Supporting information for

Lewis acid-catalyzed 2-arylquinazoline formation from *N*'-arylbenzimidamides and paraformaldehyde

Xiufang Cheng,[a] Huamin Wang,[a] Fuhong Xiao[a]* and Guo-Jun Deng[a]*

[a] Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, China; Fax: (+86)-731-58292251; e-mail: gjdeng@xtu.edu.cn；fhxiao@xtu.edu.cn.

Table of Contents

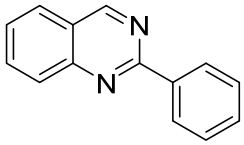
General information:

All experiments were carried out under an atmosphere of O_2. Flash column chromatography was performed over silica gel 48-75 μm. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to $SiMe_4$ or chloroform signals. MS analyses were performed on an Agilent 5975 GC-MS instrument (EI). The new compounds were characterized by ^{1}H NMR, ^{13}C NMR, MS and HRMS. The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and MS data with those of literature. The substrates **1a-1aa** were synthesized following the literature procedures[1]. All other chemicals and solvents were used as received from commercial sources without further purification.

General procedure for preparation of 2:

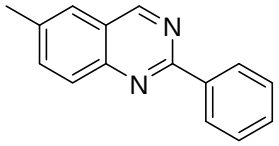
A 10 mL oven-dried reaction vessel was charged with $BF_3 \cdot Et_2O$ (2.5 uL, 0.01 mmol), K_2CO_3 27.6 mg, 0.2 mmol), (Z)-*N'*-phenylbenzimidamide (**1a**, 39.3, 0.2 mmol), paraformaldehyde (18.0 mg, 0.6 mmol) and DMSO (0.8 mL). The resulting solution was sealed under O_2 and stirred at 140 °C for 24 h. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2a** as light yellow solid; yield: 38.0 mg (92%).

2-phenylquinazoline (2a, CAS: 25855-20-3)[2]



^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.48 (s, 1H), 8.63-8.60 (m, 2H), 8.11-8.09 (m, 1H), 7.95-7.89 (m, 2H), 7.64-7.60 (m, 1H), 7.57-7.49 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.1, 160.5, 150.8, 138.0, 134.1, 130.6, 128.6, 128.6, 128.6, 127.2, 127.1, 123.6 ; MS (EI)) m/z (%) 206, 197, 179, 105 (100), 77.

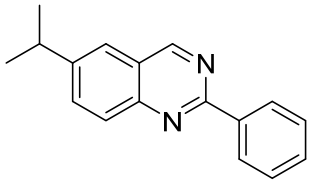
6-methyl-2-phenylquinazoline (2b, CAS: 121910-86-9)[3]



The reaction was conducted with methyl (Z)-*N*′-(p-tolyl)benzimidamide (**1b**, 42.1 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2b** as light yellow solid; yield 90%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.39 (s, 1H), 8.61-8.58 (m, 2H), 7.99 (d, J = 8.0 Hz, 1H), 7.76-7.73 (m, 1H), 7.69 (s, 1H), 7.56-7.50 (m, 3H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160, 159.7, 149.1 137.7, 137.6, 136.7, 130.5, 128.6, 128.4, 128.1, 125.8, 123.5, 21.6; MS (EI) m/z (%) 220 (100), 193, 165, 110, 77.

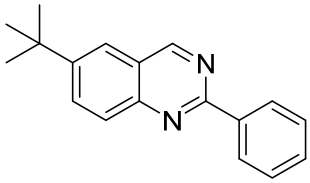
6-isopropyl-2-phenylquinazoline (2c)



The reaction was conducted with (Z)-*N*′-(4-isopropylphenyl)benzimidamide (**1c**, 47.7 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2c** as light yellow solid; yield 84%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.43-9.42 (m, 1H), 8.61-8.58 (m, 2H), 8.03 (d, J = 8.0 Hz, 1H), 7.84-7.81 (s, 1H), 7.73-7.72 (m, 1H), 7.56-7.50 (m, 3H), 3.17-3.10 (m, 1H), 1.38 (d, J = 8.0 Hz, 6H) ; ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.5, 160.0, 149.7, 148.2, 138.2, 134.2, 130.4, 128.6, 128.4, 123.6, 123.0, 34.1, 23.7; MS (EI) m/z (%) 248, 233 (100), 206, 103, 77; HRMS calcd. for: $C_{17}H_{16}N_2$ $[M+H]^+$ = 249.13863, found = 249.13845.

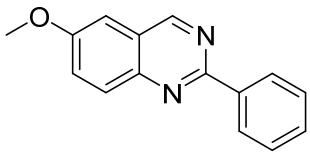
6-(*tert*-butyl)-2-phenylquinazoline (2d)



The reaction was conducted with (Z)-*N'*-(4-(tert-butyl)phenyl)benzimidamide (**1d**, 50.5 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2d** as light yellow solid; yield 90%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.44 (s, 1H), 8.61-8.58 (m, 2H), 8.03-8.02 (m, 2H), 7.84-7.83 (m, 1H), 7.54-7.50 (m, 3H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.7, 160.3, 150.4, 149.4, 138.2, 133.1, 130.3, 128.6, 128.4, 128.1, 123.4, 121.9, 35.1, 31.0; MS (EI) m/z (%) 262, 247 (100), 220, 116, 77 ; HRMS calcd. for: $C_{18}H_{18}N_2$ $[M+H]^+$ = 263.15428, found = 263.15412.

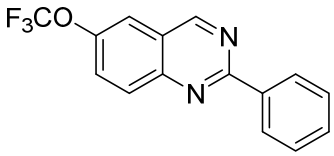
6-methoxy-2-phenylquinazoline (2e, CAS: 34637-66-6)[2]



The reaction was conducted with (Z)-*N'*-(4-methoxyphenyl)benzimidamide (**1e**, 45.3 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2e** as light yellow solid; yield 75%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) *δ* 9.37 (s, 1H), 8.58-8.56 (m, 2H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.57-7.49 (m, 4H), 7.16-7.15 (m, 1H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) *δ* 159.3, 158.8, 158.2, 146.9, 138.1, 130.2, 130.1, 128.6, 128.1, 127.2, 124.4, 103.8, 55.7; MS (EI) m/z (%) 236 (100), 221, 193, 106, 63.

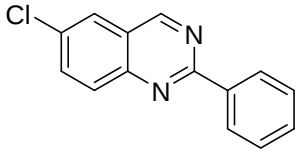
2-phenyl-6-(trifluoromethoxy)quinazoline (2f)



The reaction was conducted with (Z)-*N'*-(4-(trifluoromethoxy)phenyl)benzimidamide (**1f**, 56.1 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2f** as light yellow solid; yield 84%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.47 (s, 1H), 8.62-8.60 (m, 2H), 8.15-8.13 (m, 1H), 7.75-7.74 (m, 2H), 7.55-7.53 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.6, 160.3, 149.1, 147.1 (q, J = 2.0 Hz), 137.5, 131.2, 131.0, 128.8, 128.6, 128.3, 123.5, 121.8, 117.0; MS (EI) m/z (%) 290 (100), 263, 166, 103, 63; ^{19}F NMR (376 MHz, $CDCl_3$) δ = - 57.90 ppm; HRMS calcd. for: $C_{15}H_{10}ON_2F_3$ $[M+H]^+$ = 291.07397, found = 291.07371.

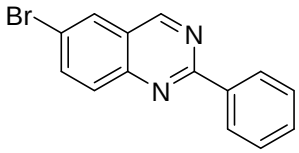
6-chloro-2-phenylquinazoline (2g, CAS: 580-53-0)[2]



The reaction was conducted with (Z)-*N'*-(4-chlorophenyl)benzimidamide (**1g**, 46.1 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2g** as light yellow solid; yield 80%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.41(s, 1H), 8.61-8.59 (m, 2H), 8.04 (d, J = 8.0 Hz, 1H), 7.92-7.92 (m, 1H), 7.85-7.83 (m, 1H), 7.57-7.52 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.2, 159.5, 149.2, 137.5, 135.0, 132.7, 130.8, 130.3, 128.7, 128.5, 125.8, 123.9; MS (EI) m/z (%) 240 (100), 213, 178, 120, 75.

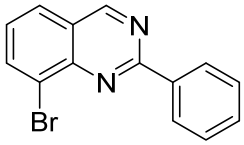
6-bromo-2-phenylquinazoline (2h)[4]



The reaction was conducted with (Z)-*N'*-(4-bromophenyl)benzimidamide (**1h**, 55.0 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2h** as light yellow solid; yield 65%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.40 (s, 1H), 8.61-8.59 (m, 2H), 8.10-8.09 (m, 1H), 7.97-7.97 (m, 2H), 7.57-7.52 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.2, 159.4, 149.3, 137.6, 137.5, 130.9, 130.4, 129.2, 128.7, 128.6, 124.4, 120.7; MS (EI) m/z (%) 284 (100), 257, 178, 151, 75.

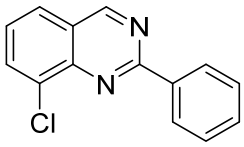
8-bromo-2-phenylquinazoline (2i)



The reaction was conducted with (Z)-*N*′-(2-bromophenyl)benzimidamide (**1i**, 55.0 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2i** as light yellow solid; yield 65%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ9.44 (s, 1H), 8.73-8.71 (m, 2H), 8.23-8.21 (m, 1H), 7.91-7.89 (m, 1H), 7.58-7.53 (m, 3H), 7,48 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.6, 160.9, 148.1, 137.5, 137.4, 131.1, 128.8, 128.7, 127.6, 126.7, 124.7, 124.3; MS (EI) m/z (%) 284 (100), 257, 178, 151, 75; HRMS calcd. for: $C_{14}H_9BrN_2$ $[M+H]^+$ = 285.00219 , found = 285.00211.

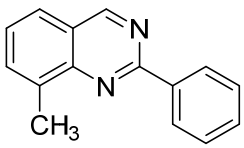
8-chloro-2-phenylquinazoline (2j, CAS: 58058-52-9)[5]



The reaction was conducted with (Z)-*N*′-(2-chlorophenyl)benzimidamide (**1j**, 46.1 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2j** as light yellow solid; yield 68%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.55-9.54 (m, 1H), 8.16-8.13 (m, 1H), 8.03-7.96 (m, 2H), 7.84-7.82 (m, 1H), 7.74-7.70 (m, 1H), 7.56-7.54 (m, 1H), 7.43-7.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.4, 160.7, 147.2, 137.5, 133.9, 133.2, 131.1, 128.8, 128.7, 127.1, 126.0, 124.6; MS (EI) m/z (%) 240 (100), 213, 178, 151, 75.

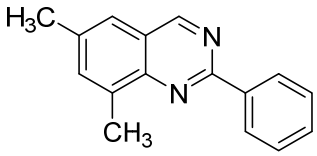
8-methyl-2-phenylquinazoline (2k, CAS: 58058-51-8)[3]



The reaction was conducted with (Z)-*N*′-(o-tolyl)benzimidamide (**1k**, 42.1 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2k** as light yellow solid; yield 91%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.43 (s, 1H), 8.68-8.66 (m, 2H), 7.77-7.73 (m, 2H), 7.56-7.48 (m, 4H), 2.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.5, 159.8, 149.6, 138.3, 137.1, 133.8, 130.4, 128.6, 128.5, 126.9, 124.8, 123.4, 16.9; MS (EI) m/z (%) 220 (100), 193, 165, 110, 77.

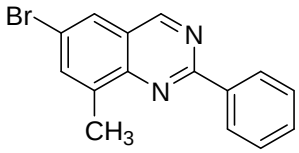
6,8-dimethyl-2-phenylquinazoline (2l)



The reaction was conducted with (Z)-*N*'-(2,4-dimethylphenyl)benzimidamide (**1l**, 44.9 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2l** as light yellow solid; yield 89%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.33 (s, 1H), 8.66-8.63 (m, 2H), 7.58 (s, 1H), 7.56-7.49 (m, 4H), 2.82 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 159.3, 158.6, 148.4, 137.9, 137.2, 136.7, 136.6, 130.4, 128.6, 128.3, 123.6, 123.3, 21.6, 16.8; MS (EI) m/z (%) 234 (100), 206, 165, 103, 77; HRMS calcd. for: $C_{16}H_{14}N_2$ $[M+H]^+$ = 235.12298, found = 235.12278.

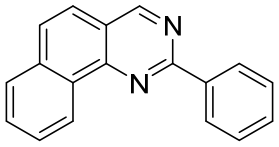
6-bromo-8-methyl-2-phenylquinazoline (2m)



The reaction was conducted with (Z)-*N*'-(4-bromo-2-methylphenyl)benzimidamide (**1m**, 57.8 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2m** as light yellow solid; yield 76%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.34 (s, 1H), 8.65-8.63 (m, 2H), 7.91-7.91 (m, 1H), 7.82-7.82 (m, 1H), 7.56-7.52 (m, 3H), 2.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.1, 159.4, 148.9, 139.6, 137.9, 137.0, 130.7, 128.6, 128.5, 126.8, 124.4, 120.4, 16.7; MS (EI) m/z (%) 298 (100), 192, 165, 89, 63; HRMS calcd. for: $C_{15}H_{11}BrN_2$ $[M+H]^+$ = 299.01784, found = 299.01812.

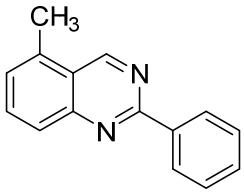
2-phenylbenzo[*h*]quinazoline (2n, CAS: 88737-72-8)[4]



The reaction was conducted with (Z)-*N*′-(naphthalen-1-yl)benzimidamide (**1n**, 49.3 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2n** as light yellow solid; yield 94%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.47-9.42 (m, 2H), 8.78-8.75 (m, 2H), 7.96-7.94 (m, 1H), 7.87-7.74 (m, 4H), 7.61-7.52 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.0, 158.5, 150.8, 138.2, 135.5, 130.6, 130.3, 130.2, 128.6, 128.6, 128.5, 128.0, 127.4, 124.9, 122.9, 121.4; MS (EI) m/z (%) 256 (100), 229, 152, 126, 76.

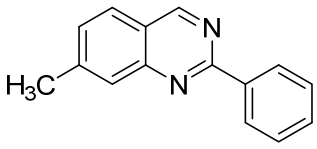
7-methyl-2-phenylquinazoline (2o)



The reaction was conducted with (Z)-*N*′-(naphthalen-1-yl)benzimidamide (**1o**, 42.1 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2o** as light yellow solid; yield 58%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.67-9.67 (m, 1H), 8.63-8.60 (m, 2H), 7.94-7.92 (m, 1H), 7.79-7.76 (m, 1H), 7.55-7.51 (m, 3H), 7.39-7.38 (m, 1H), 2.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.6, 157.5, 151.2, 138.0, 135.4, 133.9, 130.5, 128.6, 128.5, 127.8, 126.8, 122.7, 17.5; MS (EI) m/z (%) 220 (100), 193, 165, 110, 77; HRMS calcd. for: $C_{15}H_{12}N_2$ $[M+H]^+$ = 221.10732, found = 221.10700.

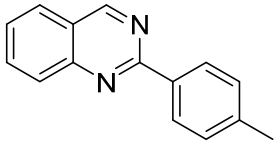
5-methyl-2-phenylquinazoline (2o', CAS: 1600535-89-4)[6]



The reaction was conducted with (Z)-*N*′-(naphthalen-1-yl)benzimidamide (**1o**, 42.1 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2o'** as light yellow solid; yield 20%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.39 (s, 1H), 8.61-8.59 (m, 2H), 7.87 (s, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.55-7.50 (m, 3H), 7.43 d, J = 8.0 Hz, 1H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.1, 159.9, 151.1, 145.2, 138.2, 130.5, 129.6, 128.6, 128.5, 127.6, 126.8, 121.9, 22.4; MS (EI) m/z (%) 220 (100), 193, 165, 110, 77.

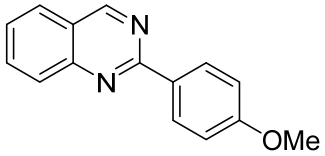
2-(*p*-tolyl)quinazoline (2p)[2]



The reaction was conducted with (Z)-4-methyl-*N*′-phenylbenzimidamide (**1p**, 42.1 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2p** as light yellow solid; yield 86%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.45 (s, 1H), 8.52-8.50 (m, 2H), 8.07 (d, J = 8.0 Hz, 1H), 7.92-7.87 (m, 2H), 7.61-7.57 (m, 1H), 7.34 (d, J = 8.0 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.1, 160.4, 150.7, 140.8, 135.3, 134.0, 129.4, 128.5, 127.1, 127.0, 123.4, 21.5; MS (EI) m/z (%) 220 (100), 193, 165, 89, 76.

2-(4-methoxyphenyl)quinazoline (2q, CAS: 67205-04-3)[2]

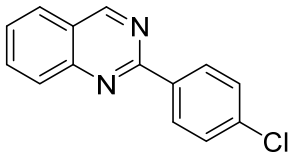


The reaction was conducted with (Z)-4-methoxy-*N*′-phenylbenzimidamide (**1q**, 45.3 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2q** as light yellow solid; yield 61%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.44 (s, 1H), 8.59 (d, J = 8.0 Hz, 2H), 8.07 (d, J = 8.0 Hz, 1H), 7.92-7.87 (m, 2H), 7.61-7.57 (m, 1H), 7.07-7.04 (m, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$, ppm) δ 161.8, 160.8, 160.4, 150.7, 134.0, 130.6, 130.2, 128.3, 127.1, 126.8, 123.3, 113.9, 55.4; MS (EI) m/z (%) 236 (100), 209, 169, 103, 76.

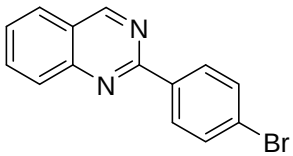
2-(4-chlorophenyl)quinazoline (2r)[2]



The reaction was conducted with (Z)-4-chloro-*N*′-phenylbenzimidamide (**1r**, 46.1 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2r** as light yellow solid; yield 88%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.47 (s, 1H), 8.60-8.57 (m, 2H), 8.10 (d, J = 8.0 Hz, 1H), 7.96-7.91 (m, 2H), 7.66-7.62 (m, 1H), 7.53-7.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.5, 160.0, 150.6, 136.8, 136.4, 134.3, 129.8, 128.8, 128.5, 127.4, 127.1, 123.5; MS (EI) m/z (%) 240 (100), 213, 178, 102, 76.

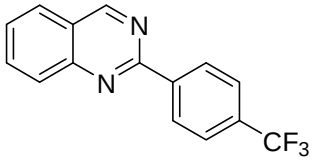
2-(4-bromophenyl)quinazoline (2s, CAS: 1222094-28-1)[2]



The reaction was conducted with (Z)-4-bromo-*N*′-phenylbenzimidamide (**1s**, 55.0 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2s** as light yellow solid; yield 85%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.47 (s, 1H), 8.53-8.51 (m, 2H), 8.11 (d, J = 8.0 Hz, 1H), 7.96-7.92 (m, 2H), 7.68-7.63 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.5, 160.1, 150.7, 136.9, 134.3, 131.8, 130.1, 128.6, 127.5, 127.1, 125.4, 123.6; MS (EI) m/z (%) 284 (100), 257, 178, 102, 76.

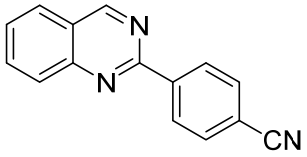
2-(4-(trifluoromethyl)phenyl)quinazoline (2t, CAS:1208258-10-2)[7]



The reaction was conducted with (Z)-*N'*-phenyl-4-(trifluoromethyl)benzimidamide (**1t**, 52.9 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2t** as light yellow solid; yield 90%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.51 (s, 1H), 8.75 (d, J = 8.0 Hz, 2H), 8.13 (d, J = 8.0 Hz, 1H), 7.99-7.94 (m, 2H), 7.80 (d, J = 8.0 Hz, 2H), 7.70-7.66 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.6, 159.6, 150.6, 141.3, 134.4, 134.4, 132.1 (q, J = 32.1 Hz), 128.8, 128.7, 127.9, 127.2, 125.5 (q, J = 3.7 Hz), 123.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.67 ppm; MS (EI) m/z (%) 274 (100), 247, 178, 102, 76.

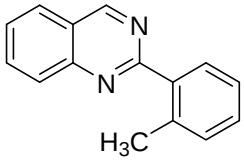
4-(quinazolin-2-yl)benzonitrile (2u)



The reaction was conducted with (Z)-*N'*-phenyl-4-(trifluoromethyl)benzimidamide (**1u**, 44.3 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2u** as light yellow solid; yield 66%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.53 (s, 1H), 8.79-8.77 (m, 2H), 8.17 (d, J = 8.0 Hz, 1H), 8.02-7.97 (m, 2H), 7.85-7.83 (m, 2H), 7.74-7.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.7, 159.1, 150.6, 142.1, 134.5, 132.4, 129.0, 128.8, 128.2, 127.2, 123.8, 118.9, 113.8; MS (EI) m/z (%) 231 (100), 204, 177, 102, 76; HRMS calcd. for: $C_{15}H_{10}N_3$ $[M+H]^+$ = 232.08692, found = 232.08693.

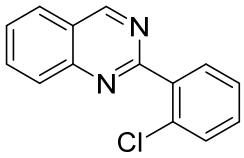
2-(o-tolyl)quinazoline (2v, CAS: 1208259-15-7)[2]



The reaction was conducted with (Z)-2-methyl-*N*′-phenylbenzimidamide (**1v**, 42.1 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2v** as light yellow solid; yield 60%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.51-9.51 (m, 1H), 8.11-8.09 (m, 1H), 7.98-7.89 (m, 3H), 7.69-7.65 (m, 1H), 7.36-7.35 (m, 3H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 164.0, 160.1, 150.3, 138.5, 137.3, 134.1, 131.3, 130.6, 129.3, 128.5, 127.5, 127.0, 126.0, 122.9, 21.0; MS (EI) m/z (%) 220 (100), 190, 165, 89, 77.

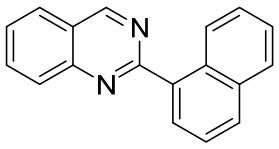
2-(2-chlorophenyl)quinazoline (2w, CAS: 1353000-32-4)[7]



The reaction was conducted with (Z)-2-methyl-*N*′-phenylbenzimidamide (**1w**, 46.1 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2w** as light yellow solid; yield 50%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.54-9.54 (m, 1H), 8.16-8.13 (m, 1H), 8.02-7.96 (m, 2H), 7.84-7.82 (m, 1H), 7.74-7.70 (m, 1H), 7.56-7.54 (m, 1H), 7.43-7.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.9, 160.2, 150.3, 138.2, 134.4, 132.9, 131.8, 130.5,m 130.3, 128.6, 128.0, 127.1, 126.9, 123.2; MS (EI) m/z (%) 240, 205 (100), 178, 102, 76.

2-(naphthalen-1-yl)quinazoline (2x, CAS: 93656-11-2)[2]

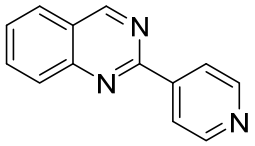


The reaction was conducted with (Z)-2-methyl-*N*′-phenylbenzimidamide (**1x**, 49.3 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2x** as light yellow solid; yield 75%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.61 (s, 1H), 8.70-8.68 (m, 1H), 8.20-8.16 (m, 2H), 8.05-7.93

(m, 4H), 7.74-7.72 (m, 1H), 7.66-7.62 (m, 1H), 7.57-7.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 163.4, 160.4, 150.5, 136.3, 134.3, 134.1, 131.1, 130.4, 129.6, 128.6, 128.5, 127.7, 127.1, 126.8, 125.9, 125.8, 125.3, 123.1; MS (EI) m/z (%) 255 (100), 228, 201, 153, 77.

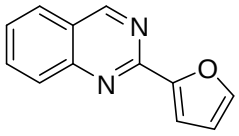
2-(pyridin-4-yl)quinazoline (2y, CAS: 1208259-13-5)[7]



The reaction was conducted with (Z)-2-methyl-*N*′-phenylbenzimidamide (**1y**, 39.4 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2y** as light yellow solid; yield 92%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.53 (s, 1H), 8.82 (d, J = 8.0 Hz, 2H), 8.49-8.48 (m, 2H), 8.16-8.14 (m, 1H), 8.01-7.96 (m, 2H), 7.74-7.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.7, 158.9, 150.5, 150.4, 145.3, 134.5, 128.8, 128.3, 127.1, 124.1, 122.3; MS (EI) m/z (%) 207 (100), 179, 153, 129, 76.

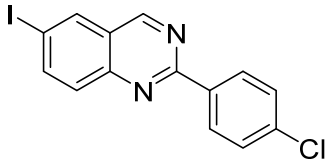
2-(furan-2-yl)quinazoline (2z)[2]



The reaction was conducted with (Z)-2-methyl-*N*′-phenylbenzimidamide (**1z**, 37.2 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2z** as light yellow solid; yield 62%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.40-9.37 (m, 1H), 8.14-8.08 (m, 1H), 7.94-7.88 (m, 2H), 7.71-7.69 (m, 1H), 7.64-7.57 (m, 1H), 7.51-7.46 (m, 1H), 6.64-6.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.7, 154.1, 152.5, 150.4, 145.3, 134.4, 128.3, 127.2, 123.3, 114.0, 112.3; MS (EI) m/z (%) 196 (100), 168, 140, 98, 76.

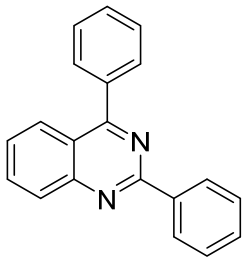
2-(4-chlorophenyl)-6-iodoquinazoline (2aa)



The reaction was conducted with (Z)-4-chloro-*N′*-(4-iodophenyl)benzimidamide (**1aa**, 71.3 mg, 0.2 mmol) and paraformaldehyde (18.0 mg, 0.6 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2aa** as light yellow solid; yield 80%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.36 (s, 1H), 8.57-8.54 (m, 2H), 8.32-8.32 (m, 1H), 8.15-8.12 (m, 1H), 7.82-7.79 (m, 1H), 7.51-7.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.3, 159.2, 149.7, 143.0, 137.2, 136.1, 135.9, 130.2, 129.9, 128.9, 125.0, 92.3; MS (EI) m/z (%) 366 (100), 339, 212, 102, 75; HRMS calcd. for: $C_{14}H_9N_2ClI$[M] = 366.94935, found = 366.94911.

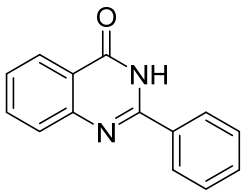
2,4-diphenylquinazoline (2ab, CAS: 31730-65-1)[8]



A 10 mL oven-dried reaction vessel was charged with $BF_3 \cdot Et_2O$ (2.5 uL, 0.01 mmol), (Z)-*N′*-phenylbenzimidamide (**1a**, 39.3, 0.2 mmol), benzaldehyde (31.8 mg, 0.3 mmol) and DMSO (0.8 mL). The resulting solution was sealed under O_2 and stirred at 140 °C for 24 h. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2ab** as light yellow solid; yield 62%.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.71-8.69 (m, 2H), 8.17-8.11 (m, 2H), 7.90-7.86 (m, 3H), 7.61-7.49 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.4, 160.3, 152.0, 138.3, 137.7, 133.6, 130.5, 130.2, 130.0, 129.2, 128.7, 128.6, 127.0, 121.7; MS (EI) m/z (%) 282 (100), 205, 179, 103, 76.

