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Supplementary Information

Cp*Rh(III)-Catalyzed Annulation of *N*-Methoxybenzamide with 1,4,2-Bisoxazol-5-one toward 2-Aryl Quinazolin-4(3*H*)-one Derivatives

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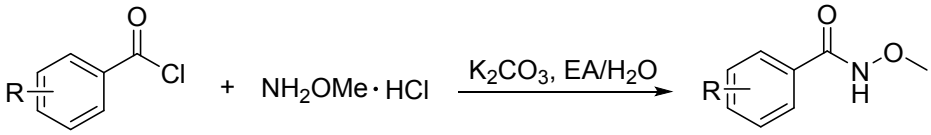
1. General Information

Unless otherwise noted, all the reactions were carried out under nitrogen atmosphere using standard Schlenk technique，and all chemicals were purchased from commercial suppliers and used without further purification. The ^{1}H NMR spectra were recorded on a 300 MHz or 400 MHz NMR spectrometer. The ^{13}C NMR spectra were recorded at 75 MHz or 100 MHz. NMR experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 or 77.26 ppm) as the internal standard. The coupling constants J are given in Hz. Column chromatography was performed using EM Silica gel 60 (300-400 mesh), and the eluent was a mixture of petroleum ether (PE) and ethyl acetate (EA).

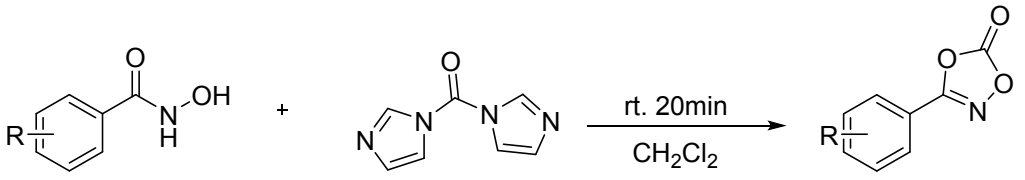
2. Synthesis and Reaction

2.1 General Procedure for Preparation of *N*-methoxybenzamides



N-Methoxybenzamides were prepared according to reported procedures.[1] In a reaction flask, a mixture of $MeONH_2 \cdot HCl$ (1.5 equiv) and K_2CO_3 (2 equiv) in a 2:1 mixture of EtOAc:H_2O (0.3 M) was stirred at 0 ^{o}C, followed by dropwise addition of the benzoyl chloride. The reaction was stirred at room temperature overnight. Afterwards, the reaction was quenched with aqueous $NaHCO_3$ solution and extracted with EtOAc. The organic phase was dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by recrystallization from EtOAc/Pentane.

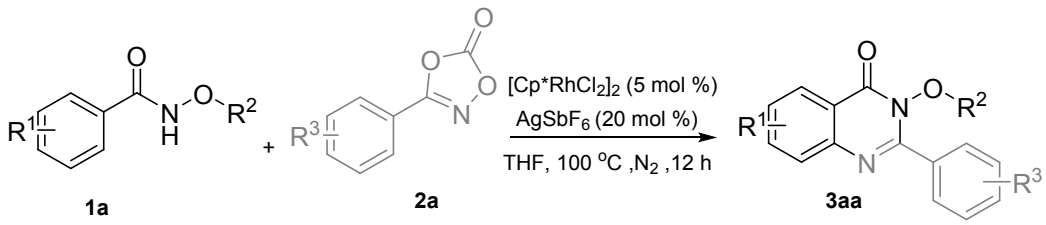
2.2 General Procedure for Preparation of 1,4,2-bisoxazol-5-one



Substituted 1,4,2-bisoxazol-5-one were prepared according to the reported procedures.[2] To a stirred solution of benzohydroxamic acid (5.0 mmol) in dichloromethane (50 mL) was added 1,1'- carbonyldiimidazole (0.81 g, 5.0 mmol) in

one portion at room temperature. After stirring for 30 min, the reaction mixture was quenched with 1 N HCl (30 mL), extracted with dichloromethane three times (50 mL × 3) and dried over magnesium sulfate. The solvent was removed under reduced pressure to afford 3-substituted 1,4,2-dioxazol-5-ones. Product was recrystallized with acetone/hexane, if necessary.

2.3 Specific Synthesis of Quinazolinone

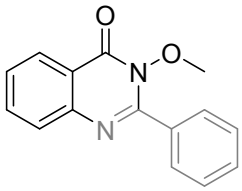


1a 2a 3aa

A 20 mL of Schlenk tube equipped with a stir bar was charged with substituted *N*-methoxybenzamide (0.10 mmol, 1.0 eq.), 1,4,2-bisoxazol-5-one (0.12 mmol, 1.2 eq.), $[Cp^*RhCl_2]_2$ (3.1 mg, 5 mol %), $AgSbF_6$ (6.9 mg, 20 mol %) and THF (2.0 ml). The tube was sealed with a PTFE cap. The reaction mixture was stirred at 100 °C for 12 h under N_2 in an oil bath. After the completion of the reaction, the mixture was then allowed to cool to room temperature. The mixture was purified by flash column chromatography on silica gel with PE-EA (V_1/V_2, 10:1) as the eluent to give the desired products.

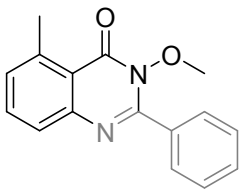
3. Characterization Data for the Products

3-methoxy-2-phenylquinazolin-4(3*H*)-one (3aa):[3]



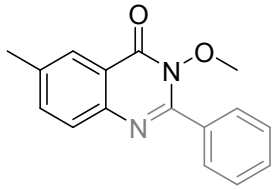
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10: 1) give **3aa** (19.6 mg, 78% yield) as a white solid. m. p. 121-122 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.35-8.31 (m, 1H), 7.92-7.88 (m, 2H), 7.78-7.76 (m, 2H), 7.55-7.48 (m, 4H), 3.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0, 153.1, 146.5, 134.4, 132.0, 130.8, 129.3, 128.3, 127.9, 127.0, 126.7, 122.5, 64.0.
MS (m/z): 252.1 $[M]^+$.

3-methoxy-5-methyl-2-phenylquinazolin-4(3*H*)-one (3ab):



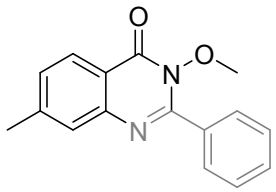
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10: 1) give **3ab** (22.1 mg, 83% yield) as a white solid. m. p. 103-104 ^{o}C ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91-7.88 (m, 2H), 7.62-7.48 (m, 6H), 3.74 (s, 3H), 2.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 152.8, 148.1, 141.4, 133.6, 132.1, 130.8, 129.5, 129.4, 128.3, 126.2, 121.0, 63.9, 22.8.
MS (m/z): 266.1 $[M]^+$.
HRMS (ESI-TOF): calculated for $C_{16}H_{15}N_2O_2^+$ 267.1128, found 267.1127

3-methoxy-6-methyl-2-phenylquinazolin-4(3*H*)-one (3ac):



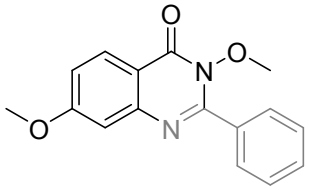
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10: 1) give **3ac** (22.1 mg, 83% yield) as a white solid. m. p. 81-82 ^{o}C ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.11 (s, 1H), 7.89-7.86 (m, 2H), 7.68-7.65 (m, 2H), 7.59-7.47 (m, 4H), 3.74 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 152.5, 144.7, 137.5, 136.1, 132.2, 130.8, 129.5, 128.4, 127.9, 126.2, 122.4, 64.2, 21.5.
MS (m/z): 266.1 $[M]^+$.
HRMS (ESI-TOF): calculated for $C_{16}H_{15}N_2O_2^+$ 267.1128, found 267.1125

3-methoxy-7-methyl-2-phenylquinazolin-4(3*H*)-one (3ad):



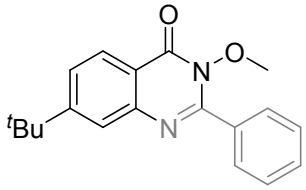
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10: 1) give **3ad** (22.6 mg, 85% yield) as a white solid. m. p. 77-78 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.13 (s, 1H), 7.90-7.88 (m, 2H), 7.59-7.67 (m, 1H), 7.61-7.48 (m, 4H), 3.75 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0, 153.2, 146.7, 145.6, 132.1, 130.8, 129.4, 128.6, 128.3, 127.7, 126.6, 120.1, 64.1, 22.0.
MS (m/z): 266.1 [M] +.
HRMS (ESI-TOF): calculated for $C_{16}H_{15}N_2O_2^+$ 267.1128, found 267.1128

3,7-dimethoxy-2-phenylquinazolin-4(3*H*)-one (3ae):[3]



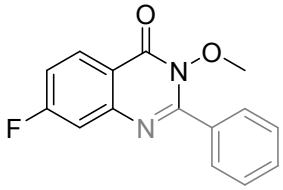
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10: 1) give **3ae** (22.3 mg, 79% yield) as a white solid. m. p. 125-126 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.16-8.11 (m, 1H), 7.85-7.81 (m, 2H), 7.49-7.42 (m, 3H), 7.10-7.07 (m, 1H), 7.03-6.98 (m, 1H), 3.84 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 157.4, 153.6, 148.5, 131.9, 130.6, 129.1, 128.1, 127.9, 117.1, 115.7, 108.2, 63.9, 55.5.
MS (m/z): 282.1 $[M]^+$.

7-(*tert*-butyl)-3-methoxy-2-phenylquinazolin-4(3*H*)-one (3af):



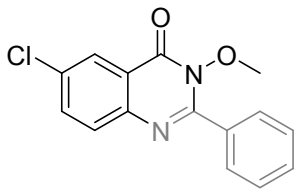
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10: 1) give **3af** (26.5 mg, 86% yield) as a white solid. m. p. 129-130 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.24-8.22 (m, 1H), 7.87-7.84 (m, 2H), 7.77-7.75 (m, 1H), 7.56-7.46 (m, 4H), 3.72 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 157.8, 153.2, 146.6, 132.2, 130.7, 129.3, 128.3, 126.4, 125.2, 124.3, 120.0, 64.0, 35.4, 31.1.
MS (m/z): 308.2 $[M]^+$.
HRMS (ESI-TOF): calculated for $C_{19}H_{21}N_2O_2^+$ 309.1598, found 309.1596

7-fluoro-3-methoxy-2-phenylquinazolin-4(3*H*)-one (3ag):



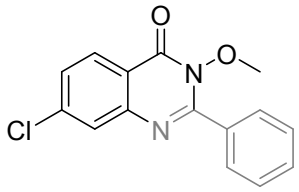
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10: 1) give **3ag** (16.5 mg, 61% yield) as a white solid. m. p. 145-146 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.33-8.28 (m, 1H), 7.90-7.87 (m, 2H), 7.55-7.47 (m, 3H), 7.41-7.37 (m, 1H), 7.23-7.17 (m, 1H), 3.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4 (d, $J_{C\text{-}F}$ = 253.5 Hz), 155.8 (d, $J_{C\text{-}F}$ = 223.5 Hz), 148.5 (d, $J_{C\text{-}F}$ = 13.5 Hz), 131.54, 131.00, 129.42, 129.33, 129.32 (d, $J_{C\text{-}F}$ = 10.5 Hz), 128.27, 119.12 (d, $J_{C\text{-}F}$ = 1.5 Hz), 115.77 (d, $J_{C\text{-}F}$ = 24.0 Hz), 113.14 (d, $J_{C\text{-}F}$ = 21.8 Hz), 64.04.
MS (m/z): 270.1 $[M]^+$.
HRMS (ESI-TOF): calculated for $C_{15}H_{12}FN_2O_2^+$ 271.0877, found 271.0880

6-chloro-3-methoxy-2-phenylquinazolin-4(3*H*)-one (3ah):



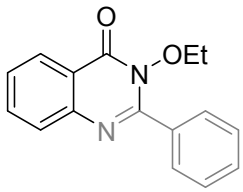
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10: 1) give **3ah** (16.6 mg, 58% yield) as a white solid. m. p. 149-150 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.30-8.29 (m, 1H), 7.91-7.88 (m, 2H), 7.71 (s, 2H), 7.56-7.50 (m, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 153.4, 145.1, 135.0, 133.0, 131.7, 131.1, 129.7, 129.5, 128.4, 126.1, 123.6, 64.2.
MS (m/z): 286.1 $[M]^+$.
HRMS (ESI-TOF): calculated for $C_{15}H_{12}ClN_2O_2^+$ 287.0582, found 287.0580

7-chloro-3-methoxy-2-phenylquinazolin-4(3*H*)-one (3ai):



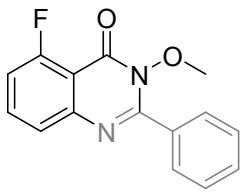
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10: 1) give **3ai** (17.4 mg, 61% yield) as a white solid. m. p. 150-151 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.23-8.20 (m, 1H), 7.89-7.87 (m, 2H), 7.74-7.73 (m, 1H), 7.55-7.41 (m, 4H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 154.4, 147.5, 140.7, 131.6, 131.2, 129.5, 128.4, 128.2, 127.6, 127.5, 121.0, 64.2.
MS (m/z): 286.1 $[M]^+$.
HRMS (ESI-TOF): calculated for $C_{15}H_{12}ClN_2O_2^+$ 287.0582, found 287.0582

3-ethoxy-2-phenylquinazolin-4(3*H*)-one (3aj):



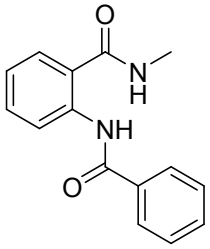
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10: 1) give **3aj** (19.4 mg, 73% yield) as a white solid. m. p. 113-114 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.35-8.32 (m, 1H), 7.92-7.90 (m, 2H), 7.78-7.77 (m, 2H), 7.54-7.49 (m, 4H), 3.99 (q, J = 7.0 MHz, 2H), 1.10 (t, J = 7.0 MHz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 153.7, 146.6, 134.5, 132.2, 130.8, 129.6, 128.2, 128.0, 127.0, 126.8, 122.6, 72.8, 13.2.
MS (m/z): 266.1 $[M]^+$.
HRMS (ESI-TOF): calculated for $C_{16}H_{15}N_2O_2^+$ 267.1128, found 267.1130

5-fluoro-3-methoxy-2-phenylquinazolin-4(3H)-one (3ak):



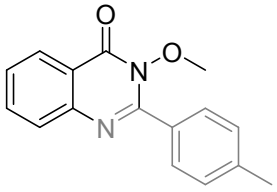
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10: 1) give **3ak** (10.0 mg, 37% yield) as a white solid. m. p. 121-122 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91-7.88 (m, 2H), 7.72-7.66 (m, 1H), 7.58-7.49(m, 4H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (d, J_{C-F} = 264.6 MHz), 155.2, 154.3, 148.6, 135.0 (d, J_{C-F} = 10.3 MHz), 131.7, 131.2, 129.6, 128.5, 124.1 (d, J_{C-F} = 4.3 MHz), 113.6 (d, J_{C-F} = 20.2 MHz), 64.2.
MS (m/z): 270.3 $[M]^+$.
HRMS (ESI-TOF): calculated for $C_{15}H_{12}FN_2O_2^+$ 271.0877, found 271.0879

2-benzamido-N-methylbenzamide (3al):[4]



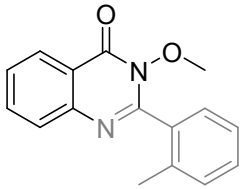
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **3al** (34.5 mg, 68% yield) as a white solid. m. p. 170-172 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 12.08 (s, 1H), 8.65-8.62 (m, 1H), 8.02-8.00 (m, 2H), 7.54-7.40 (m, 5H), 6.97-6.91 (m, 2H), 2.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 165.8, 139.3, 134.6, 132.1, 131.9, 128.8, 127.3, 126.8, 122.8, 121.4, 120.8, 26.7.
MS (m/z): 254.1 $[M]^+$.

3-methoxy-2-(*p*-tolyl)quinazolin-4(3*H*)-one (3ba):[3]



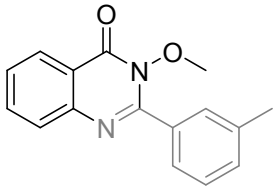
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10: 1) give **3ba** (20.2 mg, 76% yield) as a white solid. m. p. 153-154 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.21-8.19 (m, 1H), 7.90-7.87 (m, 2H), 7.56-7.47 (m, 4H), 7.33-7.30 (m, 1H), 3.74 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 153.2, 146.7, 145.6, 132.1, 130.8, 129.4, 128.6, 128.3, 127.7, 126.6, 120.1, 64.1, 22.0.
MS (m/z): 266.1 $[M]^+$.

3-methoxy-2-(o-tolyl)quinazolin-4(3*H*)-one (3ca):



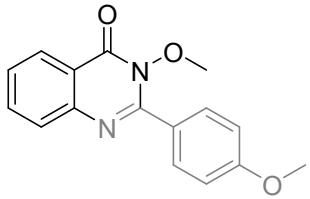
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10: 1) give **3ca** (18.9 mg, 71% yield) as a white solid. m. p. 105-106 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.38-8.36 (m, 1H), 7.82-7.77 (m, 2H), 7.58-7.52 (m, 1H), 7.49-7.40 (m, 2H), 7.34-7.30 (m, 2H), 3.74 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 154.2, 146.5, 136.9, 134.6, 132.3, 130.3, 130.2, 128.3, 128.0, 127.2, 126.8, 125.7, 122.8, 64.2, 19.6.
MS (m/z): 266.1 $[M]^+$.
HRMS (ESI-TOF): calculated for $C_{16}H_{15}N_2O_2^+$ 267.1128, found 267.1126

3-methoxy-2-(m-tolyl)quinazolin-4(3*H*)-one (3da):



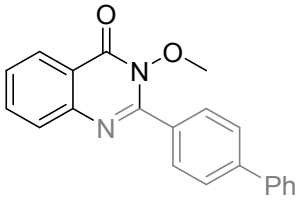
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10: 1) give **3da** (18.9 mg, 71% yield) as a white solid. m. p. 76-77 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.34-8.30 (m, 1H), 7.78-7.56 (m, 2H), 7.69-7.65 (m, 2H), 7.52-7.47 (m, 1H), 7.41-7.33 (m, 2H), 3.76 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 153.5, 146.6, 138.2, 134.5, 131.9, 131.6, 129.9 128.2 128.0, 127.0, 127.0, 126.5, 122.6, 64.1, 21.5.
MS (m/z): 266.1 $[M]^+$.
HRMS (ESI-TOF): calculated for $C_{16}H_{15}N_2O_2^+$ 267.1128, found 267.1126

3-methoxy-2-(4-methoxyphenyl)quinazolin-4(3*H*)-one (3ea):[3]



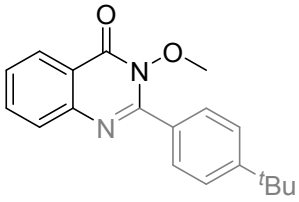
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10: 1) give **3ea** (18.9 mg, 67% yield) as a white solid. m. p. 132-133 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.32-8.29 (m, 1H), 7.94-7.91 (m, 2H), 7.76-7.74 (m, 2H), 7.50-7.45 (m, 1H), 7.02-7.00 (m, 2H), 3.88 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.6, 158.1, 152.7, 146.6, 134.4, 131.3, 127.7, 126.7, 126.6, 124.1, 122.3, 113.7, 63.8, 55.4.
MS (m/z): 282.1 $[M]^+$.

2-([1,1'-biphenyl]-4-yl)-3-methoxyquinazolin-4(3*H*)-one (3fa):



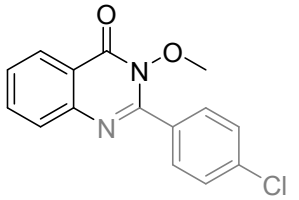
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10: 1) give **3fa** (19.5 mg, 51% yield) as a brown solid. m. p. 165-166 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.37-8.34 (m, 1H), 8.03-8.00 (m, 2H), 7.80-7.65 (m, 6H), 7.54-7.34 (m, 4H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 153.1, 146.8, 143.8, 140.2, 134.7, 130.9, 130.1, 129.1, 128.2, 128.1, 127.4, 127.2, 126.9, 122.7, 64.3.
MS (m/z): 328.1 $[M]^+$.
HRMS (ESI-TOF): calculated for $C_{21}H_{16}N_2O_2^+$ 329.1285, found 329.1288

2-(4-(*tert*-butyl)phenyl)-3-methoxyquinazolin-4(3H)-one (3ga):



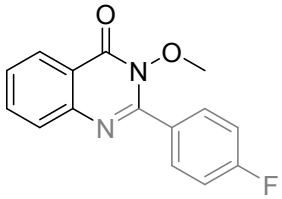
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10: 1) give **3ga** (19.5 mg, 51% yield) as a white solid. m. p. 190-191 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.32-8.28 (m, 1H), 7.85-7.83 (m, 2H), 7.75-7.73 (m, 2H), 7.52-7.44 (m, 3H), 3.77 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 154.3, 153.2, 147.0, 134.4, 129.2, 129.1, 127.9, 126.8, 126.7, 125.4, 122.5, 64.1, 35.0, 31.2.
MS (m/z): 308.2 $[M]^+$.
HRMS (ESI-TOF): calculated for $C_{19}H_{21}N_2O_2^+$ 309.1598, found 309.1598

2-(4-chlorophenyl)-3-methoxyquinazolin-4(3*H*)-one (3ha):



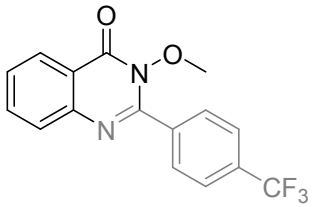
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10: 1) give **3ha** (21.2 mg, 74% yield) as a white solid. m. p. 131-132 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.33-8.31 (m, 1H), 7.89-7.87 (m, 2H), 7.78-7.75 (m, 2H), 7.54-7.48 (m, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 152.0, 146.5, 137.3, 134.6, 131.0, 130.4, 128.7, 128.0, 127.2, 126.8, 122.6, 64.2.
MS (m/z): 286.1 $[M]^+$.
HRMS (ESI-TOF): calculated for $C_{15}H_{12}ClN_2O_2^+$ 287.0582, found 287.0584

2-(4-fluorophenyl)-3-methoxyquinazolin-4(3*H*)-one (3ia):[3]



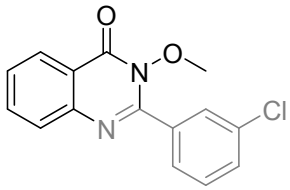
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10: 1) give **3ia** (18.9 mg, 70% yield) as a white solid. m. p. 121-122 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.32-8.29 (m, 1H), 7.95-7.92 (m, 2H), 7.76-7.74 (m, 2H), 7.51-7.47 (m, 1H), 7.21-7.16 (m, 2H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3 (d, J = 250.0 Hz), 157.9, 152.1, 146.5, 134.6, 131.9 (d, $J_{C\text{-}F}$ = 9.0 Hz), 128.0 (d, $J_{C\text{-}F}$ = 4.0 Hz), 127.9, 127.1, 126.8, 122.5, 115.6 (d, $J_{C\text{-}F}$ = 22.0 Hz), 64.1.
MS (m/z): 270.1 $[M]^+$.

