

Supporting Information

Asymmetric Total Synthesis of (+)-Waihoensene

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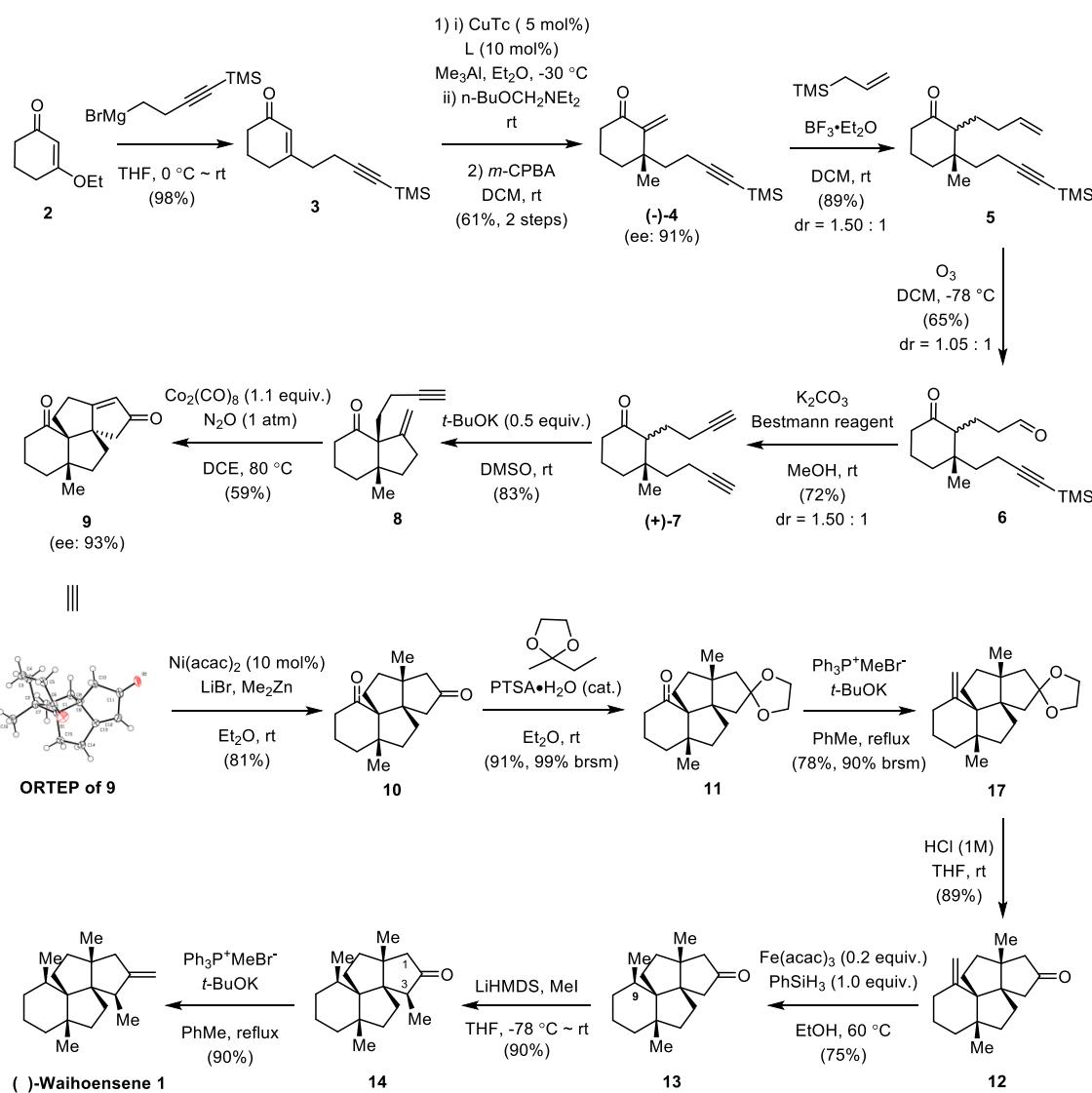
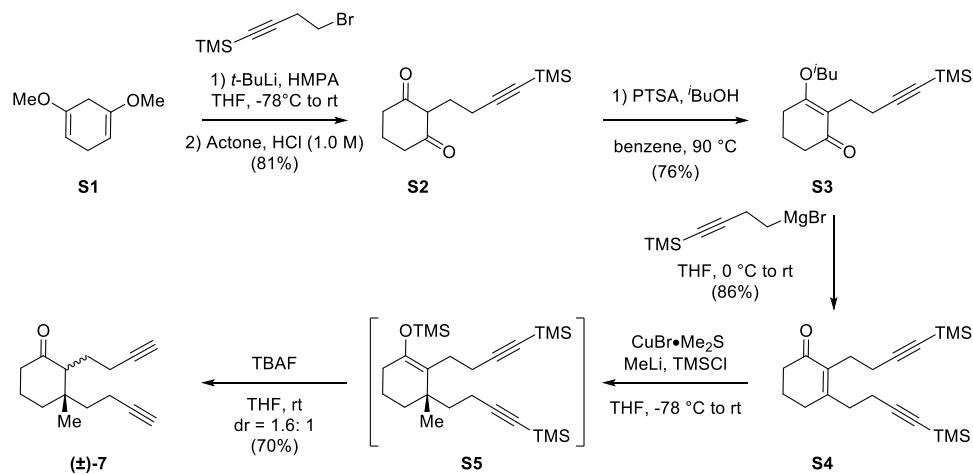
Part I: General Information

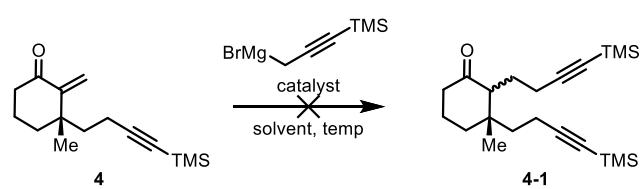
Unless otherwise mentioned, all reactions were carried out under a argon atmosphere with dry solvents, unless otherwise noted. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Solvents purification was conducted according to Purification of Laboratory Chemicals (Peerrin, D. D.; Armarego, W. L. and Perrins, D. R., Pergamon Press: Oxford, 1980). Concentration of solutions was accomplished using a Büchi rotary evaporator with a water aspirator. Yields refer to chromatographically and spectroscopically (¹H NMR) homogeneous materials. This was generally followed by removal of residual solvents on a vacuum line held at 0.1–1 torr.

Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Tsingdao silica gel plates (GF-254). Visualization on TLC was achieved by use of UV light at 254 nm, exposure to iodine vapor. Staining was performed with an ethanolic solution of phosphomolybdic acid (PMA) and cerium sulfate, or by oxidative staining with an aqueous basic potassium permanganate (KMnO₄) solution and subsequent heating. Tsingdao silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography.

NMR spectra were recorded on either a Brüker Advance 400 (¹H: 400 MHz, ¹³C: 100 MHz) or Brüker Advance 500 (¹H: 500 MHz, ¹³C: 125 MHz) and were calibrated using residual undeuterated solvent as an internal reference (CDCl₃: ¹H NMR = 7.26 ppm, ¹³C NMR = 77.00 ppm; C₆D₆: ¹H NMR = 7.15 ppm, ¹³C NMR = 128.00 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet. IR spectra were recorded on an IR Prestige-21 FTIR spectrometer with a KBr disc. High resolution mass spectrometric (HRMS) data were recorded on a Brüker Apex IV RTMS instrument and a VG Auto Spec-3000 spectrometer, respectively. Optical rotation values were recorded on a Rudolph Research Analytical Autopol I polarimeter (Rudolph Research Co.).

Part II: Experimental Procedures and Spectroscopic Data

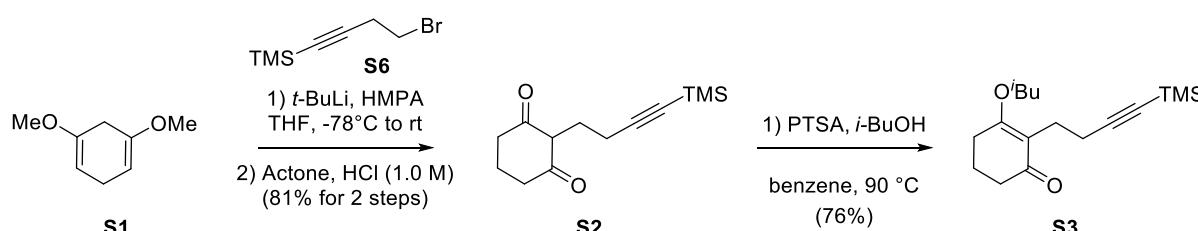




entry	catalyst	equiv.	solvent	temp (°C)	yield (%)
1	CuI	0.1	THF	-78	0
2	CuBr Me ₂ S	0.1	THF	-78 to 0	0
3	CuCN	0.1	THF	-78	0

Scheme S3: Attempted Cu-mediated 1,4-addition reactions for the synthesis of compound **4-1**.

Preparation of compound S3



Compound **S3** was prepared by following the published procedures^[1]. To a solution of *t*-BuLi (2.5 M, 6.70 mL, 16.75 mmol, 2.3 equiv.) in dry THF (28 mL) was added 1,5-dimethoxy-1,4-cyclohexadiene **S1** (1.00 g, 7.14 mmol, 1.0 equiv.) at -78 °C, and the resultant solution was stirred at the same temperature for 1 h. To this solution was added HMPA (10.70 mL, 61.50 mmol, 8.6 equiv.), and the mixture was stirred at the same temperature for 10 min. To this solution was added 4-bromo-1-trimethylsilyl-1-butyne **S6**^[2] (1.50 mL, 8.57 mmol, 1.2 equiv.) at -78 °C, and the resultant mixture was then warmed up to room temperature, and stirred for 2 h. The resultant mixture was then quenched by addition of a saturated solution of NH₄Cl (10 mL), and the mixture was extracted with hexane (150 mL). The solvent was removed under vacuum, and the residue was used in next step without further purification.

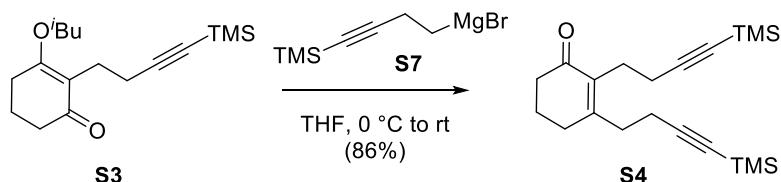
To a solution of the crude product in dry acetone (10 mL, previously purged with a stream of N₂ for 15 min) was added a solution of HCl, (1 M, 3 mL, previously purged with a stream of N₂ for 15 min) at the room temperature with vigorous stirring, and the resultant solution was stirred at the same temperature for 1 h. The reaction was worked up by addition of a saturated solution of NH₄Cl (10 mL), and the mixture was extracted with ethyl acetate (3 × 10 mL), and the combined extracts were washed with brine (2 × 5 mL), and the combined organic extracts were dried over Na₂SO₄. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 8 : 1) to afford compound **S2** (1.37 g, 81%).

To a solution of compound **S2** (2.30 g, 9.74 mmol, 1.0 equiv.) and isobutyl alcohol (16 mL, 175.32 mmol, 18.0 equiv.) in benzene (82 mL) was added PTSA·H₂O (556 mg, 2.92 mmol, 0.3 equiv.) under reflux using a Dean–Stark apparatus to trap the water for 5 h. The reaction was quenched by addition of a saturated solution of NaHCO₃ (10 mL), the resultant mixture was extracted with Et₂O (3 × 30 mL). The combined organic extracts were washed with brine (2 × 5 mL), and then dried over Na₂SO₄. The extract was filtered off through a short silica gel pad, and the filtrate was concentrated in vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 3 : 1) to give isobutyl ether **S3** (2.16 g, 76%).

R_f = 0.18 (hexane/EtOAc = 8:1, UV); ¹**H NMR** (500 MHz, CDCl₃) δ 3.74 (d, *J*=6.5, 2H), 2.58 – 2.46 (m, 4H), 2.35 – 2.28 (m, 2H), 2.25 (t, *J*=7.6, 2H), 2.04 – 1.91 (m, 3H), 0.98 (d, *J*=6.7, 6H), 0.10 (s, 9H) ppm; ¹³**C NMR** (125 MHz, CDCl₃) δ 197.8, 172.4, 117.8, 107.8, 83.5, 74.0, 36.3, 28.7,

25.5, 21.3, 20.9, 19.0, 18.9, 0.2 ppm; **HRMS (ESI)** m/z calcd for $C_{17}H_{28}NaO_2Si^+$ [M+Na⁺]: 315.1751; Found: 315.1753.

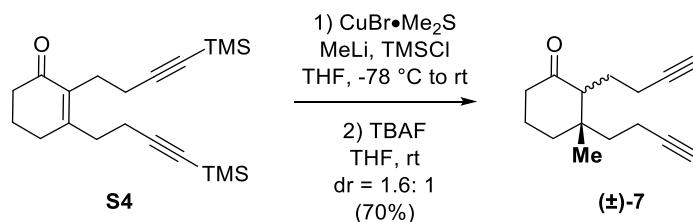
Preparation of compound S4:



To a stirred suspension of Mg turnings (2.53 g, 105.34 mmol, 3.0 equiv.) in THF (13 mL) was added iodine (ca. 50 mg), and the mixture was maintained to slightly reflux using hair drier. To this solution was added a solution of 4-bromo-1-trimethylsilyl-1-butyne **S6** (14.33 g, 70.23 mmol, 2.0 equiv.) in dry THF (84 mL) in a dropwise manner with a syringe pump, and the resultant mixture was stirred under reflux for 1 h. To a solution of isobutyl ether **S3** (10.26 g, 35.11 mmol, 1.0 equiv.) in THF (100 mL) was added the Grignard reagent **S7** made above at 0 °C, and the resultant mixture was allowed to warmed up to room temperature, and then stirred at the same temperature overnight. The reaction mixture was quenched by addition of a saturated solution of NH₄Cl (25 mL), and the mixture was extracted with Et₂O (3 × 50 mL). The combined organic phases were washed with brine (2 × 10 mL), and dried over Na₂SO₄. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 15 : 1) to give enone **S4** (10.39 g, 86%).

R_f = 0.50 (hexane/EtOAc = 8:1, UV); **¹H NMR** (500 MHz, CDCl₃) δ 2.61-2.47 (m, 4H), 2.46-2.32 (m, 6H), 2.29 (t, *J* = 7.2, 2H), 1.97-1.85 (m, 2H), 0.10 (s, 18H) ppm; **¹³C NMR** (125 MHz, CDCl₃) δ 198.7, 158.0, 134.6, 107.1, 105.3, 85.9, 84.7, 37.9, 33.8, 30.7, 24.3, 22.3, 19.5, 18.5, 0.05, -0.08 ppm; **HRMS (ESI)** m/z calcd for C₂₀H₃₂NaOSi₂⁺ [M+Na⁺]: 367.1884; Found: 367.1887.

Preparation of racemic compound 7:



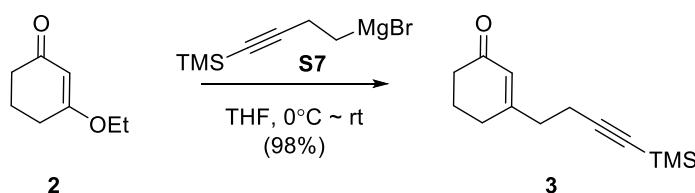
To a suspension of $\text{CuBr} \cdot \text{Me}_2\text{S}$ (0.60 g, 2.90 mmol, 2.4 equiv.) in dry THF (5 mL) was added MeLi (1.6 M, 3.60 mL, 5.76 mmol, 4.8 equiv.) at 0 °C in a dropwise manner, and the resultant mixture was stirred at the same temperature for 15 min. To this mixture was added TMSCl (0.79 g,

7.26 mmol, 6.0 equiv.) in a dropwise manner at -78 °C, and the mixture was stirred at the same temperature for 15 min. To this solution was added a solution of enone **S4** (417 mg, 1.21 mmol, 1.0 equiv.) in anhydrous THF (7 mL) at -78 °C in a dropwise manner, and the mixture was stirred at the same temperature for 1 h. The reaction mixture was warmed up to room temperature slowly, and then stirred at the same temperature overnight. The reaction was quenched by addition of a saturated solution of NH₄Cl (5 mL), and mixture was extracted with Et₂O (3 × 5 mL). The combined organic extracts were washed with brine (2 × 3 mL), and then dried over Na₂SO₄. The solvent was removed under vacuum, and the residue was used in next step without further purification.

To a solution of crude product made above in anhydrous THF (7 mL) was added TBAF (1 M solution in THF, 3.80 mL, 3.80 mmol, 3.1 equiv.) at room temperature, and the mixture was stirred at the same temperature for 1 h. The reaction was quenched by addition of water (5 mL), and the resultant mixture was extracted with Et₂O (3 × 5 mL). The combined organic phases were washed with brine (2 × 3 mL), and then dried over Na₂SO₄. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 30: 1) to give compound **7** (183 mg, 70%) as a yellow oil, which is an inconsequential 1.6 : 1 mixture.

R_f = 0.53 (hexane/EtOAc = 8:1, PMA); **¹H NMR** (500 MHz, CDCl₃) δ 2.43 (d, J = 10.7 Hz, 1.02H), 2.39 – 2.32 (m, 2.85H, overlap), 2.31 – 2.23 (m, 4.38H, overlap), 2.12 – 2.00 (m, 2.84H, overlap), 1.98 – 1.85 (m, 6.19H, overlap), 1.83 – 1.68 (m, 4.43H, overlap), 1.68 – 1.63 (m, 0.85H, overlap), 1.60 – 1.54 (m, 0.66H, overlap), 1.54 – 1.47 (m, 1.69H, overlap), 1.47 – 1.38 (m, 2.39H, overlap), 1.04 (s, 1.83H), 0.74 (s, 3H) ppm; **¹³C NMR** (125 MHz, CDCl₃) δ 211.8, 84.2, 84.1, 68.7, 60.0, 56.2, 41.7, 41.1, 34.9, 25.4, 17.6, 12.7 ppm (minor diastereomer); 212.1, 84.5, 84.3, 68.8, 68.4, 42.0, 41.6, 40.1, 35.7, 32.8, 22.5, 22.1, 20.4, 17.3, 13.0 ppm (major diastereomer); **HRMS (ESI)** m/z calcd for C₁₅H₂₀NaO⁺ [M+Na⁺]: 239.1406; Found: 239.1408.

Preparation of compound **3**:

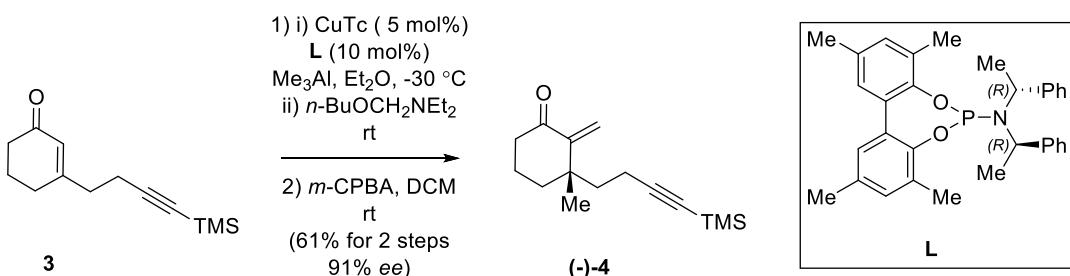


Compound **3** was prepared by the following procedure^[2]. To a solution of ethoxycyclohex-2-en-1-one **2** (7.50 g, 53.54 mmol, 1.0 equiv.) in THF (134 mL) in a flame-dried flask was added the Grignard reagent **S7** made above (144 mL, 107.08 mmol, 2.0 equiv.) at 0 °C in a dropwise manner, and the mixture was stirred at room temperature until starting material disappearance. The reaction was worked up by addition of a saturated solution of NH₄Cl (50 mL),

and the mixture was extracted with ethyl acetate (3×30 mL). The combined organic extracts were washed with brine (2×10 mL), and dried over Na_2SO_4 . The solvent was removed under vacuum, the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 8 : 1) to give enone **3** (11.60 g, 98%) as a yellow oil.

R_f = 0.73 (hexane/EtOAc = 8:1, UV); **¹H NMR** (500 MHz, CDCl₃) δ 5.88 (s, 1H), 2.42 (s, 4H), 2.37 – 2.33 (m, 2H), 2.33 – 2.29 (m, 2H), 2.02 – 1.95 (m, 2H), 0.11 (s, 9H) ppm; **¹³C NMR** (125 MHz, CDCl₃) δ 199.6, 163.7, 126.4, 105.1, 86.1, 37.3, 36.6, 29.5, 22.6, 18.0, -0.03 ppm; **HRMS (ESI)** m/z calcd for C₁₃H₂₀NaOSi⁺ [M+Na]⁺ : 243.1176; found: 243.1178.

Preparation of compound 4:



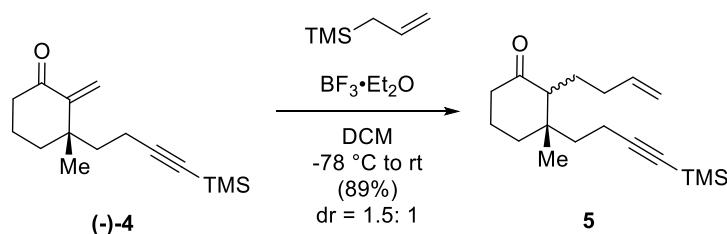
To a solution of copper(I) thiophene-2-carboxylate (29 mg, 0.15 mmol, 5 mol%) and ligand **L**^[3] (152 mg, 0.31 mmol, 10 mol%) in Et₂O (6 mL) in a flame-dried Schlenk tube was added a solution of Michael acceptor **3** (675 mg, 3.07 mmol, 1.0 equiv.) in Et₂O (6 mL) at room temperature, and the resultant mixture was stirred at the same temperature for 5 min, and then cooled to -30 °C. To this solution was added trimethylaluminium (1.6 M solution in toluene, 3.80 mL, 6.14 mmol, 2.0 equiv.) in a dropwise manner, and the reaction mixture was stirred at -30 °C overnight. To this solution was added N-(butoxymethyl)-N-ethylethanamine^[4] (1.50 mL, 7.68 mmol, 2.5 equiv.), and the mixture was warmed up to room temperature, and stirred at the same temperature for 3 h. The reaction was worked up by addition of Et₂O (6 mL) followed by addition of aqueous solution of NaOH (5%) carefully. The mixture was extracted with Et₂O (3 × 30 mL), and the combined organic extracts were dried over Na₂SO₄. The solvent was removed in vacuum, and the residue was used directly in next step without purification.

To a solution of the crude product made above in DCM (77 mL) was added *m*-CPBA (85 weight%, 935 mg, 4.61 mmol, 1.5 equiv.) at room temperature in several portions, and the mixture was stirred at the same temperature for 1 h. The reaction was worked up by addition of DCM (20 mL), and the mixture was washed with a saturated solution of NaHCO₃ (2 × 20 mL), and separated organic phase was dried over Na₂SO₄. The solvent was removed in vacuum, and the residue was purified by a column chromatography on silica gel (hexane/EtOAc = 40 : 1 to 30 : 1) to give enone **4** (460 mg, 61% with 91% ee for 2 steps) as a yellow oil (see page 25 for determination methods of

the ee value).

R_f = 0.50 (hexane/EtOAc = 8:1, UV); [α]_D²⁴ = - 61.70 (*c* 1.53, CHCl₃); **¹H NMR** (500 MHz, CDCl₃) δ 5.77 (s, 1H), 5.12 (s, 1H), 2.53 – 2.44 (m, 1H), 2.41 – 2.31 (m, 1H), 2.17 – 2.07 (m, 2H), 1.99 – 1.90 (m, 1H), 1.90 – 1.82 (m, 1H), 1.77 – 1.69 (m, 1H), 1.67 (dd, *J* = 14.2, 7.5 Hz, 2H), 1.63 – 1.56 (m, 1H), 1.11 (s, 3H), 0.11 (s, 9H) ppm; **¹³C NMR** (125 MHz, CDCl₃) δ 203.3, 153.6, 117.9, 107.1, 84.6, 40.5, 40.4, 38.3, 35.9, 25.6, 19.2, 14.7, 0.1 ppm; **IR** (thin film) 2960, 2941, 2175, 1696, 1249, 842, 759 cm⁻¹; **HRMS (ESI)** m/z calcd for C₁₅H₂₄NaOSi⁺ [M+Na]⁺ : 271.1498; found: 271.1500.

Preparation of compound 5:

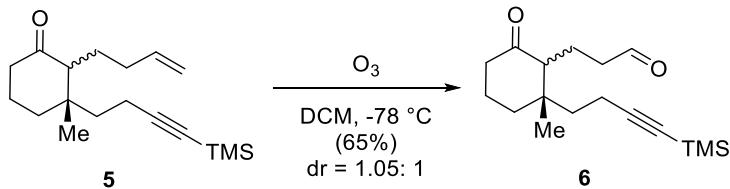


To a solution of enone **4** (444 mg, 1.79 mmol, 1.0 equiv.) in DCM (6.0 mL) was added BF₃·Et₂O (250 μL, 1.97 mmol, 1.1 equiv.) at -78 °C in a dropwise manner, and the mixture was stirred at the same temperature for 10 min. To this solution was added allyltrimethylsilane (0.43 mL, 2.68 mmol, 1.5 equiv.) at -78 °C in a dropwise manner, and the mixture was stirred at the same temperature for 1 h. After warming up to 0 °C, the resultant mixture was first stirred at the same temperature for 1 h, and then warmed up to room temperature followed by stirring for at the same temperature for 30 min. After cooling back to 0 °C, the reaction mixture was quenched by addition of a saturated solution of NaHCO₃ (3 mL), and the resultant mixture was extracted with DCM (3 × 10 mL). The combined organic extracts were dried over Na₂SO₄. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 70 : 1 to 60 : 1) to give compound **5** (460 mg, 89%) as a pair of diastereomers in a ratio of 1.5:1 in a form of yellow oil.

R_f = 0.68 (hexane/EtOAc = 8:1, PMA); [α]_D²² = + 6.22 (*c* 0.45, CHCl₃); **¹H NMR** (400 MHz, CDCl₃) δ 5.84 – 5.69 (m, 1.54H, overlap), 5.03 – 4.90 (m, 3.12H, overlap), 2.43 – 2.29 (m, 2.09H, overlap), 2.29 – 2.17 (m, 4.13H, overlap), 2.17 – 2.00 (m, 4.89H, overlap), 1.97 – 1.71 (m, 8.46H, overlap), 1.71 – 1.63 (m, 2.19H, overlap), 1.57 – 1.49 (m, 1.75H, overlap), 1.49 – 1.41 (m, 2.04H, overlap), 1.40 – 1.35 (m, 0.96H, overlap), 1.35 – 1.27 (m, 1.76H, overlap), 0.99 (s, 2H), 0.76 (s, 3H), 0.14 (s, 8.84H, overlap), 0.13 (s, 5.52H, overlap) ppm; **¹³C NMR** (100 MHz, CDCl₃) δ 212.9, 138.5, 114.9, 107.2, 84.6, 60.6, 57.6, 41.9, 41.2, 39.8, 34.9, 32.7, 22.7, 20.6, 14.5, 0.1 ppm (major diastereomer); 138.3, 107.1, 84.5, 41.6, 40.7, 34.4, 33.6, 25.07, 23.2, 22.8, 22.5, 14.1, 0.1 ppm

(minor diastereomer); **IR** (thin film) 2959, 2933, 2175, 1715, 1249, 842, 759 cm⁻¹; **HRMS (ESI)** m/z calcd for C₁₈H₃₀NaOSi⁺ [M+Na]⁺: 313.1958; found: 313.1960.

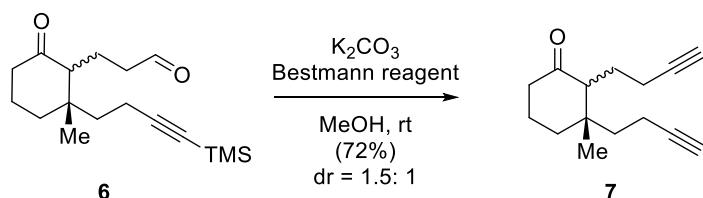
Preparation of compound 6:



To a solution of alkene **5** (266 mg, 0.92 mmol, 1.0 equiv.) in DCM (30 mL) was bubbled ozone (40% in air) at -78 °C until the starting material disappeared (TLC analysis, about 1 min), and the mixture was purged with air at -78 °C followed by addition of PPh₃ (250 mg, 0.95 mmol, 1.0 equiv.). The mixture was warmed up to room temperature slowly, and stirred at the same temperature for 12 h. After removal of the solvent, the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 5 : 1 to 3 : 1) to give compound **6** as a colorless oil (173 mg, 65%), which is an inconsequential 1.05: 1 mixture.

R_f = 0.25 (hexane/EtOAc = 8:1, PMA); $[\alpha]_D^{25} = -4.44$ (*c* 1.31, CHCl₃); **¹H NMR** (400 MHz, CDCl₃) δ 9.77 – 9.70 (m, 1.69H, overlap), 2.63 – 2.48 (m, 2.21H, overlap), 2.42 – 2.18 (m, 9.27H, overlap), 2.18 – 2.06 (m, 3.58H, overlap), 2.00 – 1.82 (m, 5.93H, overlap), 1.82 – 1.72 (m, 4.72H, overlap), 1.71 – 1.60 (m, 3.95H, overlap), 1.58 – 1.49 (m, 2.12H, overlap), 1.49 – 1.35 (m, 2.79H, overlap), 1.06 (s, 3H), 0.77 (s, 2.84H), 0.14 (s, 8.31H), 0.12 (s, 9H) ppm; **¹³C NMR** (100 MHz, CDCl₃) δ 212.4, 202.1, 106.9, 84.7, 60.8, 57.4, 42.9, 41.2, 39.9, 34.8, 25.4, 22.4, 16.1, 14.1, 0.1 ppm (major diastereomer); 212.6, 202.2, 107.1, 84.8, 42.9, 42.2, 41.9, 41.5, 35.4, 32.5, 22.6, 20.1, 15.9, 14.6, 0.1 ppm (minor diastereomer); **IR** (thin film) 2961, 2174, 1710, 1249, 1219, 842, 773 cm⁻¹; **HRMS (ESI)** m/z calcd for C₁₇H₂₈NaO₂Si⁺ [M+Na]⁺: 315.1751; found: 315.1751.

Preparation of compound 7:

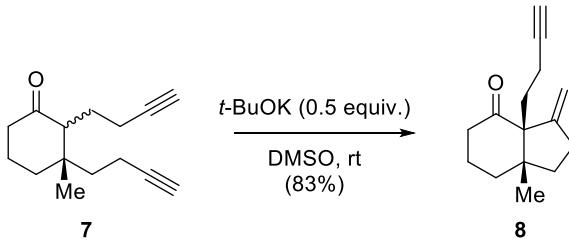


To a stirred solution of keto aldehyde **6** (2.23 g, 7.613 mmol, 1.0 equiv) in dry MeOH (109 mL) was added anhydrous K₂CO₃ (2.10 g, 15.23 mmol, 2.0 equiv) and Ohira-Bestmann reagent (1.5 mL, 9.90 mmol, 1.3 equiv) at 0 °C, and the mixture was warmed up gradually to room temperature, and the mixture was stirred at the same temperature until starting material disappeared (observed by TLC, ca. 3 h). The methanol was removed in vacuum, and the resultant mixture was dissolved in EtOAc

(30 mL), and the mixture was washed with a saturated solution of NaHCO₃ (20 mL). The aqueous phase was extracted with ethyl acetate (3 × 40 mL), and the combined organic extracts were washed with brine (2 × 20 mL), and dried over Na₂SO₄. The solvent was removed in vacuum, and residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 50 : 1 to 30 : 1) to give compound **7** (1.19 g, 72%) as a yellow oil, which is an inconsequential 1.5 : 1 mixture of diastereomers.

R_f = 0.50 (hexane/EtOAc = 8:1, PMA); [α]_D²² = + 2.56 (*c* 1.21, CHCl₃); **¹H NMR** (400 MHz, CDCl₃) δ 2.46 – 2.39 (m, 0.93H, overlap), 2.38 – 2.31 (m, 3.23H, overlap), 2.31 – 2.21 (m, 3.91H, overlap), 2.12 – 2.01 (m, 3.27H, overlap), 2.01 – 1.84 (m, 6.95H, overlap), 1.84 – 1.70 (m, 3.98H, overlap), 1.69 – 1.61 (m, 1.15H, overlap), 1.61 – 1.54 (m, 1.12H, overlap), 1.54 – 1.46 (m, 1.89H, overlap), 1.45 – 1.38 (m, 2.73H, overlap), 1.04 (s, 3H), 0.74 (s, 2H) ppm; **¹³C NMR** (100 MHz, CDCl₃) δ 211.9, 84.2, 84.1, 68.7, 68.4, 59.9, 56.0, 41.7, 41.1, 34.8, 25.4, 22.4, 22.4, 17.5, 12.7 ppm (major diastereomer); 212.2, 84.5, 84.3, 68.8, 68.4, 41.9, 41.6, 40.0, 35.6, 32.7, 22.7, 21.9, 20.4, 17.3, 12.9 ppm (minor diastereomer); **IR** (thin film) 3291, 2941, 2855, 2116, 1707, 1430, 772, 631 cm⁻¹; **HRMS (ESI)** m/z calcd for C₁₅H₂₀NaO⁺ [M+Na]⁺ : 239.1406; found: 239.1408.