2-phenylquinazolin-4(3*H*)-one (3a, CAS: 1022-45-3)[2]



A 10 mL oven-dried reaction vessel was charged with **2a** (20.6 mg, 0.1 mmol), H_2O_2 (6.8 mg, 0.2 mmol). The reaction vessel was purged three times with O_2, and HOAc (0.5 mL) was added to the sealed reaction vessel by syringe. The resulting solution was stirred at for 24 h 55 °C. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5 : 1) to give **3a** as pale yellow solid; yield: 21.1 mg (95%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 11.11 (s, 1H), 8.35-8.32 (m, 1H), 8.22-8.20 (m, 2H), 7.89-7.80 (m, 2H), 7.62-7.59 (m, 3H), 7.55-7.51 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 164.0, 151.8, 149.5, 134.9, 132.8, 131.6, 129.0, 128.0, 127.5, 126.8, 126.3, 120.8; MS (EI) m/z (%) 222, 178, 119 (100), 92, 77.

Reference

1. Velavan; Sumathi; Balasubramanian. *Eur. J. Org. Chem.* **2014** , *2014*, 5806

2. Wang, H. M.; Chen, H.; Chen, Y.; Deng, G. J. *Org. Biomol. Chem.* **2014,** *12***,** 7792**.**

3. Chen, Z. Y.; Chen, J. X.; Liu, M. C.; Ding, J. C.; Gao, W. X.; Huang, X. B.; Wu, H. Y. *J. Org. Chem.* **2013**, *78*, 11342.

4. Lv, Y. H.; Li, Y.; Xiong, T.; Pu, W. Y.; Zhang, H. W.; Sun, K.; Liu, Q.; Zhang, Q. *Chem. Commun*. **2013**, *49*, 6439.

5. Gilchrist et al. *Journal of the chemical society, Perkin Transactions 1: Oranic and Bio-Organic Chemistry* (1972-1999), **1975**, 1969.

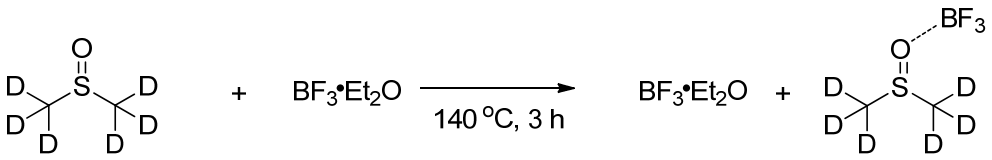
6. Omar, M. A.; Conrad, J.; Beifuss, U. *Tetrahedron* **2014**, *70*, 3061.

7. Fan, X.; Li, B.; Guo, S. H.; Wang, Y. Y.; Zhang, X. Y. *Chem. Asian J*. **2014**, *9*, 739.

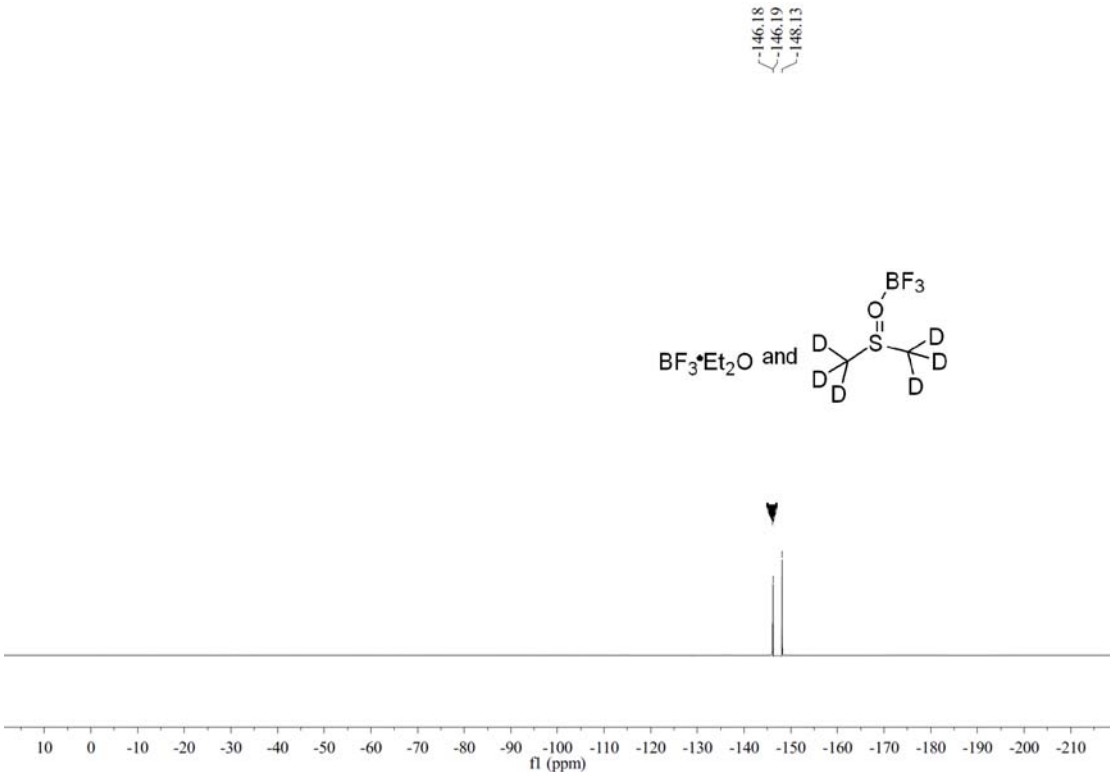
8. Su, X.; Chen, C.; Wang, Y.; Chen, J. J.; Lou, Z. B.; Li, M. *Chem. Commun.* **2013,** *49***,** 6752.

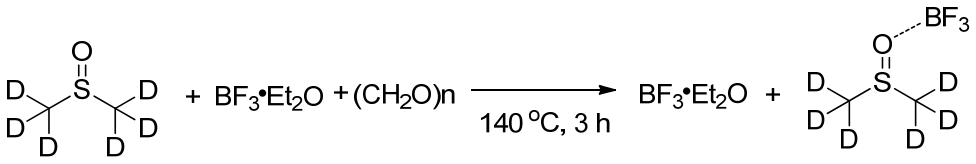
Control experiments

(1) Base effects of paraformaldehyde

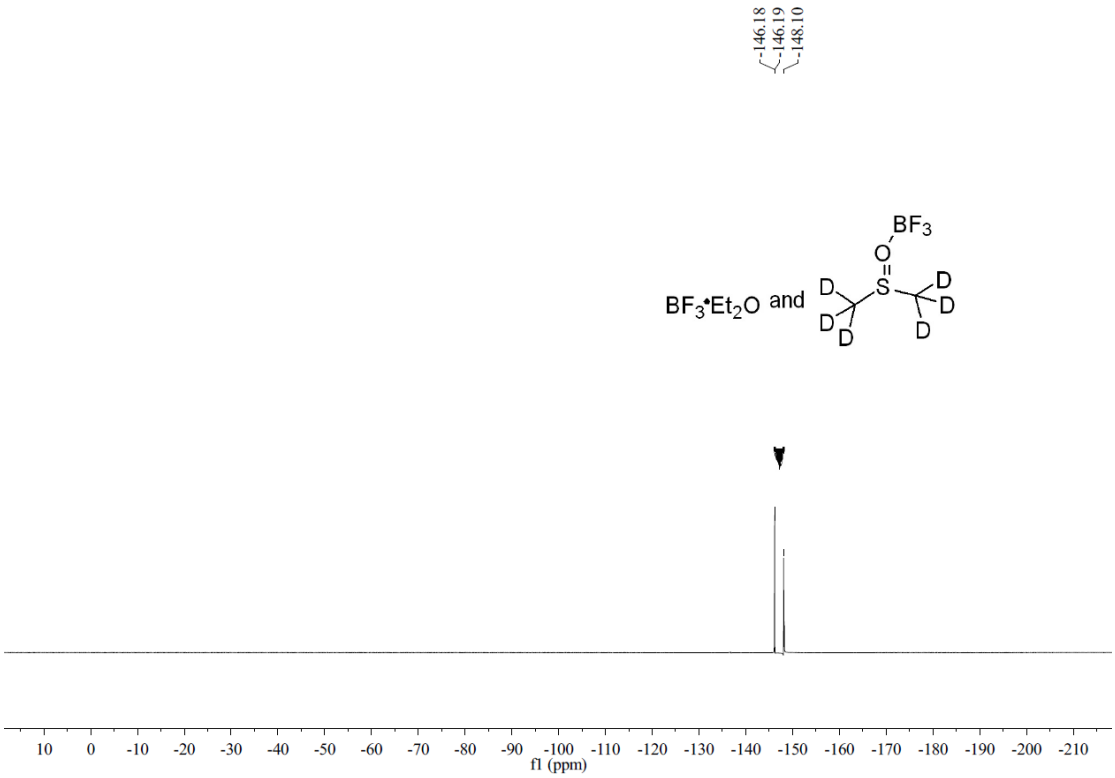


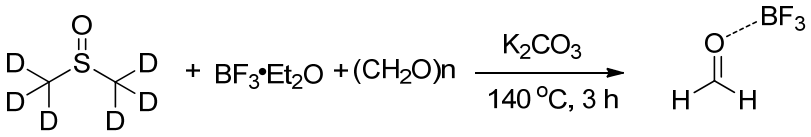
Reaction conditions: A 10 mL oven-dried reaction vessel was charged with $BF_3 \cdot Et_2O$ (0.2 mmol, 28.4 mg) and DMSO-D6 (0.4 mL). The resulting solution was stirred at 140 °C for 3 h. After cooling down to room temperature, the crude reaction mixture was detected on the base of ^{19}F NMR, the result was shown below.



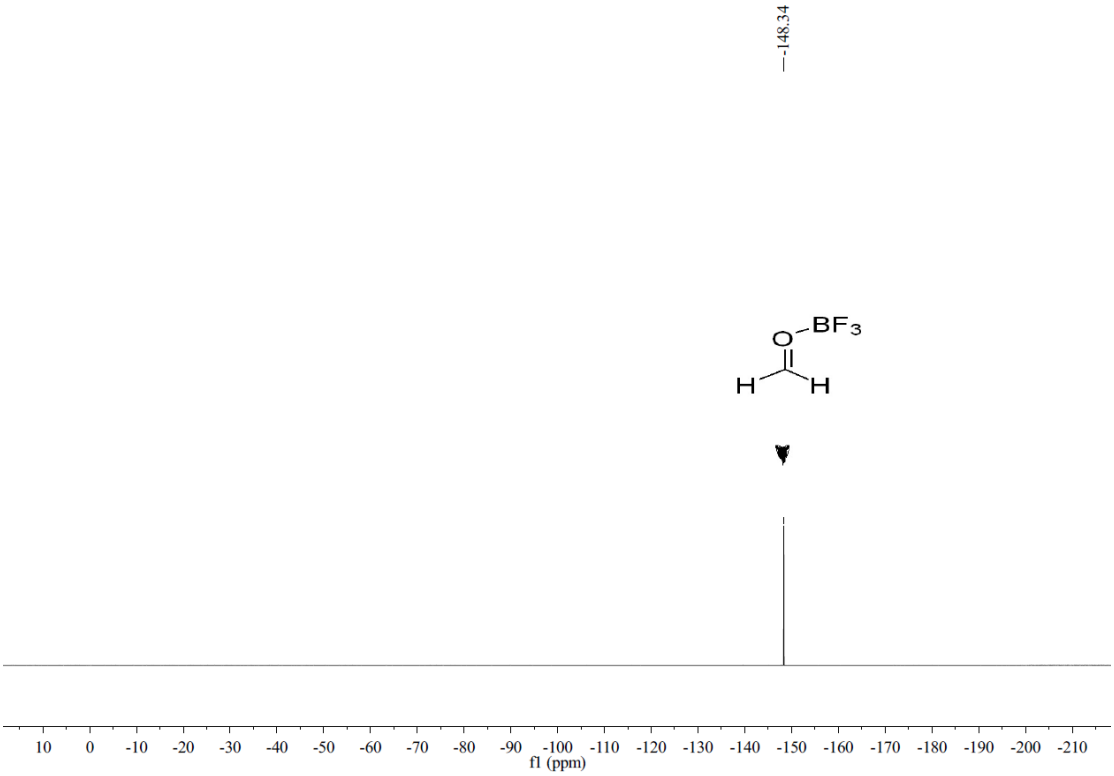


Reaction conditions: A 10 mL oven-dried reaction vessel was charged with $BF_3 \cdot Et_2O$ (0.2 mmol, 28.4 mg), paraformaldehyde (0.6 mmol, 18 mg) and DMSO-D6 (0.4 mL). The resulting solution was stirred at 140 °C for 3 h. After cooling down to room temperature, the crude reaction mixture was detected on the base of ^{19}F NMR, the result was shown below.





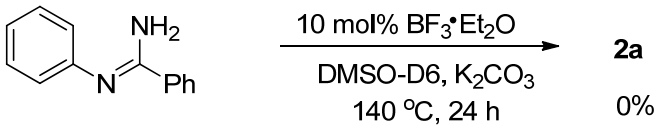
Reaction conditions: A 10 mL oven-dried reaction vessel was charged with $BF_3 \cdot Et_2O$ (0.2 mmol, 28.4 mg), paraformaldehyde (0.6 mmol, 18 mg), K_2CO_3 (0.2 mmol, 27.6 mg)and DMSO-D6 (0.4 mL). The resulting solution was stirred at 140 °C for 3 h. After cooling down to room temperature, the crude reaction mixture was detected on the base of ^{19}F NMR, the result was shown below.



These results showed that K_2CO_3 played a role, as promoting paraformaldehyde to formaldehyde.

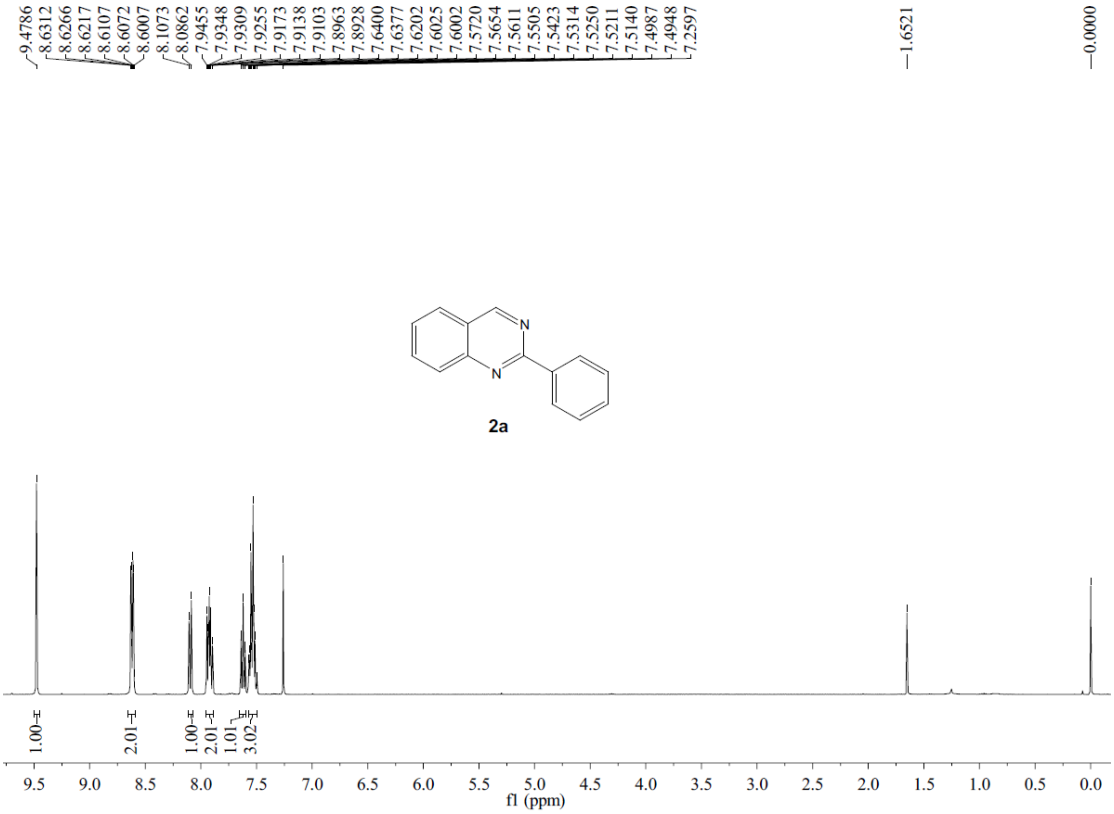
(2) The elucidation of the carbon source

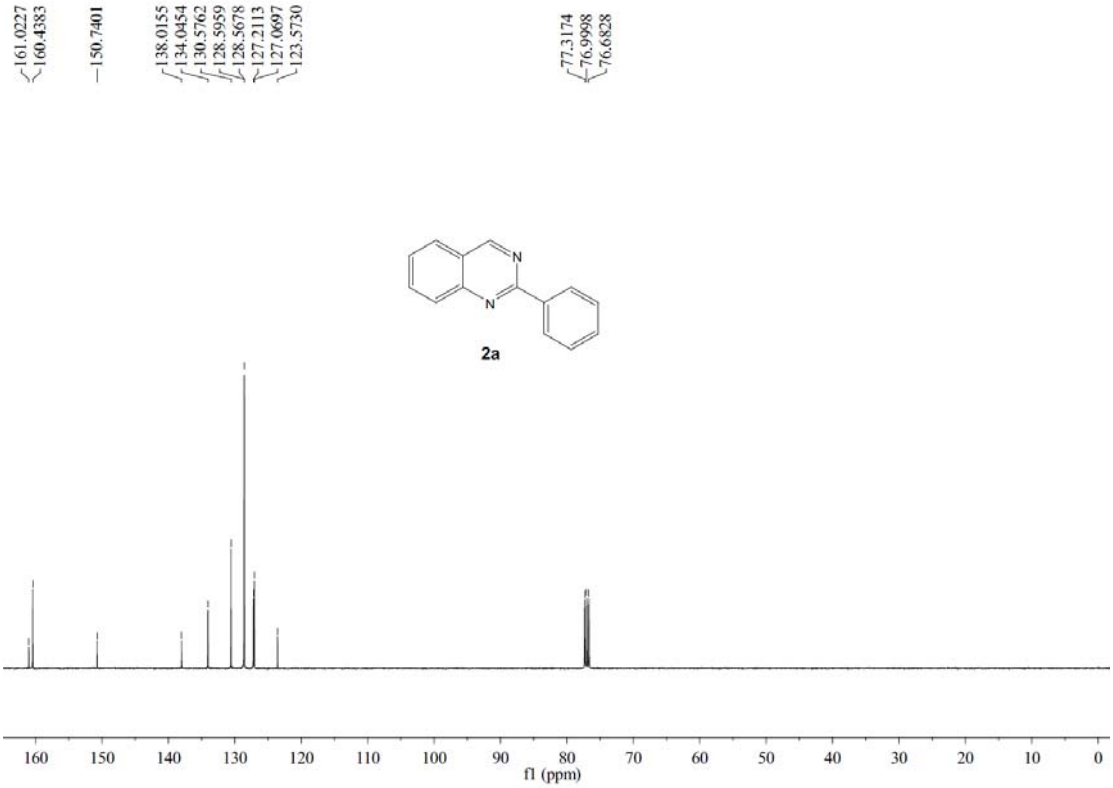
$BF_3 \cdot Et_2O$ (2.5 uL, 0.01 mmol), K_2CO_3 (27.6 mg, 0.2 mmol), (*Z*)-*N'*-phenylbenzimidamide (**1a,** 39.3, 0.2 mmol) and DMSO-D6 (0.5 mL) was sealed under O_2 and stirred at 140 °C for 24 h. After completion of the reaction, **2a** was not detected by GC-MS and materials were all recovered.

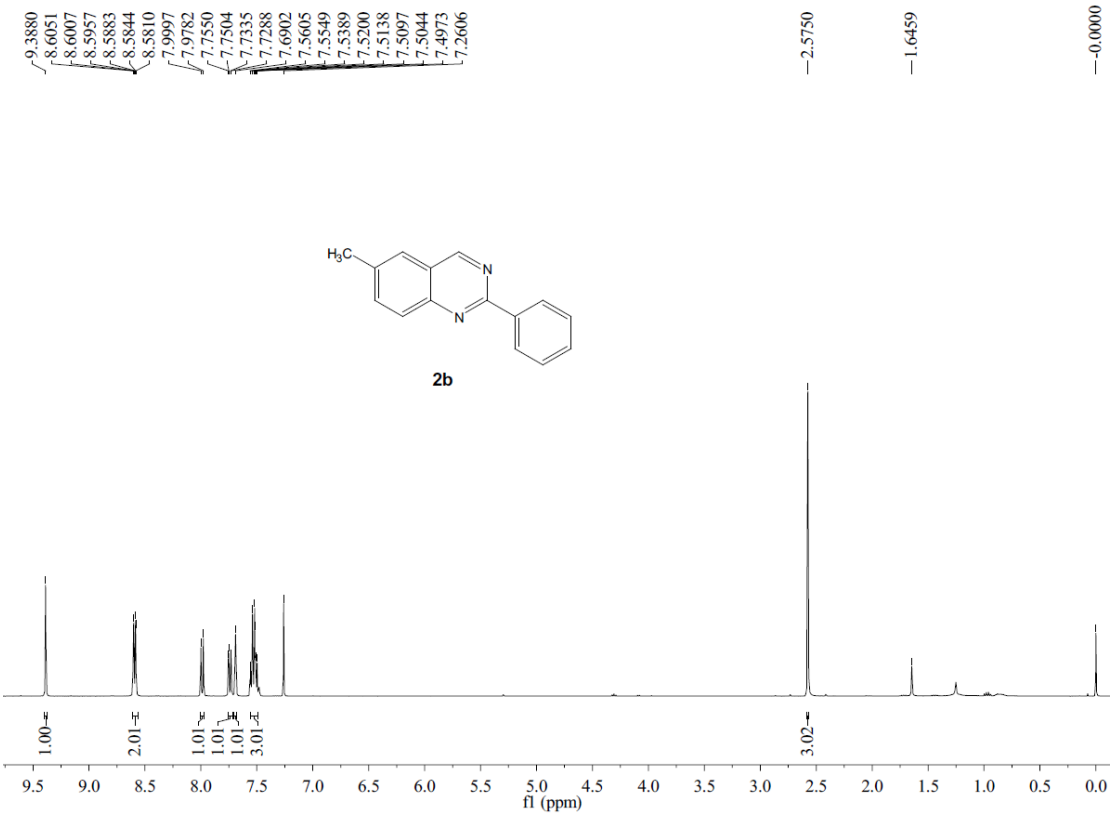


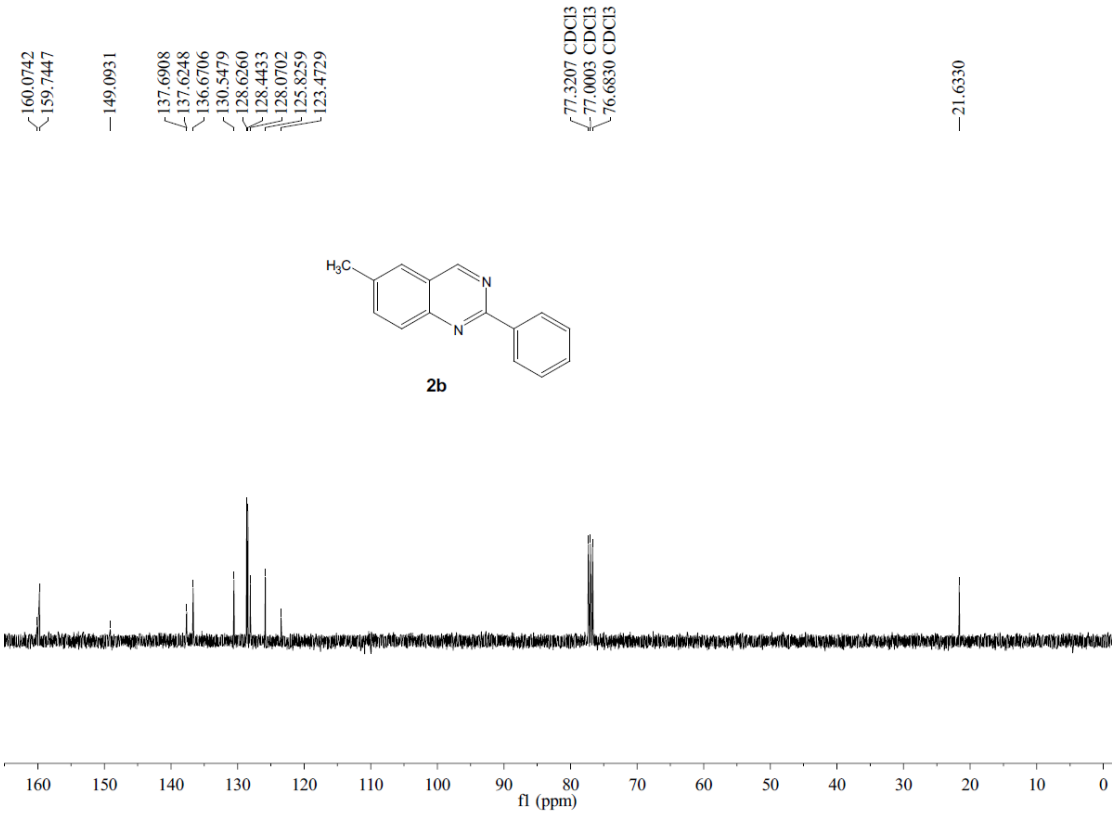
$BF_3 \cdot Et_2O$ (2.5 uL, 0.01 mmol), K_2CO_3 (27.6 mg, 0.2 mmol), (*Z*)-*N'*-phenylbenzimidamide (**1a,** 39.3, 0.2 mmol), paraformaldehyde (18.0 mg, 0.6 mmol) and DMSO-D6 (0.5 mL) was sealed under O_2 and stirred at 140 °C for 24 h. After completion of the reaction, **2a** was detected by GC-MS in 87% yield and the deuterated product **D-2a** was not detected.

