Supporting Information

Synthesis of 3-Acylquinolines through Cu-Catalyzed Double $C(sp^3)$-H Bond Functionalization of Saturated Ketones

Ze Wang, Guang Chen, Xinying Zhang*, and Xuesen Fan*

School of Chemistry and Chemical Engineering, Collaborative Innovation Centre of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Henan Normal University, Xinxiang, Henan 453007, China

E-mail: xuesen.fan@htu.cn; xinyingzhang@htu.cn

Table of Contents

I. General experimental information

Commercial reagents were used without further purification, and solvents were dried before using. Melting points were recorded with a micro melting point apparatus and uncorrected. The ^{1}H NMR spectra were recorded at 400 MHz or 600 MHz. The ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. Chemical shifts were expressed in parts per million (δ) downfield from the internal standard tetramethylsilane, and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet), m (multiplet), br s (broad singlet), etc. The coupling constants J were given in Hz. High resolution mass spectra (HRMS) were obtained *via* ESI mode by using a MicrOTOF mass spectrometer. The conversion of starting materials was monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).

II. Experimental procedures and spectroscopic sata

1. Typical procedure for the synthesis of 3a and spectroscopic data of 3a-3r

To a 15 mL reaction tube equipped with a stir bar were added 2-aminobenzaldehyde (**1a**, 60.5 mg, 0.5 mmol), toluene (3.0 mL), $Cu(OAc)_2$ (9.1 mg, 0.05 mmol), 2,2'-bipyridine (15.6 mg, 0.1 mmol), TEMPO (156.1 mg, 1 mmol) and propiophenone (**2a**, 80 μL, 0.6 mmol) with stirring. After being flushed with N_2, the tube was sealed, and the mixture was stirred at 120 ℃ for 14 h. Upon completion, the resulting mixture was diluted with DCM (20 mL), and washed with water (10 mL) and brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as the eluent to give **3a** (90.9 mg, 78%). **3b-3r** were obtained in a similar manner.

Phenyl(quinolin-3-yl)methanone (3a) [1]

Eluent: petroleum ether/ethyl acetate (10:1). White solid (90.9 mg, 78%), mp 74-76 ℃ (lit.[1] 73-75 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.54 (m, 2H), 7.59-7.66 (m, 2H), 7.81-7.83 (m, 1H), 7.85 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.53 (d, *J* = 2.0 Hz, 1H), 9.32 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.6, 127.6, 128.6, 129.2, 129.5, 130.0, 131.8, 133.1, 137.0, 138.8, 149.5, 150.3, 194.8. MS: m/z 234 $[M+H]^+$.

(6-Chloroquinolin-3-yl)(phenyl)methanone (3b)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (100.1 mg, 75%), mp 121-123 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (t, *J* = 8.0 Hz, 2H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.76 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.89 (d, *J* = 2.4 Hz, 1H), 8.12 (d, *J* = 8.8 Hz, 1H), 8.45 (d, *J* = 2.0 Hz, 1H), 9.29 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.3, 127.6, 128.7, 130.1, 130.9, 131.1, 132.7, 133.3, 133.5, 136.8, 137.6, 147.8, 150.5, 194.5. HRMS calcd for $C_{16}H_{11}ClNO$: 268.0524 $[M+H]^+$, found: 268.0528.

[1,3]Dioxolo[4,5-*g*]quinolin-7-yl(phenyl)methanone (3c)

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (109.4 mg, 79%), mp 119-120 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.15 (s, 2H), 7.09 (s, 1H), 7.41 (s, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 2H), 8.35 (d, *J* = 1.8 Hz, 1H), 9.08 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 102.3, 103.7, 105.9, 123.9, 128.56, 128.59, 130.0, 132.8, 137.2, 137.3, 148.4, 148.6, 148.7, 152.8, 194.9. HRMS calcd for $C_{17}H_{12}NO_3$: 278.0812 $[M+H]^+$, found: 278.0820.

(7-Methoxyquinolin-3-yl)(phenyl)methanone (3d) [2]

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (110.5 mg, 84%), mp 84-85 ℃ (lit.[2] 79-80 ℃). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.97 (s, 3H), 7.25 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.47 (d, *J* = 2.4 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 2H), 8.47 (d, *J* = 1.8 Hz, 1H), 9.25 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 55.7, 107.4, 120.9, 121.7, 128.0, 128.6, 129.9, 130.3, 132.8, 137.3, 138.5, 150.9, 151.6, 162.7, 194.8. MS: m/z 264 $[M+H]^+$.

(6,7-Dimethoxyquinolin-3-yl)(phenyl)methanone (3e) [2]

Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid (126.0 mg, 86%), mp 144-145 ℃ (lit.[2] 142-143 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.02 (s, 3H), 4.07 (s, 3H), 7.12 (s, 1H), 7.48 (s, 1H), 7.51-7.55 (m, 2H), 7.61-7.65 (m, 1H), 7.84-7.86 (m, 2H), 8.42 (d, *J* = 2.0 Hz, 1H), 9.13 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.1, 56.3, 106.1, 107.9, 122.3, 128.5, 129.9, 132.7, 136.8, 137.5, 147.1, 148.6, 150.5, 154.4, 195.1. MS: m/z 294 $[M+H]^+$.

(4-Bromophenyl)(quinolin-3-yl)methanone (3f) [1]

Eluent: petroleum ether/ethyl acetate (10:1). White solid (110.4 mg, 71%), mp 118-119 ℃ (lit.[1] 115-117 ℃). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.85 (t, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 8.18 (d, *J* = 9.0 Hz, 1H), 8.51 (d, *J* = 1.8 Hz, 1H), 9.29 (d, J = 1.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 126.5, 127.7, 128.3, 129.2, 129.5, 129.6, 131.5, 132.01, 132.04, 135.7, 138.7, 149.6, 150.1, 193.8. MS: m/z 312 $[M+H]^+$.

Quinolin-3-yl(4-(trifluoromethyl)phenyl)methanone (3g)

Eluent: petroleum ether/ethyl acetate (10:1). Yellow solid (108.4 mg, 72%), mp 116-117 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.69 (m, 1H), 7.82 (d, J = 8.4 Hz, 2H), 7.86-7.91 (m, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.0 Hz, 2H), 8.21 (d, J = 8.8 Hz, 1H), 8.55 (d, J = 2.0 Hz, 1H), 9.33 (d, J = 2.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 123.6 (q, $^1J_{C-F}$ = 271.2 Hz), 125.7 (q, $^3J_{C-F}$ = 4.5 Hz), 126.5, 127.9, 129.2, 129.3, 129.6, 130.2, 132.3, 134.4 (q, $^2J_{C-F}$ = 32.9 Hz), 139.1, 140.1, 149.7, 150.1, 193.8. HRMS calcd for $C_{17}H_{11}F_3NO$: 302.0787 $[M+H]^+$, found: 302.0807.

Quinolin-3-yl(p-tolyl)methanone (3h) [3]

Eluent: petroleum ether/ethyl acetate (10:1). White solid (97.6 mg, 79%), mp 93-94 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 3H), 7.30-7.33 (m, 2H), 7.59-7.63 (m, 1H), 7.77 (d, J = 8.0 Hz, 2H), 7.80-7.84 (m, 1H), 7.89 (d, J = 8.0 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H), 8.51 (d, J = 2.0 Hz, 1H), 9.30 (d, J = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 126.6, 127.5, 129.1, 129.3, 129.5, 130.3, 130.4, 131.7, 134.4, 138.5, 144.0, 149.4, 150.4, 194.5. MS: m/z 248 $[M+H]^+$.

(4-Methoxyphenyl)(quinolin-3-yl)methanone (3i) [3]

Eluent: petroleum ether/ethyl acetate (5:1). White solid (109.2 mg, 83%), mp 132-133 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3H), 7.01 (dt, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 2H), 7.61-7.65 (m, 1H), 7.81-7.85 (m, 1H), 7.88 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 2H), 7.91 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 8.51 (d, J = 2.0 Hz, 1H), 9.28 (d, J = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 114.0, 126.7, 127.5, 129.0, 129.5, 129.7, 130.8, 131.6, 132.6, 138.2, 149.3, 150.3, 163.7, 193.5. MS: m/z 264 $[M+H]^+$.

Pyridin-3-yl(quinolin-3-yl)methanone (3j)

Eluent: petroleum ether/ethyl acetate (3:1). Brown yellow solid (73.7 mg, 63%), mp 81-82 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.88 (td, J_1 = 8.4 Hz,

J_2 = 1.2 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 8.19-8.21 (m, 2H), 8.56 (d, J = 2.0 Hz, 1H), 8.88 (dd, J_1 = 4.8 Hz, J_2 = 1.6 Hz, 1H), 9.08 (d, J = 2.0 Hz, 1H), 9.34 (d, J = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.7, 126.4, 127.9, 129.1, 129.2, 129.6, 132.3, 132.6, 137.1, 139.0, 149.7, 149.9, 150.8, 153.4, 193.1. HRMS calcd for $C_{15}H_{11}N_2O$: 235.0866 $[M+H]^+$, found: 235.0878.

Quinolin-3-yl(thiophen-2-yl)methanone (3k) [1]

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (89.6 mg, 75%), mp 86-87 ℃ (lit.[1] 89-91 ℃). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (dd, J_1 = 4.8 Hz, J_2 = 3.6 Hz, 1H), 7.63-7.65 (m, 1H), 7.71 (dd, J_1 = 4.2 Hz, J_2 = 0.6 Hz, 1H), 7.79 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.83-7.85 (m, 1H), 7.94 (td, J_1 = 7.8 Hz, J_2 = 0.6 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 8.64 (d, J = 2.4 Hz, 1H), 9.34 (d, J = 1.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 126.6, 127.7, 128.4, 129.1, 129.5, 130.7, 131.8, 135.08, 135.10, 137.7, 143.2, 149.5, 149.6, 186.2. MS: m/z 240 $[M+H]^+$.

1-(Quinolin-3-yl)ethanone (3l) [1]

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (24.8 mg, 29%), mp 95-96 ℃ (lit.[1] 98-99 ℃). ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.74 (s, 3H), 7.63 (t, J = 7.8 Hz, 1H), 7.83-7.85 (m, 1H), 7.95 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 8.70 (d, J = 2.4 Hz, 1H), 9.43 (d, J = 2.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 26.8, 126.8, 127.6, 129.3, 129.4, 129.5, 132.0, 137.4, 149.2, 149.8, 196.8. MS: m/z 172 $[M+H]^+$.

Cyclohexyl(quinolin-3-yl)methanone (3m) [3]

Eluent: petroleum ether/ethyl acetate (10:1). Yellow solid (41.8 mg, 35%), mp 61-62 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.27-1.33 (m, 1H), 1.41-1.49 (m, 2H), 1.53-1.60 (m, 2H), 1.75-1.78 (m, 1H), 1.86-1.90 (m, 2H), 1.96 (d, J = 13.2 Hz, 2H), 3.37 (tt, J_1 = 11.4 Hz, J_2 = 3.6 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 7.81 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.94 (d, J = 7.8 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 8.68 (d, J = 1.8 Hz, 1H), 9.41 (d, J = 1.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 25.7, 25.9, 29.2, 46.0, 126.9, 127.4, 128.4, 129.3, 129.4, 131.8, 137.0, 149.5, 149.7, 202.5. MS: m/z 240 $[M+H]^+$.

(2-Methylquinolin-3-yl)(phenyl)methanone (3n) [4]

Eluent: petroleum ether/ethyl acetate (10:1). Yellow solid (56.8 mg, 46%), mp 134-136 ℃ (lit.[4] 131-133 ℃). ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.75 (s, 3H), 7.49 (t, J = 7.8 Hz, 2H), 7.54 (t, J = 7.8 Hz, 1H), 7.63 (t, J = 7.8 Hz, 1H), 7.76-7.79 (m, 2H), 7.85 (d, J = 7.2 Hz, 2H), 8.09 (d, J = 8.4 Hz, 1H), 8.11 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.3, 125.3, 126.7, 128.1, 128.7, 128.8, 130.2, 131.1, 132.2, 133.7, 136.8, 137.3, 148.1, 156.7, 196.7. MS: m/z 248 $[M+H]^+$.

Phenyl(2-phenylquinolin-3-yl)methanone (3o) [5]

Eluent: petroleum ether/ethyl acetate (10:1). White solid (123.6 mg, 80%), mp 138-139 ℃ (lit.[5] 135-137 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.31 (m, 5H), 7.41-7.45 (m, 1H), 7.55-7.59 (m, 1H), 7.63 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 2H), 7.69-7.71 (m, 2H), 7.78-7.82 (m, 1H), 7.86 (d, J = 8.0 Hz, 1H), 8.24 (d, J = 8.8 Hz, 1H), 8.31 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.8, 127.3, 128.2, 128.4, 128.9, 129.3, 129.7, 130.0, 131.2, 132.9, 133.4, 137.1, 137.6, 139.8, 148.4, 157.5, 196.9. MS: m/z 310 $[M+H]^+$.

11*H*-Indeno[1,2-*b*]quinolin-11-one (3p) [4]

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (42.7 mg, 37%), mp 169-171 ℃ (lit.[4] 172-174 ℃). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (t, J = 7.8 Hz, 1H), 7.54-7.59 (m, 2H), 7.63-7.66 (m, 2H), 7.75 (t, J = 7.2 Hz, 2H), 8.06 (s, 1H), 8.20 (d, J = 9.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 121.6, 124.9, 126.2, 128.5, 129.2, 129.5, 129.9, 130.1, 131.7, 133.7, 134.3, 136.1, 142.6, 148.6, 154.3, 192.3. MS: m/z 232 $[M+H]^+$.

(1,8-Naphthyridin-3-yl)(phenyl)methanone (3q)

Eluent: petroleum ether/ethyl acetate (1:1). White solid (101.8 mg, 87%), mp 102-103 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (t, J = 7.8 Hz, 2H), 7.62 (q, J = 4.2 Hz, 1H), 7.68 (t, J = 7.8 Hz, 1H), 7.87 (d, J = 7.2 Hz, 2H), 8.34 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 8.62 (d, J = 1.8 Hz, 1H) , 9.24 (q, J = 1.8 Hz, 1H) , 9.51

(d, J = 2.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 121.4, 123.2, 128.8, 130.0, 131.1, 133.4, 136.6, 138.4, 139.7, 153.6, 155.7, 157.1, 194.1. HRMS calcd for $C_{15}H_{10}N_2NaO$: 257.0685 $[M+Na]^+$, found: 257.0692.

(1,8-Naphthyridin-3-yl)(pyridin-3-yl)methanone (3r)

Eluent: petroleum ether/ethyl acetate (1:2). White solid (96.4 mg, 82%), mp 97-98 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H), 7.66 (q, J = 4.0 Hz, 1H), 8.22 (dt, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 8.37 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 8.66 (d, J = 2.8 Hz, 1H), 8.62 (dd, J_1 = 4.8 Hz, J_2 = 1.6 Hz, 1H) , 9.09 (d, J = 1.6 Hz, 1H) , 9.28 (dd, J_1 = 4.0 Hz, J_2 = 1.6 Hz, 1H), 9.54 (d, J = 2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.4, 123.4, 123.8, 130.2, 132.3, 137.2, 138.5, 140.0, 150.8, 153.2, 153.7, 156.1, 157.3, 192.4. HRMS calcd for $C_{14}H_{10}N_3O$: 236.0818 $[M+H]^+$, found: 236.0819.

2. Typical procedure for the synthesis of 5a and spectroscopic data of 5a-5l

To a 15 mL reaction tube equipped with a stir bar were added (2-aminophenyl)(phenyl)methanone (**4a**, 98.5 mg, 0.5 mmol), toluene (3.0 mL), $Cu(OAc)_2$ (9.1 mg, 0.05 mmol,), 2,2'-bipyridine (15.6 mg, 0.1 mmol), TEMPO (156.1 mg, 1 mmol) and propiophenone (**2a**, 80 μL, 0.6 mmol) with stirring. After being flushed with N_2, the tube was sealed, and the mixture was stirred at 120 ^{o}C for 36 h. Upon completion, the resulting mixture was diluted with DCM (20 mL), and washed with water (10 mL) and brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as the eluent to give **5a** (142.2 mg, 92%). **5b-5l** were obtained in a similar manner.

Phenyl(4-phenylquinolin-3-yl)methanone (5a) [1]

Eluent: petroleum ether/ethyl acetate (10:1). Yellow solid (142.2 mg, 92%), mp 105-107 ℃ (lit.[1] 108-110 ℃). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25-7.28 (m, 7H), 7.41 (d, J = 7.2 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.61 (d, J = 7.2 Hz, 2H), 7.79 (t, J = 8.4 Hz, 2H), 8.24 (d, J = 8.4 Hz, 1H), 9.00 (s, 1H). ^{13}C NMR

(150 MHz, $CDCl_3$) δ 126.5, 126.8, 127.6, 128.3, 128.6, 129.76, 129.85, 130.1, 130.5, 131.9, 133.3, 135.0, 137.4, 147.0, 148.6, 148.9, 196.9. MS: m/z 310 $[M+H]^+$.

(4-Methoxyphenyl)(4-phenylquinolin-3-yl)methanone (5b) [6]

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (159.4 mg, 94%), mp 118-120 ℃ (lit.[6] 115-116 ℃). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.79 (s, 3H), 6.77 (d, *J* = 8.4 Hz, 2H), 7.27-7.31 (m, 5H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.78 (t, *J* = 7.8 Hz, 2H), 8.23 (d, *J* = 8.4 Hz, 1H), 8.96 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 55.5, 113.6, 126.6, 126.7, 127.5, 128.2, 128.5, 129.8, 130.0, 130.3, 132.2, 132.3, 135.1, 146.6, 148.5, 148.7, 163.8, 195.1. MS: m/z 340 $[M+H]^+$.

(4-Phenylquinolin-3-yl)(4-(trifluoromethyl)phenyl)methanone (5c)

Eluent: petroleum ether/ethyl acetate (10:1). Yellow solid (147.1 mg, 78%), mp 139-141 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24-7.29 (m, 5H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.82 (t, *J* = 7.8 Hz, 2H), 8.25 (d, *J* = 8.4 Hz, 1H), 9.04 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 123.5 (q, $^1J_{C\text{-}F}$ = 271.4 Hz), 125.2 (q, $^3J_{C\text{-}F}$ = 3.3 Hz), 126.2, 126.8, 127.8, 128.4, 128.8, 129.7, 129.9, 130.2, 130.9, 131.1, 134.0 (q, $^2J_{C\text{-}F}$ = 32.9 Hz), 134.7, 140.3, 147.4, 148.5, 149.2, 196.1. HRMS calcd for $C_{23}H_{14}F_3NNaO$: 400.0920 $[M+Na]^+$, found: 400.0949.

(4-Phenylquinolin-3-yl)(thiophen-2-yl)methanone (5d) [6]

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (141.8 mg, 90%), mp 123-124 ℃ (lit.[6] 128-130 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (dd, J_1 = 4.8 Hz, J_2 = 4.0 Hz, 1H), 7.28 (dd, J_1 = 4.0 Hz, J_2 = 1.2 Hz, 1H), 7.34-7.37 (m, 5H), 7.52-7.56 (m, 1H), 7.60 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.78-7.82 (m, 2H), 8.23 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 9.04 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 126.5, 126.9, 127.6, 128.1, 128.4, 128.7, 129.8, 130.1, 130.6, 131.9, 134.9, 135.4, 135.6, 144.5, 146.8, 148.1, 148.8, 188.3. MS: m/z 316 $[M+H]^+$.

1-(4-Phenylquinolin-3-yl)ethanone (5e) [7]

Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid (63.0 mg, 51%), mp 75-76 ℃ (lit.[7] 69-71 ℃). ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.97 (s, 3H), 7.38 (dd, J_1 = 6.6 Hz, J_2 = 3.0 Hz, 2H), 7.52 (t, J = 7.8 Hz, 1H), 7.55-7.57 (m, 3H), 7.70 (d, J = 7.8 Hz, 1H), 7.78 (t, J = 7.8 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 9.09 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 30.6, 126.3, 127.1, 127.5, 128.9, 129.2, 129.69, 129.72, 130.8, 132.2, 135.8, 146.8, 148.9, 149.0, 202.3. MS: m/z 248 $[M+H]^+$.

(6-Chloro-4-phenylquinolin-3-yl)(phenyl)methanone (5f) [6]

Eluent: petroleum ether/ethyl acetate (10:1). White solid (154.4 mg, 90%), mp 175-177 ℃ (lit.[6] 181-182 ℃). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26-7.32 (m, 7H), 7.43 (t, J = 7.8 Hz, 1H), 7.60 (d, J = 7.2 Hz, 2H), 7.73 (dd, J_1 = 9.0 Hz, J_2 = 2.4 Hz, 1H), 7.75 (d, J = 2.4 Hz, 1H), 8.17 (d, J = 9.0 Hz, 1H), 8.98 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 125.5, 127.3, 128.3, 128.5, 128.9, 129.7, 130.0, 131.4, 131.5, 132.6, 133.4, 133.6, 134.3, 137.1, 146.1, 147.3, 148.7, 196.4. MS: m/z 344 $[M+H]^+$.

(4-Methylquinolin-3-yl)(phenyl)methanone (5g) [5]

Eluent: petroleum ether/ethyl acetate (10:1). White solid (70.4 mg, 57%), mp 87-89 ℃ (lit.[5] 82-86 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67 (s, 3H), 7.49 (t, J = 7.6 Hz, 2H), 7.61-7.68 (m, 2H), 7.78-7.83 (m, 1H), 7.84-7.86 (m, 2H), 8.13 (dd, J_1 = 8.4 Hz, J_2 = 0.4 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H), 8.82 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.9, 124.5, 127.3, 127.6, 128.8, 130.1, 130.2, 130.4, 131.9, 133.9, 137.5, 143.6, 148.1, 148.6, 197.0. MS: m/z 248 $[M+H]^+$.

(4-Methylquinolin-3-yl)(*p*-tolyl)methanone (5h)

Eluent: petroleum ether/ethyl acetate (10:1). Yellow solid (73.1 mg, 56%), mp 118-120 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.45 (s, 3H), 2.67 (s, 3H), 7.30 (d, J = 7.8 Hz, 2H), 7.67 (t, J = 7.8 Hz, 1H), 7.76 (d, J = 7.8 Hz, 2H), 7.81 (t, J = 7.8 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 8.82 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.9, 21.8, 124.4, 127.3, 127.7, 129.6, 130.2, 130.31, 130.34, 132.2, 135.0, 143.3, 145.0, 148.0, 148.6, 196.6. HRMS calcd for $C_{18}H_{16}NO$: 262.1226 $[M+H]^+$, found: 262.1248.

(4-Methoxyphenyl)(4-methylquinolin-3-yl)methanone (5i)

Eluent: petroleum ether/ethyl acetate (5:1). White solid (80.4 mg, 58%), mp 91-93 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.65 (s, 3H), 3.88 (s, 3H), 6.95 (d, *J* = 9.0 Hz, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 9.0 Hz, 2H), 8.11 (d, *J* = 7.8 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 8.81 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.8, 55.6, 114.1, 124.4, 127.3, 127.7, 130.2, 130.5, 132.4, 132.6, 142.9, 147.9, 148.5, 164.3, 195.5. HRMS calcd for $C_{18}H_{16}NO_2$: 278.1176 $[M+H]^+$, found: 278.1202.

(4-Chlorophenyl)(4-methylquinolin-3-yl)methanone (5j)

Eluent: petroleum ether/ethyl acetate (10:1). White solid (73.1 mg, 52%), mp 150-152 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.69 (s, 3H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.83 (t, *J* = 7.8 Hz, 2H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 8.81 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.9, 124.5, 127.5, 127.6, 129.2, 130.3, 130.6, 131.4, 131.5, 135.9, 140.5, 143.8, 148.2, 148.4, 195.7. HRMS calcd for $C_{17}H_{13}ClNO$: 282.0680 $[M+H]^+$, found: 282.0695.

(4-Methylquinolin-3-yl)(4-(trifluoromethyl)phenyl)methanone (5k)

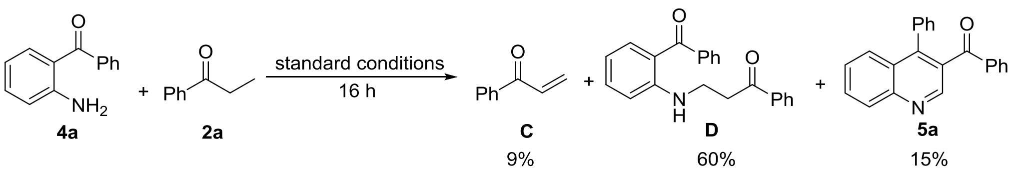
Eluent: petroleum ether/ethyl acetate (10:1). White solid (77.2 mg, 49%), mp 140-142 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.69 (s, 3H), 7.69 (t, *J* = 7.2 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.82-7.85 (m, 1H), 7.96 (d, *J* = 7.8 Hz, 2H), 8.15 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 8.81 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 16.0, 123.5 (q, $^1J_{C-F}$ = 271.2 Hz), 124.5, 125.9 (q, $^3J_{C-F}$ = 4.4 Hz), 127.56, 127.60, 130.3, 130.4, 130.8, 131.0, 135.0 (q, $^2J_{C-F}$ = 31.8 Hz), 140.3, 144.3, 148.3, 148.5, 195.9. HRMS calcd for $C_{18}H_{13}F_3NO$: 316.0944 $[M+H]^+$, found: 316.0968.

1-Benzoyl-7*H*-naphtho[1,2,3-*de*]quinolin-7-one (5l)

Eluent: petroleum ether/ethyl acetate (5:1). Orange solid (77.3 mg, 46%), mp 188-189 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41-7.45 (m, 3H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 2H), 8.02 (t, *J* = 7.8 Hz, 1H), 8.46 (d, *J* = 7.8 Hz, 1H), 8.49 (d, *J* = 8.4 Hz, 1H), 8.76 (d, *J* = 7.2 Hz, 1H), 8.93 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 123.1, 128.7, 128.8, 129.0, 129.1, 130.1, 130.4, 130.5, 130.8, 131.3, 132.8, 132.9, 133.2, 133.5, 134.6, 136.1, 136.5, 147.6, 150.0, 182.1, 197.9. HRMS calcd for $C_{23}H_{13}NNaO_2$: 358.0838 $[M+Na]^+$, found: 358.0864.

3. Control experiments (I)

3.1. To a 15 mL reaction tube equipped with a stir bar were added **4a** (98.5 mg, 0.5 mmol), toluene (3.0 mL), $Cu(OAc)_2$ (9.1 mg, 0.05 mmol), 2,2'-bipyridine (15.6 mg, 0.1 mmol), TEMPO (156.2 mg, 1 mmol) and **2a** (80 μL, 0.6 mmol) with stirring. After being flushed with N_2, the tube was sealed, and the mixture was stirred at 120 ℃ for 16 h. Afterwards, the resulting mixture was diluted with DCM (20 mL), and washed with water (10 mL) and brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as the eluent to give 1-phenylprop-2-en-1-one (**C**, 7.2 mg, 9%), 3-((2-benzoyl phenyl)amino)-1-phenylpropan-1-one (**D**, 98.7 mg, 60%), and **5a** (23.2 mg, 15%).



1-Phenylprop-2-en-1-one (C) [8]

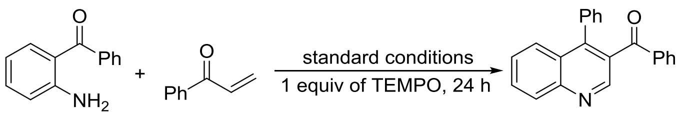
Eluent: petroleum ether/ethyl acetate (50:1). Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 (dd, J_1 = 10.8 Hz, J_2 = 1.6 Hz, 1H), 6.44 (dd, J_1 = 16.8 Hz, J_2 = 1.6 Hz, 1H), 7.16 (dd, J_1 = 16.8 Hz, J_2 = 10.4 Hz, 1H), 7.48 (td, J_1 = 6.4 Hz, J_2 = 1.2 Hz, 2H), 7.58 (tt, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.94-7.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.6, 128.7, 130.2, 132.4, 133.0, 137.3, 191.1. MS: m/z 133 $[M+H]^+$.

3-((2-Benzoylphenyl)amino)-1-phenylpropan-1-one (D)

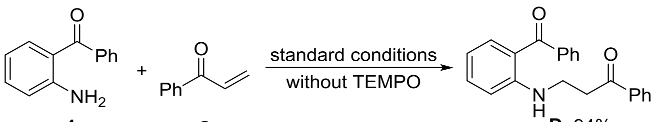
Eluent: petroleum ether/ethyl acetate (10:1). Yellow solid, mp 88-89 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.38 (t, *J* = 7.2 Hz, 2H), 3.75 (q, *J* = 6.8 Hz, 2H), 6.54 (t, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 1H), 7.37-7.51 (m, 7H), 7.53-7.59 (m, 3H), 7.97 (d, *J* = 7.6 Hz, 2H), 8.73 (br s, 1H). ^{13}C NMR (100 MHz,

$CDCl_3$) δ 37.8, 38.1, 111.4, 114.0, 117.5, 128.1, 128.7, 129.1, 130.8, 133.4, 135.1, 135.7, 136.7, 140.5, 151.5, 198.2. 199.3. HRMS calcd for $C_{22}H_{19}NNaO_2$: 352.1308 $[M+Na]^+$, found: 352.1326.

3.2. To a 15 mL reaction tube equipped with a stir bar were added **4a** (98.5 mg, 0.5 mmol), toluene (3.0 mL), $Cu(OAc)_2$ (9.1 mg, 0.05 mmol), 2,2'-bipyridine (15.6 mg, 0.1 mmol), TEMPO (78.1 mg, 0.5 mmol) and **C** (79.2 mg, 0.6 mmol) with stirring. After being flushed with N_2, the tube was sealed, and the mixture was stirred at 120 ℃ for 24 h. Afterwards, the resulting mixture was diluted with DCM (20 mL), and washed with water (10 mL) and brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as the eluent to give **5a** (142.2 mg, 92%).

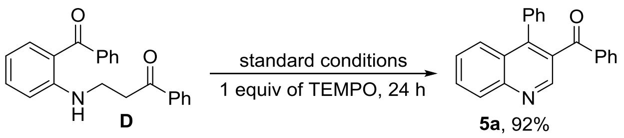


3.3. To a 15 mL reaction tube equipped with a stir bar were added **4a** (98.5 mg, 0.5 mmol), toluene (3.0 mL), $Cu(OAc)_2$ (9.1 mg, 0.05 mmol), 2,2'-bipyridine (15.6 mg, 0.1 mmol) and **C** (79.2 mg, 0.6 mmol) with stirring. After being flushed with N_2, the tube was sealed, and the mixture was stirred at 120 ℃ for 36 h. Afterwards, the resulting mixture was diluted with DCM (20 mL), and washed with water (10 mL) and brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as the eluent to give **D** (154.7 mg, 94%).

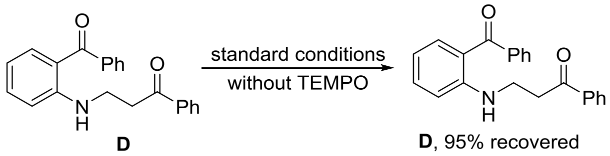


3.4. To a 15 mL reaction tube equipped with a stir bar were added **D** (164.6 mg, 0.5 mmol), toluene (3 mL), $Cu(OAc)_2$ (9.1 mg, 0.05 mmol), 2,2'-bipyridine (15.6 mg, 0.1 mmol) and TEMPO (78.1 mg, 0.5 mmol) with stirring. After being flushed with N_2, the tube was sealed, and the mixture was stirred at

120 ℃ for 24 h. Afterwards, the resulting mixture was diluted with DCM (20 mL), and washed with water (10 mL) and brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as the eluent to give **5a** (142.2 mg, 92%).

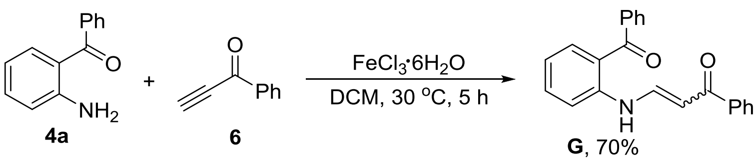


3.5. To a 15 mL reaction tube equipped with a stir bar were added **D** (164.6 mg, 0.5 mmol), toluene (3.0 mL), $Cu(OAc)_2$ (9.1 mg, 0.05 mmol) and 2,2'-bipyridine (15.6 mg, 0.1 mmol) with stirring. After being flushed with N_2, the tube was sealed, and the mixture was stirred at 120 ℃ for 36 h. From the resulting mixture, 95% of **D** were recovered.



4. Control experiments (II)

4.1. To a 50 mL reaction tube equipped with a stir bar were added 1-phenylprop-2-yn-1-one (**6**, 130.0 mg, 1 mmol), DCM (10 mL), **4a** (394.2 mg, 2 mmol) and $FeCl_3$ $6H_2O$ (13.5 mg, 0.05 mol). The mixture was then stirred at 30 ℃ for 5 h. The resulting mixture was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as the eluent to afford 3-((2-benzoylphenyl)amino)-1-phenylprop-2-en-1-one (**G**, 229.0 mg, 70%).[3]

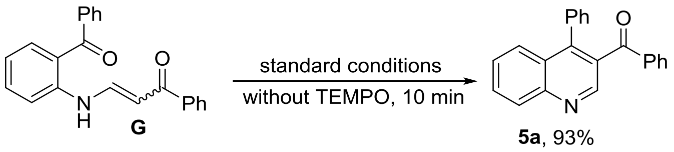


3-((2-Benzoylphenyl)amino)-1-phenylprop-2-en-1-one (G)

Eluent: petroleum ether/ethyl acetate (10:1). Yellow solid, mp 104-105 ℃. ^1H NMR (600 MHz, $CDCl_3$) δ 6.14 (d, J = 8.4 Hz, 1H), 7.02 (t, J = 7.8 Hz, 1H), 7.38-7.48 (m, 6H), 7.50-7.57 (m, 4H), 7.79 (d, J = 7.8

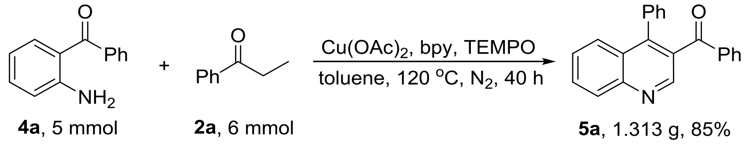
Hz, 2H), 8.02 (d, *J* = 7.8 Hz, 2H), 13.38 (d, *J* = 12.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 96.4, 115.1, 121.2, 124.0, 127.8, 128.1, 128.3, 130.3, 131.6, 132.3, 133.7, 133.8, 138.6, 139.1, 142.4, 190.4, 197.1. HRMS calcd for $C_{22}H_{17}NNaO_2$: 350.1151 $[M+Na]^+$, found: 350.1162.

4.2. To a 15 mL reaction tube equipped with a stir bar were added **G** (163.6 mg, 0.5 mmol), toluene (3.0 mL), $Cu(OAc)_2$ (9.1 mg, 0.05 mmol) and 2,2'-bipyridine (15.6 mg, 0.1 mmol) with stirring. After being flushed with N_2, the tube was sealed, and the mixture was stirred at 120 ℃ for 10 min. Afterwards, the resulting mixture was diluted with DCM (20 mL), and washed with water (10 mL) and brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as the eluent to give **5a** (143.7 mg, 93%).



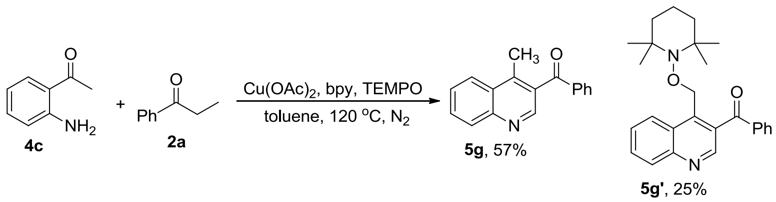
5. Gram scale synthesis of 5a

To a 100 mL reaction tube equipped with a stir bar were added **4a** (985.4 mg, 5 mmol), toluene (20 mL), $Cu(OAc)_2$ (90.8 mg, 0.5 mmol), 2,2'-bipyridine (156.1 mg, 1 mmol), TEMPO (1.56 g, 10 mmol) and **2a** (0.80 mL, 6 mmol) with stirring. After being flushed with N_2, the tube was sealed, and the mixture was stirred at 120 ℃ for 40 h. Upon completion, the resulting mixture was diluted with DCM (50 mL), and washed with water (20 mL) and brine (20 mL). The organic layer was dried over anhydrous Na_2SO_4 and contentrated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as the eluent to give **5a** (1.313 g, 85%).



