Supporting Information

Facile and General Acid-Catalyzed Deuteration at Methyl Groups of *N*-Heteroarylmethanes

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1. General information

All reactions were carried out under a dry N_2 or air atmosphere (1 atm) using standard Schlenk technique in the parallel synthesizer. All reagent/reactant were commercial available without further purified except noted. The pure products obtained were neutralized by saturated $NaHCO_3$ solution, extracted with ethyl acetate/DCM. The combined organic layer was dried by Na_2SO_4 and further evaporated. The percentage of H/D exchange was calculated by ^1H NMR spectroscopies. The ^1H NMR and ^{13}C NMR data were acquired on a Brucker ADVANCE III spectrometer (400 MHz for ^1H NMR spectroscopy and 100 MHz for ^{13}C NMR spectroscopy) by the Analytical Center of State Key Laboratory of Chemo/Biosensing and Chemometrics at Hunan University, China.

2. Experimental Section

A: Procedure for preparation of 1-benzyl-2-methyl-*1H*-indole

To a 100 mL flask charged with 2-methyl-*1H*-indole (1.31g, 10 mmol), NaH (0.36 g, 15 mmol) and a stir bar, 40 mL anhydrous DMF was added. After stirring the mixture for 30 min at 0°C, (bromomethyl)benzene (1.5 mL, 12 mmol) was added slowly. The solution was further stirred overnight at 100°C, then quenched with 15 mL H_2O at room temperature and further kept stirring for 30 min. The solution was extracted with EA (4×20 mL) and the combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure, the residue was passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate = 50/1 as eluent) to afford the analytically pure product (white solid, 1.9 g, 86%) . (S.-G. Xu, X.-M. Huang, X.-H. Hong and B. Xu, *Org. Lett.*, 2012, **14**, 4614.)

B: A typical procedure for deuteration

An oven-dried Schlenk tube containing a stir bar was charged with benzoic acid (0.015 mmol, 1.8 mg), D_2O (**2a**, 0.2 mL), and 2-methylquinoline (**1a**, 0.2 mmol, 27 uL). The mixture was allowed to stir at 80 °C (pre-heated) for 4 h under air atmosphere. Then the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL), extracted with ethyl acetate (3×3 mL), the organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3a** (yellow oil) in 94% isolated yield with 95% ratio of deuterium incorporation. The ratio of deuterium incorporation was determined by ^1H NMR spectroscopy.

C: Procedure for 500 mmol scale experiment

An oven-dried 1000 mL round-bottom flask containing a stir bar was equipped with a condenser and charged with benzoic acid (37.5 mmol, 4.5 g), D_2O (**2a**, 300 mL), and 2-methylquinoline (**1a**, 500 mmol, 67.5 mL, 71.5 g). The mixture was allowed to stir at 80 °C for 5 h under an air atmosphere. The upper water layer was neutralized with saturated $NaHCO_3$ solution (100 mL), extracted with DCM (80×2 mL). The lower organic layer was diluted with 100 mL DCM, neutralized by saturated $NaHCO_3$ solution (100 mL), extracted with DCM (80×3 mL). Then, the combined organic layer was dried by Na_2SO_4 and evaporated to afford analytically pure product **3a** (yellow oil) in 98% isolated yield (71.2 g) with 95% ratio of deuterium incorporation. The ratio of deuterium incorporation was determined by ^1H NMR spectroscopy.

3. *Reaction profile*

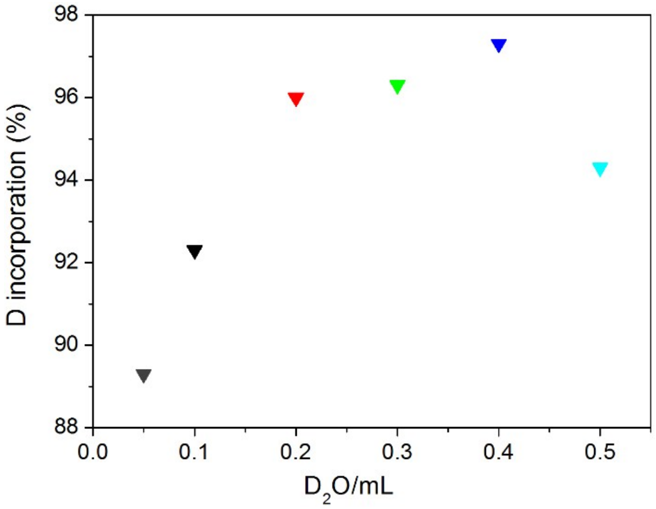


Figure 1 Concentration effect

(Reaction conditions: **1a**/0.2 mmol, PhCOOH/7.5 mmol%; 4 h; 80 °C)

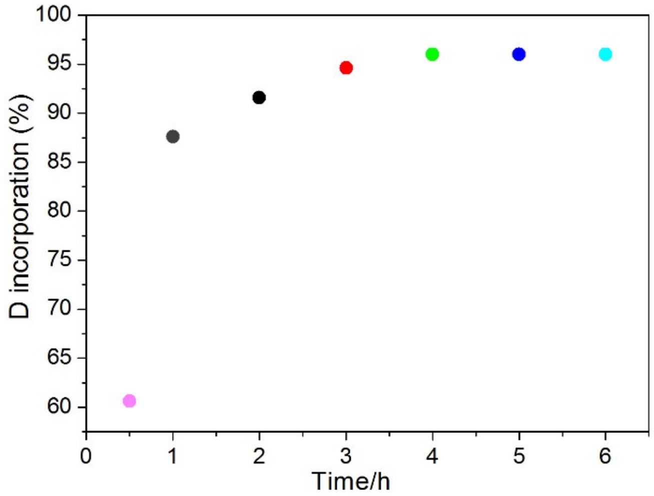
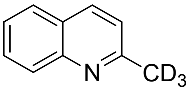


Figure 2 Time effect

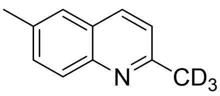
(Reaction conditions: **1a**/0.2 mmol, D_2O/0.2 mL, PhCOOH/7.5 mmol%, 80 °C)

4. *Characterization and analytical data of products*

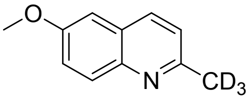


3a

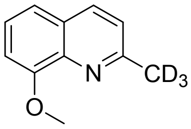
An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.015 mmol, 1.8 mg), D_2O (0.2 mL) and 2-methylquinoline (**1a**, 0.2 mmol, 27 uL). The mixture was stirred at 80 °C for 4 h under a dry N_2 or air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (3×3 mL), the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3a** (yellow oil)**.** ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.68 (dd, *J* = 7.2 Hz, *J* = 7.6 Hz, 1H), 7.47 (dd, *J* = 7.6 Hz, *J* = 7.2 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.94, 146.84, 135.16, 128.41, 127.59, 126.47, 125.49, 124.65, 120.98, 23.13-23.75 (m). (Z. Jamal and Y.-C. Teo, *Synlett*, 2014, **25**, 2049)


3b

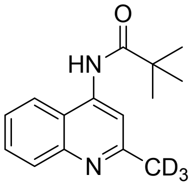
An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.02 mmol, 2.4 mg), 2,6-dimethylquinoline (**1b**, 0.2 mmol, 31.4 mg), D_2O (0.2 mL). The mixture was stirred at 80 °C for 8 h under a dry N_2 or air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (3×3 mL), the organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3b** (yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.51 (s, 1H), 7.50 (d, *J* = 9.2 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.93, 146.44, 135.54, 135.38, 131.64, 128.29, 126.51, 126.39, 121.95, 24.25-24.71 (m), 21.46. (P. M., Draper and D. B., MacLean, *Can. J. Chem.* 1970, **48**, 738)


3c

An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.02 mmol, 2.4 mg) and 6-methoxy-2-methylquinoline (**1c**, 0.2 mmol, 34.6 mg), D_2O (0.2 mL). The mixture was stirred at 100 °C for 8 h under a dry N_2 or air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (3×3 mL), the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3c** (yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.25 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 2.0 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.15, 156.29, 143.89, 135.04, 130.00, 127.33, 122.23, 121.87, 105.23, 55.49, 23.97-24.40 (m).

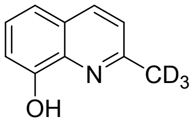

3d

An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.015 mmol, 1.8 mg), 8-methoxy-2-methylquinoline (**1d**, 0.2 mmol, 34.6 mg) and D_2O (0.2 mL). The mixture was stirred at 100 °C for 4 h under a dry N_2 or air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (3×3 mL), the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3d** (white solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.93 (m, 1H), 7.20-7.33 (m, 1.77H), 6.94 (d, *J* = 7.6 Hz, 1H), 3.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.08, 154.81, 139.70, 136.11 (d, $J_{\text{D-C}}$ = 11.0 Hz), 136.00, 127.58, 125.69, 122.60, 119.42, 107.59, 55.98, 24.25-24.71 (m). (Note: C3-H on aromatic cycle was partially deuterated, the site is determined by ^{1}H NMR analysis of **3n** and **3o**).



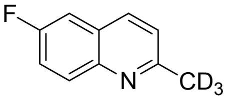
3e

An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.015 mmol, 1.8 mg), N-(2-methylquinolin-4-yl)pivalamide (**1e**, 0.2 mmol, 48.4 mg) and D_2O (0.2 mL). The mixture was stirred at 120 ^{o}C for 8 h under a dry N_2/air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (3×3 mL), the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3e** (white solid)**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.09 (bs, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.57-761 (m, 2H), 7.42 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.10, 160.13, 148.42, 140.11, 129.90, 129.32, 125.64, 118.63, 118.32, 111.49, 40.53, 27.64, 24.77-25.23 (m).



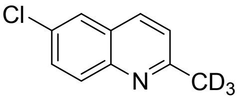
3f

An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.015 mmol, 1.8 mg), 2-methylquinolin-8-ol (**1f**, 0.2 mmol, 31.8 mg) and D_2O (0.2 mL). The mixture was stirred at 120 ^{o}C for 8 h under a dry N_2/air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (3×3 mL), the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3f** (purple solid)**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.4 Hz, 1H), 7.37 (dd, J = 8.0 Hz, J = 7.6 Hz, 1H), 7.28 (d, J = 6.4 Hz, 1H), 7.27 (d, J = 7.2 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.84, 151.69, 137.69, 136.13, 126.65, 122.72, 117.58, 109.80, 23.93-24.32 (m). (P. Addy, D. F Evans and Q. De Souza, *Polyhedron*, 1987, **6**, 2003)



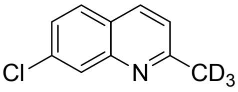
3g

An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.02 mmol, 2.4 mg), 6-fluoro-2-methylquinoline (**1g**, 0.2 mmol, 32 mg) and 0.2 mL D_2O. The mixture was stirred at 80 ^{o}C for 8 h under a dry N_2 or air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (3×3 mL), then the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3g** (yellow solid)**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.95 (m, 2H), 7.34-7.39 (m, 1H), 7.30 (d, J = 8.8 Hz, 1H), 7.2 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.96 ($J_{F\text{-}C}$ = 245.1 Hz), 158.24, 144.94, 135.50 ($J_{F\text{-}C}$ = 5.2 Hz), 131.02 ($J_{F\text{-}C}$ = 9 Hz), 126.98 ($J_{F\text{-}C}$ = 9.8 Hz), 122.75, 119.45 ($J_{F\text{-}C}$ = 25,4 Hz), 110.51 ($J_{F\text{-}C}$ = 21.4 Hz), 24.02-24.77 (m).



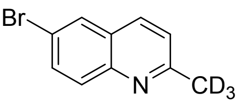
3h

An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.015 mmol, 1.8 mg), 6-chloro-2-methylquinoline (**1h**, 0.2 mmol, 35.5 mg) and 0.2 mL D_2O. The mixture was stirred at 80 ^oC for 4 h under a dry N_2/air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (3×3 mL), then the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3h** (yellow solid). ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 2H), 7.74 (s, 1H), 7.61 (d, J = 8.8 Hz, 1H), 7.30 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.31, 146.24, 135.21, 135.10, 131.30, 130.27, 127.09, 126.17, 122.87, 24.34-24.80 (m).



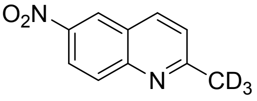
3i

An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.02 mmol, 2.4 mg), 7-chloro-2-methylquinoline (**1i**, 0.2 mmol, 35.5 mg) and 0.2 mL D_2O. The mixture was stirred at 90 ^oC for 8 h under a dry N_2 or air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (3×3 mL), then the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3i** (yellow solid). ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.34 (d, J = 8.8 Hz, 1H), 7.19 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.15, 148.24, 135.90, 135.18, 128.69, 127.76, 126.70, 124.85, 122.20, 24.38-25.03 (m). (A. W Czarnik, U.S. Pat. Appl. Publ. (2008), US 20080319007 A1 20081225)



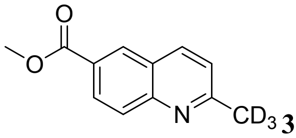
3j

An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.02 mmol, 2.4 mg), 6-bromo-2-methylquinoline (**1j**, 0.2 mmol, 44.4 mg) and 0.2 mL D_2O. The mixture was stirred at 80 ^oC for 8 h under a dry N_2 or air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (3×3 mL), then the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3j** (yellow solid). ^1H NMR (400 MHz, $CDCl_3$) δ 7.86-7.94 (m, 3H), 7.73 (d, J = 8.8 Hz, 1H), 7.28 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.44, 145.41, 134.09, 131.77, 129.38, 128.48, 126.60, 121.81, 118.33, 23.15-24.00(m).



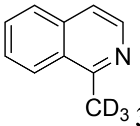
3k

An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.04 mmol, 4.8 mg), 2-methyl-6-nitroquinoline (**1k**, 0.2 mmol, 37.6 mg) and 0.2 mL D_2O. The mixture was stirred at 120 ^oC for 24 h under a dry N_2/air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (3×3 mL), then the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3k** (yellow solid)**.** ^1H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.35 (d, *J* = 9.2 Hz, 1H), 8.14 (dd, *J* = 4.4 Hz, *J* = 4.0 Hz 1H), 8.03 (d, *J* = 9.2 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 0.65H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.24, 150.00, 144.98, 137.61-137.72 (m), 130.39, 125.25, 124.34, 123.96, 122.97, 24.71-25.70 (m). (Note: C3-H on aromatic cycle was partially deuterated, the site is determined by ^1H NMR analysis of **3n** and **3o**).



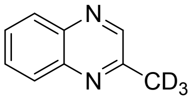
3l

An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.015 mmol, 1.8 mg), methyl 2-methylquinoline-6-carboxylate (**1l**, 0.2 mmol, 40.2 mg) and D_2O (0.2 mL). The mixture was stirred at 80 °C for 4 h under a dry N_2 or air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (3×3 mL), the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3l** (yellow solid)**.** ^1H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.18 (d, *J* = 8.8 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.73, 161.54, 149.78, 137.29, 130.69, 129.00, 128.91, 127.24, 125.61, 122.81, 52.34, 24.61-25.00 (m).



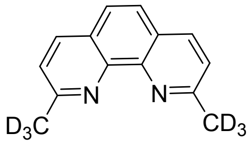
3m

An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.02 mmol, 2.4 mg), 0.2 mL D_2O and 1-methylisoquinoline (**1m**, 0.2 mmol, 27 uL). The mixture was stirred at 80 °C for 4 h under a dry N_2 or air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (3×3 mL), then the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3m** (purple oil)**.** ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 6.0 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.67 (dd, *J* = 6.8 Hz, *J* = 8.0 Hz, 1H), 7.59 (dd, *J* = 8.0 Hz, *J* = 7.2 Hz, 1H), 7.50 (d, *J* = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.57, 141.79, 135.90, 129.95, 127.54, 127.20, 127.04, 125.63,119.29, 21.19-21.86 (m). HRMS data for C10H6D3N, cal. 146.0923, found 147.1012 (M+H).



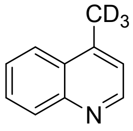
3n

An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.02 mmol, 2.4 mg), 0.2 mL D_2O and 2-methylquinoxaline (**1n**, 0.2 mmol, 24 uL). The mixture was stirred at 90 °C for 8 h under a dry N_2 or air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (3×3 mL), then the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3n** (red oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 0.45H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.61-7.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.72, 145.99, 142.06, 140.98, 130.01, 129.14, 128.94, 128.64, 21.39-22.04 (m). (Note: C3-H on aromatic cycles were deuterated, the site was determined by ^{1}H NMR analysis of **3n** and **3o**.) HRMS data for C9H5D3N2, cal. 147.0876, found 148.1024 (M+H).



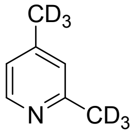
3o

An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.03 mmol, 3.6 mg), 2,9-dimethyl-1,10-phenanthroline (**1o**, 0.2 mmol, 41.6 mg) and 0.2 mL D_2O. The mixture was stirred at 90 °C for 8 h under a dry N_2 or air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (3×3 mL), then the organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3o** (yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 2H), 7.68 (s, 2H), 7.48 (d, *J* = 8.0 Hz, 1.6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.11, 145.25, 136.07-136.18 (m), 126.72, 125.38, 122.85-123.41 (m), 24.58-25.49 (m). (Note: C3-H on aromatic cycles were deuterated, the site was determined by ^{1}H NMR analysis of **3n** and **3o**)



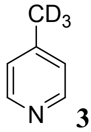
3p

An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.02 mmol, 2.4 mg), 0.2 mL D_2O and 4-methylquinoline (**1p**, 0.2 mmol, 27 uL). The mixture was stirred at 100 °C for 8 h under a dry N_2 or air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (3×3 mL) then the organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3p** (yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.4 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.63 (dd, *J* = 8.8 Hz, *J* = 8.0 Hz, 1H), 7.48 (dd, *J* = 7.2 Hz, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.16, 147.95, 144.26, 129.98, 129.13, 128.32, 126.30, 123.83,121.88, 17.68-18.33 (m). (Z. Jamal, Y.-C. Teo and L.-K., Wong, *Eur. J. of Org. Chem.* 2014, **2014**, 7343)

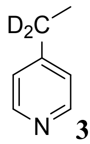


3r

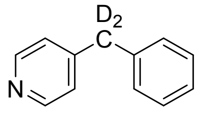
An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.04 mmol, 4.8 mg), 0.2 mL D_2O and 2,4-dimethylpyridine (**1r**, 0.2 mmol, 23 uL). The mixture was stirred at 120 °C for 24 h under a dry N_2 or air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with DCM (3×3 mL), then the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3r** (yellow oil)**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 4.8 Hz, 1H), 6.98 (s, 1H), 6.91 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.00, 148.78, 147.22, 124.20, 121.77, 23.66-24.19 (m), 19.91-20.30 (m).


3s

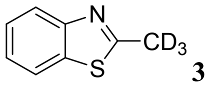
An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.04 mmol, 4.8 mg), 0.2 mL D_2O and 4-methylpyridine (**1s**, 0.2 mmol, 20 uL) was charged into the tube. Then the mixture was stirred at 120 °C for 24 h under a dry N_2 or air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with DCM (3×3 mL), then the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3s** (yellow oil)**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 5.2 Hz, 2H), 7.03 (d, *J* = 5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.47, 147.02, 124.68, 20.02-20.41 (m). (H. C.Brown and G. J.McDonald, *J. Am. Chem. Soc.* 1966, **88**, 2514)


3t

An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.04 mmol, 4.8 mg), 0.2 mL D_2O and 4-ethylpyridine (**1t**, 0.2 mmol, 23 uL). The mixture was stirred at 120 °C for 24 h under a dry N_2 or air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with DCM (3×3 mL), then the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3t** (yellow oil)**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 5.2 Hz, 2H), 7.12 (d, *J* = 5.2 Hz, 2H), 1.24-1.28 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.95, 149.60, 123.38, 27.30-27.83 (m), 14.15. HRMS data for C7H7D2N, cal. 109.0861, found 110.0933 (M+H).

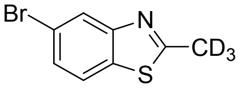

3u

An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.04 mmol, 4.8 mg), 0.2 mL D_2O and 4-benzylpyridine (**1u**, 0.2 mmol, 32 uL). The mixture was stirred at 120 °C for 24 h under a dry N_2 or air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (3×3 mL), then the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3u** (yellow oil)**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 5.6 Hz, 2H), 7.23 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 2H), 7.02 (d, *J* = 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.99, 149.82, 138.81,129.02, 128.75, 128.70, 124.21, 40.21-40.78 (m).



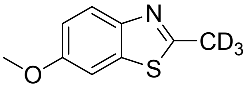
3v

An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.03 mmol, 3.6 mg), 0.2 mL D_2O and 2-methylbenzo[*d*]thiazole (**1v**, 0.2 mmol, 24 uL). The mixture was stirred at 120 ^oC for 8 h under a dry N_2 or air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (3×3 mL), then the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3v** (yellow oil)**.** ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.44 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H), 7.34 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.91, 153.39, 135.63, 125.92, 124.70, 122.40, 121.40, 19.01-19.79 (m). (G. Davidovics, J. C.Panizzi, R. Guglielmetti, G. Mille, M. Conte and J. Chouteau, Journal de Chimie Physique et de Physico-Chimie Biologique, 1974, **71**, 659)



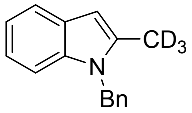
3w

An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.03 mmol, 3.6 mg), 5-bromo-2-methylbenzo[*d*]thiazole (**1w**, 0.2 mmol, 45.3 mg) and 0.2 mL D_2O. The mixture was stirred at 120 ^oC for 8 h under a dry N_2 or air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (3×3 mL), then the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3w** (yellow solid)**.** ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.70, 153.54, 133.40, 126.79, 124.31, 121.40, 118.49, 18.06-18.69 (m). HRMS data for C8H3D3BrNS, cal. 229.9593, found 230.9686 (M+H).



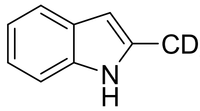
3x

An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.03 mmol, 3.6 mg), 0.2 mL D_2O and 6-methoxy-2-methylbenzo[*d*]thiazole (**1x**, 0.2 mmol, 30 uL). The mixture was stirred at 120 ^oC for 8 h under a dry N_2 or air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (3×3 mL), then the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3x** (red oil)**.** ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.8 Hz, 1H), 7.19 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.30, 157.35, 147.85, 136.84, 122.78, 114.96, 104.20, 55.78, 18.82-19.41 (m).



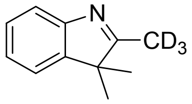
3y

An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.015 mmol, 1.8 mg), 1-benzyl-2-methyl-*1H*-indole (**1y**, 0.2 mmol, 44.2 mg) and 0.2 mL D_2O. The mixture was stirred at 120 °C for 18 h under a dry N_2 or air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (3×3 mL), then the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3y** (yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.6 Hz, 0.78H), 7.20-7.22 (m, 5H), 7.05-7.11 (m, 2H), 6.95 (d, *J* = 7.2 Hz, 2H), 5.29 (d, *J* = 8.4 Hz, 1H), 5.28 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.97, 137.24, 136.61, 128.80, 128.17-128.34 (m), 127.29, 126.04, 120.78, 119.75, 119.55, 109.24, 100.01-100.51 (m), 46.48, 11.84-12.22 (m). (Note: C3-H on the aromatic cycle was partially deuterated, the site was determined by ^{1}H NMR analysis of **3n** and **3o**)



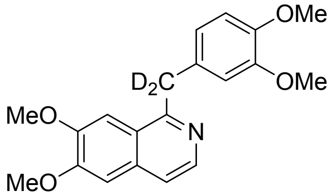
3z

An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.015 mmol, 1.8 mg), 1-benzyl-2-methyl-*1H*-indole (**1z**, 0.2 mmol, 26.2 mg) and 0.2 mL D_2O. The mixture was stirred at 120 °C for 18 h under a dry N_2 or air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (3×3 mL), then the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3z** (yellow solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 1H)), 6.99-7.05 (m, 2H), 6.14 (s, 0.15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.06, 134.93, 129.00, 120.92, 119.62, 110.23, 100.40, 12.77-13.16 (m). (Note: C3-H on the aromatic cycle was partially deuterated, the site was determined by ^{1}H NMR analysis of **3n** and **3o**) (J. C. Carry, V. Certal, F. Halley, K. A. Karlsson and L. Schio, Fr. Demande (2012), FR 2969611 A1 20120629)



3aa

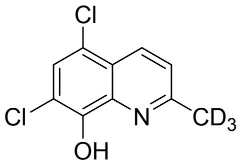
An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.02 mmol, 2.4 mg), 0.2 mL D_2O and 2,3,3-trimethyl-3*H*-indole (**1aa**, 0.2 mmol, 32 uL). The mixture was stirred at 80 °C for 8 h under a dry N_2 or air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (3×3 mL), then the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3aa** (brown oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.6 Hz, 1H), 7.20-7.22 (m, 2H), 7.10-7.14 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 1H), 1.23 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.00, 153.70, 145.65, 127.57, 125.08, 121.28, 119.89, 53.60, 23.07, 14.52-14.90 (m).



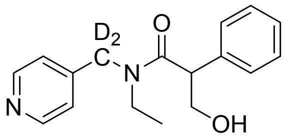
3ab

An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.1 mmol, 12.2 mg), Papaverine (**1ab**, 1 mmol, 339 mg) and 0.6 mL D_2O. The mixture was stirred at 120 °C for 18 h under a dry N_2 atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$

solution (3 mL) and extracted with ethyl acetate (3×3 mL), then the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3ab** (yellow solid)**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 5.6 Hz, 1H), 7.33 (d, *J* = 4.8 Hz, 1H), 7.25 (s, 1H), 6.95 (s, 1H), 6.73 (d, *J* = 7.2 Hz, 2H), 6.67 (d, *J* = 8.0 Hz, 1H), 3.90 (s, 3H), 3.82 (s, 3H), 3.72 (s, 3H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.78, 152.45, 149.80, 149.04, 147.54, 141.00, 133.45, 132.16, 122.94, 120.51, 118.70, 111.89, 111.22, 105.29, 104.21, 55.99, 55.86, 55.85, 55.80, 41.14-41.93 (m).

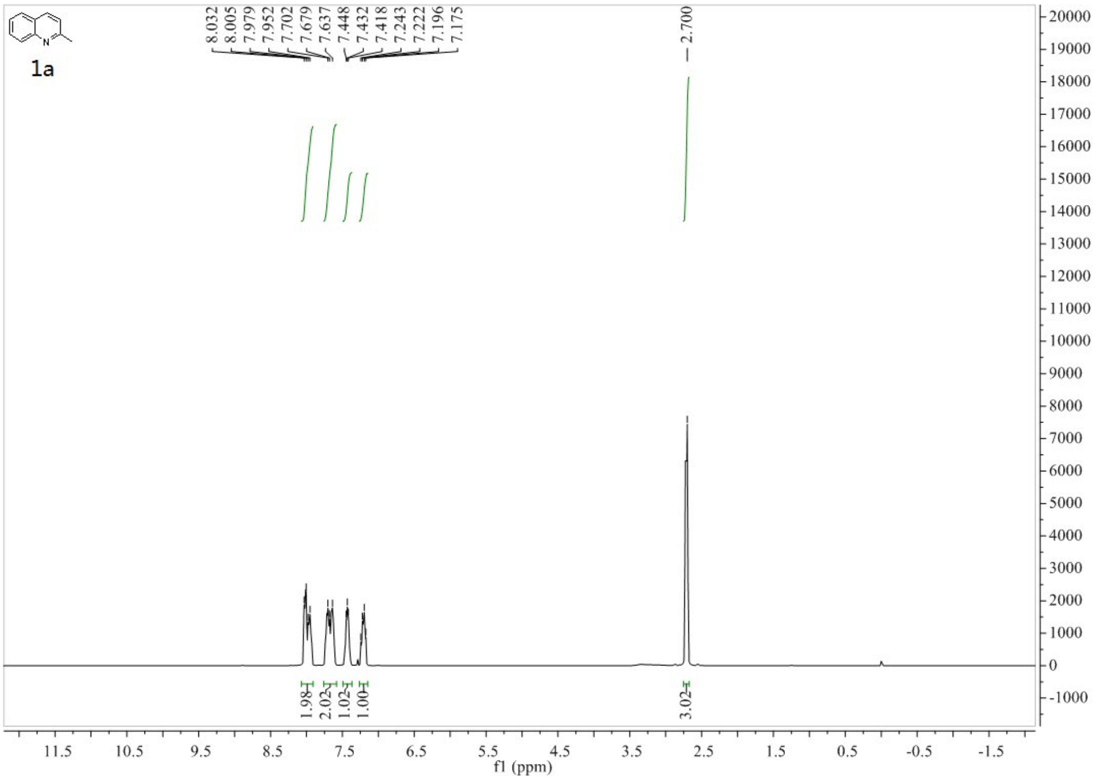

3ac

An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.04 mmol, 4.8 mg), 5,7-dichloro-2-methylquinolin-8-ol (**1ac**, 0.2 mmol, 45.2 mg) and 0.2 mL D_2O. The mixture was stirred at 120 ^{o}C for 16 h under a dry N_2 or air atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with ethyl acetate (3×3 mL), then the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3ac** (yellow solid)**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.8 Hz, 1H), 7.39 (s, 1H), 7.30 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.79, 147.06, 138.00, 133.47, 127.15, 123.46, 123.14, 120.62, 114.99, 23.86-24.40 (m).


3ad

An oven-dried Schlenk tube containing a stir bar was charged with PhCOOH (0.04 mmol, 4.8 mg), **1ad** Tropicamide (0.2 mmol, 57.2 mg) and 0.2 mL D_2O. Then the mixture was stirred at 120 ^{o}C for 16 h under a dry N_2 atmosphere. After reaction, the mixture was neutralized by saturated $NaHCO_3$ solution (3 mL) and extracted with DCM (3×3 mL), then the combined organic layer was dried by Na_2SO_4 and further evaporated to afford analytically pure product **3ad** (yellow solid)**.** ^{1}H NMR (400 MHz, DMSO-d6) δ 8.37-8.53 (m, 2H), 7.28-7.44 (m, 5H), 7.16-7.20 (m, 2H), 4.85-4.94(m, 1H), 3.91-4.21 (m, 2H), 3.36-3,41 (m, 2H), 0.98-1.04 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d6) δ 172.34 (171.93), 150.06 (149.89), 147.95 (147.42), 138.02 (137.78), 129.00, 128.65 (128.46), 127.53 (127.45), 122.65 (122.33), 65.22 (65.15), 51.16 (50.77), 48.57-48.81 (46.81-48.81) (m), 42.60 (41.10), 14.66 (12.91). (Note: Due to the intramolecular hydrogen bonds, the molecule exists in equilibrium of two isomers.)

5. ***^{1}H and ^{13}C-NMR spectrum of products***


1a
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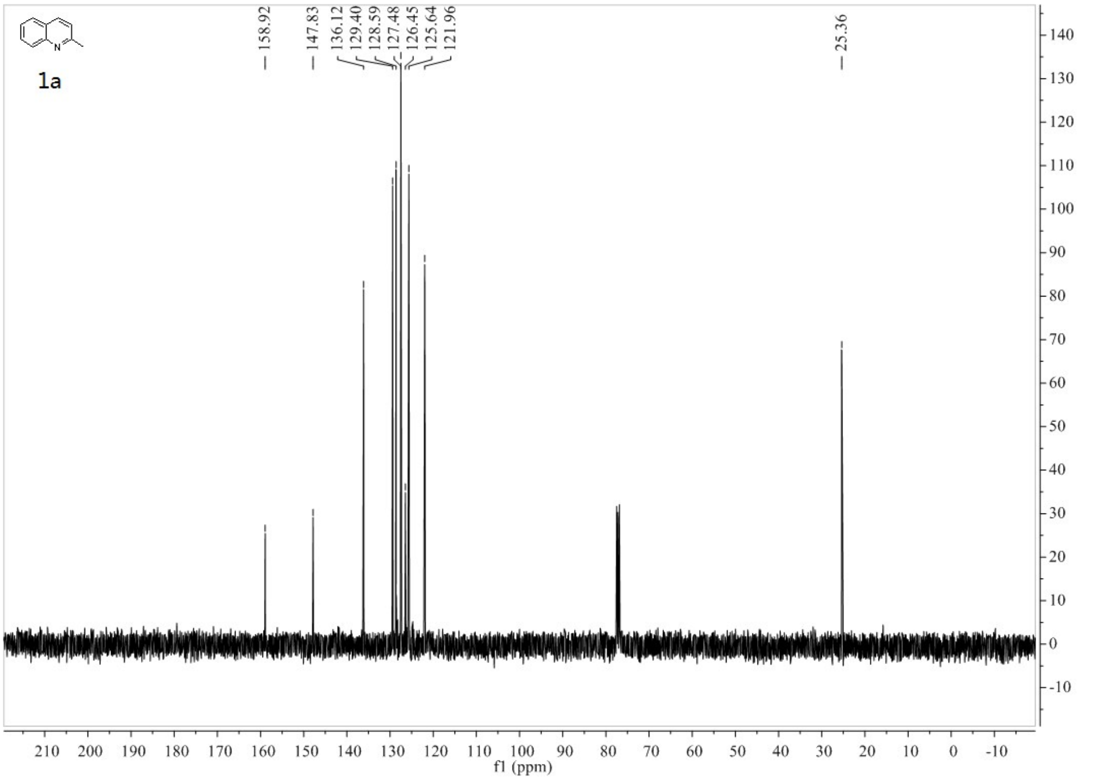
8.005
7.979
7.952
7.702
7.679
7.637
7.448
7.432
7.418
7.243
7.222
7.196
7.175
2.700
1.98
2.02
1.02
1.00
3.02
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)


1a
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147.83
136.12
129.40
128.59
127.48
126.45
125.64
121.96
25.36
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
210
200
190
180
170
160
150
140
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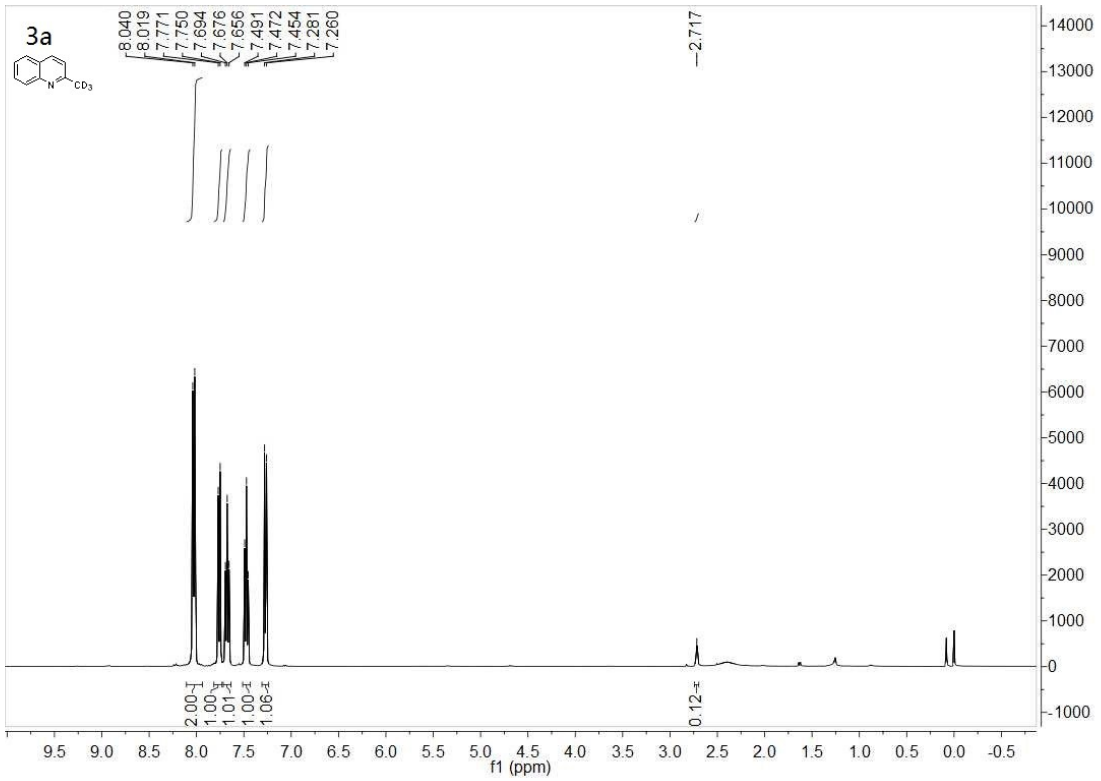
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


3a
N
CD3
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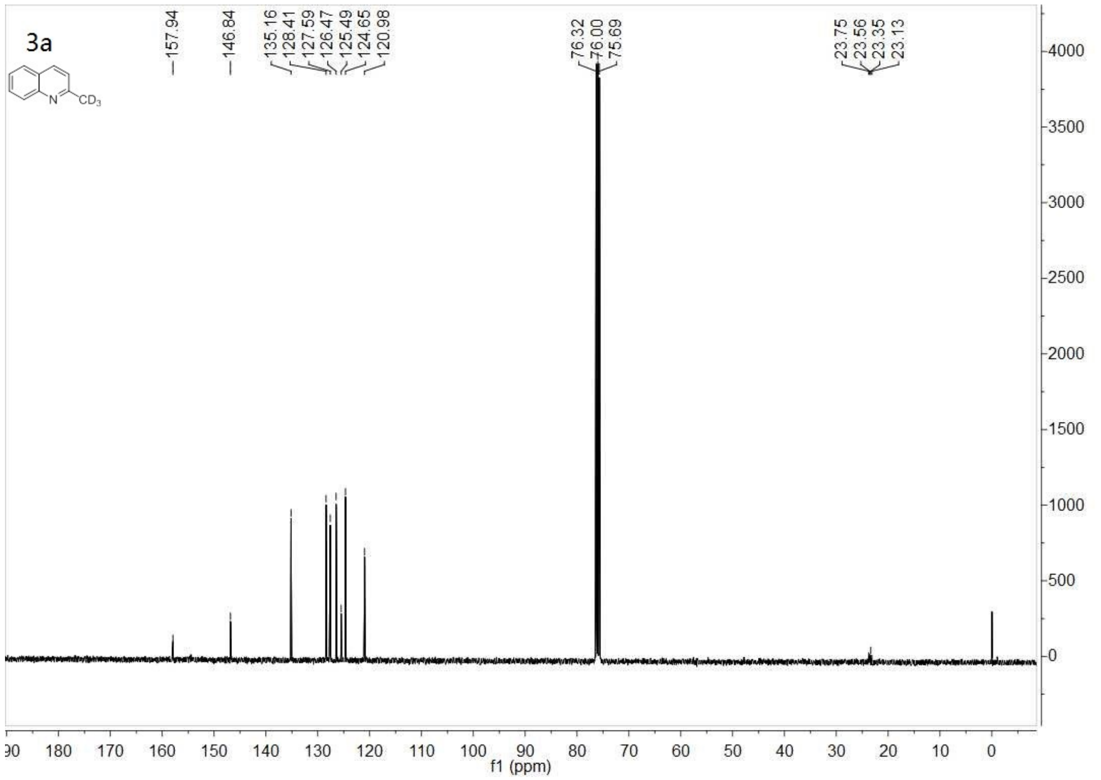
8.019
7.771
7.750
7.694
7.676
7.656
7.491
7.472
7.454
7.281
7.260
2.717
2.00
1.00
1.01
1.00
1.06
0.12
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


3a
N
CD3
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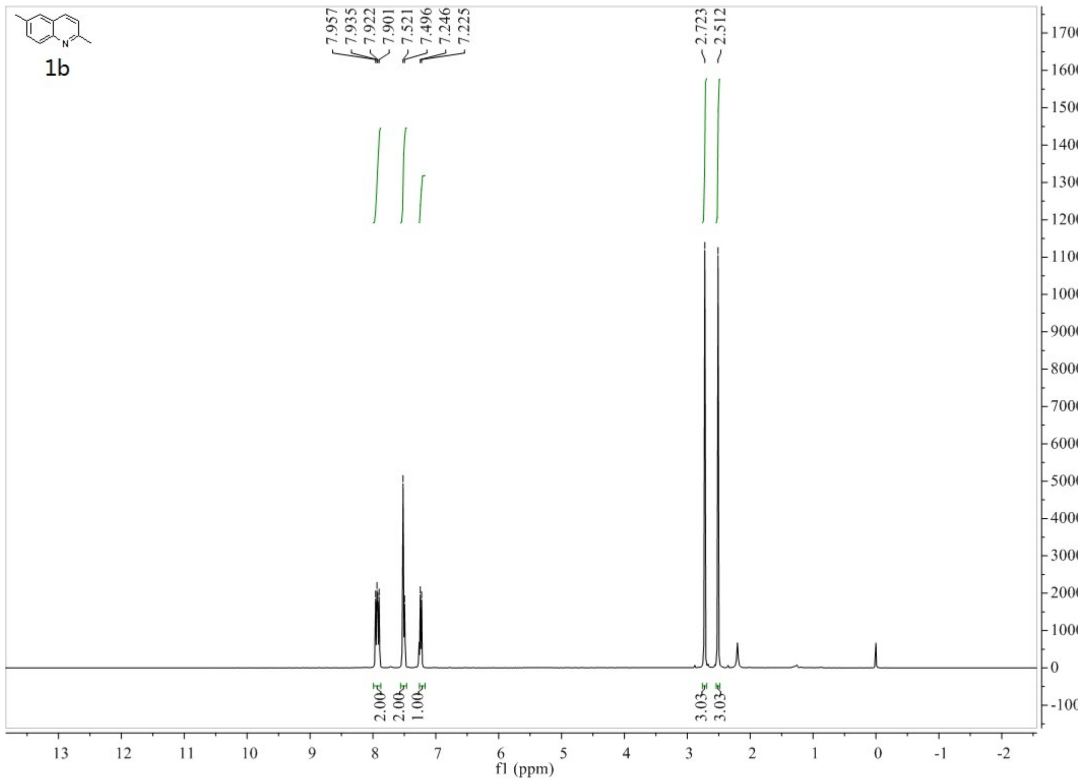
146.84
135.16
128.41
127.59
126.47
125.49
124.65
120.98
76.32
76.00
75.69
23.75
23.56
23.35
23.13
4000
3500
3000
2500
2000
1500
1000
500
0
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


