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–Supporting Information–

N-Heterocyclic Carbene Copper Catalyzed Quinolines Synthesis from 2-Aminobenzyl Alcohols and Ketones Using DMSO as an Oxidant at Room Termperature

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Table of Contents

1. General information

KOH was dried in vacuum oven at 50 ^{o}C for 24h. Toluene and DMSO were dried by distilling over CaH_2. Other reagents were of analytical grade and obtained from commercial suppliers and used without further purification. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AVANCE III HD 400 at 400 MHz and 100 MHz respectively, using $CDCl_3$ or DMSO-D_6 as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Melting points were measured using SGW X-4B and values are uncorrected. GC-MS were performed on Thermo Trace DSQ.

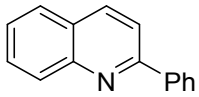
2. Typical procedure for synthesis of quinolines

A magnetic stir-bar, 2-aminobenzyl alcohol **1** (0.5mmol), ketone **2** (0.5 mmol), KOH (84.2 mg, 3 equiv), IPrCuCl (12.2mg, 5 mol%), DMSO (312.5 mg, 8 equiv) and Toluene (3 mL) were added into a 25 mL test tube and then sealed. The reaction mixture was stirred magnetically at room temperature for 6h. When the reaction was finished, 10 mL water was added. The aqueous solution was extracted with ethyl acetate (3 × 10 mL) and the combined extract was dried with anhydrous $MgSO_4$. The solvent was vacuumed and the crude product was purified by flash column chromatography on a silica gel (petroleum ether/ethyl acetate) to afford the product.

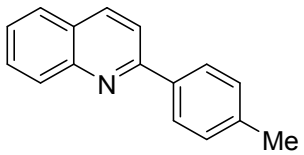
3. Mechanistic study as depicted in Eq. 1

After 2-aminobenzyl alcohol **1** reacted under the standard condition, 10 mL water was added. The aqueous solution was extracted with 10 mL ethyl acetate and the extract was analyzed by GC/MS using dodecane as an internal standard.

4. Characterization data of products

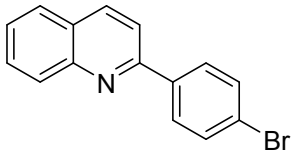


2-phenylquinoline (**3aa**) [1] According to the general procedure, **3aa** (91.3mg, 89%)was obtained from 2-aminobenzylic alcohol **1a** (61.6mg, 0.5mmol) and acetophenone **2a** (60.1mg, 0.5mmol) as a white solid, mp 82-83 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 – 8.08 (m, 4H), 7.85 (dd, J = 20.0, 8.3 Hz, 2H), 7.73 (t, J = 7.7 Hz, 1H), 7.53 (dd, J = 7.5, 4.9 Hz, 2H), 7.47 (t, J = 7.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 148.2, 139.6, 136.8, 129.7, 129.7, 129.3, 128.8, 127.6, 127.4, 127.2, 126.3, 119.0.

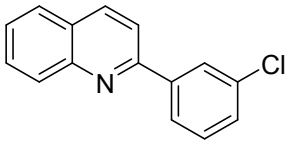


2-(p-tolyl)quinoline (**3ba**) [1] According to the general procedure, **3ba** (103.1mg, 94%)was obtained from 2-aminobenzylic alcohol **1a** (61.6mg, 0.5mmol) and 4'-methylacetophenone **2b** (67.1mg, 0.5mmol) as a white solid, mp 84-85 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, J = 8.5, 1.1 Hz, 1H), 8.01 – 7.89 (m, 3H), 7.75 – 7.60 (m, 2H), 7.56 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.34 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.18

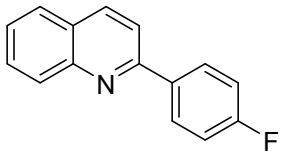
(d, J = 7.9 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 148.4, 139.4, 137.0, 136.7, 129.8, 129.6, 129.6, 127.5, 127.5, 127.2, 126.1, 118.9, 21.4.



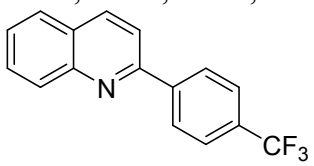
2-(4-bromophenyl)quinoline (**3ca**) [1] According to the general procedure, **3ca** (115.1mg, 81%)was obtained from 2-aminobenzylic alcohol **1a** (61.6mg, 0.5mmol) and 4'-bromoacetophenone **2c** (99.5mg, 0.5mmol) as a white solid, mp 121-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, J = 14.6, 8.6 Hz, 2H), 8.07 – 7.98 (m, 2H), 7.81 (d, J = 8.5 Hz, 2H), 7.73 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.68 – 7.61 (m, 2H), 7.53 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 148.2, 138.4, 137.0, 131.9, 129.9, 129.7, 129.1, 127.5, 127. 2, 126.5, 123.9, 118.5.



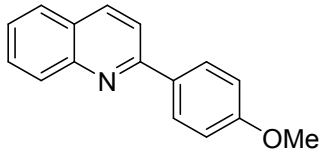
2-(3-chlorophenyl)quinoline (**3da**) [2] According to the general procedure, **3da** (93.5mg, 78%)was obtained from 2-aminobenzylic alcohol **1a** (61.6mg, 0.5mmol) and 3'-chloroacetophenone **2d** (77.3mg, 0.5mmol) as a white solid, mp 93-94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.08 (m, 3H), 7.98 (t, J = 4.5 Hz, 1H), 7.76 (dd, J = 8.4, 5.0 Hz, 2H), 7.70 (t, J = 7.8 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.39 (d, J = 4.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 148.3, 141.5, 137.0, 135.0, 130.1, 129.9, 129.8, 129.3, 127.8, 127.5, 127.4, 126.7, 125.6, 118.7.



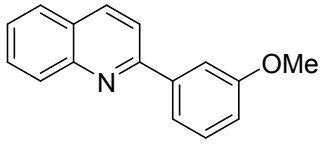
2-(4-fluorophenyl)quinoline (**3ea**) [1] According to the general procedure, **3ea** (94.9mg, 85%)was obtained from 2-aminobenzylic alcohol **1a** (61.6mg, 0.5mmol) and 4'-fluoroacetophenone **2e** (69.1mg, 0.5mmol) as a white solid, mp 91-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.07 (m, 4H), 7.78 (td, J = 5.5, 2.8 Hz, 2H), 7.71 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.50 (ddd, J = 8.0, 6.7, 1.1 Hz, 1H), 7.23 – 7.01 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 162.6, 156.2, 148.3, 137.0, 135.9, 135.8, 129.9, 129.7, 129.5, 129.4, 127.5, 127.1, 126.4, 118.6, 115.9, 115.7.



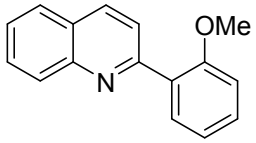
2-(4-(trifluoromethyl)phenyl)quinoline (**3fa**) [1] According to the general procedure, **3fa** (112.0mg, 82%)was obtained from 2-aminobenzylic alcohol **1a** (61.6mg, 0.5mmol) and 4'-trifluoromethylacetophenone **2f** (94.1mg, 0.5mmol) as a white solid, mp 129-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.04 (m, 4H), 7.79 – 7.68 (m, 2H), 7.69 – 7.57 (m, 3H), 7.44 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 148.3, 142.9, 142.9, 137.1, 131.2, 130.9, 123.0, 129.8, 127.8, 127.5, 127.4, 126.9, 125.8, 125.8, 125.7, 125.7, 125.6, 122.9, 118.7.



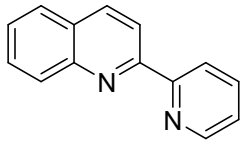
2-(4-methoxyphenyl)quinoline (**3ga**) [1] According to the general procedure, **3ga** (112.9mg, 96%)was obtained from 2-aminobenzylic alcohol **1a** (61.6mg, 0.5mmol) and 4'-methoxyacetophenone **2g** (75.1mg, 0.5mmol) as a white solid, mp 121-122 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.03 (m, 4H), 7.82 – 7.71 (m, 2H), 7.67 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.44 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.06 – 6.93 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 156.9, 148.3, 136.6, 132.2, 129.6, 129.5, 128.9, 127.4, 126.9, 125.9, 118.5, 114.2, 55.4.



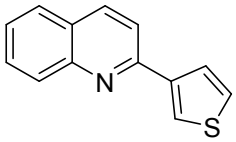
2-(3-methoxyphenyl)quinoline (**3ha**) [3] According to the general procedure, **3ha** (105.9mg, 90%)was obtained from 2-aminobenzylic alcohol **1a** (61.6mg, 0.5mmol) and 3'-methoxyacetophenone **2h** (75.1mg, 0.5mmol) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, J = 8.1, 3.3 Hz, 2H), 7.83 (dd, J = 15.4, 8.0 Hz, 2H), 7.77 (s, 1H), 7.75 – 7.67 (m, 2), 7.52 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.7 Hz, 1H), 7.01 (d, J = 7.8 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 157.3, 148.3, 141.3, 137.1, 130.07, 123.0, 129.9, 127.8, 127.5, 126.6, 120.3, 119.4, 115.7, 112.9, 55.8.



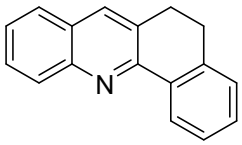
2-(2-methoxyphenyl)quinoline (**3ia**) [3] According to the general procedure, **3ia** (89.4mg, 76%)was obtained from 2-aminobenzylic alcohol **1a** (61.6mg, 0.5mmol) and 2'-methoxyacetophenone **2i** (75.1mg, 0.5mmol) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, J = 16.8, 8.5 Hz, 2H), 7.94 – 7.79 (m, 3H), 7.70 (td, J = 7.5, 6.9, 1.5 Hz, 1H), 7.59 – 7.48 (m, 1H), 7.46 – 7.37 (m, 1H), 7.13 (t, J = 7.5 Hz, 1H), 7.03 (d, J = 8.3 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 157.1, 148.3, 135.1, 131.5, 130.3, 129.7, 129.6, 129.2, 127.4, 127.1, 126.2, 123.5, 121.3, 111.5, 55.7.



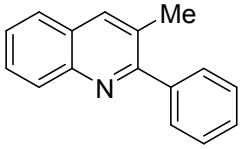
2-(pyridin-2-yl)quinoline (**3ja**) [1] According to the general procedure, **3ja** (86.6mg, 84%)was obtained from 2-aminobenzylic alcohol **1a** (61.6mg, 0.5mmol) and 1-(pyridin-2-yl)ethan-1-one **2j** (60.6mg, 0.5mmol) as a white solid, mp 94-95 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (ddd, J = 4.7, 1.9, 0.9 Hz, 1H), 8.64 (dt, J = 8.0, 1.1 Hz, 1H), 8.55 (d, J = 8.6 Hz, 1H), 8.24 (dd, J = 8.6, 0.8 Hz, 1H), 8.17 (dq, J = 8.6, 0.9 Hz, 1H), 7.88 – 7.77 (m, 2H), 7.70 (ddd, J = 8.4, 6.9, 1.5 Hz, 1H), 7.51 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.31 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 156.2, 149.2, 147.9, 136.9, 136.8, 129.8, 129.5, 128.3, 127.6, 126.7, 124.0, 121.8, 119.0.



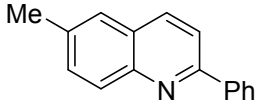
2-(thiophen-3-yl)quinoline (**3ka**) [4] According to the general procedure, **3ka** (95.1mg, 90%)was obtained from 2-aminobenzylic alcohol **1a** (61.6mg, 0.5mmol) and 1-(thiophen-3-yl)ethan-1-one **2k** (63.1mg, 0.5mmol) as a white solid, mp 123-124 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (t, J = 7.7 Hz, 2H), 8.00 (d, J = 2.7 Hz, 1H), 7.86 (d, J = 4.9 Hz, 1H), 7.70 (dq, J = 14.7, 7.9 Hz, 3H), 7.46 (t, J = 7.4 Hz, 1H), 7.40 (dd, J = 5.0, 2.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 148.3, 142.8, 136.8, 129.8, 129.6, 127.6, 127.20, 127.0, 126.6, 126.2, 124.9, 119.2.



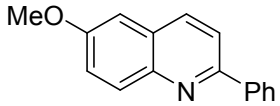
5,6-dihydrobenzo[c]acridine (**3la**) [1] According to the general procedure, **3la** (99.5mg, 86%)was obtained from 2-aminobenzylic alcohol **1a** (61.6mg, 0.5mmol) and 1-tetralone **2l** (73.1mg, 0.5mmol) as a white solid, mp 66-67 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 7.7 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.86 (s, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.63 (t, J = 7.7 Hz, 1H), 7.43 (dt, J = 11.9, 7.5 Hz, 2H), 7.35 (t, J = 7.3 Hz, 1H), 7.29 – 7.20 (m, 1H), 3.08 (dd, J = 8.3, 5.5 Hz, 2H), 2.97 (dd, J = 8.4, 5.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 147.6, 139.4, 134.7, 133.8, 130.6, 129.7, 129.4, 128.7, 128.0, 127.9, 127.4, 127.0, 126.1, 126.1, 28.9, 28.4.



3-methyl-2-phenylquinoline (**3ma**) [1] According to the general procedure, **3ma** (53.7mg, 49%)was obtained from 2-aminobenzylic alcohol **1a** (61.6mg, 0.5mmol) and propiophenone **2m** (67.1mg, 0.5mmol) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.5 Hz, 1H), 7.99 (s, 1H), 7.76 (d, J = 8.3 Hz, 1H), 7.69 – 7.62 (m, 1H), 7.59 (d, J = 7.8 Hz, 2H), 7.55 – 7.41 (m, 4H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 146.7, 141.0, 136.8, 129.4, 129.3, 129.0, 128.8, 128.4, 128.3, 128.3, 127.7, 126.8, 126.5, 20.7.

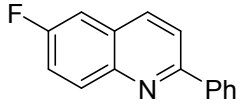


6-methyl-2-phenylquinoline (**3ab**) [1] According to the general procedure, **3ab** (102.0mg, 93%)was obtained from 2-amino-5-methylbenzylic alcohol **1b** (68.6mg, 0.5mmol) and acetophenone **2a** (60.1mg, 0.5mmol) as a white solid, mp 70-71^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.09 (m, 2H), 8.05 (d, J = 8.5 Hz, 1H), 8.00 – 7.95 (m, 1H), 7.71 (d, J = 8.6 Hz, 1H), 7.55 – 7.44 (m, 4H), 7.44 – 7.34 (m, 1H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 146.9, 139.8, 136.1, 136.1, 131.9, 129.5, 129.2, 128.8, 127.5, 127.2, 126.4, 118.9, 21.6.

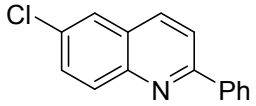


6-methoxy-2-phenylquinoline (**3ac**) [5] According to the general procedure, **3ac** (114.1mg, 97%)was obtained from 2-amino-5-methoxybenzylic alcohol **1c** (76.6mg, 0.5mmol) and acetophenone **2a** (60.1mg, 0.5mmol) as a white solid, mp 133-134^{o}C;

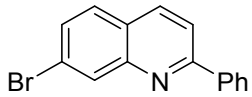
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.00 (m, 4H), 7.82 (dd, J = 8.7, 2.5 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.41 (dd, J = 24.9, 8.4 Hz, 2H), 7.08 (s, 1H), 3.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 155.0, 144.3, 139.7, 135.5, 131.1, 128.9, 128.8, 128.1, 127.3, 122.3, 119.2, 105.0, 55.5.



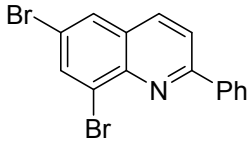
6-fluoro-2-phenylquinoline (**3ad**) [1] According to the general procedure, **3ad** (98.2mg, 88%)was obtained from 2-amino-5-fluorobenzylic alcohol **1d** (70.6mg, 0.5mmol) and acetophenone **2a** (60.1mg, 0.5mmol) as a white solid, mp 90-91^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.07 (m, 4H), 7.89 (d, J = 8.5 Hz, 1H), 7.63 – 7.34 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 159.1, 145.3, 139.3, 136.2, 136.1, 132.2, 132.1, 129.4, 128.9, 127.7, 127.4, 120.0, 119.7, 110.6, 110.4.



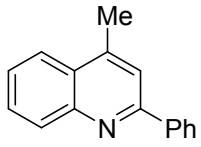
6-chloro-2-phenylquinoline (**3ae**) [1] According to the general procedure, **3ae** (103.1mg, 86%)was obtained from 2-amino-5-chlorobenzylic alcohol **1e** (78.8mg, 0.5mmol) and acetophenone **2a** (60.1mg, 0.5mmol) as a white solid, mp 111-112 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.05 (m, 2H), 8.02 (dt, J = 9.0, 0.6 Hz, 1H), 7.89 (dd, J = 8.7, 0.8 Hz, 1H), 7.70 (d, J = 8.6 Hz, 1H), 7.62 (d, J = 2.4 Hz, 1H), 7.56 (dd, J = 9.0, 2.4 Hz, 1H), 7.49 – 7.38 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 146.6, 139.2, 135.8, 131.9, 131.4, 130.5, 129.6, 129.0, 127.7, 127.6, 126.2, 119.7.



