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Electronic Supporting Information

Concise Gram-Scale Synthesis of Euphorikanin A Skeleton through a Domino Ring-Closing Metathesis Strategy

Linlin Shi [‡ a], Yingdong He[‡ a], Jianxian Gong[a] *, and Zhen Yang[a b] *

[a] State Key Laboratory of Chemical Oncogenomics, Key Laboratory of Chemical Genomics, Peking University Shenzhen Graduate School, Shenzhen, 518055, China

[b] Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education and Beijing National Laboratory for Molecular Science (BNLMS), college of chemistry, and Peking-Tsinghua Center for Life Sciences, Peking University, Beijing 100871, China

[‡]These authors contributed equally to this work.

E-mail: zyang@pku.edu.cn

E-mail: gongjx@pku.edu.cn

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1. General Information

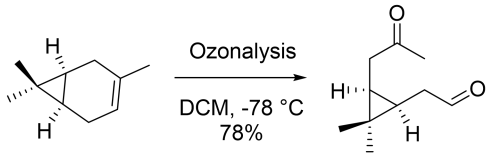
Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere under anhydrous conditions and all reagents were purchased from commercial suppliers without further purification. Anhydrous tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium-benzophenone. Dichloromethane (DCM) were distilled from calcium hydride, toluene ($PhCH_3$) and benzene (PhH) was distilled from sodium.

Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Tsingdao silica gel plates (GF-254), using UV light as visualizing agent and an ethanolic solution of phosphomolybdic acid and heat, or KMnO4 and heat as developing agents. Tsingdao silica gel (60, particle size 0.040-0.063 mm) was used for flash column chromatography.

NMR spectra were recorded on a Brüker Advance 400 (1H: 400 MHz, 13C: 100 MHz), Brüker Advance 500 (1H: 500 MHz, 13C: 125 MHz) or Brüker Advance 300 (1H: 300 MHz, 13C: 75 MHz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. IR spectra were recorded on an IRPrestige-21 FTIR spectrometer. High resolution mass spectrometric (HRMS) data were obtained using Brüker Apex IV RTMS

2. Experimental procedures for the synthesis of compounds

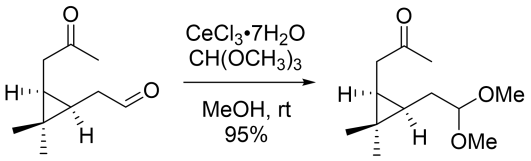
2.1. Synthesis of the compound 13



5 **6**

To a solution of (+)-3-carene[1] (50.0 g, 367.6 mmol) in DCM and MeOH (500 mL, 3:1) was induced O_3 gas slowly at -78 °C, and the mixture was stirred at the same temperature for 4.5 h. The reaction was quenched by addition of a dimethyl sulfide (50 mL) at -78 °C, and the resultant mixture was extracted with hexane (3×100 mL). The combined extracts were washed sequentially with water (100 mL) and brine (100 mL), and dried over $NaSO_4$. The extract was concentrated under reduced pressure, and the residue was purified by a flash chromatography on silica gel to give desired compound **6** (48 g, 78%) as a colorless oil. Rf = 0.6 (silica gel, 10% ethyl acetate in hexane); $[\alpha]_D^{25}$ = + 5 (c = 0.4, $CHCl_3$). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.75 (s, 1H), 2.35 - 2.29 (m, 4H), 2.14 (s, 3H), 1.12 (s, 3H), 1.00 - 0.93 (m, 2H), 0.89 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.39, 201.96, 39.77, 39.49, 29.72, 28.58, 21.34, 19.48, 17.24, 15.26. HRMS (ESI+, MeOH): m/z calcd. 191.1043 $(M + Na)^+$, found: 191.1044.

2.2. Synthesis of the compound 7

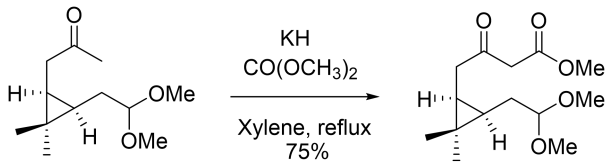


6 **7**

To a solution of aldehyde **6** (20.0 g, 119.1 mmol) in MeOH (300 mL) was added cerium(III) chloride heptahydrate (44.2 g, 1.0 equiv, 119.1 mmol) and trimethyl orthoformate (63 g, 5.0 equiv, 595.5 mmol) slowly at room temperature, and the mixture was stirred at the same temperature for 4 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (150 mL), and the resultant mixture was extracted with ethyl acetate (3×100 mL). The combined extracts were washed sequentially with water (100 mL) and brine (100 mL), and dried over $NaSO_4$. The extract was concentrated under

reduced pressure, and the residue was purified by a flash chromatography on silica gel to give desired compound **7** (24.2 g, 95%) as a colorless oil. Rf = 0.5 (silica gel, 10% ethyl acetate in hexane); $[\alpha]_D^{25}$ = + 5 (c = 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.31 (t, *J* = 5.7 Hz, 1H), 3.32 (d, *J* = 4.9 Hz, 6H), 2.41 - 2.26 (m, 2H), 2.14 (s, 3H), 1.48 (m, *J* = 14.4, 7.1, 5.7 Hz, 2H), 1.07 (s, 3H), 0.89 (s, 4H), 0.86 - 0.80 (m, 1H), 0.70 - 0.62 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.01, 105.28, 53.39, 39.57, 29.76, 28.84, 28.40, 21.55, 21.23, 16.93, 15.26. HRMS (ESI+, MeOH): m/z calcd. 237.1461 $(M + Na)^+$, found: 237.1459.

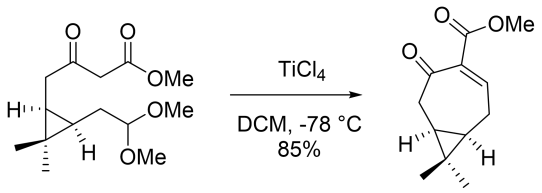
2.3. Synthesis of the compound 8



7 **8**

To a solution of ketone **7** (10.0 g, 46.7 mmol) in xylene (150 mL) was added KH (2.73 g, 1.5 equiv, 70 mmol) dimethyl carbonate (21.0 g, 5.0 equiv, 233.5 mmol) slowly at room temperature, and the mixture was stirred at 145 °C for 1.5 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (80 mL) at 0 °C, and the resultant mixture was extracted with ethyl acetate (3×80 mL). The combined extracts were washed sequentially with water (100 mL) and brine (100 mL), and dried over $NaSO_4$. The extract was concentrated under reduced pressure, and the residue was purified by a flash chromatography on silica gel to give desired compound **8** (9.5 g, 75%) as a colorless oil. Rf = 0.5 (silica gel, 10% ethyl acetate in hexane); $[\alpha]_D^{25}$ = + 9 (c = 0.4, $CHCl_3$). ^{1}H NMR (500 MHz, Chloroform-d) δ 4.32 (t, J = 5.7 Hz, 1H), 3.73 (s, 3H), 3.48 (s, 2H), 3.33 (d, J = 4.6 Hz, 6H), 2.56 - 2.41 (m, 2H), 1.56 - 1.51 (m, 1H), 1.45 (m, J = 14.1, 7.4, 6.0 Hz, 1H), 1.08 (s, 3H), 0.96 - 0.92 (m, 1H), 0.89 (s, 3H), 0.67 (dt, J = 9.1, 7.1 Hz, 1H). ^{13}C NMR (126 MHz, CDCl3) δ 202.69, 167.83, 105.32, 77.42, 53.58, 53.44, 52.45, 48.84, 39.20, 28.79, 28.44, 21.70, 20.82, 17.06, 15.26. HRMS (ESI+, MeOH): m/z calcd. 295.1516 $(M + Na)^+$, found: 295.1517.

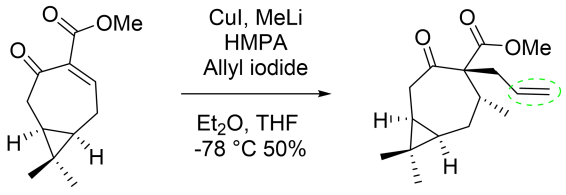
2.4. Synthesis of the compound 9



8 **9**

To a solution of ketoester **8** (10.0 g, 36.8 mmol) in DCM (100 mL) was added $TiCl_4$ (7.4 mL, 1.2 equiv, 44.2 mmol, 1.0 M in DCM) slowly at -78 °C, and the mixture was stirred at the same temperature for 2.5 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (10 mL), and the resultant mixture was extracted with DCM (3×50 mL). The combined extracts were washed sequentially with water (50 mL) and brine (50 mL), and dried over $NaSO_4$. The extract was concentrated under reduced pressure, and the residue was purified by a flash chromatography on silica gel to give desired enone **9** (6.5 g, 85%) as a colorless oil. Rf = 0.6 (silica gel, 5% ethyl acetate in hexane); $[\alpha]_D^{25}$ = + 99 (c = 0.4, $CHCl_3$). ^{1}H NMR (500 MHz, Chloroform-d) δ 7.42 (dd, J = 8.9, 3.7 Hz, 1H), 3.77 (s, 3H), 2.82 (dd, J = 13.5, 5.1 Hz, 1H), 2.72 (m, J = 17.0, 9.0, 6.2 Hz, 1H), 2.34 (dd, J = 13.4, 11.9 Hz, 1H), 2.16 (m, J = 17.0, 10.4, 3.8 Hz, 1H), 1.21 - 1.17 (m, 1H), 1.17 (s, 3H), 1.08 (s, 3H), 0.79 (m, J = 11.9, 9.1, 5.2 Hz, 1H). ^{13}C NMR (126 MHz, CDCl3) δ 197.08, 167.37, 151.82, 137.71, 52.41, 42.37, 29.87, 28.42, 26.04, 24.55, 23.15, 15.59. HRMS (ESI+, MeOH): m/z calcd. 231.0990 $(M + Na)^+$, found: 231.0992.

2.5. Synthesis of the enone 11[2]

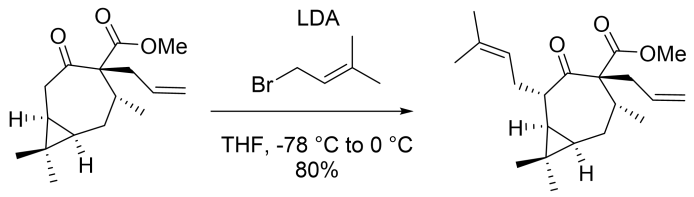


9 **11**

To a solution of Cuprous iodide (1.9 g, 1.0 equiv, 10.0 mmol) in Et_2O (30 mL) was added MeLi (15.0 mL, 1.5 equiv, 15.0 mmol, 1.0 M in THF) slowly at -78 °C, and the mixture was stirred at the same temperature for 0.5 h. To this solution was added enone **9** (2.0 g, 10.0 mmol) and allyl iodide (2.5 g, 1.5 equiv, 15.0 mmol) at -78 °C in a drop-wise manner, and the resultant mixture was then stirred at room temperature for 2.5 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (10 mL), and the resultant mixture was extracted with diethyl ether (3×20 mL). The combined

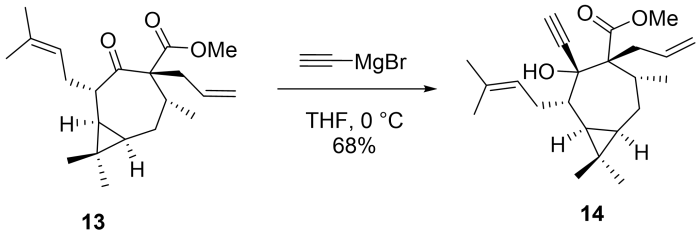
extracts were washed sequentially with water (20 mL) and brine (20 mL), and dried over $NaSO_4$. The extract was concentrated under reduced pressure, and the residue was purified by a flash chromatography on silica gel to give desired compound **11** (1.3 g, 50%) as a colorless oil. Rf = 0.5 (silica gel, 10% ethyl acetate in hexane); $[\alpha]_D^{25}$ = + 107 (c = 0.4, $CHCl_3$). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.86 (m, *J* = 17.2, 10.1, 8.5, 5.5 Hz, 1H), 5.14 - 4.94 (m, 2H), 3.66 (s, 3H), 2.84 (m, *J* = 14.3, 5.5, 1.7 Hz, 1H), 2.55 - 2.32 (m, 3H), 1.87 - 1.70 (m, 3H), 1.18 (d, *J* = 6.4 Hz, 3H), 1.05 (s, 3H), 1.02 (s, 3H), 0.77 - 0.57 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.85, 171.96, 135.24, 117.65, 66.61, 51.90, 38.75, 38.41, 38.28, 29.90, 28.37, 27.18, 21.92, 21.60, 18.26, 15.32. HRMS (ESI+, MeOH): m/z calcd. 287.1618 $(M + Na)^+$, found: 287.1619.

2.6. Synthesis of the compound 13



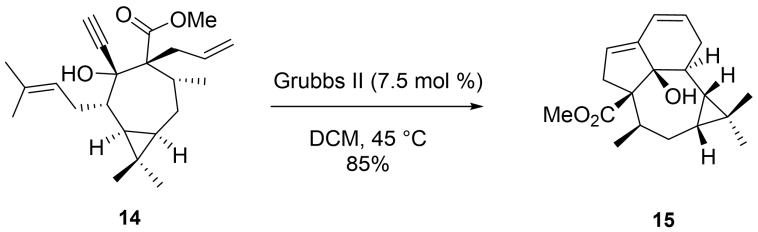
To a solution of compound **11** (300 mg, 1.1 mmol) in THF (30 mL) was added LDA (1.65 mL, 1.5 equiv, 1.65 mmol, 1.0 M in THF) slowly at -78 ºC, and the mixture was stirred at the same temperature for 1.5 h. To this solution was added allyl bromide (323 mg, 2.0 equiv, 2.2 mmol) at -78 ºC in a drop-wise manner, and the resultant mixture was then stirred at 0 ºC for 5 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (10 mL), and the resultant mixture was extracted with ethyl acetate (3×20 mL). The combined extracts were washed sequentially with water (20 mL) and brine (20 mL), and dried over $NaSO_4$. The extract was concentrated under reduced pressure, and the residue was purified by a flash chromatography on silica gel to give desired compound **14** (292 mg, 80%) as a colorless oil. Rf = 0.5 (silica gel, 10% ethyl acetate in hexane); $[\alpha]_D^{25}$ = + 133 (c = 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.62 (m, *J* = 16.5, 10.4, 7.5 Hz, 1H), 5.11 - 5.01 (m, 3H), 3.70 (s, 3H), 2.69 - 2.58 (m, 2H), 2.31 (m, *J* = 15.1, 5.7 Hz, 3H), 2.16 (m, *J* = 10.4, 7.0, 4.0 Hz, 1H), 1.90 (m, *J* = 15.4, 10.1, 8.4 Hz, 1H), 1.71 (d, *J* = 1.4 Hz, 3H), 1.66 (t, *J* = 4.5 Hz, 1H), 1.62 (d, *J* = 1.4 Hz, 3H), 1.02 (s, 3H), 1.00 - 0.93 (m, 6H), 0.71 (m, *J* = 8.8, 4.8 Hz, 1H), 0.27 (t, *J* = 9.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.40, 172.02, 132.96, 132.52, 122.00, 119.04, 77.41, 67.04, 51.79, 45.52, 39.68, 34.49, 29.85, 29.29, 29.08, 28.67, 28.31, 25.95, 22.53, 19.55, 17.90, 16.76, 15.56. HRMS (ESI+, MeOH): m/z calcd. 355.2244 $(M + Na)^+$, found: 355.2246.

2.7. Synthesis of the compound 14



To a solution of compound **13** (210 mg, 0.63 mmol) in THF (15 mL) was added ethynyl magnesium bromide (1.58 mL, 2.5 equiv, 1.58 mmol, 1.0 M in THF) slowly at 0 °C, and the mixture was stirred at the same temperature for 2.5 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (10 mL), and the resultant mixture was extracted with ethyl acetate (3×10 mL). The combined extracts were washed sequentially with water (10 mL) and brine (10 mL), and dried over $NaSO_4$. The extract was concentrated under reduced pressure, and the residue was purified by a flash chromatography on silica gel to give desired compound **14** (153 mg, 68%) as a colorless oil. Rf = 0.5 (silica gel, 5% ethyl acetate in hexane); $[\alpha]_D^{25}$ = - 36 (c = 0.4, $CHCl_3$). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.12 (m, *J* = 17.9, 9.1, 4.6 Hz, 1H), 5.39 (d, *J* = 2.0 Hz, 1H), 5.22 - 5.16 (m, 1H), 5.08 (d, *J* = 1.6 Hz, 1H), 5.05 - 5.01 (m, 1H), 3.77 (s, 3H), 3.75 - 3.66 (m, 1H), 2.86 - 2.71 (m, 2H), 2.55 (s, 1H), 2.38 - 2.27 (m, 2H), 2.19 (m, *J* = 7.5, 5.8, 1.8 Hz, 1H), 1.77 - 1.74 (m, 3H), 1.65 (t, *J* = 1.9 Hz, 3H), 1.44 - 1.26 (m, 2H), 1.21 (d, *J* = 7.3 Hz, 3H), 0.99 (s, 3H), 0.93 (s, 3H), 0.78 - 0.69 (m, 1H), 0.53 (t, *J* = 9.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.18, 136.25, 131.51, 123.64, 117.55, 87.51, 80.09, 75.12, 60.85, 52.06, 40.54, 39.26, 37.29, 32.73, 28.88, 28.52, 26.18, 25.50, 22.26, 19.96, 17.99, 17.25, 16.43. HRMS (ESI+, MeOH): m/z calcd. 381.2400 $(M + Na)^+$, found: 381.2386.

