Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Supported gold-catalyzed and ammonia-promoted selective synthesis of quinazolines in aqueous media

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Contents:

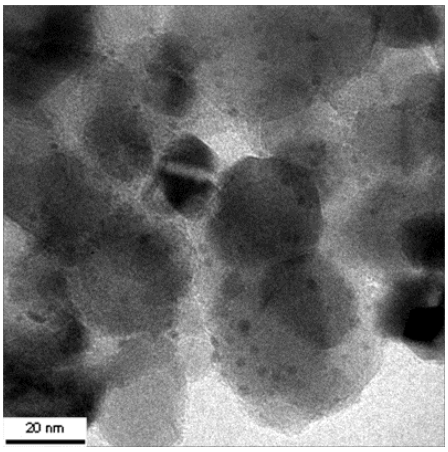
General Remarks

Unless otherwise indicated, all substrates of the alcohol were purchased commercially without further purification. CeO_2 (CAS: 1306-38-3), ZrO_2 (CAS: 1314-23-4), C (CAS: 7440-44-0), Polyvinyl pyrrolidone (PVP K-30, CAS: 9003-39-8), Polyvinyl alcohol (PVA-124, CAS: 9002-89-5) were purchased from Sinopharm Chemical Reagent Co., Ltd. TiO_2 (Degussa P25) was purchased from Ltd. Shanghai harbour plaza trade co., Ltd. Pt/C (5%) (CAS: 7440-06-4) was purchased from Shaanxi Reach Chemical Co., Ltd. Pd/C (10%) (CAS: 7440-05-3) was purchased from Shanghai Titan Technology Co., Ltd. Diatomite (CAS: 61790-53-2) was afforded by Alfa Aesar (Tianjin) chemical co., Ltd. The morphology and size of the nanoparticles were characterized on transmission electron microscopy (TEM) (JEOL–2010 and Hitachi H7650). The as-synthesized heterogenous catalysts dispersed with ethanol were used as samples directly and dried on the carbon-coated Cu grids. The accurate metal loading was directly determined by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometer) using Perkin Elmer Optima 7300 DV. ^{1}H NMR, ^{13}C NMR were recorded on a Bruker AC-400 FT (^{1}H NMR 400 MHz, ^{13}C NMR 100 MHz) using TMS as internal reference. GC-MS samples were recorded on a Shimadzu QP-5050 GC-MS system. And the yields were determined using 1,3,5-trimethylbenzene as an internal standard.

General procedures for the synthesis of heterogeneous catalysts

Preparation of Au/TiO_2

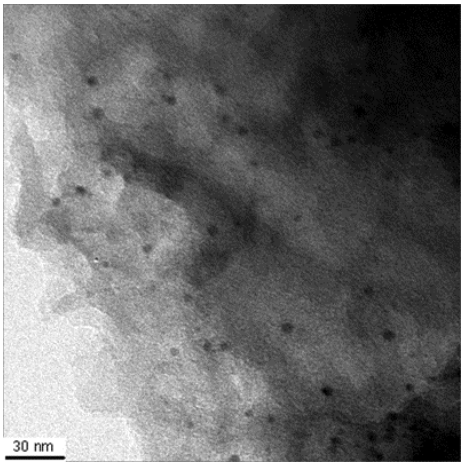
Au/TiO_2 catalyst was prepared via deposition-precipitation (DP) procedure. 1 g TiO_2 was dispersed in 20 ml of deionized water. An appropriate volume of 2.5 mM $HAuCl_4$ solution was added, and the pH value raised to 7 using 1.0 M KOH. During the aging step, the slurry pH was maintained for 2 h at 343 K under constant stirring. Au/TiO_2 solid was then filtered and exhaustively washed with deionized water until no traces of chlorides were detected by the $AgNO_3$. The catalyst was dried at 323 K under vacuum before calcination at 300 °C for 4 h.



Au/TiO_2

Preparation of Au/C

This catalyst was synthesized as followed: to an aqueous $HAuCl_4$ solution of the desired concentration, the required amount of a PVA solution (1 wt %) was added (PVA/Au (w/w) = 1.2); a freshly prepared solution of $NaBH_4$ (0.1 M, $NaBH_4$/Au (mol/mol) = 5) was then added to the mixture. After 30 min of sol generation, the colloid was immobilized by adding an appropriate amounts of activated carbon (acidified at pH 1 by sulfuric acid) under vigorous stirring conditions. After 2 h, the slurry was filtered and the catalyst was washed thoroughly with deionized water (neutral mother liquors) until no traces of chlorides were detected by the $AgNO_3$ and then dried at 120 °C for 16 h.

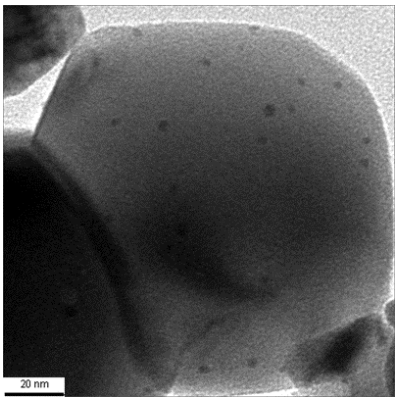


Au/C

Preparation of Au/ZrO_2

Au/ZrO_2 catalyst was prepared via deposition-precipitation (DP) procedure. 1 g ZrO_2 was dispersed in 20 ml of deionized water. An appropriate volume of 2.5 mM $HAuCl_4$

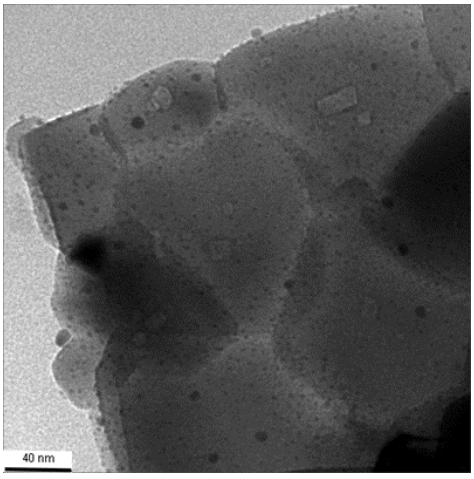
solution was added, and the pH value raised to 9 using 0.1 M Na_2CO_3. During the aging step, the slurry pH was maintained overnight at 298 K under constant stirring. Au/ZrO_2 solid was then filtered and exhaustively washed with deionized water until no traces of chlorides were detected by the $AgNO_3$. The catalyst was dried at room temperature under vacuum before calcination at 200 °C for 4 h.



Au/ZrO_2

Preparation of Au/CeO_2

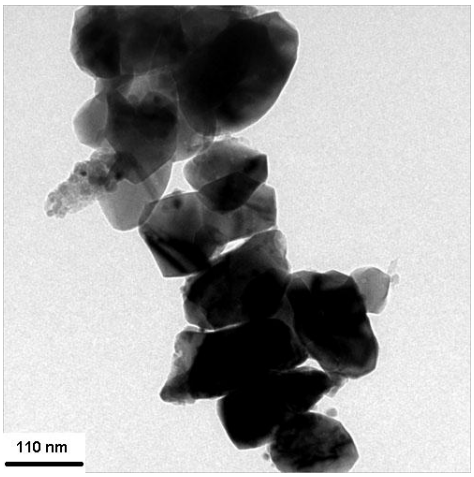
Au/CeO_2 catalyst was prepared via deposition-precipitation (DP) procedure. 1 g CeO_2 was dispersed in 20 ml of deionized water. An appropriate volume of 2.5 mM $HAuCl_4$ solution was added, and the pH value raised to 8 using 0.2 M NaOH. During the aging step, the slurry pH was maintained overnight at 298 K under constant stirring. Au/CeO_2 solid was then filtered and exhaustively washed with deionized water until no traces of chlorides were detected by the $AgNO_3$. The catalyst was dried at room temperature under vacuum before calcination at 200 °C for 4 h.



Au/CeO_2

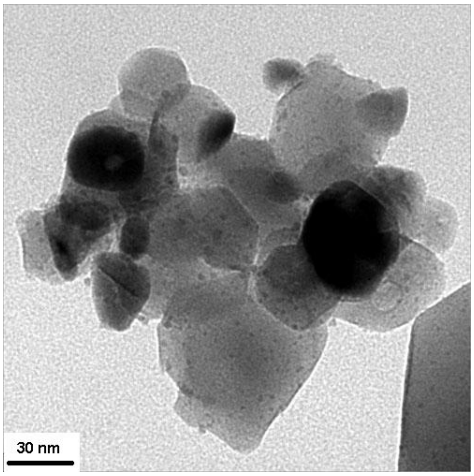
Preparation of Ni/ZrO_2

Ni/ZrO_2 catalyst was prepared via a wet impregnation method. 1 g ZrO_2 was dispersed in 25 ml of deionized water. An appropriate amount of $Ni(NO_3)_2 \cdot 6H_2O$ was added, then this slurry was stirred for 24 h. This sample was dried using a rotary evaporator at 383 K under reduced pressure and reduced at 773 K for 2 h under H_2 atmosphere.



Preparation of Ru/ZrO_2

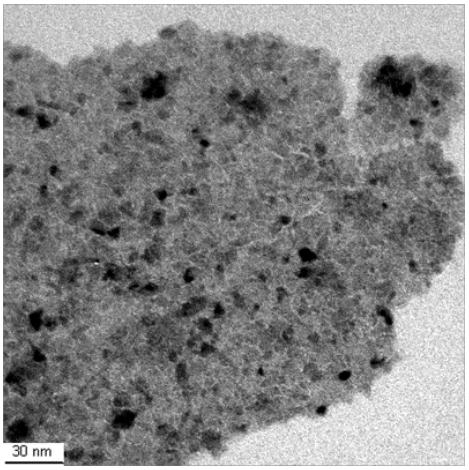
Ru/ZrO_2 catalyst was prepared via a wet impregnation method. 1 g ZrO_2 was dispersed in 25 ml of deionized water. An appropriate amount of $RuCl_3$ was added, then this slurry was stirred for 24 h. This sample was dried using a rotary evaporator at 373 K under reduced pressure and reduced at 723 K for 3.5 h under H_2 atmosphere.



Preparation of Pd/diatomite

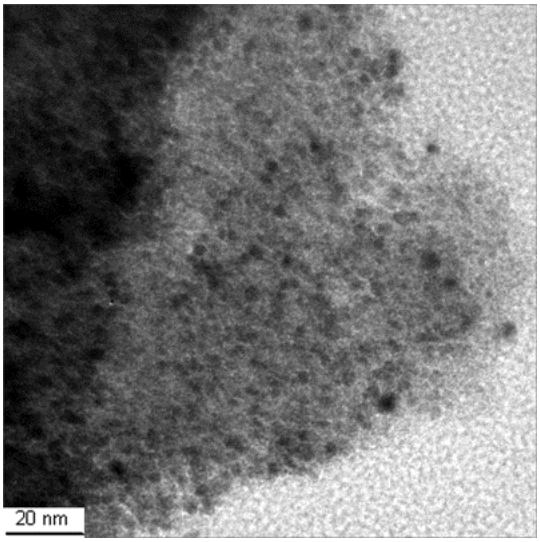
This catalyst was synthesized according to ref. [1]. by our group. 200 mg of diatomite

was added to 10 mL of water, together with 1 mmol of $SnCl_2 \cdot 2H_2O$ and 3 mmol of CF_3COOH. After the mixture was stirred for 1 h under room temperature, 200 mg of PVP (poly(vinylpyrrolidone)) and 100 mL of H_2PdCl_4 (2 mM) were added. Then, the supported Pd nanoparticles were achieved by refluxing the above mixture.

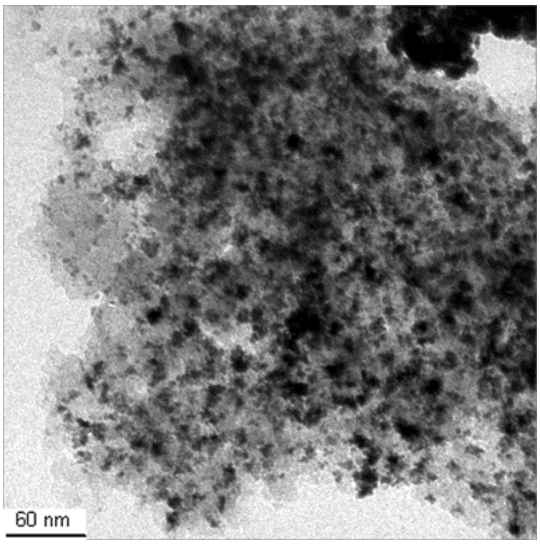


Pd/diatomite

TEM of commercial heterogeneous catalysts of Pd/C and Pt/C

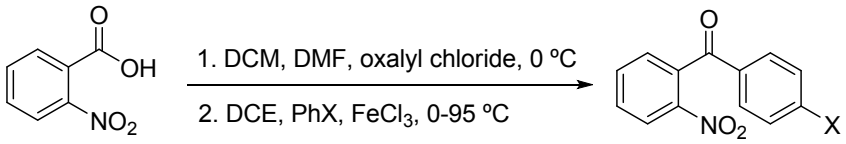


Pd/C



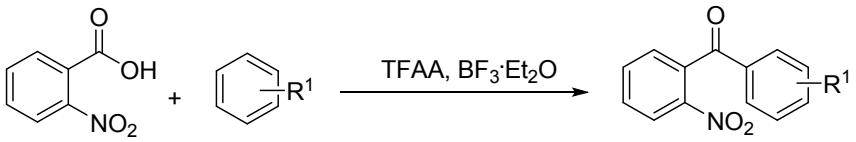
Pt/C

General procedures for preparing of the substrates



X = F, Cl, Br

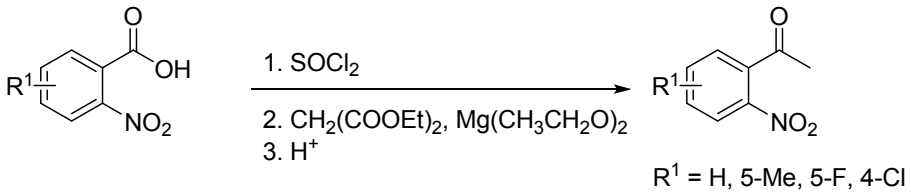
Detailed method[2],[3]: *o*-nitrobenzoic acid (5.014 g, 29.9 mmol) and anhydrous DMA (0.1 mL) were dissolved in dry DCM (105 mL) under argon. After cooling to 0 ºC, oxalyl chloride (5.2 mL, 60 mmol) was added slowly. The mixture was stirred at 0 °C for 30 min, then at ambient temperature until the reaction became clear. Subsequently, the mixture was concentrated to leave the crude acid chloride as a light yellow oil. The oil was directly dissolved in 1,2-dichloroethane (11.6 mL) and fluorobenzene (4.5 mL, 48 mmol) and cooled to 0 ºC. Anhydrous iron (III) chloride (5.35 g, 33.0 mmol) was added to the reaction in 3 portions over 30 min, and the reaction was stirred at 0 ºC for another 1 h. Then the reaction mixture was poured onto ice-water (60 mL), and heated at 95 ºC to remove 1,2-dichloroethane.When the temperature reach 75 ºC,isobutanol (20 mL) was added and the hot solution was washed with water (50 mL x 3). After cooling to room temperature, the precipitate was collected, washed with water and purified by flash column chromatography to give the ((4-fluorophenyl)(2-nitrophenyl)methanone as a light brown solid (5.792g, 79% yield).



R^1 = H, Me, 2,4,6-tri-Me

Detailed method[2],[4]: 2-Nitrobenzoic acid (1.997 g, 12 mmol) and trifluoroacetic anhydride (4 g, 19 mmol) were stirred to homogeneous. After cooling in ice bath,

boron trifluoride-ether (1.701 g, 12 mmol) was added to the solution dropwise. The deep red solution was dropped to mesitylene (2.255g, 18.75 mmol) in ice bath, and stirred for another 2 h. Then the reaction mixture was poured onto ice and extracted with chloroform. The extract was washed with aqueous sodium hydroxide (40%), dried over Na_2SO_4, and concentrated to give a greyish-white solid. After recrystallization from EtOH, mesityl(2-nitrophenyl)methanone was obtained as a white solid (1.134 g, 35% yield).



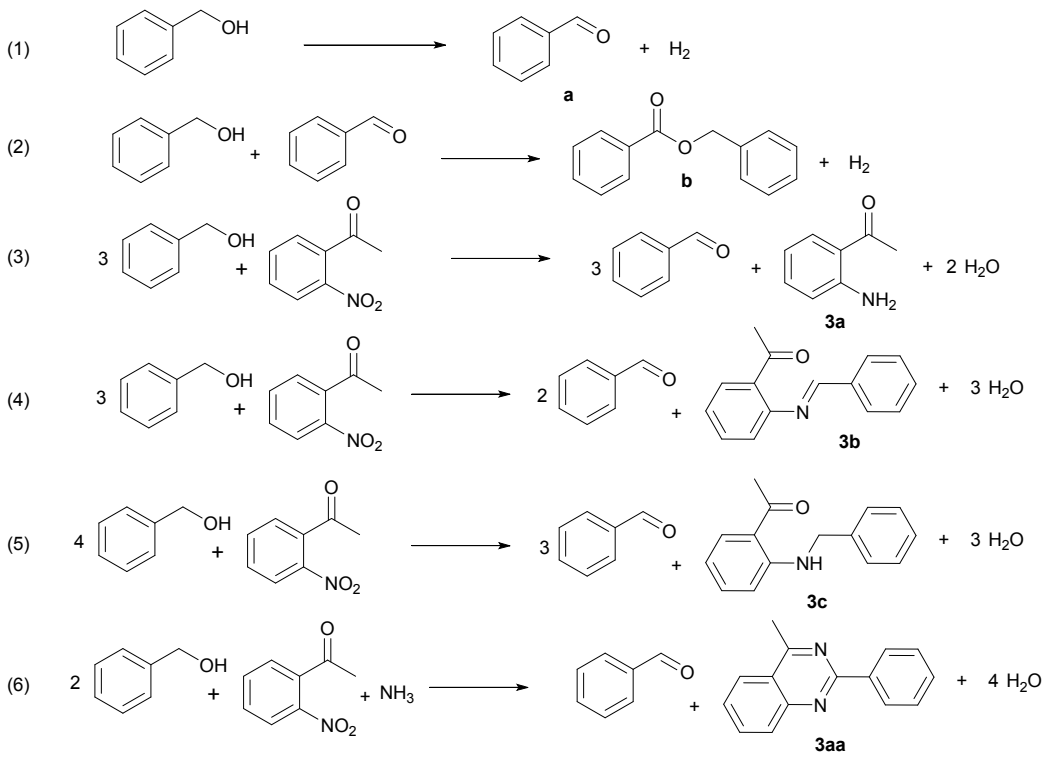
R^1 = H, 5-Me, 5-F, 4-Cl

Detailed method[5]: 2-Nitrobenzoic acid (1.67 g, 10 mmol) and 25 ml thionyl chloride was heated to 80 ºC for 3h under argon. After cooling to room temperature, the mixture was concentrated to leave the crude acid chloride as a light yellow oil. 1.66 ml diethyl malonate and magnesium ethoxide (1.1 eq., 1.25g) was refluxed in dry THF (10 ml) for 4 h, then the crude acid chloride dissolved in dry THF (5 ml) was added in the above mixture very slowly. The reaction mixture was cooled to room temperature and the solvent was removed under vacuum. The residue was dissolved in ethyl acetate and treated with dilute sulfuric acid (1.0 mL of H_2SO_4 in 10 mL of H_2O). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. Extracts were combined, and solvent was removed to yield crude diethyl-5-methyl-2-nitrobenzoylmalonate. A solution of 2 mL of glacial acetic acid and 4.0 mL of concentrated sulfuric acid was added, and the mixture was refluxed until no more carbon dioxide was evolved. The reaction mixture was cooled on an ice bath and made alkaline with NaOH solution, and the product 5-methyl-2-nitroacetophenone **3** was extracted with ethyl acetate and purified by flash column chromatography to give yellow oil. (1.337g, 81% yield).

General procedures for synthesis of quinazolines

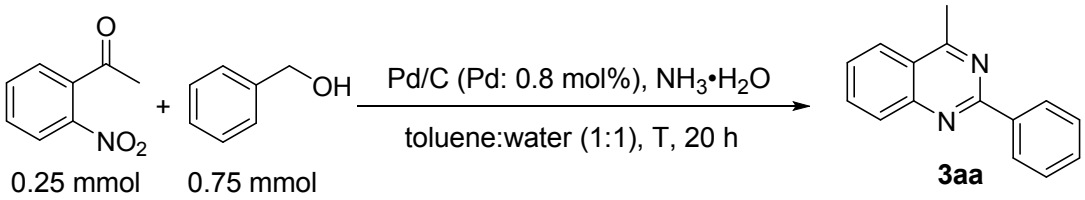
Solvent of water (0.5 ml) and toluene (0.5 ml) were added to the mixture of *o*-nitroacetophenone (41.25 mg, 0.25 mmol), benzyl alcohol (81.1 mg, 0.75 mmol), and metal catalyst (0.8 mol% metal), then ammonia (25% in H_2O, 60 μL, about 3.0 equiv.) was added in a Schlenk tube. The air in the reaction mixture was removed under vacuum and the reaction tube was refilled with N_2 under -30 °C. This procedure was repeated three times. The reaction mixture was then stirred under N_2 atmosphere at 130 °C for 20 h. After cooling to room temperature, the catalyst was recovered by filtering the solid from liquid phase and reused for the next round. Then, the liquid phase was removed under vacuum and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 15:1) to give the product as a white solid.

Analysis for the possible reactions and their stoichiometries



These were the possible reations using benzyl alcohol as the source of hydrogen and their stoichiometries of benzyl alcohol. From these reactions, we can know that **a** was the coupled product and a lot of **a** can be observed during the dehydrogenation of benzyl alcohol. Also, we can observe a trace of benzylbenzoate. But all the yield was based on *o*-nitrophenols, the possible measured products were **3a, 3b, 3c and 3aa**. From reaction (6) we can know that the real stoichiometry of benzyl alcohol to 1-(2-nitrophenyl)ethanone was 2. Through the optimization of conditions in table 1, 1.5 equiv. of benzyl alcohol was used as the optimal conditions.

