Supplementary Information (SI) for Organic Chemistry Frontiers.

Supporting Information

Dirhodium(II)-catalyzed regio- and stereoselective cycloisomerization towards 6,5,3-tricyclic skeletons containing vicinal all-carbon quaternary stereocenters

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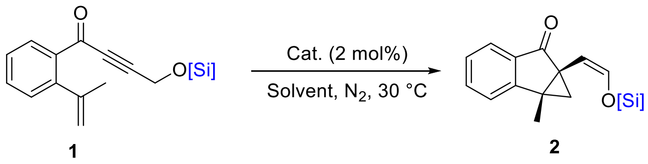
Contents

1. General information

All reactions were carried out under an inert atmosphere of dry N_2 in Schlenk tube. Tetrahydrofuran and toluene were distilled from sodium and benzophenone prior to use. Dichloromethane and dichloroethane were distilled from CaH_2 prior to use. All other reagents and solvents were used as received from commercial sources, unless specified otherwise, or prepared. **^{1}H, ^{13}C, ^{19}F NMR** spectra were recorded on Bruker AVANCE 400 MHz or 500 MHz, **^{1}H NMR** and **^{13}C NMR** chemical shifts were determined relative to internal standard TMS at δ 0.0 and **^{19}F NMR** chemical shifts were determined relative to $CFCl_3$ as external standard. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.. Melting points were determined using a hot stage apparatus. HRMS (EI) and HRMS (ESI) were determined on Waters Micromass GCT Premier, Agilent Technologies 6224 TOF LC/MS, and APEX III 7.0 TESLA FTMS spectrometers, respectively. Specific rotation [a] was determined using a polarimeter ZhuoGuang GP30 with a 1.2 mL cell, long 10 cm, $[\alpha]_D^T$ values, reported in mL g^{-1} dm^{-1}, are calculated on the average value of 3 consecutive readings. The chiral Rh_2(II) catalysts were purchased from Strem Chemicals, Inc. Enantiomeric ratios were determined by HPLC, using a chiral OD-H, OJ-H, IC, NC, INA and INC column with hexane and *i*-PrOH as solvents.

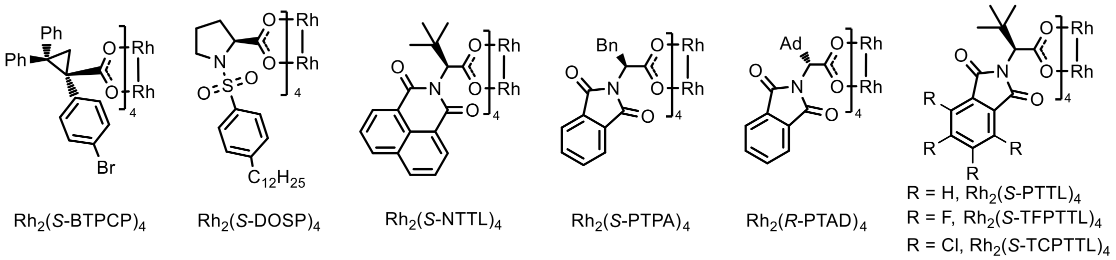
2. Optimization of reaction conditions

Table S1[a]



Entry	Cat.	[Si]	**2**	Solvent	Yield[b]	ee[c]	*Z:E*[d]
1	Rh$_2$(OPiv)$_4$	TBS	**2d**	DCE	57%	-	>99:1
2	Rh$_2$(*S*-BTPCP)$_4$	TBS	**2d**	DCE	49%	35%	>99:1
3	Rh$_2$(*S*-NTTL)$_4$	TBS	**2d**	DCE	6%	70%	>99:1
4	Rh$_2$(*S*-DOSP)$_4$	TBS	**2d**	DCE	45%	23%	>99:1
5	Rh$_2$(*S*-PTTL)$_4$	TBS	**2d**	DCE	14%	37%	>99:1
6	Rh$_2$(*S*-PTPA)$_4$	TBS	**2d**	DCE	60%	2%	>99:1
7	Rh$_2$(*R*-PTAD)$_4$	TBS	**2d**	DCE	13%	21%	>99:1
8	Rh$_2$(*S*-TFPTTL)$_4$	TBS	**2d**	DCE	66%	40%	>99:1
9	Rh$_2$(*S*-TCPTTL)$_4$	TBS	**2d**	DCE	64%	90%	>99:1
10	**Rh$_2$(*S*-TCPTTL)$_4$**	TBS	**2d**	**DCM**	**84%**[d]	**93%**	>99:1

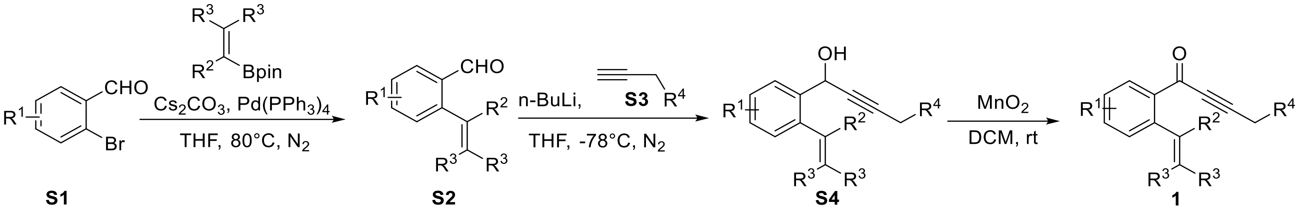
11	$Rh_2(S\text{-}TCPTTL)_4$	TBDPS	**2e**	DCM	18%	74%	>99:1
12	$Rh_2(S\text{-}TCPTTL)_4$	TIPS	**2f**	DCM	52%	83%	>99:1
13	$Rh_2(S\text{-}TCPTTL)_4$	TBS	**2d**	$CHCl_3$	64%	89%	>99:1
14	$Rh_2(S\text{-}TCPTTL)_4$	TBS	**2d**	Toluene	60%	75%	>99:1
15[g]	$Rh_2(S\text{-}TCPTTL)_4$	TBS	**2d**	DCM	57%	92%	>99:1
16[h]	$Rh_2(S\text{-}TCPTTL)_4$	TBS	**2d**	DCM	73%	93%	>99:1
17[i]	$Rh_2(S\text{-}TCPTTL)_4$	TBS	**2d**	DCM	33%	90%	>99:1



[a]Experiments were performed with **1** (0.05 mmol), catalyst (2 mol%) in solvent with stirring at the temperature for 48 h. (Cat. = catalyst; ee = enantiomeric excess, Ad = 1-admantyl). [b]NMR yield; [c]Determined by chiral HPLC; [e]DCM as solvent; [g]Raw DCM as solvent; [h]1 mol% catalyst; [i]0 °C. (TBS = *tert*-butyldimethylsilyl, TBDPS = *tert*-butyldiphenylsilyl, TIPS = triisopropylsilyl)

3. General procedure for preparation of 1,6-enynes

Typical procedure A[1]:



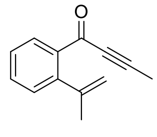
To an N_2-sparged solution of **S1** (10 mmol, 1.0 equiv), alkenylboronic acid pinacol ester (11 mmol, 1.1 equiv) and cesium carbonate (30 mmol, 3.0 equiv) in THF (50 mL) was added $Pd(PPh_3)_4$ (0.2 mmol, 2 mol%). The mixture was stirred at 80 °C for 12 h. After the reaction completed (monitored by GC-MS), it was diluted with water and extracted with EtOAc. The combined organics were washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting residue was flash chromatographed (PE: EA = 200:1) on silica gel to afford the product **S2**.

Under N_2 atmosphere, the solution of n-BuLi (6 mmol, 1.2 equiv) in hexane (1.6 mol/L) was added dropwise into the solution of **S3** (6 mmol, 1.2 equiv) in anhydrous THF at -78℃. After the 30 min, aldehyde **S2** (5 mmol, 1.0 equiv) dissolved in anhydrous THF was added and the temperature was allowed to raise to room temperature. After the complete consumption of **S3** (determined by TLC, about 1 h), the reaction was quenched by saturated NH_4Cl (aq), and extracted with EtOAc. The organic phase was washed with brine and dried with anhydrous Na_2SO_4, the solvent was removed by rotary evaporator. The resulting residue was flash chromatography (PE: EA = 10:1) on silica gel to afford the product **S4**.

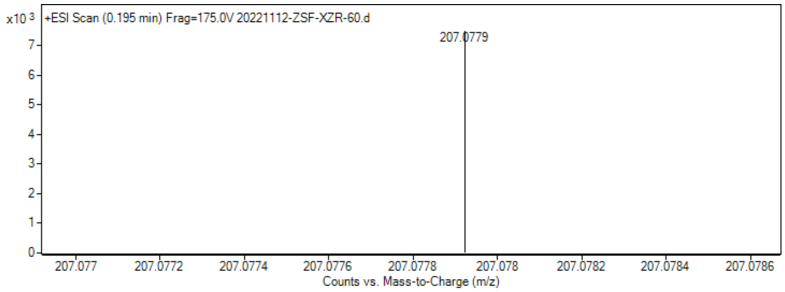
To the solution of **S4** (2 mmol, 1.0 equiv) in 10 mL DCM, activated MnO_2 (20 mmol, 10 equiv) was added and the mixture was stirred at room temperature for about 3 h. After the complete consumption of **S4** determined by TLC, the reaction mixture was filtered through silica gel and the filtrate was concentrated by rotary evaporator. The resulting residue was flash chromatographed (PE: EA = 20:1) on silica gel to afford the product **1**.

The substrates such as **1a, 1c, 1d, 1e, 1f, 1g, 1h, 1i, 1j, 1k, 1l, 1m, 1n, 1o, 1p, 1q, 1r, 1s, 1t, 1u, 1v, 1w, 1x, 1y, 3k, 3n, 3o, 3p, 3r** were synthesized according to General procedure **A.**

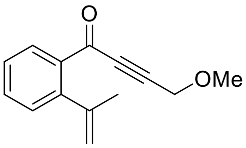
1-(2-(prop-1-en-2-yl)phenyl)but-2-yn-1-one (1a)



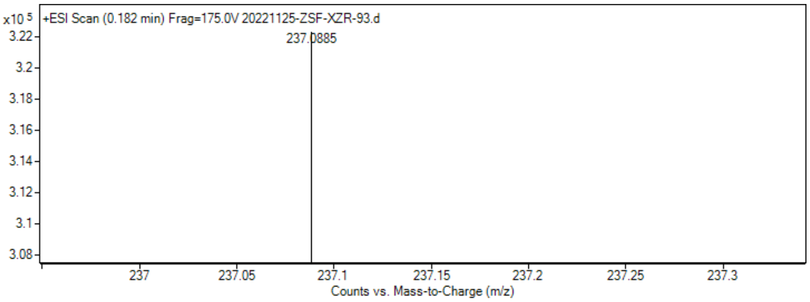
Yellow liquid, purified by chromatography (PE/EA = 20/1, Rf = 0.5); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.98 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.47 (td, *J* = 7.5, 1.5 Hz, 1H), 7.36 (td, *J* = 7.6, 1.3 Hz, 1H), 7.24 (dd, *J* = 7.6, 1.3 Hz, 1H), 5.15 (q, *J* = 1.6 Hz, 1H), 4.86 (dd, *J* = 1.9, 1.0 Hz, 1H), 2.09 (d, *J* = 2.0 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 179.8, 146.1, 145.0, 136.2, 132.3, 131.1, 129.6, 127.0, 115.0, 91.7, 80.6, 24.0, 4.3. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{13}H_{12}O\ Na^+$: 207.0780, found 207.0779.



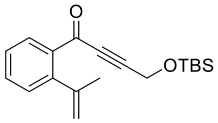
4-methoxy-1-(2-(prop-1-en-2-yl)phenyl)but-2-yn-1-one (1c)



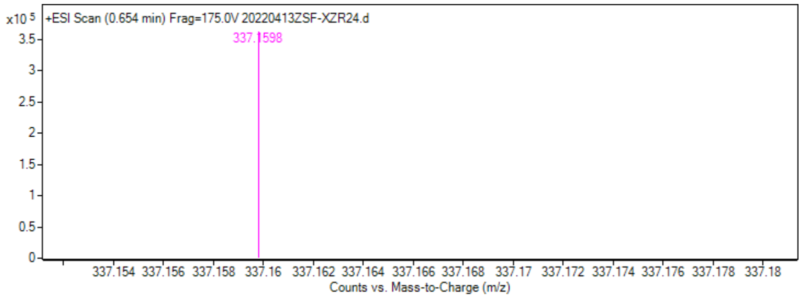
Colorless liquid, purified by chromatography (PE/EA = 20/1, Rf = 0.5); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.99 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.50 (td, *J* = 7.5, 1.4 Hz, 1H), 7.38 (td, *J* = 7.6, 1.4 Hz, 1H), 7.3 (dd, *J* = 7.6, 1.3 Hz, 1H), 5.20 – 5.12 (m, 1H), 4.89 – 4.85 (m, 1H), 4.33 (s, 2H), 3.45 (s, 3H), 2.10 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 178.9, 145.8, 145.1, 135.6, 132.8, 131.3, 129.7, 127.2, 115.4, 89.0, 85.7, 59.8, 58.2, 23.9. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{14}H_{14}O_2Na^+$:237.0886, found 237.0885.