Preparation of compound **8**:

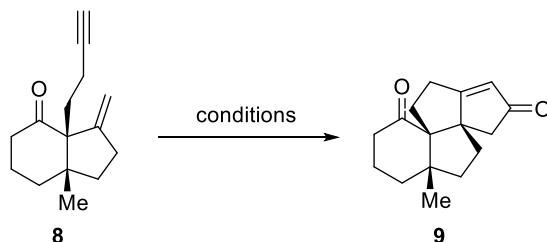


To a solution of **7** (4.48 g, 20.74 mmol, 1.0 equiv) in degassed DMSO (207 mL) was added a solution of *t*-BuOK (1.16 g, 10.37 mmol, 0.5 equiv.) in degassed DMSO (345 mL) at room temperature in a dropwise manner, and the mixture was stirred at the same temperature for 4 h. The reaction was worked up by addition of a saturated solution of NH₄Cl (5 mL), and the aqueous phase was extracted with Et₂O (3 × 50 mL). The combined organic extracts were washed with brine (2 × 10 mL), and dried over Na₂SO₄. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography over silica gel (hexane/ether = 70 : 1 to 50 : 1) to give compound **8** (3.70 g, 83%) as a yellow oil.

R_f = 0.70 (hexane/EtOAc = 8:1, PMA); [α]_D²² = - 46.28 (*c* 0.78, CHCl₃); **¹H NMR** (400 MHz, CDCl₃) δ 4.98 (t, *J* = 2.1 Hz, 1H), 4.48 (t, *J* = 2.5 Hz, 1H), 2.69 – 2.57 (m, 1H), 2.57 – 2.47 (m, 1H), 2.45 – 2.34 (m, 1H), 2.31 – 2.21 (m, 1H), 2.11 – 2.01 (m, 1H), 2.01 – 1.96 (m, 1H), 1.96 – 1.90 (m, 1H), 1.87 (t, *J* = 2.5 Hz, 1H), 1.84 – 1.71 (m, 3H), 1.66 – 1.58 (m, 1H), 1.55 – 1.45 (m, 1H), 1.37 – 1.23 (m, 2H), 0.91 (s, 3H) ppm; **¹³C NMR** (100 MHz, CDCl₃) δ 213.4, 153.1, 110.3, 85.3, 67.7, 66.4,

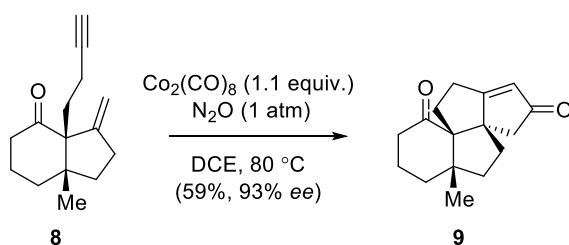
52.2, 38.3, 36.1, 35.3, 29.1, 28.8, 23.6, 19.9, 15.1 ppm; **IR** (thin film) 2960, 2925, 2854, 2116, 1700, 1261, 1016, 798 cm⁻¹; **HRMS (ESI)** m/z calcd for C₁₅H₂₁O⁺ [M+H]⁺: 217.1587; found: 217.1591.

Attempts toward the Pauson-Khand reaction



Entry	Co ₂ (CO) ₈ (equiv.)	Additive	atmosphere (1 atm.)	Solvent (0.05M)	Tem. (°C)	Time (h)	Yield (%)
1	1.1	NMO (5 equiv)	CO	PhMe	100	33	32
2	1.1	NMO (5 equiv)	CO	DCE	77	22	30
3	1.1	NMO (5 equiv)	CO	PhH	76	16	38
4	1.1	NMO (5 equiv)	CO	MeCN	77	24	trace
5	1.1	NMO (5 equiv)	CO	DCM	35	24	NR
6	1.1	DMSO (5 equiv)	CO	DCE	77	16	32
7	1.1	TMANO (5 equiv)	CO	DCE	77	16	24
8	1.1	none	CO	DCE	77	16	29
9	1.1	NMO (5 equiv), 4Å MS	CO	DCE	77	34	22
10	1.1	TMTU (1.2 equiv)	CO	PhMe	70	23	NR
11	[Rh(CO) ₂ Cl] ₂ (0.3 equiv)	none	CO	DCE	80	20	ND
12	PdCl ₂ (0.3 equiv)	TMTU (0.3 equiv) LiCl (1.2 equiv)	CO	THF	50	18	NR
13	1.1	none	N ₂ O	DCM	35	30	trace
14	1.1	none	N ₂ O	MeCN	80	24	trace
15	1.1	none	N ₂ O	THF	60	39	27
16	1.1	none	N ₂ O	PhMe	110	39	32
17	1.1	none	N ₂ O	DCE	80	20	59
18	1.1	none	N ₂ O	PhH	80	13	50

Preparation of compound 9:

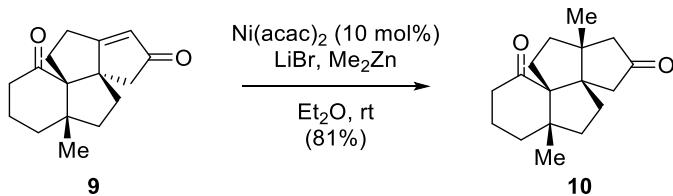


To a solution of enyne **8** (157 mg, 0.73 mmol, 1.0 equiv.) in DCE (25 mL) was added Co₂(CO)₈ (273 mg, 0.80 mmol, 1.1 equiv.) at room temperature. After stirring for 1 h at room temperature, the resultant mixture was bubbled with N₂O gently for 30 min at the same temperature. The mixture was

then stirred at 80 °C for 9 h with slowly bubbling N₂O, and then stirred at 80 °C for additional 10 h under N₂O. After cooling to room temperature, and the reaction solvent was removed in vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 2:1) to give enone **9** (105 mg, 59%).

R_f = 0.60 (hexane/EtOAc = 2:1, UV); [α]_D²² = - 26.79 (*c* 0.28, CHCl₃); **¹H NMR** (400 MHz, CDCl₃) δ 5.69 (s, 1H), 2.84 – 2.73 (m, 1H), 2.70 – 2.58 (m, 1H), 2.58 – 2.50 (m, 1H), 2.50 – 2.41 (m, 1H), 2.38 (d, *J* = 6.9 Hz, 2H), 2.27 – 2.13 (m, 1H), 2.07 – 1.98 (m, 1H), 1.98 – 1.86 (m, 4H), 1.85 – 1.72 (m, 3H), 1.60 – 1.51 (m, 1H), 1.13 (s, 3H) ppm; **¹³C NMR** (100 MHz, CDCl₃) δ 213.0, 208.9, 191.7, 122.3, 70.6, 65.7, 51.8, 49.1, 40.1, 38.8, 36.1, 30.0, 27.3, 22.9, 20.3 ppm; **IR** (thin film) 2961, 2925, 1714, 1684, 1634, 1261, 1219, 1088, 1017, 773 cm⁻¹; **HRMS (ESI)** m/z calcd for C₁₆H₂₁O₂⁺ [M+H]⁺: 245.1536; found: 245.1537.

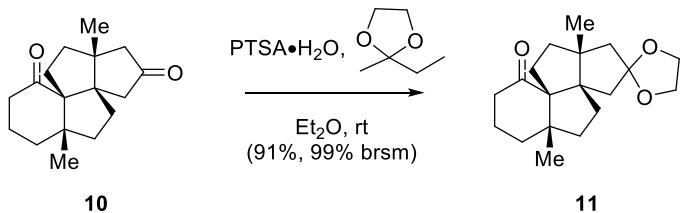
Preparation of compound **10**:



To a stirred solution of enone **9** (483 mg, 1.98 mmol, 1.0 equiv.) in Et₂O (16 mL) containing LiBr (515 mg, 5.94 mmol, 3.0 equiv.) and Ni(acac)₂ (49 mg, 0.20 mmol, 10 mol %) was added Me₂Zn (9.9 mL of 1 M solution in toluene, 9.90 mmol, 5.0 equiv.) in a dropwise manner over 10 min at 0 °C, and the reaction mixture was stirred at room temperature for 48 h. The reaction was worked up by addition of a saturated solution of NaHCO₃ (8 mL) at 0 °C, and mixture was extracted with DCM (3 × 20 mL). The combined organic extracts were washed with brine (2 × 5 mL), and then dried over Na₂SO₄. The solvent was concentrated under vacuum, the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 20 : 1) to give compound **10** (417 mg, 81%) as a yellow oil.

R_f = 0.70 (hexane/EtOAc = 2:1, PMA); [α]_D²³ = - 65.47 (*c* 0.39, CHCl₃); **¹H NMR** (400 MHz, CDCl₃) δ 2.54 (d, *J* = 18.8 Hz, 1H), 2.48 – 2.39 (m, 1H), 2.39 – 2.27 (m, 2H), 2.26 – 2.18 (m, 1H), 2.17 – 2.06 (m, 1H), 2.05 – 1.97 (m, 1H), 1.97 – 1.89 (m, 1H), 1.85 – 1.78 (m, 2H), 1.78 – 1.66 (m, 4H), 1.62 – 1.55 (m, 1H), 1.54 – 1.48 (m, 2H), 1.48 – 1.41 (m, 1H), 1.09 (s, 3H), 1.07 (s, 3H) ppm; **¹³C NMR** (100 MHz, CDCl₃) δ 217.0, 215.9, 72.3, 65.4, 51.3, 51.3, 50.1, 47.8, 41.3, 40.7, 39.9, 36.4, 33.1, 31.5, 24.5, 24.1, 19.6 ppm; **IR** (thin film) 2950, 2923, 2862, 1744, 1684, 1259, 1220, 773 cm⁻¹; **HRMS (ESI)** m/z calcd for C₁₇H₂₅O₂⁺ [M+H]⁺: 261.1849; found: 261.1849.

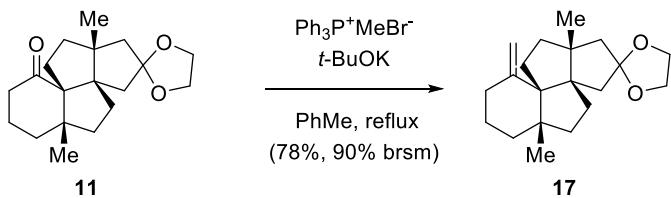
Preparation of compound **11**:



To a solution of ketone **10** (213 mg, 0.82 mmol, 1.0 equiv.) in Et₂O (4 mL) was added PTSA·H₂O (8 mg, 0.04 mmol, 0.05 equiv.) and 2-ethyl-2-methyl-3-dioxolane (512 μL, 4.10 mmol, 5.0 equiv.) at room temperature, and the reaction mixture was stirred at the same temperature for 1 h. The reaction was quenched by the addition of saturated solution of NaHCO₃ (5 mL) at 0 °C, and the mixture was extracted with Et₂O (3 × 10 mL). The combined organic extracts were washed with brine (2 × 5 mL), and dried over Na₂SO₄. The solvent was filtered off, and the filtrate was removed under vacuum, and the residue was purified by a column chromatography on silica gel (hexane/EtOAc = 10 : 1) to give compound **11** (227 mg, 91%, 99% brsm), together with the recovered compound **10** (17 mg).

R_f = 0.50 (hexane/EtOAc = 4:1, PMA); [α]_D²³ = - 12.47 (c 0.77, CHCl₃); **¹H NMR** (500 MHz, CDCl₃) δ 3.87 (dd, J=9.4, 4.1, 2H), 3.82 – 3.74 (m, 2H), 2.38 – 2.30 (m, 1H), 2.27 – 2.14 (m, 2H), 2.06 – 1.99 (m, 1H), 1.97 (d, J=12.7, 1H), 1.90 – 1.84 (m, 1H), 1.84 – 1.80 (m, 2H), 1.80 – 1.75 (m, 2H), 1.75 – 1.71 (m, 1H), 1.71 – 1.64 (m, 1H), 1.64 – 1.56 (m, 2H), 1.52 – 1.40 (m, 2H), 1.40 – 1.30 (m, 2H), 1.08 (s, 3H), 0.92 (s, 3H) ppm; **¹³C NMR** (125 MHz, CDCl₃) δ 215.3, 118.0, 72.9, 65.7, 64.3, 63.9, 52.3, 50.7, 49.7, 48.6, 43.7, 42.6, 40.9, 35.8, 35.6, 33.1, 25.4, 22.1, 21.9 ppm; **IR** (thin film) 2949, 2932, 2872, 1689, 1457, 1332, 1219, 1101, 1025, 773 cm⁻¹; **HRMS (ESI)** m/z calcd for C₁₉H₂₉O₃⁺ [M+H]⁺: 305.2111; found: 305.2113.

Preparation of compound **17**:

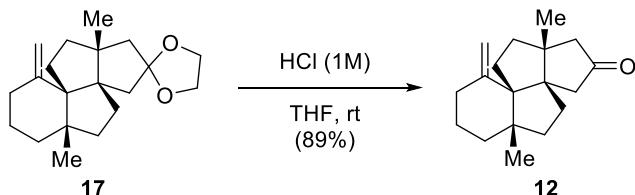


To a solution of *t*-BuOK (799 mg, 7.12 mmol, 4.9 equiv.) in anhydrous PhMe (16 mL) was added Ph₃P⁺MeBr⁻ (2.60 g, 7.27 mmol, 5.0 equiv.) at room temperature in glove box, and the mixture was stirred under reflux for 1 h. To this bright yellow solution was added a solution of ketone **11** (442 mg, 1.45 mmol, 1.0 equiv.) in anhydrous PhMe (5 mL) in a dropwise manner, and mixture was stirred under reflux for 19 h. To this solution was added acetone (0.6 mL, 7.27 mmol, 5.0 equiv.) under reflux, and the resultant mixture was stirred the same temperature for 30 min. After cooling back to room temperature, and the mixture was quenched by addition of water (5 mL), and the

mixture was extracted with Et₂O (3 × 15 mL), and the combined extracts were dried over Na₂SO₄. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 100 : 1 to 90 : 1) to give compound **17** (344 mg, 78%, 90% brsm), together with recovered compound **11** (57 mg).

R_f = 0.70 (hexane/EtOAc = 8:1, PMA); [α]_D²⁴ = - 16.67 (*c* 0.06, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 4.96 (s, 1H), 4.83 (s, 1H), 3.92 (t, *J* = 6.4 Hz, 2H), 3.81 (dd, *J* = 9.8, 4.0 Hz, 2H), 2.23 – 2.14 (m, 3H), 1.93 – 1.81 (m, 2H), 1.80 – 1.74 (m, 1H), 1.74 – 1.64 (m, 3H), 1.63 – 1.59 (m, 2H), 1.57 – 1.51 (m, 2H), 1.50 – 1.42 (m, 1H), 1.42 – 1.35 (m, 1H), 1.30 – 1.21 (m, 3H), 1.11 (s, 3H), 0.88 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 151.7, 118.9, 111.5, 64.9, 64.2, 64.0, 63.9, 52.4, 51.5, 50.2, 45.3, 43.9, 40.2, 37.6, 37.3, 35.7, 35.3, 26.2, 23.6, 21.9 ppm; IR (thin film) 2959, 2922, 2850, 1261, 1026, 1016, 801, 772 cm⁻¹; HRMS (ESI) m/z calcd for C₂₀H₃₁O₂⁺ [M+H]⁺: 303.2319; found: 303.2321.

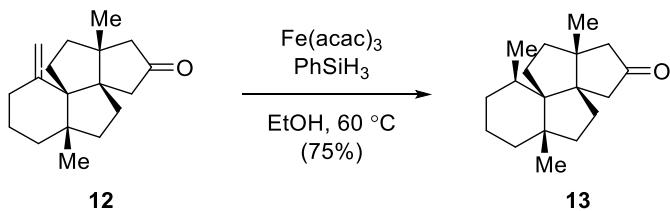
Preparation of compound **12**:



To a stirred solution of ketal **17** (185 mg, 0.61 mmol, 1.0 equiv) in THF (8 mL) was added HCl (1.60 mL of 1 M solution, 1.59 mmol, 2.6 equiv) at room temperature, and the reaction mixture was stirred overnight. The reaction mixture was quenched by addition of a saturated solution of NaHCO₃ (5 mL) at 0 °C, and the mixture was extracted with Et₂O (3 × 10 mL). The combined organic extracts were first washed with brine (2 × 5 mL), and dried over Na₂SO₄. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 20 : 1) to give compound **12** (140 mg, 89%).

R_f = 0.50 (hexane/EtOAc = 8:1, PMA); [α]_D²⁴ = - 20.00 (*c* 0.19, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 5.01 (t, *J* = 1.5 Hz, 1H), 4.88 (s, 1H), 2.84 (dd, *J* = 18.4, 1.6 Hz, 1H), 2.42 (dd, *J* = 18.8, 1.7 Hz, 1H), 2.33 – 2.19 (m, 2H), 2.14 – 2.01 (m, 2H), 2.01 – 1.89 (m, 2H), 1.77 – 1.71 (m, 2H), 1.70 – 1.64 (m, 1H), 1.64 – 1.52 (m, 4H), 1.49 – 1.39 (m, 1H), 1.39 – 1.28 (m, 2H), 1.16 (s, 3H), 0.94 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 219.1, 151.1, 113.2, 64.9, 62.9, 53.2, 52.9, 50.9, 46.0, 40.8, 39.9, 37.6, 36.9, 34.3, 33.8, 25.5, 23.1, 22.6 ppm; IR (thin film) 2962, 2929, 1261, 1025, 1015, 799, 760 cm⁻¹; HRMS (ESI) m/z calcd for C₁₈H₂₆NaO⁺ [M+Na]⁺ : 281.1876; found: 281.1876.

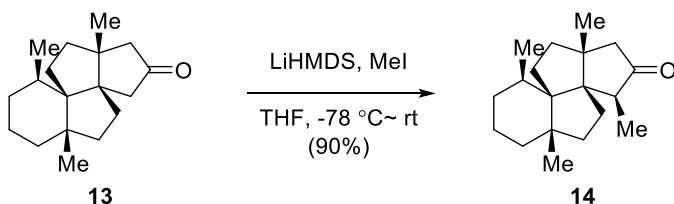
Preparation of compound **13**:



To a solution of alkene **12** (181 mg, 0.70 mmol, 1.0 equiv) in EtOH (7 mL) was added Fe(acac)₃ (49 mg, 0.42 mmol, 0.2 equiv) at room temperature, and the reaction mixture was stirred for 5 min. To this solution was added PhSiH₃ (87 μ L, 0.70 mmol, 1.0 equiv) at room temperature slowly, the reaction mixture was first purged with argon for 5 min. The reaction flask was then transferred to a preheated oil bath at 60 °C, and the mixture was stirred at 60 °C for 1 h. After cooling back to room temperature, the reaction mixture was quenched by addition of brine (3 mL), and the mixture was extracted with Et₂O (3 \times 15 mL). The combined organic extracts were washed with brine (2 \times 3 mL), and then dried over Na₂SO₄. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 70 : 1) to give compound **13** (137 mg, 75%).

R_f = 0.52 (hexane/EtOAc = 8:1, PMA); [α]_D²³ = - 25.62 (*c* 0.38, CHCl₃); ¹H NMR (500 MHz, C₆D₆) δ 2.46 (d, *J* = 20.1 Hz, 1H), 2.05 (d, *J* = 18.3 Hz, 1H), 1.98 – 1.86 (m, 2H), 1.52 – 1.44 (m, 2H), 1.44 – 1.39 (m, 2H), 1.38 – 1.30 (m, 4H), 1.23 (ddd, *J* = 12.2, 6.1, 2.5 Hz, 1H), 1.20 – 1.15 (m, 1H), 1.14 – 1.06 (m, 3H), 1.05 – 1.03 (m, 1H), 0.93 – 0.89 (m, 1H), 0.89 (s, 3H), 0.77 (s, 3H), 0.65 (d, *J* = 6.8 Hz, 3H) ppm; ¹³C NMR (125 MHz, C₆D₆) δ 216.9, 62.9, 58.9, 53.6, 49.1, 49.1, 45.6, 42.1, 40.1, 34.6, 34.2, 32.7, 28.8, 28.1, 24.7, 24.1, 19.3, 17.9 ppm; IR (thin film) 2963, 2922, 2868, 1743, 1261, 1092, 1020, 799, 776 cm⁻¹; HRMS (ESI) m/z calcd for C₁₈H₂₉O⁺ [M+H]⁺ : 261.2213; found: 261.2214.

Preparation of compound **14**:

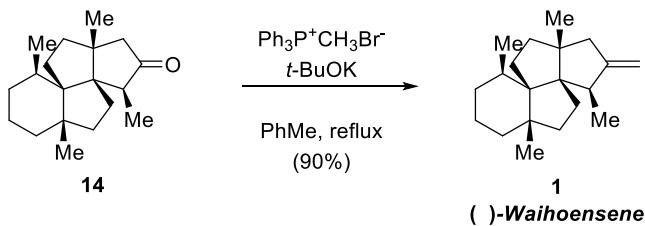


To a solution of ketone **13** (144 mg, 0.55 mmol, 1.0 equiv) in THF (11 mL) was added lithium bis(trimethylsilyl)amide (2.70 mL, 1.0 M solution in THF, 2.77 mmol, 5.0 equiv.) at -78 °C, and the mixture was warmed up to room temperature gradually, and then stirred at the same temperature for 2.5 h. After cooling back to -78 °C, to this mixture was added iodomethane (0.3 mL, 4.70 mmol, 8.5 equiv), and the reaction mixture was warmed up gradually to room temperature, and the mixture was

stirred at the same temperature for 27 h. The reaction was quenched by addition of a saturated solution of NH₄Cl (5 mL), and the mixture was extracted with Et₂O (3 × 15 mL), and the combined organic extracts were dried over Na₂SO₄. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 80 : 1) to give compound **14** (136 mg, 90%).

R_f = 0.35 (hexane/EtOAc = 20:1, PMA); [α]_D²² = + 12.38 (*c* 0.63, CHCl₃); **1H NMR** (500 MHz, C₆D₆) δ 2.37 (q, *J* = 7.7 Hz, 1H), 2.10 – 1.98 (m, 2H), 1.47 – 1.39 (m, 5H), 1.37 – 1.27 (m, 4H), 1.26 – 1.22 (m, 1H), 1.17 – 1.12 (m, 2H), 1.11 – 1.08 (m, 3H), 1.04 (d, *J* = 7.7 Hz, 3H), 0.91 (s, 3H), 0.84 (s, 3H), 0.67 (d, *J* = 6.7 Hz, 3H) ppm; **13C NMR** (125 MHz, C₆D₆) δ 220.4, 66.0, 60.5, 52.3, 49.9, 48.7, 44.9, 42.4, 41.4, 34.7, 32.9, 28.9, 28.9, 28.4, 25.3, 24.7, 19.6, 17.9, 15.5 ppm; **IR** (thin film) 2962, 2930, 2869, 1735, 1261, 1219, 1017, 801, 772 cm⁻¹; **HRMS (ESI)** m/z calcd for C₁₉H₃₀NaO⁺ [M+Na]⁺: 297.2189; found: 297.2189.

Synthesis of (+)-waihoensene (**1**):

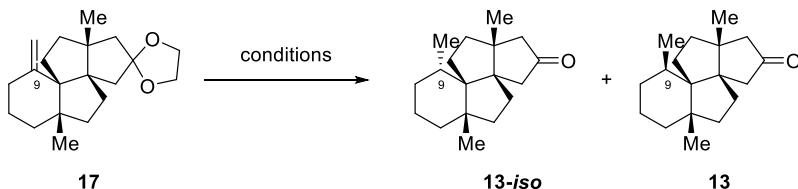


To a solution of *t*-BuOK (218 mg, 1.94 mmol, 4.8 equiv.) anhydrous PhMe (10 mL) was added Ph₃P⁺CH₃Br⁻ (723 mg, 2.02 mmol, 5.0 equiv.) in glove box, and the mixture was stirred at reflux for 1 h. To this bright yellow solution was added a solution of ketone **14** (111 mg, 0.41 mmol, 1.0 equiv.) in anhydrous PhMe (4 mL) in a dropwise manner under reflux, and mixture was stirred at the same temperature for 4 h. The reaction was quenched by addition of acetone (150 µL, 2.02 mmol, 5.0 equiv.), and the resultant mixture was further stirred under reflux for 30 min. After cooling to room temperature, the mixture was quenched by addition of water (5 mL), and the mixture was extracted with Et₂O (3 × 20 mL), and the combined organic extracts were finally dried over Na₂SO₄. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (impregnated silver nitrate) (elute with hexane) to give (+)-waihoensene **1** (100 mg, 90%) as a yellow oil.

R_f = 0.90 (hexane, I₂); [α]_D²³ = + 49.33 (*c* 0.15, CHCl₃); **1H NMR** (500 MHz, CDCl₃) δ 4.69 (q, *J* = 1.9 Hz, 2H), 2.72 (q, *J* = 7.2 Hz, 1H), 2.22 (d, *J* = 1.6 Hz, 2H), 1.84 – 1.74 (m, 1H), 1.69 – 1.60 (m, 1H), 1.60 – 1.58 (m, 1H), 1.58 – 1.56 (m, 1H), 1.55 – 1.50 (m, 2H), 1.50 – 1.46 (m, 1H), 1.45 – 1.43 (m, 1H), 1.43 – 1.40 (m, 1H), 1.40 – 1.30 (m, 2H), 1.30 – 1.27 (m, 1H), 1.27 – 1.24 (m, 1H), 1.19 – 1.15 (m, 1H), 1.14 – 1.11 (m, 1H), 1.05 (d, *J* = 7.3 Hz, 3H), 1.03 (s, 3H), 1.02 (s, 3H), 0.91 (d, *J* =

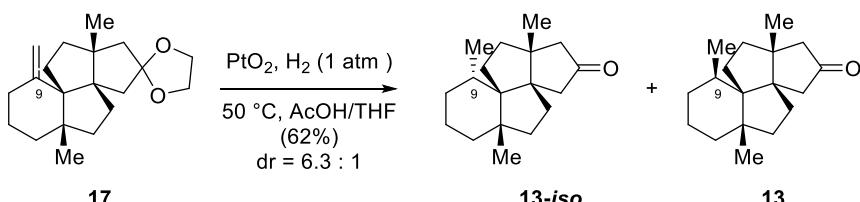
6.9 Hz, 3H) ppm; **¹³C NMR** (125 MHz, CDCl₃) δ 159.6, 102.9, 68.3, 60.4, 52.5, 48.0, 44.7, 43.8, 42.0, 40.9, 35.9, 31.8, 30.4, 30.2, 28.7, 25.3, 25.0, 19.8, 19.1, 17.5 ppm; **IR** (thin film) 2961, 2923, 2867, 2855, 1750, 1665, 1460, 1376, 1261, 1091, 1018, 875, 801, 762 cm⁻¹; **HR-MS (EI)**: Calculated for C₂₀H₃₂: 272.2504, Found: 272.2495.

Construction of chiral center at C9 from compound 17:



Entry	Conditions	Results
1	10 mol% Pd/C, 1 atm H ₂ , EtOH, 25 °C, 12 h	NR
2	10 mol% PtO ₂ , 1 atm H ₂ , EtOH, 25 °C, 12 h	NR
3	10 mol% Pd/C, 90 atm H ₂ , MeOH, 80 °C, 12 h	NR
4	10 mol% Ni, 40 atm H ₂ , MeOH/THF, 100 °C, 12 h	NR
5	10 mol% PtO ₂ , 40 atm H ₂ , MeOH/THF, 100 °C, 12 h	NR
6	10 mol% PtO ₂ , 1 atm H ₂ , AcOH/THF, 50 °C, 24 h	62% (13-<i>iso</i> : 13 = 6.3:1)
7	10 mol% RhCl(PPh ₃) ₃ , 1 atm H ₂ , PhH, 25 °C, 3 h	NR
8	10 mol% Mn(dpm) ₃ , 1 equiv. PhSiH ₃ , 1.5 equiv. TBHP, <i>i</i> -PrOH (0.5 M), 25 °C, 1 h	NR
9	1) 20 mol% Fe(acac) ₃ , 1 equiv. PhSiH ₃ , EtOH (0.1 M), 60 °C, 1 h 2) 1 M HCl, THF, 25 °C, 6 h	79% (13-<i>iso</i> : 13 = 7.7:1)

Procedure for entry 6:

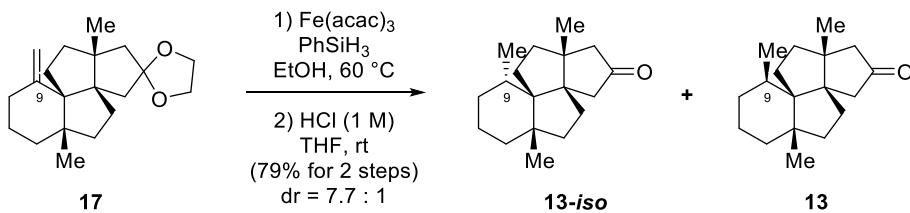


To a solution of **17** (24 mg, 0.08 mmol, 1.0 equiv) in THF (0.80 mL) and AcOH (0.80 mL) was added PtO₂ (2 mg, 83% Pt, 0.008 mmol, 0.1 equiv) at room temperature under argon, and the mixture was degassed with hydrogen gas, and then stirred at 50 °C for 24 h. The mixture was worked up by filtration of the reaction mixture through a celite-pad, and the filtrate was concentrated under vacuum. The residue was purified by a column chromatography on silica gel (hexane/EtOAc = 90: 1 to 70: 1) to give the inseparable 6.3: 1 mixture-1 (13 mg, 62%) of compound **13-*iso*** and compound **13** as colorless oil.

R_f = 0.52 (hexane/EtOAc = 8:1, PMA); **¹H NMR** (400 MHz, C₆D₆) δ 2.90 (d, *J* = 19.4, 1H, major), 2.46 (d, *J* = 19.9, 0.16H, minor, **13**), 2.19 (dd, *J* = 18.0, 1.5, 1H, major), 2.05 (d, *J* = 18.5, 0.16H, minor, **13**), 1.98 – 1.81 (m, 2.56H, overlap), 1.70 (dd, *J* = 13.9, 6.5, 1H), 1.51 – 1.48 (m,

0.16H, overlap), 1.49 – 1.45 (m, 0.92H, overlap), 1.44 – 1.39 (m, 2.69H, overlap), 1.39 – 1.32 (m, 4.05H, overlap), 1.32 – 1.28 (m, 1.22H, overlap), 1.27 – 1.22 (m, 1.69H, overlap), 1.22 – 1.13 (m, 3.99H, overlap), 1.13 – 1.09 (m, 0.56H, overlap), 1.09 – 1.02 (m, 1.90H, overlap), 1.01 (d, J = 6.7, 0.50H, overlap), 0.91 (d, J = 7.3, 3.18H, overlap), 0.89 (s, 0.57H, overlap), 0.86 (s, 3H), 0.79 (s, 3H), 0.77 (s, 0.54H, overlap), 0.66 (d, J = 6.8, 0.47H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ 216.6, 61.6, 60.2, 53.1, 51.0, 50.2, 45.7, 40.7, 40.0, 38.7, 38.3, 35.4, 35.3, 33.6, 25.6, 23.1, 23.0, 19.5 ppm (major diastereomer **13-iso**); 216.8, 62.9, 58.9, 53.6, 49.1, 49.1, 45.6, 42.1, 40.1, 34.6, 34.2, 32.8, 28.8, 28.2, 24.7, 24.1, 19.3, 17.9 ppm (minor diastereomer **13**); IR (thin film) 2963, 2922, 2868, 1743, 1261, 1092, 1020, 799, 776 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{29}\text{O}^+$ [M+H] $^+$: 261.2213; found: 261.2214.

Procedure for entry 9:



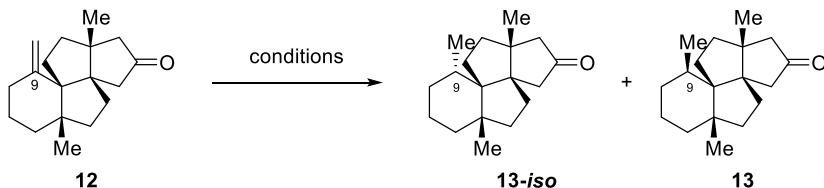
To a solution of alkene **17** (15 mg, 0.05 mmol, 1.0 equiv) in EtOH (0.50 mL) was added $\text{Fe}(\text{acac})_3$ (4 mg, 0.01 mmol, 0.2 equiv) at room temperature, and the reaction mixture was stirred for 5 min. To this solution was degassed with argon for 5 min, followed by addition of PhSiH_3 (6 μL , 0.05 mmol, 1.0 equiv) slowly at room temperature, and the reaction mixture was stirred at 60 $^\circ\text{C}$ in a preheated oil bath for 1 h. After cooling back to room temperature, the reaction mixture was quenched by addition of brine (0.3 mL), and the mixture was extracted with Et_2O (3×5 mL). The combined organic extracts were washed with brine (2×5 mL), and then dried over Na_2SO_4 . The solvent was removed under vacuum, and the residue was used in the next step without further purification.