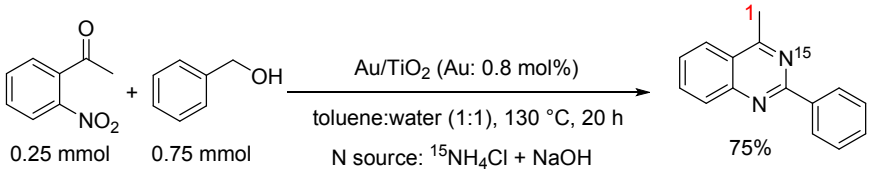
Optimization of the reaction conditions catalyzed by Pd/C



T = 130 ºC, 3**aa** = 65%
T = 160 ºC, **3aa** = 81%
T = 170 ºC, **3aa** = 83%

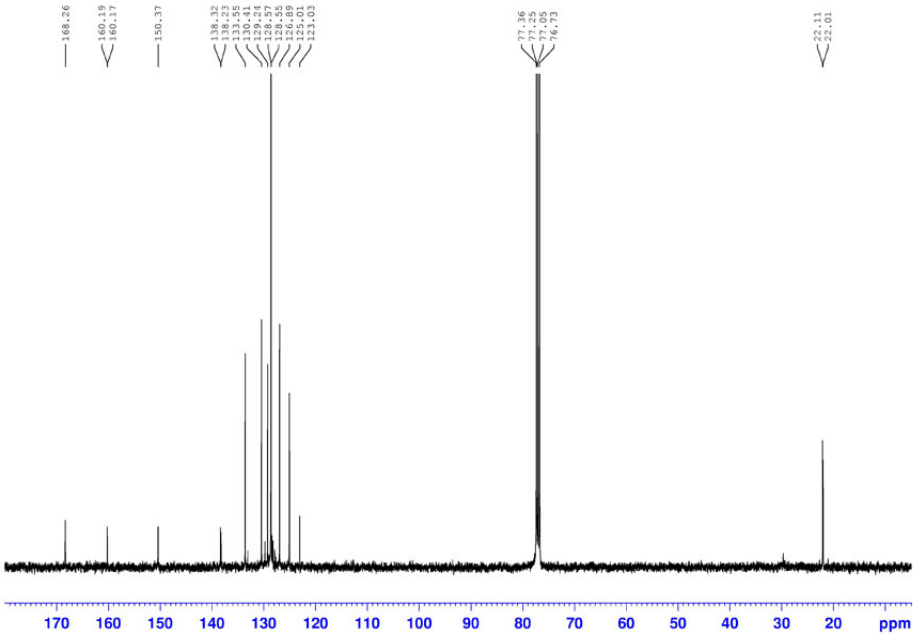
Control experiments for the reaction mechanism

^{15}N-labeling experiment



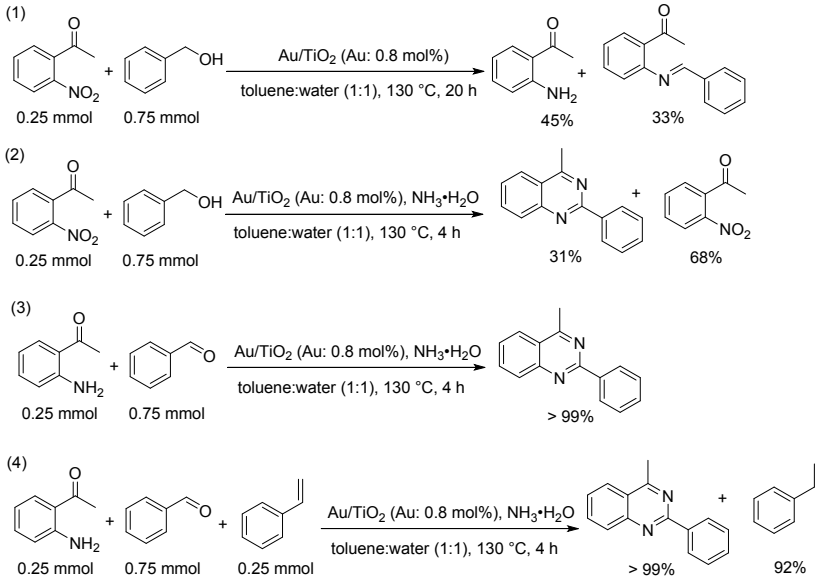
HRMS [M+] calcd for C15H12^{14}N^{15}N: 221.0971, found 221.0974.

^{13}C NMR showed two peaks of C1from the coupling interaction of C-N bond.



^{13}C NMR of the product

From these results, we can know that the additional nitrogen atom of the product was derived from nitrogen source.



Scheme S1 Some verification experiments.

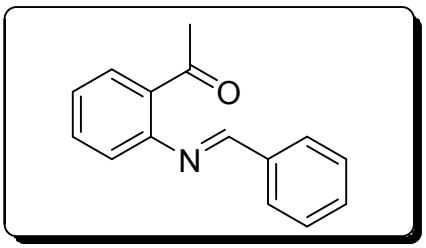
To get insight into the mechanism of the reaction, verification experiments were performed (Scheme S1). (1) When *o*-nitroacetophenone was employed as the substrate to react with benzyl alcohol under the optimal conditions, the corresponding amine and imine was obtained in a moderate yield. This indicated that benzyl alcohol could be oxidized into benzaldehyde and nitro group could be reduced into amino group in situ. Then the imine was obtained through condensation of the corresponding aldehyde and amine. This was the first hydrogen-transfer process. (2) The reaction of *o*-nitroacetophenone with benzyl alcohol for 4 h under the optimal conditions only gave the product in 31% yield, and 68% of *o*-nitroacetophenone was obtained. (3) While the substrates were *o*-aminoacetophenone and benzaldehyde, this reaction could give the product in 99% yield for 4 h under the optimal conditions. From (2) and (3), these results revealed that the rate-limiting step of the reaction was the first hydrogen-transfer process and *o*-aminoacetophenone and benzaldehyde should be the intermediate of the product **3aa**. (4) When styrene was added in this reaction, 92% of phenylethane was obtained, which indicated that the intermediate 4-methyl-2-phenyl-1,2-dihydroquinazoline (**2d**) could be oxidized into **3aa** completely and the styrene was reduced into phenylethane in situ by the hydrogen liberated from **2d**. This suggested that there was a second hydrogen-transfer process.

ICP-AES analysis after reaction with NH_4Cl as the nitrogen source

ICP-AES analysis after reaction when NH_4Cl was used as the nitrogen source showed that the amount of Au in 2 ml of solvent was 1.02 μg/ml.

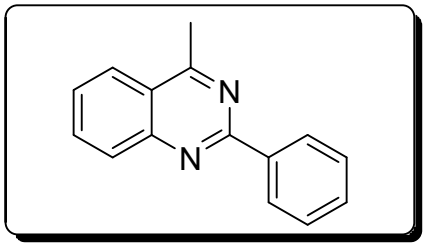
Characterization data of products

4-methyl-2-phenylquinazoline **(3b)**



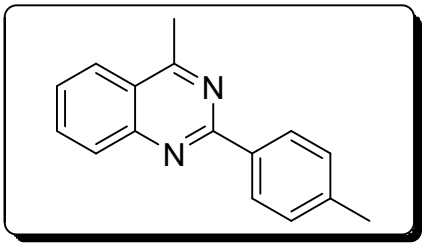
^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 9.260 (d, 6.0 Hz, 1H), 7.905-7.881 (m, 1H), 7.555-7.534 (m, 1H), 7.453-7.353 (m, 3H), 6.803 (d, 8.4 Hz, 1H), 6.725-6.687 (m, 1H), 6.282 (t, 6.4 Hz, 1H), 2.542 (s, 3H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 201.4, 148.1, 140.4, 135.1, 133.1, 129.0, 128.5, 126.4, 117.8, 115.7, 112.7, 64.5, 28.1; GC-MS (EI): 223. HRMS $(M+H)^+$ calcd for $C_{15}H_{14}NO$: 224.10699 found 224.10634. This compound was purified by recrystallization with EtOAc/petroleum ether to give the product. This compound was known.[8]

4-methyl-2-phenylquinazoline **(3aa)**



^{1}H NMR (400 MHz, d^6-DMSO): δ [ppm] = 8.579-8.556 (m, 2H), 8.285 (d, 8.0 Hz, 1H), 8.044-7.967 (m, 2H), 7.705 (t, 8.0 Hz, 1H), 7.586-7.546 (m, 3H), 2.997 (s, 3H); ^{13}C NMR (100 MHz, d^6-DMSO): δ [ppm] = 168.8, 158.8, 149.6, 137.5, 134.3, 130.6, 128.6, 128.5, 128.0, 127.4, 125.8, 122.5, 21.9; GC-MS (EI): 220. This compound was known.[6]

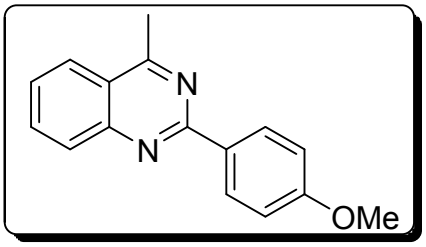
4-methyl-2-p-tolylquinazoline (**3ba**)



^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.532 (d, 8.0 Hz, 2H), 8.101-8.058 (m, 2H), 7.869-7.827 (m, 1H), 7.579-7.538 (m, 1H), 7.334 (d, 8.0 Hz, 2H), 3.007 (s, 3H), 2.444 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 168.6, 160.2, 150.2, 140.9, 135.3, 133.7, 129.5, 129.0, 128.7, 126.9,

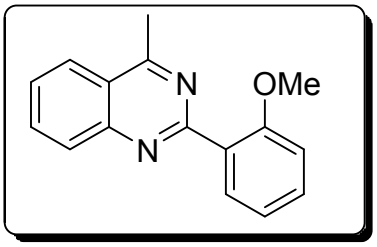
125.1, 123.0, 22.2, 21.7; GC-MS (EI): 234. This compound was known.[6]

2-(4-methoxyphenyl)-4-methylquinazoline (**3ca**)



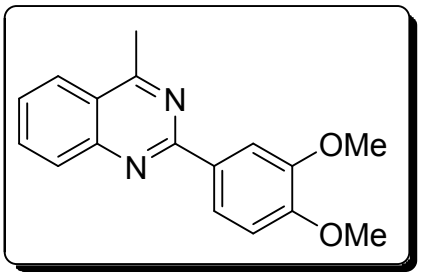
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.586 (d, 8.8 Hz, 2H), 8.018 (d, 8.8 Hz, 2H), 7.811 (t, 8.0 Hz, 1H), 7.506 (t, 7.8 HZ, 1H), 7.033 (d, 8.8 Hz, 2H), 3.881 (s, 3H), 2.967 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 168.0, 161.7, 159.9, 150.4, 133.4, 130.9, 130.2, 128.9, 126.4, 125.0, 122.7, 113.9, 55.4, 22.0; GC-MS (EI): 250. This compound was known.[6]

2-(2-methoxyphenyl)-4-methylquinazoline (**3da**)



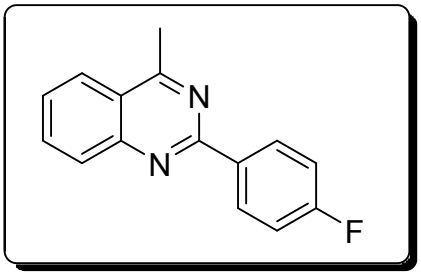
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.13-8.08 (m, 2H), 7.89-7.85 (m, 1H), 7.72-7.70 (m, 1H), 7.63-7.59 (m, 1H), 7.44-7.39 (m, 1H), 7.11-7.03 (m, 2H), 3.85 (s, 3H), 3.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 168.1, 161.8, 157.7, 150.2, 133.6, 131.6, 130.7, 129.5, 129.3, 127.3, 125.0, 122.7, 120.9, 112.2, 56.1, 22.0; IR (film, cm^{-1}): 751, 1020, 1242, 1338, 1340, 1496, 1547; GC-MS (EI): 250. HRMS (M+) calcd for $C_{16}H_{14}N_2O$: 250.1106 found 250.1099.

2-(3,4-dimethoxyphenyl)-4-methylquinazoline (**3ea**)



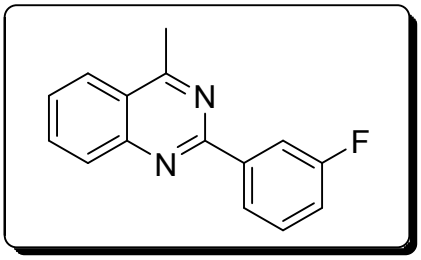
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.28-8.26 (m, 1H), 8.21 (d, 1.6 Hz, 1H), 8.07-8.03 (m, 2H), 7.86-7.82 (m, 1H), 7.56-7.52 (m, 1H), 7.01 (d, 8.0 Hz, 1H), 4.07 (s, 3H), 3.97 (s, 3H), 3.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 168.2, 160.0, 151.4, 150.6, 149.1, 133.6, 131.3, 129.1, 126.6, 125.1, 122.9, 122.1, 111.3, 110.9, 56.2, 56.1, 22.2; IR (film, cm^{-1}): 763, 1128, 1249, 1516, 1551, 1761; GC-MS (EI): 280. HRMS (M+) calcd for $C_{17}H_{16}N_2O_2$: 280.1212 found 280.1206.

2-(4-fluorophenyl)-4-methylquinazoline (**3fa**)



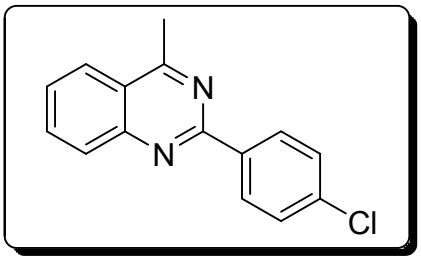
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.66-8.63 (m, 2H), 8.09-8.07 (m, 2H), 7.89-7.85 (m, 1H), 7.60-7.56 (m, 1H), 7.22-7.17 (m, 2H), 3.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 169.3, 166.2, 163.7, 158.9, 149.6, 134.3, 133.7, 131.2, 131.1, 128.7, 127.4, 125.2, 122.9, 115.8, 115.6, 22.2; GC-MS (EI): 238. This compound was known.[6]

2-(3-fluorophenyl)-4-methylquinazoline (**3ga**)



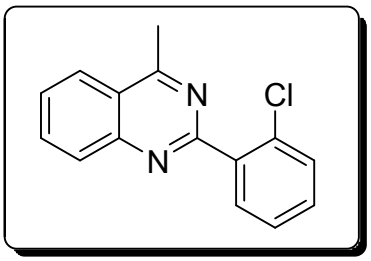
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.43 (d, 8.0 Hz, 1H), 8.36-8.32 (m, 1H), 8.10 (d, 8.8 Hz, 2H), 7.90-7.86 (m, 1H), 7.62-7.58 (m, 1H), 7.51-7.46 (m, 1H), 7.21-7.16 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 169.1, 164.6, 162.1, 158.8, 149.8, 140.3, 134.2, 130.2, 130.1, 129.0, 127.6, 125.2, 124.5, 123.2, 117.8, 117.6, 115.8, 115.6, 22.7; GC-MS (EI): 238. This compound was known.[6]

2-(4-chlorophenyl)-4-methylquinazoline (**3ha**)



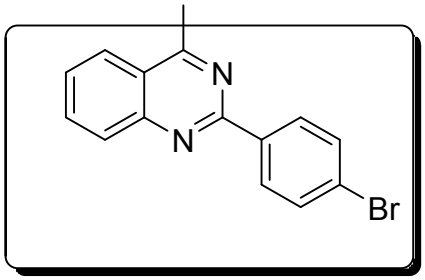
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.61-8.58 (m, 2H), 8.10-8.07 (m, 2H), 7.89-7.85 (m, 1H), 7.61-7.59 (m, 1H), 7.58-7.47 (m, 2H), 3.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 168.9, 159.1, 149.9, 137.0, 136.4, 134.1, 130.2, 129.0, 128.9, 127.4, 125.2, 123.1, 22.2; GC-MS (EI): 254. This compound was known.[6]

2-(2-chlorophenyl)-4-methylquinazoline (**3ia**)



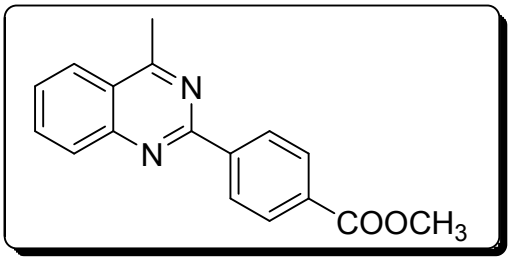
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.165-8.098 (m, 2H), 7.935-7.893 (m, 1H), 7.792-7.769 (m, 1H), 7.689-7.651 (m, 1H), 7.532-7.509 (m, 1H), 7.419-7.376 (m, 2H), 3.035 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 168.5, 161.4, 150.0, 138.7, 134.0, 132.9, 131.6, 130.6, 130.3, 129.3, 127.8, 127.0, 125.1, 122.9, 22.0; GC-MS (EI): 254. This compound was known.[6]

2-(4-bromophenyl)-4-methylquinazoline (**3ja**)



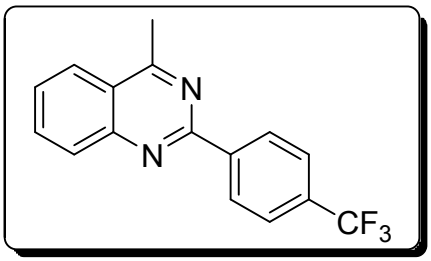
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.516 (d, 8.0 Hz, 2H), 8.089-8.059 (m, 2H), 7.887-7.846 (m, 1H), 7.654-7.541 (m, 3H); 3.004 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 169.1, 159.1, 149.8, 136.7, 134.2, 131.9, 130.5, 128.9, 127.5, 125.7, 125.2, 123.1, 22.2; GC-MS (EI): 298. This compound was known.[6]

methyl 4-(4-methylquinazolin-2-yl)benzoate (**3ka**)



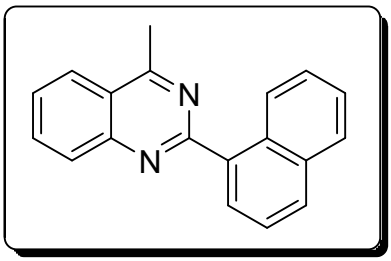
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.725-8.703 (m, 2H), 8.200-8.102 (m, 4H), 7.923-7.882 (m, 1H), 7.651-7.611 (m, 1H), 3.961 (s, 3H), 3.041 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 169.0, 167.1, 159.0, 149.9, 142.1, 134.1, 131.8, 129.9, 129.2, 128.7, 127.7, 125.5, 123.3, 52.4, 22.2; IR (film, cm^{-1}): 717, 860, 1054, 1105, 1245, 1278, 1375, 1764, 2993; GC-MS (EI): 278. HRMS (M+) calcd for $C_{17}H_{14}N_2O_2$: 278.1055 found 278.1048.

4-methyl-2-(4-(trifluoromethyl)phenyl)quinazoline (**3la**)



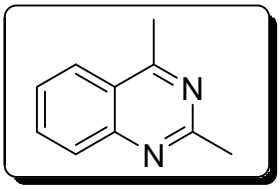
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.748 (d, 8.0 Hz, 2H), 8.109 (t, 7.2 Hz, 2H), 7.900 (t, 8.0 Hz, 1H), 7.772 (d, 8.0 Hz, 2H), 7.631 (t, 7.8 Hz, 1H), 3.035 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 168.8, 158.8, 150.3, 141.6, 134.0, 132.2, 131.9, 130.3, 129.5, 129.0, 127.6, 125.8, 125.6, 125.5, 125.5, 125.2, 123.4, 123.1, 22.2; GC-MS (EI): 288. This compound was known.[6]

4-methyl-2-(naphthalen-1-yl)quinazoline (**3ma**)



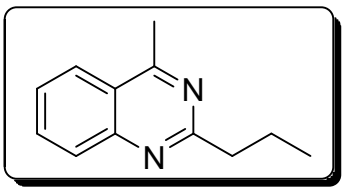
^{1}H NMR (400 MHz,$CDCl_3$): δ [ppm] = 8.637-8.613 (m, 1H), 8.242-8.148 (m, 3H), 7.996-7.915 (m, 3H), 7.708-7.611 (m, 2H), 7.545-7.515 (m, 2H), 3.100 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 168.7, 162.4, 149.8, 134.2, 134.1, 132.0, 131.2, 130.4, 129.5, 129.0, 128.5, 127.6, 126.8, 125.9, 125.8, 125.3, 125.1, 122.5, 22.0; IR (film, cm^{-1}): 760, 870, 1110, 1332, 1388, 1448, 1552, 1644, 3057, 3210; GC-MS (EI): 270. HRMS (M+) calcd for $C_{19}H_{14}N_2$: 270.1157 found 270.1156.

2,4-dimethylquinazoline (**3na**)



^{1}H NMR (400 MHz,$CDCl_3$): δ [ppm] = 8.059-8.036 (m, 1H), 7.933 (d, 8.0 Hz, 1H), 7.851-7.810 (m, 1H), 7.576-7.536 (m, 1H), 2.918 (s, 3H), 2.846 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 168.3, 163.6, 149.9, 133.8, 128.3, 126.7, 125.0, 122.3, 26.5, 21.8; GC-MS (EI): 158. This compound was known.[6]

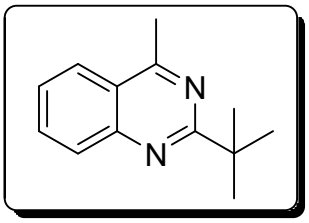
4-methyl-2-propylquinazoline (**3oa**)



^{1}H NMR (400 MHz,$CDCl_3$): δ [ppm] = 8.066-8.042 (m, 1H), 7.964-7.939 (m, 1H), 7.850-7.808

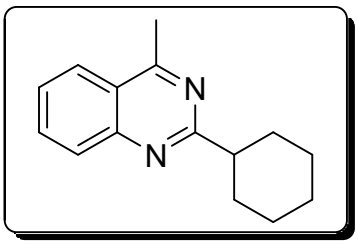
(m, 1H), 7.577-7.536 (m, 1H), 3.049-3.010 (m, 2H), 2.927 (s, 3H), 1.958-1.901 (m, 2H), 1.037 (t, 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 168.2, 166.9, 150.0, 133.6, 128.6, 126.7, 125.1, 122.6, 42.1, 22.6, 21.9, 14.2; GC-MS (EI): 186. This compound was known.[6]

2-tert-butyl-4-methylquinazoline (**3pa**)



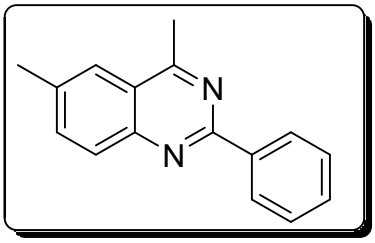
^{1}H NMR (400 MHz,$CDCl_3$): δ [ppm] = 8.036-8.014 (m, 1H), 7.972 (d, 8.0 Hz, 1H), 7.819-7.778 (m, 1H), 7.549-7.508 (m, 1H), 2.915 (s, 3H), 1.522 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 172.8, 167.4, 149.9, 133.0, 129.1, 126.4, 124.8, 122.4, 39.5, 29.8, 22.0; IR (film, cm^{-1}): 760, 1172, 1394, 1483, 1560, 1618, 2927, 2955, 3453; GC-MS (EI): 200. HRMS (M+) calcd for $C_{13}H_{16}N_2$: 200.1313 found 200.1308.

2-cyclohexyl-4-methylquinazoline (**3qa**)



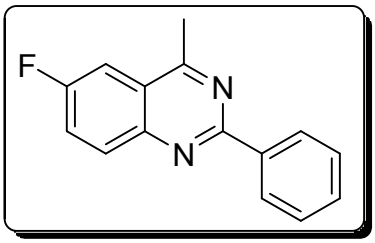
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.034 (d, 8.0 Hz, 1H), 7.960 (d, 8.0 Hz, 1H), 7.832-7.791 (m, 1H), 7.534 (t, 7.6 Hz, 1H), 3.027-2.952 (m, 1H), 2.919 (s, 3H), 2.076-2.043 (m, 2H), 1.893-1.802 (m, 2H), 1.778-1.708 (m, 3H), 1.514-1.301 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 170.1, 168.2, 150.0, 133.5, 128.6, 126.6, 125.0, 122.8, 47.9, 32.0, 26.5, 26.2, 21.9; GC-MS (EI): 226. This compound was known.[6]

4,6-dimethyl-2-phenylquinazoline (**3ab**)



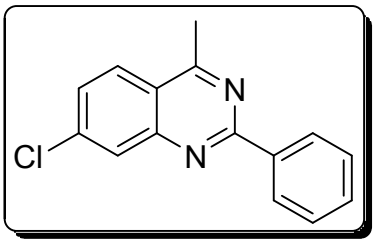
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.617-8.593 (m, 2H), 7.980 (d, 8.8 Hz, 1H), 7.822 (s, 1H), 7.697-7.671 (m, 1H), 7.548-7.481 (m, 3H), 2.982 (s, 3H), 2.565 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 167.6, 159.6, 148.9, 138.4, 137.1, 135.9, 130.3, 128.9, 128.7, 128.5, 124.0, 123.0, 22.1, 22.0; IR (film, cm^{-1}): 708, 830, 1027, 1336, 1400, 1780, 1549, 3060; GC-MS (EI): 234. HRMS (M+) calcd for $C_{16}H_{14}N_2$: 234.1157 found 234.1150.

