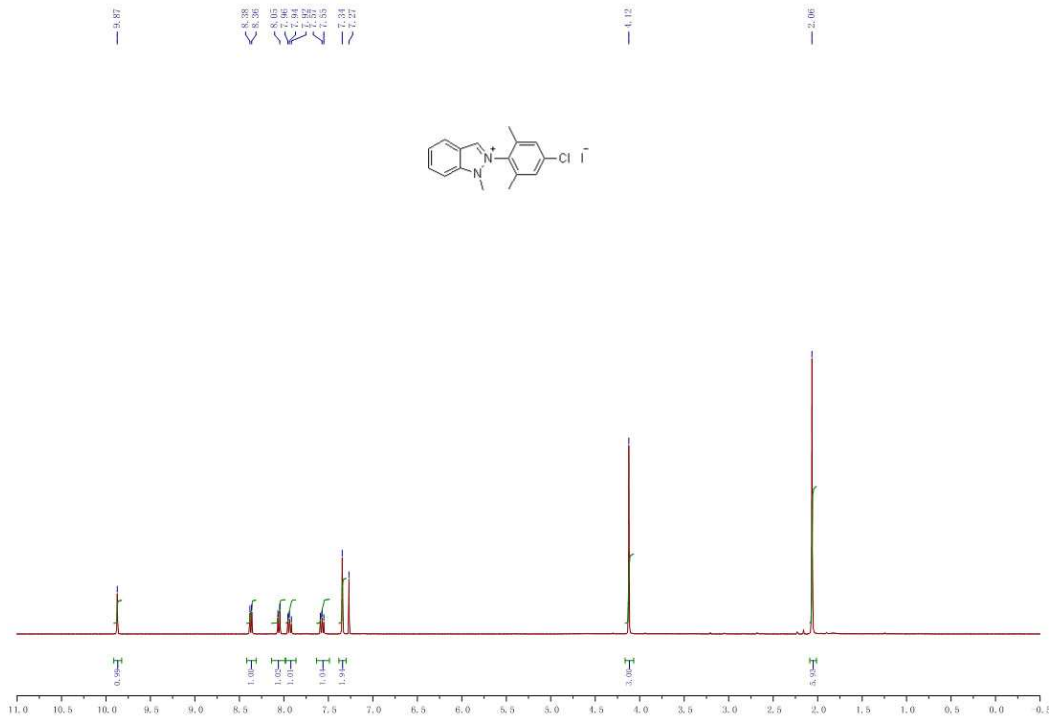
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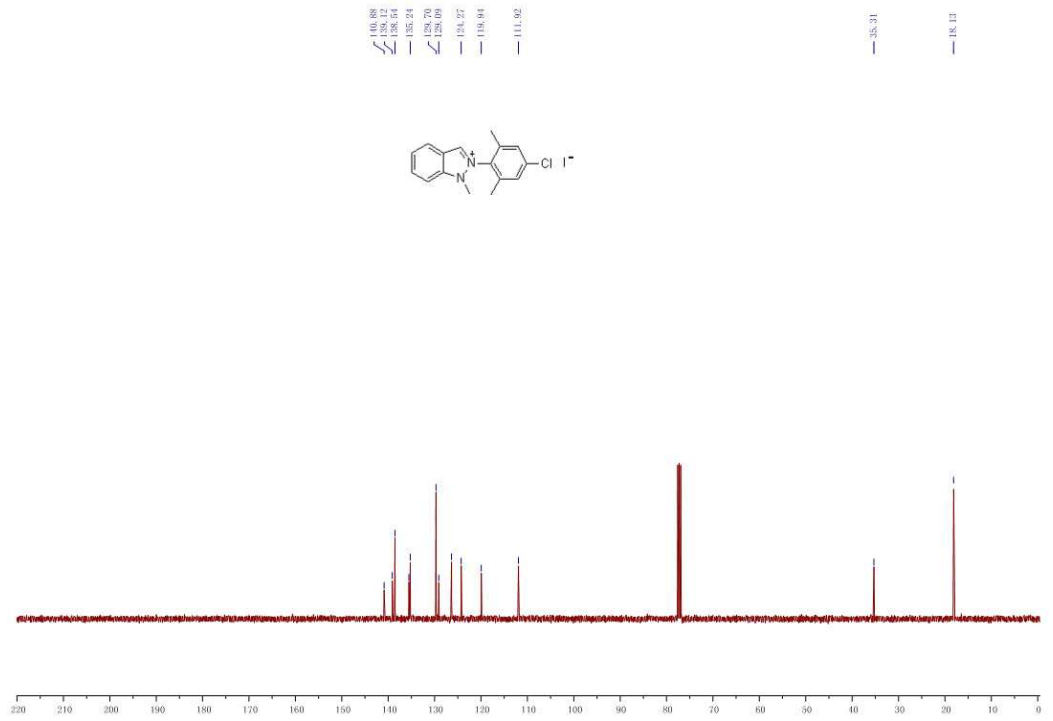
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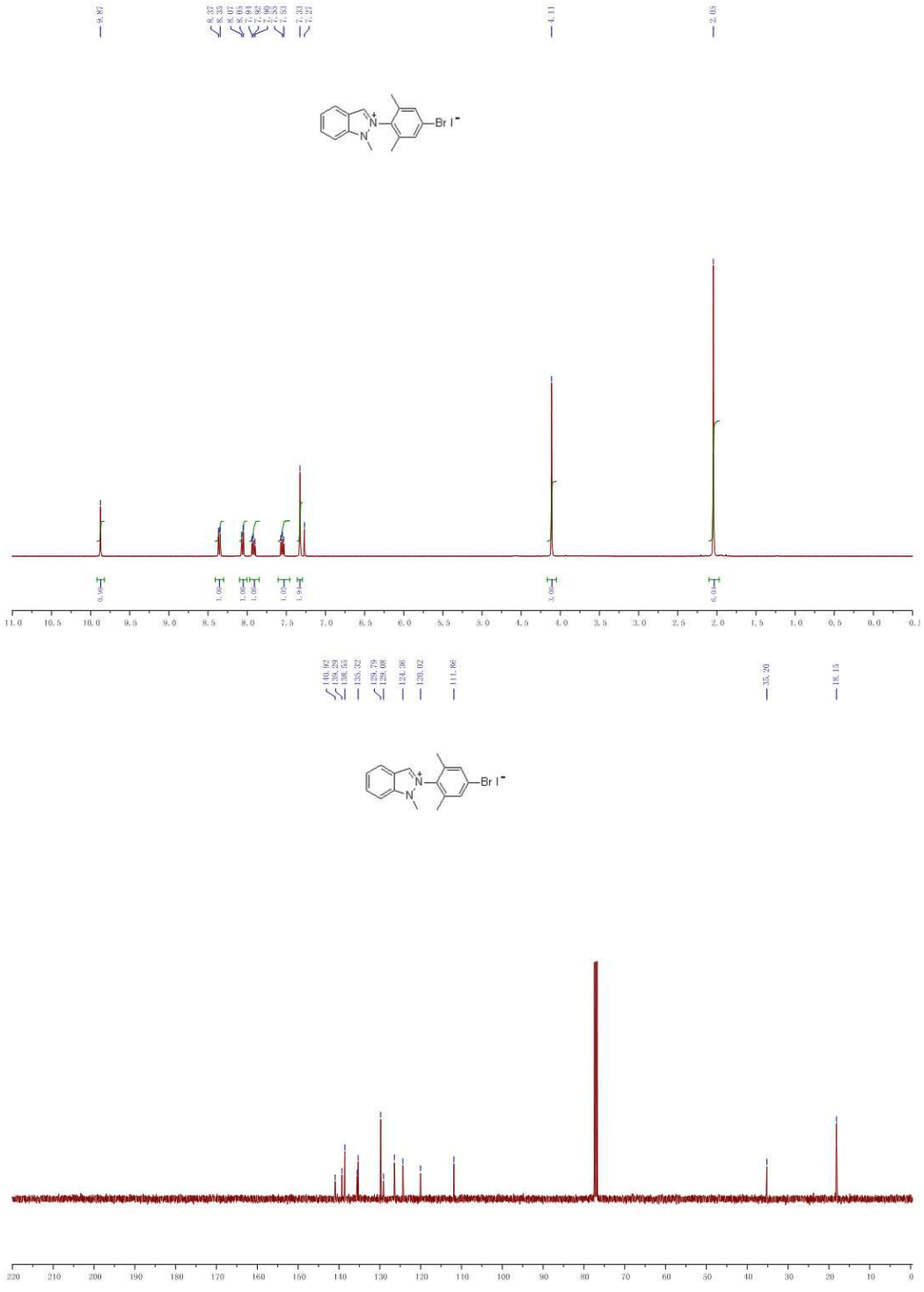
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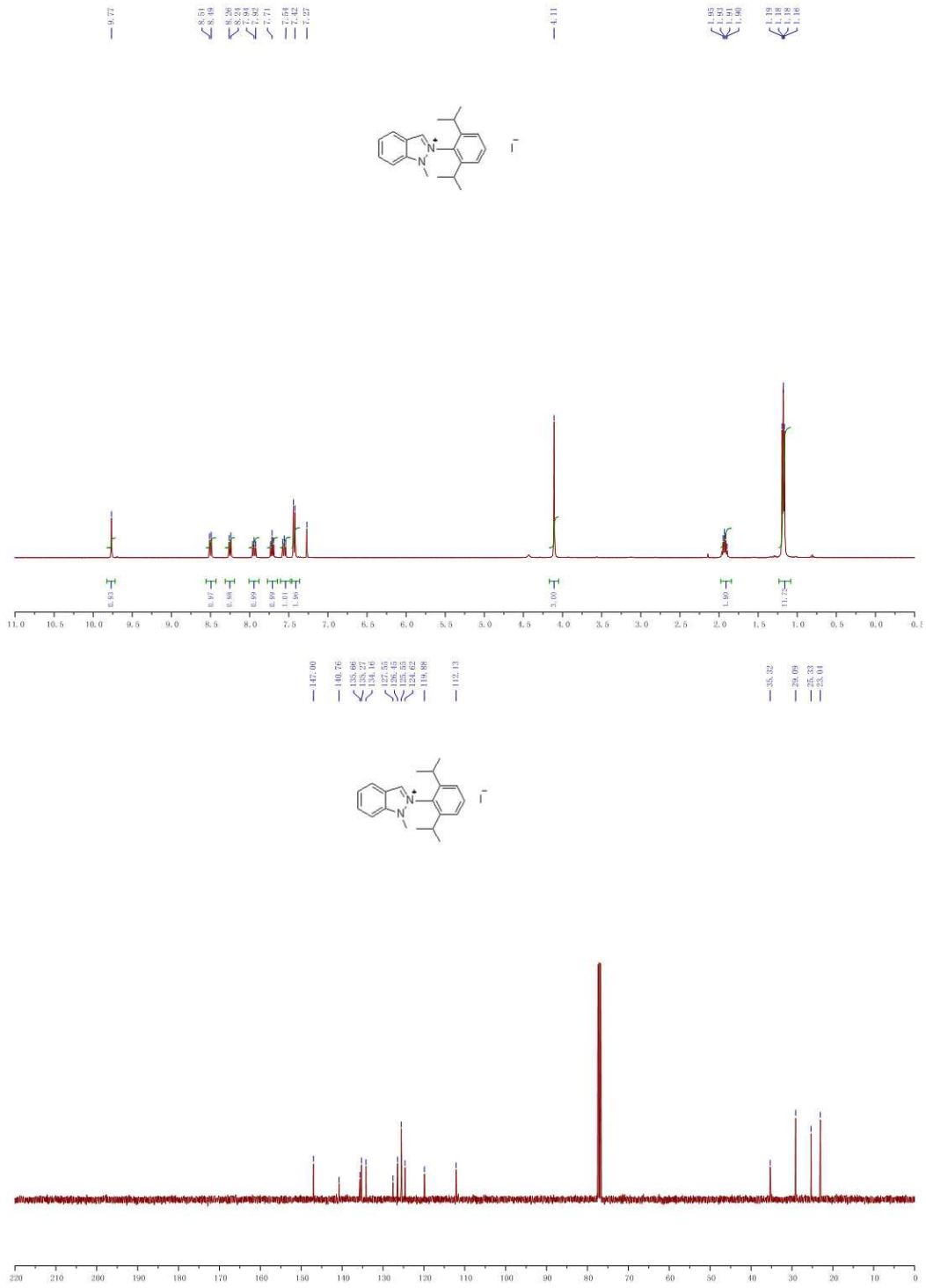

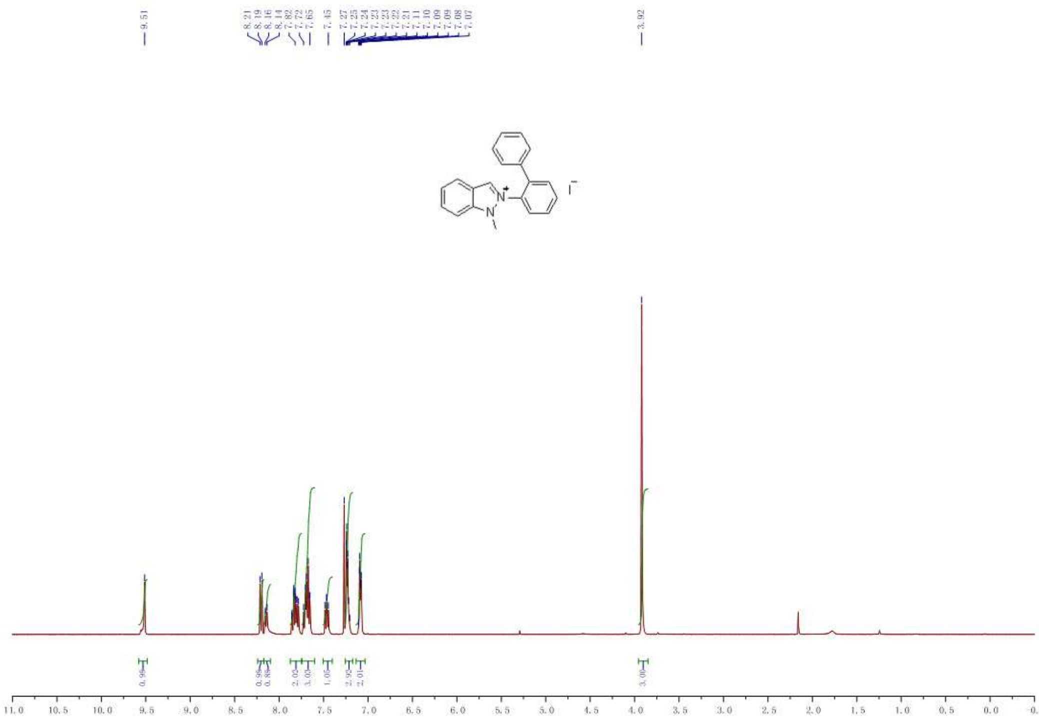

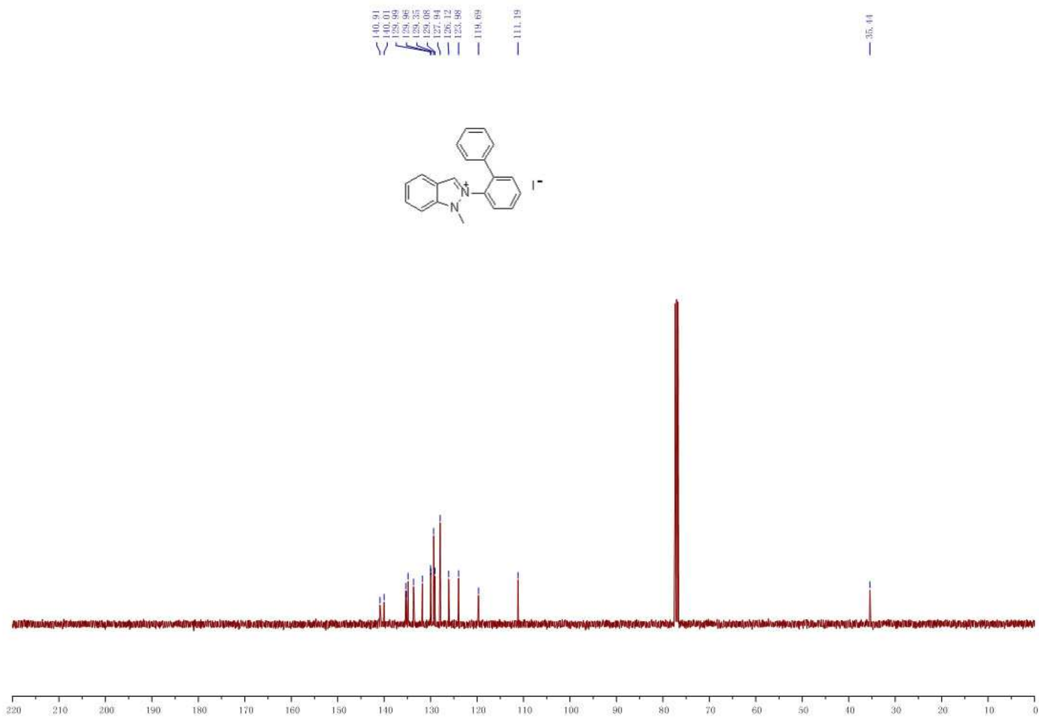

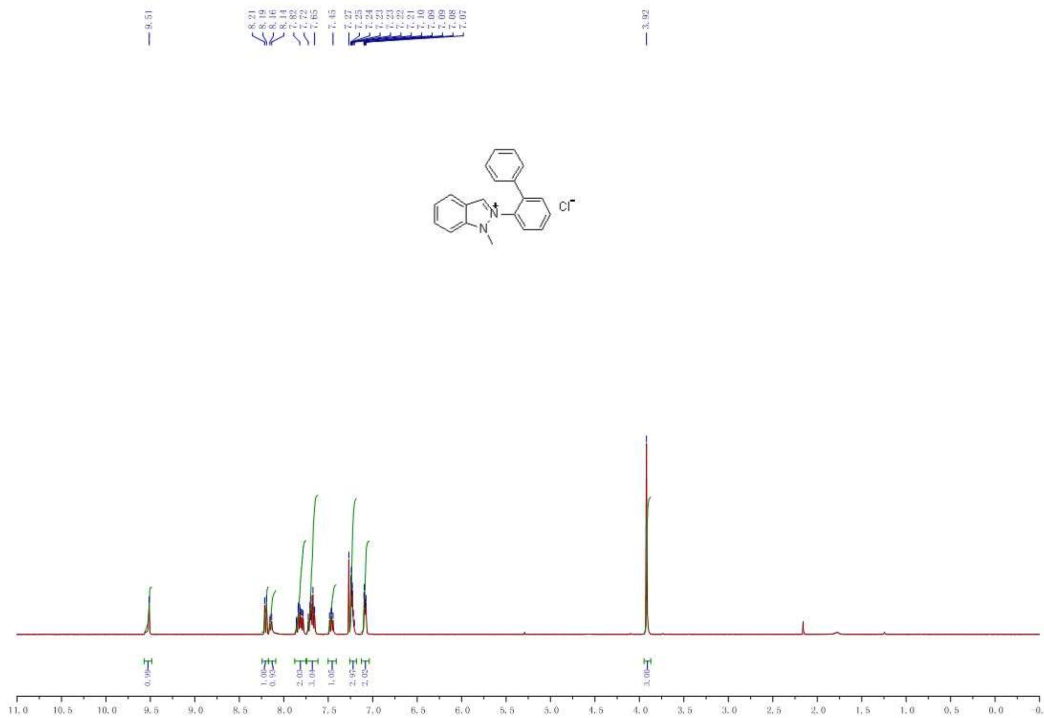
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7.07
3.92
Cl⁻
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0.93
2.03
3.01
1.05
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2.02
3.05
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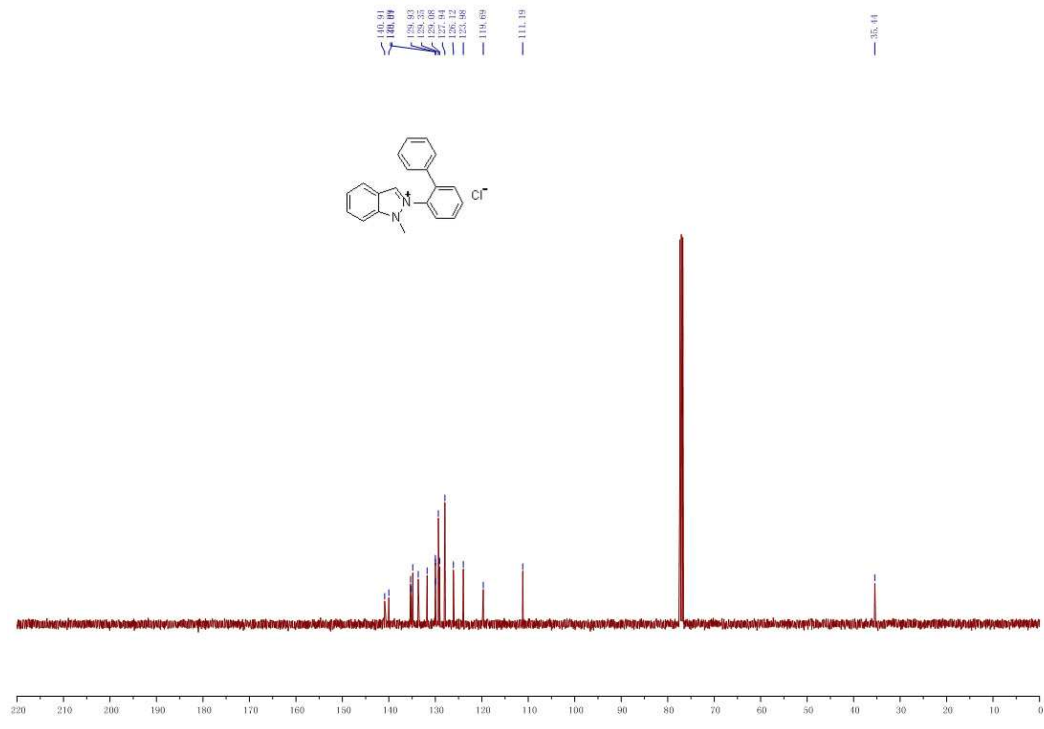