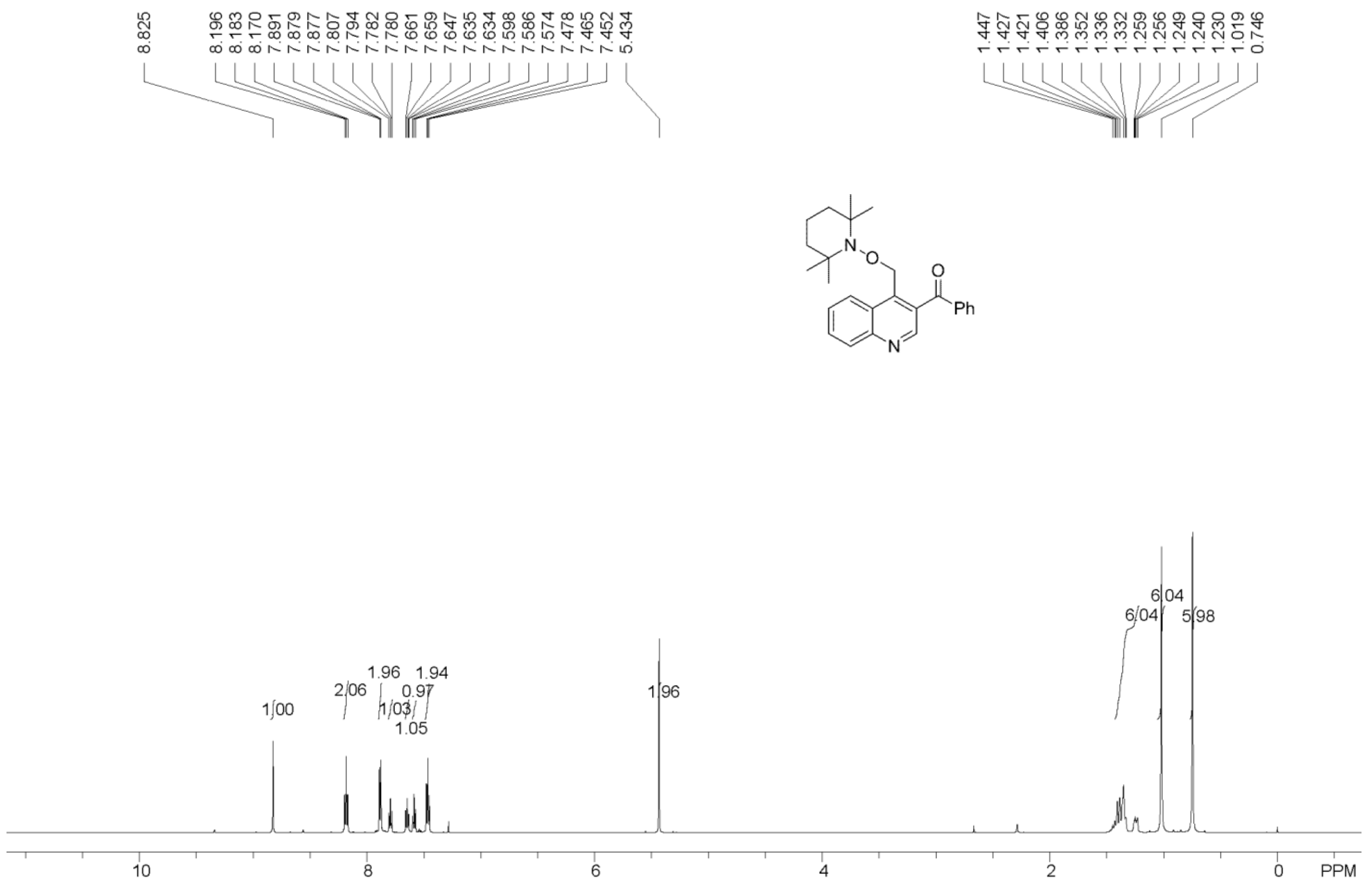
6. The formation of 5g' along with the formation of 5g

The fact that **5g-5k** were obtained only in moderate yields (see Table 3 of the main text) is mainly due to the formation of TEMPO-related side products. Taking **5g** as an example, under the standard reaction conditions, the formation of **5g** is along with the formation of phenyl(4-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)quinolin-3-yl)methanone (**5g′**) in a yield of 25%.



To a 15 mL reaction tube equipped with a stir bar were added 1-(2-aminophenyl)ethan-1-one (**4c**, 67.5 mg, 0.5 mmol), toluene (3.0 mL), $Cu(OAc)_2$ (9.1 mg, 0.05 mmol,), 2,2'-bipyridine (15.6 mg, 0.1 mmol), TEMPO (156.1 mg, 1 mmol) and propiophenone (**2a**, 80 μL, 0.6 mmol) with stirring. After being flushed with N_2, the tube was sealed, and the mixture was stirred at 120 ^{o}C for 36 h. Upon completion, the resulting mixture was diluted with DCM (20 mL), and washed with water (10 mL) and brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as the eluent to give **5g** (70.4 mg, 57%) and **5g'** (50.2 mg, 25%).

Phenyl(4-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)quinolin-3-yl)methanone (5g'): Eluent: petroleum ether/ethyl acetate (10:1). Yellow solid, mp 112-114 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 0.75 (s, 6H), 1.02 (s, 6H), 1.23-1.45 (m, 6H), 5.43 (s, 2H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.63-7.66 (m, 1H), 7.78-7.81 (m, 1H), 7.88 (t, *J* = 7.2 Hz, 2H), 8.18 (t, *J* = 7.8 Hz, 2H), 8.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.0, 20.3, 32.7, 39.7, 60.0, 124.7, 125.5, 127.4, 128.5, 130.21, 130.24, 130.3, 131.4, 133.6, 137.3, 142.3, 148.2, 148.6, 195.8. MS: m/z 403 $[M+H]^+$.



III. References

(1) S. Khong and O. Kwon, *J. Org. Chem.*, 2012, **77**, 8257.

(2) P.-K. Mahata, C. Venkatesh, U.-K.-S. Kumar, H. Ila and H. Junjappa, *J. Org. Chem.*, 2003, **68**, 3966.

(3) H. Li, X. Xu, J. Yang, X. Xie, H. Huang and Y. Li, *Tetrahedron Lett.*, 2011, **52**, 530.

(4) E. Cini, E. Petricci, G.-I. Truglio, M. Vecchio and M. Taddei, *RSC Adv.*, 2016, **6**, 31386.

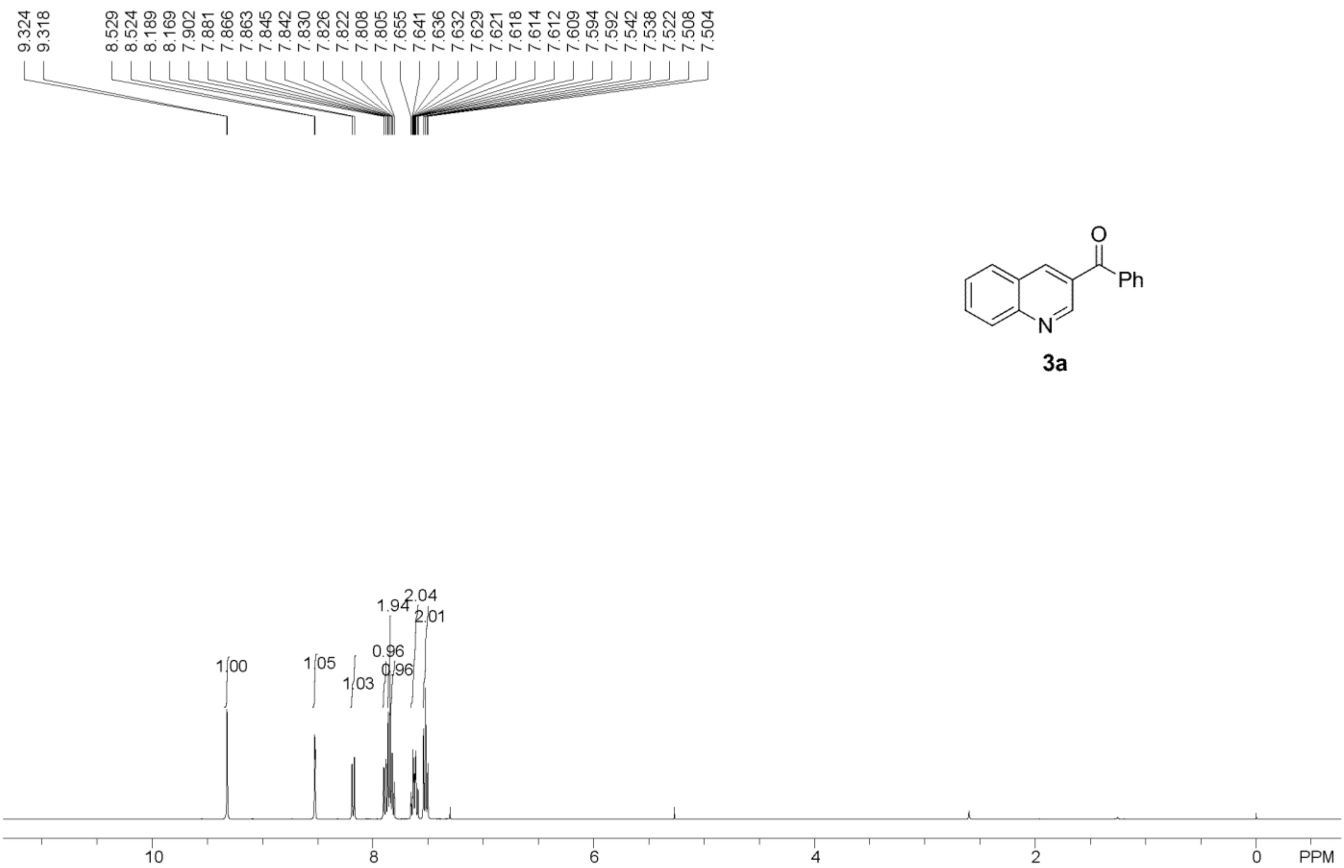
(5) N. Anand, T. Chanda, S. Koley, S. Chowdhury and M.-S.Singh, *RSC Adv.*, 2015, **5**, 7654.

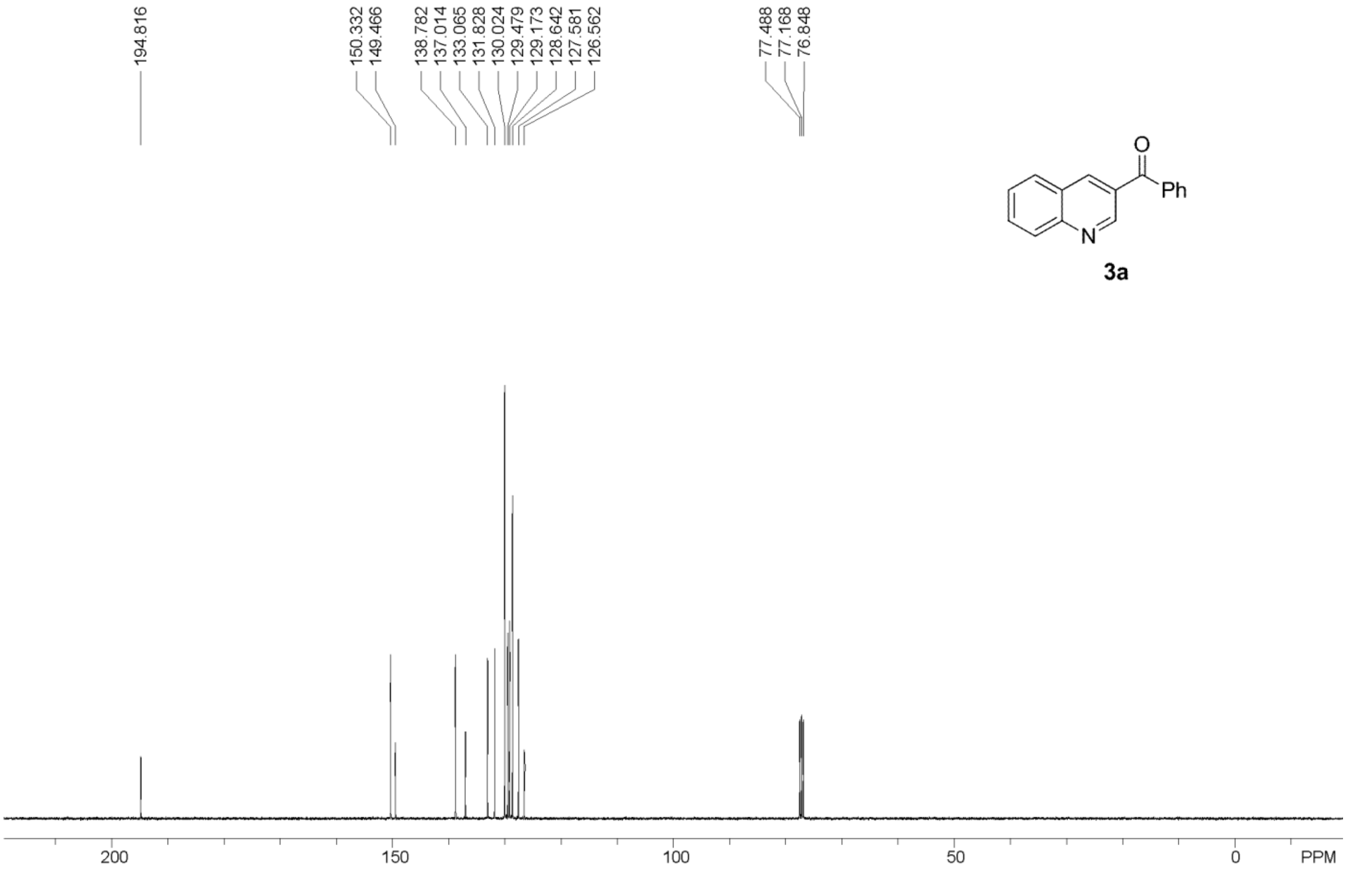
(6) L. Luo, Z. Zhou, J. Zhu, X. Lu and H. Wang, *Tetrahedron Lett.*, 2016, **57**, 4987.

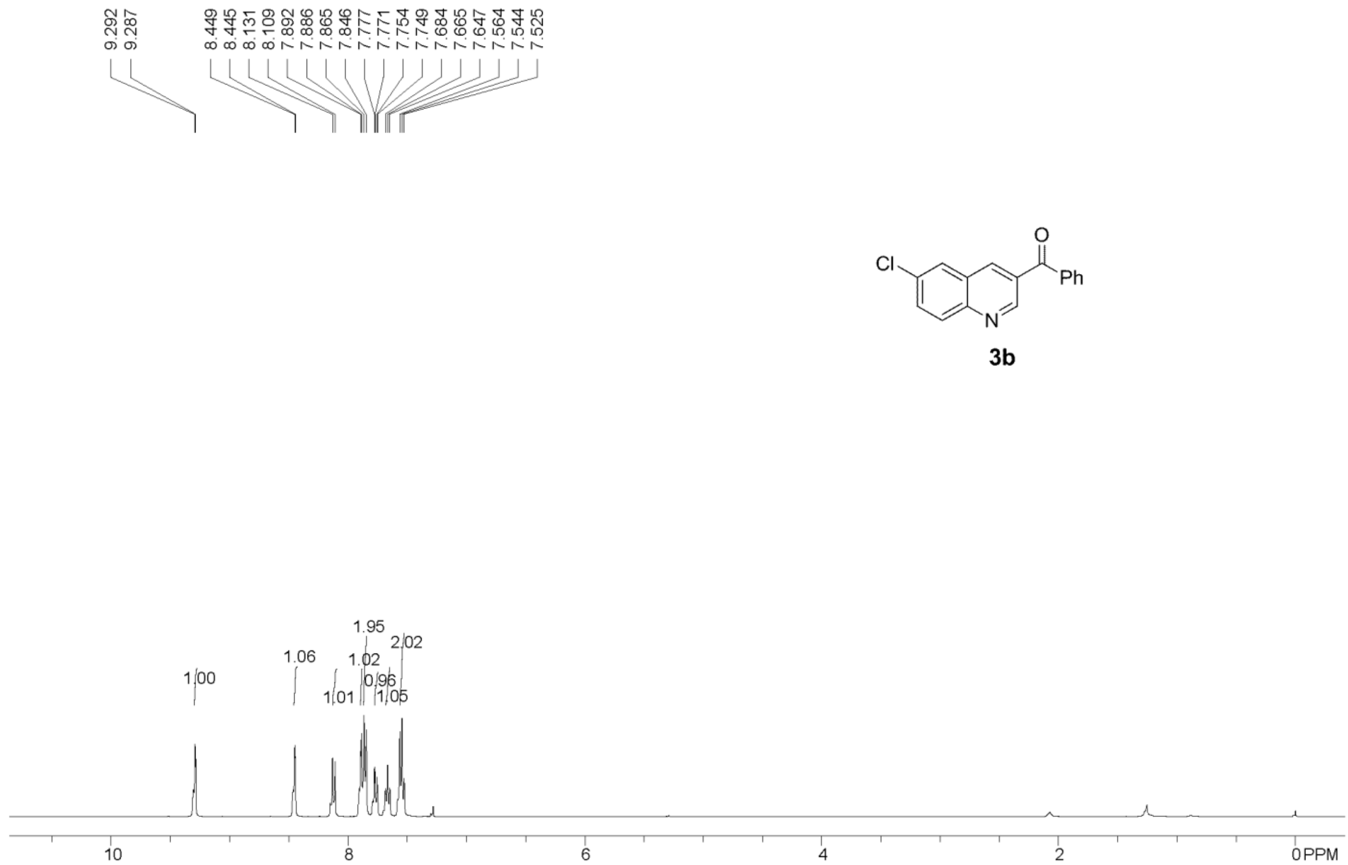
(7) W.-Y. Gao, K. Leng, L. Cash, M. Chrzanowski, C.-A. Stackhouse, Y. Sun and S. Ma, *Chem. Commun.*, 2015, **51**, 4827.

(8) X. Jie, Y. Shang, X. Zhang and W. Su, *J. Am. Chem. Soc.*, 2016, **138**, 5623.

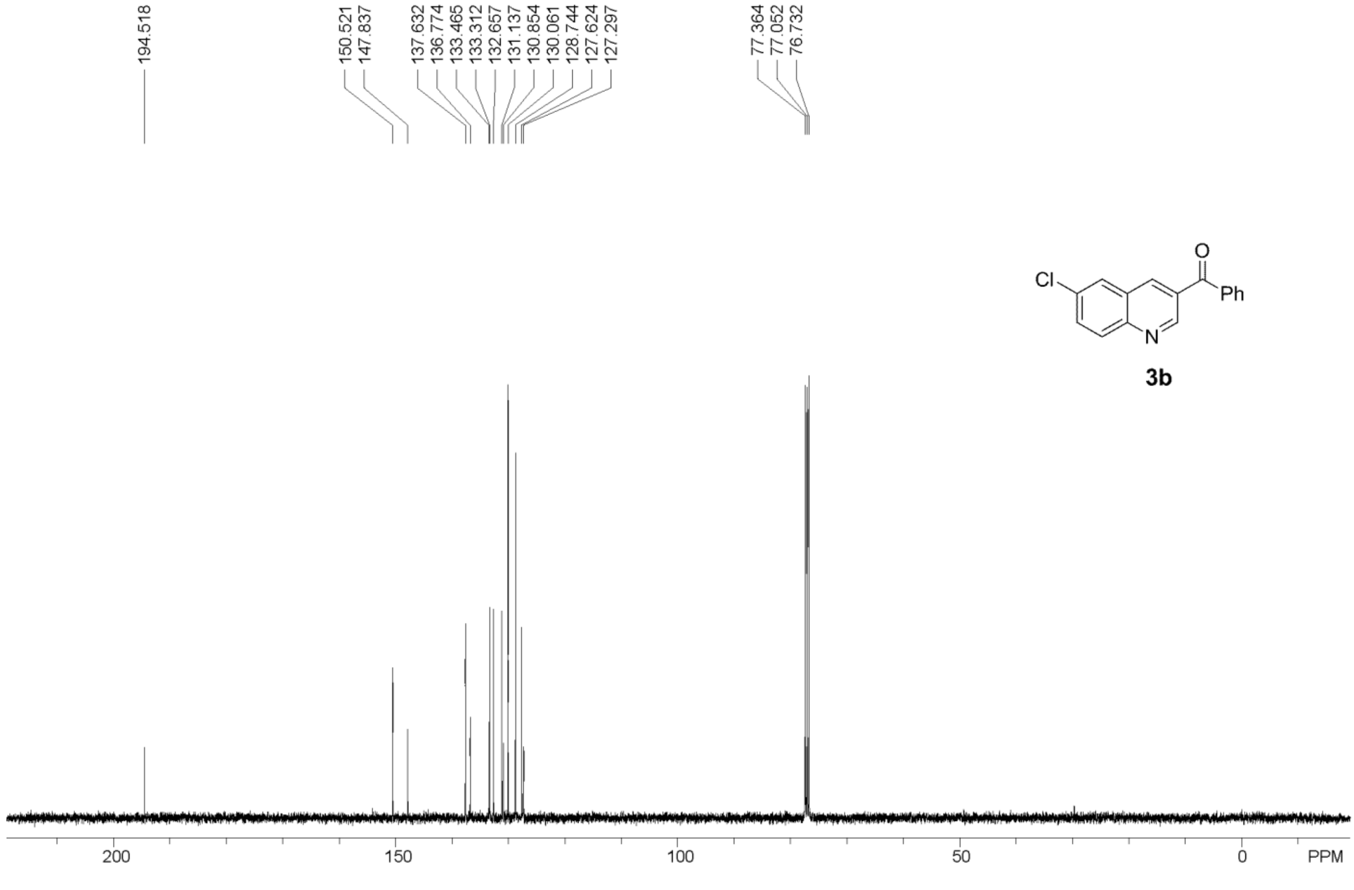
IV. Copies of ^{1}H and ^{13}C NMR spectra of 3a-3r



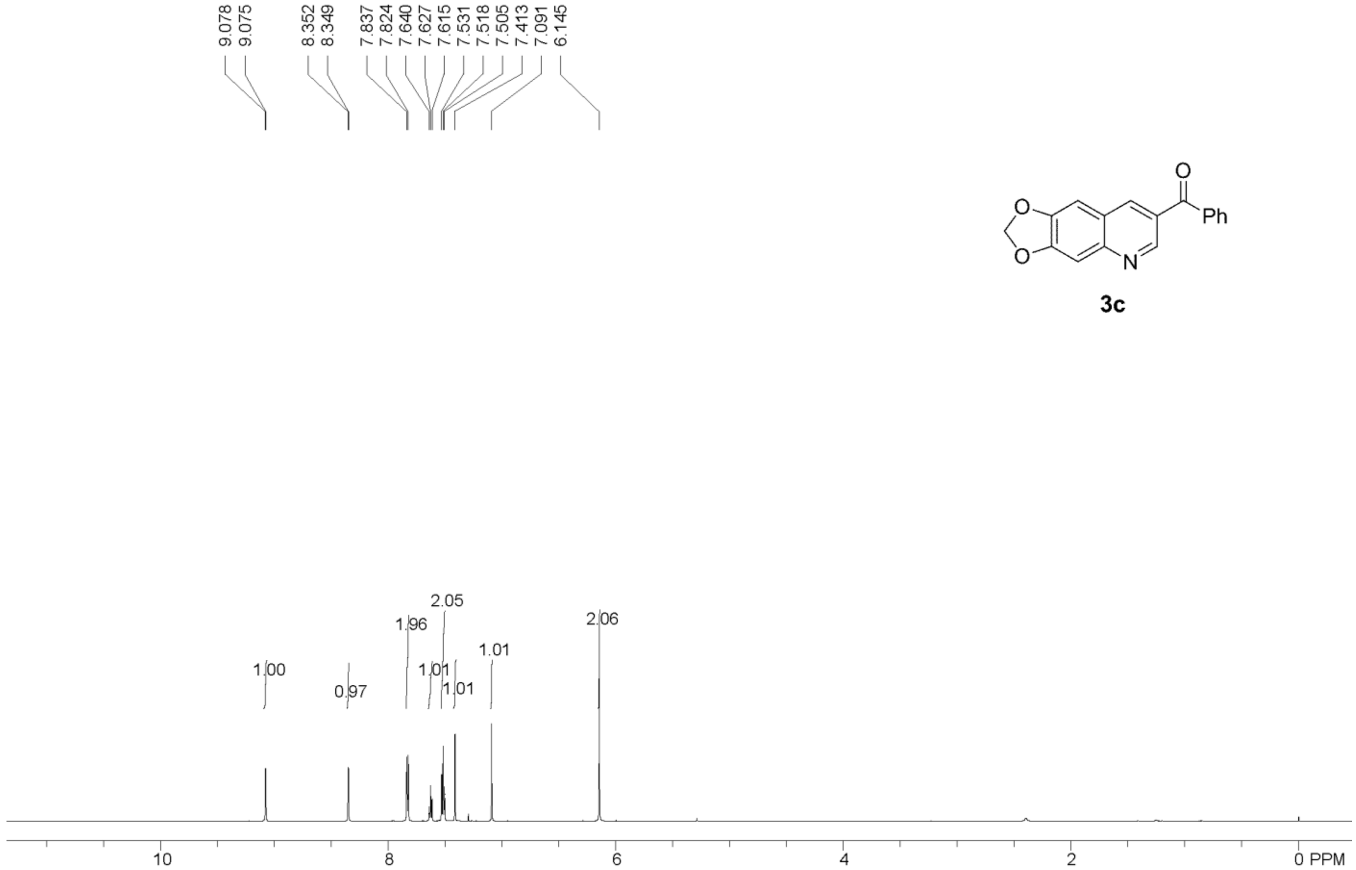


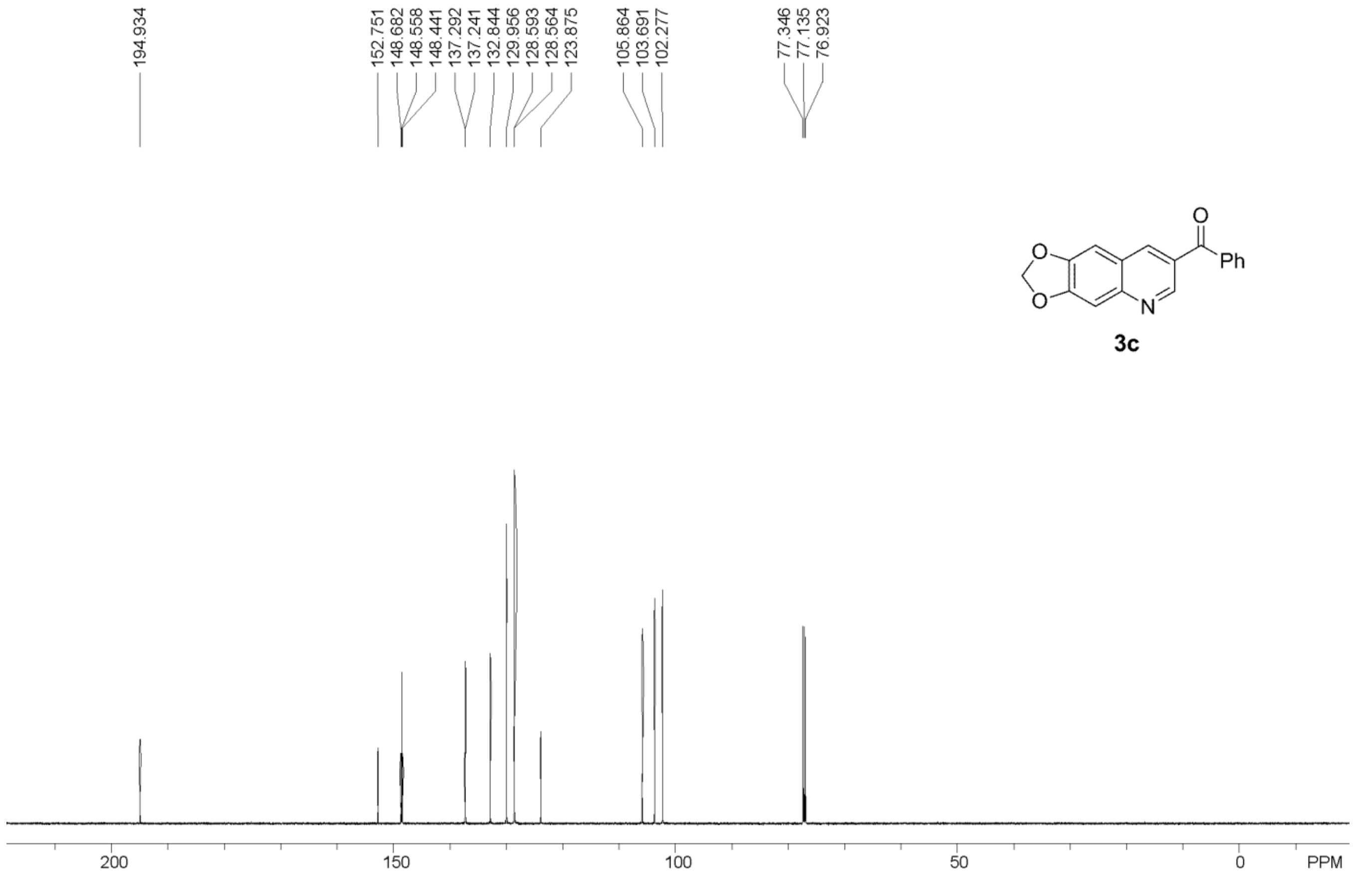

9.292
9.287
8.449
8.445
8.131
8.109
7.892
7.886
7.865
7.846
7.777
7.771
7.754
7.749
7.684
7.665
7.647
7.564
7.544
7.525
1.00
1.06
1.01
1.95
1.02
0.96
1.05
2.02
10
8
6
4
2
0 PPM

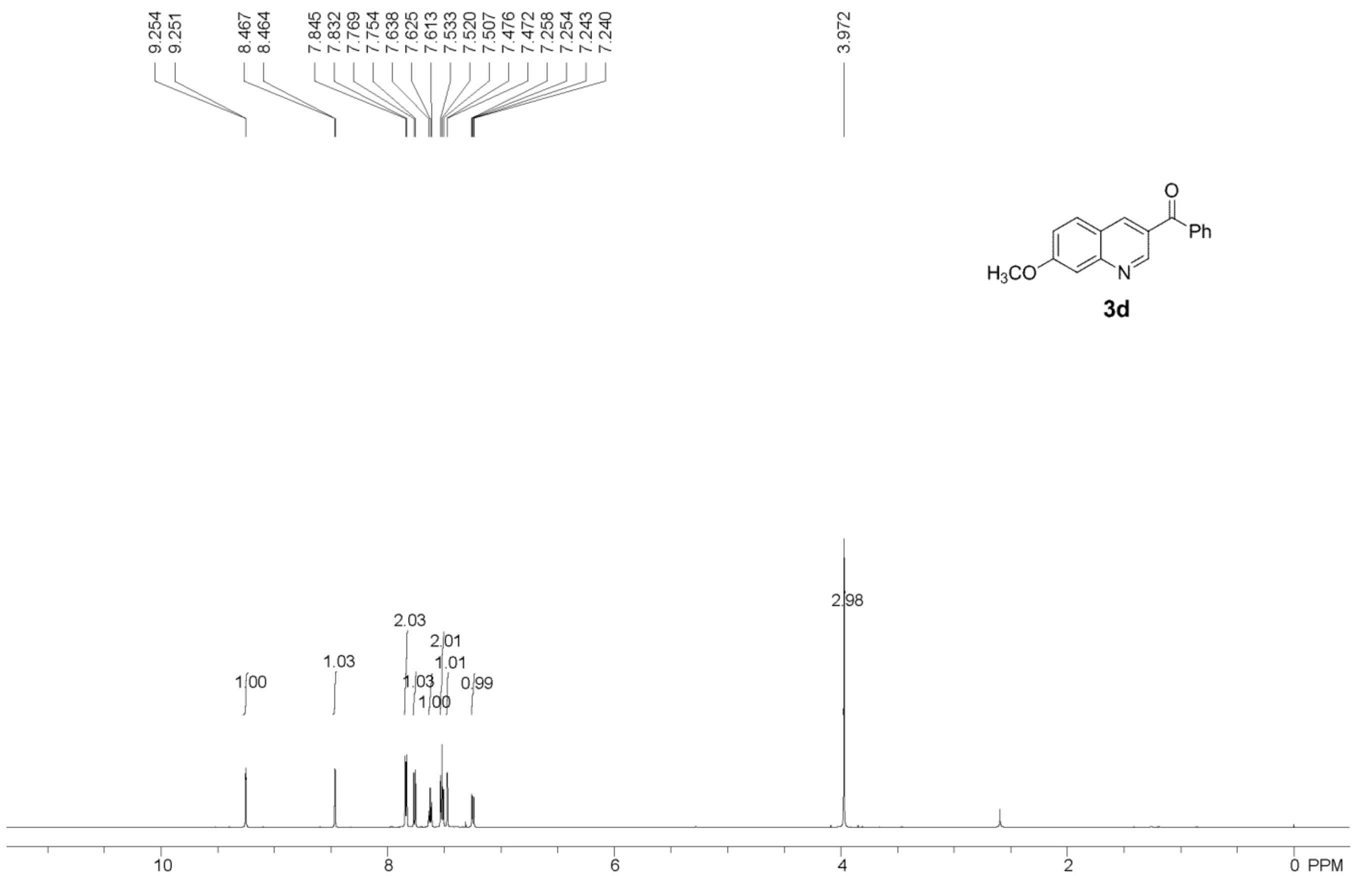
3b

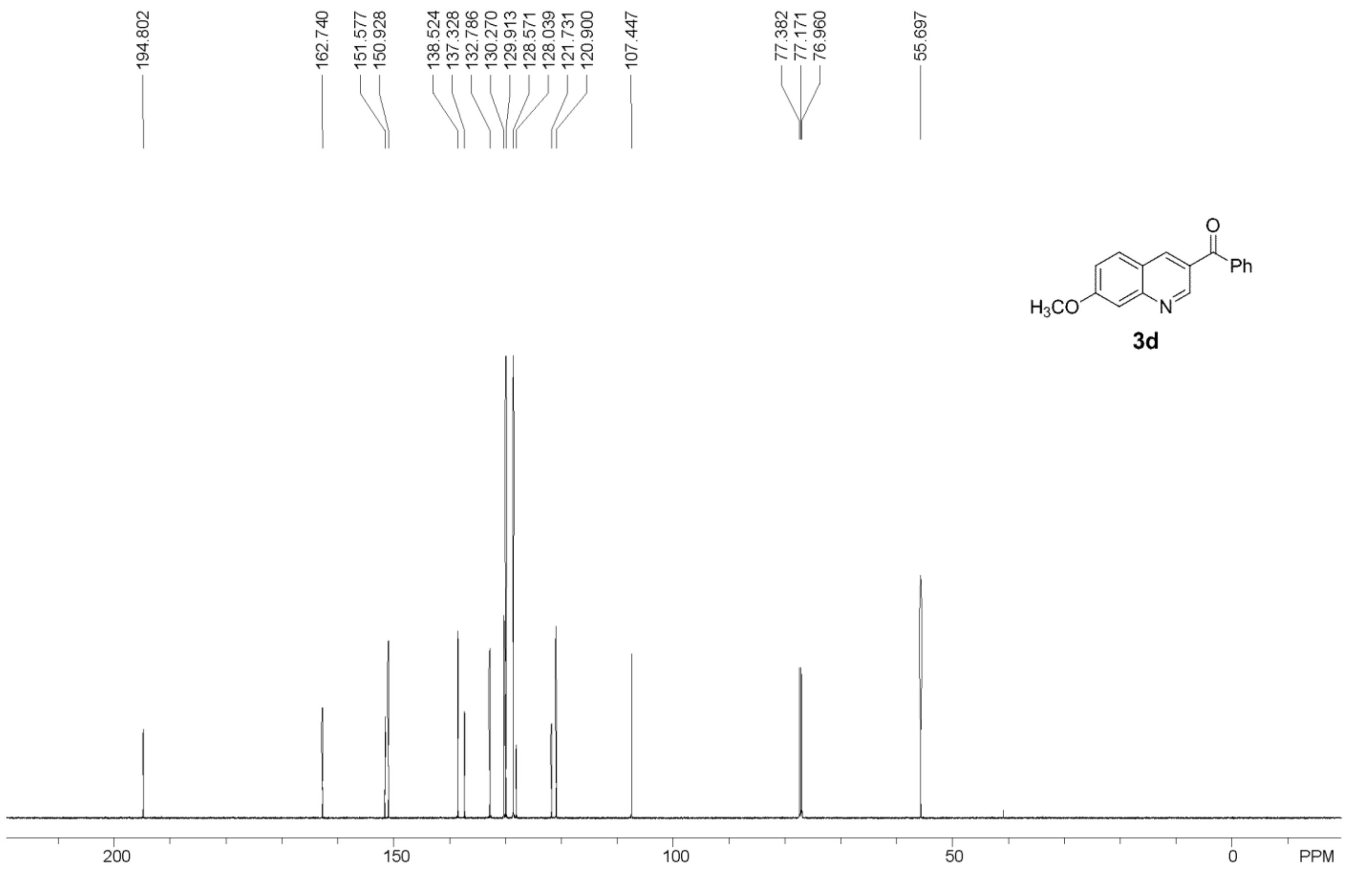

194.518
150.521
147.837
137.632
136.774
133.465
133.312
132.657
131.137
130.854
130.061
128.744
127.624
127.297
77.364
77.052
76.732
200
150
100
50
0
PPM