7-bromo-2-phenylquinoline (**3af**) [1] According to the general procedure, **3af** (126.4mg, 89%)was obtained from 2-amino-4-bromobenzylic alcohol **1f** (101.0mg, 0.5mmol) and acetophenone **2a** (60.1mg, 0.5mmol) as a white solid, mp 122-123^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.28 (m, 1H), 8.16 – 8.06 (m, 2H), 8.03 (d, J = 8.6 Hz, 1H), 7.76 (d, J = 8.5 Hz, 1H), 7.59 – 7.39 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 148.9, 139.1, 136.6, 132.0, 129.7, 128.9, 128.7, 127.6, 125.7, 123.7, 119.2.

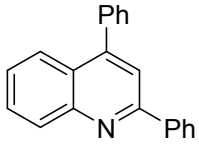


6,8-dibromo-2-phenylquinoline (**3ag**) [6] According to the general procedure, **3ag** (152.5mg, 84%)was obtained from 2-amino-3,5-dibromobenzylic alcohol **1g** (140.5mg, 0.5mmol) and acetophenone **2a** (60.1mg, 0.5mmol) as a yellow solid, mp 126-127^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.13 (m, 2H), 8.02 (d, J = 2.1 Hz, 1H), 7.86 (d, J = 8.6 Hz, 1H), 7.77 – 7.69 (m, 2H), 7.51 – 7.41 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 143.7, 138.3, 136.1, 135.8, 130.1, 129.3, 128.9, 128.7, 127.6, 126.5, 119.8, 119.3.



4-methyl-2-phenylquinoline (**3ah**) [7] According to the general procedure, **3ah** (29.6mg, 27%)was obtained from 1-(2-aminophenyl)ethan-1-ol **1h** (68.6mg, 0.5mmol)

and acetophenone **2a** (60.1mg, 0.5mmol). According the regulated procedure, a magnetic stir-bar, 1-(2-aminophenyl)ethan-1-ol **1h** (68.6mg, 0.5mmol) and acetophenone **2a** (60.1mg, 0.5mmol), KOH (84.2 mg, 3 equiv), IPrCuCl (12.2mg, 5 mol%), DMSO (2mL) and Toluene (1 mL) were added into a 25 mL test tube and then sealed. The reaction mixture was stirred magnetically at room temperature for 6h. When the reaction was finished, 10 mL water was added. The aqueous solution was extracted with ethyl acetate (3 × 10 mL) and the combined extract was dried with anhydrous $MgSO_4$. The solvent was vacuumed and the crude product was purified by flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 20 : 1) to afford the product **3ah** (83.3mg, 76%) as a white solid, mp 62-63°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.08 (m, 3H), 7.87 (dd, J = 8.4, 1.4 Hz, 1H), 7.65 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.60 (d, J = 1.1 Hz, 1H), 7.52 – 7.35 (m, 4H), 2.63 (d, J = 1.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 148.2, 144.8, 139.9, 130.3, 129.4, 129.2, 128.8, 127.6, 127.3, 126.0, 123.7, 119.7, 19.0.



2,4-diphenylquinoline (**3ai**) [8] According to the general procedure, **3ai** (19.7mg, 14%) was obtained from (2-aminophenyl)(phenyl)methanol **1i** (99.6mg, 0.5mmol) and acetophenone **2a** (60.1mg, 0.5mmol). According the regulated procedure, a magnetic stir-bar, (2-aminophenyl)(phenyl)methanol **1i** (99.6mg, 0.5mmol) and acetophenone **2a** (60.1mg, 0.5mmol), KOH (84.2 mg, 3 equiv), IPrCuCl (12.2mg, 5 mol%), DMSO (2mL) and Toluene (1 mL) were added into a 25 mL test tube and then sealed. The reaction mixture was stirred magnetically at room temperature for 6h. When the reaction was finished, 10 mL water was added. The aqueous solution was extracted with ethyl acetate (3 × 10 mL) and the combined extract was dried with anhydrous $MgSO_4$. The solvent was vacuumed and the crude product was purified by flash column chromatography on a silica gel (petroleum ether/ethyl acetate) to afford the product 3ai (91.4mg, 65%) as a white solid, mp 115-116°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, J = 8.5, 1.2 Hz, 1H), 8.19 – 8.12 (m, 2H), 7.85 (dd, J = 8.4, 1.4 Hz, 1H), 7.76 (s, 1H), 7.66 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.52 – 7.43 (m, 7H), 7.43 – 7.34 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 149.2, 148.9, 139.7, 138.5, 130.3, 129.7, 129.6, 129.4, 128.9, 128.7, 128.5, 127.7, 126.4, 125.9, 125.7, 119.4.

5. References

(1) R. Wang, H. Fan, W. Zhao and F. Li, *Org. Lett.,* 2016, **18**, 3558.

(2) N. An, C. Tanmoy, K. Suvajit, C. Sushobhan and S. M. Shankar, *RSC Adv.,* 2014, **5**, 7654.

(3) S. C. Chan and X. R. Wen, *J. Organomet. Chem*., 2007, **692**, 4182.

(4) M. Kuriyama, S. Matsuo, M. Shinozawa and O. Onomura, *Org. lett.,* 2013, **15**, 2716.

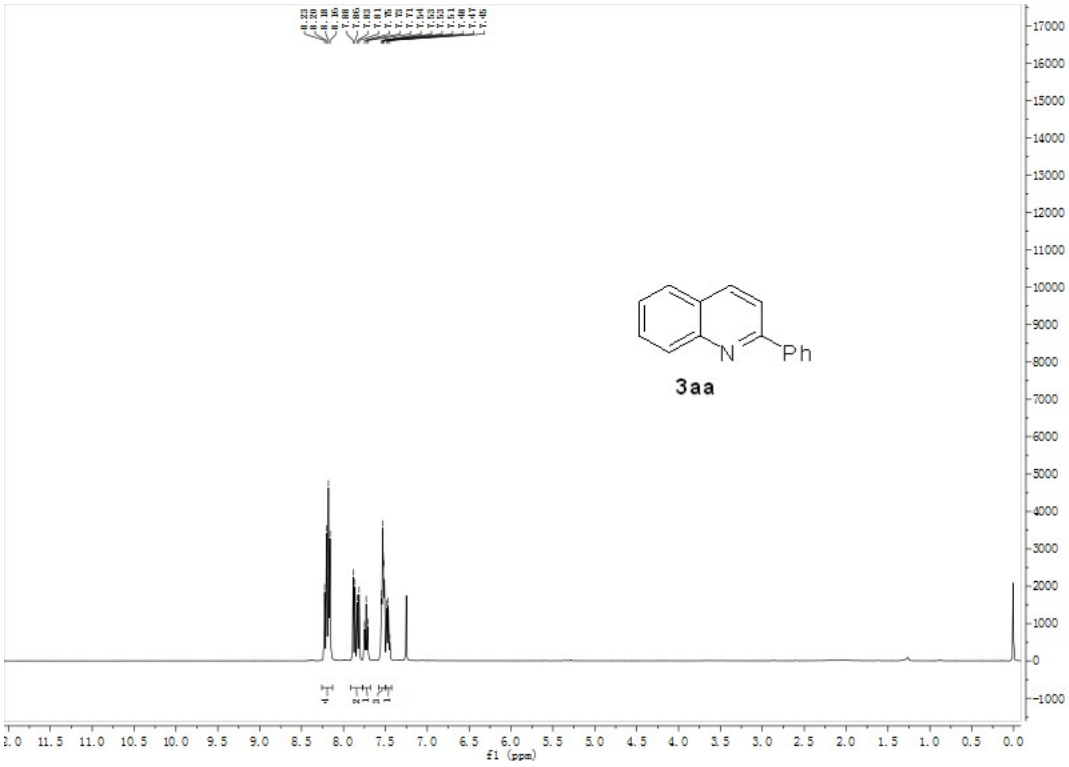
(5) X. Xu, X. Zhang, W. Liu, Q. Zhao, Z. Wang, L. Yu and F. Shi, *Tetrahedron Lett*. 2015, **56**, 3790.

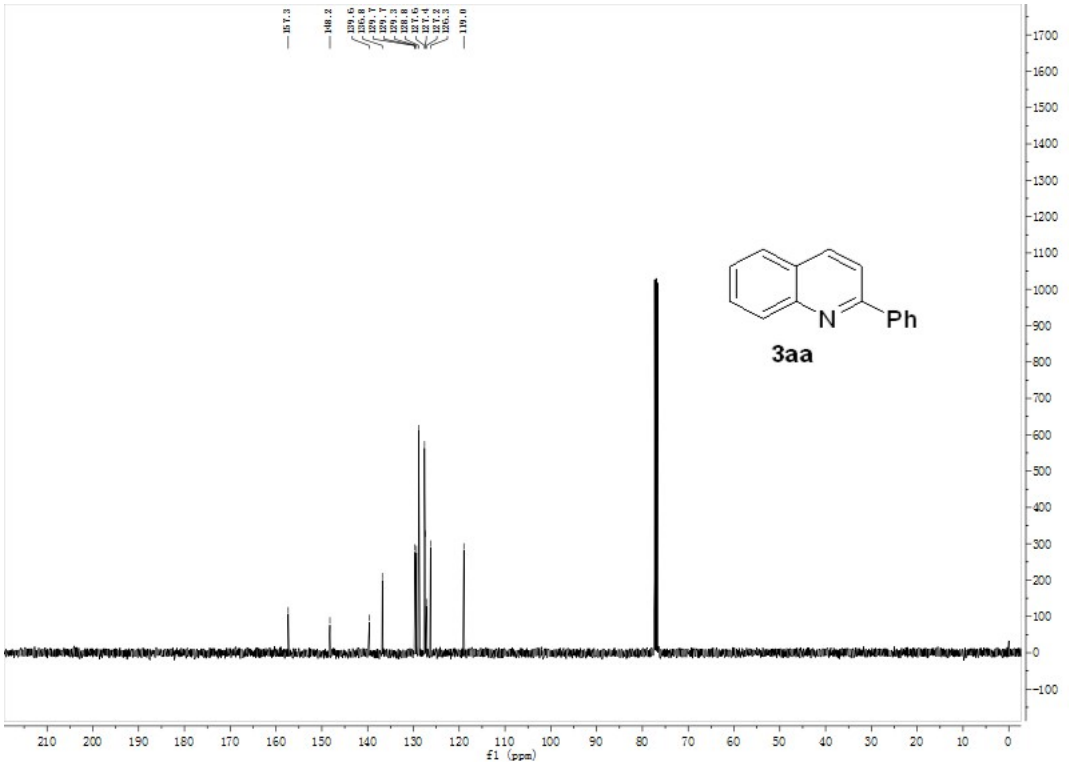
(6) J. Yu, Z. Li and W. Su, *Synth. Commun.,* 2013, **43**, 361.

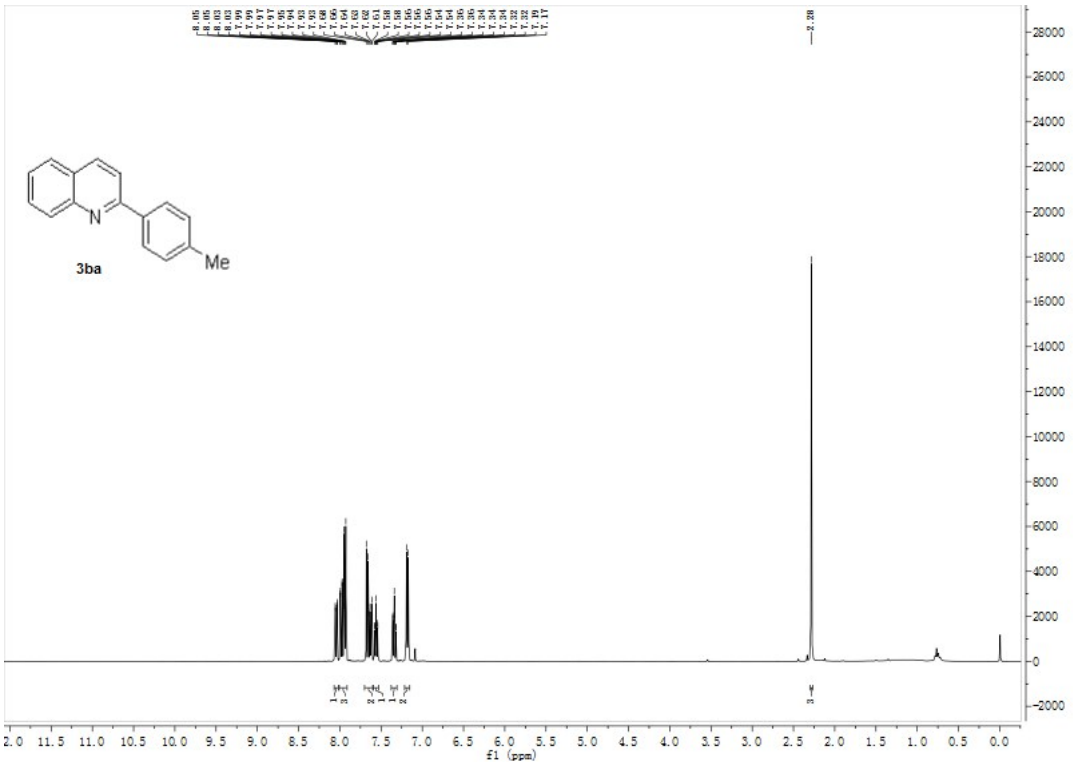
(7) Y. Zhu and C. Cai, *RSC Adv.,* 2014, **4**, 52911.

(8) R. Martínez, D. J. Ramón and M. Yus, *J. Org. Chem.,* 2008, **73**, 9778.

