Desymmetrization of cyclic 1,3-diketones via Ir-catalyzed hydrogenation: an efficient approach to cyclic hydroxy ketones with a chiral quaternary carbon

[Electronic supplementary information]

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Contents

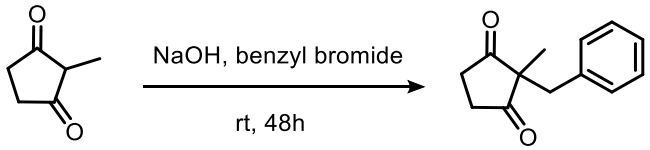
1. General remarks.

All the reactions dealing with air- or moisture- sensitive compounds were carried out in a dry reaction vessel under an argon atmosphere or in an argon-filled glove box. Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers without further purification. Toluene was dried with sodium chips and indicated by benzophenone. Other anhydrous solvents were purchased from J&K Chemical and degassed by bubbling argon over a period of 30 min. Purification of products was carried out by flash chromatography using silica gel (200-300 mesh). Thin layer chromatography was carried out using silica gel plates from Merck (GF254). $[Ir(COD)Cl]_2$ and other metal precursors were purchased from Heraeus.

^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker Avance 400 MHz or a Bruker Avance 600 MHz spectrometer with tetramethylsilane as the internal standard. Chemical shifts are reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to the $CDCl_3$ at 7.27 ppm for ^{1}H NMR or 77.0 ppm for ^{13}C NMR. Data are reported as: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in hertz (Hz) and signal area integration in natural numbers. ^{13}C NMR and ^{31}P NMR analyses were recorded with ^{1}H decoupling. Enantiomeric excess values were determined with Agilent 1290 Series HPLC instrument or Agilent 7980B Series GC instrument on a chiral stationary phase. Optical rotations were measured using a 1 mL cell with a 1 dm path length on a Rudolph Autopol I polarimeter at 589 nm.

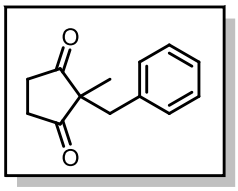
2. Preparation of cyclic diketone substrates.

General method of synthesis of alkane 1,3-diones.



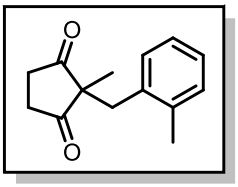
2-Methyl cyclopentane-1,3-dione (1.0 equiv.) was stirred with 1 M aq. NaOH solution (1.0 equiv.) at room temperature for 10 min. To this suspension benzyl bromide was added (2.0 equiv.) at once and the resulting bi-phasic solution was stirred vigorously. After being stirred for 48 hours, the reaction mixture was diluted with EtOAc (10 mL). The aqueous phase was back-extracted with EtOAc twice (10 mL × 2). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (silica, 15% EtOAc in petroleum ether) to obtain a white solid. (Note: Reactions were performed at room temperature for all liquid alkyl bromides and the reactions with solid alkyl bromides were carried out at the temperature slightly above melting point).

2-benzyl-2-methylcyclopentane-1,3-dione (**1a**)[1]



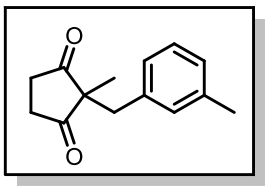
White solid. 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.16 (m, 3H), 7.05 (dd, *J* = 8.7, 6.8 Hz, 2H), 2.96 (s, 2H), 2.64 – 2.45 (m, 2H), 2.15 – 1.95 (m, 2H), 1.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.49, 135.86, 129.68, 128.67, 127.32, 58.39, 43.18, 35.92, 20.11.

2-methyl-2-(2-methylbenzyl)cyclopentane-1,3-dione (**1b**)



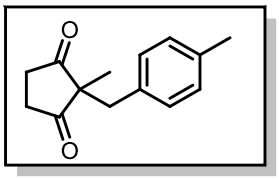
Colorless oil. 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.02 (m, 3H), 6.96 (d, *J* = 7.2 Hz, 1H), 3.03 (s, 2H), 2.61 – 2.44 (m, 2H), 2.25 (s, 3H), 2.22 – 2.06 (m, 2H), 1.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.79, 136.87, 134.36, 131.08, 129.85, 127.51, 126.14, 58.16, 40.02, 36.10, 19.96, 19.78. *m/z* (ESI–MS): calc. 217.1229 $[M+H]^+$, found 217.1223 $[M+H]^+$.

2-methyl-2-(3-methylbenzyl)cyclopentane-1,3-dione (**1c**)[2]



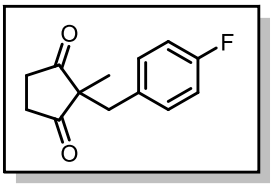
White solid. 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.03 (m, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 9.7 Hz, 2H), 2.89 (s, 2H), 2.57 – 2.44 (m, 2H), 2.25 (s, 3H), 2.12 – 1.95 (m, 2H), 1.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.57, 138.25, 135.70, 130.31, 128.52, 128.03, 126.61, 58.36, 43.29, 35.91, 21.37, 19.94. *m/z* (ESI–MS): calc. 239.1048 $[M+Na]^+$, found 239.1043 $[M+Na]^+$.

2-methyl-2-(4-methylbenzyl)cyclopentane-1,3-dione (**1d**)



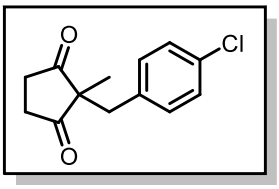
White solid. 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 7.9 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 2.91 (s, 2H), 2.61 – 2.44 (m, 2H), 2.27 (s, 3H), 2.18 – 1.97 (m, 2H), 1.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.71, 136.95, 132.72, 129.56, 129.37, 58.51, 42.99, 36.00, 21.15, 19.95. *m/z* (ESI–MS): calc. 239.1048 $[M+Na]^+$, found 239.1041 $[M+Na]^+$.

2-(4-fluorobenzyl)-2-methylcyclopentane-1,3-dione (**1e**)[2]



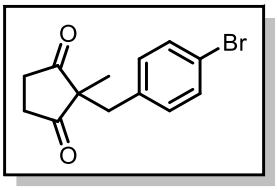
White solid. 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (dd, *J* = 8.3, 5.5 Hz, 2H), 6.91 (t, *J* = 8.5 Hz, 2H), 2.93 (s, 2H), 2.68 – 2.50 (m, 2H), 2.19 – 2.01 (m, 2H), 1.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.34, δ 161.95 (d, *J* = 246.1 Hz), 131.60 (d, *J* = 3.4 Hz), 131.26 (d, *J* = 8.0 Hz), 115.42 (d, *J* = 21.3 Hz), 58.43, 41.71, 35.87, 20.42. *m/z* (ESI–MS): calc. 221.0978 $[M+H]^+$, found 221.0972 $[M+H]^+$.

2-(4-chlorobenzyl)-2-methylcyclopentane-1,3-dione (**1f**)



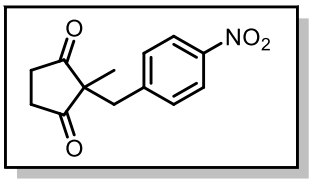
White solid. 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.15 (m, 2H), 7.01 – 6.95 (m, 2H), 2.93 (s, 2H), 2.69 – 2.52 (m, 2H), 2.22 – 2.03 (m, 2H), 1.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.10, 134.51, 133.31, 131.21, 128.83, 58.35, 41.61, 35.85, 20.59. *m/z* (ESI–MS): calc. 237.0682 $[M+H]^+$, found 237.0676 $[M+H]^+$.

2-(4-bromobenzyl)-2-methylcyclopentane-1,3-dione (**1g**)



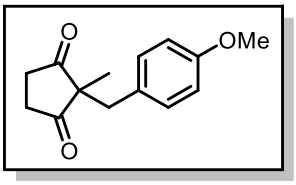
White solid. 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 6.93 – 6.87 (m, 2H), 2.90 (s, 2H), 2.69 – 2.51 (m, 2H), 2.20 – 2.03 (m, 2H), 1.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.95, 135.00, 131.75, 131.55, 121.40, 58.25, 41.57, 35.82, 20.60. *m/z* (ESI–MS): calc. 281.0177 $[M+H]^+$, found 281.0172 $[M+H]^+$.

2-methyl-2-(4-nitrobenzyl)cyclopentane-1,3-dione (**1h**)



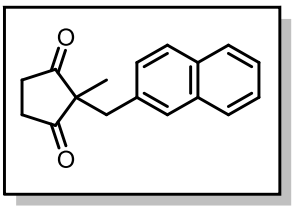
White solid. 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.05 (m, 2H), 7.31 – 7.19 (m, 2H), 3.08 (s, 2H), 2.81 – 2.62 (m, 2H), 2.31 – 2.12 (m, 2H), 1.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.97, 147.27, 143.82, 131.02, 123.75, 58.35, 40.59, 35.60, 21.43. *m/z* (ESI–MS): calc. 248.0923 $[M+H]^+$, found 248.0917 $[M+H]^+$.

2-(4-methoxybenzyl)-2-methylcyclopentane-1,3-dione (**1i**)



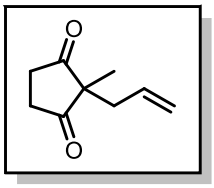
White solid. 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 – 6.86 (m, 2H), 6.81 – 6.66 (m, 2H), 3.75 (s, 3H), 2.89 (s, 2H), 2.62 – 2.43 (m, 2H), 2.19 – 1.95 (m, 2H), 1.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.82, 158.79, 130.76, 127.85, 114.02, 58.54, 55.29, 42.53, 35.98, 19.91. *m/z* (ESI–MS): calc. 255.0997 $[M+H]^+$, found 255.0991 $[M+H]^+$.

2-methyl-2-(naphthalen-2-ylmethyl)cyclopentane-1,3-dione (**1j**)



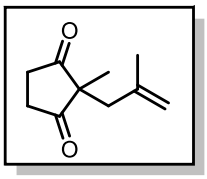
White solid. 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dt, *J* = 12.0, 6.0 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.51 (s, 1H), 7.48 – 7.40 (m, 2H), 7.16 (dd, *J* = 8.4, 1.8 Hz, 1H), 3.12 (s, 2H), 2.60 – 2.44 (m, 2H), 2.09 – 1.92 (m, 2H), 1.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.56, 133.45, 133.33, 132.45, 128.48, 128.32, 127.90, 127.79, 127.68, 126.33, 126.06, 58.54, 43.15, 35.93, 20.36.

2-allyl-2-methylcyclopentane-1,3-dione (**1k**)[3]



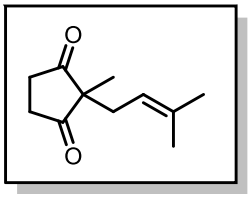
Colorless oil. 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49 – 5.34 (m, 1H), 4.94 – 4.82 (m, 2H), 2.69 – 2.45 (m, 4H), 2.15 (t, *J* = 12.5 Hz, 2H), 0.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.94, 131.41, 119.50, 77.48, 77.16, 76.84, 56.45, 39.81, 35.19, 18.48.

2-methyl-2-(2-methylallyl)cyclopentane-1,3-dione (**1l**)[4]



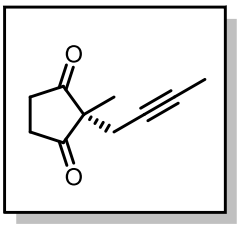
Colorless oil. 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.74 – 4.67 (s, 1H), 4.47 (s, 1H), 2.78 – 2.52 (m, 4H), 2.33 (d, *J* = 1.6 Hz, 2H), 1.54 (s, 3H), 1.10 – 0.93 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.65, 140.74, 114.97, 56.81, 43.71, 35.56, 24.02, 20.54.

2-methyl-2-(3-methylbut-2-en-1-yl)cyclopentane-1,3-dione (**1m**)[5]



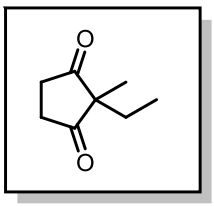
Colorless oil. 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.93 – 4.85 (m, 1H), 2.74 – 2.58 (m, 4H), 2.29 (d, *J* = 7.8 Hz, 2H), 1.63 (s, 3H), 1.54 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 216.93, 136.63, 117.11, 56.92, 35.53, 35.32, 25.84, 18.32, 17.72.

2-(but-2-yn-1-yl)-2-methylcyclopentane-1,3-dione (**1n**)[6]



Colorless oil. 85% yield (2.2g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.74 (d, *J* = 2.3 Hz, 4H), 2.33 (dd, *J* = 5.1, 2.5 Hz, 2H), 1.65 (q, *J* = 2.5 Hz, 3H), 1.03 (d, *J* = 2.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.97, 78.32, 73.48, 55.58, 35.91, 25.45, 18.79, 3.34. *m/z* (ESI–MS): calc. 165.0907 $[M+H]^+$, found 165.0910$[M+H]^+$.

2-ethyl-2-methylcyclopentane-1,3-dione (**1o**)[7]



Colorless oil. 12% yield (21.2 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.85 – 2.71 (m, 4H), 1.67 (q, *J* = 7.5 Hz, 2H), 1.10 (s, 3H), 0.85 – 0.77 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.70, 57.13, 35.25, 28.86, 18.09, 8.89. *m/z* (ESI–MS): calc. 143.1073 $[M+H]^+$, found 143.1066 $[M+H]^+$.

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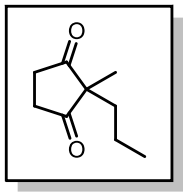
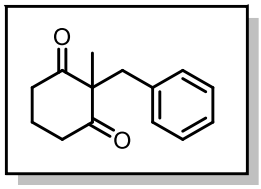
2-methyl-2-propylcyclopentane-1,3-dione (**1p**)



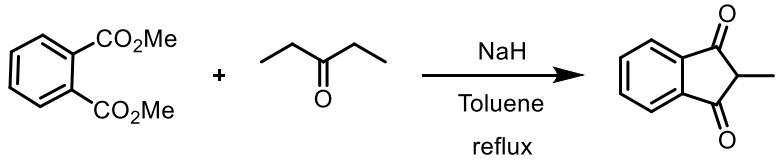
Prepared by hydrogenation of **1j**. In 10 mL Schlenk tube 200 mg of **1j** was dissolved in 2mL methanol, to which mixture 10 mg of 10% Pd/C was added in one potion. This suspension was freezed by liquid nitrogen was evacuated and back-filled with hydrogen. After warming up to room temperature, this mixture was stirred for 24 hours. LC-MS showed full conversion of the alkene moiety. The mixture was filtered through a pad of celite and the filtrate was concentrate *in vacuo* to give a colorless oil. 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.62 – 2.47 (m, 4H), 1.40 – 1.27 (m, 2H), 1.01 – 0.88 (m, 2H), 0.88 – 0.81 (m, 3H), 0.61 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.48, 56.49, 37.75, 35.00, 18.58, 17.70, 14.06.

2-benzyl-2-methylcyclohexane-1,3-dione (**1q**)



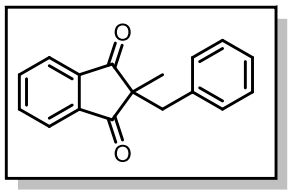
Yellow solid. 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 3H), 7.06 – 6.97 (m, 2H), 3.12 (s, 2H), 2.54 (ddd, *J* = 16.8, 7.8, 5.0 Hz, 2H), 2.31 (ddd, *J* = 16.8, 8.9, 5.2 Hz, 2H), 1.82 – 1.65 (m, 1H), 1.57 – 1.43 (m, 1H), 1.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.56, 136.72, 129.98, 128.50, 127.09, 77.48, 77.16, 76.84, 65.38, 43.95, 39.39, 22.26, 16.66.

Synthesis of 2-Methyl-1H-indene-1,3(2H)-dione



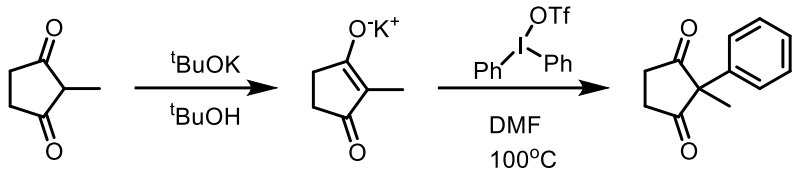
Under an atmosphere of argon NaH (1.2 g, 60% suspension in mineral oil, 30 mmol) was suspended in anhydrous toluene. 3-Pentanone (2.15 g, 25 mmol) and diethyl phthalate (4.85 g, 103 mmol) were added dropwise. The reaction mixture was stirred for 1 hour at rt and refluxed for 2 d. After cooling the solid was filtered, washed with benzene. The solid was dissolved in water and the solution was acidified with conc. HCl to obtain a yellow oil from which product crystallized as a yellow solid. The solid was filtered and dried *in vacuo* (2.48 g, 62%).

2-benzyl-2-methyl-1H-indene-1,3(2H)-dione (**1r**)[8]



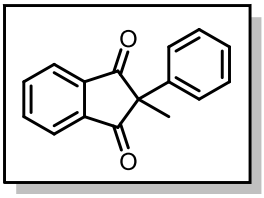
Yellow solid, 72% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (dt, *J* = 6.8, 3.4 Hz, 2H), 7.71 – 7.65 (m, 2H), 7.04 – 7.00 (m, 2H), 6.97 (dd, *J* = 10.7, 4.3 Hz, 3H), 3.15 (s, 2H), 1.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 204.14, 141.64, 135.96, 135.63, 129.83, 128.16, 126.79, 123.14, 55.98, 41.66, 20.28.

Synthesis of 2-methyl-2-phenylcyclopentane-1,3-dione



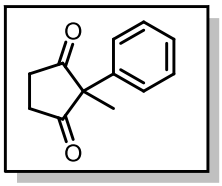
In an oven and vacuum dried round-bottom flask 2-methyl-cyclopentane-1,3-dione (100mg, 0.89 mmol, 1.0 equiv.) was taken with 8.0 mL of tert-butanol under positive argon pressure, potassium tert-butoxide (120 mg, 1.07 mmol, 1.2 equiv.) was added and the resulting suspension was stirred at r.t. for 2 h. Solvent was removed under vacuum, the residue was taken with 8.0 mL of dry DMF, diphenyliodonium triflate (920 mg, 2.14 mmol, 2.4 equiv.) was added and the resulting solution was stirred at 100 °C. After 7 h reaction mixture was cooled to r.t., quenched with 10 mL of distilled water and 15 mL of EtOAc was added. Organic phase was separated from aqueous phase, aqueous phase was back-extracted with EtOAc (2 × 10 mL). Combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The ridue was purified by silica gel column chromatography (5-7% EtOAc in petroleum ether) to obtain a colorless thick oil (61 mg, 0.324mmol, 36% yield)

2-methyl-2-phenyl-1H-indene-1,3(2H)-dione (**1s**)[9]



White solid, 34% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 2H), 7.92 – 7.84 (m, 2H), 7.38 – 7.21 (m, 5H), 1.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.08, 141.46, 137.86, 136.17, 128.95, 127.76, 126.81, 124.04, 58.06, 20.16.

2-methyl-2-phenylcyclopentane-1,3-dione (**1t**)[10]



Colorless oil, 35% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 3H), 7.22 (dd, *J* = 5.3, 3.3 Hz, 2H), 2.97 – 2.82 (m, 2H), 2.82 – 2.66 (m, 2H), 1.43 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 213.19, 137.06, 129.42, 128.10, 126.46, 62.09, 35.37, 19.89.

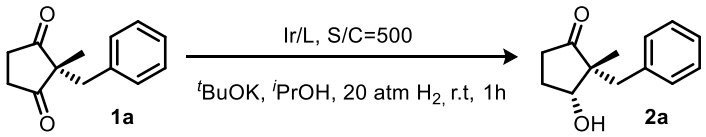
3. General procedure of desymmetrization of cyclic diketones via asymmetric hydrogenation.

Procedure of condition screening:

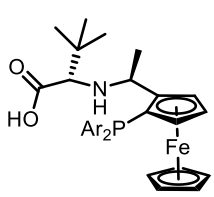
In an argon-filled glove box, a 4.0 mL vial was charged with the metal precursor $[Ir(COD)Cl]_2$ (3.4 mg, 5.0×10^{-3} mmol), ligand (10.5×10^{-3} mmol) and anhydrous ^{i}PrOH (1.0 mL). The mixture (0.010 M) was stirred for 1.0 h at 25 ^{o}C, giving an orange-red solution. The resulting solution (10 μL) and a solution of ^{t}BuOK in ^{i}PrOH (10 μL, c = 0.10 M) transferred by a syringe into a 5.0 mL vial charged with cyclic diketone (0.1 mmol) in 1.0 mL anhydrous solvent. The vial was transferred to an autoclave, which was then pressurized with 20 atm of H_2 and stirred at room temperature for the indicated period of time. The hydrogen gas was released slowly in a well-ventilated hood and the solution was passed through a short column of silica gel to remove the metal complex. The crude product was analyzed by HPLC for ee and dr values.

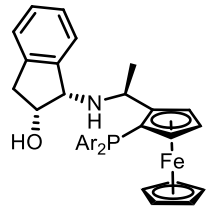
Detailed condition screening:

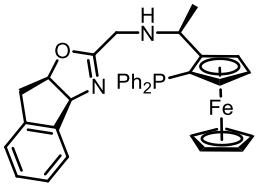
Table S1. Screening of ligands.



entry	ligand	conversion (%)	ee (%)	dr(%)
1	f-amphox	24	93	88:12
2	indan-f-amphox	11	28	76:14
3	f-amphol	50	37	81:19
4	f-ampha	84	95	91:9


f-ampha


f-amphol


indan-f-amphox

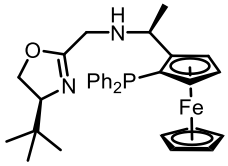
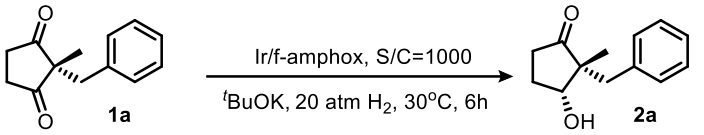
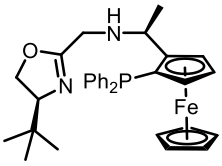

f-amphox

Table S2. Screening of solvents with f-amphox.

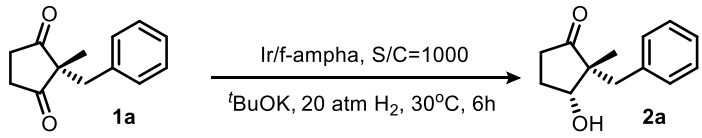


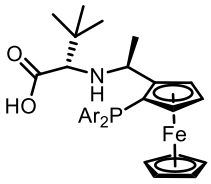


f- Amphox

entry	solvent	conversion (%)	ee (%)	dr(%)
1	^{i}PrOH	<5		
2	MeOH	<5		
3	EtOH	<5		
4	DCM	26	90	96:4
5	TOL	16	93	93:7
6	THF	15	96	93:7
7	DCE	<5		

Table S3. Screening of solvents with f-ampha.

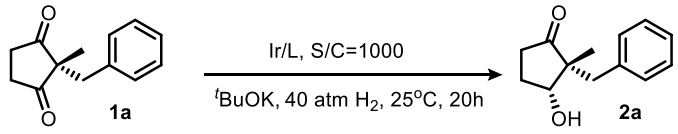




f- Ampha

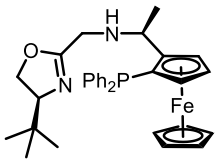
entry	solvent	conversion (%)	ee (%)	dr(%)
1	^{i}PrOH	82	92	91:9
2	MeOH	<5		
3	EtOH	<5		
4	DCM	39	97	93:7
5	TOL	95	96	87:13
6	THF	74	93	84:16
7	DCE	<5		

Table S4. Screening of bases with different alkali metals.



L = f-Amphox, solvent = THF

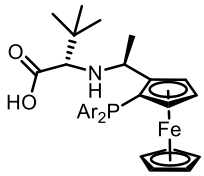
entry	base	conversion (%)	ee (%)	dr(%)
1	KO^{t}Bu	>95	97	94:6
2	NaO^{t}Bu	>95	96	95:5
3	LiO^{t}Bu	<5		



f- Amphox

L =f -Ampha, solvent = DCM

entry	base	conversion (%)	ee (%)	dr(%)
1	KO^{t}Bu	70	97	94:6
2	NaO^{t}Bu	>95	99	96:4
3	LiO^{t}Bu	14	97	89:11



f- Ampha

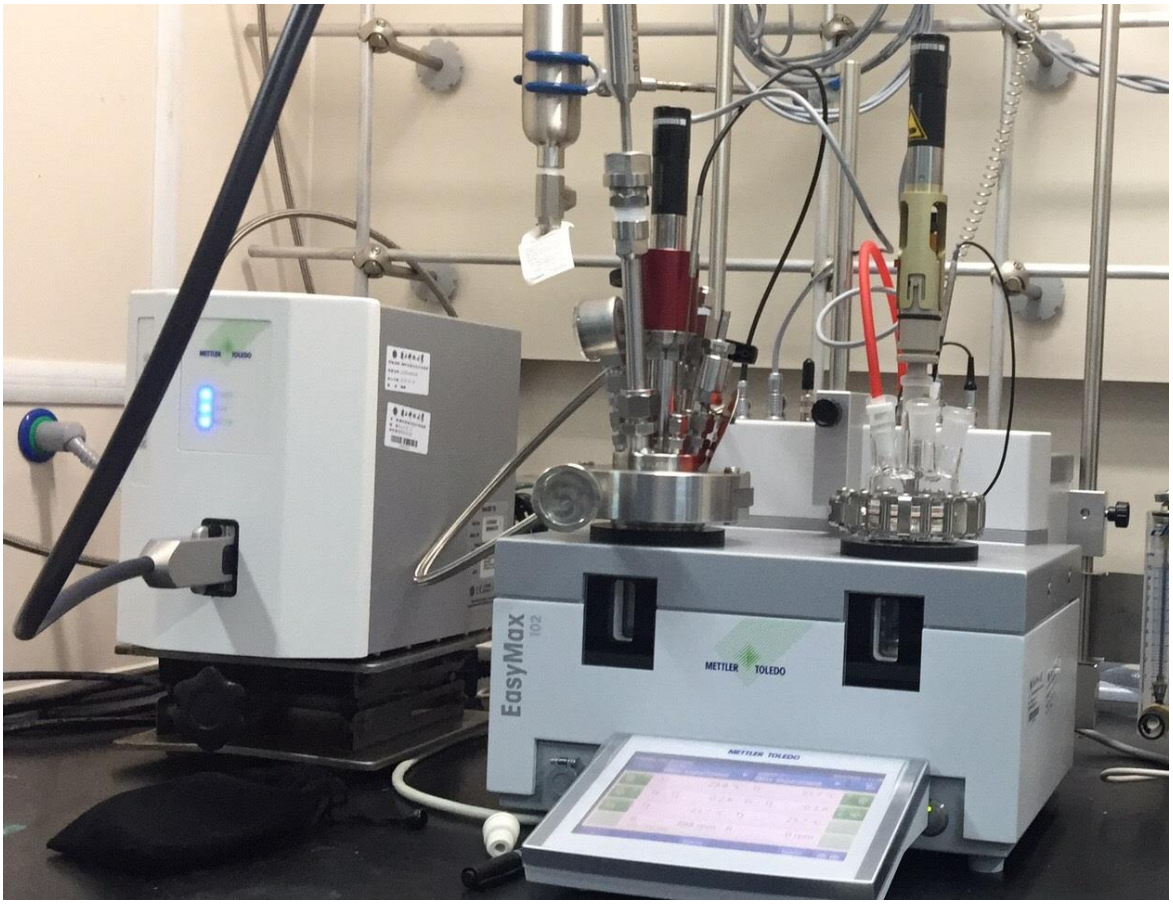
Procedure of the optimized condition for substrate scope:

In an argon-filled glove box, a 4.0 mL vial was charged with the metal precursor $[Ir(COD)Cl]_2$ (3.4 mg, 5.0×10^{-3} mmol), f-ampha (8.8 mg, 10.5×10^{-3} mmol) and anhydrous ^{i}PrOH (1.0 mL). The mixture (0.010 M) was stirred for 1.0 h at 25 °C, giving an orange-red solution. The resulting solution (20 μL) and a solution of ^{t}BuOK in ^{i}PrOH (20 μL, 0.10 M) transferred by a syringe into a 5.0 mL vial charged with cyclic diketone (0.2 mmol) in 1.0 mL anhydrous dichloromethane. The vial was transferred to an autoclave, which was then pressurized with 40 atm of H_2 and stirred at room temperature for 1 h. The hydrogen gas was released slowly in a well-ventilated hood. The crude product was purified by flash chromatography (silica, hexanes/EtOAc). The ee and dr values was determined by HPLC or GC on a chiral stationary phase.

Absolute configurations of chiral cyclic hydroxy ketones were determined by (1) comparison of the ^{1}H NMR spectra and optical rotations with known compounds reported in literature; (2) single crystal analysis (**2a** and **2s**) and (3) analogy.

Procedure of the scale-up reaction:

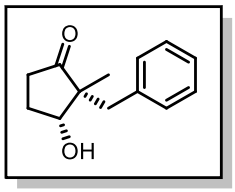
Scale-up reaction was performed on a Mettler-Toledo Easymax-102 reaction station with a 100 mL Hastelloy C-22 pressure reactor with was equipped with mechanical stirring.



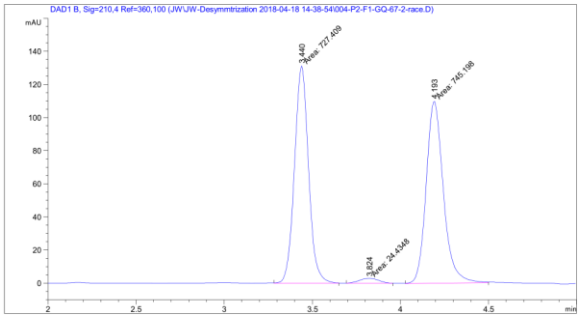
In an argon-filled glove box, a 4.0 mL vial was charged with the metal precursor $[Ir(COD)Cl]_2$ (3.4 mg, 5.0×10^{-3} mmol), f-ampha (8.8 mg, 10.5×10^{-3} mmol) and anhydrous ^{i}PrOH (1.0 mL). The mixture (0.010 M) was stirred for 1.0 h at 25 ^{o}C, giving an orange-red solution. The resulting solution (0.80 mL) and a solution of ^{t}BuOK in ^{i}PrOH (2.0 mL, 0.10 M) transferred by a syringe into a 50 mL Erlenmeyer flask which was charged with cyclic diketone (20.0 mmol) in 38 mL anhydrous dichloromethane (40 mL in total). The mixture was stirred for 3 min and transfered to the pressure reactor via a 50 mL syringe. This reactor was degassed and back filled with argon before adding reaction mixture. The reactor was sealed and pressurized with hydrogen gas to 40 atm. The reaction was stirred at 300 rpm and monitored with in situ AFT-FTIR. After 4 hours, in situ IR indicated the end point of this reaction and the hydrogen gas was released slowly in a well-ventilated hood. The crude product was purified by flash chromatography (silica, hexanes/EtOAc). The ee and dr values was determined by HPLC or GC on a chiral stationary phase.

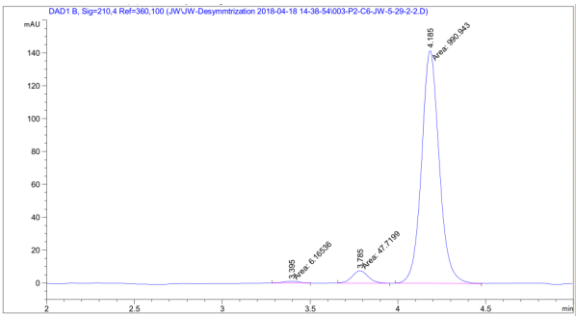
4. Characterization of chiral cyclic hydroxy ketones.

(2*R*,3*R*)-2-benzyl-3-hydroxy-2-methylcyclopentan-1-one (**2a**)[1]



White solid. 95% yield (38.7 mg), $[\alpha]^{25}_{D}$ -63.55° (c 2.0, MeOH, 99% ee, 21:1 dr). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 4H), 7.25 – 7.18 (m, 1H), 4.07 – 4.02 (m, 1H), 3.06 (d, *J* = 13.7 Hz, 1H), 2.72 (d, *J* = 13.7 Hz, 1H), 2.51 (dt, *J* = 18.8, 9.3 Hz, 1H), 2.36 (ddd, *J* = 19.2, 9.2, 3.4 Hz, 1H), 2.16 (tdd, *J* = 13.9, 9.1, 4.5 Hz, 1H), 1.89 (ddt, *J* = 12.8, 9.5, 3.2 Hz, 1H), 0.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.82, 138.04, 130.51, 128.23, 126.35, 76.43, 54.91, 35.80, 33.83, 28.32, 19.72. *m/z* (ESI–MS): calc. 205.1228 $[M+H]^+$, found 205.1225 $[M+H]^+$. HPLC (Daicel Chiralpak IA-U, hexanes/i-PrOH = 95/5, Flow rate = 0.6 ml/min, UV = 210 nm): t_1 = 3.4 min, t_2 = 3.8 min, t_3 = 4.2 min.





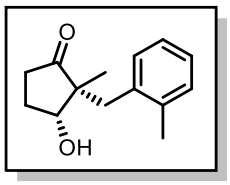
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.440	MM T	0.0923	727.40863	131.37578	48.5898
2	3.824	MM T	0.1356	24.43477	3.00412	1.6322
3	4.193	MM T	0.1128	745.19775	110.07211	49.7780

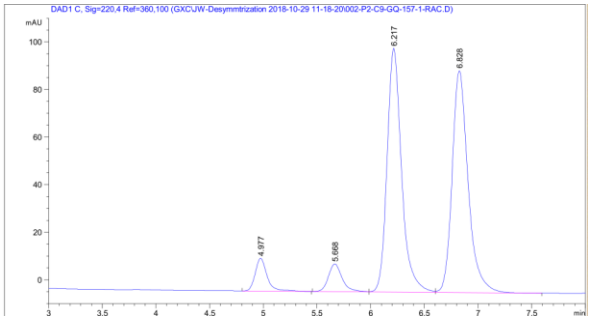
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

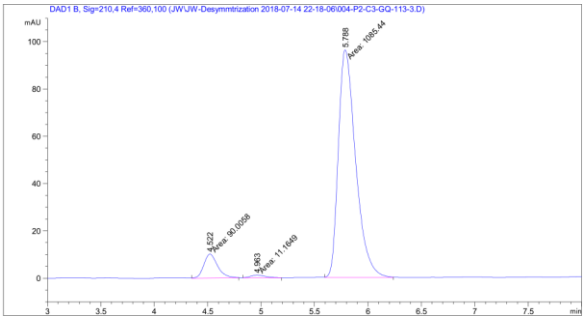
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.395	MM T	0.0974	6.16536	1.05446	0.5901
2	3.785	MM	0.1057	47.71986	7.52358	4.5672
3	4.185	MM	0.1163	990.94281	141.96001	94.8427

(2*R*,3*R*)-3-hydroxy-2-methyl-2-(2-methylbenzyl)cyclopentan-1-one (**2b**)



Colorless oil. 93% yield (41mg), $[\alpha]^{25}_{D}$ -34.63° (c 1.75, MeOH, 97% ee, 14:1 dr). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 1H), 7.18 – 7.05 (m, 3H), 4.16 (t, *J* = 3.8 Hz, 1H), 3.01 – 2.85 (m, 2H), 2.61 – 2.46 (m, 1H), 2.42 – 2.30 (m, 4H), 2.28 – 2.16 (m, 1H), 1.97 (ddt, *J* = 13.4, 9.7, 3.6 Hz, 1H), 0.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.65, 137.38, 136.52, 130.63, 130.55, 126.34, 125.82, 76.56, 55.39, 33.71, 30.79, 28.20, 20.42, 18.92. *m/z* (ESI–MS): calc. 219.1377 $[M+H]^+$, found 219.1375 $[M+H]^+$. HPLC (Daicel Chiralpak IA-U, hexanes/i-PrOH = 95/5, Flow rate = 0.6 ml/min, UV = 210 nm): t_1 = 4.5 min, t_2 = 5.0 min, t_3 = 5.8 min.





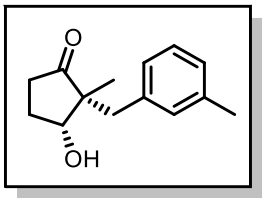
Signal 1: DAD1 C, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.977	BB	0.1156	106.24710	13.83762	4.9667
2	5.668	BV	0.1357	103.73180	11.66903	4.8491
3	6.217	VV	0.1436	962.90033	102.52978	45.0120
4	6.828	VB	0.1568	966.33118	93.30305	45.1723

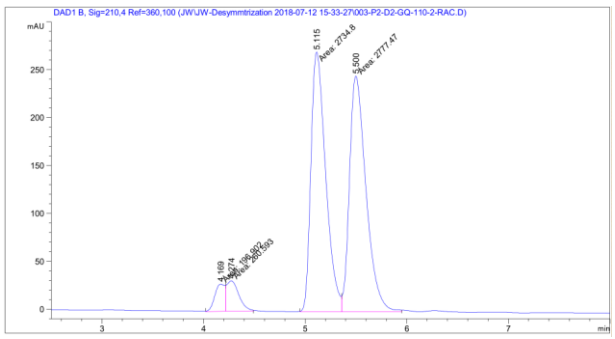
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

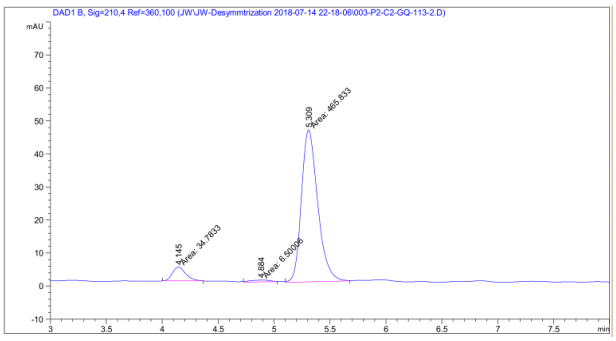
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.522	MM T	0.1480	90.00583	10.13390	7.5851
2	4.963	MM T	0.1609	11.16494	1.15659	0.9409
3	5.788	MM T	0.1877	1085.43787	96.37545	91.4740

(2*R*,3*R*)-3-hydroxy-2-methyl-2-(3-methylbenzyl)cyclopentan-1-one (**2c**)



White solid. 93% yield (40mg), $[\alpha]^{25}_{D}$ -61.66° (c 1.45, MeOH, 98% ee, 14:1 dr). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.13 (m, 1H), 7.05 (dd, *J* = 14.0, 7.2 Hz, 3H), 4.06 (dd, *J* = 6.5, 2.8 Hz, 1H), 3.01 (d, *J* = 13.8 Hz, 1H), 2.70 (d, *J* = 13.8 Hz, 1H), 2.57 – 2.43 (m, 1H), 2.41 – 2.34 (m, 1H), 2.33 (s, 3H), 2.25 – 2.09 (m, 1H), 1.94 – 1.80 (m, 1H), 0.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.39, 138.00, 137.88, 131.24, 128.24, 127.51, 127.20, 76.71, 54.92, 35.88, 33.85, 28.39, 21.61, 19.93. *m/z* (ESI–MS): calc. 241.1204 $[M+Na]^+$, found 241.1197 $[M+Na]^+$;mp 118℃. HPLC (Daicel Chiralpak IB-U, hexanes/i-PrOH = 98/2, Flow rate = 0.8 ml/min, UV = 210 nm): t_1 = 4.1 min, t_2 = 4.9 min, t_3 = 5.3 min.





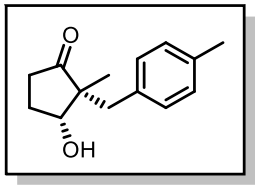
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.169	MF T	0.1153	196.90242	28.45325	3.2983
2	4.274	FM T	0.1371	260.59344	31.67639	4.3652
3	5.115	MF T	0.1682	2734.79614	270.98126	45.8108
4	5.500	FM T	0.1883	2777.46899	245.84483	46.5256

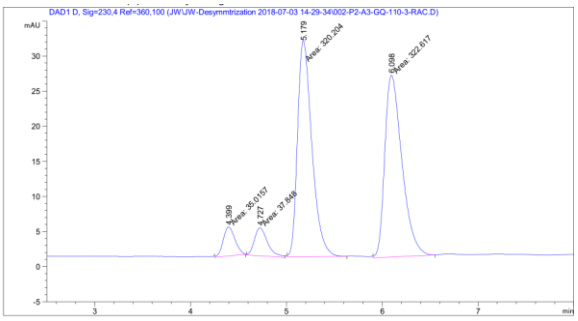
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

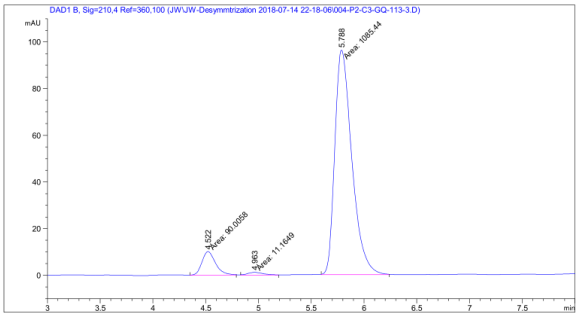
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.145	MM T	0.1369	34.78330	4.23452	6.8590
2	4.884	MM T	0.2041	6.50006	5.30747e-1	1.2818
3	5.309	MM T	0.1688	465.83279	45.98860	91.8592

(2*R*,3*R*)-3-hydroxy-2-methyl-2-(4-methylbenzyl)cyclopentan-1-one (**2d**)



White solid. 92% yield (41mg), $[\alpha]^{25}_{D}$ -58.39° (c 1.55, MeOH, 98% ee, 16:1 dr). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 4.05 (s, 1H), 3.00 (d, *J* = 13.8 Hz, 1H), 2.70 (d, *J* = 13.9 Hz, 1H), 2.58 – 2.43 (m, 1H), 2.40 – 2.33 (m, 1H), 2.32 (s, 3H), 2.17 (dtd, *J* = 13.7, 9.2, 4.5 Hz, 1H), 1.92 – 1.83 (m, 1H), 0.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.47, 135.96, 134.86, 130.37, 130.03, 129.39, 129.05, 76.77, 54.91, 35.57, 33.93, 28.39, 21.16, 19.92. *m/z* (ESI–MS): calc. 241.1204 $[M+Na]^+$, found 241.1197 $[M+Na]^+$;mp 95°C. HPLC (Daicel Chiralpak IB-U, hexanes/i-PrOH = 98/2, Flow rate = 0.8 ml/min, UV = 210 nm): t_1 = 4.5 min, t_2 = 5.0 min, t_3 = 5.8 min.





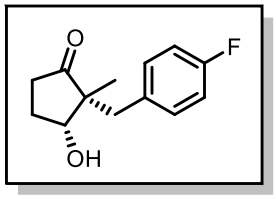
Signal 1: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.399	MM T	0.1415	35.01569	4.12572	4.8926
2	4.727	MM T	0.1580	37.84802	3.99142	5.2884
3	5.179	MM T	0.1733	320.20432	30.80330	44.7409
4	6.098	MM T	0.2075	322.61716	25.91156	45.0781

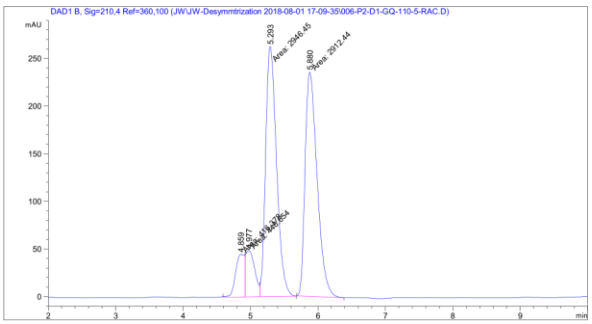
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

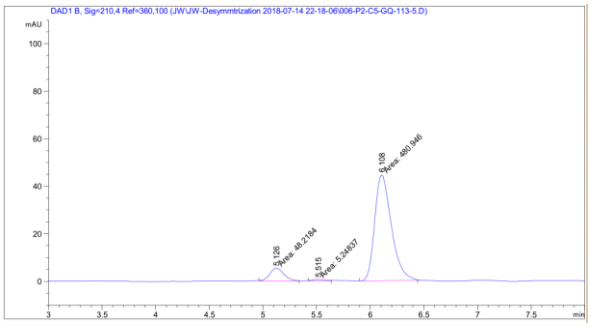
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.522	MM T	0.1480	90.00583	10.13390	7.5851
2	4.963	MM T	0.1609	11.16494	1.15659	0.9409
3	5.788	MM T	0.1877	1085.43787	96.37545	91.4740

(2*R*,3*R*)-2-(4-fluorobenzyl)-3-hydroxy-2-methylcyclopentan-1-one (**2e**)



White solid. 93% yield (44mg), $[\alpha]^{25}_{D}$ -54.75° (c 0.4, MeOH 98% ee, 11:1 dr). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.18 (m, 3H), 7.02 – 6.90 (m, 2H), 4.04 (s, 1H), 3.03 (d, *J* = 13.8 Hz, 1H), 2.69 (d, *J* = 13.8 Hz, 1H), 2.50 (dt, *J* = 15.3, 9.3 Hz, 1H), 2.37 (ddd, *J* = 19.2, 9.2, 3.4 Hz, 1H), 2.25 – 2.15 (m, 1H), 1.87 (dtd, *J* = 18.7, 6.2, 2.9 Hz, 1H), 0.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.23, 162.96-160.53(d, *J* = 245.4Hz,), 133.70 (d, *J* = 3.2 Hz), 131.98 (d, *J* = 7.7 Hz), 115.12-114.92 (d, *J* = 20.2 Hz), 76.46, 54.79, 35.06, 33.83, 28.61, 19.70. *m/z* (ESI–MS): calc. 223.1126 $[M+H]^+$, found 223.1125 $[M+H]^+$;mp 93°C. HPLC (Daicel Chiralpak IB-U, hexanes/i-PrOH = 98/2, Flow rate = 0.8 ml/min, UV = 210 nm): t_1 = 5.1 min, t_2 = 5.5 min, t_3 = 6.1 min.





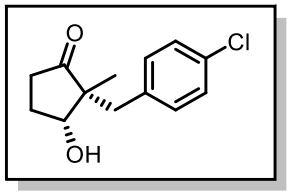
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.859	MF T	0.1547	416.37830	44.86858	6.1925
2	4.977	FM T	0.1539	448.65372	48.58003	6.6725
3	5.293	FM T	0.1870	2946.44580	262.65884	43.8203
4	5.880	MM T	0.2061	2912.44458	235.46411	43.3147

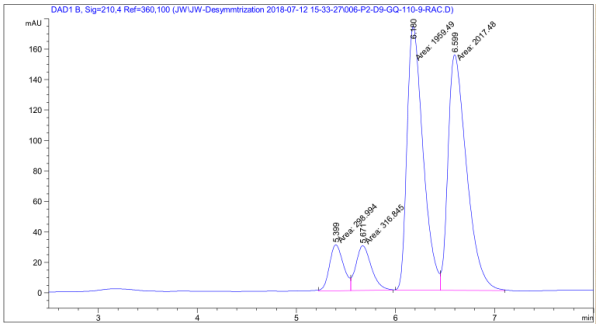
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

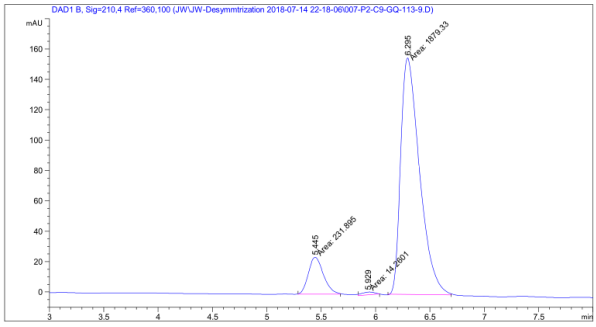
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.126	MM T	0.1502	48.21841	5.34877	9.0227
2	5.515	MM T	0.1458	5.24837	6.00004e-1	0.9821
3	6.108	MM T	0.1796	480.94644	44.63055	89.9952

(2*R*,3*R*)-2-(4-chlorobenzyl)-3-hydroxy-2-methylcyclopentan-1-one (**2f**)



White solid. 95% yield (45mg), $[\alpha]^{25}_{D}$ -52.69° (c 1.6, MeOH, 99% ee, 8:1 dr). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.19 (m, 4H), 4.03 (s, 1H), 3.03 (d, *J* = 13.7 Hz, 1H), 2.68 (d, *J* = 13.7 Hz, 1H), 2.55 – 2.44 (m, 1H), 2.38 (ddd, *J* = 19.2, 9.3, 3.3 Hz, 1H), 2.26 – 2.13 (m, 1H), 1.88 (ddt, *J* = 12.4, 9.4, 3.0 Hz, 1H), 0.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.07, 136.62, 131.95, 129.72, 128.37, 76.46, 54.73, 35.21, 33.75, 28.65, 19.65.*m/z* (ESI–MS): calc. 239.0831 $[M+H]^+$, found 239.0831 $[M+H]^+$;mp 74℃. HPLC (Daicel Chiralpak IB-U, hexanes/i-PrOH = 98/2, Flow rate = 0.8 ml/min, UV = 210 nm): t_1 = 5.4 min, t_2 = 5.9 min, t_3 = 6.3 min.





