Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

# *Supporting Information*

## An Improved Synthesis of [5.6.7]-Tricyclic Core of Cyrneine B and Glaucopine C

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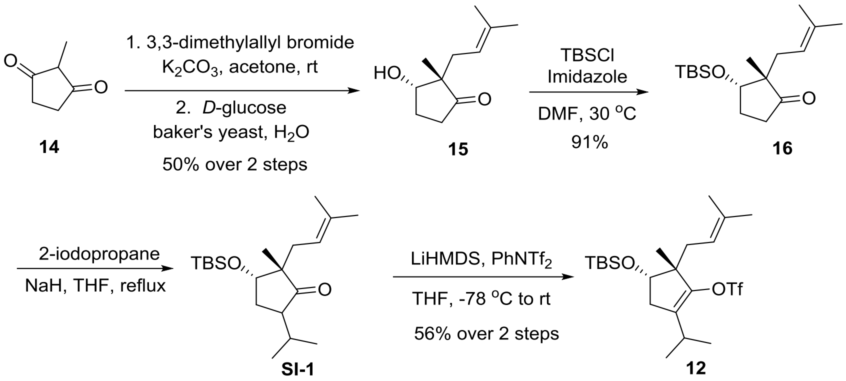
## 1. General Information

Unless otherwise stated, all oxygen or moisture sensitive reactions were conducted in flame-dried glassware under an atmosphere of nitrogen or argon. All solvents were purified and dried according to standard methods prior to use. Reagents were purchased from commercial sources and were used without further purification.

Analytical thin layer chromatography (TLC) was performed on 0.2 mm thick silica gel 60-F254 plates (Merck) and visualized by exposure to ultraviolet light, or an ethanolic solution of phosphomolybdic acid. Chromatographic purification of products was accomplished using forced-flow chromatography on 200–300 mesh silica gel. The $^{1}$H NMR spectra were recorded on Bruker AV at 300, 400, or 600 MHz and $^{13}$C NMR spectra were recorded at 75 MHz. Chemical shifts are given relative to TMS or the appropriate solvent peak. High resolution mass spectra (HRMS) were obtained on an IonSpec Ultima 7.0 T FT-ICR-MS (IonSpec, USA) using ESI as ionization method.

## 2. 2. Experimental Procedures and Characterization Data

### 2.1 Synthesis of compound 12



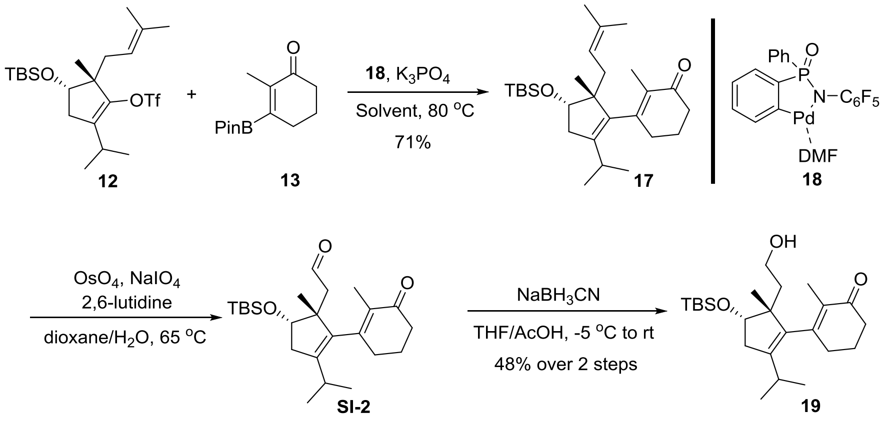
Compound **15** was prepared in 50% yield as white solid from **14** using previously described protocols.[1]

To a solution of compound **15** (5.83 g, 32 mmol) in DMF (30 mL) was added imidazole (2.83 g, 41.6 mmol, 1.3 equiv) and TBSCl (5.79 g, 38.4 mmol, 1.2 equiv). The mixture was stirred at 30 °C overnight. The reaction mixture was poured into aqueous $NaHCO_3$ (50 mL) and extracted with EtOAc (3 × 120 mL). The combined organic layers were washed with brine (5 × 30 mL), dried over $Na_2SO_4$ and evaporated to dryness. The resulting crude residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc = 30/1) to afford **16** (8.61 g, 91%) as colorless oil. $R_f$ = 0.4 (petroleum ether/EtOAc = 15/1); $[\alpha]_D^{20}$ = + 40.8 (*c* 1.23, $CHCl_3$); **$^1$H NMR** (300 MHz, $CDCl_3$) δ 5.14–5.05 (m, 1H), 4.04 (t, *J* = 5.1 Hz, 1H), 2.48–2.35 (m, 1H), 2.27–2.03 (m, 4H), 1.97–1.85 (m, 1H), 1.70 (s, 3H), 1.59 (s, 3H), 0.92 (s, 3H), 0.88 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 221.1, 133.8, 119.8, 78.0, 54.0, 34.4, 29.1, 28.4, 26.1, 25.8, 19.4, 18.1, 17.9, -4.2, -4.9; **HRMS** (ESI) m/z calcd for $C_{17}H_{32}NaO_2Si^+$ $[M+Na]^+$: 319.2064, found 319.2062.

To a stirred suspension of NaH (60% dispersion in mineral oil, 5.8 g, 145 mmol, 5.0 equiv) in THF (120 mL) was added dropwise a solution of **16** (8.6 g, 29 mmol) in THF (20 mL) at 0 °C, then 2-iodopropane (29 mL, 290 mmol, 10.0 equiv) was added. The reaction mixture was refluxed overnight. The resulting mixture was quenched at 0 ℃ by adding $H_2O$. Then 2 M HCl (80 mL) was added, and the mixture was stirred at room temperature for 1 h. Then brine was added to the reaction mixture, and the layers were separated. The aqueous layer was extracted with EtOAc (3 × 100 mL), and the combined organic layers were washed with 10% aqueous $Na_2S_2O_3$ (50 mL) and brine (2 × 50 mL), dried over $Na_2SO_4$ and concentrated under reduced pressure. The resulting crude residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/$CH_2Cl_2$ = 5/1) to afford **SI-1** (6.59 g, 67% yield) as colorless oil.

To a solution of ketone **SI-1** (6.59 g, 19.46 mmol) in THF (25 mL) was added LiHMDS (1.0 M in THF, 25.3 mL, 25.3 mmol, 1.3 equiv) at -78 ℃. The clear solution was stirred at this temperature for 0.5 h. Then $PhNTf_2$ (7.65 g, 21.41 mmol, 1.3 equiv) in THF (25 mL) was slowly added and the mixture was allowed to warm to room temperature and stirred for 6.5 h. Then brine (50 mL) was added to the reaction mixture, and the layers were separated. The aqueous layer was extracted with EtOAc (3 × 50 mL), and the combined organic layers were dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: petroleum ether/$CH_2Cl_2$ = 50/1) to afford **12** (7.62 g, 83% yield) as colorless oil. $R_f = 0.5$ (petroleum ether/$CH_2Cl_2$ = 12/1); $[\alpha]_D^{20} = -45.6$ (*c* 0.83, $CHCl_3$); **$^1$H NMR** (300 MHz, $CDCl_3$) δ 5.27–5.18 (m, 1H), 4.02 (t, *J* = 7.6 Hz, 1H), 2.81 (sept, *J* = 6.9 Hz, 1H), 2.41 (dd, *J* = 15.3, 7.8 Hz, 1H), 2.21–2.04 (m, 3H), 1.66 (s, 3H), 1.56 (s, 3H), 1.09 (s, 3H), 1.01 (d, *J* = 6.9 Hz, 3H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.92 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 143.3, 135.7 133.3, 121.0, 118.8 (q, *J* = 317 Hz), 77.4, 50.5, 34.8, 33.0, 26.1, 25.9, 25.6, 22.9, 20.4, 20.3, 18.1, 17.7, -4.3, -4.8; HRMS (ESI) m/z calcd for $C_{21}H_{38}F_3O_4SSi^+$ [M+H]$^+$: 471.2207, found 471.2197.

### 2.2 Synthesis of compound 19



Compound **13** was prepared in 80% yield as white solid from 2-methyl-1,3-cyclohexanedione using previously described protocols.[2] The product was isolated by flash chromatography on silica gel without further purification by Kugelrohr distillation.

To a solution of vinyl triflate **12** (2.71 g, 5.75 mmol) in the mixed solvents of DMF (10 mL) and *t*-BuOH (10 mL) was added **13** (2.04 g, 8.62 mmol, 1.5 equiv), palladacycle **18** (0.32 g, 10 mol%), $K_3PO_4$ (2.44 g, 11.5 mmol, 2.0 equiv) at room temperature under nitrogen. The resulting mixture was stirred at 80 °C for 16 h. The reaction mixture was then filtered through a celite bed and the filter cake was washed with EtOAc. The combined filtrate was washed with brine (5 × 15 mL), dried over $Na_2SO_4$ and concentrated under vacuum. The residue was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 50/1) to afford the desired cross-coupling product **17** (1.75 g, 71%) as an inseparable mixture of rotamers (colorless oil). $R_f$ = 0.3 (petroleum ether/EtOAc = 15/1).

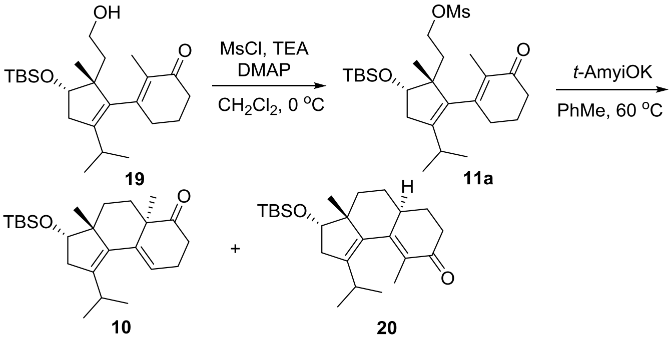
To a solution of **17** (1.20 g, 2.79 mmol) in dioxane (16 mL) was added $NaIO_4$ (2.09 g, 9.75 mmol, 3.5 equiv), 2,6-lutidine (0.60 g, 5.57 mmol, 2 equiv) and 3.5 mL of $OsO_4$ solution (0.04 M in $H_2O$). The mixture was stirred at 65 $^oC$ for 5 h. The reaction mixture was then filtered through a thin celite bed and the filter cake was washed with EtOAc. The combined filtrate was washed with brine, dried over $Na_2SO_4$ and concentrated under vacuum. The resulting crude residue was purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 20/1) to afford crude **SI-2** (0.74 g, 66%) as grey solid. $R_f$ = 0.5 and 0.45 for separable rotamers (petroleum ether/EtOAc = 8/1).

