# Supporting Information For:

## Chiral Phosphoric Acid-Catalyzed Asymmetric Transfer Hydrogenation of Quinolin-3-amines

*Xian-Feng Cai,*[a,b] *Ran-Ning Guo,*[b] *Guang-Shou Feng,*[b] *Bo Wu,*[b] *Yong-Gui Zhou*[b,*]

[a]Department of Chemistry, Dalian University of Technology, Dalian 116012, P. R. China

[b]State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics

Chinese Academy of Sciences, Dalian 116023, P. R. China;

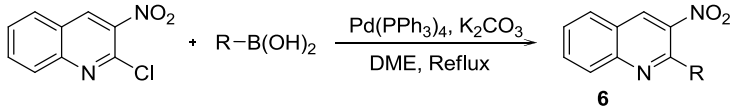
## Table of Contents

## 1. General:

Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. $^{1}H$ NMR, $^{13}C$ NMR and $^{19}F$ NMR spectra were recorded at room temperature in $CDCl_3$ or DMSO-$d_6$ on 400 MHz instrument with tetramethylsilane (TMS) as internal standard. Enantiomeric excess was determined by HPLC analysis, using chiral column described below in detail. Optical rotations were measured by polarimeter. Flash column chromatography was performed on silica gel (200-300 mesh).

## 2. Synthesis of 3-Nitroquinolines 6

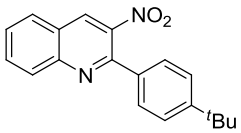
3-Nitroquinoline derivatives can be conveniently synthesized according to the known literature procedure.[1,2] The compounds 2-phenyl-3-nitroquinoline (**6a**), 2-*m*-tolyl-3-nitroquinoline (**6b**), 2-*p*-tolyl-3-nitroquinoline (**6c**), 2-(4-methoxyphenyl)-3-nitroquinoline (**6e**), 2-(4-chlorophenyl)-3-nitroquinoline (**6f**), 2-(4-bromophenyl)-3-nitroquinoline (**6g**), 2-(4-fluorophenyl)-3-nitroquinoline (**6h**), 2-(4-trifluoromethylphenyl)-3-nitroquinoline (**6i**), 2-naphthyl-3-nitroquinoline (**6j**), 2-phenyl-6-fluoro-3-nitroquinoline (**6k**) are known compounds.



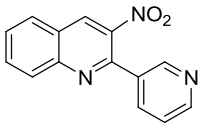
**6**

A mixture of 2-chloro-3-nitroquinoline (50 mg, 0.24 mmol), boronic acid (0.29 mmol), $Pd(PPh_3)_4$ (17 mg, 0.01 mmol) and $K_2CO_3$ (99 mg, 0.72 mmol) in DME (dimethoxyethane, 6 mL) was stirred at reflux for 2 h, then cooled to rt, diluted with water (15mL), then extracted with $CH_2Cl_2$ (15 mL×3). The combined organic layers were dried with $Na_2SO_4$. After filtration, the solvent was removed under the reduced pressure and the residue was purified by flash chromatography on silica gel to yield the corresponding products.

**2-(4-*tert*-Butylphenyl)-3-nitroquinoline (6d):** 97% yield, light yellow solid, mp 134-136 $^{o}$C, $R_f$ = 0.60 (petroleum ether/EtOAc 10:1). $^{1}H$ NMR (400 MHz, $CDCl_3$) δ = 8.63 (s, 1H), 8.21 (d, *J* = 8.5, 1H), 7.95 (d, *J* = 8.2, 1H), 7.88 (dd, *J* = 8.3, 7.2, 1H), 7.66 (t, *J* = 7.6, 1H), 7.63-7.57 (m, 2H), 7.51 (d, *J* = 8.3, 2H), 1.36 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 152.9, 152.1, 148.5, 144.1, 134.1, 132.7, 132.4, 129.8, 128.5, 128.3, 127.9, 125.8, 125.5, 34.8, 31.3; HRMS Calculated for $C_{19}H_{19}N_2O_2$ $[M+H]^+$ 307.1447, found 307.1443.



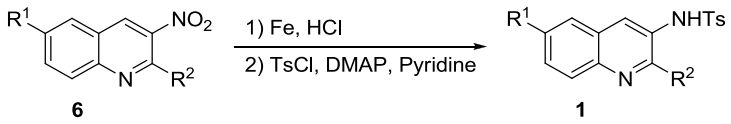

**2-(Pyridin-3-yl)-3-nitroquinoline (6l):** 97% yield, yellowish-brown solid, mp 207-209 $^{o}$C, $R_f$ = 0.30 (petroleum ether/EtOAc 1:1). $^{1}H$ NMR (400 MHz, $CDCl_3$) δ = 8.91 (s, 1H), 8.80 (s, 1H), 8.74 (d, *J* = 4.0, 1H), 8.24 (d, *J* = 8.5, 1H), 8.02 (d, *J* = 8.1, 1H), 7.95 (t, *J* = 7.7, 2H), 7.74 (t, *J* = 7.5, 1H), 7.43 (dd, *J* = 7.3, 5.1, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 150.4, 149.4, 149.1, 148.6, 143.4, 135.6, 133.4, 133.4, 133.3, 129.9, 129.0, 128.8, 125.8, 123.2; HRMS Calculated for $C_{14}H_{10}N_3O_2$ $[M+H]^+$ 252.0773, found 252.0775.




1 Yan, M.-C.; Tu, Z.; Lin, C.; Ko, S.; Hsu, J.; Yao, C.-F. *J. Org. Chem.* **2004**, *69*, 1565.

2 Cai, X.-F.; Chen, M.-W.; Ye, Z.-S.; Guo, R.-N.; Shi, L.; Li, Y.-Q.; Zhou, Y.-G. *Chem. Asian J.* **2013**, *8*, 1381

## 3. Synthesis of Quinolin-3-amines 1

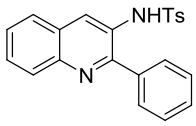



**6** **1**

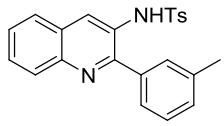
To a solution of **6** (0.60 mmol) in a mixed solvent of ethanol and $H_2O$ with a ratio of 4/1 (5 mL) was added iron powder (134 mg, 2.40 mmol) followed by HCl (0.1 M, 0.3 mL, 0.03 mmol), and the resulting mixture was vigorously stirred at 85 $^oC$ for 0.5-1.5 h. When the reduction reaction was complete (determined by TLC), saturated $NaHCO_3$ (5 mL) was added and the mixture was filtered through celite. The combined organic layers were dried ($Na_2SO_4$). After filtration, the solvent was removed under reduced pressure and the crude product was pure enough for further reaction.

In a 25 mL round-bottom flask, the crude product, 4-methylbenzene-1-sulfonyl chloride (TsCl, 137 mg, 0.72 mmol) and 4-dimethylaminopyridine (DMAP, 22 mg, 0.18 mmol, 30 mol%) were combined in pyridine (5 mL). The resulting mixture was refluxed for 18 h. The solvent was removed under reduced pressure, the residue was resolved in $CH_2Cl_2$ (10 mL) and washed with water (15 mL). The combined organic layers were dried ($Na_2SO_4$). After filtration, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to yield the product.

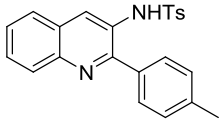
**4-Methyl-*N*-(2-phenylquinolin-3-yl)benzenesulfonamide (1a):** 79% yield, white solid, mp 207-209 $^oC$, $R_f$ = 0.30 (petroleum ether/EtOAc 5:1). $^1H$ NMR (400 MHz, $CDCl_3$) δ = 8.45 (s, 1H), 8.03 (d, *J* = 8.2, 1H), 7.85 (d, *J* = 8.0, 1H), 7.65 (t, *J* = 7.2, 1H), 7.60-7.47 (m, 3H), 7.42 (d, *J* = 7.2, 3H), 7.15 (dd, *J* = 15.9, 7.0, 4H), 6.85 (s, 1H), 2.36 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 153.5, 145.3, 144.6, 136.8, 136.1, 130.0, 129.5, 129.5, 129.4, 129.3, 128.6, 128.6, 127.9, 127.7, 127.5, 127.3, 126.6, 21.7; HRMS Calculated for $C_{22}H_{19}N_2O_2S$ $[M+H]^+$ 375.1167, found 375.1174.




**4-Methyl-*N*-(2-*m*-tolylquinolin-3-yl)benzenesulfonamide (1b):** 53% yield, white solid, mp 217-219 $^oC$, $R_f$ = 0.40 (petroleum ether/EtOAc 5:1). $^1H$ NMR (400 MHz, $CDCl_3$) δ = 8.47 (s, 1H), 8.03 (d, *J* = 8.4, 1H), 7.86 (d, *J* = 8.0, 1H), 7.66 (dd, *J* = 11.2, 4.1, 1H), 7.56 (t, *J* = 7.5, 1H), 7.49 (d, *J* = 8.2, 2H), 7.31 (t, *J* = 7.5, 1H), 7.26 (d, *J* = 3.9, 1H), 7.17 (d, *J* = 8.1, 2H), 6.92 (d, *J* = 7.3, 1H), 6.87 (s, 1H), 6.80 (s, 1H), 2.37 (s, 3H), 2.35 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 153.5, 145.1, 144.3, 139.2, 136.5, 136.0, 130.2, 129.8, 129.2, 129.2, 129.1, 129.0, 128.5, 127.7, 127.5, 127.3, 127.1, 126.3, 125.3, 21.5, 21.4; HRMS Calculated for $C_{23}H_{21}N_2O_2S$ $[M+H]^+$ 389.1324, found 389.1332.

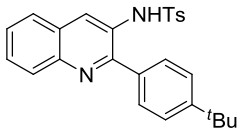



**4-Methyl-*N*-(2-*p*-tolylquinolin-3-yl)benzenesulfonamide (1c):** 55% yield, white solid, mp 281-283 $^oC$, $R_f$ = 0.40 (petroleum ether/EtOAc 5:1). $^1H$ NMR (400 MHz, $CDCl_3$) δ = 8.43 (s, 1H), 8.01 (d, *J* = 8.4, 1H), 7.84 (d, *J* = 8.0, 1H), 7.64 (t, *J* = 7.5, 1H), 7.54 (t, *J* = 8.1, 3H), 7.21 (dd, *J* = 22.6, 7.9, 4H), 7.04 (d, *J* = 7.7, 2H), 6.82 (s, 1H), 2.42 (s, 3H), 2.37 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 153.2, 145.1, 144.4, 139.5, 135.9, 133.7, 130.0, 129.8, 129.2, 129.0, 128.6, 128.3, 127.7,



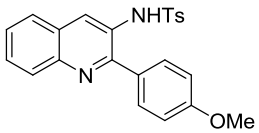
127.4, 127.2, 127.2, 125.6, 21.5, 21.3; HRMS Calculated for $C_{23}H_{21}N_2O_2S$ $[M+H]^+$ 389.1324, found 389.1331.

***N*-(2-(4-*tert*-Butylphenyl)quinolin-3-yl)-4-methylbenzenesulfonamide (1d):** 65% yield, white solid, mp 193-195 °C, $R_f$ = 0.40 (petroleum ether/EtOAc 5:1). $^1$H NMR (400 MHz, $CDCl_3$)



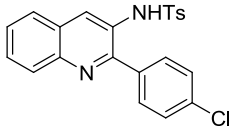

δ = 8.42 (s, 1H), 8.02 (d, *J* = 8.4, 1H), 7.84 (d, *J* = 8.1, 1H), 7.68–7.61 (m, 1H), 7.58–7.50 (m, 3H), 7.45 (d, *J* = 8.3, 2H), 7.18 (d, *J* = 8.1, 2H), 7.12 (d, *J* = 8.2, 2H), 6.89 (s, 1H), 2.38 (s, 3H), 1.38 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 153.1, 152.6, 145.1, 144.3, 135.9, 133.7, 129.8, 129.2, 129.0, 128.5, 128.1, 127.7, 127.4, 127.2, 127.2, 126.3, 125.6, 34.8, 31.3, 21.5; HRMS Calculated for $C_{26}H_{27}N_2O_2S$ $[M+H]^+$ 431.1793, found 431.1788.

***N*-(2-(4-Methoxyphenyl)quinolin-3-yl)-4-methylbenzenesulfonamide (1e):** 62% yield, white solid, mp 243-245 °C, $R_f$ = 0.50 (petroleum ether/EtOAc 2:1). $^1$H NMR (400 MHz,



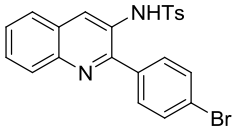

DMSO-$d_6$) δ = 9.90 (s, 1H), 8.09-7.84 (m, 3H), 7.80-7.67 (m, 1H), 7.53 (dd, *J* = 24.5, 7.3, 5H), 7.26 (d, *J* = 7.2, 2H), 6.96 (d, *J* = 7.8, 2H), 3.84 (s, 3H), 2.36 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ = 160.1, 156.6, 146.0, 143.5, 137.8, 133.1, 131.2, 131.1, 130.2, 130.0, 129.0, 128.7, 128.0, 127.3, 127.1, 127.1, 113.7, 55.7, 21.5; HRMS Calculated for $C_{23}H_{21}N_2O_3S$ $[M+H]^+$ 405.1273, found 405.1269.

***N*-(2-(4-Chlorophenyl)quinolin-3-yl)-4-methylbenzenesulfonamide (1f):** 42% yield, white solid, mp 260-262 °C, $R_f$ = 0.40 (petroleum ether/EtOAc 5:1). $^1$H NMR (400 MHz, DMSO-$d_6$) δ =



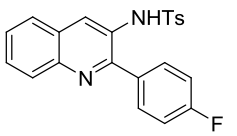

10.02 (s, 1H), 8.08 (s, 1H), 7.97 (dd, *J* = 18.3, 8.2, 2H), 7.76 (t, *J* = 7.3, 1H), 7.67-7.52 (m, 3H), 7.45 (t, *J* = 6.9, 4H), 7.25 (d, *J* = 7.8, 2H), 2.36 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ = 156.0, 146.0, 143.7, 137.6, 137.5, 134.1, 133.8, 131.6, 130.5, 130.0, 129.1, 128.6, 128.2, 128.1, 127.8, 127.5, 127.0, 21.5; HRMS Calculated for $C_{22}H_{18}ClN_2O_2S$ $[M+H]^+$ 409.0778, found 409.0766.

***N*-(2-(4-Bromophenyl)quinolin-3-yl)-4-methylbenzenesulfonamide (1g):** 55% yield, white solid, mp 281-283 °C, $R_f$ = 0.15 (petroleum ether/EtOAc 10:1). $^1$H NMR (400 MHz, DMSO-$d_6$) δ




= 10.02 (s, 1H), 8.07 (s, 1H), 7.97 (dd, *J* = 16.1, 8.2, 2H), 7.76 (t, *J* = 7.4, 1H), 7.60 (dd, *J* = 17.0, 7.9, 3H), 7.46 (dd, *J* = 15.0, 8.2, 4H), 7.25 (d, *J* = 7.9, 2H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ = 156.1, 146.0, 143.6, 137.9, 137.7, 134.0, 131.9, 131.2, 130.5, 130.0, 129.1, 128.7, 128.1, 127.8, 127.5, 127.0, 122.6, 21.5; HRMS Calculated for $C_{22}H_{18}BrN_2O_2S$ $[M+H]^+$ 453.0272, found 453.0267.

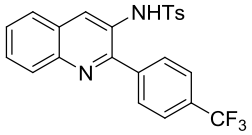
***N*-(2-(4-Fluorophenyl)quinolin-3-yl)-4-methylbenzenesulfonamide (1h):** 51% yield, white solid, mp 278-280 °C, $R_f$ = 0.40 (petroleum ether/EtOAc 10:1). $^1$H NMR (400 MHz, $CDCl_3$) δ =



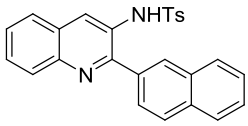

8.44 (s, 1H), 8.02 (d, *J* = 8.4, 1H), 7.86 (d, *J* = 8.1, 1H), 7.67 (dd, *J* = 11.2, 4.1, 1H), 7.62-7.48 (m, 3H), 7.20 (d, *J* = 8.1, 2H), 7.13 (p, *J* = 8.8, 4H), 6.68 (s, 1H), 2.39 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ = 162.8 (d, $^1J_{FC}$ = 245.6 Hz), 156.2, 146.0, 143.6, 137.7, 135.1 (d, $^4J_{FC}$ = 2.2 Hz),

133.9, 132.0 (d, $^{3}J_{FC}$ = 8.6 Hz), 130.4, 130.0, 129.1, 128.6, 128.1, 127.7, 127.4, 127.0, 115.1 (d, $^{2}J_{FC}$ = 21.3 Hz), 21.4; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -111.2; HRMS Calculated for $C_{22}H_{18}FN_2O_2S$ $[M+H]^+$ 393.1073, found 393.1065.

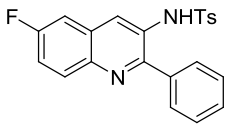
**4-Methyl-*N*-(2-(4-(trifluoromethyl)phenyl)quinolin-3-yl)benzenesulfonamide (1i):** 47% yield, white solid, mp 252-254 °C, $R_f$ = 0.15 (petroleum ether/EtOAc 10:1). $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 8.46 (s, 1H), 8.03 (d, *J* = 8.4, 1H), 7.88 (d, *J* = 8.1, 1H), 7.65 (tt, *J* = 15.0, 7.4, 4H), 7.49 (d, *J* = 8.1, 2H), 7.29 (d, *J* = 7.9, 2H), 7.19 (d, *J* = 8.0, 2H), 6.64 (s, 1H), 2.39 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 152.1, 145.4, 144.6, 140.5, 136.0, 131.6, 131.2, 130.9, 129.9, 129.6, 129.3, 129.1, 128.2, 128.0, 127.9, 127.8, 127.6, 127.1, 126.1, 126.1, 126.0, 126.0, 125.2, 122.4, 21.5; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -62.9; HRMS Calculated for $C_{23}H_{18}F_3N_2O_2S$ $[M+H]^+$ 443.1041, found 443.1037.



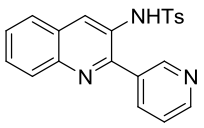

**4-Methyl-*N*-(2-(naphthalen-2-yl)quinolin-3-yl)benzenesulfonamide (1j):** 52% yield, white solid, mp 292-294 °C, $R_f$ = 0.30 (petroleum ether/EtOAc 5:1). $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ = 10.06 (s, 1H), 8.19 (s, 1H), 8.01 (dd, *J* = 16.1, 7.4, 4H), 7.91 (dd, *J* = 10.2, 5.6, 2H), 7.77 (t, *J* = 7.5, 1H), 7.70-7.55 (m, 4H), 7.42 (d, *J* = 8.1, 2H), 7.09 (d, *J* = 8.0, 2H), 2.26 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ = 156.8, 146.0, 143.5, 137.7, 136.1, 133.3, 133.2, 133.0, 130.3, 129.9, 129.1, 129.1, 129.0, 128.8, 128.1, 127.9, 127.6, 127.6, 127.6, 127.5, 127.1, 126.9, 126.6, 21.4; HRMS Calculated for $C_{26}H_{21}N_2O_2S$ $[M+H]^+$ 425.1324, found 425.1317.



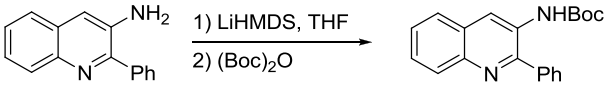

***N*-(6-Fluoro-2-phenylquinolin-3-yl)-4-methylbenzenesulfonamide (1k):** 60% yield, white solid, mp 216-218 °C, $R_f$ = 0.15 (petroleum ether/$CH_2Cl_2$ 1:3). $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 8.36 (s, 1H), 8.01 (dd, *J* = 8.0, 5.2, 1H), 7.54 (d, *J* = 7.5, 2H), 7.42 (dd, *J* = 21.4, 7.7, 5H), 7.18 (dd, *J* = 14.8, 6.8, 4H), 6.83 (s, 1H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 161.1 (d, $^{1}J_{FC}$ = 249.3 Hz), 152.3 (d, $^{4}J_{FC}$ = 2.9 Hz), 144.6, 142.1, 136.3, 135.9, 131.8 (d, $^{3}J_{FC}$ = 9.4 Hz), 129.9, 129.5, 129.4, 129.3, 128.6, 128.4, 127.2, 124.7 (d, $^{3}J_{FC}$ = 5.4 Hz), 119.3 (d, $^{2}J_{FC}$ = 25.9 Hz), 110.4 (d, $^{2}J_{FC}$ = 22.2 Hz), 21.5; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -112.1; HRMS Calculated for $C_{22}H_{18}FN_2O_2S$ $[M+H]^+$ 393.1073, found 393.1065.




**4-Methyl-*N*-(2-(pyridin-3-yl)quinolin-3-yl)benzenesulfonamide (1l):** 58% yield, white solid, mp 192-194 °C, $R_f$ = 0.30 (petroleum ether/EtOAc 5:1). $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 8.62 (d, *J* = 4.5, 1H), 8.43 (s, 2H), 8.03 (d, *J* = 8.4, 1H), 7.86 (d, *J* = 8.1, 1H), 7.70 (t, *J* = 7.6, 1H), 7.57 (dd, *J* = 21.7, 8.3, 4H), 7.41 (s, 1H), 7.31 (dd, *J* = 7.5, 5.0, 1H), 7.20 (d, *J* = 8.0, 2H), 2.39 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 151.0, 150.0, 149.4, 145.6, 144.5, 136.4, 136.2, 133.2, 129.9, 129.6, 129.3, 128.9, 128.5, 127.9, 127.7, 127.6, 127.1, 123.5, 21.5; HRMS Calculated for $C_{21}H_{18}N_3O_2S$ $[M+H]^+$ 376.1120, found 376.1116.



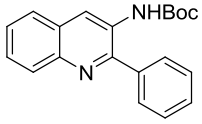
## 4. Synthesis of *tert*-butyl 2-phenylquinolin-3-ylcarbamate 7



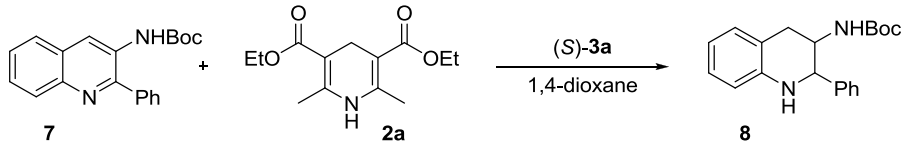

**7**

Under an nitrogen atmosphere and at 0 °C, a solution of 2-phenylquinolin-3-amine (100 mg, 0.45 mol) in THF (5 mL) was charged with 1.0 M lithium bis(trimethylsilyl)amide in THF/PhEt (1.1 mL, 1.1 mmol), followed by di-*tert*-butyl dicarbonate ($(Boc)_2O$, 119 mg, 0.55 mmol) in THF (4 mL). The cold bath was removed and the viscous mixture was allowed to stir for 5 h. The solvent was evaporated, dissolved in dichloromethane (10 mL) and washed with 0.05 M HCl (10 mL) and brine. The combined organic layers were dried ($Na_2SO_4$). After filtration, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to yield the product.

***tert*-Butyl 2-phenylquinolin-3-ylcarbamate (7):** 71% yield, white solid, mp 144-146 °C, $R_f$ = 0.70 (petroleum ether/EtOAc 5:1). $^1$H NMR (400 MHz, $CDCl_3$) δ = 8.92 (s, 1H), 8.05 (d, *J* = 8.0, 1H), 7.81 (d, *J* = 7.5, 1H), 7.71-7.45 (m, 7H), 6.80 (s, 1H), 1.51 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 152.9, 151.6, 144.3, 137.7, 130.2, 129.5, 129.4, 129.3, 129.1, 128.3, 128.2, 127.5, 127.2, 123.3, 81.5, 28.5; HRMS Calculated for $C_{20}H_{21}N_2O_2$ $[M+H]^+$ 321.1603, found 321.1600.



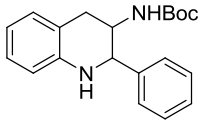

## 5. Asymmetric Transfer Hydrogenation of 7



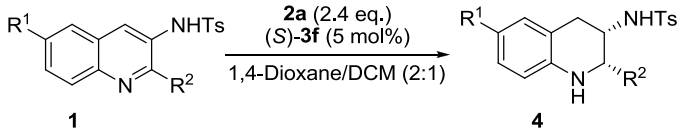

**7** **2a** **8**

A mixture of **7** (0.125 mmol), Hantzsch ester **2a** (76 mg, 0.30 mmol, 2.4 equiv), and chiral phosphoric acid (*S*)-**3a** (3.2 mg, 0.00625 mmol, 5 mol%) in 1,4-dioxane (3 mL) was stirred at 25 °C under nitrogen for 24 h. After the reaction was completed (determined by TLC), the solvent was removed under reduced pressure. Purification was performed by a silica gel column to give the desired product. The enantiomeric excesses were determined by chiral HPLC.

***tert*-Butyl 2-phenyl-1,2,3,4-tetrahydroquinolin-3-ylcarbamate (8):** 70% yield, 42% ee, white solid, mp 55-57 °C, $[\alpha]^{20}_D$ = -41.5 (*c* 0.20, $CH_2Cl_2$), $R_f$ = 0.70 (petroleum ether/$CH_2Cl_2$/EtOAc 10:10:1). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.40-7.29 (m, 5H), 7.04 (dd, *J* = 16.2, 7.9, 2H), 6.72 (t, *J* = 7.3, 1H), 6.60 (d, *J* = 7.9, 1H), 4.89 (d, *J* = 9.1, 1H), 4.59 (s, 1H), 4.27 (d, *J* = 4.9, 1H), 4.02 (s, 1H), 3.20 (dd, *J* = 16.4, 4.6, 1H), 2.79 (dd, *J* = 16.4, 3.7, 1H), 1.30 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 155.3, 143.9, 140.6, 130.4, 128.5, 127.8, 127.3, 126.9, 118.4, 118.4, 114.3, 79.1, 58.3, 47.9, 33.7, 28.3; HRMS Calculated for $C_{20}H_{25}N_2O_2$ $[M+H]^+$ 325.1916, found 325.1910; HPLC: Chirapak OJ-H column, 254 nm, 30 °C, *n*-hexane/*i*-propanol = 70/30, flow = 0.7 mL/min, retention time 7.5 min and 10.3 min (major).



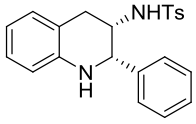
## 6. Asymmetric Transfer Hydrogenation of Quinolin-3-amines 1



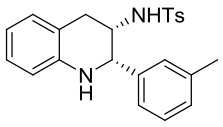

1 4

A mixture of quinolin-3-amine **1** (0.125 mmol), Hantzsch ester **2a** (76 mg, 0.30 mmol, 2.4 equiv), and chiral phosphoric acid (*S*)-**3f** (4.7 mg, 0.00625 mmol, 5 mol%) in 1,4-dioxane/$CH_2Cl_2$ (2:1, 3 mL) was stirred at 25 $^oC$ under nitrogen for 24 h. After the reaction was completed (determined by TLC), the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel to yield desire product. The enantiomeric excesses were determined by chiral HPLC.

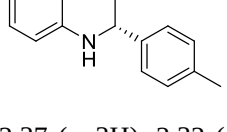
**4-Methyl-*N*-((2*S*,3*S*)-2-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)benzenesulfonamide (4a)[2]:** 94% yield, 95% ee, white solid, mp 175-177 $^oC$, $[\alpha]^{20}_D$ = +73.2 (*c* 0.88, $CH_2Cl_2$) [lit.[2]: $[\alpha]^{18}_D$ = +82.9 (*c* 0.14, $CHCl_3$) for >99% ee (2*S*,3*S*)], $R_f$ = 0.40 (petroleum ether/EtOAc 5:1). $^1H$ NMR (400 MHz, $CDCl_3$) δ = 7.35 (d, *J* = 8.2, 2H), 7.25-7.17 (m, 5H), 7.04 (t, *J* = 8.8, 3H), 6.93 (d, *J* = 7.4, 1H), 6.72 (t, *J* = 7.4, 1H), 6.60 (d, *J* = 7.9, 1H), 4.84 (d, *J* = 8.7, 1H), 4.49 (s, 1H), 3.99 (s, 1H), 3.84 (dd, *J* = 7.8, 3.5, 1H), 3.07 (dd, *J* = 16.2, 3.9, 1H), 2.89 (dd, *J* = 16.5, 4.2, 1H), 2.36 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 143.6, 142.9, 139.7, 137.6, 130.6, 129.6, 128.7, 128.0, 127.6, 126.9, 126.8, 119.0, 118.2, 114.7, 58.4, 51.6, 34.4, 21.6; HPLC: Chirapak AD-H column, 254 nm, 30 $^oC$, *n*-hexane/*i*-propanol = 70/30, flow = 0.7 mL/min, retention time 15.0 min (major) and 20.1 min.




**4-Methyl-*N*-((2*S*,3*S*)-2-*m*-tolyl-1,2,3,4-tetrahydroquinolin-3-yl)benzenesulfonamide (4b):** 96% yield, 97% ee, white solid, mp 197-199 $^oC$, $[\alpha]^{20}_D$ = +71.3 (*c* 0.94, $CH_2Cl_2$), $R_f$ = 0.45 (petroleum ether/EtOAc 5:1). $^1H$ NMR (400 MHz, $CDCl_3$) δ = 7.31 (d, *J* = 7.9, 2H), 7.15-6.90 (m, 8H), 6.72 (t, *J* = 7.3, 1H), 6.59 (d, *J* = 7.9, 1H), 4.86 (d, *J* = 8.4, 1H), 4.43 (s, 1H), 3.93 (s, 1H), 3.81 (d, *J* = 4.1, 1H), 3.11 (dd, *J* = 16.4, 3.3, 1H), 2.96 (dd, *J* = 16.4, 2.9, 1H), 2.35 (s, 3H), 2.24 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 143.5, 142.5, 139.5, 138.2, 137.5, 130.5, 129.3, 128.6, 128.5, 127.4, 127.3, 126.6, 123.6, 118.9, 118.2, 114.6, 58.1, 51.6, 34.6, 21.4, 21.4; HRMS Calculated for $C_{23}H_{25}N_2O_2S$ $[M+H]^+$ 393.1637, found 393.1632; HPLC: Chirapak AD-H column, 254 nm, 30 $^oC$, *n*-hexane/*i*-propanol = 70/30, flow = 0.7 mL/min, retention time 12.8 min (major) and 16.3 min.

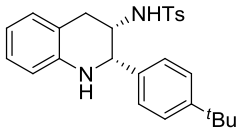



**4-Methyl-*N*-((2*S*,3*S*)-2-*p*-tolyl-1,2,3,4-tetrahydroquinolin-3-yl)benzenesulfonamide (4c):** 98% yield, 91% ee, white solid, mp 240-242 $^oC$, $[\alpha]^{20}_D$ = +59.5 (*c* 0.92, $CH_2Cl_2$), $R_f$ = 0.45 (petroleum ether/EtOAc 5:1). $^1H$ NMR (400 MHz, $CDCl_3$) δ = 7.35 (d, *J* = 8.2, 2H), 7.11-6.96 (m, 7H), 6.93 (d, *J* = 7.5, 1H), 6.71 (t, *J* = 7.4, 1H), 6.58 (d, *J* = 7.9, 1H), 4.82 (d, *J* = 8.3, 1H), 4.44 (s, 1H), 3.94 (s, 1H), 3.80 (td, *J* = 7.0, 4.0, 1H), 3.07 (dd, *J* = 16.4, 4.0, 1H), 2.89 (dd, *J* = 16.5, 4.1, 1H), 2.37 (s, 3H), 2.32 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 143.5, 142.5, 137.6, 136.5, 130.4, 129.2, 129.2, 127.4, 126.7, 126.5, 118.8, 118.1, 114.5, 57.9, 51.5, 34.3, 21.5, 21.1; HRMS Calculated for $C_{23}H_{25}N_2O_2S$ $[M+H]^+$ 393.1637, found 393.1635; HPLC: Chirapak AD-H column,

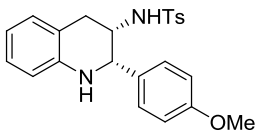


254 nm, 30 °C, *n*-hexane/*i*-propanol = 70/30, flow = 0.7 mL/min, retention time 14.1 min (major) and 21.2 min.

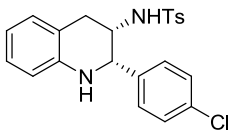
***N*-((2*S*,3*S*)-2-(4-*tert*-Butylphenyl)-1,2,3,4-tetrahydroquinolin-3-yl)-4-methylbenzenesulfonamide (4d):** 93% yield, 94% ee, white solid, mp 201-203 °C, $[\alpha]^{20}_D$ = +28.7 (*c* 1.00, $CH_2Cl_2$), $R_f$ = 0.30 (petroleum ether/EtOAc 10:1). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.42 (d, *J* = 8.2, 2H), 7.27 (d, *J* = 8.3, 2H), 7.17 (d, *J* = 8.3, 2H), 7.11-7.00 (m, 3H), 6.90 (d, *J* = 7.4, 1H), 6.70 (t, *J* = 7.4, 1H), 6.56 (d, *J* = 7.9, 1H), 4.78 (d, *J* = 8.8, 1H), 4.46 (d, *J* = 2.3, 1H), 4.00 (s, 1H), 3.84 (td, *J* = 8.1, 4.6, 1H), 3.01 (dd, *J* = 16.4, 4.1, 1H), 2.88 (dd, *J* = 16.5, 5.0, 1H), 2.35 (s, 3H), 1.32 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 151.0, 143.5, 142.7, 137.7, 136.6, 130.3, 129.3, 127.5, 126.9, 126.7, 125.5, 118.6, 118.0, 114.4, 58.0, 51.2, 34.5, 33.7, 31.4, 21.5; HRMS Calculated for $C_{26}H_{31}N_2O_2S$ $[M+H]^+$ 435.2106, found 435.2095; HPLC: Chirapak AD-H column, 254 nm, 30 °C, *n*-hexane/*i*-propanol = 70/30, flow = 0.7 mL/min, retention time 10.4 min (major) and 19.5 min.



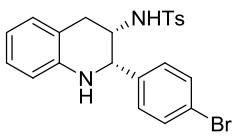

***N*-((2*S*,3*S*)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinolin-3-yl)-4-methylbenzenesulfonamide (4e):** 96% yield, 99% ee, white solid, mp 195-197 °C, $[\alpha]^{20}_D$ = +49.2 (*c* 0.98, $CH_2Cl_2$), $R_f$ = 0.15 (petroleum ether/EtOAc 10:1). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.36 (d, *J* = 8.2, 2H), 7.09 (d, *J* = 8.6, 2H), 7.03 (t, *J* = 6.7, 3H), 6.93 (d, *J* = 7.5, 1H), 6.71 (t, *J* = 7.6, 3H), 6.57 (d, *J* = 7.9, 1H), 4.82 (d, *J* = 8.6, 1H), 4.42 (d, *J* = 1.7, 1H), 3.94 (s, 1H), 3.79 (d, *J* = 6.5, 4H), 3.07 (dd, *J* = 16.4, 4.0, 1H), 2.87 (dd, *J* = 16.5, 4.1, 1H), 2.36 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 159.4, 143.5, 142.7, 137.6, 131.5, 130.4, 129.3, 127.7, 127.4, 126.7, 118.8, 118.0, 114.5, 113.9, 57.6, 55.2, 51.6, 34.3, 21.4; HRMS Calculated for $C_{23}H_{25}N_2O_3S$ $[M+H]^+$ 409.1586, found 409.1573; HPLC: Chirapak AD-H column, 254 nm, 30 °C, *n*-hexane/*i*-propanol = 70/30, flow = 0.7 mL/min, retention time 17.8 min (major) and 30.1 min.




***N*-((2*S*,3*S*)-2-(4-Chlorophenyl)-1,2,3,4-tetrahydroquinolin-3-yl)-4-methylbenzenesulfonamide (4f):** 97% yield, 95% ee, white solid, mp 260-262 °C, $[\alpha]^{20}_D$ = +52.0 (*c* 0.88, $CH_2Cl_2$), $R_f$ = 0.20 (petroleum ether/EtOAc 10:1). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.33 (d, *J* = 8.2, 2H), 7.13-7.04 (m, 7H), 6.99 (d, *J* = 7.4, 1H), 6.76 (t, *J* = 7.4, 1H), 6.61 (d, *J* = 8.1, 1H), 4.87 (d, *J* = 8.9, 1H), 4.47 (s, 1H), 3.90 (s, 1H), 3.80 (d, *J* = 5.6, 1H), 3.17 (dd, *J* = 16.6, 4.1, 1H), 2.96 (dd, *J* = 16.5, 3.4, 1H), 2.41 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ = 144.7, 142.8, 140.4, 138.5, 132.2, 129.9, 129.8, 129.8, 128.0, 127.5, 126.7, 117.4, 116.6, 113.9, 57.0, 51.1, 31.8, 21.5; HRMS Calculated for $C_{22}H_{22}ClN_2O_2S$ $[M+H]^+$ 413.1091, found 413.1076; HPLC: Chirapak AD-H column, 254 nm, 30 °C, *n*-hexane/*i*-propanol = 70/30, flow = 0.7 mL/min, retention time 12.4 min (major) and 23.1 min.

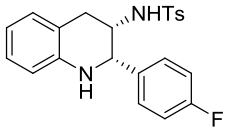



***N*-((2*S*,3*S*)-2-(4-Bromophenyl)-1,2,3,4-tetrahydroquinolin-3-yl)-4-methylbenzenesulfonamide (4g):** 99% yield, 96% ee, white solid, mp 264-266 °C, $[\alpha]^{20}_D$ = +33.6 (*c* 0.80, $CH_2Cl_2$), $R_f$ = 0.20 (petroleum ether/EtOAc 10:1). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.33 (d, *J* = 8.3, 2H), 7.27 (d, *J* = 7.2, 2H), 7.07 (dd, *J* = 13.3, 8.2, 5H), 6.98 (d, *J* = 7.6, 1H), 6.76 (t, *J* = 7.0, 1H), 6.61 (d, *J* = 7.9, 1H), 4.85 (d, *J* = 8.9, 1H), 4.45 (s, 1H), 3.89 (s, 1H), 3.80 (dd, *J* = 8.5, 3.3, 1H), 3.15 (dd, *J* = 16.6, 4.0, 1H), 2.95 (dd, *J* = 16.6, 3.5, 1H), 2.43 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ = 144.7, 142.8, 140.8, 138.5, 130.9, 130.3, 129.8, 129.8, 127.5, 126.7, 120.8, 117.4, 116.6, 113.9,

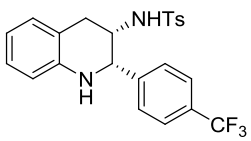


57.0, 51.1, 31.7, 21.5. HRMS Calculated for $C_{22}H_{22}BrN_2O_2S$ $[M+H]^+$ 457.0585, found 457.0579; HPLC: Chirapak AD-H column, 254 nm, 30 °C, *n*-hexane/*i*-propanol = 70/30, flow = 0.7 mL/min, retention time 13.1 min (major) and 24.8 min.

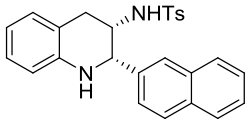
***N*-((2*S*,3*S*)-2-(4-Fluorophenyl)-1,2,3,4-tetrahydroquinolin-3-yl)-4-methylbenzenesulfonamide (4h):** 93% yield, 98% ee, white solid, mp 249-251 °C, $[\alpha]^{20}_D$ = +45.0 (*c* 0.88, $CH_2Cl_2$), $R_f$ = 0.40 (petroleum ether/EtOAc 7:1). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.35 (d, *J* = 8.2, 2H), 7.15 (dd, *J* = 8.5, 5.4, 2H), 7.05 (t, *J* = 8.5, 3H), 6.94 (d, *J* = 7.5, 1H), 6.83 (t, *J* = 8.6, 2H), 6.73 (t, *J* = 7.4, 1H), 6.59 (d, *J* = 8.0, 1H), 4.84 (d, *J* = 8.9, 1H), 4.47 (s, 1H), 3.92 (s, 1H), 3.80 (dd, *J* = 8.3, 3.2, 1H), 3.11 (dd, *J* = 16.5, 4.0, 1H), 2.88 (dd, *J* = 16.5, 3.7, 1H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 162.5 (d, $^1J_{FC}$ = 246.4 Hz), 143.3, 142.9, 137.5, 135.3 (d, $^4J_{FC}$ = 3.1 Hz), 130.5, 129.4, 128.3 (d, $^3J_{FC}$ = 8.1 Hz), 127.5, 126.6, 119.1, 117.8, 115.3 (d, $^2J_{FC}$ = 21.4 Hz), 114.7, 57.6, 51.7, 34.5, 21.4; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -114.3. HRMS Calculated for $C_{22}H_{22}FN_2O_2S$ $[M+H]^+$ 397.1386, found 397.1368; HPLC: Chirapak AD-H column, 254 nm, 30 °C, *n*-hexane/*i*-propanol = 70/30, flow = 0.7 mL/min, retention time 12.2 min (major) and 20.8 min.




**4-Methyl-*N*-((2*S*,3*S*)-2-(4-(Trifluoromethyl)phenyl)-1,2,3,4-tetrahydroquinolin-3-yl)benzenesulfonamide (4i):** 99% yield, 98% ee, white solid, 214-216 °C, $[\alpha]^{20}_D$ = +65.9 (*c* 0.94, $CH_2Cl_2$), $R_f$ = 0.20 (petroleum ether/EtOAc 10:1). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.42 (d, *J* = 8.2, 2H), 7.36-7.29 (m, 4H), 7.07 (t, *J* = 7.6, 1H), 7.00 (dd, *J* = 13.4, 7.8, 3H), 6.77 (t, *J* = 7.4, 1H), 6.63 (d, *J* = 8.0, 1H), 4.88 (d, *J* = 8.8, 1H), 4.55 (s, 1H), 3.96 (s, 1H), 3.85 (d, *J* = 3.2, 1H), 3.16 (dd, *J* = 16.6, 4.0, 1H), 2.96 (dd, *J* = 16.6, 3.5, 1H), 2.34 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 143.6, 143.1, 143.0, 137.2, 130.6, 130.2, 129.9, 129.3, 127.6, 127.1, 126.6, 125.3, 125.3, 125.3, 125.2, 122.6, 119.5, 117.8, 114.9, 58.0, 51.5, 34.6, 21.3; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -62.4. HRMS Calculated for $C_{23}H_{22}F_3N_2O_2S$ $[M+H]^+$ 447.1354, found 447.1344; HPLC: Chirapak AD-H column, 254 nm, 30 °C, *n*-hexane/*i*-propanol = 70/30, flow = 0.7 mL/min, retention time 9.1 min (major) and 17.1 min.

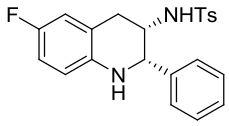



**4-Methyl-*N*-((2*S*,3*S*)-2-(Naphthalen-2-yl)-1,2,3,4-tetrahydroquinolin-3-yl)benzenesulfonamide (4j):** 91% yield, 83% ee, white solid, mp 225-227 °C, $[\alpha]^{20}_D$ = +27.2 (*c* 0.98, $CH_2Cl_2$), $R_f$ = 0.20 (petroleum ether/EtOAc 10:1). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.79-7.73 (m, 1H), 7.73-7.67 (m, 1H), 7.62 (s, 1H), 7.55 (d, *J* = 8.5, 1H), 7.52-7.46 (m, 2H), 7.15 (dd, *J* = 8.5, 1.6, 1H), 7.07 (dd, *J* = 12.8, 8.1, 3H), 7.01 (d, *J* = 7.5, 1H), 6.76 (td, *J* = 7.5, 0.8, 1H), 6.65 (d, *J* = 7.9, 1H), 6.50 (d, *J* = 8.1, 2H), 5.00 (d, *J* = 8.4, 1H), 4.58 (d, *J* = 1.2, 1H), 4.03 (s, 1H), 3.91-3.83 (m, 1H), 3.21 (dd, *J* = 16.5, 4.0, 1H), 3.06 (dd, *J* = 16.5, 3.2, 1H), 2.06 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 143.4, 142.3, 136.9, 136.8, 133.2, 133.1, 130.6, 128.8, 128.3, 128.0, 127.5, 127.4, 126.3, 126.3, 126.1, 125.0, 124.5, 119.2, 118.3, 114.9, 58.1, 51.7, 35.2, 21.3; HRMS Calculated for $C_{26}H_{25}N_2O_2S$ $[M+H]^+$ 429.1637, found 429.1625; HPLC: Chirapak AD-H column, 254 nm, 30 °C, *n*-hexane/*i*-propanol = 70/30, flow = 0.7 mL/min, retention time 17.5 min (major) and 22.8 min.

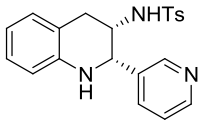



***N*-((2*S*,3*S*)-6-Fluoro-2-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)-4-methylbenzenesulfonamide (4k):** 94% yield, 73% ee, white solid, mp 204-206 °C, $[\alpha]^{20}_D$ = +66.7 (*c* 0.92, $CH_2Cl_2$), $R_f$ = 0.25 ($CH_2Cl_2$/petroleum ethe 3:1). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.33 (d, *J* = 8.2, 2H), 7.22 (dd, *J* = 7.4, 2.6, 5H), 7.03 (d, *J* = 8.1, 2H), 6.78 (td, *J* = 8.5, 2.8, 1H), 6.67 (d, *J* = 9.0, 1H), 6.55 (dd, *J*

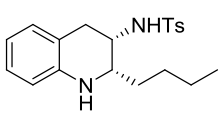
= 8.7, 4.7, 1H), 4.88 (d, *J* = 8.4, 1H), 4.45 (s, 1H), 3.88 (s, 1H), 3.82 (dd, *J* = 7.3, 3.6, 1H), 3.10 (dd, *J* = 16.8, 4.0, 1H), 2.92 (dd, *J* = 16.7, 3.2, 1H), 2.36 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ = 154.7 (d, $^{1}J_{FC}$ = 231.3 Hz), 142.7, 141.5 (d, $^{4}J_{FC}$ = 1.3 Hz), 138.6, 129.9, 128.2, 128.2, 127.4, 126.7, 118.9 (d, $^{3}J_{FC}$ = 7.2 Hz), 115.7 (d, $^{2}J_{FC}$ = 21.9 Hz), 114.6 (d, $^{3}J_{FC}$ = 7.5 Hz), 114.1 (d, $^{2}J_{FC}$ = 22.1 Hz), 57.7, 51.0, 31.5, 21.4; $^{19}$F NMR (376 MHz, DMSO-$d_6$) δ = -129.3. HRMS Calculated for $C_{22}H_{22}FN_2O_2S$ $[M+H]^+$ 397.1386, found 397.1373; HPLC: Chirapak AD-H column, 254 nm, 30 $^{o}$C, *n*-hexane/*i*-propanol = 40/60, flow = 0.2 mL/min, retention time 31.9 min (major) and 33.4 min.



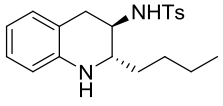

**4-Methyl-*N*-((2*S*,3*S*)-2-(Pyridin-3-yl)-1,2,3,4-tetrahydroquinolin-3-yl)benzenesulfonamide (4l):** 70% yield, 97% ee, colorless oil, $[\alpha]^{20}_{D}$ = +65.0 (*c* 0.50, $CH_2Cl_2$), $R_f$ = 0.40 (pure EtOAc). $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 8.53-8.38 (m, 2H), 7.60 (d, *J* = 7.9, 1H), 7.44 (d, *J* = 8.2, 2H), 7.17-7.02 (m, 4H), 6.93 (d, *J* = 7.4, 1H), 6.74 (t, *J* = 7.3, 1H), 6.61 (d, *J* = 8.0, 1H), 5.14 (d, *J* = 7.7, 1H), 4.54 (s, 1H), 4.01 (s, 1H), 3.92-3.83 (m, 1H), 3.09 (dd, *J* = 16.5, 4.0, 1H), 2.85-2.74 (m, 1H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 149.1, 148.6, 143.1, 143.0, 137.6, 135.3, 134.7, 130.5, 129.6, 127.7, 126.6, 123.3, 119.2, 117.4, 114.7, 56.6, 51.2, 33.9, 21.5; HRMS Calculated for $C_{21}H_{22}N_3O_2S$ $[M+H]^+$ 380.1433, found 380.1420; HPLC: Chirapak AD-H column, 254 nm, 30 $^{o}$C, *n*-hexane/*i*-propanol = 70/30, flow = 0.7 mL/min, retention time 18.9 min and 65.3 min (major).