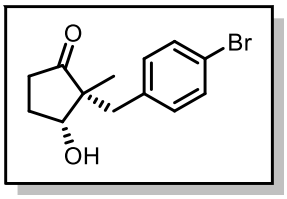
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.399	MF T	0.1648	298.99438	30.23049	6.5100
2	5.671	FM T	0.1794	316.84546	29.43496	6.8987
3	6.180	MF T	0.1885	1959.49316	173.26263	42.6643
4	6.599	FM T	0.2175	2017.48010	154.62370	43.9269

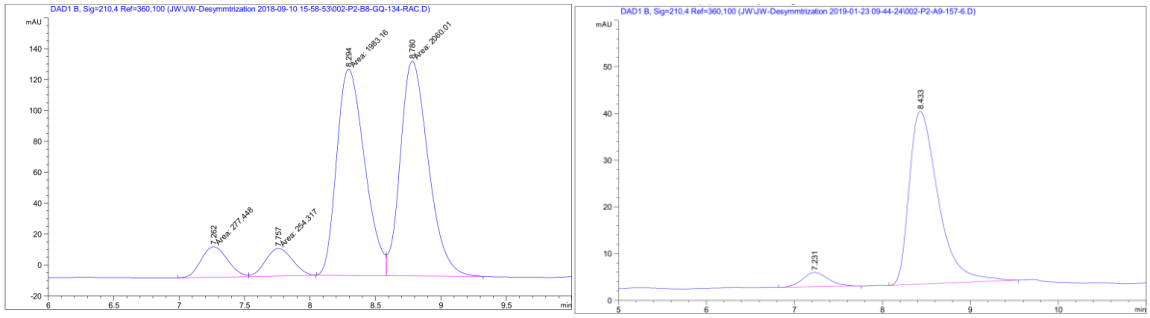
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.445	MM T	0.1597	231.89523	24.20850	10.9102
2	5.929	MM T	0.1294	14.26010	1.83640	0.6709
3	6.295	MM T	0.2012	1879.32727	155.70601	88.4188

(2*R*,3*R*)-2-(4-bromobenzyl)-3-hydroxy-2-methylcyclopentan-1-one (**2g**)



White solid. 94% yield (51mg), $[\alpha]^{25}_{D}$ -53.47° (c 2.45, MeOH, > 99% ee, 9:1 dr). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 4.03 (dd, *J* = 6.6, 2.8 Hz, 1H), 3.01 (d, *J* = 13.7 Hz, 1H), 2.67 (d, *J* = 13.7 Hz, 1H), 2.57 – 2.44 (m, 1H), 2.38 (ddd, *J* = 19.2, 9.3, 3.3 Hz, 1H), 2.25 – 2.15 (m, 1H), 1.92 – 1.83 (m, 1H), 0.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.11, 137.15, 132.37, 131.33, 120.35, 76.31, 54.68, 35.23, 33.72, 28.65, 19.61. *m/z* (ESI–MS): calc. 239.0831 $[M+H]^+$, found 239.0831 $[M+H]^+$;mp 135℃. HPLC (Daicel Chiralpak IB-U, hexanes/i-PrOH = 98/2, Flow rate = 0.8 ml/min, UV = 210 nm): t_1 = 7.8 min, t_2 = 9.2 min.



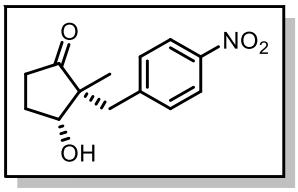
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.262	MF T	0.2342	277.44754	19.74212	6.0645
2	7.757	FM T	0.2375	254.31667	17.84942	5.5589
3	8.294	MF T	0.2475	1983.15674	133.52451	43.3484
4	8.780	FM T	0.2470	2060.00708	139.00076	45.0282

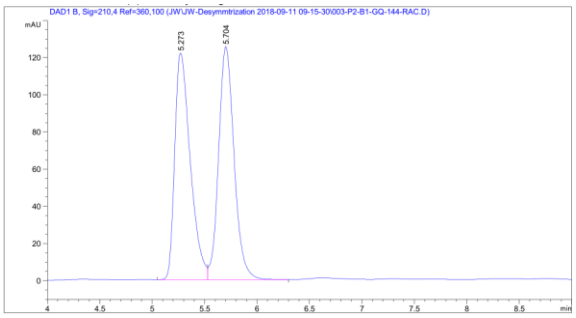
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.231	BB	0.3121	62.86595	3.08092	6.9142
2	8.433	BB	0.3507	846.36047	37.02058	93.0858

(2*R*,3*R*)-3-hydroxy-2-methyl-2-(4-nitrobenzyl)cyclopentan-1-one (**2h**)

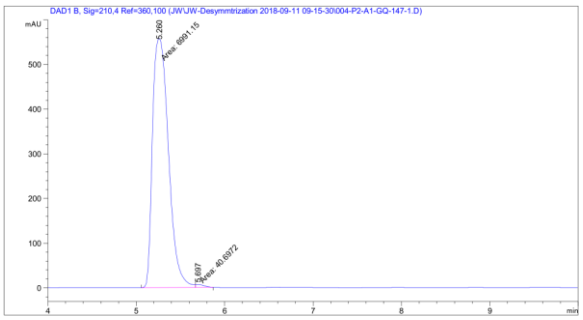


White solid. 84% yield (44mg), $[\alpha]^{25}_{D}$ -76.64° (c 1.40, MeOH, 99% ee, >30:1 dr). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 4.04 (s, 1H), 3.18 (d, *J* = 13.4 Hz, 1H), 2.80 (d, *J* = 13.4 Hz, 1H), 2.54 (dt, *J* = 19.1, 9.5 Hz, 1H), 2.41 (ddd, *J* = 19.2, 9.2, 3.0 Hz, 1H), 2.30 – 2.14 (m, 1H), 1.91 (ddt, *J* = 14.4, 9.3, 2.7 Hz, 1H), 0.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 219.26, 146.49, 131.50, 123.40, 76.06, 54.68, 35.72, 33.51, 28.86, 19.48. *m/z* (ESI–MS): calc. 250.1071 $[M+H]^+$, found 250.1073 $[M+H]^+$;mp 165℃. HPLC (Daicel Chiralpak IA-U, hexanes/i-PrOH = 90/10, Flow rate = 0.5 ml/min, UV = 210 nm): t_1 = 5.3 min, t_2 = 5.7 min.



Signal 1: DAD1 B, Sig=210,4 Ref=360,100

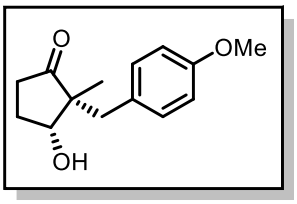
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.273	BV	0.1581	1255.40723	121.99220	49.3949
2	5.704	VB	0.1577	1286.16296	125.40067	50.6051



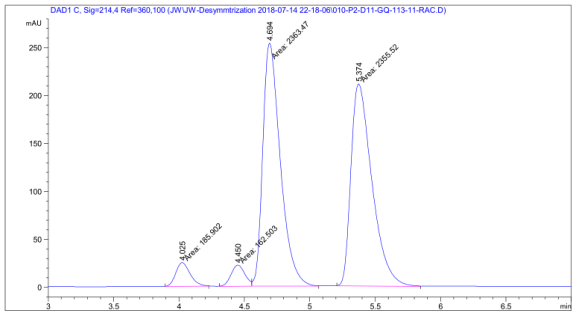
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.260	MF T	0.2092	6991.15039	557.01642	99.4212
2	5.697	FM T	0.1100	40.69722	6.16648	0.5788

(2*R*,3*R*)-3-hydroxy-2-(4-methoxybenzyl)-2-methylcyclopentan-1-one (**2i**)

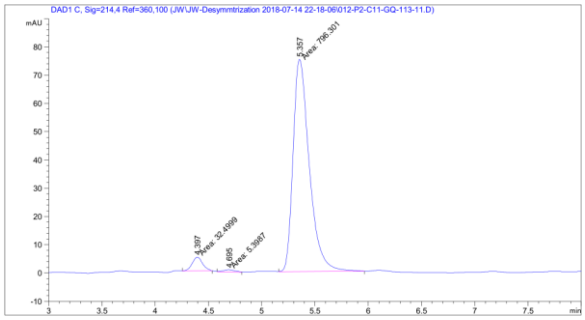


White solid. 84% yield (45mg), $[\alpha]^{25}_{D}$ -65.22° (c 1.15, MeOH, 99% ee, >25:1 dr). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 5.7 Hz, 2H), 6.86 – 6.75 (m, 2H), 4.05 (s, 1H), 3.79 (s, 3H), 2.98 (d, *J* = 13.9 Hz, 1H), 2.68 (d, *J* = 13.9 Hz, 1H), 2.49 (dt, *J* = 18.7, 9.2 Hz, 1H), 2.35 (ddd, *J* = 19.2, 9.2, 3.6 Hz, 1H), 2.18 (dtd, *J* = 13.7, 9.1, 4.5 Hz, 1H), 1.86 (ddt, *J* = 13.2, 9.4, 3.4 Hz, 1H), 0.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.55, 158.28, 131.45, 129.98, 113.74, 76.78, 55.36, 54.93, 35.16, 33.99, 28.45, 19.93. *m/z* (ESI–MS): calc. 257.1154 $[M+Na]^+$, found 257.1146 $[M+Na]^+$;mp 114℃. HPLC (Daicel Chiralpak IB-U, hexanes/i-PrOH = 96/4, Flow rate = 0.8 ml/min, UV = 210 nm): t_1 = 4.4 min, t_2 = 4.7 min, t_3 = 5.4 min.



Signal 1: DAD1 C, Sig=214,4 Ref=360,100

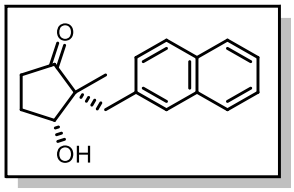
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.025	MM T	0.1259	185.90157	24.61358	3.6686
2	4.450	MF T	0.1228	162.50316	22.04795	3.2068
3	4.694	FM T	0.1554	2363.46948	253.54683	46.6407
4	5.374	MM T	0.1864	2355.51855	210.65172	46.4838



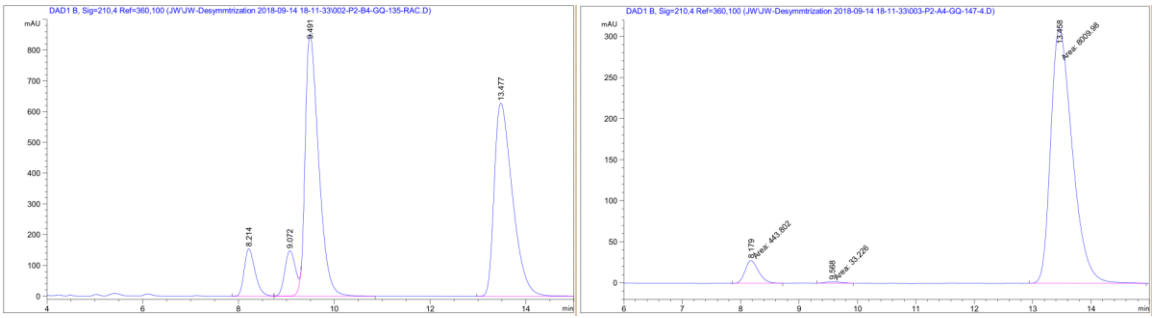
Signal 1: DAD1 C, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.397	MM T	0.1122	32.49989	4.82565	3.8959
2	4.695	MM T	0.1234	5.39870	7.28908e-1	0.6472
3	5.357	MM T	0.1766	796.30066	75.14021	95.4569

(2*R*,3*R*)-3-hydroxy-2-methyl-2-(naphthalen-2-ylmethyl)cyclopentan-1-one (**2j**)



White solid. 90% yield (48mg), $[\alpha]^{25}_{D}$ -58.31° (c 0.65, MeOH, 99% ee, 21:1 dr). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.74 (m, 3H), 7.72 (s, 1H), 7.49 – 7.41 (m, 3H), 4.09 (s, 1H), 3.23 (d, *J* = 13.7 Hz, 1H), 2.90 (d, *J* = 13.7 Hz, 1H), 2.60 – 2.49 (m, 1H), 2.39 (ddd, *J* = 19.2, 9.2, 3.3 Hz, 1H), 2.23 – 2.13 (m, 1H), 1.89 (ddt, *J* = 11.7, 8.3, 2.6 Hz, 1H), 0.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.55, 135.78, 133.54, 132.27, 129.04, 128.97, 127.74, 127.69, 126.04, 125.53, 76.55, 55.09, 36.01, 33.80, 28.54, 19.90. *m/z* (ESI–MS): calc. 277.1205 $[M+Na]^+$, found 277.1199 $[M+Na]^+$;mp 145°C. HPLC (Daicel Chiralpak OJ-3, hexanes/i-PrOH = 85/15, Flow rate = 0.6 ml/min, UV = 210 nm): t_1 = 8.2 min, t_2 = 9.6 min, t_3 = 13.5 min.



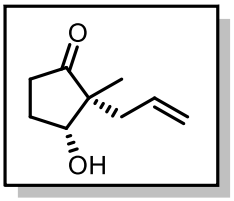
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.214	BV	0.2439	2454.91895	154.07060	6.4544
2	9.072	VV E	0.2378	2223.52368	147.58543	5.8460
3	9.491	VB R	0.3017	1.67790e4	852.17719	44.1147
4	13.477	BBA	0.4058	1.65775e4	628.26288	43.5849

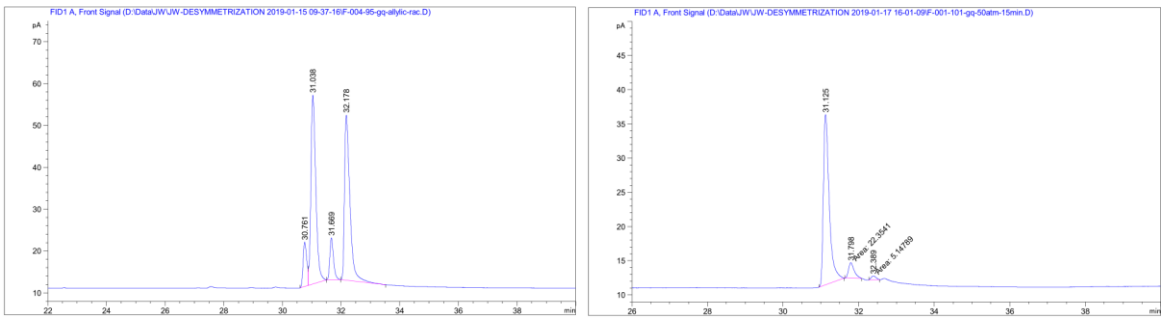
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.179	MM T	0.2673	443.80167	27.66827	5.2292
2	9.568	MM T	0.3258	33.22599	1.69978	0.3915
3	13.458	MM T	0.4303	8009.98438	310.24335	94.3793

(2*R*,3*R*)-2-allyl-3-hydroxy-2-methylcyclopentan-1-one (**2k**)[11]



Colorless oil. 93% yield (28.8 mg), $[\alpha]^{25}_{D}$ -69.75° (c 0.4, $CHCl_3$, 98% ee, 19 dr). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (ddt, *J* = 17.2, 10.1, 7.4 Hz, 1H), 5.22 – 5.07 (m, 2H), 4.12 (dd, *J* = 7.4, 3.2 Hz, 1H), 2.48 (dt, *J* = 18.6, 9.2 Hz, 1H), 2.41 – 2.13 (m, 4H), 1.97 (ddt, *J* = 13.4, 9.6, 3.5 Hz, 1H), 1.82 (d, *J* = 3.0 Hz, 1H), 1.00 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 220.66, 134.52, 118.30, 77.61, 53.30, 35.61, 34.12, 27.91, 19.84. *m/z* (ESI–MS): calc. 155.1072 $[M+H]^+$, found 155.1067 $[M+H]^+$. GC (Supelco β-DEX-325, 30 m × 0.25 mm, d_f 0.25 μm): t_1 = 31.1 min, t_2 = 31.8 min, t_3 = 32.4 min.



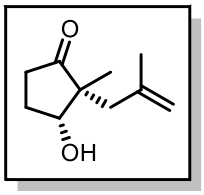
Signal 1: FID1 A, Front Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	30.761	BV	0.1304	91.98411	10.58697	7.62133
2	31.038	VB	0.1706	521.18005	45.16122	43.18227
3	31.669	BB	0.1343	87.84919	10.02110	7.27873
4	32.178	BB	0.1895	505.91727	39.47858	41.91768

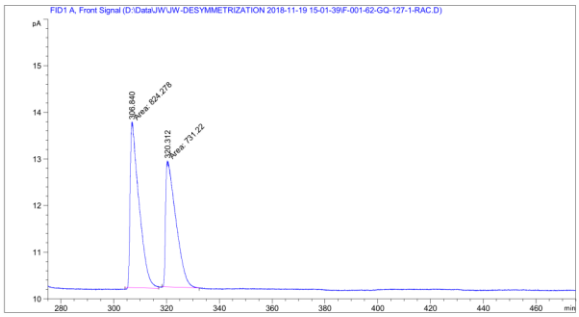
Signal 1: FID1 A, Front Signal

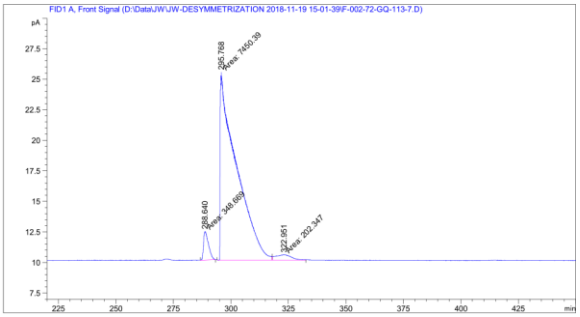
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	31.125	BB	0.1597	268.19336	24.88792	90.69922
2	31.798	MM T	0.1693	22.35408	2.20118	7.55984
3	32.389	MM T	0.1528	5.14789	5.61669e-1	1.74095

(2*R*,3*R*)-3-hydroxy-2-methyl-2-(2-methylallyl)cyclopentan-1-one (**2l**)[4]



Colorless oil. 93% yield (31.0 mg), $[\alpha]^{25}_{D}$ -63.85° (c 0.65, MeOH, 95% ee, 22:1 dr.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.84 (d, *J* = 20.5 Hz, 2H), 4.20 (s, 1H), 2.53 – 2.39 (m, 1H), 2.38 – 2.34 (m, 1H), 2.34 – 2.24 (m, 2H), 2.18 (dtd, *J* = 13.8, 9.3, 4.5 Hz, 1H), 1.98 (ddt, *J* = 12.8, 9.6, 2.9 Hz, 1H), 1.78 (s, 3H), 0.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.74, 143.18, 114.55, 77.57, 53.65, 38.27, 33.50, 27.98, 24.31, 20.06. *m/z* (ESI–MS): calc. 169.1220 $[M+Na]^+$, found 169.1224 $[M+Na]^+$. GC (Supelco β-DEX-325, 30 m × 0.25 mm, d_f 0.25 μm): t_1 = 288.6 min, t_2 = 295.7 min, t_3 = 322.9 min.





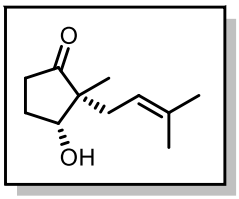
Signal 1: FID1 A, Front Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	306.840	MM T	3.8634	824.27802	3.55592	52.99127
2	320.312	MM T	4.5006	731.21973	2.70786	47.00873

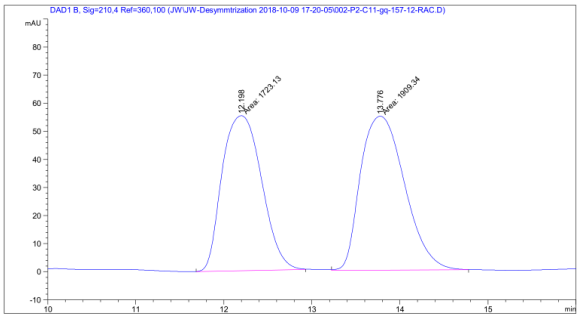
Signal 1: FID1 A, Front Signal

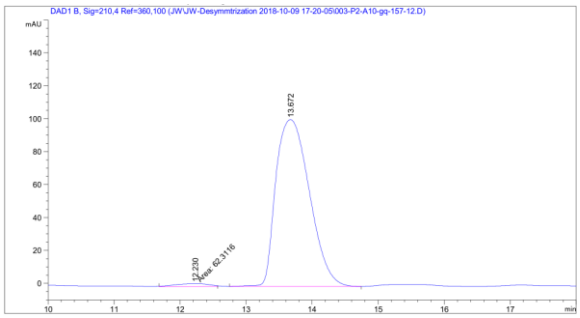
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	288.640	MM T	2.4638	348.66916	2.35862	4.35760
2	295.768	MF	8.0698	7450.39014	15.38737	93.11351
3	322.951	FM	7.9121	202.34674	4.26237e-1	2.52889

(*2R*,*3R*)-3-hydroxy-2-methyl-2-(3-methylbut-2-en-1-yl)cyclopentan-1-one (**2m**)[5]



Colorless oil. 93% yield (31.0 mg), $[\alpha]^{25}_{D}$ -31.53° (c 0.85, MeOH, 98% ee, >25:1 dr,). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.20 (dddd, *J* = 8.8, 6.0, 2.7, 1.3 Hz, 1H), 4.14 (s, 1H), 2.49 (dt, *J* = 18.7, 9.3 Hz, 1H), 2.37 – 2.14 (m, 4H), 2.03 – 1.94 (m, 1H), 1.74 (s, 3H), 1.66 (s, 3H), 1.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.35, 135.09, 119.28, 77.66, 53.76, 34.27, 29.55, 27.75, 26.15, 19.93, 18.03. *m/z* (ESI–MS): calc. 183.1385 $[M+Na]^+$, found 183.1380 $[M+Na]^+$. HPLC (Daicel Chiralpak IB-U, hexanes/i-PrOH = 99/1, Flow rate = 0.3 ml/min, UV = 210 nm): t_1 = 12.2 min, t_2 = 13.7min.





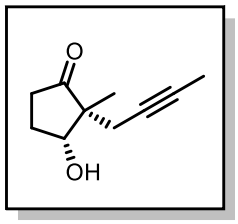
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.198	MM T	0.5206	1723.13342	55.16226	47.4369
2	13.776	MM T	0.5807	1909.33923	54.79670	52.5631

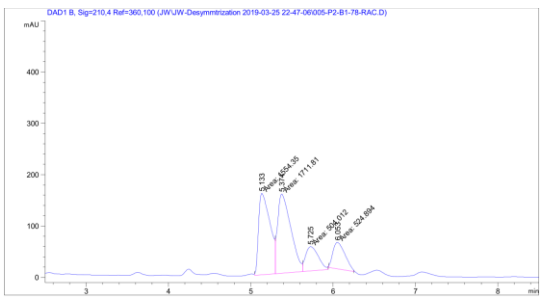
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

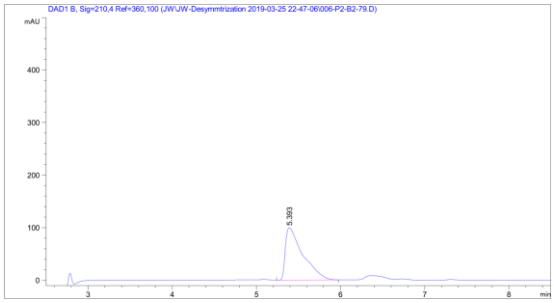
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.230	MM T	0.6010	62.31162	1.72797	1.7106
2	13.672	BB	0.5743	3580.27612	101.30632	98.2894

(*2R*,*3R*)-2-(but-2-yn-1-yl)-3-hydroxy-2-methylcyclopentan-1-one (**2n**)



Colorless oil. 95% yield, $[\alpha]^{25}_{D}$ -57.29° (c 3.4, MeOH, 99% ee, 3:1 dr). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.26 – 4.22 (m, 1H), 2.56 – 2.44 (m, 1H), 2.38 – 2.29 (m, 4H), 2.27 – 2.14 (m, 1H), 2.04 (ddt, *J* = 12.9, 8.6, 3.0 Hz, 1H), 1.80 (t, *J* = 2.6 Hz, 3H), 1.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.43, 78.33, 77.35, 75.41, 53.59), 34.51, 27.34, 21.43, 20.33, 3.66. *m/z* (ESI–MS): calc. 167.1064 $[M+H]^+$, found 167.1066 $[M+H]^+$. HPLC (Daicel Chiralpak IA-U, hexanes/i-PrOH = 96/4, Flow rate = 0.5 ml/min, UV = 210 nm): t_1 = 5.39 min.





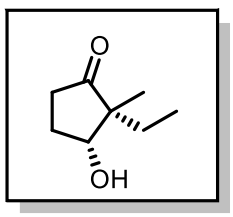
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.133	MF T	0.1631	1554.35486	158.84517	36.1892
2	5.374	FM T	0.1848	1711.81494	154.34892	39.8553
3	5.725	FM T	0.1782	504.01239	47.13634	11.7347
4	6.053	MM T	0.1702	524.89386	51.38817	12.2208

Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.393	BB	0.2095	1427.69934	99.44354	100.0000
Totals :				1427.69934	99.44354	

(*2R*,*3R*)-2-ethyl-3-hydroxy-2-methylcyclopentan-1-one (**2o**)

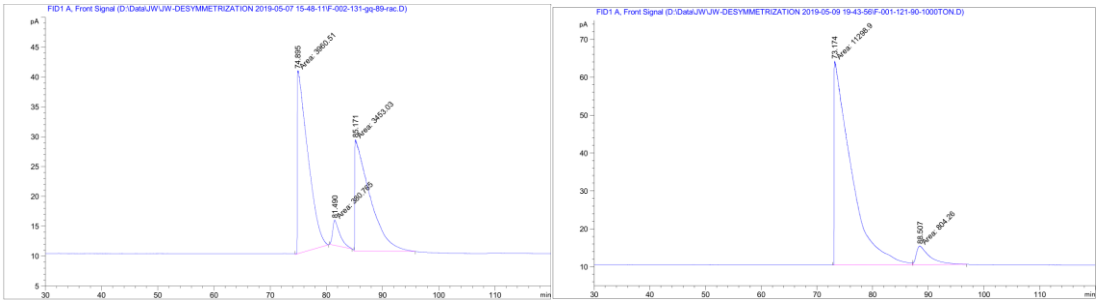


Colorless oil. 82% yield (21.2 mg), $[\alpha]^{25}_{D}$ -49.29° (c 1.1, MeOH, 85% ee, 10.1:1 dr,). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.11 (t, *J* = 4.4 Hz, 1H), 2.53 – 2.38 (m, 1H), 2.32 – 2.13 (m, 2H), 1.97 – 1.87 (m, 2H), 1.63 – 1.46 (m, 2H), 0.96 (s, 3H), 0.90 (t, *J* = 7.6 Hz, 3H). ^{13}C

NMR (101 MHz, $CDCl_3$) δ 221.27, 77.42, 53.52, 34.26, 27.86, 22.73, 18.77, 8.35. *m/z* (ESI–MS): calc. 141.0916 $[M+H]^+$, found 141.0909 $[M+H]^+$;

Due to poor separation on GC capillary column, ee and dr are determined separately:

ee (the pair of minor diastereomers are buried in the first peak): GC (Supelco β-DEX-325 30 m × 0.25 mm, d_f 0.25 μm): t_1 = 73.17 min, t_2 = 88.51min.



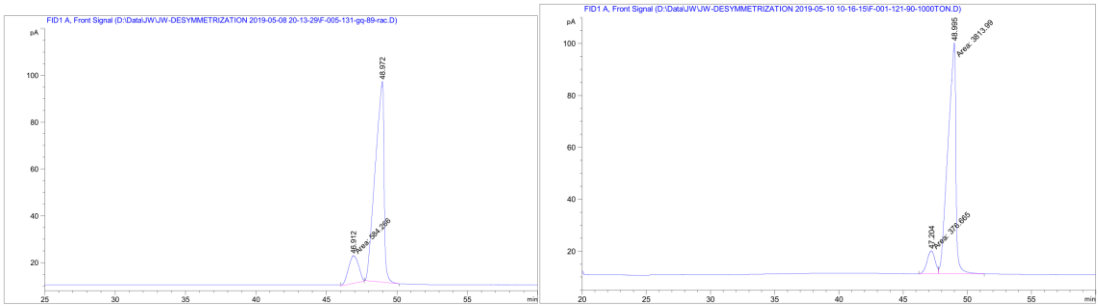
Signal 1: FID1 A, Front Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	74.895	MM T	2.1558	3960.51025	30.61937	50.81289
2	81.490	MM T	1.5051	380.76480	4.21650	4.88517
3	85.171	MM T	3.0893	3453.02661	18.62913	44.30194

Signal 1: FID1 A, Front Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	73.174	MF T	3.4997	1.12989e4	53.80828	93.35494
2	88.507	FM T	2.7323	804.26001	4.90581	6.64506

dr: GC (Supelco γ-DEX-325 30 m × 0.25 mm, d_f 0.25 μm): t_1 = 47.20 min, t_2 = 49.00 min.



Signal 1: FID1 A, Front Signal

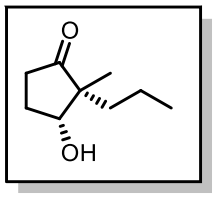
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	46.912	MM T	0.8175	584.26569	11.91165	13.52854
2	48.972	BB	0.5121	3734.49951	85.74135	86.47146

Signal 1: FID1 A, Front Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	47.204	MF T	0.7131	376.66458	8.80322	8.98820
2	48.995	FM T	0.7146	3813.99243	88.95226	91.01180

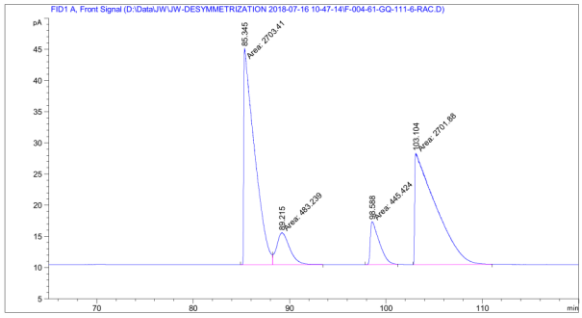
ee = (93.35-8.99-6.65)/91.01*100% = 85%

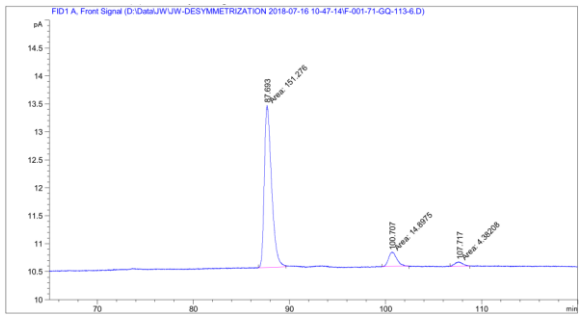
(*2R,3R*)-3-hydroxy-2-methyl-2-propylcyclopentan-1-one (**2p**)



Colorless oil. 93% yield (29.1 mg), $[\alpha]^{25}_D$ -38.91° (c 1.1, MeOH, 99% ee, 10:1 dr,). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.08 (t, *J* = 4.5 Hz, 1H), 2.49 – 2.36 (m, 1H), 2.27 (td, *J* = 9.3, 4.4 Hz, 1H), 2.23 – 2.12 (m, 1H), 1.96 – 1.87 (m, 1H), 1.53 – 1.41 (m, 2H), 1.42 – 1.21 (m, 2H), 0.97 (s, 3H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.22, 77.69, 53.37, 34.15,

32.42, 27.90, 19.40, 17.26, 14.92. *m/z* (ESI–MS): calc. 157.1220 $[M+Na]^+$, found 157.1224 $[M+Na]^+$. GC (Supelco β-DEX-325, 30 m × 0.25 mm, d_f 0.25 μm): t_1 = 87.7 min, t_2 = 100.7 min, t_3 = 107.7 min.





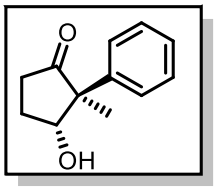
Signal 1: FID1 A, Front Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	85.345	MM T	1.2414	2573.68848	34.55423	42.80081
2	89.215	MM T	1.3099	327.53497	4.16752	5.44695
3	98.588	MM T	1.0153	401.37411	6.58863	6.67491
4	103.104	MM T	2.4818	2710.57983	18.20282	45.07733

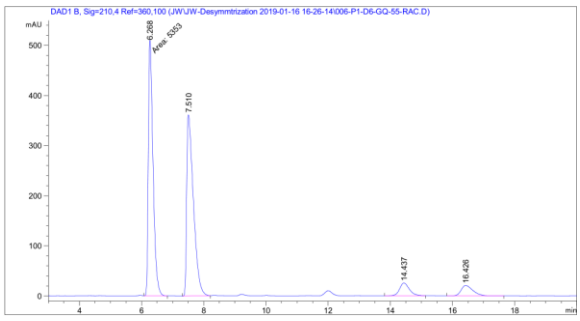
Signal 1: FID1 A, Front Signal

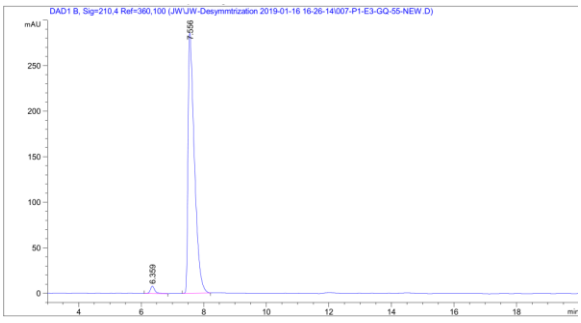
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	87.693	MM T	0.8680	151.27576	2.90472	88.69599
2	100.707	MM T	0.9792	14.89752	2.53576e-1	8.73471
3	107.717	MM T	0.9007	4.38208	8.10844e-2	2.56930

(*2S*,*3R*)-3-hydroxy-2-methyl-2-phenylcyclopentan-1-one (**2q**)



Yellow oil. 90% yield (34 mg), $[\alpha]^{25}_D$ -158.40° (c 3.8, $CHCl_3$, ee 96%, dr >50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 5H), 4.17 (dt, *J* = 4.4, 2.4 Hz, 1H), 2.65 (dt, *J* = 19.2, 9.6 Hz, 1H), 2.48 (ddd, *J* = 19.1, 8.7, 3.1 Hz, 1H), 2.30 – 2.18 (m, 1H), 2.10 – 2.01 (m, 1H), 1.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 219.29, 138.39, 128.78, 128.17, 127.46, 78.97, 59.03, 35.47, 27.02, 22.04. *m/z* (ESI–MS): calc. 213.0892 $[M+Na]^+$, found 213.0885 $[M+Na]^+$; HPLC (Daicel Chiralpak IB-U, hexanes/i-PrOH = 98/2, Flow rate = 0.7 ml/min, UV = 210 nm): t_1 = 6.4 min, t_2 = 7.5 min.





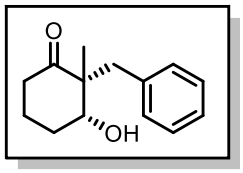
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.268	MM T	0.2012	5352.99902	509.83777	45.1507
2	7.510	BB	0.2241	5394.30371	361.44928	45.4991
3	14.437	BB	0.3331	553.96216	25.33819	4.6725
4	16.426	BB	0.4045	554.59039	20.83511	4.6778

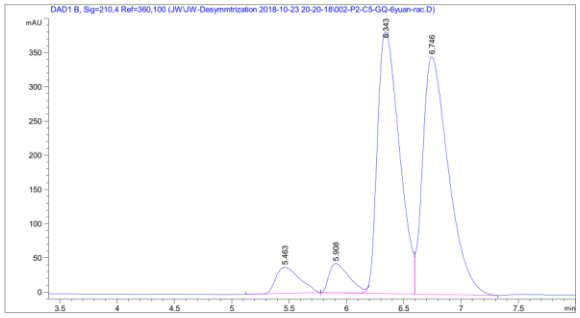
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

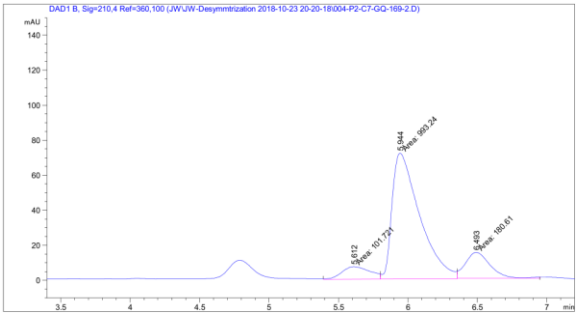
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.359	BB	0.1471	78.49958	7.95854	1.9166
2	7.556	BB	0.2099	4017.21851	286.03275	98.0834

(2*R*,3*R*)-2-benzyl-3-hydroxy-2-methylcyclohexan-1-one (**2r**)



White solid. 93% yield (41.0 mg), $[\alpha]^{25}_{D}$ -6.39° (c 0.36, MeOH, 81% ee, 6:1 dr). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.3 Hz, 2H), 7.20 (dd, *J* = 15.1, 7.1 Hz, 3H), 3.87 – 3.77 (m, 1H), 3.13 (d, *J* = 13.6 Hz, 1H), 2.87 (d, *J* = 13.6 Hz, 1H), 2.52 – 2.41 (m, 2H), 2.11 – 2.04 (m, 1H), 2.02 – 1.93 (m, 1H), 1.87 (ddd, *J* = 17.5, 8.6, 4.3 Hz, 1H), 1.67 – 1.58 (m, 1H), 1.14 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 213.77, 137.91, 130.54, 128.38, 126.62, 74.21, 55.92, 41.15, 37.84, 28.87, 20.24, 18.35. *m/z* (ESI–MS): calc. 241.1205 $[M+Na]^+$, found 241.1198 $[M+Na]^+$; HPLC (Daicel Chiralpak IB-U, hexanes/i-PrOH = 96/4, Flow rate = 0.5 ml/min, UV = 210 nm): t_1 = 5.6 min, t_2 = 5.9 min, t_3 = 6.5 min.





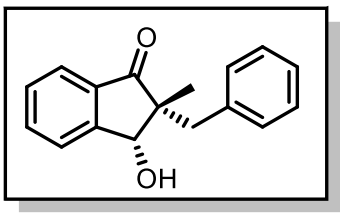
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.463	BB	0.2263	550.70203	38.17267	4.7632
2	5.908	BV E	0.1877	519.77100	42.80208	4.4957
3	6.343	VV R	0.2064	5064.66748	382.75339	43.8064
4	6.746	VB	0.2383	5426.34717	347.20944	46.9347

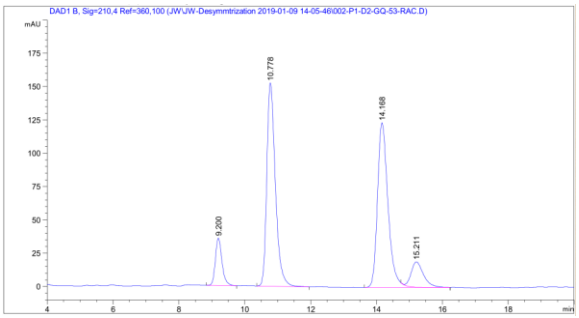
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

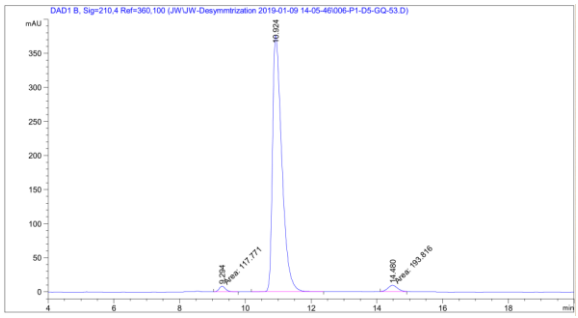
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.612	MF T	0.2361	101.72125	7.18069	7.9746
2	5.944	MF T	0.2301	993.23950	71.92735	77.8663
3	6.493	MM T	0.2044	180.60991	14.72712	14.1591

(2*R*,3*R*)-2-benzyl-3-hydroxy-2-methyl-2,3-dihydro-1H-inden-1-one (**2s**)



White solid. 91% yield (46.1 mg), $[\alpha]^{25}_{D}$ -34.2° (c 2.3, $CHCl_3$, ee 94%, dr >50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.70 – 7.61 (m, 2H), 7.51 – 7.43 (m, 1H), 7.24 – 7.12 (m, 5H), 4.97 (d, *J* = 7.2 Hz, 1H), 3.13 (d, *J* = 13.8 Hz, 1H), 2.88 (d, *J* = 13.7 Hz, 1H), 1.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.31, 152.72, 137.63, 135.32, 135.05, 130.69, 129.69, 128.17, 126.51, 125.63, 123.96, 78.31, 56.10, 38.65, 29.84, 21.69. *m/z* (ESI–MS): calc. 253.1228 $[M+H]^+$, found 253.1222 $[M+H]^+$; HPLC (Daicel Chiralpak IB-U, hexanes/i-PrOH = 98/2, Flow rate = 0.7 ml/min, UV = 210 nm): t_1 = 9.3 min, t_2 = 10.9 min, t_3 = 14.5 min.





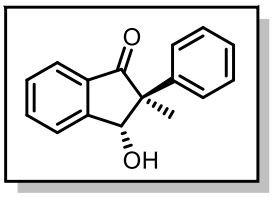
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.200	BB	0.2137	499.16660	35.57295	7.7137
2	10.778	BB	0.2740	2744.06323	152.44646	42.4047
3	14.168	BV R	0.3361	2733.08667	123.55569	42.2351
4	15.211	VB E	0.3937	494.81314	19.00987	7.6465

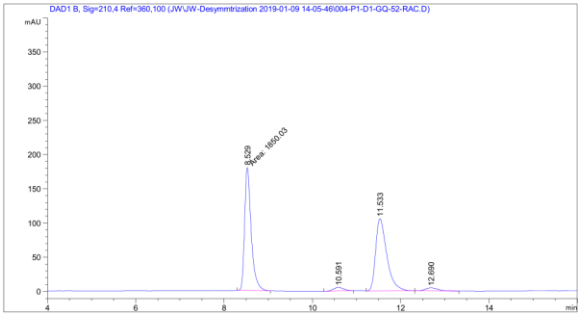
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

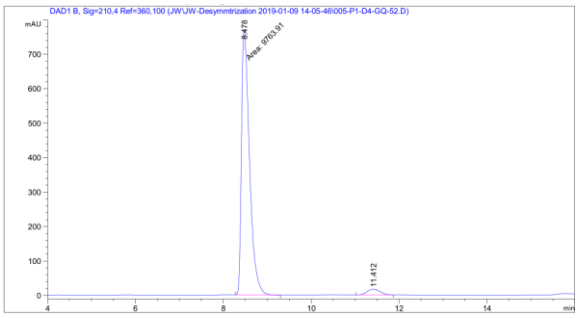
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.294	MM T	0.2350	117.77148	8.35416	1.5304
2	10.924	BB	0.3009	7384.07813	376.37921	95.9511
3	14.480	MM T	0.3506	193.81566	9.21254	2.5185

(*2S*,*3R*)-3-hydroxy-2-methyl-2-phenyl-2,3-dihydro-1H-inden-1-one (**2t**)



White solid. 88% yield (42 mg), $[\alpha]^{25}_{D}$ 89.5° (c 2.6, $CHCl_3$, ee 93%, dr >50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.7 Hz, 1H), 7.78 – 7.68 (m, 2H), 7.61 – 7.49 (m, 1H), 7.36 – 7.22 (m, 4H), 7.19 – 7.11 (m, 2H), 5.09 (d, *J* = 8.5 Hz, 1H), 1.74 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 206.40, 153.39, 138.82, 136.00, 135.88, 129.85, 128.94, 128.09, 127.74, 126.46, 124.08, 79.18, 59.46, 29.84, 22.12. *m/z* (ESI–MS): calc. 239.1072 $[M+Na]^+$, found 239.1065 $[M+Na]^+$; HPLC (Daicel Chiralpak IB-U, hexanes/i-PrOH = 98/2, Flow rate = 0.7 ml/min, UV = 210 nm): t_1 = 8.5 min, t_2 = 11.4 min.





Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.529	MM T	0.1719	1850.02979	179.40266	47.6826
2	10.591	BB	0.2568	84.80727	5.18529	2.1858
3	11.533	BB	0.2649	1854.27954	105.59505	47.7921
4	12.690	BB	0.3107	90.77126	4.55035	2.3395

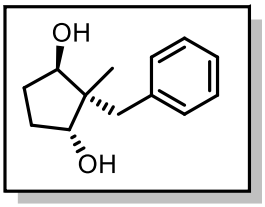
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.478	MM T	0.2119	9763.90625	767.97437	96.6458
2	11.412	BB	0.3280	338.86780	16.60778	3.3542

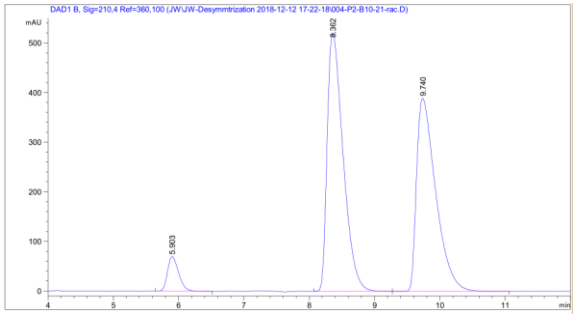
5. Elaboration on the cyclic hydroxy ketone to prepare chiral diol.

In a 10 mL flask **2a** (102 mg, 0.5 mmol) was dissolved in 3 mL anhydrous methanol. This mixture was stirred at 0 °C for 10 min, after which period of time sodium borohydride (1 eq.) was added in three potions. TLC indicated the completion of the reaction. 10 mL of saturated ammonium chloride solution was added to the resulting mixture was stirred vigorously. The mixture was extracted with ethyl acetate (10 mL × 3) and the combined organic phase was dried over sodium sulfate. After concentration *in vavuo*, the residue was purified by flash chromatography to give the diol **3a**.