To a solution of **SI-2** (0.74 g, 1.83 mmol) in THF (12 mL) and AcOH (1.2 mL) was added $NaBH_3CN$ (0.345 g, 5.49 mmol, 3.0 equiv) in three portions within 5 min at -5 $^oC$. The mixture was allowed to warm to room temperature and stirred for 20 min. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ carefully at 0 ℃ and extracted with EtOAc. The combined organic layers were dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: petroleum ether/$CH_2Cl_2$/$Et_2O$ = 7/1/1 → 4/1/1 ) to afford **19** (0.54 g, 72% yield) as a separable mixture of rotamers. **19a:** $R_f$ = 0.5 (petroleum ether/$CH_2Cl_2$/$Et_2O$ = 1/1/1); $[\alpha]_D^{20}$ = + 38.6 (*c* 2.85, $CHCl_3$); **$^1$H NMR** (300 MHz, $CDCl_3$) δ 4.12 (t, *J* = 8.4 Hz, 1H), 3.77–3.47 (m, 3H), 2.55–2.25 (m, 6H), 2.19–2.05 (m, 1H), 2.02–1.78 (m, 3H), 1.73–1.61 (m, 4H), 0.98 (d, *J* = 6.9 Hz, 3H), 0.98 (s, 3H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.94 (s, 9H), 0.13 (s, 3H), 0.13 (s, 3H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 199.5, 154.2, 141.3, 137.7, 134.2, 81.0, 58.9, 54.0, 39.5, 38.2, 36.8, 32.5, 28.6, 26.0, 25.9, 23.1, 22.0, 20.2, 18.1, 14.0, -4.5, -4.8. **19b:** $R_f$ = 0.45 (petroleum ether/$CH_2Cl_2$/$Et_2O$ = 1/1/1); $[\alpha]_D^{20}$ = – 12.8 (*c* 0.92, $CHCl_3$); **$^1$H NMR** (300 MHz, $CDCl_3$) δ 4.00 (t, *J* = 6.6 Hz, 1H), 3.77–3.56 (m, 2H), 3.08 (bs, 1H), 2.52–2.25 (m, 6H), 2.19–2.06 (m, 1H), 2.02–1.89 (m, 2H), 1.86–1.75 (m, 1H), 1.70–1.48 (m, 4H), 1.10 (s, 3H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.92 (s, 9H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.13 (s, 3H), 0.13 (s, 3H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 199.7, 154.4, 139.9, 139.5, 133.8, 81.0, 59.2, 54.3, 38.2, 37.3, 36.6, 33.3, 28.2, 25.9, 25.0, 23.1, 21.6, 20.2, 18.1, 13.5, -4.3, -4.8. **HRMS** (ESI) m/z calcd for $C_{24}H_{42}NaO_3Si^+$ $[M+Na]^+$: 429.2795, found 429.2790.

### 2.3 Synthesis of compound 10

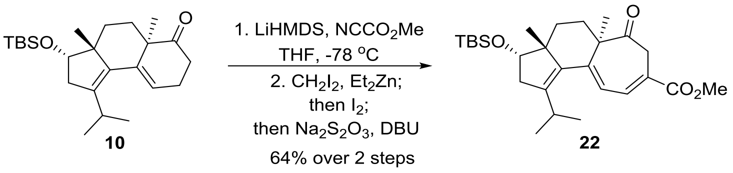
To a solution of compound **19** (707 mg, 1.74 mmol), DMAP (10 mg, 0.05 equiv), and TEA (0.73 mL, 5.2 mmol, 3 equiv) in $CH_2Cl_2$ (12 mL) was added MsCl (0.175 mL, 2.26 mmol, 1.3

equiv) at 0 $^o$C. The mixture was stirred at the same temperature for 0.5 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ carefully at 0 ℃ and extracted with $CH_2Cl_2$. And the combined organic layers were dried over $Na_2SO_4$ and concentrated under reduced pressure. The resulting residue was employed in the next step without further purification.



To a solution of compound **11a** obtained above in PhMe (15 mL) was added *t*-AmylOK (0.54 g, 4.25 mmol, 2.5 equiv) and the mixture was stirred at 60 ℃ for 4 h. Then water was added, and the layers were separated. The aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic layers were dried over $Na_2SO_4$. The solvent was removed under reduced pressure. Purification of the residue by flash chromatography on silica gel (eluent: petroleum ether/$Et_2O$ = 100/1) afforded **10** (515 mg, 76% over 2 steps) as white solid. **10**: $R_f$ = 0.35 (petroleum ether/$Et_2O$ = 15/1); $[\alpha]_D^{20}$ = + 243.5 (*c* 0.77, $CHCl_3$); **$^1$H NMR** (600 MHz, $CDCl_3$) δ 5.49–5.46 (m, 1H), 3.81 (d, *J* = 4.8 Hz, 1H), 2.89 (sept, *J* = 6.6 Hz, 1H), 2.74–2.68 (m, 1H), 2.62 (dd, *J* = 16.2, 4.8 Hz, 1H), 2.54–2.41 (m, 3H), 2.26 (td, *J* = 13.8, 5.4 Hz, 1H), 2.13 (d, *J* = 16.2 Hz, 1H), 1.80–1.69 (m, 2H), 1.13 (s, 3H), 1.10 (dt, *J* = 13.8, 3.6 Hz, 1H), 0.98 (d, *J* = 6.6 Hz, 3H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.88 (s, 9H), 0.85(s, 3H), 0.05 (s, 3H), 0.03 (s, 3H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 215.8, 139.7, 139.6, 135.9, 121.0, 78.4, 52.5, 48.6, 39.0, 35.9, 30.8, 26.4, 26.0, 25.9, 25.7, 22.6, 22.5, 21.6, 21.4, 18.2, -4.6, -4.8; **HRMS** (ESI) m/z calcd for $C_{24}H_{40}NaO_2Si^+$ $[M+Na]^+$: 411.2690, found 411.2699. **20**: $R_f$ = 0.15 (petroleum ether/$Et_2O$ = 15/1); $[\alpha]_D^{20}$ = + 369.6 (*c* 1.15, $CHCl_3$); **$^1$H NMR** (400 MHz, $CDCl_3$) δ 4.05 (dd, *J* = 7.0, 5.2 Hz, 1H), 2.71 (dd, *J* = 16.4, 7.2 Hz, 1H), 2.46 (dt, *J* = 16.0, 4.0 Hz, 1H), 2.36 (dd, *J* = 14.8, 4.8 Hz, 1H), 2.33–2.23 (m, 2H), 2.19 (dd, *J* = 16.8, 4.8 Hz, 1H), 2.08–1.98 (m, 1H), 1.93–1.81 (m, 2H), 1.70 (d, *J* = 2.4 Hz, 3H), 1.68–1.48 (m, 2H), 1.43–1.35 (m, 1H), 0.99 (s, 3H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.91 (s, 9H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.07 (s, 3H), 0.06 (s, 3H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 200.0, 156.4, 140.3, 137.5, 130.5, 79.5, 54.2, 40.8, 39.1, 37.1, 32.2, 31.4, 29.2, 27.8, 26.0, 23.4, 21.8, 19.4, 18.3, 13.7, -4.4, -4.7; **HRMS** (ESI) m/z calcd for $C_{24}H_{40}NaO_2Si^+$ $[M+Na]^+$: 411.2690, found 411.2688.

### 2.4 Synthesis of compound 22



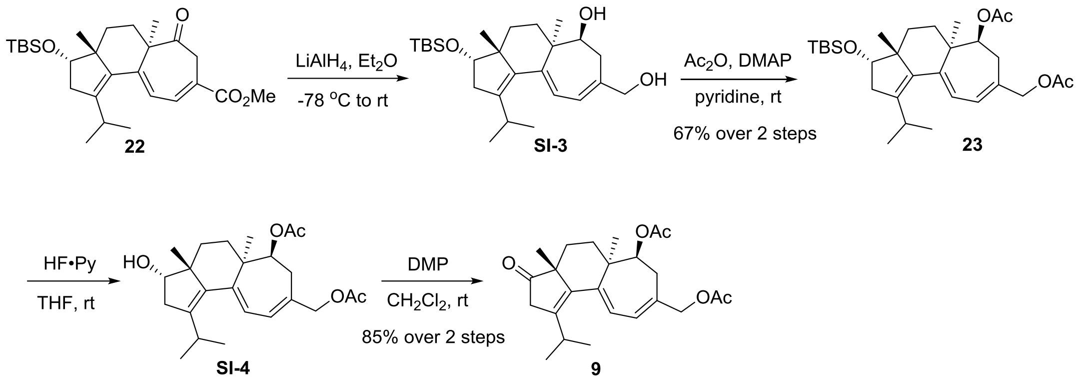
To a solution of compound **10** (194 mg, 0.5 mmol) in dry THF (2 mL) at -78 $^{o}$C was added LiHMDS (1M in THF, 1.5 mL, 1.5 mmol, 3 equiv) and the resulting solution was stirred for 15 min at -78 $^{o}$C and then 15 min at 0 $^{o}$C. Then methyl carbonocyanidate (0.16 mL, 2 mmol, 4 equiv) was added at -78 $^{o}$C and the mixture was stirred for 2 h at the same temperature. The reaction mixture was quenched by addition of water. The organic phase was collected, and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over $Na_2SO_4$ and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel yielded crude β-keto ester as colorless oil.

To a solution of diethyl zinc (1.0 M in hexanes, 2.7 mL, 2.7 mmol, 6.0 equiv) in $CH_2Cl_2$ (3 mL) was added $CH_2I_2$ (0.22 mL, 2.7 mmol, 6.0 equiv) at 0 ℃. After the mixture was stirred for 10 min, β-keto ester obtained above was added as a solution in 3 mL of $CH_2Cl_2$. The mixture was stirred for 2 h at room temperature. Then iodine (0.91 g, 3.6 mmol) was added to the reaction mixture in a single portion and allowed to stir until a pink color persisted for 10 min. A saturated solution of $Na_2S_2O_3$ was added and the mixture was stirred until the pink color had disappeared. To this solution was added DBU (1.0 mL, 6.7 mmol, 15 equiv). The mixture was stirred for 0.5 h at room temperature and quenched by addition of saturated $NH_4Cl$. The mixture was extracted with $Et_2O$ and the combined organic layers were dried with $Na_2SO_4$ and concentrated under reduced pressure. The residue was chromatographed on silica (eluent:petroleum ether/$CH_2Cl_2$/$Et_2O$ = 100/10/1) to yield **22** (146 mg, 64% over 2 steps) as light yellow oil. $R_f$= 0.4 (petroleum ether/$CH_2Cl_2$/$Et_2O$ = 7/3/1); $[\alpha]_D^{20}$ = + 94.1 (*c* 0.71, $CHCl_3$); **$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 6.3, 1.5 Hz, 1H), 5.95 (d, *J* = 6.3 Hz, 1H), 3.88 (dd, *J* = 5.4, 1.8 Hz, 1H), 3.85 (d, *J* = 11.7 Hz, 1H), 3.79 (s, 3H), 3.38 (d, *J* = 11.7 Hz, 1H), 2.89 (sept, *J* = 6.9 Hz, 1H), 2.68 (dd, *J* = 16.5, 5.4 Hz, 1H), 2.25–2.14 (m, 2H), 1.99 (td, *J* = 12.9, 3.9 Hz, 1H), 1.55 (dt, *J* = 13.2, 4.5 Hz, 1H), 1.15 (s, 3H), 1.02 (d, *J* = 6.9 Hz, 3H), 0.98 (d, *J* = 6.9 Hz, 3H), 0.94 (s, 3H), 0.88 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 206.4, 166.2, 149.2, 141.7, 138.5, 136.0, 123.7, 122.1, 79.0, 57.1, 53.2, 52.4, 41.2, 39.3, 33.8, 27.2, 26.8, 25.9, 23.3, 23.0, 21.6, 21.4, 18.1, -4.5, -4.9; **HRMS** (ESI) m/z calcd for $C_{27}H_{42}NaO_4Si^+$ $[M+Na]^+$: 481.2745, found 481.2745.