6-fluoro-4-methyl-2-phenylquinazoline (**3ac**)



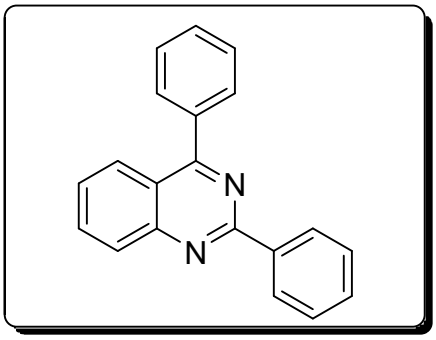
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.609-8.585 (m, 2H), 8.101-8.065 (m, 1H), 7.684-7.602 (m, 2H), 7.552-7.493 (m, 3H), 2.972 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 167.9, 167.8, 161.5, 159.9, 159.8, 159.0, 147.5, 137.9, 131.9, 131.8, 130.6, 128.7, 128.5, 124.0, 123.7, 123.5, 123.4, 108.8, 108.5, 22.2; IR (film, cm^{-1}): 707, 837, 1185, 1224, 1399, 1436, 1500, 1549, 1582, 3064; GC-MS (EI): 238. HRMS (M+) calcd for $C_{15}H_{11}FN_2$: 238.0906 found 238.0908.

7-chloro-4-methyl-2-phenylquinazoline (**3ad**)



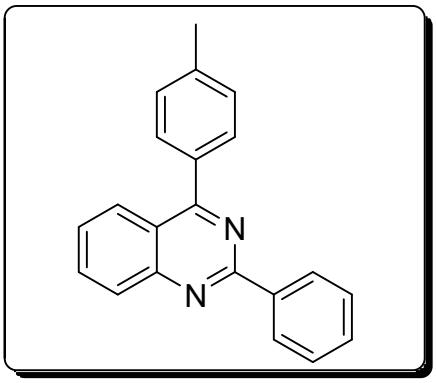
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.620-8.596 (m, 2H), 8.077-7.995 (m, 2H), 7.545-7.500 (m, 4H), 2.988 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 168.6, 161.0, 150.9, 140.0, 137.6, 131.0, 128.8, 128.7, 128.1, 126.6, 121.4, 22.2; IR (film, cm^{-1}): 703, 760, 913, 1096, 1338, 1546, 1569, 1602, 3430; GC-MS (EI): 254. HRMS (M+) calcd for $C_{15}H_{11}ClN_2$: 254.0611 found 254.0609.

2,4-diphenylquinazoline (**3ae**)



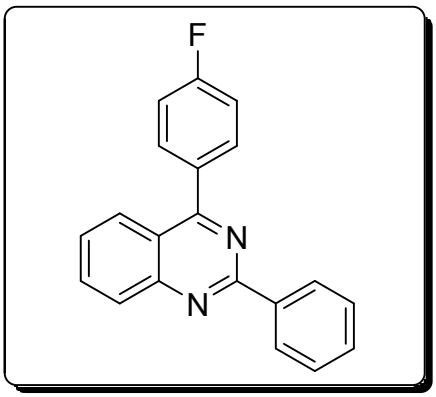
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.722-8.699 (m, 2H), 8.194-8.128 (m, 2H), 7.913-7.879 (m, 3H), 7.638-7.489 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 168.5, 160.4, 152.0, 138.3, 137.8, 133.7, 130.7, 130.3, 130.1, 129.2, 128.8, 128.7, 128.6, 128.4, 127.2, 121.8; GC-MS (EI): 282. This compound was known.[2]

2-phenyl-4-p-tolylquinazoline (**3af**)



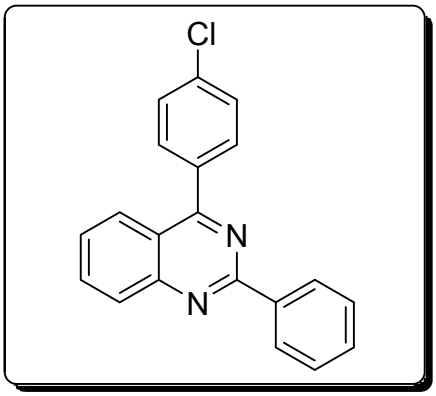
^{1}H NMR (400 MHz,$CDCl_3$): δ [ppm] = 8.761-8.735 (m, 2H), 8.176 (d, 8.7 Hz, 2H), 7.892-7.824 (m, 3H), 7.570-7.524 (m, 4H), 7.438 (d, 7.8 Hz, 2H), 2.527 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 168.3, 160.2, 152.0, 140.1, 138.4, 134.9, 133.4, 130.4, 130.2, 129.2, 129.1, 128.7, 128.5, 127.1, 126.8, 121.7, 21.5; GC-MS (EI): 296. This compound was known.[2]

4-(4-fluorophenyl)-2-phenylquinazoline (**3ag**)



^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.687-8.6682 (m, 2H), 8.164-8.071 (m, 2H), 7.921-7.862 (m, 3H), 7.571-7.493 (m, 4H), 7.315-7.248 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 167.2, 165.3, 162.8, 160.2, 152.1, 138.2, 133.9, 133.8, 133.7, 132.3, 132.2, 130.6, 129.4, 128.7, 128.6, 127.2, 126.7, 121.6, 115.8, 115.6; GC-MS (EI): 300. This compound was known.[2]

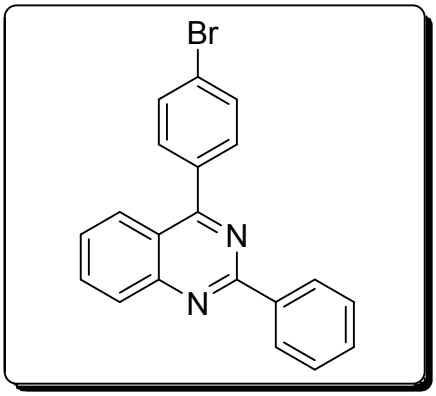
4-(4-chlorophenyl)-2-phenylquinazoline (**3ah**)



^{1}H NMR (400 MHz,$CDCl_3$): δ [ppm] = 8.705-8.681 (m, 2H), 8.218 (d, 8.0 Hz, 1H), 8.094-8.073 (m, 1H), 7.932-7.890 (m, 1H), 7.862-7.835 (m, 2H), 7.599-7.513 (m, 6H); ^{13}C NMR (100

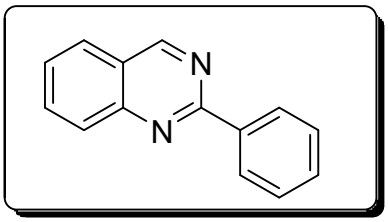
MHz,$CDCl_3$): δ [ppm] = 167.8, 160.0, 151.2, 137.3, 136.7, 135.9, 134.3, 131.7, 131.1, 129.0, 129.0, 128.8, 127.6, 126.8, 121.5; GC-MS (EI): 316. This compound was known.[10]

4-(4-bromophenyl)-2-phenylquinazoline (**3ai**)



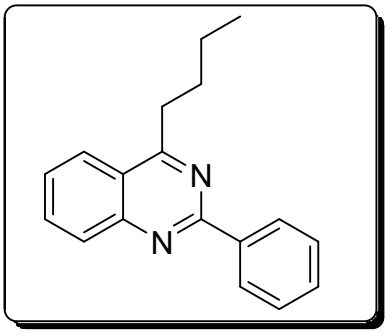
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.697-8.665 (m, 2H), 8.166 (d, 8.7 Hz, 1H), 8.072 (d, 8.7 Hz, 1H), 7.927-7.900 (m, 1H), 7.895-7.726 (m, 4H), 7.590-7.506 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 167.0, 160.0, 152.1, 138.0, 136.5, 133.7, 131.8, 131.7, 130.6, 129.3, 128.6, 128.5, 127.2, 126.5, 124.6, 121.4; GC-MS (EI): 360. This compound was known.[11]

2-phenylquinazoline (**3ak**)



^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 9.481 (s, 1H), 8.633-8.609 (m, 2H), 8.102 (d, 8.0 Hz, 1H), 7.949-7.895 (m, 2H), 7.623 (t, 7.8 Hz, 1H), 7.570-7.494 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 160.0, 159.4, 149.4, 136.9, 133.1, 129.5, 127.6, 127.5, 126.2, 126.1, 122.5; GC-MS (EI): 206. This compound was known.[7]

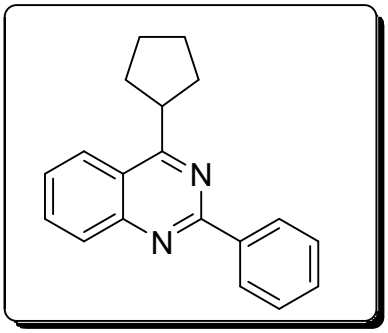
4-butyl-2-phenylquinazoline (**3al**)



^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.663-8.632 (m, 2H), 8.133-8.066 (m, 2H), 7.874-7.819 (m, 1H), 7.595-7.490 (m, 4H), 3.339 (t, 7.8 Hz, 2H), 2.003-1.952 (m, 2H), 1.585-1.511 (m, 2H), 1.030 (t, 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 171.6, 160.2, 150.9, 138.7, 133.4,

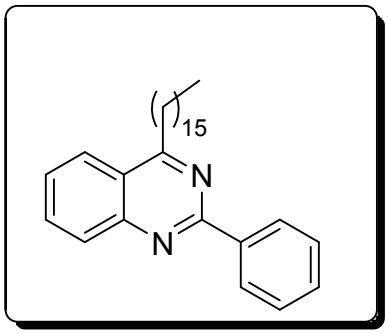
130.5, 129.5, 128.7, 128.7, 126.8, 124.8, 122.7, 34.5, 30.8, 23.0, 14.2; GC-MS (EI): 262. This compound was known.[2]

4-cyclopentyl-2-phenylquinazoline (**3am**)



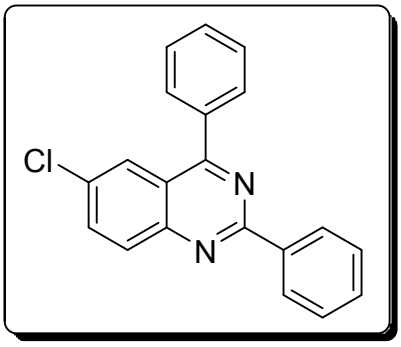
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.690-8.666 (m, 2H), 8.186-8.162 (m, 1H), 8.082 (d, 8.0 Hz, 1H), 7.858-7.816 (m, 1H), 7.583-7.489 (m, 4H), 4.072 (t, 8.0 Hz, 1H), 2.243-2.169 (m, 4H), 1.990-1.979 (m, 2H), 1.842-1.813 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 174.4, 159.9, 150.9, 138.7, 133.1, 130.4, 129.5, 128.7, 128.5, 126.6, 124.7, 122.6, 42.6, 32.7, 26.3; GC-MS (EI): 274. This compound was known.[2]

4-hexadecyl-2-phenylquinazoline (**3an**)



^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.662-8.639 (m, 2H), 8.127-8.071 (m, 2H), 7.865-7.823 (m, 1H), 7.586-7.472 (m, 4H), 3.329 (t, 7.8 Hz, 2H), 2.026-1.950 (m, 2H), 1.606-1.479 (m, 2H), 1.420 (d, 6.4 Hz, 2H), 1.393-1.214 (m, 22H), 0.886 (t, 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 171.6, 160.2, 150.8, 138.6, 133.3, 130.4, 129.5, 128.7, 128.6, 126.7, 124.7, 122.6, 34.7, 32.0, 29.8, 29.8, 29.7, 29.6, 29.5, 28.6, 22.8, 14.2; GC-MS (EI): 430. This compound was known.[2]

6-chloro-2,4-diphenylquinazoline (**3ao**)



^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.698-8.674 (m, 2H), 8.138-8.099 (m, 2H), 7.886-7.811 (m, 3H), 7.635-7.609 (m, 3H), 7.563-7.516 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] = 167.9, 160.4, 150.2, 137.5, 137.1, 134.8, 132.9, 131.1, 130.7, 130.5, 130.2, 128.9, 128.7, 125.9, 122.3; GC-MS (EI): 316. This compound was known.[2]

References:

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[4] D. G. Kawkins, O. Meth-Cohn, *J. Chem. Soc., Perkin Trans., 1* 1983, 2077.

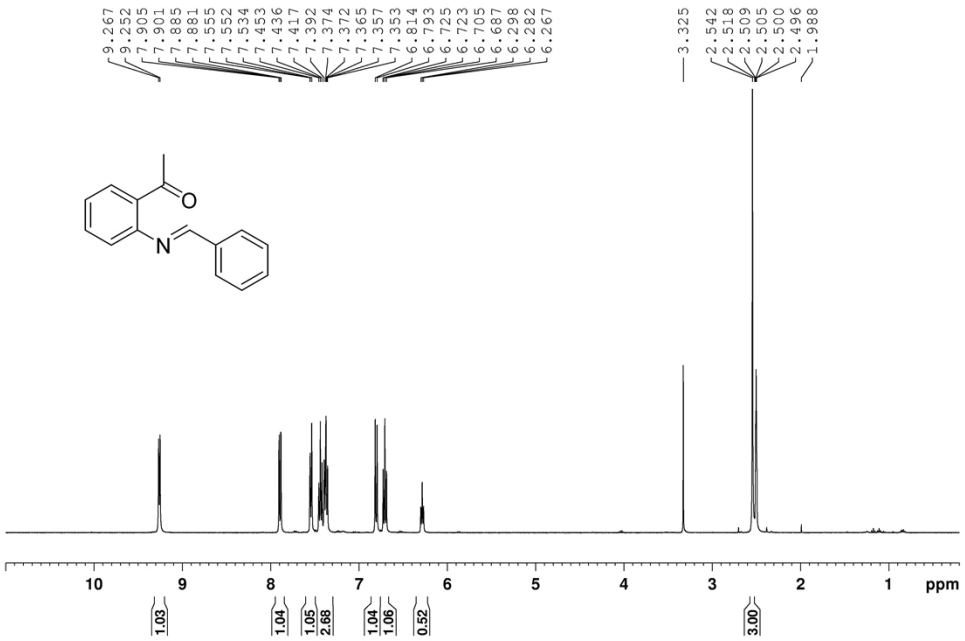
[5] D. Saran and D. H. Burke, *Bioconjugate Chem*. 2007, **18**, 275.

[6] J. Ju, R. Hua, J. Su, *Tetrahedron*, 2012, **68**, 9364.

[7] Z. Cheng, J. Chen, M. Liu, J. Ding, W. Gao, X. Huang, H. Wu, *J. Org. Chem.,* 2013, **78**, 11342.

[8] K. Kanagaraj and K. Pichumani, *J. Org. Chem.,* 2013, **78**, 744.

NMR Spectra of products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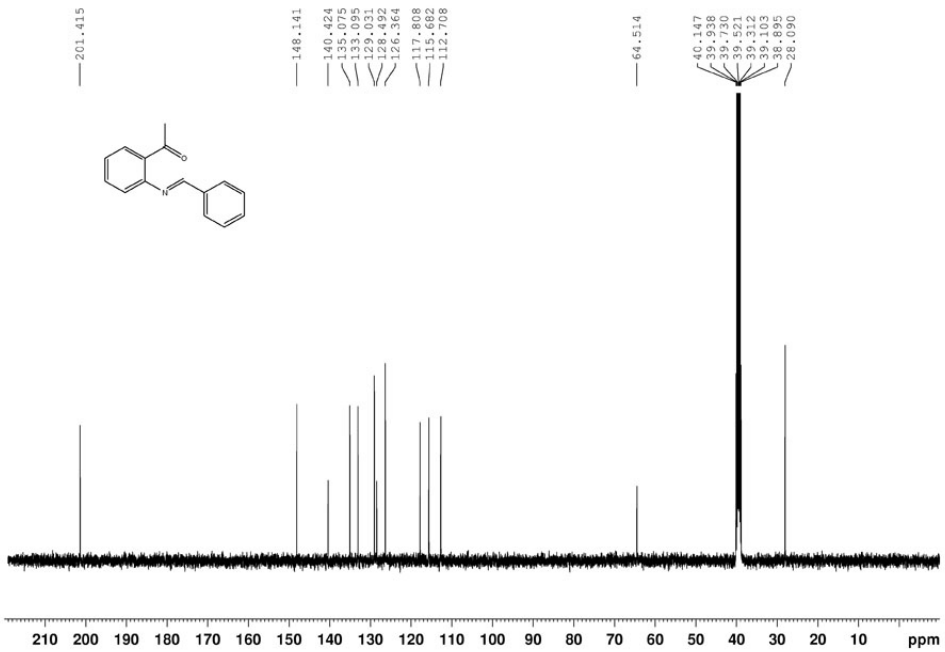
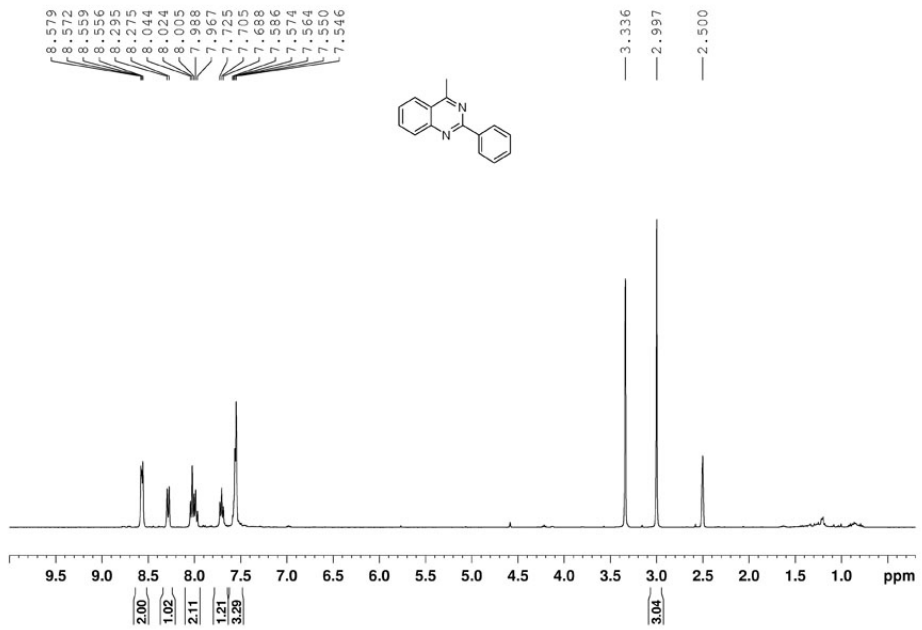
9.252
7.905
7.901
7.885
7.881
7.555
7.552
7.534
7.453
7.436
7.417
7.392
7.374
7.372
7.365
7.357
7.353
6.814
6.793
6.725
6.723
6.705
6.687
6.298
6.282
6.267
3.325
2.542
2.518
2.509
2.505
2.500
2.496
1.988
O
N
10
9
8
7
6
5
4
3
2
1
ppm
1.03
1.04
1.05
2.68
1.04
1.06
0.52
3.00