(1*R*,3*R*)-2-benzyl-2-methylcyclopentane-1,3-diol (***trans*-3a**)

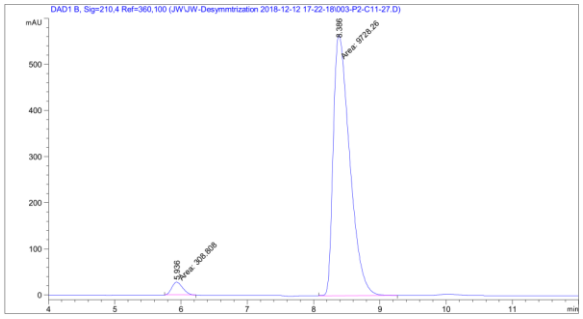


Colorless solid. 95% yield (93 mg), $[\alpha]^{25}_{D}$ -22.18° (c 7.8, $CHCl_3$, > 99% ee, dr 97/3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 5H), 7.24 – 7.19 (m, 1H), 4.26 (t, *J* = 7.3 Hz, 1H), 3.89 (d, *J* = 3.7 Hz, 1H), 2.93 (d, *J* = 13.2 Hz, 1H), 2.69 (d, *J* = 13.2 Hz, 1H), 2.35 – 2.23 (m, 1H), 2.22 – 2.11 (m, 1H), 1.63 – 1.47 (m, 3H), 0.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.39, 130.31, 128.29, 126.15, 78.83, 77.73, 49.74, 39.39, 30.19, 29.61, 16.62. *m/z* (ESI–MS): calc. 229.1205 $[M+Na]^+$, found 229.1200 $[M+Na]^+$; HPLC (Daicel Chiralpak IB-U, hexanes/i-PrOH = 96/2, Flow rate = 0.5 ml/min, UV = 210 nm): t_1 = 5.9 min, t_2 = 9.4 min.



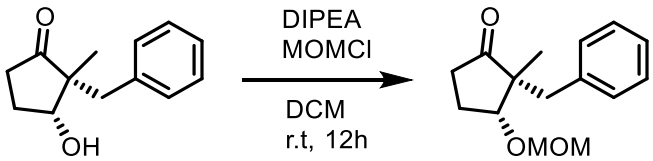
Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.903	BB	0.1848	816.71503	69.63821	4.6662
2	8.362	BB	0.2586	8781.45996	520.99609	50.1723
3	9.740	BB	0.3092	7904.43604	388.85977	45.1615



Signal 1: DAD1 B, Sig=210,4 Ref=360,100

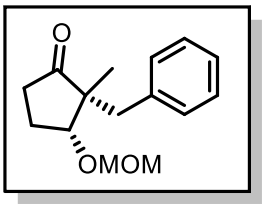
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.936	MM T	0.1883	308.80807	27.33491	3.0767
2	8.386	MM T	0.2871	9728.26172	564.76520	96.9233



In a 10 mL flask **2a** (102 mg, 0.5 mmol) was dissolved in 3 mL anhydrous dichloromethane. This mixture was stirred at 0 °C for 10 min, then diisopropylethylamine (5 eq.) and MOMCl (5 eq.) were sequentially added dropwise into the mixture at the same temperature. After being stirred for 12 hours at room temperature, 10 mL of saturated

ammonium chloride solution was added. The mixture was extracted with dichloromethane (10 mL × 3) and the combined organic phase was dried over sodium sulfate. After concentration *in vavuo*, the residue was purified by flash chromatography to give the **2a-MOM**

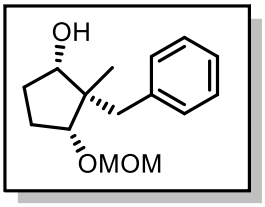
(*2R,3R*)-2-benzyl-3-(methoxymethoxy)-2-methylcyclopentan-1-one (**2a-MOM**)



Colorless oil. 99% yield (142 mg), (> 99% ee, dr 93/7). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 9.8, 5.0 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 3H), 4.84 (d, *J* = 6.8 Hz, 1H), 4.73 (d, *J* = 6.8 Hz, 1H), 3.90 (t, *J* = 4.9 Hz, 1H), 3.44 (s, 3H), 3.00 (d, *J* = 13.7 Hz, 1H), 2.79 (d, *J* = 13.7 Hz, 1H), 2.42 – 2.33 (m, 1H), 2.28 (ddd, *J* = 19.2, 9.0, 5.5 Hz, 1H), 2.07 (ddd, *J* = 16.4, 10.9, 6.5 Hz, 1H), 1.99 (dq, *J* = 10.0, 5.2 Hz, 1H), 0.94 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 219.85, 138.09, 130.60, 128.09, 126.37, 96.35, 83.42, 56.11, 54.27, 36.50, 34.34, 25.02, 20.41. *m/z* (ESI–MS): calc.271.1305 $[M+Na]^+$, found 271.1301 [M+Na]

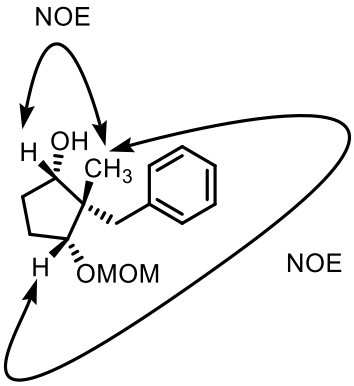
The reduction of **2a-MOM** was performed with the same procedure as reduction of **2a**.

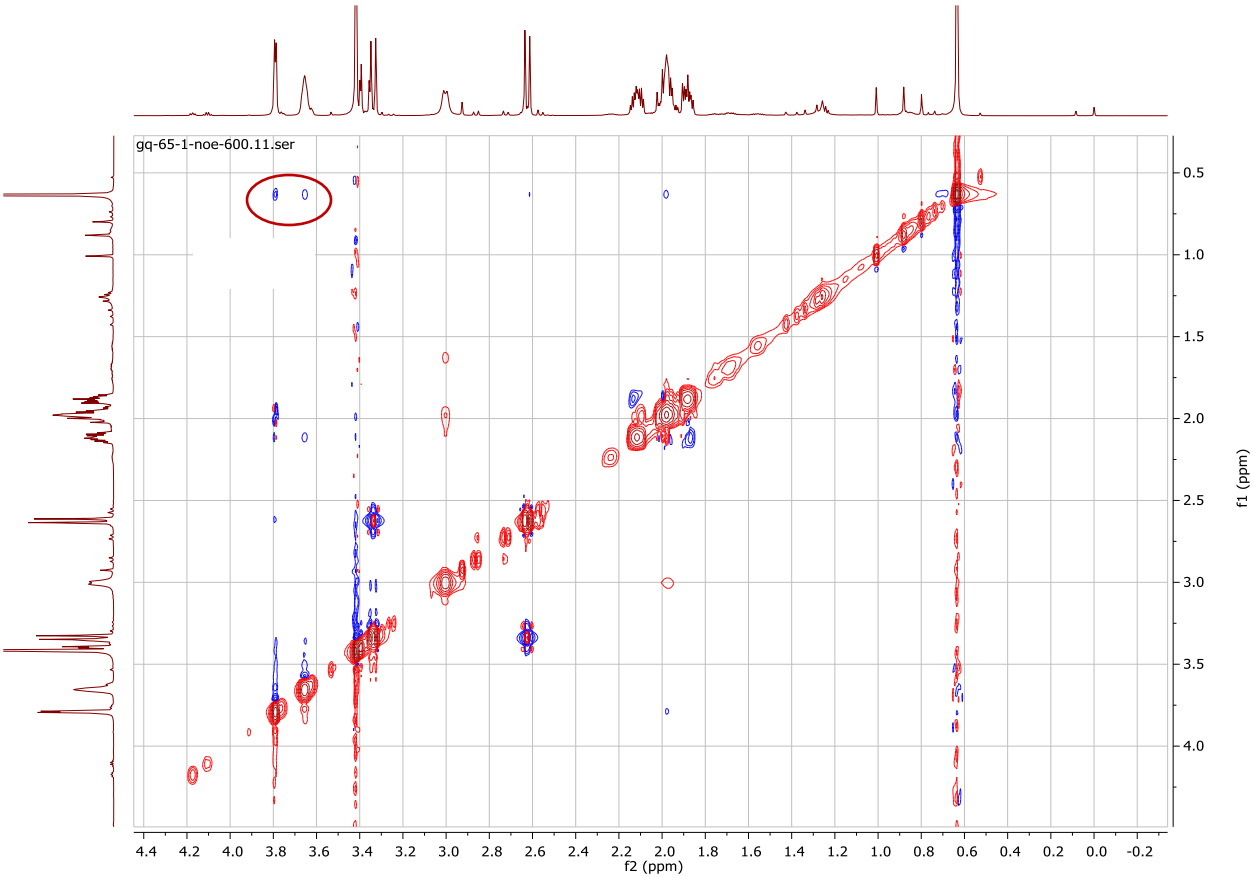
(*1S,2S,3R*)-2-benzyl-3-(methoxymethoxy)-2-methylcyclopentan-1-ol (***cis*-3a-MOM**)



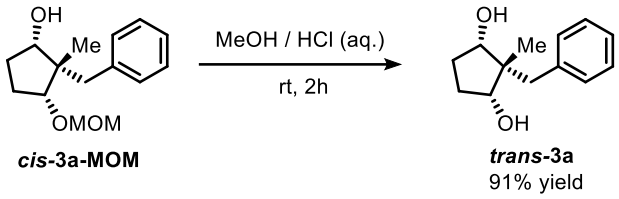
Colorless oil. 99% yield (142 mg), (dr 93/7). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.1 Hz, 2H), 7.30 – 7.24 (m, 2H), 7.22 – 7.16 (m, 1H), 4.79 – 4.74 (m, 1H), 4.63 (d, *J* = 6.8 Hz, 1H), 3.81 (d, *J* = 4.1 Hz, 1H), 3.67 (dd, *J* = 11.4, 5.7 Hz, 1H), 3.43 (s, 3H), 3.34 (d, *J* = 13.4 Hz, 1H), 2.98 (d, *J* = 11.4 Hz, 1H), 2.63 (d, *J* = 13.4 Hz, 1H), 2.18 – 2.08 (m, 1H), 2.02 – 1.96 (m, 2H), 1.93 – 1.85 (m, 1H), 0.65 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.77, 130.63, 128.08, 125.90, 95.47, 86.66, 79.22, 56.09, 51.54, 36.89, 32.35, 28.50, 21.24. *m/z* (ESI–MS): calc. 273.1461 $[M+Na]^+$, found 273.1458 $[M+Na]^+$.

The absolute configuration of was determined by (Nuclear Overhauser effect) NOESY NMR spectroscopy.



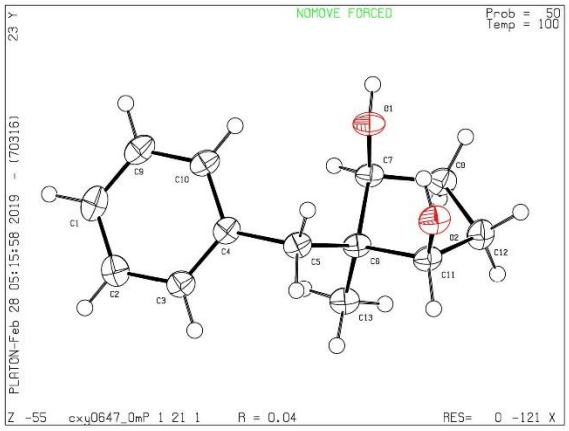


In addition, the absolute configuration could also be confirmed by the single crystal data of the corresponding diol after removal of MOM.

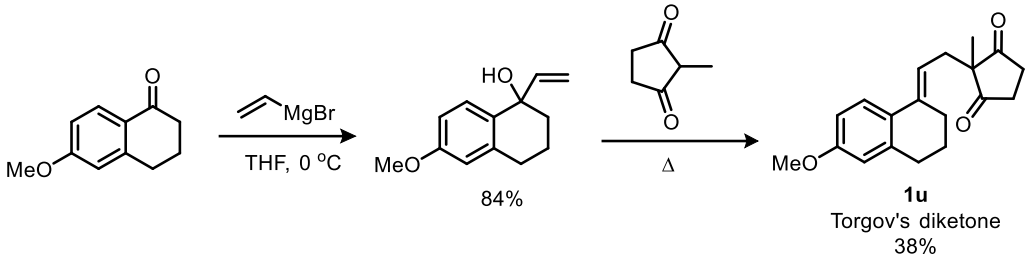


***cis*-3a-MOM**

***trans*-3a**
91% yield



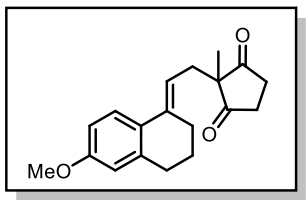
6. Application of desymmetrization in the synthesis of estrone.



To an ice-cooled solution of vinyl magnesium bromide (1 M in THF, 3.8 equiv, 85 mL), a 0.57 M solution of ketone (3.92 g, 22.2 mmol) in THF was added dropwise. After complete addition, the ice-bath was removed and the reaction was stirred at 40 °C for 6 h. The reaction mixture was then cooled to 0 °C and a saturated aqueous solution of NH4Cl was carefully added, followed by EtOAc. The layers were separated and the aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with brine, dried over MgSO4 and concentrated in vacuo. The residue was purified by flash chromatography (hexane/EtOAc) and the vinyl carbinol was obtained 3.8 g (84% yield) as a colorless liquid. The characterization data were in accordance with literature.

The vinyl carbinol (2 g, 10 mmol) was dissolved in a 2/1 mixture of xylene/^{t}BuOH (c = 0.6 M). 2-methylcyclopentane-1,3-dione (1.68 g, 15 mmol) was added and, after stirring 15 min at room temperature, a 40% solution of Triton B in MeOH (0.2 equiv) was added. The mixture was stirred under reflux for 5 h. At 0 °C Et_2O (5 mL/1 mmol of SM) was added and the mixture was stirred at 0 °C for 30 min. The mixture was filtrated and washed with Et_2O. The combined filtrates were washed with a 5% potassium hydroxide solution and with water, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography (hexane/EtOAc), and then Torgov's diketone was obtained (1.13 g, 38% yield) as a white solid.

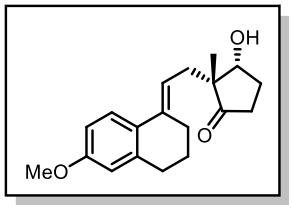
(*E*)-2-(2-(6-methoxy-3,4-dihydronaphthalen-1(2H)-ylidene)ethyl)-2-methylcyclopentane-1,3-dione (**1u**, Torgov's diketone)[1]



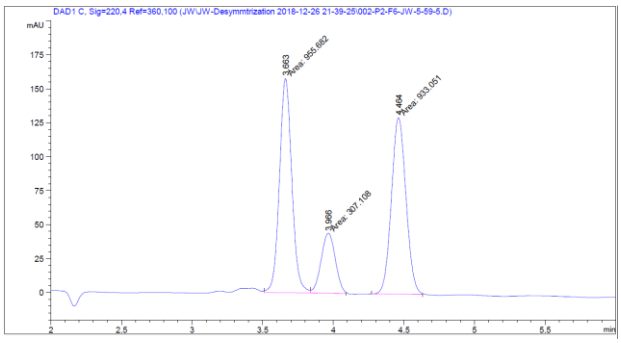
White solid, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.8 Hz, 1H), 6.69 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.59 (d, *J* = 2.7 Hz, 1H), 5.64 (t, *J* = 8.1 Hz, 1H), 3.77 (s, 3H), 2.76 – 2.67 (m, 6H), 2.55 (d, *J* = 8.1 Hz, 2H), 2.45 – 2.40 (m, 2H), 1.81 – 1.73 (m, 2H), 1.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.13, 158.98, 139.25, 138.26, 128.43, 125.24, 114.12, 113.30, 112.63, 57.27, 55.35, 35.75, 35.30, 30.74, 26.58, 23.41, 18.98.

Desymmetrization of **1u** via hydrogenation was performed using the standard procedure with 0.1 mol% catalyst. The reaction mixture was concentrated and the crude product **2u** was of high purity which was used directly for the next step.

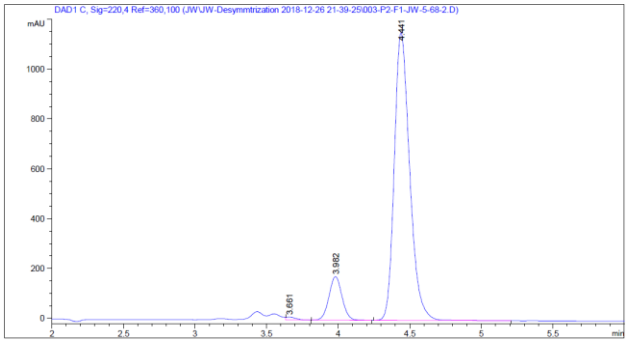
(2*R*,3*R*)-3-hydroxy-2-(2-((*E*)-6-methoxy-3,4-dihydronaphthalen-1(2H)-ylidene)ethyl)-2-methylcyclopentan-1-one (**2u**)[1]



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.7 Hz, 1H), 6.72 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.62 (d, *J* = 2.7 Hz, 1H), 6.00 – 5.87 (m, 1H), 4.19 (dt, *J* = 5.5, 3.0 Hz, 1H), 3.79 (s, 3H), 2.75 (t, *J* = 6.2 Hz, 2H), 2.56 – 2.40 (m, 4H), 2.40 – 2.29 (m, 1H), 2.22 (dtd, *J* = 14.1, 9.1, 4.9 Hz, 1H), 2.05 – 1.95 (m, 1H), 1.82 (dt, *J* = 7.5, 5.6 Hz, 3H), 1.62 (s, 1H), 1.06 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 221.05, 158.57, 138.81, 136.73, 128.86, 125.08, 116.51, 113.11, 112.53, 77.44, 55.26, 53.92, 34.13, 30.75, 29.41, 27.87, 26.76, 23.22, 19.97. HPLC (Daicel Chiralpak IE-3, hexanes/i-PrOH = 80/20, Flow rate = 0.5 ml/min, UV = 220 nm): t_1 = 3.6 min, t_2 = 4.0 min, t_3 = 4.5 min.



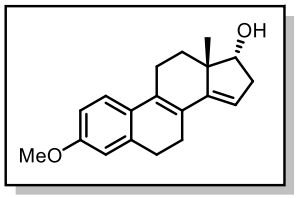
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.663	MM	0.1008	955.68195	158.04115	43.5224
2	3.966	MM	0.1156	307.10831	44.26190	13.9859
3	4.464	MM	0.1195	933.05090	130.10844	42.4917



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.661	VB	0.0746	50.31933	10.37135	0.5140
2	3.982	BB	0.0977	1103.05615	174.60709	11.2672
3	4.441	BB	0.1152	8636.56152	1155.80176	88.2188

To a solution of this hydroxy ketone **2u** in MeOH (7 mL) was added a solution of HCl (1.0 M in ^{i}PrOH, 1 eq.) at 23 °C. The resulting solution was heated at 60 °C for 1 h. After cooling to room temperature, the volatile was removed under vacuum, and the solid residue was purified by flash chromatography to give an alcohol **3u** as a white foam.

(13*S*,17*R*)-3-methoxy-13-methyl-7,11,12,13,16,17-hexahydro-6H-cyclopenta[a]phenanthren-17-ol (**3u**)[1]

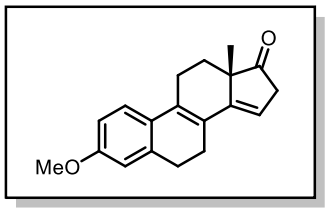


White foam, 80% yield (451 mg) for two steps. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.27 – 7.24 (m, 1H), 6.75 (dt, *J* = 8.5, 1.7 Hz, 1H), 6.73 – 6.70 (m, 1H), 5.58 (s, 1H), 4.01 (d, *J* = 4.5 Hz, 1H), 3.81 (d, *J* = 1.4 Hz, 3H), 2.98 (dt, *J* = 18.2, 2.9 Hz, 1H), 2.79 – 2.72 (m, 2H), 2.66 (d, *J* = 8.3 Hz, 2H), 2.61 – 2.55 (m, 1H), 2.37 – 2.25 (m, 2H), 2.03 – 1.96 (m, 1H), 1.72 – 1.67 (m, 1H), 1.51 (br, 1H) 0.94 (d, *J* = 1.4 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.37, 146.17, 138.06, 129.47, 129.27, 126.13, 124.01, 117.19, 113.45, 111.08, 79.91, 55.29, 48.29, 40.83, 28.60, 26.95, 23.65, 23.57, 20.97.

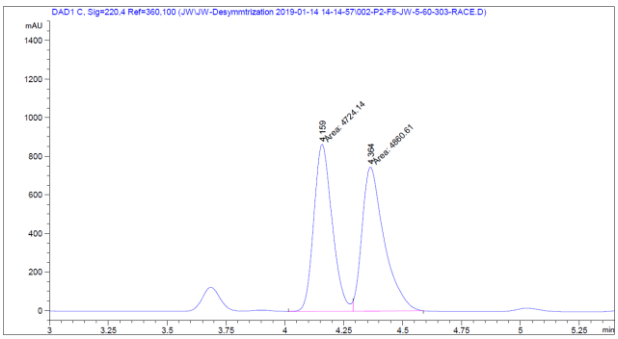
To a solution of the above alcohol (451 mg, 1.6 mmol) in DMSO (10 mL) was added 1-hydroxy-1,2-benziodoxol-3(1*H*)-one (3.2 mmol) at 23 °C. After stirring for 2 h at the same temperature, the solution was clear and diluted with EtOAc (10 mL × 2). Water (10 mL) was added slowly to the vigorously stirred mixture giving a white precipitate which was removed by filtration. The filtrate was extracted with EtOAc (10 mL × 2). The combined

extracts were washed with brine (10 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica, hexanes/EtOAc) to give Torgov's diene **4u** as a white solid.

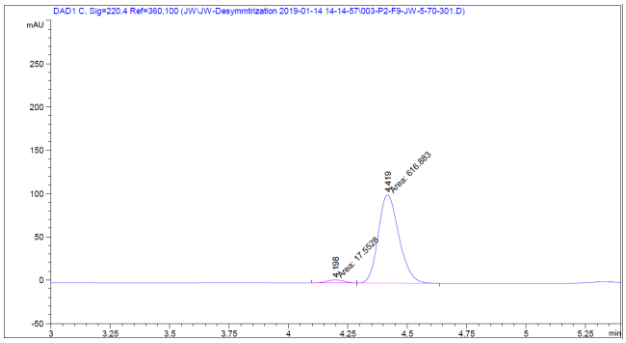
(*S*)-3-methoxy-13-methyl-6,7,11,12,13,16-hexahydro-17H-cyclopenta[a]phenanthren-17-one (**4u**, Torgov's diene)[1]



White solid, 86% yield (387 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (s, 1H), 6.76 (d, *J* = 2.8 Hz, 1H), 6.74 – 6.70 (m, 3H), 5.86 (t, *J* = 2.7 Hz, 2H), 3.82 (s, 6H), 3.32 (dd, *J* = 23.8, 2.0 Hz, 2H), 2.99 – 2.86 (m, 2H), 2.84 – 2.76 (m, 4H), 2.69 – 2.55 (m, 5H), 2.38 – 2.24 (m, 2H), 2.04 (ddd, *J* = 12.9, 4.7, 2.6 Hz, 2H), 1.64 – 1.54 (m, 5H), 1.14 (s, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 220.05, 158.67, 146.92, 138.19, 129.87, 128.61, 125.34, 124.14, 114.69, 113.63, 111.15, 55.30, 49.07, 41.98, 28.46, 27.35, 22.98, 22.77, 20.62. HPLC (Daicel Chiralpak IE-3, hexanes/i-PrOH = 95/5, Flow rate = 0.5 ml/min, UV = 220 nm): t_1 = 4.2 min, t_2 = 4.4 min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.159	MF	0.0907	4724.14355	868.53351	49.2881
2	4.364	FM	0.1081	4860.60547	749.38263	50.7119



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.198	MM	0.0832	17.55283	3.51576	2.7667
2	4.419	MM	0.1004	616.88312	102.36624	97.2333

7. Single crystal data for 2a, 2s and *cis*-3a

Single crystal of **2a** was obtained from hexane/EtOAc, for more details see the cif file.

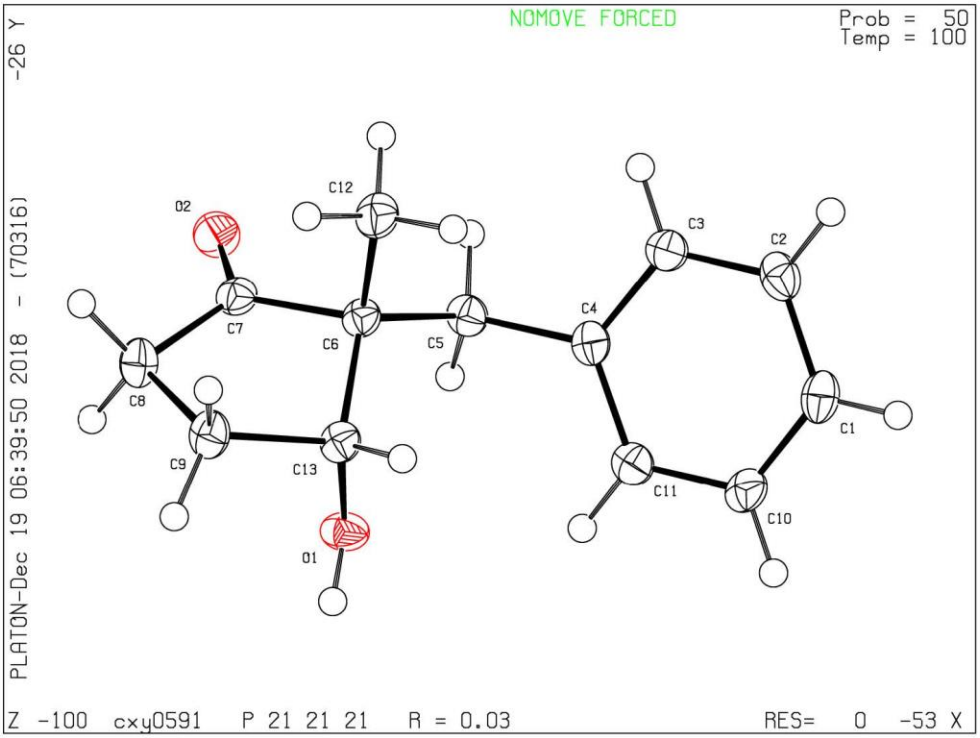


Table S5. Crystal data and structure refinement for **2a**.

Identification code	cxy0591
Empirical formula	C13H16O2
Formula weight	204.26
Temperature/K	100.01
Crystal system	orthorhombic
Space group	P212121
a/Å	6.2989(3)
b/Å	10.0377(5)
c/Å	17.5539(9)
α/°	90
β/°	90
γ/°	90
Volume/Å3	1109.87(10)
Z	4
ρcalcg/cm3	1.222
μ/mm-1	0.644
F(000)	440.0
Crystal size/mm3	0.42 × 0.35 × 0.26

Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	10.078 to 137.212
Index ranges	-7 ≤ h ≤ 7, -12 ≤ k ≤ 10, -20 ≤ l ≤ 18
Reflections collected	16724
Independent reflections	2026 [Rint = 0.0406, Rsigma = 0.0207]
Data/restraints/parameters	2026/0/139
Goodness-of-fit on F2	1.098
Final R indexes [I>=2σ (I)]	R1 = 0.0268, wR2 = 0.0675
Final R indexes [all data]	R1 = 0.0269, wR2 = 0.0676
Largest diff. peak/hole / e Å-3	0.19/-0.12
Flack parameter	-0.09(8)

Table S6. Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for cxy0591. Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

Atom	x	y	z	U(eq)
O1	101.7(17)	5983.9(11)	2939.3(7)	24.1(3)
O2	5888.9(18)	6772.6(12)	2688.6(6)	26.5(3)
C1	164(3)	3745.2(15)	5800.7(9)	24.3(4)
C2	2186(3)	4282.8(16)	5884.3(10)	25.0(4)
C3	3279(3)	4754.8(15)	5251.3(9)	21.9(4)
C4	2380(3)	4701.9(14)	4523.9(9)	19.0(3)
C5	3558(3)	5212.5(15)	3831.1(9)	20.0(4)
C6	3095(2)	6687.5(15)	3651.7(8)	18.1(4)
C7	4200(2)	7176.0(15)	2931.3(9)	19.5(3)
C8	2885(3)	8261.5(16)	2560.9(9)	23.8(4)
C9	856(3)	8345.8(15)	3042.4(9)	23.4(4)
C10	-744(3)	3676.1(15)	5080.5(9)	23.0(4)
C11	353(2)	4157.8(14)	4450.7(9)	21.3(4)
C12	3906(3)	7595.7(16)	4295.6(9)	24.5(4)
C13	775(2)	6995.3(14)	3458.1(9)	19.5(3)

Single crystal of **2s** was obtained from hexane/EtOAc, for more details see the cif file.

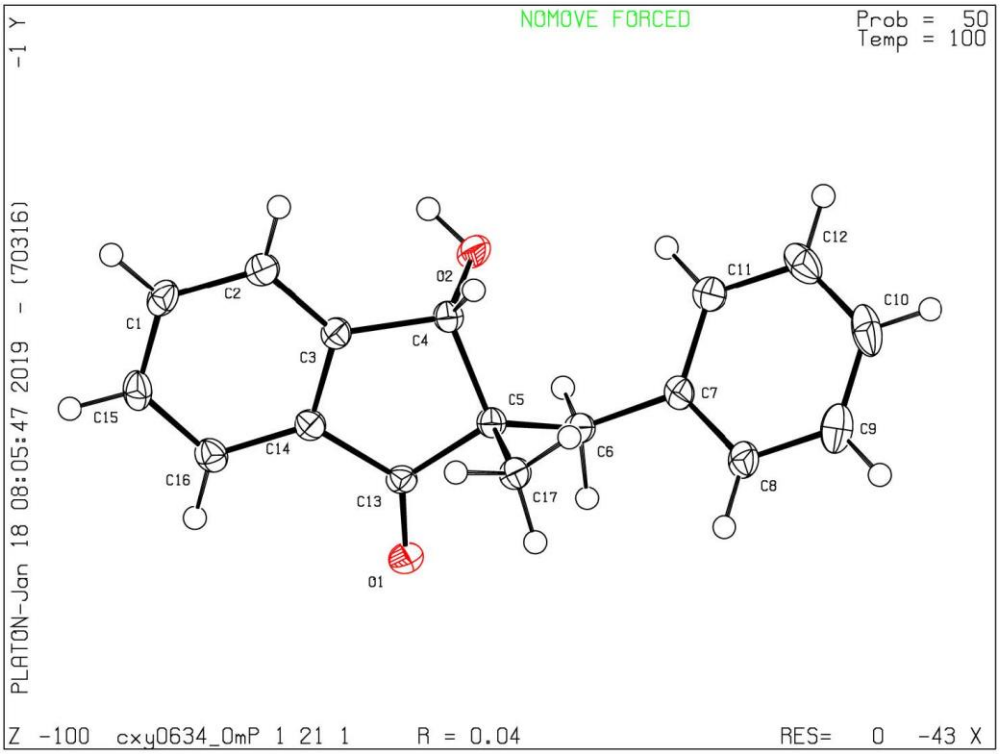


Table S7. Crystal data and structure refinement for **2s**.

Identification code	cxy0634_0m
Empirical formula	C17H16O2
Formula weight	252.30
Temperature/K	100
Crystal system	monoclinic
Space group	P21
a/Å	6.1412(2)
b/Å	6.7002(3)
c/Å	15.7738(6)
α/°	90
β/°	94.466(2)
γ/°	90
Volume/Å3	647.08(4)
Z	2
ρcalcg/cm3	1.295
μ/mm-1	0.664
F(000)	268.0
Crystal size/mm3	0.42 × 0.29 × 0.28
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.62 to 136.184

Index ranges	$-6 \leq h \leq 7$, $-8 \leq k \leq 8$, $-18 \leq l \leq 18$
Reflections collected	7757
Independent reflections	2302 [Rint = 0.0475, Rsigma = 0.0474]
Data/restraints/parameters	2302/1/175
Goodness-of-fit on F2	1.050
Final R indexes [I>=2σ (I)]	R1 = 0.0392, wR2 = 0.1028
Final R indexes [all data]	R1 = 0.0398, wR2 = 0.1039
Largest diff. peak/hole / e Å-3	0.21/-0.19
Flack parameter	0.40(17)

Table S8. Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for cxy0634_0m. Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

Atom	x	y	z	U(eq)
O1	-368(3)	5340(3)	1212.3(11)	21.4(4)
O2	6130(3)	4065(3)	2138.1(13)	26.8(5)
C1	6052(4)	10111(4)	965.9(16)	22.1(5)
C2	6415(4)	8762(4)	1632.0(16)	20.4(5)
C3	4791(4)	7384(4)	1777.3(15)	17.5(5)
C4	4843(4)	5677(4)	2411.5(15)	19.0(6)
C5	2417(4)	5024(4)	2410.9(15)	17.0(5)
C6	1996(4)	2759(4)	2458.0(15)	17.8(5)
C7	2526(4)	1804(4)	3317.3(15)	17.8(5)
C8	936(4)	1667(4)	3899.1(17)	22.1(6)
C9	1390(5)	734(4)	4683.8(17)	29.9(7)
C10	3419(5)	-93(4)	4891.6(18)	32.4(7)
C11	4574(4)	973(4)	3534.6(17)	22.0(6)
C12	5017(5)	20(4)	4314.4(18)	29.1(6)
C13	1395(4)	5843(4)	1559.3(14)	16.3(5)
C14	2844(4)	7397(4)	1263.8(15)	17.7(5)
C15	4080(4)	10103(4)	450.1(16)	22.4(6)
C16	2452(4)	8755(4)	599.4(16)	20.4(6)
C17	1336(4)	6175(4)	3110.2(16)	19.3(5)

Single crystal of ***cis*-3a** was obtained from hexane/EtOAc, for more details see the cif file.

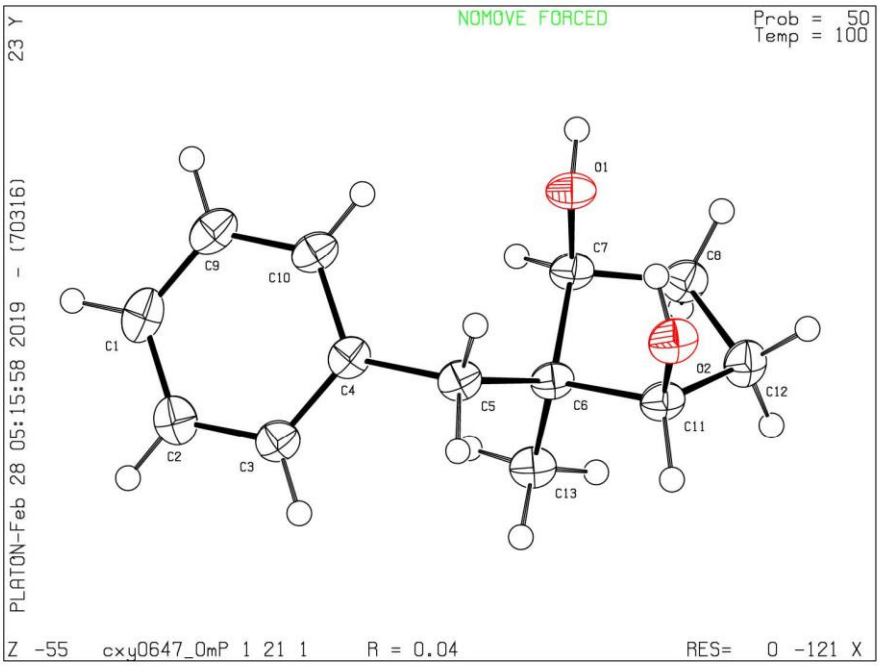


Table S9. Crystal data and structure refinement for ***cis*-3a**.

Identification code	cxy0647_0m
Empirical formula	$C_{13}H_{18}O_2$
Formula weight	206.27
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	6.9109(7)
b/Å	9.9938(9)
c/Å	8.2507(8)
α/°	90
β/°	92.496(5)
γ/°	90
Volume/Å^3	569.30(9)
Z	2
ρ_{calc}g/cm^3	1.203
μ/mm^{-1}	0.628
F(000)	224.0
Crystal size/mm^3	0.36 × 0.32 × 0.25
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	10.732 to 136.98
Index ranges	$-8 \le h \le 8$, $-12 \le k \le 12$, $-9 \le l \le 9$
Reflections collected	7567

Independent reflections	2079 [R_{int} = 0.0493, R_{sigma} = 0.0434]
Data/restraints/parameters	2079/1/139
Goodness-of-fit on F^2	1.123
Final R indexes [I>=2σ (I)]	R_1 = 0.0394, wR_2 = 0.1254
Final R indexes [all data]	R_1 = 0.0417, wR_2 = 0.1315
Largest diff. peak/hole / e $Å^{-3}$	0.17/-0.21
Flack parameter	0.1(2)

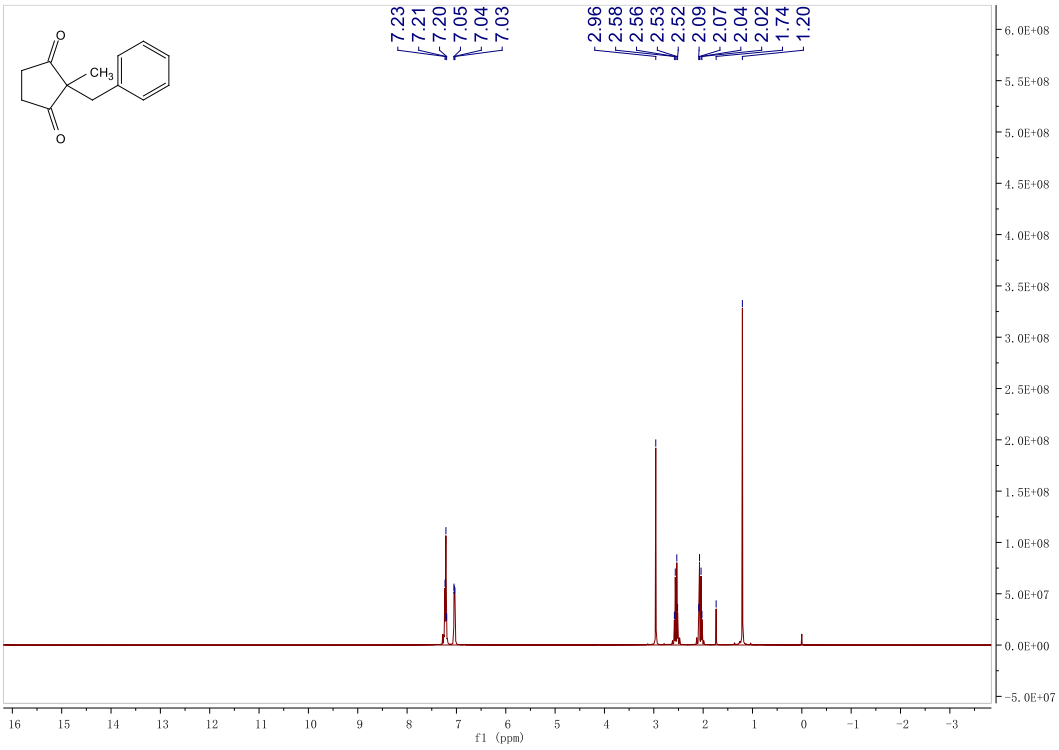
Table S10. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for cxy0647_0m. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O1	9181(2)	4344(2)	4226(2)	28.5(5)
O2	9005(3)	6910.2(18)	5361(2)	31.0(5)
C1	2726(4)	3262(3)	46(3)	33.8(7)
C2	1761(4)	4263(3)	845(3)	32.0(6)
C3	2774(4)	5098(3)	1931(3)	28.0(6)
C4	4764(4)	4945(3)	2246(3)	24.7(6)
C5	5869(4)	5877(3)	3400(3)	25.6(6)
C6	6258(3)	5332(2)	5133(3)	23.4(5)
C7	7563(4)	4086(2)	5223(3)	24.0(6)
C8	8250(4)	4005(3)	7015(3)	29.2(6)
C9	4701(4)	3081(3)	359(3)	31.9(6)
C10	5705(4)	3918(3)	1440(3)	27.6(6)
C11	7445(4)	6322(3)	6223(3)	26.2(6)
C12	8231(4)	5470(3)	7651(3)	30.0(6)
C13	4333(4)	5032(3)	5931(3)	28.2(6)