6. Copies of NMR spectra



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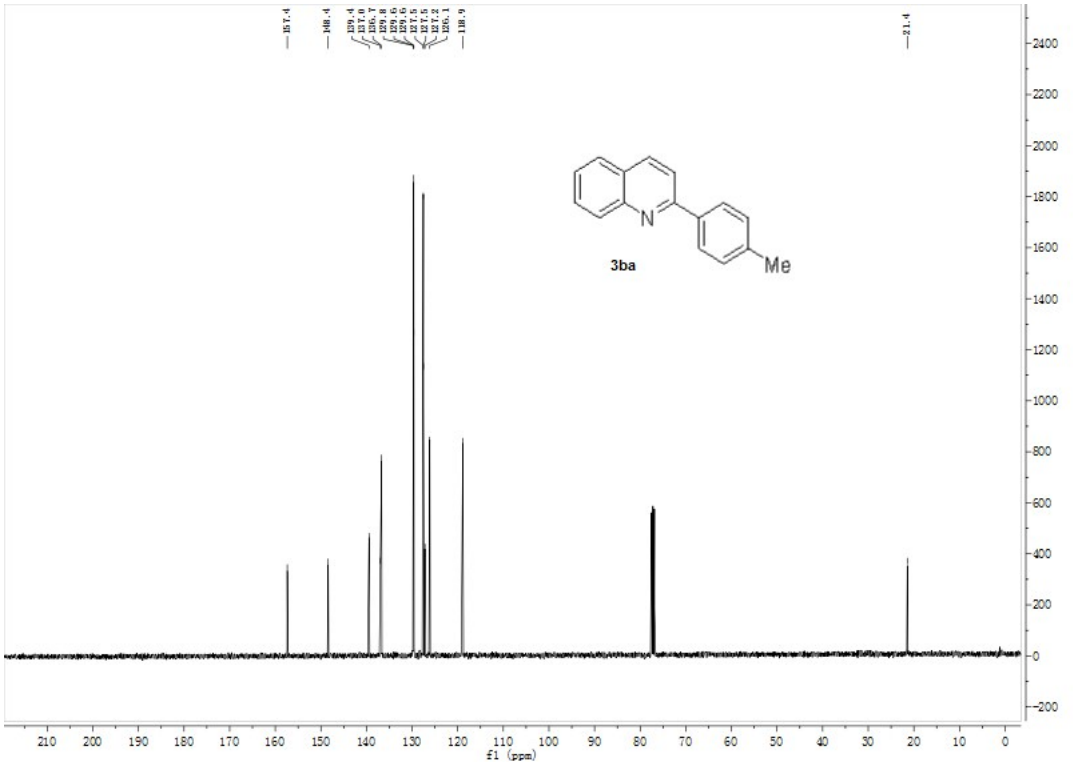
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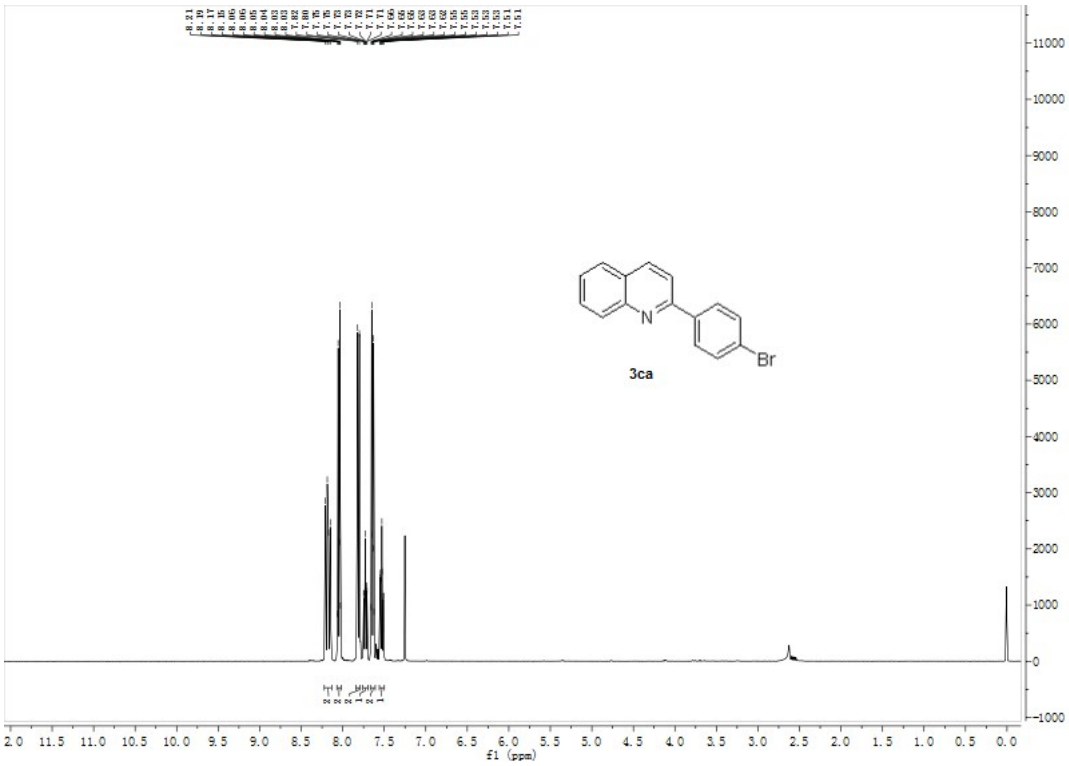
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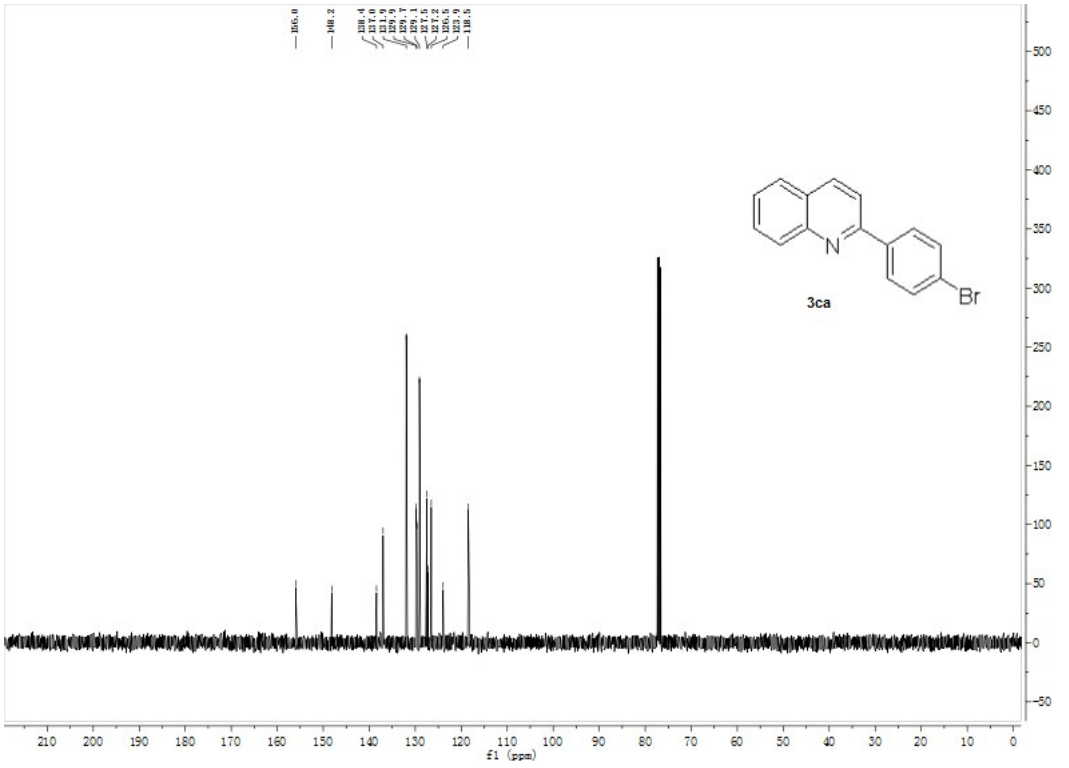
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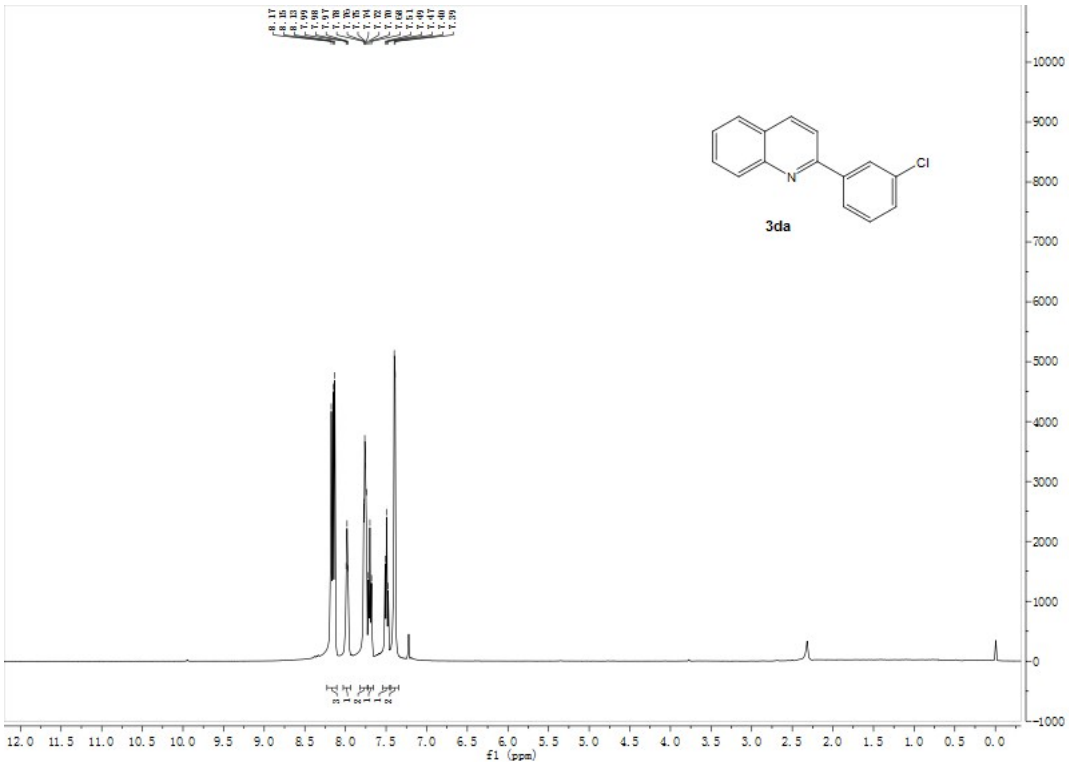
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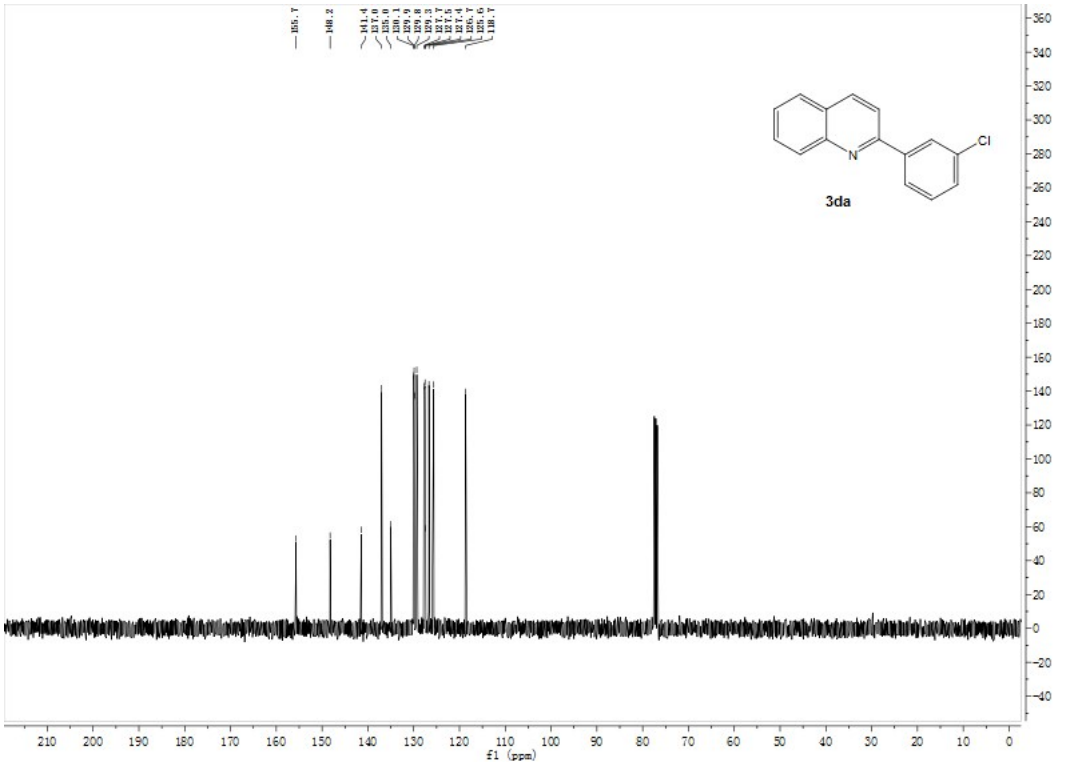
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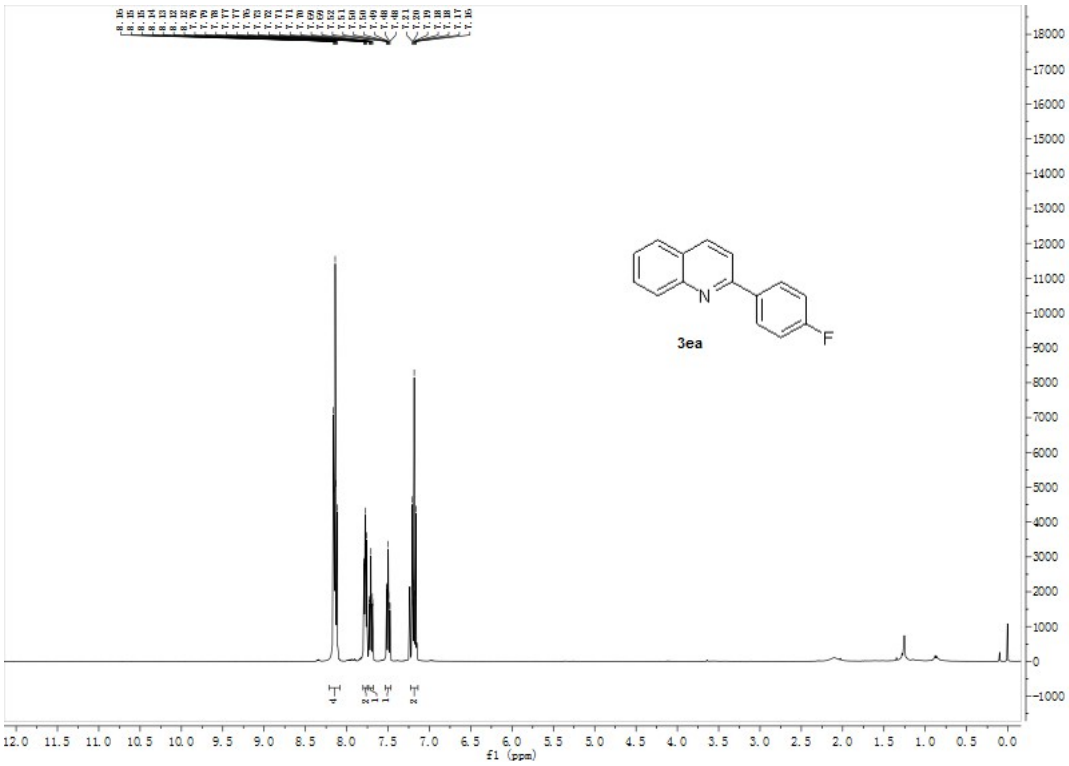
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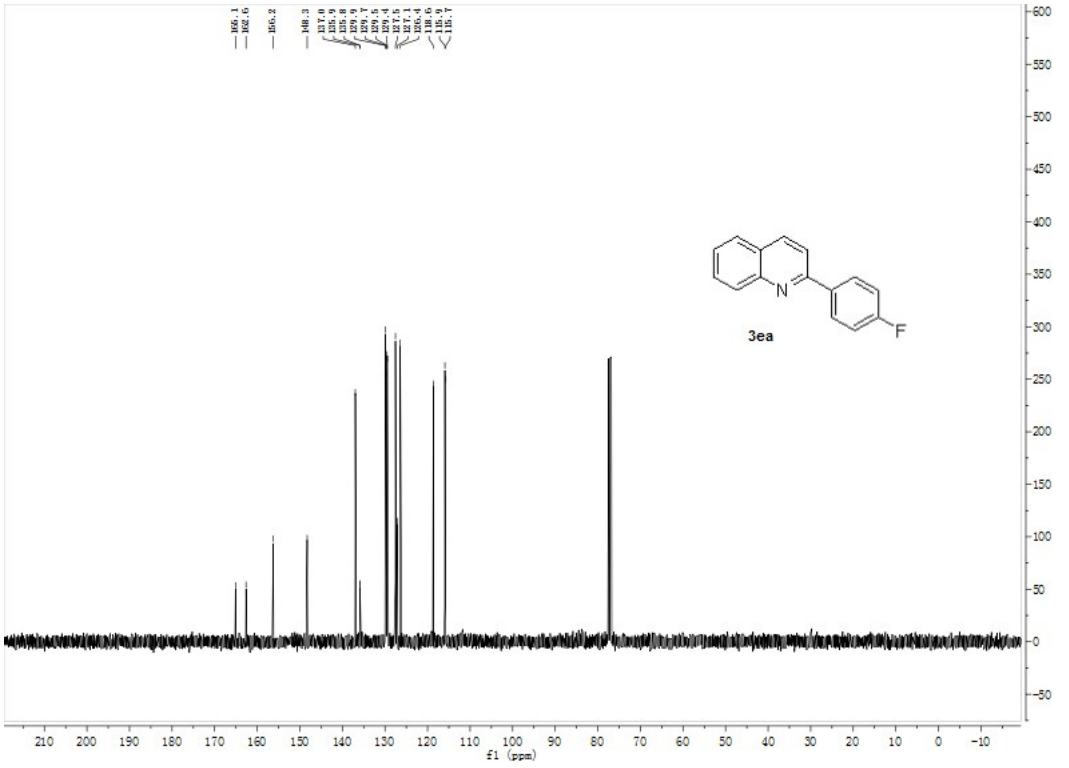
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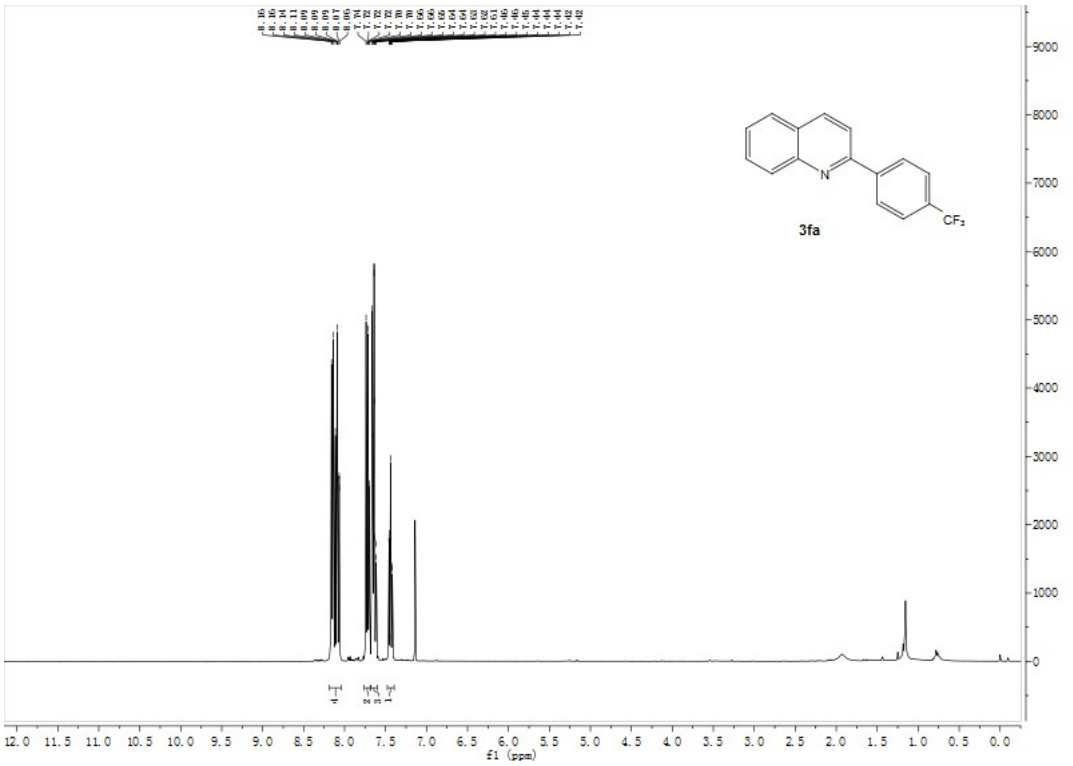