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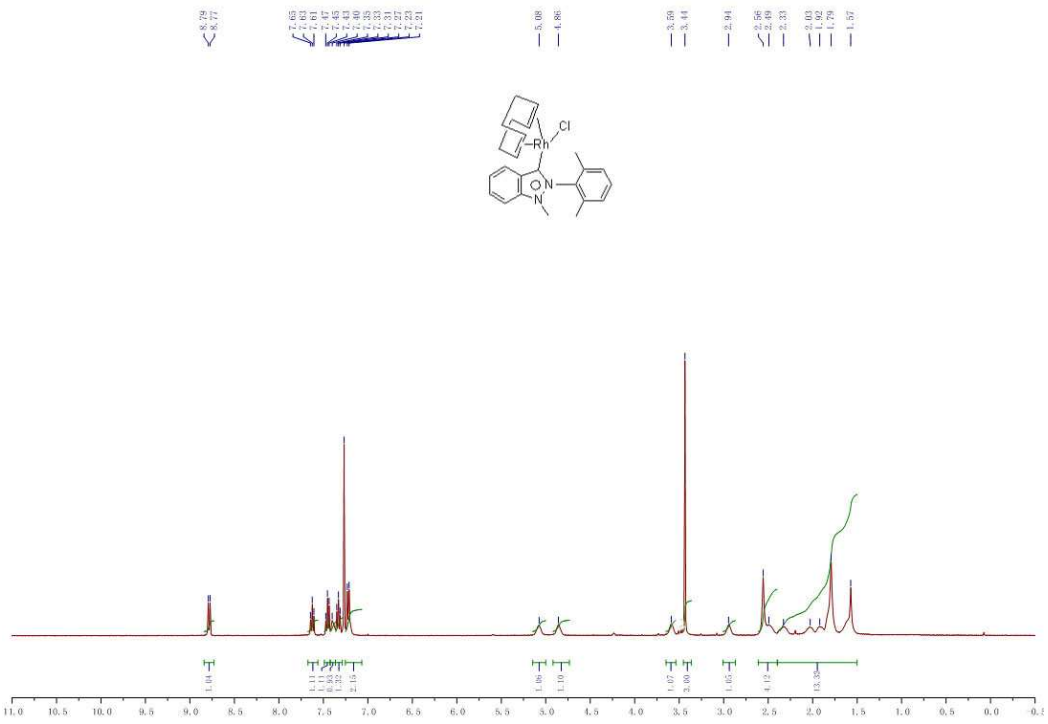
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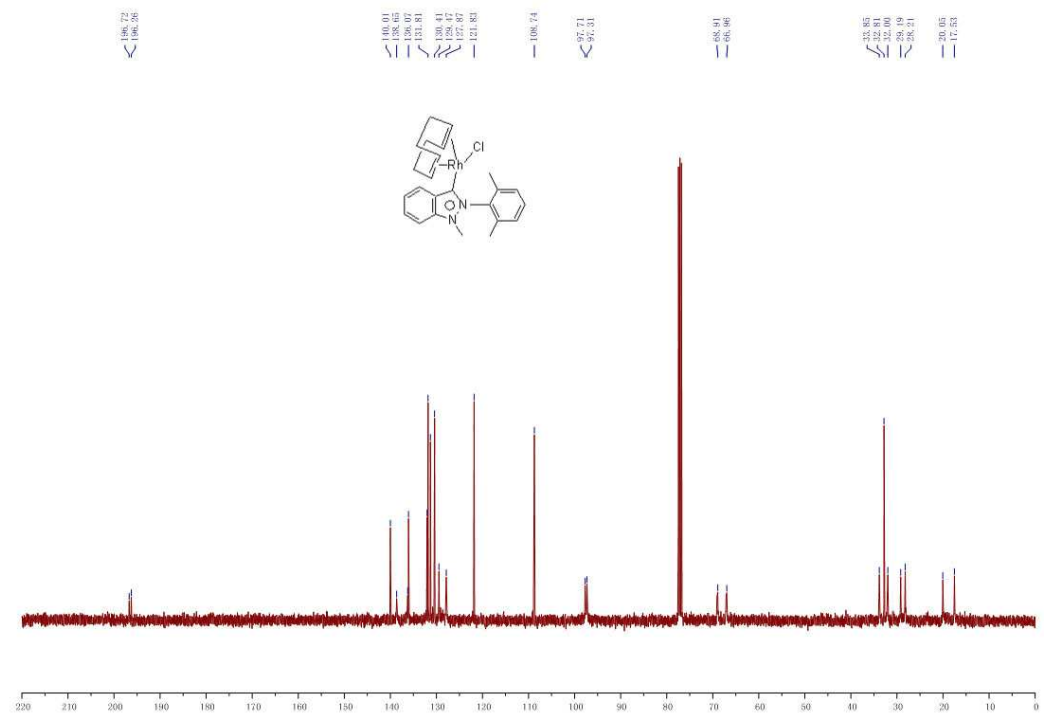
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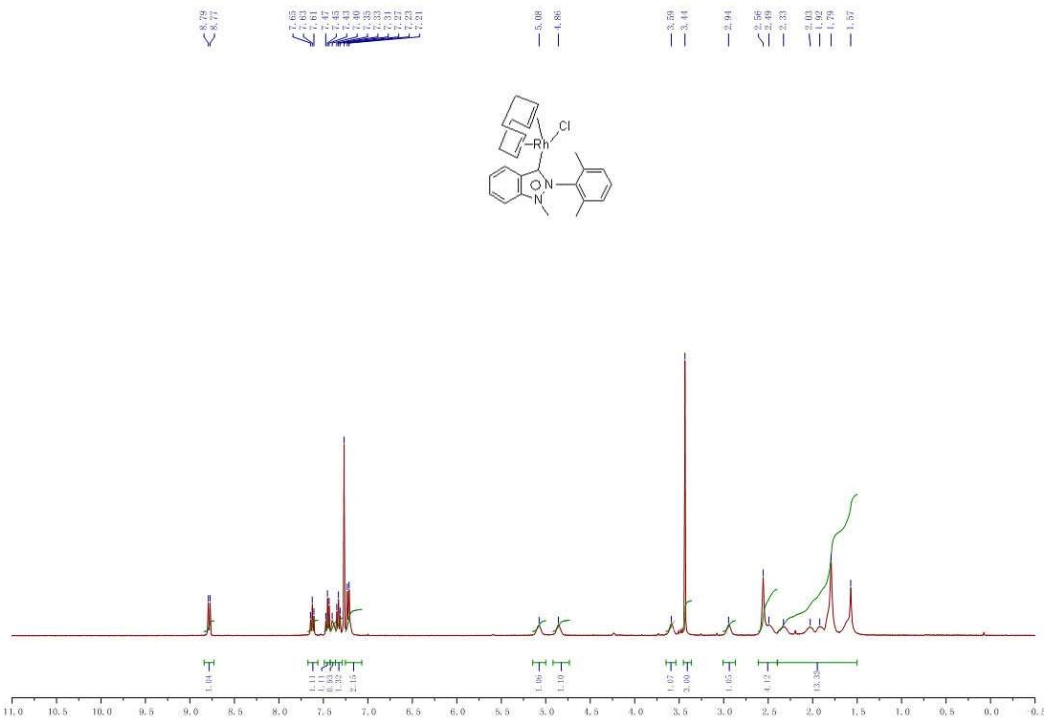
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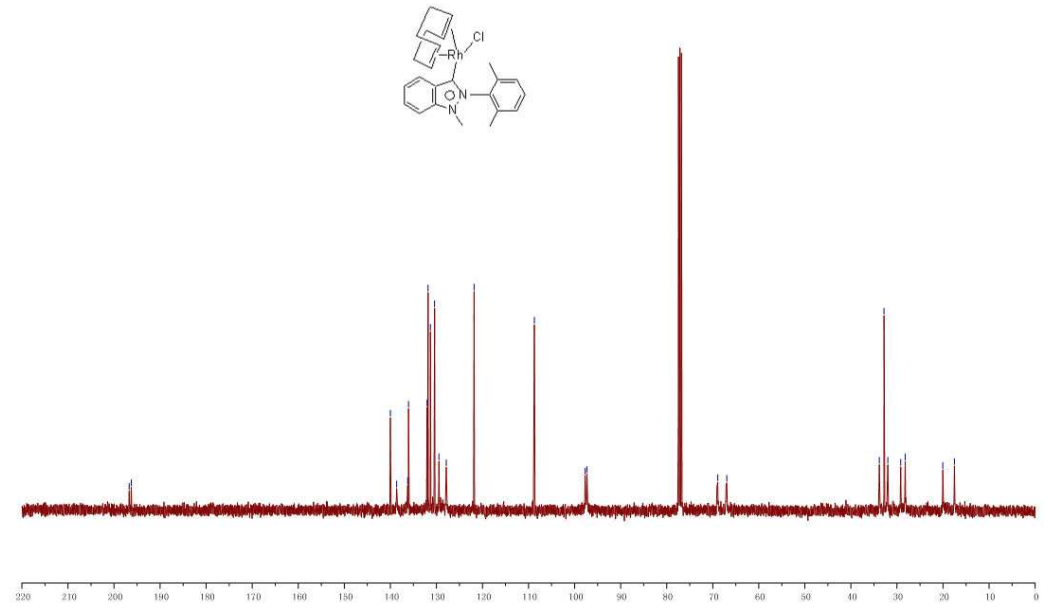
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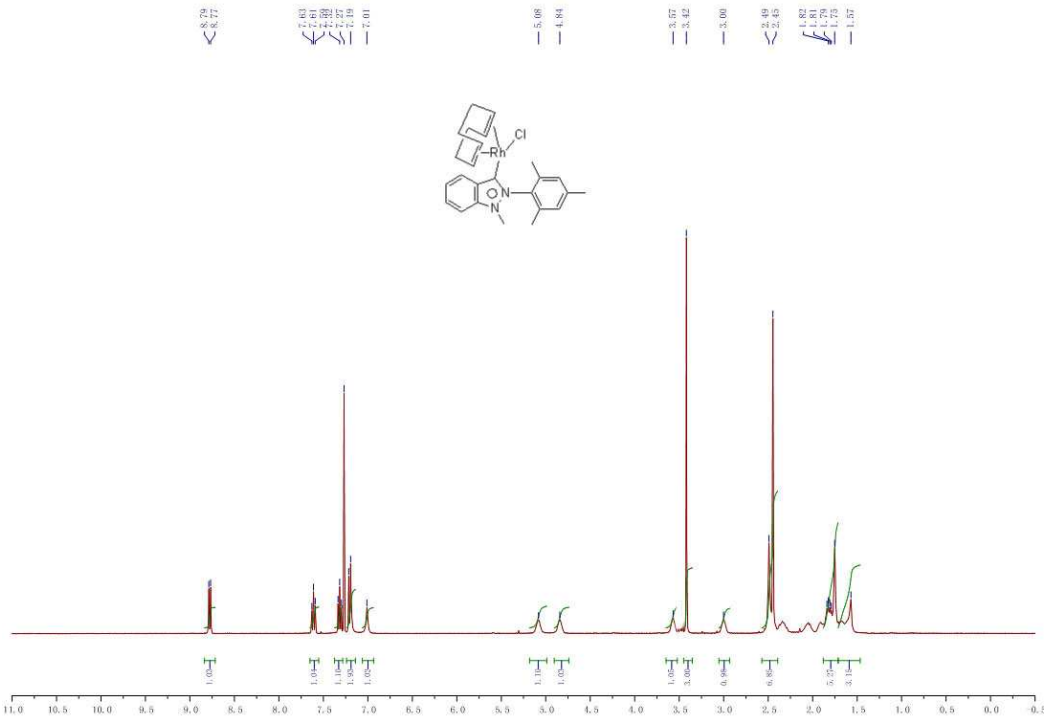
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Cl
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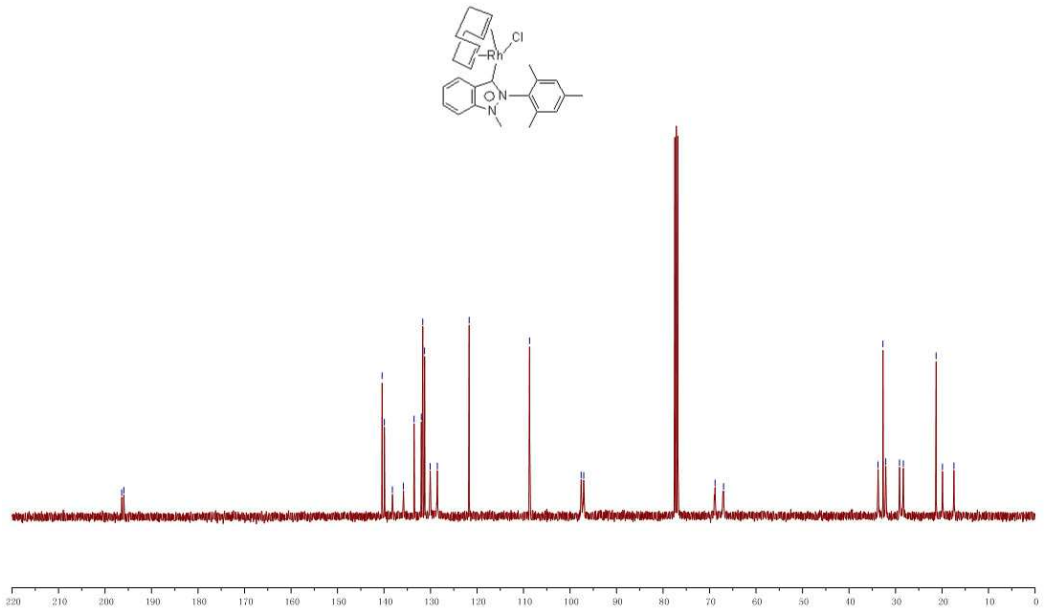
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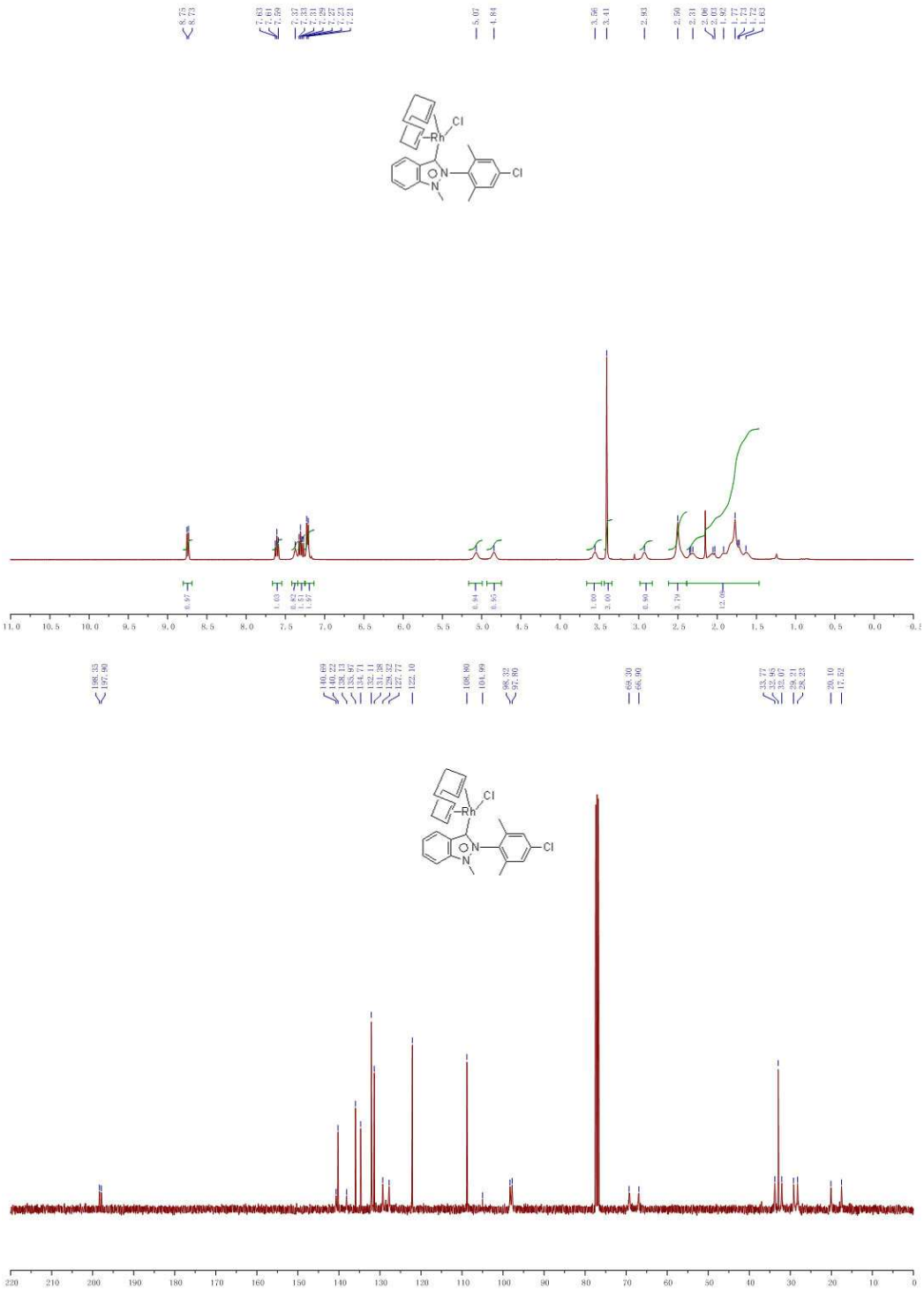

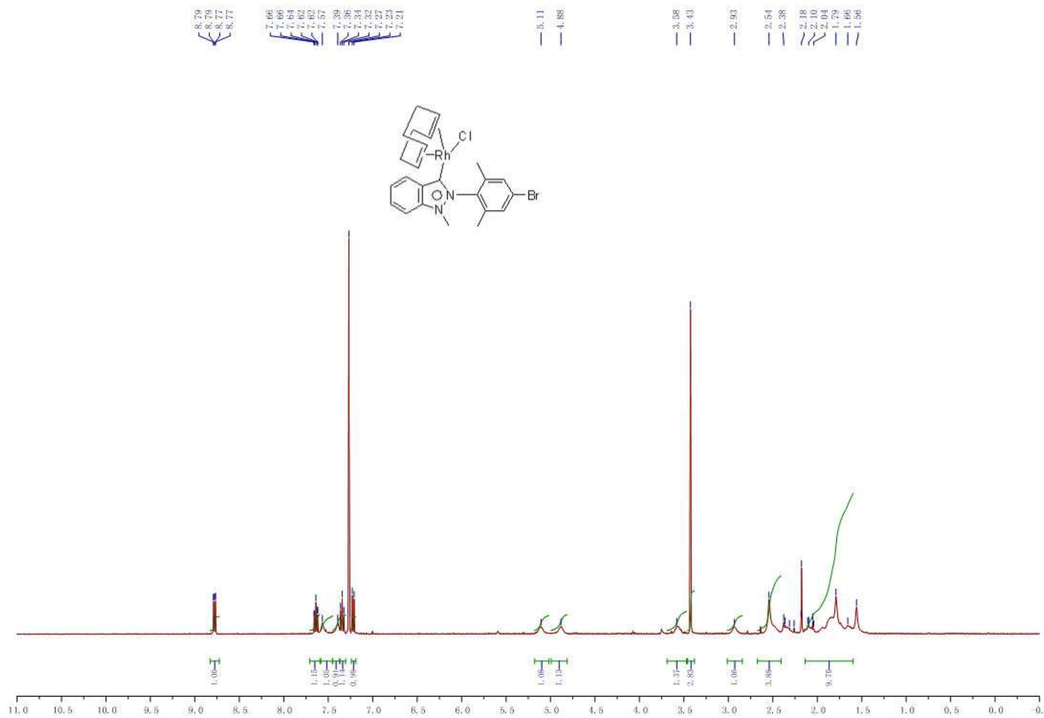
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2.54 2.38