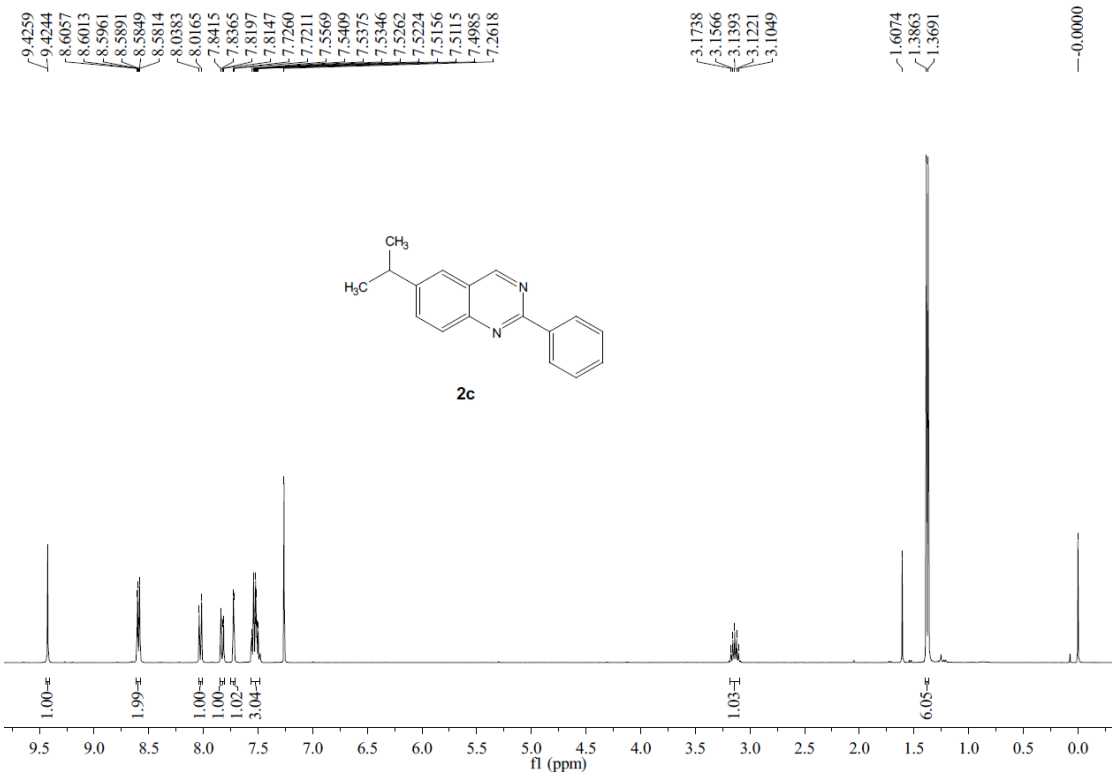
^{1}H NMR and ^{13}C NMR spectra for all products

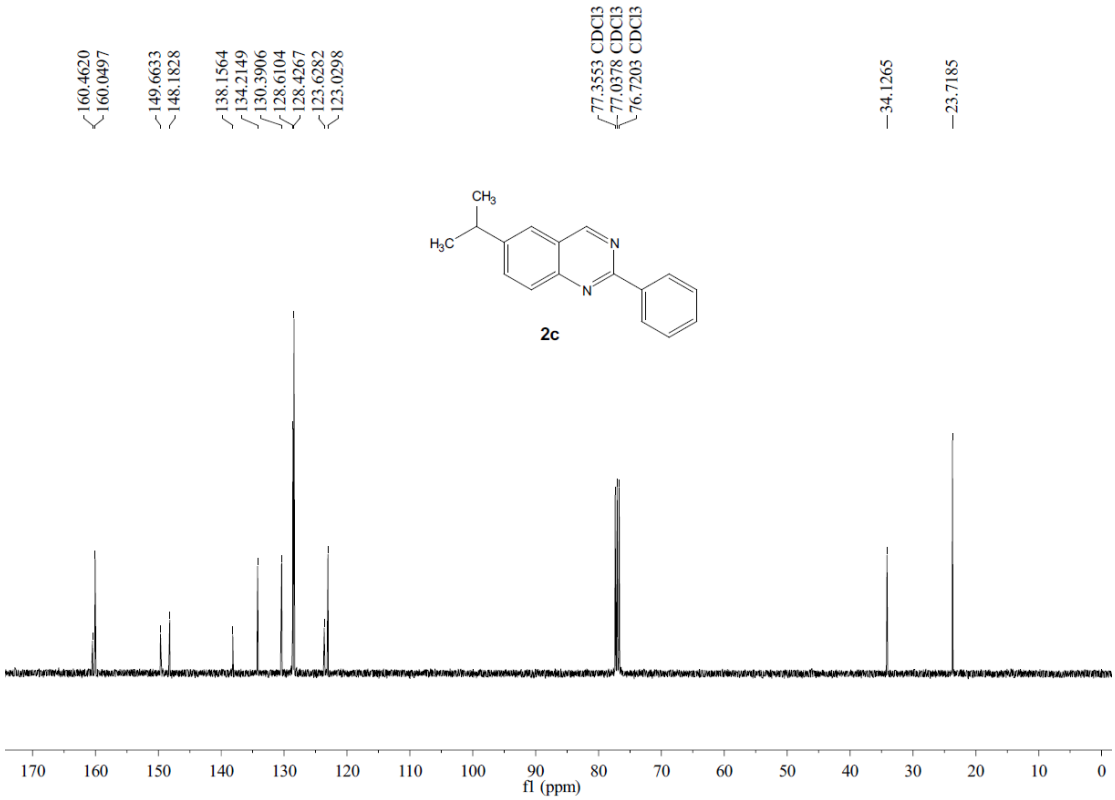


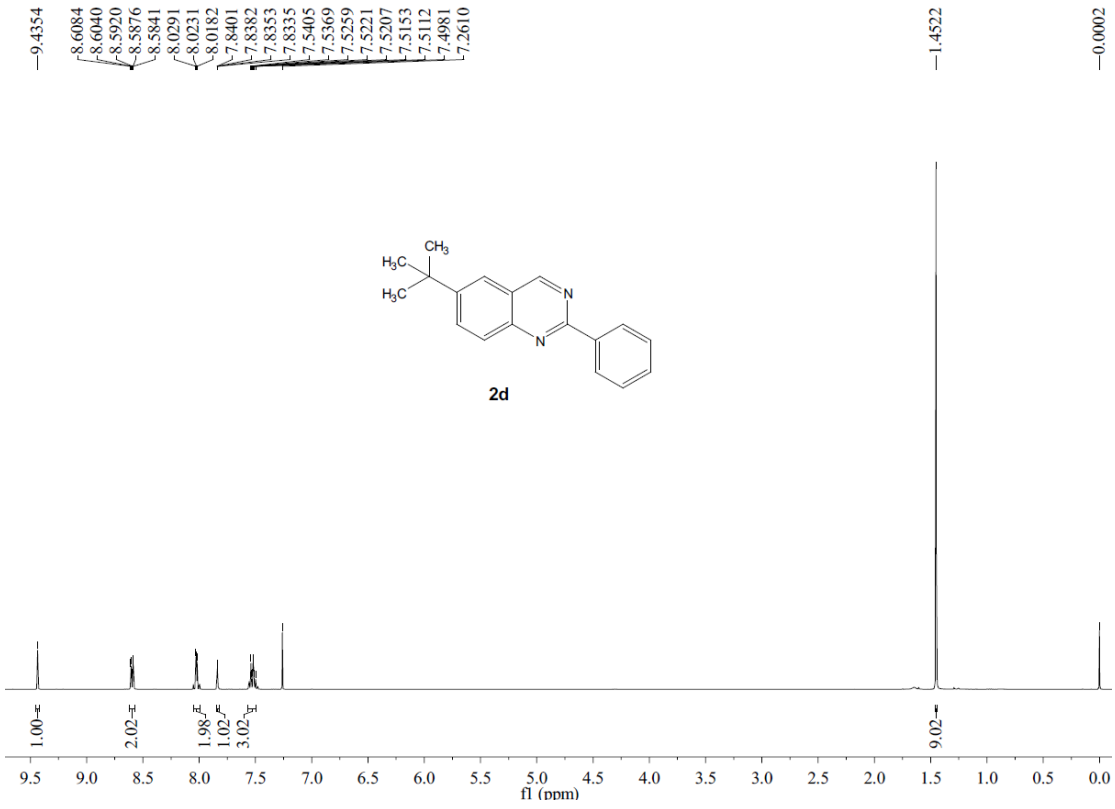

161.0227
160.4383
150.7401
138.0155
134.0454
130.5762
128.5959
128.5678
127.2113
127.0697
123.5730
77.3174
76.9998
76.6828
2a
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

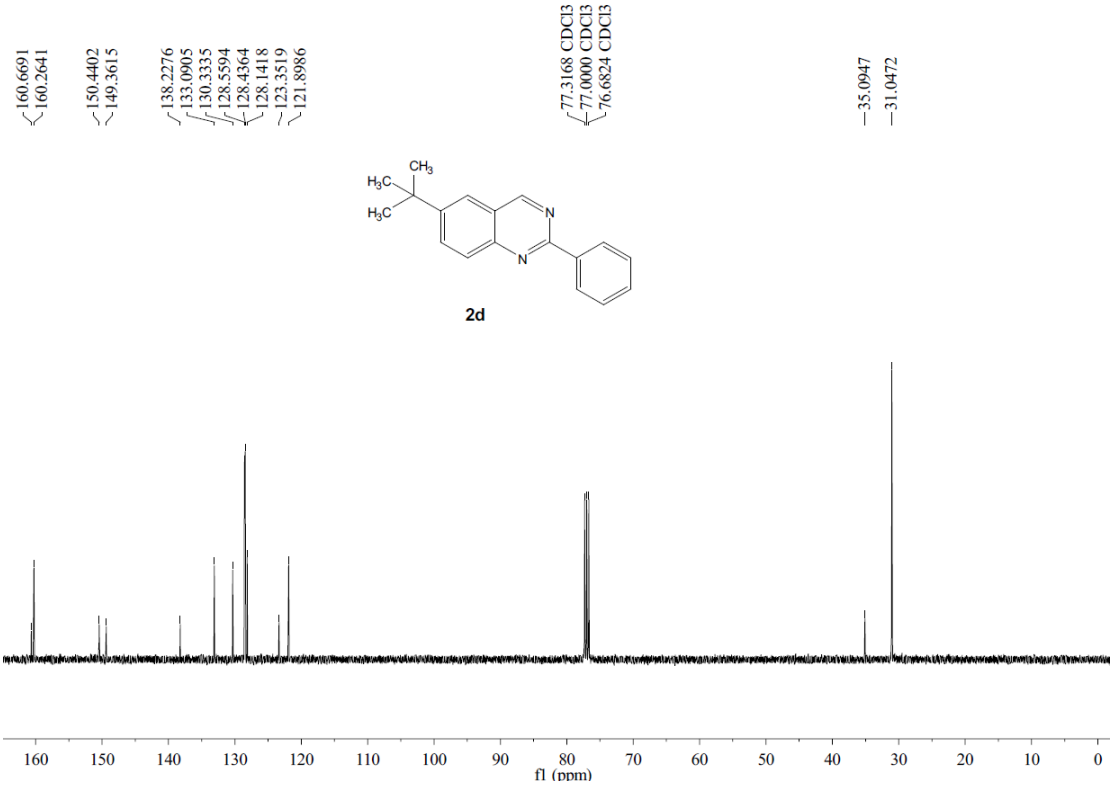

9.3880
8.6051
8.6007
8.5957
8.5883
8.5844
8.5810
7.9997
7.9782
7.7550
7.7504
7.7335
7.7288
7.6902
7.5605
7.5549
7.5389
7.5200
7.5138
7.5097
7.5044
7.4973
7.2606
2.5750
1.6459
0.0000
2b
1.00
2.01
1.01
1.01
1.01
3.01
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

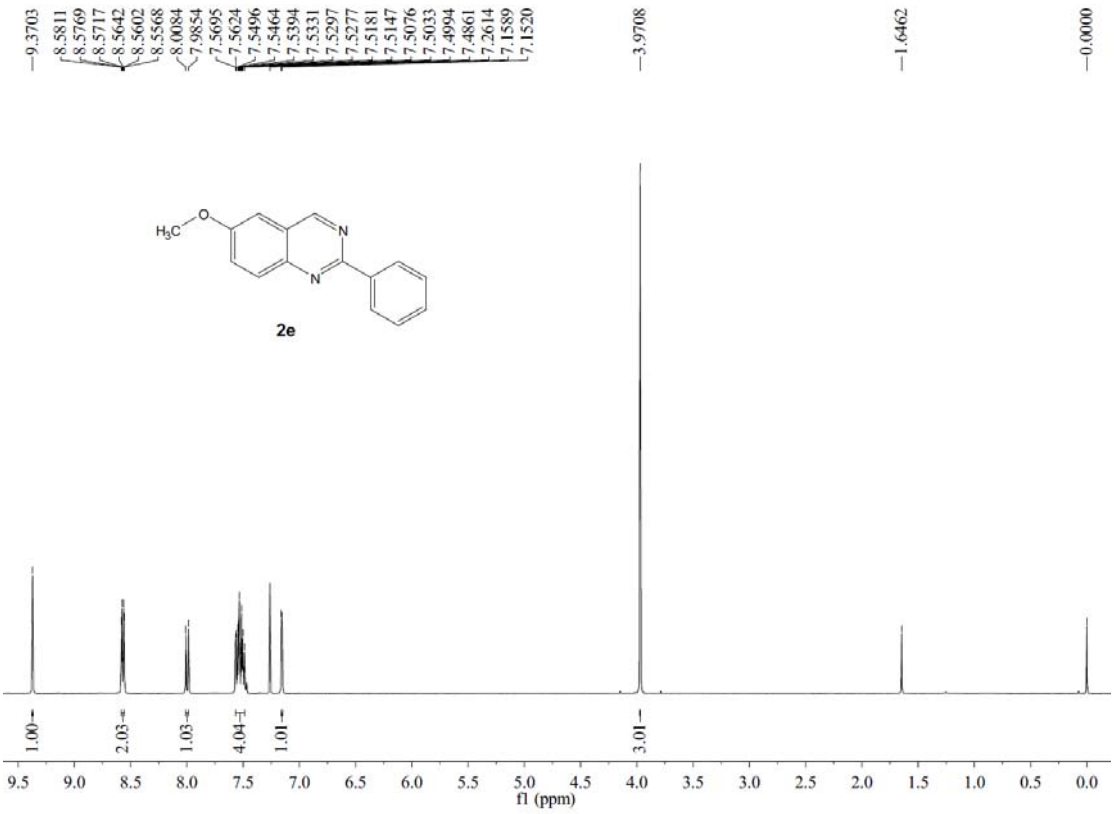

160.0742
159.7447
149.0931
137.6908
137.6248
136.6706
130.5479
128.6260
128.4433
128.0702
125.8259
123.4729
77.3207 CDCl3
77.0003 CDCl3
76.6830 CDCl3
21.6330
H3C
N
N
2b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.4259
9.4244
8.6057
8.6013
8.5961
8.5891
8.5849
8.5814
8.0383
8.0165
7.8415
7.8365
7.8197
7.8147
7.7260
7.7211
7.5569
7.5409
7.5375
7.5346
7.5262
7.5224
7.5156
7.5115
7.4985
7.2618
3.1738
3.1566
3.1393
3.1221
3.1049
1.6074
1.3863
1.3691
0.0000
CH3
H3C
N
N
2c
1.00
1.99
1.00
1.02
3.04
1.03
6.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

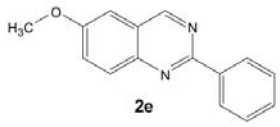

160.4620
160.0497
149.6633
148.1828
138.1564
134.2149
130.3906
128.6104
128.4267
123.6282
123.0298
77.3553 CDCl3
77.0378 CDCl3
76.7203 CDCl3
34.1265
23.7185
CH3
H3C
N
N
2c
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.4354
8.6084
8.6040
8.5920
8.5876
8.5841
8.0291
8.0231
8.0182
7.8401
7.8382
7.8353
7.8335
7.5405
7.5369
7.5259
7.5221
7.5207
7.5153
7.5112
7.4981
7.2610
1.4522
0.0002
CH3
H3C
H3C
N
N
2d
1.00
2.02
1.98
1.02
3.02
9.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

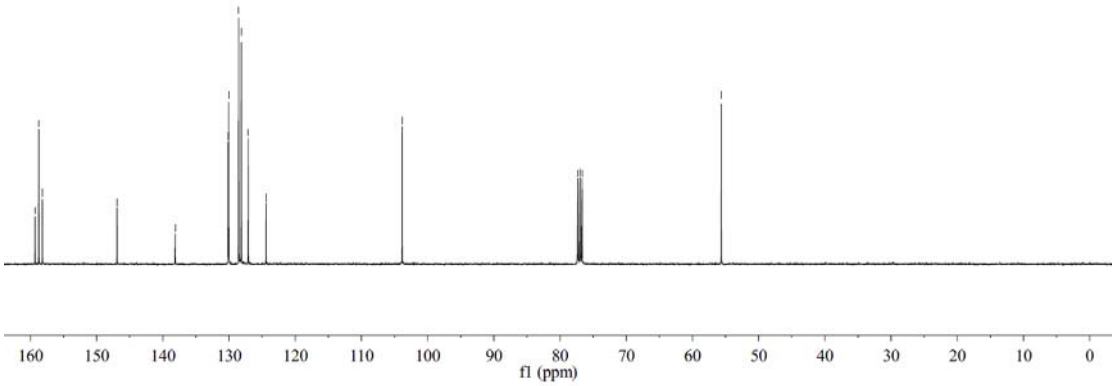

160.6691
160.2641
150.4402
149.3615
138.2276
133.0905
130.3335
128.5594
128.4364
128.1418
123.3519
121.8986
77.3168 CDCl3
77.0000 CDCl3
76.6824 CDCl3
35.0947
31.0472
CH3
H3C
H3C
N
N
2d
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.3703
8.5811
8.5769
8.5717
8.5642
8.5602
8.5568
8.0084
7.9854
7.5695
7.5624
7.5496
7.5464
7.5394
7.5331
7.5297
7.5277
7.5181
7.5147
7.5076
7.5033
7.4994
7.4861
7.2614
7.1589
7.1520
3.9708
1.6462
0.0000
H3C
O
N
N
2e
1.00
2.03
1.03
4.04
1.01
3.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

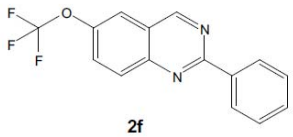

159.3109
158.7289
158.1913
146.9276
138.1322
130.1275
130.0607
128.5367
128.1546
127.0941
124.4018
103.8553
77.3180
77.0003
76.6823
55.6427


H3C
O
N
N

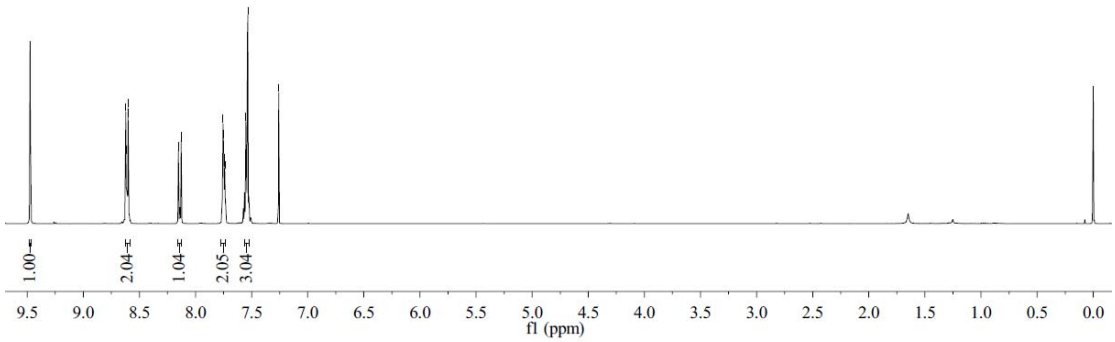
2e

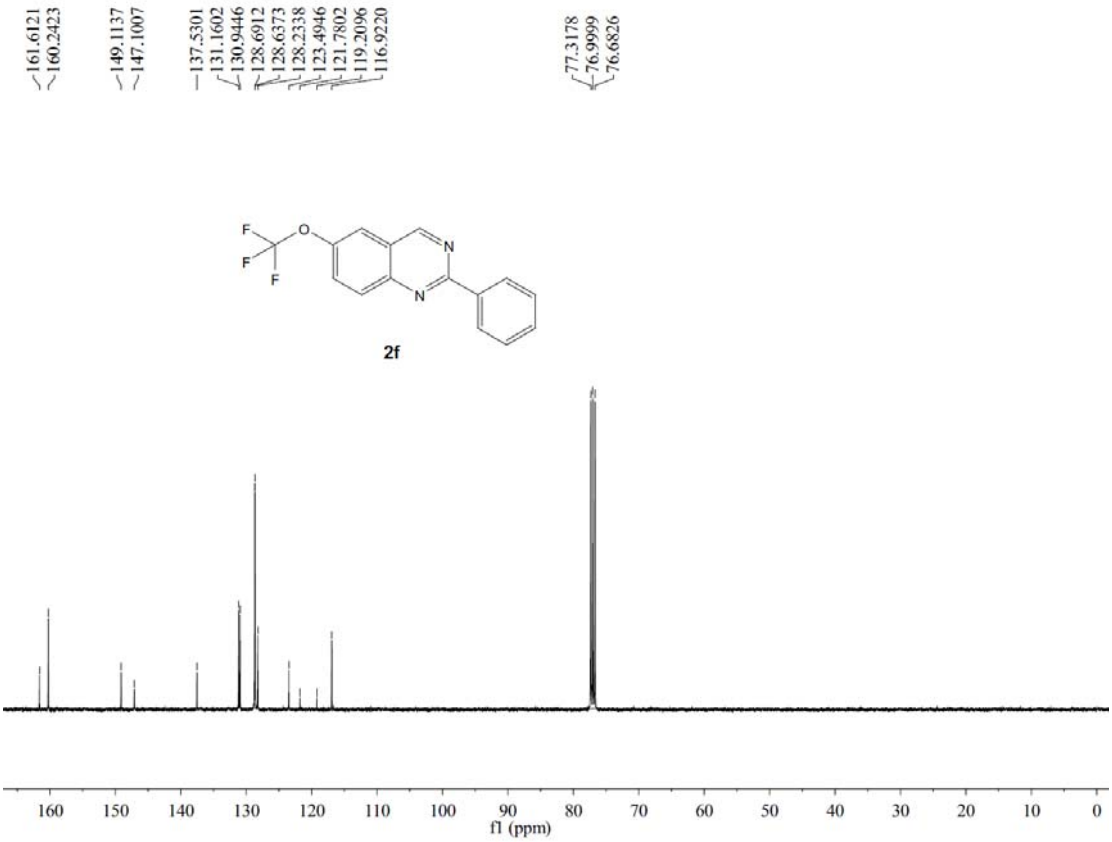

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.47
8.62
8.61
8.60
8.60
8.15
8.15
8.13
8.13
7.75
7.75
7.75
7.75
7.74
7.74
7.55
7.55
7.54
7.54
7.53
7.53
7.53
7.26
0.00


F
F
F
O
N
N

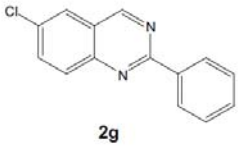
2f


1.00
2.04
1.04
2.05
3.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

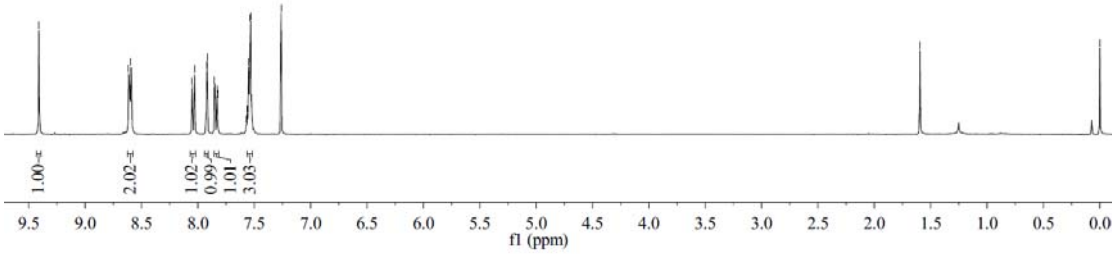

161.6121
160.2423
149.1137
147.1007
137.5301
131.1602
130.9446
128.6912
128.6373
128.2338
123.4946
121.7802
119.2096
116.9220
77.3178
76.9999
76.6826
F
F
F
O
N
N
2f
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

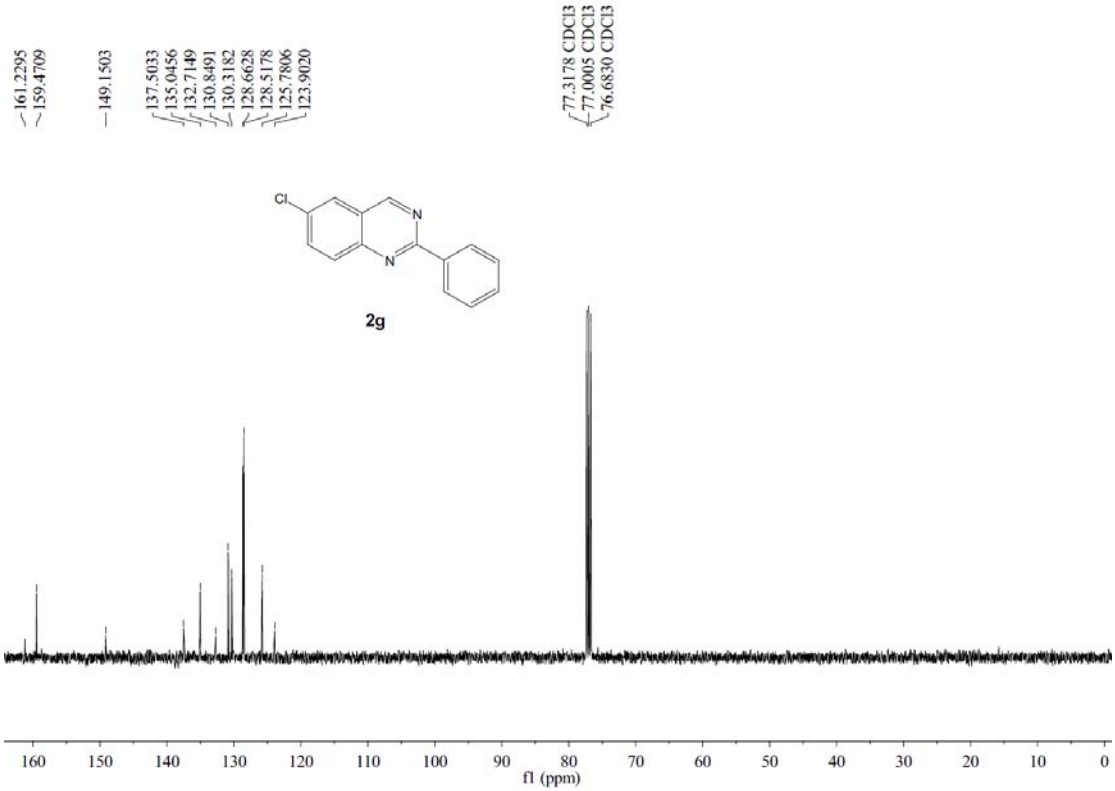

-57.8970
F
F
F
O
N
N
2f
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


9.4103
8.6137
8.6074
8.6010
8.5988
8.5938
8.5894
8.0519
8.0295
7.9235
7.9180
7.8532
7.8475
7.8308
7.8250
7.5722
7.5624
7.5585
7.5500
7.5417
7.5352
7.5315
7.5242
7.2620
1.5958
0.0000