3-methoxy-2-(4-(trifluoromethyl)phenyl)quinazolin-4(3*H*)-one (3ja):[3]



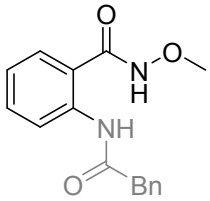
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10: 1) give **3ja** (26.9 mg, 84% yield) as a white solid. m. p. 113-114 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.32-8.28 (m, 1H), 8.04-8.01 (m, 2H), 7.77-7.73 (m, 4H), 7.53-7.48 (m, 1H), 3.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.6, 151.6, 146.2, 135.3 (d, $J_{C\text{-}F}$ = 1.5 Hz), 134.6, 132.4 (q, $J_{C\text{-}F}$ = 32.3 Hz), 129.9, 128.0, 127.4, 126.7, 125.2 (q, $J_{C\text{-}F}$ = 3.8 Hz), 123.6 (q, $J_{C\text{-}F}$ = 270.0 Hz), 122.6, 64.2.
MS (m/z): 320.1 $[M]^+$.

2-(3-chlorophenyl)-3-methoxyquinazolin-4(3*H*)-one (3ka):



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10: 1) give **3ka** (18.0 mg, 63% yield) as a white solid. m. p. 142-143 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.25-8.20 (m, 1H), 7.87-7.84 (m, 1H), 7.78-7.68 (m, 3H), 7.48-7.36 (m, 3H), 3.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.70, 151.64, 146.29, 134.56, 134.29, 133.58, 130.92, 129.60, 129.55, 127.97, 127.66, 127.27, 126.72, 122.59, 64.23.
MS (m/z): 286.1 $[M]^+$.
HRMS (ESI-TOF): calculated for $C_{15}H_{12}ClN_2O_2^+$ 287.0582, found 287.0580

***N*-methoxy-2-(2-phenylacetamido)benzamide (3la):**



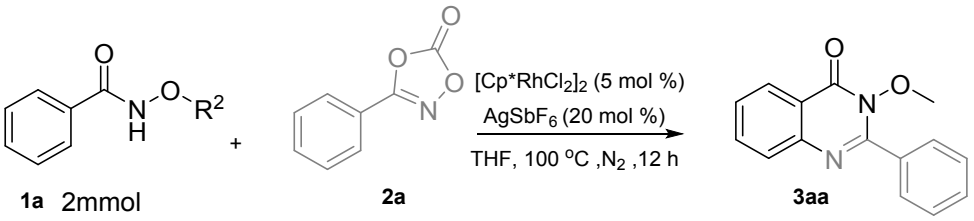
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10: 1) give **3la** (23.5 mg, 87% yield) as a white solid. m. p. 117-118 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.75 (s, 1H), 7.78-7.50 (m, 2H), 7.54-7.50 (m, 1H), 7.45-7.41 (m, 2H), 7.37-7.25 (m, 5H), 4.56 (d, J = 5.7 MHz, 2H), 3.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ171.6, 152.0, 137.9, 133.2, 132.1, 129.1, 128.9, 128.9, 128.2, 127.9, 127.7, 64.6, 44.7.

MS (m/z): 284.1 $[M]^+$.

HRMS (ESI-TOF): calculated for $C_{16}H_{17}N_2O_3^+$ 285.1234, found 285.1234

4. Larger-Scale Preparation and Transformations

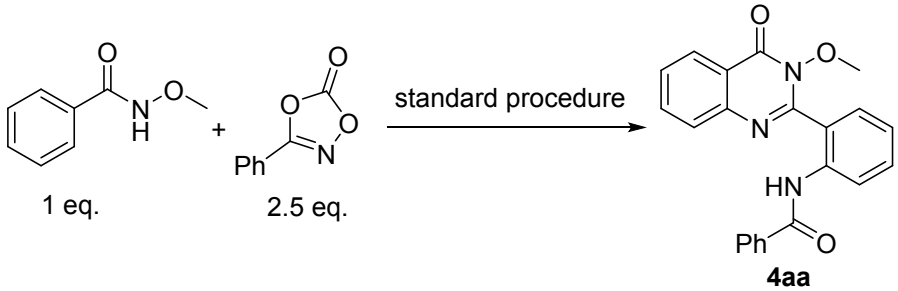
4.1 Larger-Scale Preparation of 3a



1a 2mmol **2a** **3aa**

A 20 mL of Schlenk tube equipped with a stir bar was charged with substituted *N*-methoxybenzamide (2 mmol, 1.0 eq.), 1,4,2-bisoxazol-5-one (2.4 mmol, 1.2 eq.), $[Cp^*RhCl_2]_2$ (61.8 mg, 5 mol %), $AgSbF_6$ (143.1 mg, 20 mol %) and THF (20 ml). The tube was sealed with a PTFE cap. The reaction mixture was stirred at 100 °C for 12 h under N_2 in an oil bath. After the completion of the reaction, the mixture was then allowed to cool to room temperature. The mixture was purified by flash column chromatography on silica gel with petroleum ether-EtOAc (V_1/V_2, 10:1) as the eluent to afford the product as a white soild (403.2 mg, yield: 80%).

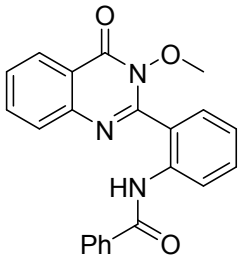
4.2 Transformations of 4aa



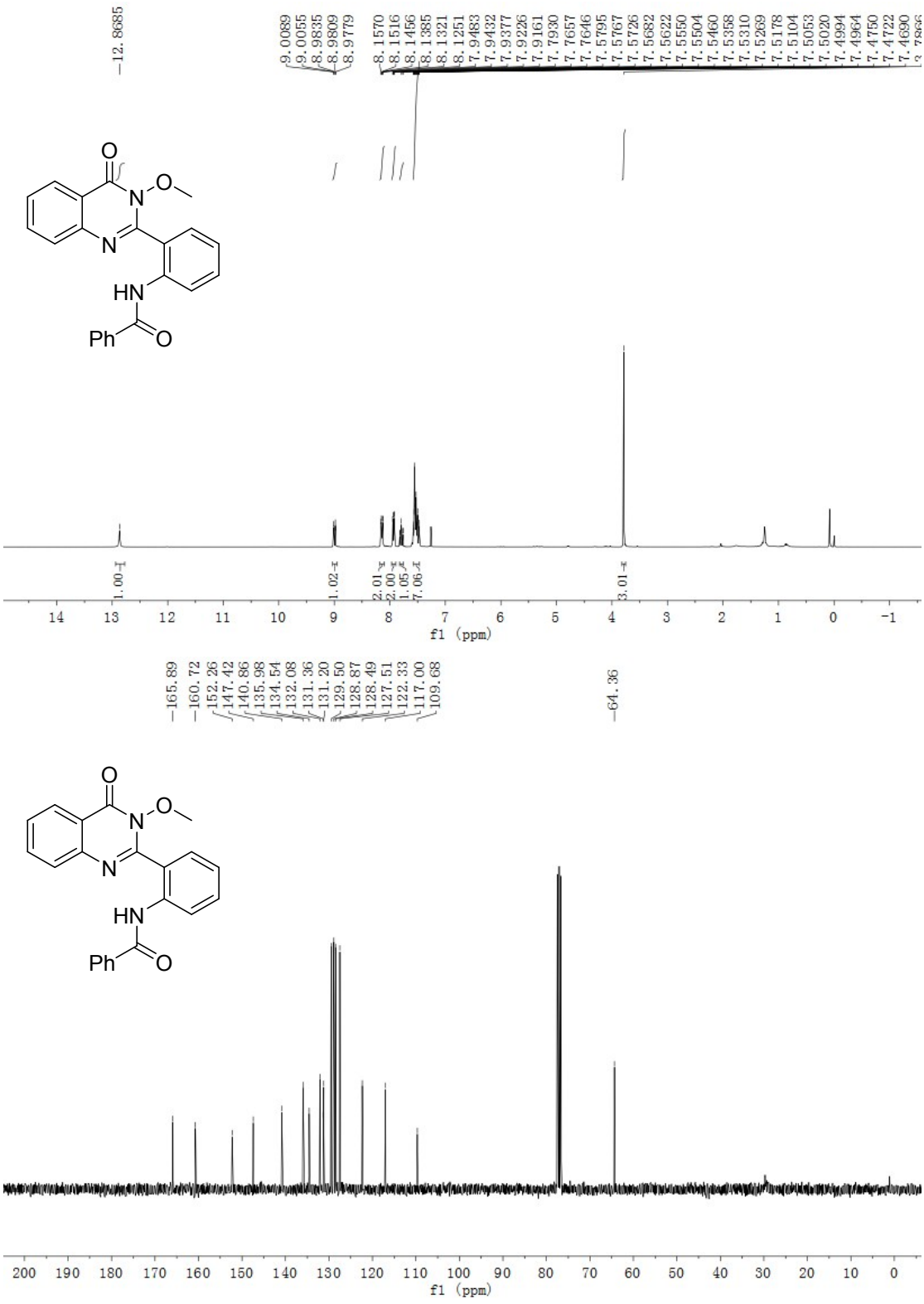
1 eq. 2.5 eq. **4aa**

A 20 mL of Schlenk tube equipped with a stir bar was charged with substituted *N*-methoxybenzamide (0.10 mmol, 1.0 eq.), 1,4,2-bisoxazol-5-one (0.25 mmol, 2.5 eq.), $[Cp^*RhCl_2]_2$ (3.1 mg, 5 mol %), $AgSbF_6$ (6.9 mg, 20 mol %) and THF (2.0 ml). The tube was sealed with a PTFE cap. The reaction mixture was stirred at 100 °C for 12 h under N_2 in an oil bath. After the completion of the reaction, the mixture was then allowed to cool to room temperature. The mixture was purified by flash column chromatography on silica gel with petroleum ether-EtOAc (V_1/V_2, 10:1) as the eluent to give the desired products.

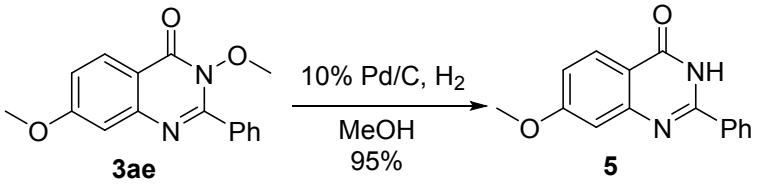
***N*-(2-(3-methoxy-4-oxo-3,4-dihydroquinazolin-2-yl)phenyl)benzamide (4aa):**



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 10: 1) give **4aa** (26.3 mg, 71% yield) as a white solid. m. p. 168-169 ^oC. ^1H NMR ($CDCl_3$, 300 MHz) δ 12.87 (s, 1H), 9.07-9.98 (m, 1H), 8.16-8.13 (m, 2H), 7.95-7.92 (m, 2H), 7.82-7.76 (1H), 7.58-7.47 (m, 7H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 160.7, 152.3, 147.4, 140.9, 136.0, 134.5, 132.1, 131.4, 131.2, 129.5, 128.9, 128.5, 127.5, 122.3, 117.0, 109.7, 64.4.
MS (m/z): 371.1 $[M]^+$.
HRMS (ESI-TOF): calculated for $C_{22}H_{18}N_3O_3^+$ 372.1343, found 372.1345

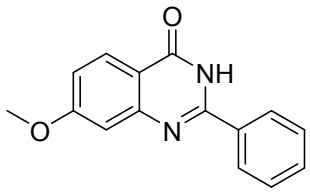


4.3 Transformation of 5

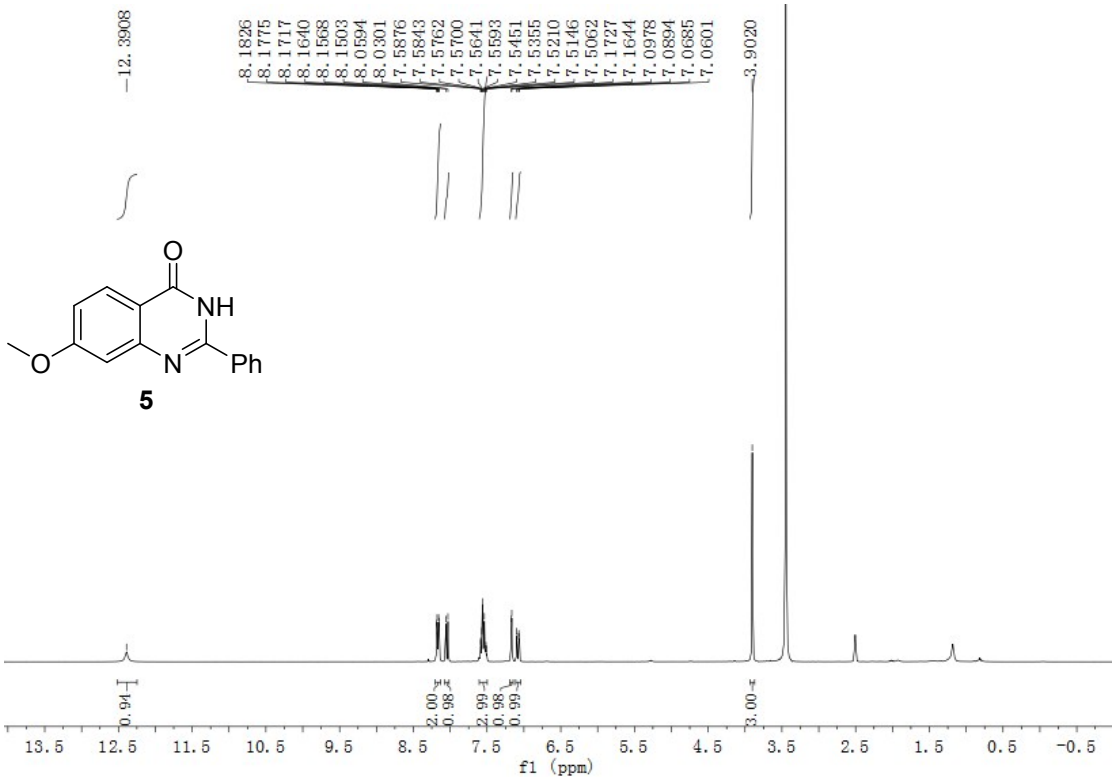


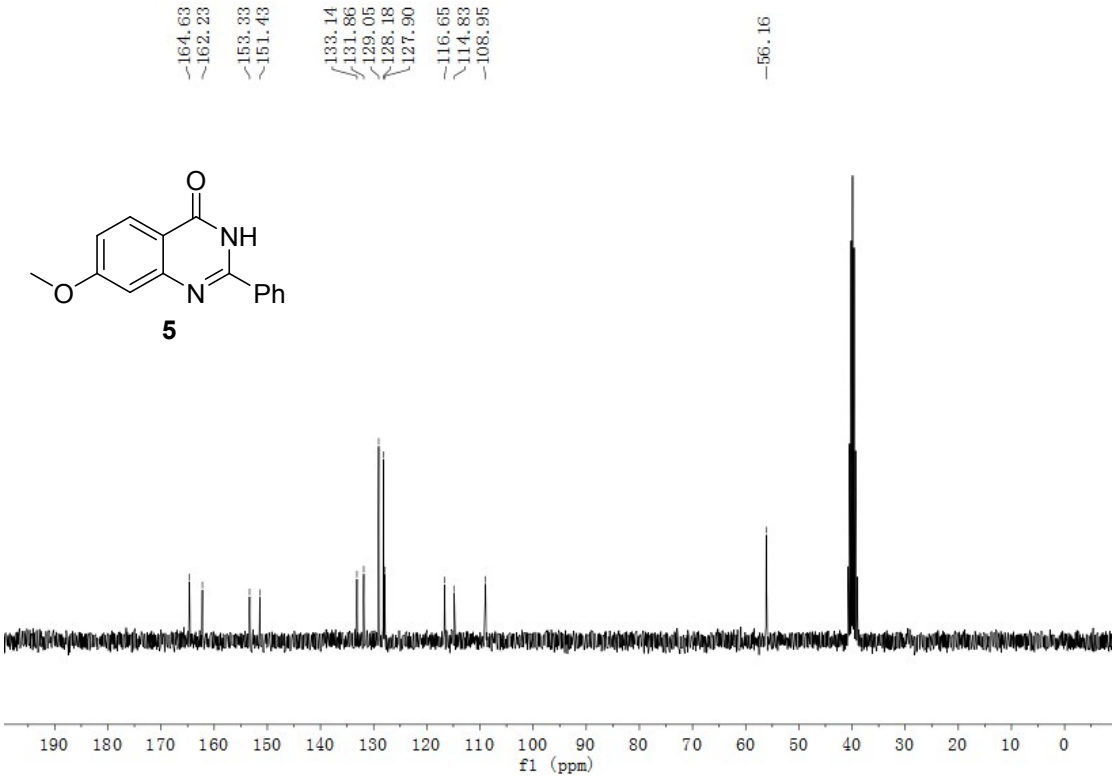
A 20 mL of Schlenk tube equipped with a stir bar was charged with substituted **3ae** (0.2 mmol, 1.0 eq.), 10% Pd/C (5.6 mg), and MeOH (2 ml). The tube was sealed with a PTFE cap. The reaction mixture was stirred for 12 h under H_2 at room temperature. After the completion of the reaction, the mixture was purified by flash column chromatography on silica gel with petroleum ether-EtOAc (V_1/V_2, 5:1) as the eluent to afford the product as a white soild (47.8 mg, yield: 95%).

7-methoxy-2-phenylquinazolin-4(3H)-one (5):[5]



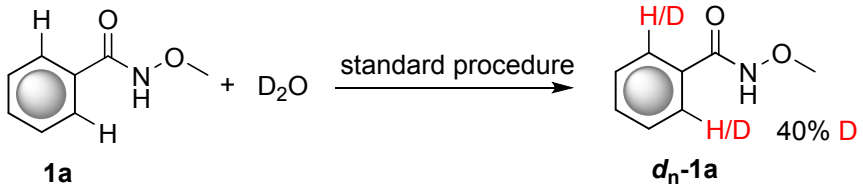
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5: 1) give **5** (47.8 mg, 95% yield) as a white solid. m. p. 221-223 ^{o}C. ^{1}H NMR (DMSO-d_6, 300 MHz) δ 12.39 (s, 1H), 8.12-8.15 (m, 2H), 8.06-8.03 (m, 1H), 7.59-7.51 (m, 3H), 7.17-7.16 (m, 1H), 7.10-7.06 (m, 1H), 3.90 (s, 3H) ; ^{13}C NMR (75 MHz, DMSO-d_6) δ 164.6, 162.2, 153.3, 151.4, 133.1, 131.9, 129.1, 128.2, 127.9, 116.7 114.8, 109.0, 56.2. MS (m/z): 252.1 $[M]^+$.





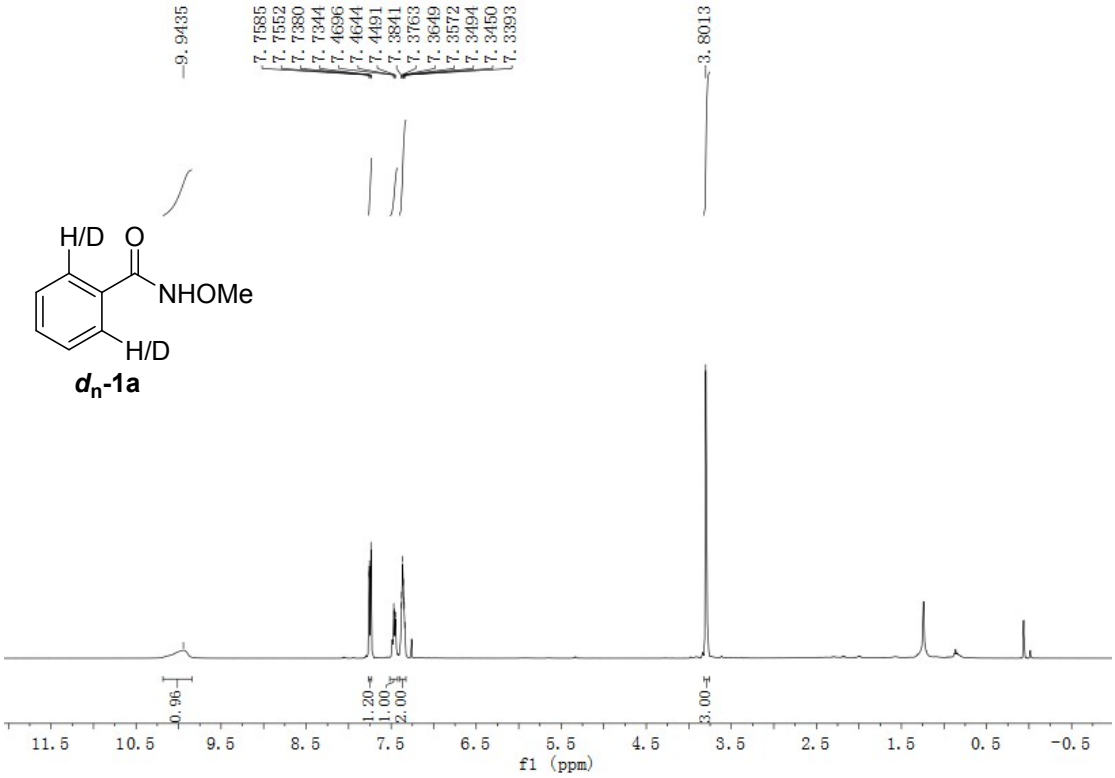
5. Mechanism Study

5.1 Deuterium Labeling Experiments



1a **d_n-1a**

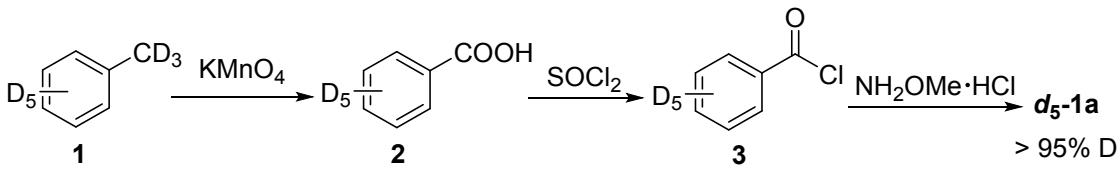
A pressure tube was charged with **3a** (15.1 mg, 0.1 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 5% mmol), $AgSbF_6$ (3.9 mg, 20% mmol) and D_2O (20 mg, 1 mmol) were dissolved in THF (1 mL) under N_2 atmosphere. The reaction mixture was stirred at 100°C for 12 h. After that, the crude product was purified by silica gel chromatography using PE/EA(V_1/V_2 = 3:1) to afford an oily liquid (***d*$_n$-1a**), which was characterized by ^1H NMR spectroscopy.