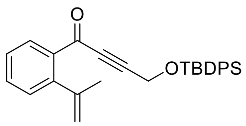
4-((tert-butyldimethylsilyl)oxy)-1-(2-(prop-1-en-2-yl)phenyl)but-2-yn-1-one (1d)



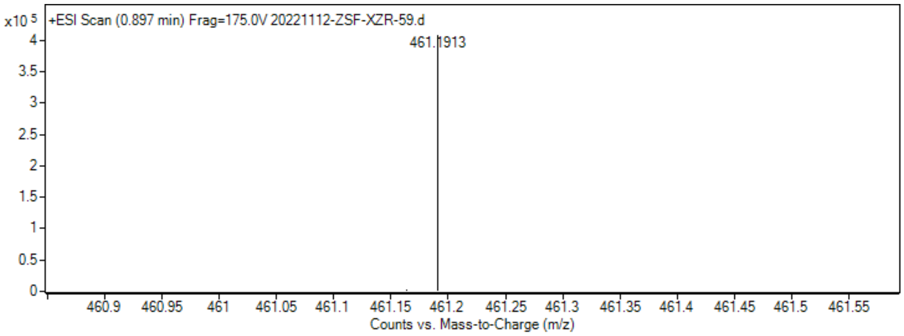
Yellow liquid, purified by chromatography (PE/EA = 20/1, Rf = 0.5); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.49 (td, *J* = 7.5, 1.4 Hz, 1H), 7.37 (td, *J* = 7.6, 1.3 Hz, 1H), 7.26 (d, *J* = 1.1 Hz, 1H), 5.15 (p, *J* = 1.6 Hz, 1H), 4.86 (dt, *J* = 1.9, 0.9 Hz, 1H), 4.54 (s, 2H), 2.10 (dd, *J* = 1.5, 0.9 Hz, 3H), 0.92 (s, 9H), 0.14 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.1, 146.0, 145.1, 135.7, 132.6, 131.4, 129.7, 127.0, 115.2, 91.8, 84.2, 51.7, 25.7, 23.9, 18.3, -5.2. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{19}H_{26}O_2SiNa^+$: 337.1594, found 337.1598.



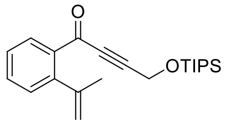
4-((tert-butyldiphenylsilyl)oxy)-1-(2-(prop-1-en-2-yl)phenyl)but-2-yn-1-one (1e)



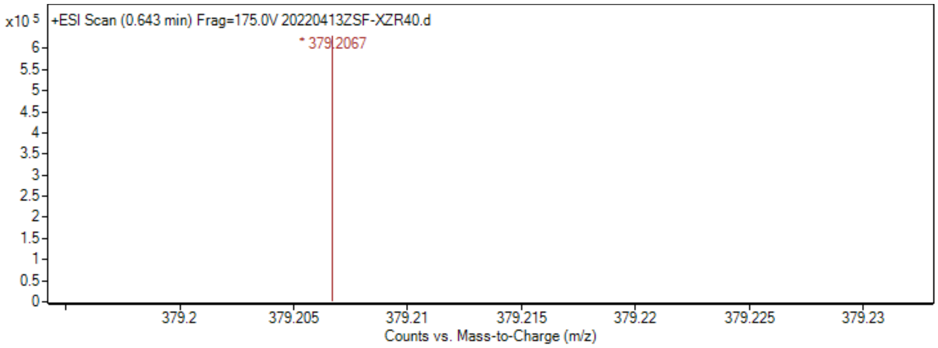
Yellow liquid, purified by chromatography (PE/EA = 20/1, Rf = 0.5); ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.95 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.75 (dt, *J* = 6.7, 1.6 Hz, 4H), 7.57 – 7.34 (m, 8H), 7.29 (dd, *J* = 7.4, 1.4 Hz, 1H), 5.18 (t, *J* = 1.6 Hz, 1H), 4.90 (s, 1H), 4.58 (s, 2H), 2.12 (t, *J* = 1.1 Hz, 3H), 1.12 (s, 9H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 179.1, 146.0, 145.1, 135.8, 135.6, 132.6, 132.5, 131.4, 130.1, 129.7, 127.9, 127.1, 115.2, 91.5, 84.4, 52.7, 26.7, 24.0, 19.2. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{29}H_{30}O_2SiNa^+$: 461.1907, found 461.1913.



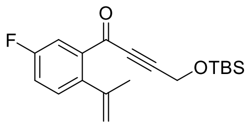
1-(2-(prop-1-en-2-yl)phenyl)-4-((triisopropylsilyl)oxy)but-2-yn-1-one (1f)



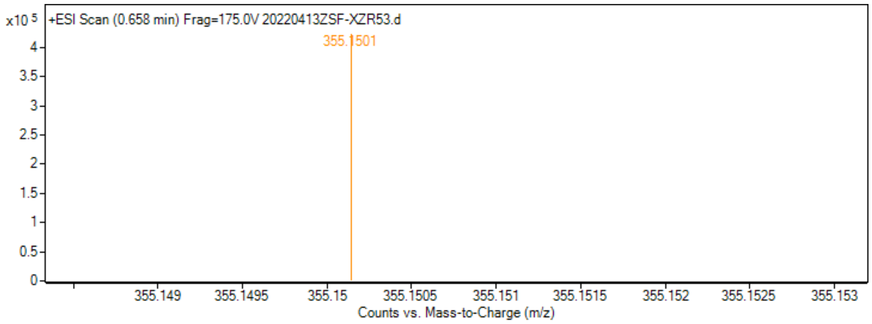
Yellow liquid, purified by chromatography (PE/EA = 20/1, Rf = 0.5); ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 8.03 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.51 (td, *J* = 7.5, 1.4 Hz, 1H), 7.38 (td, *J* = 7.6, 1.3 Hz, 1H), 7.27 (dd, *J* = 7.7 Hz, 1.4H), 5.17 (t, *J* = 1.6 Hz, 1H), 4.88 (dd, *J* = 1.8, 1.0 Hz, 1H), 4.64 (s, 3H), 2.12 (t, *J* = 1.1 Hz, 4H), 1.12 (s, 18H), 1.11 (s, 3H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 179.1, 145.9, 145.1, 135.8, 132.5, 131.4, 129.6, 127.0, 115.2, 91.9, 84.0, 52.1, 23.9, 17.9, 12.0. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{22}H_{32}O_2SiNa^+$: 379.2063, found 379.2067.



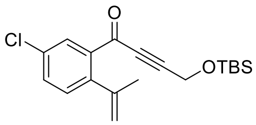
4-((tert-butyldimethylsilyl)oxy)-1-(5-fluoro-2-(prop-1-en-2-yl)phenyl)but-2-yn-1-one (1g)



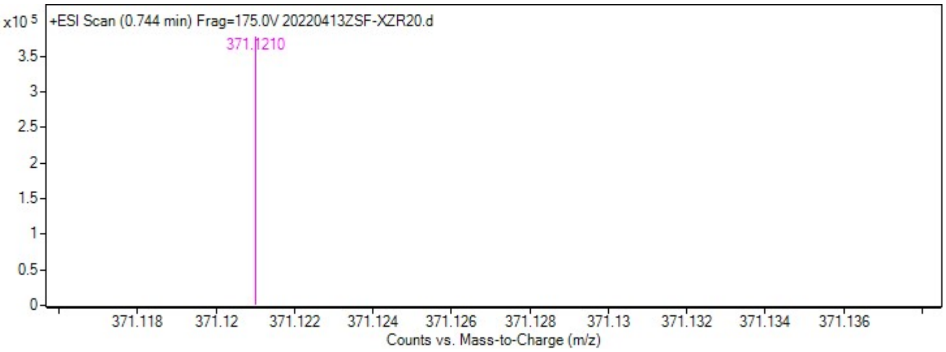
Yellow liquid, purified by chromatography (PE/EA = 20/1, Rf = 0.5); ^{1}**H NMR** (500 MHz, Chloroform-*d*) δ 7.66 (dd, *J* = 9.1, 2.7 Hz, 1H), 7.23 (dd, *J* = 8.4, 5.5 Hz, 1H), 7.20 (dd, *J* = 7.9, 2.7 Hz, 1H), 2.07 (t, *J* = 1.2 Hz, 3H), 0.92 (s, 9H), 0.15 (s, 6H). ^{13}**C NMR** (126 MHz, Chloroform-d) δ 177.7 (d, *J* = 2.3 Hz), 161.3 (d, *J* = 247.7 Hz), 144.8, 141.0 (d, *J* = 3.6 Hz), 137.2 (d, *J* = 6.3 Hz), 131.4 (d, *J* = 7.2 Hz), 119.5 (d, J = 21.1 Hz), 117.7 (d, *J* = 23.0 Hz), 115.9, 92.5, 83.7, 51.7, 25.7, 24.0, 18.3, -5.3. ^{19}**F NMR** (471 MHz, $CDCl_3$) δ -114.5. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{19}H_{25}FO_2SiNa^+$: 355.1500, found 355.1501.



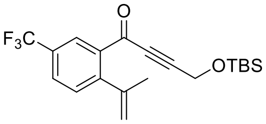
4-((tert-butyldimethylsilyl)oxy)-1-(5-chloro-2-(prop-1-en-2-yl)phenyl)but-2-yn-1-one (1h)



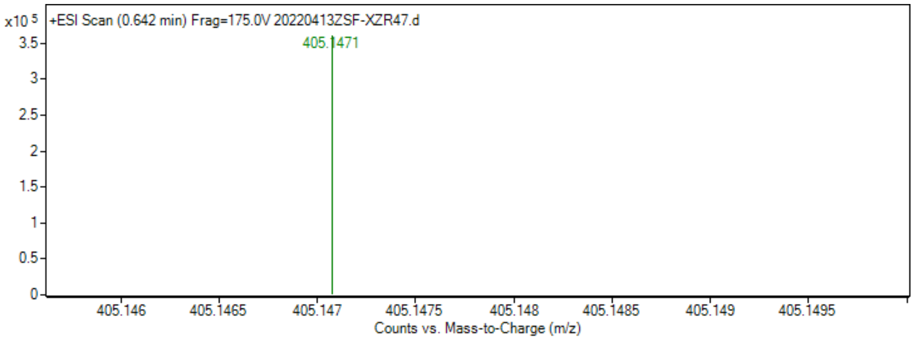
Yellow liquid, purified by chromatography (PE/EA = 20/1, Rf = 0.5); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 2.3 Hz, 1H), 7.47 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 5.39 – 5.08 (m, 1H), 4.87 (dd, *J* = 1.6, 0.9 Hz, 1H), 4.56 (s, 2H), 2.09 (t, *J* = 1.2 Hz, 3H), 0.95 (s, 9H), 0.17 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.7, 144.7, 143.4, 137.0, 133.0, 132.4, 131.1, 130.9, 115.9, 92.8, 83.7, 51.7, 25.7, 23.8, 18.2, -5.2. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{19}H_{25}ClO_2SiNa^+$: 371.1204, found 371.1210.