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Br
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1.09 1.13
1.31 2.83
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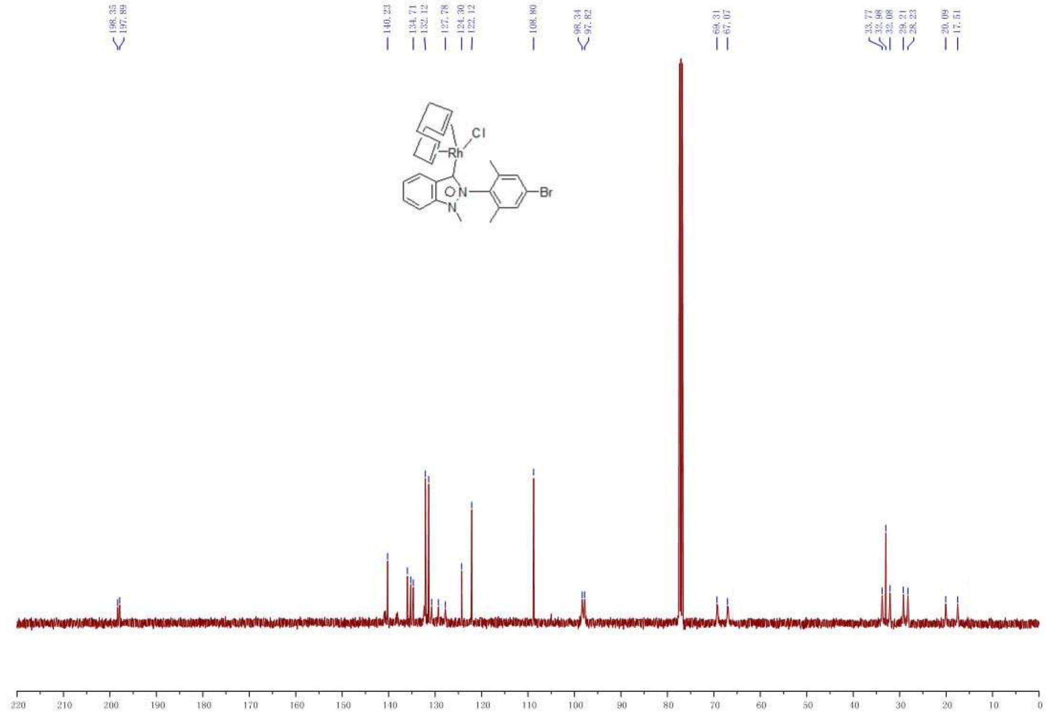
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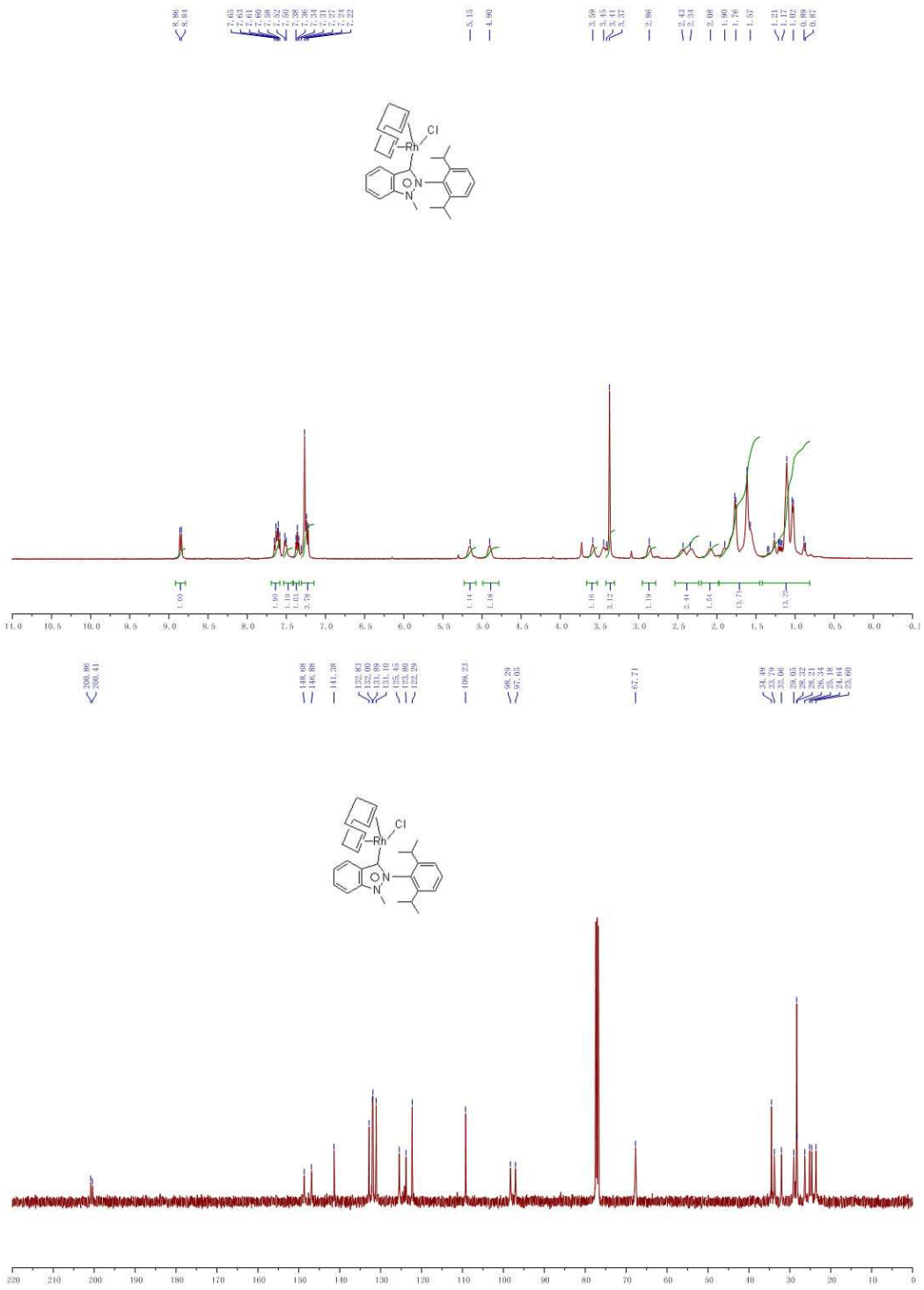

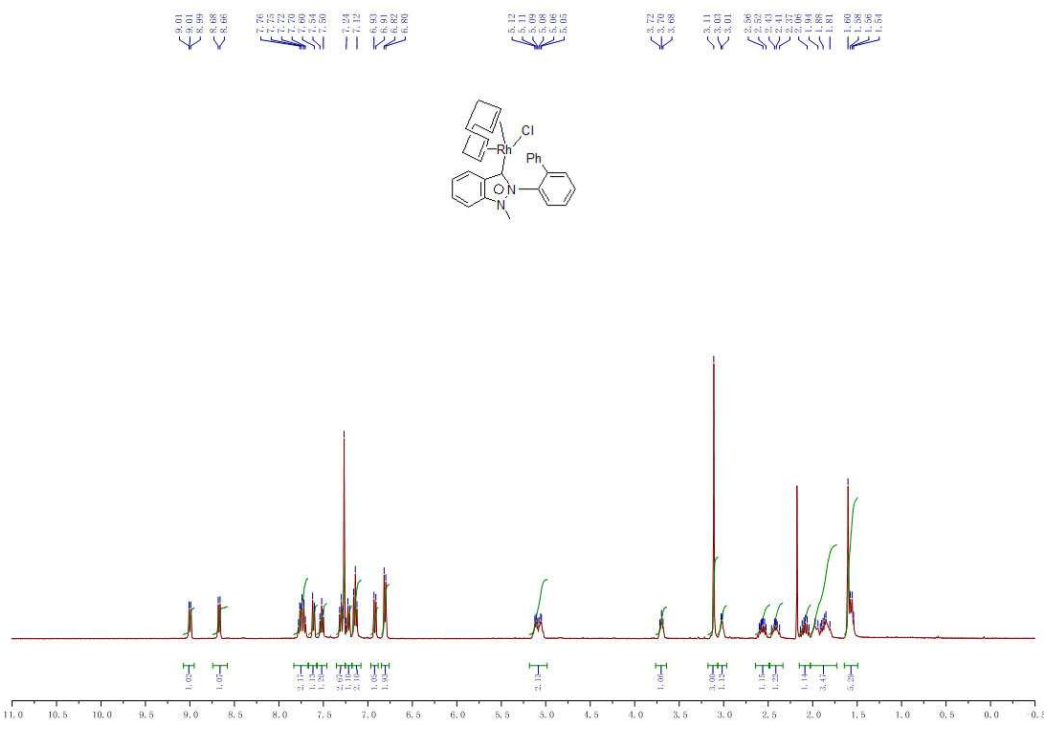
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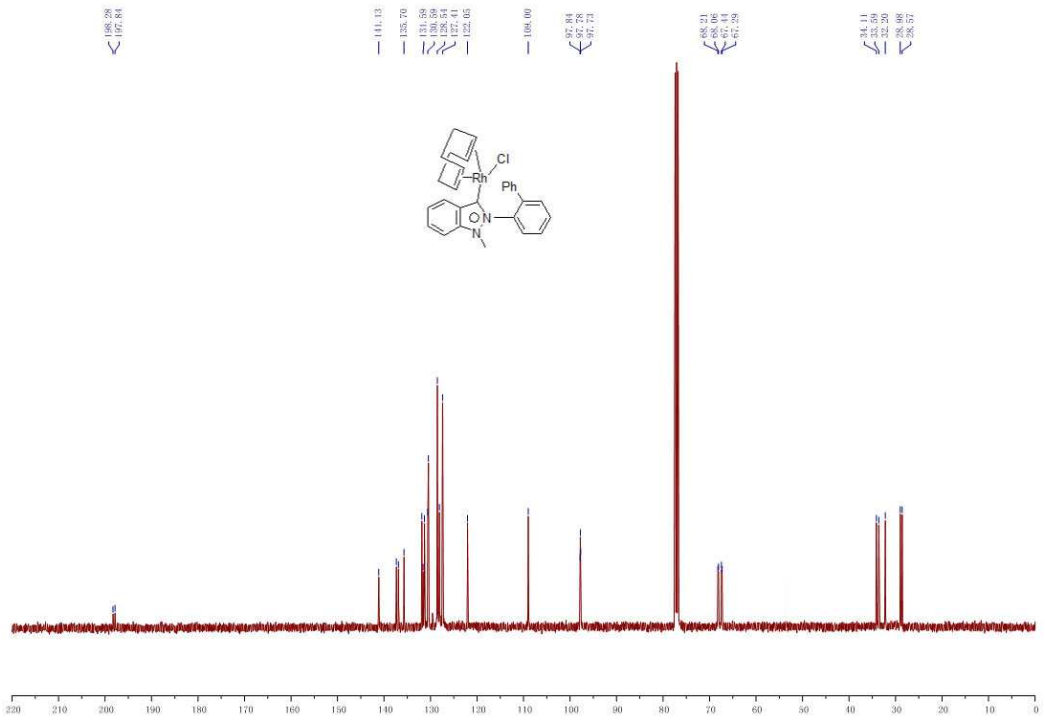
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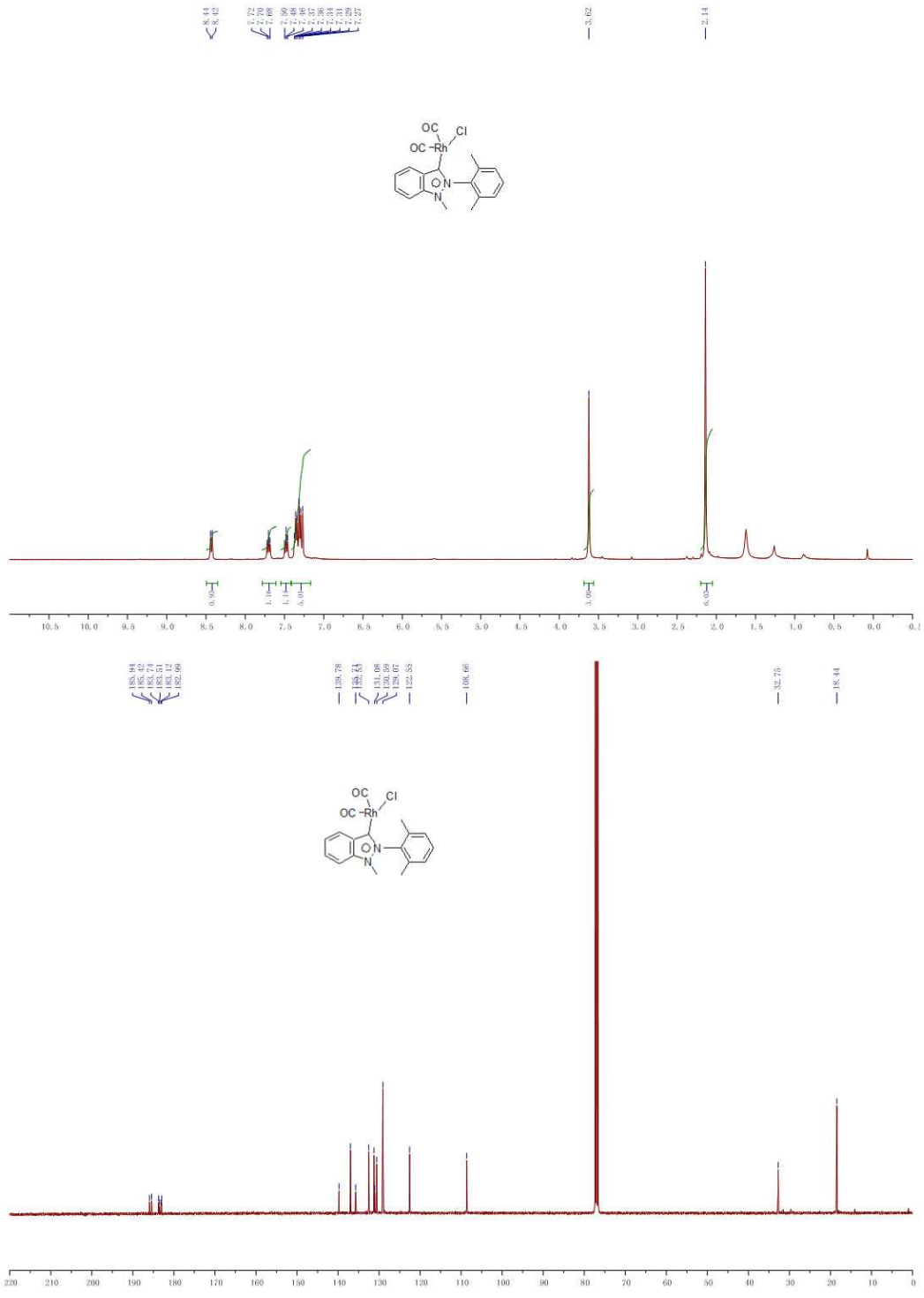
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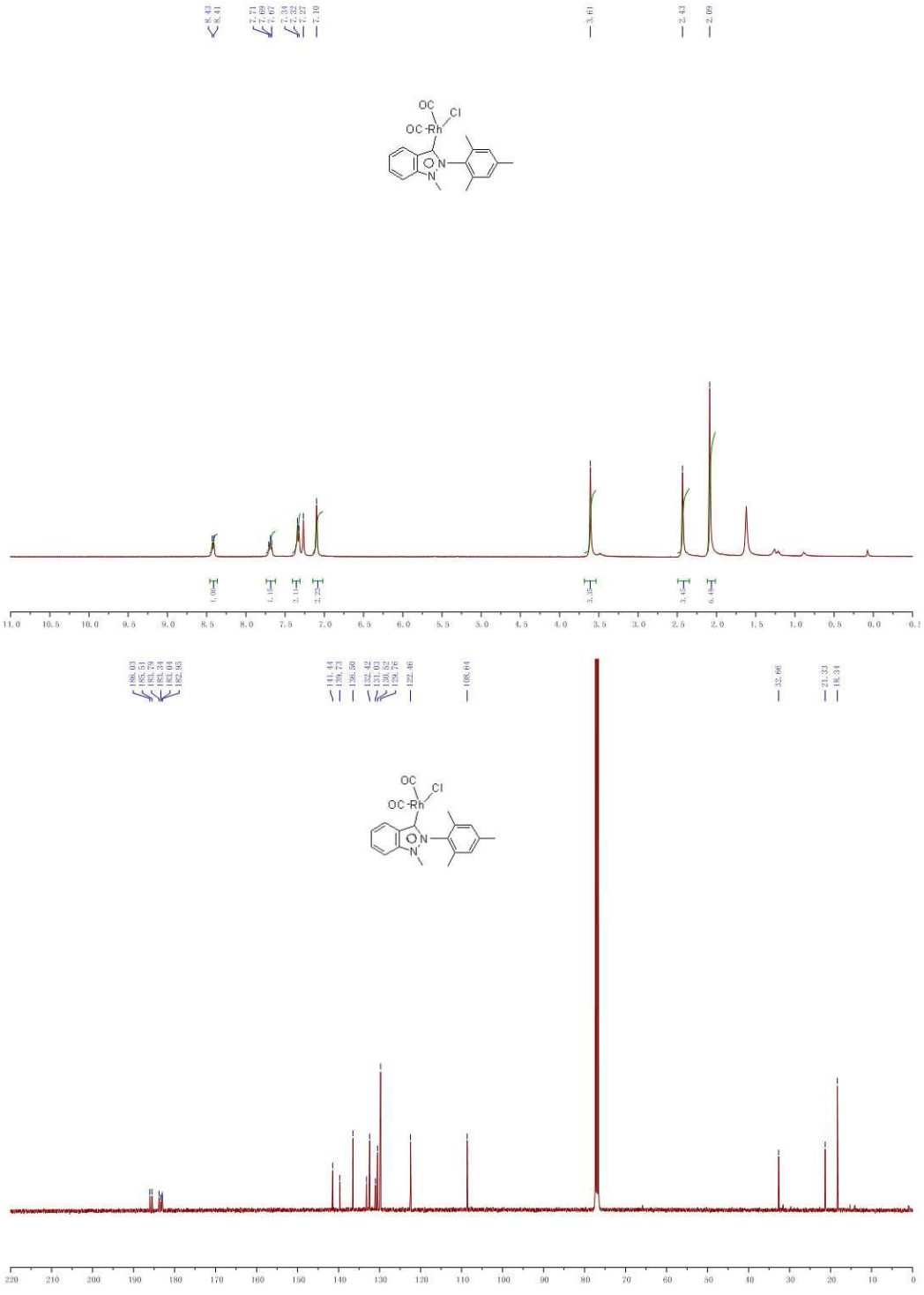
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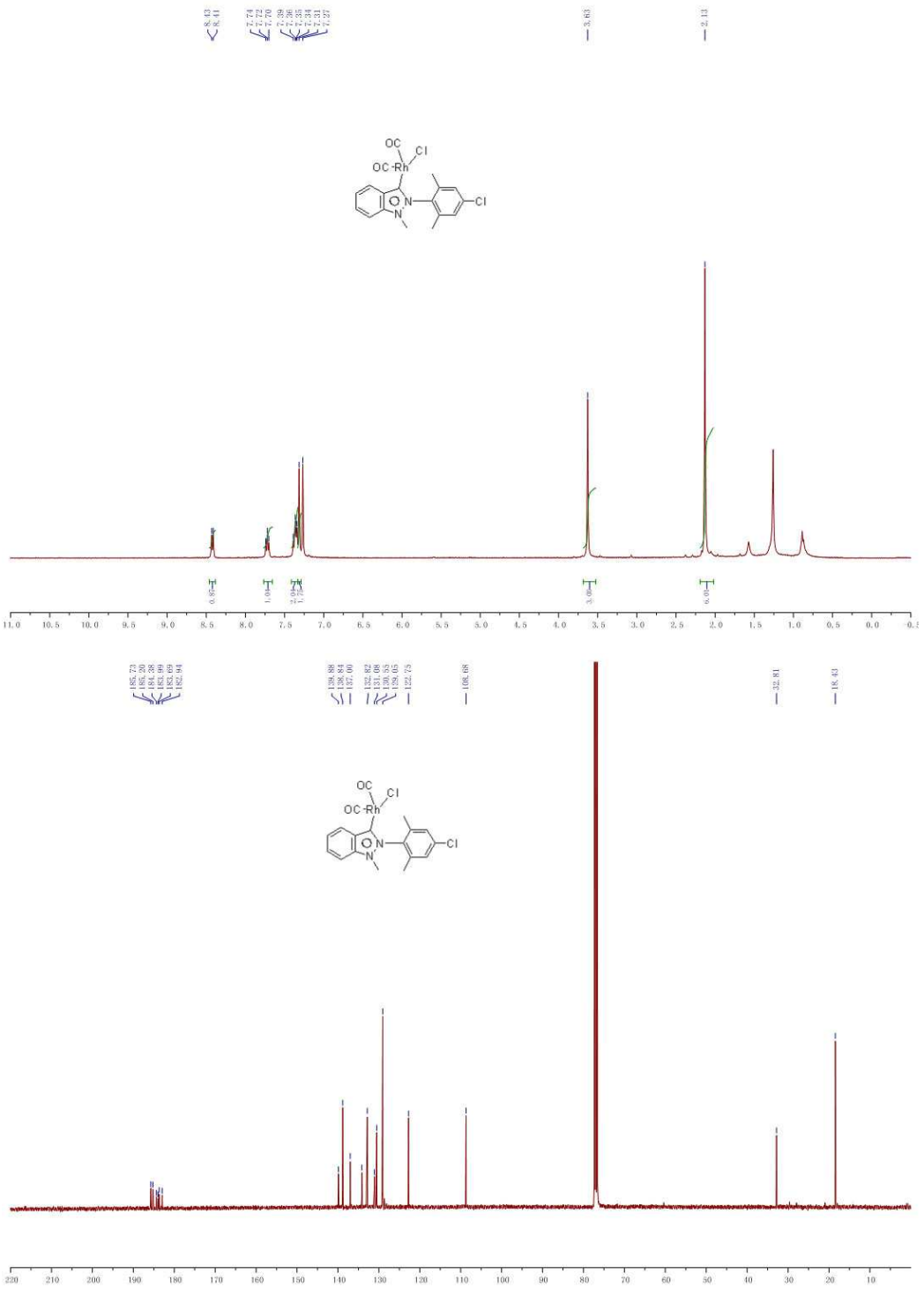
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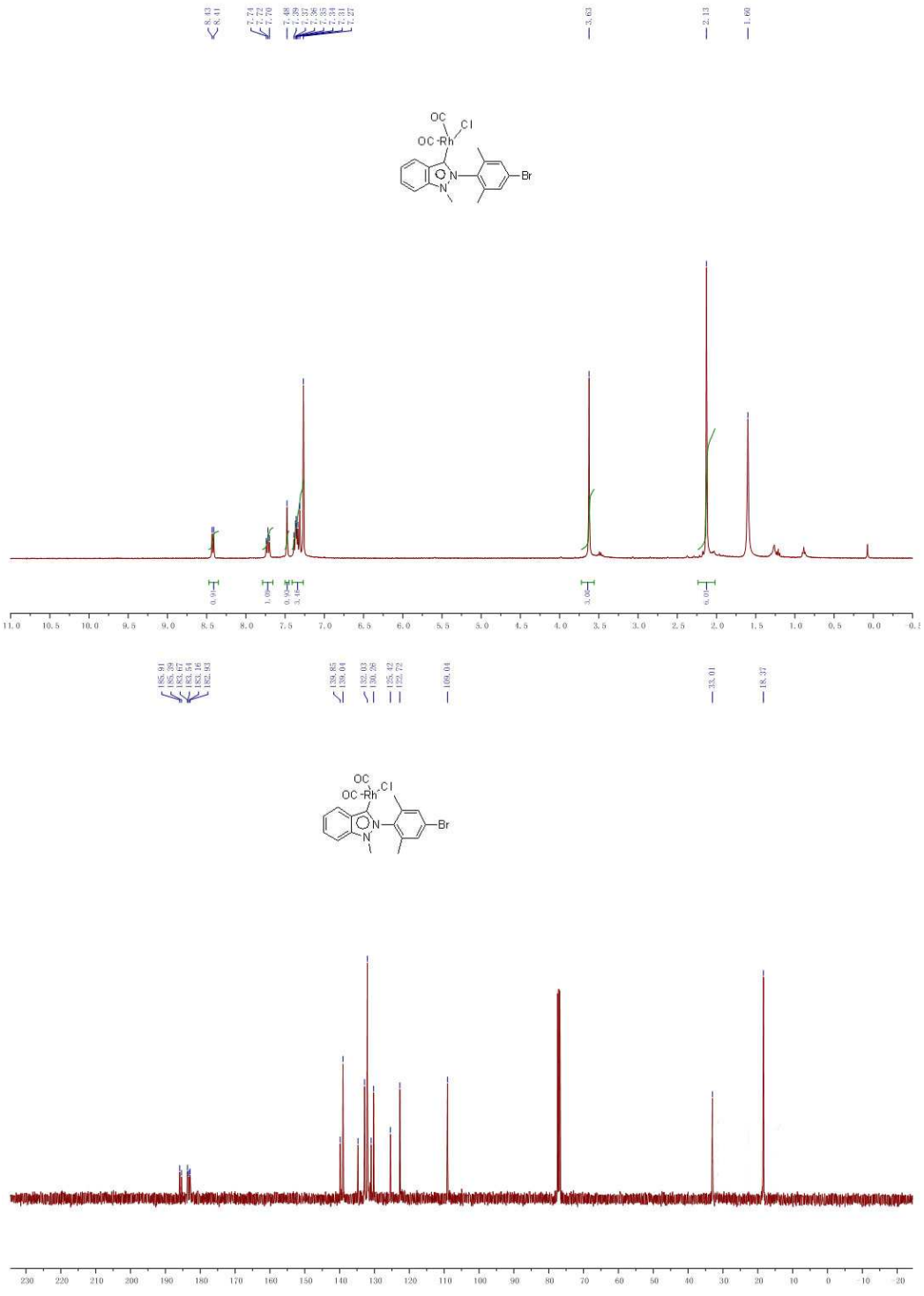