1b
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7.935
7.922
7.901
7.521
7.496
7.246
7.225
2.723
2.512
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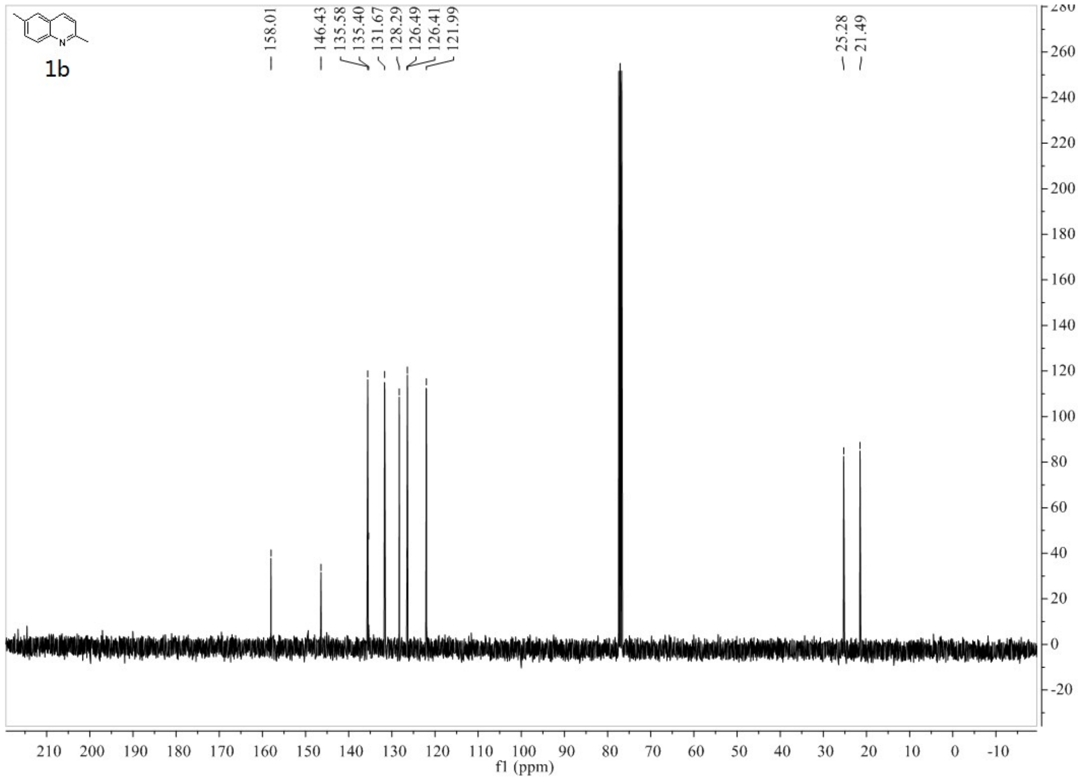
1.00
3.03
3.03
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)


1b
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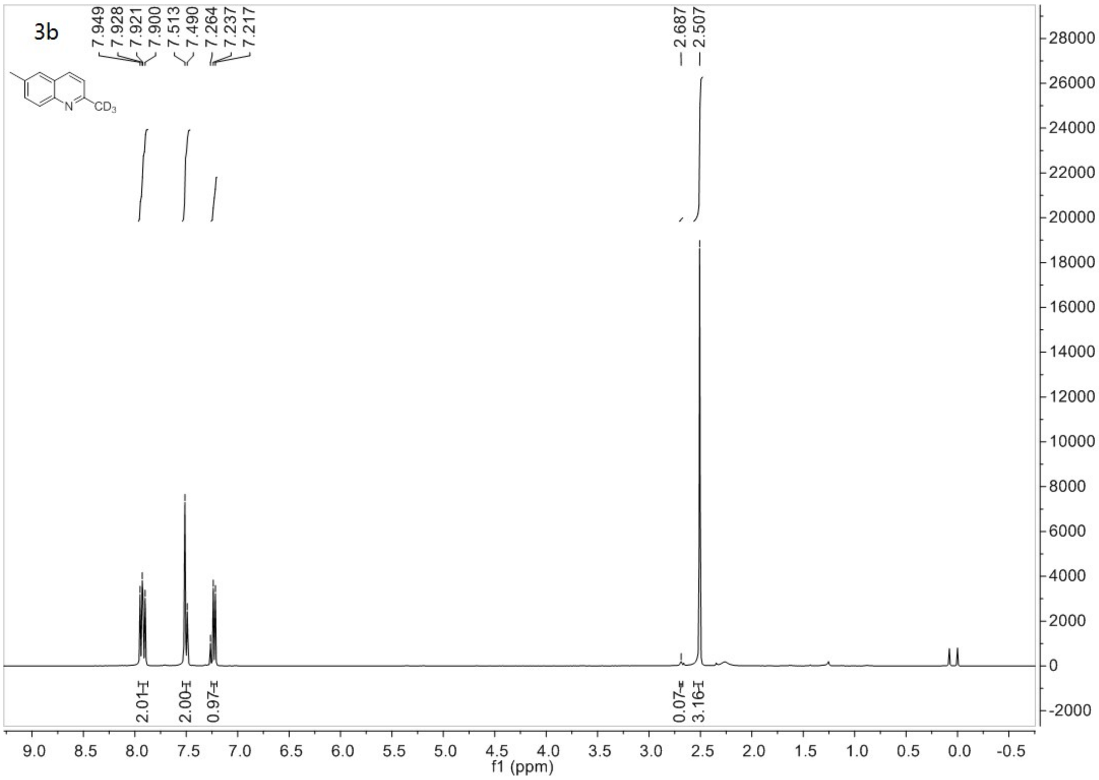
135.58
135.40
131.67
128.29
126.49
126.41
121.99
25.28
21.49
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


3b
N
CD3
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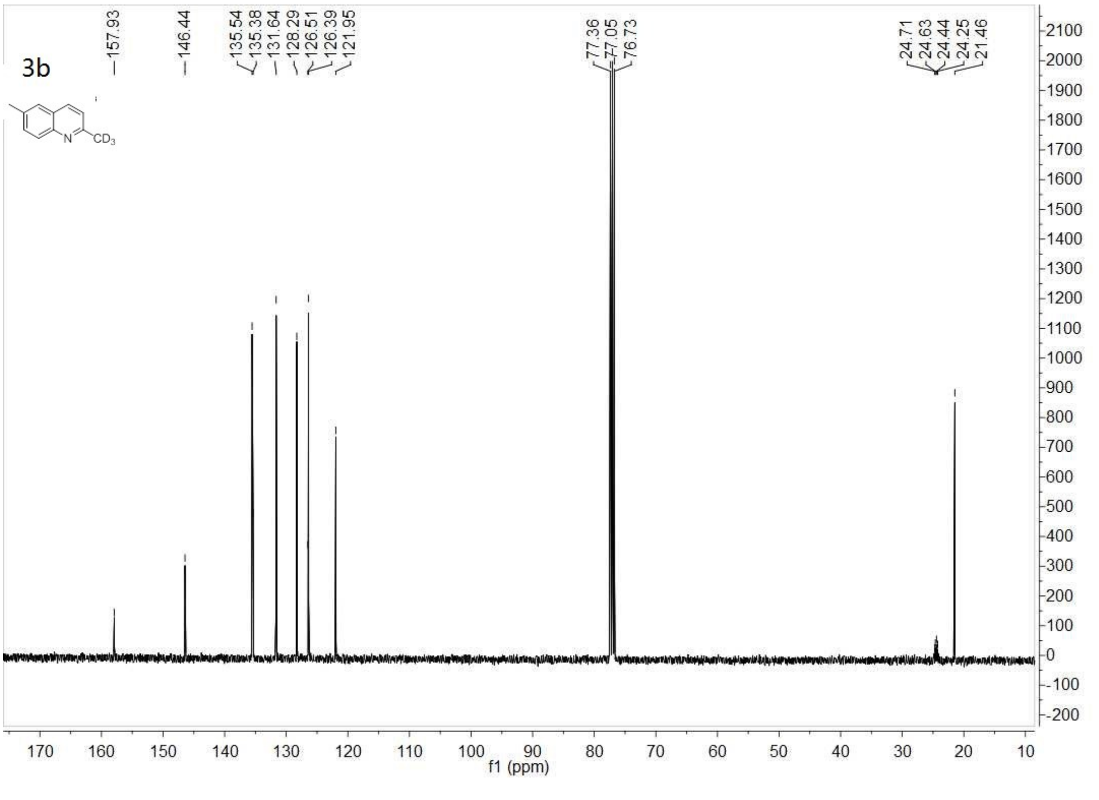
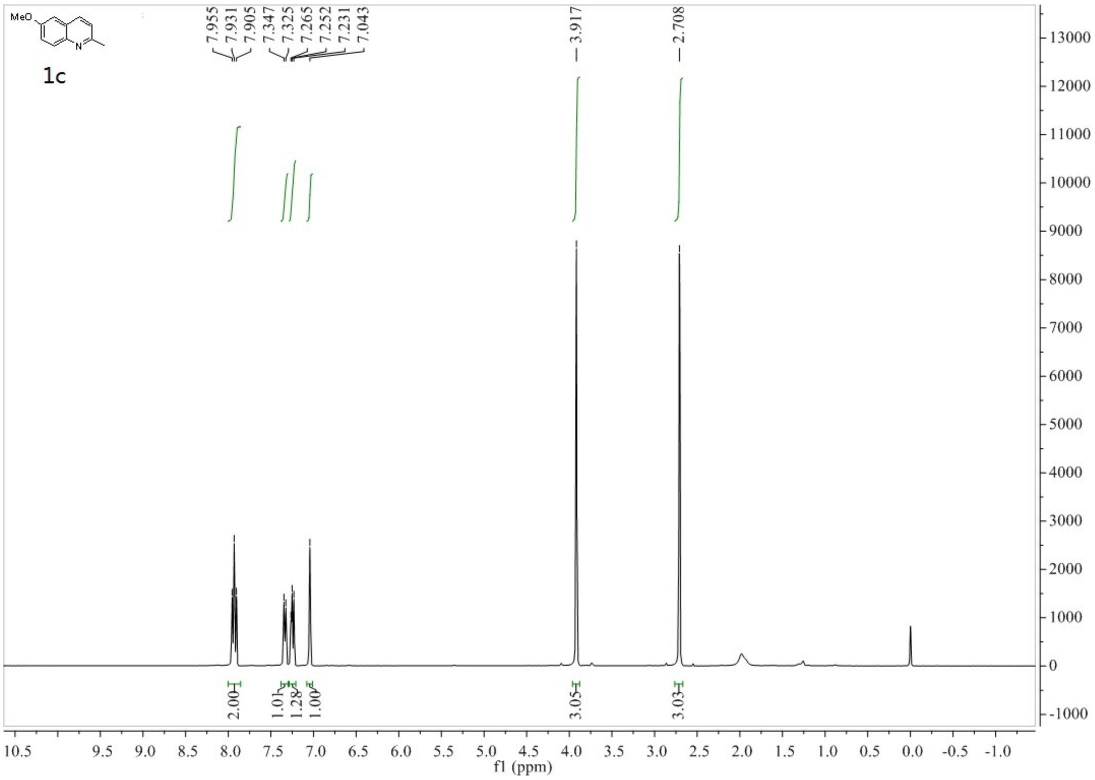
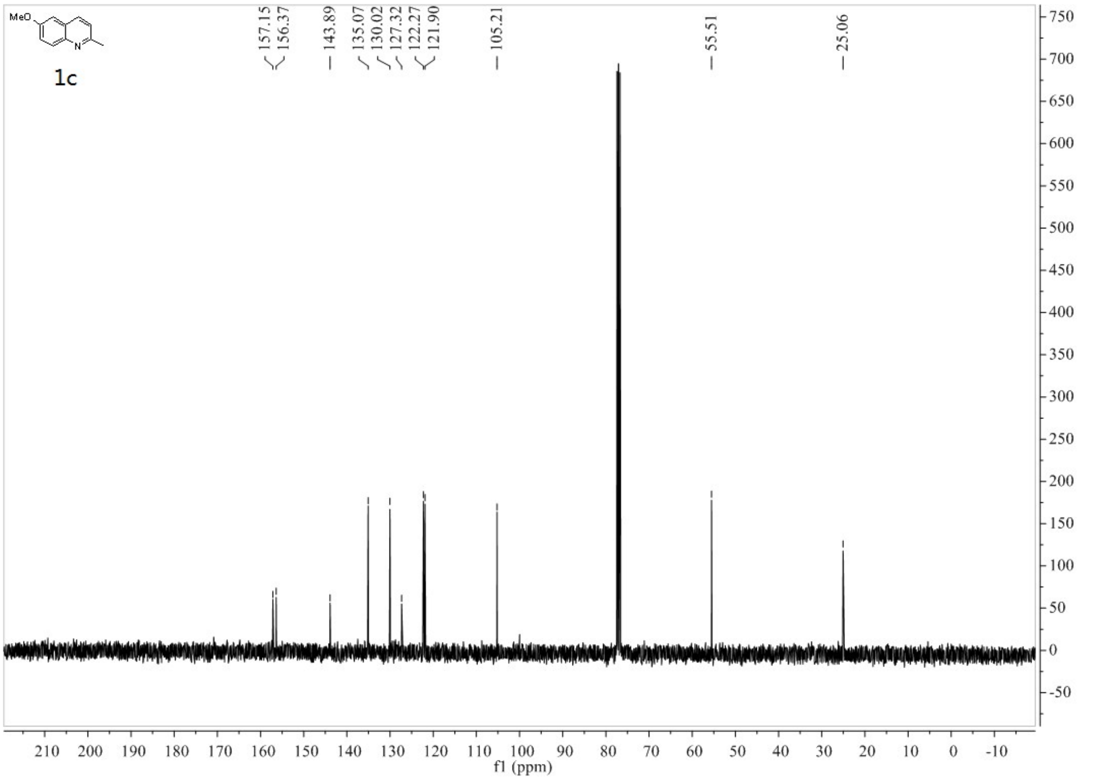
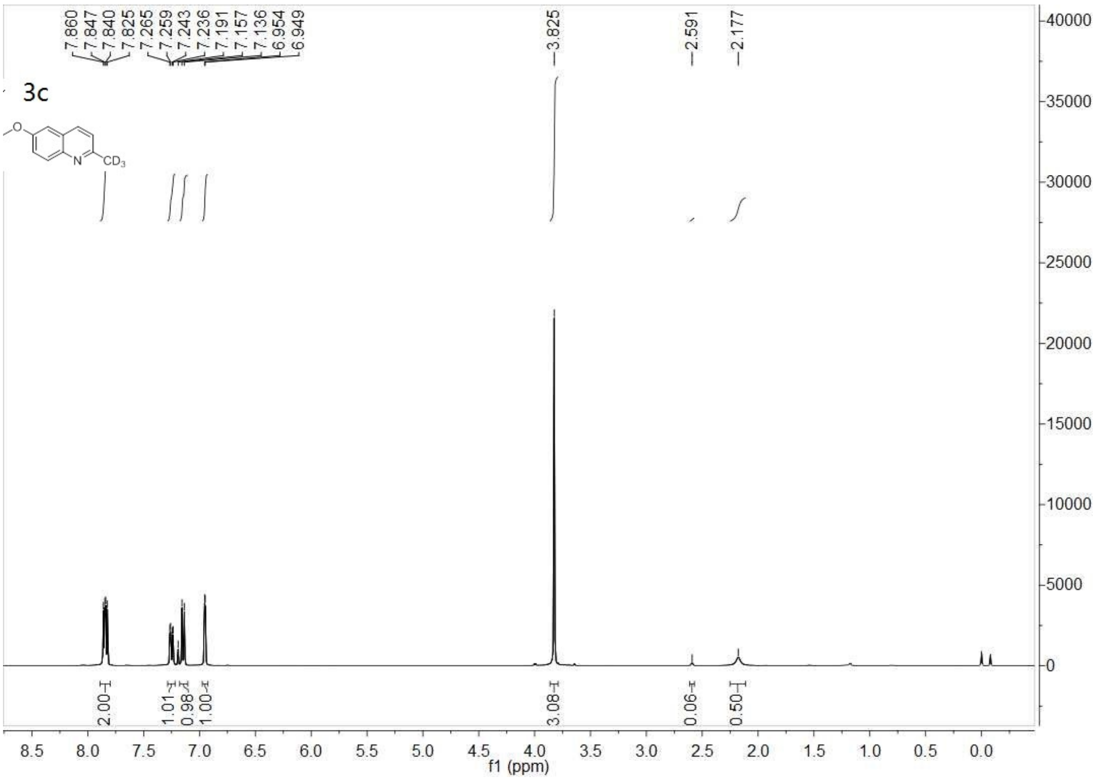
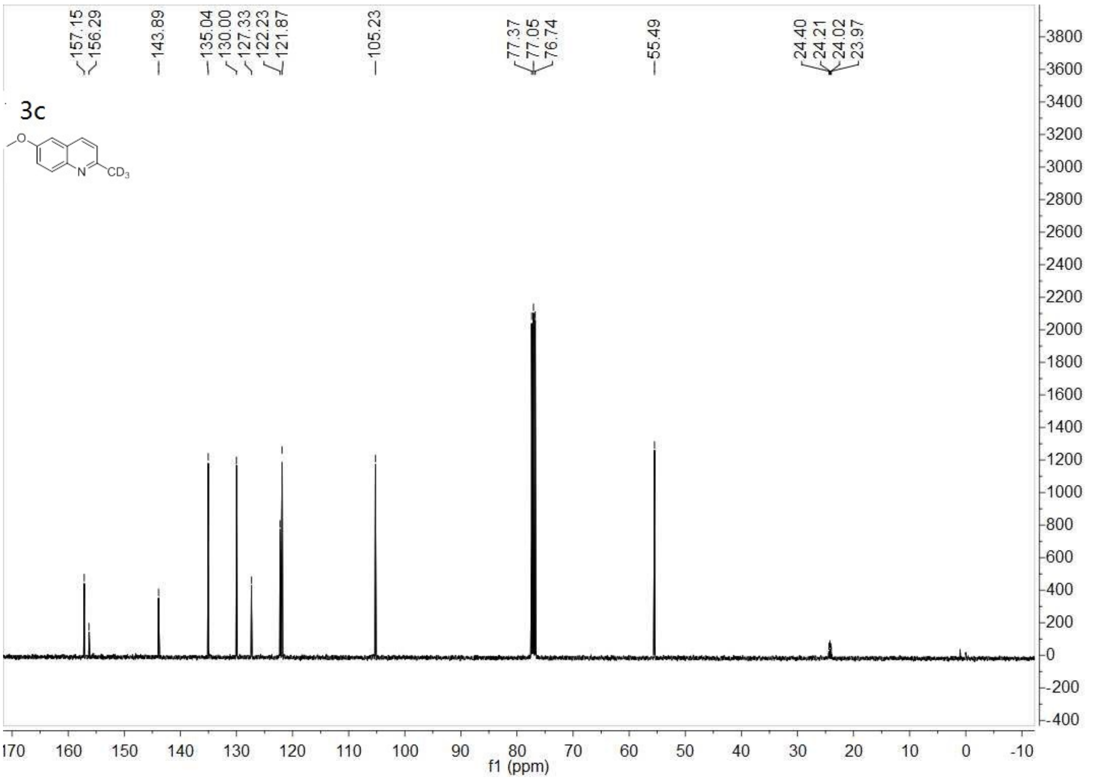
7.928
7.921
7.900
7.513
7.490
7.264
7.237
7.217
2.687
2.507
2.01
2.00
0.97
0.07
3.16
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

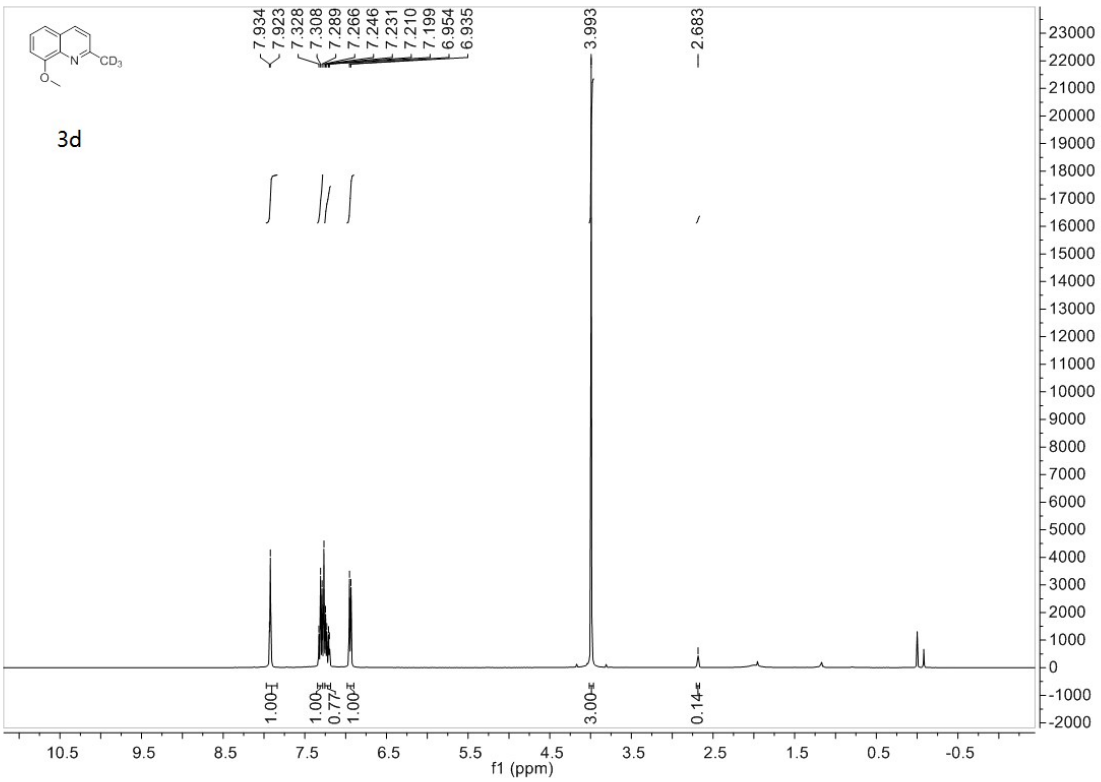

3b
N
CD3
157.93
146.44
135.54
135.38
131.64
128.29
126.51
126.39
121.95
77.36
77.05
76.73
24.71
24.63
24.44
24.25
21.46
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

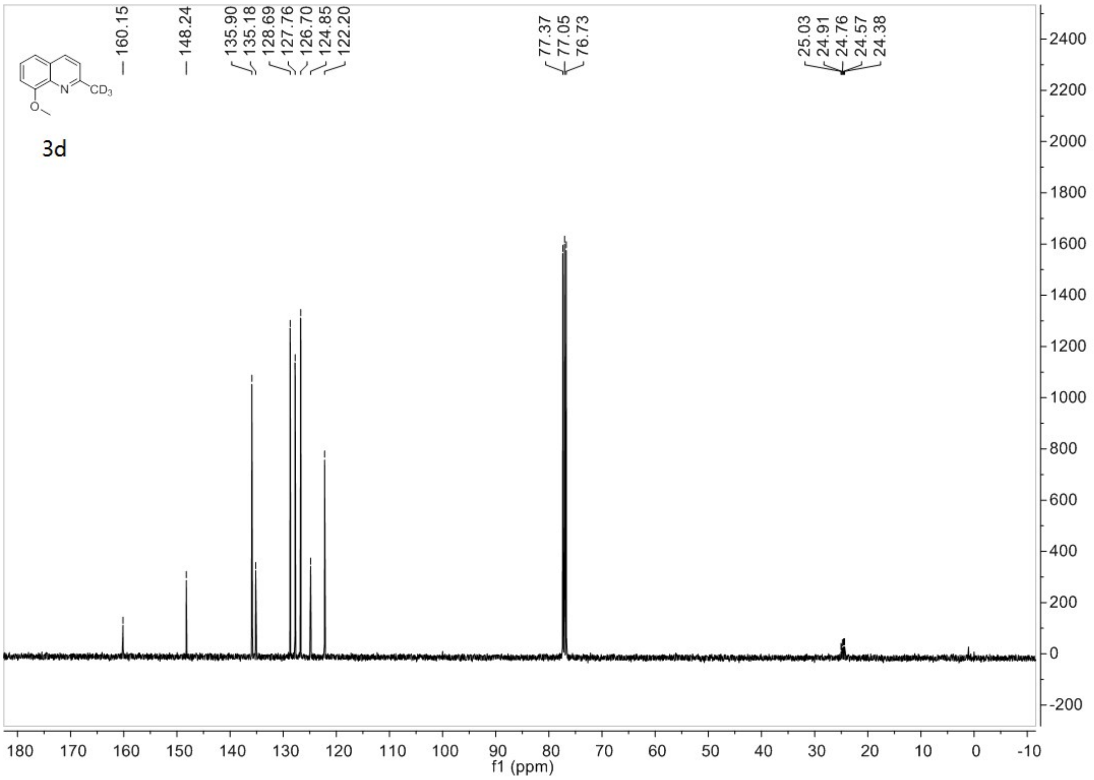

MeO
N
1c
7.955
7.931
7.905
7.347
7.325
7.265
7.252
7.231
7.043
3.917
2.708
2.00
1.01
1.28
1.00
3.05
3.03
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

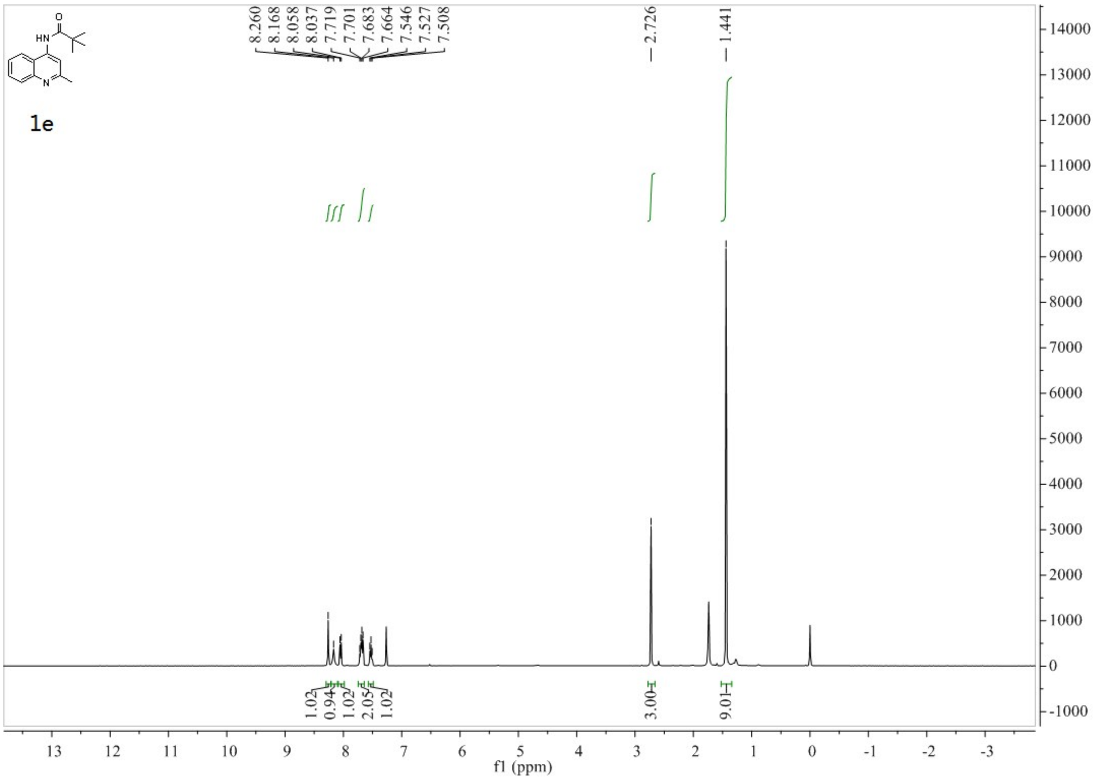

MeO
N
1c
157.15
156.37
143.89
135.07
130.02
127.32
122.27
121.90
105.21
55.51
25.06
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

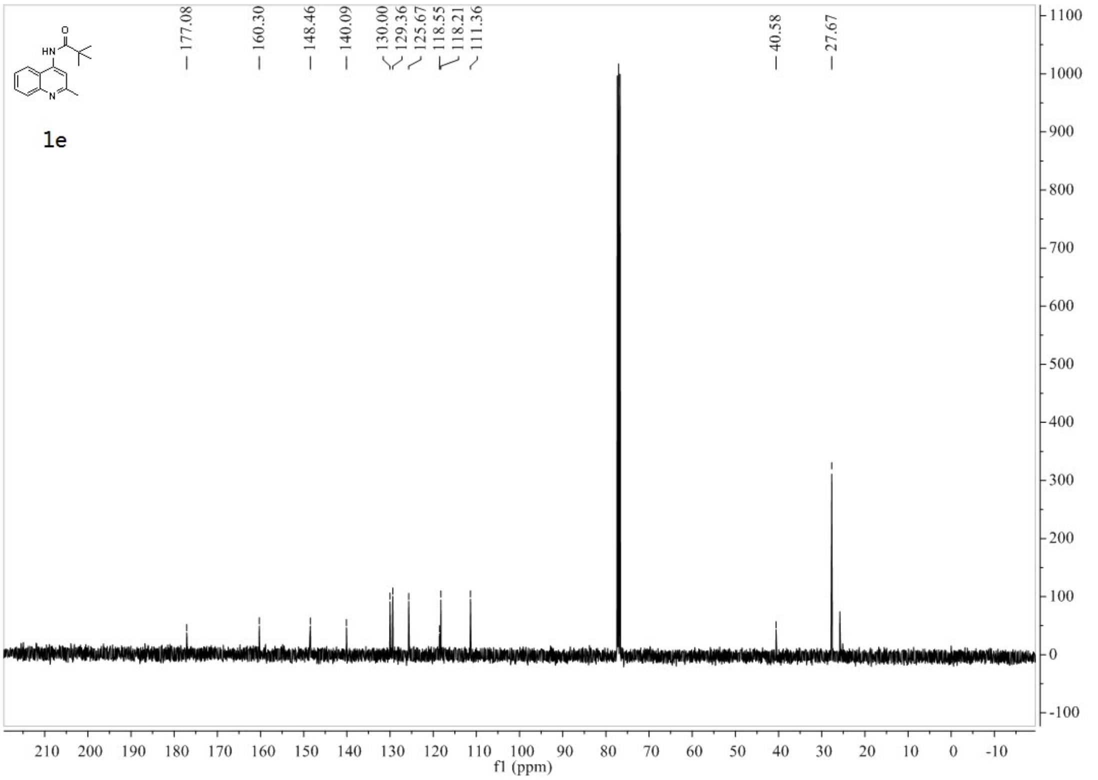

7.860
7.847
7.840
7.825
7.265
7.259
7.243
7.236
7.191
7.157
7.136
6.954
6.949
3.825
2.591
2.177
3c
O
N
CD3
2.00
1.01
0.98
1.00
3.08
0.06
0.50
40000
35000
30000
25000
20000
15000
10000
5000
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

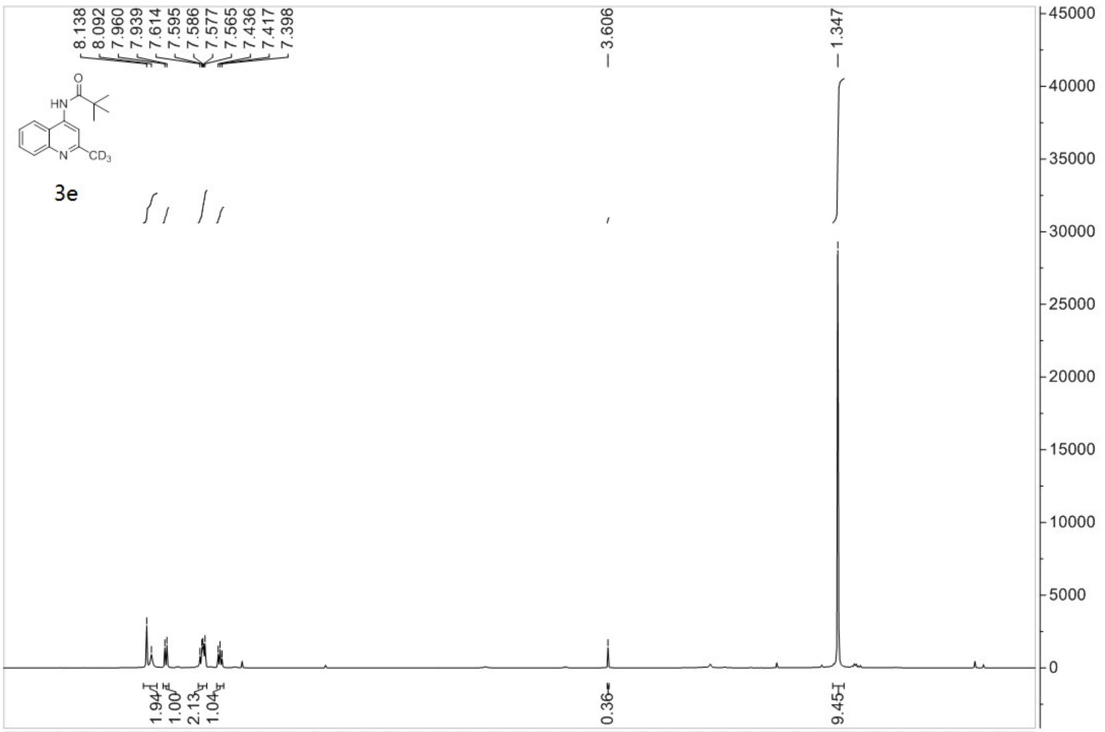

157.15
156.29
143.89
135.04
130.00
127.33
122.23
121.87
105.23
77.37
77.05
76.74
55.49
24.40
24.21
24.02
23.97
3c
O
N
CD3
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

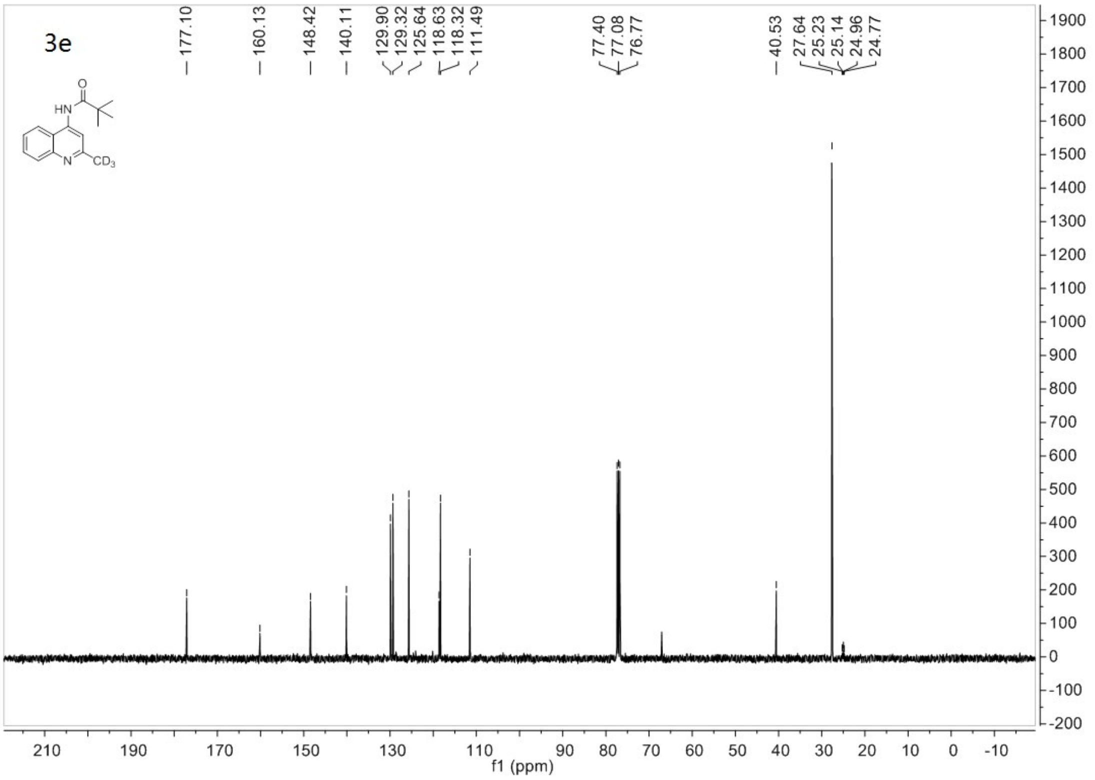

CD3
3d
7.934
7.923
7.328
7.308
7.289
7.266
7.246
7.231
7.210
7.199
6.954
6.935
3.993
2.683
1.00
1.00
0.77
1.00
3.00
0.14
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

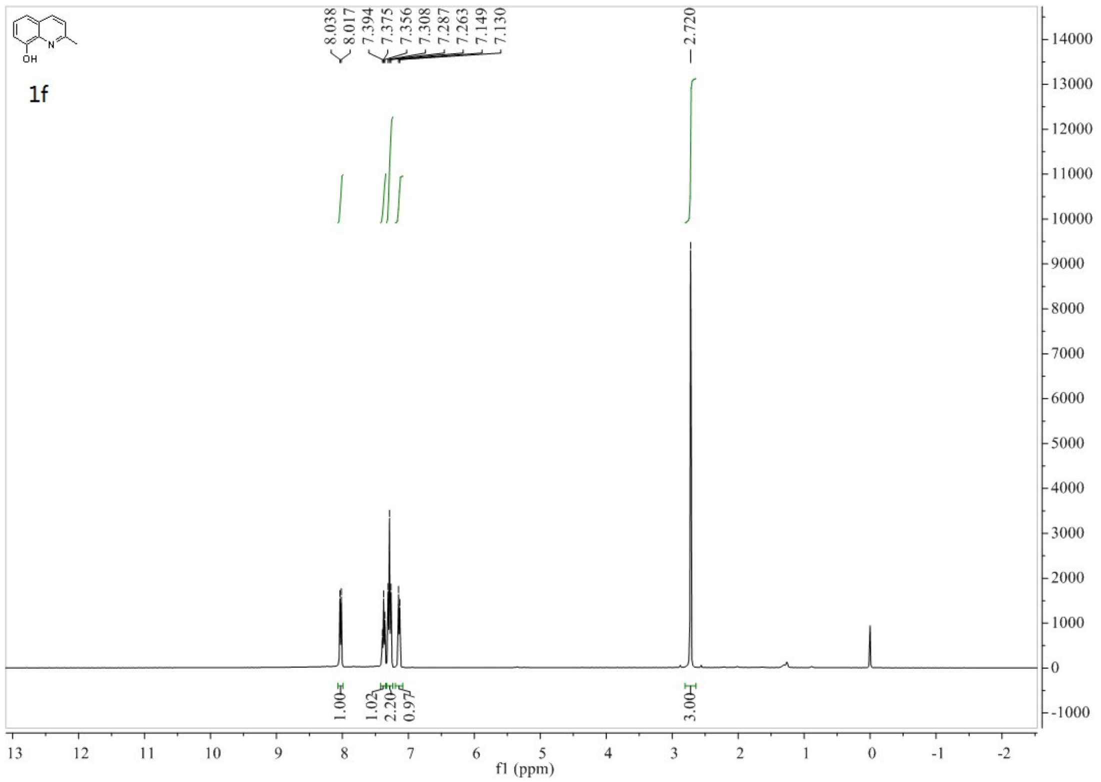

CD3
3d
160.15
148.24
135.90
135.18
128.69
127.76
126.70
124.85
122.20
77.37
77.05
76.73
25.03
24.91
24.76
24.57
24.38
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


1e
8.260
8.168
8.058
8.037
7.719
7.701
7.683
7.664
7.546
7.527
7.508
2.726
1.441
1.02
0.94
1.02
2.05
1.02
3.00
9.01
f1 (ppm)
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

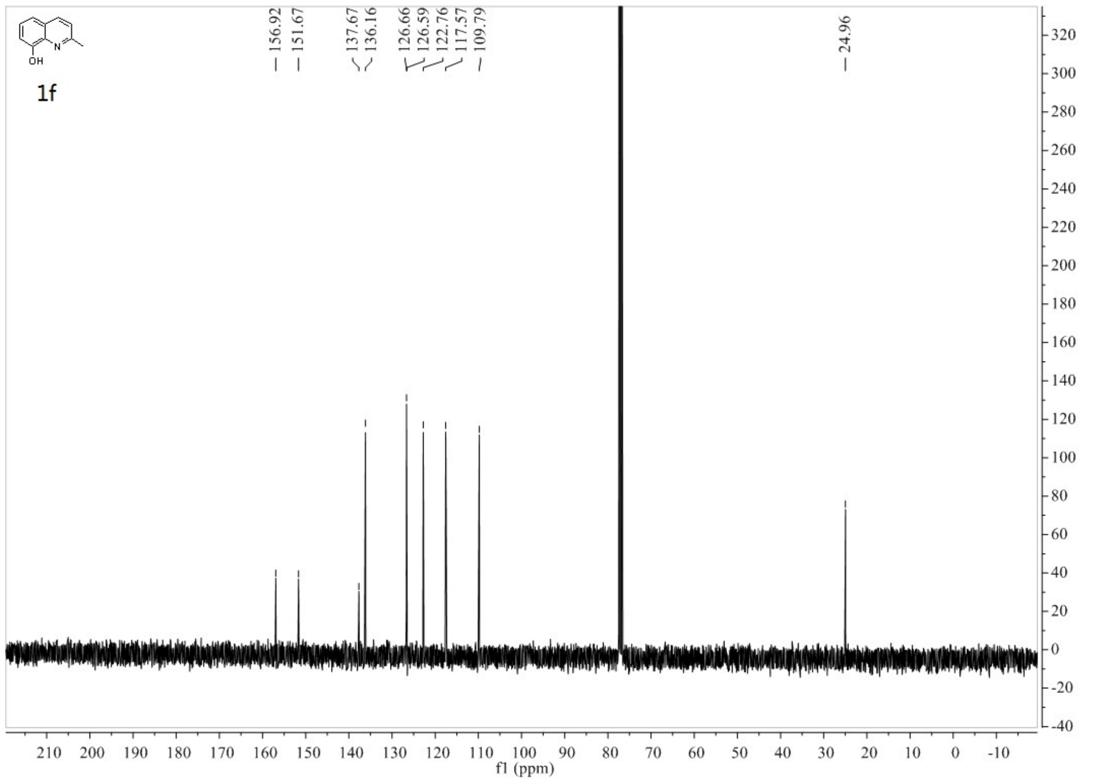

1e
177.08
160.30
148.46
140.09
130.00
129.36
125.67
118.55
118.21
111.36
40.58
27.67
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
1100
1000
900
800
700
600
500
400
300
200
100
0
-100