d_n-1a

5.2 Kinetic Isotope Effect Experiments

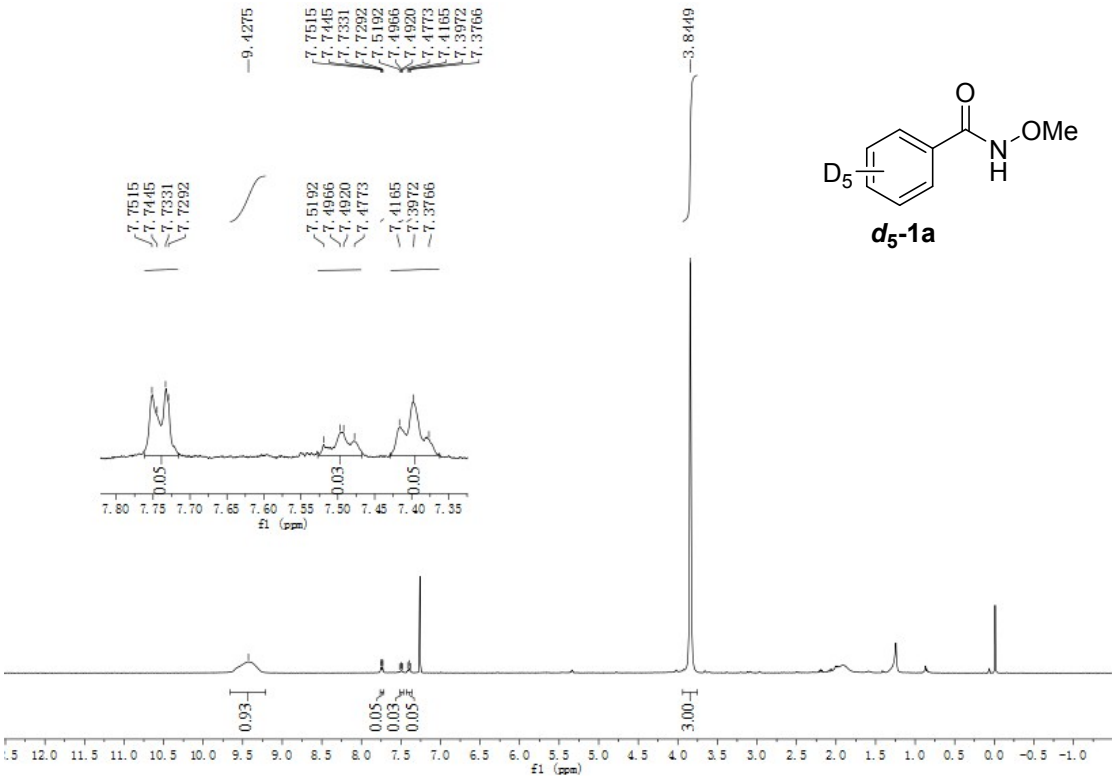
5.2.1 General Procedure for Preparation of Deuterated *N*-methoxybenzamides



1 **2** **3**

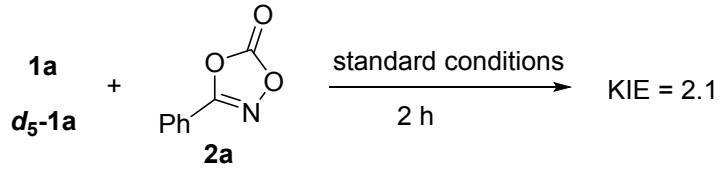
A 250ml single-mouth bottle was charged with H_2O (100 ml), deuterated toluene

1 (99.5% D, 2 ml), TBAB (2.4 g), $KMnO_4$ (8 g). The reaction mixture was stirred at 120°C for 6 h. After the reaction was completed, saturated Na_2SO_3 solution was added dropwise to make the reaction solution purple disappear. After hot filtration, the filtrate was acidified with concentrated hydrochloric acid to give a white solid **2** (1 g, yield 50%). Then dissolve **2** (254 mg, 2 mmol) in 5ml MeCN and add $SOCl_2$ (0.5 ml) to reflux overnight. After the reaction is complete, concentrate the reaction solution to obtain crude product **3**. In a reaction flask, a mixture of $MeONH_2 \cdot HCl$ (1.5 equiv) and K_2CO_3 (2 equiv) in a 2:1 mixture of EtOAc:H_2O (0.3 M) was stirred at 0 ^oC, followed by dropwise addition of crude **3**. The reaction was stirred at room temperature overnight. Afterwards, the reaction was quenched with aqueous $NaHCO_3$ solution and extracted with EtOAc. The organic phase was dried over Na_2SO_4 and evaporated under reduced pressure. The mixture was purified by flash column chromatography on silica gel with petroleum ether-EtOAc (V_1/V_2, 1:1) as the eluent to give the desired products (***d*$_5$-1a)**, which was characterized by ^1H NMR spectroscopy.

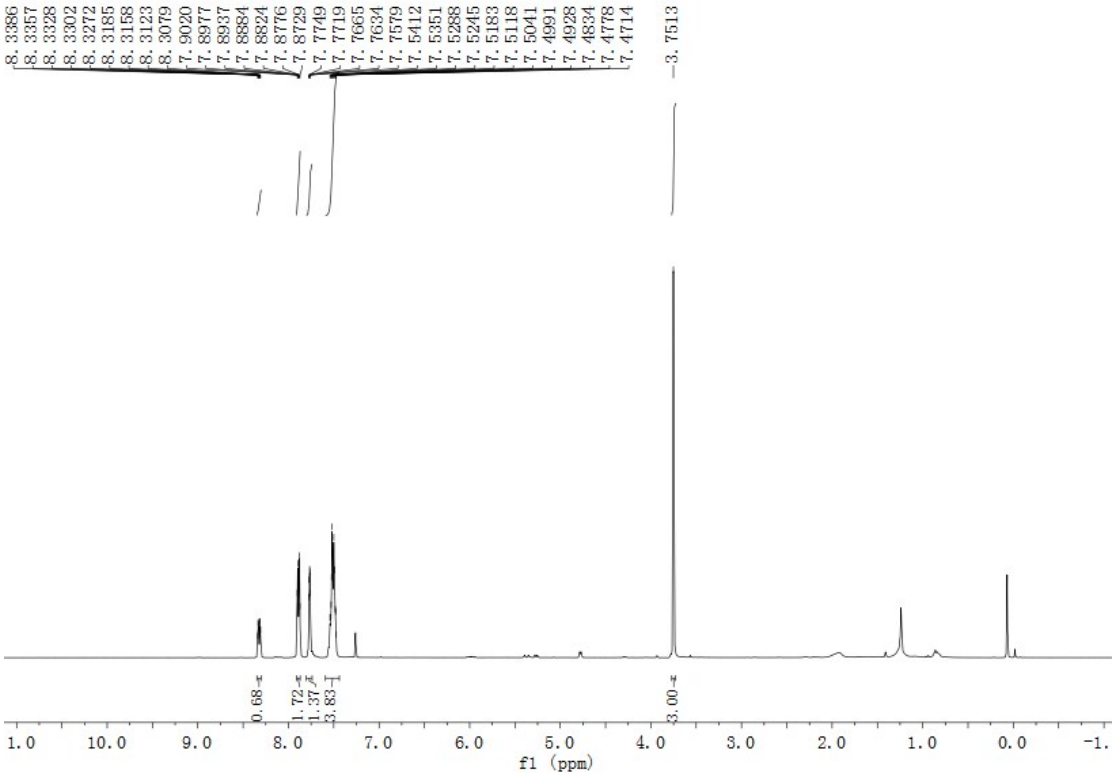


5.2.2 Control Experiments

5.2.2.1 Intermolecular Competition

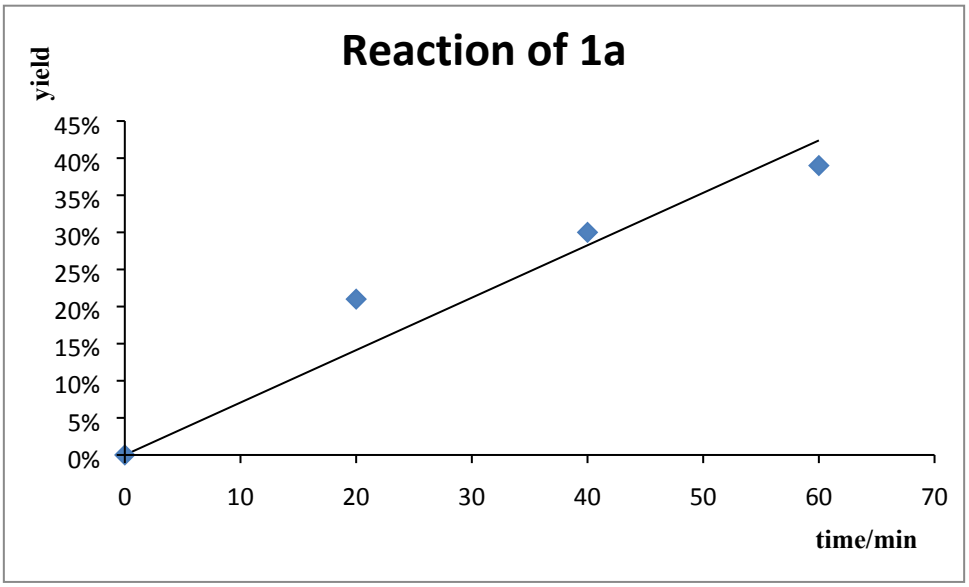


A 20 mL of Schlenk tube equipped with a stir bar was charged with substituted *N*-methoxybenzamide (**1a**, 15.1 mg, 0.10 mmol, 1.0 eq.), *N*-methoxybenzamide-2, 3, 4, 5, 6-d_5 (***d*$_5$-1a**,15.6 mg, 0.10 mmol, 1.0 eq.), 1,4,2-bisoxazol-5-one (39.1 mg, 0.24 mmol, 1.2 eq.), $[Cp^*RhCl_2]_2$ (6.2 mg, 5 mol %), $AgSbF_6$ (13.7 mg, 20 mol %) and THF (4.0 ml). The tube was sealed with a PTFE cap. The reaction mixture was stirred at 100 °C for 2 h under N_2 in an oil bath. After that, the mixture was then allowed to cool to room temperature. The mixture was purified by flash column chromatography on silica gel with petroleum ether-EtOAc (V_1/V_2, 10:1) as the eluent to give the mixture of **3aa** and ***d*$_4$-3aa**, the KIE value was determined to be *k*H/*k*D = 2.1 on the basis of ^{1}H NMR analysis.



5.2.2.2 Parallel Reaction

Six 20 mL of Schlenk tube equipped with a stir bar were charged with substituted *N*-methoxybenzamide (**1a**, 15.1 mg, 0.10 mmol, 1.0 eq.), *N*-methoxybenzamide-2, 3, 4, 5, 6-d_5 (***d*$_5$-1a**,15.6 mg, 0.10 mmol, 1.0 eq.), 1,4,2-bisoxazol-5-one (39.1 mg, 0.24 mmol, 1.2 eq.), $[Cp^*RhCl_2]_2$ (6.2 mg, 5 mol %), $AgSbF_6$ (13.7 mg, 20 mol %) and THF (4.0 ml) (three experiments for each). Then the reaction was quenched by EtOAc in specified time. The mixture was analyzed by GC-MS to give the yield of product. A significant intermolecular kinetic isotope effect (k_H/k_D = 2.2:1) was observed. The results were listed below:



6. Reference

[1] a) J.Vaitla, A. Bayer, K. H. Hopmann, *Angew. Chem. Int. Ed.,* 2017, **56**, 4277; *Angew. Chem.,* 2017, **129**, 4341. b) Y. Xu, X. Yang, X. Zhou, L. Kong and X. Li, *Org. Lett.,* 2017, **19**, 4307.

[2] Y. Park, K. Park, J. Kim, S. Chang, *J. Am. Chem. Soc.,* 2015, **137**, 4534.

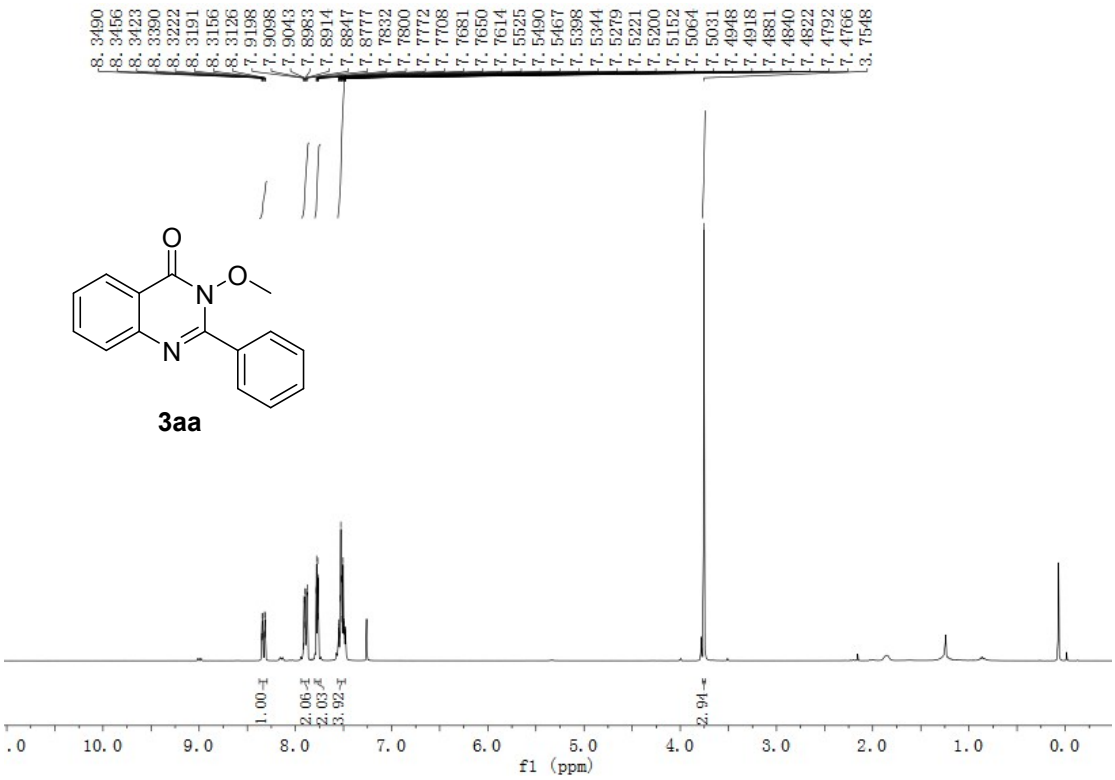
[3] R. Cheng, T. Guo, D. Zhang-Negrerie, Y. Du, K. Zhao, *synthesi,* 2013, **45**, 2998.

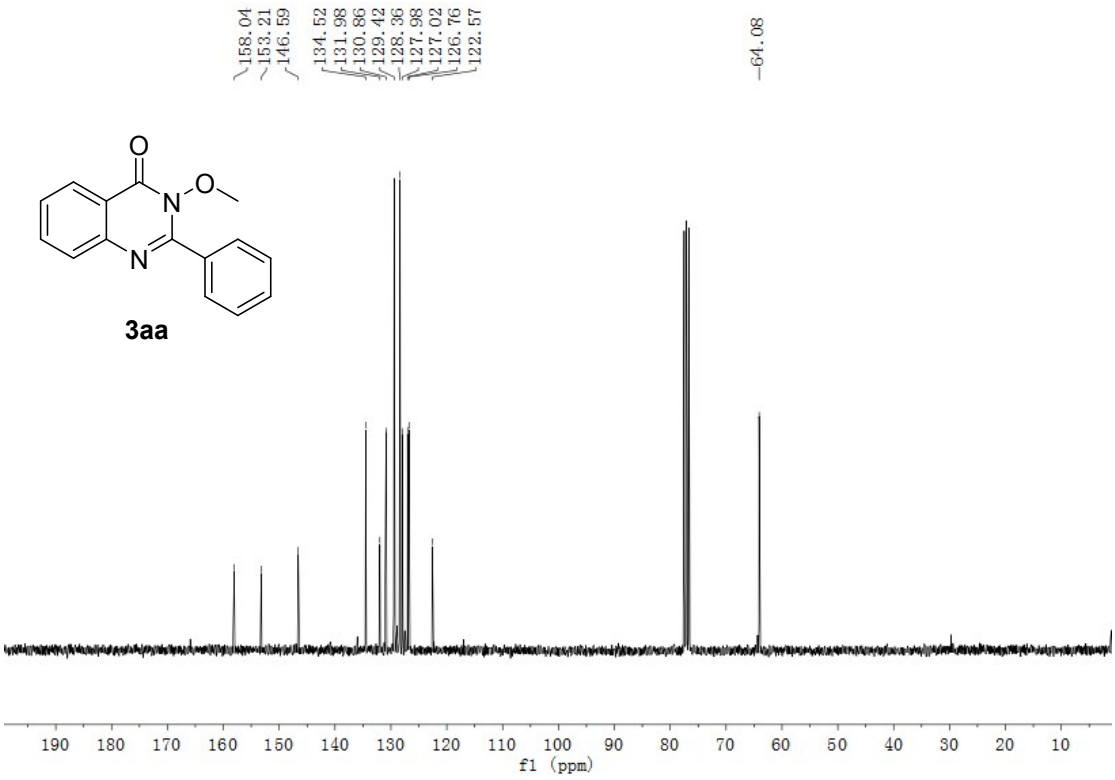
[4] J. Park, S. Chang, *Angew. Chem*., 2015, **127**, 14309. *Angew. Chem. Int. Rd*., 2015, **54**, 14103.

[5] a) M. Hayakawa, H. Kaizawa, H. Moritomo, T. Koizumi, T. Ohishi, M. Okada, M. Ohta, S. Tsukamoto, P. Paker, P. Workman, M. Waterfield. *Bioorg. Med. Chem.,* 2006, **14**, 6847. b) R. Cheng, L. Tang, T. Guo, D. Zhang-Negrerie, Y. Du, K. Zhao, *RSC Adv.,* 2014, **4**, 26434.

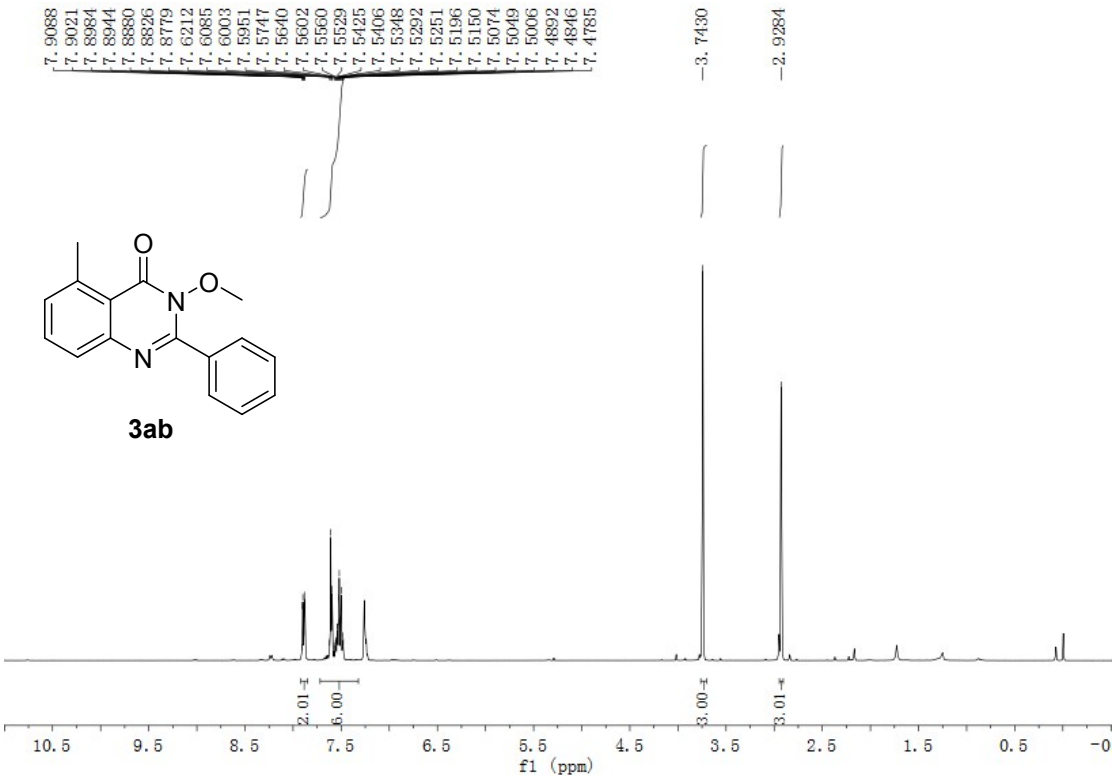
7. ^{1}H NMR, ^{13}C NMR Spectra

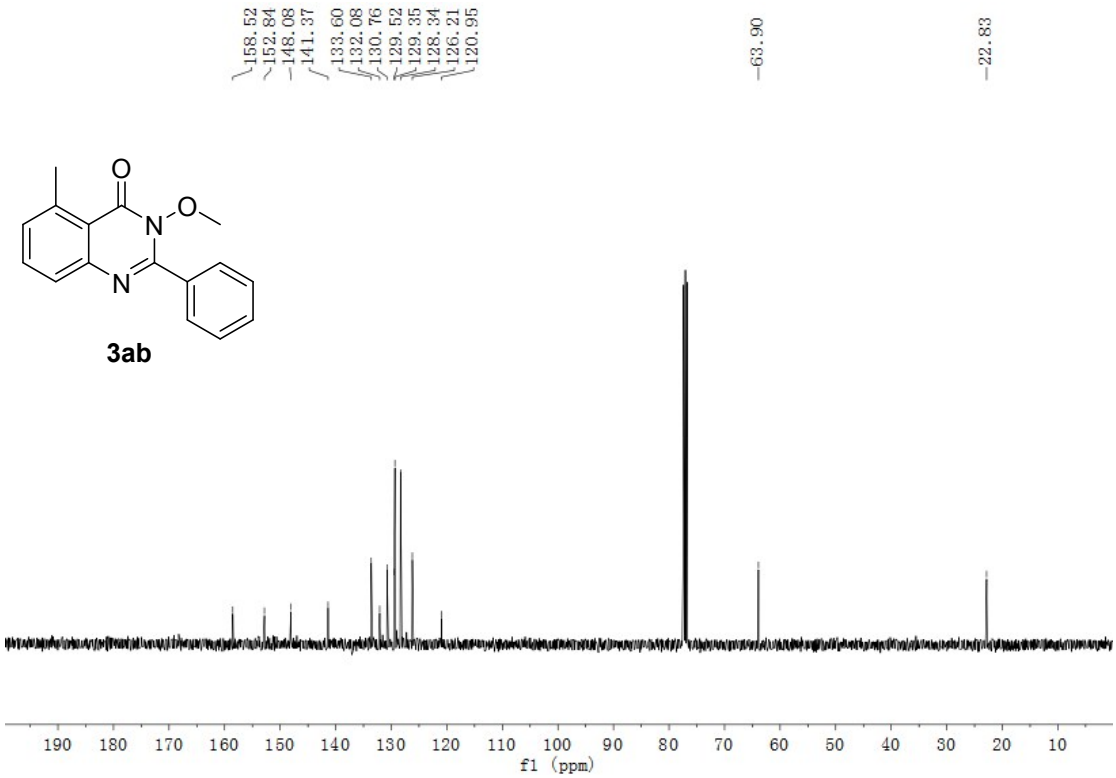
3-methoxy-2-phenylquinazolin-4(3*H*)-one (3aa):