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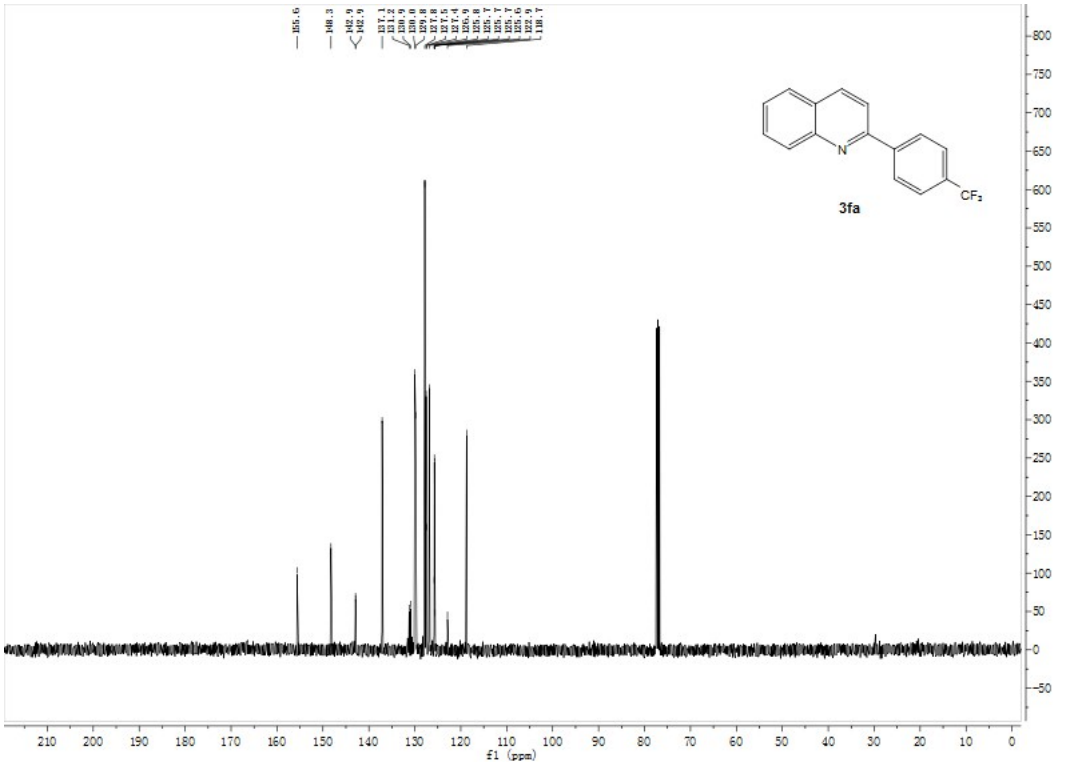
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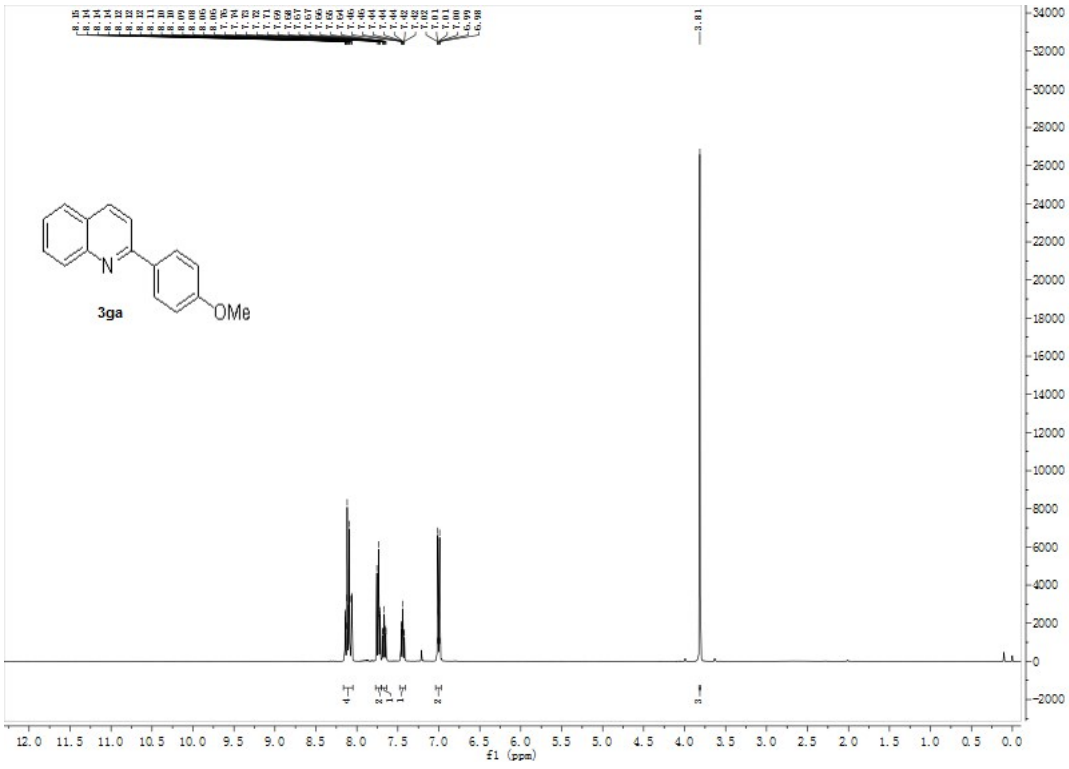
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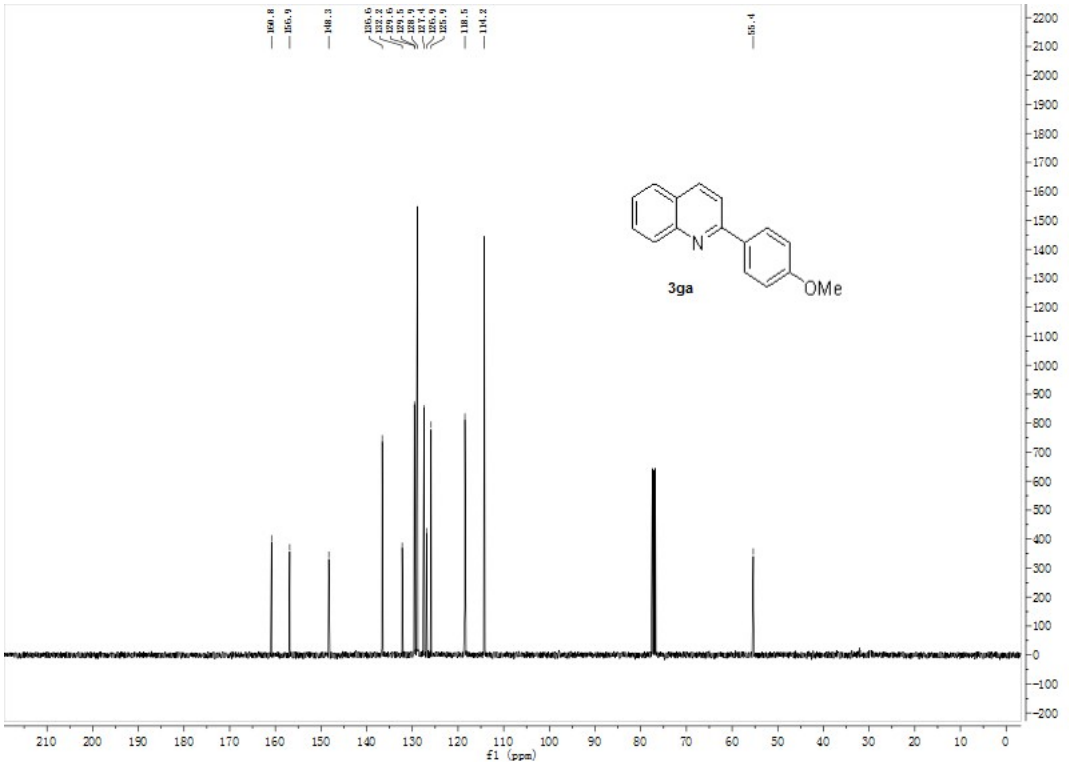
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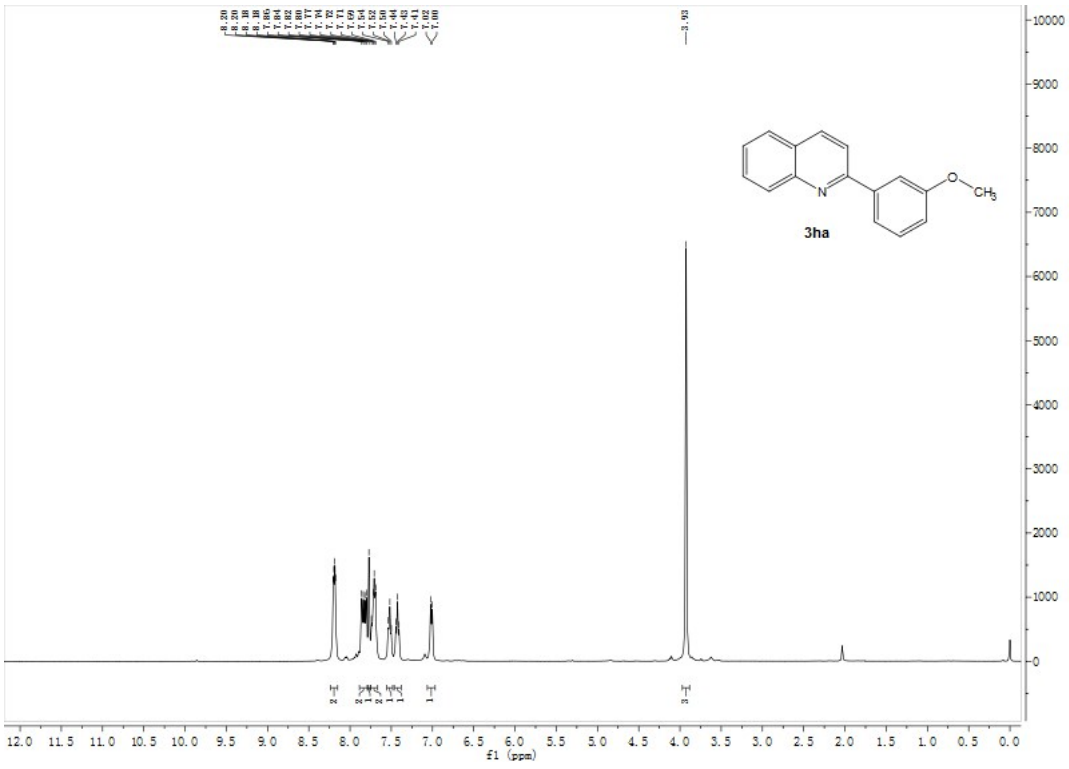
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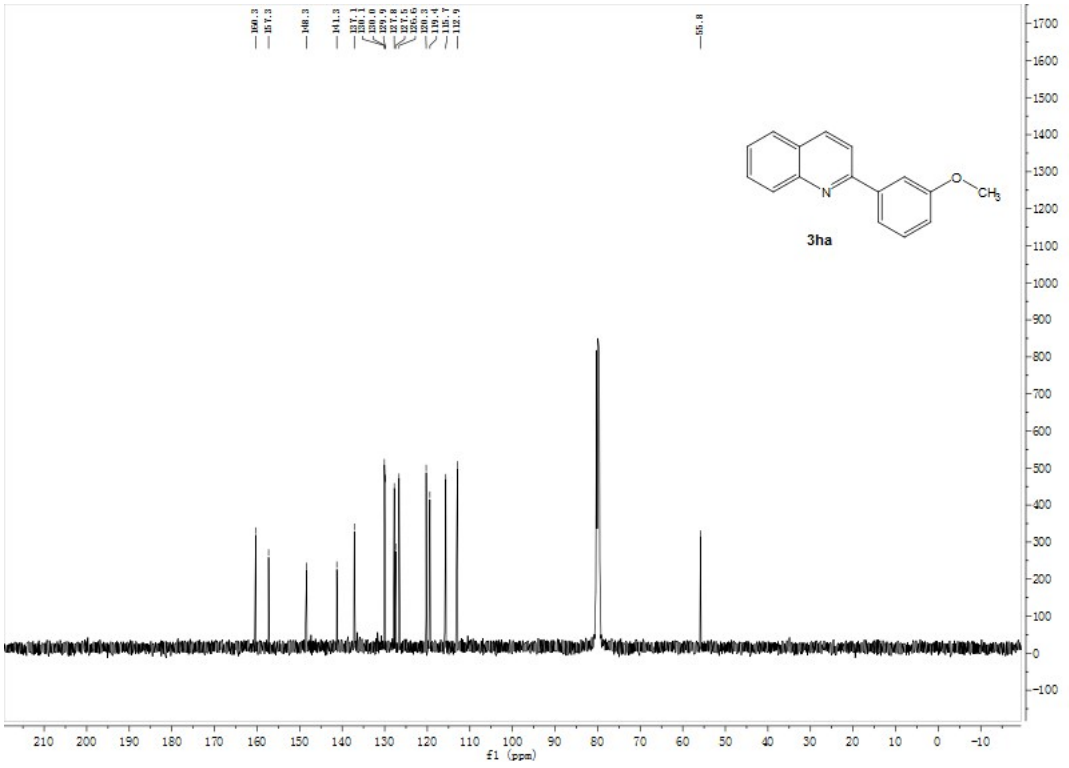
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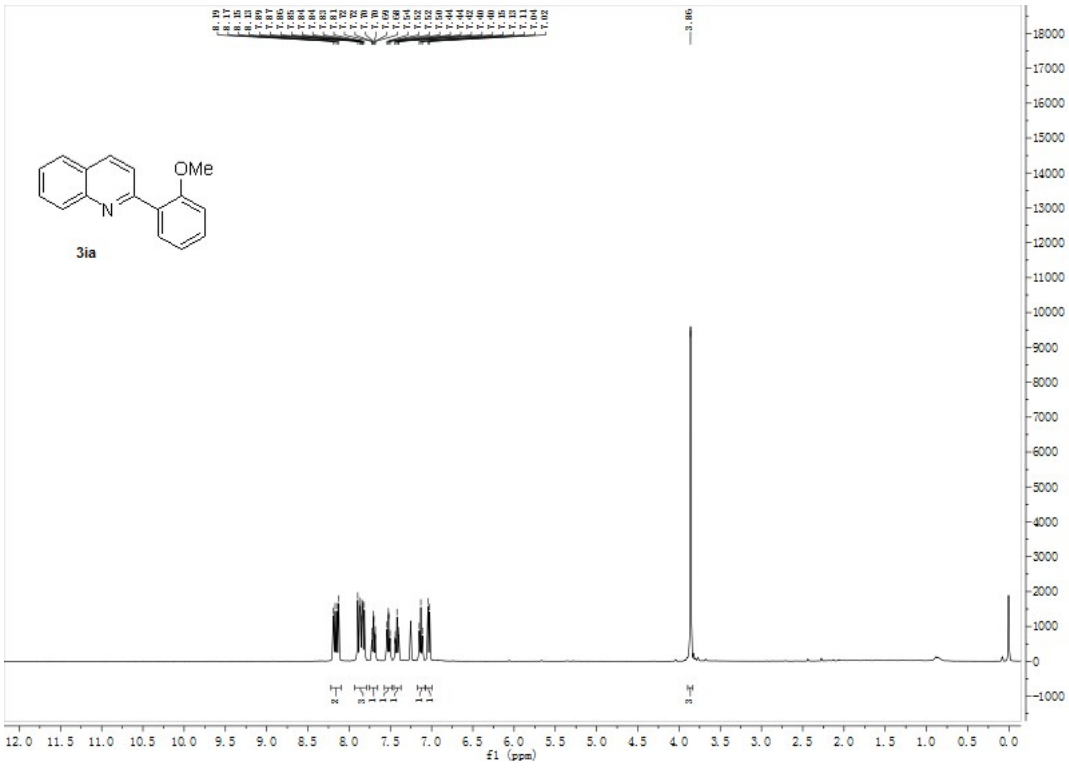
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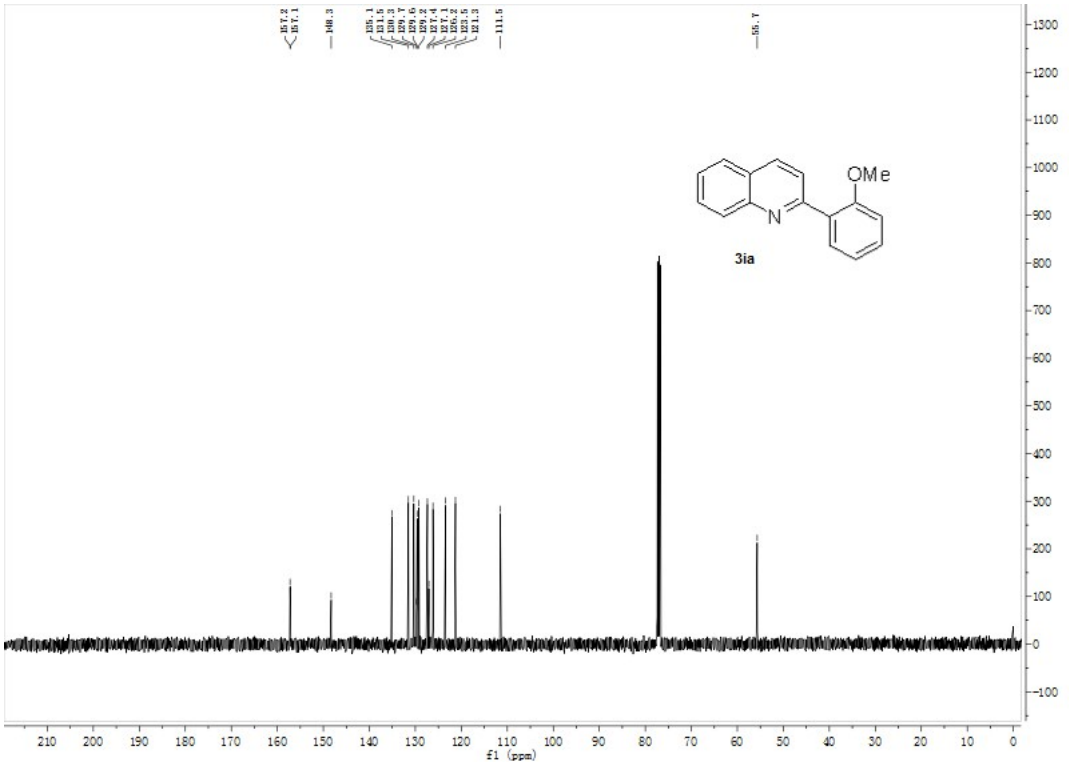
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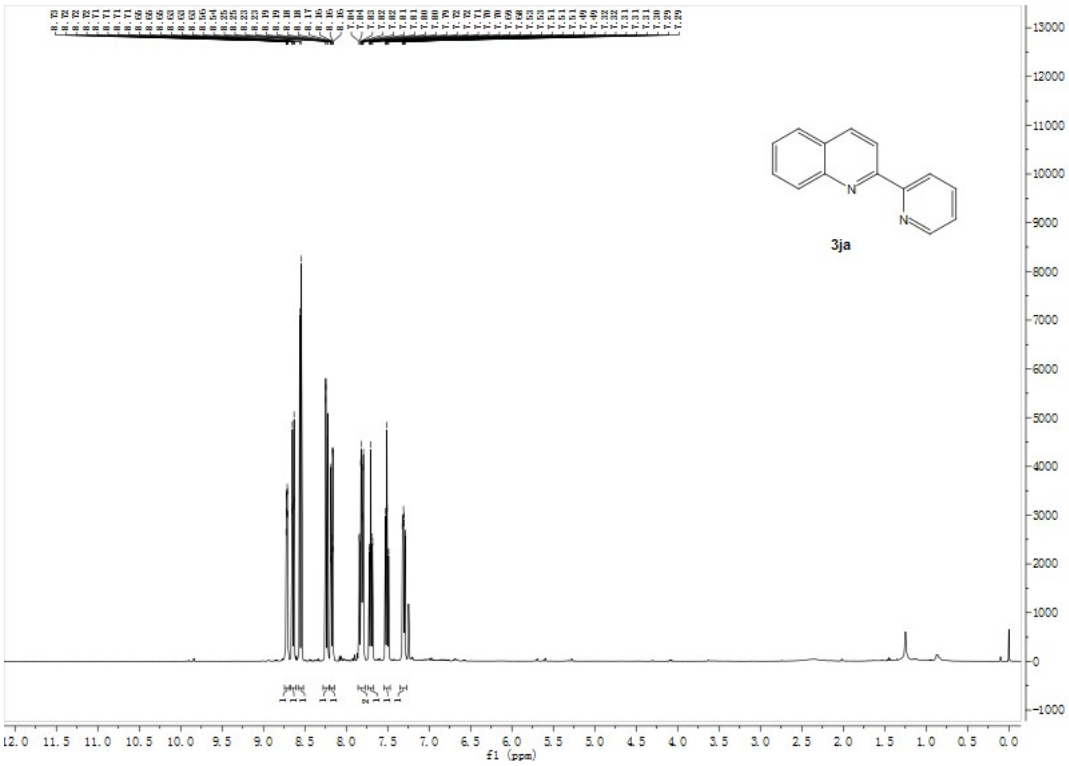