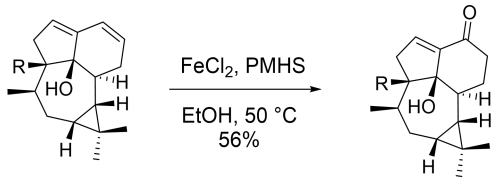
2.8. Synthesis of the compound 15



To a solution of tetracyclic compound **14** (3 g, 8.4 mmol) in DCM (200 mL) was added Grubbs second generation catalyst (535 mg, 7.5 mol %, 0.6 mmol) slowly at room temperature, and the mixture was fully degassed and stirred at the 45 °C for 2.5 h. The reaction was quenched by addition

of a saturated aqueous NH_4Cl solution (100 mL), and the resultant mixture was extracted with ethyl acetate (3×100 mL). The combined extracts were washed sequentially with water (100 mL) and brine (100 mL), and dried over $NaSO_4$. The extract was concentrated under reduced pressure, and the residue was purified by a flash chromatography on silica gel to give desired compound **15** (2.23 g, 88%) as a colorless oil. Rf = 0.6 (silica gel, 10% ethyl acetate in hexane); $[\alpha]_D^{25}$ = + 78 (c = 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.17 (dd, *J* = 9.8, 2.7 Hz, 1H), 5.86 (m, *J* = 9.6, 5.8, 1.9 Hz, 1H), 5.54 (t, *J* = 2.9 Hz, 1H), 5.13 (s, 1H), 3.76 (s, 3H), 2.90 - 2.61 (m, 2H), 2.42 (m, *J* = 17.6, 10.7, 2.6, 1.3 Hz, 1H), 2.03 (m, *J* = 18.2, 5.2 Hz, 1H), 1.81 (m, *J* = 12.7, 6.4 Hz, 1H), 1.69 - 1.53 (m, 3H), 0.75 (dd, *J* = 11.3, 9.1 Hz, 1H), 0.48 (m, *J* = 9.5, 3.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.96, 142.34, 131.13, 123.04, 122.40, 86.20, 58.66, 51.49, 37.92, 37.60, 33.21, 31.02, 30.56, 28.97, 28.60, 22.05, 19.81, 19.29, 15.13. HRMS (ESI+, MeOH): m/z calcd. 325.1774 $(M + Na)^+$, found: 325.1774.

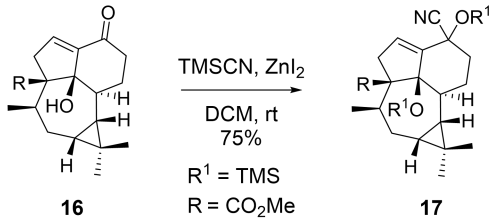
2.9. Synthesis of the compound 16



15 **16**

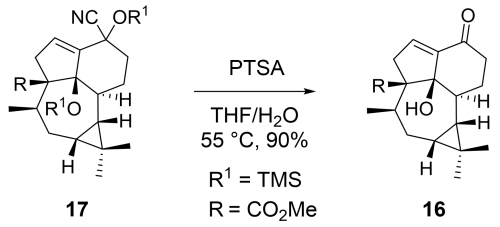
To a solution of compound **15** (40 mg, 0.13 mmol) in EtOH (2 mL) was added $FeCl_2$ (1 mg, 5 mol %, 0.007 mmol), and poly(methylhydrosiloxane) (0.1 ml, 6.5 equiv, 0.86 mmol). The reaction mixture was stirred under air atmosphere at 50 °C until the reaction was complete. After the mixture was cooled to room temperature, the reaction was concentrated under reduced pressure, and the residue was purified by a flash chromatography on silica gel to give desired compound **16** (23.3 mg, 56%) as a colorless oil. Rf = 0.4 (silica gel, 10% ethyl acetate in hexane); $[\alpha]_D^{25}$ = + 43 (c = 0.4, $CHCl_3$). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.81 (d, *J* = 2.0 Hz, 1H), 5.59 (s, 1H), 3.80 (s, 3H), 2.86 (dd, *J* = 16.8, 12.2 Hz, 1H), 2.79 - 2.67 (m, 1H), 2.47 - 2.33 (m, 2H), 2.23 (dd, *J* = 16.9, 4.0 Hz, 1H), 1.98 - 1.89 (m, 2H), 1.74 - 1.65 (m, 3H), 1.05 - 1.01 (m, 6H), 0.96 (s, 3H), 0.77 (dd, *J* = 11.4, 8.8 Hz, 1H), 0.47 (m, *J* = 9.2, 4.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.65, 178.18, 169.74, 124.19, 83.24, 77.42, 76.91, 58.85, 52.02, 39.75, 39.52, 33.32, 32.38, 30.02, 28.98, 28.88, 28.29, 22.36, 20.50, 18.68, 15.07. HRMS (ESI+, MeOH): m/z calcd. 341.1723 $(M + Na)^+$, found: 341.1724.

2.10. Synthesis of the compound 17



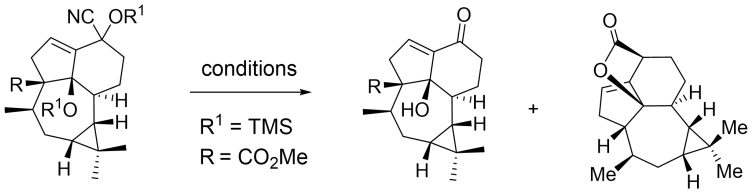
To a solution of compound **16** (18.9 mg, 0.06 mmol) in CH_2Cl_2 (1 mL) was added ZnI_2 (11.4 mg, 0.6 equiv, 0.036 mmol) and trimethylsilyl cyanide (70 μL, 10.0 equiv, 0.59 mmol) at 0 °C under argon. The reaction was allowed to slowly warm to room temperature and stirred for 15 h. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (1 mL), and the resultant mixture was extracted with ethyl acetate (3×2 mL). The combined extracts were washed sequentially with water (2 mL) and brine (3 mL), and dried over $NaSO_4$. The extract was concentrated under reduced pressure, and the residue was purified by a flash chromatography on silica gel to give desired compound **17** (21.8 mg, 75%) as a colorless oil. Rf = 0.8 (silica gel, 20% ethyl acetate in hexane); $[\alpha]_D^{25}$ = - 73 (c = 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.41 (d, *J* = 1.7 Hz, 1H), 3.69 (s, 3H), 2.66 - 2.54 (m, 2H), 2.13 - 2.07 (m, 3H), 1.68 (m, *J* = 11.0, 6.5 Hz, 2H), 1.48 (dd, *J* = 12.0, 6.1 Hz, 1H), 1.06 (s, 3H), 1.04 (s, 3H), 1.01 - 0.97 (m, 1H), 0.87 - 0.79 (m, 2H), 0.75 (d, *J* = 6.4 Hz, 3H), 0.57 (t, *J* = 10.1 Hz, 1H), 0.27 (s, 9H), 0.08 (d, *J* = 1.8 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.27, 150.16, 121.73, 120.32, 82.95, 77.48, 69.11, 65.39, 51.13, 41.19, 39.86, 37.62, 37.42, 31.74, 31.65, 29.05, 27.97, 23.10, 19.98, 17.99, 15.27, 2.78, 1.55. HRMS (ESI+, MeOH): m/z calcd. 512.2623 $(M + Na)^+$, found: 512.2621.

2.11. Synthesis of the compound 16



To a solution of compound **17** (45 mg, 0.1 mmol) in 10% aqueous THF (1 mL) was added PTSA (2 mg, 10 mol %, 0.01 mmol) and the reaction was heated at 55 °C for 20 h. After the mixture was cooled to room temperature, the reaction was quenched by addition of a saturated aqueous NH_4Cl solution (2 mL), and the resultant mixture was extracted with ethyl acetate (2×2 mL). The combined

extracts were washed sequentially with water (1 mL) and brine (2 mL), and dried over $NaSO_4$. The extract was concentrated under reduced pressure, and the residue was purified by a flash chromatography on silica gel to give compound **16** (5.7 mg, 90%) as a colorless oil. Rf = 0.4 (silica gel, 10% ethyl acetate in hexane); $[\alpha]_D^{25}$ = + 43 (c = 0.4, $CHCl_3$). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.81 (d, *J* = 2.0 Hz, 1H), 5.59 (s, 1H), 3.80 (s, 3H), 2.86 (dd, *J* = 16.8, 12.2 Hz, 1H), 2.79 - 2.67 (m, 1H), 2.47 - 2.33 (m, 2H), 2.23 (dd, *J* = 16.9, 4.0 Hz, 1H), 1.98 - 1.89 (m, 2H), 1.74 - 1.65 (m, 3H), 1.05 - 1.01 (m, 6H), 0.96 (s, 3H), 0.77 (dd, *J* = 11.4, 8.8 Hz, 1H), 0.47 (m, *J* = 9.2, 4.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.65, 178.18, 169.74, 124.19, 83.24, 77.42, 76.91, 58.85, 52.02, 39.75, 39.52, 33.32, 32.38, 30.02, 28.98, 28.88, 28.29, 22.36, 20.50, 18.68, 15.07. HRMS (ESI+, MeOH): m/z calcd. 341.1723 $(M + Na)^+$, found: 341.1724.

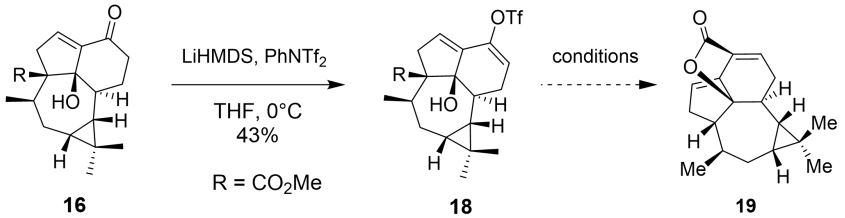


17 **16** **20**

Table 1. Lactonization conditions by cyano condensation

Entry	Conditions	Yield [%]	
		16	17
1	PTSA, acetone/H_2O, 0°C, 6h	97	-
2	PTSA, acetone/H_2O, 0°C, 12 h	97	-
3	PTSA, THF/H_2O, 0°C, 2 h	96	6
4	PTSA, THF/H_2O, 25°C, 12 h	75	23
5	PTSA, THF/H_2O, 50°C, 20 h	95	-
5	HCl, THF/H_2O, 50°C, 20 h	61	-
5	HCl, THF/H_2O, rt, 10 h	66	-
5	H_2SO_4, THF/H_2O, rt, 10 h	70	-

2.12. Synthesis of the compound 18



Pd-catalyzed carbonylation lactonization conditions screening

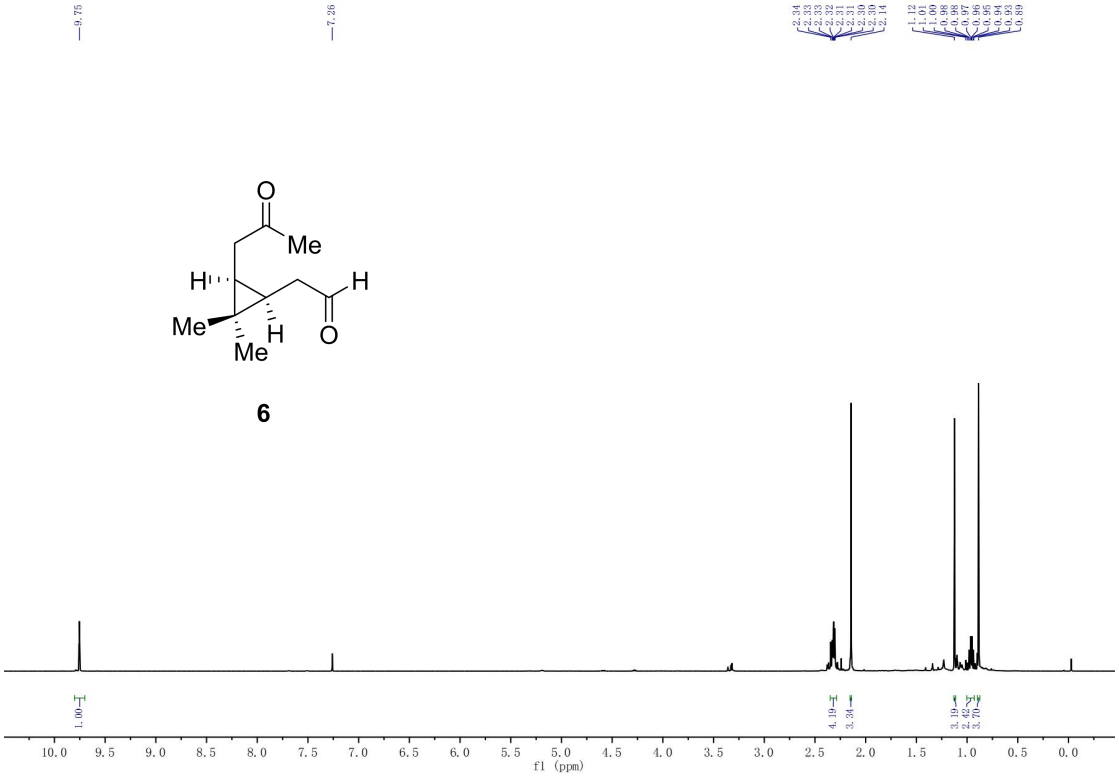
E	Conditions	Results
1	$Pd(OAc)_2$, PPh_3, Et_3N, CO, CH_3CN, 60 °C, 6h	-
2	$Pd(OAc)_2$, PPh_3, Et_3N, CO, EtOH, 80 °C, 6h	-
3	$Pd(OAc)_2$, dppp, Et_3N, CO, CH_3CN, 60 °C, 6h	-
4	$Pd(OAc)_2$, dppp, Et_3N, CO, DMF, 100 °C, 6h	mixture
5	$Pd(PPh_3)_4$, n-Bu_3N, CO, LiCl, CH_3CN, 80 °C, 10h	mixture
6	$Pd(PPh_3)_4$, Et_3N, CO, LiCl, CH_3CN, 80 °C, 10h	mixture

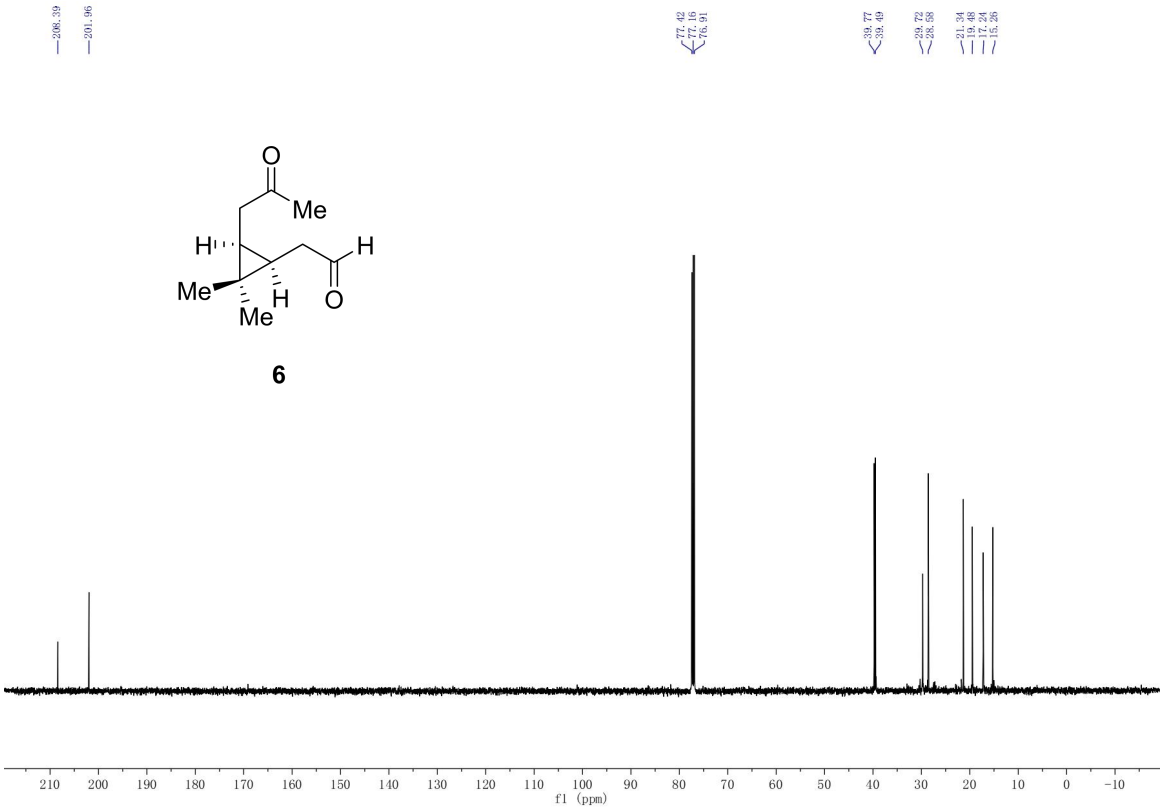
To a solution of compound **16** (25 mg, 0.08 mmol) in dry THF (1 mL) was added LiHMDS (0.16 mL, 2.0 equiv, 0.16 mmol, 1.0 M in THF) slowly at 0 °C, and the mixture was stirred at 0 °C for 30 min. To this solution was added N-phenyl-bis(trifluromethanesulfonimide) (57.2 mg, 1.5 equiv, 0.13 mmol) at 0 °C, and the resultant mixture was then stirred at room temperature overnight. The reaction was quenched by addition of a saturated aqueous NH_4Cl solution (1 mL), and the resultant mixture was extracted with ethyl acetate (3×2 mL). The combined extracts were washed sequentially with water (2 mL) and brine (3 mL), and dried over $NaSO_4$. The extract was concentrated under reduced pressure, and the residue was purified by a flash chromatography on silica gel to give desired compound **18** (15.4 mg, 43%) as a colorless oil. Rf = 0.5 (silica gel, 20% ethyl acetate in hexane); $[\alpha]_D^{25}$ = + 97 (c = 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.19 (d, J = 2.2 Hz, 1H), 5.78 (s, 1H), 5.34 (s, 1H), 3.78 (s, 3H), 2.90 - 2.75 (m, 3H), 2.23 (dd, J = 17.0, 4.6 Hz, 1H), 1.76 - 1.62 (m, 4H), 1.06 (s, 3H), 1.01 (d, J = 6.2 Hz, 3H), 0.96 (s, 3H), 0.77 (m, J = 11.3, 9.1 Hz, 1H), 0.52 (m, J = 9.5, 3.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.52, 151.43, 139.19, 129.82, 128.09, 113.95, 85.31, 77.48, 57.92, 51.80, 38.94, 37.74, 33.21, 32.60, 30.77, 28.73, 27.80, 22.06, 20.16, 19.26, 14.93. HRMS (ESI+, MeOH): m/z calcd. 473.1216 $(M + Na)^+$, found: 473.1216.