3e
HN
O
N
CD3
8.138
8.092
7.960
7.939
7.614
7.595
7.586
7.577
7.565
7.436
7.417
7.398
3.606
1.347
1.94
1.00
2.13
1.04
0.36
9.45
45000
40000
35000
30000
25000
20000
15000
10000
5000
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
-0.5
f1 (ppm)

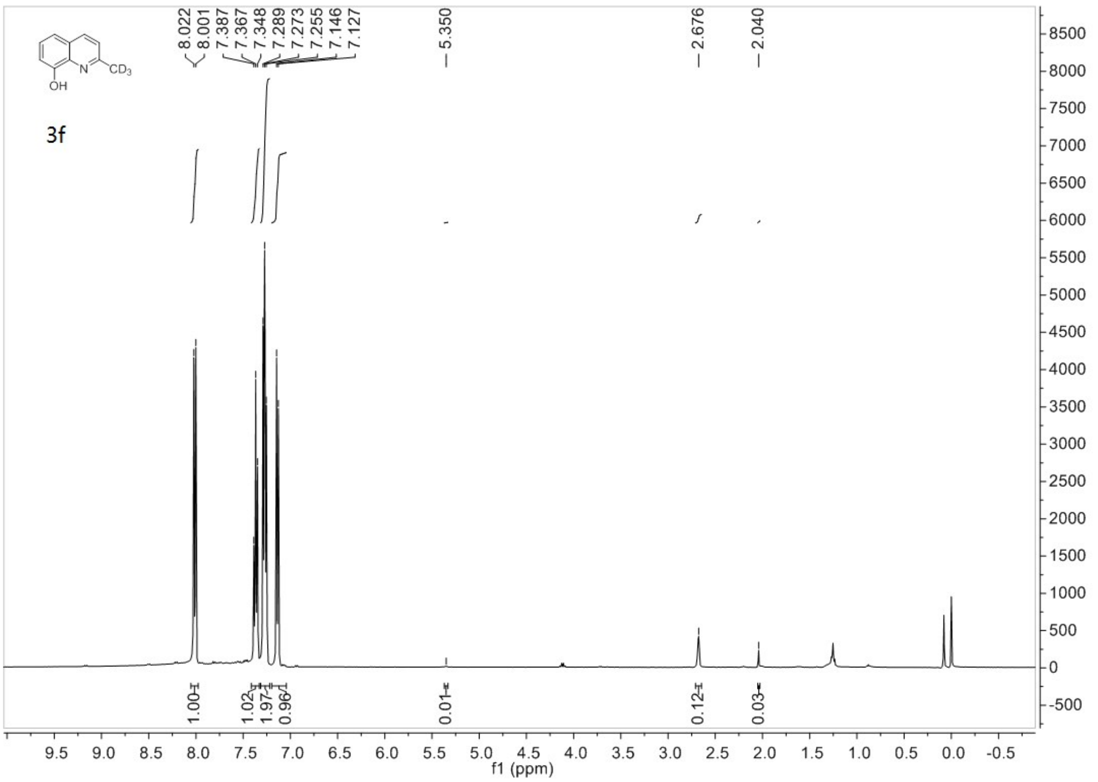

3e
HN
O
N
CD3
177.10
160.13
148.42
140.11
129.90
129.32
125.64
118.63
118.32
111.49
77.40
77.08
76.77
40.53
27.64
25.23
25.14
24.96
24.77
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

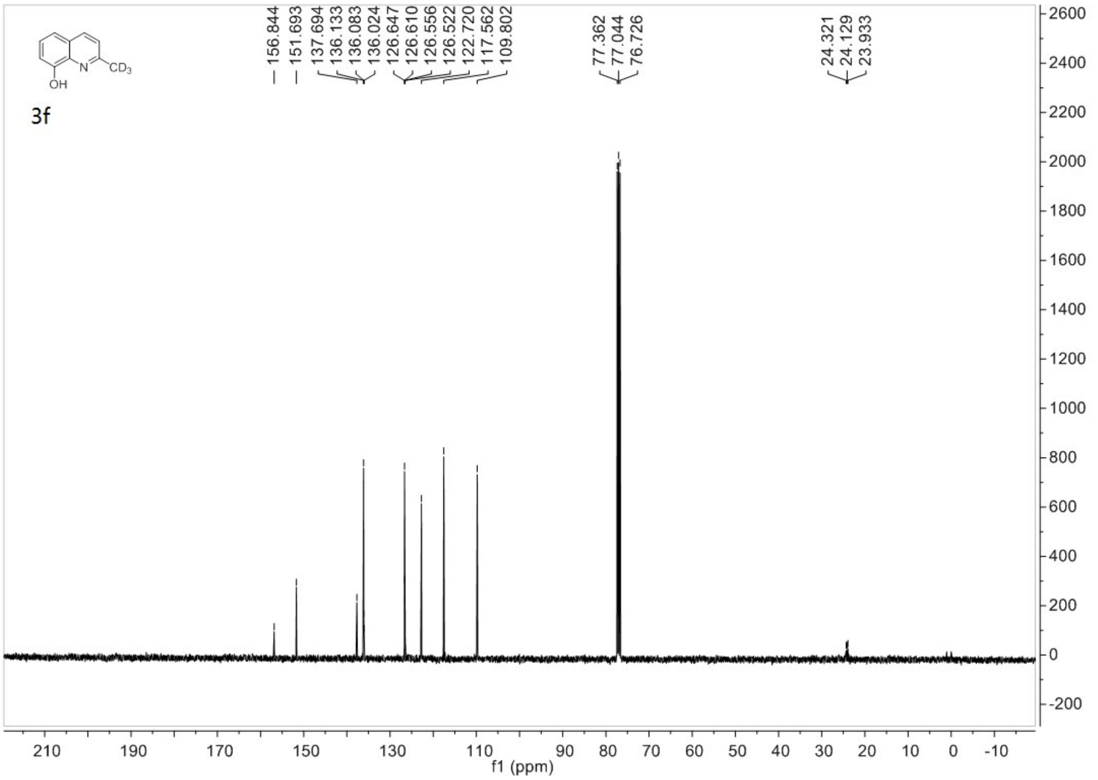


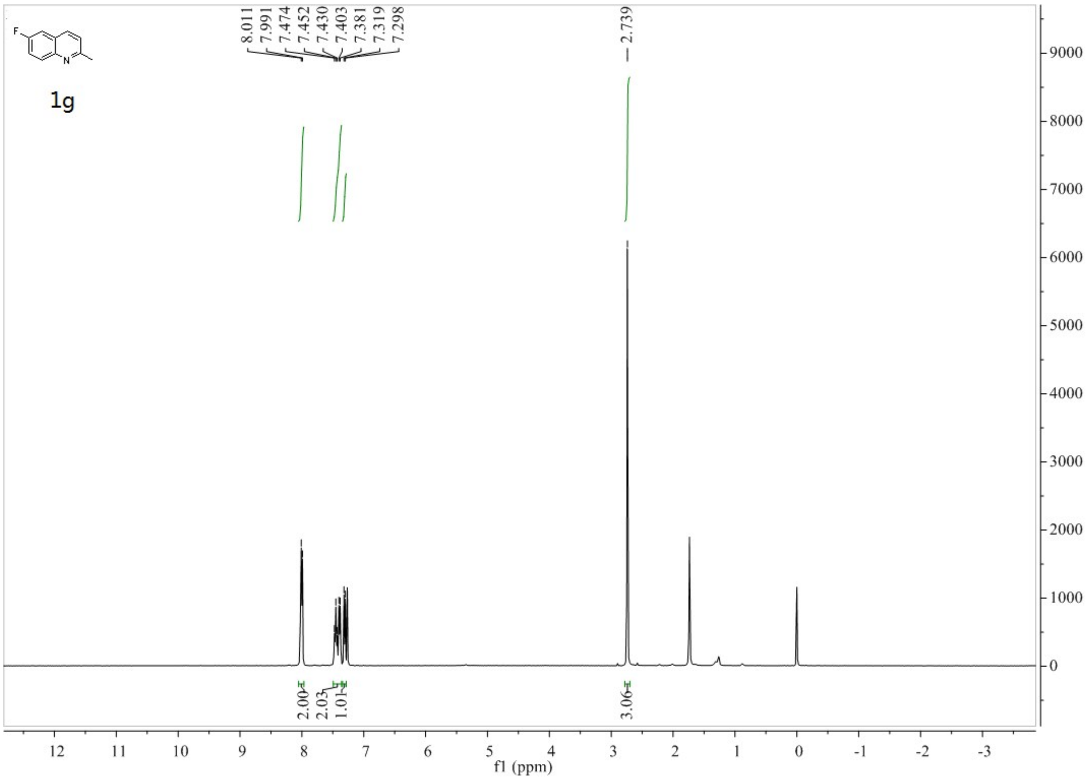
OH
N
1f
8.038
8.017
7.394
7.375
7.356
7.308
7.287
7.263
7.149
7.130
2.720
1.00
1.02
2.20
0.97
3.00
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

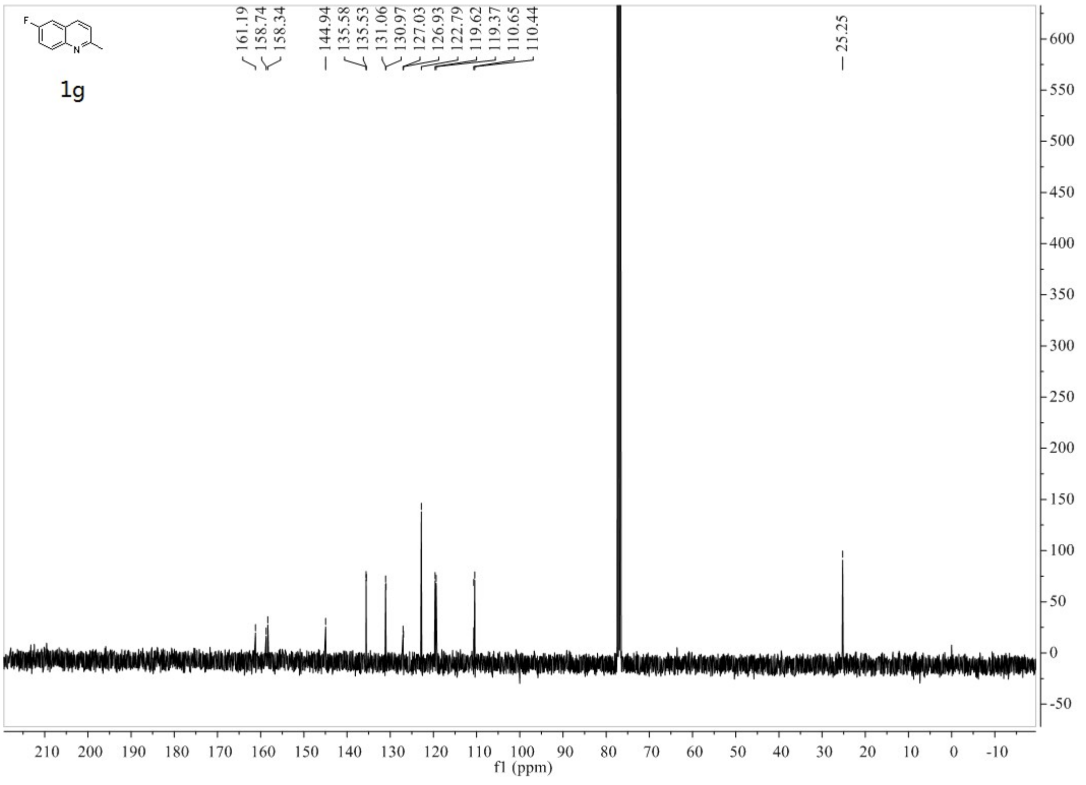


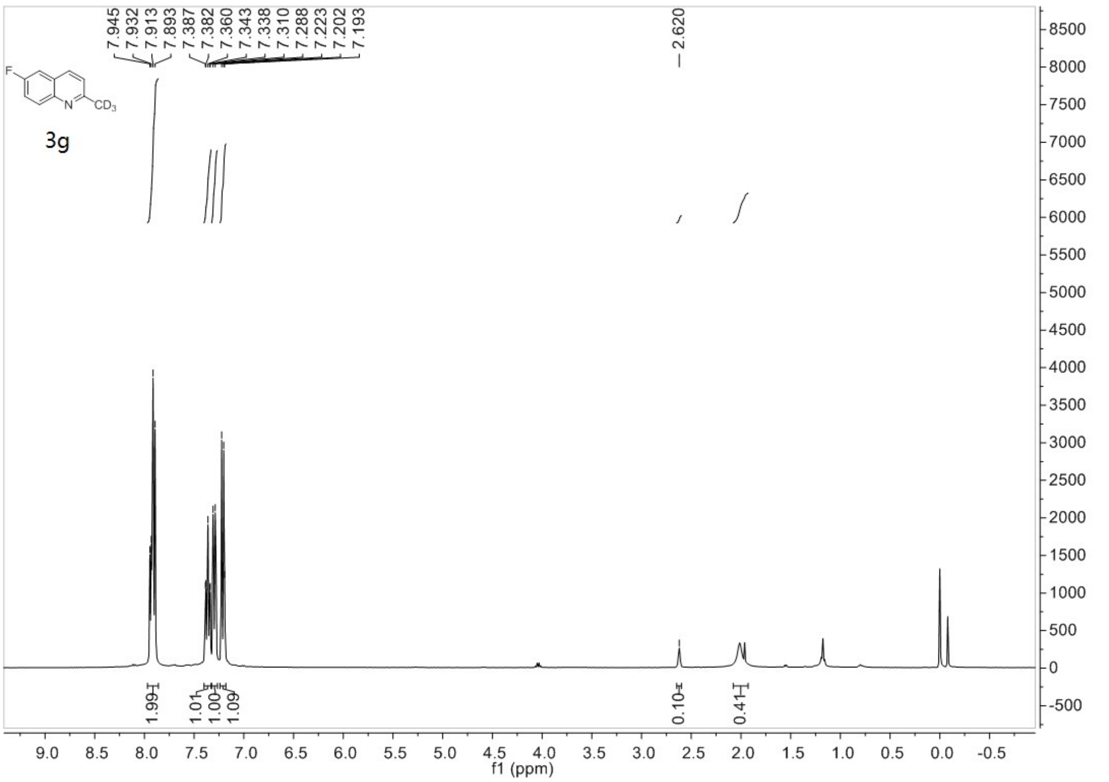
OH
N
1f
156.92
151.67
137.67
136.16
126.66
126.59
122.76
117.57
109.79
24.96
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

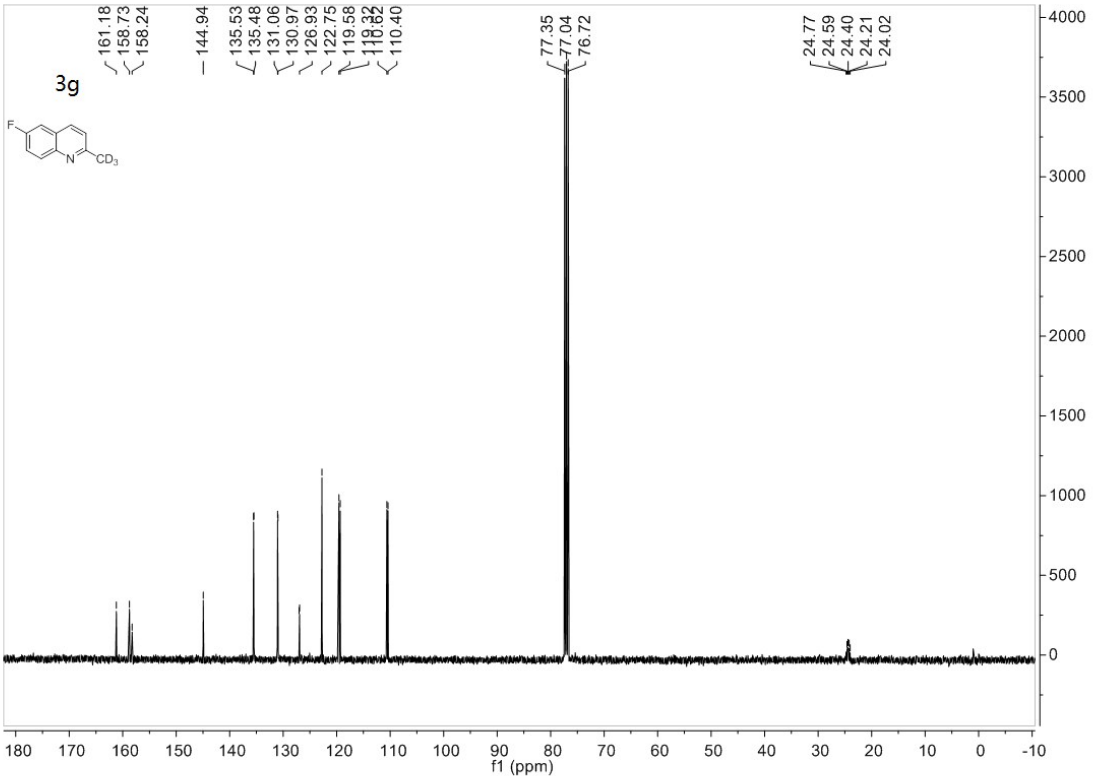

8.022
8.001
7.387
7.367
7.348
7.289
7.273
7.255
7.146
7.127
5.350
2.676
2.040
OH
N
CD3
3f
1.00
1.02
1.97
0.96
0.01
0.12
0.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
8500 8000 7500 7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500

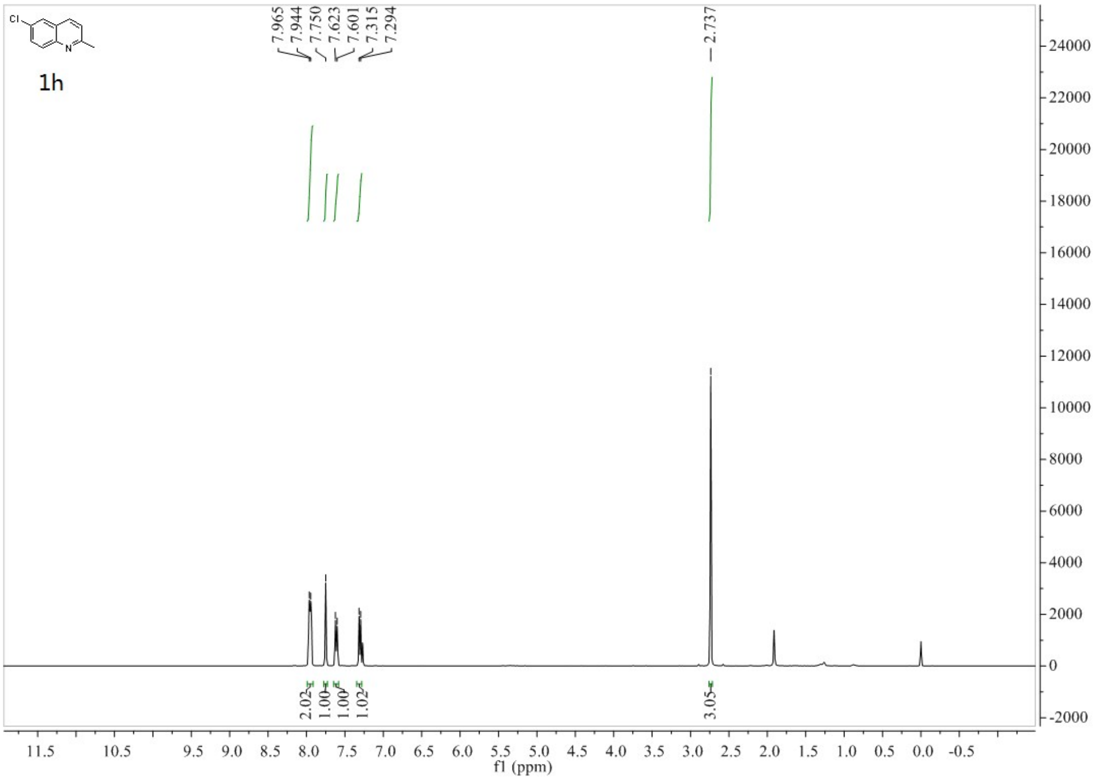

156.844
151.693
137.694
136.133
136.083
136.024
126.647
126.610
126.556
126.522
122.720
117.562
109.802
77.362
77.044
76.726
24.321
24.129
23.933
OH
N
CD3
3f
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200

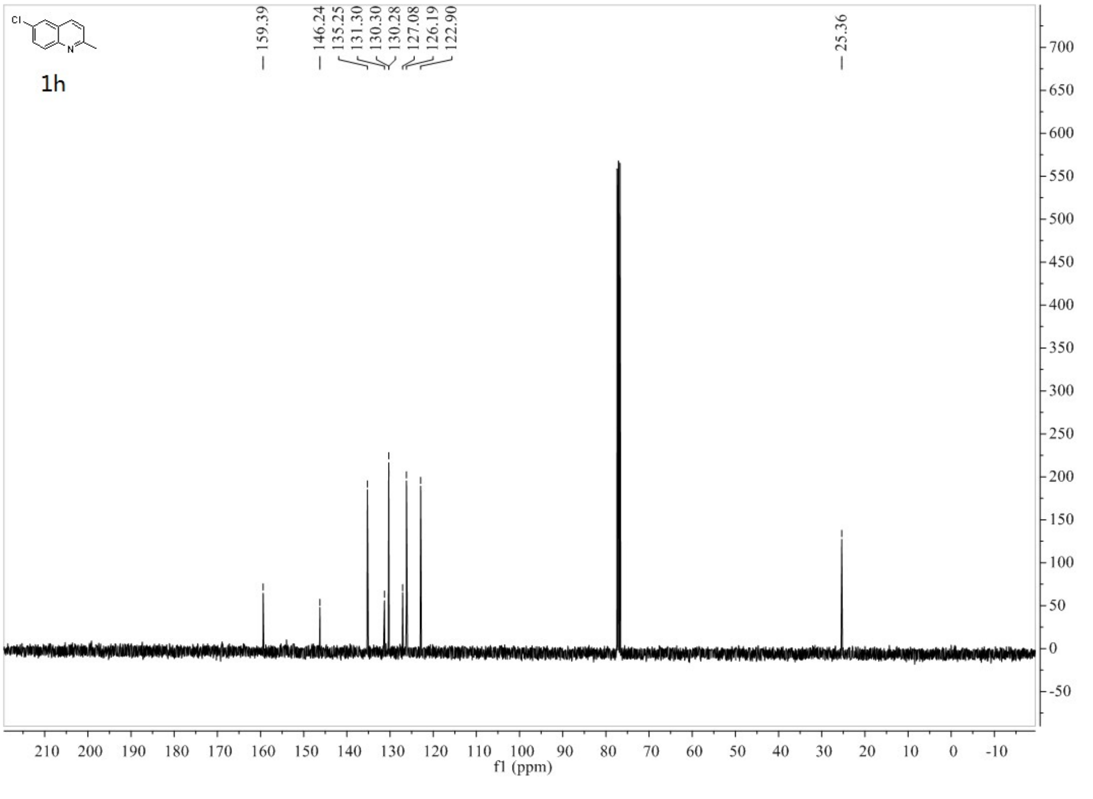

F
N
1g
8.011
7.991
7.474
7.452
7.430
7.403
7.381
7.319
7.298
2.739
2.00
2.03
1.01
3.06
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

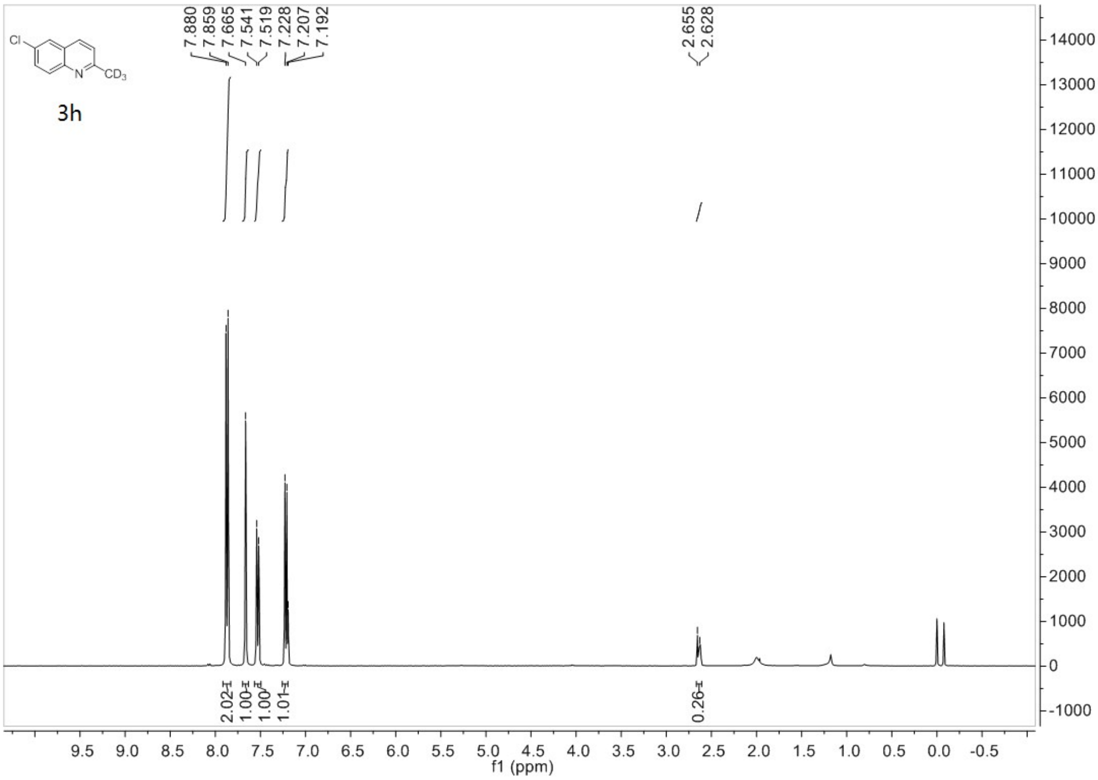

F
N
1g
161.19
158.74
158.34
144.94
135.58
135.53
131.06
130.97
127.03
126.93
122.79
119.62
119.37
110.65
110.44
25.25
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

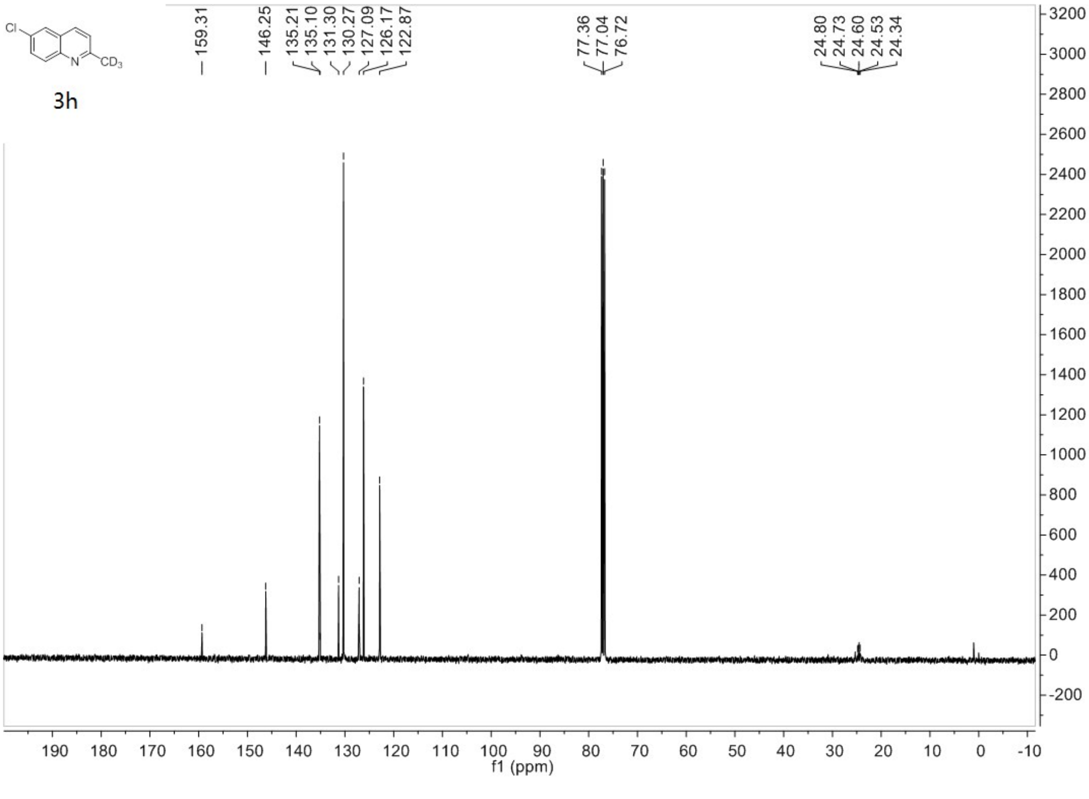

7.945
7.932
7.913
7.893
7.387
7.382
7.360
7.343
7.338
7.310
7.288
7.223
7.202
7.193
2.620
F
N
CD3
3g
1.99
1.01
1.00
1.09
0.10
0.41
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
8500 8000 7500 7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500

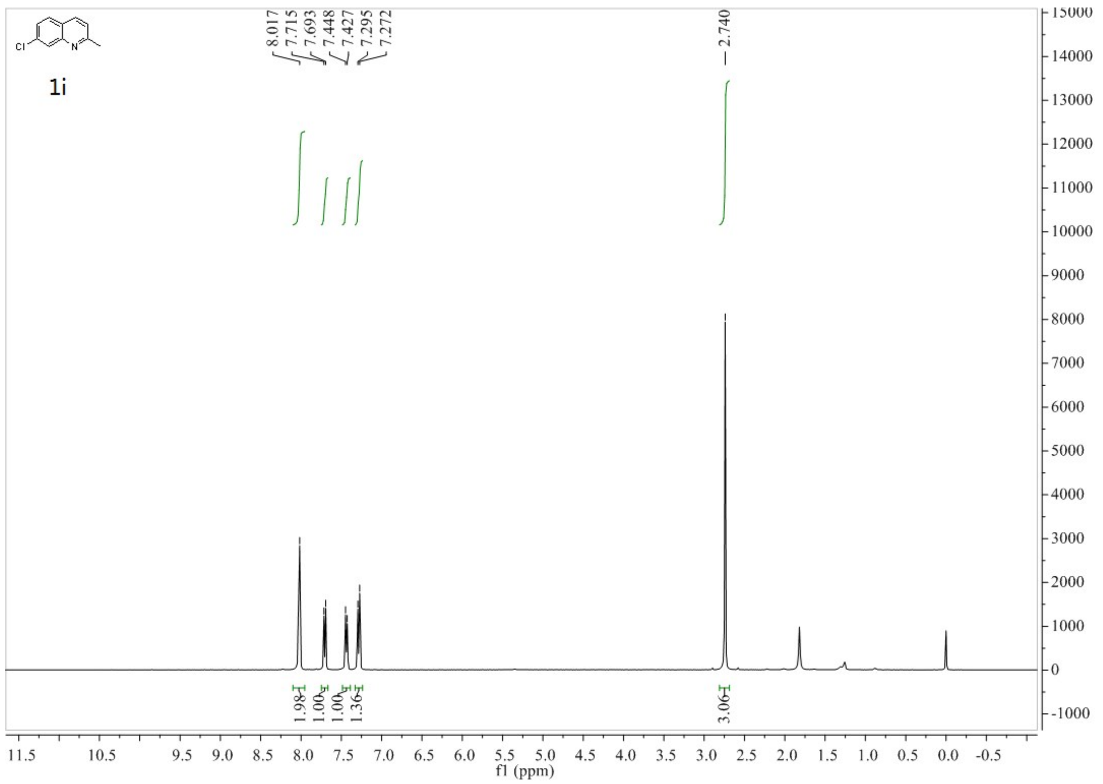

161.18
158.73
158.24
144.94
135.53
135.48
131.06
130.97
126.93
122.75
119.58
119.32
110.52
110.40
77.35
77.04
76.72
24.77
24.59
24.40
24.21
24.02
3g
F
N
CD3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
4000 3500 3000 2500 2000 1500 1000 500 0


Cl
N
1h
7.965
7.944
7.750
7.623
7.601
7.315
7.294
2.737
2.02
1.00
1.00
1.02
3.05
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
11.5 10.5 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 -0.5
f1 (ppm)

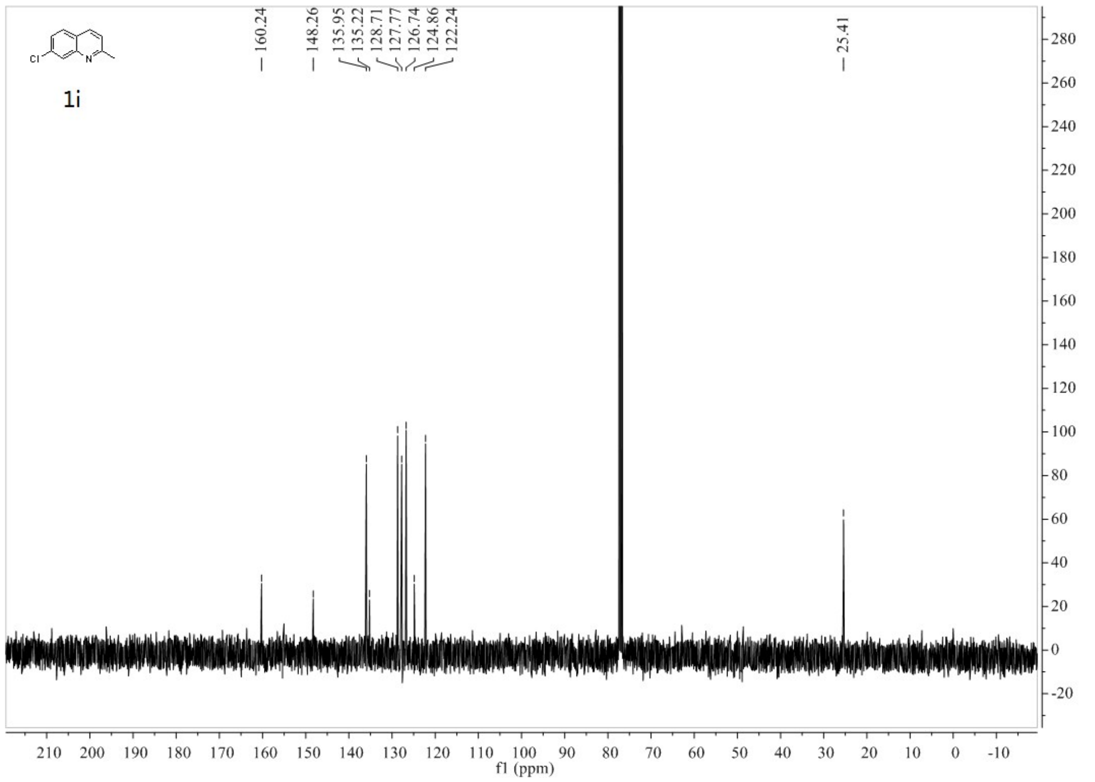

Cl
N
1h
159.39
146.24
135.25
131.30
130.30
130.28
127.08
126.19
122.90
25.36
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Cl
N
CD3
3h
7.880
7.859
7.665
7.541
7.519
7.228
7.207
7.192
2.655
2.628
2.02
1.00
1.00
1.01
0.26
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
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
-0.5
f1 (ppm)

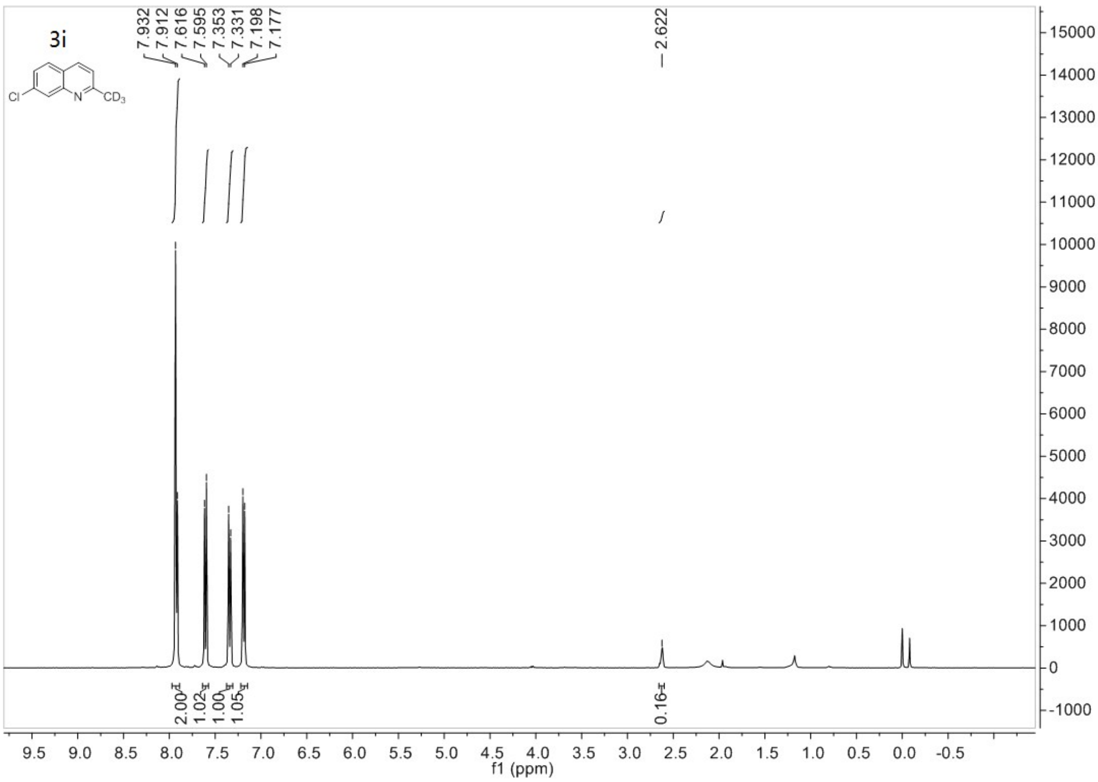

Cl
N
CD3
3h
159.31
146.25
135.21
135.10
131.30
130.27
127.09
126.17
122.87
77.36
77.04
76.72
24.80
24.73
24.60
24.53
24.34
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

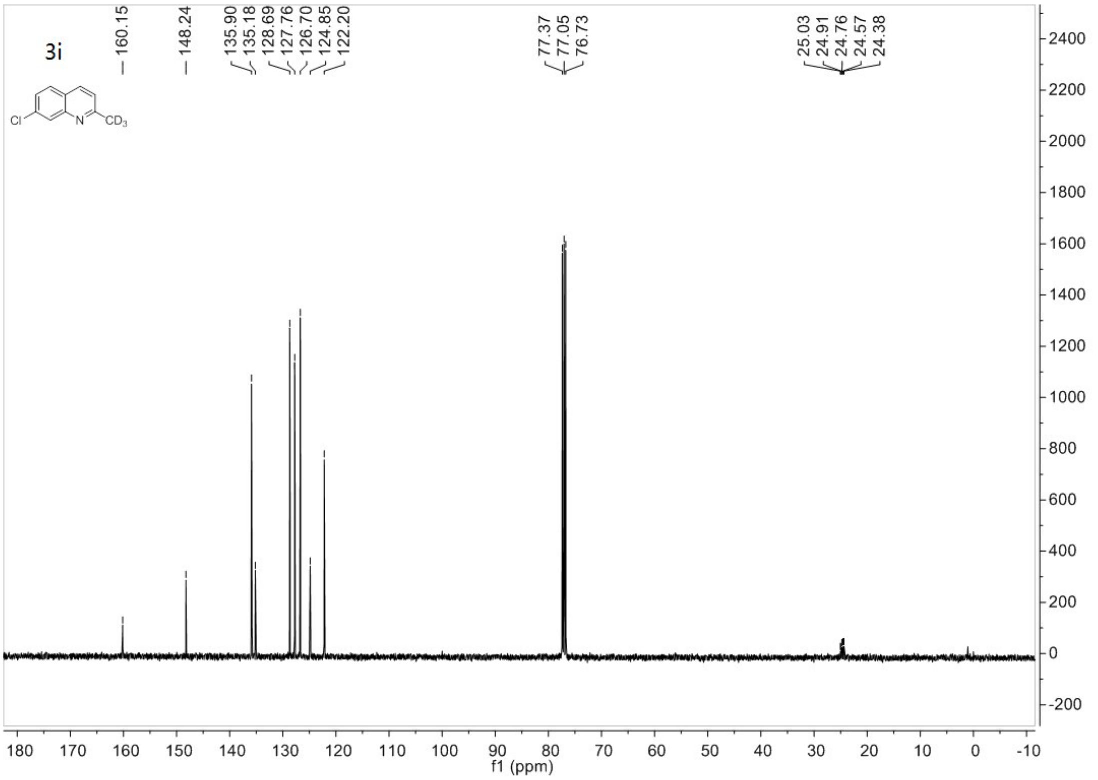


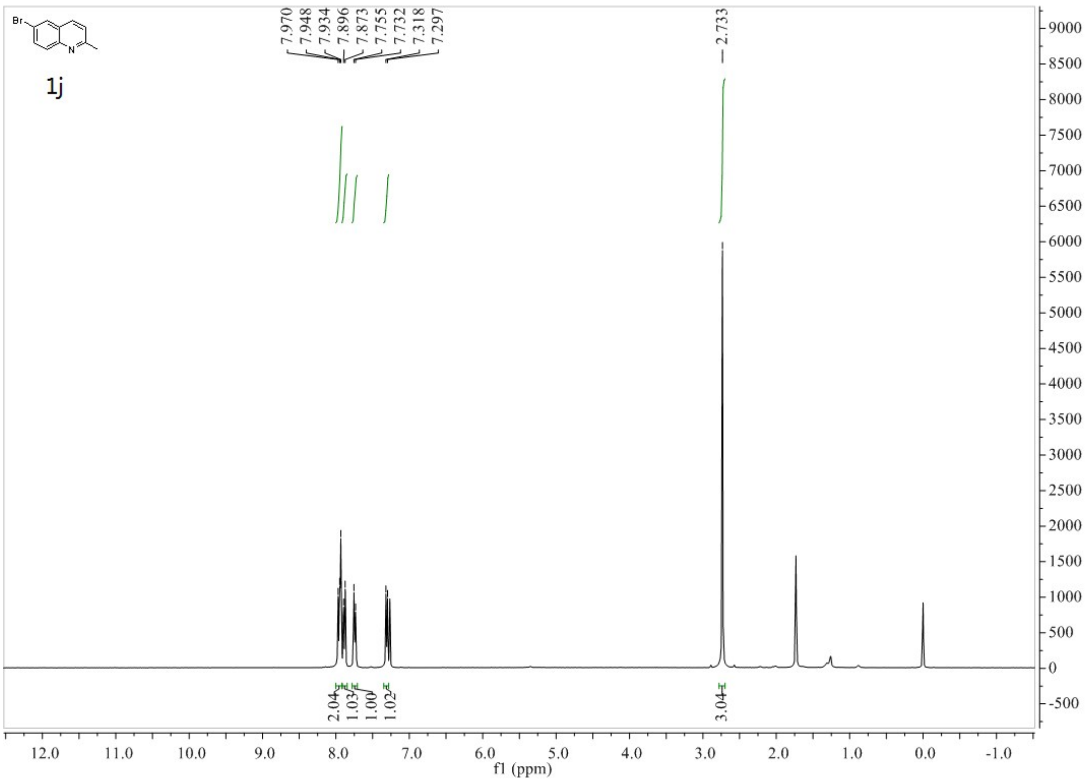
1i
Cl
N
8.017
7.715
7.693
7.448
7.427
7.295
7.272
2.740
1.98
1.00
1.00
1.36
3.06
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