## 2.5 Synthesis of compound 9

To a solution of **22** (120 mg, 0.26 mmol) in $Et_2O$ (6 mL) was added $LiAlH_4$ (59 mg, 1.56

mmol, 6.0 equiv) at -78 ℃. The reaction mixture was stirred for 20 min at -78 ℃ under nitrogen atmosphere and the solution was warmed to room temperature. The reaction mixture was quenched by the addition of $H_2O$. Brine (10 mL) and $Et_2O$ (30 mL) was added to the reaction mixture and the layers were separated. The aqueous layer was extracted with $Et_2O$ (2 × 10 mL). The combined organic layers were washed with brine (30 mL), dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent:petroleum ether/EtOAc = 3/1) to give compound **SI-3** (92 mg, 82%) as colorless oil. $R_f$ = 0.3 (petroleum ether/EtOAc = 1/1).



To a stirred solution of **SI-3** (92 mg, 0.213 mmol) in pyridine (1.2 mL) containing DMAP (5 mg, 0.2 equiv) was added $Ac_2O$ (0.3 mL, 3.2 mmol, 15 equiv) dropwise at 0 °C, and the reaction mixture was stirred at room temperature for 30 min. The reaction mixture was poured into aqueous $NaHCO_3$ and extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (4 × 15 mL), dried over $Na_2SO_4$ and evaporated to dryness. The resulting crude residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc = 30/1→10/1) to afford **23** (90 mg, 67% over 2 steps) as colorless oil. $R_f$ = 0.3 (petroleum ether/EtOAc = 8/1); $[\alpha]_D^{20}$ = + 351.6 (*c* 0.9, $CHCl_3$); **$^1$H NMR** (300 MHz, $CDCl_3$) δ 5.94 (d, *J* = 7.8 Hz, 1H), 5.51 (d, *J* = 7.8 Hz, 1H), 4.80 (dd, *J* = 6.9, 1.5 Hz, 1H), 4.55 (d, *J* = 12.3 Hz, 1H), 4.45 (d, *J* = 12.3 Hz, 1H), 3.87 (dd, *J* = 5.7, 2.4 Hz, 1H), 2.83 (sept, *J* = 6.9 Hz, 1H), 2.71 (dd, *J* = 17.1, 6.9 Hz, 1H), 2.62 (dd, *J* = 16.5, 5.7 Hz, 1H), 2.53 (d, *J* = 17.1 Hz, 1H), 2.21–2.08 (m, 2H), 2.07(s, 3H), 2.04 (s, 3H), 1.97 (td, *J* = 13.5, 4.2 Hz, 1H), 1.39 (dt, *J* = 13.2, 3.6 Hz, 1H), 1.15 (dt, *J* = 13.2, 3.6 Hz, 1H), 1.01 (s, 3H), 0.97 (d, *J* = 6.9 Hz, 3H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.90 (s, 3H), 0.88 (s, 9H), 0.05 (s, 3H), 0.03 (s, 3H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 171.0, 170.8, 144.0, 140.4, 139.7, 132.6, 125.5, 120.0, 78.9, 77.3, 70.1, 52.4, 45.7, 39.1, 31.8, 31.3, 26.8, 26.5, 25.9, 23.0, 21.7, 21.3, 21.3, 21.1, 18.2, -4.5, -4.8; **HRMS** (ESI) m/z calcd for $C_{30}H_{48}NaO_5Si^+$ $[M+Na]^+$: 539.3163, found 539.3163.

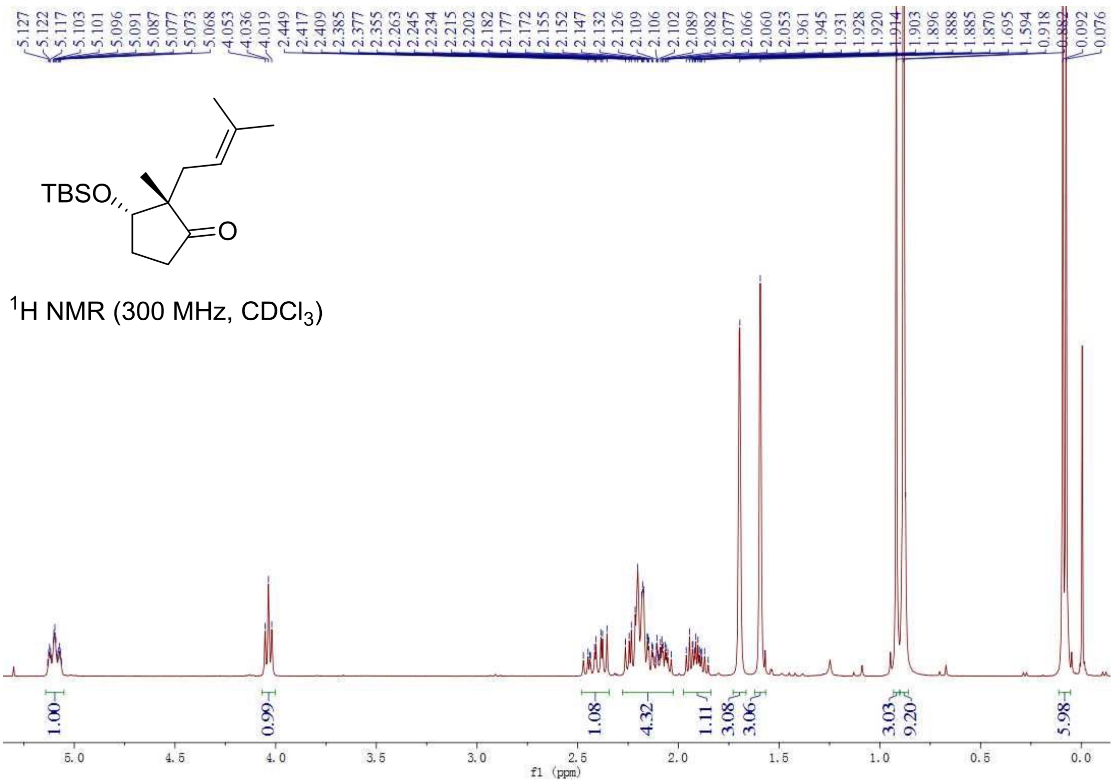
To a stirred solution of **23** (76 mg, 0.147 mmol) in THF (2 mL) was added HF •Py (75%, 0.6 mL) dropwise at 0 °C under argon atmosphere, and the reaction mixture was stirred at room temperature for 2 h. The reaction mixture was poured into aqueous $NaHCO_3$, and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with aqueous $NaHCO_3$ (3 × 5 mL) and brine (15 mL), dried over $Na_2SO_4$, and evaporated to dryness. The resulting crude residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc = 6/1→3/1) to afford **SI-4** (55 mg, 93%) as colorless oil. $R_f = 0.3$ (petroleum ether/EtOAc = 2/1).

To a stirred solution of **SI-4** (55 mg, 0.137 mmol) in $CH_2Cl_2$ (1.5 mL) was added DMP (116 mg, 0.274 mmol, 2.0 equiv) at room temperature. The reaction mixture was stirred at the same temperature for 4 h and quenched by addition of saturated aqueous $Na_2SO_3/NaHCO_3$. The organic phase was collected, and the aqueous layer was extracted with $CH_2Cl_2$ (2 × 10 mL). The combined organic layers were dried over $Na_2SO_4$ and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (eluent: petroleum ether/EtOAc = 10/1) yielded **9** (50 mg, 85% over 2 steps) as colorless oil. $R_f = 0.5$ (petroleum ether/EtOAc = 2/1); $[\alpha]_D^{20} = +368.8$ ($c$ 0.093, $CH_2Cl_2$); **$^1$H NMR** (300 MHz, $CDCl_3$) δ 5.98 (d, *J* = 7.8 Hz, 1H), 5.65 (d, *J* = 7.8 Hz, 1H), 4.81–4.75 (m, 1H), 4.56 (d, *J* = 12.6 Hz, 1H), 4.47 (d, *J* = 12.6 Hz, 1H), 3.04 (d, *J* = 22.8 Hz, 1H), 3.00 (sept, *J* = 6.9 Hz, 1H), 2.91 (d, *J* = 22.8 Hz, 1H), 2.74 (dd, *J* = 17.4, 6.6 Hz, 1H), 2.58 (d, *J* = 17.4 Hz, 1H), 2.13–2.01 (m, 1H), 2.08 (s, 3H), 2.04 (s, 3H), 1.68–1.61 (m, 2H), 1.38 (dt, *J* = 13.8, 3.3 Hz, 1H), 1.07 (d, *J* = 6.9 Hz, 3H), 1.04 (s, 3H), 1.01 (s, 3H), 0.96 (d, *J* = 6.9 Hz, 3H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 220.7, 170.9, 170.7, 141.3, 141.3, 137.9, 134.0, 124.8, 121.5, 76.3, 69.8, 53.3, 45.3, 39.8, 31.1, 30.8, 28.6, 26.3, 25.8, 21.8, 21.2, 21.1, 21.1, 19.7.

## References

1. (*a*) G.-J. Wu, Y.-H. Zhang, D.-X. Tan and F.-S. Han, *Nat. Commun.*, 2018, **9**, 2148; (*b*) G.-J. Wu, Y.-H. Zhang, D.-X. Tan, L. He, B.-C. Cao, Y.-P. He and F.-S. Han, *J. Org. Chem.*, 2019, **84**, 3223.
2. (*a*) J. Takagi, A. Kamon, T. Ishiyama and N. Miyaura, *Synlett*, 2002, **11**, 1880; (*b*) T. Ishiyama, J. Takagi, A. Kamon and N. Miyaura, *J. Organomet. Chem.*, 2003, **687**, 284; (*c*) X. Zhao, C. Song and J. D. Rainier, *Org. Lett.*, 2019, **21**, 8611.