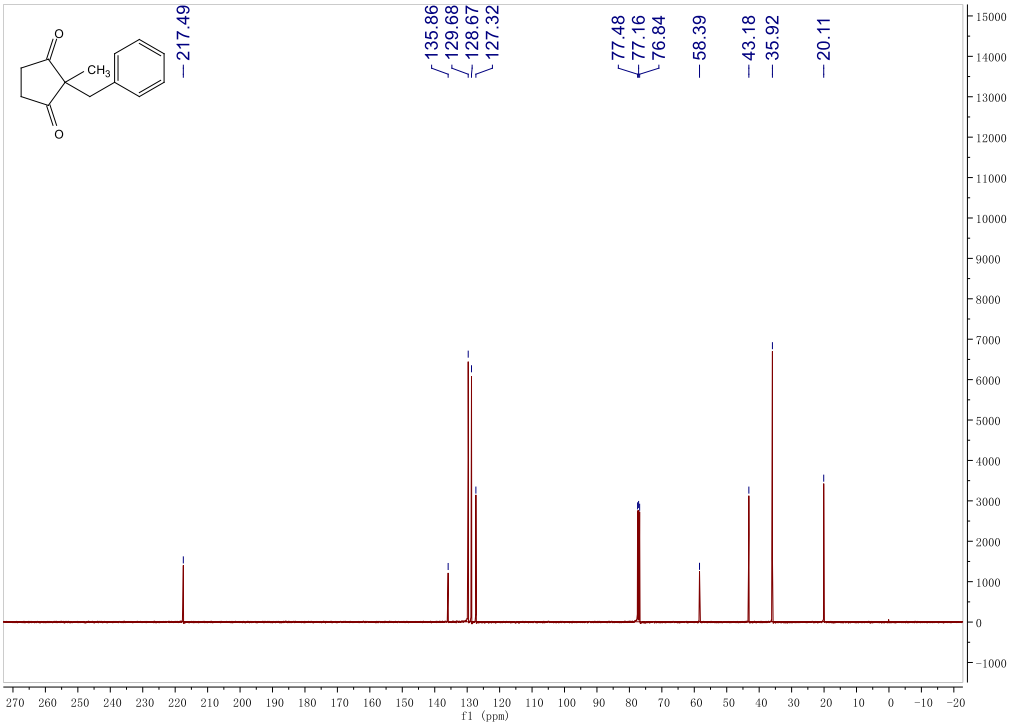
8. NMR spectra of compounds

1a 2-benzyl-2-methylcyclopentane-1,3-dione

^{1}H NMR

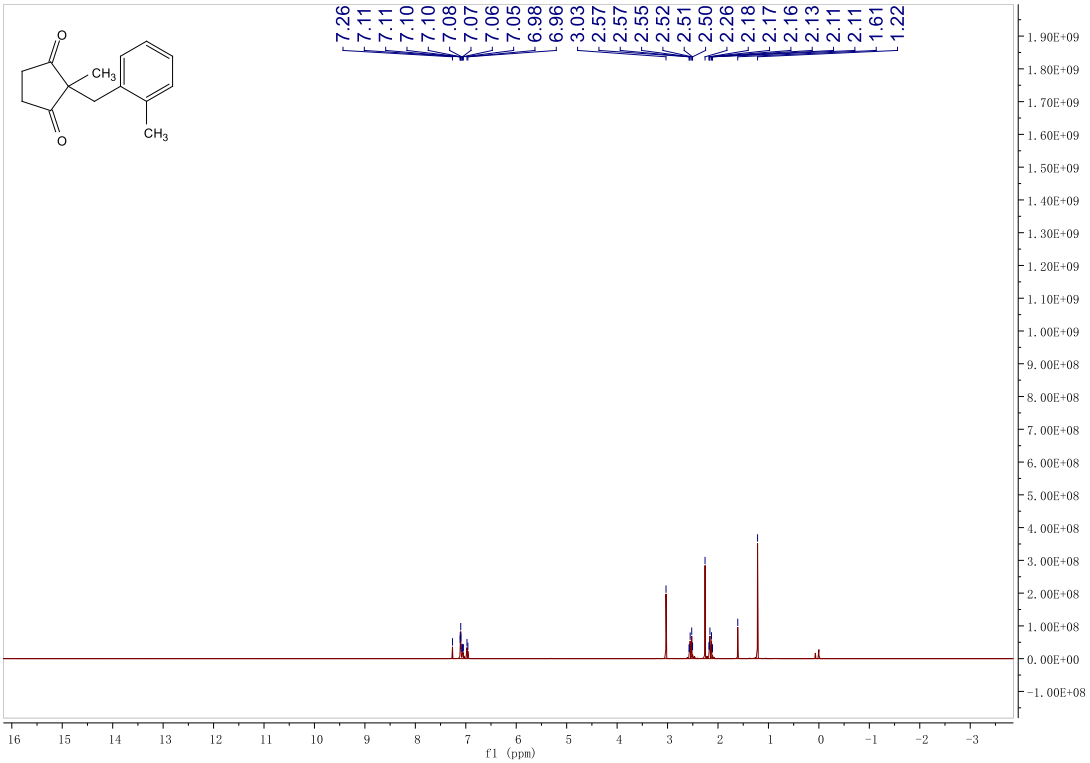


^{13}C NMR

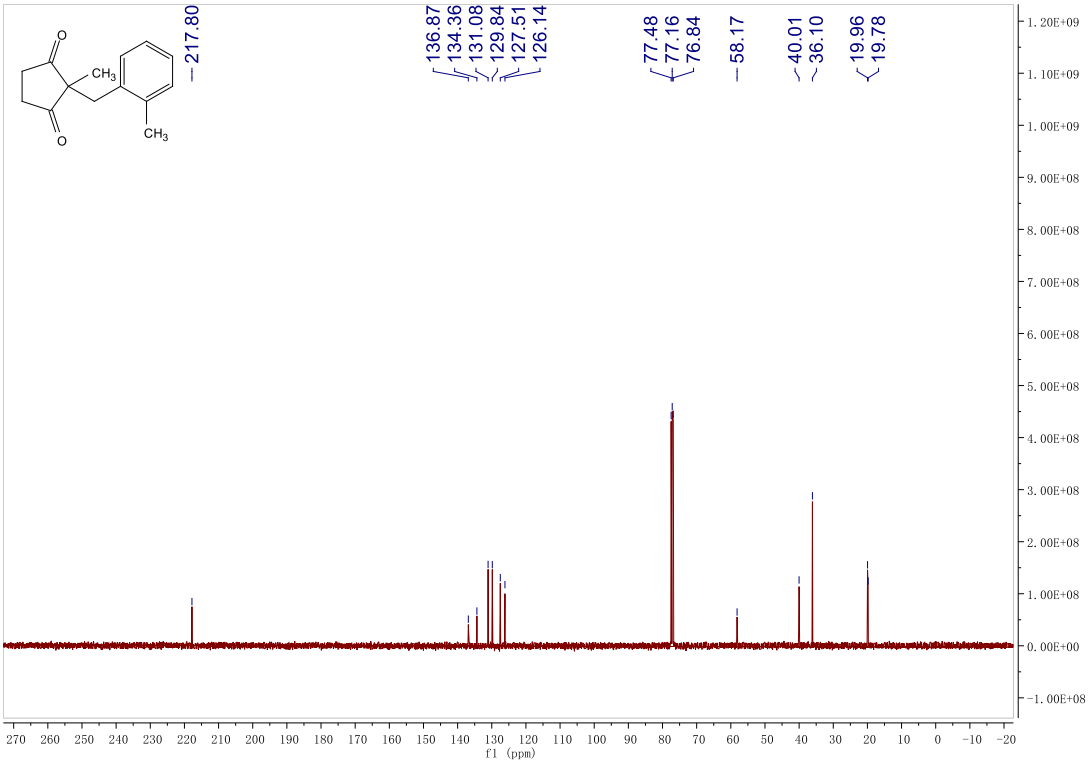


1b 2-methyl-2-(2-methylbenzyl)cyclopentane-1,3-dione

^{1}H NMR

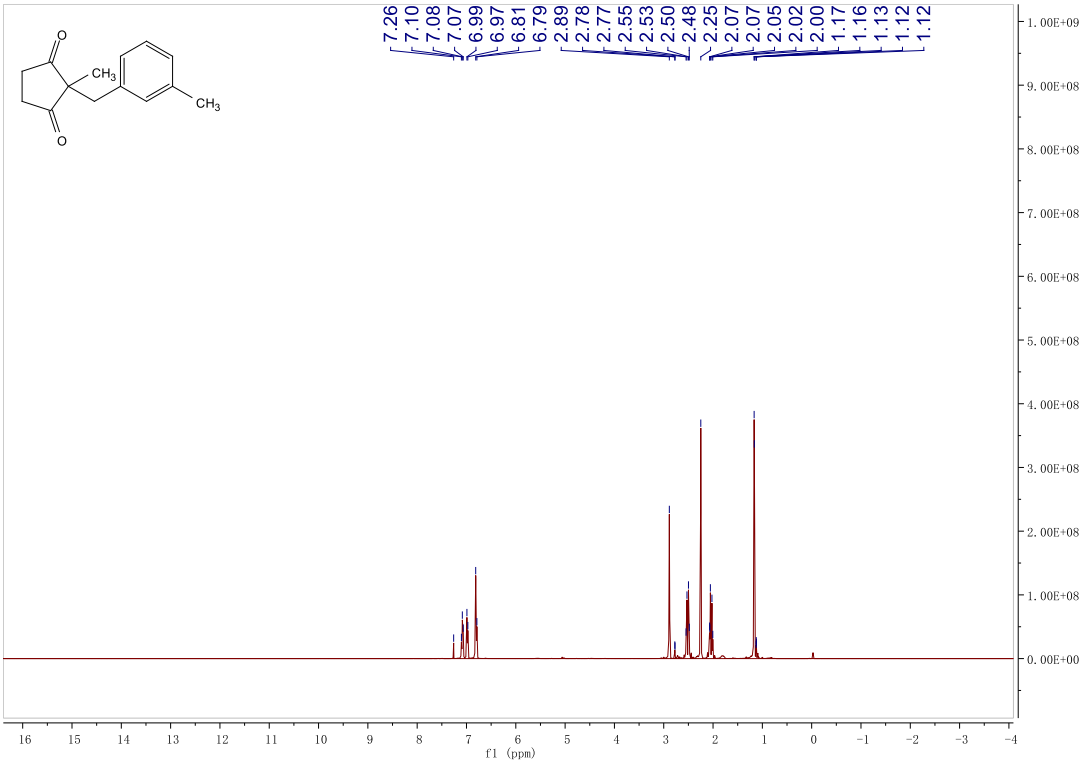


^{13}C NMR

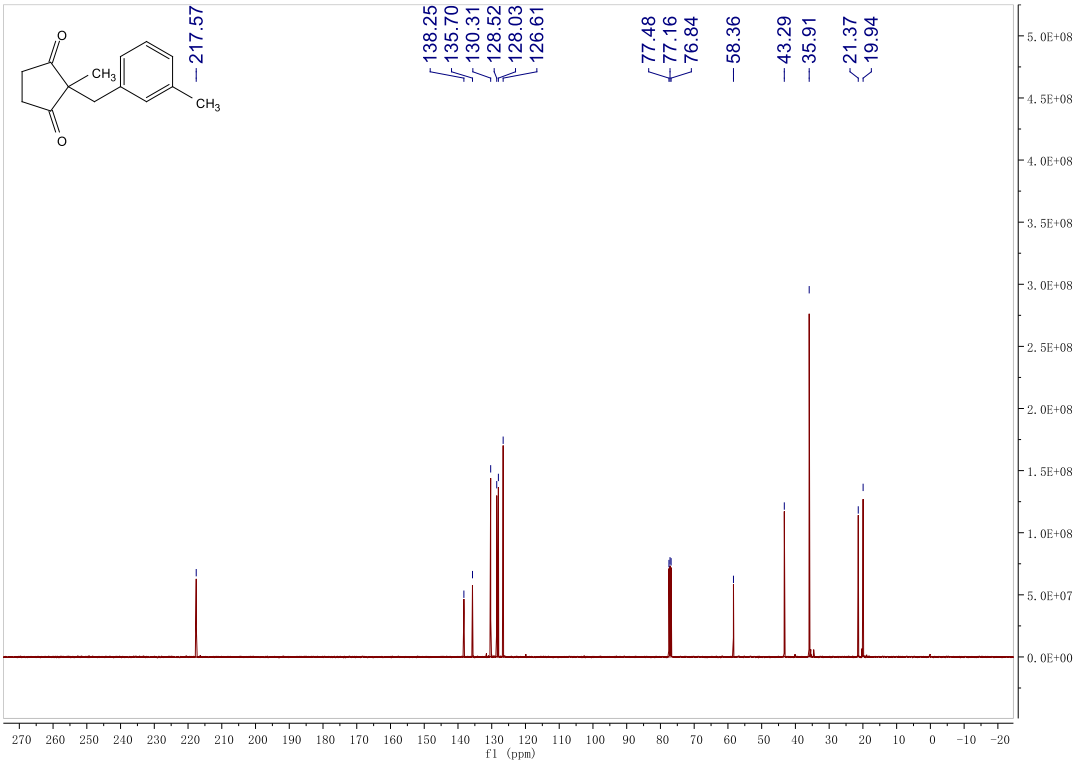


1c 2-methyl-2-(3-methylbenzyl)cyclopentane-1,3-dione

^{1}H NMR

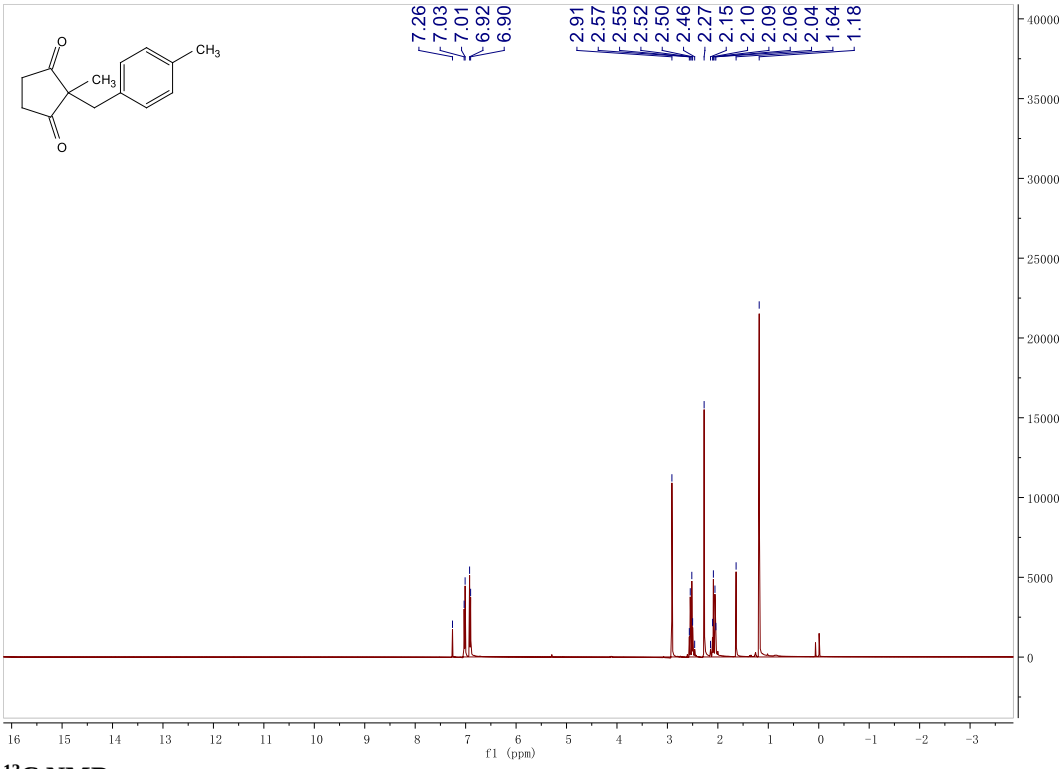


^{13}C NMR

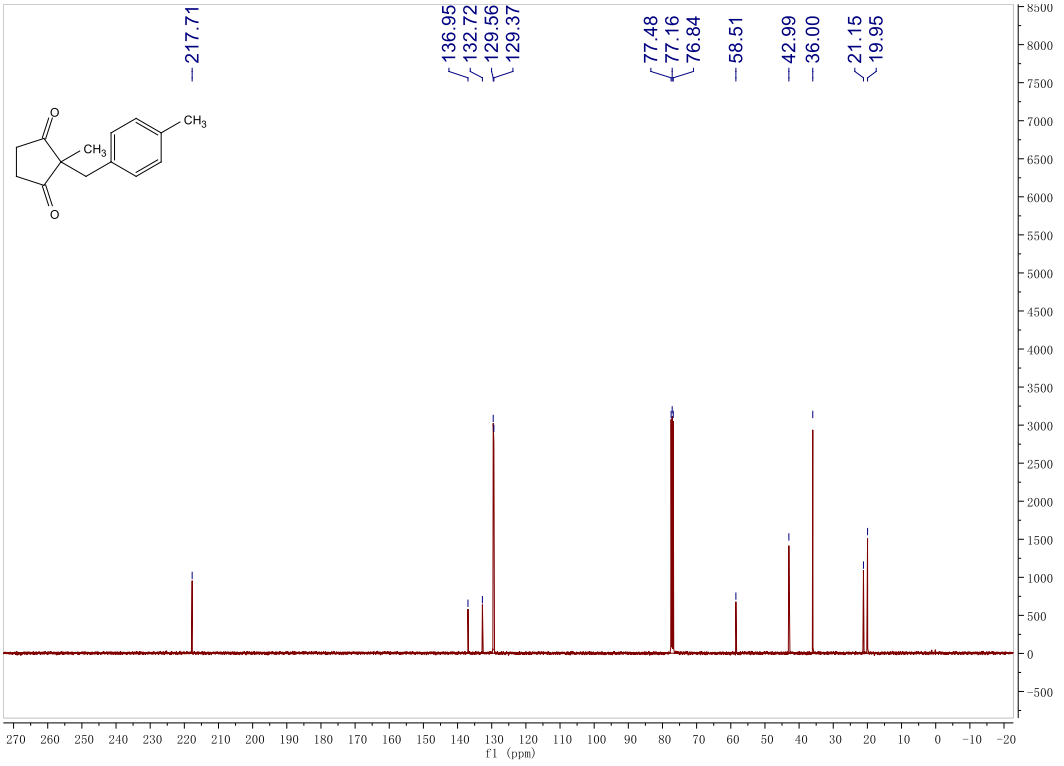


1d 2-methyl-2-(4-methylbenzyl)cyclopentane-1,3-dione

^{1}H NMR

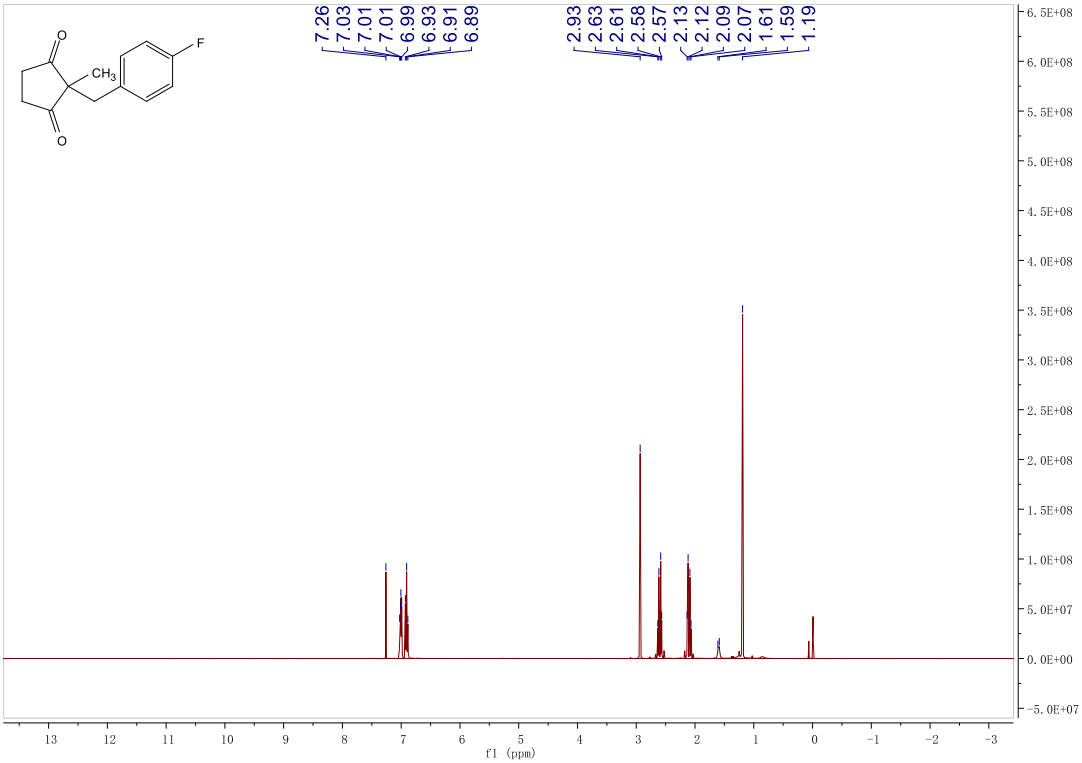


^{13}C NMR

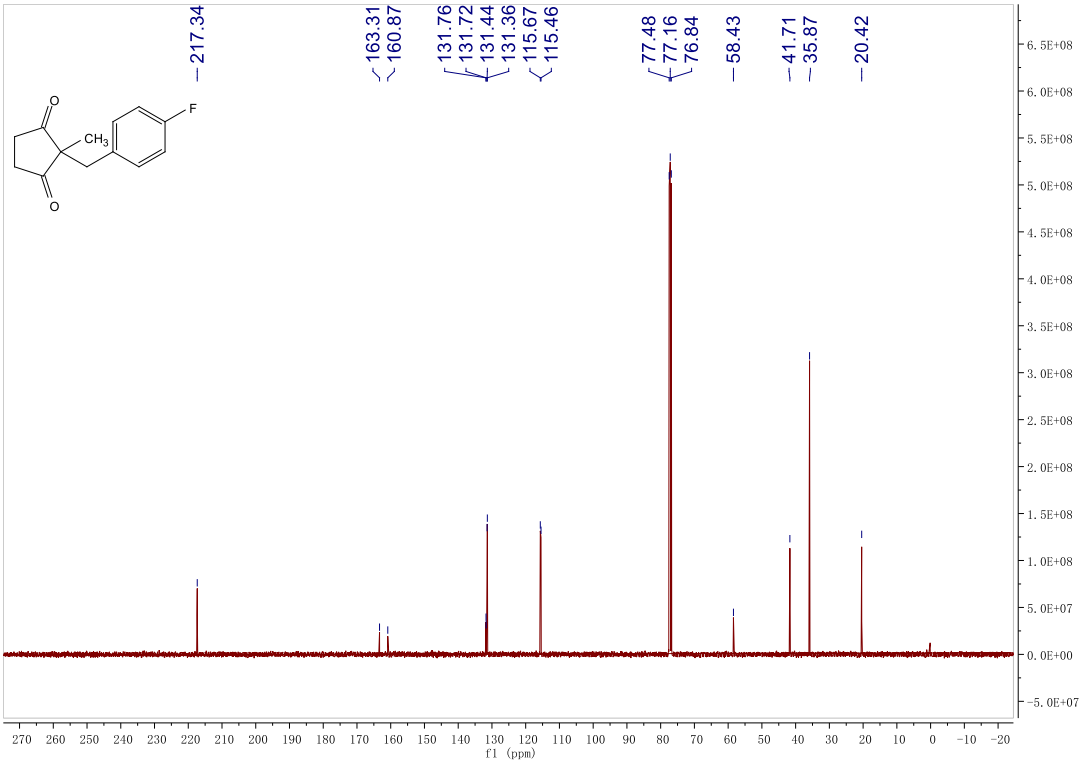


1e 2-(4-fluorobenzyl)-2-methylcyclopentane-1,3-dione

^{1}H NMR

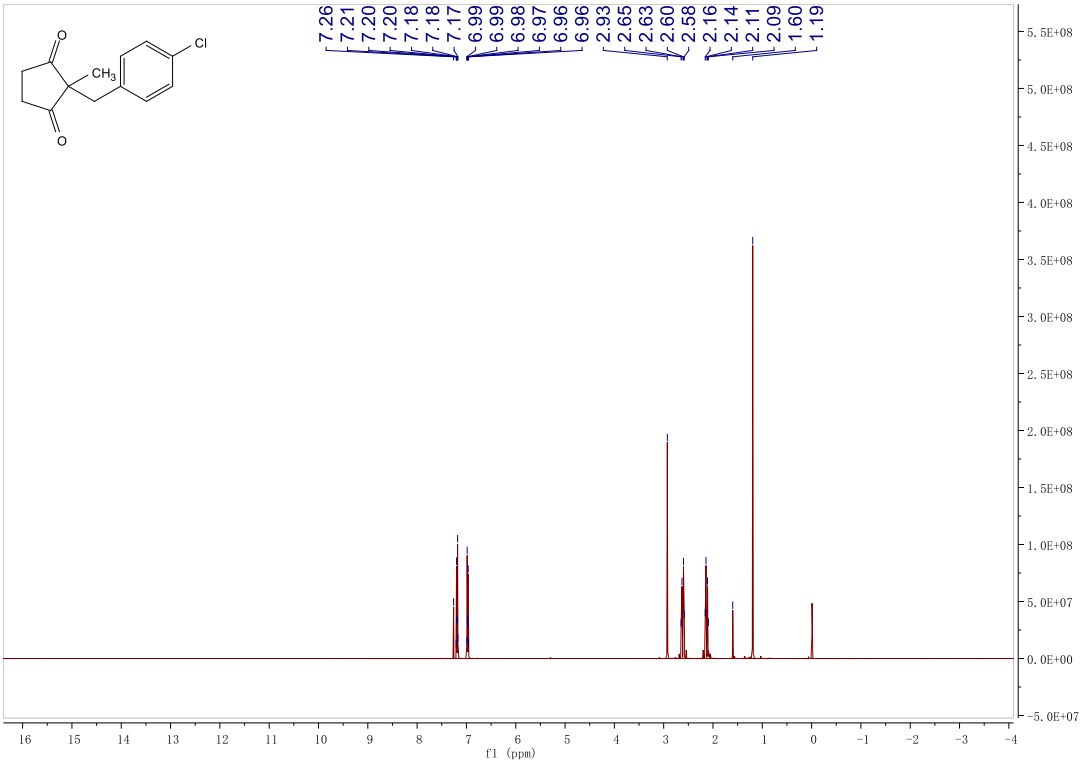


^{13}C NMR

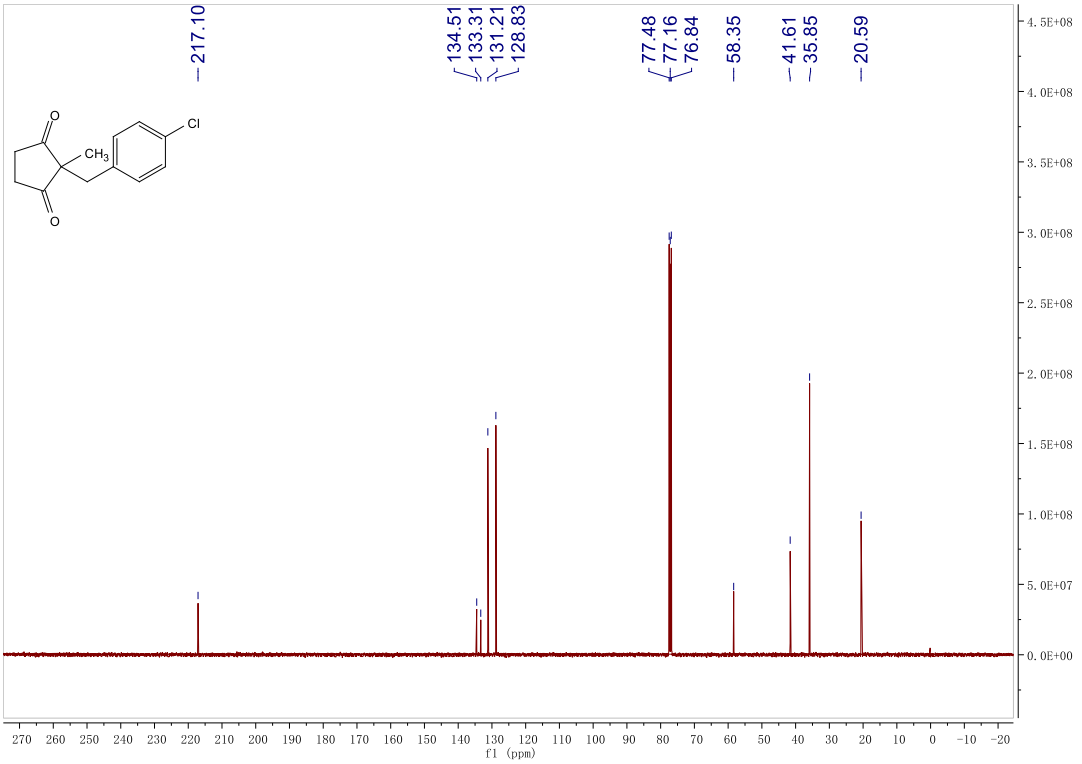


1f 2-(4-chlorobenzyl)-2-methylcyclopentane-1,3-dione

^{1}H NMR

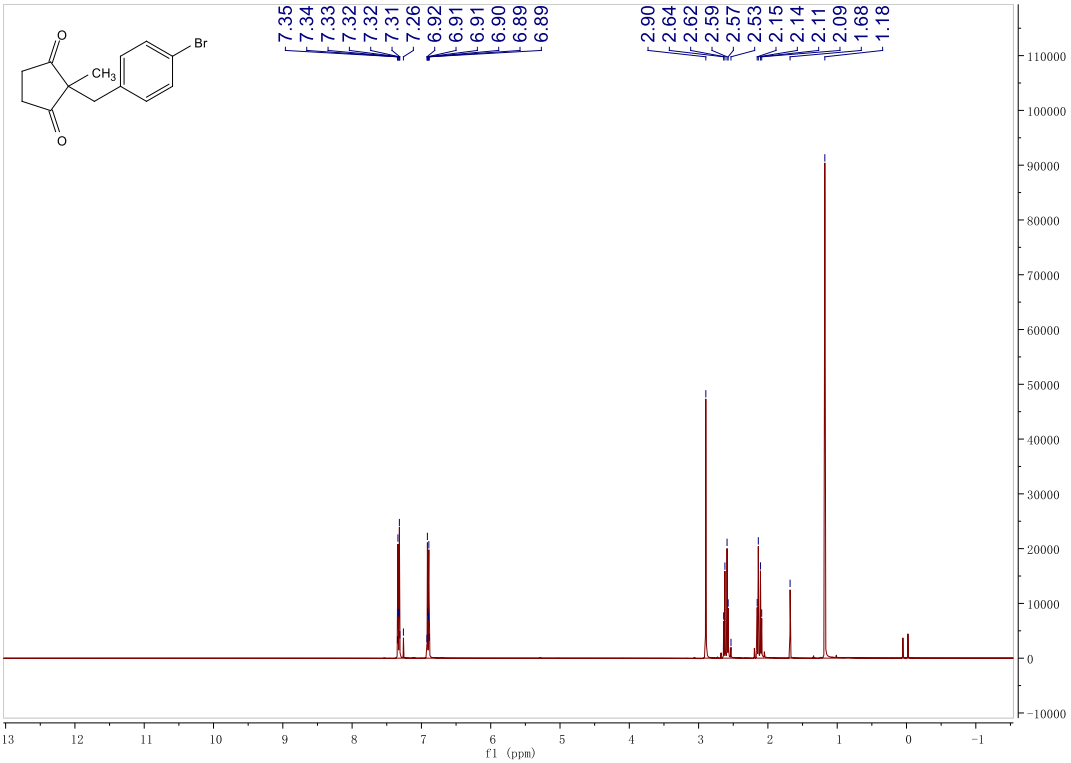


^{13}C NMR

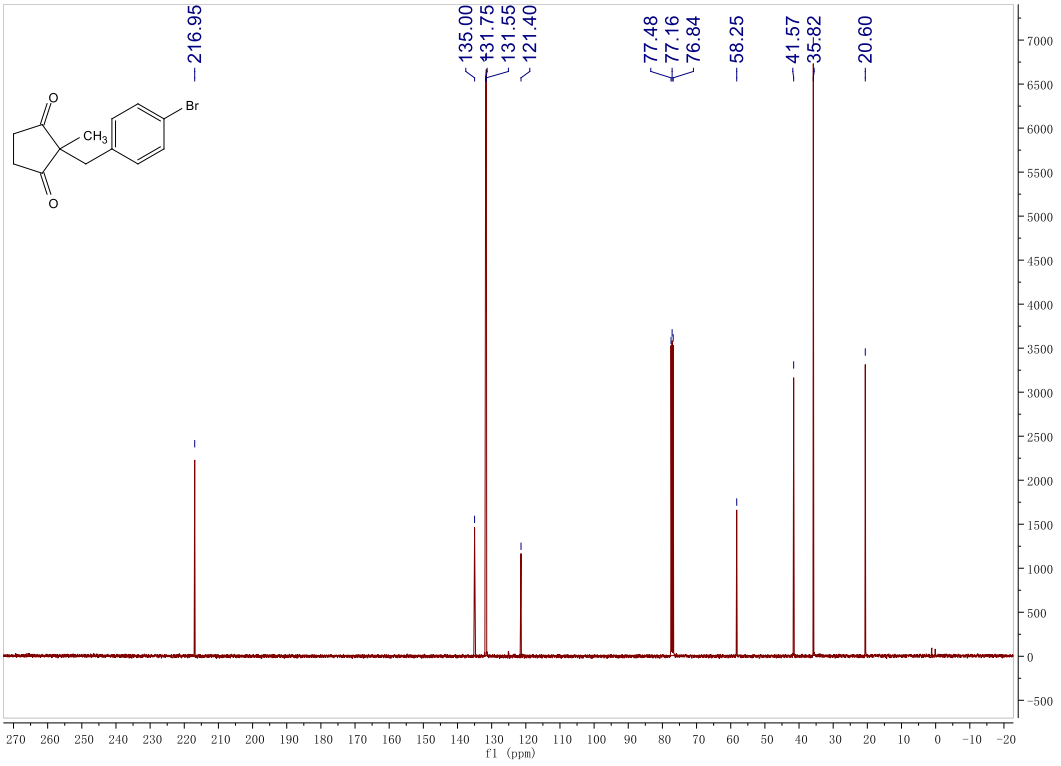


1g 2-(4-bromobenzyl)-2-methylcyclopentane-1,3-dione

^{1}H NMR

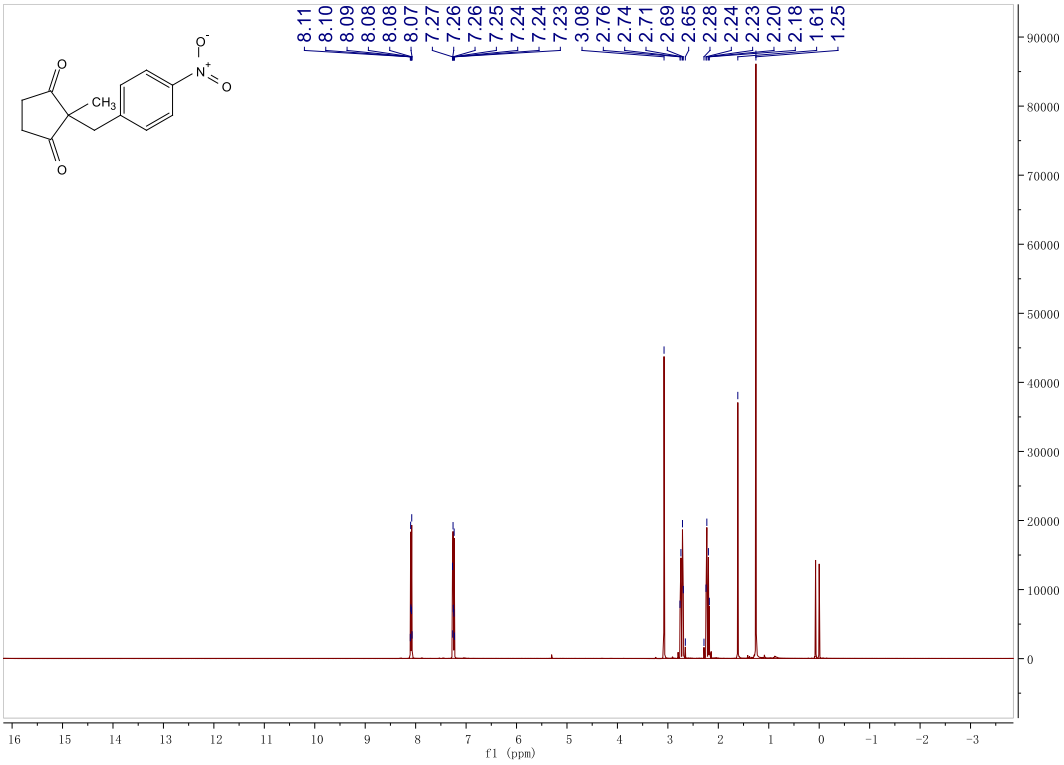


^{13}C NMR

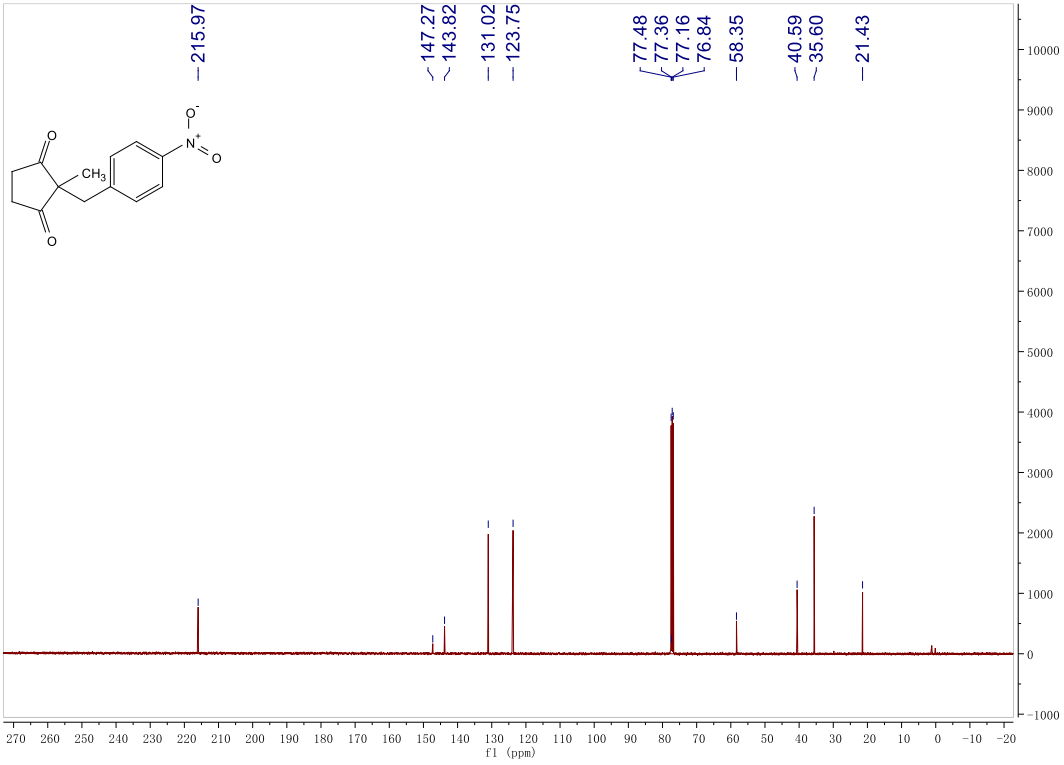


1h 2-methyl-2-(4-nitrobenzyl)cyclopentane-1,3-dione

^{1}H NMR

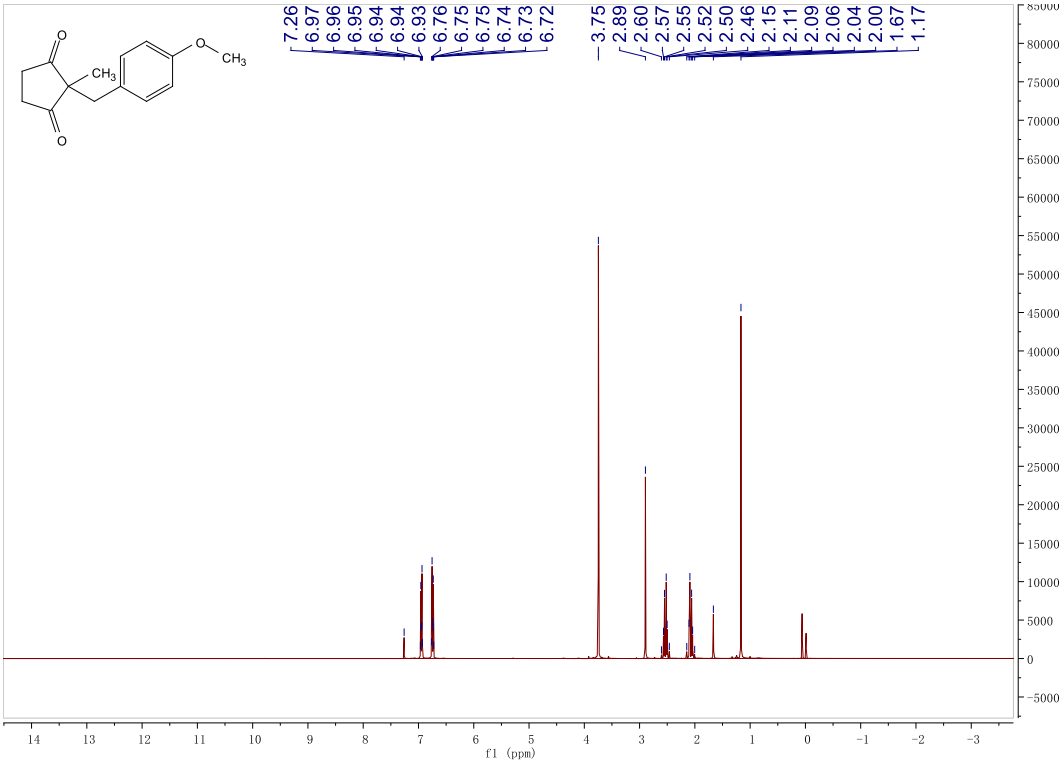


^{13}C NMR

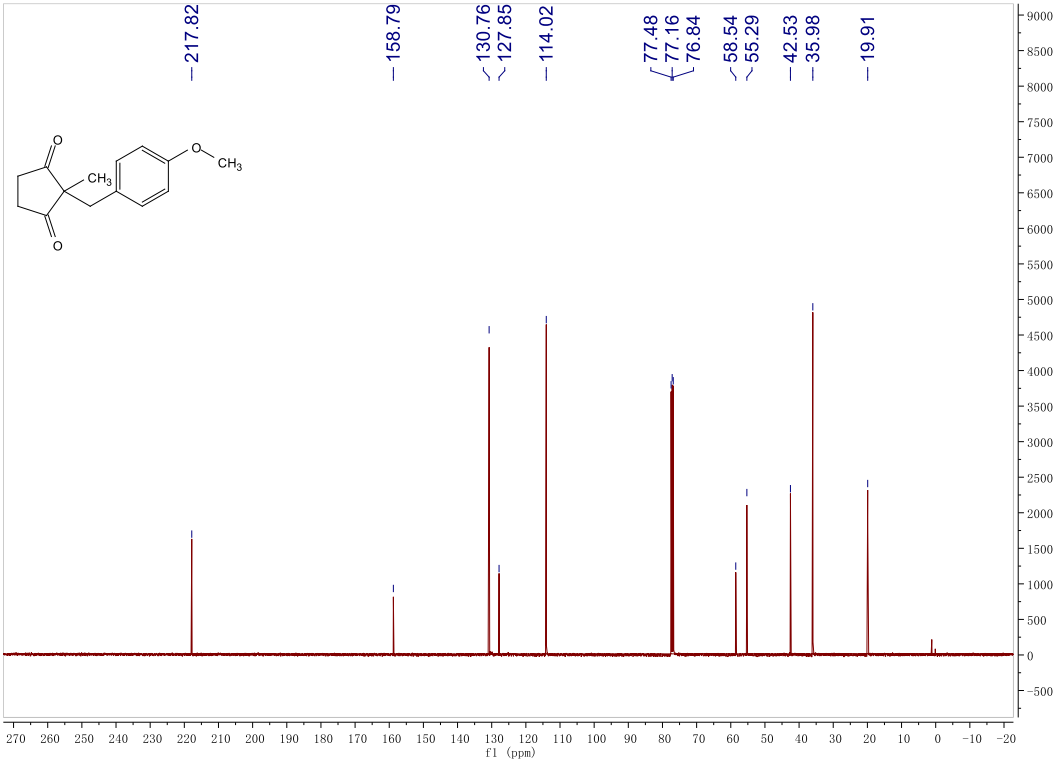


1i 2-(4-methoxybenzyl)-2-methylcyclopentane-1,3-dione

^{1}H NMR

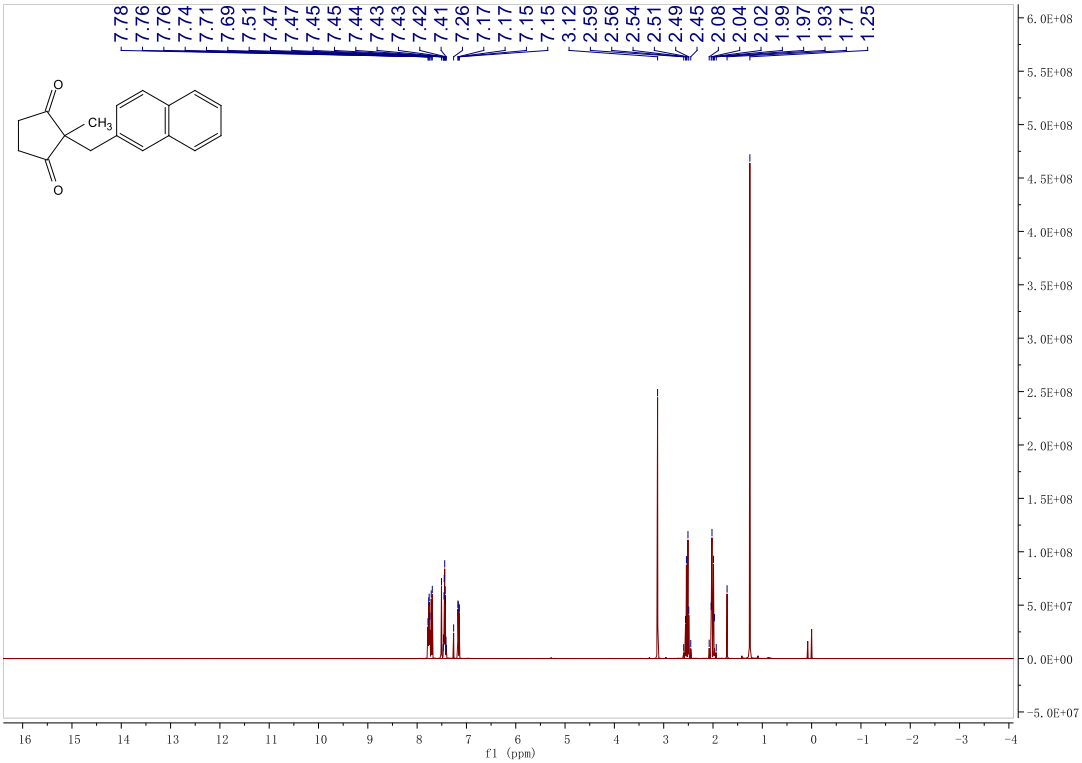


^{13}C NMR

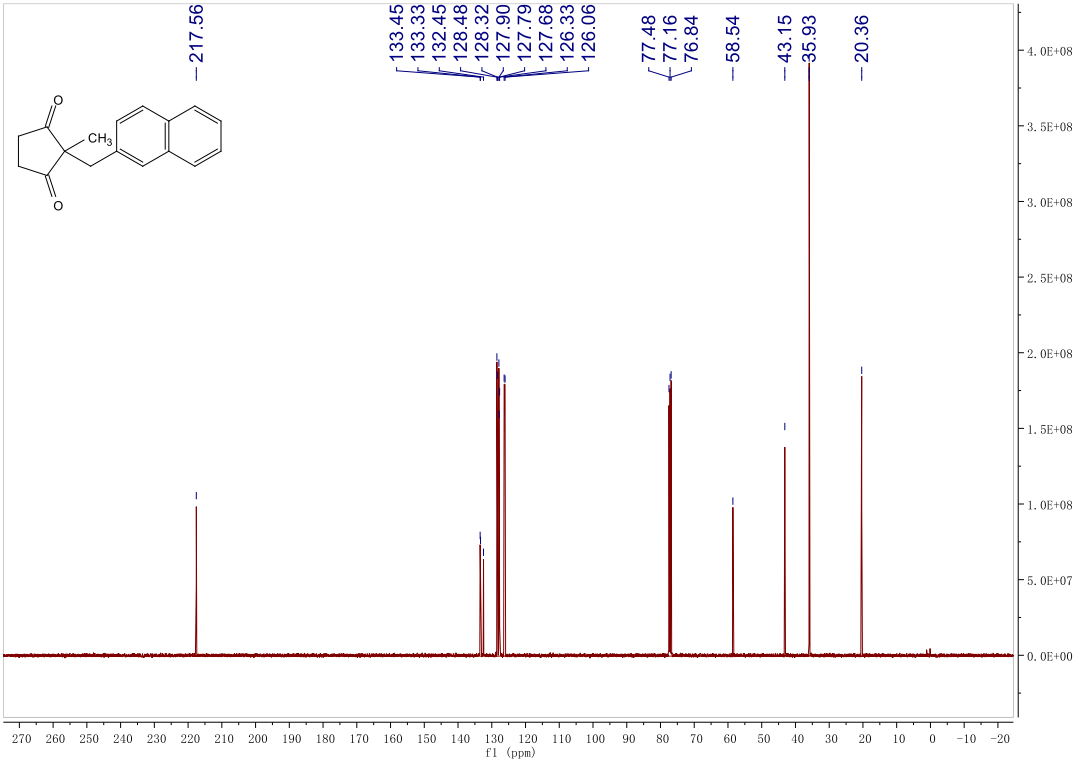


1j 2-methyl-2-(naphthalen-2-ylmethyl)cyclopentane-1,3-dione

^{1}H NMR

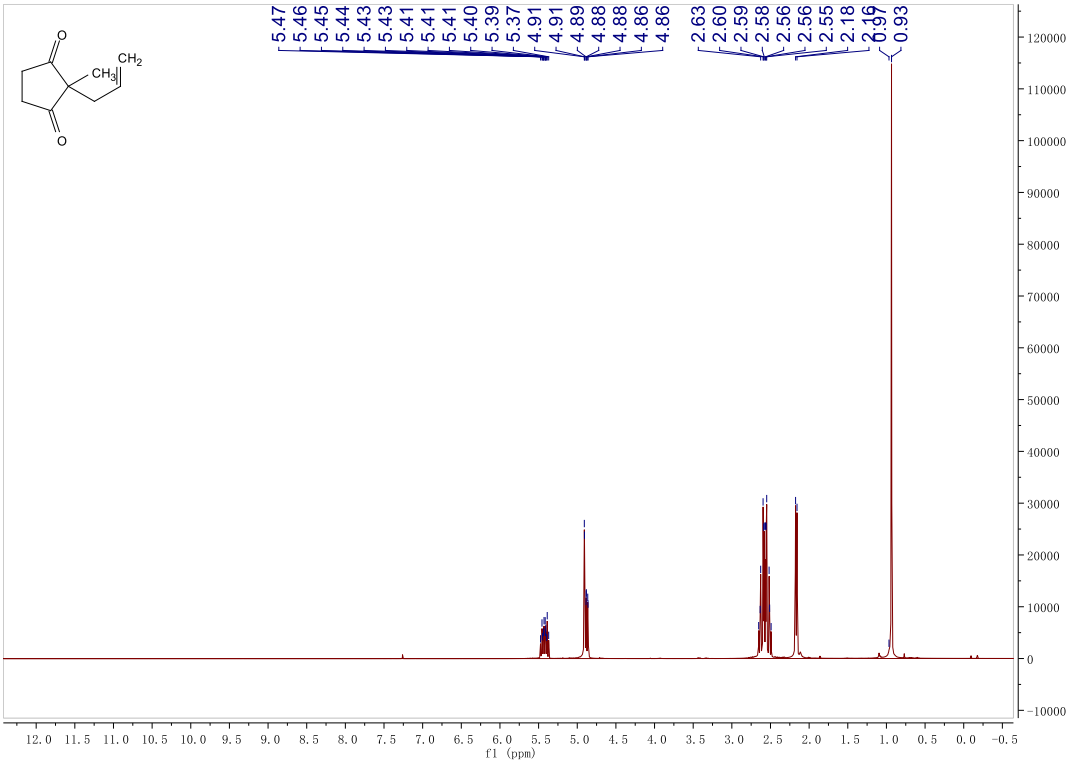


^{13}C NMR

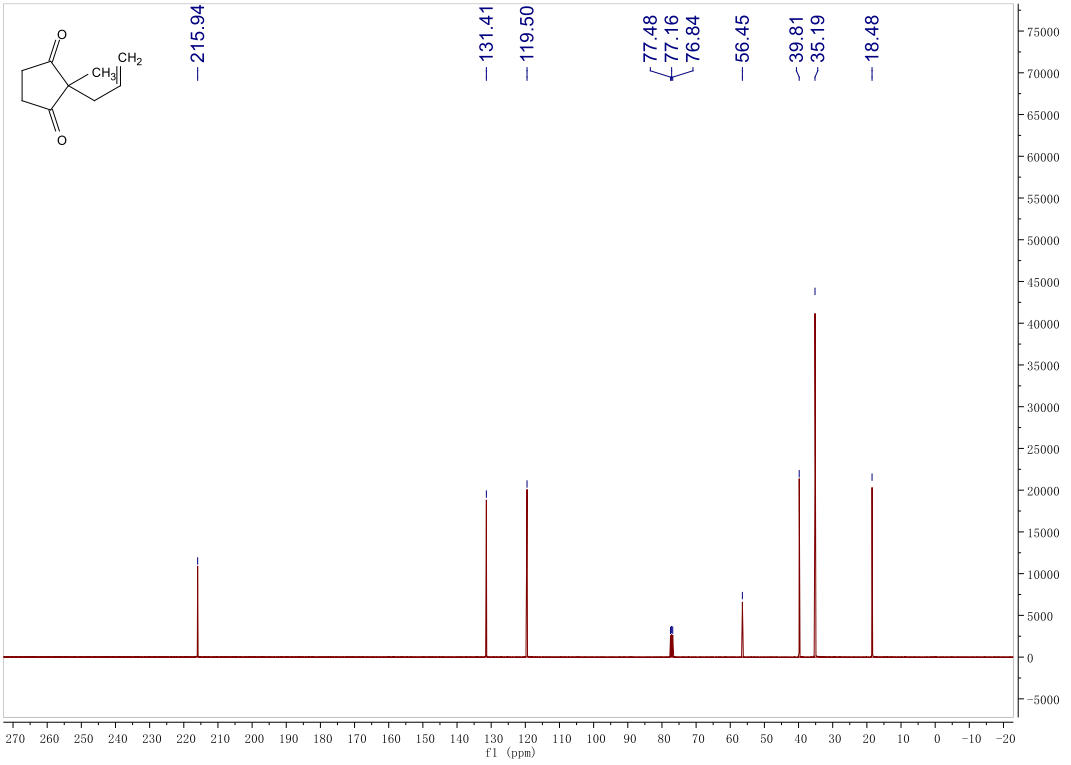