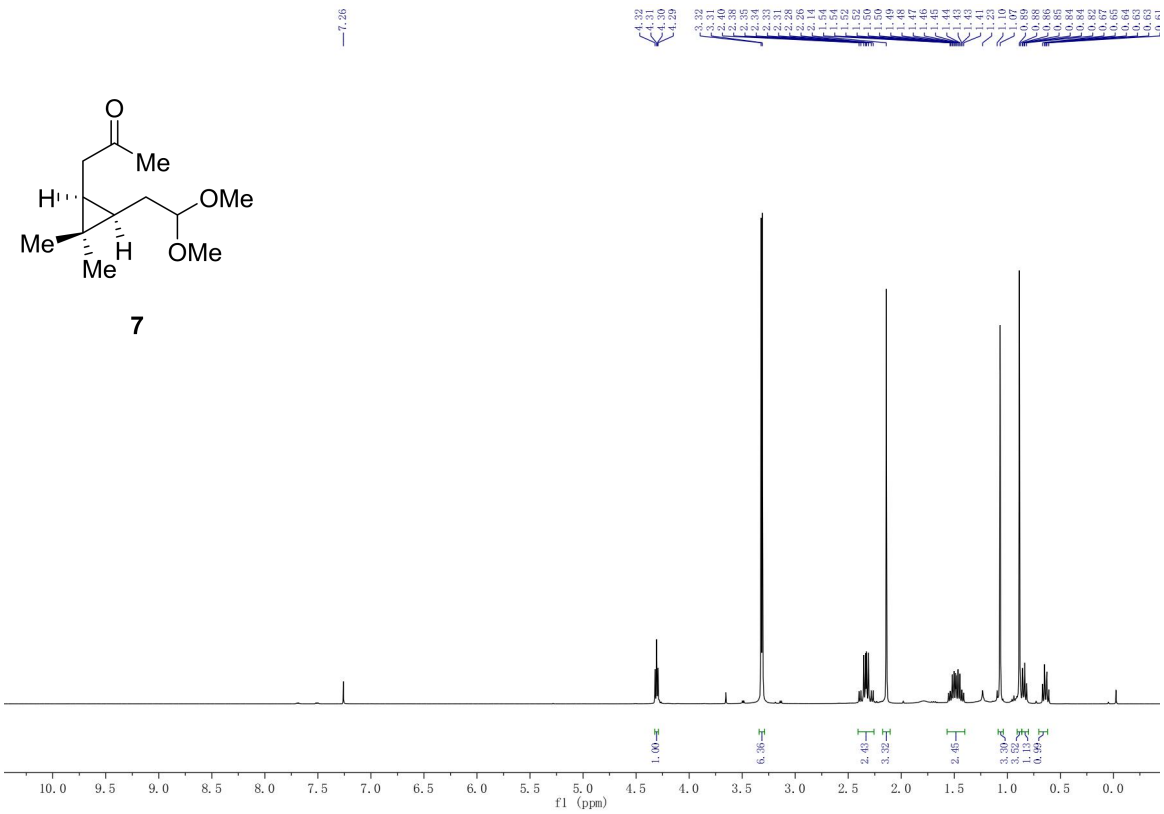
3. References

1. T. Satoh, Y. Kaneko, T. Okuda, S. Uwaya and K. Yamakawa, *Chem. Pharm. Bull.*, 1984, **32**, 3452.
2. (a) A. Olmstead, M. Parvez and R. Funk, *J. Am. Chem. Soc.*, 1988, **110**, 3298. (b) H. F. Tang, N. Naeem and J. L. Wood, *Org. Lett.*, 2001, **3**, 1563.