## 3. Copies of NMR Spectra



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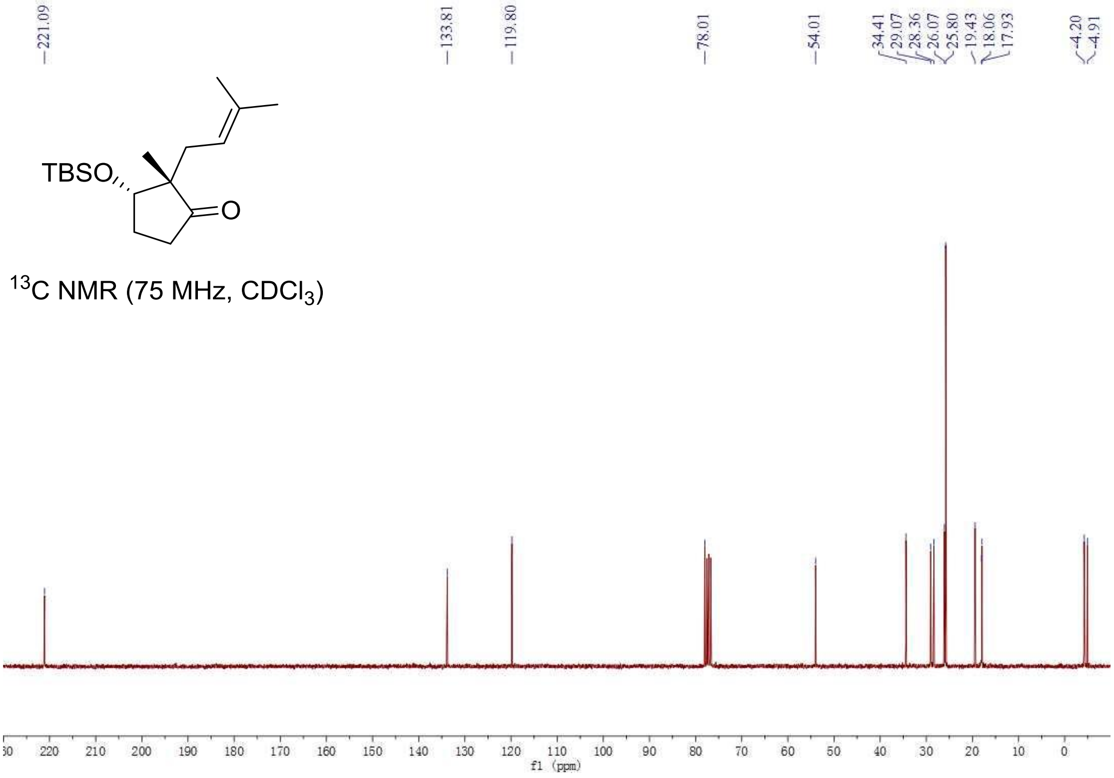

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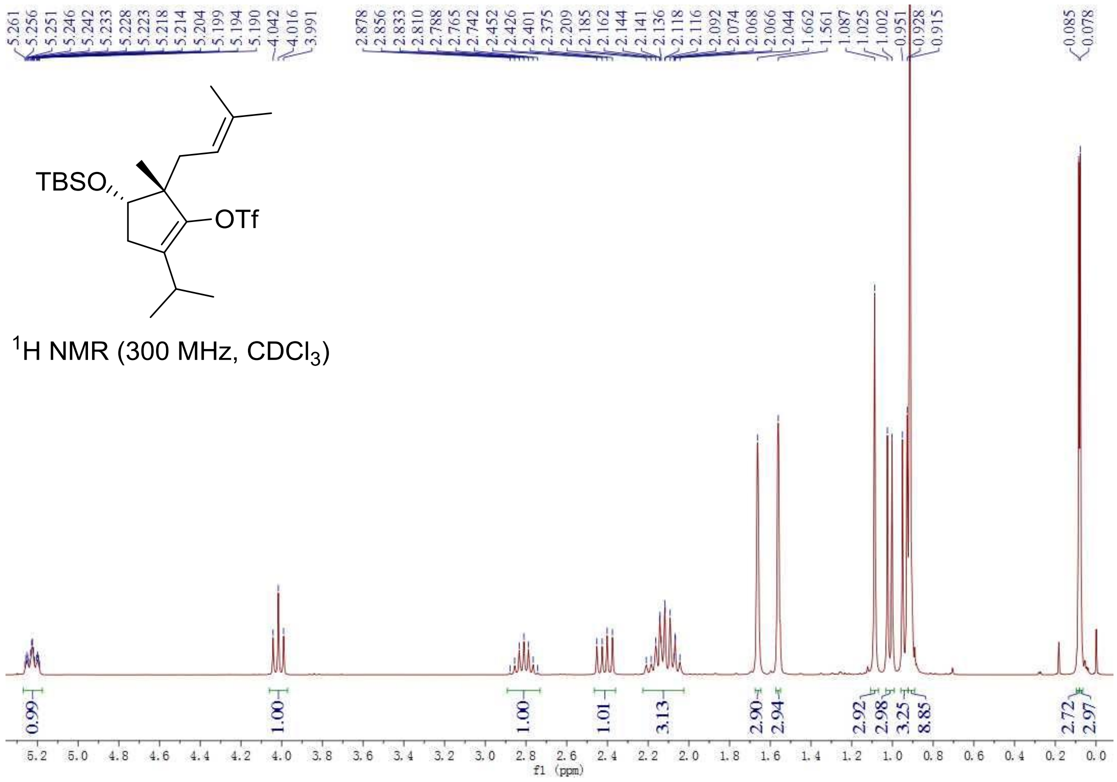

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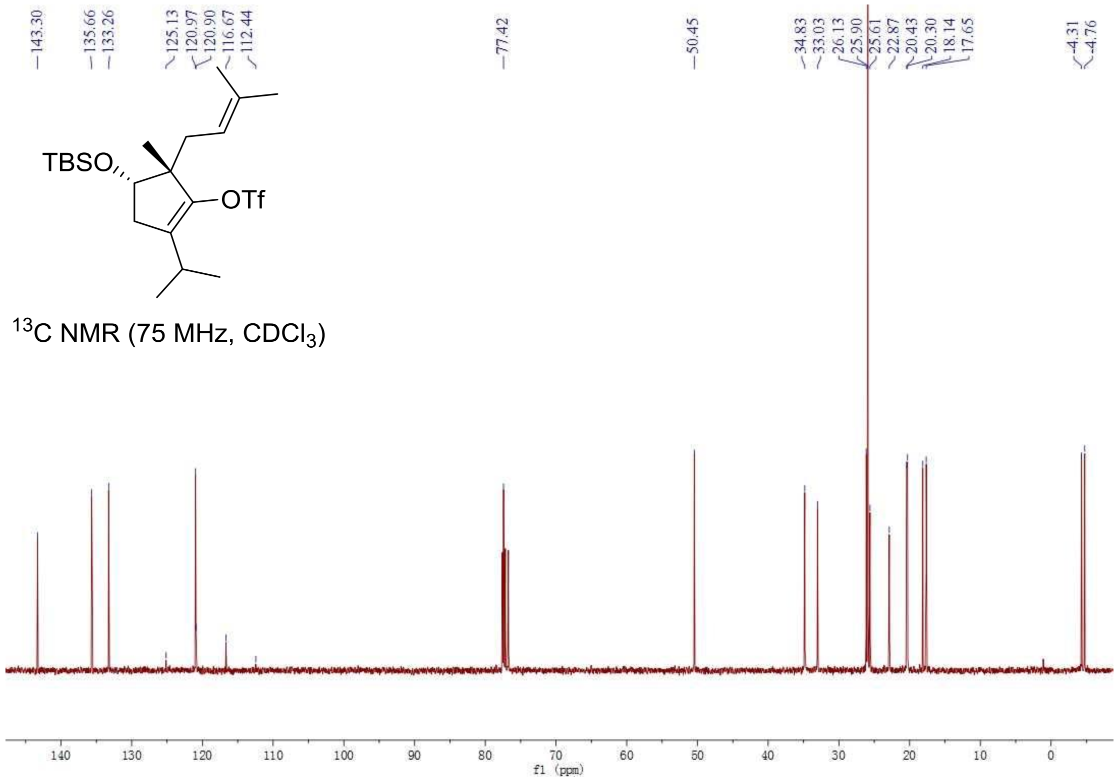

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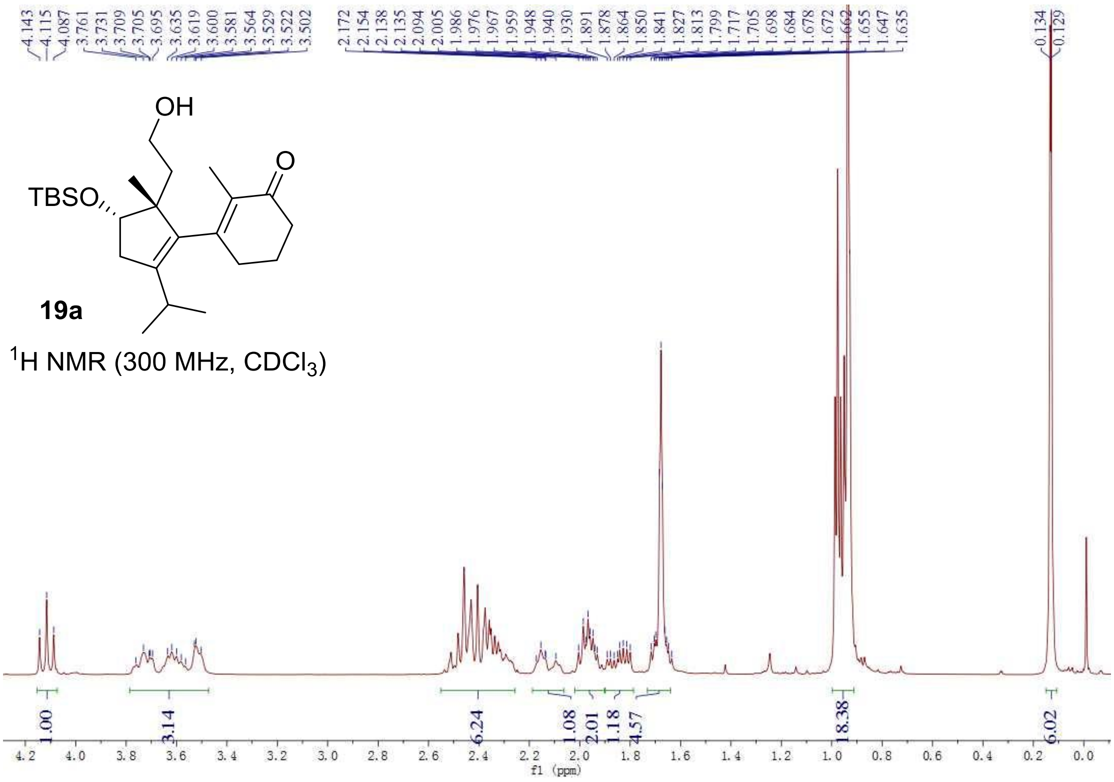