1k 2-allyl-2-methylcyclopentane-1,3-dione

^{1}H NMR

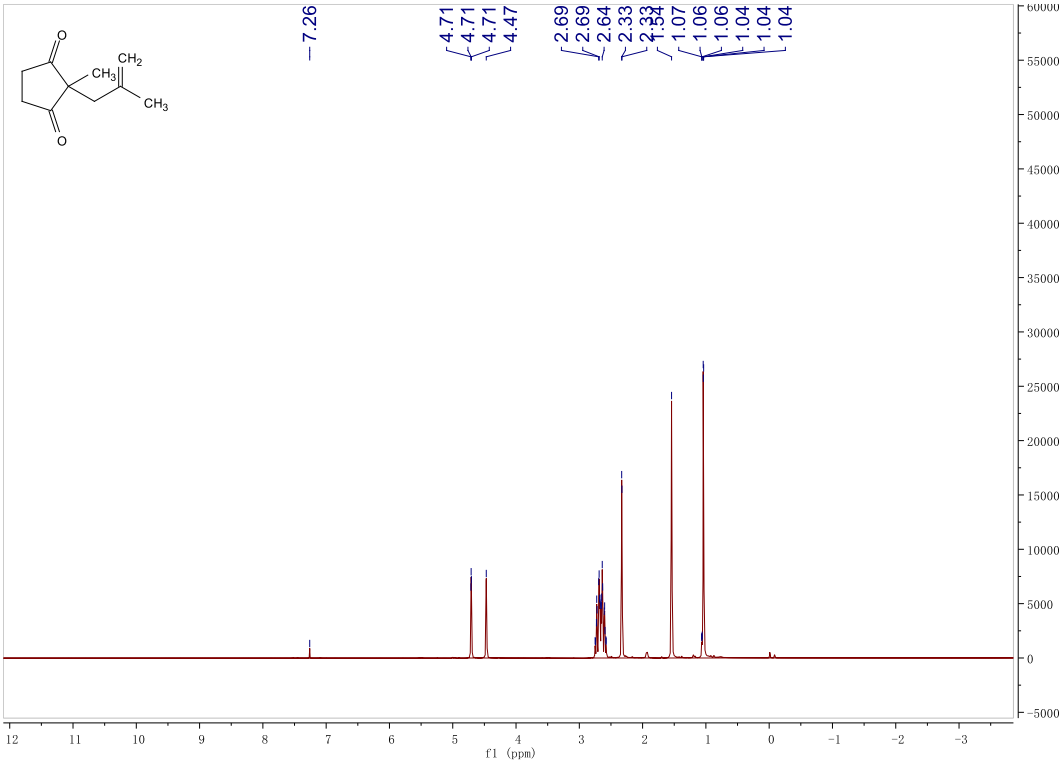


^{13}C NMR

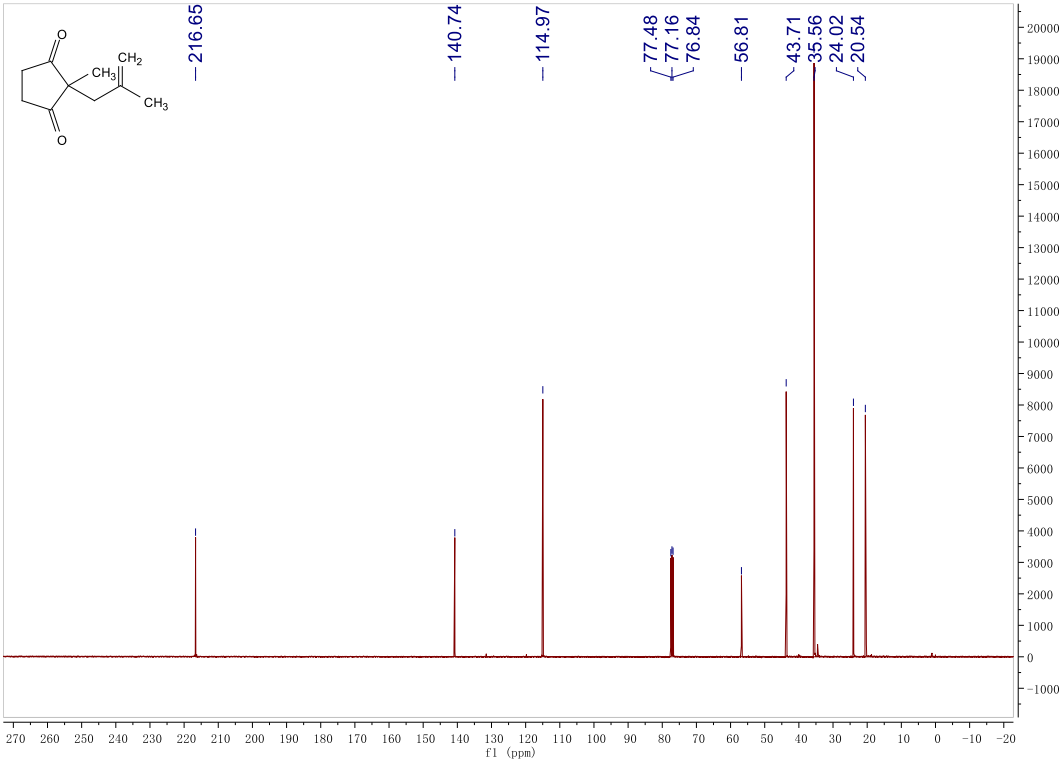


1l 2-methyl-2-(2-methylallyl)cyclopentane-1,3-dione

^{1}H NMR

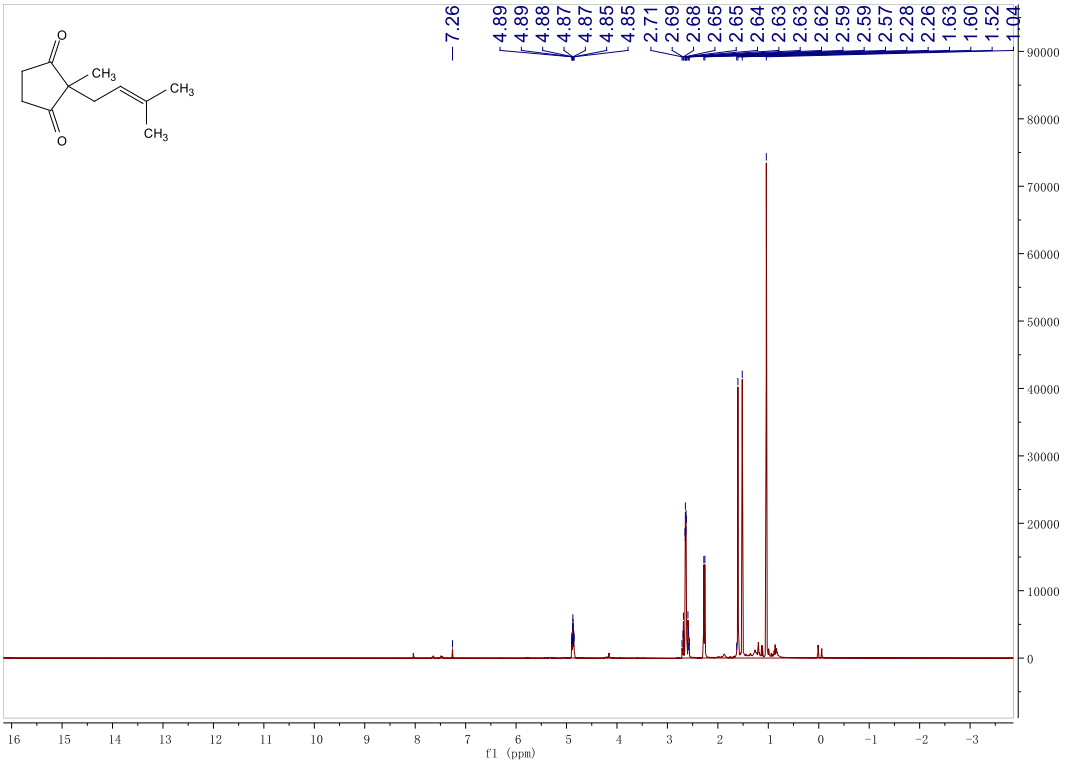


^{13}C NMR

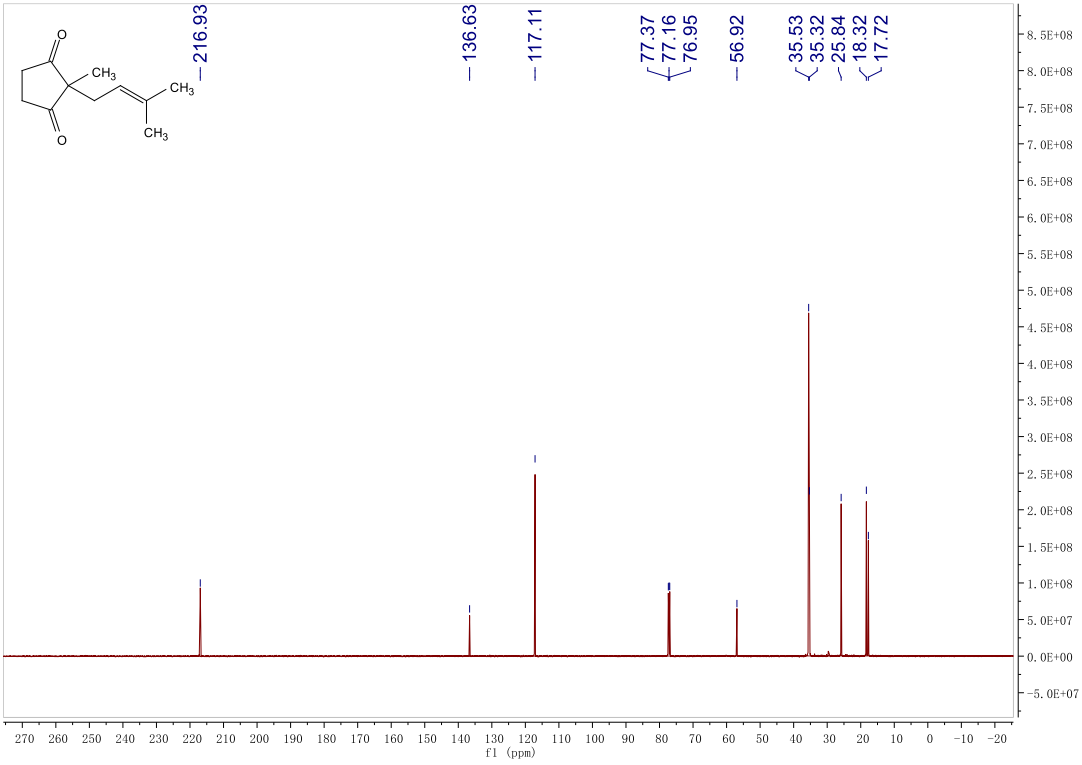


1m 2-methyl-2-(3-methylbut-2-en-1-yl)cyclopentane-1,3-dione

^{1}H NMR

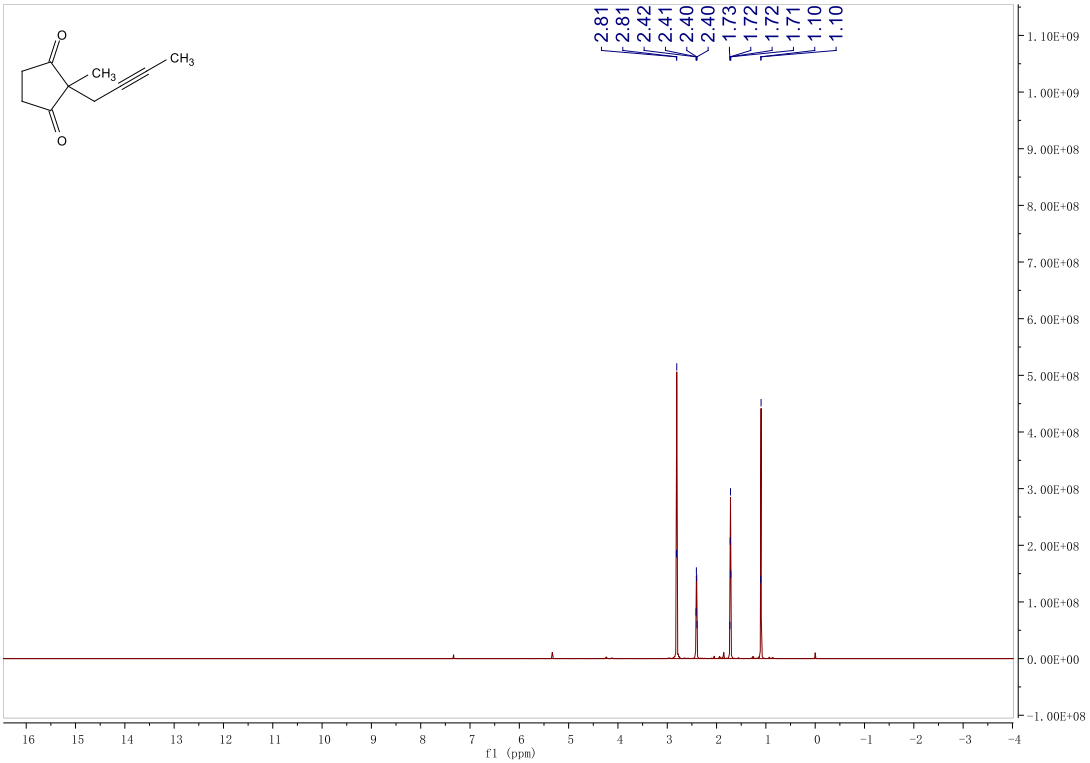


^{13}C NMR

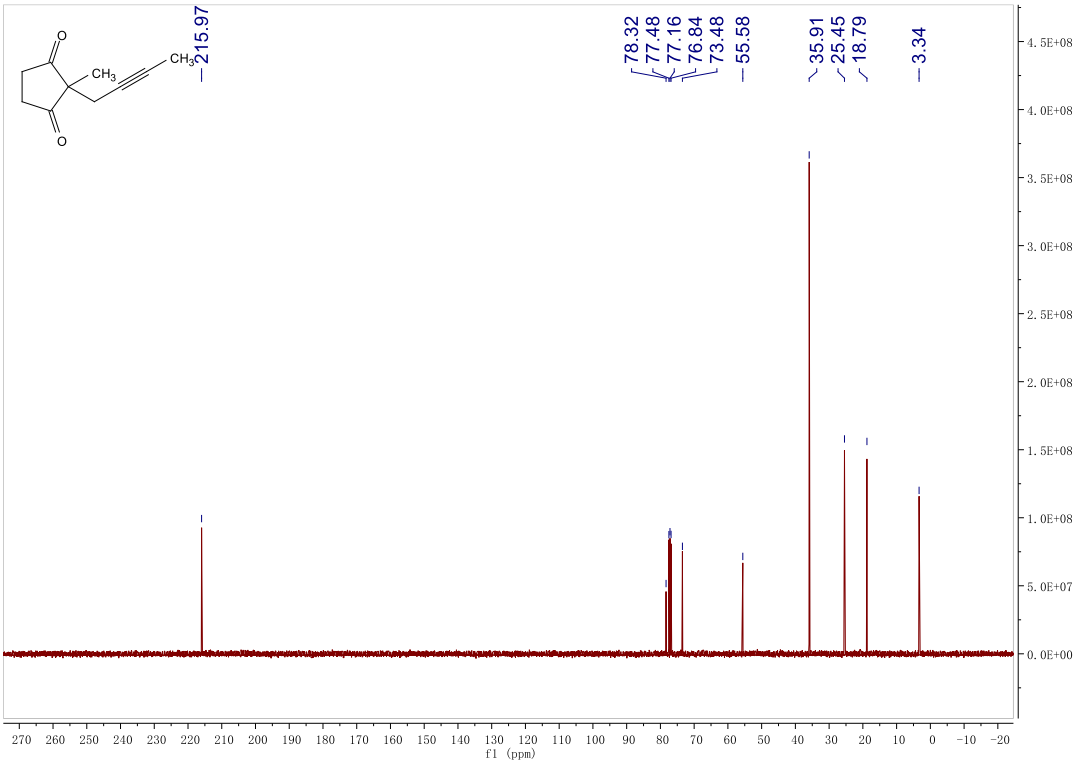


1n 2-(but-2-yn-1-yl)-2-methylcyclopentane-1,3-dione

^{1}H NMR

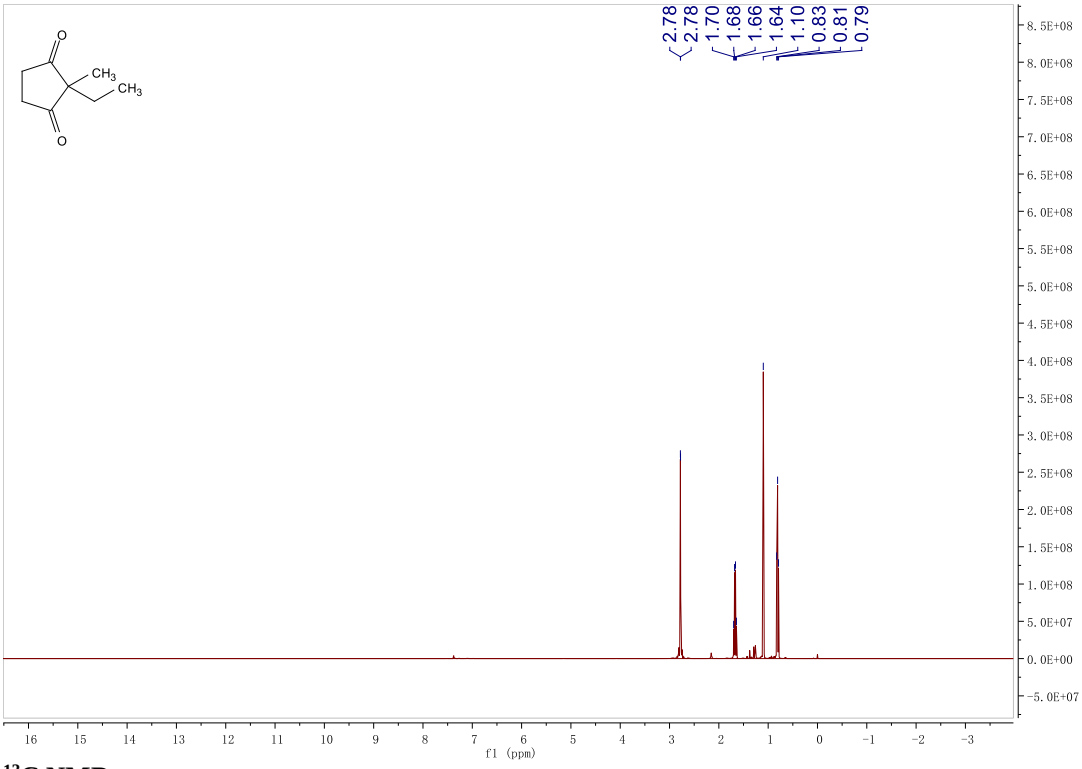


^{13}C NMR

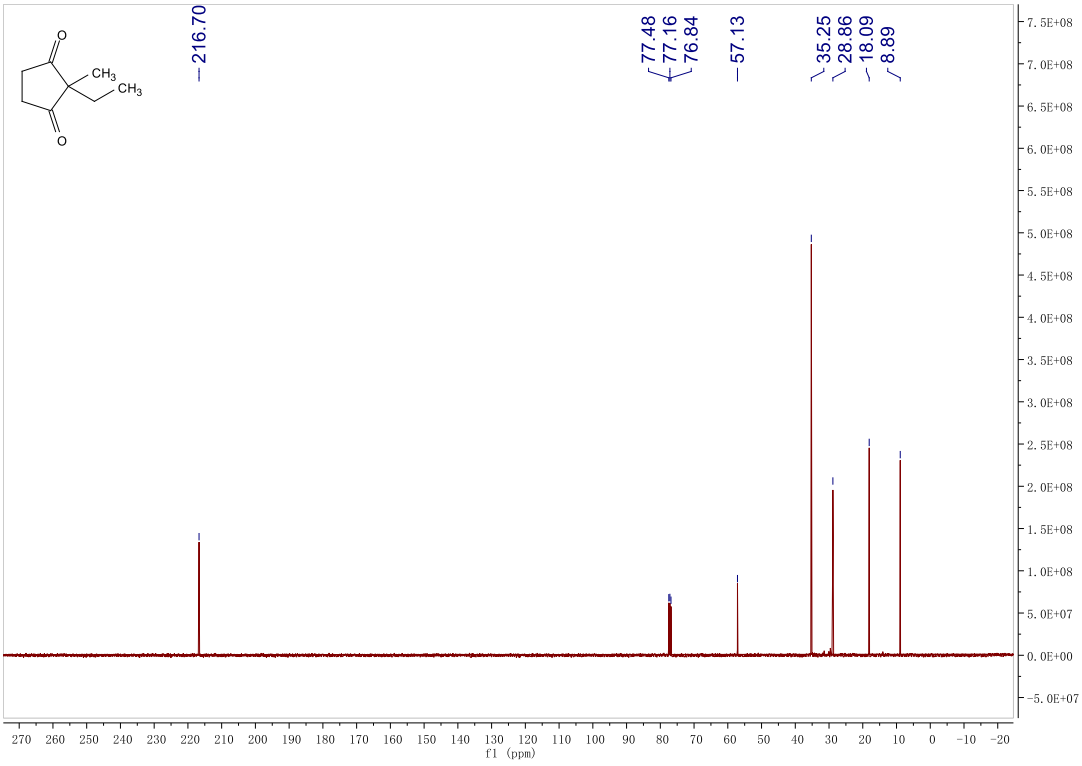


1o 2-methyl-2-ethylcyclopentane-1,3-dione

^{1}H NMR

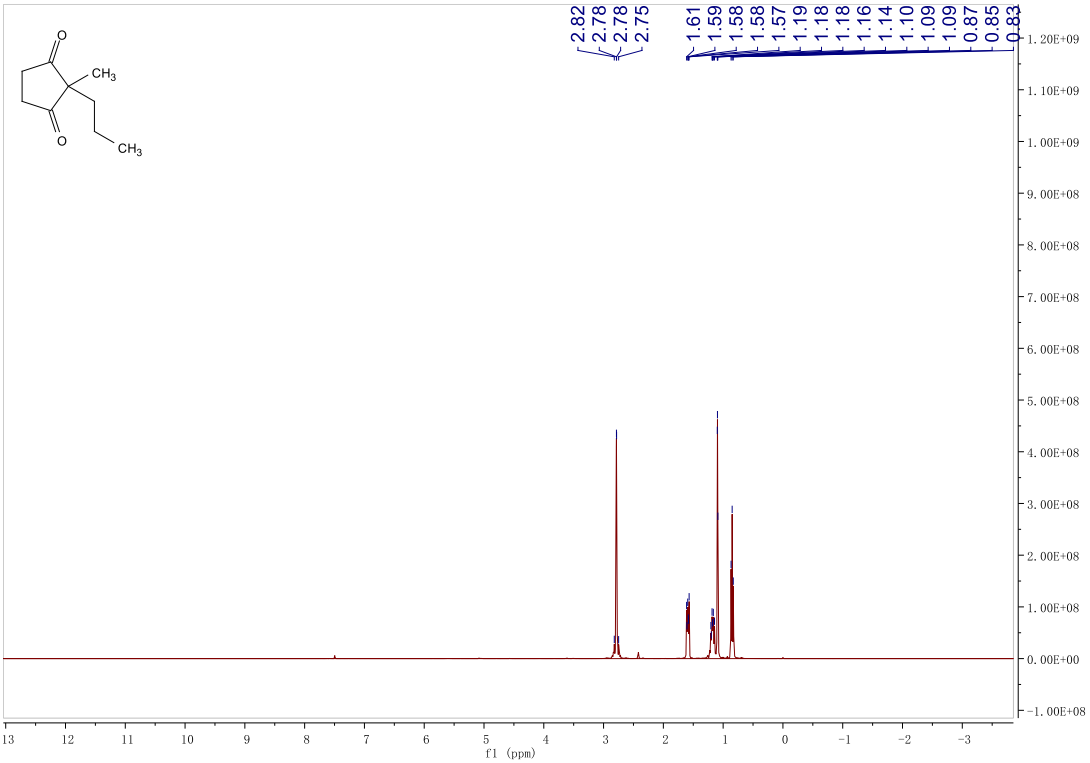


^{13}C NMR

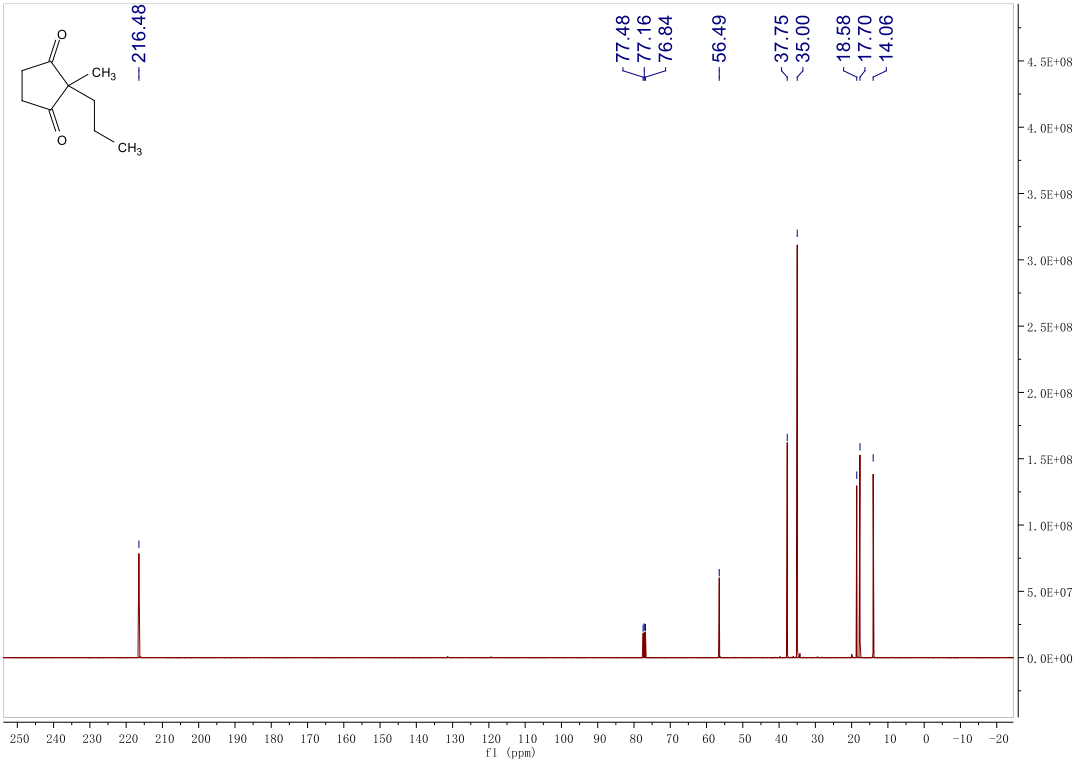


1p 2-methyl-2-propylcyclopentane-1,3-dione

^{1}H NMR

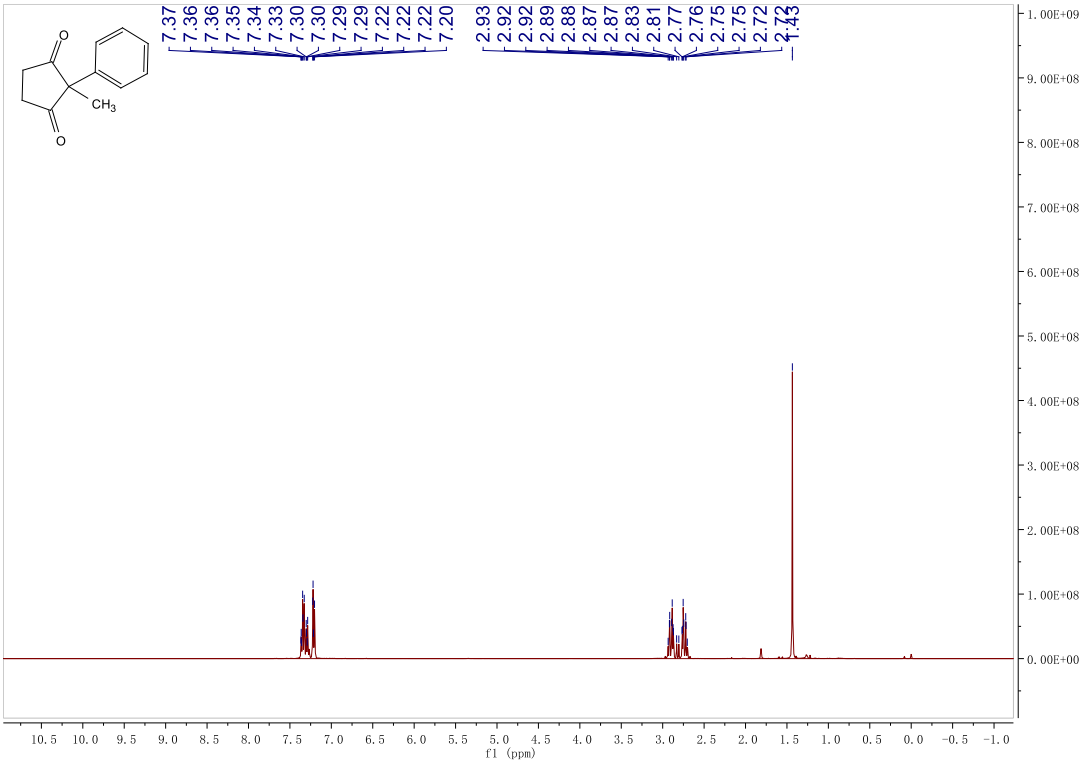


^{13}C NMR

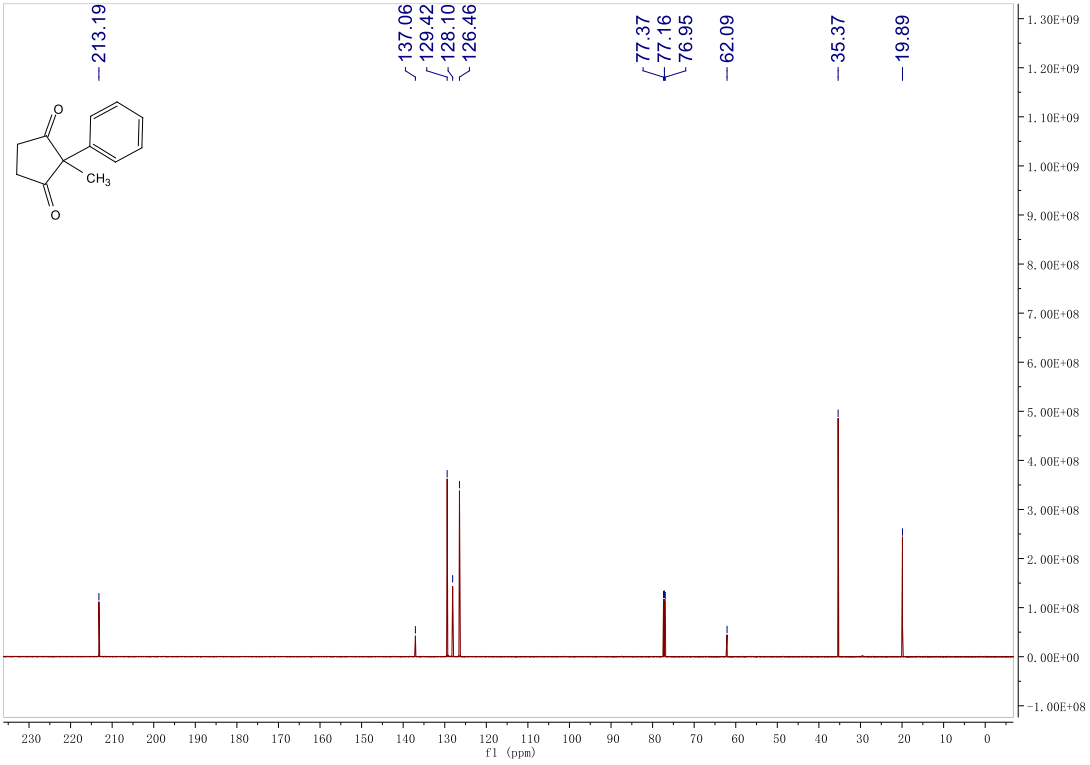


1q 2-benzyl-2-methylcyclohexane-1,3-dione

^{1}H NMR

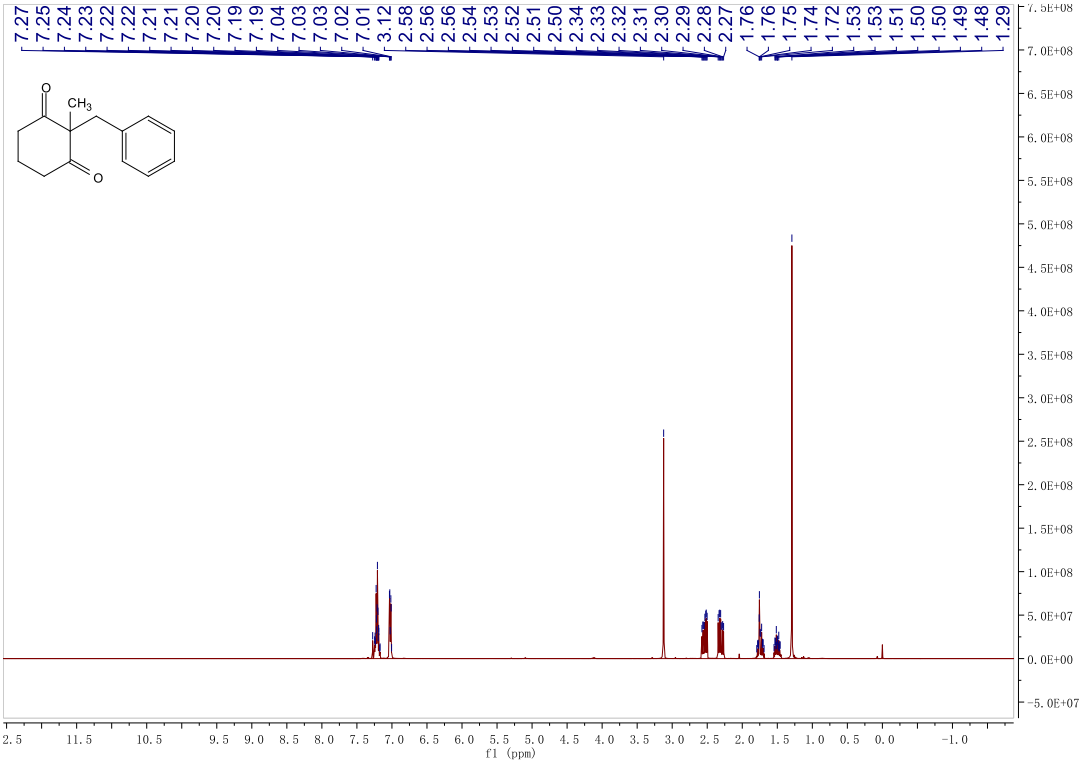


^{13}C NMR

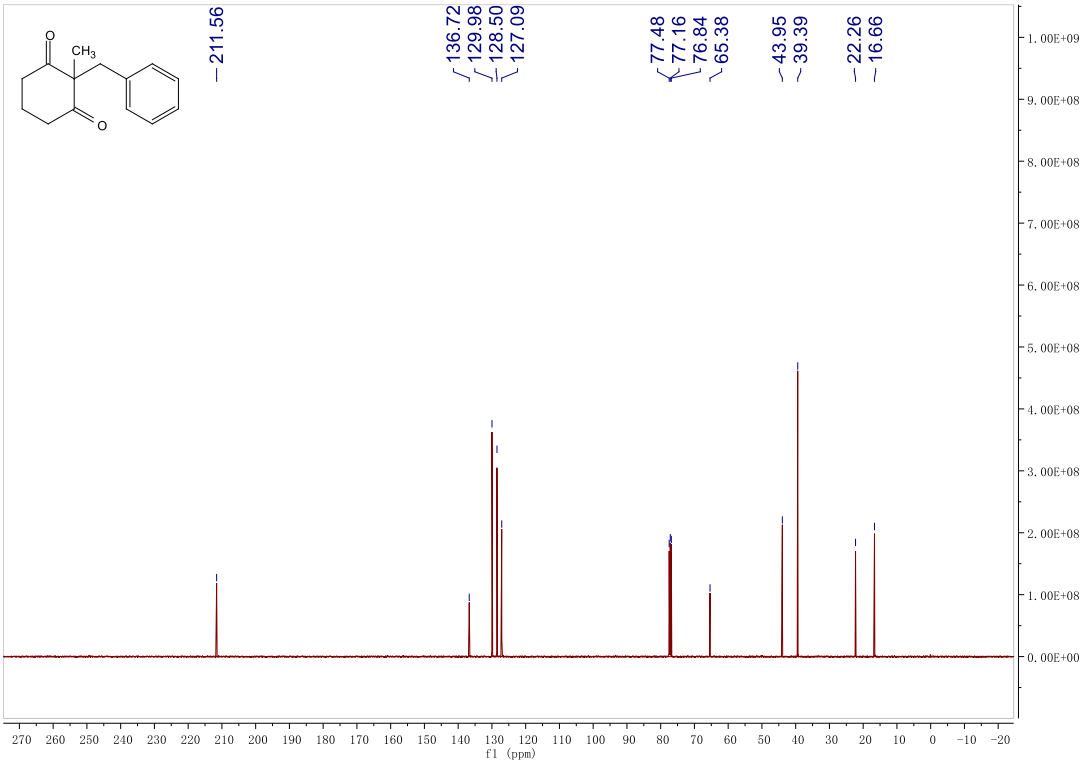


1r 2-benzyl-2-methyl-1H-indene-1,3(2H)-dione

^{1}H NMR

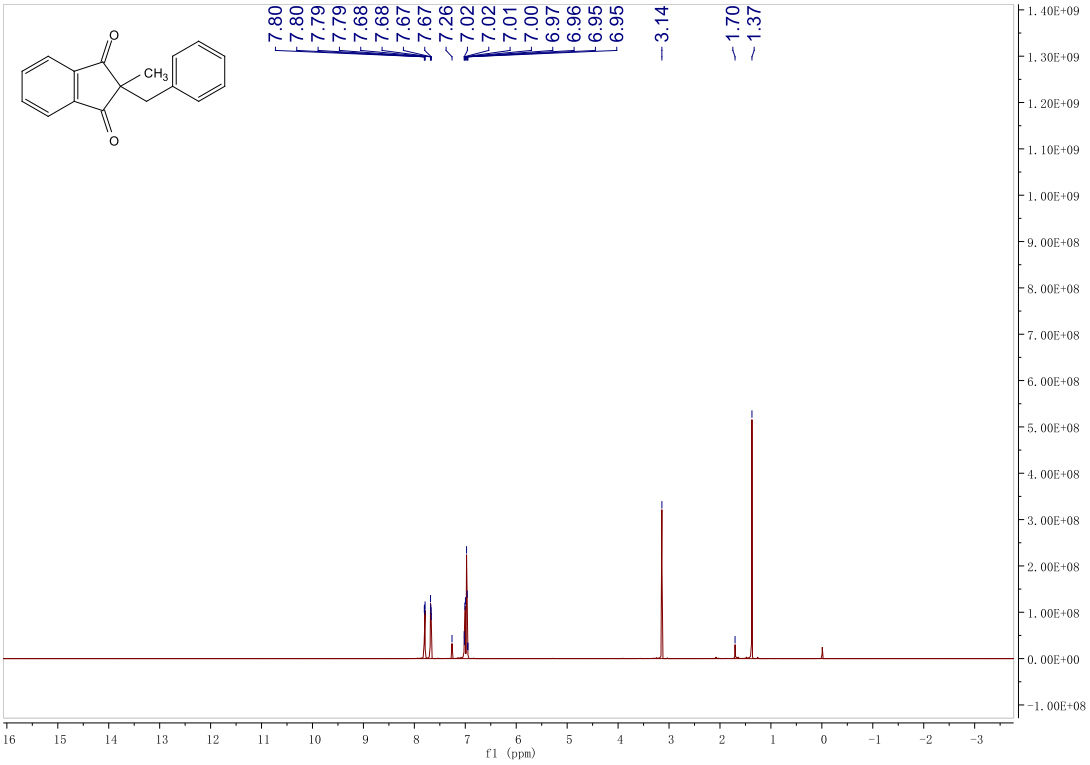


^{13}C NMR

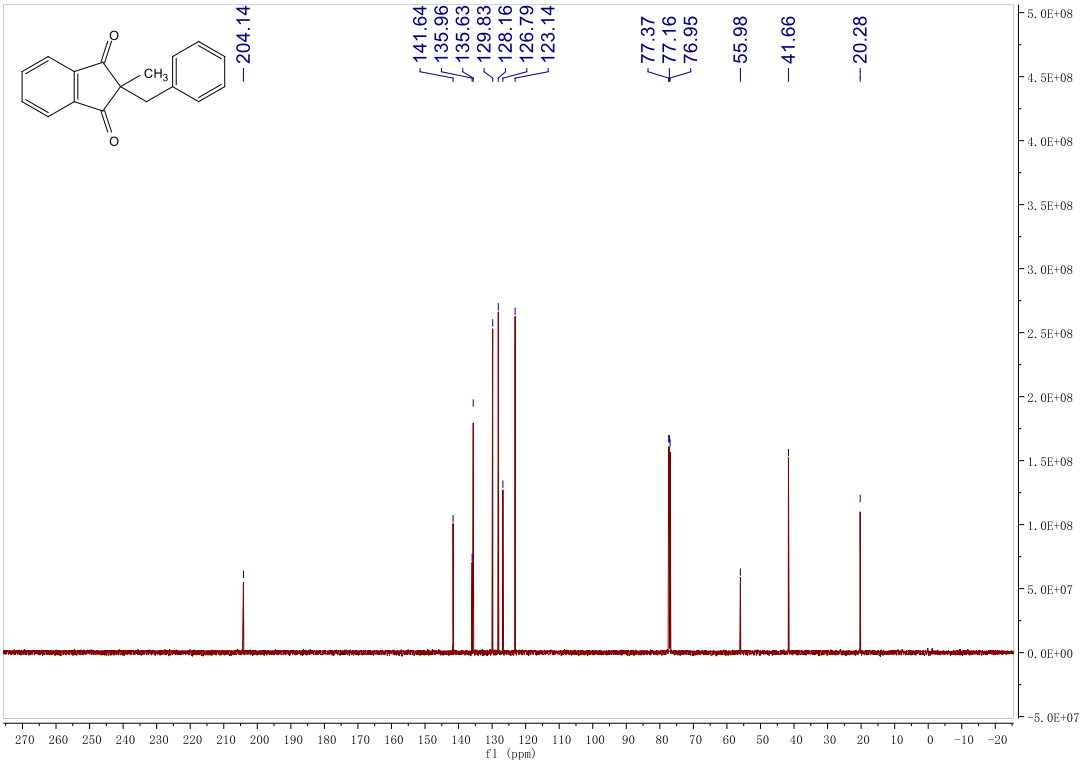


1s 2-methyl-2-phenyl-1H-indene-1,3(2H)-dione

^{1}H NMR

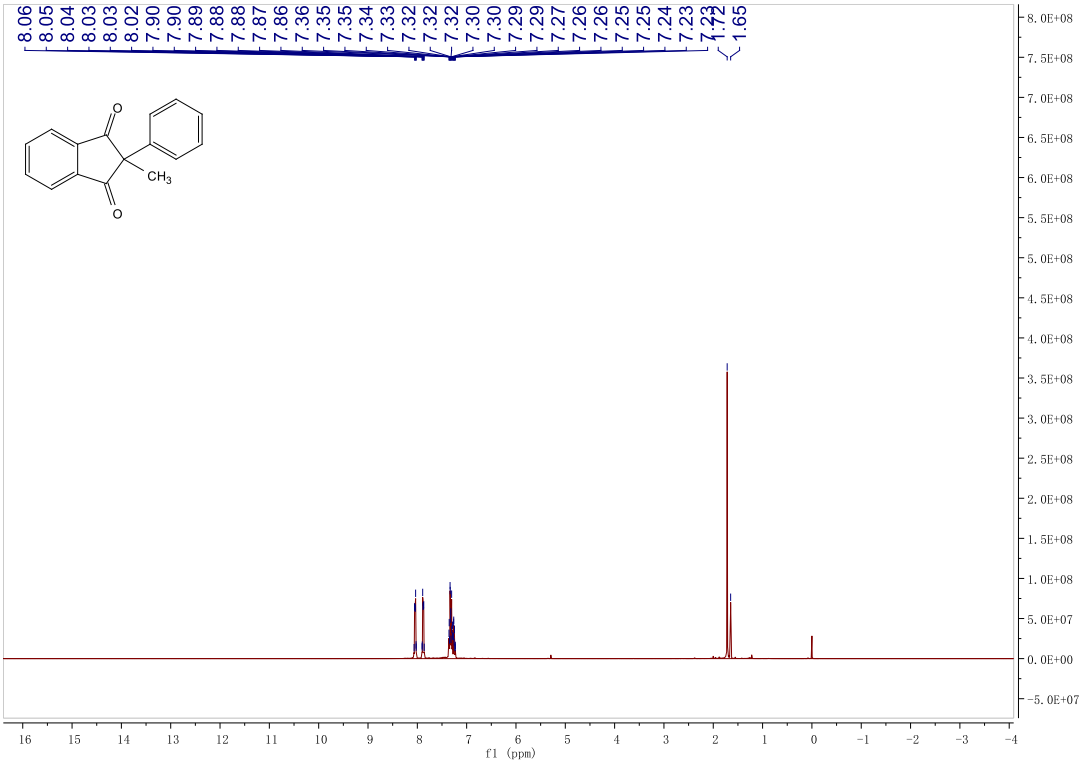


^{13}C NMR

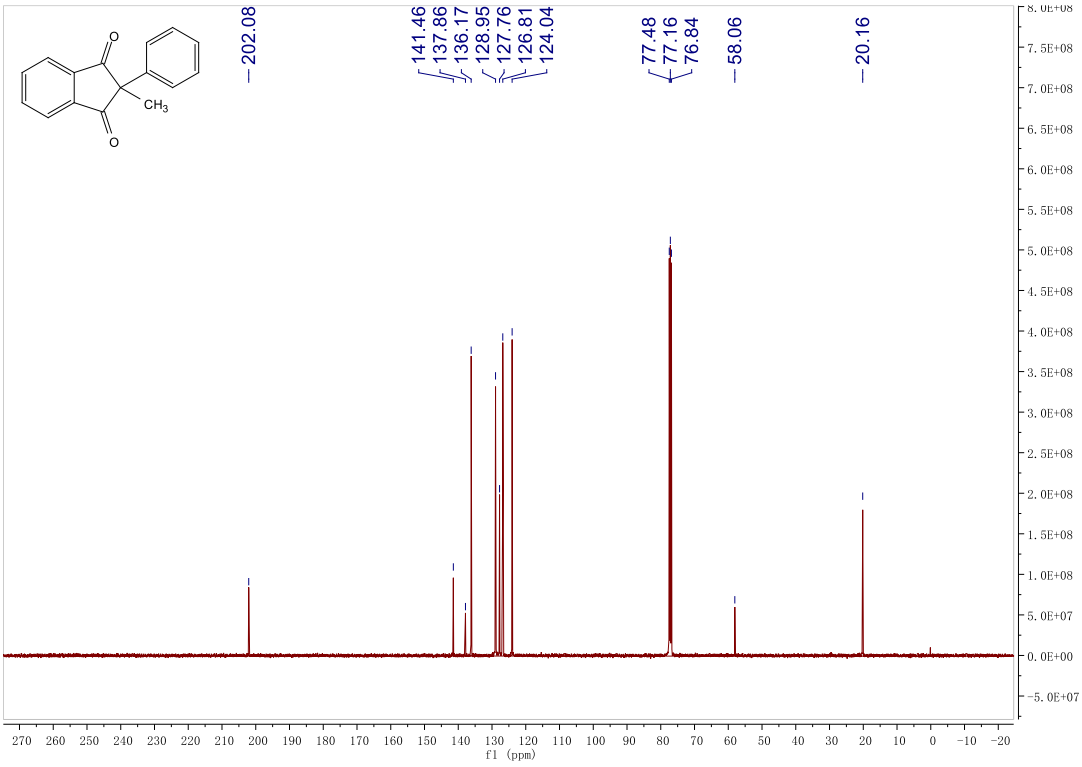


1t 2-methyl-2-phenylcyclopentane-1,3-dione

^{1}H NMR

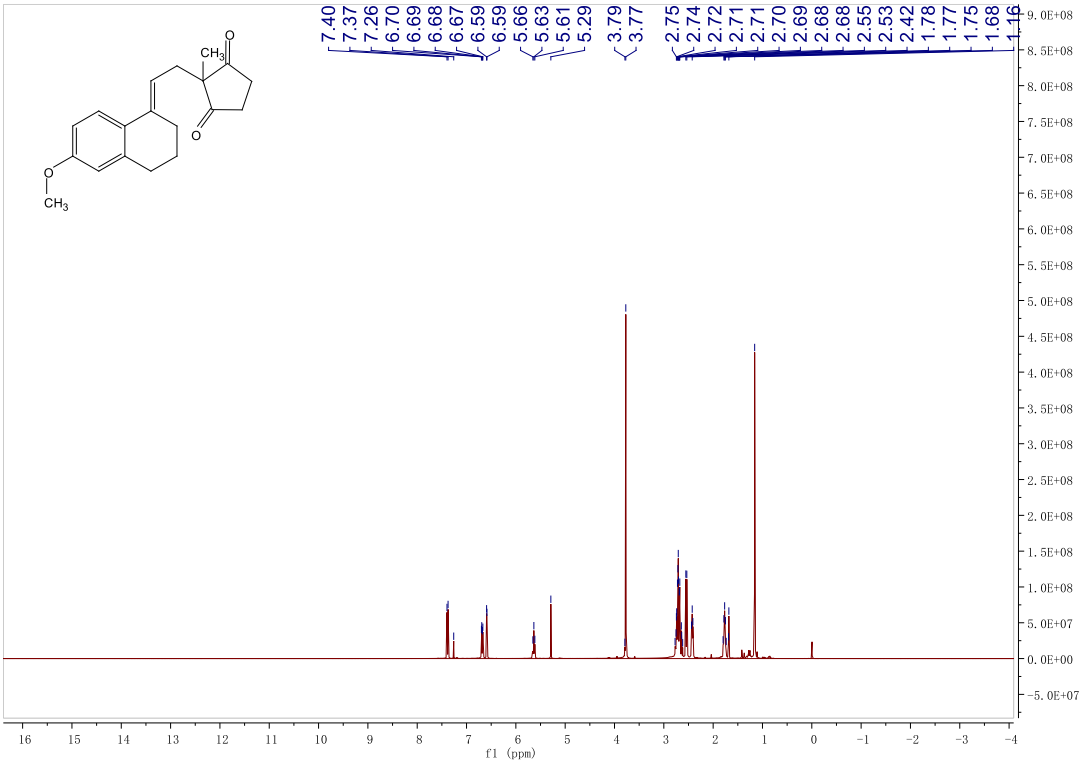


^{13}C NMR

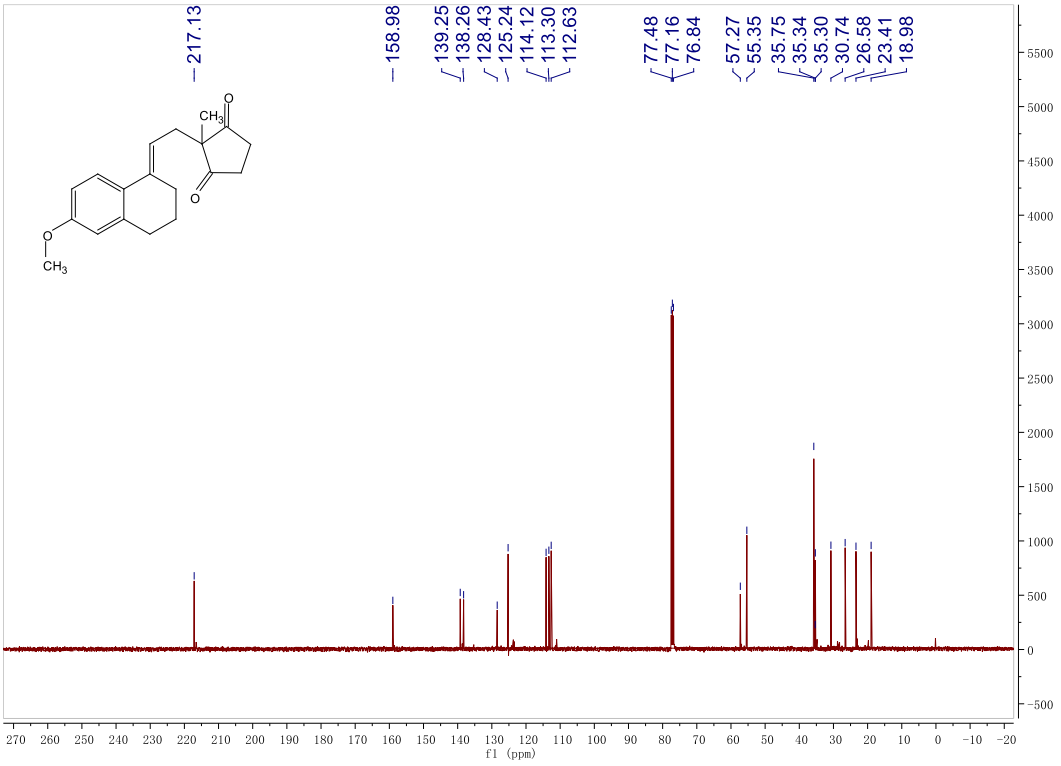


1u (*E*)-2-(2-(6-methoxy-3,4-dihydronaphthalen-1(2H)-ylidene)ethyl)-2-methylcyclopentane-1,3-dione