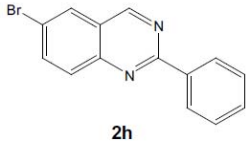

Cl
N
N

2g

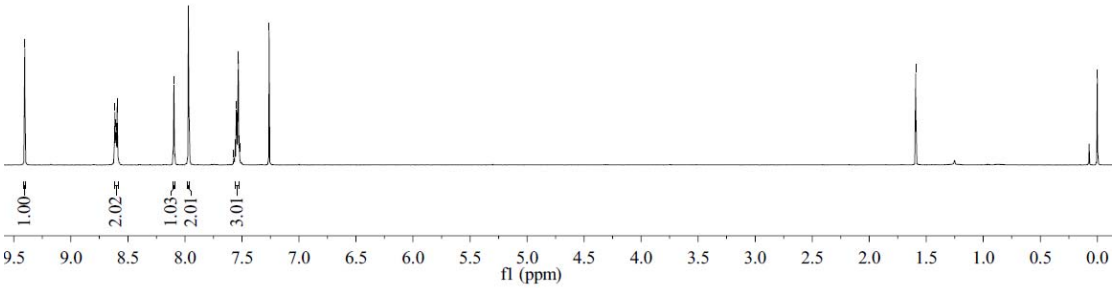

1.00
2.02
1.02
0.99
1.01
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


161.2295
159.4709
149.1503
137.5033
135.0456
132.7149
130.8491
130.3182
128.6628
128.5178
125.7806
123.9020
77.3178 CDCl3
77.0005 CDCl3
76.6830 CDCl3
Cl
N
N
2g
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

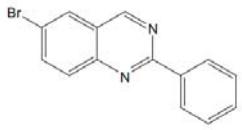

9.4041
8.6148
8.6075
8.6032
8.5950
8.5903
8.0996
8.0964
8.0930
7.9697
7.9664
7.5720
7.5607
7.5569
7.5493
7.5447
7.5429
7.5356
7.5311
7.5259
7.5237
7.5199
7.2619
1.5922
0.0000


Br
N
N

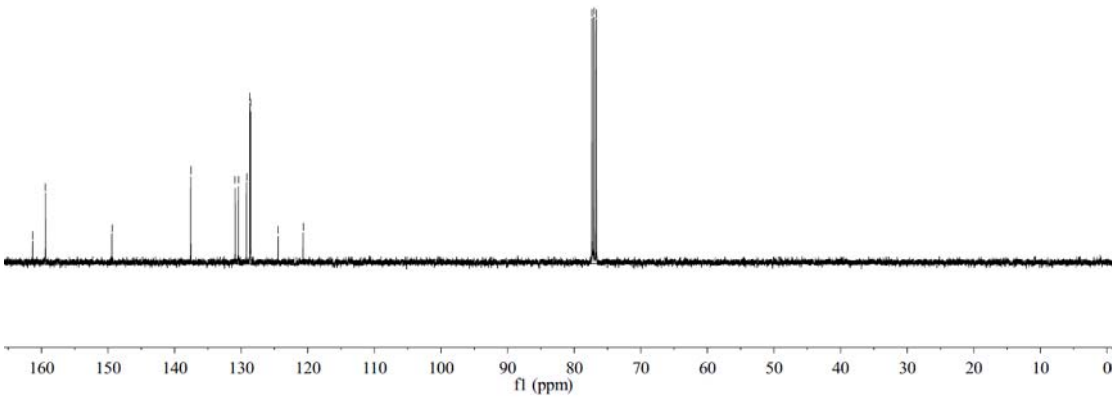
2h

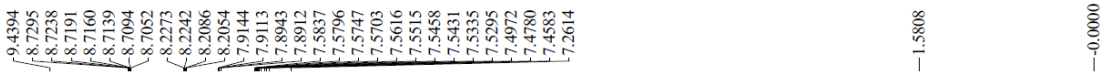

1.00
2.02
1.03
2.01
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

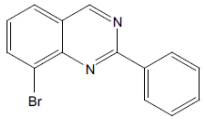

161.3140
159.3715
149.4231
137.5831
137.4843
130.8899
130.4348
129.2074
128.6782
128.5936
124.4594
120.7126
77.3179
77.0004
76.6827


Br
N
N

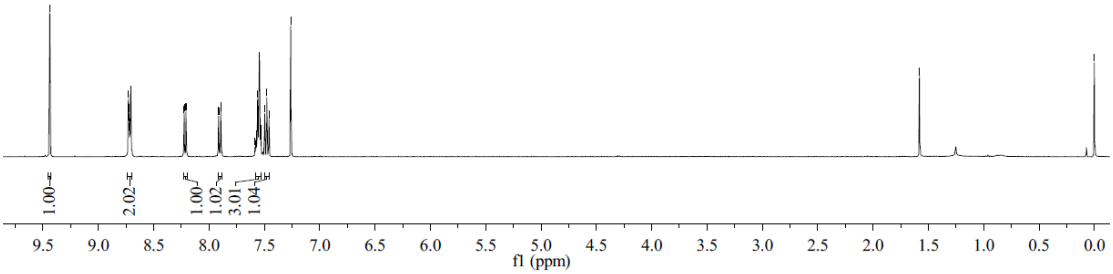
2h

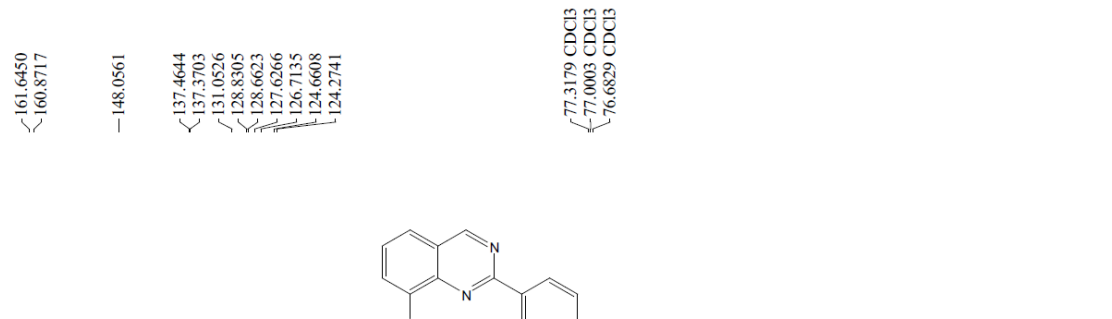

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.4394
8.7295
8.7238
8.7191
8.7160
8.7139
8.7094
8.7052
8.2273
8.2242
8.2086
8.2054
7.9144
7.9113
7.8943
7.8912
7.5837
7.5796
7.5747
7.5703
7.5616
7.5515
7.5458
7.5431
7.5335
7.5295
7.4972
7.4780
7.4583
7.2614
1.5808
0.0000


N
N
Br

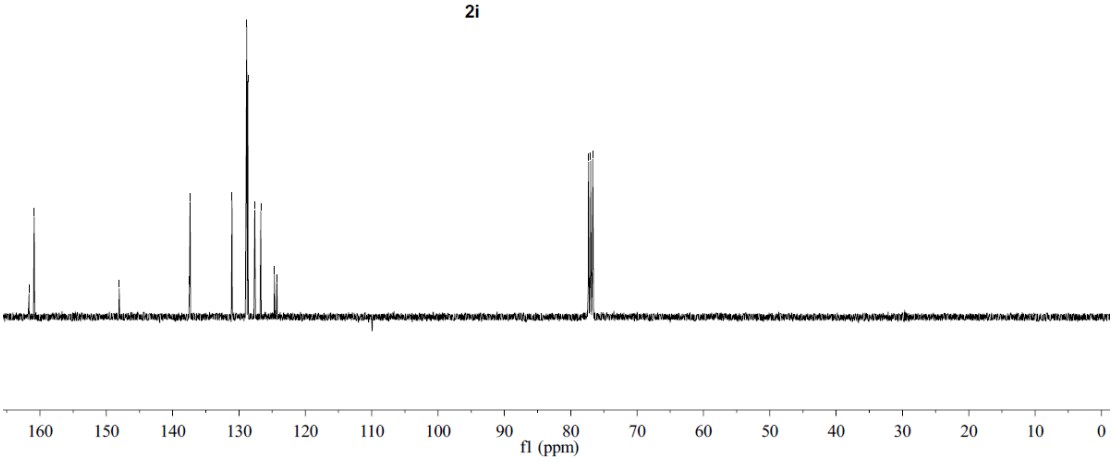
2i

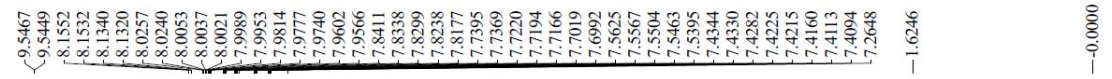

1.00
2.02
1.00
1.02
3.01
1.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

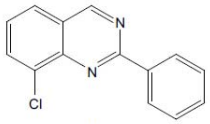

161.6450
160.8717
148.0561
137.4644
137.3703
131.0526
128.8305
128.6623
127.6266
126.7135
124.6608
124.2741
77.3179 CDCl3
77.0003 CDCl3
76.6829 CDCl3

N
N
Br

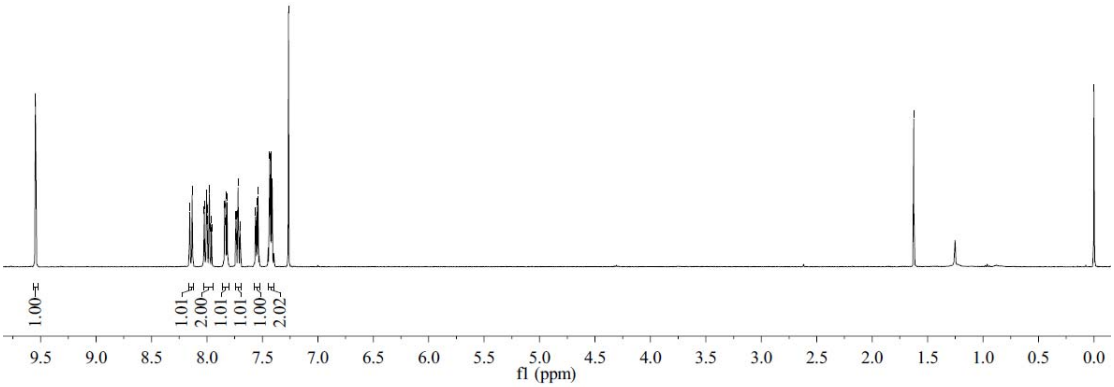
2i

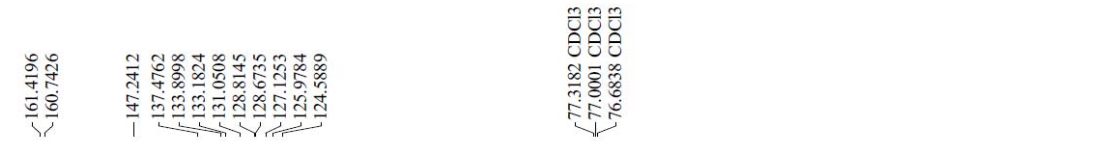

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

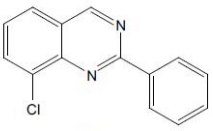

9.5467
9.5449
8.1552
8.1532
8.1340
8.1320
8.0257
8.0240
8.0053
8.0037
8.0021
7.9989
7.9953
7.9814
7.9777
7.9740
7.9602
7.9566
7.8411
7.8338
7.8299
7.8238
7.8177
7.7395
7.7369
7.7220
7.7194
7.7166
7.7019
7.6992
7.5625
7.5567
7.5504
7.5463
7.5395
7.4344
7.4330
7.4282
7.4225
7.4215
7.4160
7.4113
7.4094
7.2648
1.6246
0.0000


N
N
Cl

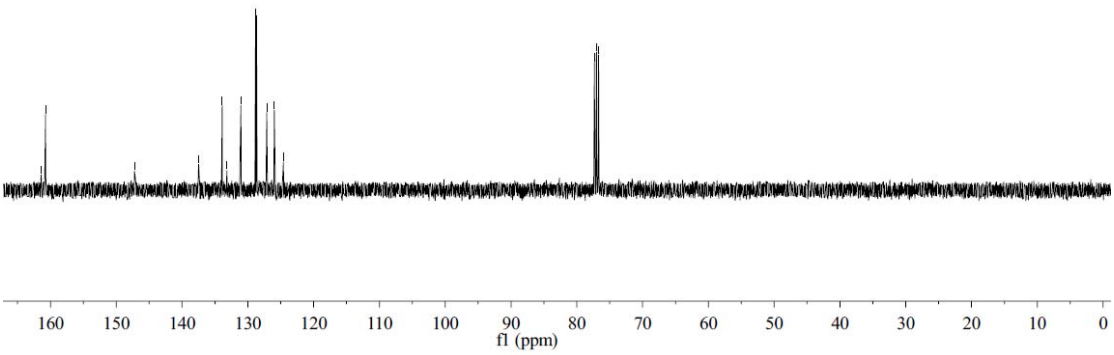
2j

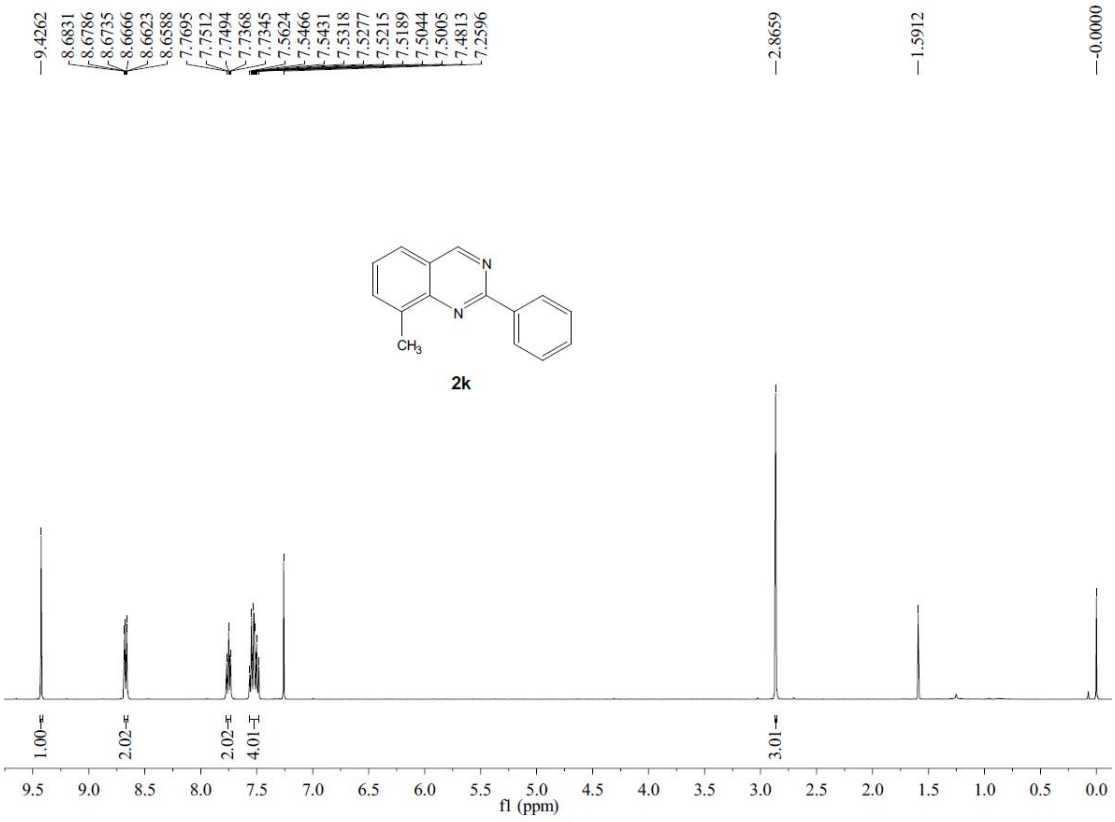

1.00
1.01
2.00
1.01
1.01
1.00
2.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

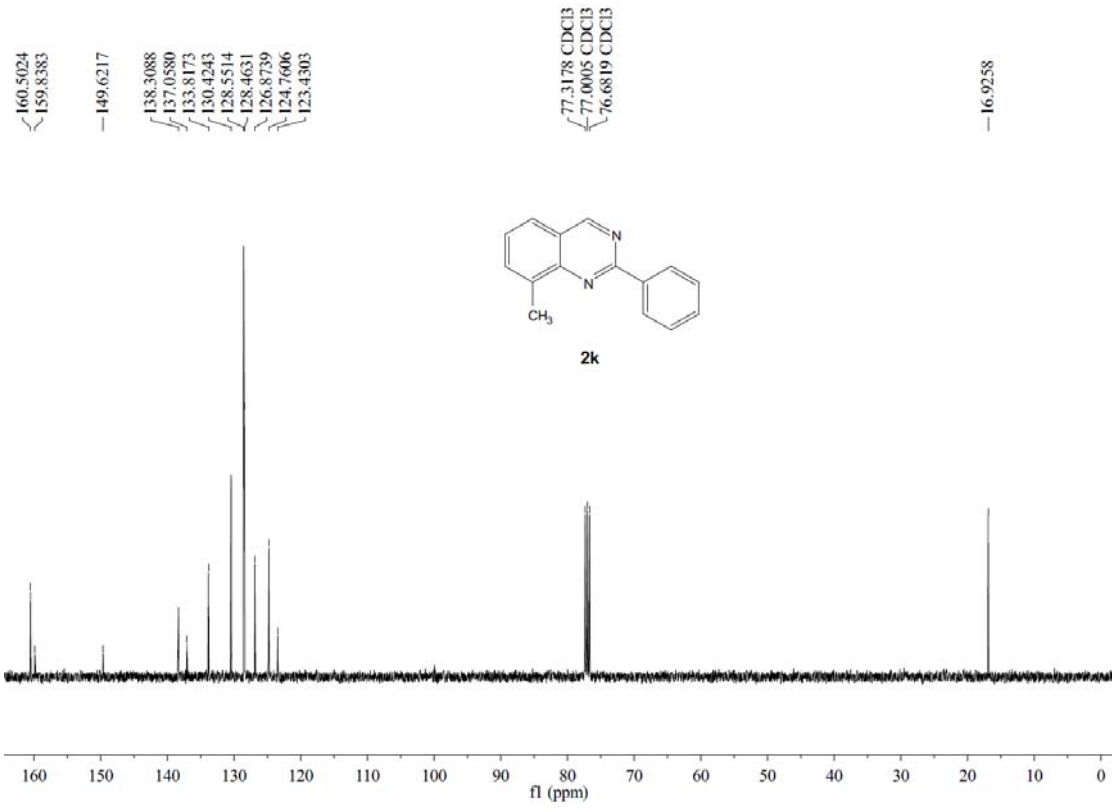

161.4196
160.7426
147.2412
137.4762
133.8998
133.1824
131.0508
128.8145
128.6735
127.1253
125.9784
124.5889
77.3182 CDCl3
77.0001 CDCl3
76.6838 CDCl3

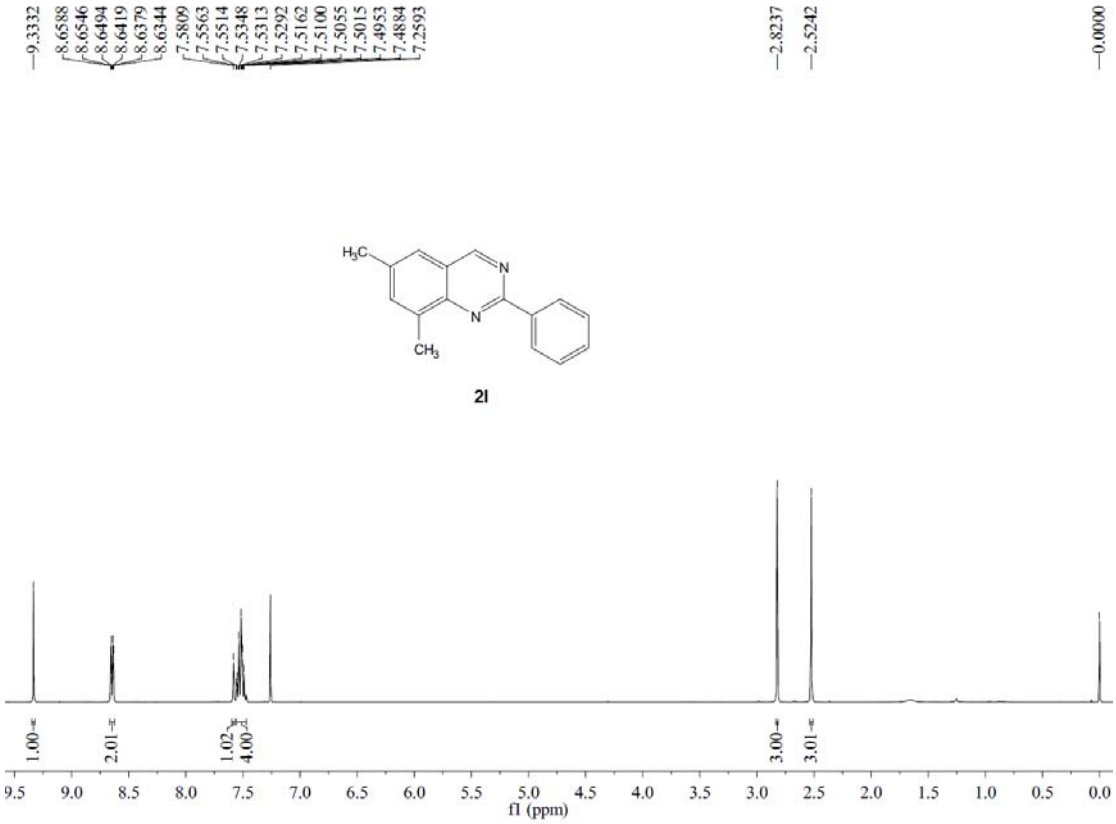

N
N
Cl

2j

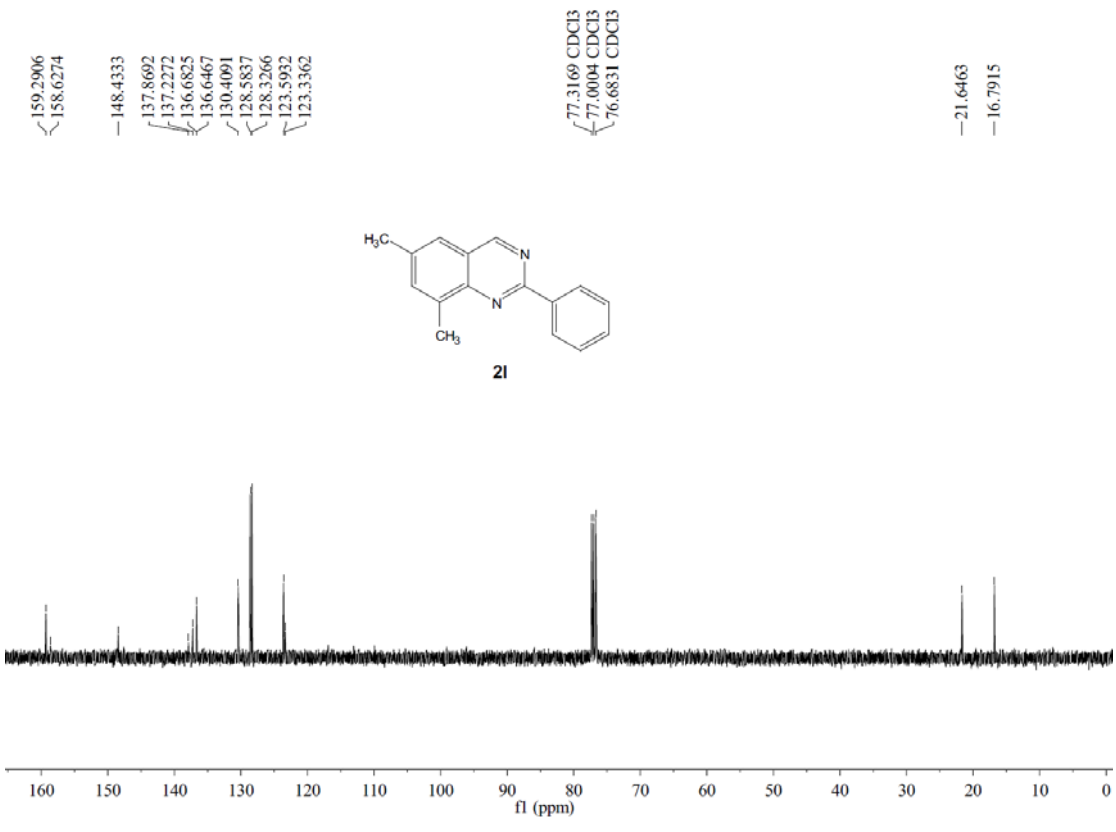

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.4262
8.6831
8.6786
8.6735
8.6666
8.6623
8.6588
7.7695
7.7512
7.7494
7.7368
7.7345
7.5624
7.5466
7.5431
7.5318
7.5277
7.5215
7.5189
7.5044
7.5005
7.4813
7.2596
2.8659
1.5912
0.0000
N
N
CH3
2k
1.00
2.02
2.02
4.01
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

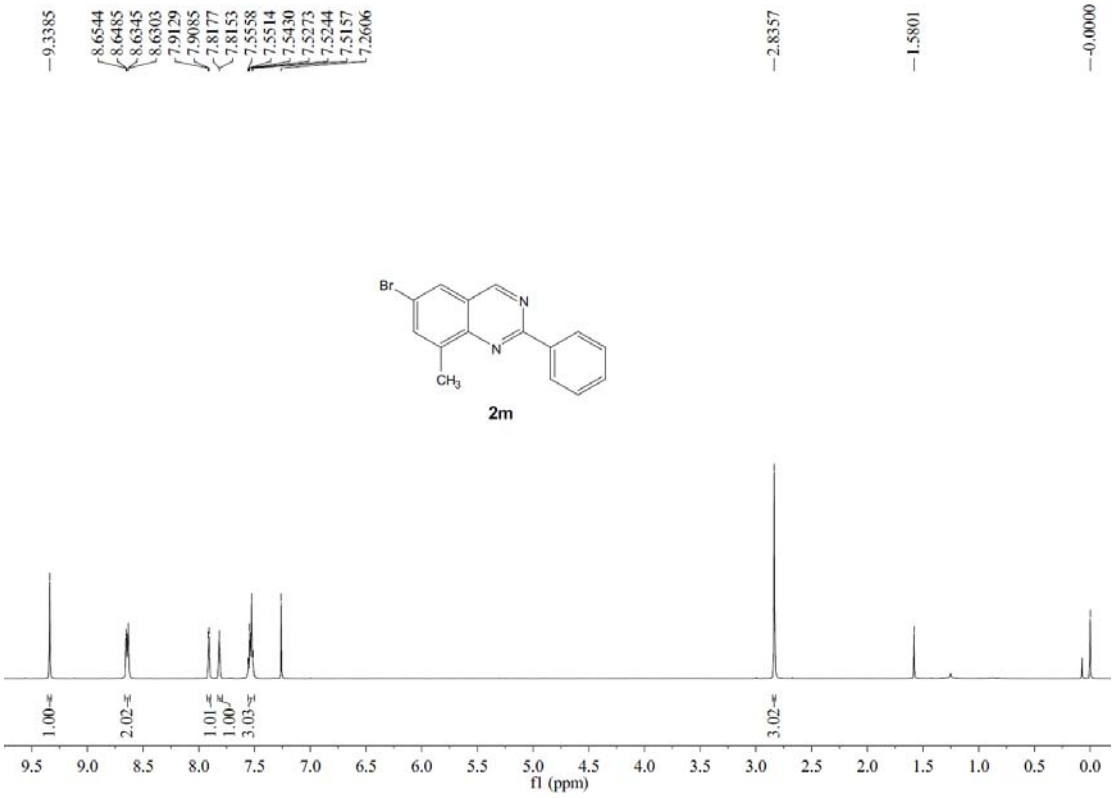

160.5024
159.8383
149.6217
138.3088
137.0580
133.8173
130.4243
128.5514
128.4631
126.8739
124.7606
123.4303
77.3178 CDCl3
77.0005 CDCl3
76.6819 CDCl3
16.9258
N
N
CH3
2k
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