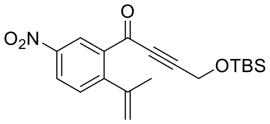
4-((tert-butyldimethylsilyl)oxy)-1-(2-(prop-1-en-2-yl)-5-(trifluoromethyl)phenyl)but-2-yn-1-one (1i)



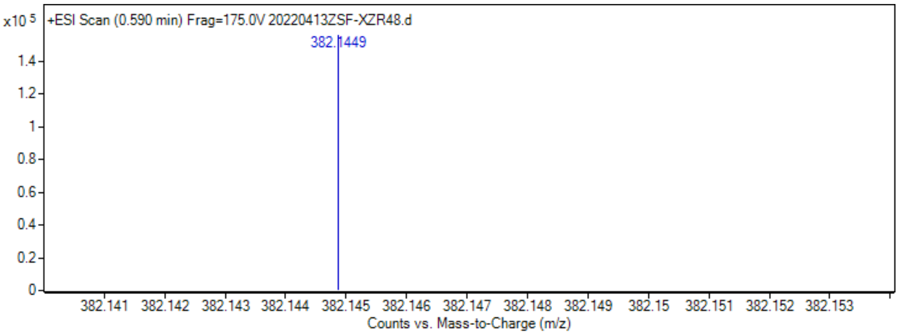
Yellow liquid, purified by chromatography (PE/EA = 20/1, Rf = 0.5); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 2.0 Hz, 1H), 7.94 – 7.69 (m, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 5.22 (t, *J* = 1.5 Hz, 1H), 4.90 (t, *J* = 1.2 Hz, 1H), 4.56 (s, 2H), 2.11 (t, *J* = 1.2 Hz, 3H), 0.92 (s, 9H), 0.15 (s, 6H).). **^{13}C NMR** (126 MHz, Chloroform) δ 177.7, 148.5, 144.6, 136.2, 130.4, 129.61 (q, *J* = 33.3 Hz), 128.9 (q, *J* = 3.6 Hz), 128.0 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 272.16 Hz), 116.4, 93.2, 83.6, 51.7, 25.7, 23.7, 18.2, -5.3. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.68. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{20}H_{25}F_3O_2SiNa^+$: 405.1468, found 405.1471.



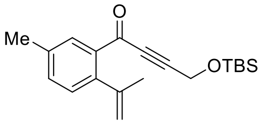
4-((tert-butyldimethylsilyl)oxy)-1-(5-nitro-2-(prop-1-en-2-yl)phenyl)but-2-yn-1-one(1j)



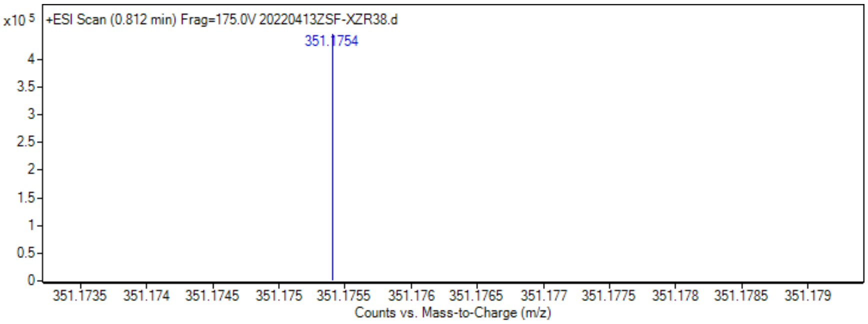
Orange liquid, purified by chromatography (PE/EA = 20/1, Rf = 0.5); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.81 (d, *J* = 2.4 Hz, 1H), 8.34 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 5.28 (p, *J* = 1.5 Hz, 1H), 5.08 – 4.90 (m, 1H), 4.59 (s, 2H), 2.14 (dd, *J* = 1.6, 0.9 Hz, 3H), 0.94 (s, 9H), 0.17 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.8, 151.1, 146.7, 144.0, 136.8, 131.0, 126.7, 125.9, 117.2, 94.0, 83.3, 51.7, 25.7, 23.5, 18.2, -5.3. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{19}H_{25}NO_4SiNa^+$: 382.1445, found 382.1449.



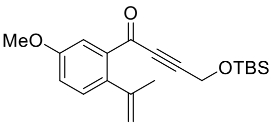
4-((tert-butyldimethylsilyl)oxy)-1-(5-methyl-2-(prop-1-en-2-yl)phenyl)but-2-yn-1-one (1k)



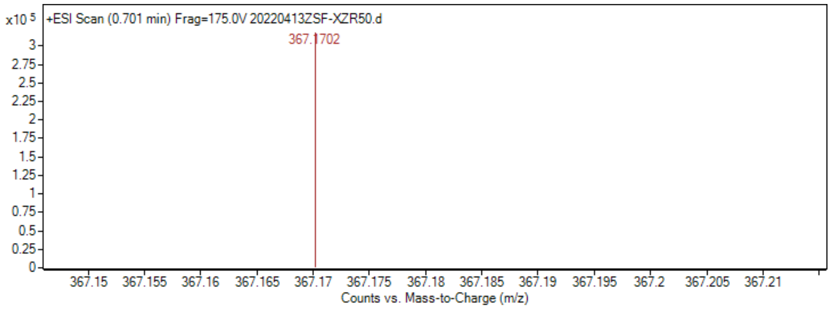
Yellow liquid, purified by chromatography (PE/EA = 20/1, Rf = 0.5); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 1.9 Hz, 1H), 7.30 (ddd, *J* = 7.7, 2.0, 0.9 Hz, 1H), 7.14 (d, *J* = 7.7 Hz, 1H), 5.12 (p, *J* = 1.6 Hz, 1H), 4.83 (dd, *J* = 1.9, 1.0 Hz, 1H), 4.54 (s, 2H), 2.39 (s, 3H), 2.07 (d, *J* = 1.3 Hz, 3H), 0.93 (s, 9H), 0.15 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 179.2, 145.9, 142.4, 136.9, 135.6, 133.3, 131.8, 129.6, 115.0, 91.7, 84.2, 51.8, 25.7, 24.0, 20.9, 18.3, -5.2. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{20}H_{28}O_2SiNa^+$: 351.1751, found 351.1754.



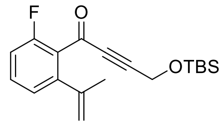
4-((tert-butyldimethylsilyl)oxy)-1-(5-methoxy-2-(prop-1-en-2-yl)phenyl)but-2-yn-1-one (1l)



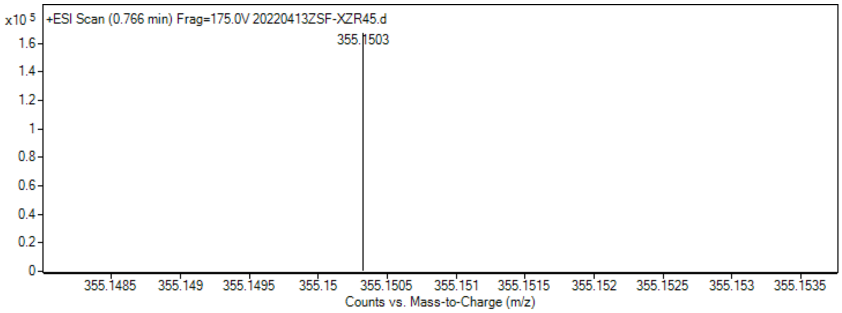
Yellow liquid, purified by chromatography (PE/EA = 10/1, Rf = 0.5);**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 2.7 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.02 (dd, *J* = 8.4, 2.8 Hz, 1H), 5.13 (p, *J* = 1.5 Hz, 1H), 4.83 (dd, *J* = 1.8, 0.9 Hz, 1H), 4.52 (s, 2H), 3.85 (s, 3H), 2.68 – 1.76 (m, 3H), 0.91 (s, 9H), 0.14 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.1, 158.4, 145.2, 137.5, 136.9, 130.7, 118.5, 115.6, 91.9, 84.1, 77.3, 77.1, 76.7, 55.5, 51.7, 25.7, 24.1, 18.2, -5.2. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{20}H_{28}O_3SiNa^+$: 367.1700, found 367.1702.



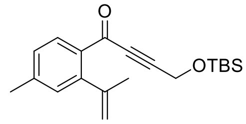
4-((tert-butyldimethylsilyl)oxy)-1-(2-fluoro-6-(prop-1-en-2-yl)phenyl)but-2-yn-1-one (1m)



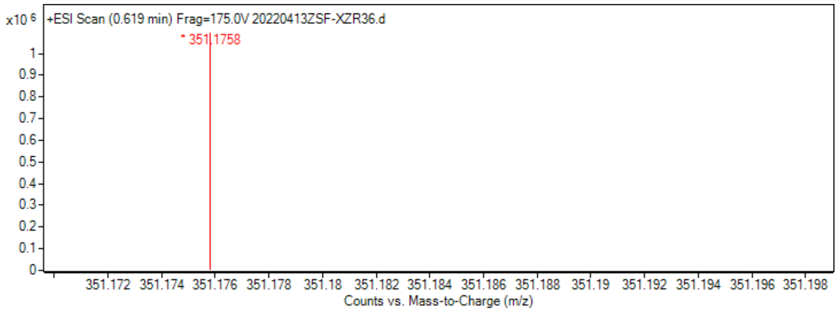
Yellow liquid, purified by chromatography (PE/EA = 20/1, Rf = 0.5); ^{1}**H NMR** (500 MHz, Chloroform-*d*) δ 7.39 (td, *J* = 8.0, 5.5 Hz, 1H), 7.09 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.04 (ddd, *J* = 9.5, 8.3, 1.0 Hz, 1H), 5.48 – 5.12 (m, 1H), 4.97 (t, *J* = 1.2 Hz, 1H), 4.51 (s, 2H), 2.14 (t, *J* = 1.3 Hz, 3H), 0.90 (s, 9H), 0.12 (s, 6H). ^{13}**C NMR** (126 MHz, Chloroform-*d*) δ 177.1, 159.5 (d, *J* = 253.1 Hz), 144.8 (d, *J* = 1.9 Hz), 142.8 (d, *J* = 2.1 Hz), 131.7 (d, *J* = 9.1 Hz), 126.9 (d, *J* = 13.8 Hz), 123.9 (d, *J* = 3.3 Hz), 118.3, 114.7 (d, *J* = 21.5 Hz), 92.6 (d, *J* = 1.4 Hz), 85.1, 51.7, 25.7, 24.0, 18.2, -5.3. ^{19}**F NMR** (471 MHz, $CDCl_3$) δ -115.33. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{19}H_{25}FO_2SiNa^+$: 355.1500, found 355.1503.



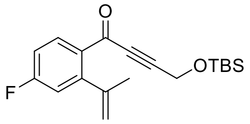
4-((tert-butyldimethylsilyl)oxy)-1-(4-methyl-2-(prop-1-en-2-yl)phenyl)but-2-yn-1-one(1n)



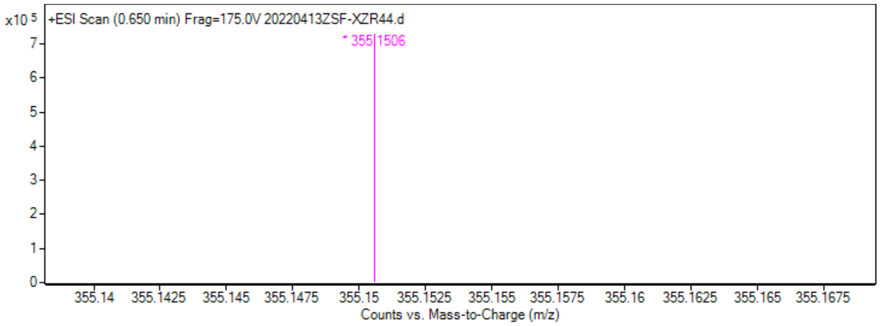
Yellow liquid, purified by chromatography (PE/EA = 10/1, Rf = 0.5); ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 7.9 Hz, 1H), 7.19 (ddd, *J* = 7.9, 1.8, 0.8 Hz, 1H), 7.07 (d, *J* = 1.8 Hz, 1H), 5.14 (t, *J* = 1.6 Hz, 1H), 4.86 (dd, *J* = 1.9, 1.0 Hz, 1H), 4.56 (s, 2H), 2.42 (s, 3H), 2.09 (t, *J* = 1.1 Hz, 3H), 0.95 (s, 9H), 0.17 (s, 6H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 178.3, 146.5, 145.5, 143.7, 132.9, 132.2, 130.6, 127.7, 114.4, 91.3, 84.2, 51.7, 25.7, 23.9, 21.6, 18.3, -5.2. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{20}H_{28}O_2SiNa^+$: 351.1751, found 351.1758.