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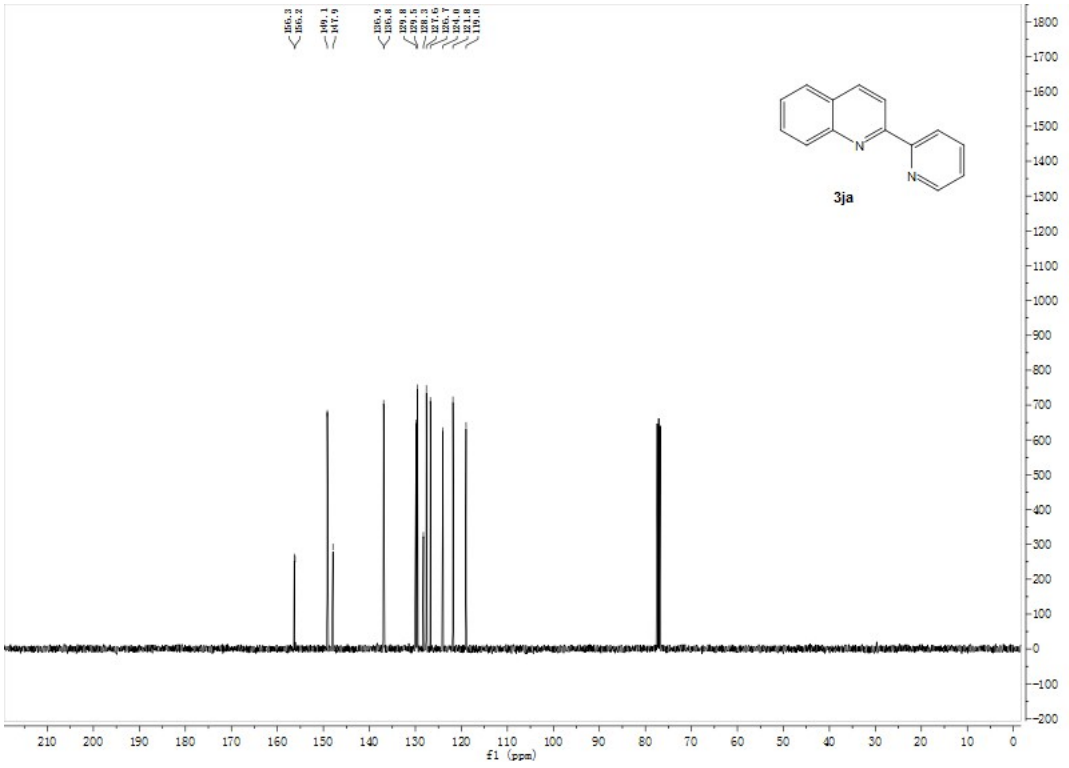
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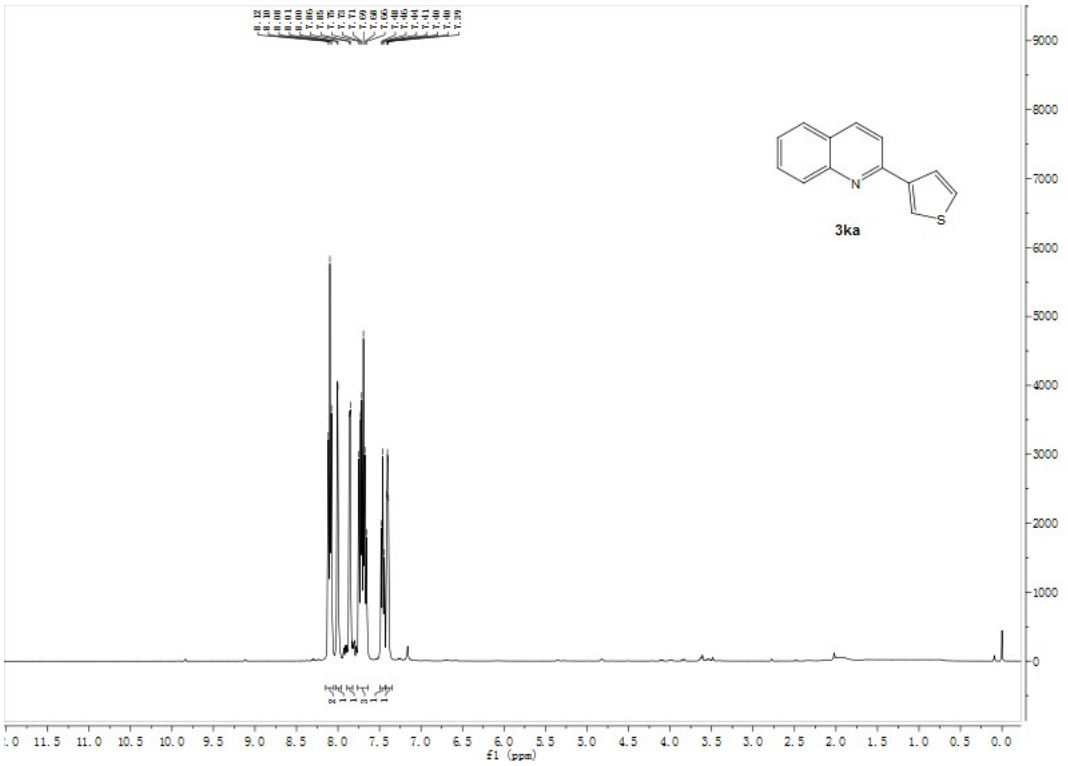
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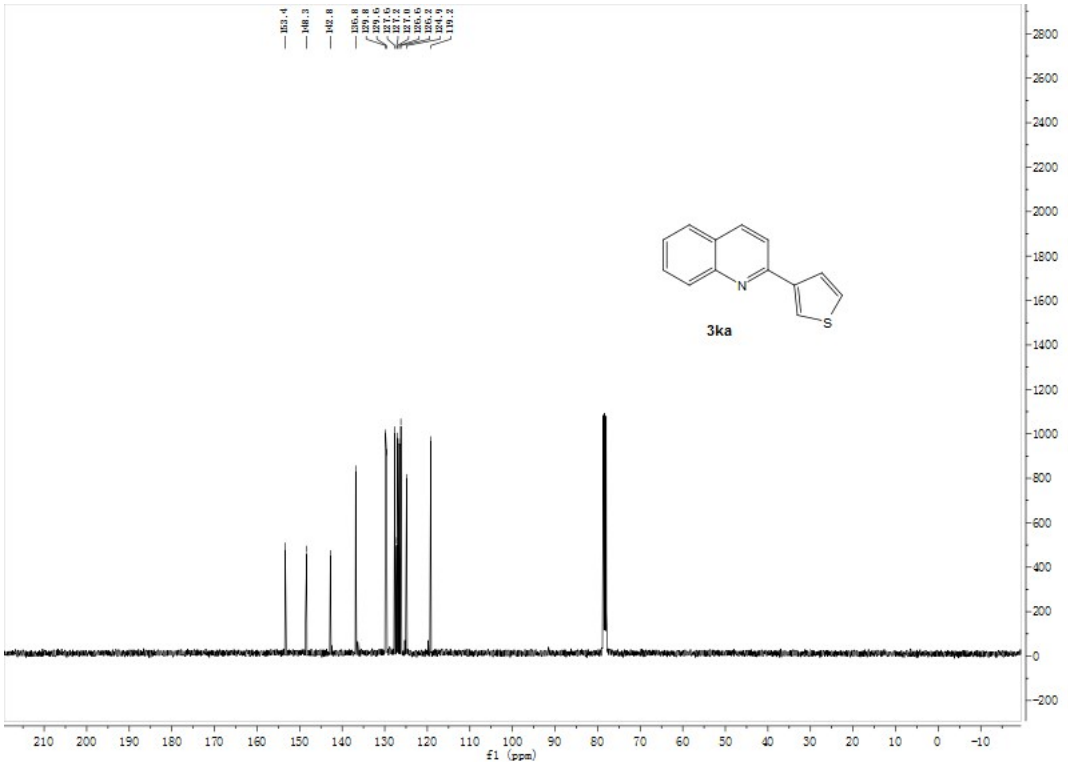
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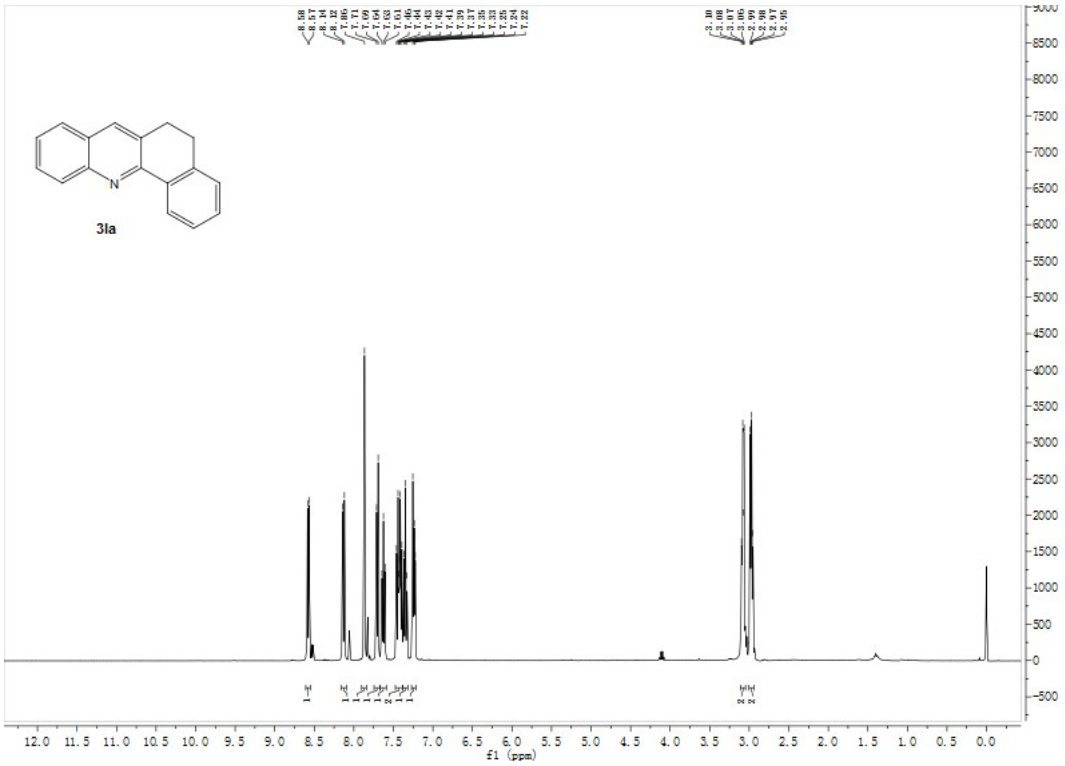
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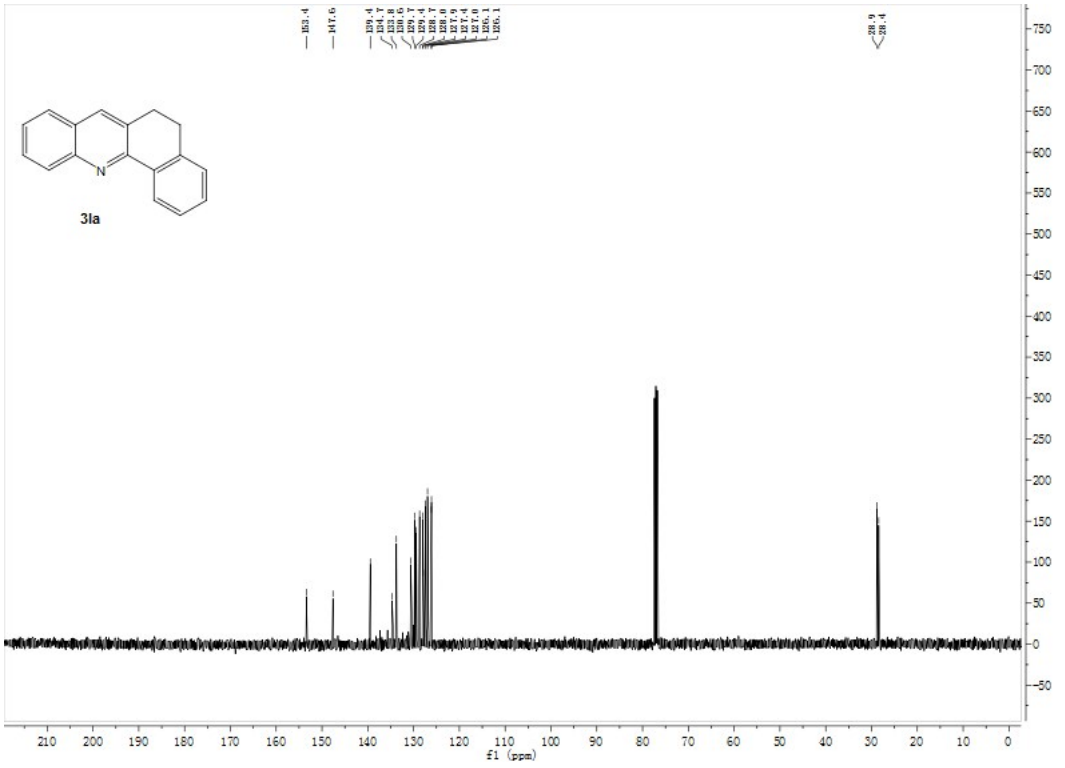
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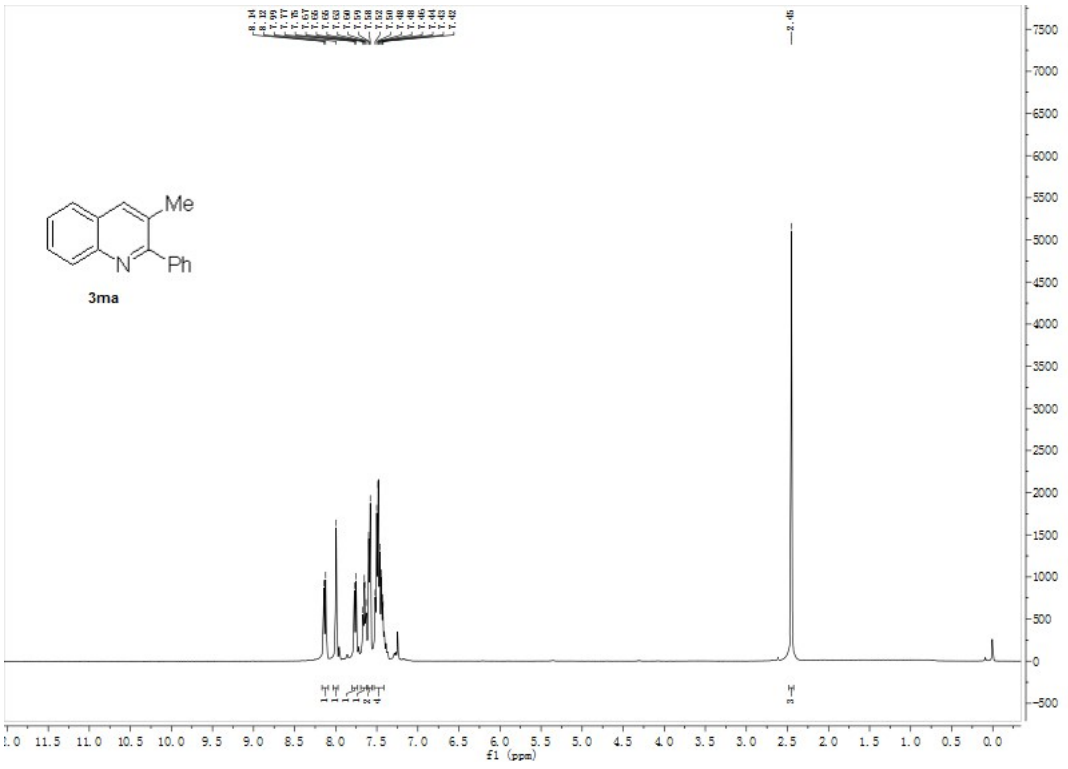
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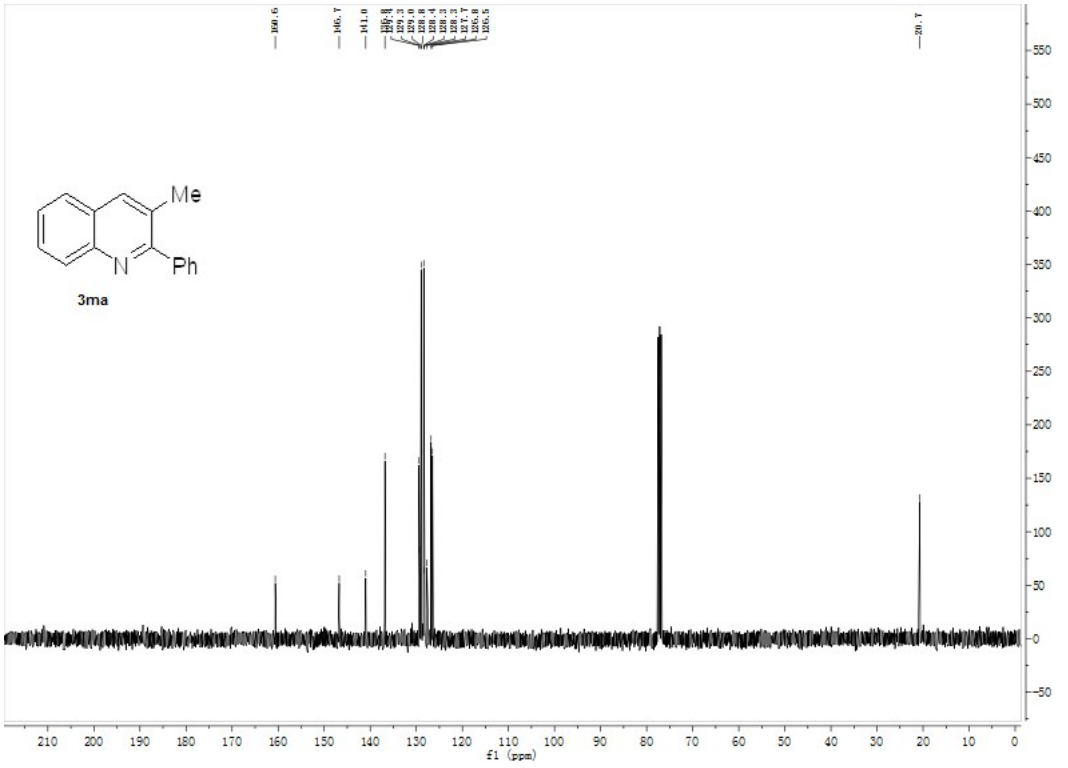
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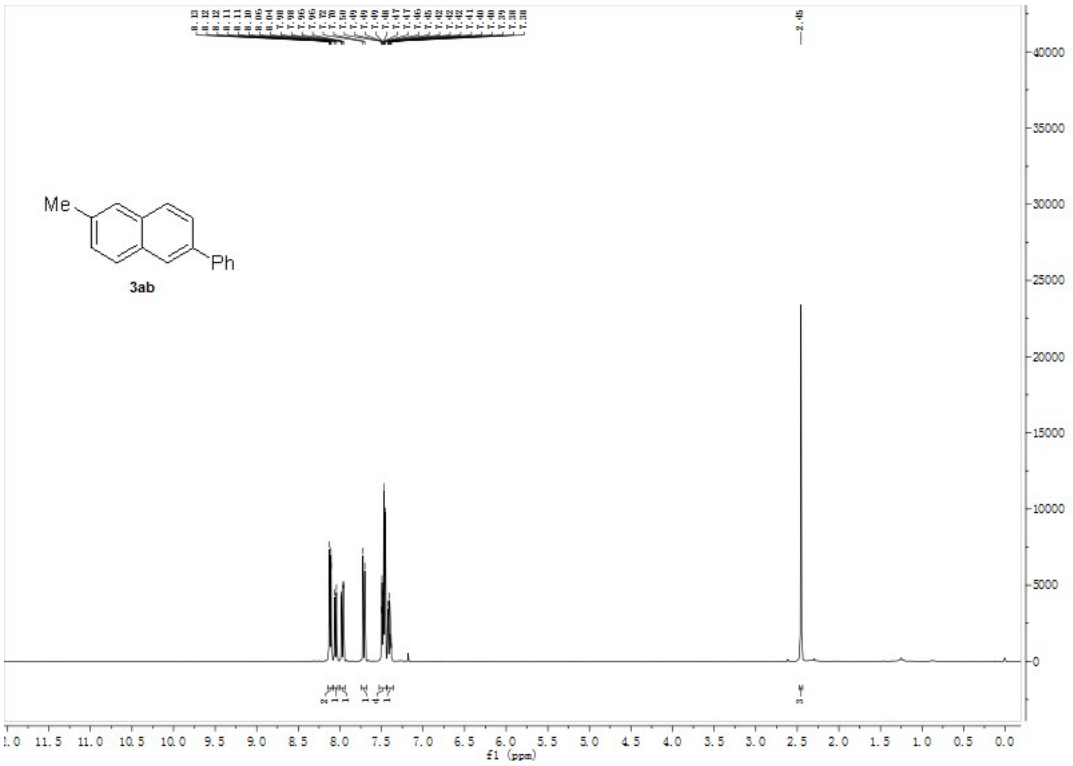