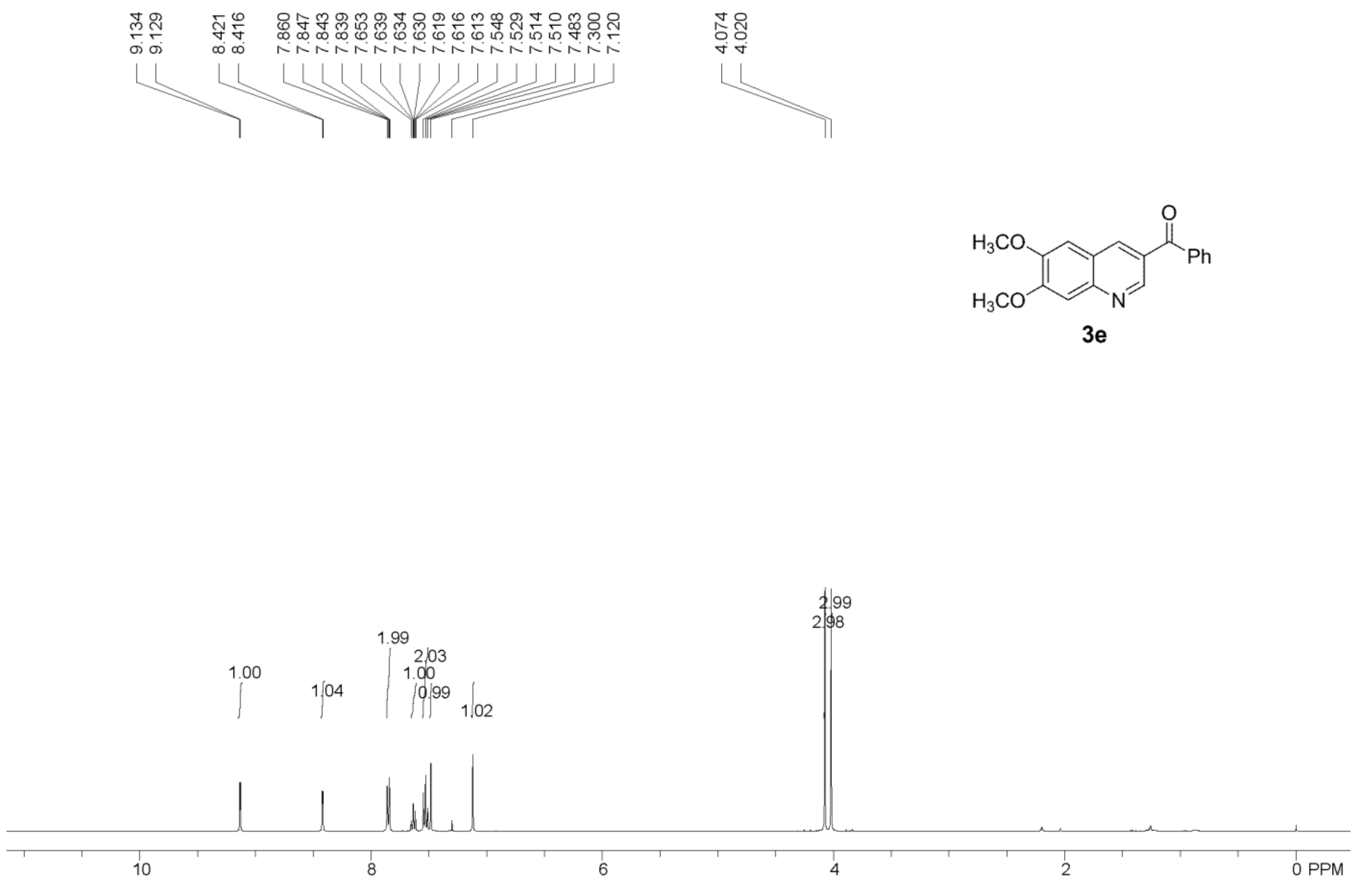
3b

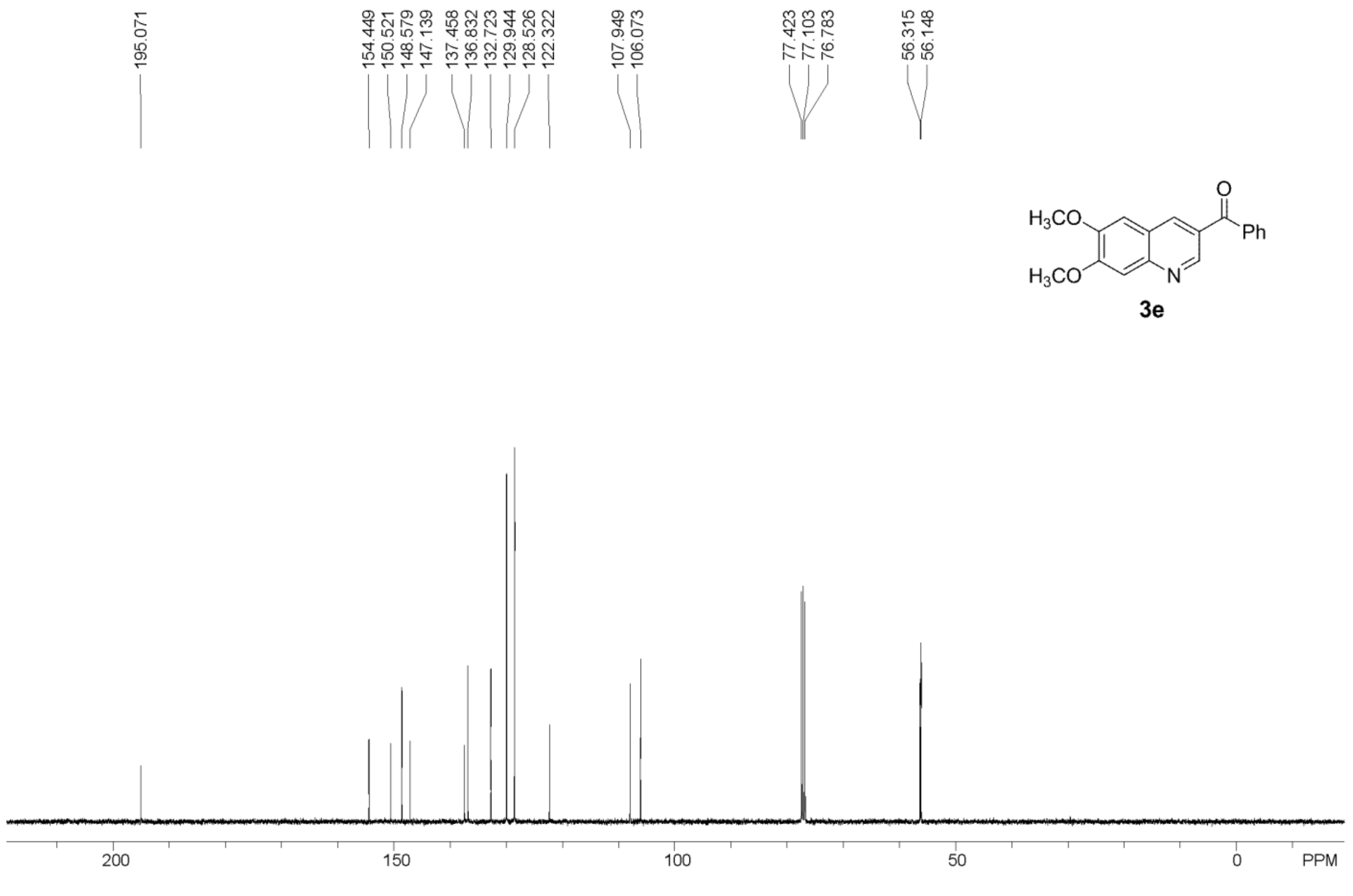

9.078
9.075
8.352
8.349
7.837
7.824
7.640
7.627
7.615
7.531
7.518
7.505
7.413
7.091
6.145
O
Ph
O
O
N
3c
1.00
0.97
1.96
2.05
1.01
1.01
1.01
2.06
10
8
6
4
2
0 PPM

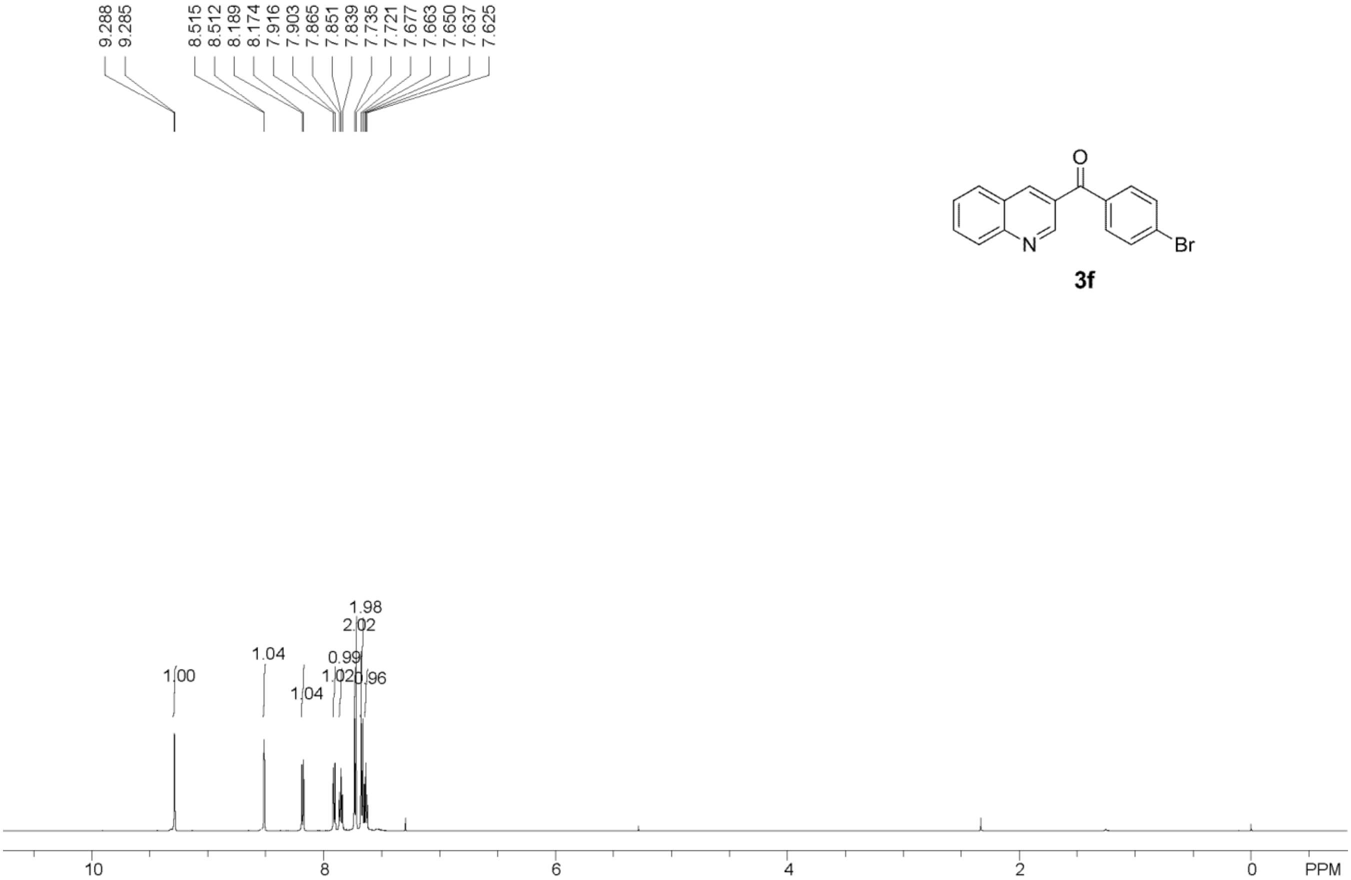

194.934
152.751
148.682
148.558
148.441
137.292
137.241
132.844
129.956
128.593
128.564
123.875
105.864
103.691
102.277
77.346
77.135
76.923
O
Ph
O
O
N
3c
200
150
100
50
0
PPM


9.254
9.251
8.467
8.464
7.845
7.832
7.769
7.754
7.638
7.625
7.613
7.533
7.520
7.507
7.476
7.472
7.258
7.254
7.243
7.240
3.972
Ph
H3CO
N
3d
1.00
1.03
2.03
1.03
1.00
2.01
1.01
0.99
2.98
10
8
6
4
2
0 PPM


194.802
162.740
151.577
150.928
138.524
137.328
132.786
130.270
129.913
128.571
128.039
121.731
120.900
107.447
77.382
77.171
76.960
55.697
Ph
H3CO
N
3d
200
150
100
50
0
PPM

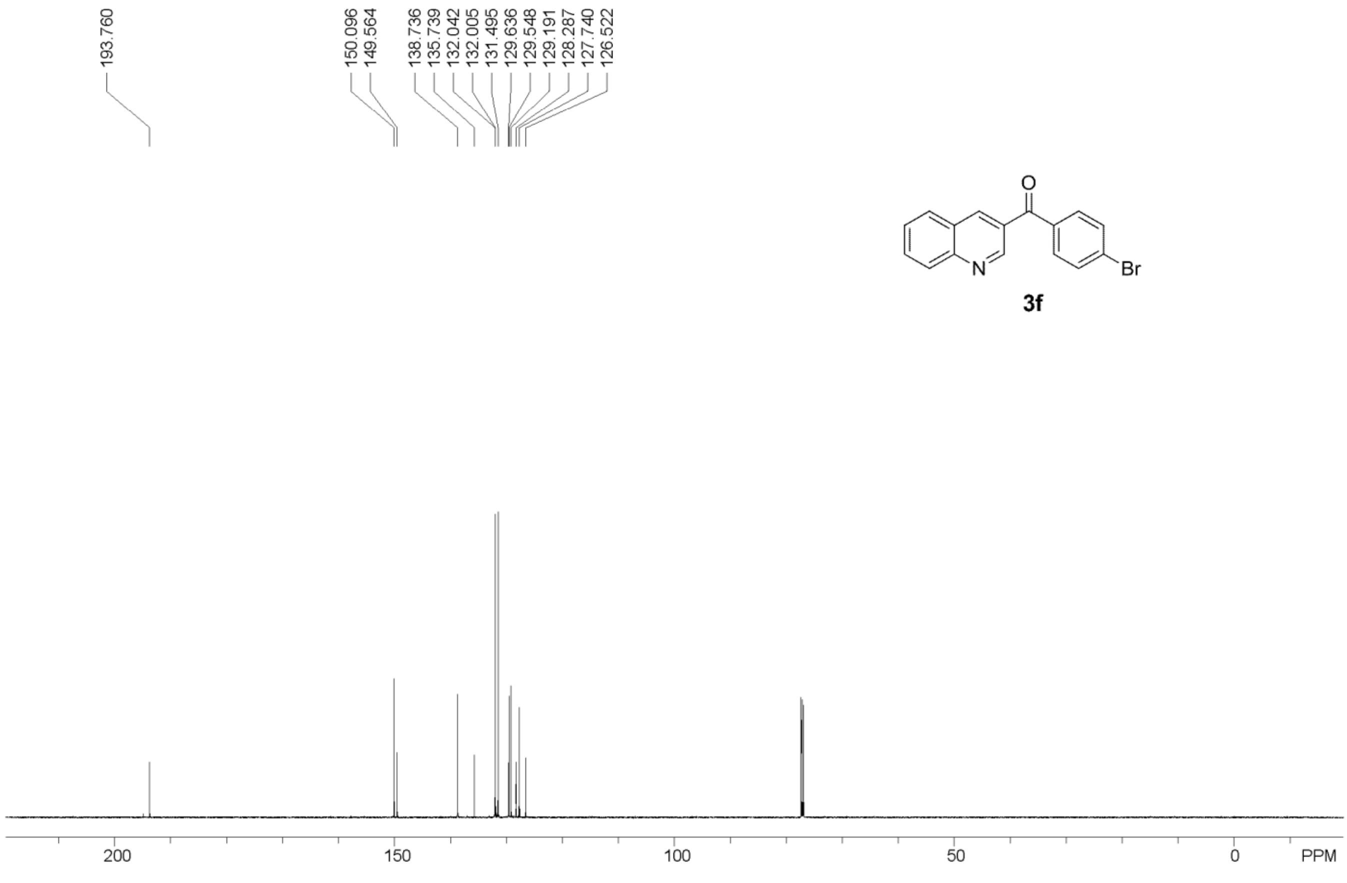

9.134
9.129
8.421
8.416
7.860
7.847
7.843
7.839
7.653
7.639
7.634
7.630
7.619
7.616
7.613
7.548
7.529
7.514
7.510
7.483
7.300
7.120
4.074
4.020
H_3CO
H_3CO
O
Ph
N
3e
1.00
1.04
1.99
2.03
1.00
0.99
1.02
2.99
2.98
10
8
6
4
2
0 PPM


195.071
154.449
150.521
148.579
147.139
137.458
136.832
132.723
129.944
128.526
122.322
107.949
106.073
77.423
77.103
76.783
56.315
56.148
H_3CO
H_3CO
O
Ph
N
3e
200
150
100
50
0
PPM



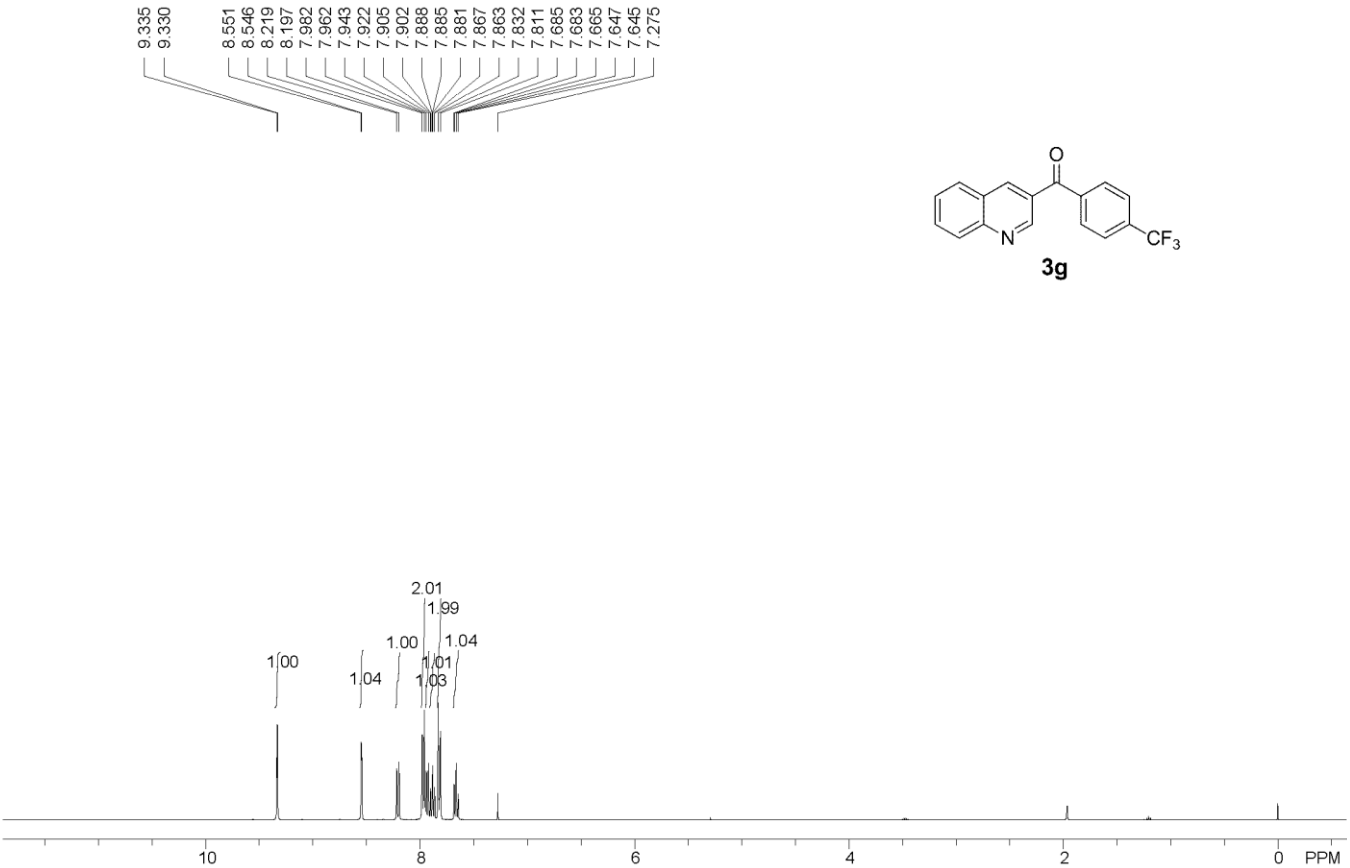
9.288
9.285
8.515
8.512
8.189
8.174
7.916
7.903
7.865
7.851
7.839
7.735
7.721
7.677
7.663
7.650
7.637
7.625
1.00
1.04
1.04
0.99
1.02
0.96
2.02
1.98
10
8
6
4
2
0
PPM
O
N
Br

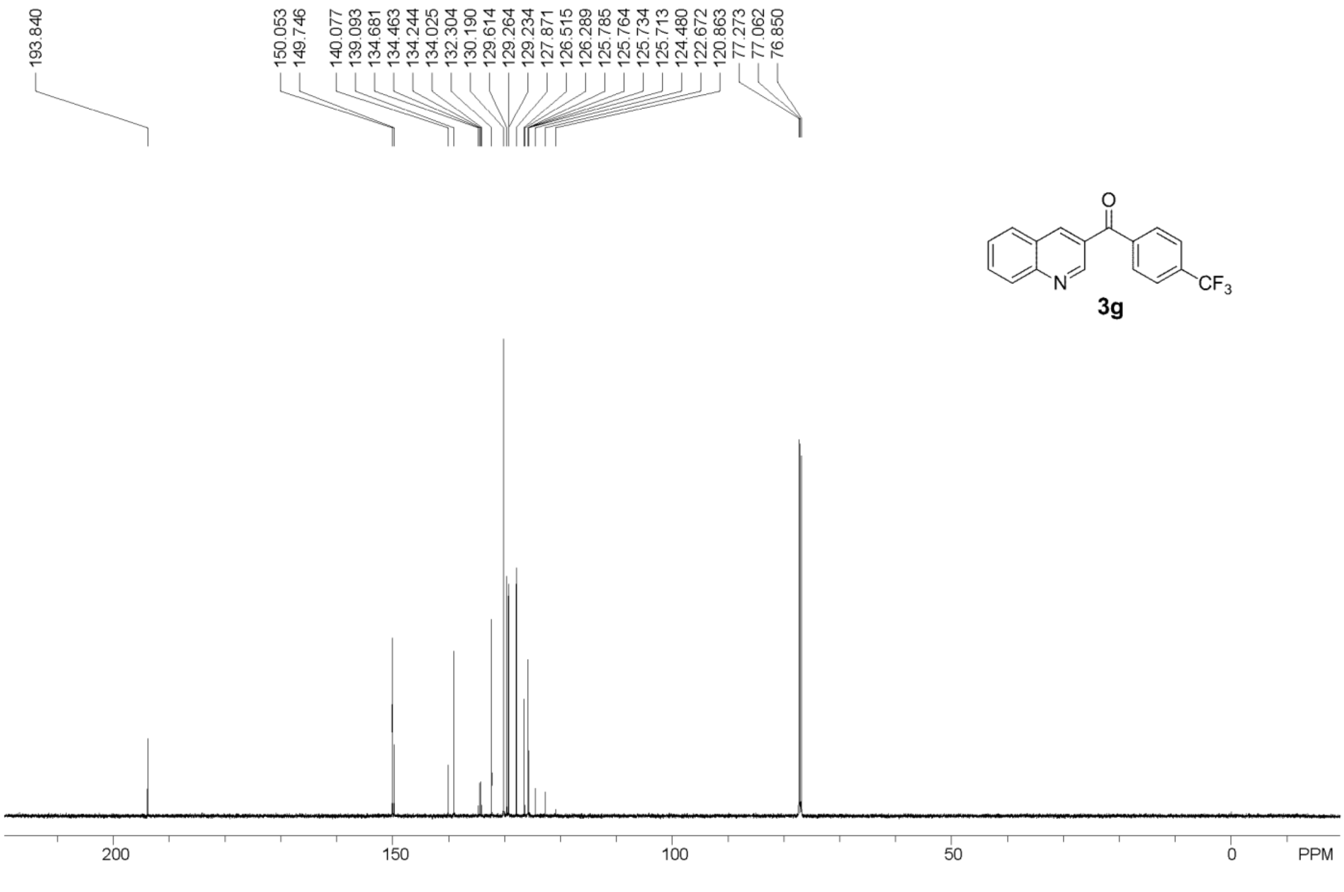
3f

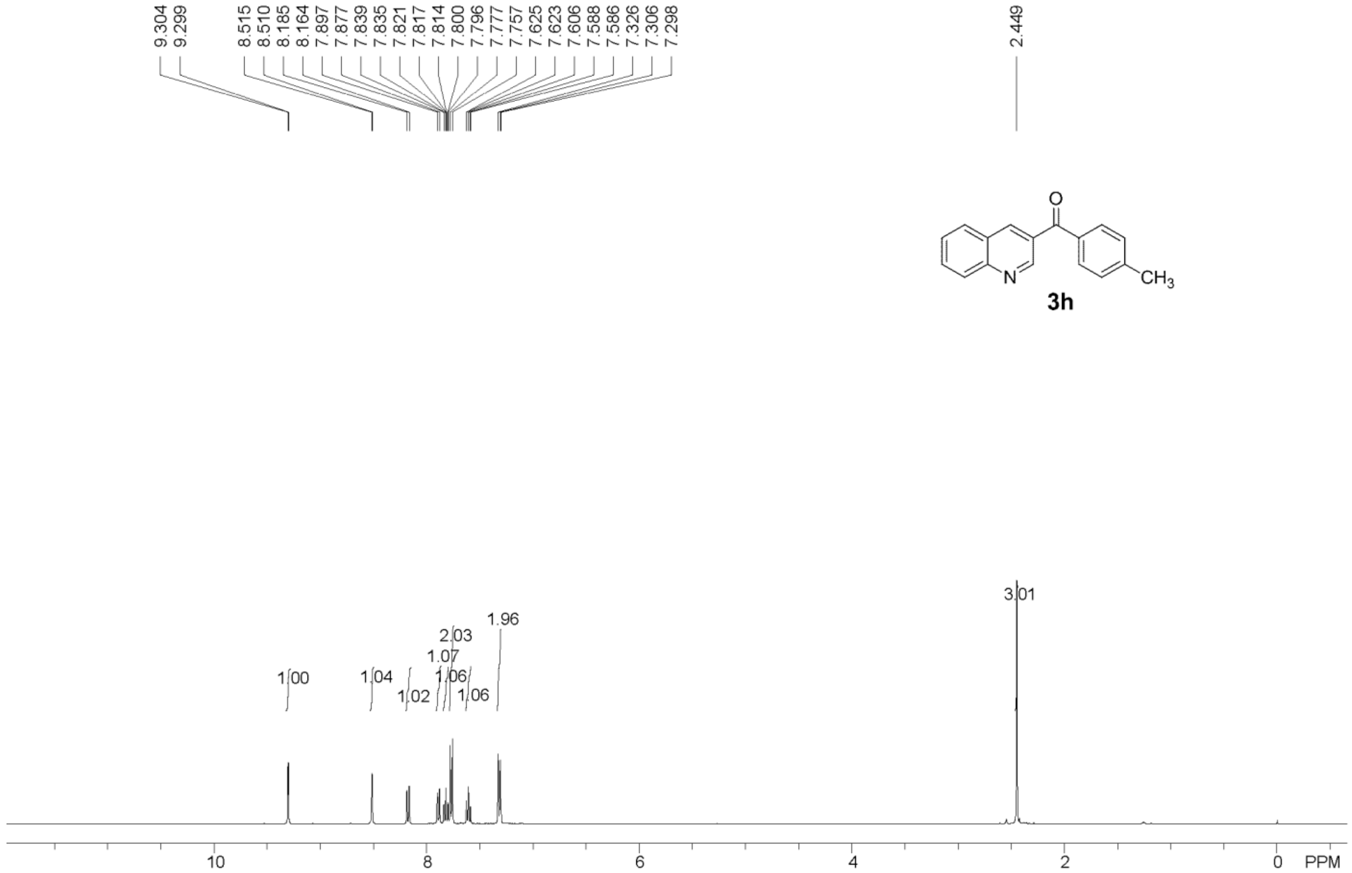


193.760
150.096
149.564
138.736
135.739
132.042
132.005
131.495
129.636
129.548
129.191
128.287
127.740
126.522
200
150
100
50
0
PPM
O
N
Br

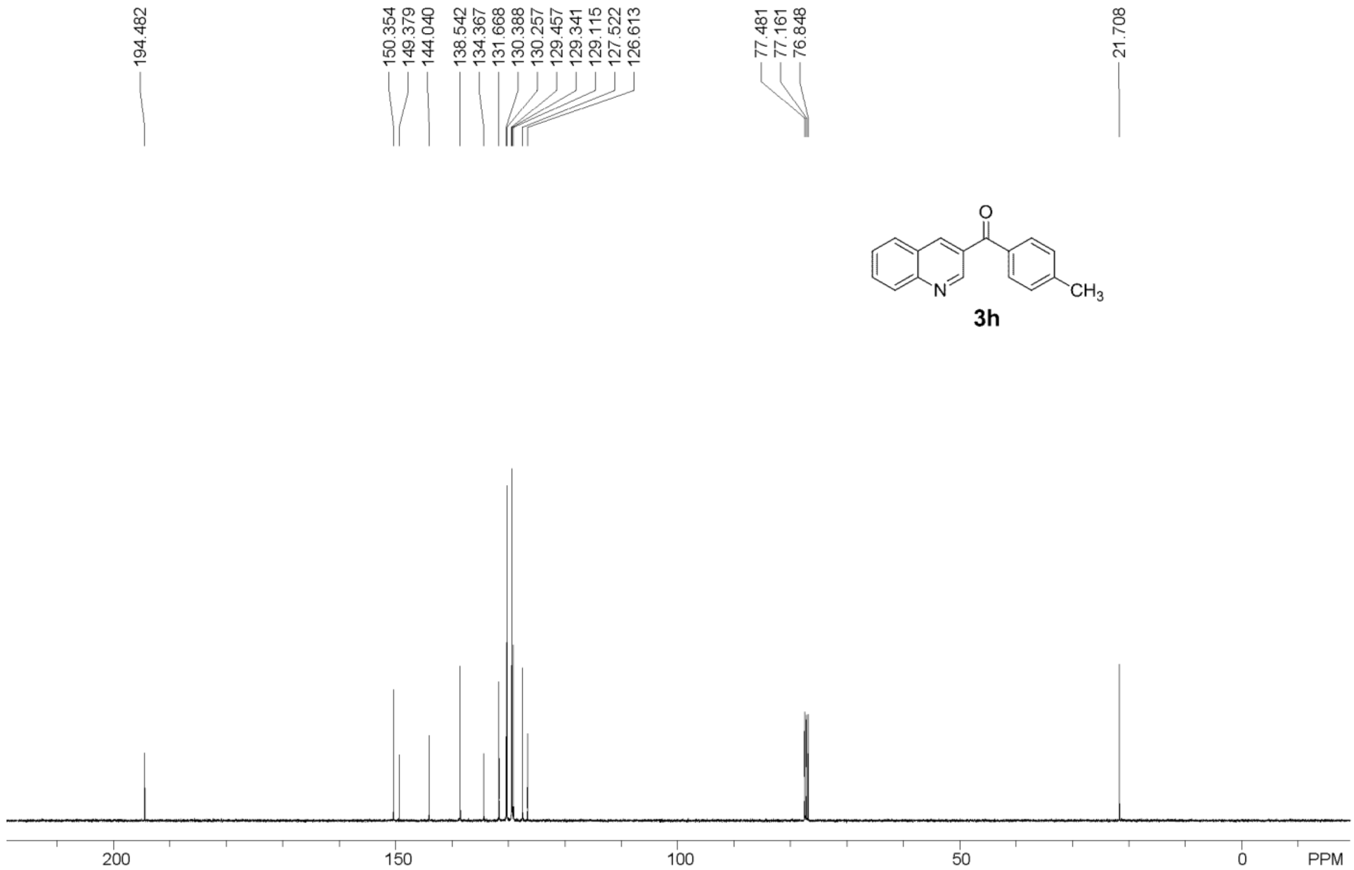
3f


9.335
9.330
8.551
8.546
8.219
8.197
7.982
7.962
7.943
7.922
7.905
7.902
7.888
7.885
7.881
7.867
7.863
7.832
7.811
7.685
7.683
7.665
7.647
7.645
7.275
O
N
CF3
3g
2.01
1.99
1.00
1.04
1.00
1.01
1.04
1.03
1.00
10
8
6
4
2
0
PPM

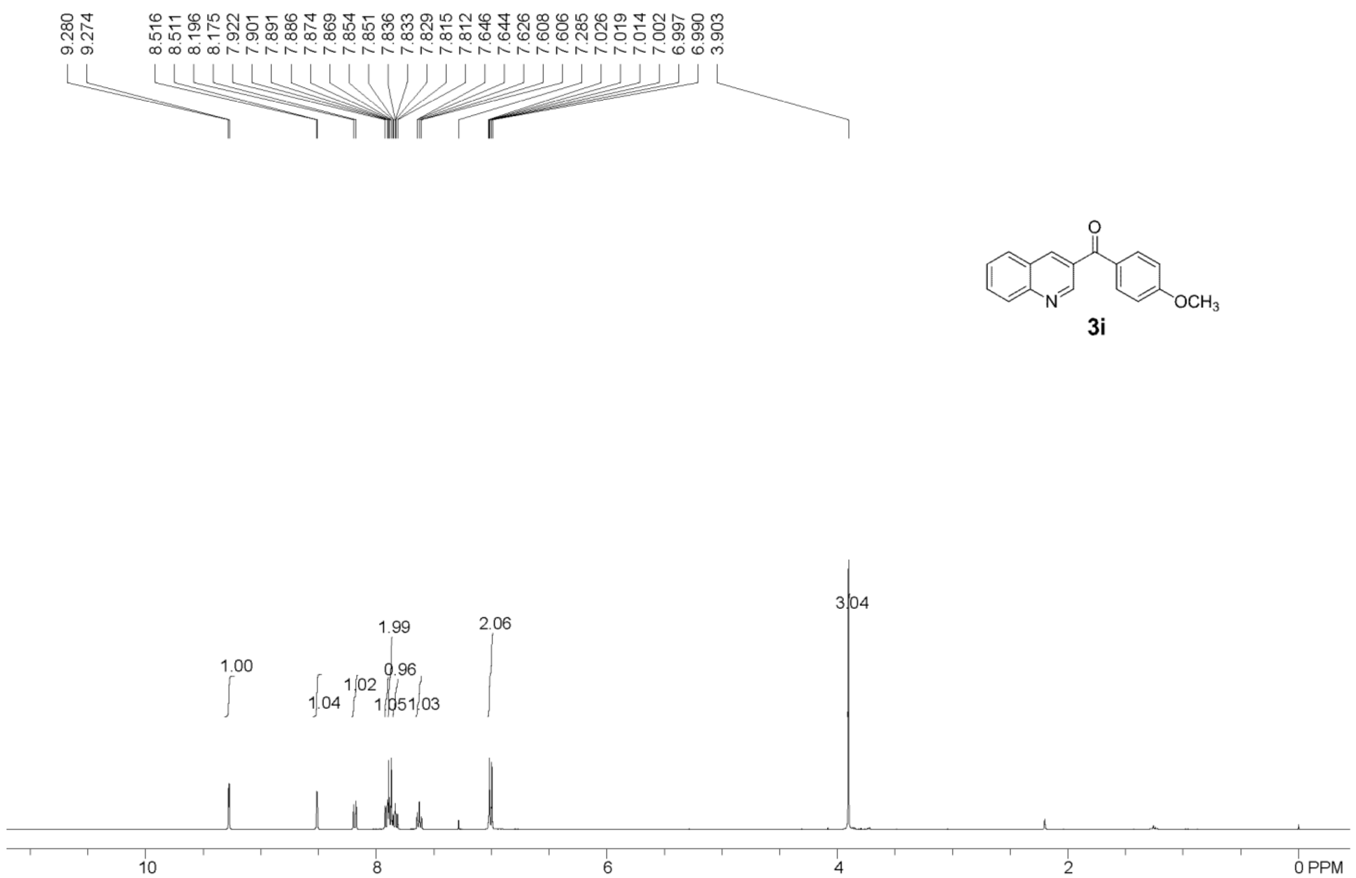

193.840
150.053
149.746
140.077
139.093
134.681
134.463
134.244
134.025
132.304
130.190
129.614
129.264
129.234
127.871
126.515
126.289
125.785
125.764
125.734
125.713
124.480
122.672
120.863
77.273
77.062
76.850
O
N
CF3
3g
200
150
100
50
0
PPM

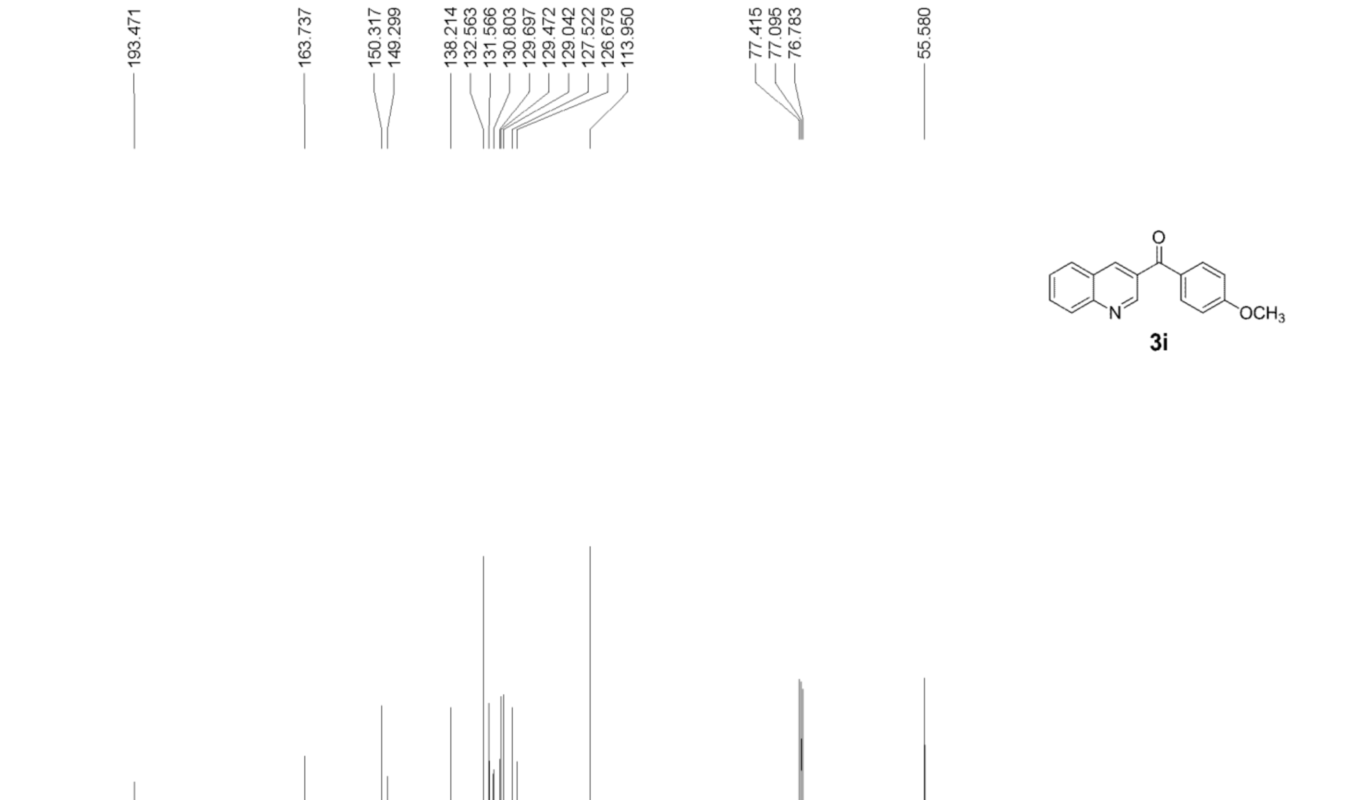

9.304
9.299
8.515
8.510
8.185
8.164
7.897
7.877
7.839
7.835
7.821
7.817
7.814
7.800
7.796
7.777
7.757
7.625
7.623
7.606
7.588
7.586
7.326
7.306
7.298
2.449
O
N
CH3
1.00
1.04
1.02
1.07
2.03
1.06
1.06
1.96
3.01
10
8
6
4
2
0
PPM