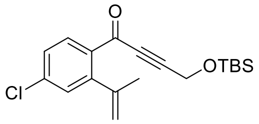
4-((tert-butyldimethylsilyl)oxy)-1-(4-fluoro-2-(prop-1-en-2-yl)phenyl)but-2-yn-1-one (1o)



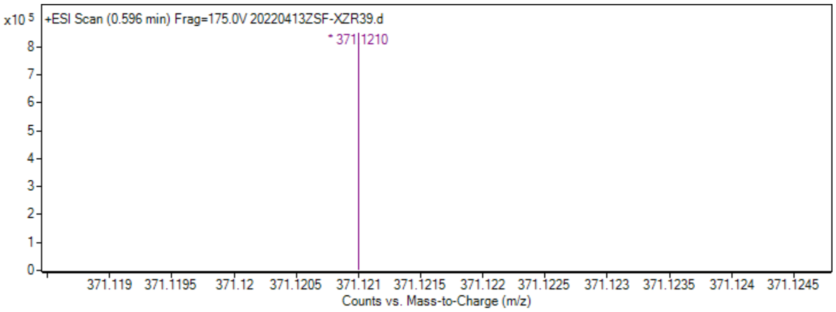
Yellow liquid, purified by chromatography (PE/EA = 20/1, Rf = 0.5); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.07 (dd, *J* = 8.7, 5.8 Hz, 1H), 7.05 (ddd, *J* = 8.7, 7.9, 2.6 Hz, 1H), 6.95 (dd, *J* = 9.3, 2.6 Hz, 1H), 5.16 (p, *J* = 1.6 Hz, 1H), 4.93 – 4.82 (m, 1H), 4.54 (s, 2H), 2.08 (t, *J* = 1.2 Hz, 3H), 0.93 (s, 9H), 0.15 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 177.2, 164.9 (d, *J* = 256.3 Hz), 148.5 (d, *J* = 8.9 Hz), 145.8 – 142.9 (m), 134.5 (d, *J* = 9.8 Hz), 131.9 (d, *J* = 2.8 Hz), 117.0 (d, *J* = 21.7 Hz), 115.5, 114.0 (d, *J* = 21.6 Hz), 92.0, 83.8, 51.7, 25.7, 23.6, 18.3, -5.2. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -105.23. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{19}H_{25}FO_2SiNa^+$: 355.1500, found 355.1506.



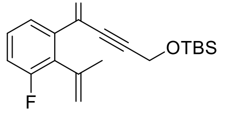
4-((tert-butyldimethylsilyl)oxy)-1-(4-chloro-2-(prop-1-en-2-yl)phenyl)but-2-yn-1-one (1p)



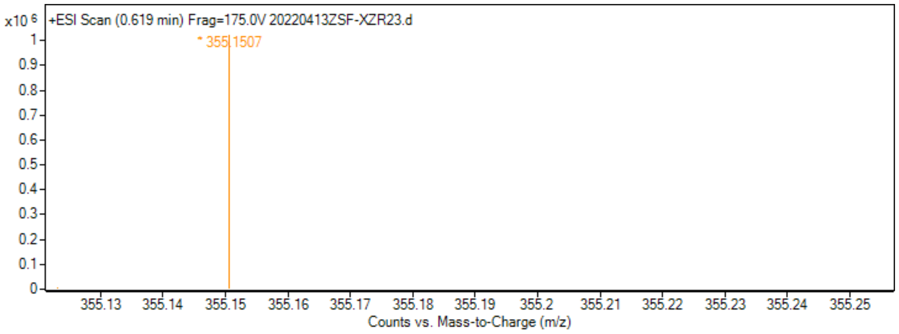
Yellow liquid, purified by chromatography (PE/EA = 10/1, Rf = 0.5); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.4 Hz, 1H), 7.34 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.25 (d, *J* = 2.1 Hz, 1H), 5.17 (t, *J* = 1.5 Hz, 1H), 4.95 – 4.79 (m, 1H), 4.54 (s, 2H), 2.07 (t, *J* = 1.1 Hz, 3H), 0.92 (s, 9H), 0.14 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.6, 146.9, 144.8, 138.9, 133.9, 133.0, 129.9, 127.2, 115.8, 92.3, 83.8, 51.7, 25.7, 23.7, 18.3, -5.2. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{19}H_{25}ClO_2SiNa^+$: 371.1204, found 371.1210.



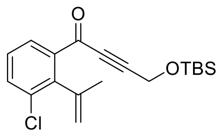
4-((tert-butyldimethylsilyl)oxy)-1-(3-fluoro-2-(prop-1-en-2-yl)phenyl)but-2-yn-1-one (1q)



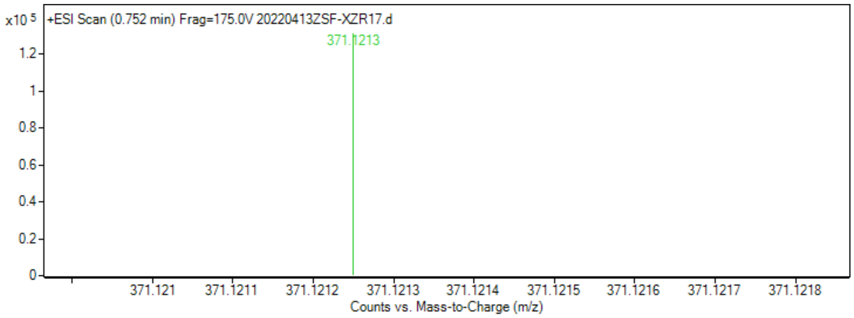
Yellow liquid, purified by chromatography (PE/EA = 20/1, Rf = 0.5); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.74 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.34 (td, *J* = 8.0, 5.2 Hz, 1H), 7.27 – 7.21 (m, 1H), 5.28 (p, *J* = 1.6 Hz, 1H), 4.86 (t, *J* = 1.2 Hz, 1H), 4.53 (s, 2H), 2.15 (t, *J* = 1.2 Hz, 3H), 0.92 (s, 9H), 0.14 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 178.0 (d, *J* = 3.3 Hz), 159.6 (d, *J* = 246.4 Hz), 138.8, 138.4 (d, *J* = 3.7 Hz), 131.8 (d, *J* = 18.4 Hz), 128.2 (d, *J* = 8.6 Hz), 126.4 (d, *J* = 3.2 Hz), 119.8(d, *J* = 23.7 Hz), 117.6(d, *J* = 1.0 Hz), 92.4, 84.1, 51.7, 25.7, 23.6(d, *J* = 2.0 Hz), 18.2, -5.6. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.08. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{19}H_{25}FO_2SiNa^+$: 355.1500, found 355.1507.



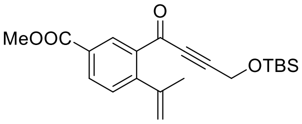
4-((tert-butyldimethylsilyl)oxy)-1-(3-chloro-2-(prop-1-en-2-yl)phenyl)but-2-yn-1-one (1r)



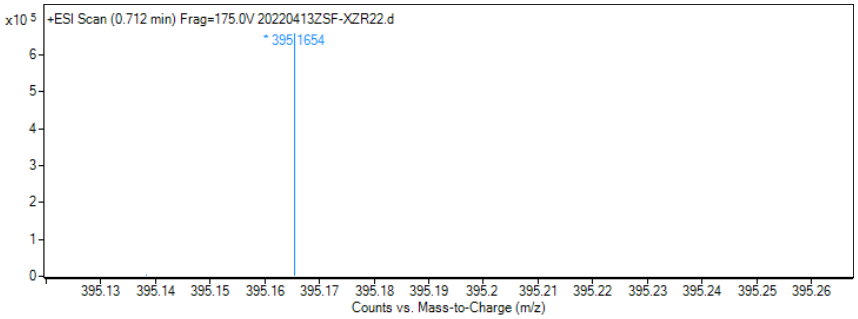
Yellow liquid, purified by chromatography (PE/EA = 20/1, Rf = 0.5); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.55 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 5.26 (p, *J* = 1.5 Hz, 1H), 4.79 (t, *J* = 1.3 Hz, 1H), 4.54 (s, 2H), 2.17 (t, *J* = 1.3 Hz, 3H), 0.92 (s, 9H), 0.14 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.1, 142.6, 142.4, 138.4, 134.0, 133.5, 129.2, 127.8, 116.8, 92.6, 84.0, 77.3, 77.0, 76.8, 51.7, 25.7, 23.2, 18.2, -5.2. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{19}H_{25}ClO_2SiNa^+$: 371.1204, found 371.1213.



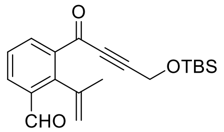
Methyl 3-(4-((tert-butyldimethylsilyl)oxy)but-2-ynoyl)-4-(prop-1-en-2-yl)benzoate (1s)



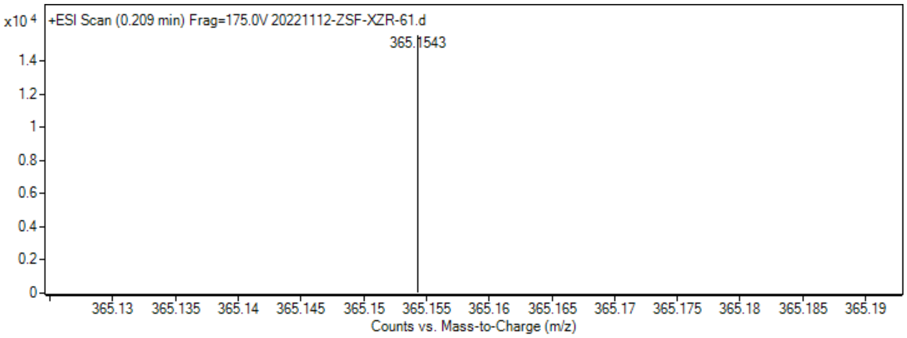
Yellow liquid, purified by chromatography (PE/EA = 10/1, Rf = 0.5); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.61 (d, *J* = 1.8 Hz, 1H), 8.15 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 5.21 (q, *J* = 1.5 Hz, 1H), 4.91 (t, *J* = 1.2 Hz, 1H), 4.57 (s, 2H), 3.96 (s, 3H), 2.11 (t, *J* = 1.2 Hz, 3H), 0.93 (s, 10H), 0.16 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.3, 166.0, 149.4, 145.0, 136.0, 133.3, 132.2, 130.0, 129.2, 116.1, 92.7, 83.8, 52.4, 51.7, 25.7, 23.7, 18.2, -5.2. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{21}H_{28}O_4SiNa^+$: 395.1649, found 395.1654.



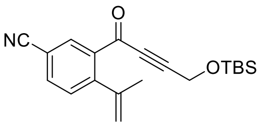
3-(4-((tert-butyldimethylsilyl)oxy)but-2-ynoyl)-2-(prop-1-en-2-yl)benzaldehyd (1t)



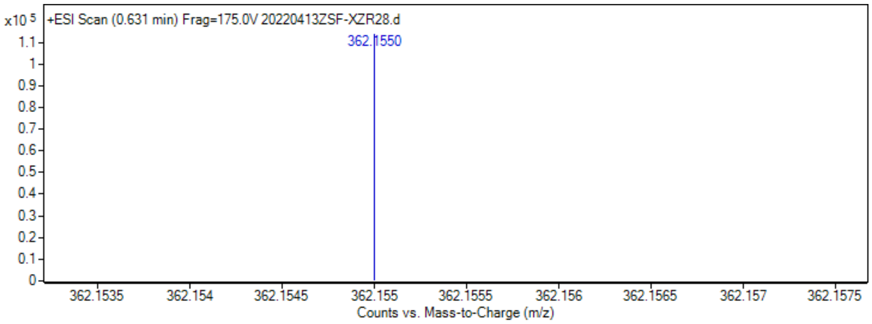
Yellow solid, M.P. = 102-103 °C, purified by chromatography (PE/EA = 20/1, Rf = 0.5); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 10.27 (d, *J* = 0.8 Hz, 1H), 8.33 (dd, *J* = 7.7, 1.4 Hz, 1H), 8.14 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.55 (td, *J* = 7.8, 0.9 Hz, 1H), 5.50 – 5.40 (m, 1H), 4.94 (t, *J* = 1.3 Hz, 1H), 4.58 (s, 2H), 2.22 (t, *J* = 1.2 Hz, 3H), 0.95 (s, 9H), 0.17 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.6, 177.5, 147.6, 140.9, 136.9, 136.3, 134.1, 131.8, 127.5, 118.4, 92.8, 83.9, 51.7, 26.1, 25.7, 18.3, -5.2. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{20}H_{26}O_3SiNa^+$: 365.1543, found 365.1543.