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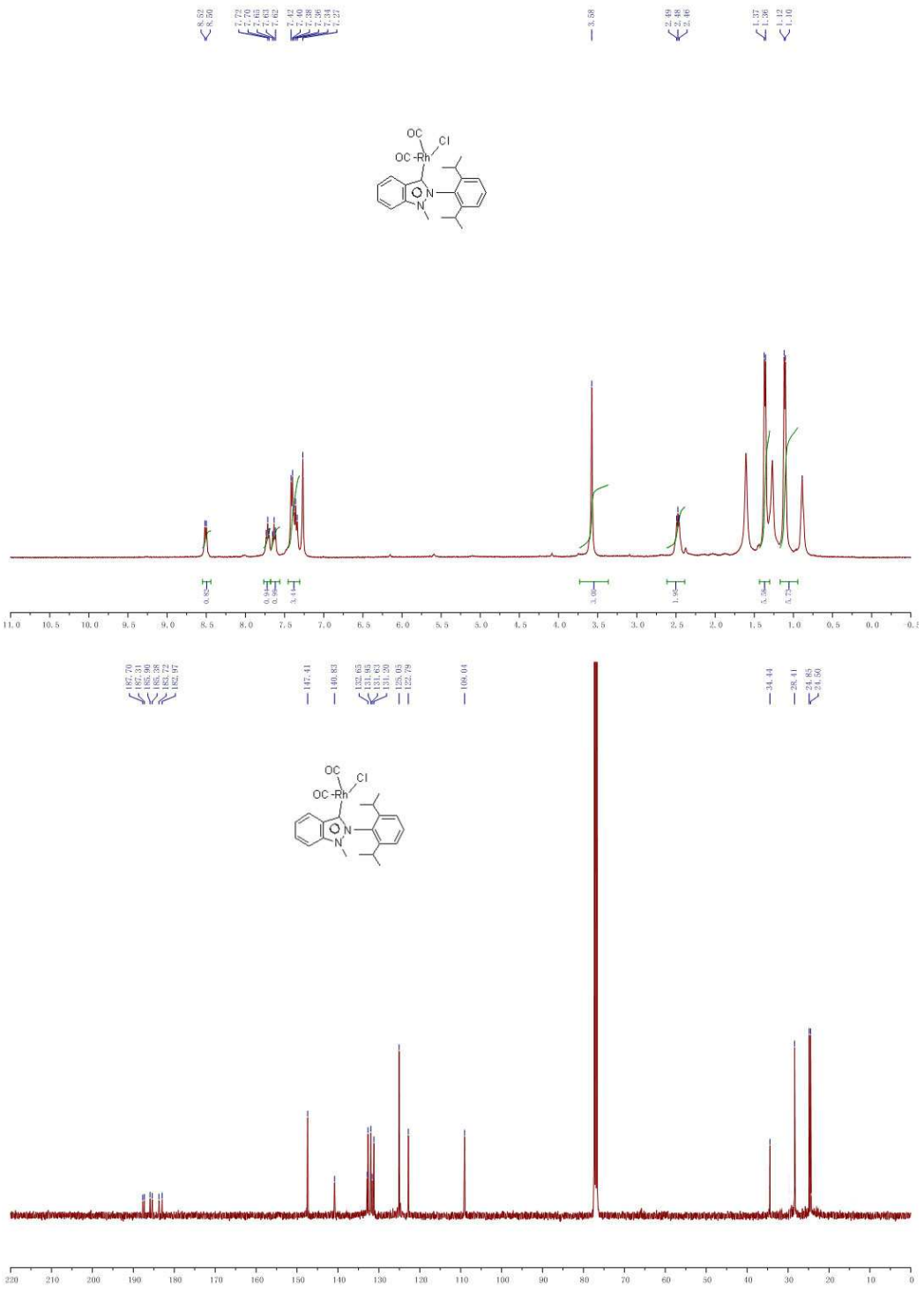

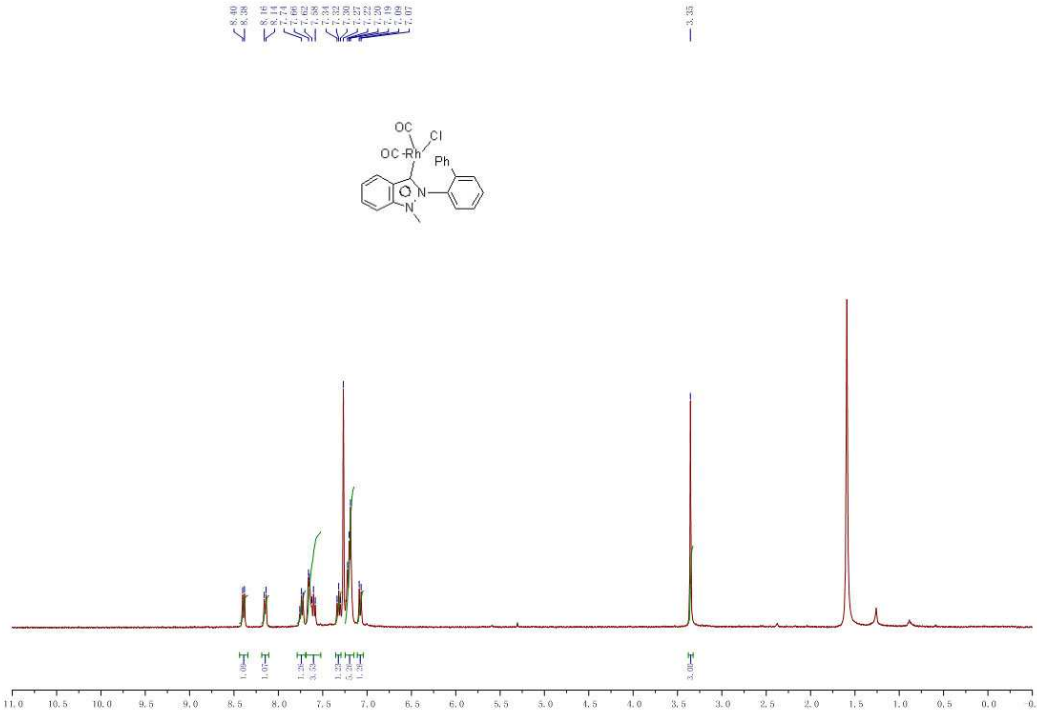
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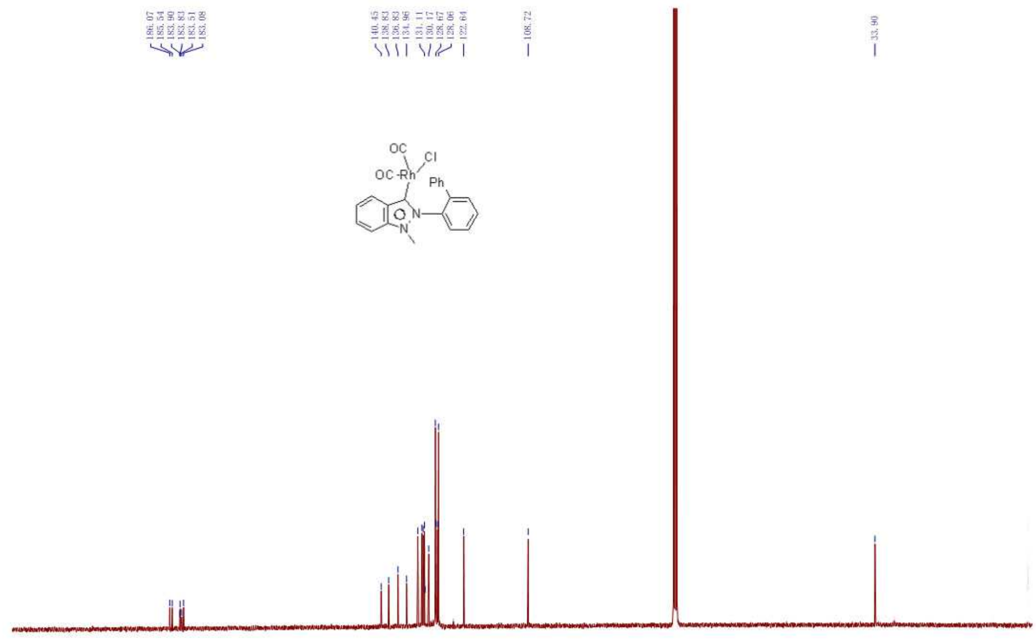
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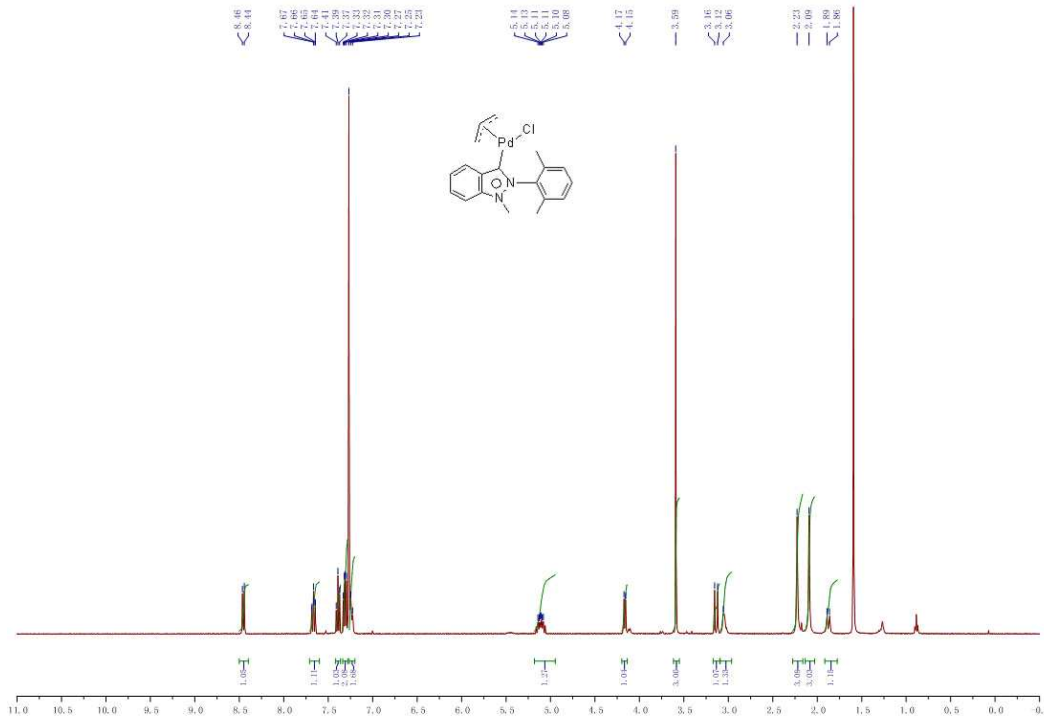
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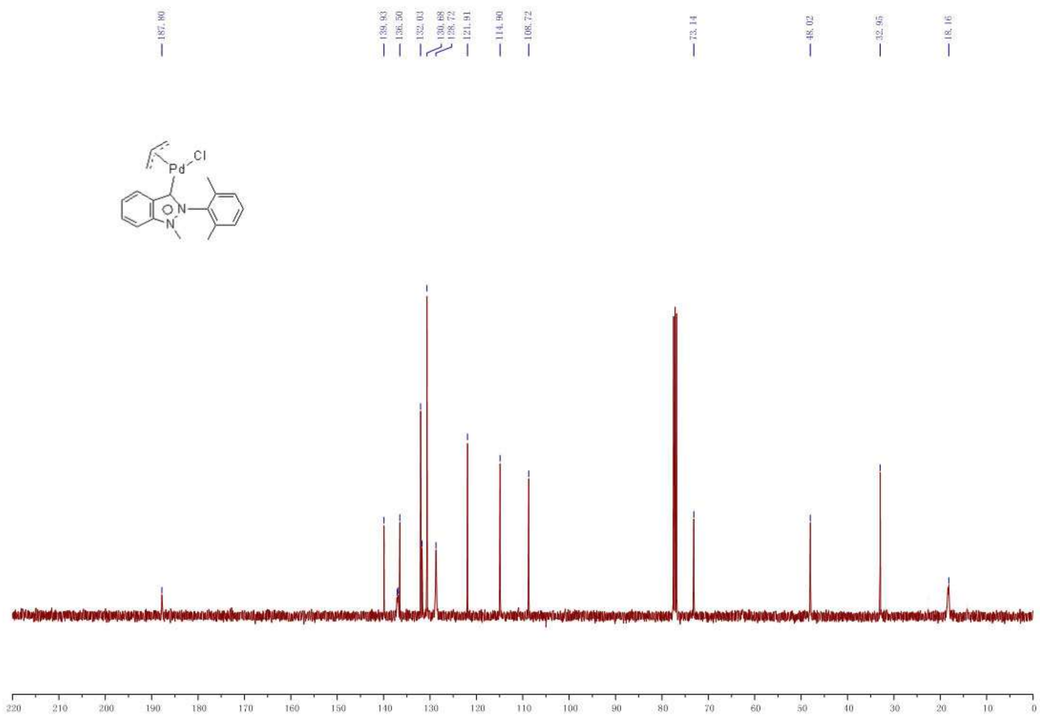
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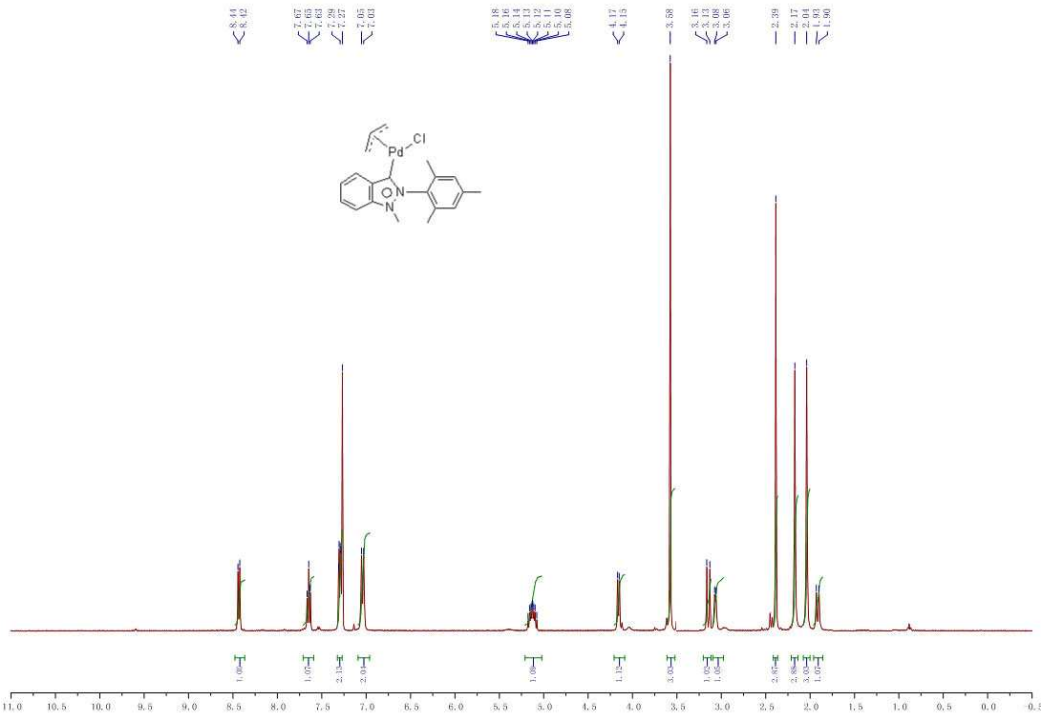
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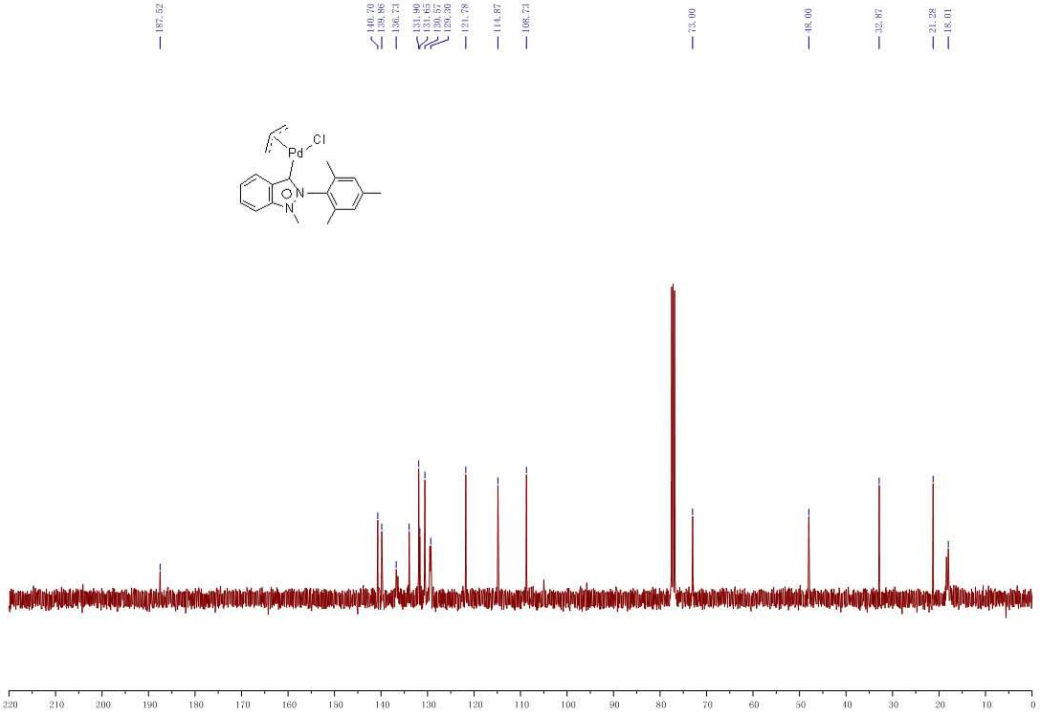
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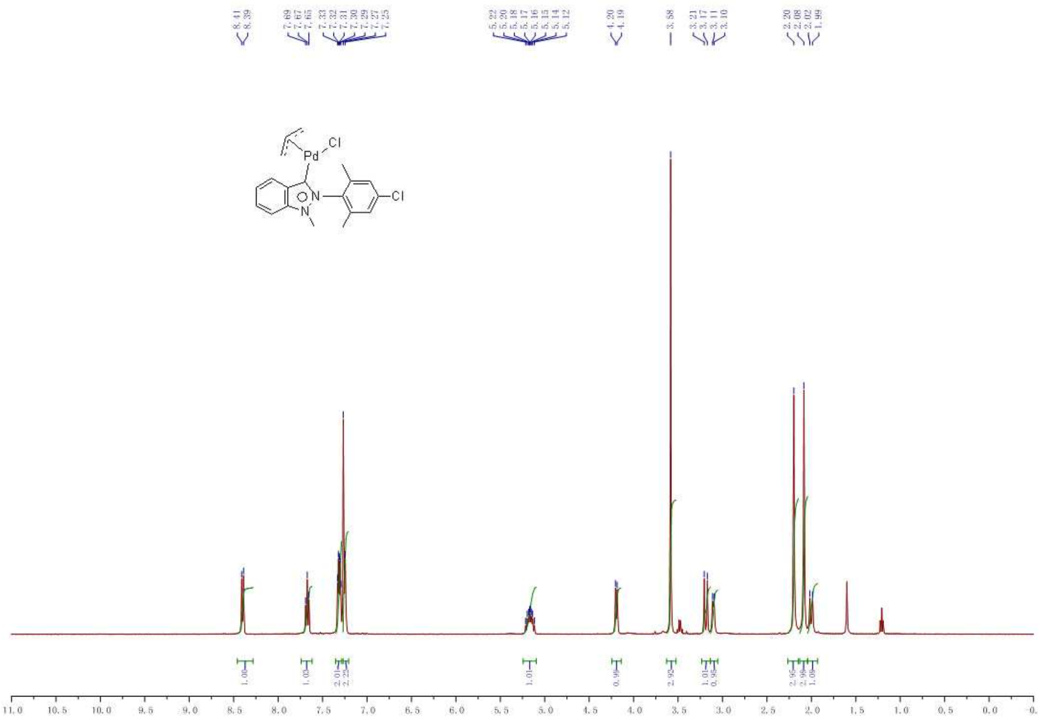