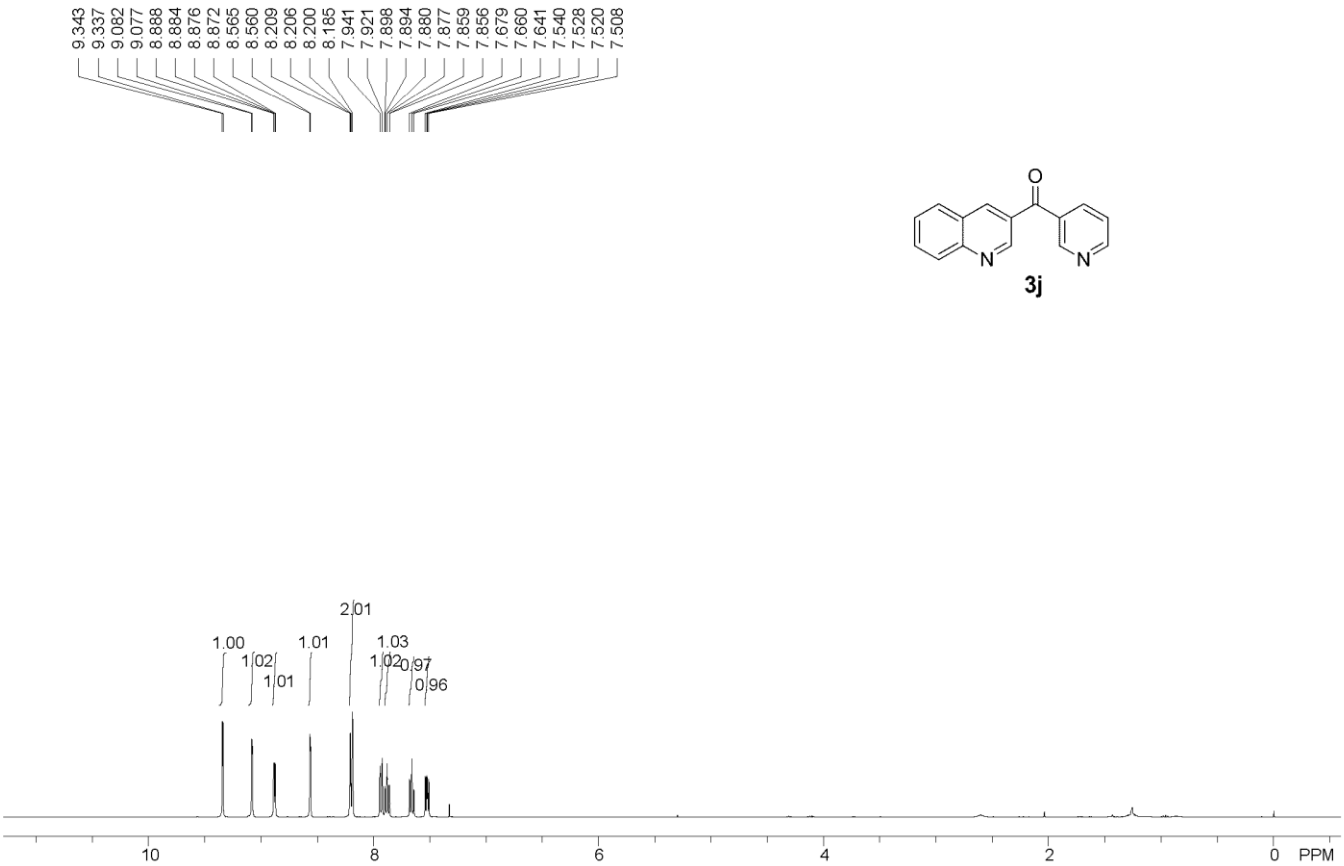
3h

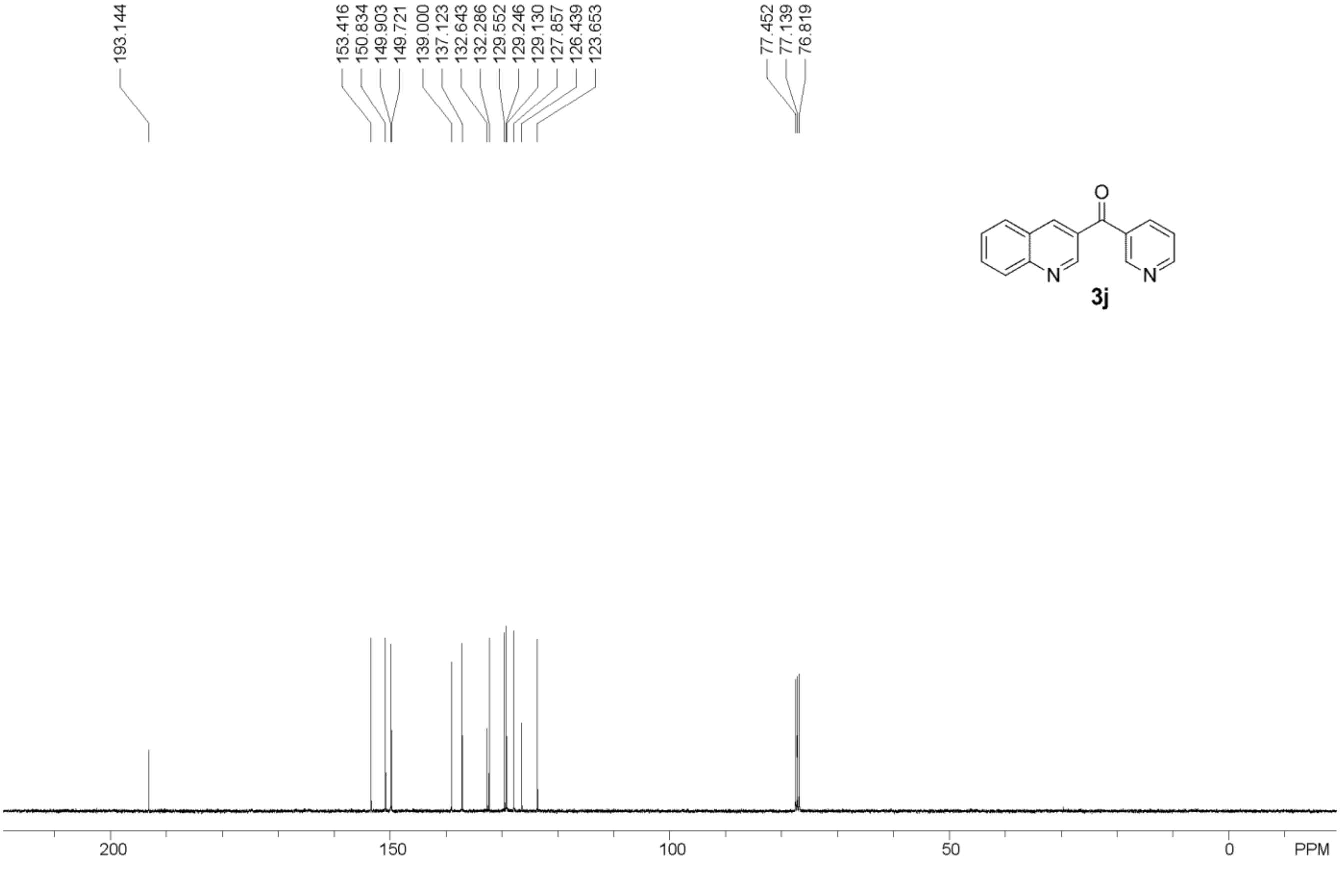

194.482
150.354
149.379
144.040
138.542
134.367
131.668
130.388
130.257
129.457
129.341
129.115
127.522
126.613
77.481
77.161
76.848
21.708
O
N
CH3
200
150
100
50
0
PPM

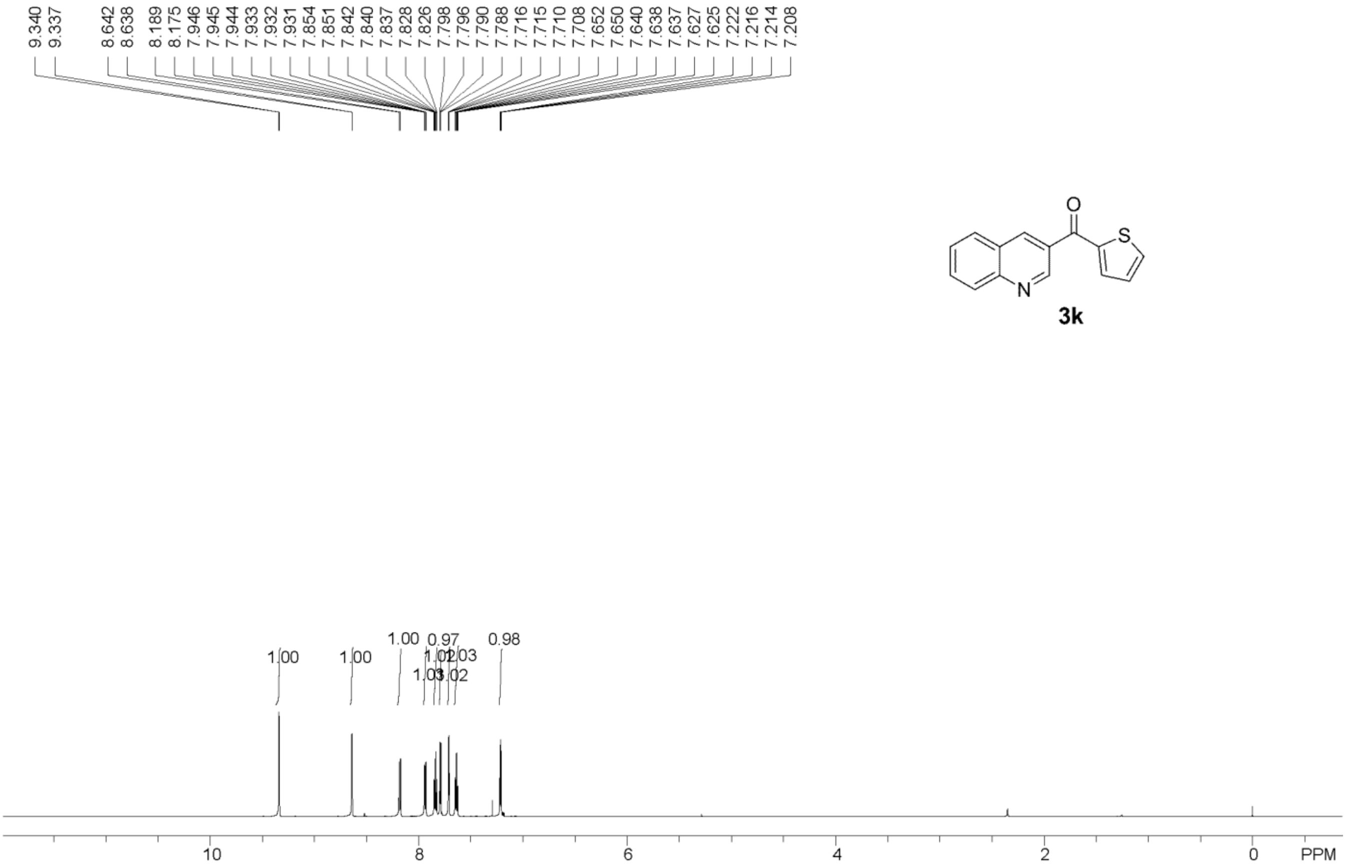
3h


9.280 9.274 8.516 8.511 8.196 8.175 7.922 7.901 7.891 7.886 7.874 7.869 7.854 7.851 7.836 7.833 7.829 7.815 7.812 7.646 7.644 7.626 7.608 7.606 7.285 7.026 7.019 7.014 7.002 6.997 6.990 3.903
O
N
OCH3
3i
1.00
1.04
1.02
1.99
0.96
1.05
1.03
2.06
3.04
10 8 6 4 2 0 PPM

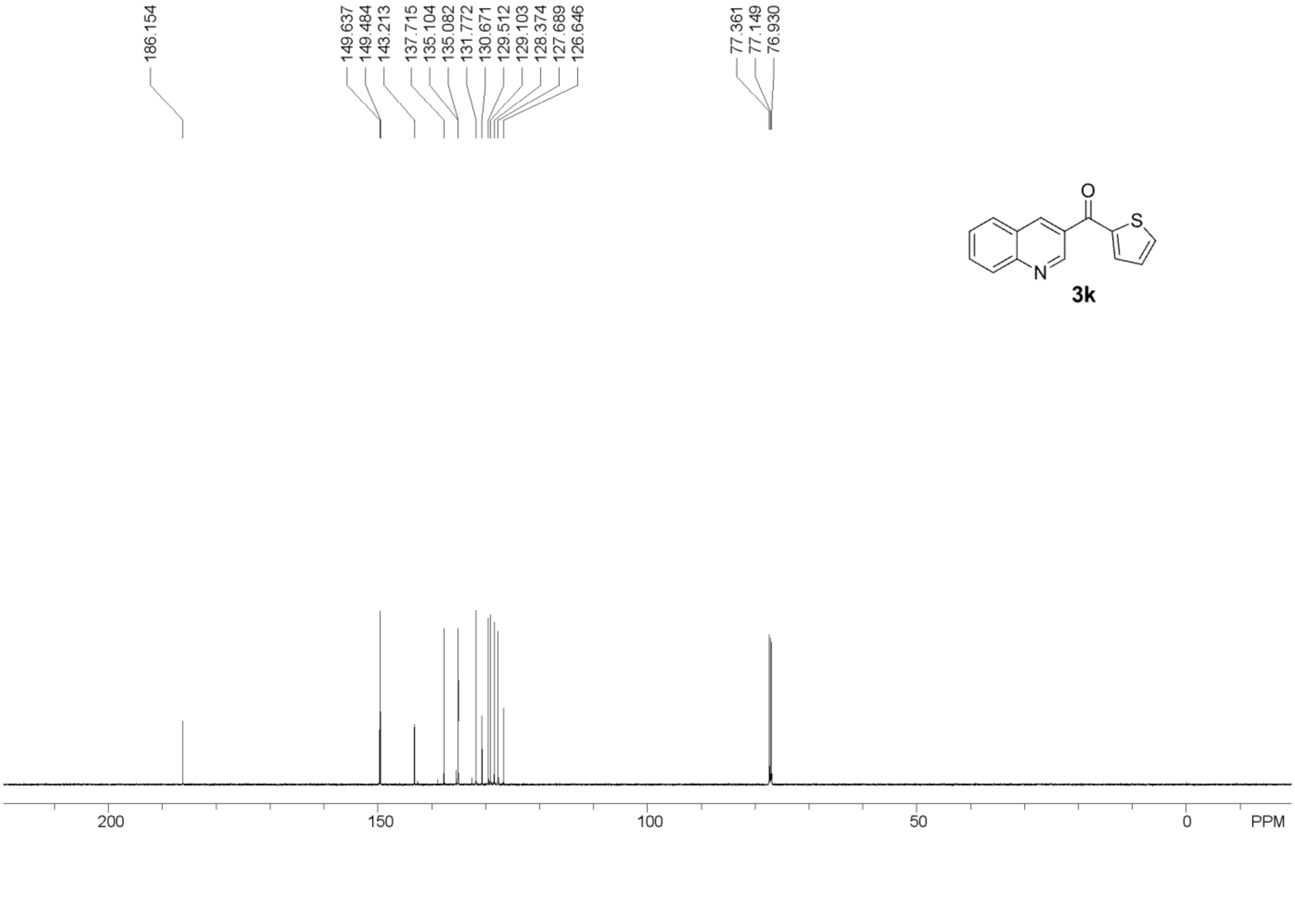

193.471 163.737 150.317 149.299 138.214 132.563 131.566 130.803 129.697 129.472 129.042 127.522 126.679 113.950 77.415 77.095 76.783 55.580
O
N
OCH3
3i
200 150 100 50 0 PPM


9.343
9.337
9.082
9.077
8.888
8.884
8.876
8.872
8.565
8.560
8.209
8.206
8.200
8.185
7.941
7.921
7.898
7.894
7.880
7.877
7.859
7.856
7.679
7.660
7.641
7.540
7.528
7.520
7.508
O
N
N
3j
1.00
1.02
1.01
1.01
2.01
1.03
1.02
0.97
0.96
10
8
6
4
2
0
PPM

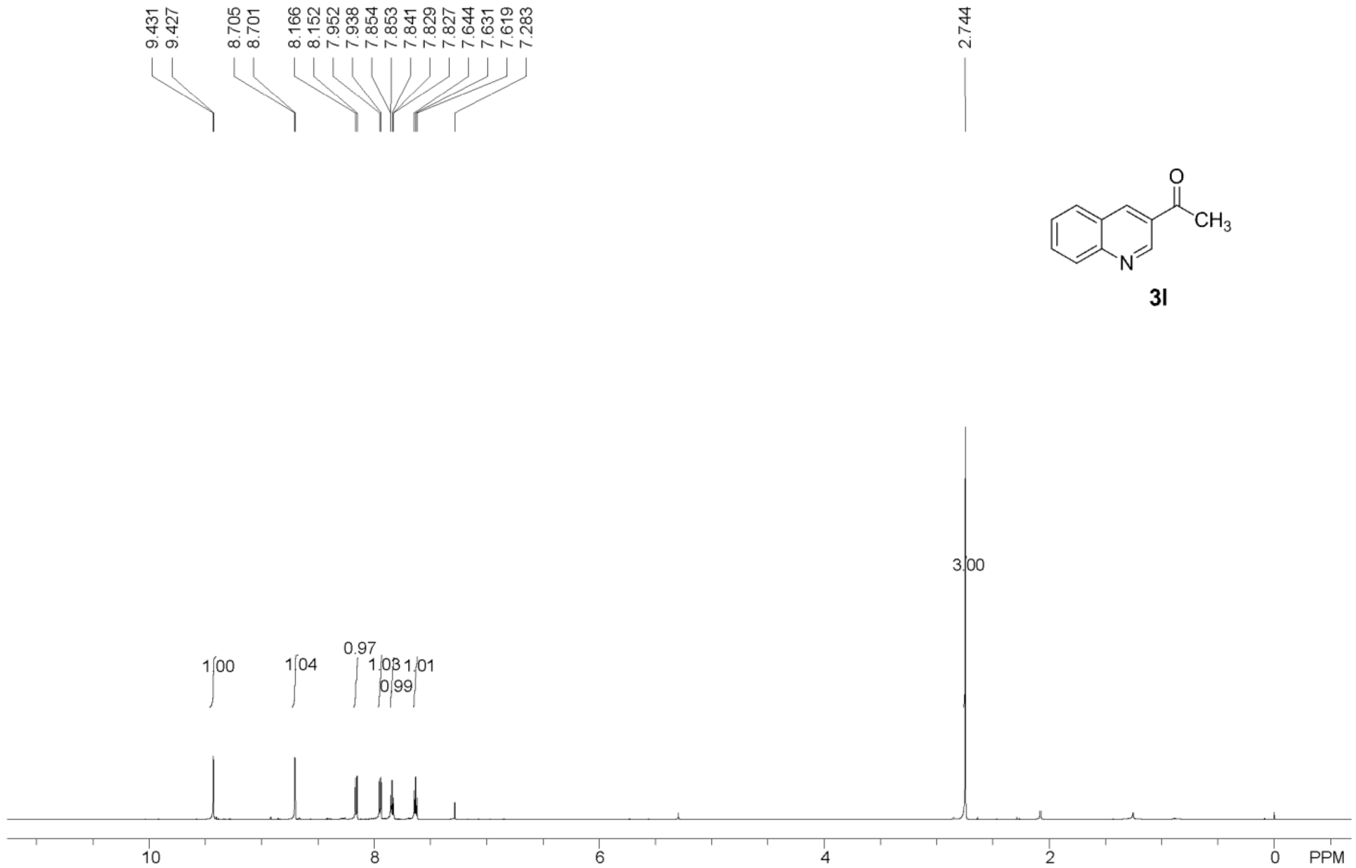

193.144
153.416
150.834
149.903
149.721
139.000
137.123
132.643
132.286
129.552
129.246
129.130
127.857
126.439
123.653
77.452
77.139
76.819
O
N
N
3j
200
150
100
50
0
PPM


9.340
9.337
8.642
8.638
8.189
8.175
7.946
7.945
7.944
7.933
7.932
7.931
7.854
7.851
7.842
7.840
7.837
7.828
7.826
7.798
7.796
7.790
7.788
7.716
7.715
7.710
7.708
7.652
7.650
7.640
7.638
7.637
7.627
7.625
7.222
7.216
7.214
7.208
O
S
N
1.00
1.00
1.00
0.97
1.02
1.03
1.03
1.02
0.98
10
8
6
4
2
0
PPM

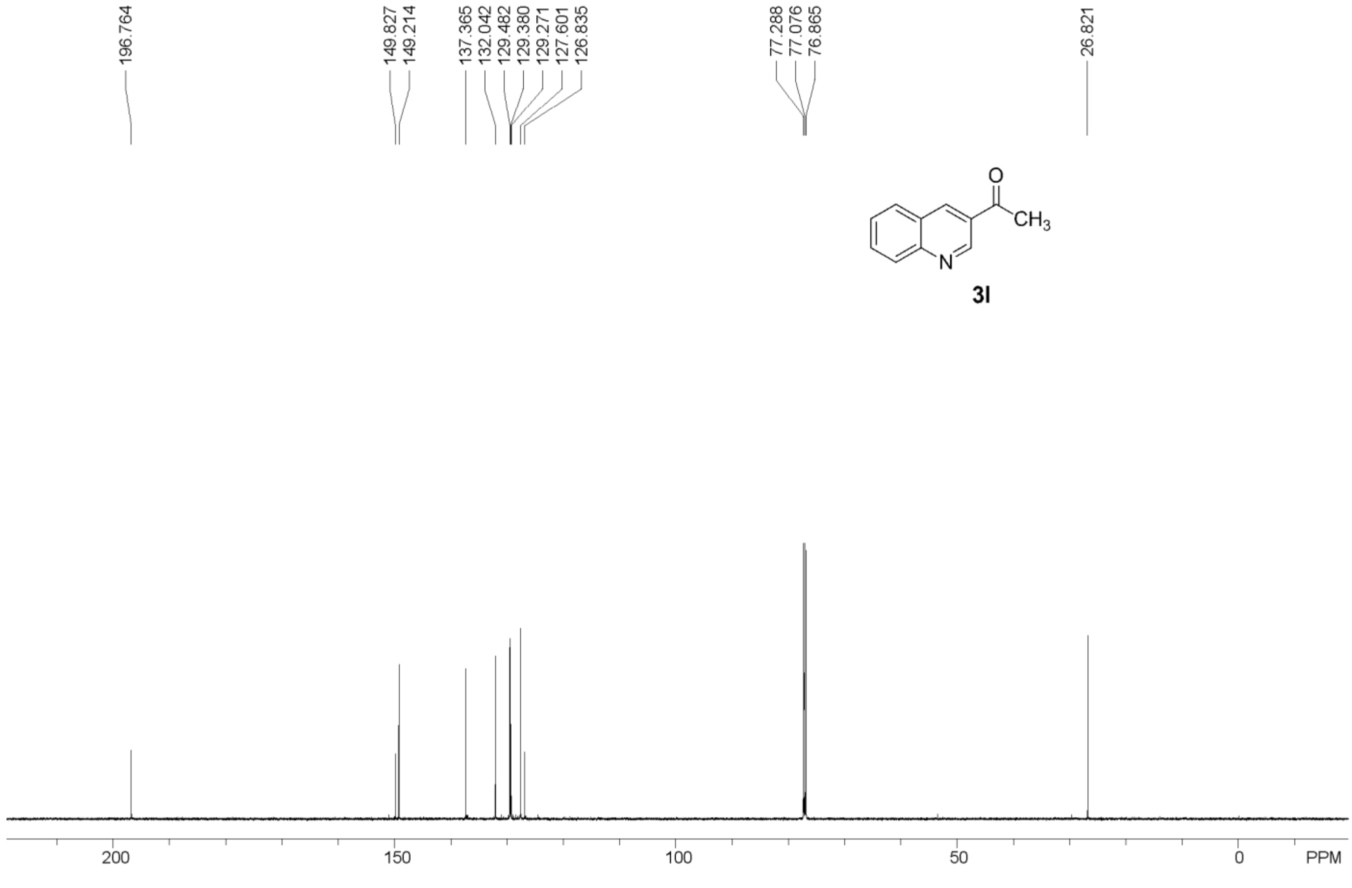
3k


186.154
149.637
149.484
143.213
137.715
135.104
135.082
131.772
130.671
129.512
129.103
128.374
127.689
126.646
77.361
77.149
76.930
O
S
N
200
150
100
50
0
PPM

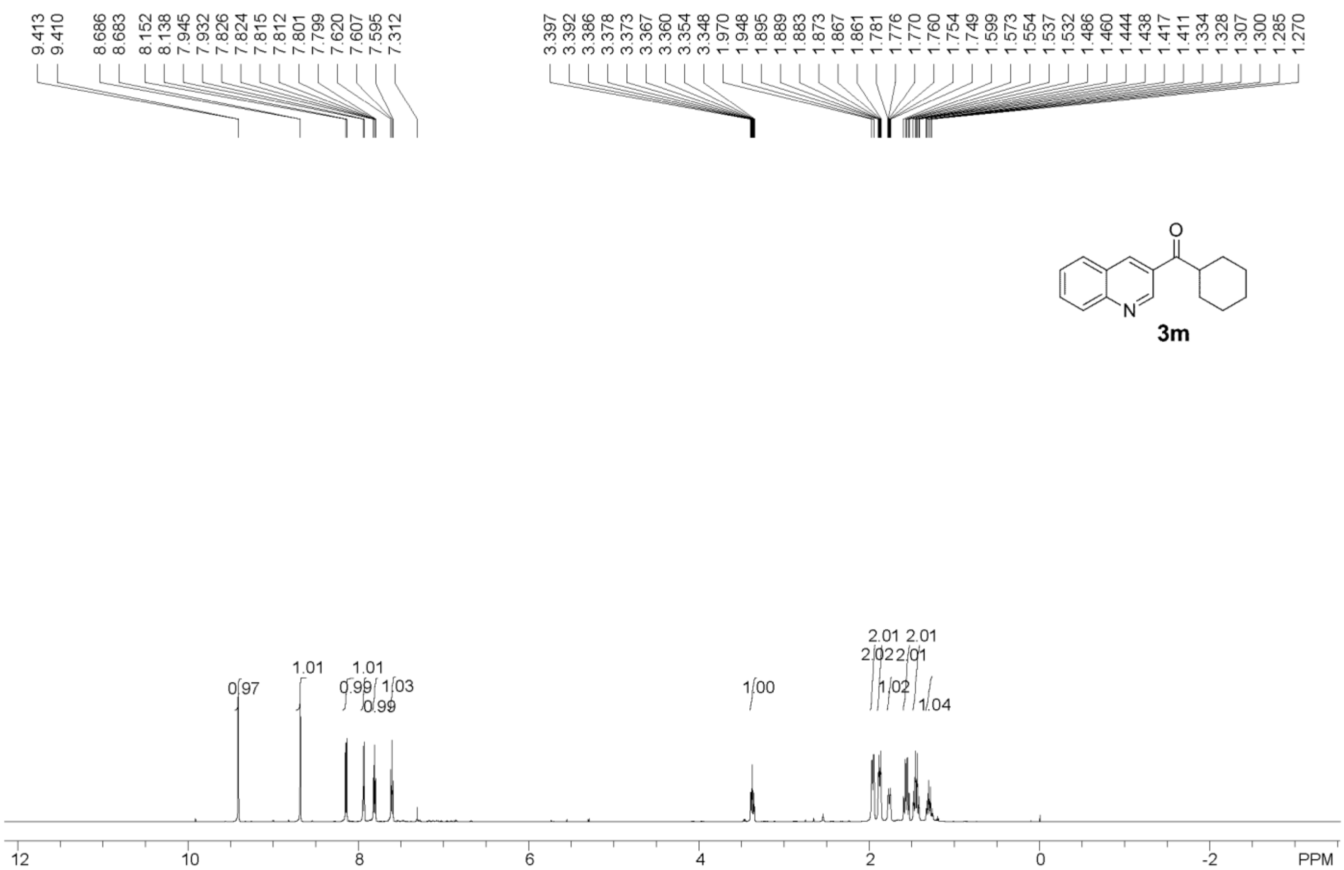
3k


9.431
9.427
8.705
8.701
8.166
8.152
7.952
7.938
7.854
7.853
7.841
7.829
7.827
7.644
7.631
7.619
7.283
2.744
1.00
1.04
0.97
1.03
1.01
0.99
3.00
10
8
6
4
2
0
PPM

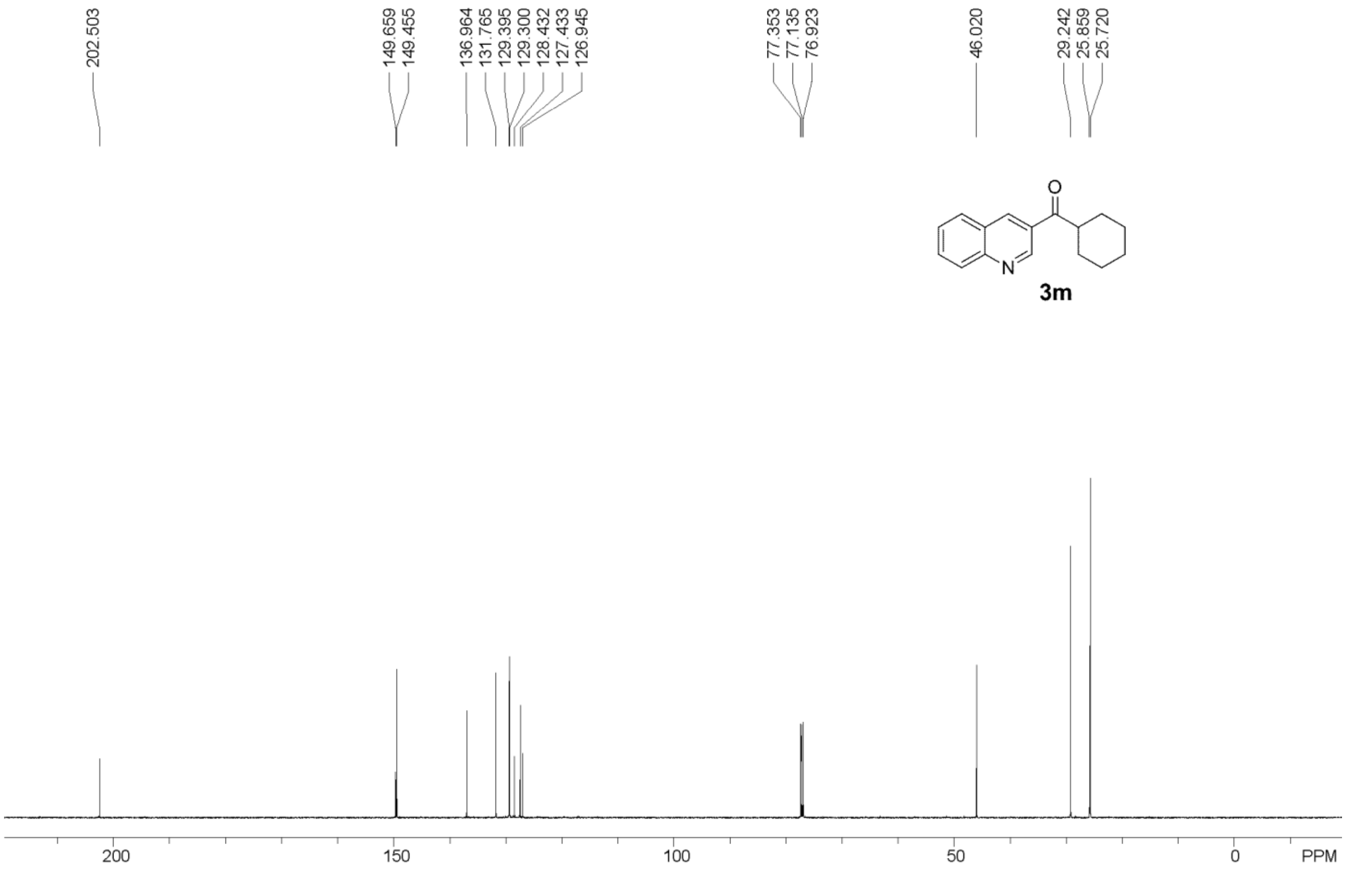
3l


196.764
149.827
149.214
137.365
132.042
129.482
129.380
129.271
127.601
126.835
77.288
77.076
76.865
26.821
200
150
100
50
0
PPM

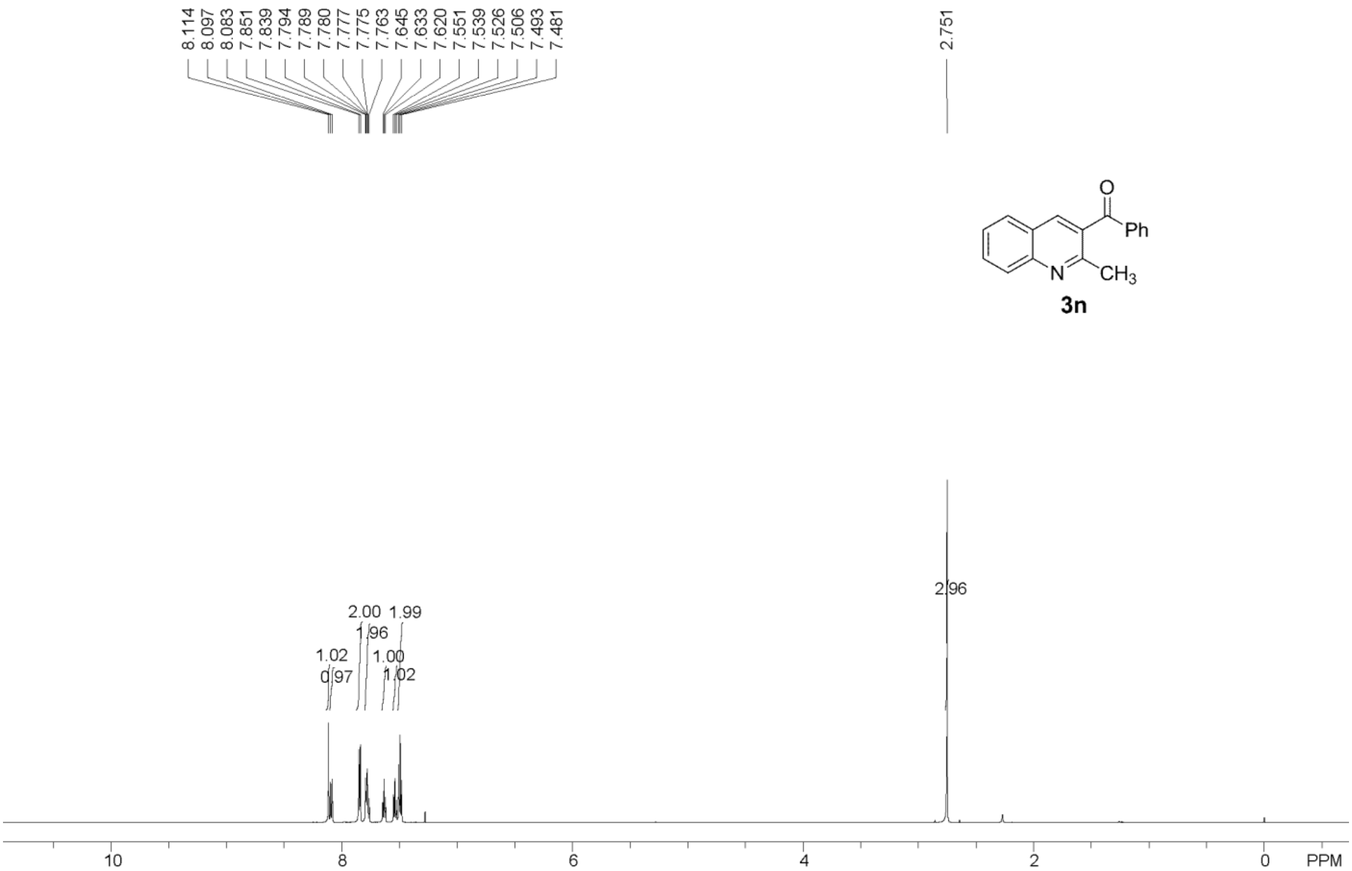
3l

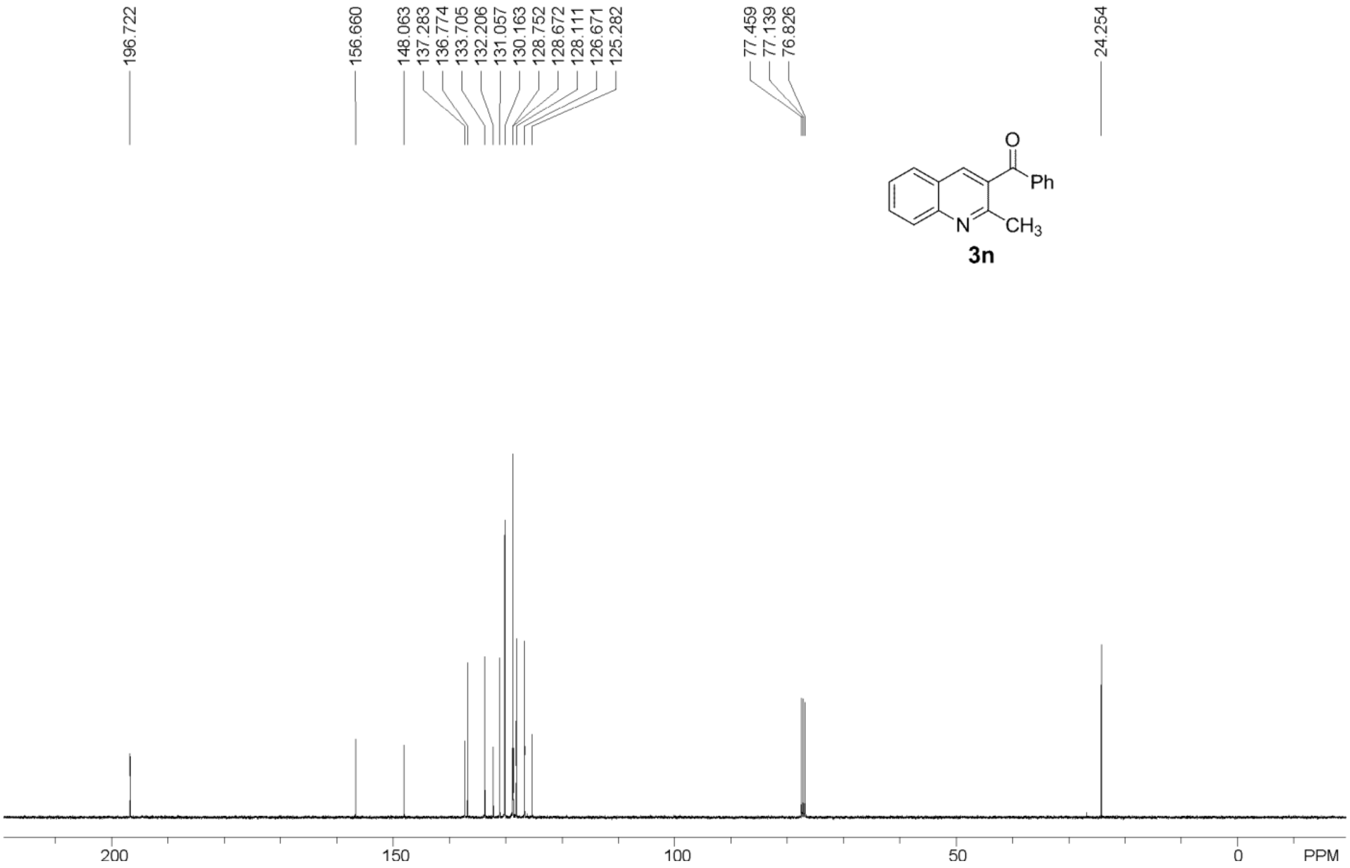

9.413
9.410
8.686
8.683
8.152
8.138
7.945
7.932
7.826
7.824
7.815
7.812
7.801
7.799
7.620
7.607
7.595
7.312
3.397
3.392
3.386
3.378
3.373
3.367
3.360
3.354
3.348
1.970
1.948
1.895
1.889
1.883
1.873
1.867
1.861
1.781
1.776
1.770
1.760
1.754
1.749
1.599
1.573
1.554
1.537
1.532
1.486
1.460
1.444
1.438
1.417
1.411
1.334
1.328
1.307
1.300
1.285
1.270
0.97
1.01
0.99
1.01
0.99
1.03
1.00
2.01
2.02
2.01
2.01
1.02
1.04
12
10
8
6
4
2
0
-2
PPM
O
N