**19a**

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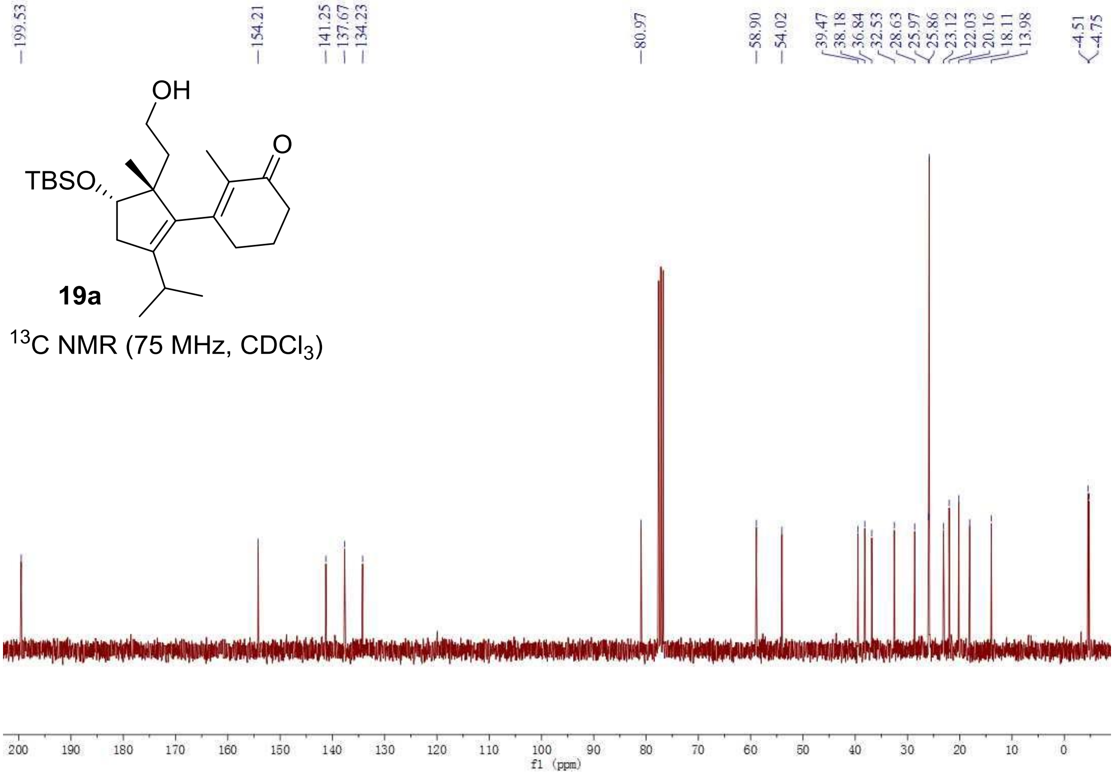

**19a**

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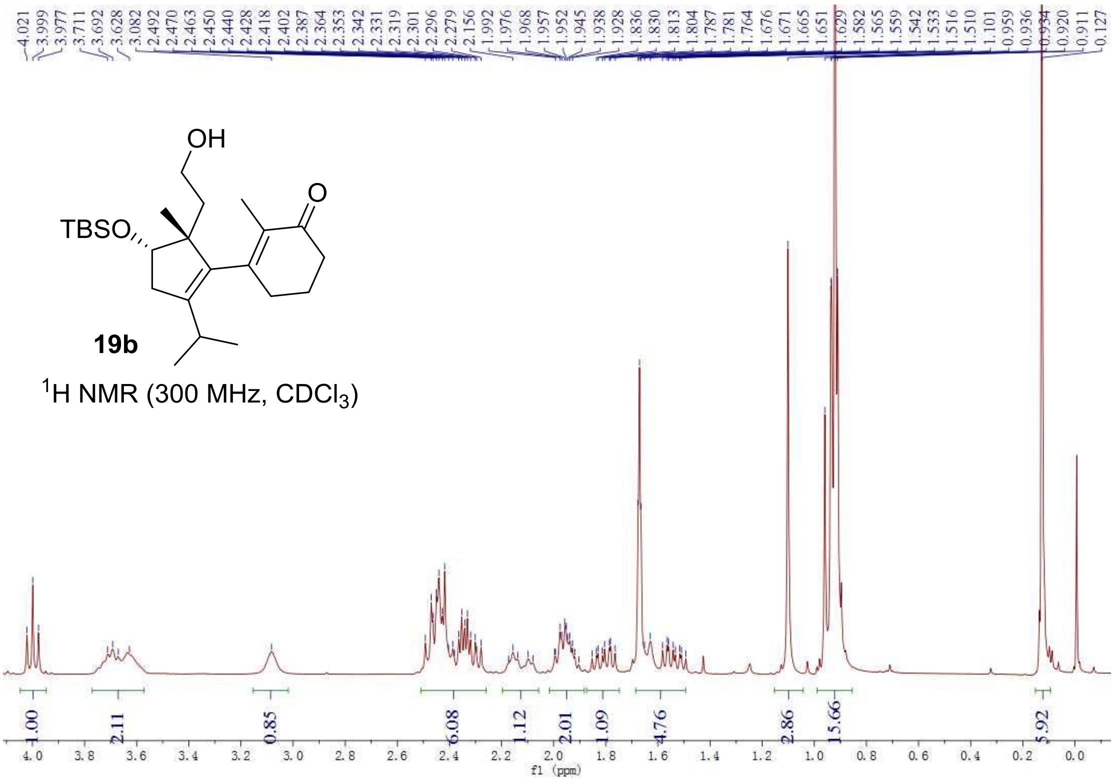

**19b**

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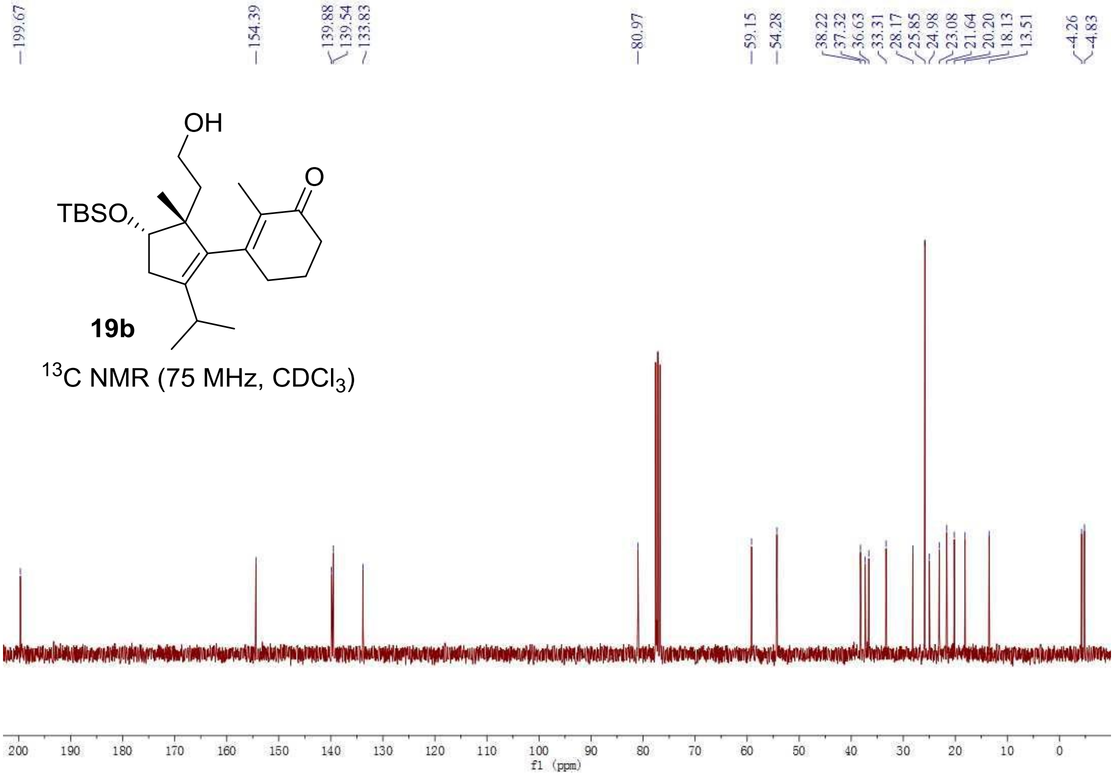

**19b**

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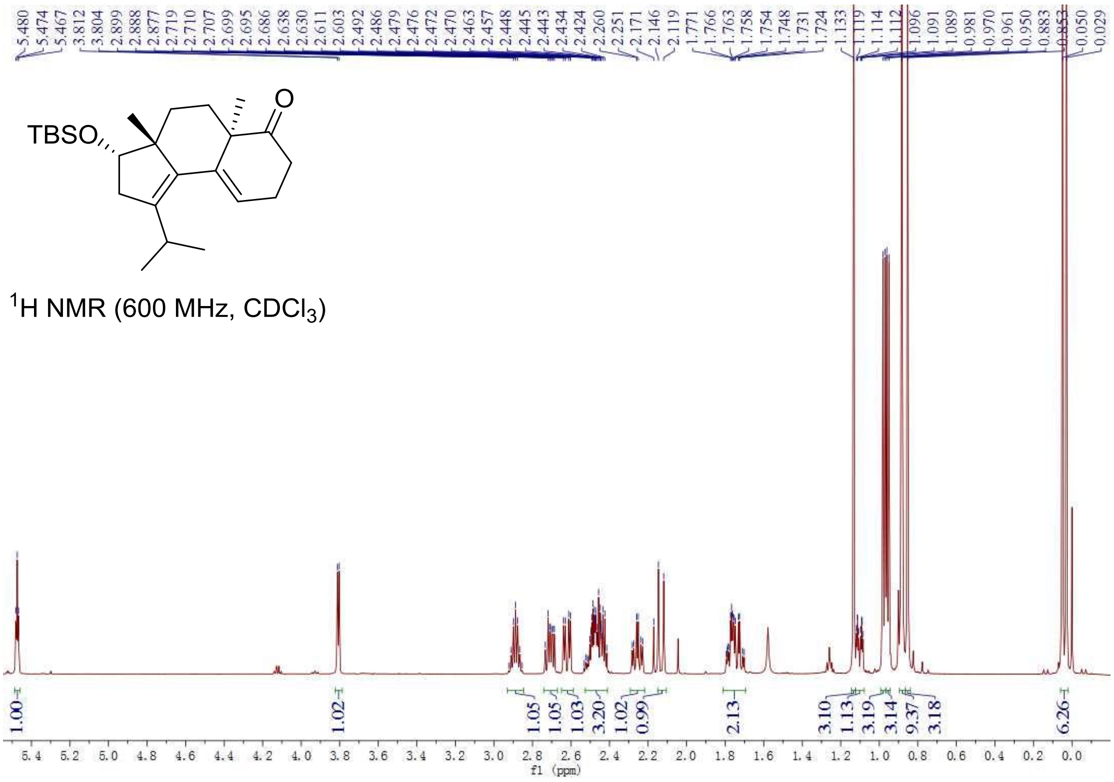