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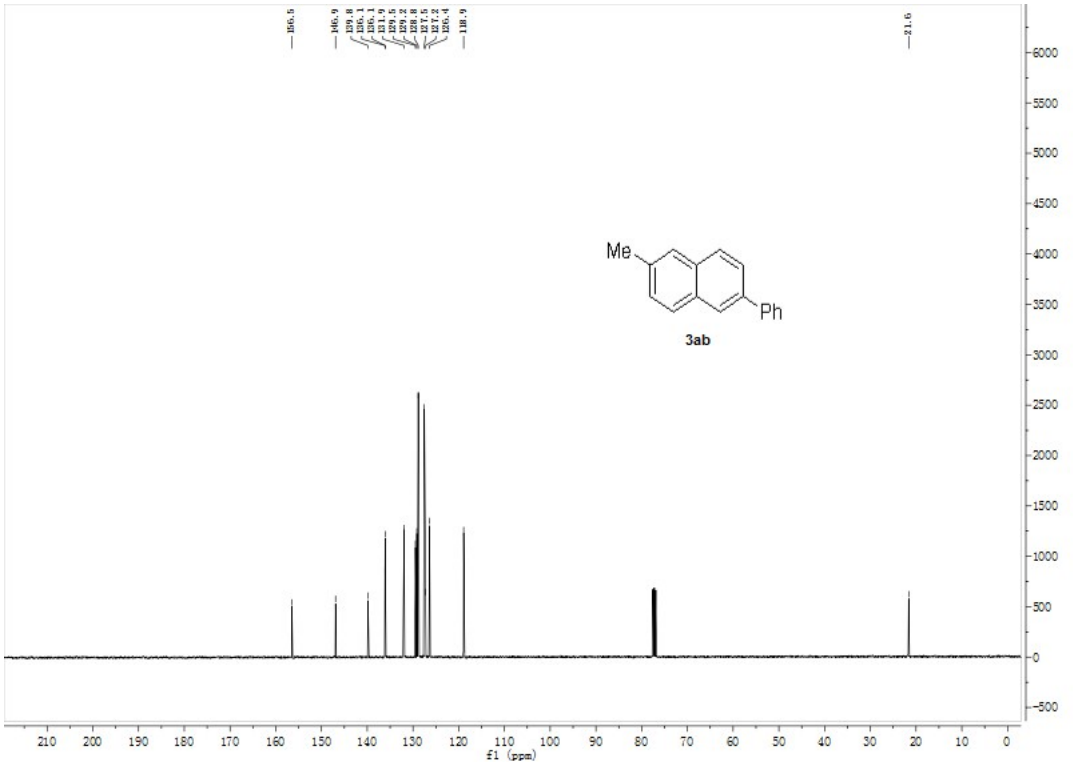
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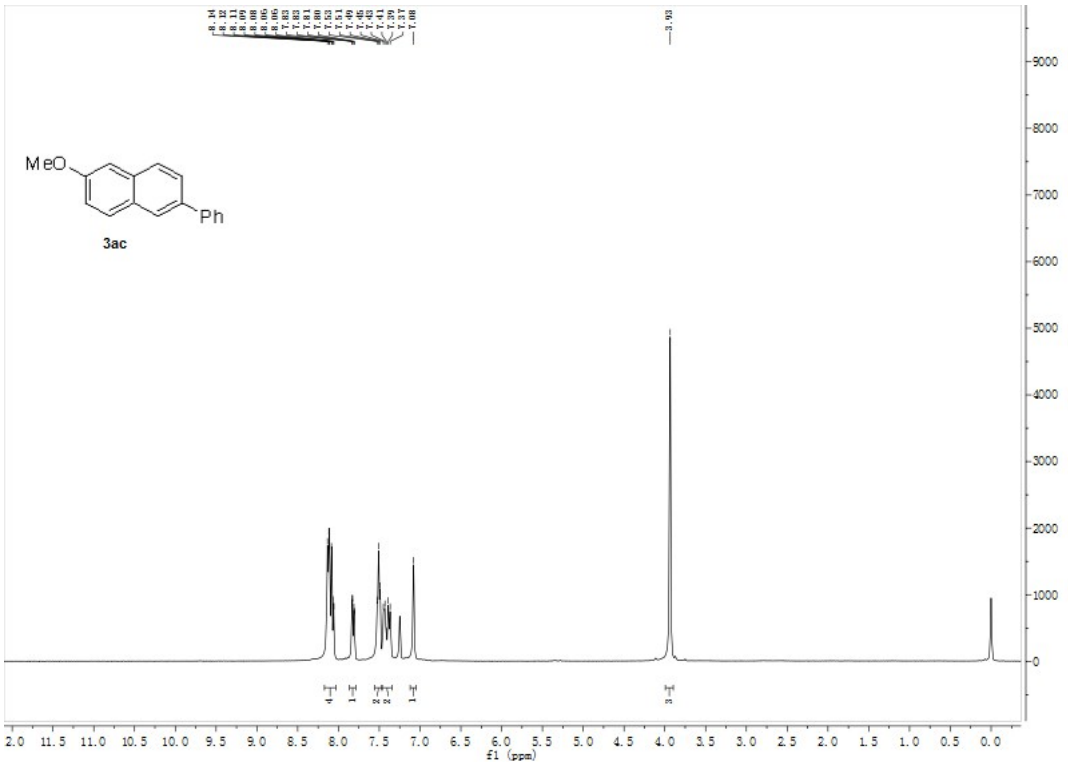
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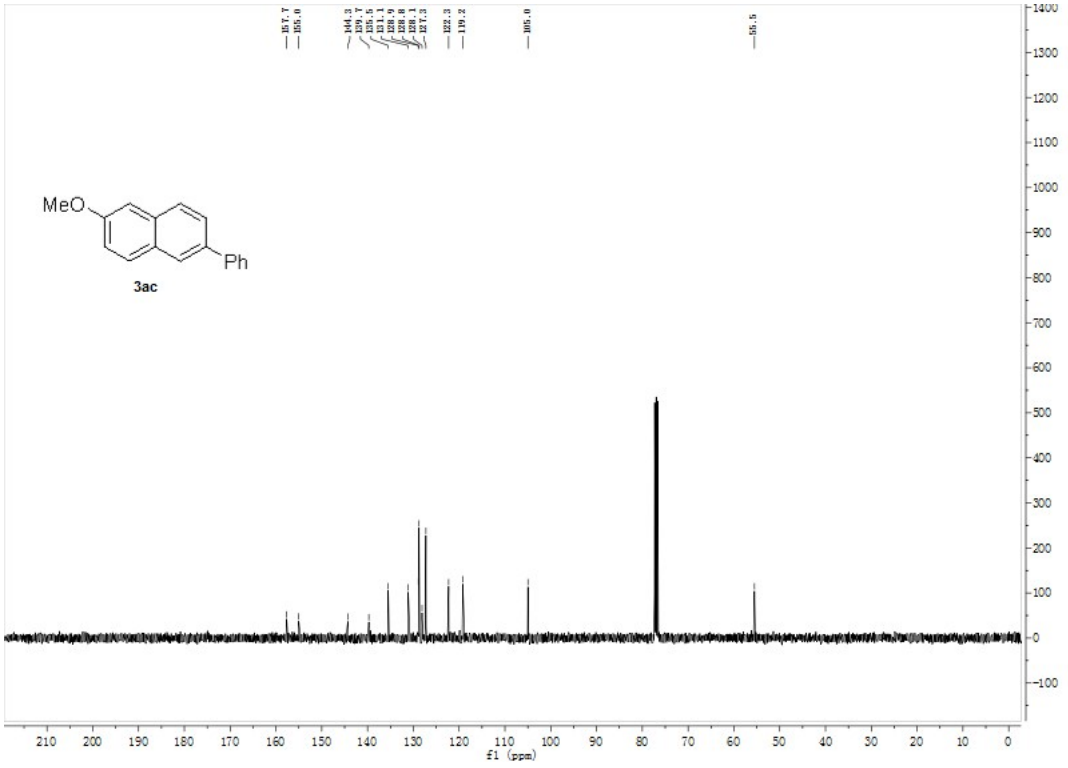
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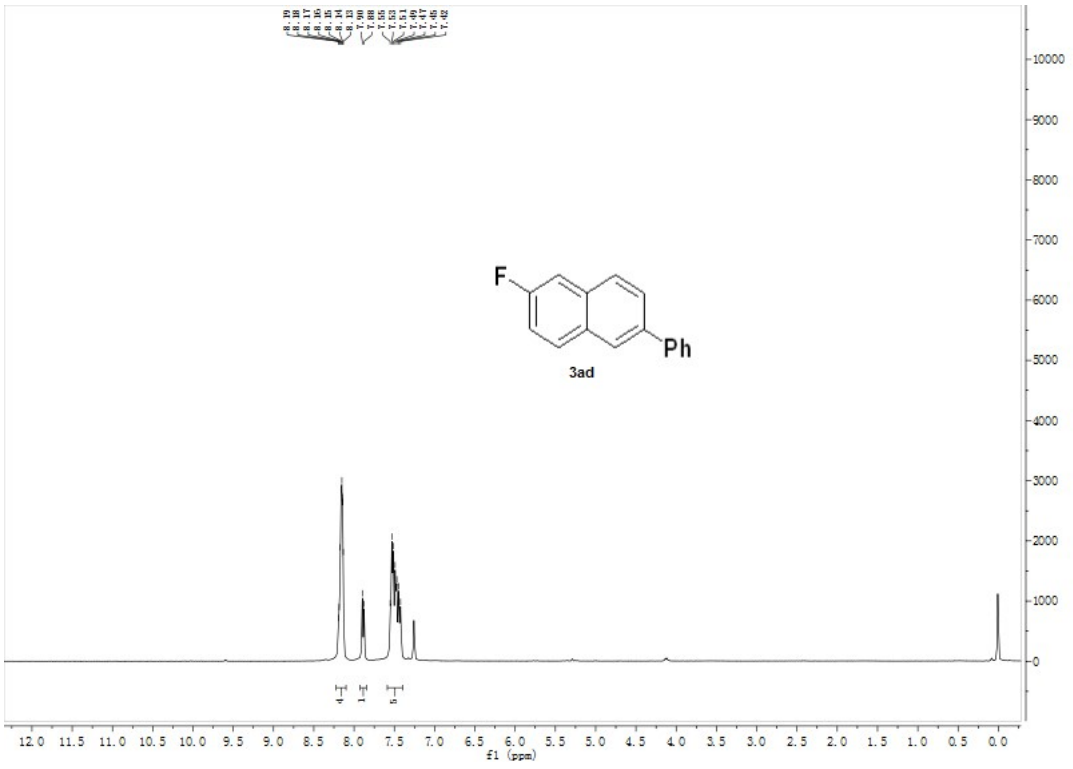
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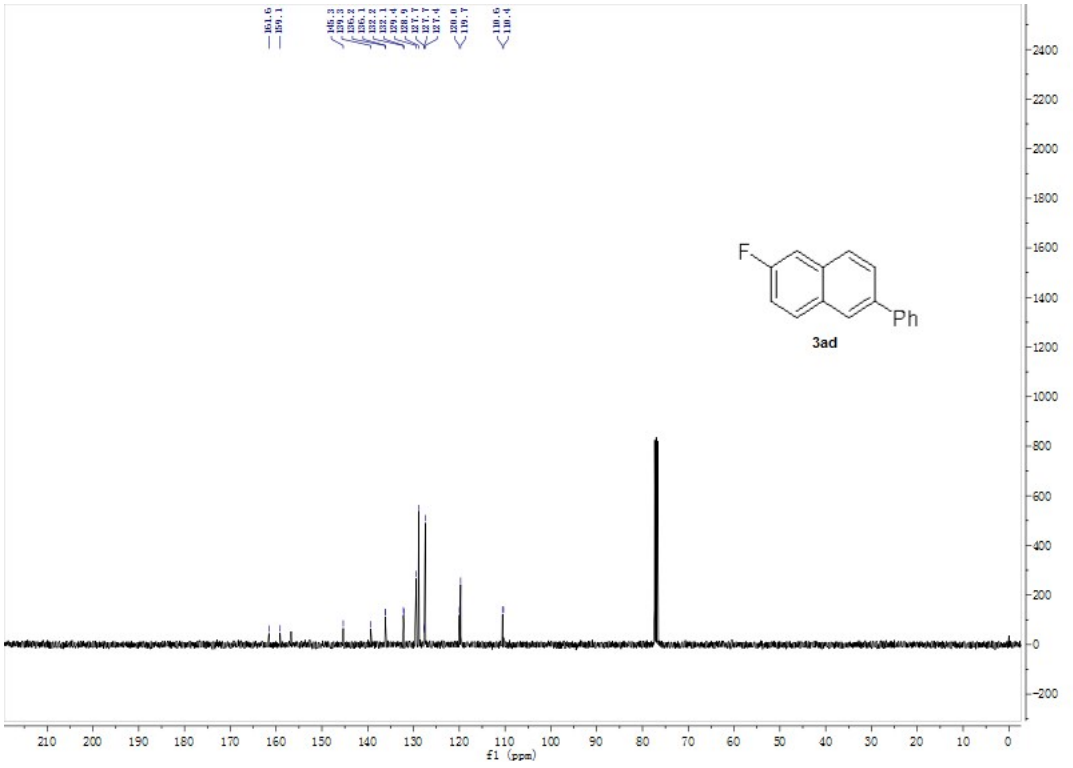
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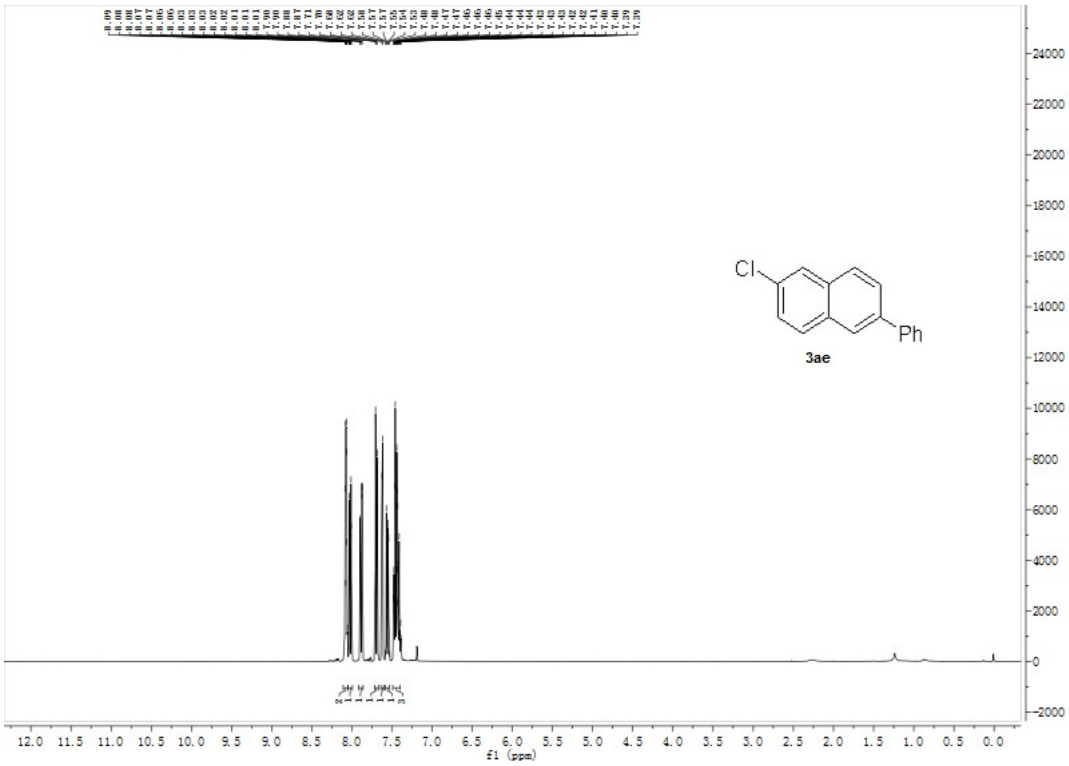
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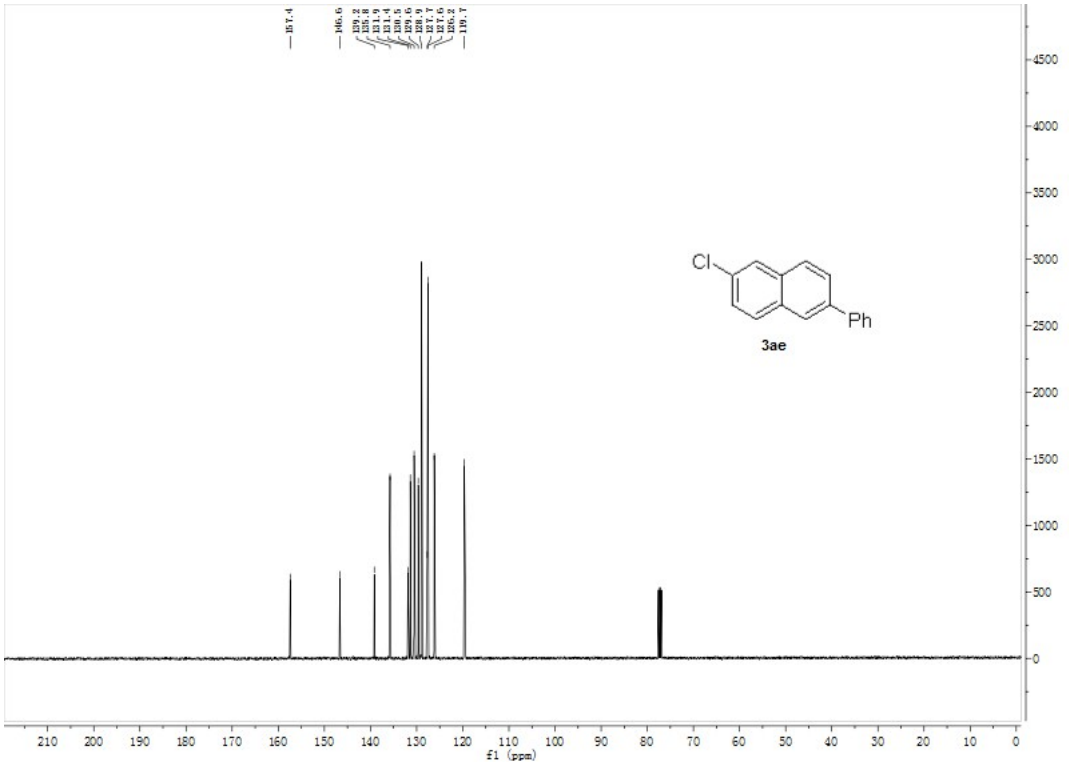
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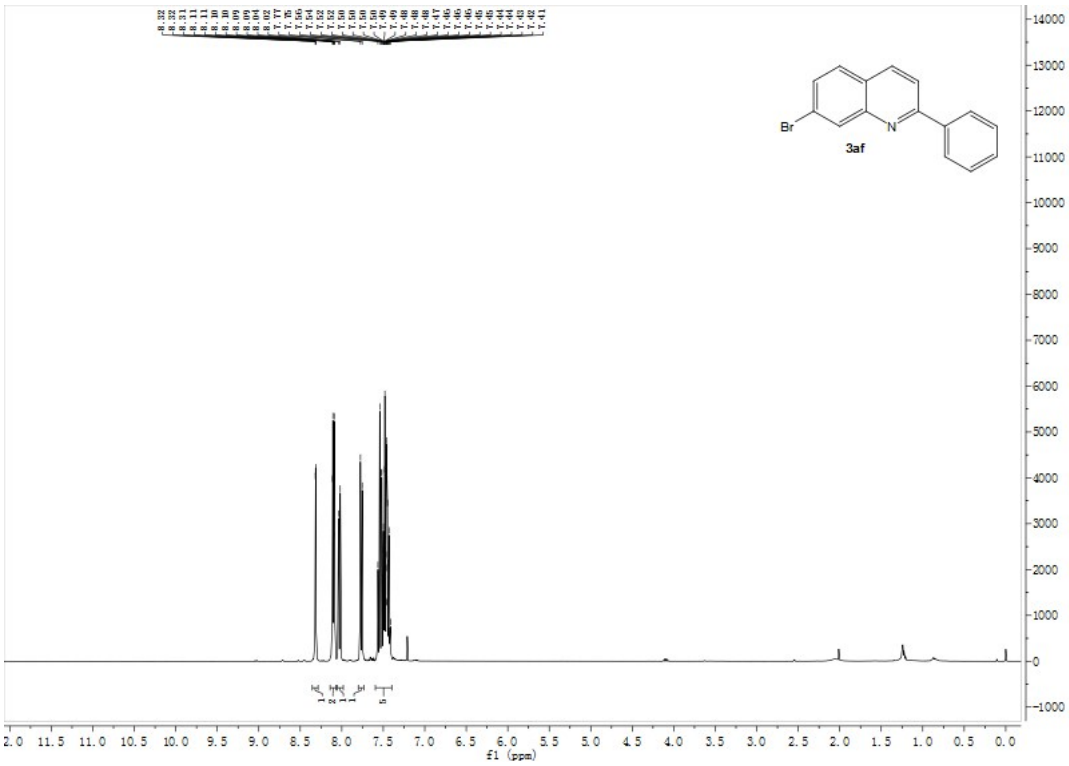
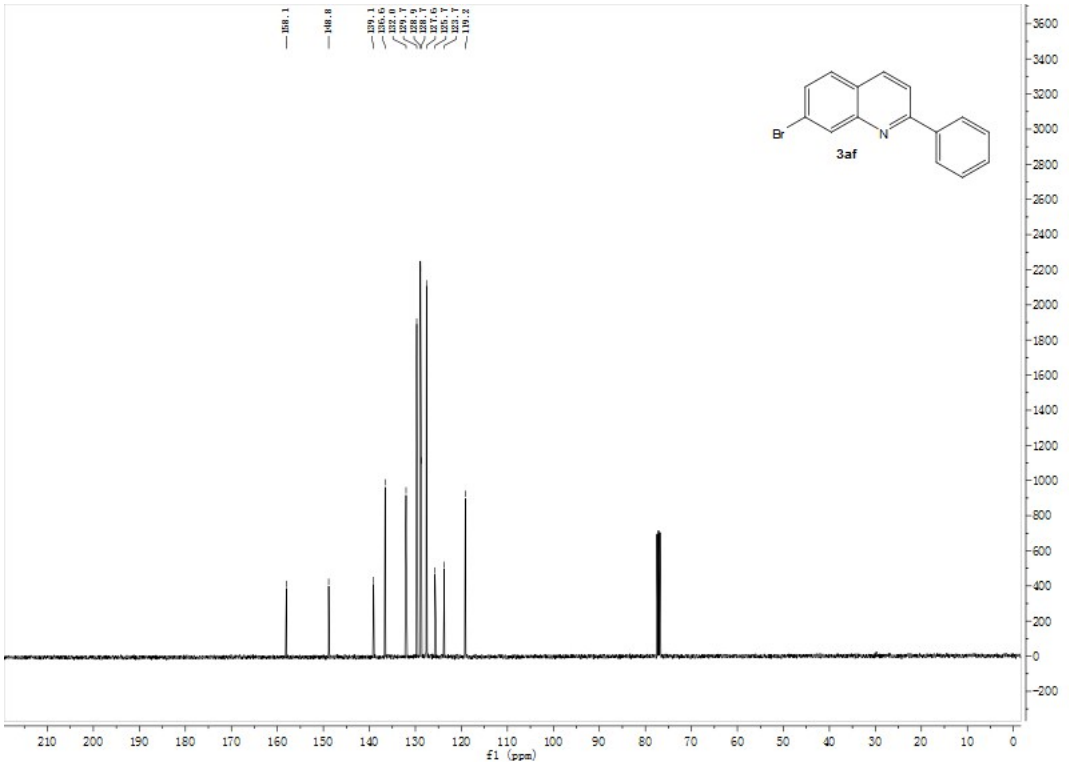