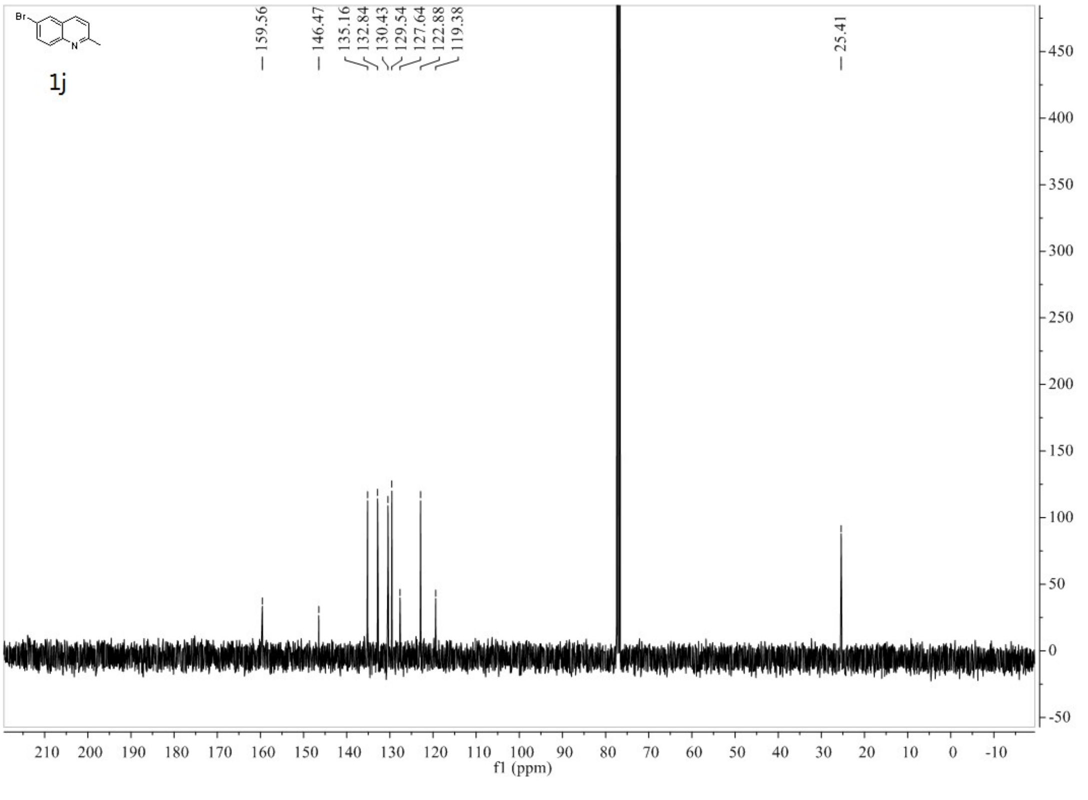


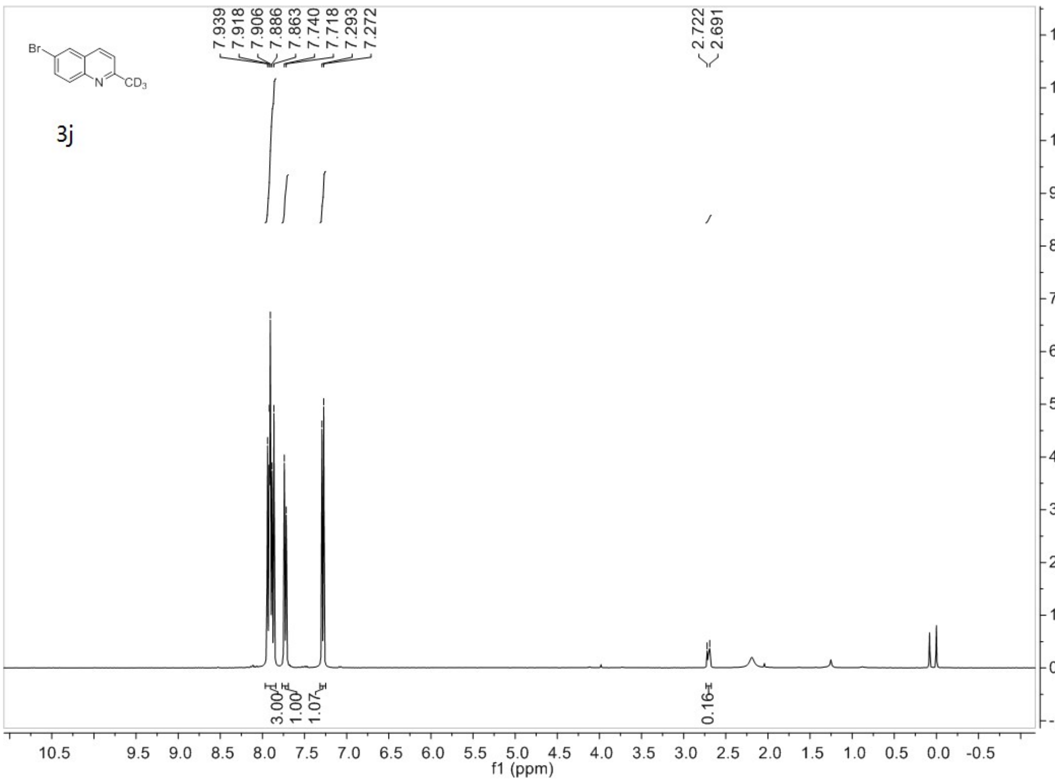
1i
Cl
N
160.24
148.26
135.95
135.22
128.71
127.77
126.74
124.86
122.24
25.41
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

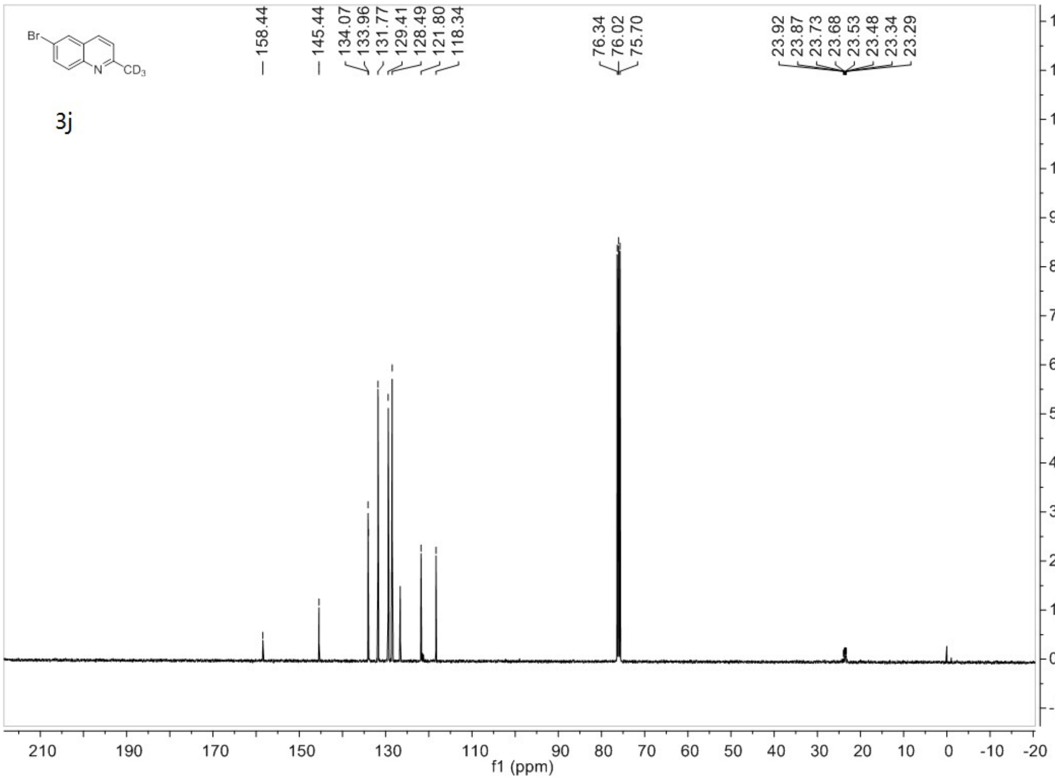

3i
Cl
N
CD3
7.932
7.912
7.616
7.595
7.353
7.331
7.198
7.177
2.622
2.00
1.02
1.00
1.05
0.16
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

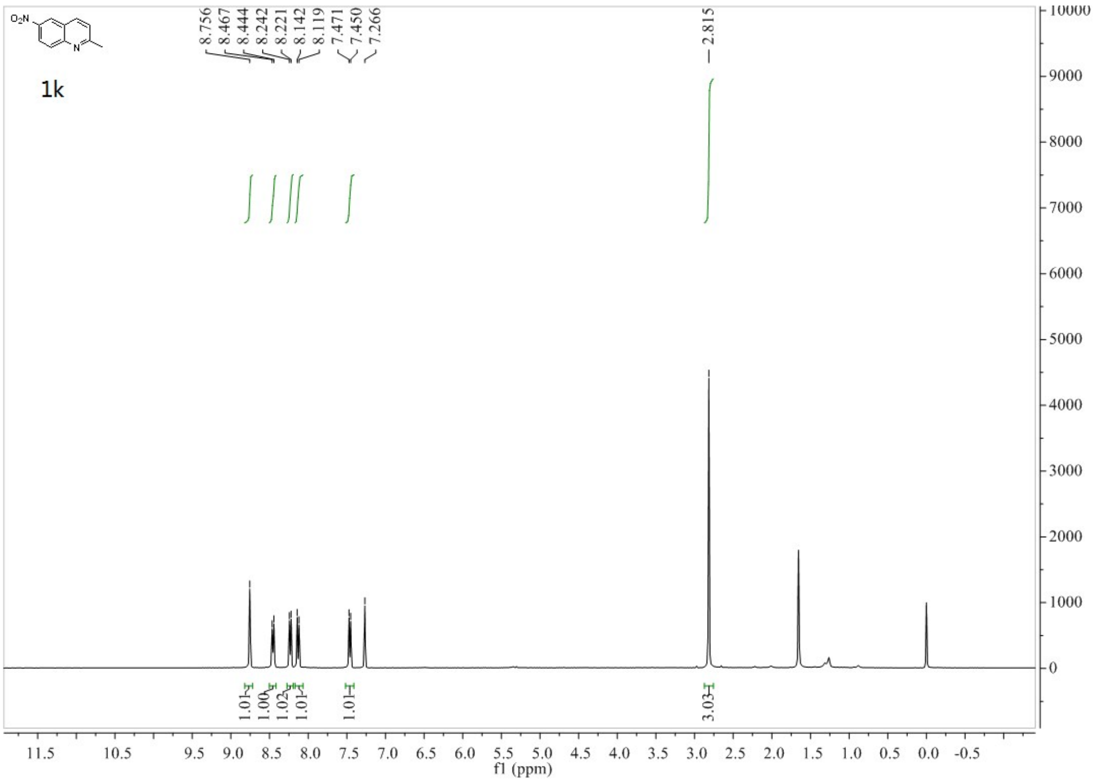

3i
Cl
N
CD3
160.15
148.24
135.90
135.18
128.69
127.76
126.70
124.85
122.20
77.37
77.05
76.73
25.03
24.91
24.76
24.57
24.38
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

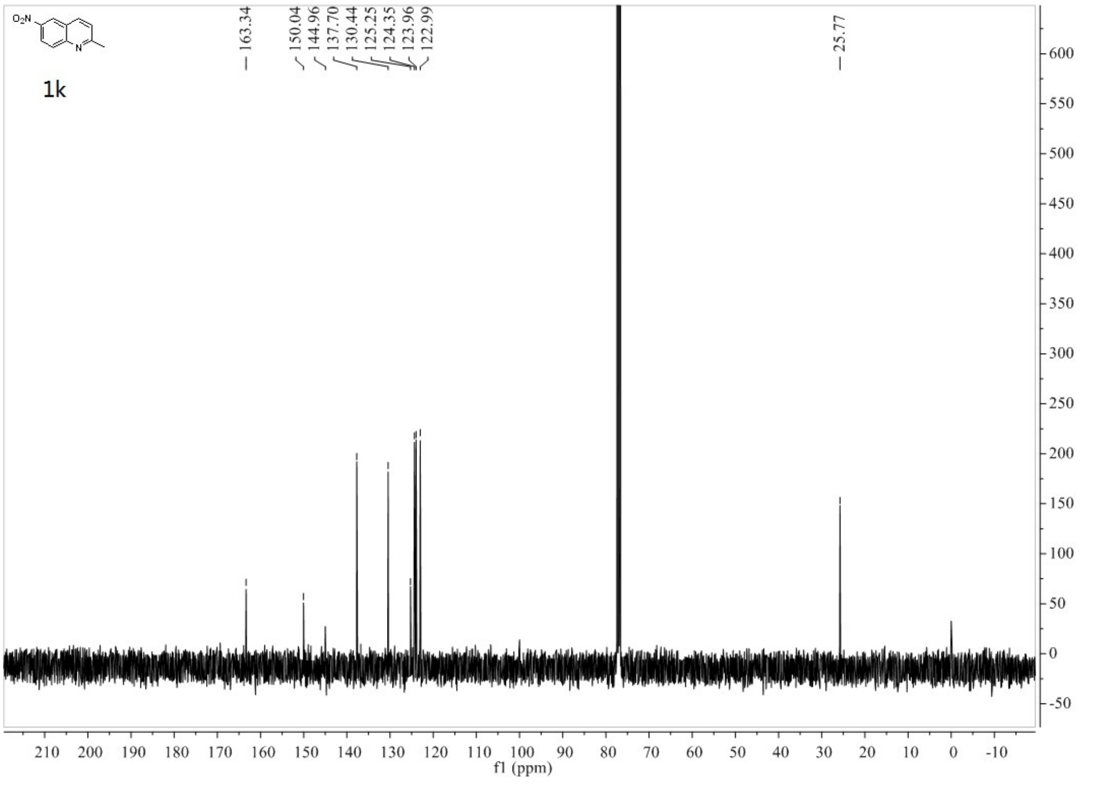

Br
N
1j
7.970
7.948
7.934
7.896
7.873
7.755
7.732
7.318
7.297
2.733
2.04
1.03
1.00
1.02
3.04
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

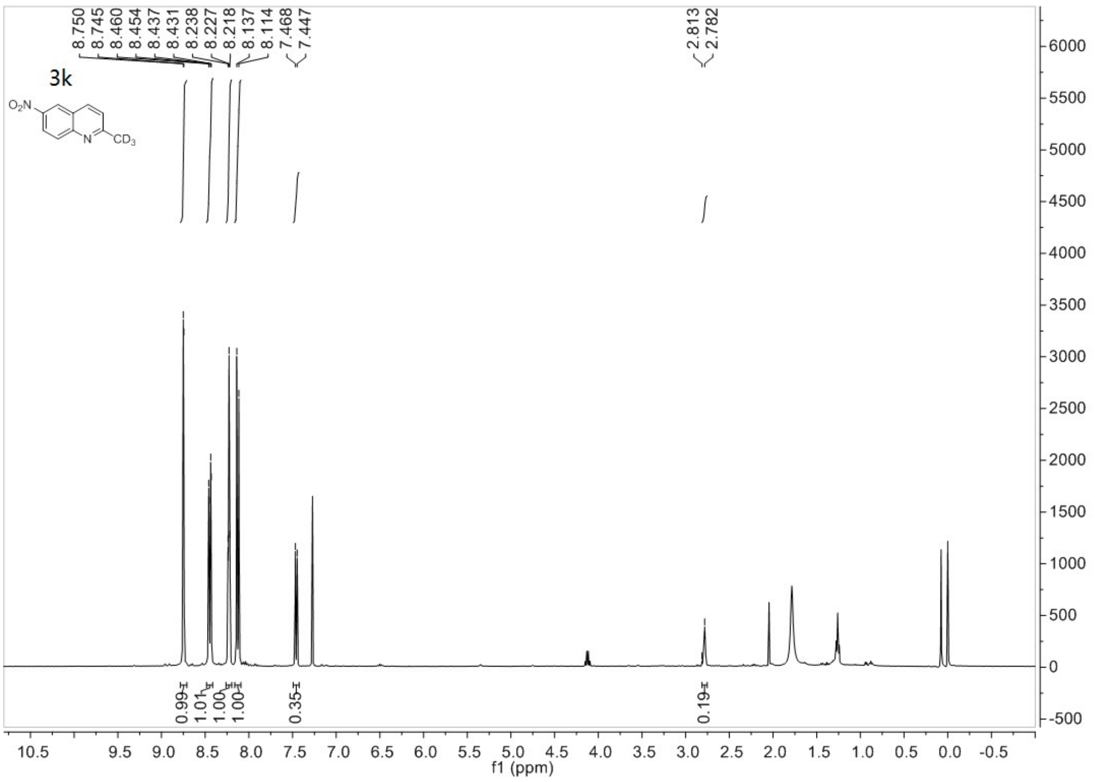

Br
N
1j
159.56
146.47
135.16
132.84
130.43
129.54
127.64
122.88
119.38
25.41
450
400
350
300
250
200
150
100
50
0
-50
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

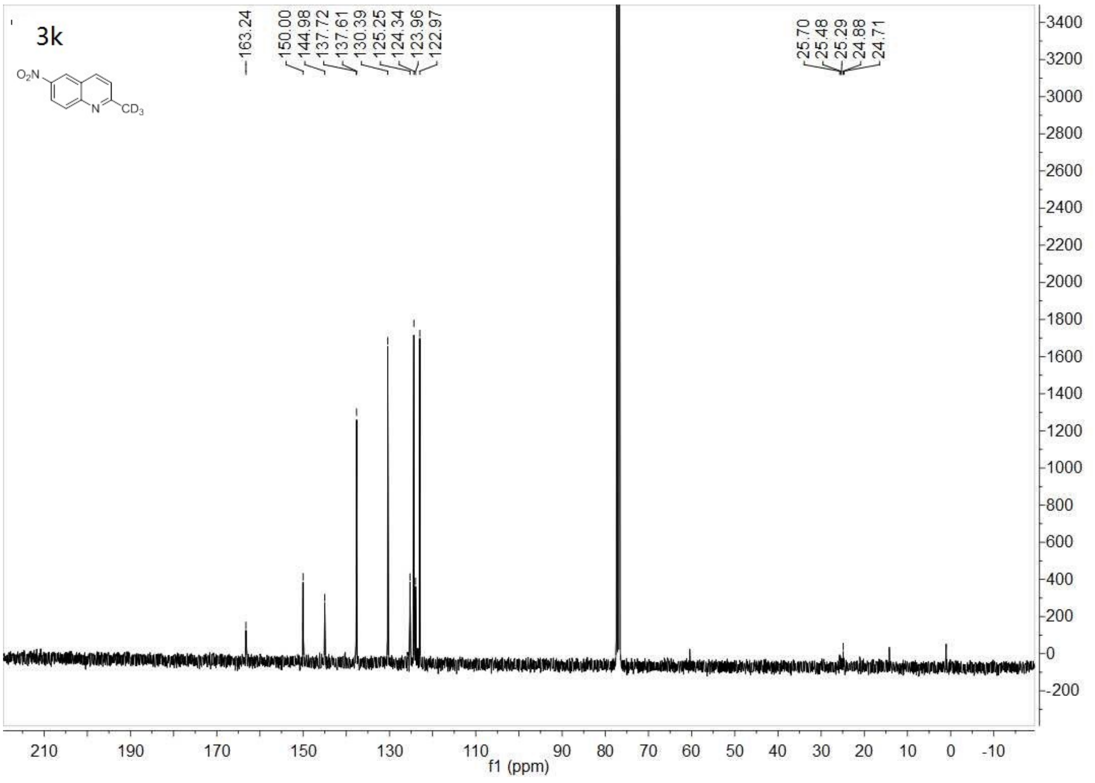

Br
N
CD3
3j
7.939
7.918
7.906
7.886
7.863
7.740
7.718
7.293
7.272
2.722
2.691
3.00
1.00
1.07
0.16
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

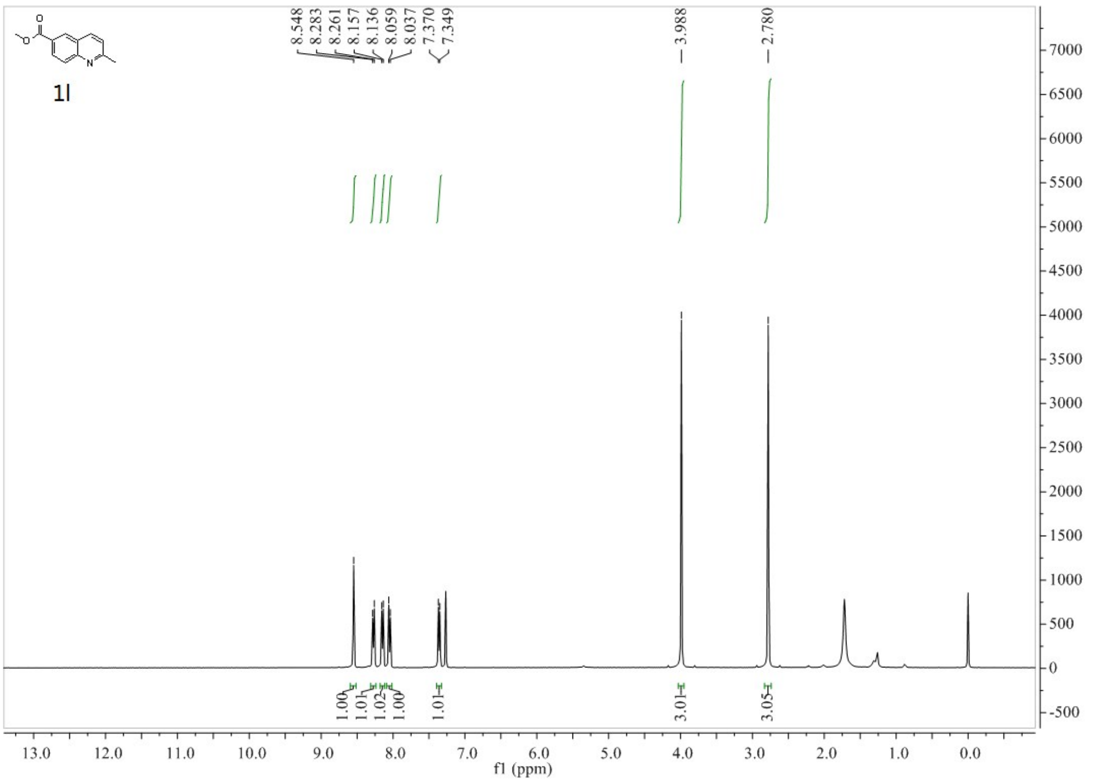

Br
N
CD3
3j
158.44
145.44
134.07
133.96
131.77
129.41
128.49
121.80
118.34
76.34
76.02
75.70
23.92
23.87
23.73
23.68
23.53
23.48
23.34
23.29
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

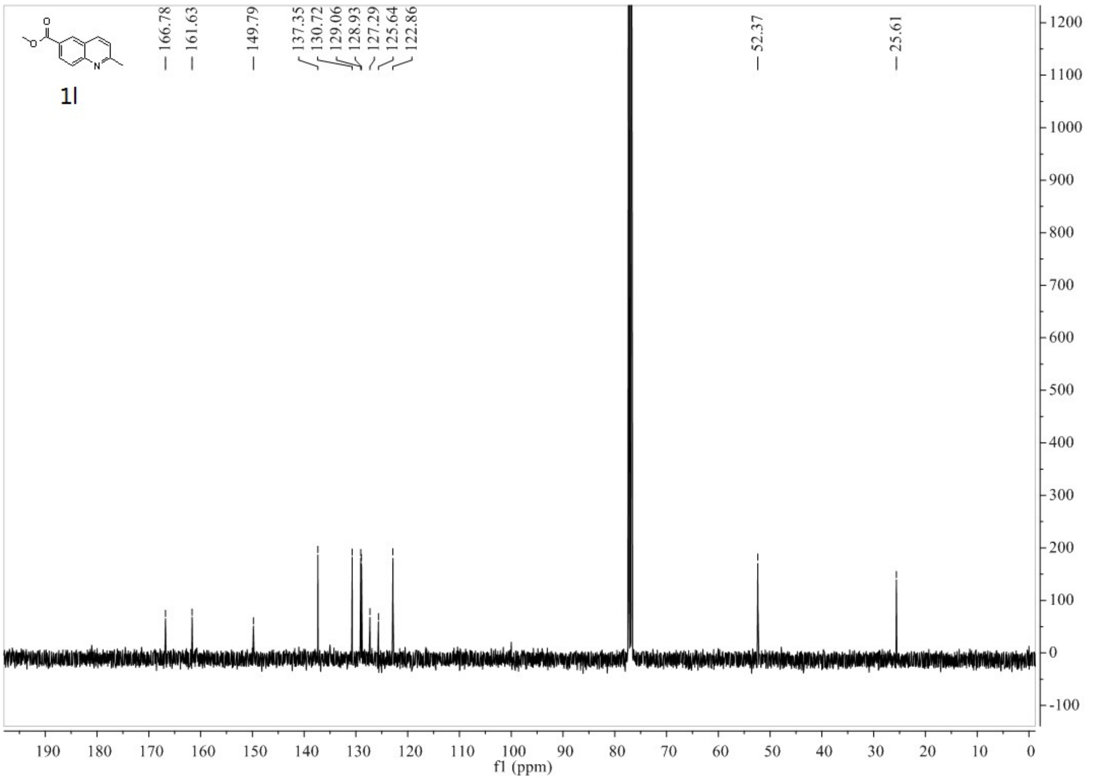

O2N
N
1k
8.756
8.467
8.444
8.242
8.221
8.142
8.119
7.471
7.450
7.266
2.815
1.01
1.00
1.02
1.01
1.01
3.03
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

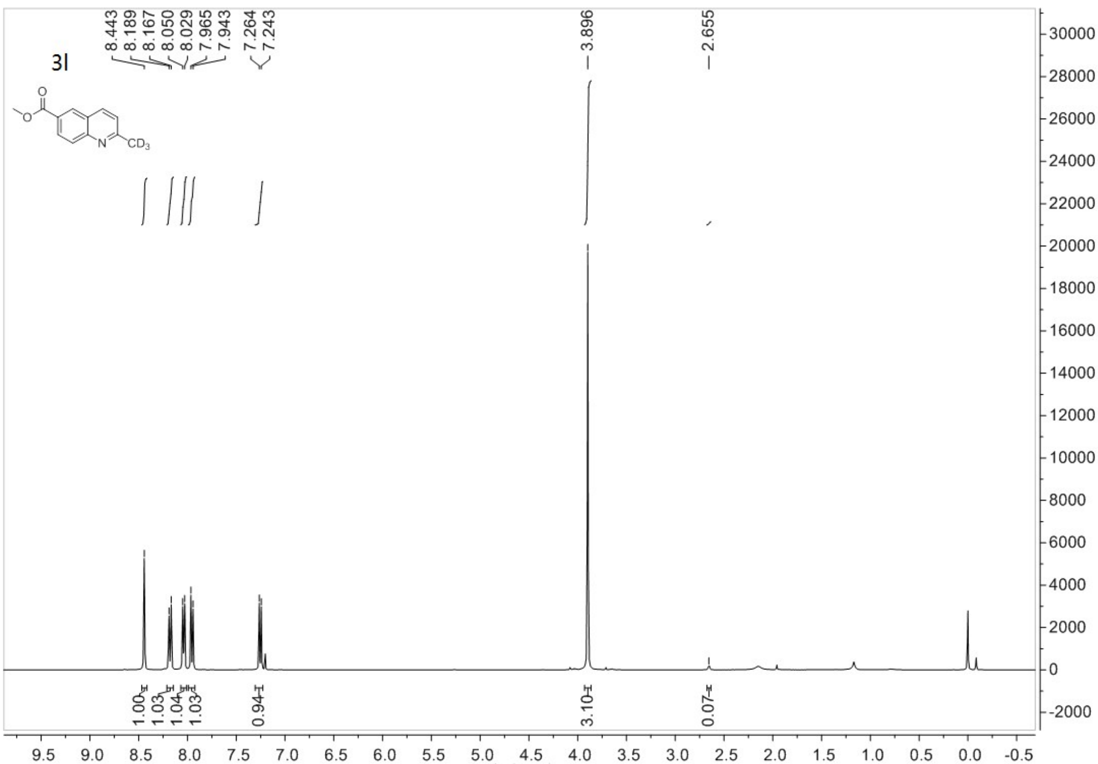

O2N
N
1k
163.34
150.04
144.96
137.70
130.44
125.25
124.35
123.96
122.99
25.77
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

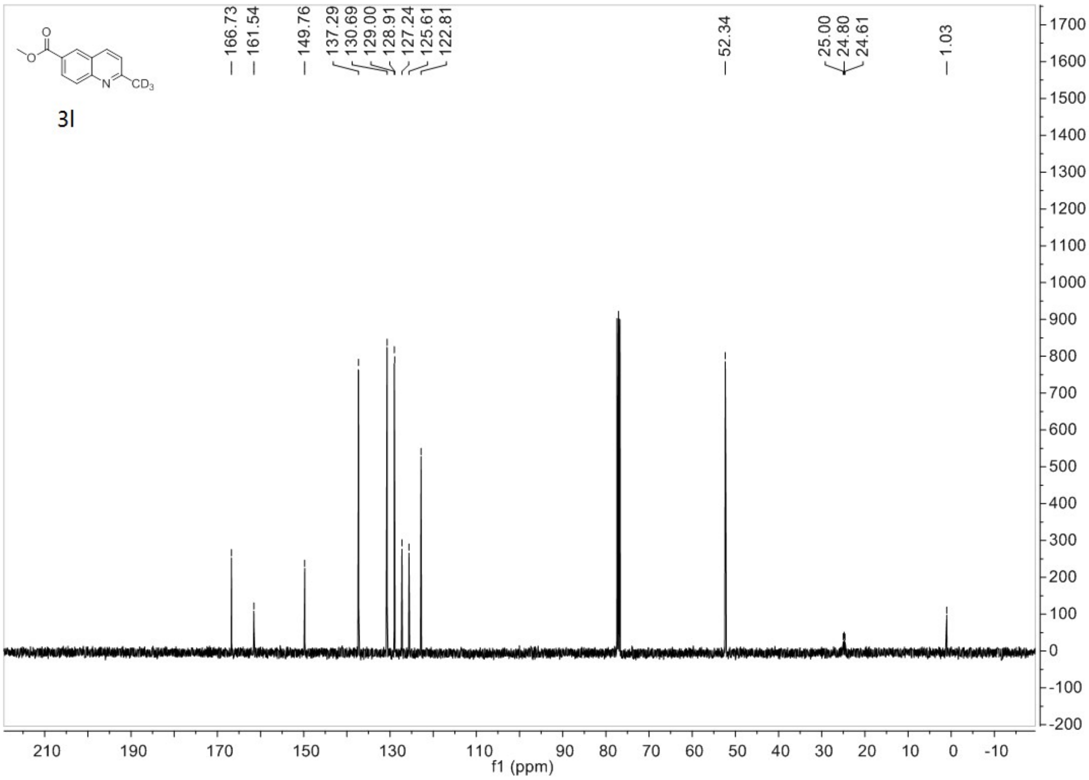

3k
O_2N
N
CD_3
8.750
8.745
8.460
8.454
8.437
8.431
8.238
8.227
8.218
8.137
8.114
7.468
7.447
2.813
2.782
0.99
1.01
1.00
1.00
0.35
0.19
f1 (ppm)
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500

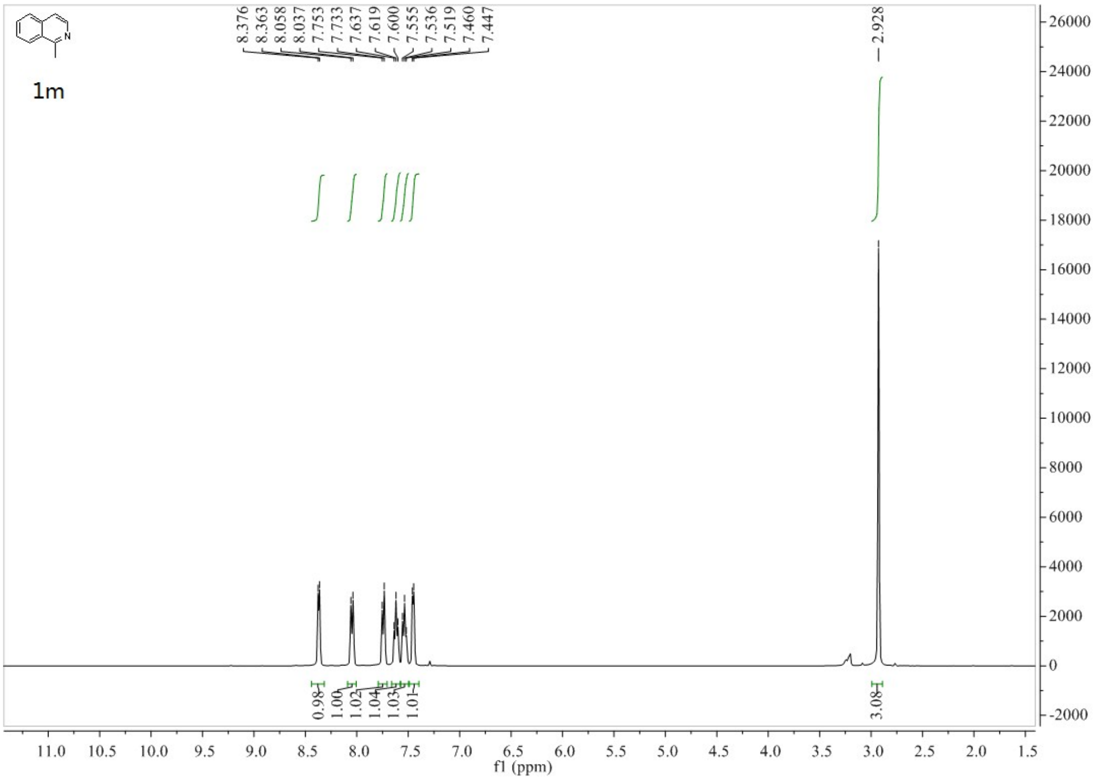

3k
O_2N
N
CD_3
163.24
150.00
144.98
137.72
137.61
130.39
125.25
124.34
123.96
122.97
25.70
25.48
25.29
24.88
24.71
f1 (ppm)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200

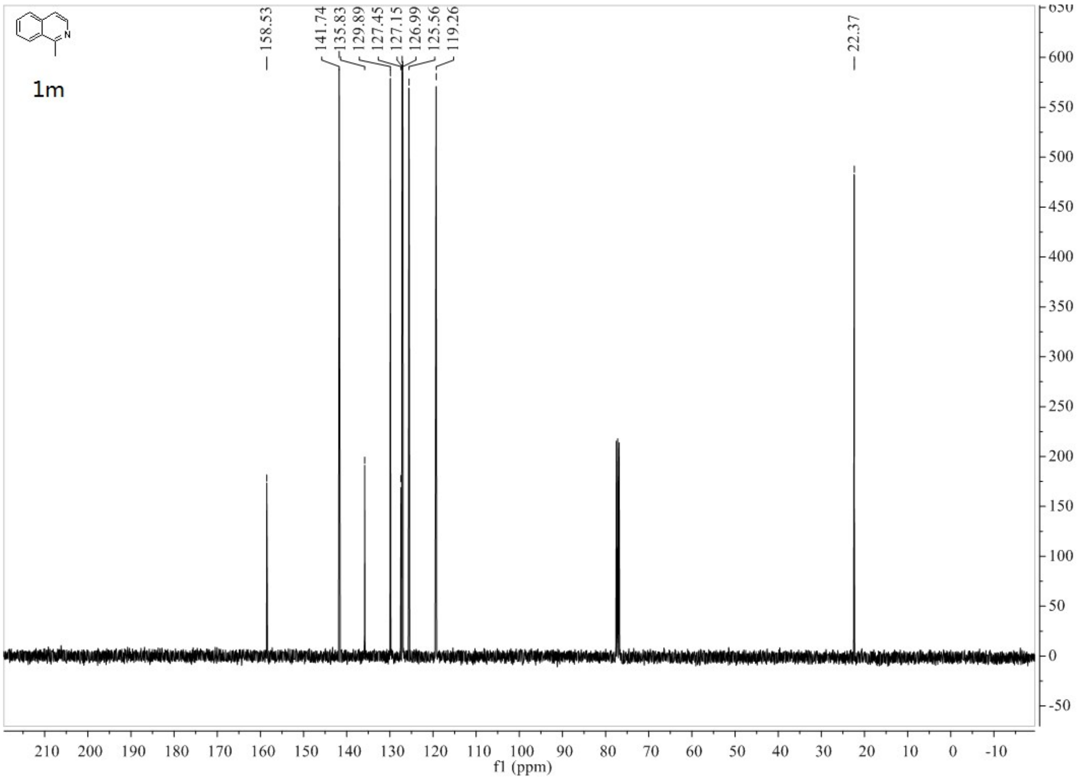

1l
8.548
8.283
8.261
8.157
8.136
8.059
8.037
7.370
7.349
3.988
2.780
1.00
1.01
1.02
1.00
1.01
3.01
3.05
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

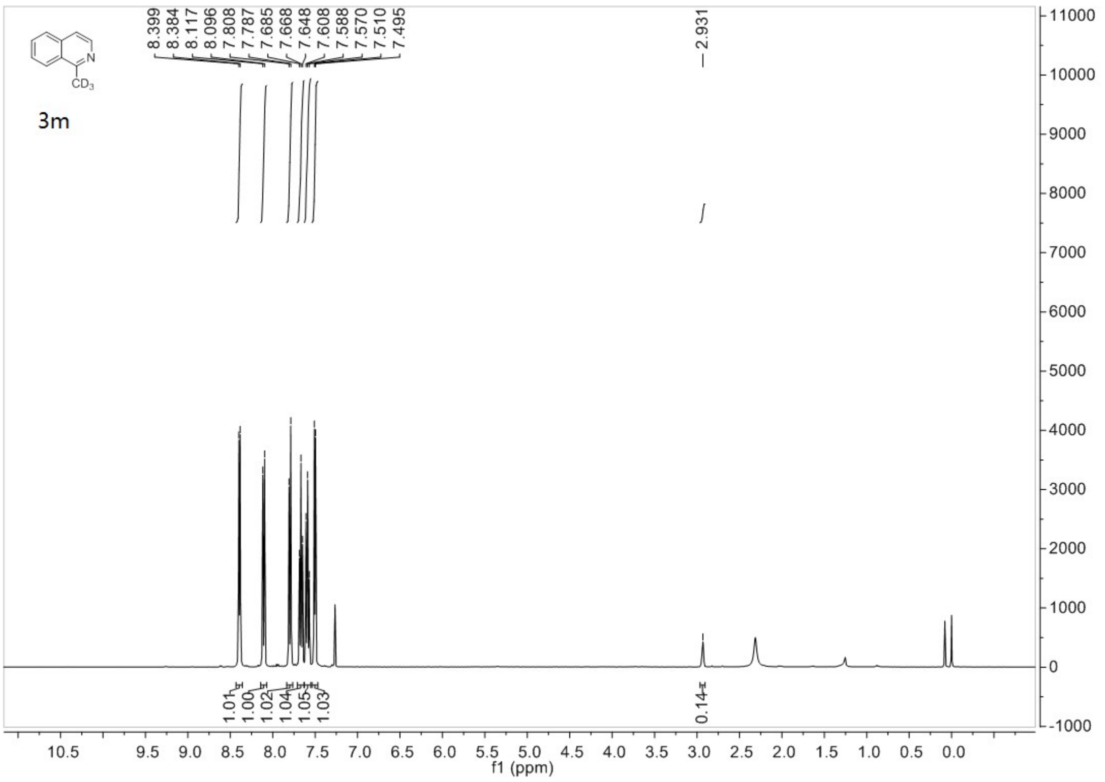

1l
166.78
161.63
149.79
137.35
130.72
129.06
128.93
127.29
125.64
122.86
52.37
25.61
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


3l
CD3
N
O
8.443
8.189
8.167
8.050
8.029
7.965
7.943
7.264
7.243
3.896
2.655
1.00
1.03
1.04
1.03
0.94
3.10
0.07
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 -0.5
f1 (ppm)
30000 28000 26000 24000 22000 20000 18000 16000 14000 12000 10000 8000 6000 4000 2000 0 -2000