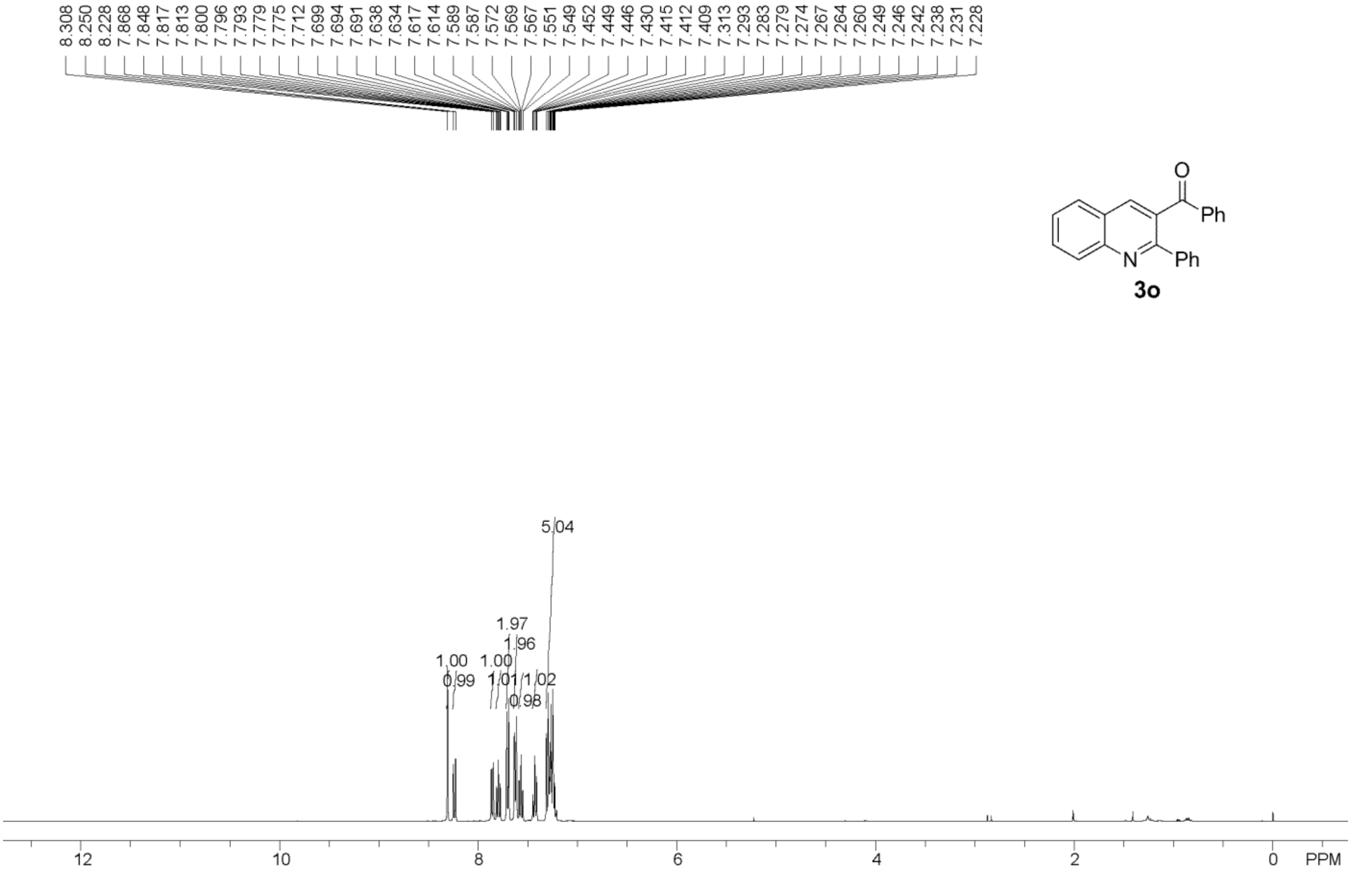
3m

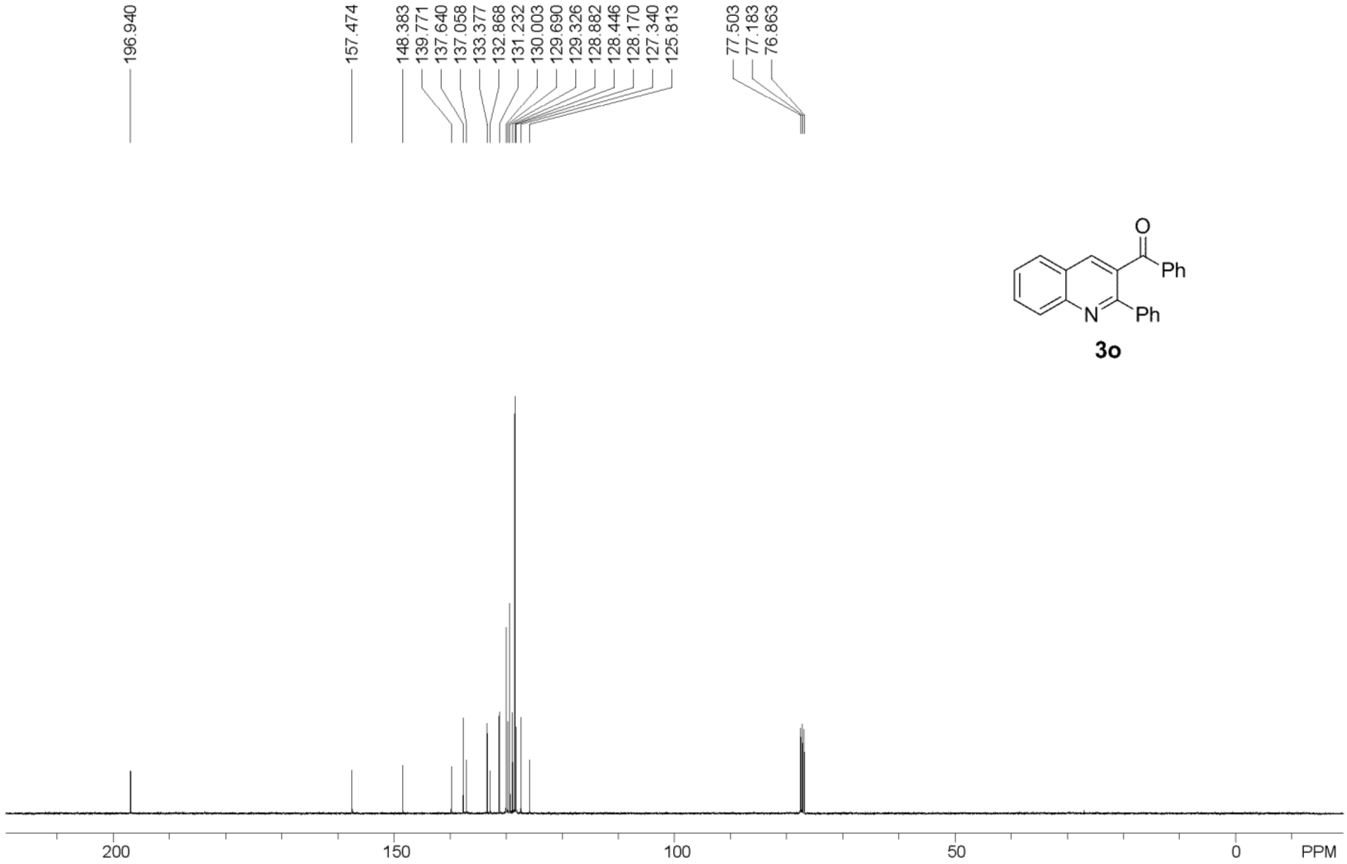

202.503
149.659
149.455
136.964
131.765
129.395
129.300
128.432
127.433
126.945
77.353
77.135
76.923
46.020
29.242
25.859
25.720
200
150
100
50
0
PPM
O
N

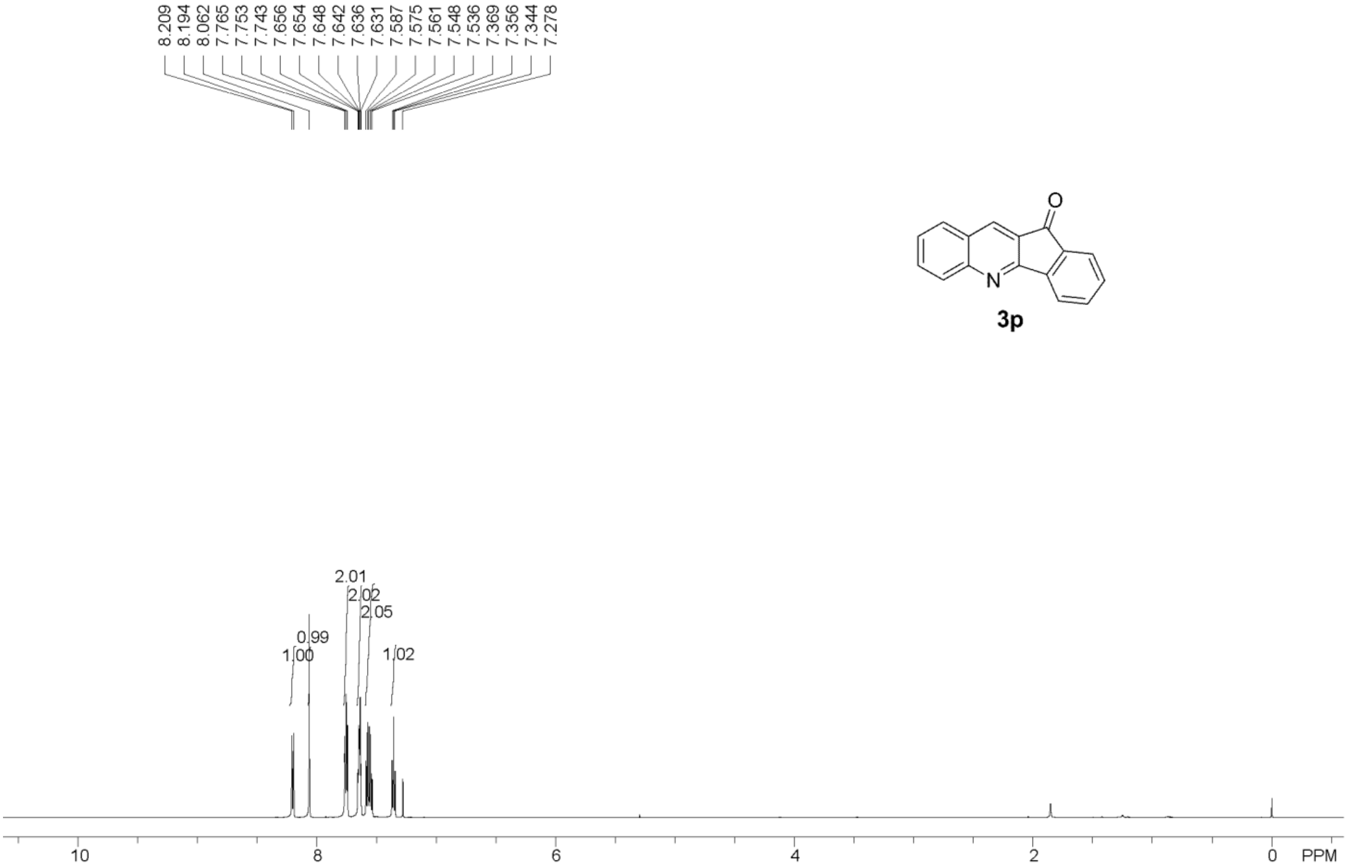
3m


8.114
8.097
8.083
7.851
7.839
7.794
7.789
7.780
7.777
7.775
7.763
7.645
7.633
7.620
7.551
7.539
7.526
7.506
7.493
7.481
2.751
O
Ph
N
CH3
3n
2.00 1.99
1.96
1.02
1.00
0.97
1.02
2.96
10
8
6
4
2
0
PPM

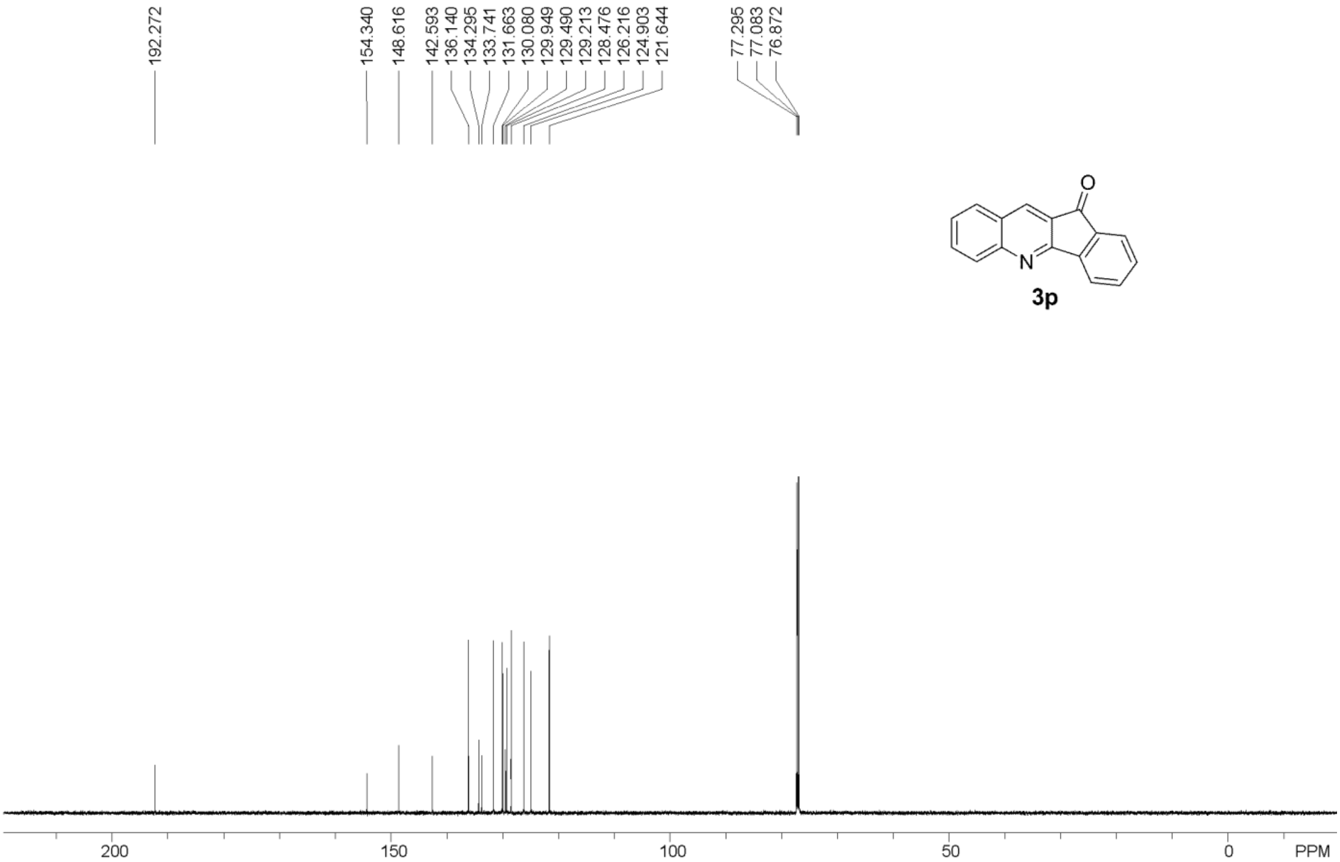

196.722
156.660
148.063
137.283
136.774
133.705
132.206
131.057
130.163
128.752
128.672
128.111
126.671
125.282
77.459
77.139
76.826
24.254
O
Ph
N
CH3
3n
200
150
100
50
0
PPM


8.308
8.250
8.228
7.868
7.848
7.817
7.813
7.800
7.796
7.793
7.779
7.775
7.712
7.699
7.694
7.691
7.638
7.634
7.617
7.614
7.589
7.587
7.572
7.569
7.567
7.551
7.549
7.452
7.449
7.446
7.430
7.415
7.412
7.409
7.313
7.293
7.283
7.279
7.274
7.267
7.264
7.260
7.249
7.246
7.242
7.238
7.231
7.228
O
Ph
N
Ph
3o
5.04
1.97
1.96
1.00
1.00
0.99
1.01
1.02
0.98
12
10
8
6
4
2
0
PPM

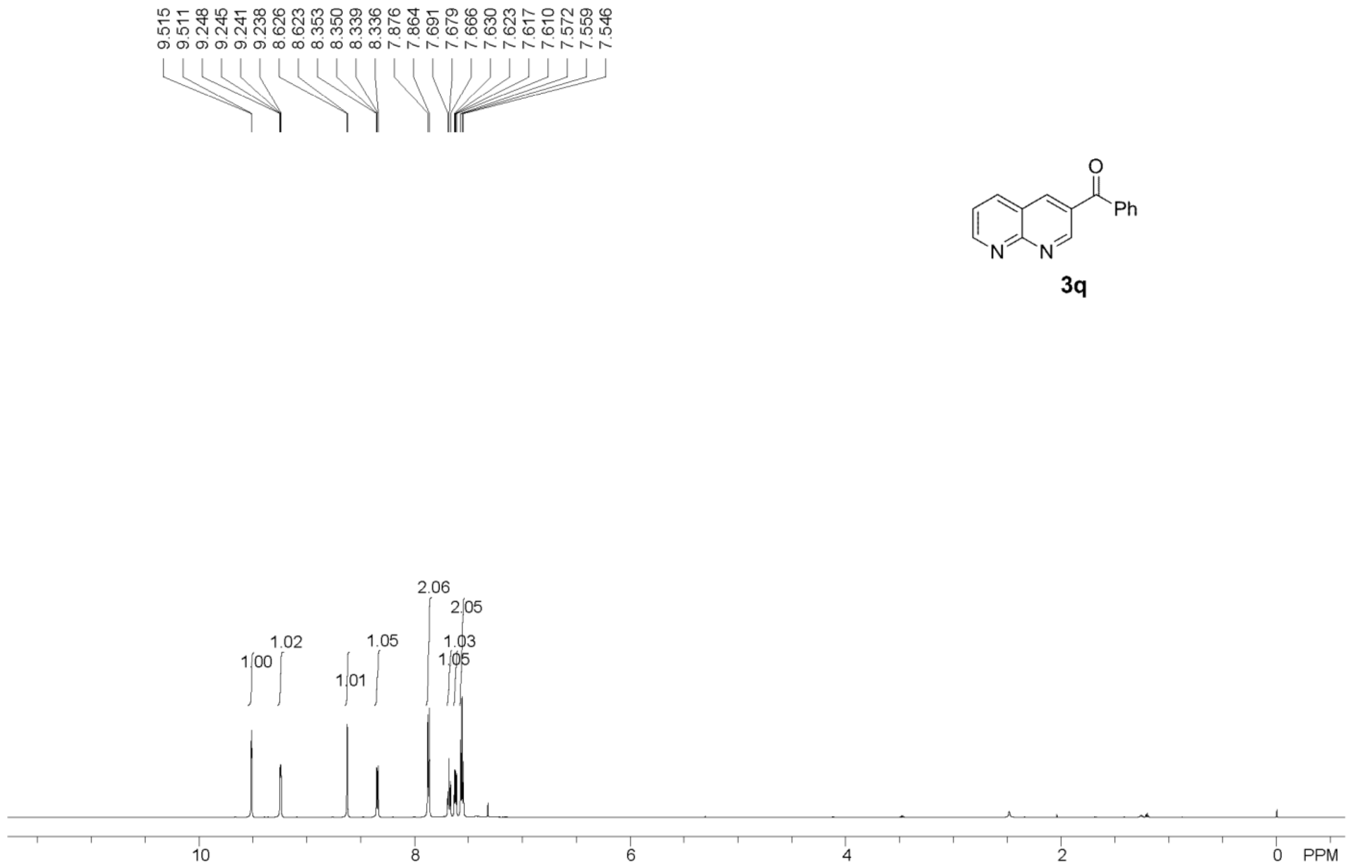

196.940
157.474
148.383
139.771
137.640
137.058
133.377
132.868
131.232
130.003
129.690
129.326
128.882
128.446
128.170
127.340
125.813
77.503
77.183
76.863
O
Ph
N
Ph
3o
200
150
100
50
0
PPM

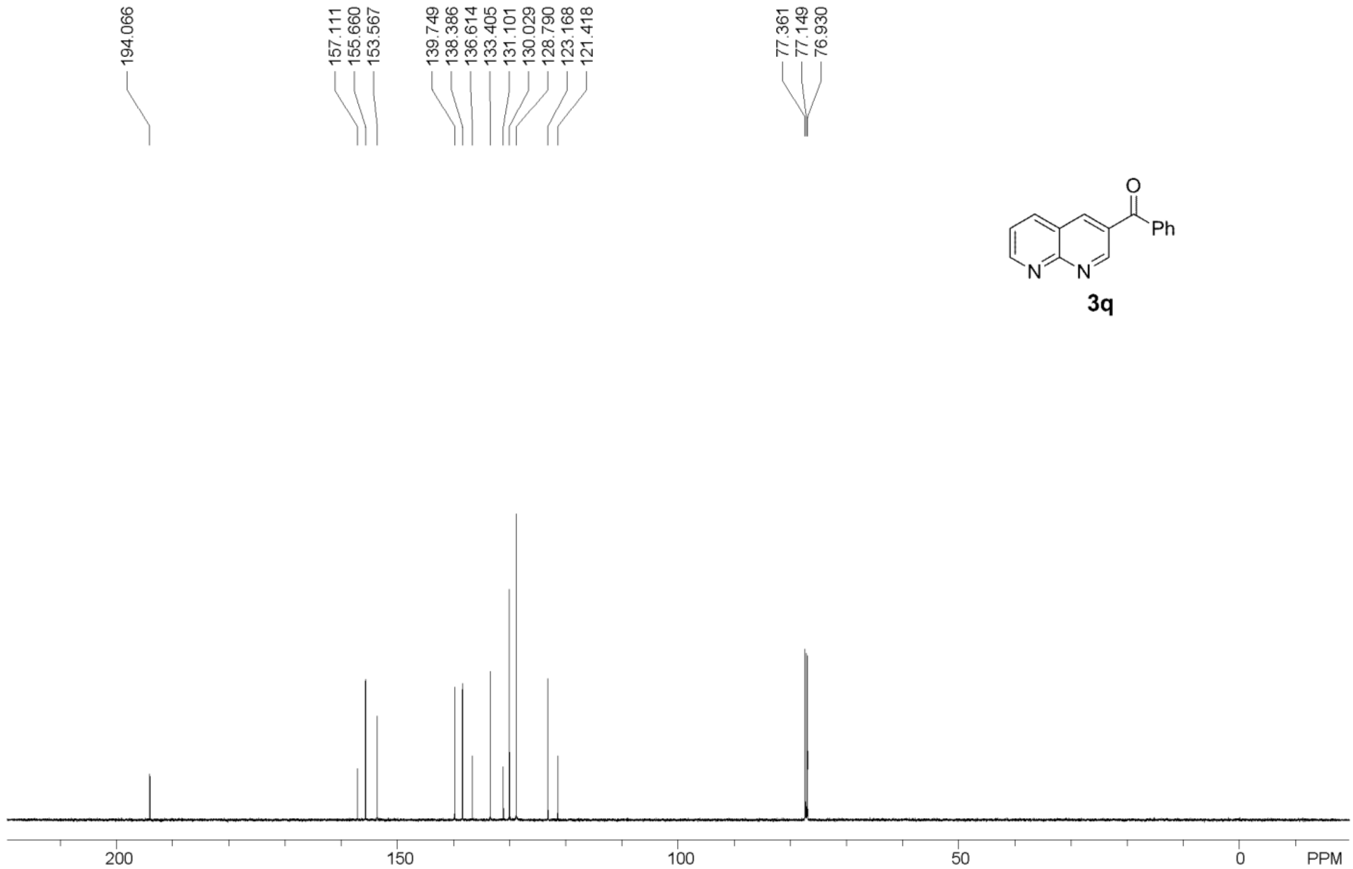

8.209
8.194
8.062
7.765
7.753
7.743
7.656
7.654
7.648
7.642
7.636
7.631
7.587
7.575
7.561
7.548
7.536
7.369
7.356
7.344
7.278
2.01
2.02
2.05
0.99
1.00
1.02
10
8
6
4
2
0
PPM

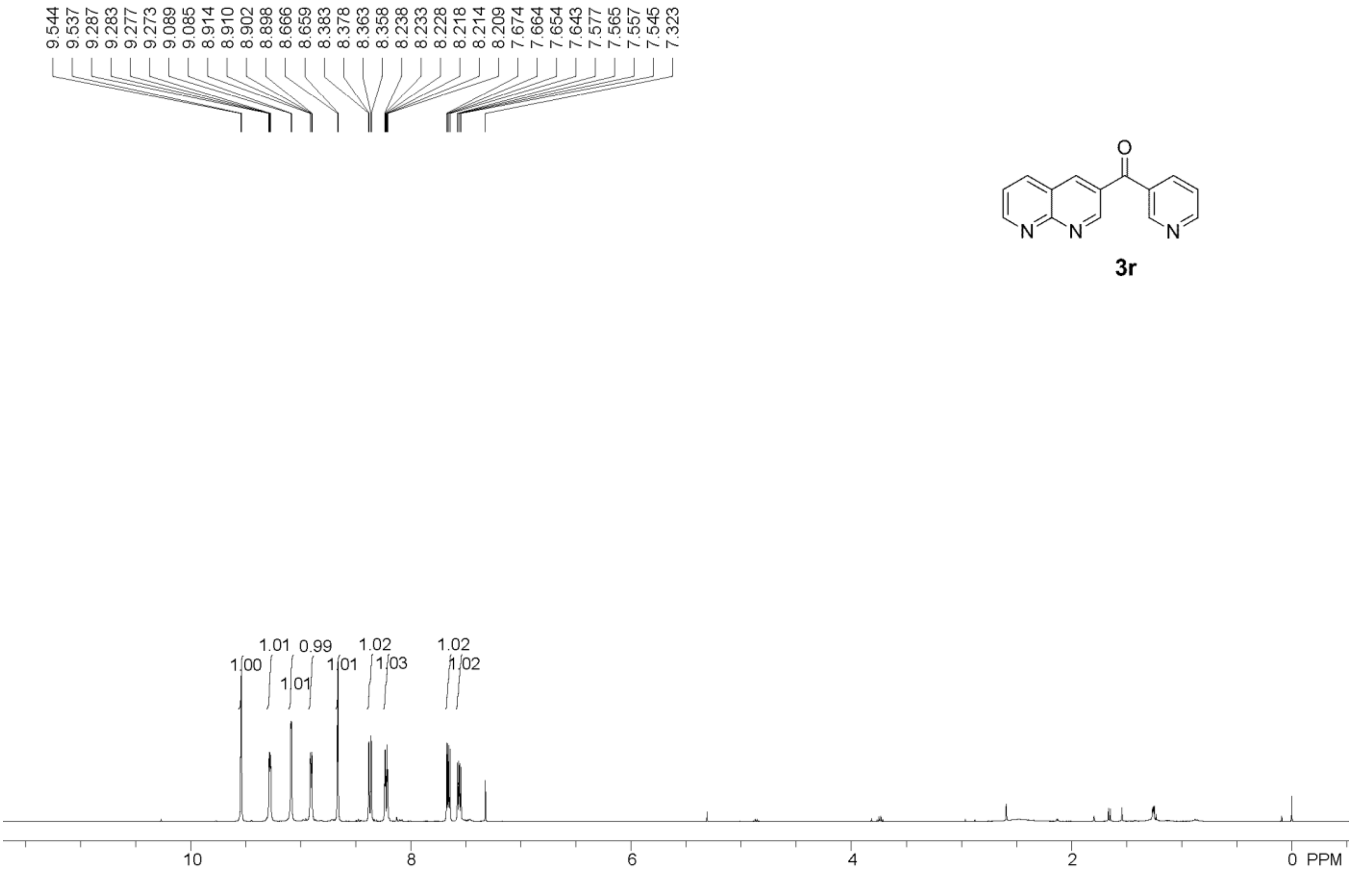
3p

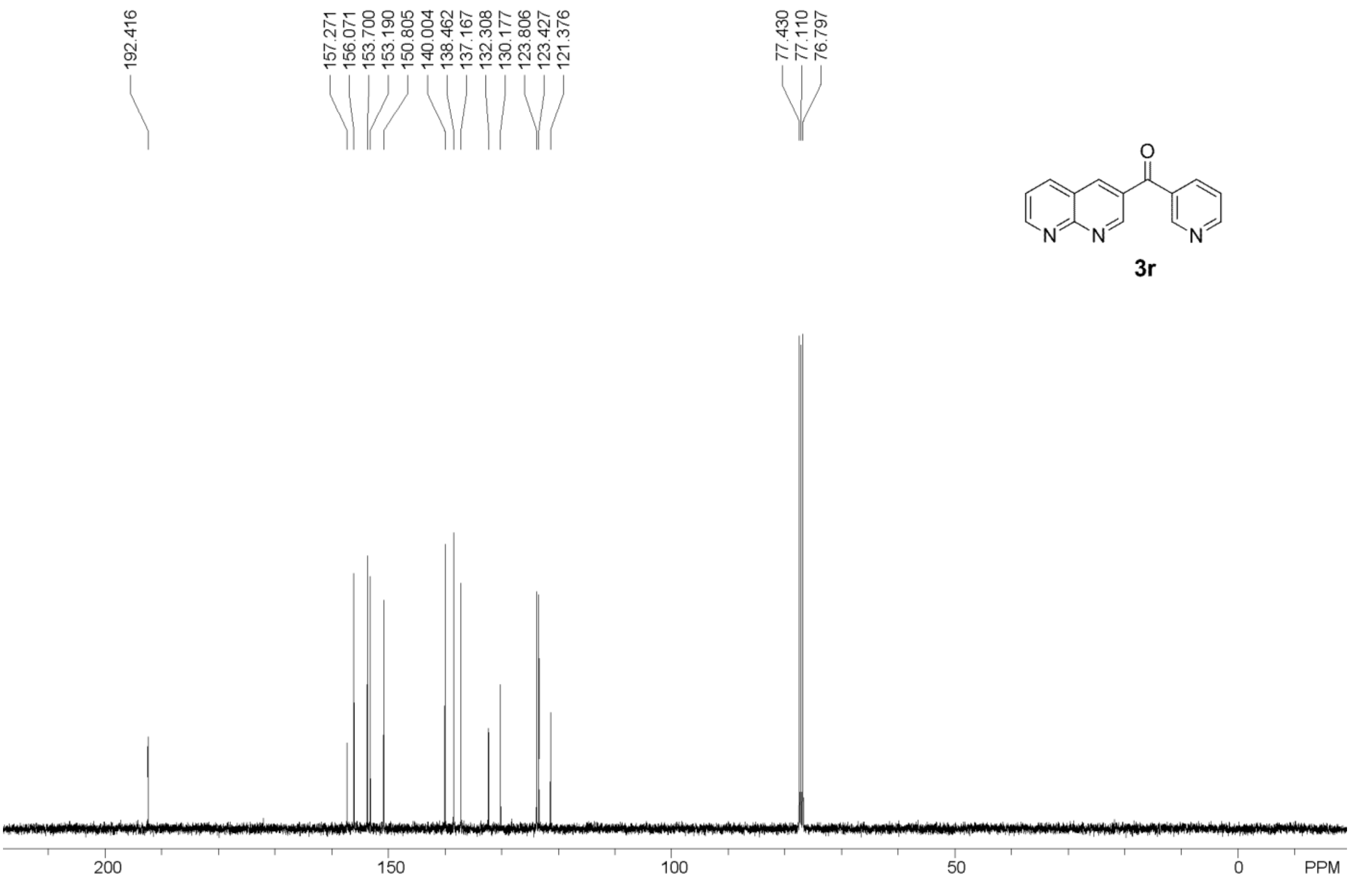

192.272
154.340
148.616
142.593
136.140
134.295
133.741
131.663
130.080
129.949
129.490
129.213
128.476
126.216
124.903
121.644
77.295
77.083
76.872
200
150
100
50
0
PPM

3p

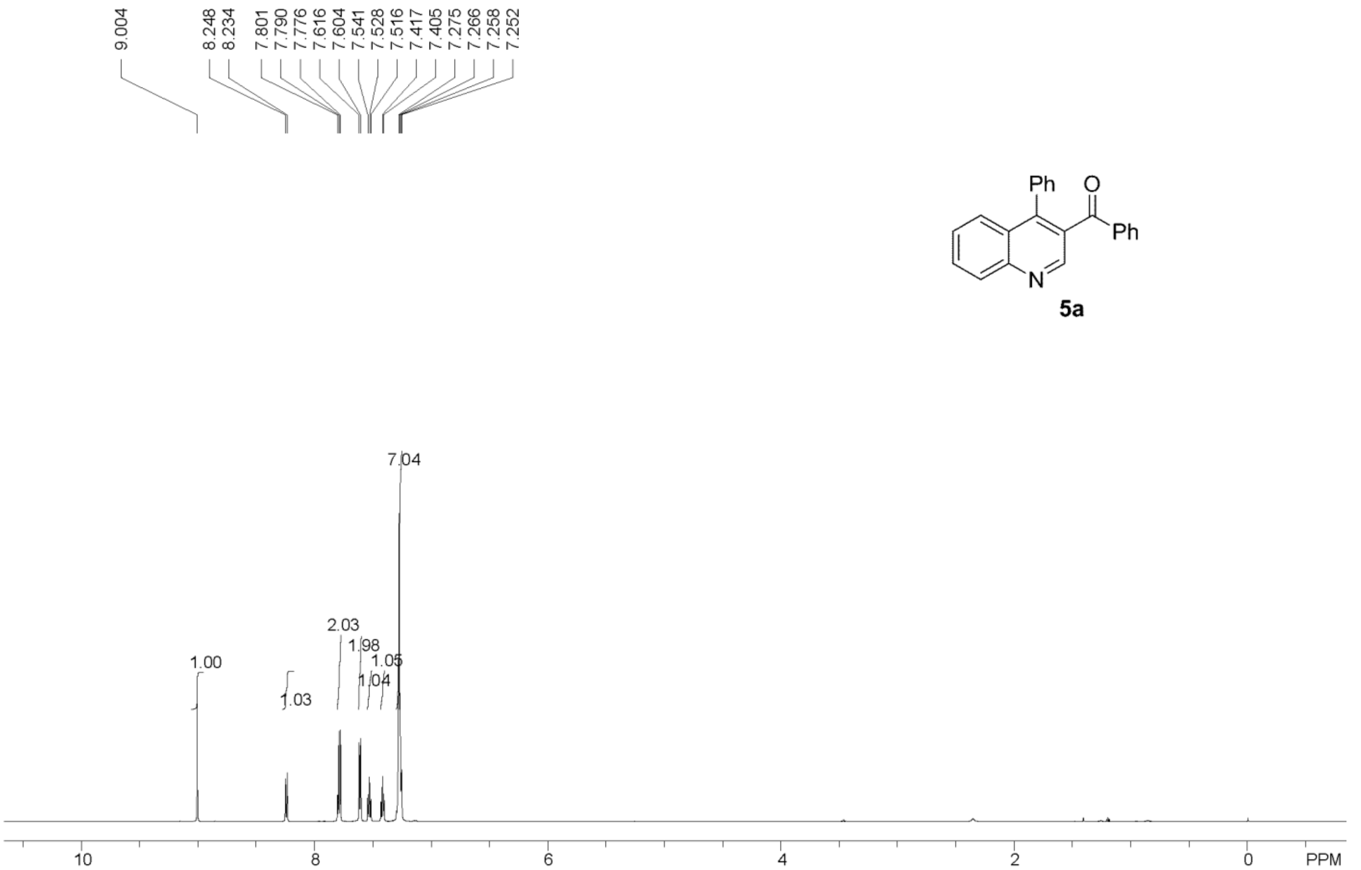

9.515
9.511
9.248
9.245
9.241
9.238
8.626
8.623
8.353
8.350
8.339
8.336
7.876
7.864
7.691
7.679
7.666
7.630
7.623
7.617
7.610
7.572
7.559
7.546
1.00
1.02
1.01
1.05
2.06
2.05
1.03
1.05
10
8
6
4
2
0
PPM
O
Ph
N
N
3q