To a solution of the crude product made above in THF (0.80 mL) was added HCl (50 μL of 1 M solution, 0.05 mmol, 1.0 equiv) at room temperature, and the reaction mixture was stirred overnight. The reaction mixture was quenched by addition of saturated solution of NaHCO_3 (0.3 mL) at 0 $^\circ\text{C}$, and the residue was extracted with Et_2O (3×5 mL). The combined organic extracts were washed with brine (2×2 mL), and dried over Na_2SO_4 . The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 30 : 1) to give the inseparable 7.7:1 mixture-2 (10 mg, 79% for 2 steps) of compound **13-iso** and compound **13** as a colorless oil.

\mathbf{R}_f = 0.52 (hexane/EtOAc = 8:1, PMA); ^1H NMR (400 MHz, C_6D_6) δ 2.90 (d, J = 19.3, 1H,

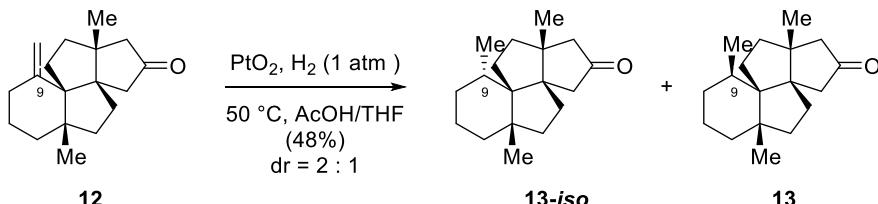
major), 2.46 (d, $J = 20.0$, 0.13H, minor, **13**), 2.19 (dd, $J = 18.0$, 1.6, 1H, major), 2.09 – 2.01 (m, 0.13H, minor, **13**), 1.98 – 1.82 (m, 2.3 H, overlap), 1.70 (dd, $J = 13.9$, 6.5, 1H, major), 1.51 – 1.48 (m, 0.13H, overlap), 1.49 – 1.45 (m, 0.81H, overlap), 1.45 – 1.39 (m, 2.51H, overlap), 1.39 – 1.32 (m, 3.54H, overlap), 1.32 – 1.27 (m, 1.25H, overlap), 1.27 – 1.21 (m, 1.54H, overlap), 1.21 – 1.13 (m, 3.90H, overlap), 1.13 – 1.09 (m, 0.47H, overlap), 1.08 – 1.03 (m, 1.82H, overlap), 1.01 (d, $J = 6.6$, 0.51H), 0.91 (d, $J = 7.3$, 3H), 0.89 (s, 0.45H, overlap), 0.86 (s, 3H), 0.79 (s, 3H), 0.77 (s, 0.44H, overlap), 0.66 (d, $J = 6.8$, 0.38H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ 216.6, 61.6, 60.2, 53.1, 51.0, 50.2, 45.7, 40.7, 40.0, 38.7, 38.3, 35.4, 35.3, 33.6, 25.6, 23.1, 23.0, 19.5 ppm (major diastereoisomer **13-iso**); 216.8, 62.9, 58.9, 53.6, 49.1, 49.1, 45.6, 42.1, 40.1, 34.6, 34.2, 32.8, 28.8, 28.2, 24.7, 24.1, 19.3, 17.9 ppm (minor diastereoisomer **13**); IR (thin film) 2963, 2922, 2868, 1743, 1261, 1092, 1020, 799, 776 cm^{-1} ; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{29}\text{O}^+$ [M+H]⁺: 261.2213; found: 261.2214.

Construction of chiral center at C9 from compound **12**:



Entry	Conditions	Results
1	PtO ₂ (10 mol%), H ₂ (1 atm), AcOH/THF, 50 °C, 24 h	48% (13-iso : 13 = 2.0: 1.0)
2	PtO ₂ (10 mol%), H ₂ (1 atm), EtOH, RT, 12 h	not detected
3	Co(acac) ₂ (20 mol%), PhSiH ₃ (1.0 equiv), EtOH, 60 °C, 2 h	NR
4	Rh(PPh ₃)Cl (10 mol%), H ₂ (1 atm), PhH, 60 °C, 12 h	trace
5	Mn(dpm) ₃ (10 mol%), PhSiH ₃ (1.0 equiv), TBHP (1.5 equiv), i-PrOH, RT, 2 h	76% (13-iso : 13 = 1.0: 7.7)

Procedure for entry 1:

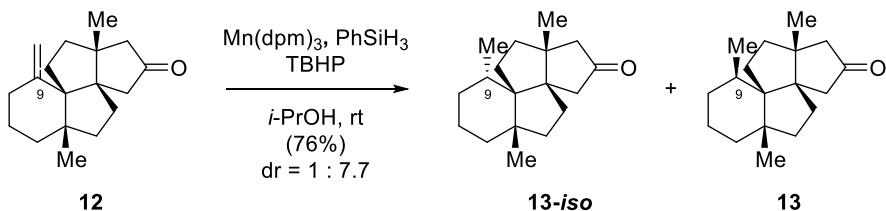


To a solution of **12** (21 mg, 0.08 mmol, 1.0 equiv) in THF (0.8 mL) and AcOH (0.8 mL) was added PtO₂ (2 mg, 83% Pt, 0.008 mmol, 0.1 equiv) at room temperature under argon atmosphere, and the mixture was degassed with hydrogen gas, and then stirred at 50 °C for 24 h. The reaction was worked up by filtration of the reaction mixture through a pad of silica gel, and the filtrate was concentrated under vacuum. The residue was purified by a flash column chromatography on silica

gel (hexane/EtOAc = 30 : 1) to give the inseparable 2:1 mixture-3 (10 mg, 48%) of compound **13-iso** and compound **13** as colorless oil.

R_f = 0.52 (hexane/EtOAc = 8:1, PMA); **1H NMR** (500 MHz, C₆D₆) δ 2.89 (dd, J = 19.1, 1.2, 1H, major), 2.46 (d, J = 18.7, 0.5H, minor, **13**), 2.19 (dd, J = 18.1, 1.6, 1H, major), 2.05 (d, J = 18.7, 0.5H, minor, **13**), 1.97 – 1.82 (m, 3.32H, overlap), 1.70 (dd, J = 14.0, 6.5, 1H), 1.53 – 1.49 (m, 0.5H, overlap), 1.49 – 1.45 (m, 1.5H, overlap), 1.45 – 1.42 (m, 1.93H, overlap), 1.42 – 1.38 (m, 2.33H, overlap), 1.38 – 1.31 (m, 4.55H, overlap), 1.31 – 1.28 (m, 1.29H, overlap), 1.28 – 1.21 (m, 2.33H, overlap), 1.21 – 1.16 (m, 4H, overlap), 1.15 – 1.09 (m, 1.41H, overlap), 1.09 – 1.03 (m, 2.67H, overlap), 1.02 (d, J = 6.8, 0.57H, overlap), 0.91 (d, J = 7.4, 3.32H), 0.89 (s, 1.63H), 0.86 (s, 3H), 0.80 (s, 3H), 0.78 (s, 1.5H), 0.66 (d, J = 6.8, 1.5H) ppm; **13C NMR** (125 MHz, C₆D₆) δ 216.4, 61.7, 60.3, 53.1, 51.0, 50.3, 45.8, 40.8, 40.1, 38.8, 38.3, 35.5, 35.3, 33.6, 25.6, 23.0, 23.0, 19.5 ppm (major diastereoisomer **13-iso**); 216.6, 62.9, 59.0, 53.6, 49.2, 49.2, 45.6, 42.1, 40.2, 34.8, 34.2, 32.9, 29.0, 28.4, 24.8, 24.1, 19.3, 17.9 ppm (minor diastereoisomer **13**); **IR** (thin film) 2963, 2922, 2868, 1743, 1261, 1092, 1020, 799, 776 cm⁻¹; **HRMS (ESI)** m/z calcd for C₁₈H₂₉O⁺ [M+H]⁺ : 261.2213; found: 261.2214.

Procedure for entry 5:

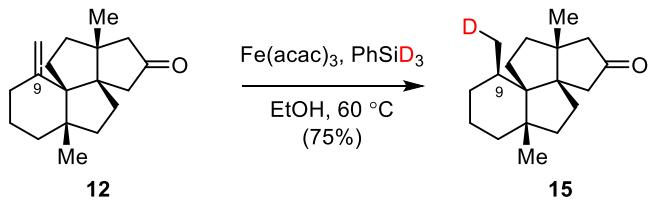


To a solution of compound **12** (23 mg, 0.09 mmol, 1.0 equiv.) in anhydrous *i*-PrOH (0.20 mL) was added phenylsilane (11 μ L, 0.09 mmol, 1.0 equiv.) and TBHP (13 μ L, 0.13 mmol, 1.5 equiv.) at room temperature under argon, and the resultant mixture was degassed by bubbling argon through the solution for 10 minutes. To this solution was Mn(dpm)₃ (6 mg, 0.01 mmol, 10 mol%) in one portion and the reaction was then degassed with argon for an additional half h. The reaction mixture was then stirred at room temperature for 2 h. The solvent was removed under vacuum, and the residue was purified directly on a flash column chromatography on silica gel to give the inseparable 1: 7.7 mixture-4 (18 mg, 76%) of compound **13-iso** and compound **13**.

R_f = 0.52 (hexane/EtOAc = 8:1, PMA); **1H NMR** (500 MHz, C₆D₆) δ 2.90 (d, J = 19.3, 0.13H, minor), 2.46 (d, J = 20.4, 1H, major, **13**), 2.19 (dd, J = 18.1, 1.6, 0.13H, minor), 2.05 (d, J = 18.6, 1H, major, **13**), 1.98 – 1.82 (m, 2.34H, overlap), 1.70 (dd, J = 14.0, 6.6, 0.15H), 1.53 – 1.46 (m, 1.69H, overlap), 1.46 – 1.39 (m, 2.79H, overlap), 1.39 – 1.28 (m, 5.17H, overlap), 1.28 – 1.20 (m, 1.63H, overlap), 1.20 – 1.15 (m, 1.44H, overlap), 1.15 – 1.00 (m, 4.63H, overlap), 0.91 (d, J =7.2, 1.11H,

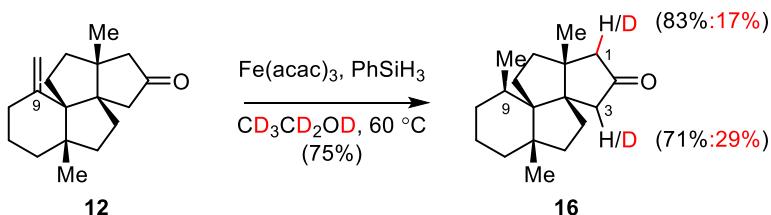
overlap), 0.89 (s, 3.48H, overlap), 0.86 (s, 0.46H, overlap), 0.79 (s, 0.49H, overlap), 0.77 (s, 3.06H, overlap), 0.66 (d, $J=6.8$, 3H) ppm; **^{13}C NMR** (125 MHz, C_6D_6) δ 216.6, 62.9, 59.0, 53.6, 49.2, 49.2, 45.6, 42.1, 40.2, 34.8, 34.2, 32.8, 28.9, 28.4, 24.7, 24.1, 19.3, 17.9 ppm (major diastereoisomer **13**); 216.4, 61.7, 60.3, 53.1, 51.0, 50.3, 45.8, 40.8, 40.1, 38.8, 38.3, 35.5, 35.3, 33.6, 25.6, 23.0, 23.0, 19.5 ppm (minor diastereoisomer **13-iso**); **IR** (thin film) 2963, 2922, 2868, 1743, 1261, 1092, 1020, 799, 776 cm^{-1} ; **HRMS (ESI)** m/z calcd for $\text{C}_{18}\text{H}_{29}\text{O}^+$ [$\text{M}+\text{H}]^+$: 261.2213; found: 261.2214.

Deuteration experiments:



To a solution of alkene **12** (21 mg, 0.08 mmol, 1.0 equiv) in dry EtOH (0.90 mL) was added $\text{Fe}(\text{acac})_3$ (6 mg, 0.02 mmol, 0.2 equiv) at room temperature, and the reaction mixture was stirred for 5 min followed by degassed with argon for 5 min. To this solution was added PhSiD_3 (10 μL , 0.08 mmol, 1.0 equiv) slowly at room temperature, and the mixture was stirred at 60 °C for 1 h in a preheated oil bath. After cooling back to room temperature, the reaction mixture was quenched by addition of brine (0.3 mL), and mixture was extracted with Et_2O (3×5 mL). The combined organic phases were washed with brine (2×1.5 mL), and then dried over Na_2SO_4 . The solvent was removed under vacuum, and the residue was purified by a column chromatography on silica gel (hexane/EtOAc = 70 : 1) to give deuterated compound **15** (16 mg, 75%).

$\text{R}_f = 0.52$ (hexane/EtOAc = 8:1, PMA); **^1H NMR** (500 MHz, C_6D_6) δ 2.47 (d, $J=20.4$, 1H), 2.05 (d, $J = 18.7$, 1H), 1.99 – 1.85 (m, 2H), 1.53 – 1.44 (m, 2H), 1.44 – 1.39 (m, 2H), 1.38 – 1.30 (m, 4H), 1.27 – 1.21 (m, 1H), 1.21 – 1.15 (m, 1H), 1.15 – 1.06 (m, 3H), 1.06 – 1.03 (m, 1H), 0.93 – 0.90 (m, 1H), 0.89 (s, 3H), 0.77 (s, 3H), 0.66 – 0.62 (m, 2H) ppm; **^{13}C NMR** (125 MHz, C_6D_6) δ 216.8, 62.9, 58.9, 53.5, 49.2, 49.1, 45.5, 42.1, 40.2, 34.7, 34.2, 32.7, 28.9, 28.2, 24.7, 24.1, 18.9 (m), 17.9 ppm; **IR** (thin film) 2996, 2963, 2924, 2850, 1769, 1758, 1375, 1258, 1247, 1241, 1097, 1057, 1019, 800 cm^{-1} ; **HRMS (ESI)** m/z calcd for $\text{C}_{18}\text{H}_{28}\text{DO}^+$ [$\text{M}+\text{H}]^+$: 262.2276; found: 262.2274.



To a stirred solution of alkene **12** (26 mg, 0.10 mmol, 1.0 equiv) in dry $\text{CD}_3\text{CD}_2\text{OD}$ (0.90 mL)

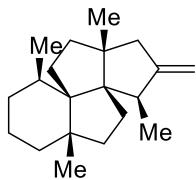
at room temperature was added Fe(acac)₃ (7 mg, 0.02 mmol, 0.2 equiv), and the reaction mixture was stirred for 5 min followed by degassed with argon for 5 min. To this solution was added PhSiH₃ (12 μ L, 0.10 mmol, 1.0 equiv) slowly at room temperature, and the mixture was stirred at 60 °C for 1 h in a preheated oil bath. After cooling back to room temperature, the reaction mixture was quenched by addition of brine (0.3 mL), and the mixture was extracted with Et₂O (3 \times 5 mL). The combined organic extracts were washed with brine (2 \times 1.5 mL), and dried over Na₂SO₄. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 70 : 1) to give deuterated compound **16** (20 mg, 75%).

R_f = 0.52 (hexane/EtOAc = 8:1, PMA); **¹H NMR** (400 MHz, C₆D₆) δ 2.48 (s, 0.21H), 2.43 (s, 0.72H), 2.07 (s, 0.24H), 2.02 (s, 0.52H), 1.96 (d, *J* = 1.7, 0.26H), 1.92 (s, 0.42H), 1.91 (d, *J* = 1.9, 0.23H), 1.87 (s, 0.49H), 1.54 – 1.44 (m, 2H), 1.44 – 1.38 (m, 2H), 1.38 – 1.28 (m, 4H), 1.27 – 1.22 (m, 1H), 1.20 – 1.15 (m, 1H), 1.15 – 1.06 (m, 3H), 1.06 – 1.02 (m, 1H), 0.93 – 0.90 (m, 1H), 0.89 (s, 3H), 0.77 (s, 3H), 0.64 (d, *J*=6.7, 3H) ppm; **¹³C NMR** (100 MHz, C₆D₆) δ 216.9, 216.9, 62.9, 62.8, 58.9, 58.9, 53.6, 49.2, 49.1, 48.9, 48.9, 45.6, 42.1, 40.1, 40.1, 34.6, 34.2, 34.1, 32.8, 28.8, 28.2, 24.7, 24.1, 19.3, 17.9 ppm (peak overlap); **IR** (thin film) 2996, 2963, 2924, 2850, 1770, 1759, 1383, 1247, 1241, 1097, 1057, 1021, 800 cm⁻¹; **HRMS (ESI)** m/z calcd for C₁₈H₂₈DO⁺ [M+H]⁺: 262.2276; found: 262.2270. (**Note:** Hydrogen with straight underline belongs to C3; hydrogen with wavy underline belongs to C1.)



To a solution of alkene **13** (20 mg, 0.08 mmol, 1.0 equiv) in dry CD₃CD₂OD (1.00 mL) at room temperature was added Fe(acac)₃ (6 mg, 0.02 mmol, 0.2 equiv), and the reaction mixture was stirred for 5 min followed by degassed with argon for 5 min. To this solution was added PhSiH₃ (9 µL, 0.08 mmol, 1.0 equiv) slowly at room temperature, the reaction mixture was stirred at 60 °C for 1 h in a preheated oil bath. After cooling back to room temperature, the reaction mixture was quenched by addition of brine (0.3 mL), and then extracted with Et₂O (3 × 5 mL). The combined organic extracts were washed with brine (2 × 1.5 mL), and then dried over Na₂SO₄. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (hexane/EtOAc = 70 : 1) to recover **13** (18 mg, 90%).

Part III. Comparison of the Spectra of Isolated and Synthetic (+)-Waihoensene*



1
(+)-Waihoensene

$[\alpha]_D^{23} = +49.33^\circ$ ($c = 0.15$, CHCl_3)

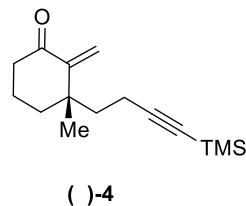
lit. $[\alpha]_D^{22} = +43.9^\circ$ ($c = 0.09$, CHCl_3)

¹ H [δ H (ppm), mult, J (Hz)]		¹³ C (ppm)	
Isolated ^[5]	Synthetic 500 MHz	Isolated	Synthetic 125 MHz
0.89 (d, $J = 7.0$ Hz, 3H)	0.91 (d, $J = 6.9$ Hz, 3H)	17.6	17.5
0.99 (s, 3H)	1.02 (s, 3H)	19.2	19.1
1.00 (s, 3H)	1.03 (s, 3H)	19.9	19.8
1.02 (d, $J = 7.0$ Hz, 3H)	1.05 (d, $J = 7.3$ Hz, 3H)	25.1	25.0
1.12 (m, 1H)	1.14-1.11 (m, 1H)	25.4	25.3
1.15 (m, 1H)	1.19-1.15 (m, 1H)	28.8	28.7
1.25 (m, 1H)	1.27-1.24 (m, 1H)	30.3	30.2
1.27 (m, 1H)	1.30-1.27 (m, 1H)	30.5	30.4
1.36 (m, 2H)	1.40-1.30 (m, 2H)	31.9	31.8
1.42 (m, 1H)	1.43-1.40 (m, 1H)	36.0	35.9
1.43 (m, 1H)	1.45-1.43 (m, 1H)	41.0	40.9
1.50 (m, 1H)	1.50-1.46 (m, 1H)	42.1	42.0
1.54 (m, 2H)	1.55-1.50 (m, 2H)	44.0	43.8
1.55 (m, 1H)	1.58-1.56 (m, 1H)	44.8	44.7
1.56 (m, 1H)	1.60-1.58 (m, 1H)	48.1	48.0
1.64 (m, 1H)	1.69-1.60 (m, 1H)	52.6	52.5
1.79 (m, 1H)	1.84-1.74 (m, 1H)	60.5	60.4
2.20 (br s, 2H)	2.22 (d, $J = 1.6$ Hz, 2H)	68.4	68.3
2.69 (q, $J = 7$ Hz, 1H)	2.72 (q, $J = 7.2$ Hz, 1H)	103.0	102.9
4.69 (q, $J = 2$ Hz, 2H)	4.69 (q, $J = 1.9$ Hz, 2H)	159.7	159.6

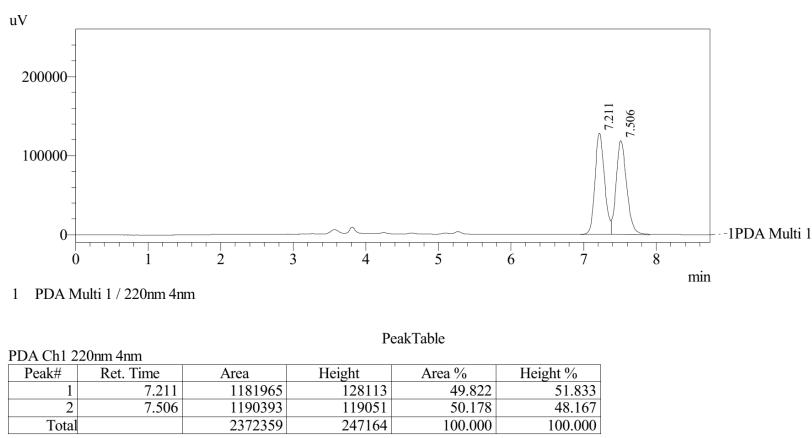
* Spectrum measured in CDCl_3 .

Part IV: Analysis for Optical Purity of Compound 4

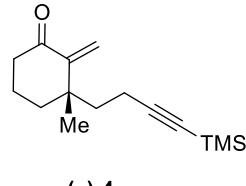
Racemic compound 4:



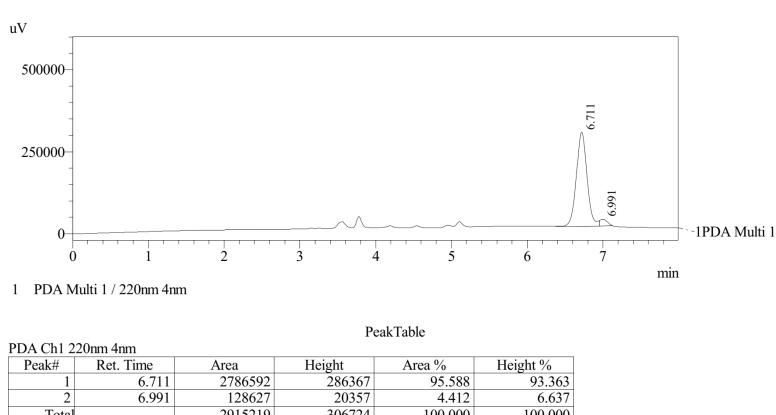
HPLC (DAICEL Chiralpak- IA column, hexane/ ethanol = 99.8:0.2, flow rate: 1.0 mL/min): $t_1 = 7.211$ min; $t_2 = 7.506$ min.



Optically active compound 4:



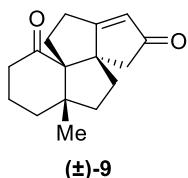
HPLC (DAICEL Chiralpak- IA column, hexane/ ethanol = 99.8:0.2, flow rate: 1.0 mL/min): $t_{\text{major}} = 6.711$ min; $t_{\text{minor}} = 6.991$ min.



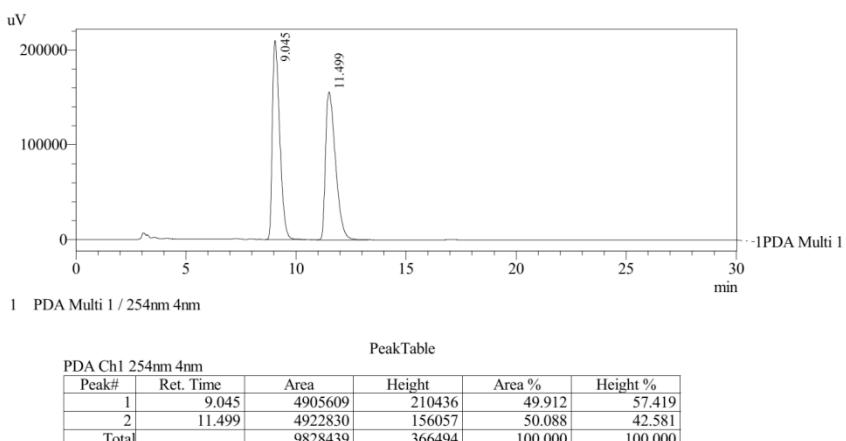
Compound (-)-4: $ee = 95.6\% - 4.4\% = 91.2\%$

Analysis for Optical Purity of Compound 9

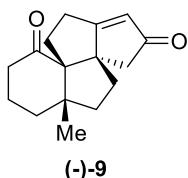
Racemic compound 9:



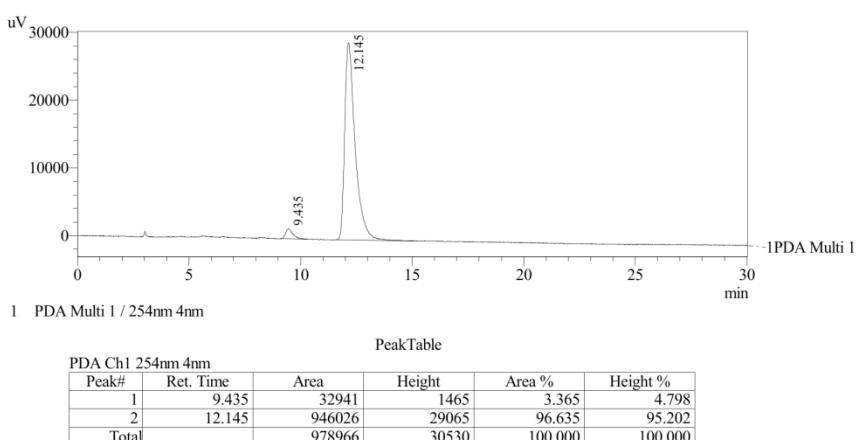
HPLC (DAICEL Chiralpak- OJ column, hexane/ ethanol = 90:10, flow rate: 1.0 mL/min): $t_1 = 9.045$ min; $t_2 = 11.499$ min.



Optically active compound 9:



HPLC (DAICEL Chiralpak- OJ column, hexane/ ethanol = 90:10, flow rate: 1.0 mL/min): $t_{\text{minor}} = 9.435$ min; $t_{\text{major}} = 12.145$ min.



Compound (-)-9: $ee = 96.6\% - 3.4\% = 93.2\%$

Part V. X-ray for the Synthesized Compounds

Crystal structure report for optically active enone 9:

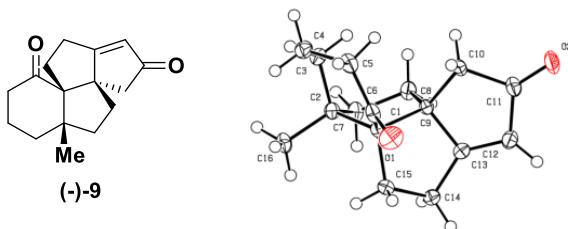


Table of crystal data and structure refinement for (-)-9.

Identification code	L-4-2
Empirical formula	C ₁₆ H ₂₀ O ₂
Formula weight	244.32
Temperature/K	108(12)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	7.36180(10)
b/Å	12.5083(2)
c/Å	27.8448(4)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	2564.05(7)
Z	8
ρ _{calc} g/cm ³	1.266
μ/mm ⁻¹	0.643
F(000)	1056.0
Crystal size/mm ³	0.14 × 0.12 × 0.11
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	6.348 to 147.156
Index ranges	-9 ≤ h ≤ 6, -15 ≤ k ≤ 14, -32 ≤ l ≤ 34
Reflections collected	13368
Independent reflections	5059 [R _{int} = 0.0283, R _{sigma} = 0.0307]
Data/restraints/parameters	5059/0/327
Goodness-of-fit on F ²	1.073
Final R indexes [I>=2σ (I)]	R ₁ = 0.0440, wR ₂ = 0.1161
Final R indexes [all data]	R ₁ = 0.0453, wR ₂ = 0.1173
Largest diff. peak/hole / e Å ⁻³	0.50/-0.24
Flack/Hooft parameter	-0.05(8)/-0.05(8)

Crystal structure report for racemic ketone 11:

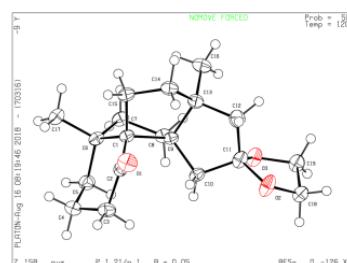
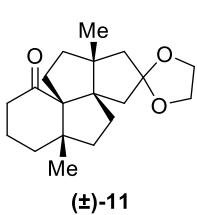


Table of crystal data and structure refinement for (±)-11.

Identification code	qyz
Empirical formula	C ₁₉ H ₂₈ O ₃
Formula weight	304.41
Temperature/K	120.00(10)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	10.2573(3)
b/Å	11.5170(3)
c/Å	14.0879(3)
α/°	90
β/°	106.200(3)
γ/°	90
Volume/Å ³	1598.16(8)
Z	4
ρ _{calc} g/cm ³	1.265
μ/mm ⁻¹	0.660
F(000)	664.0
Crystal size/mm ³	0.15 × 0.13 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.518 to 147.274
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 13, -17 ≤ l ≤ 17
Reflections collected	6102
Independent reflections	3129 [R _{int} = 0.0220, R _{sigma} = 0.0254]
Data/restraints/parameters	3129/0/209
Goodness-of-fit on F ²	1.028
Final R indexes [I>=2σ (I)]	R ₁ = 0.0471, wR ₂ = 0.1249
Final R indexes [all data]	R ₁ = 0.0498, wR ₂ = 0.1283
Largest diff. peak/hole / e Å ⁻³	0.27/-0.25

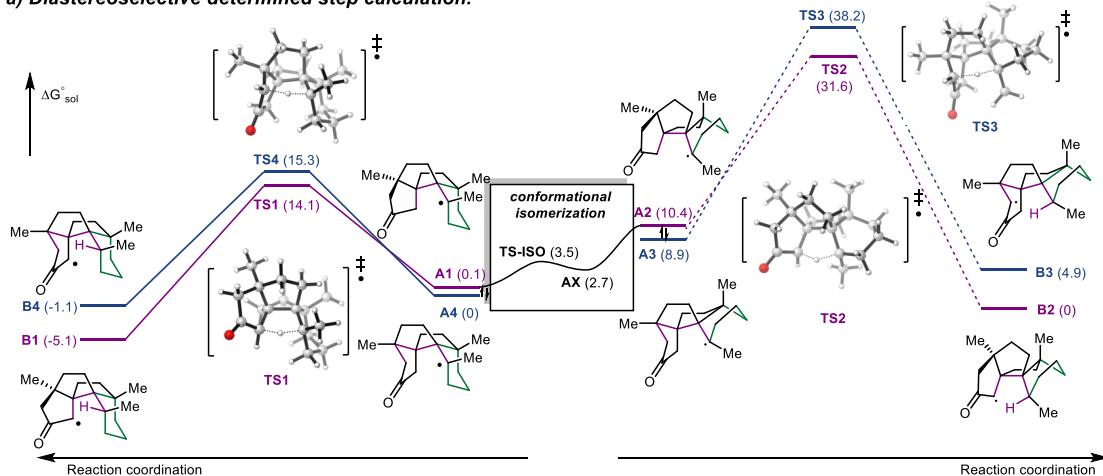
Part VI. Computational Studies for the HAT Process

Computational details

The molecular geometries of the complexes were optimized using density functional theory (DFT) calculations at the B3LYP-D3 level.^[6] Frequency calculations were also performed at the same level of theory to identify all the stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency), and the free energies at 333.15 K. An IRC^[7] analysis was performed to confirm that all the stationary points were smoothly connected to each other. The 6-31G**^[8] basis set was used for the C, H and O atoms. Solvation energies (in EtOH, 333.15 K) were evaluated by a self-consistent reaction field (SCRF) using the SMD model.^[9] The 6-311++G** basis set was used for all atoms. Extensive conformational searches for the intermediates and transition states have been conducted, and only the lowest energy conformers and isomers are shown in this work. The three-dimensional images of the optimized structures were prepared using CYLview.^[10] All calculations were performed using the Gaussian 09 package.^[11]

Results and Discussion

a) Diastereoselective determined step calculation.



b) conformational isomerization

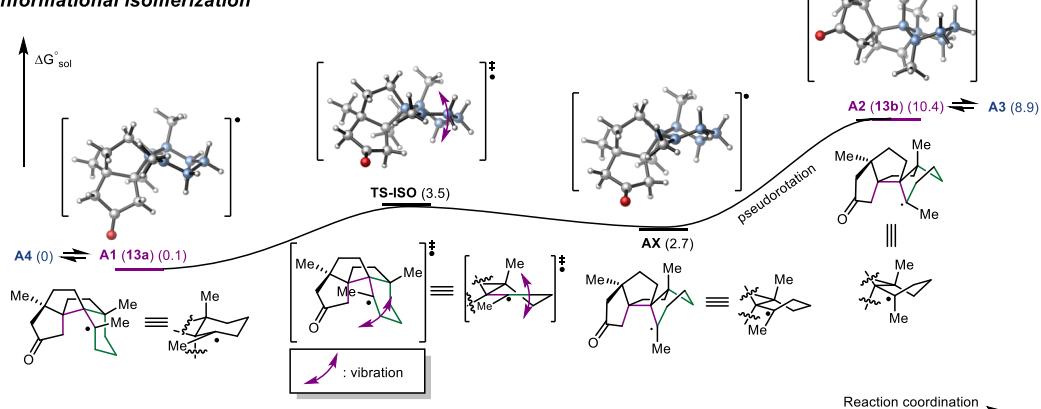


Figure S1. a) Diastereoselective determined step calculation. b). Conformational isomerization calculation, the six-membered ring were highlighted in blue.