4. NMR spectra and X-ray for the synthesized compounds



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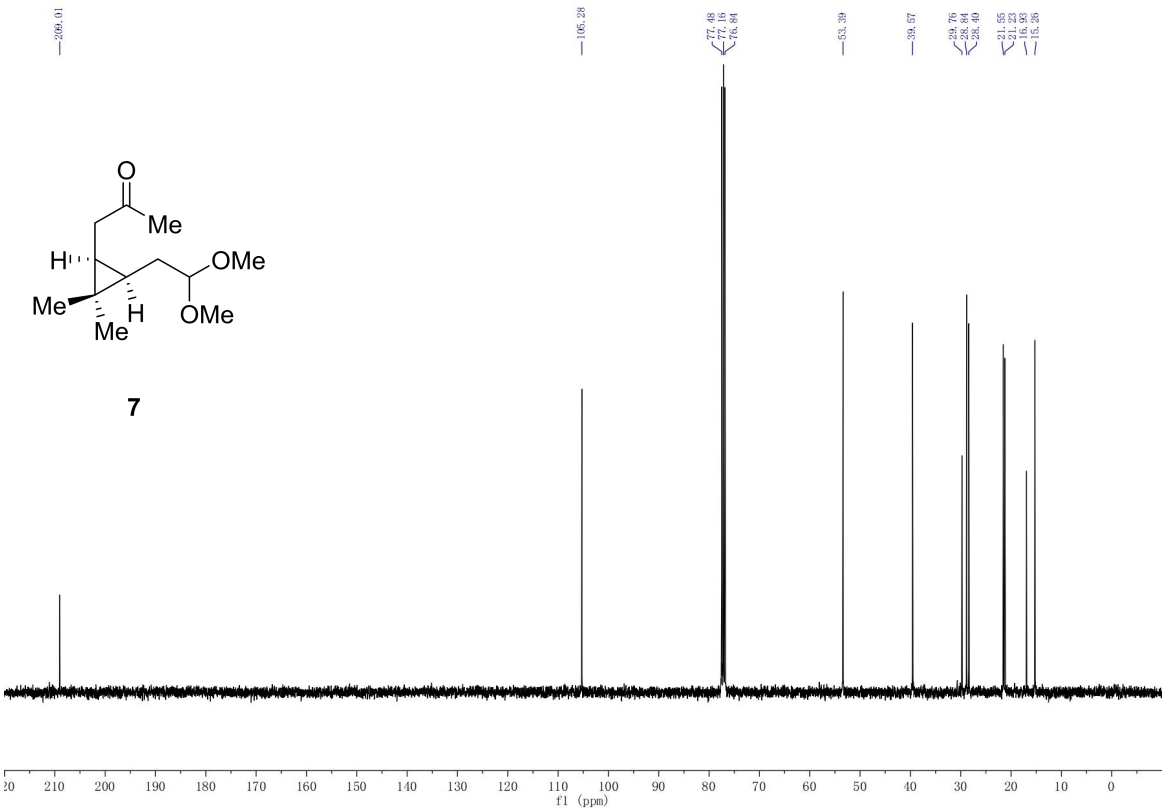
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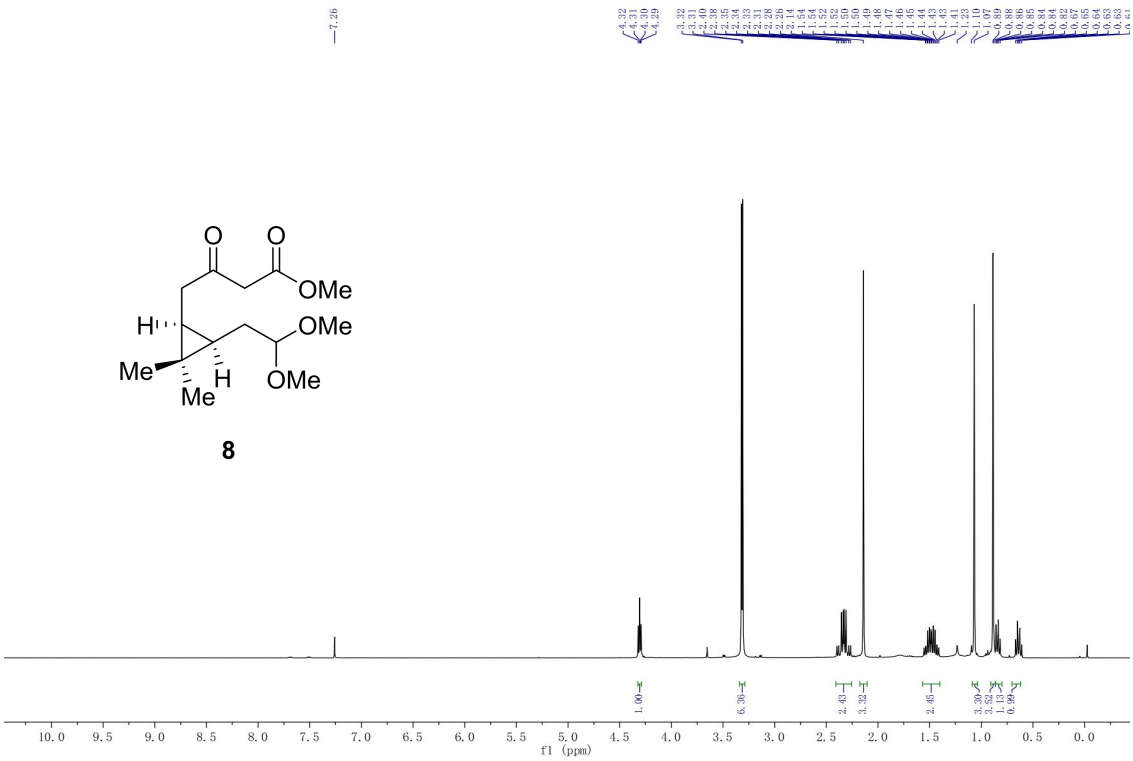
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H
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Me
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Me
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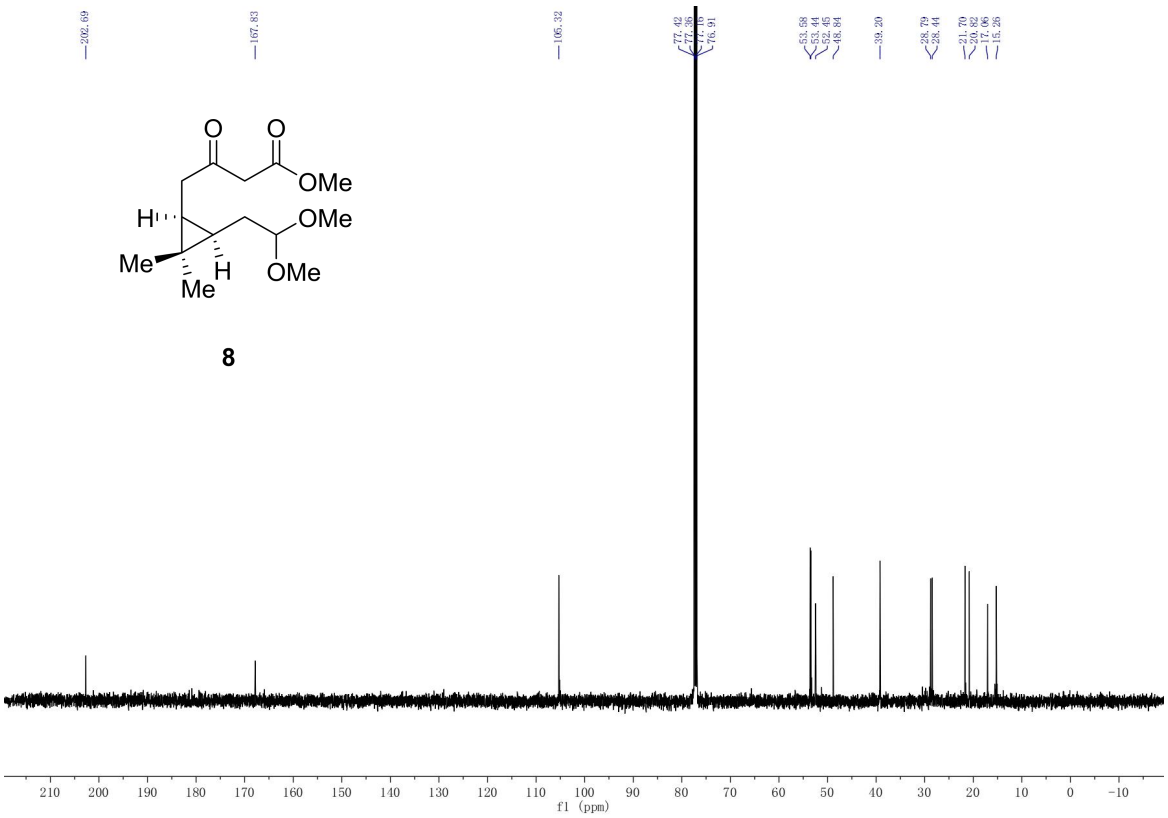
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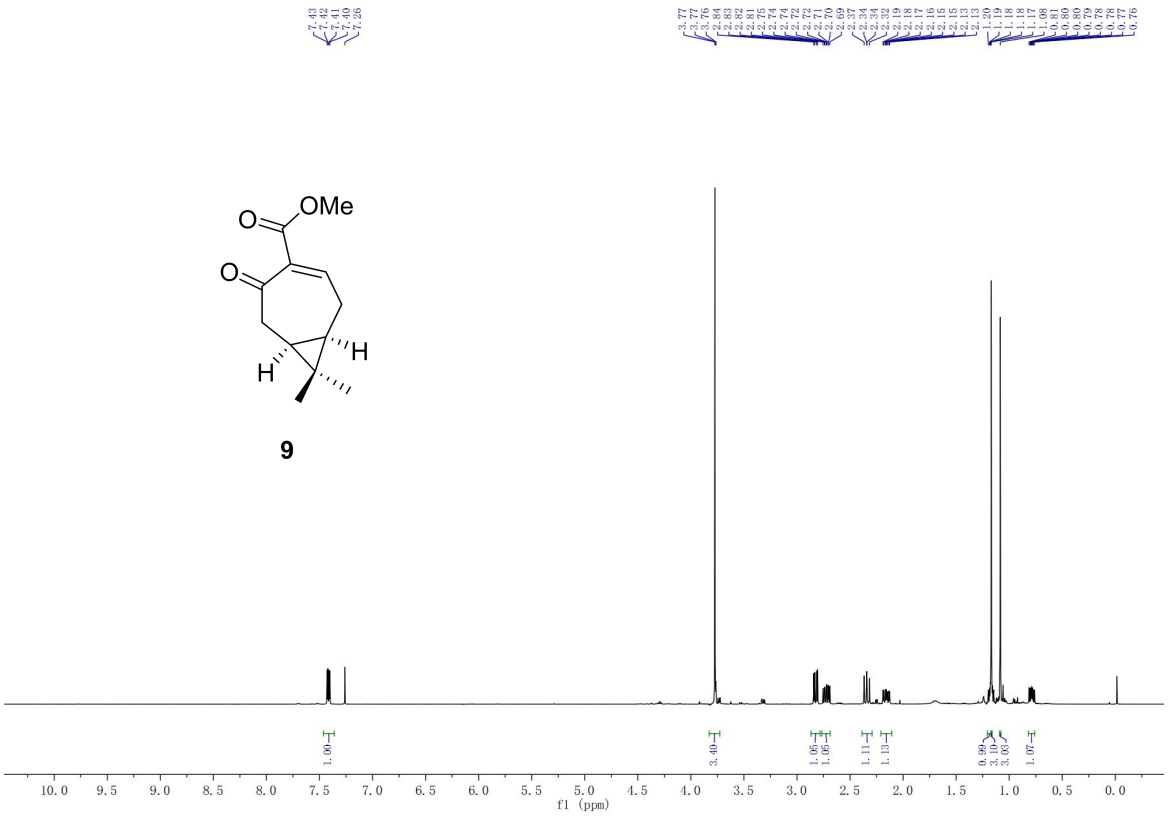
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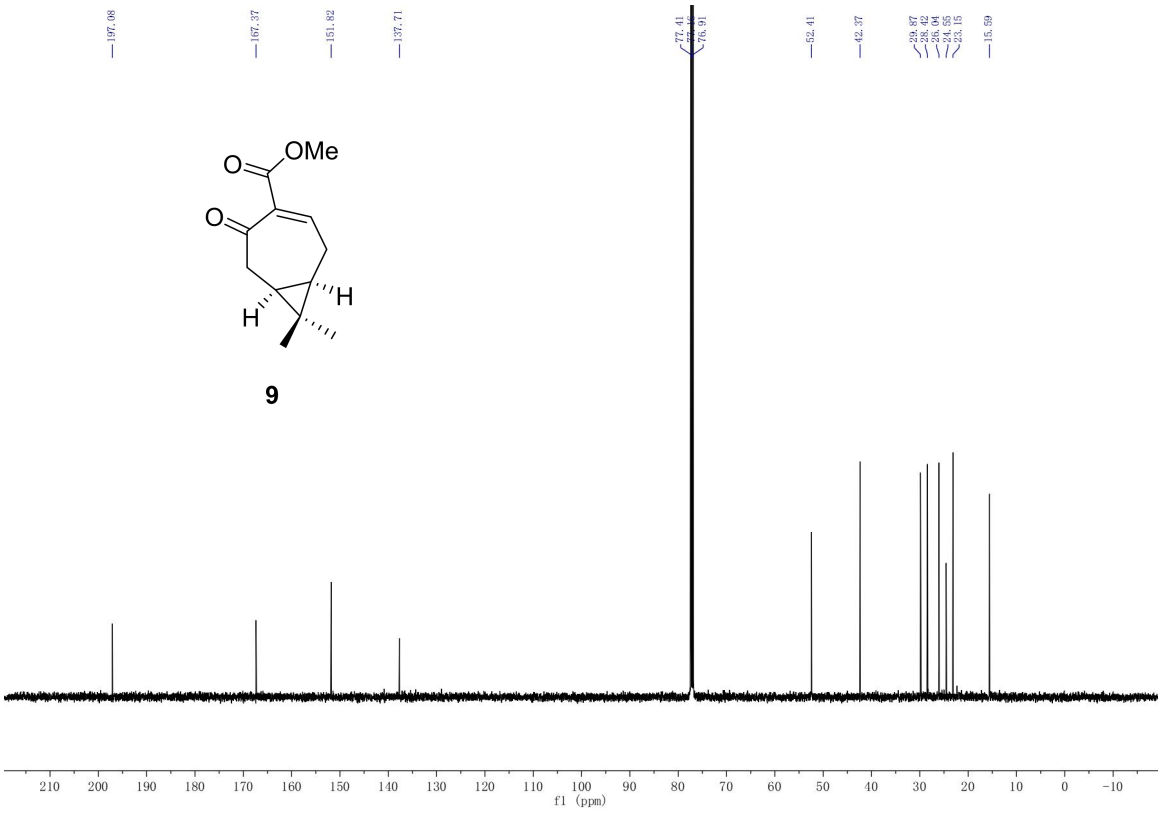
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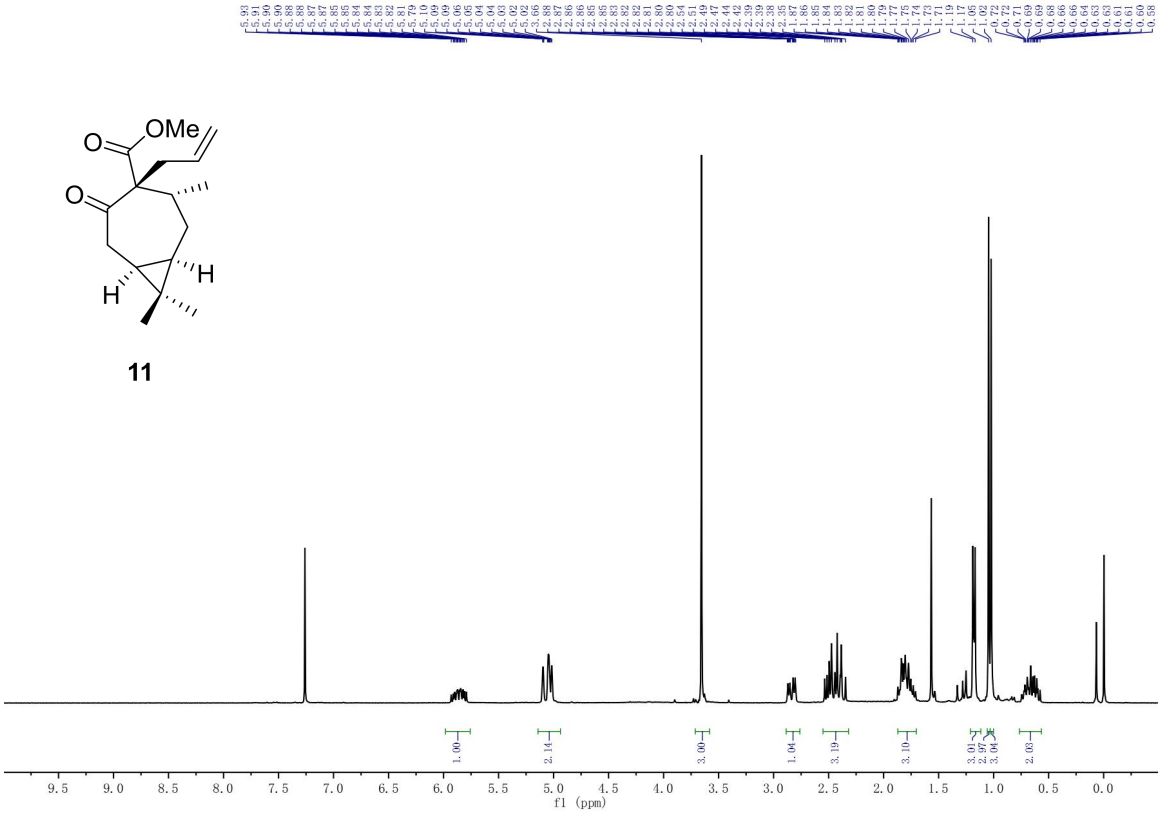
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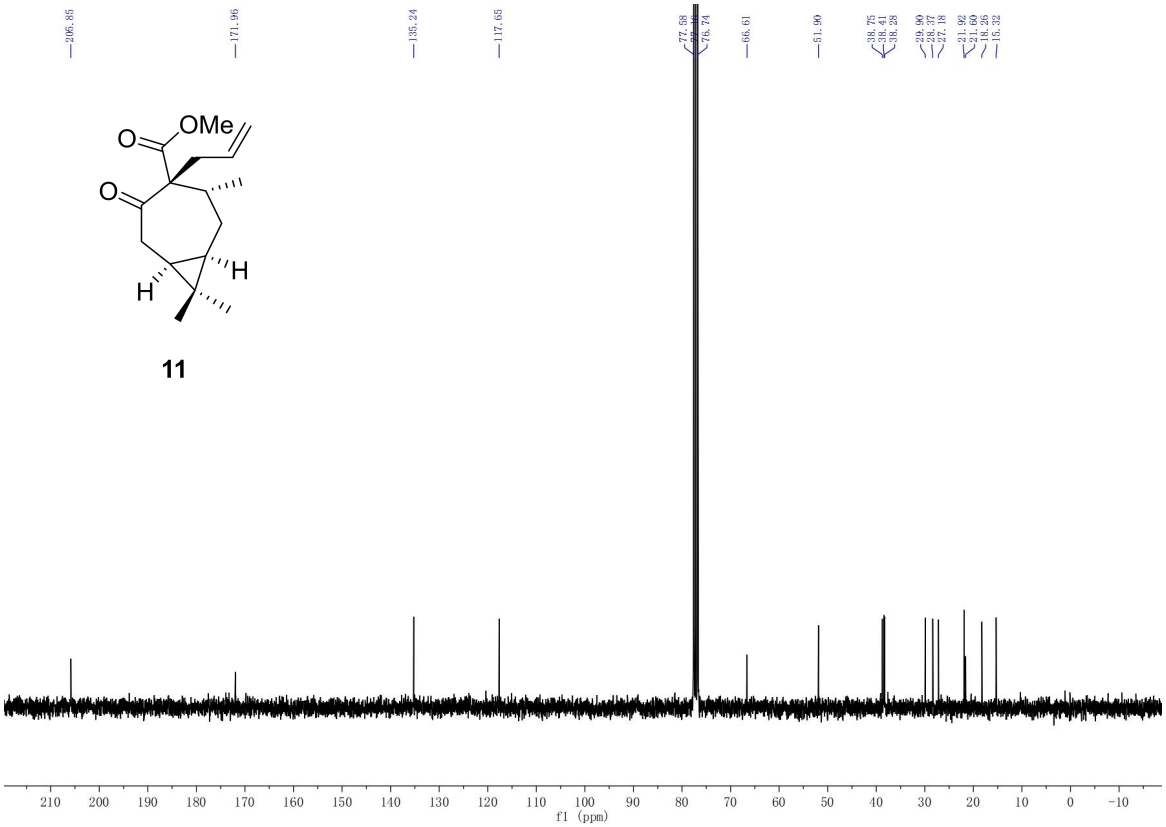
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77.58
76.74
66.61
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38.41
38.28
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21.92
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18.26
15.32