194.066
157.111
155.660
153.567
139.749
138.386
136.614
133.405
131.101
130.029
128.790
123.168
121.418
77.361
77.149
76.930
200
150
100
50
0
PPM
O
Ph
N
N
3q

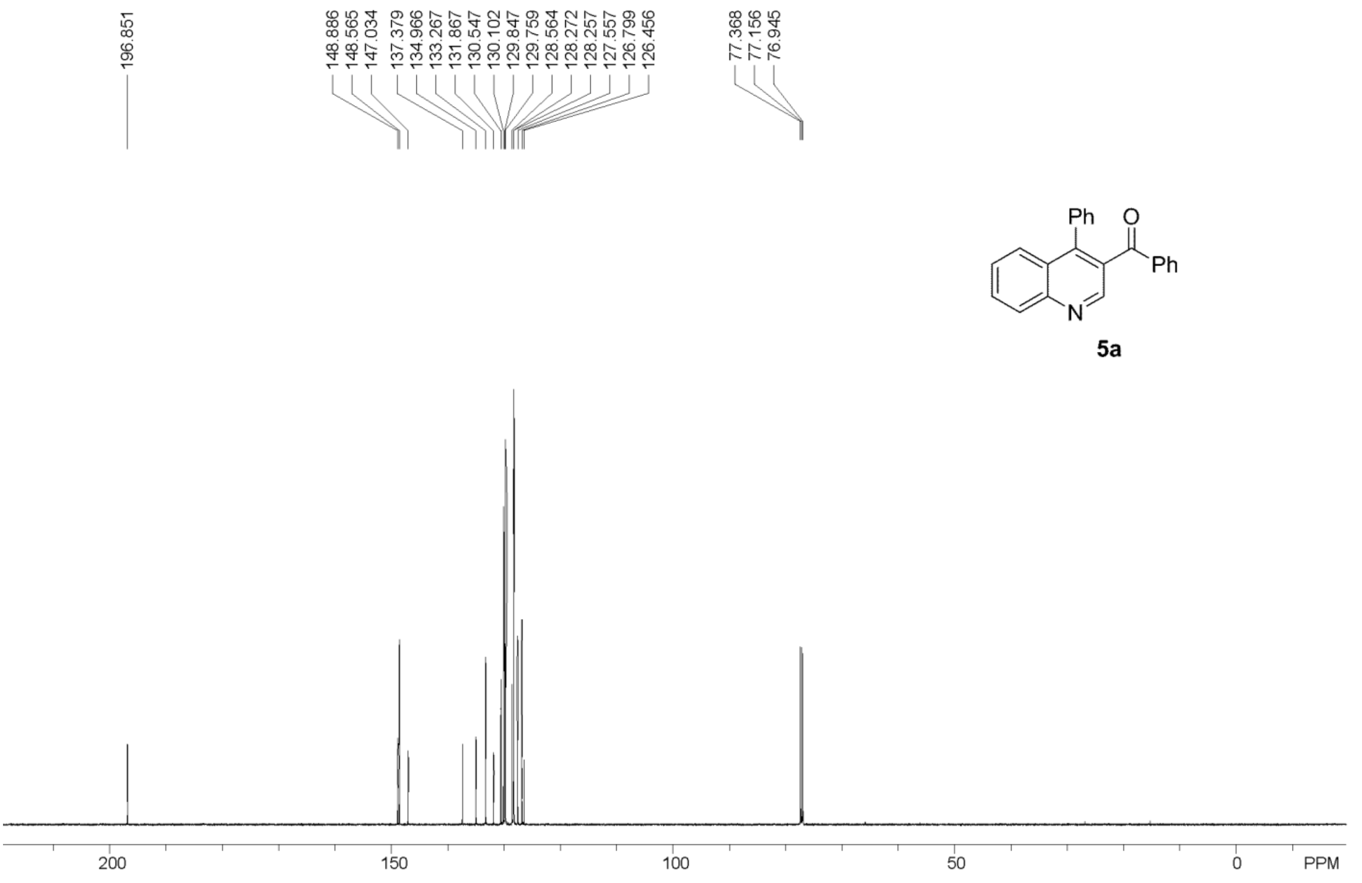

9.544
9.537
9.287
9.283
9.277
9.273
9.089
9.085
8.914
8.910
8.902
8.898
8.666
8.659
8.383
8.378
8.363
8.358
8.238
8.233
8.228
8.218
8.214
8.209
7.674
7.664
7.654
7.643
7.577
7.565
7.557
7.545
7.323
O
N
N
N
3r
1.00
1.01
1.01
0.99
1.01
1.02
1.03
1.02
1.02
10
8
6
4
2
0 PPM


192.416
157.271
156.071
153.700
153.190
150.805
140.004
138.462
137.167
132.308
130.177
123.806
123.427
121.376
77.430
77.110
76.797
O
N
N
N
3r
200
150
100
50
0
PPM

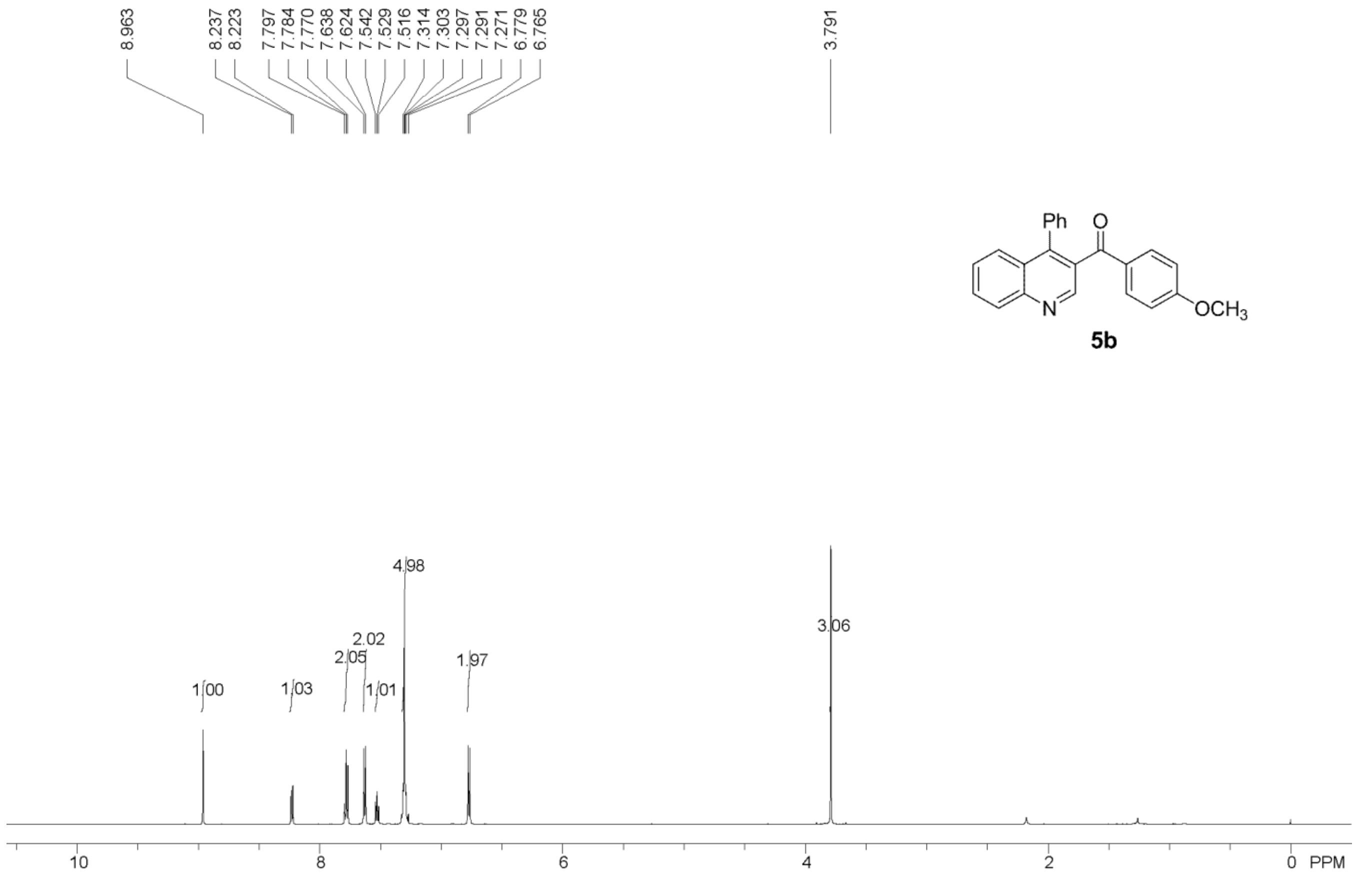
V. Copies of ^{1}H and ^{13}C NMR spectra of 5a-5l



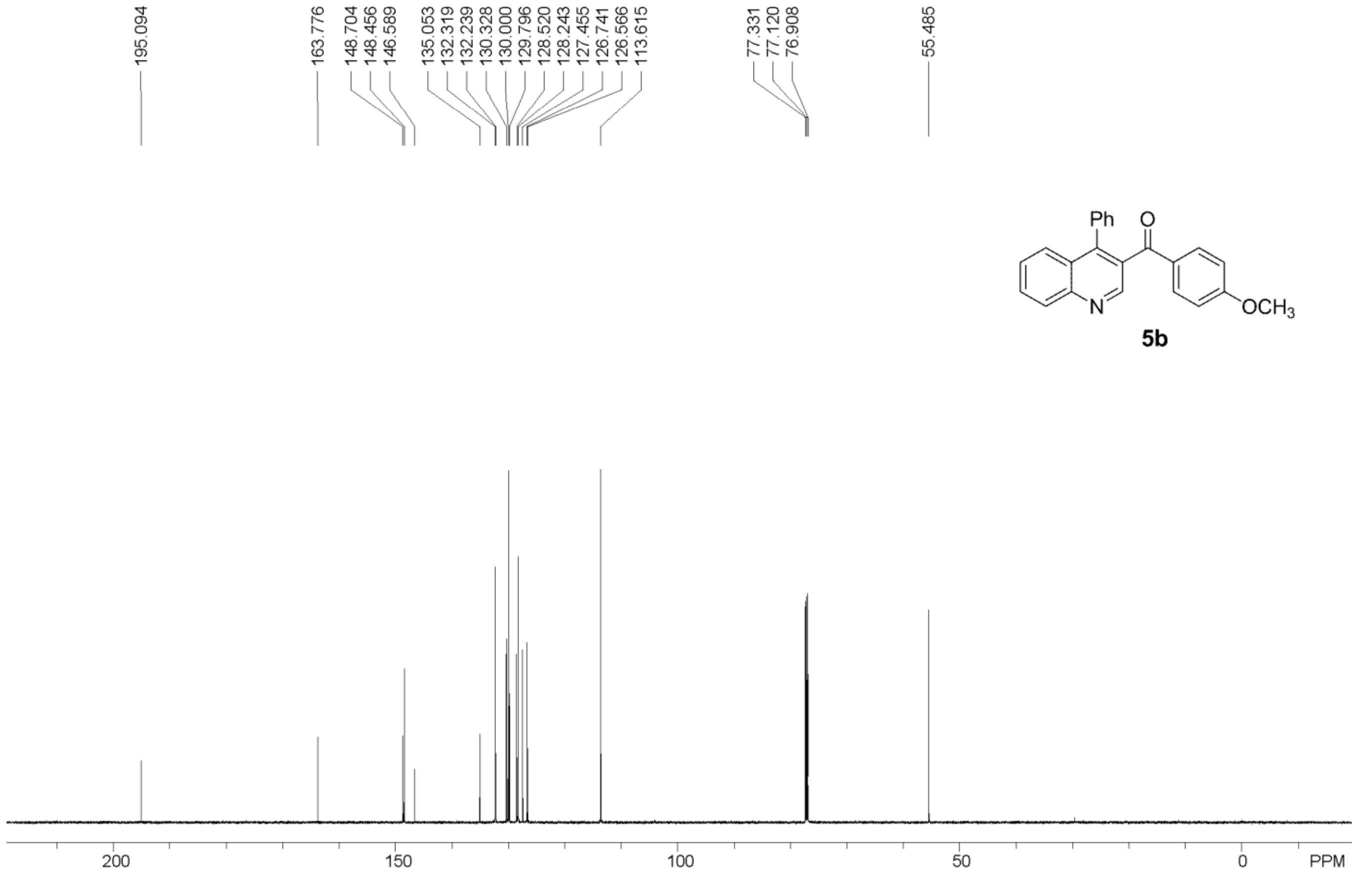
5a



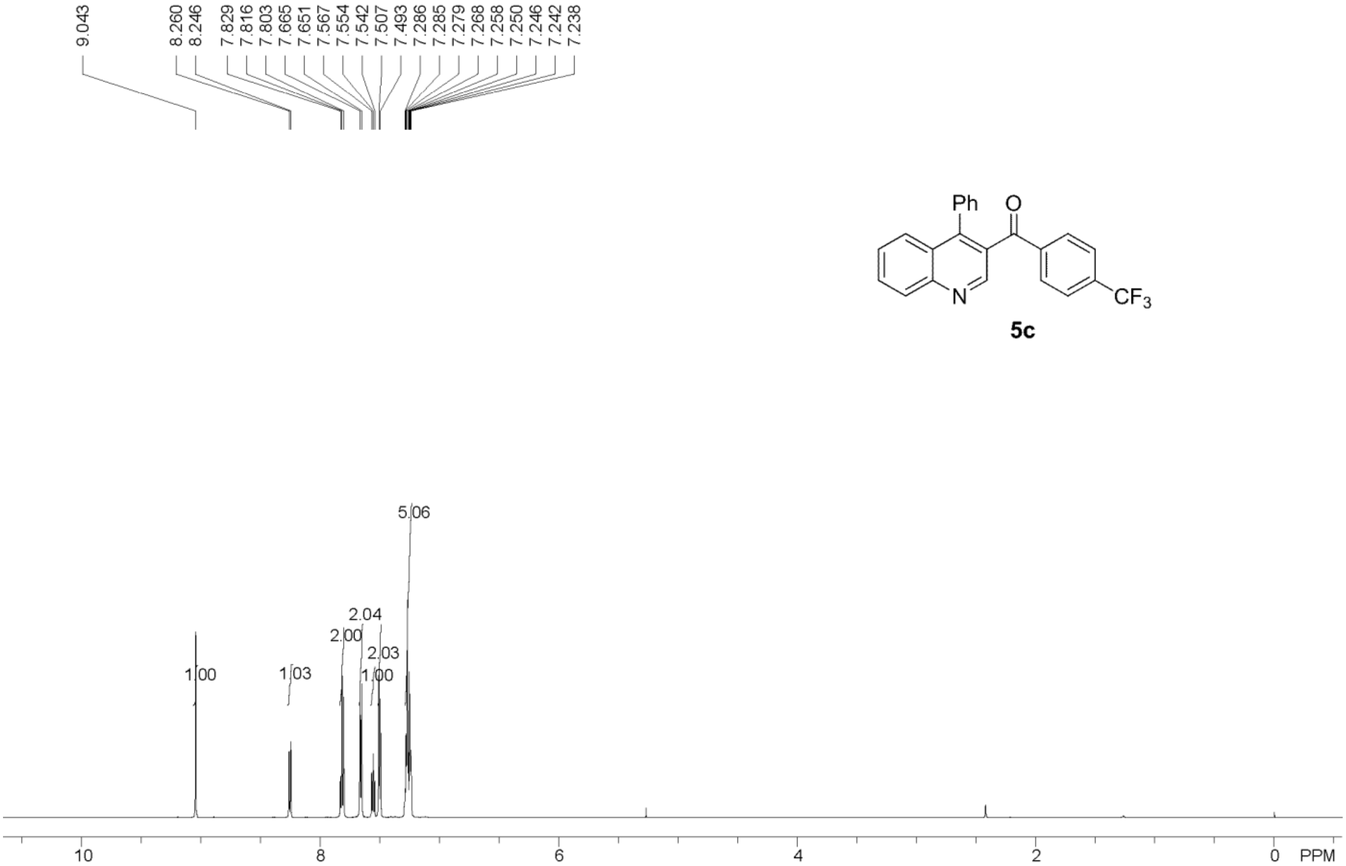
5a

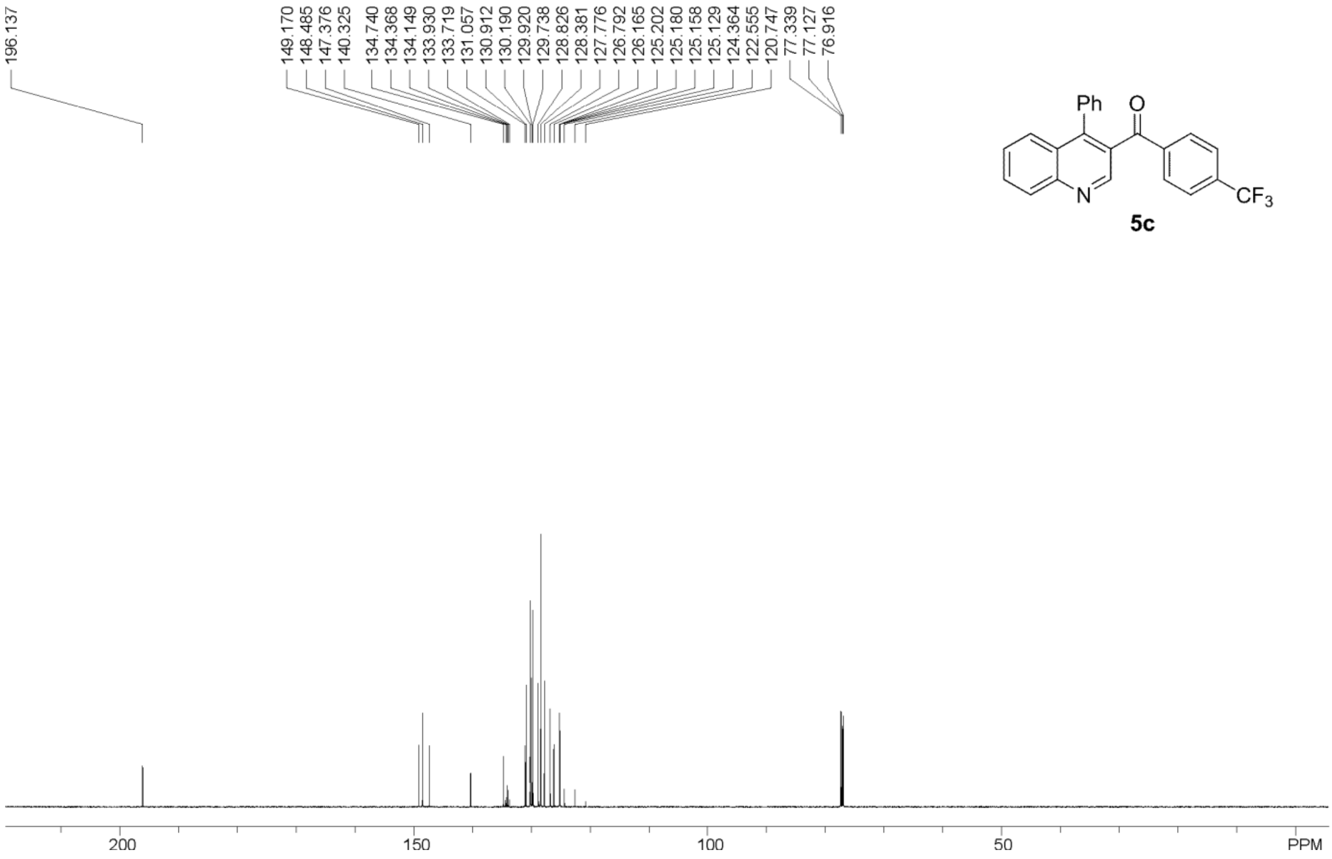


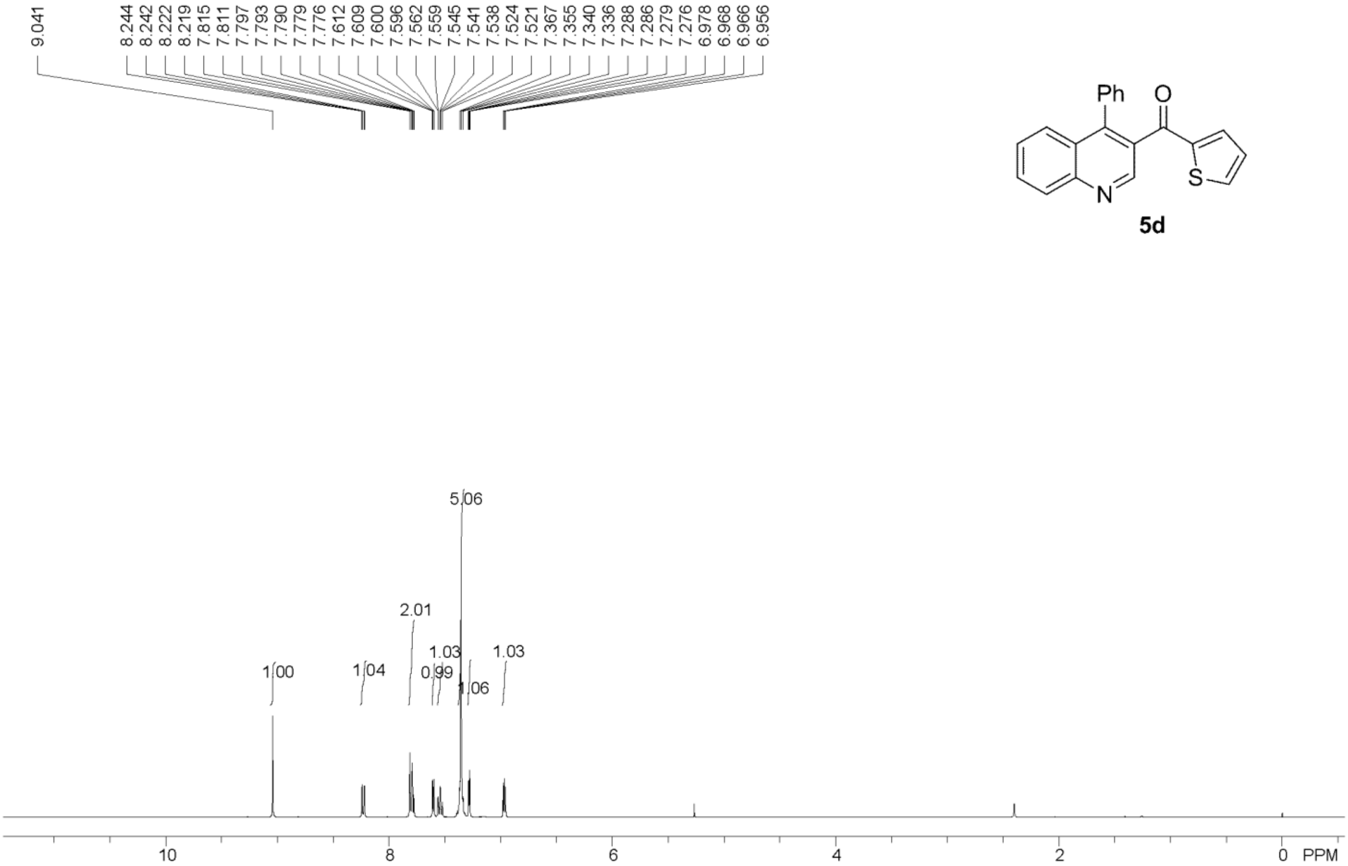
8.963
8.237 8.223 7.797 7.784 7.770 7.638 7.624 7.542 7.529 7.516 7.314 7.303 7.297 7.291 7.271 6.779 6.765
3.791
Ph
O
N
OCH3
5b
1.00 1.03 2.05 2.02 1.01 4.98 1.97 3.06
10 8 6 4 2 0 PPM

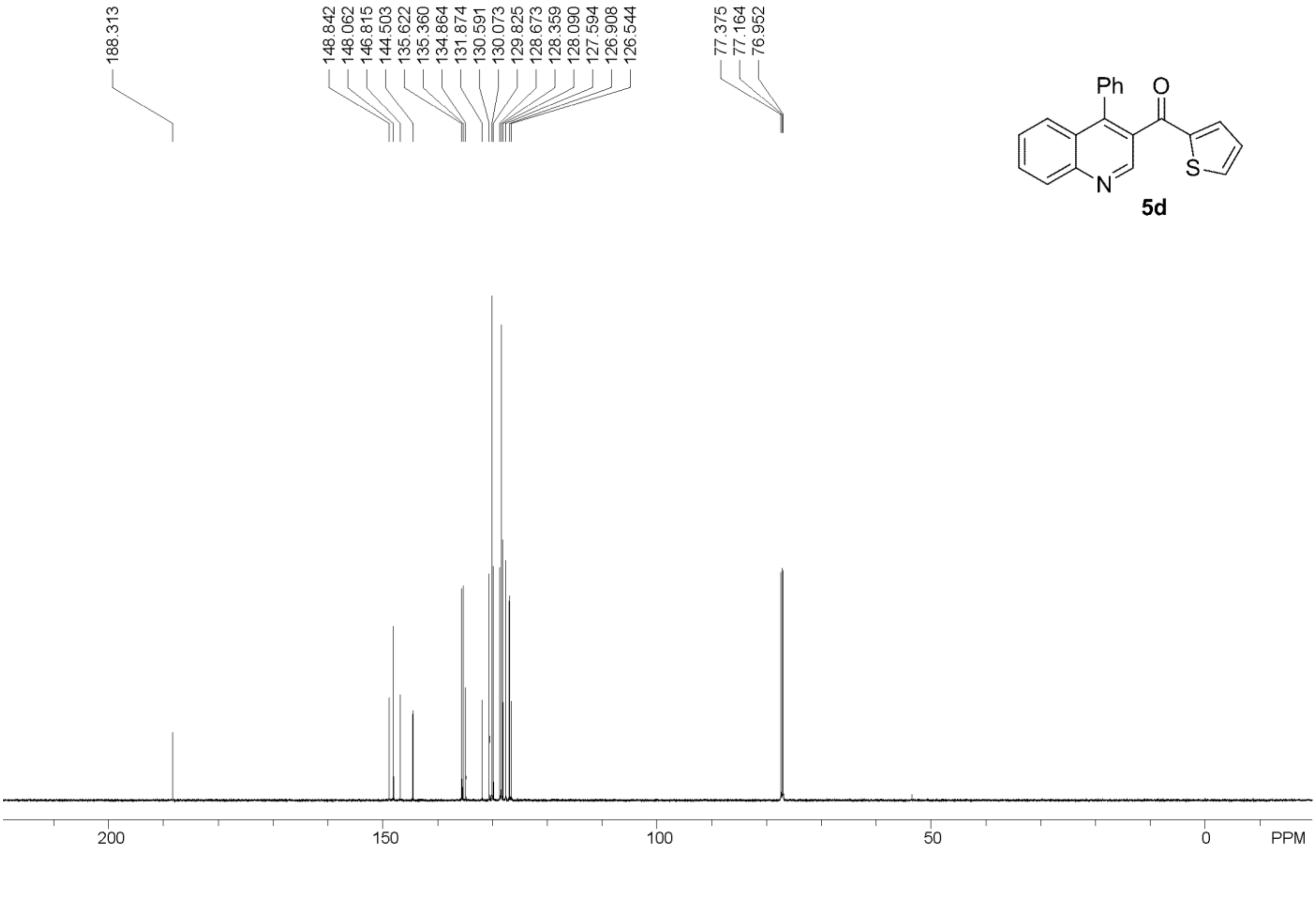


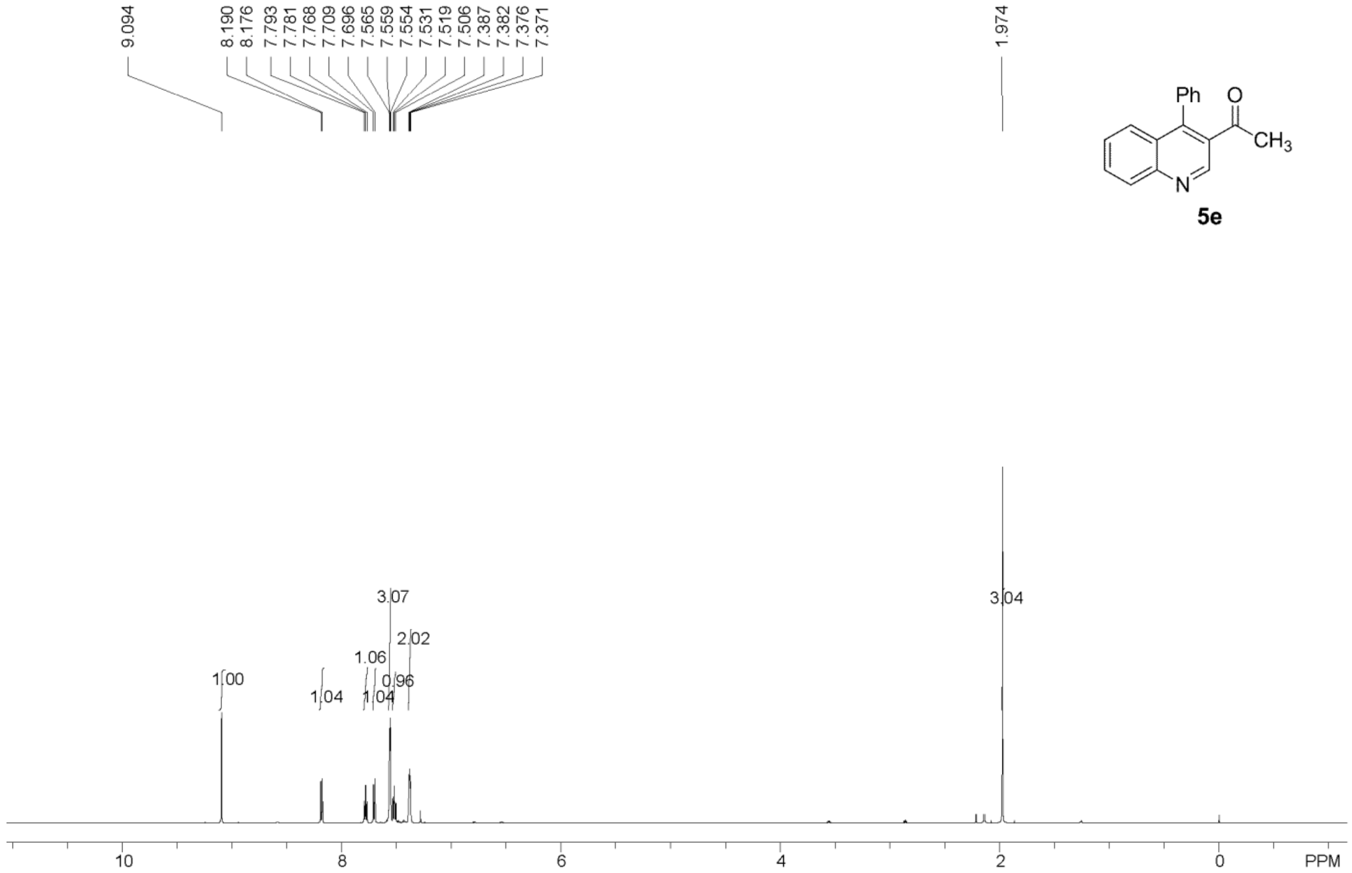
195.094
163.776
148.704 148.456 146.589
135.053 132.319 132.239 130.328 130.000 129.796 128.520 128.243 127.455 126.741 126.566 113.615
77.331 77.120 76.908
55.485
Ph
O
N
OCH3
5b
200 150 100 50 0 PPM


9.043
8.260
8.246
7.829
7.816
7.803
7.665
7.651
7.567
7.554
7.542
7.507
7.493
7.286
7.285
7.279
7.268
7.258
7.250
7.246
7.242
7.238
5.06
2.04
2.00
2.03
1.00
1.03
1.00
10
8
6
4
2
0 PPM
Ph
O
N
CF3
5c

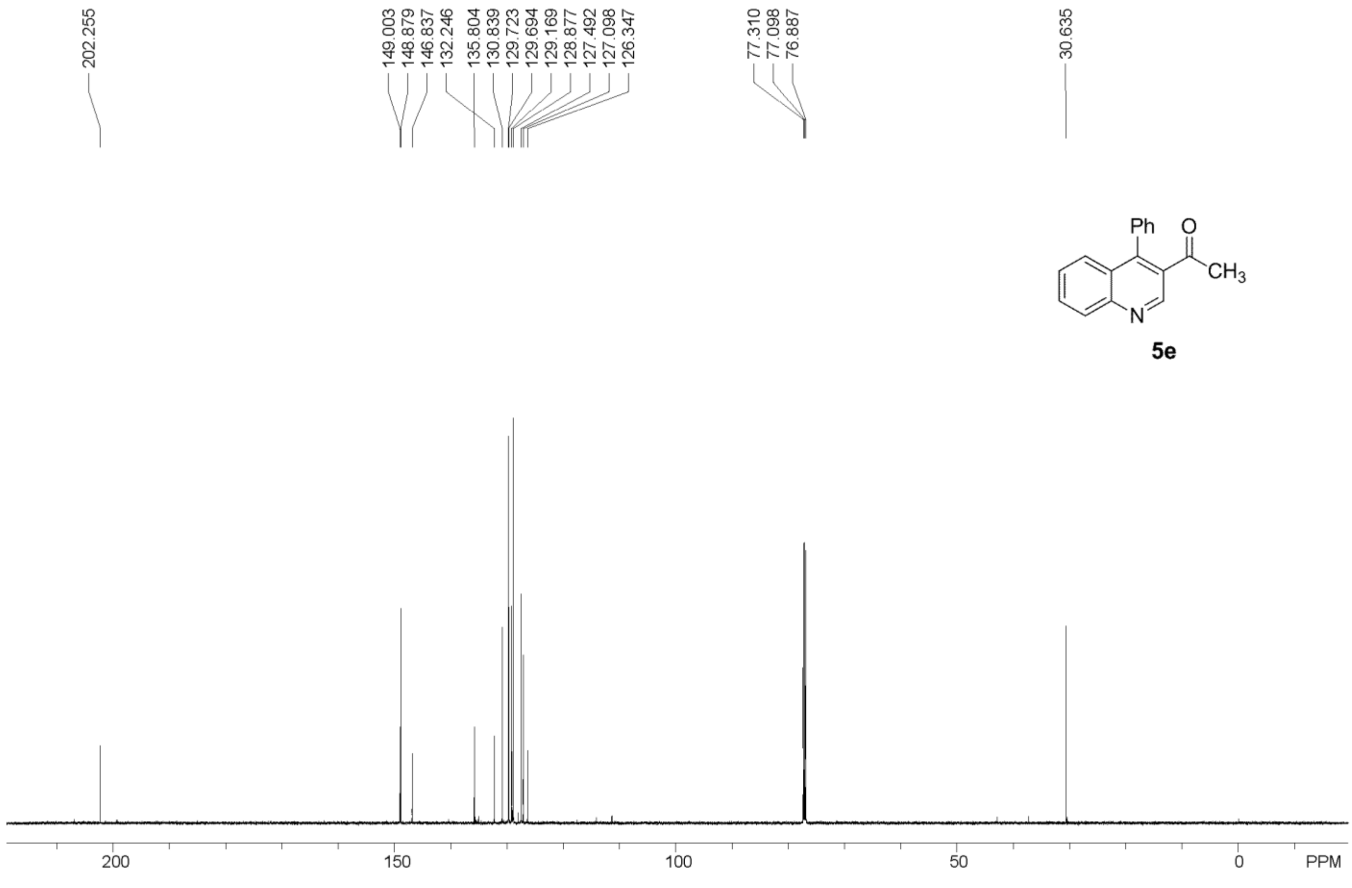

196.137
149.170
148.485
147.376
140.325
134.740
134.368
134.149
133.930
133.719
131.057
130.912
130.190
129.920
129.738
128.826
128.381
127.776
126.792
126.165
125.202
125.180
125.158
125.129
124.364
122.555
120.747
77.339
77.127
76.916
200
150
100
50
PPM
Ph
O
N
CF3
5c


9.041
8.244 8.242 8.222 8.219 7.815 7.811 7.797 7.793 7.790 7.779 7.776 7.612 7.609 7.600 7.596 7.562 7.559 7.545 7.541 7.538 7.524 7.521 7.367 7.355 7.340 7.336 7.288 7.286 7.279 7.276 6.978 6.968 6.966 6.956
Ph
O
N
S
5d
1.00
1.04
2.01
1.03
0.99
5.06
1.06
1.03
10
8
6
4
2
0
PPM


188.313
148.842 148.062 146.815 144.503 135.622 135.360 134.864 131.874 130.591 130.073 129.825 128.673 128.359 128.090 127.594 126.908 126.544
77.375 77.164 76.952
Ph
O
N
S
5d
200
150
100
50
0
PPM