We carried out density functional theory (DFT) experiment to reveal the excellent diastereoselective. Take the most stable conformation of 3° carbon-centered radical intermediate **A4** as the reference point (0 kcal/mol). As shown in figure S1b, **13a** (**A1**) could afford the twist conformational isomer **AX** via the half-twist transition state **TS-ISO** bearing an energy barrier of 3.5 kcal/mol, and **AX** could give other conformational isomers (**A2** and **A3**) via a subsequent pseudorotation.^[12] As the energy barrier of conformational isomerization is relative low ($\Delta G^\ddagger = 3.5$ kcal/mol), indicating that the conformational isomers can interconvert.

As shown in figure S1a, **A1** (**13a**) can undergoes the 1,4-HAT process via 5-membered transition state **TS1** to give radical species **B1** bearing an energy barrier of 14.1 kcal/mol (**A4** as the reference point, the same below). On the other hand, **A4** can give radical species **B4** through 6-membered transition state **TS4** with an energy barrier of 15.3 kcal/mol. Both of **TS1** and **TS4** can lead to **13**, and the little difference of the energy barriers between 1,4- and 1,5-HAT processes ($\Delta\Delta G^\ddagger = 1.2$ kcal/mol) accounts for the results of deuterium labeling studies. Moreover, the tendency of further reductive SET also has been predicted by the vertical electron affinities calculation, which reveals that enol radical species ($VEA_{B1} = 82.3$ kcal/mol and $VEA_{B4} = 81.5$ kcal/mol) is more feasible to undergo the reductive SET process than 3° carbon-centered radical intermediate ($VEA_{A1} = 36.5$ kcal/mol and $VEA_{A4} = 40.7$ kcal/mol).

Conformations **A2** and **A3** with higher energies could give intermediate **B2** and **B3** via HAT process, respectively. Both of the energy barriers of 1,4-HAT transition state **TS2** ($\Delta\Delta G^\ddagger = 17.5$ kcal/mol) and 1,5-HAT transition state **TS3** ($\Delta\Delta G^\ddagger = 24.1$ kcal/mol) are much higher than that via **TS1** ($\Delta\Delta G^\ddagger = 0$) and **TS4** ($\Delta\Delta G^\ddagger = 1.2$ kcal/mol). Therefore, the transition state **TS2** and **TS3** that leading to **13-iso** are disfavor, which accounts for the excellent diastereoselectivity.

To account for the formation **13-iso** as the major product via the HAT reaction of ketal **17**, we then carried out a computational experiment, and the results are listed in the following Figure S2.

Accordingly, since the pathway that was proposed to afford **13-iso** via **TS6** requires an energy barrier of 38.3 kcal/mol, which is kinetically disfavor. Therefore, this intramolecular HAT pathway for the formation of **13-iso** can be ruled out.

In the reaction pathway via **TS5**, even though this intramolecular HAT process via **TS5** can afford **B5**, however, due to the bond dissociation energy of α C-H of ketal ($BDE > 95$ kcal/mol),^[13] which is higher than the BDE of α C-H of cyclopentanone ($BDE = 88$ kcal/mol)^[14], this process requires an energy barrier of 22.0 kcal/mol, which is 7.9 kcal/mol higher than that of **TS1** associated with the formation of **13** from **12** (see Figure 2 in main TEXT). The increased energy barrier makes the intramolecular 1,4-HAT process of **A5** less favour, and the intermolecular HAT reaction process (see Figure S2, b) turns out to be competitive, as a result, product **13-iso** becomes a major product.

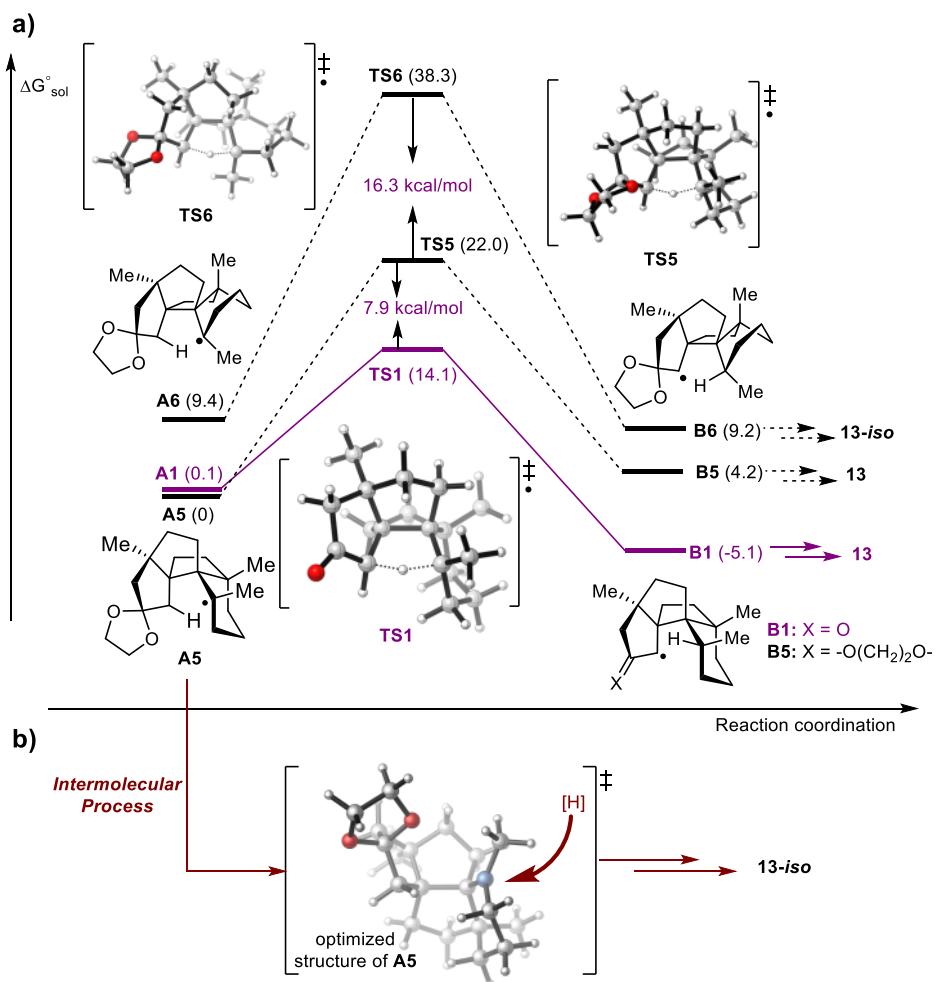


Figure S2. a) Energy profiles intramolecular 1,4-HAT, Solvated Gibbs free energies were given in kcal/mol. b) Proposed intermolecular process that lead to *13-iso*.

Calculated imaginary frequencies of all transition states species

Species	Frequencies
TS1	-1617.29
TS2	-1852.03
TS3	-1955.18
TS4	-1648.06
TS5	-1790.43
TS6	-2071.09
TS-ISO	-98.13

Table of energy values

Species	E ₀	E	H	G	G _(sol, EtOH, 333.15 K)
A1	-777.036585	-777.014868	-777.013813	-777.087621	-777.267436
A2	-777.021434	-777.000039	-776.998984	-777.071289	-777.2511363
A3	-777.024347	-777.002991	-777.001936	-777.074328	-777.2535333
A4	-777.03858	-777.016673	-777.015618	-777.089468	-777.2676732
A5	-930.817442	-930.792359	-930.791304	-930.873162	-931.0865759
A6	-930.80295	-930.778373	-930.777318	-930.856978	-931.0716217
AX	-777.034267	-777.012603	-777.011548	-777.084537	-777.2634289
<hr/>					
B1	-777.045297	-777.024089	-777.023034	-777.095696	-777.2758313
B2	-777.037272	-777.015882	-777.014827	-777.087492	-777.2677181
B3	-777.030331	-777.009088	-777.008033	-777.080054	-777.2598962
B4	-777.039361	-777.017916	-777.016861	-777.089623	-777.2694168
B5	-930.810612	-930.785821	-930.784766	-930.865189	-931.0799609
B6	-930.802189	-930.777308	-930.776253	-930.85682	-931.0718457
<hr/>					
TS-ISO	-777.034153	-777.013329	-777.012274	-777.083321	-777.2620366
TS1	-777.015883	-776.995038	-776.993983	-777.064786	-777.2452012
TS2	-776.98835	-776.967826	-776.966771	-777.036968	-777.2173418
TS3	-776.97902	-776.958359	-776.957304	-777.02757	-777.2067212
TS4	-777.01449	-776.993602	-776.992547	-777.063182	-777.2432449
TS5	-930.784048	-930.75996	-930.758905	-930.837232	-931.0514484
TS6	-930.757531	-930.733536	-930.732481	-930.810658	-931.0254664
<hr/>					
Vertical electron affinities calculation (based on the optimized geometry, charge = -1)					
A1(VEA)	-777.082246	-777.062495	-777.06144	-777.129448	-777.6877998
A4(VEA)	-777.090809	-777.070598	-777.069543	-777.139436	-777.6934879
B1(VEA)	-777.160117	-777.139734	-777.138679	-777.208299	-777.7738198
B4(VEA)	-777.152029	-777.131313	-777.130258	-777.200718	-777.7653284

E_0 = Sum of electronic and zero-point Energies

E = Sum of electronic and thermal Energies

H = Sum of electronic and thermal Enthalpies

G = Sum of electronic and thermal Free Energies

$G_{(\text{sol, EtOH, } 333.15 \text{ K})}$ = Solvated Gibbs free energy in EtOH at 333.15 K.

Cartesian coordination

A1

C 1.98187500 -2.06231500 -0.06228200

C 3.09708800 -1.27605800 -0.76367500

C 2.48586400 -0.04474700 -1.42433100

C 1.76738900 0.91307500 -0.43604200

C 0.70540000 0.15769500 0.47067700

C 1.20536800 -1.20913000 0.90542400

C 0.79622300 -1.87472900 2.18868100

C 0.89277600 1.87630700 -1.26457400

C -0.33292400 1.03930000 -1.65215100

C -0.65936200 0.15785800 -0.41813300

C -1.82131300 0.75005500 0.52818400

C -1.19553900 0.67865700 1.93598200

C 0.27605100 1.01347700 1.69869000

C -1.18159100 -1.23354800 -0.83042200

C -3.05429400 -0.16942500 0.33501700

C -2.23579300 2.20174800 0.22740700

C 2.83129900 1.65237900 0.39159700

C -2.68546600 -1.16121600 -0.74884300

O -3.47642300 -1.79700300 -1.43038900

H 2.39479600 -2.93404300 0.45936100

H 1.31732200 -2.46873100 -0.84596600

H 3.59042700 -1.90477100 -1.51563400

H 3.86541700 -0.98942400 -0.03514000

H 3.24995900 0.53146400 -1.96212000

H 1.77718900 -0.39649500 -2.18330400

H -0.89183000 -1.99125400 -0.08965900

H 0.63569400 -1.18029900 3.01728700

H -0.13718200 -2.45692200 2.08539700

H 1.56277100 -2.59174800 2.50803100

H 0.59570900 2.73835000 -0.65688100

H 1.42968500 2.26907300 -2.13635200

H -0.08500400 0.39562300 -2.50176800

H -1.17693300 1.65123400 -1.97782600

H -1.68057100 1.36380900 2.64125700

H -1.30450500 -0.33180800 2.34135700

H 0.91345400 0.84851800 2.57180500

H 0.35273900 2.07743600 1.45812200

H -0.84235800 -1.58873700 -1.80669000

H -3.96892100 0.36378100 0.05759300

H -3.28652700 -0.74704700 1.23994300

H -2.69704100 2.30262600 -0.75958400

H -2.98014600 2.52133400 0.96580100

H -1.39690100 2.90092900 0.28121800

H 3.57363400 2.11775700 -0.26778900

H 2.39766200 2.44773500 1.00392000

H 3.36452800 0.97132700 1.06349000

A2

C -2.52672400 -1.41642800 -1.27945900

C -3.42904300 -0.19710200 -0.90394600

C -3.08588400 0.30497800 0.50591600

C -1.61173300 0.78845400 0.63887400

C -0.62023100 -0.08560300 -0.27622200

C -1.29184100 -1.44325400 -0.40540400

C -1.30361600 -2.50773300 0.66082300

C -1.03534000 0.51759800 2.04540500

C 0.48946700 0.56091100 1.87335900

C 0.79410200 -0.01479700 0.45605400

C 1.73159500 0.91611300 -0.48085700

C 0.80592300 1.48954000 -1.56928400

C -0.33989400 0.48570700 -1.69873400

C 1.56376000 -1.36721700 0.53292100

C 2.93325100 -1.13187400 -0.05064000

C 2.77703200 -0.05472800 -1.08883400

O 3.96351300 -1.71165000 0.26144400

C 2.49497200 2.02766900 0.25231400

C -1.57371300 2.30291600 0.35844200

H -2.26893800 -1.36306200 -2.34572700

H -3.08685600 -2.34859800 -1.14410700

H -4.48696900 -0.47802200 -0.95995000

H -3.28891600 0.61703700 -1.62379500

H -3.76295200 1.12034500 0.78781700

H -3.27647600 -0.50453200 1.22080600

H 1.10953200 -2.11260800 -0.13344700

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H -2.27532000 -2.53664000 1.17967200

H -1.17947900 -3.50610300 0.21403900

H -1.39454700 1.24385300 2.78477700

H -1.35130000 -0.47118900 2.39208800

H 1.00798500 0.00150700 2.65870700

H 0.82776000 1.59355600 1.96192600

H 0.43560000 2.47282600 -1.27282700

H 1.34085000 1.62975600 -2.51599300

H -0.01779400 -0.34599900 -2.33735200

H -1.22321900 0.91940800 -2.17252900

H	1.62188900	-1.81032800	1.52928700	H	1.49950500	-1.50951800	2.62003400
H	3.72564400	0.41653000	-1.35793500	H	0.07942400	0.41112600	2.30000500
H	2.37504100	-0.54618700	-1.98662600	H	-1.08557700	-0.88798300	2.20910800
H	3.13131100	1.62935100	1.05188600	H	2.41280000	0.20253300	-1.88177700
H	3.14493600	2.55210700	-0.45779400	H	1.09407400	1.35652400	-1.95210700
H	1.82501700	2.77390500	0.68818200	H	3.65766100	0.29404900	1.14066600
H	-2.25356400	2.81422900	1.05023400	H	3.50846100	-1.51609400	-0.75929400
H	-0.58134800	2.73490200	0.50482400	H	3.57030400	-2.17884800	0.87729300
H	-1.90176600	2.54074900	-0.65864200	H	2.41776100	-2.83263900	-0.29208200
				H	-2.72139100	-2.74818000	-0.42722800
				H	-1.15563000	-2.81595300	0.38032900
A3							
C	-2.16676200	1.64677000	1.17211500	H	-2.52328400	-2.03800300	1.17251000
C	-3.32941900	0.68669800	0.74531300	H	2.17141100	0.87968600	1.86796100
C	-2.98835200	-0.01605600	-0.57622800				
C	-1.68621400	-0.84637600	-0.48341900	A4			
C	-0.49983600	-0.00443000	0.23813800	C	-1.46314800	2.11443300	-0.02455600
C	-0.95950600	1.44913200	0.28116500	C	-2.72337500	1.48080200	-0.63870000
C	-0.78361100	2.46011400	-0.82294600	C	-2.43456000	0.08453100	-1.19226900
C	-1.07557900	-1.13925700	-1.86808300	C	-1.83513100	-0.87571100	-0.13674100
C	0.37575100	-1.50208700	-1.55979700	C	-0.51078800	-0.28242300	0.48335100
C	0.83891600	-0.41507400	-0.56338600	C	-0.65970000	1.18098300	0.84637100
C	1.86272700	-0.88643800	0.54446400	C	-0.05542400	1.81763400	2.06261000
C	0.97094600	-1.43621900	1.66217300	C	-1.34690800	-2.16234000	-0.83911900
C	-0.21020800	-0.46555500	1.71256700	C	0.09098900	-1.88132000	-1.33517200
C	1.63235400	0.69468400	-1.28066900	C	0.61834100	-0.60954000	-0.60420800
C	2.37839400	1.40861000	-0.18310200	C	1.95359600	-0.74428800	0.24070700
C	2.58500300	0.42821300	0.95916700	C	1.51288300	-1.22474500	1.64878100
O	2.75150800	2.57339800	-0.19530900	C	-0.02822900	-1.15520500	1.68399500
C	2.89332000	-1.91144500	0.05737500	C	0.94743800	0.52817400	-1.58731400
C	-2.02868700	-2.18366200	0.20825900	C	2.53664000	0.70340400	0.25928600
H	-1.92152000	1.46193100	2.22511700	C	2.99266600	-1.68603800	-0.38439200
H	-2.50089400	2.68750000	1.11493700	C	-2.90286200	-1.17709400	0.92909400
H	-4.26503700	1.24729900	0.63993000	H	-1.74620100	2.99737100	0.56366500
H	-3.50553000	-0.06190900	1.52599600	H	-0.83002400	2.50991400	-0.83653900
H	-3.81389000	-0.67258200	-0.88015500	H	-3.11613800	2.12887700	-1.43177800
H	-2.89281300	0.73949100	-1.36574600	H	-3.50678400	1.41816000	0.12593000
H	0.19056800	2.96710600	-0.79727400	H	-3.35804600	-0.36378100	-1.58164600
H	-0.88310700	2.02248700	-1.82608200	H	-1.75581200	0.16537300	-2.04844000
H	-1.54447200	3.24354200	-0.74193100	H	2.44773200	1.20412500	1.22659200
H	-1.61557600	-1.92630600	-2.40800100	H	0.59560800	1.16015300	2.64030300
H	-1.10722100	-0.23405500	-2.48799700	H	0.53399500	2.70571900	1.78462500
H	1.01173700	-1.54301600	-2.45001600	H	-0.83930000	2.18385300	2.74603900
H	0.41293600	-2.49383100	-1.09784600	H	-1.34929200	-3.00115200	-0.13506000
H	0.64181100	-2.44727100	1.39748000	H	-2.01835900	-2.44652800	-1.65740600

H	0.10061000	-1.70911900	-2.41589700	H	0.96530300	-2.77188300	2.41075000				
H	0.72985900	-2.74979800	-1.15945100	H	-0.01946400	-1.32589600	2.64034700				
H	1.85085000	-2.25052000	1.83180700	H	2.49022900	2.40827000	-0.23120200				
H	1.97232800	-0.60833700	2.42827600	H	3.21475500	1.77255200	-1.70672200				
H	-0.42023200	-0.79121800	2.63750500	H	1.07353700	0.91855400	-2.49128200				
H	-0.41706600	-2.16821300	1.56510000	H	0.63129000	2.48083900	-1.85253800				
H	1.61027500	0.12528900	-2.36857600	H	-0.56107900	2.00354200	2.60028900				
H	0.10645500	1.00216800	-2.09072200	H	-1.02222000	0.37727700	2.09670300				
H	3.60291400	0.72611000	-0.00001900	H	1.43812900	0.26357800	2.62776500				
H	3.25148000	-1.38100500	-1.40548600	H	1.68387000	1.71734200	1.68342500				
H	3.91430700	-1.67045600	0.20929100	H	-1.09877200	0.29923500	-2.25969900				
H	2.64383700	-2.72221300	-0.41783000	H	-2.50771600	2.14332900	-0.76801500				
H	-3.82587400	-1.53193600	0.45458300	H	-2.88825400	1.61684500	0.87869700				
H	-2.57715200	-1.95285200	1.62789200	H	-0.61619200	3.62758100	-0.67766600				
H	-3.15232700	-0.28850000	1.51812700	H	-1.05914200	3.77671700	1.02132800				
C	1.77789500	1.49533500	-0.78654700	H	0.62195300	3.46266400	0.57752500				
O	1.84130200	2.70861800	-0.94524400	H	4.73463600	0.34538700	0.24883100				
A5											
C	1.41616900	-2.52172900	-0.31754700	H	3.80157700	-0.65362400	1.37182200				
C	2.84544900	-2.27047900	-0.81615400	O	-3.38704000	-0.15251300	-1.35977200				
C	2.94038100	-0.83655500	-1.32827100	O	-2.35429600	-0.94005000	0.51726500				
C	2.61814800	0.23271100	-0.25044300	C	-4.23447900	-1.14922300	-0.77225000				
C	1.20353200	-0.00997600	0.43517400	C	-3.75224900	-1.20062100	0.67129500				
C	0.96071500	-1.48871800	0.68254500	H	-5.27977300	-0.84130500	-0.87204900				
C	0.29406800	-2.06182200	1.90039700	H	-4.09107200	-2.11492800	-1.27563400				
C	2.43425600	1.59011200	-0.95796100	H	-4.23350600	-0.42619900	1.28491900				
C	1.03346800	1.50551800	-1.56769800	H	-3.87323900	-2.17425100	1.15112600				
C	0.13964300	0.76737600	-0.53562000	A6							
C	-0.72375100	1.72726400	0.41995700	C	-3.02230300	-1.79121700	-1.10074500				
C	-0.38706400	1.22891400	1.84370200	C	-4.08122200	-0.71454500	-0.70572600				
C	1.07657900	0.81064500	1.75225400	C	-3.73854400	-0.12062400	0.66687100				
C	-0.92295900	-0.10188300	-1.25546600	C	-2.35745500	0.59974100	0.68876000				
C	-2.19726800	1.47242800	0.04147700	C	-1.30086600	-0.11963500	-0.28146200				
C	-0.41623100	3.22930200	0.32176200	C	-1.73685700	-1.57576000	-0.33093600				
C	3.77192000	0.25902300	0.76698900	C	-1.45650000	-2.59970600	0.73563600				
C	-2.24442500	0.04601500	-0.50747800	C	-1.65266400	0.45261700	2.05664600				
H	1.33680200	-3.52145700	0.12762400	C	-0.15983200	0.70586600	1.79001900				
H	0.75621300	-2.53944600	-1.20260700	C	0.12539400	0.21505600	0.33756500				
H	3.09980000	-2.97862800	-1.61511200	C	0.79747100	1.31385100	-0.64613400				
H	3.56012400	-2.44122100	-0.00171000	C	-0.26390700	1.62638700	-1.72233200				
H	3.94275500	-0.62918400	-1.72515500	C	-1.21372500	0.42876400	-1.73769300				
H	2.24959300	-0.73966500	-2.17443900	C	1.12482600	-0.97723600	0.29251800				
H	-0.65257400	-1.15142000	-1.36459300	C	2.44967600	-0.41953600	-0.19753500				
H	-0.60031600	-2.64010400	1.62294600	C	2.02315100	0.58789900	-1.25709600				

C	-2.76754300	1.53355900	-0.69604500	H	-3.46826800	-0.78171800	0.85643100	
C	-2.34356700	0.26706600	-1.44257300					
C	-1.74276300	-0.82183600	-0.51612300	B2				
C	-0.59628800	-0.24493600	0.38965800	C	-2.24099700	-1.64093900	-1.20958000	
C	-0.87635800	1.17879100	0.99633400	C	-3.33011700	-0.61813500	-0.79810700	
C	-1.68061300	1.15956800	2.31184600	C	-3.03357900	0.03864200	0.55504300	
C	-1.00326900	-1.86445400	-1.38195900	C	-1.68034600	0.79406100	0.54245300	
C	0.34399100	-1.22234600	-1.73401900	C	-0.55198100	0.00008700	-0.25999700	
C	0.74502000	-0.28958900	-0.53665300	C	-0.91743200	-1.51488200	-0.40024800	
C	1.93389900	-0.77642900	0.44112900	C	-0.97822200	-2.38833700	0.86985500	
C	1.25716800	-0.89317200	1.82786400	C	-1.05975300	0.94386100	1.94813100	
C	-0.18714300	-1.24489500	1.50208700	C	0.39870700	1.30492100	1.67169900	
C	1.23946000	0.99755300	-1.06996100	C	0.83529700	0.33374400	0.54434900	
C	3.01913500	0.33126600	0.39524200	C	1.82898500	0.89794200	-0.55522800	
C	2.54416100	-2.12870300	0.04817600	C	0.91637300	1.49685600	-1.62911900	
C	-2.88781200	-1.49388800	0.26423500	C	-0.27821100	0.54201900	-1.70207300	
C	2.49724400	1.41440400	-0.53182100	C	1.59054600	-0.81994500	1.08872400	
O	3.08703200	2.47981600	-0.79703800	C	2.60595200	-1.28229400	0.18746700	
H	-1.82669800	3.06574600	0.52831500	C	2.58884500	-0.37066300	-1.03134500	
H	-0.83326500	2.45028400	-0.77384000	O	3.36683700	-2.25090400	0.36556900	
H	-3.20348600	2.25468400	-1.39868600	C	2.84334100	1.90705700	-0.00503400	
H	-3.54979300	1.30442100	0.03794000	C	-1.96408700	2.20715800	-0.02036500	
H	-3.19210000	-0.16968100	-1.98467500	H	-2.02703200	-1.52591600	-2.27727200	
H	-1.60749200	0.55443200	-2.20398300	H	-2.61927300	-2.66222600	-1.08934800	
H	0.09937200	1.61436900	1.24673100	H	-4.31393500	-1.10047500	-0.77112100	
H	-1.14037900	0.66264700	3.12206700	H	-3.40107300	0.16848600	-1.55894200	
H	-1.86987200	2.18819400	2.63929600	H	-3.83300600	0.74651600	0.80699100	
H	-2.65092700	0.66581300	2.20678100	H	-3.04905300	-0.71889400	1.34345300	
H	-0.85277200	-2.79070500	-0.81640700	H	-0.12292800	-1.96099900	-1.01229400	
H	-1.58165800	-2.13020400	-2.27473000	H	0.00449600	-2.51846700	1.32652000	
H	0.23579200	-0.61183400	-2.63601300	H	-1.65188400	-2.01302700	1.64123000	
H	1.11506300	-1.95902000	-1.96119400	H	-1.32860800	-3.39001400	0.59437400	
H	1.74849400	-1.64008500	2.46136800	H	-1.57892000	1.69163400	2.55890400	
H	1.30273600	0.06234800	2.36270900	H	-1.11040600	-0.00979700	2.48692700	
H	-0.85076600	-1.22166700	2.36752800	H	1.04117900	1.22264000	2.55431800	
H	-0.21960000	-2.26750700	1.11374000	H	0.46735600	2.34000200	1.32594000	
H	0.73674600	1.56368600	-1.84647900	H	0.60378300	2.49955700	-1.31849000	
H	3.97309500	-0.03114500	-0.00814700	H	1.42847800	1.60452400	-2.59260600	
H	3.23907800	0.75396100	1.38219200	H	-0.01569500	-0.29935300	-2.35121200	
H	2.99575800	-2.09721900	-0.94886700	H	-1.15951400	1.00527400	-2.15031600	
H	3.33568800	-2.39315500	0.75879500	H	1.46106700	-1.22726400	2.08552000	
H	1.80200300	-2.93420300	0.06125600	H	3.60374700	-0.16453200	-1.38555200	
H	-3.57890500	-1.97140300	-0.44108500	H	2.06160900	-0.88830800	-1.84252500	
H	-2.52567900	-2.27326700	0.94053200	H	3.45892300	1.46250800	0.78588200	

H	3.51568300	2.23543600	-0.80599900	H	1.01811700	1.52897300	-1.78557900
H	2.35554800	2.79716100	0.40289600	H	3.18361200	0.55734100	1.78798500
H	-2.61591800	2.74483900	0.67762900	H	3.50608800	-1.48564900	-0.84821900
H	-1.06530900	2.81103300	-0.15722000	H	3.68380400	-2.07393800	0.81331500
H	-2.48394500	2.16998400	-0.98198000	H	2.48732300	-2.81512500	-0.25924100
				H	-2.62590000	-2.80855400	-0.32802900
				H	-1.02006300	-2.84260100	0.39495900
B3				B4			
C	-2.14952400	1.63287200	1.19423900	H	-2.36191600	-2.09491400	1.26039400
C	-3.28321500	0.64687900	0.79916000	H	-0.07662400	2.01631600	0.81088400
C	-2.97787400	-0.11277000	-0.50089900				
C	-1.63595600	-0.88368700	-0.43779300				
C	-0.47717900	-0.01471400	0.24260700	C	-1.34094600	2.14047100	0.01782200
C	-0.89329400	1.49802000	0.29458700	C	-2.57814400	1.59568200	-0.70409000
C	-1.12088500	2.25837700	-1.04687400	C	-2.25795100	0.27705900	-1.41526400
C	-1.06195700	-1.18943700	-1.84079700	C	-1.74450000	-0.82455900	-0.45508800
C	0.42169900	-1.45971800	-1.58856200	C	-0.52037200	-0.31302300	0.38269600
C	0.86080600	-0.37511600	-0.57908900	C	-0.70411200	1.12348400	0.99707400
C	1.89990900	-0.85662700	0.51482900	C	-1.47330100	1.15116000	2.33407800
C	1.03929300	-1.41075100	1.65887600	C	-1.14251800	-1.99106200	-1.27761300
C	-0.14066700	-0.43840900	1.71381600	C	0.35594500	-1.68107500	-1.49250800
C	1.61424000	0.79971500	-1.24590000	C	0.74436600	-0.47831900	-0.57438100
C	2.42563500	1.42577200	-0.12377500	C	1.96930400	-0.68837900	0.43455700
C	2.59283200	0.41858100	0.88693700	C	1.33530700	-1.05585300	1.81396800
O	2.87232500	2.58619500	-0.09821900	C	-0.13023700	-1.33946500	1.48603000
C	2.95794400	-1.86744300	0.01931100	C	1.21488800	0.72093600	-1.43292500
C	-1.91451500	-2.22891000	0.27142900	C	2.62616600	0.65250700	0.47284200
H	-1.87409500	1.46976900	2.24064500	C	3.00115500	-1.74827000	-0.00956400
H	-2.50279000	2.66870300	1.13789300	C	-2.92858800	-1.34531000	0.38109400
H	-4.23614900	1.17805800	0.69461600	H	-1.60197100	3.04729100	0.57755400
H	-3.43284300	-0.08050900	1.60591600	H	-0.60818200	2.45887600	-0.72809700
H	-3.78828000	-0.82253100	-0.71048200	H	-2.93994000	2.33491300	-1.42981200
H	-2.97368700	0.58751500	-1.34050700	H	-3.39444900	1.44591800	0.01342100
H	-0.38927400	3.06474400	-1.16427100	H	-3.14819800	-0.10208300	-1.93424200
H	-1.05093700	1.62720500	-1.93306800	H	-1.50975500	0.46305100	-2.19556300
H	-2.11004600	2.72640800	-1.07406600	H	0.29698000	1.50444600	1.23623200
H	-1.57324800	-2.02905900	-2.32666900	H	-0.96324500	0.58906600	3.12095200
H	-1.17778200	-0.32025100	-2.49819600	H	-1.55547000	2.18617600	2.68489000
H	1.02474500	-1.44574300	-2.50223700	H	-2.48847700	0.75459300	2.24600500
H	0.53569700	-2.45632700	-1.14939600	H	-1.26353100	-2.93300000	-0.73235000
H	0.72020000	-2.42715100	1.40690000	H	-1.67870500	-2.11568900	-2.22532500
H	1.58962600	-1.46661600	2.60496600	H	0.55082000	-1.42211500	-2.53711500
H	0.18571100	0.45004000	2.26718000	H	0.95959600	-2.56692700	-1.28449300
H	-0.99999900	-0.83986900	2.25359600	H	1.83723800	-1.91146500	2.27677200
H	2.33636700	0.38839200	-1.96615900	H	1.41808800	-0.21734600	2.51424300