OMe
O
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H
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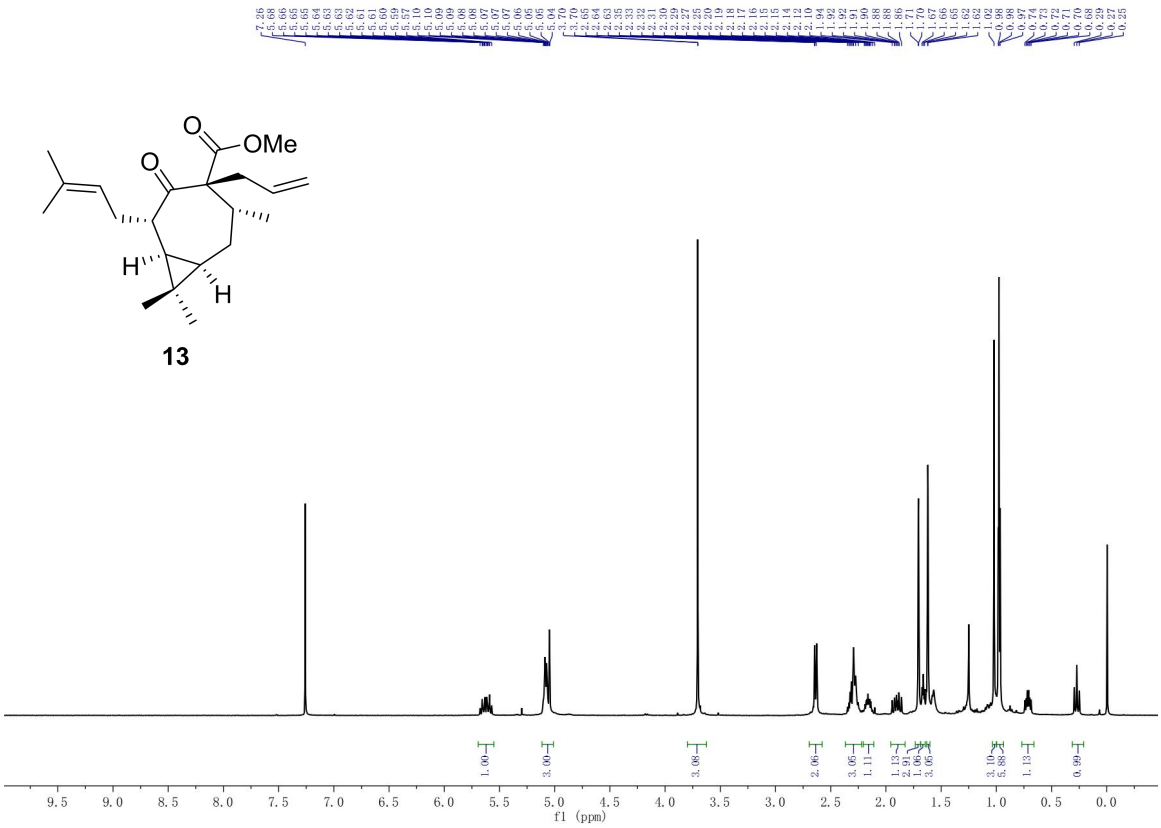
f1 (ppm)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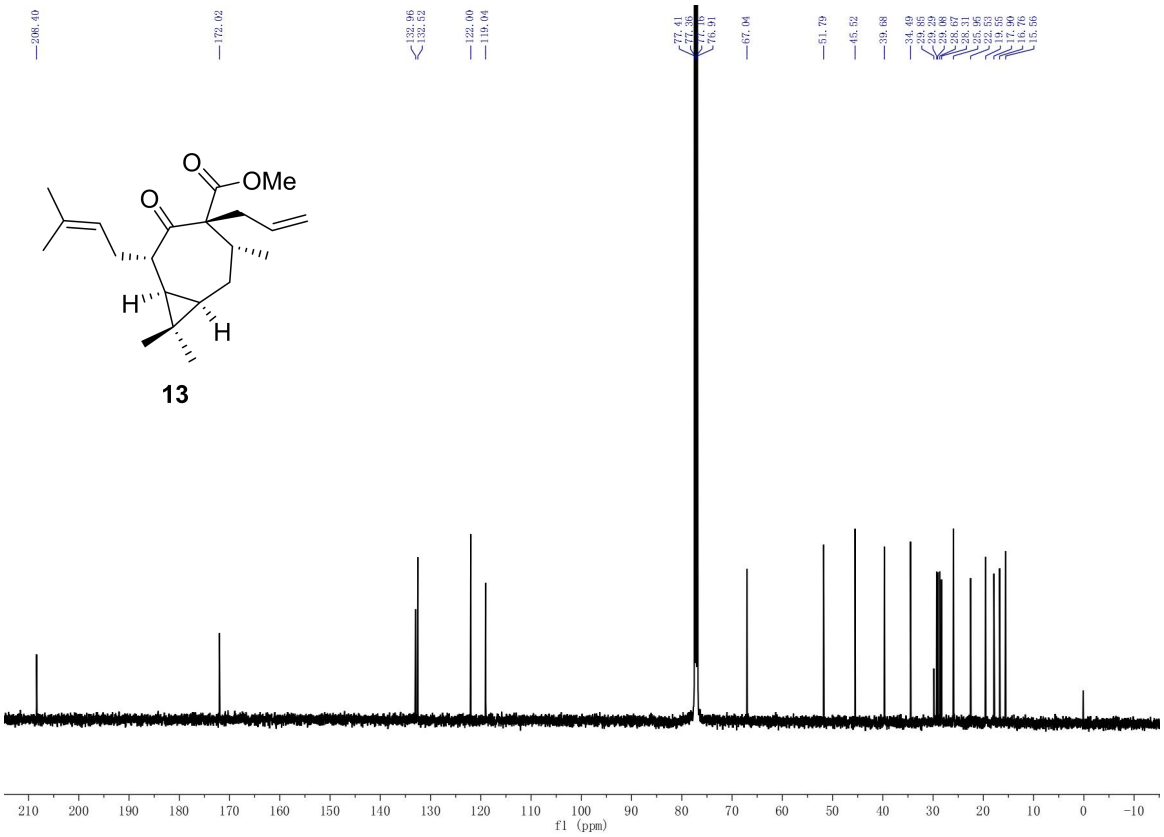
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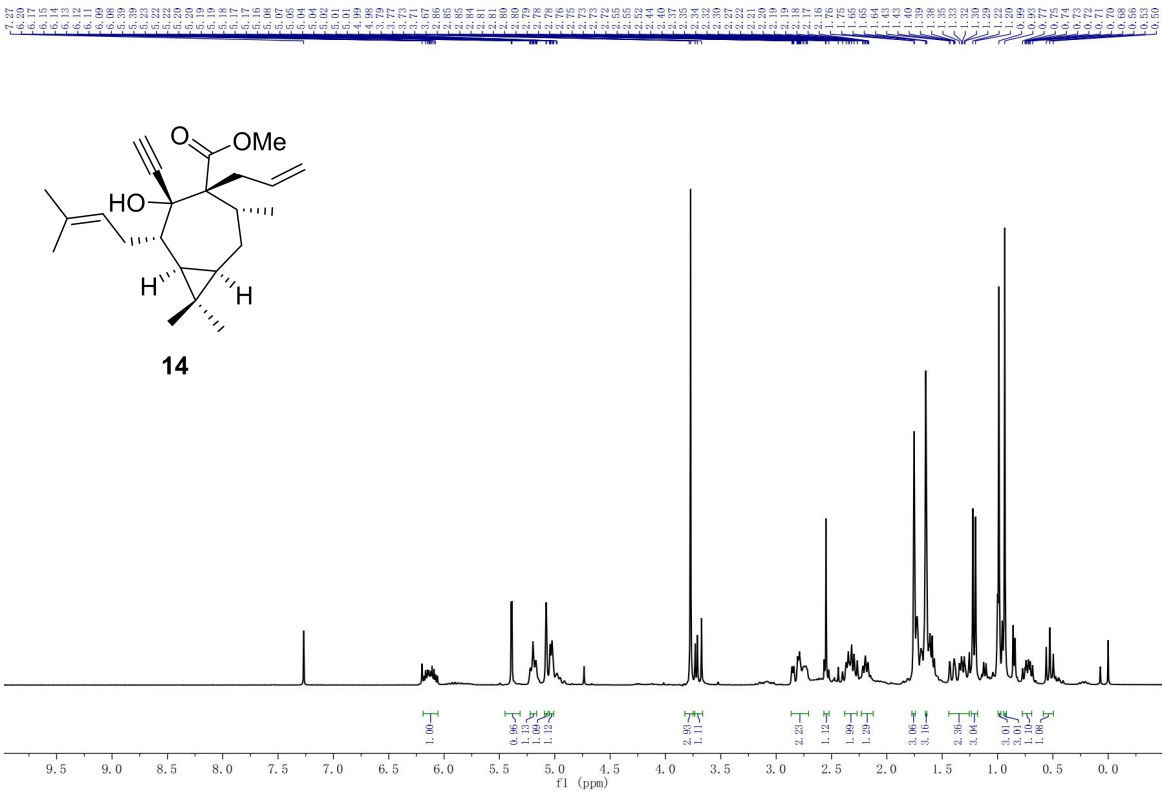
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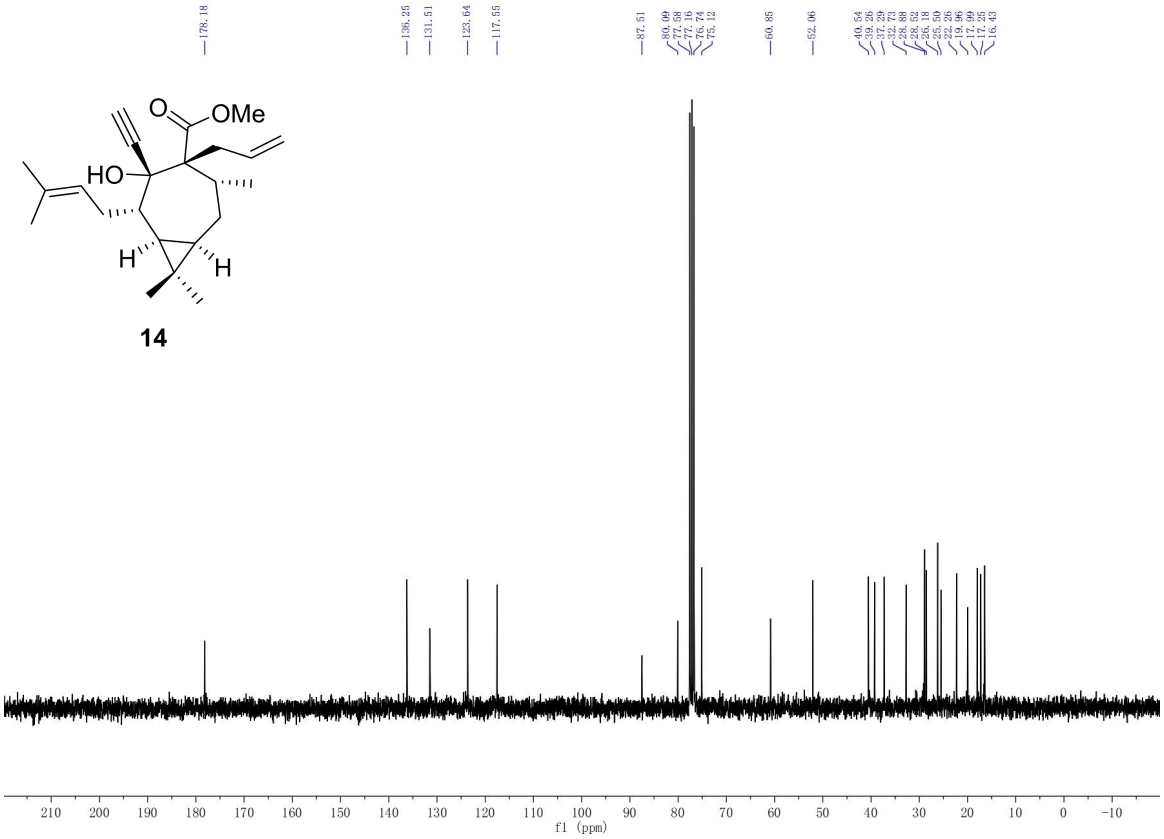
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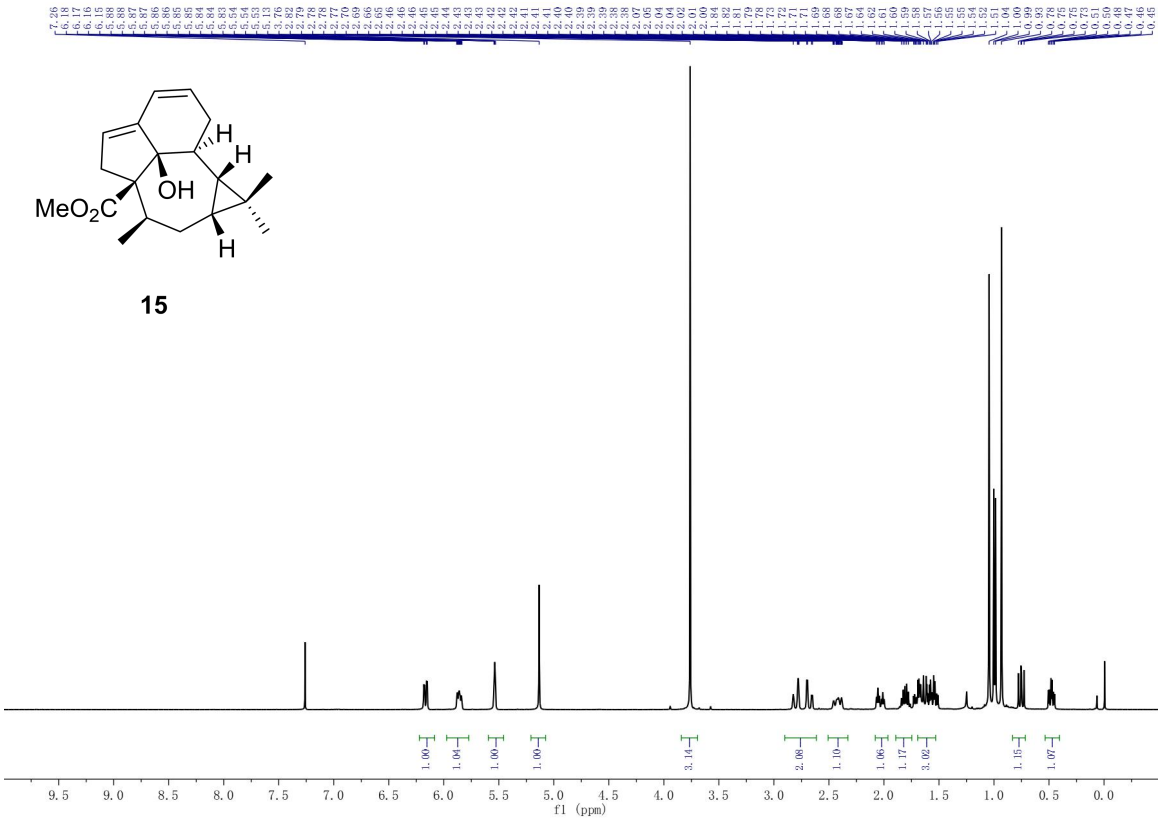
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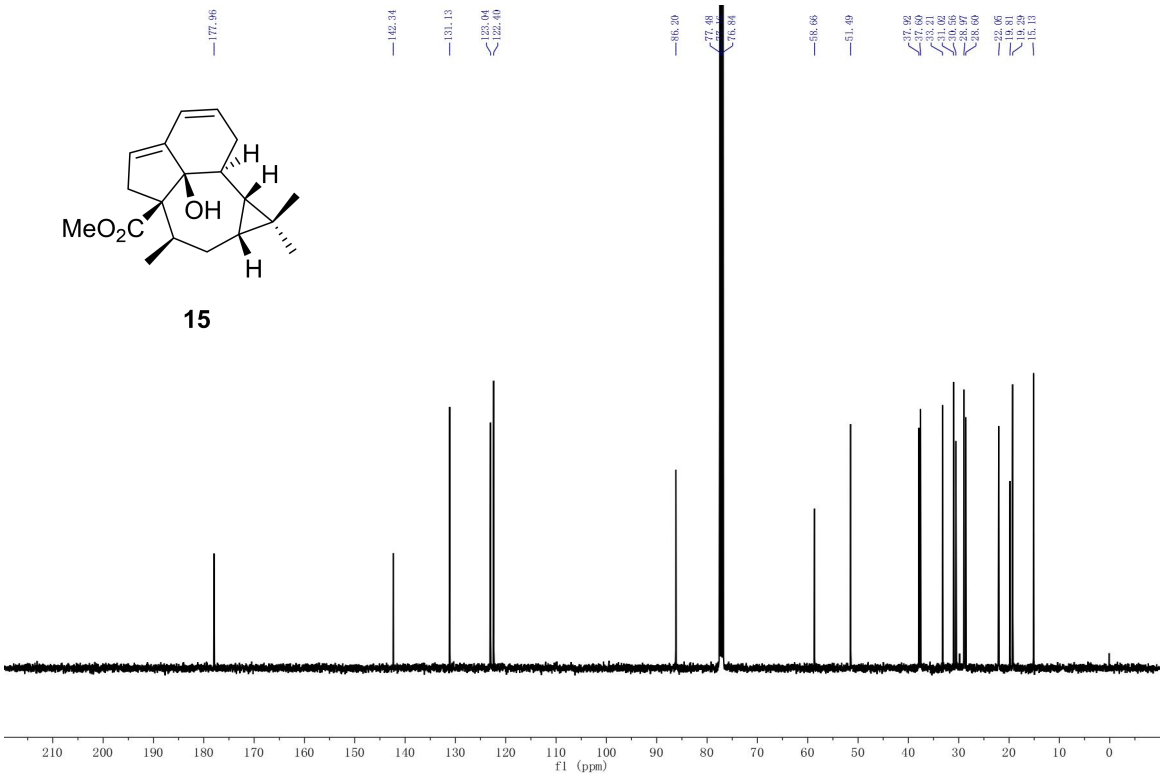
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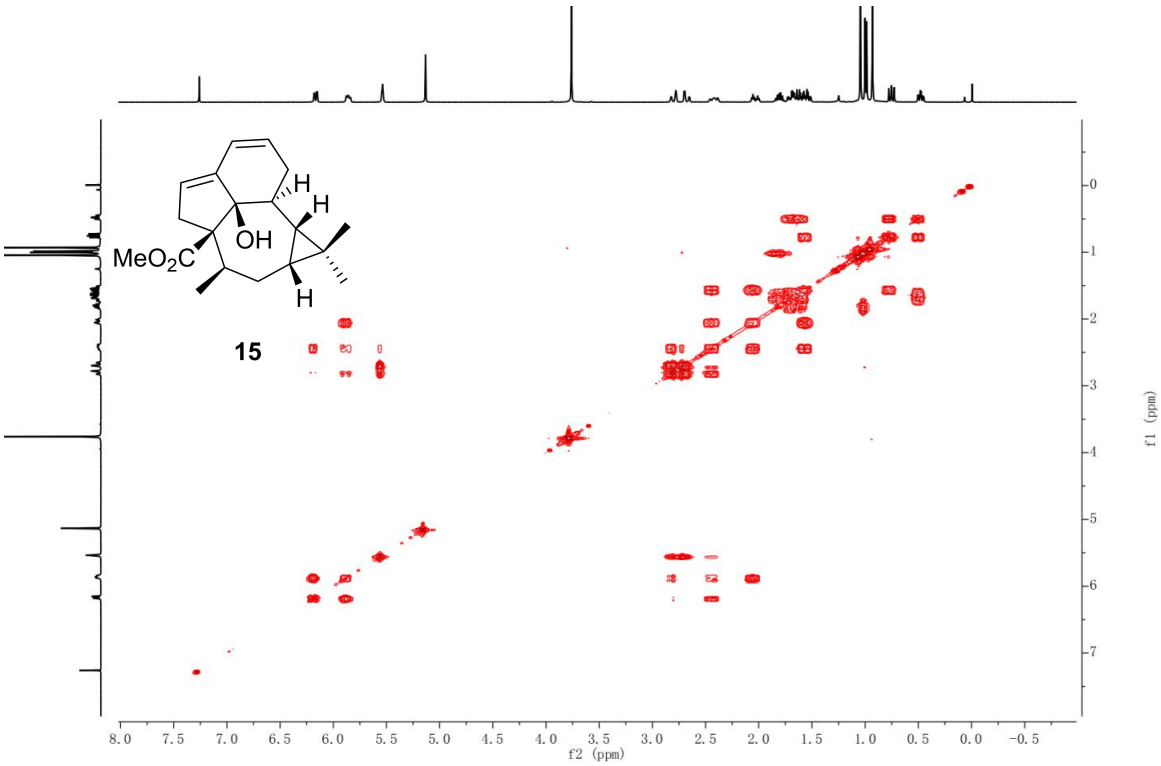
H
H
H
15
f1 (ppm)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H
H
H
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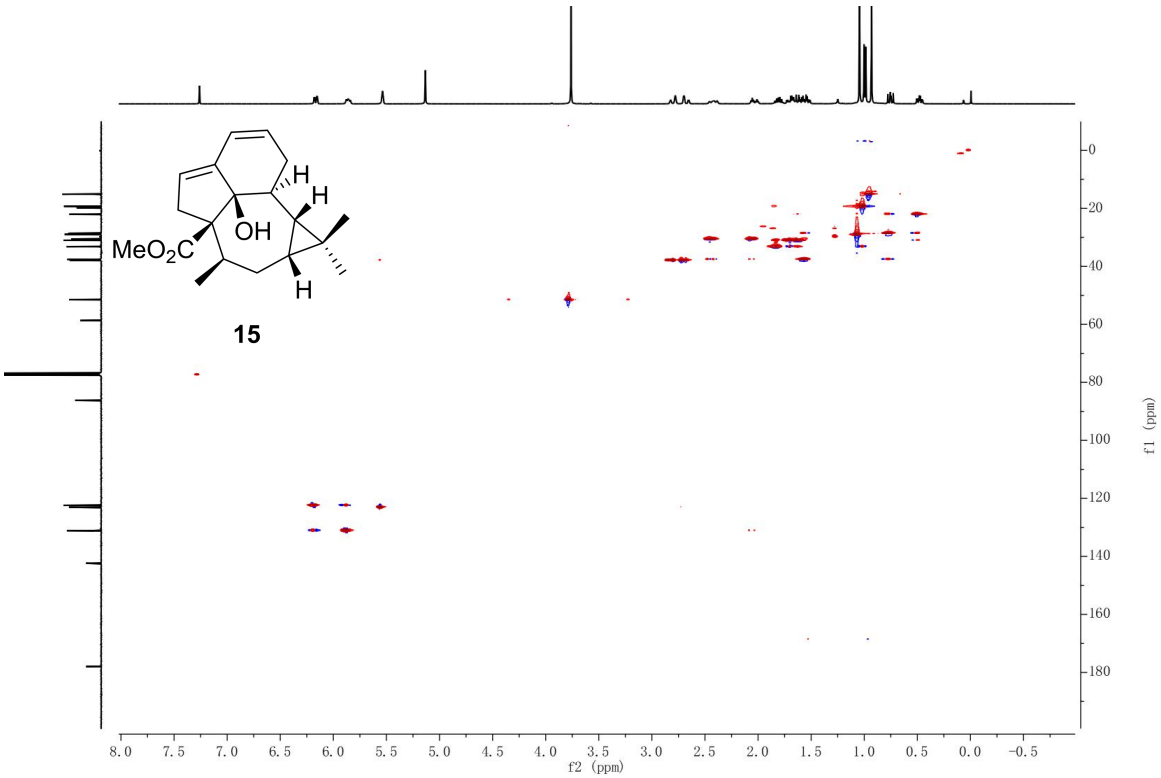
f1 (ppm)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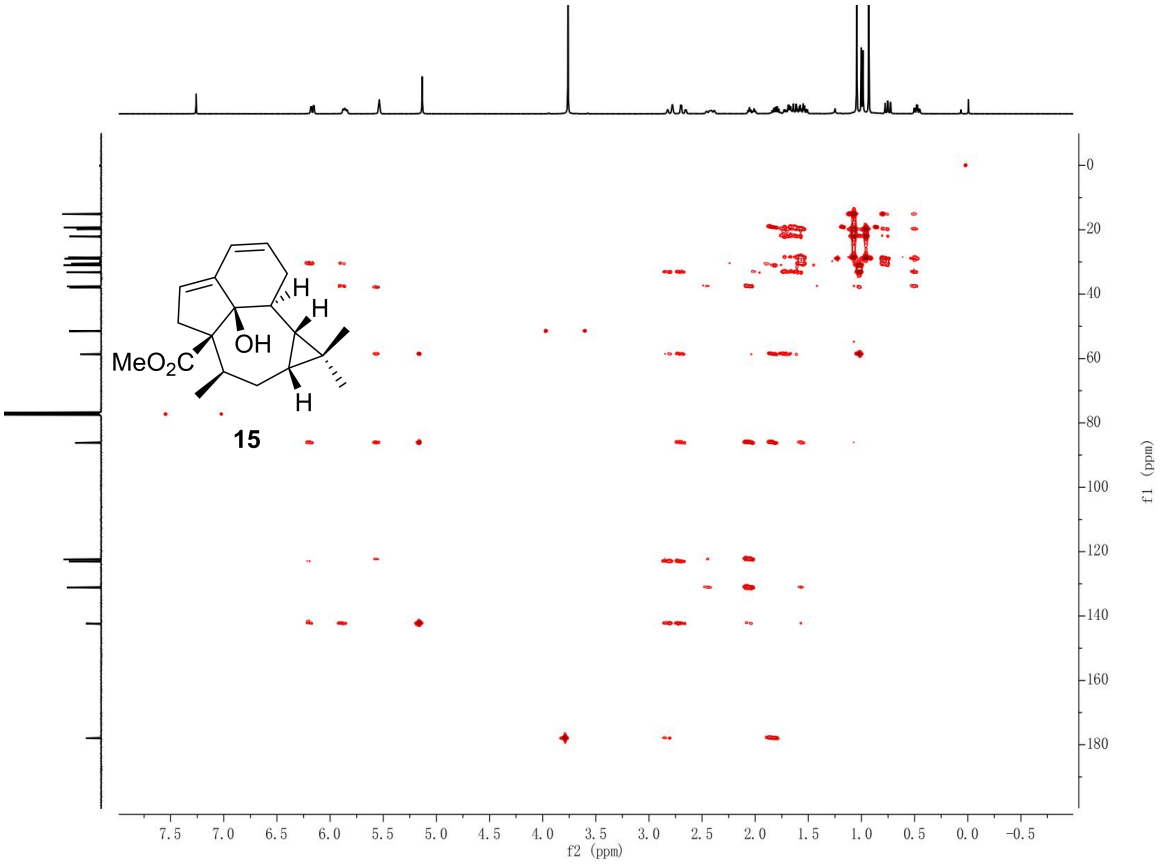
H
H
H
15
f2 (ppm)
f1 (ppm)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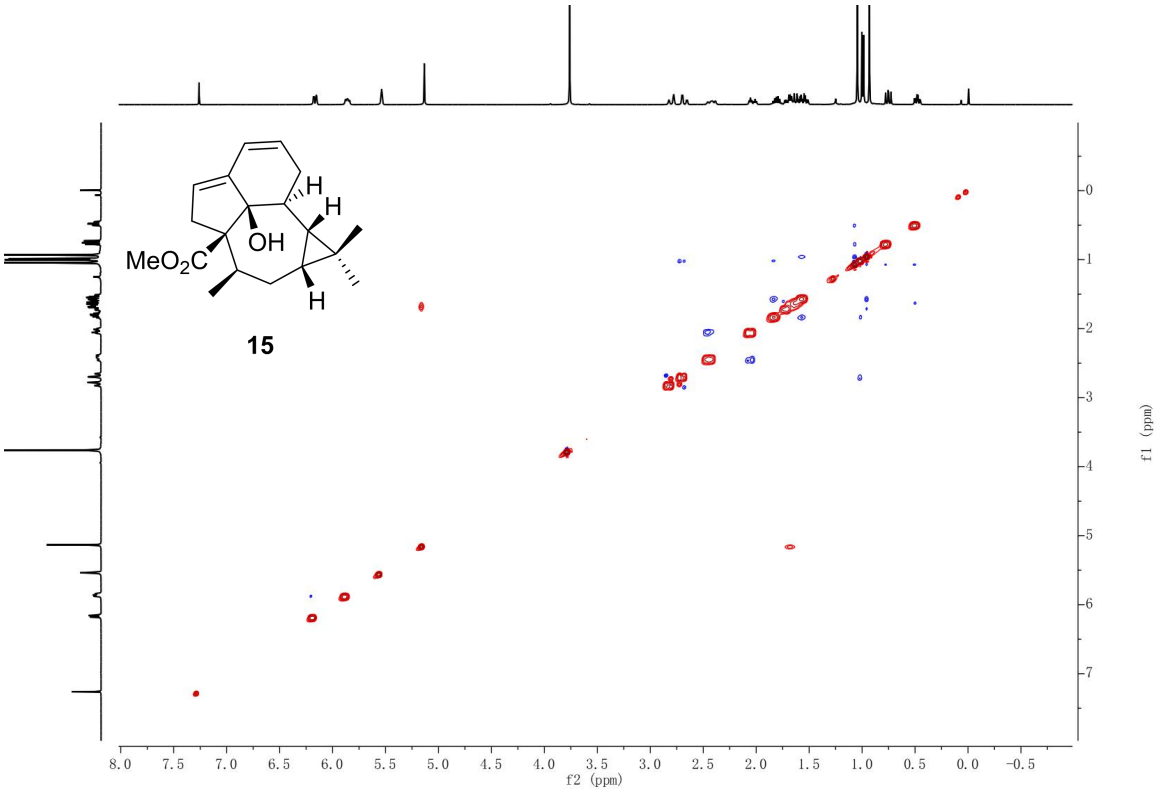
H
H
H
15
f2 (ppm)