201.415
148.141
140.424
135.075
133.095
129.031
128.492
126.364
117.808
115.682
112.708
64.514
40.147
39.938
39.730
39.521
39.312
39.103
38.895
28.090
O
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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8.559
8.556
8.295
8.275
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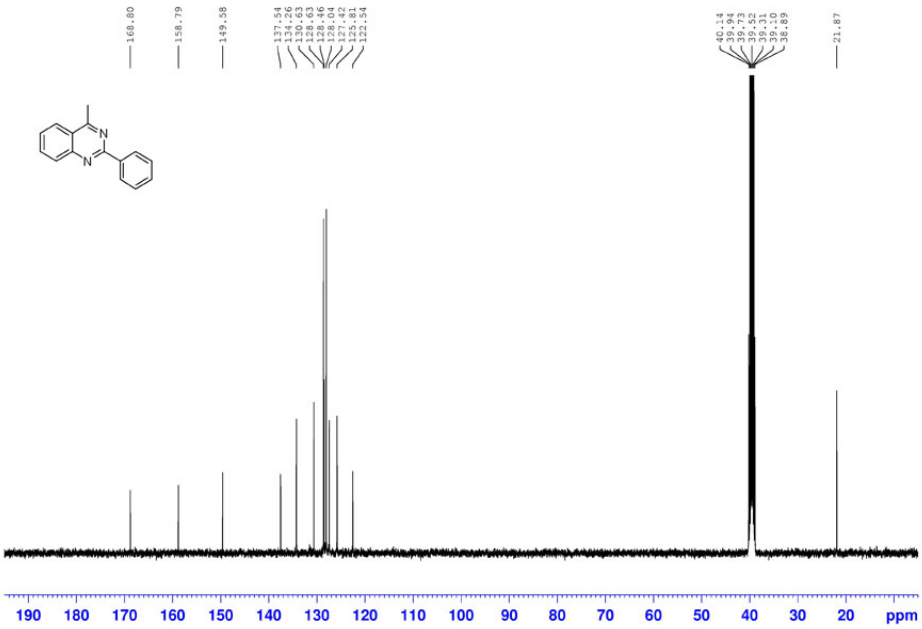
8.024
8.005
7.988
7.967
7.725
7.705
7.688
7.586
7.574
7.564
7.550
7.546
3.336
2.997
2.500
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.00
1.02
2.11
1.21
3.29
3.04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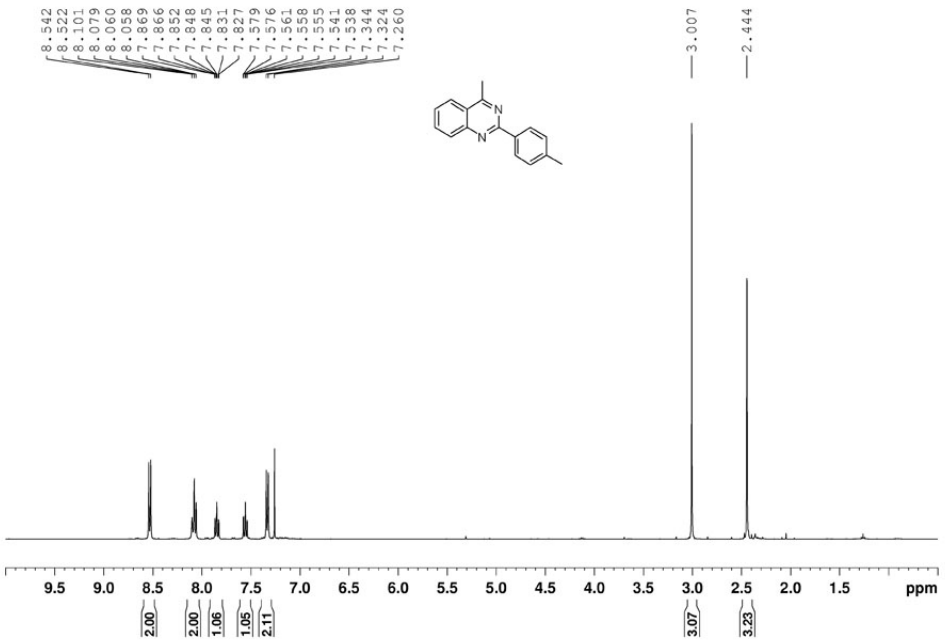
158.79
149.58
137.54
134.26
130.63
128.63
128.46
128.04
127.42
125.81
122.54
40.14
39.94
39.73
39.52
39.31
39.10
38.89
21.87
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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8.101
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8.060
8.058
7.869
7.866
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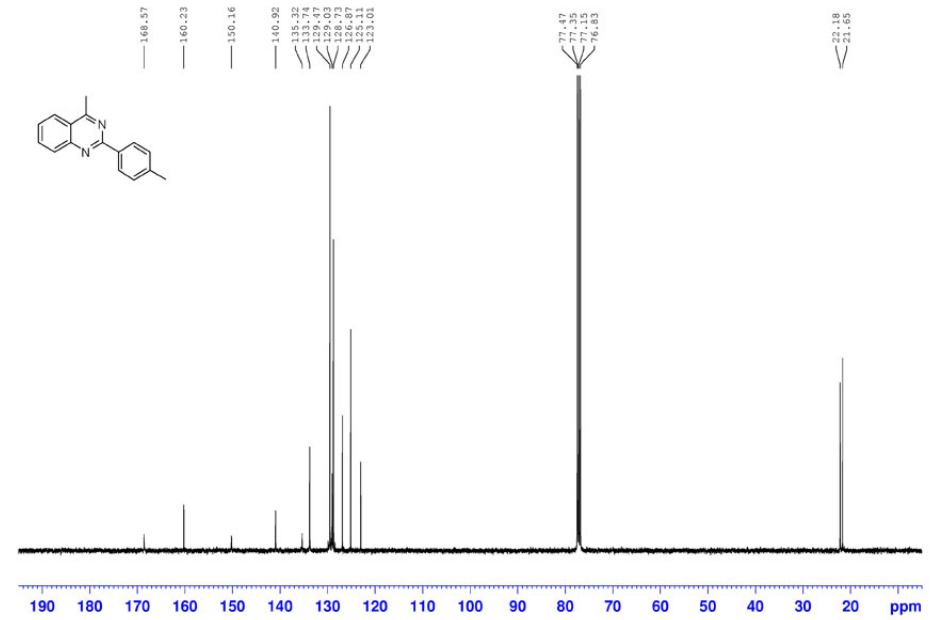
7.848
7.845
7.831
7.827
7.579
7.576
7.561
7.558
7.555
7.541
7.538
7.344
7.324
7.260
3.007
2.444
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
2.00
2.00
1.06
1.05
2.11
3.07
3.23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135.32
133.74
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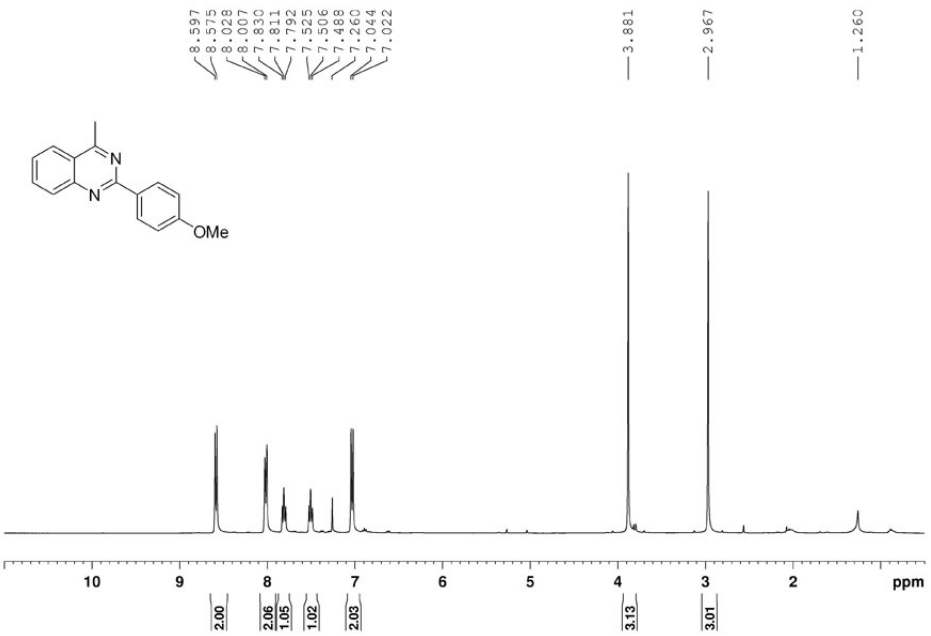
129.03
128.73
126.87
125.11
123.01
77.47
77.35
77.15
76.83
22.18
21.65
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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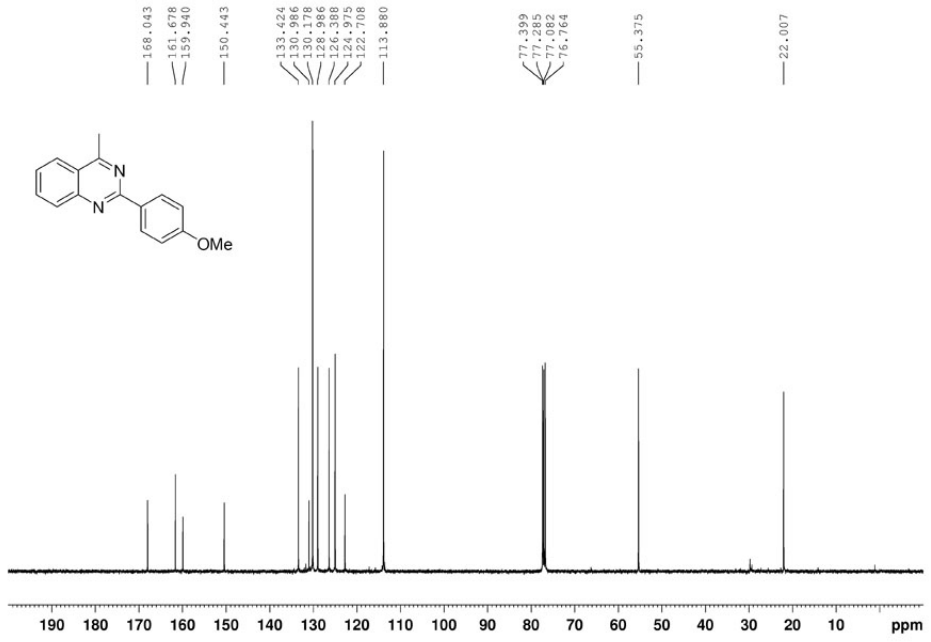
7.525
7.506
7.488
7.260
7.044
7.022
3.881
2.967
1.260
OMe
10
9
8
7
6
5
4
3
2
ppm
2.00
2.06
1.05
1.02
2.03
3.13
3.01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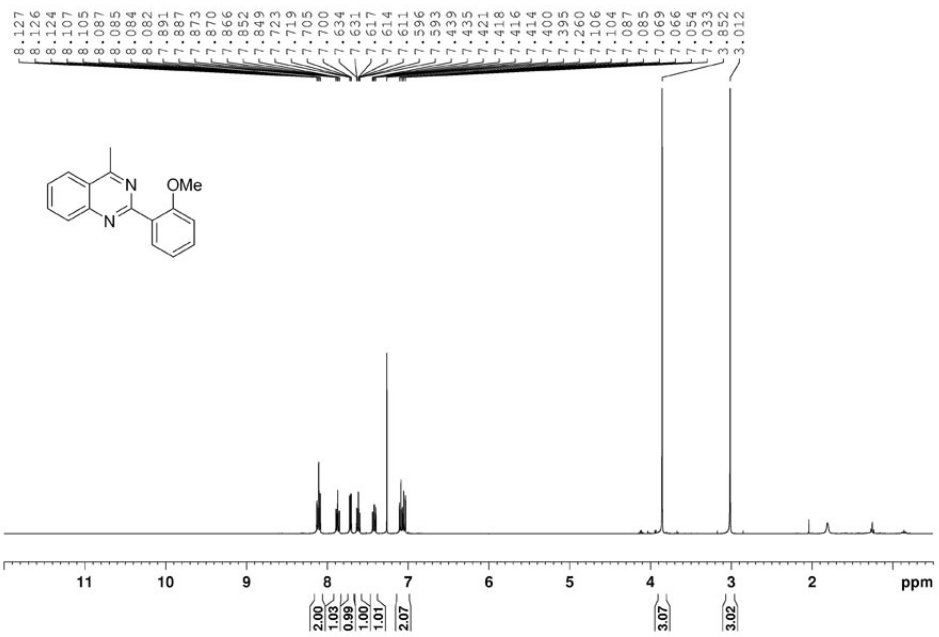
150.443
133.424
130.986
130.178
128.386
126.388
124.975
122.708
113.880
77.399
77.285
77.082
76.764
55.375
22.007
OMe
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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8.126
8.124
8.107
8.105
8.087
8.085
8.084
8.082
7.891
7.887
7.873
7.870
7.866
7.852
7.849
7.723
7.719
7.705
7.700
7.634
7.631
7.617
7.614
7.611
7.596
7.593
7.439
7.435
7.421
7.418
7.416
7.414
7.400
7.395
7.260
7.106
7.104
7.087
7.085
7.069
7.066
7.054
7.033
3.852
3.012
N
N
OMe
11
10
9
8
7
6
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2
ppm
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1.00
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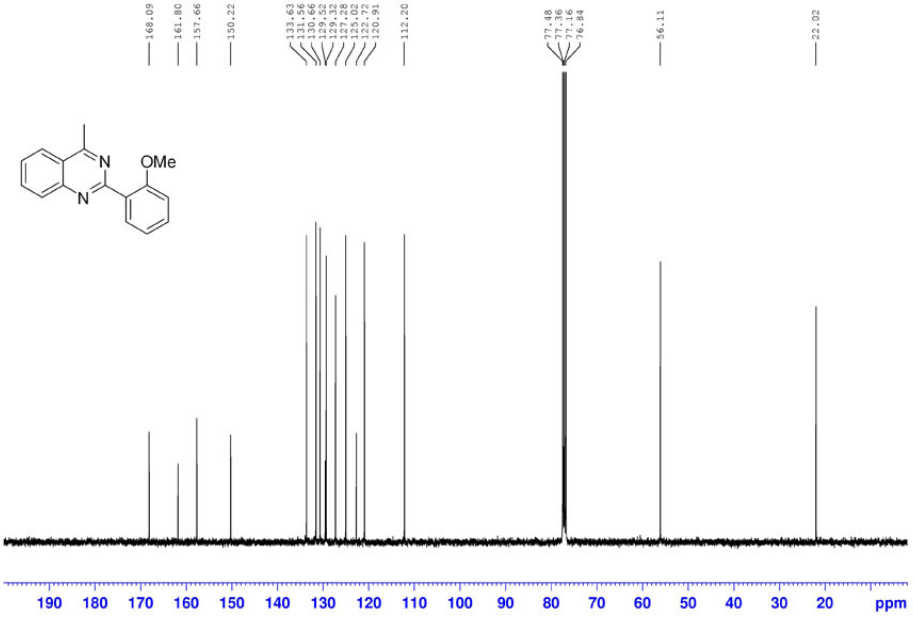
3.02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120.91
112.20
77.48
77.36
77.16
76.84
56.11
22.02
N
N
OMe
190
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160
150
140
130
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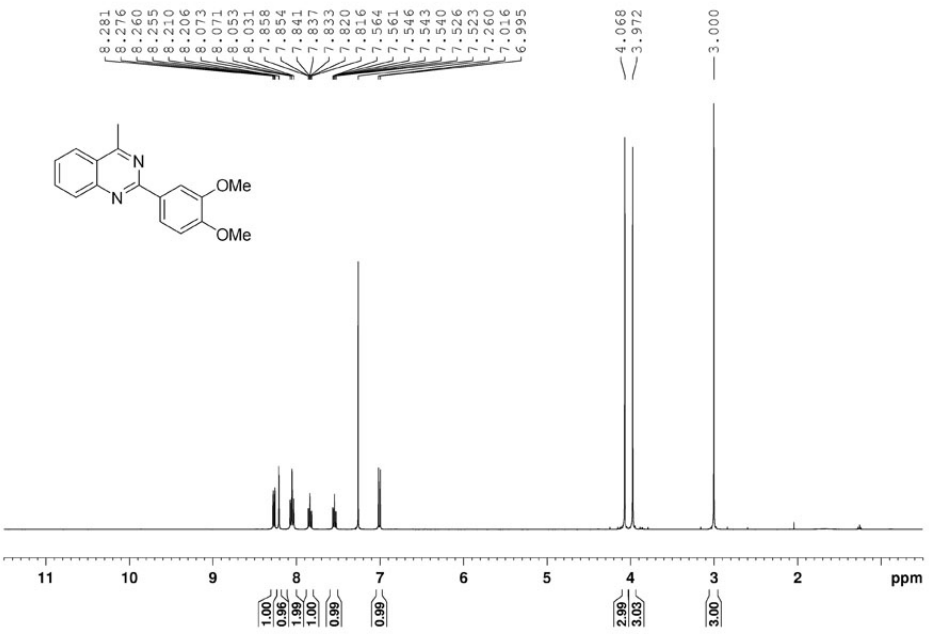
80
70
60
50
40
30
20
ppm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8.031
7.858
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7.841
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7.833
7.820
7.816
7.564
7.561
7.546
7.543
7.540
7.526
7.523
7.260
7.016
6.995
4.068
3.972
3.000
OMe
OMe
11
10
9
8
7
6
5
4
3
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ppm
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0.99
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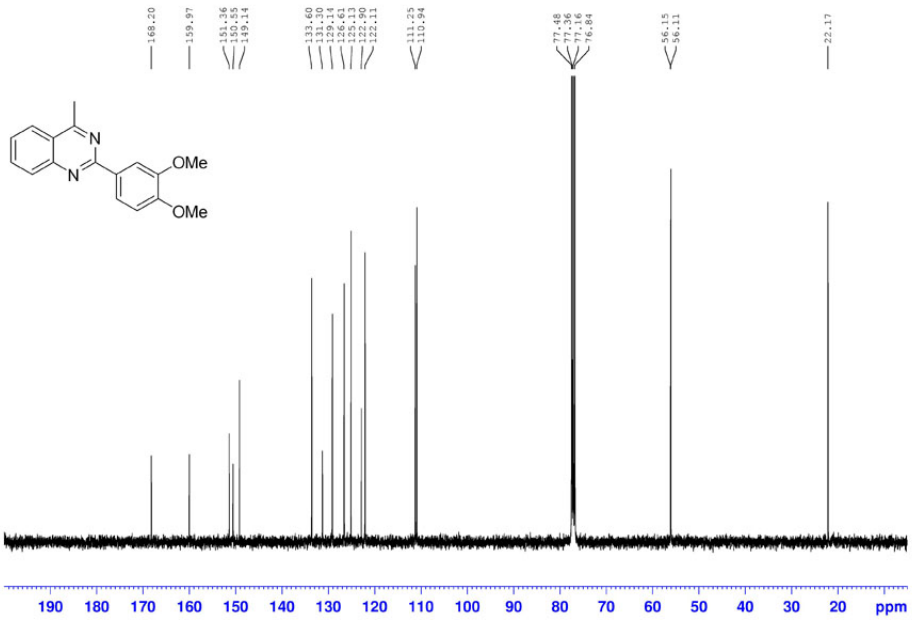
3.03
3.00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129.14
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126.13
122.90
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111.25
110.94
77.48
77.36
77.16
76.84
56.15
56.11
22.17
OMe
OMe
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170
160
150
140
130
120
110
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80
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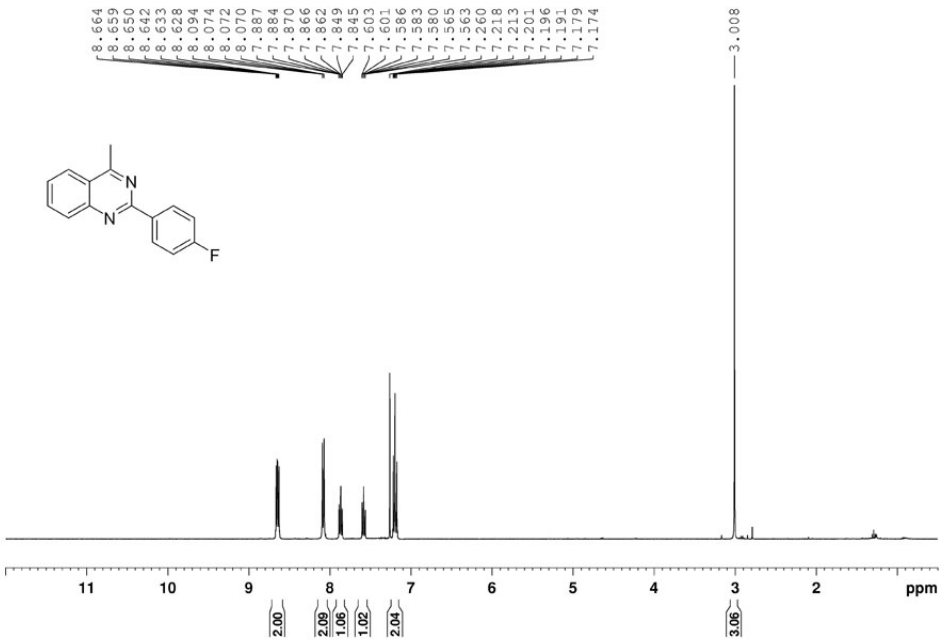
60
50
40
30
20
ppm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8.074
8.072
8.070
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7.870
7.866
7.862
7.849
7.845
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7.601
7.586
7.583
7.580
7.565
7.563
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7.213
7.201
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7.191
7.179
7.174
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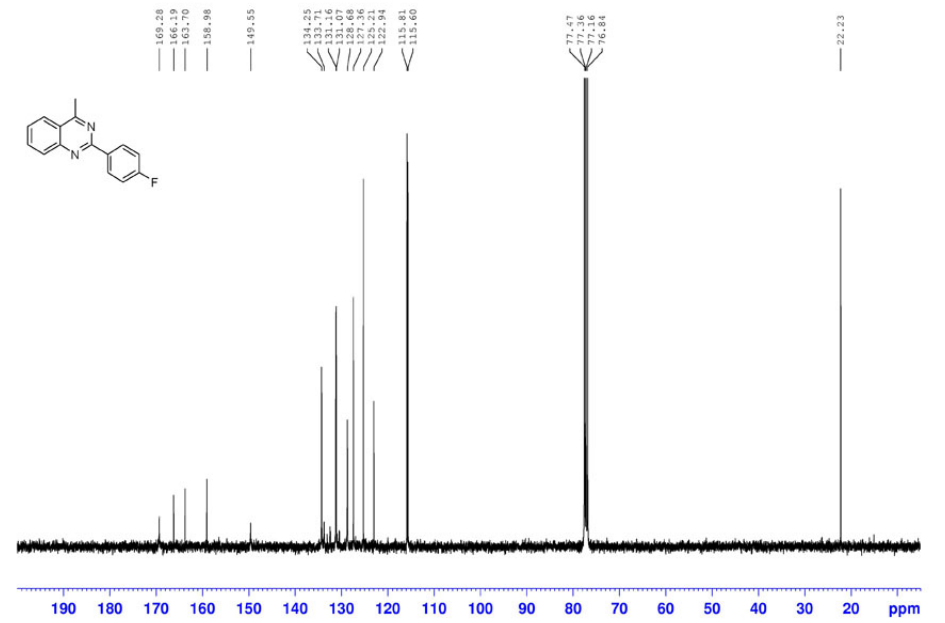
3.06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115.81
115.60
77.47
77.26
77.16
76.84
22.23
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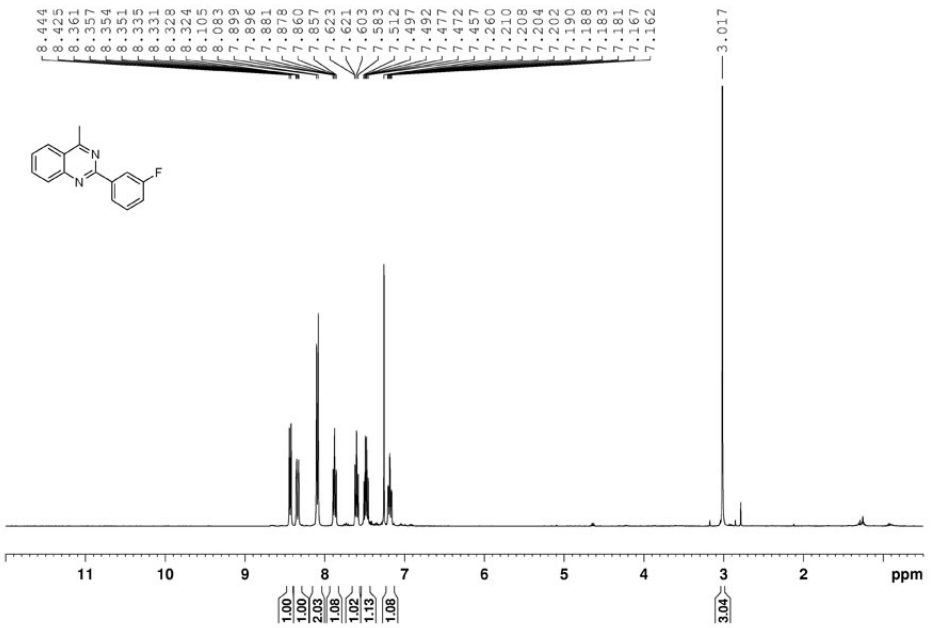
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7.860
7.857
7.623
7.621
7.603
7.583
7.512
7.497
7.492
7.477
7.472
7.457
7.260
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7.208
7.204
7.202
7.190
7.188
7.183
7.181
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7.162
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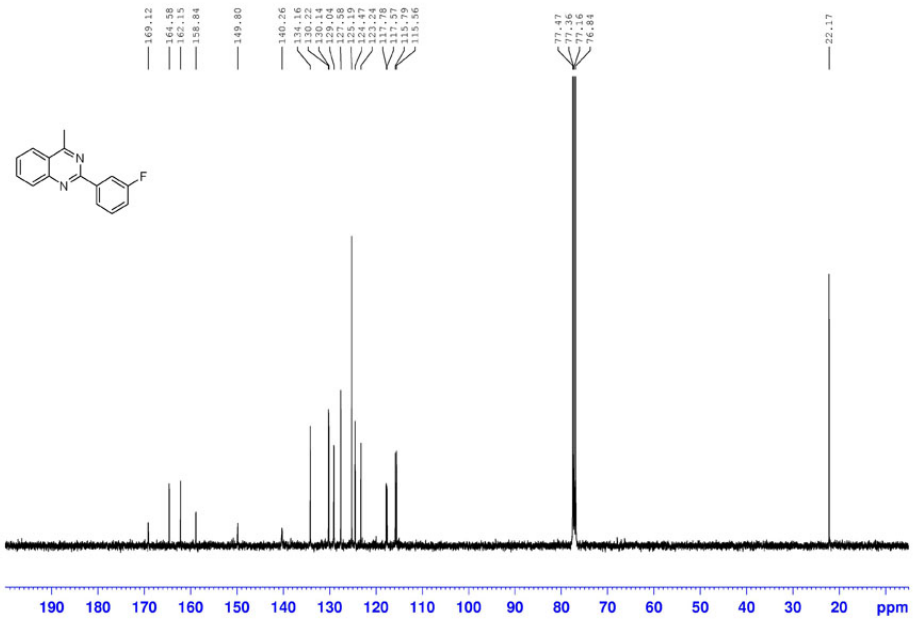
1.08
3.04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124.47
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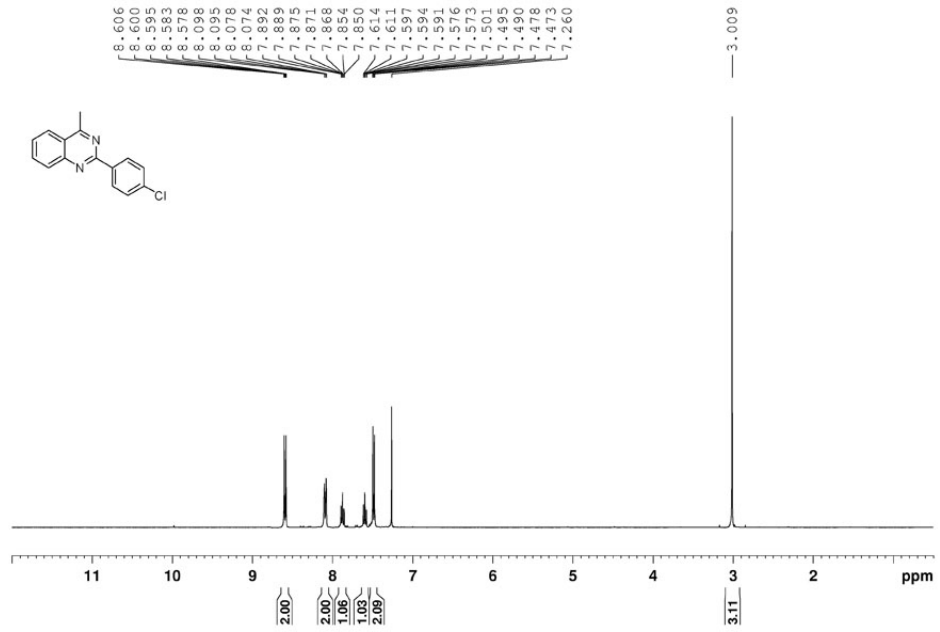
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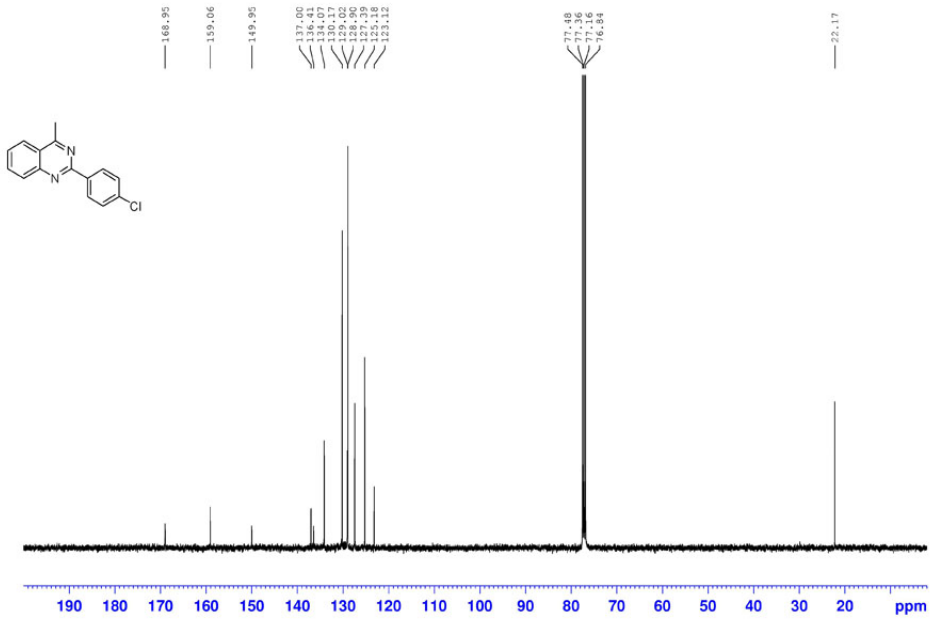
1.03
2.09
3.11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123.12
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22.17
Cl
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160
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120
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100
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80
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50
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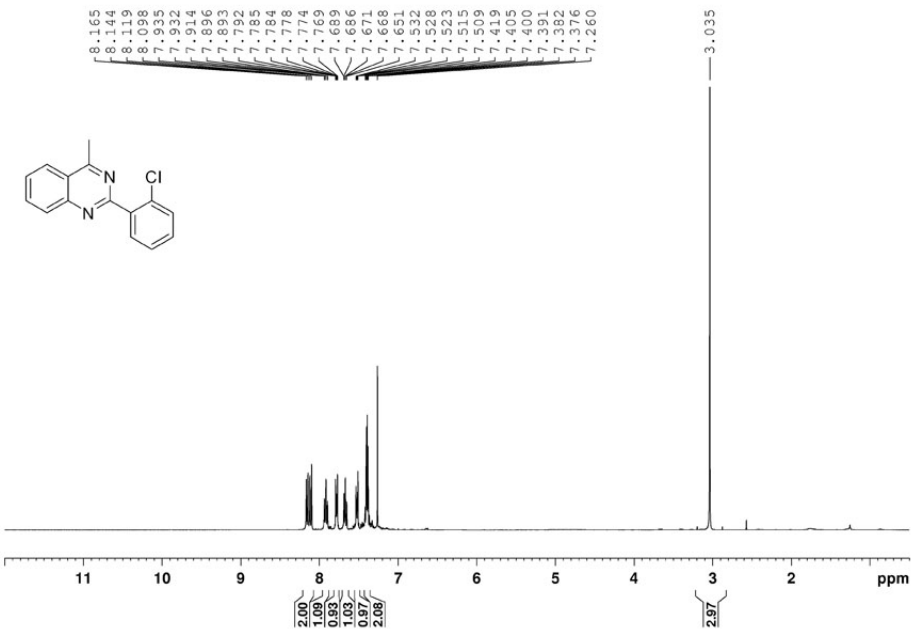
30
20
ppm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7.784
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7.774
7.769
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7.686
7.671
7.668
7.651
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7.528
7.523
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7.509
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N
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10
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6
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ppm
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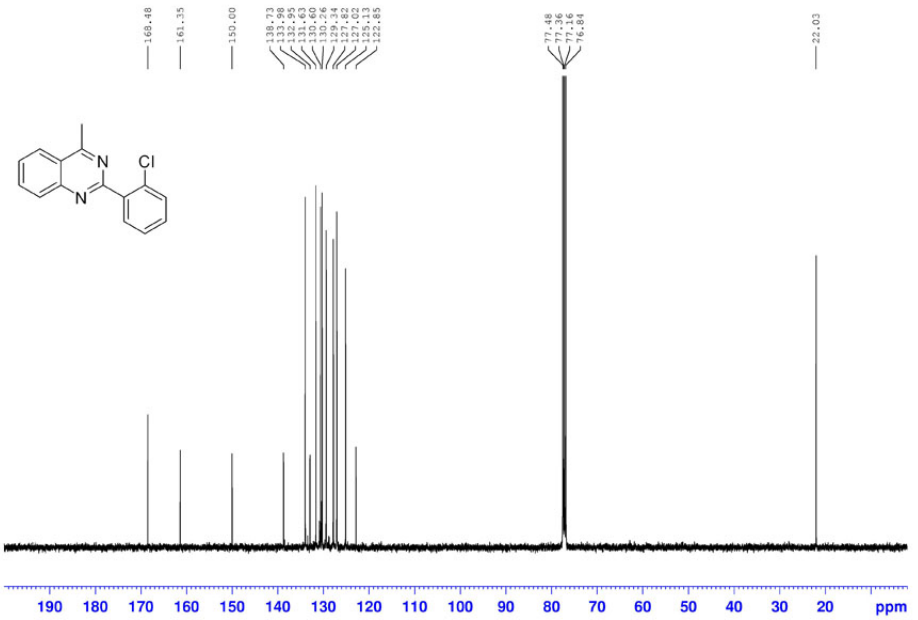
2.97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127.20
126.13
122.85
77.48
77.36
77.16
76.84
22.03
N
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Cl
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160
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120
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80