^{1}H NMR

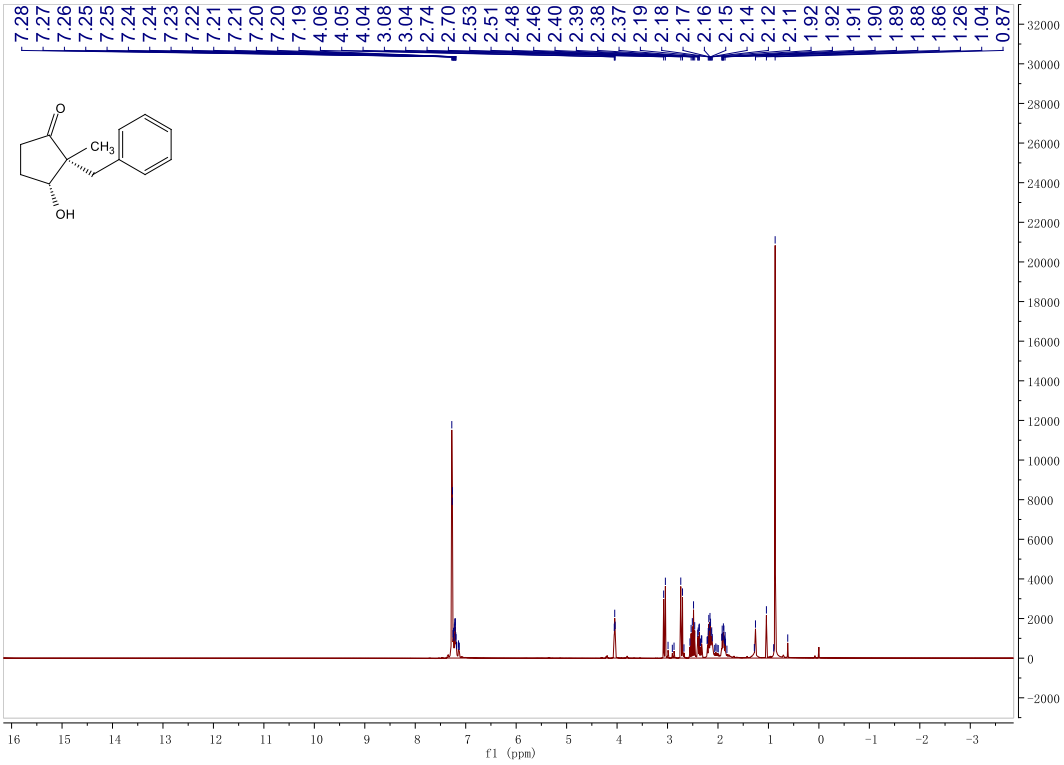


^{13}C NMR

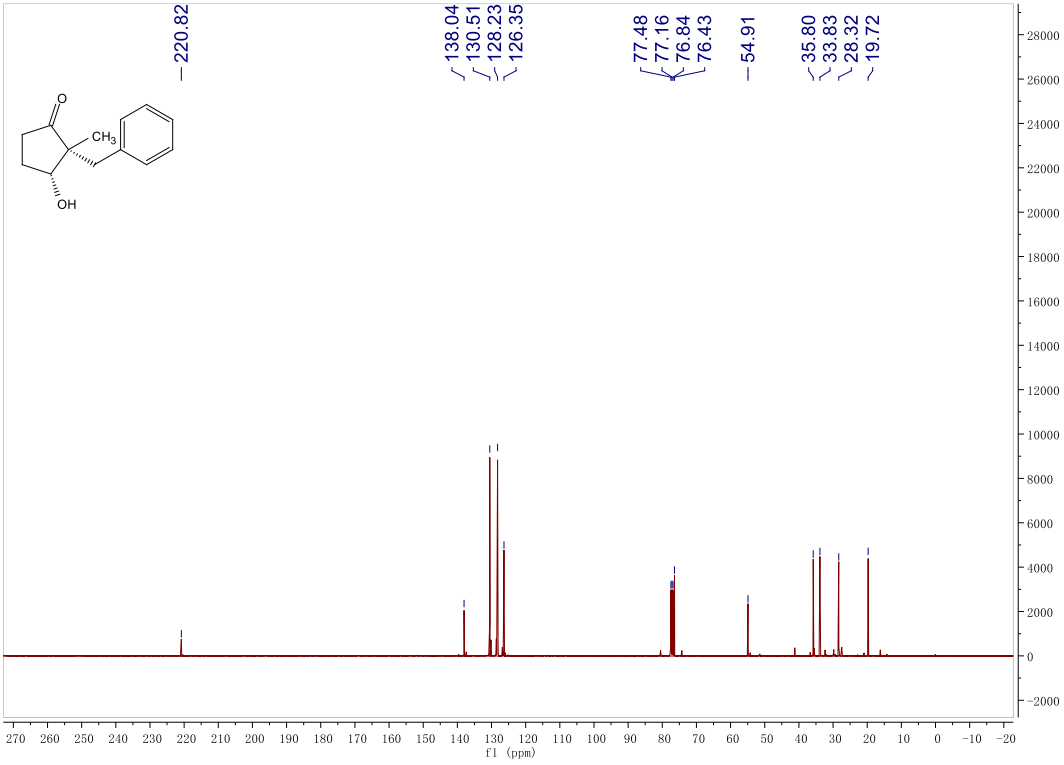


2a (2*R*,3*R*)-2-benzyl-3-hydroxy-2-methylcyclopentan-1-one

^{1}H NMR

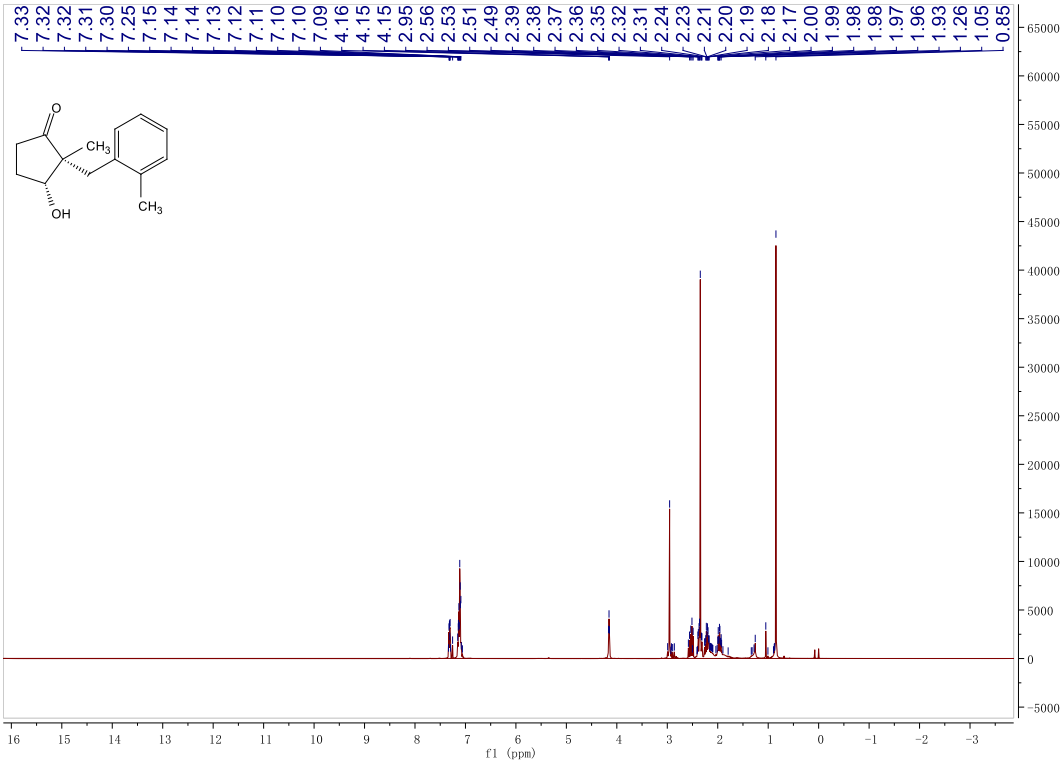


^{13}C NMR

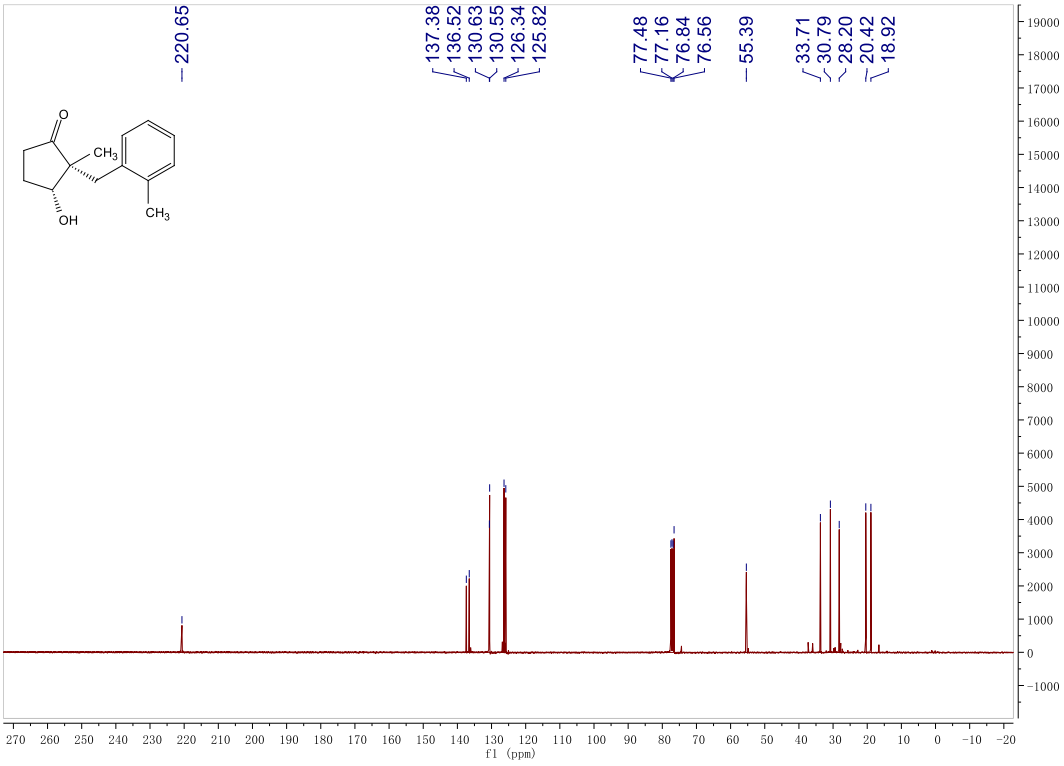


2b (2*R*,3*R*)-3-hydroxy-2-methyl-2-(2-methylbenzyl)cyclopentan-1-one

^{1}H NMR

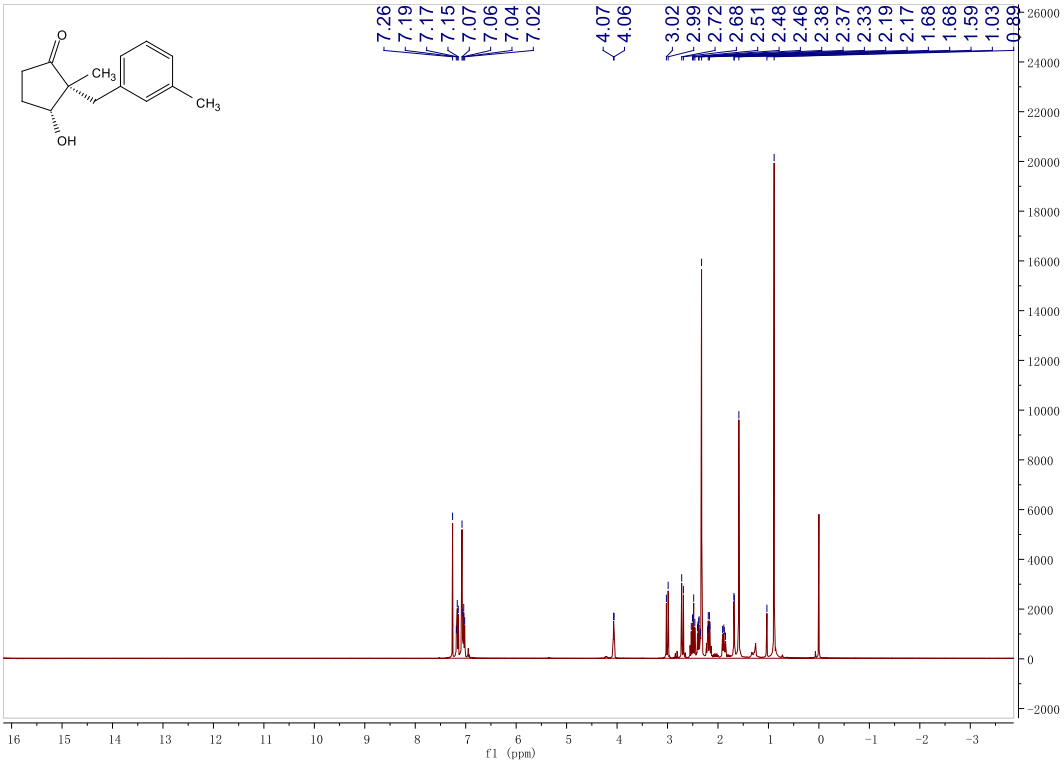


^{13}C NMR

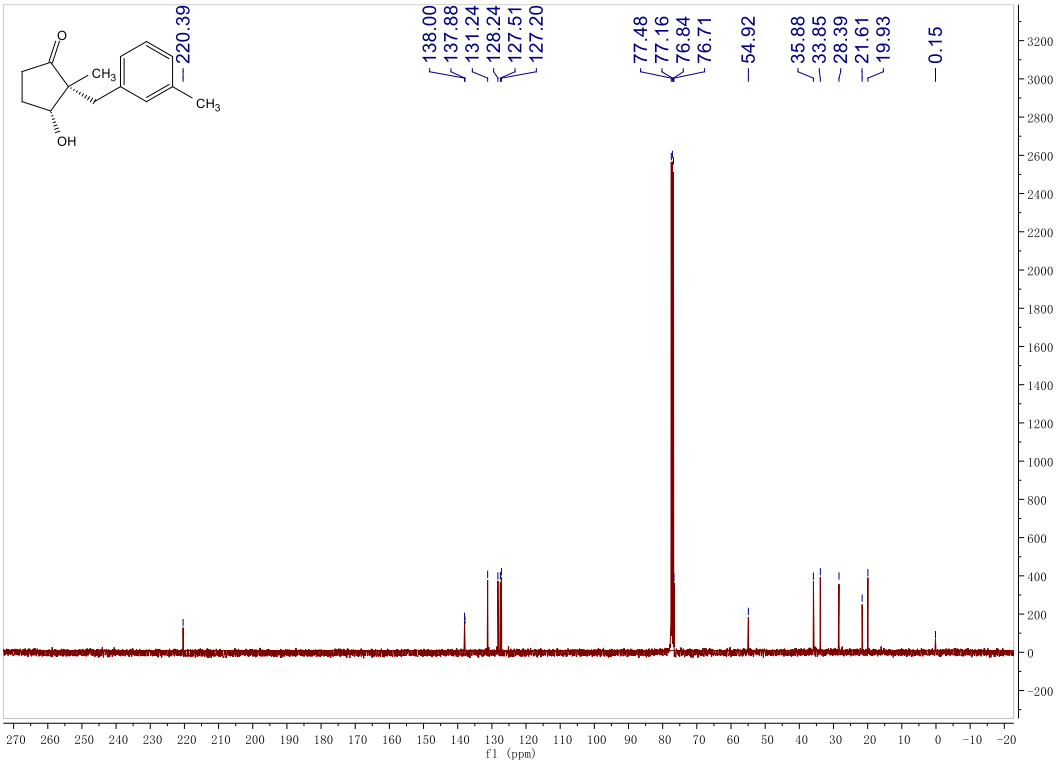


2c (2*R*,3*R*)-3-hydroxy-2-methyl-2-(3-methylbenzyl)cyclopentan-1-one

^{1}H NMR

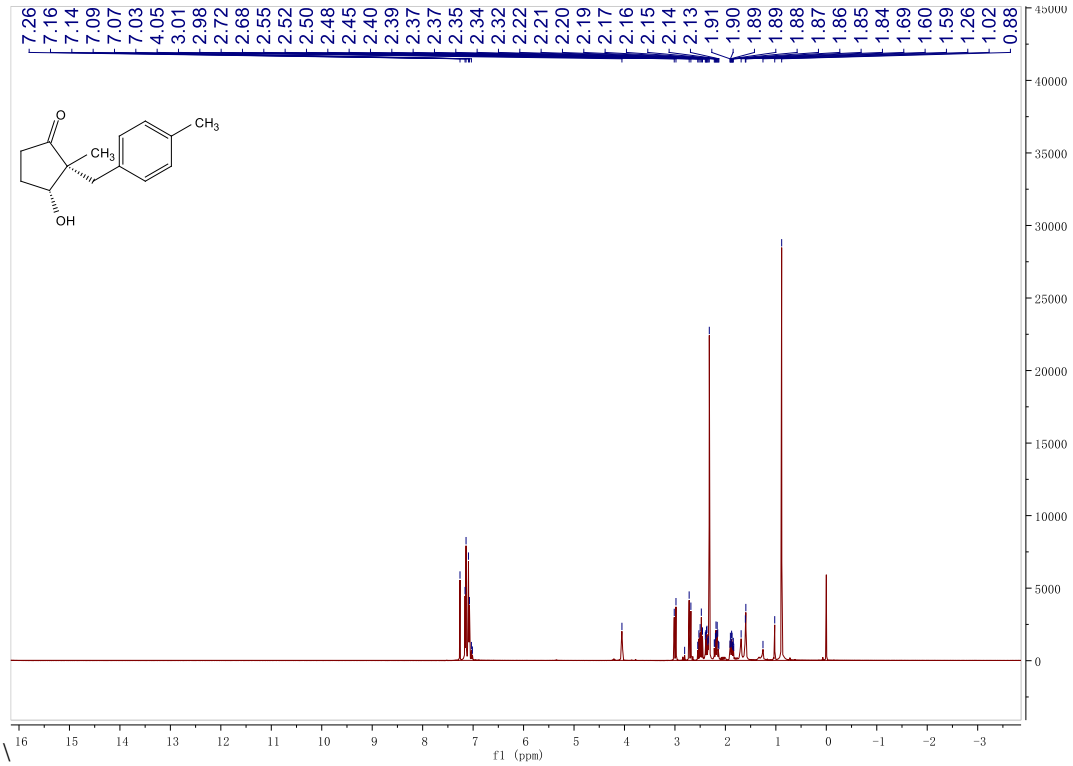


^{13}C NMR

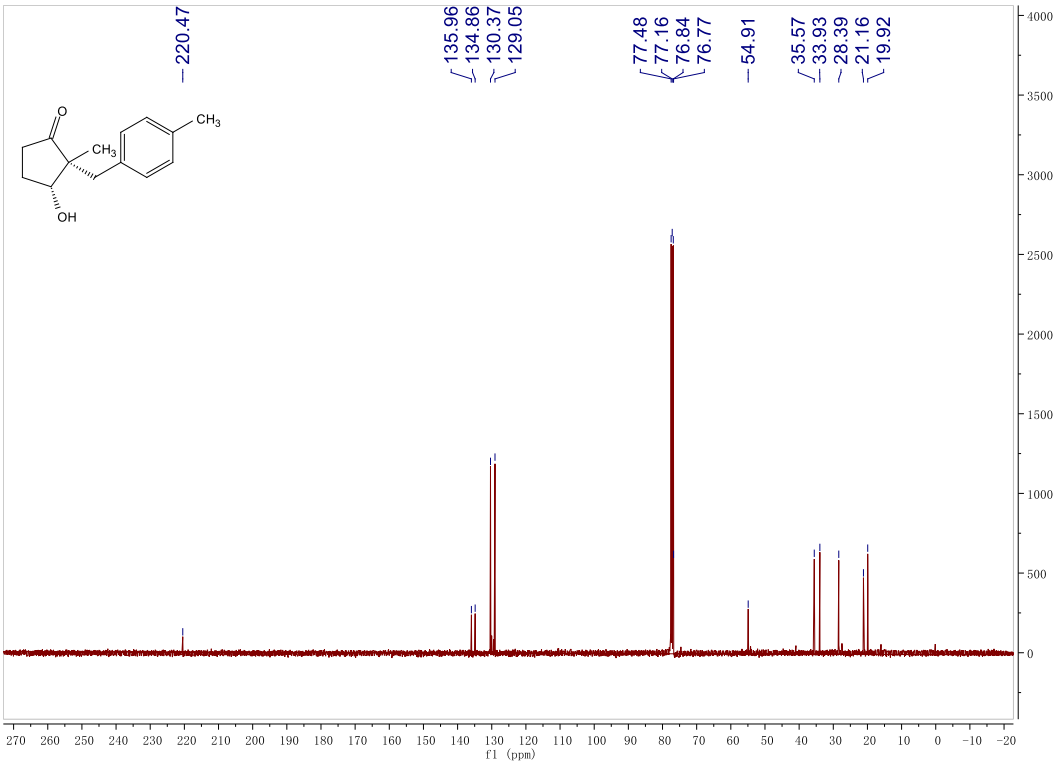


2d (2*R*,3*R*)-3-hydroxy-2-methyl-2-(4-methylbenzyl)cyclopentan-1-one

^{1}H NMR

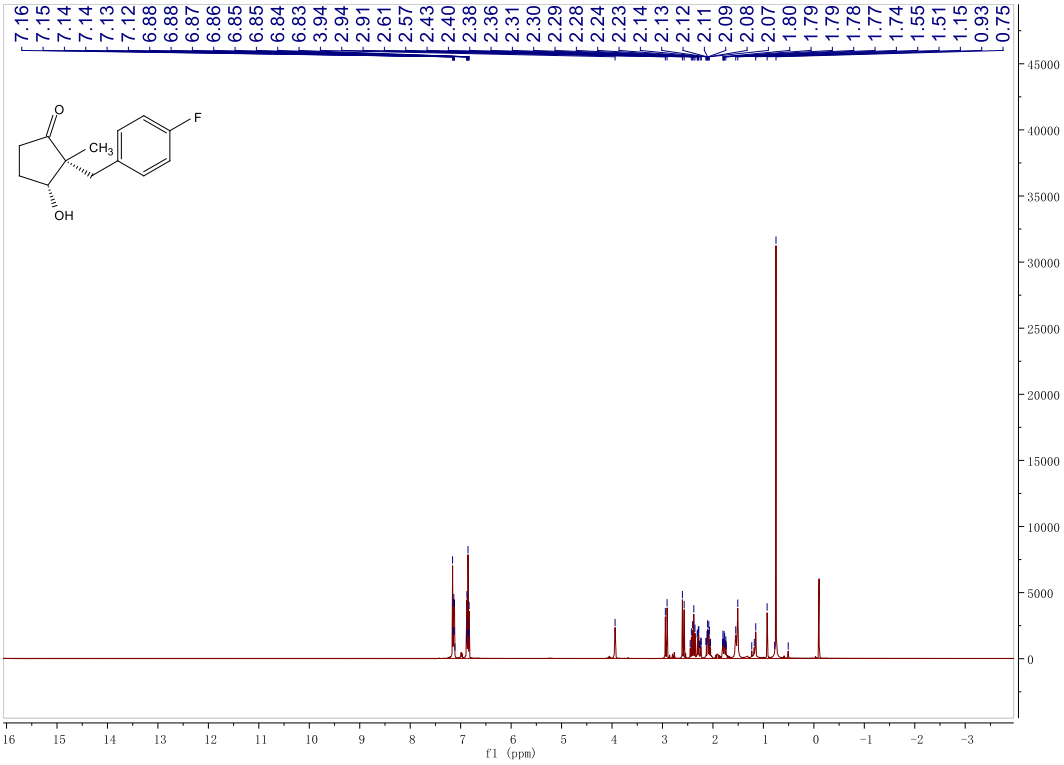


^{13}C NMR

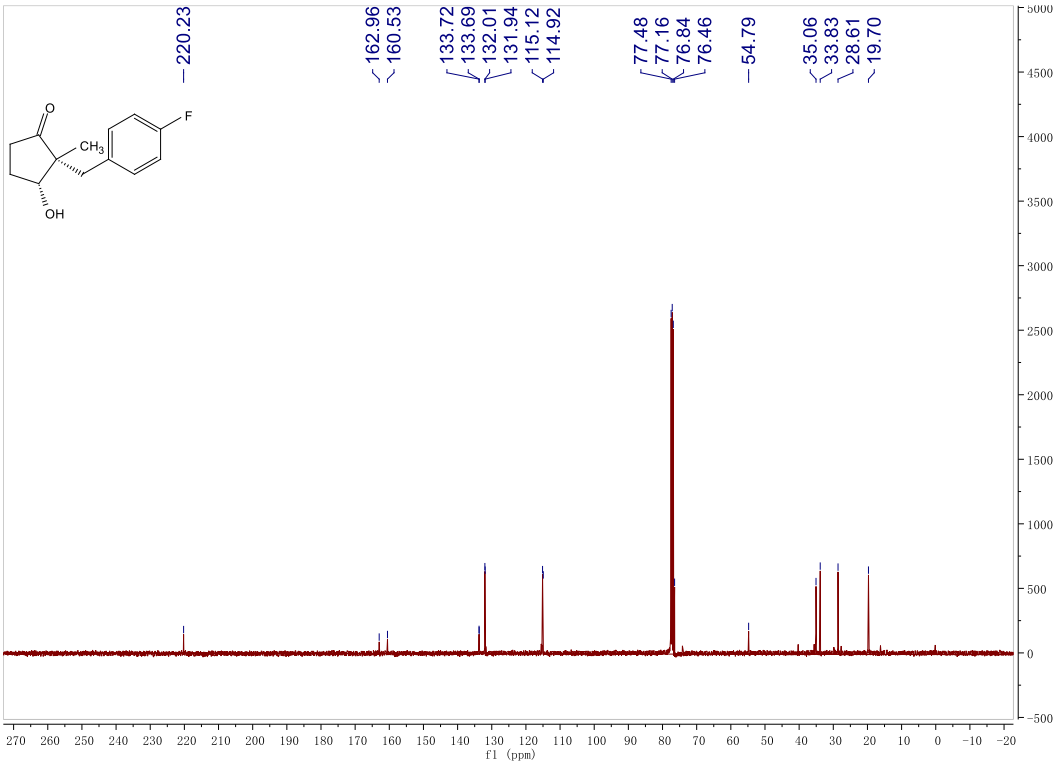


2e (2*R*,3*R*)-2-(4-fluorobenzyl)-3-hydroxy-2-methylcyclopentan-1-one

^{1}H NMR

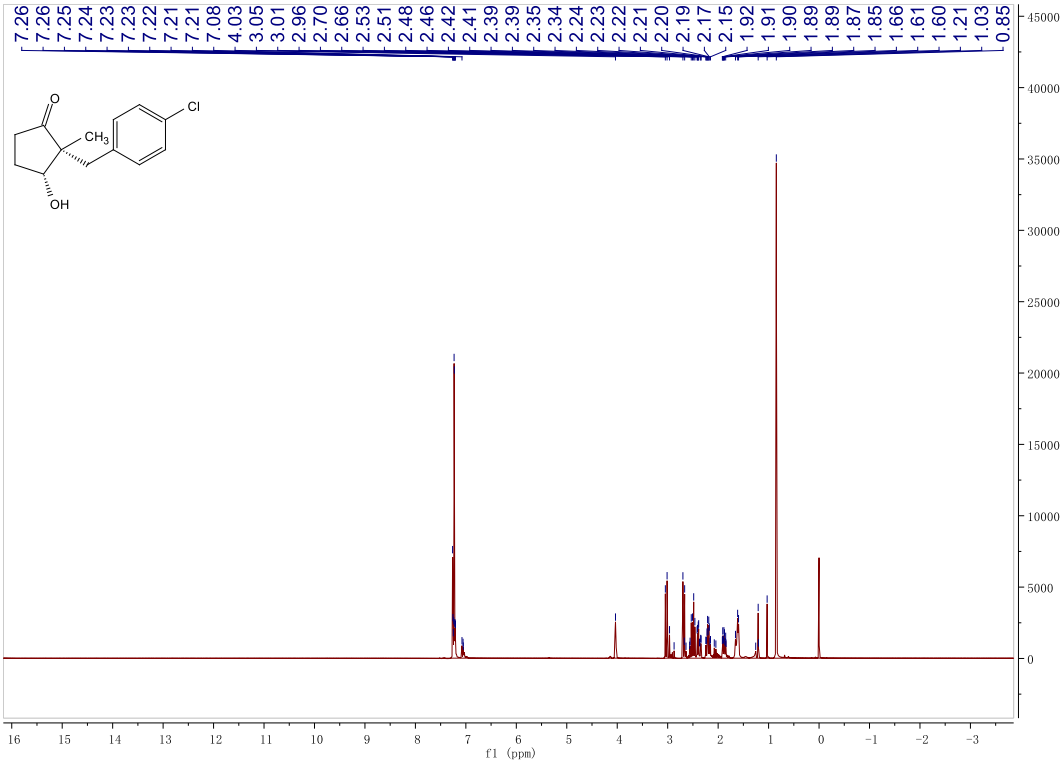


^{13}C NMR

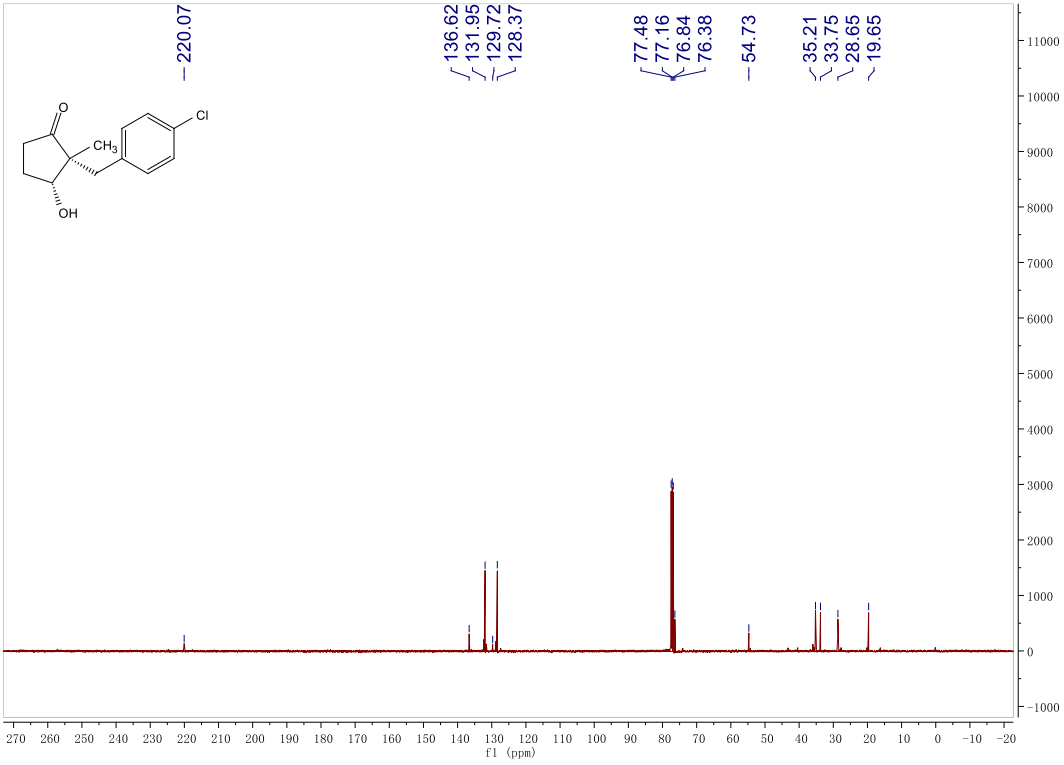


2f (2*R*,3*R*)-2-(4-chlorobenzyl)-3-hydroxy-2-methylcyclopentan-1-one

^{1}H NMR

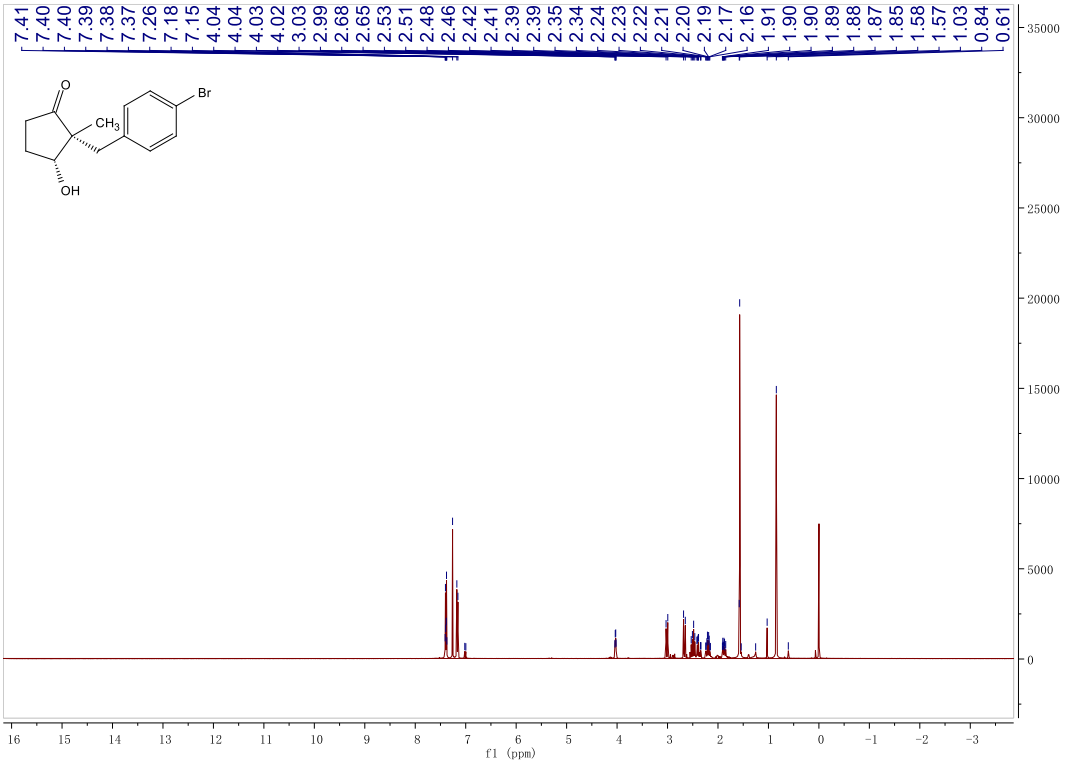


^{13}C NMR

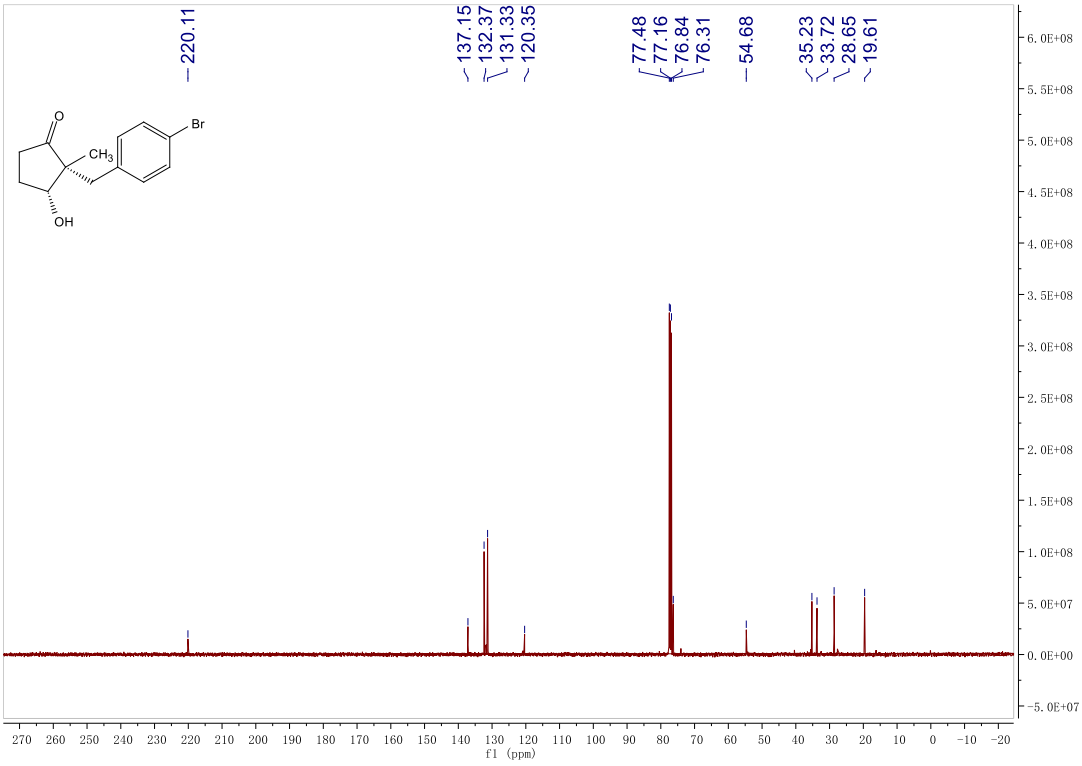


2g (2*R*,3*R*)-2-(4-bromobenzyl)-3-hydroxy-2-methylcyclopentan-1-one

^{1}H NMR

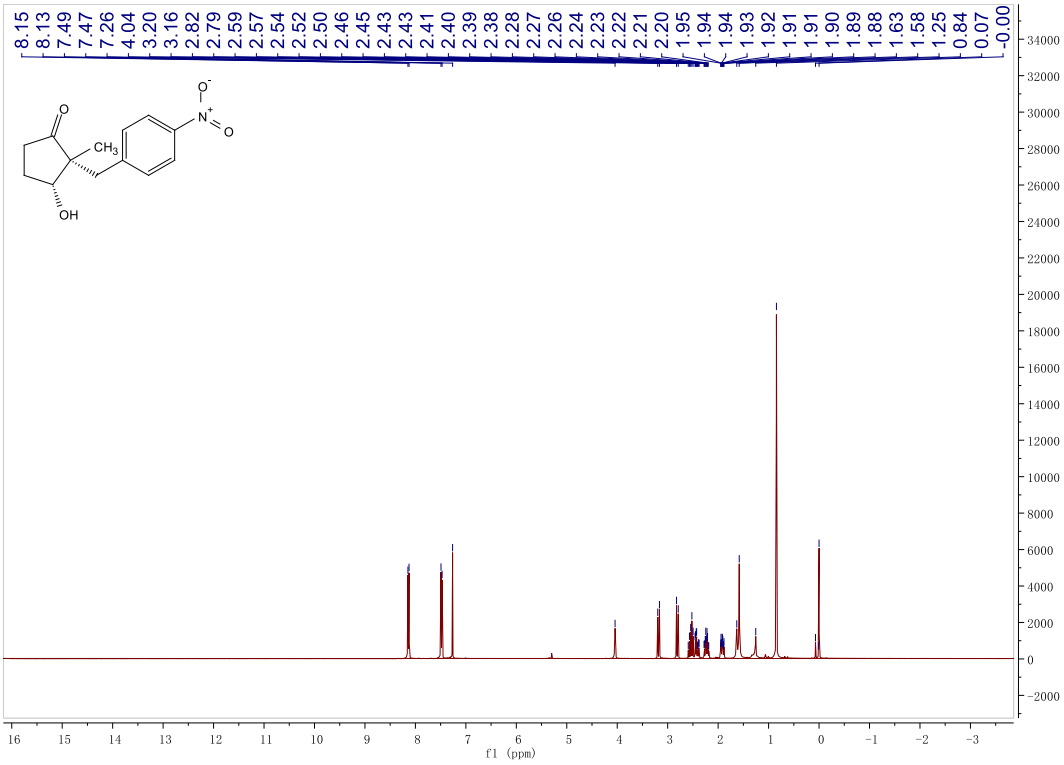


^{13}C NMR

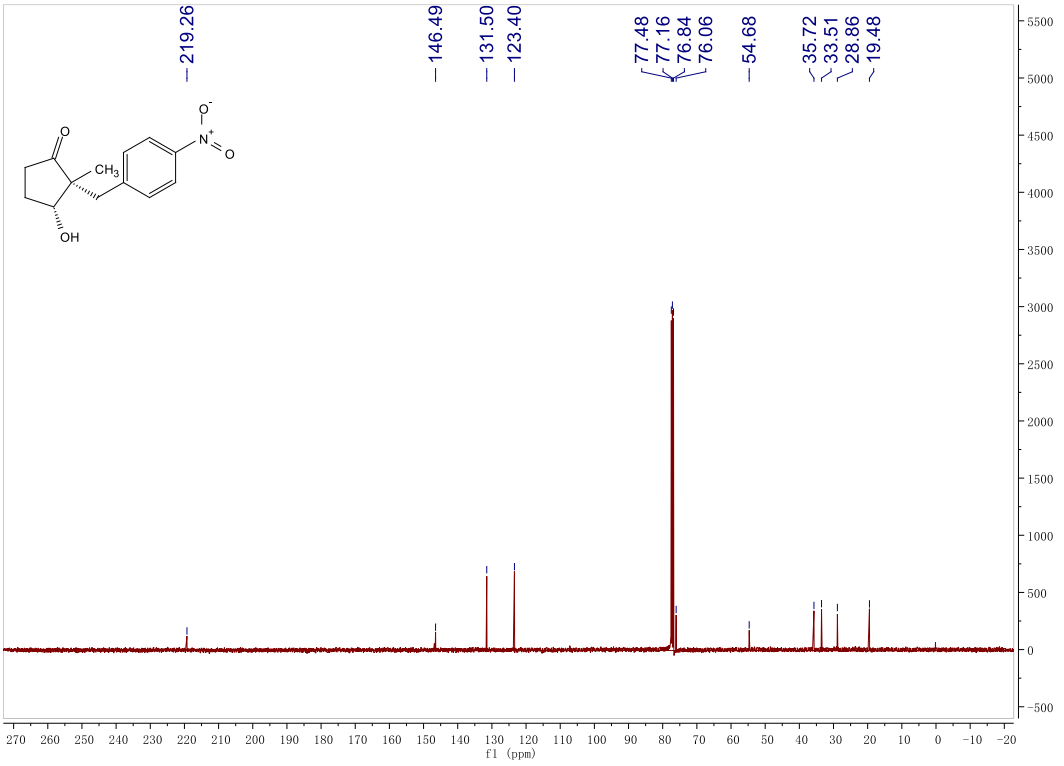


2h (2*R*,3*R*)-3-hydroxy-2-methyl-2-(4-nitrobenzyl)cyclopentan-1-one

^{1}H NMR

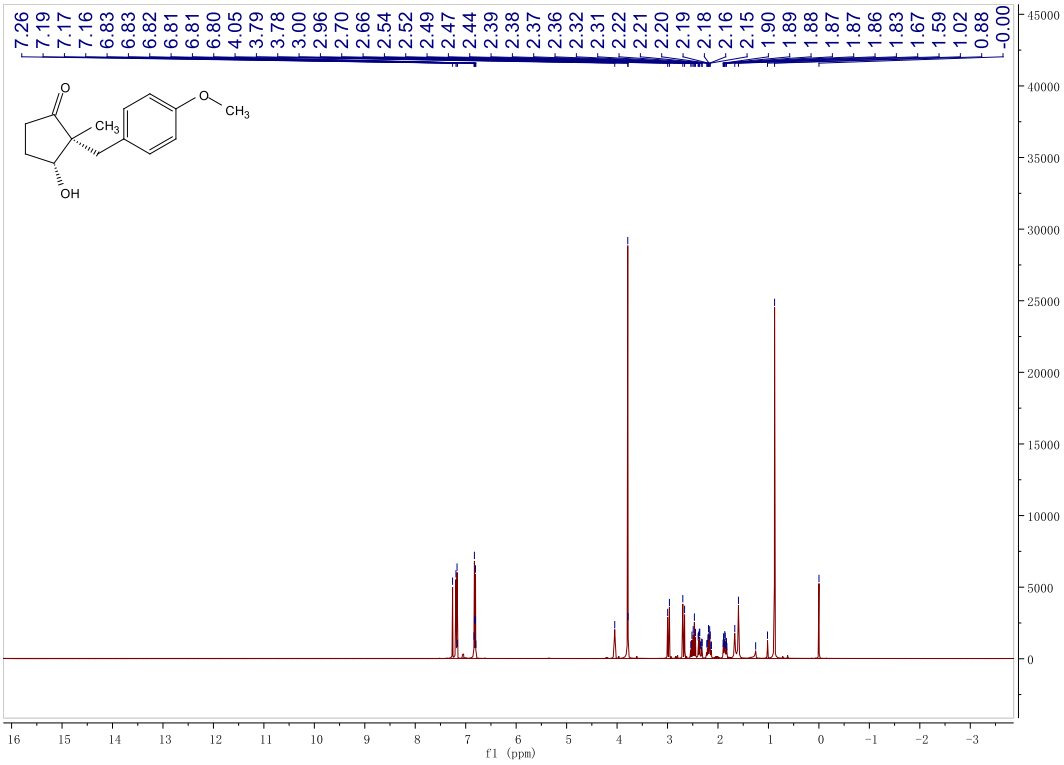


^{13}C NMR

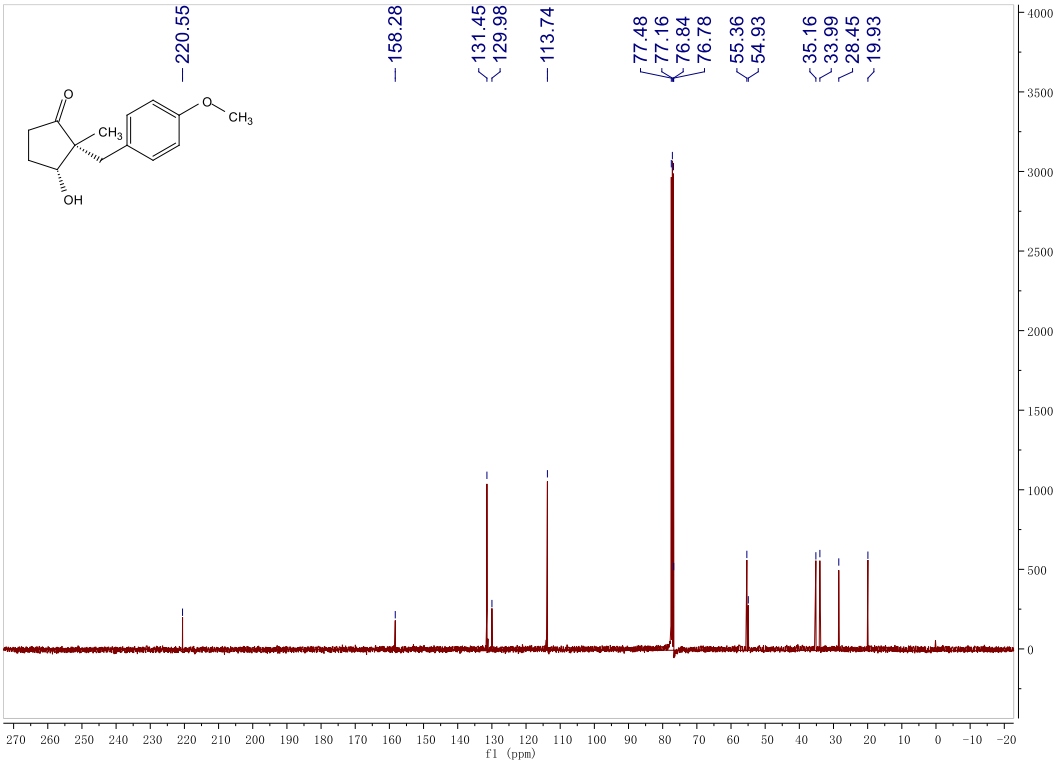


2i (2*R*,3*R*)-3-hydroxy-2-(4-methoxybenzyl)-2-methylcyclopentan-1-one