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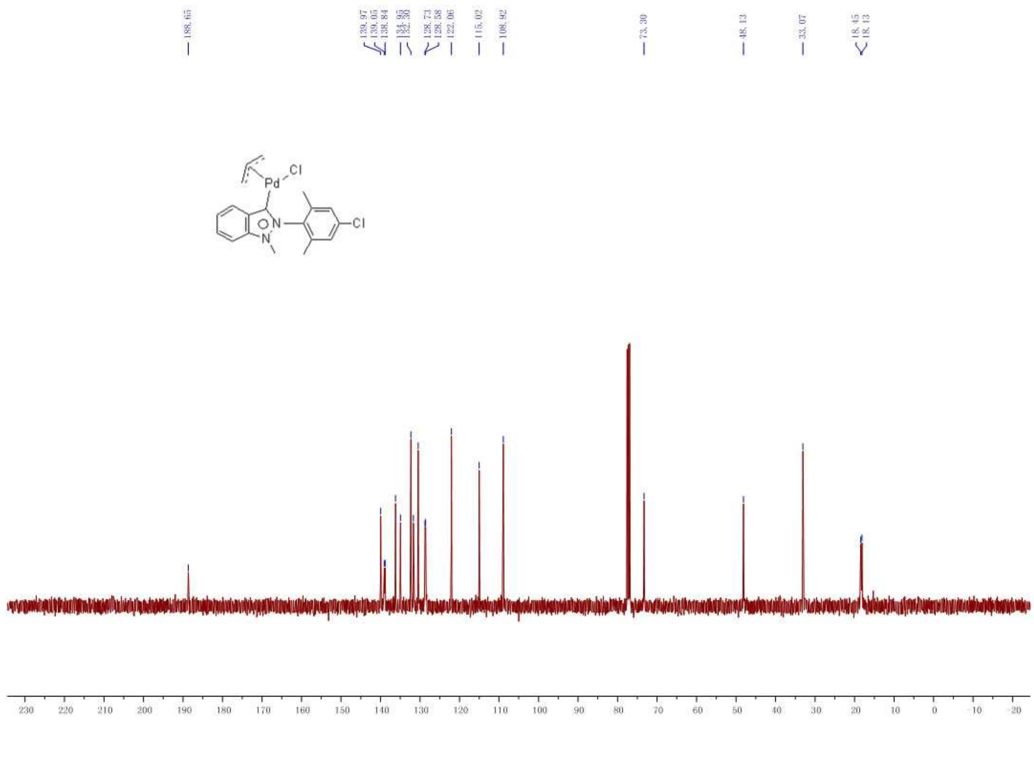

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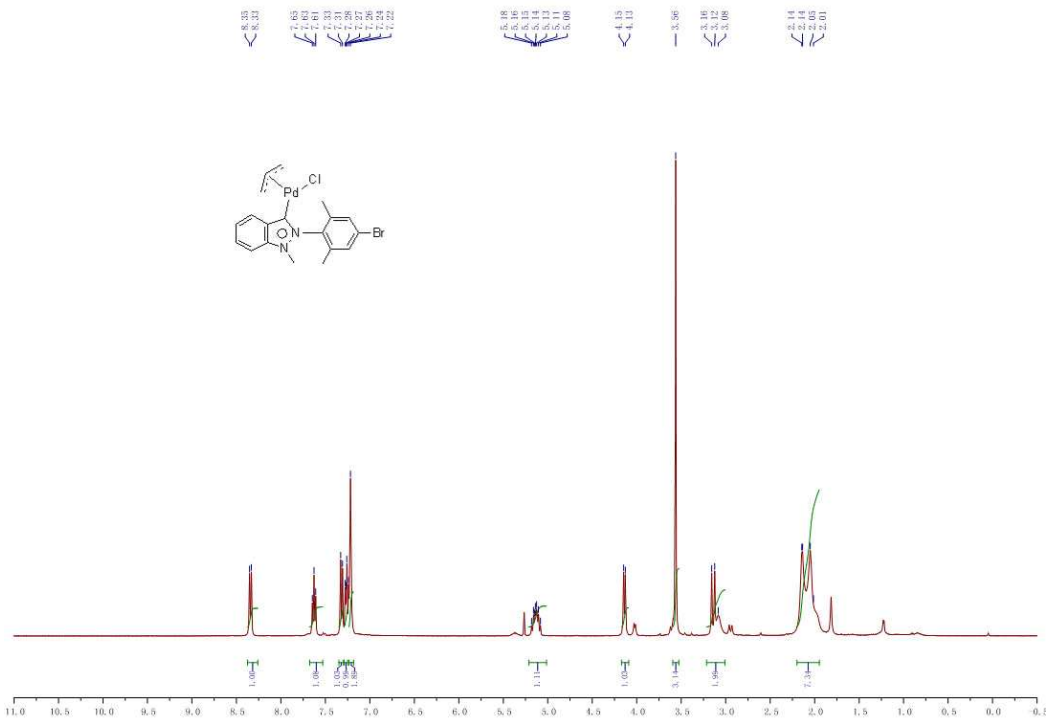
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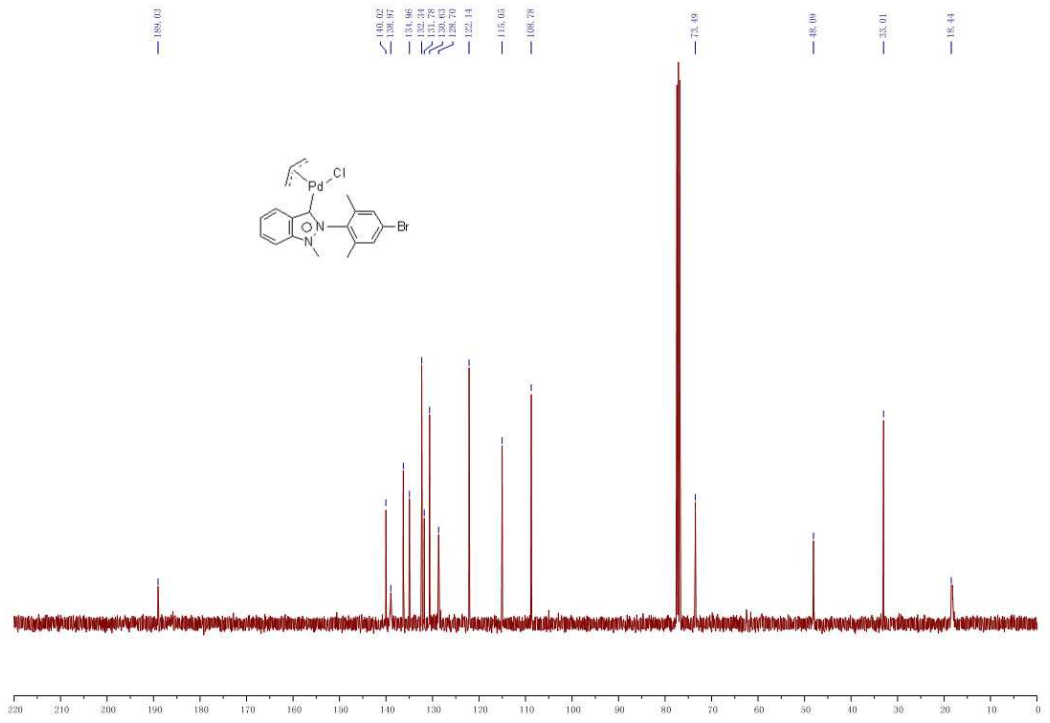
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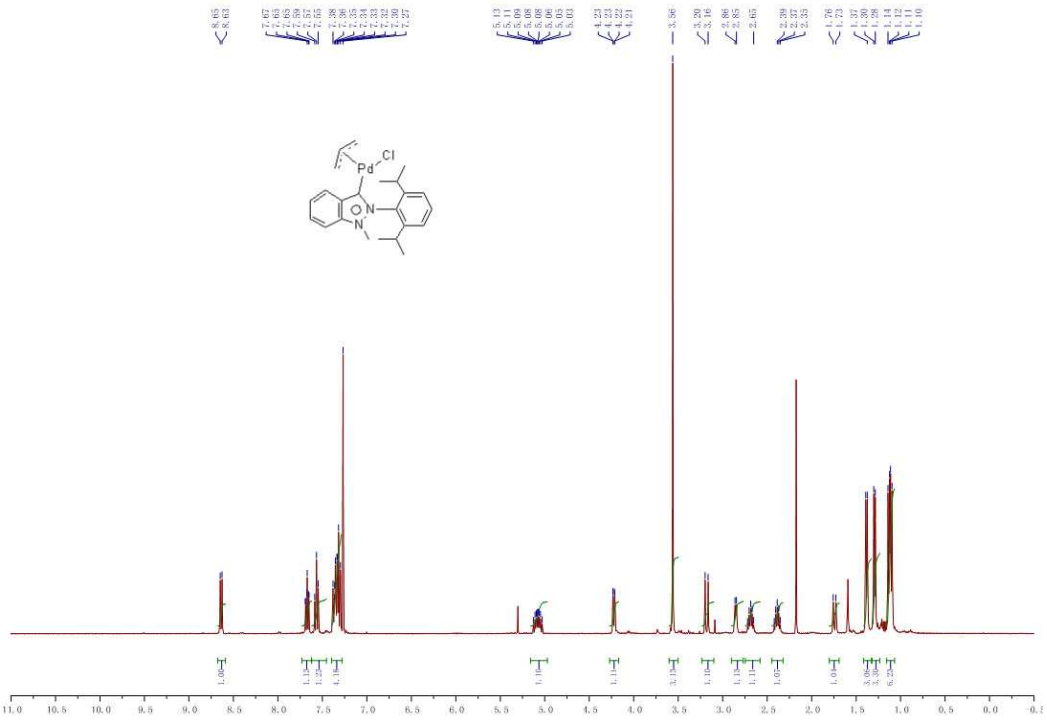
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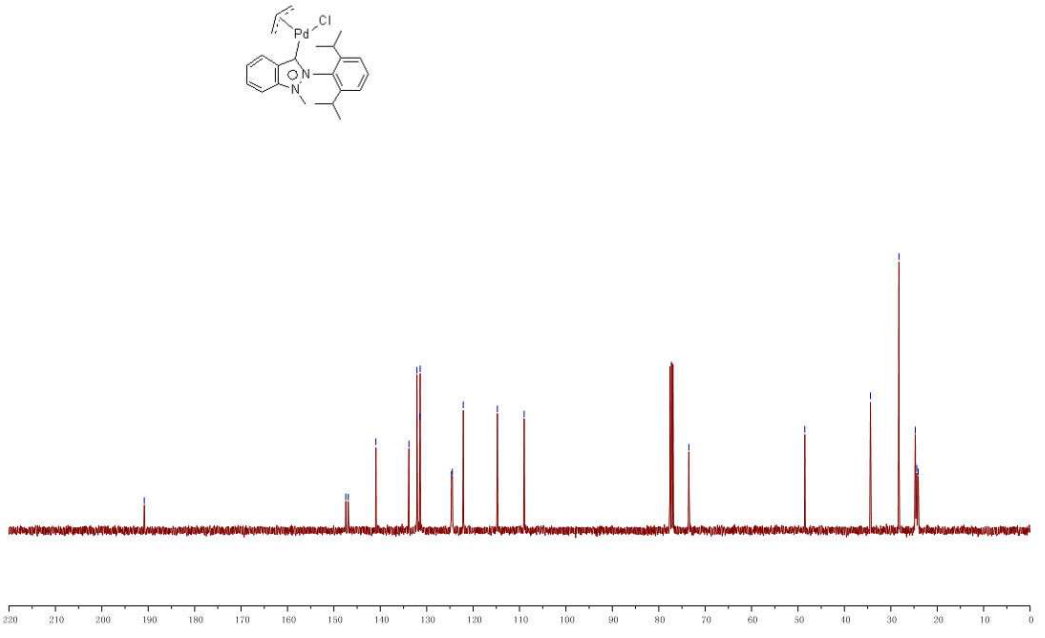
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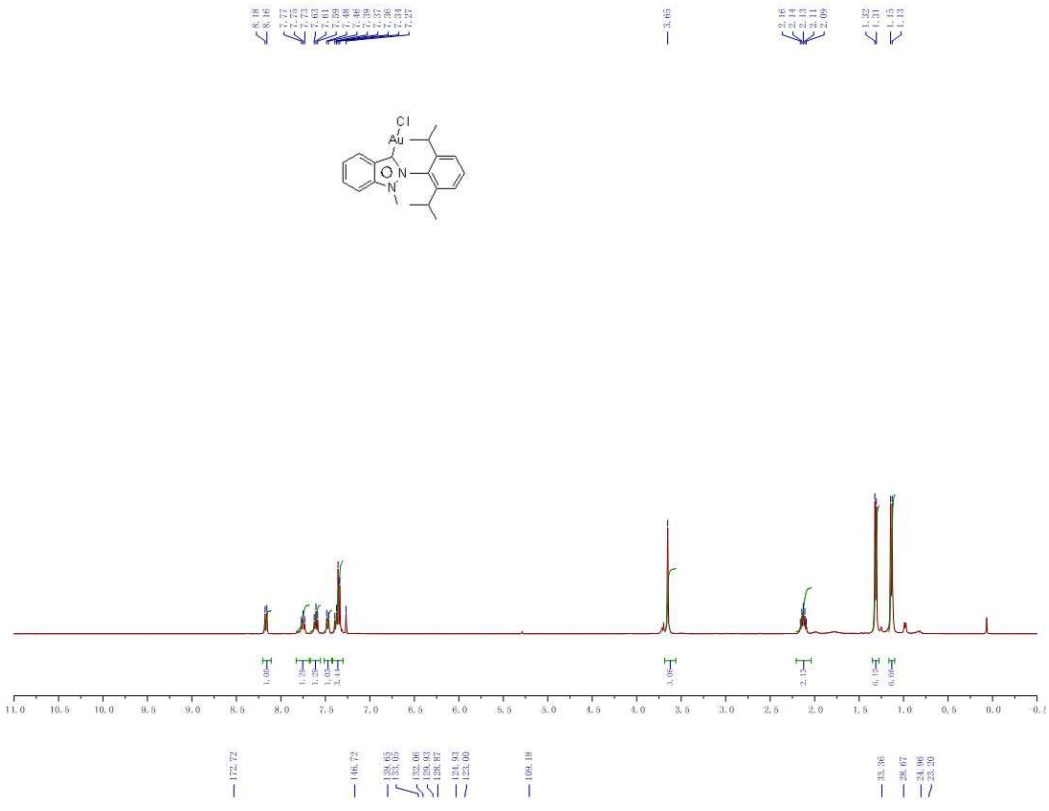

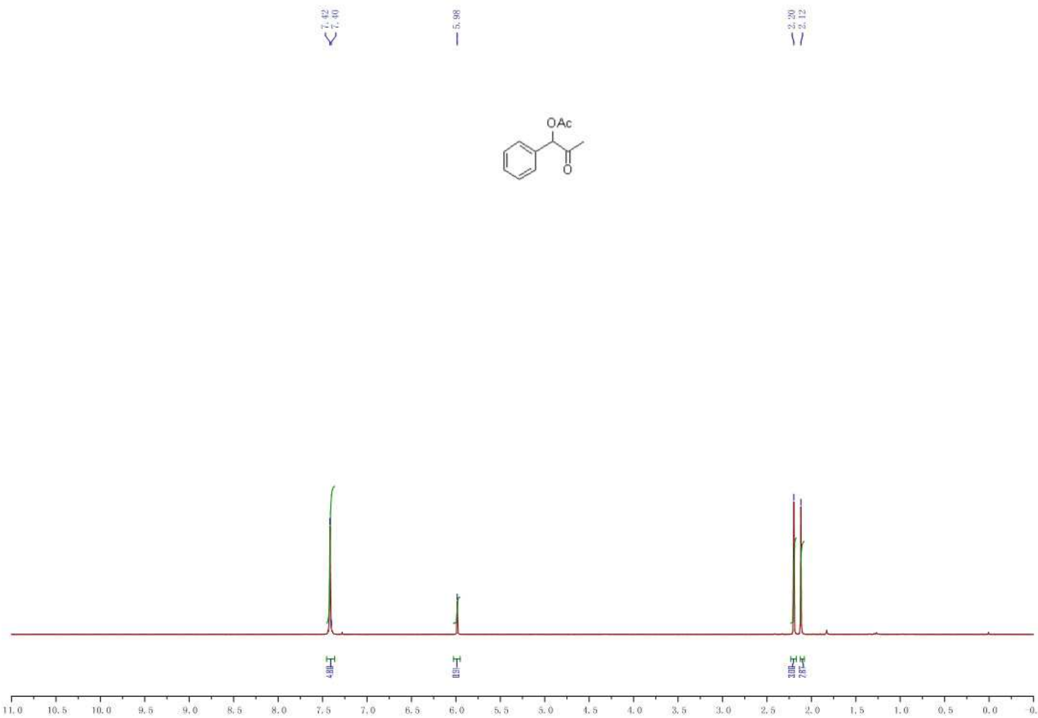
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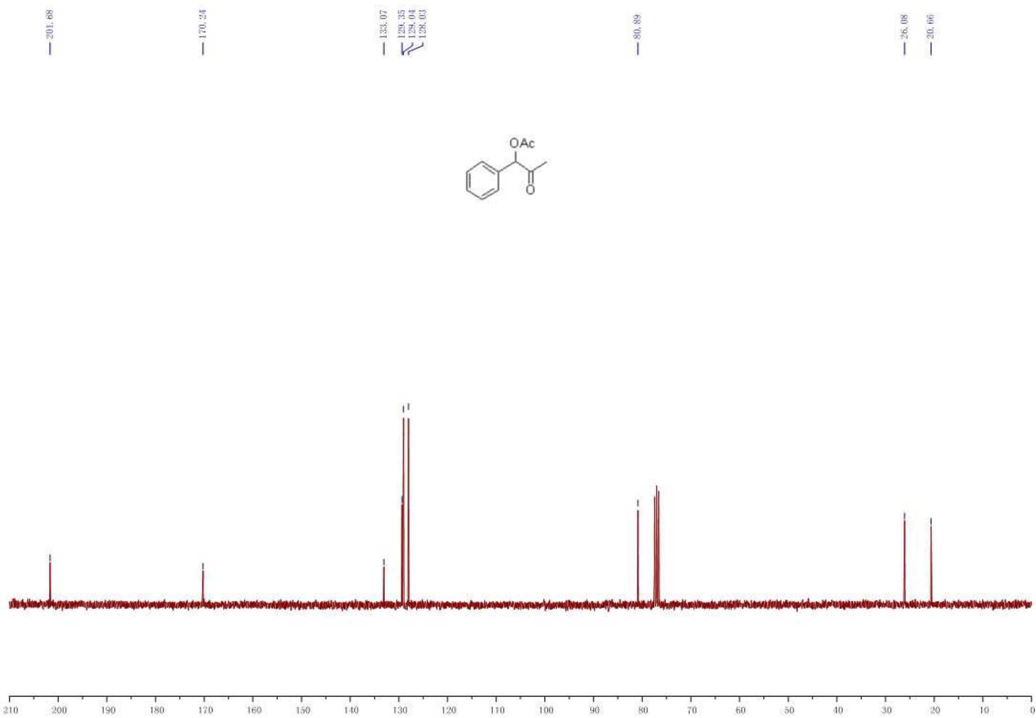
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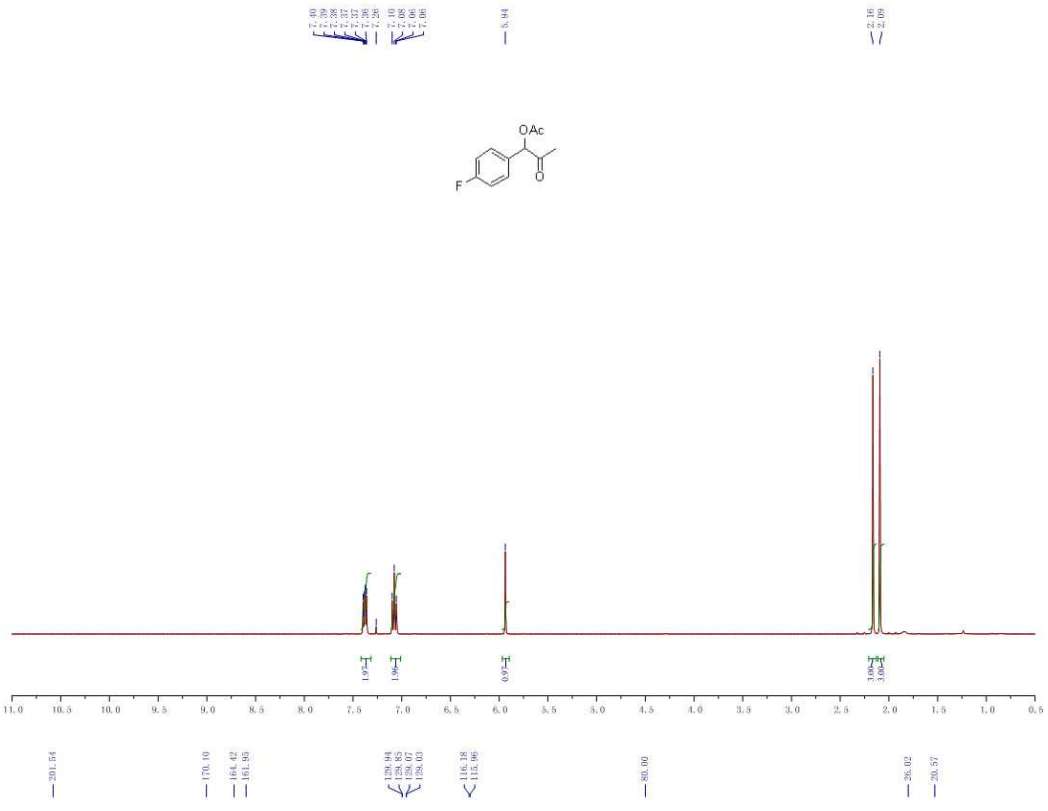
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1.96