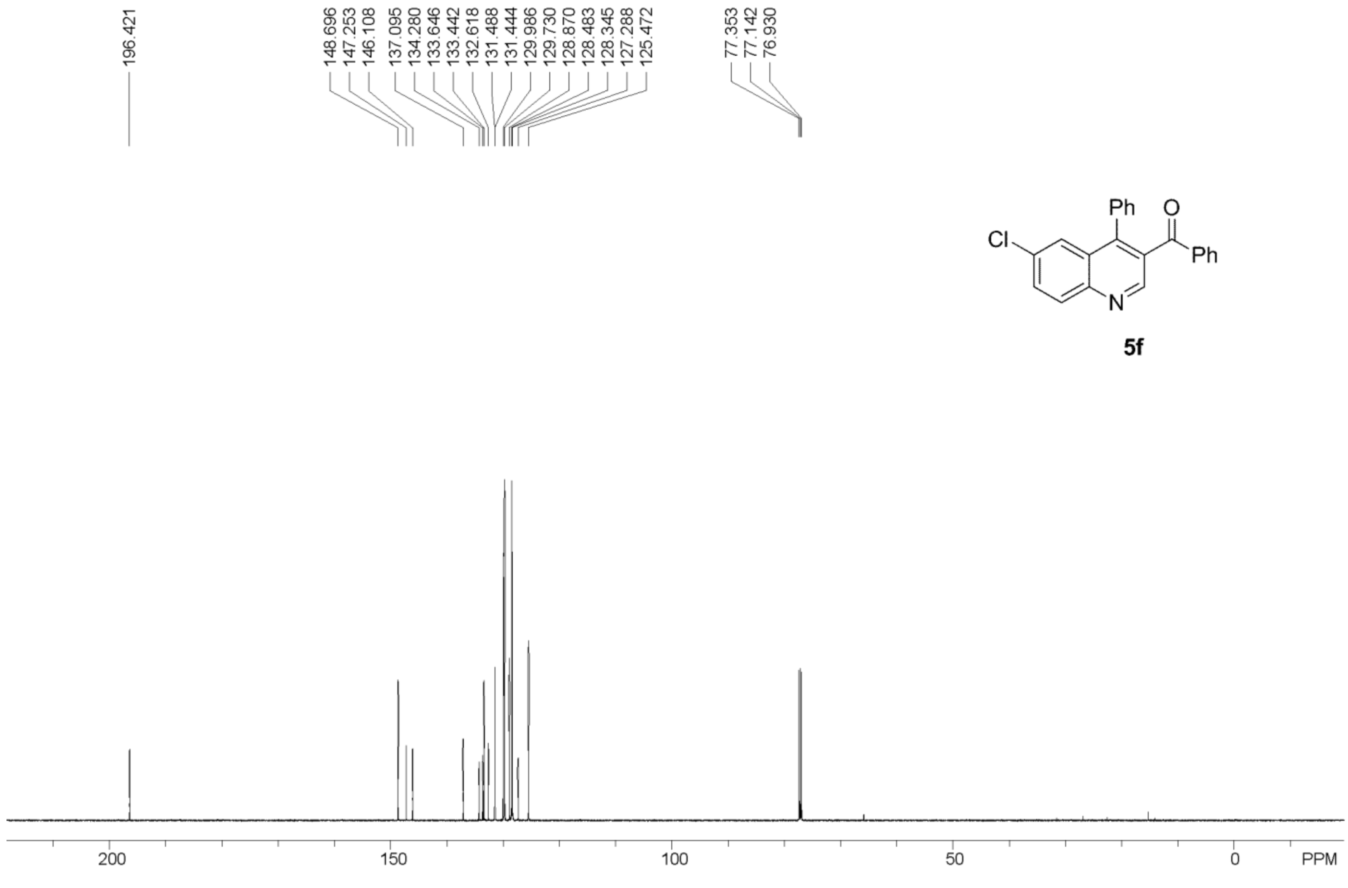
9.094
8.190
8.176
7.793
7.781
7.768
7.709
7.696
7.565
7.559
7.554
7.531
7.519
7.506
7.387
7.382
7.376
7.371
1.974
Ph
O
CH3
N
5e
3.07
2.02
1.06
0.96
1.00
1.04
1.04
3.04
10
8
6
4
2
0
PPM



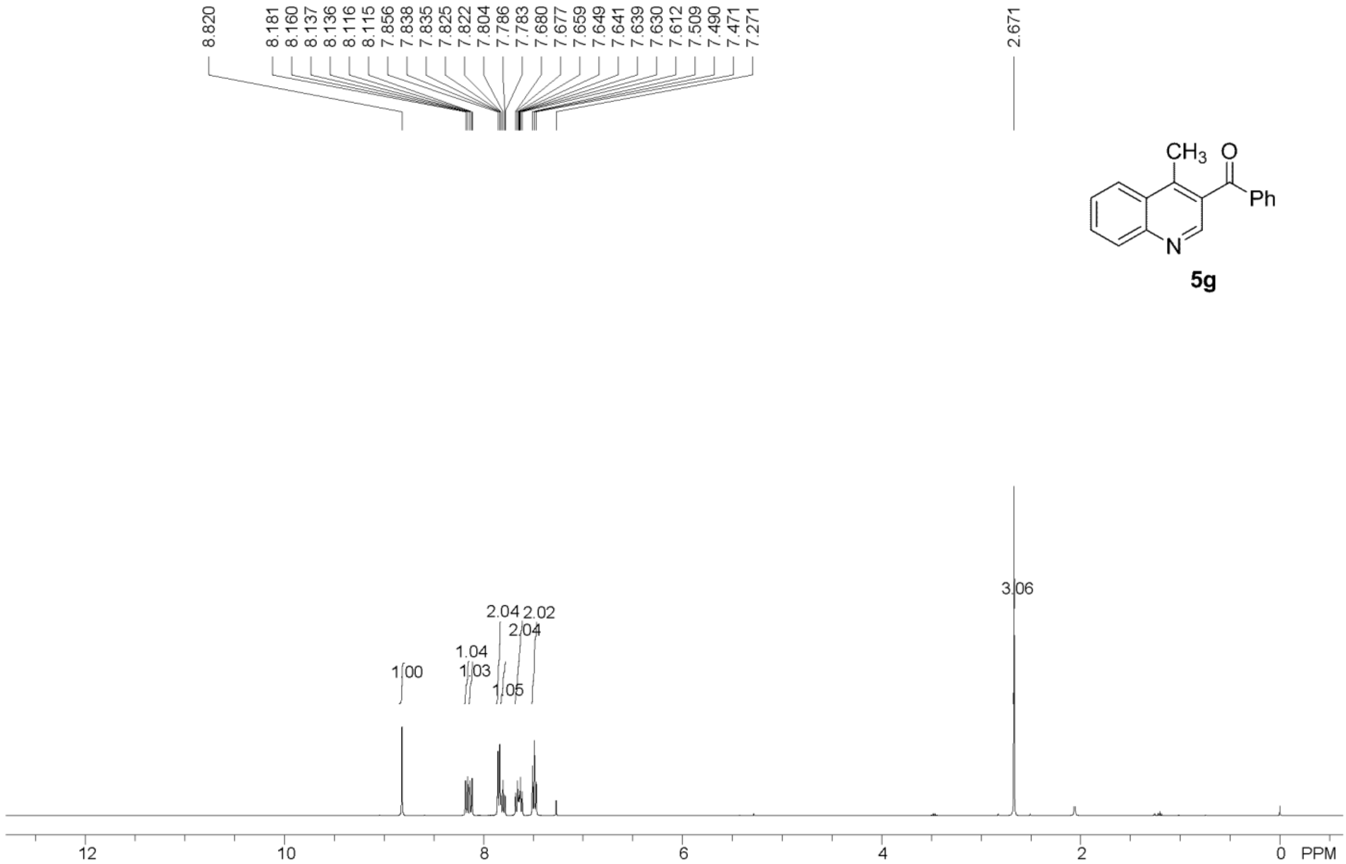
202.255
149.003
148.879
146.837
132.246
135.804
130.839
129.723
129.694
129.169
128.877
127.492
127.098
126.347
77.310
77.098
76.887
30.635
Ph
O
CH3
N
5e
200
150
100
50
0
PPM

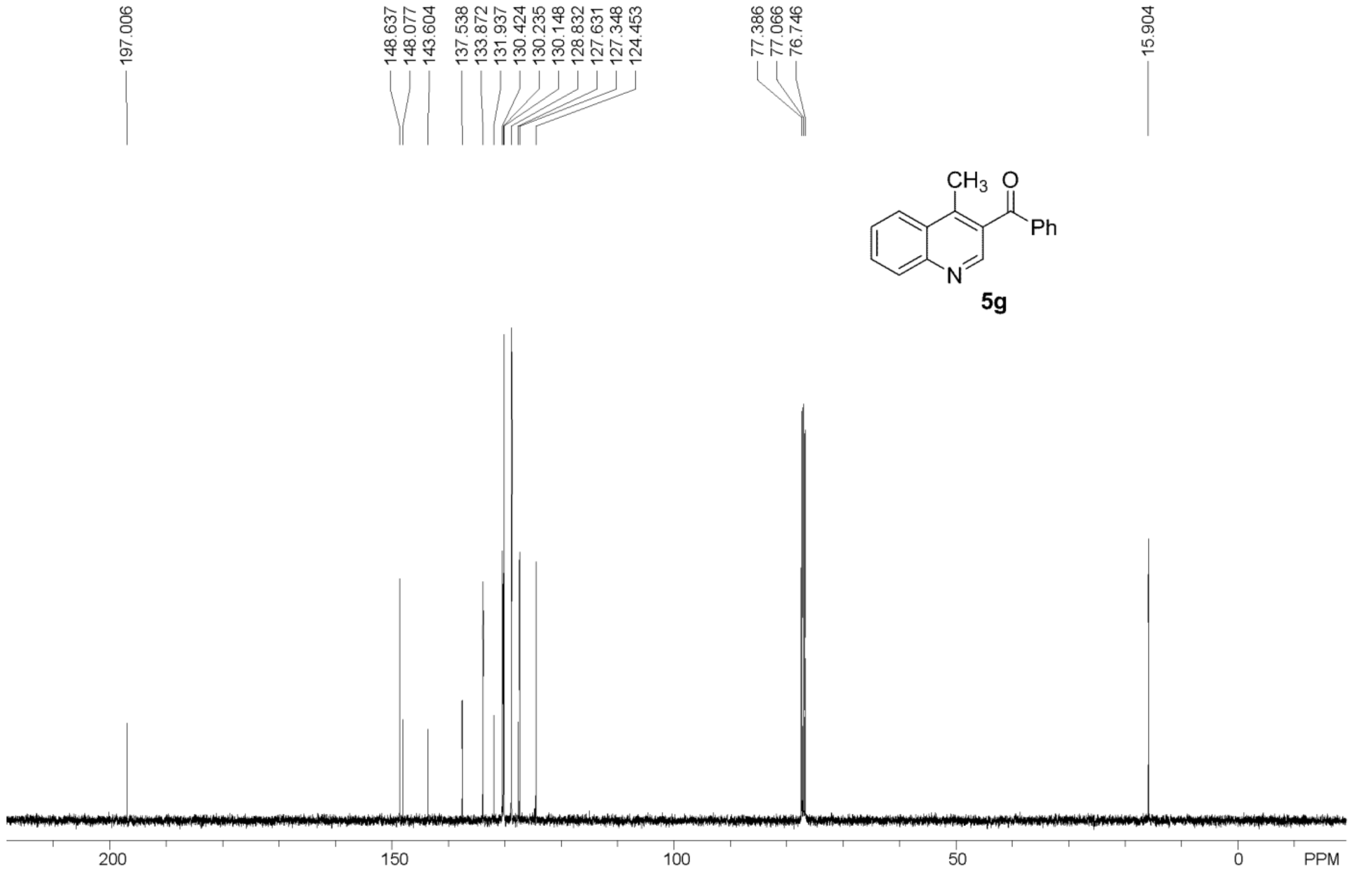

8.978
8.181 8.166 7.752 7.748 7.735 7.731 7.720 7.716 7.608 7.596 7.447 7.434 7.422 7.318 7.308 7.303 7.296 7.280 7.267 7.255
7.05
2.05
1.00
1.01
1.05
1.06
0.99
10
8
6
4
2
0
PPM
Ph
O
Cl
Ph
N

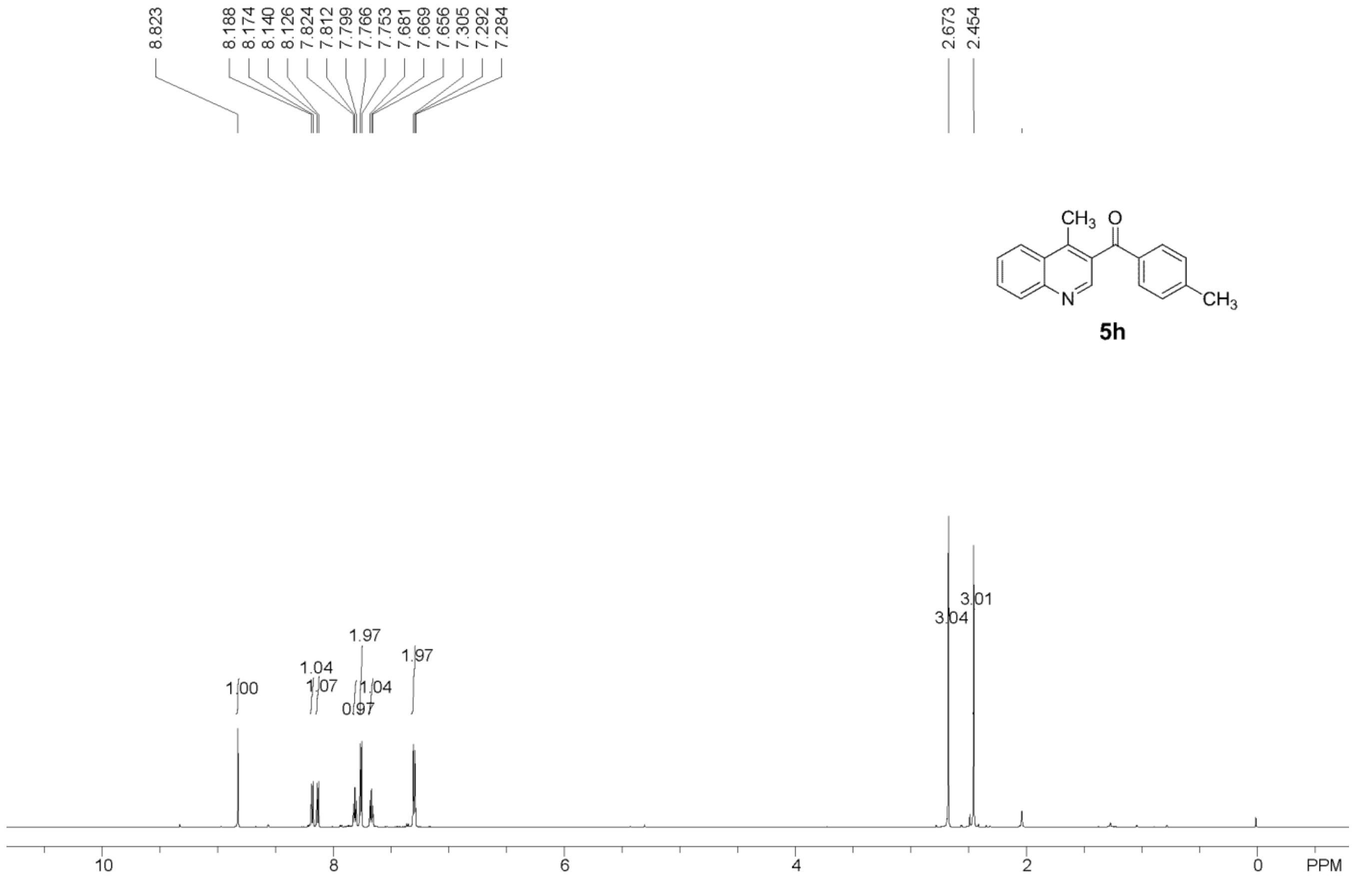
5f


196.421
148.696 147.253 146.108 137.095 134.280 133.646 133.442 132.618 131.488 131.444 129.986 129.730 128.870 128.483 128.345 127.288 125.472
77.353 77.142 76.930
200
150
100
50
0
PPM
Ph
O
Cl
Ph
N

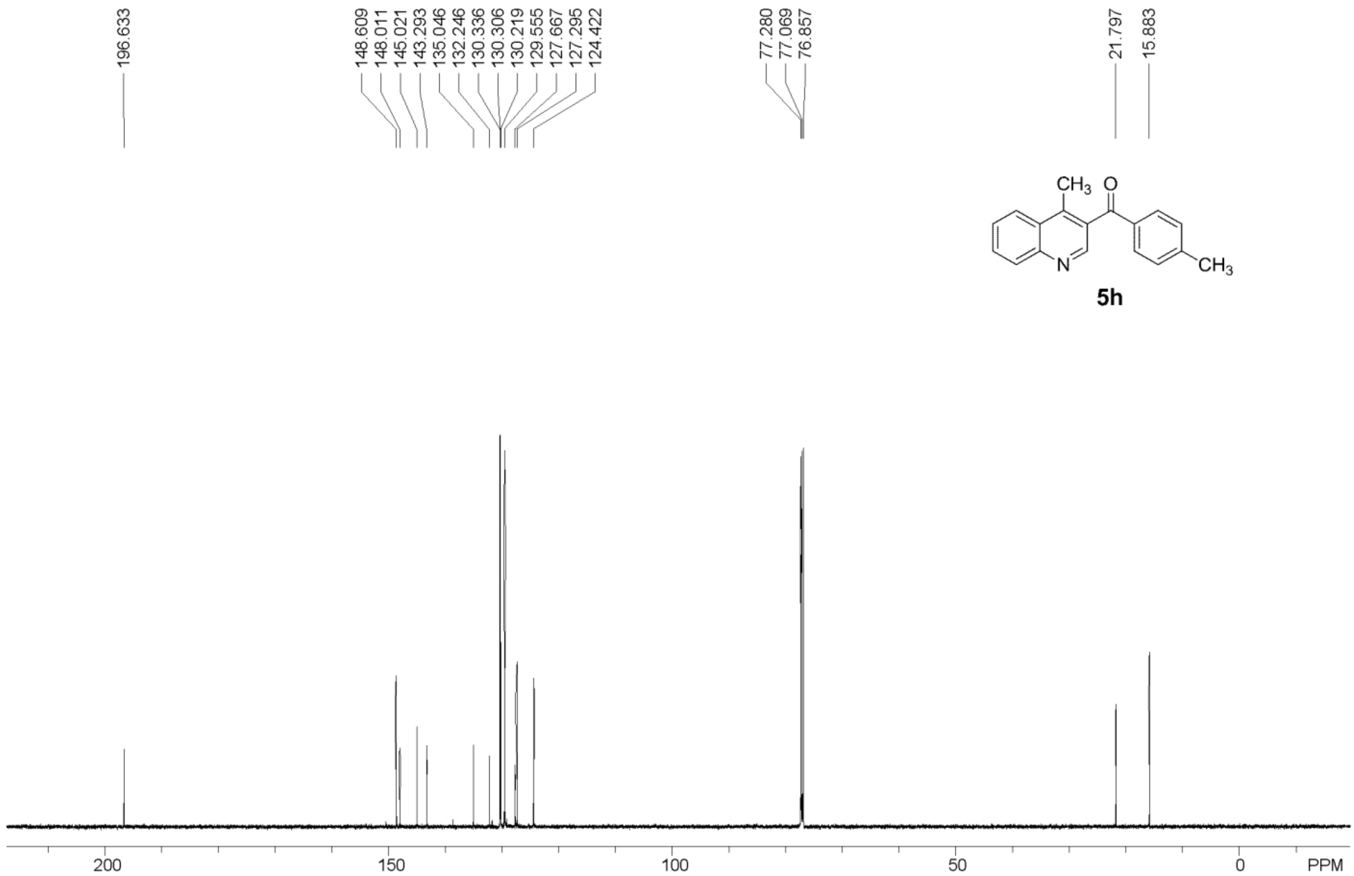
5f


8.820
8.181
8.160
8.137
8.136
8.116
8.115
7.856
7.838
7.835
7.825
7.822
7.804
7.786
7.783
7.680
7.677
7.659
7.649
7.641
7.639
7.630
7.612
7.509
7.490
7.471
7.271
2.671
CH3
O
Ph
N
5g
3.06
2.04
2.02
2.04
1.04
1.03
1.00
1.05
12
10
8
6
4
2
0
PPM

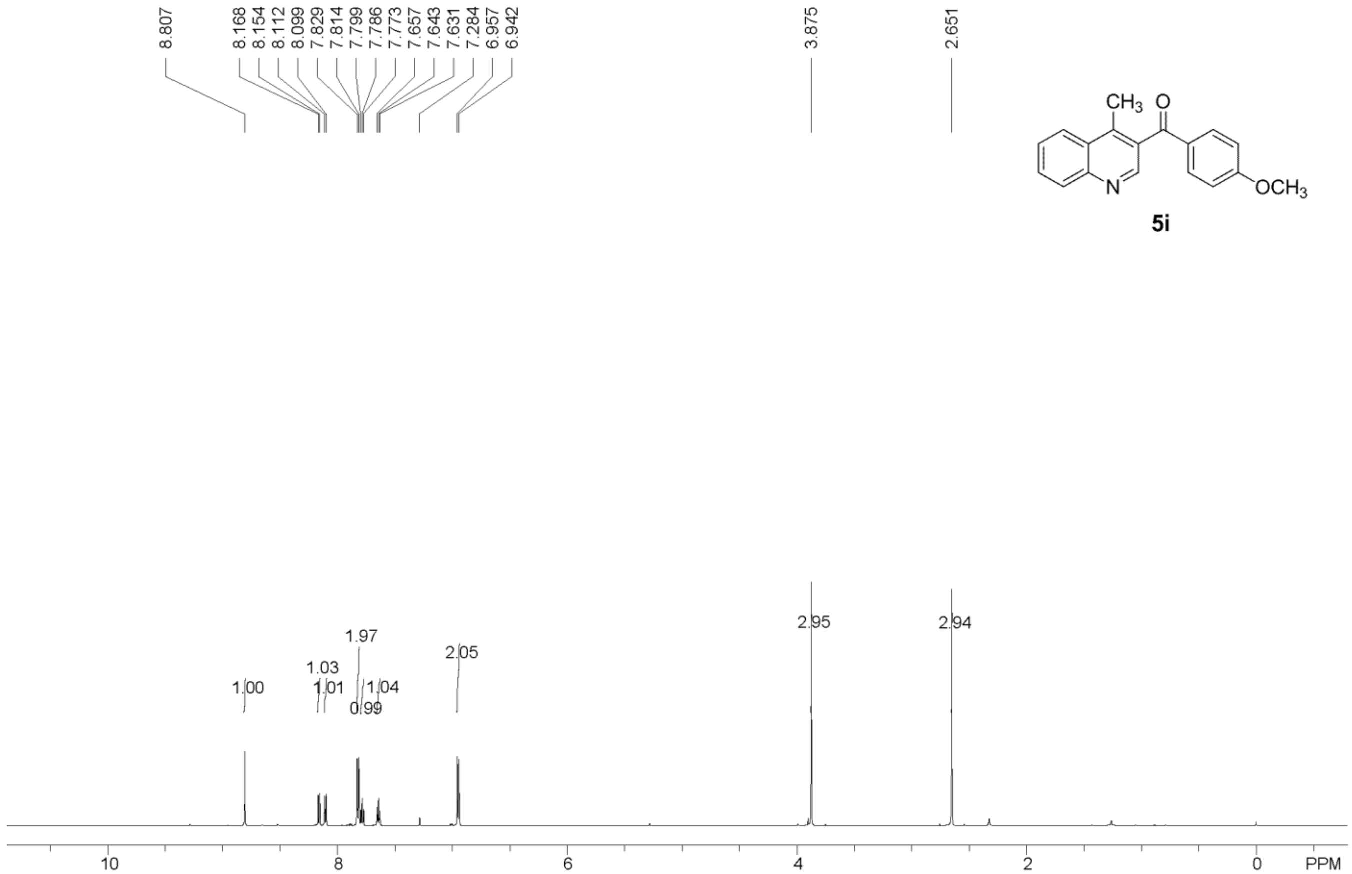

197.006
148.637
148.077
143.604
137.538
133.872
131.937
130.424
130.235
130.148
128.832
127.631
127.348
124.453
77.386
77.066
76.746
15.904
CH3
O
Ph
N
5g
200
150
100
50
0
PPM

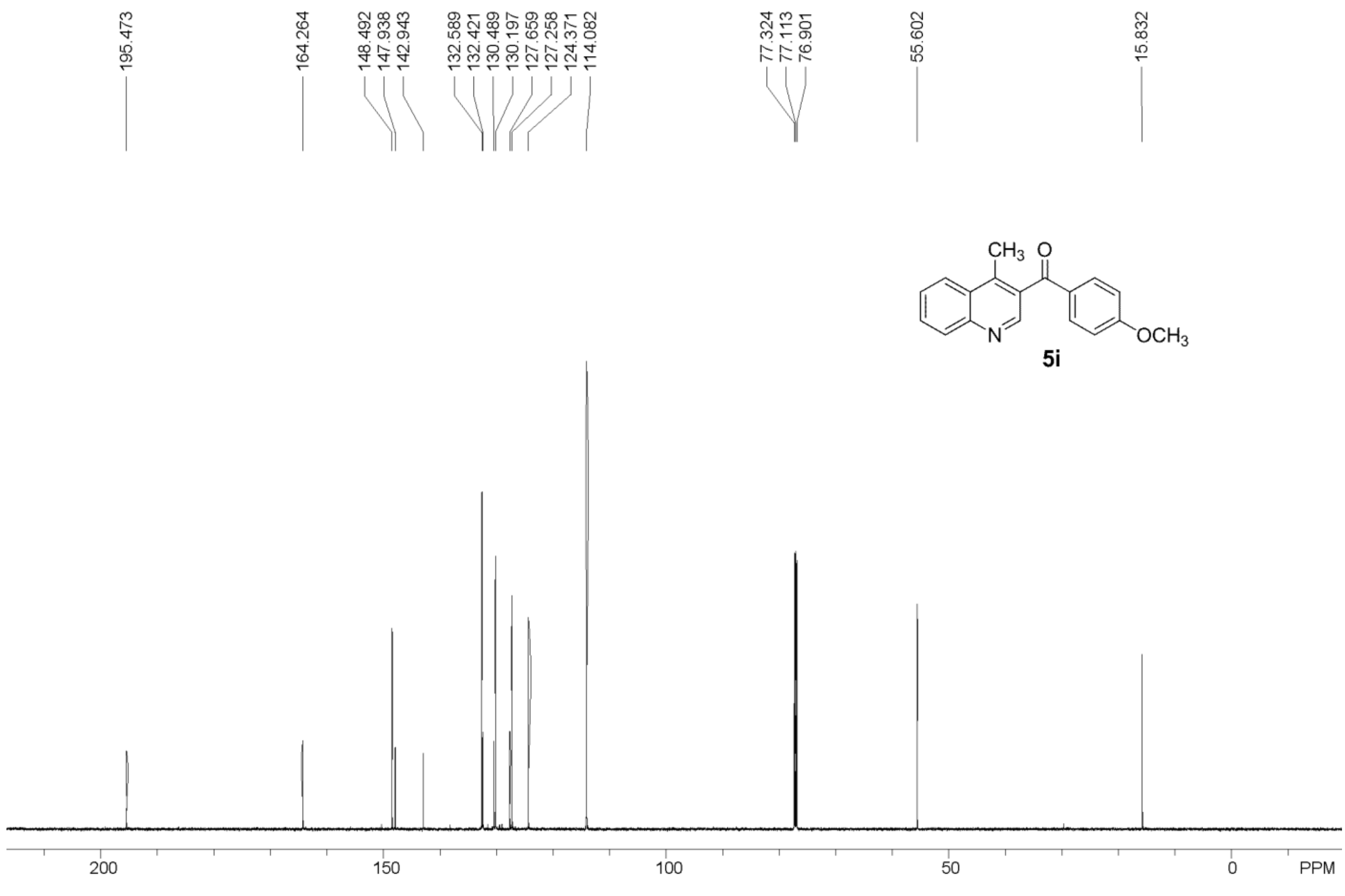

8.823
8.188 8.174 8.140 8.126 7.824 7.812 7.799 7.766 7.753 7.681 7.669 7.656 7.305 7.292 7.284
2.673 2.454
1.00 1.04 1.07 0.97 1.97 1.04 1.97 3.04 3.01
10 8 6 4 2 0 PPM

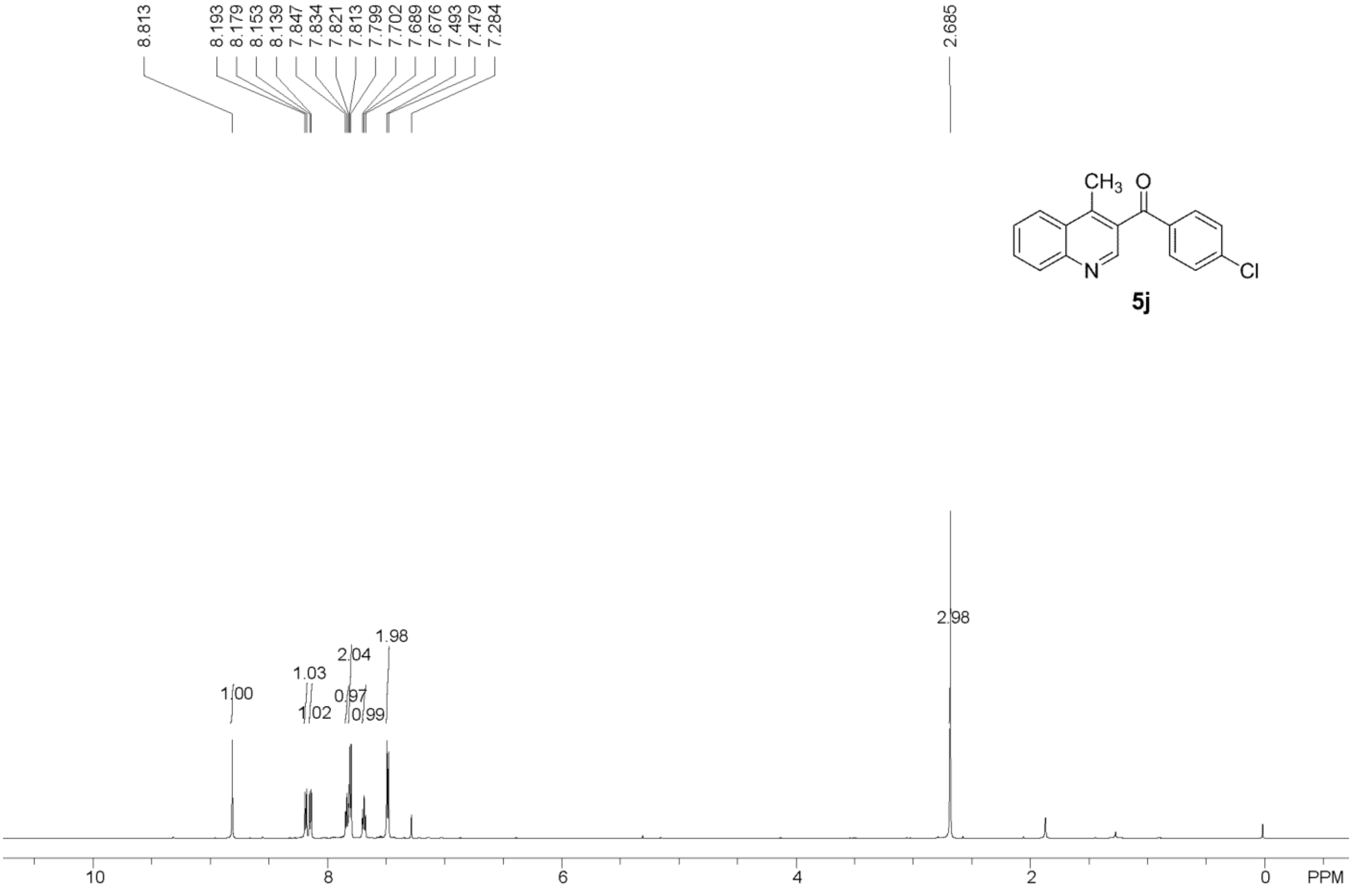
5h

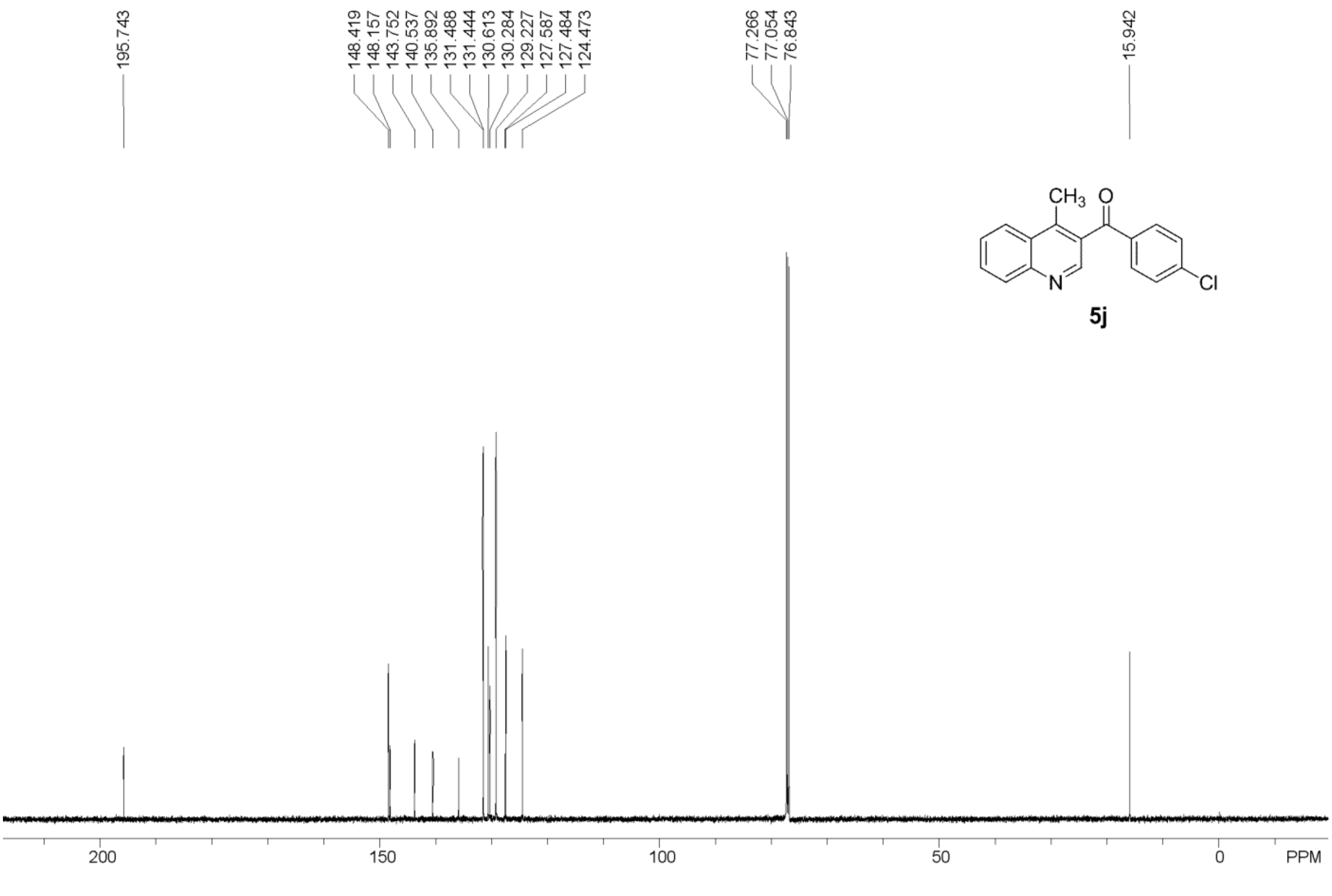

196.633
148.609 148.011 145.021 143.293 135.046 132.246 130.336 130.306 130.219 129.555 127.667 127.295 124.422
77.280 77.069 76.857
21.797 15.883
200 150 100 50 0 PPM