^{1}H NMR

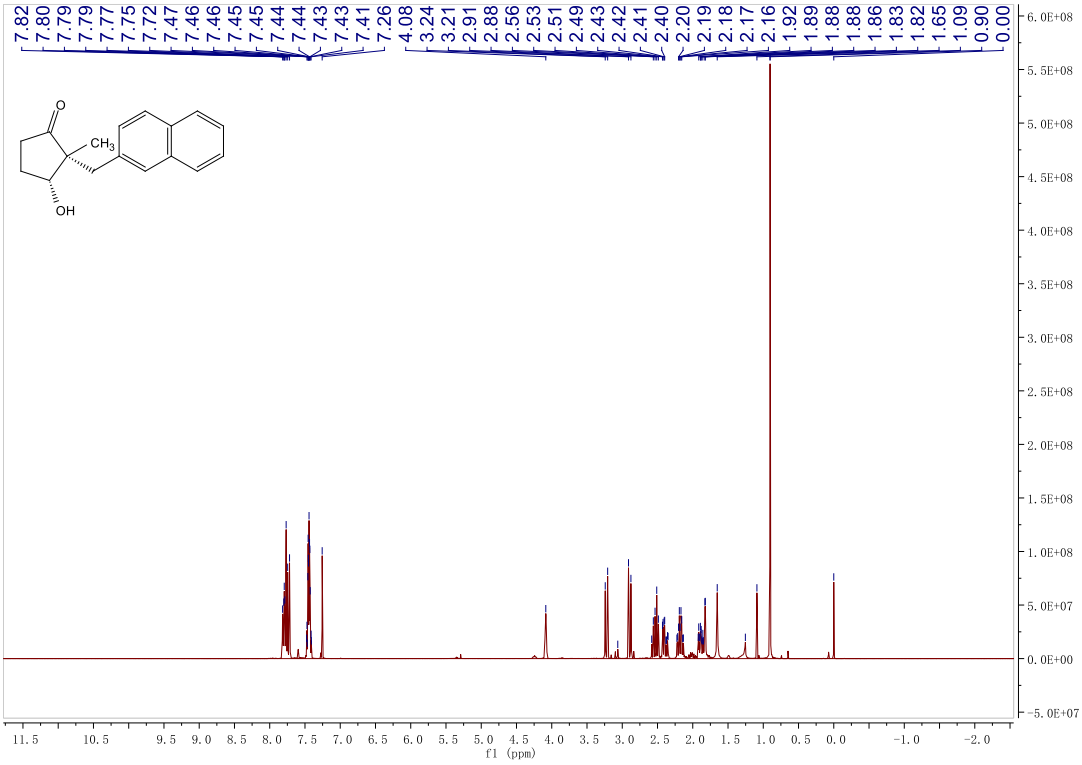


^{13}C NMR

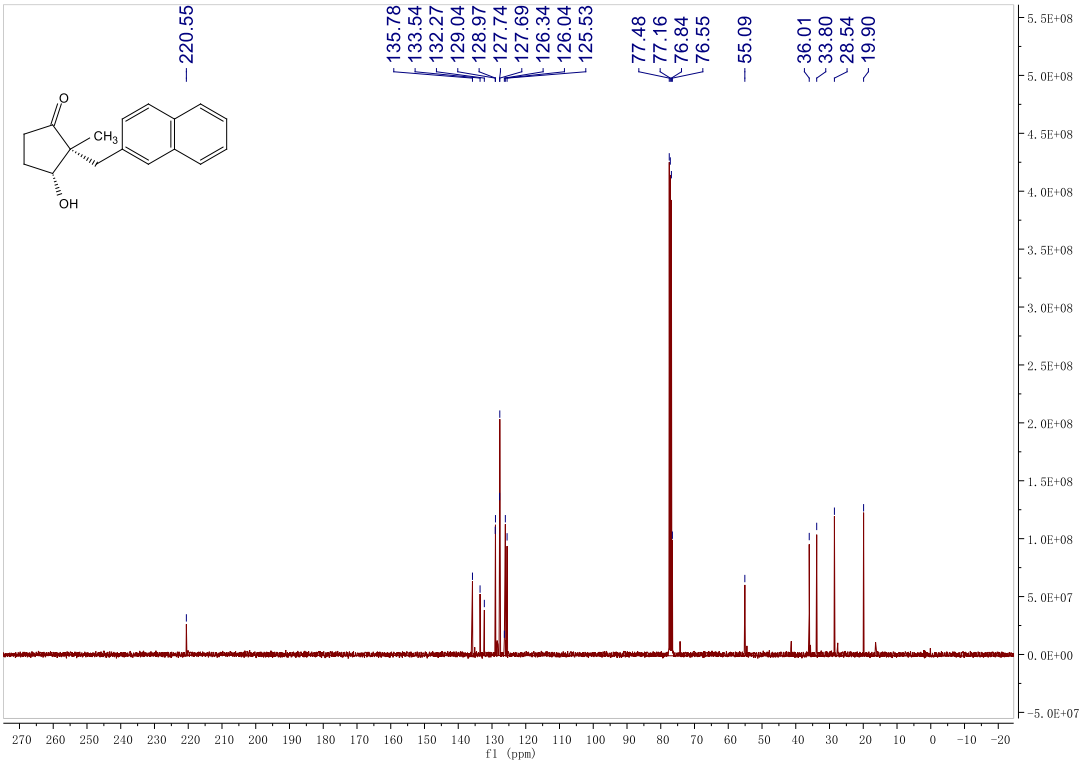


2j (2*R*,3*R*)-3-hydroxy-2-methyl-2-(naphthalen-2-ylmethyl)cyclopentan-1-one

^{1}H NMR

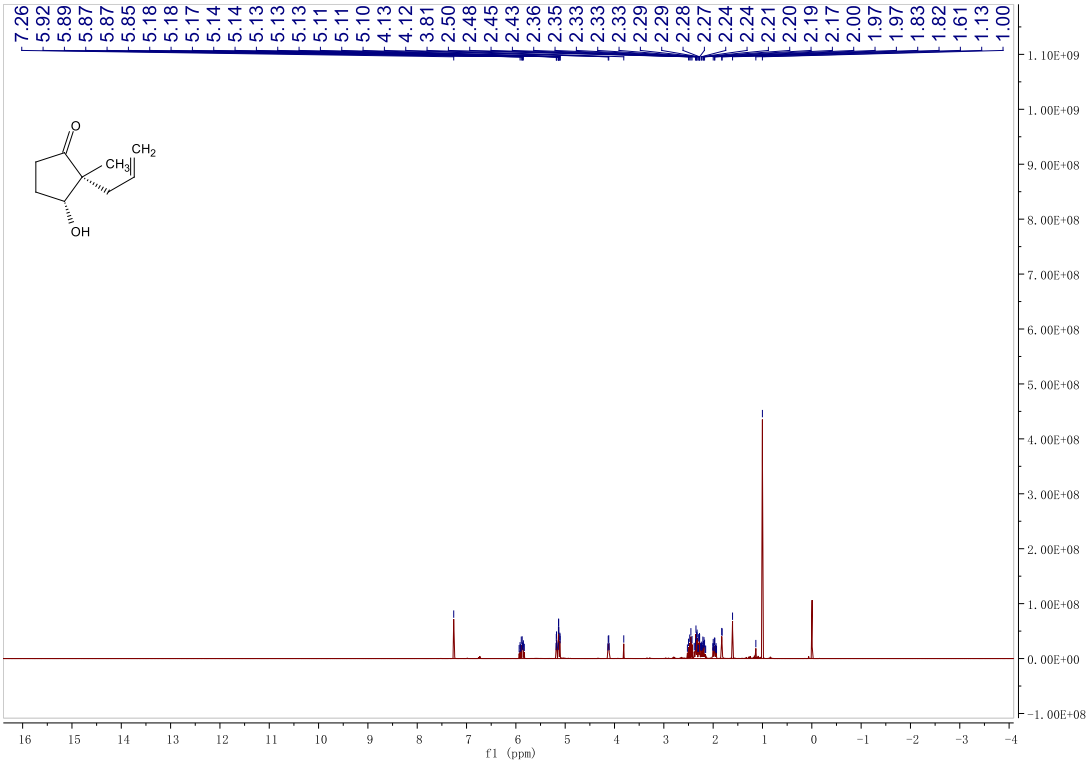


^{13}C NMR

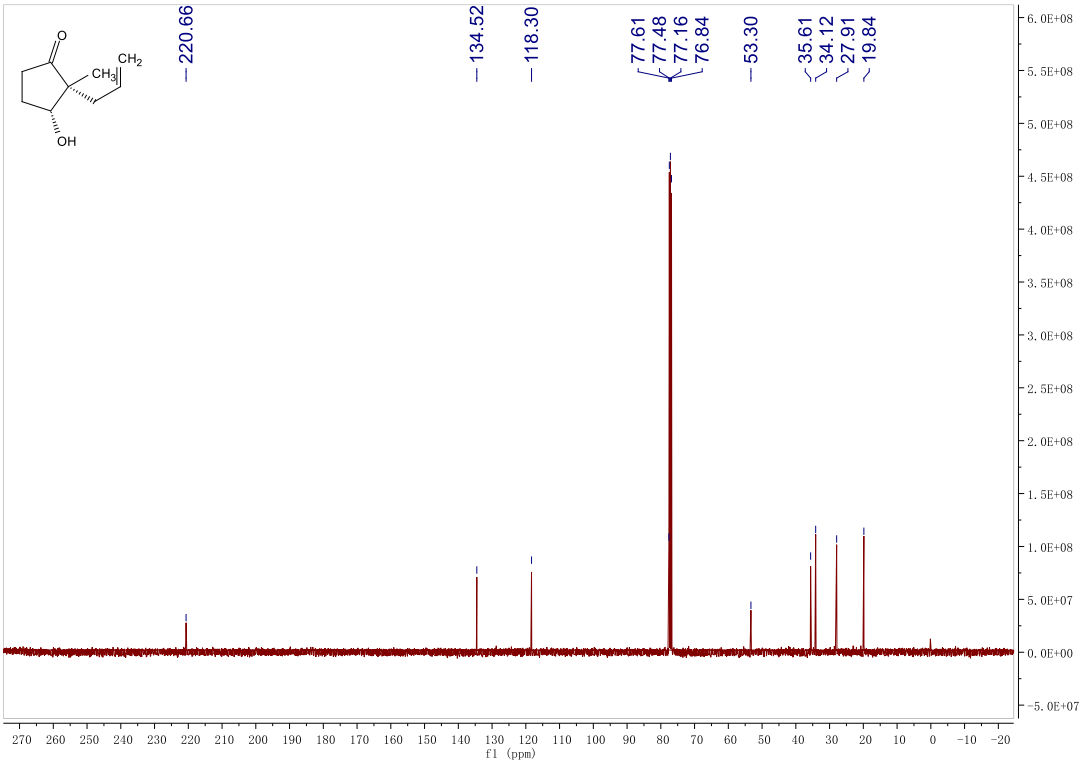


2k (2*R*,3*R*)-2-allyl-3-hydroxy-2-methylcyclopentan-1-one

^{1}H NMR

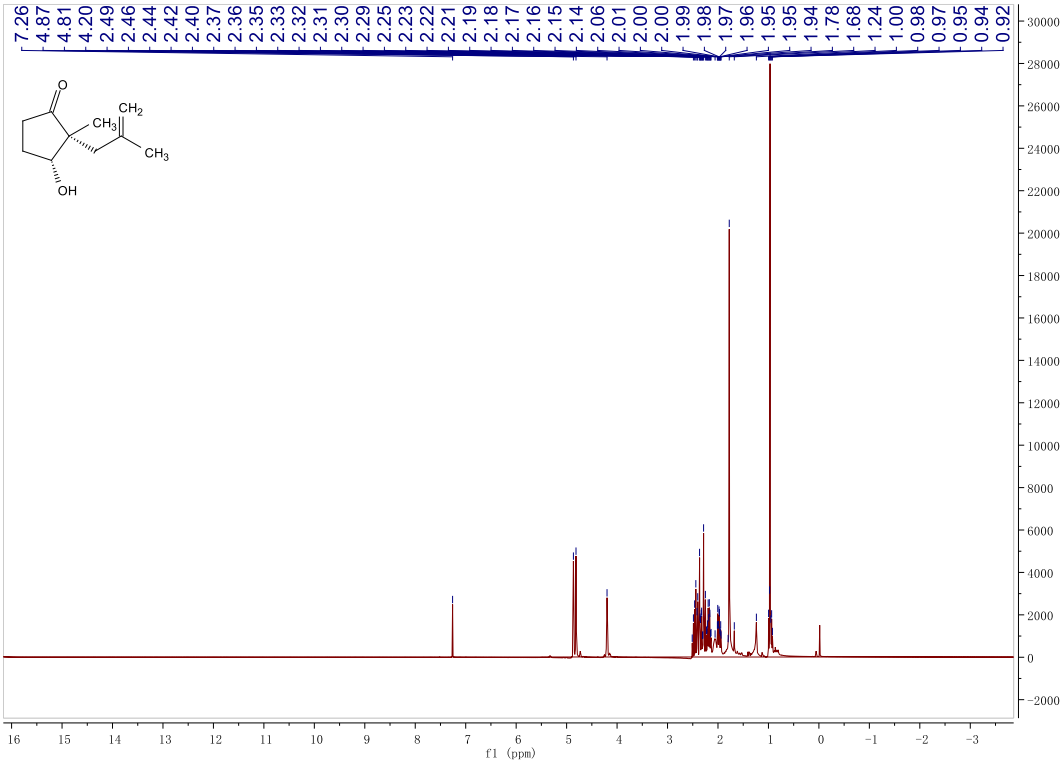


^{13}C NMR

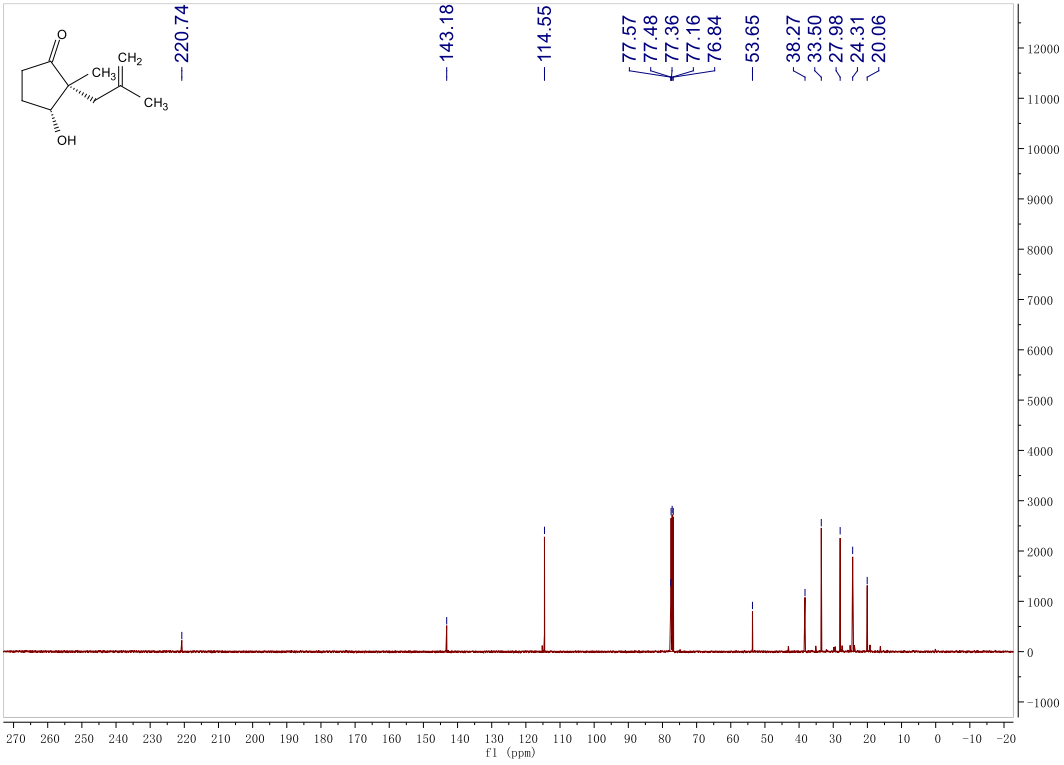


2l (2*R*,3*R*)-3-hydroxy-2-methyl-2-(2-methylallyl)cyclopentan-1-one

^{1}H NMR

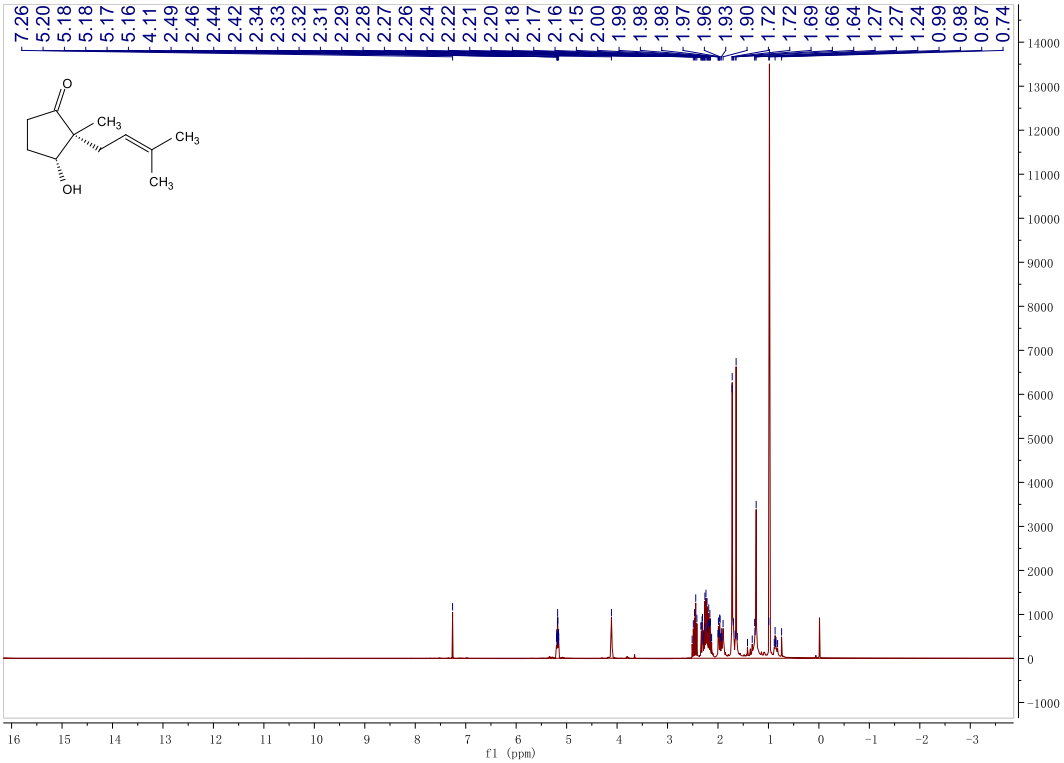


^{13}C NMR

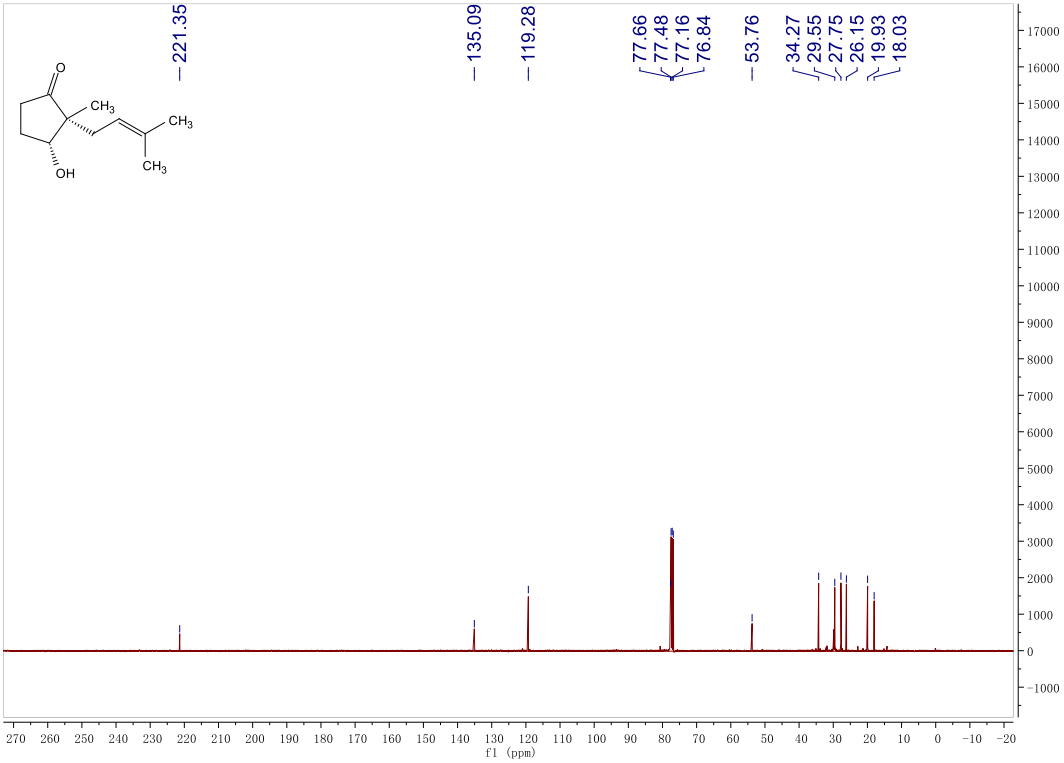


2m (*2R,3R*)-3-hydroxy-2-methyl-2-(3-methylbut-2-en-1-yl)cyclopentan-1-one

^{1}H NMR

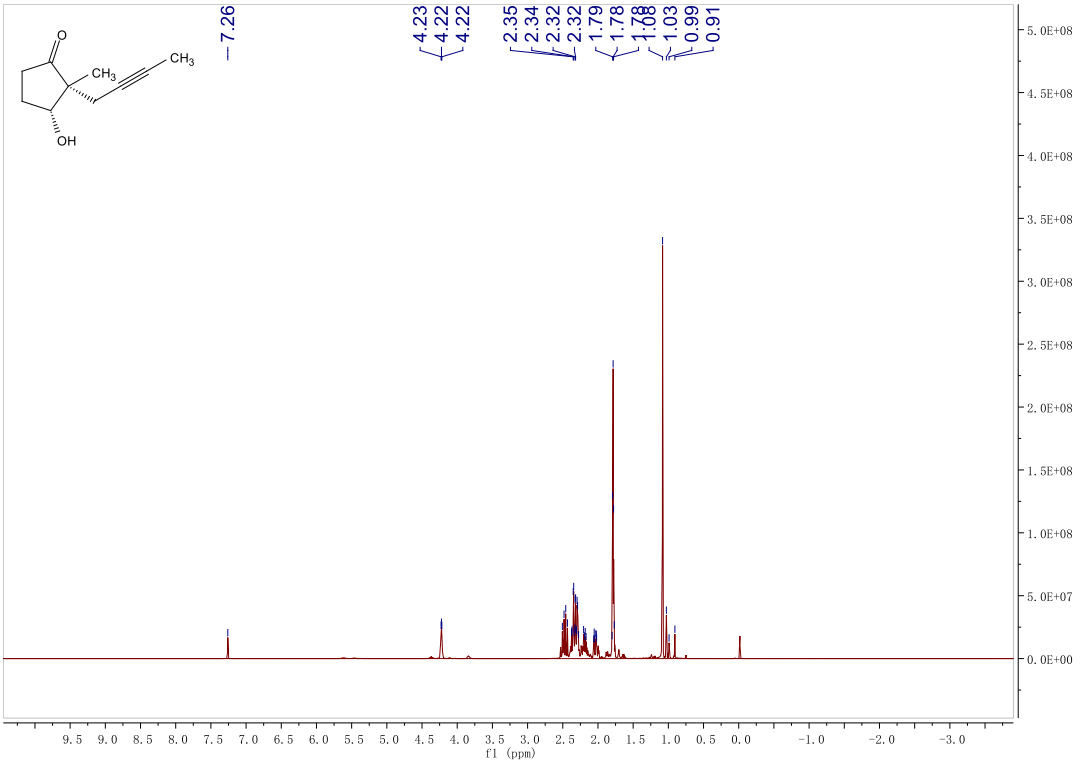


^{13}C NMR

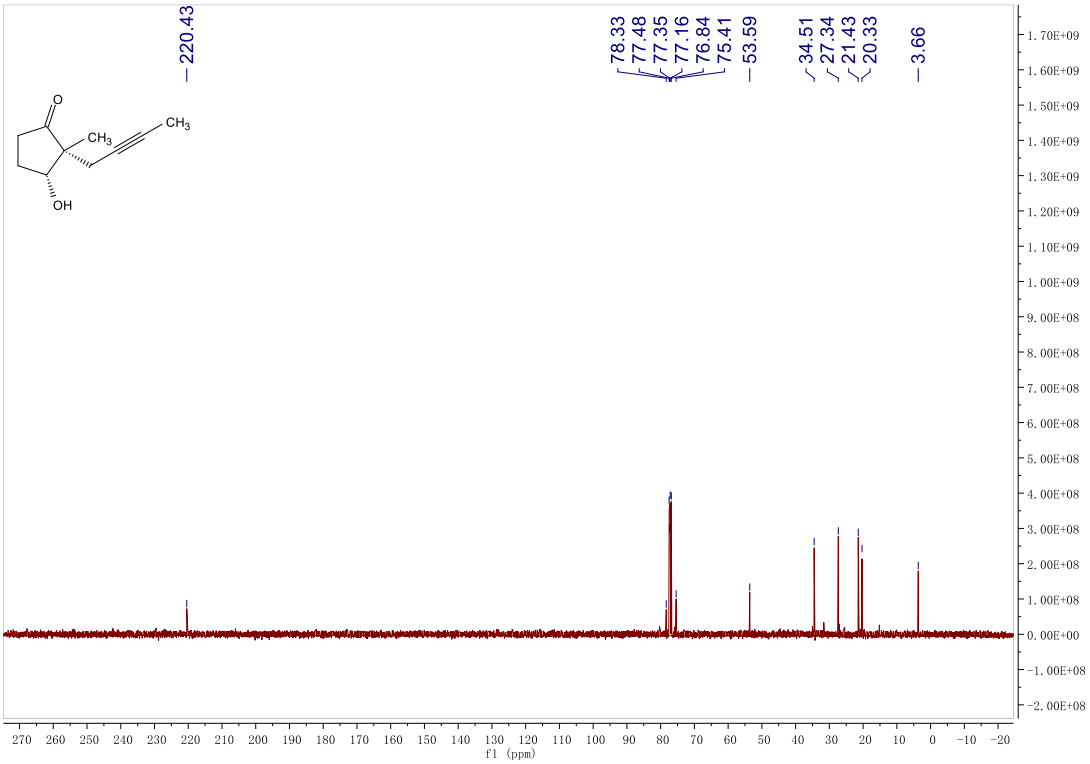


2n (2R,3R)-2-(but-2-yn-1-yl)-3-hydroxy-2-methylcyclopentan-1-one

^{1}H NMR

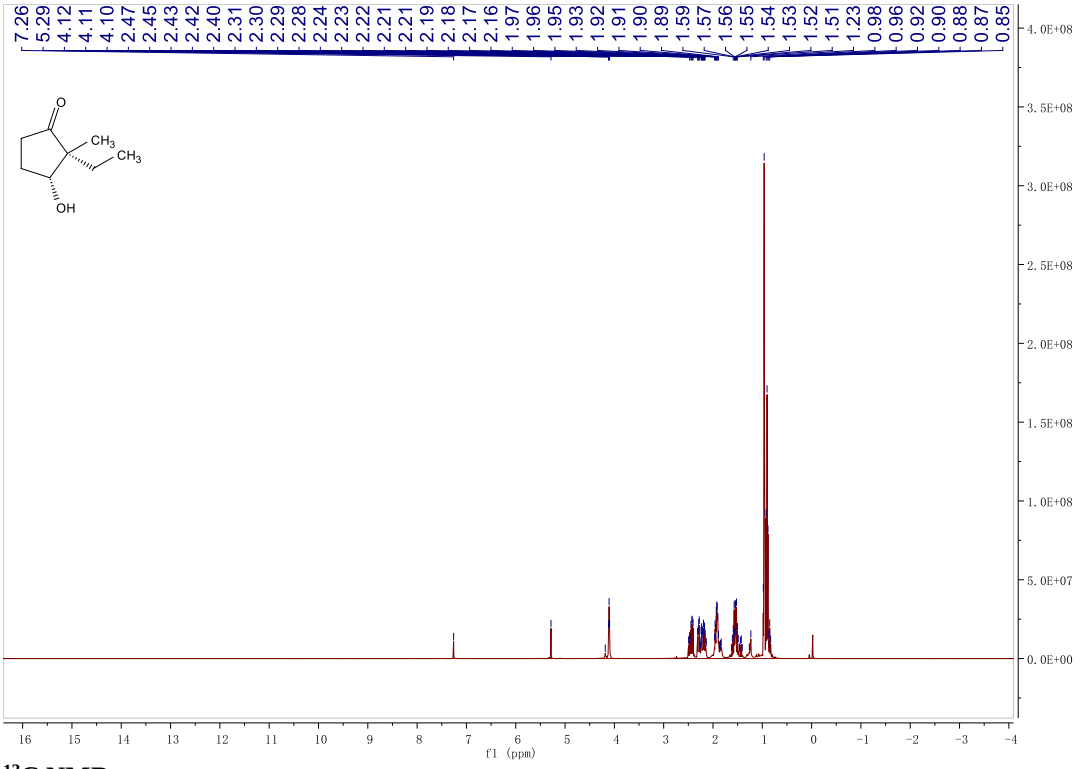


^{13}C NMR

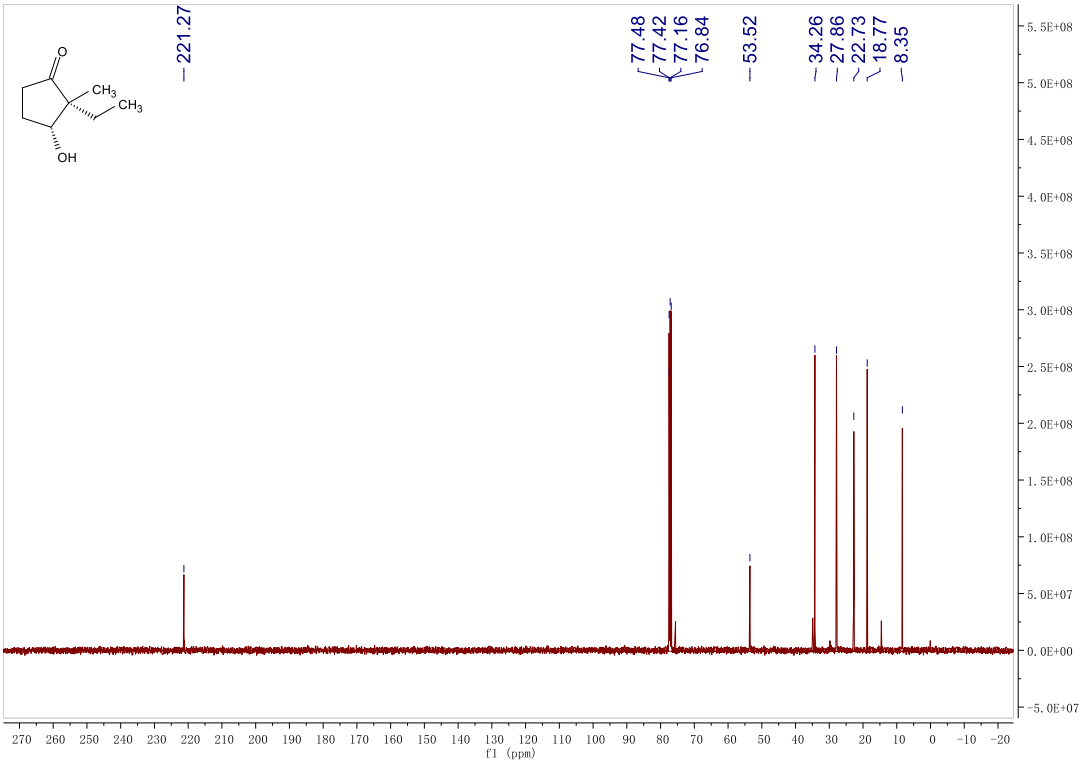


2o (*2R*,*3R*)-3-hydroxy-2-methyl-2-ethylcyclopentan-1-one

^{1}H NMR

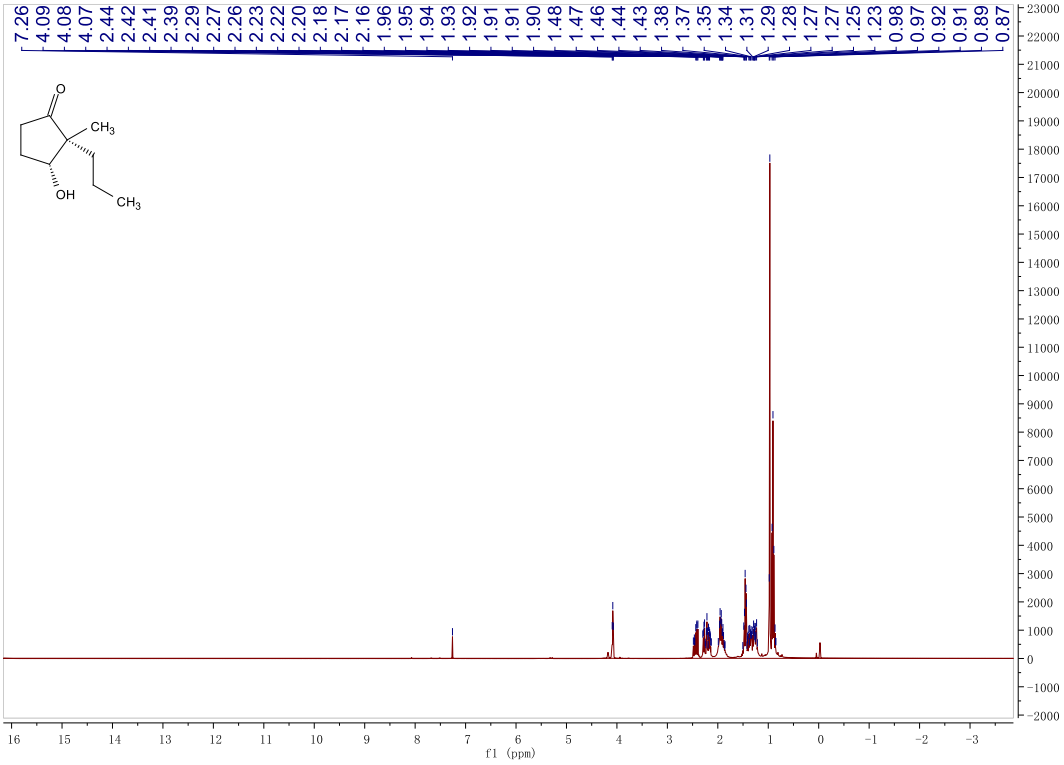


^{13}C NMR

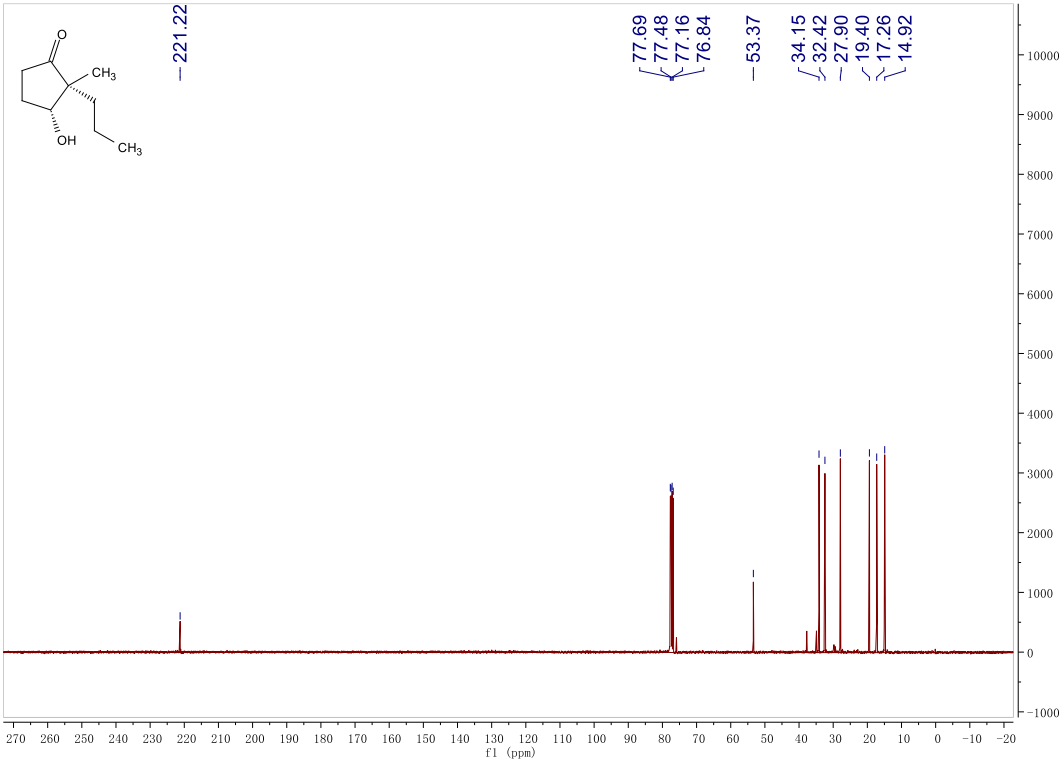


2p (*2R*,*3R*)-3-hydroxy-2-methyl-2-propylcyclopentan-1-one

^{1}H NMR

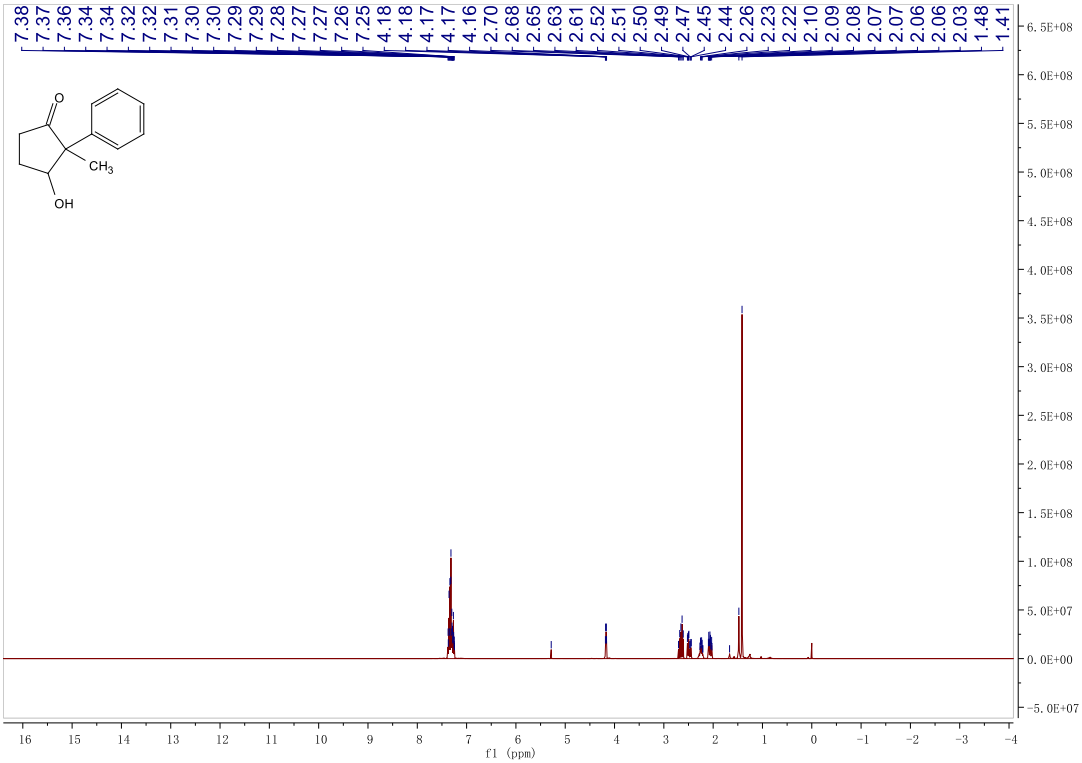


^{13}C NMR

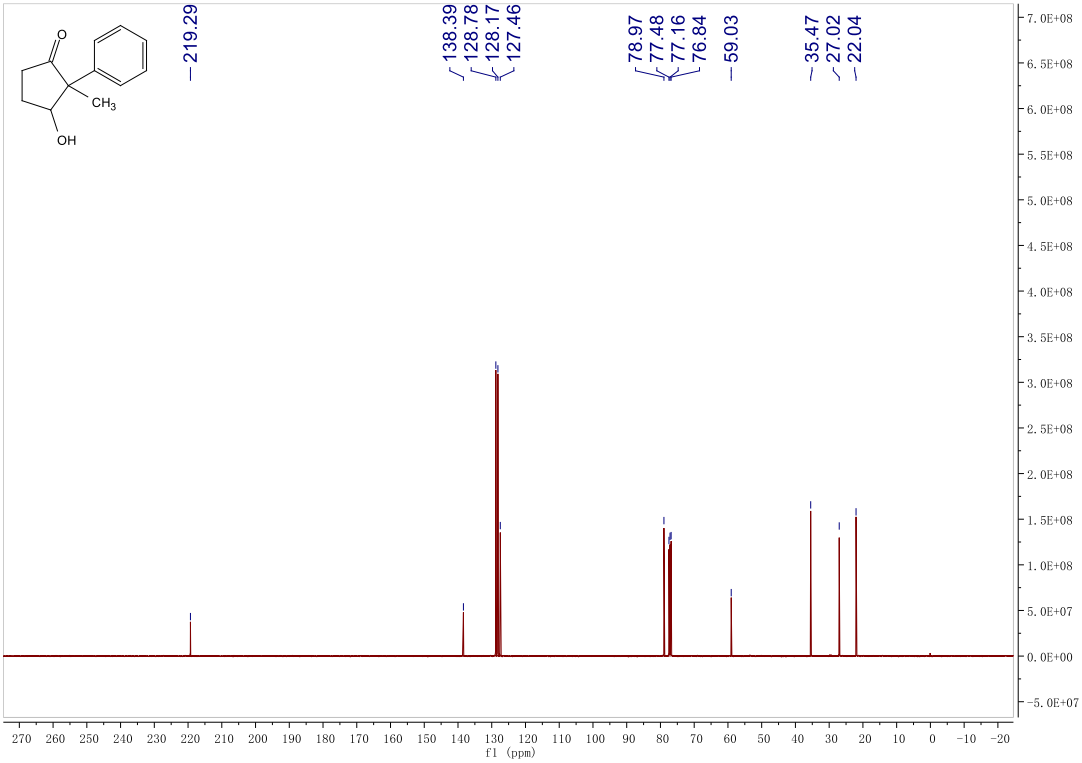


2q (*2S,3R*)-3-hydroxy-2-methyl-2-phenylcyclopentan-1-one

^{1}H NMR

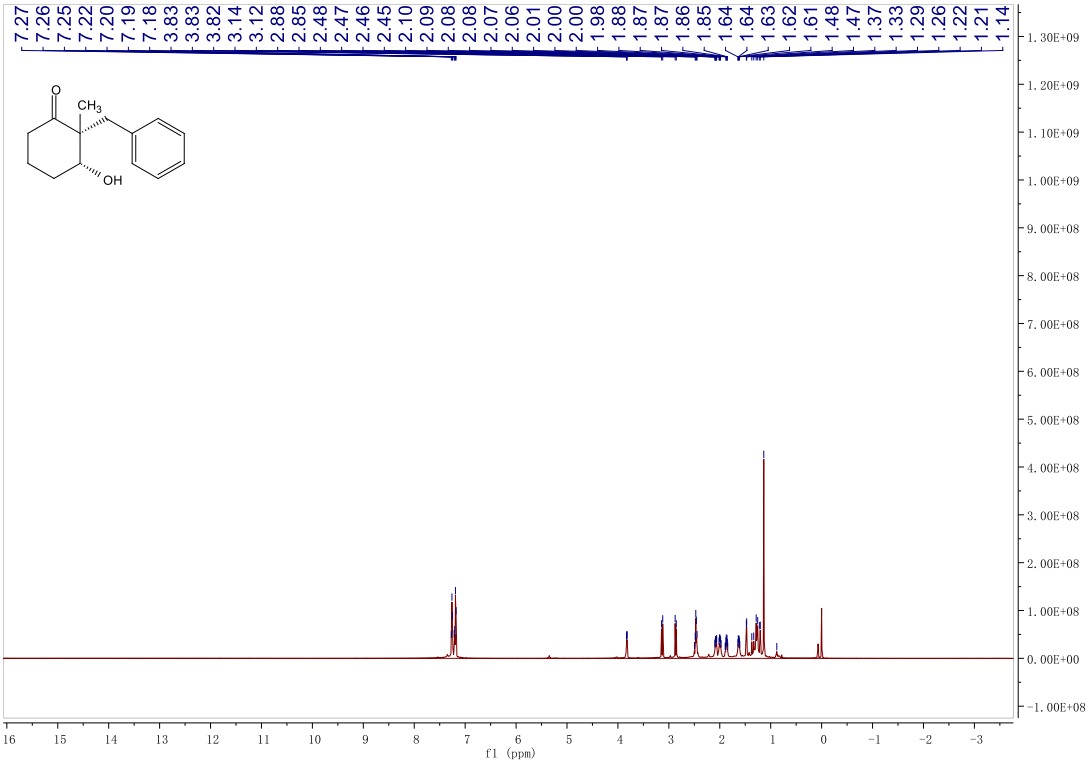


^{13}C NMR

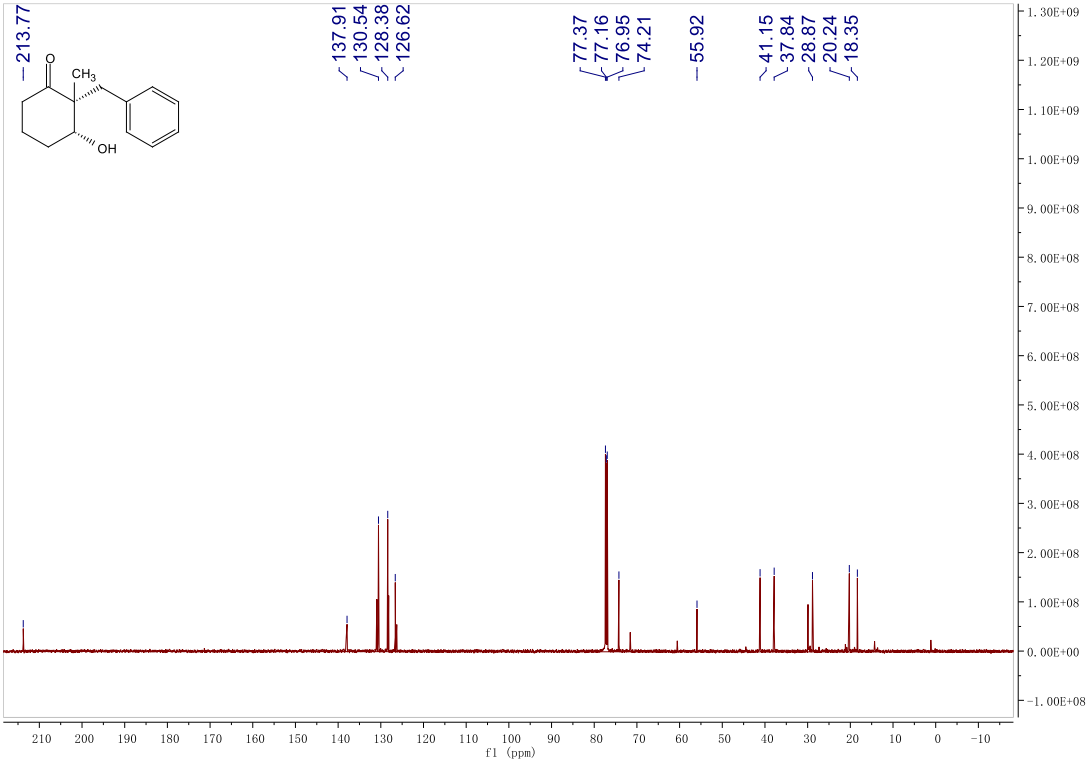


2r (2*R*,3*R*)-2-benzyl-3-hydroxy-2-methylcyclohexan-1-one

^{1}H NMR