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3.00
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9.0
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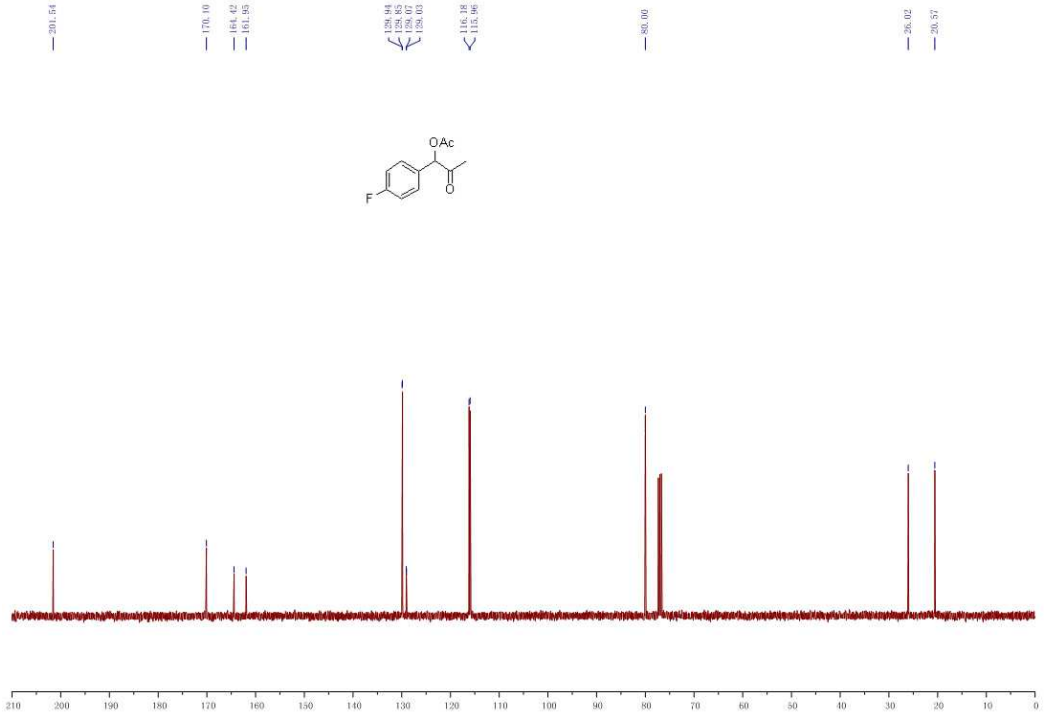
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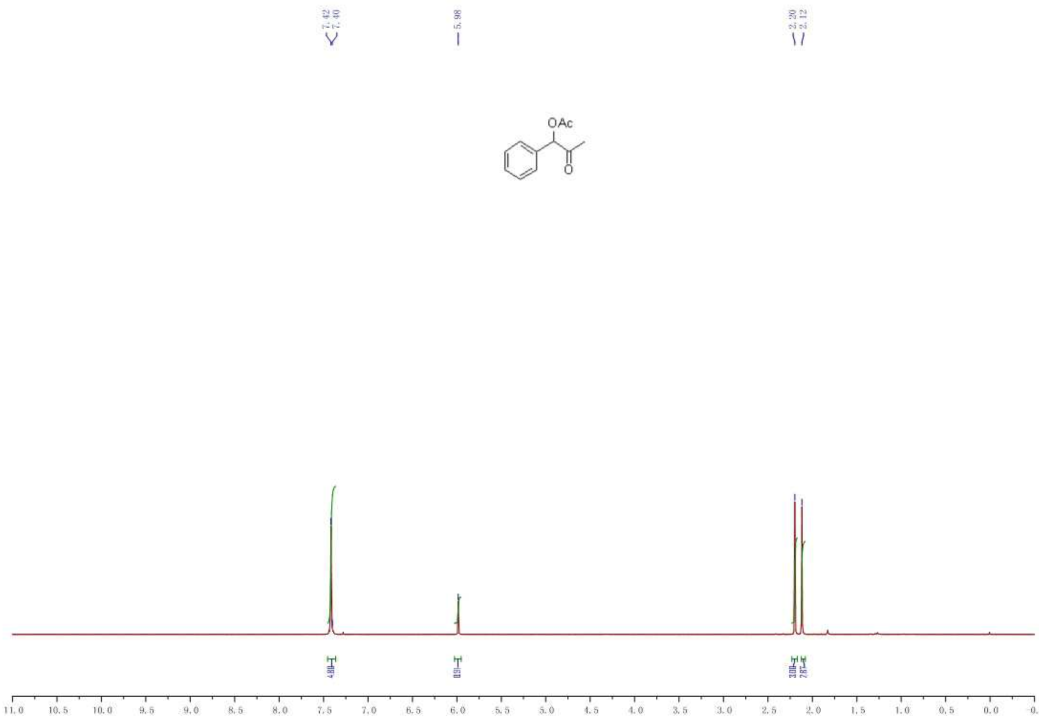
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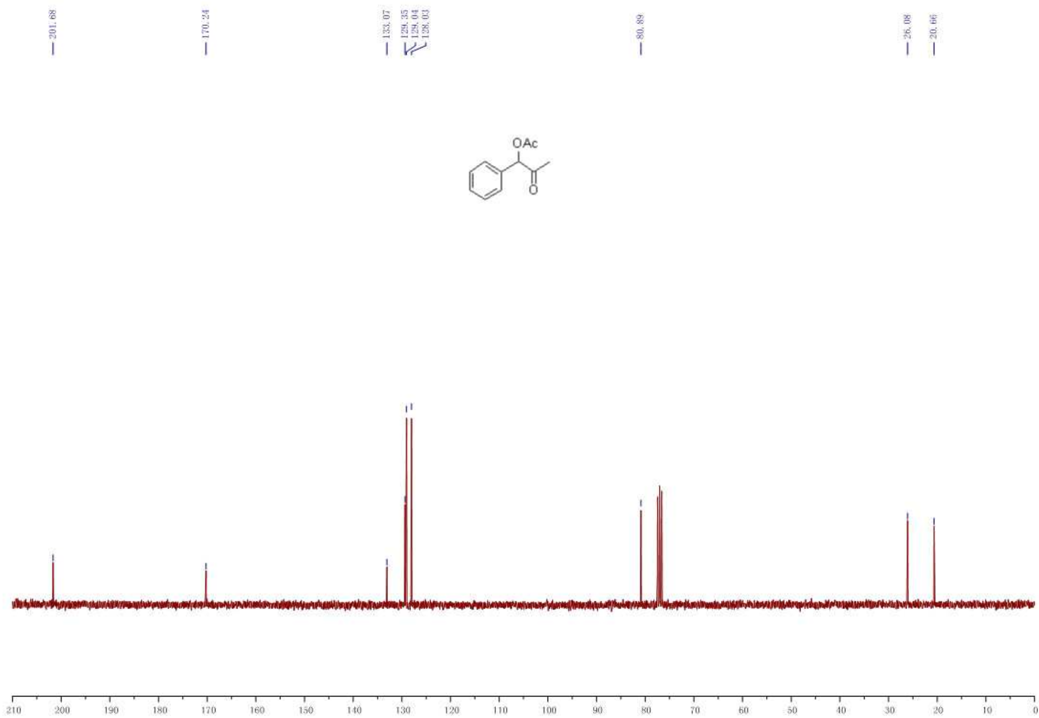
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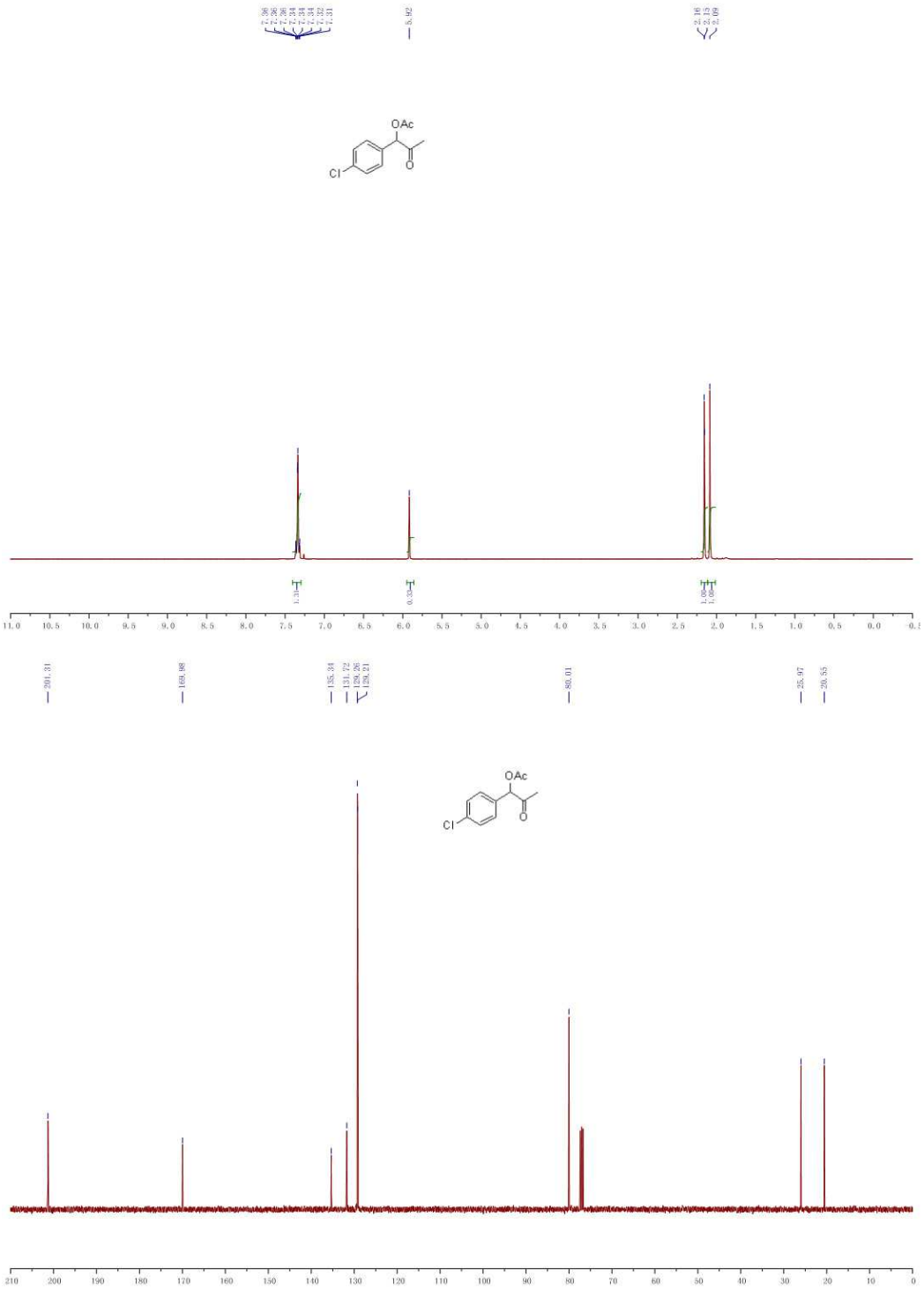
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2.0
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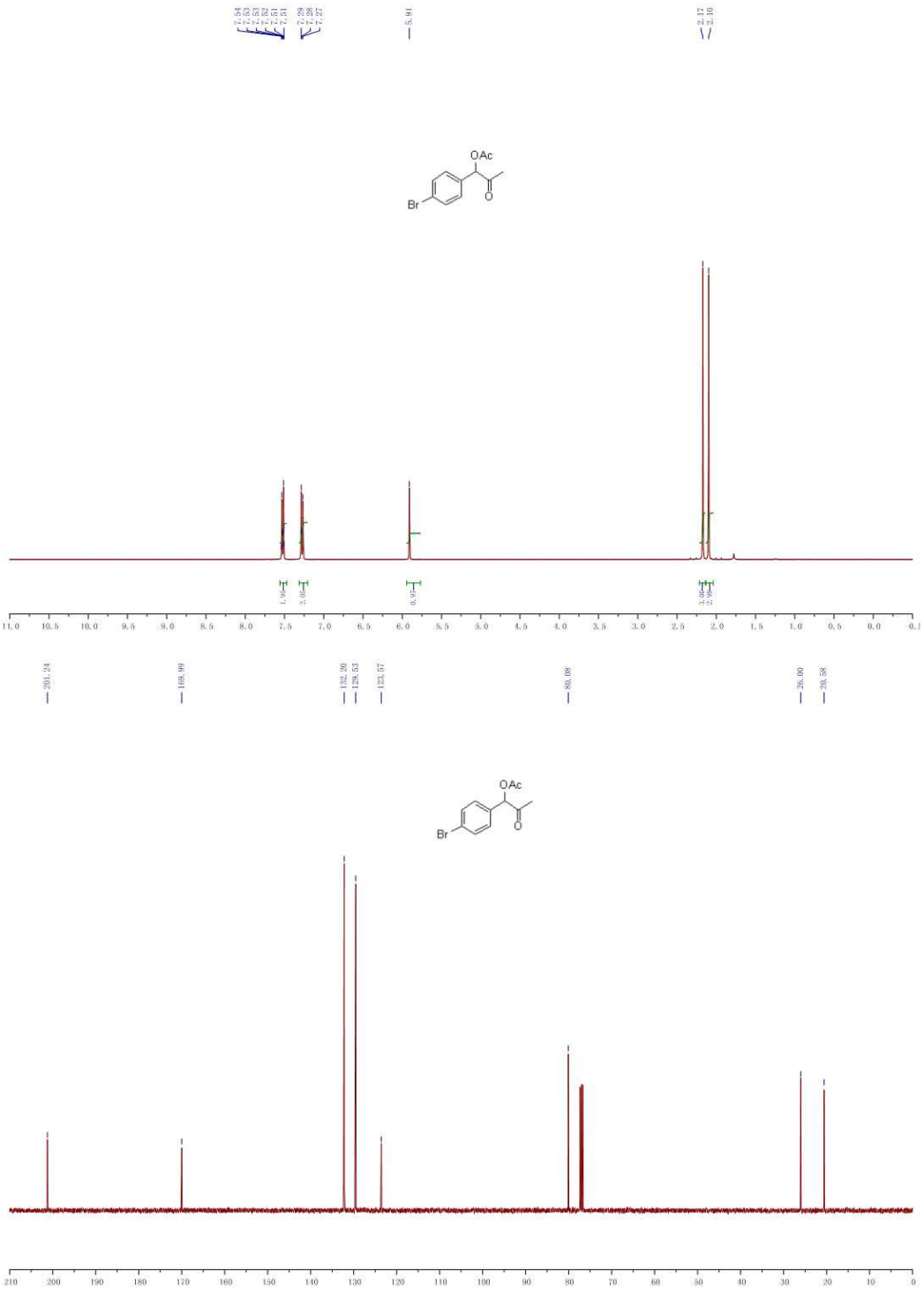
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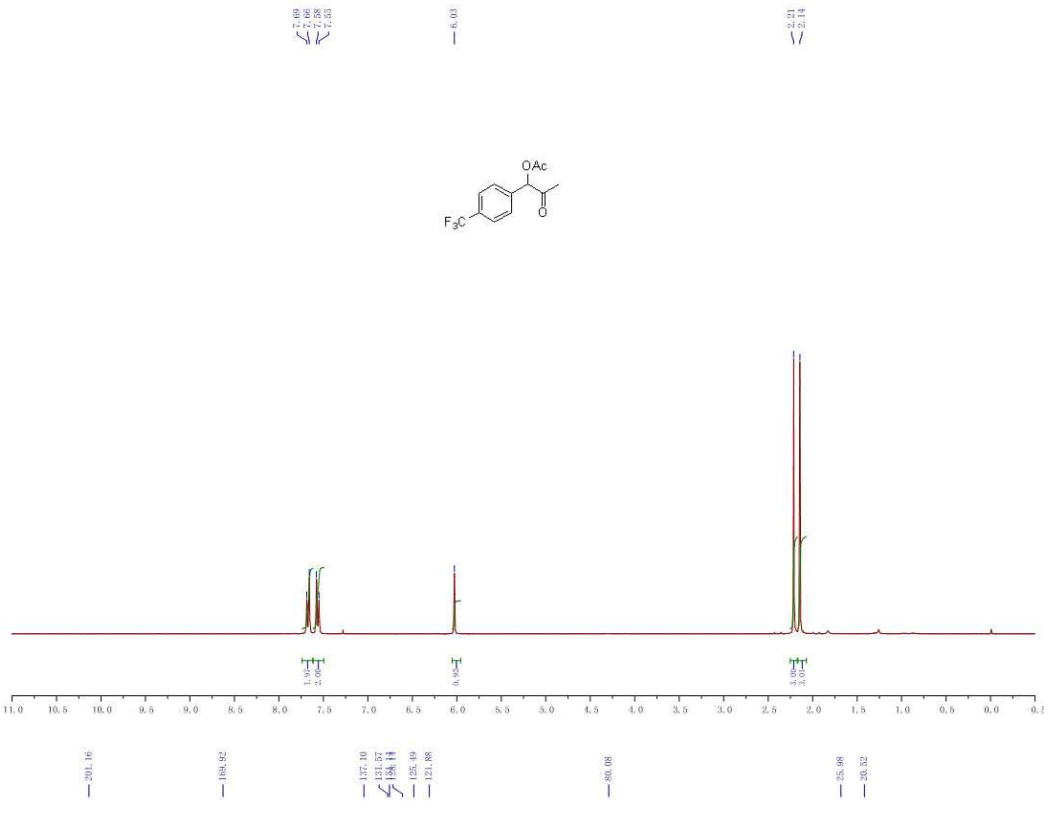