Br
N
3af
f1 (ppm)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N
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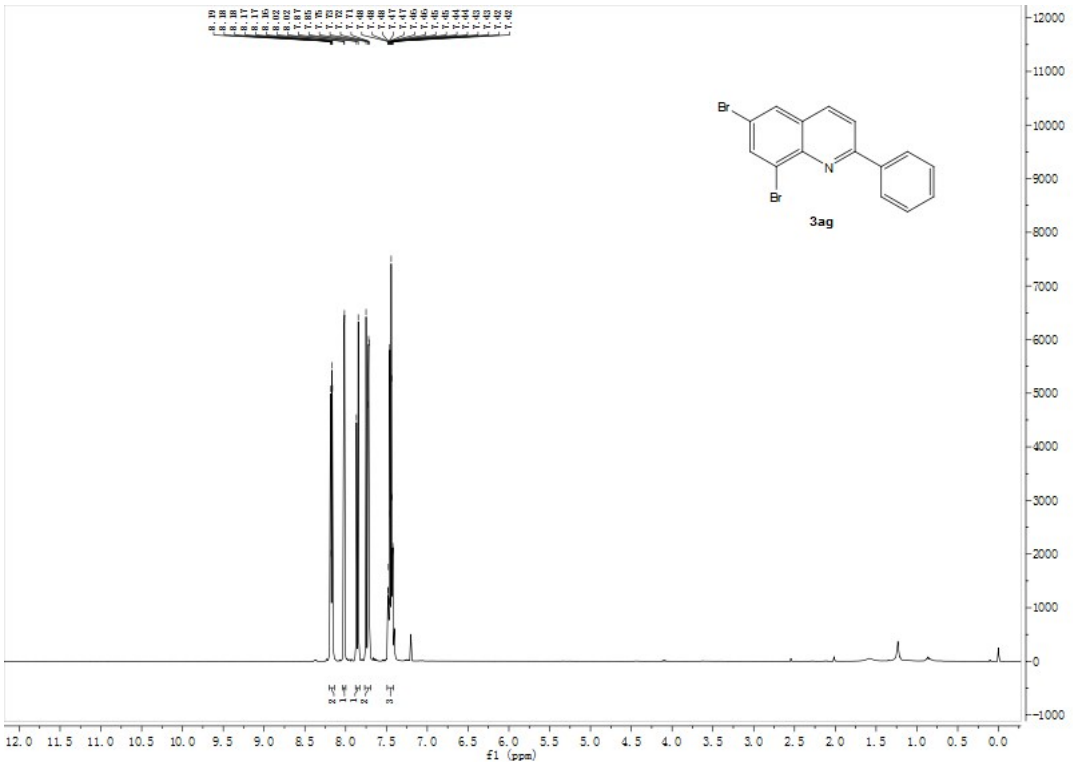
f1 (ppm)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N
Br
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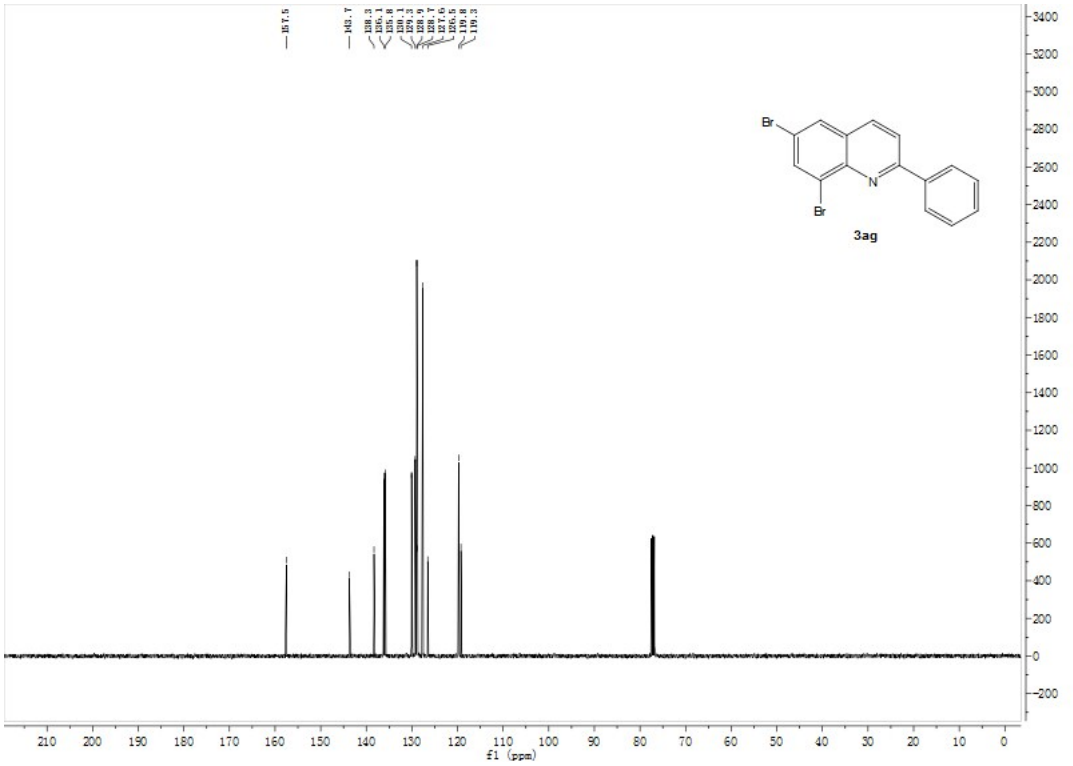
f1 (ppm)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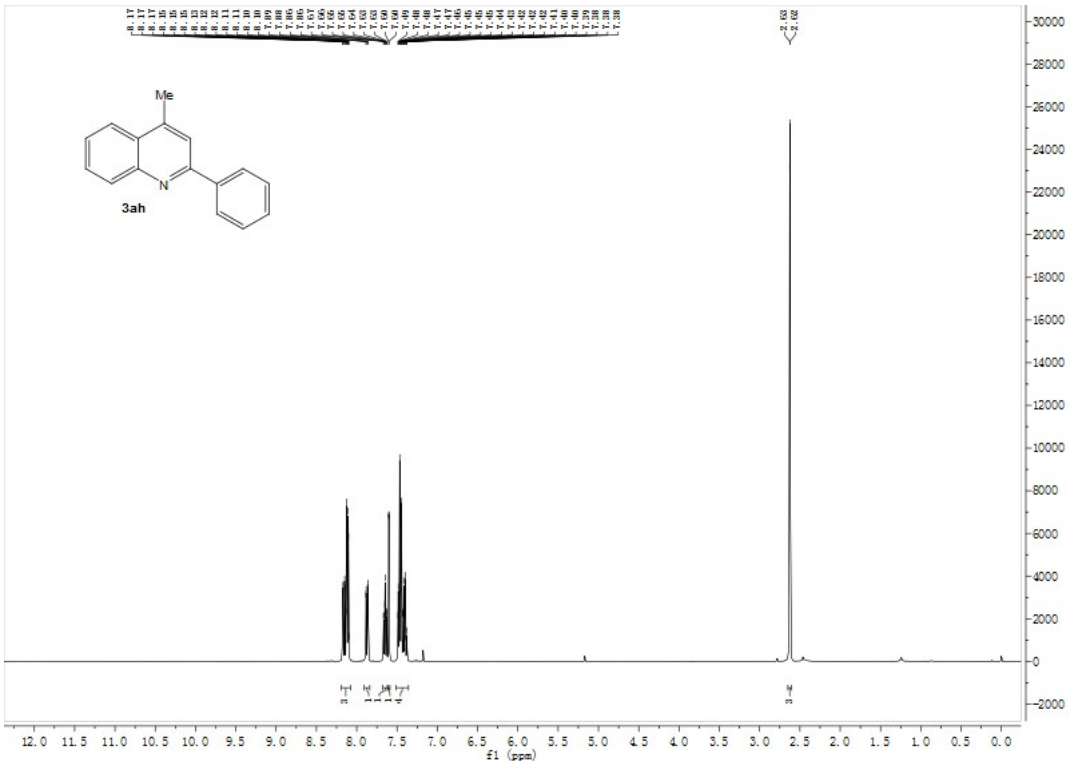
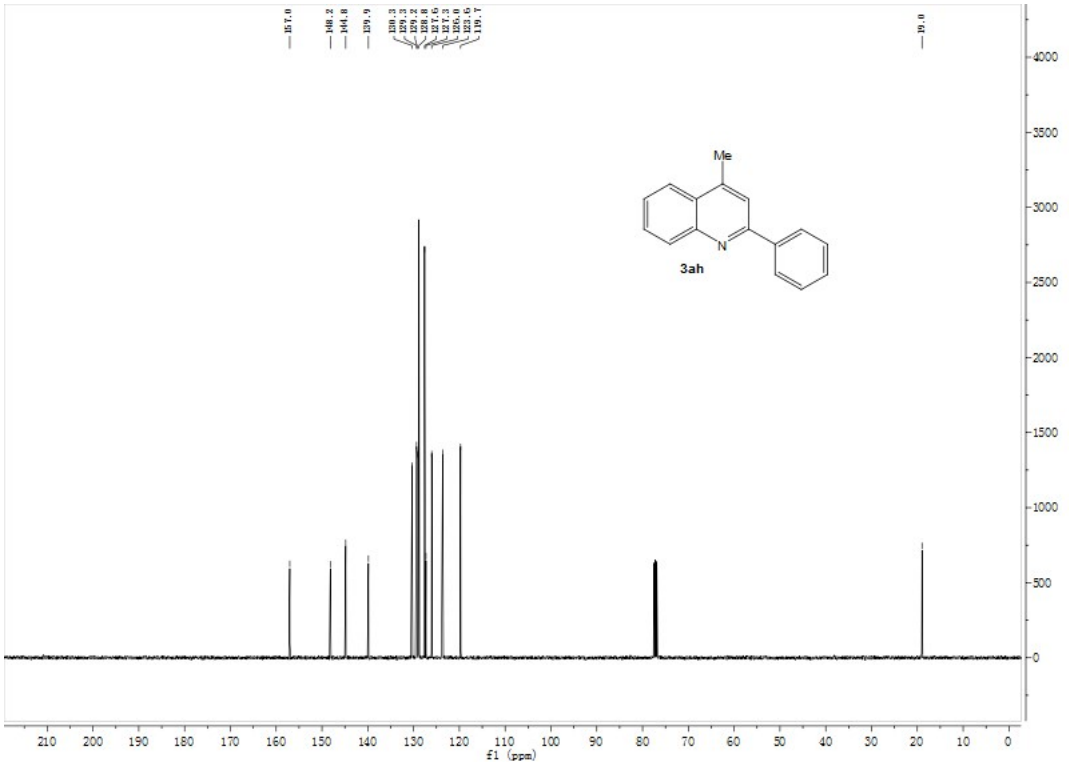
N
Br
3ag
f1 (ppm)