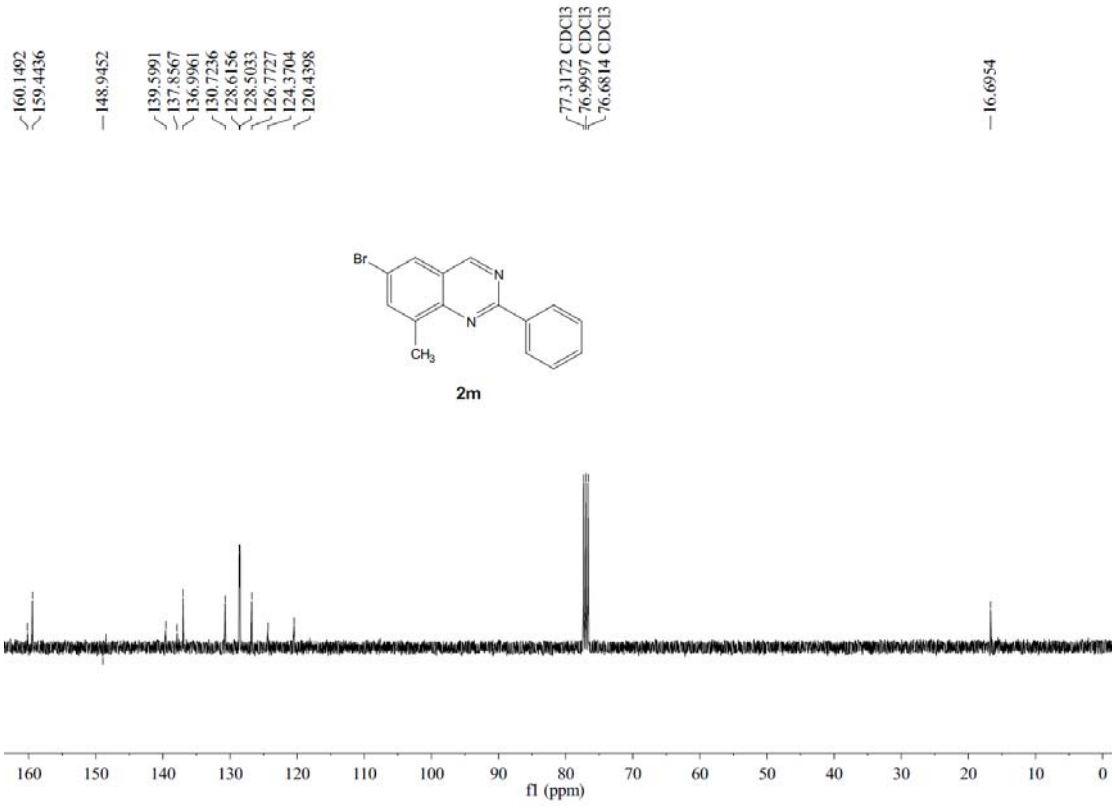

9.3332
8.6588
8.6546
8.6494
8.6419
8.6379
8.6344
7.5809
7.5563
7.5514
7.5348
7.5313
7.5292
7.5162
7.5100
7.5055
7.5015
7.4953
7.4884
7.2593
2.8237
2.5242
0.0000
H3C
N
N
CH3
1.00
2.01
1.02
4.00
3.00
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

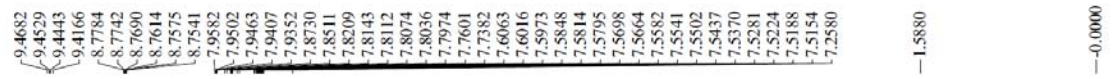
2l

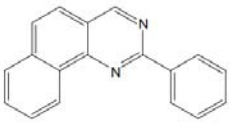

159.2906
158.6274
148.4333
137.8692
137.2272
136.6825
136.6467
130.4091
128.5837
128.3266
123.5932
123.3362
77.3169 CDCl3
77.0004 CDCl3
76.6831 CDCl3
21.6463
16.7915
H3C
N
N
CH3
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2l

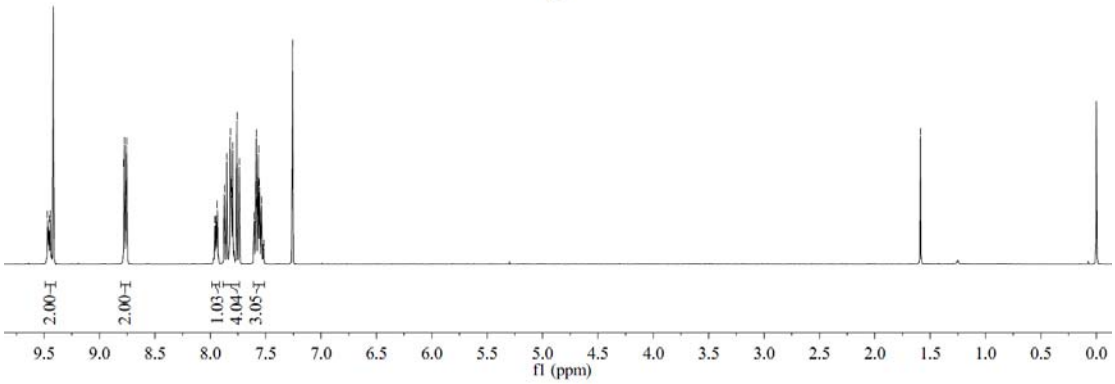

9.3385
8.6544
8.6485
8.6345
8.6303
7.9129
7.9085
7.8177
7.8153
7.5558
7.5514
7.5430
7.5273
7.5244
7.5157
7.2606
2.8357
1.5801
0.0000
Br
N
N
CH3
2m
1.00
2.02
1.01
1.00
3.03
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


160.1492
159.4436
148.9452
139.5991
137.8567
136.9961
130.7236
128.6156
128.5033
126.7727
124.3704
120.4398
77.3172 CDCl3
76.9997 CDCl3
76.6814 CDCl3
16.6954
Br
N
N
CH3
2m
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

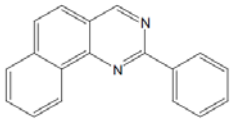

9.4682
9.4529
9.4443
9.4166
8.7784
8.7742
8.7690
8.7614
8.7575
8.7541
7.9582
7.9502
7.9463
7.9407
7.9352
7.8730
7.8511
7.8209
7.8143
7.8112
7.8074
7.8036
7.7974
7.7601
7.7382
7.6063
7.6016
7.5973
7.5848
7.5814
7.5795
7.5698
7.5664
7.5582
7.5541
7.5502
7.5437
7.5370
7.5281
7.5224
7.5188
7.5154
7.2580
1.5880
0.0000



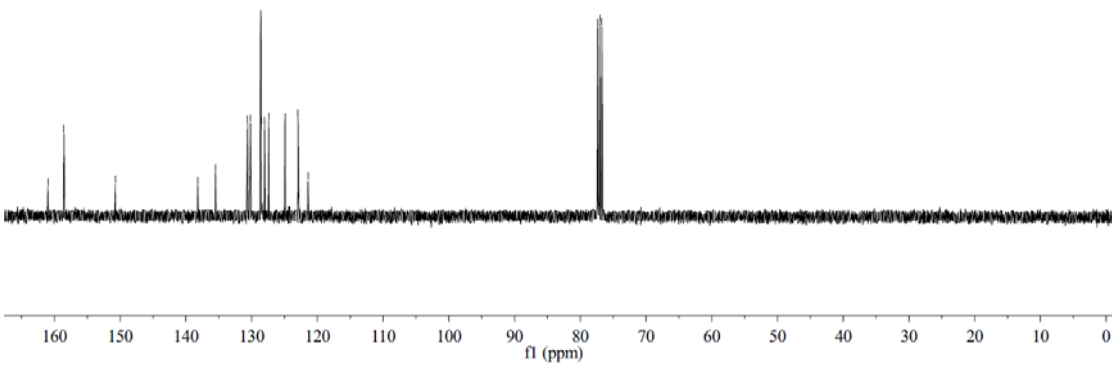
2n

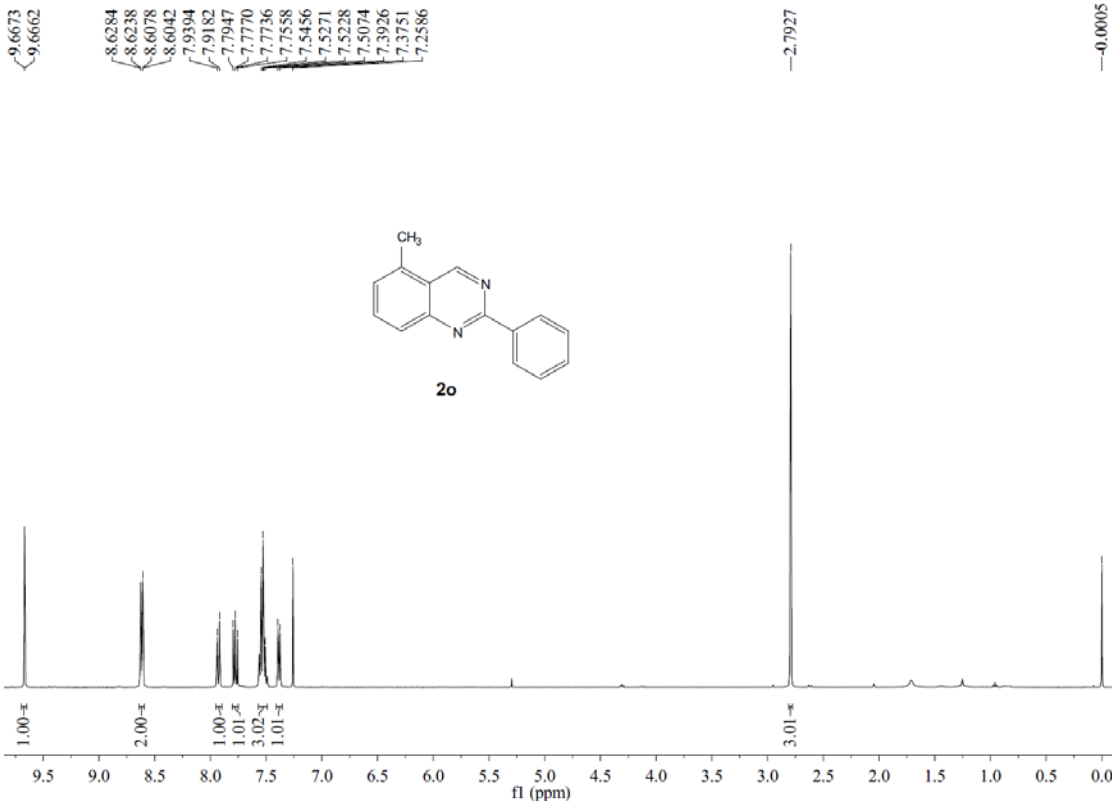

2.00
2.00
1.03
4.04
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

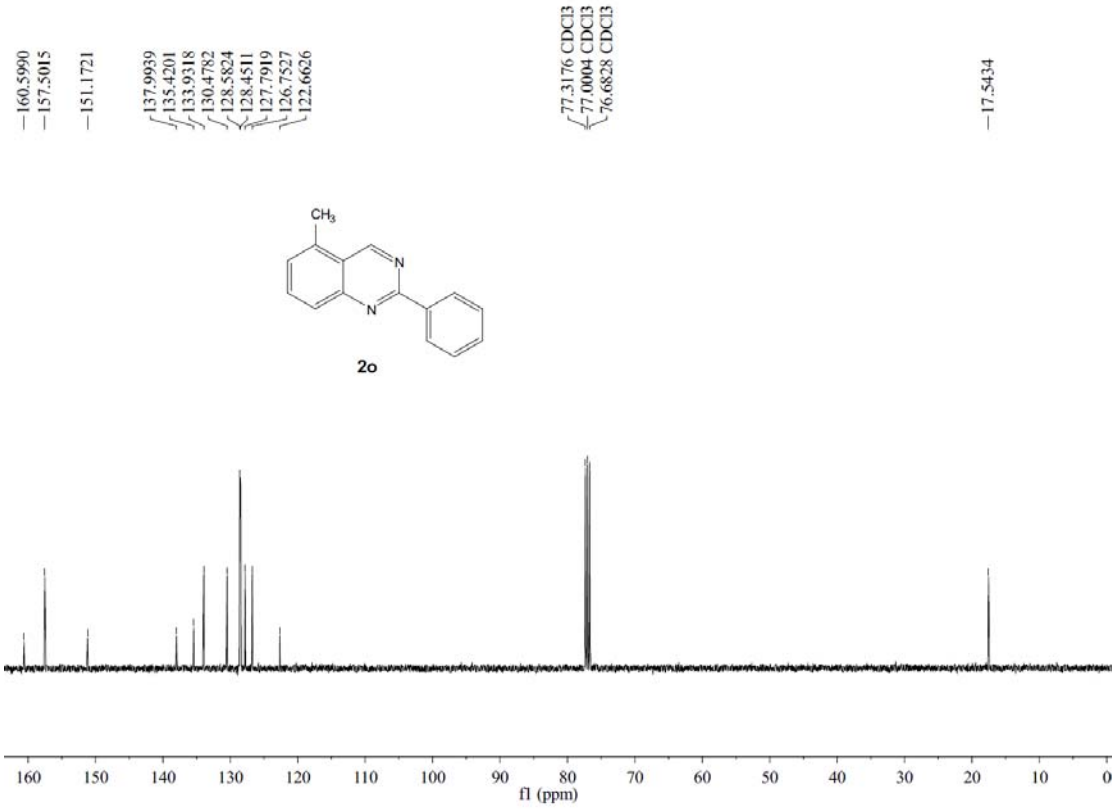

161.0048
158.5421
150.7502
138.2108
135.4976
130.6016
130.2810
130.1630
128.6399
128.5615
128.4571
128.0164
127.4087
124.9207
122.9309
121.4343
77.3513 CDCl3
77.0330 CDCl3
76.7160 CDCl3

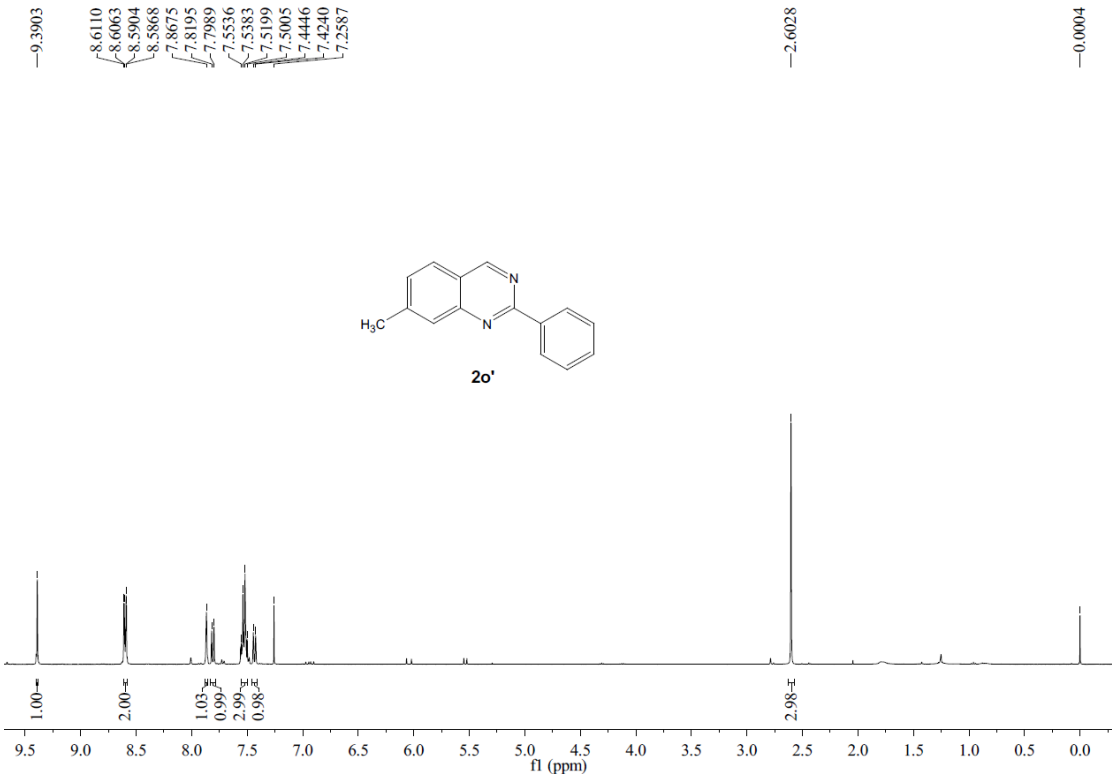


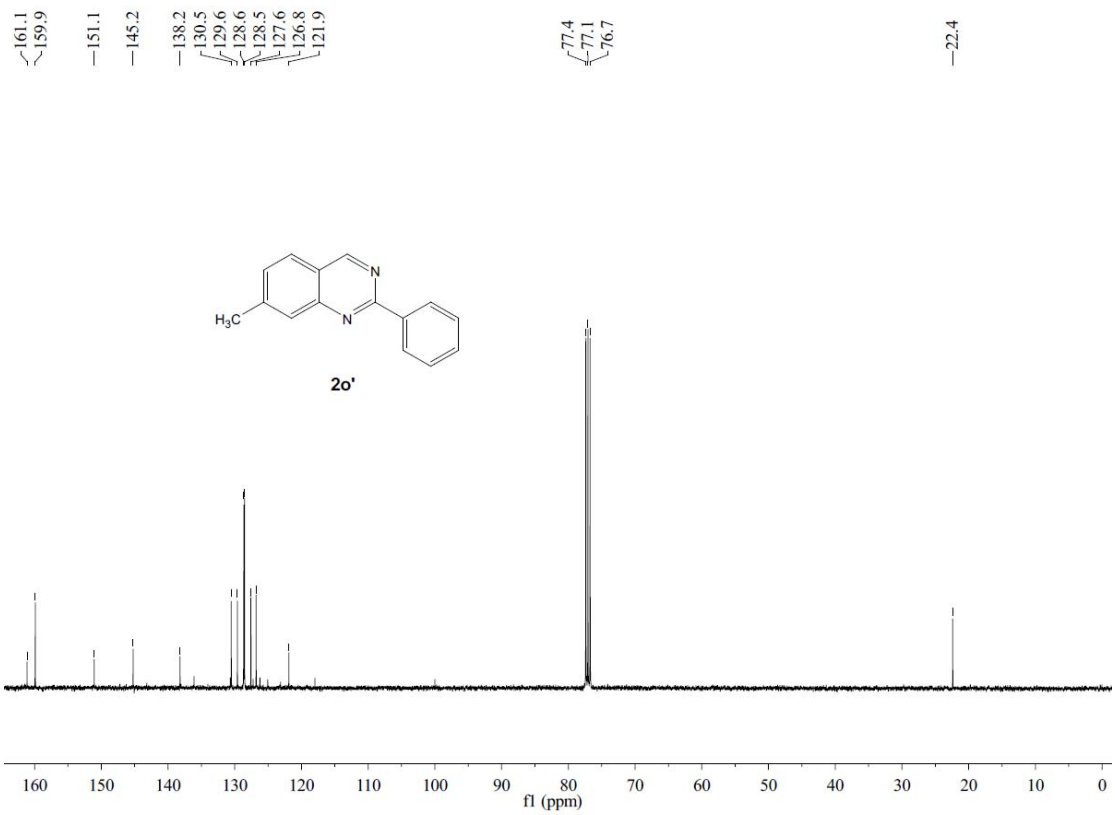
2n

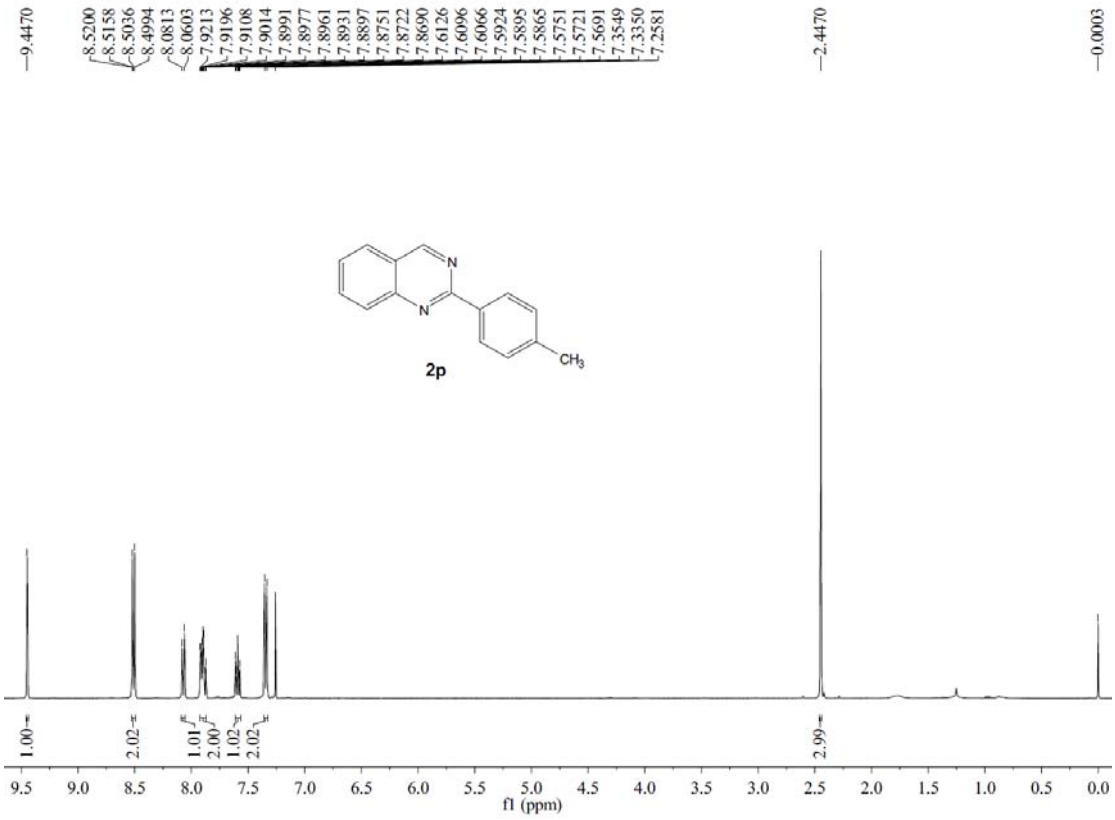

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

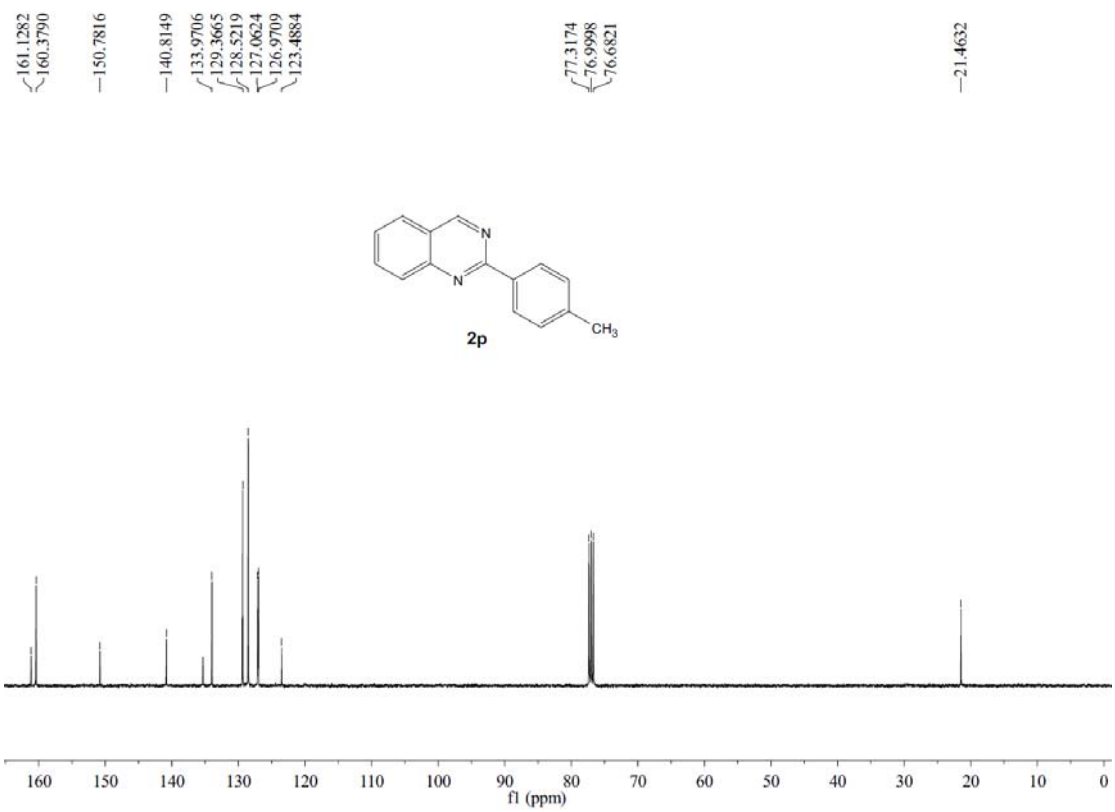

9.6673
9.6662
8.6284
8.6238
8.6078
8.6042
7.9394
7.9182
7.7947
7.7770
7.7736
7.7558
7.5456
7.5271
7.5228
7.5074
7.3926
7.3751
7.2586
2.7927
0.0005
CH3
N
N
2o
1.00
2.00
1.00
1.01
3.02
1.01
3.01
f1 (ppm)