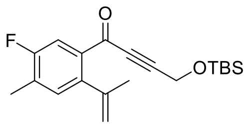
3-(4-((tert-butyldimethylsilyl)oxy)but-2-ynoyl)-4-(prop-1-en-2-yl)benzonitrile (1u)



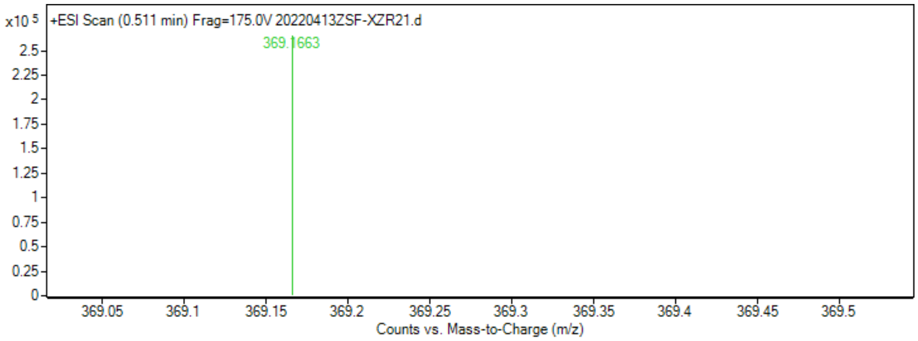
Yellow liquid, purified by chromatography (PE/EA = 10/1, Rf = 0.5); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 1.8 Hz, 1H), 7.77 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 5.25 (q, *J* = 1.5 Hz, 1H), 4.92 (d, *J* = 1.5 Hz, 1H), 4.57 (s, 2H), 2.11 (dd, *J* = 1.5, 0.9 Hz, 3H), 0.94 (s, 9H), 0.16 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.9, 149.3, 144.2, 136.7, 135.2, 134.6, 130.7, 117.7, 117.0, 111.4, 93.7, 83.4, 51.7, 25.7, 23.5, 18.2, -5.2. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{20}H_{25}NO_2SiNa^+$: 362.1547, found 362.1550.



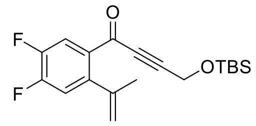
4-((tert-butyldimethylsilyl)oxy)-1-(5-fluoro-4-methyl-2-(prop-1-en-2-yl)phenyl)but-2-yn-1-one (1v)



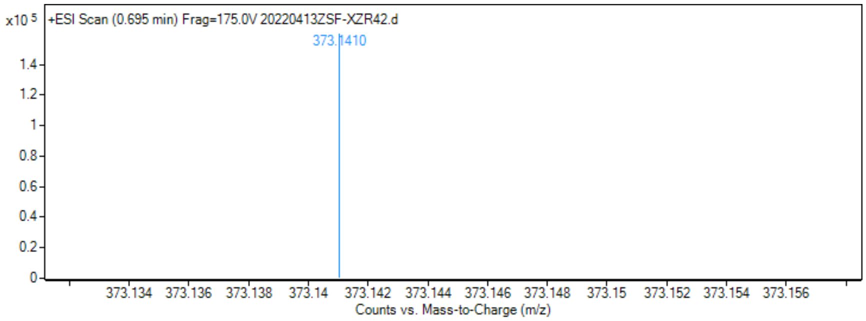
Yellow liquid, purified by chromatography (PE/EA = 20/1, Rf = 0.5); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 10.0 Hz, 1H), 7.08 (d, *J* = 7.4 Hz, 1H), 5.14 (t, *J* = 1.6 Hz, 1H), 4.84 (dd, *J* = 1.8, 1.0 Hz, 1H), 4.56 (s, 2H), 2.34 (d, *J* = 2.0 Hz, 3H), 2.07 (t, *J* = 1.2 Hz, 3H), 0.95 (s, 9H), 0.17 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 177.1 (d, *J* = 2.0 Hz), 159.8 (d, *J* = 246.2 Hz), 145.3, 141.1 (d, *J* = 3.8 Hz), 134.4 (d, *J* = 6.3 Hz), 133.0 (d, *J* = 4.6 Hz), 130.4 (d, *J* = 17.1 Hz), 117.9 (d, *J* = 24.0 Hz), 115.1, 91.9, 83.7, 51.7, 25.7, 24.0, 18.2, 14.7 (d, *J* = 3.1 Hz), -5.2. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -118.98. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{20}H_{27}FO_2SiNa^+$: 369.1656, found 369.1663.



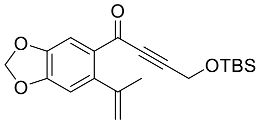
4-((tert-butyldimethylsilyl)oxy)-1-(4,5-difluoro-2-(prop-1-en-2-yl)phenyl)but-2-yn-1-one (1w)



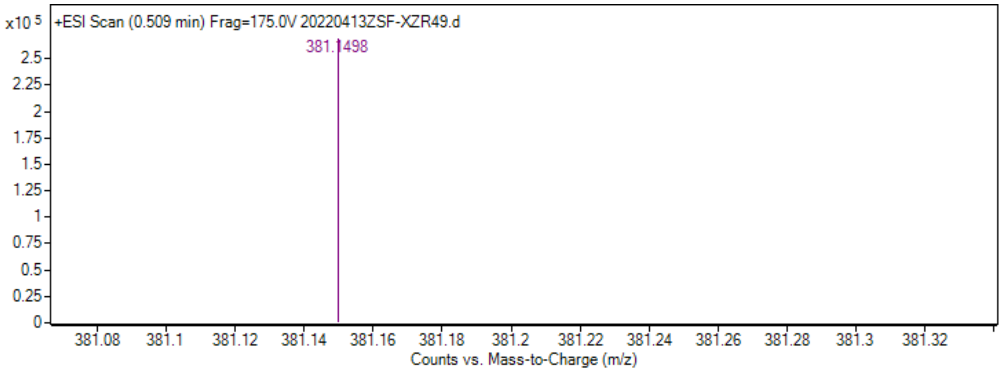
Yellow liquid, purified by chromatography (PE/EA = 10/1, Rf = 0.5); ^{1}**H NMR** (500 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 10.7, 8.0 Hz, 1H), 7.06 (dd, *J* = 10.6, 7.5 Hz, 1H), 5.17 (p, *J* = 1.5 Hz, 1H), 4.87 (t, *J* = 1.2 Hz, 1H), 4.54 (s, 2H), 2.06 (t, *J* = 1.2 Hz, 3H), 0.93 (s, 9H), 0.15 (s, 6H). ^{13}**C NMR** (126 MHz, Chloroform-*d*) δ 176.1 (d, *J* = 1.6 Hz), 152.5 (dd, *J* = 258.0, 12.7 Hz), 148.7 (dd, *J* = 250.4, 12.9 Hz), 144.1, 143.0 (dd, *J* = 7.0, 3.9 Hz), 132.0 (t, *J* = 3.7 Hz), 120.6 (dd, *J* = 18.5, 2.1 Hz), 118.9 (d, *J* = 17.5 Hz), 116.3, 92.7, 83.4, 51.7, 25.7, 23.7, 18.2, -5.3. ^{19}**F NMR** (471 MHz, Chloroform-*d*) δ -130.01 (d, *J* = 21.3 Hz), -138.56 (d, *J* = 21.6 Hz). **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{19}H_{24}F_2O_2SiNa^+$: 373.1406, found 373.1410.



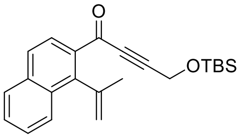
4-((tert-butyldimethylsilyl)oxy)-1-(6-(prop-1-en-2-yl)benzo[d][1,3]dioxol-5-yl)but-2-yn-1-one (1x)



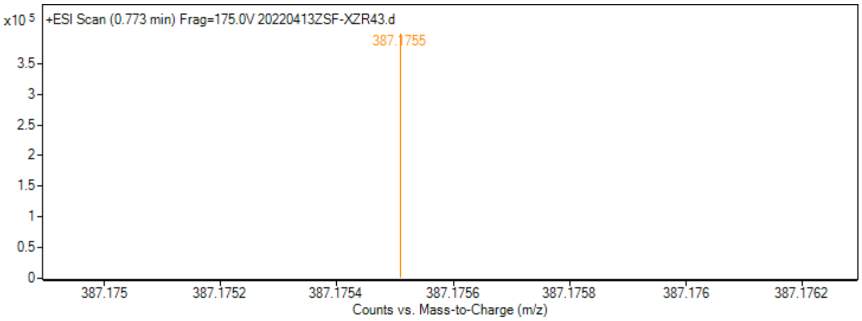
Yellow solid, M.P. = 69-70 °C, purified by chromatography (PE/EA = 20/1, Rf = 0.5);^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.51 (s, 1H), 6.69 (s, 1H), 6.05 (s, 2H), 5.11 (t, *J* = 1.6 Hz, 1H), 4.82 (dd, *J* = 1.9, 0.9 Hz, 1H), 4.52 (s, 2H), 2.06 (dd, *J* = 1.4, 0.8 Hz, 3H), 0.92 (s, 9H), 0.15 (s, 6H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 176.8, 151.2, 146.6, 146.0, 142.5, 129.5, 115.1, 111.1, 109.9, 102.1, 91.1, 84.0, 51.7, 25.7, 24.0, 18.3, -5.2. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{20}H_{26}O_4SiNa^+$: 381.1492, found 381.1498.



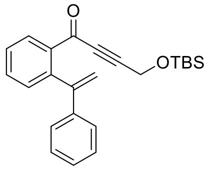
4-((tert-butyldimethylsilyl)oxy)-1-(1-(prop-1-en-2-yl)naphthalen-2-yl)but-2-yn-1-one (1y)



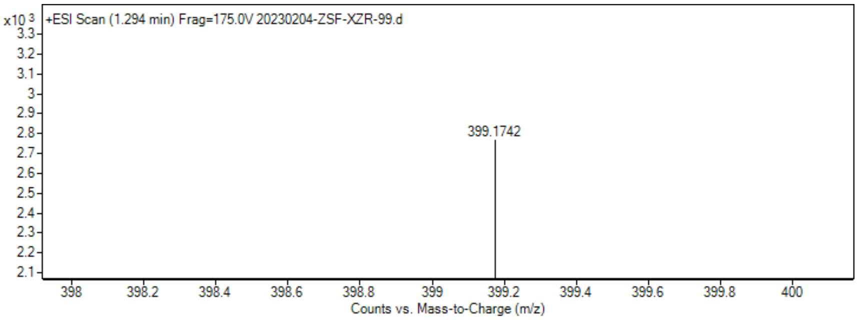
Yellow liquid, purified by chromatography (PE/EA = 10/1, Rf = 0.5); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.14 (dd, *J* = 8.6, 1.3 Hz, 1H), 8.08 (d, *J* = 8.6 Hz, 1H), 7.86 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.83 (d, *J* = 8.7 Hz, 1H), 7.56 (dddd, *J* = 19.6, 8.2, 6.8, 1.4 Hz, 2H), 5.47 (p, *J* = 1.5 Hz, 1H), 4.92 (dd, *J* = 1.8, 1.0 Hz, 1H), 4.57 (s, 2H), 2.27 (t, *J* = 1.2 Hz, 3H), 0.93 (s, 9H), 0.16 (d, *J* = 3.2 Hz, 6H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 179.0, 116.7, 92.4, 84.8, 51.8, 25.8, 25.2, 18.3, -5.2. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{23}H_{28}O_2SiNa^+$: 387.1751, found 387.1755.



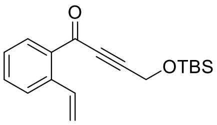
4-((tert-butyldimethylsilyl)oxy)-1-(2-(1-phenylvinyl)phenyl)but-2-yn-1-one (3k)



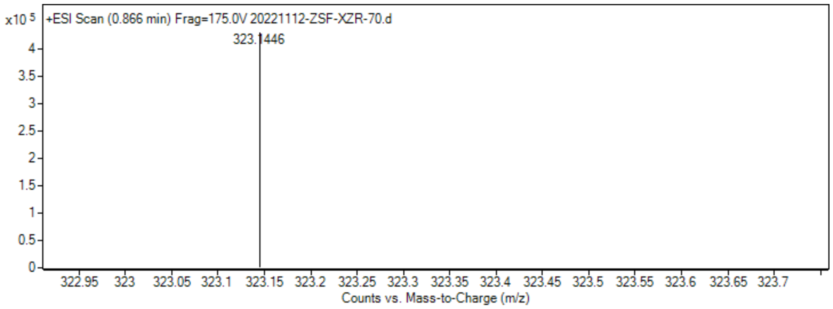
Yellow liquid, purified by chromatography (PE/EA = 20/1, Rf = 0.5); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.08 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.59 (td, *J* = 7.5, 1.4 Hz, 1H), 7.50 (td, *J* = 7.6, 1.4 Hz, 1H), 7.38 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.33 – 7.26 (m, 5H), 5.77 (d, *J* = 1.1 Hz, 1H), 5.26 (d, *J* = 0.9 Hz, 1H), 4.37 (s, 2H), 0.93 (s, 9H), 0.12 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 178.5, 149.0, 142.8, 140.6, 137.0, 132.6, 131.7, 131.3, 128.2, 127.8, 127.7, 126.9, 115.5, 92.1, 84.0, 51.6, 25.8, 18.3, -5.2. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{24}H_{28}O_2SiNa^+$: 399.1751, found 399.1742.