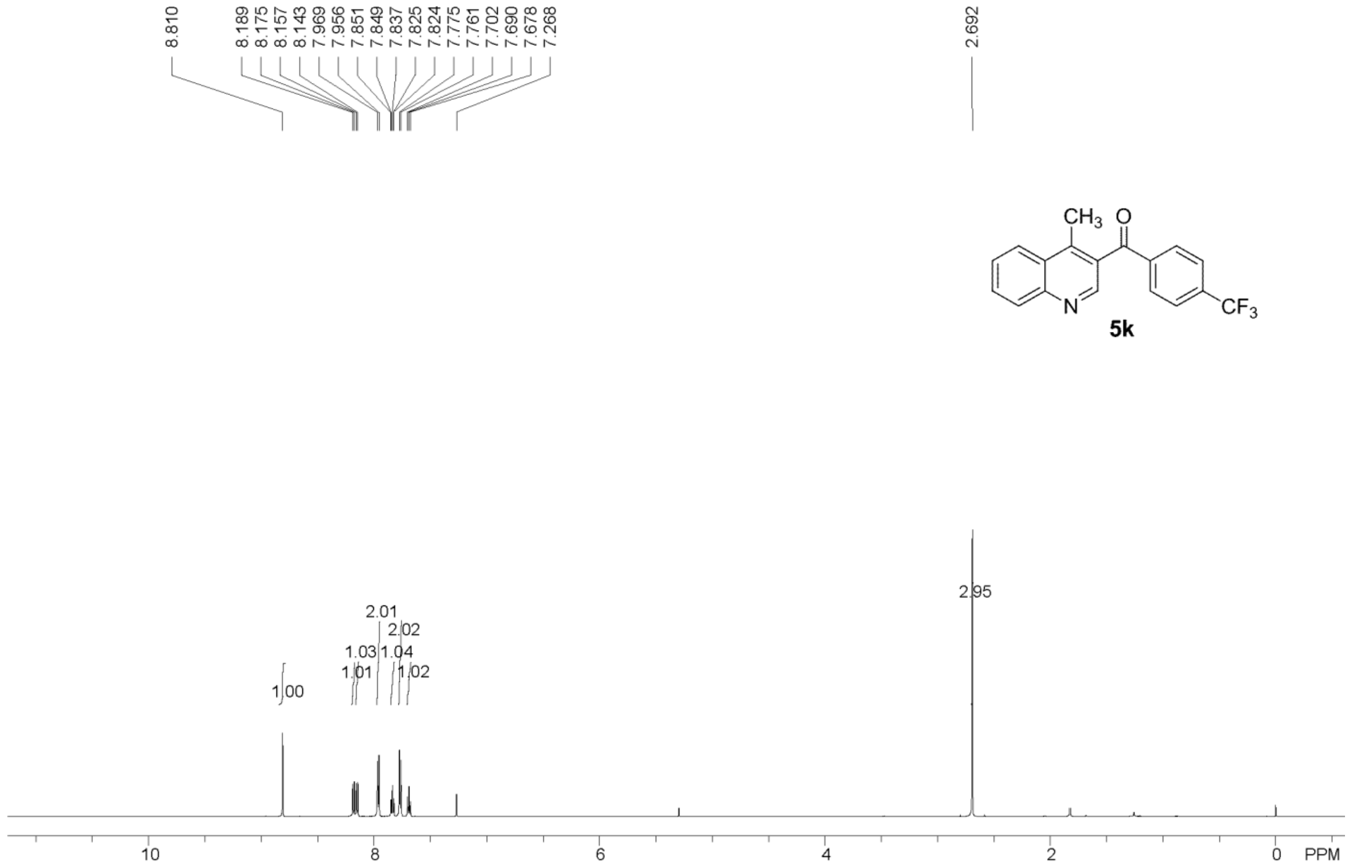
5h

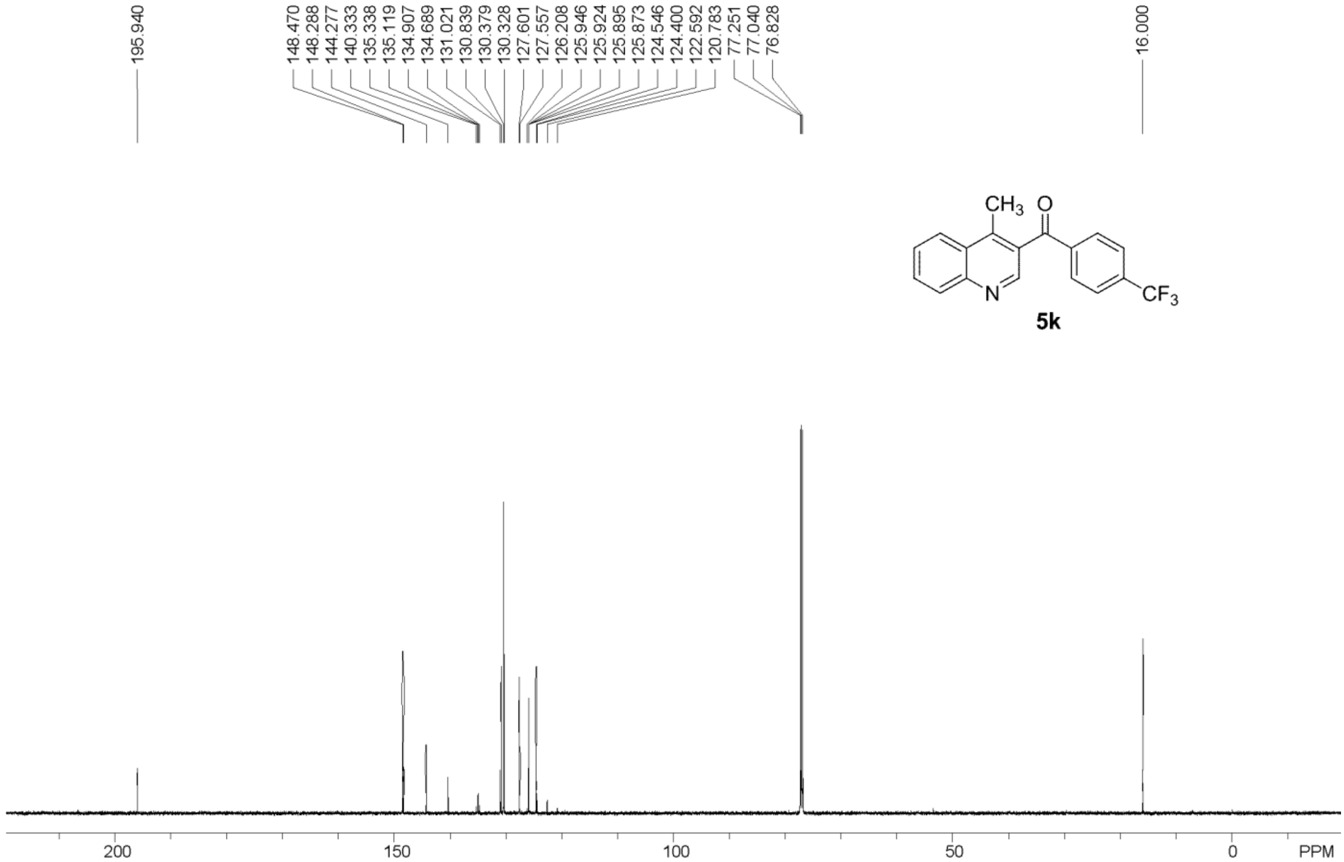

8.807
8.168 8.154 8.112 8.099 7.829 7.814 7.799 7.786 7.773 7.657 7.643 7.631 7.284 6.957 6.942
3.875
2.651
CH_3
O
N
OCH_3
5i
1.00
1.03
1.01
1.97
0.99
1.04
2.05
2.95
2.94
10
8
6
4
2
0
PPM

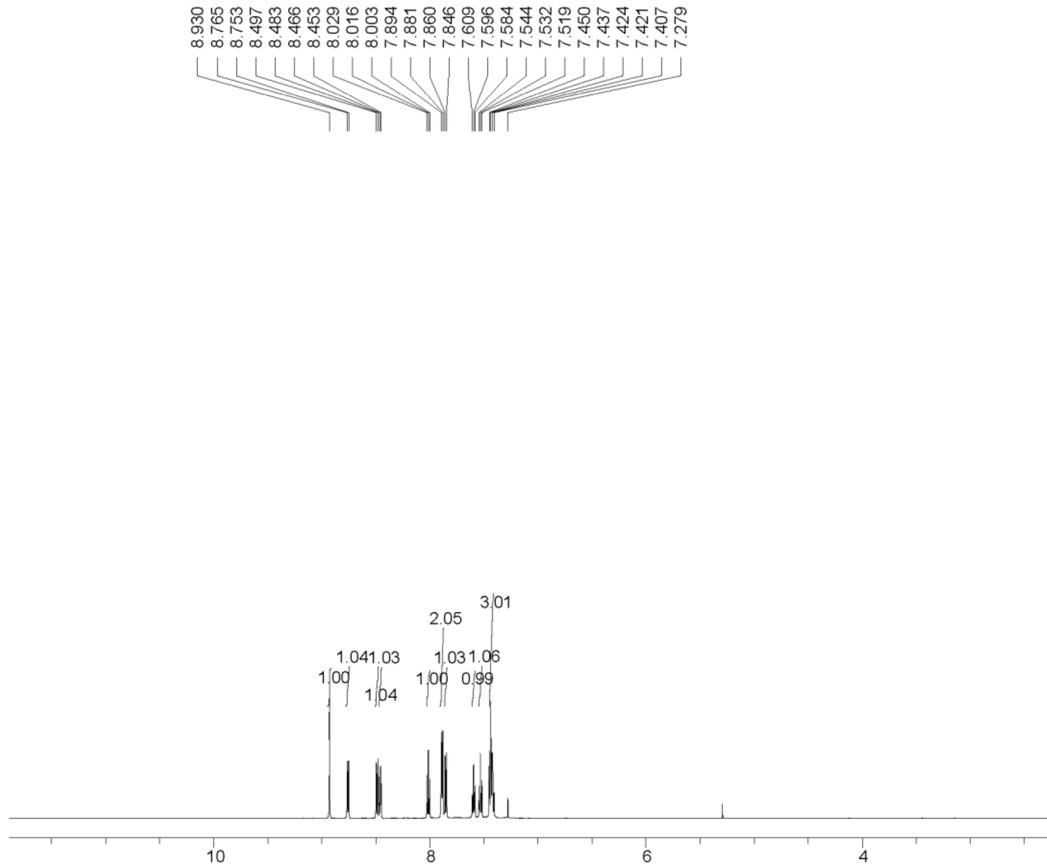

195.473
164.264
148.492 147.938 142.943
132.589 132.421 130.489 130.197 127.659 127.258 124.371 114.082
77.324 77.113 76.901
55.602
15.832
CH_3
O
N
OCH_3
5i
200
150
100
50
0
PPM

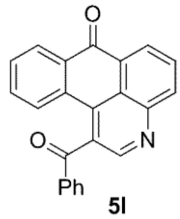

8.813
8.193
8.179
8.153
8.139
7.847
7.834
7.821
7.813
7.799
7.702
7.689
7.676
7.493
7.479
7.284
2.685
CH_3
O
N
Cl
5j
1.00
1.03
1.02
2.04
0.97
0.99
1.98
2.98
10
8
6
4
2
0
PPM


195.743
148.419
148.157
143.752
140.537
135.892
131.488
131.444
130.613
130.284
129.227
127.587
127.484
124.473
77.266
77.054
76.843
15.942
CH_3
O
N
Cl
5j
200
150
100
50
0
PPM

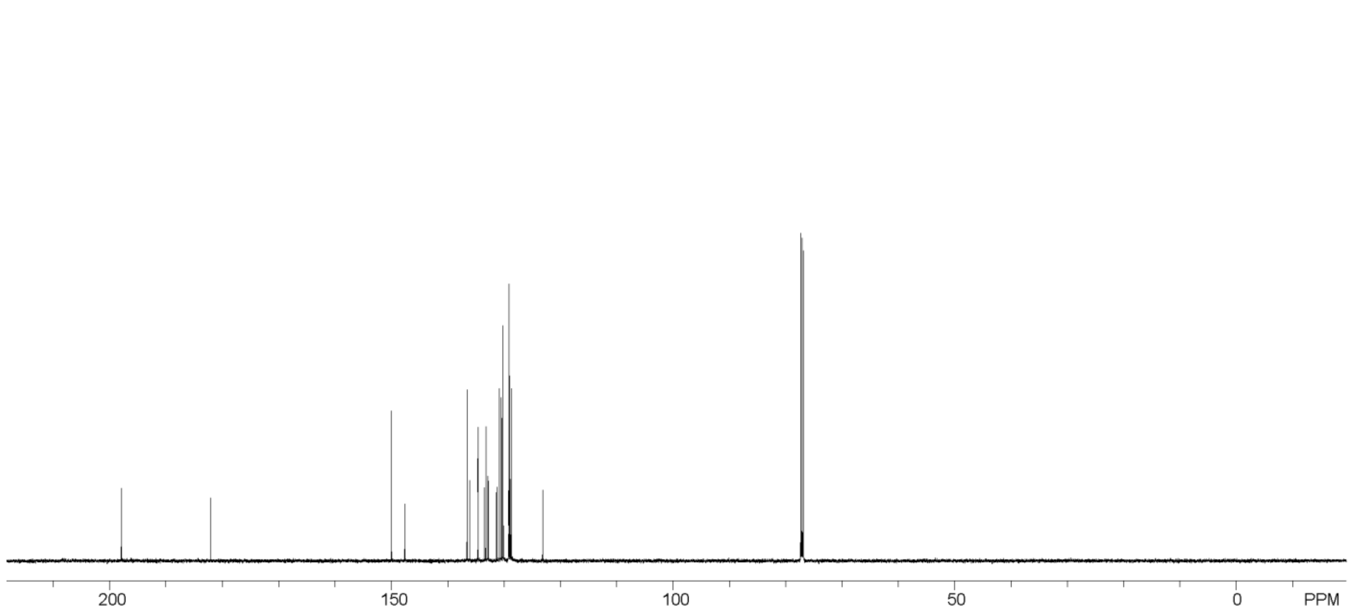

8.810
8.189 8.175 8.157 8.143 7.969 7.956 7.851 7.849 7.837 7.825 7.824 7.775 7.761 7.702 7.690 7.678 7.268
2.692
CH_3 O
N
CF_3
5k
1.00
1.01 1.03 2.01 1.04 2.02 1.02
2.95
10 8 6 4 2 0 PPM

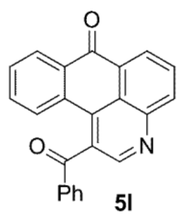

195.940
148.470 148.288 144.277 140.333 135.338 135.119 134.907 134.689 131.021 130.839 130.379 130.328 127.601 127.557 126.208 125.946 125.924 125.895 125.873 124.546 124.400 122.592 120.783 77.251 77.040 76.828
16.000
CH_3 O
N
CF_3
5k
200 150 100 50 0 PPM


8.930
8.765
8.753
8.497
8.483
8.466
8.453
8.029
8.016
8.003
7.894
7.881
7.860
7.846
7.609
7.596
7.584
7.544
7.532
7.519
7.450
7.437
7.424
7.421
7.407
7.279
3.01
2.05
1.041.03
1.031.06
1.00
1.00
0.99
1.04
10
8
6
4
2
0 PPM


O
O
N
Ph

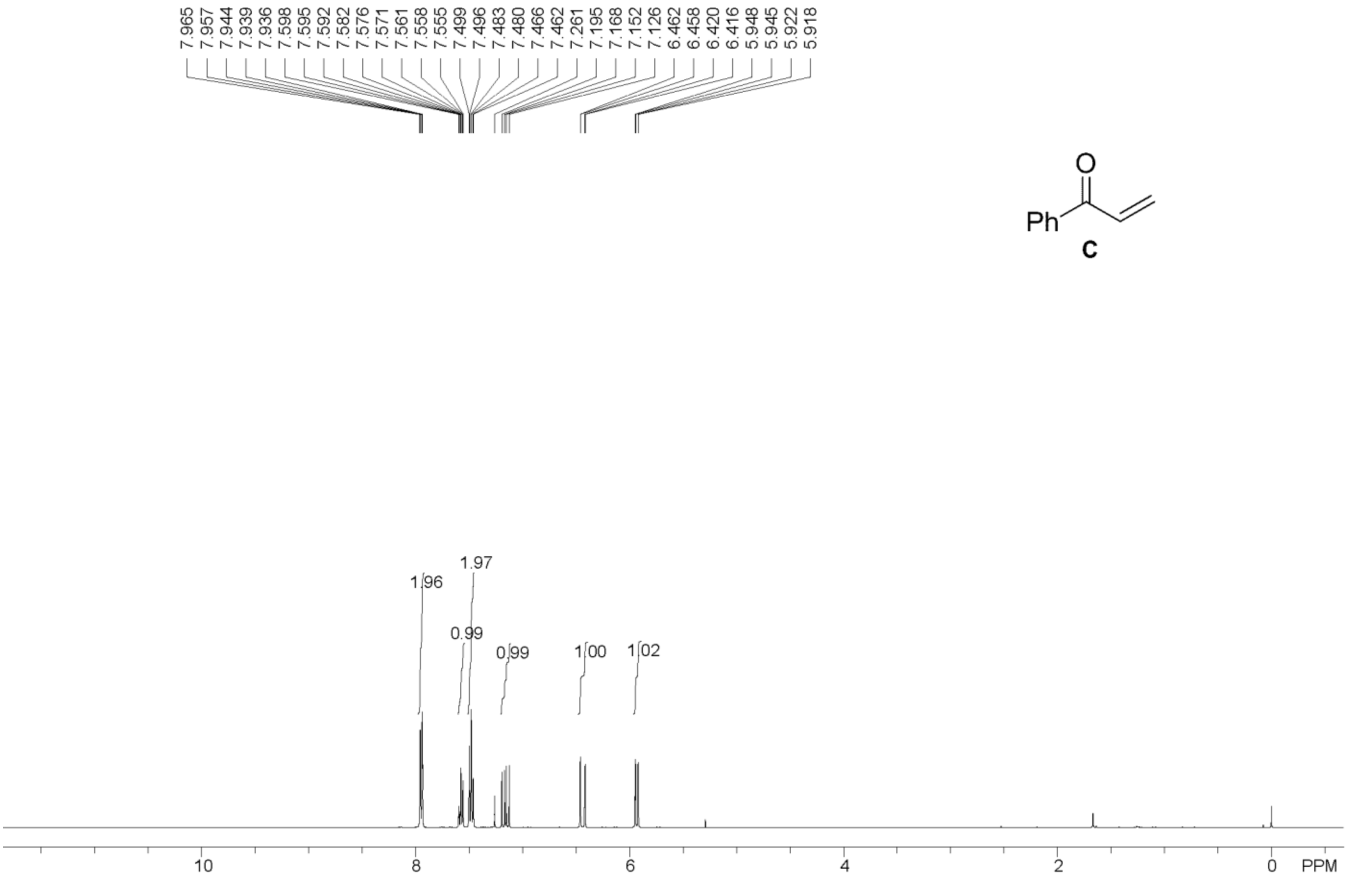
5l

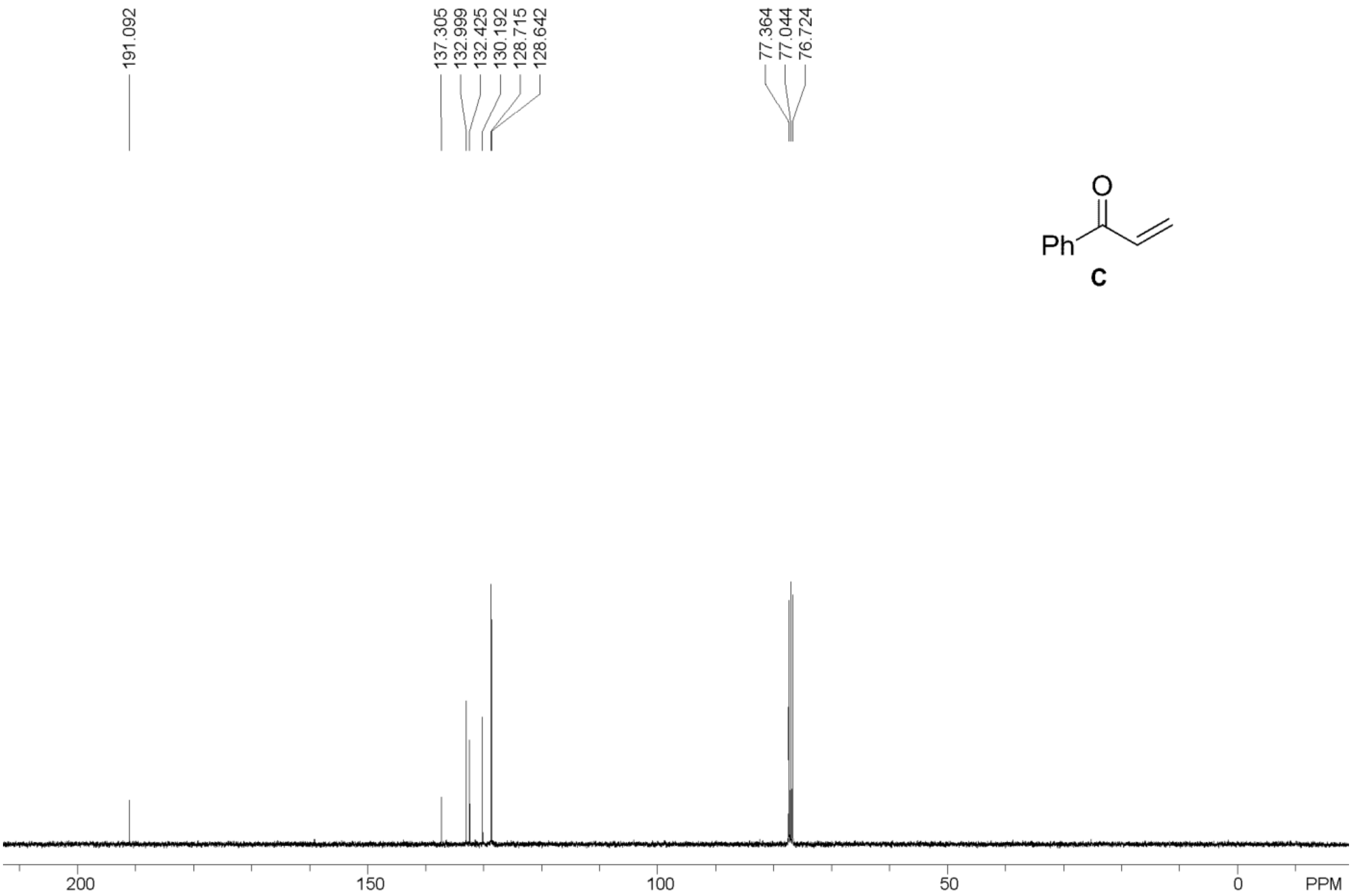

197.916
182.085
150.002
147.603
136.548
136.074
134.601
133.486
133.216
132.866
132.793
131.305
130.817
130.496
130.438
130.146
129.147
129.038
128.841
128.717
123.131
77.302
77.091
76.879
200
150
100
50
0
PPM

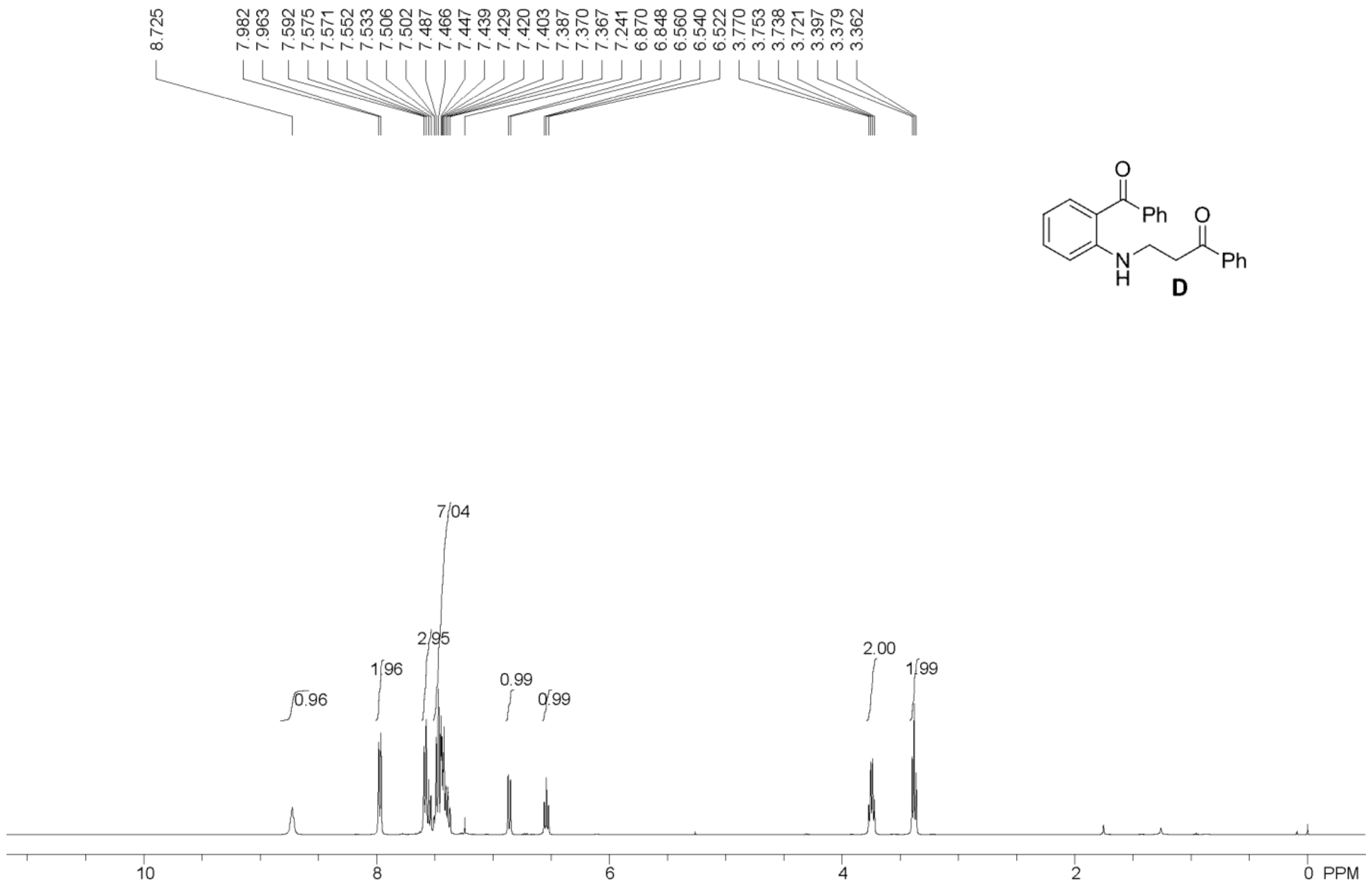

O
O
N
Ph

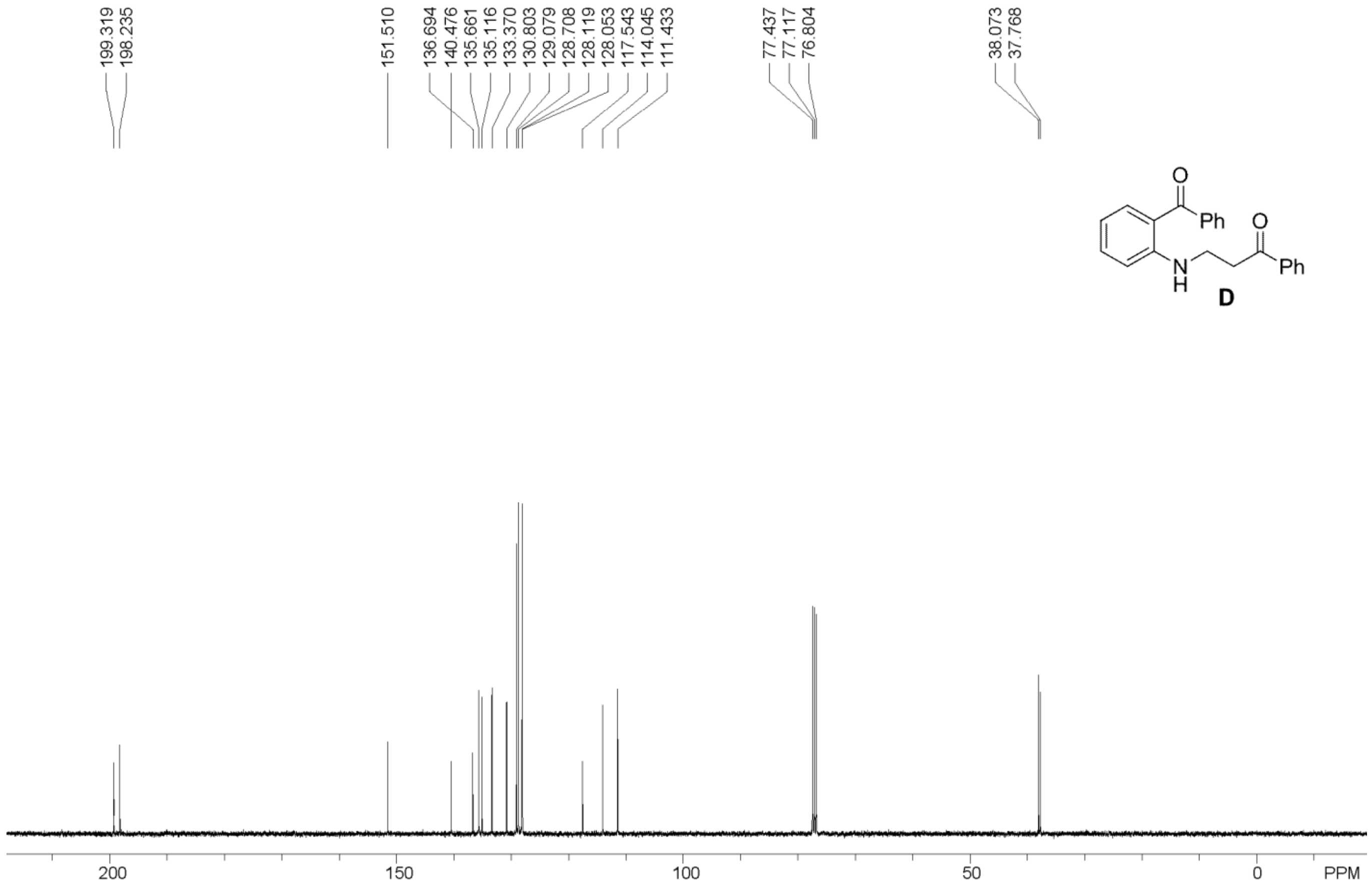
5l

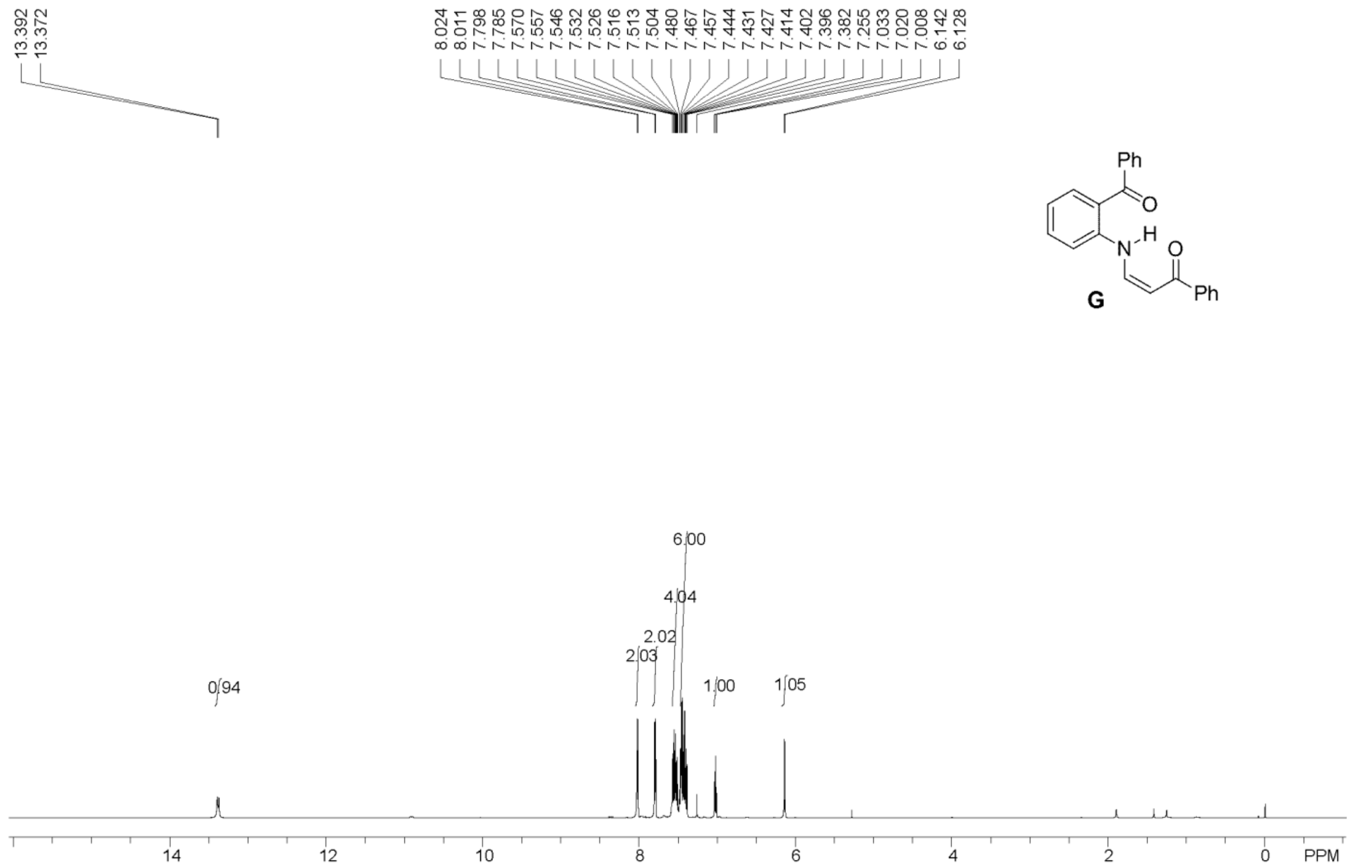
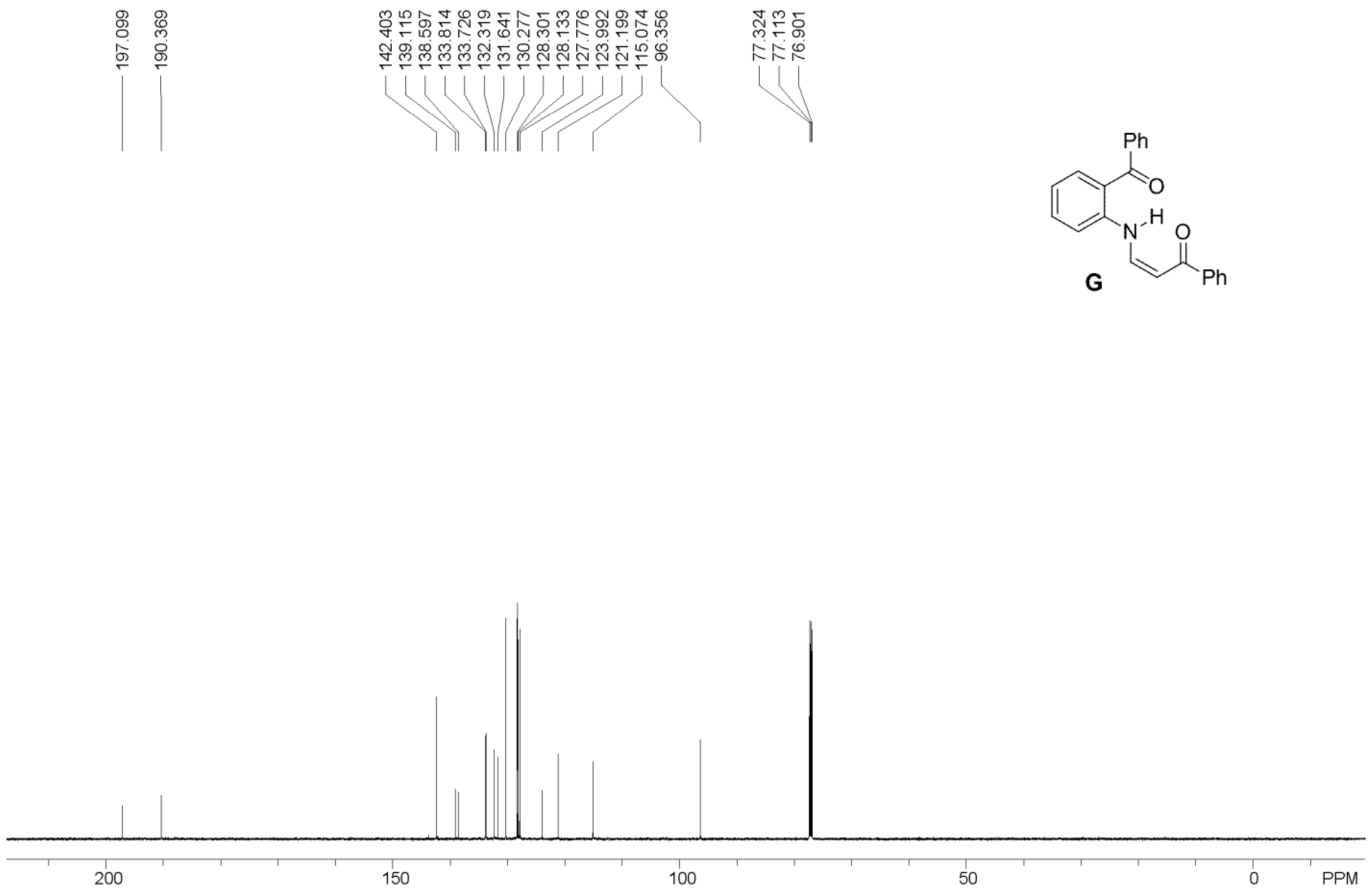
VI. Copies of ^{1}H and ^{13}C NMR spectra of intermediates C, D and G






8.725
7.982 7.963 7.592 7.575 7.571 7.552 7.533 7.506 7.502 7.487 7.466 7.447 7.439 7.429 7.420 7.403 7.387 7.370 7.367 7.241 6.870 6.848 6.560 6.540 6.522 3.770 3.753 3.738 3.721 3.397 3.379 3.362
O
Ph
O
N
H
Ph
D
7.04
2.95
1.96
0.96
0.99
0.99
2.00
1.99
10
8
6
4
2
0 PPM


199.319 198.235
151.510
136.694 140.476 135.661 135.116 133.370 130.803 129.079 128.708 128.119 128.053 117.543 114.045 111.433
77.437 77.117 76.804
38.073 37.768
O
Ph
O
N
H
Ph
D
200
150
100
50
0
PPM


13.392
13.372
8.024
8.011
7.798
7.785
7.570
7.557
7.546
7.532
7.526
7.516
7.513
7.504
7.480
7.467
7.457
7.444
7.431
7.427
7.414
7.402
7.396
7.382
7.255
7.033
7.020
7.008
6.142
6.128
Ph
O
N
H
O
Ph
G
6.00
4.04
2.02
2.03
0.94
1.00
1.05
14
12
10
8
6
4
2
0
PPM

197.099
190.369
142.403
139.115
138.597
133.814
133.726
132.319
131.641
130.277
128.301
128.133
127.776
123.992
121.199
115.074
96.356
77.324
77.113
76.901
Ph
O
N
H
O
Ph
G
200
150
100
50
0
PPM