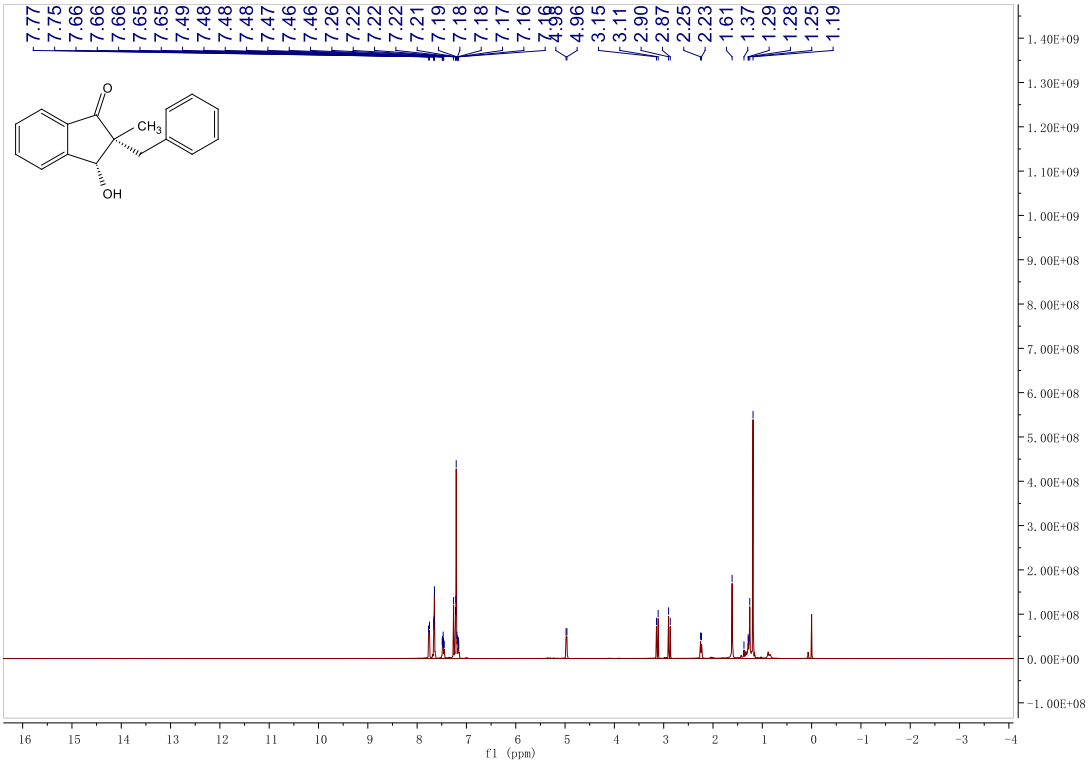


^{13}C NMR

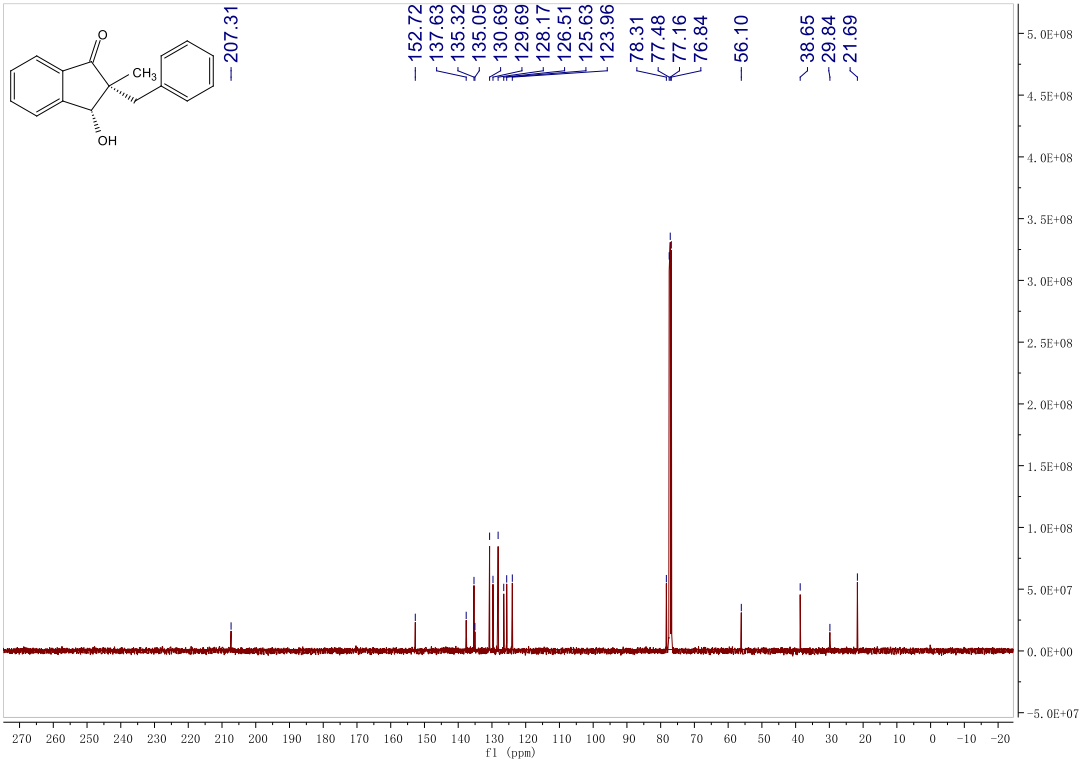


2s (2*R*,3*R*)-2-benzyl-3-hydroxy-2-methyl-2,3-dihydro-1H-inden-1-one

^{1}H NMR

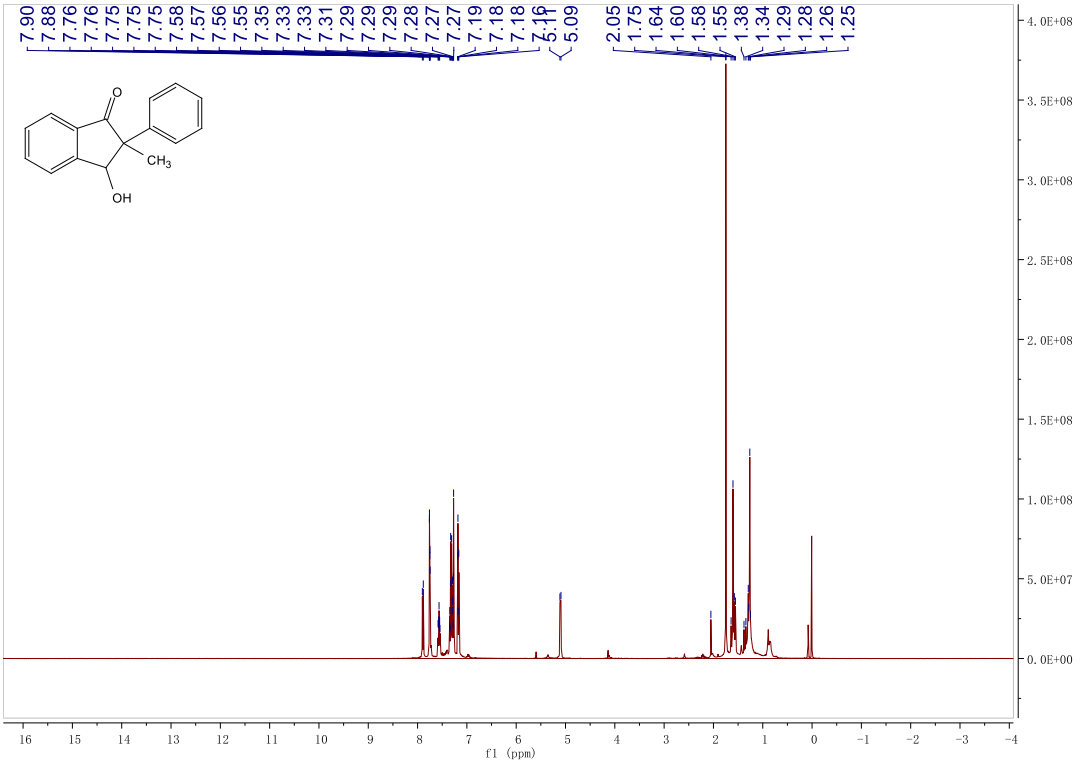


^{13}C NMR

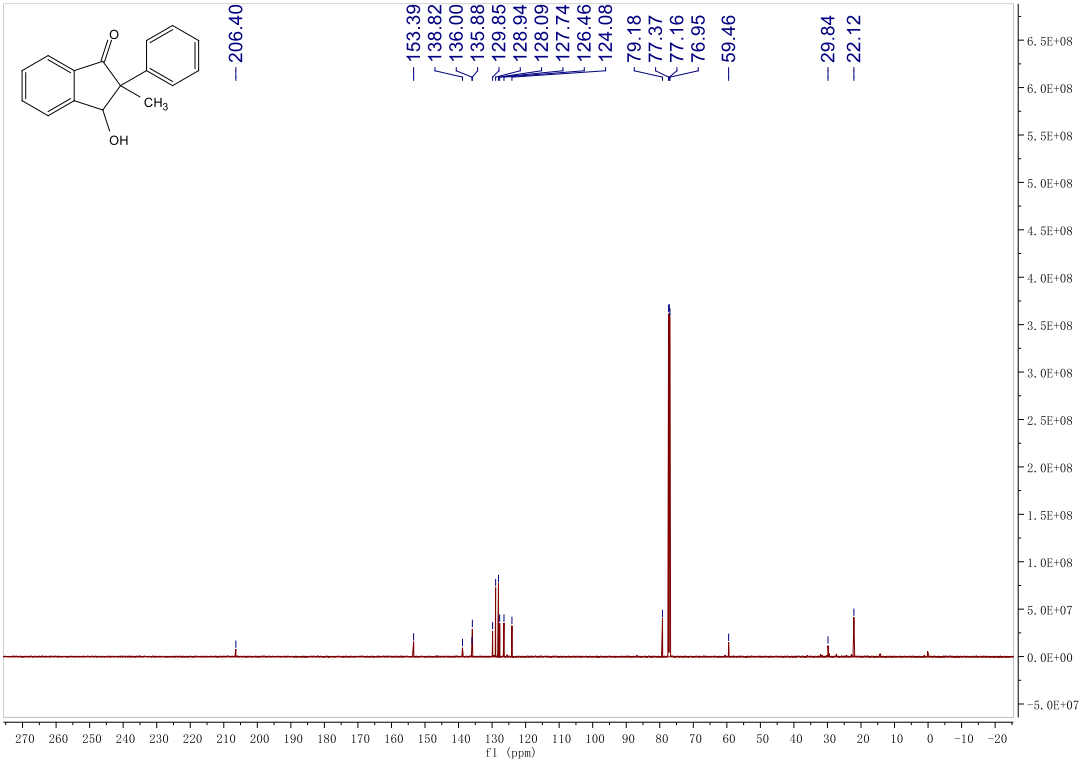


2t (*2S,3R*)-3-hydroxy-2-methyl-2-phenyl-2,3-dihydro-1H-inden-1-one

^{1}H NMR

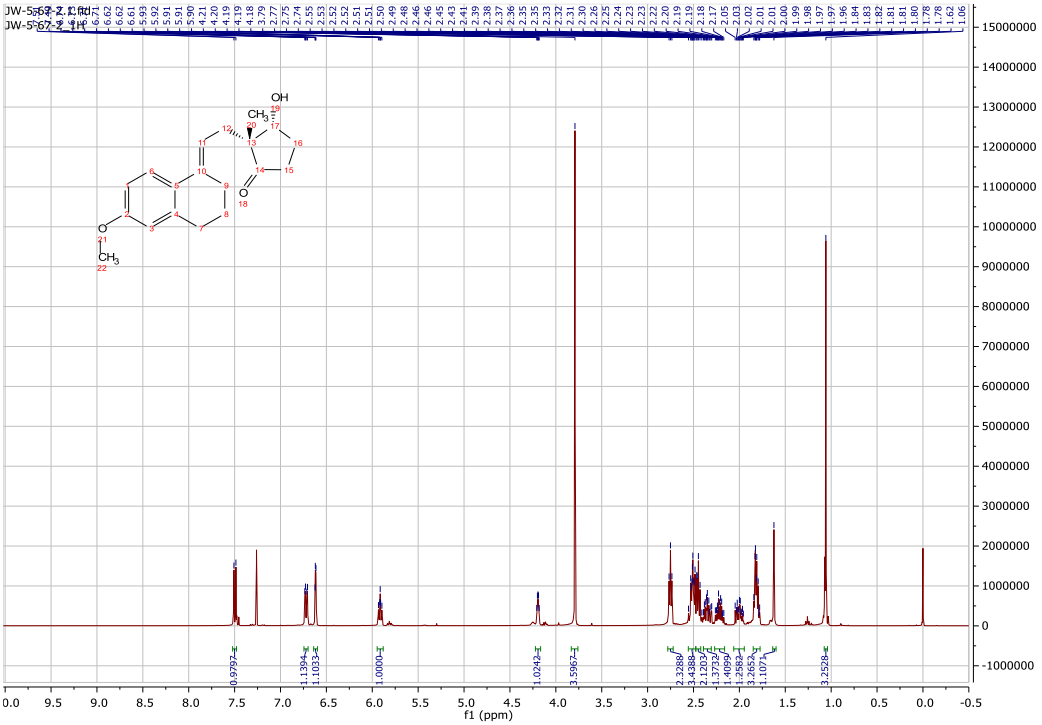


^{13}C NMR

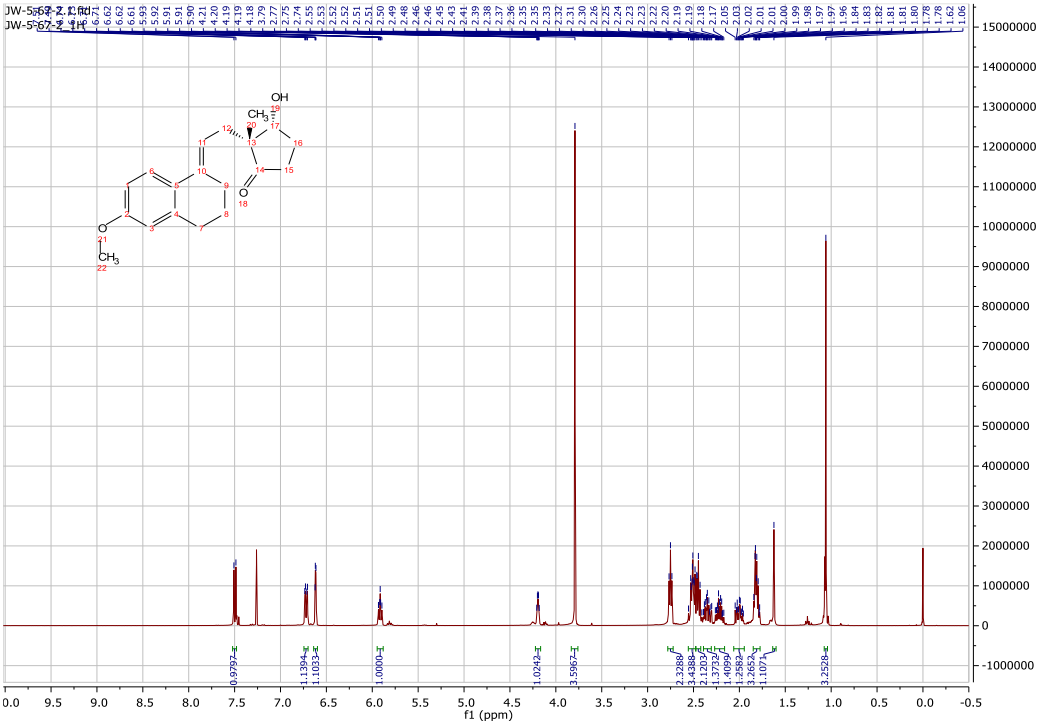


2u (2*R*,3*R*)-3-hydroxy-2-(2-((*E*)-6-methoxy-3,4-dihydronaphthalen-1(2H)-ylidene)ethyl)-2-methylcyclopentan-1-one

^{1}H NMR

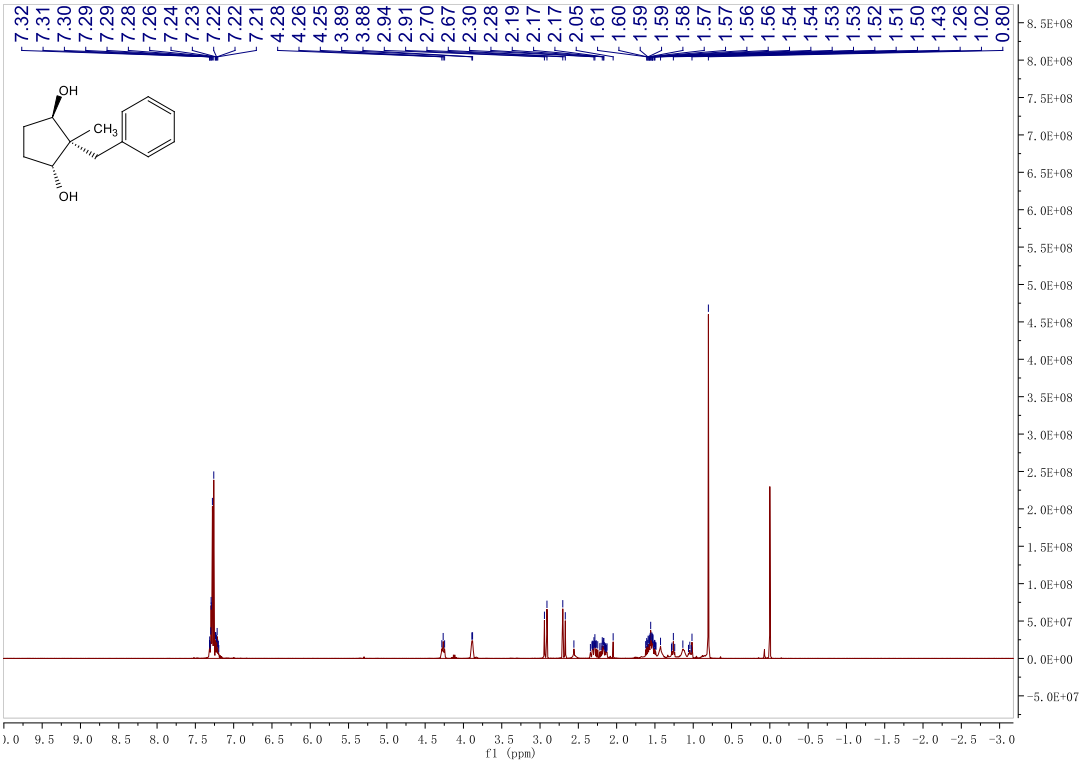


^{13}C NMR

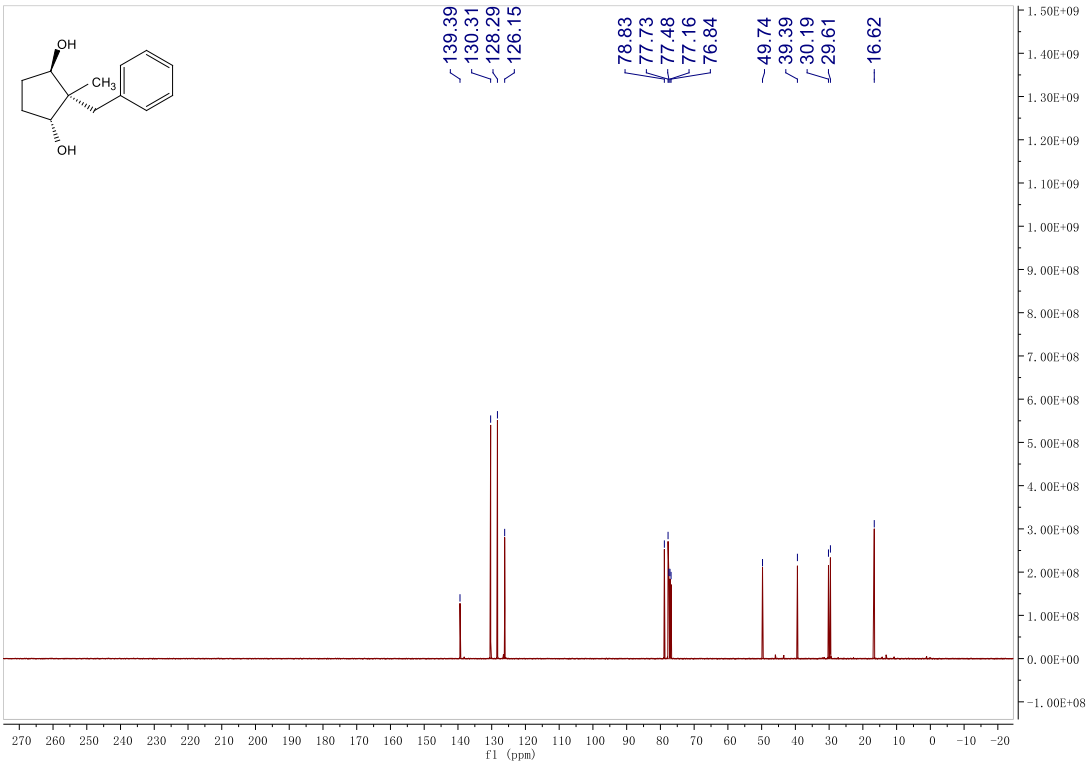


***trans*-3a** (1*R*,3*R*)-2-benzyl-2-methylcyclopentane-1,3-diol

^{1}H NMR

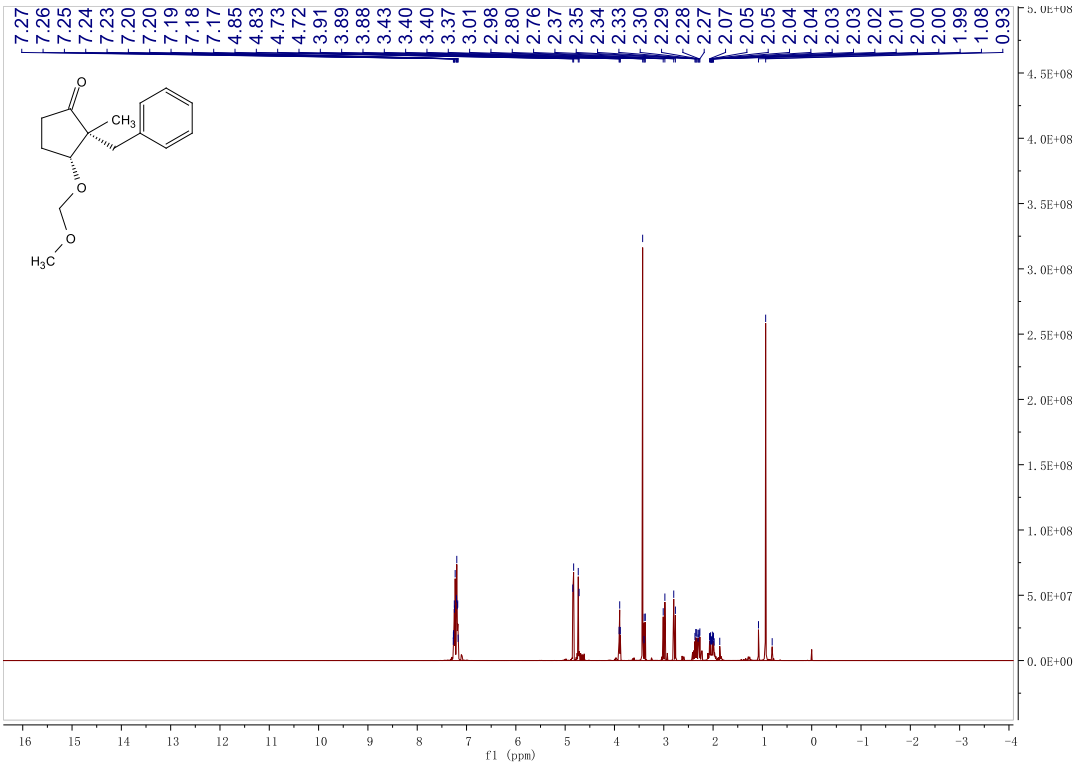


^{13}C NMR

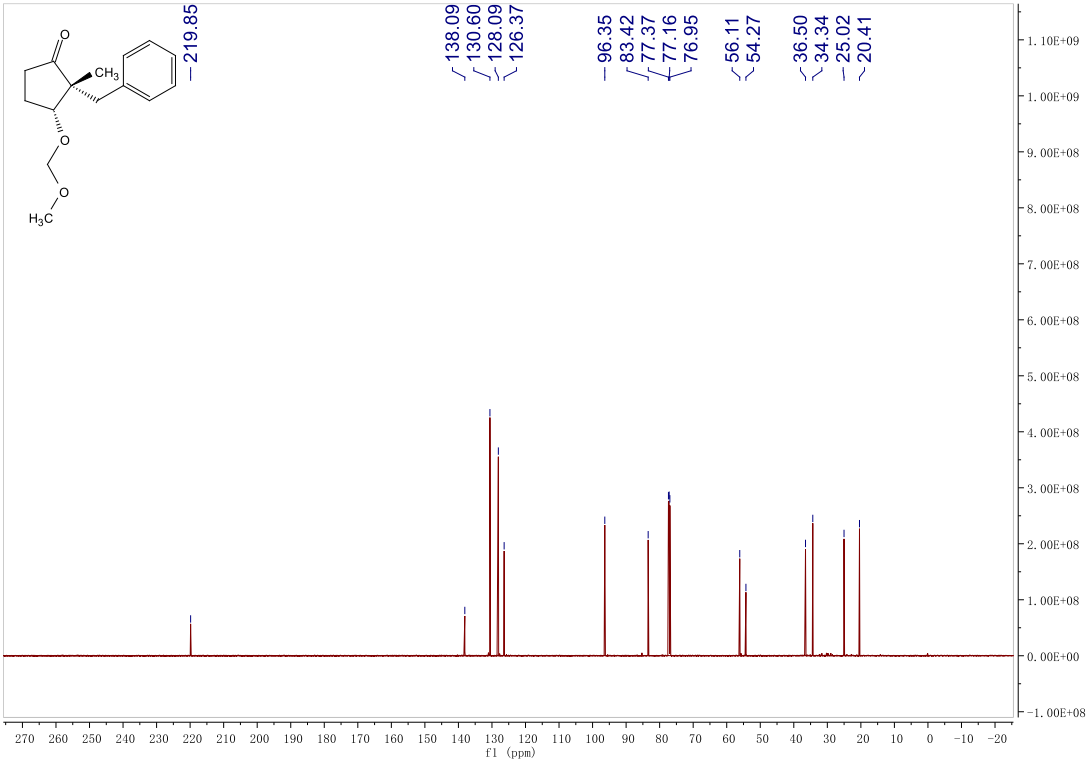


2a-MOM (2R,3R)-2-benzyl-3-(methoxymethoxy)-2-methylcyclopentan-1-one

^{1}H NMR

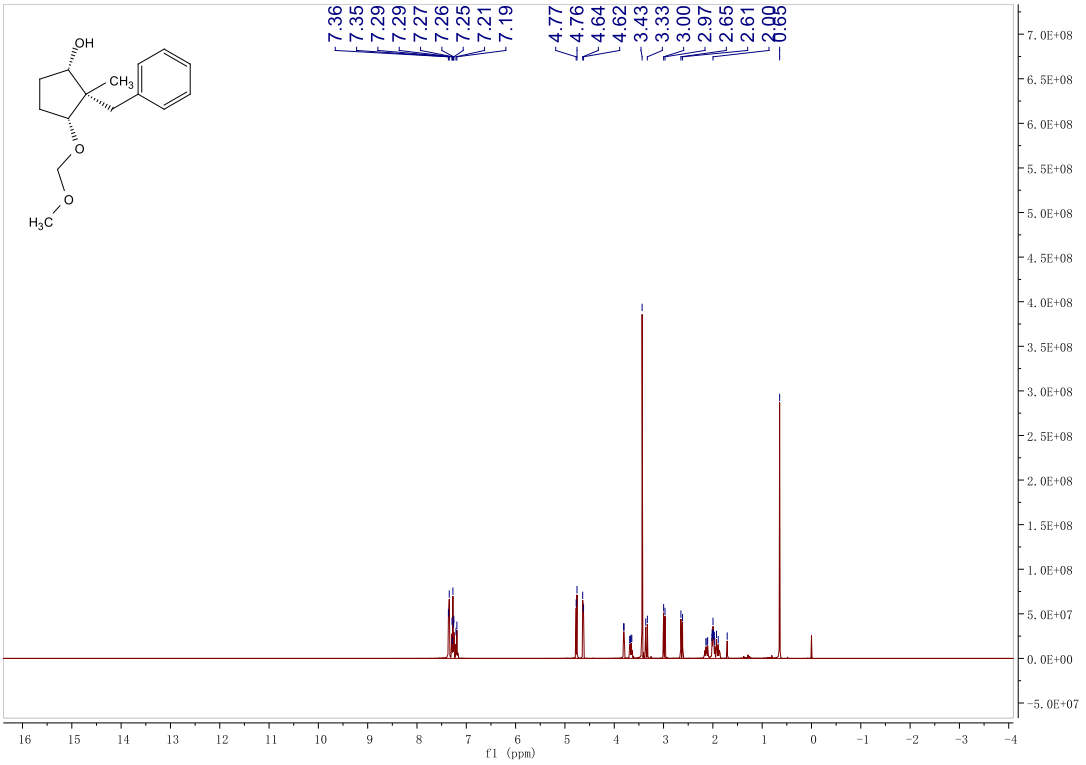


^{13}C NMR

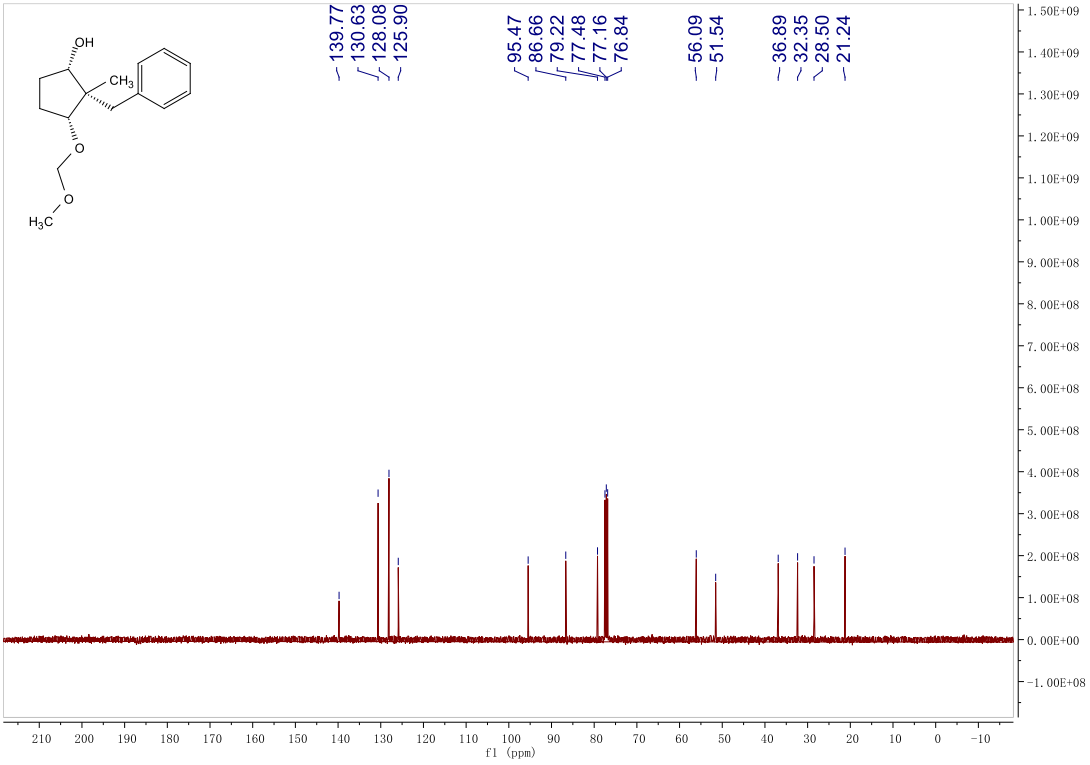


***cis*-3a-MOM** (*1S,2S,3R*)-2-benzyl-3-(methoxymethoxy)-2-methylcyclopentan-1-ol

^{1}H NMR

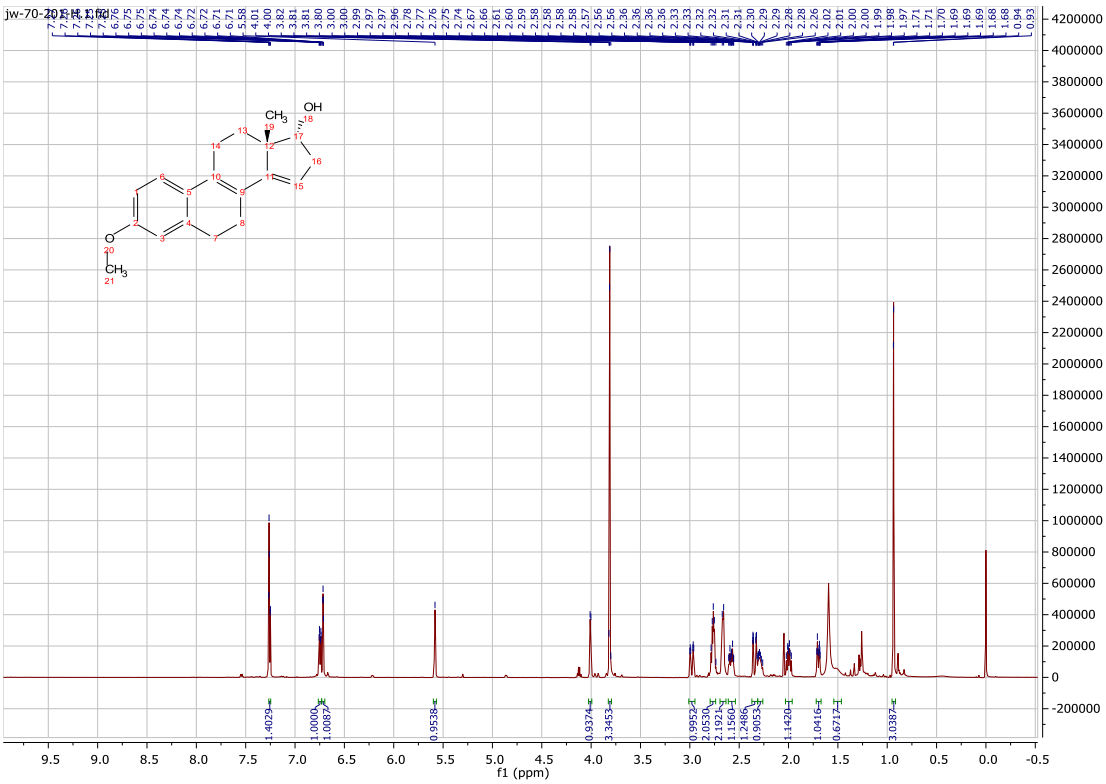


^{13}C NMR

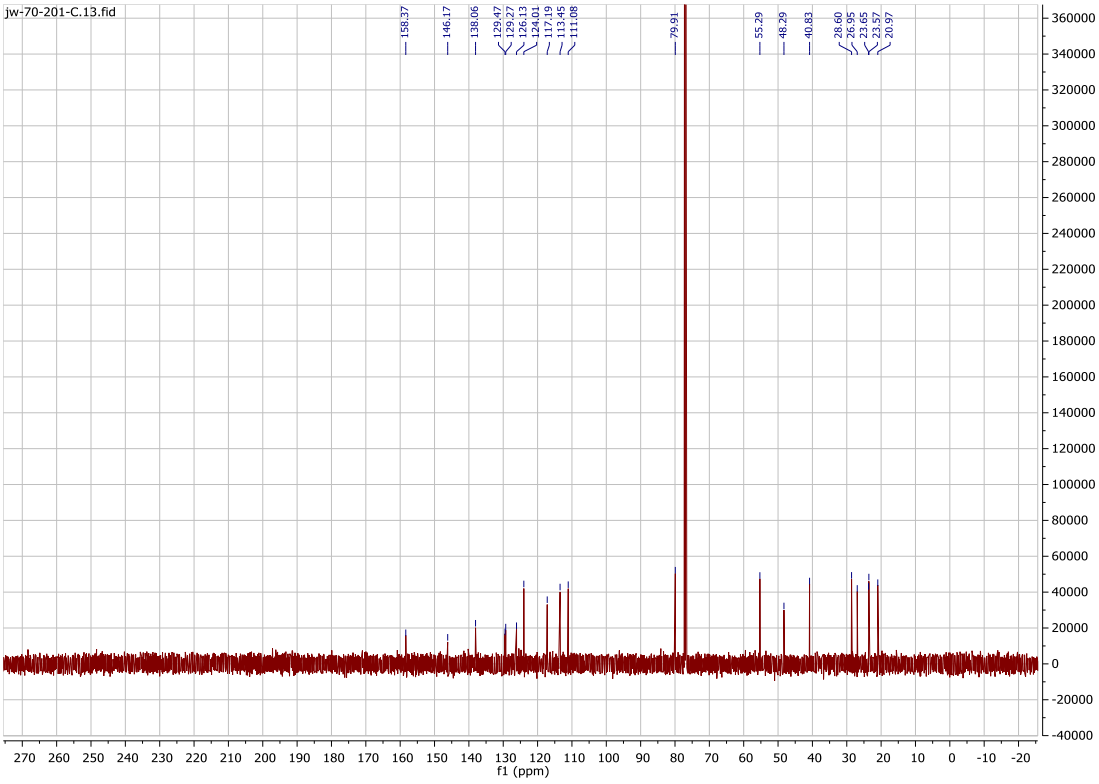


3u (13*S*,17*R*)-3-methoxy-13-methyl-7,11,12,13,16,17-hexahydro-6H-cyclopenta[a]phenanthren-17-ol

^{1}H NMR

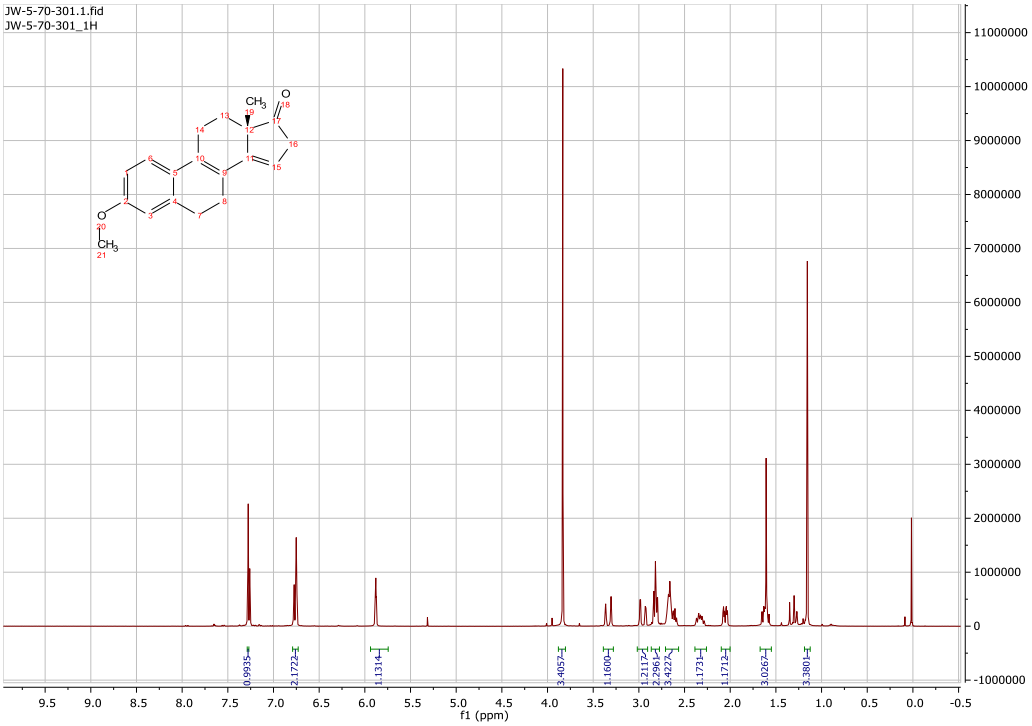


^{13}C NMR

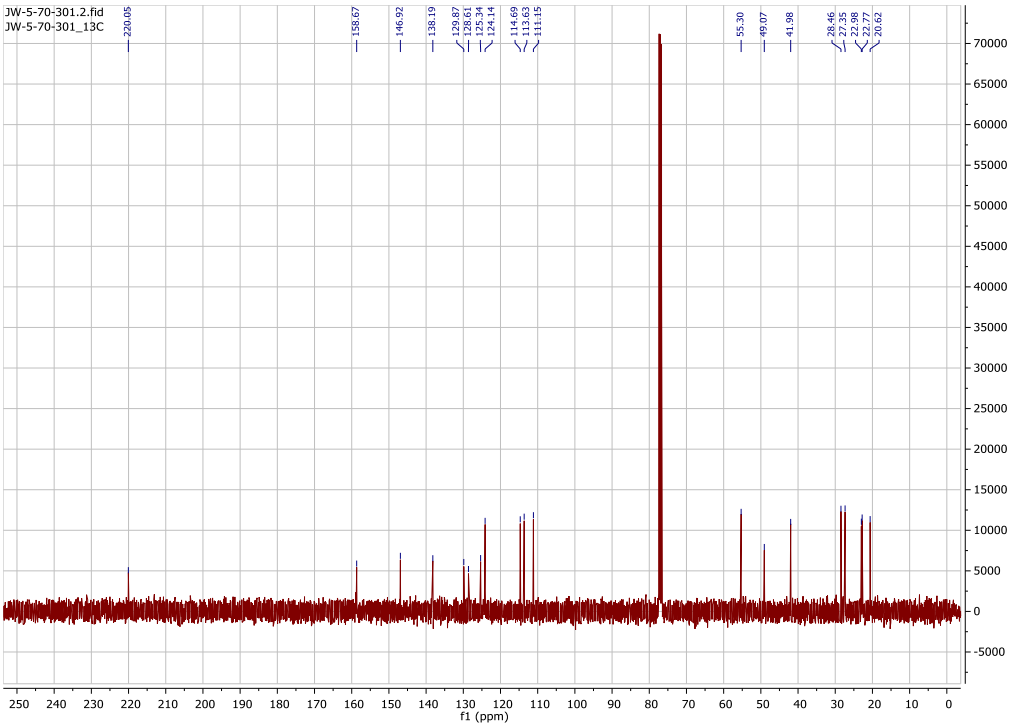


4u (*S*)-3-methoxy-13-methyl-6,7,11,12,13,16-hexahydro-17H-cyclopenta[a]phenanthren-17-one

^{1}H NMR



^{13}C NMR



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