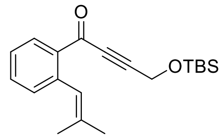
4-((tert-butyldimethylsilyl)oxy)-1-(2-vinylphenyl)but-2-yn-1-one(3n)



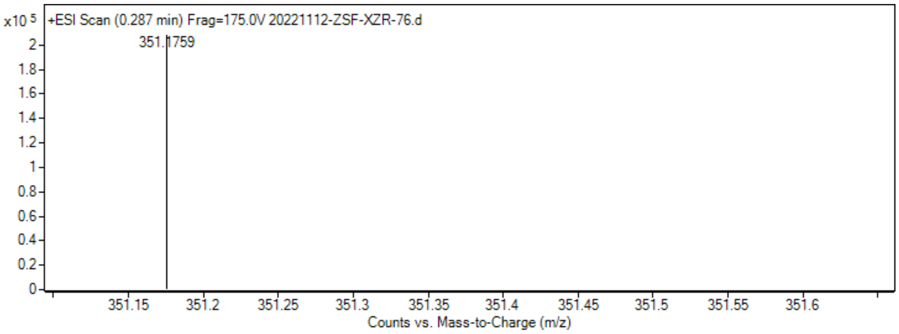
Yellow liquid, purified by chromatography (PE/EA = 20/1, Rf = 0.5); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.19 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.58 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.39 (td, *J* = 7.5, 1.4 Hz, 1H), 5.66 (dd, *J* = 17.4, 1.3 Hz, 1H), 5.38 (dd, *J* = 11.0, 1.3 Hz, 1H), 4.57 (s, 2H), 0.94 (s, 9H), 0.16 (s, 6H). **^{13}C NMR** (126 MHz, CDCl$_3$) δ 179.0, 139.8, 135.9, 134.2, 133.2, 132.9, 127.8, 127.4, 117.2, 92.2, 84.1, 51.8, 25.7, 18.3, -5.2. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{18}H_{24}$O2SiNa$^+$: 323.1438, found 323.1446.



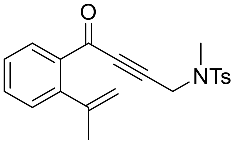
4-((tert-butyldimethylsilyl)oxy)-1-(2-(2-methylprop-1-en-1-yl)phenyl)but-2-yn-1-one(3o)



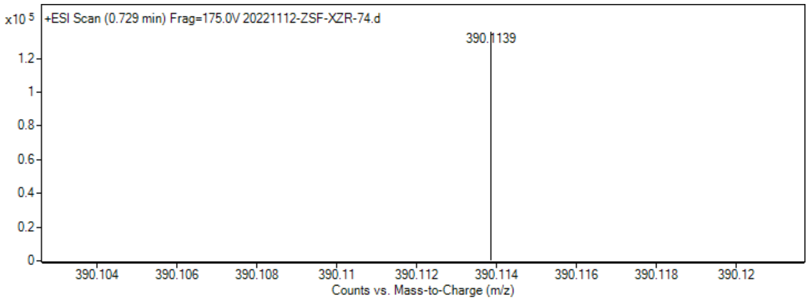
Yellow liquid, purified by chromatography (PE/EA = 20/1, Rf = 0.5); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 2.0 Hz, 1H), 7.60 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.33 – 7.22 (m, 2H), 5.45 (t, *J* = 1.1 Hz, 1H), 5.18 (q, *J* = 1.6 Hz, 2H), 4.89 (dd, *J* = 1.8, 1.0 Hz, 1H), 4.56 (s, 2H), 2.20 (dd, *J* = 1.5, 0.8 Hz, 3H), 2.12 (dd, *J* = 1.5, 0.8 Hz, 3H), 0.94 (s, 9H), 0.16 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.3, 145.5, 144.0, 141.9, 140.2, 135.8, 129.6, 129.4, 128.2, 115.5, 113.5, 92.0, 84.2, 51.7, 25.7, 23.9, 21.7, 18.2, -5.2. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{20}H_{28}O_2SiNa^+$: 351.1751, found 351.1759.



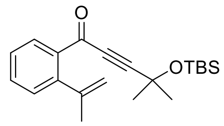
N,4-dimethyl-N-(4-oxo-4-(2-(prop-1-en-2-yl)phenyl)but-2-yn-1-yl)benzenesulfonamide(3p)



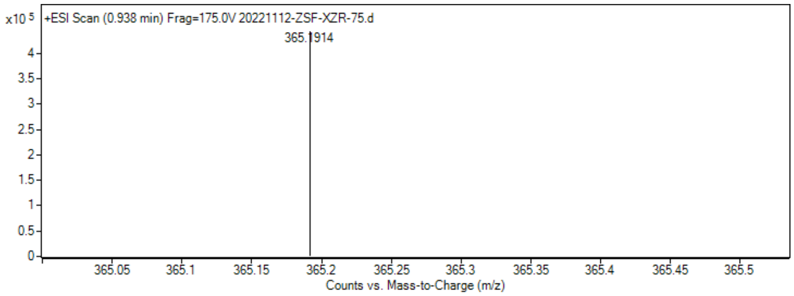
Yellow liquid, purified by chromatography (PE/EA = 3/1, Rf = 0.5); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.67 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.52 (td, *J* = 7.5, 1.4 Hz, 1H), 7.33 (td, *J* = 7.6, 1.3 Hz, 1H), 7.28 – 7.22 (m, 3H), 5.14 (t, *J* = 1.6 Hz, 1H), 4.91 – 4.71 (m, 1H), 4.30 (s, 2H), 2.91 (s, 3H), 2.31 (s, 3H), 2.05 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 178.2, 145.8, 145.2, 144.1, 135.1, 133.8, 132.9, 131.3, 129.7, 127.9, 127.0, 115.1, 85.5, 84.9, 40.2, 34.9, 23.8, 21.5. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{21}H_{21}NO_3SNa^+$: 390.1134 found 390.1139.



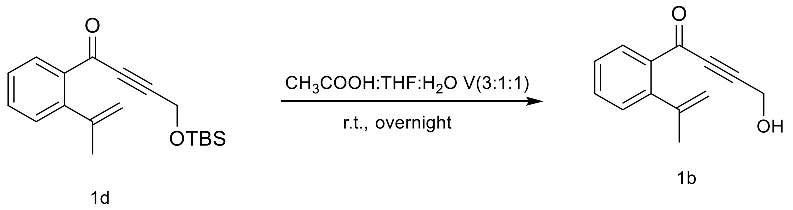
4-((tert-butyldimethylsilyl)oxy)-4-methyl-1-(2-(prop-1-en-2-yl)phenyl)pent-2-yn-1-one (3r)



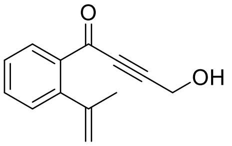
Yellow liquid, purified by chromatography (PE/EA = 10/1, Rf = 0.5); ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.95 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.49 (td, *J* = 7.5, 1.4 Hz, 1H), 7.37 (td, *J* = 7.6, 1.3 Hz, 1H), 7.27 – 7.24 (m, 1H), 5.15 (t, *J* = 1.6 Hz, 1H), 4.87 (dd, *J* = 1.8, 0.9 Hz, 1H), 2.10 (t, *J* = 1.2 Hz, 3H), 1.56 (s, 6H), 0.87 (s, 9H), 0.18 (s, 6H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 179.4, 145.8, 145.0, 136.0, 132.5, 131.1, 129.6, 127.0, 115.3, 97.8, 82.2, 66.5, 32.2, 25.6, 24.0, 17.9, -3.0. **HRMS** (ESI) [M+Na]$^{+}$ calculated for $C_{21}H_{30}O_2SiNa^{+}$: 365.1907, found 365.1914.



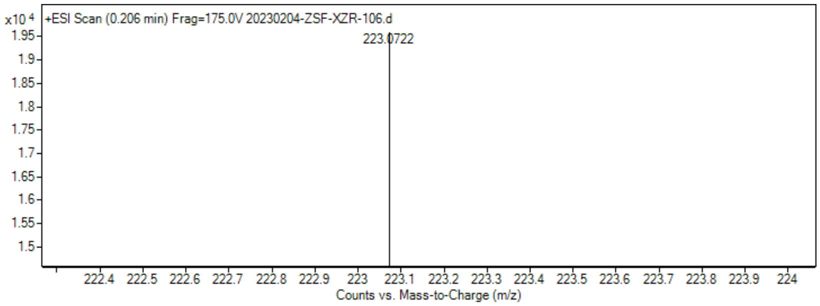
4-hydroxy-1-(2-(prop-1-en-2-yl)phenyl)but-2-yn-1-one(1b)



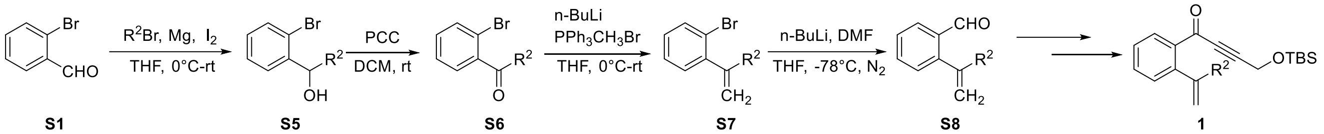
To the solution of **1d** (628 mg, 2 mmol) in 2 mL THF, acetic acid (6 mL) and H_2O (2 mL) was added and the mixture was stirred at room temperature at overnight. After the complete consumption of **1d** determined by TLC, the reaction mixture was filtered through silica gel and the filtrate was concentrated by rotary evaporator. The resulting residue was flash chromatographed (PE: EA = 5:1) on silica gel to afford the product **1b** in 80% yield, 320 mg.



Colorless liquid, purified by chromatography (PE/EA = 5/1, Rf = 0.5); ^{1}**H NMR** (500 MHz, Chloroform-*d*) δ 7.99 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.50 (td, *J* = 7.5, 1.4 Hz, 1H), 7.37 (td, *J* = 7.6, 1.3 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 5.15 (t, *J* = 1.6 Hz, 1H), 4.86 (s, 1H), 4.51 (s, 2H), 2.54 (s, 1H), 2.09 (s, 3H). ^{13}**C NMR** (126 MHz, Chloroform-*d*) δ 179.3, 145.9, 145.2, 135.4, 132.8, 131.4, 129.7, 127.2, 115.4, 91.4, 84.8, 51.0, 23.9. **HRMS** (ESI) [M+Na]$^{+}$ calculated for $C_{13}H_{12}O_2Na^{+}$:223.0729, found 223.0722.



Typical procedure B[1]**:**



Into a round-bottom flask containing of magnesium (10.5 mmol, 1.05 equiv) was equipped with a condenser, anhydrous THF (10 mL) was introduced to cover the magnesium, and I_2 (10 mg) was added. As the contents of the flask were stirred, corresponding bromide (12 mmol, 1.2 equiv, 1 M in THF) was added dropwise by syringe at 0℃. The mixture was stirred for an additional one hour at room temperature. After the formation of Grignard reagent, the reaction mixture was cooled to 0 °C and **S1** (10 mmol, 1.0 equiv) was added dropwise by syringe. The reaction was quenched with H_2O and HCl (1 M). The aqueous layer was extracted with EA and the combined organic layers were dried over Na_2SO_4, filtrated and concentrated in vacuum. The crude product was applied to flash column chromatography eluted with PE/EA = 10/1 to obtain **S5**.

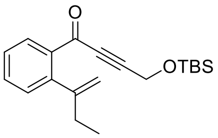
PCC (Pyridinium Chlorochromate, (9.6 mmol, 1.2 equiv)) was added into a solution of **S5** (8 mmol, 1.0 equiv) in dichlorometh-ane (DCM, 30 mL). The reaction was stirred at room temperature and monitored by TLC. After the **S5** was completely consumed, the reaction mixture was poured into water and extracted with DCM (3×10 mL). The organic phase was washed with brine and dried with anhydrous Na_2SO_4. The solvent was distilled using rotary evaporator and the product **S6** was obtained by flash column chromatography eluted with PE/EA = 20/1.

Under N_2 atmosphere, n-BuLi (7.2 mmol, 1.2 equiv, 1.6 M) in hexane was added dropwise into the suspension of CH_3PPh_3Br (7.2 mmol, 1.2 equiv) in anhydrous THF (20 mL) at 0 °C. The reaction mixture was stirred for 1 h until it turned to clear orange solution. After **S6** (6 mmol, 1.0 equiv) dissolved in anhydrous THF (4 mL) was added into the reaction dropwise, the reaction temperature was raised to room temperature and maintained until the entire consumption of **S6**. And then the reaction was quenched using 5 mL saturated NH_4Cl (aq), and extracted with EtOAc (2×20 mL). The organic phase was washed with brine and dried with anhydrous Na_2SO_4, the solvent was removed by rotary evaporator. The resulting residue was purified by chromatography (SiO_2, PE) to yield **S7.**

Under N_2 atmosphere, n-BuLi (6 mmol, 1.5 equiv 1.6 M) in hexane was added dropwise into the solution of **S7** (4 mmol, 1.0 equiv) in anhydrous THF (6 mL) at -78 °C. The reaction mixture was stirred for 1 h before DMF (8 mmol, 2.0 equiv) dissolved in anhydrous THF (1 mL) was added into the reaction dropwise. The reaction temperature was raised to room temperature and maintained until the entire consumption of **S7**. And then the reaction was quenched using 5 mL saturated NH_4Cl (aq), and extracted with EtOAc (2×20 mL). The organic phase was washed with brine and dried with anhydrous Na_2SO_4, the solvent was removed by rotary evaporator. The resulting residue was purified by chromatography (SiO_2, PE/EA = 100/1) to yield **S8**.