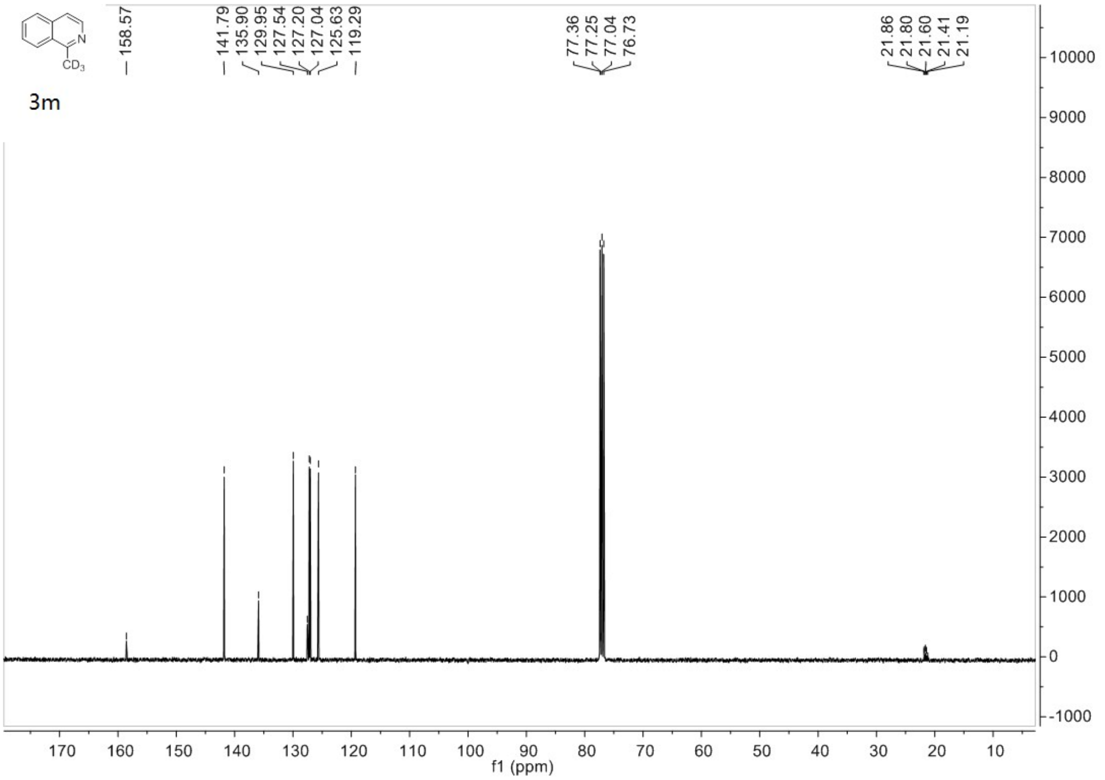

3l
CD3
N
O
166.73
161.54
149.76
137.29
130.69
129.00
128.91
127.24
125.61
122.81
52.34
25.00
24.80
24.61
1.03
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100 -200


N
1m
8.376
8.363
8.058
8.037
7.753
7.733
7.637
7.619
7.600
7.555
7.536
7.519
7.460
7.447
2.928
0.98
1.00
1.02
1.04
1.03
1.01
3.08
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
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
f1 (ppm)

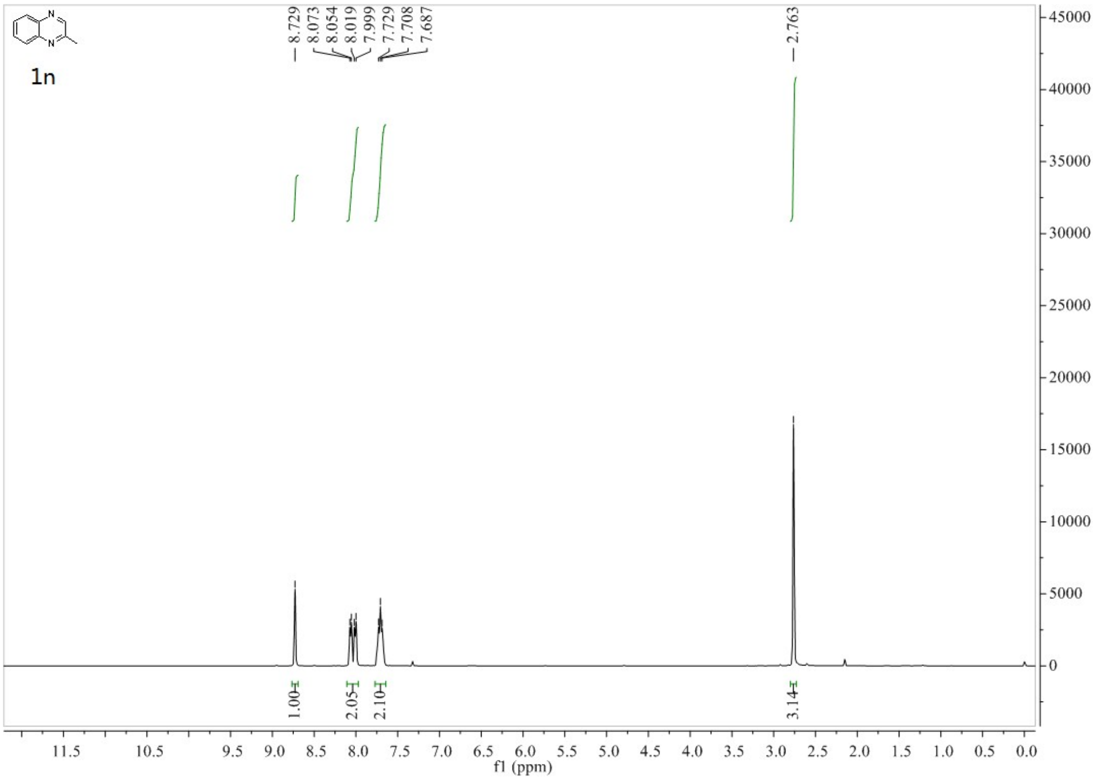

N
1m
158.53
141.74
135.83
129.89
127.45
127.15
126.99
125.56
119.26
22.37
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

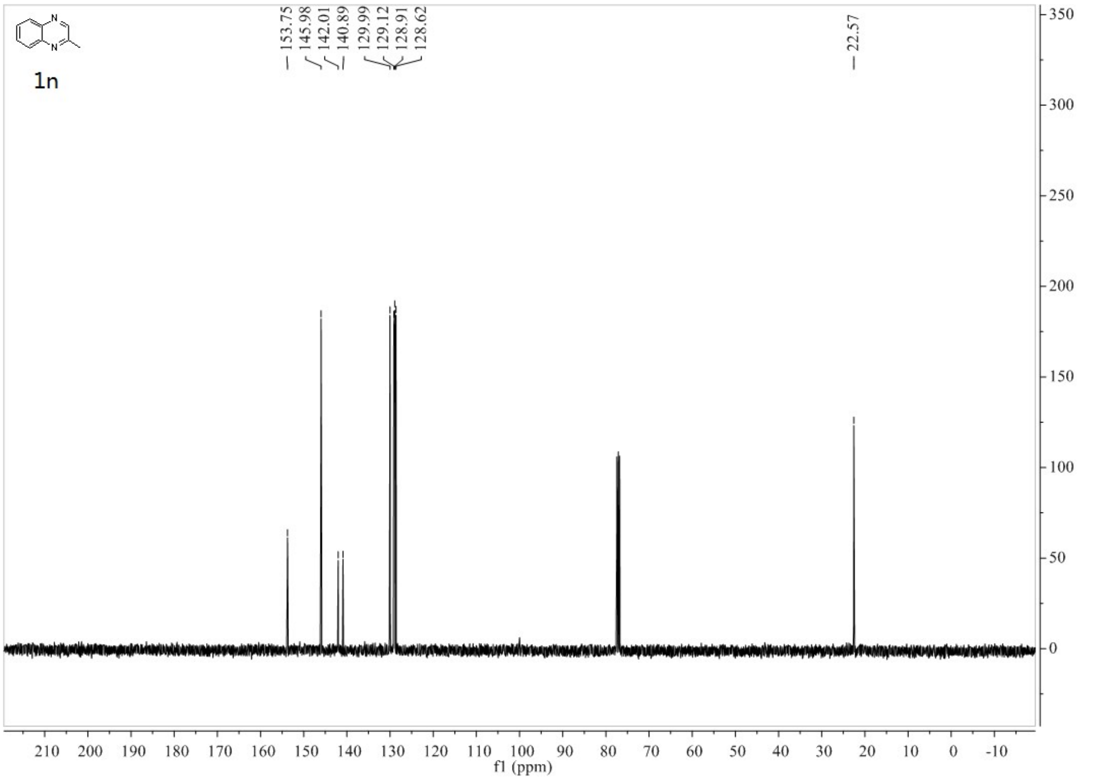

3m

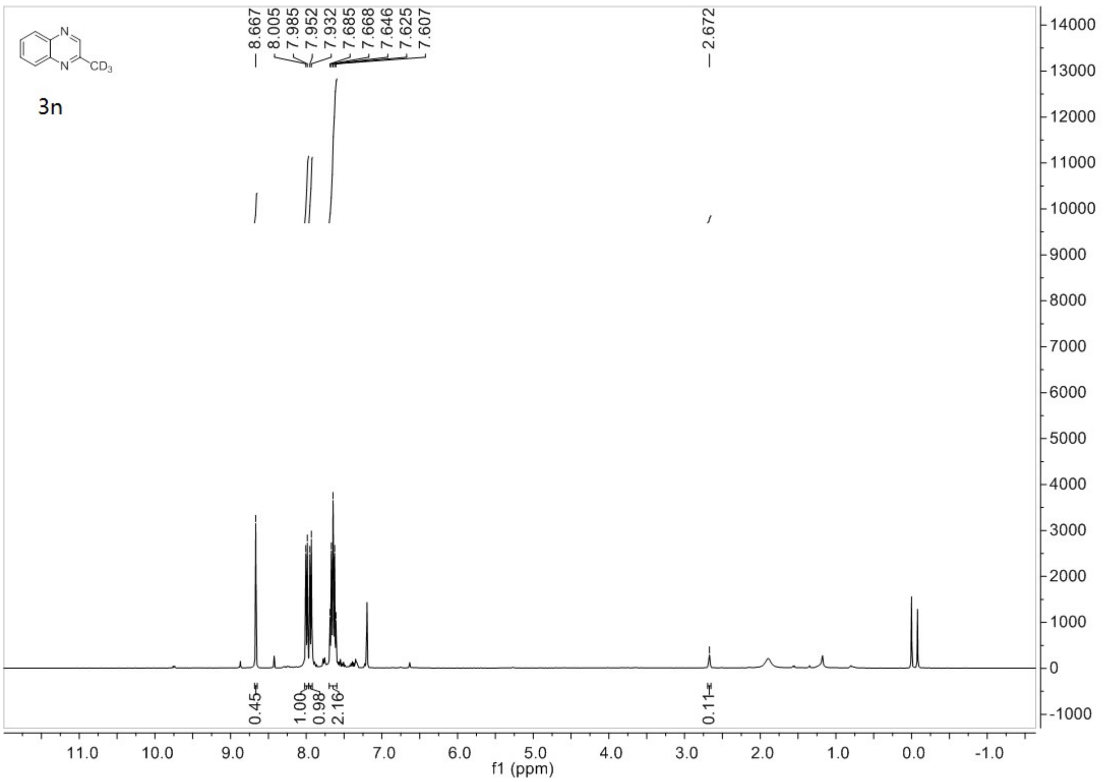
N
CD3
8.399
8.384
8.117
8.096
7.808
7.787
7.685
7.668
7.648
7.608
7.588
7.570
7.510
7.495
2.931
1.01
1.00
1.02
1.04
1.05
1.03
0.14
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

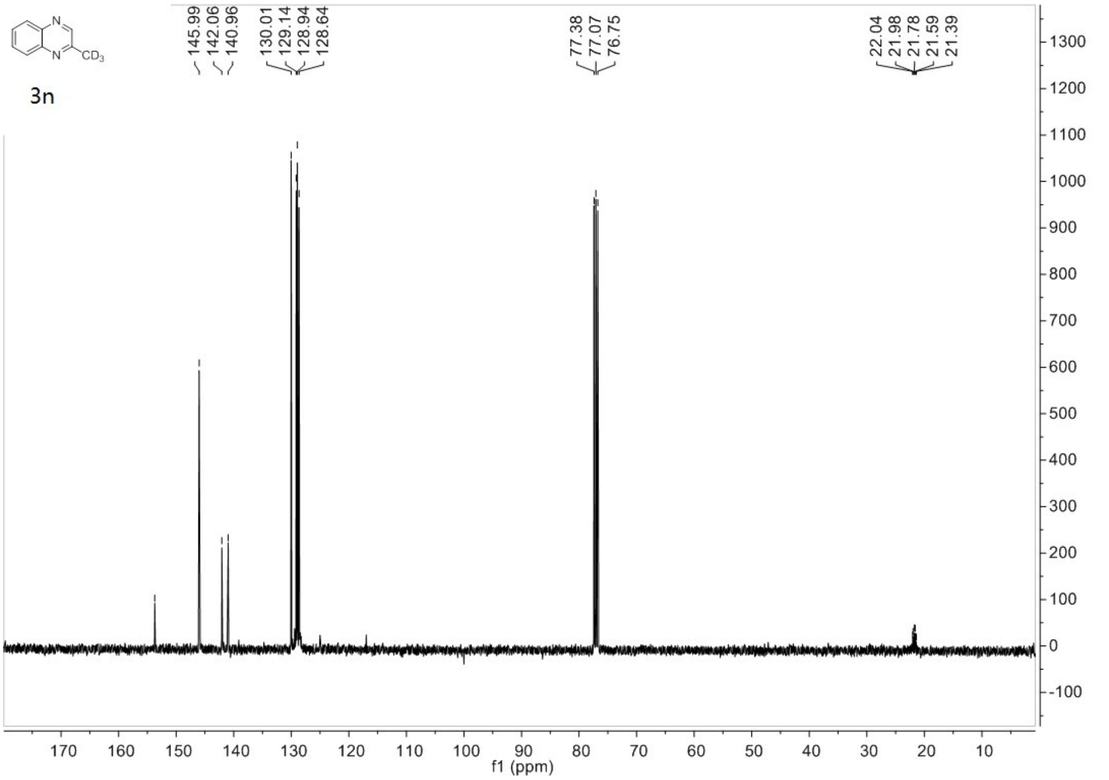

3m

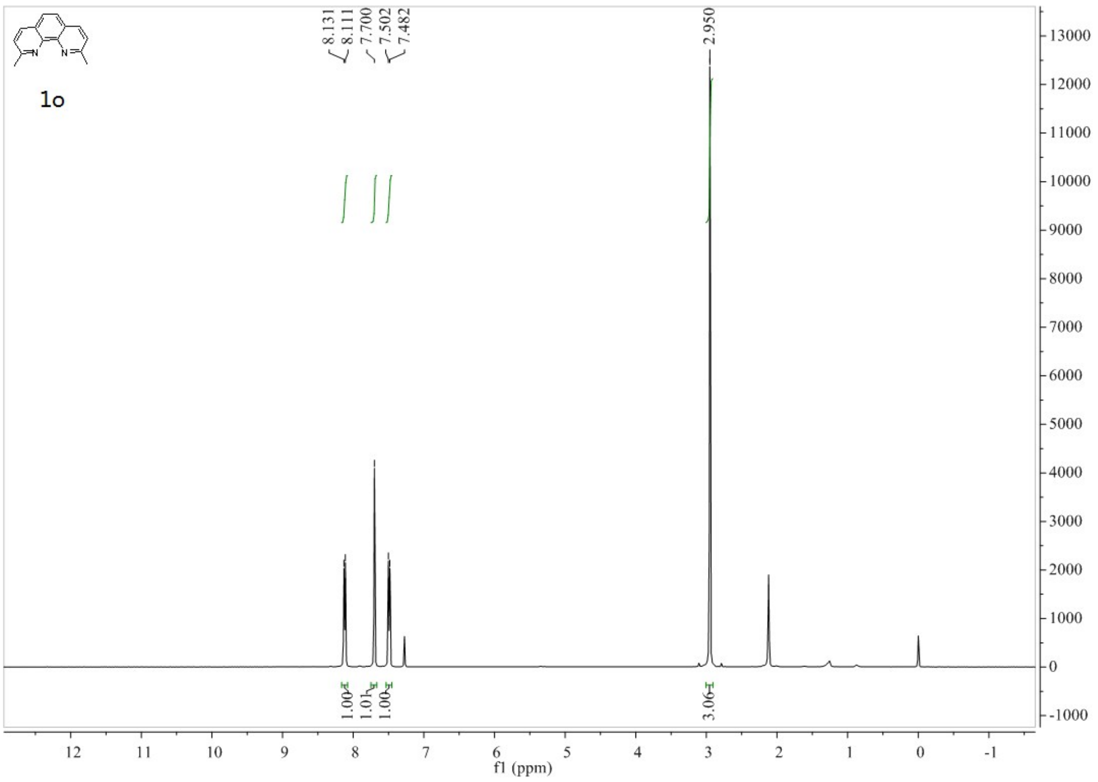
N
CD3
158.57
141.79
135.90
129.95
127.54
127.20
127.04
125.63
119.29
77.36
77.25
77.04
76.73
21.86
21.80
21.60
21.41
21.19
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

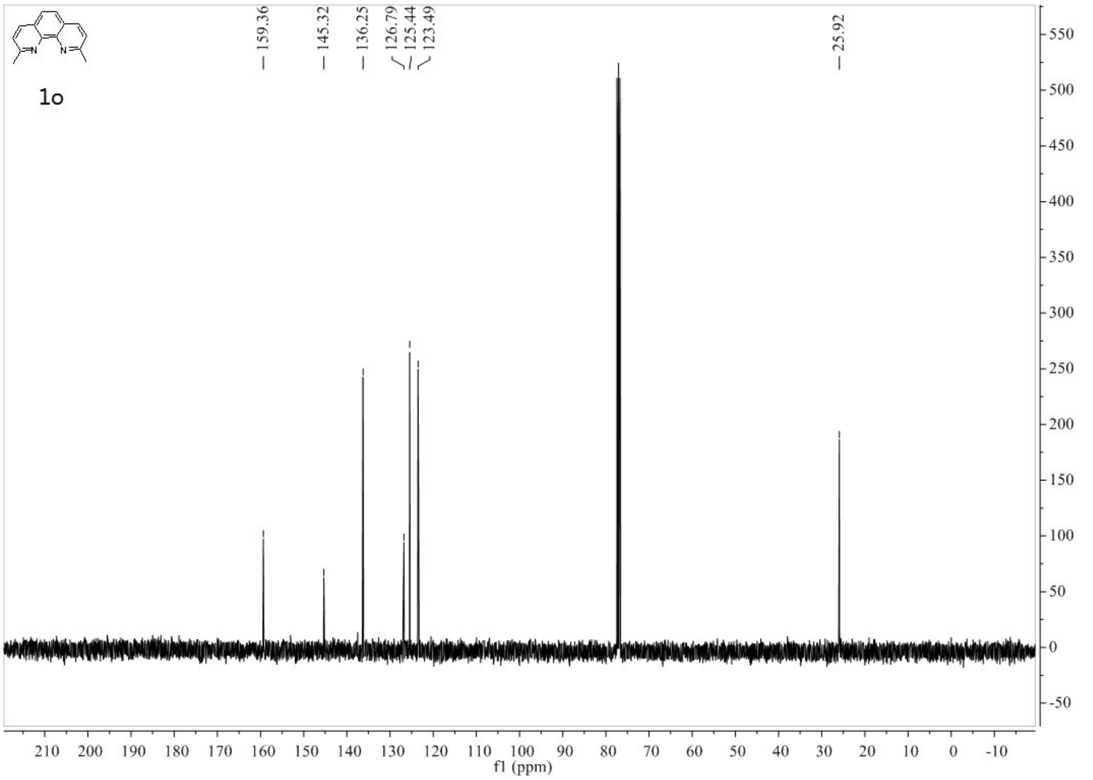

1n
8.729
8.073
8.054
8.019
7.999
7.729
7.708
7.687
2.763
1.00
2.05
2.10
3.14
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

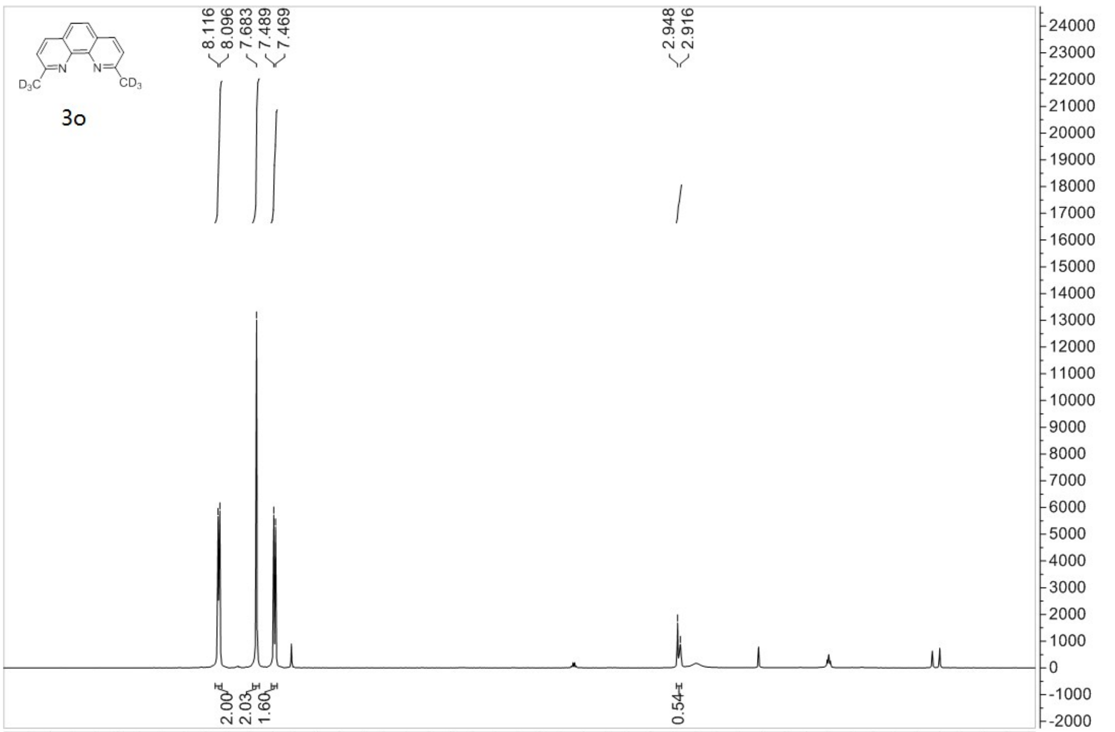

1n
153.75
145.98
142.01
140.89
129.99
129.12
128.91
128.62
22.57
350
300
250
200
150
100
50
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

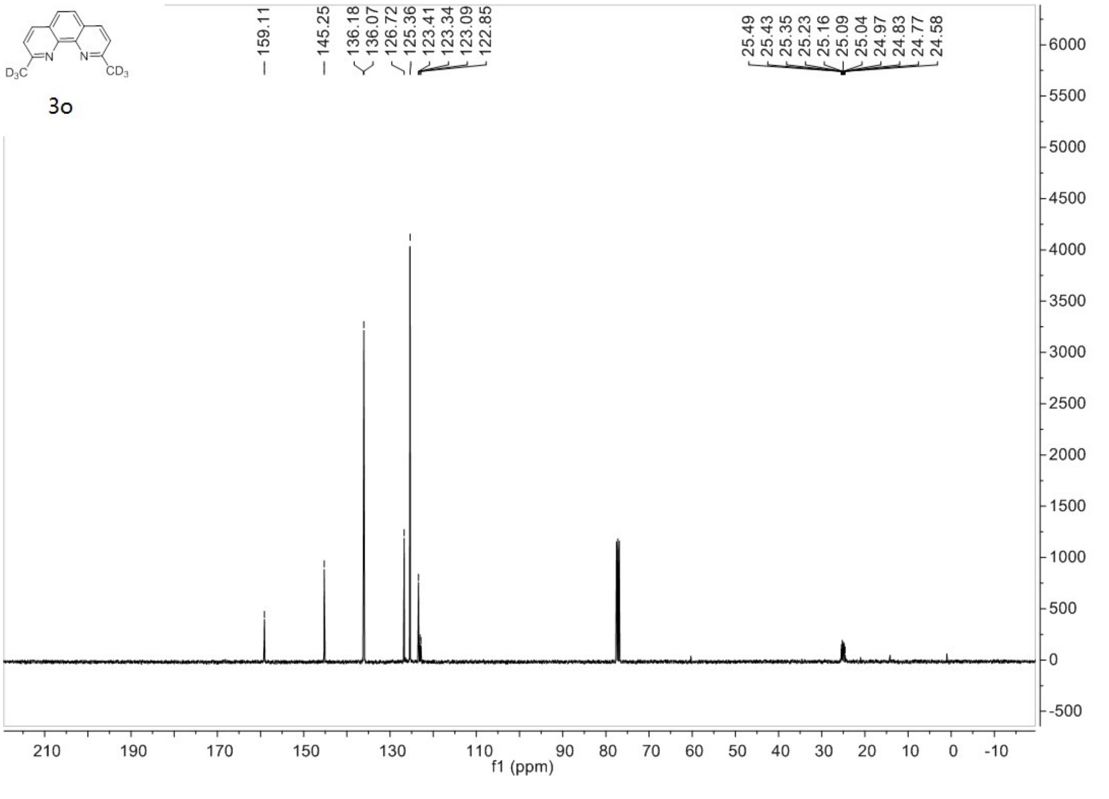

CD3
3n
8.667
8.005
7.985
7.952
7.932
7.685
7.668
7.646
7.625
7.607
2.672
0.45
1.00
0.98
2.16
0.11
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

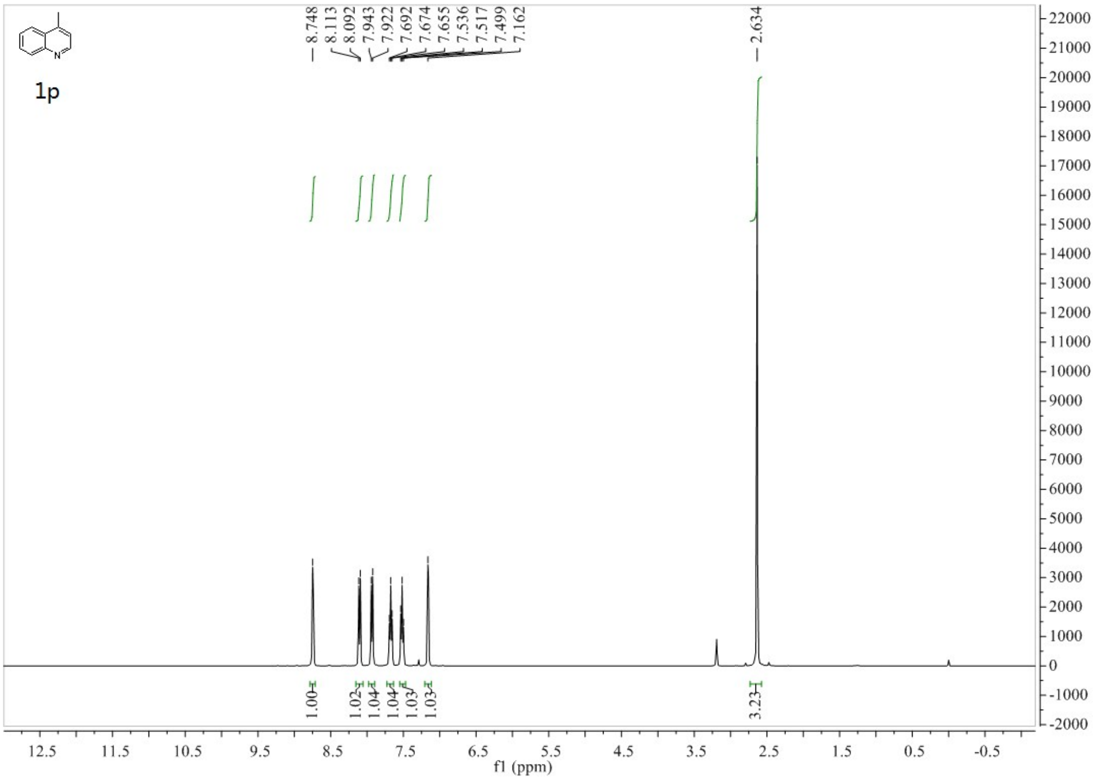

CD3
3n
145.99
142.06
140.96
130.01
129.14
128.94
128.64
77.38
77.07
76.75
22.04
21.98
21.78
21.59
21.39
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

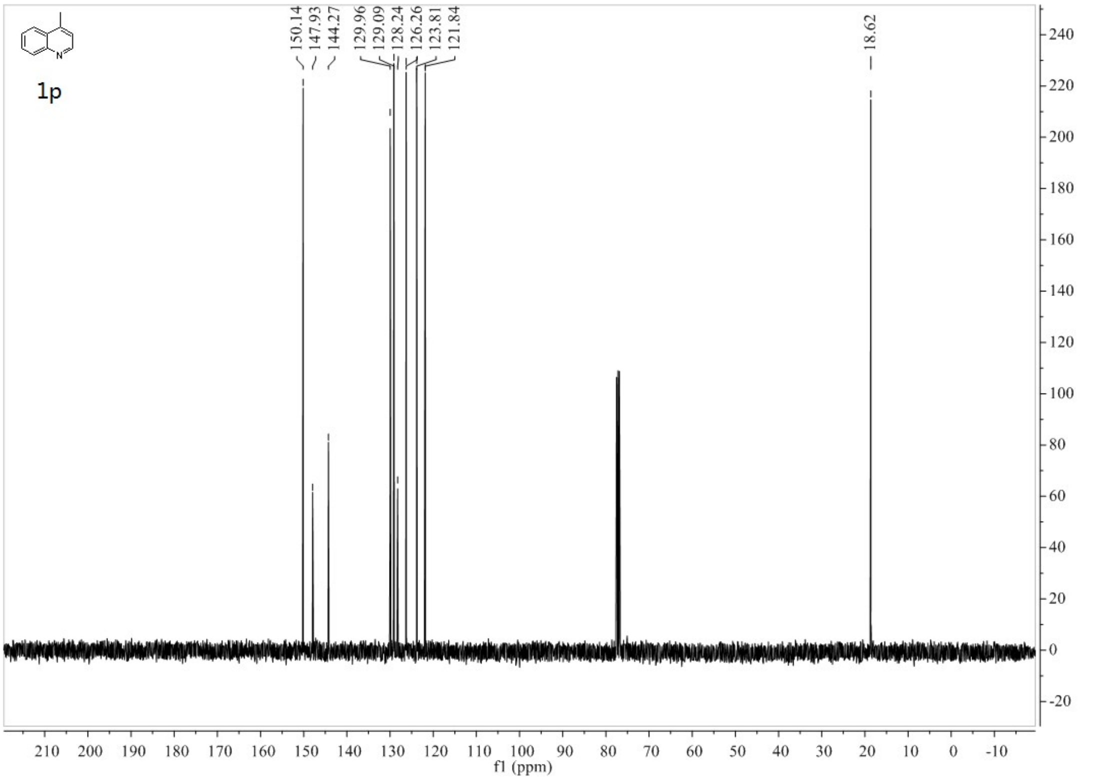

1o
8.131
8.111
7.700
7.502
7.482
2.950
1.00
1.01
1.00
3.06
f1 (ppm)
12 11 10 9 8 7 6 5 4 3 2 1 0 -1
13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000

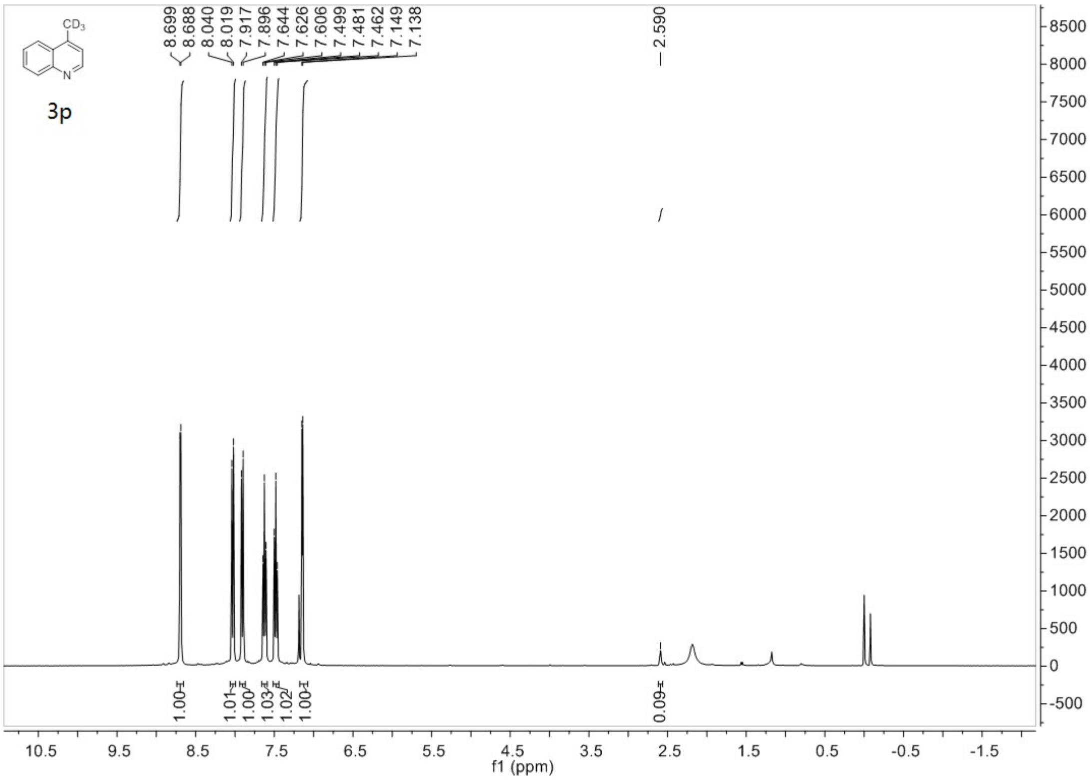

1o
159.36
145.32
136.25
126.79
125.44
123.49
25.92
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
550 500 450 400 350 300 250 200 150 100 50 0 -50

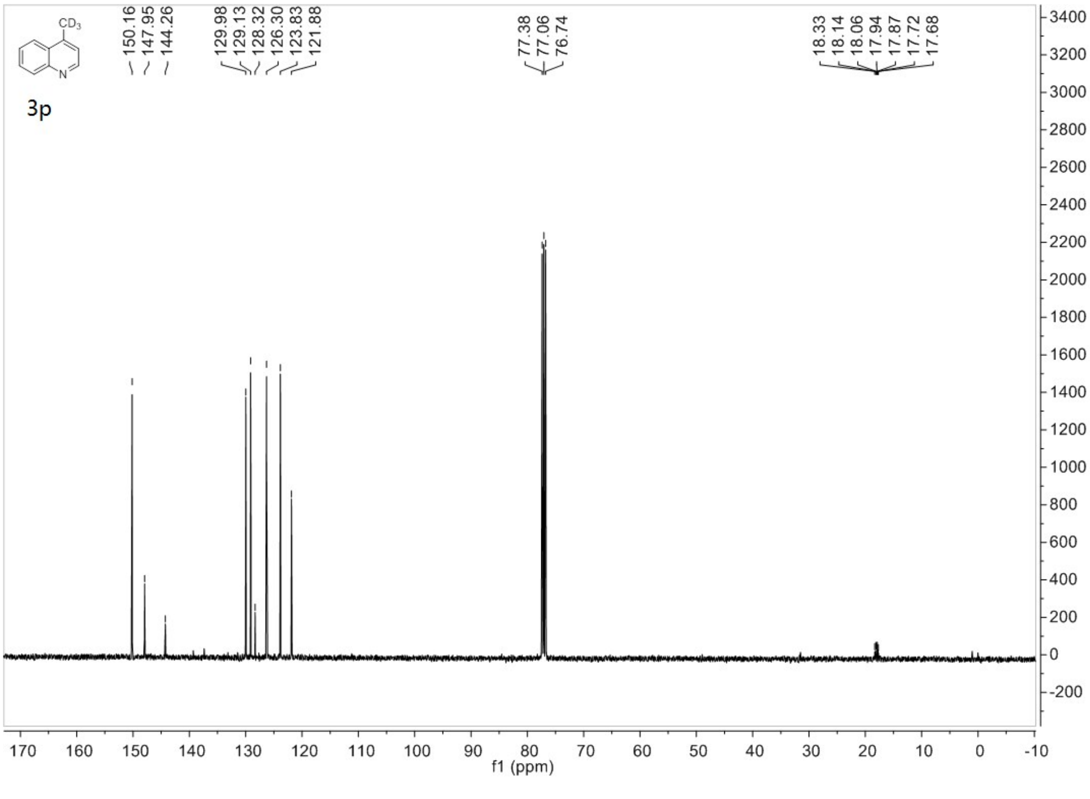

D3C
CD3
3o
8.116
8.096
7.683
7.489
7.469
2.948
2.916
2.00
2.03
1.60
0.54
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
0.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

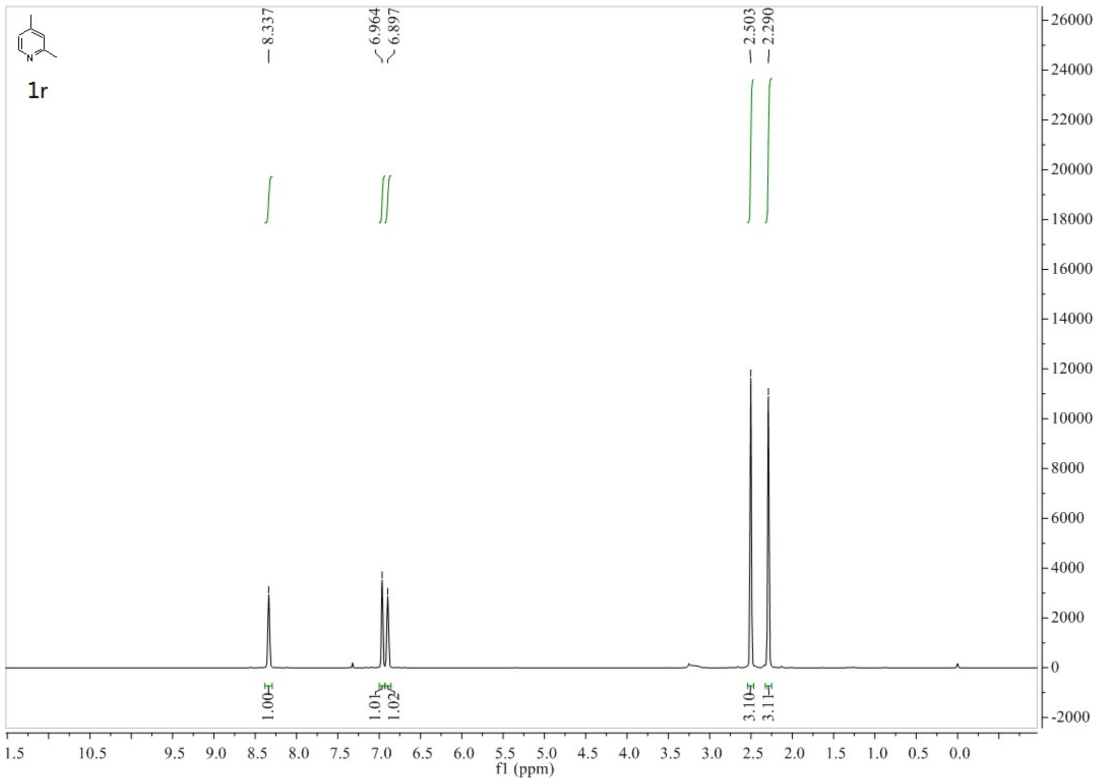

D3C
CD3
3o
159.11
145.25
136.18
136.07
126.72
125.36
123.41
123.34
123.09
122.85
25.49
25.43
25.35
25.23
25.16
25.09
25.04
24.97
24.83
24.77
24.58
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

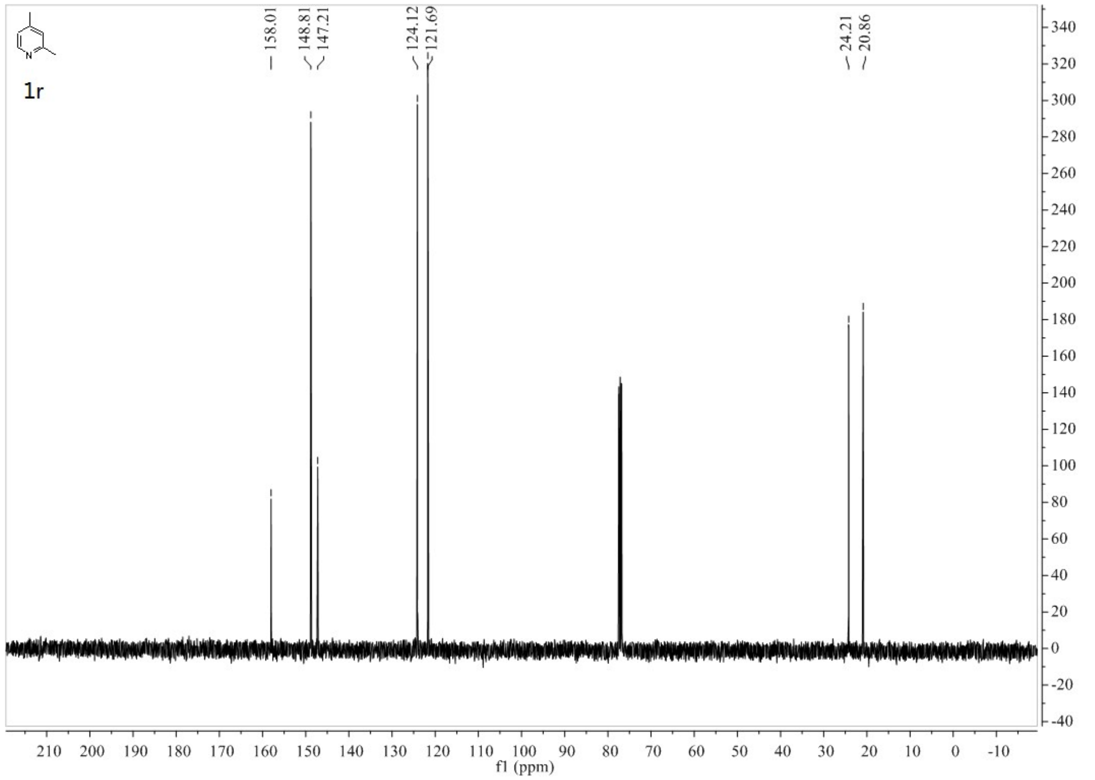

1p
8.748
8.113
8.092
7.943
7.922
7.692
7.674
7.655
7.536
7.517
7.499
7.162
2.634
1.00
1.02
1.04
1.04
1.03
1.03
3.23
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