f1 (ppm)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H
H
H
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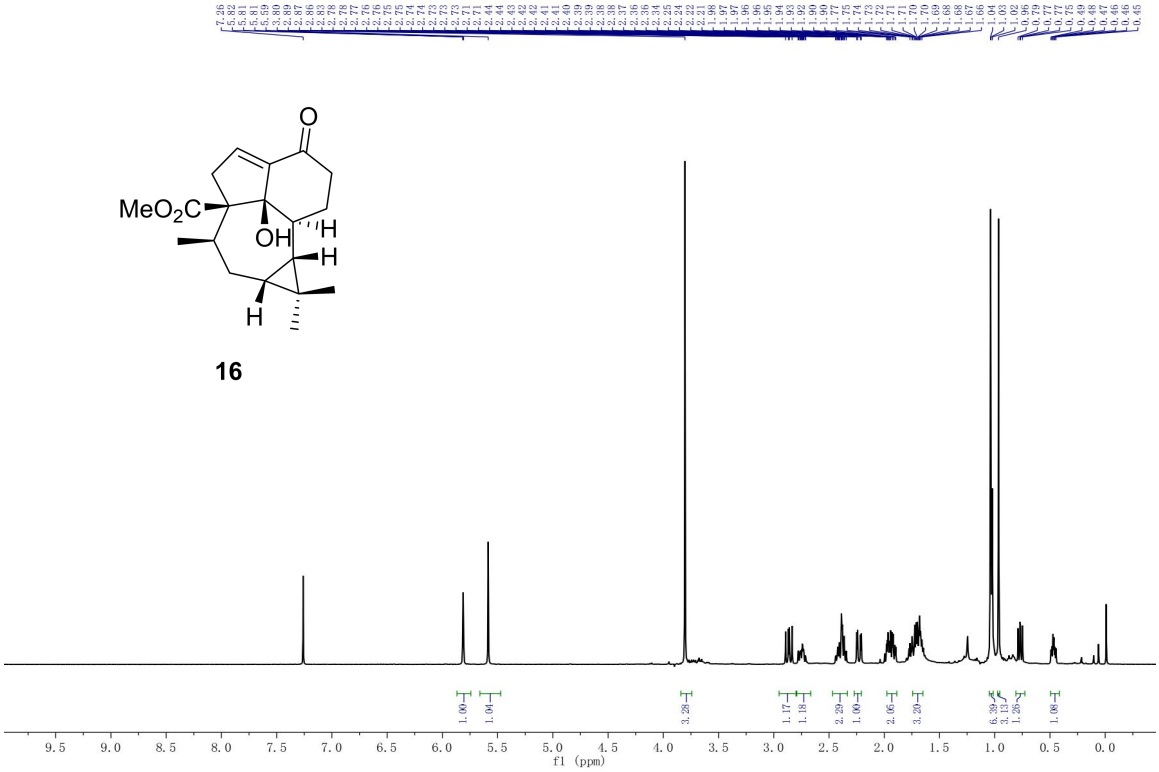
f2 (ppm)
f1 (ppm)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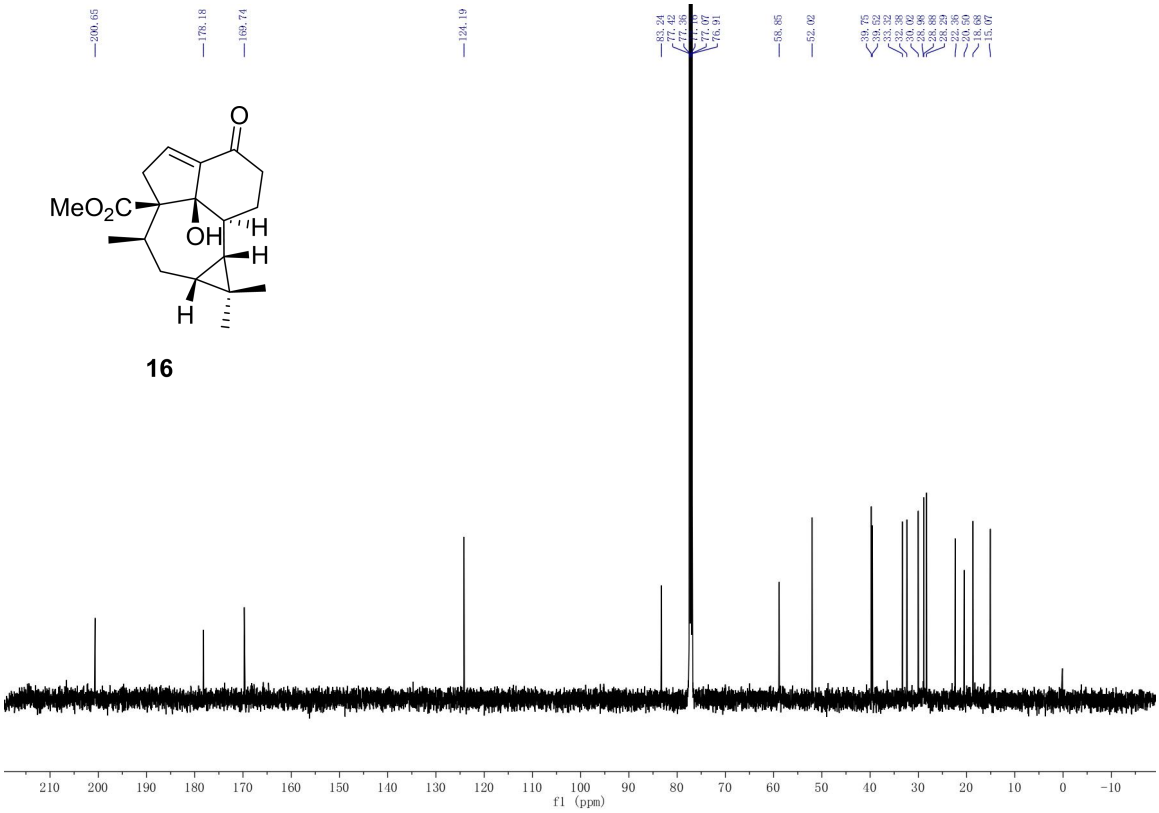
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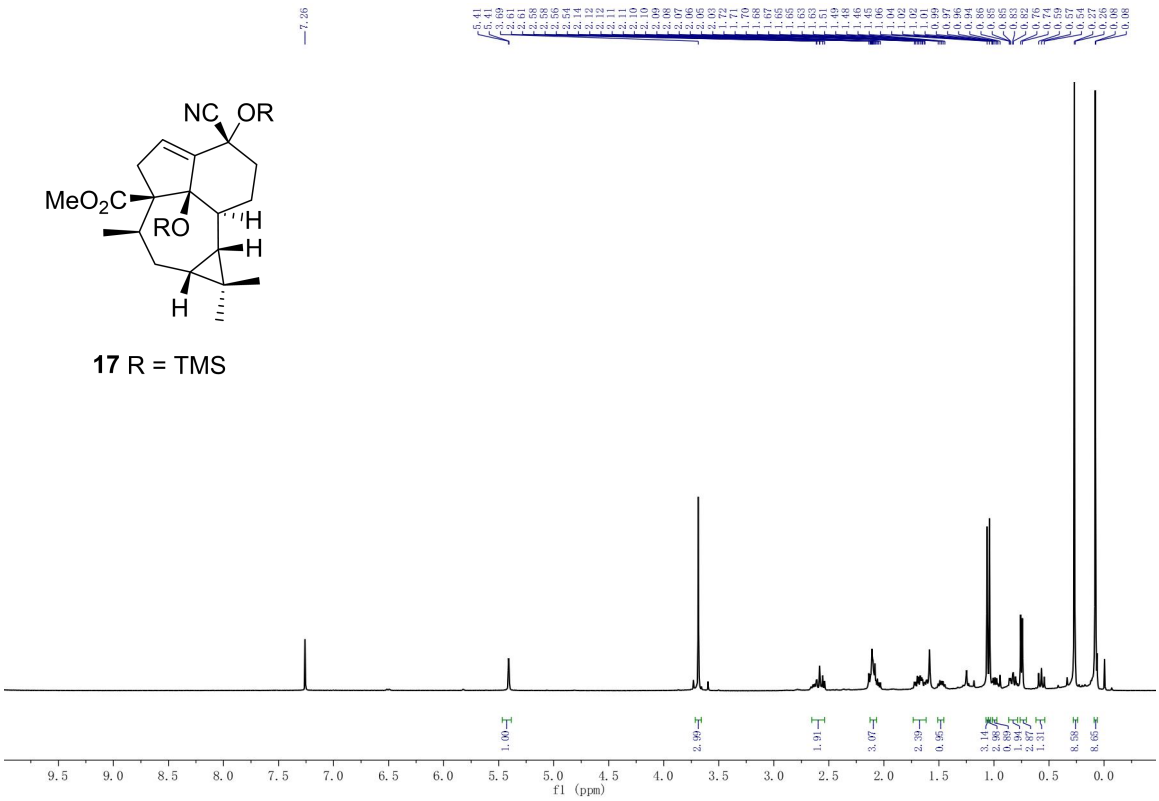
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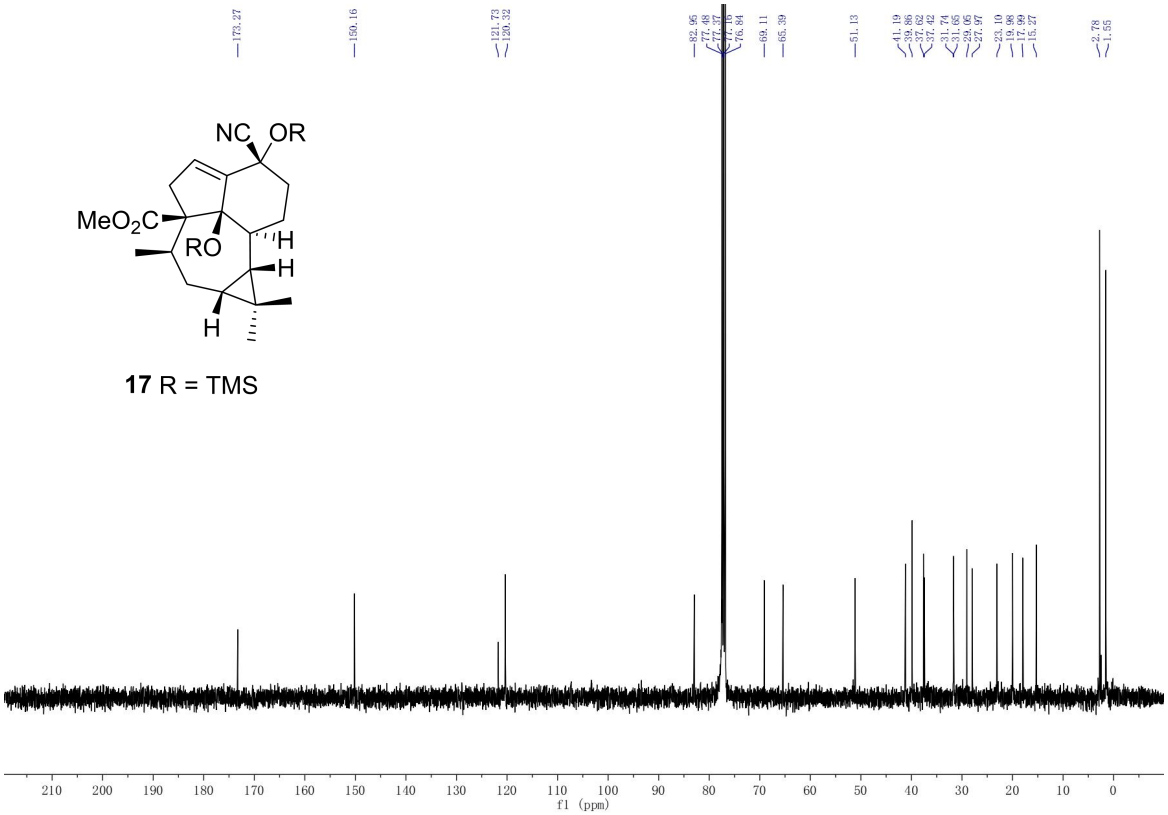
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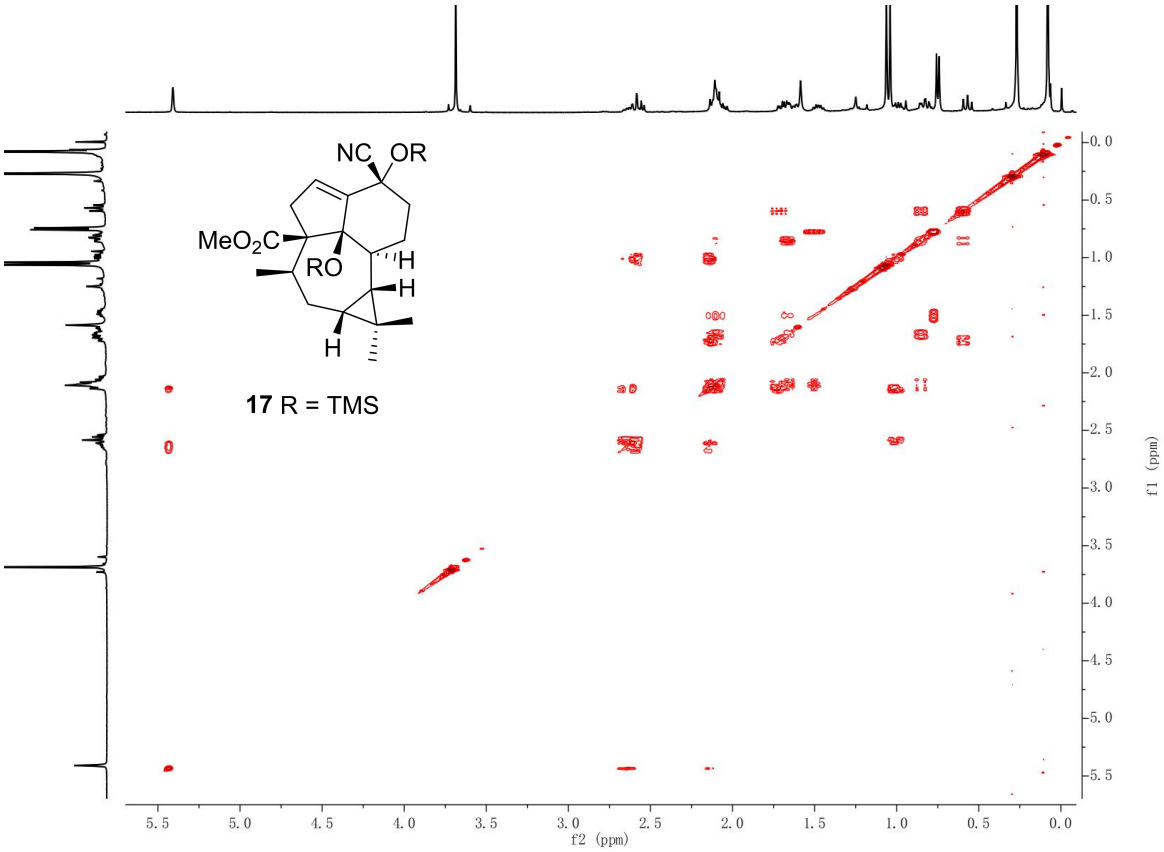
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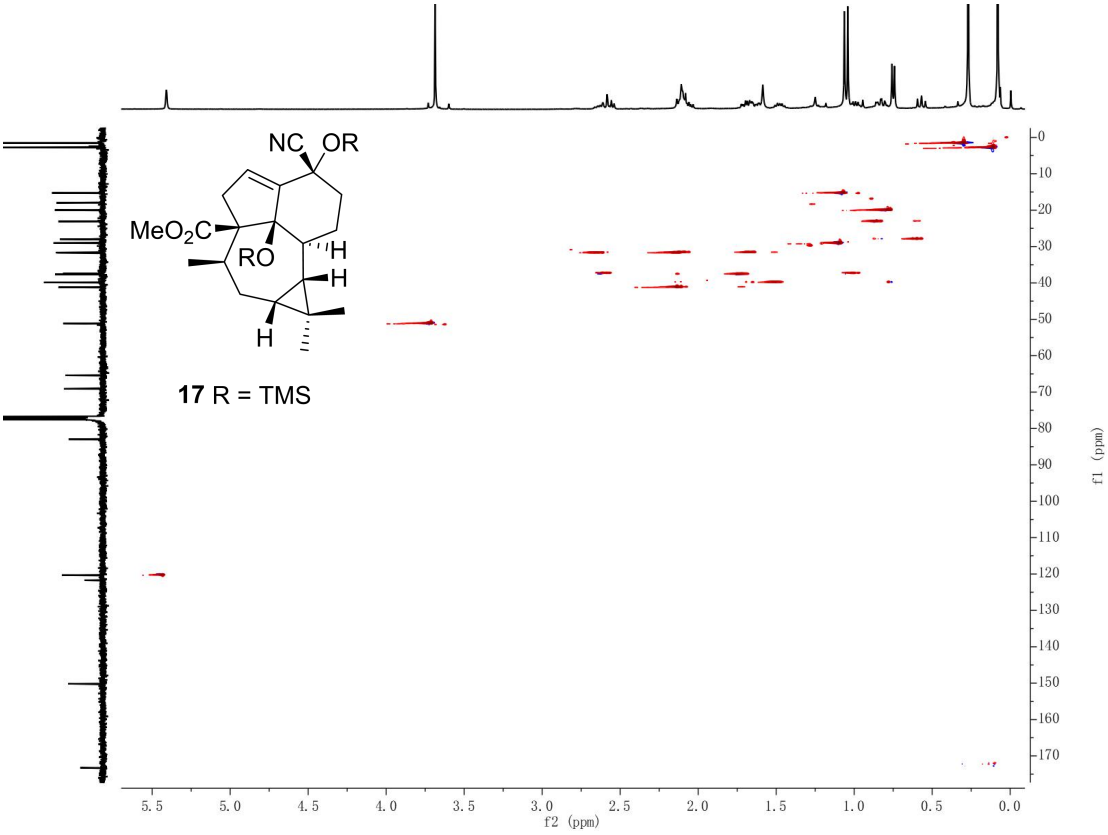
f1 (ppm)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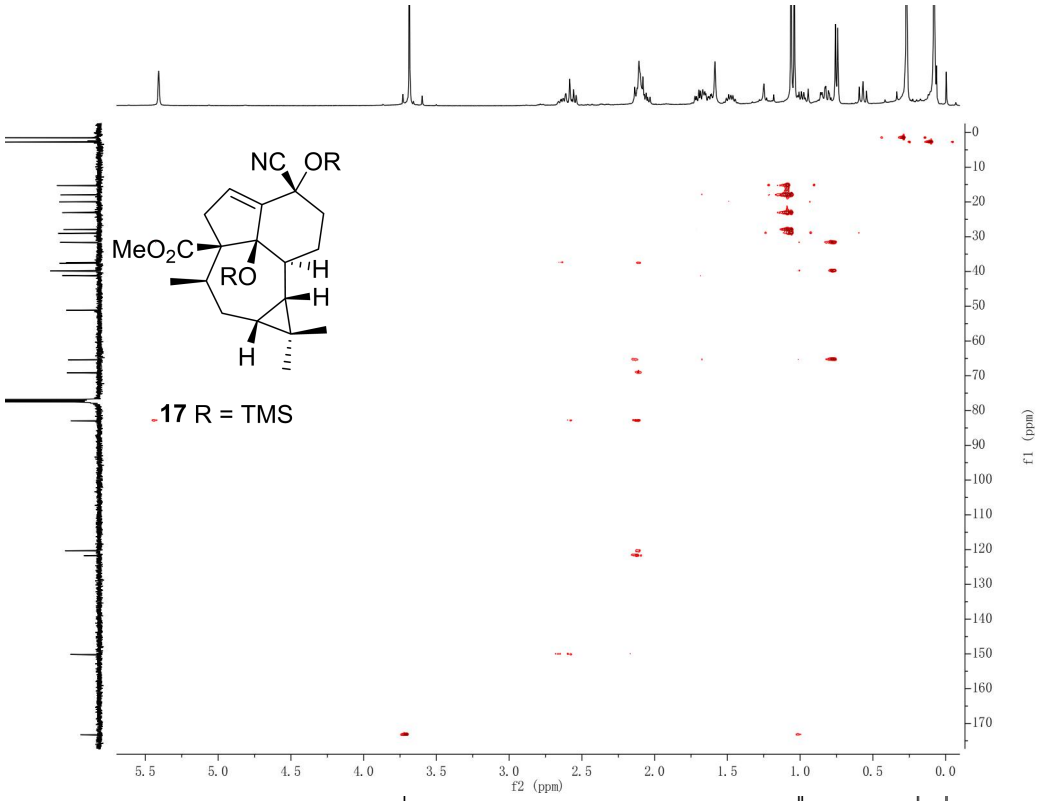
f1 (ppm)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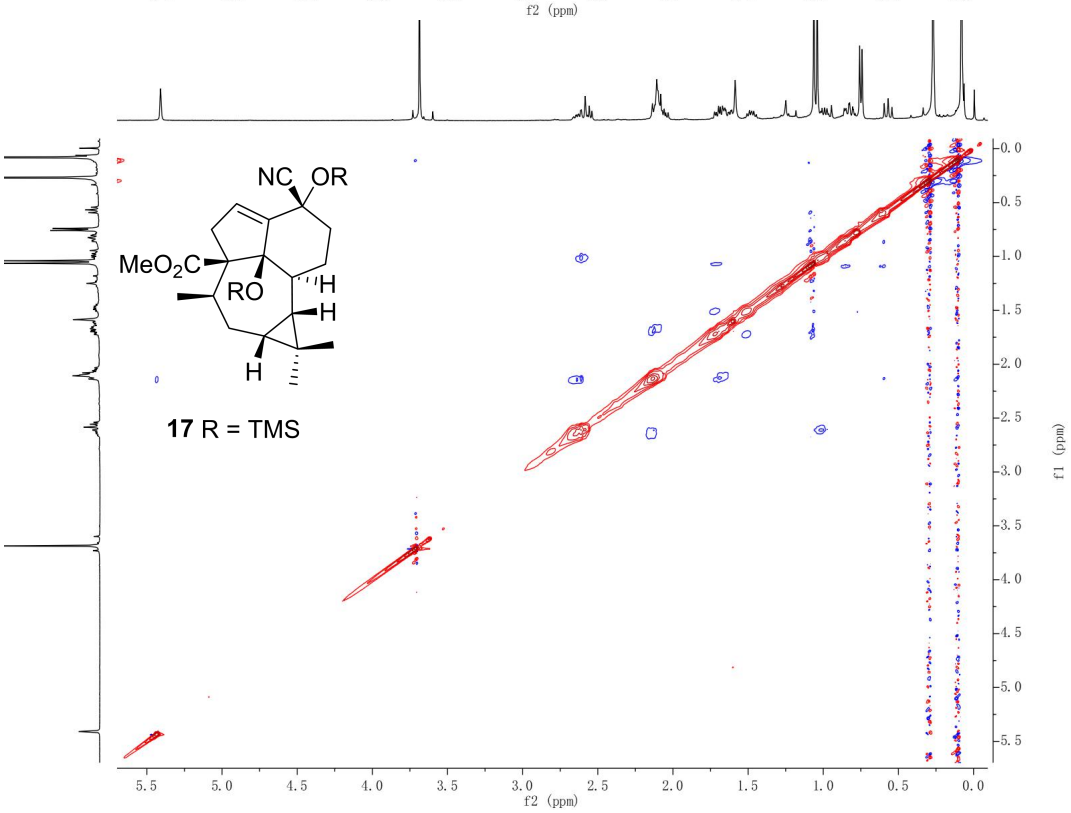
f1 (ppm)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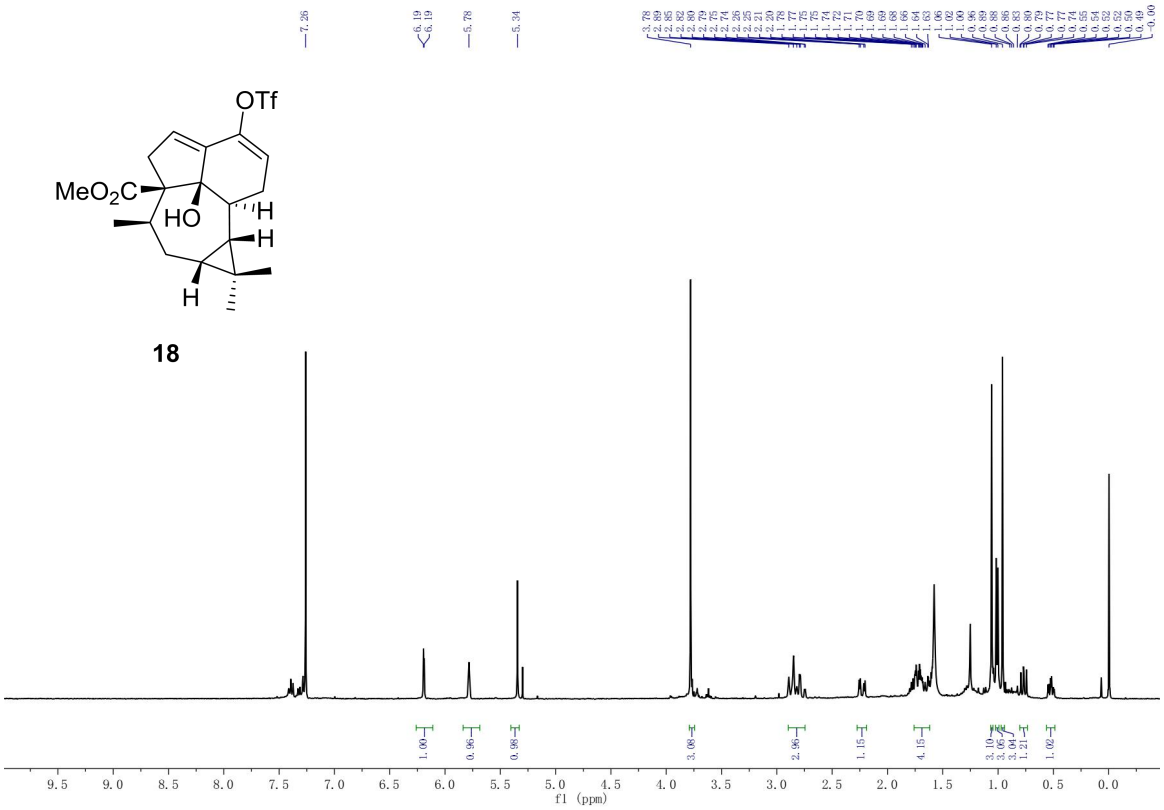
f1 (ppm)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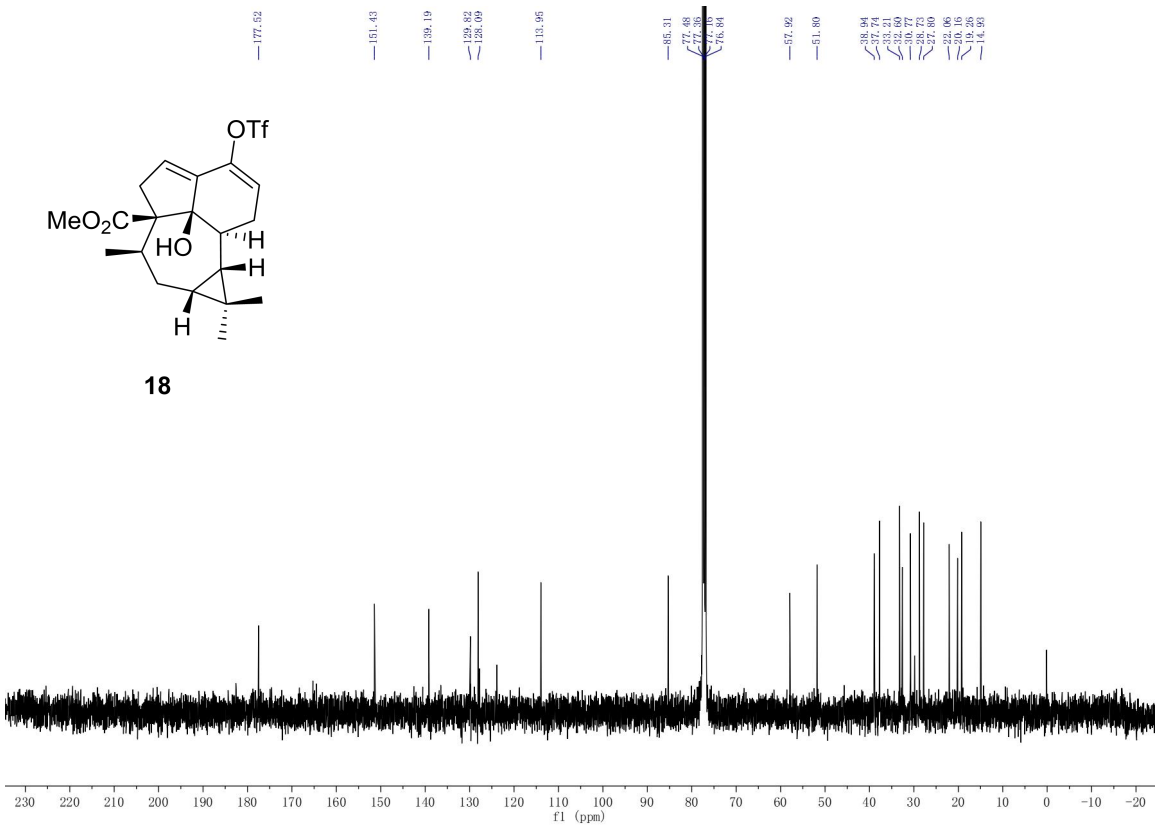
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X-ray molecular structure of 15