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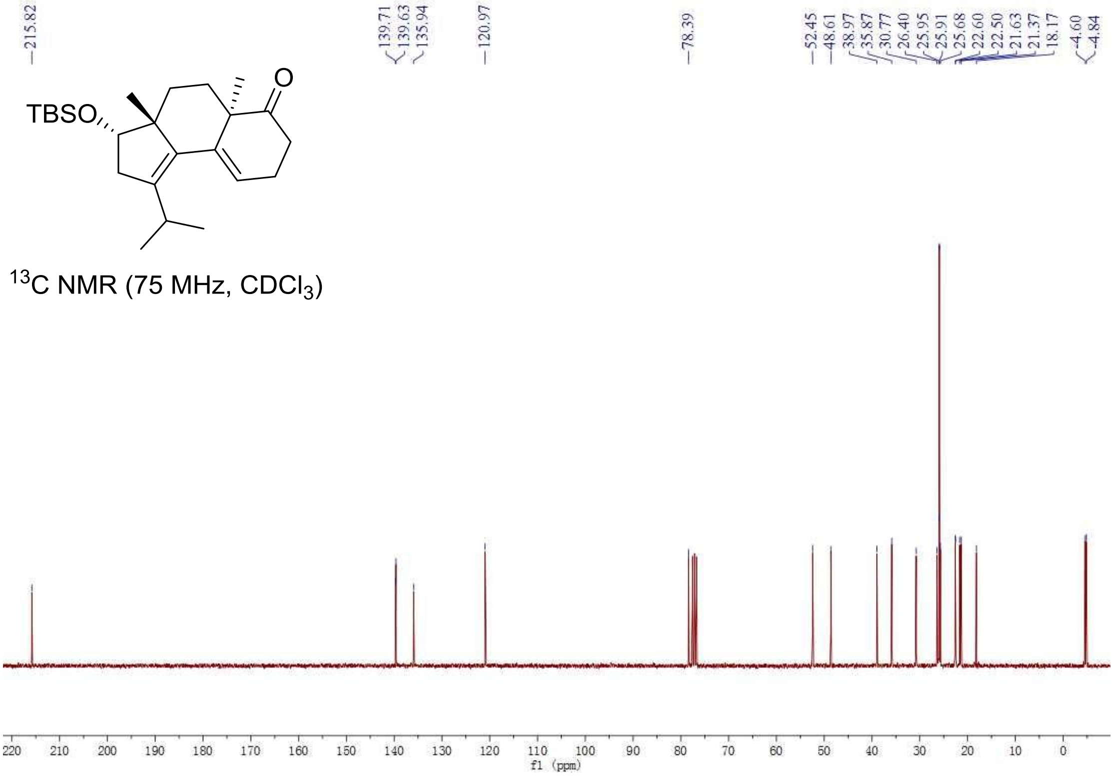

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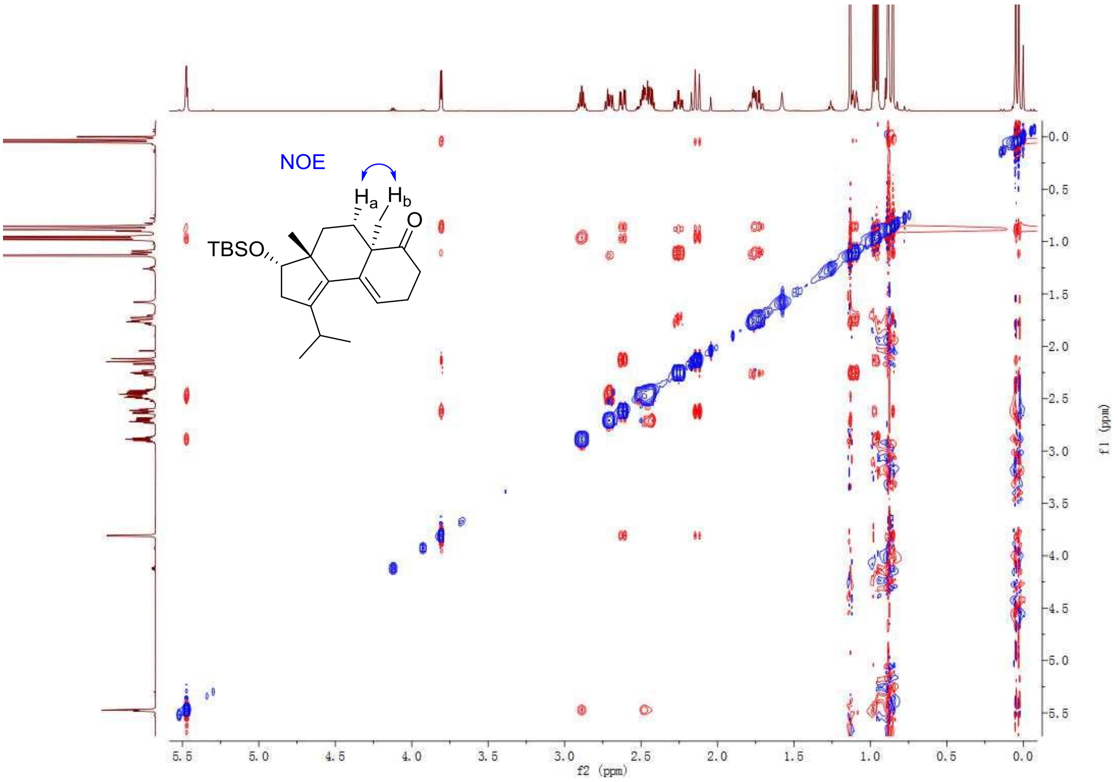
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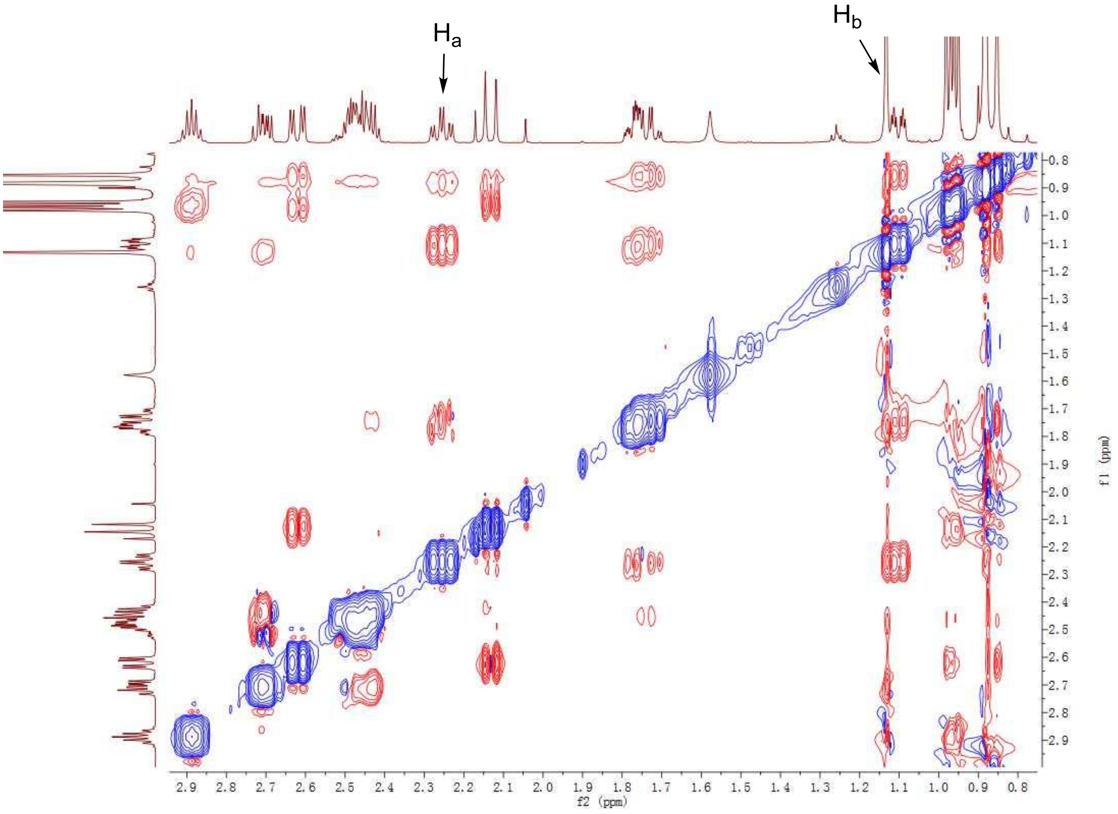
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5
f1 (ppm)