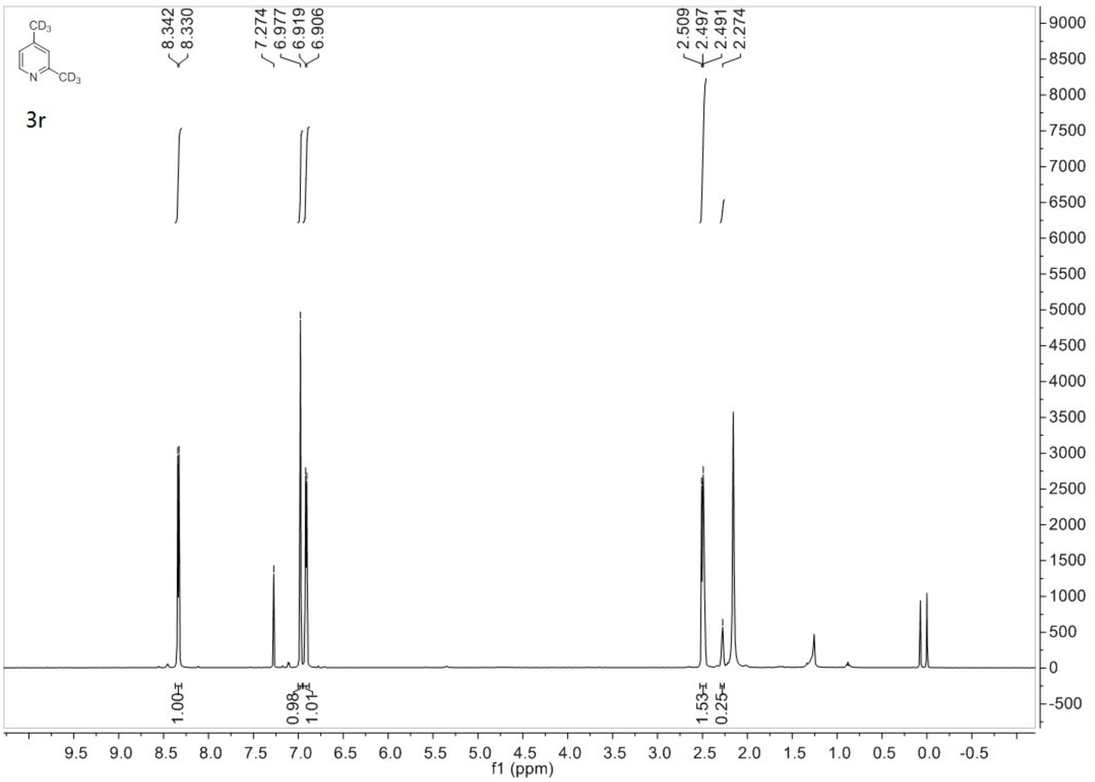

1p
150.14
147.93
144.27
129.96
129.09
128.24
126.26
123.81
121.84
18.62
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CD3
N
3p
8.699
8.688
8.040
8.019
7.917
7.896
7.644
7.626
7.606
7.499
7.481
7.462
7.149
7.138
2.590
1.00
1.01
1.00
1.03
1.02
1.00
0.09
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)

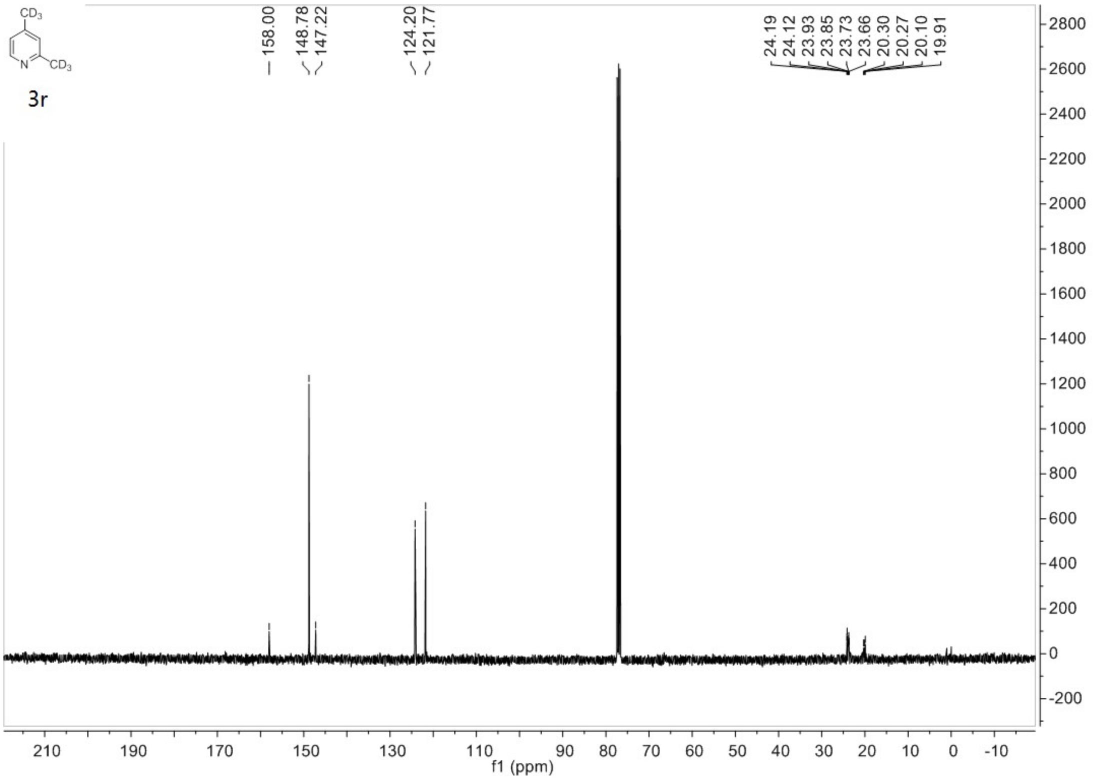

CD3
N
3p
150.16
147.95
144.26
129.98
129.13
128.32
126.30
123.83
121.88
77.38
77.06
76.74
18.33
18.14
18.06
17.94
17.87
17.72
17.68
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


N
1r
8.337
6.964
6.897
2.503
2.290
1.00
1.01
1.02
3.10
3.11
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
1.5
10.5
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)

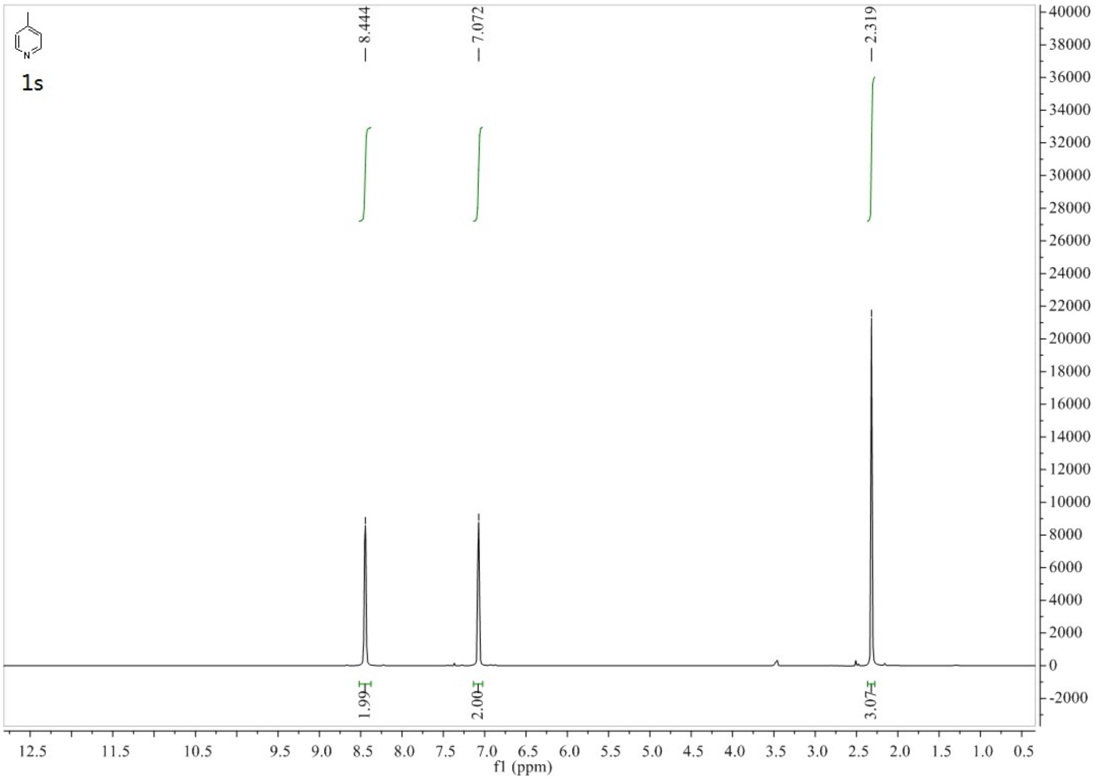

N
1r
158.01
148.81
147.21
124.12
121.69
24.21
20.86
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

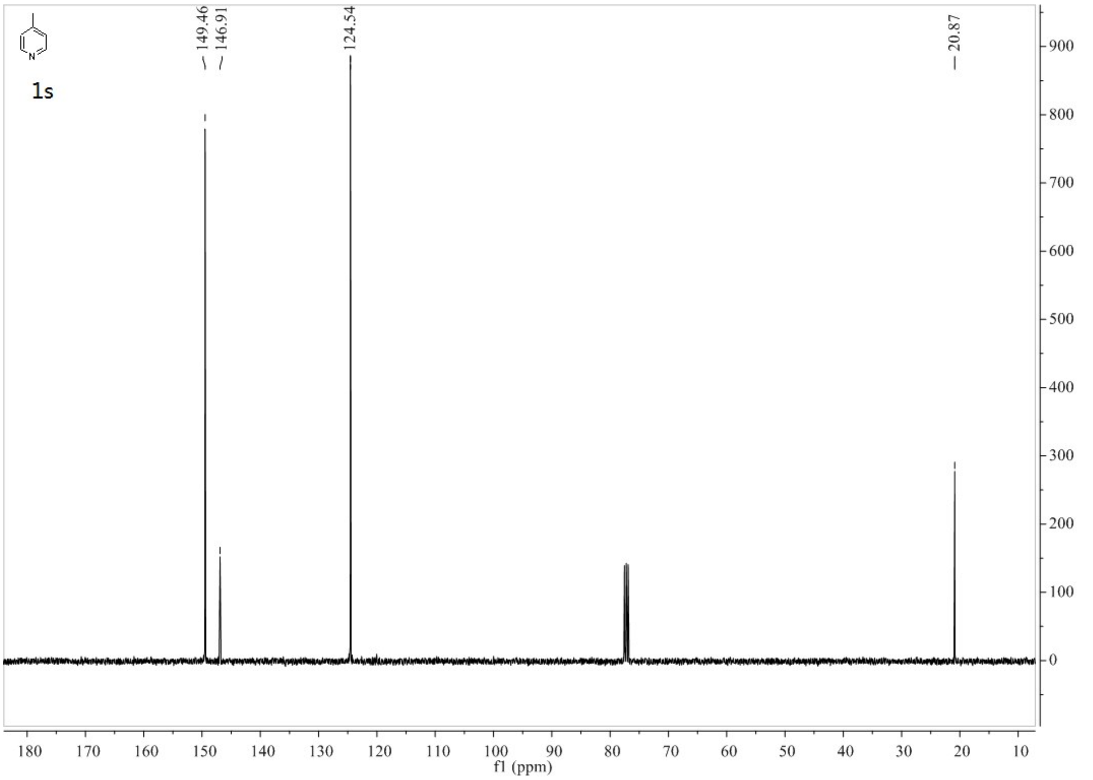


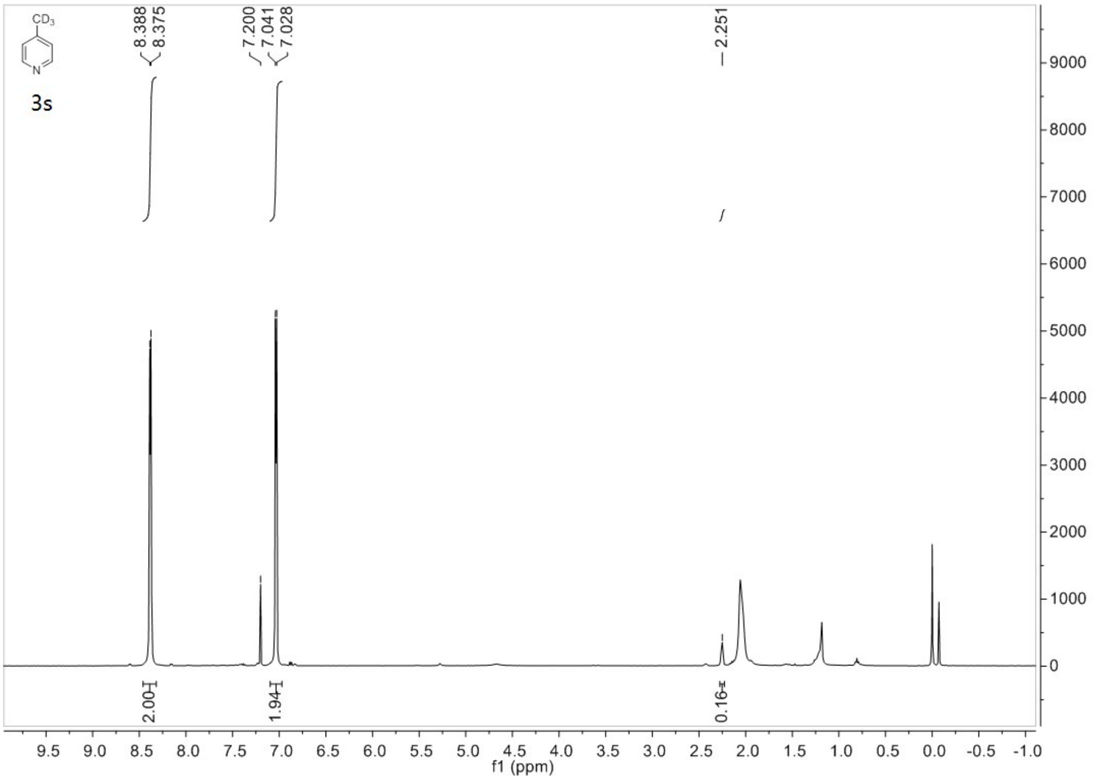
CD3
N
CD3
3r
8.342
8.330
7.274
6.977
6.919
6.906
2.509
2.497
2.491
2.274
1.00
0.98
1.01
1.53
0.25
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

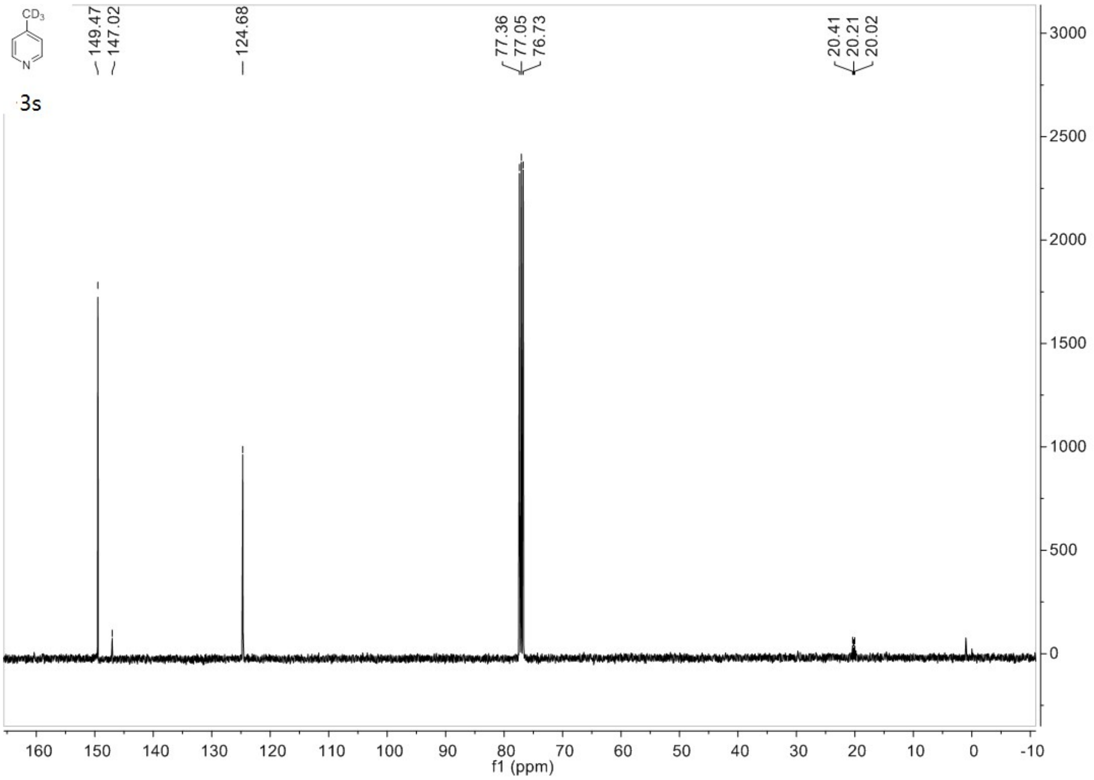


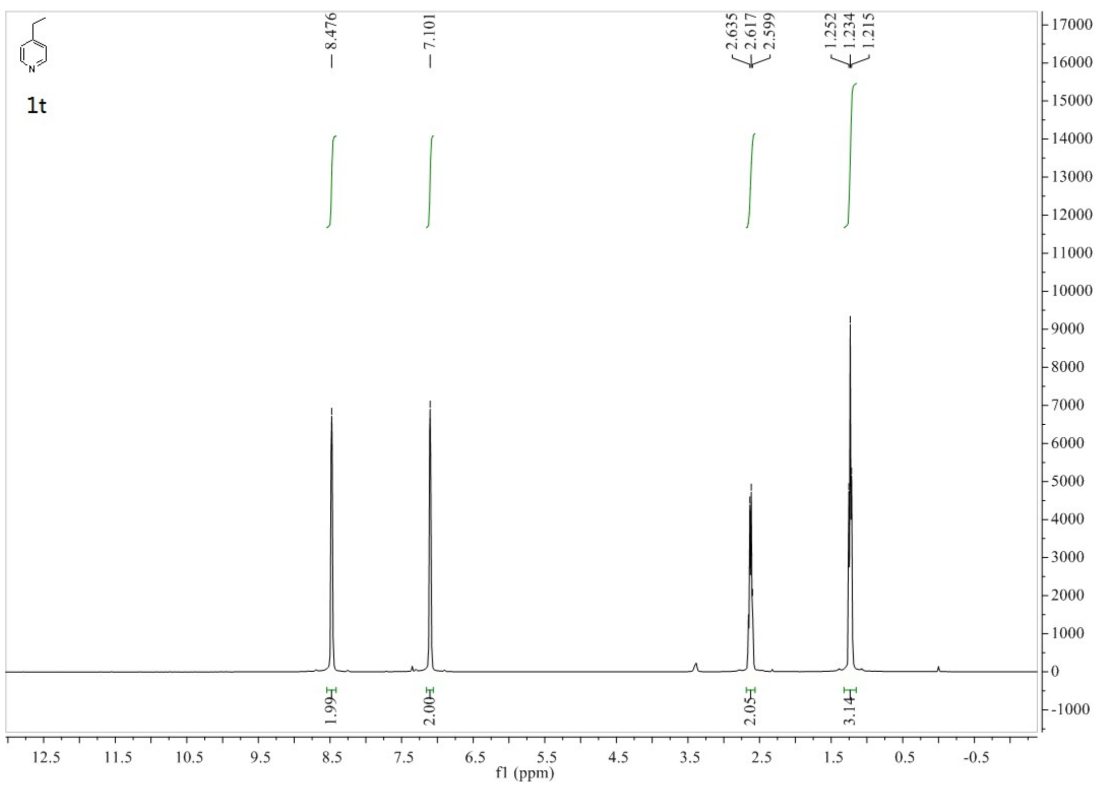
CD3
N
CD3
3r
158.00
148.78
147.22
124.20
121.77
24.19
24.12
23.93
23.85
23.73
23.66
20.30
20.27
20.10
19.91
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

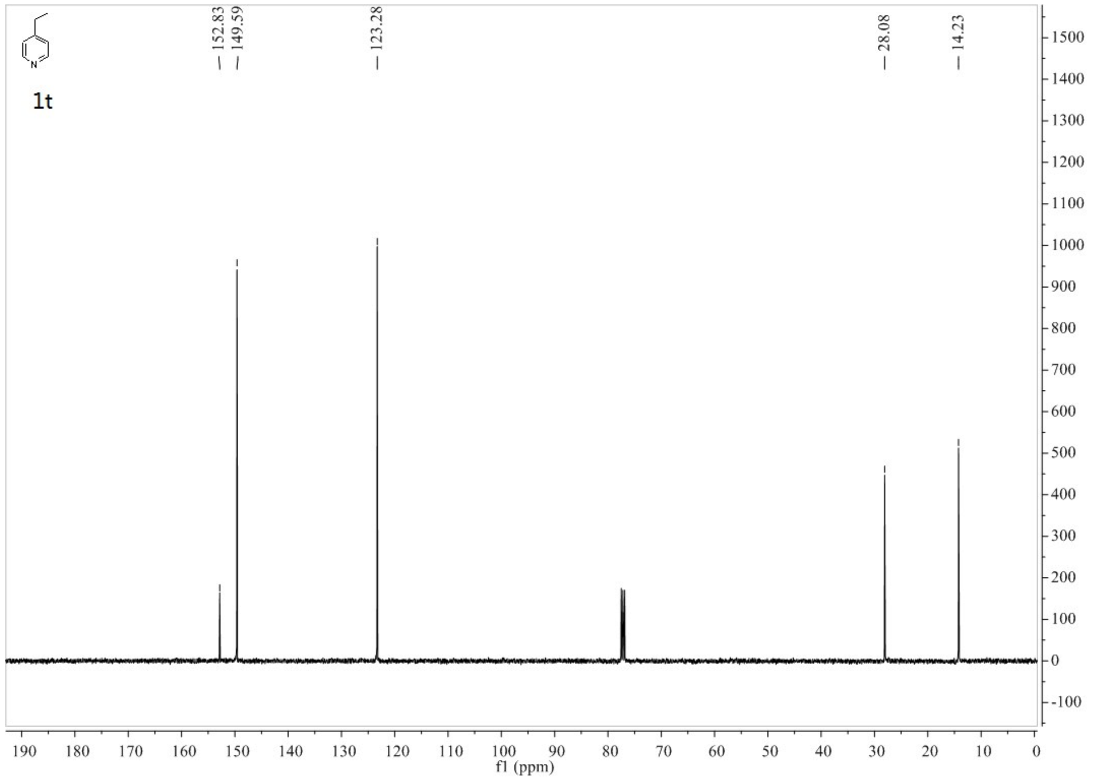

1s
8.444
7.072
2.319
1.99
2.00
3.07
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
40000 38000 36000 34000 32000 30000 28000 26000 24000 22000 20000 18000 16000 14000 12000 10000 8000 6000 4000 2000 0 -2000

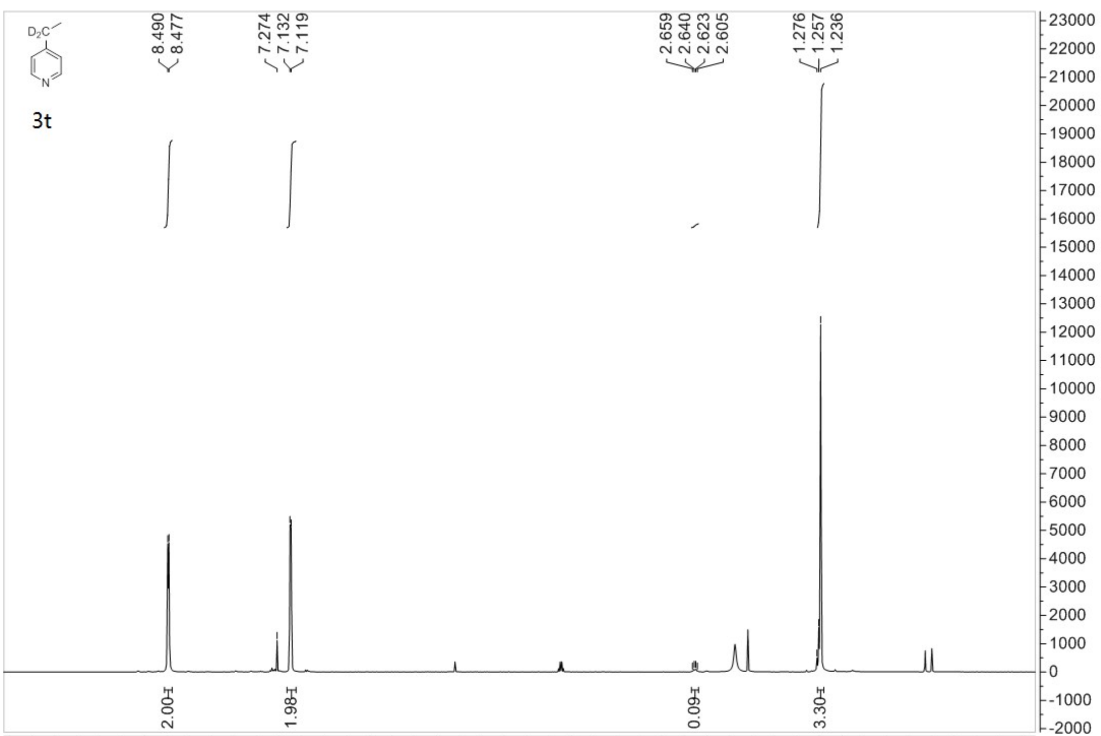

1s
149.46
146.91
124.54
20.87
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)
900 800 700 600 500 400 300 200 100 0

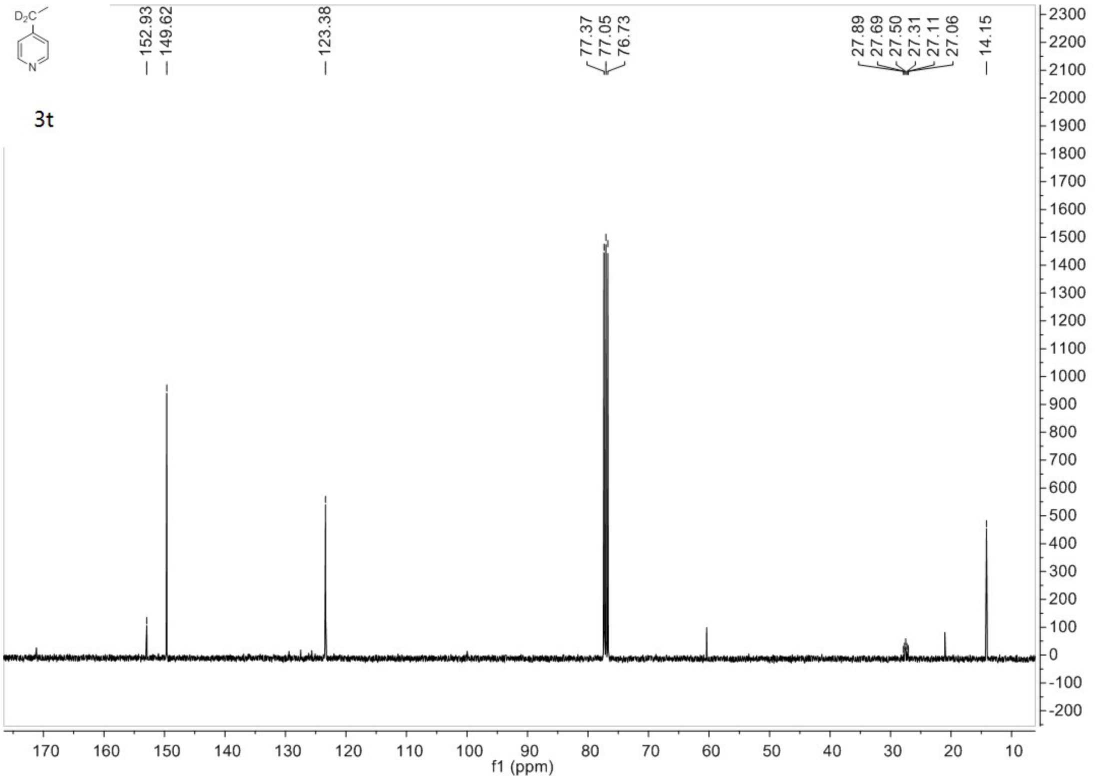

3s
CD3
N
8.388
8.375
7.200
7.041
7.028
2.251
2.00
1.94
0.16
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

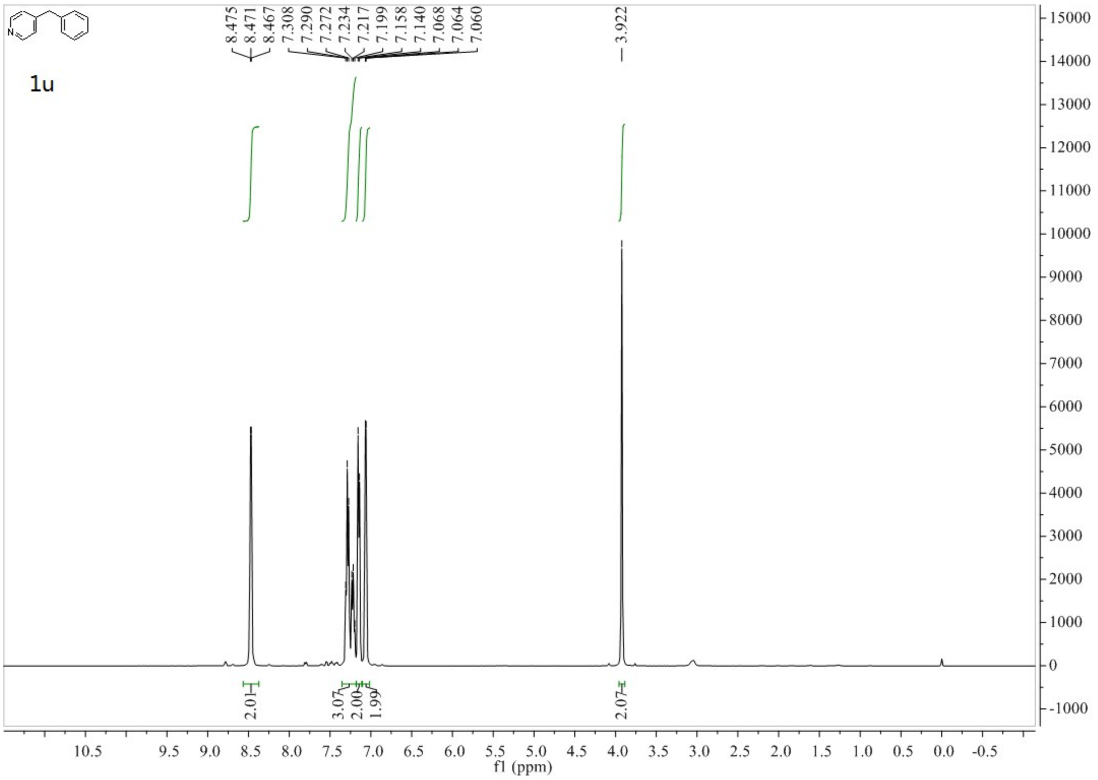

3s
CD3
N
149.47
147.02
124.68
77.36
77.05
76.73
20.41
20.21
20.02
3000
2500
2000
1500
1000
500
0
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

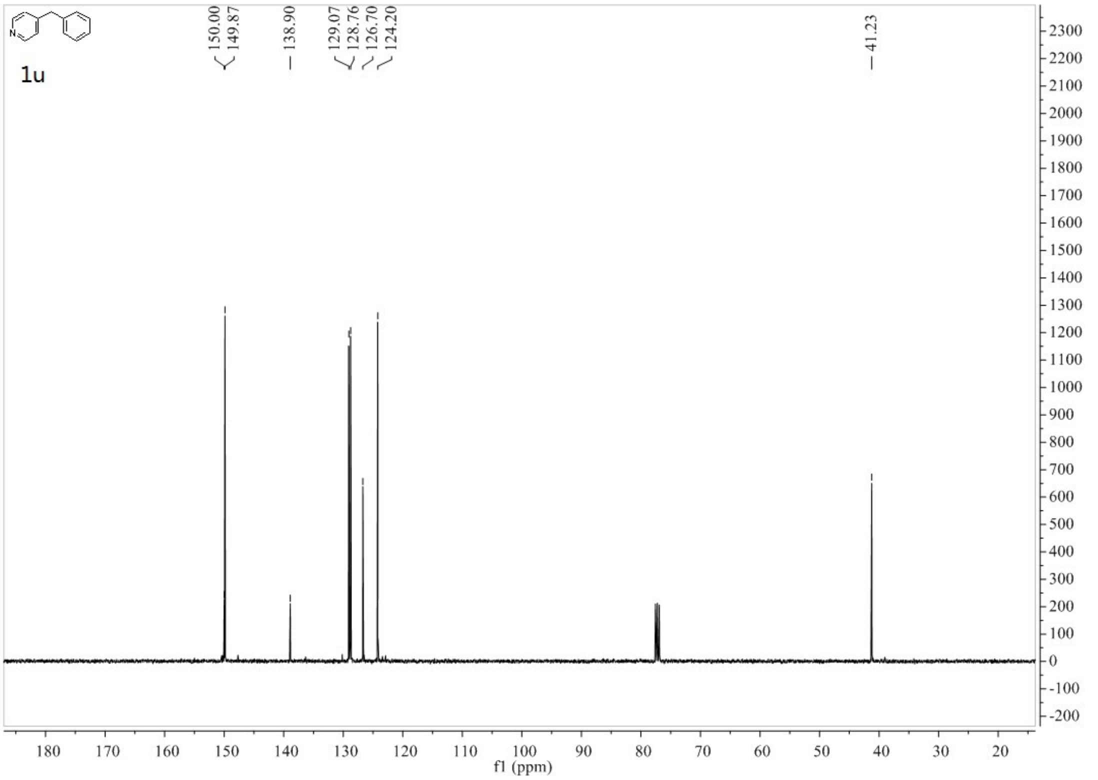

1t
8.476
7.101
2.635
2.617
2.599
1.252
1.234
1.215
1.99
2.00
2.05
3.14
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

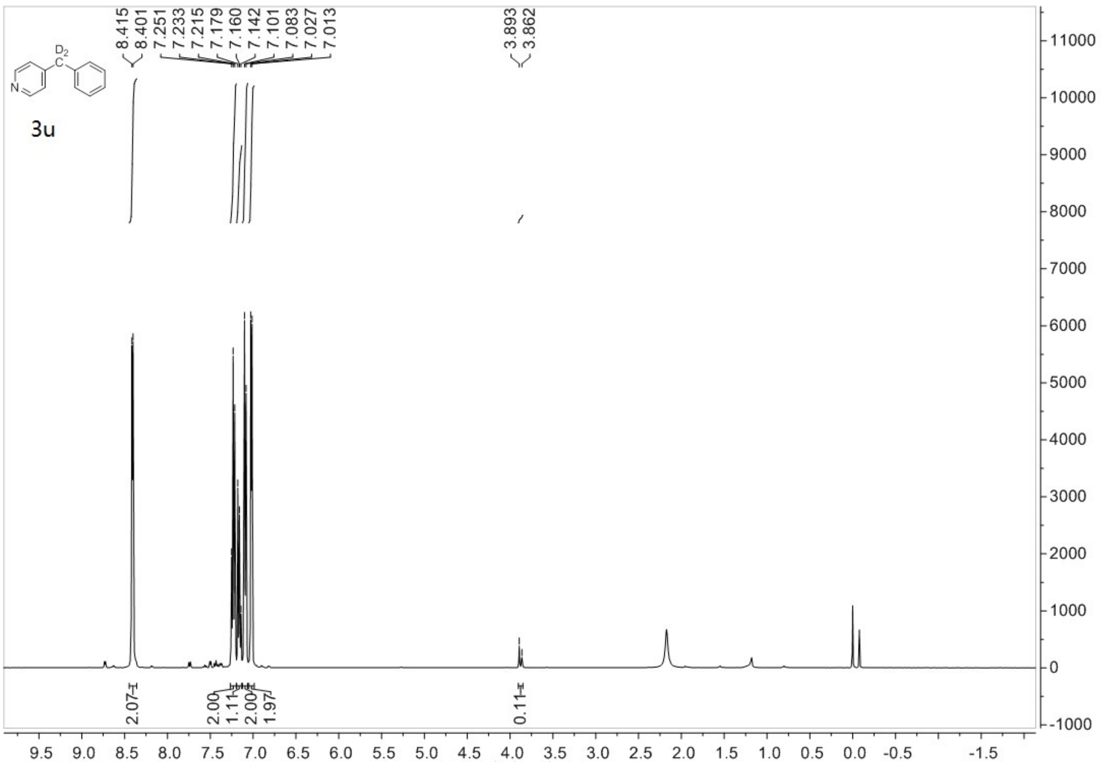

1t
152.83
149.59
123.28
28.08
14.23
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

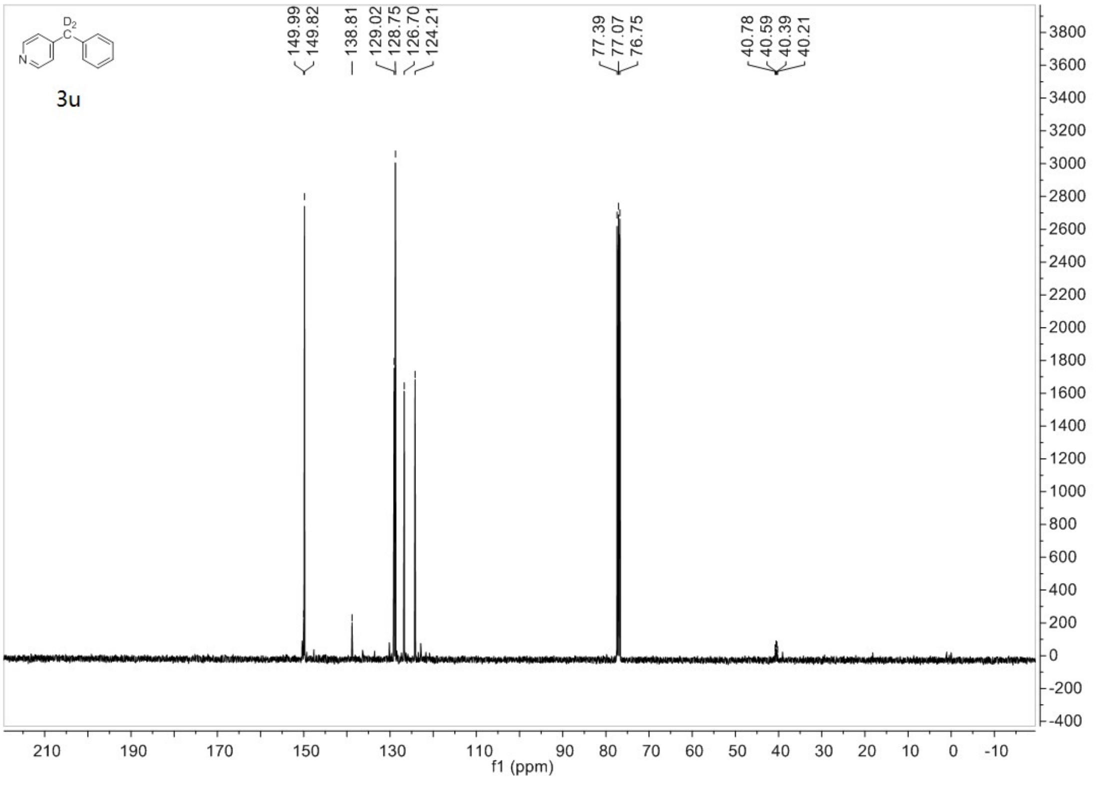

D2C
N
3t
8.490
8.477
7.274
7.132
7.119
2.659
2.640
2.623
2.605
1.276
1.257
1.236
2.00
1.98
0.09
3.30
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

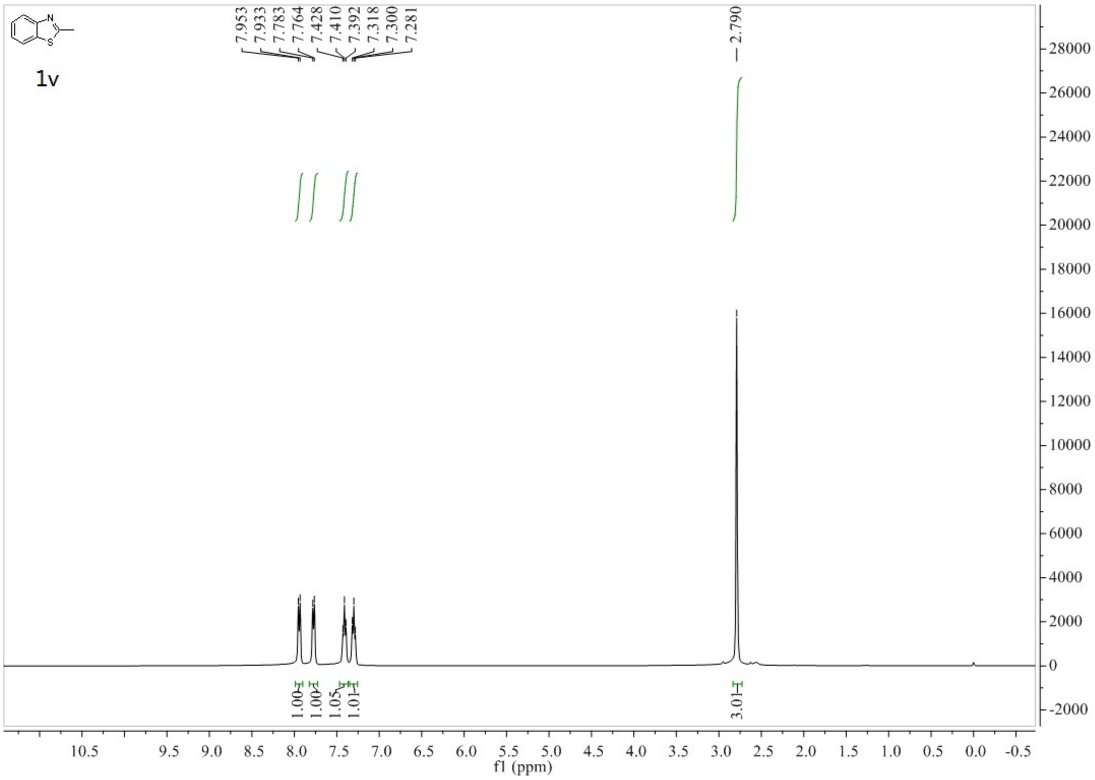

D2C
N
3t
152.93
149.62
123.38
77.37
77.05
76.73
27.89
27.69
27.50
27.31
27.11
27.06
14.15
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