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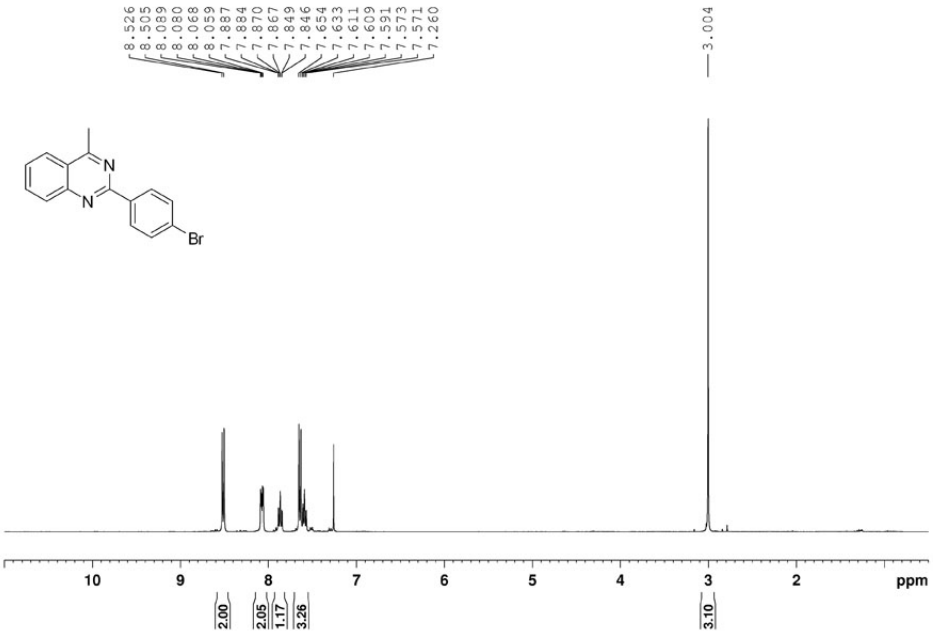
30
20
ppm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7.849
7.846
7.654
7.633
7.611
7.609
7.591
7.573
7.571
7.260
3.004
N
N
Br
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8
7
6
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4
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ppm
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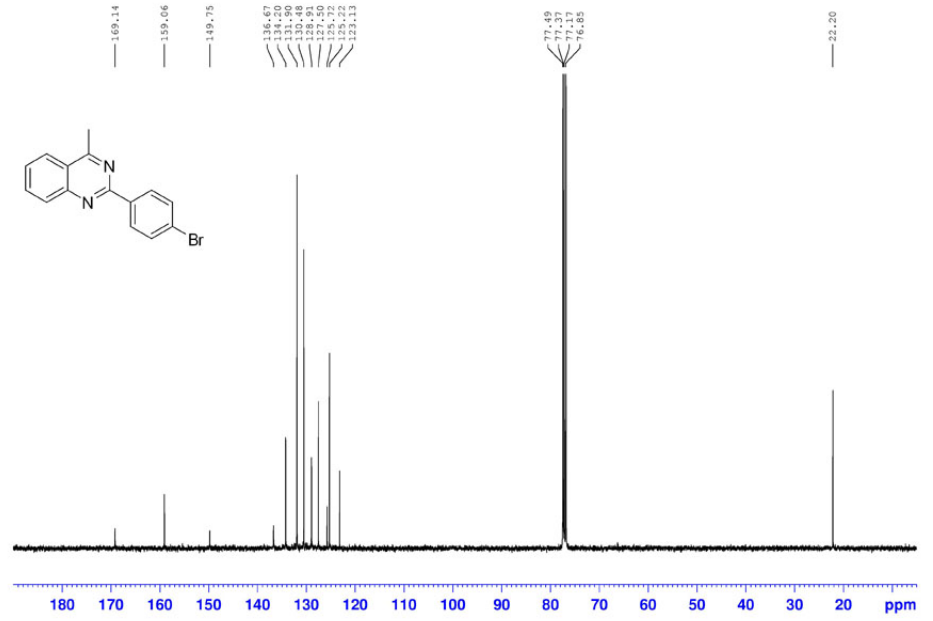
3.26
3.10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129.91
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125.22
123.13
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77.17
76.85
22.20
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80
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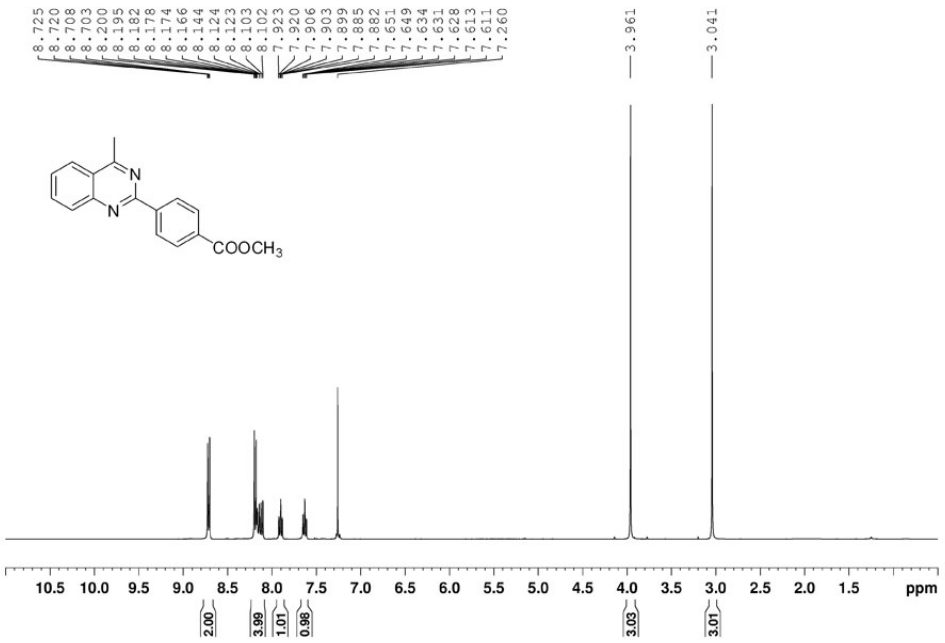
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8.178
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8.166
8.144
8.124
8.123
8.103
8.102
7.923
7.920
7.906
7.903
7.899
7.885
7.882
7.651
7.649
7.634
7.631
7.628
7.613
7.611
7.260
3.961
3.041
N
N
COOCH3
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
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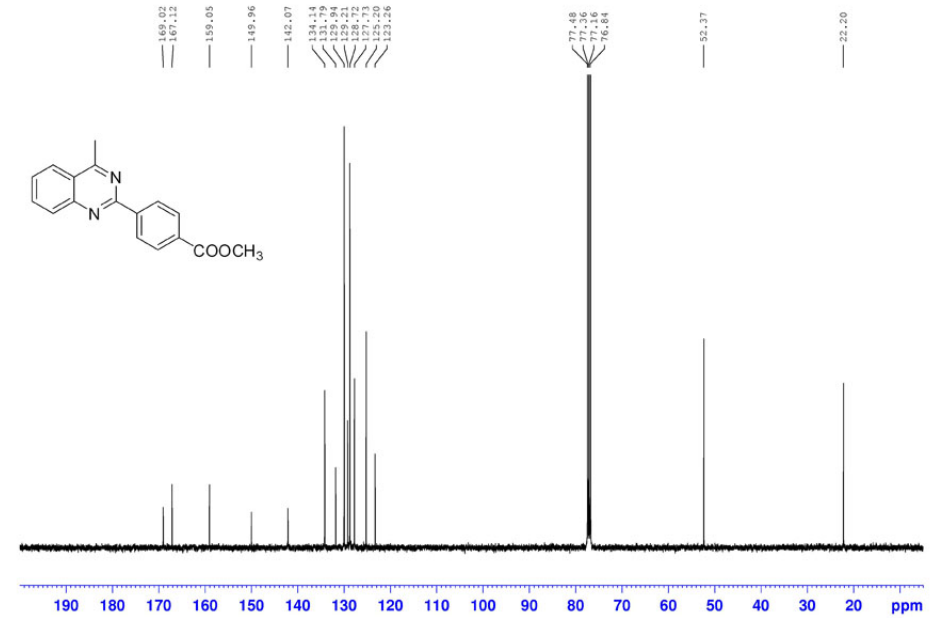
3.99
1.01
0.98
3.03
3.01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129.94
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128.72
127.73
125.20
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52.37
22.20
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COOCH3
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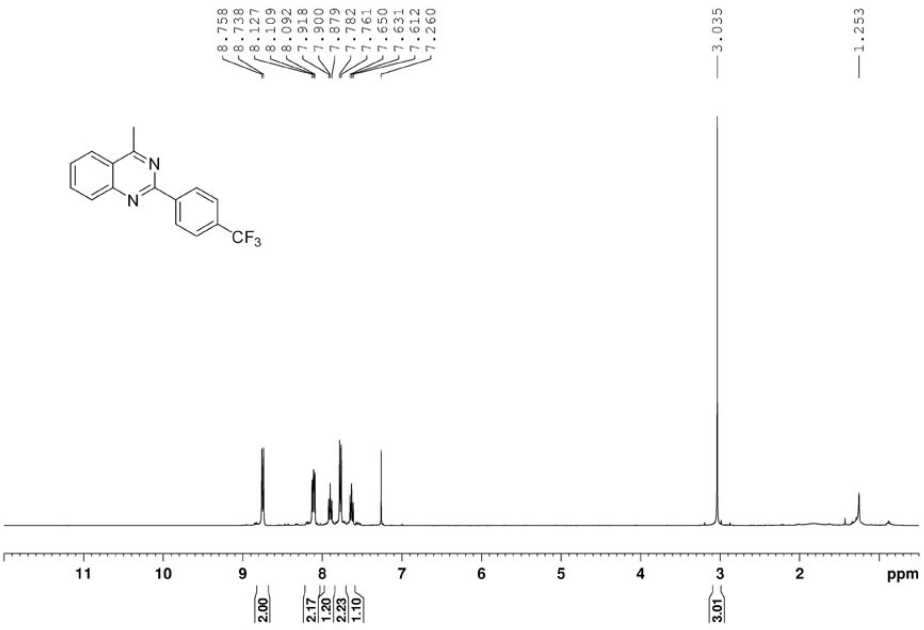
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7.761
7.650
7.631
7.612
7.260
3.035
1.253
N
N
CF3
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9
8
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6
5
4
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ppm
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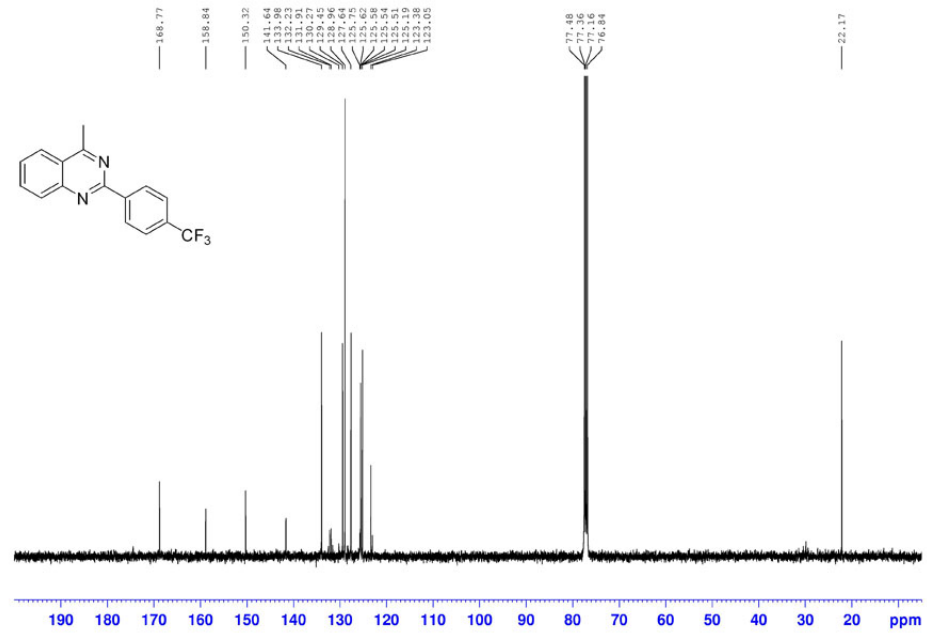
2.17
1.20
2.23
1.10
3.01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125.66
125.58
125.54
125.51
125.19
123.38
123.05
77.48
77.36
77.16
76.84
22.17
N
N
CF3
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160
150
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100
90
80
70
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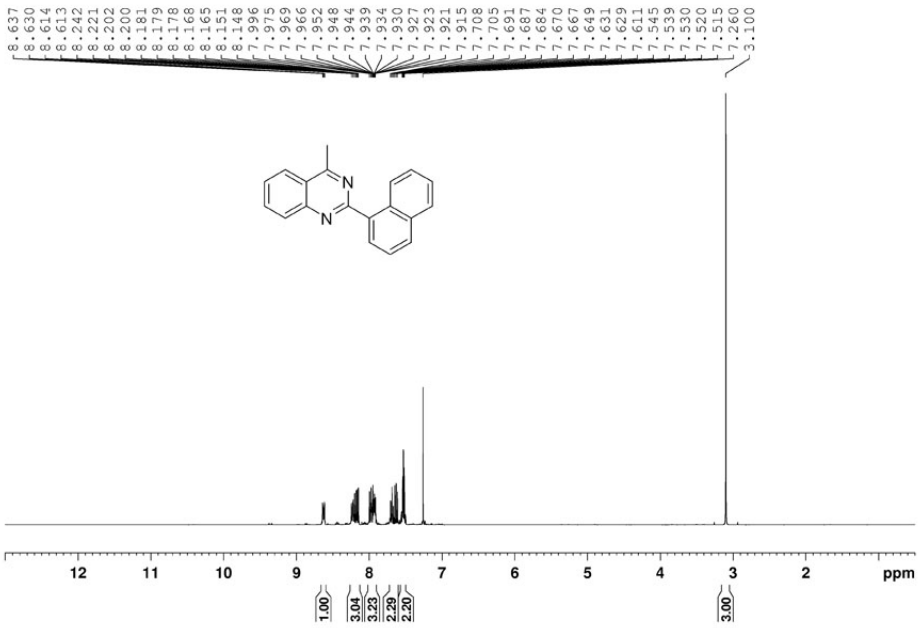
30
20
ppm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8.613
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8.202
8.200
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8.179
8.178
8.168
8.165
8.151
8.148
7.996
7.975
7.969
7.966
7.952
7.948
7.944
7.939
7.934
7.930
7.927
7.923
7.921
7.915
7.708
7.705
7.691
7.687
7.684
7.670
7.667
7.649
7.631
7.629
7.611
7.545
7.539
7.530
7.520
7.515
7.260
3.100
12
11
10
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8
7
6
5
4
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ppm
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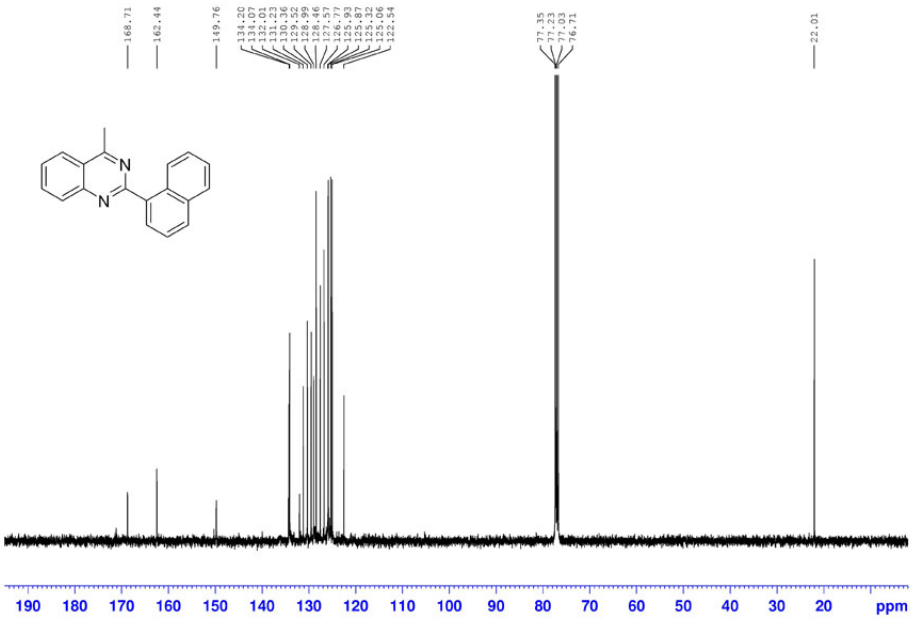
3.04
3.25
2.29
2.20
3.00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130.56
129.22
128.99
128.46
127.77
127.57
125.93
125.87
125.32
125.06
122.54
77.35
77.23
77.03
76.71
22.01
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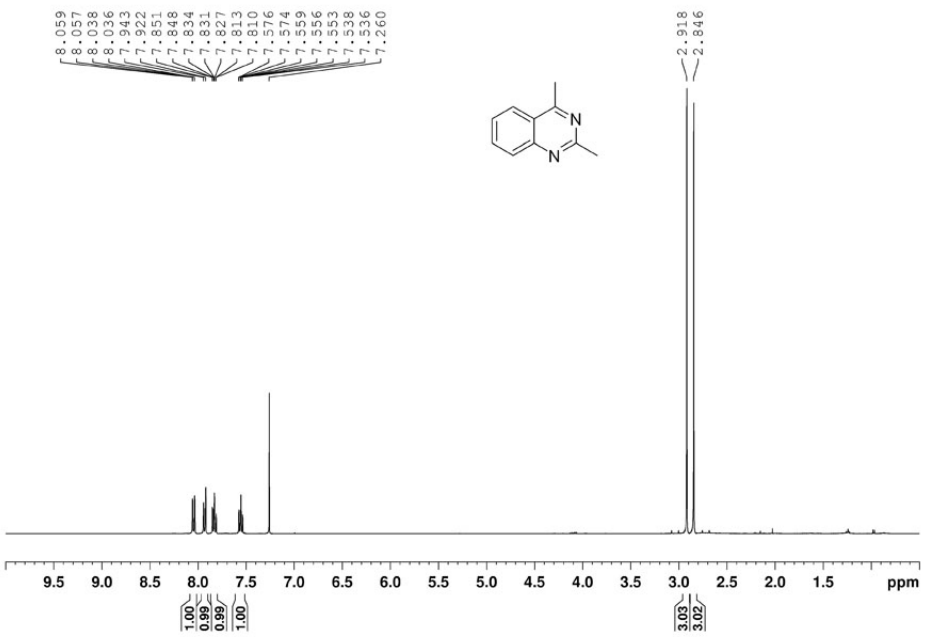
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.848
7.834
7.831
7.827
7.813
7.810
7.576
7.574
7.559
7.556
7.553
7.538
7.536
7.260
2.918
2.846
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
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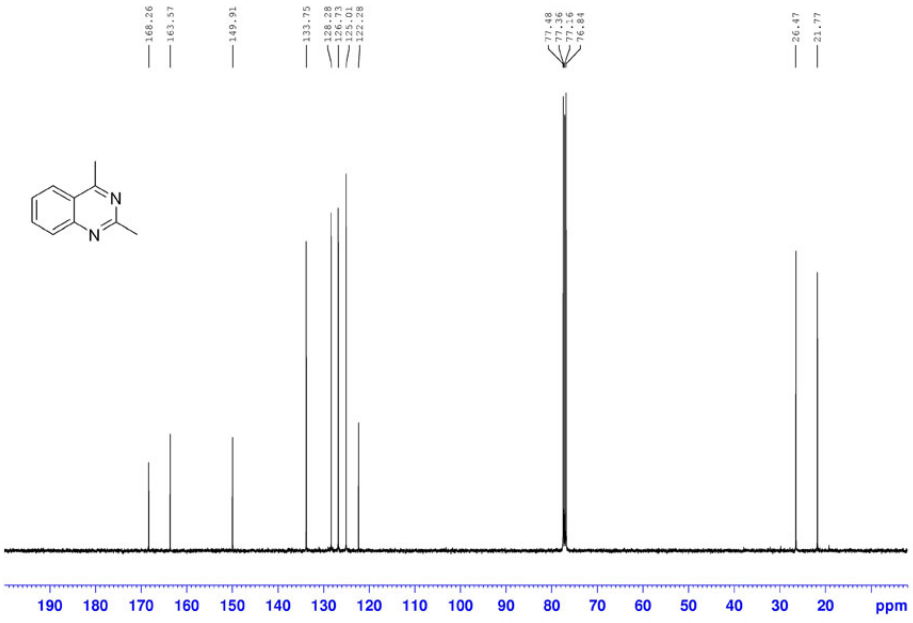
0.99
0.99
1.00
3.03
3.02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126.73
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122.28
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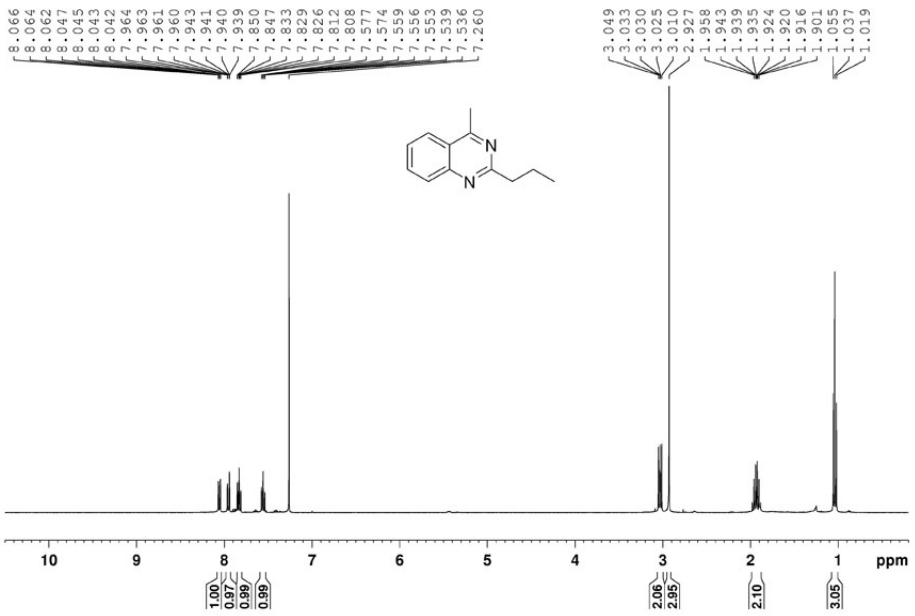
77.16
77.16
76.84
26.47
21.77
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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8.062
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8.045
8.043
8.042
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7.961
7.960
7.943
7.941
7.940
7.939
7.850
7.847
7.833
7.829
7.826
7.812
7.808
7.577
7.574
7.559
7.556
7.553
7.539
7.536
7.260
3.049
3.033
3.030
3.025
3.010
2.927
1.958
1.943
1.939
1.935
1.924
1.920
1.916
1.901
1.055
1.037
1.019
N
N
10
9
8
7
6
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2
1
ppm
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0.99
0.99
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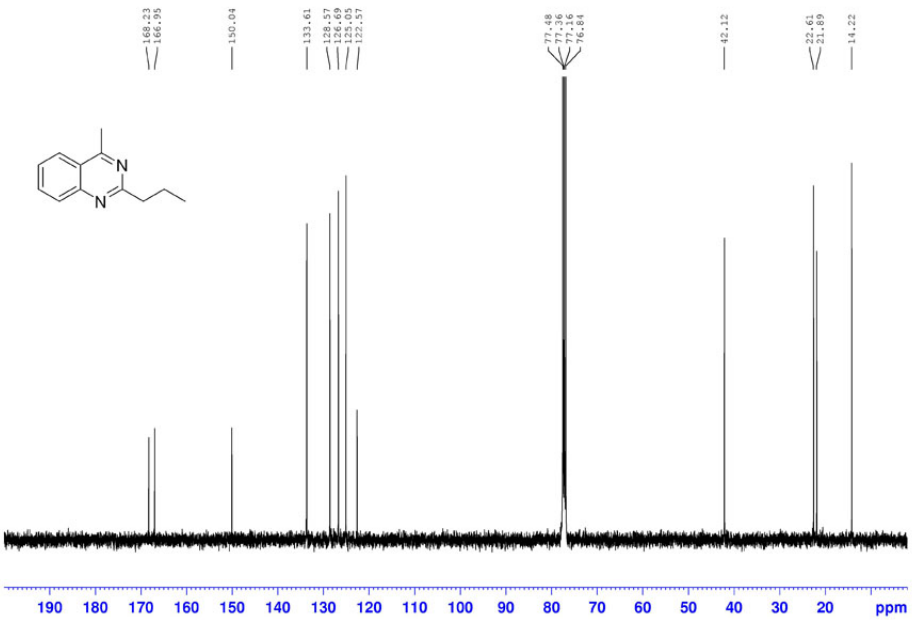
2.95
2.10
3.05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128.57
126.69
125.05
122.57
77.48
77.36
77.16
76.84
42.12
22.61
21.89
14.22
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N
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180
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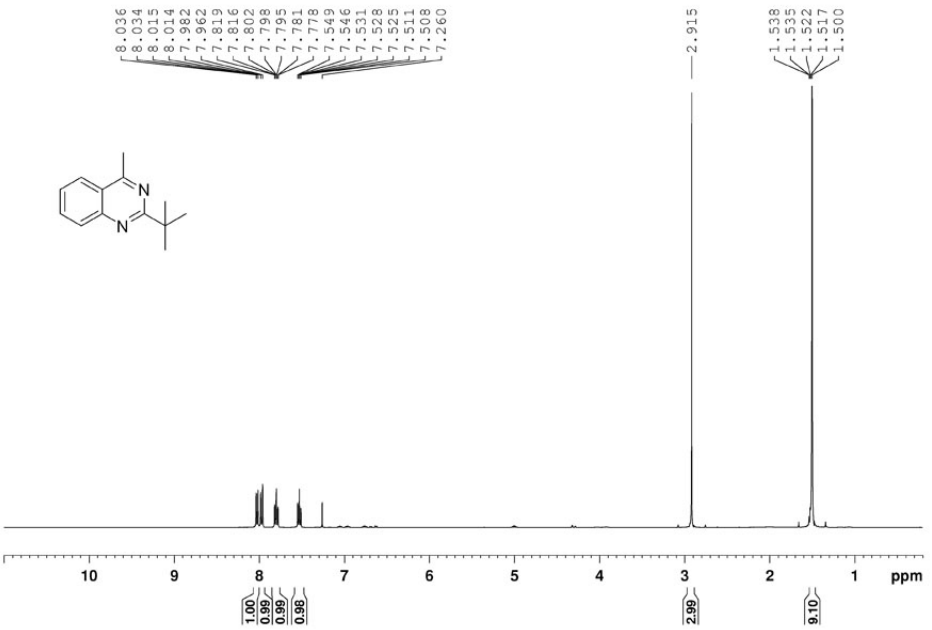
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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8.015
8.014
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7.816
7.802
7.798
7.795
7.781
7.778
7.549
7.546
7.531
7.528
7.525
7.511
7.508
7.260
2.915
1.538
1.535
1.522
1.517
1.500
10
9
8
7
6
5
4
3
2
1
ppm
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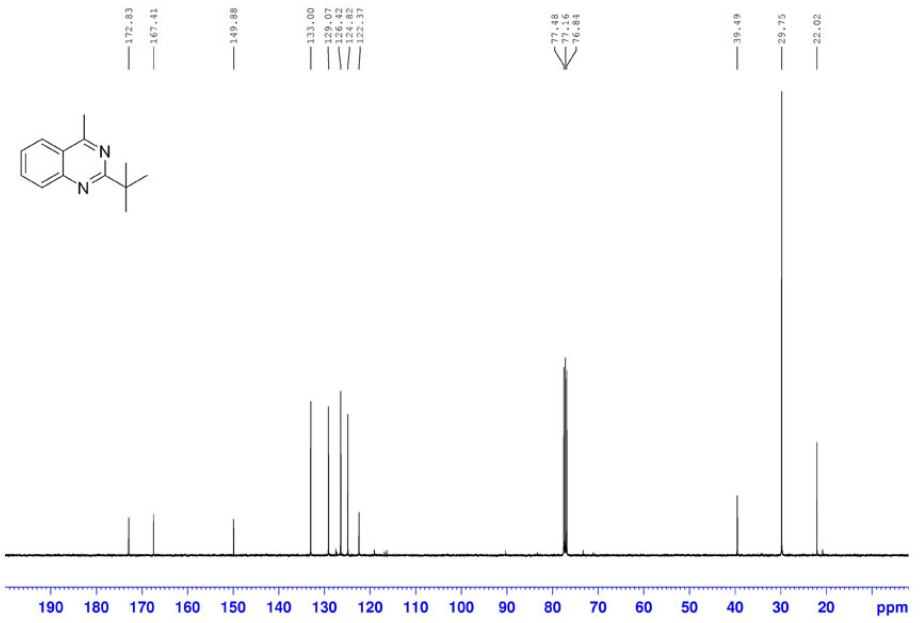
0.99
0.98
2.99
9.10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126.42
124.82
122.37
77.48
77.16
76.84
39.49
29.75
22.02
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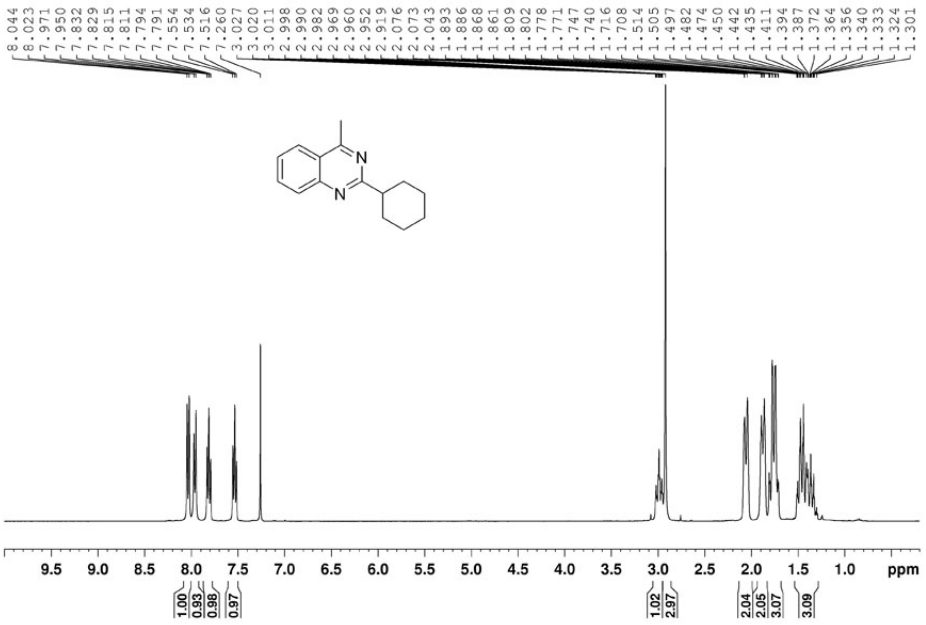
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.811
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7.791
7.554
7.534
7.516
7.260
3.027
3.020
3.011
2.998
2.990
2.982
2.969
2.960
2.952
2.919
2.076
2.073
2.043
1.893
1.886
1.868
1.861
1.809
1.802
1.778
1.771
1.747
1.740
1.716
1.708
1.514
1.505
1.497
1.482
1.474
1.450
1.442
1.435
1.411
1.394
1.387
1.372
1.364
1.356
1.340
1.333
1.324
1.301
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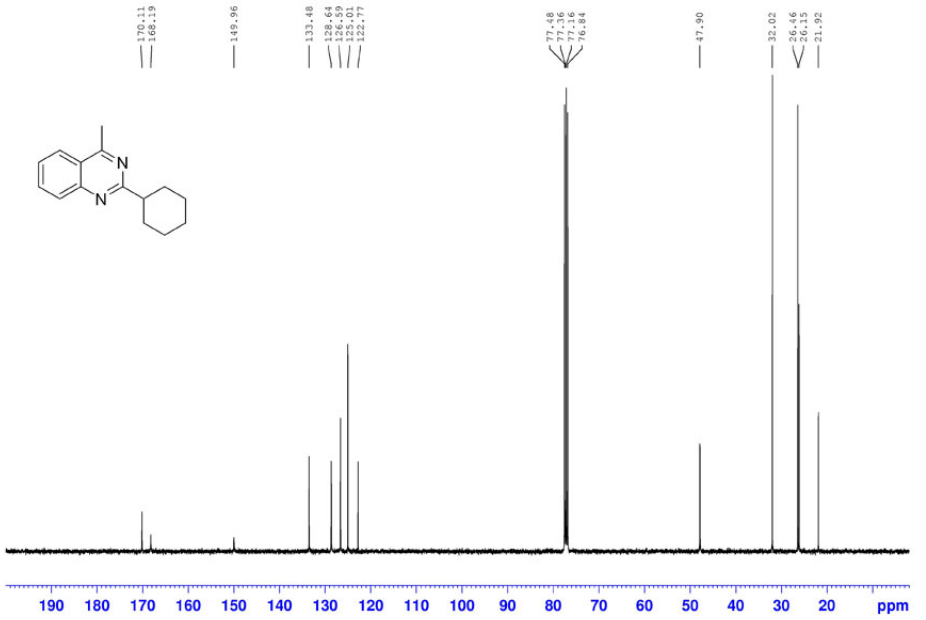
0.97
1.02
2.97
2.04
2.05
3.07
3.09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125.01
122.77
77.48
77.36
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32.02
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26.15
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N
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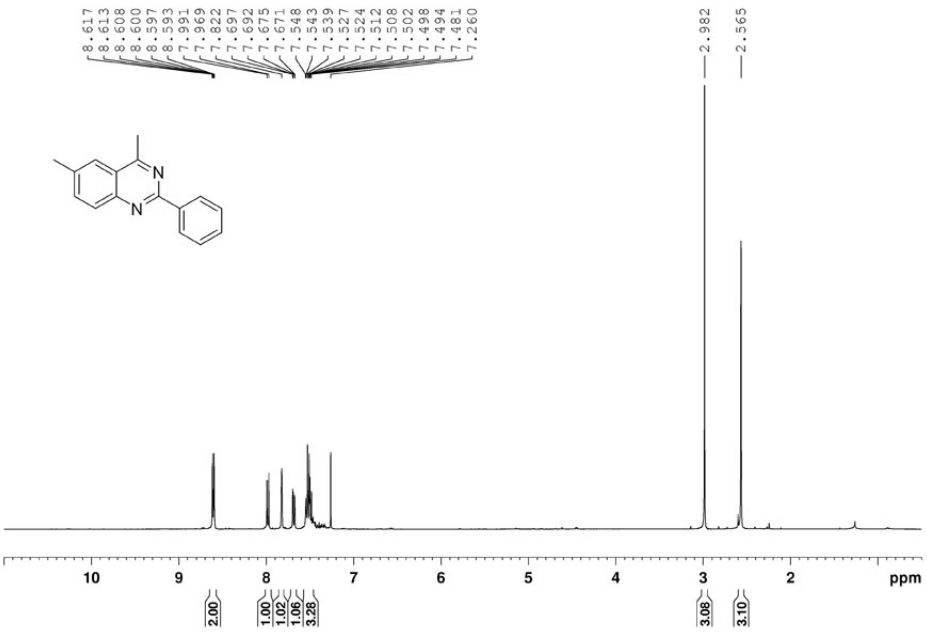
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8.597
8.593
7.991
7.969
7.822
7.697
7.692
7.675
7.671
7.548
7.543
7.539
7.527
7.524
7.512
7.508
7.502
7.498
7.494
7.481
7.260
2.982
2.565
10
9
8
7
6