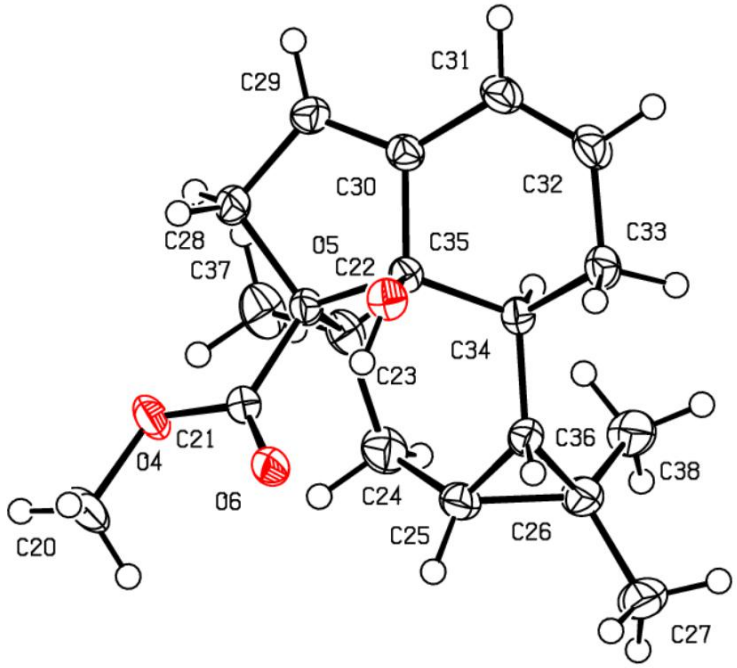

Table 1 Crystal data and structure refinement for 15

Identification code	1963179
Empirical formula	$C_{19}H_{26}O_3$
Formula weight	302.40
Temperature/K	100
Crystal system	monoclinic
Space group	C2
a/Å	17.2464(6)
b/Å	7.0762(2)
c/Å	28.1700(10)
α/°	90
β/°	103.5910(10)
γ/°	90

Volume/Å^3	3341.57(19)
Z	8
ρ_{calc}g/cm^3	1.202
μ/mm^{-1}	0.631
F(000)	1312.0
Crystal size/mm^3	0.4 × 0.35 × 0.29
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.69 to 136.938
Index ranges	$-20 \leq h \leq 19$, $-8 \leq k \leq 8$, $-33 \leq l \leq 33$
Reflections collected	17171
Independent reflections	6095 [R_{int} = 0.0309, R_{sigma} = 0.0361]
Data/restraints/parameters	6095/1/408
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0513, wR_2 = 0.1369
Final R indexes [all data]	R_1 = 0.0526, wR_2 = 0.1384
Largest diff. peak/hole / e Å^{-3}	0.20/-0.21
Flack parameter	-0.1(2)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 15. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	6938.6(12)	3793(4)	423.2(9)	44.4(6)
O2	5970.7(13)	1762(3)	482.0(8)	35.5(5)
O3	4629.4(11)	3621(3)	515.3(7)	26.4(4)
O4	3088.8(13)	6644(3)	4653.2(8)	32.4(5)

O5	5327.1(11)	6362(3)	4404.4(7)	24.1(4)
O6	4038.6(12)	4612(3)	4566.4(7)	27.9(4)
C1	7225(2)	2390(7)	132.7(14)	52.5(11)
C2	6277.4(17)	3291(5)	569.2(11)	32.0(7)
C3	5997.8(17)	4900(5)	848.8(11)	31.6(7)
C4	5121.3(15)	4623(4)	916.4(10)	23.8(6)
C5	5024.0(15)	3800(4)	1402.5(9)	23.5(6)
C6	5390(2)	1887(4)	1518.0(10)	35.3(7)
C7	5856(3)	1356(6)	2026.6(12)	56.6(12)
C8	5971(3)	2790(7)	2434.4(12)	57.3(12)
C9	6593.0(19)	5118(7)	1361.1(14)	52.8(11)
C10	6868(2)	3232(8)	1603.3(15)	66.5(15)
C11	6287(3)	1639(7)	1617.3(12)	56.6(12)
C12	4130.9(17)	3788(5)	1395.3(11)	34.5(7)
C13	3764(2)	5683(7)	1275.8(12)	46.4(10)
C14	4078(2)	6998(6)	1040.6(12)	46.0(9)
C15	4801(2)	6626(5)	873.2(11)	34.7(7)
C16	5233(3)	7751(5)	658.0(15)	53.9(11)
C17	5913(3)	6722(5)	532.6(15)	49.2(10)
C18	5769(5)	-633(7)	2194.7(15)	97(2)
C19	7344(3)	6302(11)	1358(2)	96(2)
C20	2805(2)	5213(5)	4938.7(15)	43.8(9)
C21	3723.1(16)	6147(4)	4483.4(10)	23.2(6)
C22	3954.3(15)	7735(4)	4178.0(9)	21.2(6)
C23	3267.3(15)	7961(4)	3703.0(10)	26.3(6)
C24	2933.7(18)	6033(5)	3491.7(12)	34.5(7)

C25	3484.5(17)	4422(4)	3433.3(10)	28.3(6)
C26	3781.8(19)	4118(4)	2972.8(10)	30.7(7)
C27	3807(3)	2098(5)	2804.2(12)	43.1(8)
C28	4110.2(17)	9562(4)	4493.5(10)	25.5(6)
C29	4762.3(18)	10537(4)	4316.3(10)	25.6(6)
C30	5115.1(16)	9388(4)	4058.7(9)	21.9(6)
C31	5782.6(16)	9729(4)	3831.9(10)	27.3(6)
C32	6016.1(16)	8413(5)	3558.4(10)	29.6(6)
C33	5606.0(16)	6538(4)	3452.9(10)	26.4(6)
C34	4754.6(15)	6578(4)	3527.1(9)	20.1(5)
C35	4777.9(15)	7408(4)	4035.2(9)	18.7(5)
C36	4364.0(16)	4667(4)	3446.3(9)	22.9(5)
C37	2557.9(18)	9184(5)	3755.1(12)	37.3(7)
C38	3561(2)	5531(5)	2562.9(11)	36.1(7)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 15. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	25.2(10)	66.2(17)	45.3(13)	-20.4(12)	15.3(9)	-2.6(11)
O2	37.1(12)	32.0(12)	37.9(11)	-8.5(9)	9.8(9)	6.1(10)
O3	23.7(9)	31.8(11)	22.8(9)	-1.2(8)	4.2(7)	-0.6(8)
O4	36.4(11)	29.1(11)	40.2(11)	6.2(9)	26.0(9)	1.6(9)
O5	24.2(9)	24.9(10)	22.1(9)	4.1(7)	3.6(7)	3.8(8)
O6	36.9(11)	21.4(10)	29.5(10)	2.7(8)	16.1(8)	0.0(8)
C1	34.9(17)	80(3)	46(2)	-16.9(19)	15.0(15)	16.2(19)
C2	21.8(13)	42.3(19)	32.6(15)	-11.5(13)	7.6(11)	1.4(13)