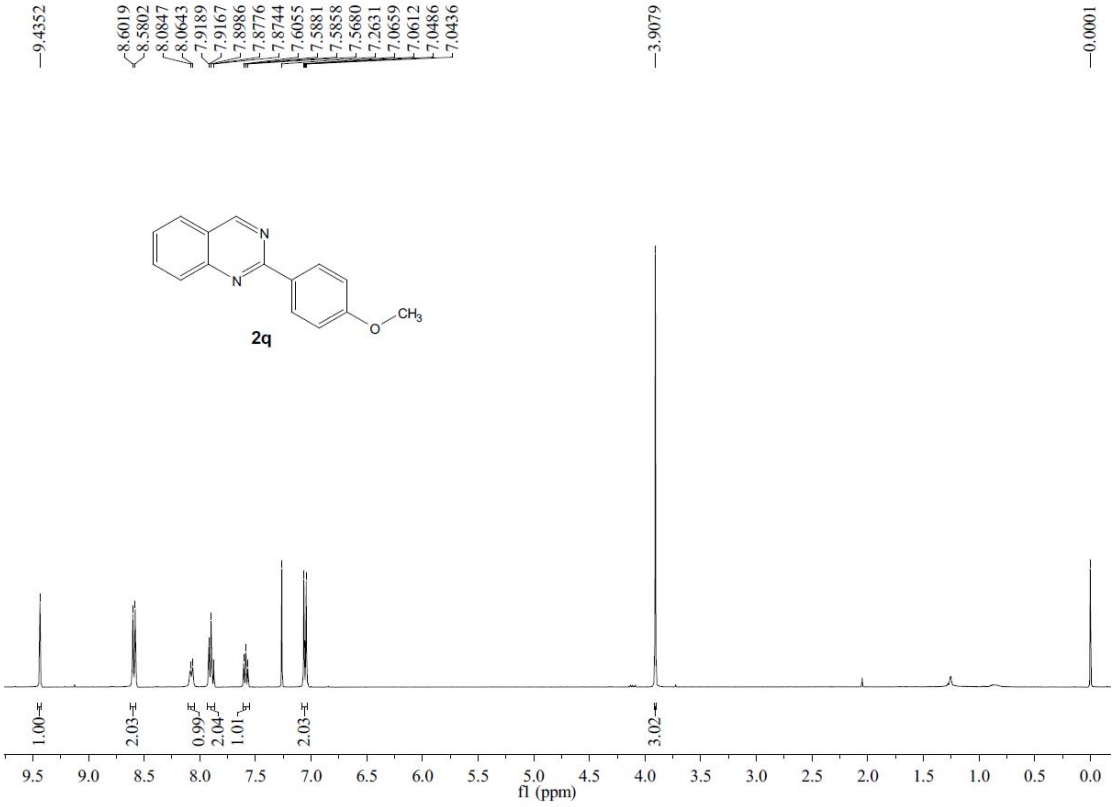

160.5990
157.5015
151.1721
137.9939
135.4201
133.9318
130.4782
128.5824
128.4511
127.7919
126.7527
122.6626
77.3176 CDCl3
77.0004 CDCl3
76.6828 CDCl3
17.5434
CH3
N
N
2o
f1 (ppm)

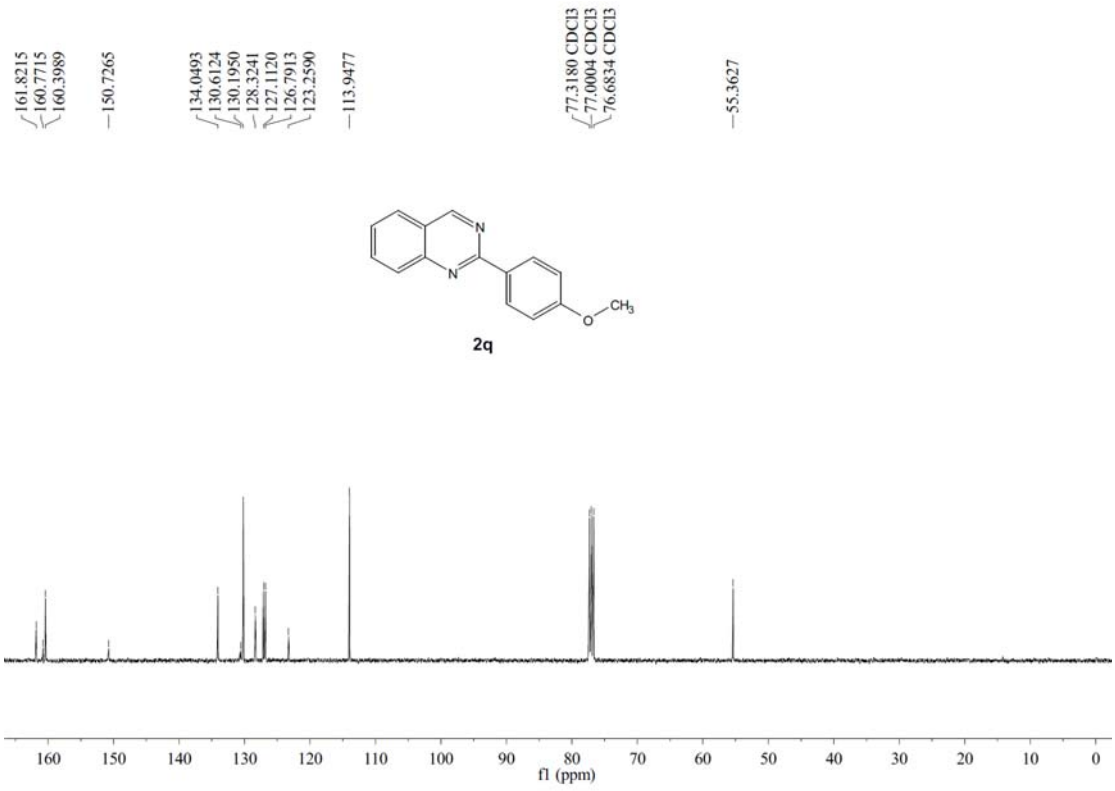

9.3903
8.6110
8.6063
8.5904
8.5868
7.8675
7.8195
7.7989
7.5536
7.5383
7.5199
7.5005
7.4446
7.4240
7.2587
2.6028
0.0004
N
N
H3C
2o'
1.00
2.00
1.03
0.99
2.99
0.98
2.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

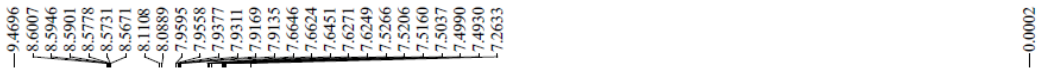

161.1
159.9
151.1
145.2
138.2
130.5
129.6
128.6
128.5
127.6
126.8
121.9
77.4
77.1
76.7
22.4
N
N
H3C
2o'
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

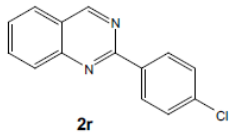

9.4470
8.5200
8.5158
8.5036
8.4994
8.0813
8.0603
7.9213
7.9196
7.9108
7.9014
7.8991
7.8977
7.8961
7.8931
7.8897
7.8751
7.8722
7.8690
7.6126
7.6096
7.6066
7.5924
7.5895
7.5865
7.5751
7.5721
7.5691
7.3549
7.3350
7.2581
2.4470
0.0003
N
N
CH3
2p
1.00
2.02
1.01
2.00
1.02
2.02
2.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


161.1282
160.3790
150.7816
140.8149
133.9706
129.3665
128.5219
127.0624
126.9709
123.4884
77.3174
76.9998
76.6821
21.4632
N
N
CH3
2p
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

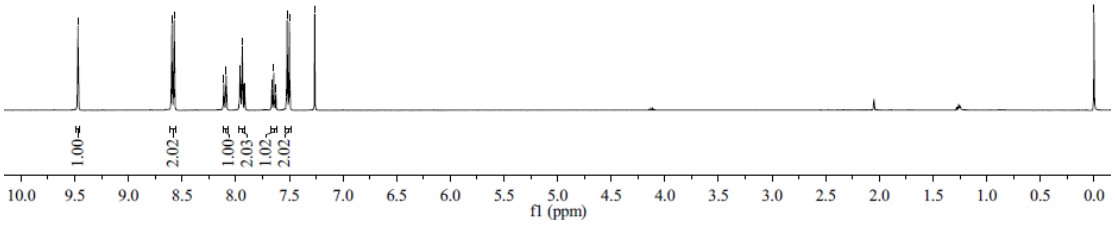

9.4352
8.6019
8.5802
8.0847
8.0643
7.9189
7.9167
7.8986
7.8776
7.8744
7.6055
7.5881
7.5858
7.5680
7.2631
7.0659
7.0612
7.0486
7.0436
3.9079
0.0001
2q
1.00
2.03
0.99
2.04
1.01
2.03
3.02
f1 (ppm)


161.8215
160.7715
160.3989
150.7265
134.0493
130.6124
130.1950
128.3241
127.1120
126.7913
123.2590
113.9477
77.3180 CDCl3
77.0004 CDCl3
76.6834 CDCl3
55.3627
2q
f1 (ppm)

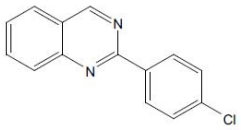

9.4696
8.6007
8.5946
8.5901
8.5778
8.5731
8.5671
8.1108
8.0889
7.9595
7.9558
7.9377
7.9311
7.9169
7.9135
7.6646
7.6624
7.6451
7.6271
7.6249
7.5266
7.5206
7.5160
7.5037
7.4990
7.4930
7.2633
0.0002


N
N
Cl

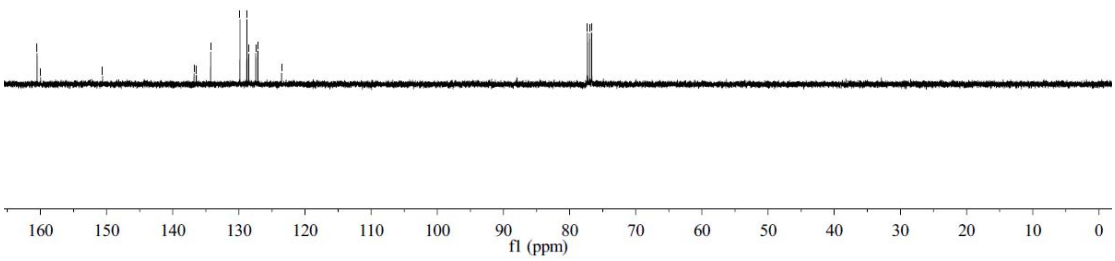
2r

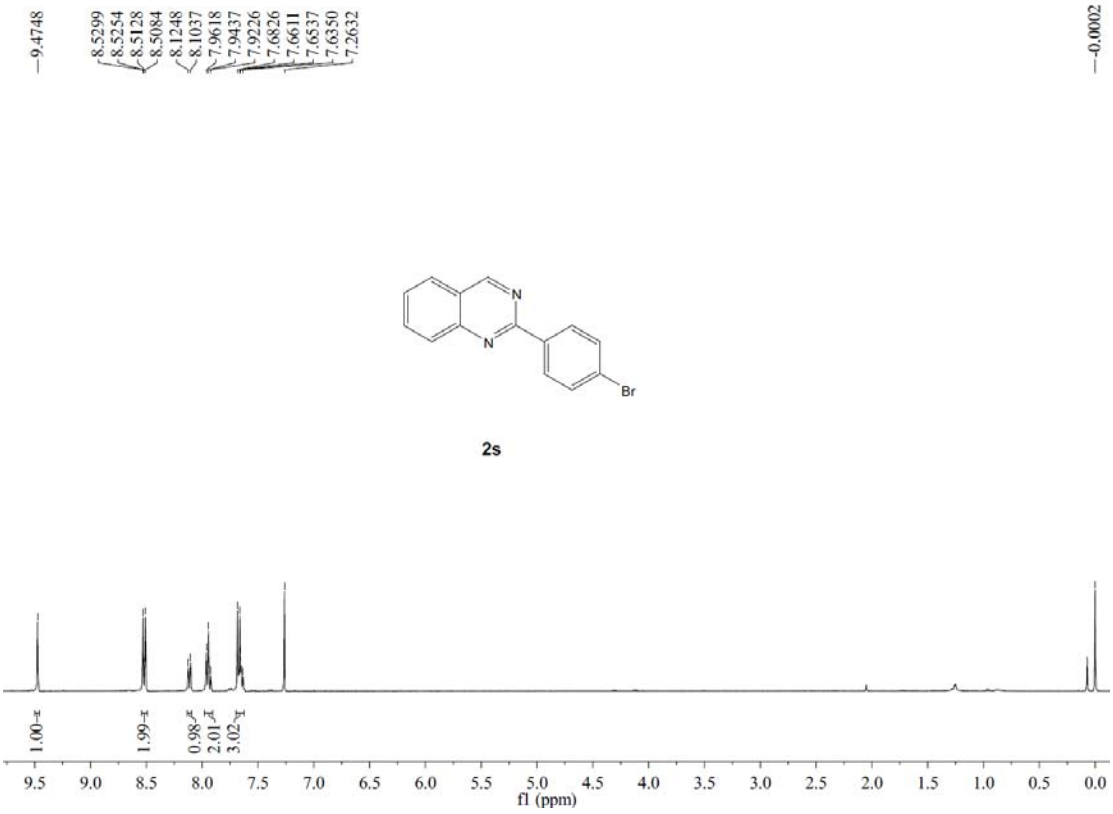

1.00
2.02
1.00
2.03
1.02
2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

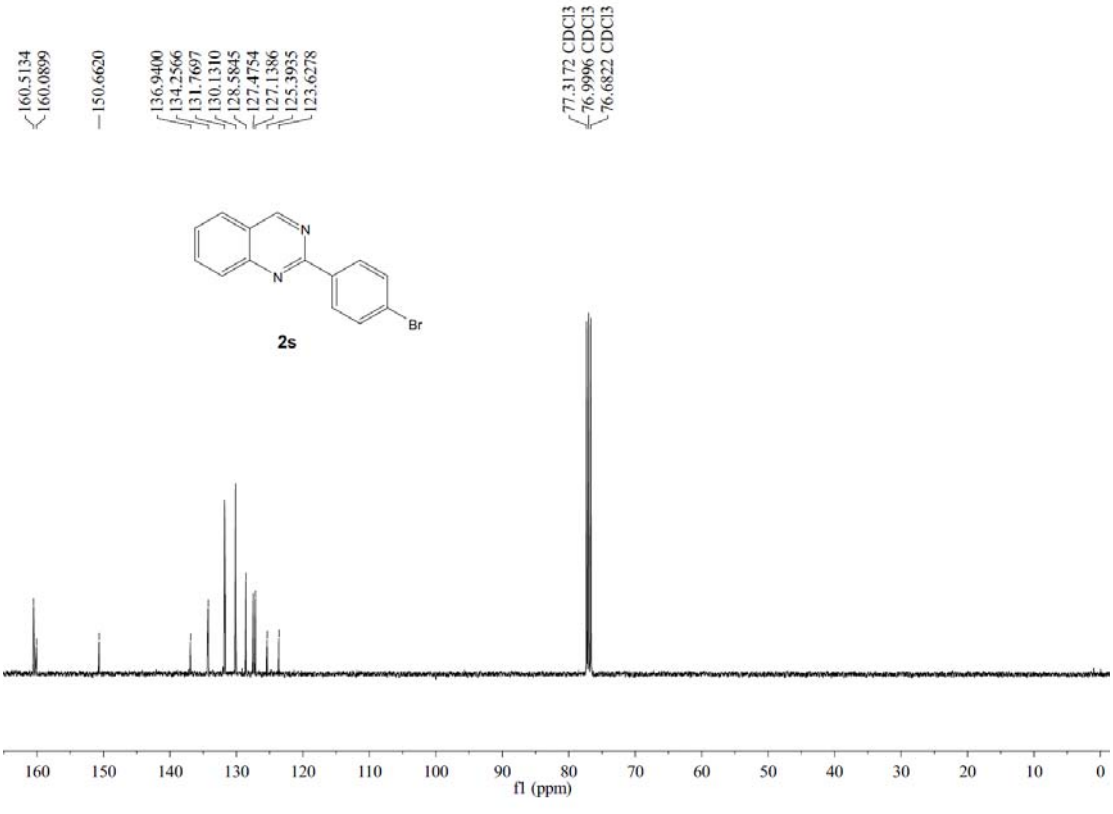

160.5067
159.9519
150.5994
136.7754
136.4292
134.2603
129.8345
128.7902
128.5191
127.4460
127.1288
123.5423
77.3176
77.0002
76.6845

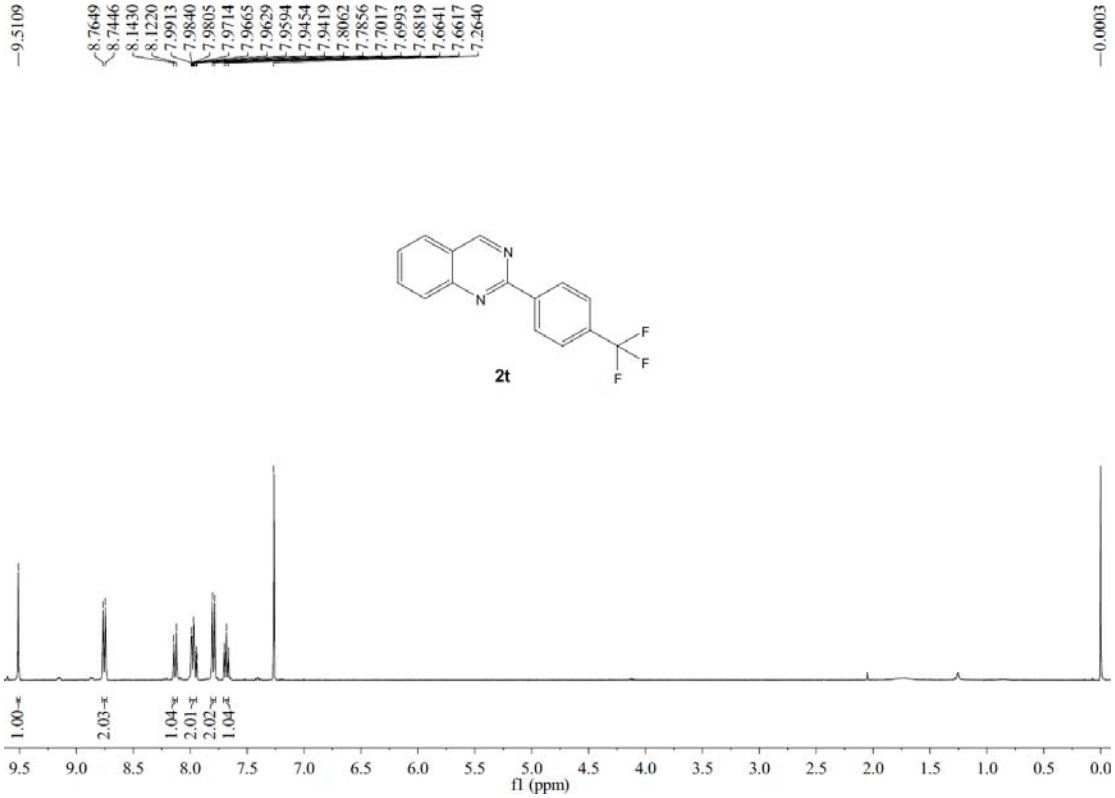

N
N
Cl

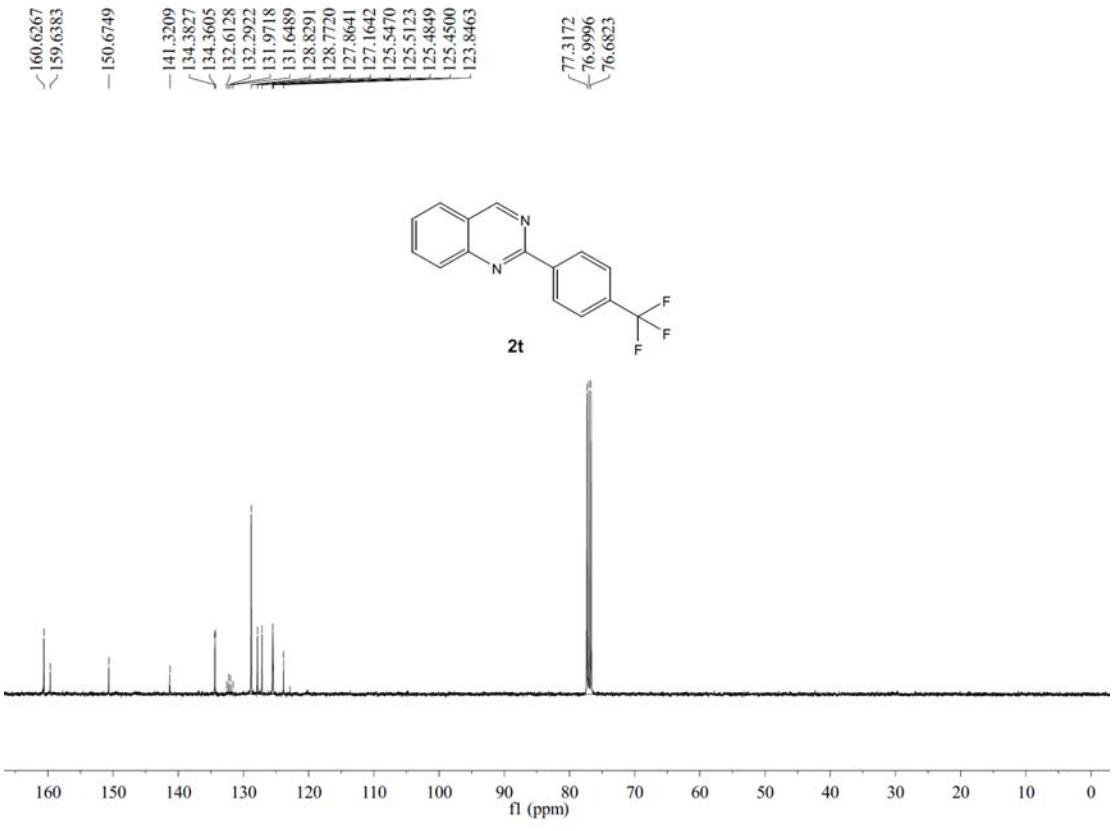
2r

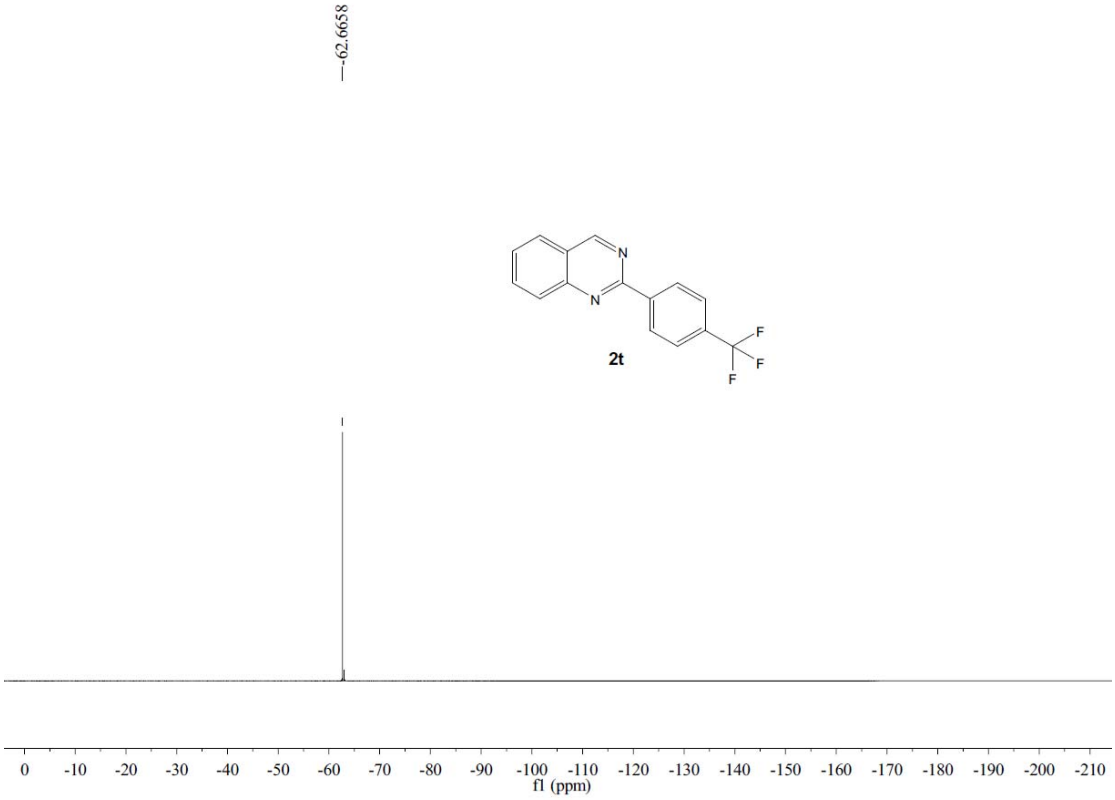

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

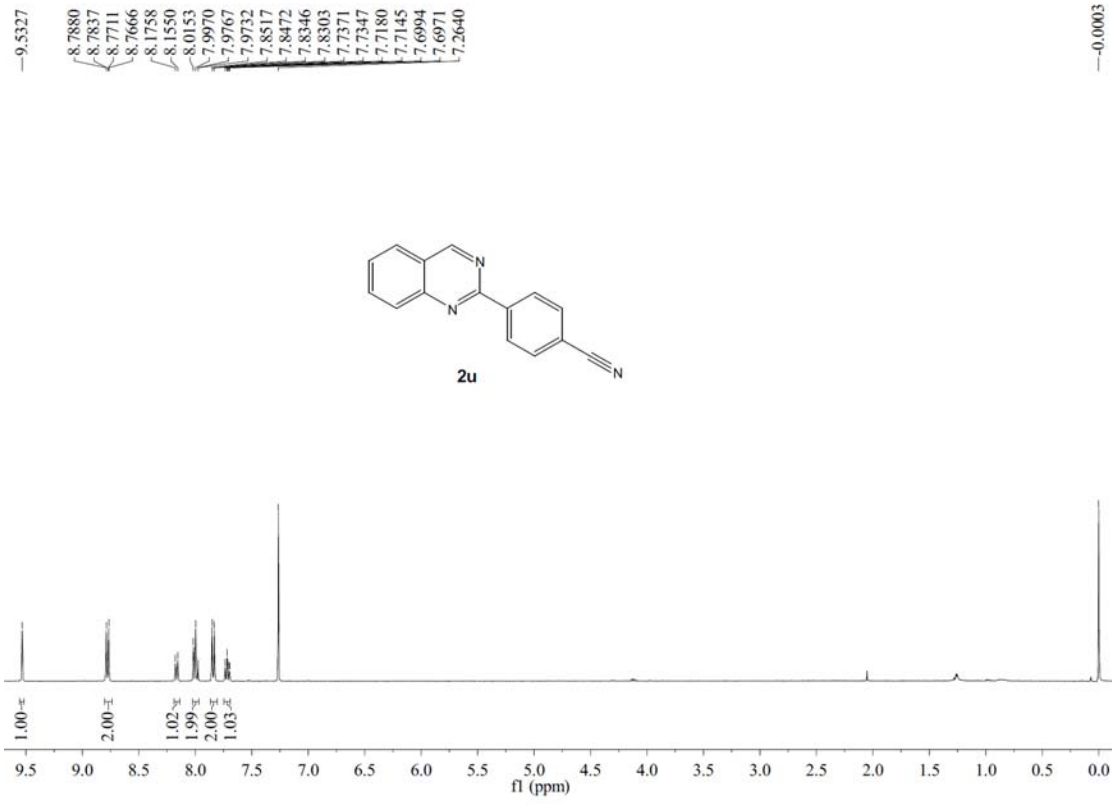

9.4748
8.5299
8.5254
8.5128
8.5084
8.1248
8.1037
7.9618
7.9437
7.9226
7.6826
7.6611
7.6537
7.6350
7.2632
0.0002
N
N
Br
2s
1.00
1.99
0.98
2.01
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