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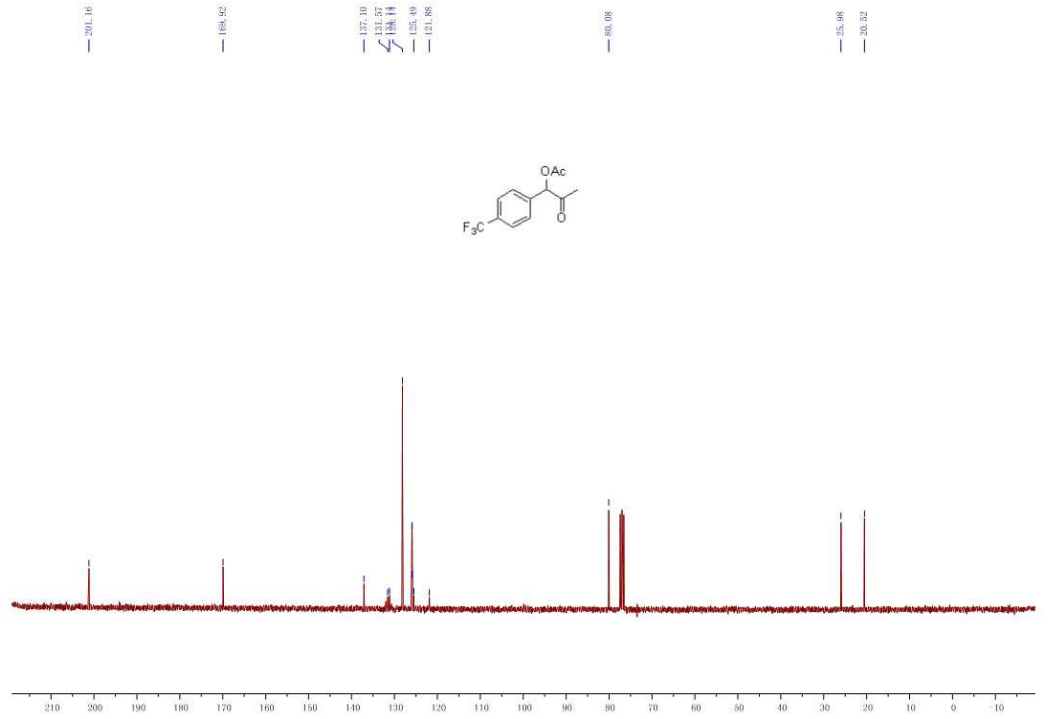
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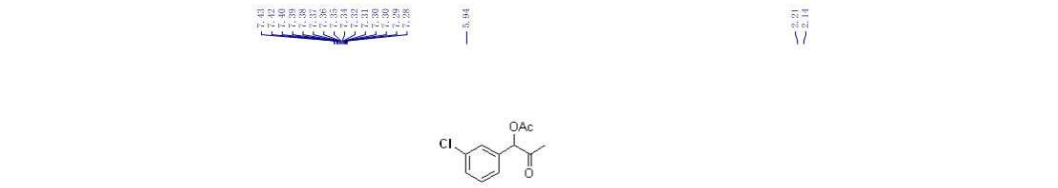
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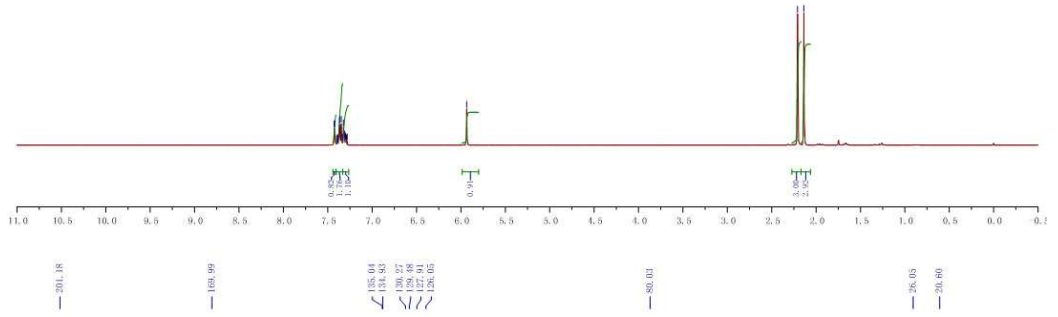
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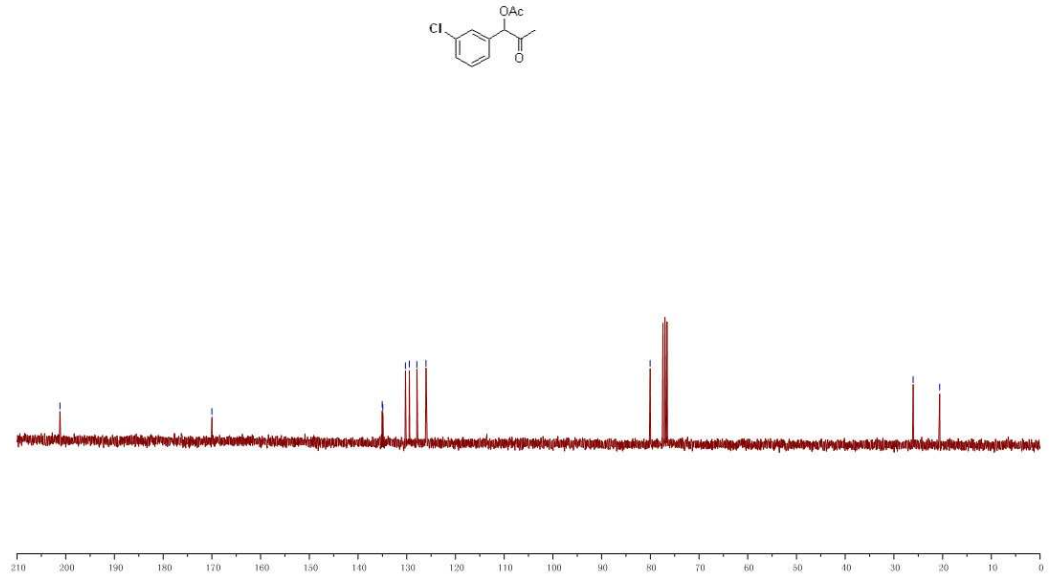
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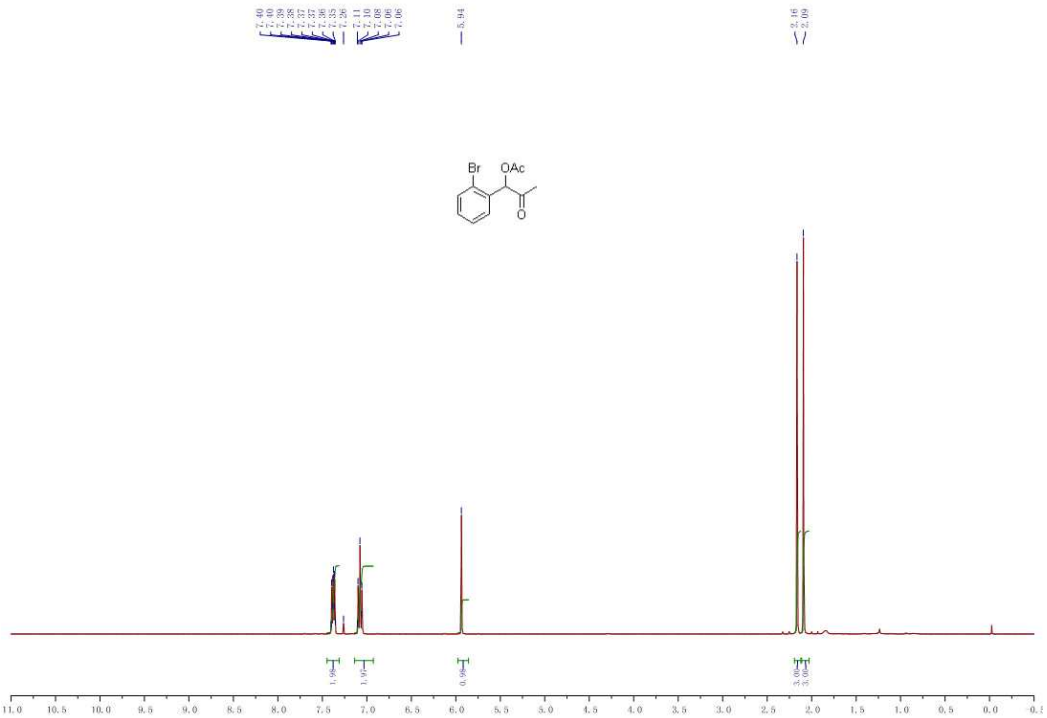
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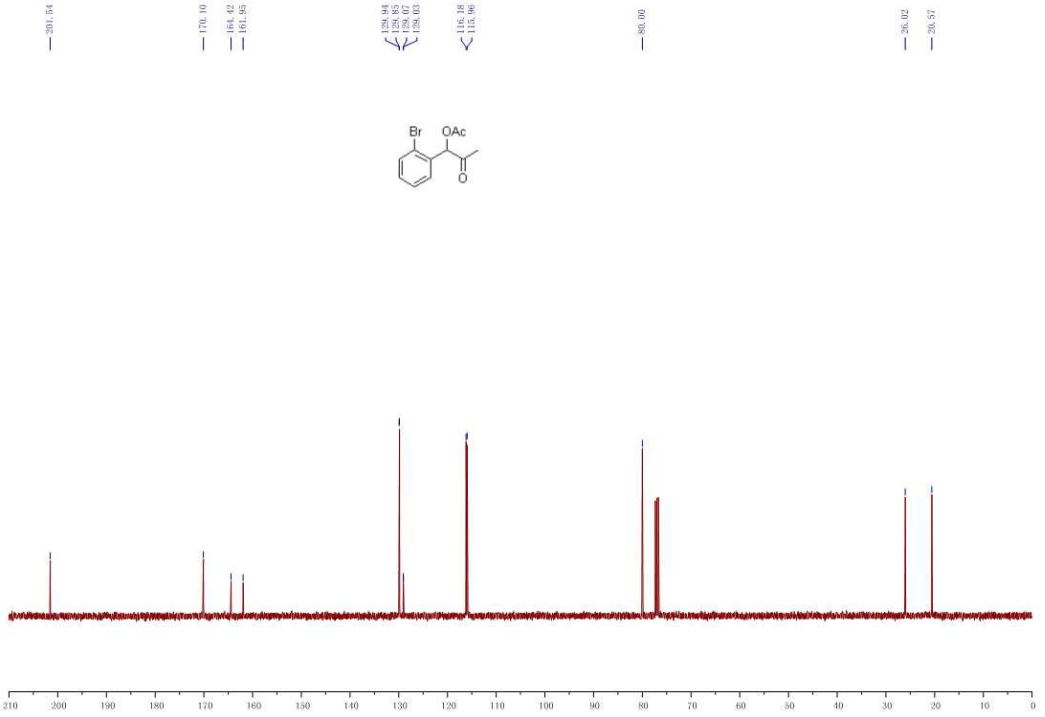
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O
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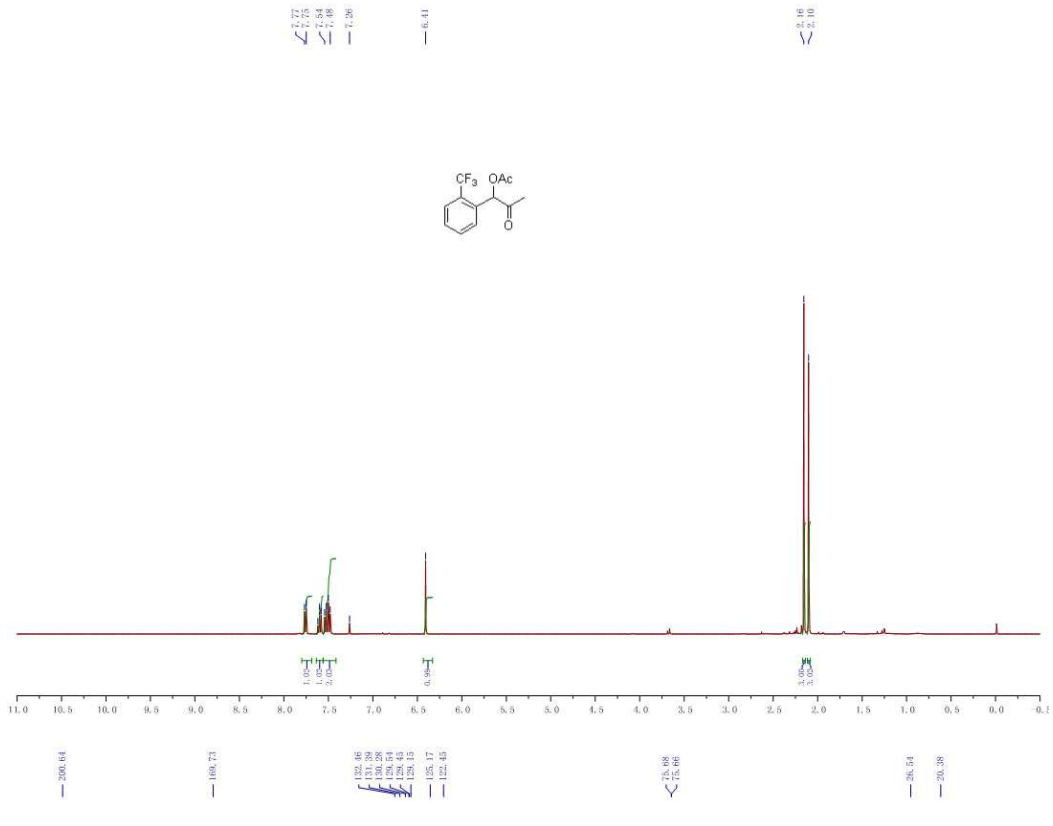
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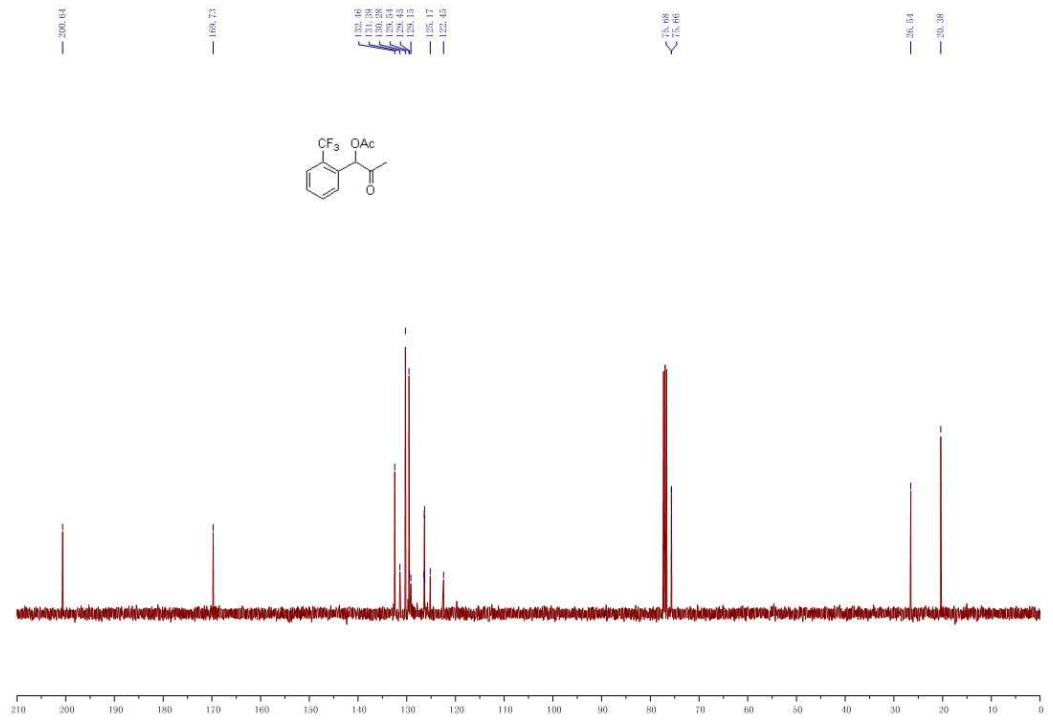