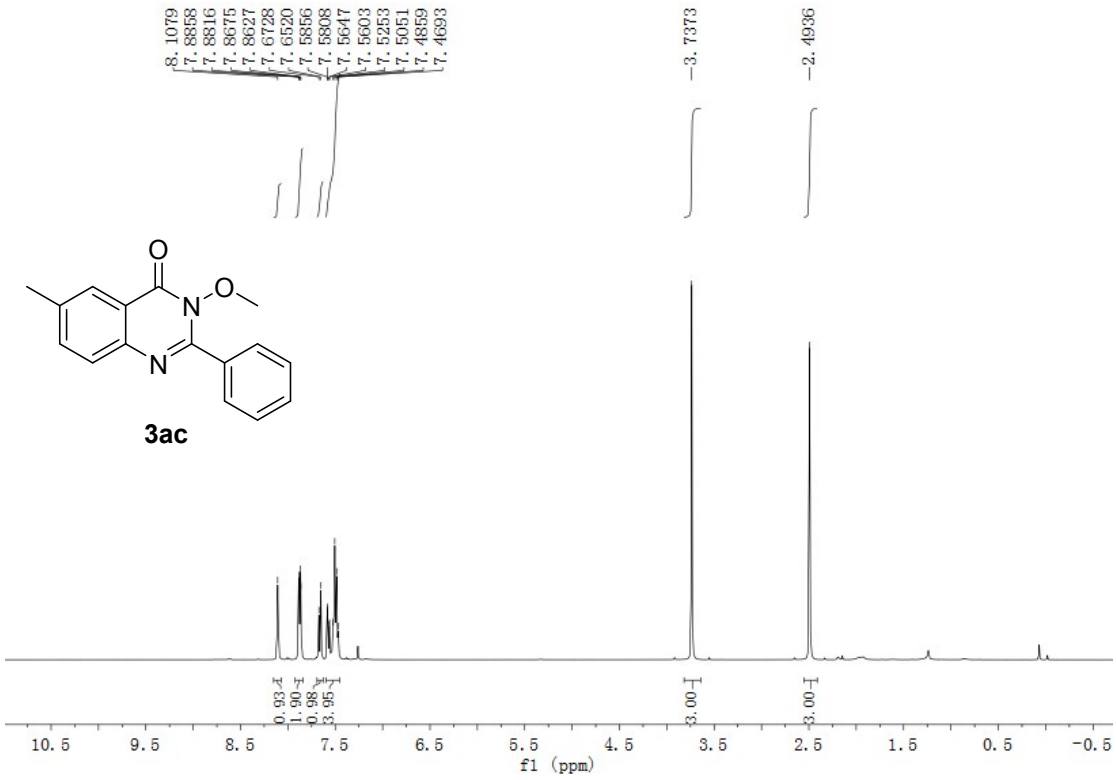


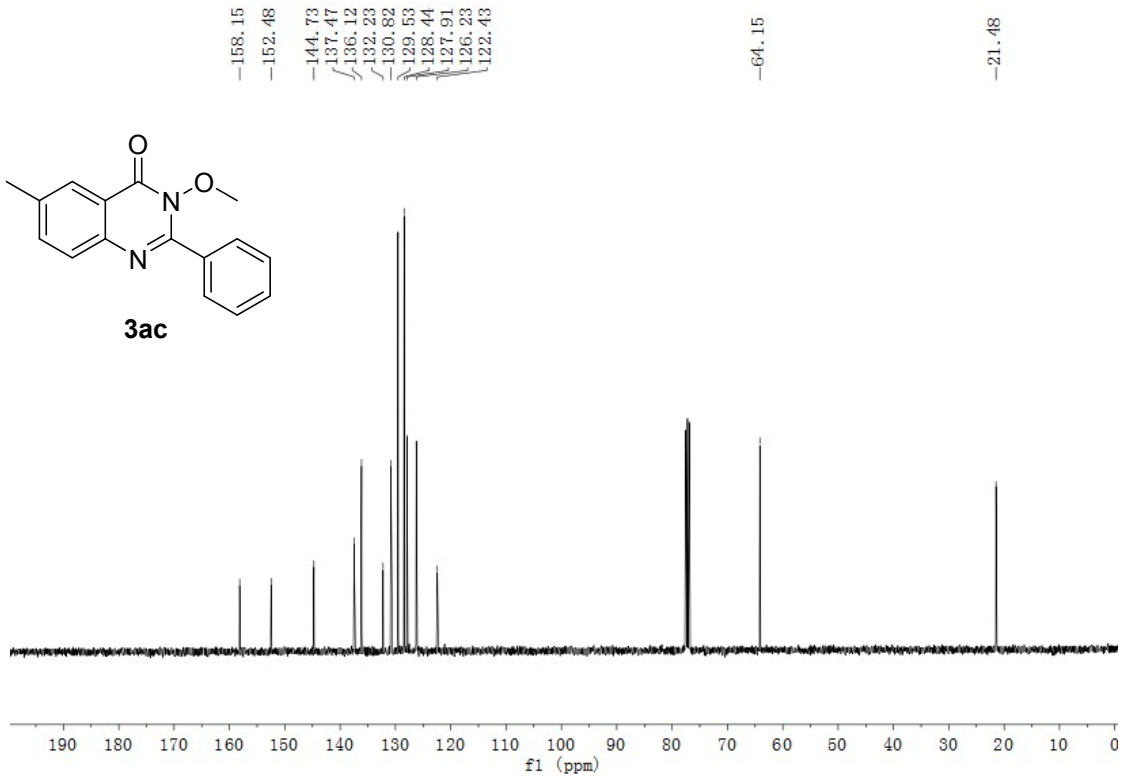
3-methoxy-5-methyl-2-phenylquinazolin-4(3*H*)-one (3ab):



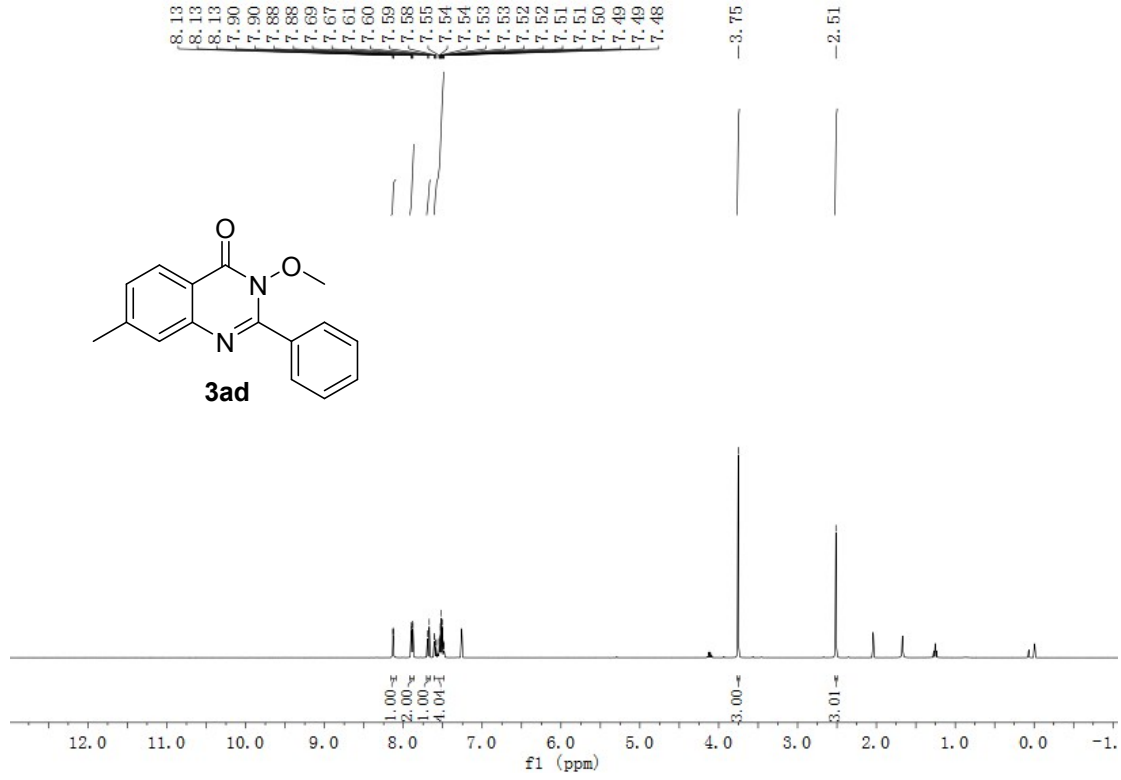


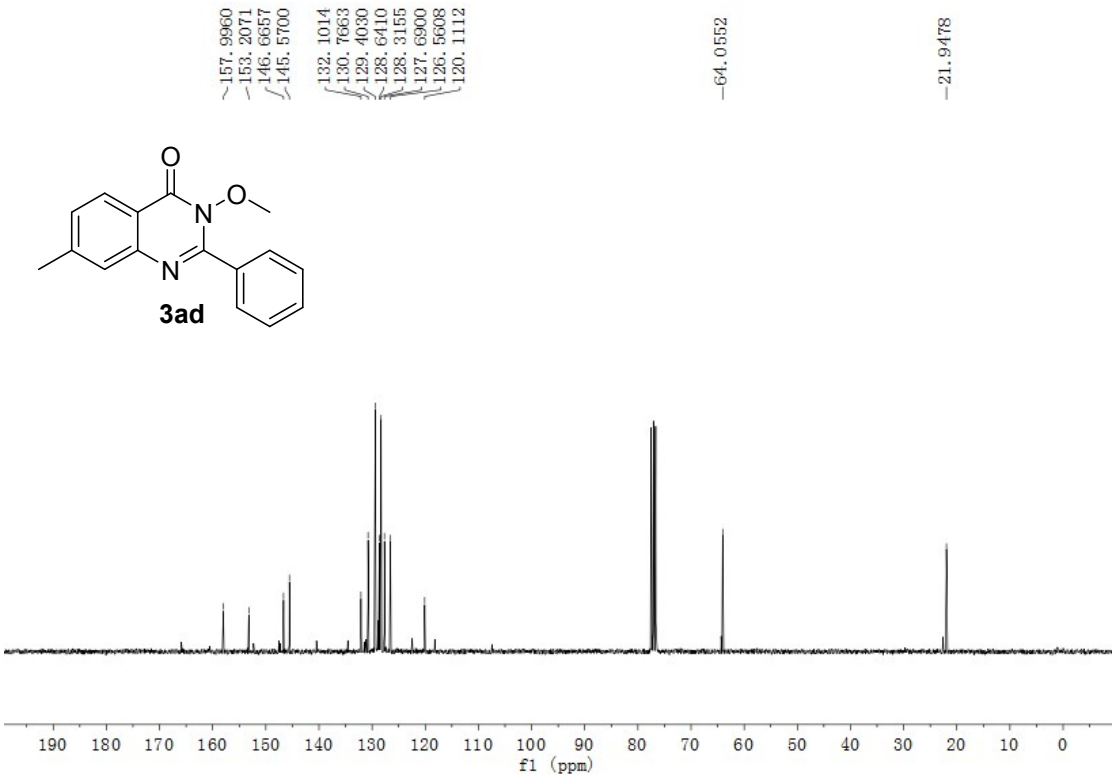
3-methoxy-6-methyl-2-phenylquinazolin-4(3*H*)-one (3ac):



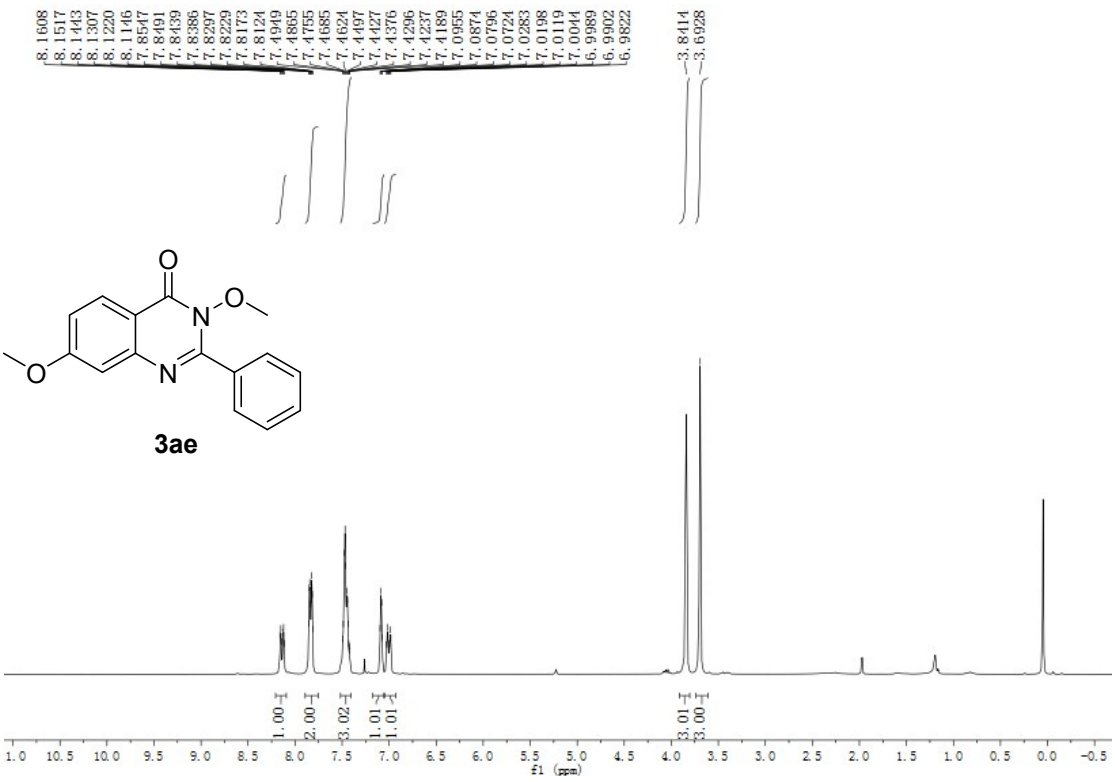


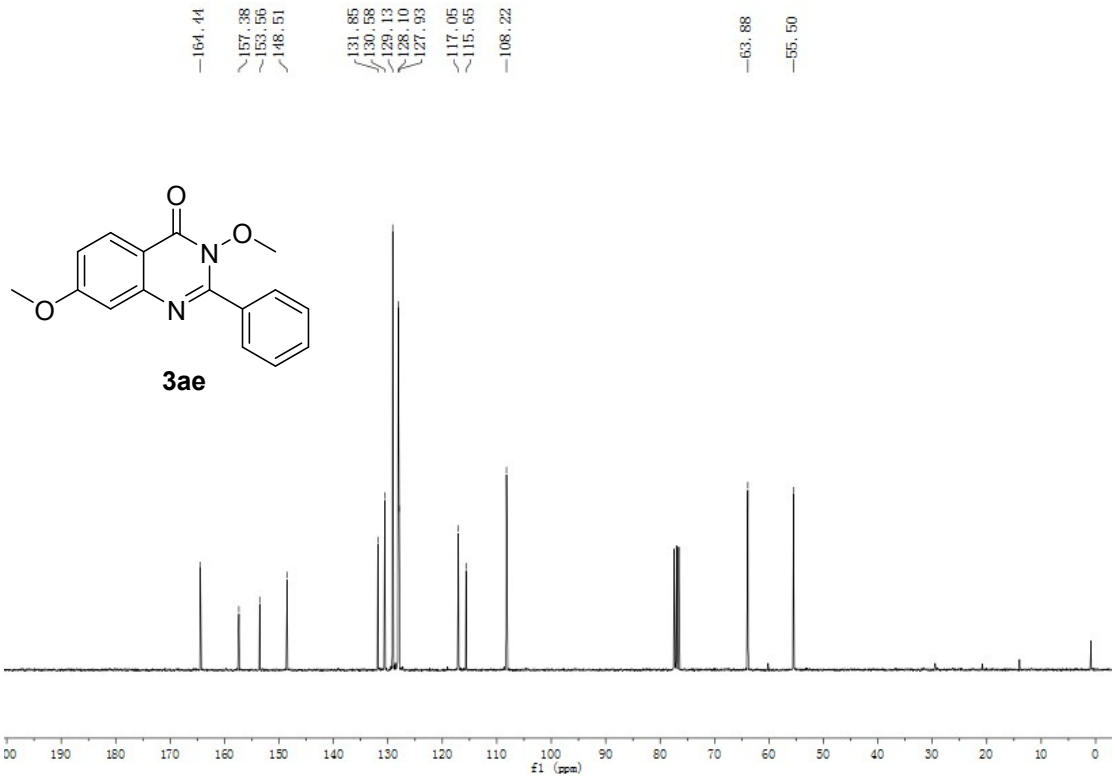
3-methoxy-7-methyl-2-phenylquinazolin-4(3*H*)-one (3ad):



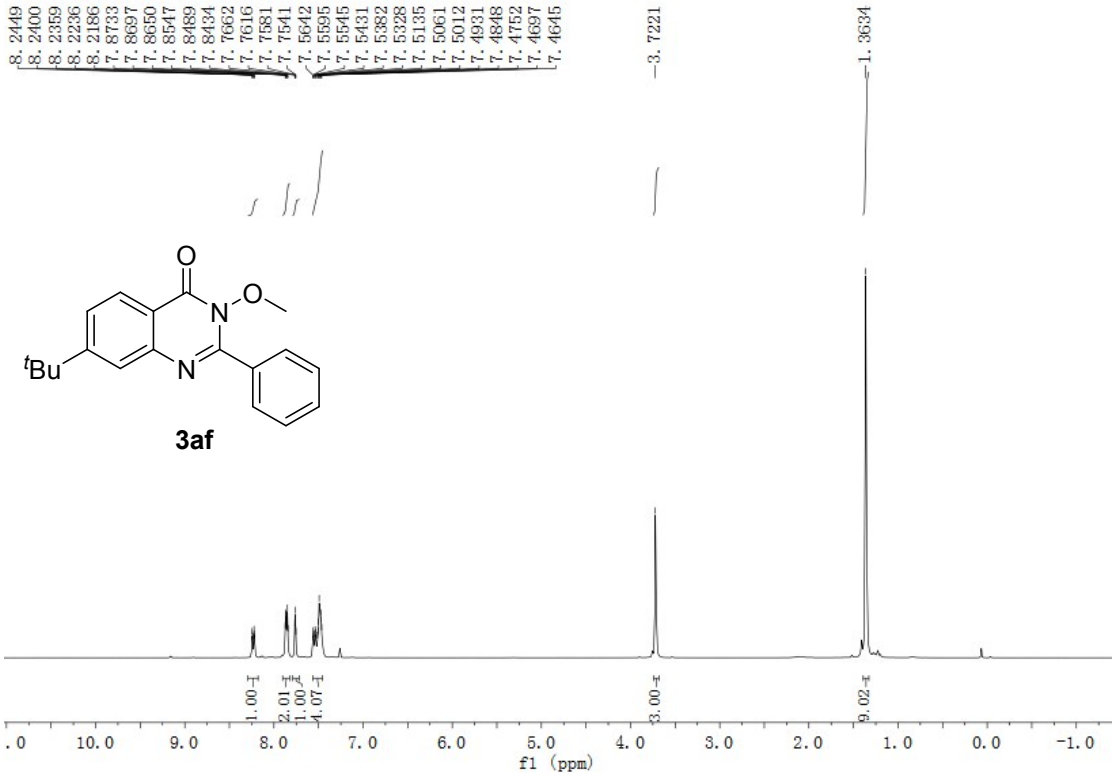


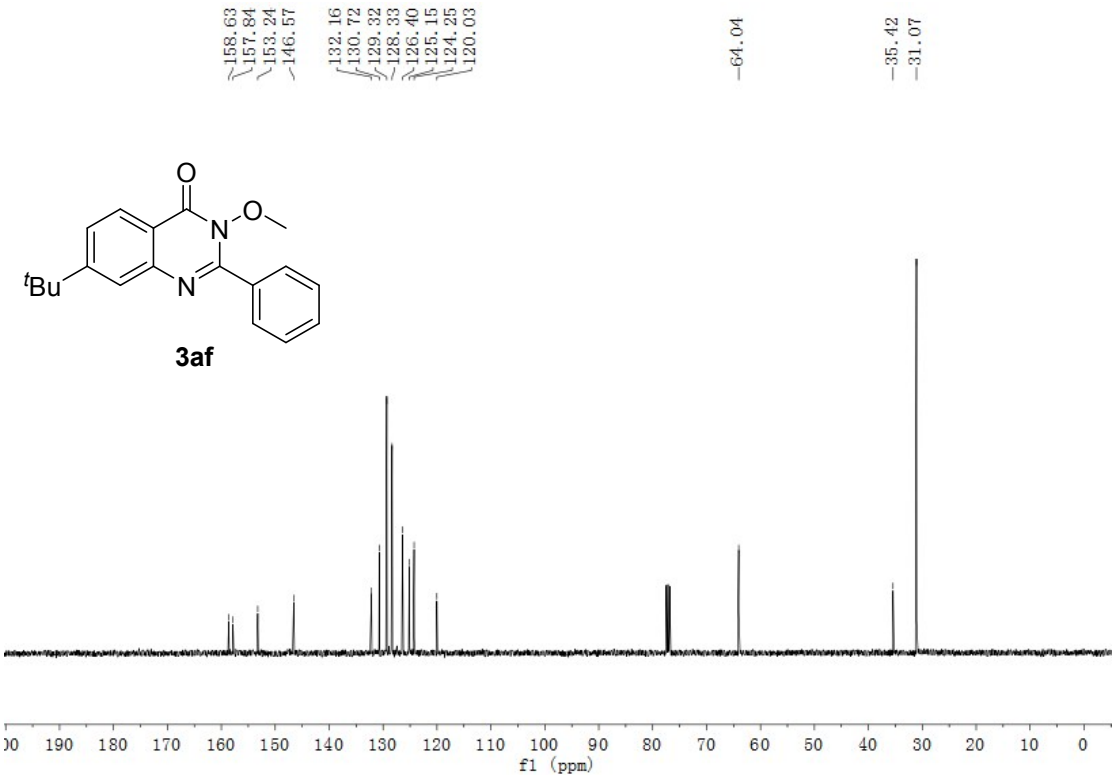
3,7-dimethoxy-2-phenylquinazolin-4(3*H*)-one (3ae):