C3	26.5(14)	32.7(16)	39.4(16)	-13.9(13)	15.5(12)	-7.7(12)
C4	20.8(12)	24.7(14)	26.1(13)	-2.5(11)	6.0(10)	-0.2(11)
C5	22.1(13)	24.9(14)	22.0(12)	-2.0(10)	2.2(10)	-1.4(11)
C6	54(2)	27.3(15)	21.3(14)	-3.2(11)	2.0(13)	5.4(14)
C7	93(3)	46(2)	24.1(15)	-1.7(15)	-0.3(17)	39(2)
C8	71(3)	64(3)	25.2(16)	-11.6(16)	-11.4(16)	38(2)
C9	22.7(15)	85(3)	52(2)	-40(2)	10.6(14)	-14.2(18)
C10	29.3(18)	113(4)	49(2)	-28(2)	-7.7(16)	28(2)
C11	67(3)	67(3)	28.6(17)	-7.2(17)	-3.4(16)	48(2)
C12	23.9(14)	56(2)	24.5(14)	-0.5(13)	7.1(11)	-5.2(14)
C13	28.3(16)	83(3)	28.2(15)	2.8(17)	7.8(13)	22.5(17)
C14	51(2)	55(2)	32.3(16)	4.5(15)	10.9(15)	34.0(18)
C15	46.7(18)	28.6(16)	32.1(15)	1.0(13)	16.1(13)	9.4(14)
C16	100(3)	21.8(16)	53(2)	-2.1(15)	44(2)	1.6(18)
C17	70(2)	31.0(18)	61(2)	-15.3(17)	46(2)	-21.1(18)
C18	206(7)	51(3)	30.3(19)	8.3(19)	17(3)	58(4)
C19	41(2)	170(6)	87(3)	-84(4)	35(2)	-56(3)
C20	53(2)	34.4(17)	57(2)	8.1(15)	38.8(18)	-5.1(16)
C21	26.6(13)	22.1(13)	23.3(12)	-1.3(10)	10.7(10)	-1.4(11)
C22	23.1(13)	19.9(13)	23.0(12)	0.6(10)	10.4(10)	1.7(10)
C23	19.1(12)	32.2(15)	28.8(14)	5.4(11)	8.1(11)	4.0(11)
C24	22.3(14)	45.0(18)	36.2(15)	-5.3(14)	6.8(12)	-8.0(13)
C25	31.6(14)	29.1(15)	24.4(13)	-1.6(11)	7.3(11)	-10.0(12)
C26	38.3(16)	30.1(16)	23.1(13)	-2.7(11)	6.2(11)	-9.5(13)
C27	67(2)	31.4(18)	31.6(16)	-7.2(13)	13.0(15)	-14.9(16)
C28	31.7(14)	19.9(13)	28.5(13)	0.0(11)	14.6(11)	3.6(11)

C29	33.6(15)	19.1(13)	24.8(12)	0.5(10)	8.4(11)	-0.2(11)
C30	22.9(12)	22.4(14)	20.0(12)	1.5(10)	4.2(10)	-2.1(10)
C31	23.5(13)	30.4(14)	28.3(13)	-0.1(11)	7.0(10)	-7.8(12)
C32	22.2(13)	38.5(17)	30.7(14)	-0.8(12)	11.3(11)	-5.3(12)
C33	23.8(13)	29.5(15)	29.0(13)	-1.2(11)	12.1(11)	2.5(12)
C34	20.4(12)	21.2(13)	19.6(12)	0.7(10)	6.4(9)	1.5(10)
C35	17.5(11)	19.6(12)	19.3(12)	1.2(9)	4.7(9)	1.2(9)
C36	27.9(13)	21.5(12)	20.0(12)	-1.4(10)	7.1(10)	-0.1(11)
C37	23.8(14)	46.5(19)	43.9(17)	7.2(15)	12.5(12)	10.7(14)
C38	44.3(18)	37.3(17)	23.2(13)	-0.5(12)	0.9(12)	-6.7(14)

Table 4 Bond Lengths for 15.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C1	1.445(4)	C13	C14	1.330(6)
O1	C2	1.347(4)	C14	C15	1.457(5)
O2	C2	1.204(4)	C15	C16	1.329(5)
O3	C4	1.431(3)	C16	C17	1.493(6)
O4	C20	1.448(4)	C21	C22	1.524(4)
O4	C21	1.340(3)	C22	C23	1.573(4)
O5	C35	1.436(3)	C22	C28	1.556(4)
O6	C21	1.213(4)	C22	C35	1.582(3)
C2	C3	1.525(4)	C23	C24	1.544(4)
C3	C4	1.579(4)	C23	C37	1.533(4)
C3	C9	1.570(5)	C24	C25	1.518(5)
C3	C17	1.554(5)	C25	C26	1.518(4)

C4	C5	1.533(4)	C25	C36	1.519(4)
C4	C15	1.516(4)	C26	C27	1.511(4)
C5	C6	1.497(4)	C26	C36	1.519(4)
C5	C12	1.536(4)	C26	C38	1.507(4)
C6	C7	1.516(4)	C28	C29	1.501(4)
C6	C11	1.517(5)	C29	C30	1.329(4)
C7	C8	1.511(5)	C30	C31	1.462(4)
C7	C11	1.525(6)	C30	C35	1.512(4)
C7	C18	1.503(7)	C31	C32	1.330(4)
C9	C10	1.523(7)	C32	C33	1.500(4)
C9	C19	1.544(6)	C33	C34	1.531(3)
C10	C11	1.515(8)	C34	C35	1.539(3)
C12	C13	1.487(5)	C34	C36	1.504(4)

Table 5 Bond Angles for 15.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	O1	C1	114.7(3)	C16	C17	C3	104.0(3)
C21	O4	C20	115.2(2)	O4	C21	C22	110.6(2)
O1	C2	C3	110.7(3)	O6	C21	O4	122.2(2)
O2	C2	O1	122.5(3)	O6	C21	C22	127.2(2)
O2	C2	C3	126.8(3)	C21	C22	C23	108.1(2)
C2	C3	C4	113.4(2)	C21	C22	C28	108.9(2)
C2	C3	C9	109.3(3)	C21	C22	C35	113.9(2)
C2	C3	C17	108.8(3)	C23	C22	C35	109.9(2)
C9	C3	C4	109.8(2)	C28	C22	C23	113.3(2)
C17	C3	C4	102.0(3)	C28	C22	C35	102.8(2)

C17	C3	C9	113.5(3)	C24	C23	C22	112.1(2)
O3	C4	C3	111.9(2)	C37	C23	C22	115.7(2)
O3	C4	C5	110.3(2)	C37	C23	C24	107.6(2)
O3	C4	C15	105.2(2)	C25	C24	C23	121.3(2)
C5	C4	C3	117.6(2)	C24	C25	C26	123.0(3)
C15	C4	C3	102.4(2)	C24	C25	C36	124.0(2)
C15	C4	C5	108.2(2)	C26	C25	C36	60.05(18)
C4	C5	C12	108.1(2)	C25	C26	C36	59.99(17)
C6	C5	C4	114.1(2)	C27	C26	C25	116.3(3)
C6	C5	C12	111.6(3)	C27	C26	C36	117.1(3)
C5	C6	C7	122.1(3)	C38	C26	C25	119.0(3)
C5	C6	C11	120.3(3)	C38	C26	C27	114.1(3)
C7	C6	C11	60.4(3)	C38	C26	C36	119.9(3)
C6	C7	C11	59.8(2)	C29	C28	C22	103.6(2)
C8	C7	C6	119.9(3)	C30	C29	C28	112.0(2)
C8	C7	C11	119.1(4)	C29	C30	C31	130.3(3)
C18	C7	C6	117.4(4)	C29	C30	C35	111.7(2)
C18	C7	C8	113.2(3)	C31	C30	C35	117.9(2)
C18	C7	C11	117.6(4)	C32	C31	C30	121.0(3)
C10	C9	C3	113.2(3)	C31	C32	C33	122.8(2)
C10	C9	C19	107.7(4)	C32	C33	C34	112.3(2)
C19	C9	C3	114.6(4)	C33	C34	C35	108.5(2)
C11	C10	C9	121.7(3)	C36	C34	C33	111.9(2)
C6	C11	C7	59.8(3)	C36	C34	C35	113.4(2)
C10	C11	C6	124.1(3)	O5	C35	C22	111.71(19)
C10	C11	C7	124.1(3)	O5	C35	C30	105.3(2)

C13	C12	C5	111.7(3)	O5	C35	C34	110.2(2)
C14	C13	C12	122.8(3)	C30	C35	C22	102.3(2)
C13	C14	C15	121.0(3)	C30	C35	C34	108.6(2)
C14	C15	C4	117.8(3)	C34	C35	C22	117.6(2)
C16	C15	C4	111.4(3)	C25	C36	C26	59.96(18)
C16	C15	C14	130.8(3)	C34	C36	C25	121.0(2)
C15	C16	C17	111.8(3)	C34	C36	C26	122.9(2)

Table 6 Torsion Angles for 15.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C2	C3	C4	165.6(3)	C17	C3	C4	C15	-27.1(3)
O1	C2	C3	C9	-71.5(4)	C17	C3	C9	C10	-162.5(3)
O1	C2	C3	C17	52.8(3)	C17	C3	C9	C19	-38.4(5)
O2	C2	C3	C4	-14.4(5)	C18	C7	C11	C6	107.2(5)
O2	C2	C3	C9	108.4(4)	C18	C7	C11	C10	-139.8(5)
O2	C2	C3	C17	-127.2(4)	C19	C9	C10	C11	-173.1(3)
O3	C4	C5	C6	71.1(3)	C20	O4	C21	O6	-0.5(4)
O3	C4	C5	C12	-53.7(3)	C20	O4	C21	C22	178.4(3)
O3	C4	C15	C14	78.4(3)	C21	C22	C23	C24	-40.1(3)
O3	C4	C15	C16	-98.5(3)	C21	C22	C23	C37	83.7(3)
O4	C21	C22	C23	-67.0(3)	C21	C22	C28	C29	146.4(2)
O4	C21	C22	C28	56.4(3)	C21	C22	C35	O5	-31.6(3)
O4	C21	C22	C35	170.5(2)	C21	C22	C35	C30	-143.8(2)
O6	C21	C22	C23	111.8(3)	C21	C22	C35	C34	97.3(3)
O6	C21	C22	C28	-124.7(3)	C22	C23	C24	C25	-46.5(4)
O6	C21	C22	C35	-10.6(4)	C22	C28	C29	C30	-15.5(3)

C1	O1	C2	O2	3.1(5)	C23	C22	C28	C29	-93.3(3)
C1	O1	C2	C3	-176.9(3)	C23	C22	C35	O5	-153.1(2)
C2	C3	C4	O3	-31.7(4)	C23	C22	C35	C30	94.7(2)
C2	C3	C4	C5	97.6(3)	C23	C22	C35	C34	-24.2(3)
C2	C3	C4	C15	-143.9(3)	C23	C24	C25	C26	-90.1(3)
C2	C3	C9	C10	-41.0(4)	C23	C24	C25	C36	-16.4(4)
C2	C3	C9	C19	83.1(5)	C24	C25	C26	C27	-139.2(3)
C2	C3	C17	C16	146.9(3)	C24	C25	C26	C36	113.2(3)
C3	C4	C5	C6	-58.9(3)	C24	C25	C26	C38	3.5(4)
C3	C4	C5	C12	176.3(2)	C24	C25	C36	C26	-111.7(3)
C3	C4	C15	C14	-164.5(3)	C24	C25	C36	C34	0.8(4)
C3	C4	C15	C16	18.6(4)	C25	C26	C36	C34	-109.6(3)
C3	C9	C10	C11	-45.3(5)	C26	C25	C36	C34	112.5(3)
C4	C3	C9	C10	84.0(3)	C27	C26	C36	C25	-106.2(3)
C4	C3	C9	C19	-151.9(4)	C27	C26	C36	C34	144.2(3)
C4	C3	C17	C16	26.8(3)	C28	C22	C23	C24	-160.9(2)
C4	C5	C6	C7	138.2(4)	C28	C22	C23	C37	-37.0(3)
C4	C5	C6	C11	66.1(3)	C28	C22	C35	O5	86.0(2)
C4	C5	C12	C13	-53.2(3)	C28	C22	C35	C30	-26.2(2)
C4	C15	C16	C17	-1.2(5)	C28	C22	C35	C34	-145.1(2)
C5	C4	C15	C14	-39.6(4)	C28	C29	C30	C31	-178.2(3)
C5	C4	C15	C16	143.5(3)	C28	C29	C30	C35	-2.2(3)
C5	C6	C7	C8	-0.8(6)	C29	C30	C31	C32	-175.4(3)
C5	C6	C7	C11	-109.2(4)	C29	C30	C35	O5	-98.4(2)
C5	C6	C7	C18	143.3(4)	C29	C30	C35	C22	18.5(3)
C5	C6	C11	C7	112.1(3)	C29	C30	C35	C34	143.5(2)

C5	C6	C11	C10	-0.7(5)	C30	C31	C32	C33	1.7(4)
C5	C12	C13	C14	22.1(4)	C31	C30	C35	O5	78.1(3)
C6	C5	C12	C13	-179.4(2)	C31	C30	C35	C22	-165.0(2)
C6	C7	C11	C10	112.9(4)	C31	C30	C35	C34	-39.9(3)
C7	C6	C11	C10	-112.8(4)	C31	C32	C33	C34	20.7(4)
C8	C7	C11	C6	-109.6(4)	C32	C33	C34	C35	-51.2(3)
C8	C7	C11	C10	3.3(5)	C32	C33	C34	C36	-177.0(2)
C9	C3	C4	O3	-154.2(3)	C33	C34	C35	O5	-55.0(3)
C9	C3	C4	C5	-25.0(4)	C33	C34	C35	C22	175.4(2)
C9	C3	C4	C15	93.5(3)	C33	C34	C35	C30	60.0(3)
C9	C3	C17	C16	-91.2(4)	C33	C34	C36	C25	-171.8(2)
C9	C10	C11	C6	-16.3(5)	C33	C34	C36	C26	-99.6(3)
C9	C10	C11	C7	-90.3(4)	C35	C22	C23	C24	84.8(3)
C11	C6	C7	C8	108.3(5)	C35	C22	C23	C37	-151.4(2)
C11	C6	C7	C18	-107.6(5)	C35	C22	C28	C29	25.3(2)
C12	C5	C6	C7	-98.9(4)	C35	C30	C31	C32	8.8(4)
C12	C5	C6	C11	-171.0(3)	C35	C34	C36	C25	65.1(3)
C12	C13	C14	C15	1.7(5)	C35	C34	C36	C26	137.3(3)
C13	C14	C15	C4	7.8(5)	C36	C25	C26	C27	107.5(3)
C13	C14	C15	C16	-176.0(4)	C36	C25	C26	C38	-109.8(3)
C14	C15	C16	C17	-177.6(4)	C36	C34	C35	O5	70.0(3)
C15	C4	C5	C6	-174.2(3)	C36	C34	C35	C22	-59.7(3)
C15	C4	C5	C12	61.0(3)	C36	C34	C35	C30	-175.1(2)
C15	C16	C17	C3	-17.1(5)	C37	C23	C24	C25	-174.8(3)
C17	C3	C4	O3	85.1(3)	C38	C26	C36	C25	108.3(3)
C17	C3	C4	C5	-145.6(3)	C38	C26	C36	C34	-1.3(4)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 15.

Atom	*x*	*y*	*z*	U(eq)
H3	4865.62	2635.88	460.44	40
H5A	5093.22	5422.7	4488.51	36
H1A	7324.56	1201.53	315.36	79
H1B	7721.23	2834.31	58.12	79
H1C	6822.8	2184.33	-172.32	79
H5	5293.72	4679.74	1668.11	28
H6	5075.04	827.71	1330.71	42
H8A	5482.68	2877.46	2554.06	86
H8B	6090.42	4027.06	2312.03	86
H8C	6415.26	2396.96	2701.83	86
H9	6299.09	5788.9	1577.61	63
H10A	7277.01	2728.7	1442.7	80
H10B	7142.79	3509.61	1946	80
H11	6447.57	421.58	1487.23	68
H12A	3854.45	2860.69	1150.13	41
H12B	4059.91	3384.96	1718.95	41
H13	3283.91	5965.76	1371.52	56
H14	3827.77	8198.84	980.78	55
H16	5121.29	9052.25	592.04	65
H17A	6407.42	7487.2	616.33	59
H17B	5794.71	6408.45	180.43	59

H18A	6266.08	-1024.87	2420.66	146
H18B	5654.47	-1481.1	1911.79	146
H18C	5330.49	-688.69	2361.11	146
H19A	7715.42	6229.06	1679.63	144
H19B	7190.53	7621.4	1283.42	144
H19C	7603.09	5805.77	1109.43	144
H20A	2632.71	4097.3	4735.04	66
H20B	2353.52	5713.42	5055.88	66
H20C	3235.5	4859.69	5218.48	66
H23	3506.97	8579.64	3451.91	32
H24A	2586.04	5561.37	3699.85	41
H24B	2583.85	6280.72	3165.18	41
H25	3363.91	3216.5	3586.73	34
H27A	3268.82	1692.02	2637.79	65
H27B	4010.16	1281.67	3087.21	65
H27C	4159.85	2009.05	2578.26	65
H28A	3625.36	10357.84	4439.69	31
H28B	4284.63	9252.47	4845.23	31
H29	4905.74	11824.12	4380.74	31
H31	6053.47	10907.58	3880.55	33
H32	6461.35	8671.66	3424.21	36
H33A	5918.16	5568.79	3670.06	32
H33B	5589.57	6173.26	3111.39	32
H34	4436.23	7460.6	3278.77	24
H36	4709.15	3605.26	3608.65	27
H37A	2161.73	9223.12	3442.49	56

H37B	2743.3	10468.95	3850.24	56
H37C	2315.38	8641.66	4005.93	56
H38A	3493.65	6780.7	2697.76	54
H38B	3060.25	5145.54	2339.59	54
H38C	3985.02	5585.33	2384.95	54