H	-0.77696900	-1.30661200	2.36380600	H	0.68198700	0.72875600	-2.59488000	
H	-0.20915900	-2.35421900	1.08310000	H	0.38041400	2.35471700	-2.03249500	
H	1.82699300	0.33424600	-2.26088300	H	-0.34629900	2.22117000	2.57811000	
H	0.43191200	1.32423800	-1.88773300	H	-0.77691100	0.54441900	2.22990100	
H	3.37409800	0.93509400	1.20832600	H	1.74475400	0.63166700	2.47091400	
H	3.33828200	-1.57483800	-1.03689700	H	1.78024100	1.95655300	1.33377300	
H	3.87735200	-1.71840700	0.64711800	H	-0.99053400	-0.85875800	-1.76280200	
H	2.57561200	-2.75490400	0.04950500	H	-2.65269600	2.20754200	-0.51304000	
H	-3.66629400	-1.81271300	-0.28309600	H	-2.82533200	1.68883500	1.17269900	
H	-2.61733200	-2.10435100	1.10461400	H	-0.75538200	3.60511000	-0.80688500	
H	-3.44352300	-0.55372400	0.93058300	H	-0.98226100	3.90260900	0.91575800	
C	2.15877600	1.52757500	-0.56296300	H	0.62898300	3.52895100	0.29123900	
O	2.48335000	2.71614000	-0.73701300	H	4.65145900	0.50219800	-0.34219100	
B5								
C	1.07624500	-2.45037600	-0.22962100	H	4.03904000	-0.60868600	0.88392800	
C	2.48183400	-2.37731700	-0.82578500	O	-3.52481000	-0.03082800	-1.09653400	
C	2.66858900	-1.00614900	-1.47425900	O	-2.55732700	-0.84624500	0.81549200	
C	2.50971500	0.18426900	-0.48912000	C	-3.97085800	-1.38118400	-0.93543600	
C	1.20026500	0.07677600	0.38467000	C	-3.73990800	-1.61108000	0.55163400	
C	0.84171200	-1.38028500	0.85882600	H	-5.01784100	-1.44176200	-1.24127600	
C	1.54382400	-1.81880900	2.16152600	H	-3.36837000	-2.06925700	-1.54527800	
C	2.26301600	1.46641300	-1.31571600	H	-4.58010000	-1.22722900	1.14629900	
C	0.79006800	1.38931900	-1.72847300	H	-3.56105200	-2.65941200	0.80881400	
C	0.02217500	0.76968900	-0.52218400	B6				
C	-0.73242200	1.80513300	0.44793900	C	-2.29118000	-2.11352300	-1.17832700	
C	-0.22195700	1.41013200	1.85105600	C	-3.62027700	-1.51062700	-0.65691500	
C	1.23632300	1.04473100	1.59862100	C	-3.46217600	-0.84213400	0.71430600	
C	-1.08247100	-0.11763000	-0.97681200	C	-2.43344000	0.31757000	0.67107700	
C	-2.24442600	1.54287300	0.25673900	C	-1.17831700	-0.01997600	-0.25324200	
C	-0.43390400	3.28958600	0.19047900	C	-1.02821800	-1.56487300	-0.45418000	
C	3.80771000	0.30631200	0.33094900	C	-0.69733000	-2.44576400	0.76795400	
C	-2.37284200	0.11666200	-0.26944500	C	-1.77611600	0.60026700	2.03866800	
H	0.88380600	-3.44146100	0.20072600	C	-0.54979400	1.44275500	1.68752700	
H	0.35233400	-2.32467500	-1.04232000	C	0.08533200	0.72632600	0.46572800	
H	2.62107900	-3.16770700	-1.57433600	C	0.71629500	1.64638000	-0.65652500	
H	3.23851000	-2.54783900	-0.04966400	C	-0.43572300	1.93551700	-1.62459900	
H	3.65413700	-0.92724300	-1.95139400	C	-1.23782900	0.62999800	-1.67416900	
H	1.93050800	-0.92065400	-2.28080700	C	1.24969900	-0.10909600	0.87181900	
H	-0.23060400	-1.38814200	1.07676000	C	2.33873900	-0.13050300	-0.14624100	
H	1.19688800	-1.25097100	3.02911500	C	1.79869000	0.73072800	-1.29004500	
H	1.31874200	-2.87268000	2.36349000	C	1.37791300	2.91851700	-0.11365800	
H	2.63240900	-1.72034500	2.11469200	C	-3.21262300	1.58161900	0.23510200	
H	2.44184300	2.35471700	-0.69866000	H	-2.21068600	-1.92510400	-2.25424600	
H	2.94120300	1.53268100	-2.17535700	H	-2.30462600	-3.20382000	-1.06541800	

H	-4.39577900	-2.28398100	-0.60952300	C	0.65774700	-0.31709400	-0.53769600
H	-3.98672100	-0.76021400	-1.36783300	C	1.84833400	-0.88642400	0.36251900
H	-4.43049500	-0.44803800	1.04772800	C	1.36779600	-0.56359800	1.79667900
H	-3.17537300	-1.59010300	1.45881800	C	-0.13882300	-0.80775800	1.74015200
H	-0.17638800	-1.69617200	-1.13365400	C	1.15374100	1.07458000	-0.91503500
H	0.25012000	-2.16478200	1.22793800	C	3.09506700	-0.06479400	-0.02135000
H	-1.46403100	-2.43333600	1.54414300	C	2.13268700	-2.38813300	0.22736700
H	-0.59578700	-3.48554200	0.43364600	C	-2.76279100	-1.59116100	0.73217400
H	-2.45754700	1.09982100	2.73783700	C	2.58713200	1.21367200	-0.66656400
H	-1.45980300	-0.33974200	2.50645100	O	3.29161000	2.18902600	-0.95629200
H	0.15895200	1.54251400	2.51597800	H	-1.98444700	3.11332600	0.01686200
H	-0.86393300	2.45537300	1.41787900	H	-1.28583000	2.25368800	-1.34651500
H	-1.04226700	2.75899300	-1.23267600	H	-3.70866100	1.85863800	-1.26852000
H	-0.07775100	2.24612800	-2.61390700	H	-3.58395500	1.16632400	0.34702700
H	-0.76578800	-0.04563700	-2.39473400	H	-3.54066300	-0.60697700	-1.50609500
H	-2.25946700	0.77938000	-2.02990700	H	-2.10098000	0.17158000	-2.13684100
H	1.40161900	-0.50259300	1.87126000	H	0.42459900	1.70553300	0.02581800
H	2.60270100	1.28923200	-1.77786900	H	-0.05394000	1.65508000	2.64953100
H	1.36113900	0.05668100	-2.03067600	H	-0.75465100	3.10391800	1.92197000
H	2.16623500	2.67912100	0.60826400	H	-1.80517800	1.79423300	2.46735600
H	1.83773900	3.48311900	-0.93339300	H	-0.70501300	-2.79344200	-0.48836700
H	0.65552400	3.57880800	0.37573500	H	-1.68650700	-2.39759600	-1.89873500
H	-3.95004600	1.82944300	1.00733000	H	-0.14518500	-0.58091600	-2.53395200
H	-2.57901200	2.45949800	0.09781700	H	0.93947700	-1.88229700	-2.08364800
H	-3.76345500	1.42420100	-0.69685700	H	1.87534100	-1.17616300	2.55050100
O	3.57333000	0.40593300	0.35659700	H	1.58593500	0.48474300	2.03220000
O	2.66415600	-1.47772400	-0.57197200	H	-0.68156500	-0.46745600	2.62580600
C	3.99378100	-1.79608200	-0.13875700	H	-0.30152500	-1.88677600	1.67576700
C	4.30132900	-0.70683600	0.88300300	H	0.76079800	1.57568200	-1.80043100
H	4.68579700	-1.75034800	-0.99030000	H	3.69797200	-0.58374400	-0.77994300
H	4.01049200	-2.80447600	0.28639600	H	3.76105400	0.14489400	0.82354600
H	5.35829300	-0.43665900	0.94165700	H	2.42206300	-2.65944900	-0.79256200
H	3.93792200	-0.97901500	1.88396500	H	2.96622100	-2.66127500	0.88509200
				H	1.27493900	-3.00556200	0.50936500
TS1				H	-3.53834700	-2.14201600	0.18719900
C	-1.75891000	2.11212200	-0.36573500	H	-2.25994700	-2.30765300	1.38623700
C	-3.04096800	1.30596900	-0.59620400	H	-3.26704200	-0.85664000	1.36964200
C	-2.65243400	-0.03483900	-1.21142200				
C	-1.80044100	-0.91994700	-0.26455900	TS2			
C	-0.61175100	-0.13289900	0.42605800	C	2.01906200	1.81103400	-1.16119300
C	-0.80093500	1.40830500	0.59539100	C	3.11431600	0.67651900	-1.12754800
C	-0.84061100	2.01390000	1.98398600	C	3.07064900	-0.23953500	0.12128700
C	-1.04340200	-1.96578600	-1.12236000	C	1.67526900	-0.90040900	0.38807600
C	0.16892000	-1.21142800	-1.69472900	C	0.55610200	-0.00599900	-0.23968100

C	0.97517100	1.47488800	-0.11143700	C	-3.11710400	1.20386200	0.49583200
C	1.34146000	2.13887600	1.21926000	C	-2.78314700	0.40789800	-0.79222300
C	1.24139800	-0.93254400	1.88445700	C	-1.76828700	-0.73688500	-0.56880700
C	-0.31168100	-0.86696800	1.89988000	C	-0.52264800	-0.19726300	0.26993300
C	-0.76982700	-0.18355800	0.57689500	C	-0.61145600	1.31309400	0.56787200
C	-1.79966400	-0.97647000	-0.37325700	C	-0.46424500	2.41170400	-0.49877900
C	-0.94510200	-1.41646000	-1.58124900	C	-1.08947800	-1.26764000	-1.86163800
C	0.14299200	-0.34601300	-1.69868900	C	0.28445800	-1.78590700	-1.38882500
C	-1.37514900	1.22021900	0.69701700	C	0.78966000	-0.61926100	-0.53058200
C	-2.66385100	1.31010000	0.02402400	C	1.80383500	-0.81882100	0.63965100
C	-2.86006800	0.07162400	-0.82034800	C	1.02014400	-1.56906000	1.70608400
O	-3.46790200	2.24805800	0.10561800	C	-0.34776100	-0.89154100	1.69086100
C	-2.50937000	-2.16508600	0.28182000	C	1.53515000	0.43775300	-1.38658700
C	1.71419100	-2.35269100	-0.12509400	C	2.29868600	1.28648400	-0.36952800
H	1.59167900	1.86277000	-2.16694300	C	2.05534600	0.67705000	0.94467500
H	2.47244600	2.78601100	-0.95554200	O	2.97181700	2.28839200	-0.62927300
H	4.10853700	1.13120900	-1.19806600	C	3.11307300	-1.54492400	0.28913000
H	3.00169800	0.05218100	-2.01966400	C	-2.52760500	-1.91188100	0.08253500
H	3.82814000	-1.02094800	-0.00974000	H	-1.90107500	0.98720200	2.30137000
H	3.38915500	0.32832600	1.00071100	H	-1.92936700	2.63008500	1.68849100
H	-0.39687500	1.83695200	-0.07163100	H	-3.64821000	2.11618800	0.20481400
H	0.75084100	1.80810500	2.07264700	H	-3.81490200	0.62538700	1.11084600
H	2.39780200	1.99844300	1.46642400	H	-3.71502000	-0.00127500	-1.20227400
H	1.19007700	3.22028900	1.11190400	H	-2.40390200	1.09341000	-1.55446400
H	1.60938400	-1.83458000	2.38685000	H	0.52574800	2.87398700	-0.50130200
H	1.66651500	-0.08613700	2.42674300	H	-0.65267900	2.06044300	-1.51478300
H	-0.68005600	-0.32691100	2.77865700	H	-1.17874700	3.21577400	-0.30061900
H	-0.71680100	-1.87782100	1.97013300	H	-1.68889500	-2.03316100	-2.36687100
H	-0.51008600	-2.40122700	-1.40075800	H	-0.93950000	-0.44741500	-2.57472800
H	-1.54695800	-1.50144400	-2.49327600	H	0.95941900	-2.03200700	-2.21486800
H	-0.29158000	0.54877800	-2.16148000	H	0.15490900	-2.69333400	-0.78755900
H	0.97849200	-0.65553600	-2.33026800	H	0.95374700	-2.62498000	1.41704200
H	-1.28563500	1.78816900	1.62146400	H	1.50226800	-1.53195900	2.68926700
H	-3.88916500	-0.28882600	-0.71602900	H	-0.35575200	-0.13290400	2.47352100
H	-2.73792500	0.35906400	-1.87310200	H	-1.14913700	-1.58334000	1.93720100
H	-3.07906300	-1.85875800	1.16713300	H	2.27508800	-0.08242600	-2.00911600
H	-3.21433100	-2.61316600	-0.42840900	H	0.93982600	1.04071400	-2.06920700
H	-1.80806800	-2.95040700	0.58044500	H	2.65755700	0.98634600	1.79881200
H	2.53430700	-2.88342700	0.37225800	H	3.70034800	-1.02741900	-0.47553000
H	0.79413600	-2.89818600	0.10318600	H	3.74390000	-1.63681700	1.18059300
H	1.89115700	-2.41254900	-1.20390500	H	2.89694400	-2.55554900	-0.07606000
				H	-3.31251000	-2.24980100	-0.60430200
TS3				H	-1.88131300	-2.77113900	0.28765000
C	-1.87018300	1.57996600	1.38615000	H	-3.01698200	-1.62747000	1.01897800

H	0.71308200	1.24655700	1.12274800	H	-3.86302200	-1.41055600	-0.32741500
				H	-2.78859800	-2.05973500	0.91226700
TS4							
C	-1.03809900	2.17902200	0.15849000	C	2.04047700	1.41335500	-0.64861400
C	-2.38150800	1.82632500	-0.50988800	O	2.52069500	2.49902200	-0.98983400
C	-2.25638000	0.54392900	-1.33816900				
TS5							
C	-1.81930500	-0.68998500	-0.50743000	C	1.46715100	-2.49088100	-0.40079400
C	-0.55913700	-0.36476200	0.36626700	C	2.95161500	-2.22450500	-0.65658200
C	-0.53855200	1.02895500	1.02861700	C	3.07707600	-0.83436300	-1.27233000
C	-0.97651000	1.16075600	2.47755800	C	2.63373800	0.30525100	-0.31615700
C	-1.31121700	-1.82712000	-1.45657600	C	1.25518500	0.01590100	0.41261900
C	0.24251000	-1.87728200	-1.37333400	C	0.84456100	-1.48637200	0.57390200
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C	1.84323200	-0.72879000	0.45808600	C	2.30207700	1.55299700	-1.17421100
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C	-0.28926700	-1.46526700	1.43339100	C	0.11807100	0.68776600	-0.51270800
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C	2.10371600	0.77031700	0.66454600	C	-0.36854000	1.18590600	1.83324600
C	3.10824600	-1.44832600	-0.03081600	C	1.11080000	0.80938400	1.73932200
C	-3.02107500	-1.16368300	0.33063500	C	-0.90783700	-0.39301800	-0.84302800
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H	-0.31967200	2.43163600	-0.62696600	C	-0.34981900	3.18084900	0.28964500
H	-2.70080300	2.65778800	-1.15020000	C	3.80504300	0.57341000	0.64741200
H	-3.15468700	1.70952600	0.25953500	C	-2.29465300	-0.00808500	-0.38494200
H	-3.21228200	0.31135400	-1.82530100	H	1.30728700	-3.50740200	-0.02334700
H	-1.54207400	0.71790100	-2.15012700	H	0.95511300	-2.43844200	-1.37239100
H	0.85940400	1.14629400	1.06689800	H	3.35879700	-2.98340500	-1.33677700
H	-0.42442900	0.50676700	3.15638400	H	3.52394300	-2.29556600	0.27734900
H	-0.83080200	2.19012500	2.82101100	H	4.10772400	-0.63176200	-1.58917400
H	-2.04530700	0.92678800	2.59212400	H	2.46976900	-0.82120900	-2.18601700
H	-1.74043500	-2.79200100	-1.16783500	H	-0.35660400	-1.31158600	0.03140900
H	-1.64773100	-1.63657500	-2.48153100	H	0.08007200	-1.44915700	2.63318300
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H	0.56473200	-2.78419600	-0.85262800	H	1.67021700	-2.19932100	2.45661000
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H	-0.55181500	-2.44431200	1.02587900	H	0.40868000	2.21403800	-2.09441200
H	1.84070000	0.06983800	-2.29309800	H	-0.56882900	1.94524600	2.59852500
H	0.42259600	1.06993100	-2.06938800	H	-0.98164900	0.31202100	2.07303100
H	2.81833400	1.11930800	1.40968900	H	1.49118900	0.27502800	2.61402100
H	3.53904200	-0.97480400	-0.91980500	H	1.68603000	1.73627500	1.67326600
H	3.87542700	-1.44116700	0.75198700	H	-0.85807800	-0.88933500	-1.81194500
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H	-0.48245000	3.55391800	-0.73062500	H	-2.43165200	1.23321600	2.65089800
H	-1.01489300	3.76443400	0.93744200	H	-1.89981000	-0.43029100	2.51353800
H	0.67724500	3.39754800	0.59636700	H	0.25146900	0.63709300	2.63946900
H	4.71669200	0.78751900	0.07692100	H	-0.35500200	2.09763000	1.88872000
H	3.62670500	1.43114900	1.30011600	H	-1.03899600	2.65916700	-1.28086600
H	4.01260100	-0.29199200	1.28659300	H	0.03518200	2.15287000	-2.57529000
O	-3.30302400	-0.17628200	-1.40004800	H	-0.56581100	-0.17919300	-2.30862900
O	-2.71082700	-0.84882300	0.70922700	H	-2.12199000	0.62186400	-2.17959400
C	-4.29079100	-1.09838700	-0.92225000	H	1.24944700	-1.21861300	1.33270400
C	-4.12646900	-1.00479000	0.58654400	H	2.73706600	1.52960000	-1.49889500
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H	-4.07798900	-2.11482000	-1.28173800	H	1.96349000	2.68222400	0.86215000
H	-4.65935500	-0.13311900	0.99331600	H	1.67218900	3.53295300	-0.66267900
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TS6

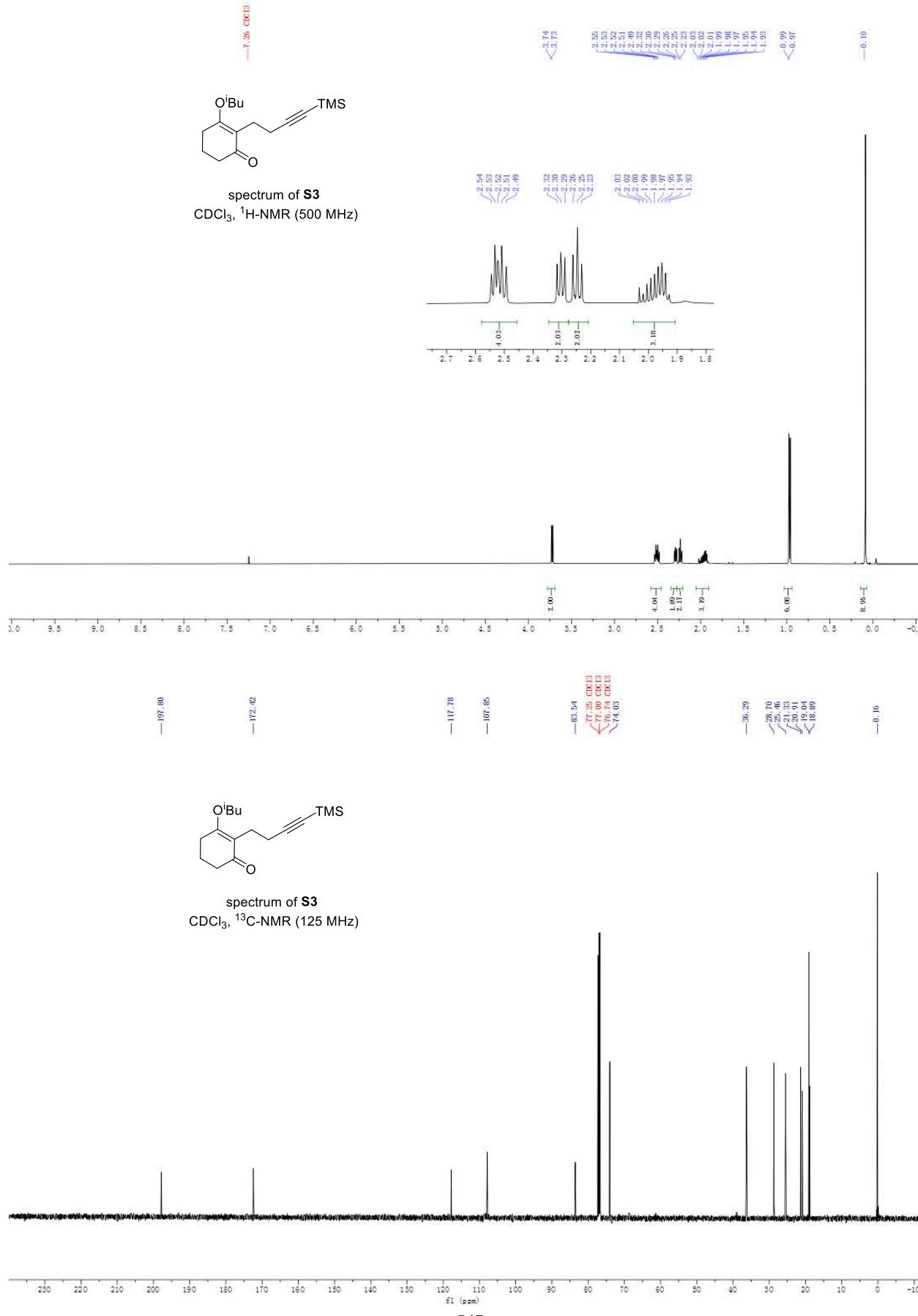
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C	-1.22635400	-0.02424900	-0.24308200	C	4.19953100	-0.68810500	1.03792700
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C	-1.15760300	-2.39785000	1.06746300	H	5.10099500	-0.89886200	-0.93005000
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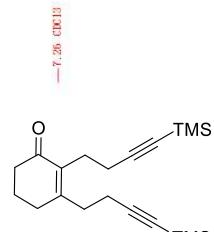
TS-ISO

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C	1.08871200	-0.64575100	0.42025100	C	-1.80479100	-0.89399400	-0.16338000
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C	1.21150700	2.88441700	0.09193900	C	-0.05175900	2.39310600	1.22051200
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H	-1.92637300	-1.99210500	-2.23062700	C	0.10493700	-1.50088600	-1.52097000
H	-2.30807600	-3.21630600	-1.03035500	C	0.65256200	-0.40450700	-0.57012100
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H	-3.77729800	-0.72307400	-1.73192900	C	1.40493500	-0.42644600	1.79895100
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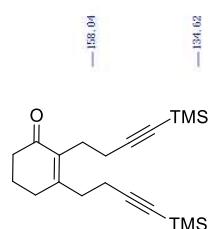
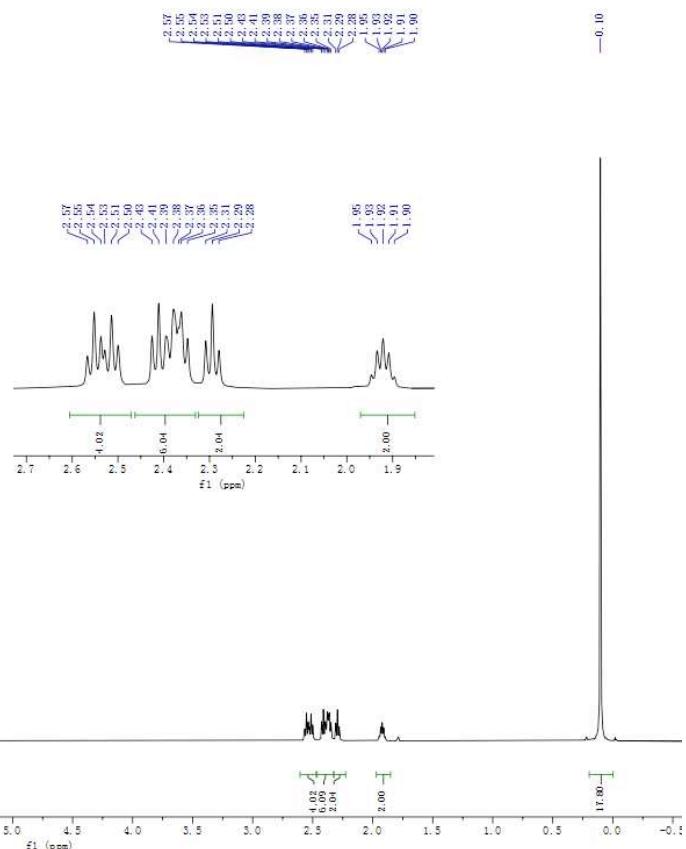
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H	-0.79908400	-2.81976000	-0.05211100
H	-1.77955700	-2.63907300	-1.50573900
H	-0.21083400	-1.03596500	-2.46063800
H	0.86044200	-2.24313900	-1.78998500
H	1.88638900	-1.02030700	2.58457300
H	1.68778100	0.61460000	1.97411100
H	-0.60724900	-0.08833200	2.62905100
H	-0.34633400	-1.65260400	1.87329800
H	1.43983300	0.48728100	-2.40823400
H	3.64751600	-0.65641800	-0.84849200
H	3.80622000	0.15517800	0.71671600
H	2.45600800	-2.75331800	-0.57886300
H	2.97977500	-2.57863500	1.09472200
H	1.29354100	-2.96903900	0.74081200
H	-3.69467200	-1.79554000	0.43055900
H	-2.38973800	-2.09270600	1.57806000
H	-3.16685500	-0.51038400	1.52489000

Part VII. NMR Spectra for the Synthesized Compounds

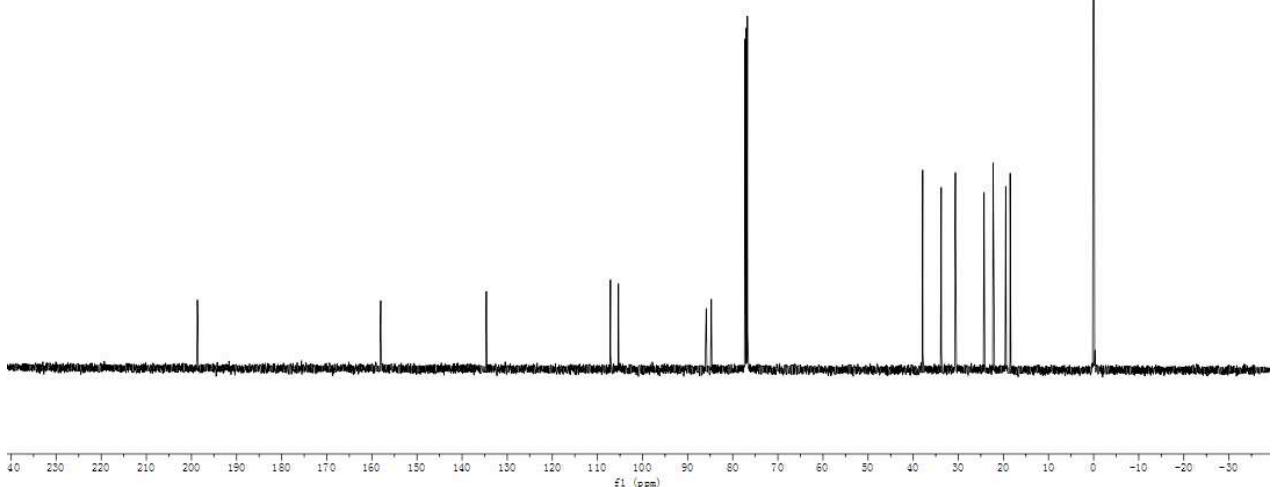


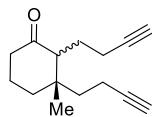


spectrum of **S4**
 CDCl_3 , $^1\text{H-NMR}$ (500 M)

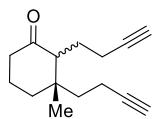
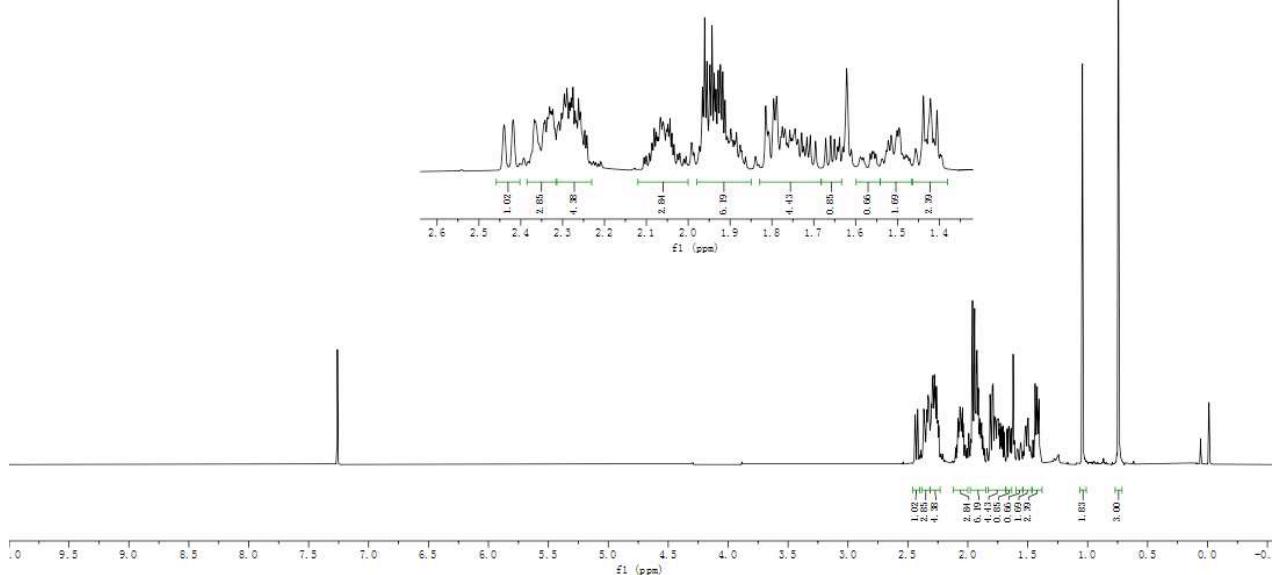


spectrum of **S4**
 CDCl_3 , ^{13}C -NMR (125 MHz)