Ha
Hb
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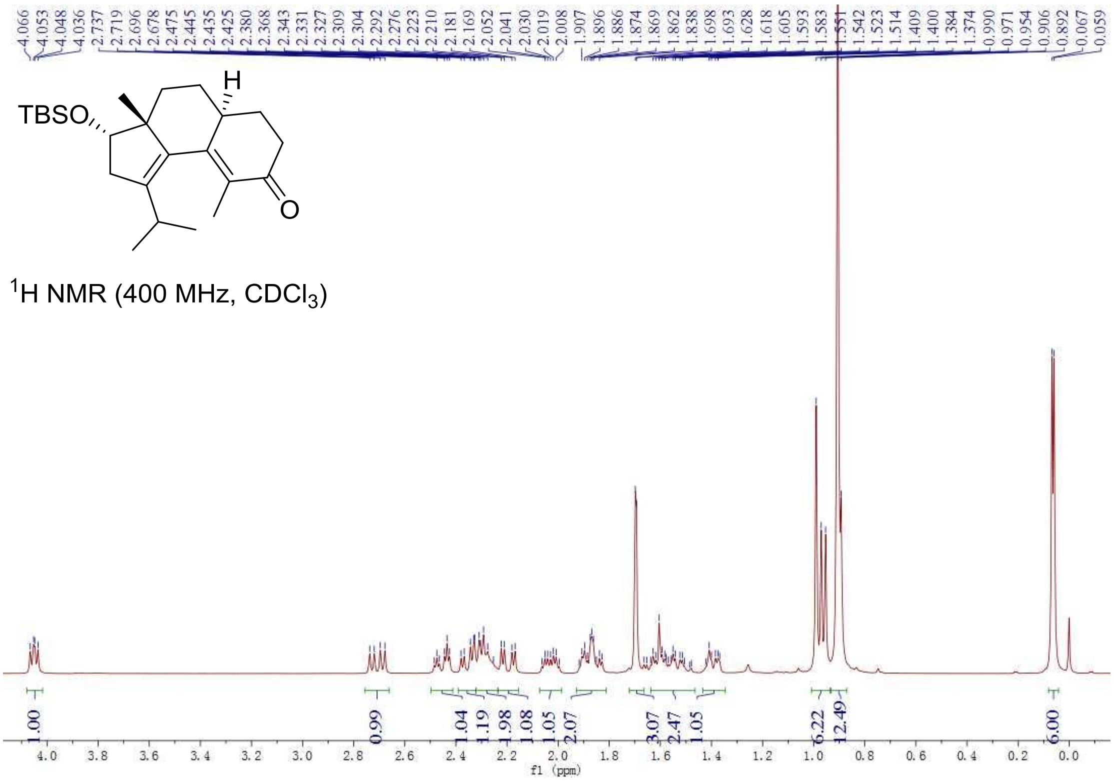
f2 (ppm)
0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6 2.7 2.8 2.9
f1 (ppm)



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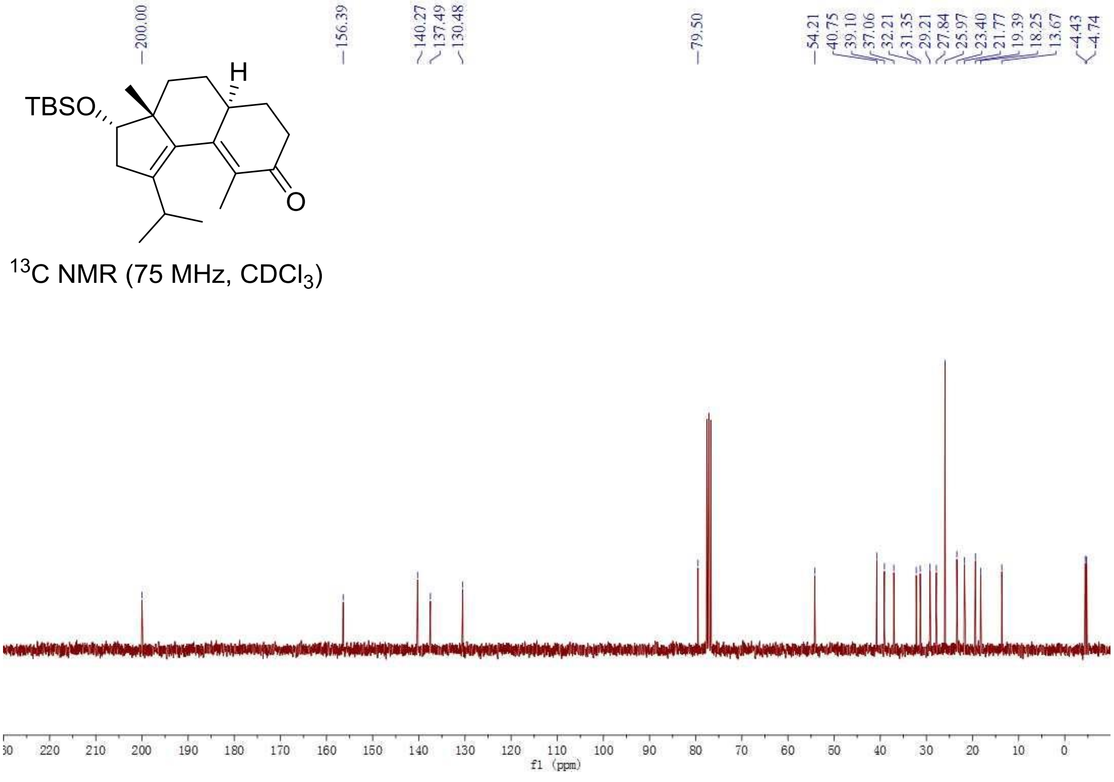

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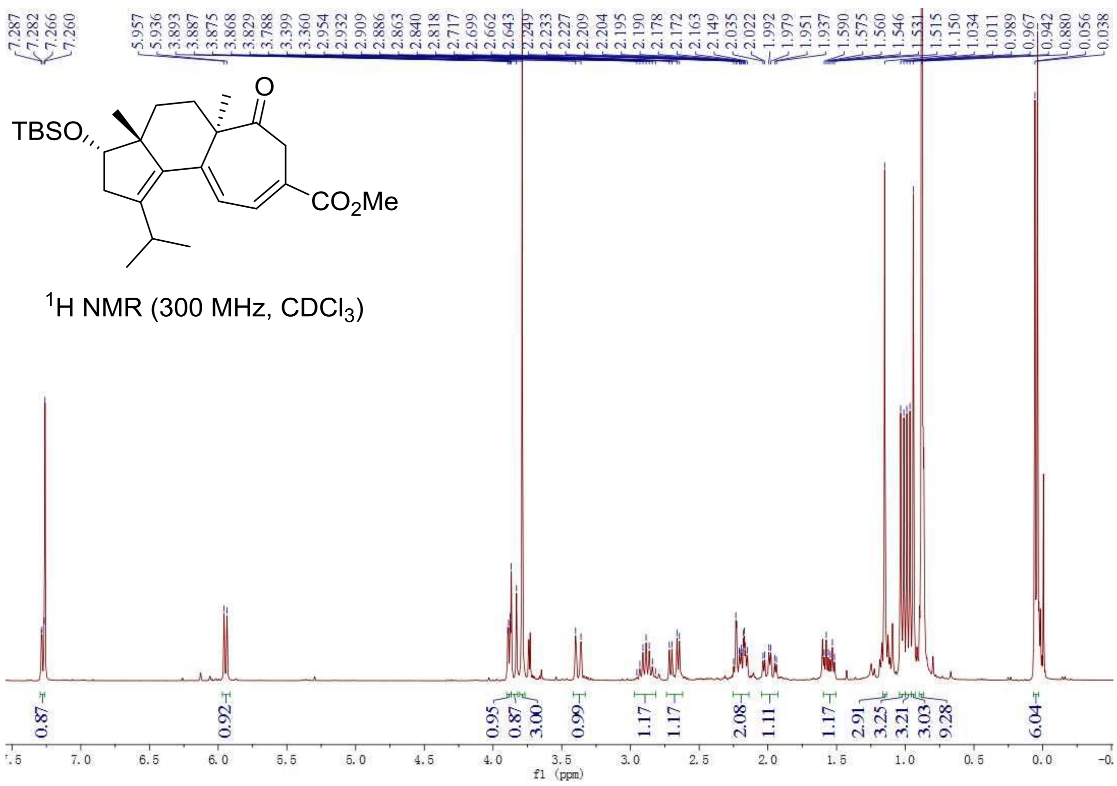
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2.932
2.909
2.886
2.863
2.840
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2.717
2.699
2.662
2.643
2.249
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2.149
2.035
2.022
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1.560
1.546
1.531
1.515
1.150
1.034
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0.056
0.038
TBSO
O
CO2Me
1H NMR (300 MHz, CDCl3)
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0.87
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0.99
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1.17
2.08
1.11
1.17
2.91
3.25
3.21
3.03
9.28
6.04
7.5
7.0
6.5
6.0
5.5
5.0
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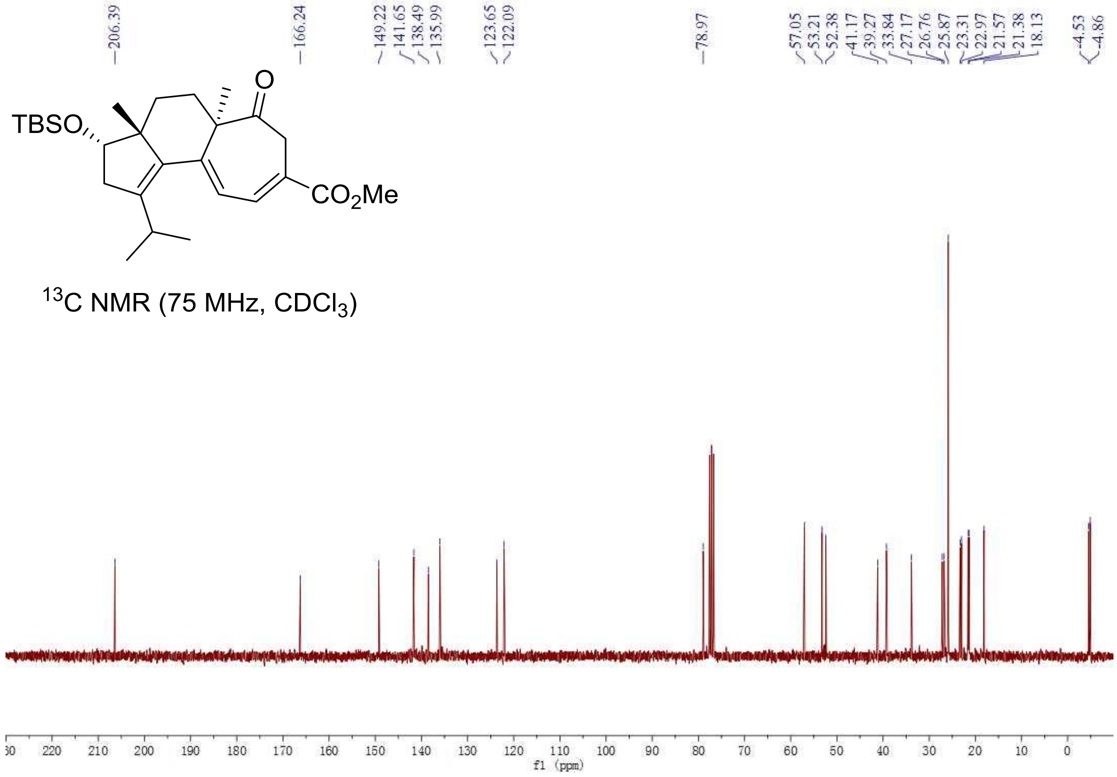
-0.
f1 (ppm)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39.27
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26.76
25.87
23.31
22.97
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21.38
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13C NMR (75 MHz, CDCl3)
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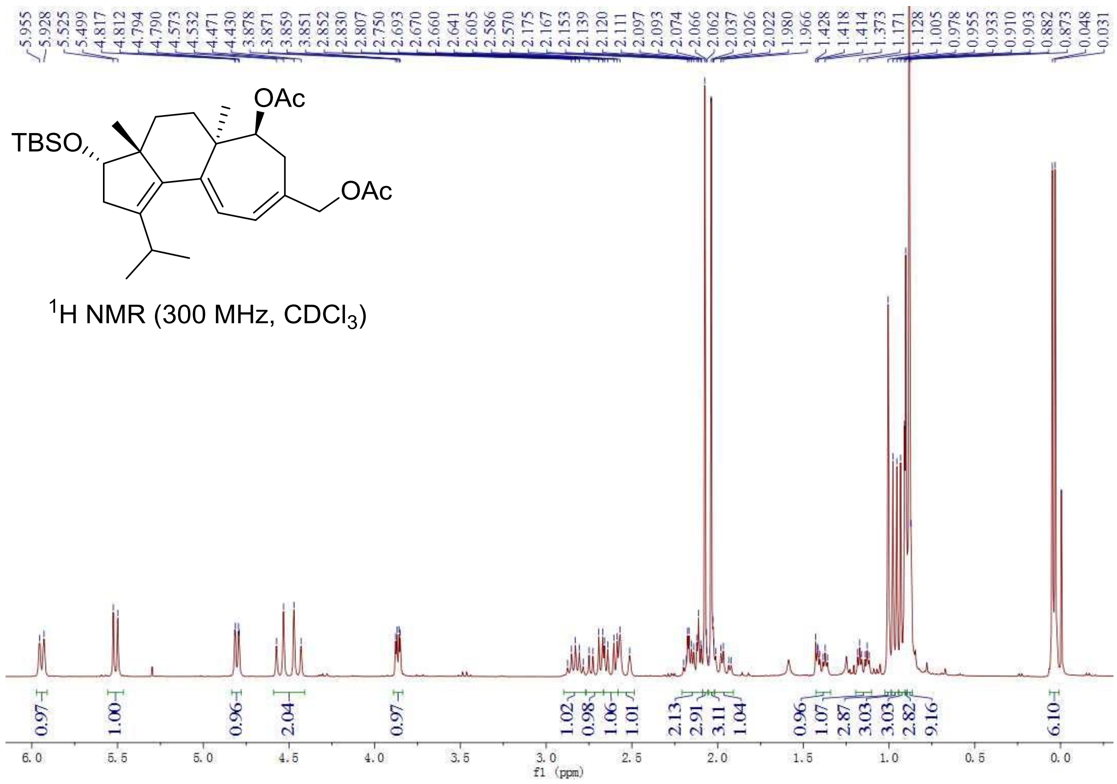