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4
3
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ppm
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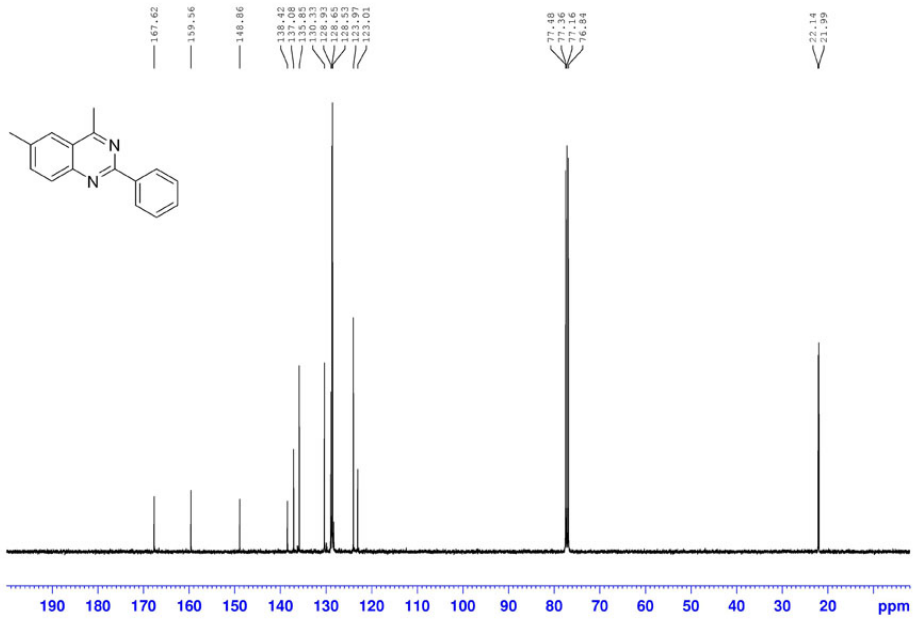
1.00
1.02
1.06
3.28
3.08
3.10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130.33
128.93
128.65
128.53
127.97
123.01
77.48
77.36
77.16
76.84
22.14
21.99
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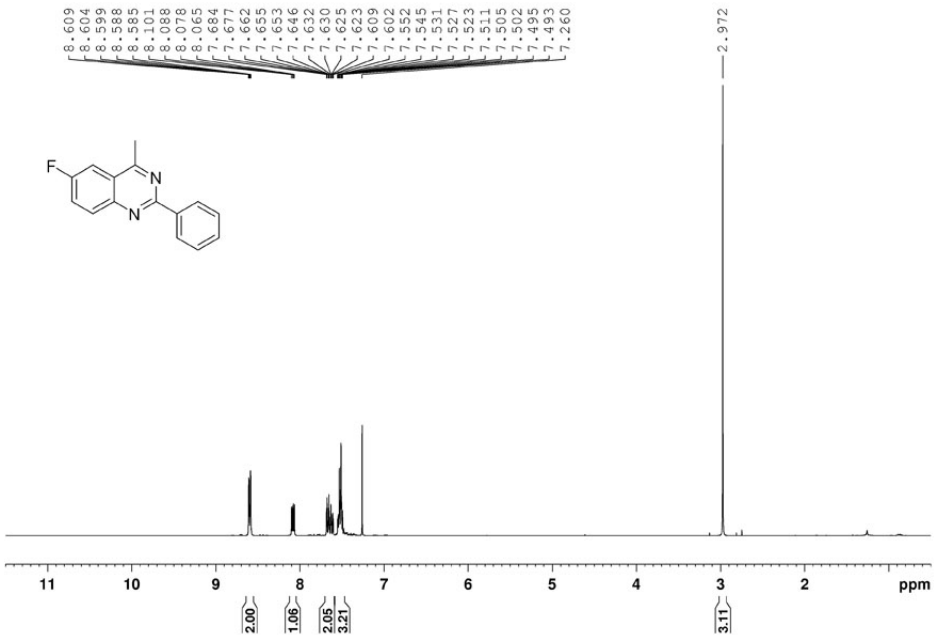
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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8.101
8.088
8.078
8.065
7.684
7.677
7.662
7.655
7.653
7.646
7.632
7.630
7.625
7.623
7.609
7.602
7.552
7.545
7.531
7.527
7.523
7.511
7.505
7.502
7.495
7.493
7.260
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F
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2.05
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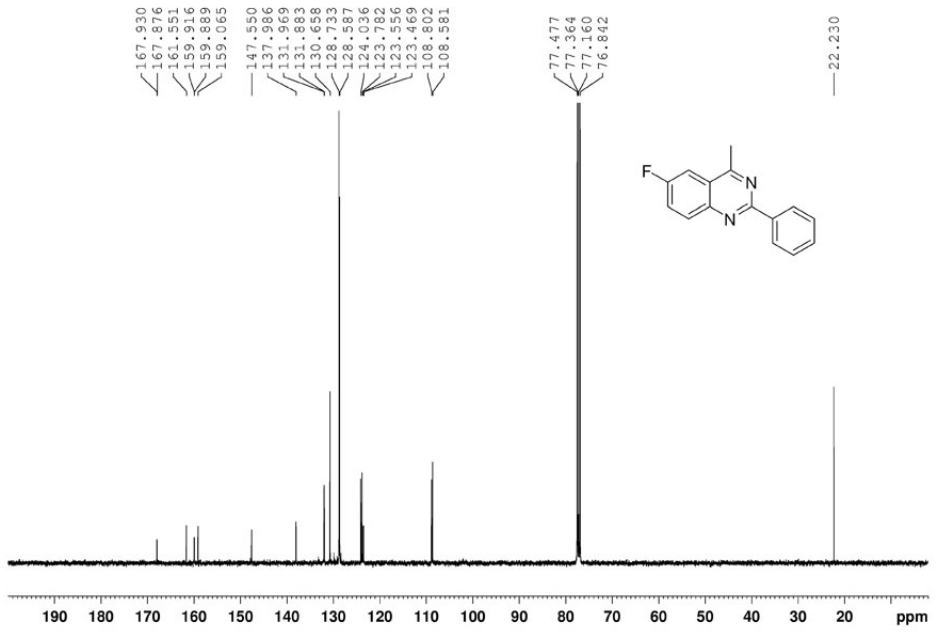
3.11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130.658
128.733
128.587
124.036
123.782
123.556
123.469
108.802
108.581
77.477
77.364
77.160
76.842
22.230
F
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N
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160
150
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120
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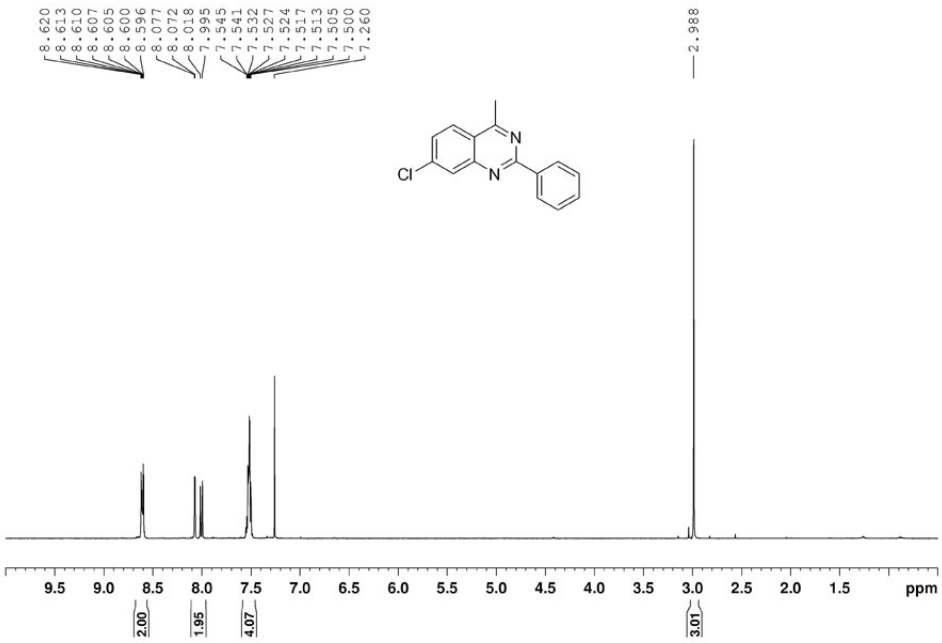
90
80
70
60
50
40
30
20
ppm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8.607
8.605
8.600
8.596
8.077
8.072
8.018
7.995
7.545
7.541
7.532
7.527
7.524
7.517
7.513
7.505
7.500
7.260
2.988
Cl
N
N
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm
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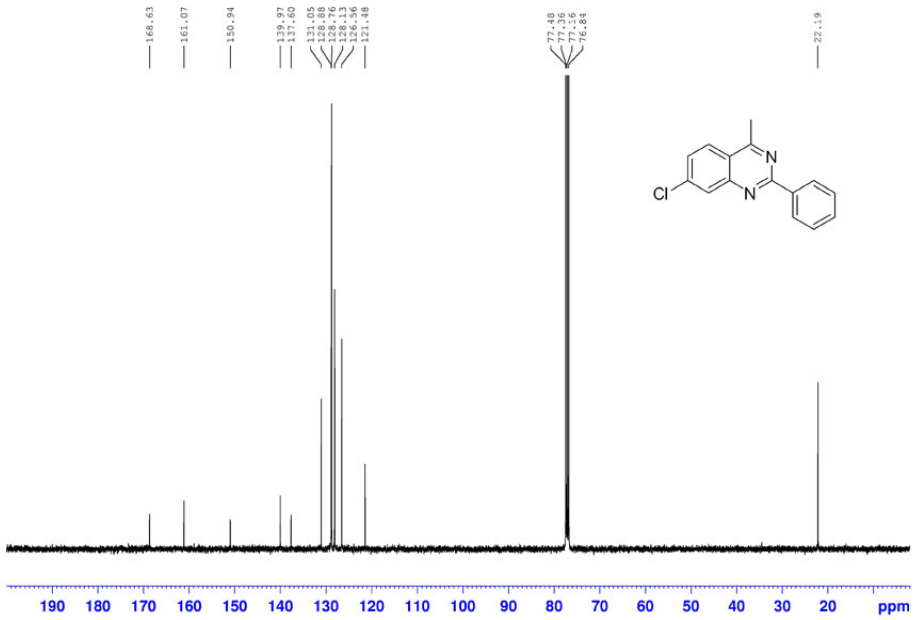
1.95
4.07
3.01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131.05
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128.76
128.13
126.46
121.48
77.48
77.36
77.16
76.84
22.19
Cl
N
N
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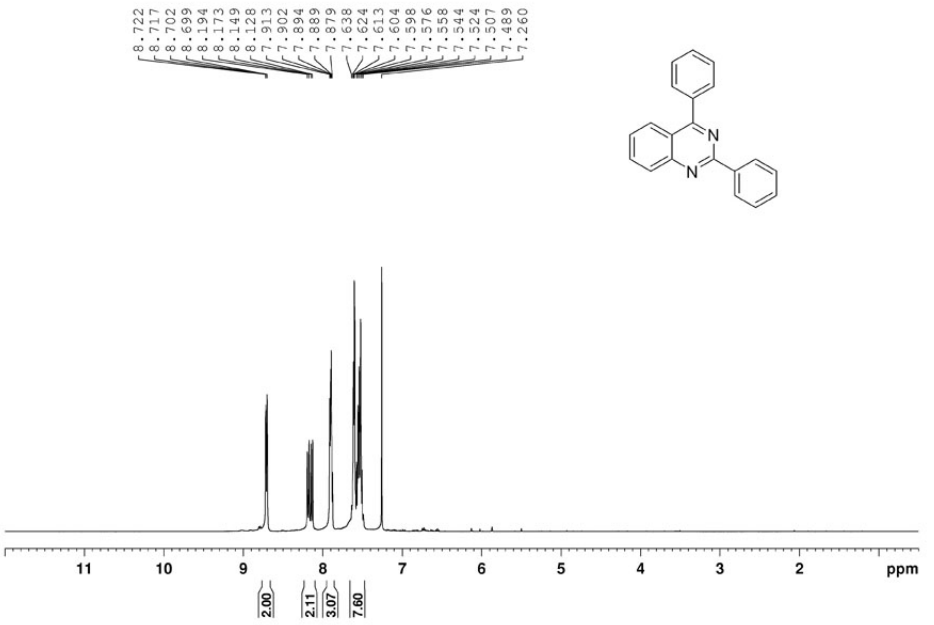
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8.128
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7.889
7.879
7.638
7.624
7.613
7.604
7.598
7.576
7.558
7.544
7.524
7.507
7.489
7.260
N
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11
10
9
8
7
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3
2
ppm
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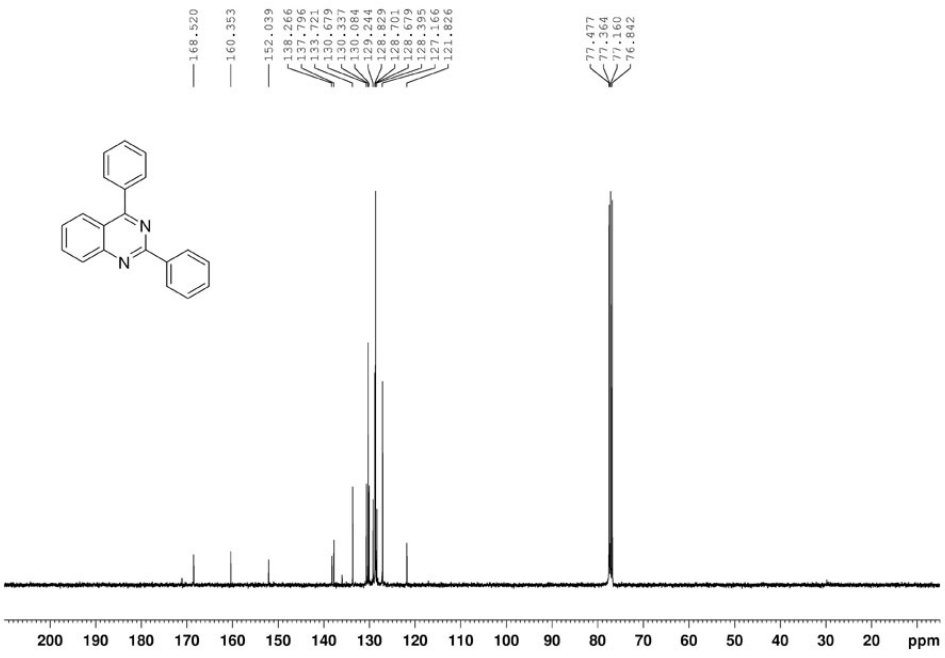
2.11
3.07
7.60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130.337
130.084
129.244
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128.679
128.395
127.166
121.826
77.477
77.364
77.160
76.842
N
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200
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150
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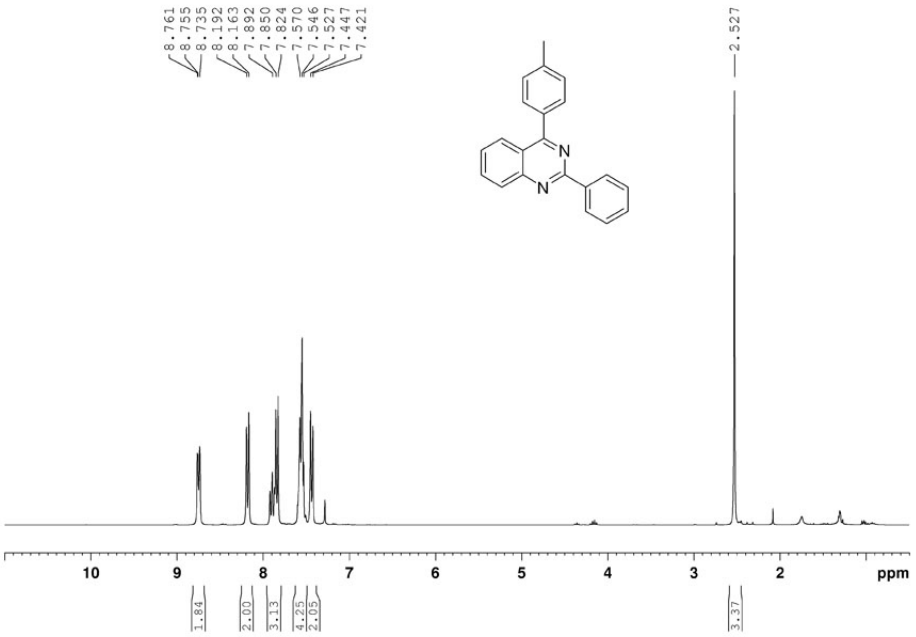
80
70
60
50
40
30
20
ppm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8.755
8.735
8.192
8.163
7.892
7.850
7.824
7.570
7.546
7.527
7.447
7.421
2.527
N
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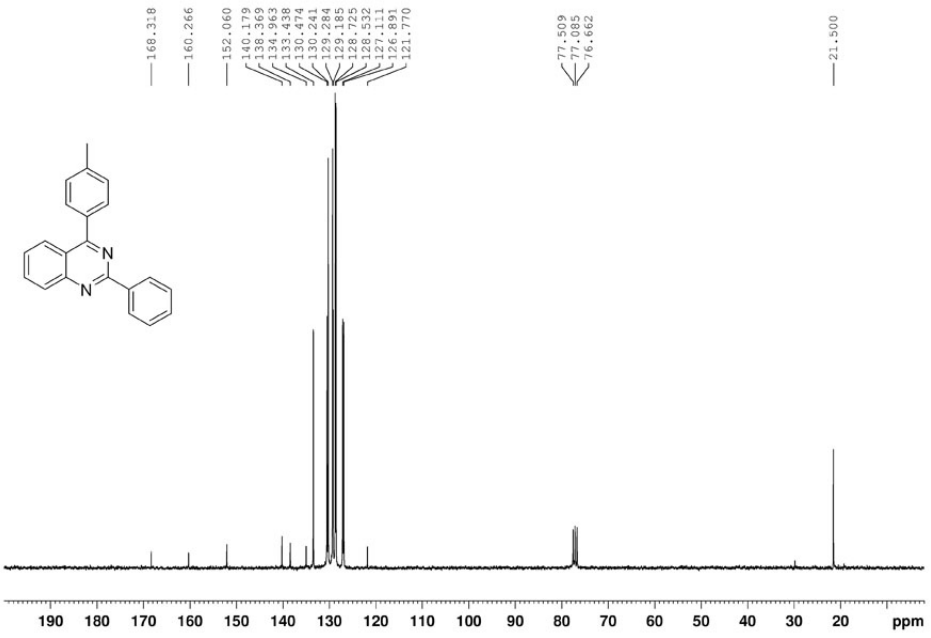
3.37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128.532
127.111
126.891
121.770
77.509
77.085
76.662
21.500
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150
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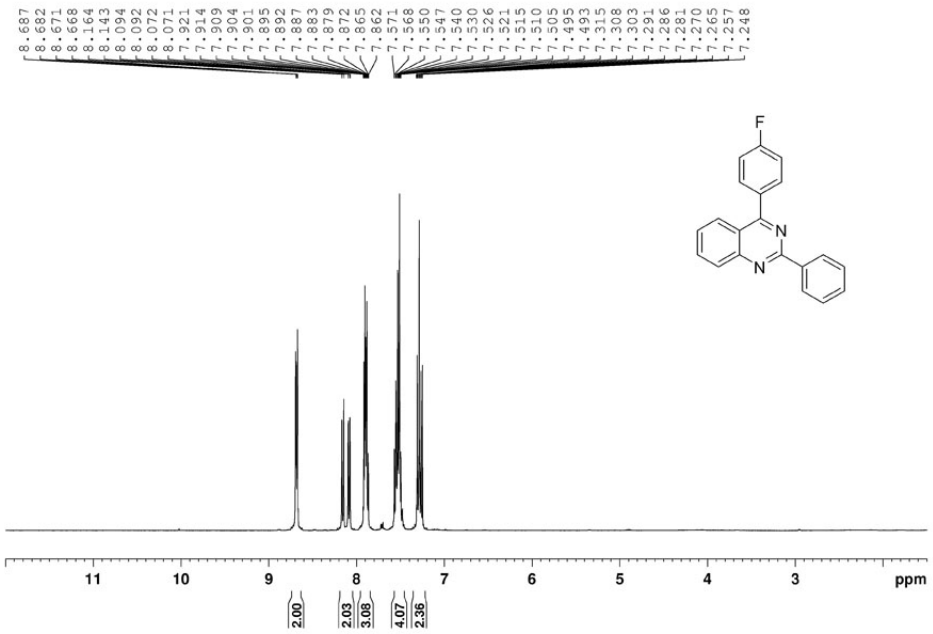
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8.668
8.164
8.143
8.094
8.092
8.072
8.071
7.921
7.914
7.909
7.904
7.901
7.895
7.892
7.887
7.883
7.879
7.872
7.865
7.862
7.571
7.568
7.550
7.547
7.540
7.530
7.526
7.521
7.515
7.510
7.505
7.495
7.493
7.315
7.308
7.303
7.291
7.286
7.281
7.270
7.265
7.257
7.248
F
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9
8
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3
ppm
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3.08
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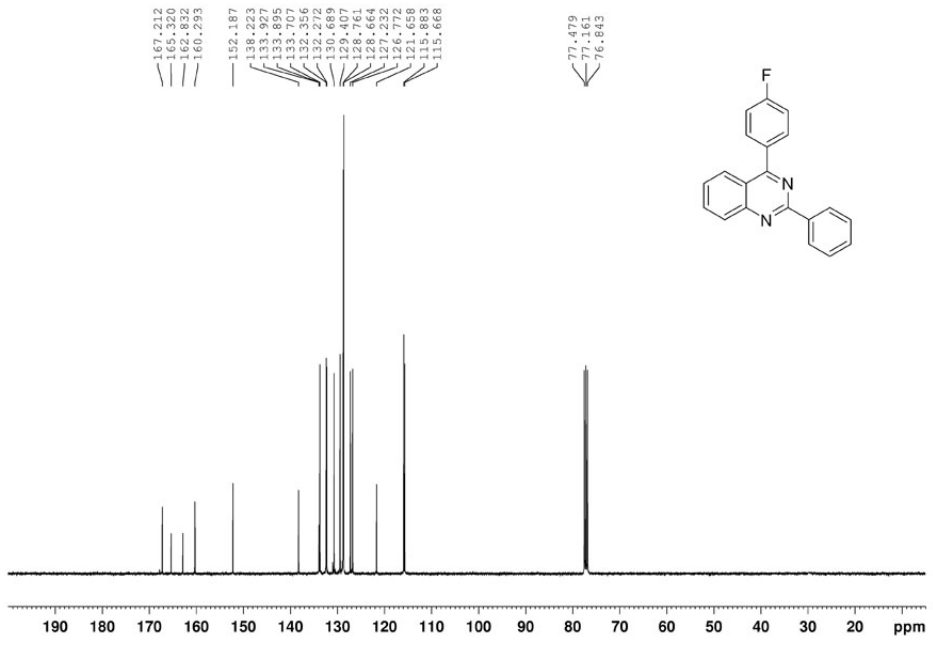
2.36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133.927
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132.356
132.272
130.689
129.407
128.761
128.664
127.232
126.772
121.658
115.883
115.668
77.479
77.161
76.843
F
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150
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80
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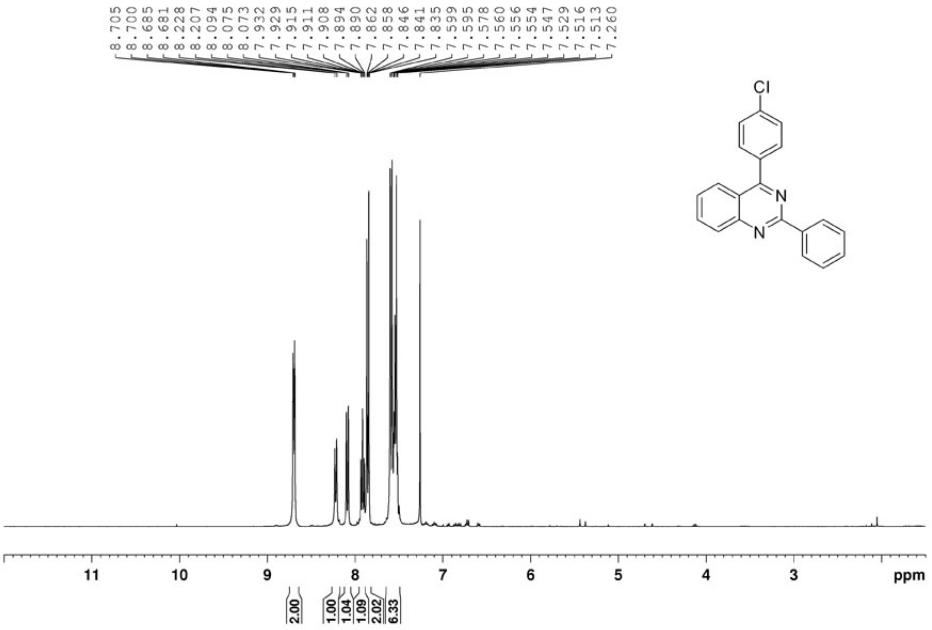
50
40
30
20
ppm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8.700
8.685
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8.207
8.094
8.075
8.073
7.932
7.929
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7.911
7.908
7.894
7.890
7.862
7.858
7.846
7.841
7.835
7.599
7.595
7.578
7.560
7.556
7.554
7.547
7.529
7.516
7.513
7.260
Cl
N
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7
6
5
4
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ppm
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1.00
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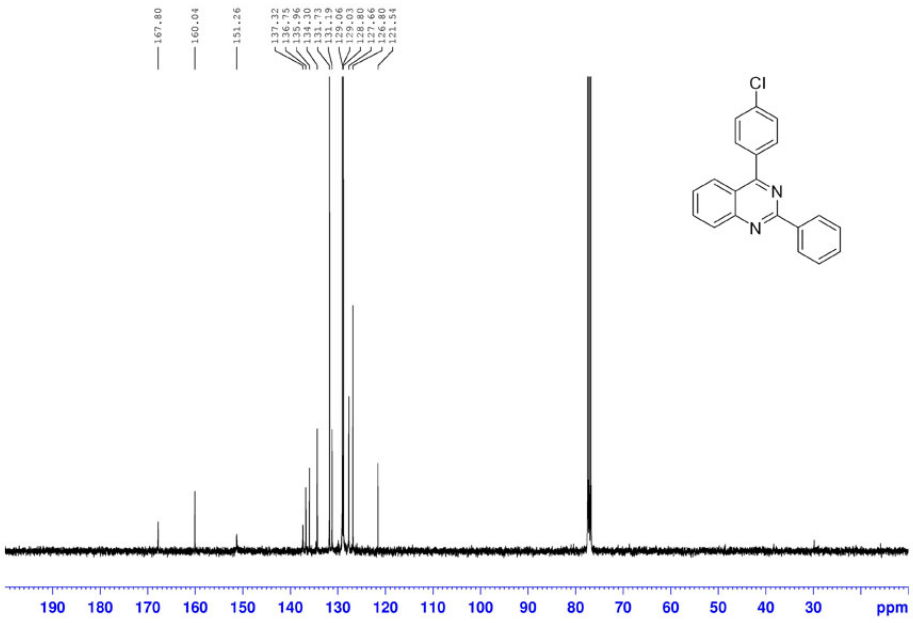
1.09
2.02
6.33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160.04
151.26
137.32
136.75
135.96
134.30
131.73
131.18
129.06
129.03
128.80
127.66
126.80
121.54
Cl
N
N
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180
170
160
150
140
130
120
110
100
90
80
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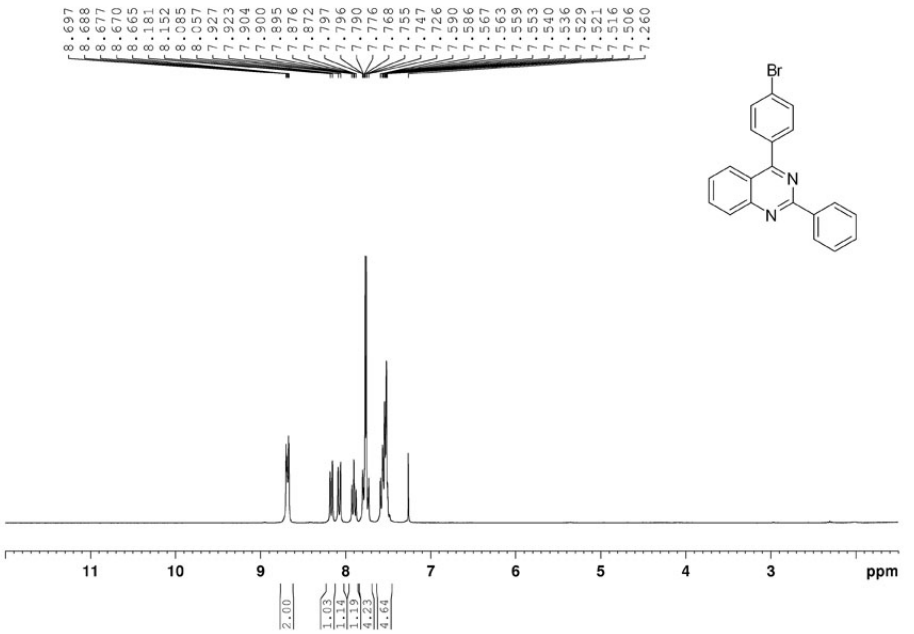
60
50
40
30
ppm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8.670
8.665
8.181
8.152
8.085
8.057
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7.923
7.904
7.900
7.895
7.876
7.872
7.797
7.796
7.790
7.776
7.768
7.755
7.747
7.726
7.590
7.586
7.567
7.563
7.559
7.553
7.540
7.536
7.529
7.521
7.516
7.506
7.260
Br
N
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8
7
6
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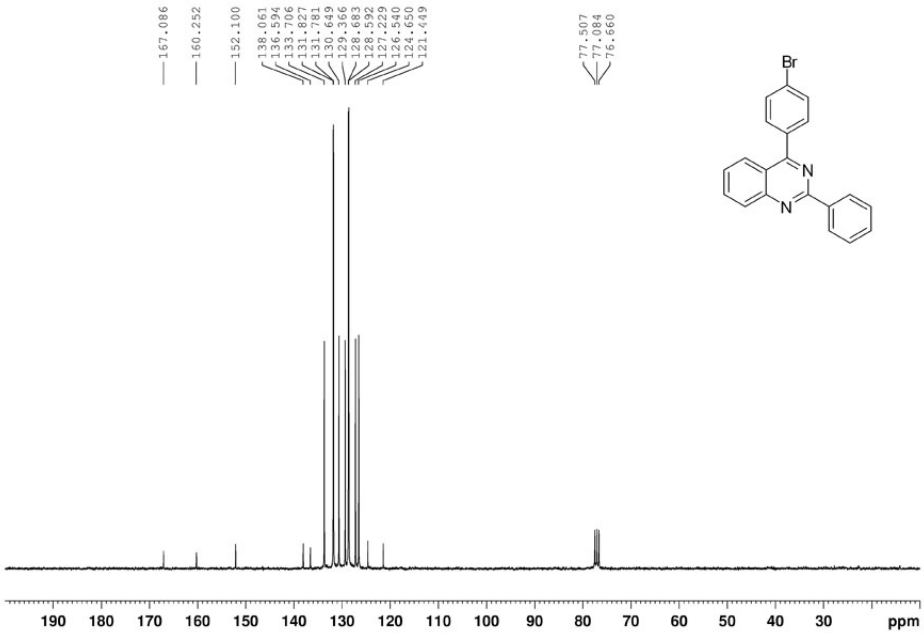
1.19
4.23
4.64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160.252
152.100
138.061
136.594
133.706
131.827
131.781
130.649
129.366
128.683
128.592
127.229
126.540
124.650
121.449
77.507
77.084
76.660
Br
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N
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180
170
160
150
140
130
120
110
100
90
80
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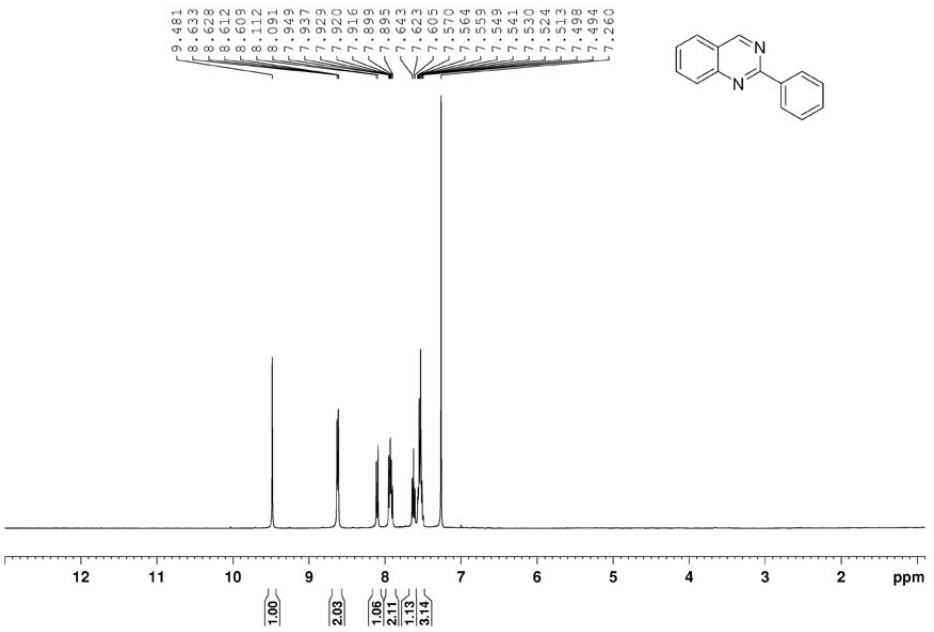
60
50
40
30
ppm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8.628
8.612
8.609
8.112
8.091
7.949
7.937
7.929
7.920
7.916
7.899
7.895
7.643
7.623
7.605
7.570
7.564
7.559
7.549
7.541
7.530
7.524
7.513
7.498
7.494
7.260
N
N
12
11
10
9
8
7
6
5
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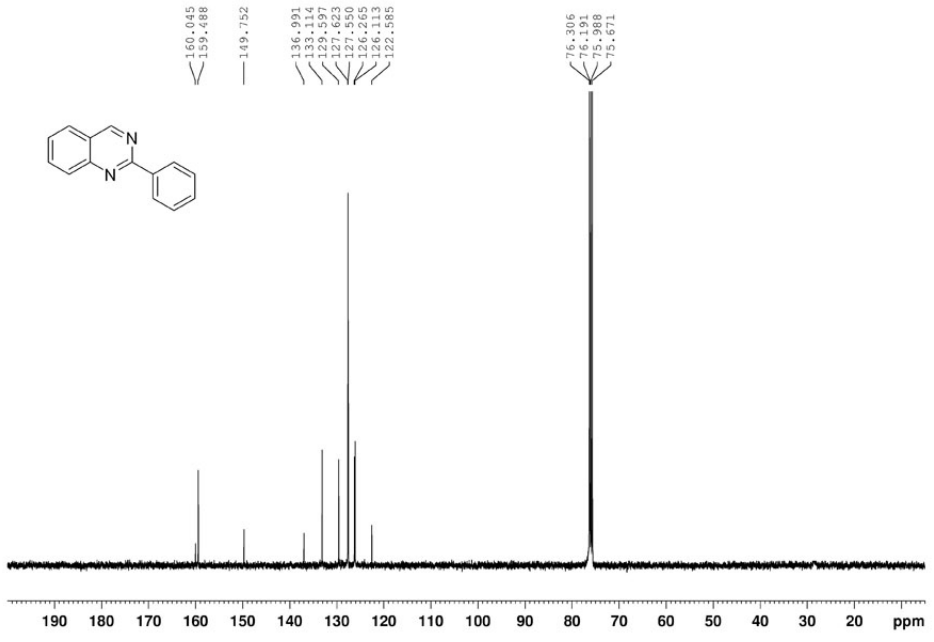
2.03
1.06
2.11
1.13
3.14