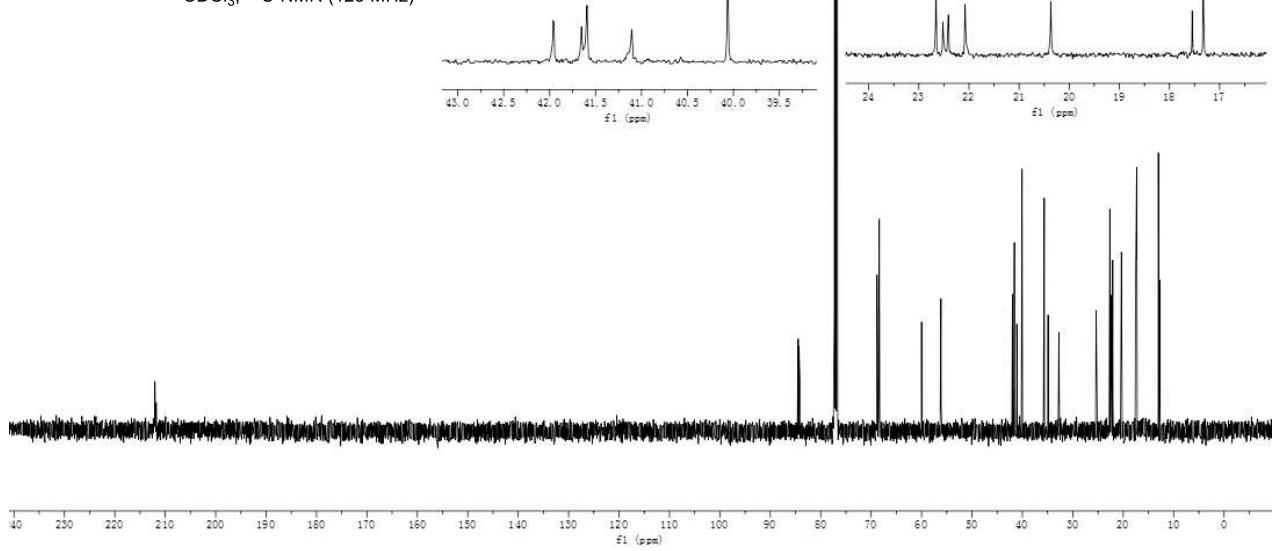


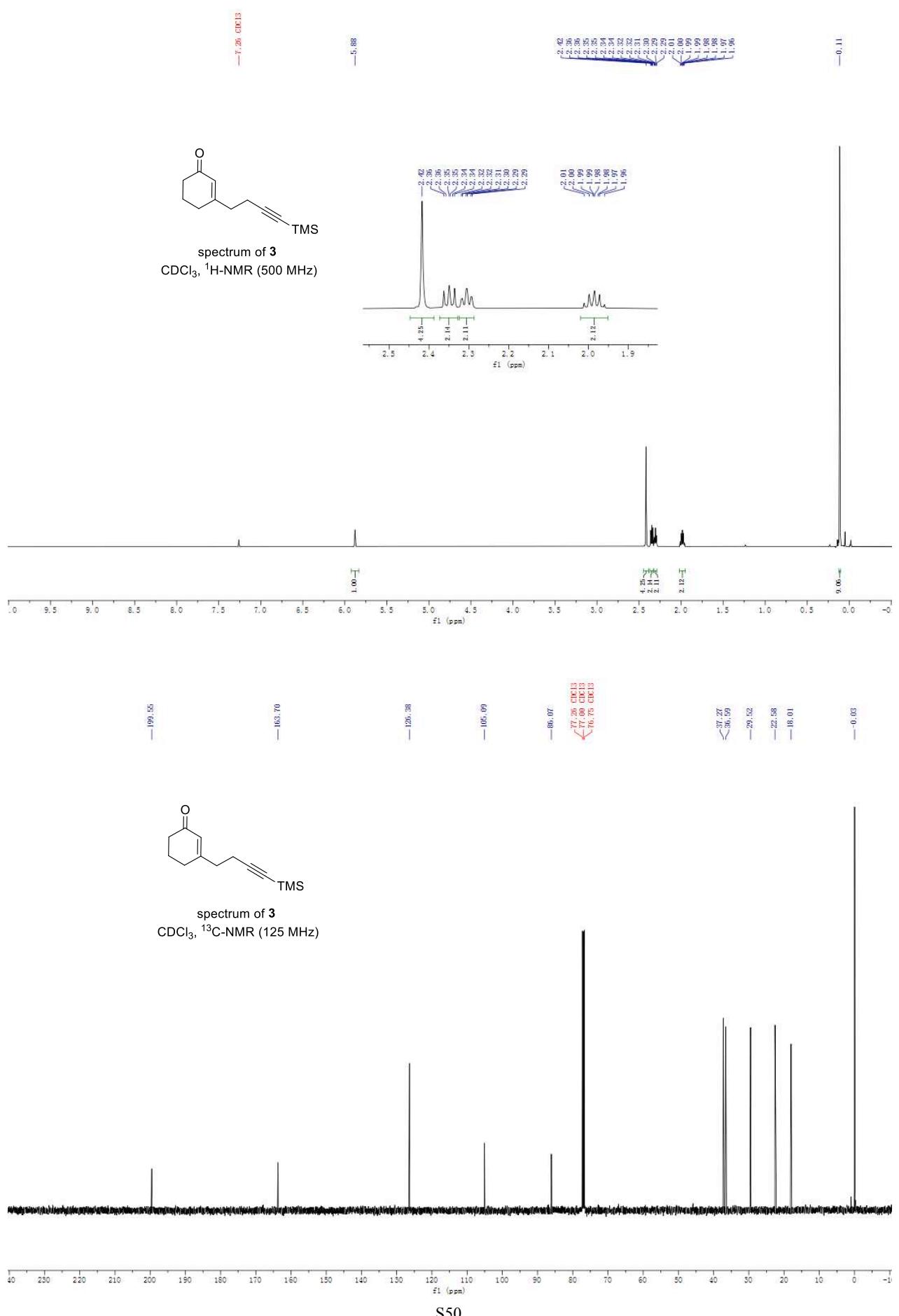


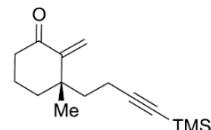
spectrum of (\pm)-7
CDCl₃, ¹H-NMR (500MHz)



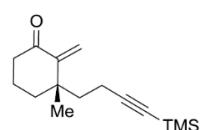
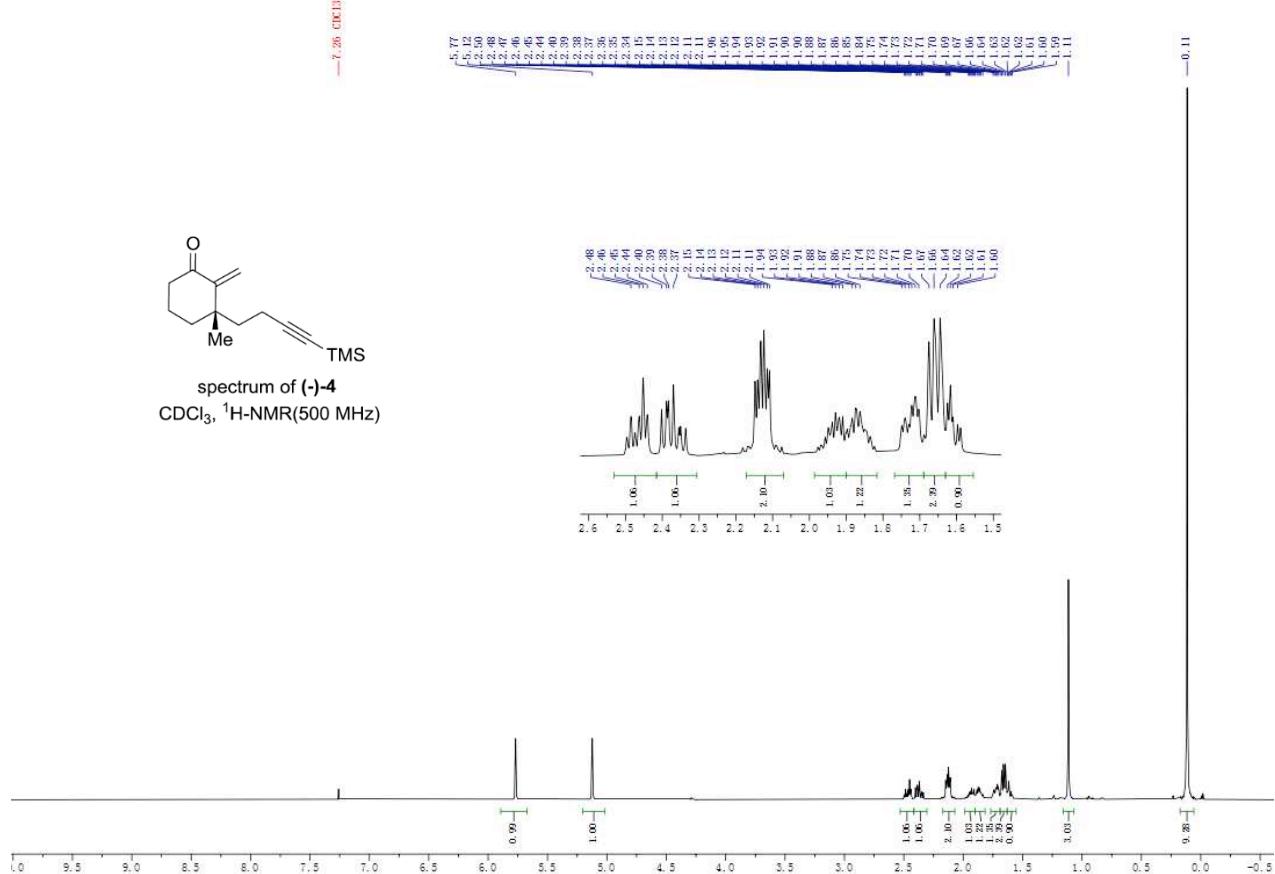
spectrum of (\pm)-7
CDCl₃, ¹³C-NMR (125 MHz)



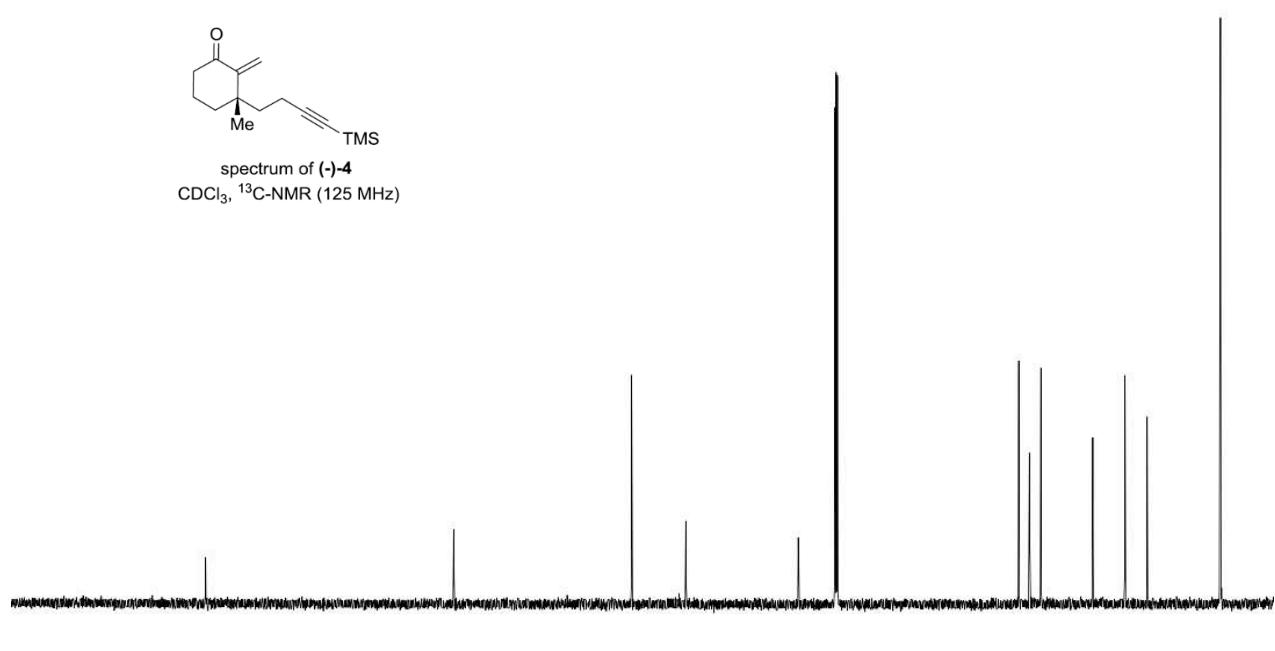


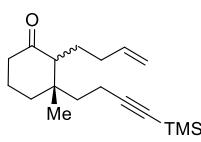
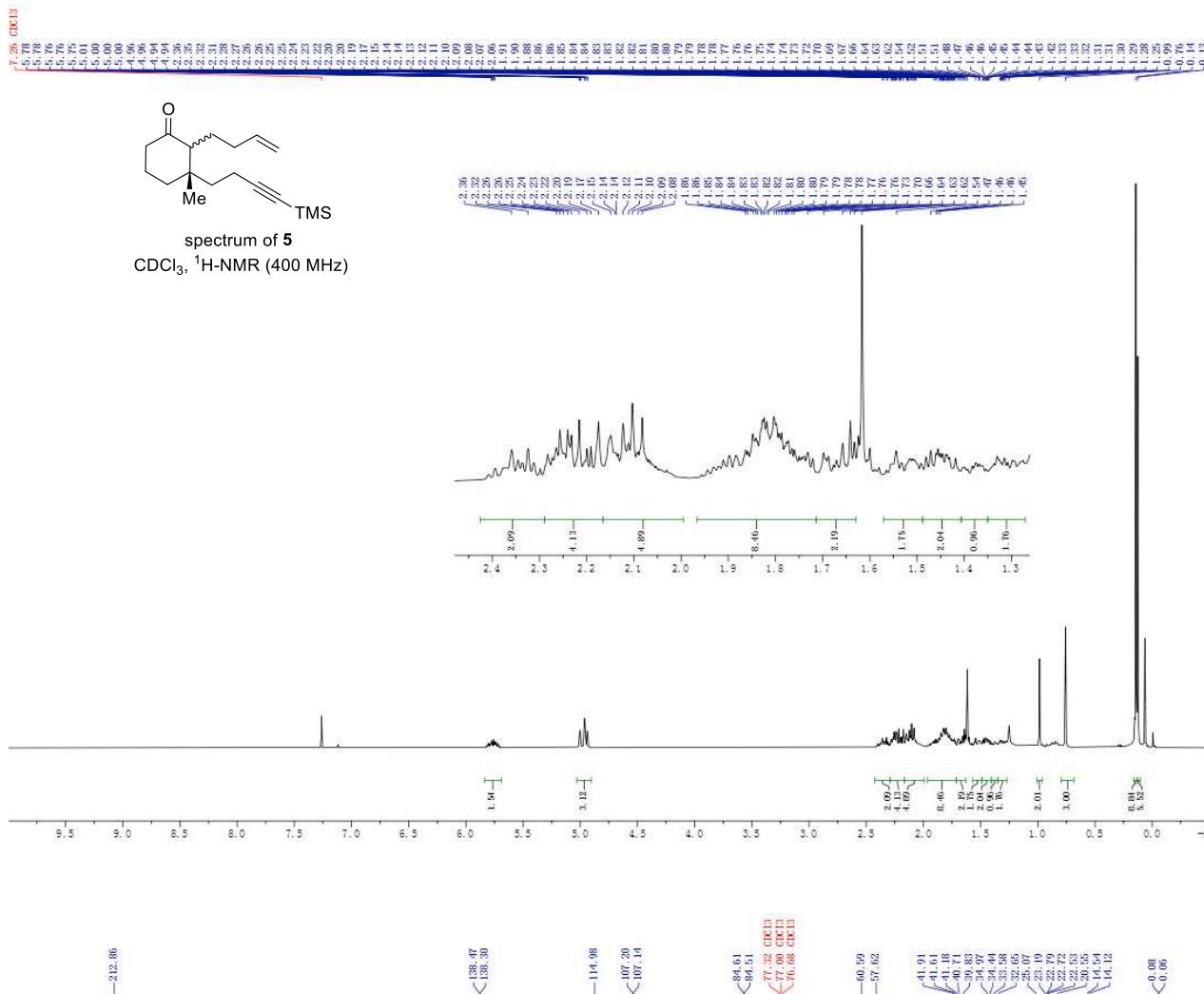


spectrum of (-)-4
 CDCl_3 , $^1\text{H-NMR}$ (500 MHz)

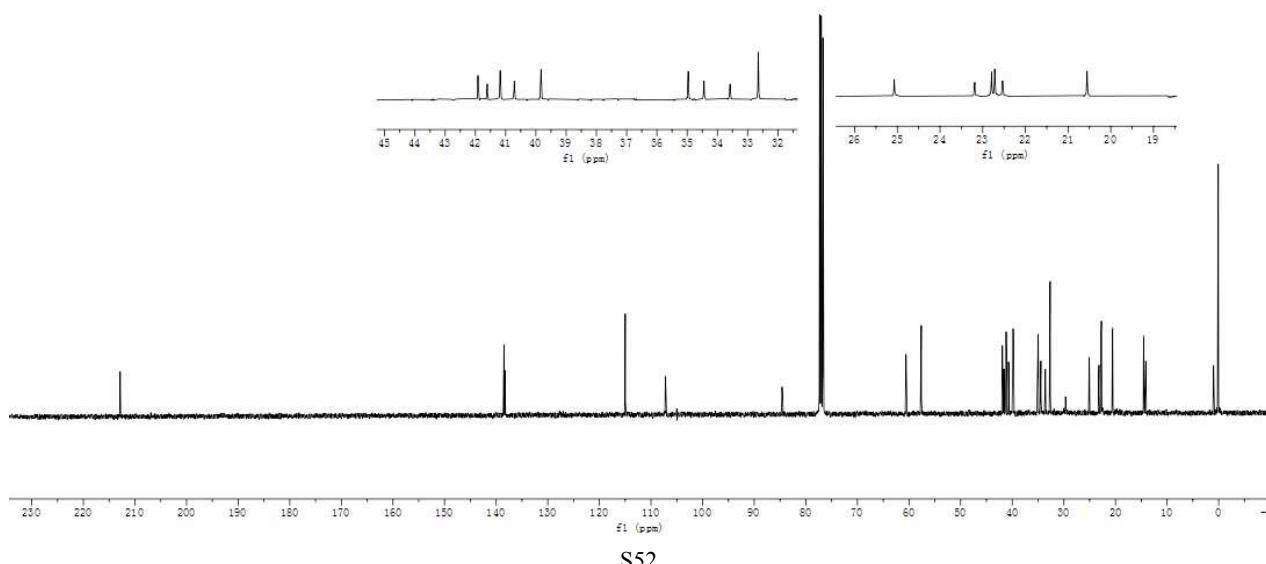


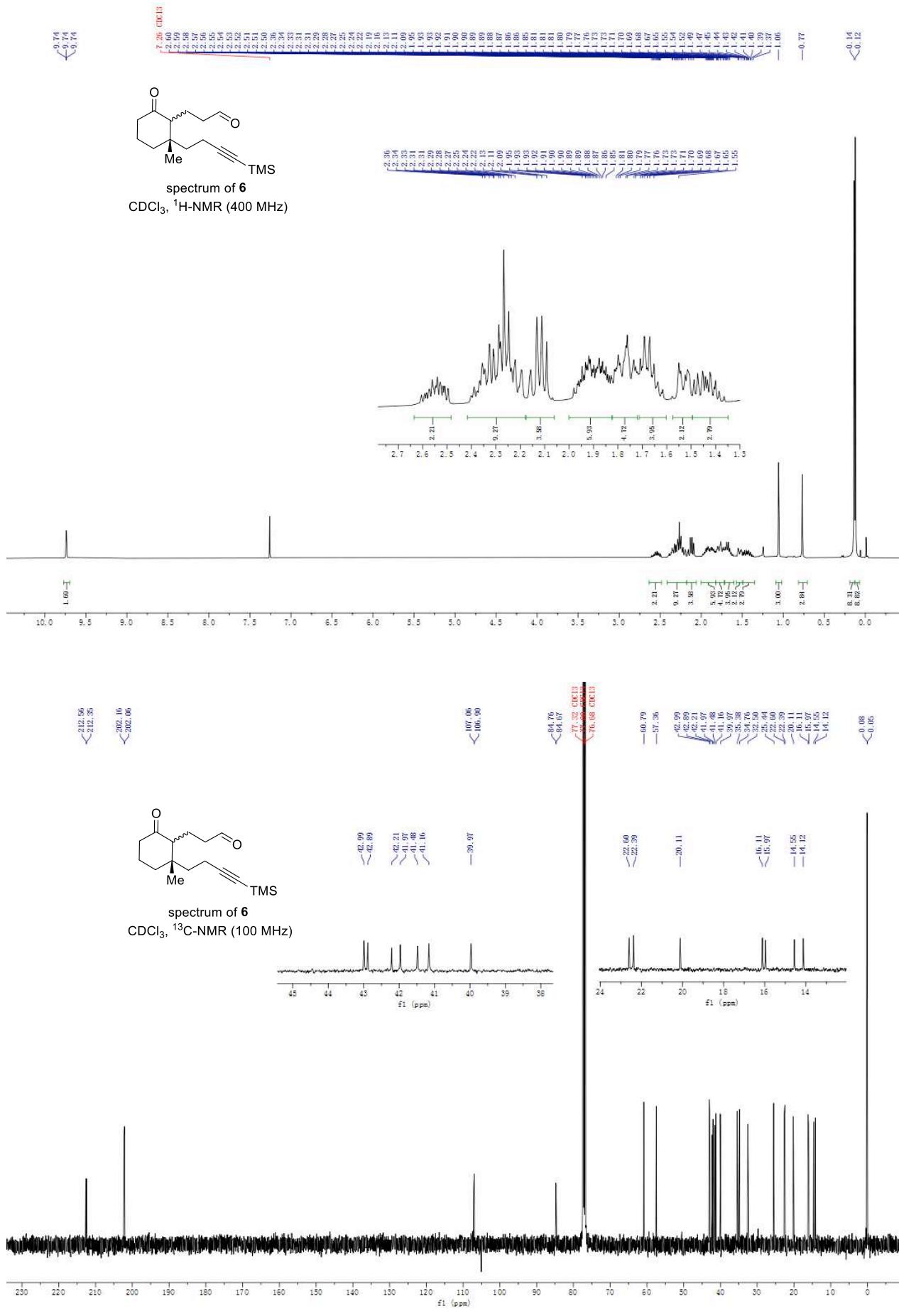
spectrum of (-)-4
CDCl₃, ¹³C-NMR (125 MHz)

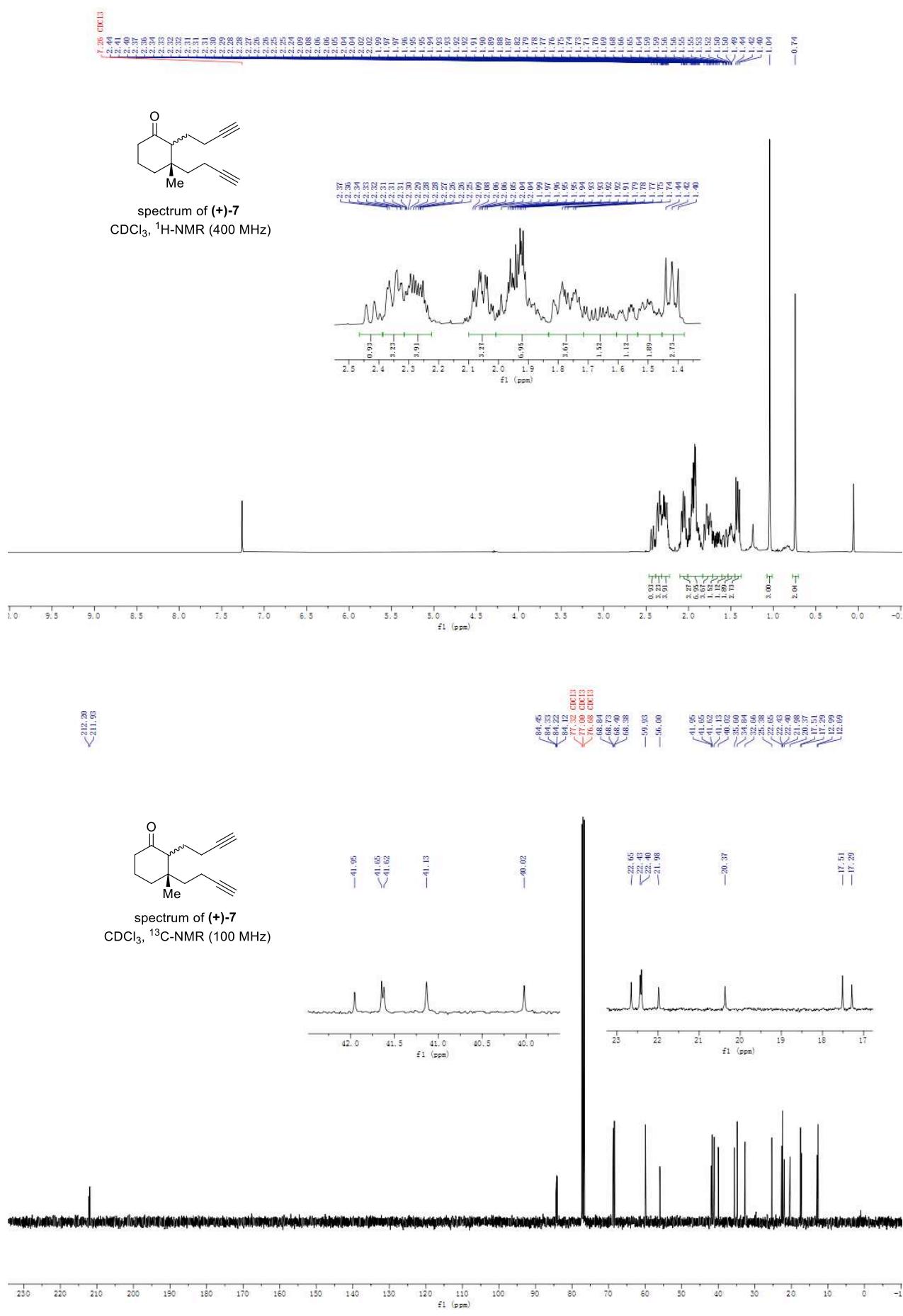


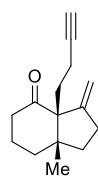


spectrum of 5
CDCl₃, ¹³C-NMR (100 MHz)

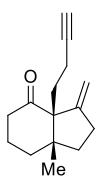
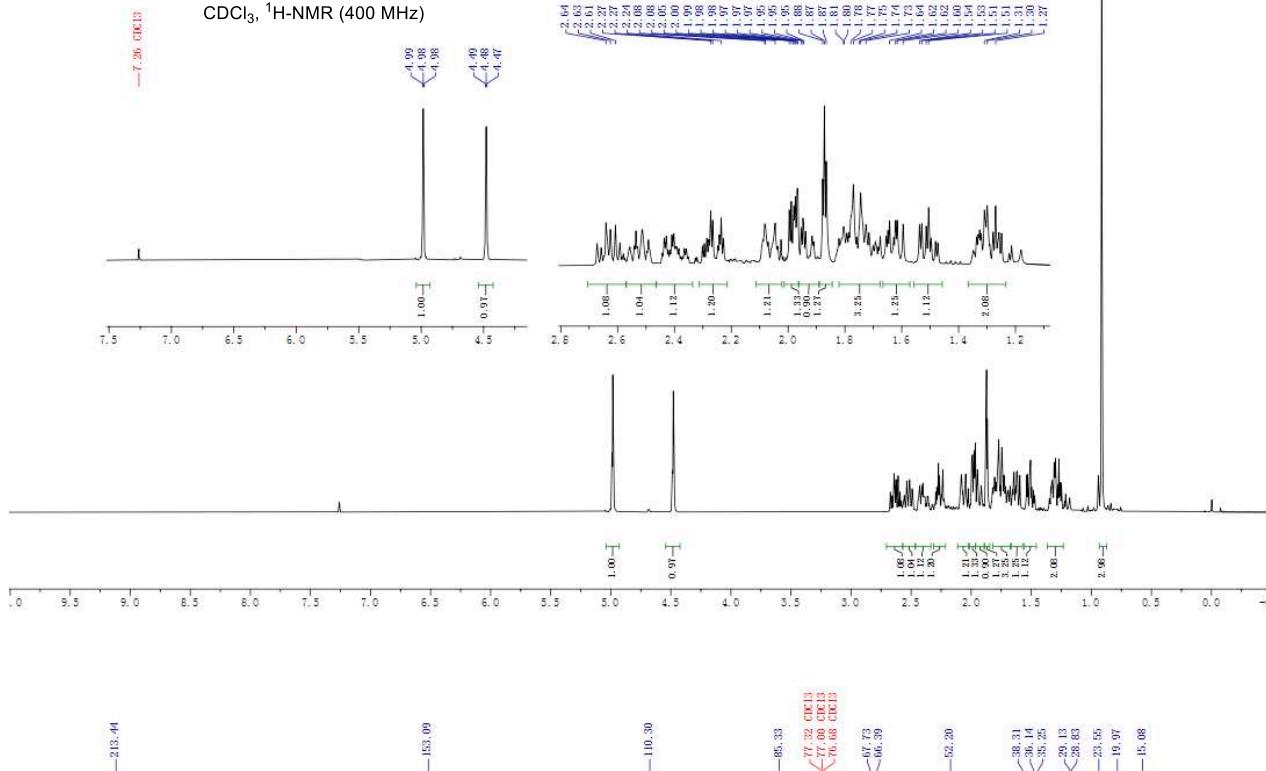




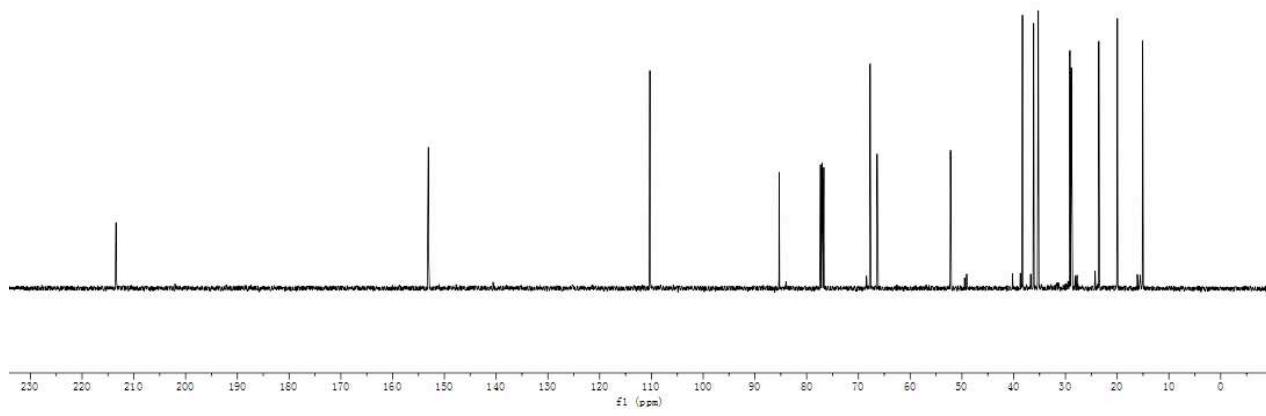


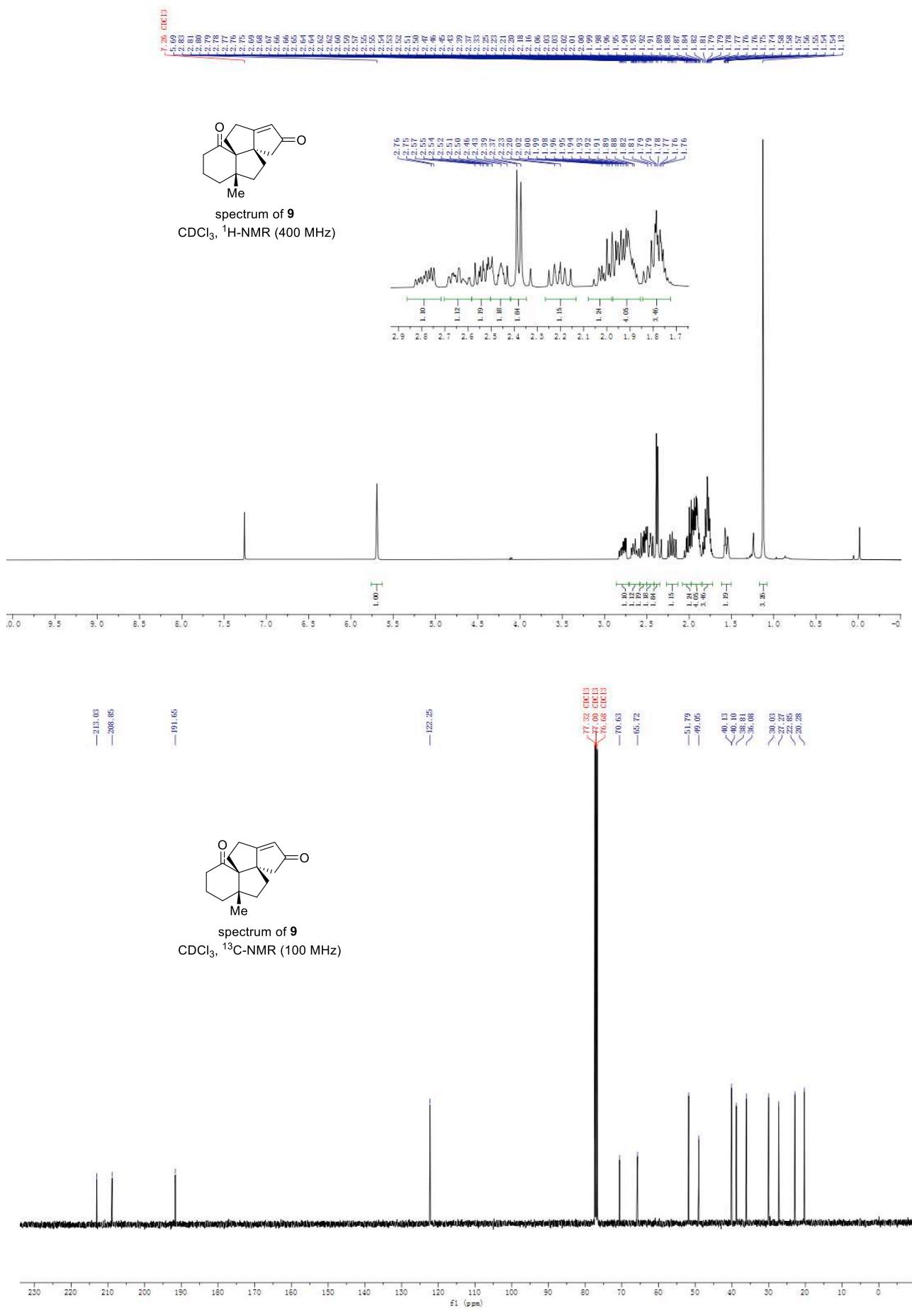


spectrum of **8**
 CDCl_3 , $^1\text{H-NMR}$ (400 MHz)

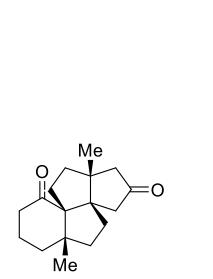
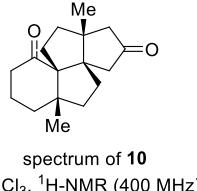