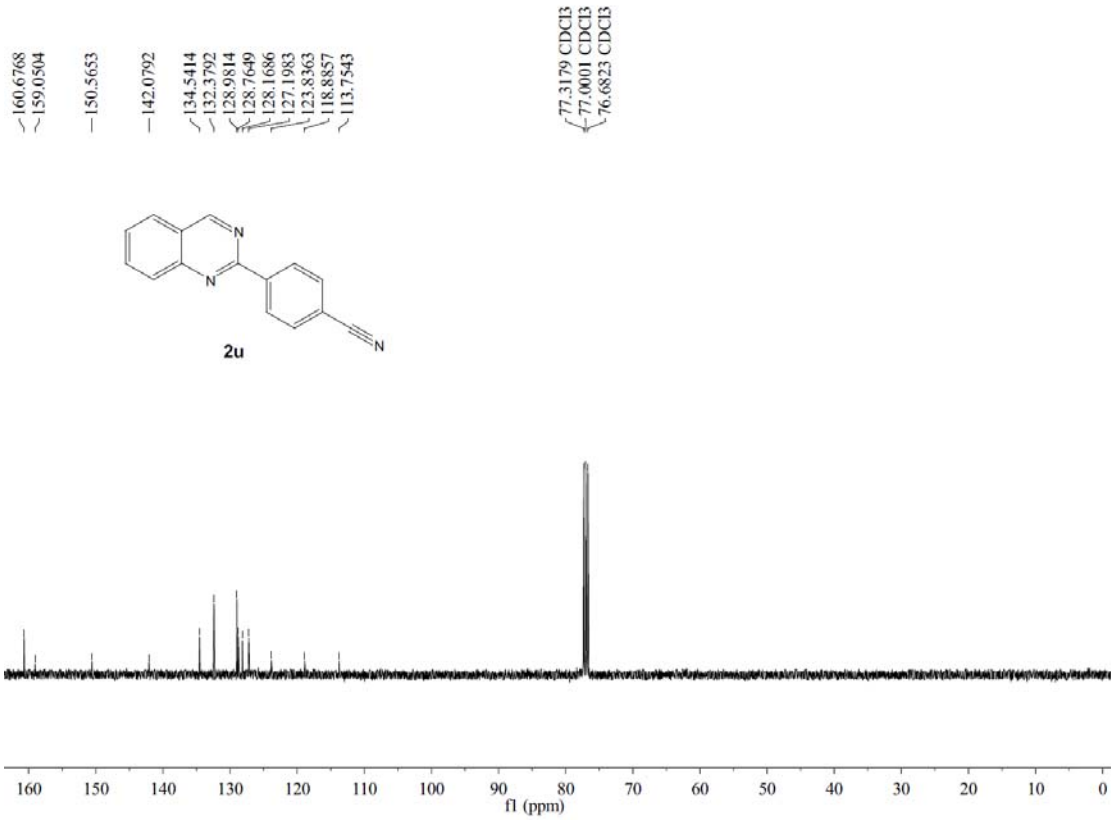

160.5134
160.0899
150.6620
136.9400
134.2566
131.7697
130.1310
128.5845
127.4754
127.1386
125.3935
123.6278
77.3172 CDCl3
76.9996 CDCl3
76.6822 CDCl3
N
N
Br
2s
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

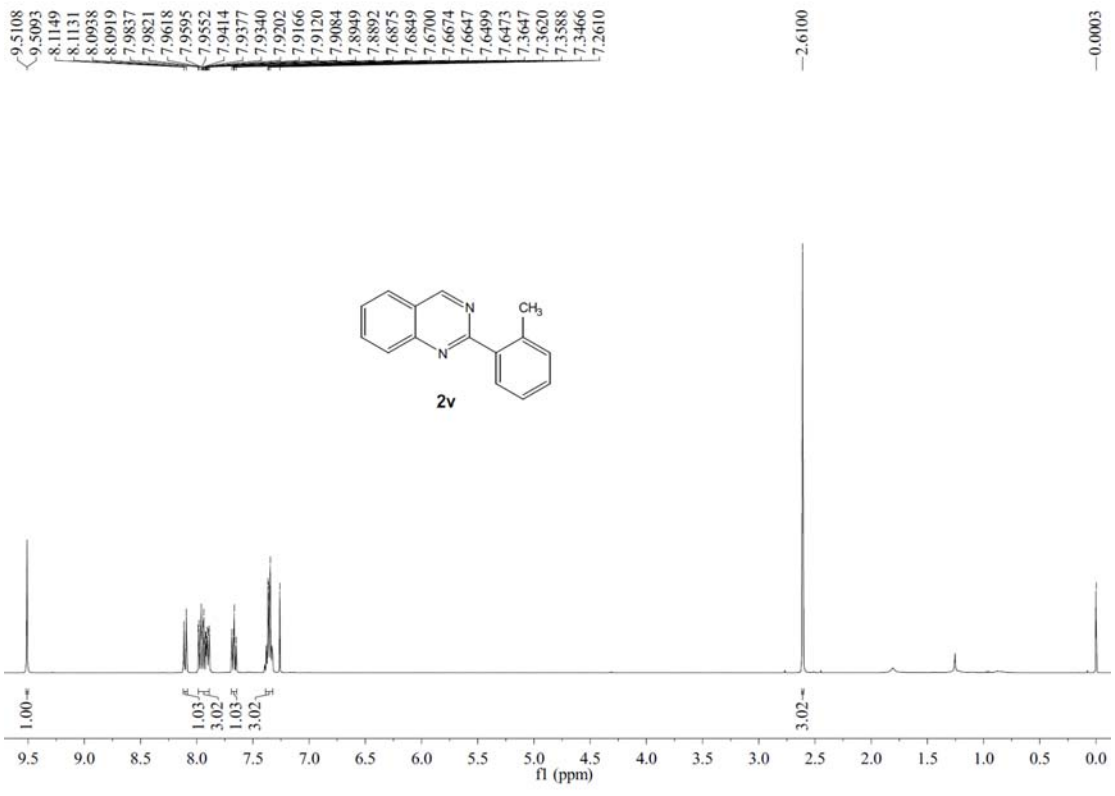

9.5109
8.7649
8.7446
8.1430
8.1220
7.9913
7.9840
7.9805
7.9714
7.9665
7.9629
7.9594
7.9454
7.9419
7.8062
7.7856
7.7017
7.6993
7.6819
7.6641
7.6617
7.2640
0.0003
N
N
F
F
F
2t
1.00
2.03
1.04
2.01
2.02
1.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

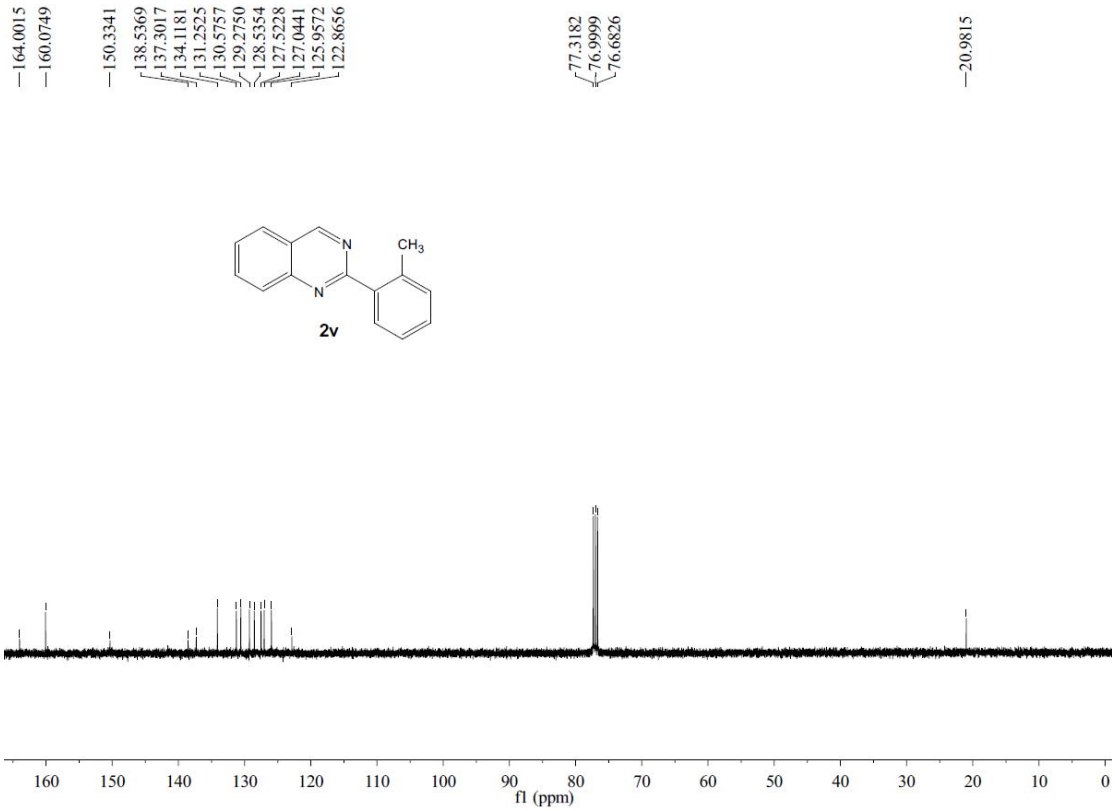

160.6267
159.6383
150.6749
141.3209
134.3827
134.3605
132.6128
132.2922
131.9718
131.6489
128.8291
128.7720
127.8641
127.1642
125.5470
125.5123
125.4849
125.4500
123.8463
77.3172
76.9996
76.6823
N
N
F
F
F
2t
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

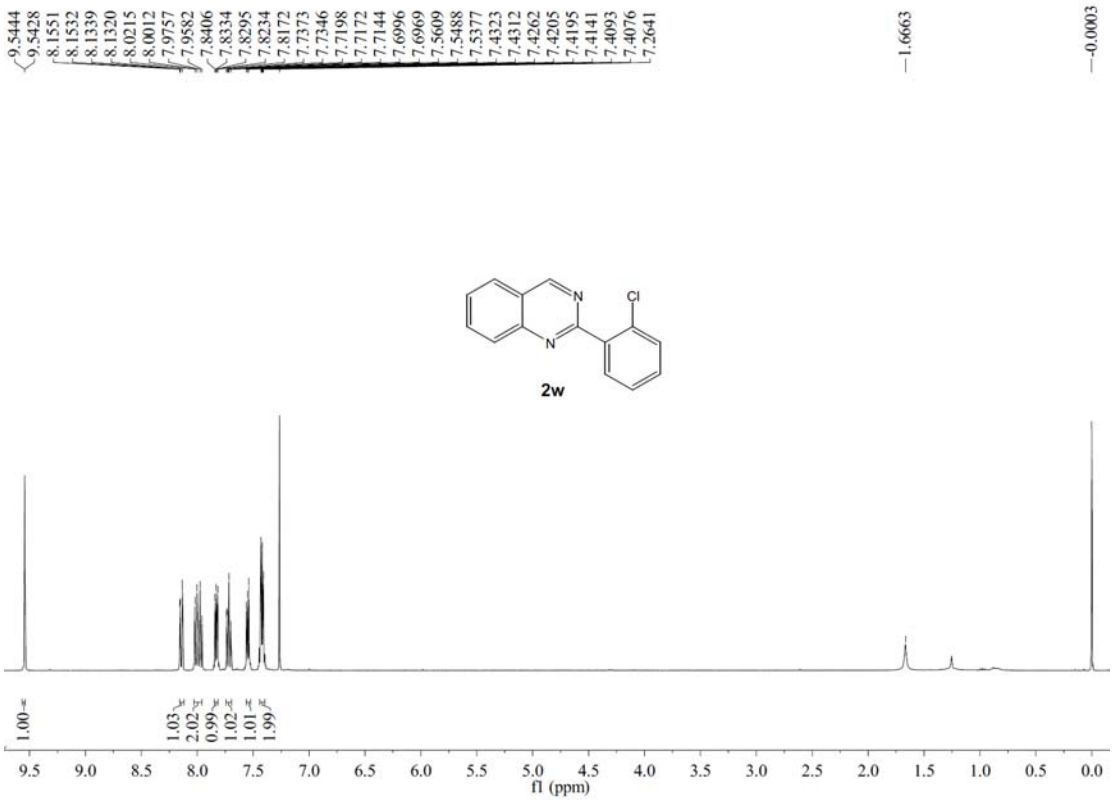

-62.6658
2t
F
F
F
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

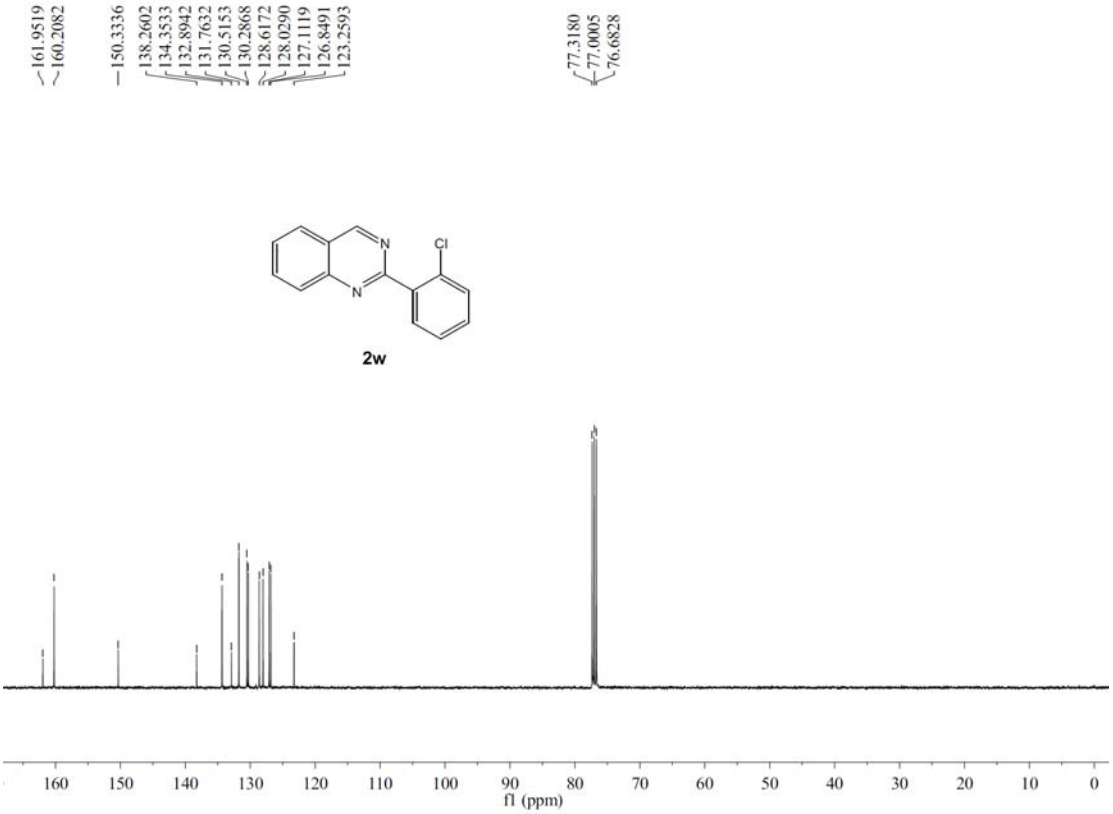

9.5327
8.7880
8.7837
8.7711
8.7666
8.1758
8.1550
8.0153
7.9970
7.9767
7.9732
7.8517
7.8472
7.8346
7.8303
7.7371
7.7347
7.7180
7.7145
7.6994
7.6971
7.2640
0.0003
2u
1.00
2.00
1.02
1.99
2.00
1.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

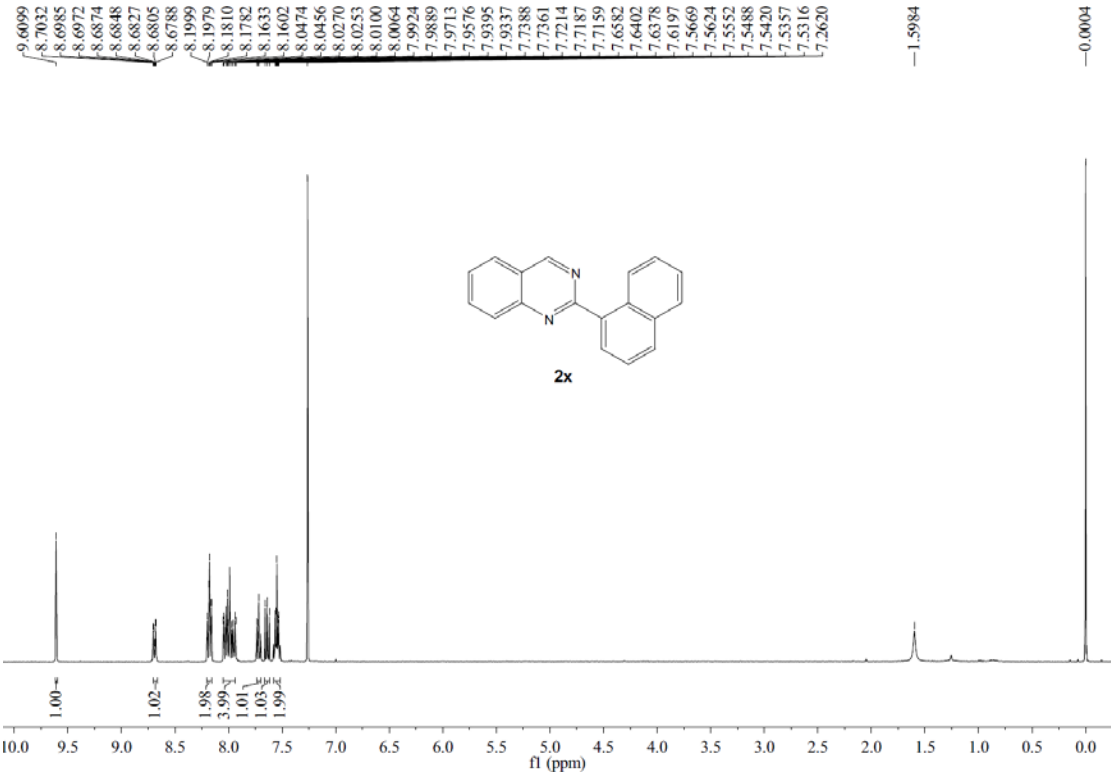

160.6768
159.0504
150.5653
142.0792
134.5414
132.3792
128.9814
128.7649
128.1686
127.1983
123.8363
118.8857
113.7543
77.3179 CDCl3
77.0001 CDCl3
76.6823 CDCl3
N
N
N
2u
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

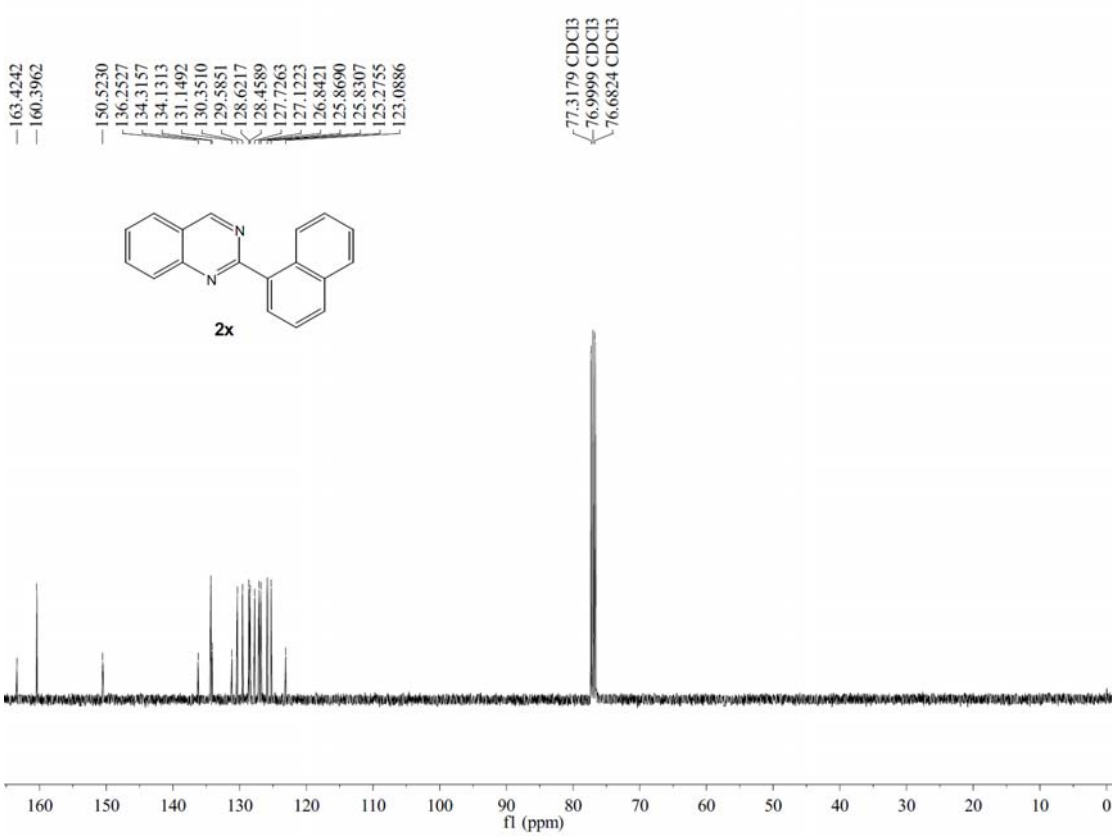

9.5108
9.5093
8.1149
8.1131
8.0938
8.0919
7.9837
7.9821
7.9618
7.9595
7.9552
7.9414
7.9377
7.9340
7.9202
7.9166
7.9120
7.9084
7.8949
7.8892
7.6875
7.6849
7.6700
7.6674
7.6647
7.6499
7.6473
7.3647
7.3620
7.3588
7.3466
7.2610
2.6100
0.0003
N
N
CH3
2v
1.00
1.03
3.02
1.03
3.02
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

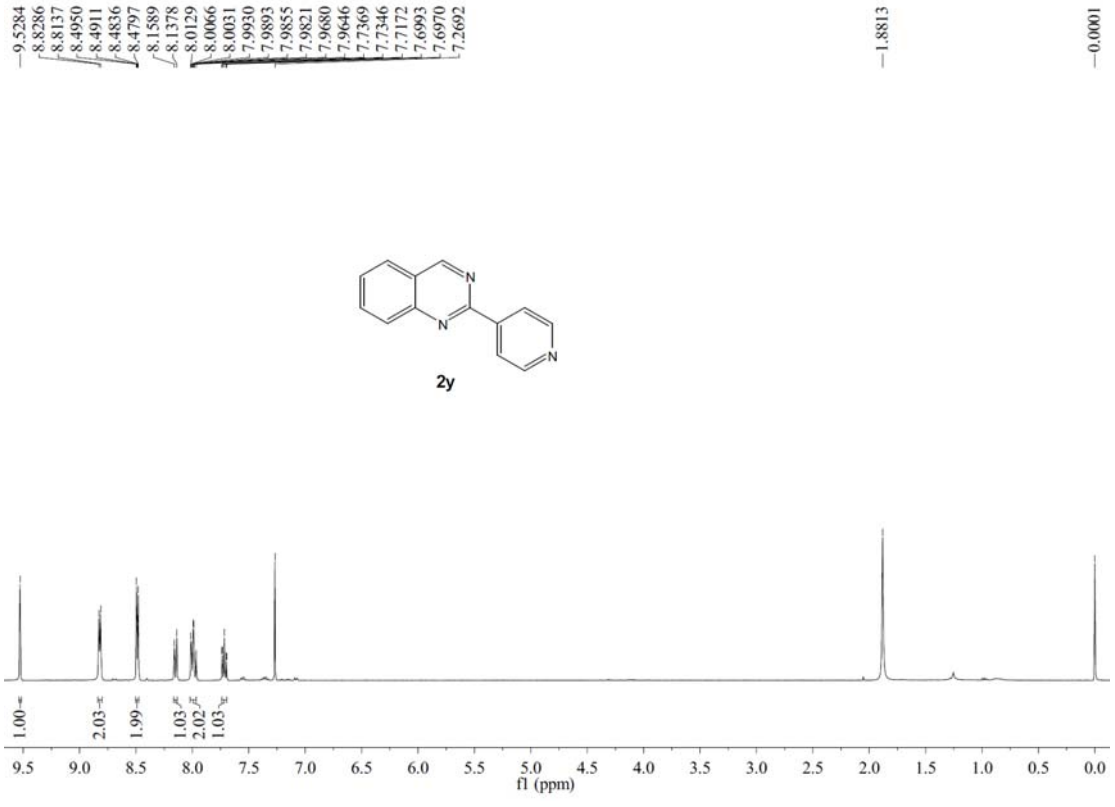

164.0015
160.0749
150.3341
138.5369
137.3017
134.1181
131.2525
130.5757
129.2750
128.5354
127.5228
127.0441
125.9572
122.8656
77.3182
76.9999
76.6826
20.9815
N
N
CH3
2v
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

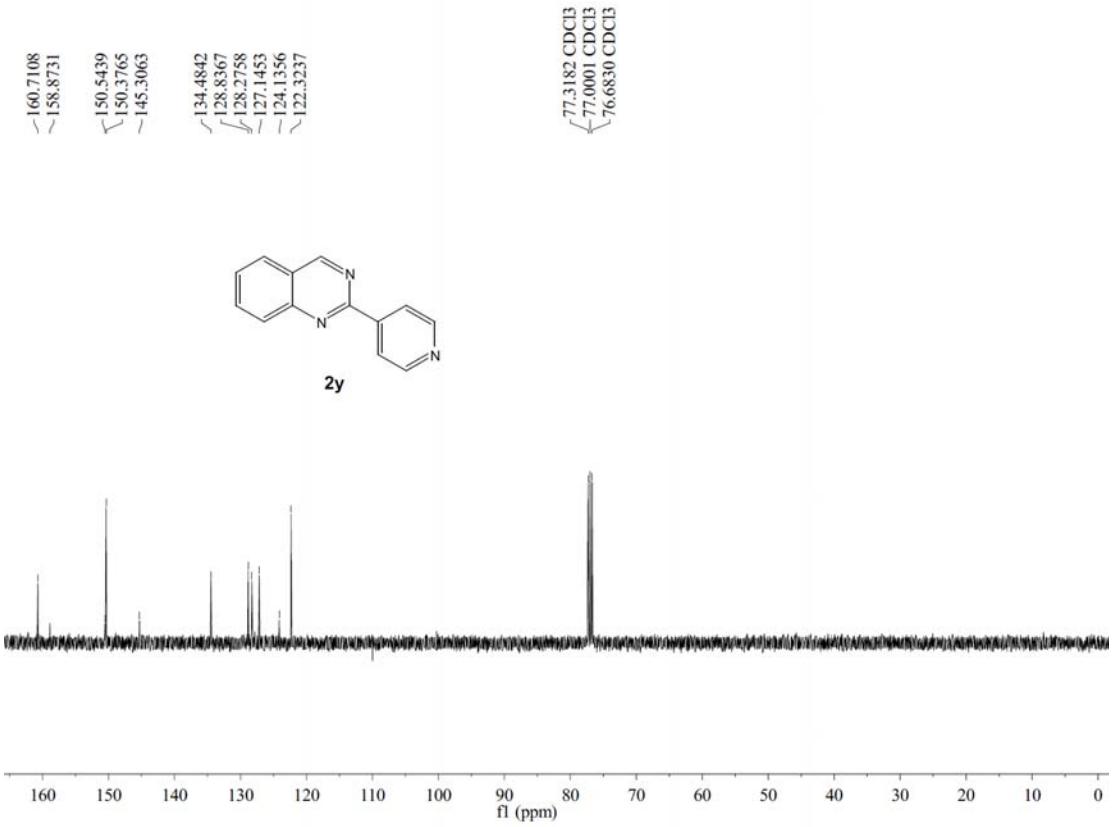

9.5444
9.5428
8.1551
8.1532
8.1339
8.1320
8.0215
8.0012
7.9757
7.9582
7.8406
7.8334
7.8295
7.8234
7.8172
7.7373
7.7346
7.7198
7.7172
7.7144
7.6996
7.6969
7.5609
7.5488
7.5377
7.4323
7.4312
7.4262
7.4205
7.4195
7.4141
7.4093
7.4076
7.2641
1.6663
0.0003
N
N
Cl
2w
1.00
1.03
2.02
0.99
1.02
1.01
1.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