160.045
159.488
149.752
136.991
133.114
129.597
127.623
127.550
126.265
126.113
122.585
76.306
76.191
75.988
75.671
N
N
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180
170
160
150
140
130
120
110
100
90
80
70
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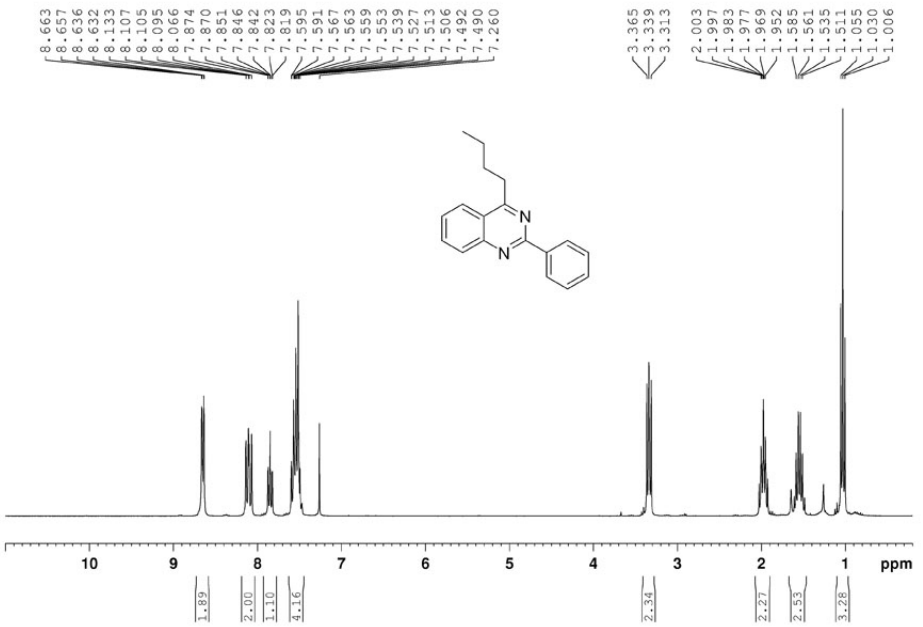
50
40
30
20
ppm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8.636
8.632
8.133
8.107
8.105
8.095
8.066
7.874
7.870
7.851
7.846
7.842
7.823
7.819
7.595
7.591
7.567
7.563
7.559
7.553
7.539
7.527
7.513
7.506
7.492
7.490
7.260
3.365
3.339
3.313
2.003
1.997
1.983
1.977
1.969
1.952
1.585
1.561
1.535
1.511
1.055
1.030
1.006
10
9
8
7
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1
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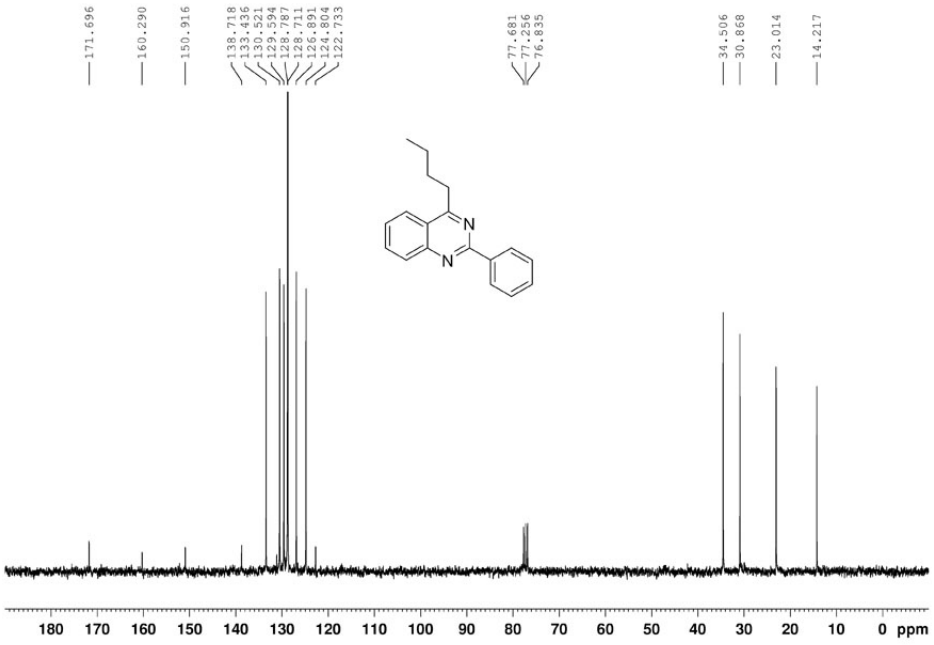
2.53
3.28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129.594
128.787
128.711
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124.804
122.733
77.681
77.256
76.835
34.506
30.868
23.014
14.217
180
170
160
150
140
130
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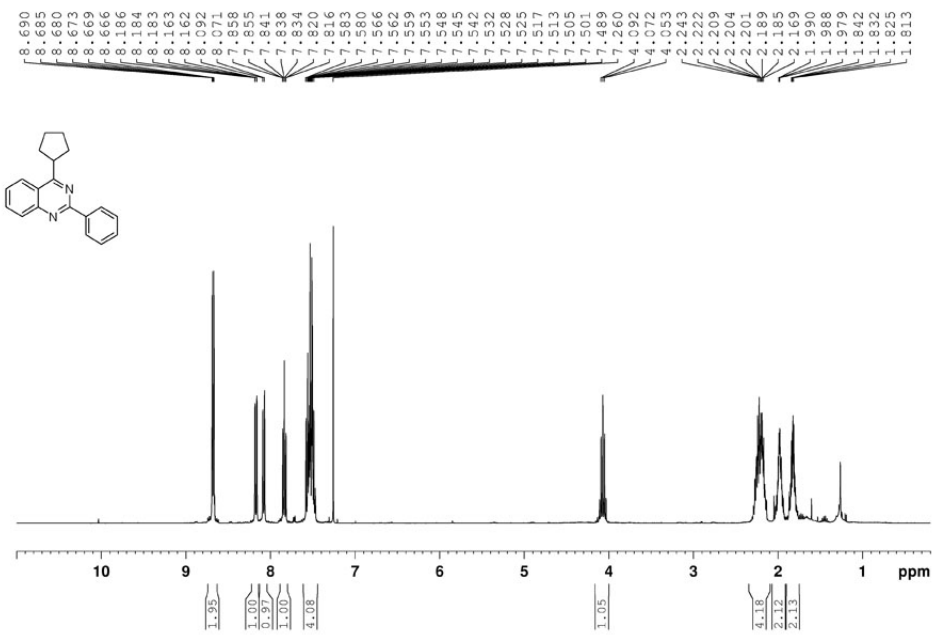
110
100
90
80
70
60
50
40
30
20
10
0 ppm