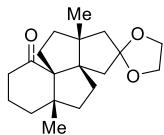
spectrum of **8**
 CDCl_3 , ^{13}C -NMR (100 MHz)



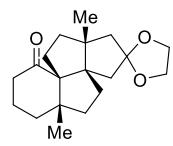
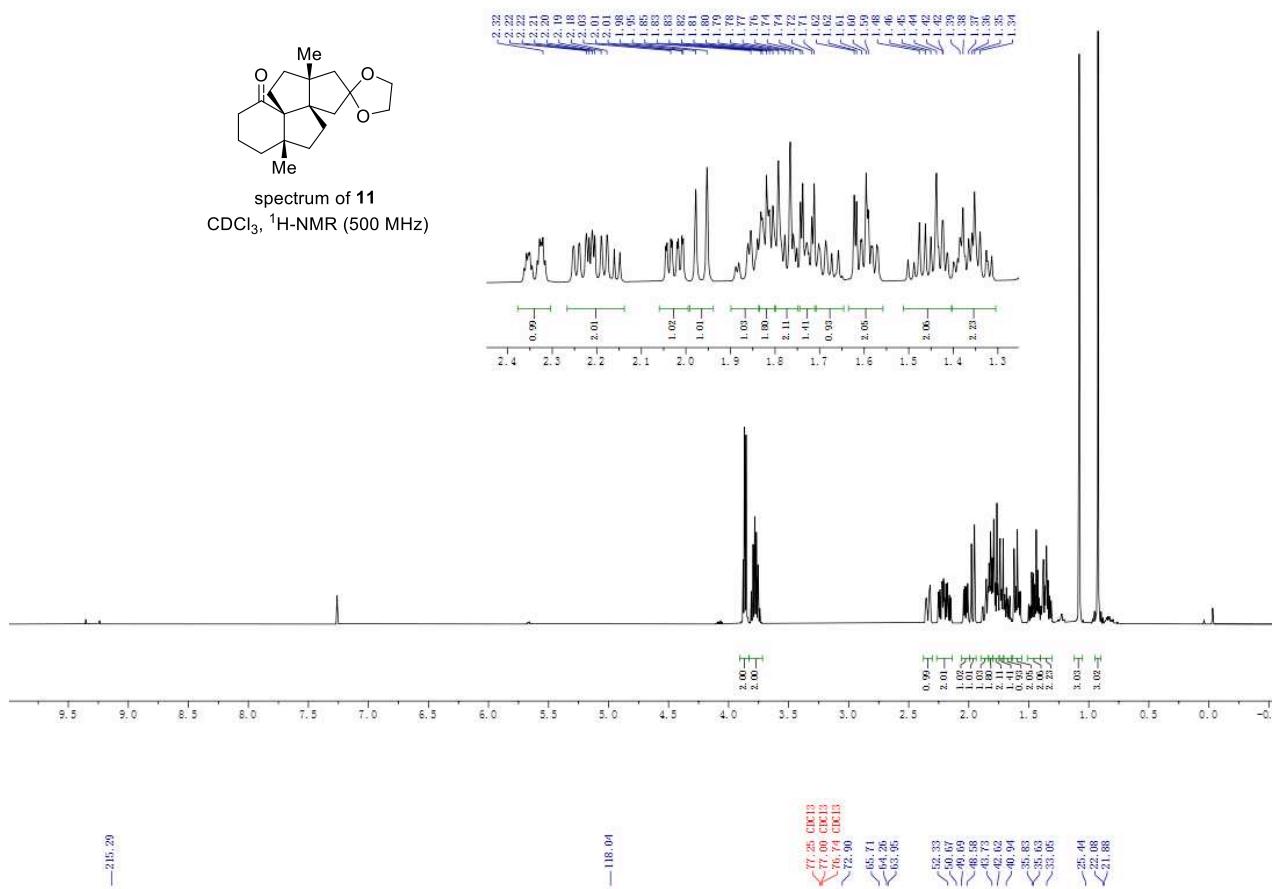


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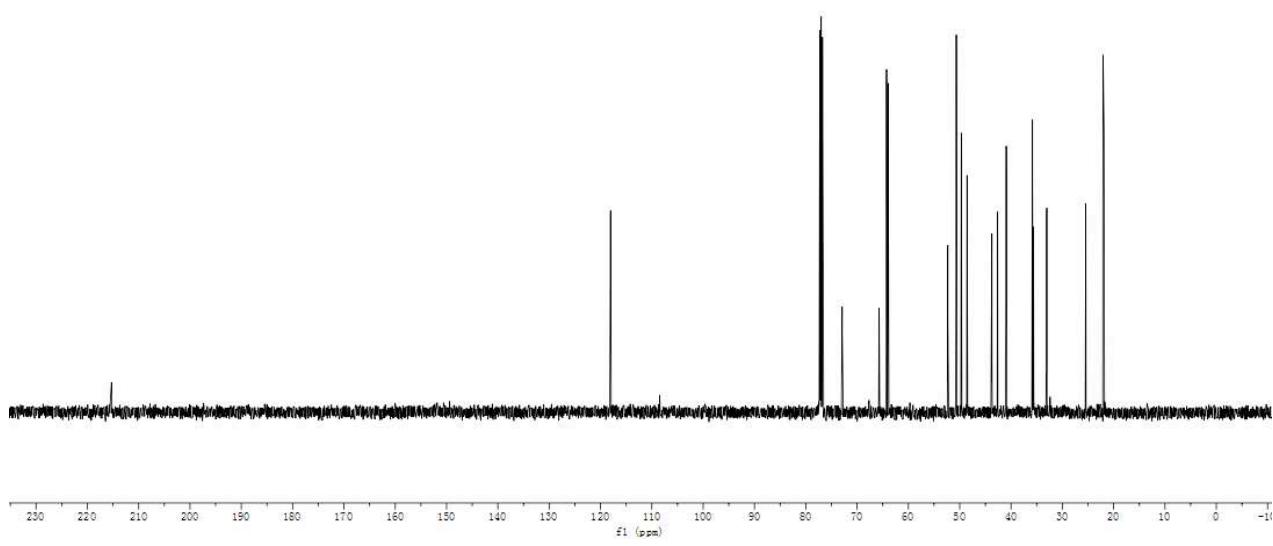


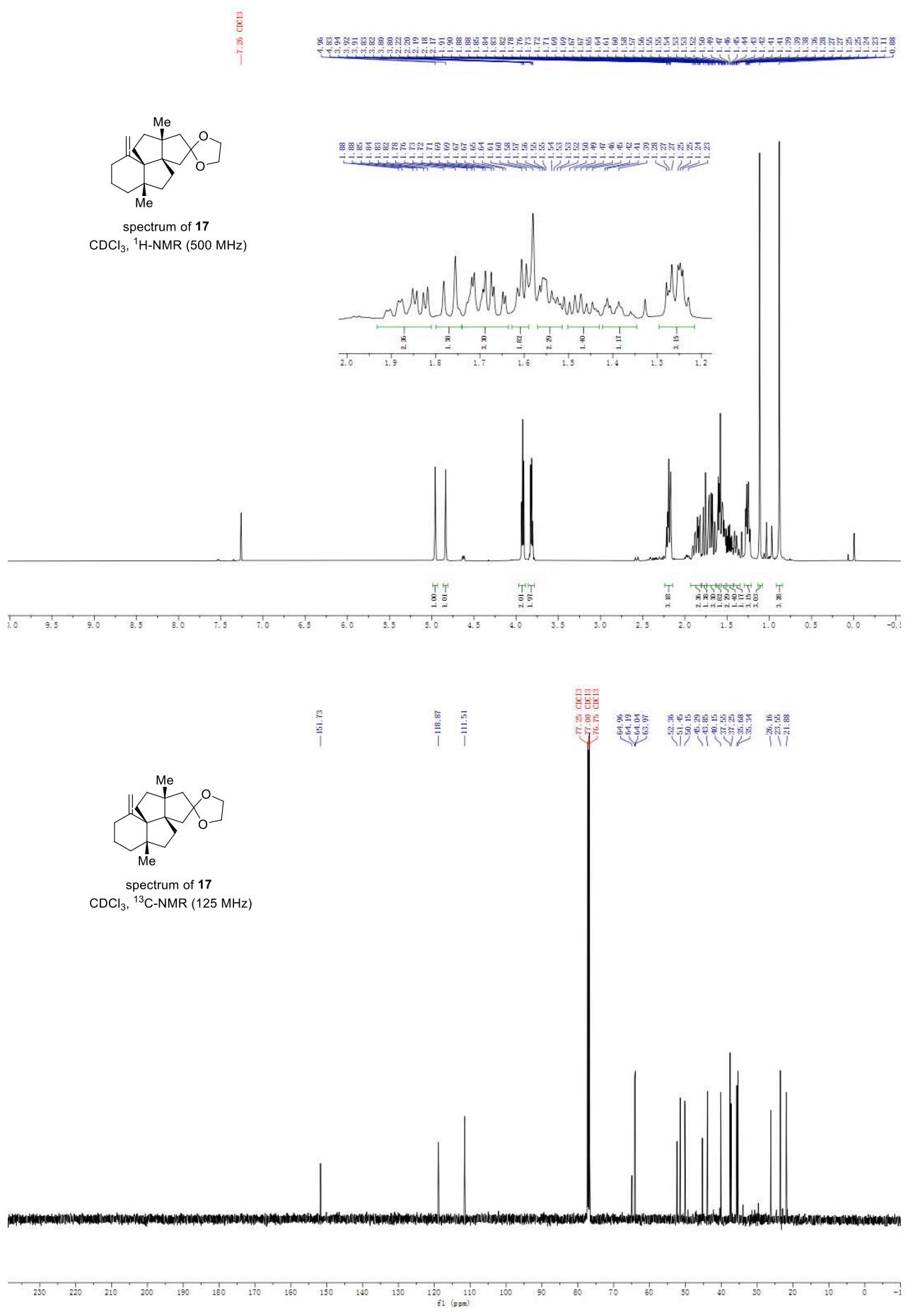


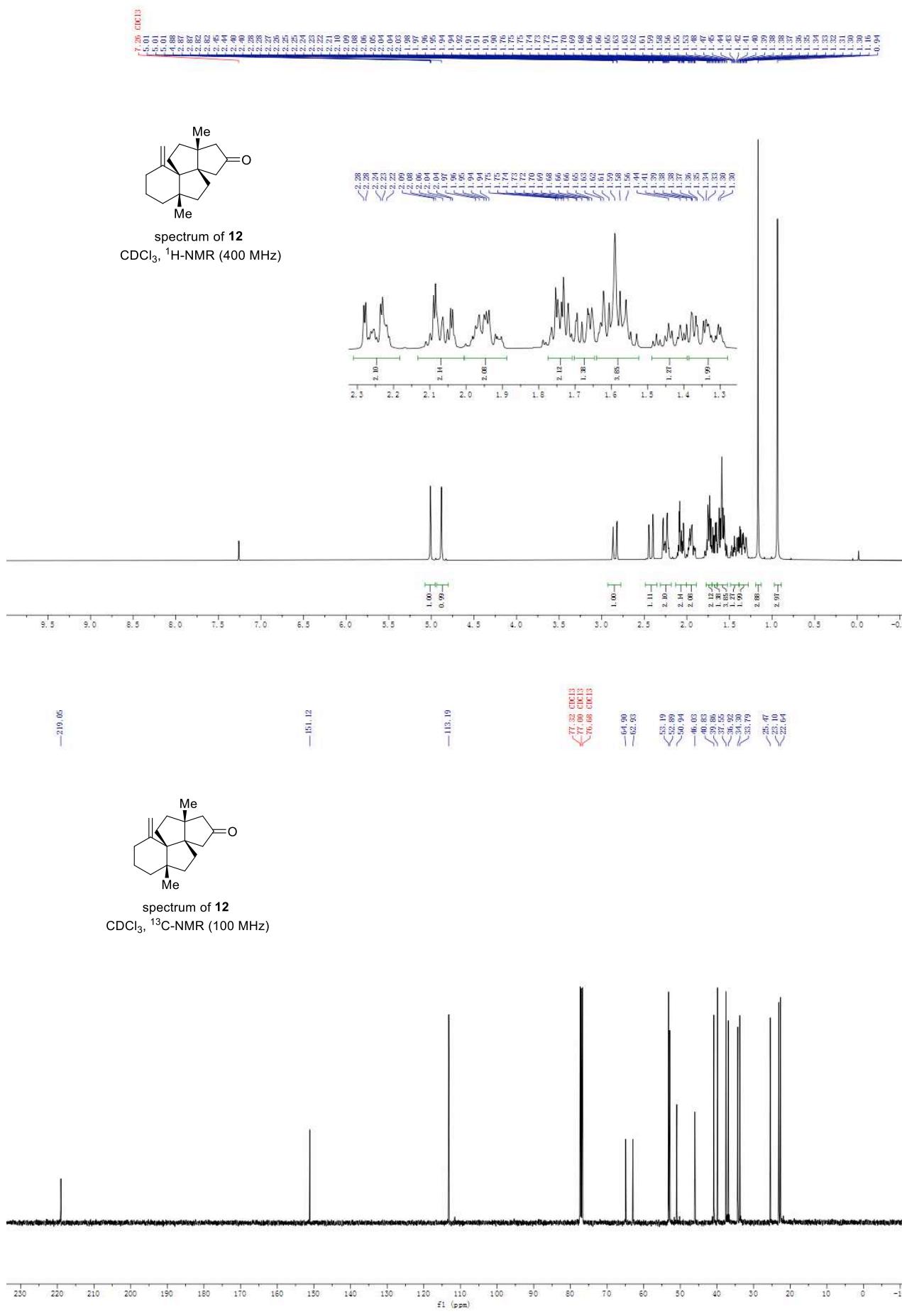
spectrum of **11**
 CDCl_3 , $^1\text{H-NMR}$ (500 MHz)

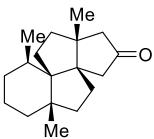


spectrum of **11**
 CDCl_3 , ^{13}C -NMR (125 MHz)

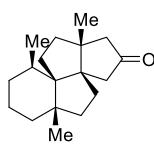
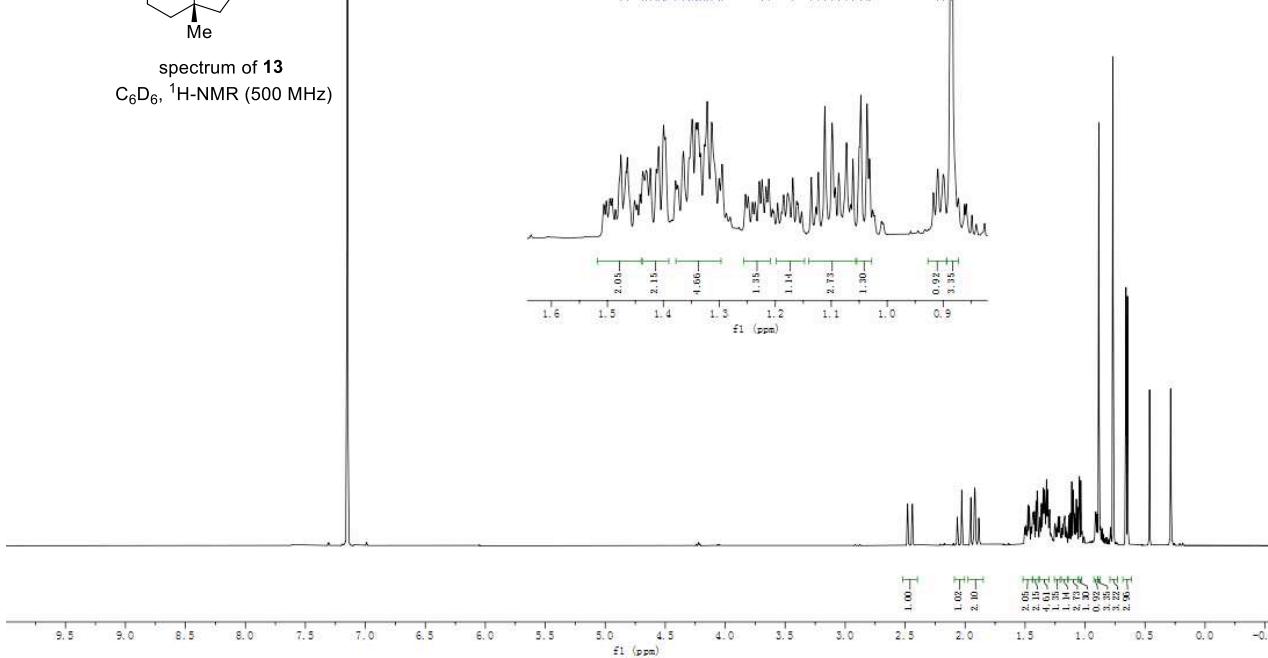




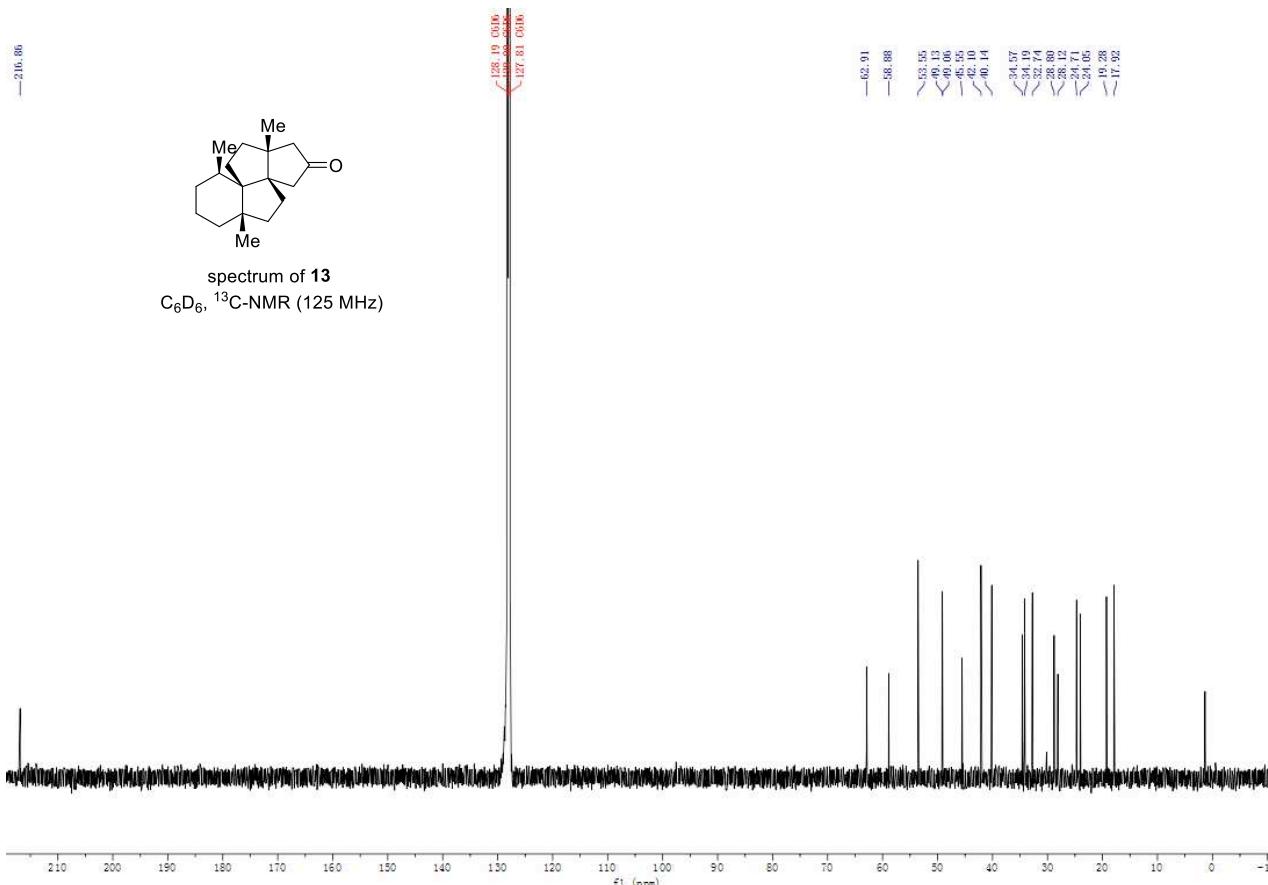


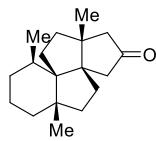


spectrum of **13**

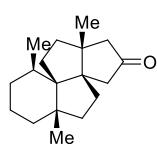
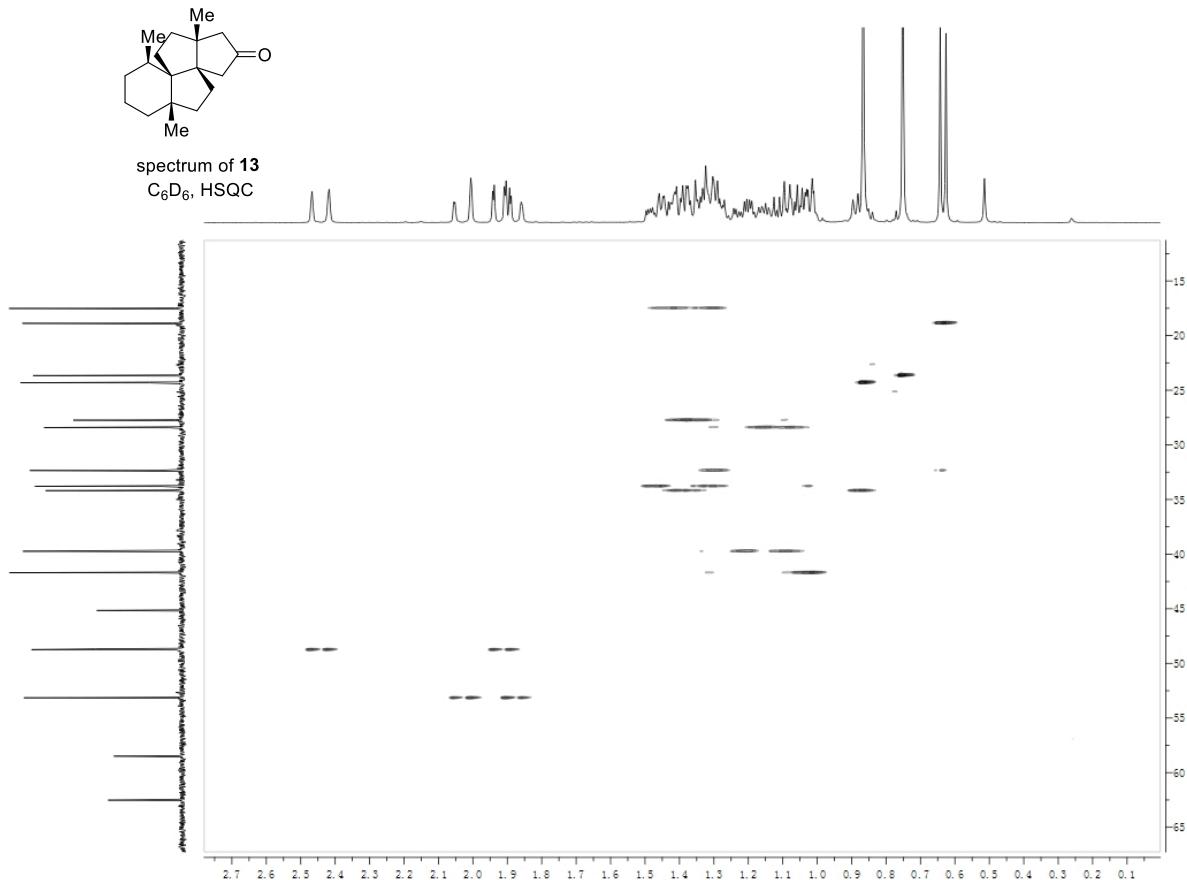


spectrum of **13**
 C_6D_6 , ^{13}C -NMR (125 MHz)

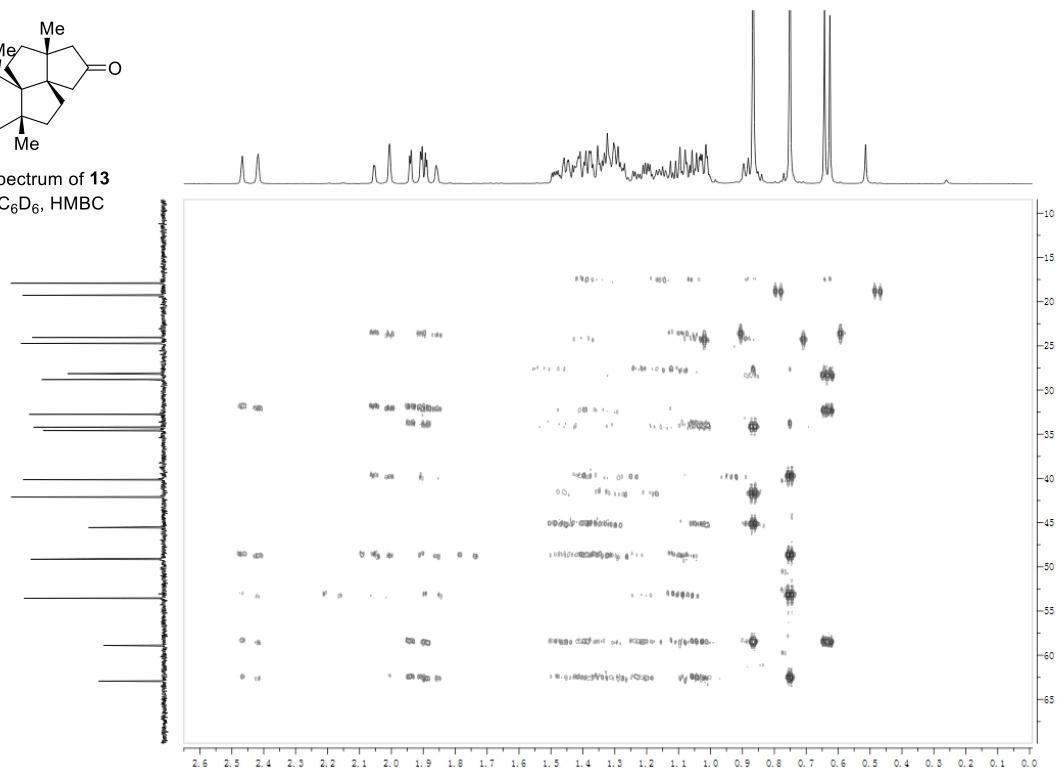


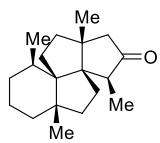


spectrum of **13**
C₆D₆, HSQC

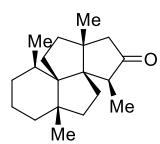
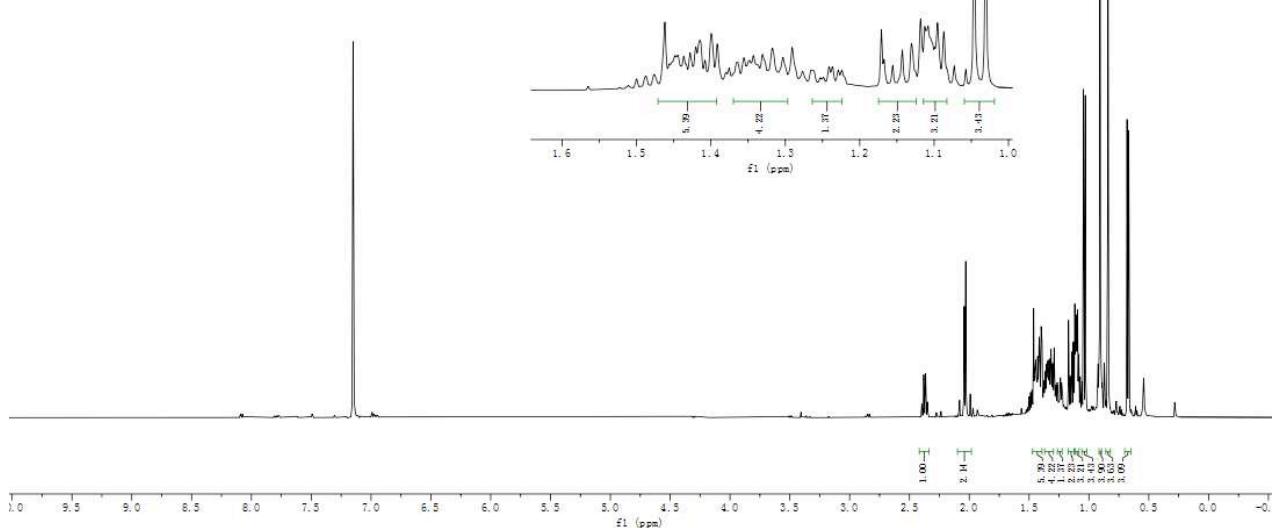


spectrum of **13**
C₆D₆, HMBC

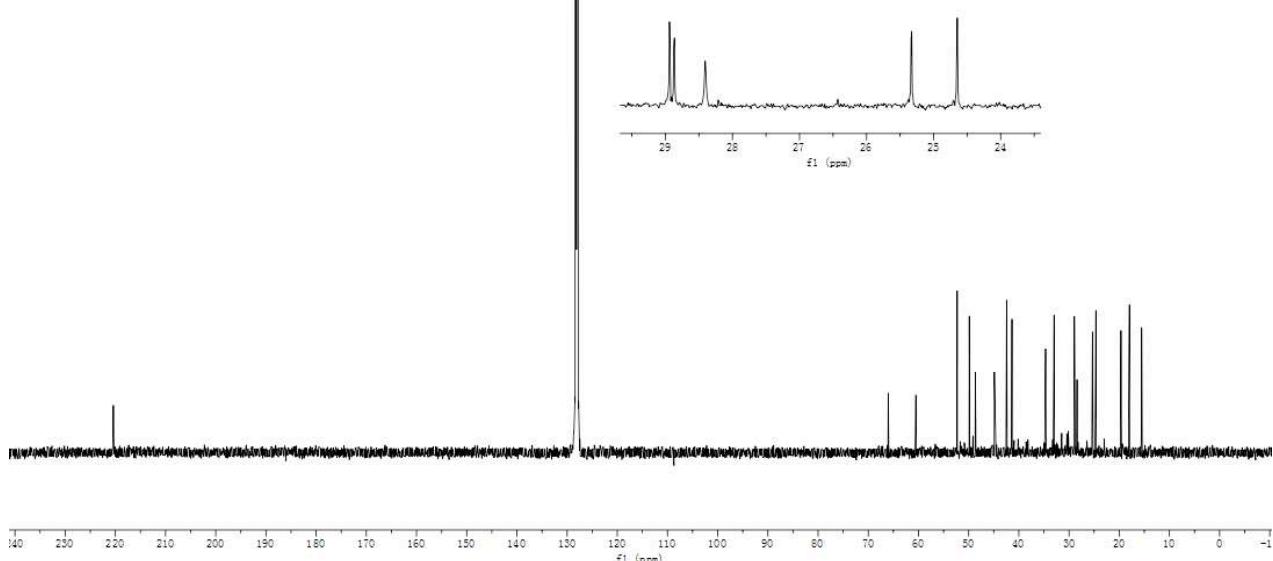


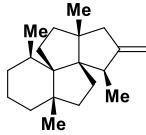


spectrum of **14**

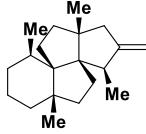
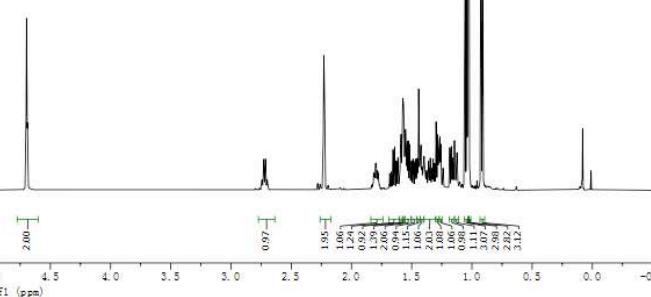
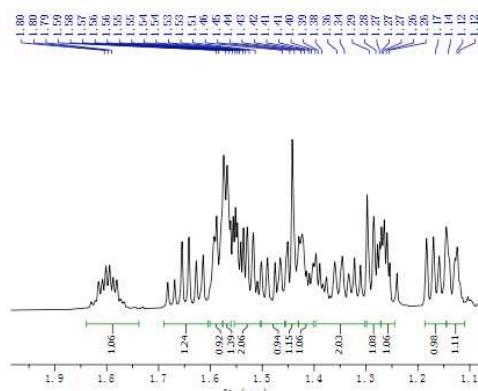


spectrum of **14**

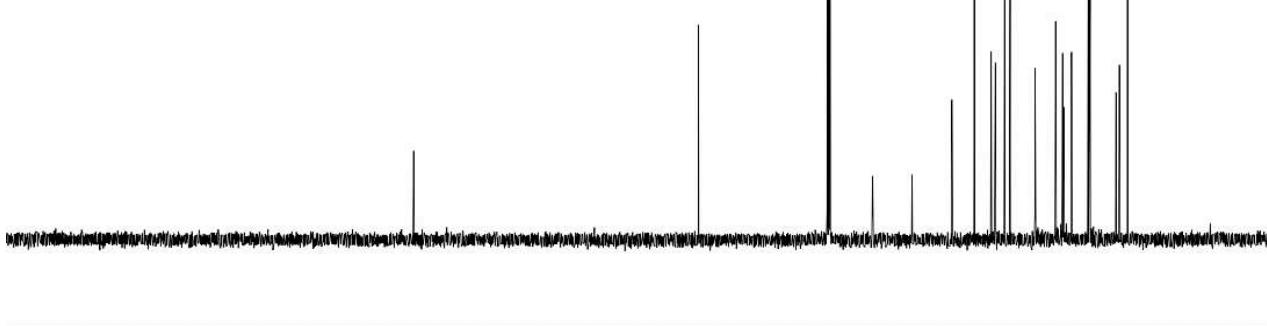
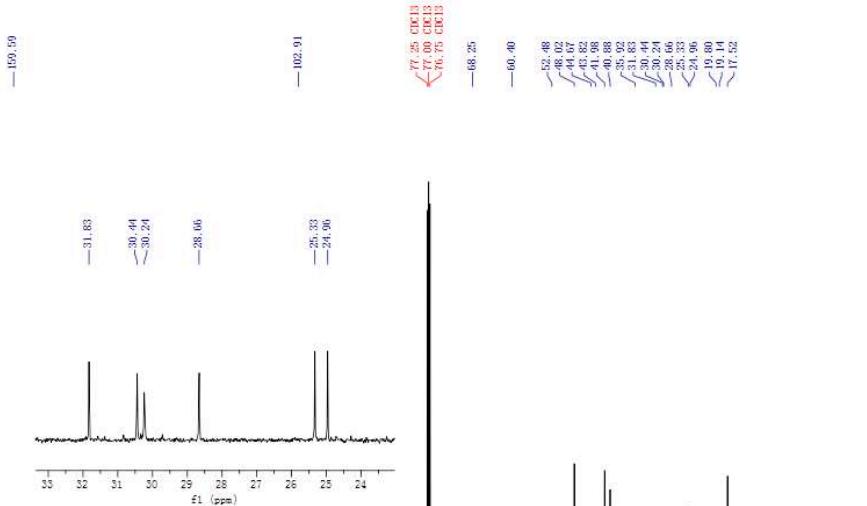