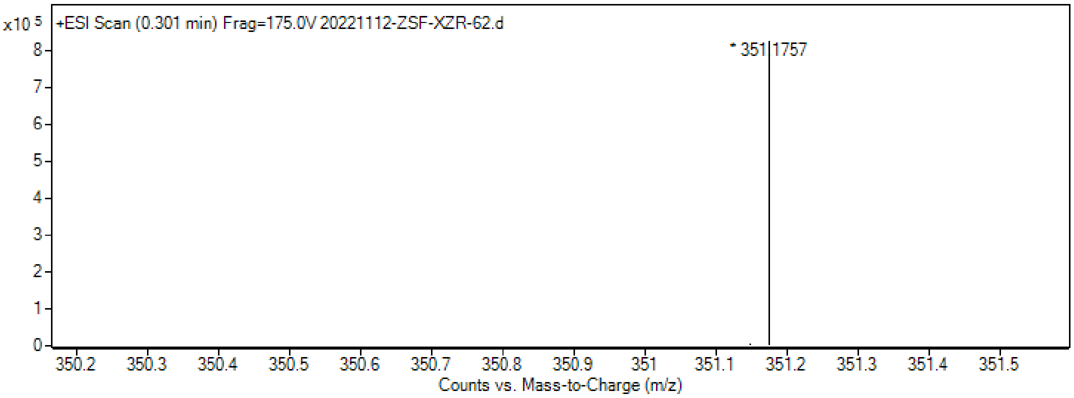
The substrates such as **3a, 3b, 3g**and **3h** were synthesized according to **General procedure B.**

1-(2-(but-1-en-2-yl)phenyl)-4- ((tert-butyldimethylsilyl)oxy)but-2-yn-1-one (3a)

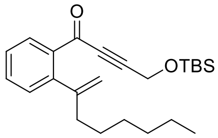


Yellow liquid, purified by chromatography (PE/EA = 10/1, Rf = 0.5); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.02 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.49 (td, *J* = 7.5, 1.4 Hz, 1H), 7.37 (td, *J* = 7.6, 1.3 Hz, 1H), 7.22 (dd, *J* = 7.6, 1.3 Hz, 1H), 5.14 (q, *J* = 1.6 Hz, 1H), 4.88 (q, *J* = 1.2 Hz, 1H), 4.53 (s, 2H), 2.38 (qt, *J* = 7.4, 1.4

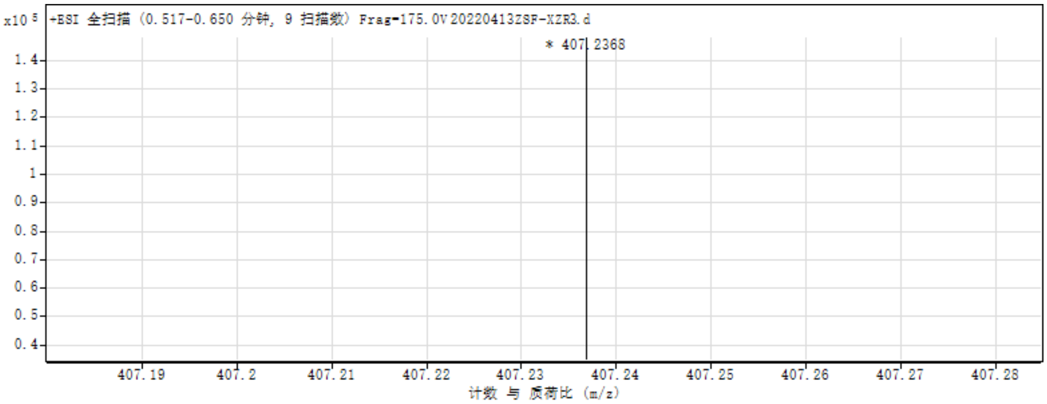
Hz, 2H), 1.07 (t, *J* = 7.4 Hz, 3H), 0.92 (s, 9H), 0.14 (s, 6H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 179.0, 151.8, 144.9, 135.6, 132.5, 131.6, 130.3, 127.0, 112.6, 91.8, 84.2, 51.7, 30.1, 25.7, 18.3, 12.5, -5.2. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{20}H_{28}O_2SiNa^+$: 351.1751, found 351.1757.



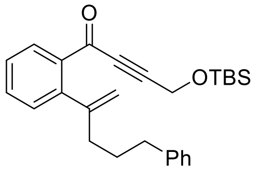
4-((tert-butyldimethylsilyl)oxy)-1-(2-(oct-1-en-2-yl)phenyl)but-2-yn-1-one (3b)



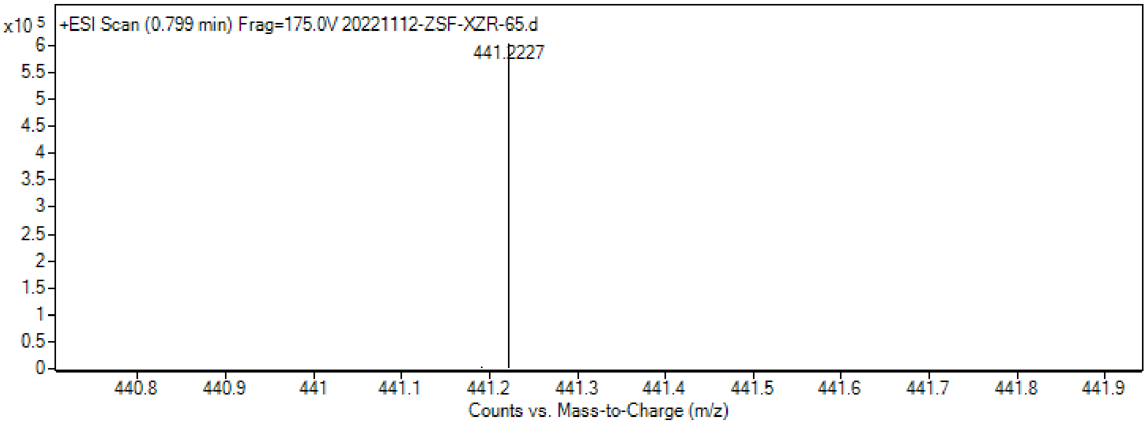
Colorless liquid, purified by chromatography (PE/EA = 10/1, Rf = 0.5); ^{1}**H NMR** (500 MHz, Chloroform-*d*) δ 8.02 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.46 (td, *J* = 7.5, 1.4 Hz, 1H), 7.34 (td, *J* = 7.6, 1.3 Hz, 1H), 7.18 (dd, *J* = 7.6, 1.3 Hz, 1H), 5.10 (d, *J* = 1.5 Hz, 1H), 4.86 (d, *J* = 1.6 Hz, 1H), 4.51 (s, 2H), 2.37 – 2.27 (m, 2H), 1.37 (q, *J* = 7.9 Hz, 2H), 1.30 – 1.20 (m, 6H), 0.90 (s, 9H), 0.83 (t, *J* = 6.9 Hz, 3H), 0.12 (s, 6H). ^{13}**C NMR** (126 MHz, Chloroform-*d*) δ 178.9, 150.8, 144.9, 135.5, 132.5, 131.7, 130.5, 127.0, 113.3, 91.9, 84.2, 51.8, 37.4, 31.8, 29.1, 28.2, 25.7, 22.6, 18.3, 14.1, -5.2. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{24}H_{36}O_2SiNa^+$: 407.2377, found 407.2368.



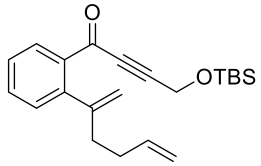
4-((tert-butyldimethylsilyl)oxy)-1-(2-(5-phenylpent-1-en-2-yl)phenyl)but-2-yn-1-one (3g)



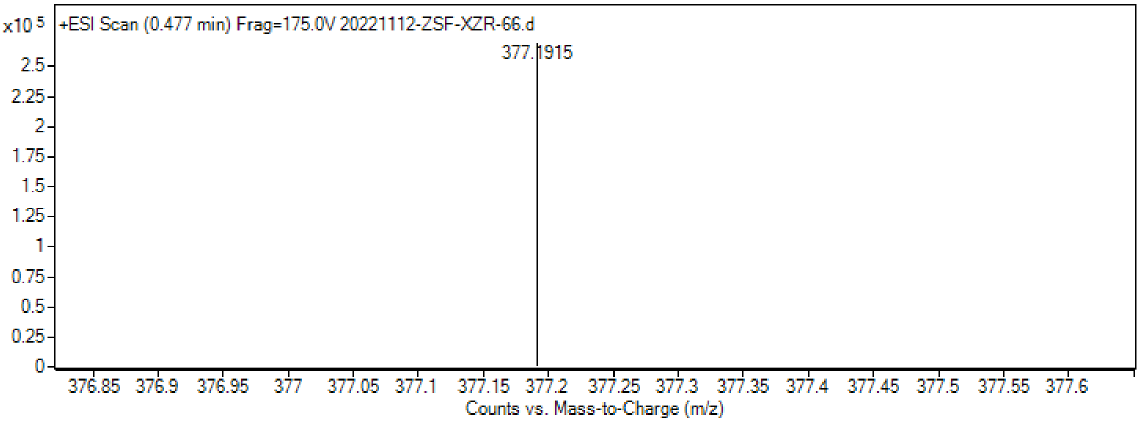
Yellow liquid, purified by chromatography (PE/EA = 10/1, Rf = 0.5); ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.48 (td, *J* = 7.5, 1.4 Hz, 1H), 7.38 (td, *J* = 7.6, 1.3 Hz, 1H), 7.26 – 7.23 (m, 2H), 7.21 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.18 – 7.11 (m, 3H), 5.15 (q, *J* = 1.5 Hz, 1H), 4.92 (d, *J* = 1.5 Hz, 1H), 4.52 (s, 2H), 2.69 – 2.54 (m, 2H), 2.42 (t, *J* = 7.8 Hz, 2H), 1.85 – 1.63 (m, 2H), 0.93 (s, 9H), 0.15 (s, 6H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 178.8, 150.2, 144.6, 142.4, 135.5, 132.9, 131.9, 130.5, 128.4, 128.3, 127.1, 125.9, 113.7, 91.9, 84.1, 51.7, 37.0, 35.6, 30.0, 25.7, 18.3, -5.2. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{27}H_{34}O_2SiNa^+$: 441.2220, found 441.2227.



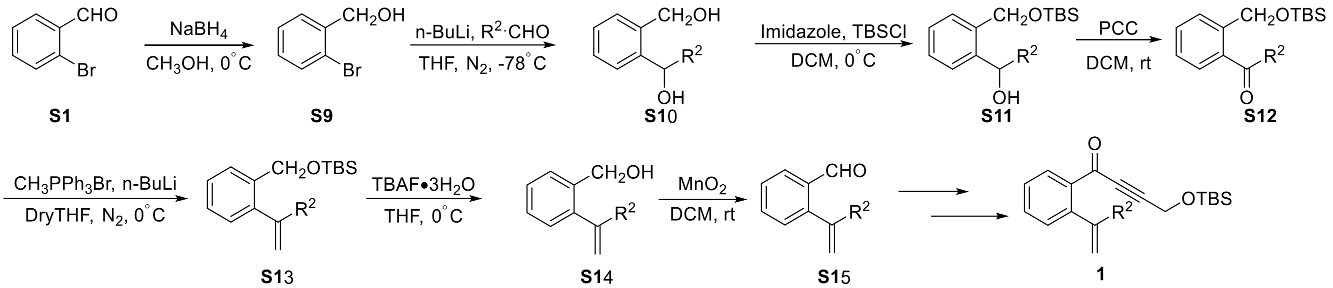
4-((tert-butyldimethylsilyl)oxy)-1-(2-(hexa-1,5-dien-2-yl)phenyl)but-2-yn-1-one (3h)



Yellow liquid, purified by chromatography (PE/EA = 10/1, Rf = 0.5); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.06 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.49 (td, *J* = 7.5, 1.4 Hz, 1H), 7.38 (td, *J* = 7.6, 1.3 Hz, 1H), 7.21 (dd, *J* = 7.6, 1.4 Hz, 1H), 5.88 – 5.74 (m, 1H), 5.15 (q, *J* = 1.5 Hz, 1H), 5.00 (dd, *J* = 17.1, 1.8 Hz, 1H), 4.95 (dt, *J* = 10.2, 1.6 Hz, 1H), 4.92 – 4.90 (m, 1H), 4.54 (s, 2H), 2.46 (dd, *J* = 9.1, 6.5 Hz, 2H), 2.24 – 2.11 (m, 2H), 0.93 (s, 9H), 0.15 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 178.7, 149.9, 144.5, 138.2, 135.4, 132.6, 131.9, 130.6, 127.1, 114.7, 113.7, 91.9, 51.7, 36.5, 32.3, 25.7, 18.3, -5.2. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{22}H_{30}O_2SiNa^+$: 377.1907, found 377.1915.



