Supporting Information

Rh(III)-Catalyzed C−H Functionalization/Aromatization Cascade with 1,3-Dienes: A Redox-Neutral and Regioselective Access to Isoquinolines

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1 General information

Unless otherwise noted, all reactions were carried out under an atmosphere of argon in flame-dried glassware. Reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under argon.

Commercially available chemicals were obtained from Acros Organics, Aldrich Chemical Co., Strem Chemicals, Alfa Aesar, ABCR and TCI Europe and used as received unless otherwise stated.

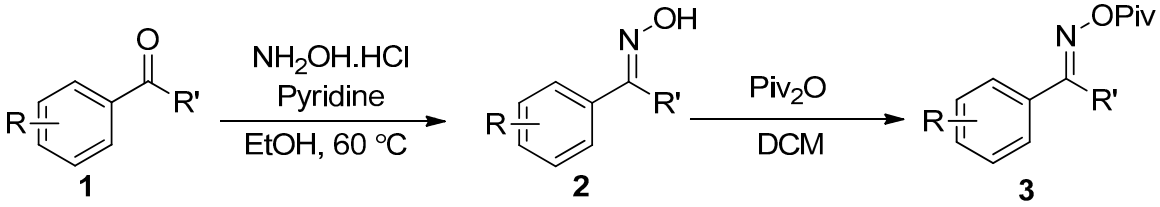
Analytical thin layer chromatography was performed on Polygram SIL G/UV_{254} plates. Flash chromatography was either performed on Merck silica gel (40-63 mesh) by standard technique eluting with solvents as indicated.

GC-MS Spectra were recorded on an Agilent Technologies 7890A GC-system with an Agilent 5975C VL MSD or an Agilent 5975 inert Mass Selective Detector (EI) and a HP-5MS column (0.25 mm × 30 m, Film: 0.25 μm). The major signals are quoted in m/z with the relative intensity in parentheses.

^{1}H and ^{13}C-NMR spectra were recorded on a Bruker AV 300 or AV 400, Varian 500 MHz INOVA or Varian Unity plus 600 in solvents as indicate. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm). ESI mass spectra were recorded on a Bruker Daltonics MicroTof. No attempts were made to optimize yields for substrate synthesis.

2 Synthesis of *O*-pivaloyl arylketoximes and diverse 1,3-dienes

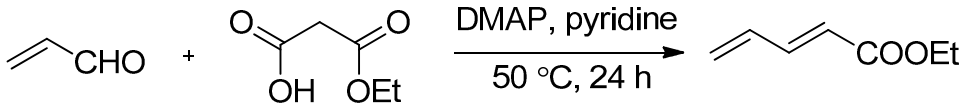
2.1 General procedure for the synthesis of *O*-pivaloyl arylketoximes [1]



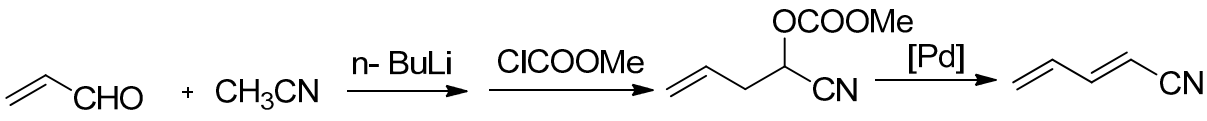
To a solution of aryl ketone (22.0 mmol) and pyridine (5.0 mL, 61.8 mmol) in EtOH (10 mL) was added NH_2OH•HCl (2.29 g, 33.0 mmol) in one portion and the reaction mixture was stirred at 60 °C for 1 h. The reaction was quenched by adding water and the organic materials were extracted twice with ethyl acetate. The combined extracts were washed with 1N aqueous HCl and brine, and dried over $MgSO_4$. Volatile materials were removed in vacuo to give aryl ketone oxime **2**, which was used for the next acetylation without further purification.

Pivalic anhydride (2.23 mL, 11 mmol, 1.1 equiv.) was added to a solution of aryl ketone oxime **2** (1.35 g, 10 mmol, 1 equiv.) in dichloromethane (30 mL). The reaction mixture was allowed to stir for 16 h at room temperature after which it was diluted with more dichloromethane and washed with sat. $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered and evaporated under reduced pressure to afford **7** in an analytically pure form.

2.2 General procedure for the synthesis of 1,3-dienes



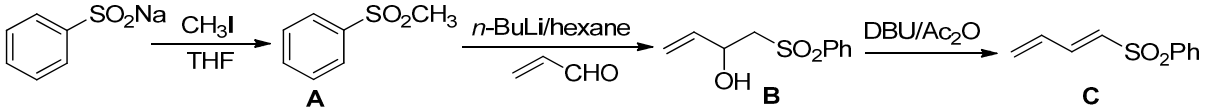
It was prepared as described procedure by Rodriguez & Waegell, *Synthesis*, **1988**, *7*, 534. Acrolein (20 mmol) and DMAP (184 mg, 15 mmol) are successively and rapidly added to a solution of monoethyl malonate 2 (3.54 g, 30 mmol) in pyridine (6 mL), and the solution is warmed to 50 °C for 24 h. Then, the reaction mixture is poured into water and extracted with ether. The ether extract is washed with 15% HCl, and dried (Na_2SO_4) and the ether extract is removed under reduced pressure. The residue was purified by flash chromatography on silica gel using ether/pentane (10:90) as eluent.



It was prepared as described procedure by M. Braun, S. Mroß, I. Schwarz, *Synthesis*, **1998**, 83-88. Under Ar atmosphere, a 1.6 M solution of BuLi in hexane (6.6 mL, 10.5 mmol)

was stirred in a 50 mL two-necked flask, equipped with a magnetic stirrer, a septum, and a thermocouple. After cooling to –20°C, anhyd THF (8 mL) was added, and the mixture was cooled to –78°C. In a second flask, a solution of MeCN (0.52 mL, 10 mmol) in anhyd THF (2 mL) was prepared under Argon and also cooled to –78°C. The solution of MeCN was transferred by a cannula into the slightly evacuated flask containing the solution of BuLi. The temperature was allowed to reach –50°C, and a white precipitate formed gradually. The mixture was cooled to –78°C, and acrolein (0.8 mL, 12 mmol) was injected in one portion whereby the temperature reached –50°C. The cooling bath was removed, so that the mixture warmed up to –20°C. Methyl chloroformate (0.92 mL, 12 mmol) was injected rapidly, and the temperature rose to 15°C within 1 min. After stirring for 18 h at r.t., Sat. aq NH_4Cl (10 mL) and H_2O (10 mL) were added and the mixture was extracted with Et_2O. The combined organic layers were washed with H_2O (20 mL) and brine (20 mL) and dried ($MgSO_4$). The solvent was removed in a rotary evaporator and the residue was purified by column chromatography.

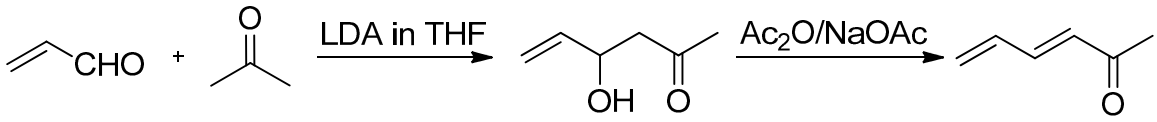
A 5 mL two-necked flask was equipped with a magnetic stirrer and charged with the crude product (5.0 mmol). $Pd(PPh_3)_4$ (0.058–0.289 g; 0.05–0.25 mmol) was added, and the mixture was stirred under N_2 at 25 to 35 °C until the evolution of CO_2 ceased. The crude product was purified by distillation or column chromatography.



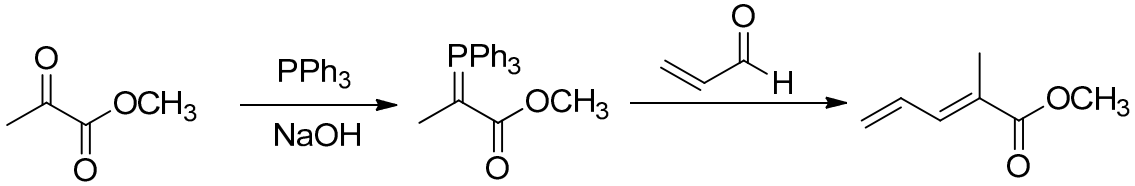
Prepared as described by S. H. Hwang, M. J. Kurth, *Tet. Lett*. **2002**, *43*, 53-56. The CH_3I (5 equiv.) was added to the solution of sodium benzenesulfinate (30.3 mmol) in THF (80 mL) under Argon atmosphere. The reaction mixture was stirred and allowed to warm to reflux for 12 h. Then, the reaction mixture was concentrated and then dissolved in dichloromethane, washed with water and brine, dried with $MgSO_4$, filtered, and concentrated under reduced pressure to give the product A.

n-BuLi (1.6 M in hexanes, 48 mmol)) was added to a cooled (-78 °C), stirred solution of the product **A** (40 mmol) in dry THF (50 mL). After 1 h stirring at the same temperature, acrolein (2.93 mL, 44 mmol) in THF (5 mL) was added dropwise. After 5 min stirring at -78 °C, the reaction was allowed to room temperature for 30 min, and then quenched by addition of sat. NH_4Cl. The mixture was then poured onto ether, washed with sat. NaCl, the organic phase separated, dried over $MgSO_4$, filtered and evaporated, furnishing the corresponding aldol product in quantitative yield, which was used in the next reaction with no

further purification. The crude product obtained (40 mmol) was treated with Ac_2O (3 equiv.) and DBU (4 equiv.). The mixture was stirred at room temperature for 24 h. Then, the reaction was treated with sat $NaHCO_3$, extracted with Et_2O, the organic phase dried over $MgSO_4$, filtered and evaporated. Chromatographic purification of the product furnished the 1,3- diene product as a yellow liquid.



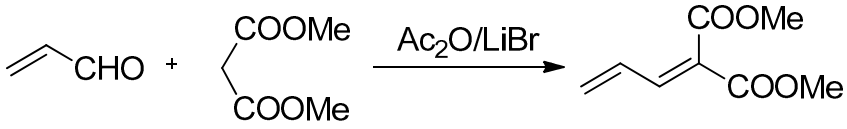
Prepared as described by Bernardi, L *et al.; J. Am. Chem. Soc*. **2007**, *129*, 5772. Acetone (2.94 mL, 40 mmol) in dry THF (5 mL) was added to a cooled (-78 °C), stirred solution of LDA (freshly prepared from diisopropylamine (6.7 mL, 48 mmol) and *n*-BuLi (1.6 M in hexanes, 48 mmol)) in dry THF (50 mL). After 1 h stirring at the same temperature, acrolein (2.93 mL, 44 mmol) in THF (5 mL) was added dropwise. After 5 min stirring at -78 °C, the reaction was quenched by addition of sat. NH_4Cl. The mixture was then poured onto ether, washed with sat. NaCl, the organic phase separated, dried over $MgSO_4$, filtered and evaporated, furnishing the corresponding aldol product in quantitative yield, which was used in the next reaction with no further purification. The crude product obtained (40 mmol) was treated with Ac_2O (10.2 mL, 80 mmol) and NaOAc (2.0 g). The mixture was stirred overnight at room temperature then heated at 100 °C for 1 h. After cooling, the reaction was treated with sat $NaHCO_3$, extracted with Et_2O, the organic phase dried over $MgSO_4$, filtered and carefully evaporated (p >300 mbar, T <30 °C). Chromatographic purification of the product (pentane /Et_2O, removed at p >300 mbar, T <30 °C) furnished the product as a pale yellow liquid.



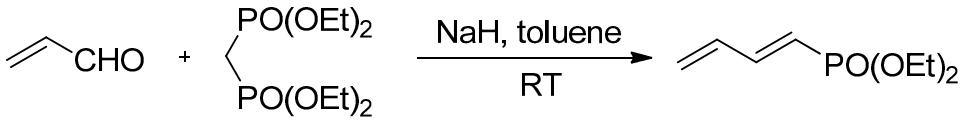
A mixture of triphenylphosphine (14.8 g, 56.4 mmol) and methyl-2-bromopropionate (7.00 mL, 62.7 mmol) in H_2O was stirred at 70 °C for 24 h. The yellow mixture was cooled to room temperature and a solution of NaOH (5.02 g, 125.5 mmol) in H_2O (147 mL) was added. The resulting mixture was swirled for 5 min at room temperature and CH_2Cl_2 was added to dissolve the yellow sticky solid that formed. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The solid residue was triturated with hexane and filtered. The resulting solid was dried *in vacuo* to give the ylide (18.3 g, 93 %) as a

yellow solid.

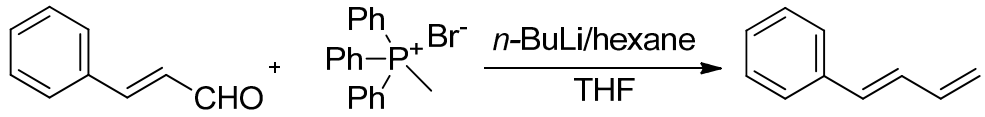
To acrolein (1.46 mL, 22 mmol) in CH_2Cl_2 (50 mL) was added the ylide (8.9 g, 25.5 mmol) at 0 °C. The resulting mixture was stirred from 0 °C to room temperature over 12 h before it was concentrated *in vacuo*. Flash column chromatography of the crude product over silica gel afforded the 1,3-diene as a colorless liquid.



Prepared as described by M. Sylla, D. Joseph, E. Chevallier, C. Camara, F. Dumas, *Synthesis* **2006**, 1045. Ac_2O (1.6 mL, 20 mmol), anhyd LiBr (170 mg, 2 mmol) and malonate (10 mmol) were placed in a round-bottomed flask (10 mL) equipped with a magnetic stirrer and a vapor condenser fitted with a septum-held gas-inlet tube. The resulting mixture was stirred for 10 min to 4 h (see Table 1) at 80 °C under nitrogen. Then, acrolein (1.7 mL, 30 mmol) was added in one portion through the vapor condenser and the solution was stirred at 80 °C until full consumption of malonate. The reaction mixture was allowed to cool to r.t. and slowly decomposed in a sat. solution of Na_2CO_3 (25 mL). The aqueous phase was extracted with Et_2O (2 × 15 mL) and the combined organic phases were washed with brine and, after drying, were evaporated under reduced pressure. The residue was purified using flash chromatography.



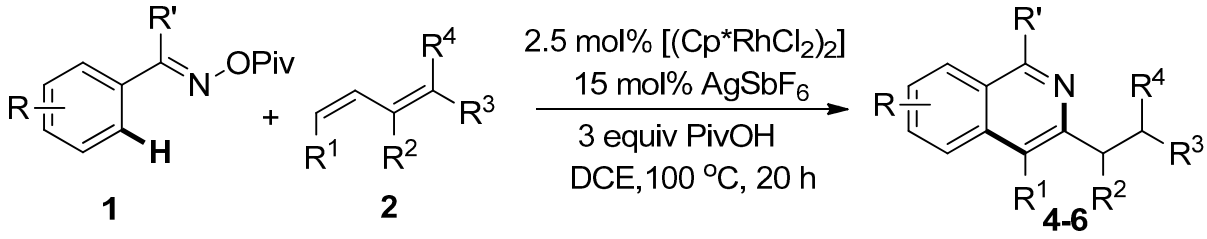
Prepared as described by E. Villemin, K. Robeyns, R. Robiette, M.-F. Herent, J. Marchand-Brynaert, *Tetrahedron* **2013**, *69*, 1138. To a suspension of sodium hydride (60% oil dispersed, 0.15 g, 3.65 mmol) in dry toluene (8 mL) was added tetrabenzyl methylenediphosphonate (1.96 g, 3.65 mmol) at room temperature. After about 15 min (end of gaseous dihydrogen evolution), a solution of acrolein (213 mL, 0.17 g, 3.04 mmol) in dry toluene (8 mL) was added dropwise to the solution and the mixture was stirred for two additional hours. After addition of water, the aqueous layer was extracted with dichloromethane and the combined organic portions were dried over magnesium sulfate. Filtration and concentration under reduced pressure gave the crude diene, which is purified by silica gel chromatography with ethyl acetate.



To a suspension of methyltriphenylphosphonium bromide (3.57 g, 10 mmol) in THF (50 ml) at 0 °C was added dropwise n-butyllithium (2 M in cyclohexane, 5 mL, 10 mmol). The reaction mixture was stirred for 15 min and the cinnamaldehyde (1.0 ml, 8 mmol) was added as a solution in THF (10 mL). After 1 h the solution was warmed to room temperature and stirred for additional 1 h. A saturated solution of NH_4Cl (50 mL) was added and the mixture was extracted with Et_2O (3×100 mL). The combined organic phases were washed with brine (100 ml), dried over $MgSO_4$, and the solvents were removed under reduced pressure (300 mbar, 40 ºC). The residue was applied to a plug of silica, eluted with hexane, and the solvent was removed carefully under reduced pressure (300 mbar, 40 ºC) to obtain the title compound (1.00 g, 96%) as a colorless liquid.

3 Rh(III)-catalyzed redox-neutral C-H/N-H annulation/isomerisation to isoquinoline from 1,3-dienes

3.1 General procedure for Rh(III)-catalyzed redox-neutral C-H/N-H annulation/isomerisation to isoquinoline from 1,3-dienes

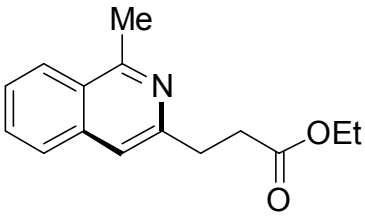


To a 50 mL screw-capped vial equipped with a 10 x 5 mm spinvane-shaped Teflon stir bar were charged with **1** (0.2 mmol), 1,3-diene **2** (0.25 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (15 mol%), PivOH (3.0 equiv.), and 1,2-dichloroethane (1.0 mL) under the Argon atmosphere. The resulting mixture was sealed with a Teflon-lined cap and stirred at 100 °C for 20 h in an oil bath. The reaction was cooled to room temperature, diluted with dichloromethane (15 mL) and washed with saturated $NaHCO_3$ solution. The organic phase was concentrate under the reduce pressure. The desired product was obtained by column chromatography using an appropriate eluent.

3.2 Procedure for the gram scale preparation of isoquinoline 3a

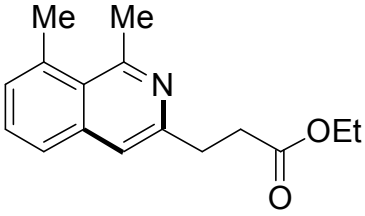
To a 100 mL screw-capped vial equipped with a 10 x 5 mm spinvane-shaped Teflon stir bar were charged with *O*-pivaloyl phenylketoxime (1.095 g, 5 mmol),, (E)-ethyl penta-2,4-dienoate (787.5 mg, 6.25 mmol), $[Cp^*RhCl_2]_2$ (77.5 mg, 0.125 mmol), $AgSbF_6$ (257.5 mg, 0.03 mmol), acetic acid (720 μL, 12 mmol), and 1,2-dichloroethane (20 mL) under the Argon atmosphere. The resulting mixture was sealed with a Teflon-lined cap and stirred at 100 °C for 20 h in an oil bath. The reaction was cooled to room temperature, diluted with dichloromethane (25 mL) and washed with saturated $NaHCO_3$ solution. The desired product was obtained by column chromatography. Ethyl 3-(1-methylisoquinolin-3-yl)propanoate **(3a)** was formed in 81% yield (984 mg).

Ethyl 3-(1-methylisoquinolin-3-yl)propanoate (3a)



Following the general procedure, the C-H activation/cyclization/isomerization reaction was carried out with *O*-pivaloyl phenylketoxime (43.8 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), (E)-ethyl penta-2,4-dienoate (31.5 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. Ethyl 3-(1-methylisoquinolin-3-yl)propanoate **(3a)** was formed in 86% yield. **R_f** (pentane/ethyl acetate 2:1): 0.25; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.09 – 7.99 (m, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.60 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.50 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.35 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.20 (t, *J* = 7.6 Hz, 2H), 2.91 (s, 3H), 2.84 (t, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.27, 158.38, 152.22, 136.61, 129.97, 126.95, 126.40, 126.11, 125.59, 117.03, 60.40, 34.24, 33.06, 22.42, 14.32. **HRMS**: m/z (ESI) calcd for $[C_{16}H_{23}NO_3P]^+$: 308.1416, found: 308.1421.

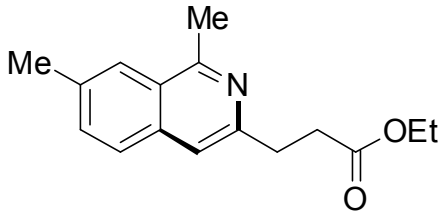
Ethyl 3-(1,8-dimethylisoquinolin-3-yl)propanoate (3b)



Following the general procedure, the C-H activation/cyclization/ isomerization reaction was carried out with *O*-pivaloyl *m*-tolylketoxime (46.6 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), (E)-ethyl penta-2,4-dienoate (31.5 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. Ethyl 3-(1,8-

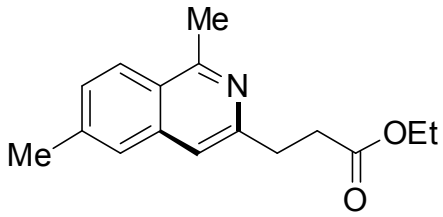
dimethylisoquinolin-3-yl)propanoate (**3b**) was formed in 63% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 2:1): 0.3; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.55 (d, *J* = 8.1 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.32 (s, 1H), 7.29 (d, *J* = 7.0 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.17 (t, *J* = 7.6 Hz, 2H), 3.11 (s, 3H), 2.95 – 2.88 (m, 3H), 2.88 – 2.78 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.37, 158.49, 151.11, 138.85, 136.27, 130.03, 129.46, 127.09, 126.06, 118.19, 60.46, 34.10, 32.52, 29.37, 25.92, 14.38. **HRMS**: m/z (ESI) calcd for $[C_{16}H_{20}NO_2]^+$ 258.1494, found 258.1495.

Ethyl 3-(1,7-dimethylisoquinolin-3-yl)propanoate (3c)



Following the general procedure, the C-H activation/cyclization/ isomerization reaction was carried out with *O*-pivaloyl *m*-tolylketoxime (46.6 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), (E)-ethyl penta-2,4-dienoate (31.5 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. Ethyl 3-(1,7-dimethylisoquinolin-3-yl)propanoate (**3c**) was formed in 81% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 2:1): 0.25; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.45 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.31 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.19 (t, *J* = 7.6 Hz, 2H), 2.90 (s, 3H), 2.83 (t, *J* = 7.6 Hz, 2H), 2.53 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$):** δ 173.33, 157.65, 151.43, 136.23, 134.91, 132.22, 126.83, 126.33, 124.58, 116.87, 60.39, 34.36, 33.03, 22.38, 22.07, 14.36. **HRMS**: m/z (ESI) calcd for $[C_{16}H_{20}NO_2]^+$ 258.1494, found 258.1491.

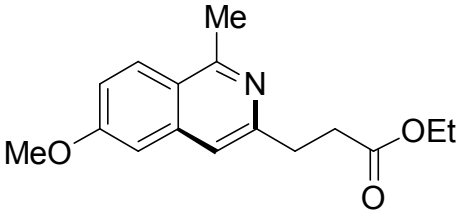
Ethyl 3-(1,6-dimethylisoquinolin-3-yl)propanoate (3d)



Following the general procedure, the C-H activation/cyclization/ isomerization reaction was carried out with *O*-pivaloyl *p*-tolylketoxime (46.6 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), (E)-ethyl penta-2,4-dienoate (31.5 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. Ethyl 3-(1,6-dimethylisoquinolin-3-yl)propanoate (**3d**) was formed in 91% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 2:1): 0.22; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.72 (d, *J* = 8.5 Hz, 1H), 7.12 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.05 (s, 1H), 3.91 (q, *J* = 7.1 Hz, 2H), 2.97 (t, *J* = 7.6 Hz, 2H), 2.67 (s, 3H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.29 (s, 3H), 1.01 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101**

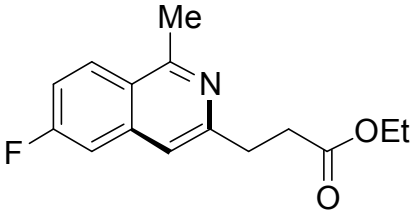
MHz, $CDCl_3$): δ 173.32, 158.04, 152.28, 140.22, 136.98, 128.63, 125.92, 125.48, 124.53, 116.61, 60.41, 34.32, 33.11, 22.35, 21.93, 14.35. **HRMS:** m/z (ESI) calcd for $[C_{16}H_{20}NO_2]^+$ 258.1494, found 258.1492.

Ethyl 3-(6-methoxy-1-methylisoquinolin-3-yl)propanoate (3e)



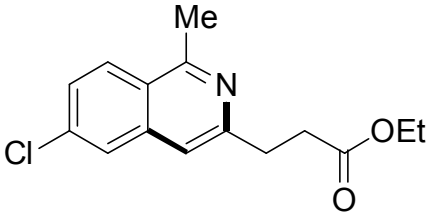
Following the general procedure, the C-H activation/cyclization/isomerization reaction was carried out with *O*-pivaloyl *p*-methoxyphenyl ketoxime (49.8 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), (E)-ethyl penta-2,4-dienoate (31.5 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. Ethyl 3-(6-methoxy-1-methylisoquinolin-3-yl)propanoate (**3e**) was formed in 88% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 2:1): 0.20; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.87 (d, *J* = 9.2 Hz, 1H), 7.19 (s, 1H), 7.05 (dd, *J* = 9.2, 2.5 Hz, 1H), 6.90 (d, *J* = 2.5 Hz, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 3.10 (t, *J* = 7.5 Hz, 2H), 2.79 (s, 3H), 2.75 (t, *J* = 7.6 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 4H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 173.33, 160.74, 157.72, 152.93, 138.80, 127.48, 121.83, 119.10, 116.63, 104.69, 60.40, 55.50, 34.29, 33.09, 22.26, 14.35. **HRMS**: m/z (ESI) calcd for $[C_{16}H_{20}NO_3]^+$: 274.1443, found: 274.1437.

Ethyl 3-(6-fluoro-1-methylisoquinolin-3-yl)propanoate (3f)



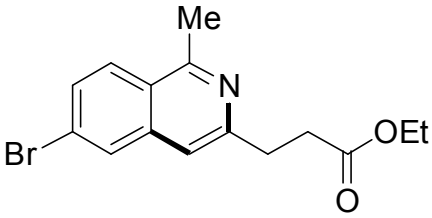
Following the general procedure, the C-H activation/cyclization/ isomerization reaction was carried out with *O*-pivaloyl *p*-fluorophenyl ketoxime (47.4 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), (E)-ethyl penta-2,4-dienoate (31.5 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. Ethyl 3-(6-fluoro-1-methylisoquinolin-3-yl)propanoate (**3f**) was formed in 86% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 2:1): 0.30; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.07 (dd, *J* = 9.1, 5.5 Hz, 1H), 7.38 – 7.19 (m, 3H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.18 (t, *J* = 7.5 Hz, 2H), 2.90 (s, 3H), 2.83 (t, *J* = 7.5 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.22, 164.41, 161.92, 158.35, 153.48, 138.41, 138.30, 128.79, 128.69, 123.39, 116.89, 116.84, 116.80, 116.55, 110.27, 110.07, 60.49, 34.07, 33.02, 22.58, 14.36. **HRMS**: m/z (ESI) calcd for $[C_{15}H_{17}FNO_2]^+$: 262.1243, found 262.1244.

Ethyl 3-(6-chloro-1-methylisoquinolin-3-yl)propanoate (3g)



Following the general procedure, the C-H activation/cyclization/ isomerization reaction was carried out with *O*-pivaloyl *p*-chlorophenyl ketoxime (50.6 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), (E)-ethyl penta-2,4-dienoate (31.5 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. Ethyl 3-(6-chloro-1-methylisoquinolin-3-yl)propanoate (**3g**) was formed in 82% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 2:1): 0.20; **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.99 (dt, *J* = 8.9, 0.7 Hz, 1H), 7.69 (d, *J* = 2.1 Hz, 1H), 7.44 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.27 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.19 (t, *J* = 7.5 Hz, 2H), 2.90 (s, 3H), 2.83 (t, *J* = 7.5 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 173.18, 158.49, 153.58, 137.56, 136.24, 127.45, 127.41, 125.74, 124.38, 116.33, 60.51, 34.05, 33.00, 22.44, 14.37. **HRMS**: m/z (ESI) calcd for $[C_{15}H_{17}ClNO_2]^+$ 278.0948, found 278.0948.

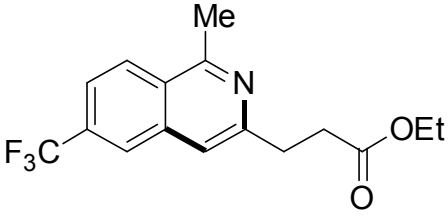
Ethyl 3-(6-bromo-1-methylisoquinolin-3-yl)propanoate (3h)



Following the general procedure, the C-H activation/cyclization/ isomerization reaction was carried out with *O*-pivaloyl *p*-bromophenyl ketoxime (59.6 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), (E)-ethyl penta-2,4-dienoate (31.5 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. Ethyl 3-(6-bromo-1-methylisoquinolin-3-yl)propanoate (**3h**) was formed in 79% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 2:1): 0.20; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.99 – 7.82 (m, 2H), 7.58 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.26 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.19 (t, *J* = 7.5 Hz, 2H), 2.90 (s, 3H), 2.83 (t, *J* = 7.5 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$):** ä 173.16, 158.60, 153.56, 137.88, 129.94, 129.09, 127.42, 124.79, 124.56, 116.16, 60.51, 34.04, 33.01, 22.41, 14.37.

HRMS: m/z (ESI) calcd for $[C_{15}H_{17}BrNO_2]^+$: 322.0443, found 322.0424.

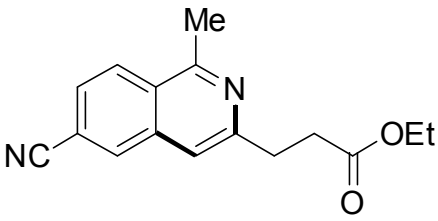
Ethyl 3-(1-methyl-6-(trifluoromethyl)isoquinolin-3-yl)propanoate (3i)



Following the general procedure, the C-H activation/cyclization/ isomerization reaction was carried out with *O*-pivaloyl *p*-trifluoromethylphenyl ketoxime

(57.4 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), (E)-ethyl penta-2,4-dienoate (31.5 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. Ethyl 3-(1-methyl-6-(trifluoromethyl)isoquinolin-3-yl)propanoate (**3i**) was formed in 83% yield. **R_f** (pentane/ethyl acetate 2:1): 0.20; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.18 (d, *J* = 8.7 Hz, 1H), 8.03 (s, 1H), 7.68 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.45 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.23 (t, *J* = 7.4 Hz, 2H), 2.96 (s, 3H), 2.86 (t, *J* = 7.4 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.14, 158.74, 153.94, 135.84, 131.83, 131.51, 126.95, 125.30, 124.79, 124.75, 122.59, 122.12, 117.63, 60.56, 33.96, 32.99, 22.56, 14.36. **HRMS:** m/z (ESI) calcd for $[C_{16}H_{17}F_3NO_2]^+$: 312.1211, found 312.1211.

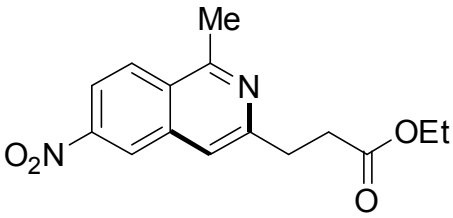
Ethyl 3-(6-cyano-1-methylisoquinolin-3-yl)propanoate (3j)



Following the general procedure, the C-H activation/cyclization/ isomerization reaction was carried out with *O*-pivaloyl *p*-cyanophenyl ketoxime (48.8 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), (E)-ethyl penta-2,4-dienoate (31.5 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. Ethyl 3-(6-cyano-1-methylisoquinolin-3-yl)propanoate (**3j**) was formed in 64% yield. **R_f** (pentane/ethyl acetate 1:1): 0.20; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.16 (dt, *J* = 8.7, 0.9 Hz, 1H), 8.11 (d, *J* = 1.5 Hz, 1H), 7.66 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.41 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.22 (t, *J* = 7.4 Hz, 2H), 2.95 (d, *J* = 0.6 Hz, 3H), 2.85 (t, *J* = 7.4 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 173.03, 158.96, 154.52, 135.70, 133.02, 127.11, 127.08, 126.72, 118.46, 116.89, 113.69, 60.57, 33.77, 32.92, 22.50, 14.35.

HRMS: m/z (ESI) calcd for $[C_{16}H_{17}N_2O_2]^+$: 269.1290, found 269.1280.

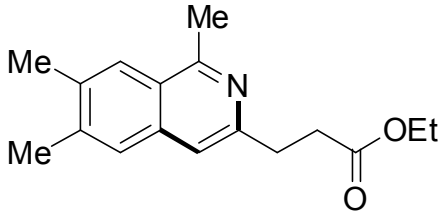
Ethyl 3-(1-methyl-6-nitroisoquinolin-3-yl)propanoate (3k)



Following the general procedure, the C-H activation/cyclization/ isomerization reaction was carried out with *O*-pivaloyl *p*-nitrophenyl ketoxime (52.8 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), (E)-ethyl penta-2,4-dienoate (31.5 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. Ethyl 3-(6-Ethyl 3-(1-methyl-6-nitroisoquinolin-3-yl)propanoate (**3k**) was formed in 64% yield. **R_f** (pentane/ethyl acetate 1:1): 0.20; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.64 (d, *J* = 1.8 Hz, 1H),

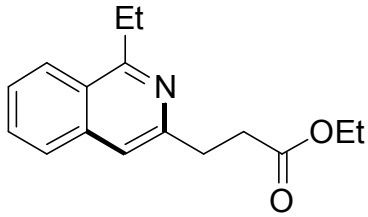
8.31 – 8.17 (m, 2H), 7.55 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.25 (t, *J* = 7.4 Hz, 2H), 2.99 (s, 3H), 2.87 (t, *J* = 7.4 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 173.02, 159.03, 154.84, 148.22, 136.02, 127.83, 127.74, 123.29, 119.82, 118.34, 60.60, 33.75, 32.89, 22.71, 14.37, 1.15. **HRMS:** m/z (ESI) calcd for $[C_{15}H_{17}N_2O_4]^+$ 289.1188, found 289.1179.

Ethyl 3-(1,6,7-trimethylisoquinolin-3-yl)propanoate (3l)



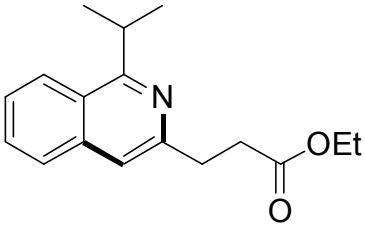
Following the general procedure, the C-H activation/cyclization/ isomerization reaction was carried out with *O*-pivaloyl 3,4-dimethylphenyl ketoxime (49.4 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), (E)-ethyl penta-2,4-dienoate (31.5 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. Ethyl 3-(6- Ethyl 3-(1-methyl-6-nitroisoquinolin-3-yl)propanoate (**3l**) was formed in 80% yield. **R_f** (pentane/ethyl acetate 1:1): 0.20; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.78 (s, 1H), 7.46 (s, 1H), 7.24 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.18 (t, *J* = 7.6 Hz, 2H), 2.88 (s, 3H), 2.82 (t, *J* = 7.6 Hz, 2H), 2.43 (d, *J* = 6.7 Hz, 6H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 173.36, 157.29, 151.39, 140.29, 136.21, 135.66, 126.51, 125.13, 116.25, 60.37, 34.42, 33.10, 22.31, 20.56, 20.43, 14.36. **HRMS:** m/z (ESI) calcd for $[C_{17}H_{22}NO_2]^+$ 272.1651, found 272.1655.

Ethyl 3-(1-ethylisoquinolin-3-yl)propanoate (3m)



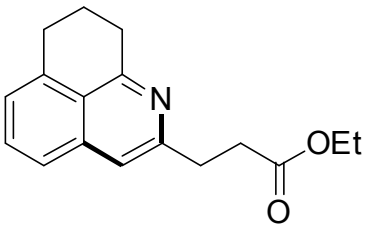
Following the general procedure, the C-H activation/cyclization/ isomerization reaction was carried out with propiophenone O-pivaloyl oxime (46.6 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), (E)-ethyl penta-2,4-dienoate (31.5 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. Ethyl 3-(1-ethylisoquinolin-3-yl)propanoate (**3m**) was formed in 88% yield. **R_f** (pentane/ethyl acetate 1:1): 0.20; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.66 – 7.55 (m, 1H), 7.50 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.35 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.39 – 3.10 (m, 4H), 2.86 (t, *J* = 7.5 Hz, 2H), 1.42 (t, *J* = 7.6 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 173.38, 162.93, 152.32, 137.04, 129.77, 127.18, 126.32, 125.32, 125.25, 116.90, 60.38, 34.17, 33.07, 28.57, 14.34, 13.86. **HRMS**: m/z (ESI) calcd for $[C_{16}H_{20}NO_2]^+$ 258.1494, found 258.1489.

Ethyl 3-(1-isopropylisoquinolin-3-yl)propanoate (3n)



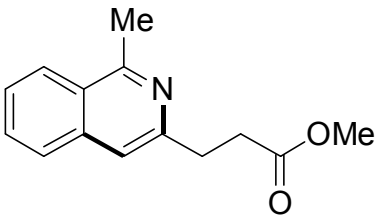
Following the general procedure, the C-H activation/cyclization/ isomerization reaction was carried out with 2-methyl-1-phenylpropan-1-one *O*-pivaloyl oxime (49.4 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), (E)-ethyl penta-2,4-dienoate (31.5 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. Ethyl 3-(1-isopropylisoquinolin-3-yl)propanoate (**3n**) was formed in 73% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 5:1): 0.25; **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.59 (t, *J* = 7.1 Hz, 1H), 7.54 – 7.45 (m, 1H), 7.32 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.90 (p, *J* = 6.7 Hz, 1H), 3.23 (t, *J* = 7.4 Hz, 2H), 2.89 (t, *J* = 7.5 Hz, 2H), 1.41 (d, *J* = 6.8 Hz, 6H), 1.24 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 173.73, 165.74, 152.11, 137.14, 129.45, 127.31, 126.11, 124.81, 124.74, 116.59, 60.40, 33.79, 32.91, 31.17, 22.37, 14.38. **HRMS**: m/z (ESI) calcd for $[C_{17}H_{22}NO_2]^+$: 272.1651, found 272.1652.

Ethyl 3-(8,9-dihydro-7H-benzo[de]quinolin-2-yl)propanoate (3o)



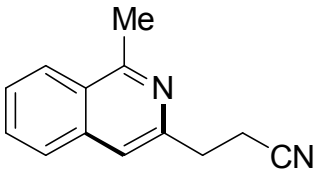
Following the general procedure, the C-H activation/cyclization/ isomerization reaction was carried out with 3,4-dihydronaphthalen-1(2H)-one O-pivaloyl oxime (49 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), (E)-ethyl penta-2,4-dienoate (31.5 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. Ethyl 3-(8,9-dihydro-7H-benzo[de]quinolin-2-yl)propanoate (**3o**) was formed in 82% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 5:1): 0.25; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.57 – 7.46 (m, 2H), 7.32 (s, 1H), 7.29 – 7.21 (m, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.27 – 3.15 (m, 4H), 3.14 – 3.03 (m, 2H), 2.83 (dd, *J* = 8.0, 7.3 Hz, 2H), 2.17 (p, *J* = 6.2 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 173.30, 160.10, 152.24, 138.76, 136.88, 130.13, 124.43, 124.14, 123.92, 116.80, 60.45, 34.40, 33.16, 30.54, 23.41, 14.36. **HRMS**: m/z (ESI) calcd for $[C_{17}H_{20}NO_2]^+$: 270.1494, found 270.1494.

Methyl 3-(1-methylisoquinolin-3-yl)propanoate (4a)



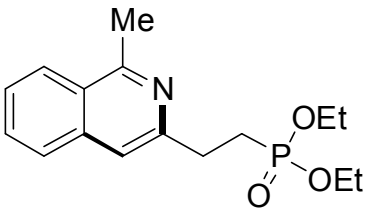
Following the general procedure, the C-H activation/cyclization/ isomerization reaction was carried out with *O*-pivaloyl phenylketoxime (43.8 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), methyl penta-2,4-dienoate (22.4 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. Methyl 3-(1-methylisoquinolin-3-yl)propanoate (**4a**) was formed in 84% yield. $\mathbf{R_f}$ (pentane/ethyl acetate): 0.20; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.09 – 8.03 (m, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.62 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.51 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.36 (s, 1H), 3.67 (s, 3H), 3.20 (t, *J* = 7.5 Hz, 2H), 2.92 (s, 3H), 2.86 (t, *J* = 7.5 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.78, 158.46, 152.16, 136.64, 130.01, 127.01, 126.46, 126.17, 125.64, 117.07, 51.70, 33.99, 33.05, 22.49. **HRMS**: m/z (ESI) calcd for $[C_{14}H_{16}NO_2]^+$: 230.1181, found: 230.1178.

3-(1-Methylisoquinolin-3-yl)propanenitrile (4b)



Following the general procedure, the C-H activation/cyclization/ isomerization reaction was carried out with *O*-pivaloyl phenylketoxime (43.8 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), penta-2,4-dienenitrile (15.8 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. 3-(1-Methylisoquinolin-3-yl)propanenitrile (**4b**) was formed in 72% yield. $\mathbf{R_f}$ (pentane/ethyl acetate): 0.20; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.72 – 7.63 (m, 1H), 7.58 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.43 (s, 1H), 3.20 (t, *J* = 7.2 Hz, 2H), 2.95 (s, 3H), 2.91 (t, *J* = 7.2 Hz, 2H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 159.12, 149.22, 136.56, 130.50, 127.21, 127.13, 126.57, 125.76, 119.71, 117.92, 33.62, 22.42, 17.61. **HRMS**: m/z (ESI) calcd for $[C_{13}H_{13}N_2]^+$: 197.1079, found: 197.1081.

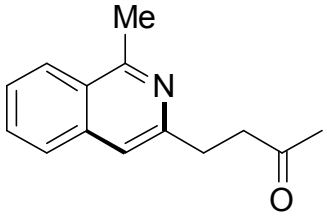
Diethyl (2-(1-methylisoquinolin-3-yl)ethyl)phosphonate (4c)



Following the general procedure, the C-H activation/cyclization/ isomerization reaction was carried out with *O*-pivaloyl phenylketoxime (43.8 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), (E)-diethyl buta-1,3-dien-1-ylphosphonate (38 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. Diethyl (2-(1-methylisoquinolin-3-yl)ethyl)phosphonate (**4c**) was formed in 80% yield. $\mathbf{R_f}$

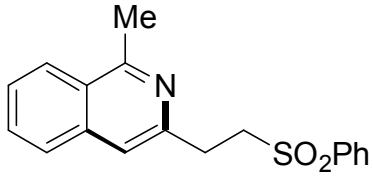
(ethyl acetate): 0.20; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.62 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.52 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.36 (s, 1H), 4.18 – 3.98 (m, 4H), 3.22 – 3.08 (m, 2H), 2.92 (s, 3H), 2.39 – 2.21 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 158.54, 152.50, 152.33, 136.66, 130.11, 127.00, 126.56, 126.20, 125.66, 116.86, 61.61, 30.93, 30.89, 26.47, 25.08, 22.47, 16.58, 16.52. **^{31}P NMR (121 Hz, $CDCl_3$):** δ 31.56. **HRMS:** m/z (ESI) calcd for $[C_{16}H_{23}NO_3P]^+$: 308.1416, found 308.1421.

4-(1-Methylisoquinolin-3-yl)butan-2-one (4d)



Following the general procedure, the C-H activation/cyclization/ isomerization reaction was carried out with *O*-pivaloyl phenylketoxime (43.8 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), (E)-hexa-3,5-dien-2-one (24 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. 4-(1-Methylisoquinolin-3-yl)butan-2-one (**4d**) was formed in 62% yield. **R_f** (pentane/ethyl acetate 3:1): 0.30; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.10 – 8.02 (m, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.63 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.52 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.37 (s, 1H), 3.16 (t, *J* = 7.4 Hz, 2H), 2.99 (t, *J* = 7.4 Hz, 2H), 2.93 (s, 3H), 2.18 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 208.42, 158.40, 152.47, 136.73, 130.15, 127.02, 126.49, 126.11, 125.67, 117.33, 43.47, 31.92, 30.25, 22.41. **HRMS**: m/z (ESI) calcd for $[C_{14}H_{16}NO]^+$: 214.1232, found: 214.1230.

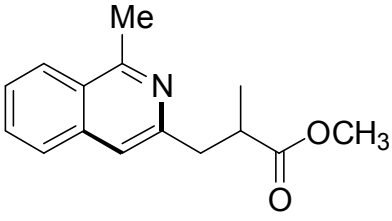
2-(1-Methylisoquinolin-3-yl)ethyl benzenesulfinate (4e)



Following the general procedure, the C-H activation/cyclization/ isomerization reaction was carried out with *O*-pivaloyl phenylketoxime (43.8 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), (E)-buta-1,3-dien-1-yl benzenesulfinate (48.5 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. 2-(1-Methylisoquinolin-3-yl)ethyl benzenesulfinate (**4e**) was formed in 66% yield. **R_f** (pentane/ethyl acetate 1:1): 0.20; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.93 – 7.85 (m, 2H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.68 – 7.60 (m, 1H), 7.54 (dddd, *J* = 8.1, 6.1, 4.5, 1.3 Hz, 2H), 7.50 – 7.41 (m, 2H), 7.32 (s, 1H), 3.78 – 3.61 (m, 2H), 3.30 (dd, *J* = 9.3, 6.5 Hz, 2H), 2.82 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 158.76, 149.06, 139.37, 136.48, 133.56, 130.31, 129.17, 128.23, 127.00, 126.91,

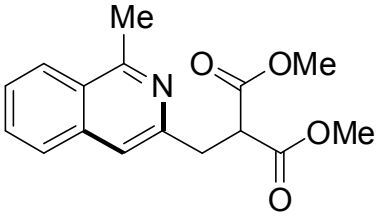
126.30, 125.63, 117.85, 55.81, 31.16, 22.35. **HRMS**: m/z (ESI) calcd for $[C_{18}H_{18}NO_2S]^+$: 312.1058, found: 312.1057.

Methyl 2-methyl-3-(1-methylisoquinolin-3-yl)propanoate (4f)



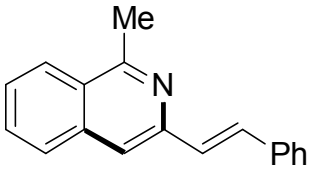
Following the general procedure, the C-H activation/cyclization/isomerization reaction was carried out with *O*-pivaloyl phenylketoxime (43.8 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), methyl 2-methylpenta-2,4-dienoate (31.5 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. Methyl 2-methyl-3-(1-methylisoquinolin-3-yl)propanoate (**4f**) was formed in 86% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 1:1): 0.20; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.10 – 8.00 (m, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.62 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.52 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.37 (s, 1H), 4.18 (t, *J* = 7.6 Hz, 1H), 3.71 (s, 6H), 3.48 (d, *J* = 7.6 Hz, 2H), 2.90 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 169.83, 158.50, 149.57, 136.51, 130.05, 127.09, 126.67, 126.30, 125.63, 117.92, 77.48, 77.16, 76.84, 52.64, 51.62, 36.69, 22.49. **HRMS**: m/z (ESI) calcd for $[C_{15}H_{18}NO_2]^+$: 244.1338, found: 244.1340.

Dimethyl 2-((1-methylisoquinolin-3-yl)methyl)malonate (4g)



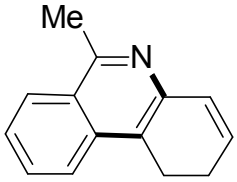
Following the general procedure, the C-H activation/cyclization/ isomerization reaction was carried out with *O*-pivaloyl phenylketoxime (43.8 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), dimethyl 2-allylidenemalonate (42.5 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. Dimethyl 2-((1-methylisoquinolin-3-yl)methyl)malonate (**4g**) was formed in 81% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 1:1): 0.20; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.09 – 8.00 (m, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.61 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.51 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.31 (s, 1H), 3.63 (s, 3H), 3.29 (dd, *J* = 13.5, 7.3 Hz, 1H), 3.13 (h, *J* = 7.0 Hz, 1H), 2.91 (d, *J* = 4.1 Hz, 4H), 1.21 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 176.98, 158.42, 151.33, 136.51, 129.97, 126.99, 126.45, 126.15, 125.63, 117.87, 51.66, 41.75, 39.83, 22.52, 17.21. **HRMS**: m/z (ESI) calcd for $[C_{16}H_{18}NO_4]^+$: 288.1236, found: 288.1227.

(E)-1-Methyl-3-styrylisoquinoline (4h)



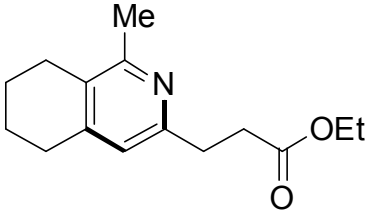
Following the general procedure, the C-H activation/cyclization/ isomerization reaction was carried out with *O*-pivaloyl phenylketoxime (43.8 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), (E)-buta-1,3-dien-1-ylbenzene (32.5 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), AgOAc (67 mg, 0.4 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. (E)-1-Methyl-3-styrylisoquinoline (**4h**) was formed in 44% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 9:1): 0.20; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.08 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 15.9 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.67 – 7.59 (m, 3H), 7.56 – 7.46 (m, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.28 (dt, *J* = 17.5, 3.5 Hz, 2H), 3.01 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 158.82, 148.24, 137.31, 136.70, 131.58, 130.23, 128.77, 128.39, 127.97, 127.46, 127.10, 126.96, 126.76, 125.91, 117.62, 22.83. HRMS m/z (ESI) calcd for $[C_{18}H_{16}N]^+$: 246.1283, found: 246.1283.

6-Methyl-1,2-dihydrophenanthridine (4l)



Following the general procedure, the C-H activation/cyclization/ isomerization reaction was carried out with *O*-pivaloyl phenylketoxime (43.8 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), cyclohexa-1,3-diene (20 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), AgOAc (67 mg, 0.4 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. 6-Methyl-1,2-dihydrophenanthridine (**4l**) was formed in 63% yield. $\mathbf{R_f}$ (pentane/ethyl acetate 9:1): 0.20; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.71 – 7.62 (m, 1H), 7.50 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 6.75 (dt, *J* = 9.7, 1.9 Hz, 1H), 6.34 – 6.18 (m, 1H), 3.18 (t, *J* = 8.8 Hz, 2H), 2.92 (s, 3H), 2.48 (tdd, *J* = 8.7, 4.3, 1.9 Hz, 2H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 156.23, 145.28, 134.51, 130.96, 130.01, 129.84, 126.61, 126.37, 125.77, 122.99, 121.70, 22.88, 22.46, 21.91. HRMS m/z (ESI) calcd for $[C_{14}H_{14}N]^+$: 196.1126, found: 196.1121.

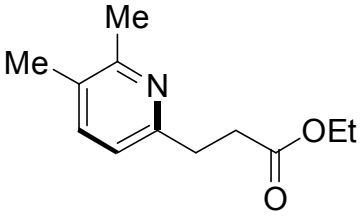
Ethyl 3-(1-methyl-5,6,7,8-tetrahydroisoquinolin-3-yl)propanoate (5a)



Following the general procedure, the C-H activation/cyclization/ isomerization reaction was carried out with (E)-1-(cyclohex-1-en-1-yl)ethanone O-pivaloyl oxime (44.6 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), (E)-ethyl penta-2,4-dienoate (31.5 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20

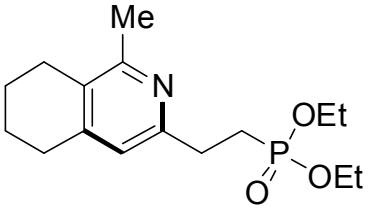
h. Ethyl 3-(1-methyl-5,6,7,8-tetrahydroisoquinolin-3-yl)propanoate (**5a**) was formed in 65% yield. $\mathbf{R_f}$ (DCM/ethyl acetate 1:1): 0.20; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.74 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.99 (t, *J* = 7.6 Hz, 2H), 2.70 (dt, *J* = 15.5, 6.9 Hz, 4H), 2.58 (t, *J* = 6.3 Hz, 2H), 2.40 (s, 3H), 1.89 – 1.64 (m, 4H), 1.31 – 1.14 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.36, 156.45, 155.22, 146.78, 128.76, 121.16, 60.44, 34.30, 32.48, 29.58, 27.33, 25.84, 23.20, 22.26, 21.93, 14.38. HRMS m/z (ESI) calcd for $[C_{15}H_{22}NO_2]^+$: 248.1651, found: 248.1651.

Ethyl 3-(5,6-dimethylpyridin-2-yl)propanoate (5b)



Following the general procedure, the C-H activation/cyclization/isomerization reaction was carried out with (E)-3-methylbut-3-en-2-one O-pivaloyl oxime (36.6 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), (E)-ethyl penta-2,4-dienoate (31.5 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. Ethyl 3-(5,6-dimethylpyridin-2-yl)propanoate (**5b**) was formed in 71% yield. $\mathbf{R_f}$ (DCM/ethyl acetate 1:1): 0.20; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.30 (d, *J* = 7.7 Hz, 1H), 6.91 (d, *J* = 7.7 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.03 (t, *J* = 7.6 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.45 (s, 3H), 2.23 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.34, 156.72, 156.58, 137.69, 128.93, 120.26, 60.45, 34.20, 32.77, 22.63, 18.91, 14.37. HRMS m/z (ESI) calcd for $[C12H18NO2]^+$: 208.1338, found: 208.1337.

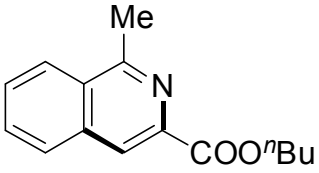
Diethyl (2-(1-methyl-5,6,7,8-tetrahydroisoquinolin-3-yl)ethyl)phosphonate (5c)



Following the general procedure, the C-H activation/cyclization/isomerization reaction was carried out with (E)-1-(cyclohex-1-en-1-yl)ethanone O-pivaloyl oxime (44.6 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), (E)-diethyl buta-1,3-dien-1-ylphosphonate (38 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. Diethyl (2-(1-methyl-5,6,7,8-tetrahydroisoquinolin-3-yl)ethyl)phosphonate (**5c**) was formed in 71% yield. $\mathbf{R_f}$ (DCM/ethyl acetate 1:1): 0.20; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.75 (s, 1H), 4.14 – 4.03 (m, 4H), 3.10 – 2.86 (m, 2H), 2.69 (t, *J* = 6.1 Hz, 2H), 2.58 (t, *J* = 6.3 Hz, 2H), 2.41 (s, 3H), 2.27 – 2.08 (m,

2H), 1.92 – 1.64 (m, 4H), 1.29 (t, J = 7.1 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 156.63, 155.62, 155.44, 146.51, 128.69, 120.75, 61.56, 30.52, 30.48, 29.53, 26.47, 25.86, 25.08, 23.22, 22.27, 22.22, 16.58, 16.52. **^{31}P NMR (121 Hz, $CDCl_3$):** δ 31.50. HRMS m/z (ESI) calcd for $[C_{16}H_{27}NO_3P]^+$: 312.1729, found: 312.1726.

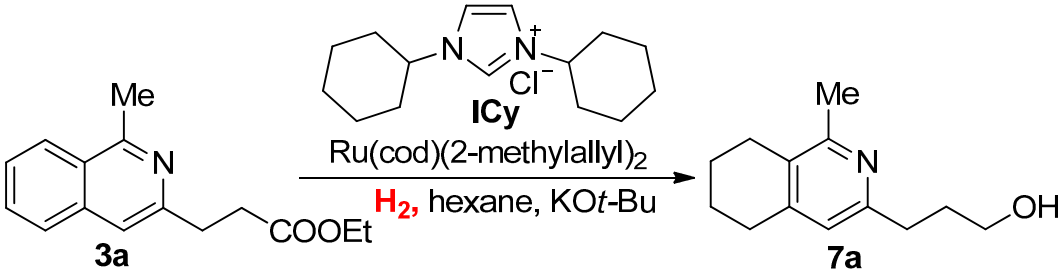
Butyl 1-methylisoquinoline-3-carboxylate (6a)



Following the general procedure, the C-H activation/cyclization/isomerization reaction was carried out with *O*-pivaloyl phenylketoxime (43.8 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), butyl acrylate (32 mg, 0.25 mmol), $AgSbF_6$ (10.3 mg, 0.03 mmol), AgOAc (67 mg, 0.4 mmol), PivOH (61.2 mg, 0.6 mmol) and 1,2-dichloroethane (1 mL) at 100 ºC for 20 h. Diethyl (2-(1-methyl-5,6,7,8-tetrahydroisoquinolin-3-yl)ethyl)phosphonate (**5c**) was formed in 71% yield. **R_f** (DCM/ethyl acetate 1:1): 0.20; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 8.39 (s, 1H), 8.22 – 8.11 (m, 1H), 7.92 (dd, J = 6.7, 2.6 Hz, 1H), 7.78 – 7.64 (m, 2H), 4.44 (t, J = 6.9 Hz, 2H), 3.02 (s, 3H), 1.82 (dt, J = 14.7, 7.0 Hz, 2H), 1.48 (dq, J = 14.6, 7.4 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.07, 159.47, 140.76, 135.53, 130.68, 129.38, 128.98, 128.74, 125.85, 122.78, 65.64, 30.89, 22.80, 19.31, 13.90. **HRMS**: m/z (ESI) calcd for $[C_{16}H_{27}NO_3P]^+$: 312.1729, found: 312.1726.

4 Synthetic Utilization of Isoquinoline

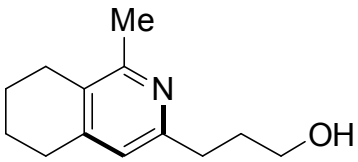
4.1 General procedure for the hydrogenation of isoquinoline 3a



To a flame-dried screw-capped tube equipped with a magnetic stir bar was added [Ru(cod)(2-methylallyl)$_2$] (4.8 mg, 0.015 mmol), imidazolium salt **ICy** (8.6 mg, 0.032 mmol) and dry KO*t*-Bu (5.0 mg, 0.045 mmol) in a glove box. The mixture was suspended in hexane (1 mL) and stirred at 70 °C for 16 h under argon. Then the mixture was transferred under argon to a glass vial containing flavones or isoquinoline **3a** (015-0.3 mmol) and a magnetic stirring bar. Then, the glass vial was placed in a 150 mL stainless-steel reactor. The autoclave was

carefully pressurized/depressurized with hydrogen gas three times before the reaction pressure of 100 bar was adjusted. The hydrogenation was performed at 60 °C for 20 h. The autoclave was depressurized carefully and the crude mixture was purified by Column . chromatography on silica gel.

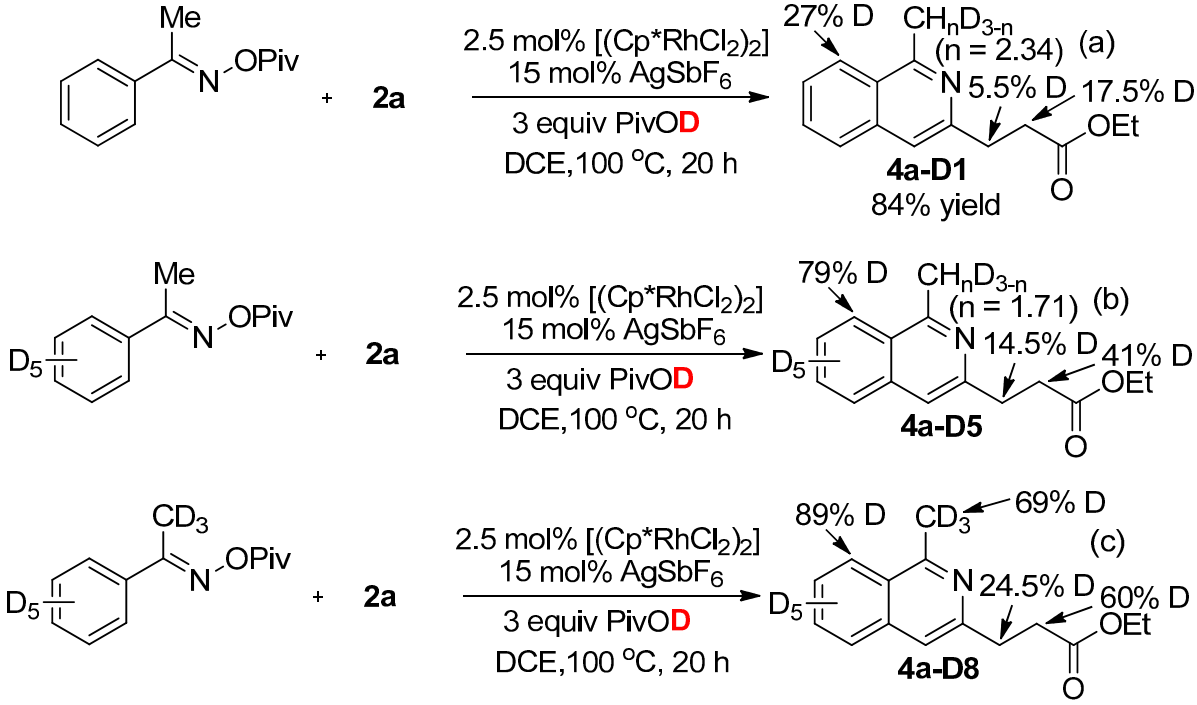
3-(1-Methyl-5,6,7,8-tetrahydroisoquinolin-3-yl)propan-1-ol (7a)



Following the procedure, 3-(1-methyl-5,6,7,8-tetrahydroisoquinolin-3-yl)propan-1-ol (**7a**) was formed in 99% yield. **R_f** (DCM/methanol 12:1): 0.20; **^{1}H NMR (300 MHz, $CDCl_3$):** δ 6.71 (s, 1H), 5.34 (s, 1H), 3.84 – 3.60 (m, 2H), 2.93 – 2.78 (m, 2H), 2.66 (t, *J* = 6.2 Hz, 2H), 2.55 (t, *J* = 6.3 Hz, 2H), 2.37 (s, 3H), 2.00 – 1.62 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.34, 155.82, 146.99, 128.36, 121.31, 62.71, 35.50, 31.52, 29.51, 25.68, 23.13, 22.21, 21.78.

5 Mechanistic Experiments

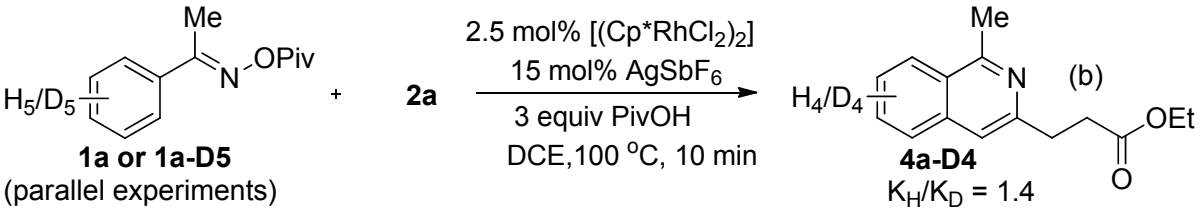
5.1 Isotope experiments



To a 10 mL Schlenk tube was added $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (10.3 mg, 0.03 mmol), *O*-pivaloyl phenylketoxime (0.20 mmol), **2a** (0.25 mmol) PivOD (0.6 mmol) and the tube was purged with Ar for three times, followed by addition of1,2-dichloroethane (1 mL). The formed mixture was stirred at 100 ºC under Ar for 20 h as monitored by TLC. The

solution was then cooled to rt, and the solvent was removed under vaccum directly. The crude product was purified by column chromatography on silica gel (eluent: pentane/ethyl acetate = 2:1) to afford the desired product. The ratio was determined by ^{1}H NMR.

5.2 Deuteration experiments

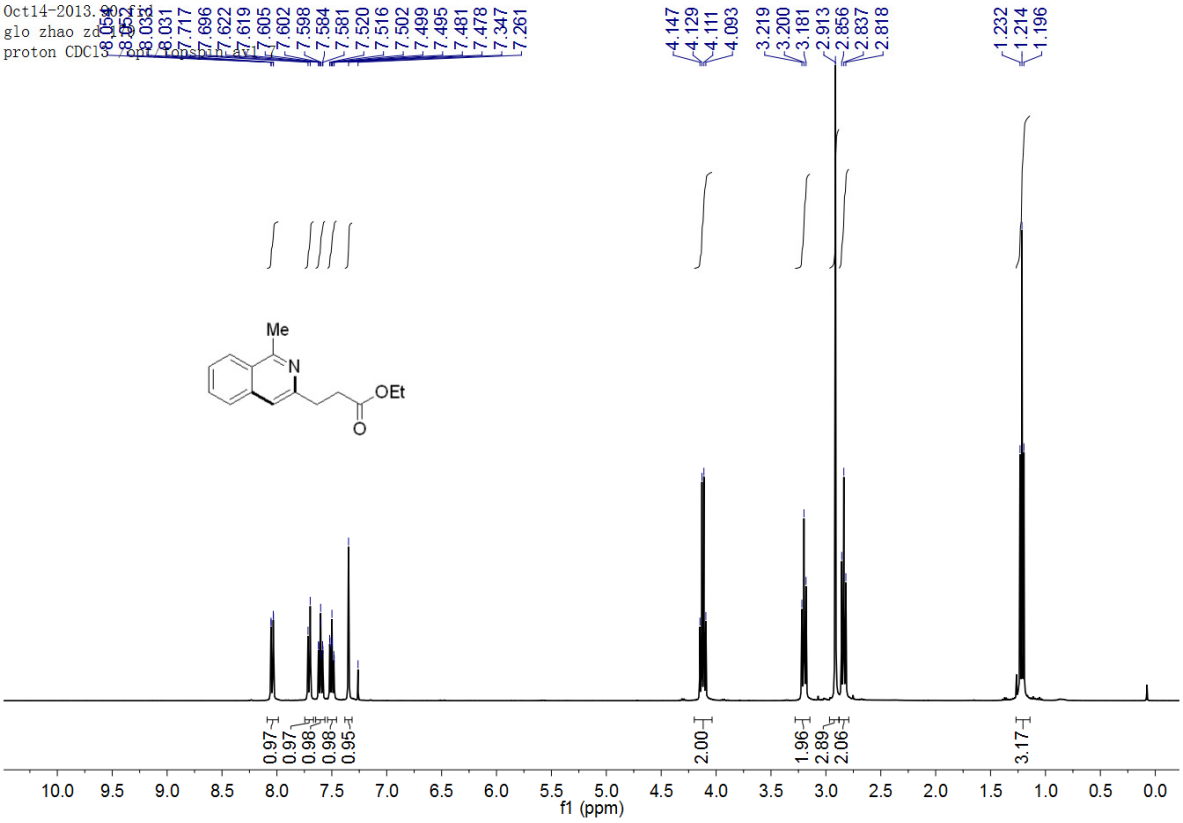


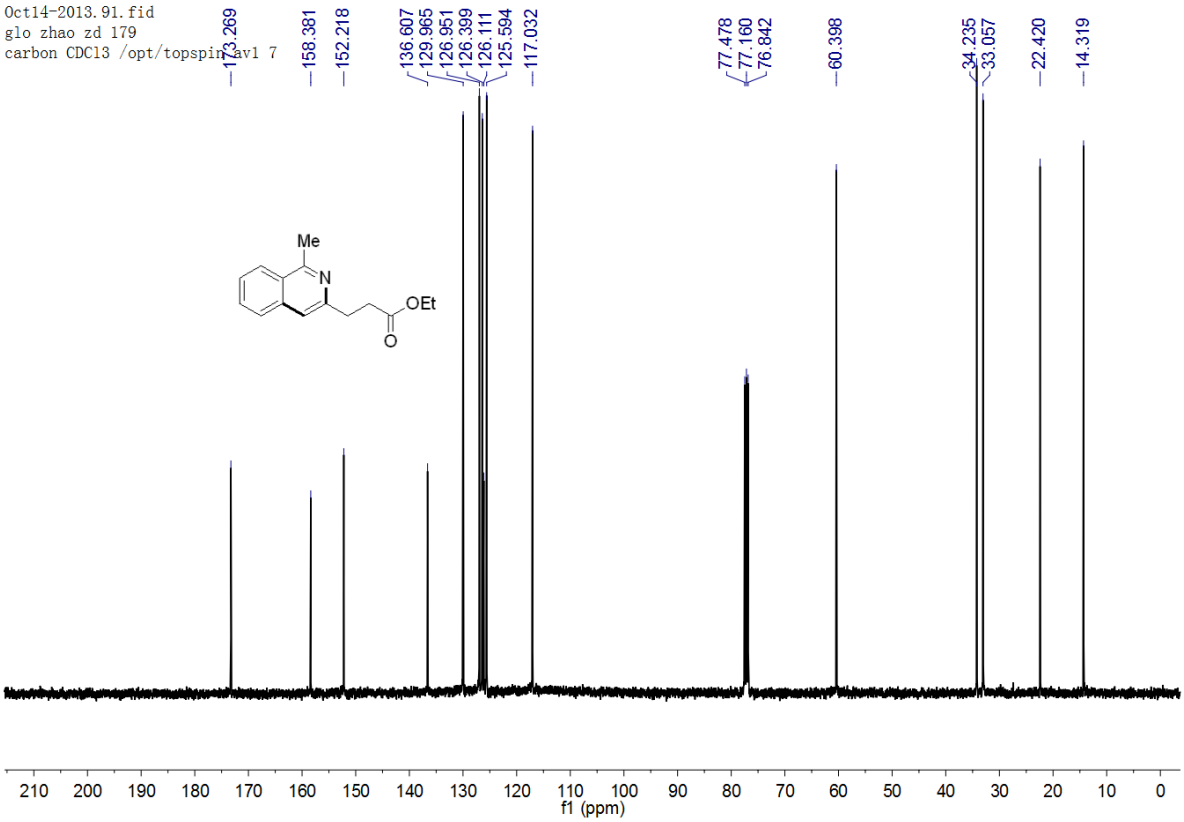
$[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %), $AgSbF_6$ (10.3 mg, 0.03 mmol), PivOH (0.6 mmol), **1a** (0.20 mmol) or **1a-D5** (0.20 mmol), **2a** (40.0 mg, 0.25 mmol) and DCE (1.0 mL) were added in two separated Schlenk tubes. They were stirred at 100 ºC under Ar for 10 minutes, then immediately quenched with DCM at the same time. Then two reaction mixtures were combined and the volatiles were removed under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: pentane/ethyl acetate = 2:1) to afford **4a** and **4a-D4**. The ratio of **4a** and **4a-D4** was determined by ^{1}H NMR to be 1.4 : 1 (The details in the way to calculate KIE and deuterium scrambling is presented in the Page S54).

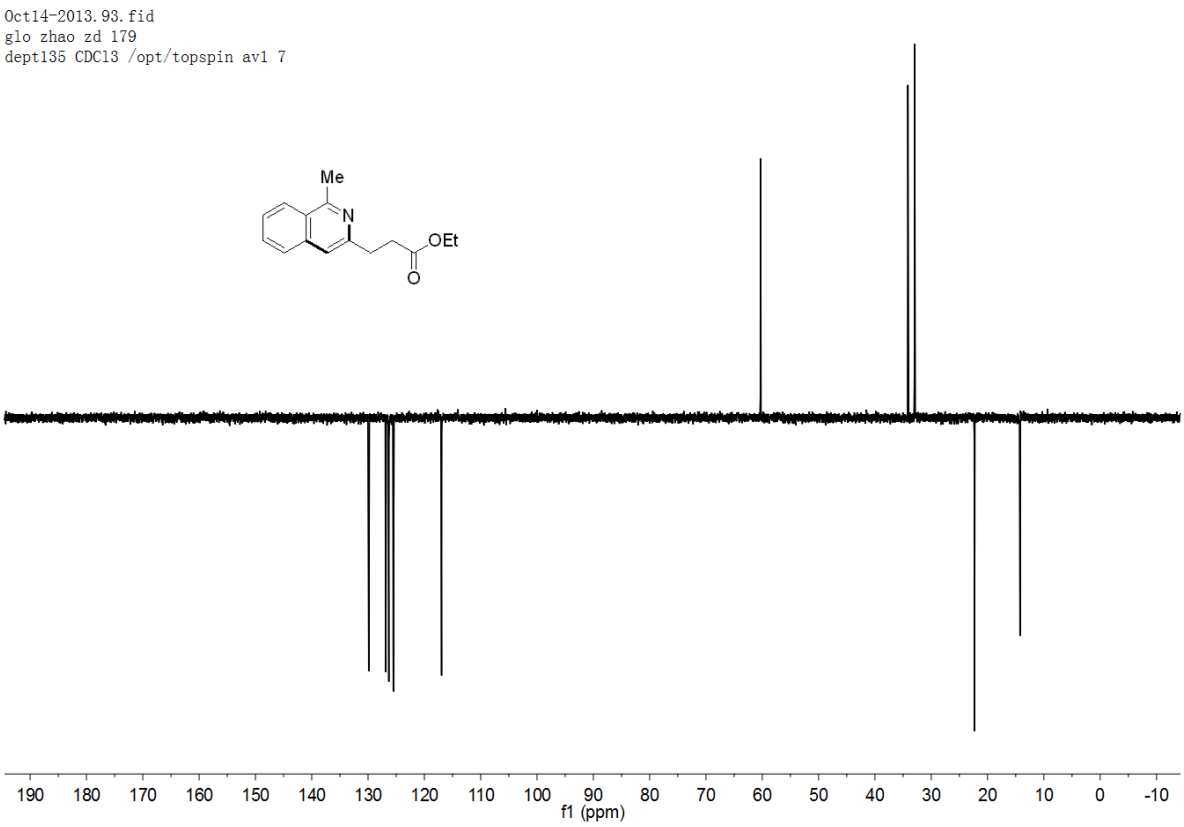
6 References

[1] a) P. C. Too, Y.-F. Wang, S. Chiba, *Org.Lett.* **2010**, *12*, 5688; b) N. Guimond, S. Gorelsky, K. Fagnou, *J. Am. Chem. Soc.* **2011**, *133*, 6449.

7 NMR spectra



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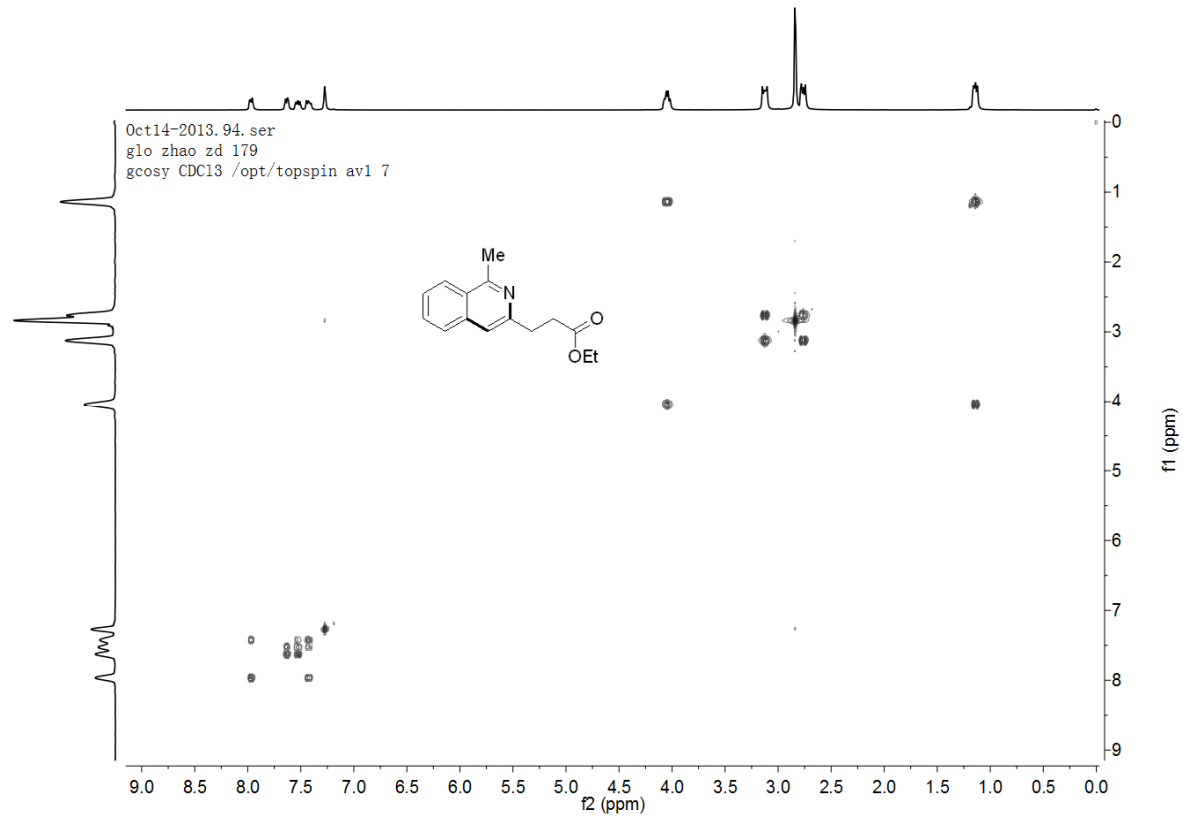
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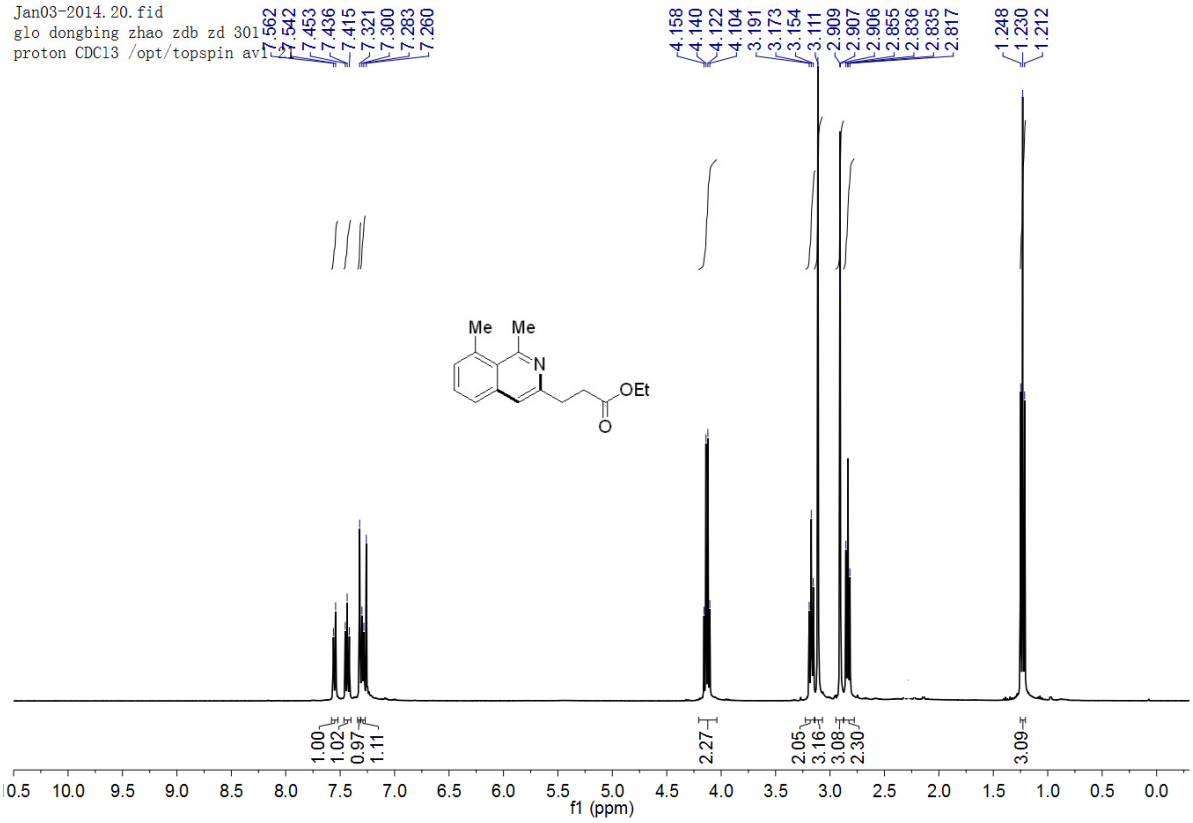
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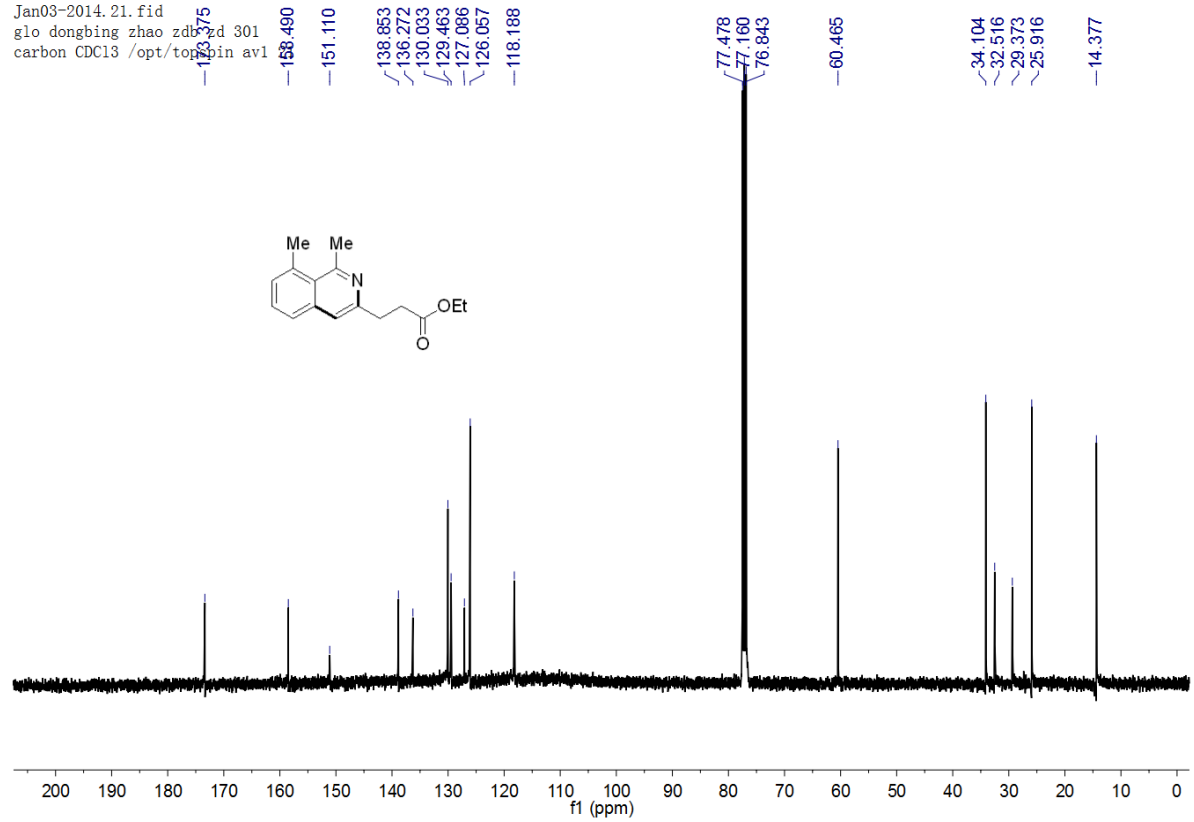
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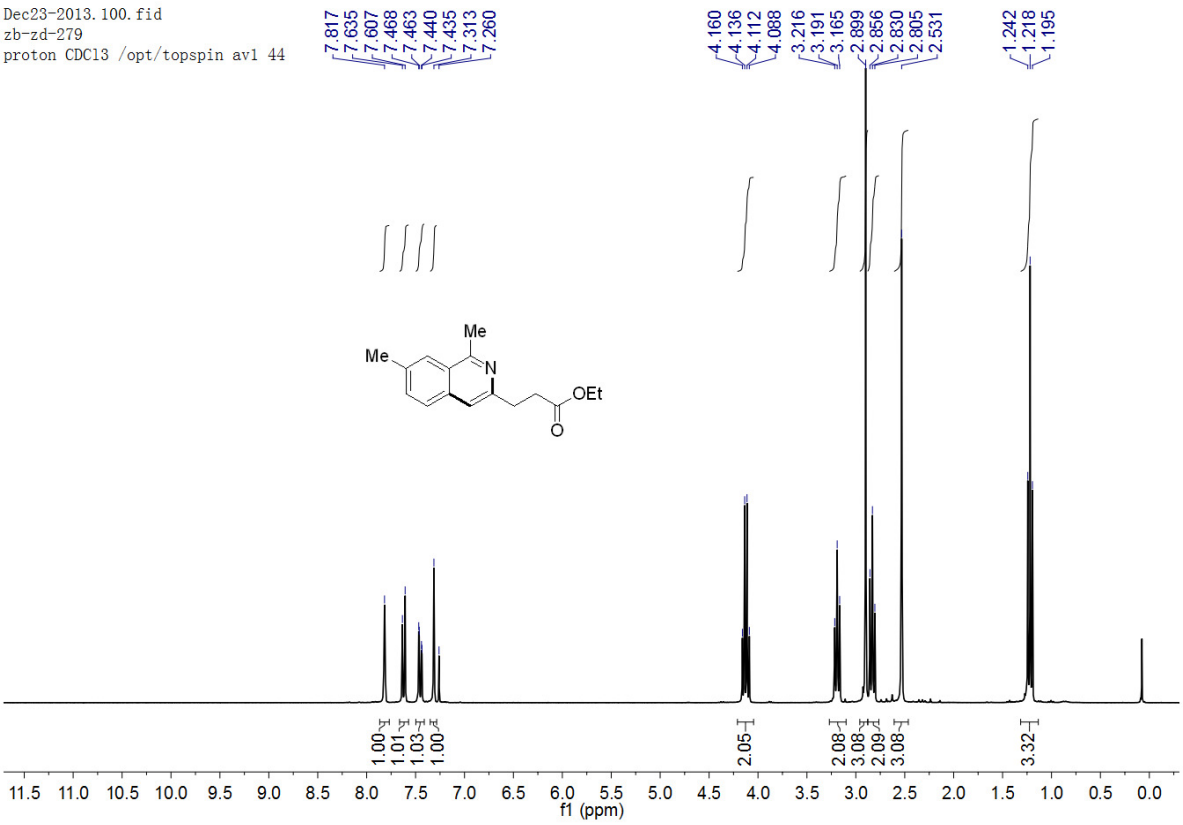
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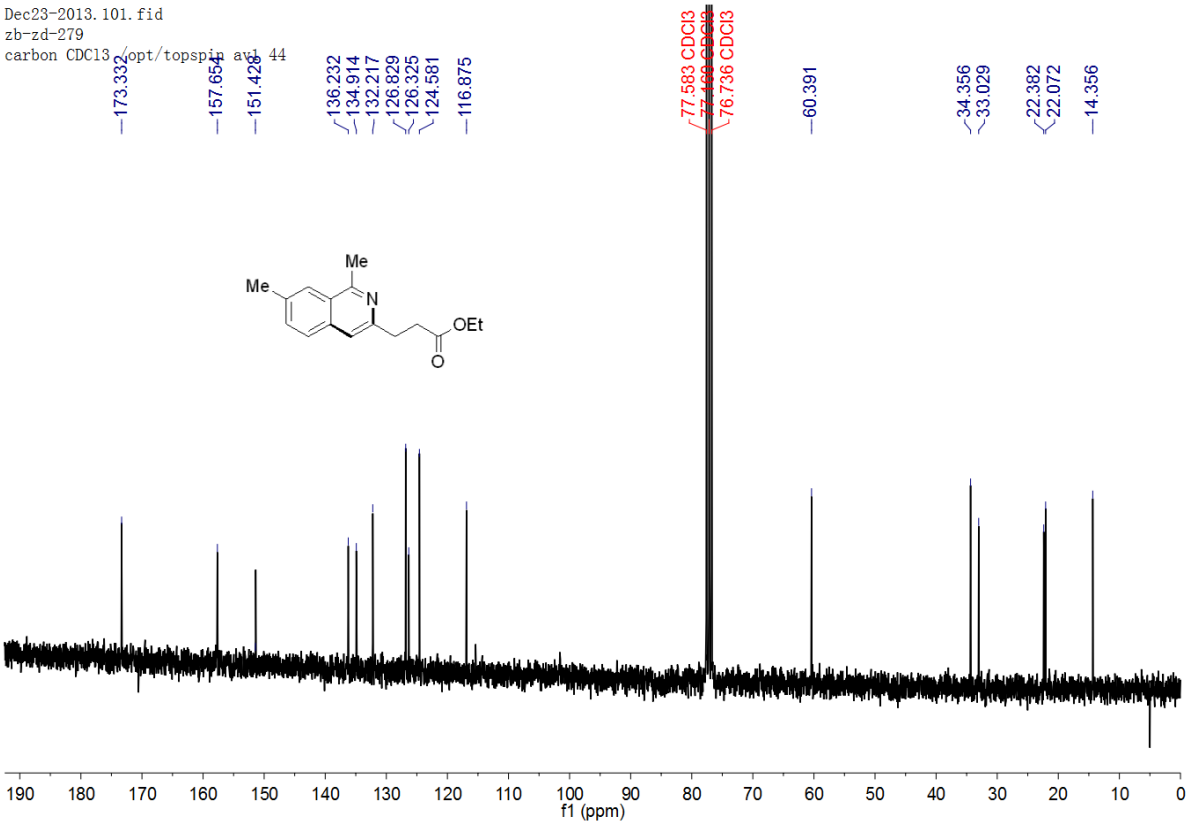
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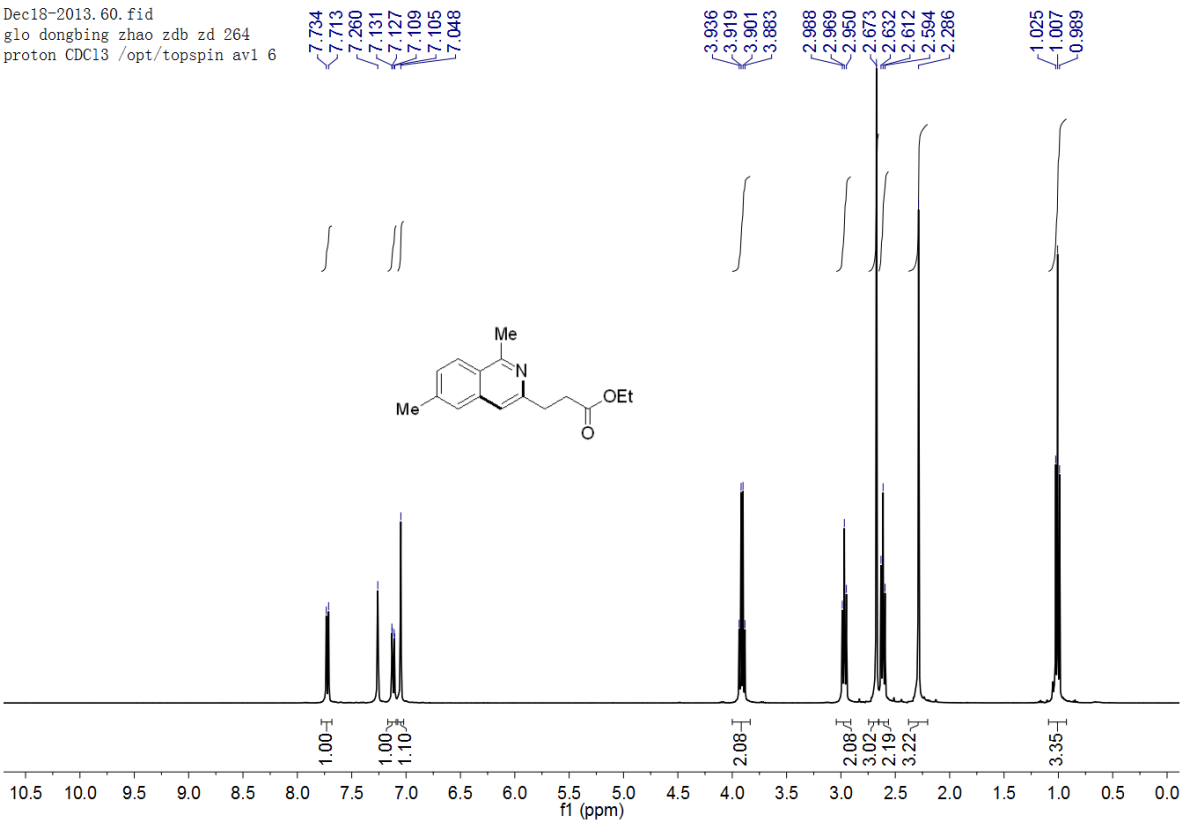
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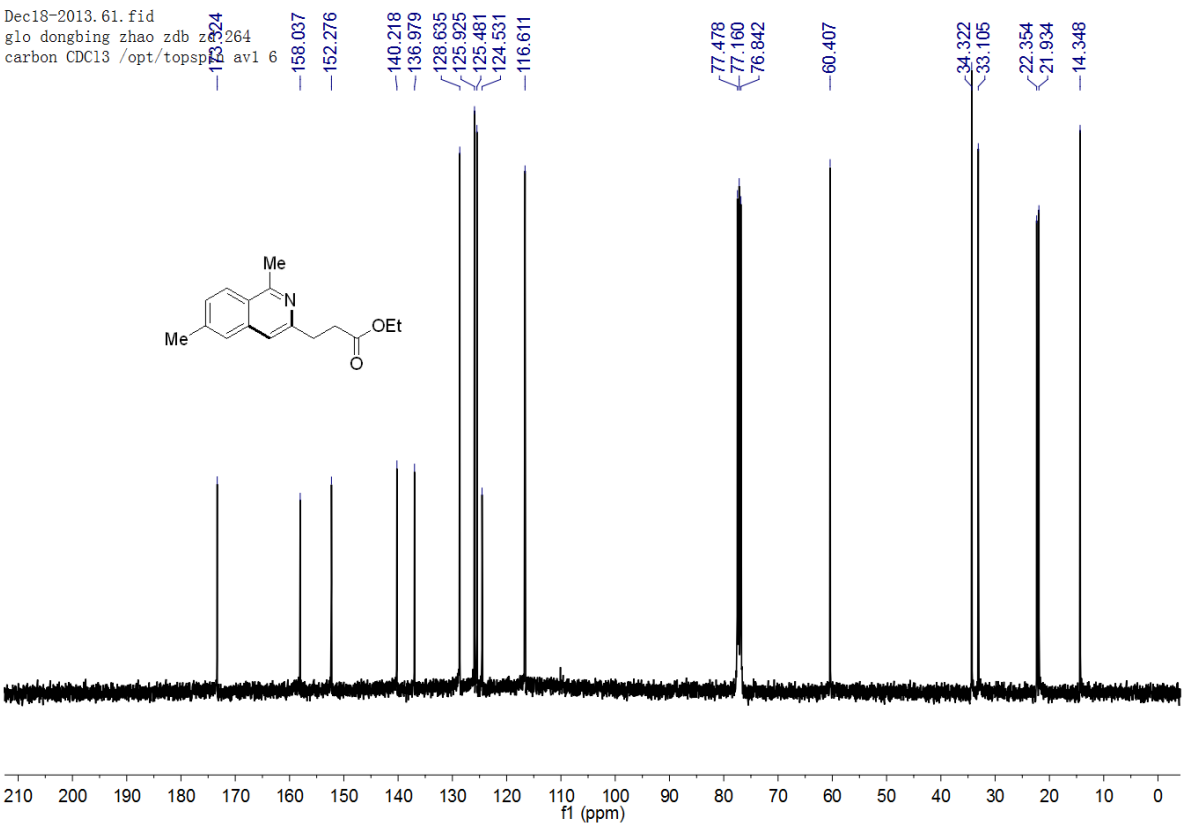
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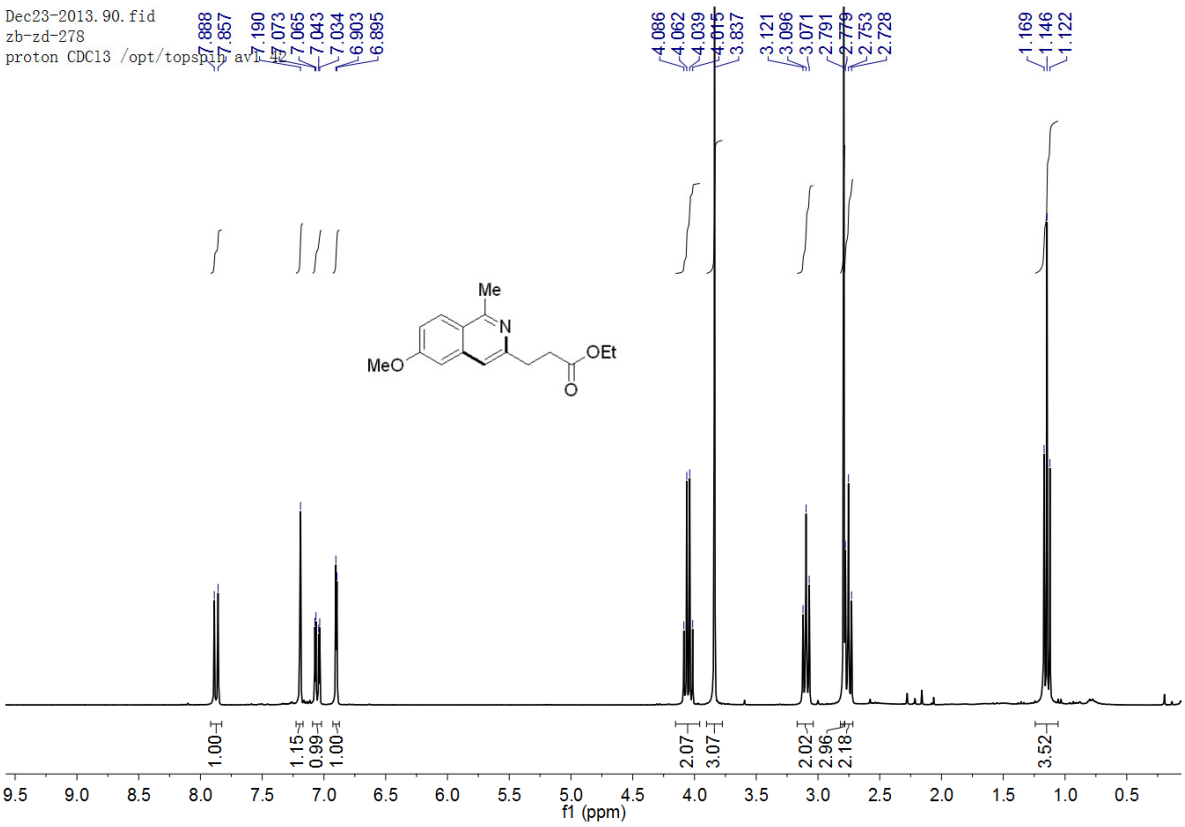
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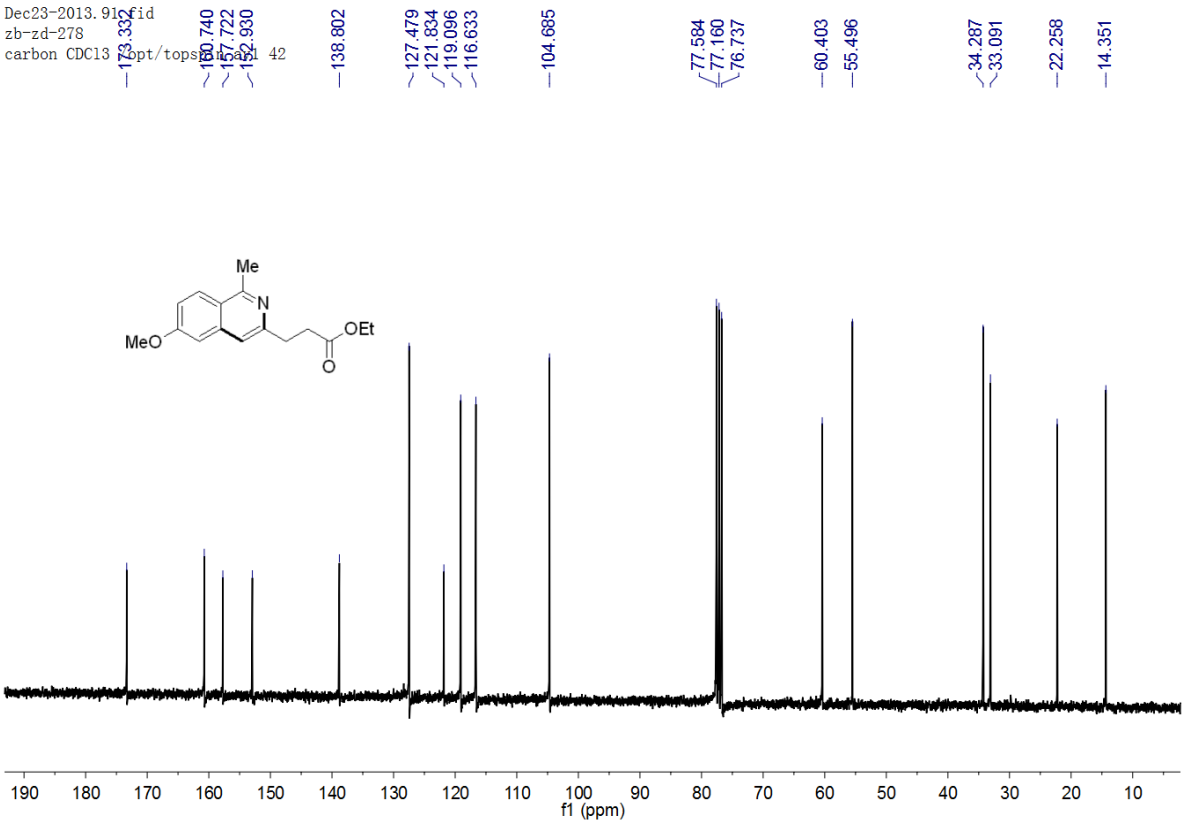
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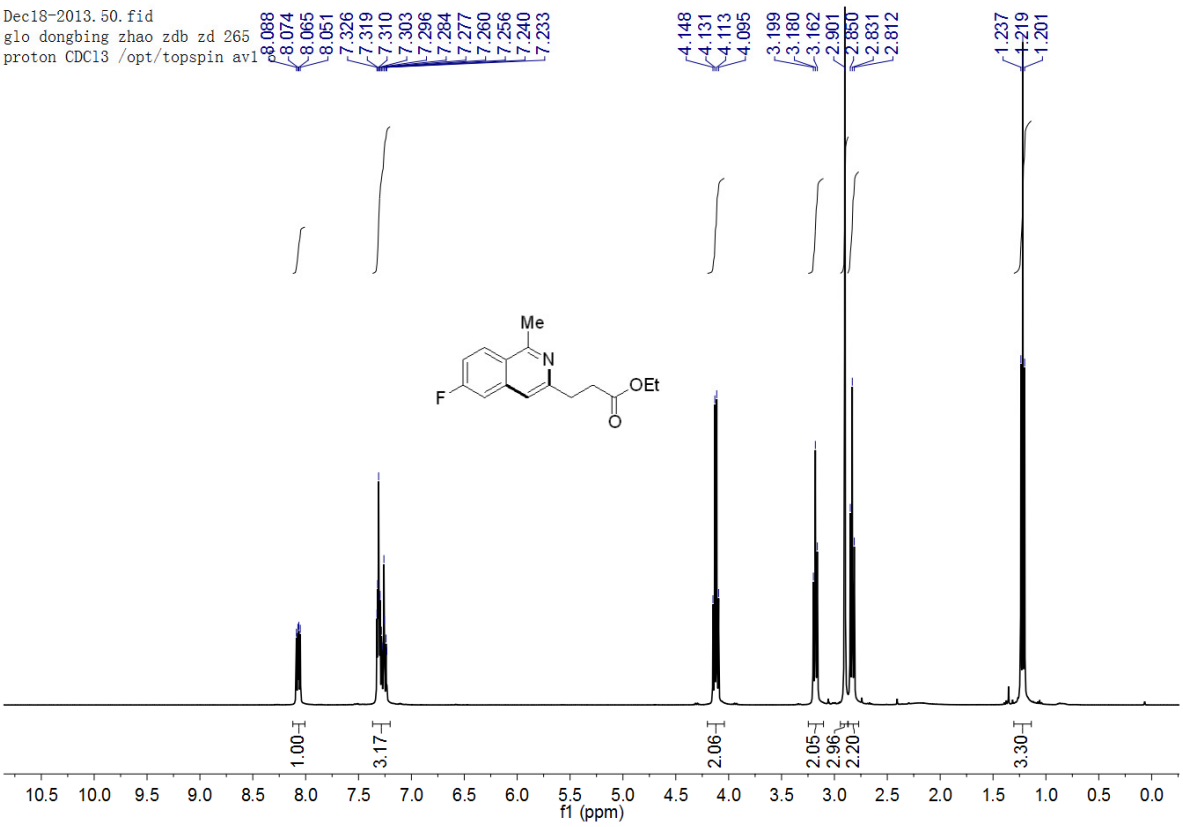
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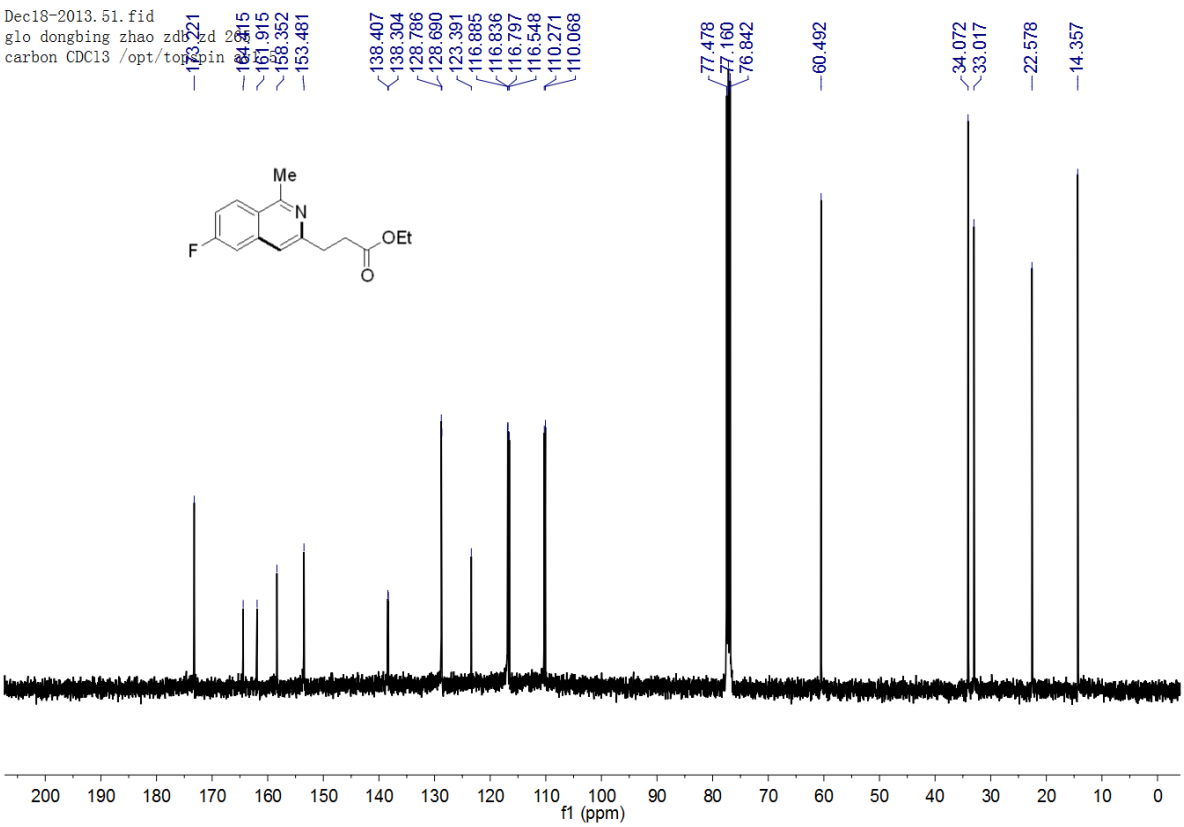
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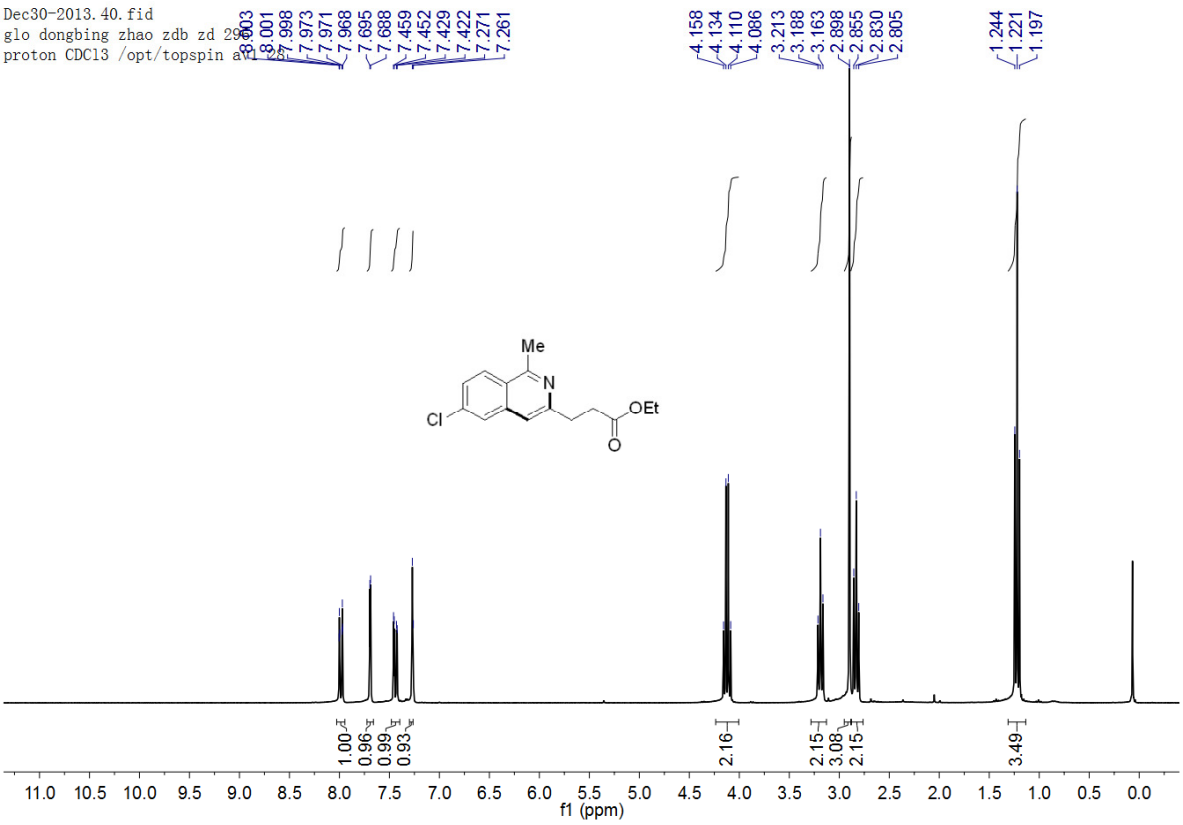
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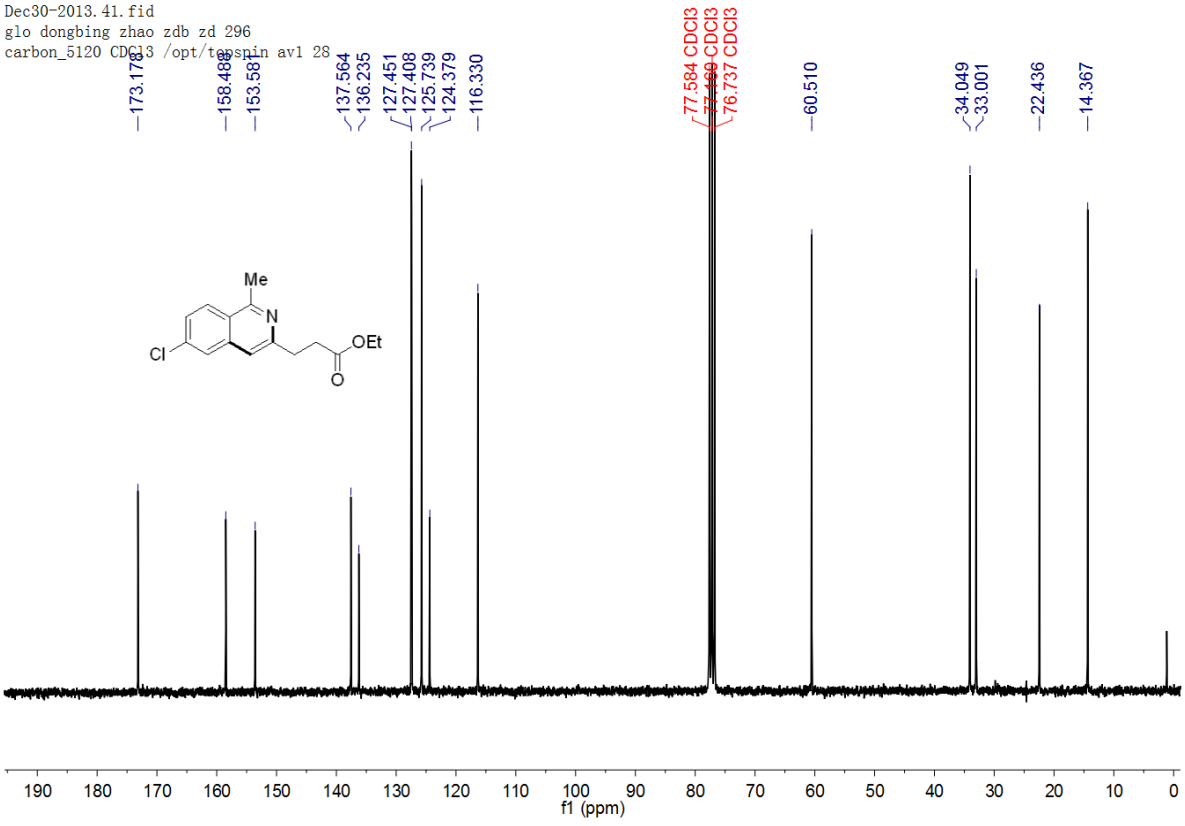
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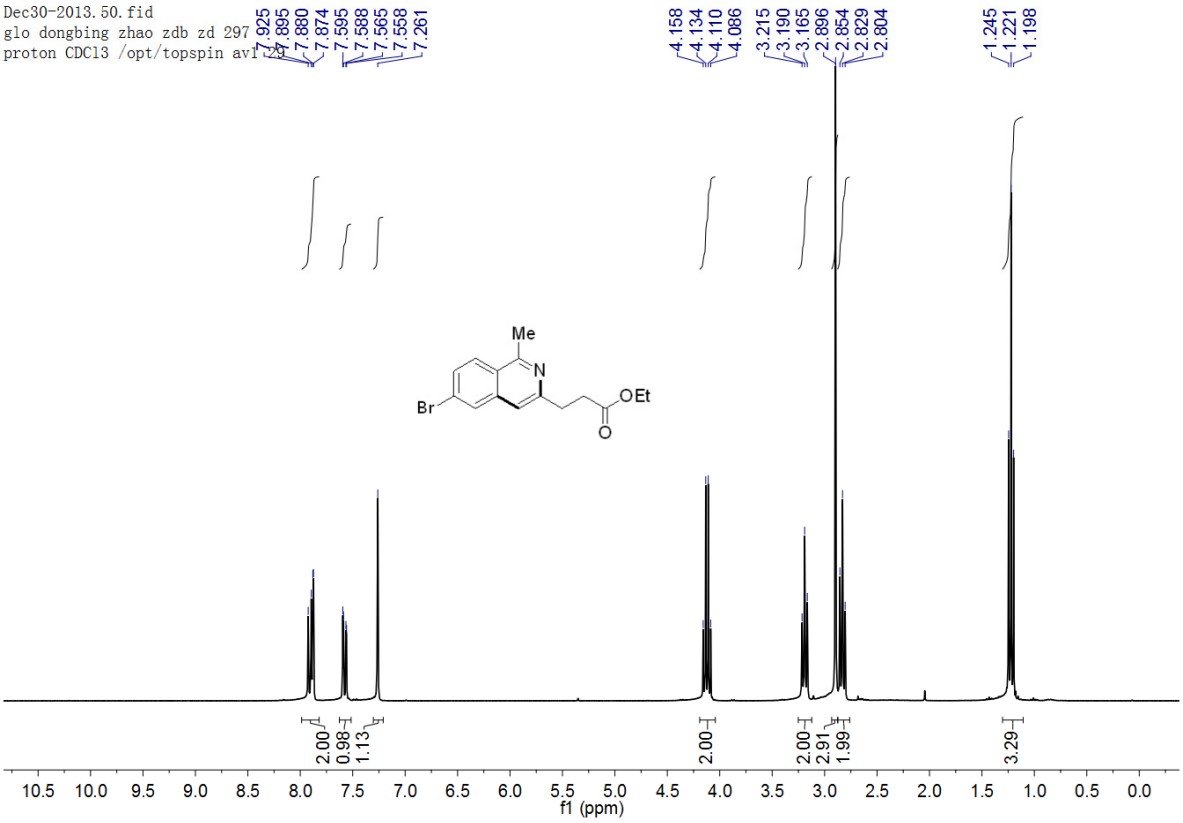
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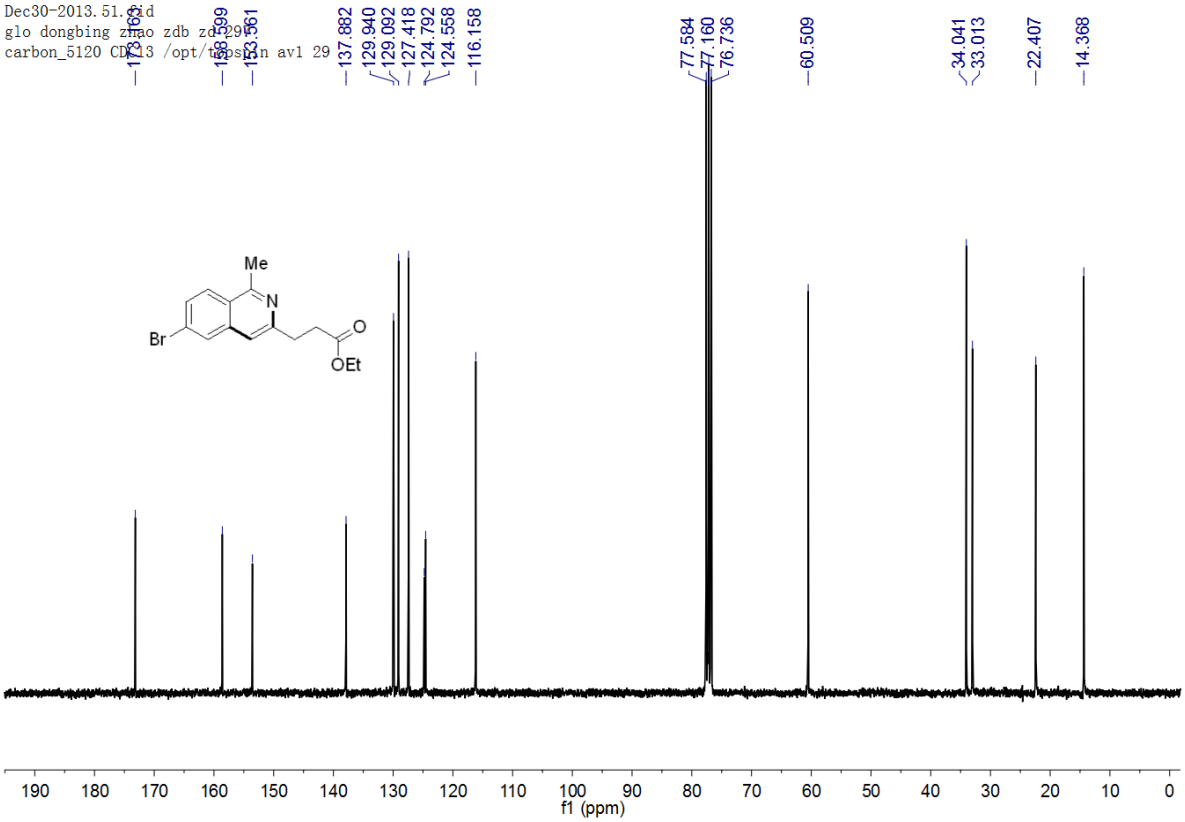
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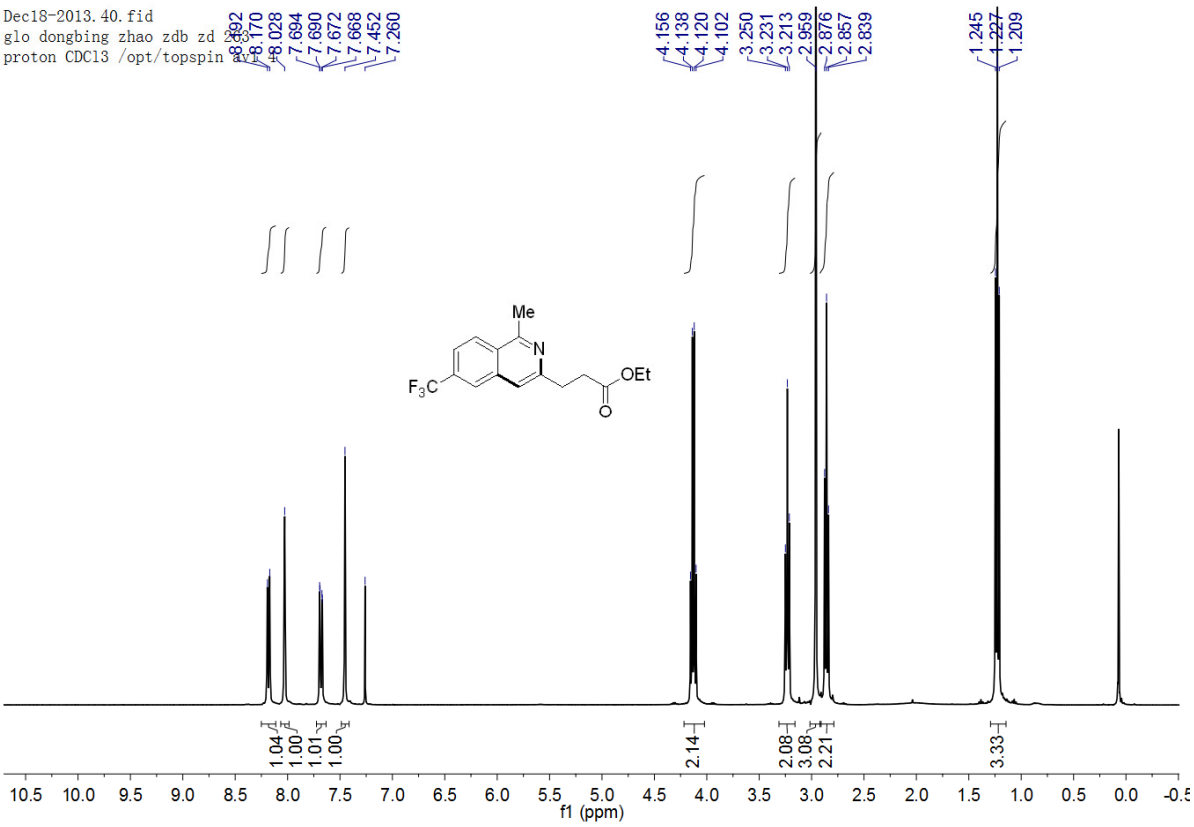
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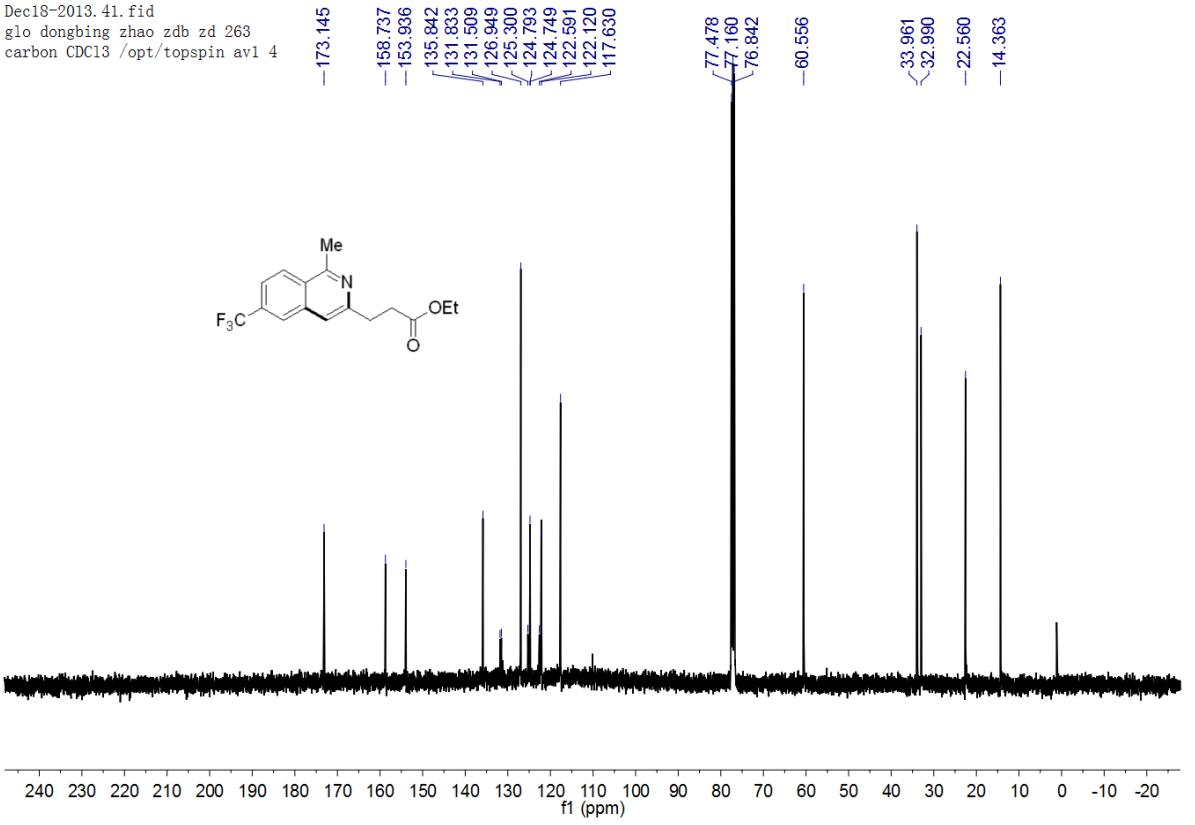
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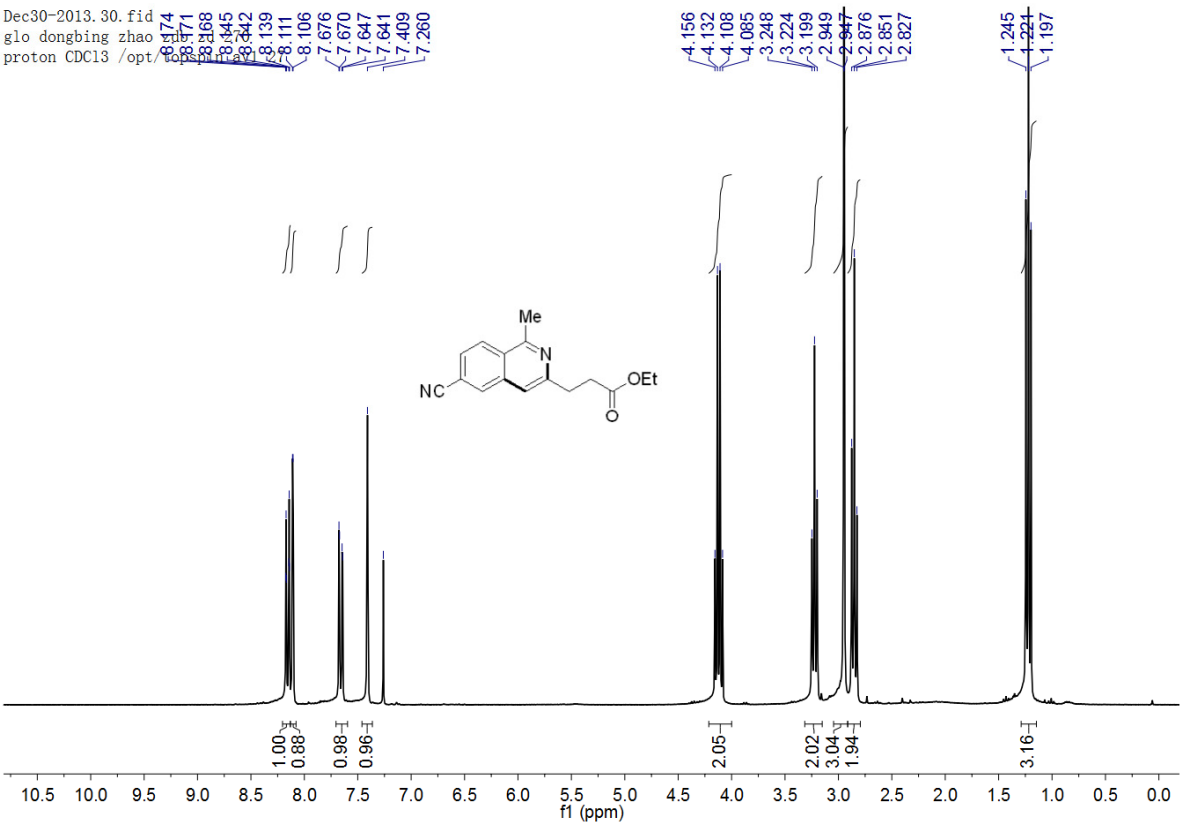
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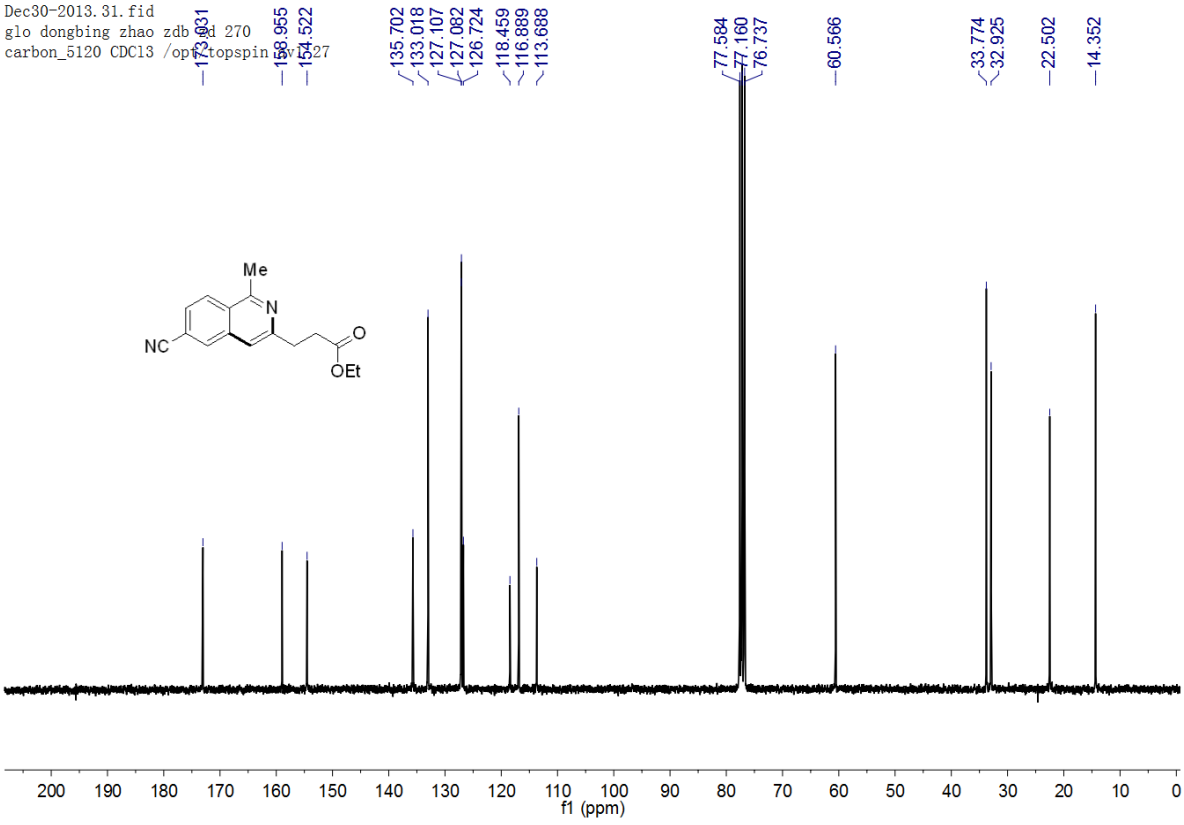
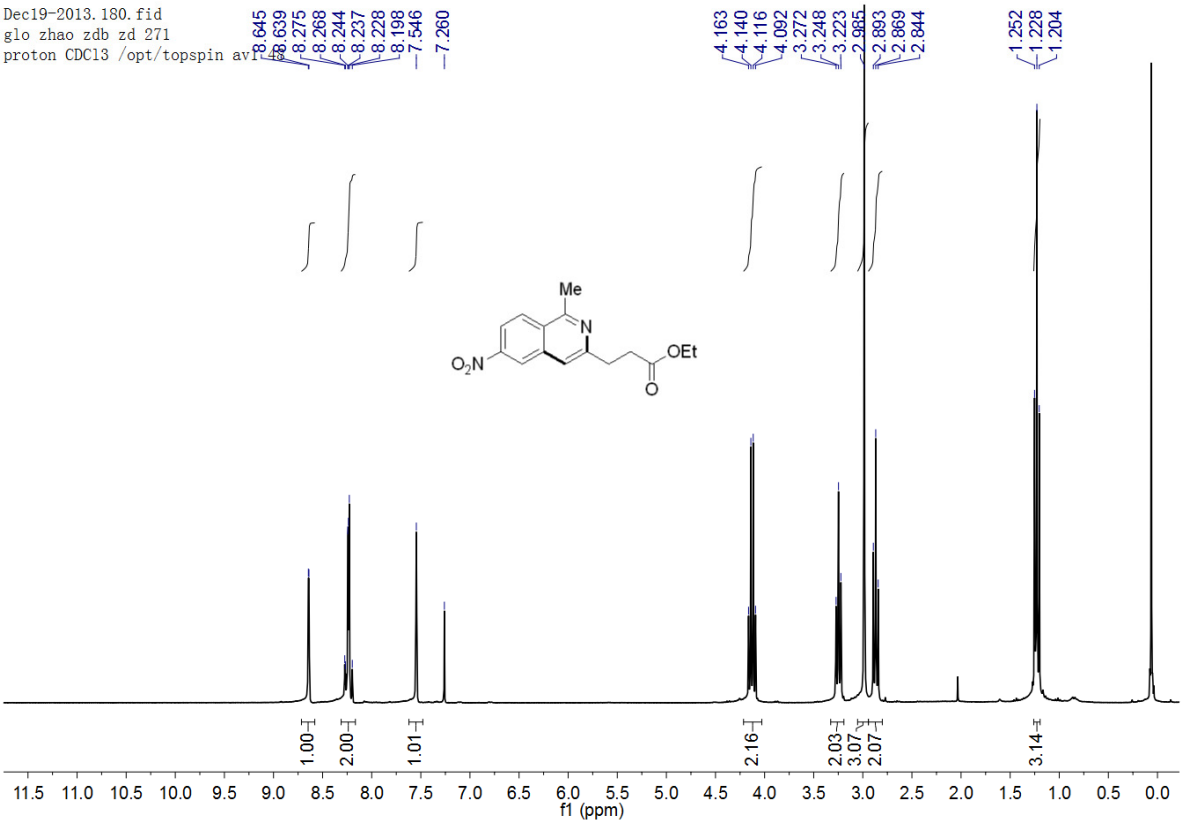
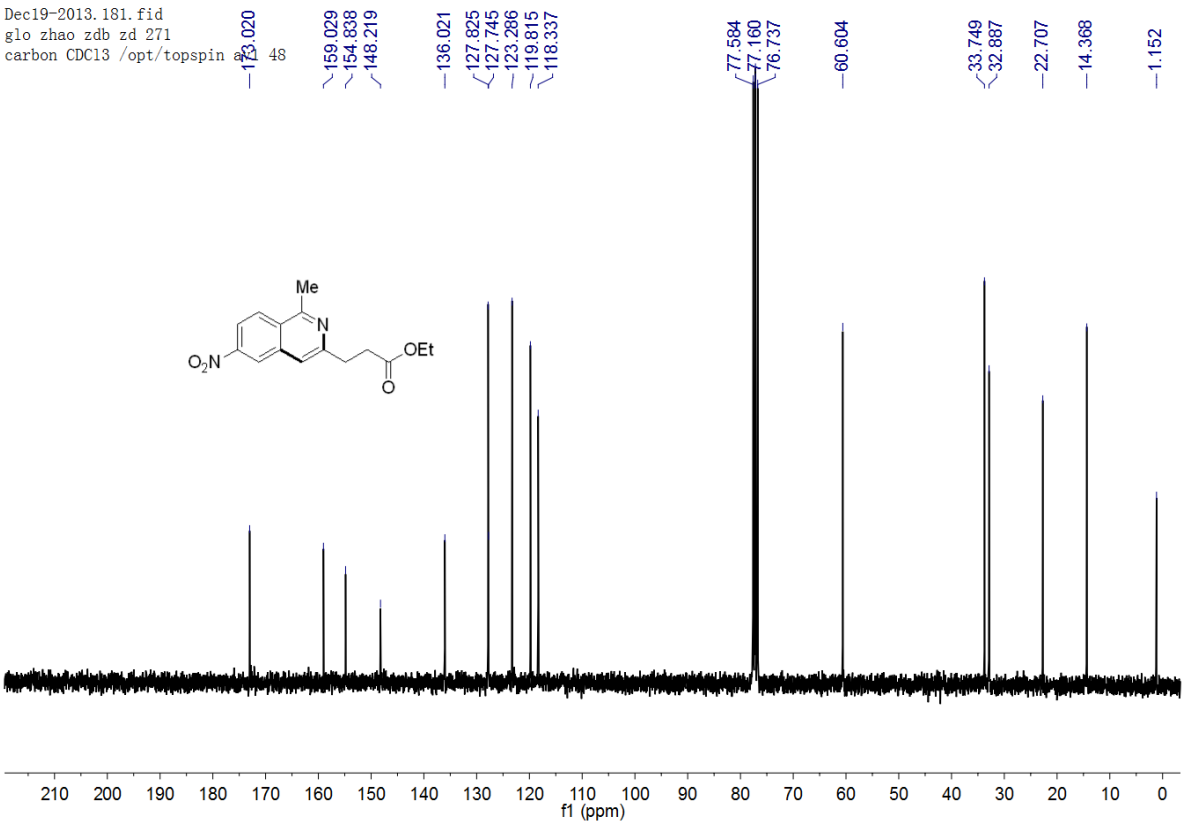
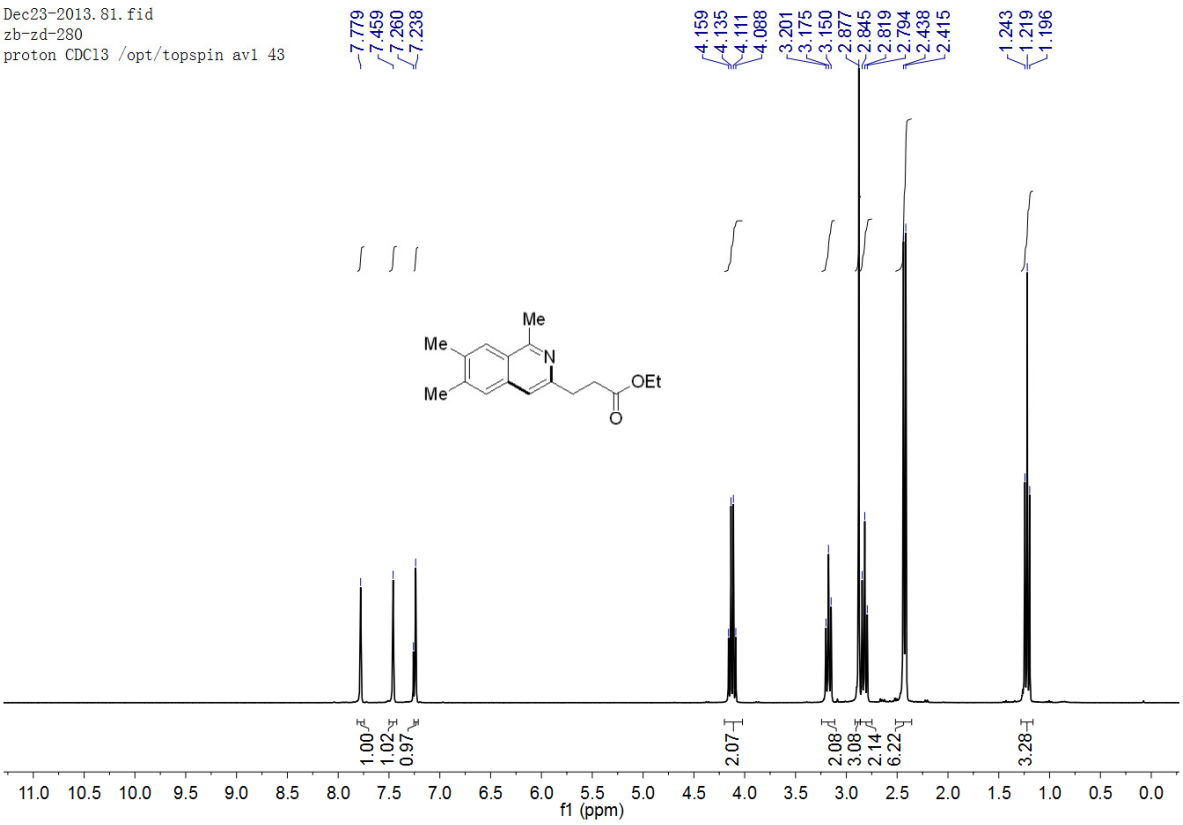
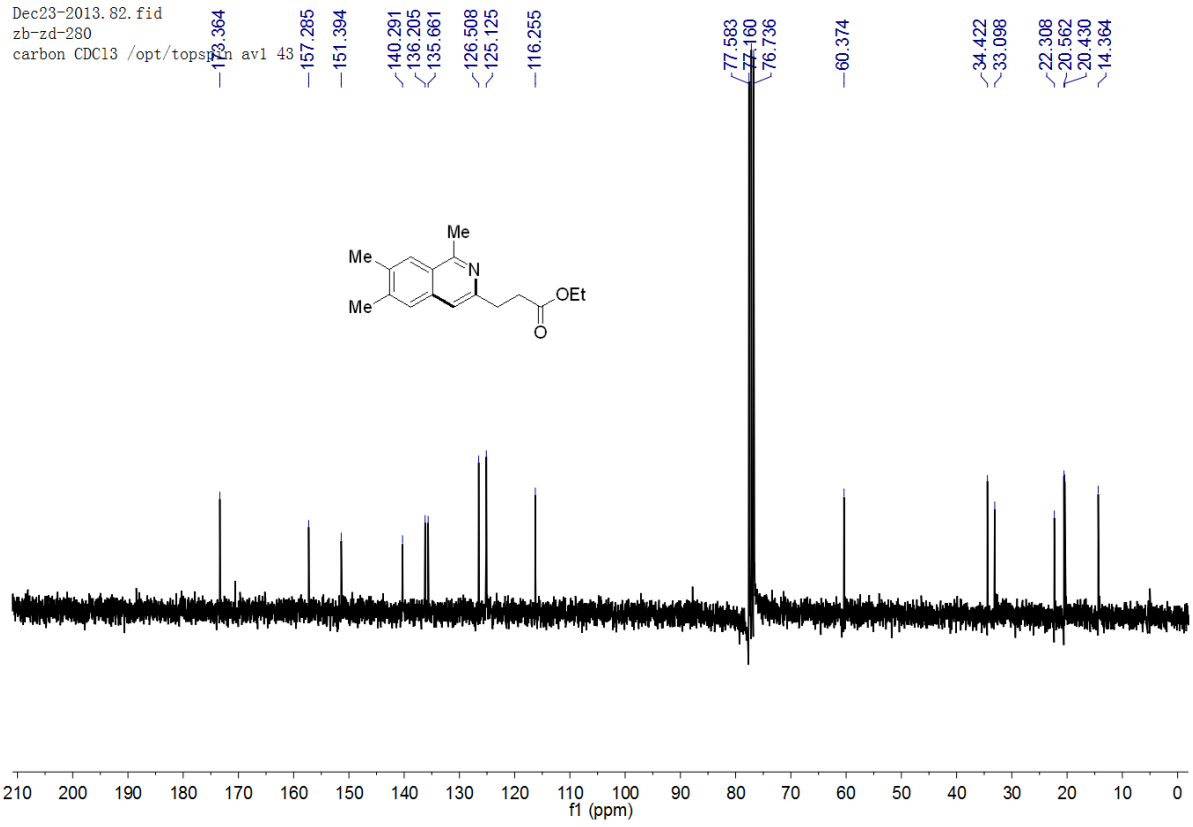
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

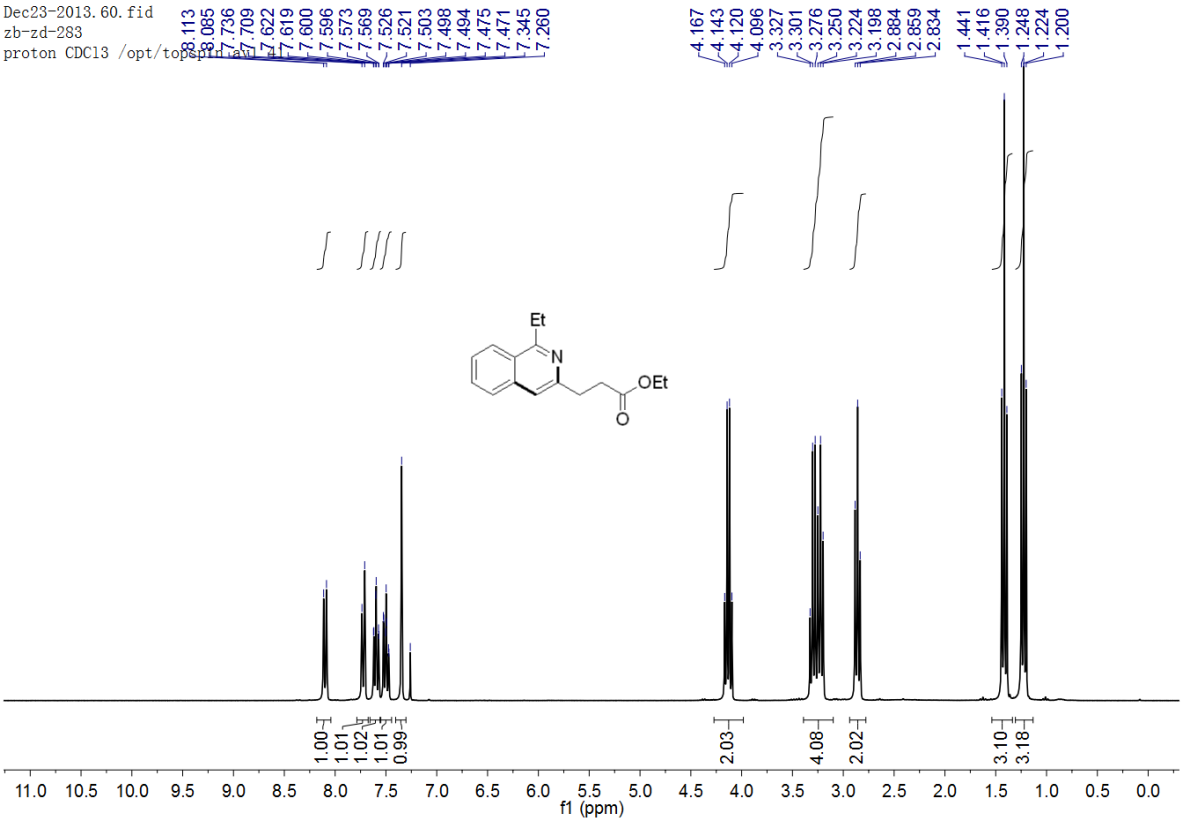

Dec30-2013.31.fid
glo dongbing zhao zdb 90 270
carbon_5120 CDCl3 /opt/topspin4.0.7
173.031
158.955
154.522
135.702
133.018
127.107
127.082
126.724
118.459
116.889
113.688
77.584
77.160
76.737
60.566
33.774
32.925
22.502
14.352
Me
N
NC
O
OEt
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

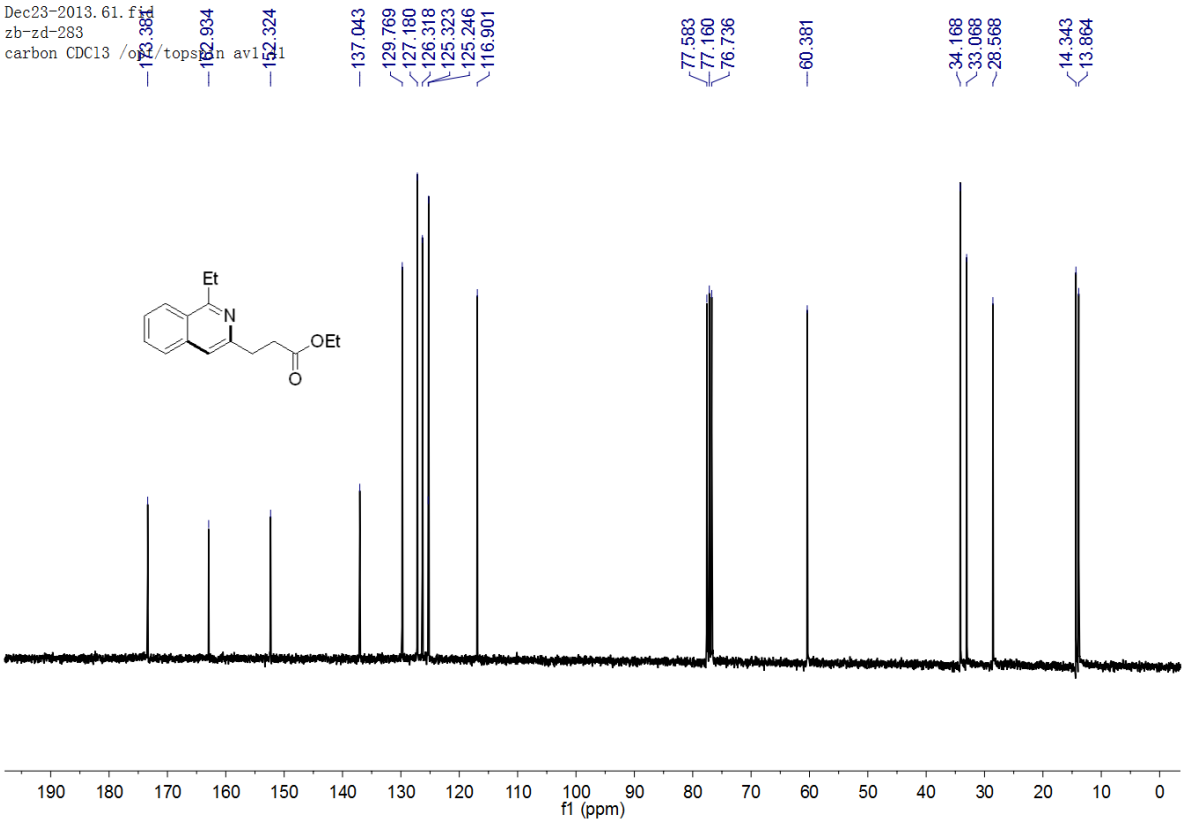

Dec19-2013.180.fid
glo zhao zdb zd 271
proton CDCl3 /opt/topspin av
8.645
8.639
8.275
8.268
8.244
8.237
8.228
8.198
7.546
7.260
4.163
4.140
4.116
4.092
3.272
3.248
3.223
2.985
2.893
2.869
2.844
1.252
1.228
1.204
Me
N
O2N
OEt
O
1.00
2.00
1.01
2.16
2.03
3.07
2.07
3.14
f1 (ppm)

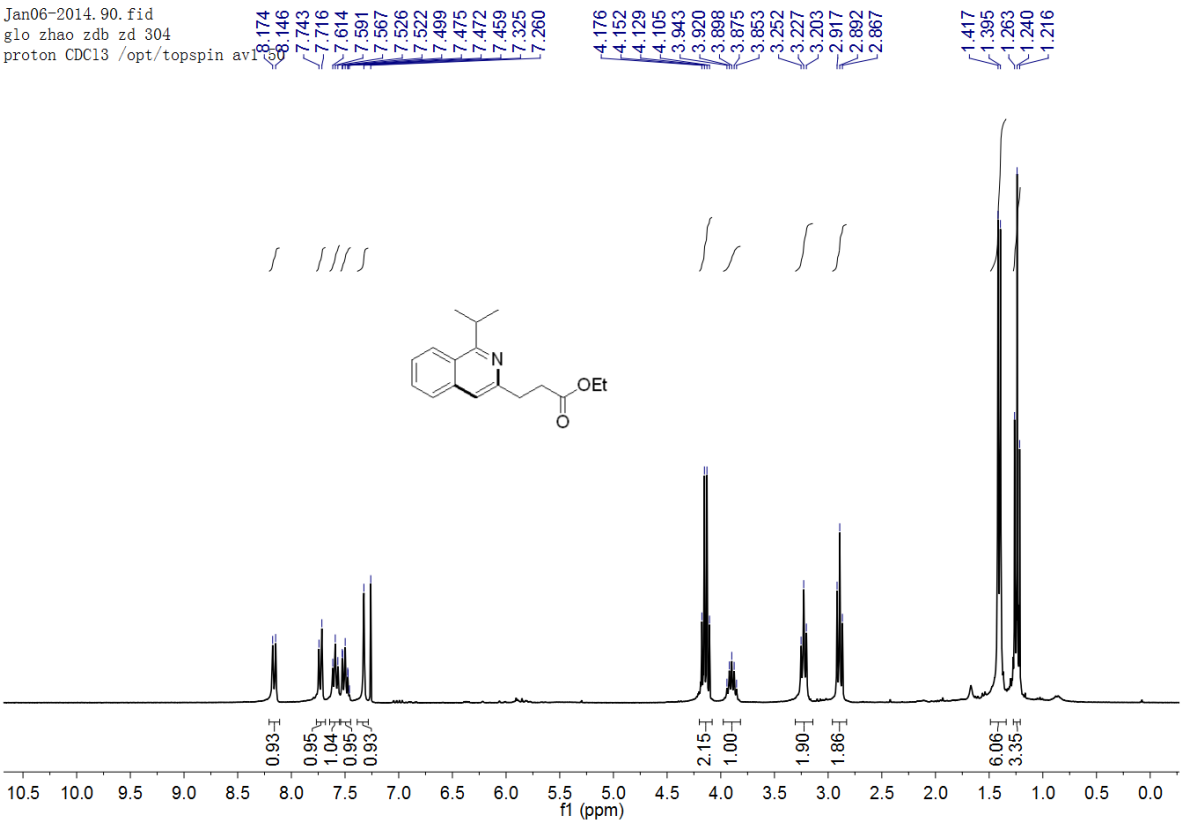

Dec19-2013.181.fid
glo zhao zdb zd 271
carbon CDCl3 /opt/topspin a
48
173.020
159.029
154.838
148.219
136.021
127.825
127.745
123.286
119.815
118.337
77.584
77.160
76.737
60.604
33.749
32.887
22.707
14.368
1.152
Me
N
O2N
OEt
O
f1 (ppm)

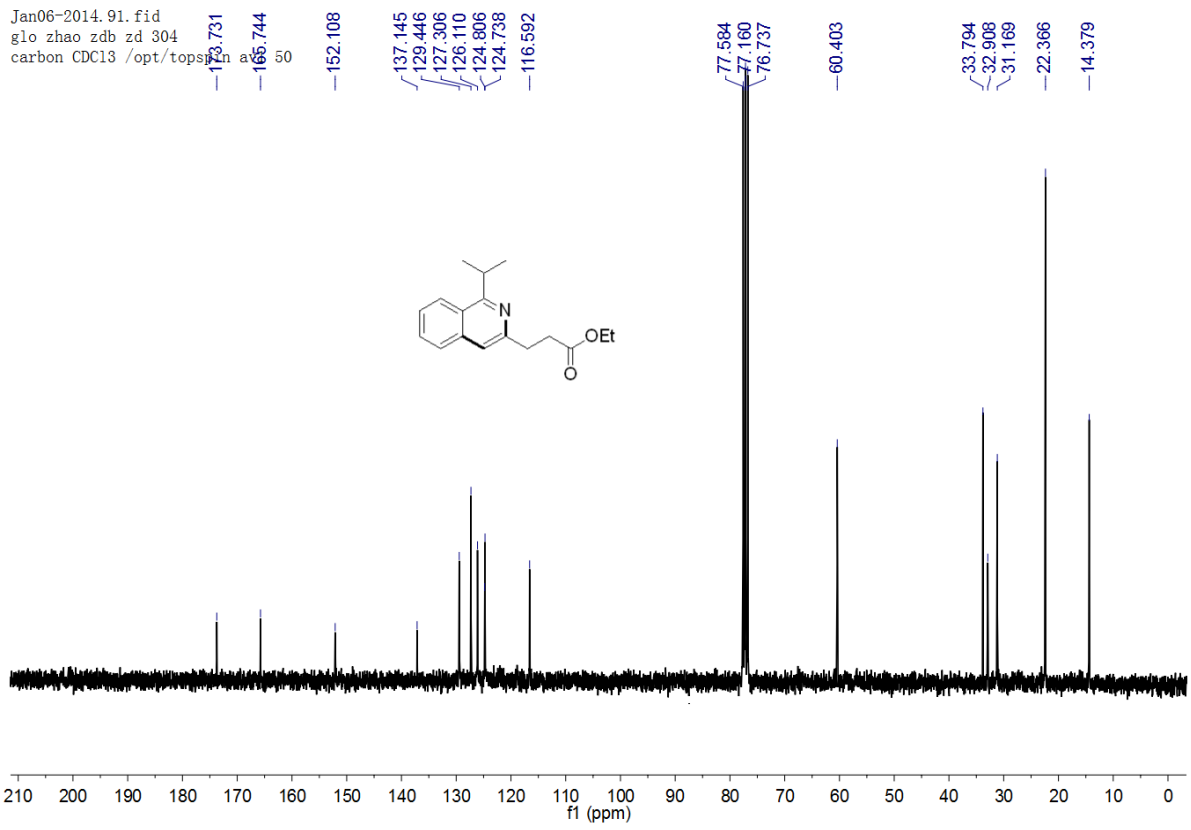

Dec23-2013.81.fid
zb-zd-280
proton CDCl3 /opt/topspin av1 43
7.779
7.459
7.260
7.238
4.159
4.135
4.111
4.088
3.201
3.175
3.150
2.877
2.845
2.819
2.794
2.438
2.415
1.243
1.219
1.196
Me
Me
Me
N
OEt
O
1.00
1.02
0.97
2.07
2.08
3.08
2.14
6.22
3.28
f1 (ppm)

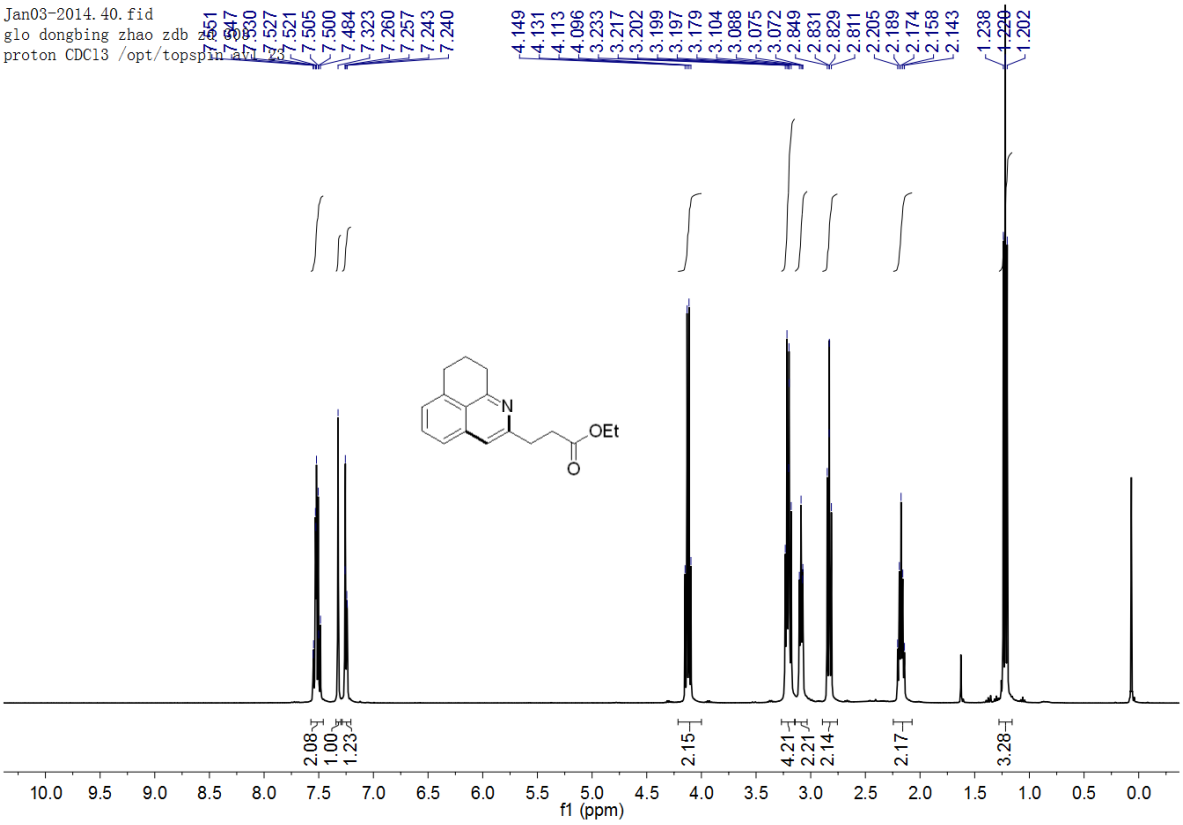

Dec23-2013.82.fid
zb-zd-280
carbon CDCl3 /opt/topspin av1 43
173.364
157.285
151.394
140.291
136.205
135.661
126.508
125.125
116.255
77.583
77.160
76.736
60.374
34.422
33.098
22.308
20.562
20.430
14.364
Me
Me
Me
N
OEt
O
f1 (ppm)

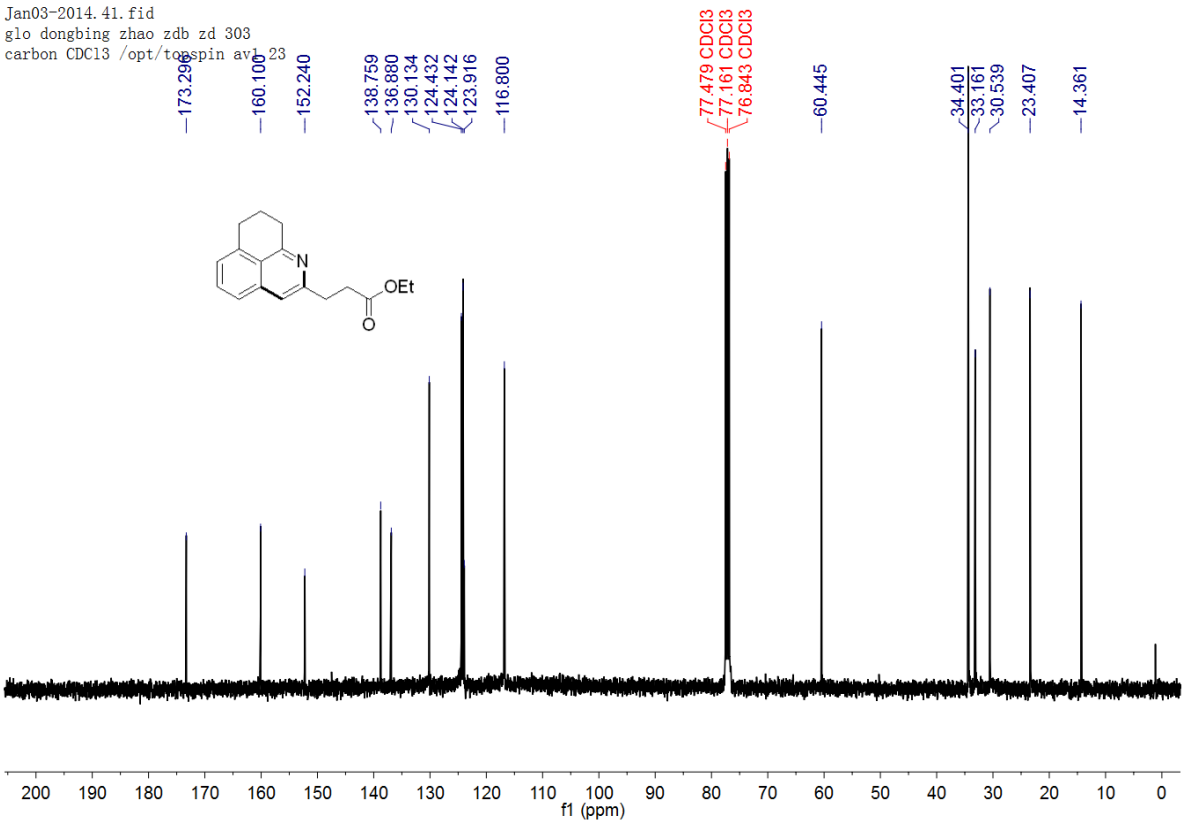

Dec23-2013.60.fid
zb-zd-283
proton CDCl3 /opt/topspin avi 1
8.113
8.085
7.736
7.709
7.622
7.619
7.600
7.596
7.573
7.569
7.526
7.521
7.503
7.498
7.494
7.475
7.471
7.345
7.260
4.167
4.143
4.120
4.096
3.327
3.301
3.276
3.250
3.224
3.198
2.884
2.859
2.834
1.441
1.416
1.390
1.248
1.224
1.200
Et
N
OEt
O
1.00
1.01
1.02
1.01
0.99
2.03
4.08
2.02
3.10
3.18
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

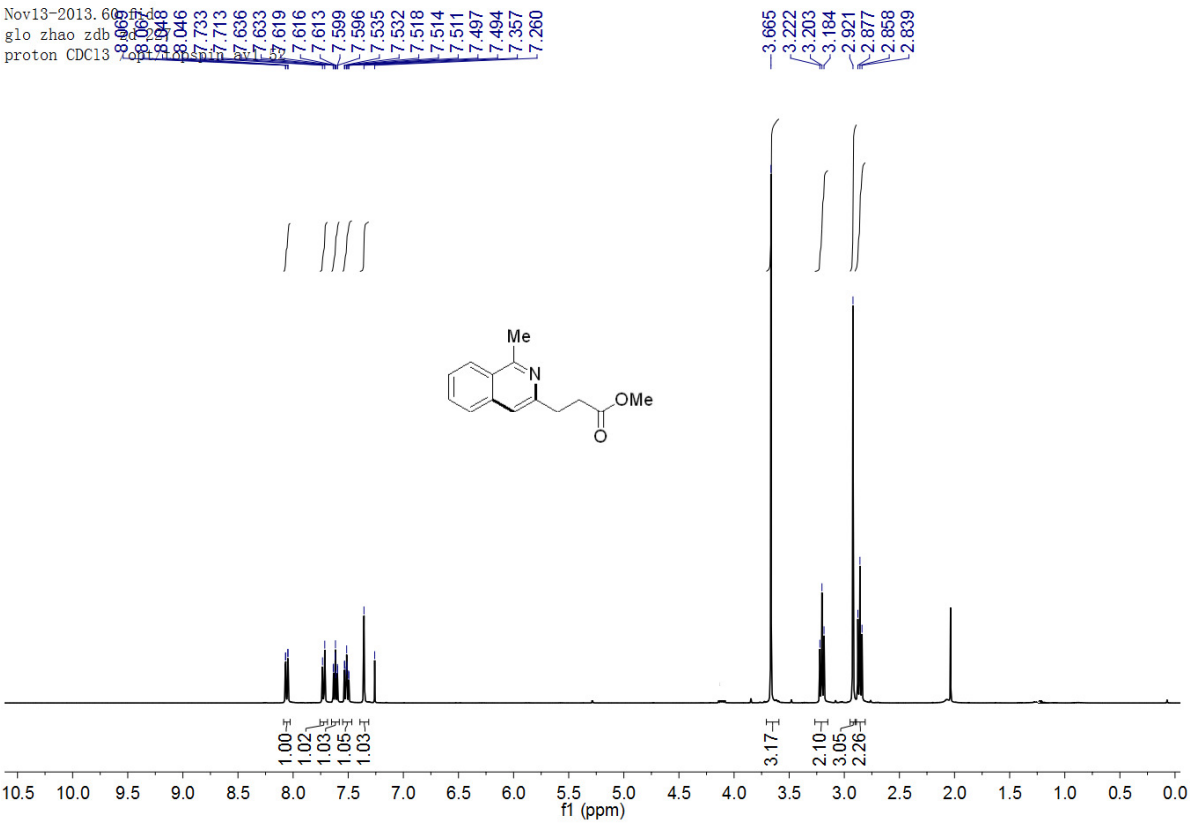

Dec23-2013.61.fid
zb-zd-283
carbon CDCl3 /opt/topspin avi 1
173.384
152.934
152.324
137.043
129.769
127.180
126.318
125.323
125.246
116.901
77.583
77.160
76.736
60.381
34.168
33.068
28.568
14.343
13.864
Et
N
OEt
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

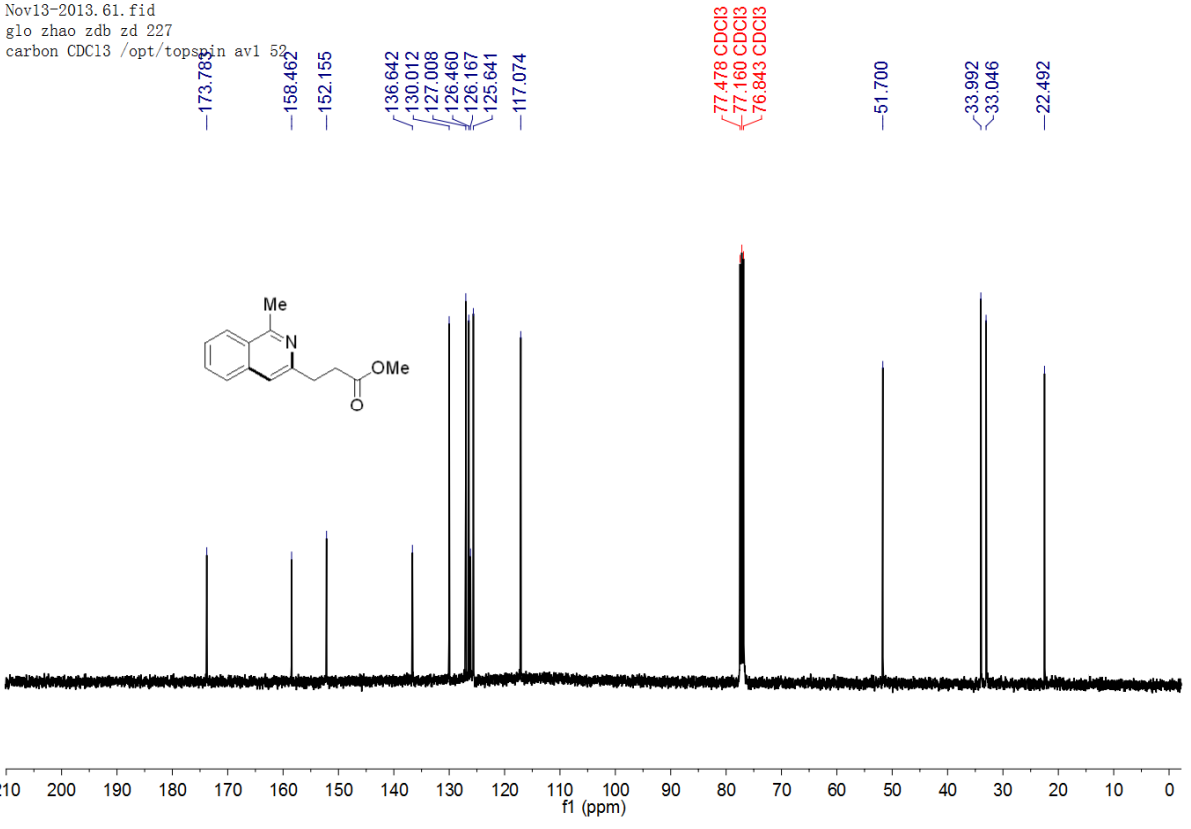

Jan06-2014.90.fid
glo zhao zdb zd 304
proton CDCl3 /opt/topspin avl
8.174
8.146
7.743
7.716
7.614
7.591
7.567
7.526
7.522
7.499
7.475
7.472
7.459
7.325
7.260
4.176
4.152
4.129
4.105
3.943
3.920
3.898
3.875
3.853
3.252
3.227
3.203
2.917
2.892
2.867
1.417
1.395
1.263
1.240
1.216
N
OEt
O
0.93
0.95
1.04
0.95
0.93
2.15
1.00
1.90
1.86
6.06
3.35
f1 (ppm)

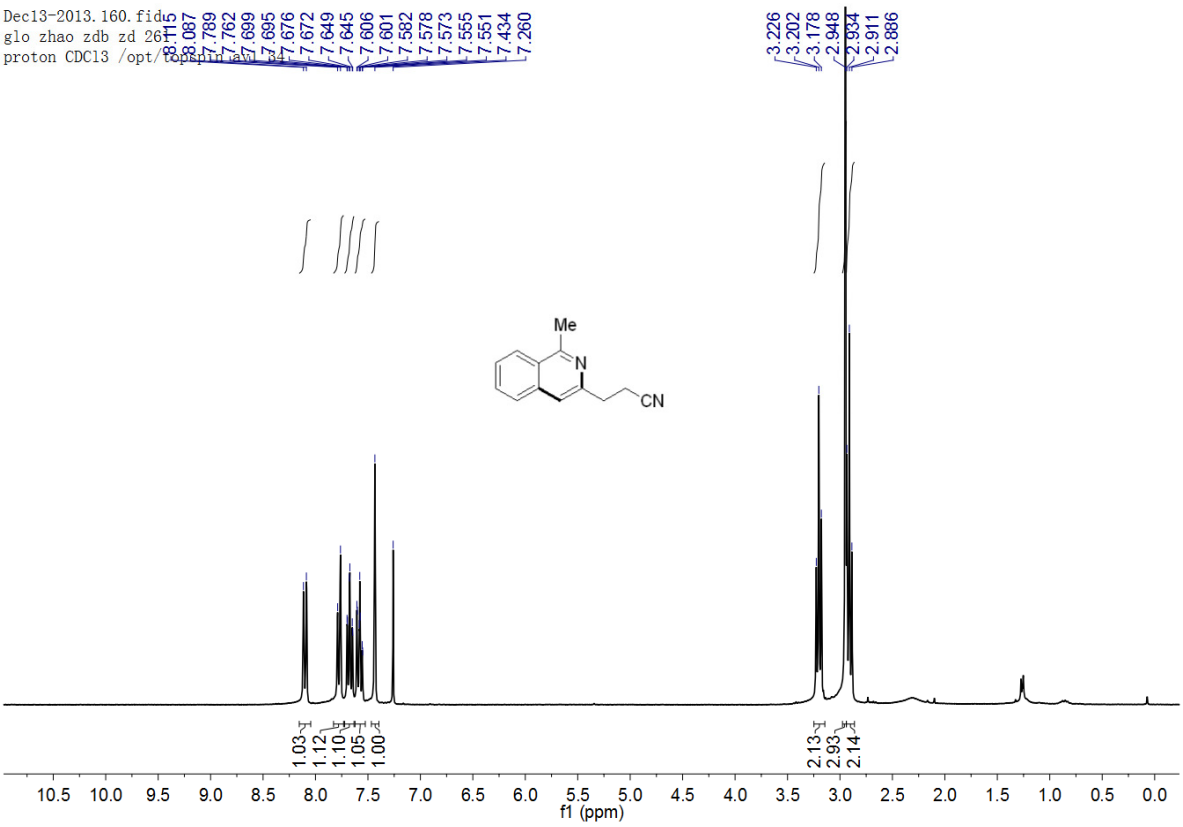

Jan06-2014.91.fid
glo zhao zdb zd 304
carbon CDCl3 /opt/topspin avl 50
173.731
165.744
152.108
137.145
129.446
127.306
126.110
124.806
124.738
116.592
77.584
77.160
76.737
60.403
33.794
32.908
31.169
22.366
14.379
N
OEt
O
f1 (ppm)

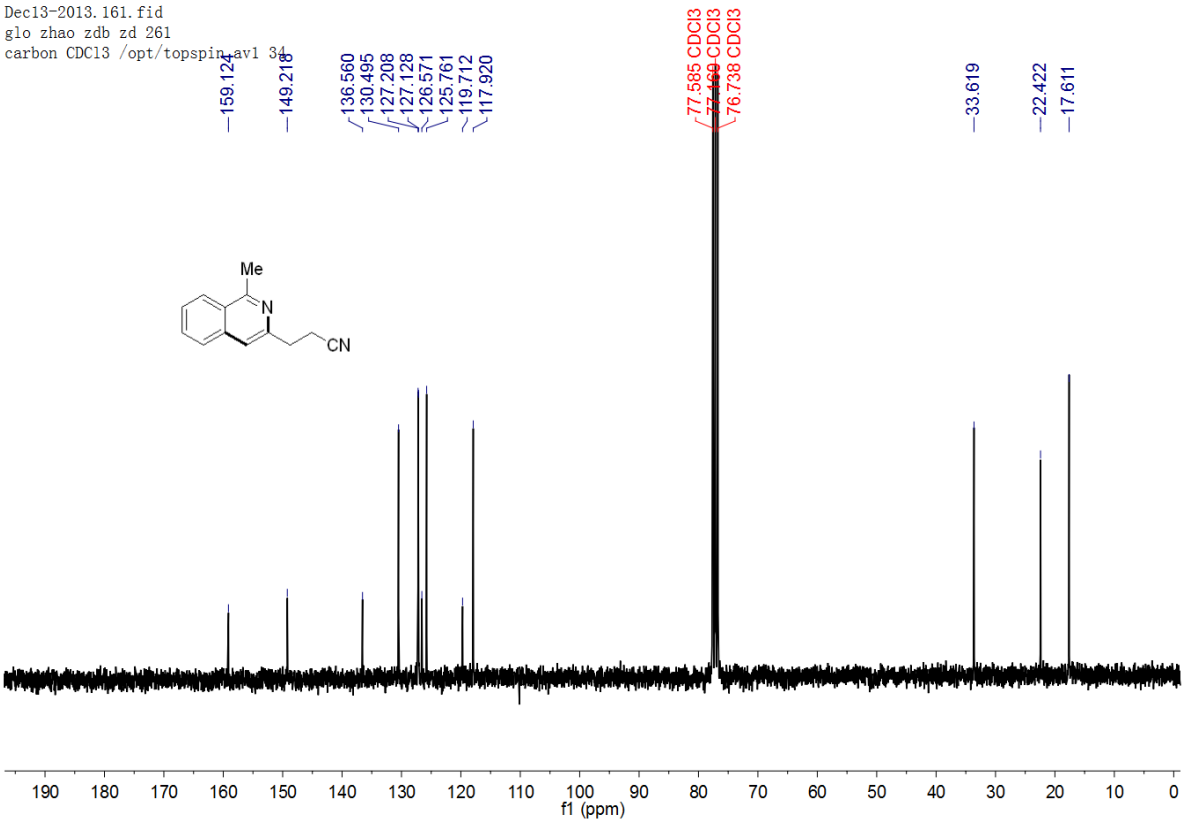

Jan03-2014.40.fid
glo dongbing zhao zdb zd 303
proton CDCl3 /opt/topspin avl 23
7.751
7.747
7.530
7.527
7.521
7.505
7.500
7.484
7.323
7.260
7.257
7.243
7.240
4.149
4.131
4.113
4.096
3.233
3.217
3.202
3.199
3.197
3.179
3.104
3.088
3.075
3.072
2.849
2.831
2.829
2.811
2.205
2.189
2.174
2.158
2.143
1.238
1.220
1.202
N
OEt
O
2.08
1.00
1.23
2.15
4.21
2.21
2.14
2.17
3.28
f1 (ppm)

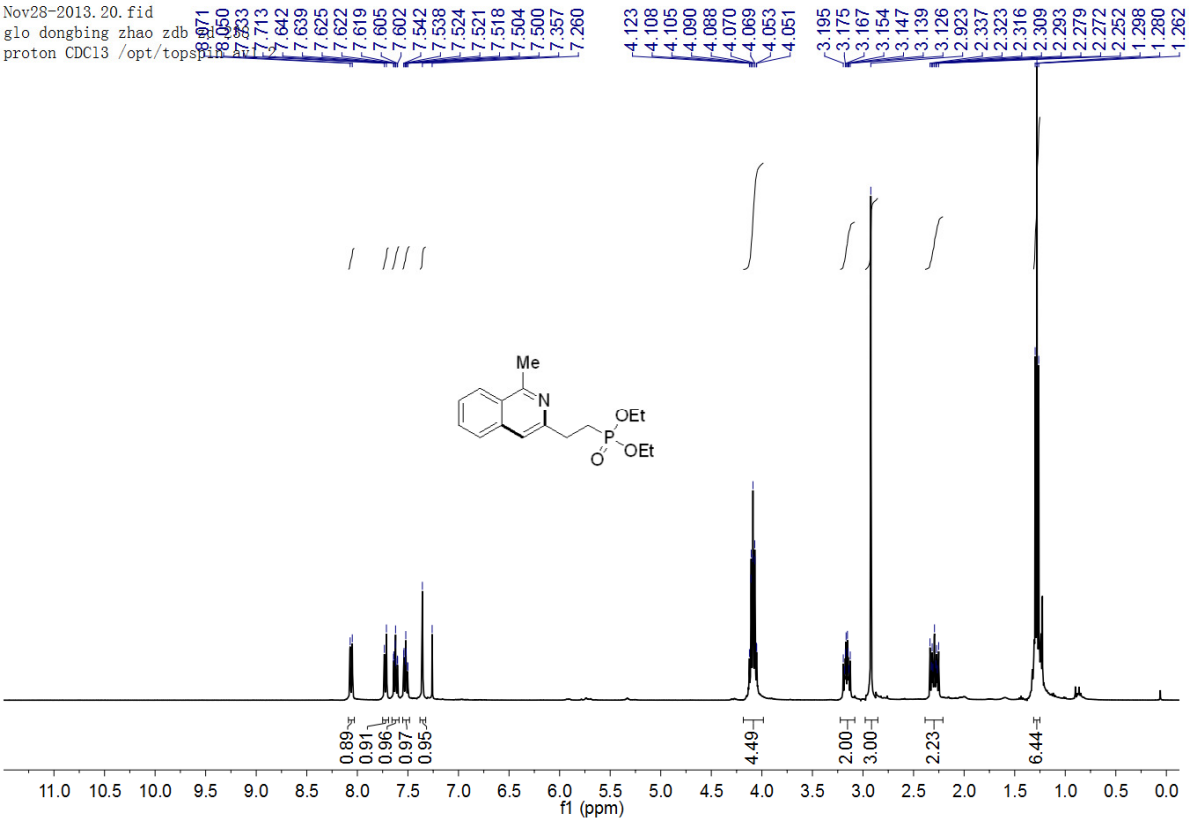

Jan03-2014.41.fid
glo dongbing zhao zdb zd 303
carbon CDCl3 /opt/topspin avl 23
173.296
160.100
152.240
138.759
136.880
130.134
124.432
124.142
123.916
116.800
77.479 CDCl3
77.161 CDCl3
76.843 CDCl3
60.445
34.401
33.161
30.539
23.407
14.361
N
OEt
O
f1 (ppm)

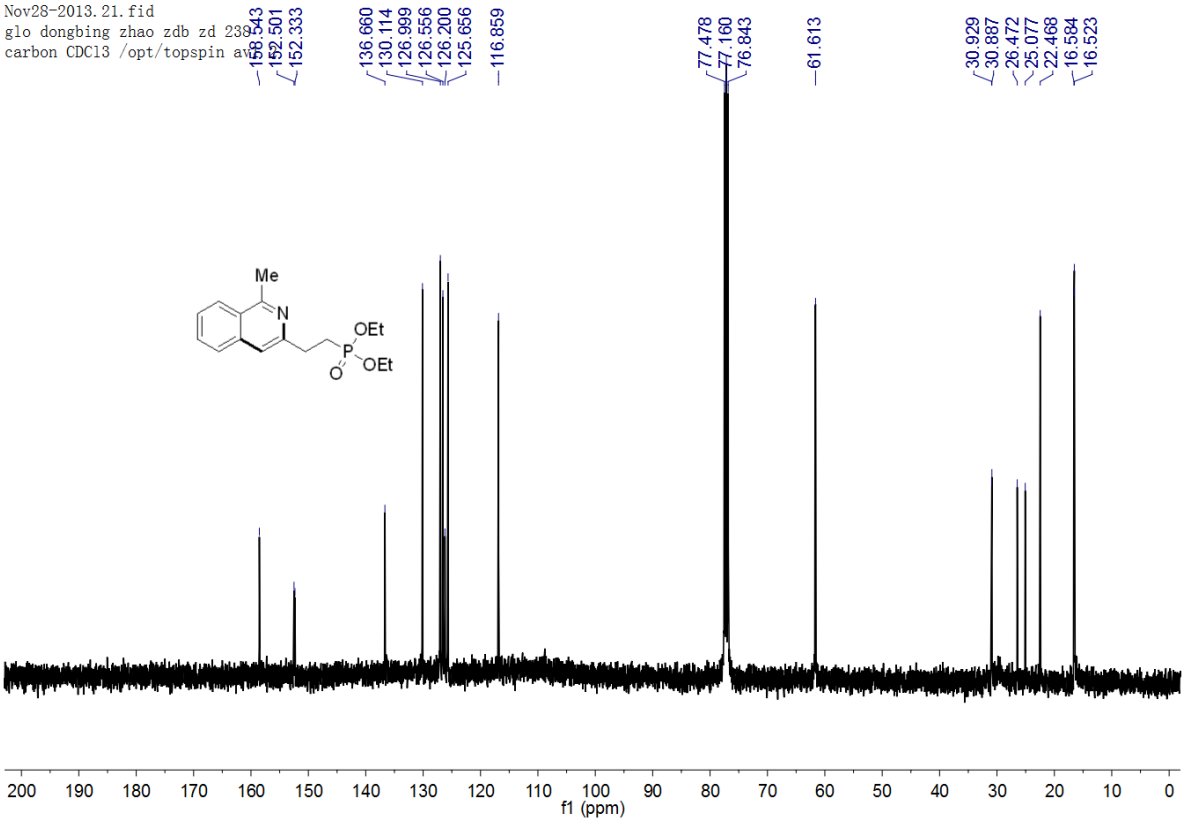

Nov13-2013.60.fid
glo zhao zdb zd 227
proton CDCl3 /opt/topspin av1 52
8.069
8.062
8.048
8.046
7.733
7.713
7.636
7.633
7.619
7.616
7.613
7.599
7.596
7.535
7.532
7.518
7.514
7.511
7.497
7.494
7.357
7.260
3.665
3.222
3.203
3.184
2.921
2.877
2.858
2.839
Me
N
OMe
O
1.00
1.02
1.03
1.05
1.03
3.17
2.10
3.05
2.26
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

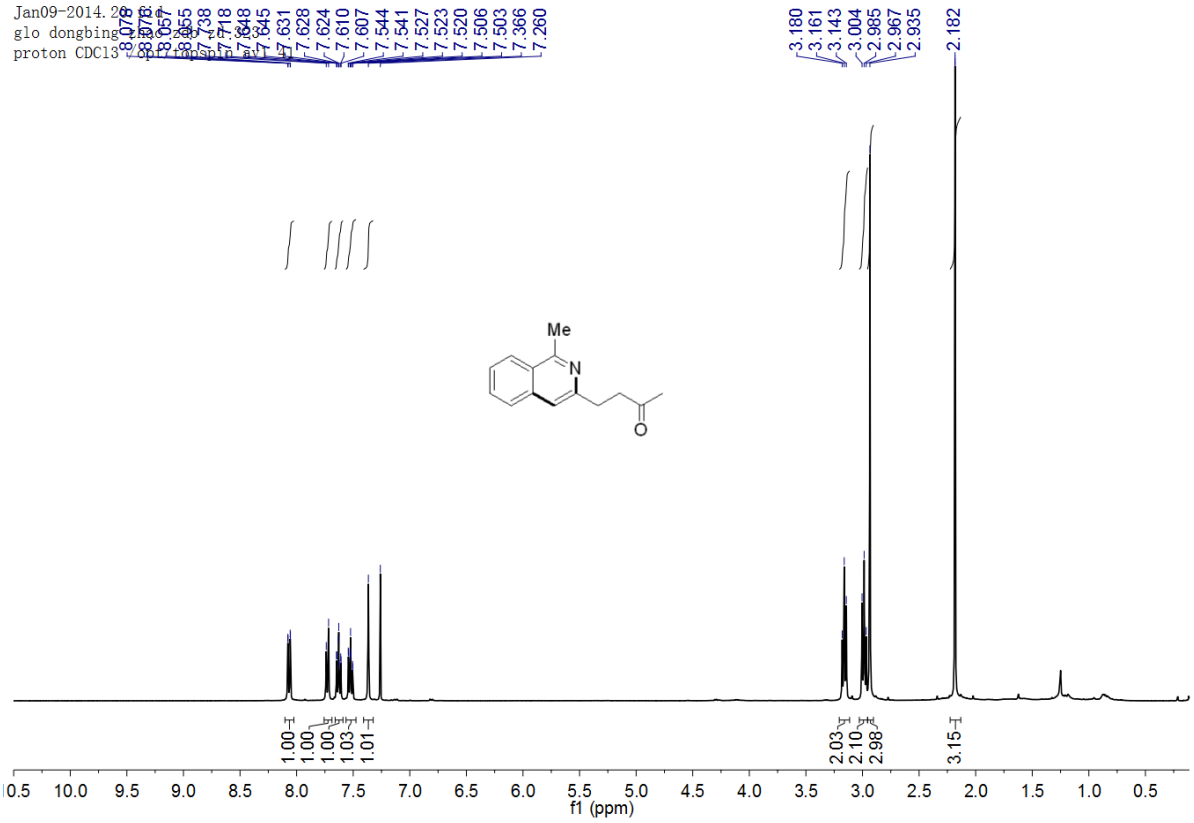

Nov13-2013.61.fid
glo zhao zdb zd 227
carbon CDCl3 /opt/topspin av1 52
173.783
158.462
152.155
136.642
130.012
127.008
126.460
126.167
125.641
117.074
77.478 CDCl3
77.160 CDCl3
76.843 CDCl3
51.700
33.992
33.046
22.492
Me
N
OMe
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

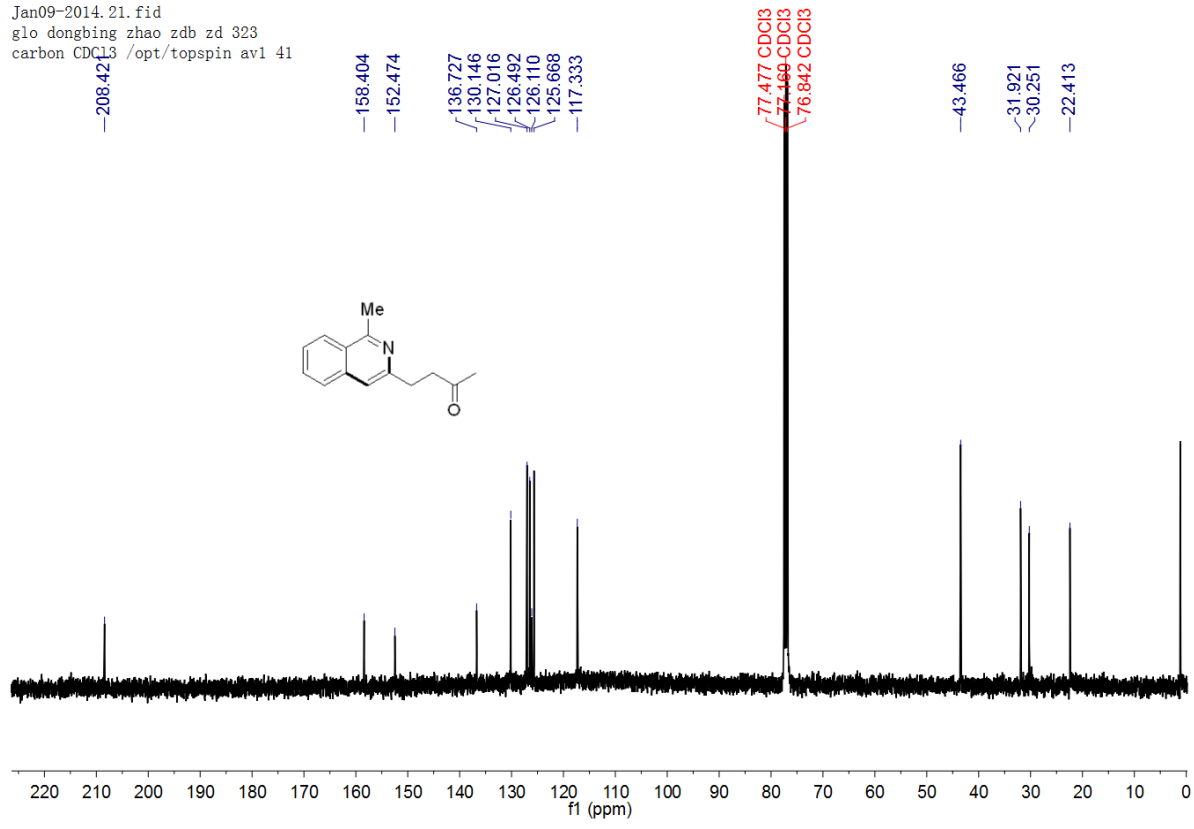

Dec13-2013.160.fid
glo zhao zdb zd 261
proton CDCl3 /opt/topspin
8.115
8.087
7.789
7.762
7.699
7.695
7.676
7.672
7.649
7.645
7.606
7.601
7.582
7.578
7.573
7.555
7.551
7.434
7.260
3.226
3.202
3.178
2.948
2.934
2.911
2.886
Me
N
CN
1.03
1.12
1.10
1.05
1.00
2.13
2.93
2.14
f1 (ppm)

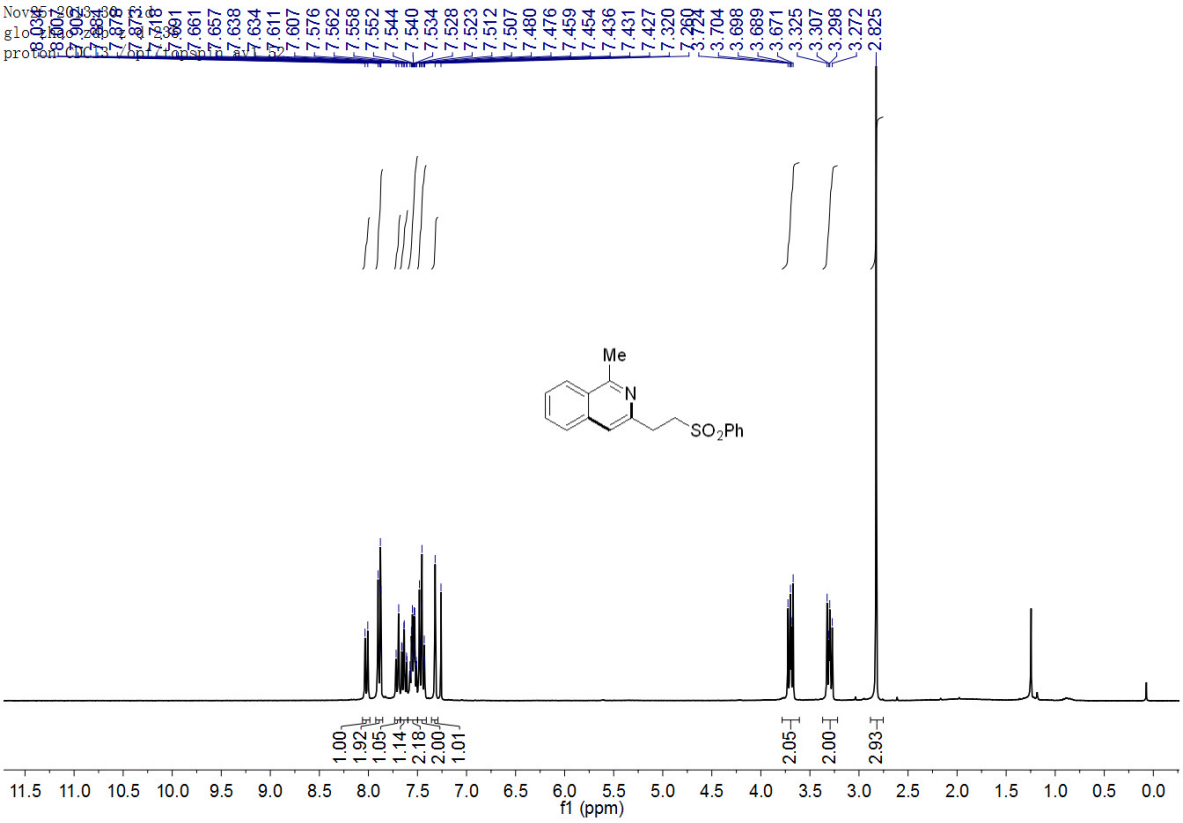

Dec13-2013.161.fid
glo zhao zdb zd 261
carbon CDCl3 /opt/topspin
159.124
149.218
136.560
130.495
127.208
127.128
126.571
125.761
119.712
117.920
77.585 CDCl3
77.169 CDCl3
76.738 CDCl3
33.619
22.422
17.611
Me
N
CN
f1 (ppm)

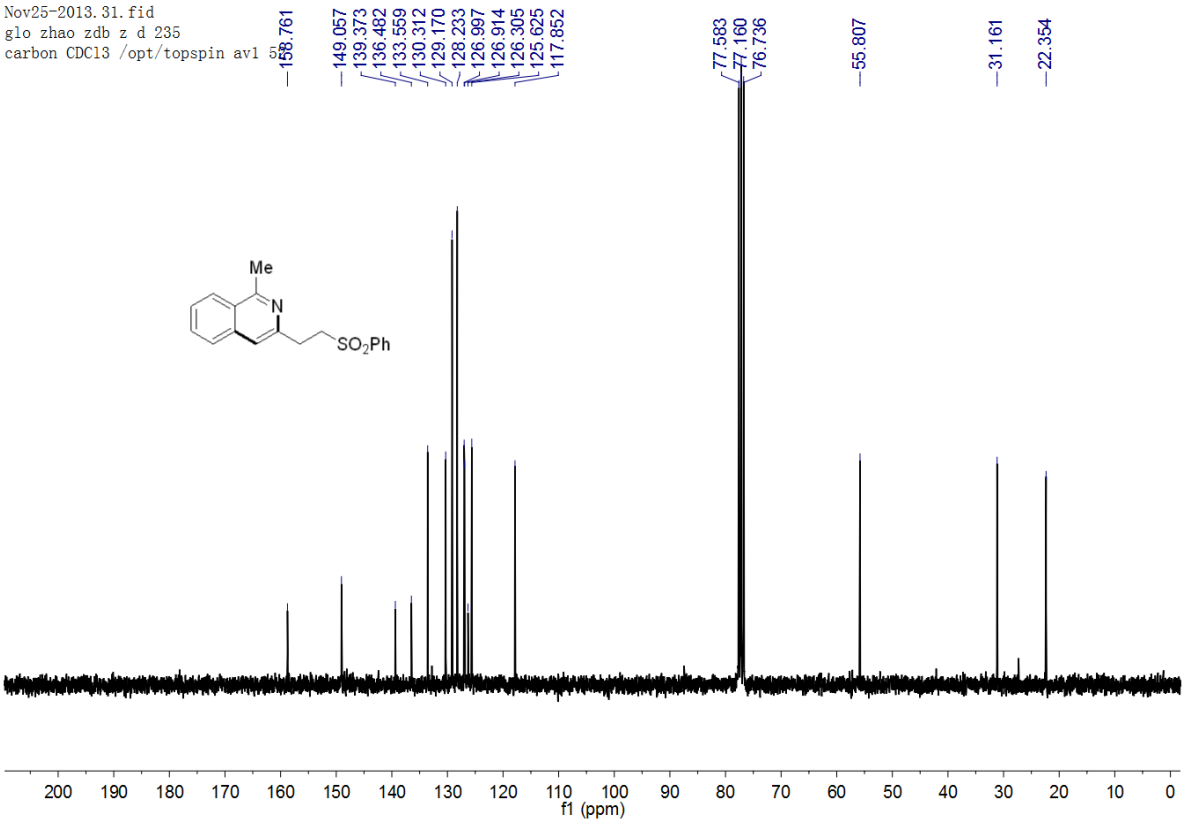

Nov28-2013.20.fid
glo dongbing zhao zdb gd
proton CDCl3 /opt/topspin
8.071
8.050
8.033
7.713
7.642
7.639
7.625
7.622
7.619
7.605
7.602
7.542
7.538
7.524
7.521
7.518
7.504
7.500
7.357
7.260
4.123
4.108
4.105
4.090
4.088
4.070
4.069
4.053
4.051
3.195
3.175
3.167
3.154
3.147
3.139
3.126
2.923
2.337
2.323
2.316
2.309
2.293
2.279
2.272
2.252
1.298
1.280
1.262
Me
N
OEt
P
O
OEt
0.89
0.91
0.96
0.97
0.95
4.49
2.00
3.00
2.23
6.44
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

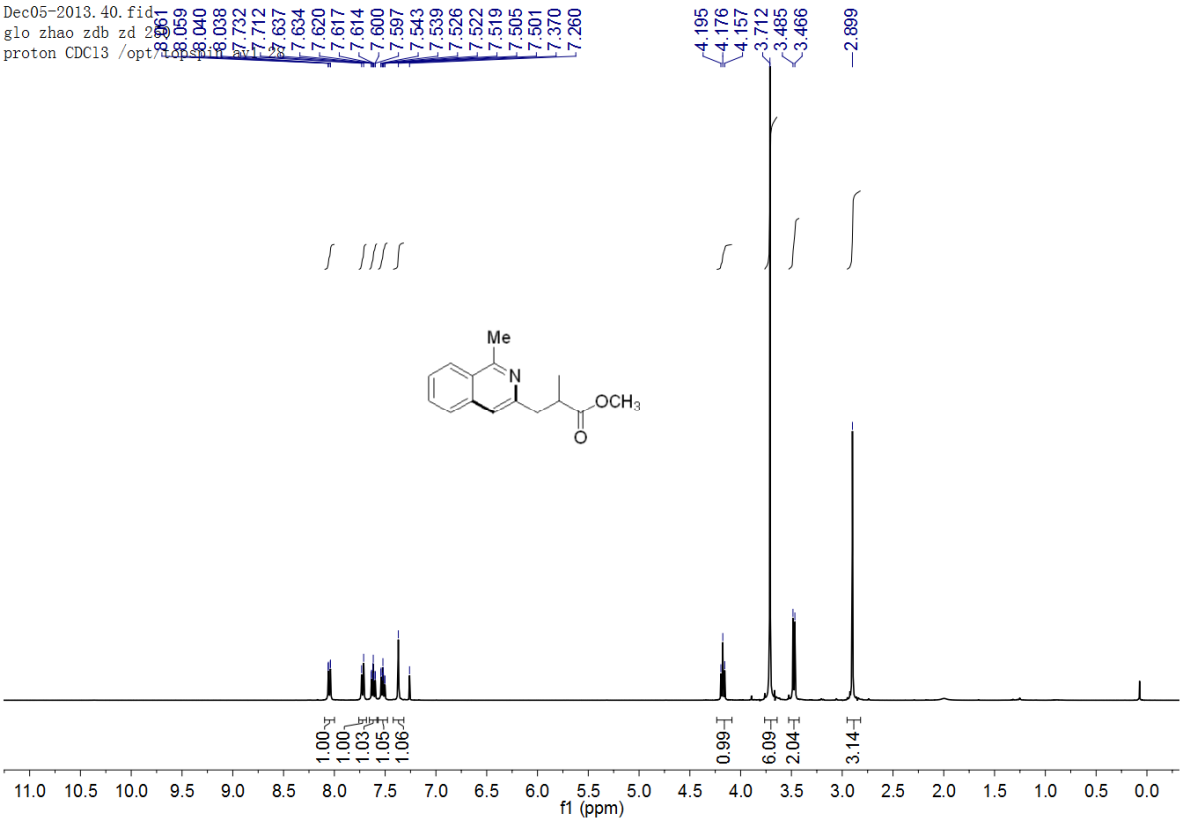

Nov28-2013.21.fid
glo dongbing zhao zdb zd 239
carbon CDCl3 /opt/topspin
158.543
152.501
152.333
136.660
130.114
126.999
126.556
126.200
125.656
116.859
77.478
77.160
76.843
61.613
30.929
30.887
26.472
25.077
22.468
16.584
16.523
Me
N
OEt
P
O
OEt
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Jan09-2014.20
glo dongbing zhao zdb zd 323
proton CDCl3 /opt/topspin av1 41
8.078
8.076
8.057
8.055
7.738
7.718
7.648
7.645
7.631
7.628
7.624
7.610
7.607
7.544
7.541
7.527
7.523
7.520
7.506
7.503
7.366
7.260
3.180
3.161
3.143
3.004
2.985
2.967
2.935
2.182
Me
N
O
1.00
1.00
1.00
1.03
1.01
2.03
2.10
2.98
3.15
f1 (ppm)


Jan09-2014.21.fid
glo dongbing zhao zdb zd 323
carbon CDCl3 /opt/topspin av1 41
208.421
158.404
152.474
136.727
130.146
127.016
126.492
126.110
125.668
117.333
77.477 CDCl3
77.160 CDCl3
76.842 CDCl3
43.466
31.921
30.251
22.413
Me
N
O
f1 (ppm)


Me
N
SO2Ph
8.037
8.001
7.905
7.873
7.718
7.661
7.657
7.638
7.634
7.611
7.607
7.576
7.562
7.558
7.552
7.544
7.540
7.534
7.528
7.523
7.512
7.507
7.480
7.476
7.459
7.454
7.436
7.431
7.427
7.320
3.704
3.698
3.689
3.671
3.325
3.307
3.298
3.272
2.825
1.00
1.92
1.05
1.14
2.18
2.00
1.01
2.05
2.00
2.93
f1 (ppm)


Nov25-2013.31.fid
glo zhao zdb z d 235
carbon CDCl3 /opt/topspin av1 5
158.761
149.057
139.373
136.482
133.559
130.312
129.170
128.233
126.997
126.914
126.305
125.625
117.852
77.583
77.160
76.736
55.807
31.161
22.354
Me
N
SO2Ph
f1 (ppm)


Dec05-2013.40.fid
glo zhao zdb zd 250
proton CDCl3 /opt/topspin_av1 28
8.061
8.059
8.040
8.038
7.732
7.712
7.637
7.634
7.620
7.617
7.614
7.600
7.597
7.543
7.539
7.526
7.522
7.519
7.505
7.501
7.370
7.260
4.195
4.176
4.157
3.712
3.485
3.466
2.899
Me
N
OCH3
O
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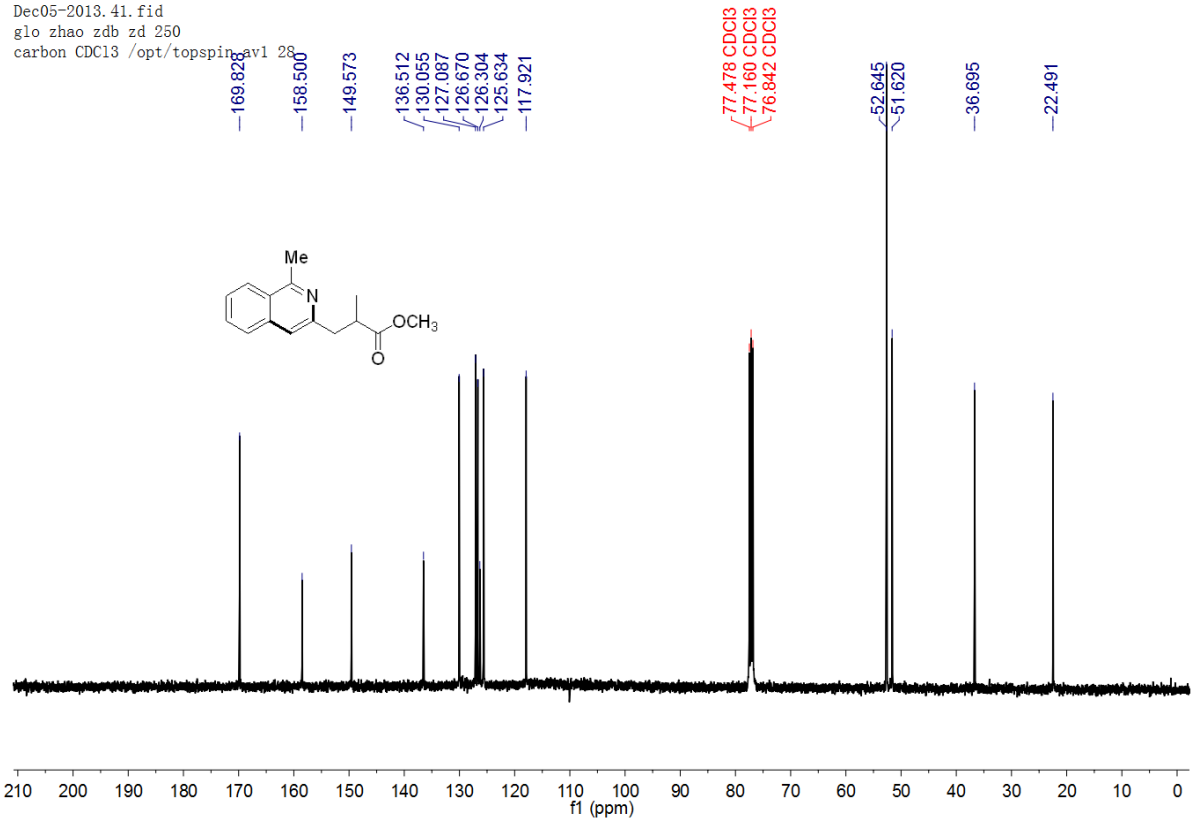
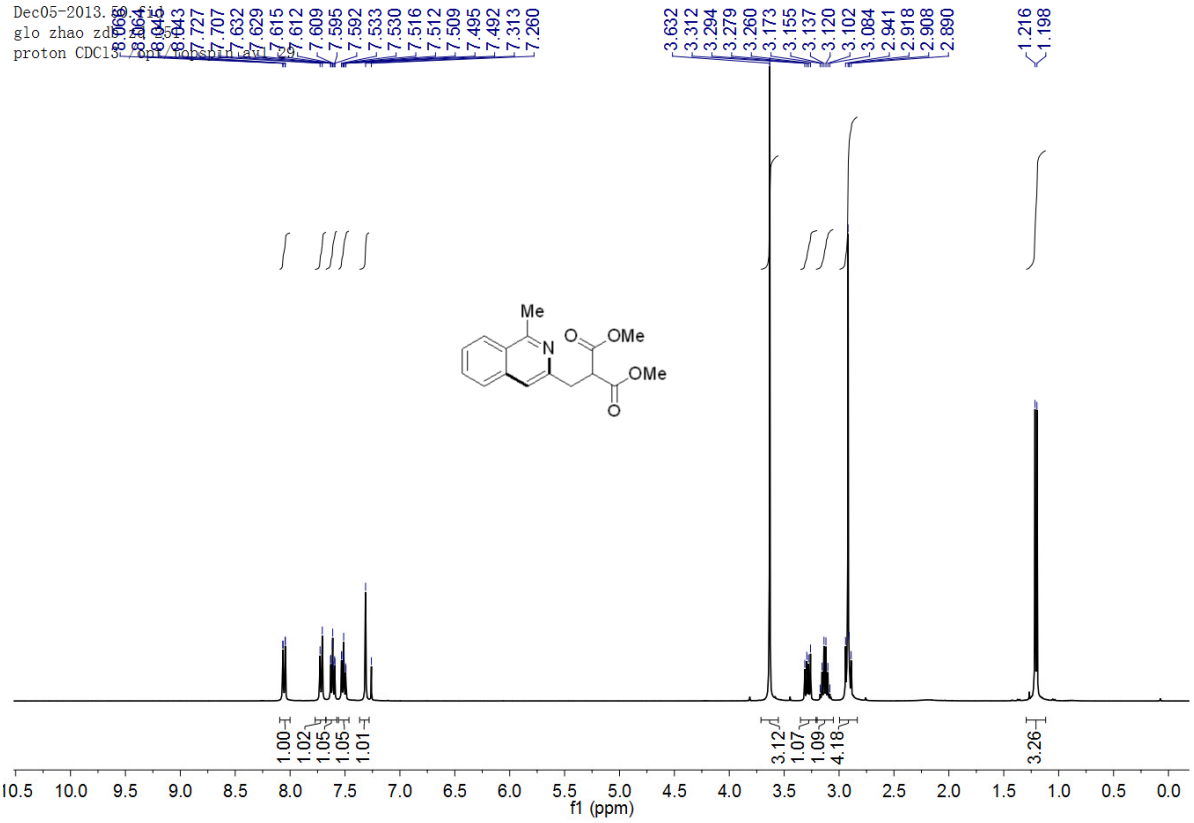
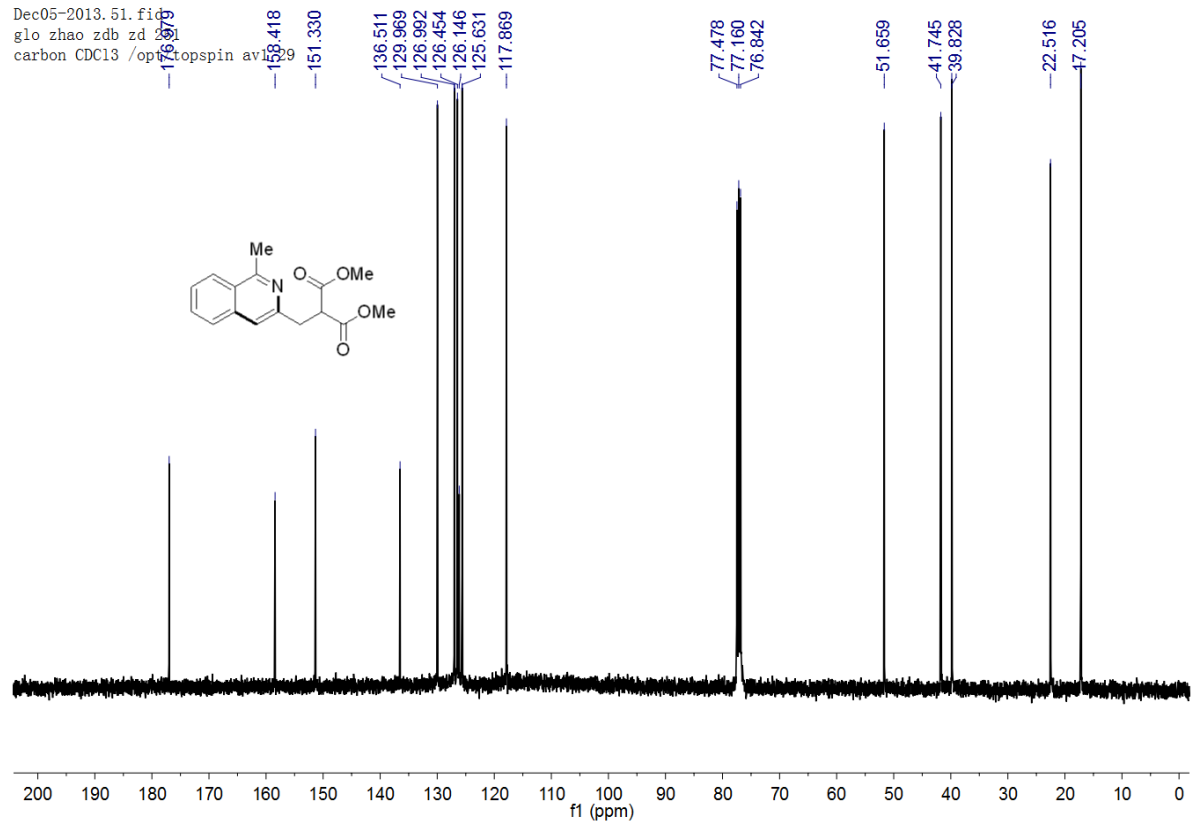
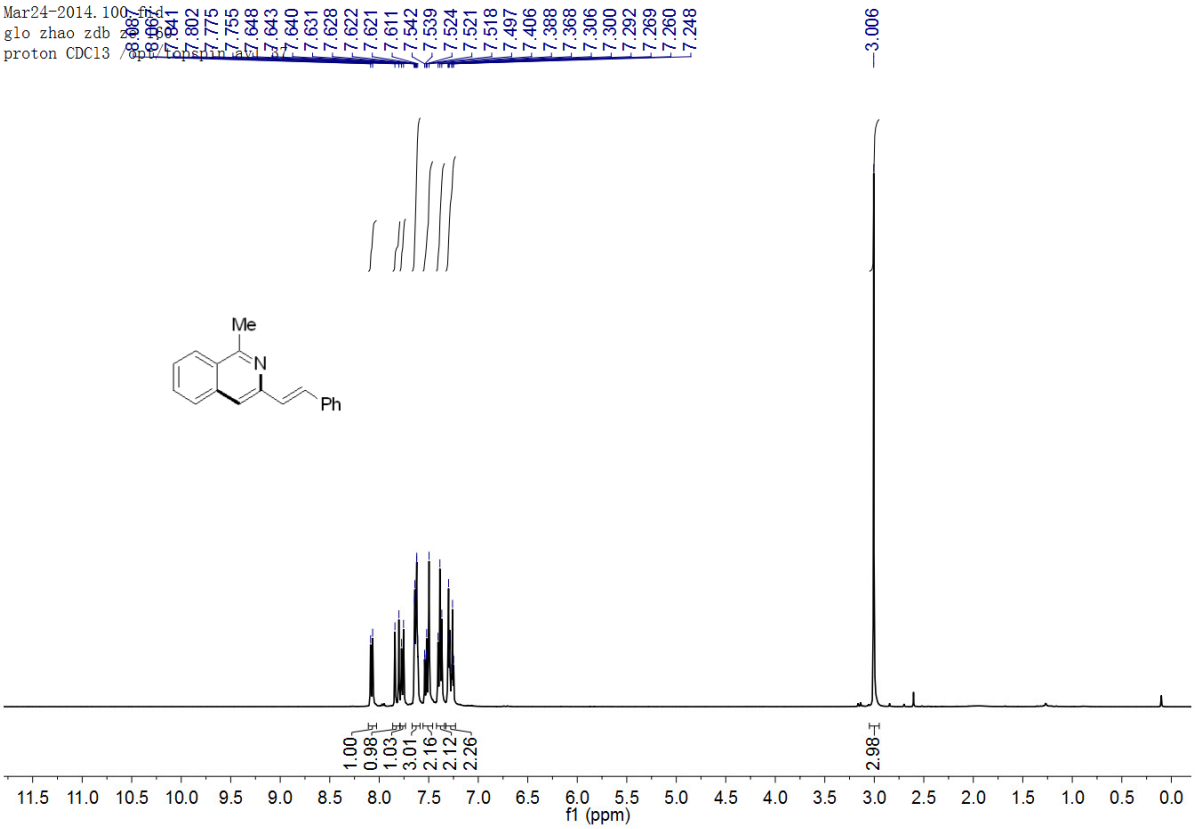
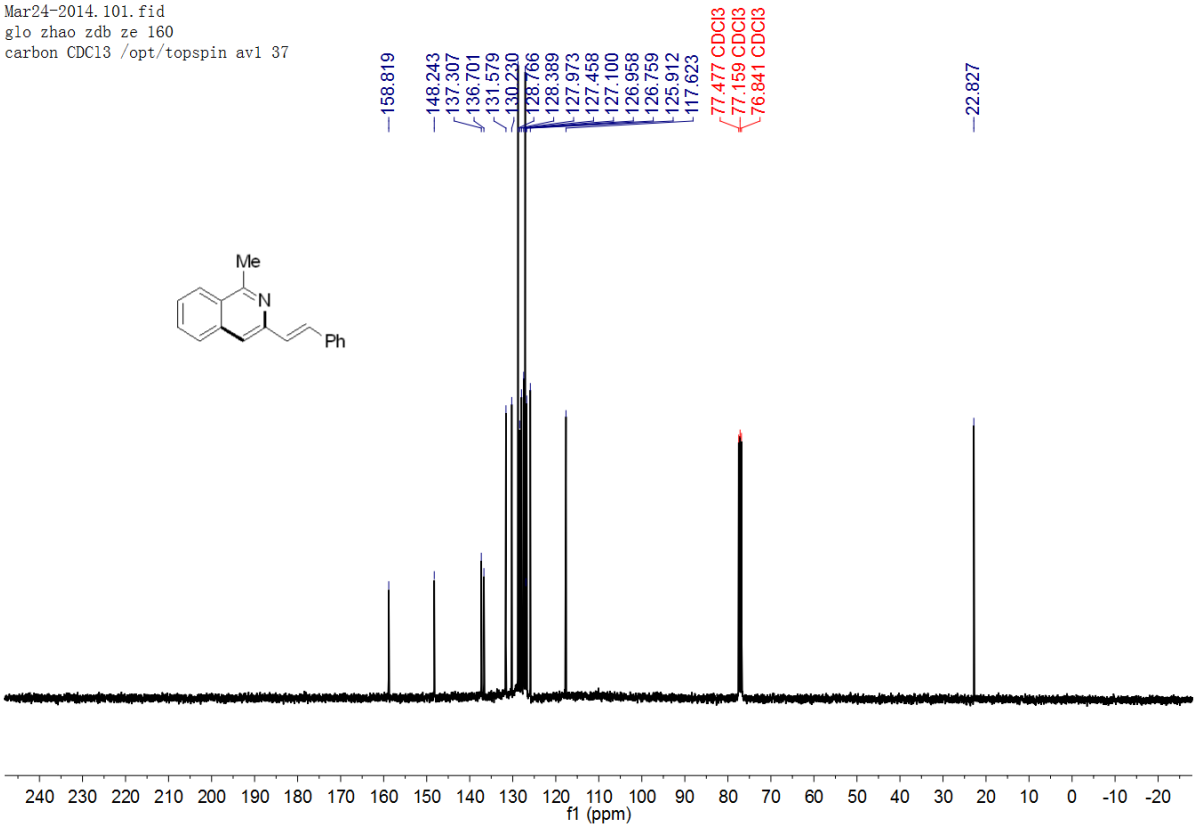
1.00
1.03
1.05
1.06
0.99
6.09
2.04
3.14
f1 (ppm)

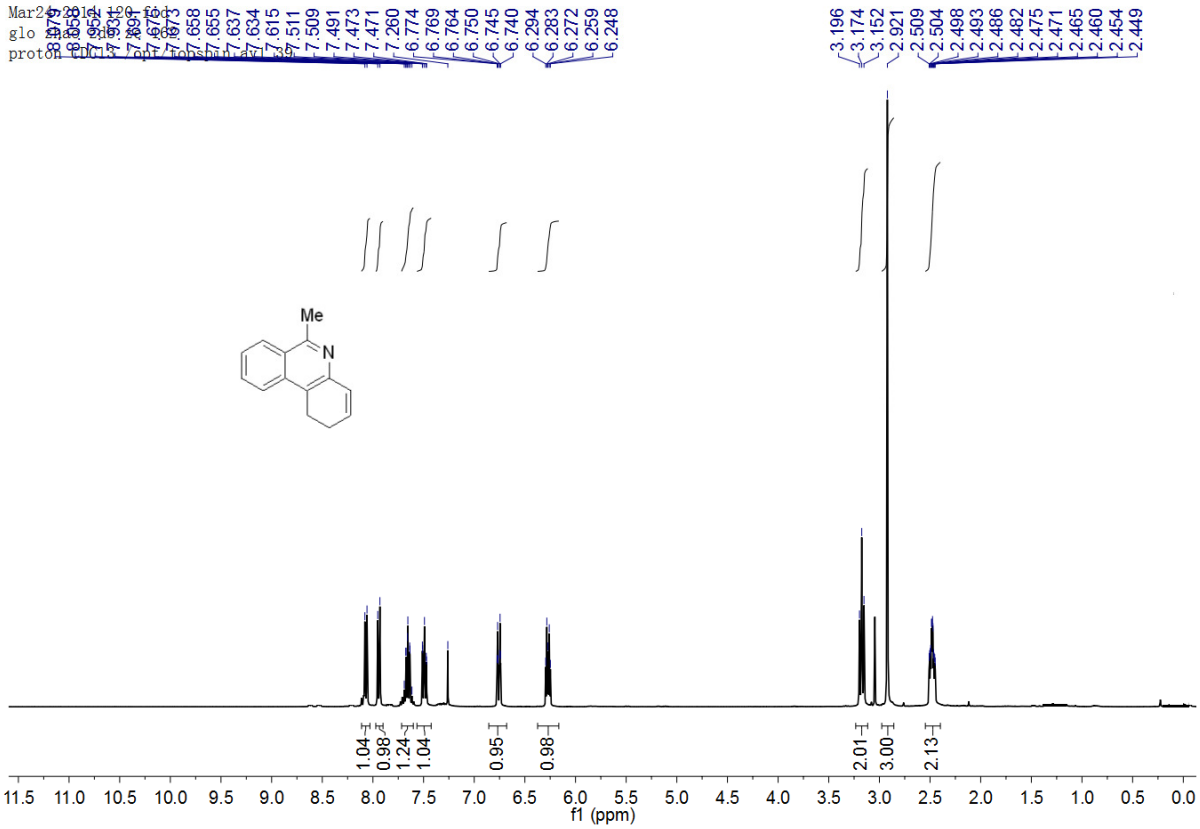

Dec05-2013.41.fid
glo zhao zdb zd 250
carbon CDCl3 /opt/topspin_av1 28
169.828
158.500
149.573
136.512
130.055
127.087
126.670
126.304
125.634
117.921
77.478 CDCl3
77.160 CDCl3
76.842 CDCl3
52.645
51.620
36.695
22.491
Me
N
OCH3
O
f1 (ppm)

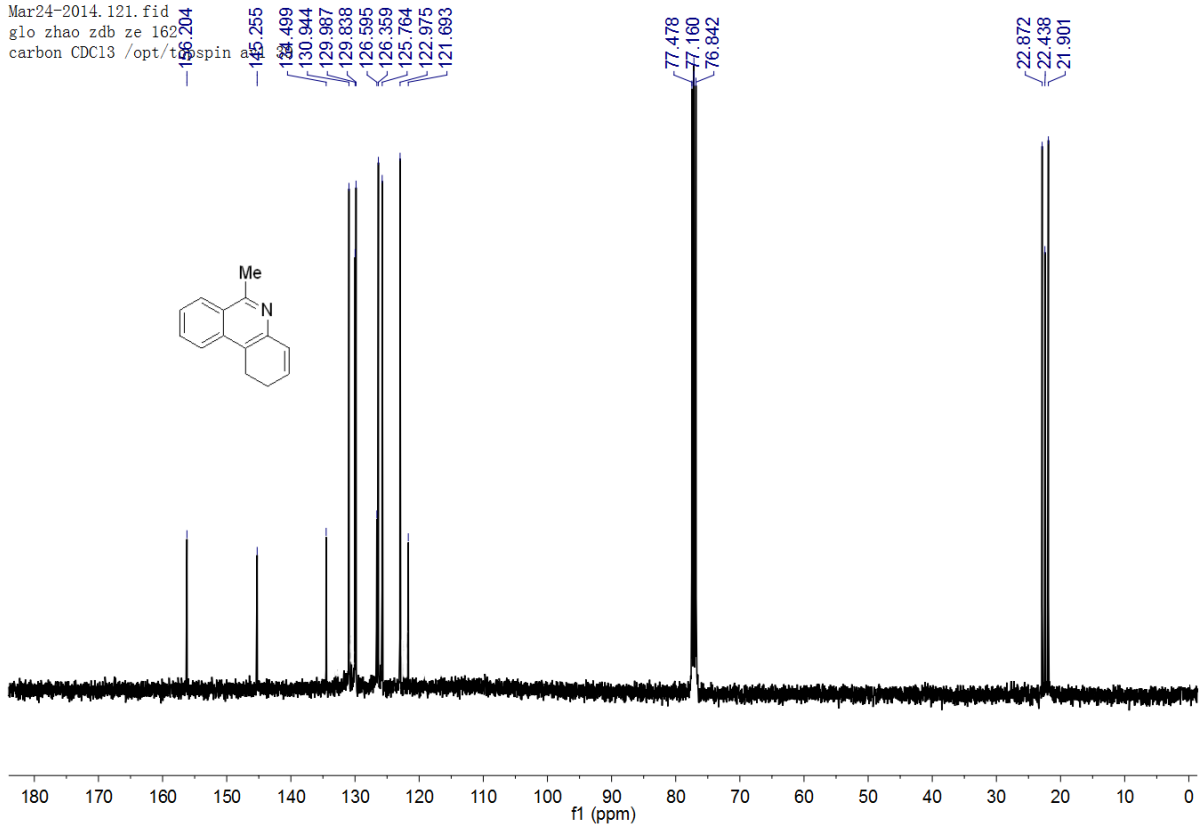

Dec05-2013.50.fid
glo zhao zdb zd 291
proton CDCl3 /opt/topspin avii 29
8.068
8.064
8.045
8.043
7.727
7.707
7.632
7.629
7.615
7.612
7.609
7.595
7.592
7.533
7.530
7.516
7.512
7.509
7.495
7.492
7.313
7.260
3.632
3.312
3.294
3.279
3.260
3.173
3.155
3.137
3.120
3.102
3.084
2.941
2.918
2.908
2.890
1.216
1.198
Me
N
O
OMe
OMe
O
1.00
1.02
1.05
1.05
1.01
3.12
1.07
1.09
4.18
3.26
f1 (ppm)

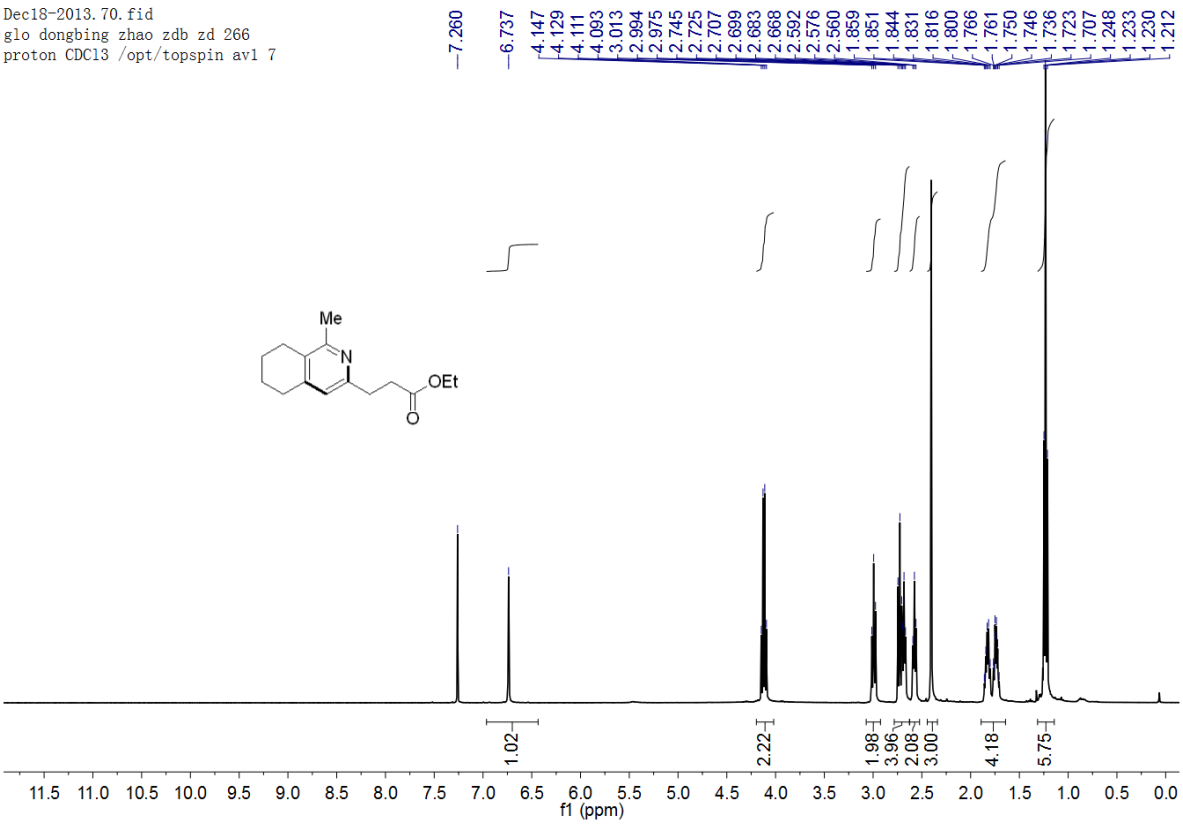

Dec05-2013.51.fid
glo zhao zdb zd 291
carbon CDCl3 /opt/topspin avii 29
176.979
158.418
151.330
136.511
129.969
126.992
126.454
126.146
125.631
117.869
77.478
77.160
76.842
51.659
41.745
39.828
22.516
47.205
Me
N
O
OMe
OMe
O
f1 (ppm)

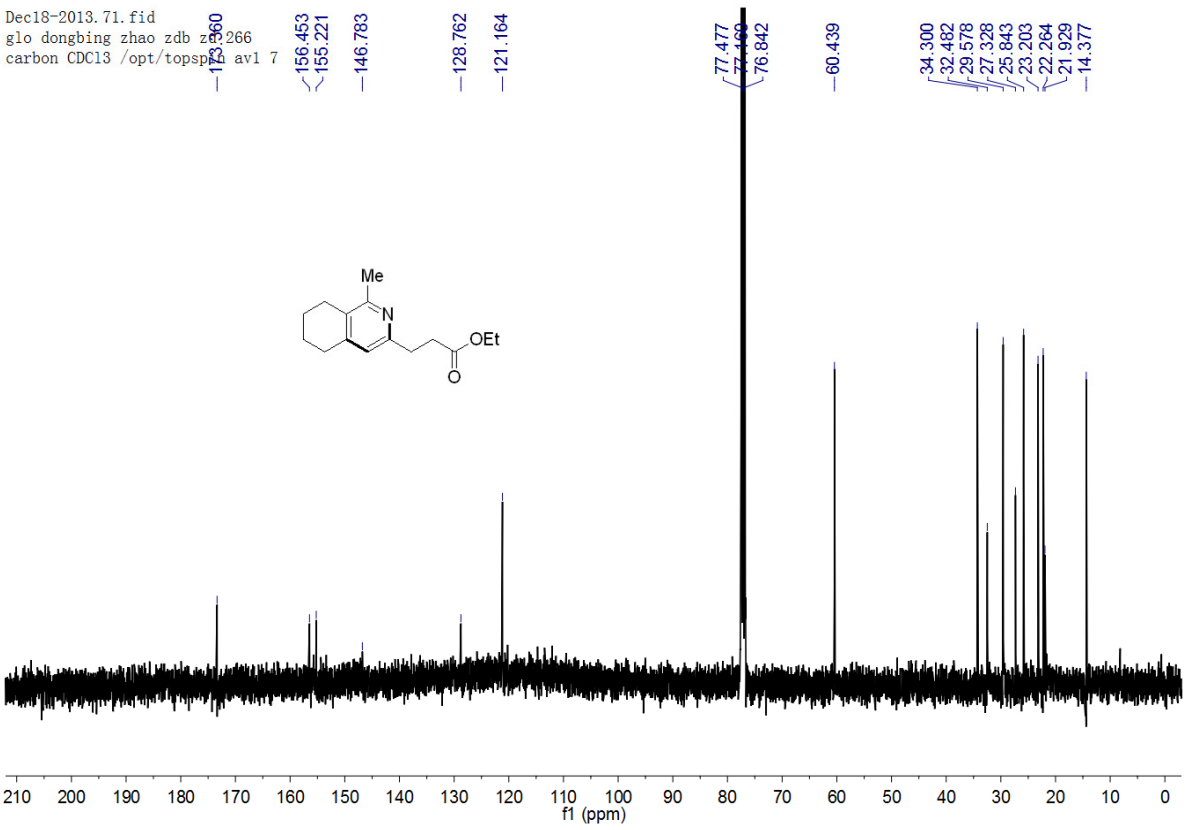

Mar24-2014.100.fid
glo zhao zdb ze 160
proton CDCl3 /opt/topspin av1 37
8.087
8.067
7.841
7.802
7.775
7.755
7.648
7.643
7.640
7.631
7.628
7.622
7.621
7.611
7.542
7.539
7.524
7.521
7.518
7.497
7.406
7.388
7.368
7.306
7.300
7.292
7.269
7.260
7.248
3.006
Me
N
Ph
1.00
0.98
1.03
3.01
2.16
2.12
2.26
2.98
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

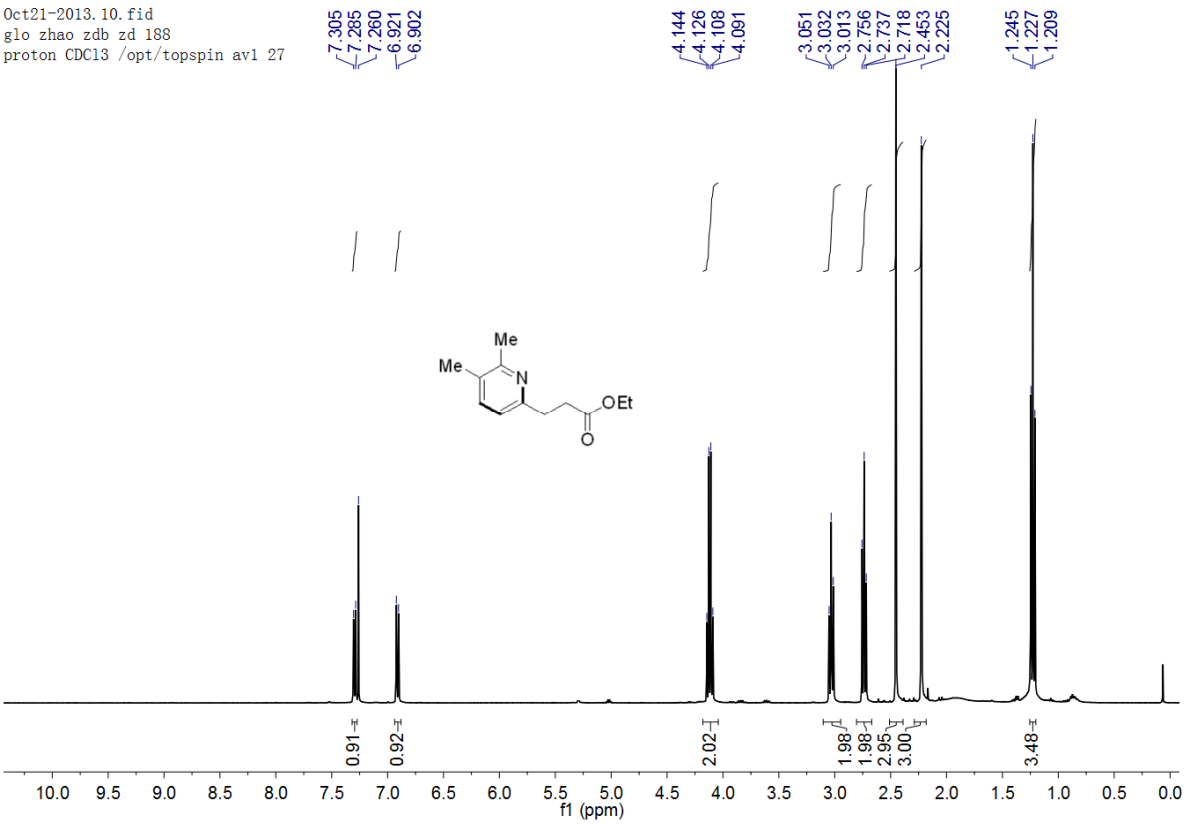

Mar24-2014.101.fid
glo zhao zdb ze 160
carbon CDCl3 /opt/topspin av1 37
158.819
148.243
137.307
136.701
131.579
130.230
128.766
128.389
127.973
127.458
127.100
126.958
126.759
125.912
117.623
77.477 CDCl3
77.159 CDCl3
76.841 CDCl3
22.827
Me
N
Ph
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

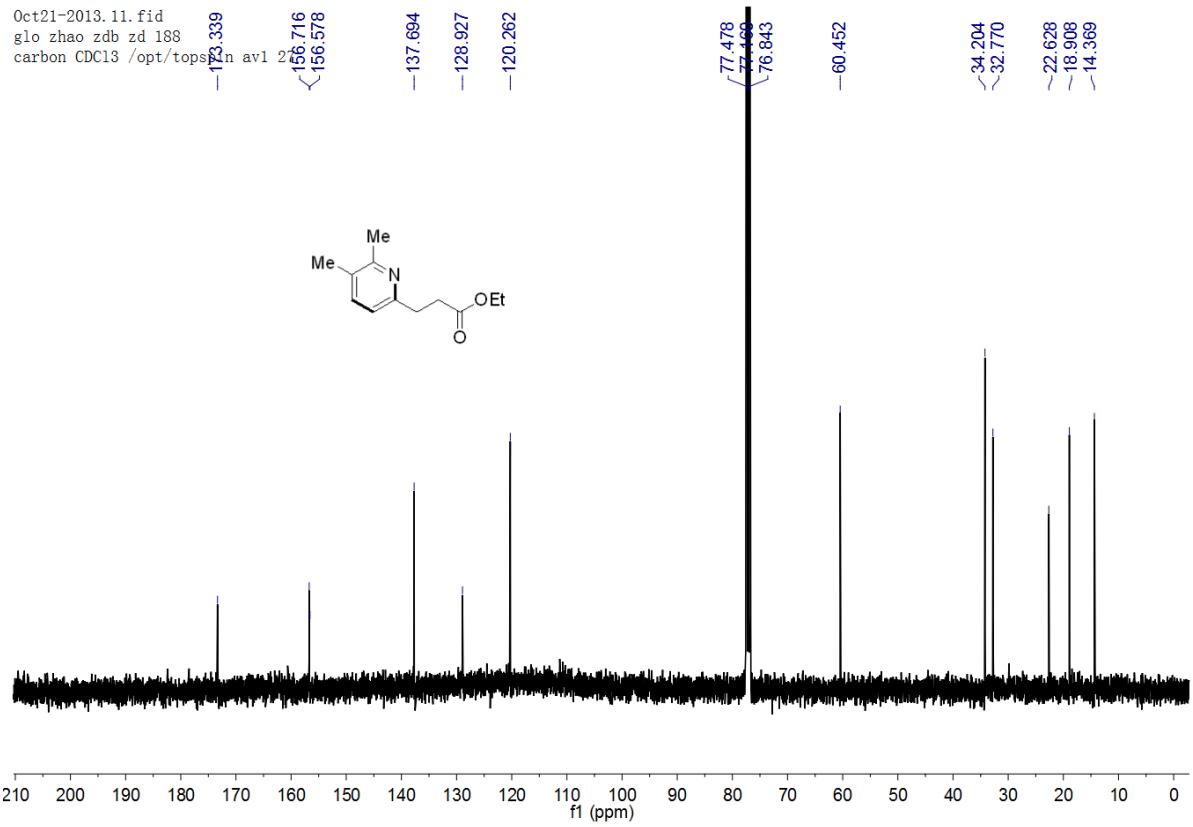

Me
N
1.04
0.98
1.24
1.04
0.95
0.98
2.01
3.00
2.13
f1 (ppm)

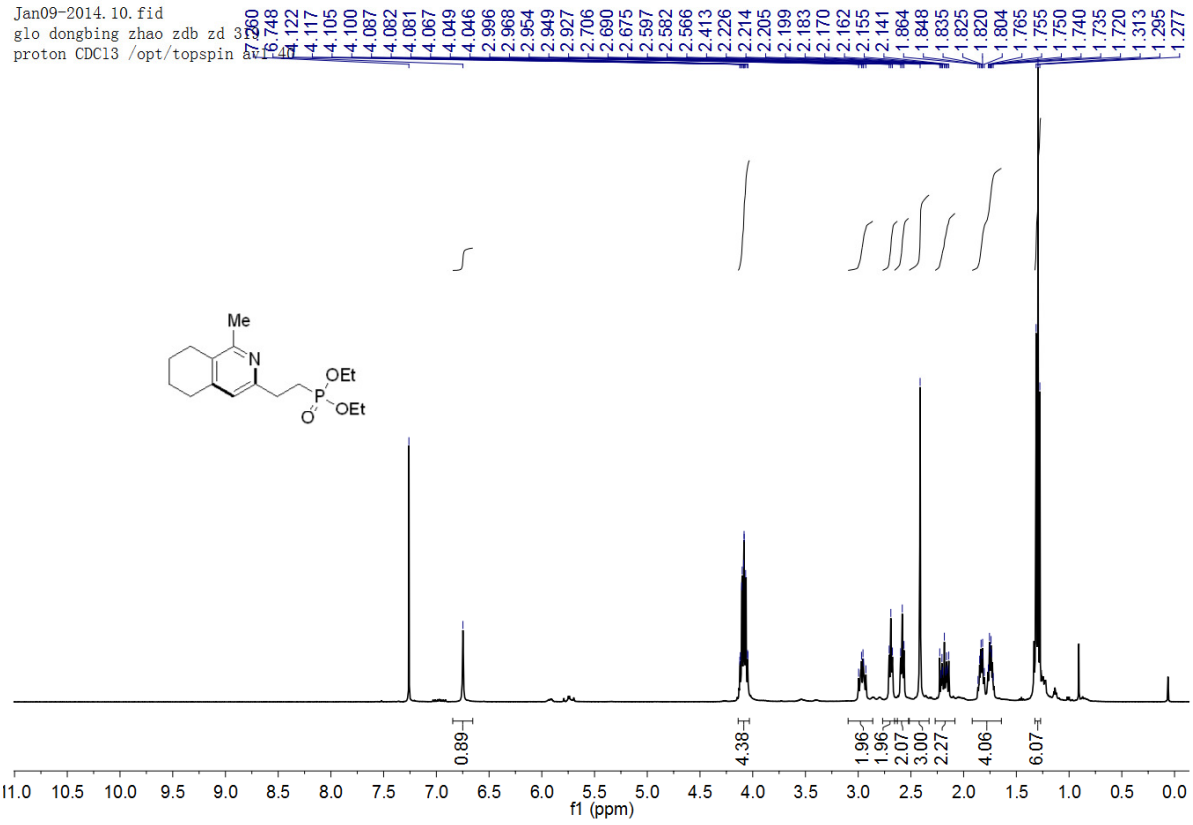

Me
N
77.478
77.160
76.842
22.872
22.438
21.901
f1 (ppm)

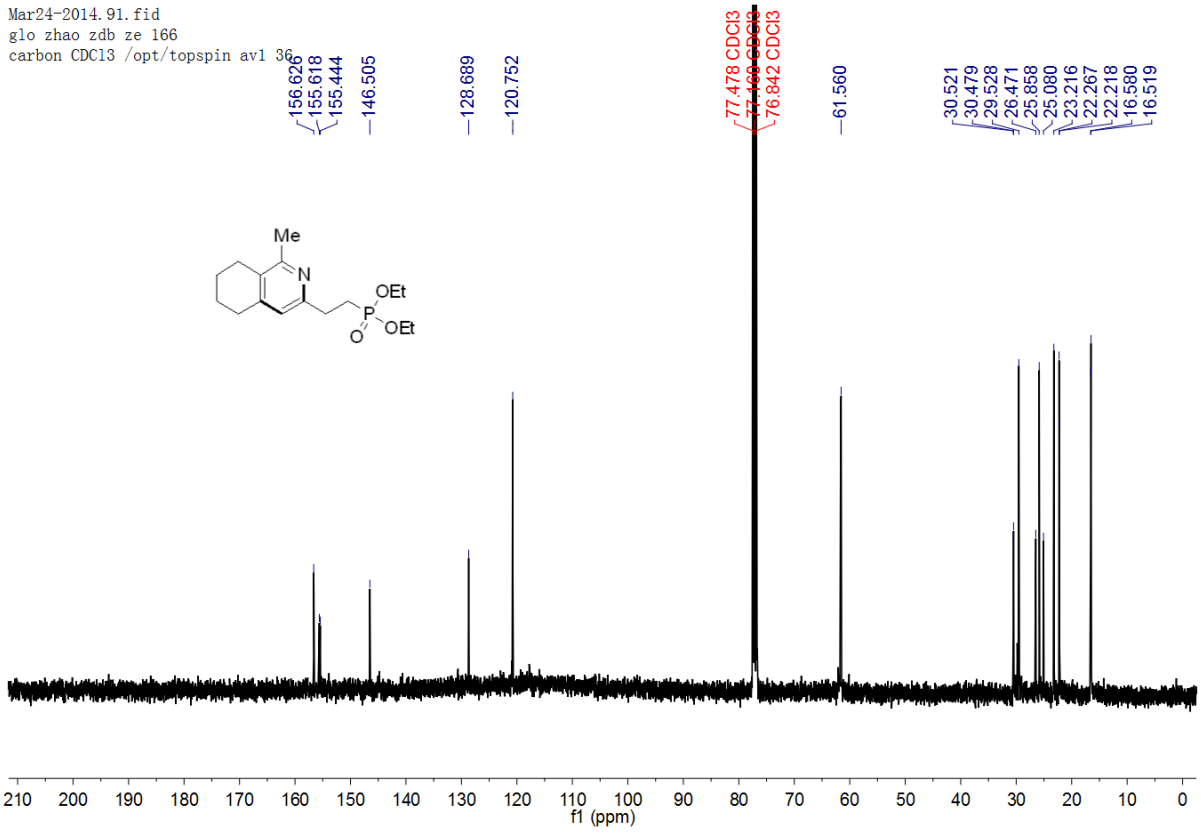

Dec18-2013.70.fid
glo dongbing zhao zdb zd 266
proton CDCl3 /opt/topspin av1 7
7.260
6.737
4.147
4.129
4.111
4.093
3.013
2.994
2.975
2.745
2.725
2.707
2.699
2.683
2.668
2.592
2.576
2.560
1.859
1.851
1.844
1.831
1.816
1.800
1.766
1.761
1.750
1.746
1.736
1.723
1.707
1.248
1.233
1.230
1.212
Me
N
OEt
O
1.02
2.22
1.98
3.96
2.08
3.00
4.18
5.75
f1 (ppm)

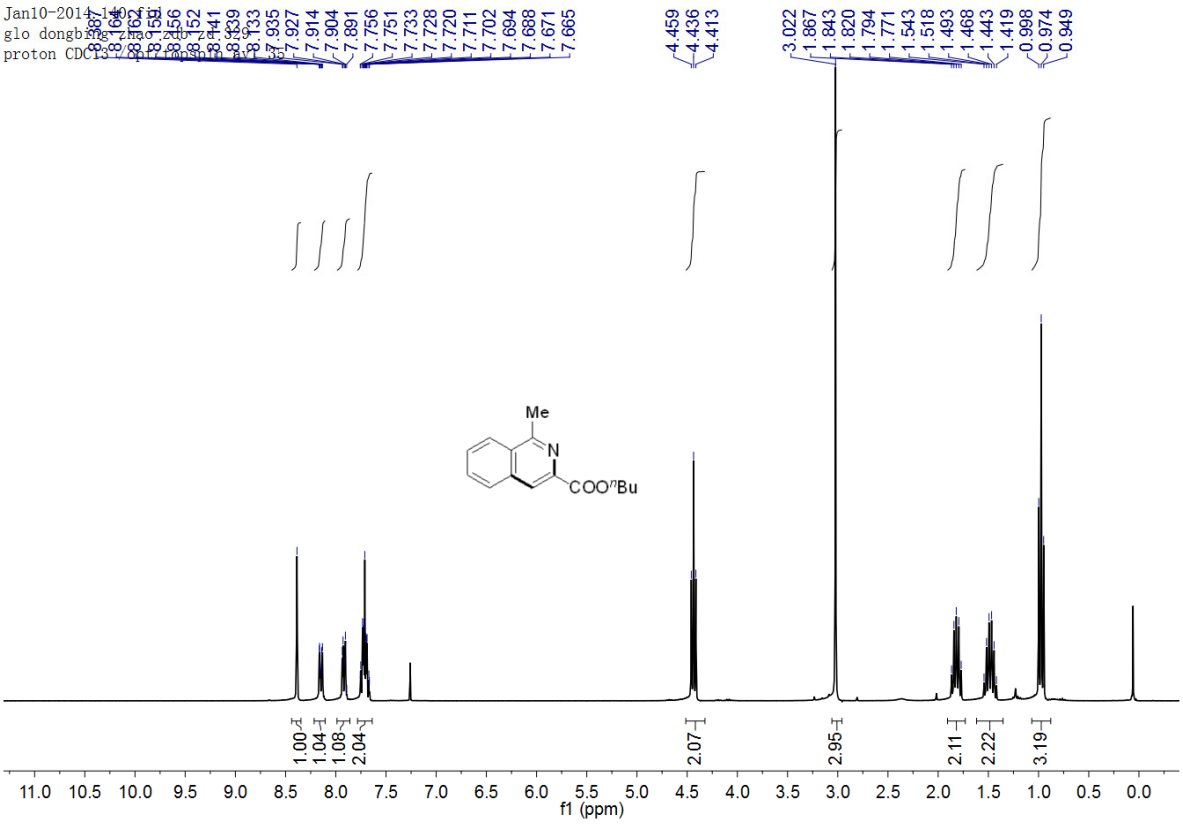

Dec18-2013.71.fid
glo dongbing zhao zdb zd 266
carbon CDCl3 /opt/topspin av1 7
173.360
156.453
155.221
146.783
128.762
121.164
77.477
77.160
76.842
60.439
34.300
32.482
29.578
27.328
25.843
23.203
22.264
21.929
14.377
Me
N
OEt
O
f1 (ppm)

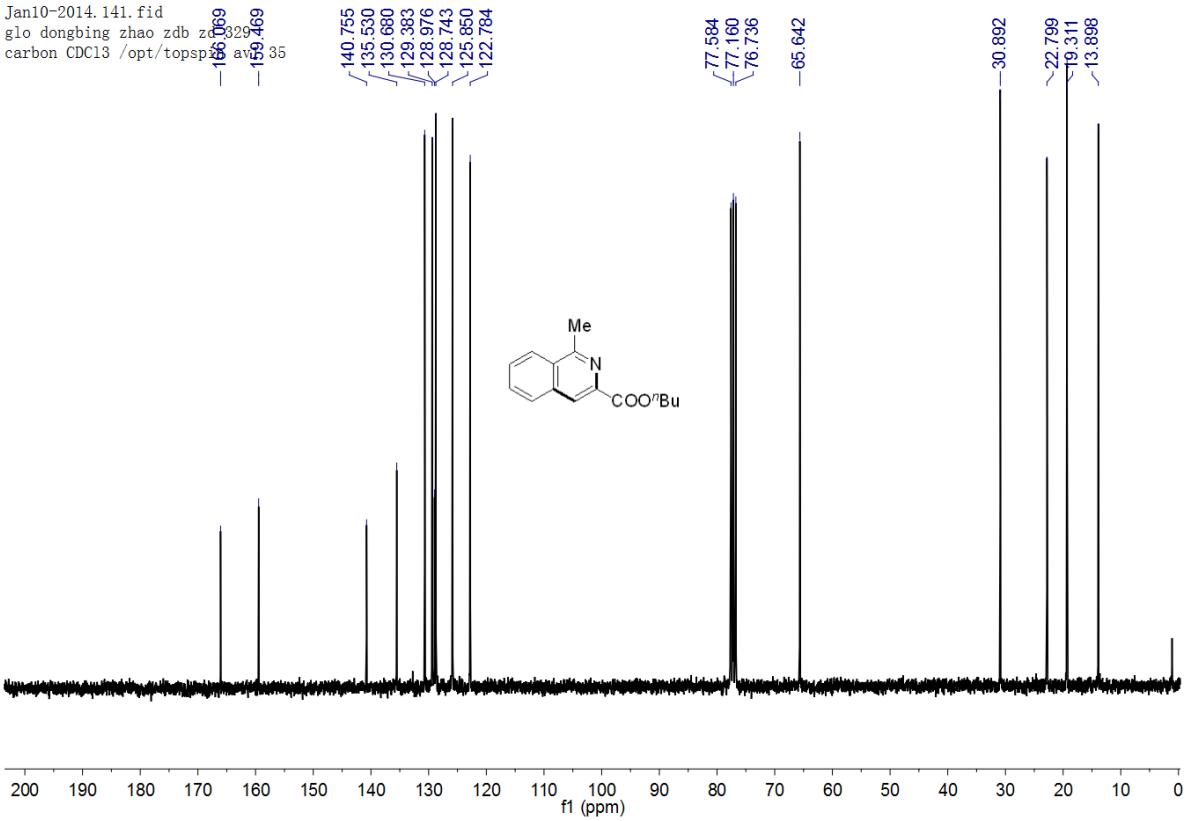

Oct21-2013.10.fid
glo zhao zdb zd 188
proton CDCl3 /opt/topspin av1 27
7.305
7.285
7.260
6.921
6.902
4.144
4.126
4.108
4.091
3.051
3.032
3.013
2.756
2.737
2.718
2.453
2.225
1.245
1.227
1.209
Me
Me
N
OEt
O
0.91
0.92
2.02
1.98
1.98
2.95
3.00
3.48
f1 (ppm)

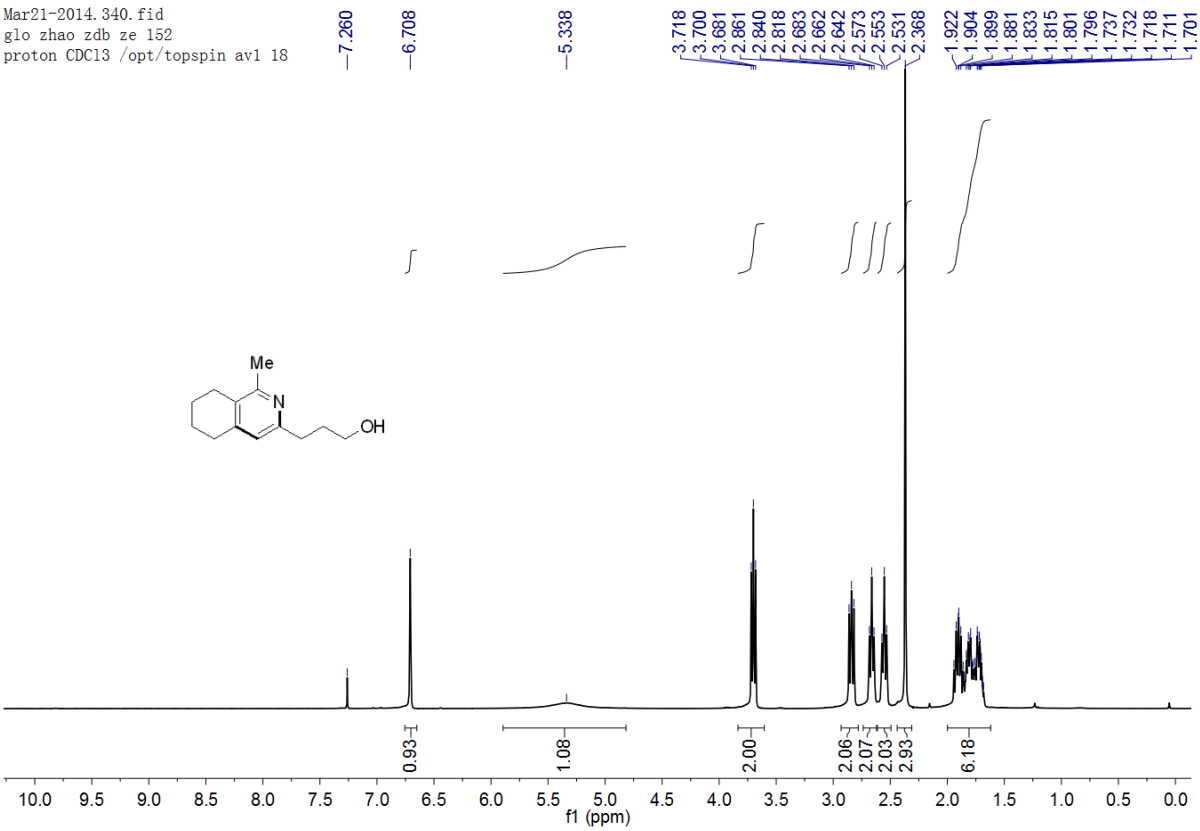

Oct21-2013.11.fid
glo zhao zdb zd 188
carbon CDCl3 /opt/topspin av1 27
173.339
156.716
156.578
137.694
128.927
120.262
77.478
77.160
76.843
60.452
34.204
32.770
22.628
18.908
14.369
Me
Me
N
OEt
O
f1 (ppm)

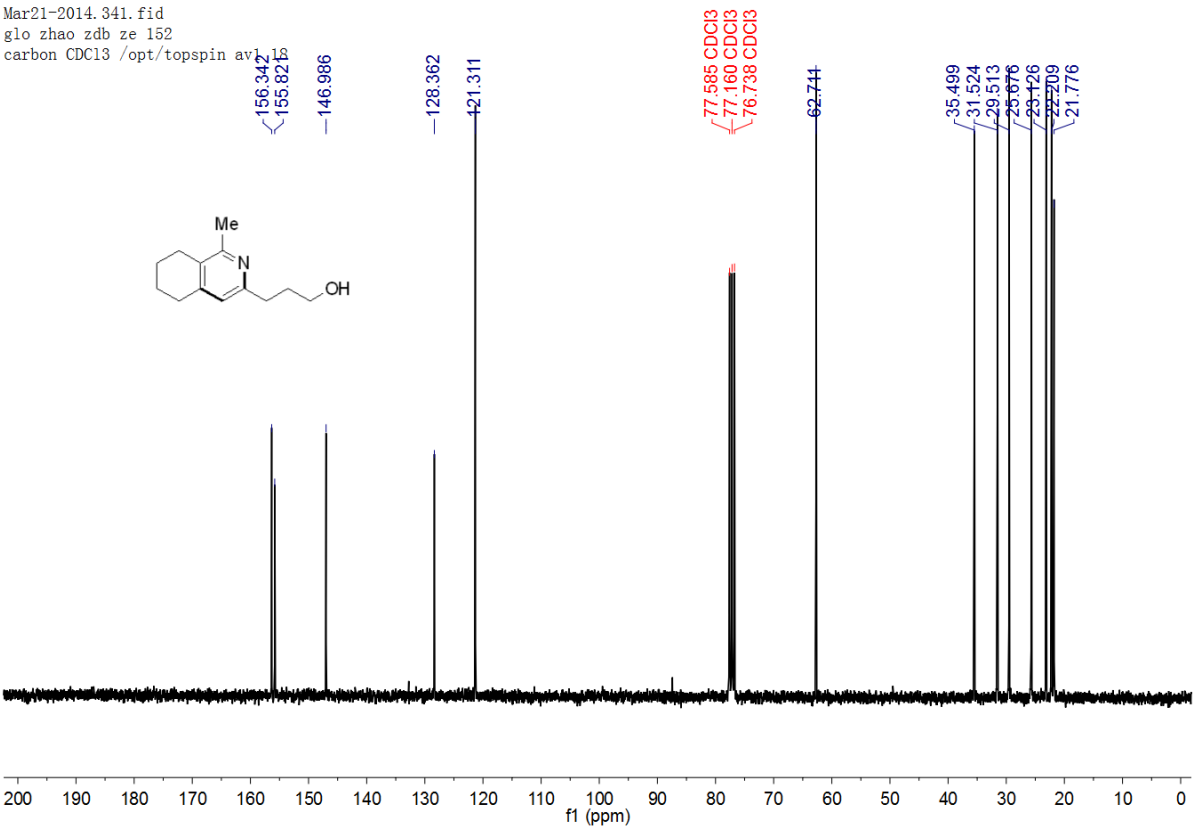

Jan09-2014.10.fid
glo dongbing zhao zdb zd 313
proton CDCl3 /opt/topspin av1 40
Me
N
OEt
P
O
OEt
0.89
4.38
1.96
1.96
2.07
3.00
2.27
4.06
6.07
f1 (ppm)

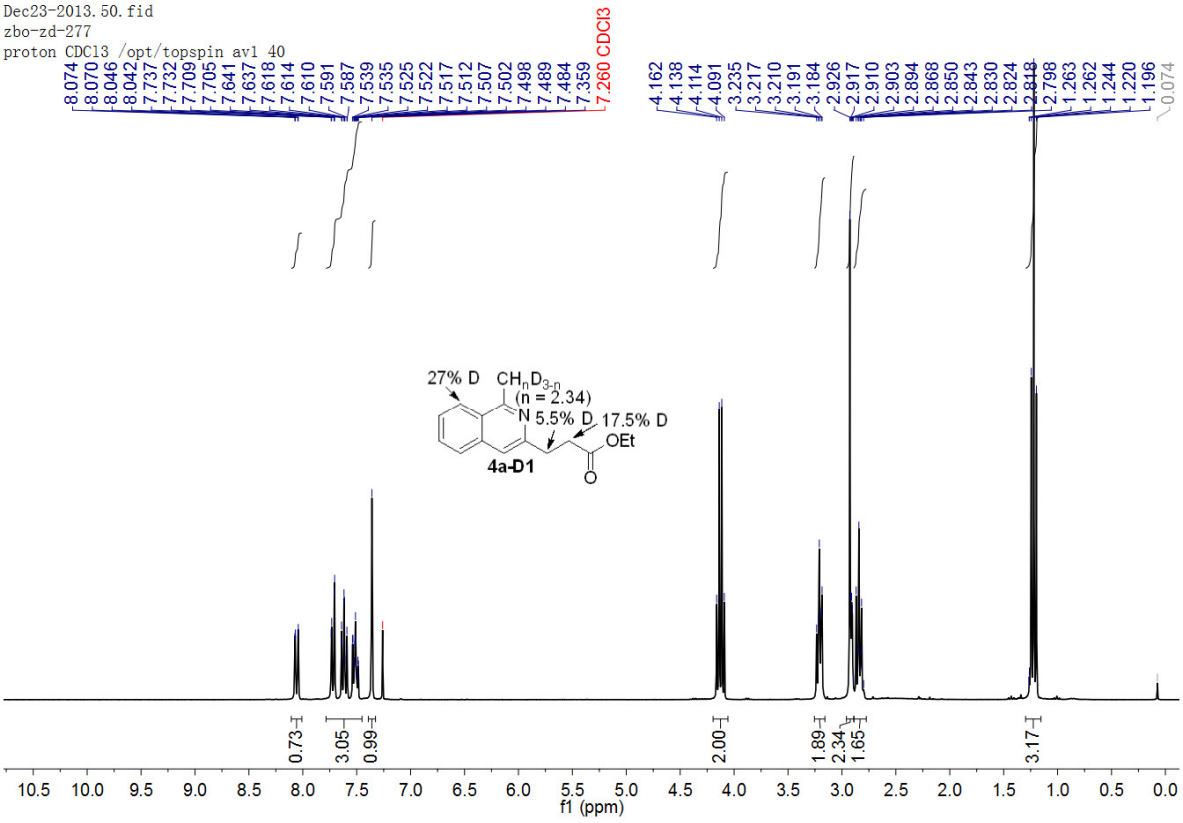

Mar24-2014.91.fid
glo zhao zdb ze 166
carbon CDCl3 /opt/topspin av1 36
156.626
155.618
155.444
146.505
128.689
120.752
77.478 CDCl3
77.160 CDCl3
76.842 CDCl3
61.560
30.521
30.479
29.528
26.471
25.858
25.080
23.216
22.267
22.218
16.580
16.519
Me
N
OEt
P
O
OEt
f1 (ppm)

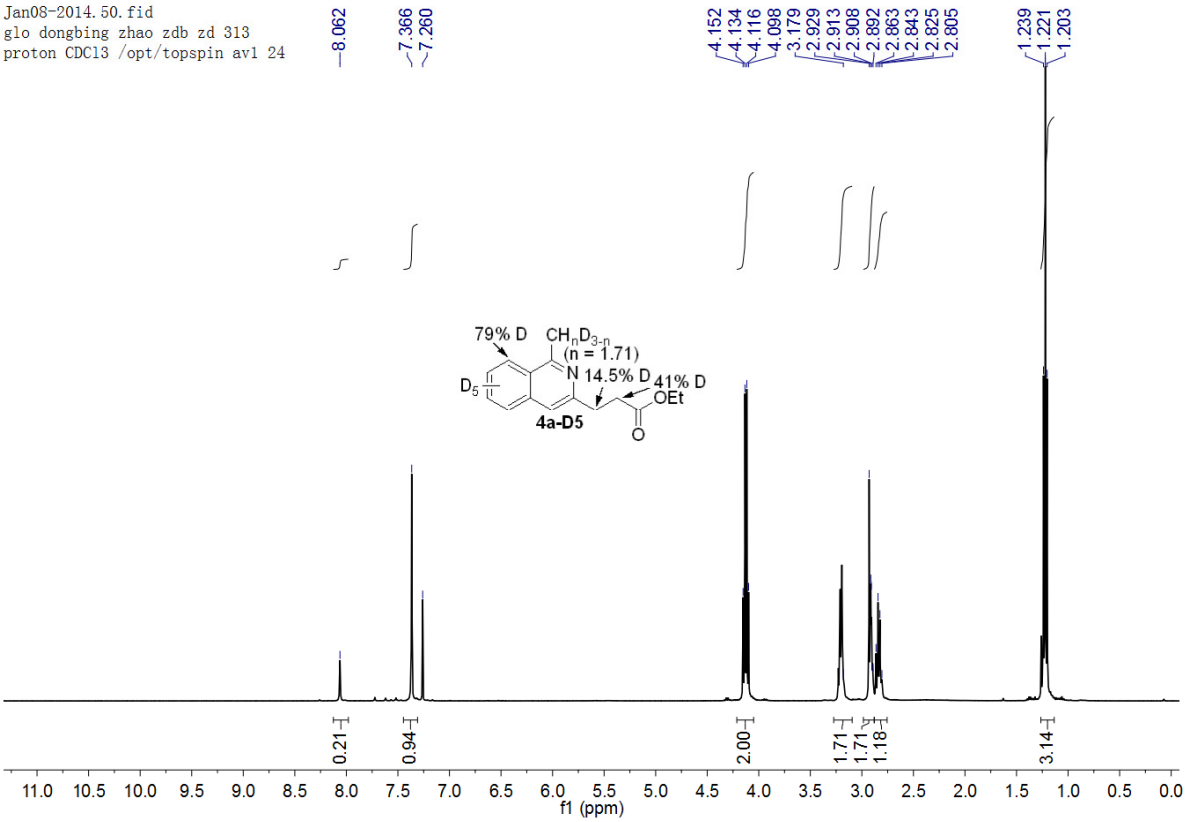

Jan10-2014.140
glo dongbing zhao zdb zd 0329
proton CDCl3 /opt/topspin3.5pl6/exp/stan
8.887
8.664
8.662
8.559
8.556
8.552
8.441
8.439
8.133
8.131
7.935
7.933
7.927
7.914
7.904
7.891
7.756
7.751
7.733
7.728
7.720
7.711
7.702
7.694
7.688
7.671
7.665
4.459
4.436
4.413
3.022
1.867
1.843
1.820
1.794
1.771
1.543
1.518
1.493
1.468
1.443
1.419
0.998
0.974
0.949
Me
N
COO^{n}Bu
1.00
1.04
1.08
2.04
2.07
2.95
2.11
2.22
3.19
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

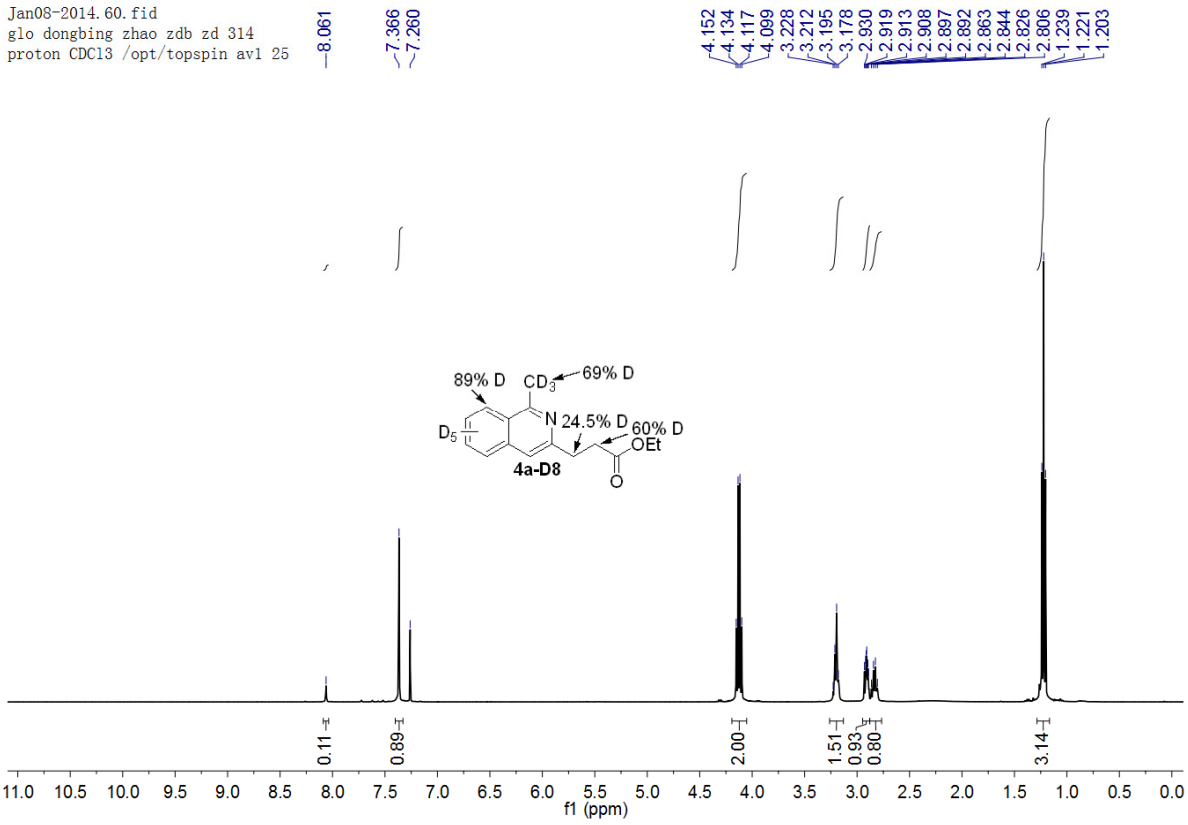

Jan10-2014.141.fid
glo dongbing zhao zdb zd 0329
carbon CDCl3 /opt/topspin3.5pl6/exp/stan
166.069
159.469
140.755
135.530
130.680
129.383
128.976
128.743
125.850
122.784
77.584
77.160
76.736
65.642
30.892
22.799
19.311
13.898
Me
N
COO^{n}Bu
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

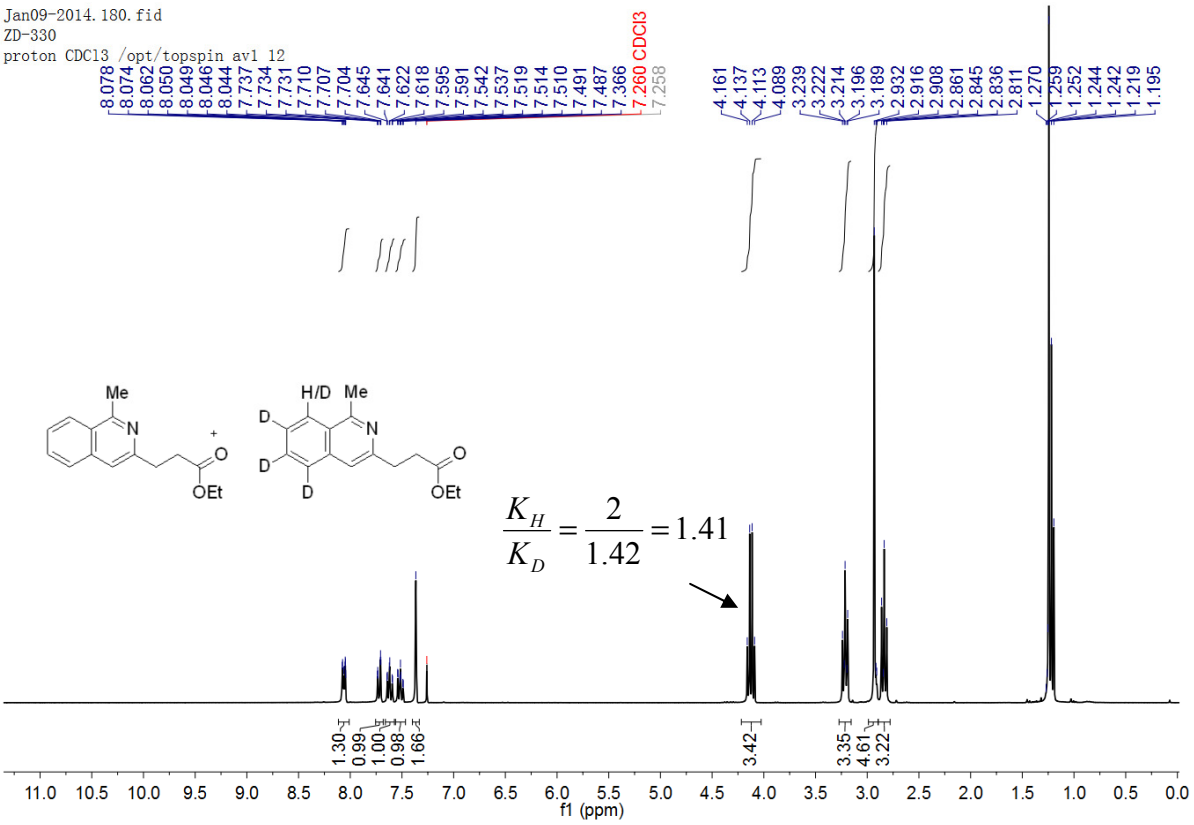

Mar21-2014.340.fid
glo zhao zdb ze 152
proton CDCl3 /opt/topspin av1 18
7.260
6.708
5.338
3.718
3.700
3.681
2.861
2.840
2.818
2.683
2.662
2.642
2.573
2.553
2.531
2.368
1.922
1.904
1.899
1.881
1.833
1.815
1.801
1.796
1.737
1.732
1.718
1.711
1.701
Me
N
OH
0.93
1.08
2.00
2.06
2.07
2.03
2.93
6.18
f1 (ppm)


Mar21-2014.341.fid
glo zhao zdb ze 152
carbon CDCl3 /opt/topspin av1 18
156.342
155.821
146.986
128.362
121.311
77.585 CDCl3
77.160 CDCl3
76.738 CDCl3
62.741
35.499
31.524
29.513
25.676
23.126
22.209
21.776
Me
N
OH
f1 (ppm)


Dec23-2013.50.fid
zbo-zd-277
proton CDCl3 /opt/topspin av1 40
7.260 CDCl3
27% D
CHnD3-n
(n = 2.34)
N
5.5% D
17.5% D
OEt
O
4a-D1
0.73
3.05
0.99
2.00
1.89
2.34
1.65
3.17
f1 (ppm)


Jan08-2014.50.fid
glo dongbing zhao zdb zd 313
proton CDCl3 /opt/topspin av1 24
7.366
7.260
79% D
CHnD3-n
(n = 1.71)
D5
N
14.5% D
41% D
OEt
O
4a-D5
0.21
0.94
2.00
1.71
1.71
1.18
3.14
f1 (ppm)


Jan08-2014.60.fid
glo dongbing zhao zdb zd 314
proton CDCl3 /opt/topspin av1 25
8.061
7.366
7.260
4.152
4.134
4.117
4.099
3.228
3.212
3.195
3.178
2.930
2.919
2.913
2.908
2.897
2.892
2.863
2.844
2.826
2.806
1.239
1.221
1.203
89% D
CD3
69% D
D5
N
24.5% D
60% D
OEt
O
4a-D8
0.11
0.89
2.00
1.51
0.93
0.80
3.14
f1 (ppm)


Jan09-2014.180.fid
ZD-330
proton CDCl3 /opt/topspin av1 12
7.260 CDCl3
7.258
4.161
4.137
4.113
4.089
3.239
3.222
3.214
3.196
3.189
2.932
2.916
2.908
2.861
2.845
2.836
2.811
1.270
1.259
1.252
1.244
1.242
1.219
1.195
Me
N
O
OEt
H/D
D
$\frac{K_H}{K_D} = \frac{2}{1.42} = 1.41$
1.30
0.99
1.00
0.98
1.66
3.42
3.35
4.61
3.22
f1 (ppm)