***N*-(*cis*-2-Butyl-1,2,3,4-tetrahydroquinolin-3-yl)-4-methylbenzenesulfonamide (4ma)[3]:** 13% yield, 60% ee, white solid, mp 164-166 $^{o}$C, $[\alpha]^{20}_{D}$ = +13.0 (*c* 0.20, $CH_2Cl_2$), [lit.[3]: $[\alpha]^{20}_{D}$ = -46.5 (*c* 0.20, $CH_2Cl_2$) for >99% ee (2*S*,3*S*)], $R_f$ = 0.55 (petroleum ether/EtOAc 5:1). $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 8.2, 2H), 7.27 (d, *J* = 8.1, 2H), 6.98 (t, *J* = 7.5, 1H), 6.77 (d, *J* = 7.4, 1H), 6.63 (t, *J* = 7.2, 1H), 6.48 (d, *J* = 7.9, 1H), 4.87 (d, *J* = 9.2, 1H), 3.80-3.69 (m, 1H), 3.61 (s, 1H), 3.18 (t, *J* = 6.6, 1H), 2.87 (dd, *J* = 16.6, 3.9, 1H), 2.57 (dd, *J* = 16.6, 2.1, 1H), 2.42 (s, 3H), 1.46-1.25 (m, 2H), 1.24-1.06 (m, 4H), 0.84 (t, *J* = 6.9, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 143.5, 143.2, 138.8, 130.5, 129.6, 127.3, 127.0, 118.5, 117.8, 114.2, 54.8, 48.4, 34.3, 31.7, 27.7, 22.6, 21.5, 13.9. HPLC: Chirapak AD-H column, 254 nm, 30 $^{o}$C, *n*-hexane/*i*-propanol = 80/20, flow = 0.9 mL/min, retention time 11.6 min and 13.2 min (major).

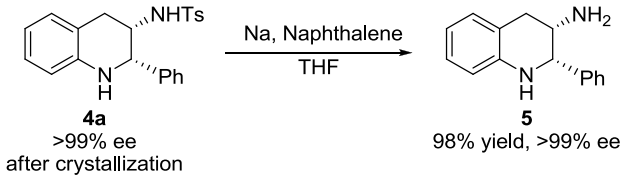



***N*-(*trans*-2-Butyl-1,2,3,4-tetrahydroquinolin-3-yl)-4-methylbenzenesulfonamide (4mb)[3]:** 76% yield, 13% ee, colorless oil, $[\alpha]^{20}_{D}$ = -8.0 (*c* 0.66, $CH_2Cl_2$), $R_f$ = 0.50 (petroleum ether/EtOAc 5:1). $^{1}$H NMR (400 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 8.2, 2H), 7.28 (d, *J* = 8.1, 2H), 6.98 (t, *J* = 7.5, 1H), 6.78 (d, *J* = 7.4, 1H), 6.61 (t, *J* = 7.3, 1H), 6.47 (d, *J* = 8.0, 1H), 4.91 (d, *J* = 9.3, 1H), 3.98 (s, 1H), 3.62 (td, *J* = 7.9, 3.7, 1H), 3.06-2.94 (m, 1H), 2.82 (dd, *J* = 16.7, 4.5, 1H), 2.52-2.38 (m, 4H), 1.35-1.17 (m, 6H), 0.84 (t, *J* = 6.9, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 143.3, 142.0, 138.6, 130.3, 129.7, 127.5, 126.9, 117.7, 116.5, 114.3, 55.0, 49.0, 33.8, 29.7, 27.7, 22.4, 21.5, 13.9. HPLC: Chirapak AD-H column, 254 nm, 30 $^{o}$C, *n*-hexane/*i*-propanol = 75/25, flow = 0.8 mL/min, retention time 10.6 min (major) and 12.4 min.




3 Cai, X.-F.; Guo, R.-N.; Chen, M.-W.; Shi, L.; Zhou, Y.-G. *Chem. Eur. J.* **2014**, DOI: 10.1002/chem.201402592.

## 7. Removal of Ts Group

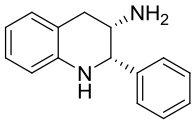



**4a**
>99% ee
after crystallization

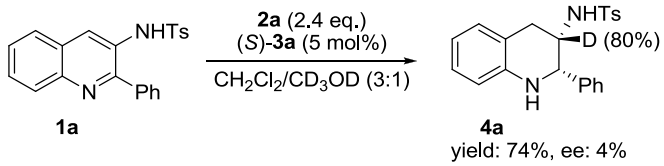
**5**
98% yield, >99% ee

Naphthalene (256 mg, 2.0 mmol) was added to a vigorously stirred suspension of sodium (46 mg, 2.0 mmol; washed free of oil in hexanes) in tetrahydrofuran (4 mL) under nitrogen at 25 °C. The resulting green suspension was stirred for 1 h at 25 °C, then was transferred to a solution of 4-methyl-*N*-((2*S*,3*S*)-2-phenyl-1,2,3,4-tetrahydroquinolin-3-yl)benzenesulfonamide **4a** (38 mg, 0.1 mmol) in THF (4 mL) cooled at -78 °C; portion-wise addition of this suspension to the reaction solution was ceased upon formation of a persistent, dark-green reaction solution. The dark-green solution was stirred at -78 °C for 1 h. Water (1 mL) was added to the solution at -78 °C. The resulting suspension was stirred at -78 °C for 2 min, then warm to ambient temperature. The organic layer was separated, and the aqueous later was extracted with $CH_2Cl_2$. The combined organic layers were dried ($Na_2SO_4$). After filtration, the solvent was removed under reduced pressure, the residue was purified by flash chromatography on silica gel to yield the product.

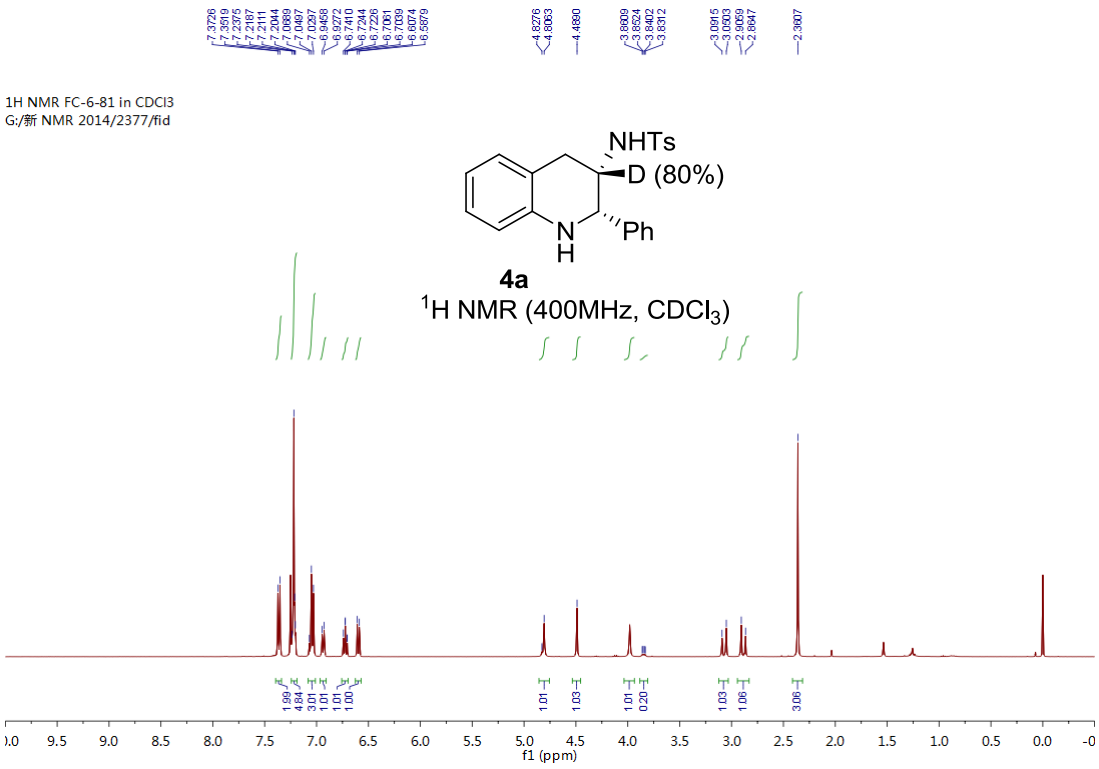
**(2*S*,3*S*)-2-Phenyl-1,2,3,4-tetrahydroquinolin-3-amine (5)**: 98% yield, >99% ee, white solid, mp 98-100 $^oC$, $[\alpha]^{20}_D$ = +56.4 (*c* 0.44, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$) δ = 7.44-7.27 (m, 5H), 7.09-6.98 (m, 2H), 6.73-6.65 (m, 1H), 6.62-6.54 (m, 1H), 4.55 (s, 1H), 3.99 (s, 1H), 3.36-3.18 (m, 2H), 2.74 (d, *J* = 15.8, 1H), 1.26 (s, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ = 144.0, 141.7, 130.6, 128.8, 127.9, 127.3, 127.1, 118.6, 118.1, 114.2, 60.2, 49.5, 35.7; HRMS Calculated for $C_{15}H_{17}N_2$ $[M+H]^+$ 225.1392, found 225.1380; HPLC (corresponding *N*-4-toluenesulfonyl derivative): Chirapak AD-H column, 254 nm, 30 $^oC$, *n*-hexane/*i*-propanol = 70/30, flow = 0.7 mL/min, retention time 14.7 min (single).



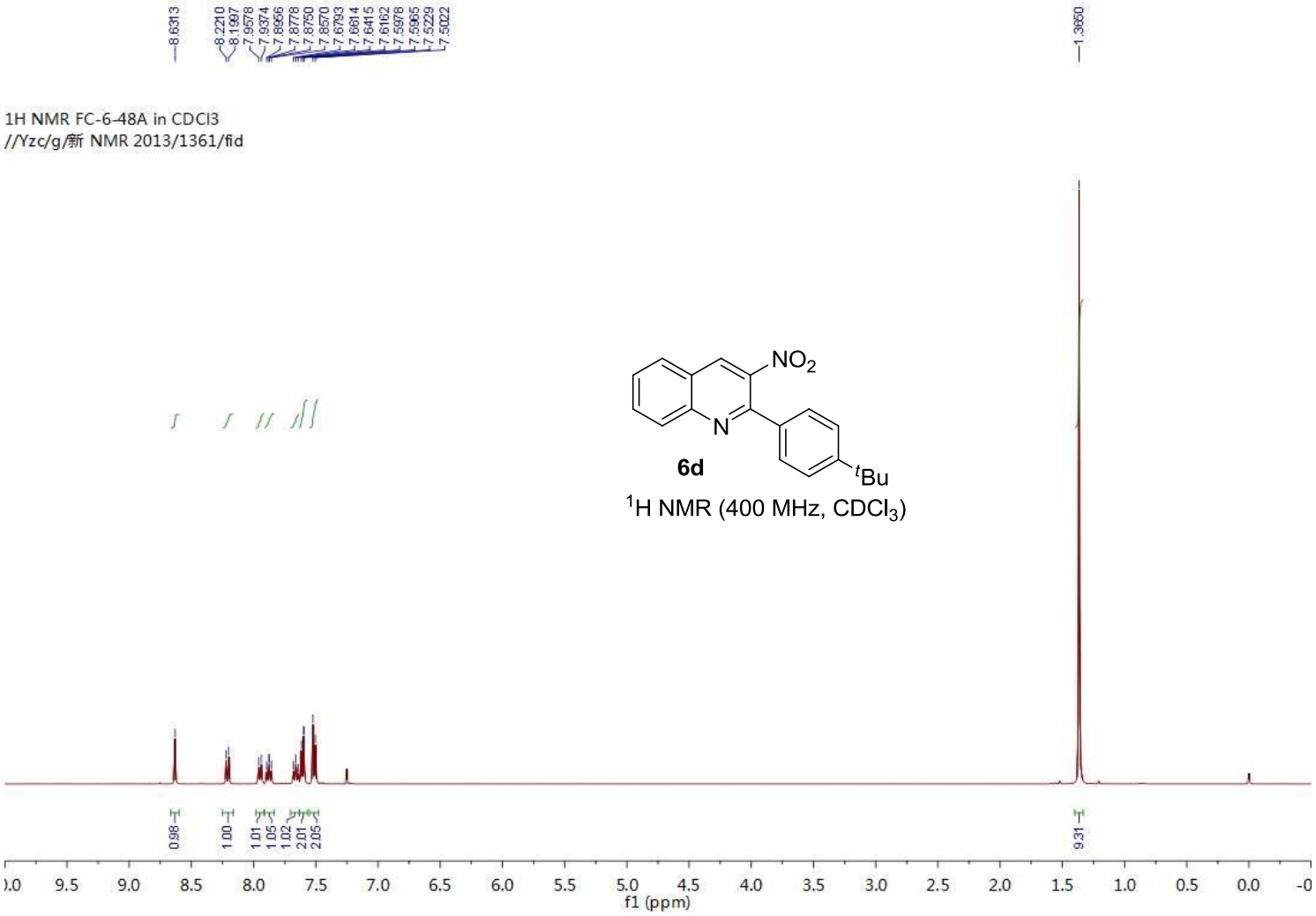
## 8. Isotopic Labeling Experiment

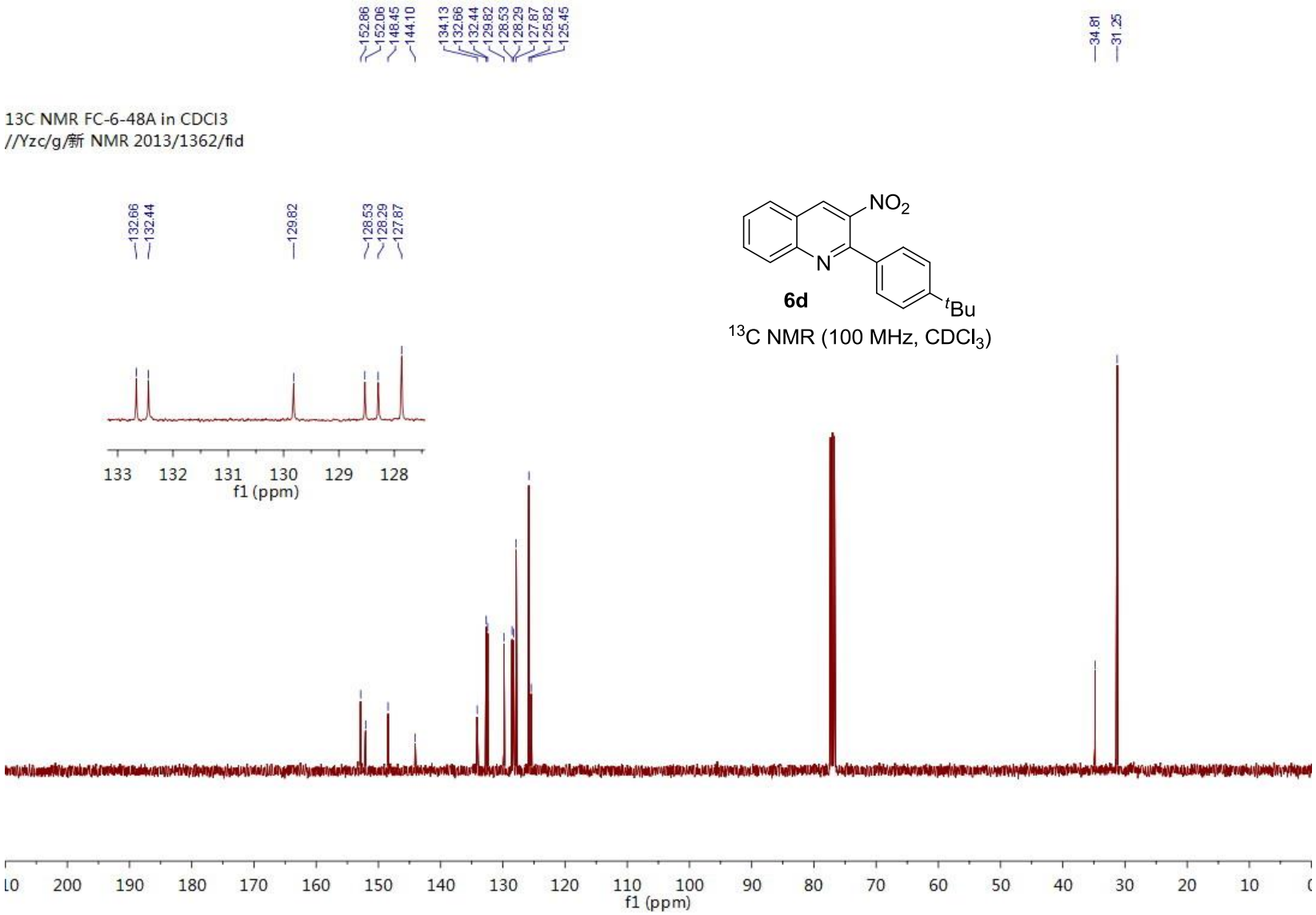



A mixture of **1a** (47 mg, 0.125 mmol), Hantzsch ester **2a** (76 mg, 0.30 mmol, 2.4 equiv), and chiral phosphoric acid (*S*)-**3a** (3.2 mg, 0.00625 mmol, 5 mol%) in $CH_2Cl_2/CD_3OD$ (3:1, 3 mL) was stirred at 30 °C under nitrogen for 24 h. The solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel to give product **4a**.

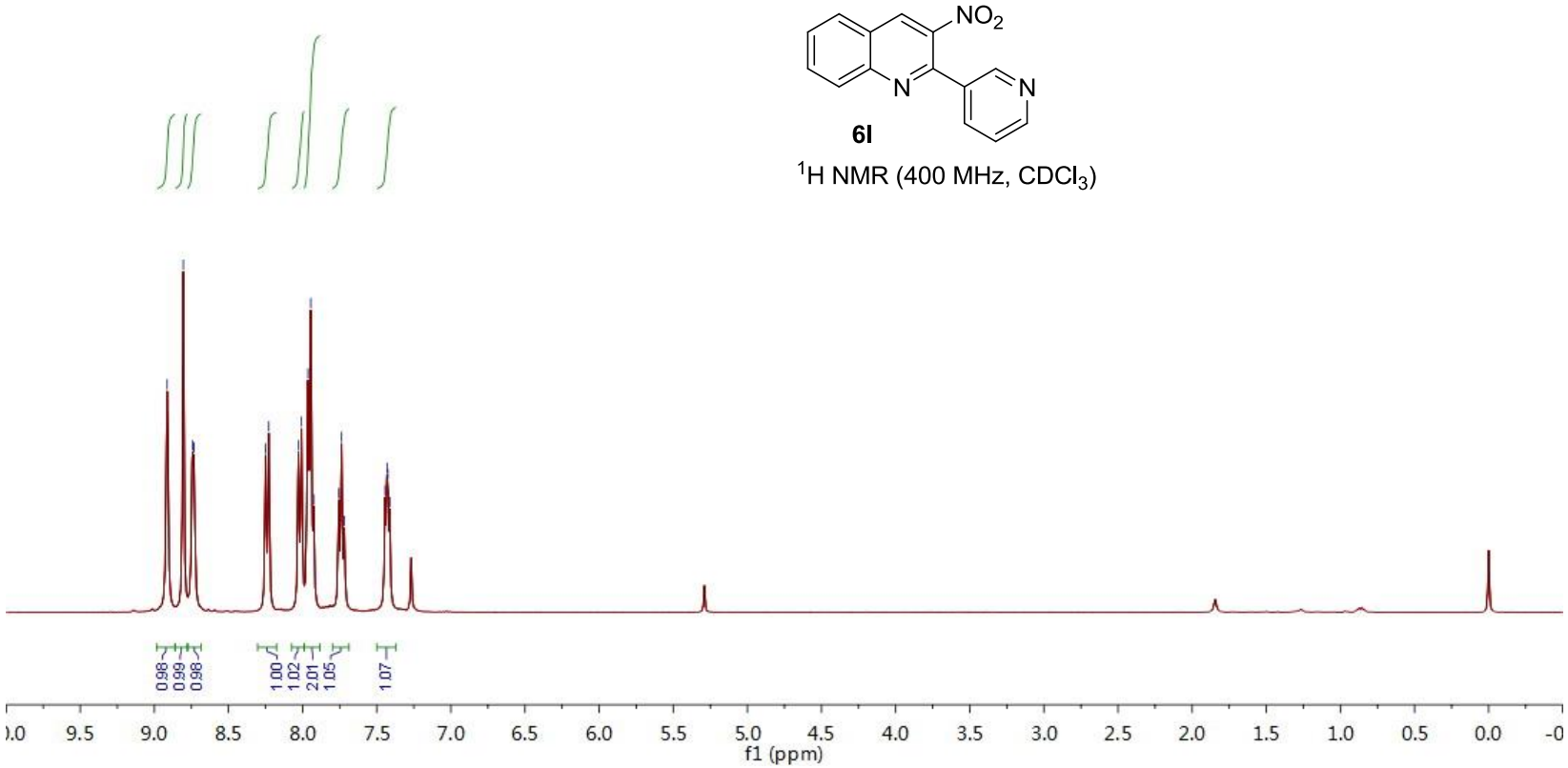


## 9. Copy of NMR and HPLC for Racemic and Chiral Compounds




152.86
152.06
148.45
144.10
134.13
132.66
132.44
129.82
128.53
128.29
127.87
125.82
125.45
34.81
31.25
13C NMR FC-6-48A in CDCl3
//Yzc/g/新 NMR 2013/1362/fid
132.66
132.44
129.82
128.53
128.29
127.87
133
132
131
130
129
128
f1 (ppm)
NO2
N
6d
tBu
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


1H NMR FC-6-48C in CDCl3
//Yzc/g/新 NMR 2013/1363/fid

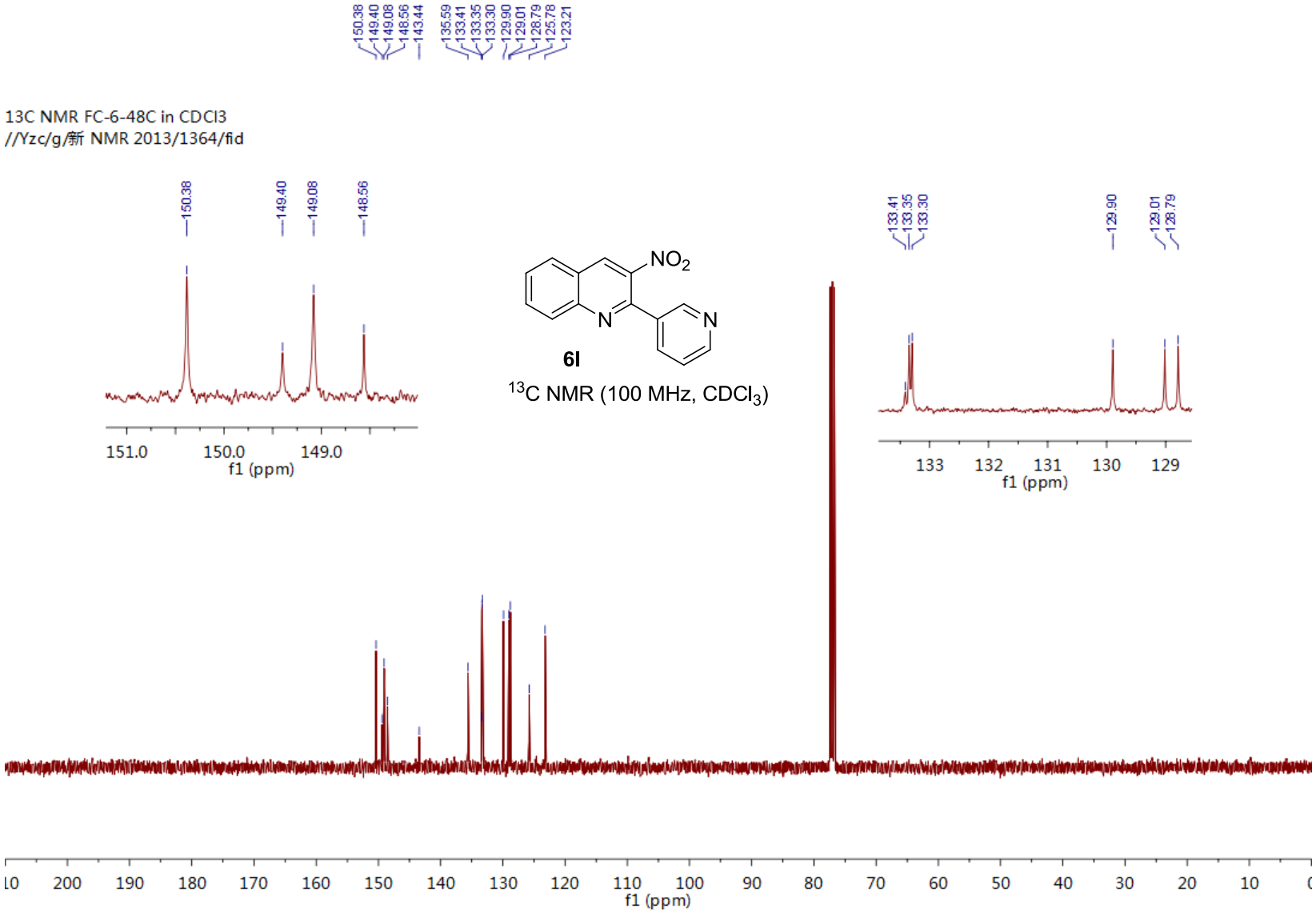


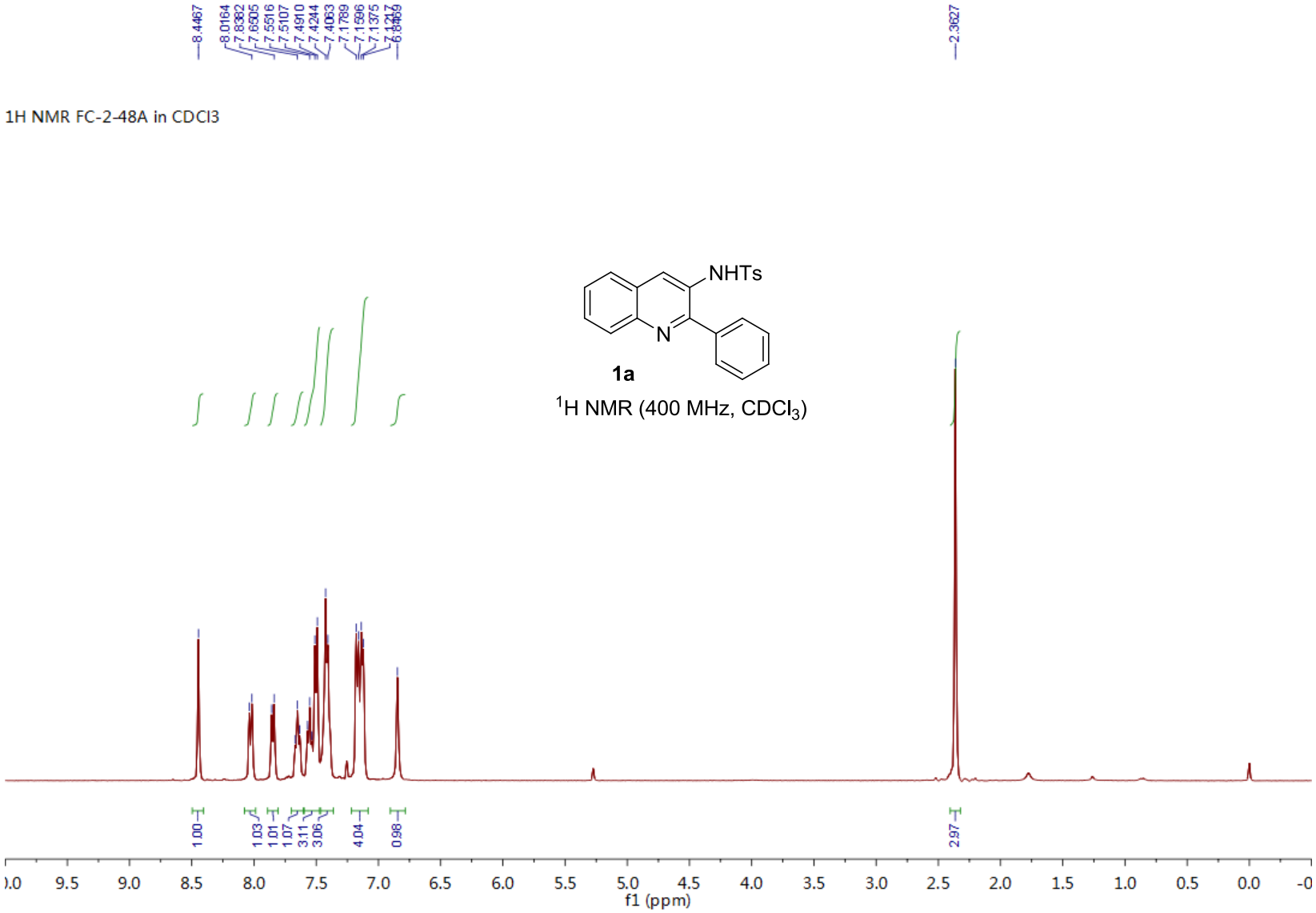


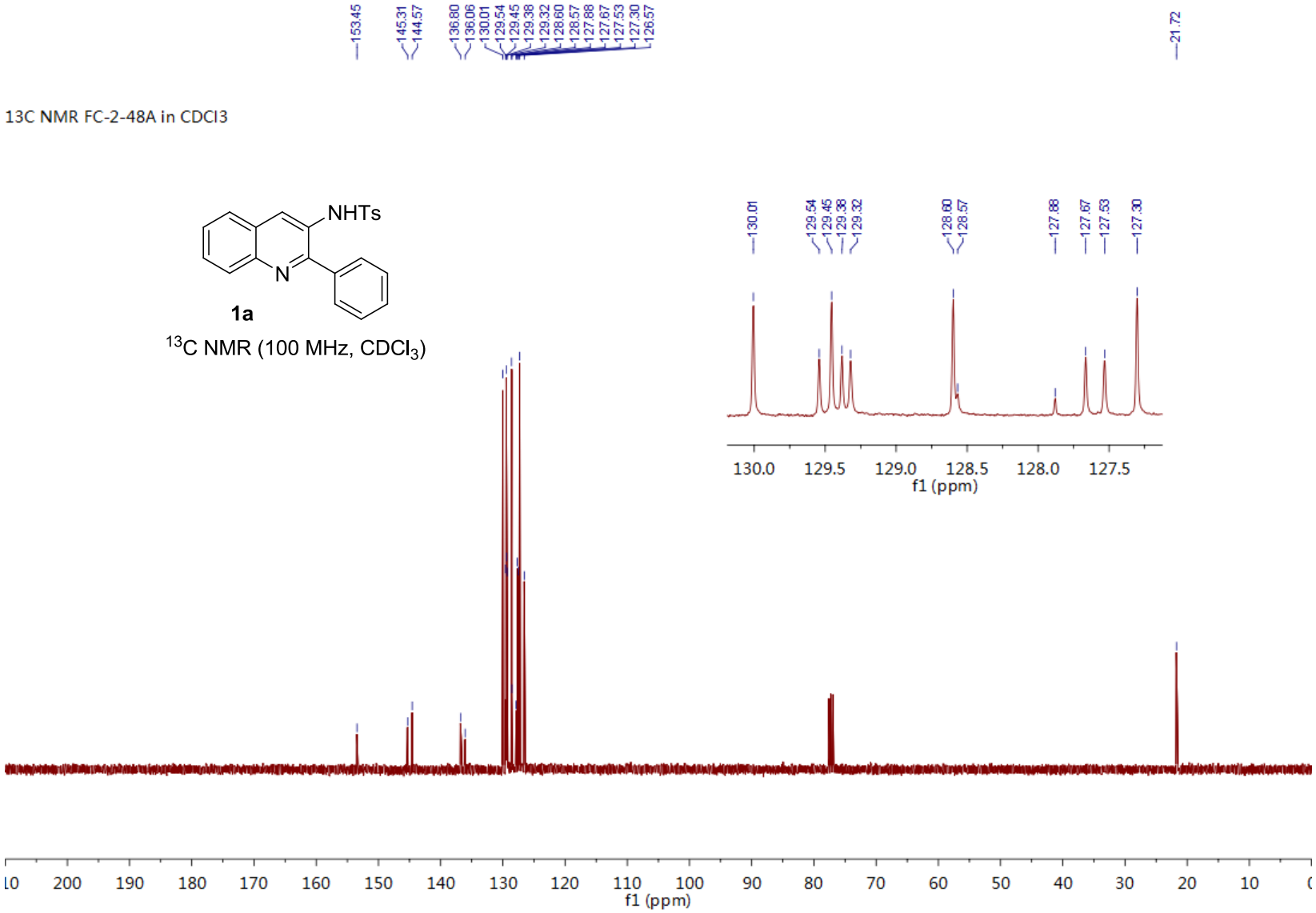


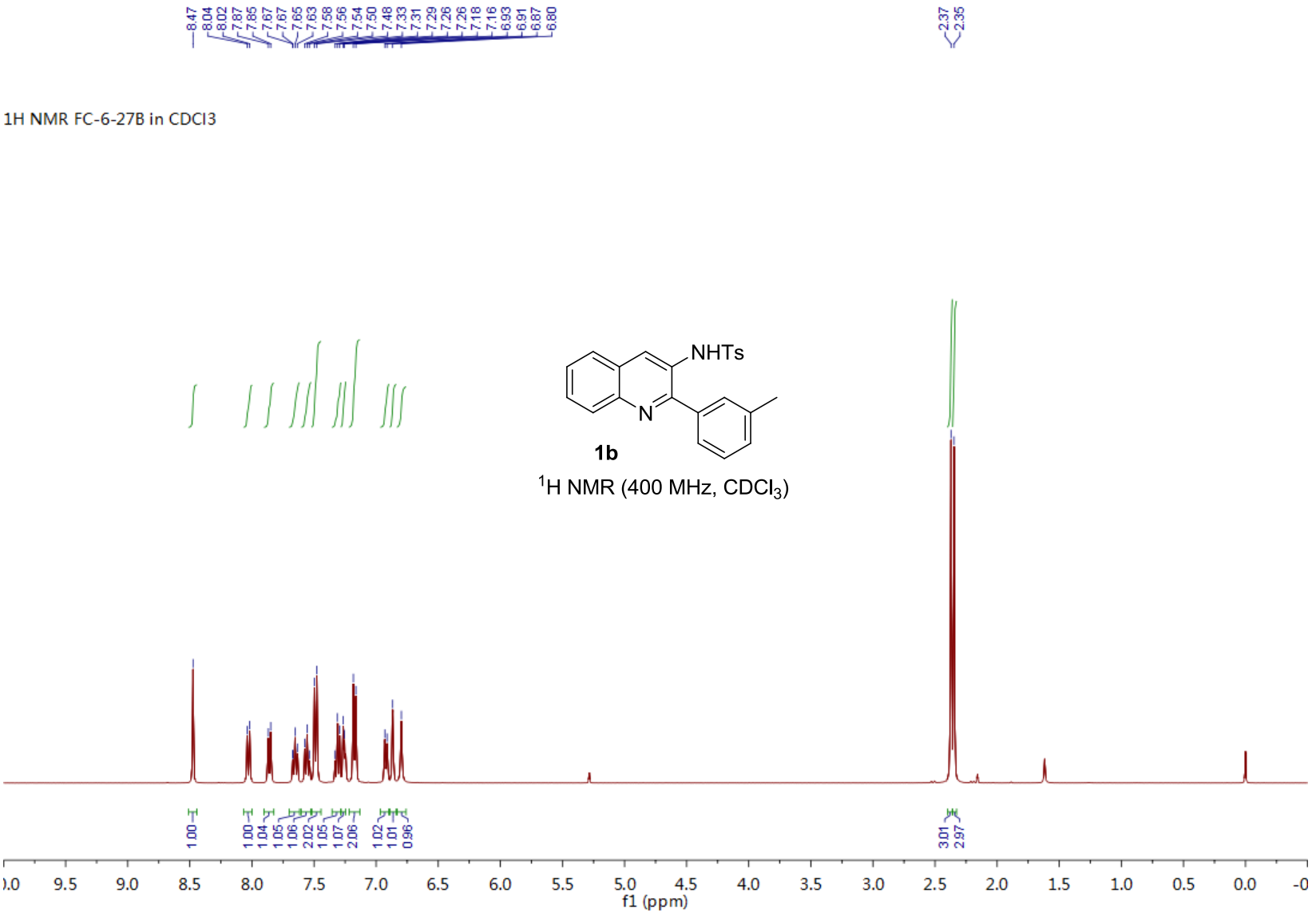
**6l**

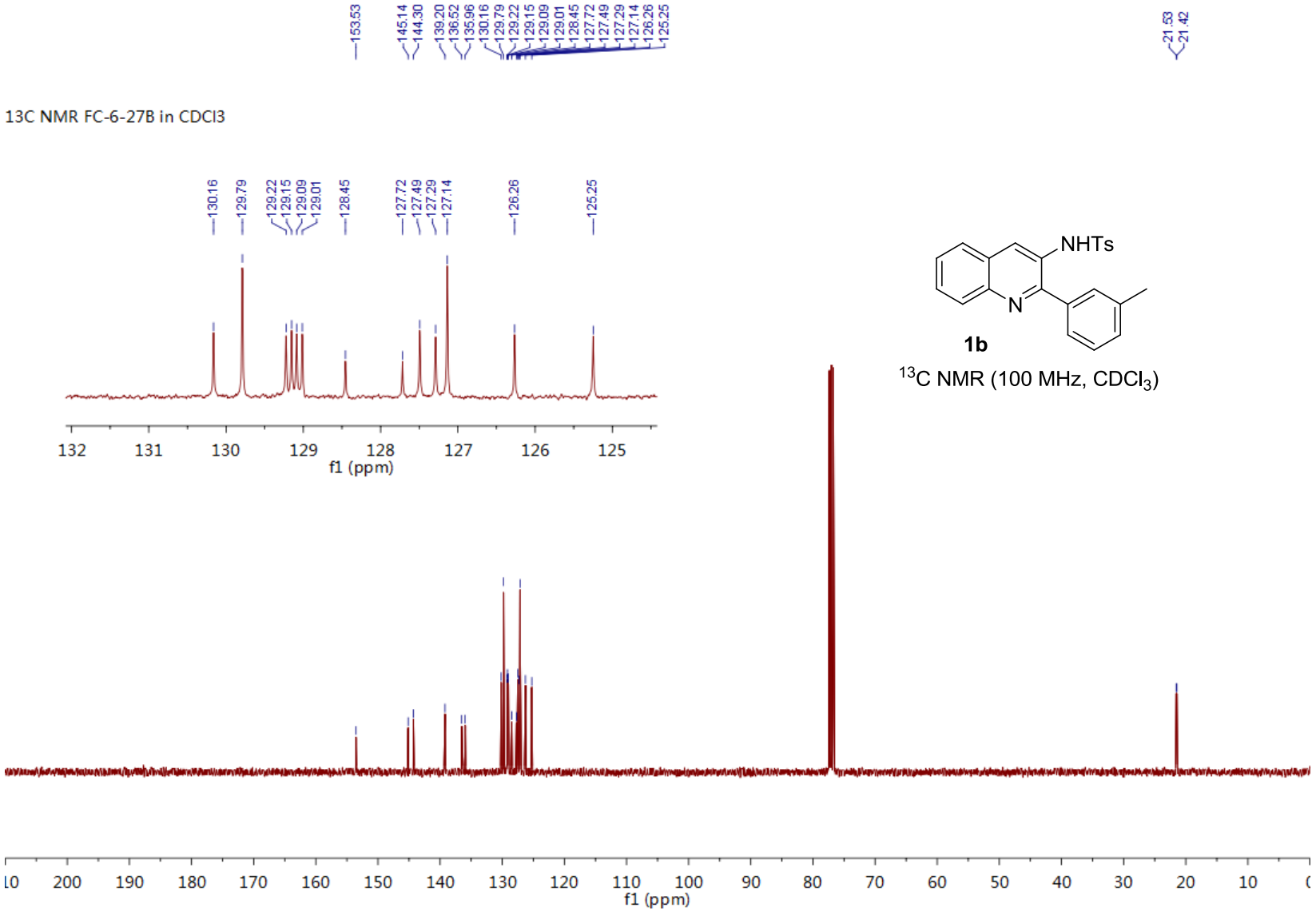
$^1$H NMR (400 MHz, $CDCl_3$)

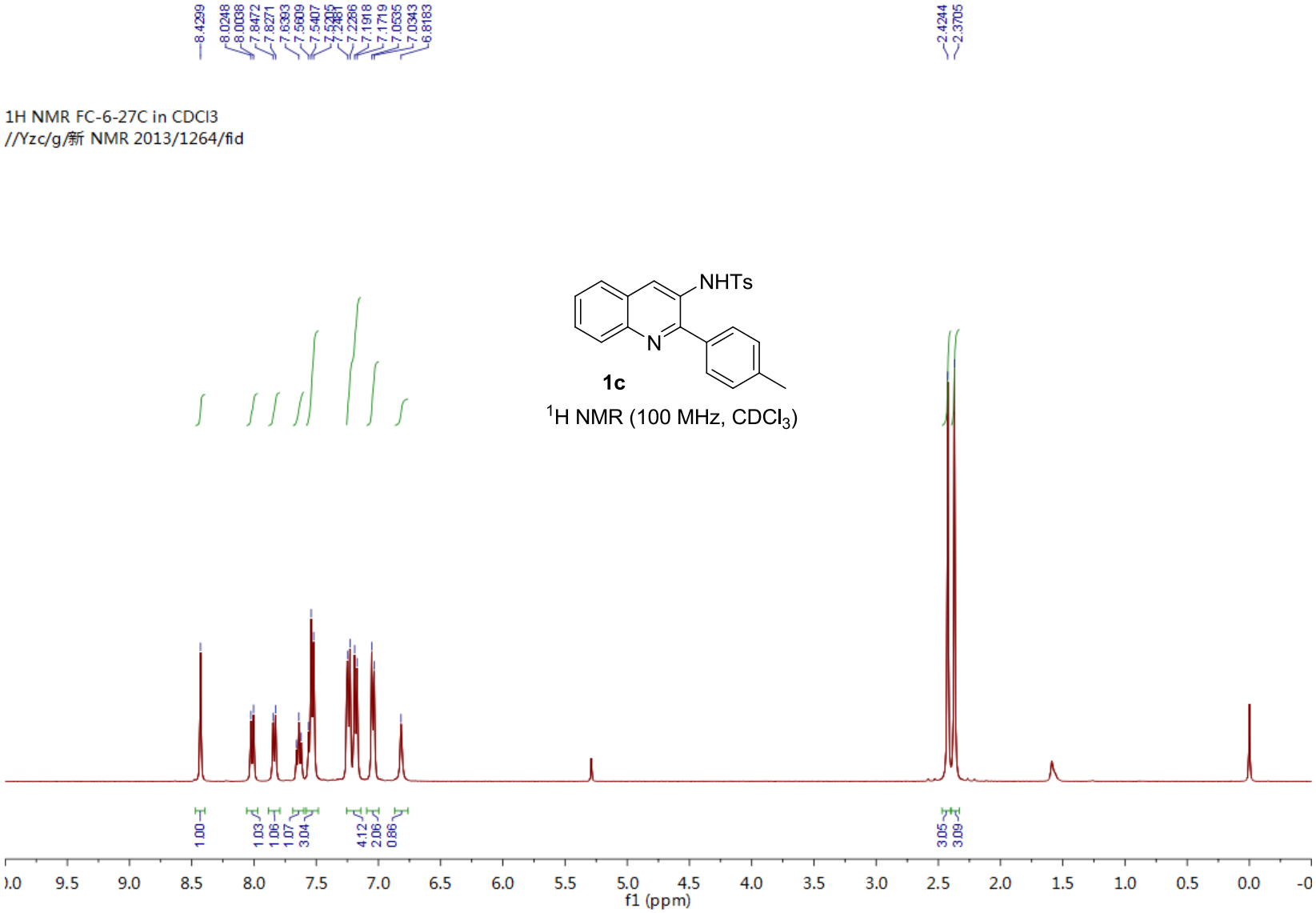

150.38
149.40
149.08
148.56
143.44
135.59
133.41
133.35
133.30
129.90
129.01
128.79
125.78
123.21
13C NMR FC-6-48C in CDCl3
//Yzc/g/新 NMR 2013/1364/fid
150.38
149.40
149.08
148.56
151.0
150.0
149.0
f1 (ppm)
NO2
N
N
6l
13C NMR (100 MHz, CDCl3)
133.41
133.35
133.30
129.90
129.01
128.79
133
132
131
130
129
f1 (ppm)
f1 (ppm)

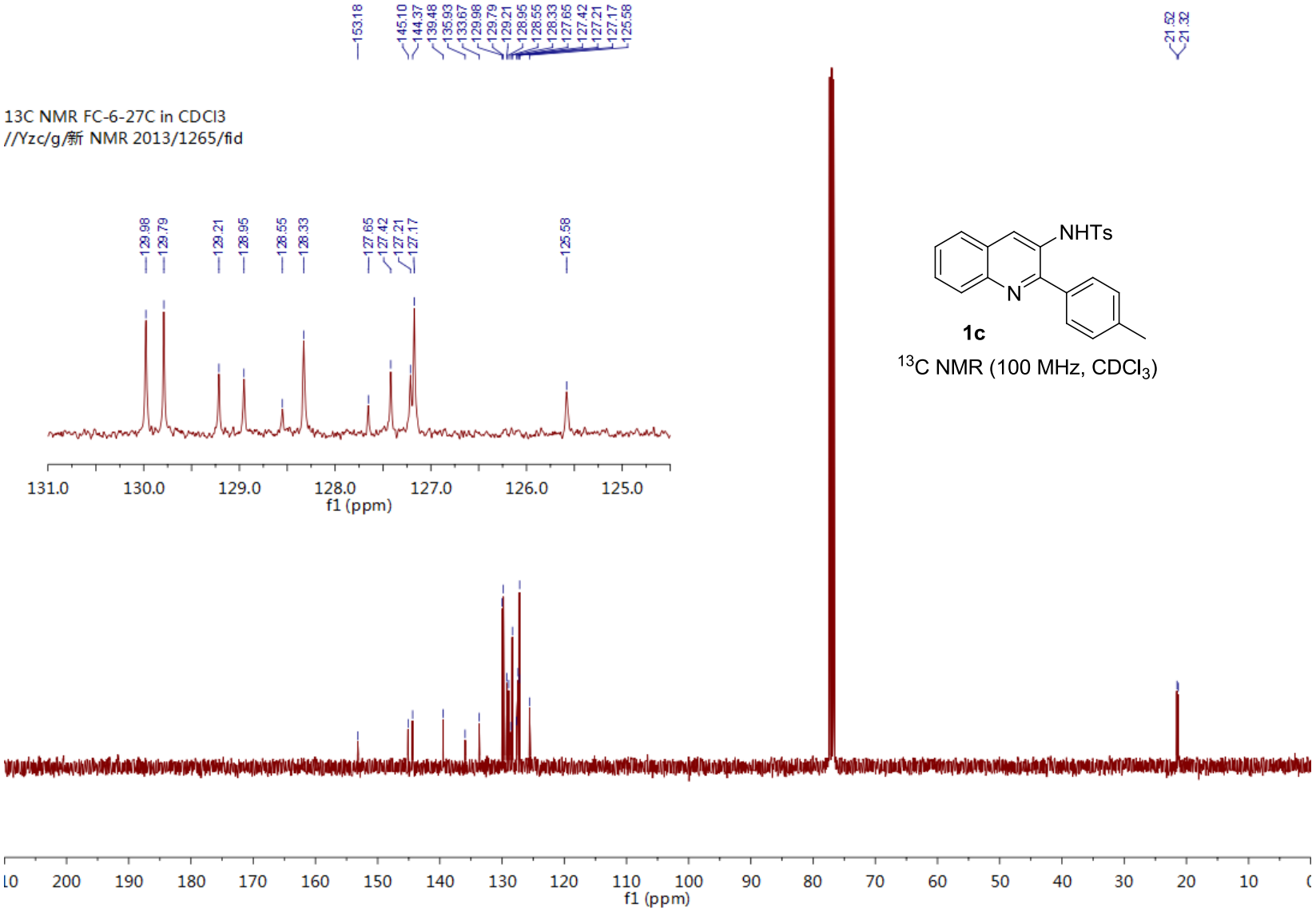

8.4467
8.0164
7.8382
7.6505
7.5516
7.5107
7.4910
7.4244
7.4063
7.1789
7.1596
7.1375
2.3627
1H NMR FC-2-48A in CDCl3
NHTs
N
1a
1H NMR (400 MHz, CDCl3)
1.00
1.03
1.01
1.07
3.11
3.06
4.04
0.98
2.97
f1 (ppm)

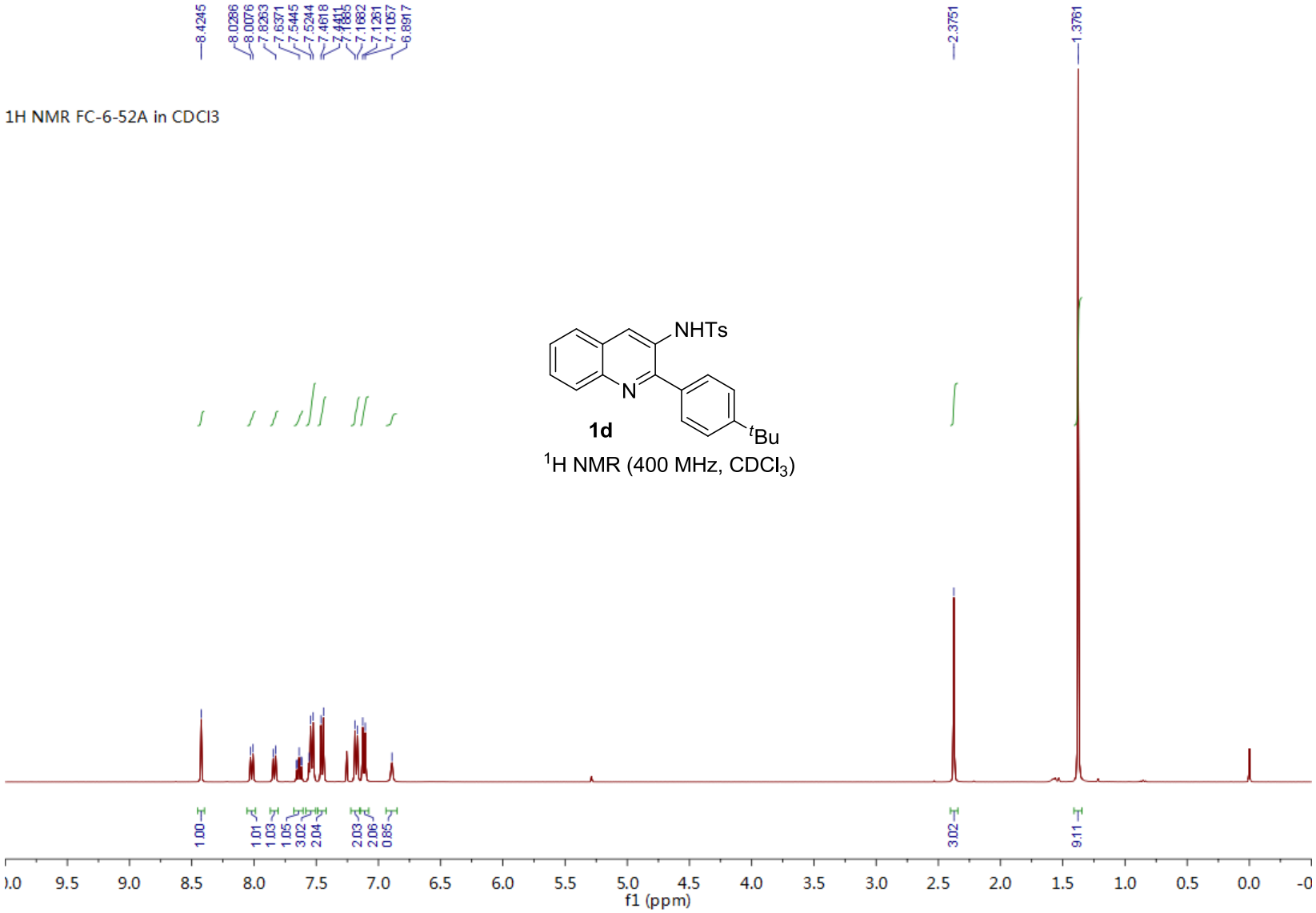

153.45
145.31
144.57
136.80
136.06
130.01
129.54
129.45
129.38
129.32
128.60
128.57
127.88
127.67
127.53
127.30
126.57
21.72
13C NMR FC-2-48A in CDCl3
NHTs
N
1a
13C NMR (100 MHz, CDCl3)
130.01
129.54
129.45
129.38
129.32
128.60
128.57
127.88
127.67
127.53
127.30
130.0
129.5
129.0
128.5
128.0
127.5
f1 (ppm)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

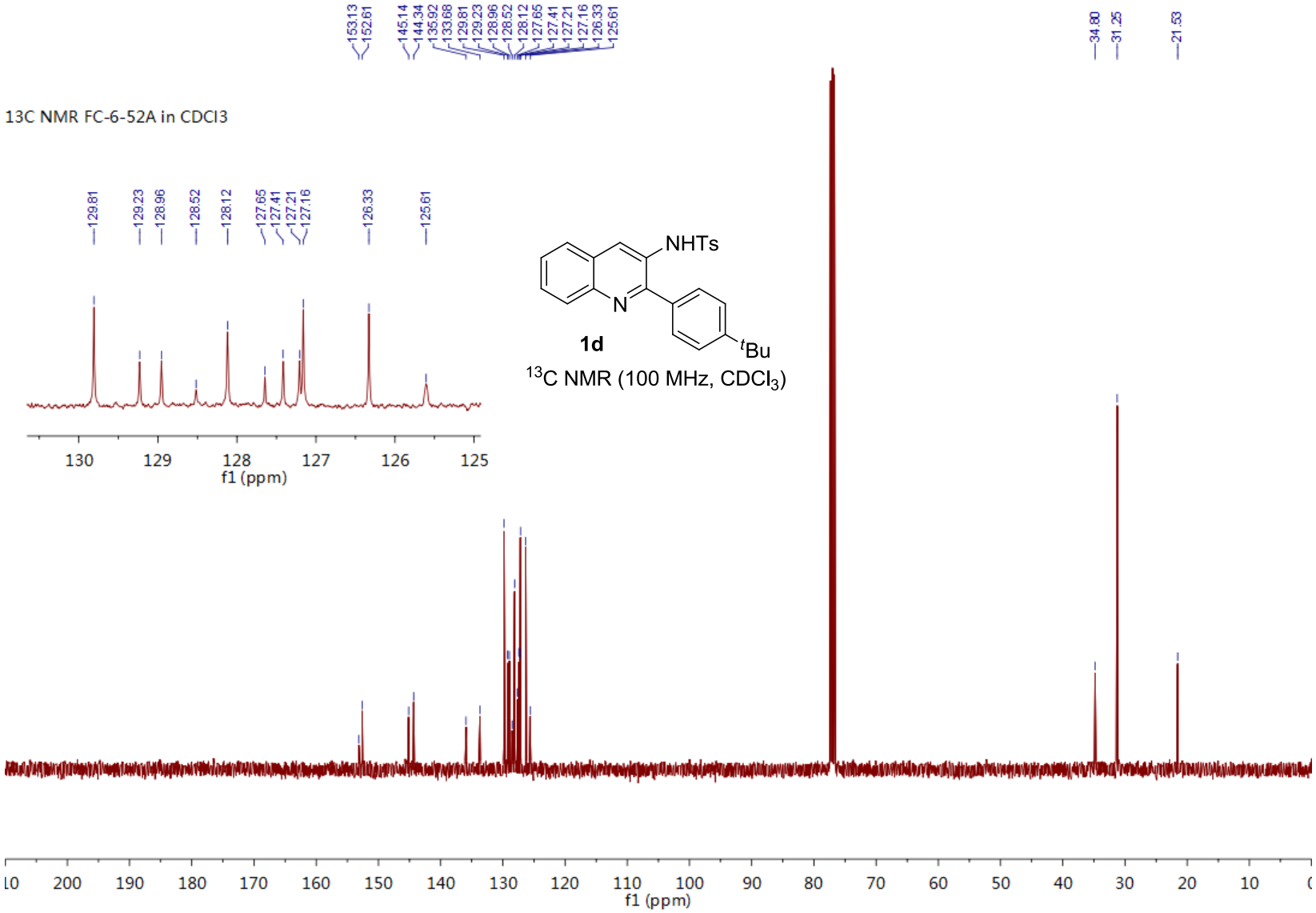

8.47
8.04
8.02
7.87
7.85
7.67
7.67
7.65
7.63
7.58
7.56
7.54
7.50
7.48
7.33
7.31
7.29
7.26
7.26
7.18
7.16
6.93
6.91
6.87
6.80
2.37
2.35
1H NMR FC-6-27B in CDCl3
NHTs
N
1b
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.04
1.05
1.06
2.02
1.05
1.07
2.06
1.02
1.01
0.96
3.01
2.97
f1 (ppm)

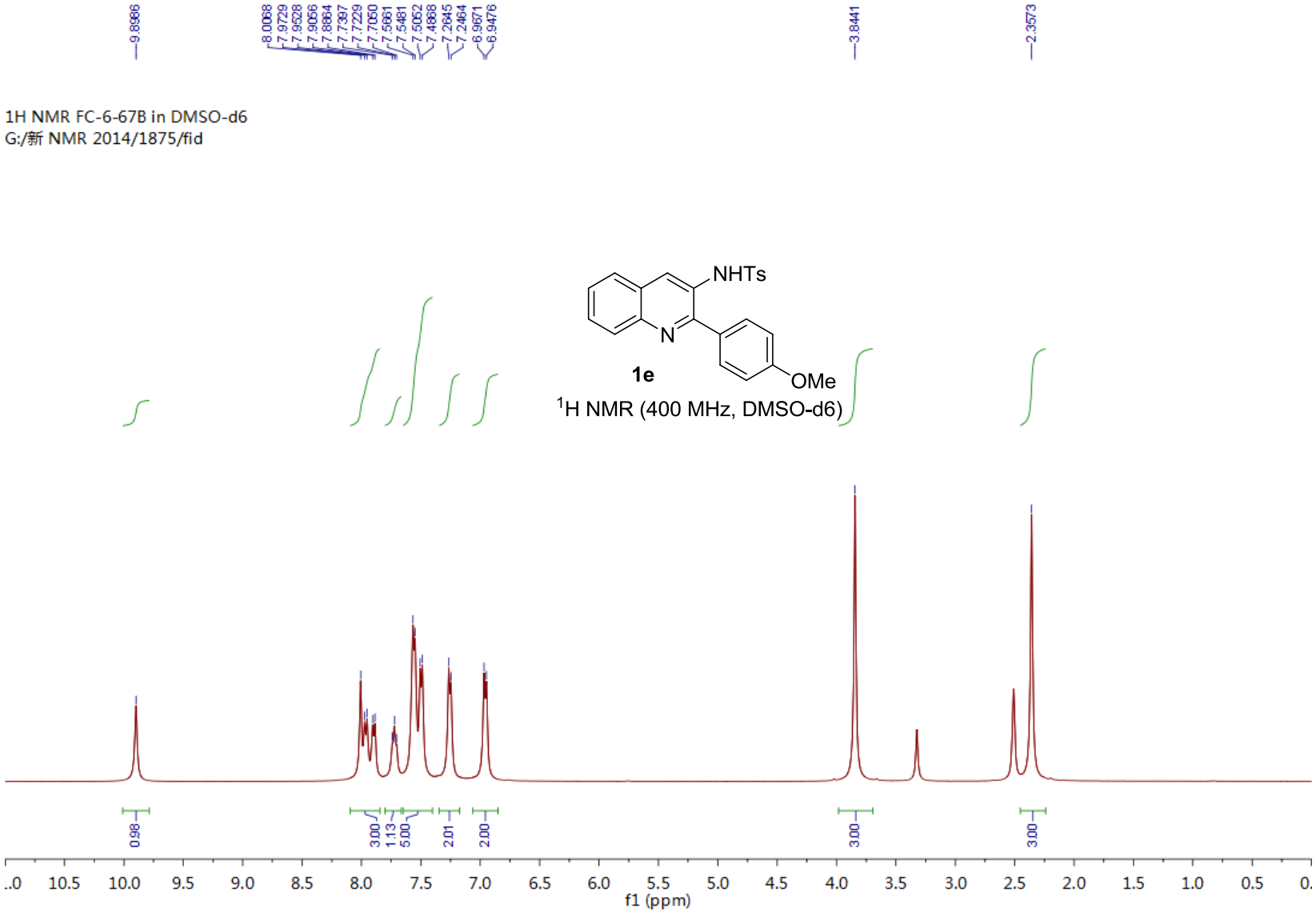

153.53
145.14
144.30
139.20
136.52
135.96
130.16
129.79
129.22
129.15
129.09
129.01
128.45
127.72
127.49
127.29
127.14
126.26
125.25
21.53
21.42
13C NMR FC-6-27B in CDCl3
NHTs
N
1b
13C NMR (100 MHz, CDCl3)
f1 (ppm)
f1 (ppm)

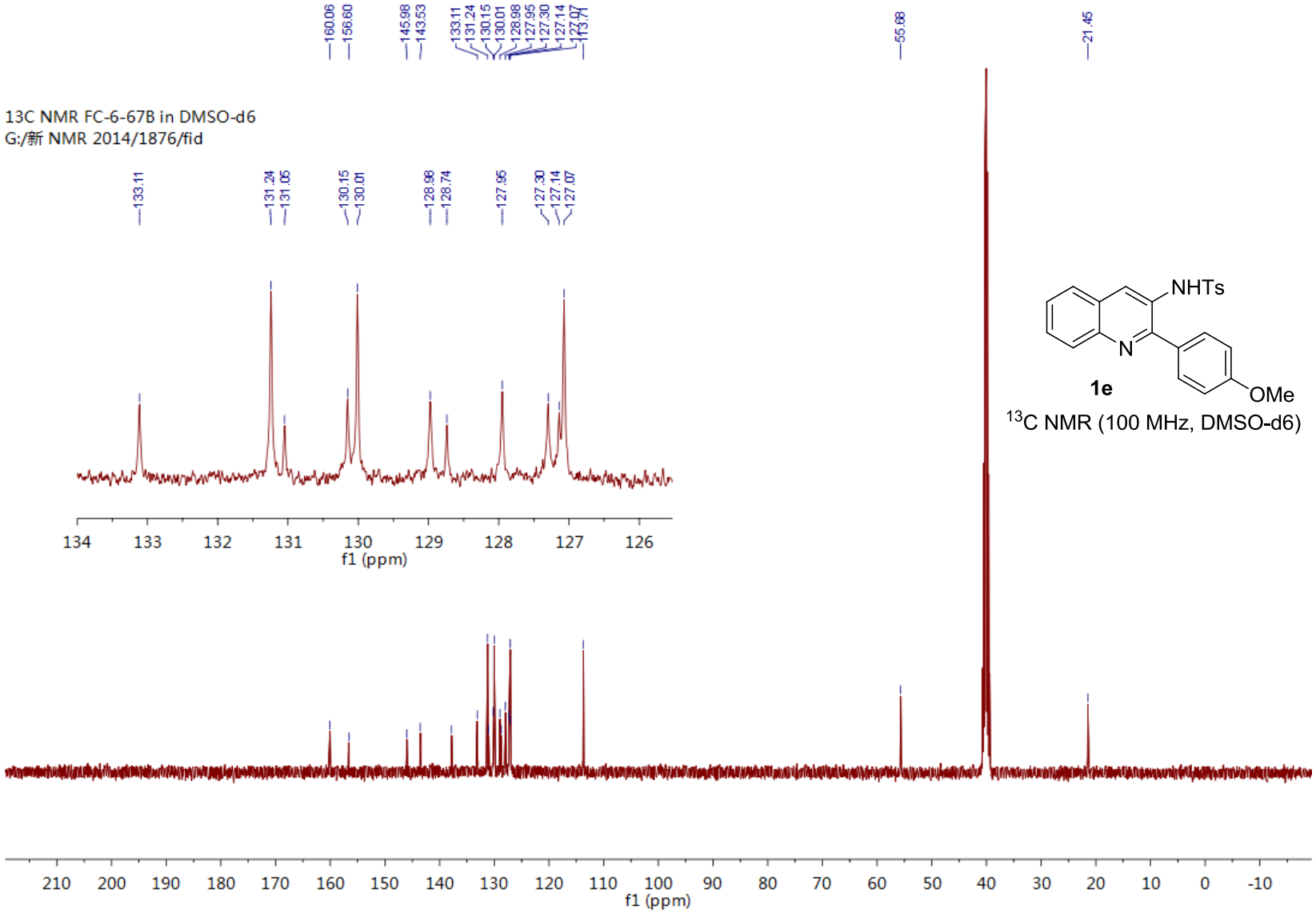

8.4299
8.0248
8.0038
7.8472
7.8271
7.6393
7.5609
7.5407
7.5205
7.2481
7.2286
7.1918
7.1719
7.0535
7.0343
6.8183
2.4244
2.3705
1H NMR FC-6-27C in CDCl3
//Yzc/g/新 NMR 2013/1264/fid
NHTs
N
1c
1H NMR (100 MHz, CDCl3)
1.00
1.03
1.06
1.07
3.04
4.12
2.06
0.88
3.05
3.09
f1 (ppm)

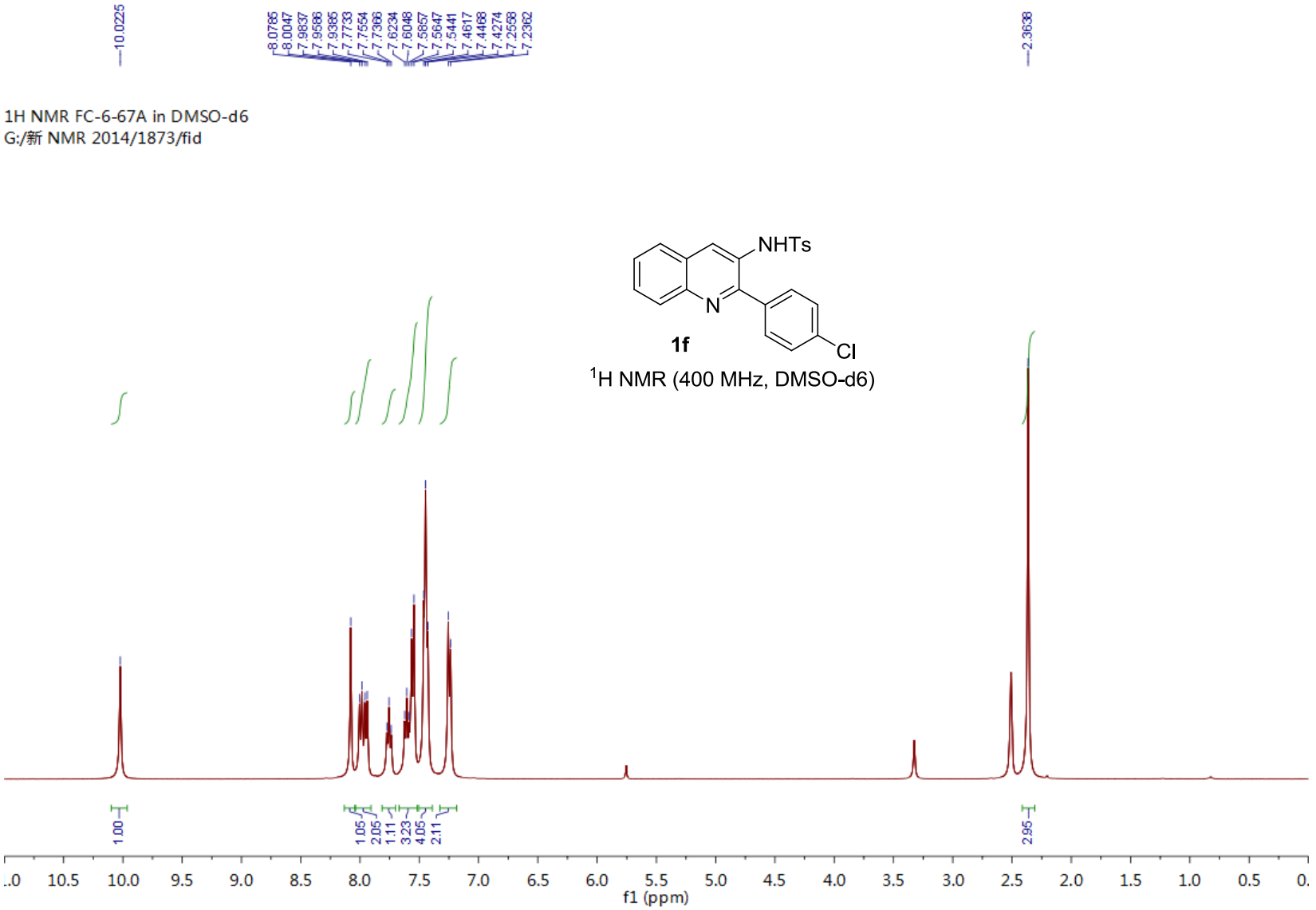

153.18
145.10
144.37
139.48
135.93
133.67
129.98
129.79
129.21
128.95
128.55
128.33
127.65
127.42
127.21
127.17
125.58
21.52
21.32
13C NMR FC-6-27C in CDCl3
//Yzc/g/新 NMR 2013/1265/fid
129.98
129.79
129.21
128.95
128.55
128.33
127.65
127.42
127.21
127.17
125.58
131.0
130.0
129.0
128.0
127.0
126.0
125.0
f1 (ppm)
NHTs
N
1c
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

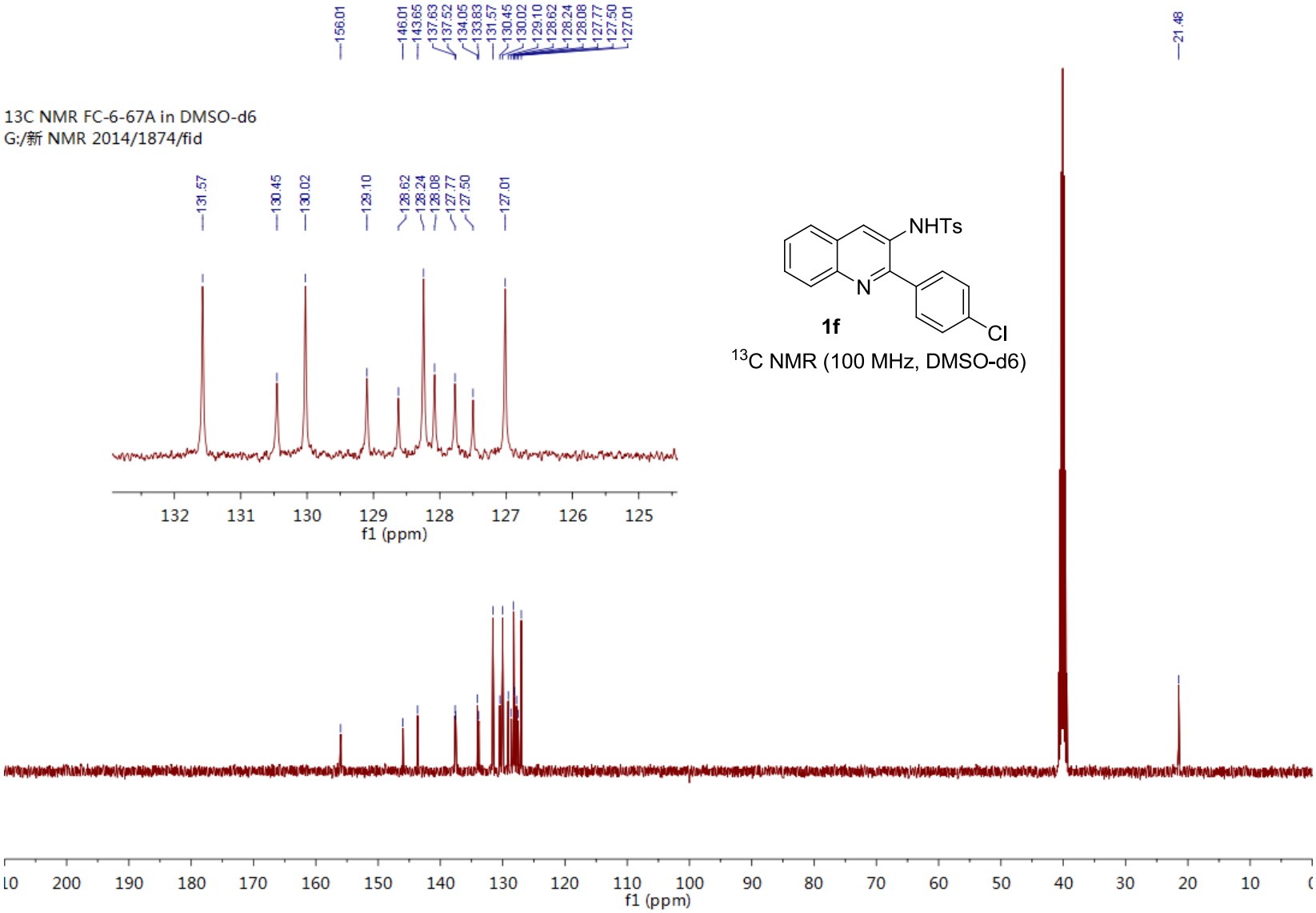

1H NMR FC-6-52A in CDCl3
8.4245
8.0286
8.0076
7.8263
7.6371
7.5445
7.5244
7.4618
7.4411
7.1885
7.1682
7.1261
7.1057
6.8917
2.3751
1.3761
NHTs
N
1d
tBu
1H NMR (400 MHz, CDCl3)
1.00
1.01
1.03
1.05
3.02
2.04
2.03
2.06
0.85
3.02
9.11
f1 (ppm)

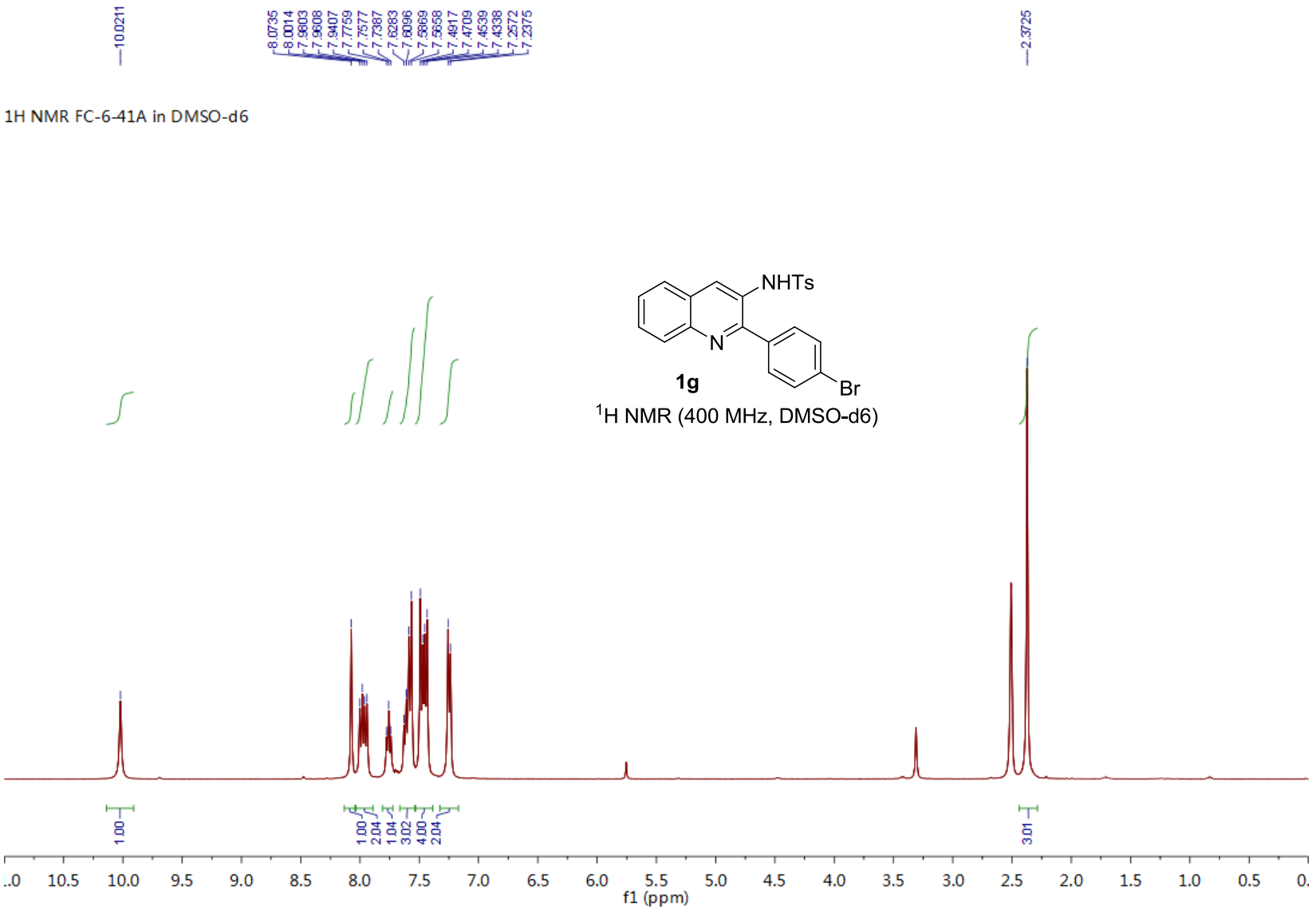

153.13
152.61
145.14
144.34
135.92
133.68
129.81
129.23
128.96
128.52
128.12
127.65
127.41
127.21
127.16
126.33
125.61
34.80
31.25
21.53
13C NMR FC-6-52A in CDCl3
129.81
129.23
128.96
128.52
128.12
127.65
127.41
127.21
127.16
126.33
125.61
130
129
128
127
126
125
f1 (ppm)
NHTs
N
tBu
1d
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

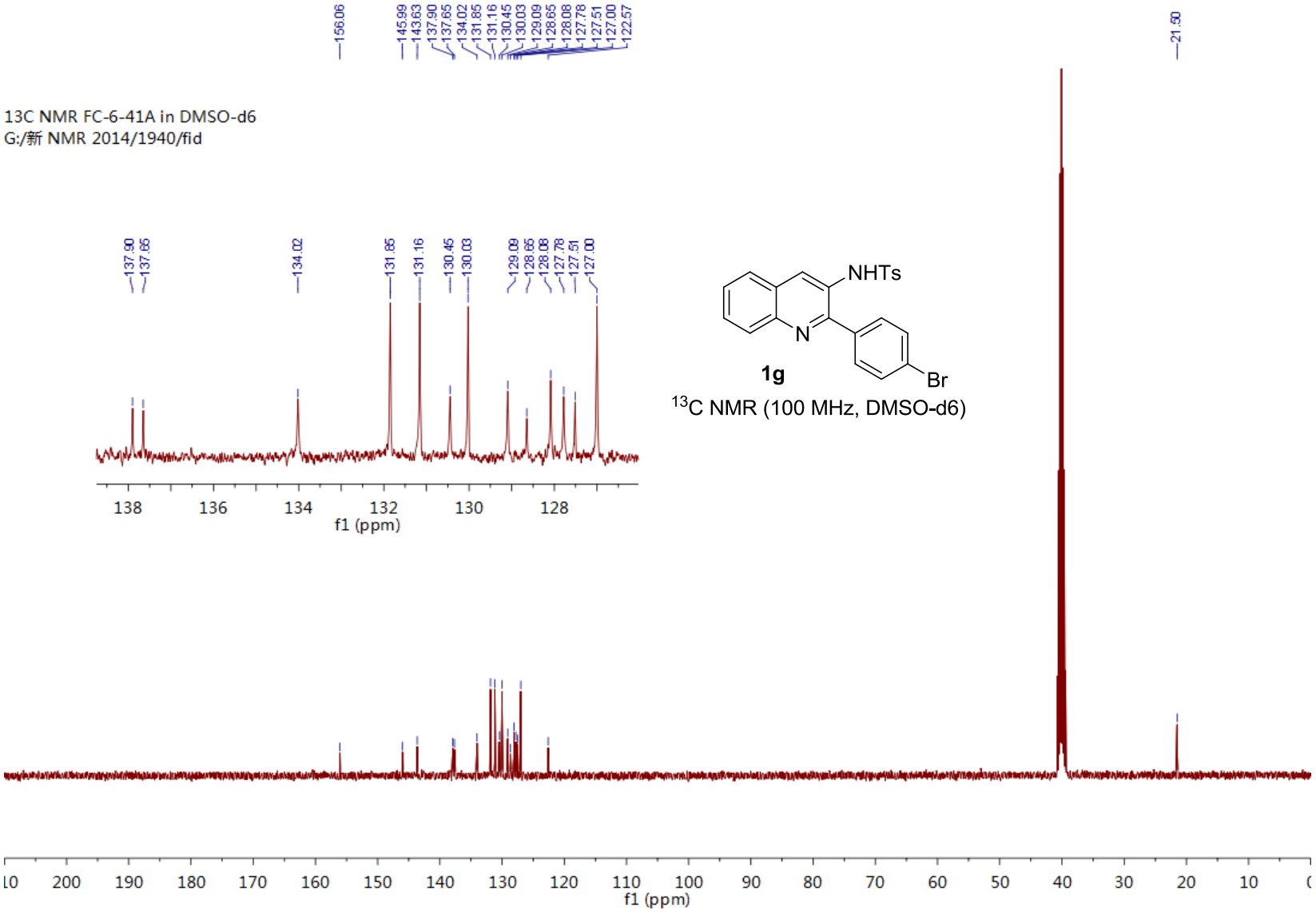

9.8966
8.0068
7.9729
7.9528
7.9056
7.8864
7.7397
7.7229
7.7050
7.5661
7.5481
7.5052
7.4868
7.2645
7.2464
6.9671
6.9476
3.8441
2.3573
1H NMR FC-6-67B in DMSO-d6
G:/新 NMR 2014/1875/fid
NHTs
N
OMe
1e
1H NMR (400 MHz, DMSO-d6)
0.98
3.00
1.13
5.00
2.01
2.00
3.00
3.00
f1 (ppm)

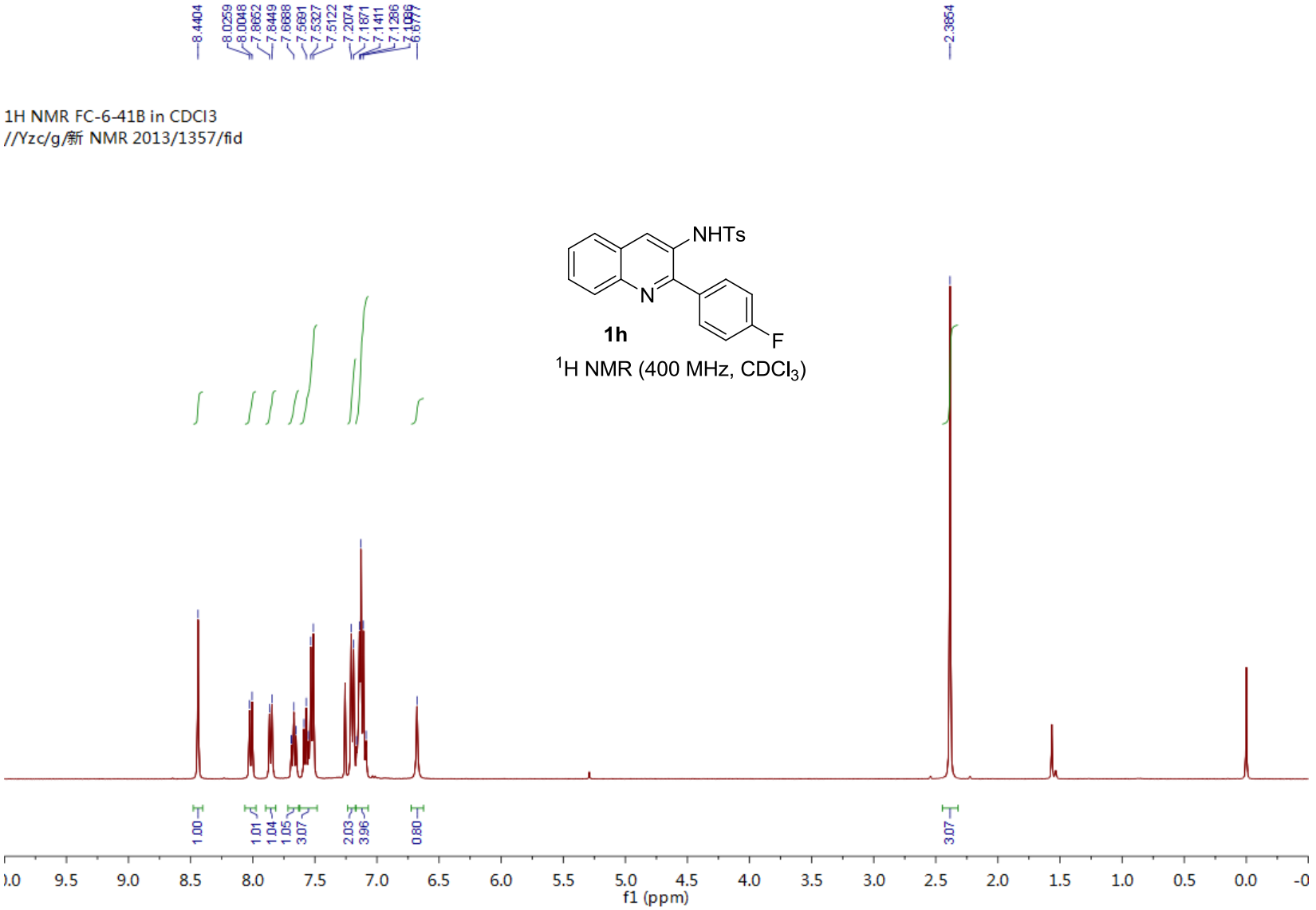

13C NMR FC-6-67B in DMSO-d6
G:/新 NMR 2014/1876/fid
160.06
156.60
145.98
143.53
133.11
131.24
130.15
130.01
128.98
127.95
127.30
127.14
127.07
55.68
21.45
NHTs
N
OMe
1e
13C NMR (100 MHz, DMSO-d6)
f1 (ppm)
f1 (ppm)

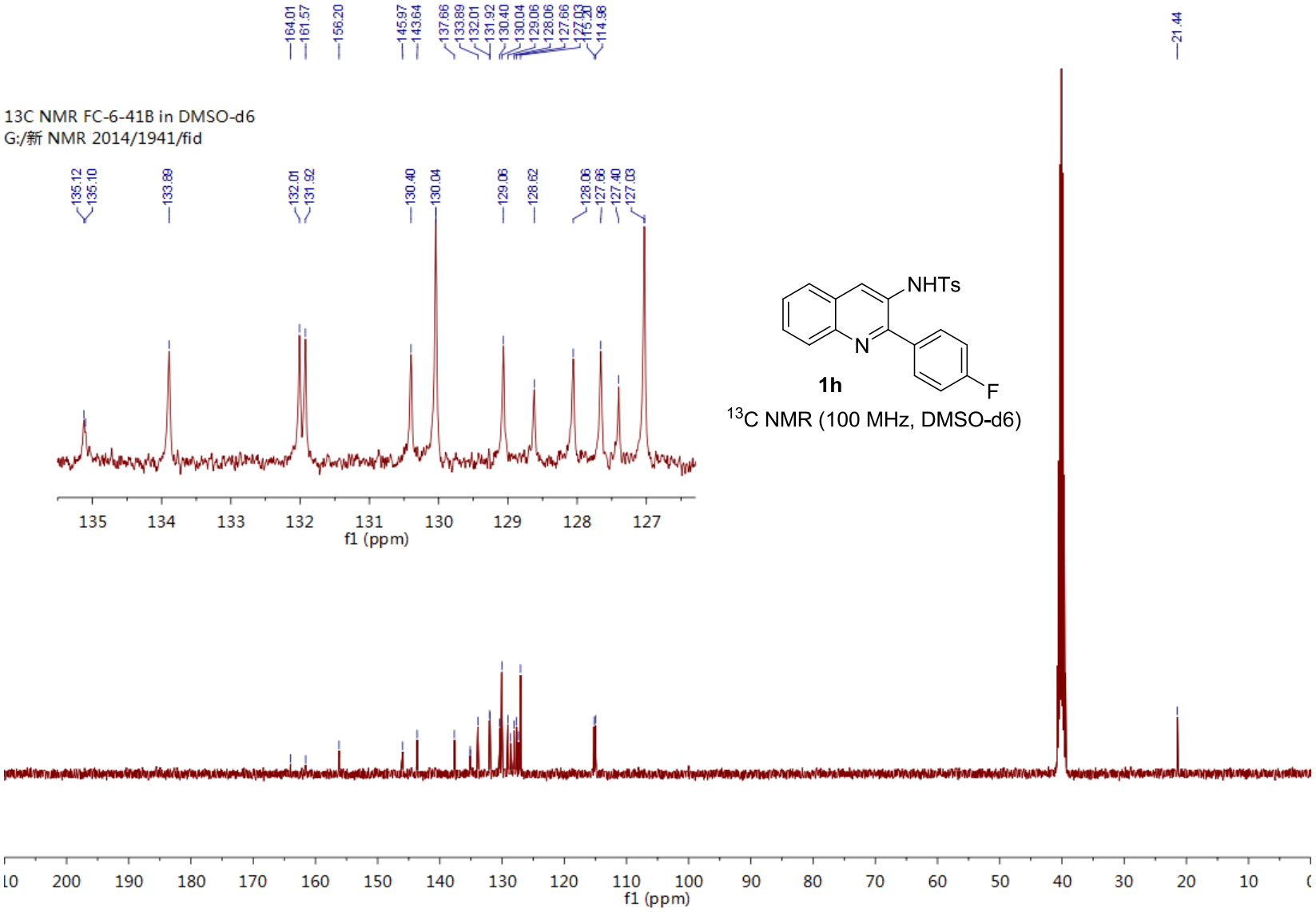

10.0225
8.0785
8.0047
7.9837
7.9586
7.9385
7.7733
7.7554
7.7366
7.6234
7.6048
7.5857
7.5647
7.5441
7.4617
7.4488
7.4274
7.2558
7.2362
2.3638
1H NMR FC-6-67A in DMSO-d6
G:/新 NMR 2014/1873/fid
NHTs
N
Cl
1f
1H NMR (400 MHz, DMSO-d6)
1.00
1.05
2.05
1.11
3.23
4.05
2.11
2.95
f1 (ppm)

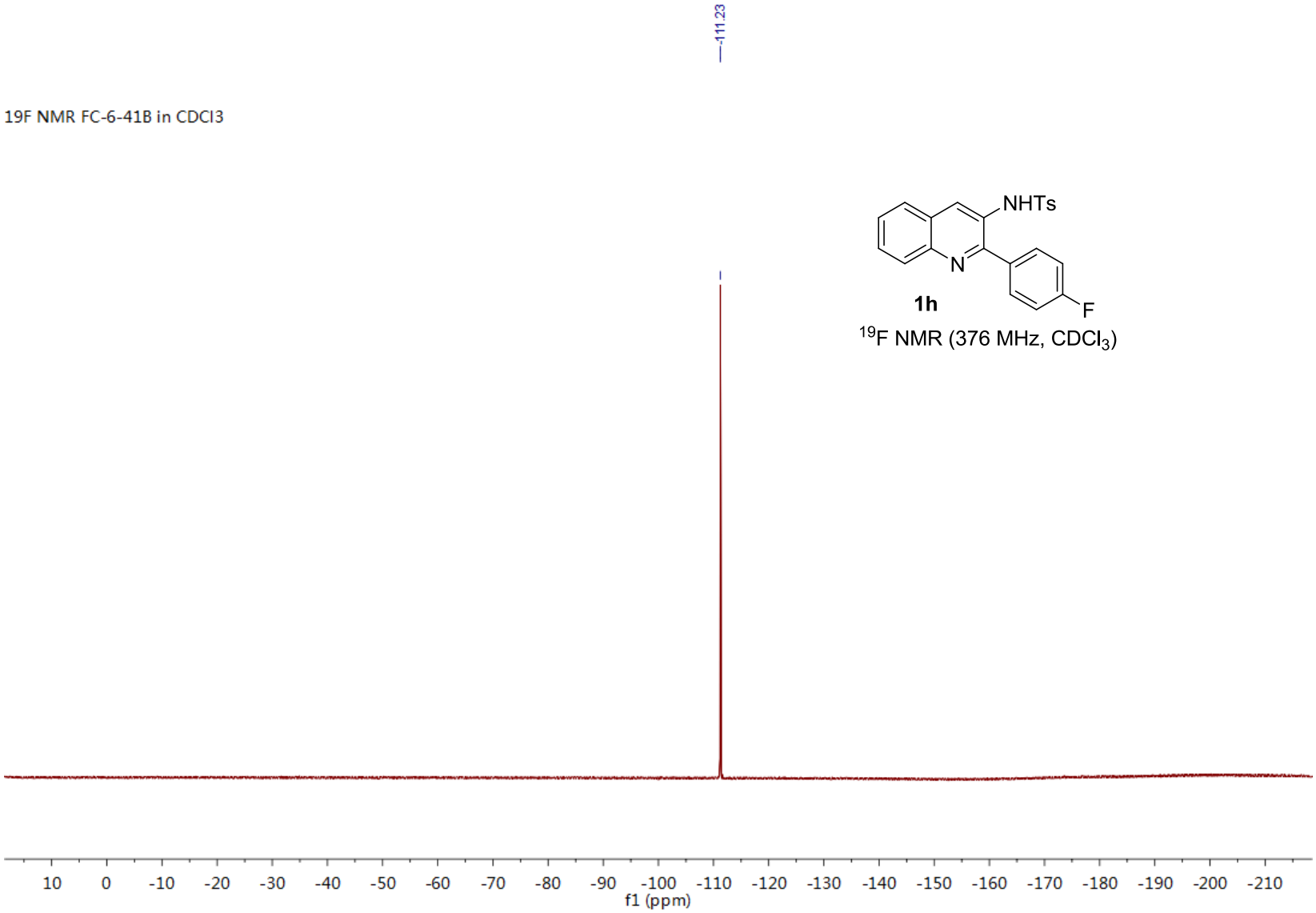

13C NMR FC-6-67A in DMSO-d6
G:/新 NMR 2014/1874/fid
156.01
146.01
143.65
137.63
137.52
134.05
133.83
131.57
130.45
130.02
129.10
128.62
128.24
128.08
127.77
127.50
127.01
21.48
NHTs
N
Cl
1f
13C NMR (100 MHz, DMSO-d6)
f1 (ppm)

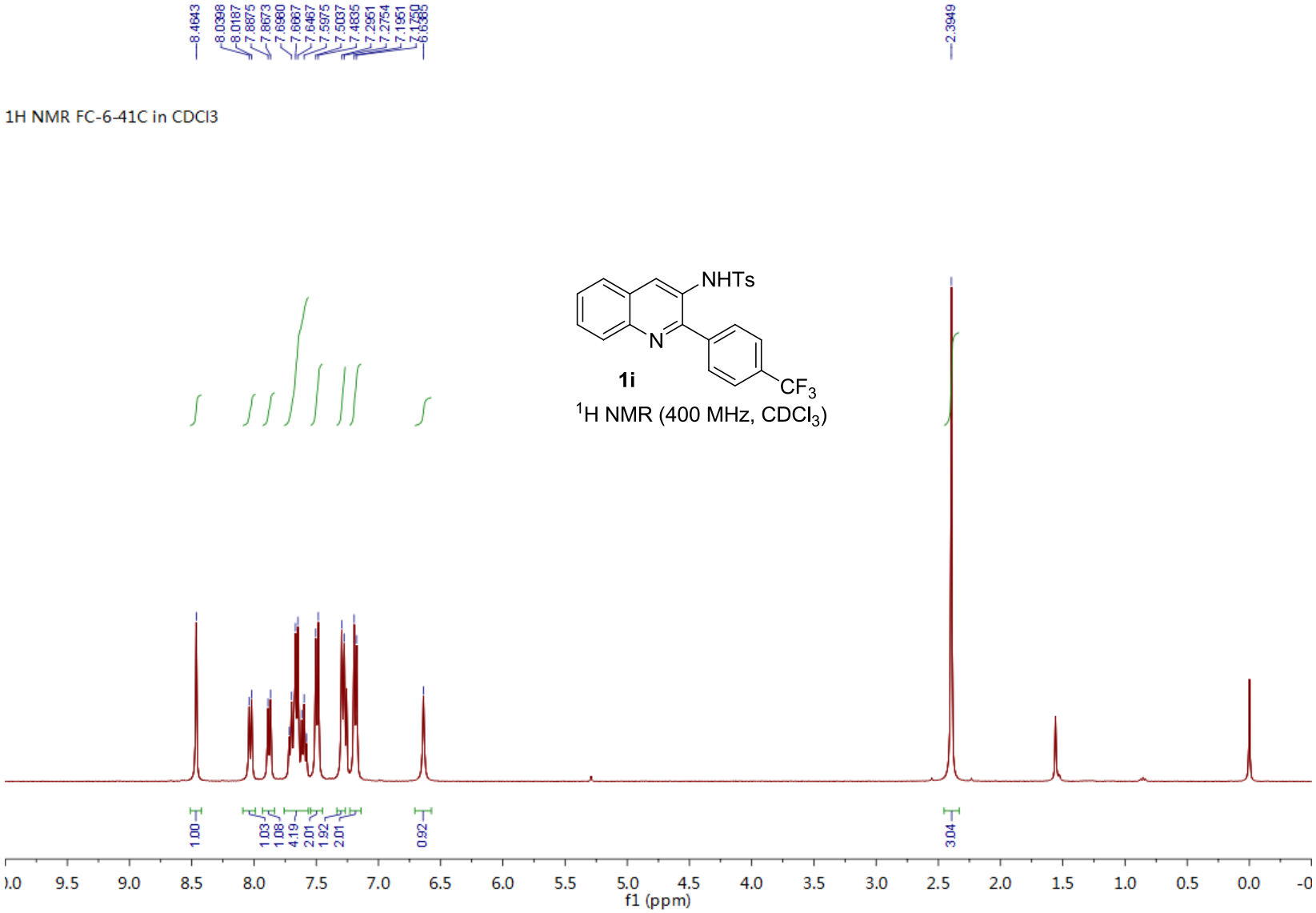

10.0211
8.0735
8.0014
7.9803
7.9608
7.9407
7.7759
7.7577
7.7387
7.6283
7.6096
7.5869
7.5658
7.4917
7.4709
7.4539
7.4338
7.2572
7.2375
2.3725
1H NMR FC-6-41A in DMSO-d6
NHTs
N
Br
1g
1H NMR (400 MHz, DMSO-d6)
1.00
1.00
2.04
1.04
3.02
4.00
2.04
3.01
f1 (ppm)

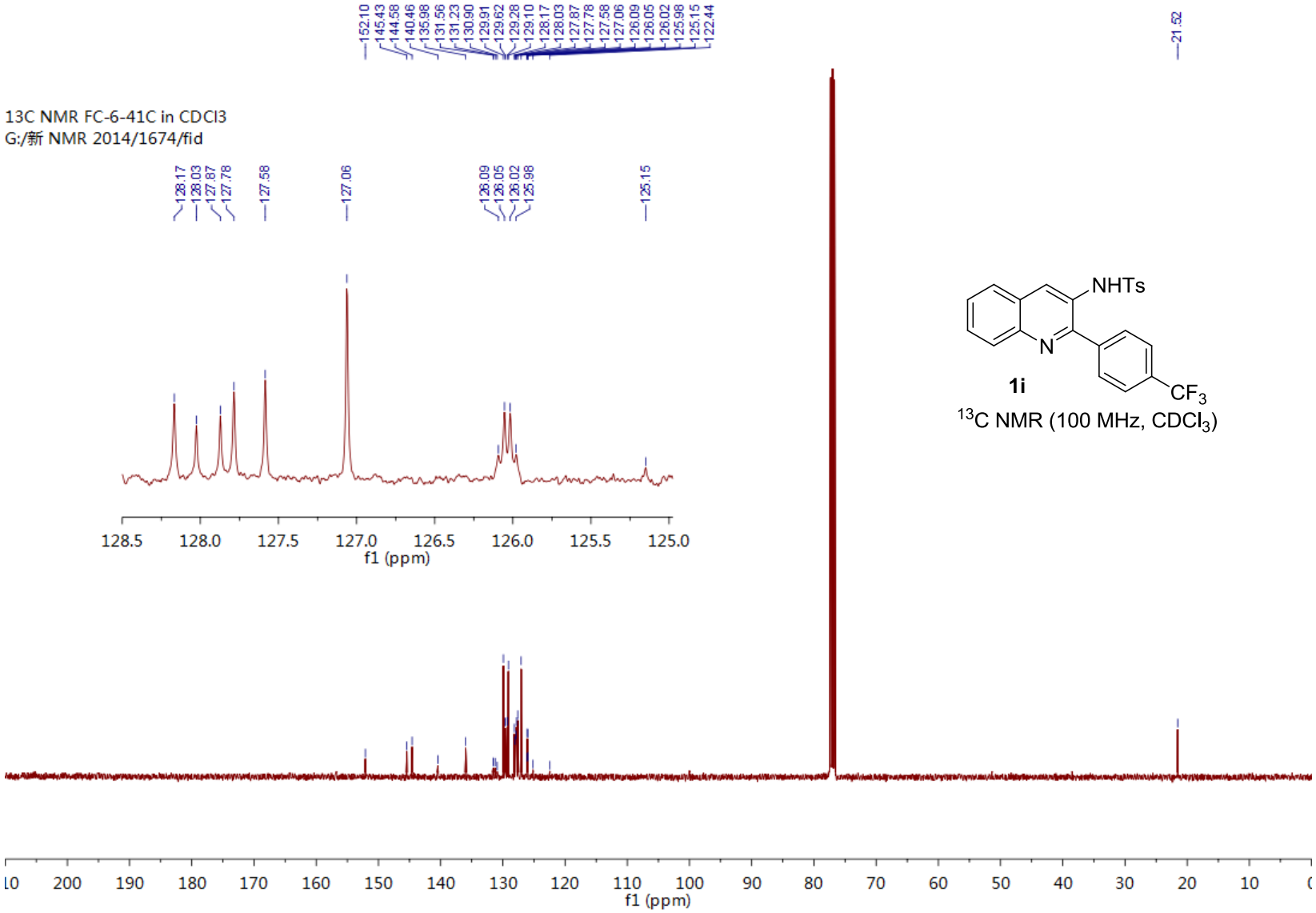

13C NMR FC-6-41A in DMSO-d6
G:/新 NMR 2014/1940/fid
156.06
145.99
143.63
137.90
137.65
134.02
131.85
131.16
130.45
130.03
129.09
128.65
128.08
127.78
127.51
127.00
122.57
21.50
NHTs
N
Br
1g
13C NMR (100 MHz, DMSO-d6)
f1 (ppm)
f1 (ppm)

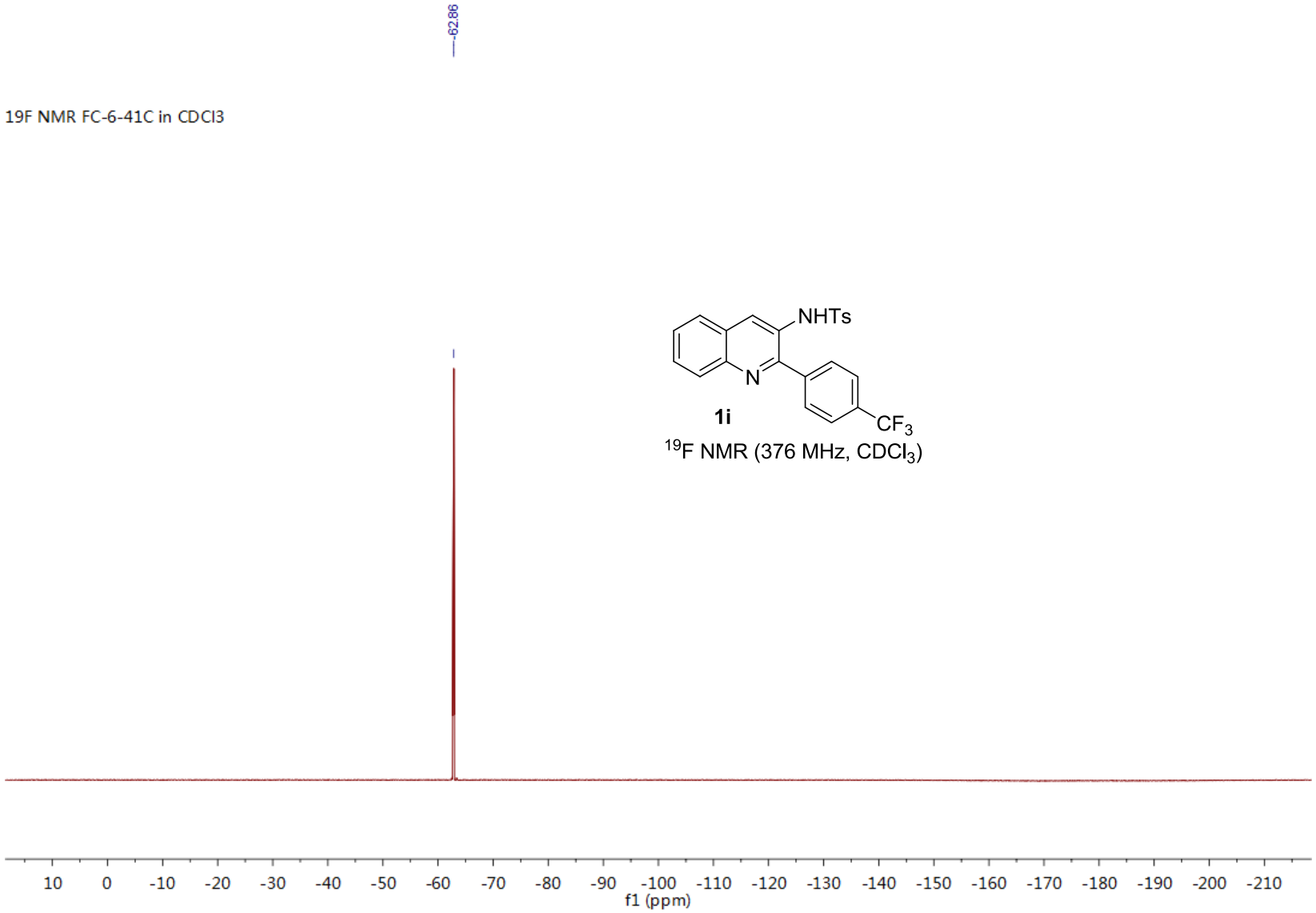

8.4404
8.0259
8.0048
7.8652
7.8449
7.6688
7.5691
7.5327
7.5122
7.2074
7.1871
7.1411
7.1286
2.3854
1H NMR FC-6-41B in CDCl3
//Yzc/g/新 NMR 2013/1357/fid
NHTs
N
F
1h
1H NMR (400 MHz, CDCl3)
1.00
1.01
1.04
1.05
3.07
2.03
3.96
0.80
3.07
f1 (ppm)

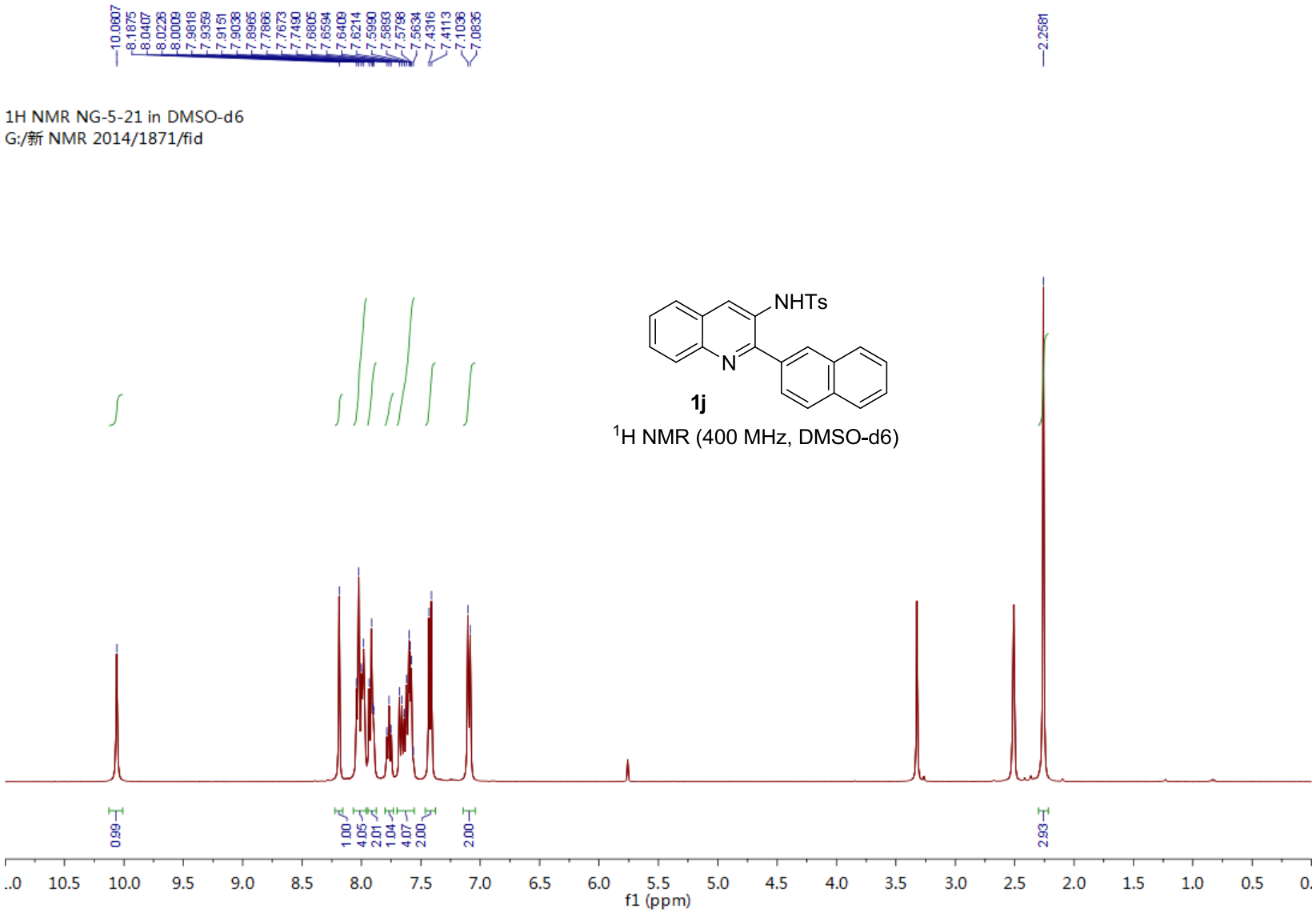

13C NMR FC-6-41B in DMSO-d6
G:/新 NMR 2014/1941/fid
164.01
161.57
156.20
145.97
143.64
137.66
133.89
132.01
131.92
130.40
130.04
129.06
128.06
127.66
114.98
21.44
135.12
135.10
133.89
132.01
131.92
130.40
130.04
129.06
128.62
128.06
127.66
127.40
127.03
NHTs
N
F
1h
13C NMR (100 MHz, DMSO-d6)
f1 (ppm)
f1 (ppm)

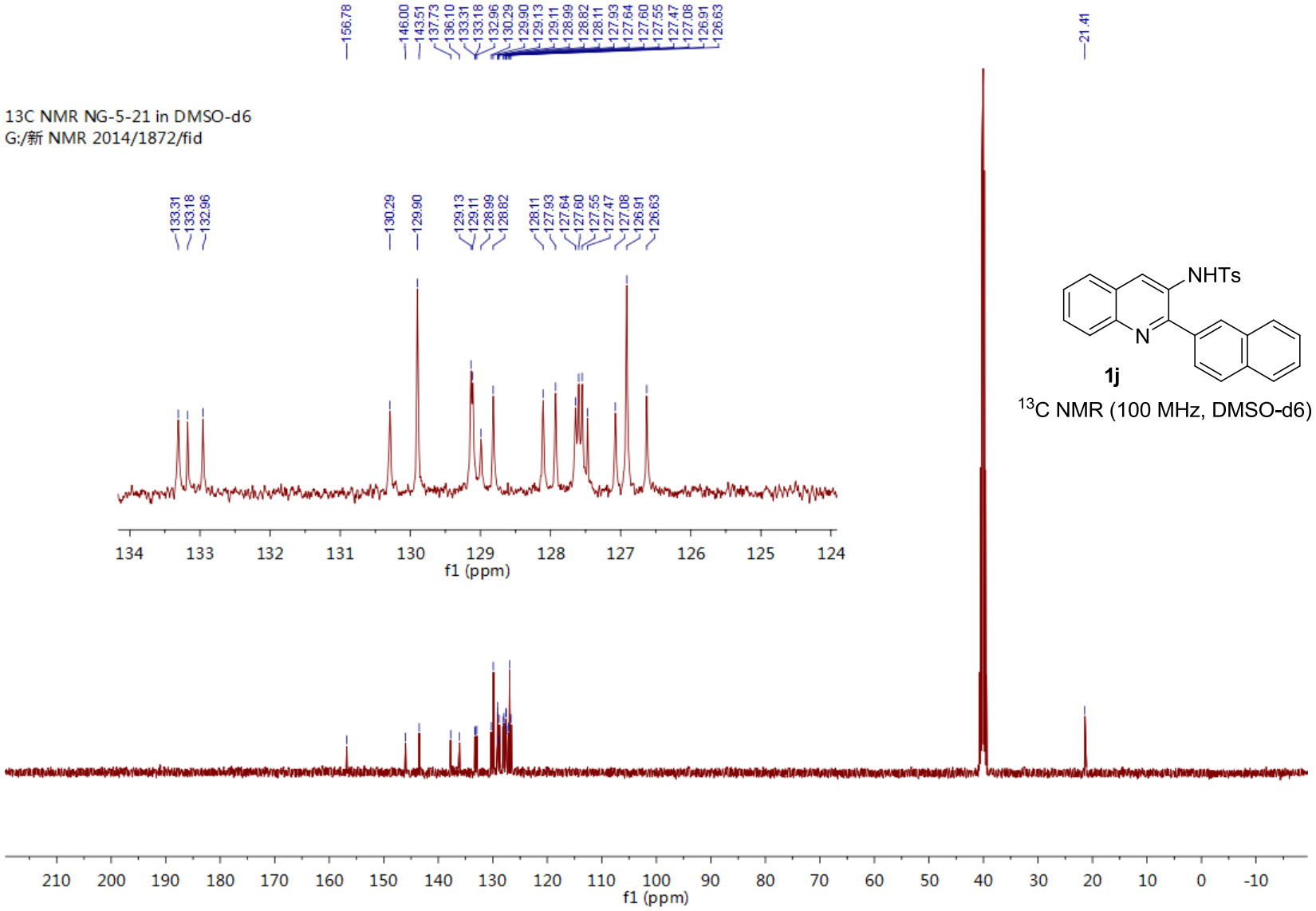

19F NMR FC-6-41B in CDCl3
-111.23
NHTs
N
F
1h
$^{19}$F NMR (376 MHz, $CDCl_3$)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

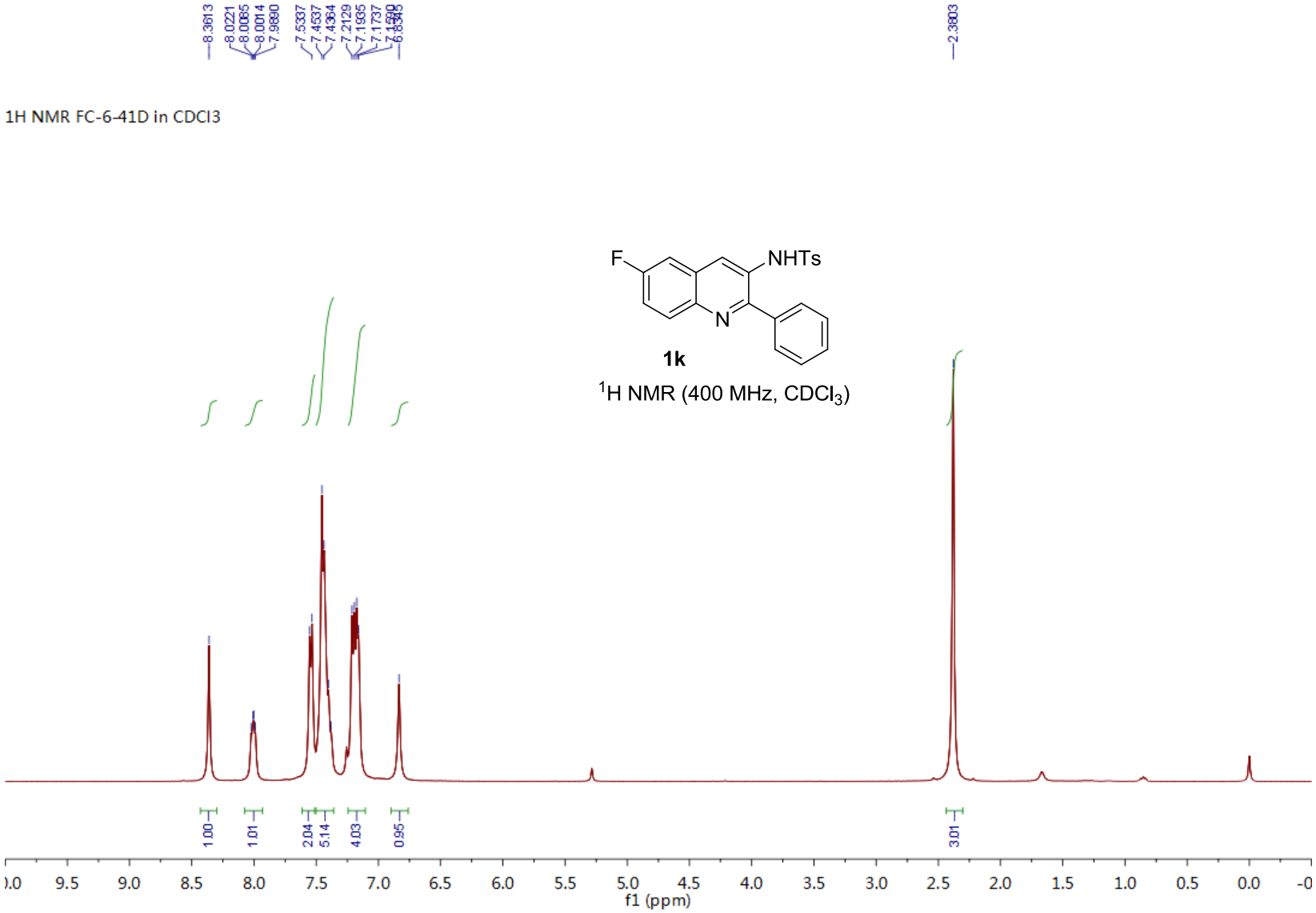

8.4643
8.0398
8.0187
7.8875
7.8673
7.6980
7.6667
7.6467
7.5975
7.5037
7.4635
7.2951
7.2754
7.1951
7.1750
6.6385
2.3949
1H NMR FC-6-41C in CDCl3
NHTs
N
1i
CF3
1H NMR (400 MHz, CDCl3)
1.00
1.03
1.08
4.19
2.01
1.92
2.01
0.92
3.04
f1 (ppm)

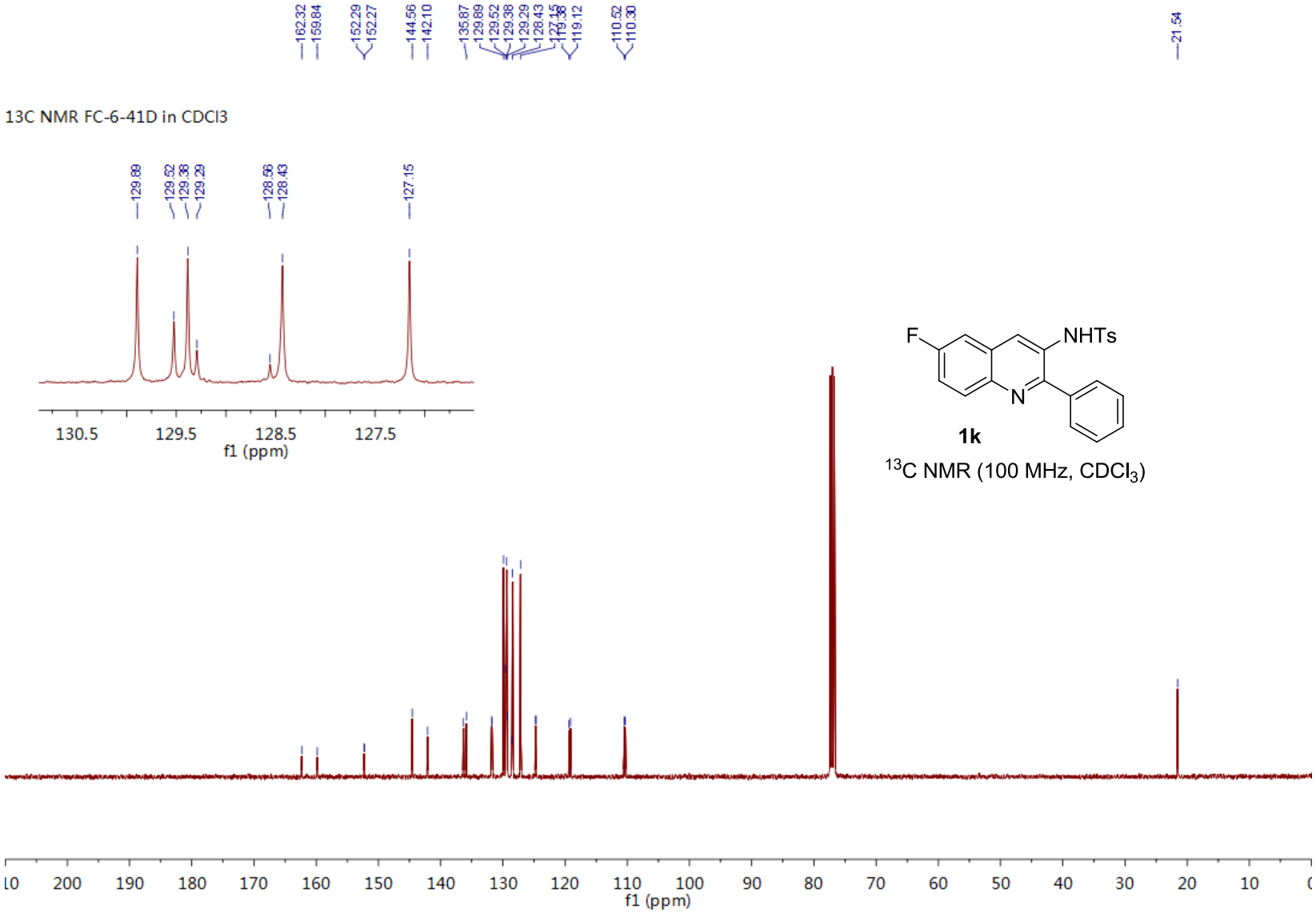

13C NMR FC-6-41C in CDCl3
G:/新 NMR 2014/1674/fid
152.10
145.43
144.58
140.46
135.98
131.56
131.23
130.90
129.91
129.62
129.28
129.10
128.17
128.03
127.87
127.78
127.58
127.06
126.09
126.05
126.02
125.98
125.15
122.44
21.52
128.17
128.03
127.87
127.78
127.58
127.06
126.09
126.05
126.02
125.98
125.15
128.5
128.0
127.5
127.0
126.5
126.0
125.5
125.0
f1 (ppm)
NHTs
N
CF3
1i
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

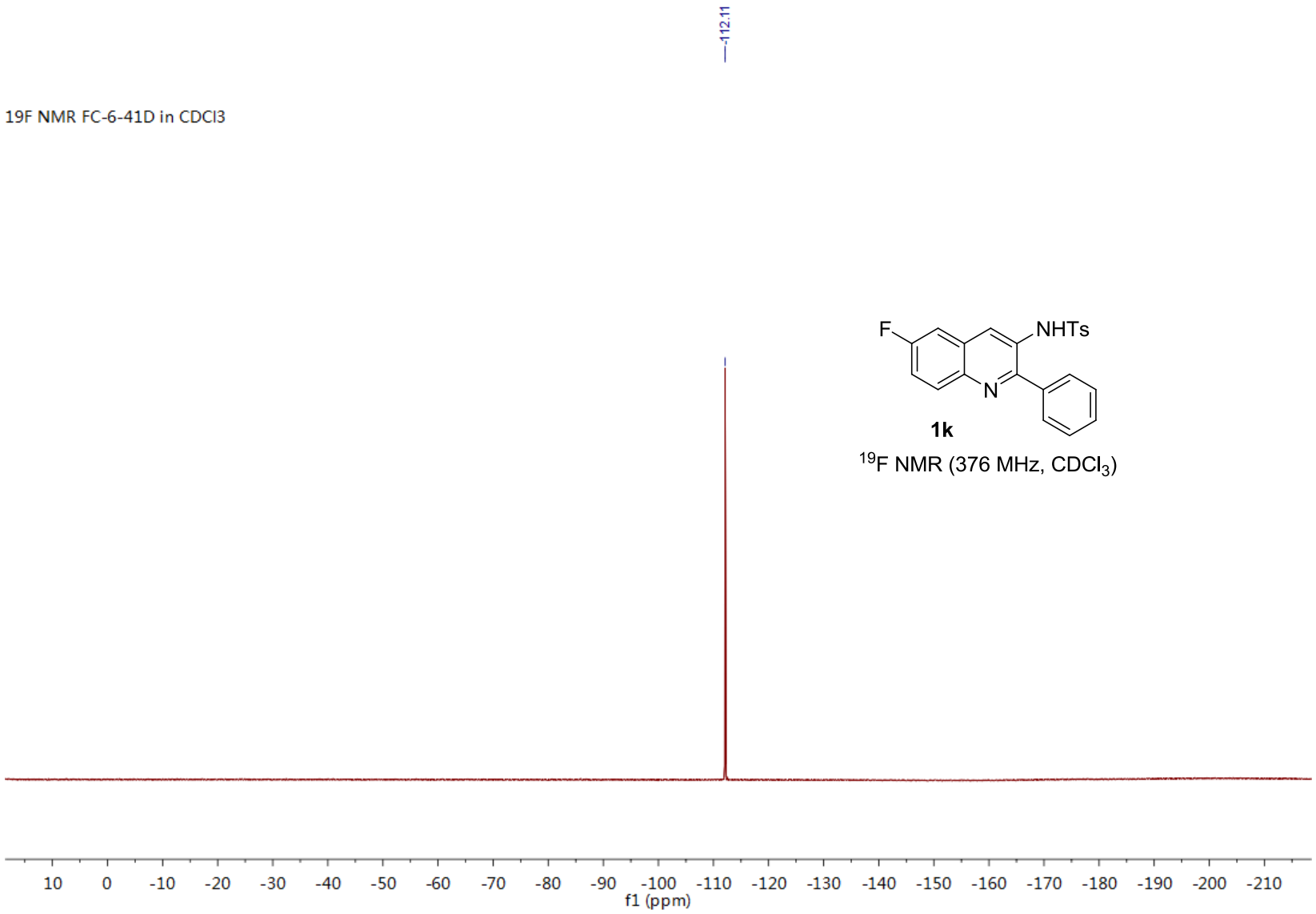

-62.86
19F NMR FC-6-41C in CDCl3
NHTs
N
CF3
1i
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


10.0807
8.1875
8.0407
8.0226
8.0009
7.9818
7.9359
7.9151
7.9038
7.8965
7.7866
7.7673
7.7490
7.6805
7.6594
7.6409
7.6214
7.5990
7.5893
7.5798
7.5634
7.4316
7.4113
7.1036
7.0835
2.2581
1H NMR NG-5-21 in DMSO-d6
G:/新 NMR 2014/1871/fid
NHTs
N
1j
1H NMR (400 MHz, DMSO-d6)
0.99
1.00
4.05
2.01
1.04
4.07
2.00
2.00
2.93
f1 (ppm)


13C NMR NG-5-21 in DMSO-d6
G:/新 NMR 2014/1872/fid
156.78
146.00
143.51
137.73
136.10
133.31
133.18
132.96
130.29
129.90
129.13
129.11
128.99
128.82
128.11
127.93
127.64
127.60
127.55
127.47
127.08
126.91
126.63
21.41
NHTs
N
1j
13C NMR (100 MHz, DMSO-d6)
f1 (ppm)
f1 (ppm)


8.3613
8.0221
8.0085
8.0014
7.9890
7.5337
7.4537
7.4364
7.2129
7.1935
7.1737
2.3803
1H NMR FC-6-41D in CDCl3
F
NHTs
N
1k
1H NMR (400 MHz, CDCl3)
1.00
1.01
2.04
5.14
4.03
0.95
3.01
f1 (ppm)

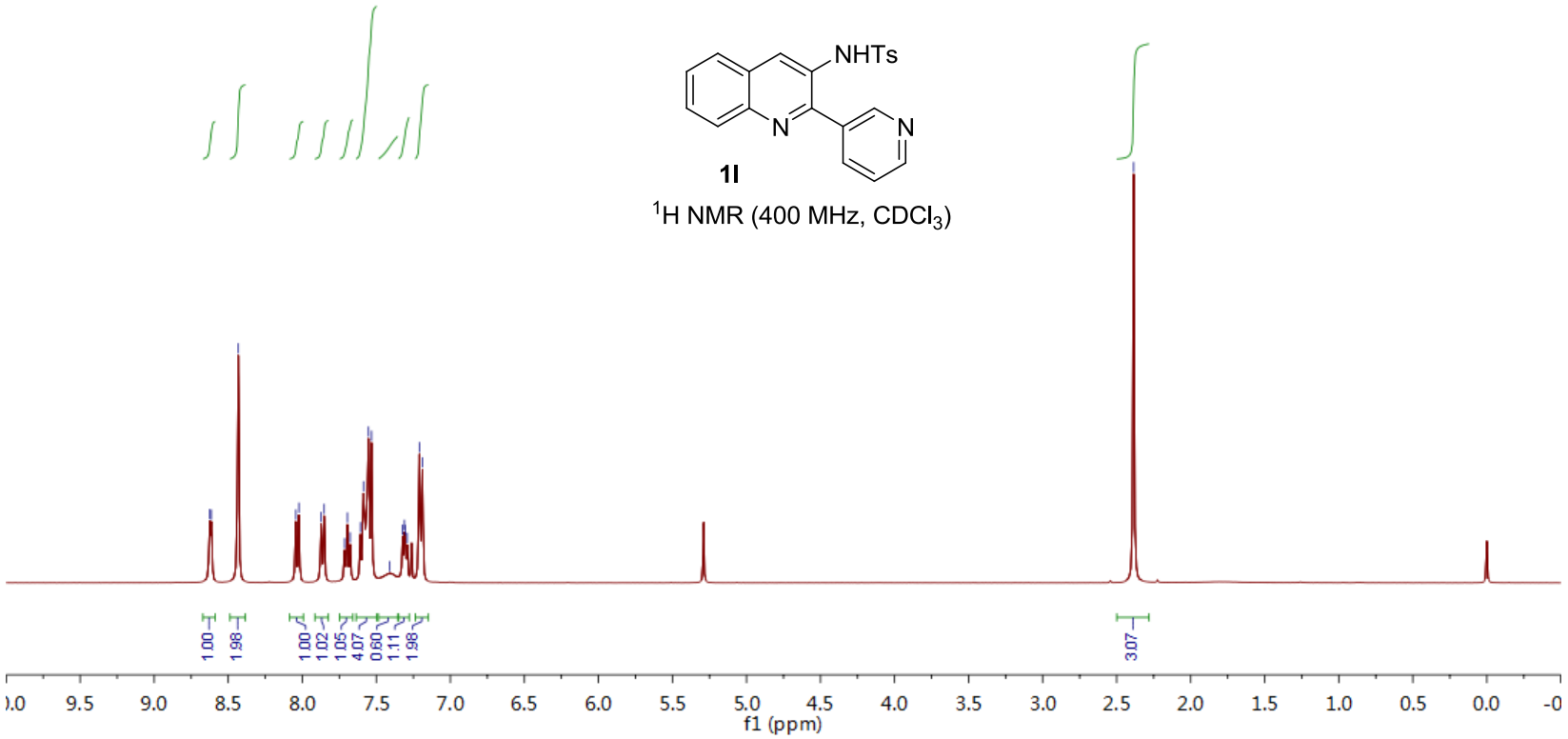

13C NMR FC-6-41D in CDCl3
162.32
159.84
152.29
152.27
144.56
142.10
135.87
129.89
129.52
129.38
129.29
128.43
127.15
119.12
110.52
110.30
21.54
129.89
129.52
129.38
129.29
128.66
128.43
127.15
130.5
129.5
128.5
127.5
f1 (ppm)
F
NHTs
N
1k
13C NMR (100 MHz, CDCl3)
f1 (ppm)




**1k**

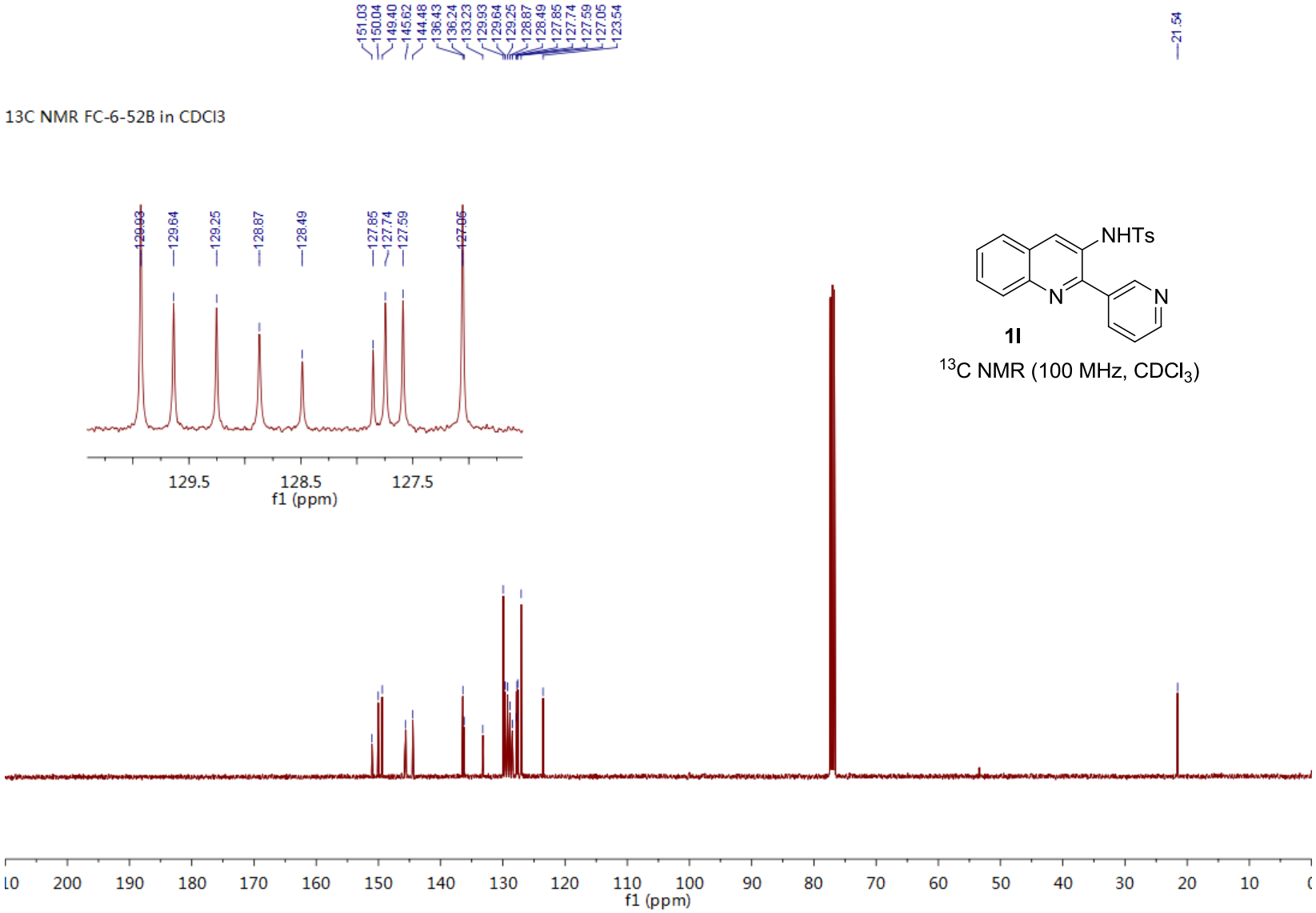
$^{19}F$ NMR (376 MHz, $CDCl_3$)

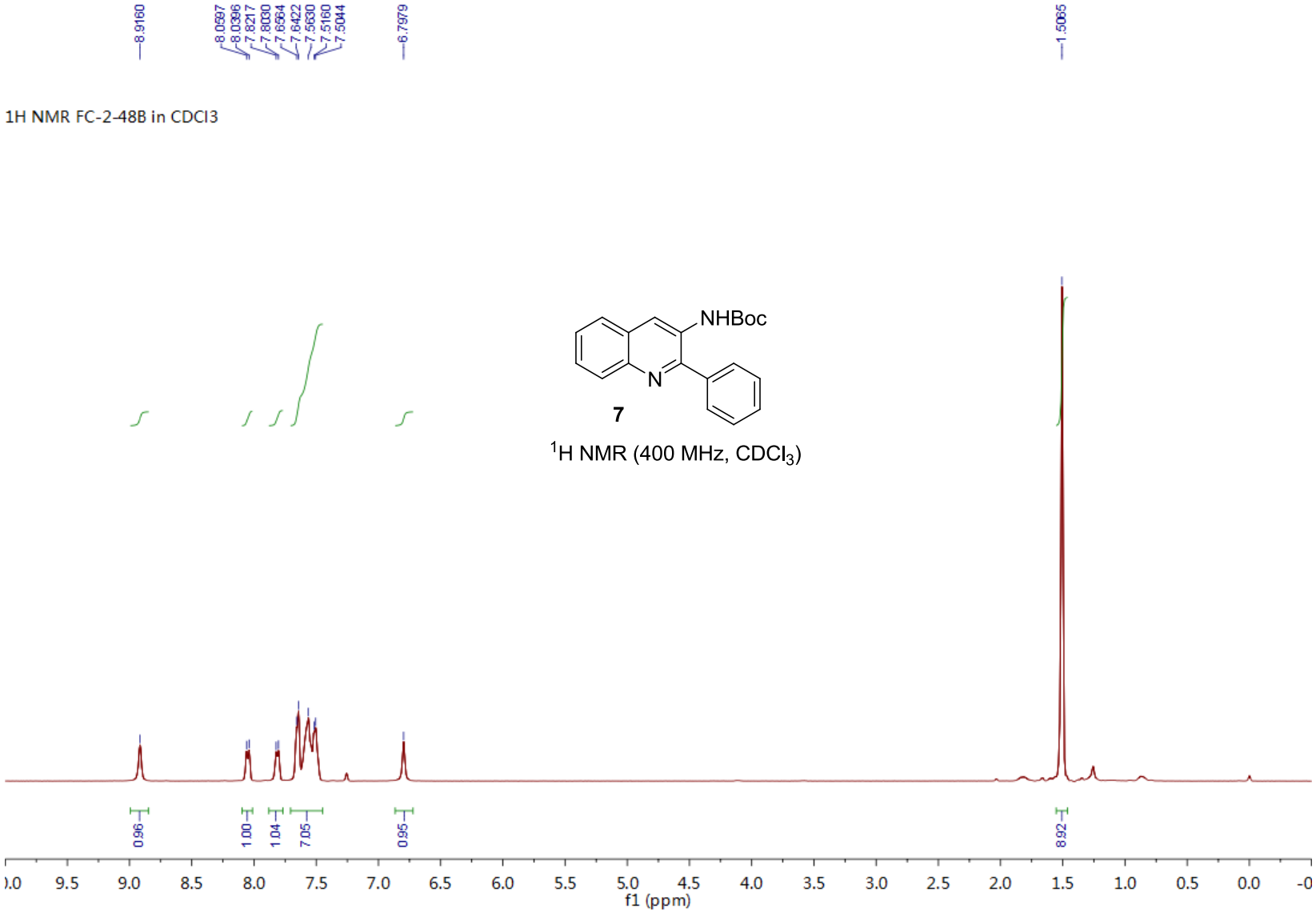

1H NMR FC-6-52B in CDCl3

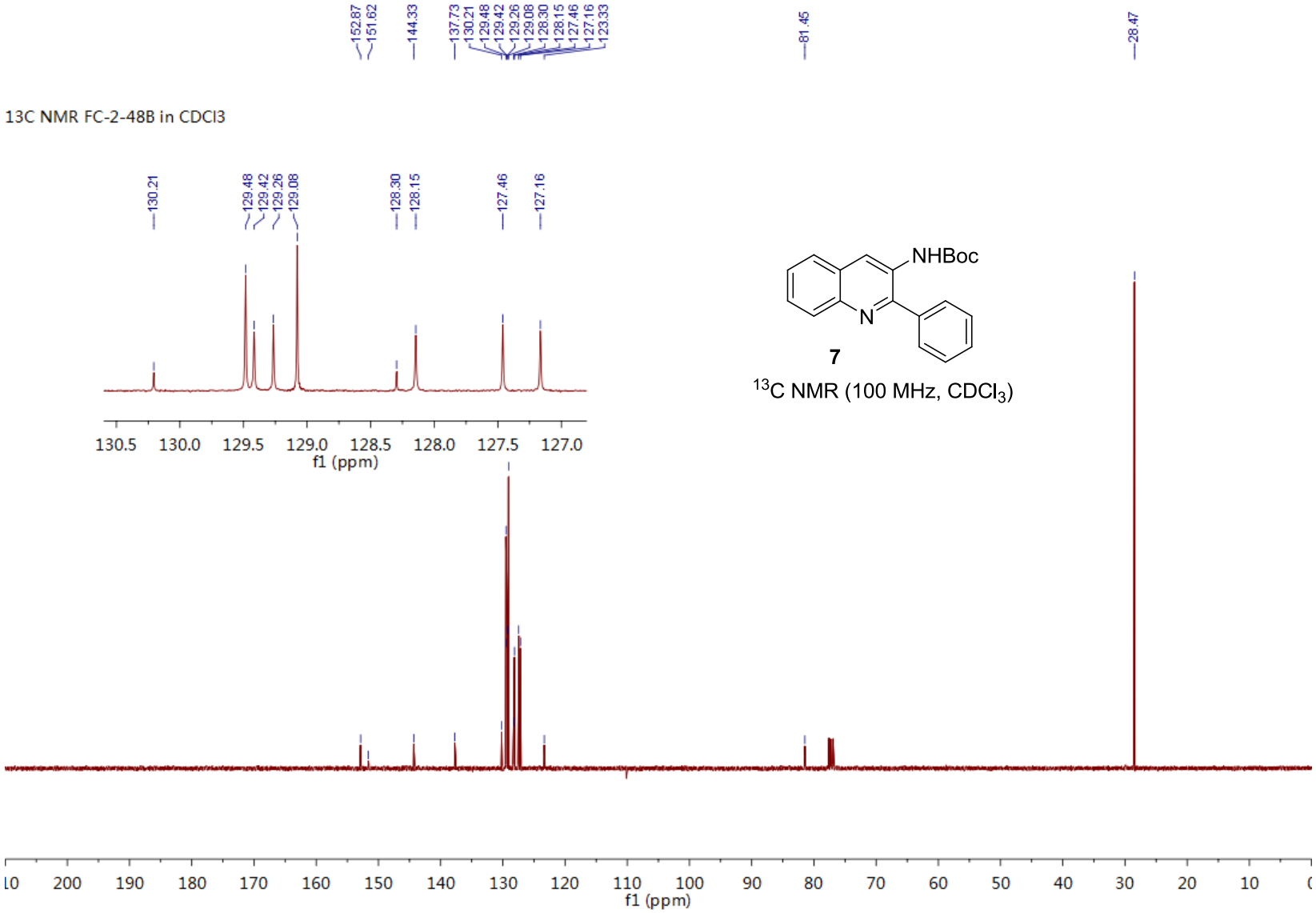


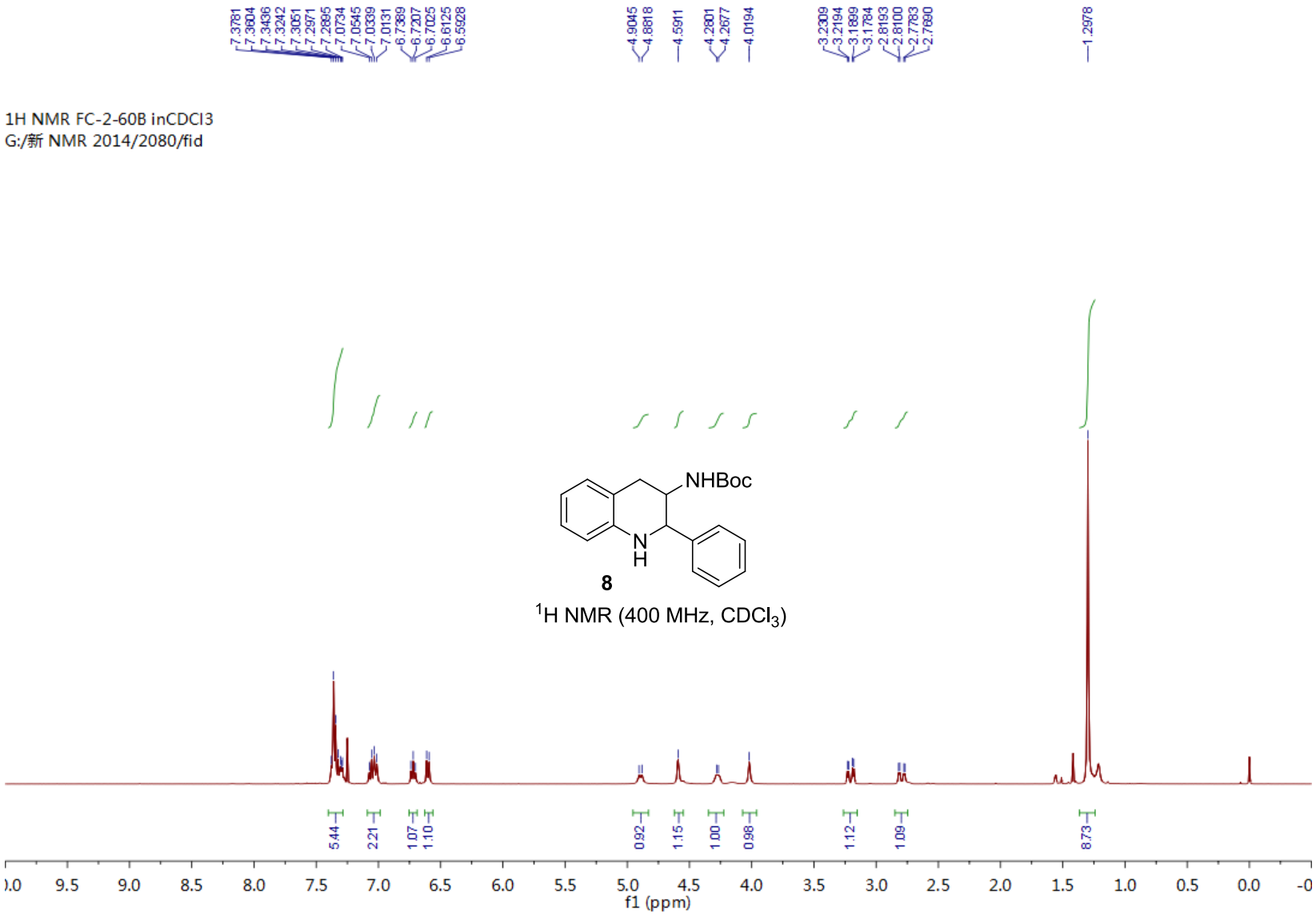

**1l**

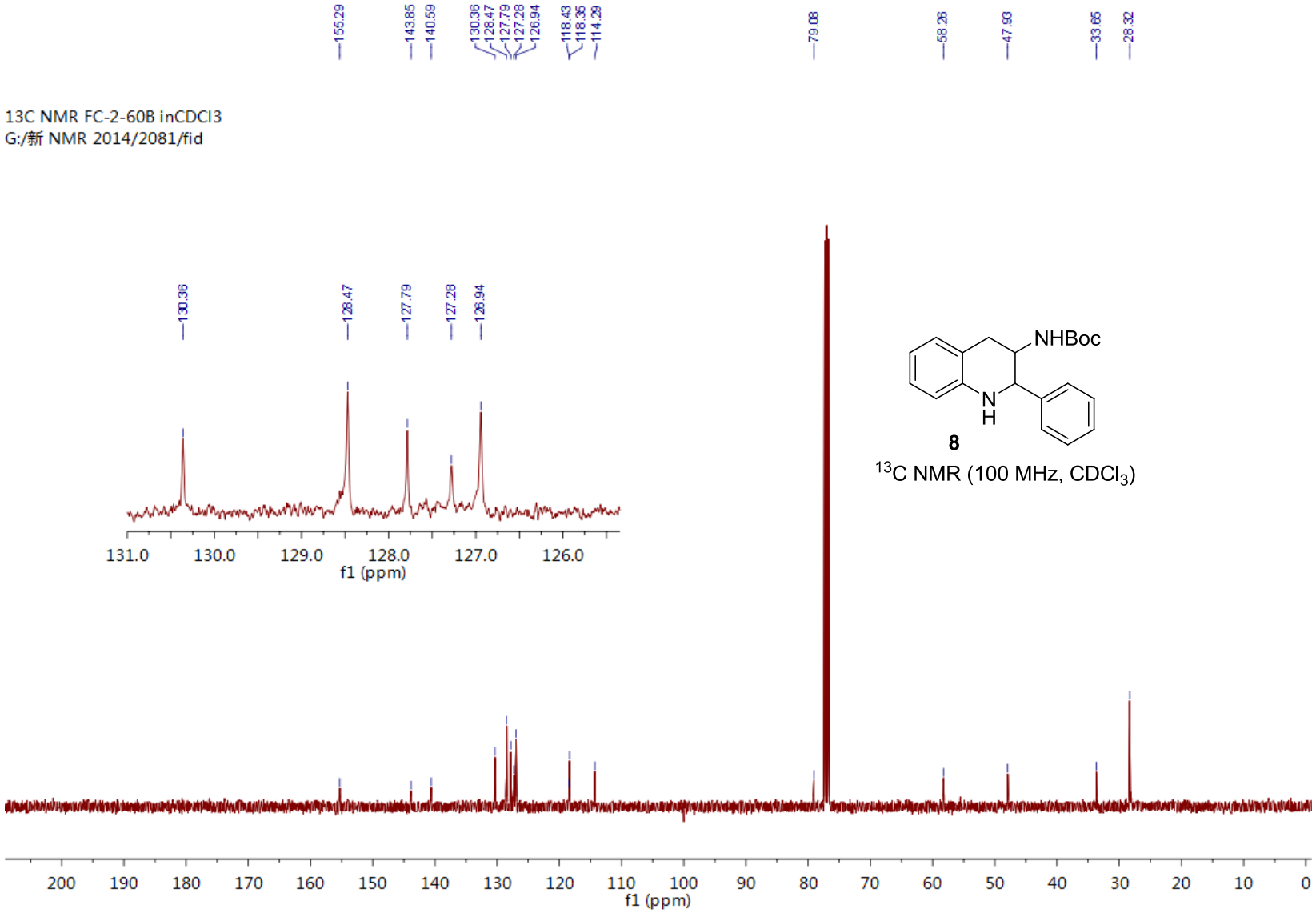
$^1$H NMR (400 MHz, $CDCl_3$)


151.03
150.04
149.40
145.62
144.48
136.43
136.24
133.23
129.93
129.64
129.25
128.87
128.49
127.85
127.74
127.59
127.05
123.54
21.54
13C NMR FC-6-52B in CDCl3
129.64
129.25
128.87
128.49
127.85
127.74
127.59
129.5
128.5
127.5
f1 (ppm)
NHTs
N
N
1l
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

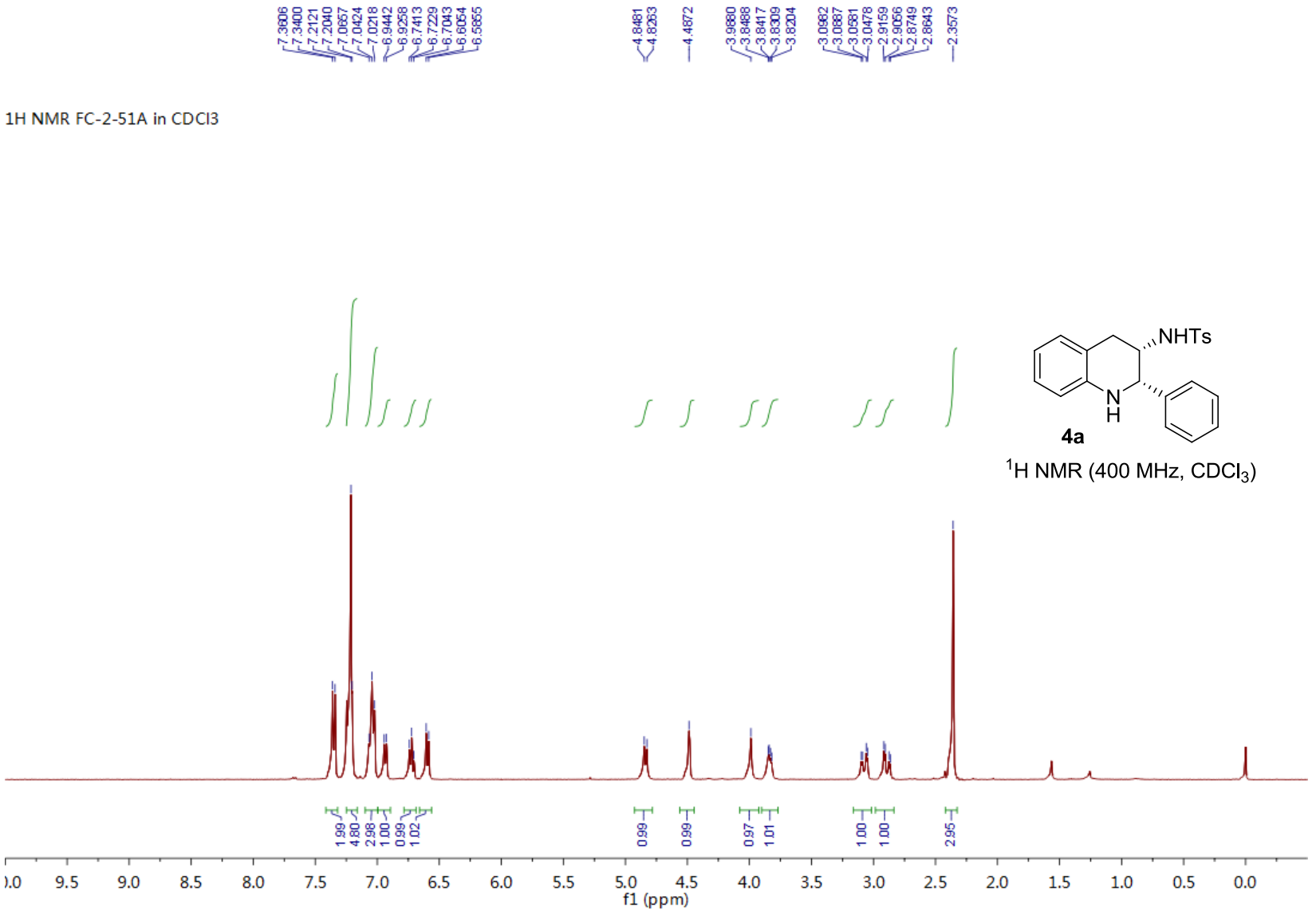

8.9160
8.0597
8.0396
7.8217
7.8030
7.6564
7.6422
7.5630
7.5160
7.5044
6.7979
1.5065
1H NMR FC-2-48B in CDCl3
NHBoc
N
7
1H NMR (400 MHz, CDCl3)
0.96
1.00
1.04
7.05
0.95
8.92
f1 (ppm)

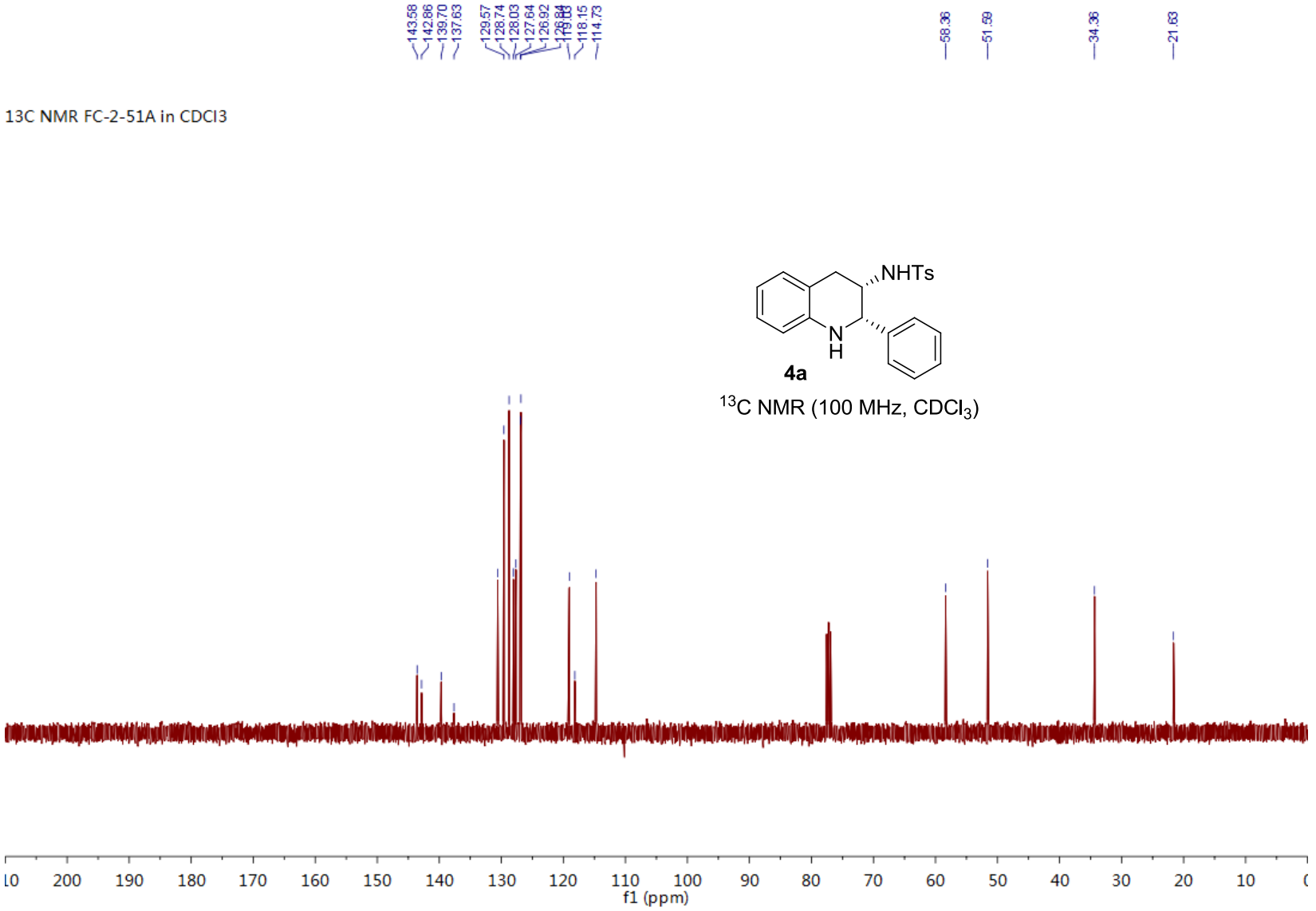

152.87
151.62
144.33
137.73
130.21
129.48
129.42
129.26
129.08
128.30
128.15
127.46
127.16
123.33
81.45
28.47
13C NMR FC-2-48B in CDCl3
130.21
129.48
129.42
129.26
129.08
128.30
128.15
127.46
127.16
130.5
130.0
129.5
129.0
128.5
128.0
127.5
127.0
f1 (ppm)
NHBoc
N
7
13C NMR (100 MHz, CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.3781
7.3604
7.3436
7.3242
7.3051
7.2971
7.2895
7.0734
7.0545
7.0339
7.0131
6.7389
6.7207
6.7025
6.6125
6.5928
4.9045
4.8818
4.5911
4.2801
4.2677
4.0194
3.2309
3.2194
3.1889
3.1784
2.8193
2.8100
2.7783
2.7690
1.2978
1H NMR FC-2-60B inCDCl3
G:/新 NMR 2014/2080/fid
NHBoc
N
H
8
1H NMR (400 MHz, CDCl3)
5.44
2.21
1.07
1.10
0.92
1.15
1.00
0.98
1.12
1.09
8.73
f1 (ppm)

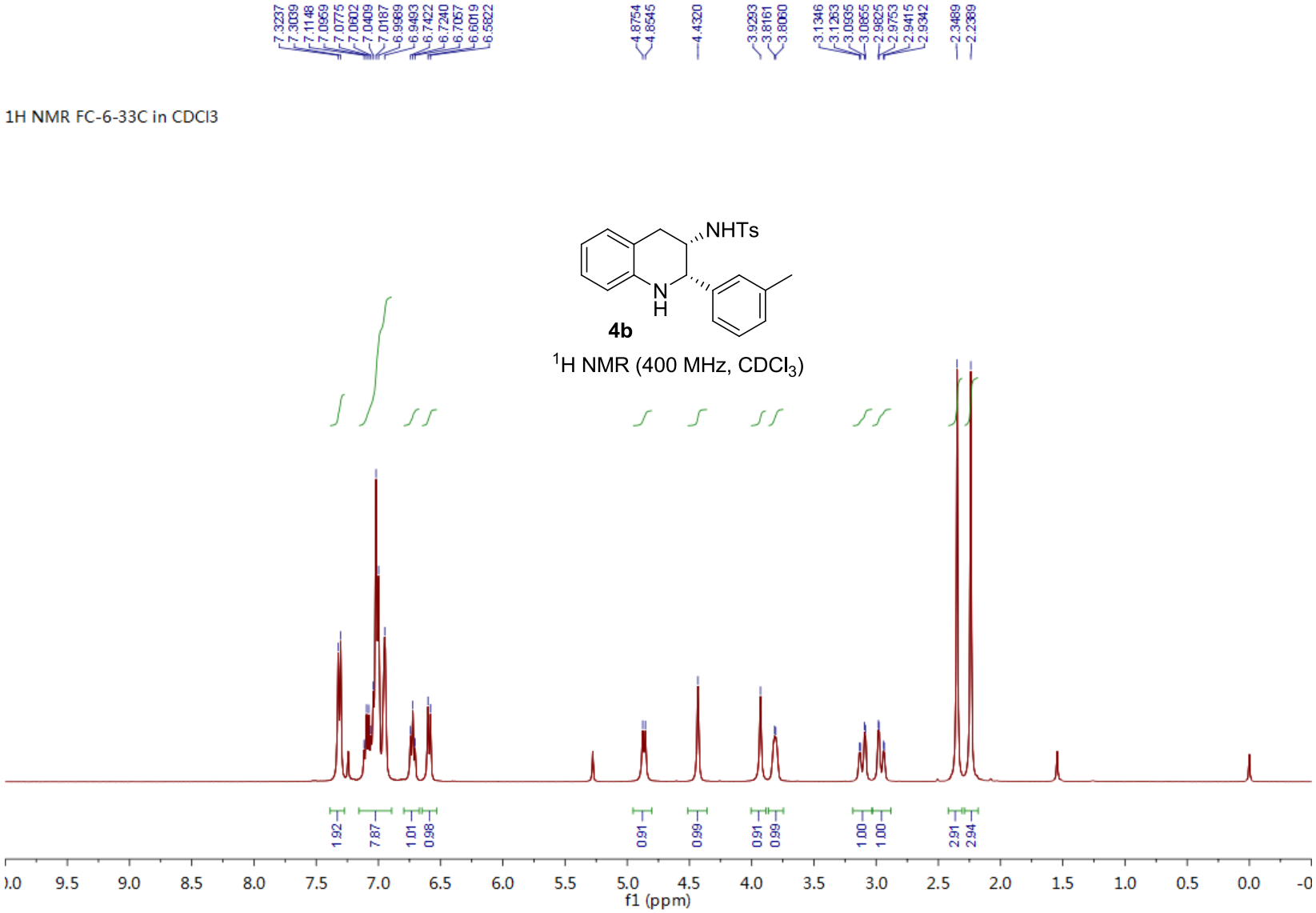

155.29
143.85
140.59
130.36
128.47
127.79
127.28
126.94
118.43
118.35
114.29
79.08
58.26
47.93
33.65
28.32
13C NMR FC-2-60B inCDCl3
G:/新 NMR 2014/2081/fid
NHBoc
N
H
8
13C NMR (100 MHz, CDCl3)
f1 (ppm)

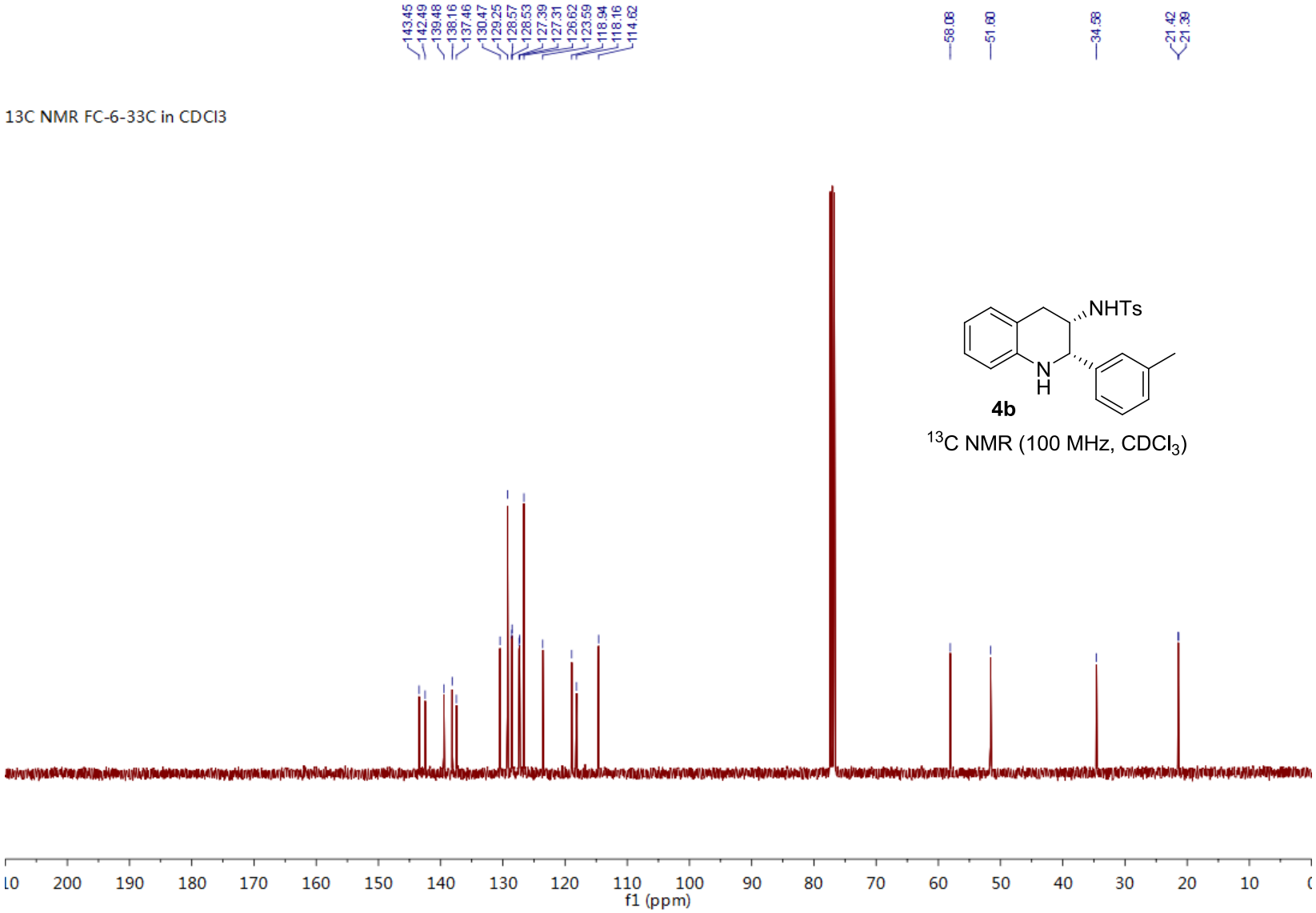
1H NMR FC-2-51A in CDCl3



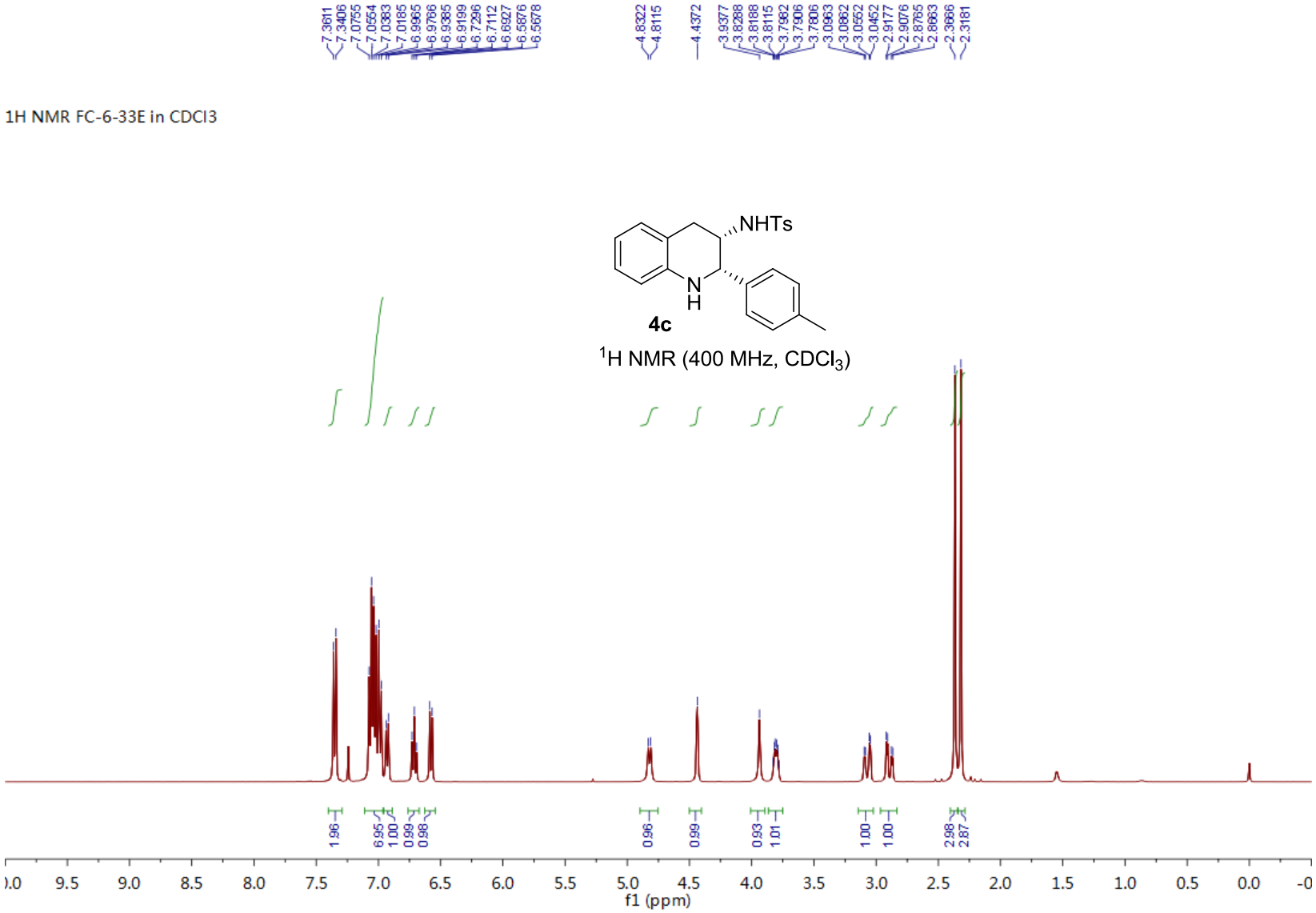

143.58
142.86
139.70
137.63
129.57
128.74
128.03
127.64
126.92
118.15
114.73
58.36
51.59
34.36
21.63
13C NMR FC-2-51A in CDCl3
NHTs
N
H
4a
13C NMR (100 MHz, CDCl3)
f1 (ppm)

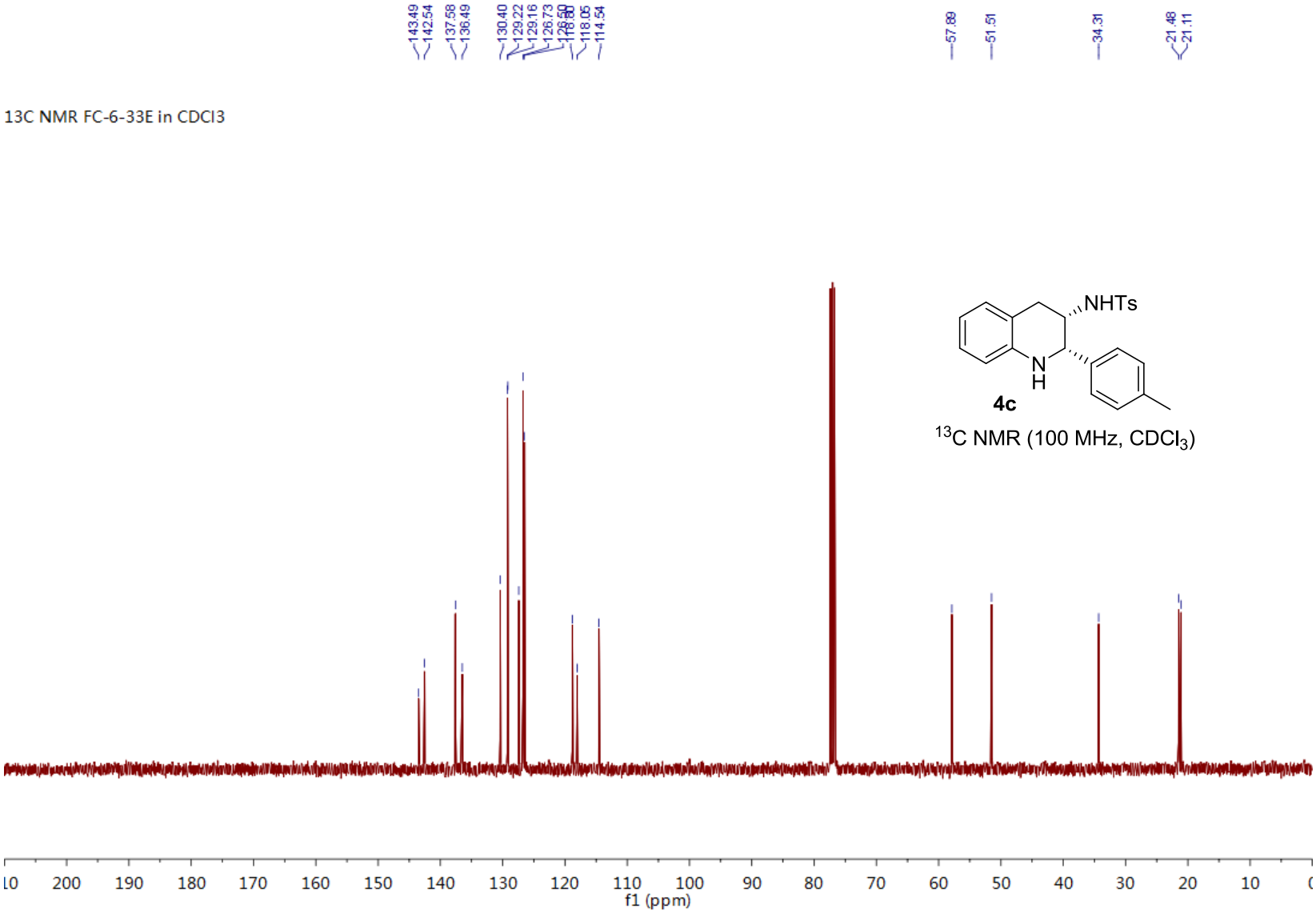
1H NMR FC-6-33C in CDCl3

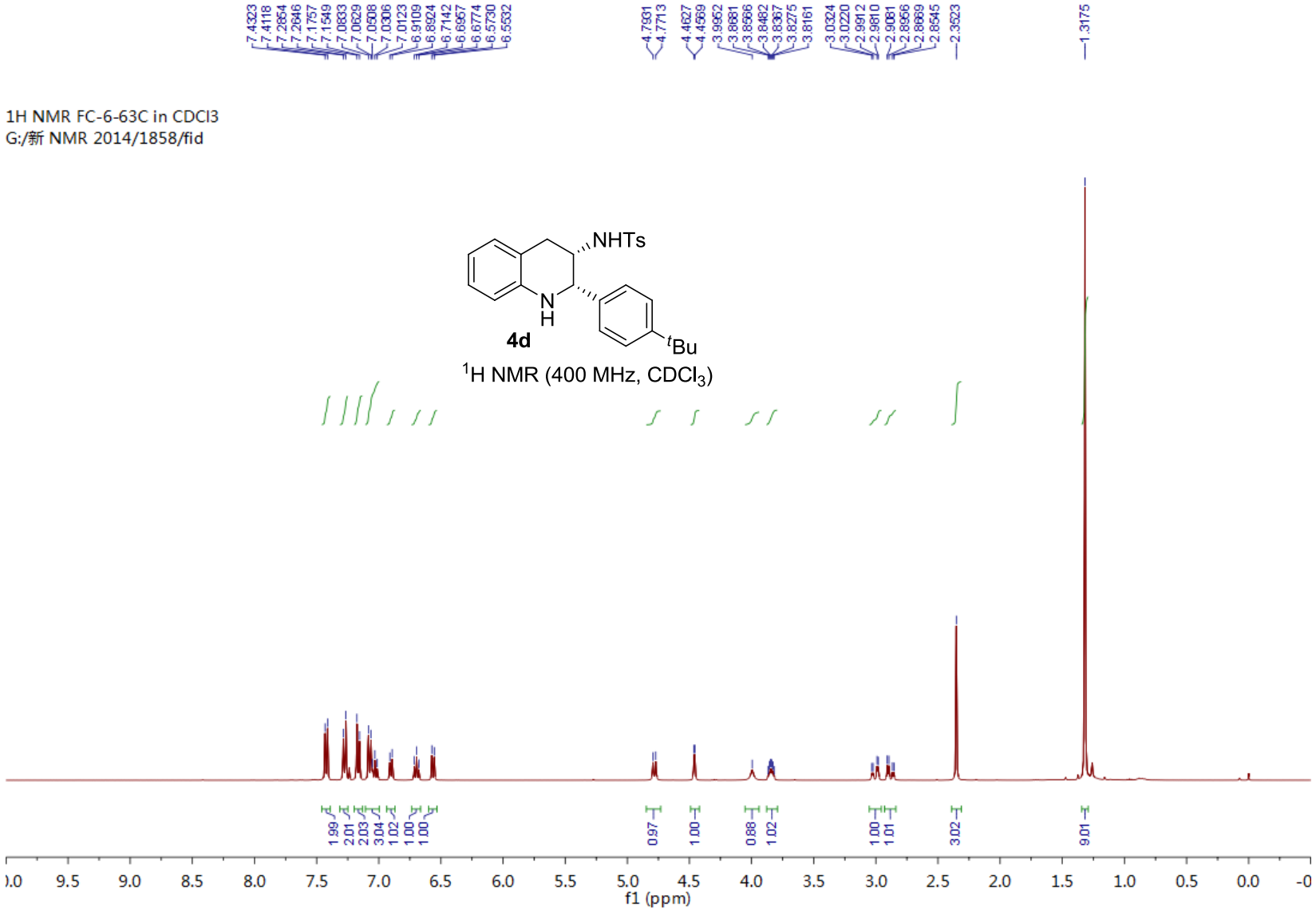



143.45
142.49
139.48
138.16
137.46
130.47
129.25
128.57
128.53
127.39
127.31
126.62
123.59
118.94
118.16
114.62
58.08
51.80
34.58
21.42
21.39
13C NMR FC-6-33C in CDCl3
NHTs
N
H
4b
13C NMR (100 MHz, CDCl3)
f1 (ppm)

1H NMR FC-6-33E in CDCl3

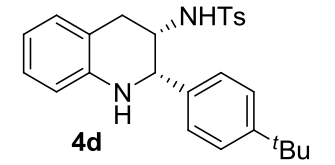



143.49
142.54
137.58
136.49
130.40
129.22
129.16
126.73
118.05
114.54
57.89
51.51
34.31
21.48
21.11
13C NMR FC-6-33E in CDCl3
NHTs
N
H
4c
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.4323
7.4118
7.2854
7.2646
7.1757
7.1549
7.0833
7.0629
7.0308
7.0306
7.0123
6.9109
6.8924
6.7142
6.6957
6.6774
6.5730
6.5532
4.7931
4.7713
4.4627
4.4569
3.9952
3.8881
3.8666
3.8482
3.8367
3.8275
3.8161
3.0324
3.0220
2.9912
2.9810
2.9081
2.8866
2.8669
2.8545
2.3523
1.3175
1H NMR FC-6-63C in CDCl3
G:/新 NMR 2014/1858/fid
NHTs
N
H
4d
tBu
1H NMR (400 MHz, CDCl3)
1.99
2.01
2.03
3.04
1.02
1.00
1.00
0.97
1.00
0.88
1.02
1.00
1.01
3.02
9.01
f1 (ppm)

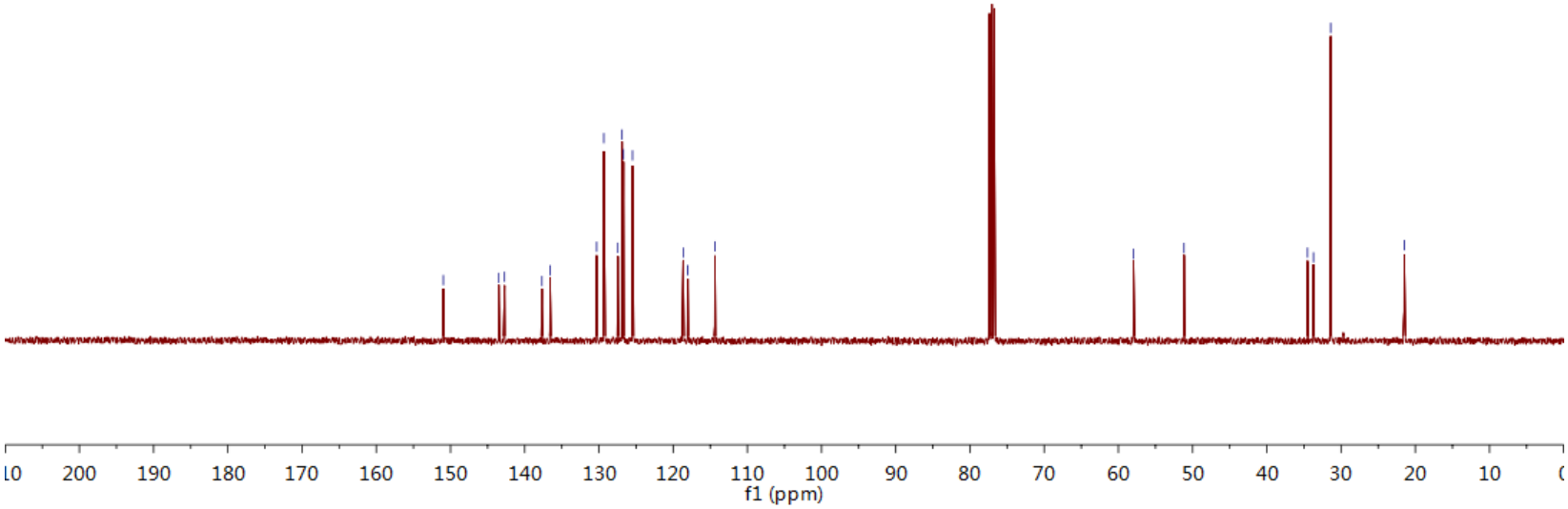
150.96
143.49
142.72
137.68
136.58
130.31
129.34
127.45
126.88
126.68
125.48
118.64
118.01
114.37
57.96
51.16
34.53
33.72
31.40
21.49

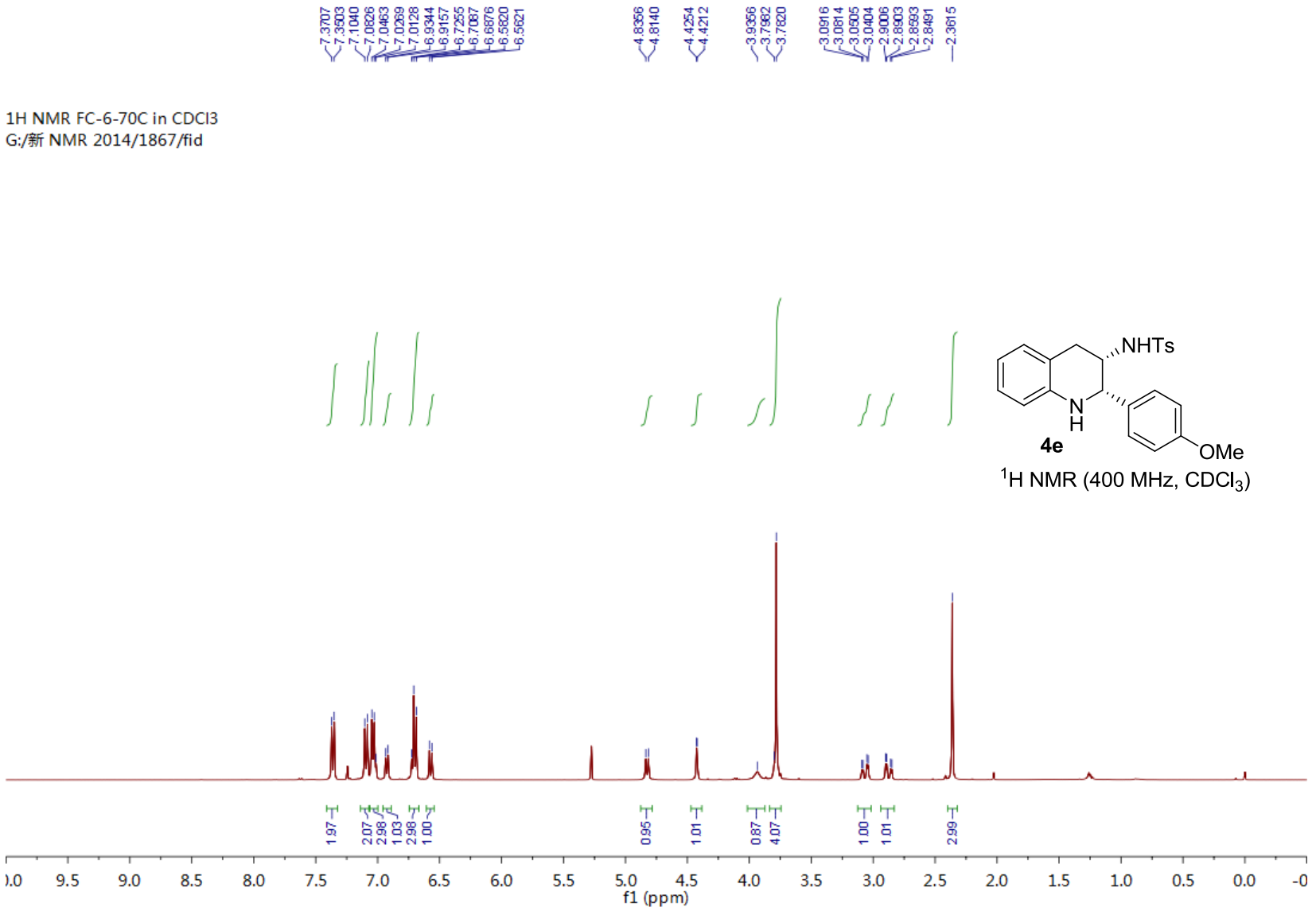
13C NMR FC-6-63C in CDCl3
G:/新 NMR 2014/1859/fid




**4d**

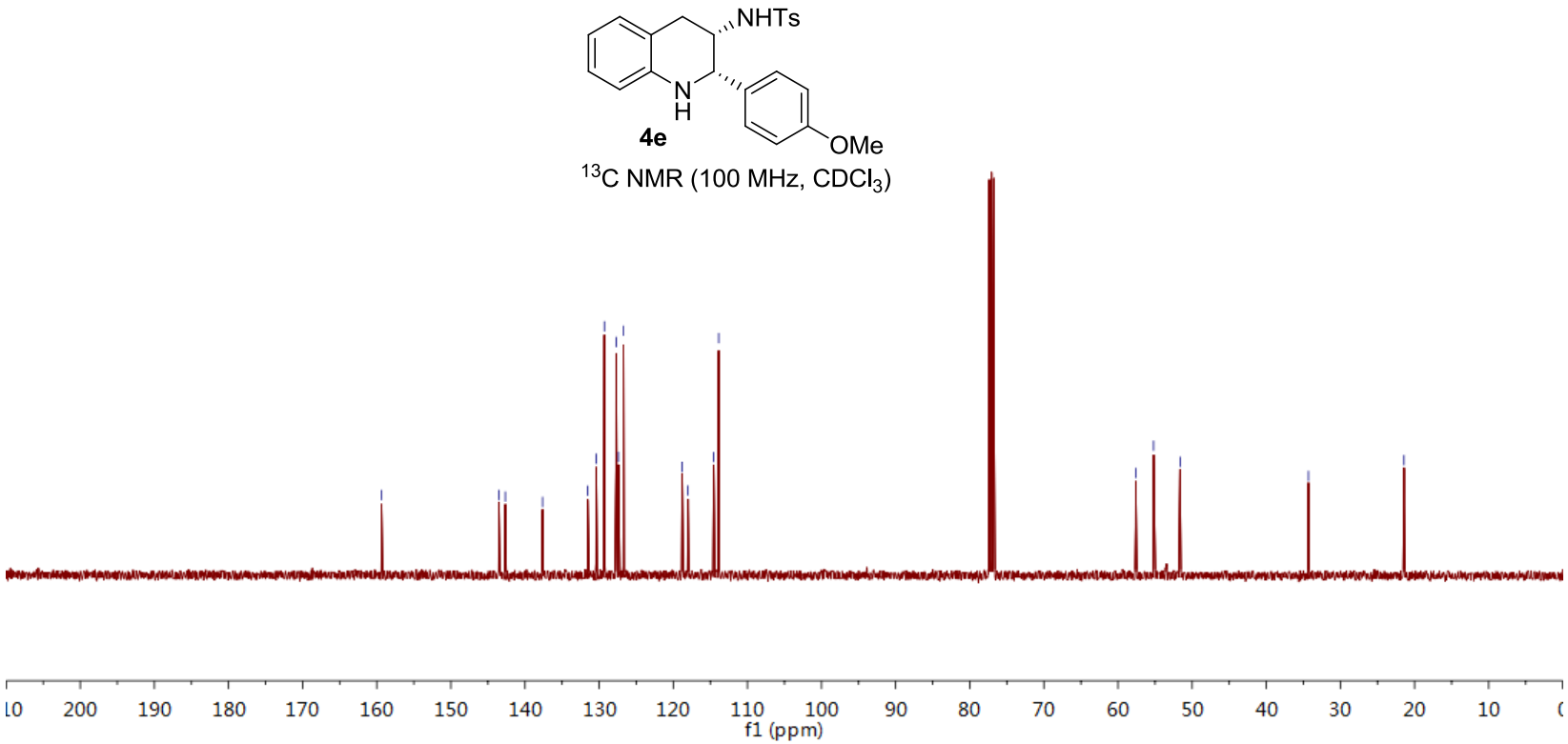
$^{13}C$ NMR (100 MHz, $CDCl_3$)

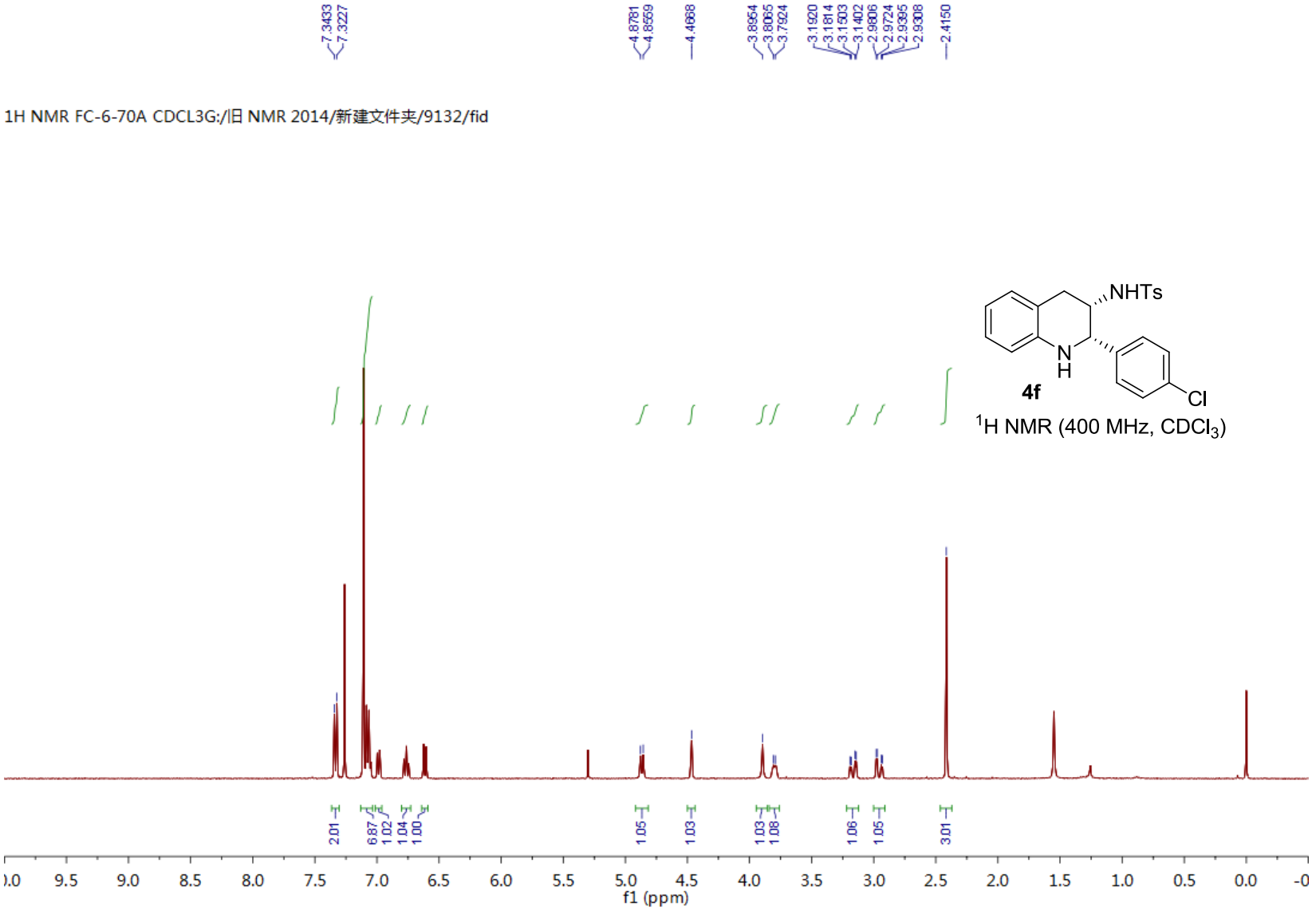


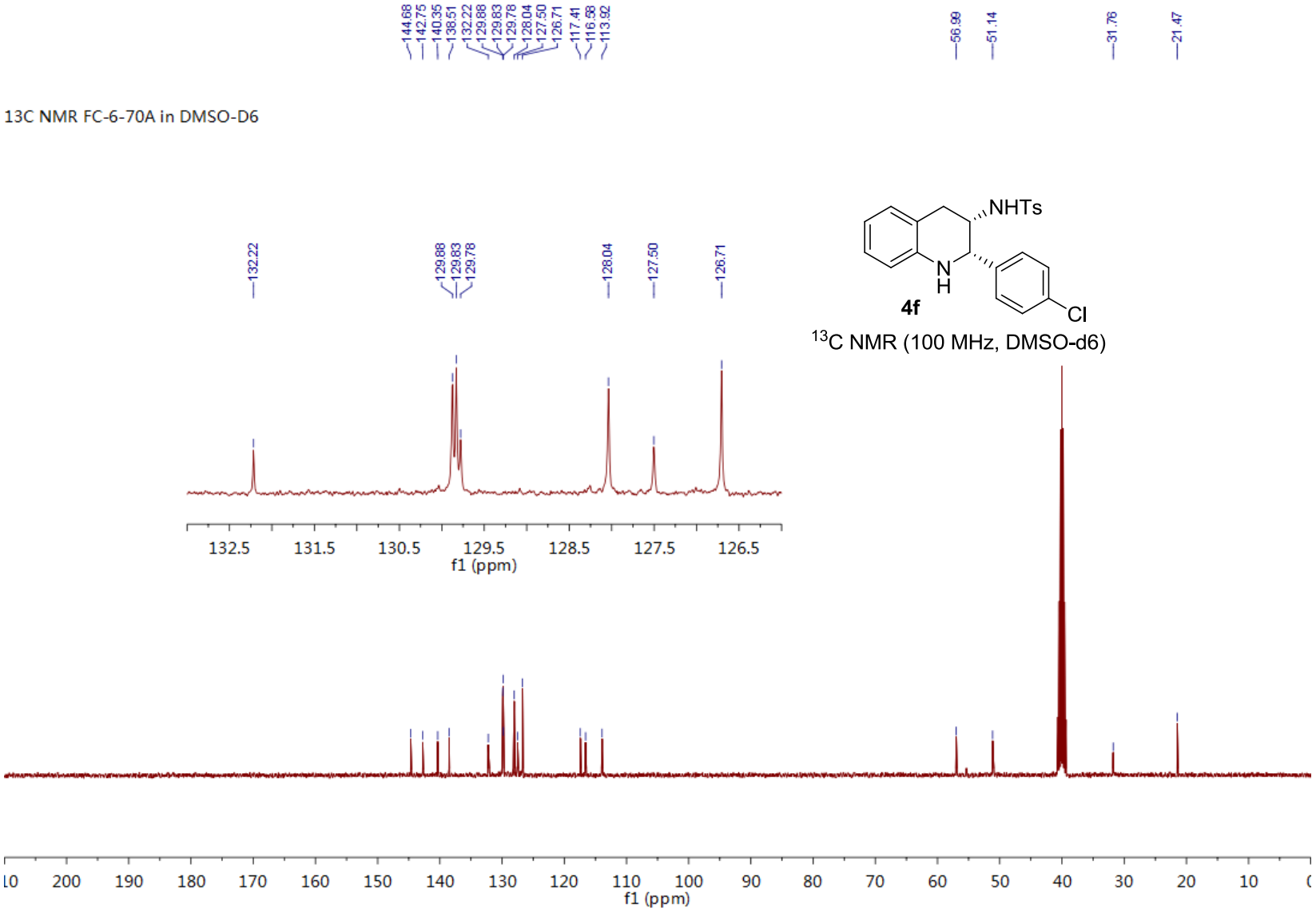

7.3707
7.3503
7.1040
7.0826
7.0463
7.0269
7.0128
6.9344
6.9157
6.7255
6.7087
6.6876
6.5820
6.5621
4.8356
4.8140
4.4254
4.4212
3.9356
3.7982
3.7820
3.0916
3.0814
3.0505
3.0404
2.9006
2.8903
2.8593
2.8491
2.3615
1H NMR FC-6-70C in CDCl3
G:/新 NMR 2014/1867/fid
NHTs
N
H
OMe
4e
1H NMR (400 MHz, CDCl3)
1.97
2.07
2.98
1.03
2.98
1.00
0.95
1.01
0.87
4.07
1.00
1.01
2.99
f1 (ppm)

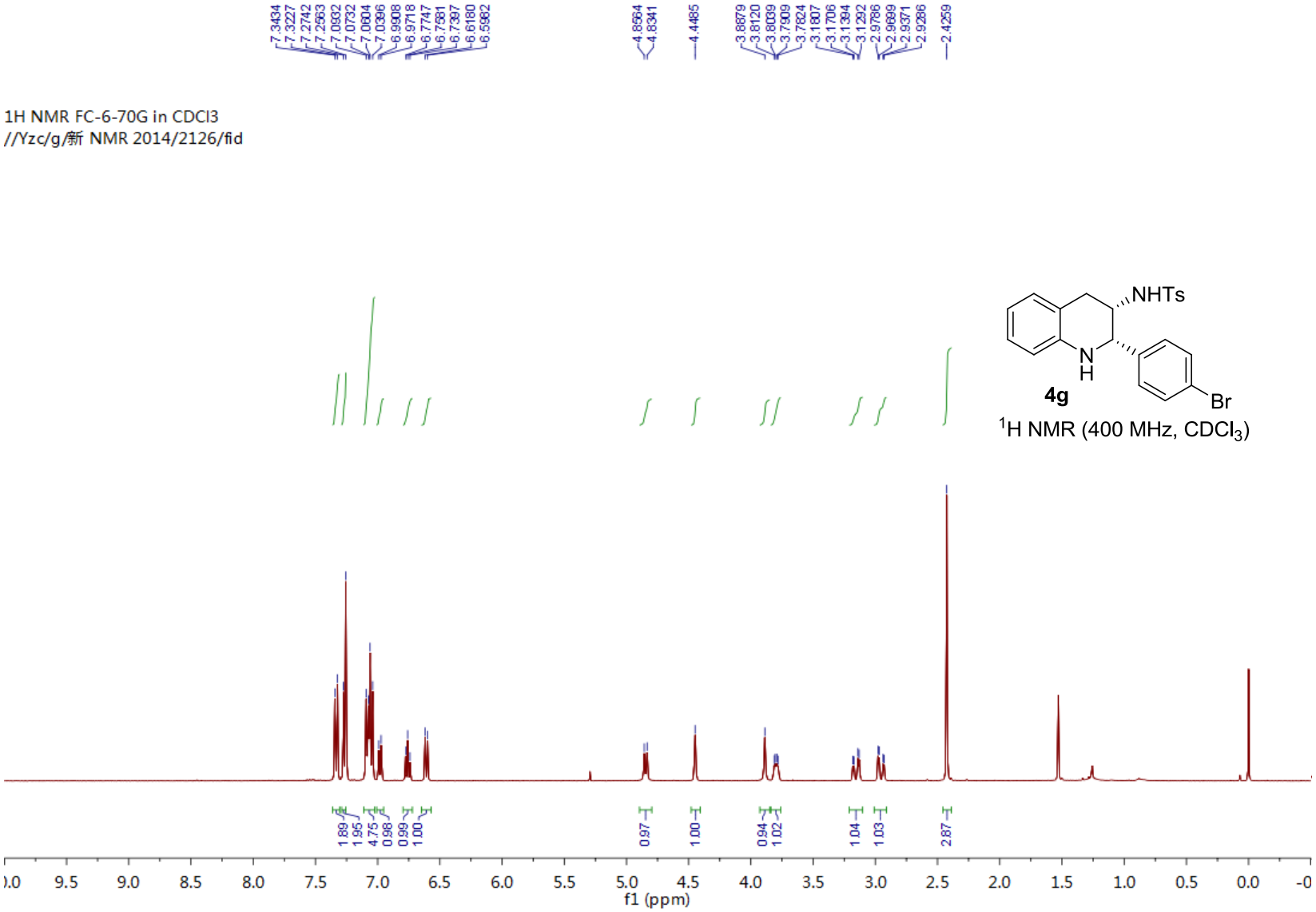
159.35
143.52
142.65
137.62
131.52
130.40
129.29
127.71
127.41
126.71
118.80
118.01
114.54
113.87
57.60
55.20
51.62
34.32
21.41

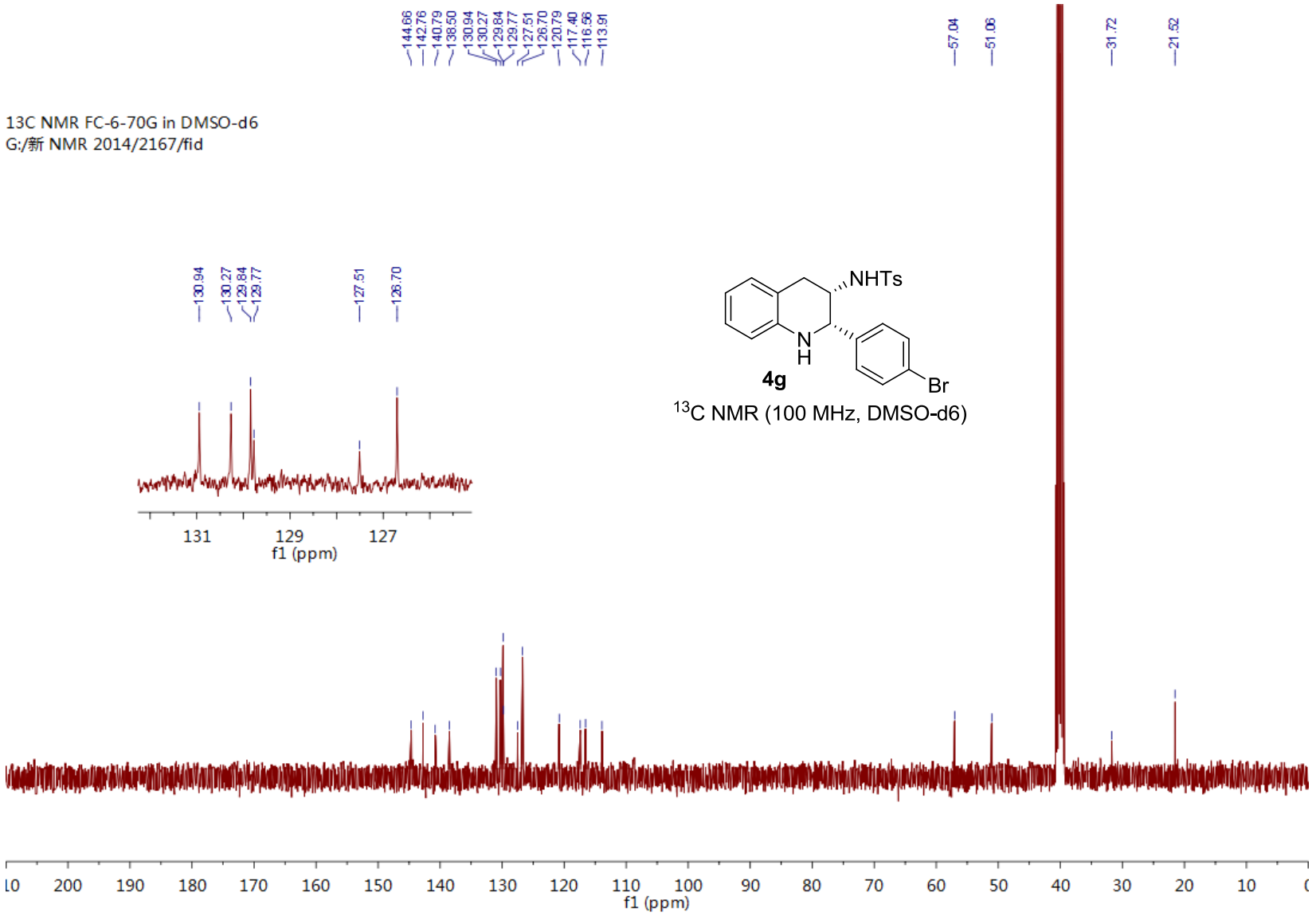
13C NMR FC-6-70C in CDCl3
G:/新 NMR 2014/1868/fid

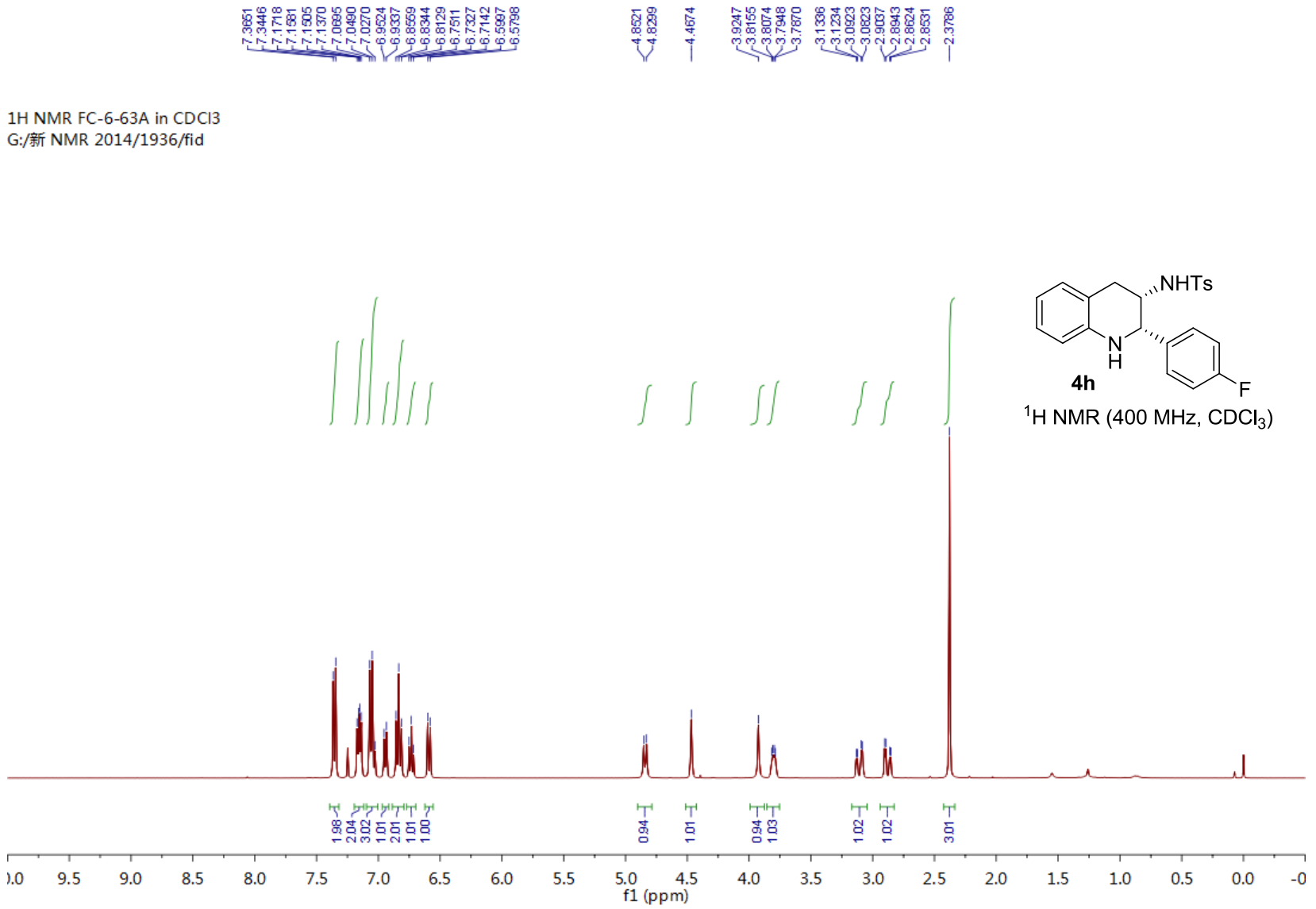


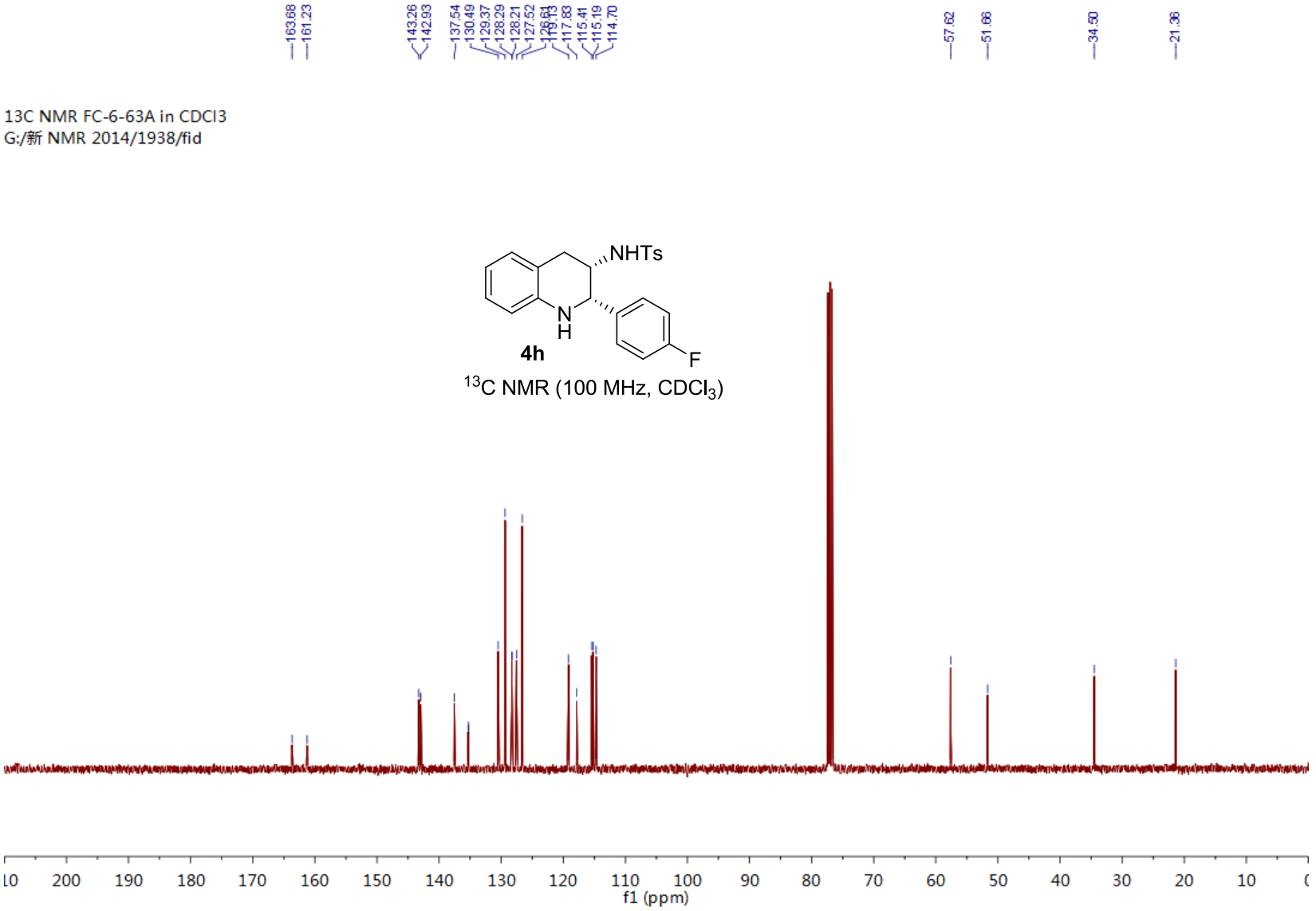

7.3433
7.3227
4.8781
4.8559
4.4668
3.8954
3.8065
3.7924
3.1920
3.1814
3.1503
3.1402
2.9806
2.9724
2.9395
2.9308
2.4150
1H NMR FC-6-70A CDCL3G:/旧 NMR 2014/新建文件夹/9132/fid
NHTs
N
H
Cl
4f
1H NMR (400 MHz, CDCl3)
2.01
6.87
1.02
1.04
1.00
1.05
1.03
1.03
1.08
1.06
1.05
3.01
f1 (ppm)


144.68
142.75
140.35
138.51
132.22
129.88
129.83
129.78
128.04
127.50
126.71
117.41
116.58
113.92
56.99
51.14
31.76
21.47
13C NMR FC-6-70A in DMSO-D6
NHTs
N
H
Cl
4f
13C NMR (100 MHz, DMSO-d6)
f1 (ppm)
f1 (ppm)

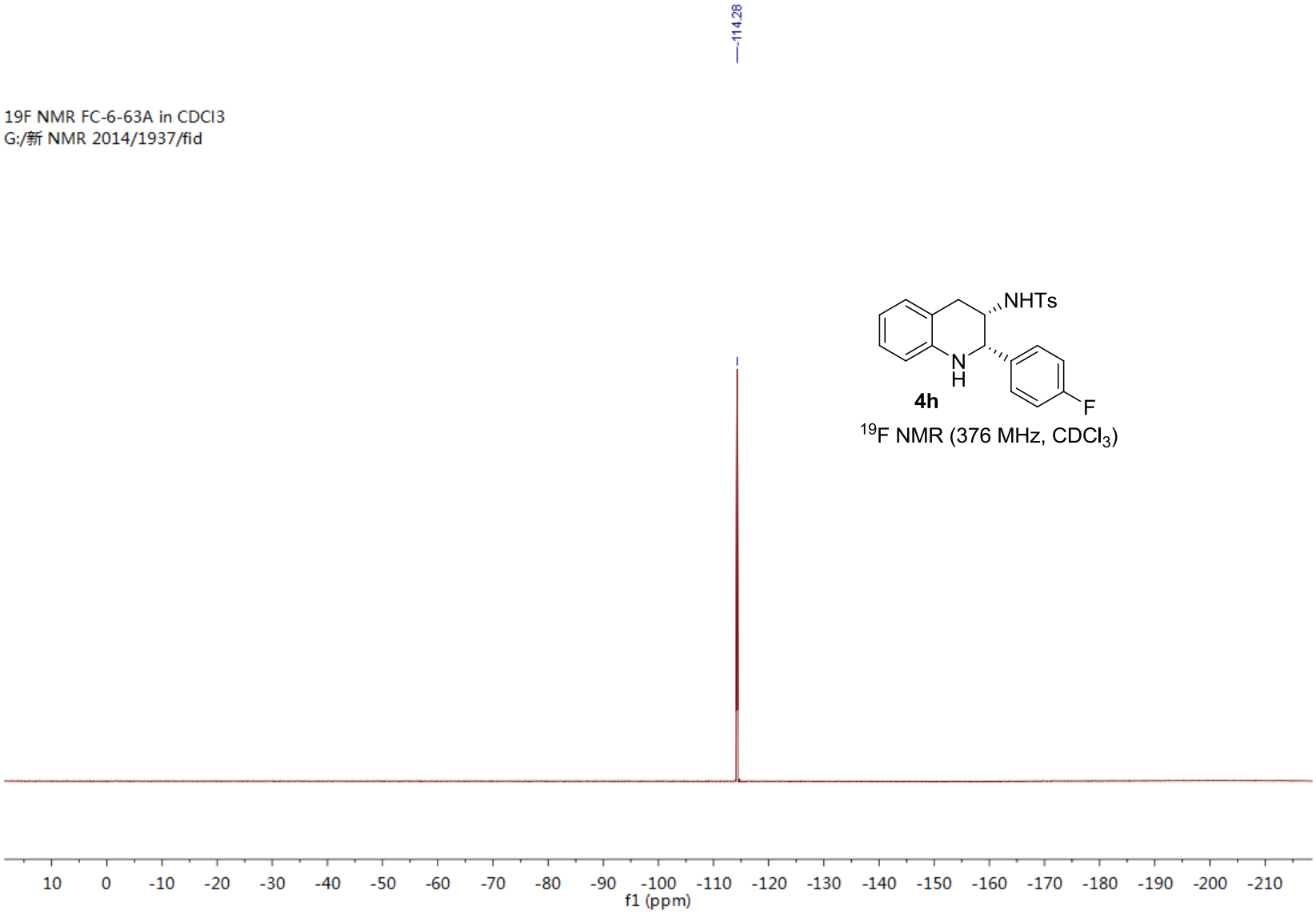

7.3434
7.3227
7.2742
7.2563
7.0932
7.0732
7.0604
7.0396
6.9908
6.9718
6.7747
6.7581
6.7397
6.6180
6.5982
4.8564
4.8341
4.4485
3.8879
3.8120
3.8039
3.7909
3.7824
3.1807
3.1706
3.1394
3.1292
2.9786
2.9699
2.9371
2.9286
2.4259
1H NMR FC-6-70G in CDCl3
//Yzc/g/新 NMR 2014/2126/fid
NHTs
N
H
Br
4g
1H NMR (400 MHz, CDCl3)
1.89
1.95
4.75
0.98
0.99
1.00
0.97
1.00
0.94
1.02
1.04
1.03
2.87
f1 (ppm)


13C NMR FC-6-70G in DMSO-d6
G:/新 NMR 2014/2167/fid
144.66
142.76
140.79
138.50
130.94
130.27
129.84
129.77
127.51
126.70
120.79
117.40
116.56
113.91
57.04
51.06
31.72
21.52
NHTs
N
H
Br
4g
13C NMR (100 MHz, DMSO-d6)
f1 (ppm)


7.3651
7.3446
7.1718
7.1581
7.1505
7.1370
7.0695
7.0490
7.0270
6.9524
6.9337
6.8559
6.8344
6.8129
6.7511
6.7327
6.7142
6.5997
6.5798
4.8521
4.8299
4.4674
3.9247
3.8155
3.8074
3.7948
3.7870
3.1336
3.1234
3.0923
3.0823
2.9037
2.8943
2.8624
2.8531
2.3786
1H NMR FC-6-63A in CDCl3
G:/新 NMR 2014/1936/fid
NHTs
N
H
F
4h
1H NMR (400 MHz, CDCl3)
1.98
2.04
3.02
1.01
2.01
1.01
1.00
0.94
1.01
0.94
1.03
1.02
1.02
3.01
f1 (ppm)


163.68
161.23
143.26
142.93
137.54
130.49
129.37
128.29
128.21
127.52
117.83
115.41
115.19
114.70
57.62
51.66
34.50
21.36
13C NMR FC-6-63A in CDCl3
G:/新 NMR 2014/1938/fid
NHTs
N
H
F
4h
13C NMR (100 MHz, CDCl3)
f1 (ppm)

19F NMR FC-6-63A in CDCl3
G:/新 NMR 2014/1937/fid



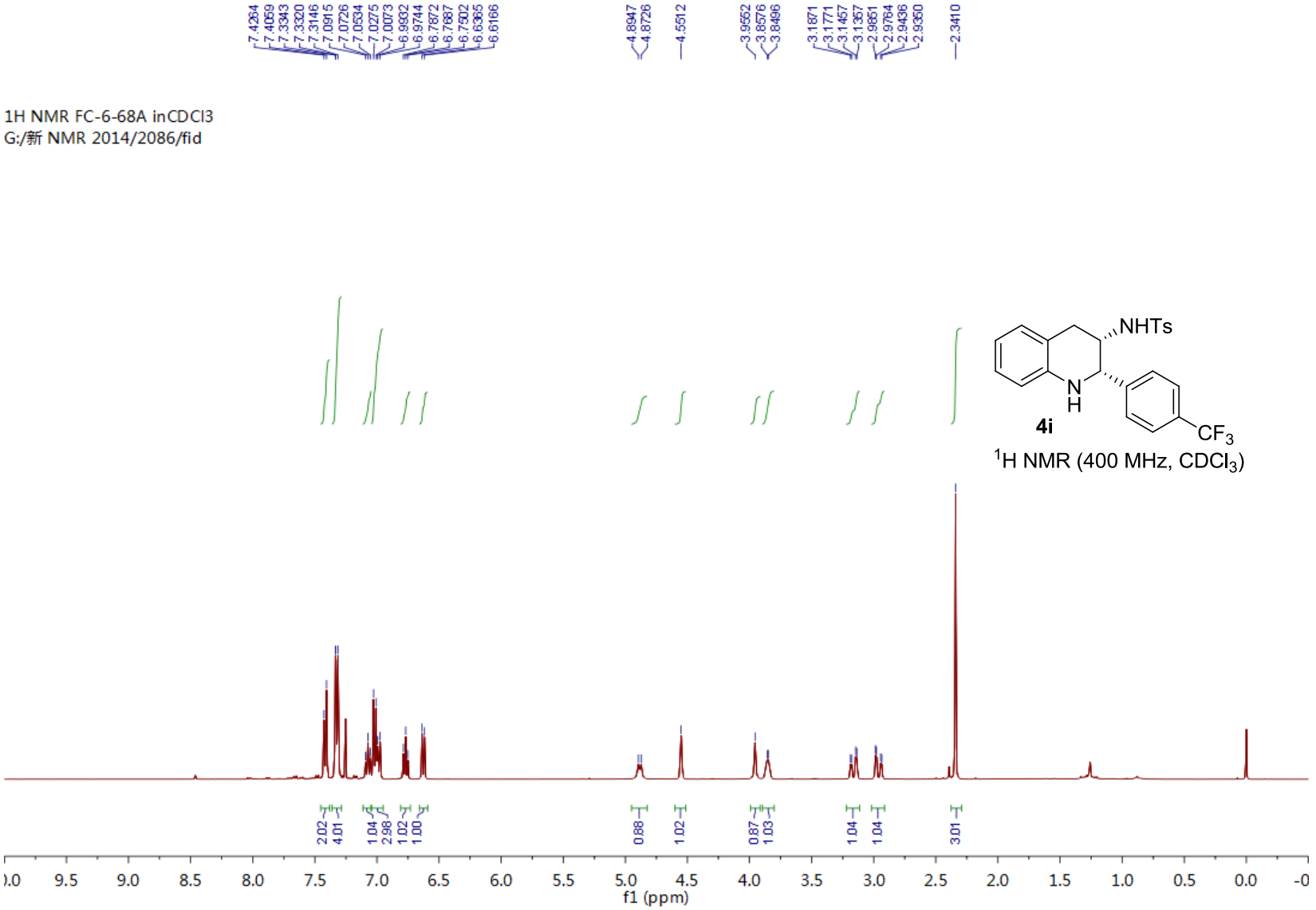


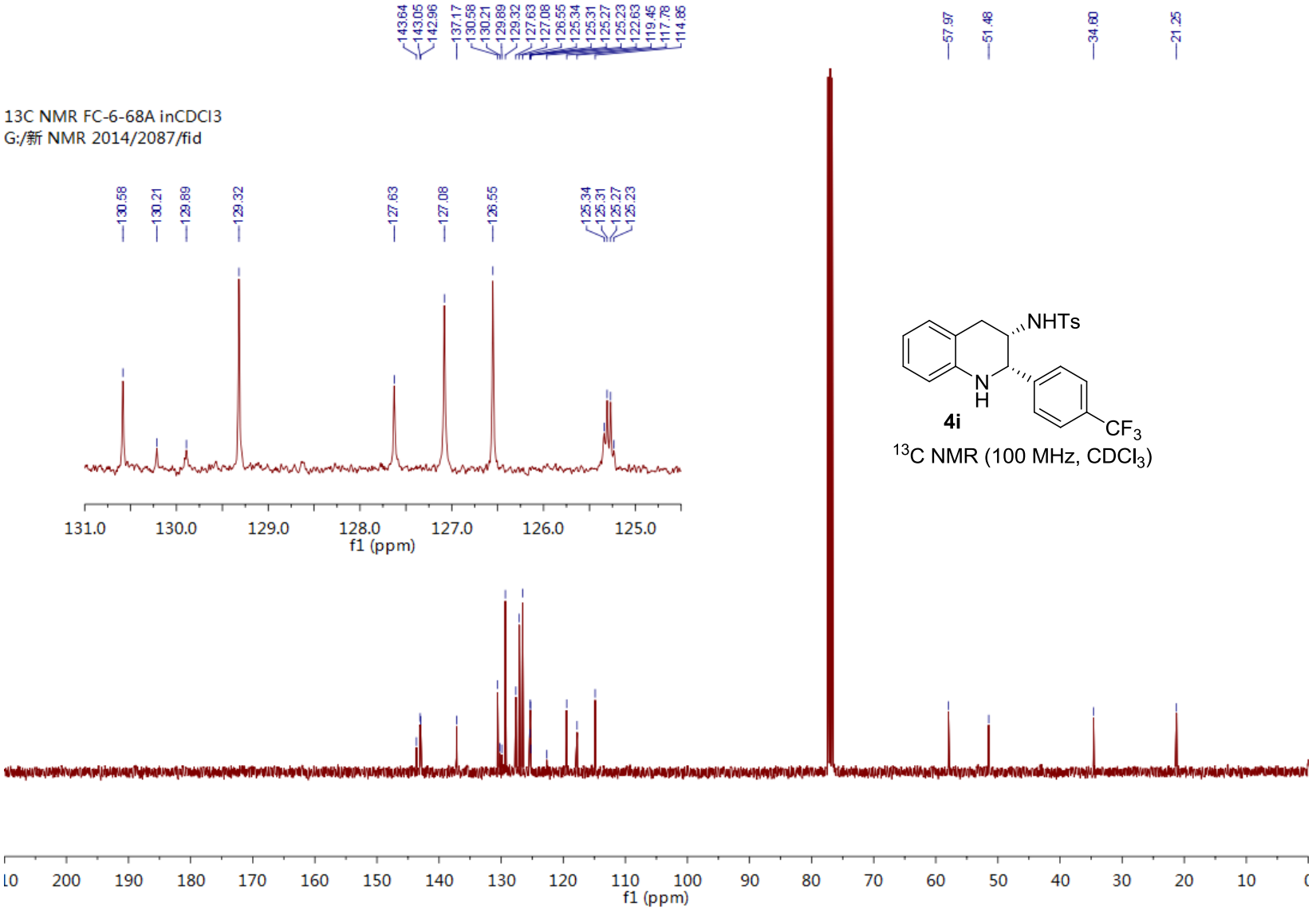


**4h**

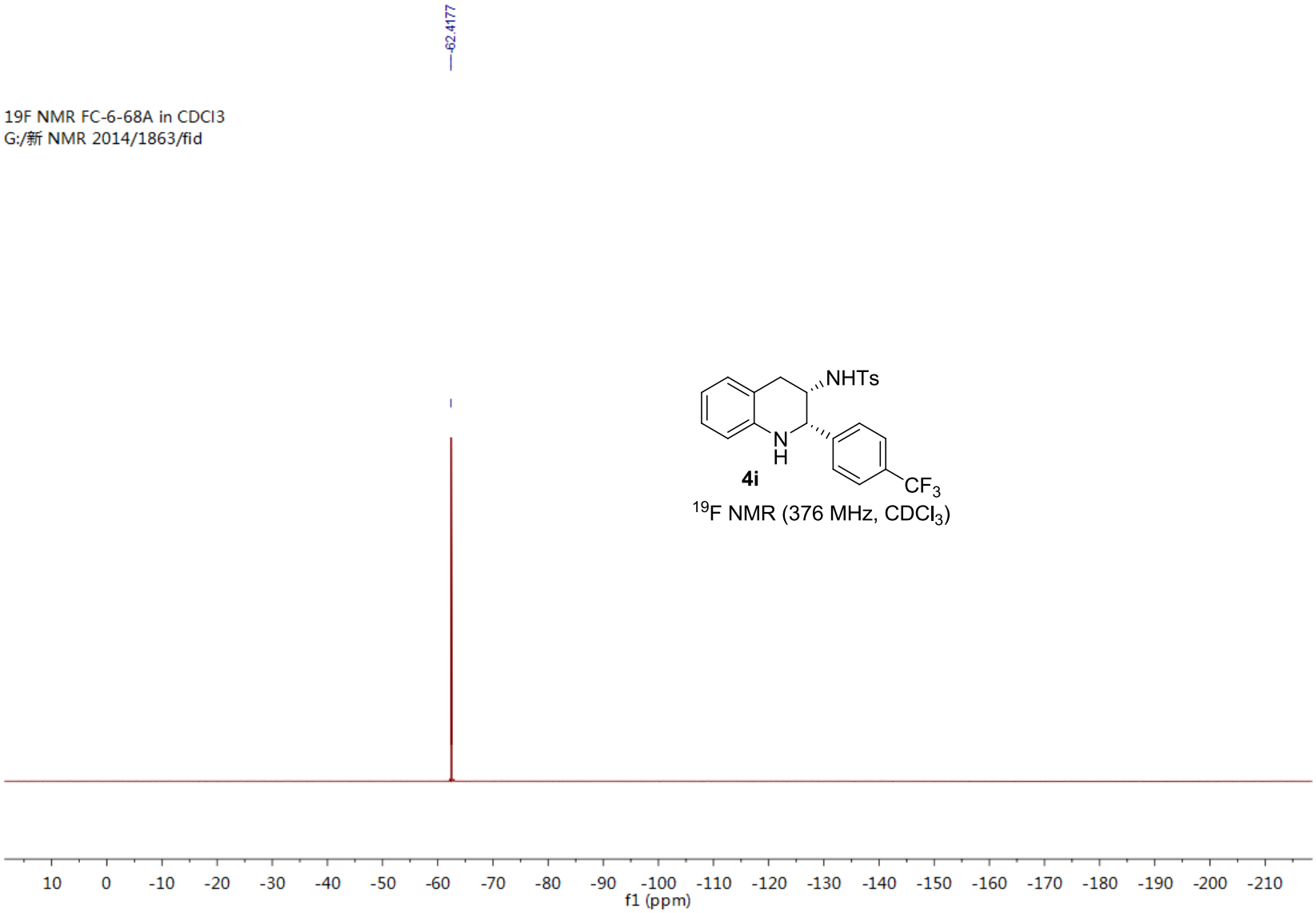
$^{19}F$ NMR (376 MHz, $CDCl_3$)

1H NMR FC-6-68A inCDCl3
G:/新 NMR 2014/2086/fid




13C NMR FC-6-68A inCDCl3
G:/新 NMR 2014/2087/fid
143.64
143.05
142.96
137.17
130.58
130.21
129.89
129.32
127.63
127.08
126.55
125.34
125.31
125.27
125.23
122.63
119.45
117.78
114.85
57.97
51.48
34.60
21.25
f1 (ppm)
NHTs
N
H
CF3
4i
13C NMR (100 MHz, CDCl3)

19F NMR FC-6-68A in CDCl3
G:/新 NMR 2014/1863/fid



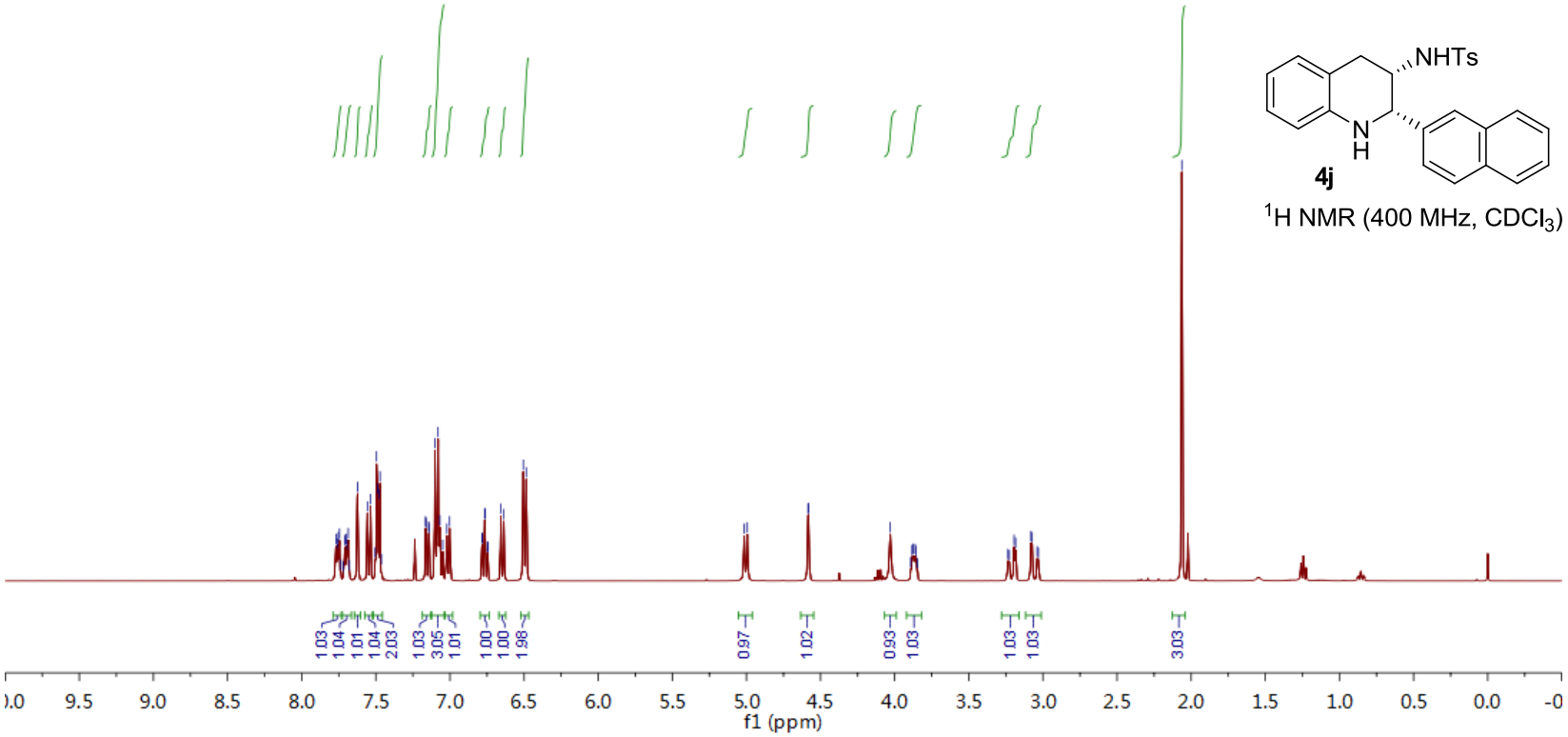




**4i**

$^{19}$F NMR (376 MHz, $CDCl_3$)


1H NMR FC-6-70E in CDCl3
G:/新 NMR 2014/1869/fid

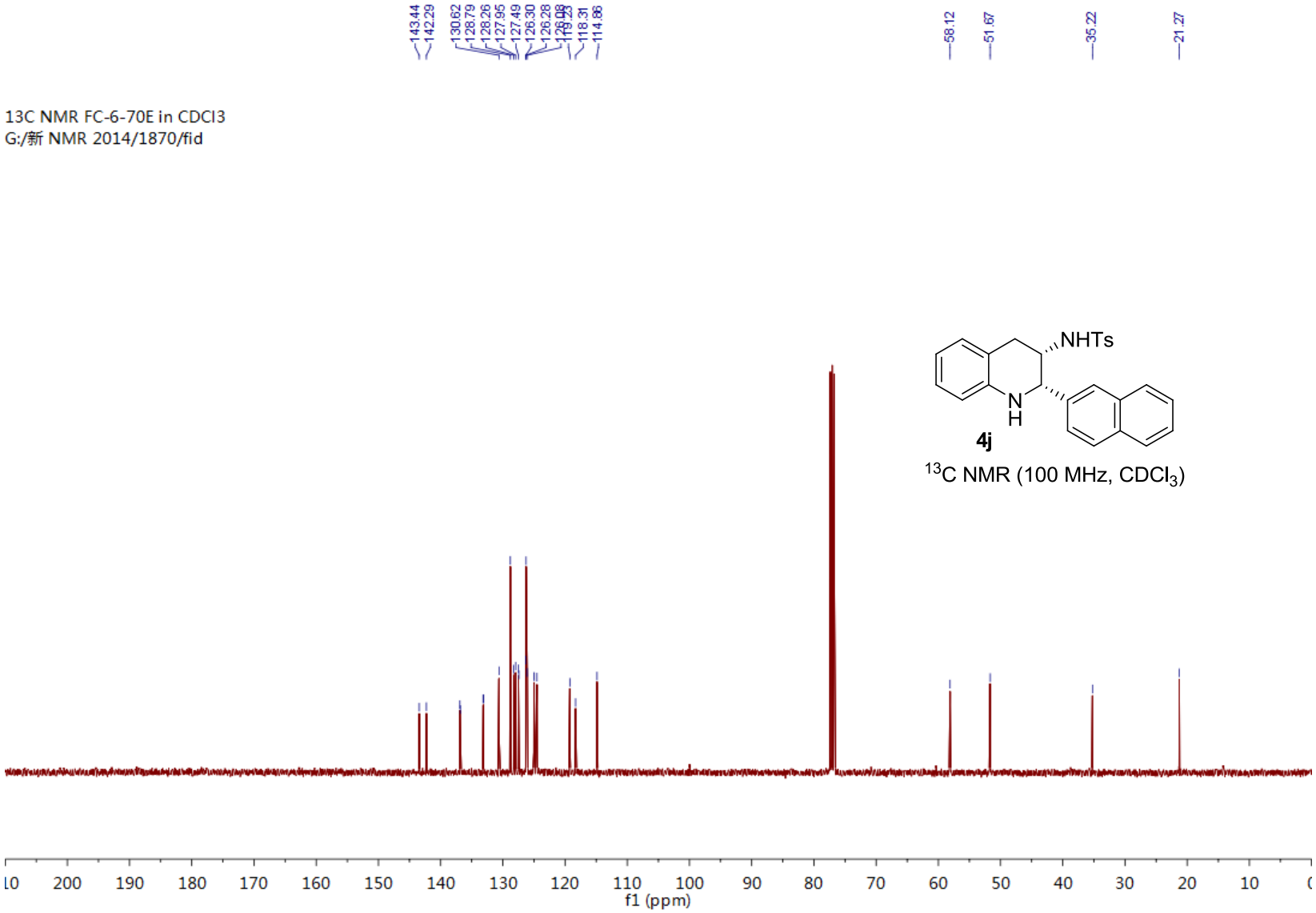


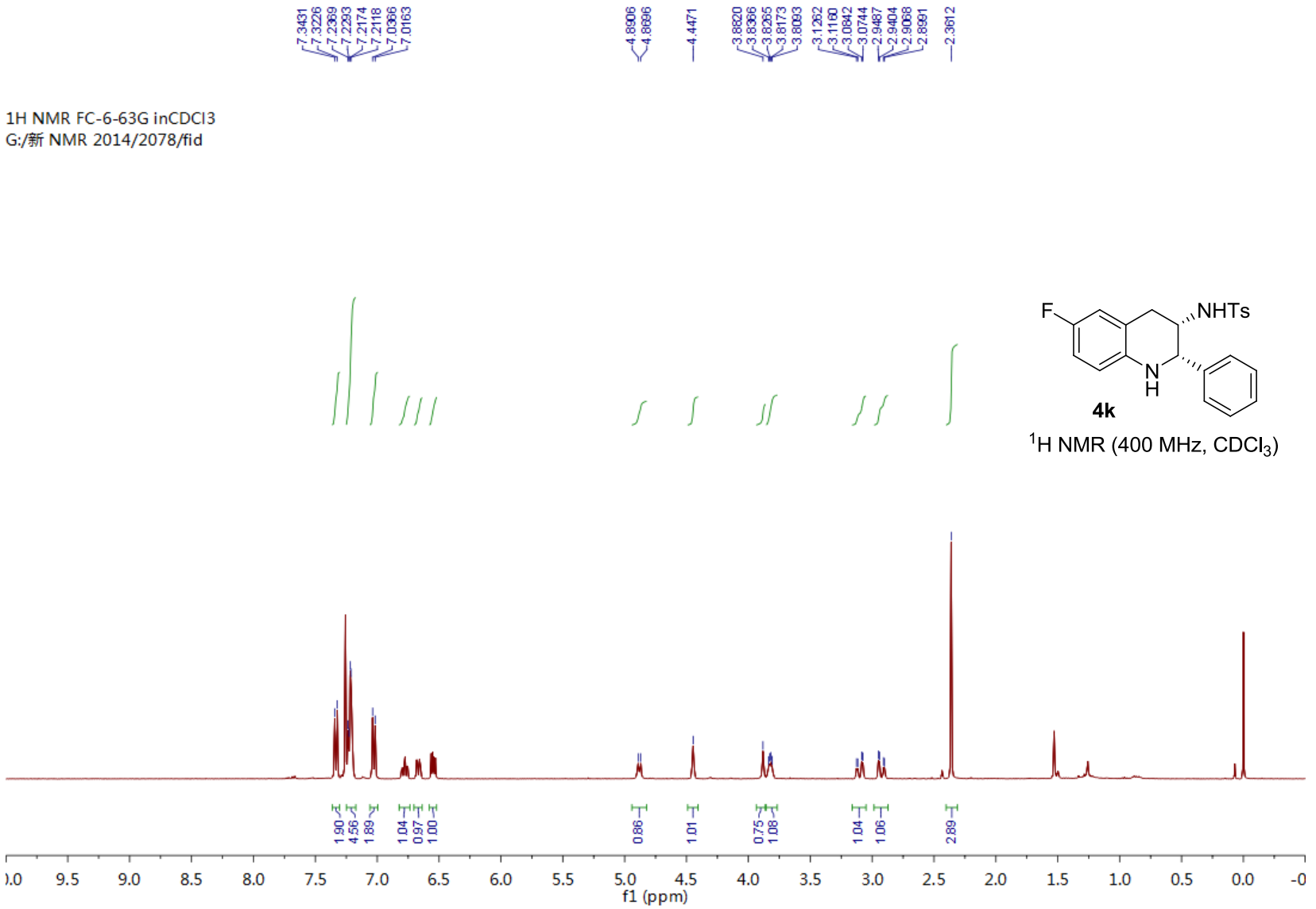


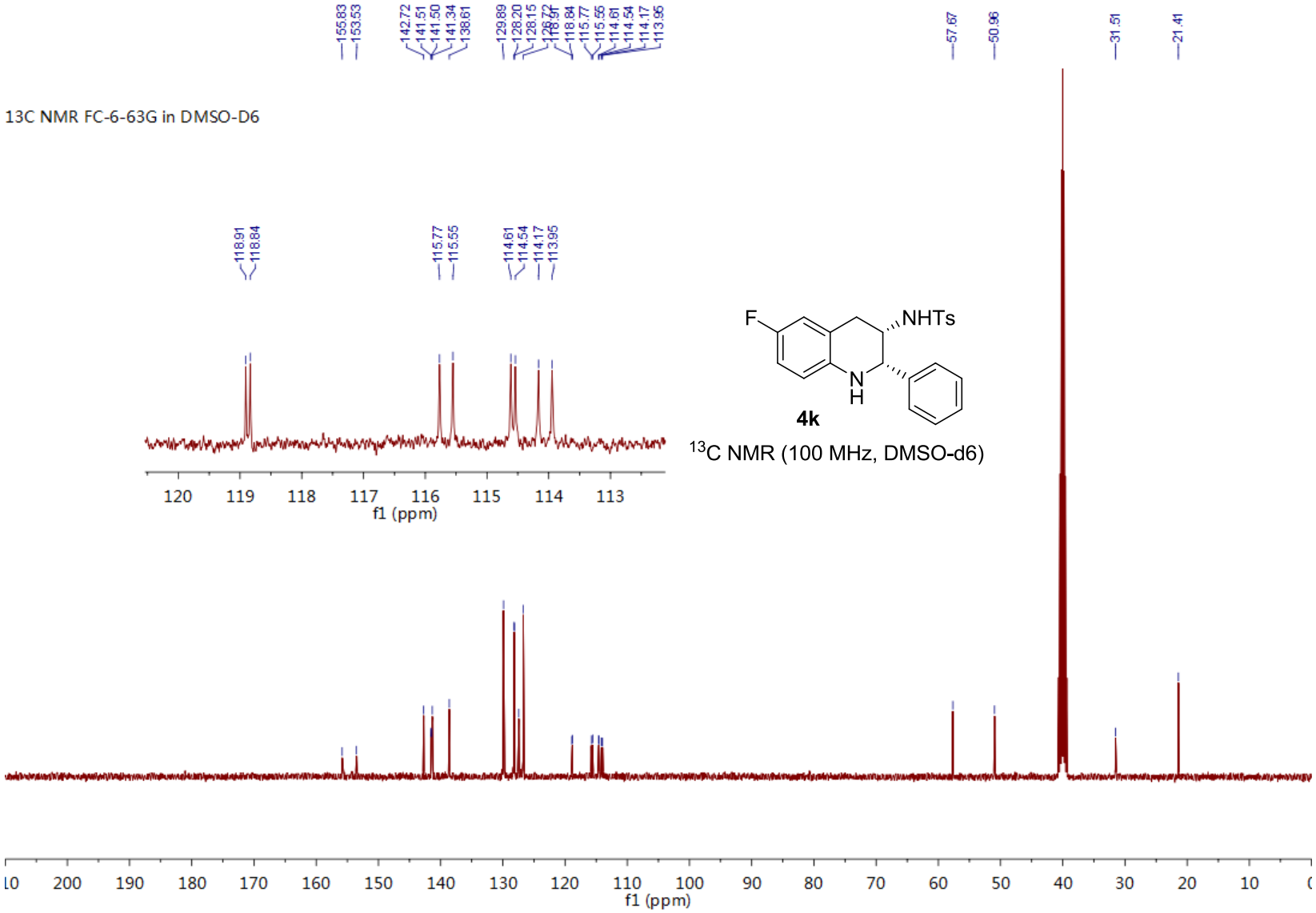


**4j**

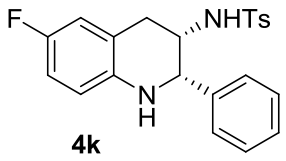
$^1$H NMR (400 MHz, $CDCl_3$)


143.44
142.29
130.62
128.79
128.26
127.95
127.49
126.30
126.28
118.31
114.86
58.12
51.67
35.22
21.27
13C NMR FC-6-70E in CDCl3
G:/新 NMR 2014/1870/fid
NHTs
N
H
4j
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.3431
7.3226
7.2369
7.2293
7.2174
7.2118
7.0366
7.0163
4.8906
4.8696
4.4471
3.8820
3.8366
3.8265
3.8173
3.8093
3.1262
3.1160
3.0842
3.0744
2.9487
2.9404
2.9068
2.8891
2.3612
1H NMR FC-6-63G inCDCl3
G:/新 NMR 2014/2078/fid
F
NHTs
N
H
4k
1H NMR (400 MHz, CDCl3)
1.90
4.56
1.89
1.04
0.97
1.00
0.86
1.01
0.75
1.08
1.04
1.06
2.89
f1 (ppm)

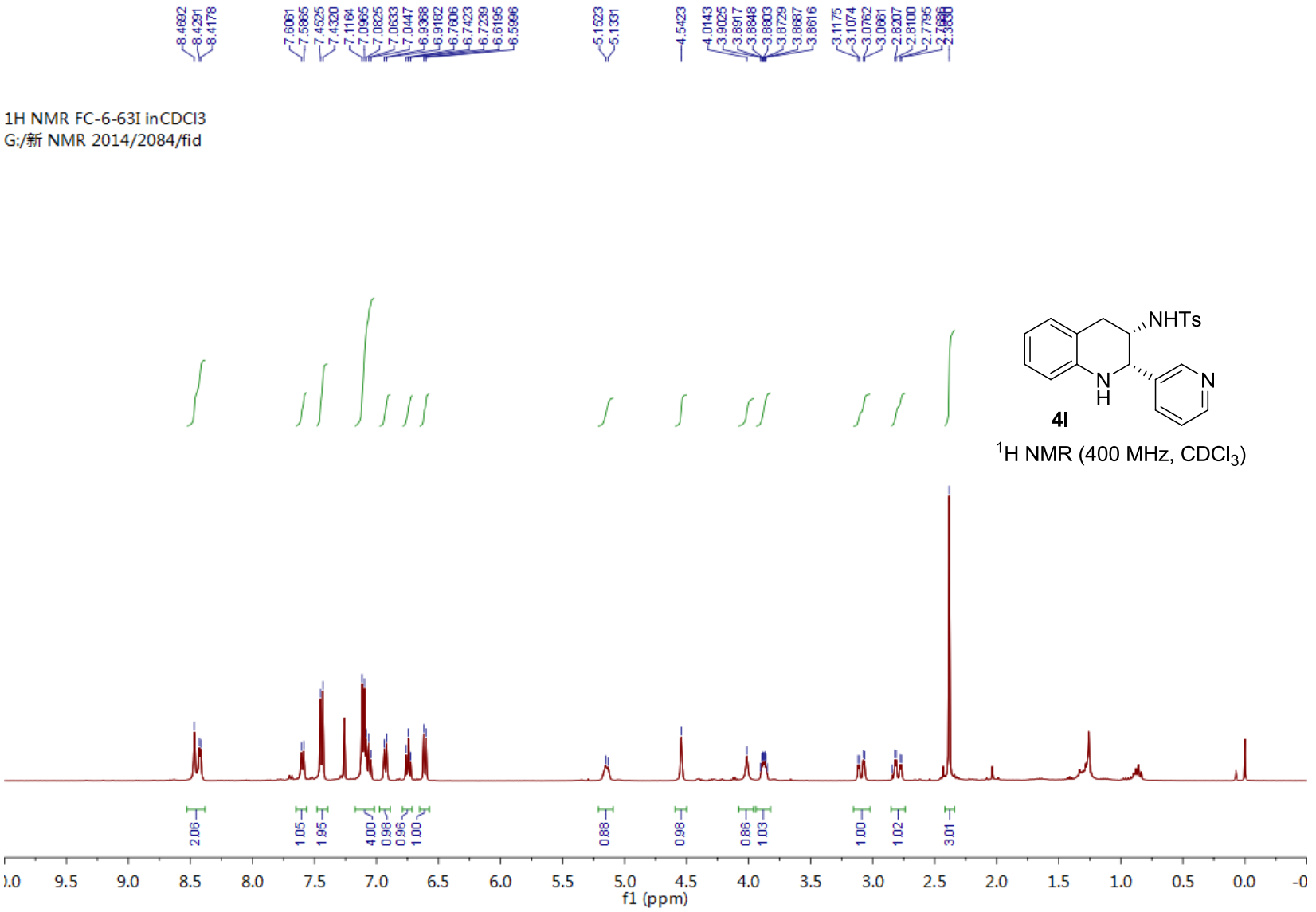

13C NMR FC-6-63G in DMSO-D6
155.83
153.53
142.72
141.51
141.50
141.34
138.61
129.89
128.20
128.15
118.84
115.77
115.55
114.61
114.54
114.17
113.95
57.67
50.96
31.51
21.41
118.91
118.84
115.77
115.55
114.61
114.54
114.17
113.95
120
119
118
117
116
115
114
113
f1 (ppm)
F
NHTs
N
H
4k
13C NMR (100 MHz, DMSO-d6)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

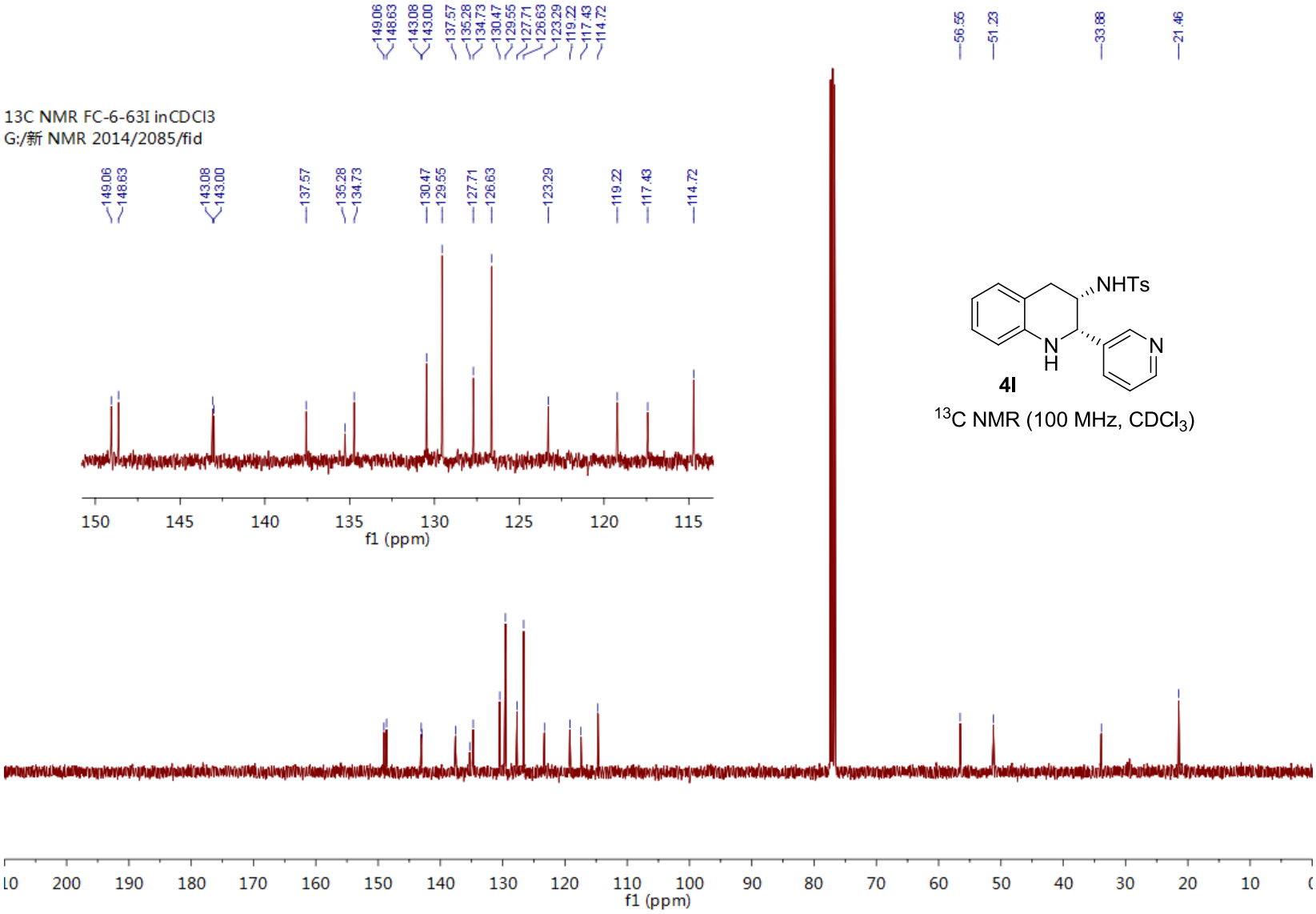
19F NMR FC-6-63G in DMSO-D6
G:/新 NMR 2014/2014/fid



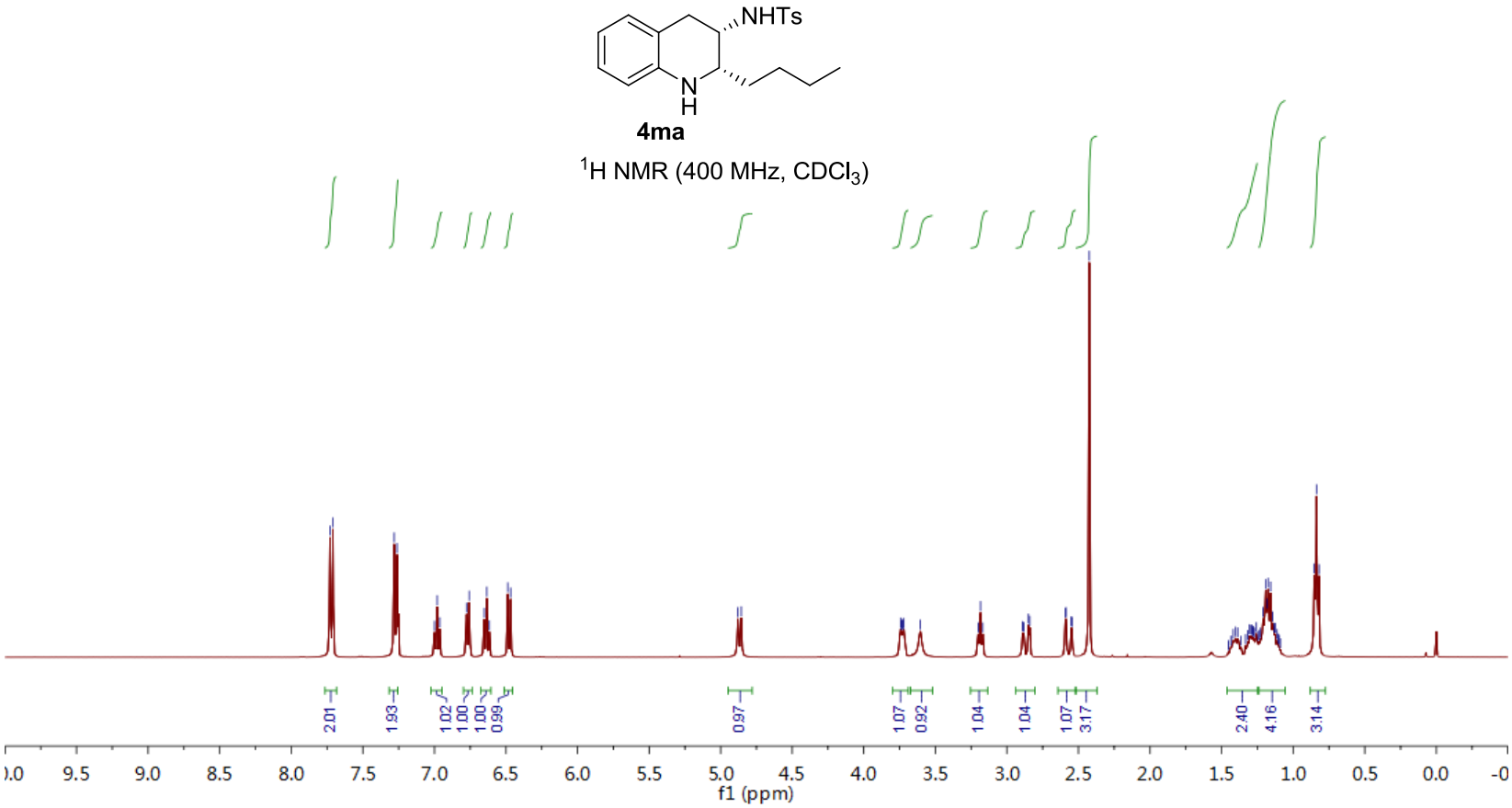

**4k**

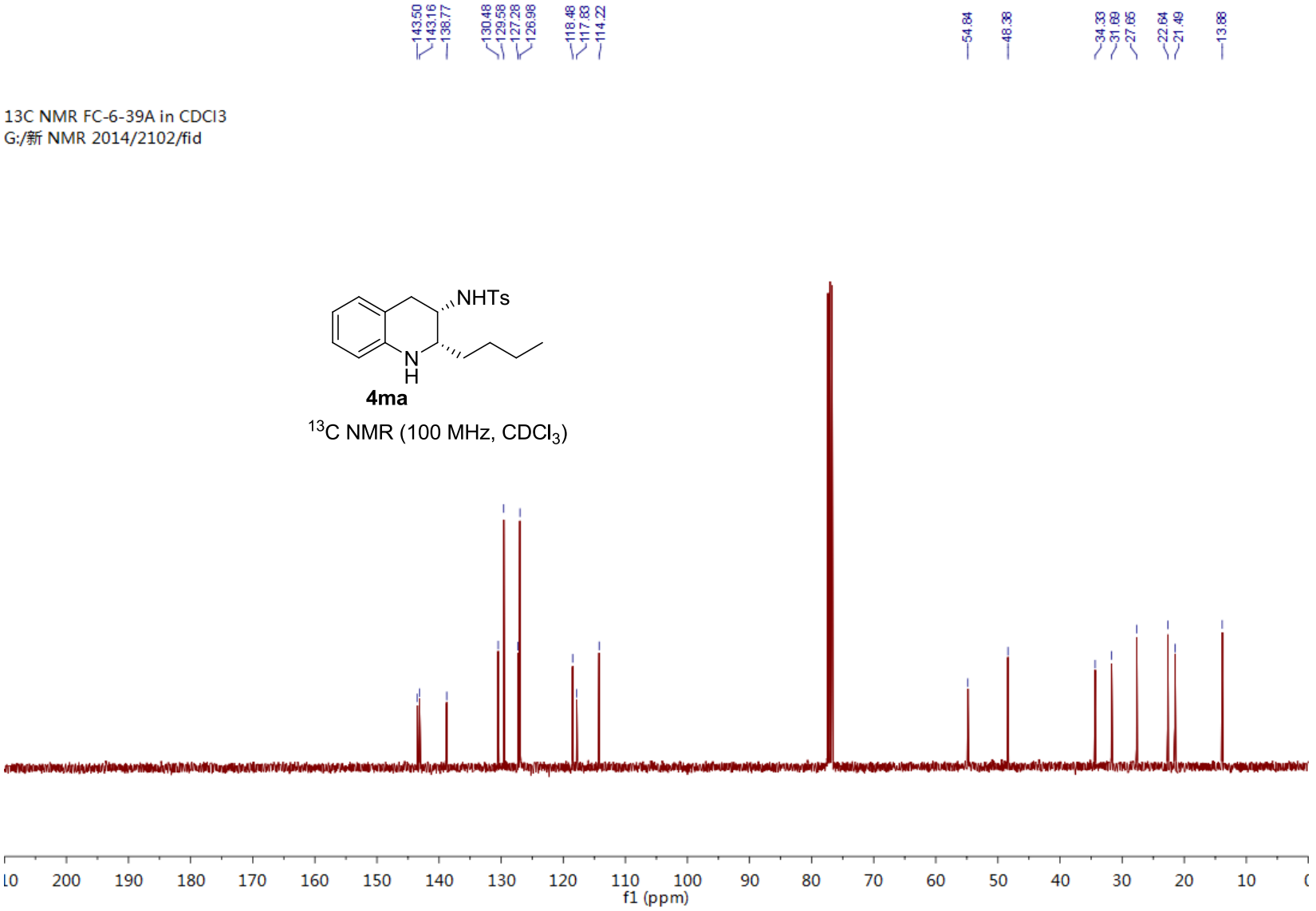
$^{19}$F NMR (376 MHz, DMSO-d6)


8.4692
8.4291
8.4178
7.6061
7.5985
7.4525
7.4320
7.1164
7.0965
7.0825
7.0633
7.0447
6.9368
6.9182
6.7806
6.7423
6.7239
6.6195
6.5996
5.1523
5.1331
4.5423
4.0143
3.9025
3.8917
3.8848
3.8803
3.8729
3.8687
3.8616
3.1175
3.1074
3.0762
3.0661
2.8207
2.8100
2.7795
1H NMR FC-6-63I inCDCl3
G:/新 NMR 2014/2084/fid
NHTs
N
H
N
4l
1H NMR (400 MHz, CDCl3)
2.06
1.05
1.95
4.00
0.98
0.96
1.00
0.88
0.98
0.86
1.03
1.00
1.02
3.01
f1 (ppm)

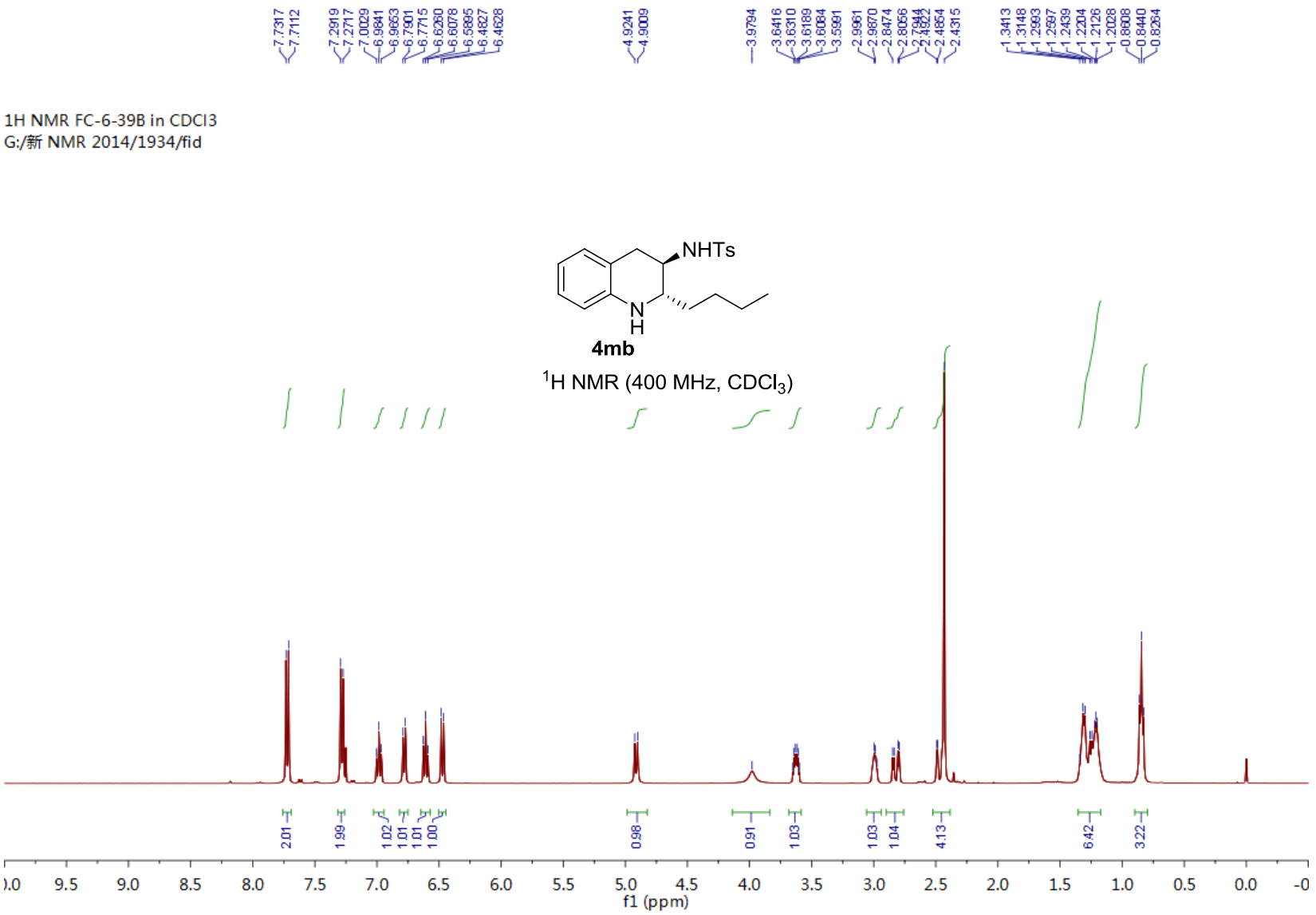

13C NMR FC-6-63I inCDCl3
G:/新 NMR 2014/2085/fid
149.06
148.63
143.08
143.00
137.57
135.28
134.73
130.47
129.55
127.71
126.63
123.29
119.22
117.43
114.72
56.55
51.23
33.88
21.46
f1 (ppm)
NHTs
N
H
N
4l
13C NMR (100 MHz, CDCl3)

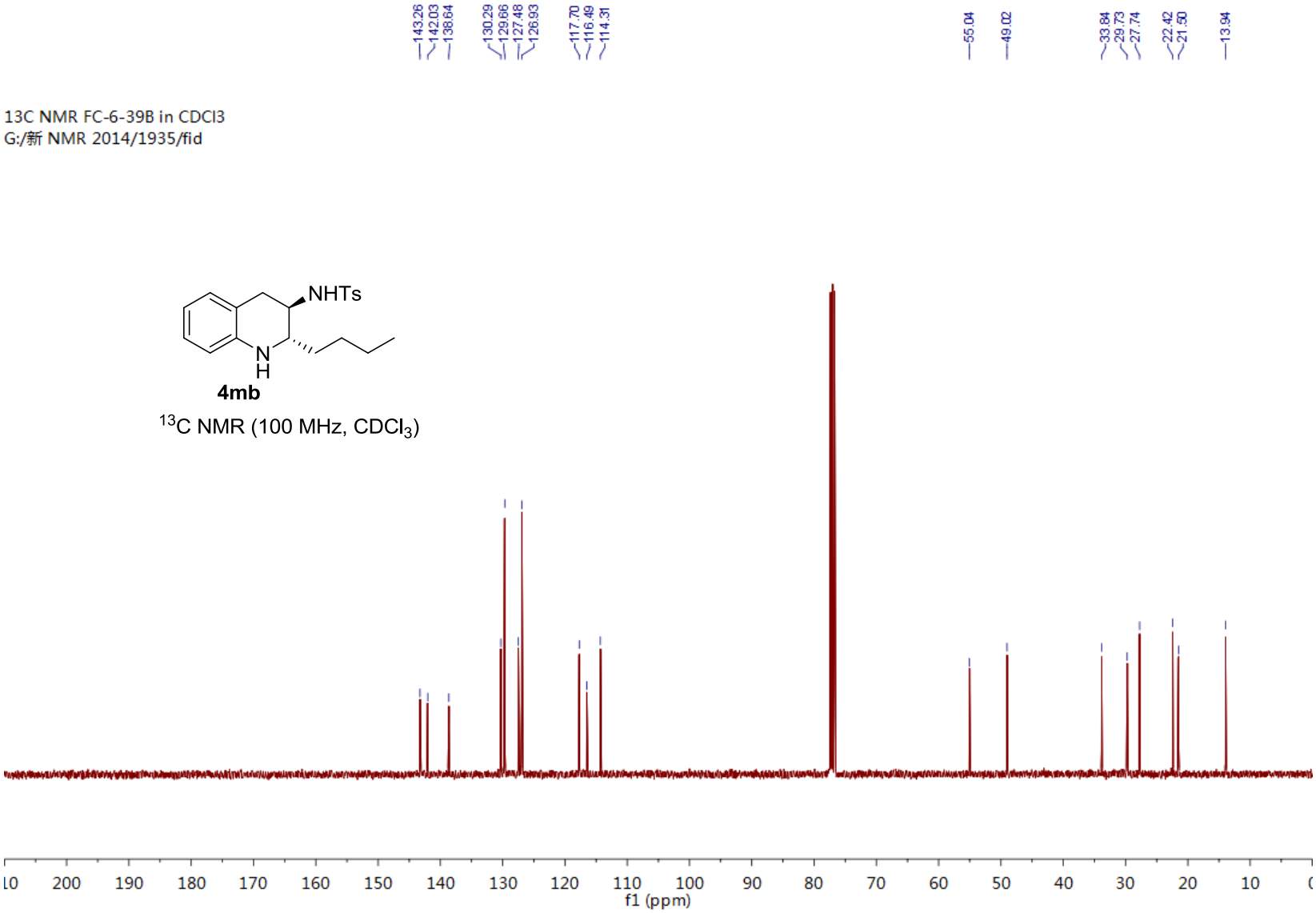
1H NMR FC-6-39A in CDCl3
G:/新 NMR 2014/2101/fid

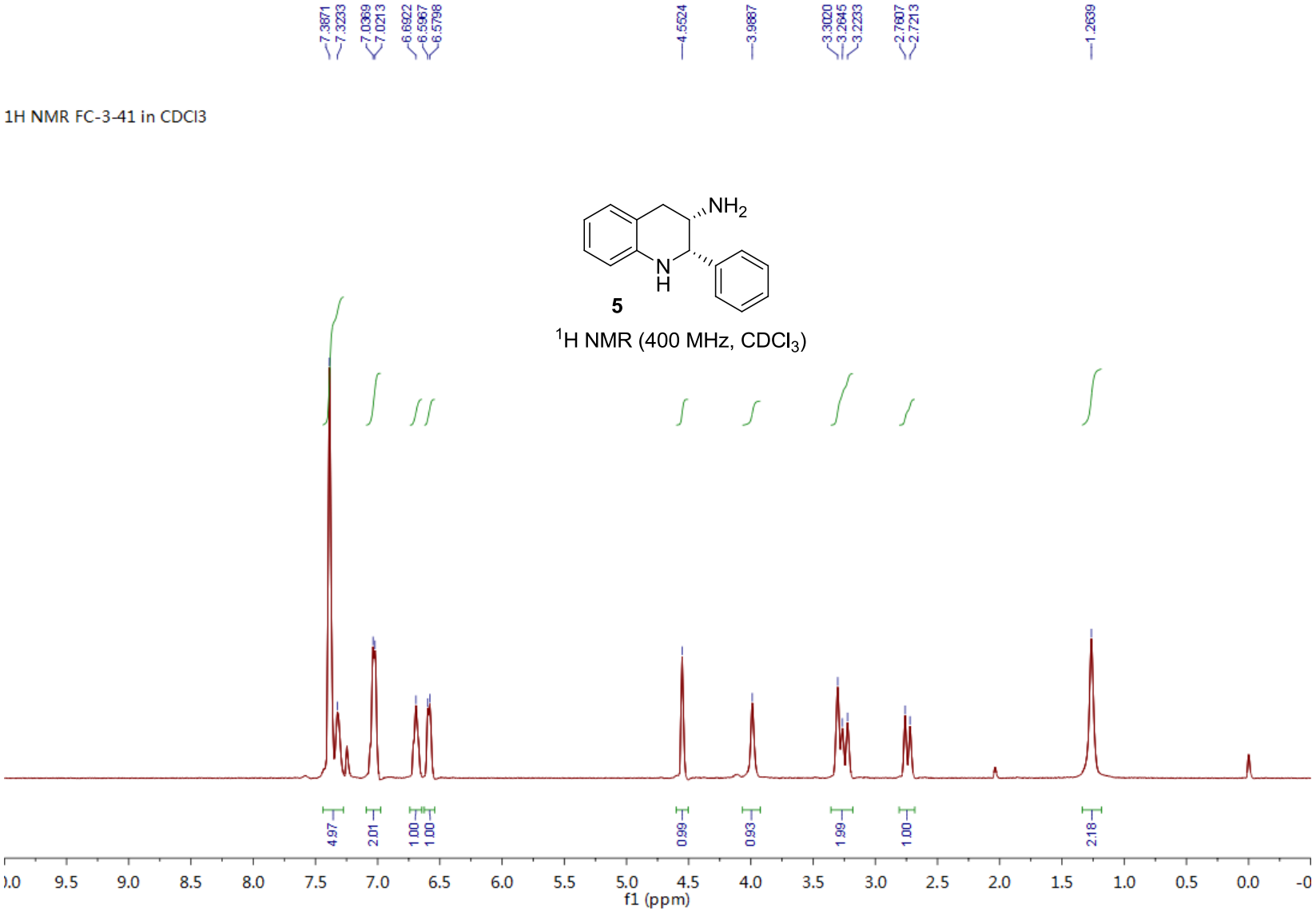



143.50
143.16
138.77
130.48
129.58
127.28
126.98
118.48
117.83
114.22
54.84
48.38
34.33
31.69
27.65
22.64
21.49
13.88
13C NMR FC-6-39A in CDCl3
G:/新 NMR 2014/2102/fid
NHTs
N
H
4ma
13C NMR (100 MHz, CDCl3)
f1 (ppm)

1H NMR FC-6-39B in CDCl3
G:/新 NMR 2014/1934/fid

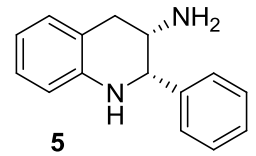



143.26
142.03
138.64
130.29
129.66
127.48
126.93
117.70
116.49
114.31
55.04
49.02
33.84
29.73
27.74
22.42
21.90
13.94
13C NMR FC-6-39B in CDCl3
G:/新 NMR 2014/1935/fid
NHTs
N
H
4mb
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.3871
7.3233
7.0369
7.0213
6.6922
6.5967
6.5798
4.5524
3.9887
3.3020
3.2645
3.2233
2.7607
2.7213
1.2639
1H NMR FC-3-41 in CDCl3
NH2
N
H
5
1H NMR (400 MHz, CDCl3)
4.97
2.01
1.00
1.00
0.99
0.93
1.99
1.00
2.18
f1 (ppm)

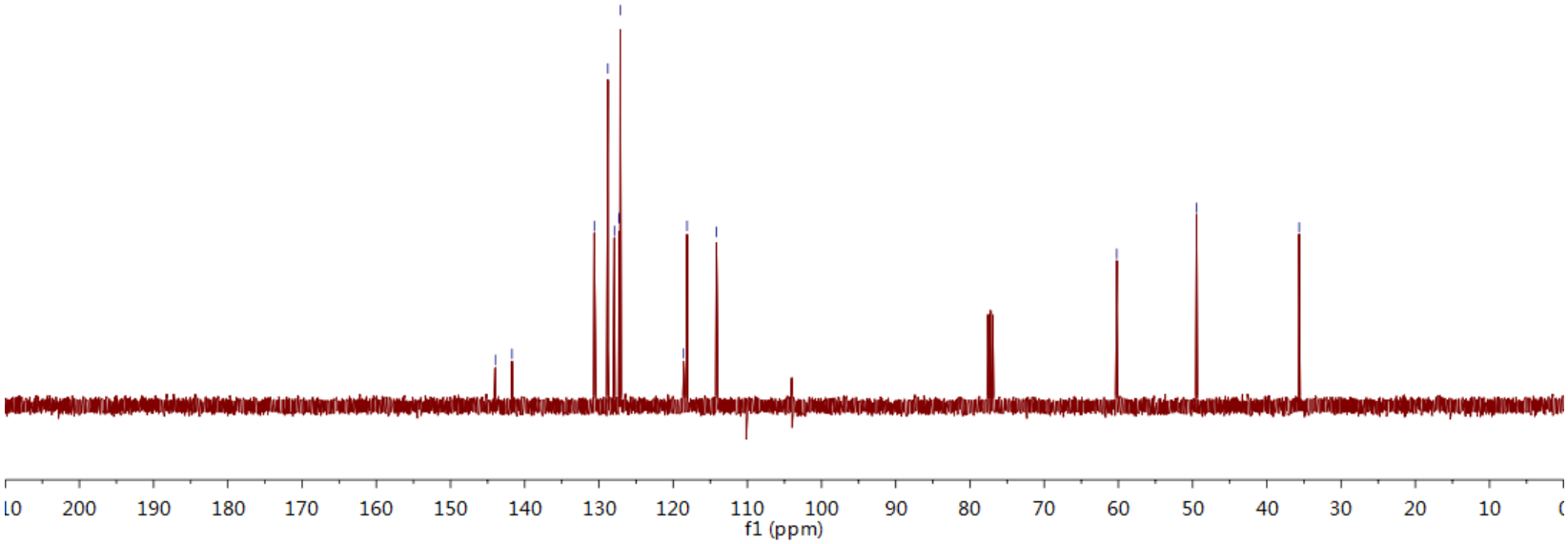
143.95
141.71
130.62
128.79
127.92
127.30
127.13
118.58
118.14
114.17
60.22
49.48
35.65

13C NMR FC-3-41 in CDCl3F:/蔡先锋/实验测试数据/NMR/FC-3/41 1767/fid



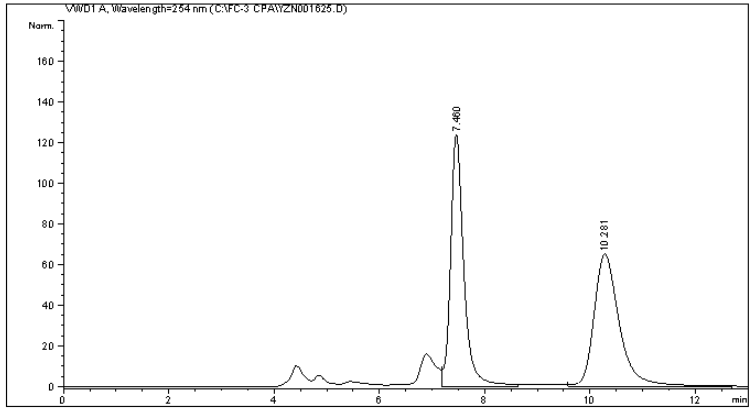

**5**

$^{13}C$ NMR (100 MHz, $CDCl_3$)

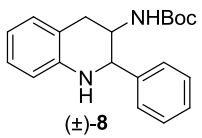


Data File C:\FC-3 CPA\YZN001625.D
Sample Name: FC-2-53B

```
==========================================================================
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 5/10/2012 10:05:16 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 5/10/2012 9:54:41 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 3:07:38 PM by Z
                  (modified after loading)
Sample Info     : OJ-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   7.460 VV    0.2624 2169.06055  123.94372  49.9235
   2  10.281 BB    0.5062 2175.70752   65.13602  50.0765

Totals :                  4344.76807  189.07974


==========================================================================
                        *** End of Report ***
```

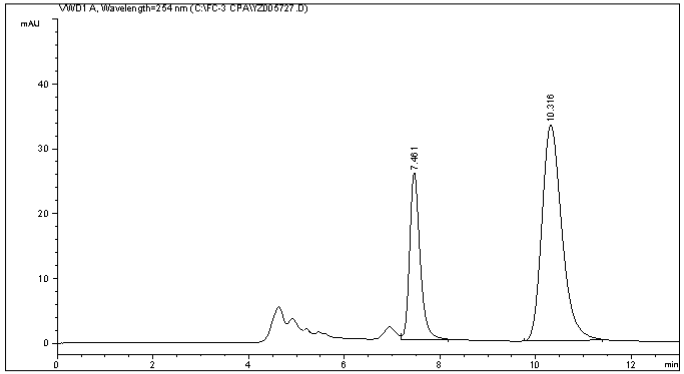



(±)-**8**

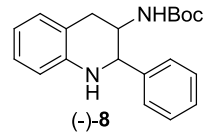


Data File C:\FC-3 CPA\YZ005727.D
Sample Name: FC-6-67C

```
==========================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 3/30/2014 12:34:12 PM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC1.M
Last changed    : 3/30/2014 12:22:43 PM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/29/2014 10:10:40 PM by Z
                  (modified after loading)
Sample Info     : OJ-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```



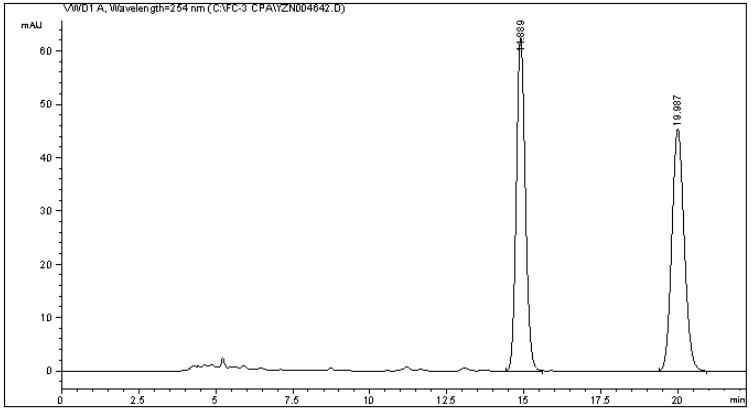

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   7.461 VB    0.2309  390.37231   25.73003  28.8163
   2  10.316 BB    0.4431  964.32111   33.25895  71.1837

Totals :                  1354.69342   58.98897


==========================================================================
                        *** End of Report ***
```



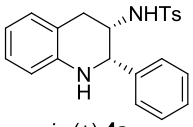

(-)-**8**

Data File C:\FC-3 CPA\YZN004642.D
Sample Name: FC-2-51A

```
==========================================================================
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 3/18/2014 11:05:24 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 10:58:34 AM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 1:34:59 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30,  0.7 mL/min, 30 oC, 254 nm
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|-------|
   1  14.889 BB    0.3137 1270.76526   62.68732  49.9832
   2  19.987 BB    0.4328 1271.62073   45.43267  50.0168

Totals :                  2542.38599  108.12000

==========================================================================
                        *** End of Report ***
```

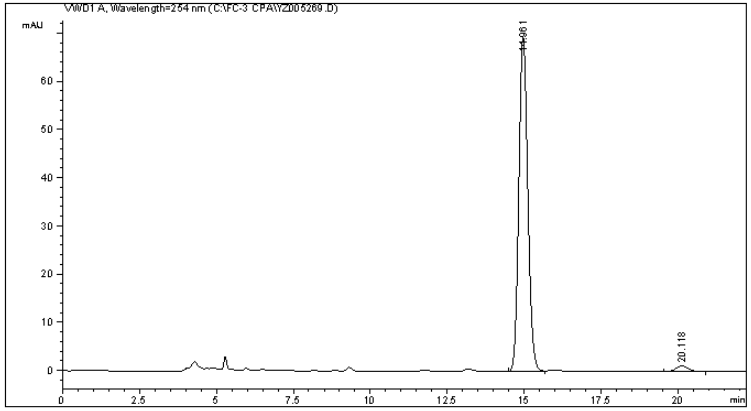



*cis*-(±)-**4a**

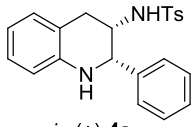


Data File C:\FC-3 CPA\YZ005269.D
Sample Name: FC-6-23D

```
==========================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 11/15/2013 1:46:51 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEMOCAL2.M
Last changed    : 11/15/2013 12:51:59 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 1:53:26 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.70 mL/min, 30 oC, 254nm
```



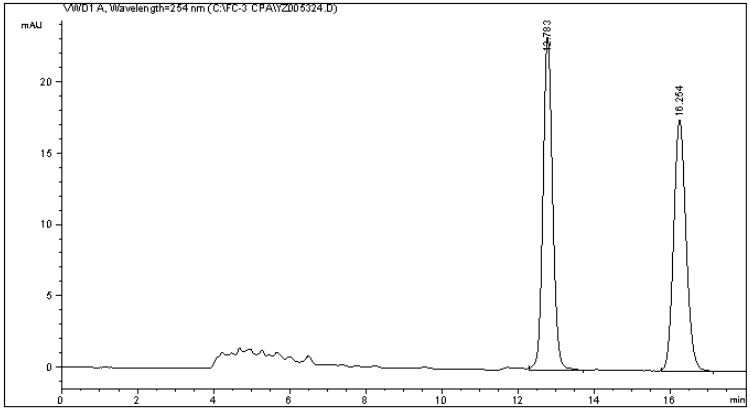

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|-------|
   1  14.961 BV    0.3148 1405.02979   69.39191  97.6604
   2  20.118 BB    0.4442   33.66003    1.19818   2.3396

Totals :                  1438.68981   70.59009

==========================================================================
                        *** End of Report ***
```



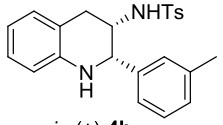

*cis*-(+)-**4a**

Data File C:\FC-3 CPA\YZ005324.D
Sample Name: FC-6-33D

```
==========================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 11/25/2013 11:27:43 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEMOCAL2.M
Last changed    : 11/25/2013 10:46:57 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 1:57:05 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]     %
----|-------|----|-------|---------|---------|-------|
   1  12.783 BB    0.2723  411.56372   23.38140  50.8108
   2  16.254 BB    0.3483  398.42828   17.61535  49.1892

Totals :                   809.99200   40.99675

==========================================================================
                        *** End of Report ***
```

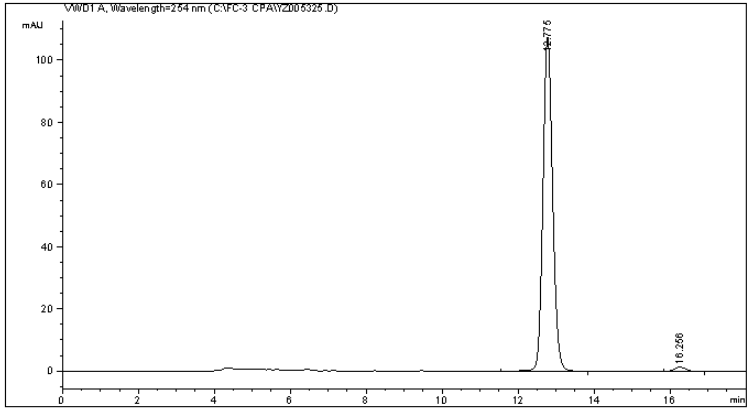



*cis*-(±)-**4b**

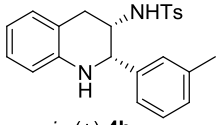


Data File C:\FC-3 CPA\YZ005325.D
Sample Name: FC-6-33C

```
==========================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 11/25/2013 11:52:03 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEMOCAL2.M
Last changed    : 11/25/2013 10:46:57 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 1:57:05 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```



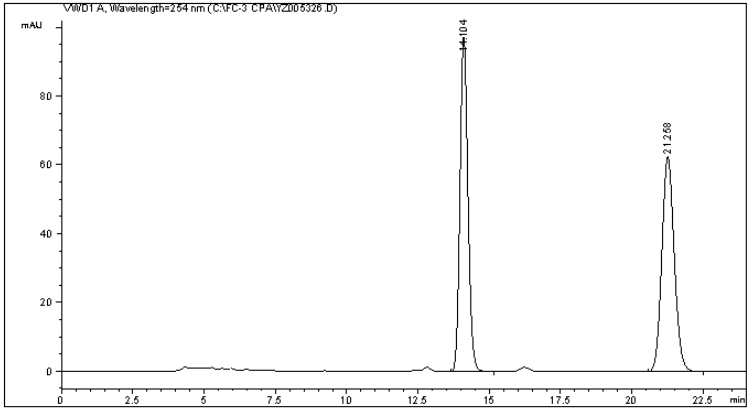

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]     %
----|-------|----|-------|---------|---------|-------|
   1  12.775 BB    0.2749 1918.63892  107.64784  98.2779
   2  16.256 BB    0.3522   33.61895    1.48077   1.7221

Totals :                  1952.25787  109.12861

==========================================================================
                        *** End of Report ***
```




*cis*-(+)-**4b**

Data File C:\FC-3 CPA\YZ005326.D
Sample Name: FC-6-33F

```
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 11/25/2013 12:11:46 PM
Acq. Method     : C:\HPCHEM\1\METHODS\DEMOCAL2.M
Last changed    : 11/25/2013 10:46:57 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 2:02:19 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```

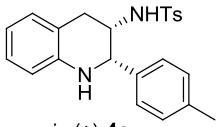



Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 14.104 | BB | 0.2991 | 1887.34253 | 97.30272 | 49.9685 |
| 2 | 21.258 | BB | 0.4694 | 1889.72144 | 62.46243 | 50.0315 |
| Totals : | | | | 3777.06396 | 159.76515 | |



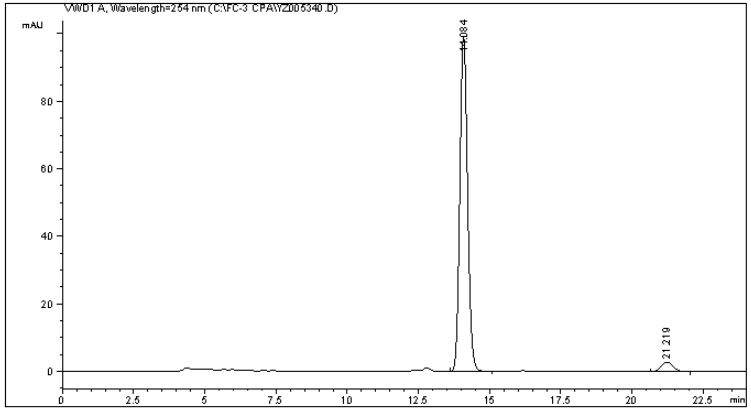

*cis*-(±)-**4c**

*** End of Report ***



Data File C:\FC-3 CPA\YZ005340.D
Sample Name: FC-6-33E

```
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 11/26/2013 11:26:38 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEMOCAL2.M
Last changed    : 11/26/2013 10:15:46 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 2:02:19 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.70 mL/min, 30 oC, 254 nm
```

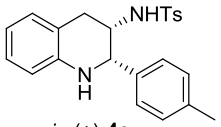



Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 14.084 | BB | 0.2934 | 1873.15735 | 99.05981 | 95.6111 |
| 2 | 21.219 | BB | 0.4658 | 85.98560 | 2.87138 | 4.3889 |
| Totals : | | | | 1959.14294 | 101.93118 | |

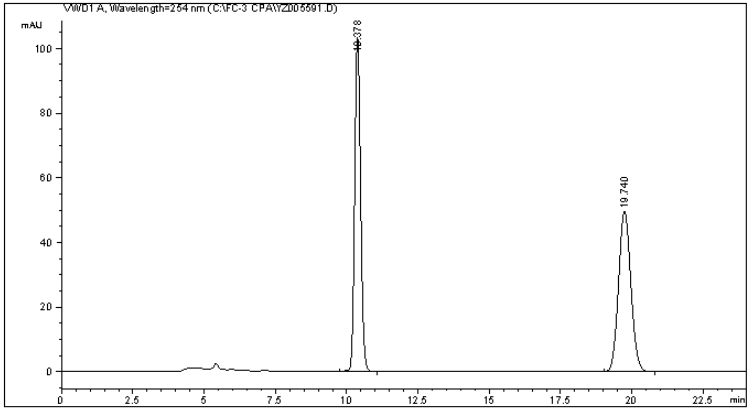



*cis*-(+)-**4c**

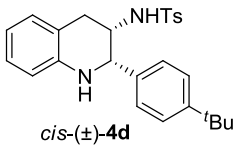
*** End of Report ***

Data File C:\FC-3 CPA\YZ005591.D
Sample Name: FC-6-63D

```
==========================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 1/22/2014 7:45:32 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC1.M
Last changed    : 1/22/2014 7:44:56 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 2:06:37 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]     %
----|-------|----|-------|---------|---------|-------|
   1  10.378 VB    0.2237 1492.69055  103.45294  50.0228
   2  19.740 BB    0.4669 1491.33228   49.65612  49.9772

Totals :                  2984.02283  153.10906

==========================================================================
                        *** End of Report ***
```

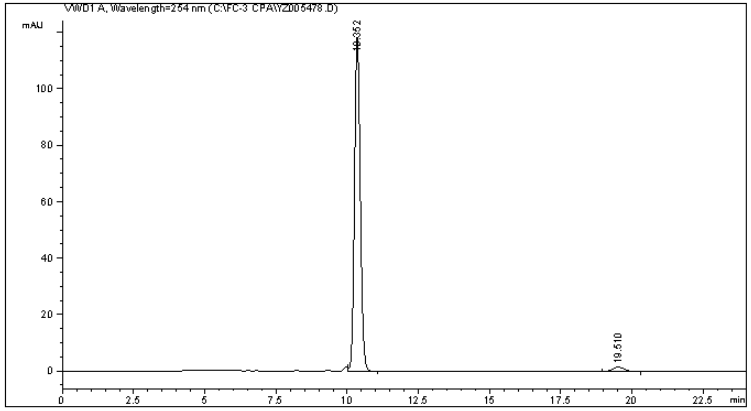



*cis*-(±)-**4d**

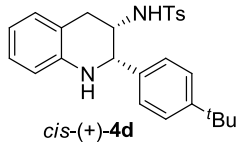


Data File C:\FC-3 CPA\YZ005478.D
Sample Name: FC-6-63C

```
==========================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 1/5/2014 1:26:50 PM
Acq. Method     : C:\HPCHEM\1\METHODS\DEMOCAL2.M
Last changed    : 1/5/2014 1:25:13 PM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 2:06:37 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```



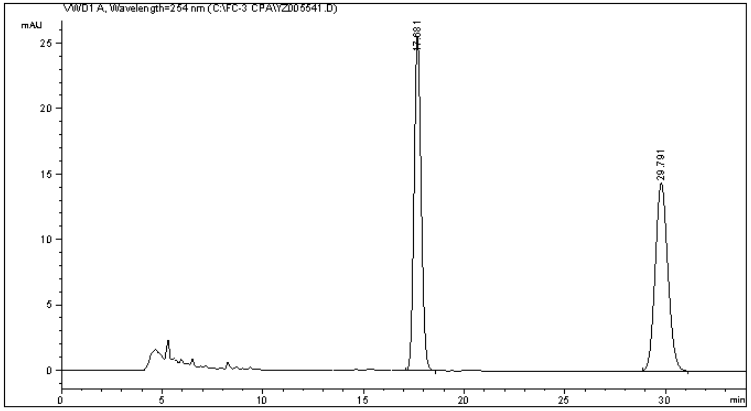

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]     %
----|-------|----|-------|---------|---------|-------|
   1  10.352 VB    0.2214 1686.70862  118.47600  97.1974
   2  19.510 BB    0.4508   48.63408    1.68231   2.8026

Totals :                  1735.34269  120.15831

==========================================================================
                        *** End of Report ***
```



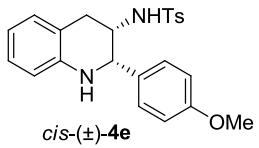

*cis*-(+)-**4d**

Data File C:\FC-3 CPA\YZ005541.D
Sample Name: FC-6-70D

```
==========================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 1/14/2014 2:58:17 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEMOCAL2.M
Last changed    : 1/14/2014 12:53:56 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 2:27:15 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|-------|
   1  17.681 BB    0.3835  628.14948   25.49725  50.0066
   2  29.791 BB    0.6737  627.98407   14.34720  49.9934

Totals :                  1256.13354   39.84445

==========================================================================
                        *** End of Report ***
```

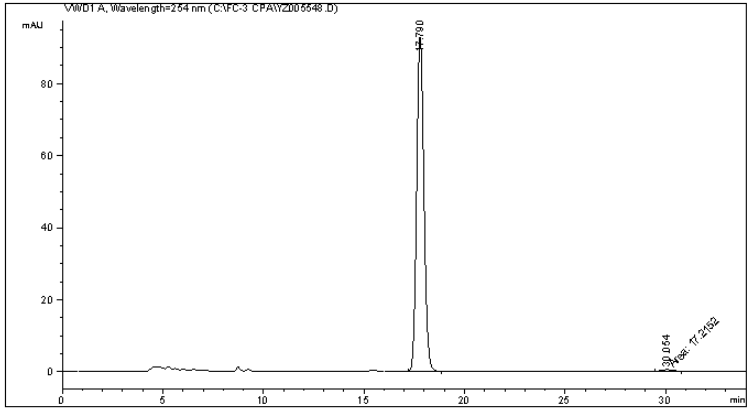



*cis*-(±)-**4e**

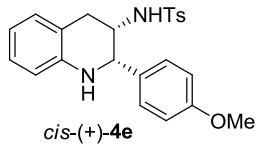


Data File C:\FC-3 CPA\YZ005548.D
Sample Name: FC-6-70C

```
==========================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 1/14/2014 9:12:35 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEMOCAL2.M
Last changed    : 1/14/2014 5:40:24 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 2:29:16 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```



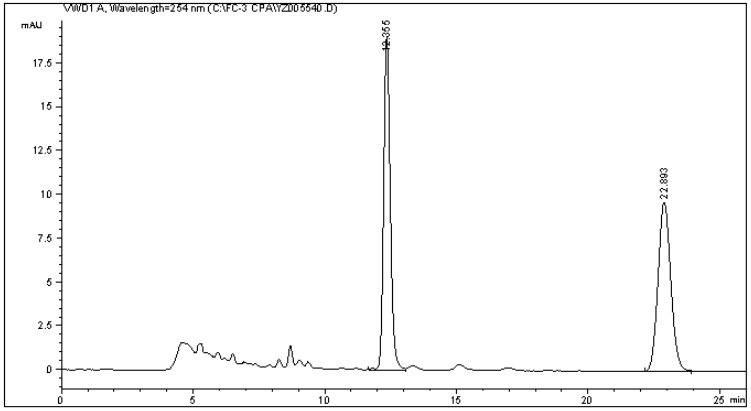

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|-------|
   1  17.790 BB    0.3913 2326.19849   92.84051  99.2654
   2  30.054 MM    0.6602   17.21516 4.34596e-1   0.7346

Totals :                  2343.41365   93.27510

==========================================================================
                        *** End of Report ***
```



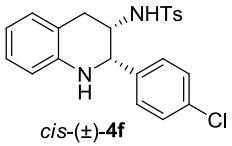

*cis*-(+)-**4e**

Data File C:\FC-3 CPA\YZ005540.D
Sample Name: FC-6-70B

```
    ======================================================================
    Acq. Operator   : ZHOU
    Acq. Instrument : Instrument 1                    Location : Vial 1
    Injection Date  : 1/14/2014 2:31:35 AM
    Acq. Method     : C:\HPCHEM\1\METHODS\DEMOCAL2.M
    Last changed    : 1/14/2014 12:53:56 AM by ZHOU
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
    Last changed    : 3/18/2014 2:21:07 PM by Z
                      (modified after loading)
    Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```




```
    ======================================================================
                               Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier:                   :      1.0000
    Dilution:                     :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]  mAU   *s   [mAU   ]     %
    ----|-------|----|-------|---------|---------|-------|
       1  12.355 BV    0.2691  333.97614   19.00358  50.6426
       2  22.893 BB    0.5175  325.50116    9.67990  49.3574

    Totals :                   659.47729   28.68347

    ======================================================================
                               *** End of Report ***
```

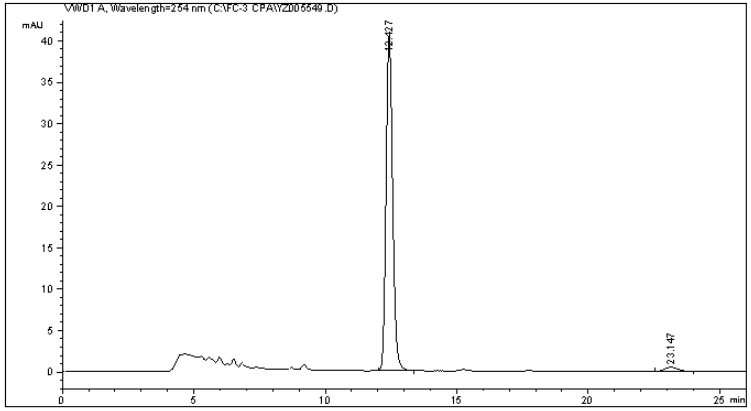



*cis*-(±)-**4f**

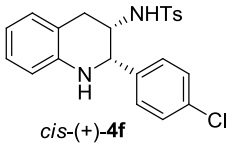


Data File C:\FC-3 CPA\YZ005549.D
Sample Name: FC-6-70A

```
    ======================================================================
    Acq. Operator   : ZHOU
    Acq. Instrument : Instrument 1                    Location : Vial 1
    Injection Date  : 1/14/2014 9:54:41 AM
    Acq. Method     : C:\HPCHEM\1\METHODS\DEMOCAL2.M
    Last changed    : 1/14/2014 5:40:24 AM by ZHOU
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
    Last changed    : 3/18/2014 2:21:07 PM by Z
                      (modified after loading)
    Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```



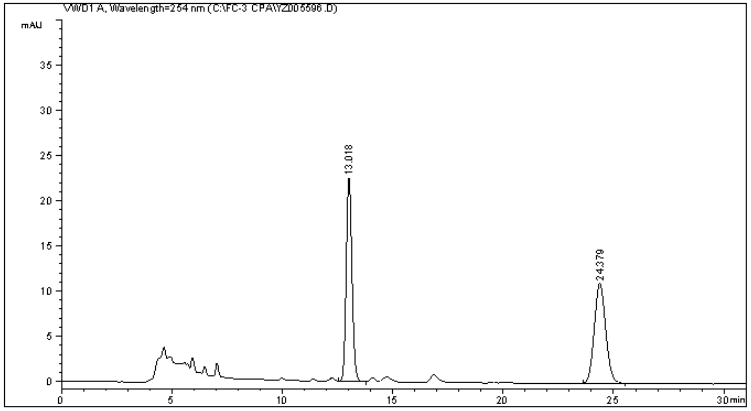

```
    ======================================================================
                               Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier:                   :      1.0000
    Dilution:                     :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]       [min]  mAU   *s   [mAU   ]     %
    ----|-------|----|-------|---------|---------|-------|
       1  12.427 BB    0.2714  706.96075   40.34700  97.7270
       2  23.147 BB    0.5051   16.44262 4.86270e-1   2.2730

    Totals :                   723.40337   40.83327

    ======================================================================
                               *** End of Report ***
```



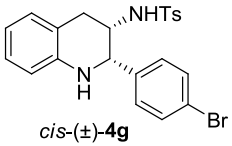

*cis*-(+)-**4f**

Data File C:\FC-3 CPA\YZ005596.D
Sample Name: FC-6-70H

```
==========================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 1/22/2014 2:39:31 PM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC1.M
Last changed    : 1/22/2014 2:38:08 PM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 2:48:28 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|-------|
   1  13.018 VB    0.2782  406.94235   22.48080  50.5561
   2  24.379 BB    0.5597  397.99048   11.05800  49.4439

Totals :                  804.93283   33.53880

==========================================================================
                        *** End of Report ***
```

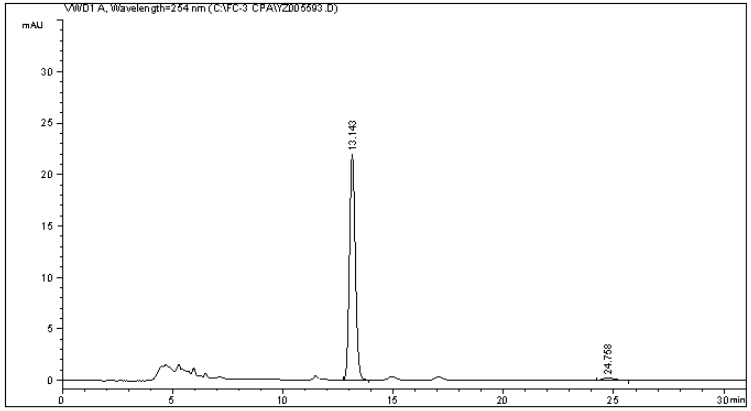



*cis*-(±)-**4g**

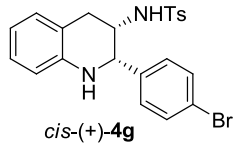


Data File C:\FC-3 CPA\YZ005593.D
Sample Name: FC-6-70G

```
==========================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 1/22/2014 8:42:14 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC1.M
Last changed    : 1/22/2014 8:39:34 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 2:50:25 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```



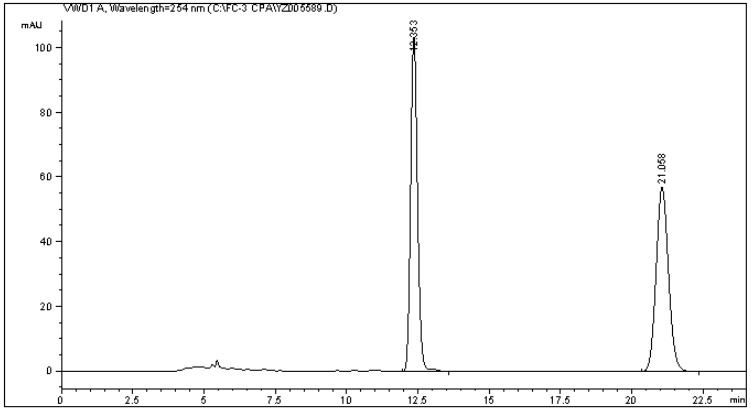

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|-------|
   1  13.143 BB    0.2853  405.00034   21.93711  97.7815
   2  24.758 BB    0.4569    9.18890 2.55844e-1   2.2185

Totals :                  414.18924   22.19296

==========================================================================
                        *** End of Report ***
```



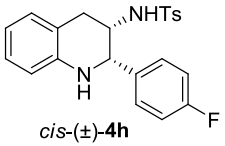

*cis*-(+)-**4g**

Data File C:\FC-3 CPA\YZ005589.D
Sample Name: FC-6-63B

```
==========================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 1/22/2014 6:49:54 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC1.M
Last changed    : 1/22/2014 6:19:21 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 2:06:37 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|-------|
   1  12.353 BB    0.2598 1735.14807  103.44108  50.2183
   2  21.058 BB    0.4656 1720.06079   57.00267  49.7817

Totals :                  3455.20886  160.44374

==========================================================================
                        *** End of Report ***
```

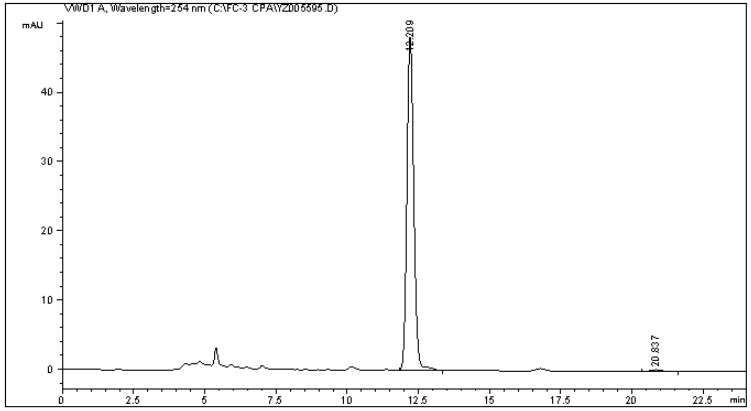



*cis*-(±)-**4h**

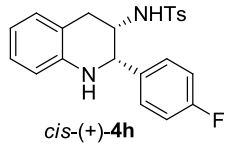


Data File C:\FC-3 CPA\YZ005595.D
Sample Name: FC-6-63a

```
==========================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 1/22/2014 2:12:15 PM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC1.M
Last changed    : 1/22/2014 2:11:15 PM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 2:06:37 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```



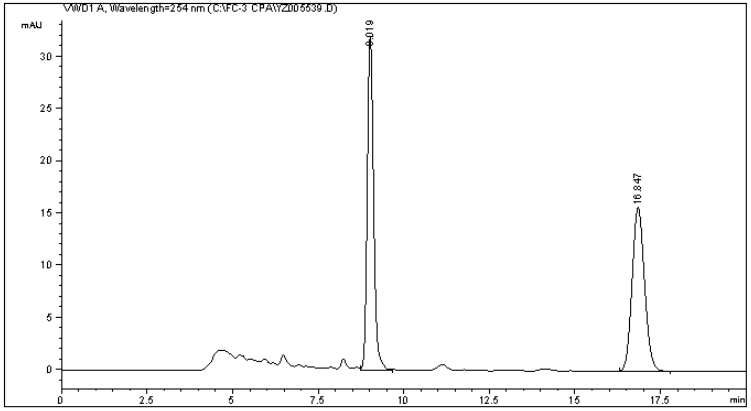

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|-------|
   1  12.209 BB    0.2587  803.82300   48.17765  99.0518
   2  20.837 BB    0.4334    7.69460 2.61642e-1   0.9482

Totals :                  811.51760   48.43929

==========================================================================
                        *** End of Report ***
```



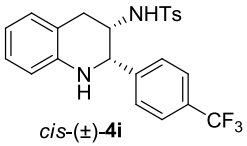

*cis*-(+)-**4h**

Data File C:\FC-3 CPA\YZ005539.D
Sample Name: FC-6-70B

```
==========================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 1/14/2014 2:08:16 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEMOCAL2.M
Last changed    : 1/14/2014 12:53:56 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 2:15:53 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]     %
----|-------|----|-------|---------|---------|-------|
   1   9.019 VB    0.1999  411.22815   31.89465  50.8654
   2  16.847 BB    0.3946  397.23495   15.67905  49.1346

Totals :                   808.46310   47.57370

==========================================================================
                        *** End of Report ***
```

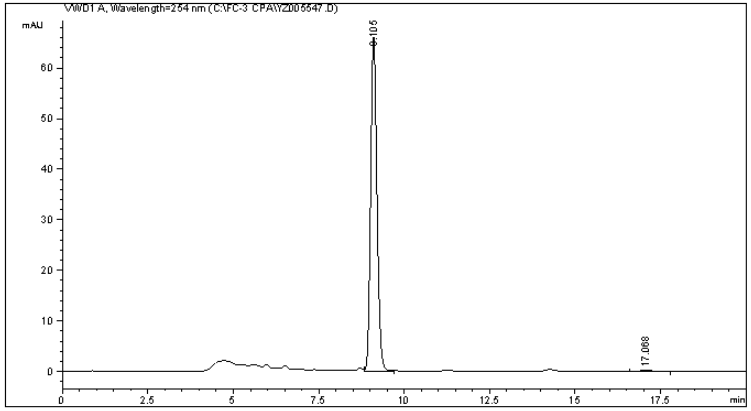



*cis*-(±)-**4i**

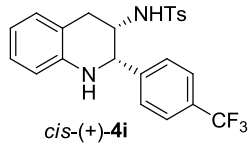


Data File C:\FC-3 CPA\YZ005547.D
Sample Name: FC-6-68A

```
==========================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 1/14/2014 8:47:44 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEMOCAL2.M
Last changed    : 1/14/2014 5:40:24 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 2:15:53 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```



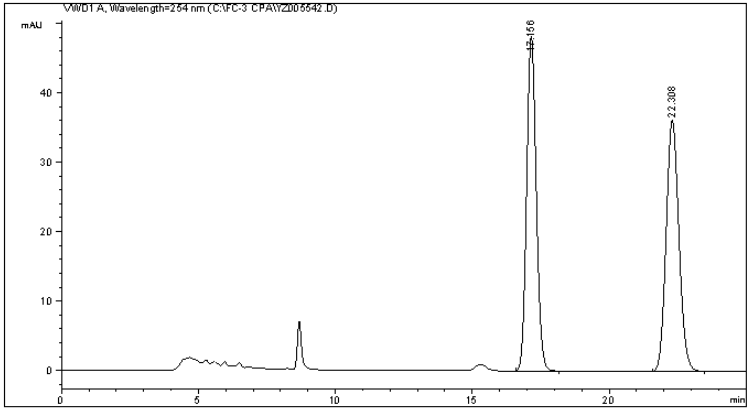

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]     %
----|-------|----|-------|---------|---------|-------|
   1   9.105 VB    0.1995  849.16541   66.05899  99.0140
   2  17.068 BB    0.3968    8.45644 3.31246e-1   0.9860

Totals :                   857.62184   66.39024

==========================================================================
                        *** End of Report ***
```



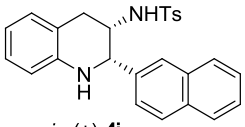

*cis*-(+)-**4i**

Data File C:\FC-3 CPA\YZ005542.D
Sample Name: FC-6-70F

```
==========================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 1/14/2014 6:03:40 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEMOCAL2.M
Last changed    : 1/14/2014 5:40:24 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 2:30:41 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|-------|
   1  17.156 BB    0.3813 1176.00781   48.10852  49.9920
   2  22.308 BB    0.5046 1176.38208   36.17297  50.0080

Totals :                  2352.38989   84.28149

==========================================================================
                        *** End of Report ***
```

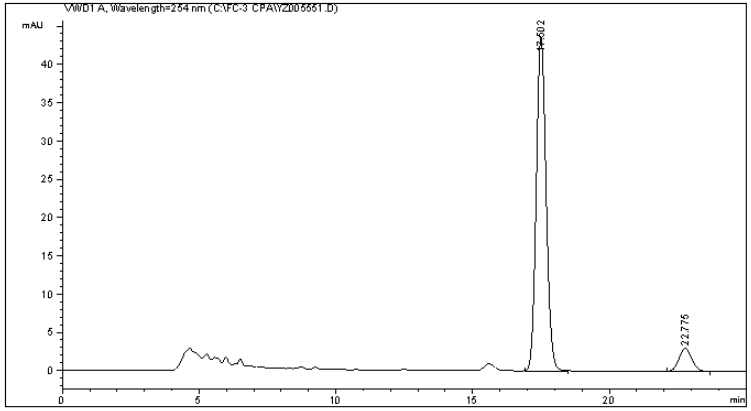



*cis*-(±)-**4j**

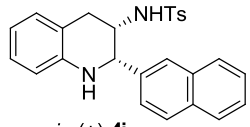


Data File C:\FC-3 CPA\YZ005551.D
Sample Name: FC-6-70E

```
==========================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 1/14/2014 10:59:20 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEMOCAL2.M
Last changed    : 1/14/2014 5:40:24 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 2:30:41 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```



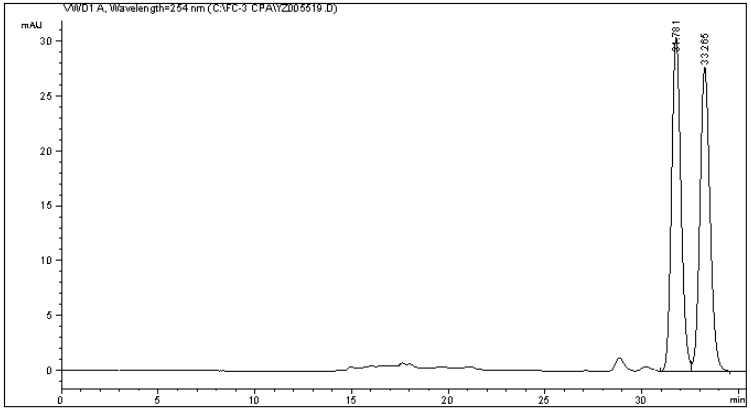

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|-------|
   1  17.502 BB    0.3875 1089.59229   43.62450  91.6042
   2  22.775 BB    0.5149   99.86411    3.01218   8.3958

Totals :                  1189.45640   46.63668

==========================================================================
                        *** End of Report ***
```



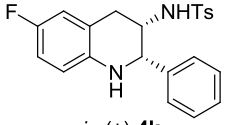

*cis*-(+)-**4j**

Data File C:\FC-3 CPA\YZ005519.D
Sample Name: FC-6-63H

```
==========================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 1/11/2014 2:40:24 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEMOCAL2.M
Last changed    : 1/11/2014 1:08:50 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 2:14:01 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 40/60, 0.2 mL/min, 30 oC, 254 nm
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|-------|
   1  31.781 VV    0.5263 1034.51758   30.53680  50.6963
   2  33.265 VB    0.5571 1006.09845   27.73657  49.3037

Totals :                  2040.61603   58.27337

==========================================================================
                        *** End of Report ***
```

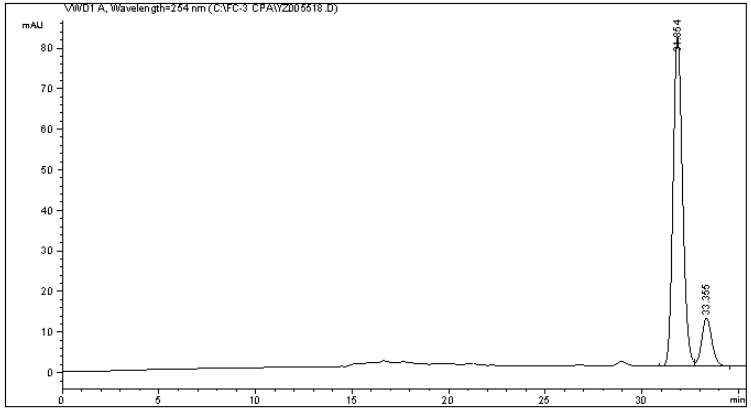



*cis*-(±)-**4k**

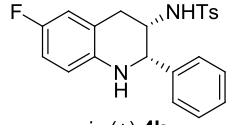


Data File C:\FC-3 CPA\YZ005518.D
Sample Name: FC-6-63G

```
==========================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 1/11/2014 1:58:45 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEMOCAL2.M
Last changed    : 1/11/2014 1:08:50 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 2:12:36 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 40/60, 0.2 mL/min, 30 oC, 254 nm
```



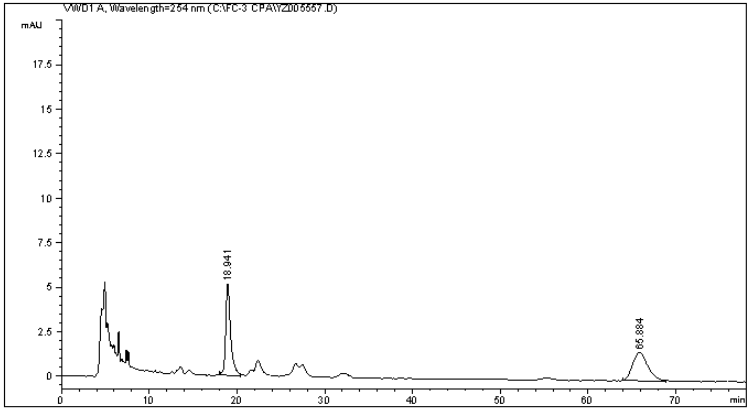

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|-------|
   1  31.854 VV    0.5277 2779.33521   81.15327  86.3785
   2  33.355 VB    0.5651  438.28717   11.86086  13.6215

Totals :                  3217.62238   93.01413

==========================================================================
                        *** End of Report ***
```



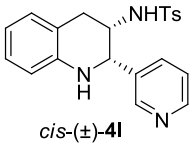

*cis*-(+)-**4k**

Data File C:\FC-3 CPA\YZ005557.D
Sample Name: FC-6-63F

```
==========================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 1/15/2014 10:28:49 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC1.M
Last changed    : 1/15/2014 10:26:19 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 2:45:00 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|-------|
   1  18.941 BB    0.5771  199.79399    5.12526  51.0451
   2  65.884 BB    1.4707  191.61284    1.58922  48.9549

Totals :                   391.40683    6.71448

==========================================================================
                        *** End of Report ***
```

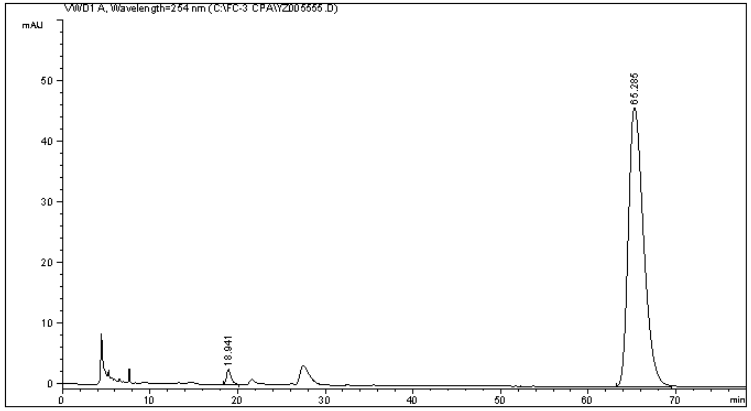



*cis*-(±)-**4l**

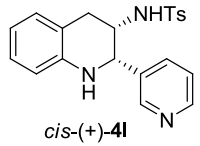


Data File C:\FC-3 CPA\YZ005555.D
Sample Name: FC-6-63I

```
==========================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 1/15/2014 6:29:31 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC1.M
Last changed    : 1/15/2014 5:52:38 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 2:46:22 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```



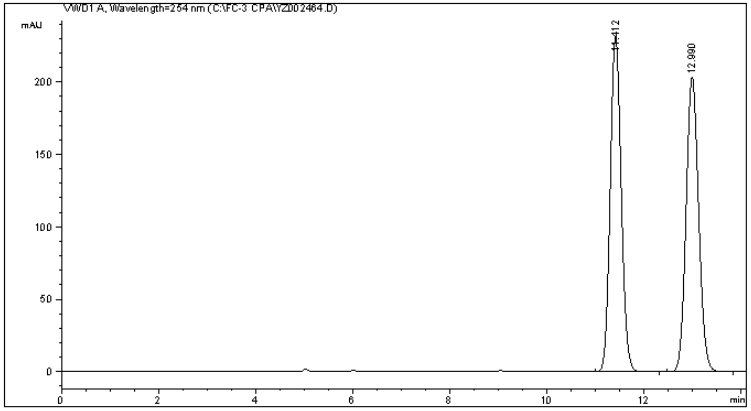

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|-------|
   1  18.941 BB    0.5339   90.60173    2.49732   1.6056
   2  65.285 BB    1.8656 5552.16455   46.08743  98.3944

Totals :                  5642.76628   48.58475

==========================================================================
                        *** End of Report ***
```



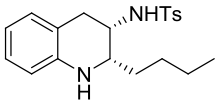

*cis*-(+)-**4l**

Data File C:\FC-3 CPA\YZ002464.D
Sample Name: FC-2-76E1

```
======================================================================
Acq. Operator   : ZX
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 6/19/2012 12:50:34 AM
Acq. Method     : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 6/19/2012 12:48:57 AM by ZX
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 2:55:05 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 80/20, 0.9mL/min, 30 oC, 254 nm
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]     %
----|-------|----|-------|---------|---------|-------|
   1  11.412 BB    0.2478 3642.36719  231.23615  49.9690
   2  12.990 BB    0.2790 3646.87964  203.42197  50.0310

Totals :                  7289.24683  434.65811

======================================================================
                        *** End of Report ***
```

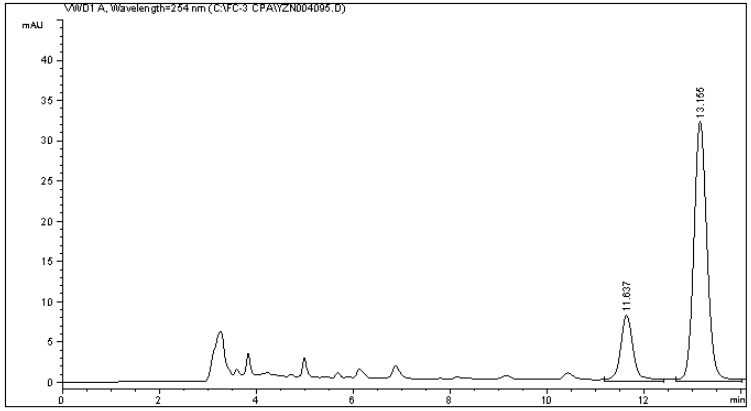



*cis*-(±)-**4ma**

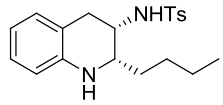


Data File C:\FC-3 CPA\YZN004095.D
Sample Name: FC-6-39A

```
======================================================================
Acq. Operator   : B
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 11/30/2013 9:48:03 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 11/30/2013 9:29:28 PM by B
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 2:56:50 PM by Z
                  (modified after loading)
Sample Info     : OD-H, H/i-PrOH/ = 80/20, 0.9 mL/min, 30 oC, 254 nm
```



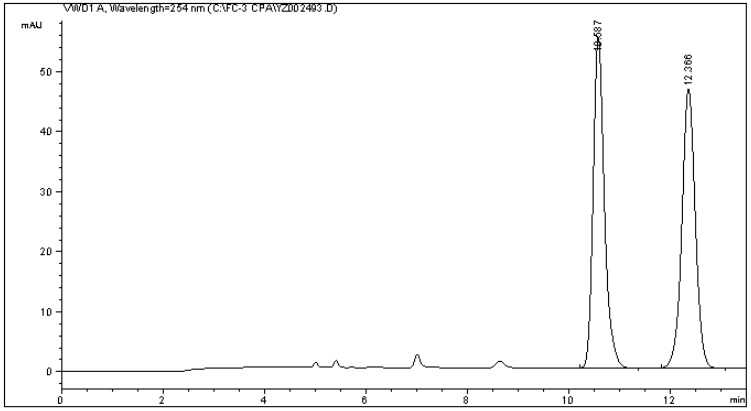

```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]     %
----|-------|----|-------|---------|---------|-------|
   1  11.637 BB    0.2824  154.48215    8.25452  20.1900
   2  13.155 BB    0.2932  610.66058   32.32342  79.8100

Totals :                  765.14273   40.57794

======================================================================
                        *** End of Report ***
```



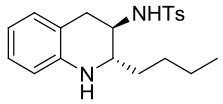

*cis*-(+)-**4ma**

Data File C:\FC-3 CPA\YZ002493.D
Sample Name: FC-2-76E2

```
======================================================================
Acq. Operator   : ZX
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 6/19/2012 9:47:14 AM
Acq. Method     : C:\HPCHEM\1\METHODS\SW.M
Last changed    : 6/19/2012 9:44:21 AM by ZX
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 3:00:15 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 75/25, 0.8 mL/min, 30 oC, 254 nm
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]     %
----|-------|----|-------|---------|---------|-------|
   1  10.587 BB    0.2348  848.72638   55.16675  49.8889
   2  12.366 BB    0.2806  852.50793   46.54912  50.1111

Totals :                  1701.23431  101.71587

======================================================================
                        *** End of Report ***
```

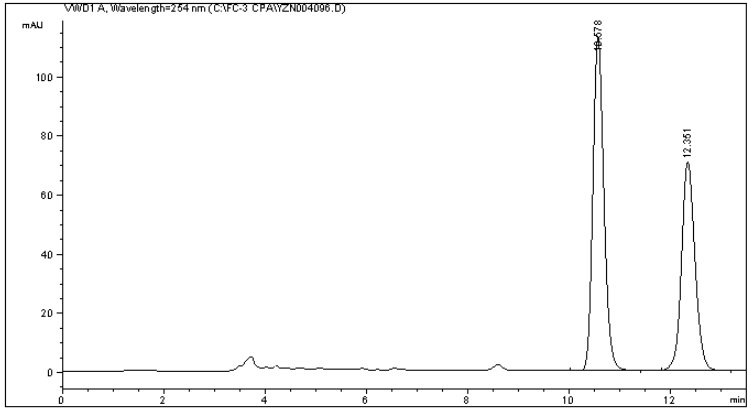



*trans*-(±)-**4mb**

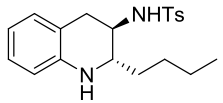


Data File C:\FC-3 CPA\YZN004096.D
Sample Name: FC-6-39B

```
======================================================================
Acq. Operator   : B
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 11/30/2013 10:07:37 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 11/30/2013 10:02:46 PM by B
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 3:00:15 PM by Z
                  (modified after loading)
Sample Info     : OD-H, H/i-PrOH/ = 75/25, 0.8 mL/min, 30 oC, 254 nm
```



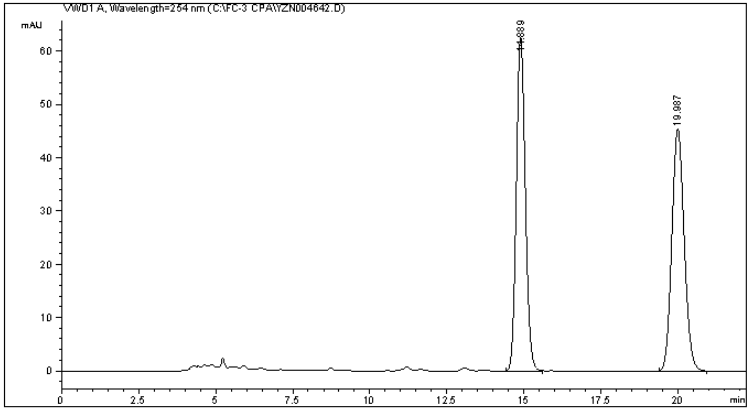

```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]     %
----|-------|----|-------|---------|---------|-------|
   1  10.578 VB    0.2347 1710.33679  113.06089  56.6928
   2  12.351 BB    0.2852 1306.51233   70.78194  43.3072

Totals :                  3016.84912  183.84283

======================================================================
                        *** End of Report ***
```



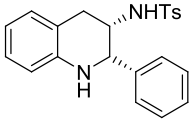

*trans*-(-)-**4mb**

Data File C:\FC-3 CPA\YZN004642.D
Sample Name: FC-2-51A

```
==========================================================================
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 3/18/2014 11:05:24 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 10:58:34 AM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 1:34:59 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30,  0.7 mL/min, 30 oC, 254 nm
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|-------|
   1  14.889 BB    0.3137 1270.76526   62.68732  49.9832
   2  19.987 BB    0.4328 1271.62073   45.43267  50.0168

Totals :                  2542.38599  108.12000

==========================================================================
                        *** End of Report ***
```

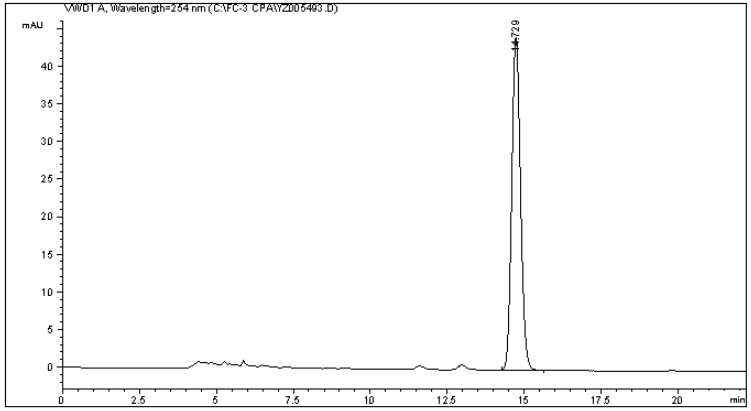



*cis*-(±)-**4a**

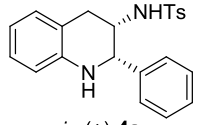


Data File C:\FC-3 CPA\YZ005493.D
Sample Name: FC-6-69

```
==========================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 1/8/2014 1:53:00 PM
Acq. Method     : C:\HPCHEM\1\METHODS\DEMOCAL2.M
Last changed    : 1/8/2014 1:18:55 PM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 1:53:26 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```



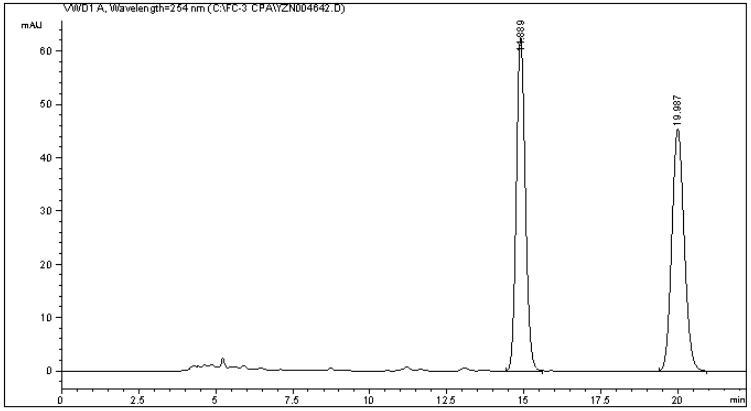

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|-------|
   1  14.729 BB    0.3104  880.09540   44.30888 100.0000

Totals :                   880.09540   44.30888

==========================================================================
                        *** End of Report ***
```



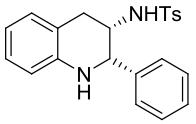

*cis*-(+)-**4a**
HPLC for **5**

Data File C:\FC-3 CPA\YZN004642.D
Sample Name: FC-2-51A

```
==========================================================================
Acq. Operator   : Z
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 3/18/2014 11:05:24 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 10:58:34 AM by Z
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 3/18/2014 1:34:59 PM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30,  0.7 mL/min, 30 oC, 254 nm
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|-------|
   1  14.889 BB    0.3137 1270.76526   62.68732  49.9832
   2  19.987 BB    0.4328 1271.62073   45.43267  50.0168

Totals :                  2542.38599  108.12000

==========================================================================
                        *** End of Report ***
```

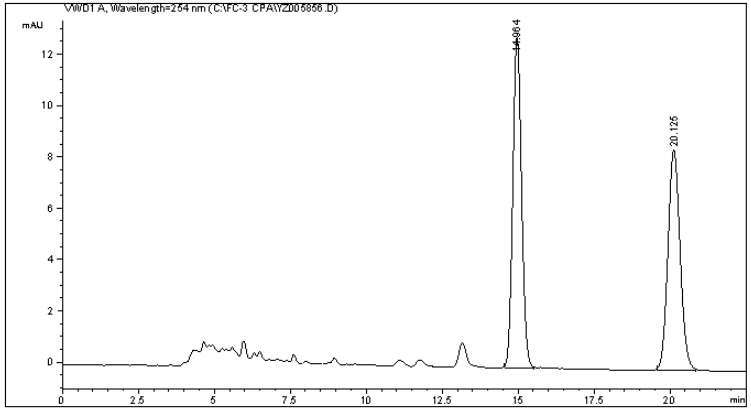



*cis*-(±)-**4a**

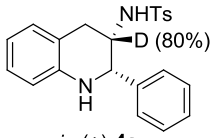


Data File C:\FC-3 CPA\YZ005856.D
Sample Name: FC-6-81

```
==========================================================================
Acq. Operator   : ZHOU
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 4/18/2014 1:43:13 AM
Acq. Method     : C:\HPCHEM\1\METHODS\DEF LC1.M
Last changed    : 4/18/2014 1:15:47 AM by ZHOU
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF LC.M
Last changed    : 4/17/2014 11:28:44 AM by Z
                  (modified after loading)
Sample Info     : AD-H, H/i-PrOH = 70/30, 0.7 mL/min, 30 oC, 254 nm
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|---------|-------|
   1  14.964 BB    0.3093  258.07516   12.89238  52.0050
   2  20.125 BB    0.4286  238.17561    8.58202  47.9950

Totals :                   496.25078   21.47440

==========================================================================
                        *** End of Report ***
```




*cis*-(+)-**4a**