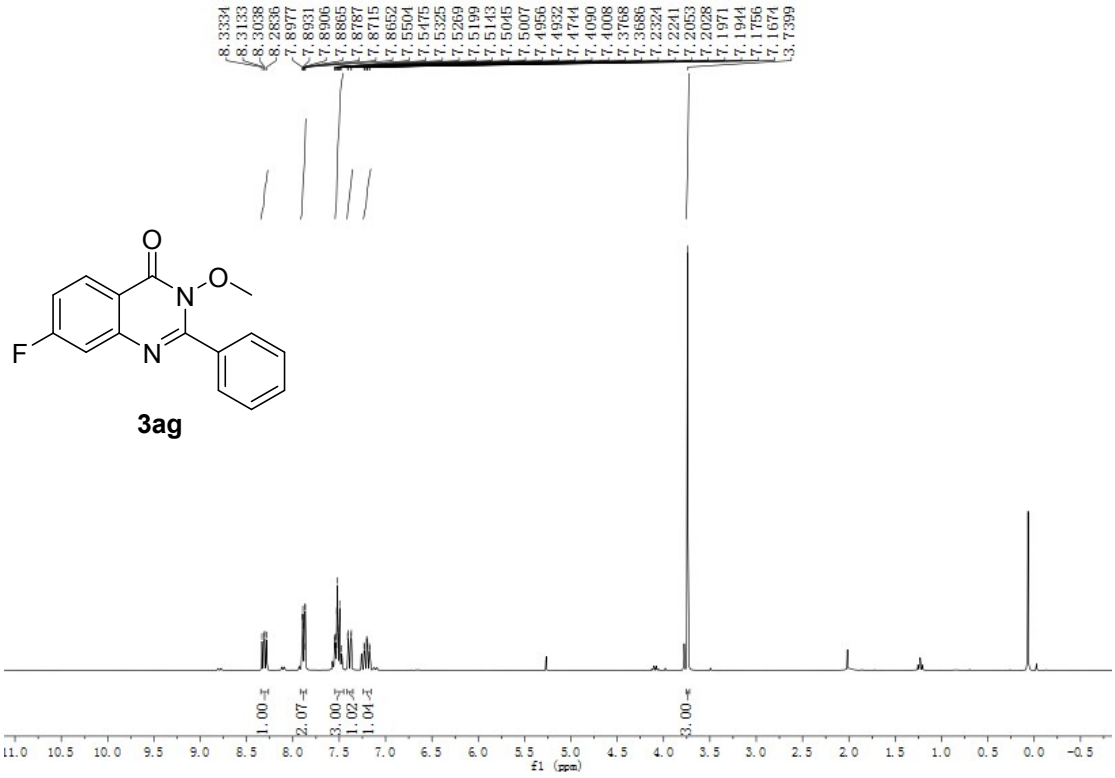
7-(tert-butyl)-3-methoxy-2-phenylquinazolin-4(3*H*)-one (3af):



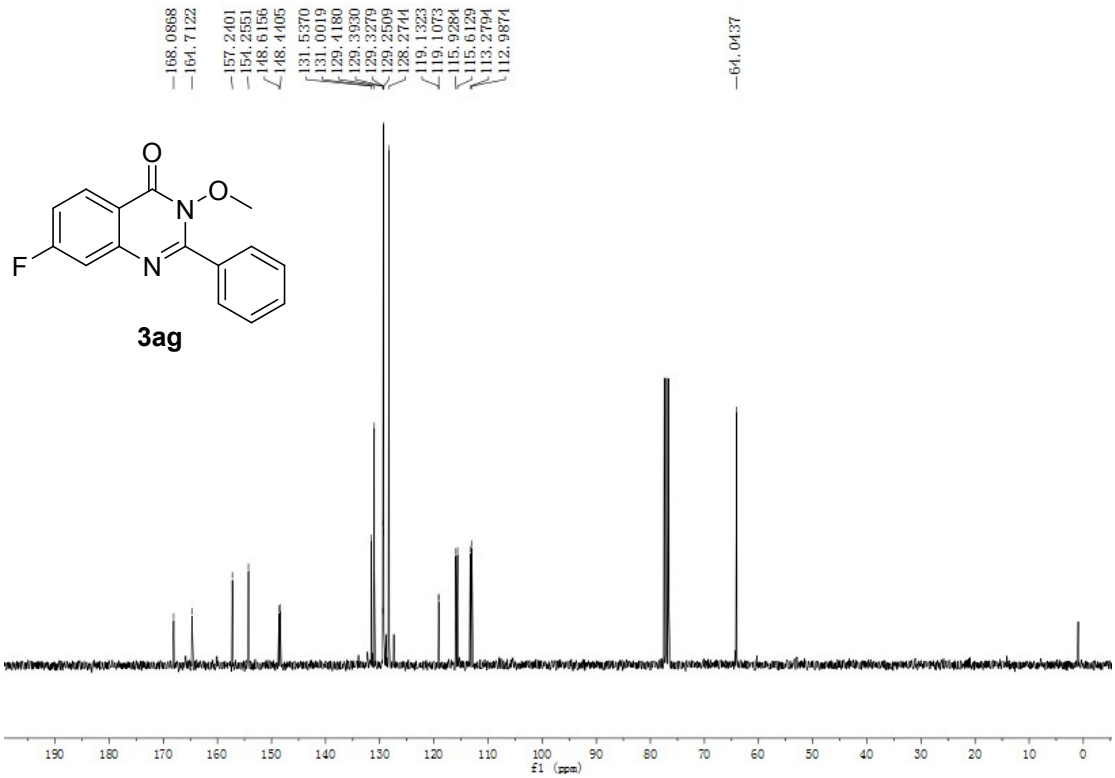


3af

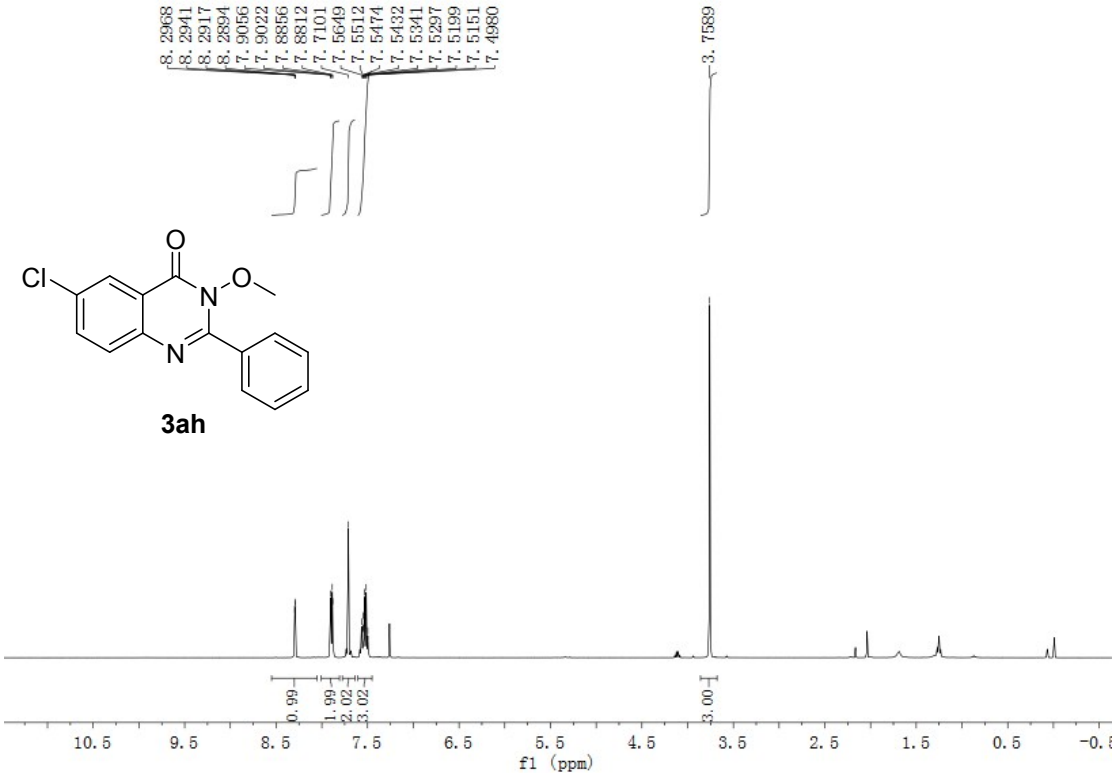
7-fluoro-3-methoxy-2-phenylquinazolin-4(3*H*)-one (3ag):

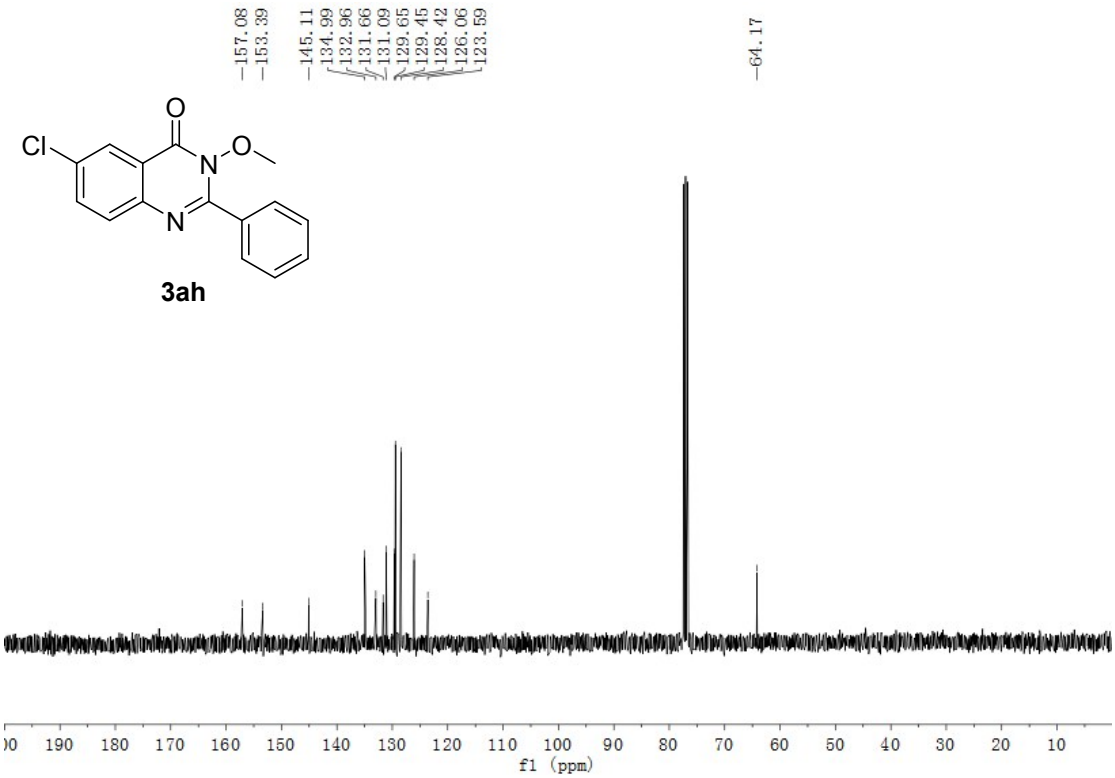


3ag



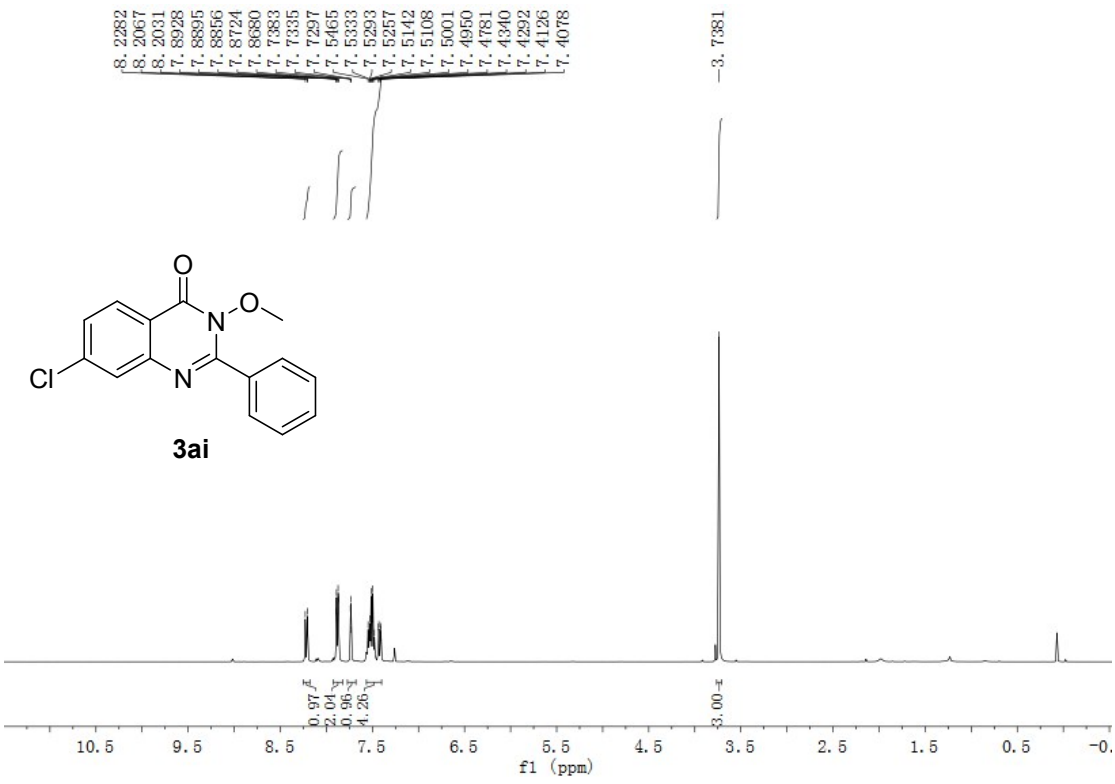
6-chloro-3-methoxy-2-phenylquinazolin-4(3*H*)-one (3ah):



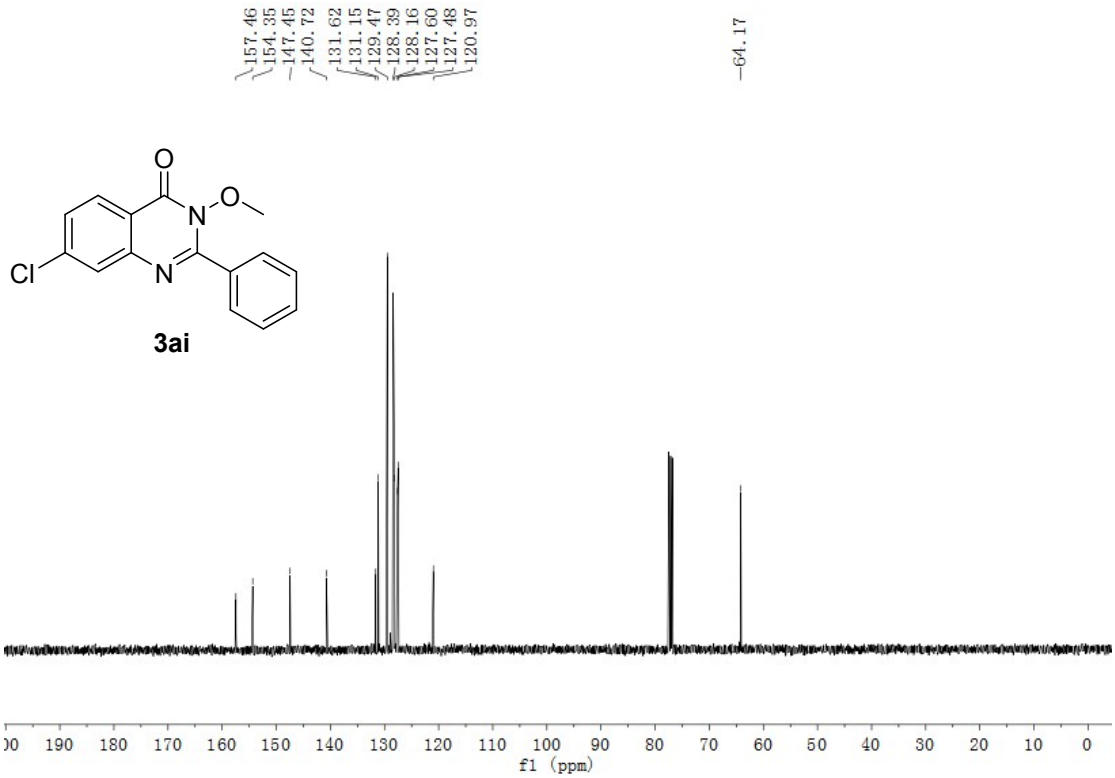


3ah

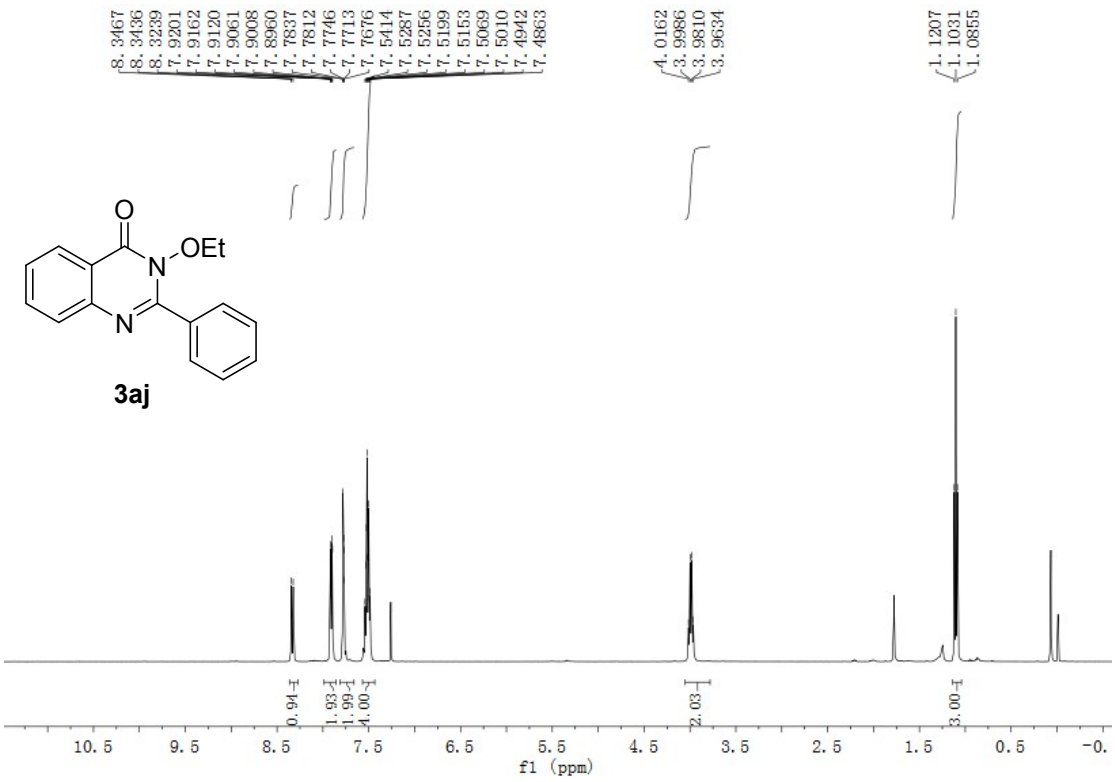
7-chloro-3-methoxy-2-phenylquinazolin-4(3*H*)-one (3ai):

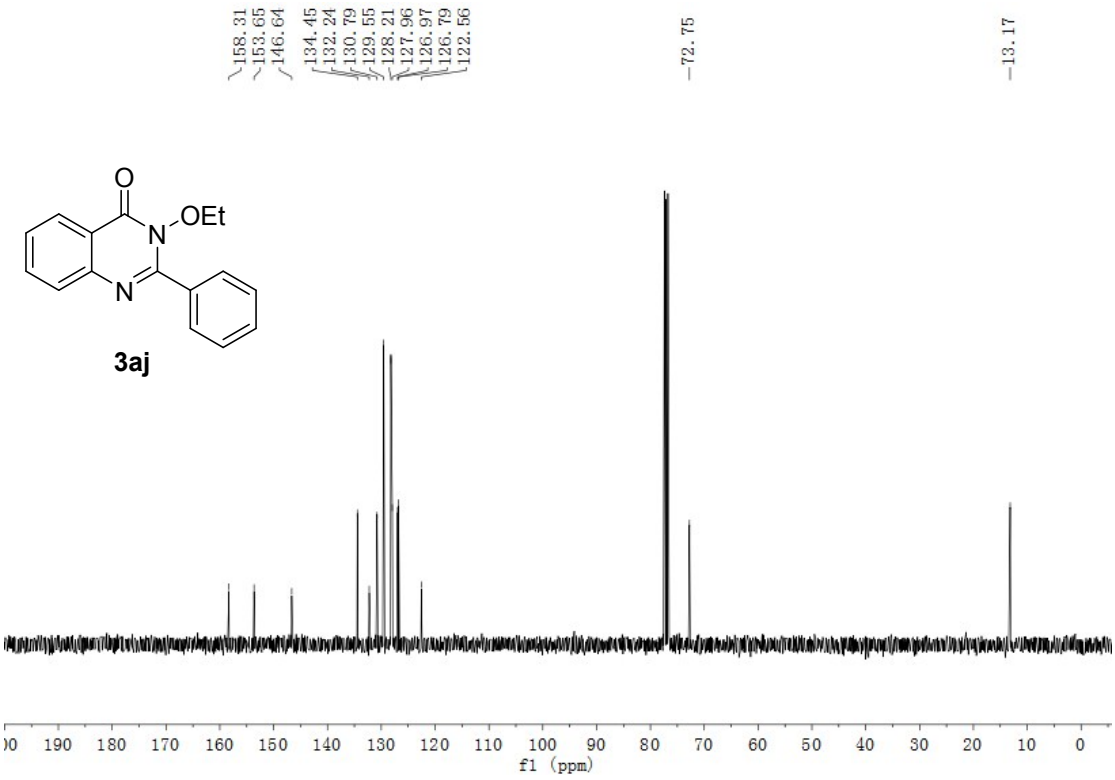


3ai



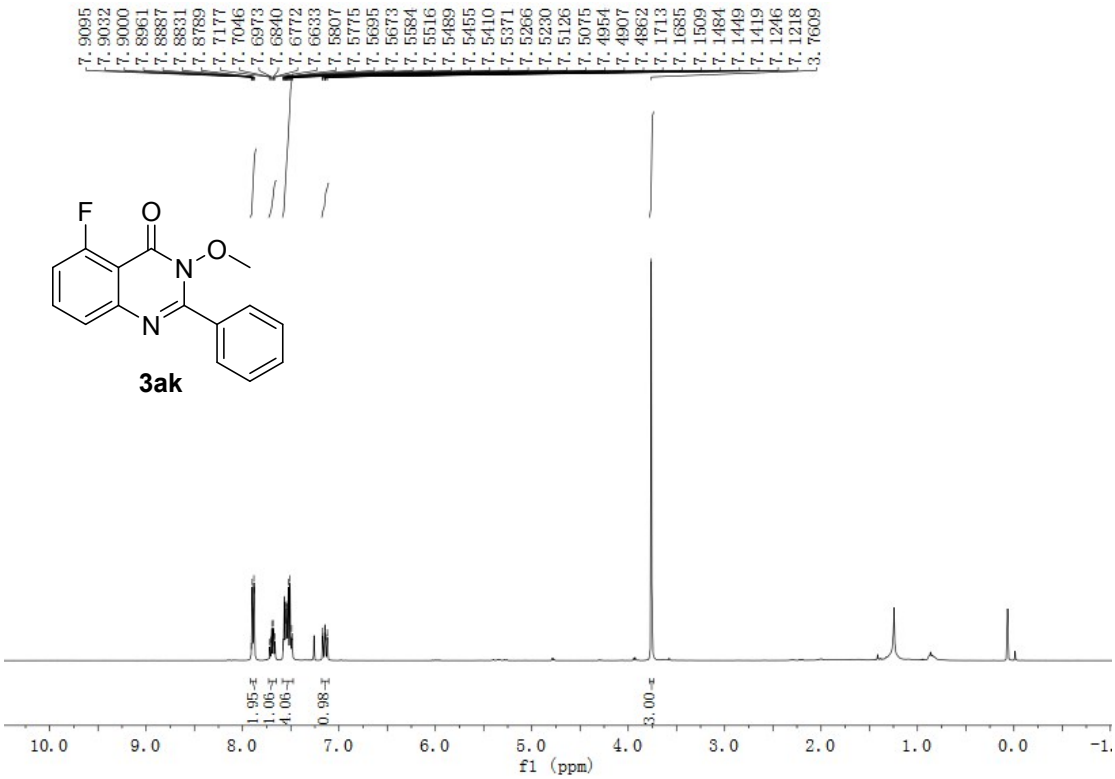
3-ethoxy-2-phenylquinazolin-4(3*H*)-one (3aj):