8.690
8.685
8.680
8.673
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8.666
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8.184
8.183
8.163
8.162
8.092
8.071
7.858
7.855
7.841
7.838
7.834
7.820
7.816
7.583
7.580
7.566
7.562
7.559
7.553
7.548
7.545
7.542
7.532
7.528
7.525
7.517
7.513
7.505
7.501
7.489
7.260
4.092
4.072
4.053
2.243
2.222
2.209
2.204
2.201
2.189
2.185
2.169
1.990
1.988
1.979
1.842
1.832
1.825
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10 9 8 7 6 5 4 3 2 1 ppm
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1.05
4.18
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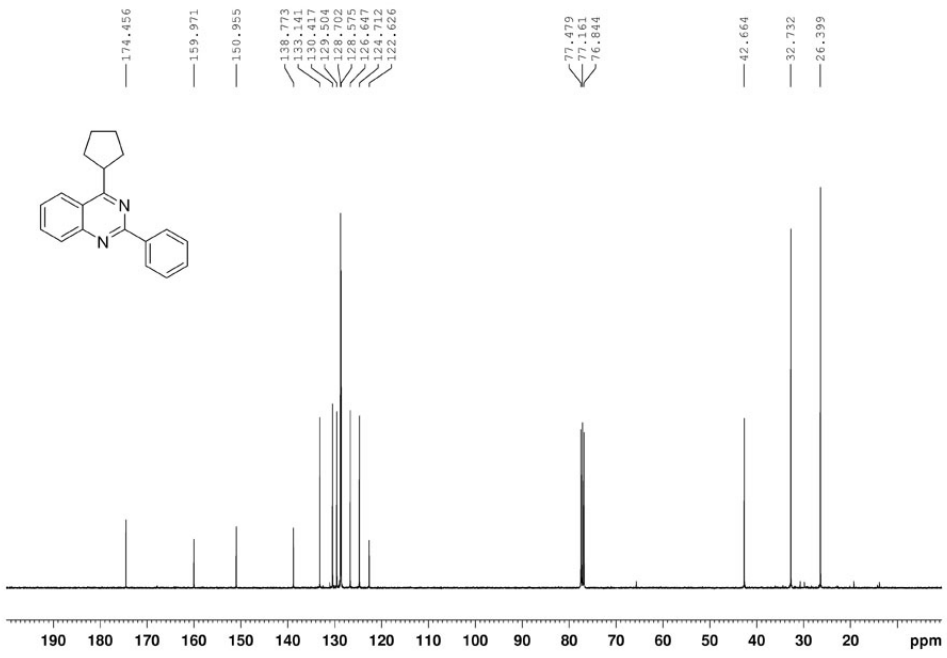
2.13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128.702
128.575
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77.161
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42.664
32.732
26.399
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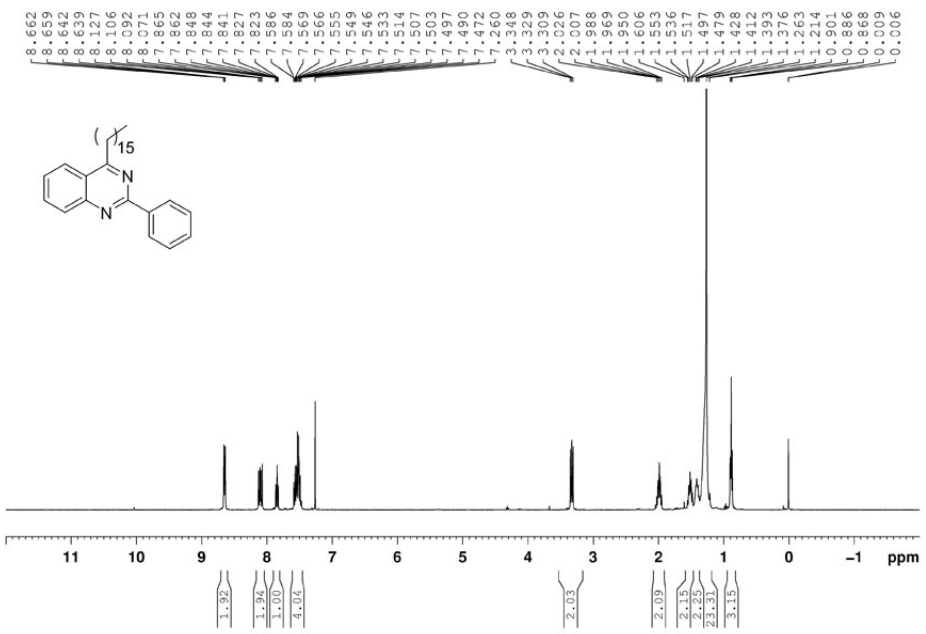
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8.092
8.071
7.865
7.862
7.848
7.844
7.841
7.827
7.823
7.586
7.584
7.569
7.566
7.555
7.549
7.546
7.533
7.514
7.507
7.503
7.497
7.490
7.472
7.260
3.348
3.329
3.309
2.026
2.007
1.988
1.969
1.950
1.606
1.553
1.536
1.517
1.497
1.479
1.428
1.412
1.393
1.376
1.263
1.214
0.901
0.886
0.868
0.009
0.006
15
N
N
11 10 9 8 7 6 5 4 3 2 1 0 −1 ppm
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1.94
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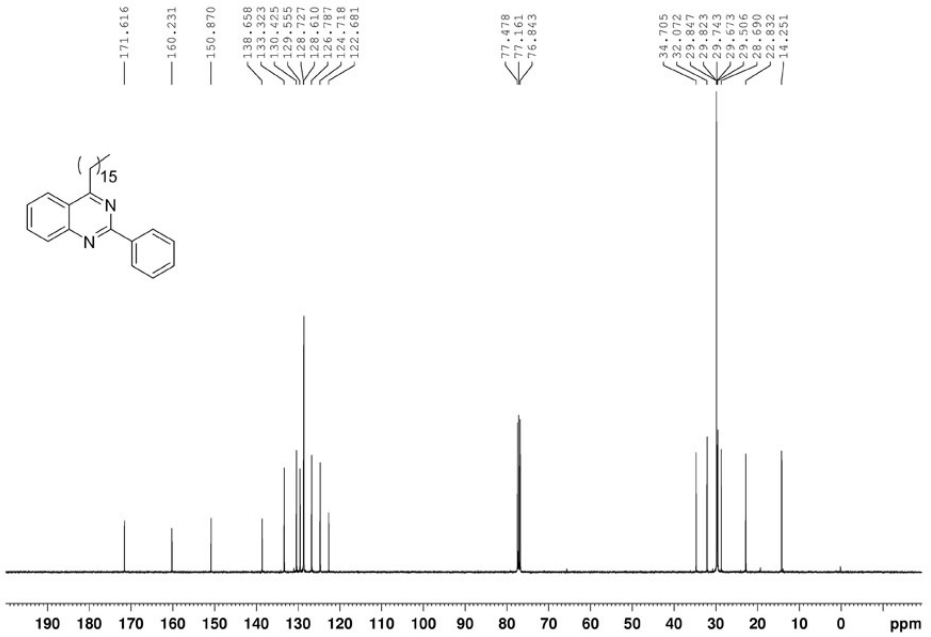
2.09
2.15
2.25
23.31
3.15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133.323
130.425
129.555
128.727
128.610
126.787
124.718
122.681
77.478
77.161
76.843
34.705
32.072
29.847
29.823
29.743
29.673
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28.690
22.832
14.251
15
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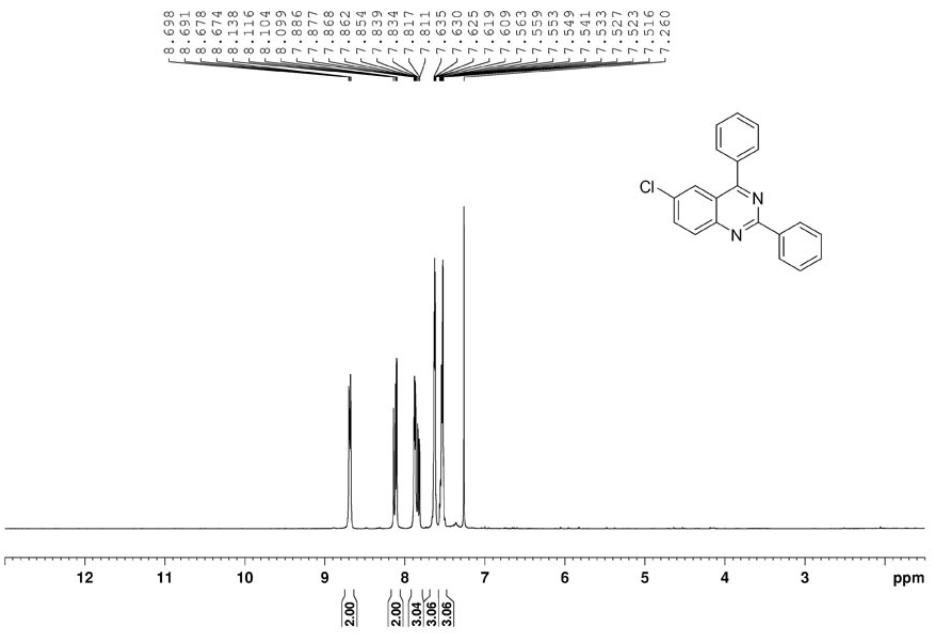
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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8.104
8.099
7.886
7.877
7.868
7.862
7.854
7.839
7.834
7.817
7.811
7.635
7.630
7.625
7.619
7.609
7.563
7.559
7.553
7.549
7.541
7.533
7.527
7.523
7.516
7.260
Cl
N
N
12
11
10
9
8
7
6
5
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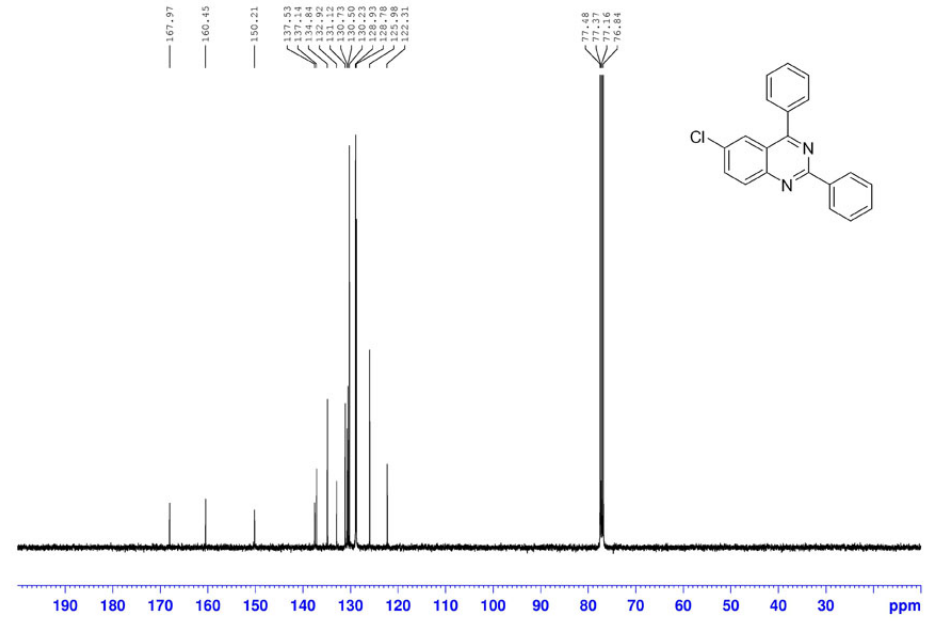
ppm
2.00
2.00
3.04
3.06
3.06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130.23
128.93
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128.08
122.31
77.48
77.37
77.16
76.84
Cl
N
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm