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Electronic Supplementary Information

Iron porphyrin-catalyzed C(sp^3)–H amination with alkyl azides for the synthesis of complex nitrogen-containing compounds

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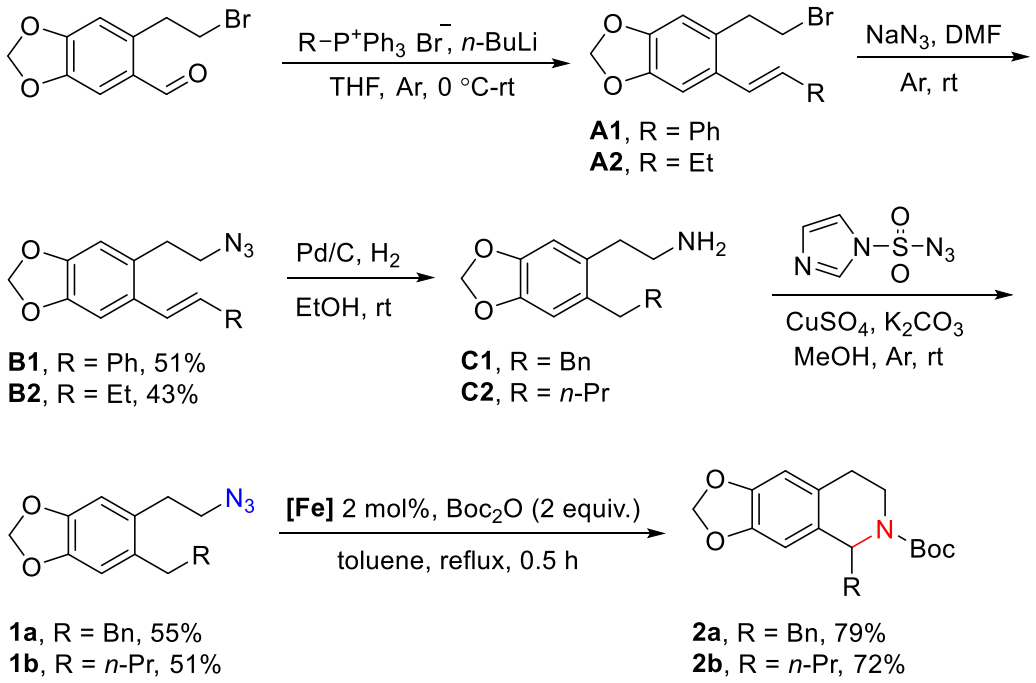
1. General information

All catalytic reactions were performed using the standard Schlenk technique under an argon atmosphere. Reagents obtained commercially were used without further purification unless indicated otherwise. Anhydrous toluene and dichloromethane (DCM) were freshly distilled with Na/benzophenone and CaH_2, respectively. TLC analysis was performed on silica gel 60 F_{254} pre-coated plates. ^1H, ^{13}C NMR and ^{19}F spectra were measured on either a Bruker DPX-500 or DPX-400 spectrometer. Chemical shifts (δ ppm) were determined with tetramethylsilane (TMS) as internal reference or nondeuterated solvent residual signal, and coupling constants (*J*) were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High resolution ESI-MS experiment was conducted using Q Exactive Mass Spectrometers (MS) (Thermo Fisher).

2. Nitrene insertion into benzylic C(sp^3)–H bonds to construct tetrahydroisoquinoline skeletons

Preparation of N-Boc-2-benzyl tetrahydroisoquinoline 2a and N-Boc-2-propyl tetrahydroisoquinoline 2b



Preparation of B1, B2. *n*-BuLi (0.62 mL, 2.50 mol/L) in hexane was added to a cooled (0 °C) Wittig reagent (1.56 mmol) in anhydrous THF in a round-bottomed flask under a nitrogen atmosphere. The resulting mixture was stirred for 1 h, then 6-(2-bromoethyl) benzo[*d*][1,3]dioxole-5-carbaldehyde (1.30 mmol, synthesized according

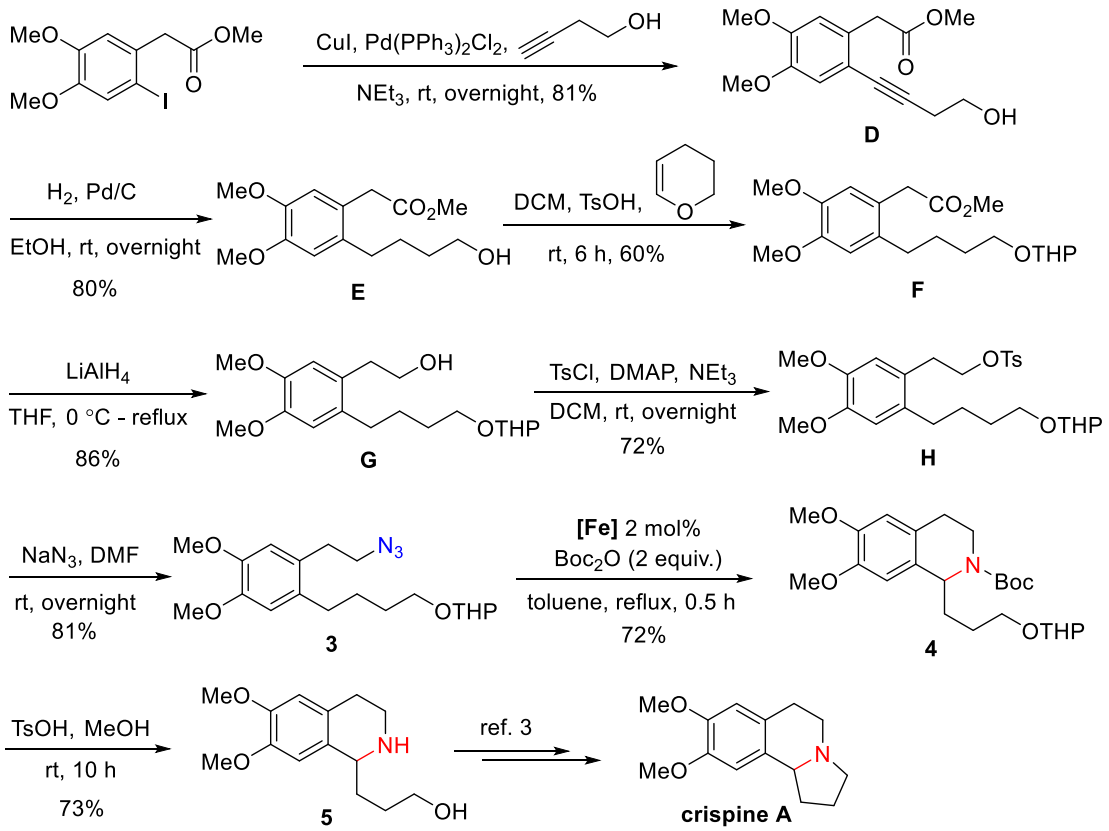
to the literature method.[1]) in anhydrous THF was added. After that, the mixture is stirred at room temperature for 12 h before it was poured into ice-water. The reaction mixture was extracted with DCM and the combined organic layer was washed sequentially with saturated $NaHCO_3$ solution (30 mL × 2), H_2O (30 mL × 3), and brine, dried over anhydrous $MgSO_4$. After evaporation under reduced pressure, the crude **A1**, **A2** were directly used for the next step.

To a solution of **A1**, **A2** (1.00 mmol) in DMF (5.0 mL) was added sodium azide (98 mg, 1.50 mmol). The reaction mixture was stirred overnight at 80 °C (oil bath). Water was added to the reaction mixture, and the crude product was extracted with diethyl ether (10 mL × 3). The combined organic layer was washed with H_2O (10 mL × 4), dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to give **B1** (51%) and **B2** (43%).

Preparation of azides 1a, 1b. To a round-bottomed flask containing **B** (0.80 mmol) and Pd/C (0.12 mmol, 10 wt%), EtOH (15.0 mL) was injected under hydrogen atmosphere (1 atm). The resulting mixture was stirred at room temperature for 12 h. After that, the mixture was filtered and washed with DCM. The filtrate was concentrated under reduced pressure and the crude product **C** was directly used without purification for next step. 1H-imidazole-1-sulfonyl azide (0.96 mmol) was added to a solution of **C** in methanol (8.0 mL). Then, K_2CO_3 (1.44 mmol) and anhydrous $CuSO_4$ (0.04 mmol) were added. The resulting mixture was stirred at room temperature overnight. After evaporation under reduced pressure, the residue was purified by flash column chromatography on silica gel (PE: EA = 10 :1) to afford **1a** (55%) and **1b** (51%).

Preparation of 2a, 2b. Azide 1 (0.20 mmol), $(Boc)_2O$ (87 mg, 0.40 mmol) and $[Fe^{III}(TDCPP)(IMe)_2]I$ (0.004 mmol) were added to a round-bottomed flask, then the reaction flask was purged and refilled with argon for three times. Then, toluene (3.0 mL) was injected to the flask and the resulting mixture was stirred at 150 °C (oil bath) for 0.5 h. TLC analysis showed the complete consumption of azide **1**. After evaporation under reduced pressure, the residue was purified by flash column chromatography on silica gel to afford the corresponding tetrahydroisoquinoline (**2a**, 79% yield; **2b**, 72% yield).

Preparation of crispine A



Preparation of D. A 25 mL round-bottomed flask was charged with methyl 2-(2-iodo-4,5-dimethoxyphenyl) acetate (2.877 g, 8.56 mmol, synthesized according to the literature method.[2]), $Pd(PPh_3)_2Cl_2$ (300 mg, 0.43 mmol), and CuI (245 mg, 1.28 mmol). The flask was purged and refilled with argon for three times. Triethylamine (10 mL) and but-3-yn-1-ol (720 mg, 10.27 mmol) were added by syringe subsequently, and the resulting reaction mixture was stirred at rt for 24 h. Then, triethylamine was removed under reduced pressure, and the resulting brown residue was purified by flash chromatography to afford **D** as an orange oil (yield 81%).

Preparation of E. To a round-bottomed flask containing **D** (1.90 g, 6.83 mmol) and Pd/C (0.68 mmol, 10% w/t) was added EtOH (10 mL) under hydrogen atmosphere (1atm). The mixture is stirred at room temperature for 12 h. After that, the mixture was filtered and washed with DCM. The filtrate was concentrated under reduced pressure. The obtained residue was purified by flash column chromatography to afford **E** (yield 80%).

Preparation of F. To a solution of **E** (1.545 g, 5.45 mmol) in CH_2Cl_2(15.0 mL) followed was added 3,4-dihydro-2H-pyran (918 mg, 10.91 mmol) and *p*-toluenesulfonic acid (94 mg, 0.55 mmol) subsequently. After stirring for 30 min, the reaction mixture was quenched with an aqueous solution of $NaHCO_3$ (satd., 5.0 mL),

extracted with EtOAc (20 mL × 3), dried (Na_2SO_4), filtered and evaporated. The residue was purified by flash column chromatography to afford **F** (yield 60%).

Preparation of G. To a solution of **F** (1.20 g, 3.27 mmol) in THF at 0 °C (ice bath) was added $LiAlH_4$ (187 mg, 4.91 mmol). The resulting mixture was stirred at 70 °C until complete consumption of the **F** (TLC monitoring). Then, after adding a minimum amount of H_2O carefully to quench the excess amount of $LiAlH_4$, the reaction mixture was filtered and washed with ethyl acetate. The combined organic fraction was dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to afford **G** as a colorless oil (yield 86%).

Preparation of H. To a solution of **G** (951 mg, 2.81 mmol) in dichloroethane (10.0 mL) was added *p*-toluenesulfonyl chloride (803 mg, 4.21 mmol), triethylamine (426 mg, 4.21 mmol) and 4-(dimethylamino) pyridine (35 mg, 0.28 mmol), and the resulting mixture was stirred at room temperature under atmosphere of argon for 12 h. After adding 20 mL of H_2O to quench the reaction, the mixture was extracted with ethyl acetate (30 mL × 2). The combined organic fraction was washed with a saturated solution of $NaHCO_3$ (10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford **H** as a colorless oil (yield 72%).

Preparation of azide 3. To a solution of **H** (1.00 g, 1.95 mmol) in DMF (10.0 mL) was added sodium azide (190 mg, 2.93 mmol). The reaction mixture was stirred overnight at rt. Water was added to the reaction mixture, and the crude product was extracted with diethyl ether (10 mL × 3). The combined organic layer was washed with H_2O (10 mL × 4), dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to give **3** (yield 81%).

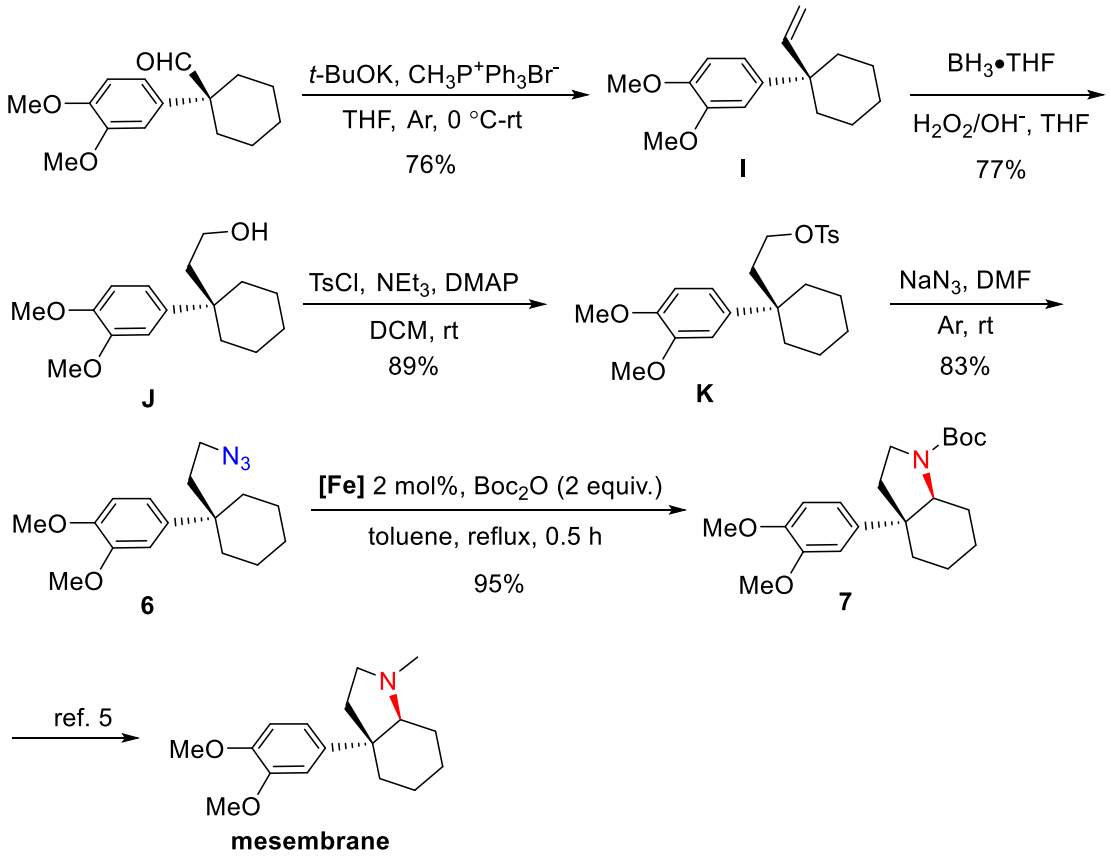
Preparation of tetrahydroisoquinoline 4. Azide **3** (218 mg, 0.60 mmol), $(Boc)_2O$ (262 mg, 1.20 mmol) and $[Fe^{III}(TDCPP)(IMe)_2]I$ (15.4 mg, 0.012 mmol) were added to a round-bottomed flask, then the reaction flask was purged and refilled with argon for three times. Then, toluene (3.0 mL) was injected to the flask and the resulting mixture was stirred at 150 °C (oil bath) for 0.5 h. TLC analysis showed the complete consumption of azide **3**. After evaporation under reduced pressure, the residue was purified by flash column chromatography on silica gel to afford the corresponding tetrahydroisoquinoline **4** (yield 72%).

Preparation of 5. A mixture of tetrahydroisoquinoline **4** (190 mg, 0.44 mmol) and a catalytic amount of recrystallised 4-toluene sulphonic acid (7.6 mg, 0.044 mmol) in methanol (8.8 mL) was stirred for 10 h at 25 °C. Subsequently, sodium bicarbonate was added, and the solution was concentrated to one third. After diluting with brine, the aqueous suspension was extracted 4 times with diethyl ether. The combined ether

extracts were dried with magnesium sulphate, filtered and concentrated under reduced pressure. The residue was purified by column chromatography to afford the product **5** (yield 73%). Crispine A could be synthesized from **5** according to the literature method.[3]

3. Nitrene insertion into unactivated C(sp^3)–H bonds

Preparation of mesembrane



Preparation of I. A mixture of $Ph_3P^+CH_3Br^-$ (4.144 g, 11.60 mmol) and *t*-BuOK (1.301 g, 11.60 mmol) in anhydrous THF was stirred under argon atmosphere for half an hour. Then, 1-(3,4-dimethoxyphenyl) cyclohexane-1-carbaldehyde (2.399 g, 9.66 mmol, synthesized according to the literature method.[4]) in THF was added and the reaction mixture was further stirred at rt for 18 h. After dilution with water, the mixture was extracted with DCM, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel to afford **I** (yield 76%).

Preparation of J. To a stirred solution of **I** (700 mg, 2.84 mmol) in THF (30 mL) under a nitrogen atmosphere at 0 °C was added BH_3•THF (3.41 mL, 3.41 mmol, 1.0 mol/L), and the resulting mixture was stirred for 3 h at room temperature. Then, the mixture is cooled to 0 °C, water (2.0 mL) is added dropwise and followed by addition of 10% aqueous sodium hydroxide solution (5 mL) and 35% H_2O_2 solution (1.5 mL). After stirring for another 30 min, the reaction mixture was extracted with diethyl ether

(20 mL × 3). The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel to afford **J** (yield 77%).

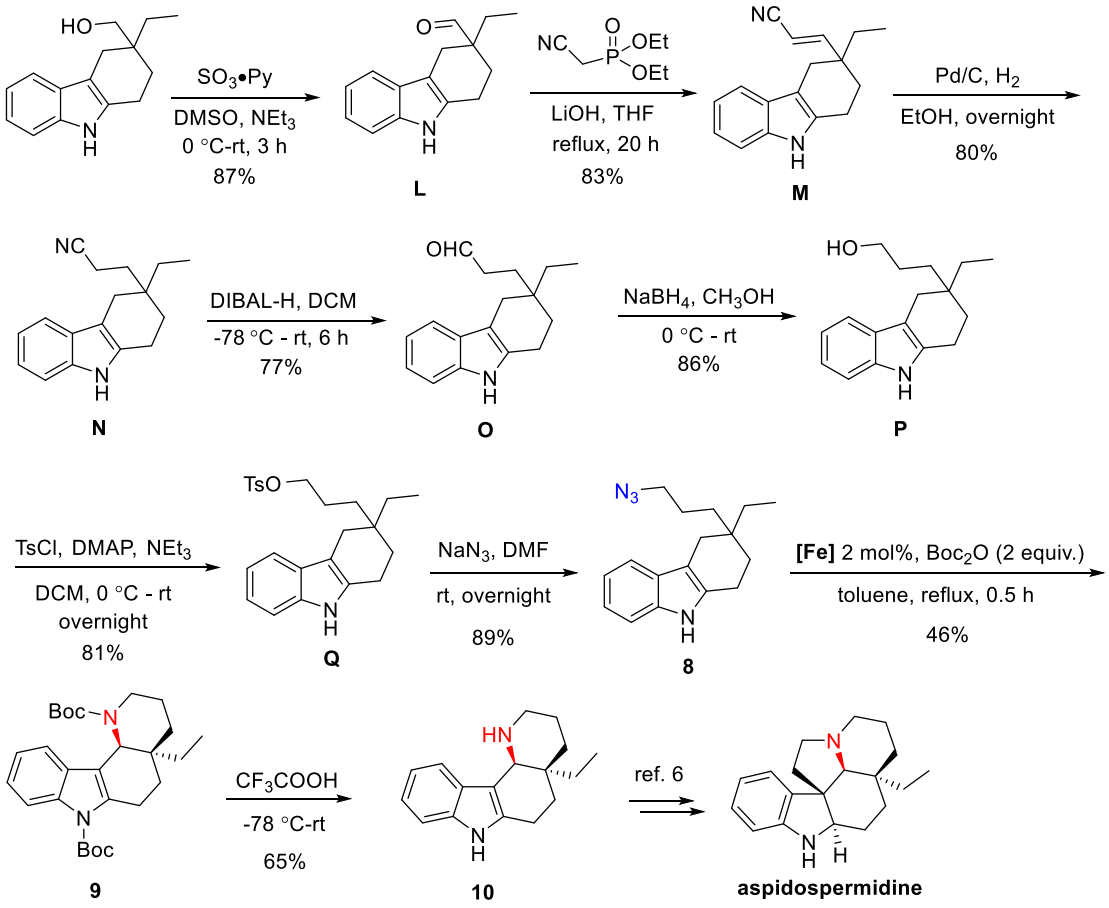
Preparation of K. To a solution of **J** (500 mg, 1.89 mmol) in dichloroethane (10.0 mL) was added *p*-toluenesulfonyl chloride (541 mg, 2.83 mmol), triethylamine (286 mg, 2.83 mmol) and 4-(dimethylamino) pyridine (23 mg, 0.189 mmol), and the resulting mixture was stirred at room temperature under atmosphere of argon for 12 h. After adding 20 mL of H_2O to quench the reaction, the mixture was extracted with ethyl acetate (30 mL × 2). The combined organic fraction was washed with a saturated solution of $NaHCO_3$ (10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford **K** as a colorless oil (yield 89%).

Preparation of azide 6. To a solution of **K** (700 mg, 1.67 mmol) in DMF (10.0 mL) was added sodium azide (163 mg, 2.51 mmol). The reaction mixture was stirred overnight at rt. Water was added to the reaction mixture, and the crude product was extracted with diethyl ether (10 mL × 3). The combined organic layer was washed with H_2O (10 mL × 4), dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to give **6** (yield 83%).

Preparation of 7. Azide **6** (58 mg, 0.20 mmol), $(Boc)_2O$ (87 mg, 0.40 mmol) and $[Fe^{III}(TDCPP)(IMe)_2]I$ (5.1 mg, 0.004 mmol) were added to a round-bottomed flask, then the reaction flask was purged and refilled with argon for three times. Then, toluene (3.0 mL) was injected to the flask and the resulting mixture was stirred at 150 °C (oil bath) for 0.5 h. TLC analysis showed the complete consumption of azide **6**. After evaporation under reduced pressure, the residue was purified by flash column chromatography on silica gel to afford **7** (yield 95%). Mesembrane could be synthesized from **7** according to the literature method.[5]

4. Preparation of polycyclic compounds

Preparation of aspidospermidine



Preparation of L. To a stirred solution of (3-ethyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl) methanol (1.147 g, 5.00 mmol, synthesized according to the literature method.[6]) in dry DCM (10.0 mL) were added dry DMSO (5.0 mL) and dry triethylamine (5.0 mL) at 0 °C under argon. After adding solid SO_3·Py (955 mg, 6.00 mmol) portionwise at the same temperature, the reaction mixture was slowly warmed to room temperature and stirred for 2 h. Aqueous NH_4Cl was added to the reaction mixture and extracted with DCM (20 mL × 3), the combined organic fraction was washed with water, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography to afford **L** (yield 87%).

Preparation of M. To a solution of **L** (950 mg, 4.18 mmol), diethyl cyanomethylphosphonate (1.051 g, 5.93 mmol) in 5.0 mL of anhydrous THF was added lithium hydroxide (150 mg, 6.27 mmol). The reaction mixture was heated to reflux for 20 h under argon atmosphere and then concentrated under reduce pressure. Diethyl ether (20 mL) was added to the resulting residue and washed with water (10 mL × 2) and brine (10 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated

under reduced pressure. The residue was purified by silica-gel column chromatography to afford **M** (yield 83%).

Preparation of N. To a round-bottomed flask containing **M** (850 mg, 3.40 mmol) and Pd/C (0.40 mmol, 10 wt % Pd), EtOH (10.0 mL) was injected under hydrogen atmosphere (1 atm). The resulting mixture was stirred at room temperature for 18 h. After that, the mixture was filtered and washed with EtOH. The filtrate was concentrated under reduced pressure and the was purified by flash column chromatography on silica gel to afford **N** (yield 80%).[7]

Preparation of O. To a solution of **N** (601 mg, 2.38 mmol) in DCM (5.0 mL) was added diisobutyl aluminium hydride (677 mg, 4.76 mmol) dropwise at -78 °C and further stirred for 2 h at this temperature, and then gradually rose to room temperature. The reaction mixture was quenched with saturated sodium bicarbonate, extracted with DCM (15 mL × 3), dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford **O** (yield 77%).

Preparation of P. To a solution of **O** (450 mg, 1.76 mmol) in MeOH (5.0 mL) was added $NaBH_4$ (100 mg, 2.64 mmol) in portion at 0 °C, then the reaction mixture was stirred at room temperature overnight. After that, the reaction mixture was diluted with water, extracted with DCM (10 mL × 3), dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash colunmn chromatography on silica gel to afford **P** (yield 86%).

Preparation of Q. To a solution of **P** (350 mg, 1.36 mmol) in anhydrous DCM (5.0 mL) were added DMAP (17 mg, 0.13 mmol), TsCl (389 mg, 2.04 mmol) and triethylamine (206 mg, 2.04 mmol) at 0 °C, and the resulting mixture was stirred at room temperature under atmosphere of argon overnight. After adding 20 mL of H_2O to quench the reaction, the mixture was extracted with DCM (10 mL × 3), dried over $MgSO_4$ and concentrated under reduced pressure. The obtained residue was purified by flash colunmn chromatography on silica gel to afford **Q** (yield 81%).

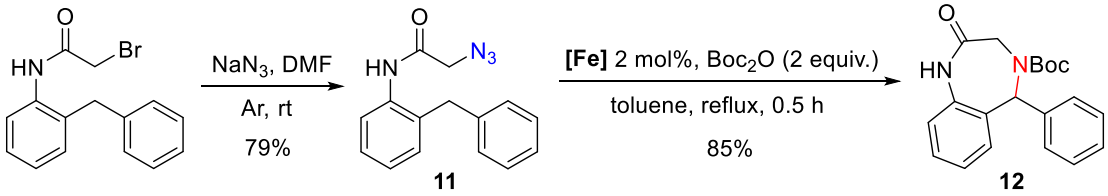
Preparation of azide 8. To a solution of **Q** (400 mg, 0.97 mmol) in anhydrous DMF (6.0 mL) was added NaN_3 (95 mg, 1.46 mmol) in portion. The mixture was stirred at room temperature overnight. Water was added to the reaction mixture, and the crude product was extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed with water to remove DMF, dried over $MgSO_4$ filtered, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to afford **8** (yield 89%).

Preparation of 9. Azide **8** (87 mg, 0.40 mmol), $(Boc)_2O$ (0.80 mmol) and $[Fe^{III}(TDCPP)(IMe)_2]I$ (5.1 mg, 0.0040 mmol) were added to a round-bottomed flask,

then the reaction flask was purged and refilled with argon for three times. Then, toluene (2.0 mL) was injected to the flask and the resulting mixture was stirred at 150 °C (oil bath) for 0.5 h. TLC analysis showed the complete consumption of azide **3**. After evaporation under reduced pressure, the residue was purified by flash column chromatography on silica gel to afford **9** (yield 46%).

Preparation of 10. A solution of **9** (40 mg, 0.088 mmol) in anhydrous DCM (2.0 mL) was added CF_3COOH (0.5 mL) at -78 °C. The reaction mixture was stirred at -78 °C for one hour, and then warmed to room temperature and further stirred for 6 h. After addition of saturated Na_2CO_3 dropwise to adjust the pH around 8~9, the reaction mixture was extracted with DCM, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford **10** (yield 65%). Crystals of **10•HCl** suitable for X-ray diffraction were grown by layering hexane onto a concentrated dichloromethane solution at room temperature. Aspidospermidine could be synthesized from **10** according to the literature method.[6]

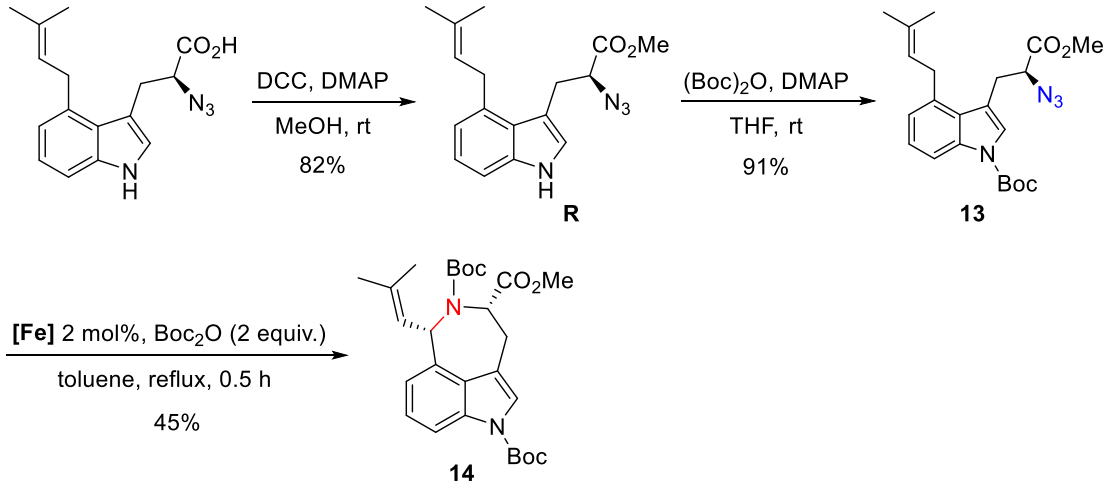
Preparation of benzodiazepine



Preparation of azide 11. To a solution of *N*-(2-benzylphenyl)-2-bromoacetamide (304 mg, 1.00 mmol, synthesized according to the literature method.[8]) in DMF (5.0 mL) was added NaN_3 (98 mg, 1.50 mmol) and the reaction mixture was stirred at room temperature for 18 h. The reaction mixture was poured into water (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layer was washed with H_2O (10 mL × 4), dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to afford **11** (yield 79%).

Preparation of benzodiazepine 12. Azide **11** (54 mg, 0.20 mmol), $(Boc)_2O$ (87 mg, 0.40 mmol) and $[Fe^{III}(TDCPP)(IMe)_2]I$ (5.1 mg, 0.004 mmol) were added to a round-bottomed flask, then the reaction flask was purged and refilled with argon for three times. Then, toluene (3.0 mL) was injected to the flask and the resulting mixture was stirred at 150 °C (oil bath) for 0.5 h. TLC analysis showed the complete consumption of azide. After evaporation under reduced pressure, the residue was purified by flash column chromatography on silica gel to afford **12** (85% yield).

Preparation of clavicipitic acid derivative

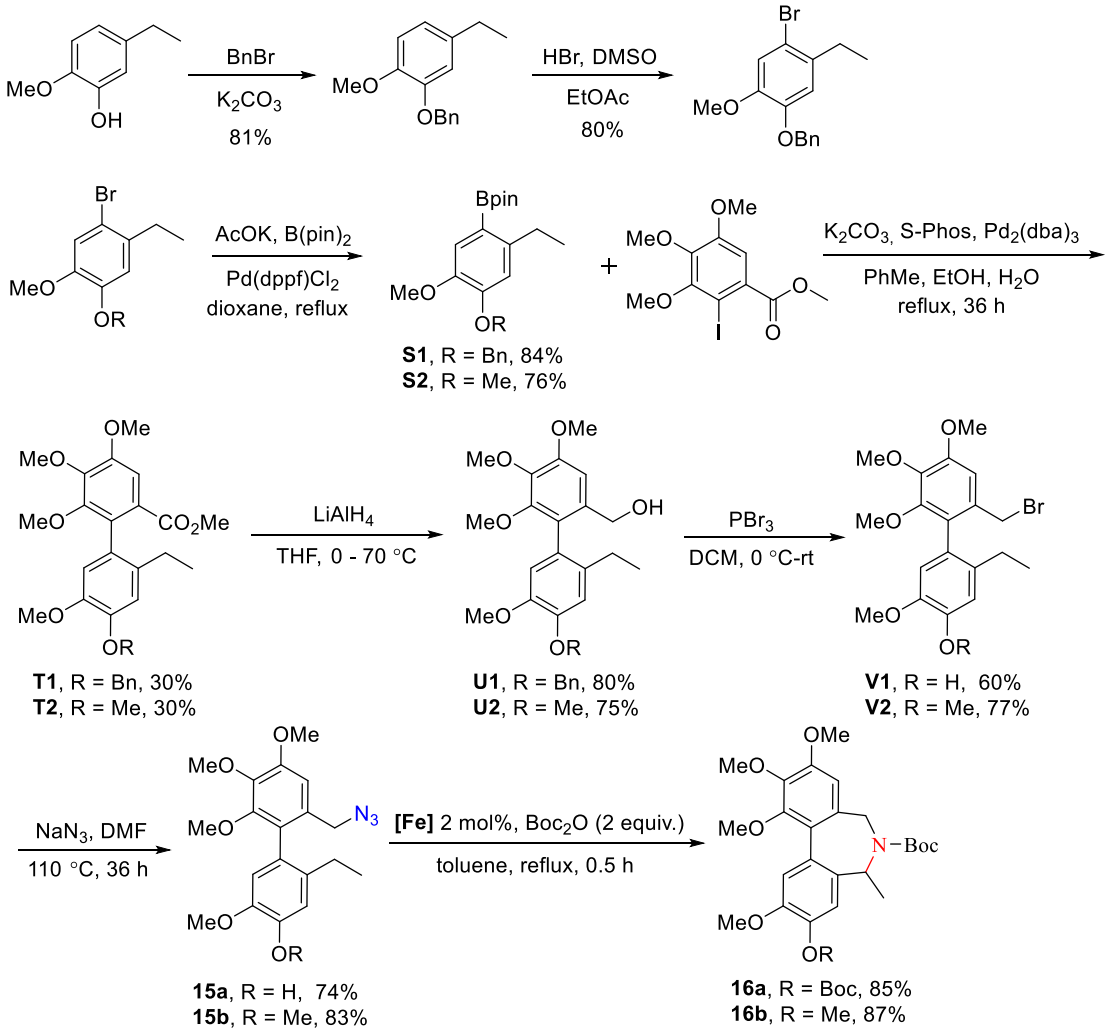


Preparation of R. To a solution of (*S*)-2-azido-3-(4-(3-methylbut-2-en-1-yl)-1H-indol-3-yl) propanoic acid (119 mg, 0.40 mmol, synthesized according to the literature method.[9]) in anhydrous MeOH were added dimethylaminopyridine (9.8 mg, 0.08 mmol) and dicyclohexylcarbodiimide (165 mg, 0.80 mmol), and the reaction mixture was stirred at room temperature overnight. Upon reaction completion checked by TLC, the reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel to afford **R** (yield 82%).

Preparation of 13. To a solution of **R** (81 mg, 0.26 mmol) in anhydrous THF were added dimethylaminopyridine (6.4 mg, 0.052 mmol) and di-tert-butyl-dicarbonate (63 mg, 0.29 mmol), and the reaction mixture was stirred at room temperature overnight. Upon reaction completion checked by TLC, the reaction mixture concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel to afford azide **13** (yield 91%).

Preparation of clavicipitic acid derivative 14. Azide **13** (83 mg, 0.20 mmol), $(Boc)_2O$ (0.40 mmol) and $[Fe^{III}(TDCPP)(IMe)_2]I$ (5.1 mg, 0.004 mmol) were added to a round-bottomed flask, then the reaction flask was purged and refilled with argon for three times. Then, toluene (3.0 mL) was injected to the flask and the resulting mixture was stirred at 150 °C (oil bath) for 0.5 h. TLC analysis showed the complete consumption of azide. After evaporation under reduced pressure, the residue was purified by flash column chromatography on silica gel to afford **14** (45% yield).[10]

Preparation of dibenz[c,e]azepines



Preparation of 2-(benzyloxy)-4-ethyl-1-methoxybenzene. A mixture of (bromomethyl) benzene (3.70 g, 21.68 mmol), 5-ethyl-2-methoxyphenol (3.00 g, 19.71 mmol) and K_2CO_3 (8.16 g, 59.14 mmol) in CH_3CN (20.0 mL) was stirred at 80 °C overnight. Then, the reaction mixture was concentrated under reduced pressure, diluted with water, extracted with ethyl acetate (3 × 20 mL), dried over Na_2SO_4, filtered and evaporated. The residue was purified by flash column chromatography to afford 2-(benzyloxy)-4-ethyl-1-methoxybenzene in 81% yield.

Preparation of 1-(benzyloxy)-4-bromo-5-ethyl-2-methoxybenzene. To a solution of 2-(benzyloxy)-4-ethyl-1-methoxybenzene (2.00 g, 8.25 mmol) in ethyl acetate (10.0 mL) were added HBr (735 mg, 48 wt% in H_2O, 19.71 mmol) and DMSO (709 mg, 9.07 mmol) and the reaction mixture was stirred at 60 °C overnight. Then, the reaction mixture was extracted with ethyl acetate (3 × 20 mL), dried over Na_2SO_4, filtered and evaporated. The residue was purified by flash column chromatography to afford 1-(benzyloxy)-4-bromo-5-ethyl-2-methoxybenzene in 80% yield.

Preparation of S1, S2 (With S2 as an example). To a solution of 1-bromo-2-ethyl-4,5-dimethoxybenzene (2.50 g, 10.20 mmol) in anhydrous dioxane (20 mL) were added AcOK (3.003 g, 30.6 mmol), $B(pin)_2$ (3.108 g, 12.24 mmol) and $Pd(dpppf)Cl_2$ (746 mg, 1.02 mmol) under argon. The resulting reaction mixture was stirred with reflux overnight. After adding water, the mixture was extracted with DCM, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford **S2** (yield 76%).

Preparation of T1, T2 (With T2 as an example). A flask charged with **S2** (2.00 g, 6.84 mmol), methyl 2-iodo-3,4,5-trimethoxybenzoate (2.408 g, 6.84 mmol, synthesized according to the literature method.[11]), $Pd_2(dba)_3$ (314 mg, 0.342 mmol), S-Phos (280 mg, 0.684 mmol) and K_2CO_3 (4726 mg, 34.1 mmol) was purged and refilled three times with argon. Then, PhMe (30 mL), EtOH (10 mL), H_2O (10 mL) were added to the reaction mixture and the resulting mixture was stirred with reflux for 36 h. The reaction mixture was extracted with ethyl acetate, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford **T2** (yield 30%).

Preparation of U1, U2 (With U2 as an example). To a solution of **T2** (800 mg, 2.05 mmol) in THF (4.0 mL) at 0 °C (ice bath) was added $LiAlH_4$ (156 mg, 4.10 mmol) in THF (4.0 mL) under argon, The resulting mixture was stirred at 70 °C until complete consumption of the **T2** (TLC monitoring). Then, the reaction mixture was quenched with isopropanol, filtered and washed with ethyl acetate. The combined organic fraction was purified by flash column chromatography on silica gel to afford **U2** (yield 75%).

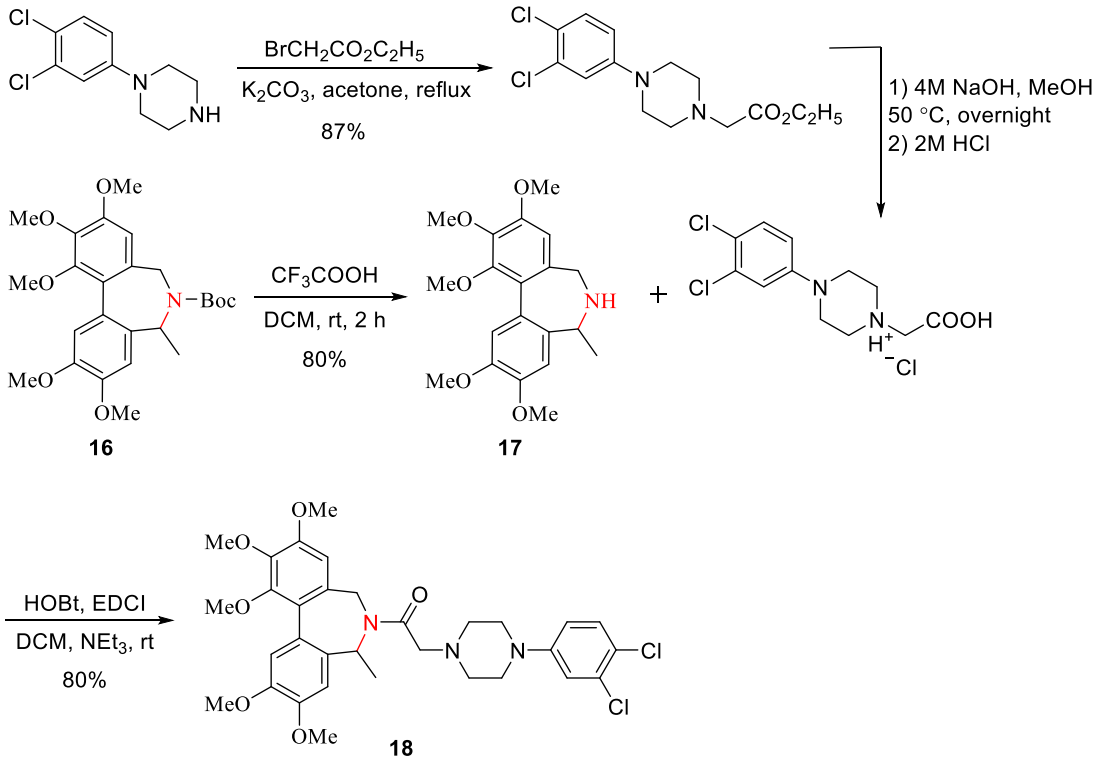
Preparation of V1, V2 (With V2 as an example). To a solution of **U2** (550 mg, 1.293 mmol) in anhydrous DCM (13.0 mL) was added PBr_3 (420 mg, 1.55 mmol) at 0 °C under argon. The mixture was stirred from ice-water bath to rt for 3 h. After that, the reaction mixture was diluted with saturated $NaHCO_3$, extracted with ethyl acetate, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford **V2** (yield 77%).

Preparation of azide 15a, 15b (With 15b as an example). To a solution of **V2** (425 mg, 1.00 mmol) in DMF (10.0 mL) was added to NaN_3 (98 mg, 1.50 mmol). The reaction mixture was stirred overnight at 110 °C for 36 h (monitoring by GC-MS). Upon reaction completion checked by TLC, the reaction mixture was diluted with water, extracted with ethyl acetate. The combined organic phase was washed with water, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to azide **15b** (yield 83%).

Preparation of dibenz[c,e]azepine 16a, 16b (With 16b as an example). Azide **15b** (300 mg, 0.774 mmol), $(Boc)_2O$ (338 mg, 1.549 mmol) and $[Fe^{III}(TDCPP)(IMe)_2]I$ (19.9 mg, 1.54% mmol) were added to a round-bottomed flask, then the flask was

purged and refilled with argon for three times. Then, toluene (7.0 mL) was injected to the flask and the resulting mixture was stirred at 150 °C (oil bath) for 0.5 h. TLC analysis showed the complete consumption of azide. After evaporation under reduced pressure, the residue was purified by flash column chromatography on silica gel to afford **16b** (yield 87%).

Preparation of dibenz[c,e]azepine derivative



Preparation of ethyl 2-(4-(3,4-dichlorophenyl) piperazin-1-yl) acetate. To a mixture of 1-(3,4-dichlorophenyl) piperazine (462 mg, 2.0 mmol) and K_2CO_3 (414 mg, 3.0 mmol) in anhydrous acetone was added ethyl 2-bromoacetate (400 mg, 2.40 mmol) under argon. The reaction mixture was stirred with reflux for 8 h. Upon reaction completion checked by TLC, the reaction mixture was diluted with water, extracted with DCM, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column on silica gel to afford ethyl 2-(4-(3,4-dichlorophenyl) piperazin-1-yl) acetate (yield 87%).

Preparation of 2-(4-(3,4-dichlorophenyl) piperazin-1-yl) acetic acid hydrochloride.[12] A solution of ethyl 2-(4-(3,4-dichlorophenyl) piperazin-1-yl) acetate (500 mg, 1.58 mmol) in 4M NaOH (5.0 mL) and MeOH (5.0 mL) was stirred at 50 °C overnight. Upon reaction completion checked by TLC, the reaction mixture was acidified to pH 2 by 2M HCl at 0 °C and stirred for another 0.5 h. Then, the reaction mixture was washed with petroleum ether and the aqueous phase was concentrated under reduced pressure. The residue was dissolved with methanol, filtered through

Celite545® and concentrated to afford 2-(4-(3,4-dichlorophenyl) piperazin-1-yl) acetic acid hydrochloride as a white amorphous powder and was used for the next step directly.

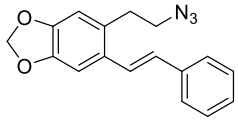
Preparation of 17. To a solution of **16** (300 mg, 0.652 mmol) in DCM (6.0 mL) was added CF_3COOH (2.0 mL) at room temperature, and the resulting reaction mixture was stirred for 2 h. After addition of saturated Na_2CO_3 dropwise to adjust the pH around 8~9, the reaction mixture was extracted with DCM, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column on silica gel to afford **17** (yield 80%).

Preparation of 18. A mixture of 2-(4-(3,4-dichlorophenyl) piperazin-1-yl) acetic acid (72 mg, 0.22 mmol), 1-hydroxybenzotriazole (30 mg, 0.22 mmol) and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (42 mg, 0.22 mmol) in anhydrous DCM was stirred at room temperature for 2 h under argon. Then, a solution of **17** (36 mg, 0.10 mmol) in DMF (2.0 mL) was added and further stirred at rt overnight. The reaction mixture was diluted with water, extracted with ethyl acetate. The combined organic layer was washed with water, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column on silica gel to afford **18** (80% yield).

5. Determination of cytotoxicity

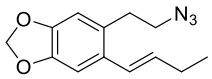
The antiproliferative property *in vitro* evaluation of compound **18** against large cell lung carcinoma (NCI-H460) cell line was carried out by using a method of 3-(4,5-dimethylthiazol- 2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay for 72 h using flat-bottomed 96-well plate. The supplemented culture medium with cells (1×10^4 cells/well) was seeded to the wells for 12 h. Compound **18** dissolved in DMSO were diluted with medium to various concentrations (1-100 μM), which contained no more than 1% DMSO(v/v) in the end. After 72 h incubation, the medium in each well was replaced by 100 μL of medium containing 10% MTT solution (0.5 mg/mL in phosphate-buffered saline). After incubation for an additional 2 h, the medium/MTT mixture was removed, and the resulting purple formazan crystals were dissolved with 100 μL DMSO per well. Optical Densities (OD) at a wavelength of 570 nm were measured with a microplate reader (Infinite M200, Swiss, Tecan). The quantity of vital cells was expressed in terms of the T/C value in comparison to the untreated control.

6. Characterization of substrates and products

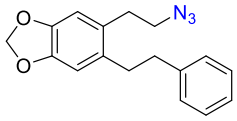


(*E*)-5-(2-Azidoethyl)-6-styrylbenzo[*d*][1,3]dioxole (B1) (*trans*:*cis* = 1:0.9). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (*cis*, d, *J* =7.2 Hz, 2H), 7.41 (*trans*, t, *J* = 7.7 Hz, 2H), 7.33 – 7.15 (*cis* or *trans*, m, 4 H); 6.94 (*trans*, d, *J* = 16.0 Hz, 1H), 6.77 (*trans*, s, 1H), 6.74 (*cis*, s, 1H), 6.68 (*trans*, s, 1H), 6.63 (*cis*, s, 1H), 6.63 (*cis*, d, *J* = 1.9 Hz, 1H), 6.00 (*cis*, s, 2H), 5.95

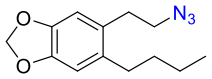
(*trans*, s, 2H), 3.48 (*cis*, t, *J* = 7.4 Hz, 2H), 3.42 (*trans*, t, *J* = 7.3 Hz, 2H), 3.00 (*cis*, t, *J* = 7.4 Hz, 2H), 2.86 (*trans*, t, *J* = 7.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.48 (*cis*), 147.20 (*cis*), 147.16, 146.56, 137.45 (*cis*), 136.45, 131.26, 130.38, 130.11 (*cis*), 129.70, 129.58 (*cis*), 129.49 (*cis*), 129.00, 128.80 (*cis*), 128.31, 128.22, 127.71 (*cis*), 127.38, 126.49 (*cis*), 125.10 (*cis*), 110.11(*cis*), 109.96, 109.60, 105.83 (*cis*), 101.23 (*cis*), 101.08, 52.18 (*cis*), 51.77, 33.09, 32.90 (*cis*). HRMS (ESI) m/z: calcd for $C_{17}H_{16}NO_2$ ($[M–N_2+H]^+$) 266.1176, found 266.1180.



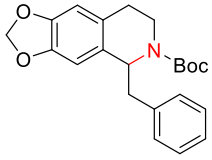
(*E*)-5-(2-Azidoethyl)-6-(but-1-en-1-yl)benzo[*d*][1,3]dioxole (B2) (*trans*:*cis* = 0.6:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96 (*trans*, s, 1H), 6.72 (*cis*, s, 1H), 6.70 (*cis*, s, 1H), 6.66 (*trans*, s, 1H), 6.52 (*trans*, dt, *J* = 15.3, 1.7 Hz, 1H), 6.39 (*cis*, dt, *J* = 11.3, 1.7 Hz, 1H), 6.07 (*trans*, dt, *J* = 15.5, 6.6 Hz, 1H), 5.96 (*cis*, s, 2H), 5.94 (*trans*, s, 2H), 5.72 (*cis*, dt, *J* = 11.3, 7.4 Hz, 2H), 3.42 (*trans*, t, *J* = 7.5 Hz, 2H), 3.38 (*cis*, t, *J* = 7.4 Hz, 2H), 2.90 (*trans*, t, *J* = 7.5 Hz, 2H), 2.83 (*cis*, t, *J* = 7.4 Hz, 2H), 2.27 (*trans*, pd, *J* = 7.5, 1.7 Hz, 2H), 2.17 (*cis*, pd, *J* = 7.5, 1.5 Hz, 2H), 1.13 (*trans*, t, *J* = 7.5 Hz, 3H), 1.04 (*cis*, t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.93, 146.72, 146.57 (*cis*), 146.08 (*cis*), 135.40 (*cis*), 133.77, 130.79, 130.20 (*cis*), 129.46 (*cis*), 128.26, 126.34 (*cis*), 125.40, 109.84 (*cis*), 109.79, 109.71 (*cis*), 106.15, 101.00, 51.92, 51.70 (*cis*), 32.93 (*cis*), 32.71, 26.31, 21.75 (*cis*), 14.25 (*cis*), 13.84. HRMS (ESI) m/z: calcd for $C_{13}H_{16}NO_2$ ($[M–N_2+H]^+$) 218.1176, found 218.1171.



5-(2-Azidoethyl)-6-phenethylbenzo[*d*][1,3]dioxole (1a). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.4 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.72 (s, 1H), 6.67 (s, 1H), 5.95 (s, 2H), 3.34 (t, *J* = 7.5 Hz, 2H), 2.87 (s, 4H), 2.77 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.54, 145.99, 141.38, 133.18, 128.64, 128.50, 128.46, 126.17, 109.57, 109.55, 100.92, 52.19, 37.96, 34.65, 31.92. HRMS (ESI) m/z: calcd for $C_{17}H_{18}NO_2$ ($[M–N_2+H]^+$) 268.1332, found 268.1335.

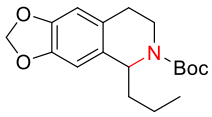


5-(2-Azidoethyl)-6-butylbenzo[*d*][1,3]dioxole (1b). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.67 (s, 1H), 6.65 (s, 1H), 5.90 (s, 2H), 3.42 (t, *J* = 7.5 Hz, 2H), 2.83 (t, *J* = 7.5 Hz, 2H), 2.55 – 2.51 (m, 2H), 1.56 – 1.49 (m, 2H), 1.43 – 1.35 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.42, 145.72, 134.41, 128.28, 109.56, 109.51, 100.82, 52.32, 33.79, 32.35, 32.01, 22.65, 14.03. HRMS (ESI) m/z: calcd for $C_{13}H_{18}NO_2$ ($[M–N_2+H]^+$) 220.1332, found 220.1335.

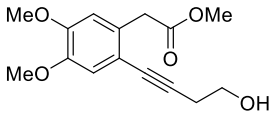


***tert*-Butyl 5-benzyl-7,8-dihydro-[1,3]dioxolo[4,5-*g*]isoquinoline-6(5*H*)-carboxylate (2a) (1:2 Diastereomers).**[13] ^{1}H NMR (500 MHz, $CDCl_3$) δ major peaks. 7.28 – 7.20 (m, 3H), 7.12 (d, *J* = 5.0 Hz, 2H), 6.59 (s, 1H), 6.51 (s, 1H), 5.92 (s, 1H), 5.90 (s, 1H), 5.10 (dd, *J* = 8.7, 5.4 Hz, 1H), 4.15 (ddd, *J* = 13.2, 5.9, 3.4 Hz, 1H), 3.26 – 3.21 (m, 1H), 3.05 – 3.02 (m, 1H), 3.00 – 2.97 (m, 1H), 2.82 (m, 1H), 2.58 (dt, *J* = 16.0, 3.9 Hz, 1H), 1.21 (s, 9H).

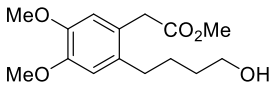
^{13}C NMR (126 MHz, $CDCl_3$) δ 154.38, 146.32, 145.88, 138.51, 130.04, 129.64, 128.36, 127.88, 126.43, 108.66, 107.18, 100.88, 79.62, 56.76, 42.97, 36.94, 28.10. HRMS (ESI) m/z: calcd for $C_{22}H_{25}NO_4Na$ ([M+Na]$^+$) 390.1676, found 390.1672.



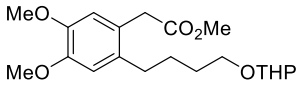
***tert*-Butyl 5-propyl-7,8-dihydro-[1,3]dioxolo[4,5-*g*]isoquinoline-6(5*H*)-carboxylate (2b) (3:2 Diastereomers).** ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.56 (s, 2H), 5.89 (s, 2H), 5.07 – 4.88 (m, 1H), 4.19 – 3.82 (m, 1H), 3.29 – 3.10 (m, 1H), 2.88 – 2.72 (m, 1H), 2.65 – 2.56 (m, 1H), 1.80 – 1.72 (m, 1H), 1.66 – 1.56 (m, 1H), 1.47 (s, 9H), 1.43 – 1.37 (m, 2H), 0.99 – 0.90 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.88, 146.06, 145.85, 131.34, 127.46, 108.65, 106.98, 100.79, 79.76, 54.54, 39.39, 36.66, 28.49, 19.64, 14.06. HRMS (ESI) m/z: calcd for $C_{13}H_{18}NO_2$ ([M–Boc+H$_2$]$^+$) 220.1332, found 220.1328.



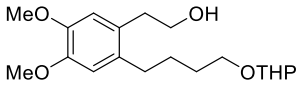
Methyl 2-(2-(4-hydroxybut-1-yn-1-yl)-4,5-dimethoxyphenyl)acetate (D). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.91 (s, 1H), 6.76 (s, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.79 (q, *J* = 6.2 Hz, 2H), 3.74 (s, 2H), 3.69 (s, 3H), 3.35 (t, *J* = 6.4 Hz, 1H), 2.67 (t, *J* = 6.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.22, 148.90, 147.71, 129.03, 115.62, 114.33, 112.78, 90.28, 80.12, 61.06, 55.86, 52.16, 39.76, 23.95. HRMS (ESI) m/z: calcd for $C_{15}H_{19}O_5$ ([M+H]$^+$) 279.1227, found 279.1224.



Methyl 2-(2-(4-hydroxybutyl)-4,5-dimethoxyphenyl)acetate (E). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (s, 1H), 6.70 (s, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.65 (s, 3H), 3.57 (s, 2H), 3.38 (t, *J* = 7.5 Hz, 2H), 2.56 (t, *J* = 7.7 Hz, 2H), 1.65 – 1.56 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.65, 147.97, 146.89, 133.38, 123.79, 113.72, 112.62, 62.04, 55.81, 55.76, 51.95, 37.83, 32.30, 27.27. HRMS (ESI) m/z: calcd for $C_{15}H_{23}O_5$ ([M+H]$^+$) 283.1540, found 283.1537.

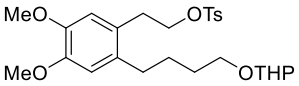


Methyl 2-(4,5-dimethoxy-2-(4-((tetrahydro-2*H*-pyran-2-yl)oxy)butyl)phenyl)acetate (F). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (s, 1H), 6.67 (s, 1H), 4.57 – 4.54 (m, 1H), 3.88 – 3.80 (m, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.79 – 3.72 (m, 1H), 3.66 (s, 3H), 3.57 (s, 2H), 3.50 – 3.44 (m, 1H), 3.43 – 3.35 (m, 1H), 2.57 (t, *J* = 7.5 Hz, 2H), 1.84 – 1.76 (m, 1H), 1.72 – 1.45 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.37, 148.06, 147.02, 133.38, 123.88, 113.62, 112.64, 98.89, 67.34, 62.33, 55.94, 55.87, 51.97, 37.93, 32.49, 30.75, 29.61, 27.92, 25.47, 19.66. HRMS (ESI) m/z: calcd for $C_{20}H_{30}O_6Na$ ([M+Na]$^+$) 389.1935, found 389.1929.

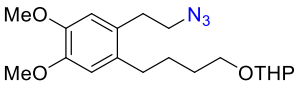


2-(4,5-Dimethoxy-2-(4-((tetrahydro-2*H*-pyran-2-yl)oxy)butyl)phenyl)ethan-1-ol (G). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.68 (s, 1H), 6.67 (s, 1H), 4.57 – 4.53 (m, 1H), 3.90– 3.83 (m, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.81 – 3.75 (m, 3H), 3.51 – 3.45 (m, 1H), 3.44 – 3.38 (m, 1H), 2.83 (t, *J* = 7.0 Hz, 2H), 2.63 – 2.56 (m, 2H), 1.95 (br s, 1H), 1.86 – 1.76 (m, 1H), 1.74 – 1.44 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.45, 147.03, 133.23, 127.84, 113.21,

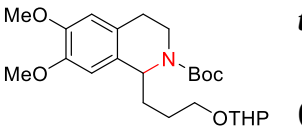
112.87, 99.18, 67.38, 63.57, 62.64, 55.97, 55.93, 35.63, 32.22, 30.79, 29.58, 28.40, 25.44, 19.82. HRMS (ESI) m/z: calcd for $C_{19}H_{30}O_5Na$ ([M+Na]$^+$) 361.1985, found 361.1982.



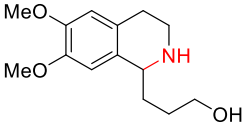
4,5-Dimethoxy-2-(4-((tetrahydro-2*H*-pyran-2-yl)oxy)butyl)phenethyl 4-methylbenzenesulfonate (H). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 6.63 (s, 1H), 6.53 (s, 1H), 4.57 (dd, *J* = 8.6, 6.1 Hz, 1H), 4.15 (d, 7.2 Hz, 2H), 3.90 – 3.84 (m, 1H), 3.85 (s, 3H), 3.79 – 3.73 (m, 1H), 3.78 (s, 3H), 3.53 – 3.49 (m, 1H), 3.44 – 3.35 (m, 1H), 2.92 (t, *J* = 7.3 Hz, 2H), 2.49 (t, *J* = 7.6 Hz, 2H), 2.43 (s, 3H), 1.86 – 1.78 (m, 1H), 1.75 – 1.68 (m, 1H), 1.66 – 1.59 (m, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.80, 147.01, 144.67, 133.13, 132.94, 129.73, 127.76, 125.45, 112.90, 112.60, 98.96, 70.47, 67.27, 62.44, 55.86, 55.85, 32.09, 31.78, 30.77, 29.56, 28.27, 25.46, 21.58, 19.74. HRMS (ESI) m/z: calcd for $C_{26}H_{36}O_7SNa$ ([M+Na]$^+$) 515.2074, found 515.2070.



2-(4-(2-(2-Azidoethyl)-4,5-dimethoxyphenyl)butoxy)tetrahydro-2*H*-pyran (3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (s, 1H), 6.64 (s, 1H), 4.56 – 4.53 (m, 1H), 3.87 – 3.81 (m, 1H), 3.82 (s, 6H), 3.78 – 3.73 (m, 1H), 3.43 – 3.38 (m, 1H), 3.42 – 3.38 (m, 1H), 3.41 (t, *J* = 7.5 Hz, 2H), 2.82 (t, *J* = 7.5 Hz, 2H), 2.57 (t, *J* = 7.7 Hz, 2H), 1.84 – 1.75 (m, 1H), 1.72 – 1.60 (m, 5H), 1.57 – 1.46 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.76, 147.15, 132.95, 127.40, 112.83, 112.79, 98.90, 67.26, 62.34, 55.97, 55.87, 52.35, 32.18, 31.81, 30.76, 29.62, 28.37, 25.48, 19.68. HRMS (ESI) m/z: calcd for $C_{19}H_{29}N_3O_4Na$ ([M+Na]$^+$) 386.2050, found 386.2044.

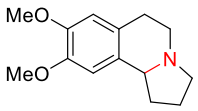


***tert*-Butyl 6,7-dimethoxy-1-(3-((tetrahydro-2*H*-pyran-2-yl)oxy)propyl)-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (4) (2:3 Diastereomers).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.61 – 6.54 (m, 2H), 5.15 – 4.90 (m, 1H), 4.55 (m, 1H), 4.26 – 3.92 (m, 1H), 3.89 – 3.70 (m, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 3.50 – 3.37 (m, 2H), 3.30 – 3.04 (m, 1H), 2.90 – 2.72 (m, 1H), 2.65 – 2.52 (m, 1H), 1.88 – 1.40 (m, 10H), 1.46 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.86, 147.33, 129.96, 126.33, 111.53, 109.97, 98.95, 79.82, 67.30, 62.36, 56.02, 55.89, 54.31, 38.24, 36.61, 33.81, 33.31, 30.77, 28.49, 26.66, 25.46, 19.68. HRMS (ESI) m/z: calcd for $C_{24}H_{37}NO_6Na$ ([M+Na]$^+$) 458.2513, found 458.2509.

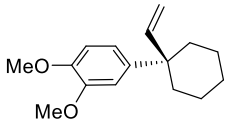


3-(6,7-Dimethoxy-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-1-ol (5).[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.59 (s, 1H), 6.56 (s, 1H), 5.00 – 4.77 (br, 2H), 3.94 (dd, *J* = 8.1, 3.1 Hz, 1H), 3.86 (s, 3H0, 3.85 (s, 3H), 3.68 – 3.64 (m, 1H), 3.59 – 3.51 (m, 1H), 3.23 – 3.16 (m, 1H), 3.08 – 3.01 (m, 1H), 2.77 (dt, *J* = 16.1, 5.6 Hz, 1H), 2.67 (dt, *J* = 16.2, 6.0 Hz, 1H), 2.00 – 1.94 (m, 2H), 1.84 – 1.66 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.51, 147.39, 130.38,

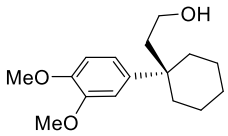
126.71, 111.69, 109.38, 62.83, 56.04, 55.84, 55.44, 39.73, 35.66, 30.65, 28.75. HRMS (ESI) m/z: calcd for $C_{14}H_{22}NO_3$ ([M+H]$^+$) 252.1594, found 252.1592.



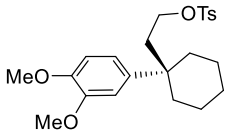
Crispine A.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 (s, 1H), 6.55 (s, 1H), 3.83, (s, 3H), 3.82 (s, 3H), 3.51 – 3.46 (m, 1H), 3.15 (ddd, *J* = 11.1, 6.0, 3.0 Hz, 1H), 3.08 – 2.94 (m, 2H), 2.76 – 2.57 (m, 3H), 2.37 – 2.27 (m, 1H), 1.99 – 1.80 (m, 2H), 1.77 – 1.67 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.41, 147.30, 130.54, 126.06, 111.33, 108.89, 62.76, 56.00, 55.89, 53.09, 48.20, 30.61, 27.82, 22.25. HRMS (ESI) m/z: calcd for $C_{14}H_{20}NO_2$ ([M+H]$^+$) 234.1489, found 234.1486.



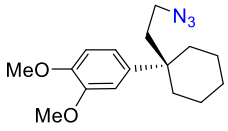
1,2-Dimethoxy-4-(1-vinylcyclohexyl)benzene (I). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 – 6.90 (m, 2H), 6.84 (d, *J* = 8.3 Hz, 1H), 5.84 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.07 (dd, *J* = 10.7, 0.8 Hz, 1H), 4.91 (dd, *J* = 17.6, 0.9 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 2.05 – 1.97 (m, 2H), 1.89 – 1.82 (m, 2H), 1.66 – 1.57 (m, 2H), 1.56 – 1.40 (m, 3H), 1.45 – 1.39 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.59, 147.59, 146.96, 139.68, 118.86, 112.25, 110.82, 110.66, 55.86, 55.78, 44.43, 36.07, 26.37, 22.58. HRMS (ESI) m/z: calcd for $C_{16}H_{23}O_2$ ([M+H]$^+$) 247.1693, found 247.1689.



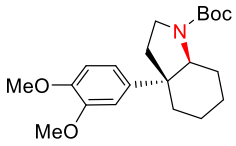
2-(1-(3,4-Dimethoxyphenyl)cyclohexyl)ethan-1-ol (J). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 – 6.82 (m, 2H), 6.83 – 6.79 (m, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.37 (t, *J* = 7.3 Hz, 2H), 2.03 (dd, *J* = 12.4, 6.4 Hz, 2H), 1.80 (t, *J* = 7.3 Hz, 2H), 1.62 – 1.51 (m, 4H), 1.44 – 1.35 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.78, 146.87, 139.03, 118.88, 110.98, 110.18, 59.37, 55.94, 55.79, 39.80, 36.71, 26.45, 22.23. HRMS (ESI) m/z: calcd for $C_{16}H_{23}O_2$ ([M–OH]$^+$) 247.1693, found 247.1688.



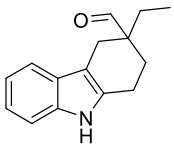
2-(1-(3,4-Dimethoxyphenyl)cyclohexyl)ethyl 4-methylbenzenesulfonate (K). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.77 – 6.71 (m, 3H), 3.86 (s, 3H), 3.83 (s, 3H), 3.73 (t, *J* = 7.4 Hz, 2H), 2.43 (s, 3H), 1.98 (dd, *J* = 12.4, 5.5 Hz, 2H), 1.87 (t, *J* = 7.4 Hz, 2H), 1.58 – 1.47 (m, 4H), 1.43 – 1.33 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.80, 147.01, 144.59, 137.64, 133.02, 129.71, 127.74, 118.84, 110.89, 109.86, 67.98, 55.84, 55.76, 39.88, 36.47, 26.21, 22.12, 21.60. HRMS (ESI) m/z: calcd for $C_{23}H_{30}O_5SNa$ ([M+Na]$^+$) 441.1706, found 441.1698.



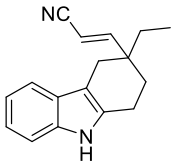
4-(1-(2-Azidoethyl)cyclohexyl)-1,2-dimethoxybenzene (6). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.84 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H), 2.94 – 2.88 (m, 2H), 2.06 (dd, *J* = 13.0, 6.1 Hz, 2H), 1.84 – 1.79 (m, 2H), 1.63 – 1.52 (m, 4H), 1.48 – 1.36 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.85, 147.02, 137.96, 118.96, 110.96, 110.02, 55.94, 55.77, 47.41, 41.99, 39.99, 36.47, 26.37, 22.22. HRMS (ESI) m/z: calcd for $C_{16}H_{24}NO_2$ ([M–N_2+H]$^+$) 262.1802, found 262.1796.



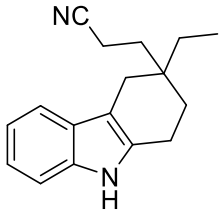
***tert*-Butyl 3a-(3,4-dimethoxyphenyl)octahydro-1*H*-indole-1-carboxylate (7) (1:1 Diastereomers).**[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (m, 3H), 4.29 – 4.06 (m, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.41 – 3.23 (m, 1H), 3.14 – 2.95 (m, 1H), 2.40 – 2.27 (m, 1H), 2.20 -2.02 (m, 2H), 1.92 – 1.81 (m, 1H), 1.72 – 1.20 (m, 6H), 1.47 (s, 4.5H), 1.41 (s, 4.5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.33, 148.60, 147.01, 140.54, 117.81, 110.92, 109.26, 78.99, 59.56, 55.83, 46.97, 43.56, 35.48, 32.22, 29.16, 28.67, 23.39, 22.43. HRMS (ESI) m/z: calcd for $C_{21}H_{31}NO_4Na$ ($[M+Na]^+$) 384.2145, found 384.2152.



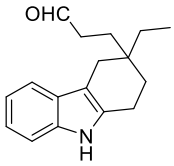
3-Ethyl-2,3,4,9-tetrahydro-1*H*-carbazole-3-carbaldehyde (L). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.77 (s, 1H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.20 – 7.13 (m, 2H), 3.16 (d, *J* = 15.1 Hz, 1H), 2.84 – 2.76 (m, 1H), 2.75 – 2.65 (m, 1H), 2.66 (d, *J* = 15.1 Hz, 1H), 2.28 – 2.21 (m, 1H), 1.87 (ddd, *J* = 13.6, 9.0, 6.4 Hz, 1H), 1.80 – 1.67 (m, 2H), 0.99 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.84, 136.22, 133.47, 127.51, 121.43, 119.29, 117.74, 110.59, 107.77, 49.63, 28.61, 27.48, 26.59, 19.98, 8.47. HRMS (ESI) m/z: calcd for $C_{15}H_{18}NO$ ($[M+H]^+$) 228.1383, found 228.1384.



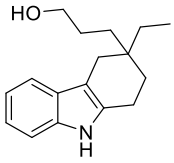
(*E*)-3-(3-ethyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-yl)acrylonitrile (M). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.31 (dd, *J* = 7.2, 0.9 Hz, 1H), 7.17 (td, *J* = 7.1, 1.2 Hz, 1H), 7.13 (td, *J* = 7.1, 1.2 Hz, 1H), 6.66 (d, *J* = 16.8 Hz, 1H), 5.17 (d, *J* = 16.8 Hz, 1H), 2.84 (d, *J* = 15.8 Hz, 1H), 2.73 (dt, *J* = 11.1, 5.0 Hz, 1H), 2.67 – 2.57 (m, 1H), 2.63 (d, *J* = 15.8 Hz, 1H), 1.95 – 1.85 (m, 2H), 1.68 – 1.56 (m, 2H), 0.94 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.34, 136.21, 132.85, 127.29, 121.49, 119.35, 117.88, 117.58, 110.66, 107.57, 99.33, 41.62, 33.11, 32.55, 28.72, 20.41, 8.38. HRMS (ESI) m/z: calcd for $C_{17}H_{19}N_2$ ($[M+H]^+$) 251.1543, found 251.1543.



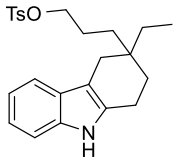
3-**(3-Ethyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-yl)propanenitrile (N).**[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.11 (td, *J* = 7.5, 1.4 Hz, 1H), 7.06 (td, *J* = 7.4, 1.3 Hz, 1H), 2.68 – 2.58 (m, 2H), 2.51 – 2.42 (m, 2H), 2.26 (t, *J* = 8.2 Hz, 2H), 1.81 – 1.61 (m, 4H), 1.47 – 1.37 (m, 1H), 1.36 – 1.27 (m, 1H), 0.87 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.25, 132.60, 127.90, 121.25, 120.63, 119.19, 117.61, 110.65, 108.02, 35.23, 31.51 (d, *J* = 15.3 Hz), 31.06, 28.32, 19.87, 11.89, 7.80. HRMS (ESI) m/z: calcd for $C_{17}H_{21}N_2$ ($[M+H]^+$) 253,1699, found 253.1700.



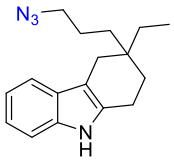
3-(3-Ethyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-yl)propanal (O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (t, *J* = 1.8 Hz, 1H), 7.73 (s, 1H), 7.46 (d, *J* = 7.4 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.16 – 7.08 (m, 2H), 2.70 (td, *J* = 6.4, 1.0 Hz, 2H), 2.54 (s, 2H), 2.50 – 2.43 (m, 2H), 1.81 – 1.66 (m, 4H), 1.53 – 1.35 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.99, 136.18, 132.78, 128.05, 121.11, 119.11, 117.60, 110.47, 108.63, 38.72, 34.81, 31.81, 31.32, 28.65, 27.75, 20.01, 7.80. HRMS (ESI) m/z: calcd for $C_{17}H_{22}NO$ ($[M+H]^+$) 256.1696, found 256.1696.



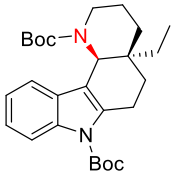
3-(3-Ethyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-yl)propan-1-ol (P). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.7 Hz, 1H), 7.13 (td, *J* = 7.2, 1.0 Hz, 1H), 7.10 (td, *J* = 7.2, 1.0 Hz, 1H), 3.73 – 3.54 (m, 2H), 2.70 (t, *J* = 6.4 Hz, 2H), 2.55 (s, 2H), 1.76 (t, *J* = 6.4 Hz, 2H), 1.66 – 1.59 (m, 2H), 1.55 – 1.46 (m, 2H), 1.45 – 1.36 (m, 2H), 0.93 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.14, 133.07, 128.20, 120.96, 119.02, 117.62, 110.42, 109.04, 63.87, 34.94, 31.99, 31.67, 36.63, 28.95, 26.83, 20.09, 7.87. HRMS (ESI) m/z: calcd for $C_{17}H_{24}NO$ ($[M+H]^+$) 258.1852, found 258.1854.



3-(3-Ethyl-2,3,4,9-tetrahydro-1*H*-carbazol-3-yl)propyl 4-methylbenzenesulfonate (Q). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.77 (s, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.13 (td, *J* = 7.2, 1.1 Hz, 1H), 7.10 (td, *J* = 7.2, 1.1 Hz, 1H), 4.09 – 3.98 (m, 2H), 2.71 – 2.60 (m, 2H), 2.51 – 2.42 (m, 2H), 2.43 (s, 3H), 1.74 – 1.65 (m, 4H), 1.48 – 1.32 (m, 3H), 1.30 – 1.21 (m, 1H), 0.87 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.74, 136.16, 133.05, 132.91, 129.85, 128.11, 127.88, 121.01, 119.03, 117.57, 110.49, 108.72, 71.51, 34.89, 31.79, 31.48, 31.25, 28.89, 23.28, 21.64, 19.97, 7.79. HRMS (ESI) m/z: calcd for $C_{24}H_{30}NO_3S$ ($[M+H]^+$) 412.1941, found 412.1942.

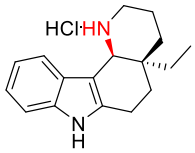


3-(3-Azidopropyl)-3-ethyl-2,3,4,9-tetrahydro-1*H*-carbazole (8). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.21 (dd, *J* = 7.0, 1.2 Hz, 1H), 7.12 – 7.04 (m, 2H), 3.28 – 3.14 (m, 2H), 2.62 (t, *J* = 6.3 Hz, 2H), 2.49 (s, 2H), 1.74 – 1.66 (m, 2H), 1.63 – 1.55 (m, 2H), 1.50 – 1.40 (m, 2H), 1.38 – 1.28 (m, 2H), 0.87 (t, *J* = 7.5 Hz, 3H). ^{3}C NMR (101 MHz, $CDCl_3$) δ 136.19, 132.99, 128.20, 121.06, 119.11, 117.68, 110.51, 108.90, 52.35, 35.13, 32.90, 31.99, 31.64, 28.90, 23.19, 20.07, 7.90. HRMS (ESI) m/z: calcd for $C_{17}H_{23}N_4$ ($[M+H]^+$) 283.1917, found 283.1918.

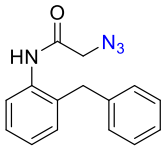


Di-*tert*-butyl-4a-ethyl-3,4,4a,5,6,11c-hexahydro-1*H*-pyrido[3,2-*c*]carbazole-1,7(2*H*)-dicarboxylate (9). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.10 (m, 1H), 7.38 – 7.31 (m, 1H), 7.26 – 7.22 (m, 1H), 7.20 – 7.14 (m, 1H), 5.28 – 5.17 (m, 1H), 4.10 – 3.85 (m, 1H), 3.17 – 3.05 (m,

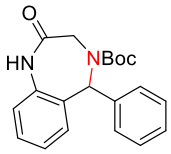
1H), 2.99 – 2.85 (m, 1H), 2.45 – 2.27 (m, 1H), 1.88 – 1.42 (m, 6H), 1.68 (s, 9H), 1.54 (s, 9H), 1.49 – 1.42 (m, 2H), 1.33 – 1.24 (m, 2H), 0.91 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.49, 150.52, 146.75, 136.30, 136.11, 128.38, 123.45, 122.92, 118.72, 115.31, 115.17, 85.21, 83.67, 79.82, 54.40, 38.66, 34.92, 31.59, 28.64, 28.33, 25.93, 27.43, 22.47, 20.57, 7.76. HRMS (ESI) m/z: calcd for $C_{27}H_{39}N_2O_4$ ($[M+H]^+$) 455.2904, found 455.2914.



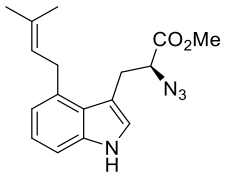
4a-Ethyl-2,3,4,4a,5,6,7,11c-octahydro-1*H*-pyrido[3,2-*c*]carbazole (10).[6] ^{1}H NMR (500 MHz, MeOD) δ 7.67 (d, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.13 (td, *J* = 7.5, 1.1 Hz, 1H), 7.09 (td, *J* = 7.6, 1.1 Hz, 1H), 4.31 (s, 1H), 3.17 (td, *J* = 12.7, 3.7 Hz, 1H), 2.95 (dd, *J* = 17.4, 6.1 Hz, 1H), 2.86 (ddd, *J* = 17.1, 11.6, 6.5 Hz, 1H), 2.40 (ddd, *J* = 14.2, 11.7, 6.9 Hz, 1H), 1.98 – 1.85 (m, 3H), 1.79 – 1.69 (m, 2H), 1.60 – 1.51 (m, 1H), 1.35 – 1.24 (m, 2H), 0.93 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, MeOD) δ 136.71, 136.62, 125.82, 121.32, 119.18, 116.83, 110.65, 103.53, 55.56, 43.82, 34.61, 32.11, 28.60, 22.95, 19.02, 17.98, 6.32. HRMS (ESI) m/z: calcd for $C_{17}H_{23}N_2$ ($[M+H]^+$) 255.1856, found 255.1854.



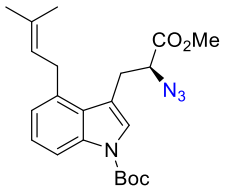
2-Azido-*N*-(2-benzylphenyl)acetamide (11). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.85 (s, 1H), 7.38 – 7.30 (m, 4H), 7.20 – 7.26 (m, 1H), 7.24 – 7.19 (m, 3H), 4.04 (s, 2H), 4.01 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.62, 138.57, 134.93, 131.42, 131.14, 128.88, 128.45, 127.75, 126.93, 125.70, 123.40, 53.06, 38.57. HRMS (ESI) m/z: calcd for $C_{15}H_{15}N_4O$ ($[M+H]^+$) 267.1240, found 267.1235.



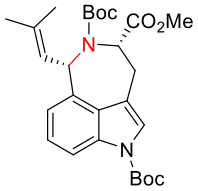
***tert*-Butyl 2-oxo-5-phenyl-1,2,3,5-tetrahydro-4*H*-benzo[e][1,4]diazepine-4-carboxylate (12).** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.1 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 3H), 7.28 – 7.23 (m, 2H), 7.17 (d, *J* = 7.4 Hz, 3H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.21 (s, 1H), 3.99 (s, 2H), 1.48 (s, 9H). ^{3}C NMR (126 MHz, $CDCl_3$) δ 153.22, 139.09, 136.27, 130.92, 130.58, 128.83, 128.70, 128.56, 128.54, 127.47, 126.58 , 126.41, 124.17, 80.34, 38.07, 38.02, 28.29. HRMS (ESI) m/z: calcd for $C_{20}H_{23}N_2O_3$ ($[M+H]^+$) 339.1703, found 339.1705.



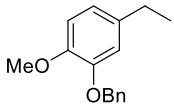
Methyl (*S*)-2-azido-3-(4-(3-methylbut-2-en-1-yl)-1*H*-indol-3-yl)propanoate (R). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.24 (d, *J* = 8.1 Hz, 1H), 7.15 – 7.09 (m, 2H), 6.92 (d, *J* = 7.2 Hz, 1H), 5.37 – 5.32 (m, 1H), 4.15 (dd, *J* = 8.6, 5.6 Hz, 1H), 3.78 (s, 3H), 3.75 (d, *J* = 6.5 Hz, 2H), 3.54 (dd, *J* = 15.1, 5.5 Hz, 1H), 3.29 (dd, *J* = 15.1, 8.6 Hz, 1H), 1.77 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.81, 136.89, 134.35, 132.56, 124.81, 123.60, 123.53, 122.40, 120.33, 110.62, 109.47, 63.18, 52.58, 32.27, 29.28, 25.65, 18.03. HRMS (ESI) m/z: calcd for $C_{17}H_{21}N_2O_2$ ($[M–N_2+H]^+$) 285.1598, found 285.1599.



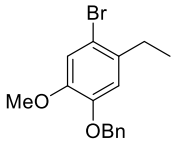
***tert*-Butyl (*S*)-3-(2-azido-3-methoxy-3-oxopropyl)-4-(3-methylbut-2-en-1-yl)-1*H*-indole-1-carboxylate (13).** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.8 Hz, 1H), 7.47 (s, 1H), 7.25 – 7.20 (m, 1H), 7.03 (d, *J* = 7.3 Hz, 1H), 5.26 (t, *J* = 6.3 Hz, 1H), 4.17 (dd, *J* = 8.8, 5.3 Hz, 1H), 3.80 (s, 3H), 3.72 – 3.66 (m, 2H), 3.46 (dd, *J* = 15.4, 5.2 Hz, 1H), 3.22 (dd, *J* = 15.4, 8.8 Hz, 1H), 1.74 (s, 6H), 1.66 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.55, 149.45, 136.28, 134.60, 132.92, 127.67, 124.75, 124.65, 123.69, 123.39, 115.37, 113.45, 83.75, 62.34, 52.74, 32.12, 29.14, 28.22, 25.67, 18.10. HRMS (ESI) m/z: calcd for $C_{22}H_{29}N_2O_4$ ($[M–N_2+H]^+$) 385.2122, found 385.2124.



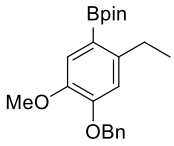
2,6-Di-tert-butyl 3-methyl 1-(2-methylprop-1-en-1-yl)-3,4-dihydro-1*H*-azepino[5,4,3-*cd*]indole-2,3,6-tricarboxylate (14) (1:1 Diastereomers).[10] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.44 (d, *J* = 12.0 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.10 (d, *J* = 7.2 Hz, 0.5H), 6.96 (d, *J* = 7.2 Hz, 0.5H), 6.44 (d, *J* = 7.5 Hz, 0.5H), 6.05 (d, *J* = 7.9 Hz, 0.5H), 5.40 (dd, *J* = 17.1, 7.8 Hz, 1H), 5.19 (dd, *J* = 12.3, 6.7 Hz, 0.5H), 4.77 (dd, *J* = 13.0, 5.1 Hz, 0.5H), 3.76 (s, 1.H), 3.74 (s, 1.5H), 3.61 – 3.52 (m, 1H), 3.38 (dd, *J* = 15.6, 5.1 Hz, 1H), 3.28 (dd, *J* = 15.6, 5.1 Hz, 1H), 1.88 (d, *J* = 4.6 Hz, 3H), 1.74 (s, 3H), 1.68 (s, 9H), 1.37 (s, 4.5 H), 1.34 (s, 4.5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.13, 154.81, 139.69, 139.18, 137.62, 124.50, 124.14, 123.27, 120.99, 120.36, 117.03, 114.11, 80.53, 60.24, 57.59, 51.98, 28.22, 27.21, 25.65, 18.97. HRMS (ESI) m/z: calcd for $C_{22}H_{29}N_2O_4$ ($[M–Boc+H_2]^+$) 385.2122, found 385. 2120.



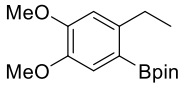
2-(Benzyloxy)-4-ethyl-1-methoxybenzene. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.88 (d, *J* = 1.8 Hz, 1H), 6.81 (dd, *J* = 8.1, 1.9 Hz, 1H), 5.18 (s, 2H), 3.91 (s, 3H), 2.72 (q, *J* = 7.6 Hz, 2H), 1.38 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.93, 146.59, 137.79, 137.66, 128.60, 127.85, 127.51, 119.78, 114.63, 112.20, 71.28, 55.89, 28.71, 16.05. HRMS (ESI) m/z: calcd for $C_{16}H_{19}O_2$ ($[M+H]^+$) 243.1380, found 243.1381.



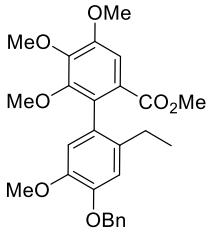
1-(Benzyloxy)-4-bromo-5-ethyl-2-methoxybenzene. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.3 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.07 (s, 1H), 6.77 (s, 1H), 5.10 (s, 2H), 3.88 (s, 3H), 2.69 (q, *J* = 7.5 Hz, 2H), 1.22 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.16, 146.88, 136.69, 136.03, 128.60, 128.02, 127.45, 118.19, 113.64, 112.88, 71.40, 56.20, 29.13, 14.59. HRMS (ESI) m/z: calcd for $C_{16}H_{17}BrO_2Na$ ($[M+Na]^+$) 343.0304, found 343.0308.



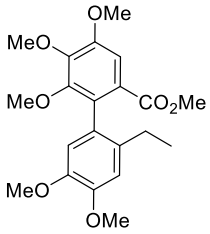
2-(4-(Benzyloxy)-2-ethyl-5-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.4 Hz, 2H), 7.40 (s, 1H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 6.76 (s, 1H), 5.14 (s, 2H), 3.91 (s, 3H), 2.89 (q, *J* = 7.5 Hz, 2H), 1.34 (s, 12H), 1.21 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.87, 146.50, 145.51, 137.50, 127.77, 127.72, 121.31, 112.33, 83.17, 71.28, 55.76, 28.51, 24.84, 17.46. HRMS (ESI) m/z: calcd for $C_{22}H_{30}BO_4$ ($[M+H]^+$) 369.2233, found 369.2234.



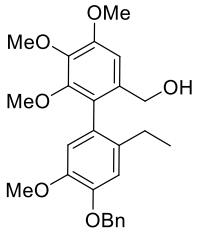
2-(2-Ethyl-4,5-dimethoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 1H), 6.71 (s, 1H), 3.90 (s, 6H), 2.88 (q, *J* = 7.1 Hz, 2H), 1.33 (s, 12H), 1.18 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.07, 145.94, 118.23, 111.83, 83.19, 55.97, 55.66, 28.49, 24.86, 17.52. HRMS (ESI) m/z: calcd for $C_{16}H_{25}BO_4Na$ ($[M+Na]^+$) 315.1738, found 315.1745.



Methyl 4'-(benzyloxy)-2'-ethyl-4,5,5',6-tetramethoxy-[1,1'-biphenyl]-2-carboxylate (T1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.1 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 5.8 Hz, 2H), 6.82 (s, 1H), 6.56 (s, 1H), 5.13 (d, *J* = 12.6 Hz, 1H), 5.08 (d, *J* = 12.6 Hz, 1H), 3.94 (s, 3H), 3.93 (s, 6H), 3.48 (s, 3H), 3.36 (s, 3H), 2.34 – 2.25 (m, 2H), 1.03 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.58, 152.12, 151.69, 148.77, 145.38, 144.88, 137.48, 135.42, 129.94, 128.41, 127.66, 127.57, 127.27, 126.30, 115.79, 111.20, 108.78, 70.87, 60.96, 60.78, 56.09, 55.85, 51.89, 26.07, 14.73. HRMS (ESI) m/z: calcd for $C_{27}H_{31}O_7$ ($[M+H]^+$) 467.2064, found 467.2070.

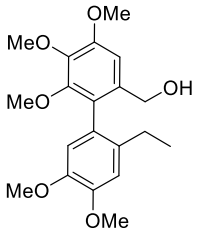


Methyl 2'-ethyl-4,4',5,5',6-pentamethoxy-[1,1'-biphenyl]-2-carboxylate (T2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (s, 1H), 6.79 (s, 1H), 6.56 (s, 1H), 3.95 (s, 3H), 3.94 (s, 3H), 3.93 (s, 3H), 3.81 (s, 3H), 3.57 (s, 3H), 3.56 (s, 3H), 2.37 – 2.27 (m, 2H), 1.05 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.74, 152.21, 151.73, 148.01, 146.10, 145.36, 134.72, 129.92, 127.59, 126.50, 112.85, 110.61, 108.72, 61.00, 60.94, 56.12, 56.00, 55.68, 51.97, 26.03, 14.82. HRMS (ESI) m/z: calcd for $C_{21}H_{27}O_7$ ($[M+H]^+$) 391.1751, found 391.1759.

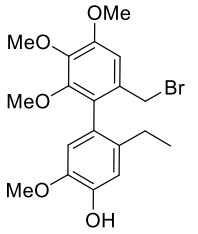


(4'-(Benzyloxy)-2'-ethyl-4,5,5',6-tetramethoxy-[1,1'-biphenyl]-2-yl)methanol (U1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.33 – 7.28 (m, 2H), 7.26 – 7.21 (m, 1H), 6.85 (s, 2H), 6.57 (s, 1H), 5.14 (s, 2H), 4.14 (s, 2H), 3.94 (s, 3H), 3.89 (s, 3H), 3.87 (s, 3H), 3.44 (s, 3H), 2.26 (q, *J* = 7.4 Hz, 2H), 1.49 (br s, 1H), 1.02 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.75, 151.37, 149.10, 145.09, 141.28, 137.25, 135.95, 134.82, 128.48, 127.67, 127.17, 126.55, 126.37, 116.42,

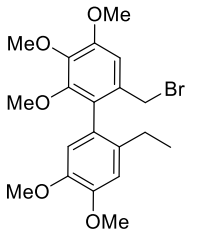
111.79, 106.52, 70.77, 62.95, 60.91, 60.85, 55.94, 25.94, 14.88. HRMS (ESI) m/z: calcd for $C_{26}H_{30}O_6Na$ ($[M+Na]^+$) 461.1935, found 461.1935.



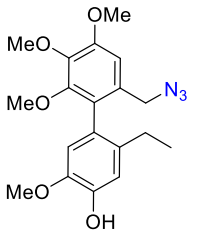
(2'-Ethyl-4,4',5,5',6-pentamethoxy-[1,1'-biphenyl]-2-yl)methanol (U2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 1H), 6.82 (s, 1H), 6.60 (s, 1H), 4.32 (d, *J* = 12.9 Hz, 1H), 4.27 (d, *J* = 12.9 Hz, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 3.89 (s, 3H), 3.80 (s, 3H), 3.62 (s, 3H), 2.29 (q, *J* = 7.6 Hz, 2H), 1.74 (br s, 1H), 1.04 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.84, 151.43, 148.32, 146.54, 141.28, 135.17, 134.87, 126.57, 126.42, 113.18, 111.16, 106.38, 63.06, 60.97, 60.93, 56..00, 55.99, 25.88, 14.99. HRMS (ESI) m/z: calcd for $C_{20}H_{26}O_6Na$ ($[M+Na]^+$) 385.1622, found 385.1630.



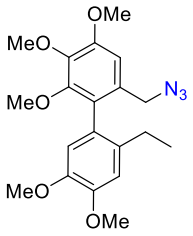
6'-(Bromomethyl)-2-ethyl-2',3',4',5-tetramethoxy-[1,1'-biphenyl]-4-ol (V1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 1H), 6.82 (s, 1H), 6.74 (s, 1H), 5.58 (s, 1H), 4.27 (d, *J* = 9.9 Hz, 1H), 4.14 (d, *J* = 9.9 Hz, 1H), 3.94 (s, 3H), 3.91 (s, 3H), 3.90 (s, 3H), 3.60 (s, 3H), 2.29 (q, *J* = 7.5 Hz, 2H), 1.06 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.83, 151.44, 146.18, 142.92, 142.30, 134.95, 131.46, 128.26, 126.86, 116.17, 110.36, 108.92, 60.99, 60.94, 56.01, 55.83, 32.39, 25.97, 14.90. HRMS (ESI) m/z: calcd for $C_{19}H_{23}BrO_5Na$ ($[M+Na]^+$) 433.0621, found 433.0626.



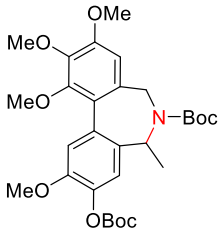
6-(Bromomethyl)-2'-ethyl-2,3,4,4',5'-pentamethoxy-1,1'-biphenyl (V2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 1H), 6.82 (s, 1H), 6.73 (s, 1H), 4.29 (d, *J* = 9.8 Hz, 1H), 4.08 (d, *J* = 9.8 Hz, 1H), 3.93 (s, 3H), 3.91 (s, 3H), 3.90 (s, 3H), 3.85 (s, 3H), 3.60 (s, 3H), 2.30 (q, *J* = 7.6 Hz, 2H), 1.04 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.94, 151.46, 148.41, 146.29, 142.38, 135.37, 131.56, 128.40, 126.06, 113.37, 111.03, 108.89, 60.96, 56.03, 55.97, 55.79, 32.67, 25.99, 14.96. HRMS (ESI) m/z: calcd for $C_{20}H_{25}BrO_5Na$ ($[M+Na]^+$) 447.0778, found 447.0787.



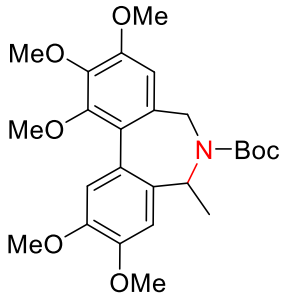
6'-(Azidomethyl)-2-ethyl-2',3',4',5-tetramethoxy-[1,1'-biphenyl]-4-ol (15a). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.86 (s, 1H), 6.81 (s, 1H), 6.70 (s, 1H), 5.60 (s, 1H), 4.09 (d, *J* = 13.8 Hz, 1H), 4.05 (d, *J* = 13.8 Hz, 1H), 3.99 (s, 3H), 3.98 (s, 3H), 3.95 (s, 3H), 3.67 (s, 3H), 2.32 (q, *J* = 7.6 Hz, 2H), 1.09 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.84, 151.67, 146.17, 143.14, 141.90, 134.80, 129.72, 127.61, 127.08, 116.23, 110.50, 107.35, 61.05, 60.95, 56.08, 55.87, 52.58, 25.95, 14.96. HRMS (ESI) m/z: calcd for $C_{19}H_{23}N_3O_5Na$ ($[M+Na]^+$) 396.1530, found 396.1533.



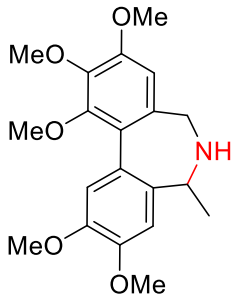
6-(Azidomethyl)-2'-ethyl-2,3,4,4',5'-pentamethoxy-1,1'-biphenyl (15b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (s, 1H), 6.74 (s, 1H), 6.57 (s, 1H), 3.97 (s, 2H), 3.89 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H), 3.79 (s, 3H), 3.59 (s, 3H), 2.25 (q, *J* = 7.6 Hz, 2H), 1.01 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.90, 151.63, 148.44, 146.55, 141.95, 135.21, 129.71, 127.86, 126.26, 113.43, 111.13, 107.55, 60.92, 60.86, 56.00, 55.92, 55.75, 52.50, 25.90, 14.92. HRMS (ESI) m/z: calcd for $C_{20}H_{25}N_3O_5Na$ ([M+Na]$^+$) 410.1686, found 410.1685.



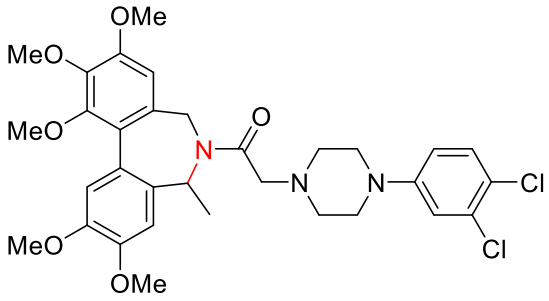
***tert*-Butyl 9-(benzyloxy)-1,2,3,10-tetramethoxy-7-methyl-5,7-dihydro-6*H*-dibenzo[*c,e*]azepine-6-carboxylate (16a) (1:1 Diastereomers).** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (s, 1H), 6.97 (s, 0.5H), 6.87 (s, 0.5H), 6.77 (s, 0.5H), 6.64 (s, 0.5H), 5.21 – 5.13 (m, 0.5H), 4.99 – 4.89 (m, 1H), 4.70 (d, *J* = 13.6 Hz, 0.5H), 3.95 – 3.98 (m, 9H), 3.96 – 3.53 (m, 4H), 1.56 (s, 9H), 1.53 (s, 9H), 0.95 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.71, 152.99, 151.50, 150.48, 150.21, 142.33, 139.07, 137.54, 131.54, 127.33, 125.74, 125.42, 113.90, 108.37, 83.42, 79.91, 61.25, 60.49, 57.79, 56.96, 56.13, 56.04, 46.57, 27.64, 20.99. HRMS (ESI) m/z: calcd for $C_{29}H_{39}NO_9Na$ ([M+Na]$^+$) 568.2517, found 568.2521.



***tert*-Butyl 1,2,3,9,10-pentamethoxy-7-methyl-5,7-dihydro-6*H*-dibenzo[*c,e*]azepine-6-carboxylate (16b) (1:1 Diastereomers).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 1H), 6.86 (s, 0.5H), 6.78 (s, 1H), 6.64 (s, 0.5H), 5.13 – 5.05 (m, 0.5H), 4.95 – 4.83 (m, 1H), 4.73 – 4.67 (m, 0.5H), 4.00 – 3.87 (m, 12H), 3.66 – 3.46 (m, 4H), 1.52 (s, 9H), 0.93 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.78, 152.84, 150.37, 148.01, 147.87, 147.69, 142.30, 131.75, 127.29, 126.25, 114.45, 112.91, 108.48, 79.79, 61.30, 60.52, 57.56, 56.14, 56.03, 55.95, 46.63, 28.65, 21.27. HRMS (ESI) m/z: calcd for $C_{25}H_{33}NO_7Na$ ([M+Na]$^+$) 482.2149, found 482.2148.

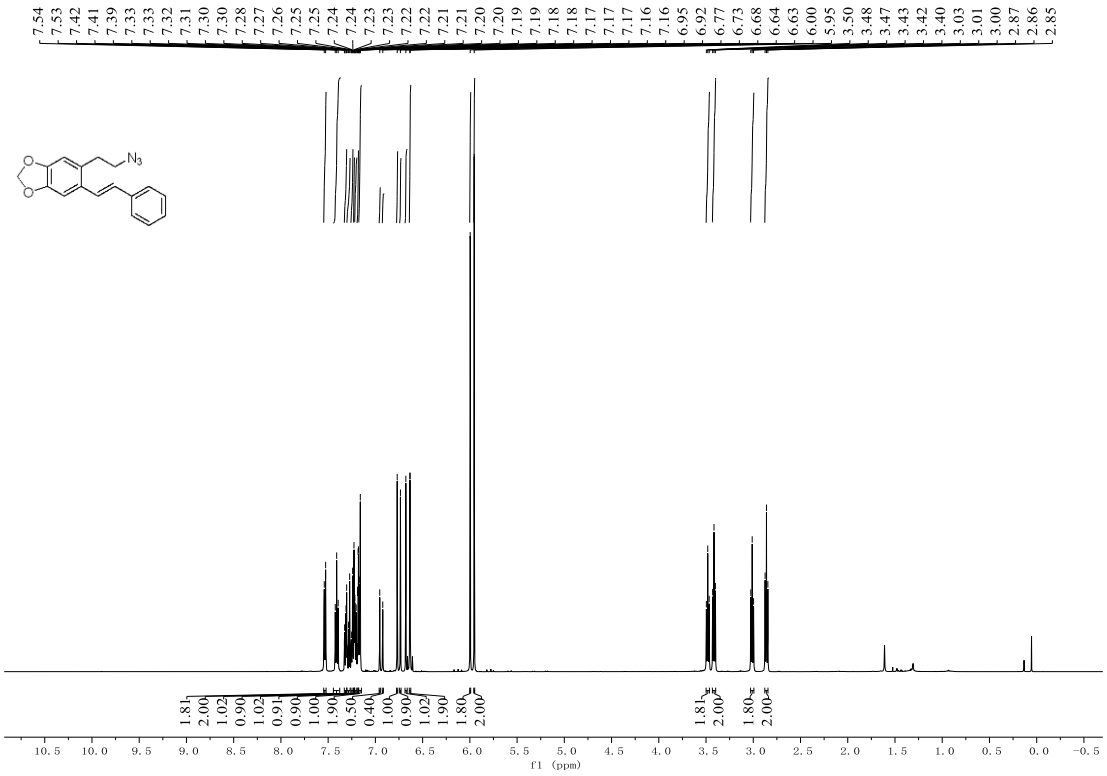


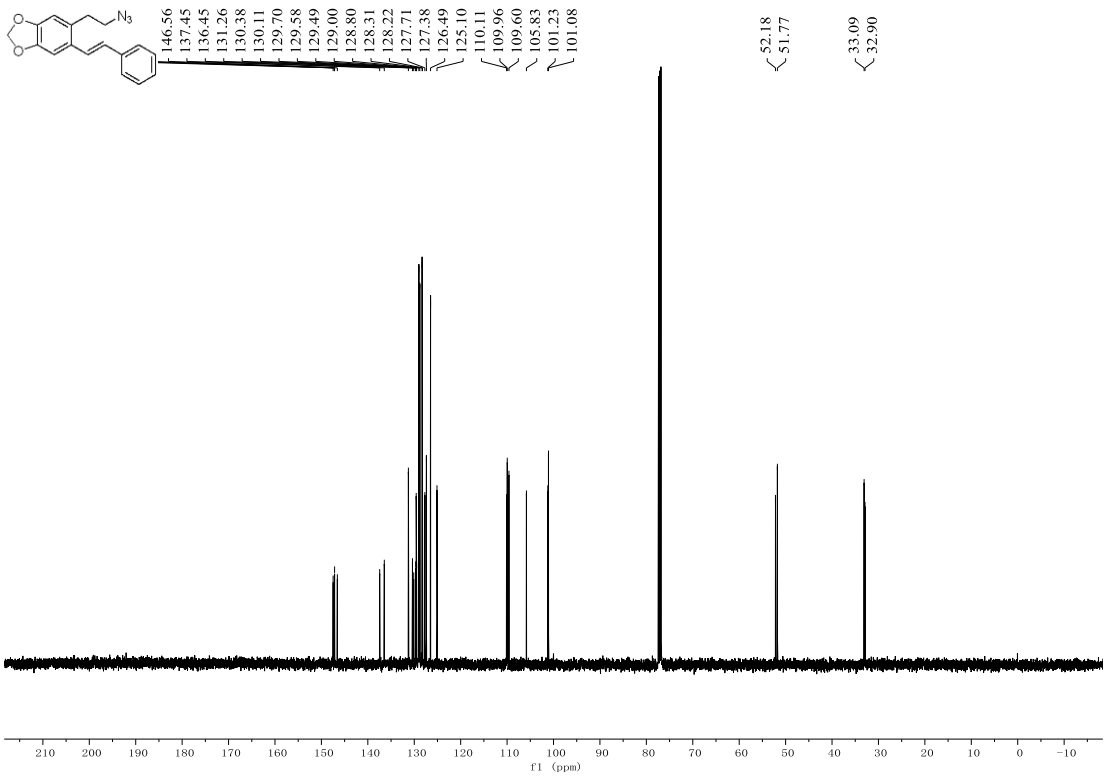
1,2,3,9,10-Pentamethoxy-7-methyl-6,7-dihydro-5*H*-dibenzo[*c,e*]azepine (17). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (s, 1H), 6.84 (s, 1H), 6.57 (s, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 3.78 (s, 3H), 3.77 (s, 3H), 3.54 (s, 3H), 3.53 (q, *J* = 6.6 Hz, 3H), 3.46 (d, *J* = 12.6 Hz, 1H), 3.19 (d, *J* = 12.5 Hz, 1H), 1.37 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.64, 150.39, 148.17, 147.31, 141.67, 132.98, 131.57, 128.99, 125.81, 112.69, 107.54, 107.46, 61.00, 60.65, 55.86, 55.73, 49.44, 49.42, 18.56. HRMS (ESI) m/z: calcd for $C_{20}H_{26}NO_5$ ([M+H]$^+$) 360.1805, found 360.1802.

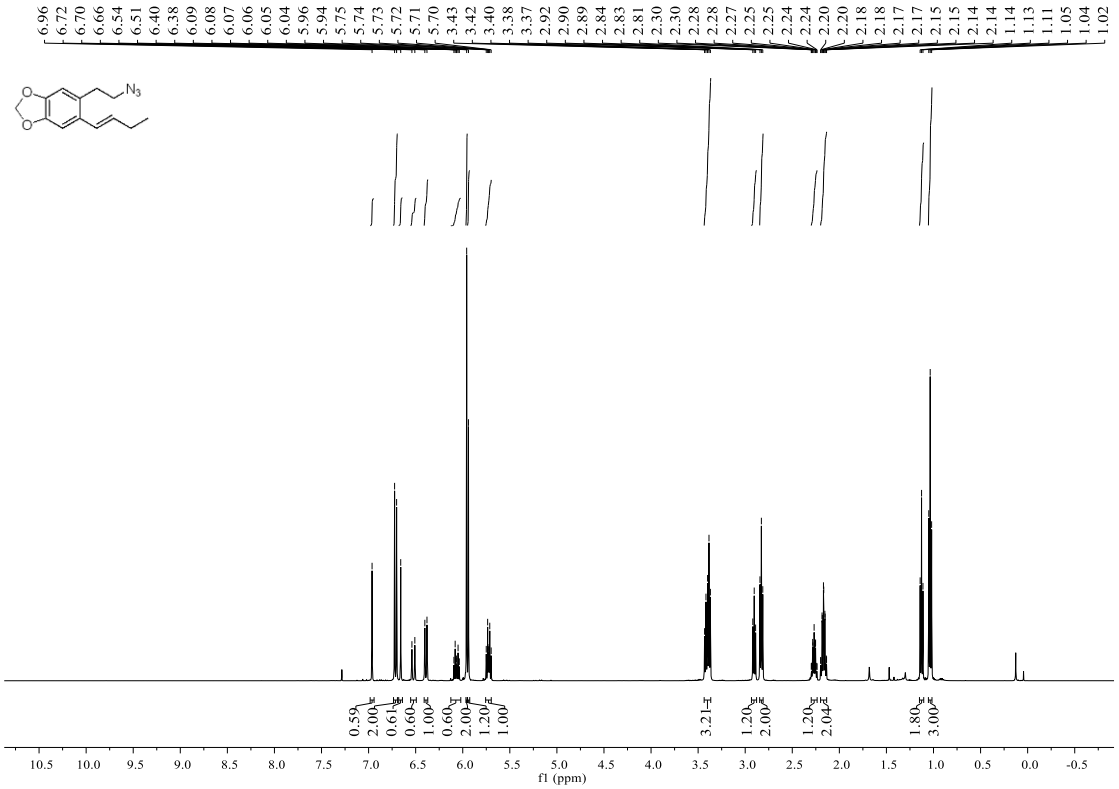


2-(4-(3,4-Dichlorophenyl)piperazin-1-yl)-1-(1,2,3,9,10-pentamethoxy-7-methyl-5,7-dihydro-6*H*-dibenzo[*c*,*e*]azepin-6-yl)ethan-1-one (18) (1:4 Diastereomers). ^{1}H NMR (500 MHz, $CDCl_3$) δ major peaks. 7.31 – 7.26 (m, 2H), 6.97 (d, *J* = 2.8 Hz, 1H), 6.87 (d, *J* = 3.8 Hz, 1H), 6.76 (dd, *J* = 8.9, 2.7 Hz, 1H), 5.45 (q, *J* = 6.8 Hz, 1H), 4.88 (d, *J* = 12.9 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H), 3.92 (s, 3H), 3.90 (d, *J* = 12.9 Hz, 1H), 3.82 (s, 3H), 3.61 (s, 3H), 3.58 (d, *J* = 12.9 Hz, 1H), 3.29 – 3.27 (m, 4H), 3.17 (d, *J* = 12.8 Hz, 1H), 2.77 – 2.75 (m, 4H), 0.94 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.22, 152.82, 150.65, 150.49, 148.15, 147.89, 142.90, 132.90, 131.11, 130.55, 130.28, 127.06, 126.97, 122.55, 117.23, 115.33, 114.18, 113.17, 108.54, 62.42, 61.36, 60.55, 56.30, 56.09, 55.99, 55.90, 52.97, 48.81, 48.41, 20.06. HRMS (ESI) m/z: calcd for $C_{32}H_{38}Cl_2N_3O_6$ ($[M+H]^+$) 630.2132, found 630.2130.

7. Copies of NMR Spectra



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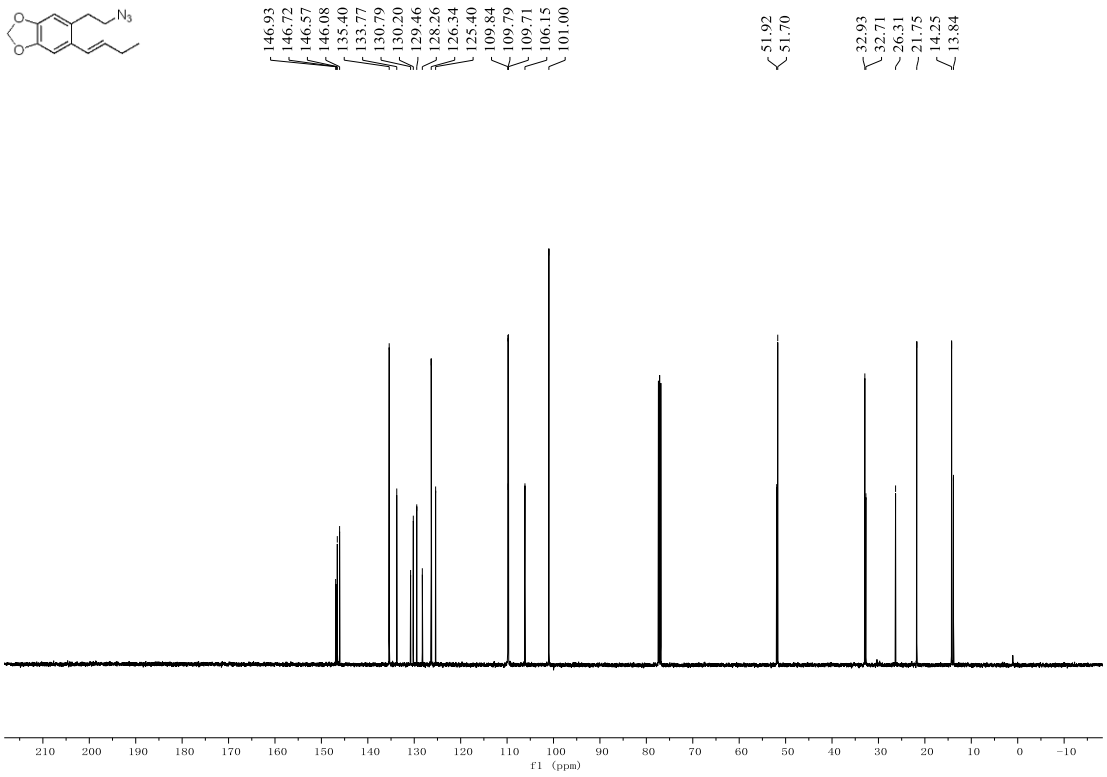
f1 (ppm)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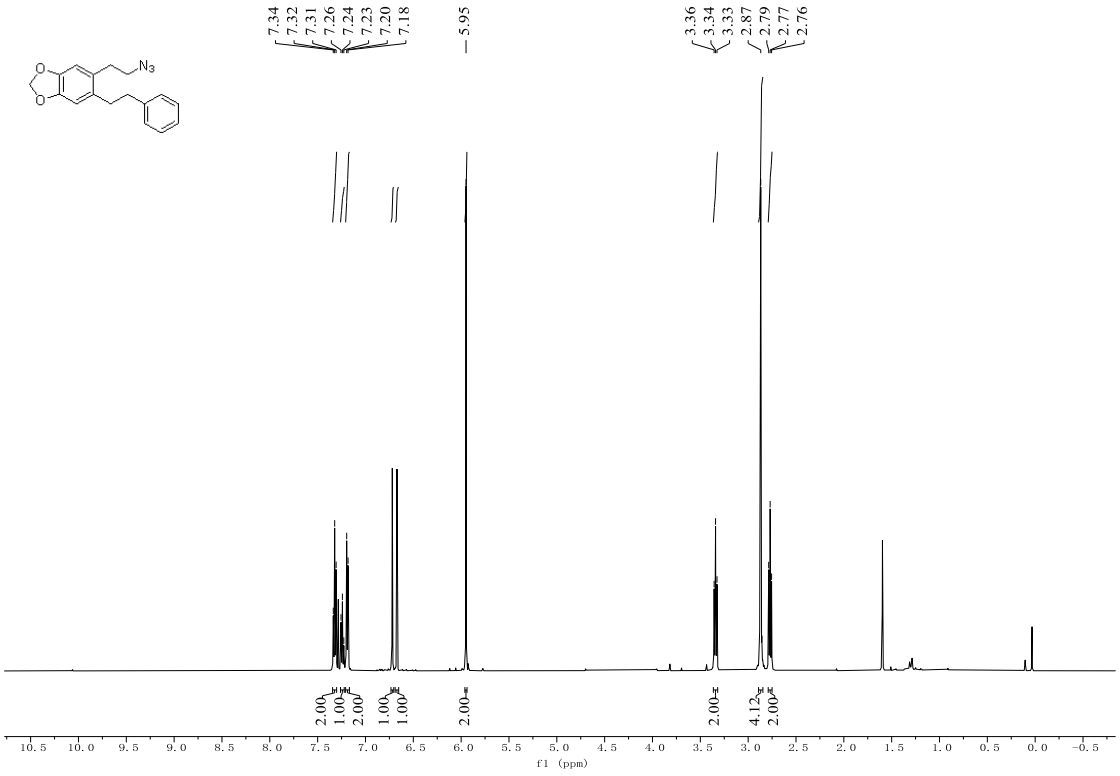
32.93 32.71 26.31 21.75 14.25 13.84
f1 (ppm)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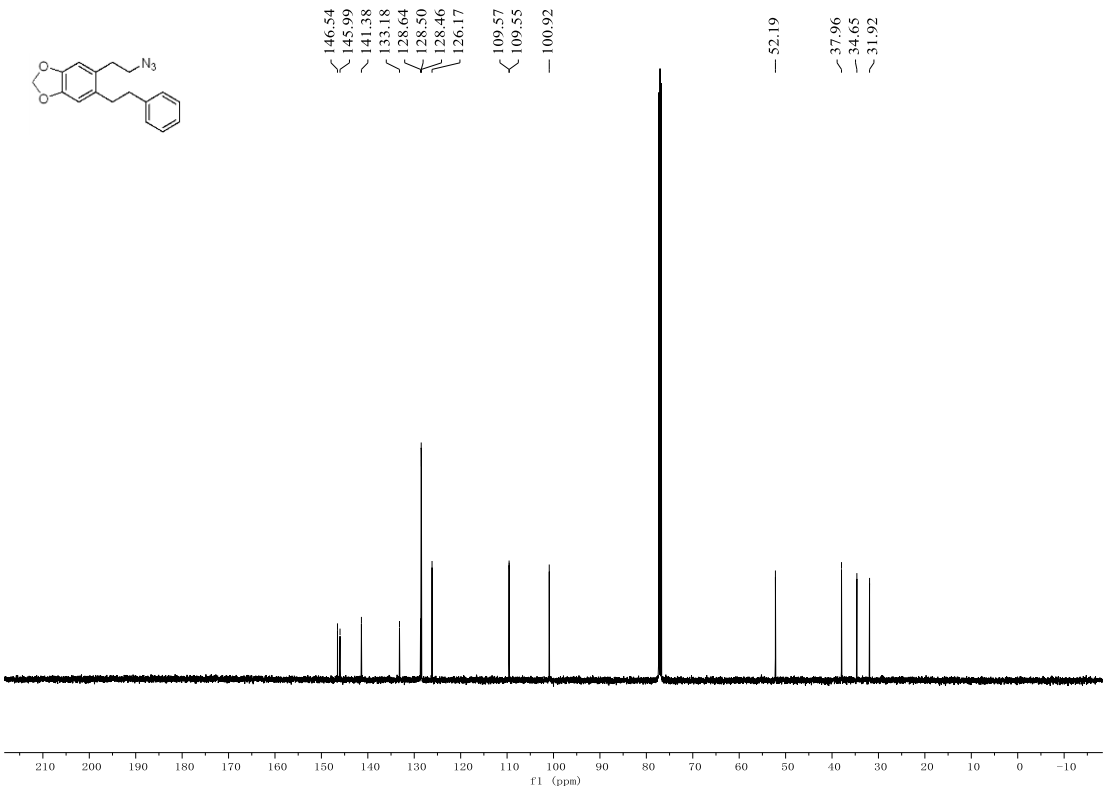
f1 (ppm)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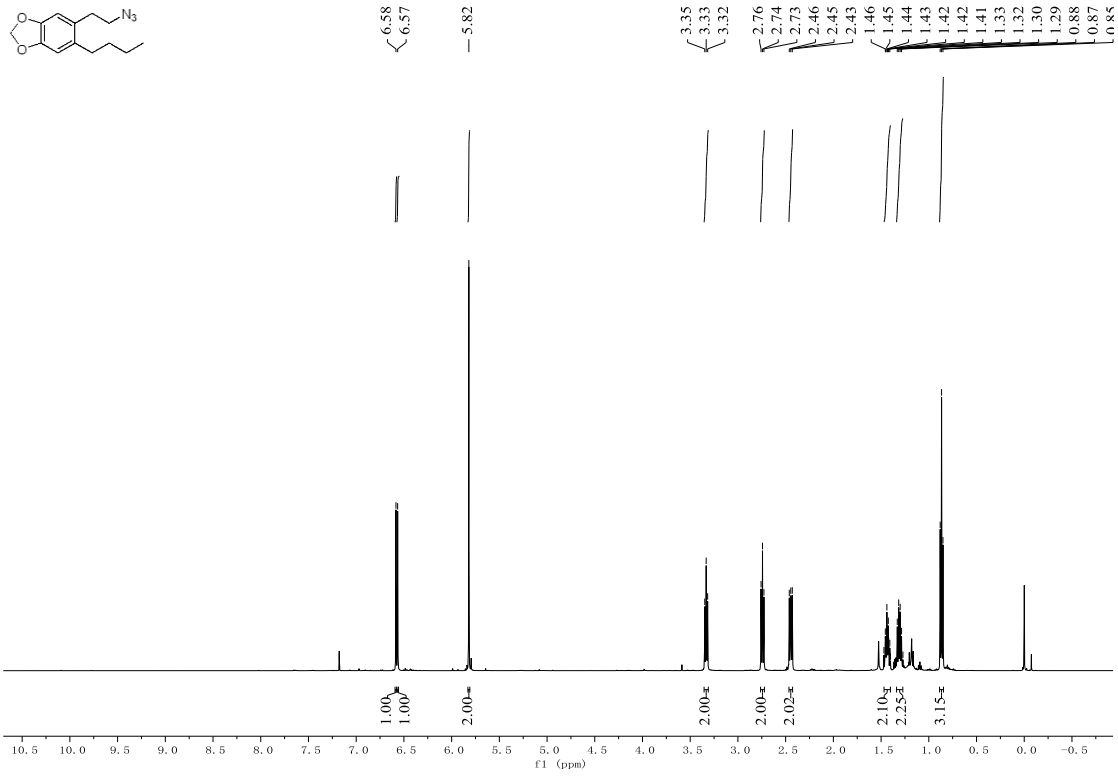
N3
f1 (ppm)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1.45
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1.42
1.42
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1.32
1.30
1.29
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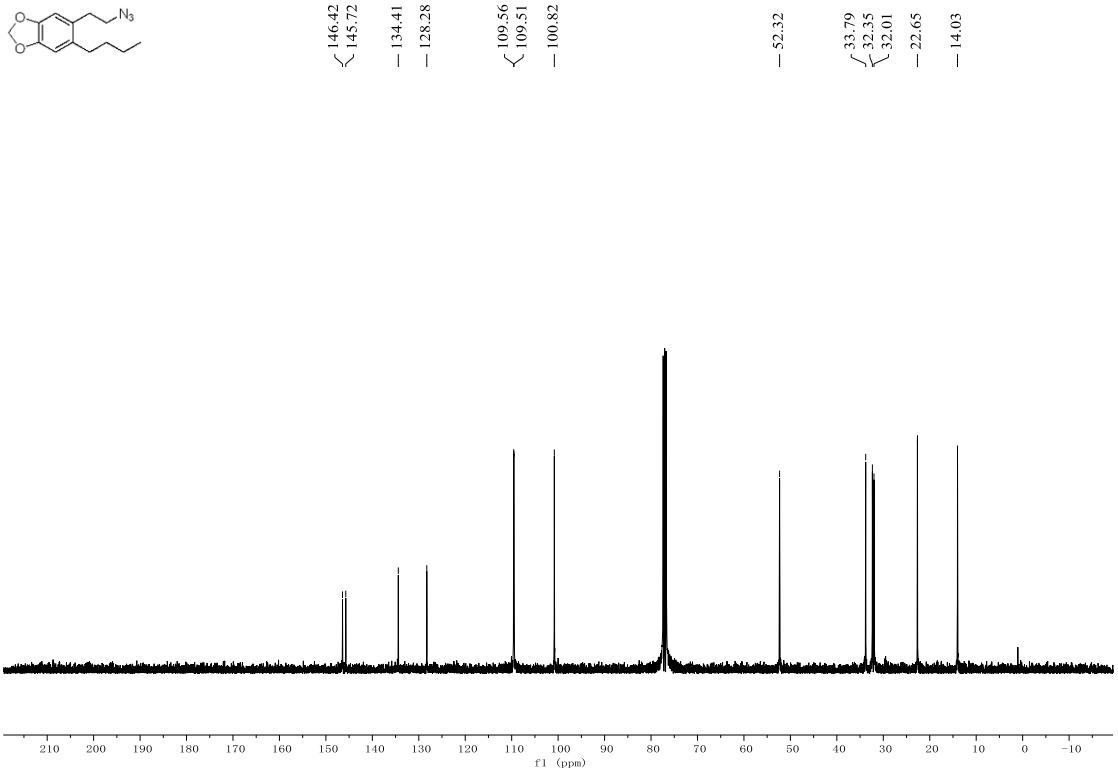
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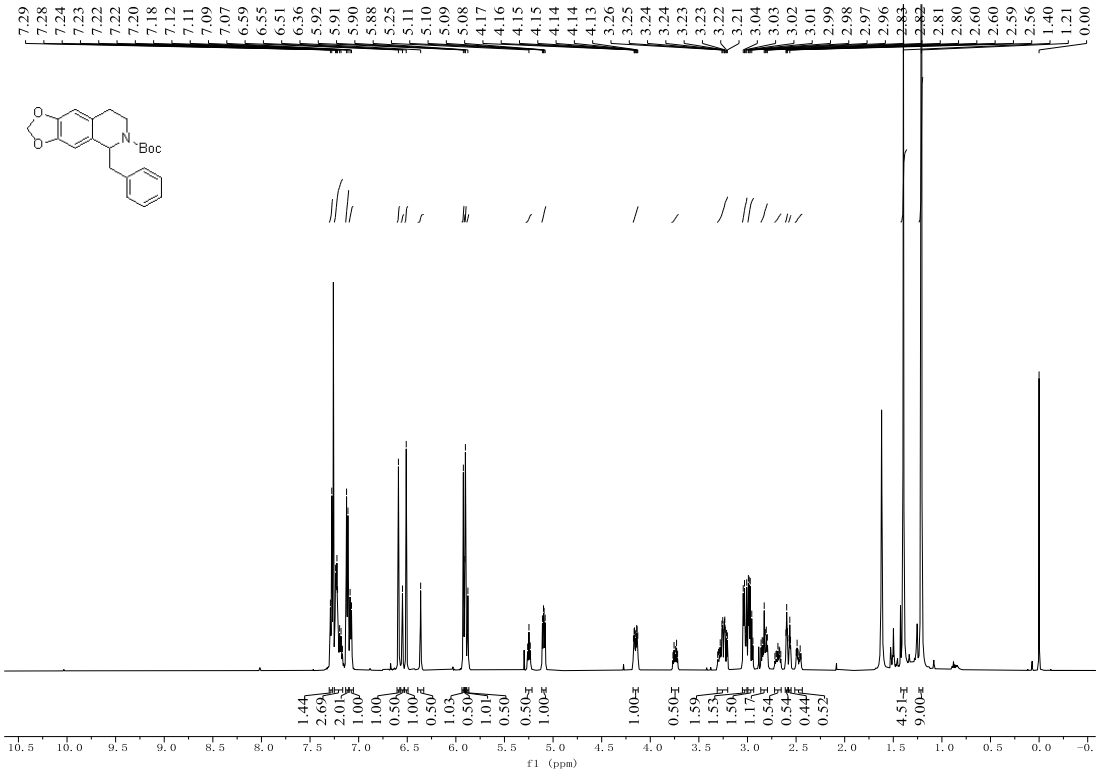
Boc
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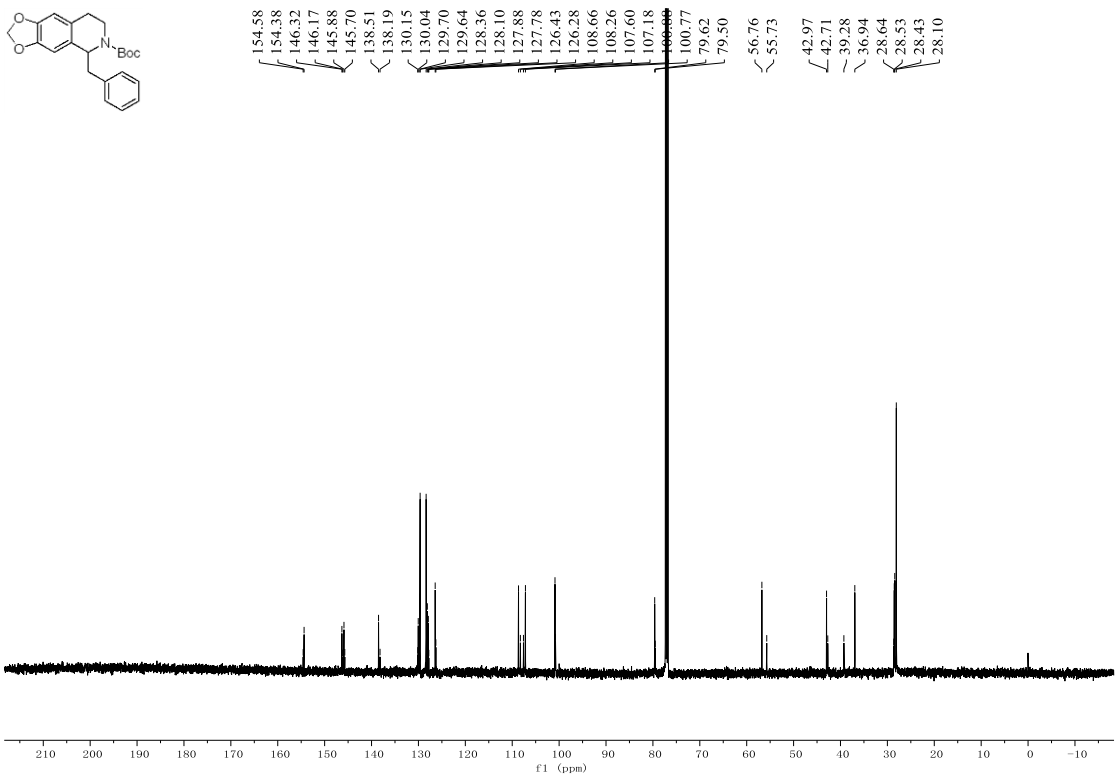
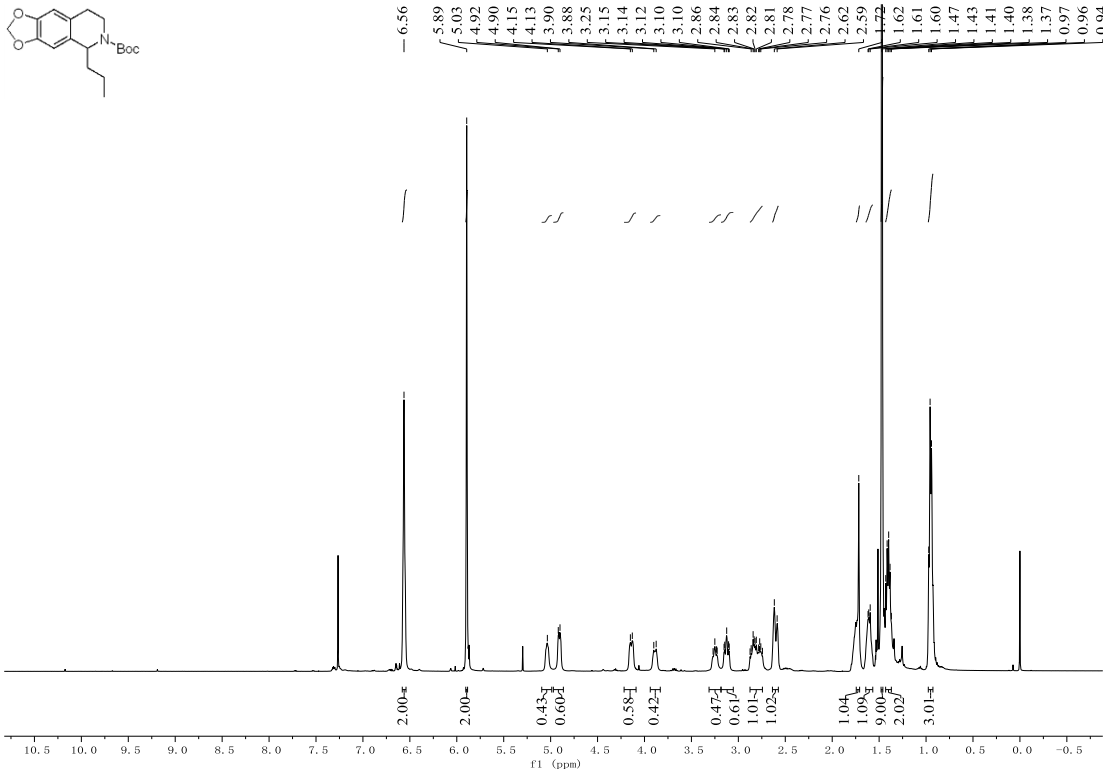

Boc
f1 (ppm)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1.40
1.38
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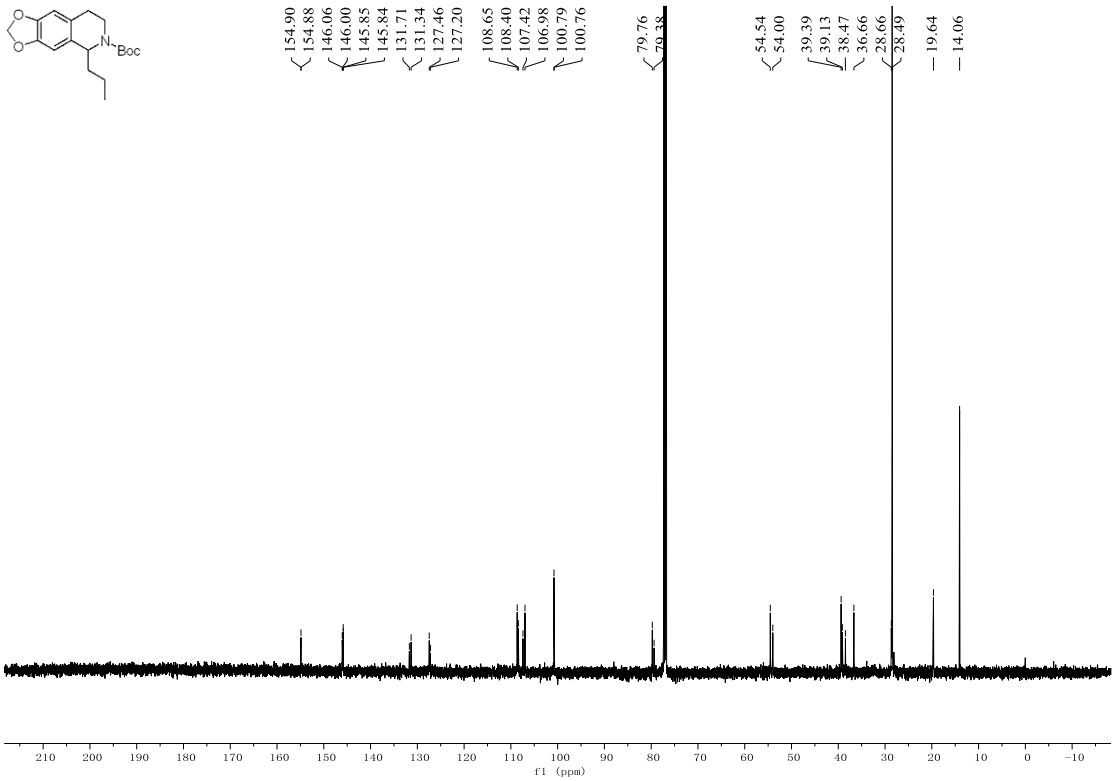
f1 (ppm)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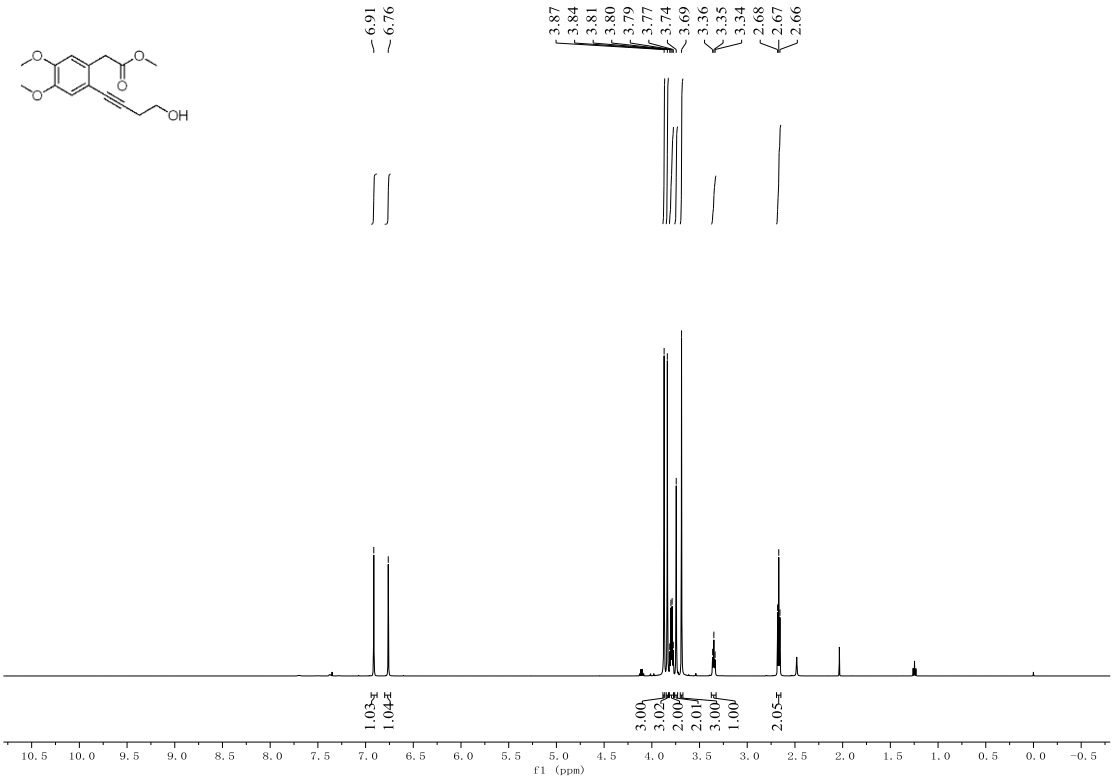
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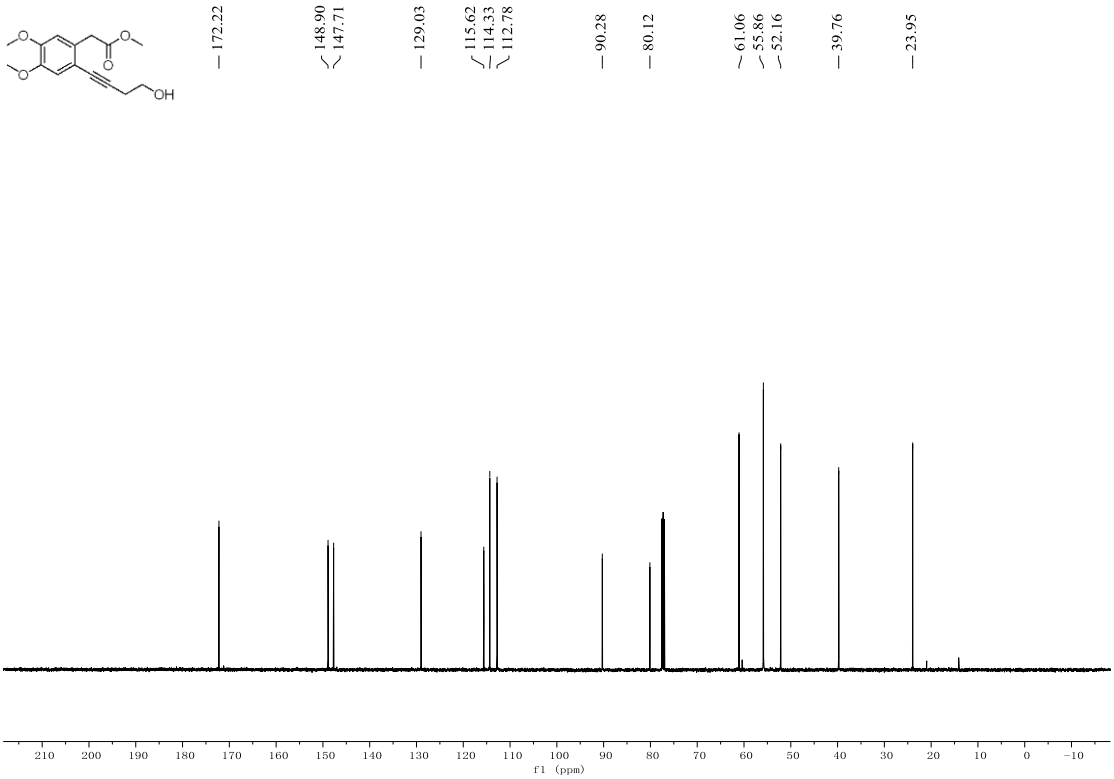
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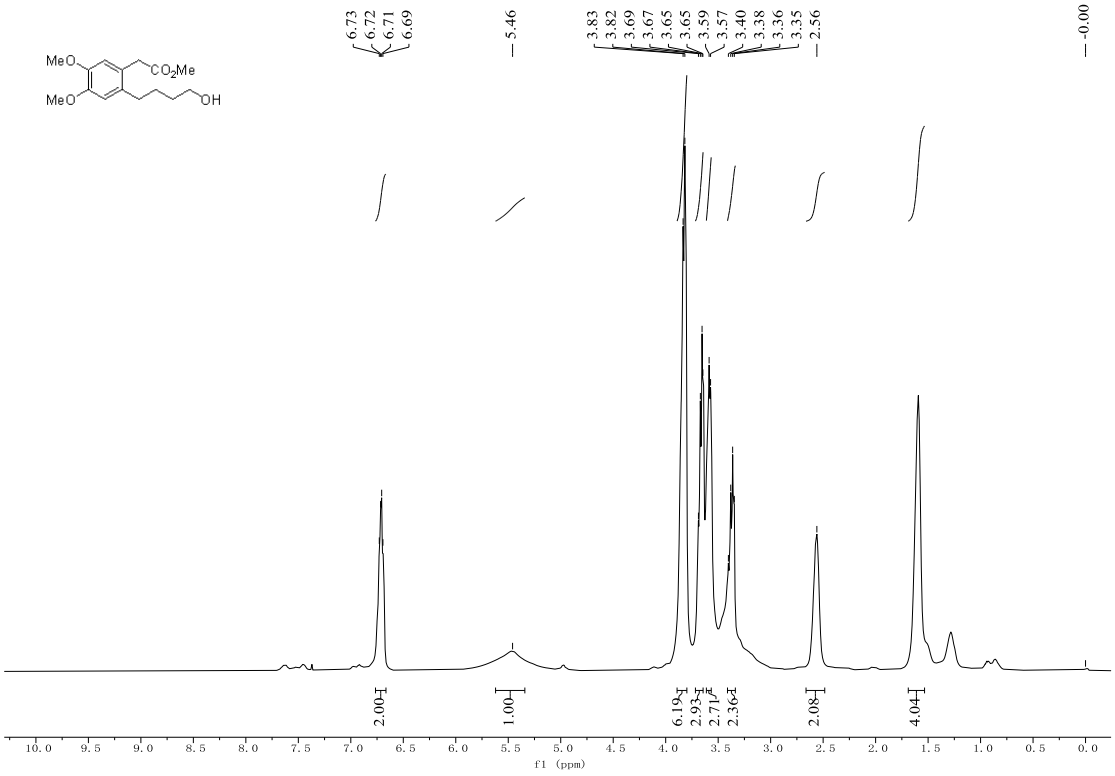
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4.04
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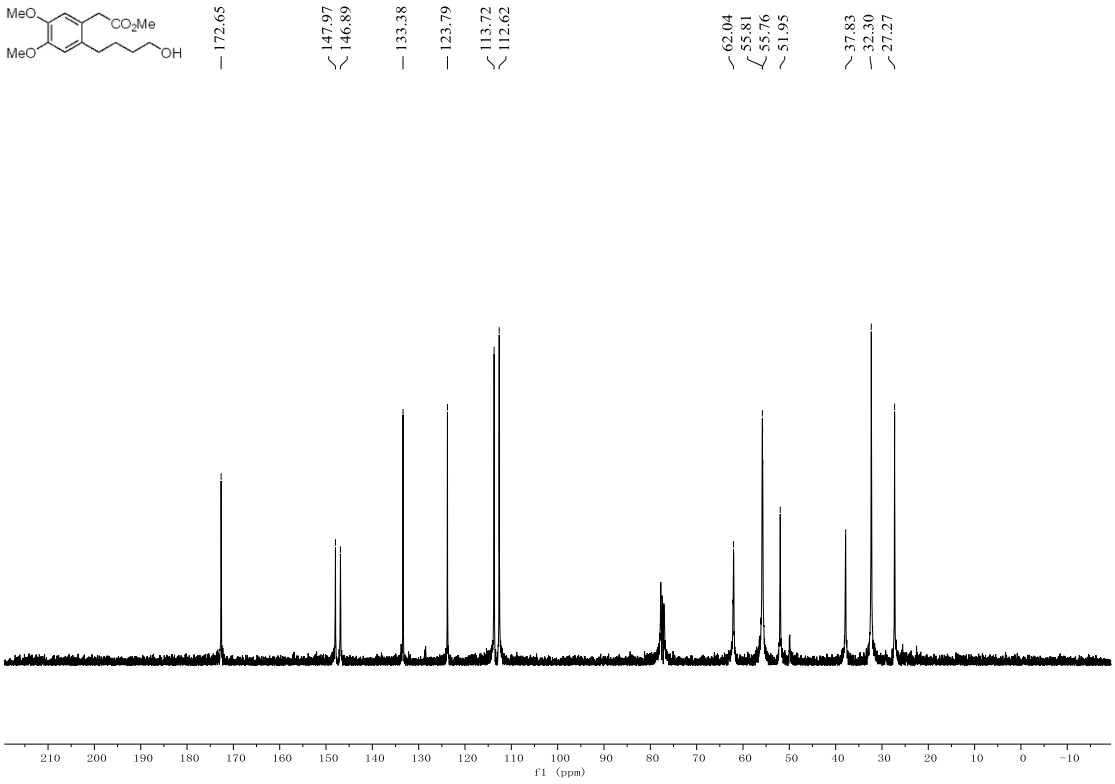
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37.83
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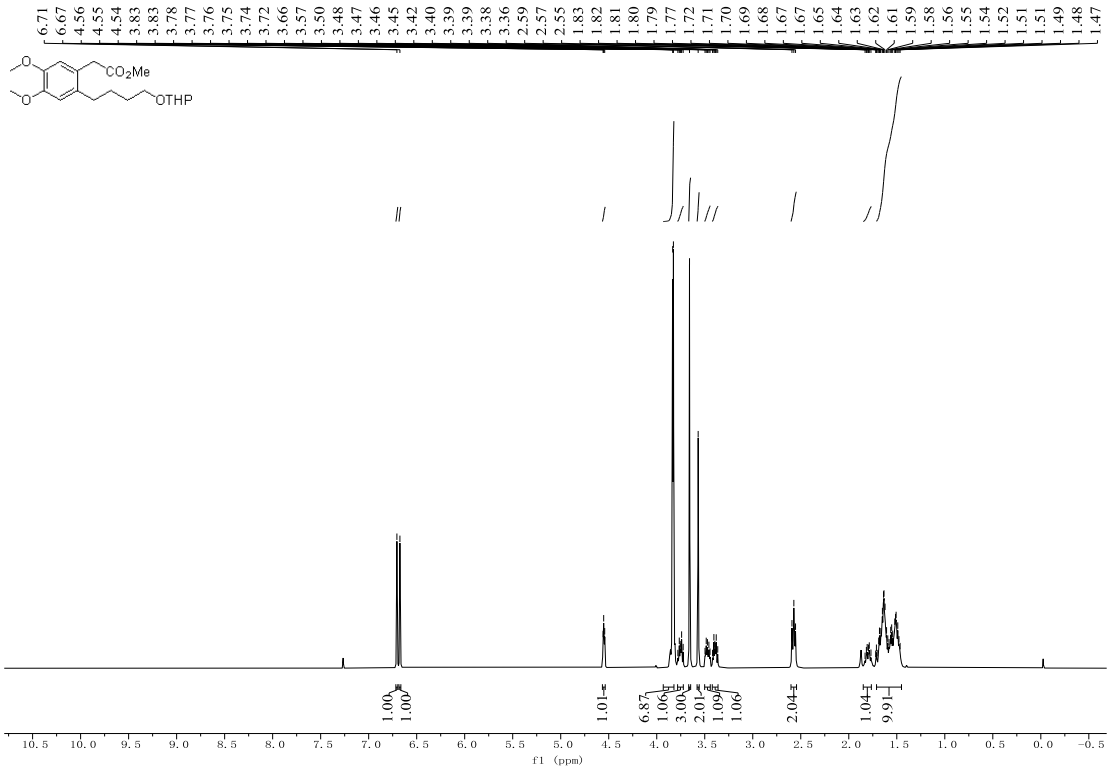
27.27
f1 (ppm)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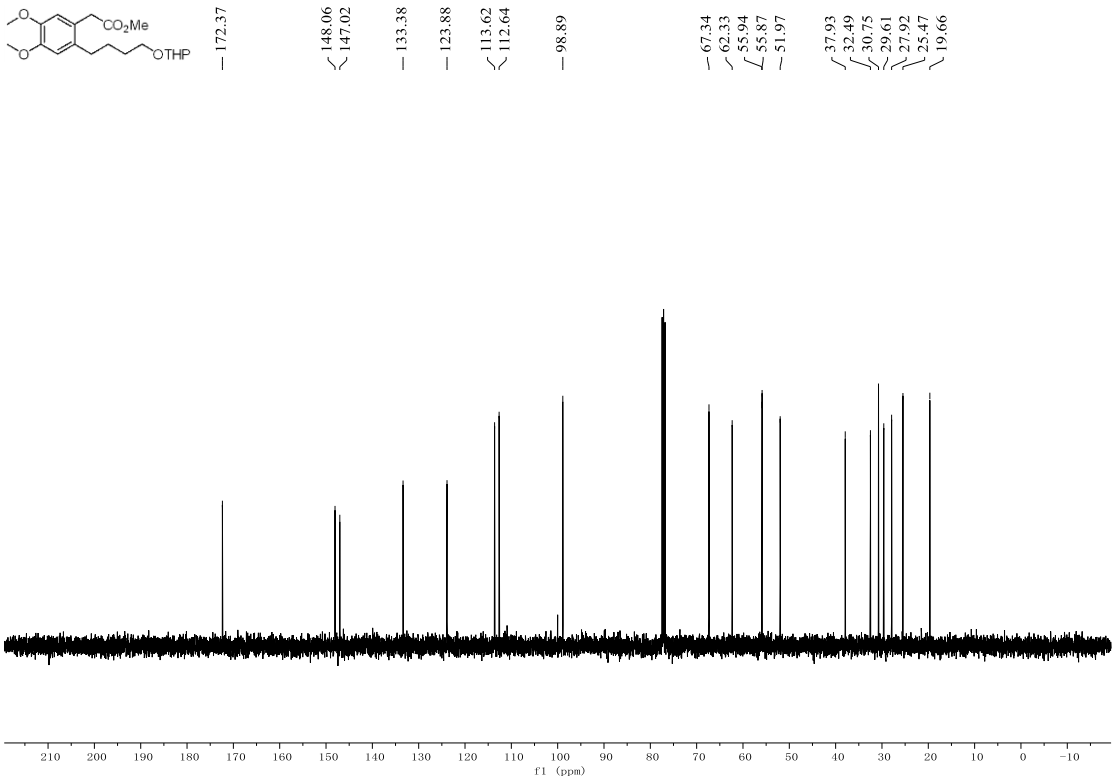
f1 (ppm)


CO2Me
OTHP
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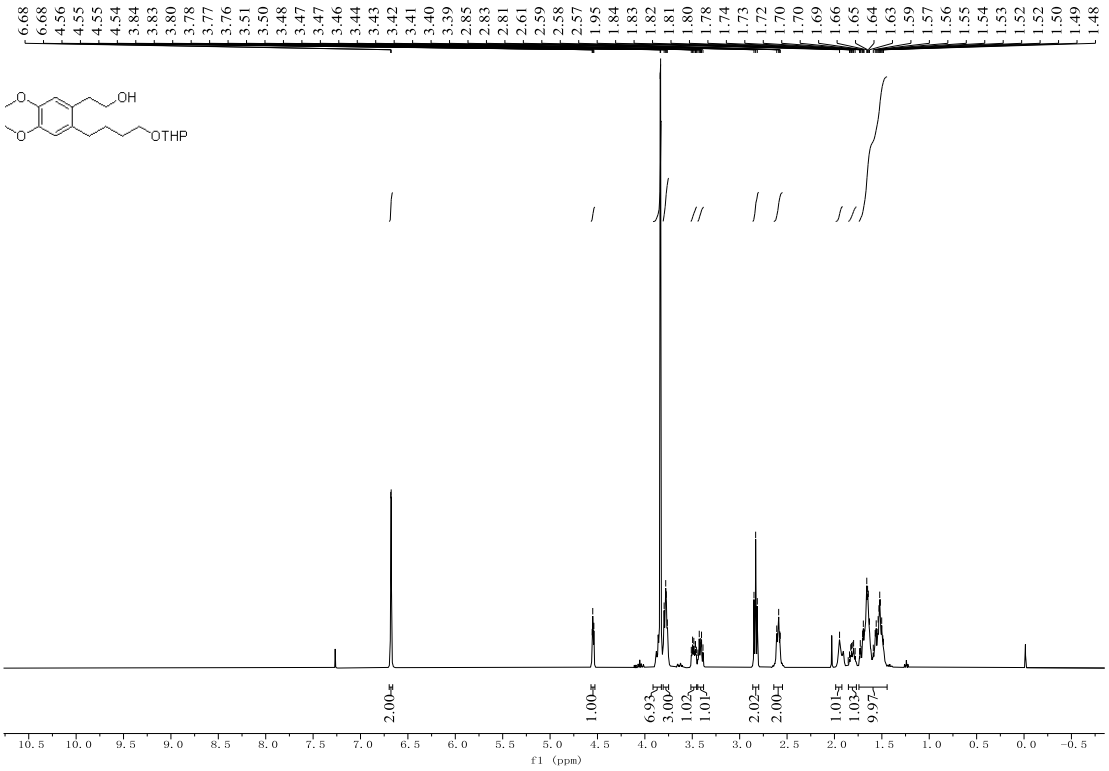
f1 (ppm)


6.68 6.68 4.56 4.55 4.55 4.54 3.84 3.83 3.80 3.78 3.77 3.76 3.51 3.50 3.48 3.47 3.47 3.46 3.44 3.43 3.42 3.41 3.40 3.39 2.85 2.83 2.81 2.61 2.59 2.58 2.57 1.95 1.84 1.83 1.82 1.81 1.80 1.78 1.74 1.73 1.72 1.70 1.70 1.69 1.66 1.65 1.64 1.63 1.59 1.57 1.56 1.55 1.54 1.53 1.52 1.52 1.50 1.49 1.48
OH
OTHP
2.00
1.00
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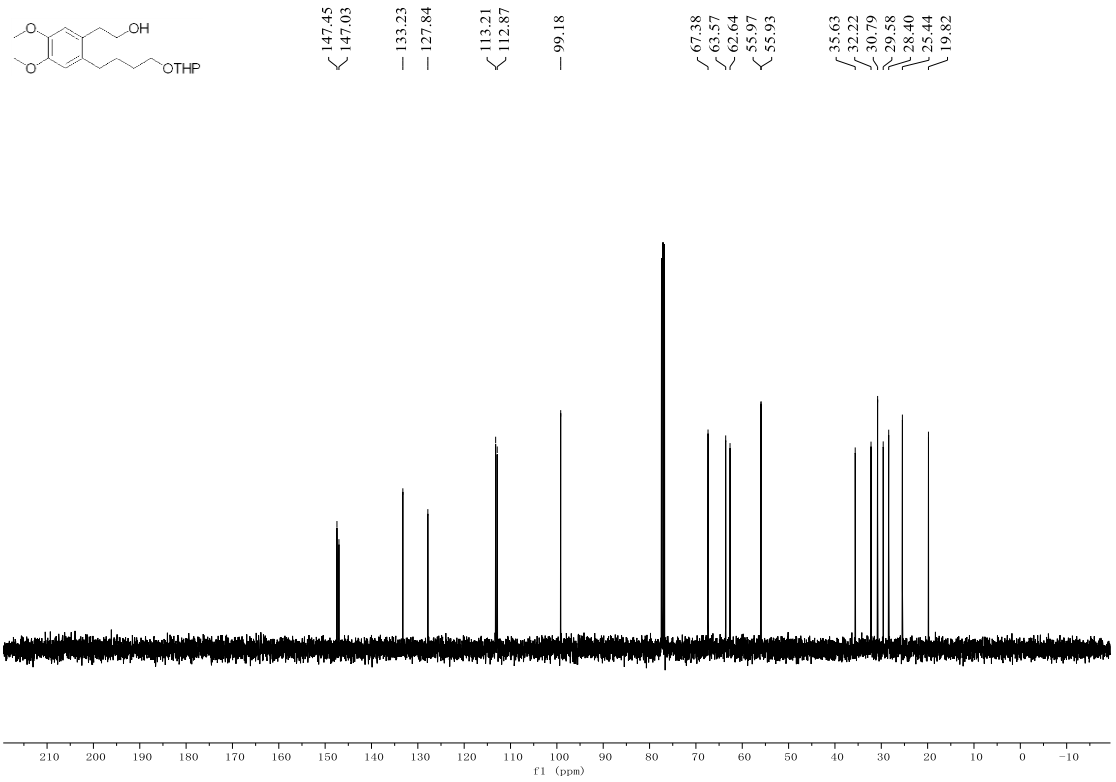
3.00
1.02
1.01
2.02
2.00
1.01
1.03
9.97
f1 (ppm)


OH
OTHP
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147.03
133.23
127.84
113.21
112.87
99.18
67.38
63.57
62.64
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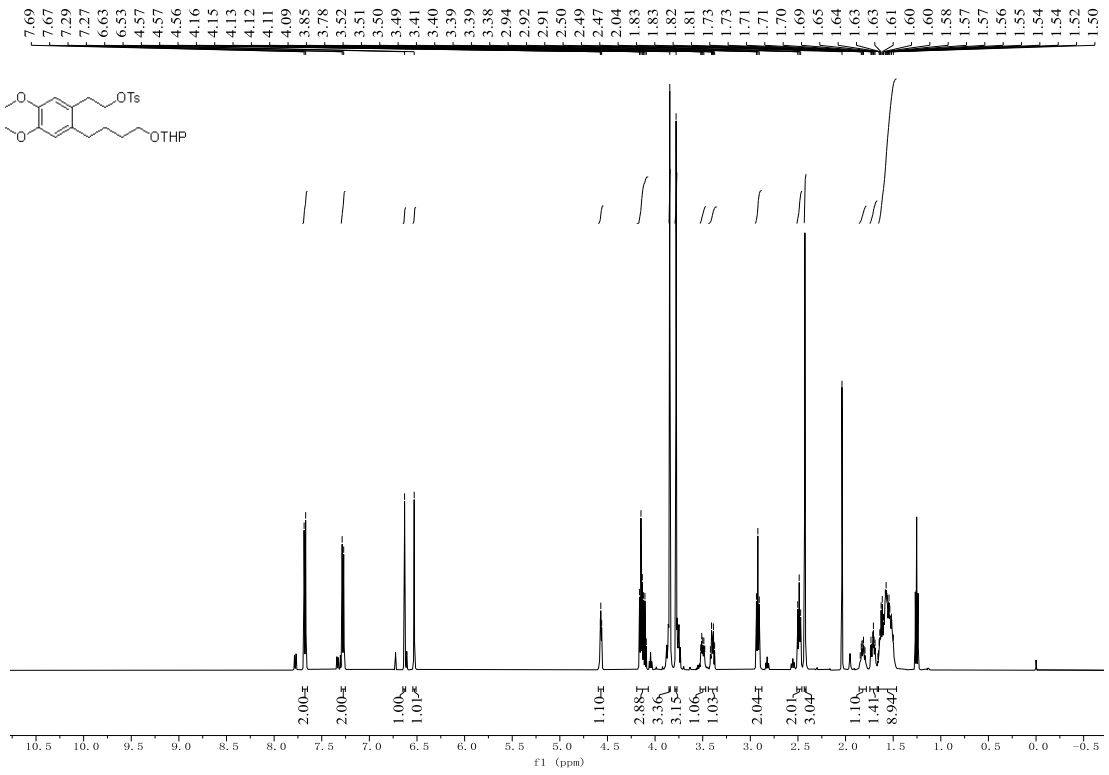
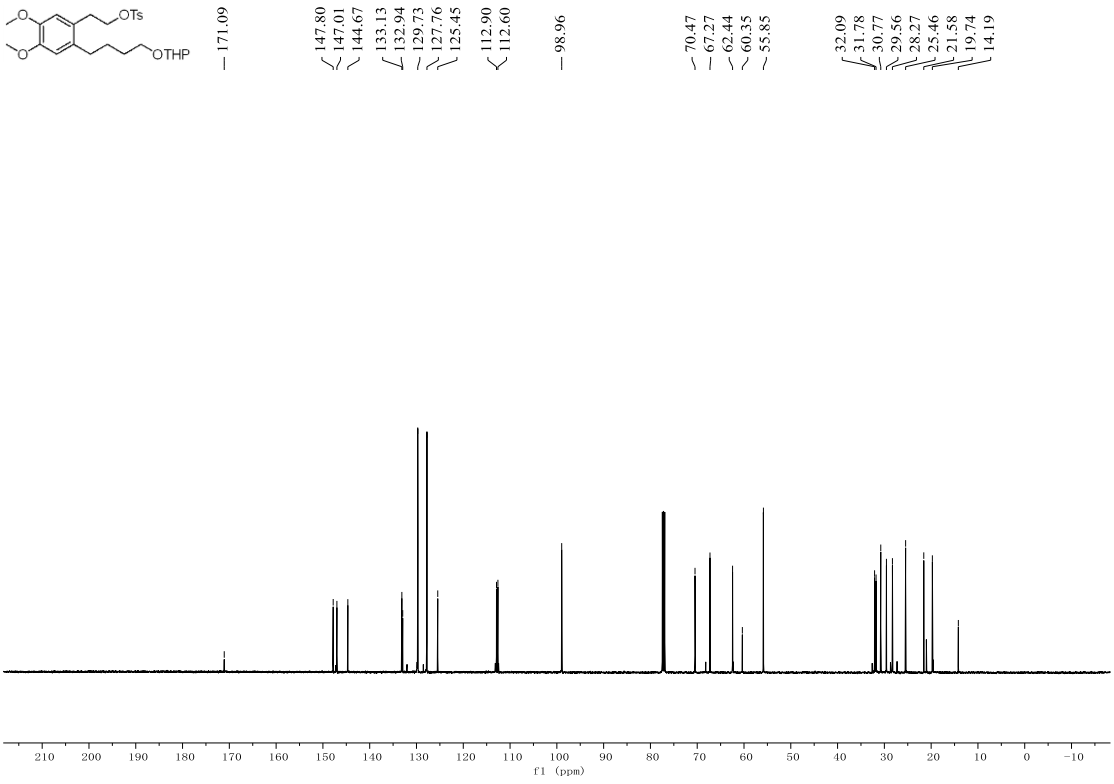
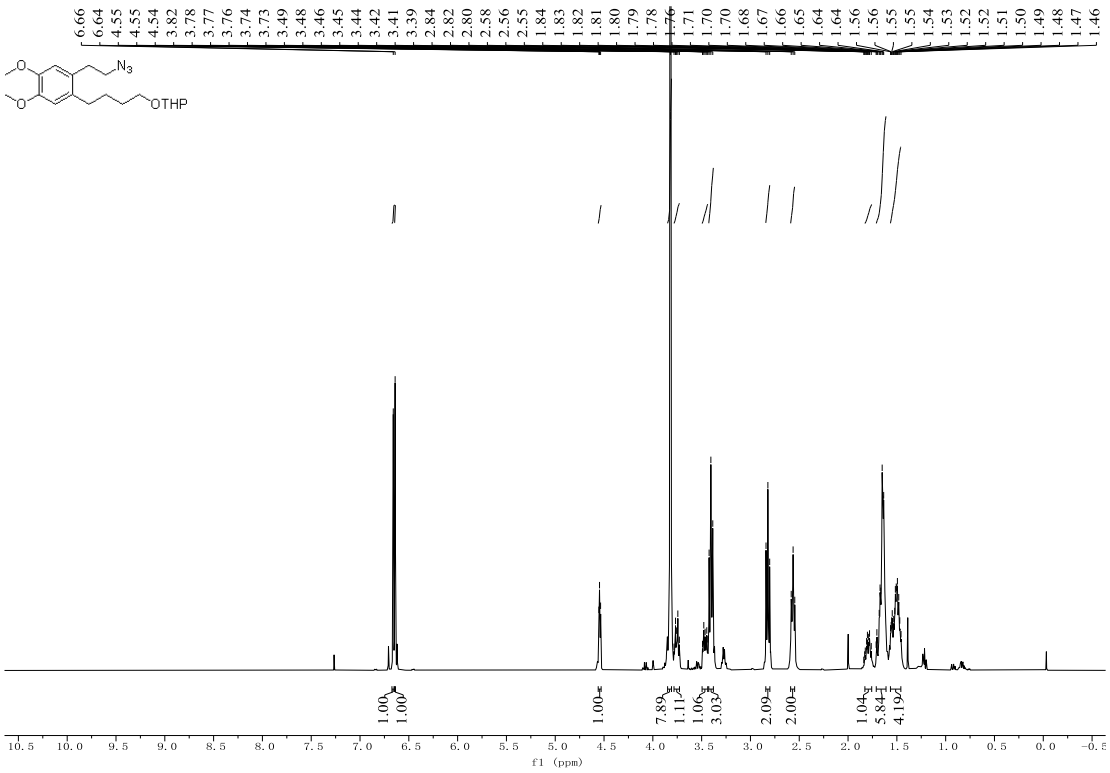
55.93
35.63
32.22
30.79
29.58
28.40
25.44
19.82
f1 (ppm)


7.69 7.67 7.29 7.27 6.63 6.53 4.57 4.57 4.56 4.16 4.15 4.13 4.12 4.11 4.09 3.85 3.78 3.52 3.51 3.50 3.49 3.41 3.40 3.39 3.39 3.38 2.94 2.92 2.91 2.50 2.49 2.47 2.04 1.83 1.83 1.82 1.81 1.73 1.73 1.71 1.71 1.70 1.69 1.65 1.64 1.63 1.63 1.61 1.60 1.60 1.58 1.57 1.57 1.56 1.55 1.54 1.54 1.52 1.50
OTs
OTHP
2.00 2.00 1.00 1.01 1.10 2.88 3.36 3.15 1.06 1.03 2.04 2.01 3.04 1.10 1.41 8.94
f1 (ppm)


OTs
OTHP
171.09
147.80 147.01 144.67 133.13 132.94 129.73 127.76 125.45 112.90 112.60 98.96 70.47 67.27 62.44 60.35 55.85 32.09 31.78 30.77 29.56 28.27 25.46 21.58 19.74 14.19
f1 (ppm)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3.77
3.76
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3.73
3.49
3.48
3.46
3.45
3.44
3.42
3.41
3.39
2.84
2.82
2.80
2.58
2.56
2.55
1.84
1.83
1.82
1.81
1.80
1.79
1.78
1.76
1.71
1.70
1.70
1.68
1.67
1.66
1.65
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1.56
1.56
1.55
1.55
1.54
1.53
1.52
1.52
1.51
1.50
1.49
1.48
1.47
1.46
N3
OTHP
1.00
1.00
1.00
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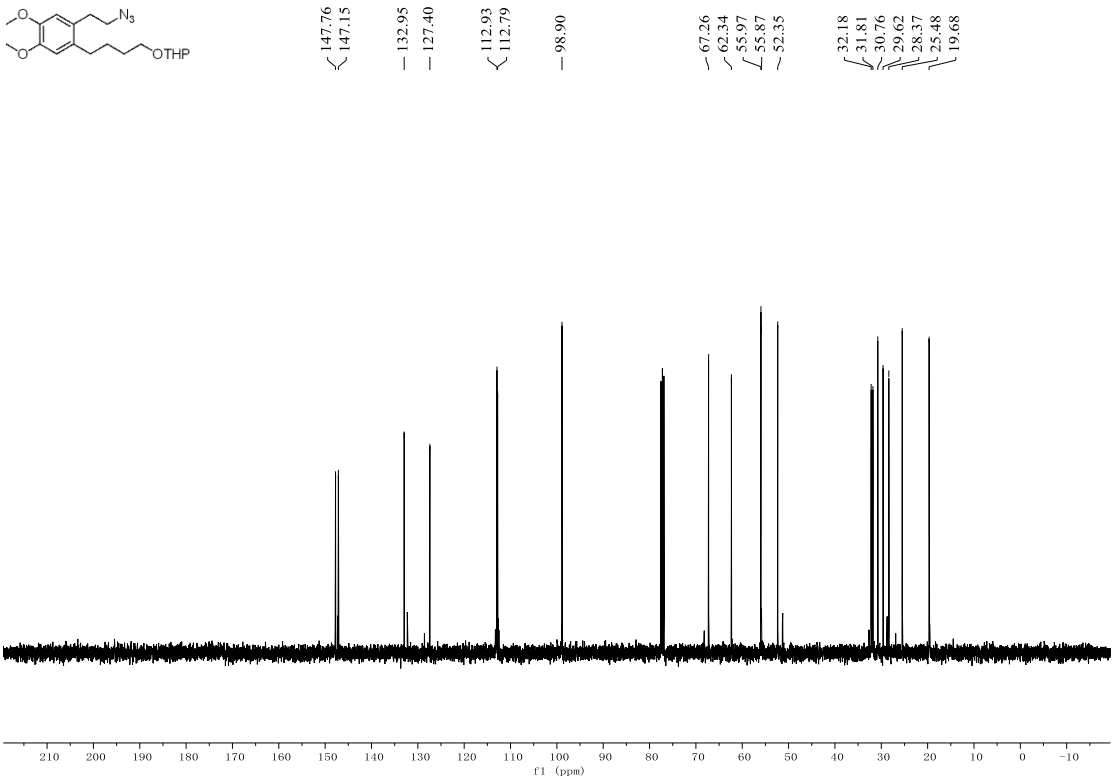
1.11
1.06
3.03
2.09
2.00
1.04
5.84
4.19
f1 (ppm)


N3
OTHP
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147.15
132.95
127.40
112.93
112.79
98.90
67.26
62.34
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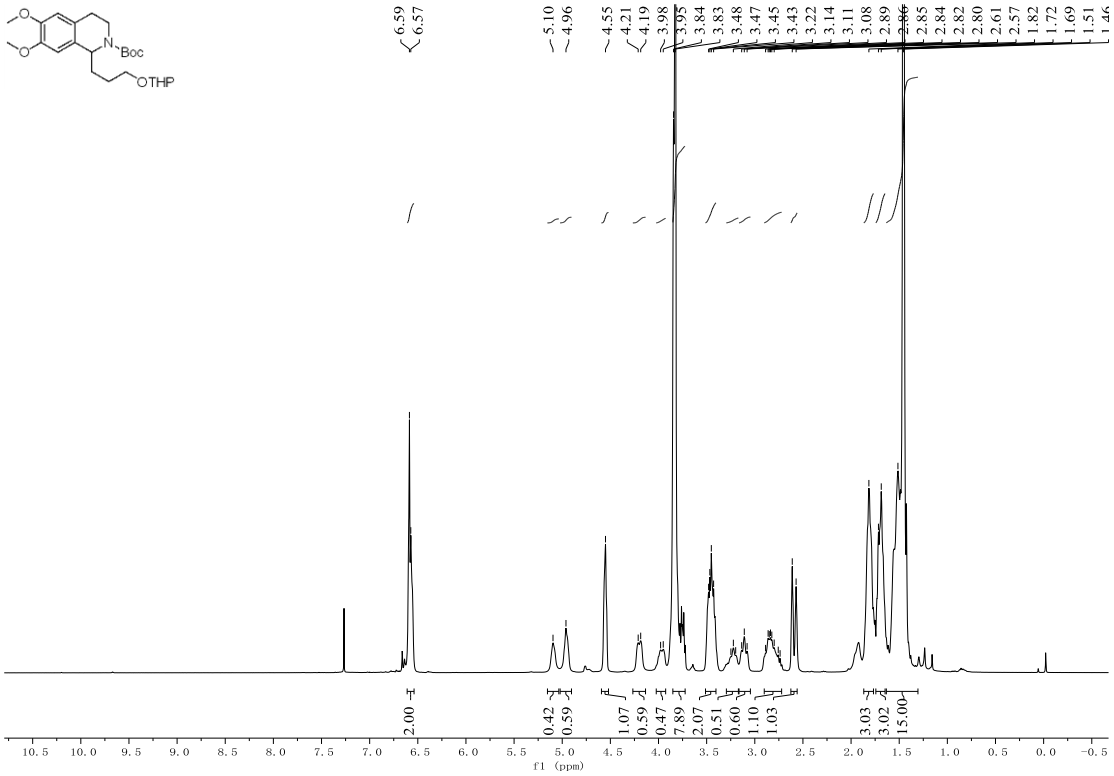
52.35
32.18
31.81
30.76
29.62
28.37
25.48
19.68
f1 (ppm)


Boc
OTHP
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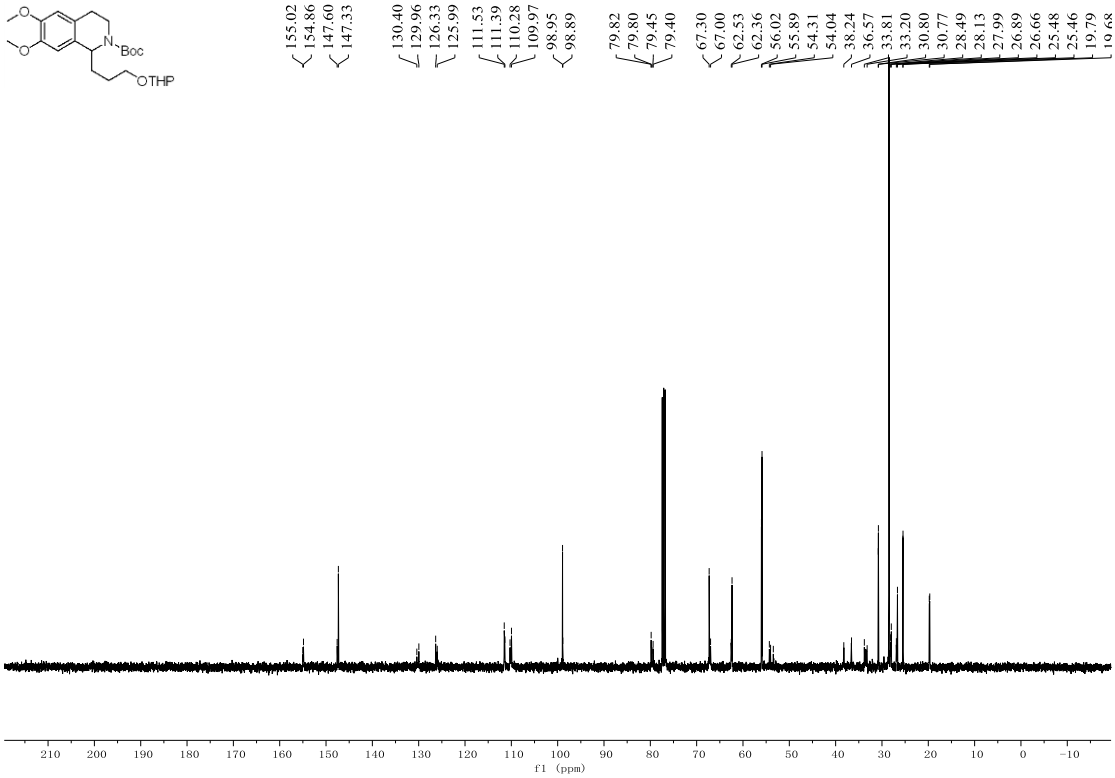
6.57
5.10
4.96
4.55
4.21
4.19
3.98
3.95
3.84
3.83
3.48
3.47
3.45
3.43
3.22
3.14
3.11
3.08
2.89
2.85
2.84
2.82
2.80
2.61
2.57
1.82
1.72
1.69
1.51
2.00
0.42
0.59
1.07
0.59
0.47
7.89
2.07
0.51
0.60
1.10
1.03
3.03
3.02
15.00
f1 (ppm)


Boc
OTHP
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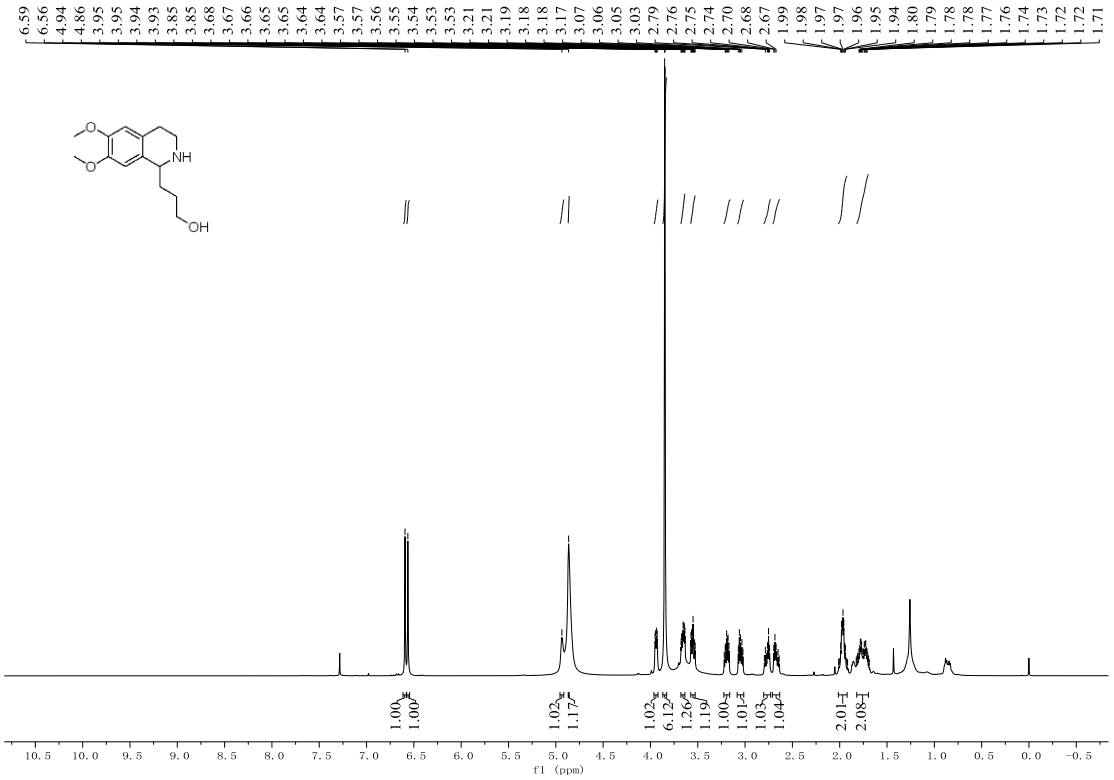
154.86
147.60
147.33
130.40
129.96
126.33
125.99
111.53
111.39
110.28
109.97
98.95
98.89
79.82
79.80
79.45
79.40
67.30
67.00
62.53
62.36
56.02
55.89
54.31
54.04
38.24
36.57
33.81
33.20
30.80
30.77
28.49
28.13
27.99
26.89
26.66
25.48
25.46
19.79
f1 (ppm)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6.56
4.94
4.86
3.95
3.95
3.94
3.93
3.85
3.85
3.68
3.67
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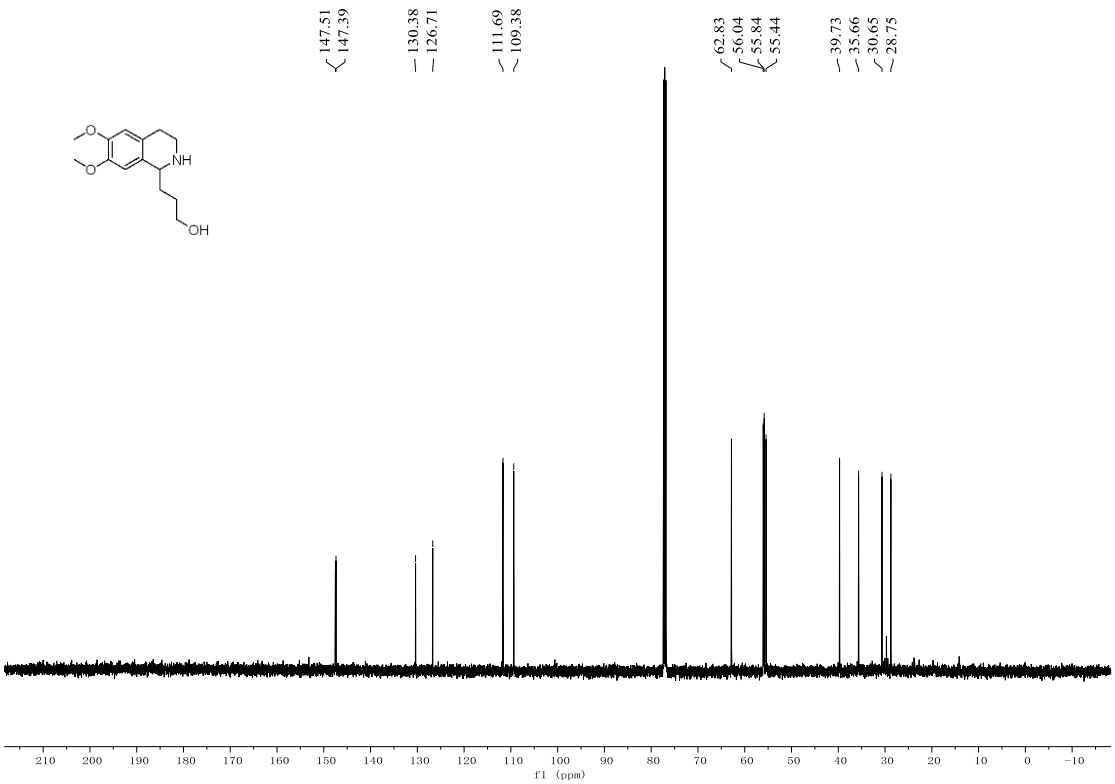
3.65
3.65
3.64
3.64
3.57
3.57
3.56
3.55
3.54
3.53
3.53
3.21
3.21
3.19
3.18
3.18
3.17
3.07
3.06
3.05
3.03
2.79
2.76
2.75
2.74
2.70
2.68
2.67
1.99
1.98
1.97
1.97
1.96
1.95
1.94
1.80
1.79
1.78
1.78
1.77
1.76
1.74
1.73
1.72
1.72
1.71
NH
OH
1.00
1.00
1.02
1.17
1.02
6.12
1.26
1.19
1.00
1.01
1.03
1.04
2.01
2.08
f1 (ppm)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147.39
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109.38
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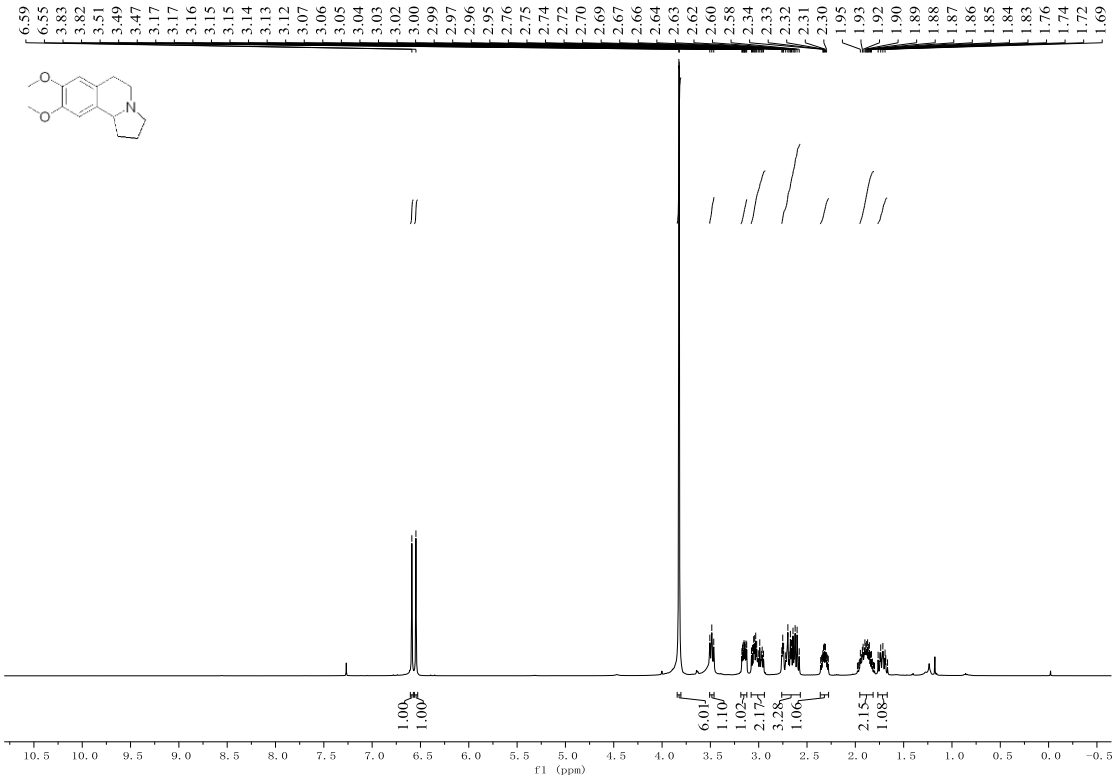
56.04
55.84
55.44
39.73
35.66
30.65
28.75
NH
OH
f1 (ppm)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6.55
3.83
3.82
3.51
3.49
3.47
3.17
3.17
3.16
3.15
3.15
3.14
3.13
3.12
3.07
3.06
3.05
3.04
3.03
3.02
3.00
2.99
2.97
2.96
2.95
2.76
2.75
2.74
2.72
2.70
2.69
2.67
2.66
2.64
2.63
2.62
2.60
2.58
2.34
2.33
2.32
2.31
2.30
1.95
1.93
1.92
1.90
1.89
1.88
1.87
1.86
1.85
1.84
1.83
1.76
1.74
1.72
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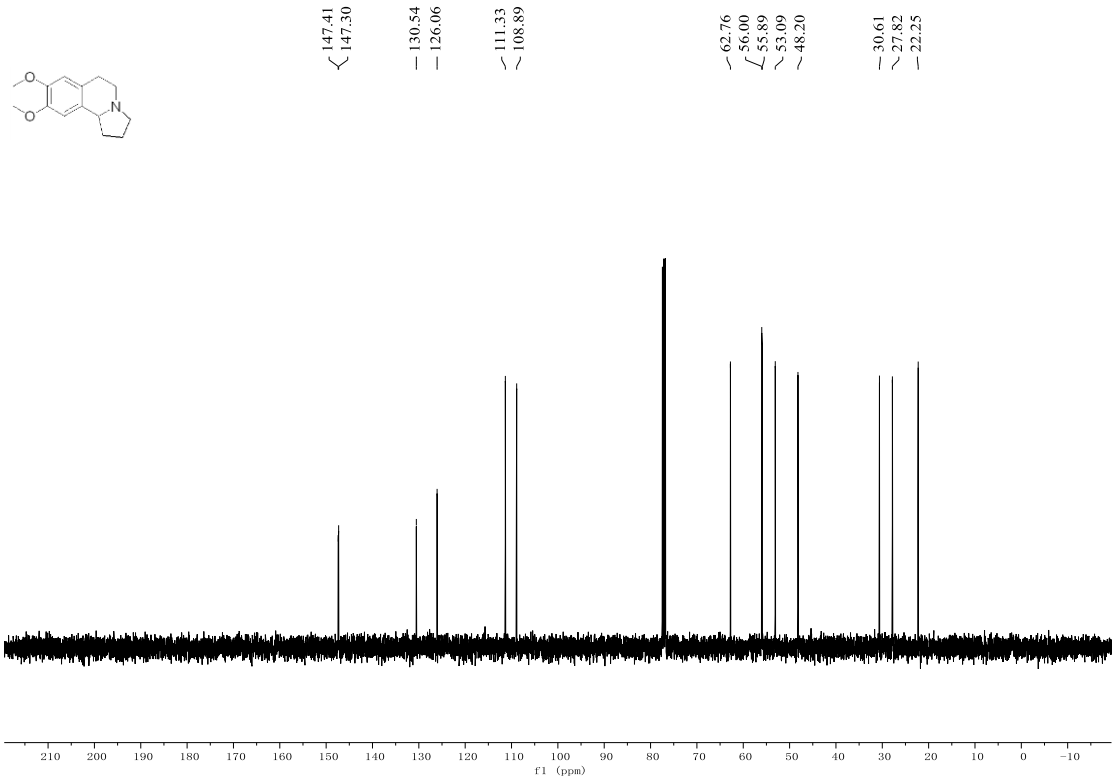
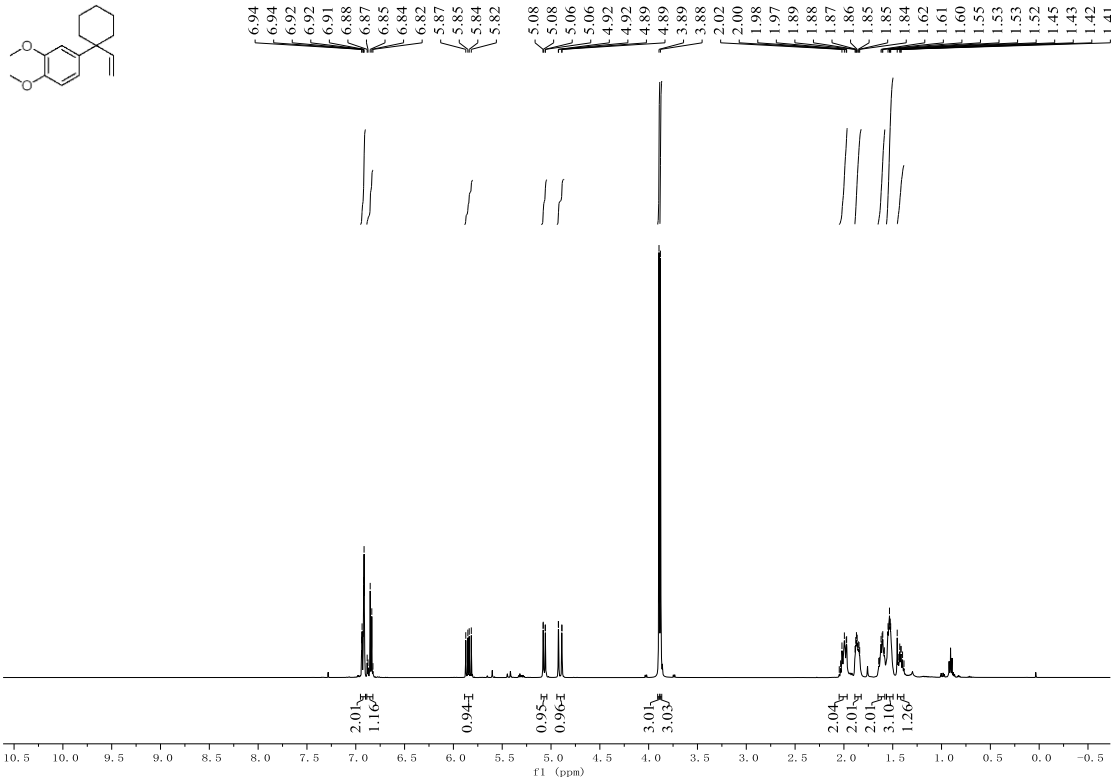
3.28
1.06
2.15
1.08
f1 (ppm)


147.41
147.30
130.54
126.06
111.33
108.89
62.76
56.00
55.89
53.09
48.20
30.61
27.82
22.25
f1 (ppm)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6.94
6.92
6.92
6.91
6.88
6.87
6.85
6.84
6.82
5.87
5.85
5.84
5.82
5.08
5.08
5.06
5.06
4.92
4.92
4.89
4.89
3.89
3.88
2.02
2.00
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1.97
1.89
1.88
1.87
1.86
1.85
1.85
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1.61
1.60
1.55
1.53
1.53
1.52
1.45
1.43
1.42
1.41
2.01
1.16
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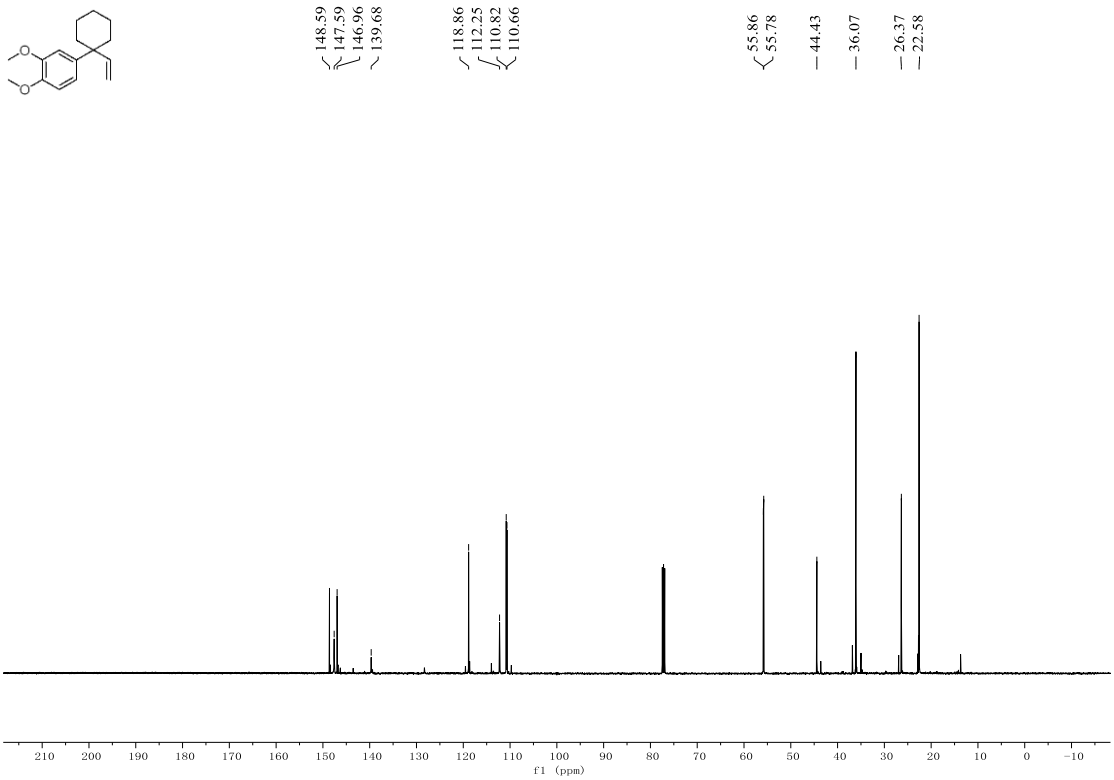
0.95
0.96
3.01
3.03
2.04
2.01
2.01
3.10
1.26
f1 (ppm)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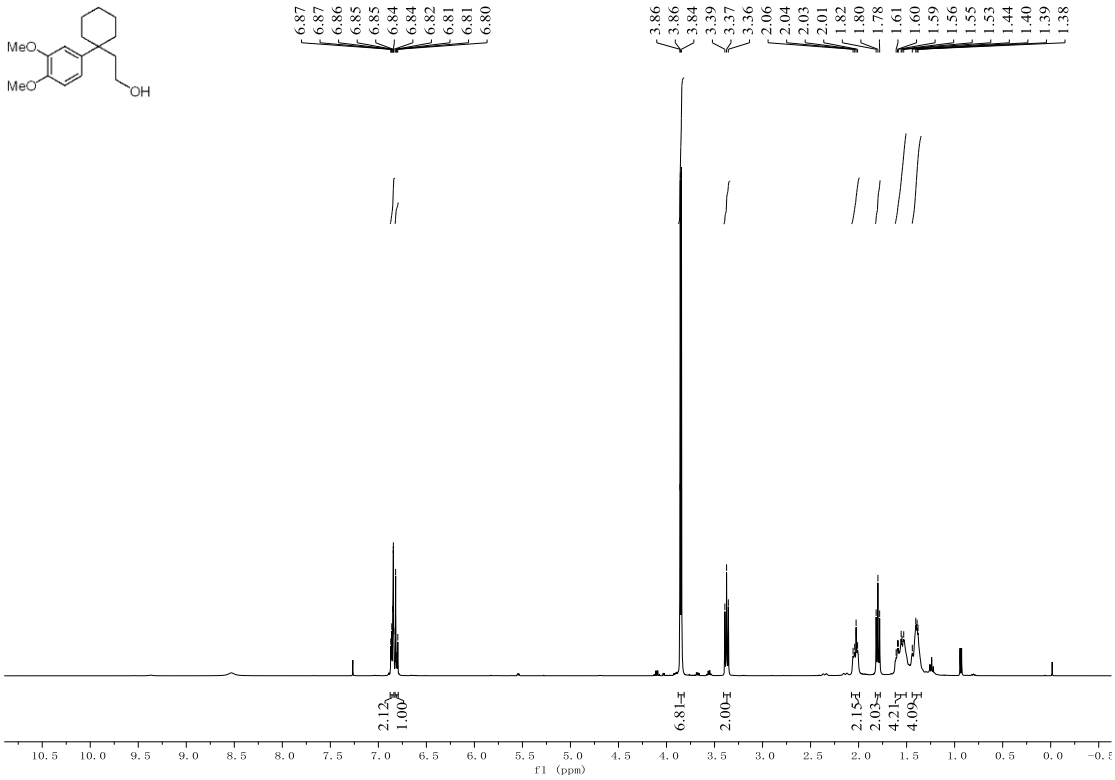
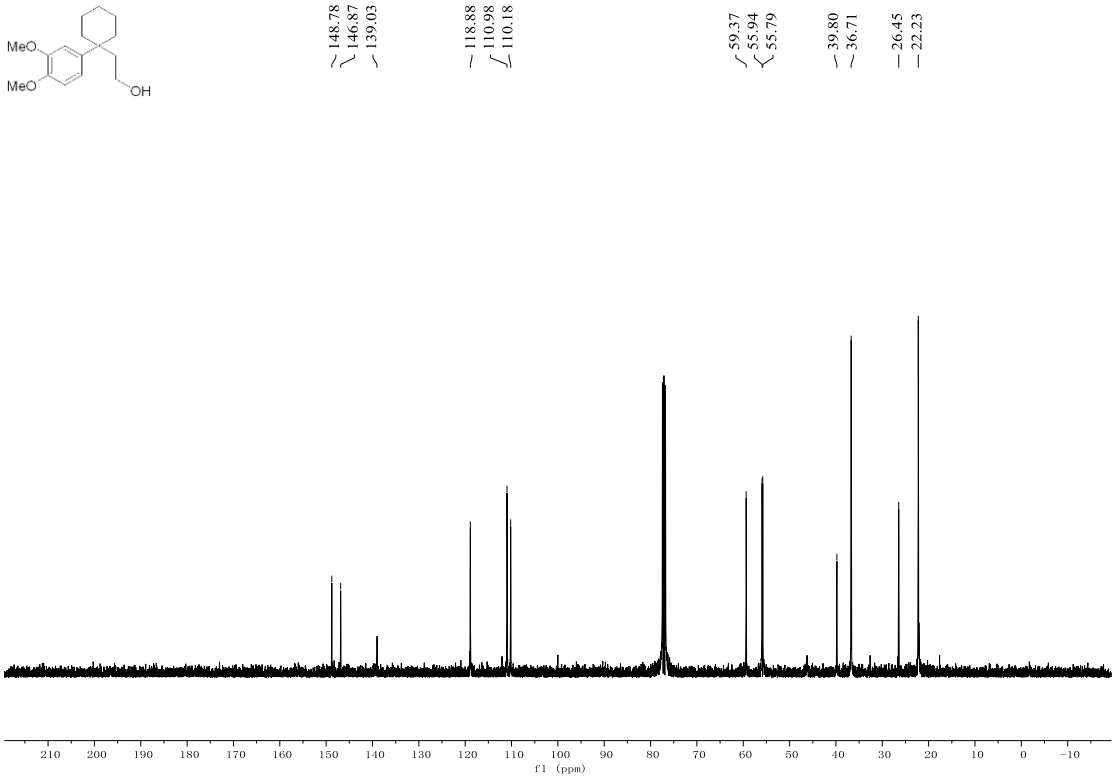
147.59
146.96
139.68
118.86
112.25
110.82
110.66
55.86
55.78
44.43
36.07
26.37
22.58
f1 (ppm)


MeO
MeO
OH
6.87
6.87
6.86
6.85
6.85
6.84
6.84
6.82
6.81
6.80
3.86
3.86
3.84
3.39
3.37
3.36
2.06
2.04
2.03
2.01
1.82
1.80
1.78
1.61
1.60
1.59
1.56
1.55
1.53
1.44
1.40
1.39
1.38
2.12
1.00
6.81
2.00
2.15
2.03
4.21
4.09
f1 (ppm)


MeO
MeO
OH
148.78
146.87
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118.88
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110.18
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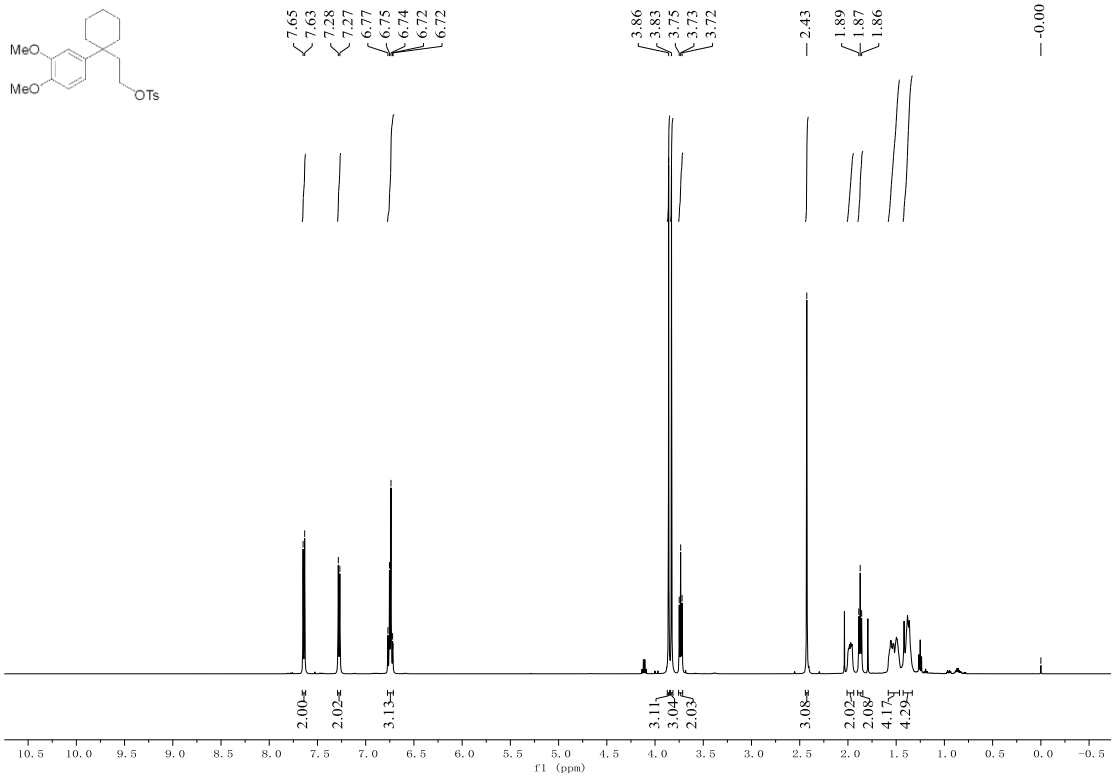
55.94
55.79
39.80
36.71
26.45
22.23
f1 (ppm)


MeO
MeO
OTs
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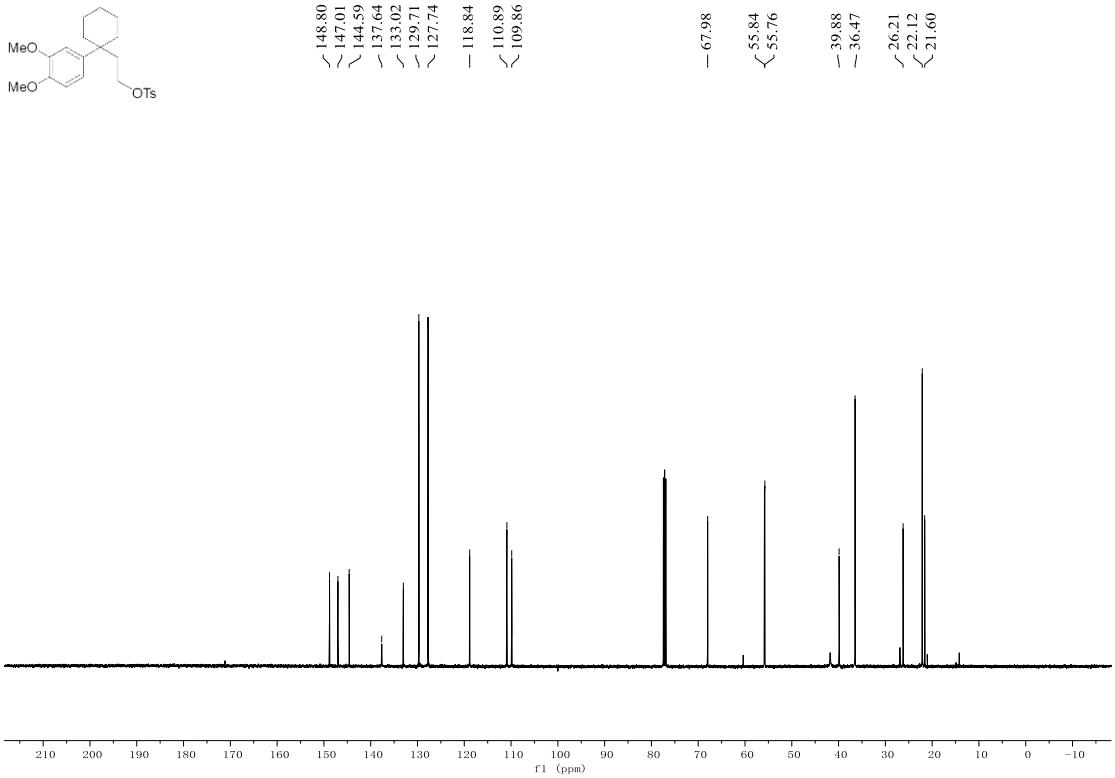
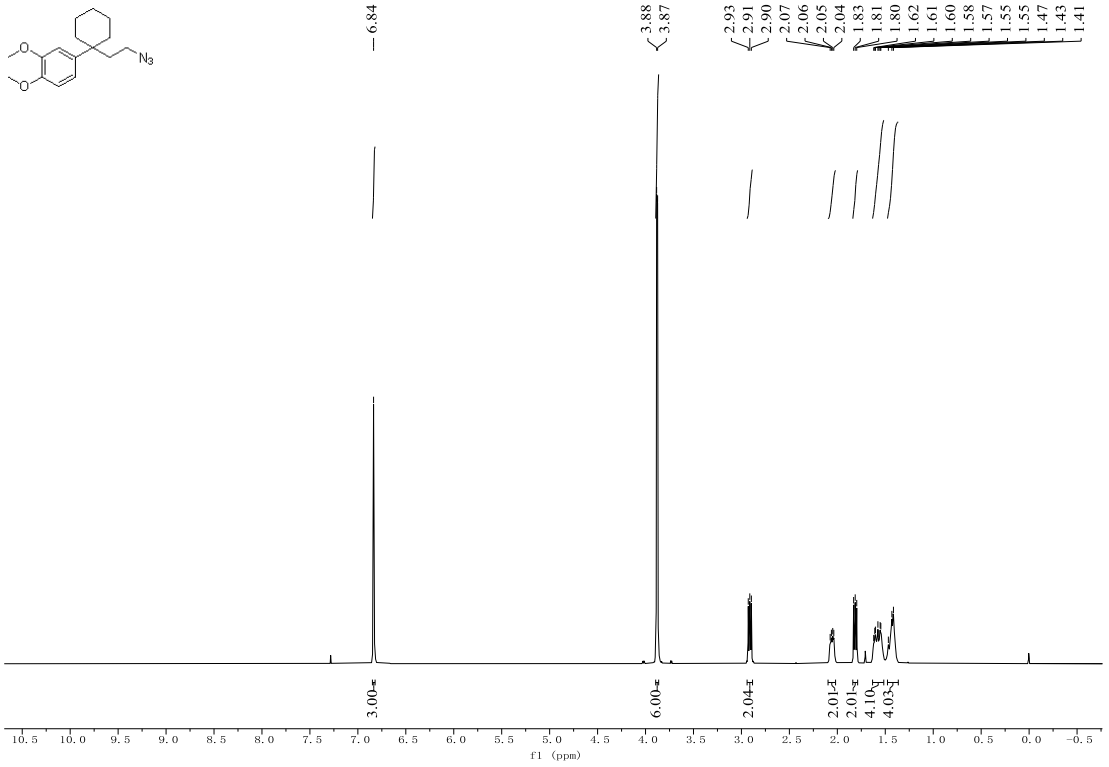
7.63
7.28
7.27
6.77
6.75
6.74
6.72
6.72
3.86
3.83
3.75
3.73
3.72
2.43
1.89
1.87
1.86
-0.00
2.00
2.02
3.13
3.11
3.04
2.03
3.08
2.02
2.08
4.17
4.29
f1 (ppm)


MeO
MeO
OTs
148.80
147.01
144.59
137.64
133.02
129.71
127.74
118.84
110.89
109.86
67.98
55.84
55.76
39.88
36.47
26.21
22.12
21.60
f1 (ppm)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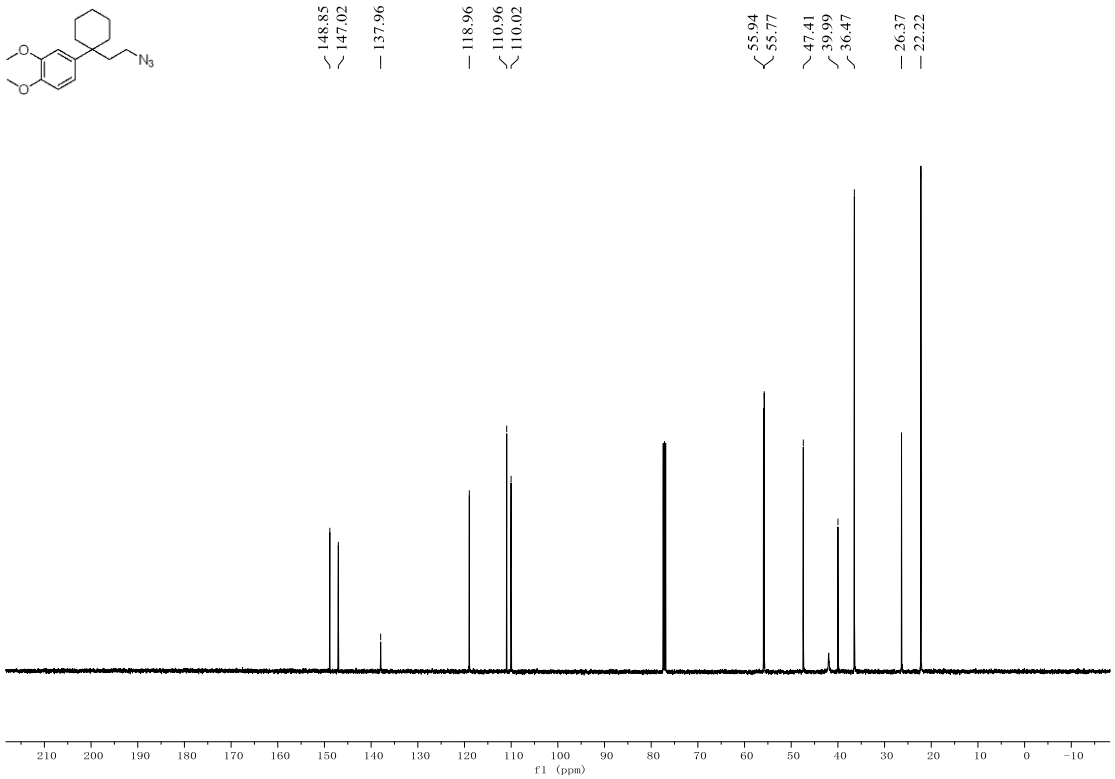
2.90
2.07
2.06
2.05
2.04
1.83
1.81
1.80
1.62
1.61
1.60
1.58
1.57
1.55
1.55
1.47
1.43
1.41
3.00
6.00
2.04
2.01
2.01
4.10
4.03
f1 (ppm)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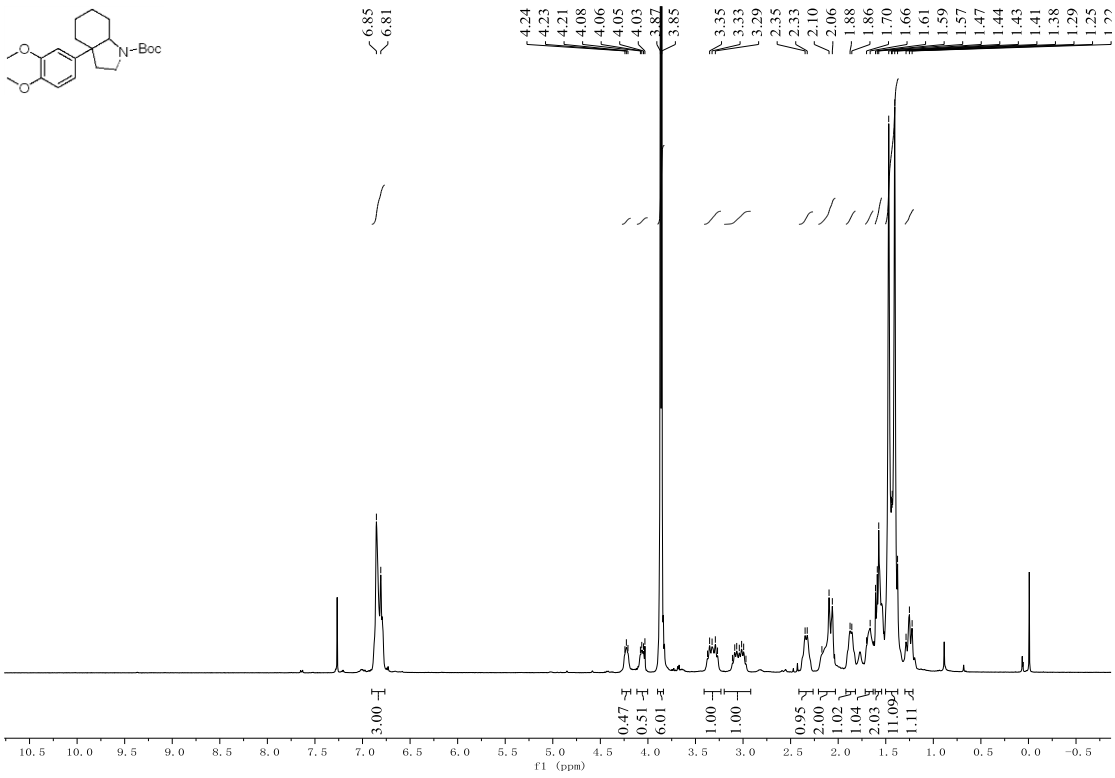
110.02
55.94
55.77
47.41
39.99
36.47
26.37
22.22
f1 (ppm)


N-Boc
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4.08
4.06
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4.03
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3.85
3.35
3.33
3.29
2.35
2.33
2.10
2.06
1.88
1.86
1.70
1.66
1.61
1.59
1.57
1.47
1.44
1.43
1.41
1.38
1.29
1.25
3.00
0.47
0.51
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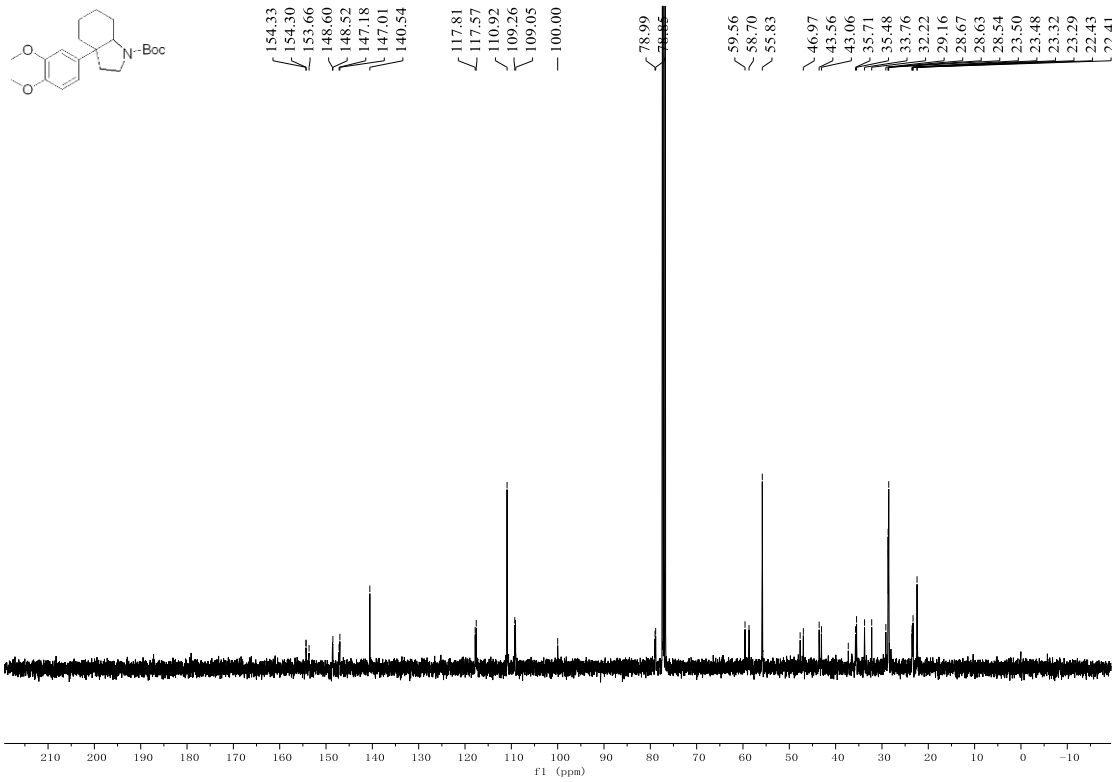
1.00
0.95
2.00
1.02
1.04
2.03
11.09
1.11
f1 (ppm)


N-Boc
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153.66
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148.52
147.18
147.01
140.54
117.81
117.57
110.92
109.26
109.05
100.00
78.99
59.56
58.70
55.83
46.97
43.56
43.06
35.71
35.48
33.76
32.22
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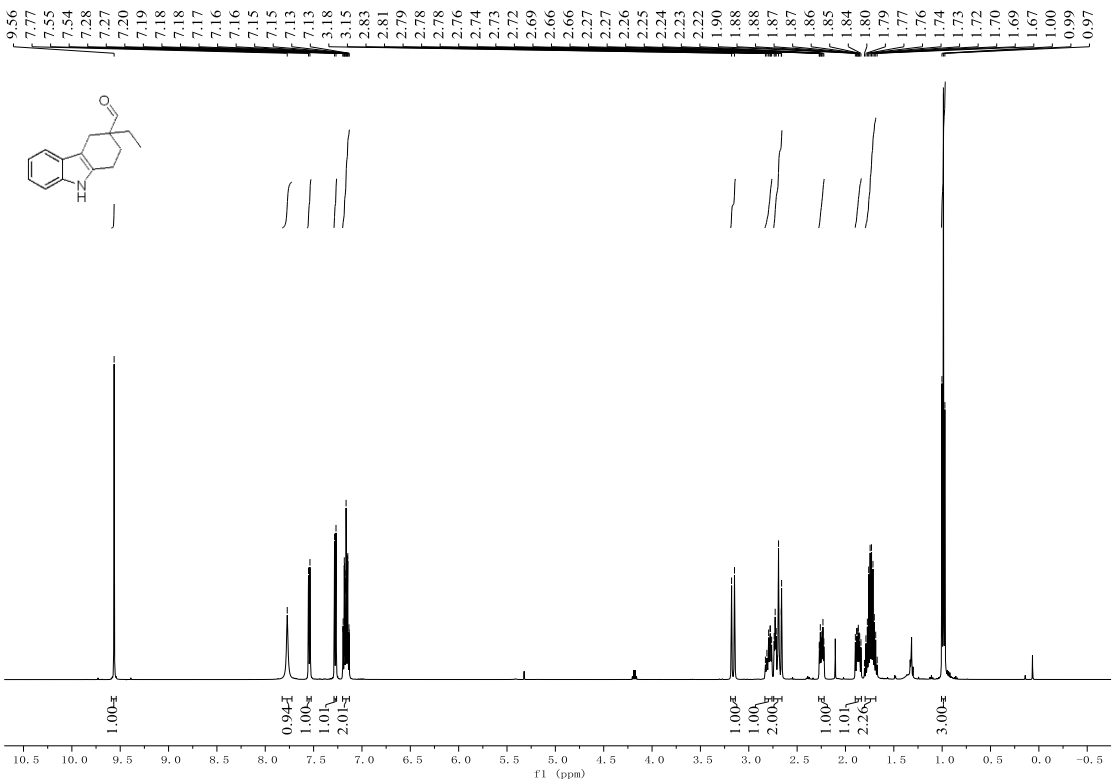
23.48
23.32
23.29
22.43
f1 (ppm)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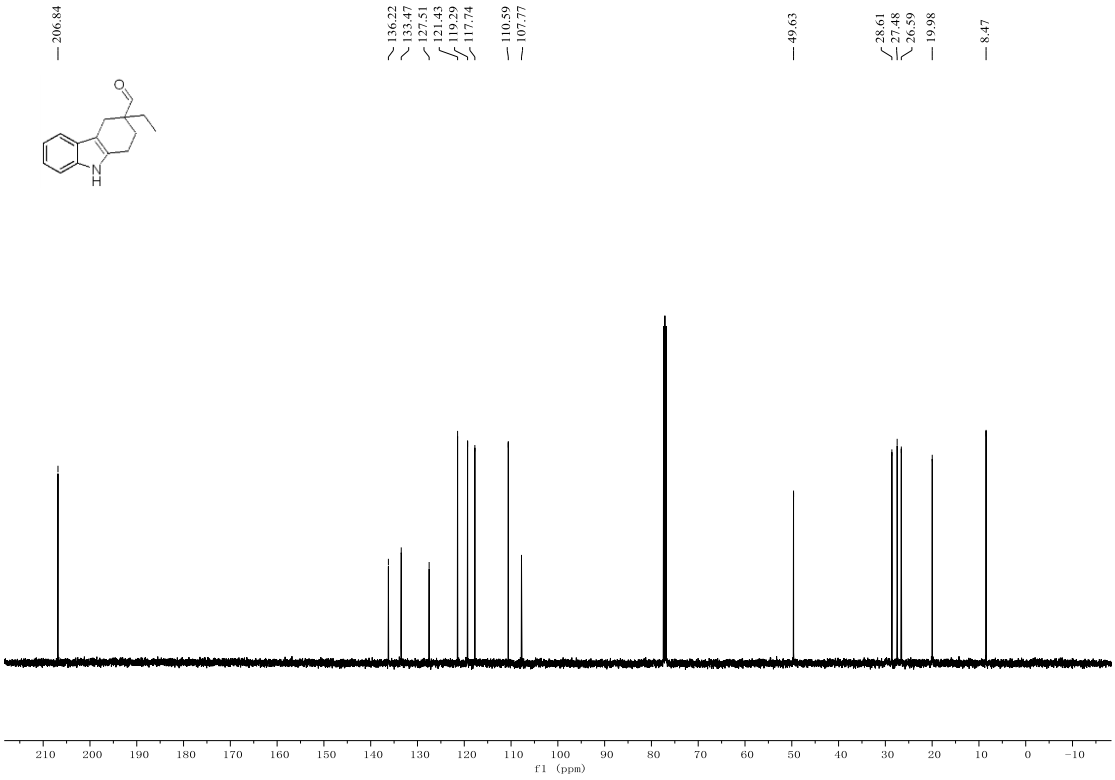
7.19
7.18
7.18
7.17
7.16
7.16
7.15
7.15
7.13
7.13
3.18
3.15
2.83
2.81
2.79
2.78
2.78
2.76
2.74
2.73
2.72
2.69
2.66
2.66
2.27
2.27
2.26
2.25
2.24
2.23
2.22
1.90
1.88
1.88
1.87
1.87
1.86
1.85
1.84
1.80
1.79
1.77
1.76
1.74
1.73
1.72
1.70
1.69
1.67
1.00
0.99
0.97
1.00
0.94
1.00
1.01
2.01
1.00
1.00
2.00
1.00
1.01
2.26
3.00
f1 (ppm)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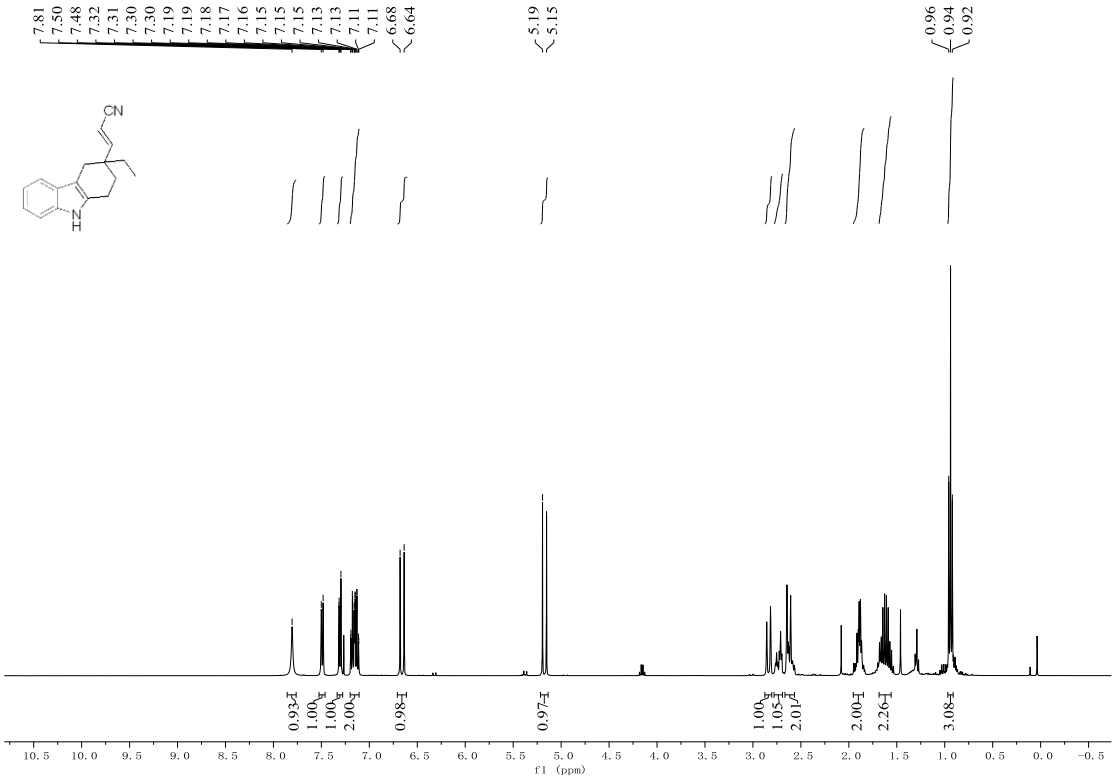
136.22
133.47
127.51
121.43
119.29
117.74
110.59
107.77
49.63
28.61
27.48
26.59
19.98
8.47
f1 (ppm)


7.81
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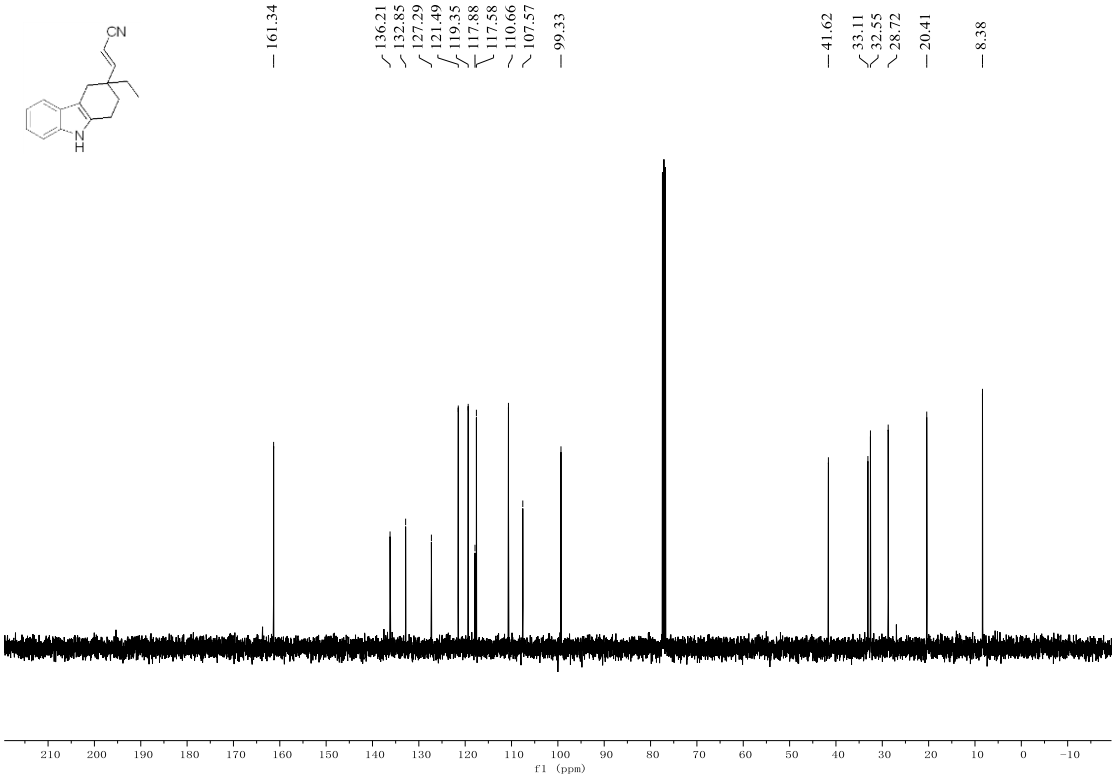
7.30
7.30
7.19
7.19
7.18
7.17
7.16
7.15
7.15
7.15
7.13
7.13
7.11
7.11
6.68
6.64
5.19
5.15
0.96
0.94
0.92
CN
N
H
0.93
1.00
1.00
2.00
0.98
0.97
1.00
1.05
2.01
2.00
2.26
3.08
f1 (ppm)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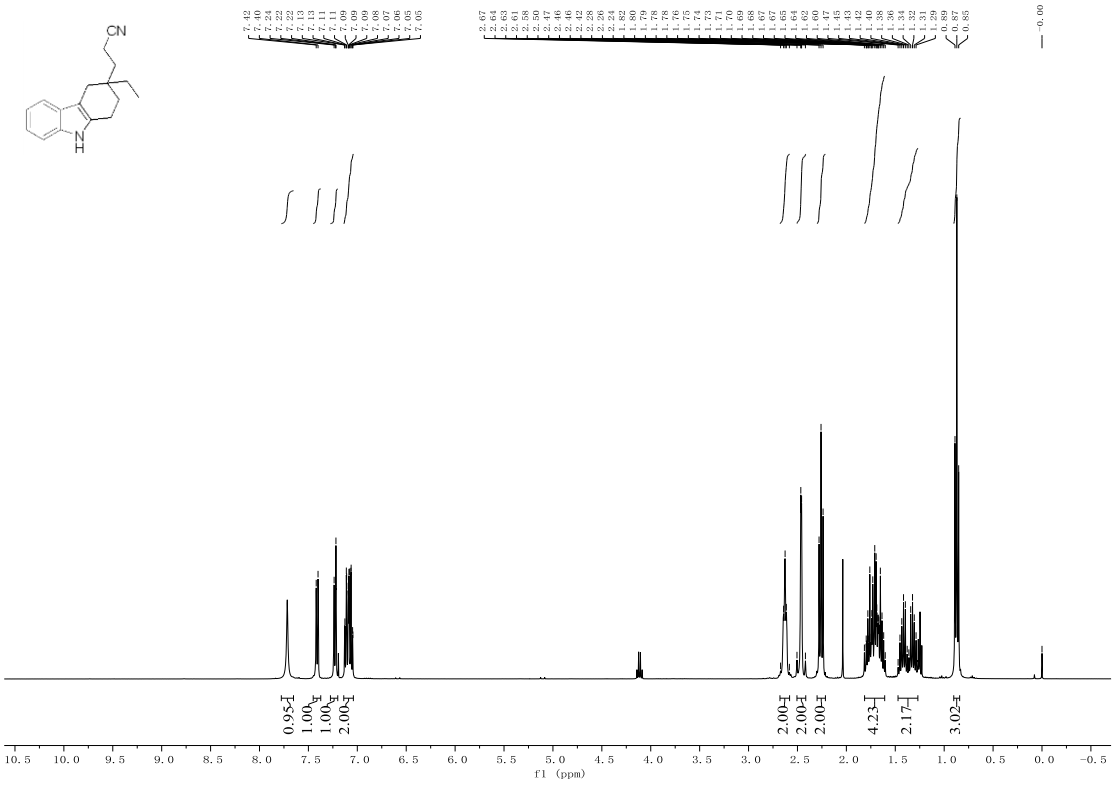
132.85
127.29
121.49
119.35
117.88
117.58
110.66
107.57
99.33
41.62
33.11
32.55
28.72
20.41
8.38
CN
N
H
f1 (ppm)


CN
N
H
7.42
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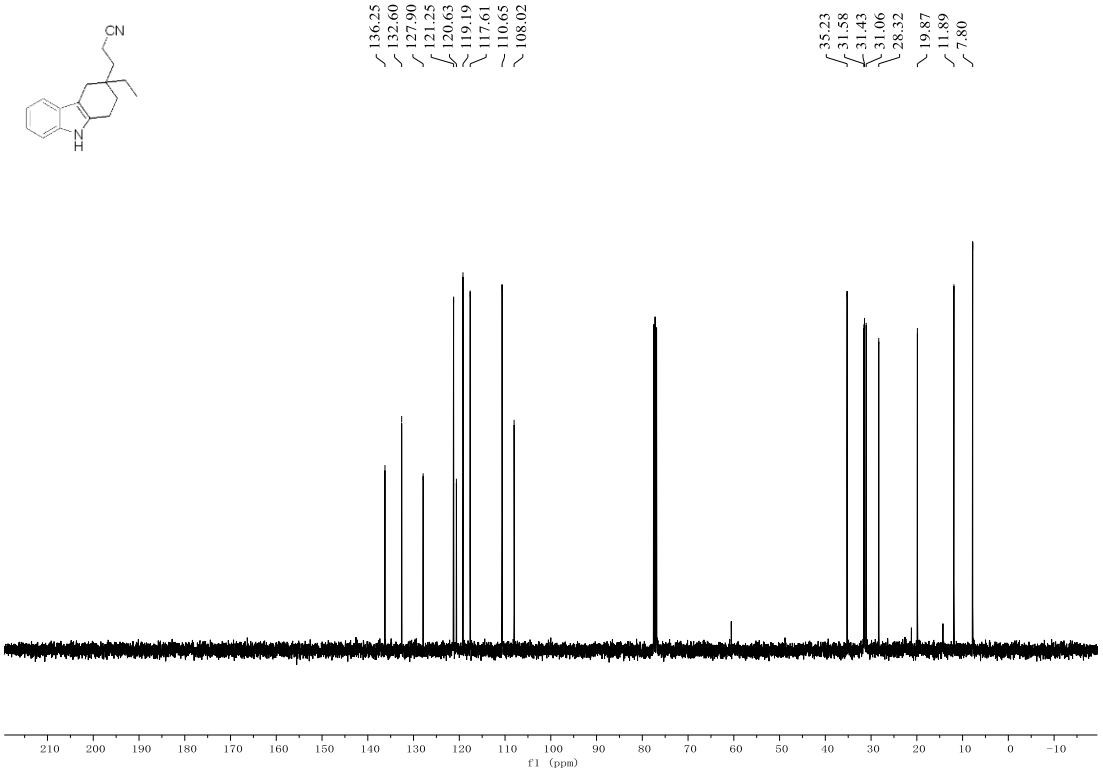
7.22
7.13
7.11
7.09
7.09
7.08
7.07
7.06
7.05
2.67
2.64
2.61
2.58
2.50
2.47
2.46
2.42
2.38
2.36
2.24
1.82
1.80
1.79
1.78
1.76
1.75
1.74
1.73
1.71
1.70
1.69
1.68
1.67
1.67
1.65
1.64
1.62
1.60
1.47
1.45
1.43
1.42
1.40
1.38
1.36
1.34
1.32
1.31
1.29
0.89
0.87
0.85
-0.00
0.95
1.00
1.00
2.00
2.00
2.00
2.00
4.23
2.17
3.02
f1 (ppm)


CN
N
H
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132.60
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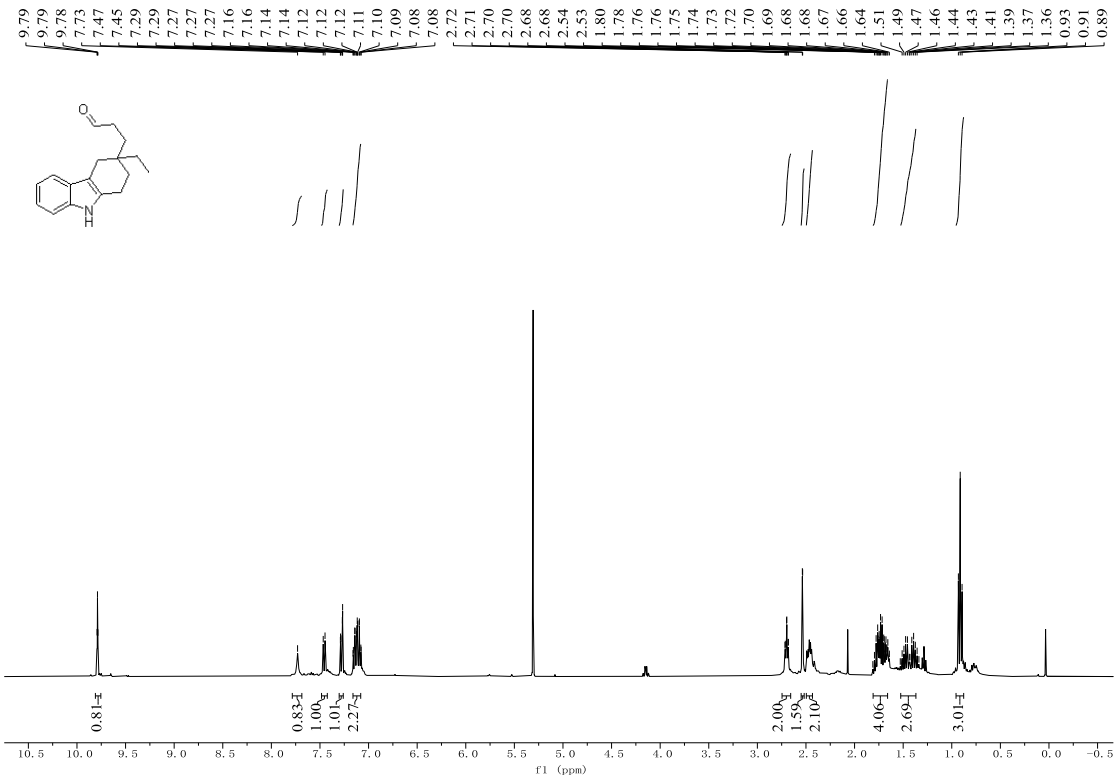
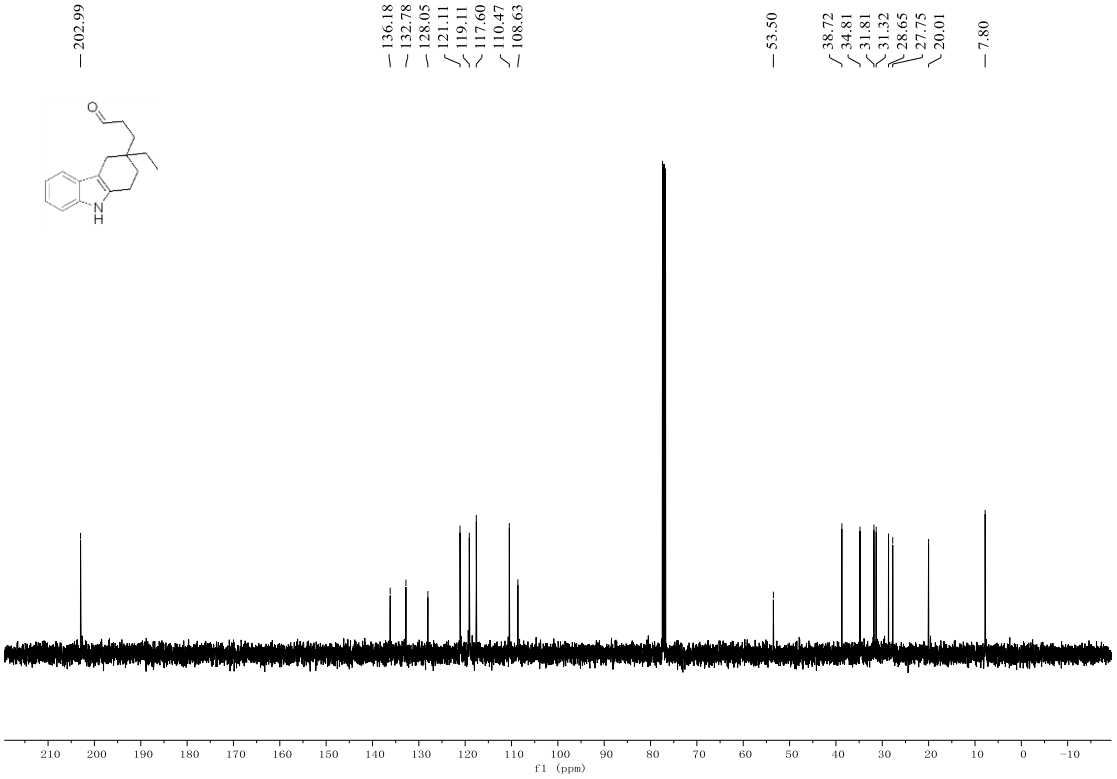
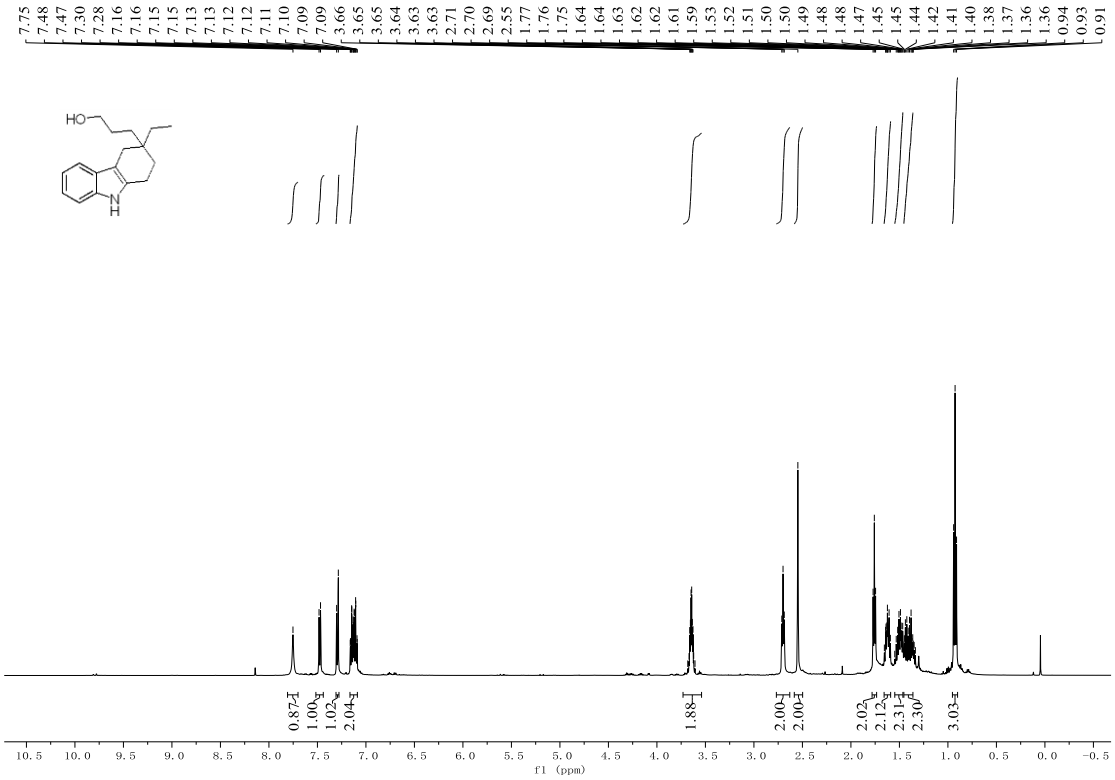
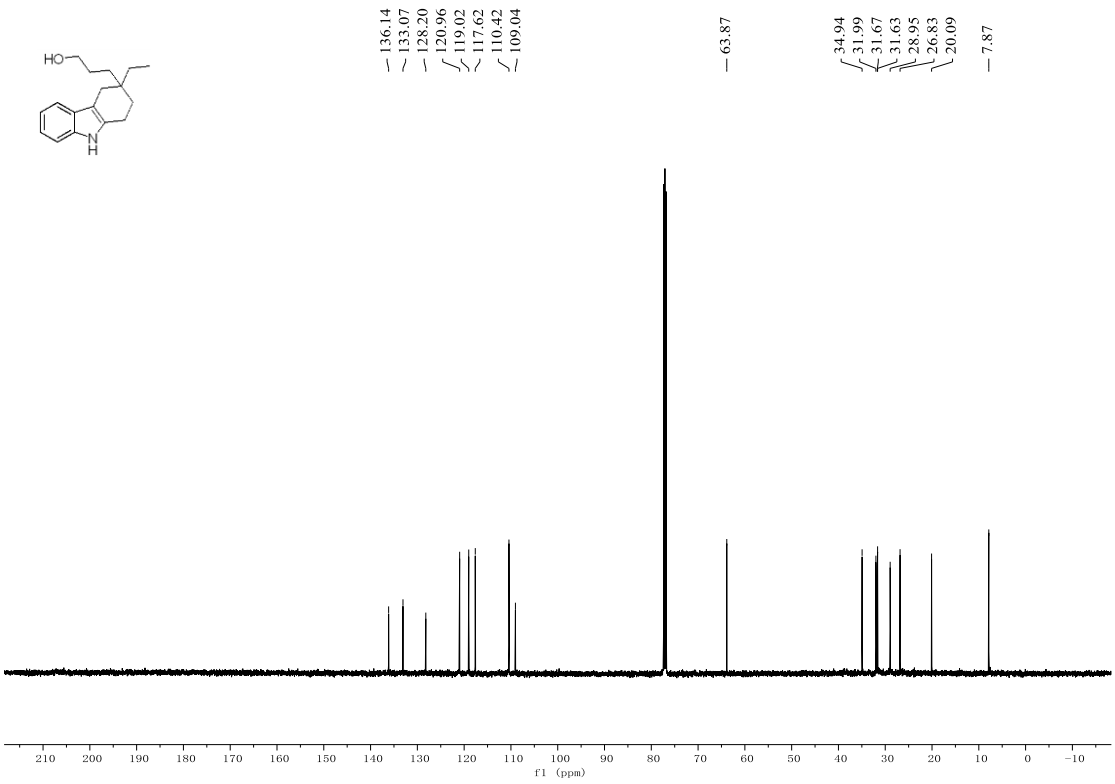
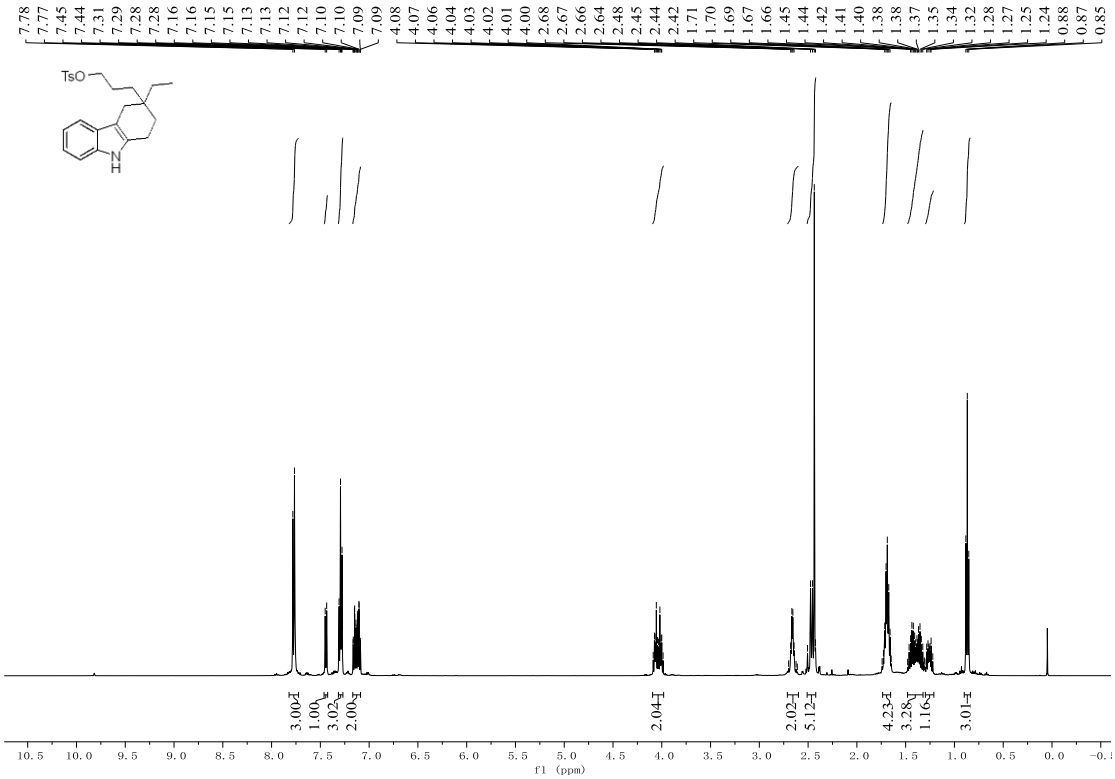
121.25
120.63
119.19
117.61
110.65
108.02
35.23
31.58
31.43
31.06
28.32
19.87
11.89
7.80
f1 (ppm)

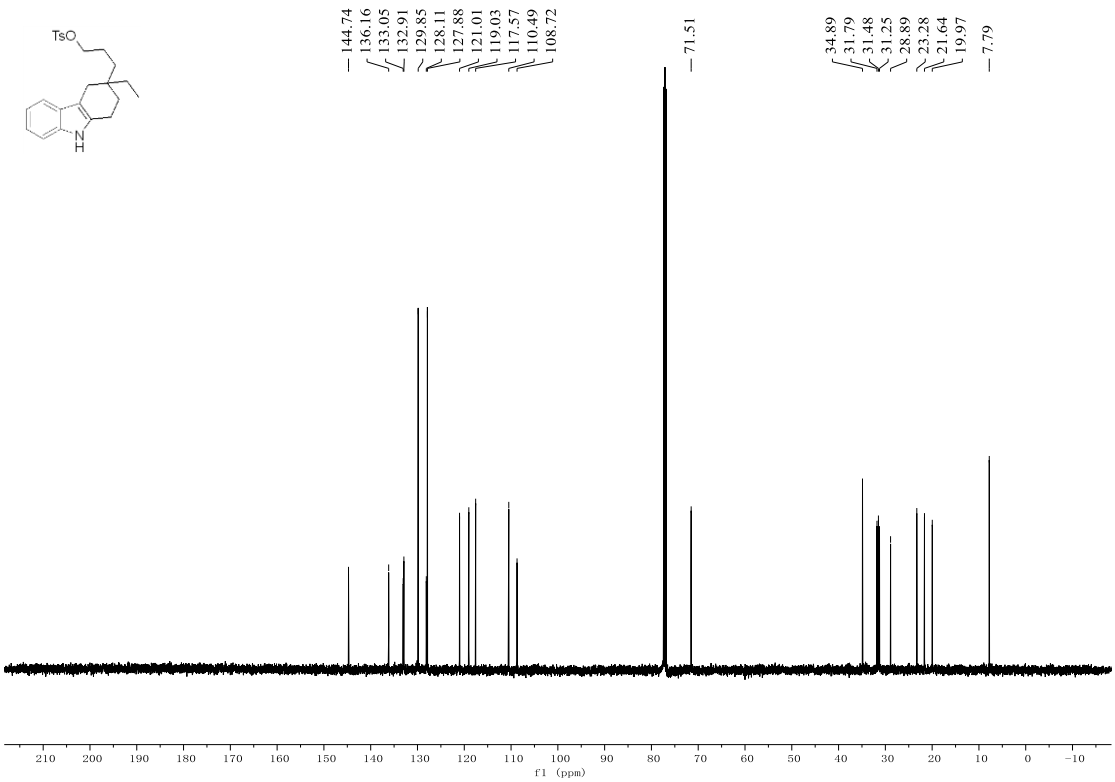

9.79
9.79
9.78
7.73
7.47
7.45
7.29
7.29
7.27
7.27
7.27
7.16
7.16
7.14
7.14
7.12
7.12
7.12
7.11
7.10
7.09
7.08
7.08
2.72
2.71
2.70
2.70
2.68
2.68
2.54
2.53
1.80
1.78
1.76
1.76
1.75
1.74
1.73
1.72
1.70
1.69
1.68
1.68
1.67
1.66
1.64
1.51
1.49
1.47
1.46
1.44
1.43
1.41
1.39
1.37
1.36
0.93
0.91
0.89
O
N
H
0.81
0.83
1.00
1.01
2.27
2.00
1.59
2.10
4.06
2.69
3.01
f1 (ppm)

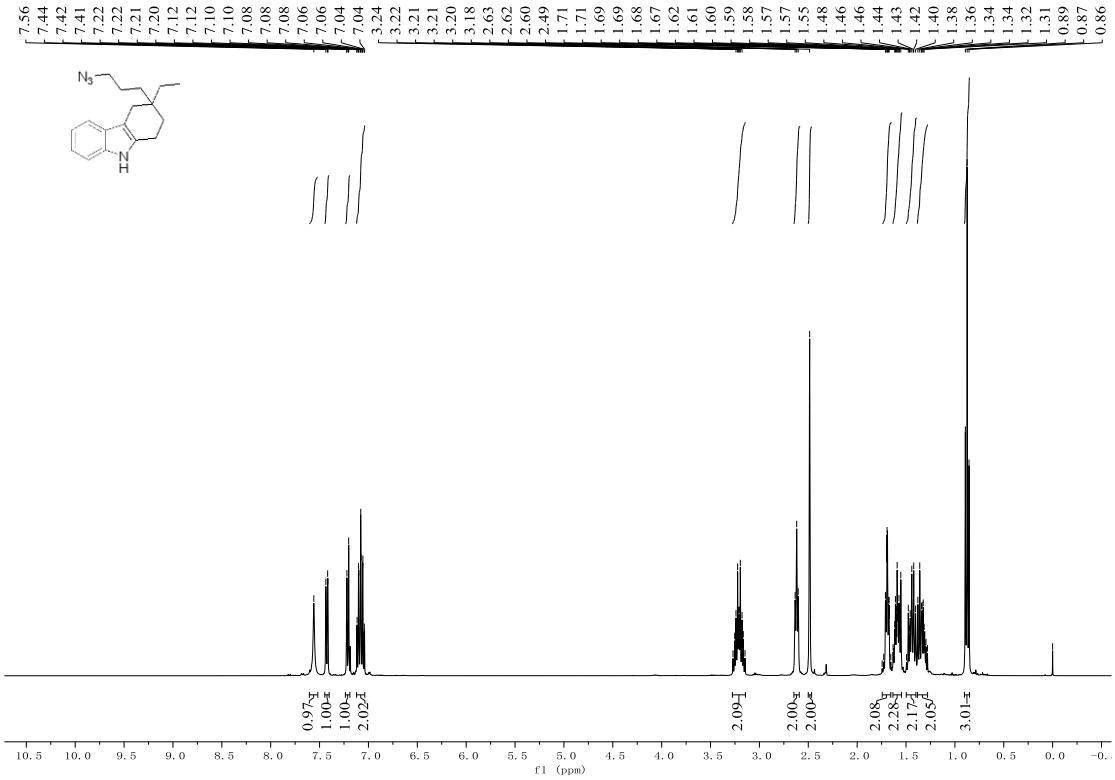

202.99
136.18
132.78
128.05
121.11
119.11
117.60
110.47
108.63
53.50
38.72
34.81
31.81
31.32
28.65
27.75
20.01
7.80
O
N
H
f1 (ppm)

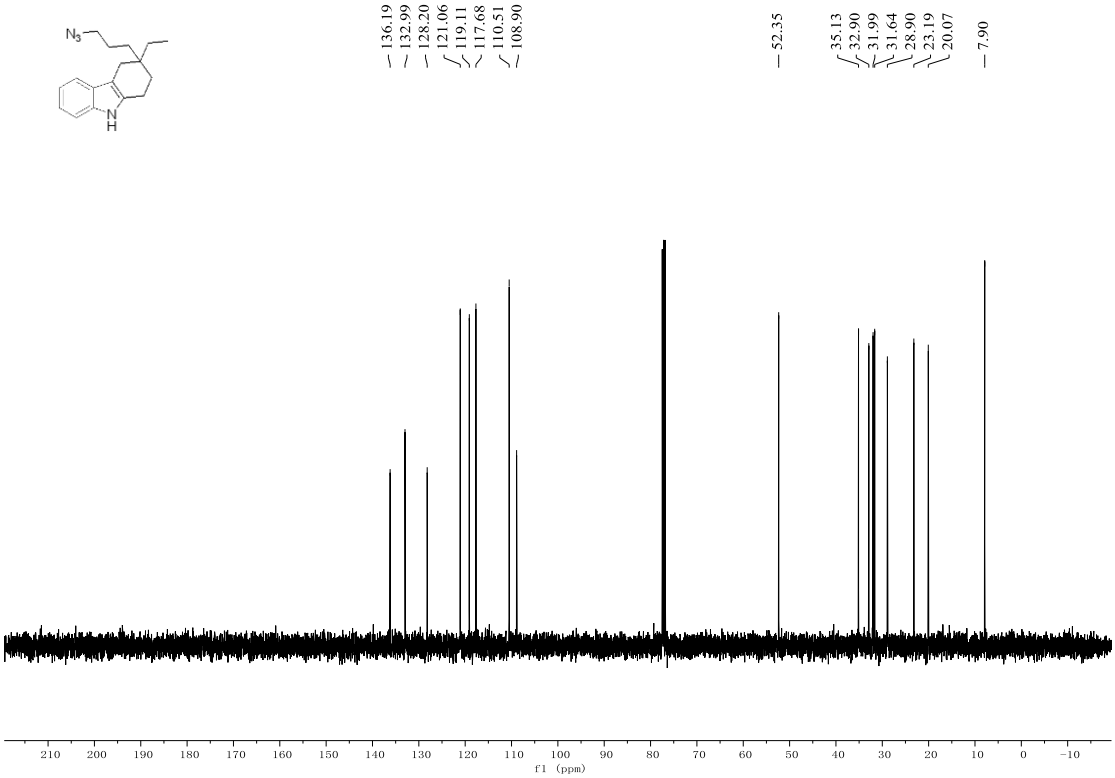

7.75 7.48 7.47 7.30 7.28 7.16 7.16 7.15 7.15 7.13 7.13 7.12 7.12 7.11 7.10 7.09 7.09 3.66 3.65 3.65 3.64 3.63 3.63 2.71 2.70 2.69 2.55 1.77 1.76 1.75 1.64 1.64 1.63 1.62 1.62 1.61 1.59 1.53 1.52 1.51 1.50 1.50 1.49 1.48 1.48 1.47 1.45 1.45 1.44 1.42 1.41 1.40 1.38 1.37 1.36 1.36 0.94 0.93 0.91
HO
N
H
0.87 1.00 1.02 2.04 1.88 2.00 2.00 2.02 2.12 2.31 2.30 3.03
f1 (ppm)

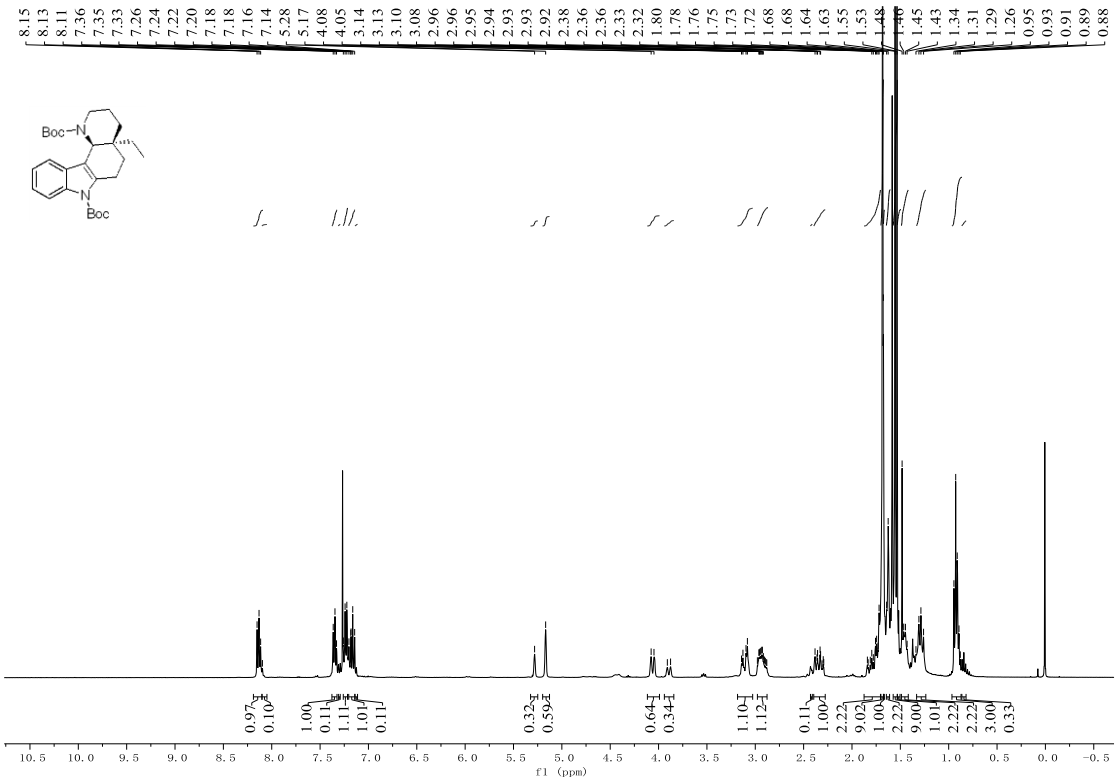

136.14 133.07 128.20 120.96 119.02 117.62 110.42 109.04 63.87 34.94 31.99 31.67 31.63 28.95 26.83 20.09 7.87
HO
N
H
f1 (ppm)


7.78 7.77 7.45 7.44 7.31 7.29 7.28 7.28 7.16 7.16 7.15 7.15 7.13 7.12 7.12 7.10 7.10 7.09 7.09
4.08 4.07 4.06 4.04 4.03 4.02 4.01 4.00 2.68 2.67 2.66 2.64 2.48 2.45 2.44 2.42 1.71 1.70 1.69 1.67 1.66 1.45 1.44 1.42 1.41 1.40 1.38 1.38 1.37 1.35 1.34 1.32 1.28 1.27 1.25 1.24 0.88 0.87 0.85
TsO
NH
3.00 1.00 3.02 2.00 2.04 2.02 5.12 4.23 3.28 1.16 3.01
f1 (ppm)


144.74 136.16 133.05 132.91 129.85 128.11 127.88 121.01 119.03 117.57 110.49 108.72
71.51
34.89 31.79 31.48 31.25 28.89 23.28 21.64 19.97
7.79
TsO
NH
f1 (ppm)


7.56 7.44 7.42 7.41 7.22 7.22 7.21 7.20 7.12 7.12 7.10 7.10 7.08 7.08 7.08 7.06 7.06 7.04 7.04
3.24 3.22 3.21 3.21 3.20 3.18 2.63 2.62 2.60 2.49 1.71 1.71 1.69 1.69 1.68 1.67 1.62 1.61 1.60 1.59 1.58 1.57 1.57 1.55 1.48 1.46 1.46 1.44 1.43 1.42 1.40 1.38 1.36 1.34 1.34 1.32 1.31 0.89 0.87 0.86
N3
N
H
0.97 1.00 1.00 2.02 2.09 2.00 2.00 2.08 2.28 2.17 2.05 3.01
f1 (ppm)


136.19 132.99 128.20 121.06 119.11 117.68 110.51 108.90
52.35
35.13 32.90 31.99 31.64 28.90 23.19 20.07
7.90
N3
N
H
f1 (ppm)


8.15
8.13
8.11
7.36
7.35
7.33
7.26
7.24
7.22
7.20
7.18
7.18
7.16
7.14
5.28
5.17
4.08
4.05
3.14
3.13
3.10
3.08
2.96
2.96
2.95
2.94
2.93
2.93
2.92
2.38
2.36
2.36
2.33
2.32
1.80
1.78
1.76
1.75
1.73
1.72
1.68
1.68
1.64
1.63
1.55
1.53
1.48
1.45
1.43
1.34
1.31
1.29
1.26
0.95
0.93
0.91
0.89
0.88
Boc
N
Boc
0.97
0.10
1.00
0.11
1.11
1.01
0.11
0.32
0.59
0.64
0.34
1.10
1.12
0.11
1.00
2.22
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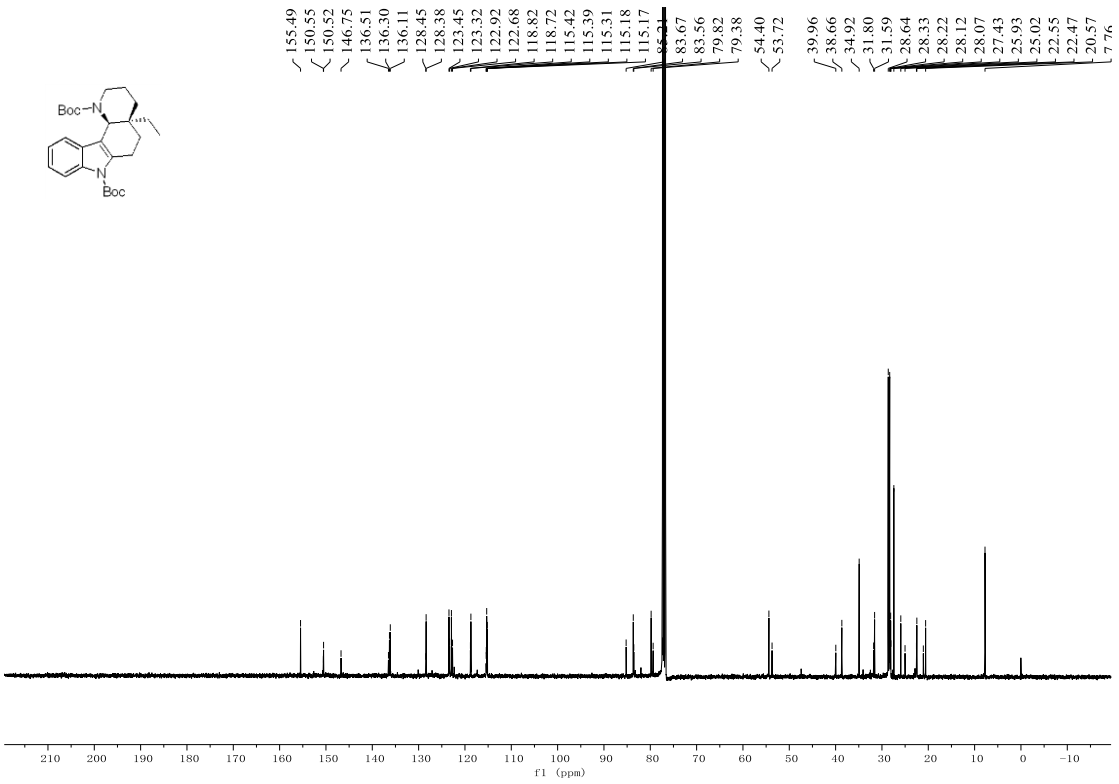
1.00
2.22
9.00
1.01
2.22
2.22
3.00
0.33
f1 (ppm)


155.49
150.55
150.52
146.75
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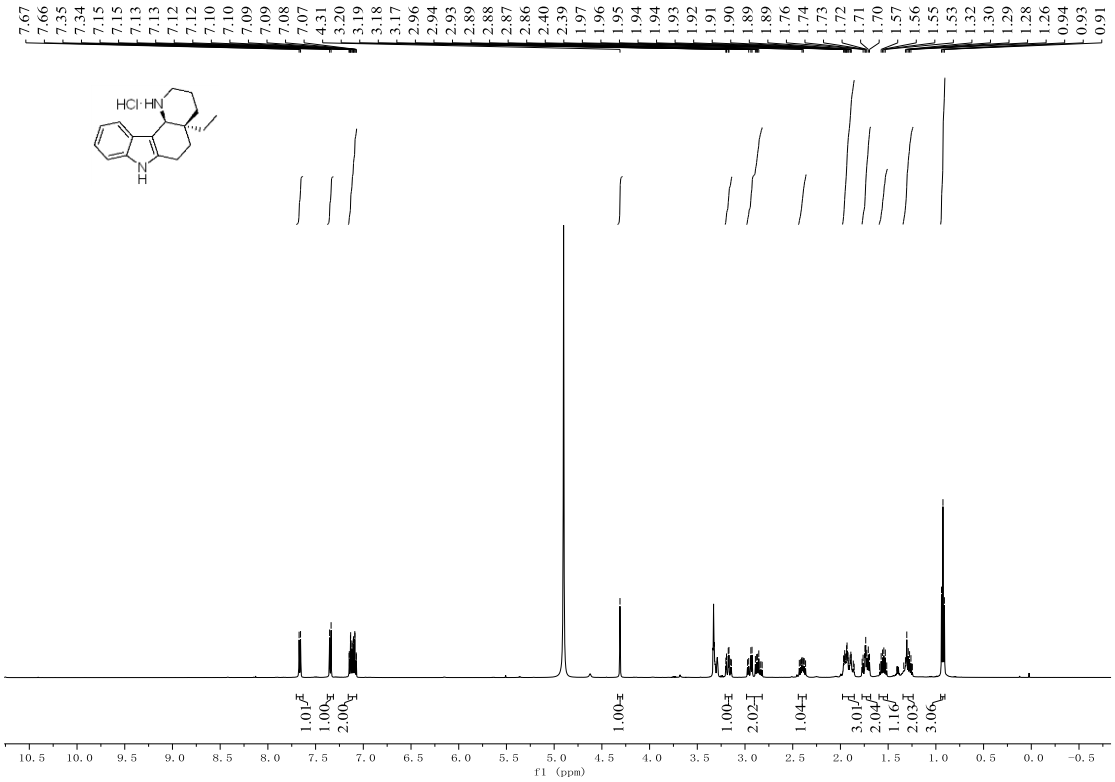
136.30
136.11
128.45
128.38
123.45
123.32
122.92
122.68
118.82
118.72
115.42
115.39
115.31
115.18
115.17
83.67
83.56
79.82
79.38
54.40
53.72
39.96
38.66
34.92
31.80
31.59
28.64
28.33
28.22
28.12
28.07
27.43
25.93
25.02
22.55
22.47
20.57
Boc
N
Boc
f1 (ppm)


7.67
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7.34
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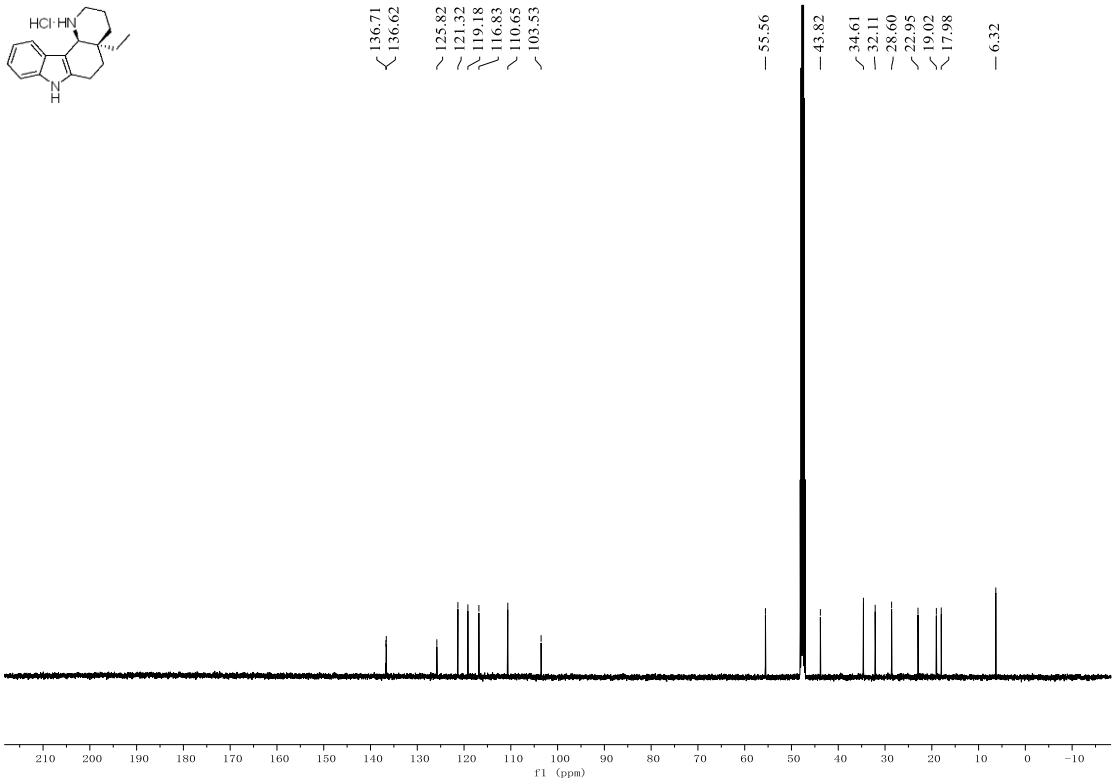
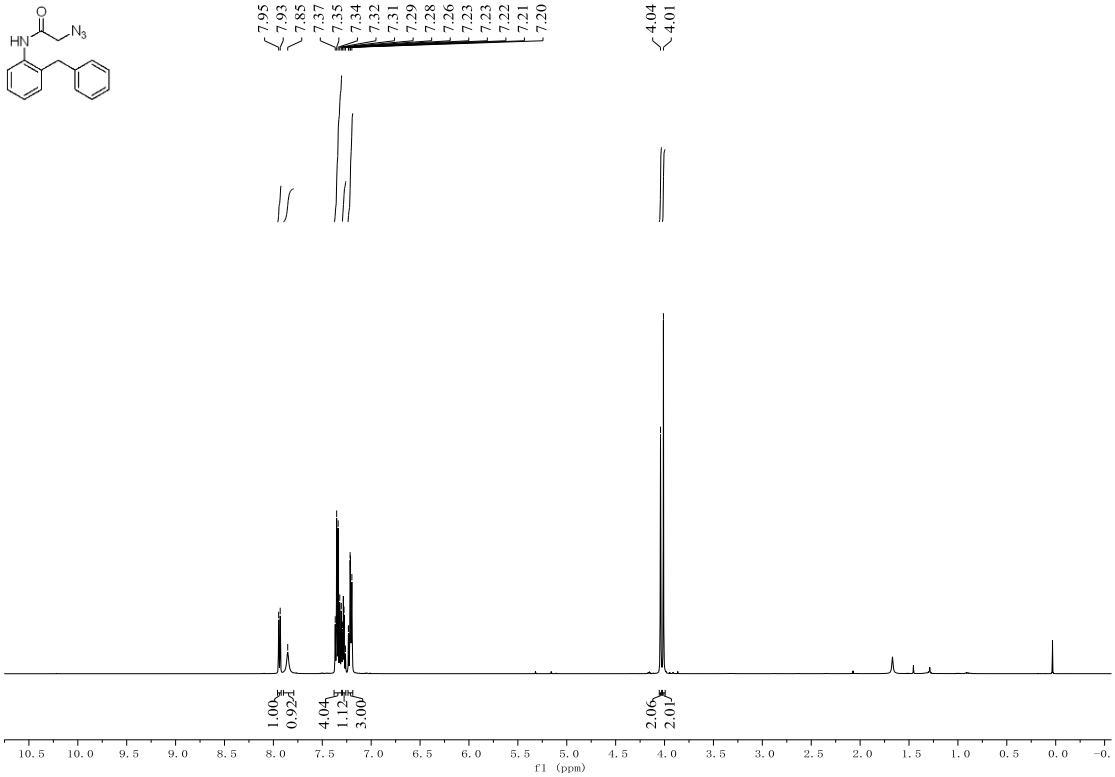
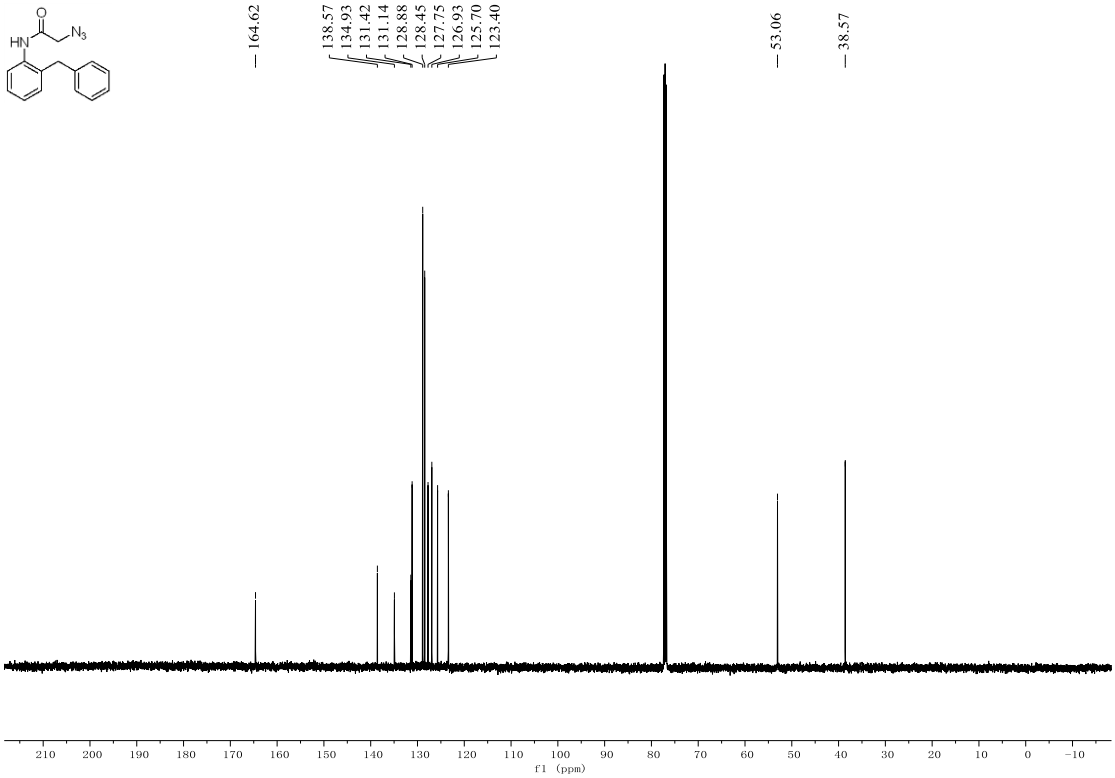
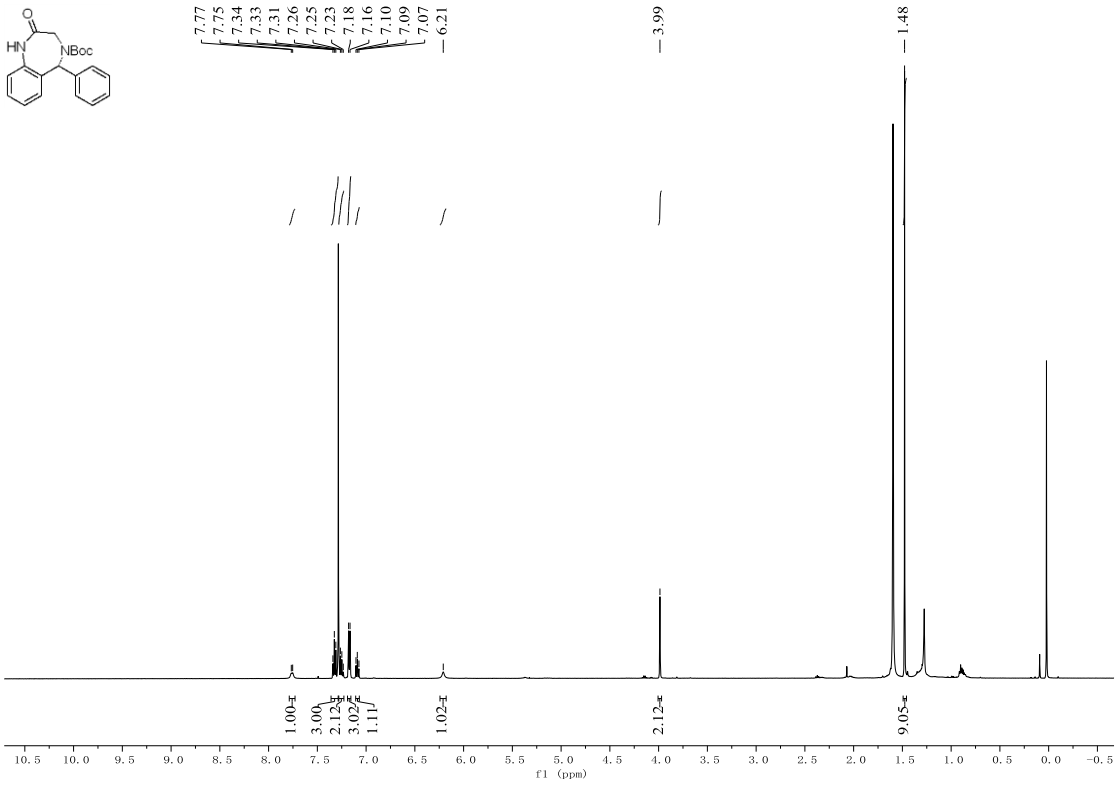
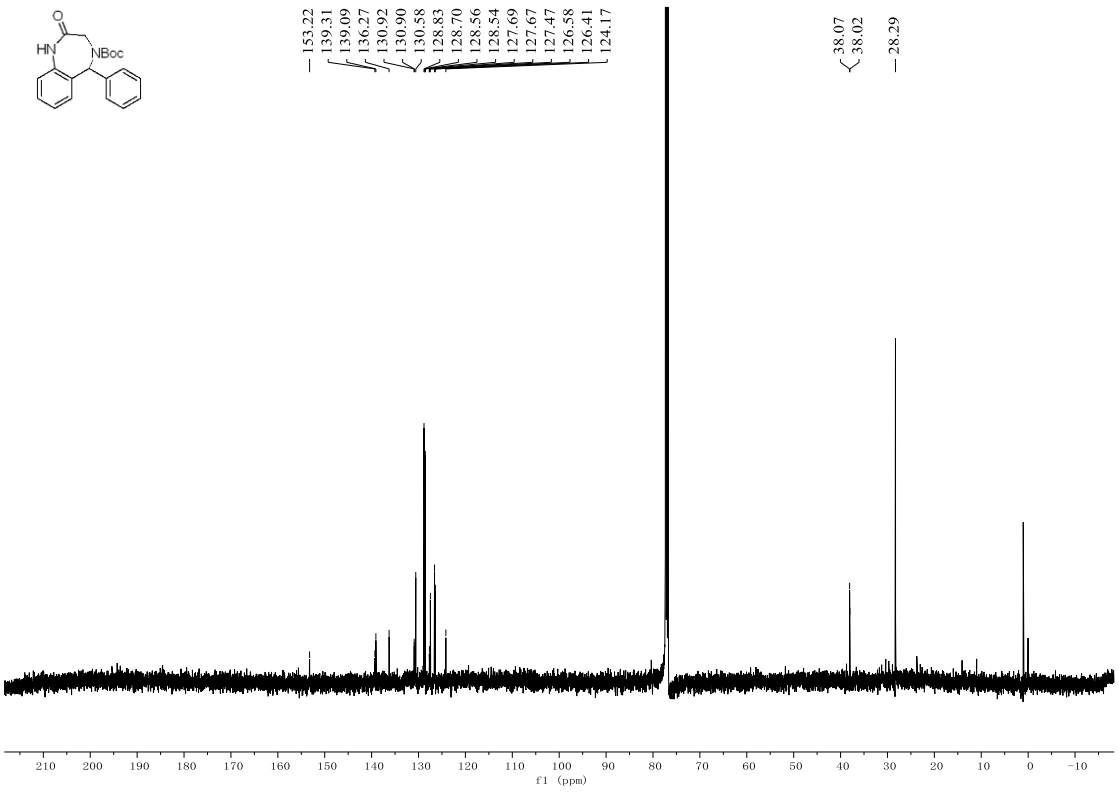
7.15
7.13
7.13
7.12
7.12
7.10
7.10
7.09
7.09
7.08
7.07
4.31
3.20
3.19
3.18
3.17
2.96
2.94
2.93
2.89
2.88
2.87
2.86
2.40
2.39
1.97
1.96
1.95
1.94
1.94
1.93
1.92
1.91
1.90
1.89
1.89
1.76
1.74
1.73
1.72
1.71
1.70
1.57
1.56
1.55
1.53
1.32
1.30
1.29
1.28
1.26
0.94
0.93
0.91
HCl·HN
1.01
1.00
2.00
1.00
1.00
2.02
1.04
3.01
2.04
1.16
2.03
3.06
f1 (ppm)

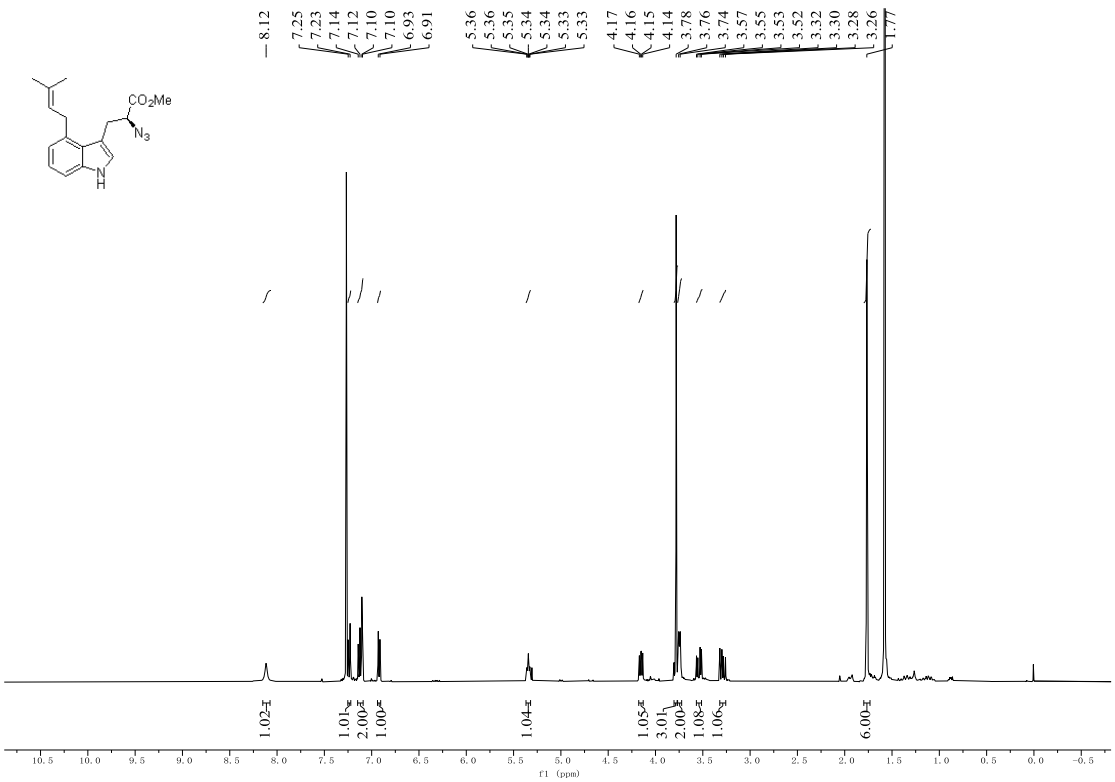

HCl·HN
136.71
136.62
125.82
121.32
119.18
116.83
110.65
103.53
55.56
43.82
34.61
32.11
28.60
22.95
19.02
17.98
6.32
f1 (ppm)

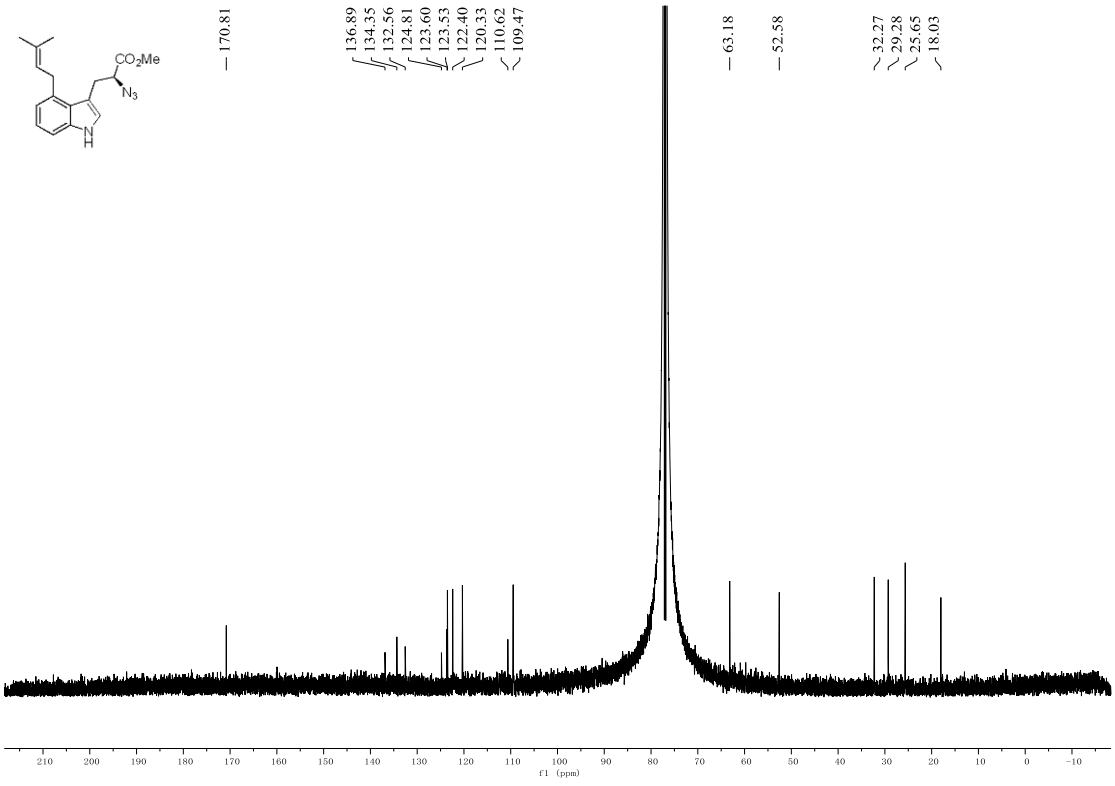

7.95
7.93
7.85
7.37
7.35
7.34
7.32
7.31
7.29
7.28
7.26
7.23
7.23
7.22
7.21
7.20
4.04
4.01
1.00
0.92
4.04
1.12
3.00
2.06
2.01
f1 (ppm)


164.62
138.57
134.93
131.42
131.14
128.88
128.45
127.75
126.93
125.70
123.40
53.06
38.57
f1 (ppm)


7.77
7.75
7.34
7.33
7.31
7.26
7.25
7.23
7.18
7.16
7.10
7.09
7.07
6.21
3.99
1.48
1.00
3.00
2.12
3.02
1.11
1.02
2.12
9.05
f1 (ppm)


153.22
139.31
139.09
136.27
130.92
130.90
130.58
128.83
128.70
128.56
128.54
127.69
127.67
127.47
126.58
126.41
124.17
38.07
38.02
28.29
f1 (ppm)


8.12
7.25
7.23
7.14
7.12
7.10
7.10
6.93
6.91
5.36
5.36
5.35
5.34
5.34
5.33
5.33
4.17
4.16
4.15
4.14
3.78
3.76
3.74
3.57
3.55
3.53
3.52
3.32
3.30
3.28
3.26
1.77
CO2Me
N3
H
1.02
1.01
2.00
1.00
1.04
1.05
3.01
2.00
1.08
1.06
6.00
f1 (ppm)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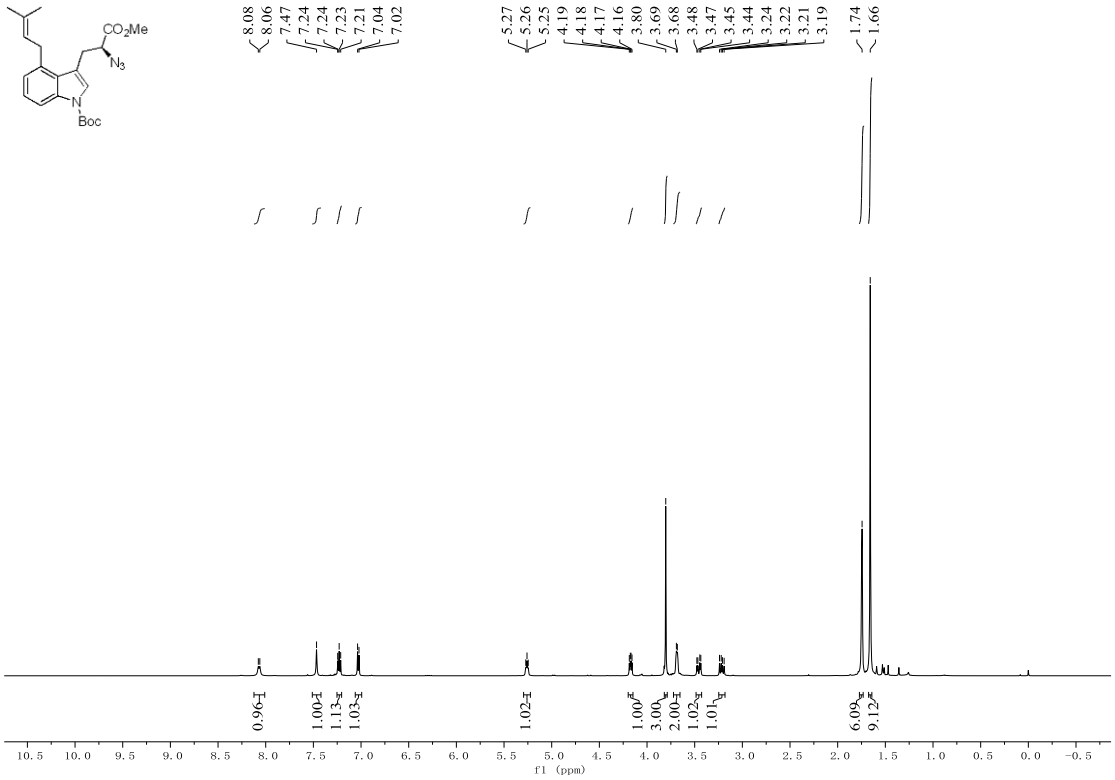
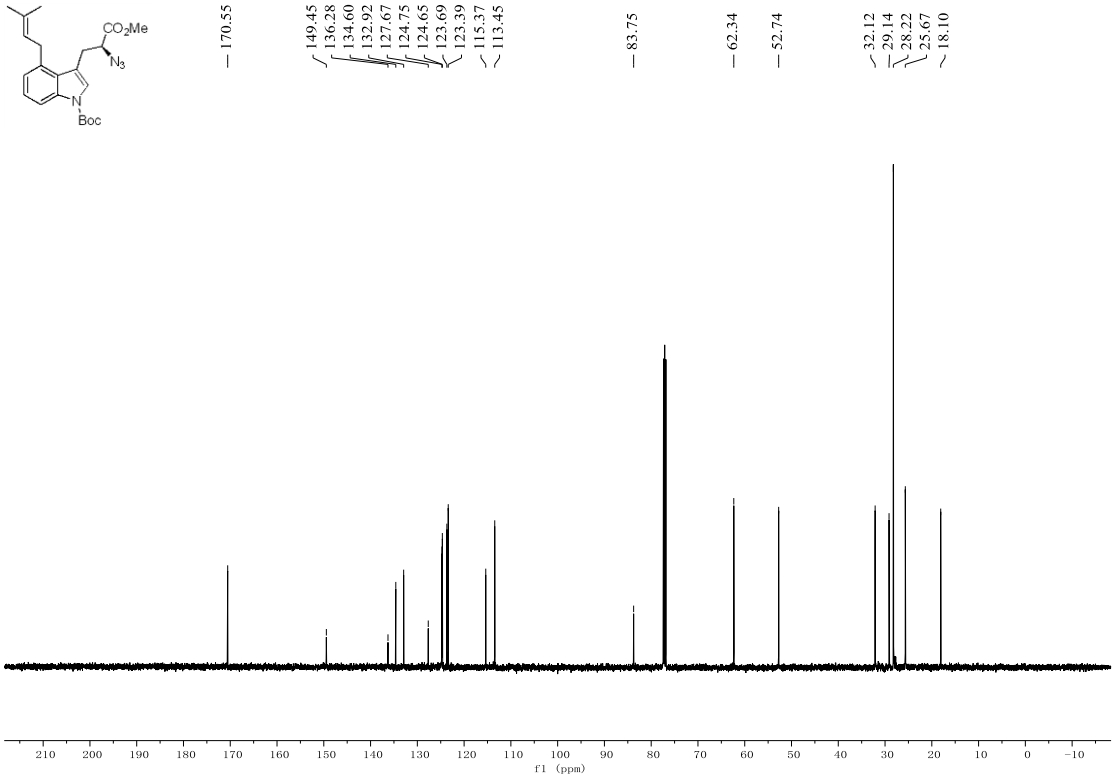
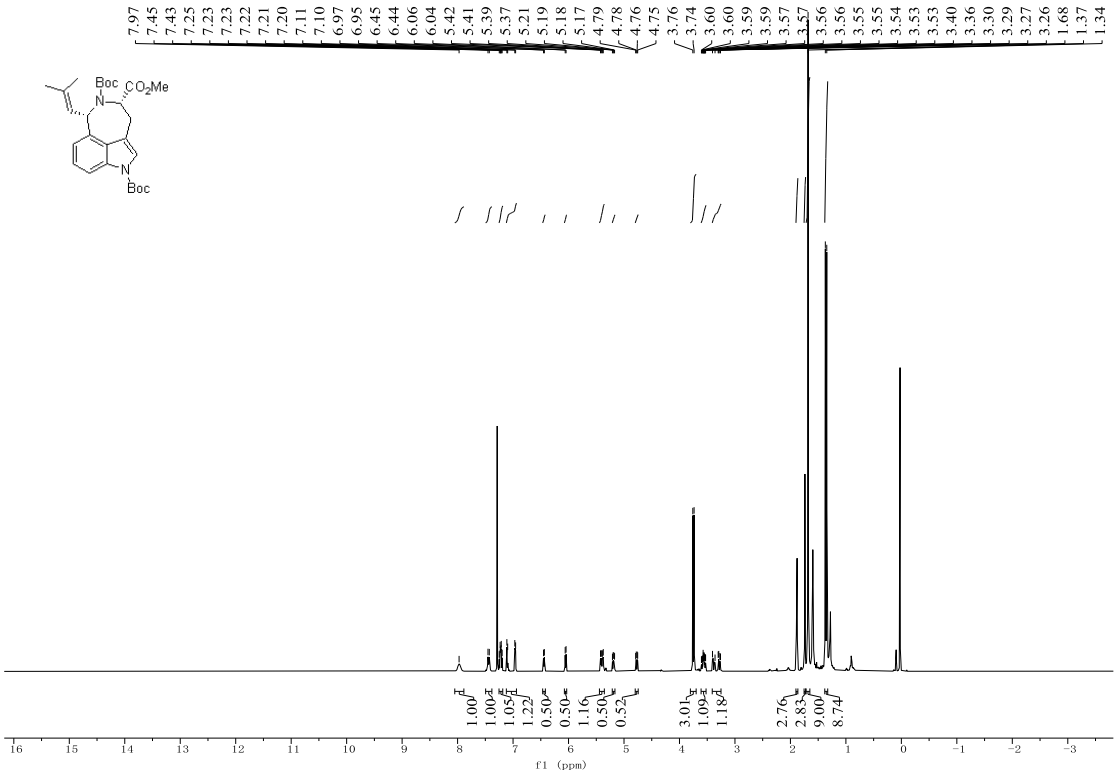
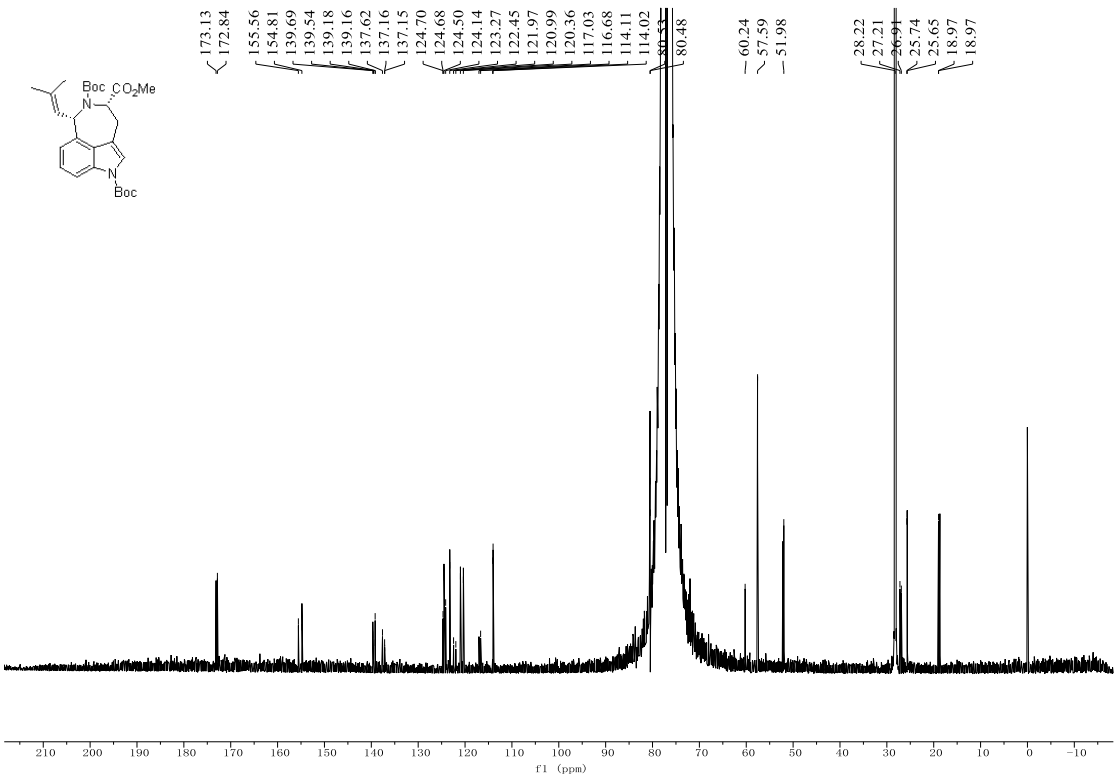
136.89
134.35
132.56
124.81
123.60
123.53
122.40
120.33
110.62
109.47
63.18
52.58
32.27
29.28
25.65
18.03
CO2Me
N3
H
f1 (ppm)


CO2Me
N3
N
Boc
8.08
8.06
7.47
7.24
7.24
7.23
7.21
7.04
7.02
5.27
5.26
5.25
4.19
4.18
4.17
4.16
3.80
3.69
3.68
3.48
3.47
3.45
3.44
3.24
3.22
3.21
3.19
1.74
1.66
0.96
1.00
1.13
1.03
1.02
1.00
3.00
2.00
1.02
1.01
6.09
9.12
f1 (ppm)


CO2Me
N3
N
Boc
170.55
149.45
136.28
134.60
132.92
127.67
124.75
124.65
123.69
123.39
115.37
113.45
83.75
62.34
52.74
32.12
29.14
28.22
25.67
18.10
f1 (ppm)


7.97
7.45
7.43
7.25
7.23
7.23
7.22
7.21
7.20
7.11
7.10
6.97
6.95
6.45
6.44
6.06
6.04
5.42
5.41
5.39
5.37
5.21
5.19
5.18
5.17
4.79
4.78
4.76
4.75
3.76
3.74
3.60
3.60
3.59
3.59
3.57
3.57
3.56
3.56
3.55
3.55
3.54
3.53
3.53
3.40
3.36
3.30
3.29
3.27
3.26
1.68
1.37
1.34
Boc
CO2Me
N
N
Boc
1.00
1.00
1.05
1.22
0.50
0.50
1.16
0.50
0.52
3.01
1.09
1.18
2.76
2.83
9.00
8.74
f1 (ppm)


173.13
172.84
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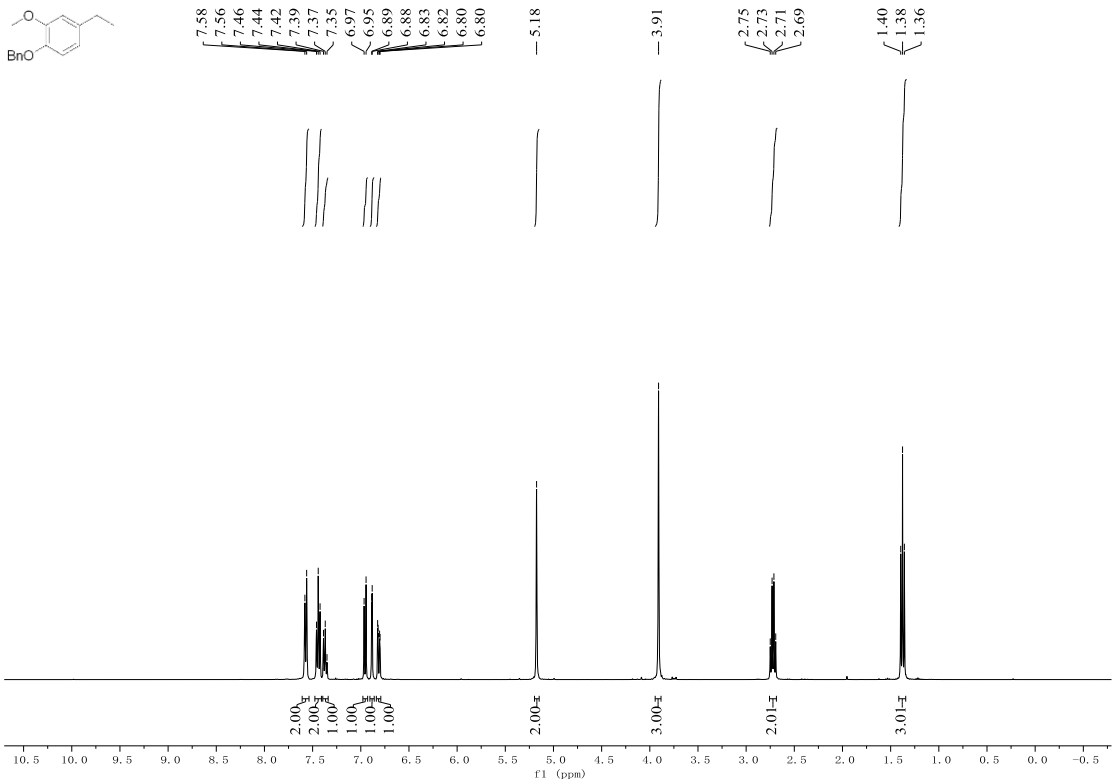
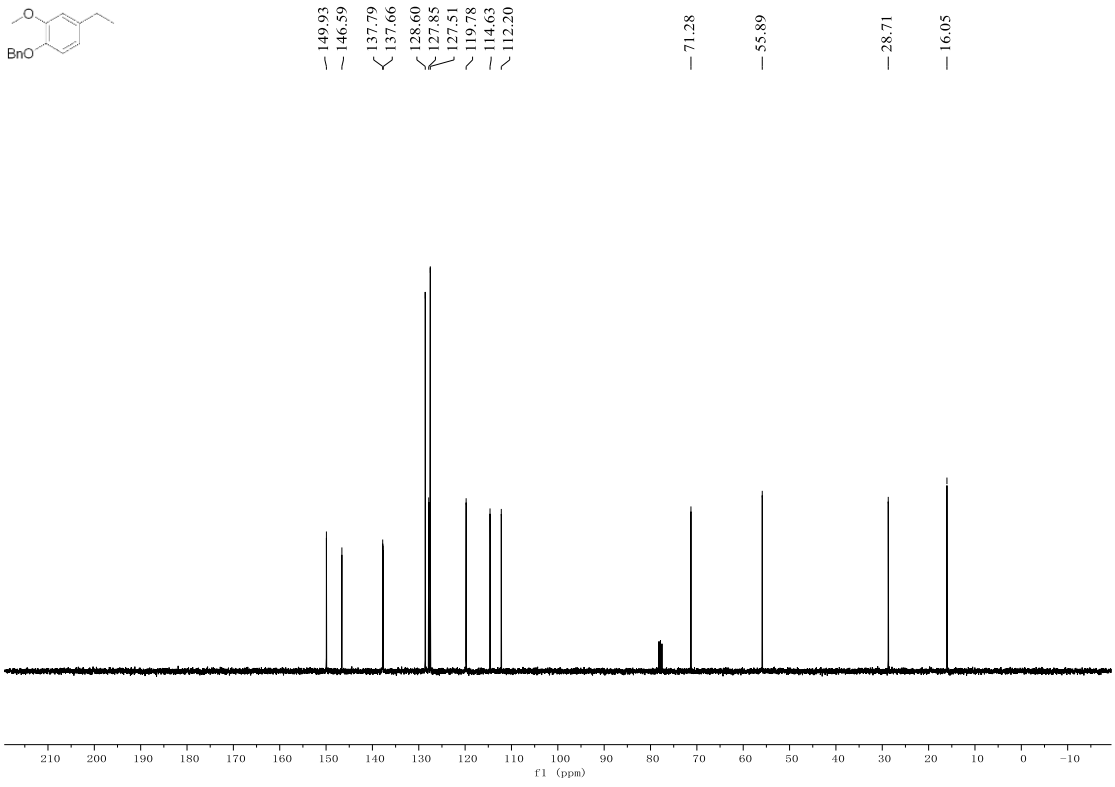
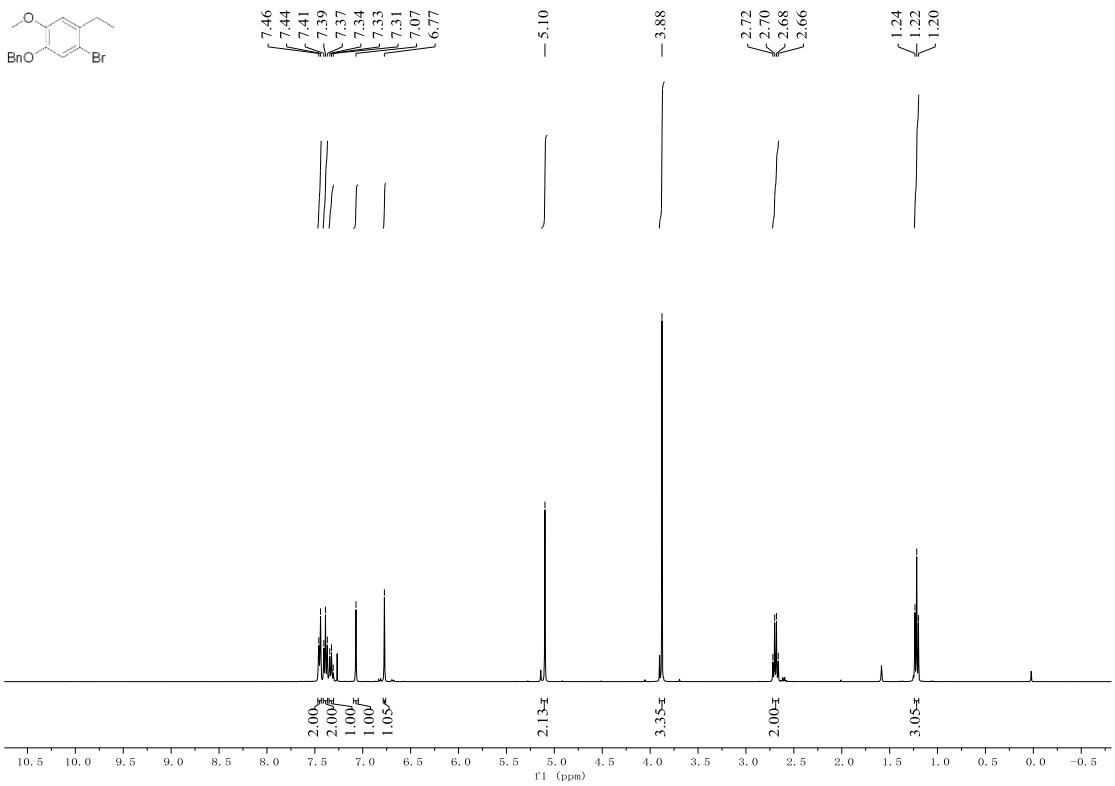
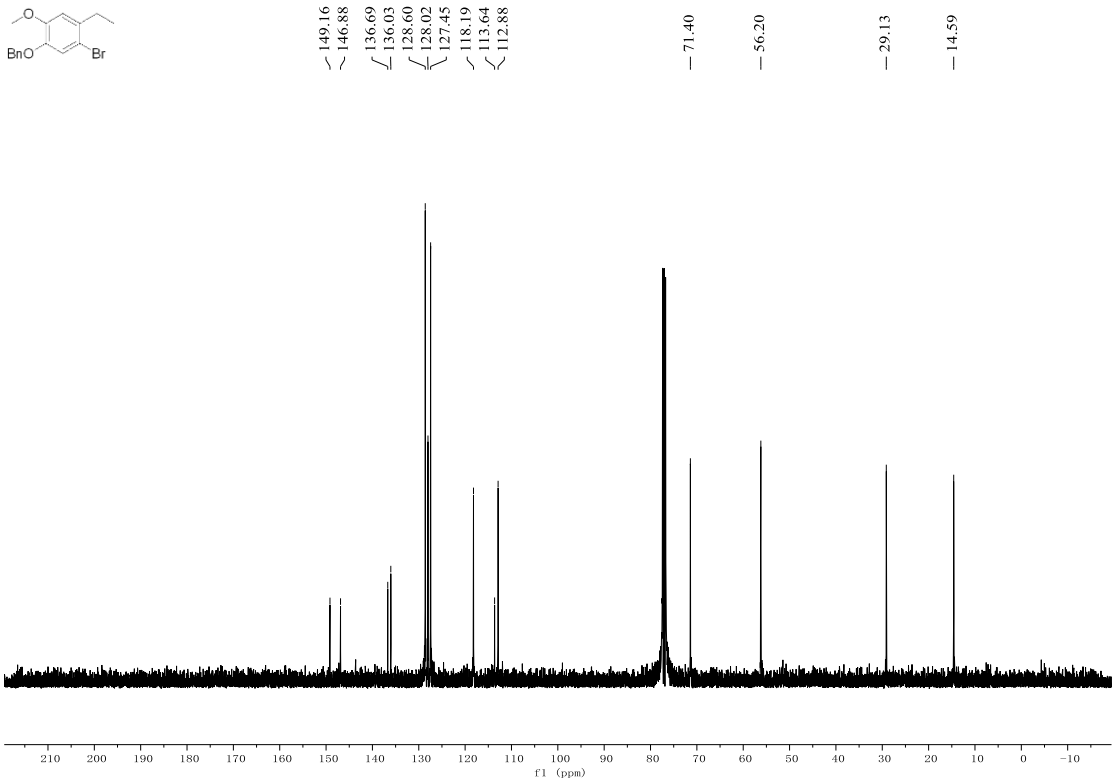
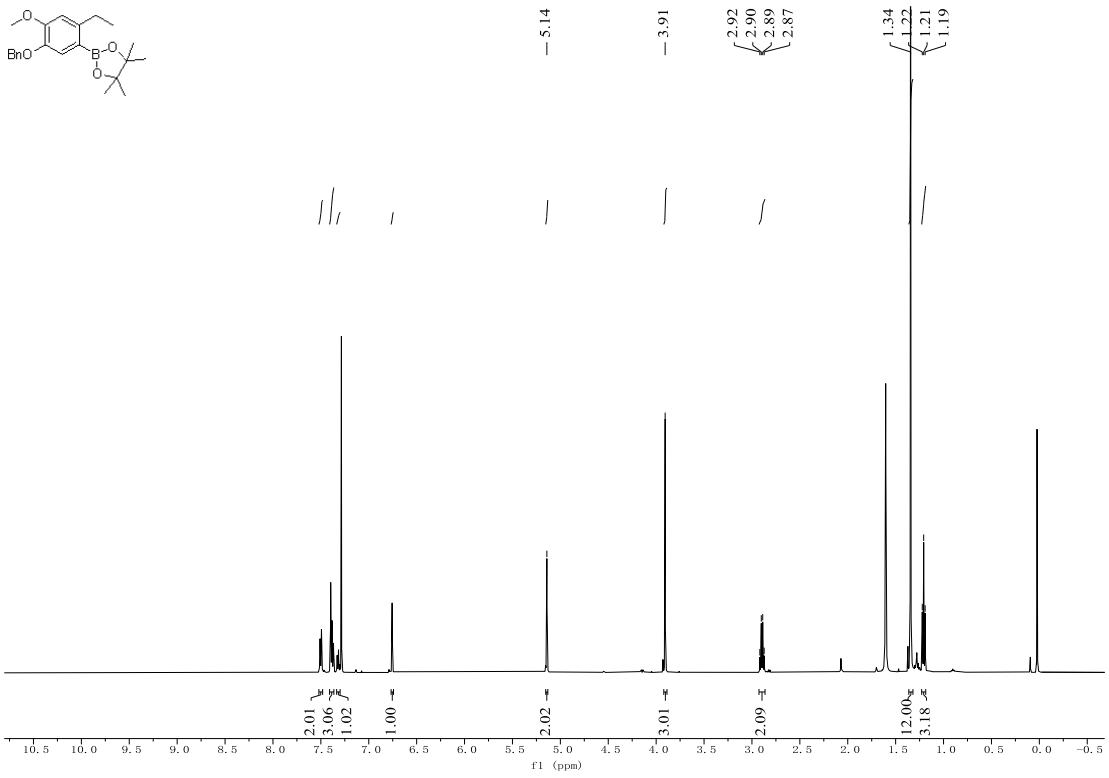
139.54
139.18
139.16
137.62
137.16
137.15
124.70
124.68
124.50
124.14
123.27
122.45
121.97
120.99
120.36
117.03
116.68
114.11
114.02
80.48
60.24
57.59
51.98
28.22
27.21
26.91
25.74
25.65
18.97
18.97
Boc
CO2Me
N
N
Boc
f1 (ppm)

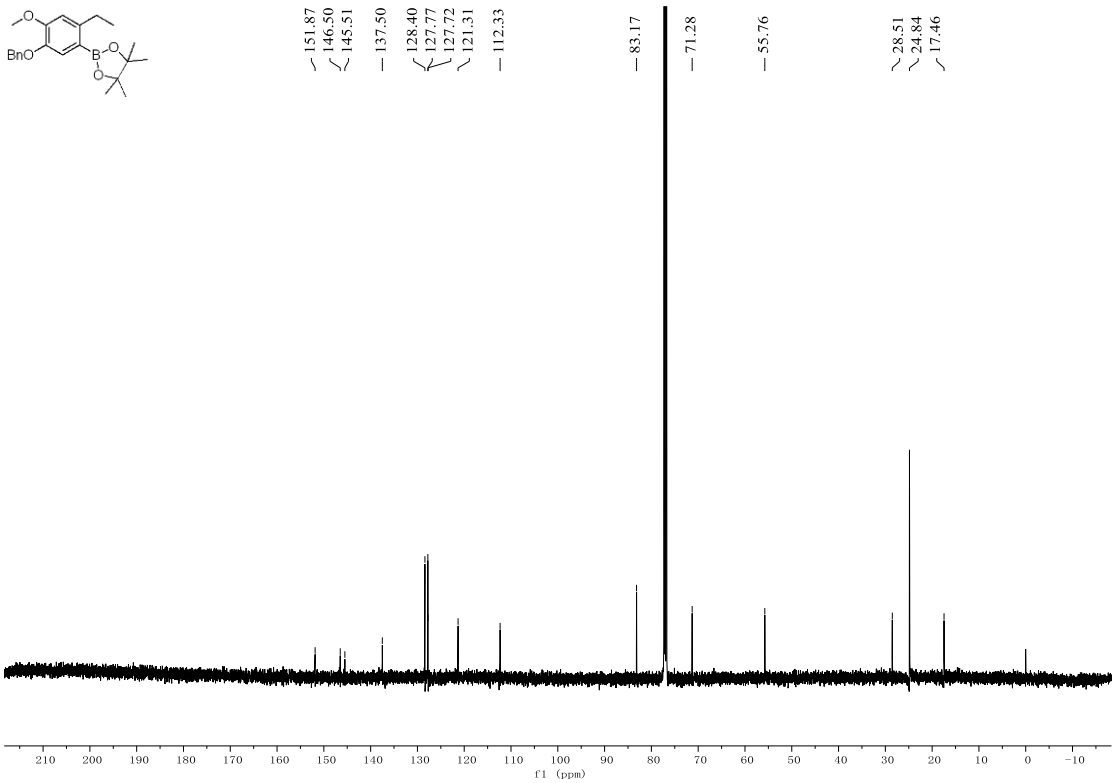

BnO
7.58
7.56
7.46
7.44
7.42
7.39
7.37
7.35
6.97
6.95
6.89
6.88
6.83
6.82
6.80
6.80
5.18
3.91
2.75
2.73
2.71
2.69
1.40
1.38
1.36
2.00
2.00
1.00
1.00
1.00
1.00
2.00
3.00
2.01
3.01
f1 (ppm)

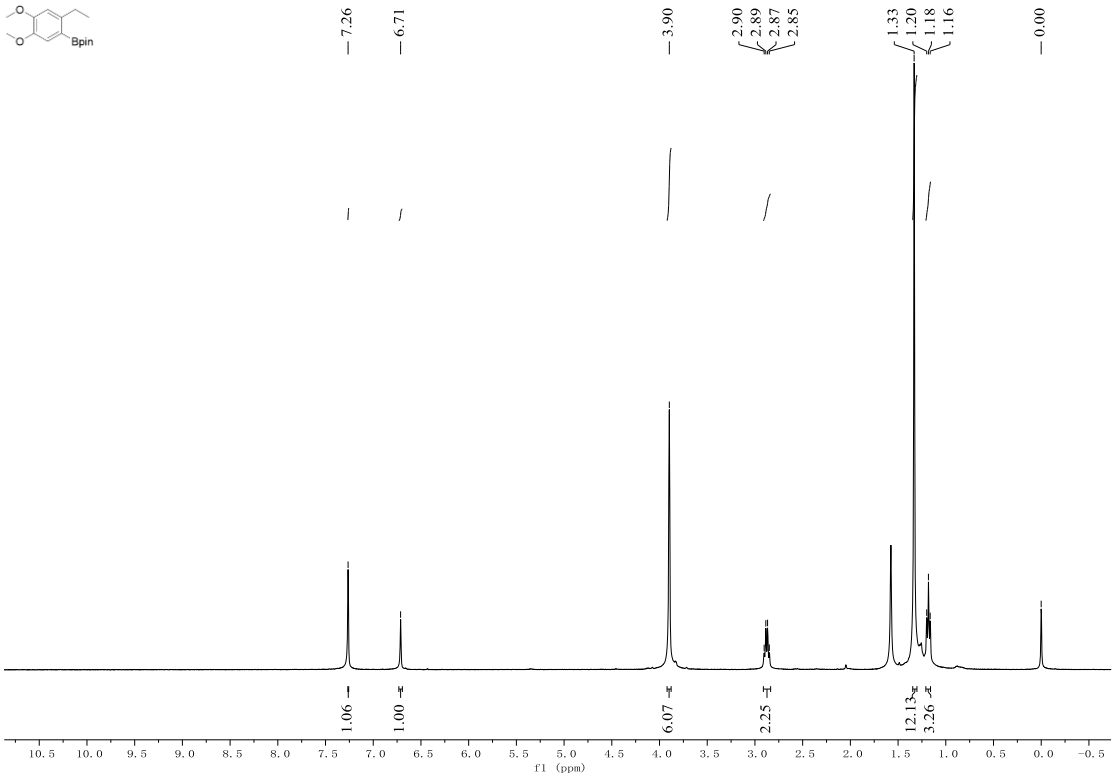

BnO
149.93
146.59
137.79
137.66
128.60
127.85
127.51
119.78
114.63
112.20
71.28
55.89
28.71
16.05
f1 (ppm)

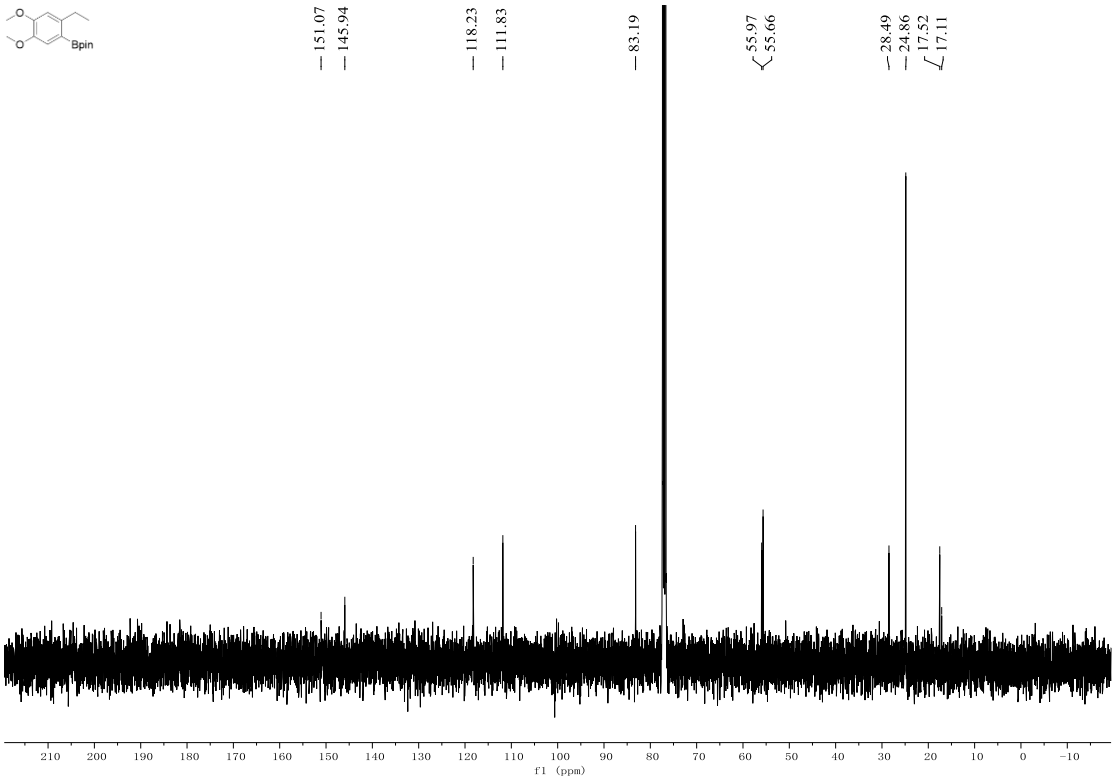

BnO
Br
7.46
7.44
7.41
7.39
7.37
7.34
7.33
7.31
7.07
6.77
5.10
3.88
2.72
2.70
2.68
2.66
1.24
1.22
1.20
2.00
2.00
1.00
1.00
1.05
2.13
3.35
2.00
3.05
f1 (ppm)

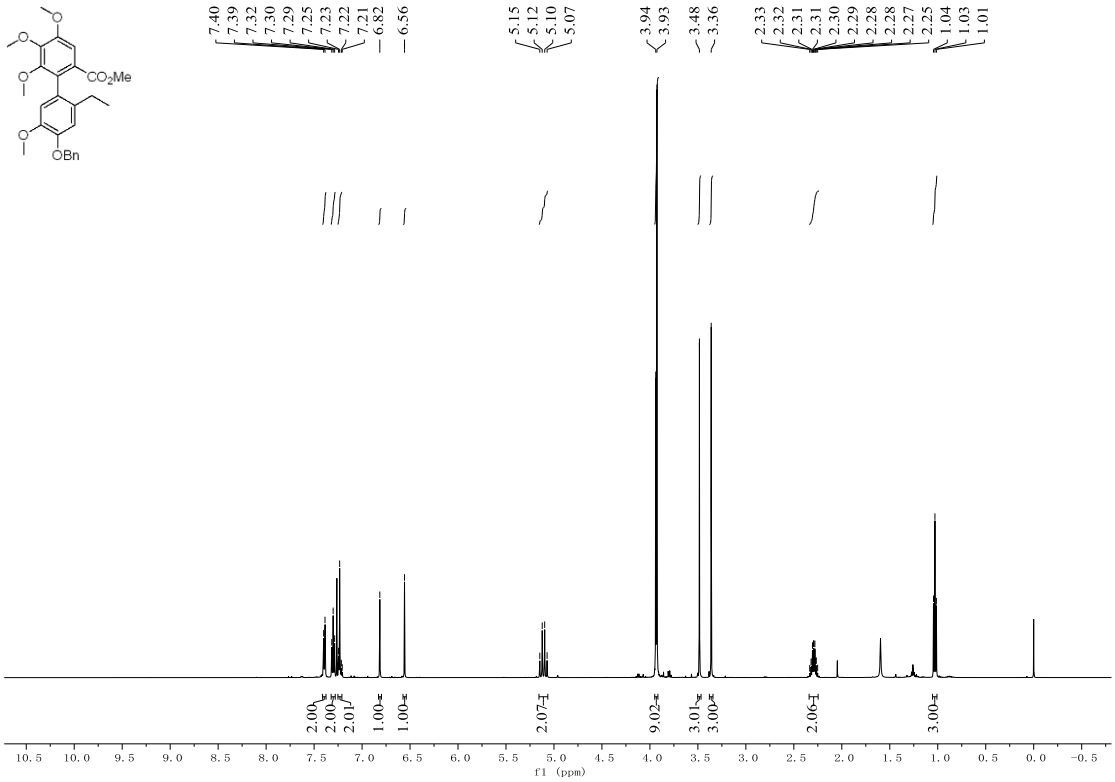

BnO
Br
149.16
146.88
136.69
136.03
128.60
128.02
127.45
118.19
113.64
112.88
71.40
56.20
29.13
14.59
f1 (ppm)

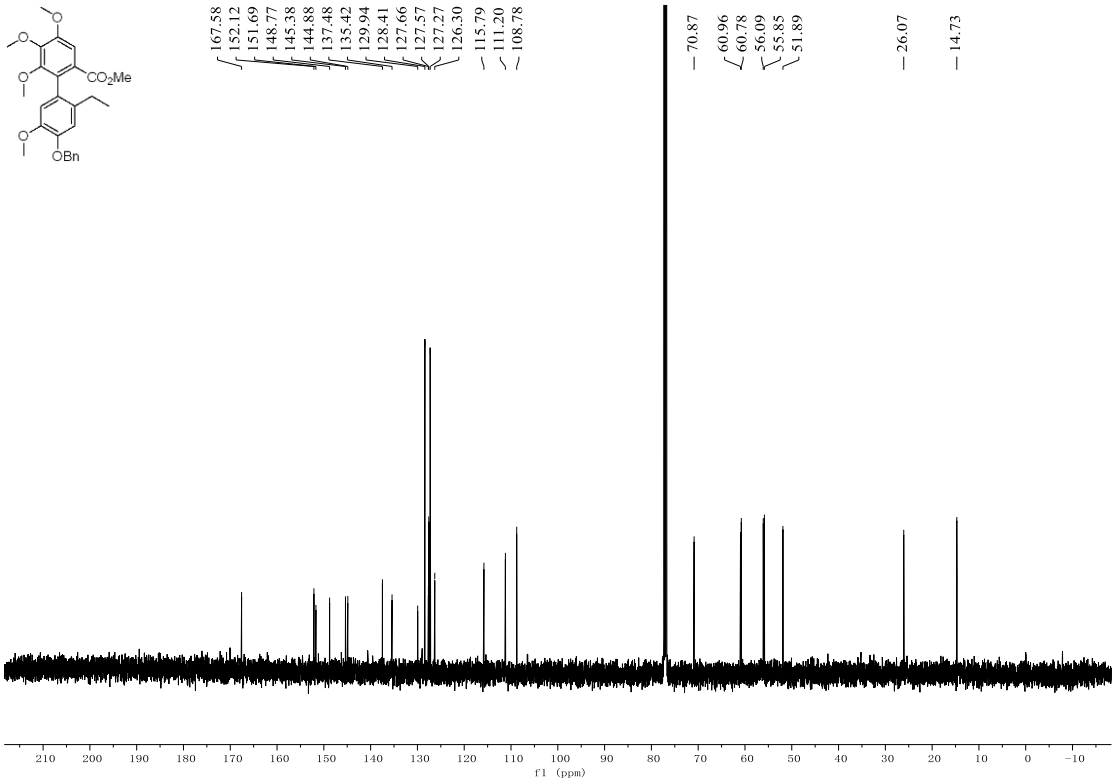

BnO
B
O
O
5.14
3.91
2.92
2.90
2.89
2.87
1.34
1.22
1.21
1.19
2.01
3.06
1.02
1.00
2.02
3.01
2.09
12.00
3.18
f1 (ppm)

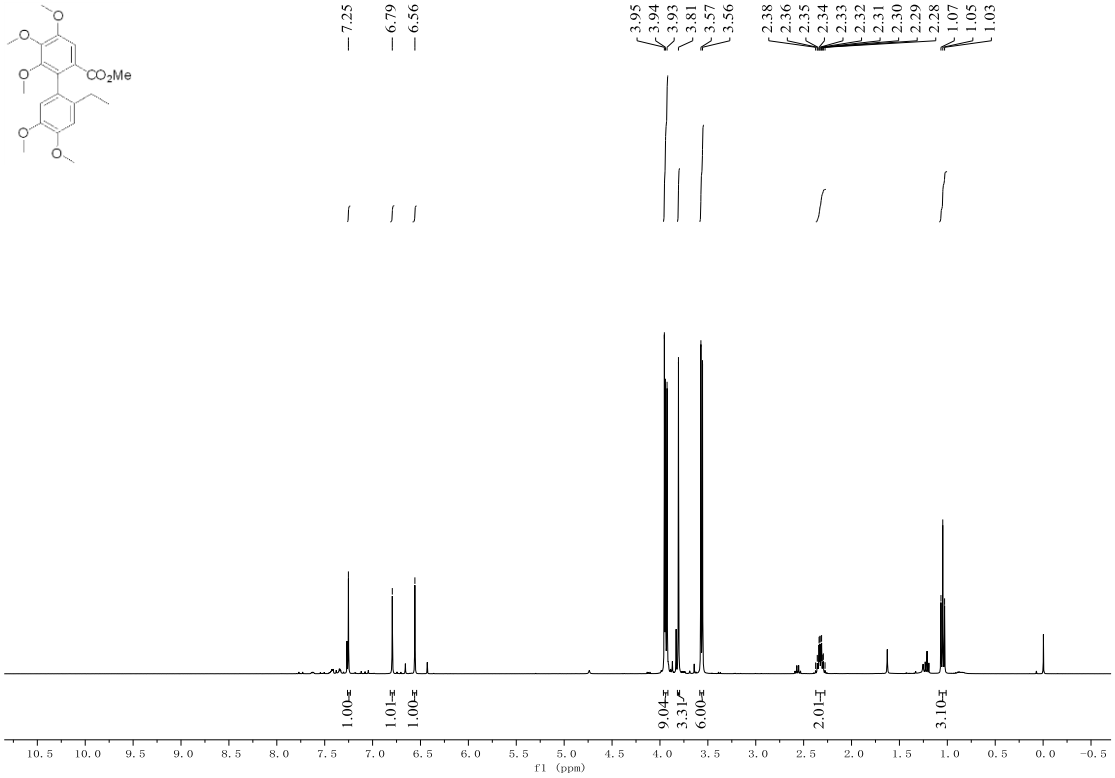

BnO
B
O
O
151.87
146.50
145.51
137.50
128.40
127.77
127.72
121.31
112.33
83.17
71.28
55.76
28.51
24.84
17.46
f1 (ppm)

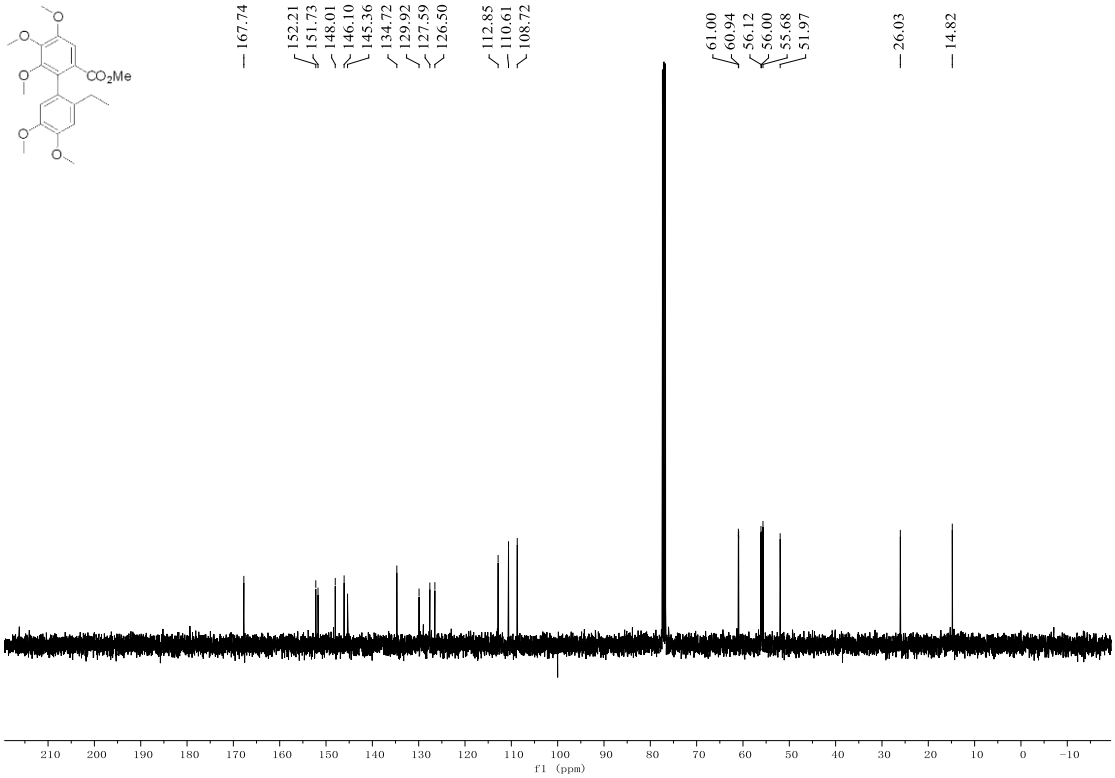

Bpin
7.26
6.71
3.90
2.90
2.89
2.87
2.85
1.33
1.20
1.18
1.16
0.00
1.06
1.00
6.07
2.25
12.13
3.26
f1 (ppm)

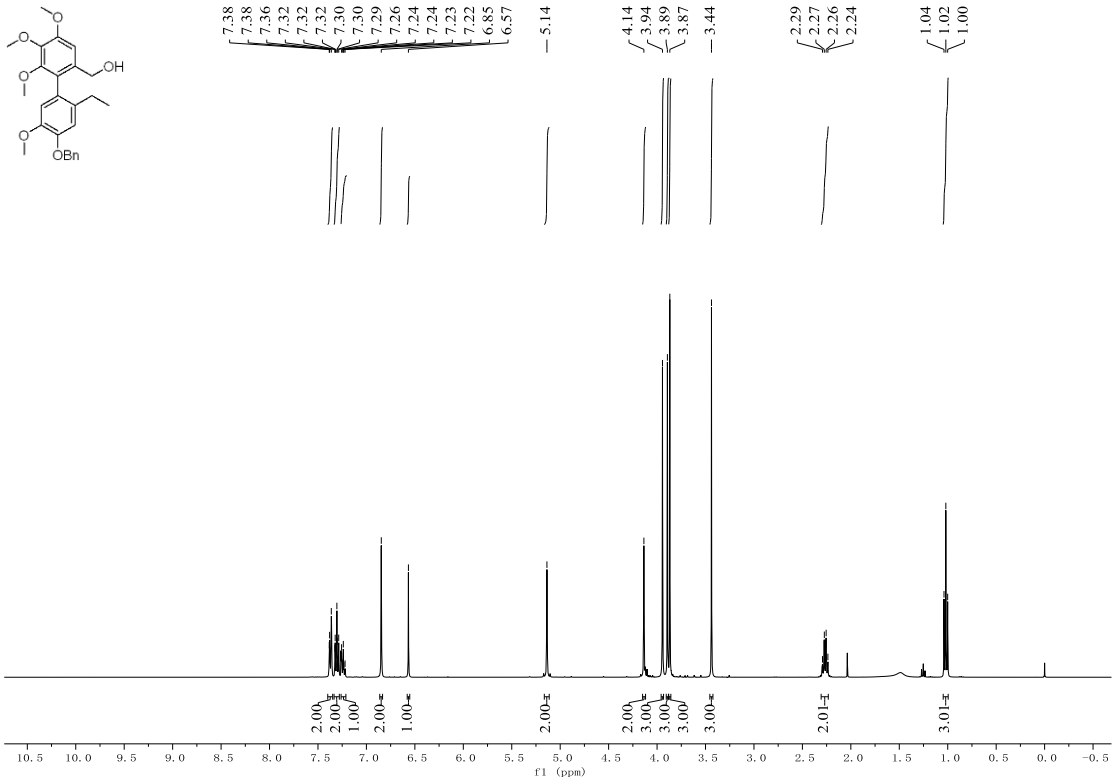

Bpin
151.07
145.94
118.23
111.83
83.19
55.97
55.66
28.49
24.86
17.52
17.11
f1 (ppm)

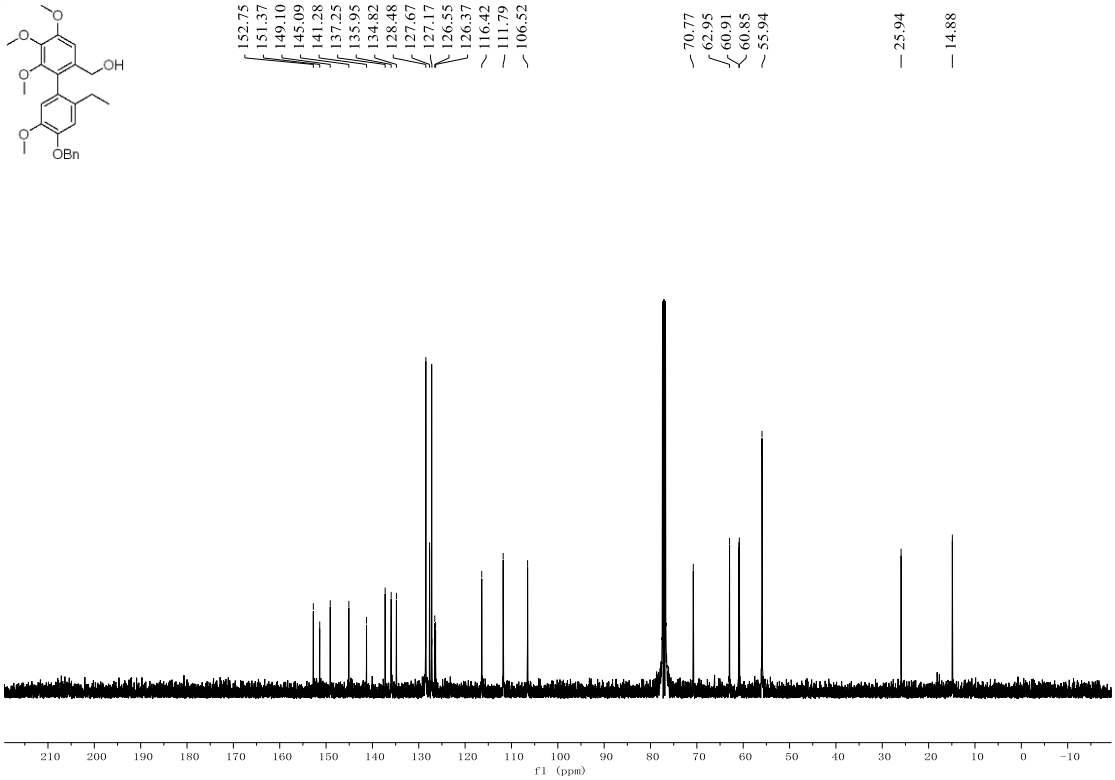

CO2Me
OBn
7.40
7.39
7.32
7.30
7.29
7.25
7.23
7.22
7.21
6.82
6.56
5.15
5.12
5.10
5.07
3.94
3.93
3.48
3.36
2.33
2.32
2.31
2.31
2.30
2.29
2.28
2.28
2.27
2.25
1.04
1.03
1.01
2.00
2.00
2.01
1.00
1.00
2.07
9.02
3.01
3.00
2.06
3.00
f1 (ppm)


CO2Me
OBn
167.58
152.12
151.69
148.77
145.38
144.88
137.48
135.42
129.94
128.41
127.66
127.57
127.27
126.30
115.79
111.20
108.78
70.87
60.96
60.78
56.09
55.85
51.89
26.07
14.73
f1 (ppm)


CO2Me
7.25
6.79
6.56
3.95
3.94
3.93
3.81
3.57
3.56
2.38
2.36
2.35
2.34
2.33
2.32
2.31
2.30
2.29
2.28
1.07
1.05
1.03
1.00
1.01
1.00
9.04
3.31
6.00
2.01
3.10
f1 (ppm)


CO2Me
167.74
152.21
151.73
148.01
146.10
145.36
134.72
129.92
127.59
126.50
112.85
110.61
108.72
61.00
60.94
56.12
56.00
55.68
51.97
26.03
14.82
f1 (ppm)


OH
OBn
7.38
7.38
7.36
7.32
7.32
7.32
7.30
7.30
7.29
7.26
7.24
7.24
7.23
7.22
6.85
6.57
5.14
4.14
3.94
3.89
3.87
3.44
2.29
2.27
2.26
2.24
1.04
1.02
1.00
2.00
2.00
1.00
2.00
1.00
2.00
2.00
3.00
3.00
3.00
2.01
3.01
f1 (ppm)


OH
OBn
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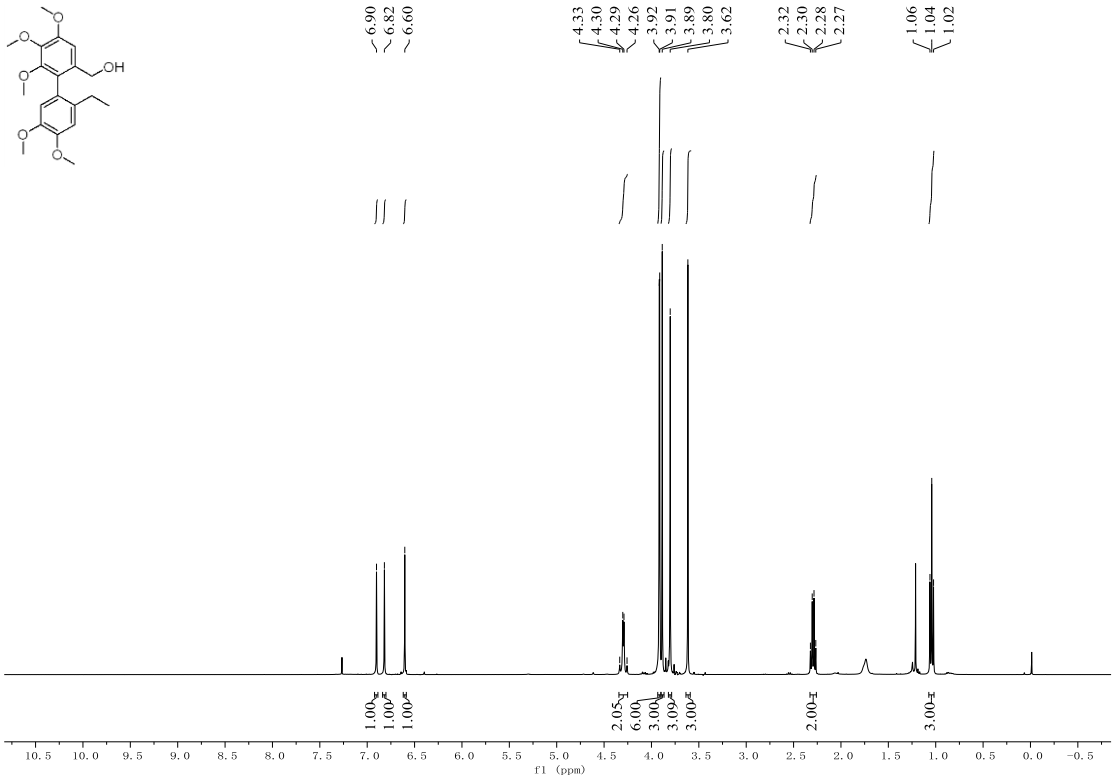
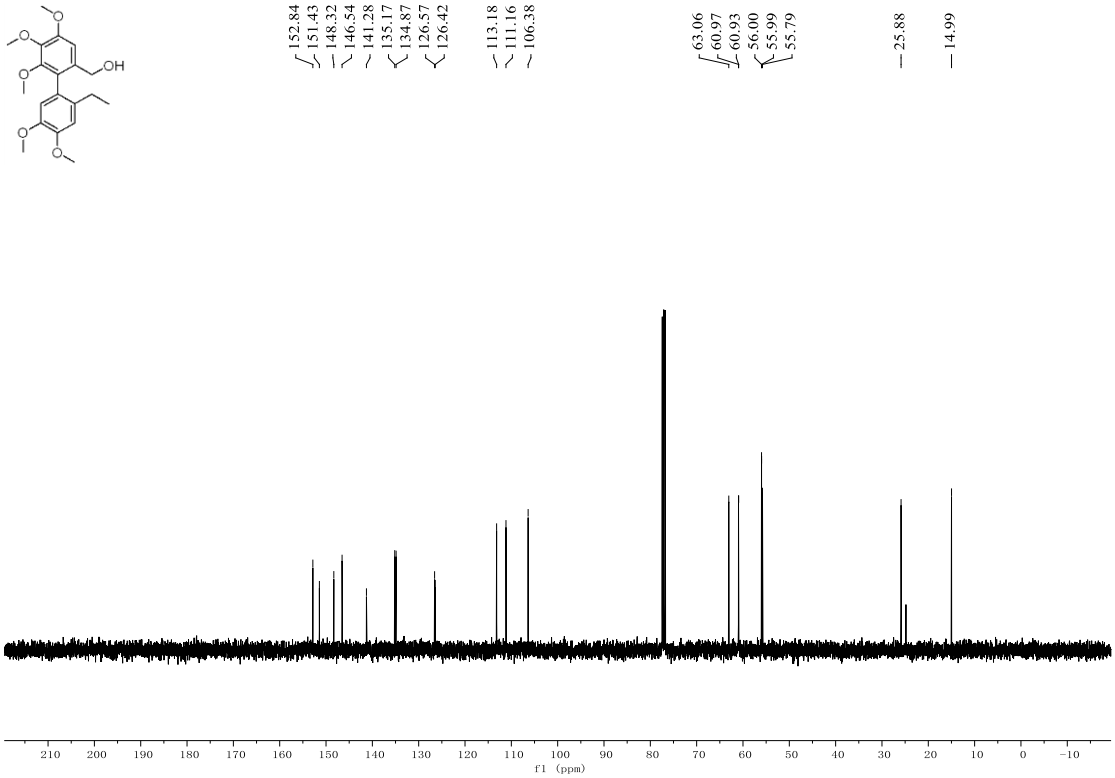
151.37
149.10
145.09
141.28
137.25
135.95
134.82
128.48
127.67
127.17
126.55
126.37
116.42
111.79
106.52
70.77
62.95
60.91
60.85
55.94
25.94
14.88
f1 (ppm)


6.90
6.82
6.60
4.33
4.30
4.29
4.26
3.92
3.91
3.89
3.80
3.62
2.32
2.30
2.28
2.27
1.06
1.04
1.02
1.00
1.00
1.00
2.05
6.00
3.00
3.09
3.00
2.00
3.00
f1 (ppm)


152.84
151.43
148.32
146.54
141.28
135.17
134.87
126.57
126.42
113.18
111.16
106.38
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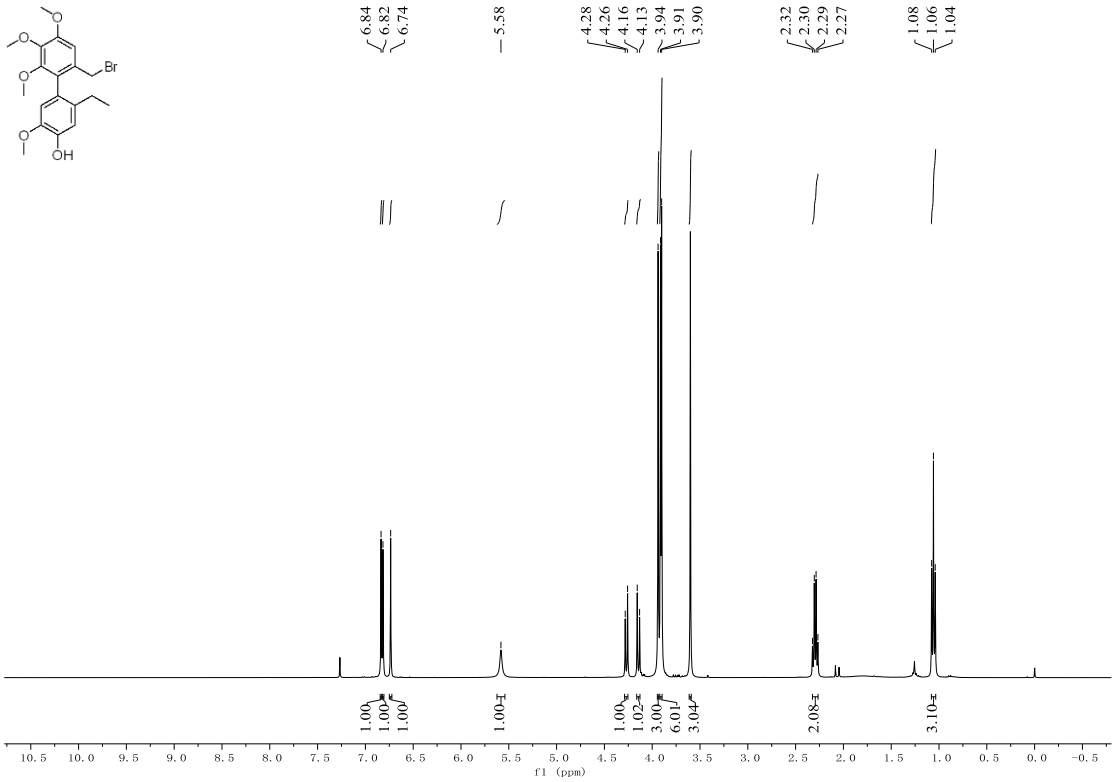
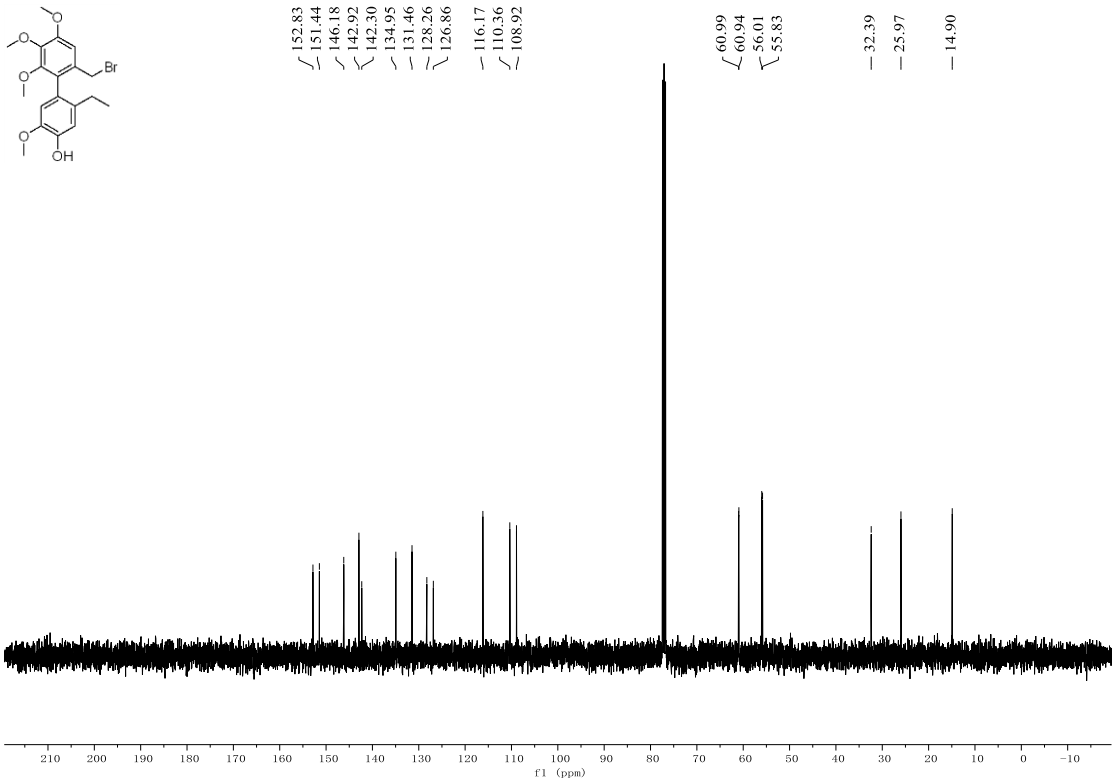
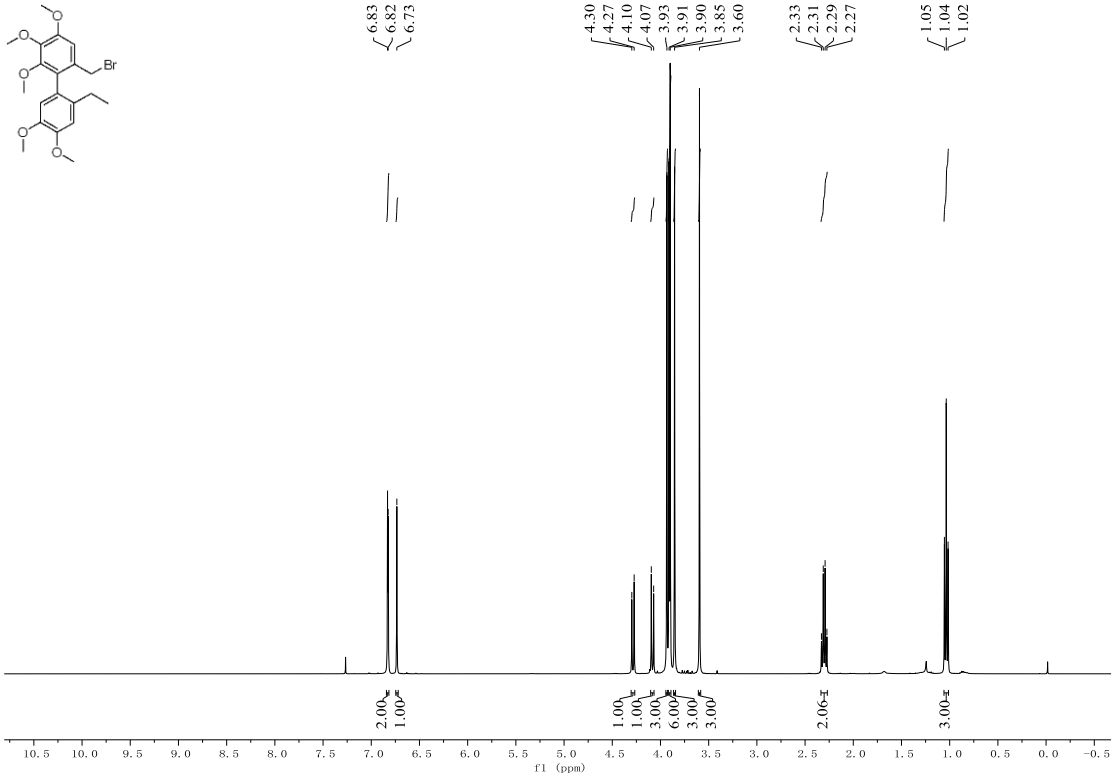
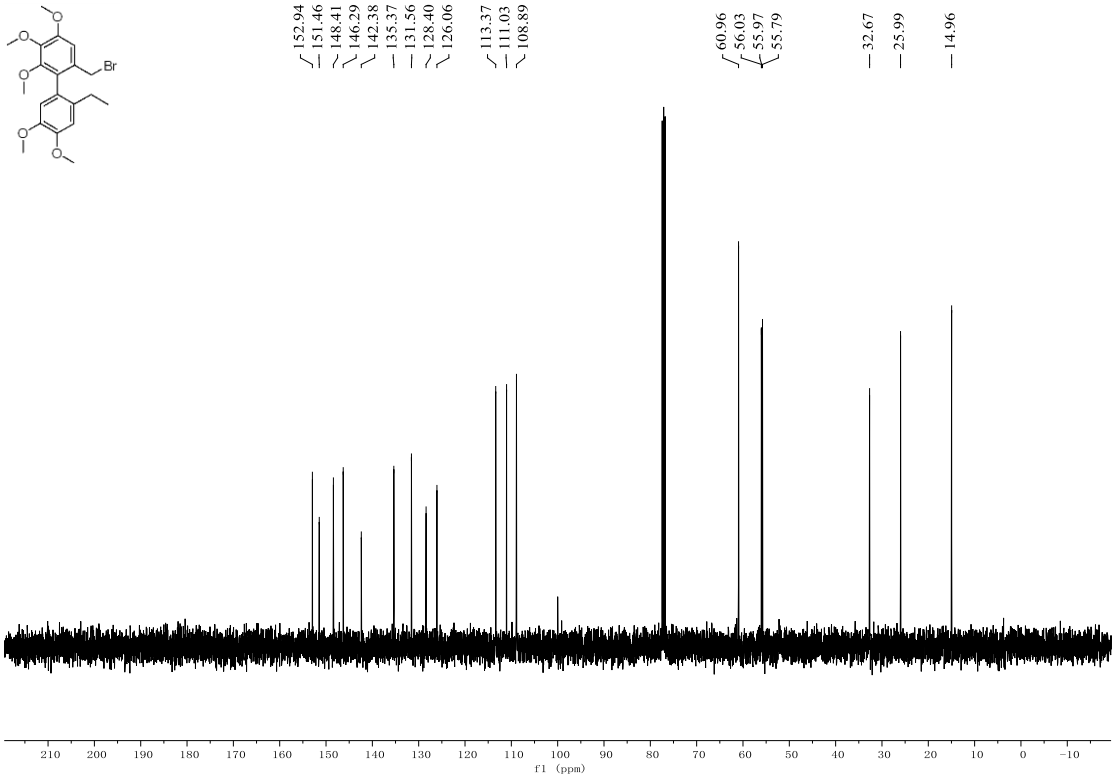
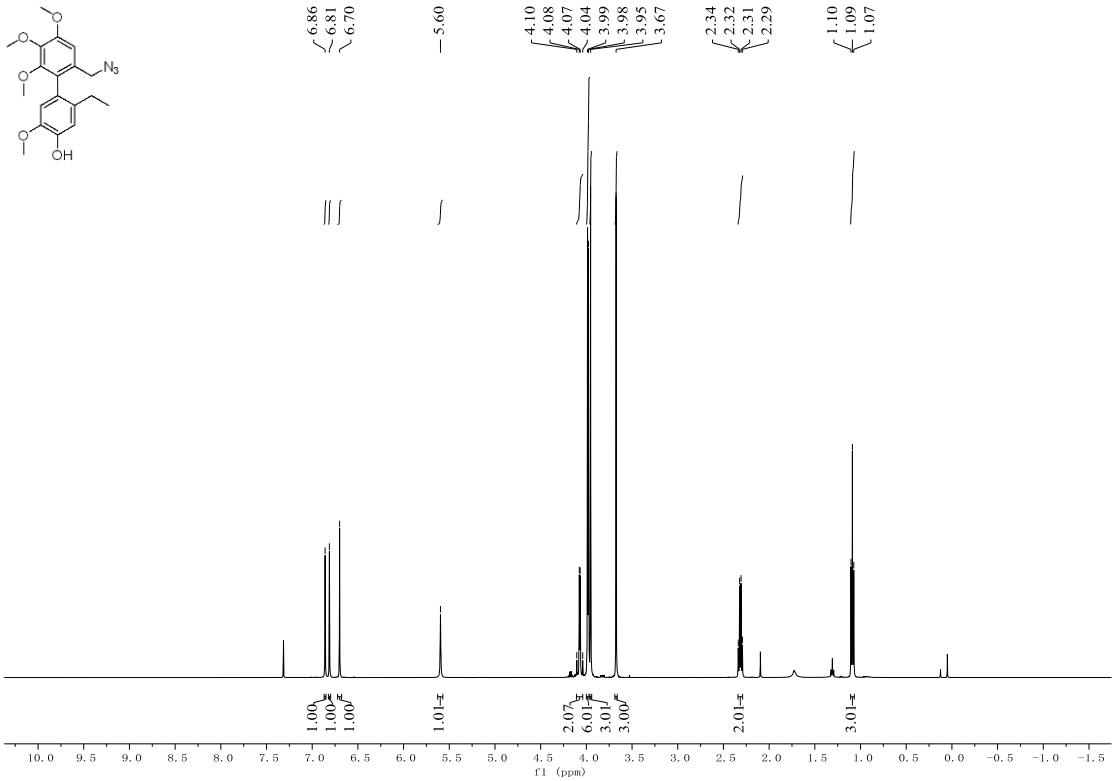
56.00
55.99
55.79
25.88
14.99
f1 (ppm)


Br
OH
6.84
6.82
6.74
5.58
4.28
4.26
4.16
4.13
3.94
3.91
3.90
2.32
2.30
2.29
2.27
1.08
1.06
1.04
1.00
1.00
1.00
1.00
1.00
1.02
3.00
6.01
3.04
2.08
3.10
f1 (ppm)


Br
OH
152.83
151.44
146.18
142.92
142.30
134.95
131.46
128.26
126.86
116.17
110.36
108.92
60.99
60.94
56.01
55.83
32.39
25.97
14.90
f1 (ppm)


Br
6.83
6.82
6.73
4.30
4.27
4.10
4.07
3.93
3.91
3.90
3.85
3.60
2.33
2.31
2.29
2.27
1.05
1.04
1.02
2.00
1.00
1.00
1.00
3.00
6.00
3.00
2.06
3.00
f1 (ppm)


Br
152.94
151.46
148.41
146.29
142.38
135.37
131.56
128.40
126.06
113.37
111.03
108.89
60.96
56.03
55.97
55.79
32.67
25.99
14.96
f1 (ppm)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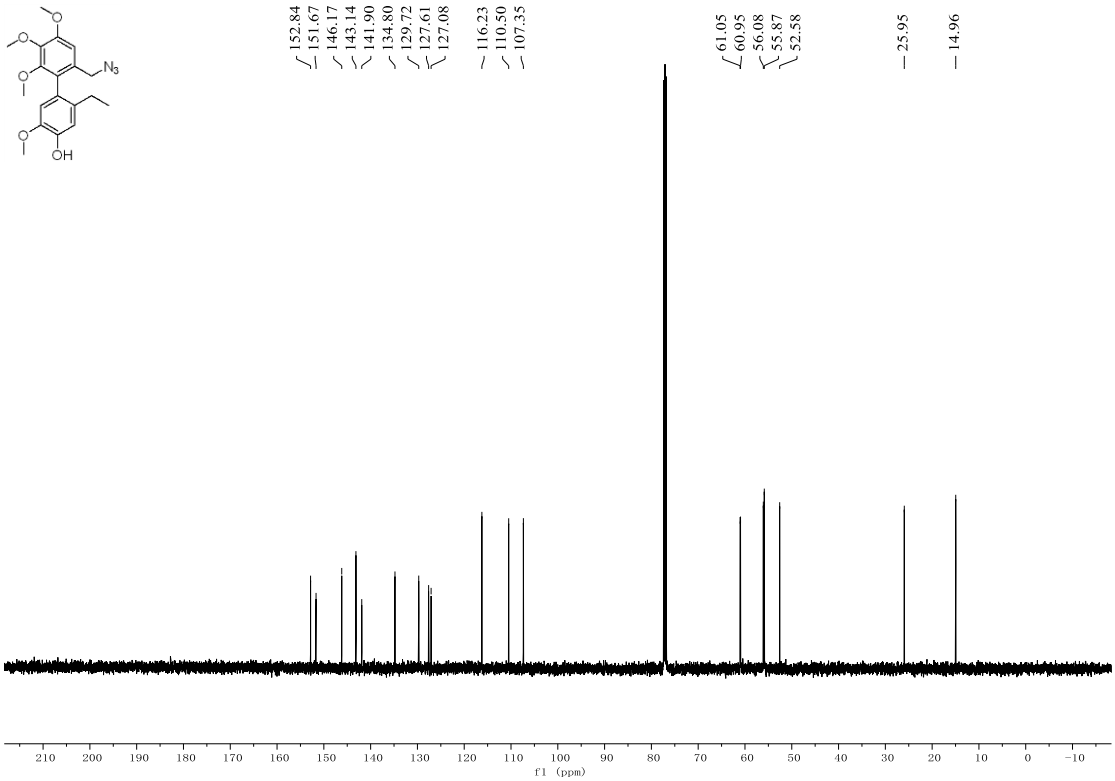
6.81
6.70
5.60
4.10
4.08
4.07
4.04
3.99
3.98
3.95
3.67
2.34
2.32
2.31
2.29
1.10
1.09
1.07
1.00
1.00
1.00
1.01
2.07
6.01
3.01
3.00
2.01
3.01
f1 (ppm)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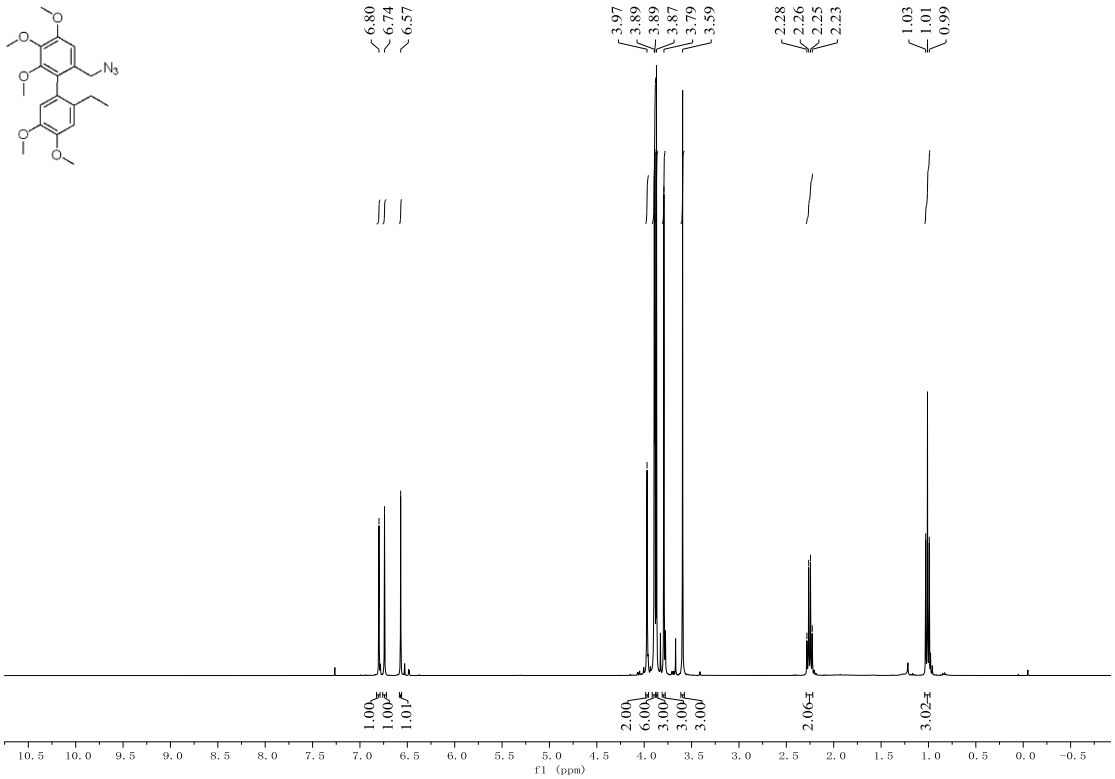
146.17
143.14
141.90
134.80
129.72
127.61
127.08
116.23
110.50
107.35
61.05
60.95
56.08
55.87
52.58
25.95
14.96
f1 (ppm)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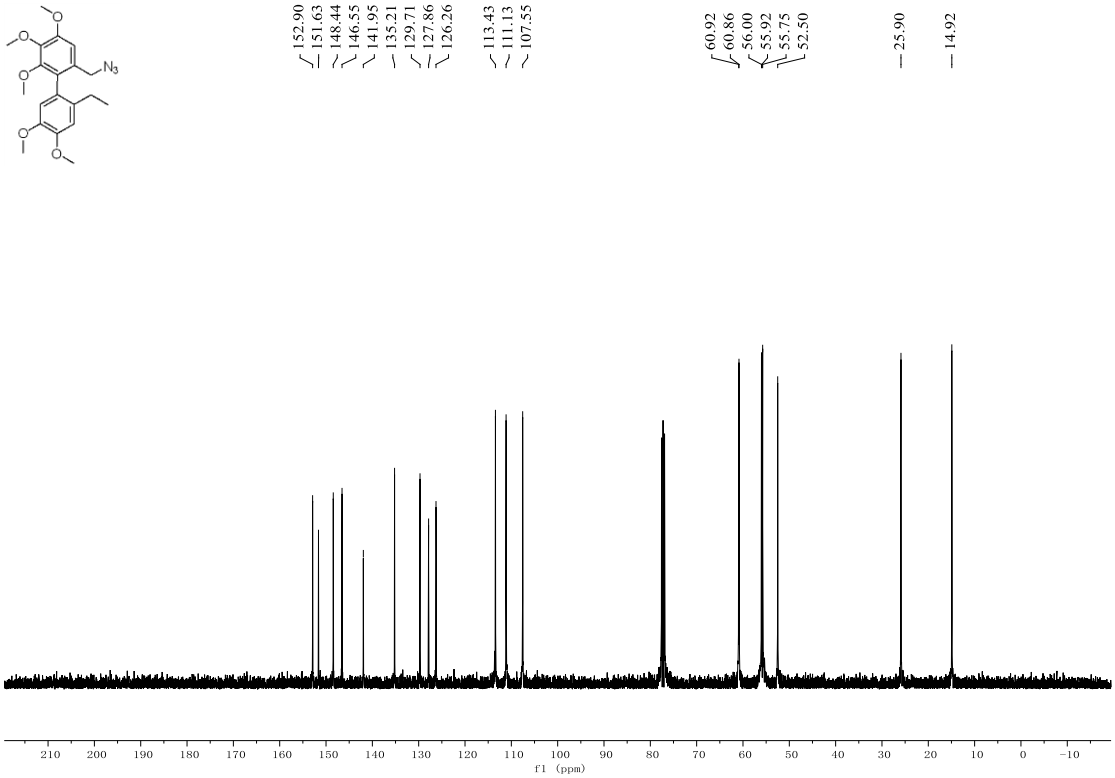
6.74
6.57
3.97
3.89
3.89
3.87
3.79
3.59
2.28
2.26
2.25
2.23
1.03
1.01
0.99
1.00
1.00
1.01
2.00
6.00
3.00
3.00
2.06
3.02
f1 (ppm)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135.21
129.71
127.86
126.26
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111.13
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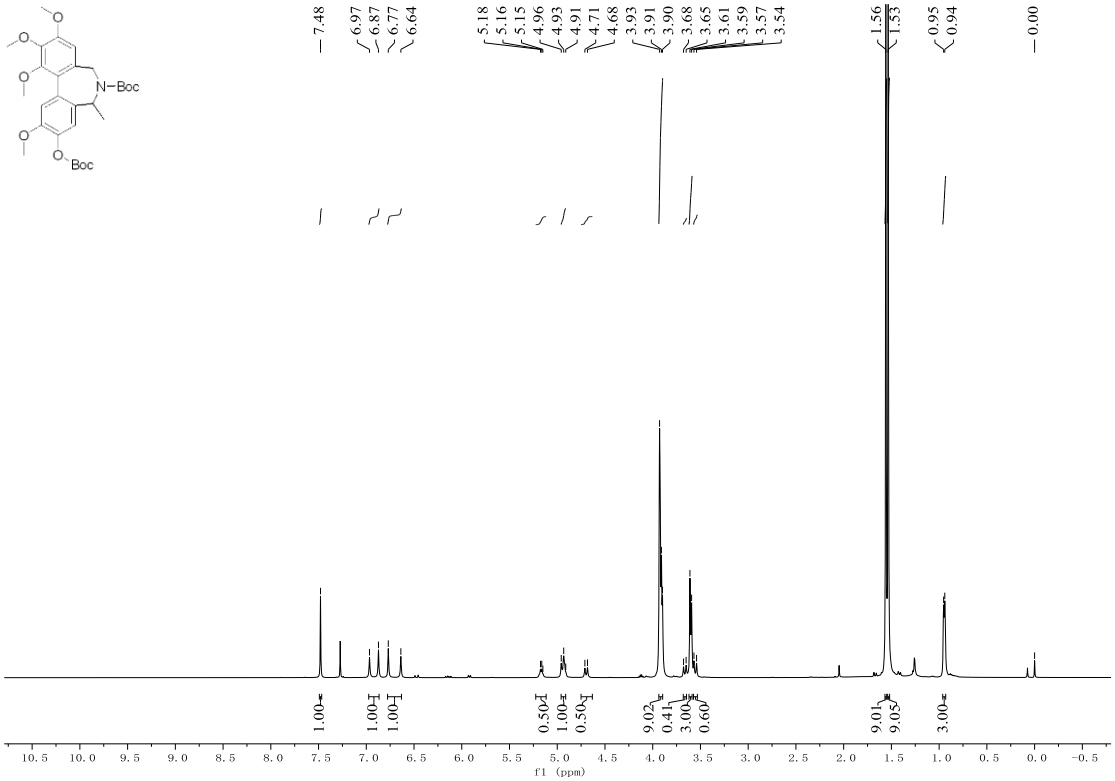
60.92
60.86
56.00
55.92
55.75
52.50
25.90
14.92
f1 (ppm)


N-Boc
Boc
7.48
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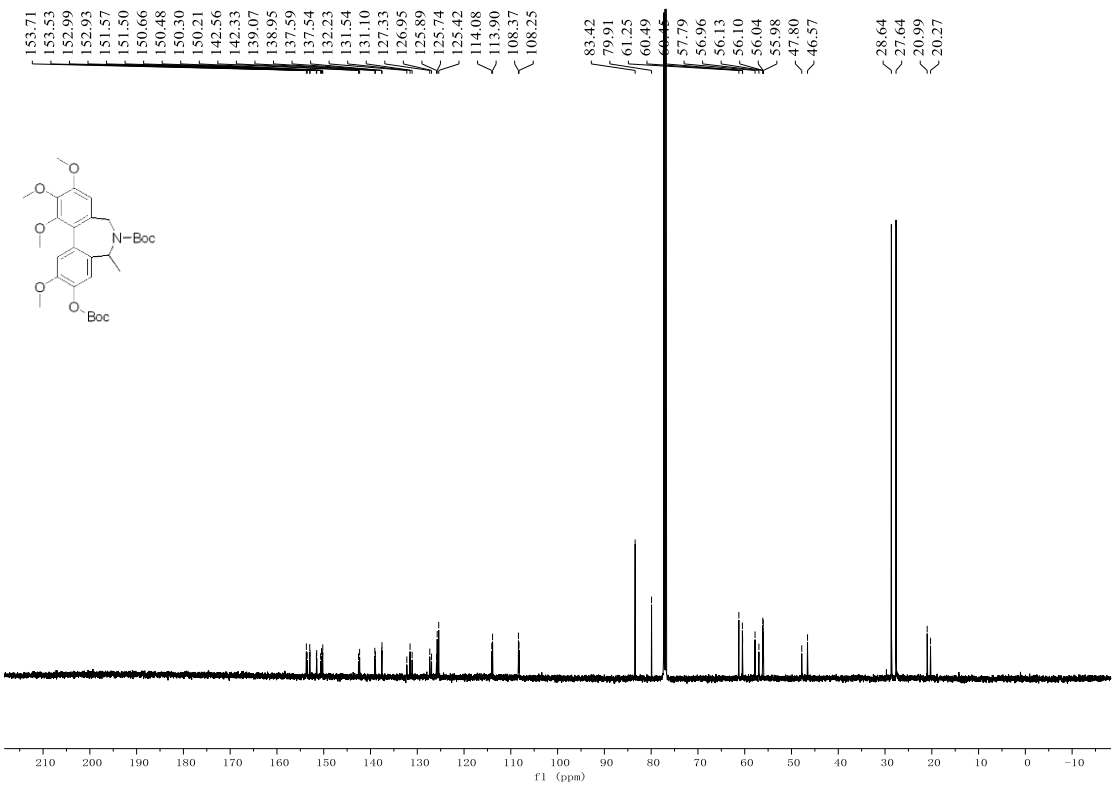
6.87
6.77
6.64
5.18
5.16
5.15
4.96
4.93
4.91
4.71
4.68
3.93
3.91
3.90
3.68
3.65
3.61
3.59
3.57
3.54
1.56
1.53
0.95
0.94
0.00
1.00
1.00
1.00
0.50
1.00
0.50
9.02
0.41
3.00
0.60
9.01
9.05
3.00
f1 (ppm)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151.50
150.66
150.48
150.30
150.21
142.56
142.33
139.07
138.95
137.59
137.54
132.23
131.54
131.10
127.33
126.95
125.89
125.74
125.42
114.08
113.90
108.37
108.25
83.42
79.91
61.25
60.49
60.48
57.79
56.96
56.13
56.10
56.04
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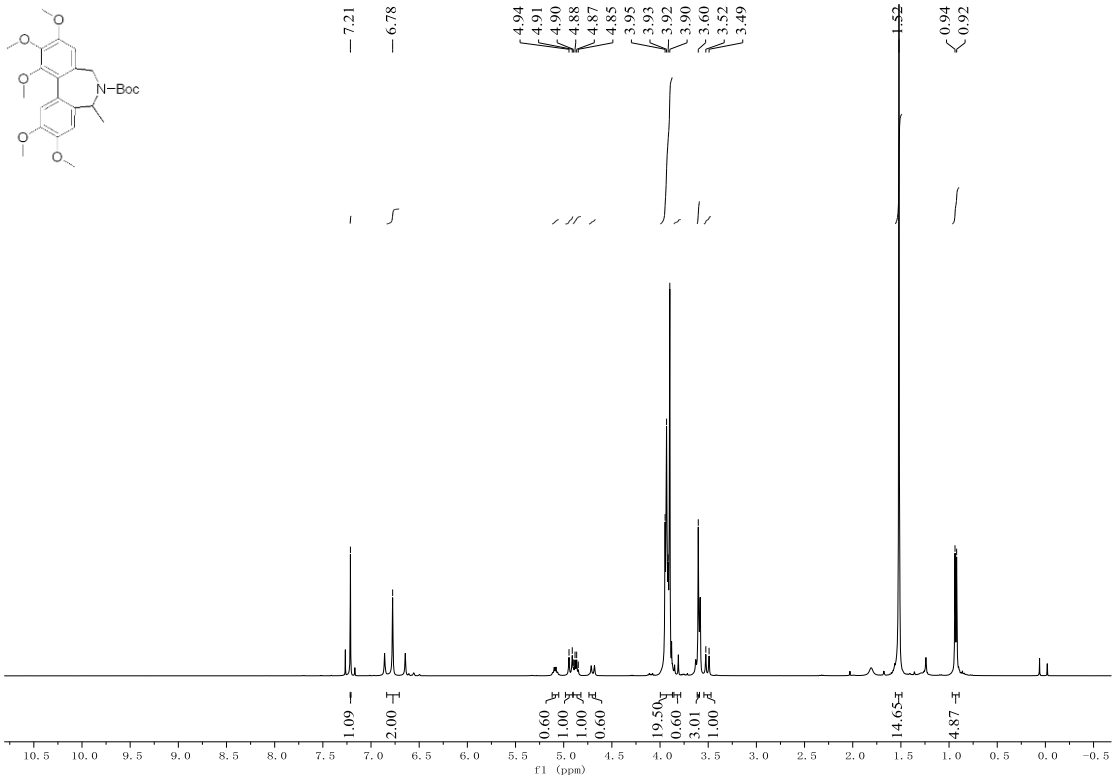
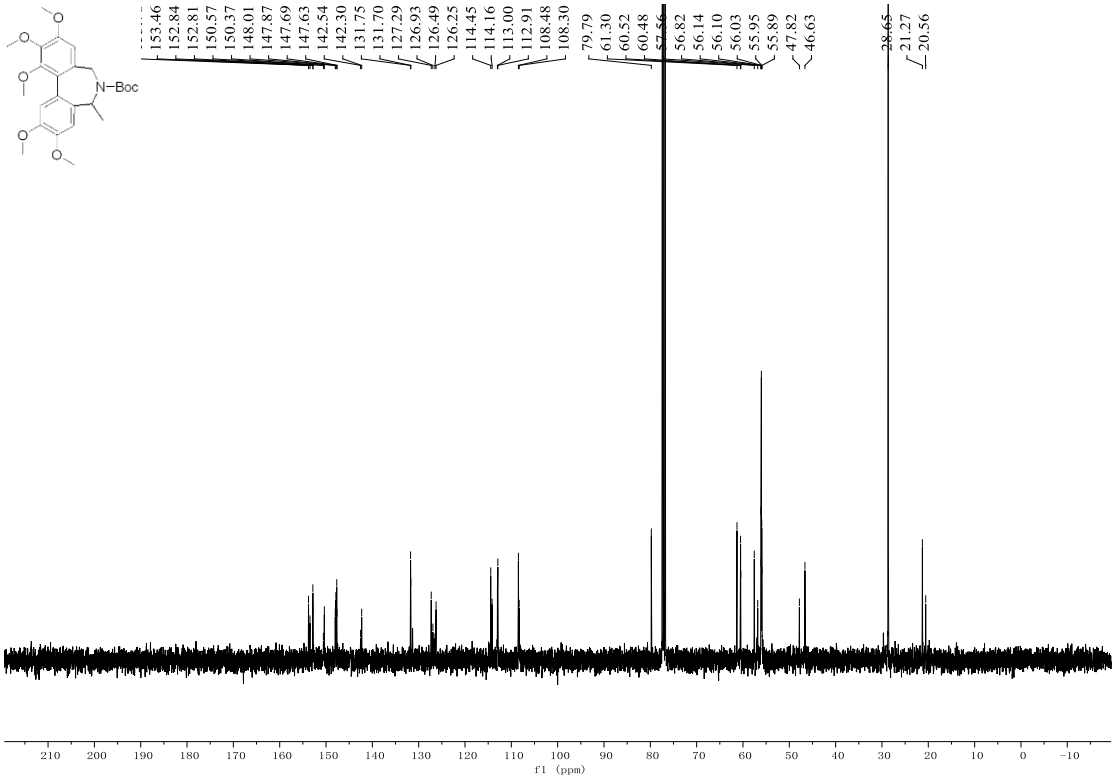
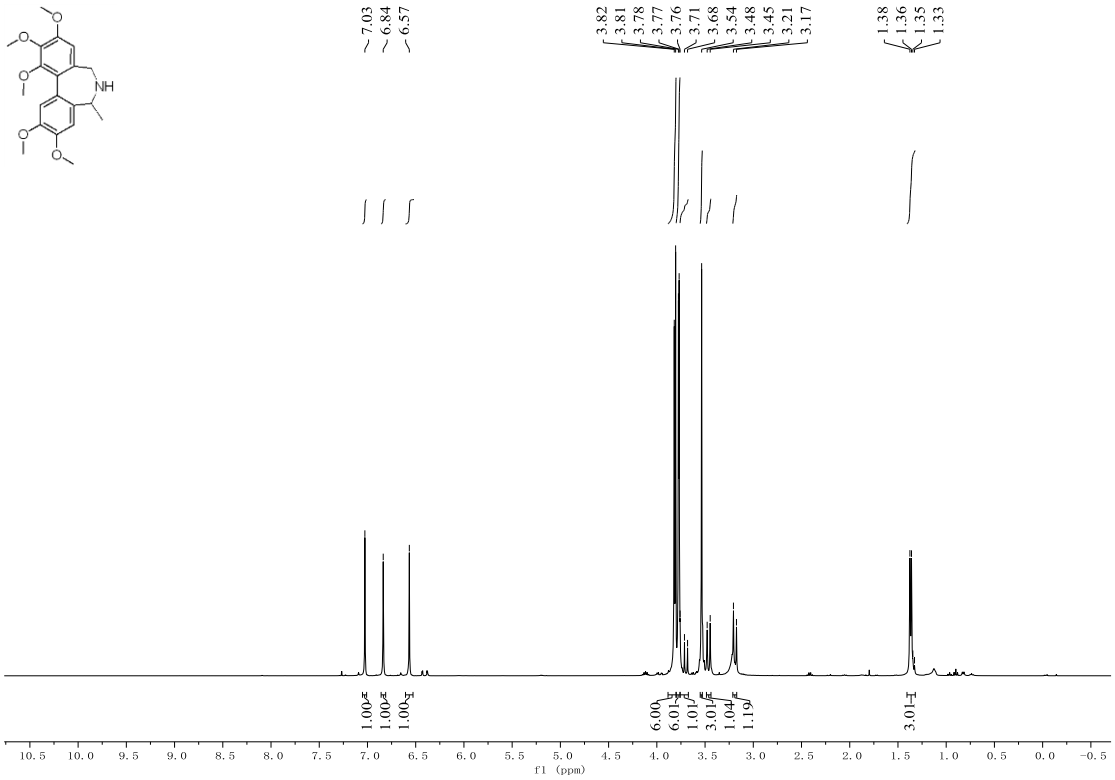
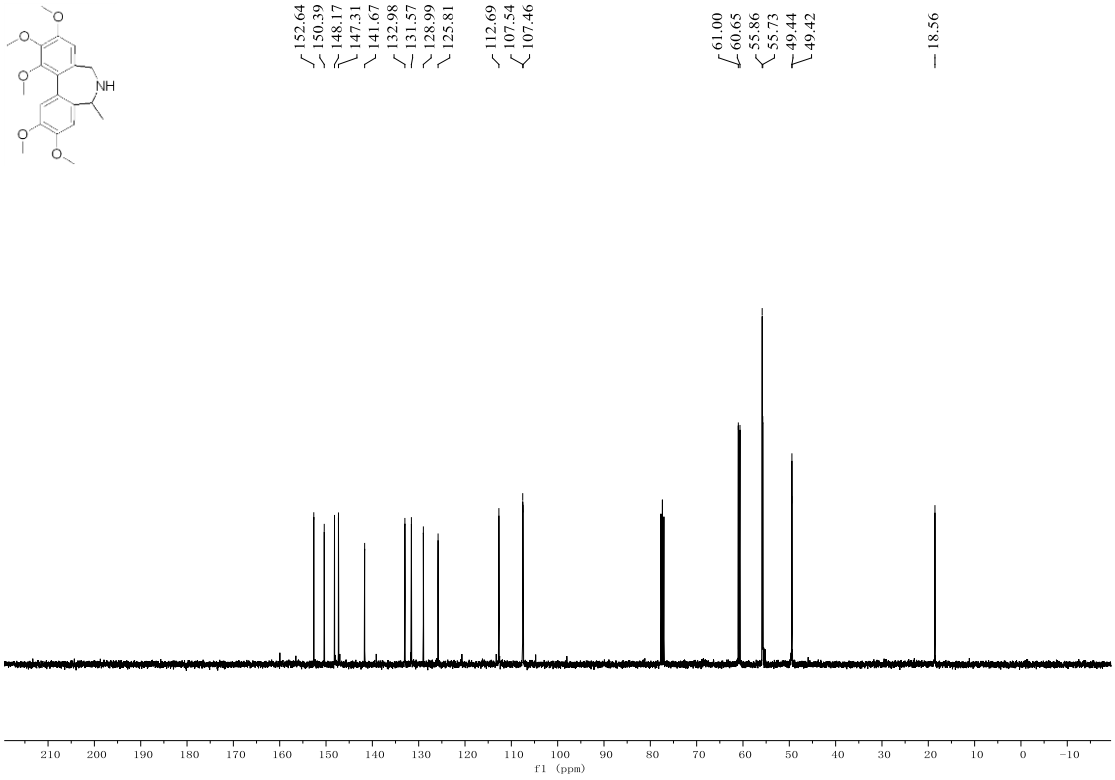
47.80
46.57
28.64
27.64
20.99
20.27
N-Boc
Boc
f1 (ppm)


N-Boc
7.21
6.78
4.94
4.91
4.90
4.88
4.87
4.85
3.95
3.93
3.92
3.90
3.60
3.52
3.49
1.52
0.94
0.92
1.09
2.00
0.60
1.00
1.00
0.60
19.50
0.60
3.01
1.00
14.65
4.87
f1 (ppm)


N-Boc
153.46
152.84
152.81
150.57
150.37
148.01
147.87
147.69
147.63
142.54
142.30
131.75
131.70
127.29
126.93
126.49
126.25
114.45
114.16
113.00
112.91
108.48
108.30
79.79
61.30
60.52
60.48
56.82
56.14
56.10
56.03
55.95
55.89
47.82
46.63
28.65
21.27
20.56
f1 (ppm)


7.03
6.84
6.57
3.82
3.81
3.78
3.77
3.76
3.71
3.68
3.54
3.48
3.45
3.21
3.17
1.38
1.36
1.35
1.33
1.00
1.00
1.00
6.00
6.01
1.01
3.01
1.04
1.19
3.01
f1 (ppm)


152.64
150.39
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147.31
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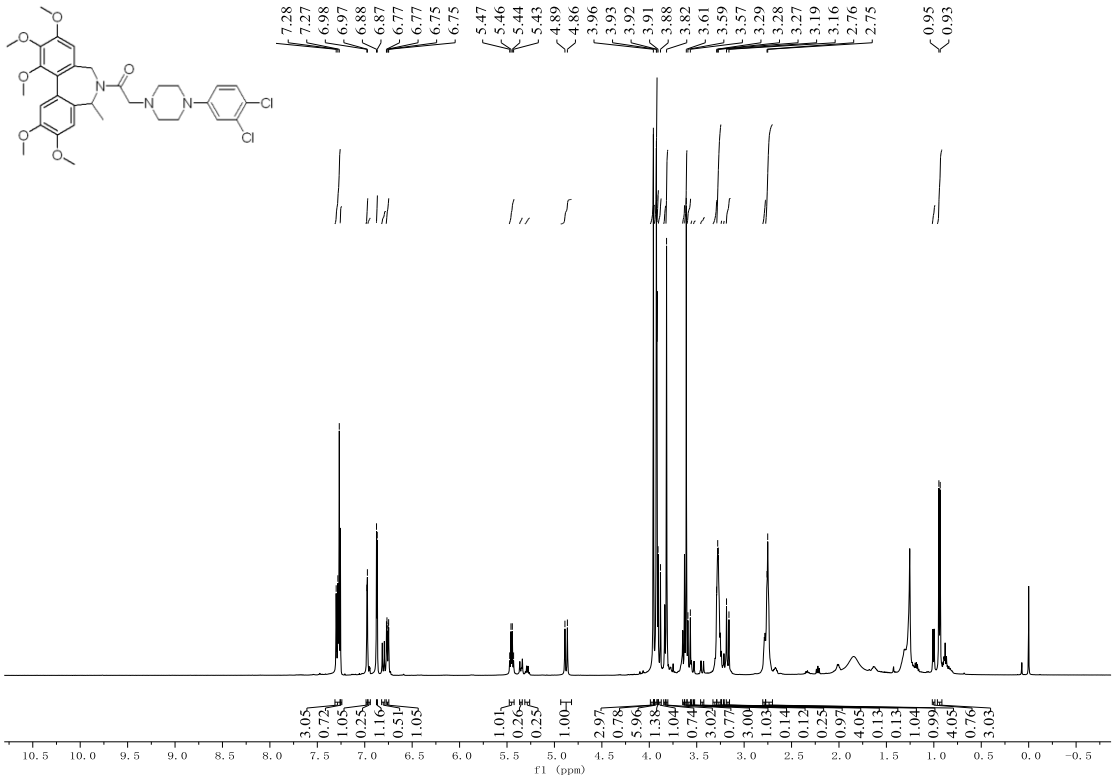
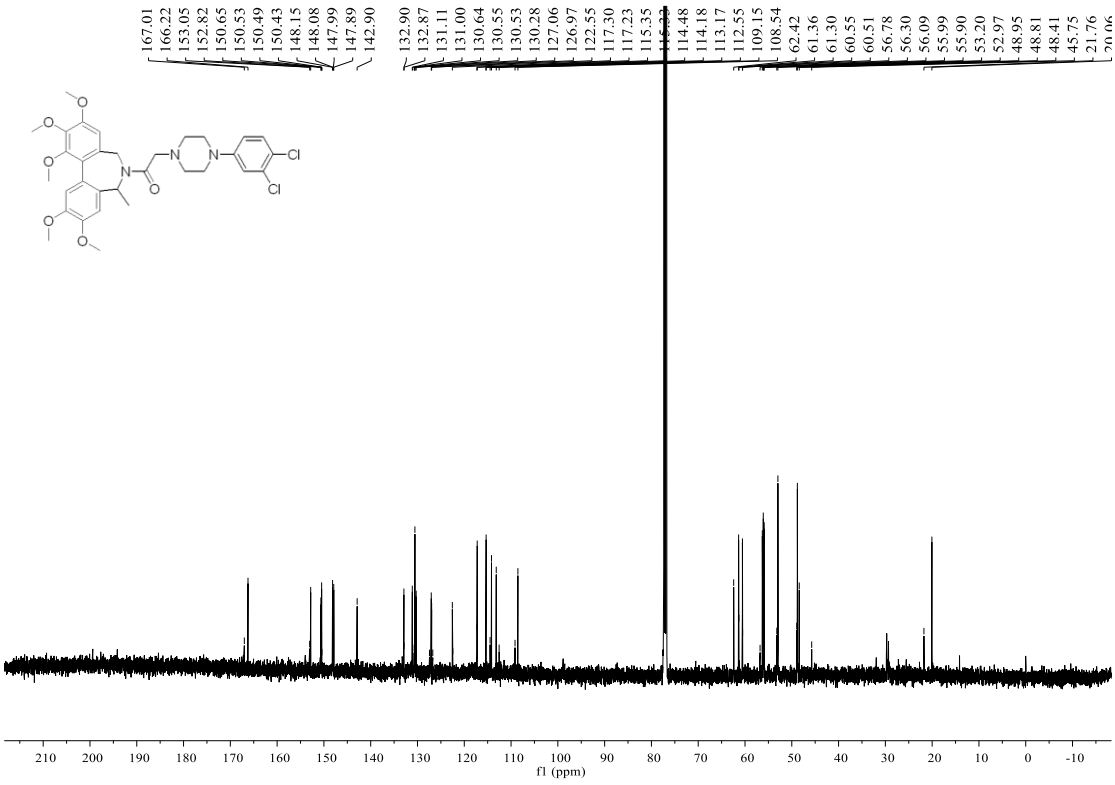
132.98
131.57
128.99
125.81
112.69
107.54
107.46
61.00
60.65
55.86
55.73
49.44
49.42
18.56
f1 (ppm)


7.28
7.27
6.98
6.97
6.88
6.87
6.77
6.77
6.75
6.75
5.47
5.46
5.44
5.43
4.89
4.86
3.96
3.93
3.92
3.91
3.88
3.82
3.61
3.59
3.57
3.29
3.28
3.27
3.19
3.16
2.76
2.75
0.95
0.93
Cl
Cl
f1 (ppm)


167.01
166.22
153.05
152.82
150.65
150.53
150.49
150.43
148.15
148.08
147.99
147.89
142.90
132.90
132.87
131.11
131.00
130.64
130.55
130.53
130.28
127.06
126.97
122.55
117.30
117.23
115.35
114.48
114.18
113.17
112.55
109.15
108.54
62.42
61.36
61.30
60.55
60.51
56.78
56.30
56.09
55.99
55.90
53.20
52.97
48.95
48.81
48.41
45.75
21.76
Cl
Cl
f1 (ppm)

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