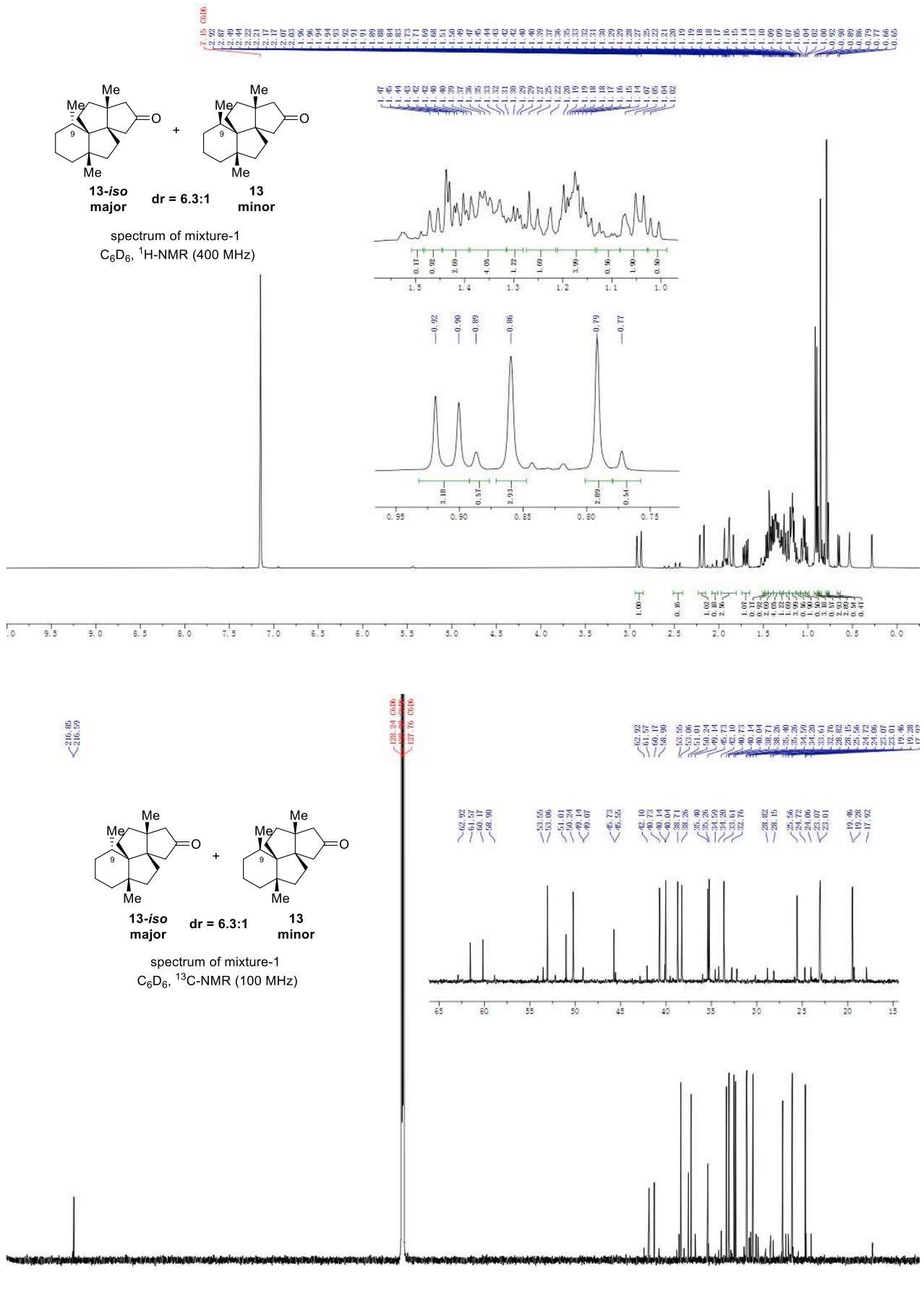


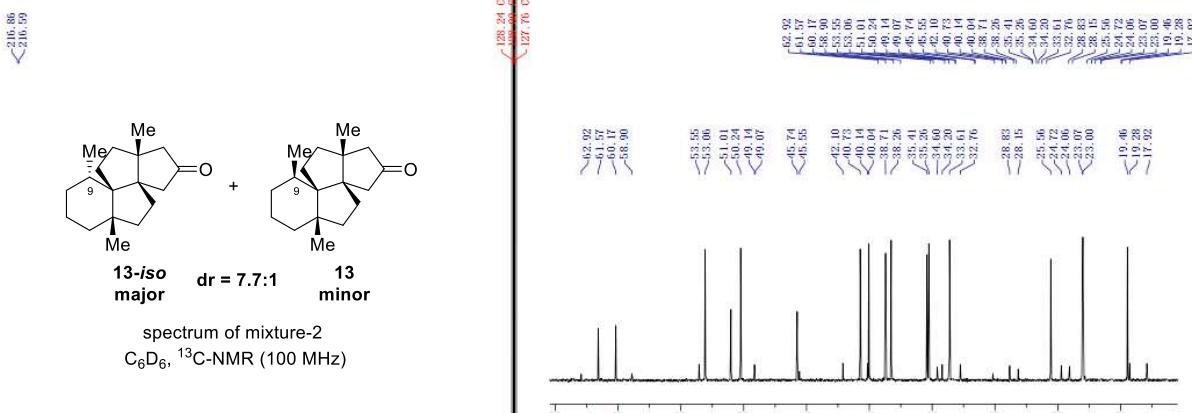
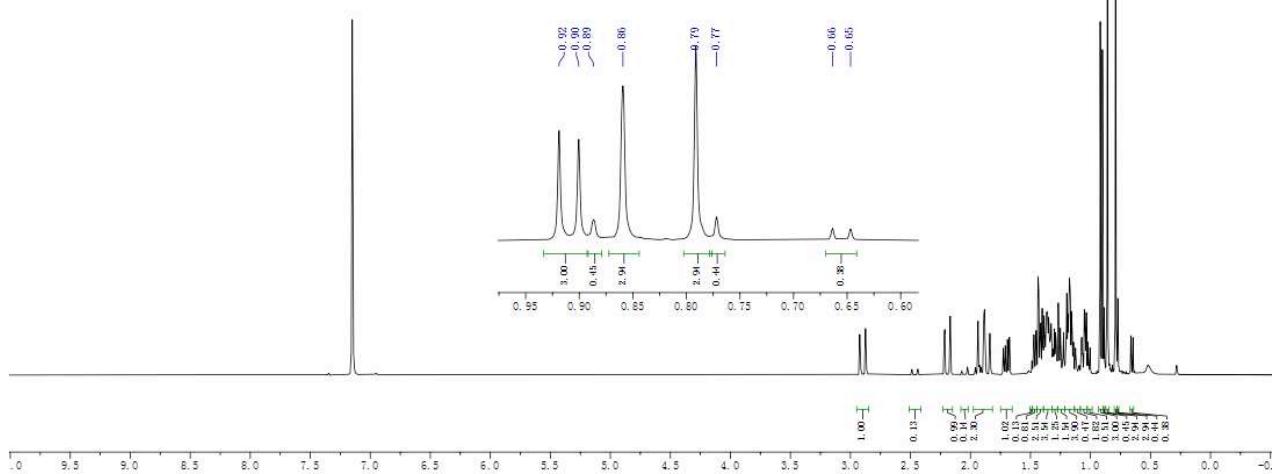
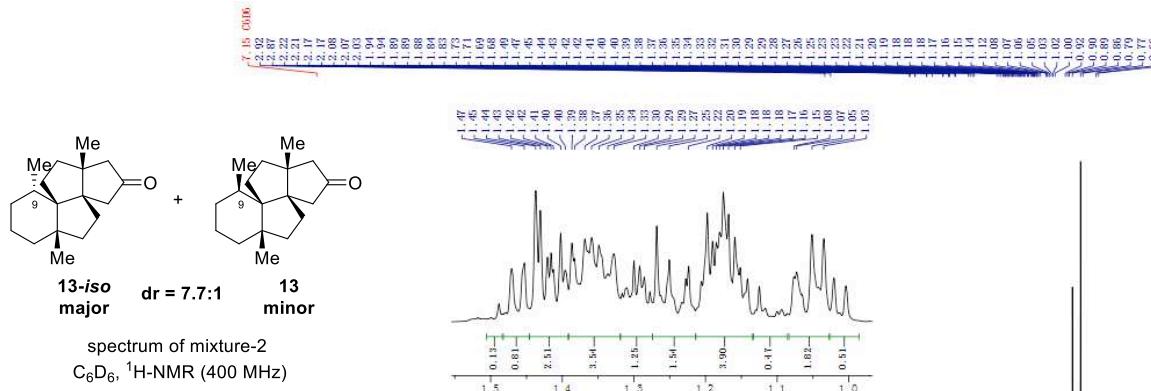
spectrum of (+)-Waihoensene 1
 CDCl_3 , $^1\text{H-NMR}$ (500 MHz)

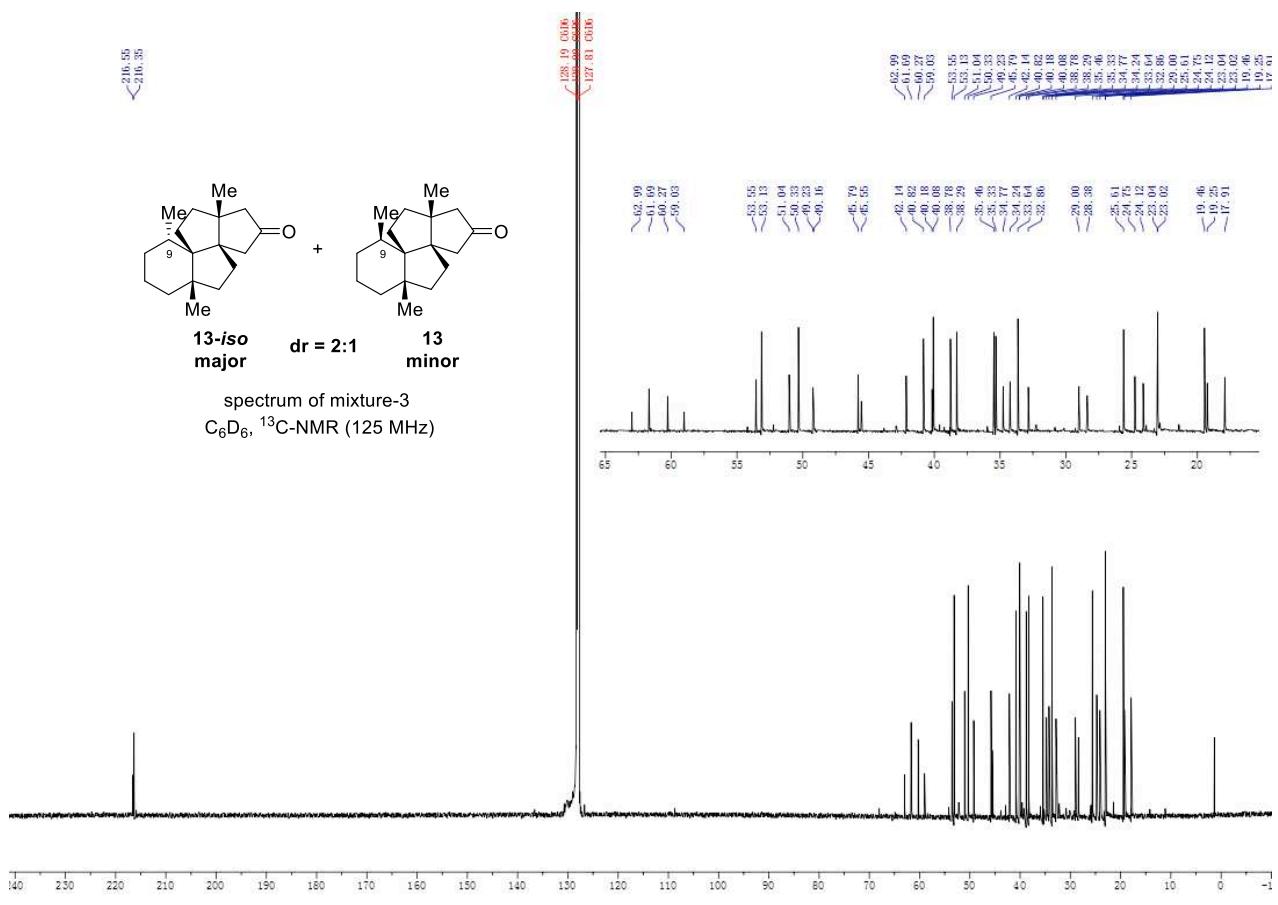
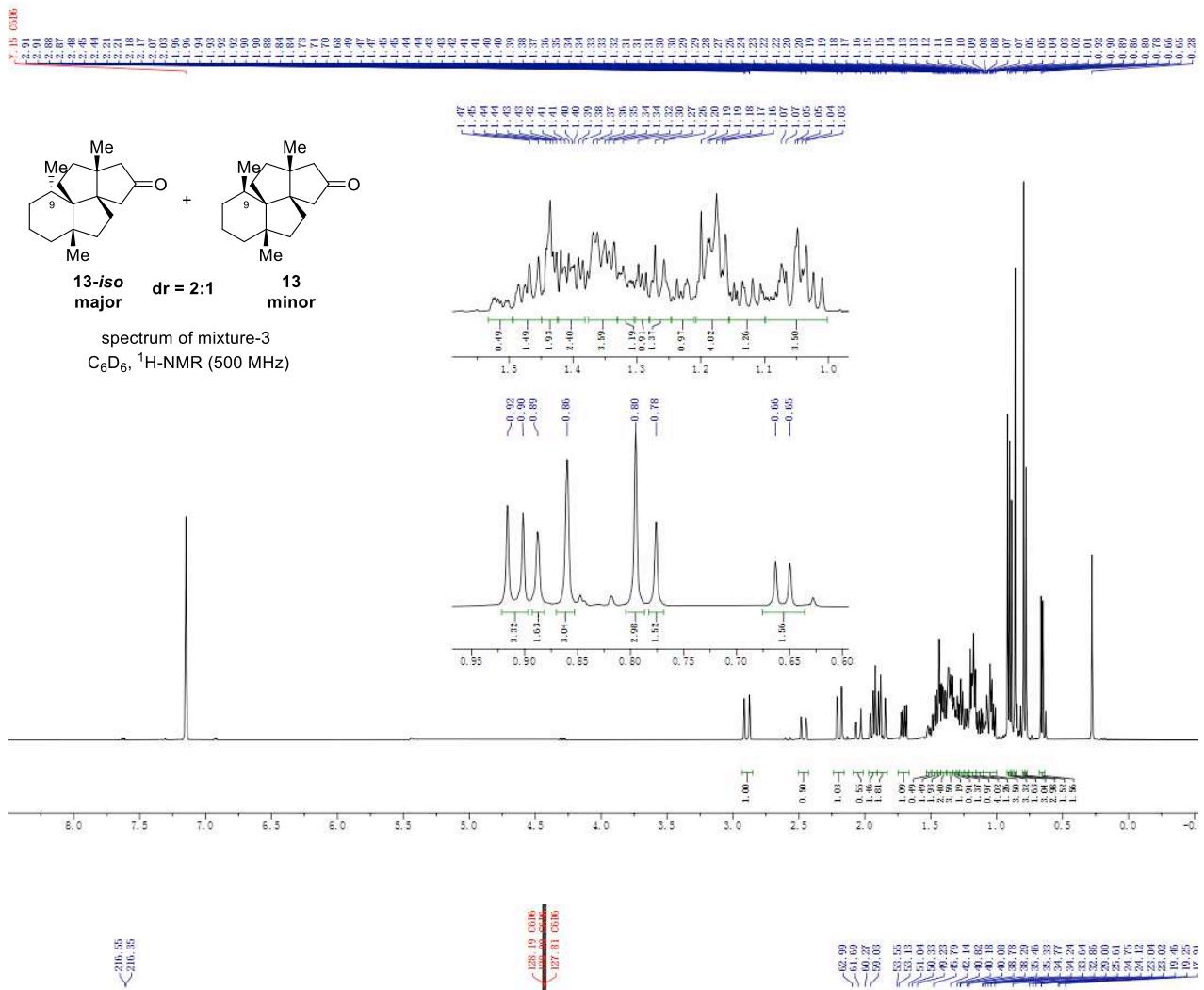


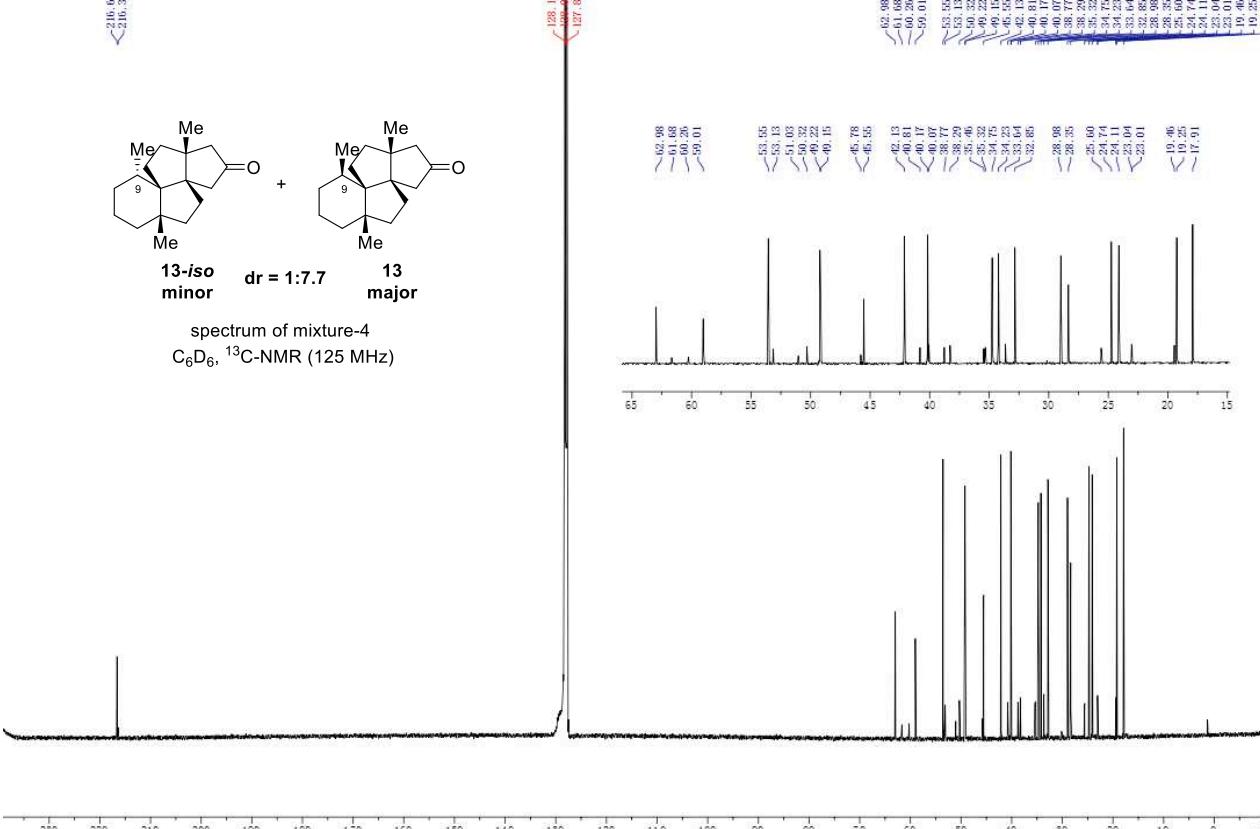
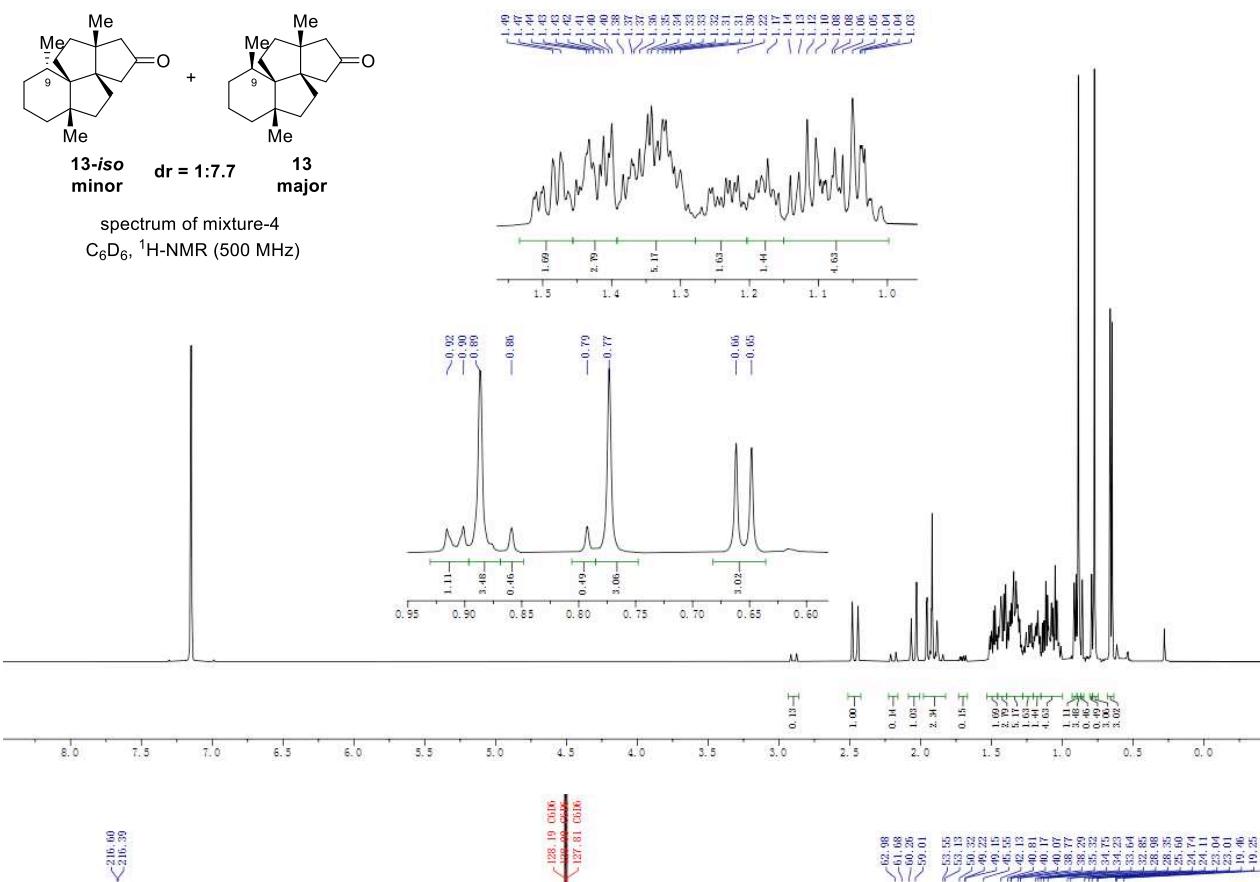
spectrum of (+)-Waihoensene 1
CDCl₃, ¹³C-NMR (125 MHz)

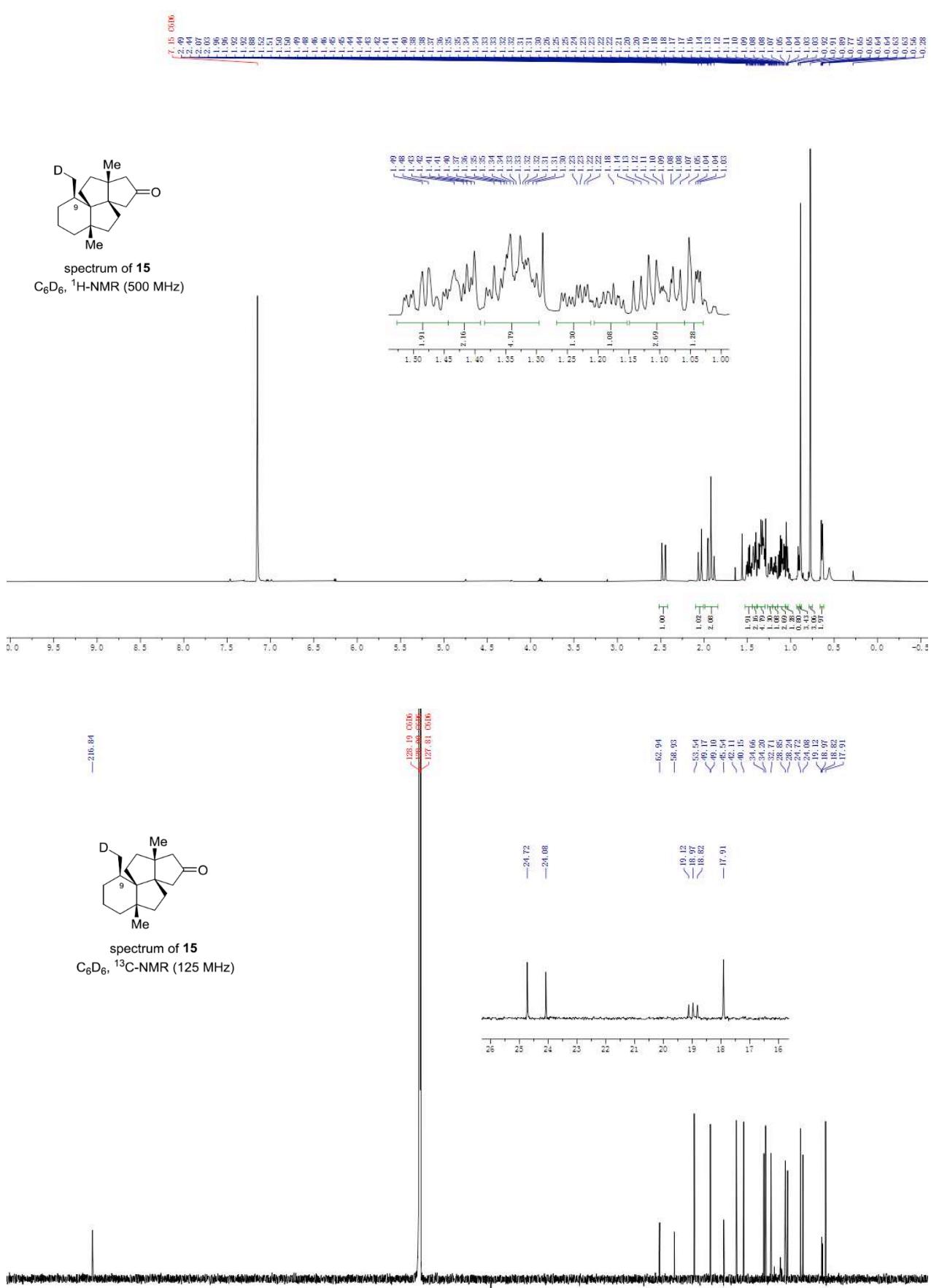


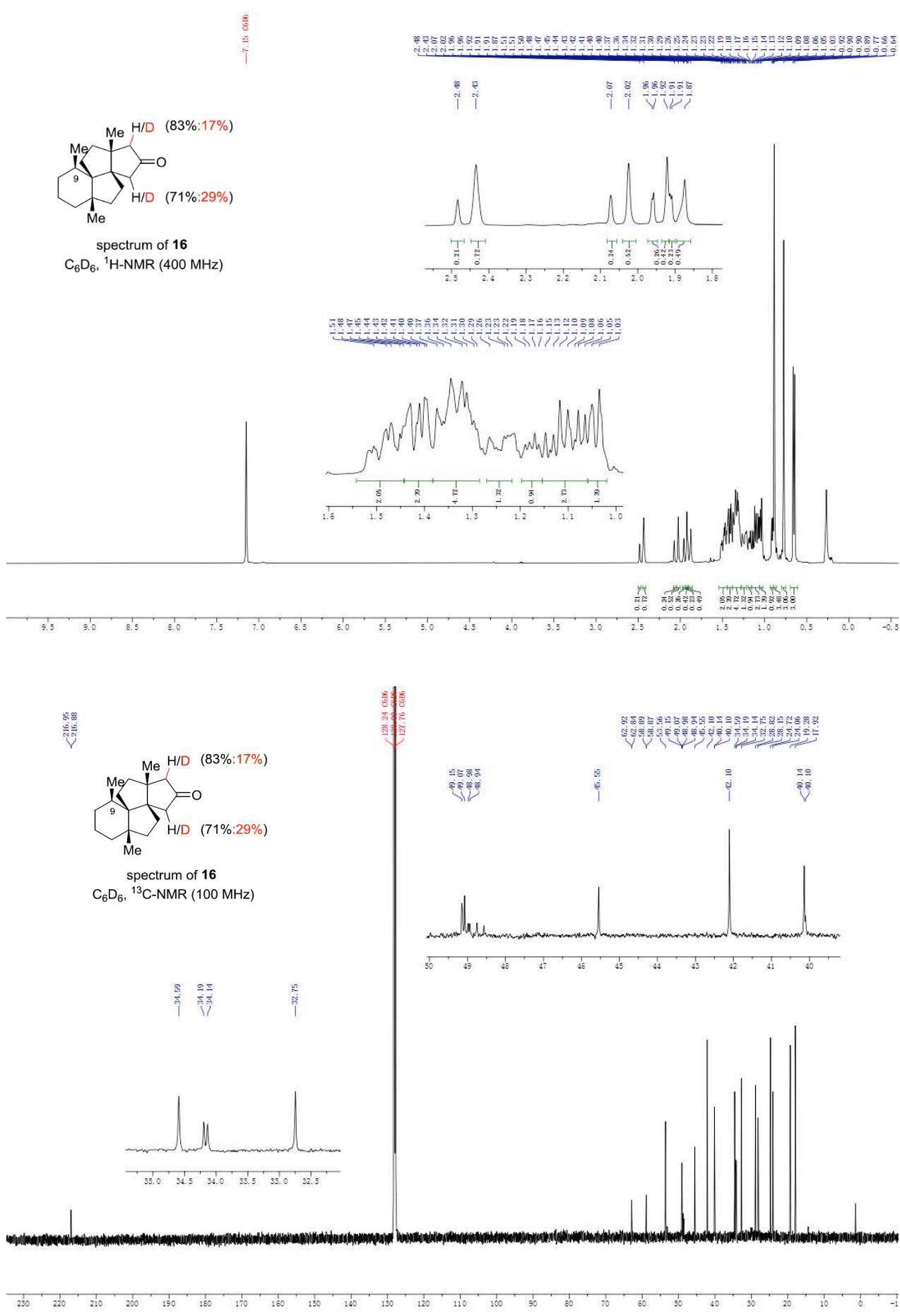












Part VIII: References

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