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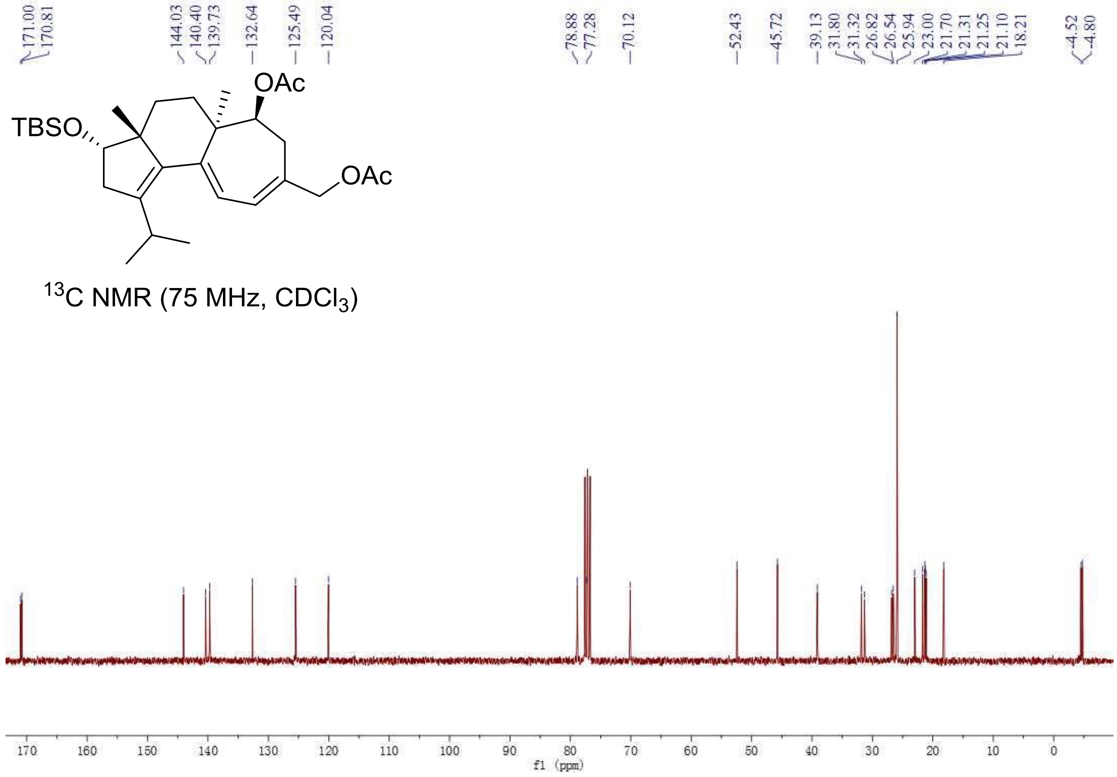

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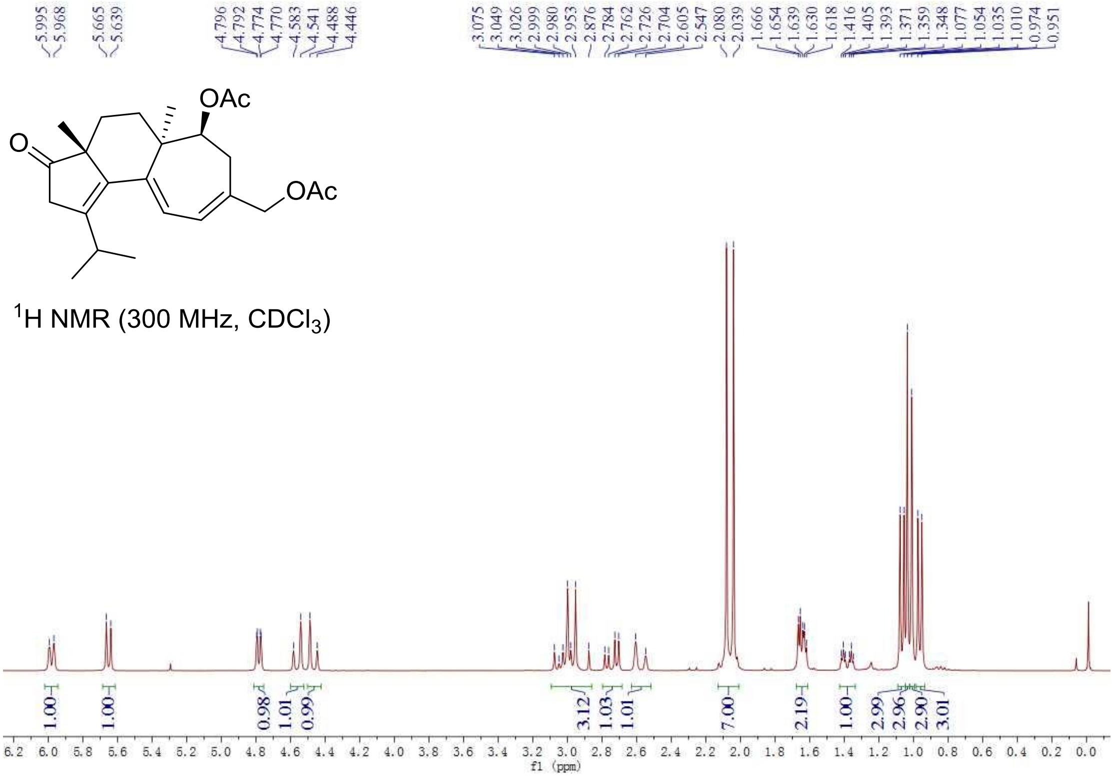

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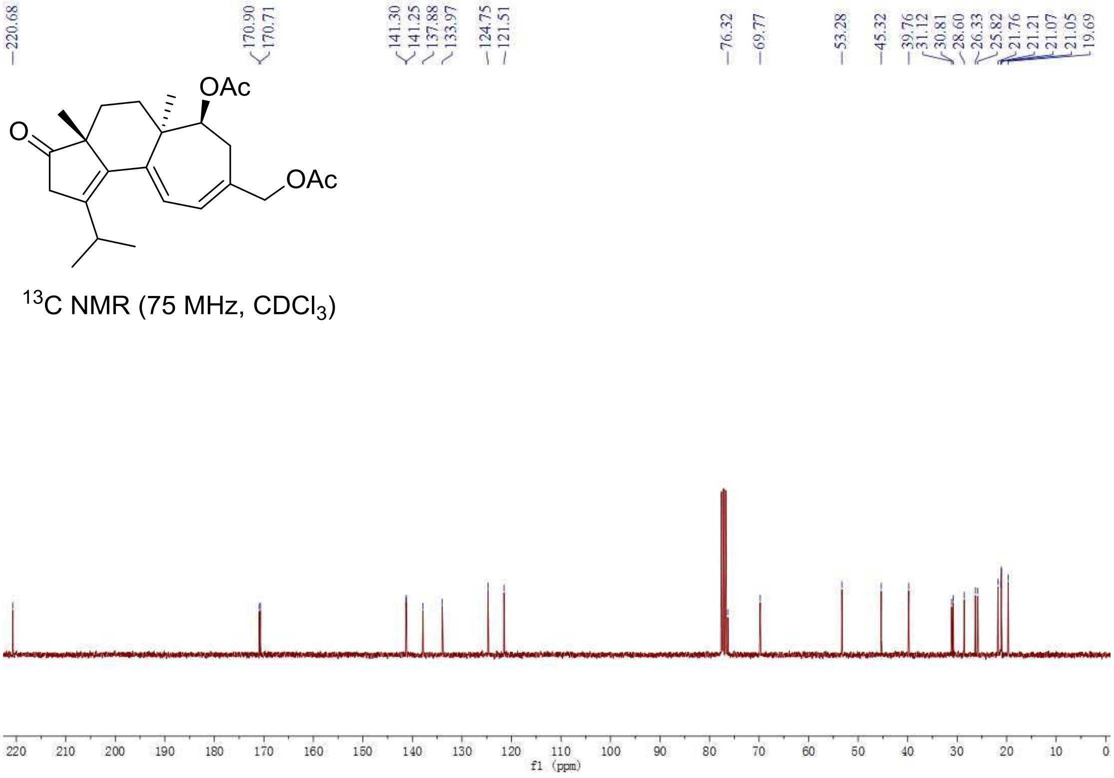

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