Me
N
3ah
f1 (ppm)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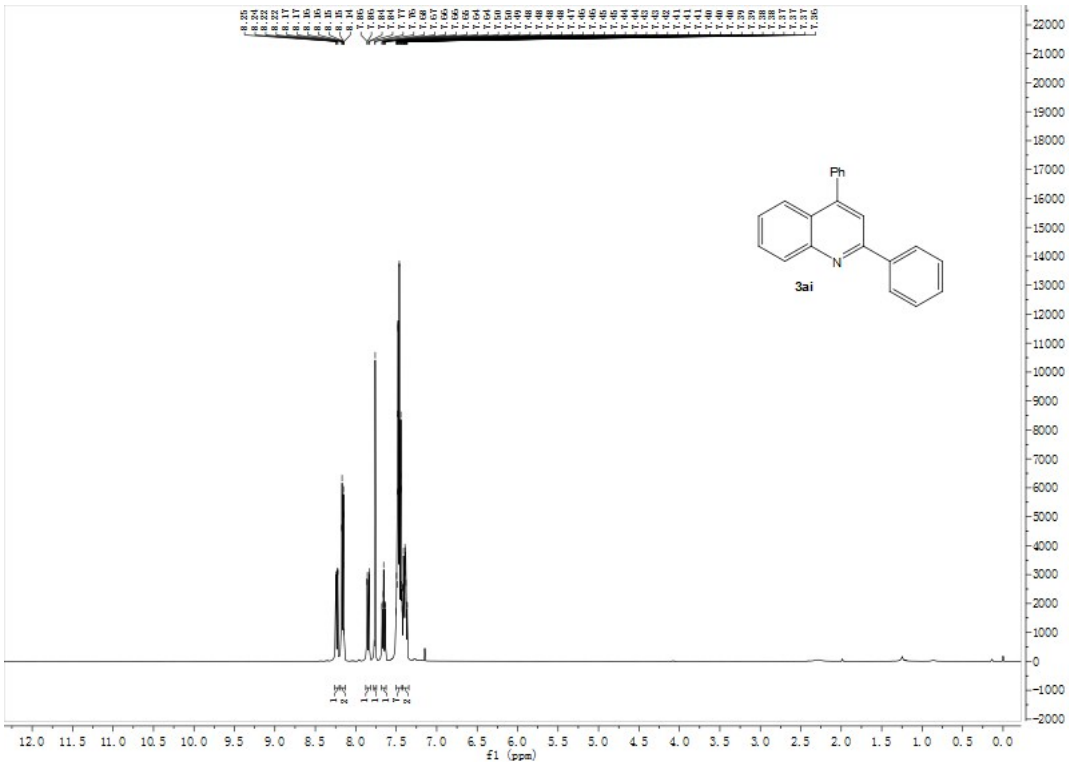
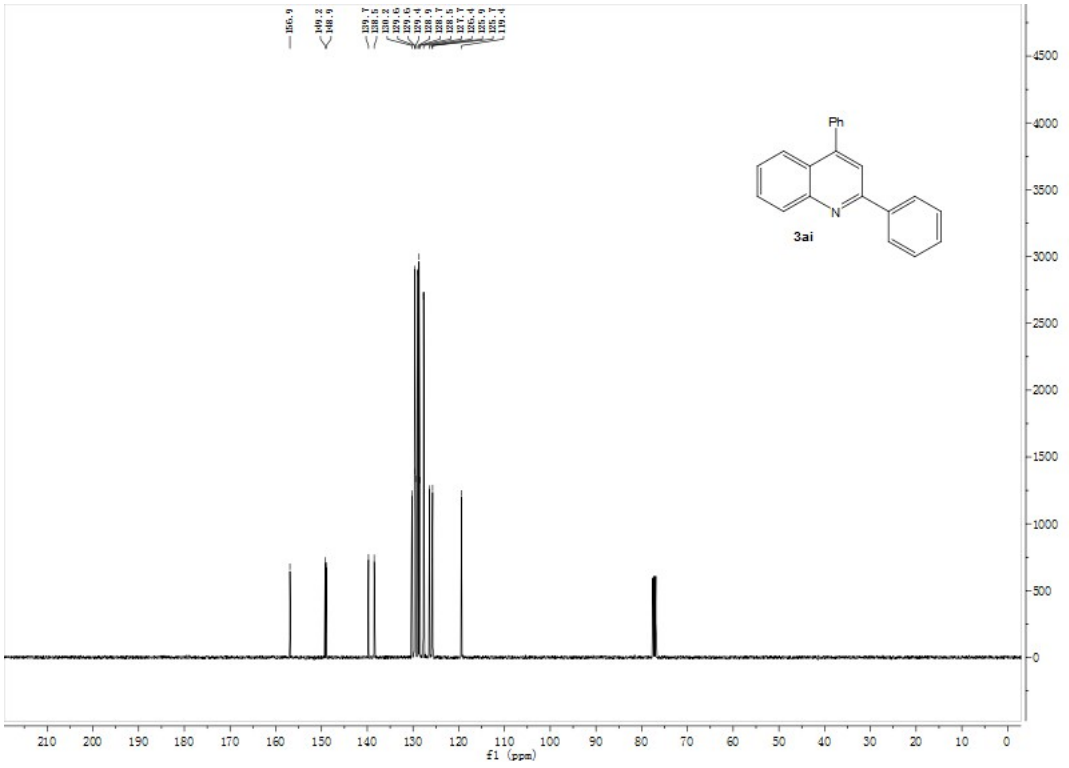

Ph
N
3ai
f1 (ppm)


Ph
N
3ai
f1 (ppm)