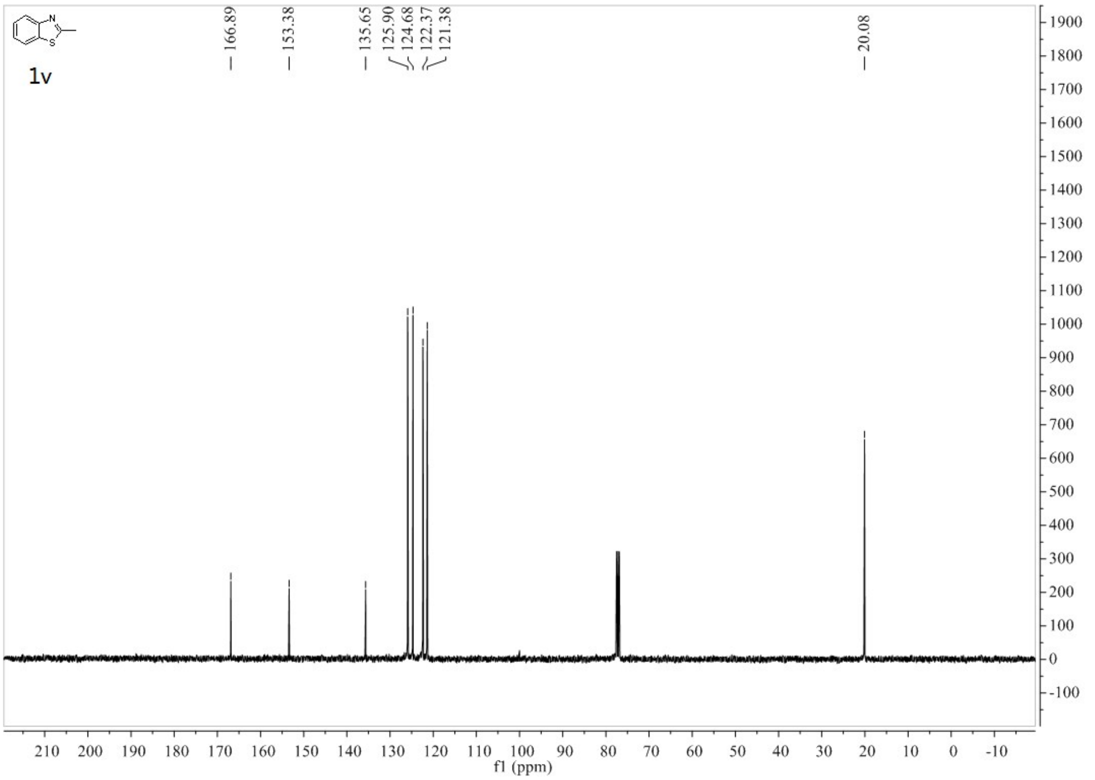

1u
8.475
8.471
8.467
7.308
7.290
7.272
7.234
7.217
7.199
7.158
7.140
7.068
7.064
7.060
3.922
2.01
3.07
2.00
1.99
2.07
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

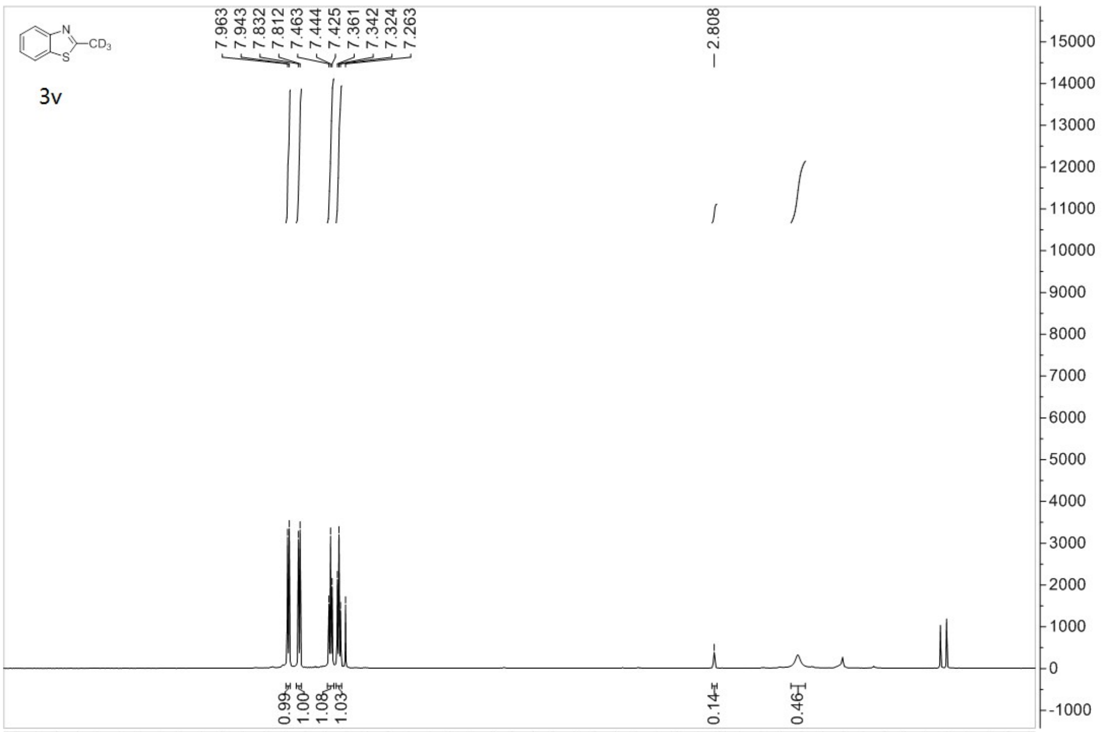

1u
150.00
149.87
138.90
129.07
128.76
126.70
124.20
41.23
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

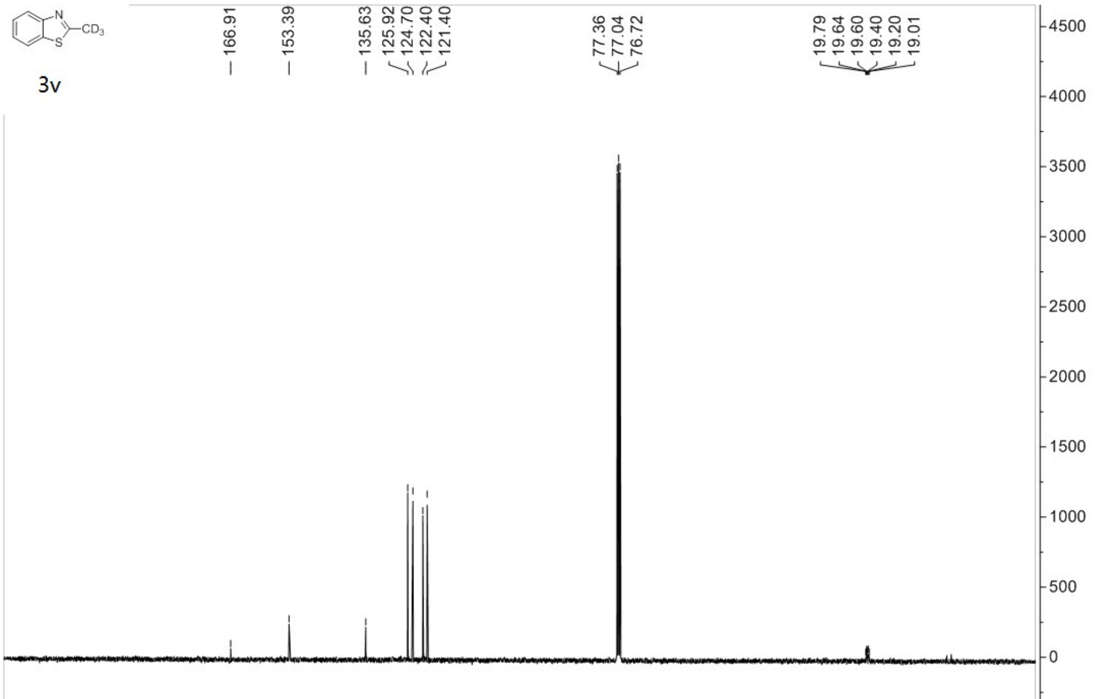

3u
D2
N
8.415
8.401
7.251
7.233
7.215
7.179
7.160
7.142
7.101
7.083
7.027
7.013
3.893
3.862
2.07
2.00
1.11
2.00
1.97
0.11
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.5
f1 (ppm)

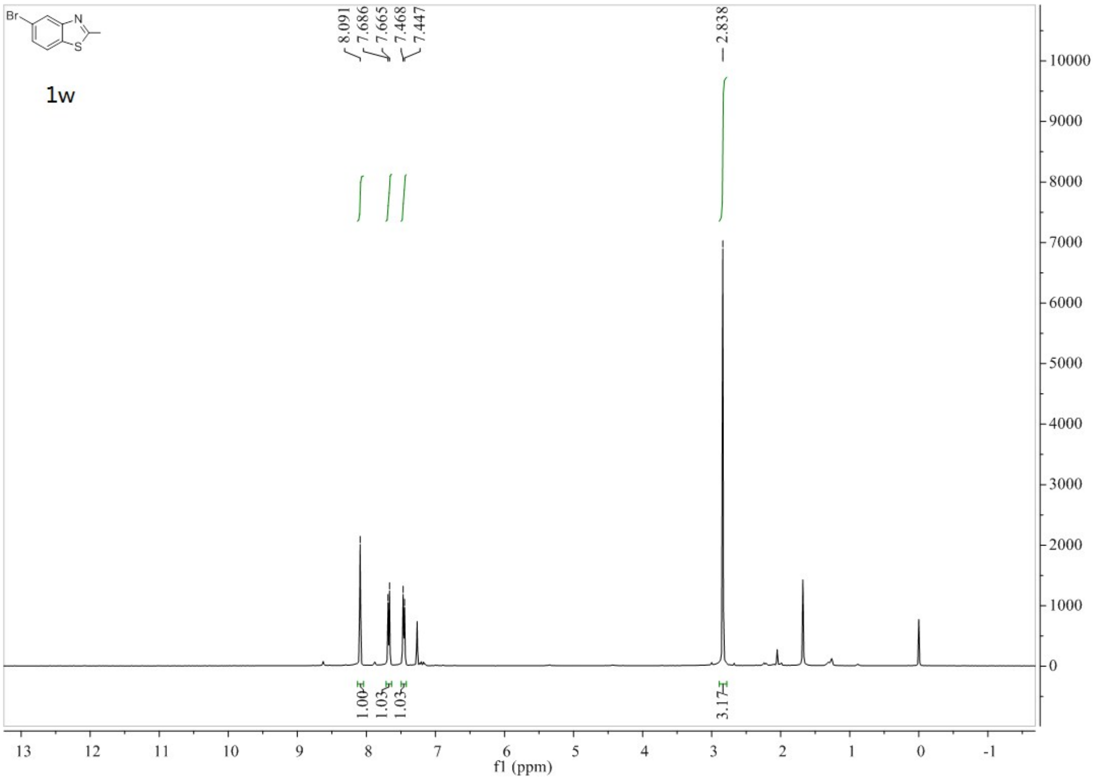

3u
D2
N
149.99
149.82
138.81
129.02
128.75
126.70
124.21
77.39
77.07
76.75
40.78
40.59
40.39
40.21
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

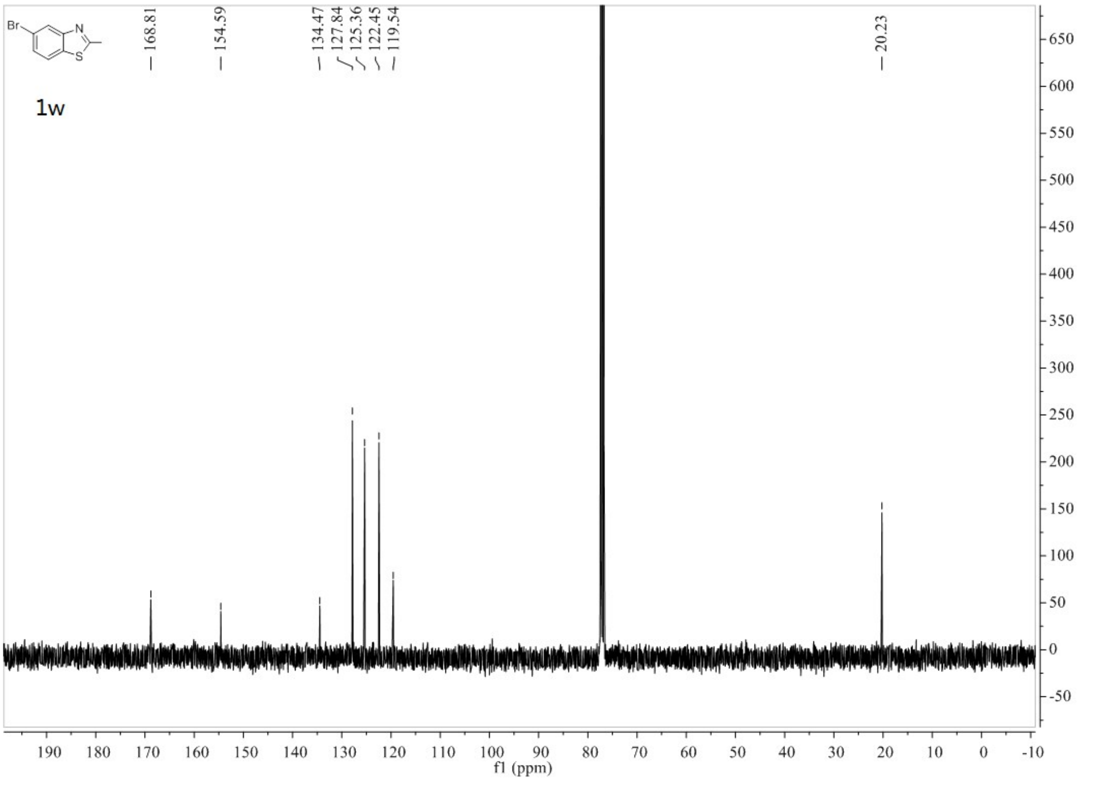

1v
N
S
7.953
7.933
7.783
7.764
7.428
7.410
7.392
7.318
7.300
7.281
2.790
1.00
1.00
1.05
1.01
3.01
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

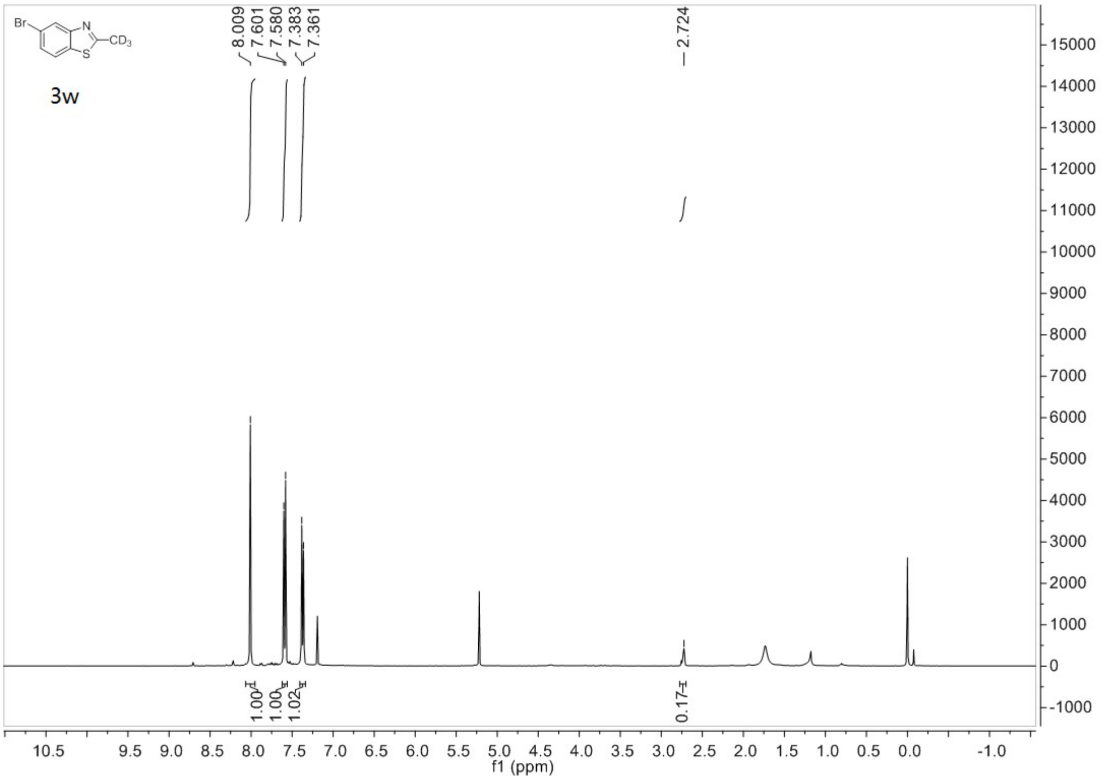

1v
N
S
166.89
153.38
135.65
125.90
124.68
122.37
121.38
20.08
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

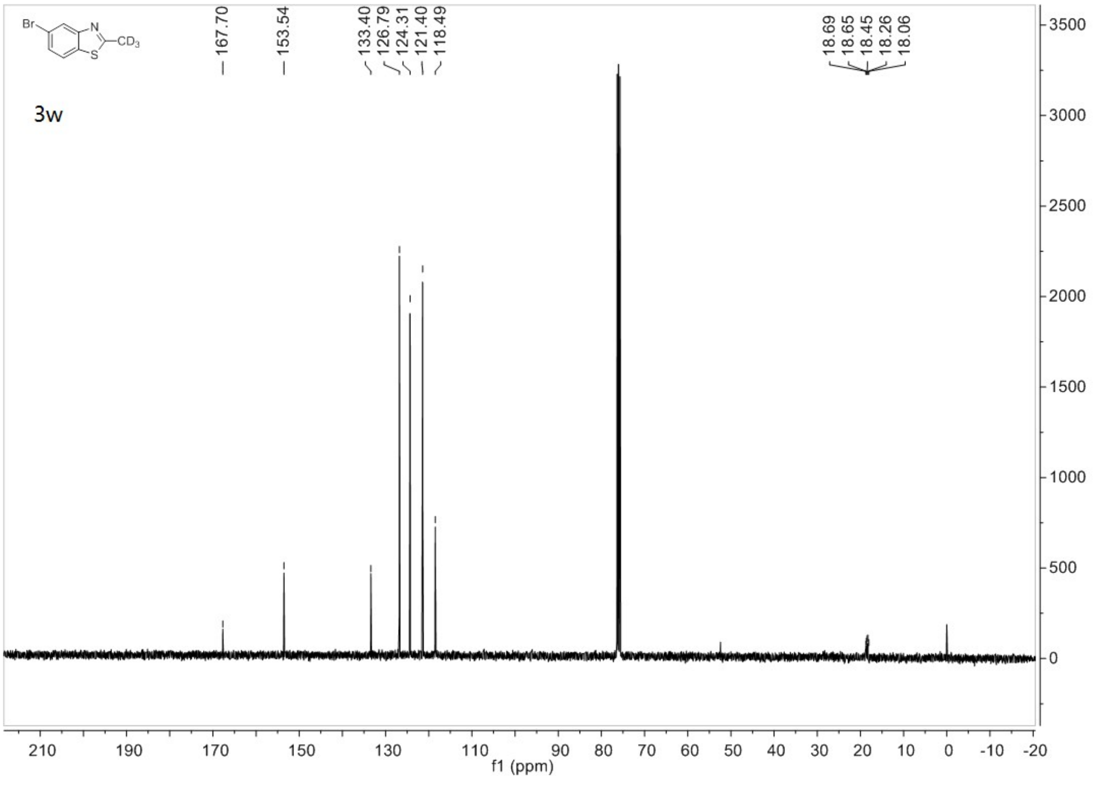

3v
N
S
CD3
7.963
7.943
7.832
7.812
7.463
7.444
7.425
7.361
7.342
7.324
7.263
2.808
0.99
1.00
1.08
1.03
0.14
0.46
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

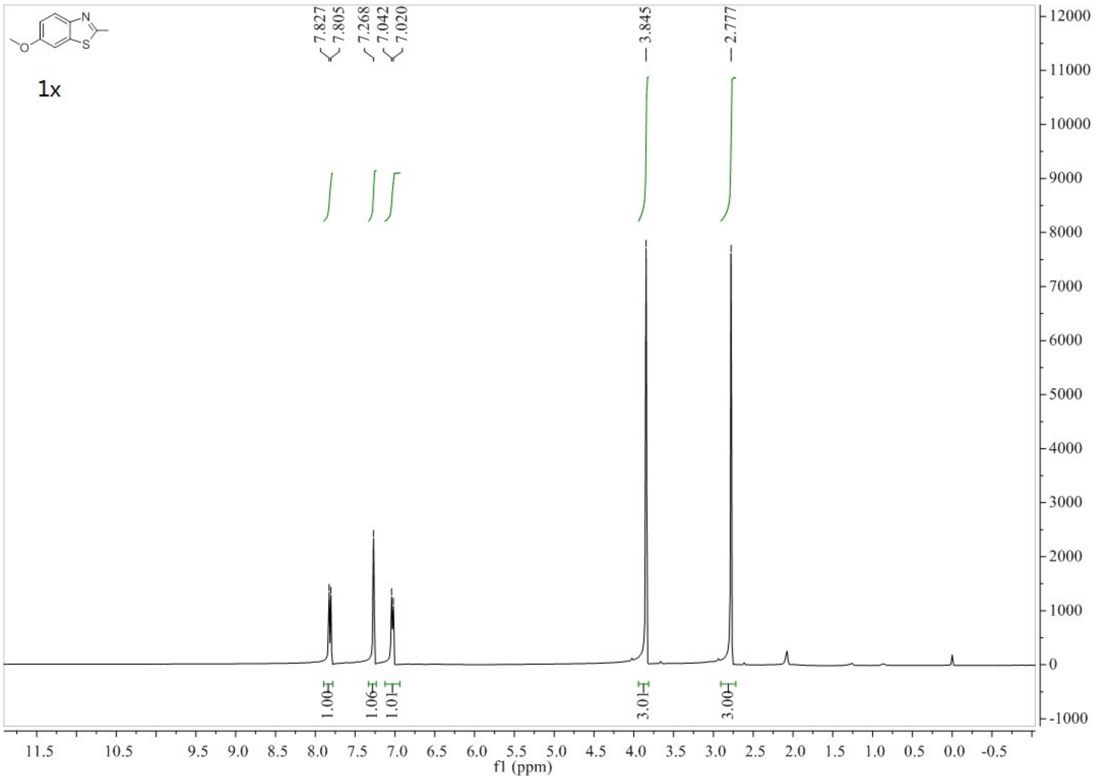

3v
N
S
CD3
166.91
153.39
135.63
125.92
124.70
122.40
121.40
77.36
77.04
76.72
19.79
19.64
19.60
19.40
19.20
19.01
4500
4000
3500
3000
2500
2000
1500
1000
500
0
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

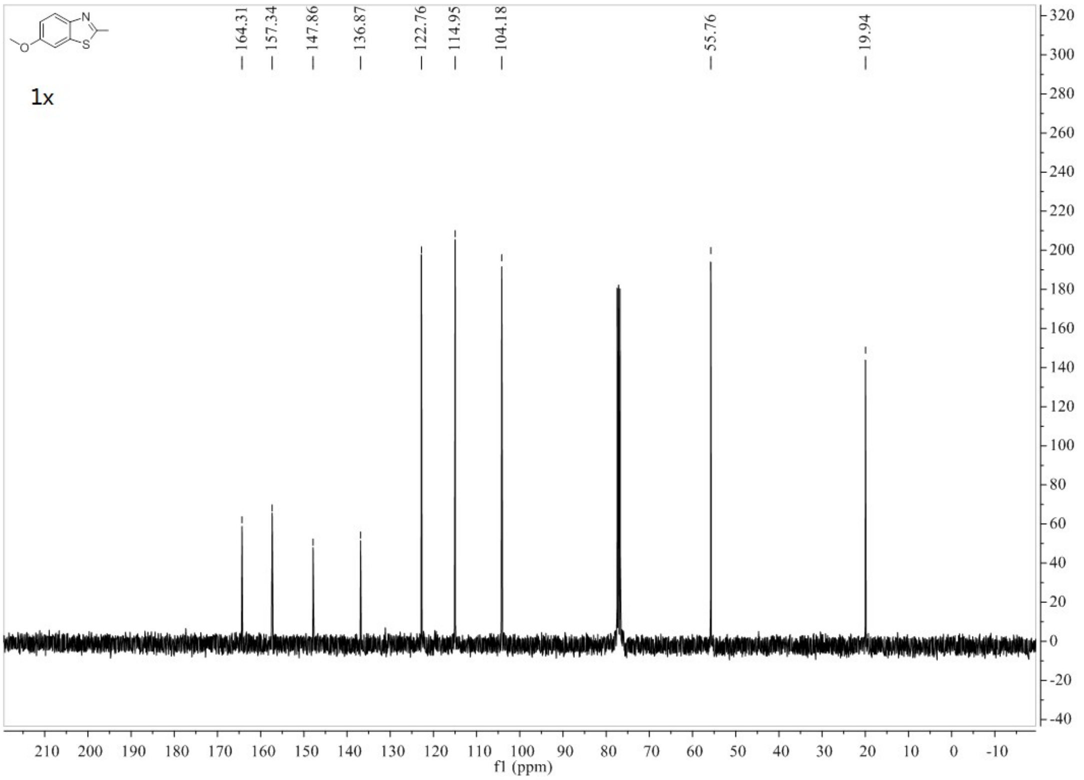

1w
8.091
7.686
7.665
7.468
7.447
2.838
1.00
1.03
1.03
3.17
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

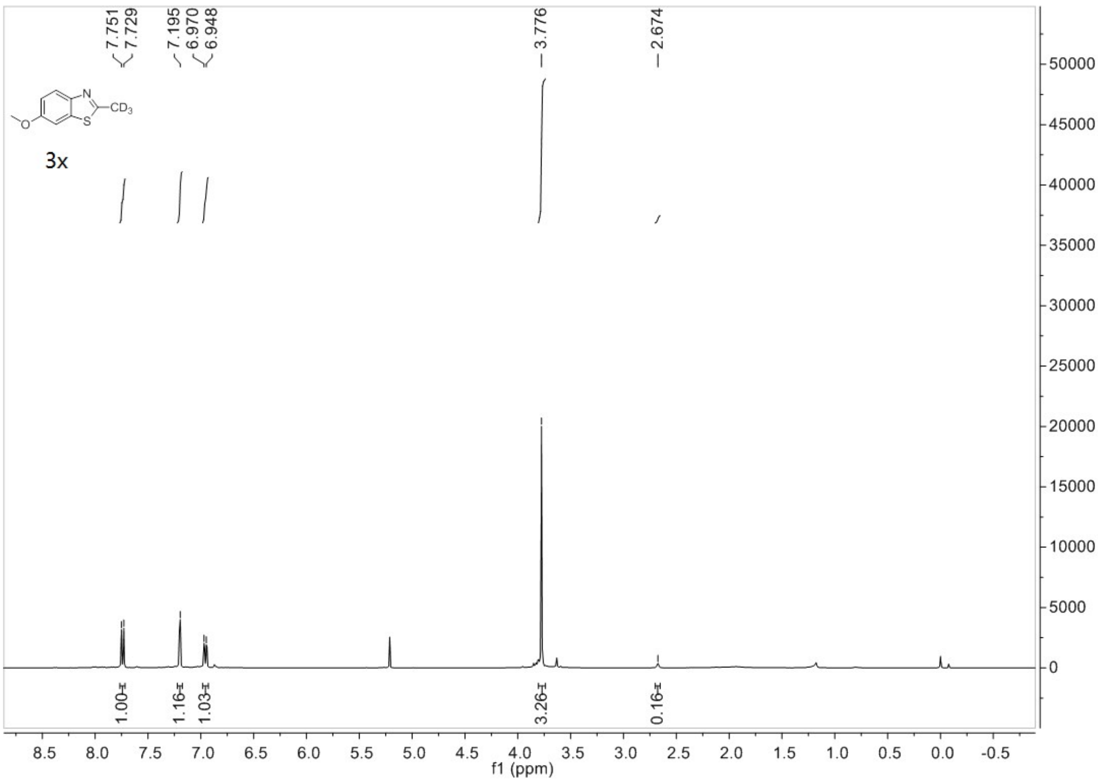

1w
168.81
154.59
134.47
127.84
125.36
122.45
119.54
20.23
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

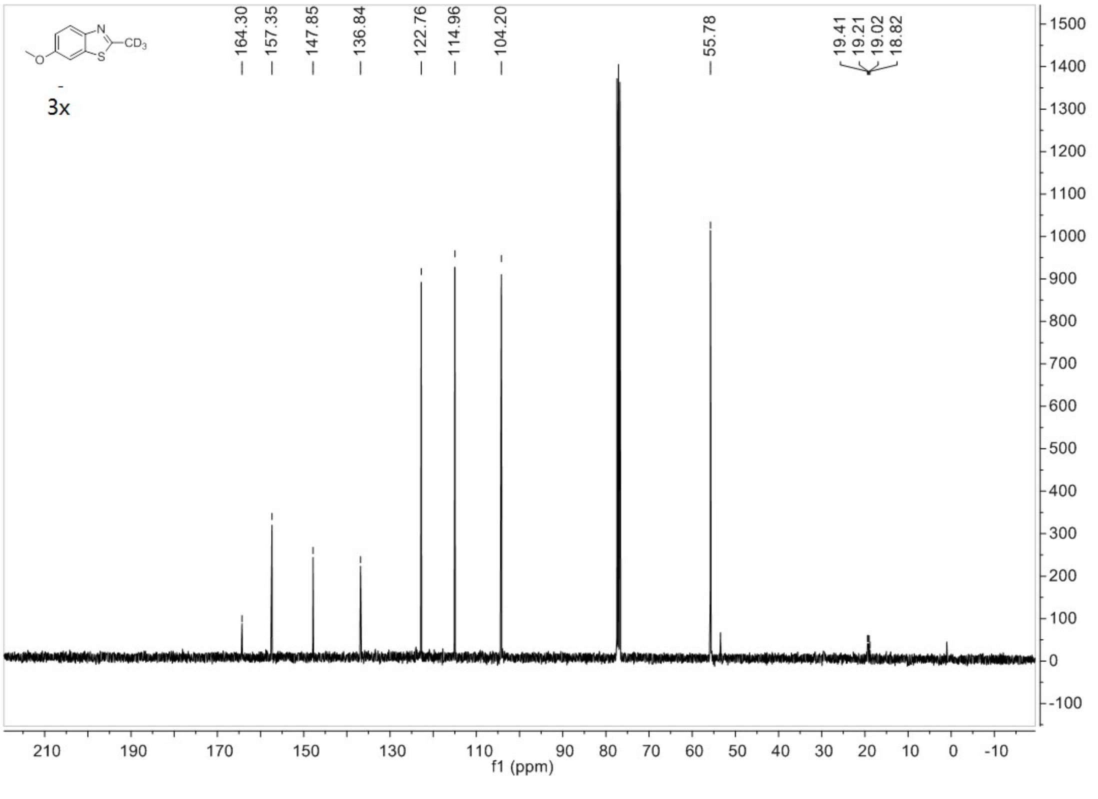

Br
N
S
CD3
3w
8.009
7.601
7.580
7.383
7.361
2.724
1.00
1.00
1.02
0.17
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0
f1 (ppm)

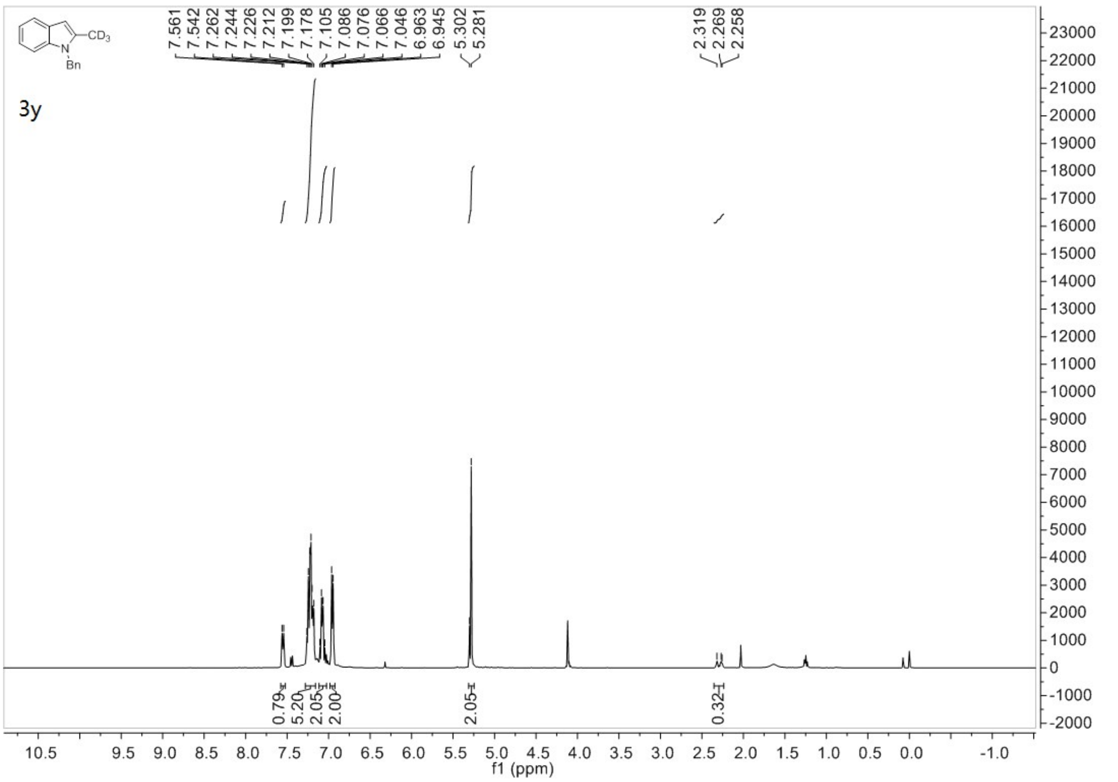

Br
N
S
CD3
3w
167.70
153.54
133.40
126.79
124.31
121.40
118.49
18.69
18.65
18.45
18.26
18.06
3500
3000
2500
2000
1500
1000
500
0
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

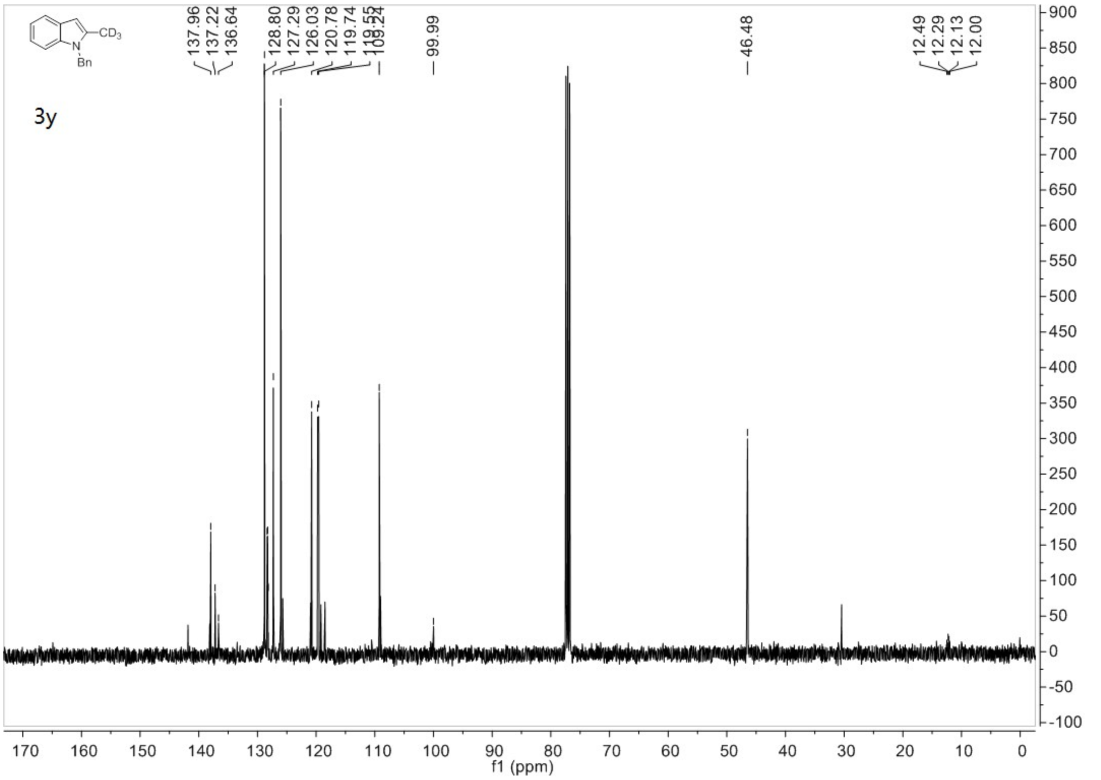

N
S
O
1x
7.827
7.805
7.268
7.042
7.020
3.845
2.777
1.00
1.06
1.01
3.01
3.00
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

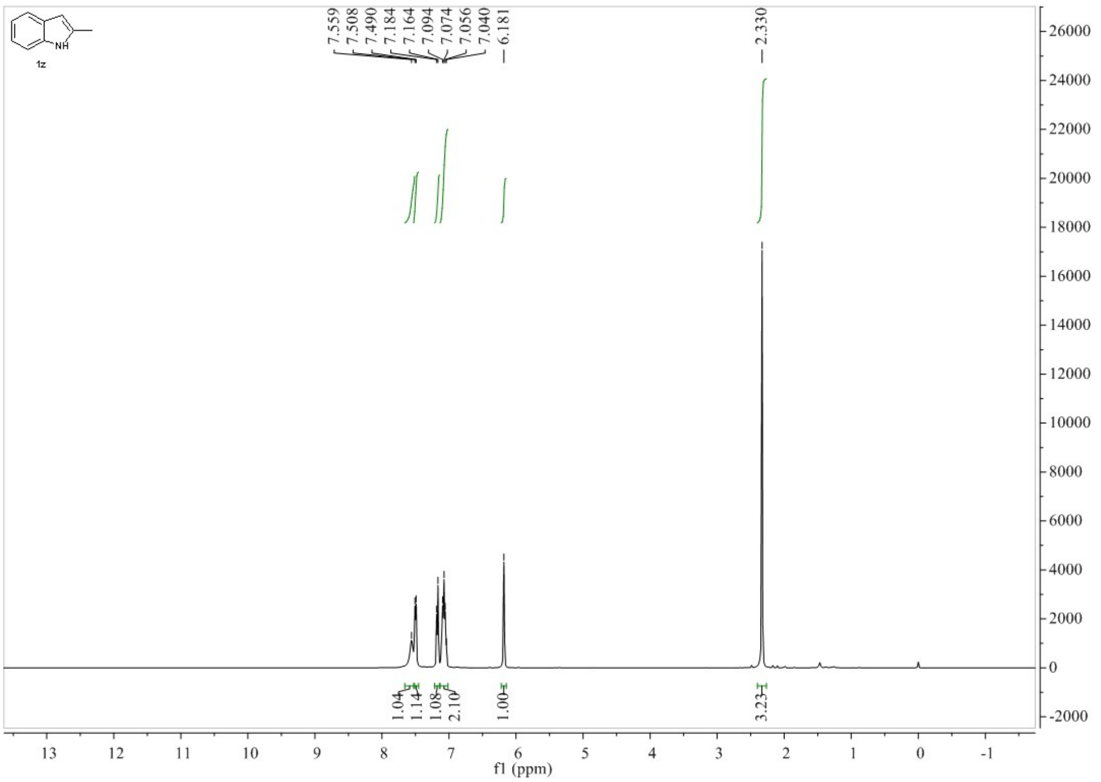

N
S
O
1x
164.31
157.34
147.86
136.87
122.76
114.95
104.18
55.76
19.94
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

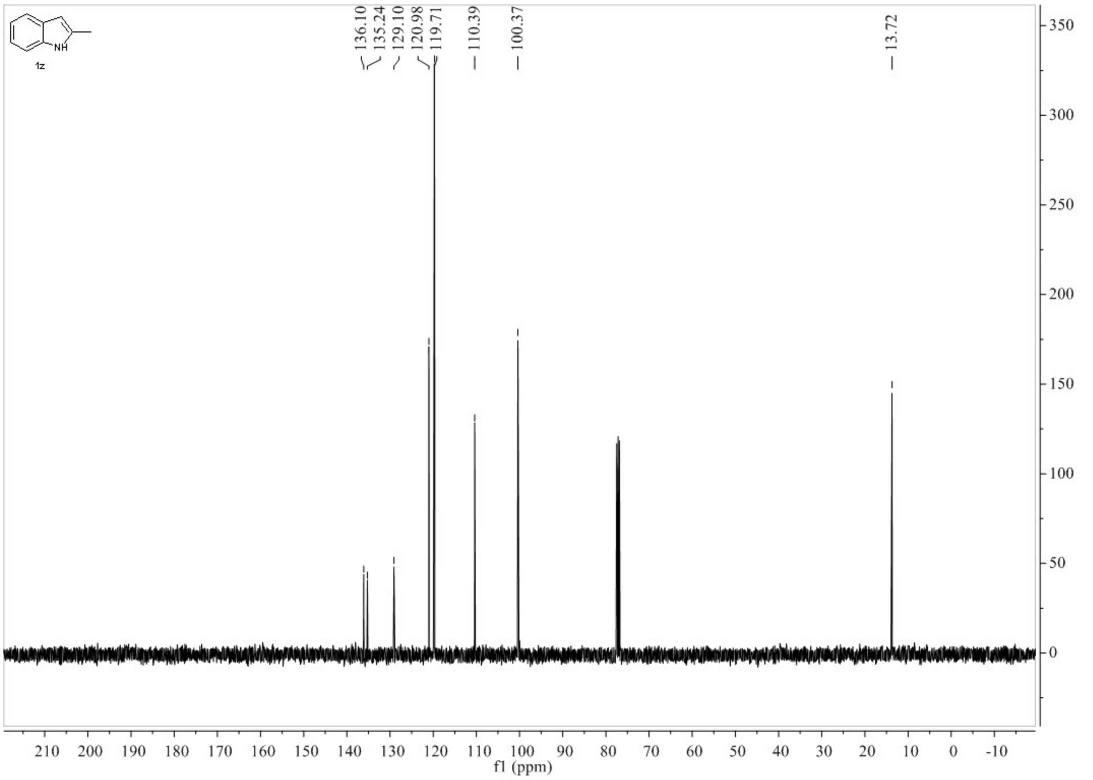

7.751
7.729
7.195
6.970
6.948
3.776
2.674
CD3
N
S
O
3x
1.00
1.16
1.03
3.26
0.16
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