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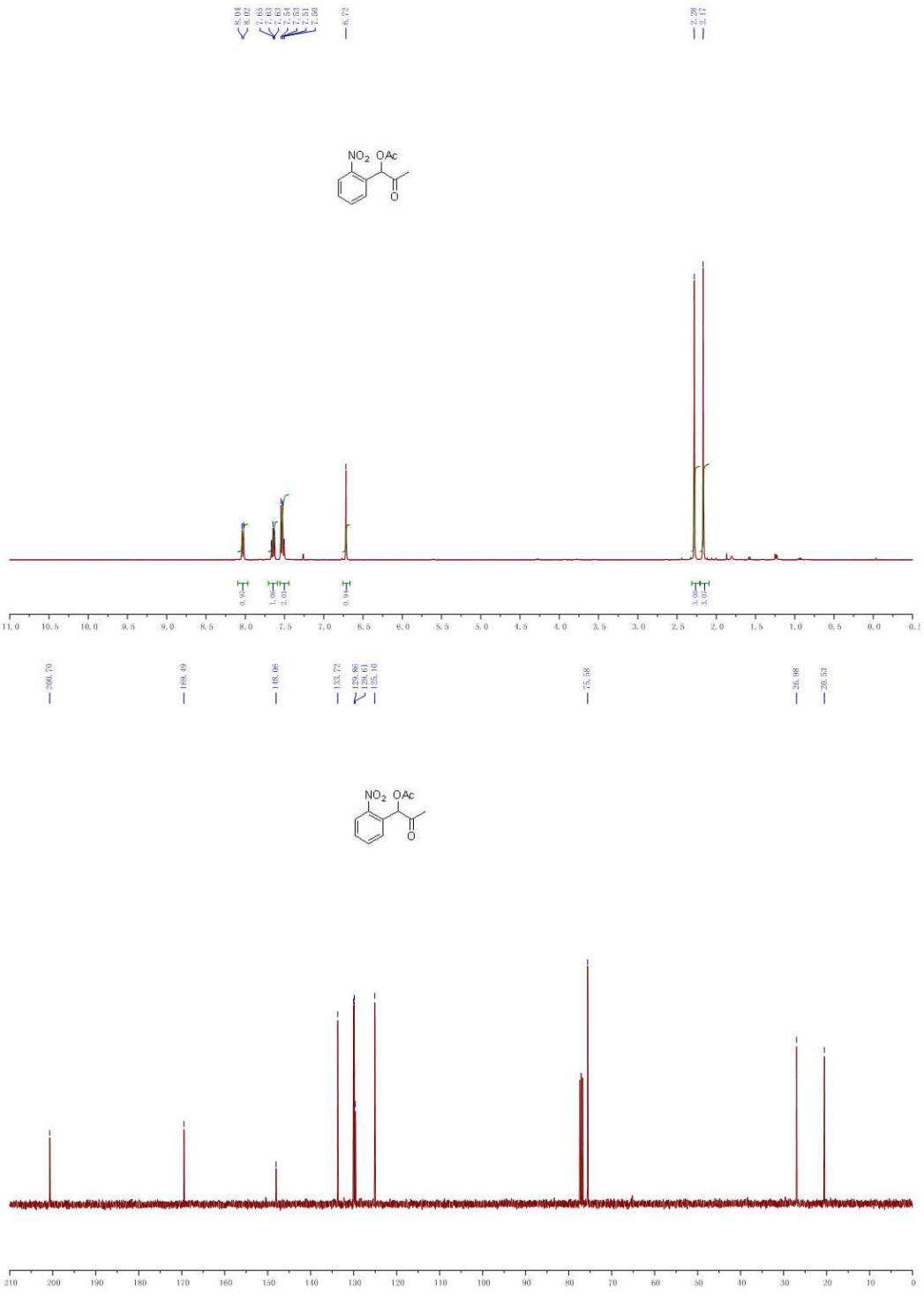
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3.00
3.07
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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O
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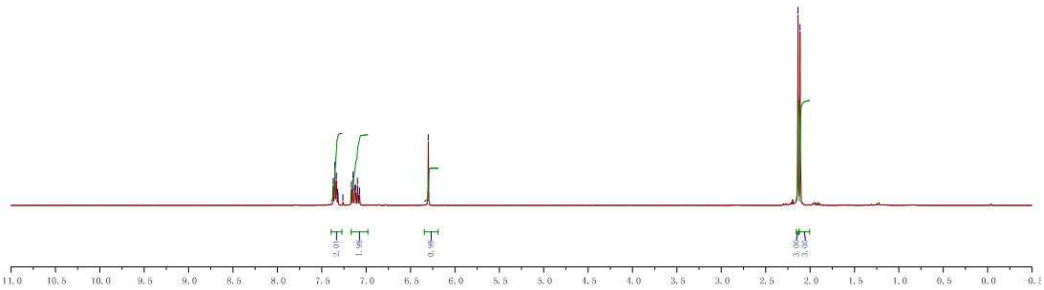
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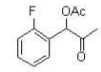
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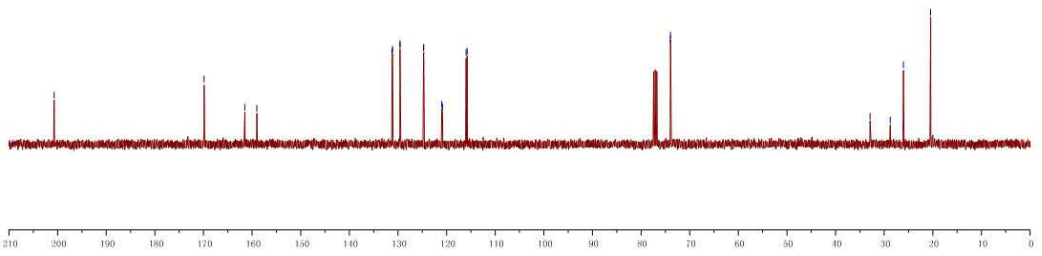
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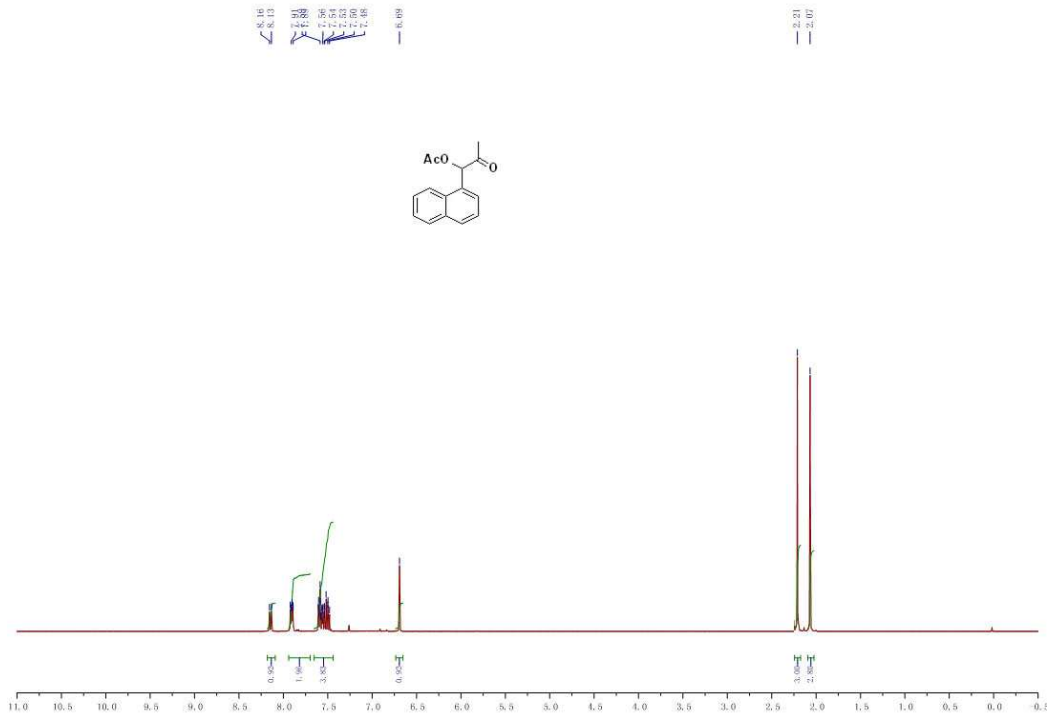
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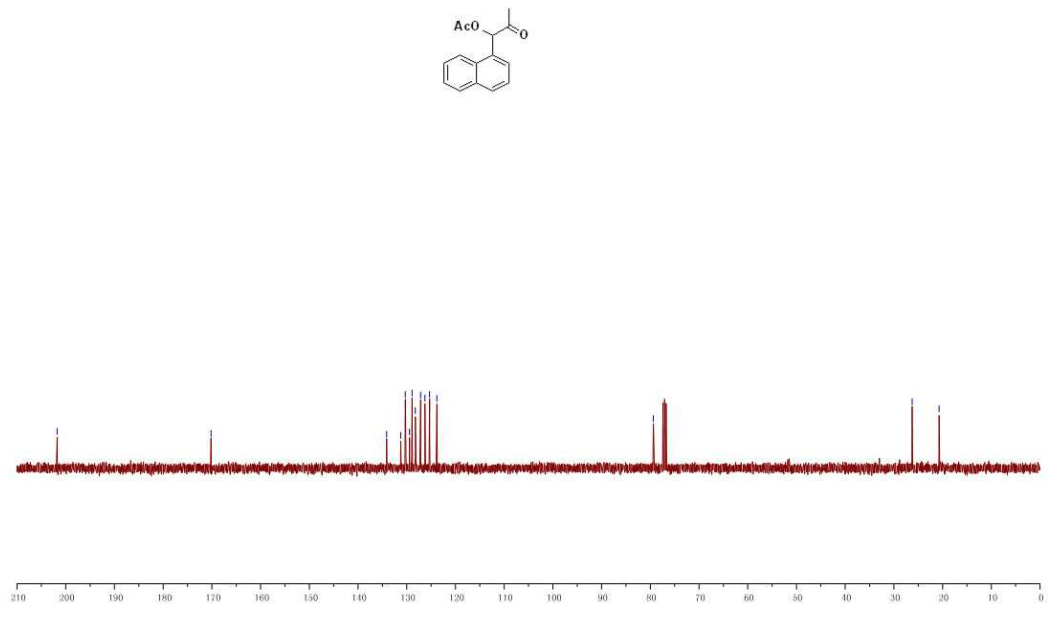
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