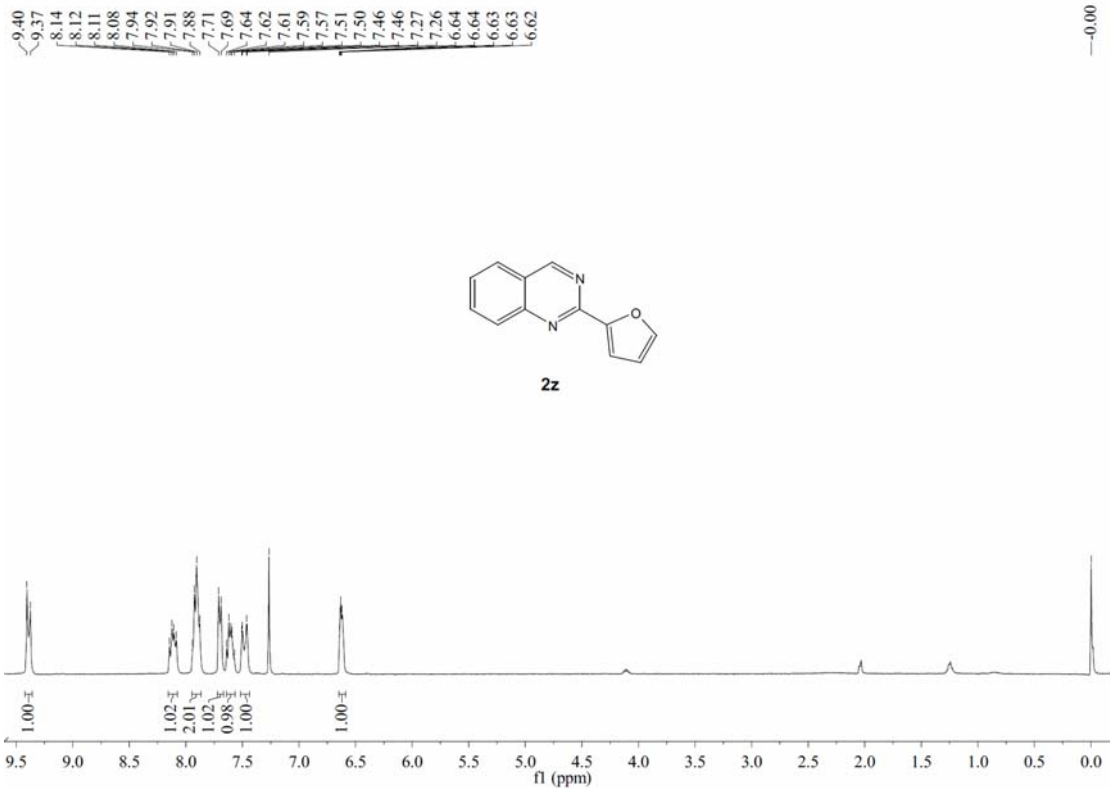

161.9519
160.2082
150.3336
138.2602
134.3533
132.8942
131.7632
130.5153
130.2868
128.6172
128.0290
127.1119
126.8491
123.2593
77.3180
77.0005
76.6828
N
Cl
N
2w
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

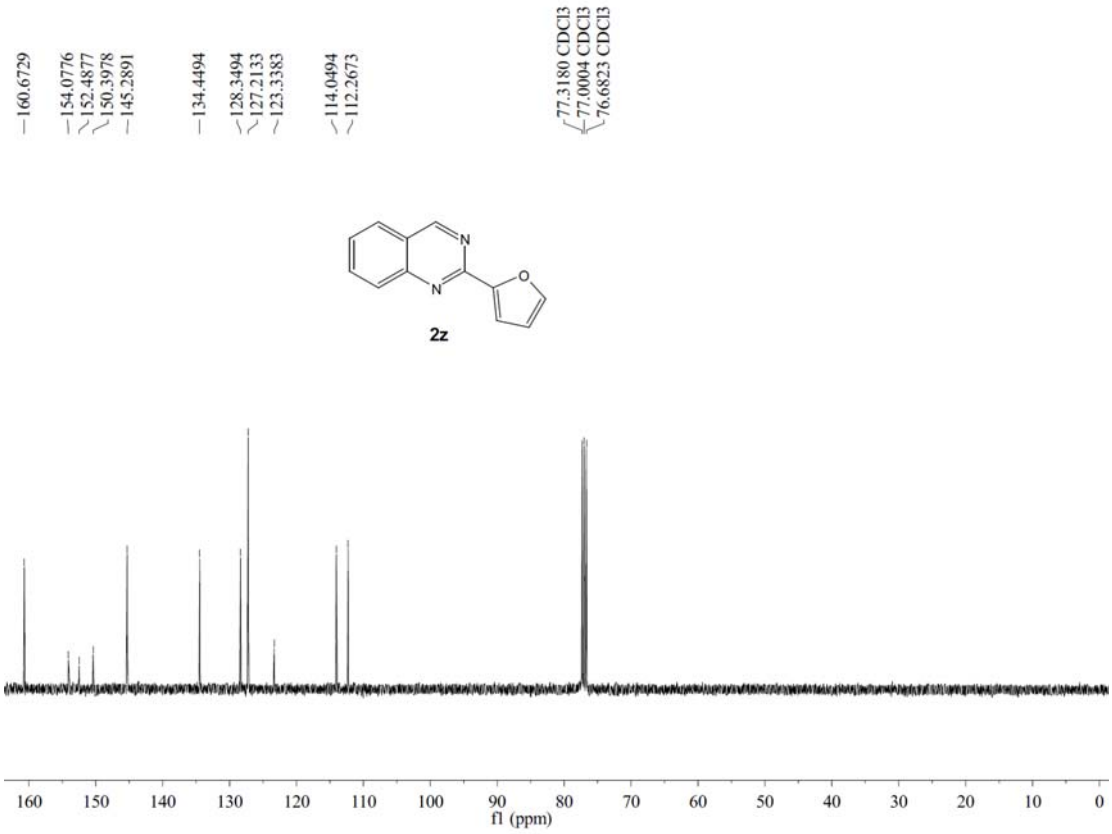

9.6099
8.7032
8.6985
8.6972
8.6874
8.6848
8.6827
8.6805
8.6788
8.1999
8.1979
8.1810
8.1782
8.1633
8.1602
8.0474
8.0456
8.0270
8.0253
8.0100
8.0064
7.9924
7.9889
7.9713
7.9576
7.9395
7.9337
7.7388
7.7361
7.7214
7.7187
7.7159
7.6582
7.6402
7.6378
7.6197
7.5669
7.5624
7.5552
7.5488
7.5420
7.5357
7.5316
7.2620
1.5984
0.0004
N
N
2x
1.00
1.02
1.98
3.99
1.01
1.03
1.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

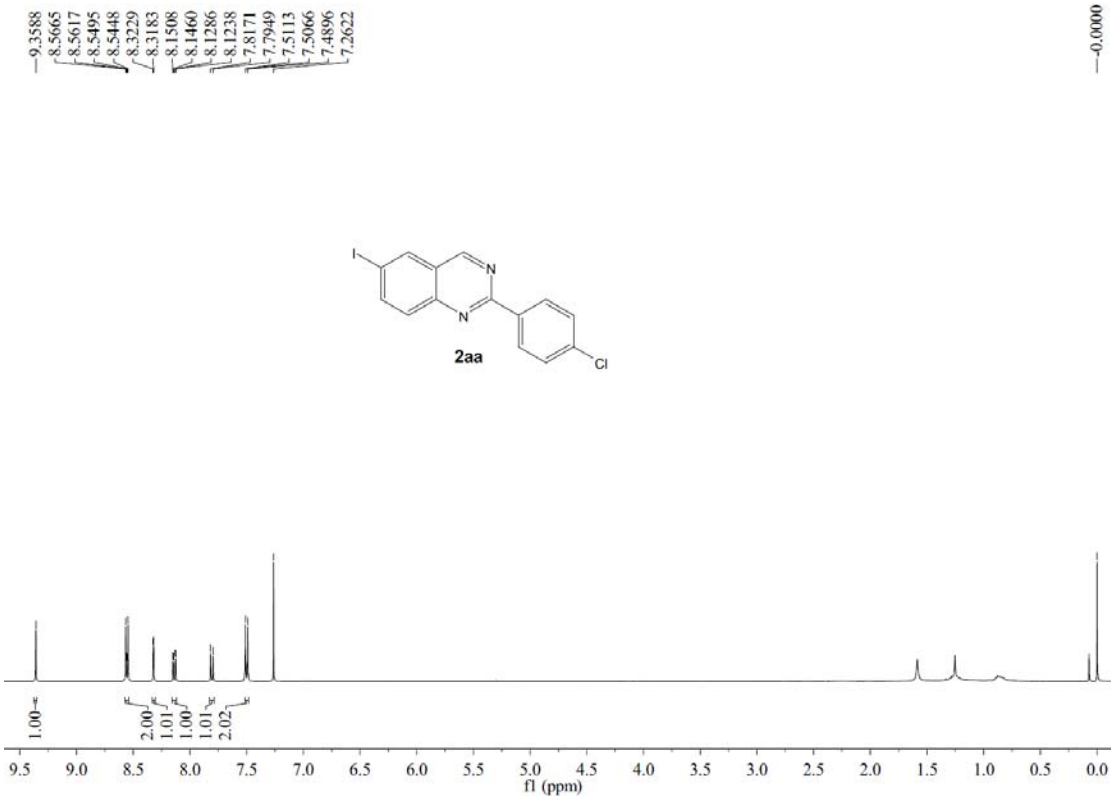

163.4242
160.3962
150.5230
136.2527
134.3157
134.1313
131.1492
130.3510
129.5851
128.6217
128.4589
127.7263
127.1223
126.8421
125.8690
125.8307
125.2755
123.0886
77.3179 CDCl3
76.9999 CDCl3
76.6824 CDCl3
N
N
2x
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

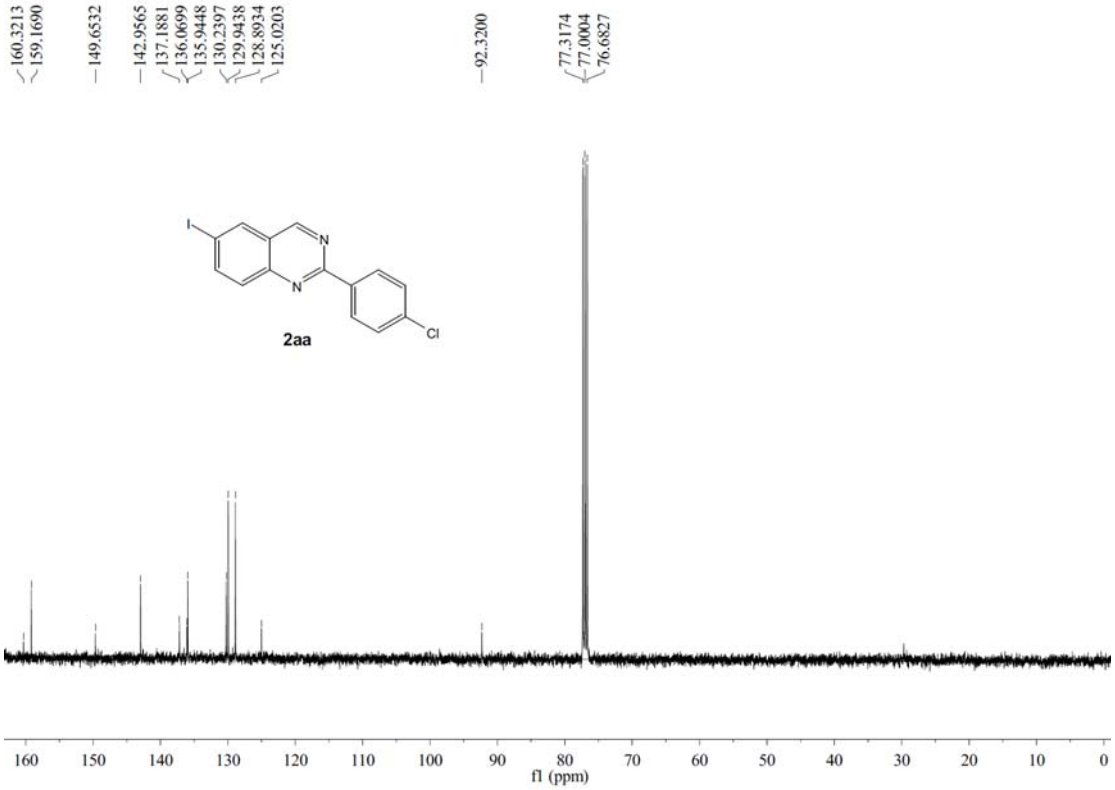

9.5284
8.8286
8.8137
8.4950
8.4911
8.4836
8.4797
8.1589
8.1378
8.0129
8.0066
8.0031
7.9930
7.9893
7.9855
7.9821
7.9680
7.9646
7.7369
7.7346
7.7172
7.6993
7.6970
7.2692
1.8813
0.0001
N
N
N
2y
1.00
2.03
1.99
1.03
2.02
1.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

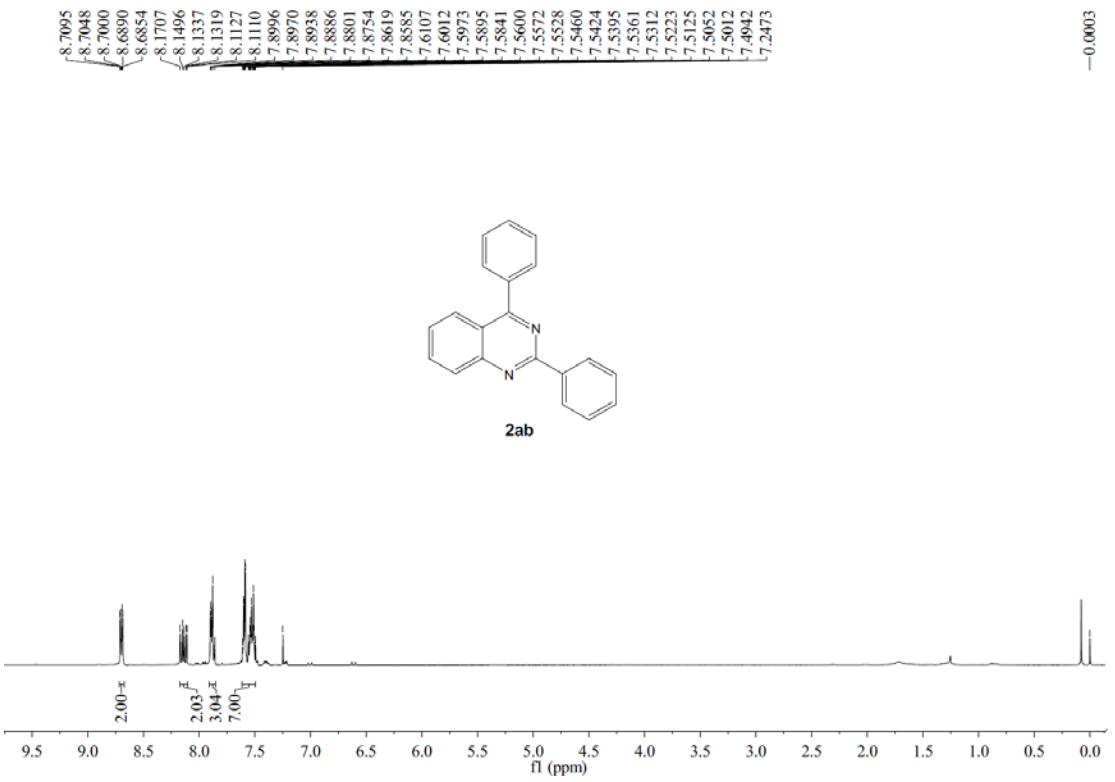

160.7108
158.8731
150.5439
150.3765
145.3063
134.4842
128.8367
128.2758
127.1453
124.1356
122.3237
77.3182 CDCl3
77.0001 CDCl3
76.6830 CDCl3
2y
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

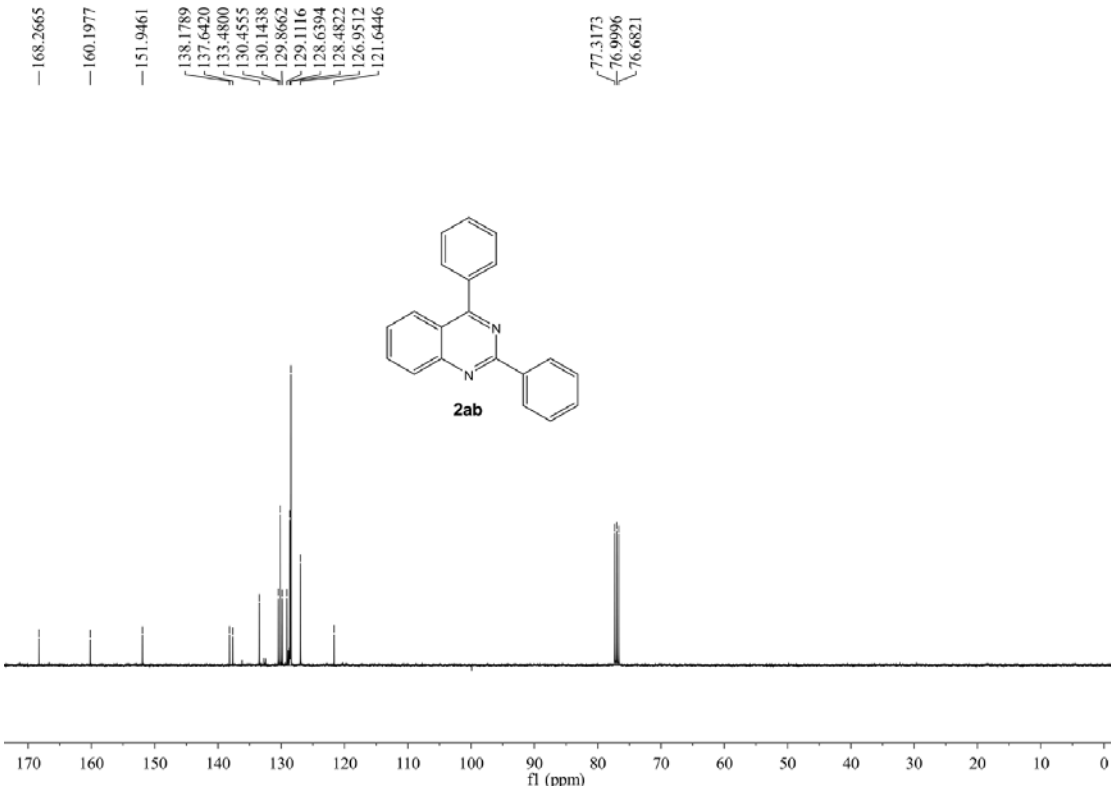

9.40
9.37
8.14
8.12
8.11
8.08
7.94
7.92
7.91
7.88
7.71
7.69
7.64
7.62
7.61
7.59
7.57
7.51
7.50
7.46
7.46
7.27
7.26
6.64
6.64
6.63
6.63
6.62
0.00
2z
1.00
1.02
2.01
1.02
0.98
1.00
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

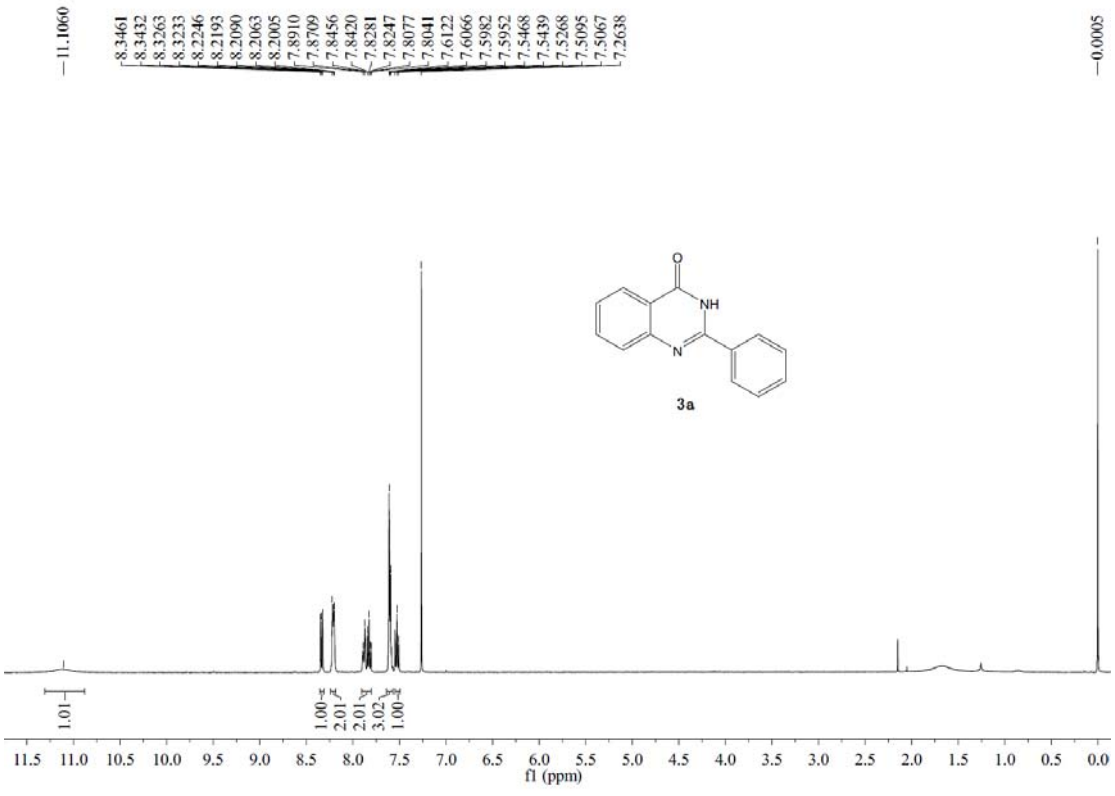

160.6729
154.0776
152.4877
150.3978
145.2891
134.4494
128.3494
127.2133
123.3383
114.0494
112.2673
77.3180 CDCl3
77.0004 CDCl3
76.6823 CDCl3
2z
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

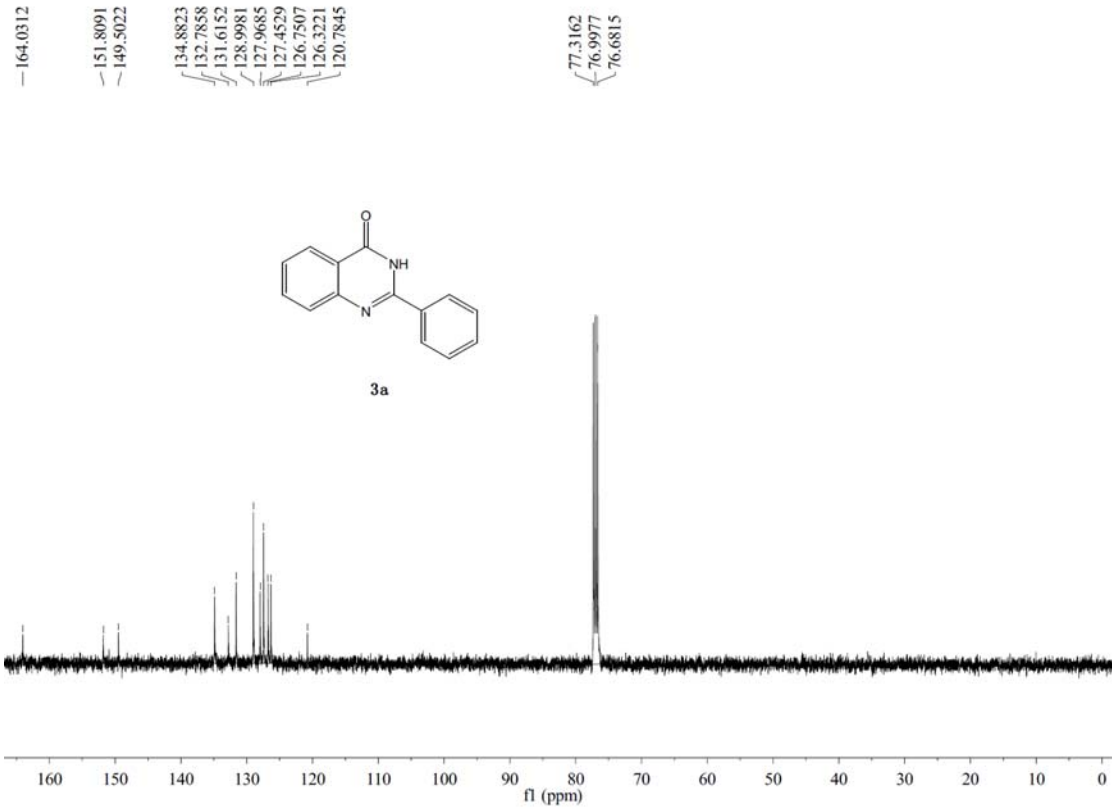

9.3588
8.5665
8.5617
8.5495
8.5448
8.3229
8.3183
8.1508
8.1460
8.1286
8.1238
7.8171
7.7949
7.5113
7.5066
7.4896
7.2622
0.0000
2aa
1.00
2.00
1.01
1.00
1.01
2.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


160.3213
159.1690
149.6532
142.9565
137.1881
136.0699
135.9448
130.2397
129.9438
128.8934
125.0203
92.3200
77.3174
77.0004
76.6827
I
N
N
Cl
2aa
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.7095
8.7048
8.7000
8.6890
8.6854
8.1707
8.1496
8.1337
8.1319
8.1127
8.1110
7.8996
7.8970
7.8938
7.8886
7.8801
7.8754
7.8619
7.8585
7.6107
7.6012
7.5973
7.5895
7.5841
7.5600
7.5572
7.5528
7.5460
7.5424
7.5395
7.5361
7.5312
7.5223
7.5125
7.5052
7.5012
7.4942
7.2473
0.0003
N
N
2ab
2.00
2.03
3.04
7.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


168.2665
160.1977
151.9461
138.1789
137.6420
133.4800
130.4555
130.1438
129.8662
129.1116
128.6394
128.4822
126.9512
121.6446
77.3173
76.9996
76.6821
2ab
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


11.1060
8.3461
8.3432
8.3263
8.3233
8.2246
8.2193
8.2090
8.2063
8.2005
7.8910
7.8709
7.8456
7.8420
7.8281
7.8247
7.8077
7.8041
7.6122
7.6066
7.5982
7.5952
7.5468
7.5439
7.5268
7.5095
7.5067
7.2638
0.0005
3a
1.01
1.00
2.01
2.01
3.02
1.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


164.0312
151.8091
149.5022
134.8823
132.7858
131.6152
128.9981
127.9685
127.4529
126.7507
126.3221
120.7845
77.3162
76.9977
76.6815
O
NH
N
3a
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)