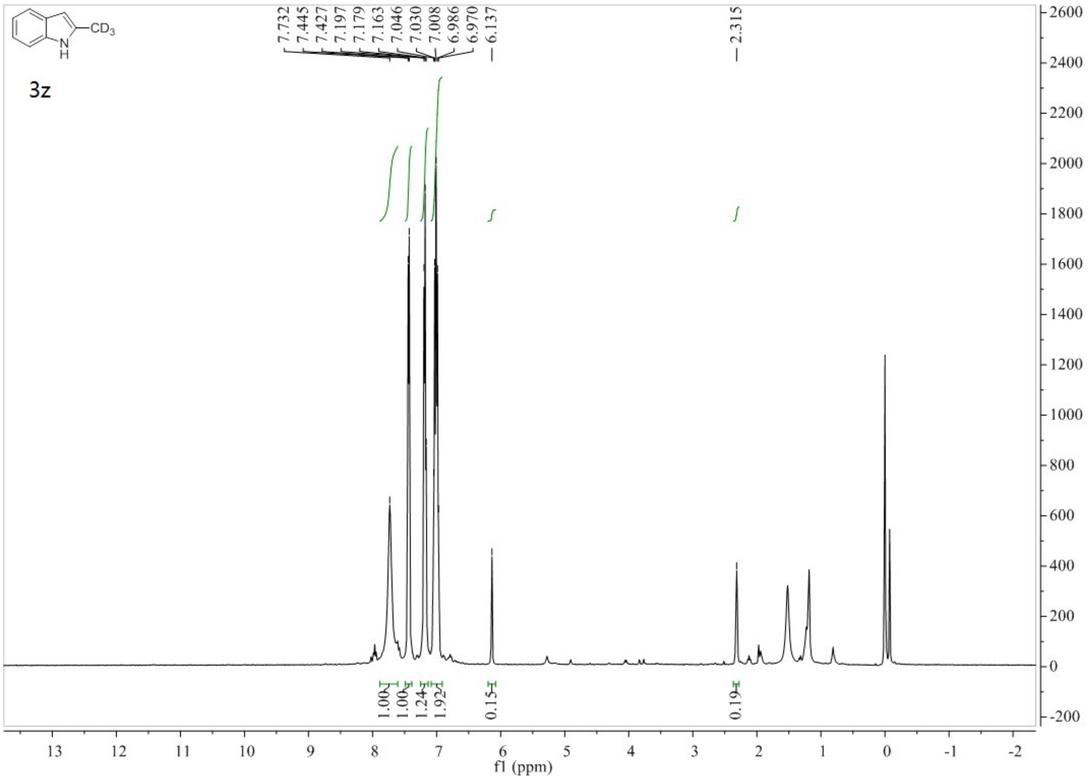

164.30
157.35
147.85
136.84
122.76
114.96
104.20
55.78
19.41
19.21
19.02
18.82
CD3
N
S
O
3x
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

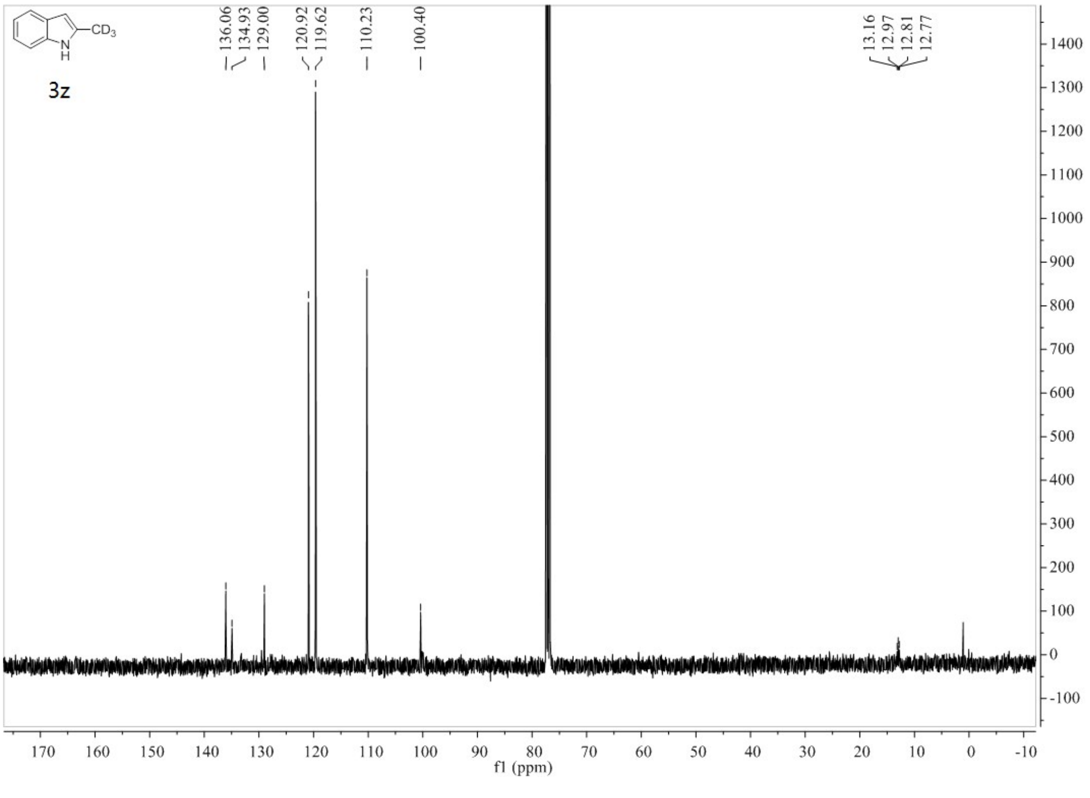

CD3
N
Bn
3y
7.561
7.542
7.262
7.244
7.226
7.212
7.199
7.178
7.105
7.086
7.076
7.066
7.046
6.963
6.945
5.302
5.281
2.319
2.269
2.258
0.79
5.20
2.05
2.00
2.05
0.32
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
10.5
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
-1.0
f1 (ppm)

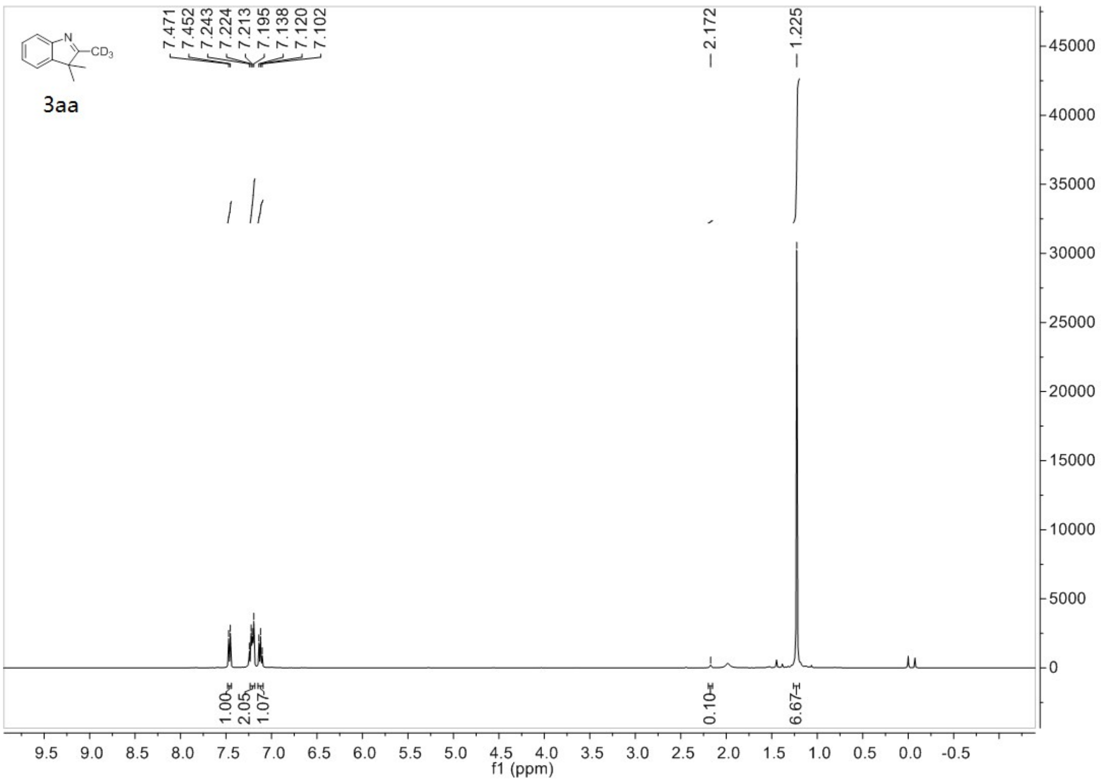

CD3
N
Bn
3y
137.96
137.22
136.64
128.80
127.29
126.03
120.78
119.74
119.55
109.24
99.99
46.48
12.49
12.29
12.13
12.00
900
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

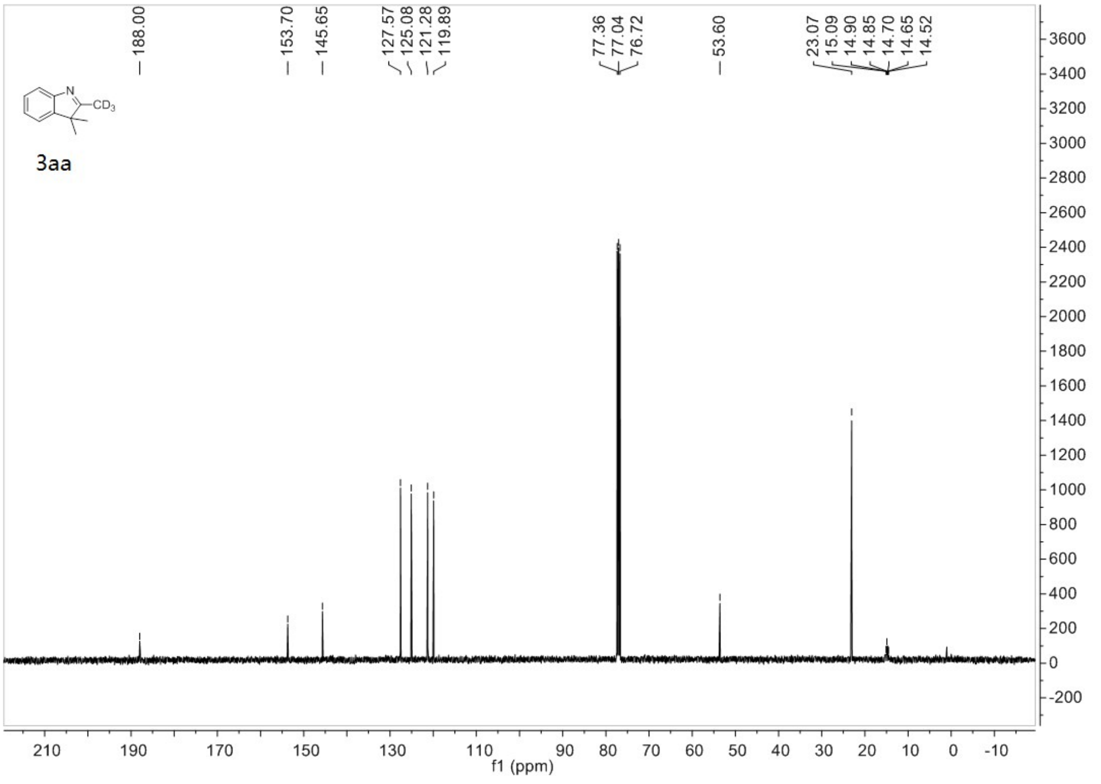

NH
1z
7.559
7.508
7.490
7.184
7.164
7.094
7.074
7.056
7.040
6.181
2.330
1.04
1.14
1.08
2.10
1.00
3.23
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

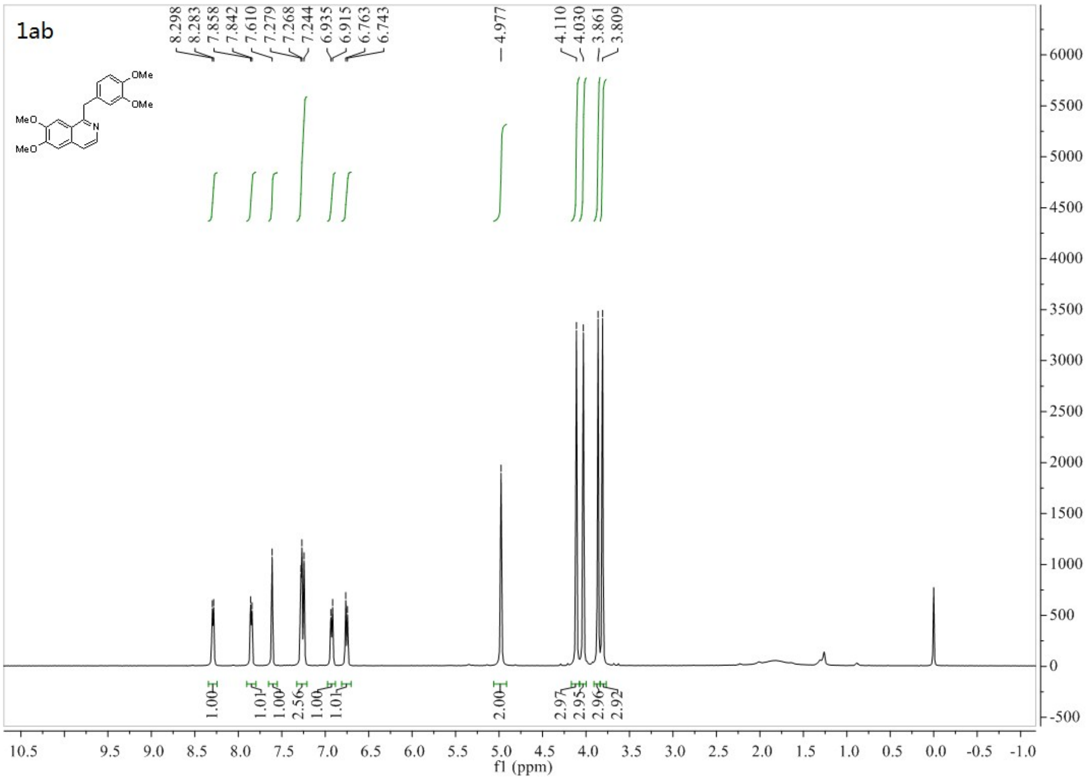

NH
1z
136.10
135.24
129.10
120.98
119.71
110.39
100.37
13.72
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
350
300
250
200
150
100
50
0

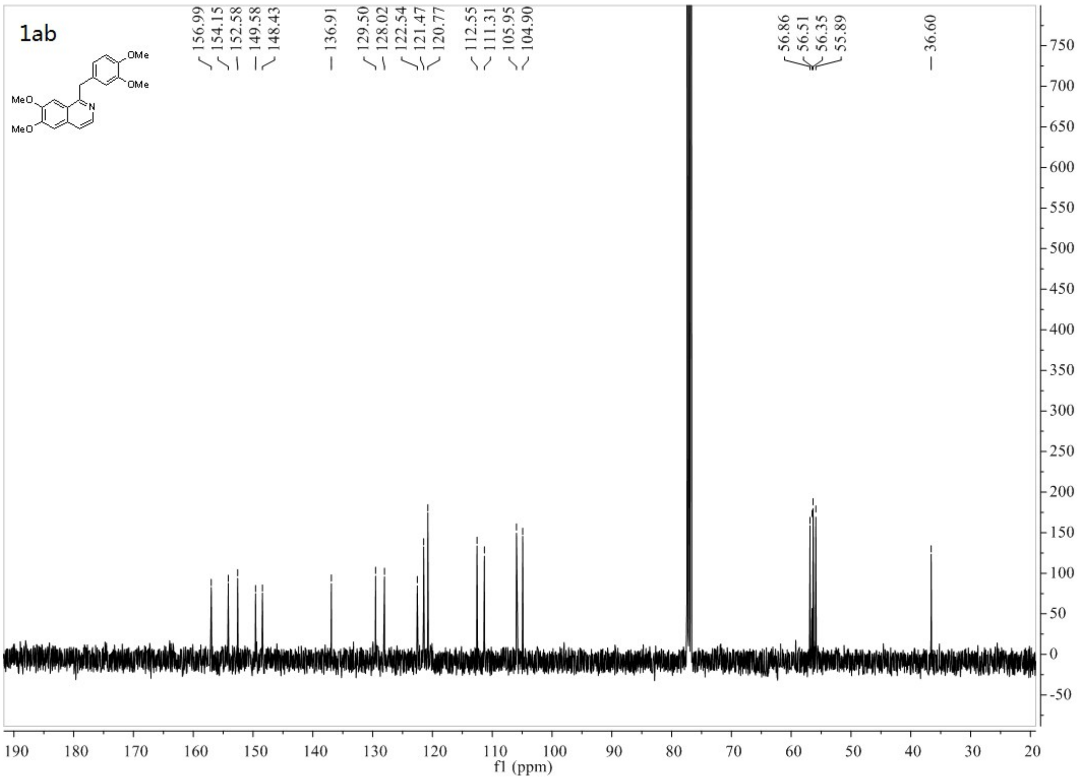

CD3
N
H
3z
7.732
7.445
7.427
7.197
7.179
7.163
7.046
7.030
7.008
6.986
6.970
6.137
2.315
1.00
1.00
1.24
1.92
0.15
0.19
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

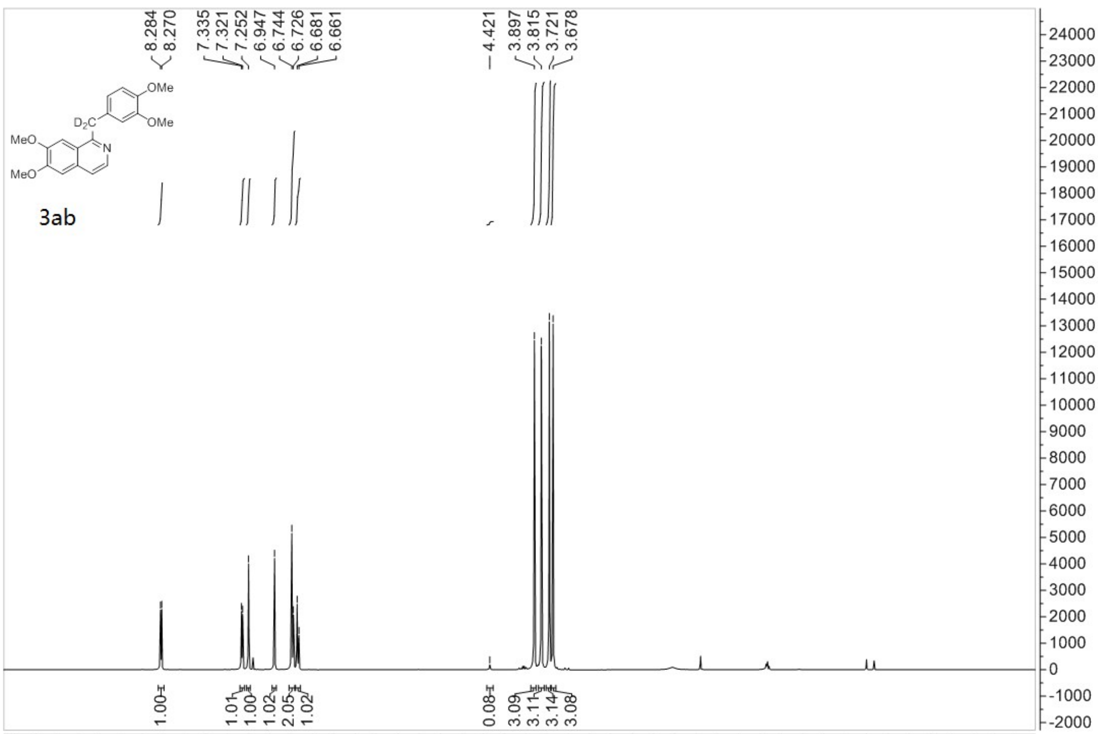

CD3
N
H
3z
136.06
134.93
129.00
120.92
119.62
110.23
100.40
13.16
12.97
12.81
12.77
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

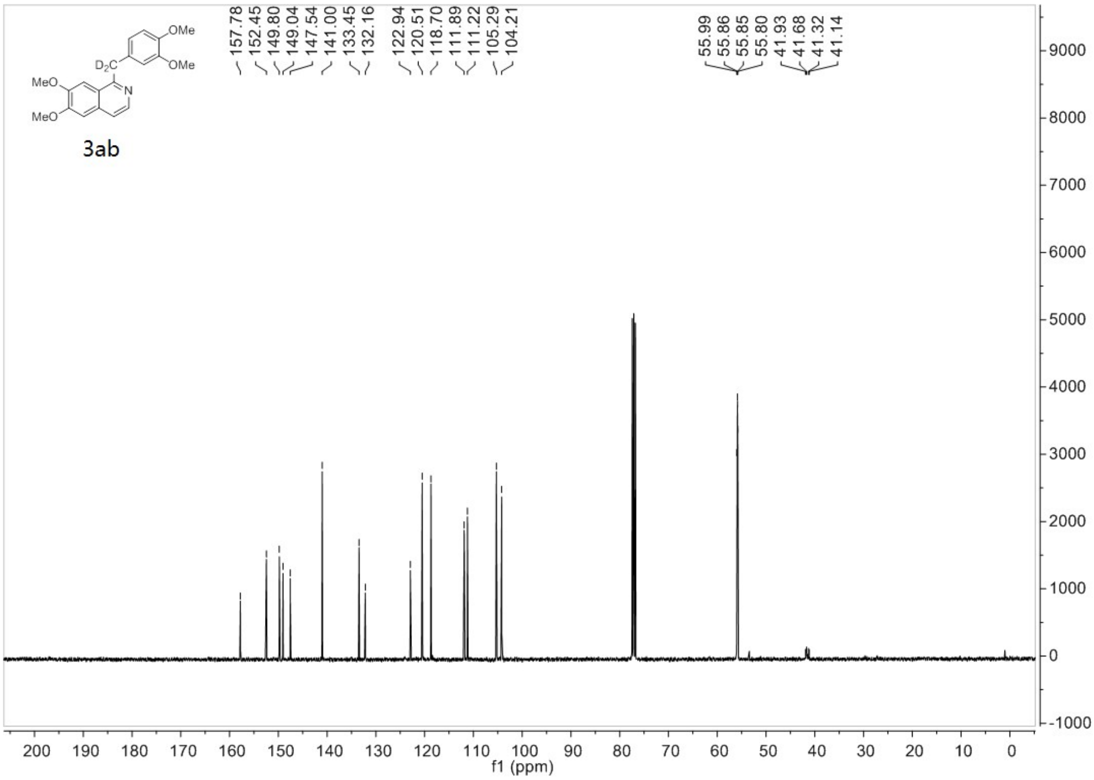

7.471
7.452
7.243
7.224
7.213
7.195
7.138
7.120
7.102
2.172
1.225
N
CD3
3aa
1.00
2.05
1.07
0.10
6.67
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

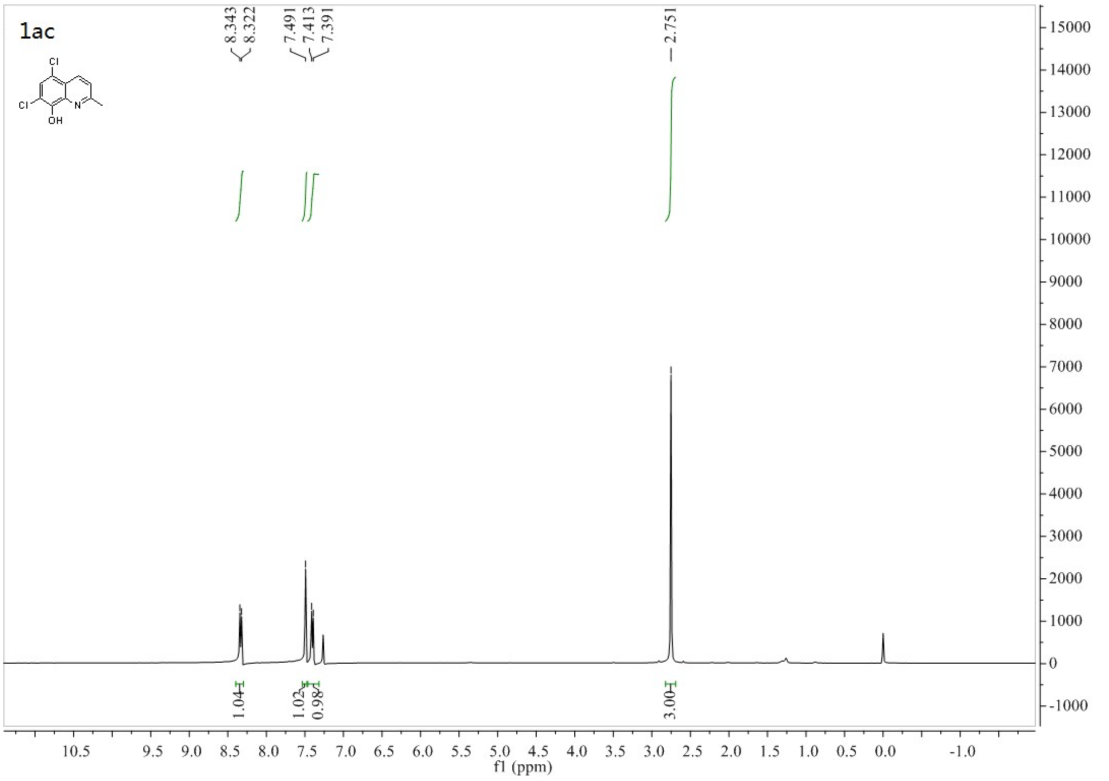

188.00
153.70
145.65
127.57
125.08
121.28
119.89
77.36
77.04
76.72
53.60
23.07
15.09
14.90
14.85
14.70
14.65
14.52
N
CD3
3aa
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

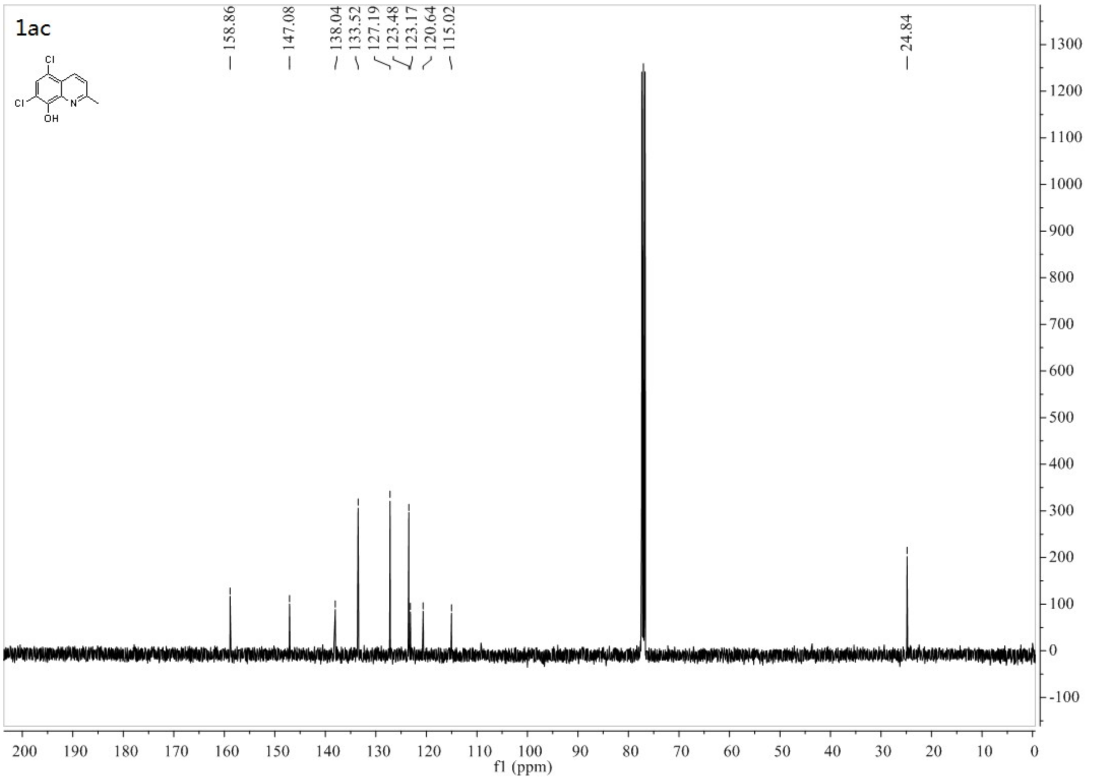

1ab
OMe
OMe
MeO
MeO
N
8.298
8.283
7.858
7.842
7.610
7.279
7.268
7.244
6.935
6.915
6.763
6.743
4.977
4.110
4.030
3.861
3.809
1.00
1.01
1.00
2.56
1.00
1.01
2.00
2.97
2.95
2.96
2.92
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

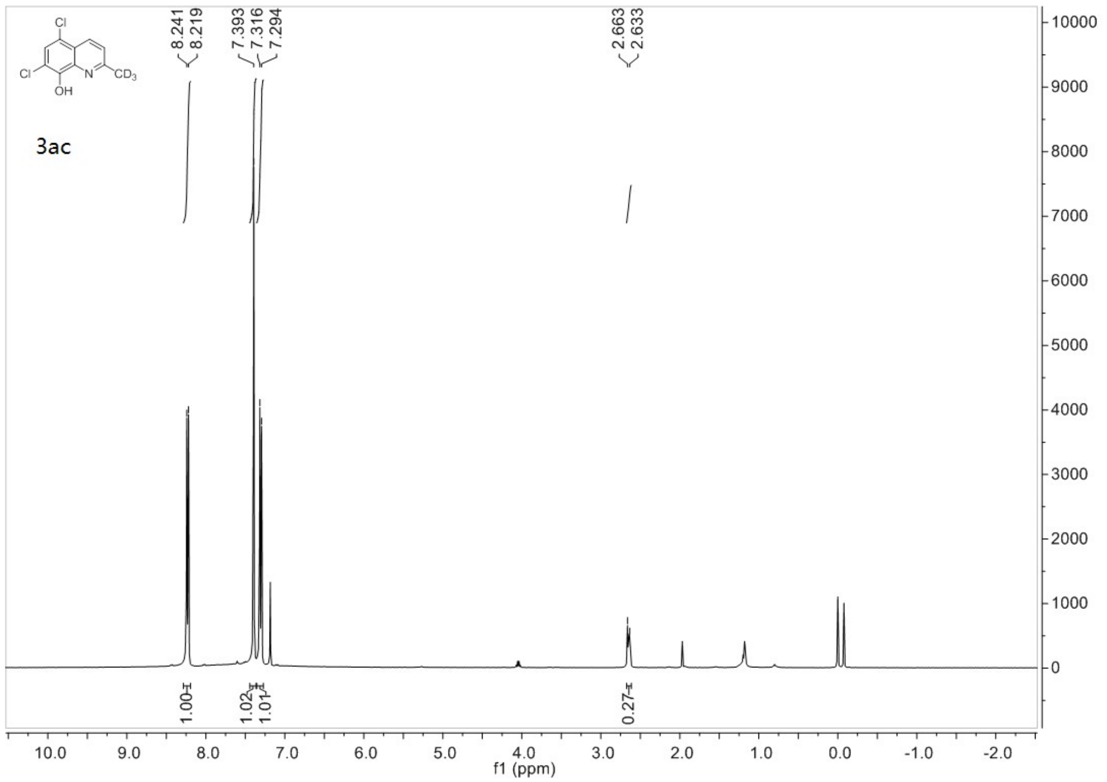

1ab
OMe
OMe
MeO
MeO
N
156.99
154.15
152.58
149.58
148.43
136.91
129.50
128.02
122.54
121.47
120.77
112.55
111.31
105.95
104.90
56.86
56.51
56.35
55.89
36.60
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


8.284
8.270
7.335
7.321
7.252
6.947
6.744
6.726
6.681
6.661
4.421
3.897
3.815
3.721
3.678
OMe
D$_2$C
OMe
MeO
N
MeO
3ab
1.00
1.01
1.00
1.02
2.05
1.02
0.08
3.09
3.11
3.14
3.08
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 -1.0
f1 (ppm)
24000 23000 22000 21000 20000 19000 18000 17000 16000 15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000 -2000

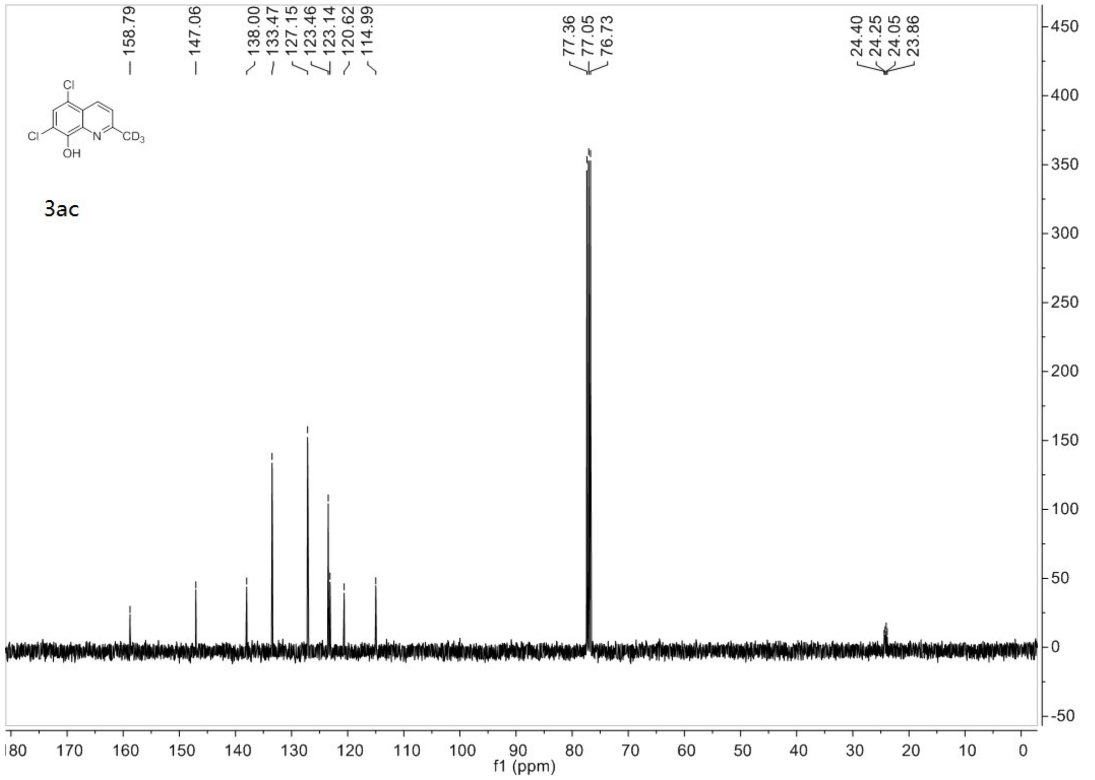

157.78
152.45
149.80
149.04
147.54
141.00
133.45
132.16
122.94
120.51
118.70
111.89
111.22
105.29
104.21
55.99
55.86
55.85
55.80
41.93
41.68
41.32
41.14
OMe
D$_2$C
OMe
MeO
N
MeO
3ab
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000


1ac
Cl
Cl
N
OH
8.343
8.322
7.491
7.413
7.391
2.751
1.04
1.02
0.98
3.00
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.5
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
-1.0
f1 (ppm)

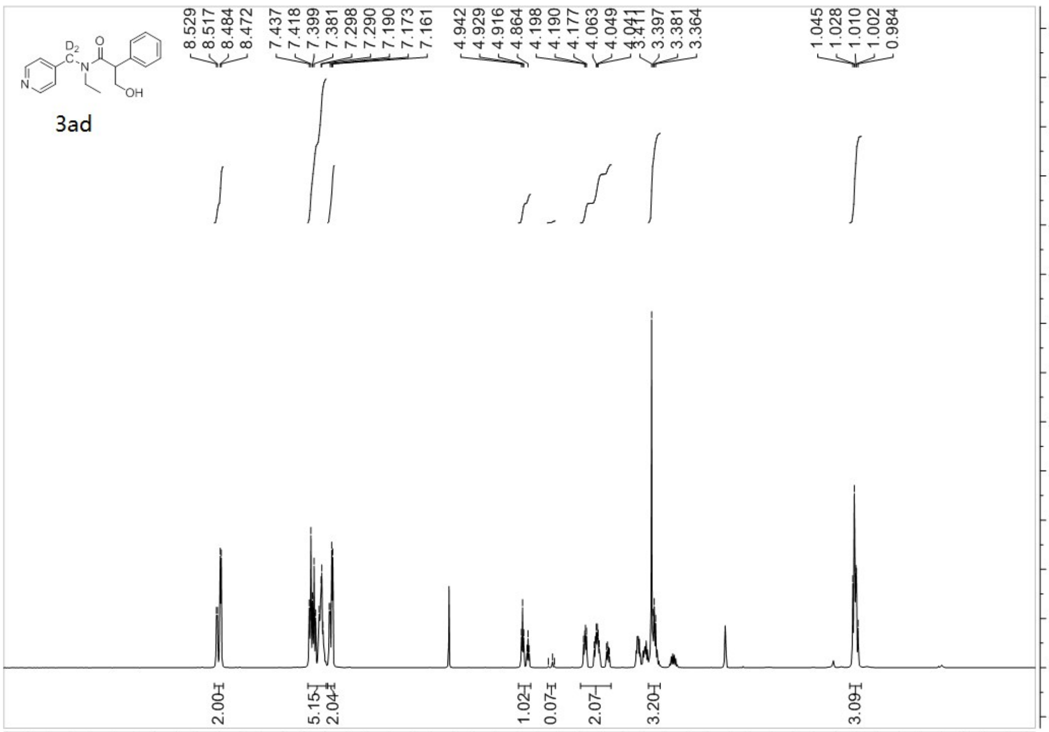

1ac
Cl
Cl
N
OH
158.86
147.08
138.04
133.52
127.19
123.48
123.17
120.64
115.02
24.84
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



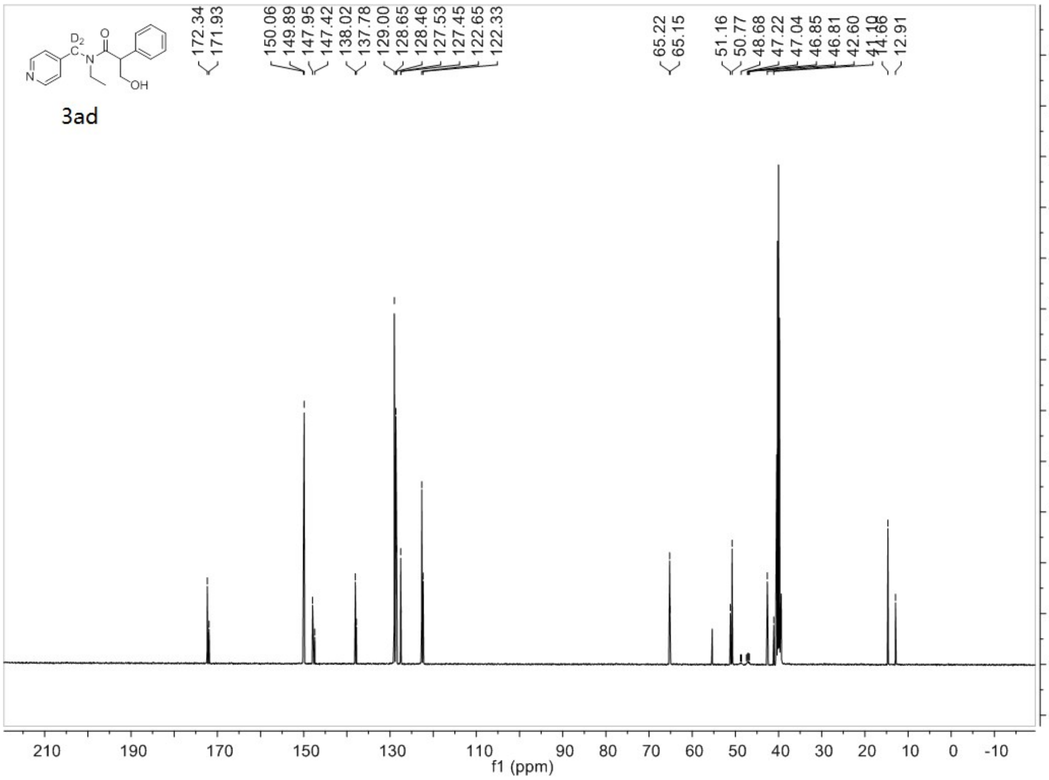
Cl
Cl
N
CD3
OH
3ac
8.241
8.219
7.393
7.316
7.294
2.663
2.633
1.00
1.02
1.01
0.27
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
f1 (ppm)



158.79
147.06
138.00
133.47
127.15
123.46
123.14
120.62
114.99
77.36
77.05
76.73
24.40
24.25
24.05
23.86
Cl
Cl
N
CD3
OH
3ac
450
400
350
300
250
200
150
100
50
0
-50
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


3ad

D2
O
N
OH
8.529
8.517
8.484
8.472
7.437
7.418
7.399
7.381
7.298
7.290
7.190
7.173
7.161
4.942
4.929
4.916
4.864
4.198
4.190
4.177
4.063
4.049
4.041
3.411
3.397
3.381
3.364
1.045
1.028
1.010
1.002
0.984
2.00
5.15
2.04
1.02
0.07
2.07
3.20
3.09
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10.5
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
-0.5
f1 (ppm)


3ad

D2
O
N
OH
172.34
171.93
150.06
149.89
147.95
147.42
138.02
137.78
129.00
128.65
128.46
127.53
127.45
122.65
122.33
65.22
65.15
51.16
50.77
48.68
47.22
47.04
46.85
46.81
42.60
41.10
14.66
12.91
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)