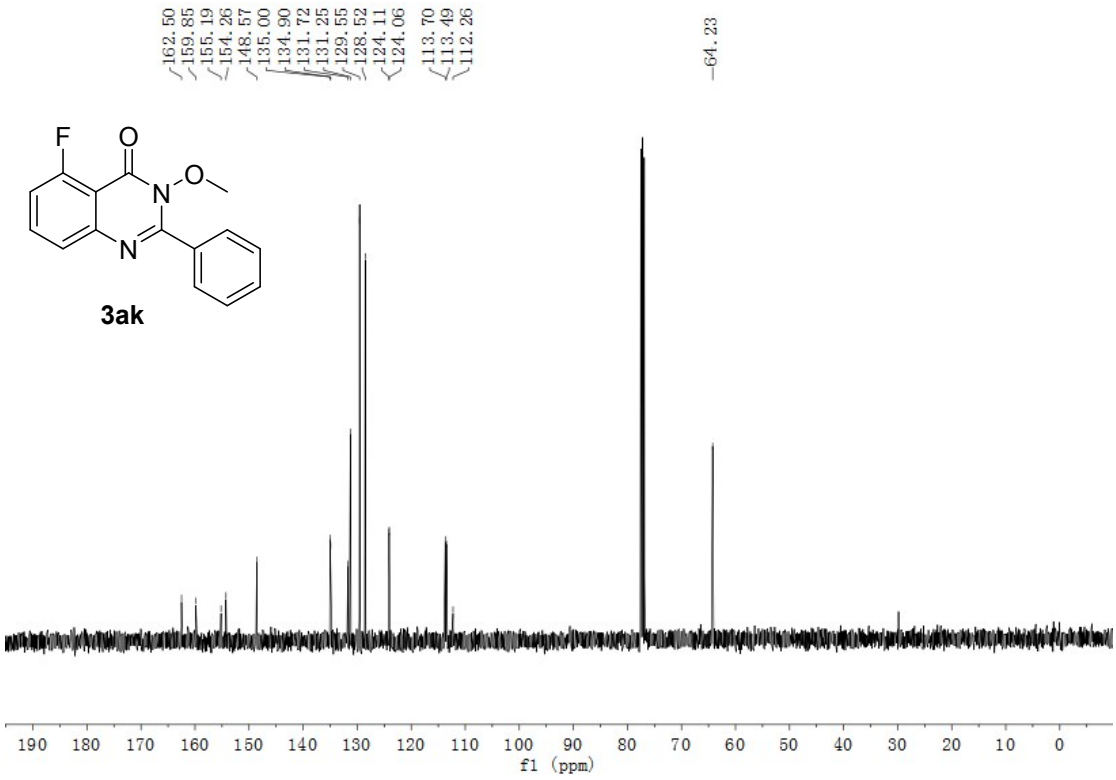


3aj

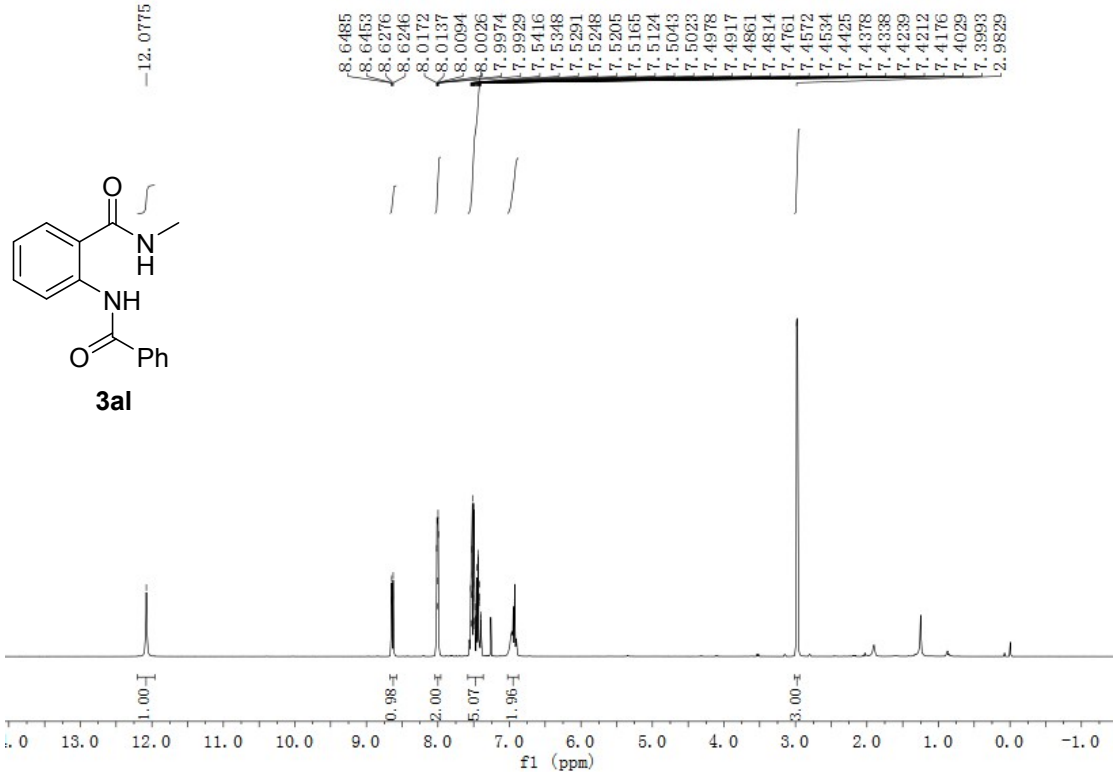
5-fluoro-3-methoxy-2-phenylquinazolin-4(3H)-one (3ak):

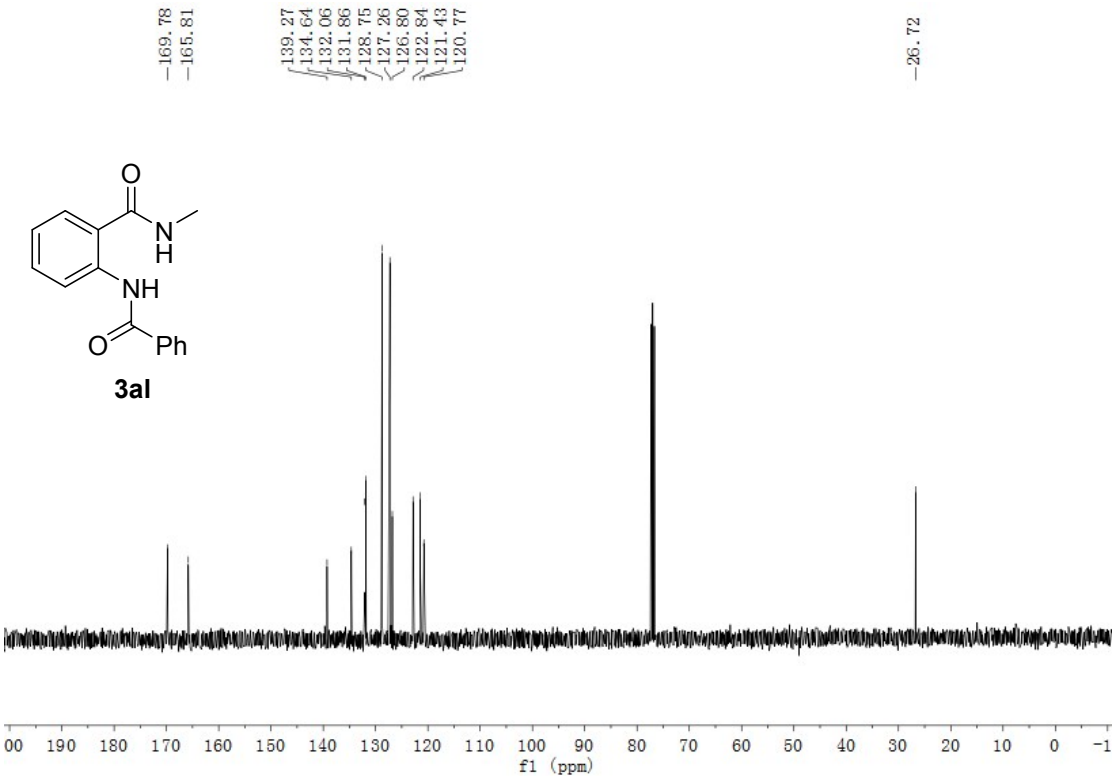


3ak

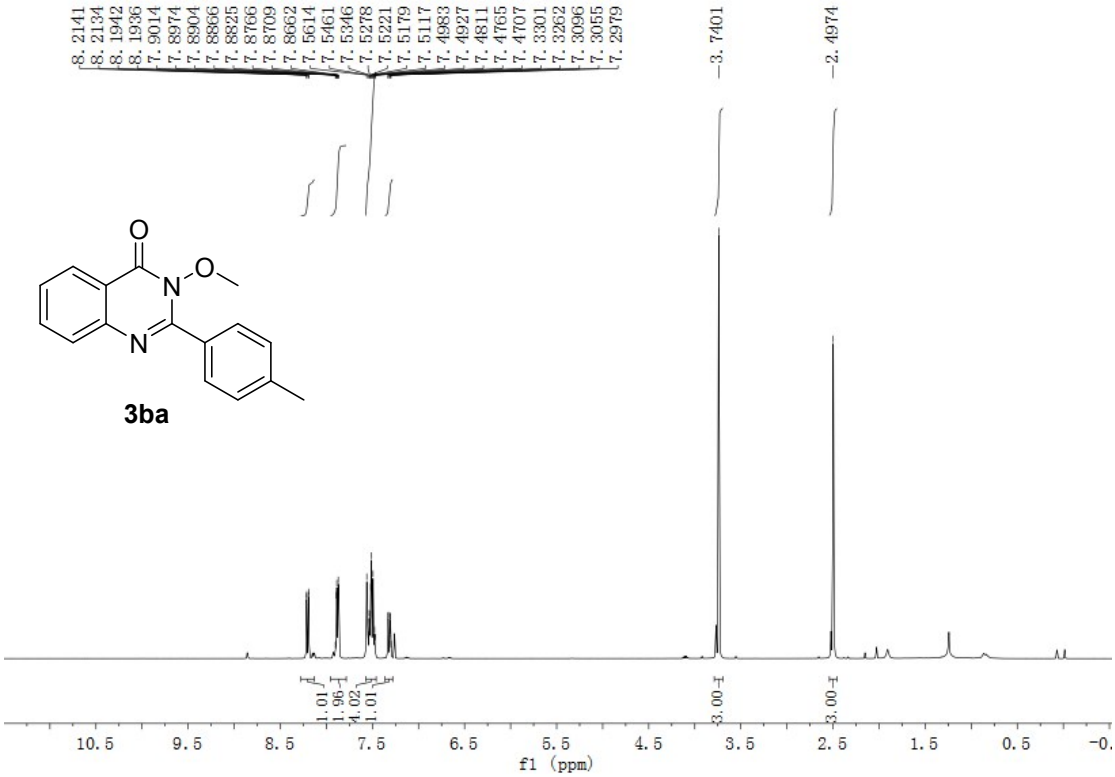


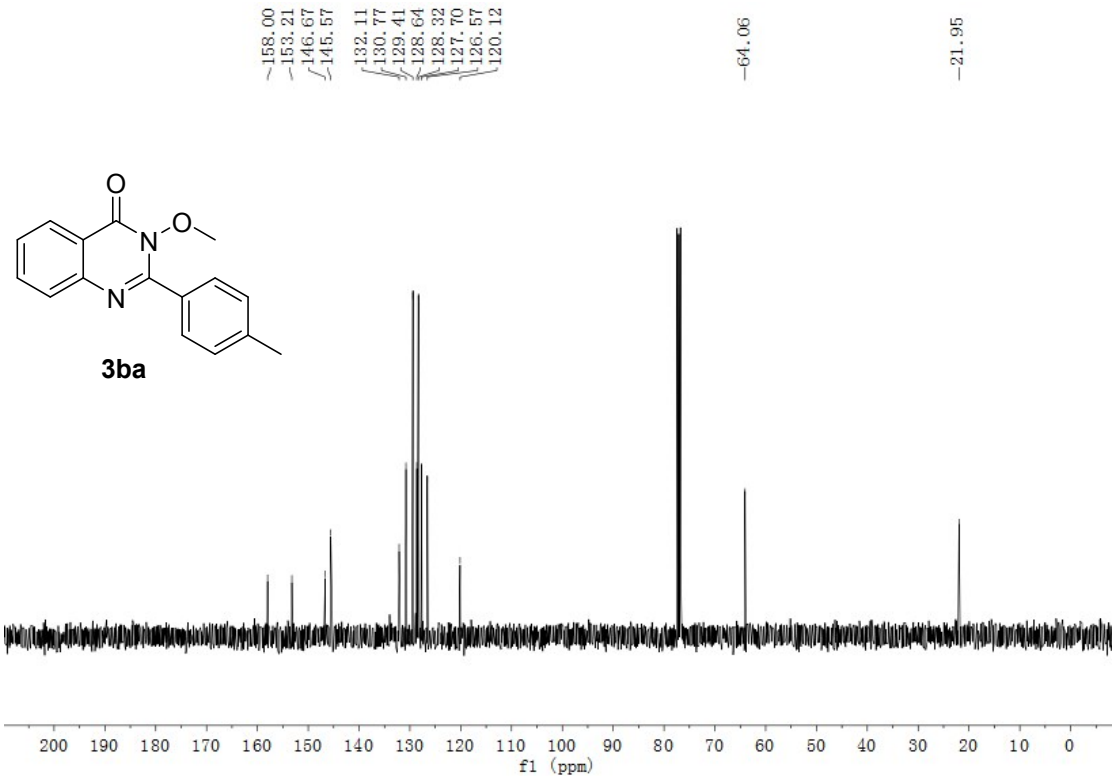
2-benzamido-N-methylbenzamide (3al):



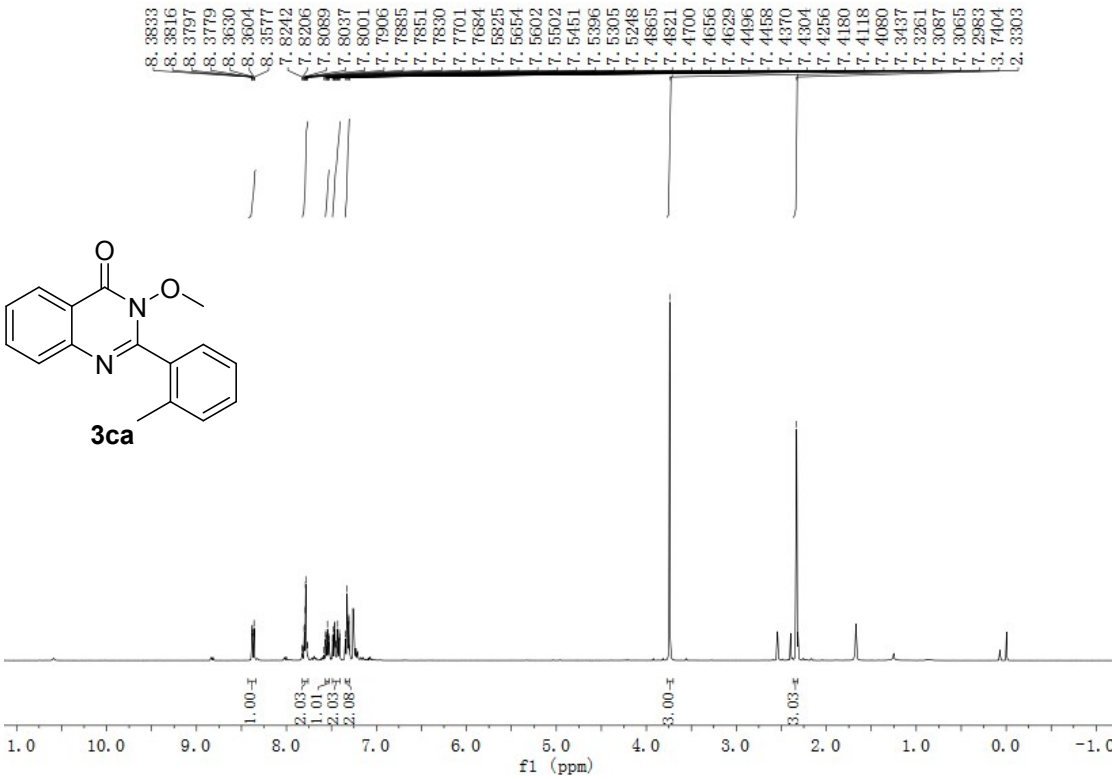


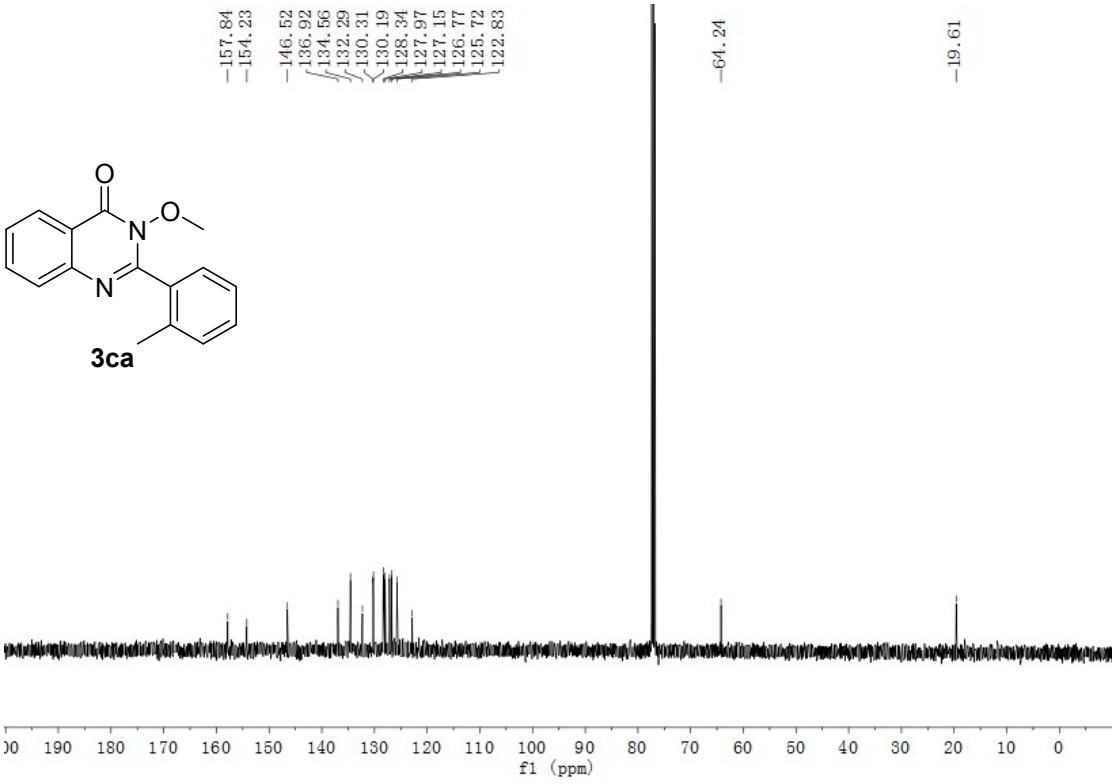
3-methoxy-2-(p-tolyl)quinazolin-4(3*H*)-one (3ba):



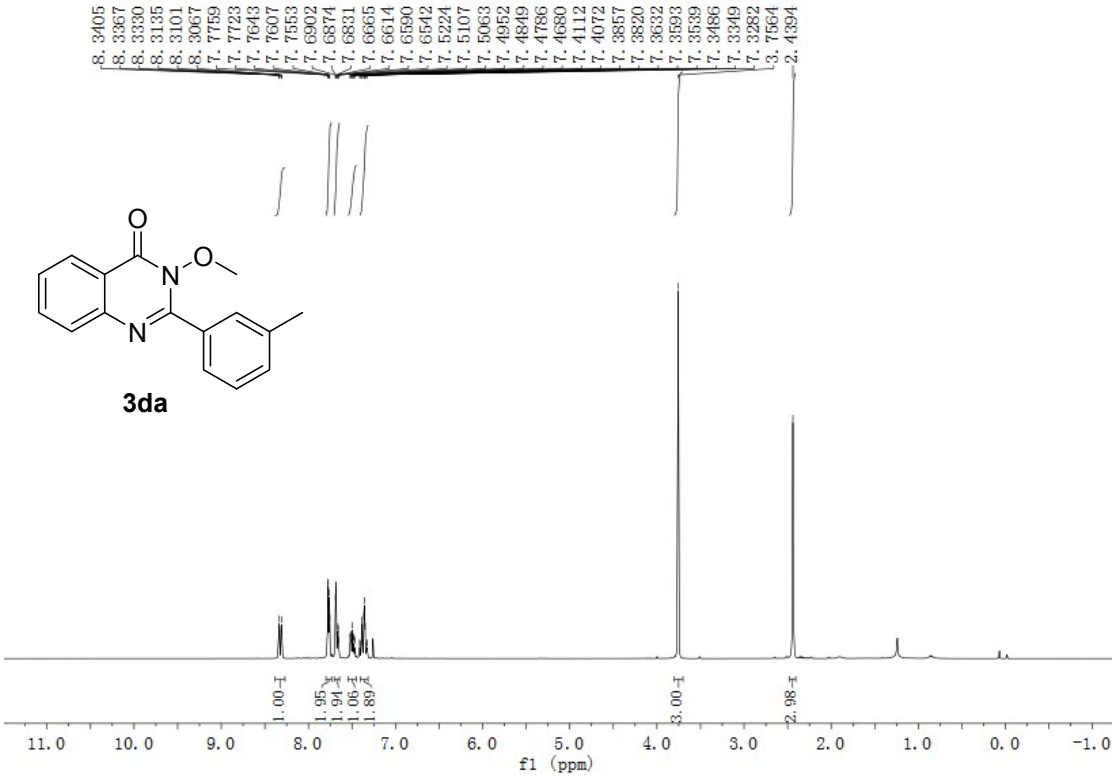


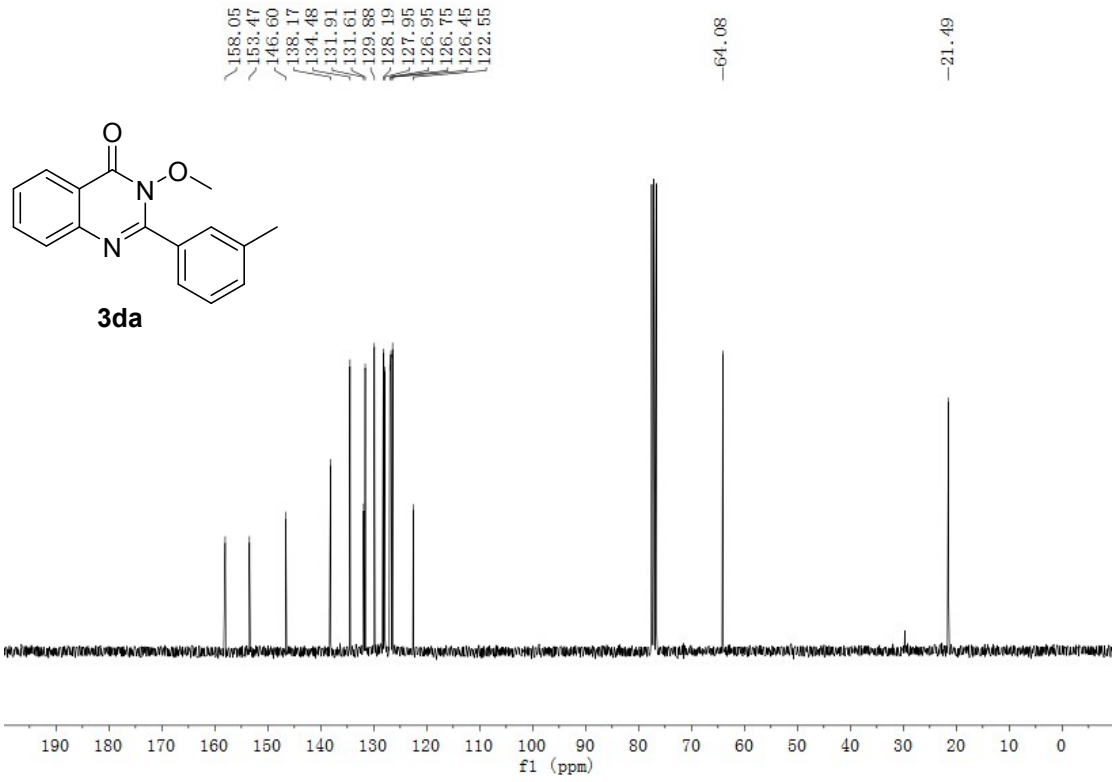
3-methoxy-2-(o-tolyl)quinazolin-4(3*H*)-one (3ca):



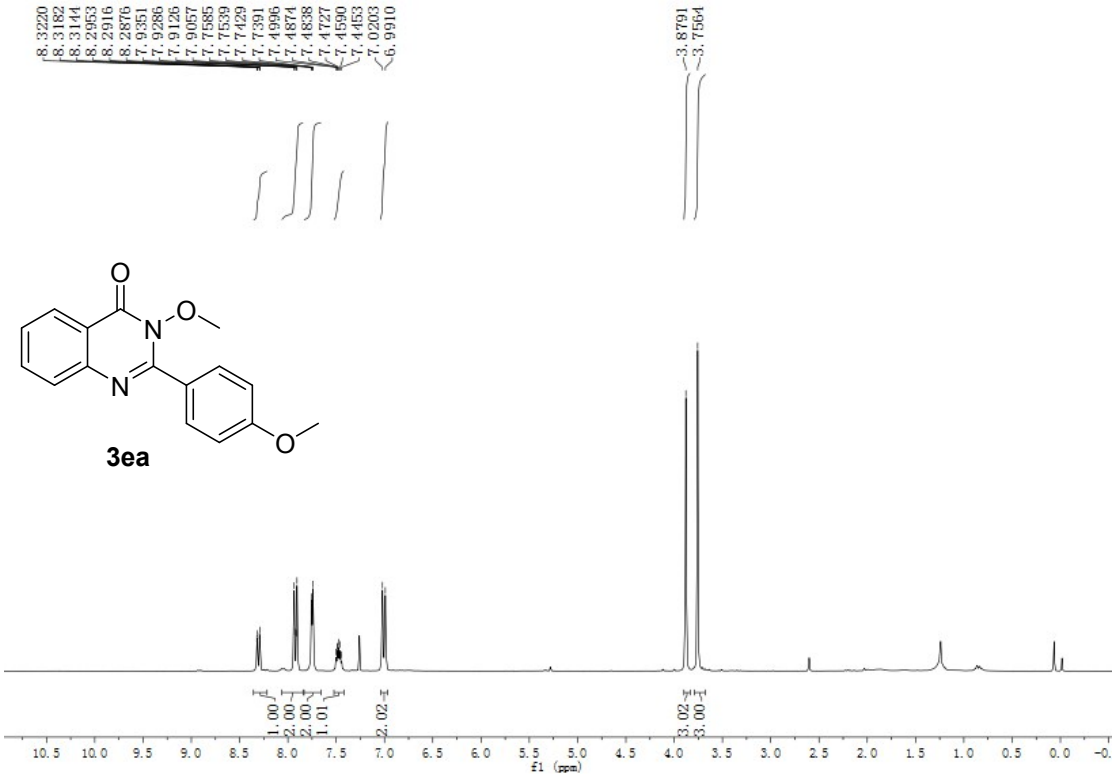


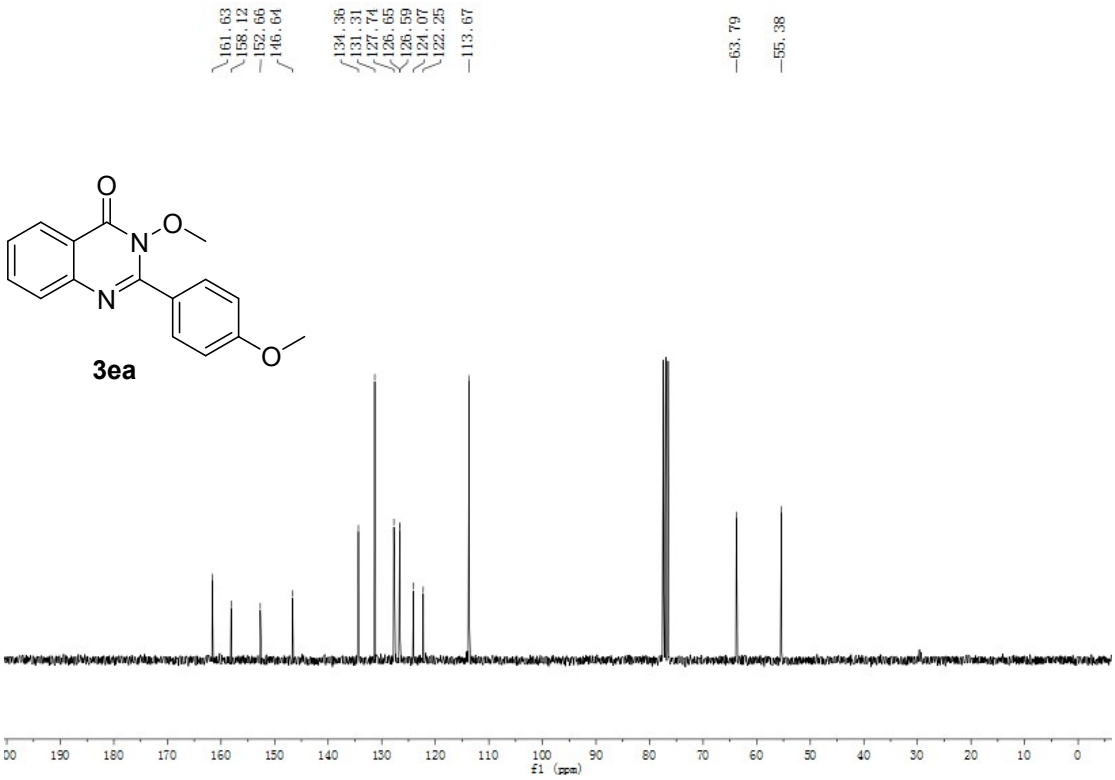
3-methoxy-2-(m-tolyl)quinazolin-4(3*H*)-one (3da):



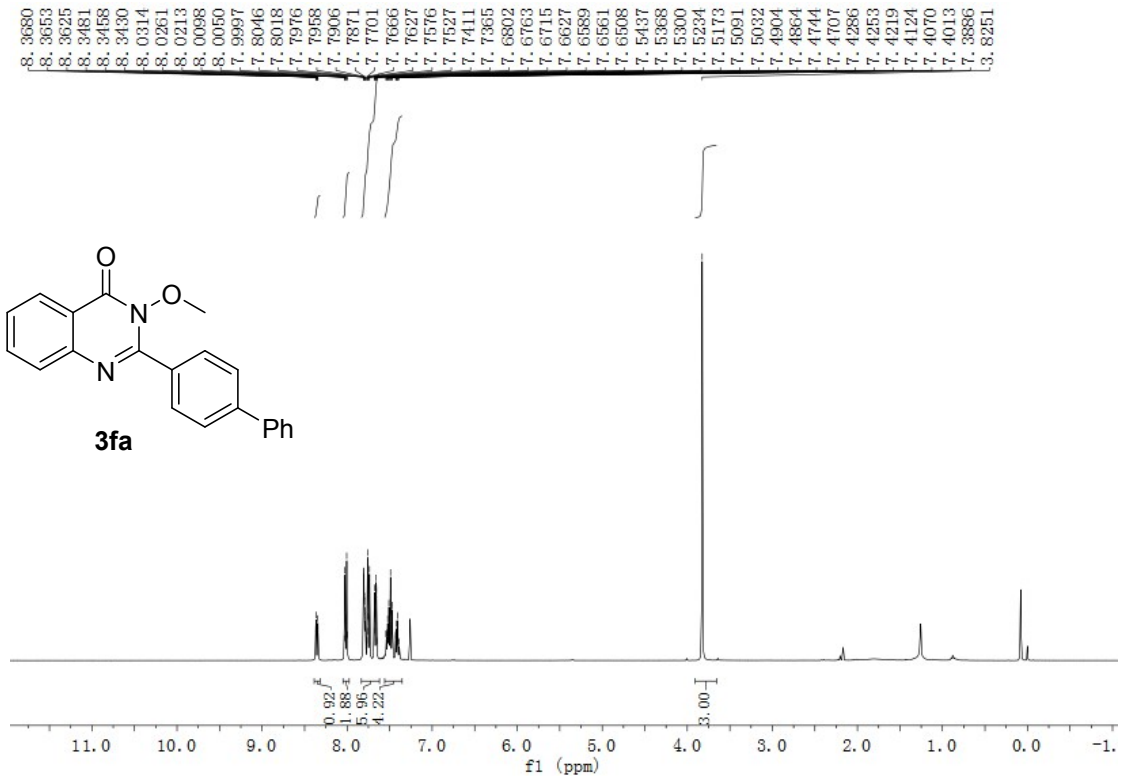


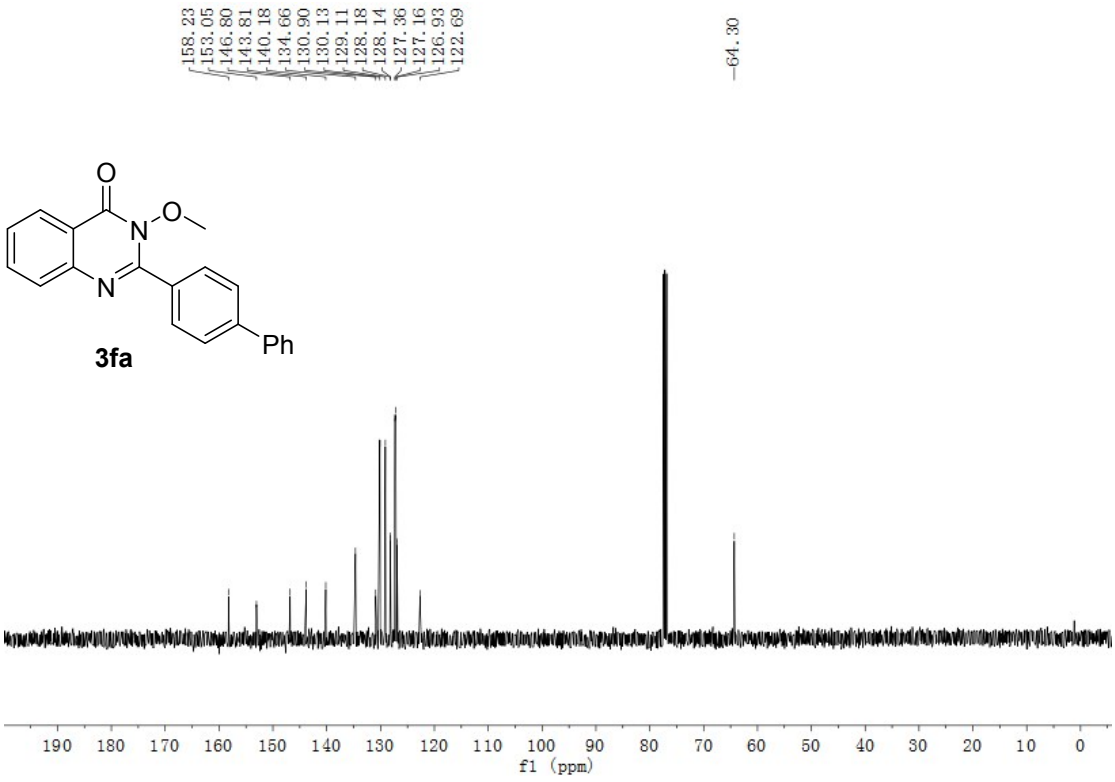
3-methoxy-2-(4-methoxyphenyl)quinazolin-4(3*H*)-one (3ea):



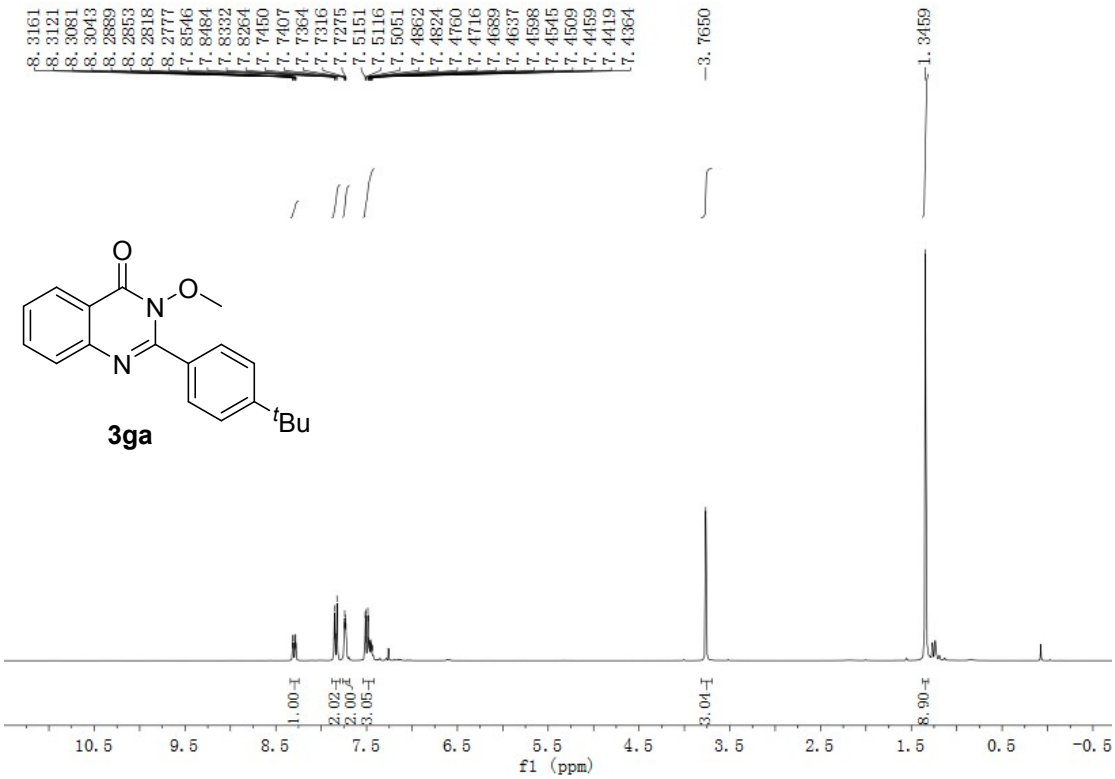


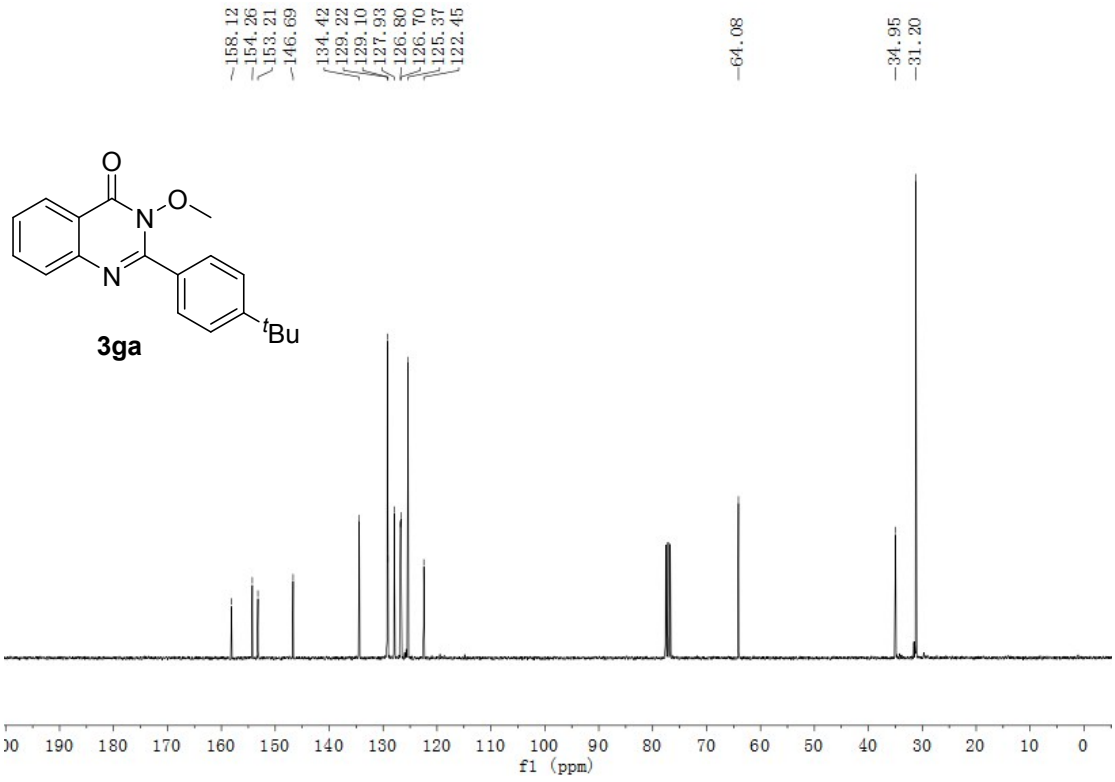
2-([1,1'-biphenyl]-4-yl)-3-methoxyquinazolin-4(3*H*)-one (3fa):



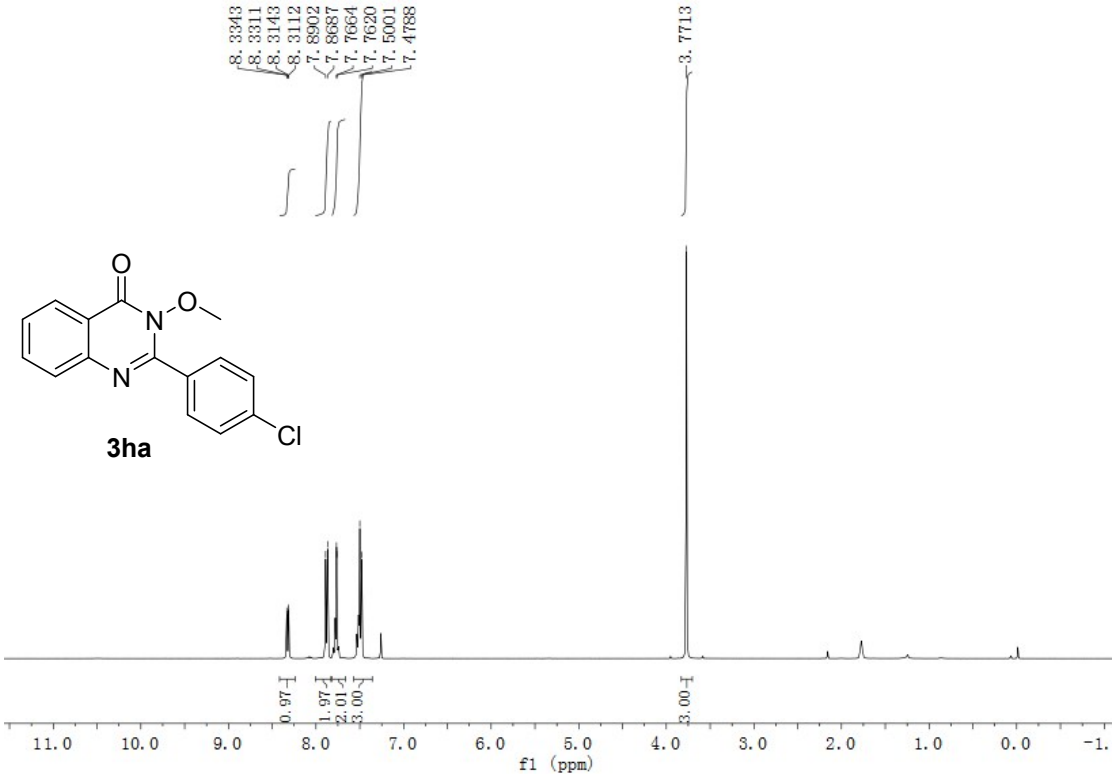


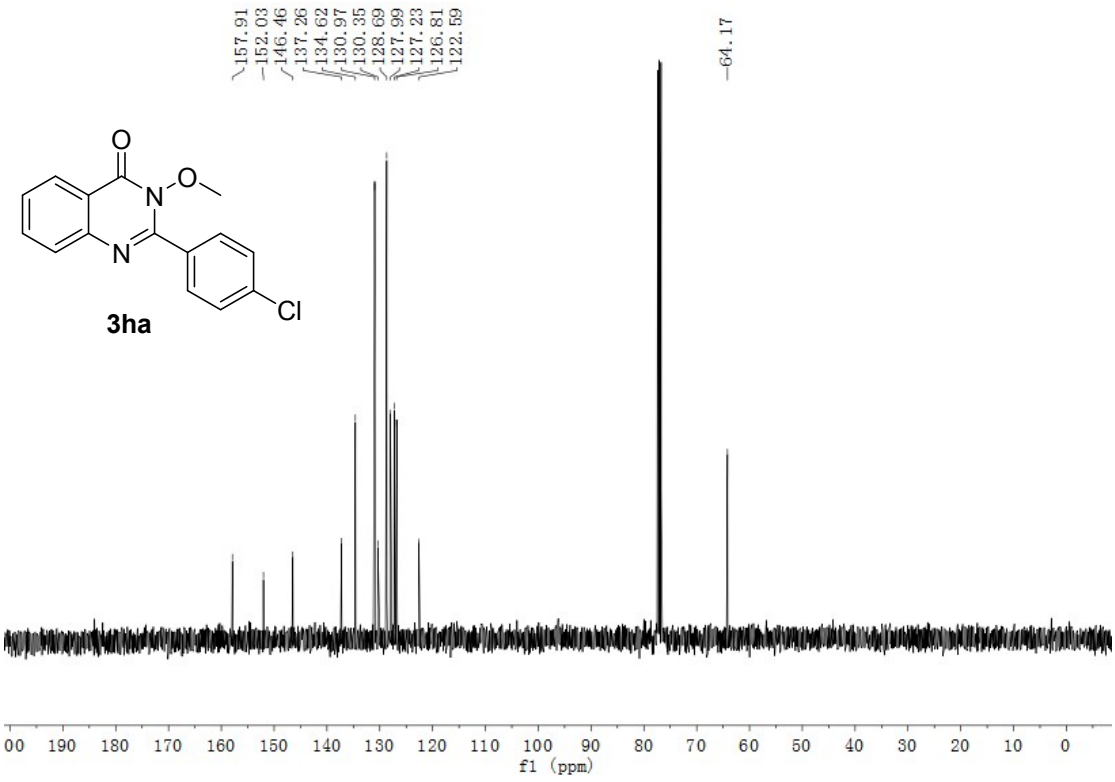
2-(4-(tert-butyl)phenyl)-3-methoxyquinazolin-4(3*H*)-one (3ga):



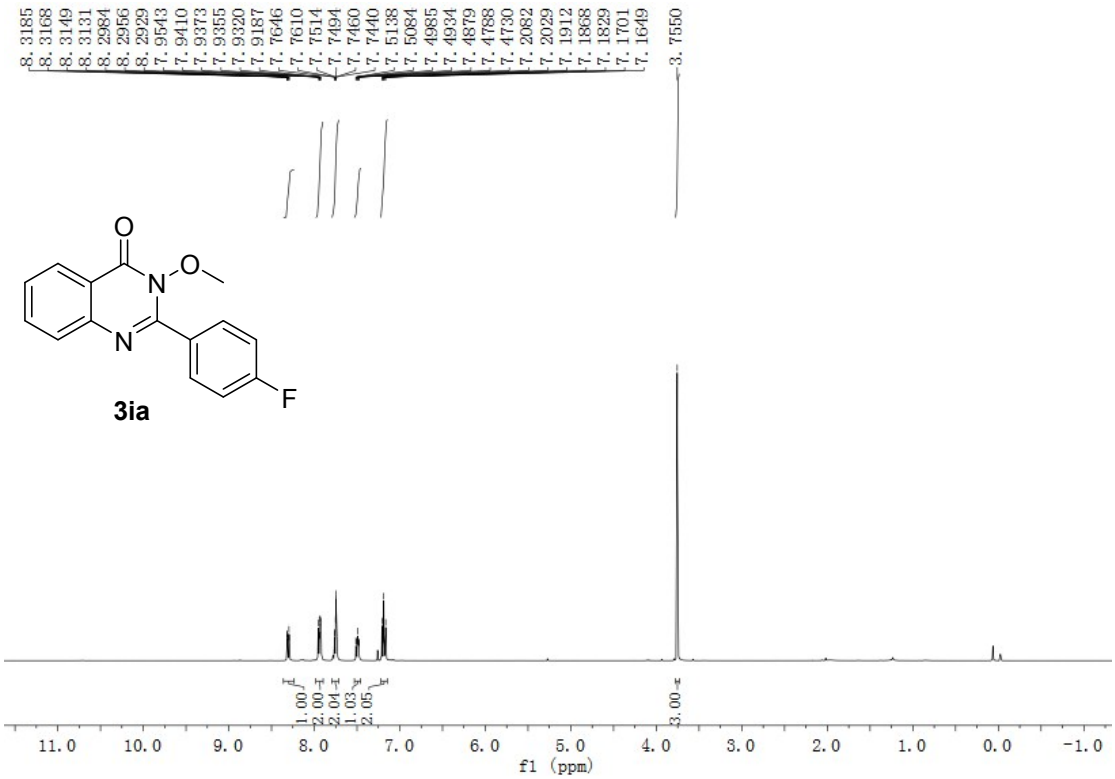


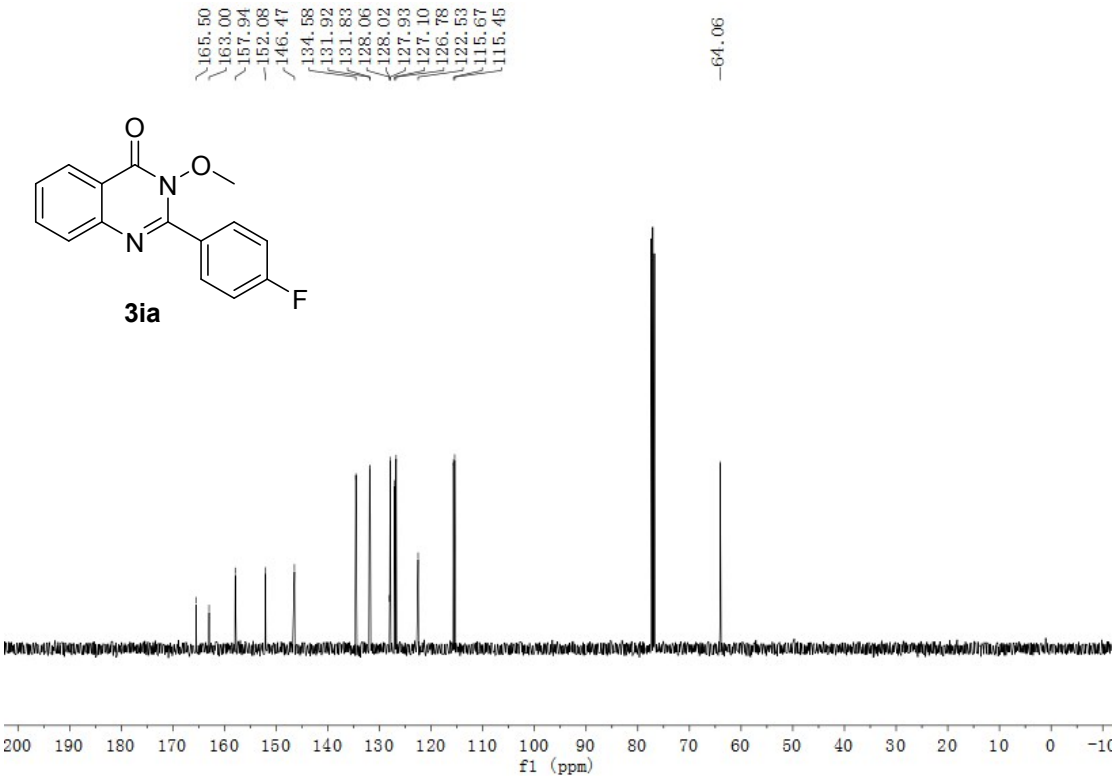
2-(4-chlorophenyl)-3-methoxyquinazolin-4(3*H*)-one (3ha):



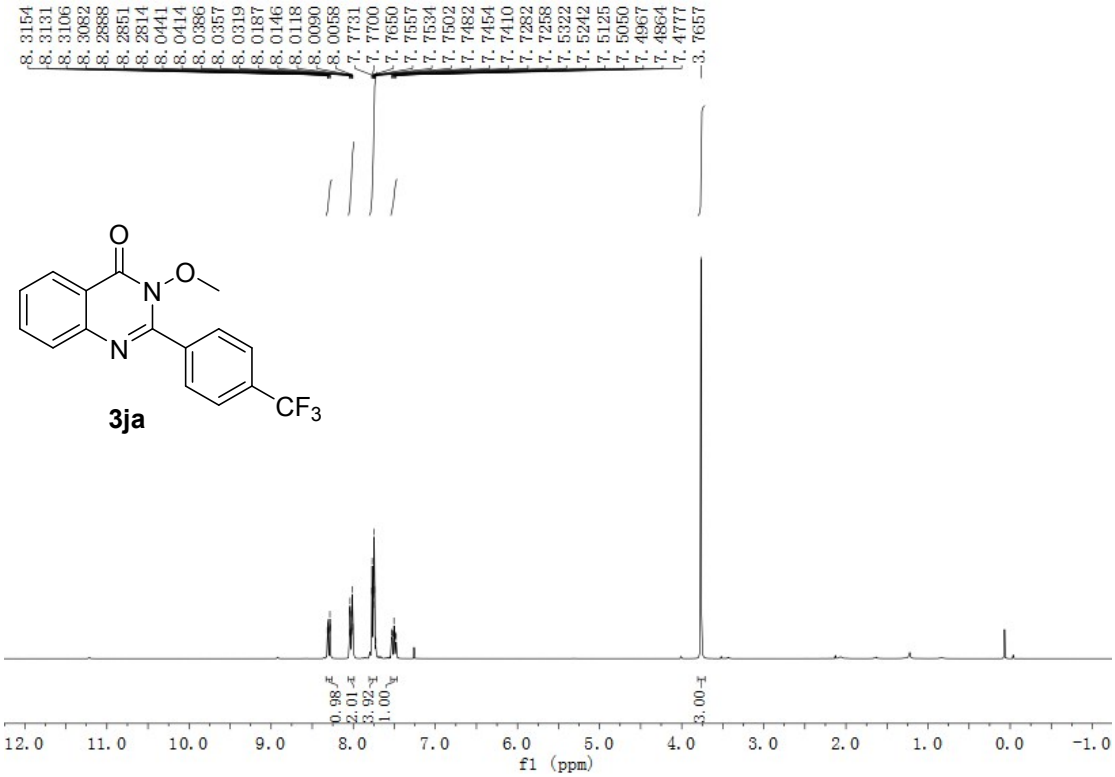


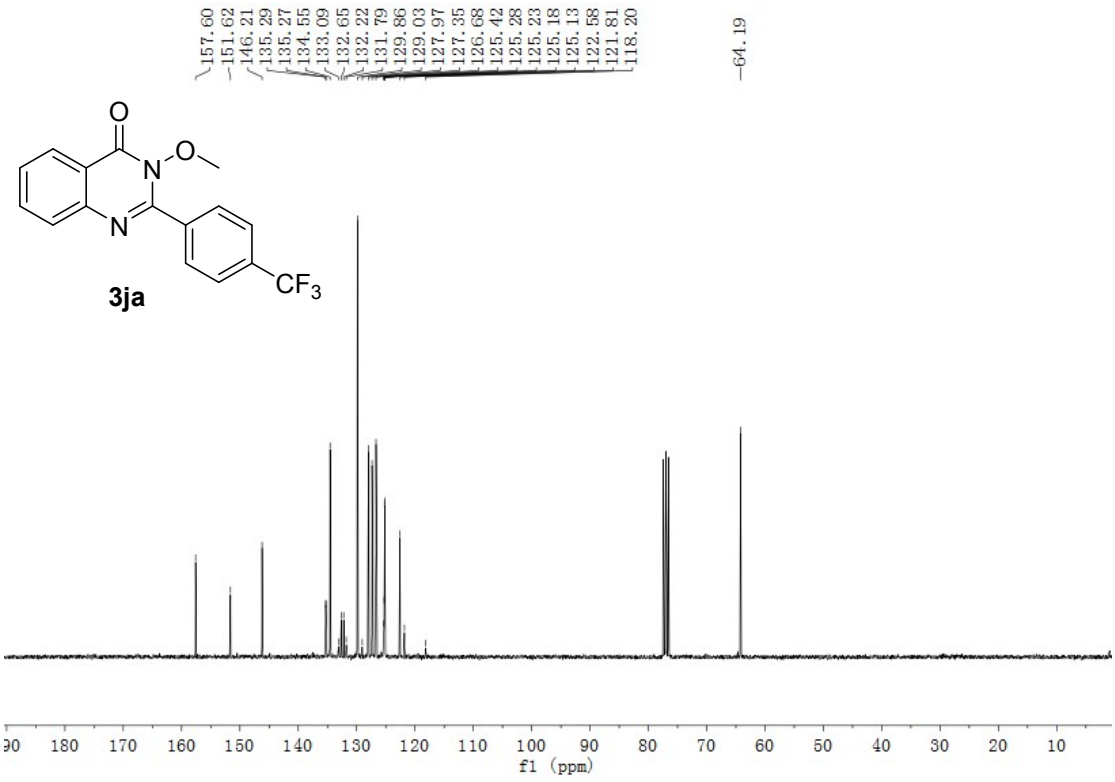
2-(4-fluorophenyl)-3-methoxyquinazolin-4(3*H*)-one (3ia):



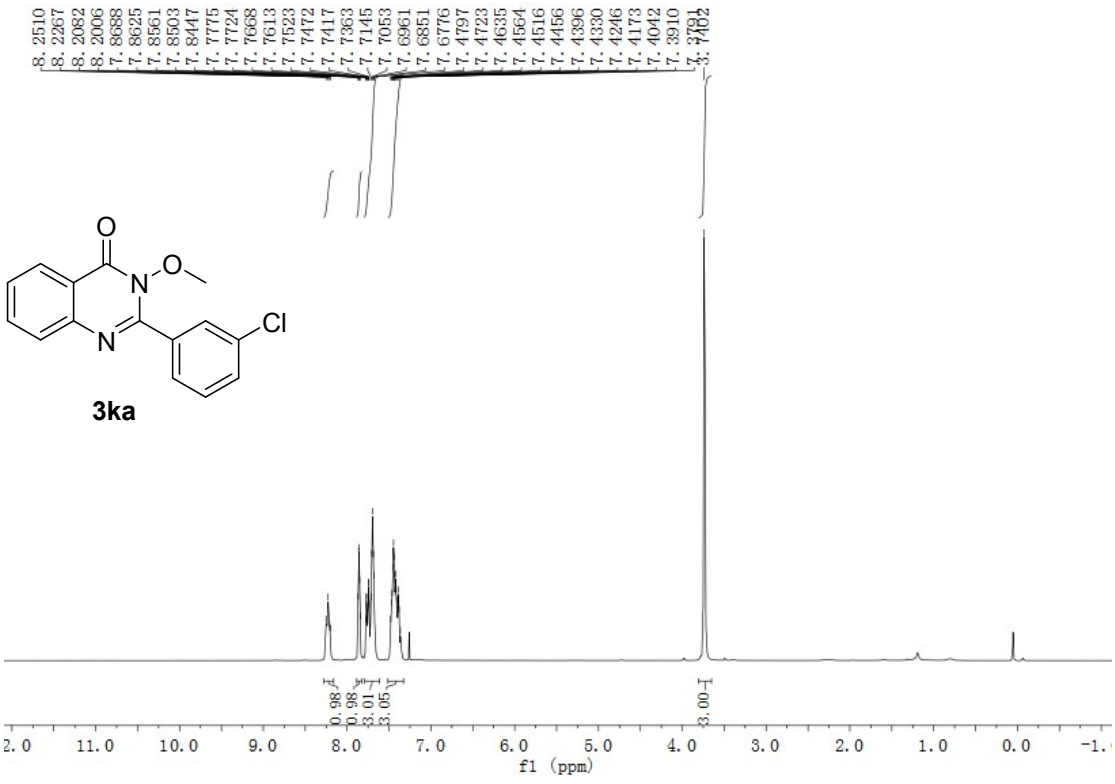


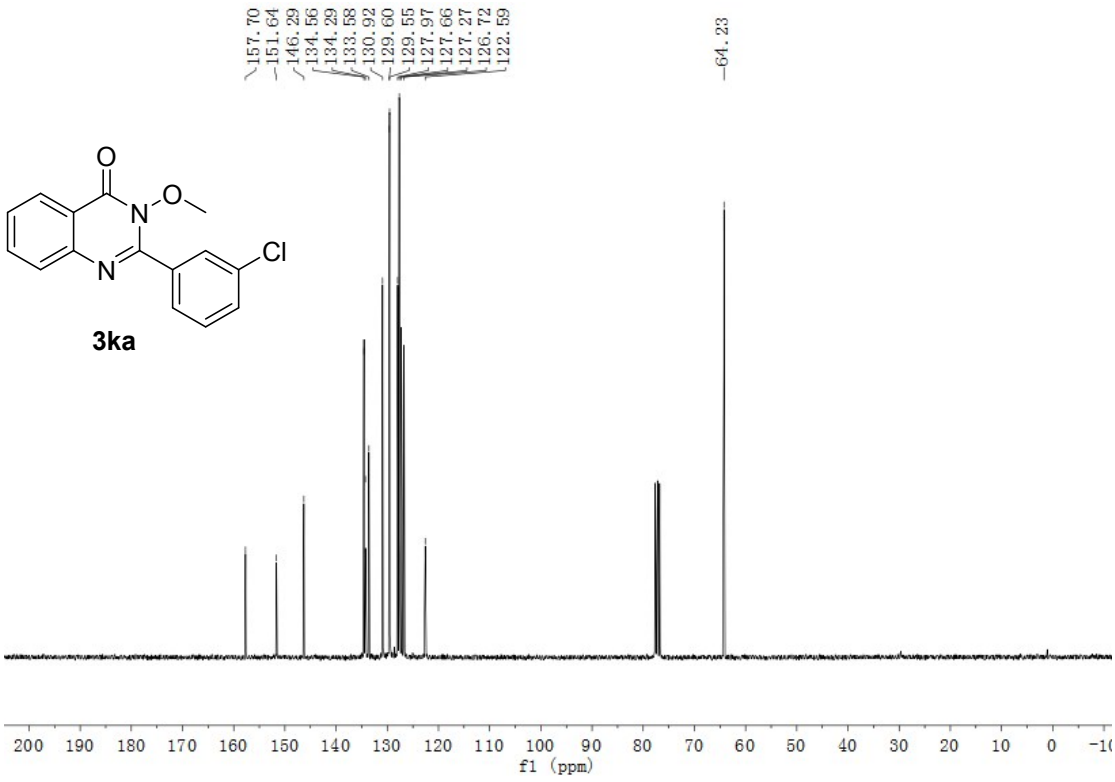
3-methoxy-2-(4-(trifluoromethyl)phenyl)quinazolin-4(3*H*)-one (3ja):



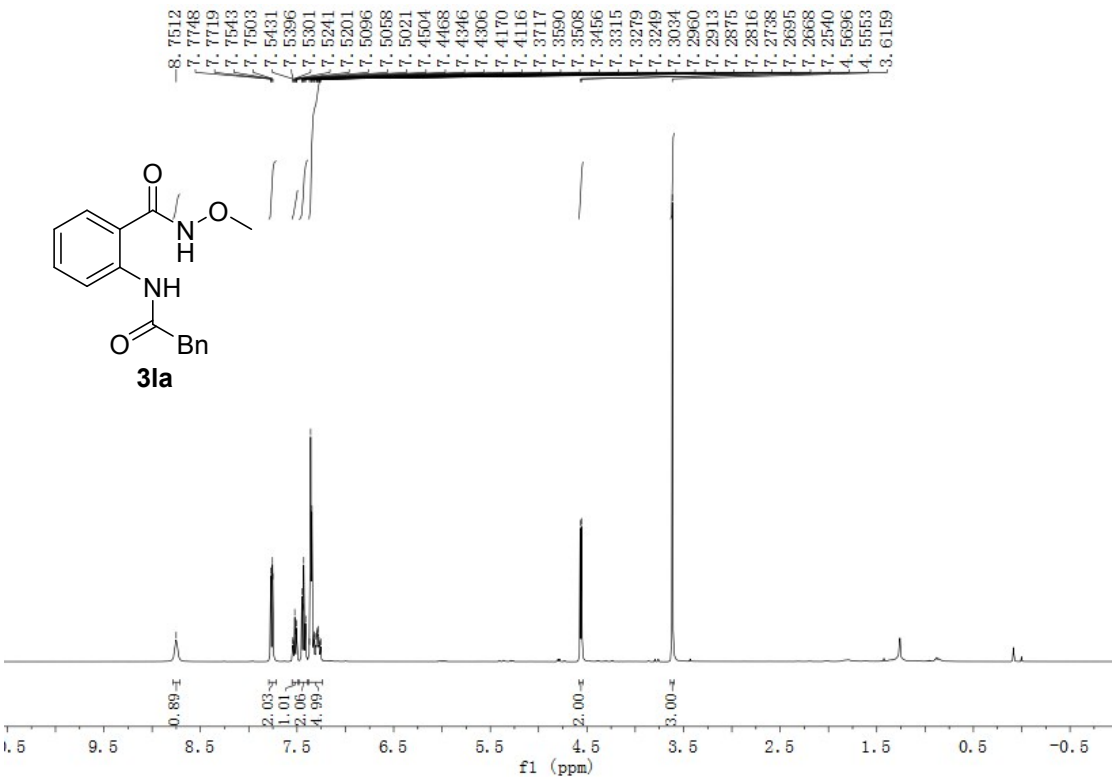


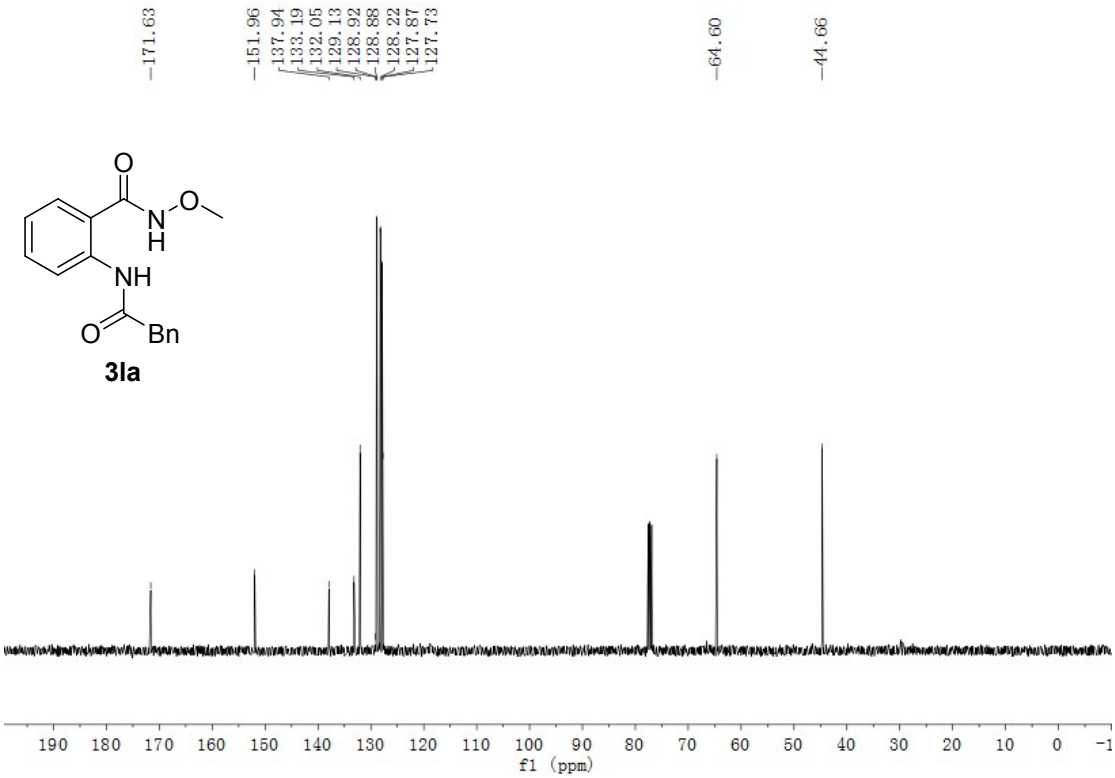
2-(3-chlorophenyl)-3-methoxyquinazolin-4(3*H*)-one (3ka):





N-methoxy-2-(2-phenylacetamido)benzamide (3la):

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133.19
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128.92
128.88
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127.87
127.73
64.60
44.66
O
N
H
O
NH
O
Bn
3la
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)