Typical procedure C:[2]



$NaBH_4$ (15 mmol, 1.5 equiv) was added into a solution of **S1** (10 mmol, 1.0 equiv) in methanol (CH_3OH, 40 mL). The reaction was stirred at 0 °C and monitored by TLC. After the **S1** was completely consumed, the reaction mixture was poured into water and extracted with EA (3×10 mL). The organic phase was washed with brine and dried with anhydrous Na_2SO_4. The solvent was distilled using rotary evaporator and the product **S9** was obtained by flash column chromatography eluted with PE/EA = 5/1.

Under N_2 atmosphere, n-BuLi (17.6 mmol, 2.2 equiv 1.6 M) in hexane was added dropwise into the solution of **S9** (8 mmol, 1.0 equiv) in anhydrous THF (40 mL) at -78 °C. The reaction mixture was stirred for 1 h before corresponding aldehyde (9.6 mmol, 1.2 equiv) dissolved in anhydrous THF (3 mL) was added into the reaction dropwise.The reaction temperature was raised to room temperature and maintained until the entire consumption of **S9**. And then the reaction was quenched using 10 mL saturated NH_4Cl (aq), and extracted with EtOAc (2×20 mL). The organic phase was washed with brine and dried with anhydrous Na_2SO_4, the solvent was removed by rotary evaporator. The resulting residue was purified by chromatography (SiO_2, PE/EA = 1/1) to yield **S10**.

To the solution of **S10** (6 mmol, 1.0 equiv) in 30 mL DCM, 1H-imidazole (7.2 mmol, 1.2 equiv), TBSCl (7.2 mmol, 1.2 equiv) was added and the mixture was stirred at room temperature for about 1 h. After the complete consumption of **S10** determined by TLC. And then the reaction was quenched using 10 mL saturated NH_4Cl (aq), and extracted with DCM (2×20 mL). The organic phase was washed with brine and dried with anhydrous Na_2SO_4, the solvent was removed by rotary evaporator. The resulting residue was purified by chromatography (SiO_2, PE/EA = 10/1) to yield **S11.**

PCC (Pyridinium Chlorochromate, (6.72 mmol, 1.2 equiv)) was added into a solution of **S11** (5.6 mmol, 1.0 equiv) in dichloromethane (DCM, 20 mL). The reaction was stirred at room temperature and monitored by TLC. After the **S11** was completely consumed, the reaction mixture was poured into water and extracted with DCM (3×10 mL). The organic phase was washed with brine and dried with anhydrous Na_2SO_4. The solvent was distilled using rotary evaporator and the product **S12** was obtained by flash column chromatography eluted with PE/EA = 20/1.

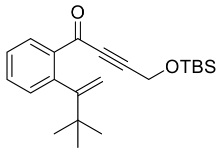
Under N_2 atmosphere, n-BuLi (6 mmol, 1.2 equiv, 1.6 M) in hexane was added dropwise into the suspension of CH_3PPh_3Br (6 mmol, 1.2 equiv) in anhydrous THF (25 mL) at 0 °C. The reaction mixture was stirred for 1 h until it turned to clear orange solution. After **S12** (5 mmol, 1.0 equiv) dissolved in anhydrous THF (4 mL) was added into the reaction dropwise, the reaction temperature was raised to room temperature and maintained until the entire consumption of **S12**. And then the reaction was quenched using 5 mL saturated NH_4Cl (aq), and extracted with EtOAc (2×20 mL). The organic phase was washed with brine and dried with anhydrous Na_2SO_4, the solvent was removed by rotary evaporator. The resulting residue was purified by chromatography (SiO_2, PE) to yield **S13.**

To a solution of **S13** (1.0 eq) in THF (0.25 M) was added TBAF•3H_2O (1.2 equiv) at room temperature and the mixture was stirred for 5 minutes. The mixture was poured into a separatory funnel and water was added. The aqueous was extracted with EtOAc for three times and the collected organic phase was washed with brine. The organic phase was dried with Na_2SO_4 and collected by vacuum into a round bottom flask. The crude product was purified by column chromatography (PE/EA=10:1) to afford **S14** in 59% yield as the yellow oil.

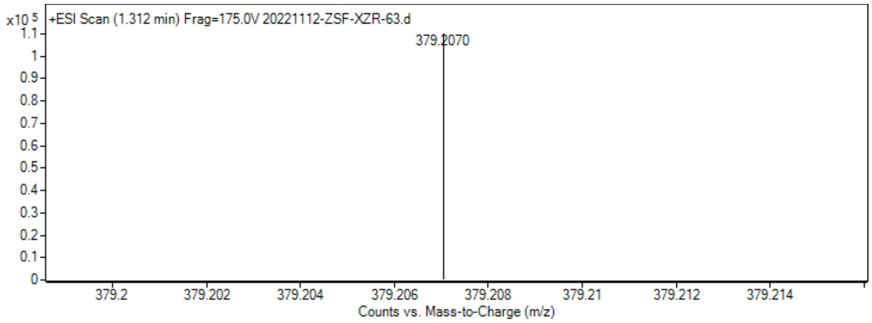
To the solution of **S14** (3 mmol, 1.0 equiv) in 10 mL DCM, activated MnO_2 (30 mmol, 10 equiv) was added and the mixture was stirred at room temperature for about 3 h. After the complete consumption of **S14** determined by TLC, the reaction mixture was filtered through silica gel and the filtrate was concentrated by rotary evaporator. The resulting residue was flash chromatographed (PE/EA = 20:1) on silica gel to afford **S15**.

The substrates such as **3c, 3d, 3e, 3f, 3l** and **3m** were synthesized according to **General procedure C.**

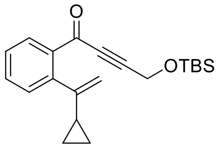
4-((tert-butyldimethylsilyl)oxy)-1-(2-(3,3-dimethylbut-1-en-2-yl)phenyl)but-2-yn-1-one (3c)



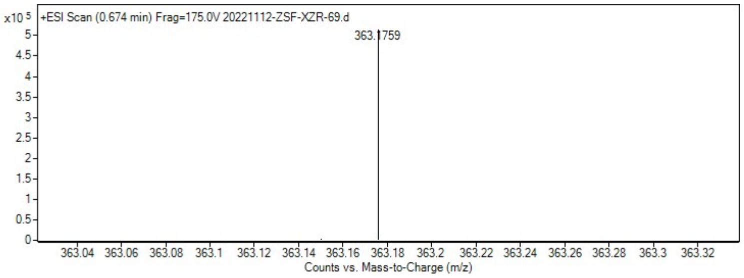
Colorless liquid, purified by chromatography (PE/EA = 10/1, Rf = 0.5); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.09 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.45 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.38 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.16 (dd, *J* = 7.6, 1.3 Hz, 1H), 5.27 (d, *J* = 1.1 Hz, 1H), 4.79 (d, *J* = 1.1 Hz, 1H), 4.54 (s, 2H), 1.12 (s, 10H), 0.92 (s, 9H), 0.14 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 178.7, 157.8, 143.8, 136.1, 131.8, 131.8, 131.0, 126.6, 112.2, 91.8, 84.4, 51.8, 36.6, 30.2, 25.7, 18.3, -5.2. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{22}H_{32}O_2SiNa^+$: 379.2064, found 379.2070.



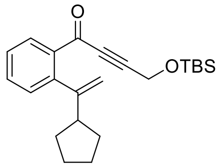
4-((tert-butyldimethylsilyl)oxy)-1-(2-(1-cyclopropylvinyl)phenyl)but-2-yn-1-one (3d)



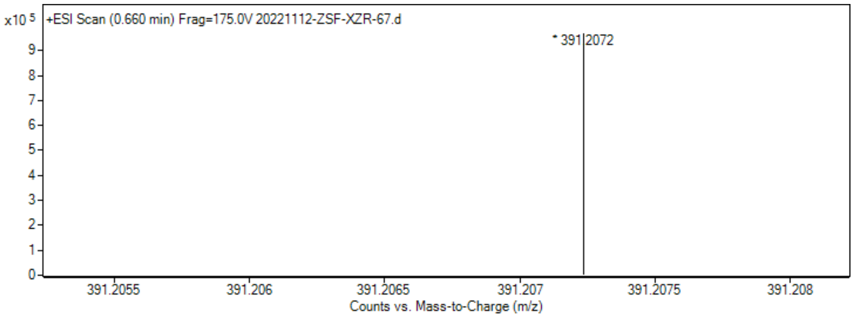
Colorless liquid, purified by chromatography (PE/EA = 10/1, Rf = 0.5); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.00 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.47 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.38 (td, *J* = 7.6, 1.3 Hz, 1H), 7.22 (dd, *J* = 7.6, 1.3 Hz, 1H), 5.06 (s, 1H), 4.82 (d, *J* = 1.2 Hz, 1H), 4.54 (s, 2H), 1.72 – 1.65 (m, 1H), 0.92 (s, 9H), 0.76 – 0.70 (m, 2H), 0.50 – 0.46 (m, 2H), 0.14 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 179.0, 151.1, 143.5, 136.1, 132.3, 131.2, 130.8, 127.1, 111.4, 92.0, 84.3, 51.8, 25.7, 18.3, 17.3, 7.1, -5.2. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{21}H_{28}O_2SiNa^+$: 363.1751, found 363.1759.



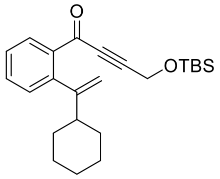
4-((tert-butyldimethylsilyl)oxy)-1-(2-(1-cyclopentylvinyl)phenyl)but-2-yn-1-one (3e)



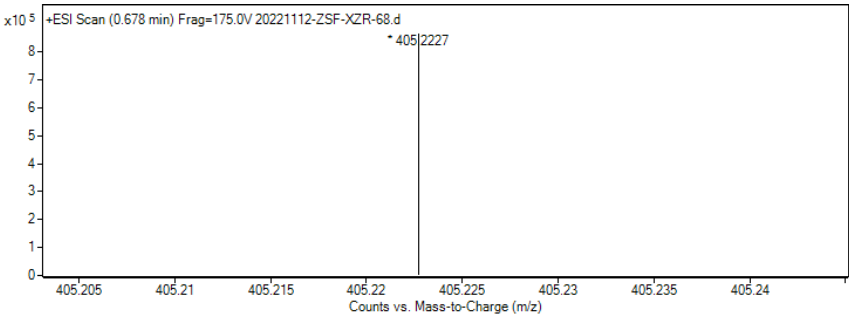
Yellow liquid, purified by chromatography (PE/EA = 10/1, Rf = 0.5); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 7.7 Hz, 1H), 7.58 – 7.45 (m, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 5.18 (s, 1H), 4.90 (s, 1H), 4.56 (s, 2H), 2.72 (p, *J* = 8.3 Hz, 1H), 1.87 – 1.76 (m, 2H), 1.70 (td, *J* = 6.6, 3.6 Hz, 2H), 1.57 (dt, *J* = 9.3, 4.7 Hz, 2H), 1.51 – 1.38 (m, 2H), 0.95 (s, 9H), 0.17 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 178.9, 154.0, 145.5, 135.3, 132.5, 131.8, 130.5, 126.8, 111.3, 91.9, 84.2, 51.8, 46.6, 32.0, 25.7, 24.7, 18.3, -5.2. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{23}H_{32}O_2SiNa^+$: 391.2064, found 391.2072.



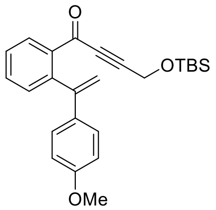
4-((tert-butyldimethylsilyl)oxy)-1-(2-(1-cyclohexylvinyl)phenyl)but-2-yn-1-one (3f)



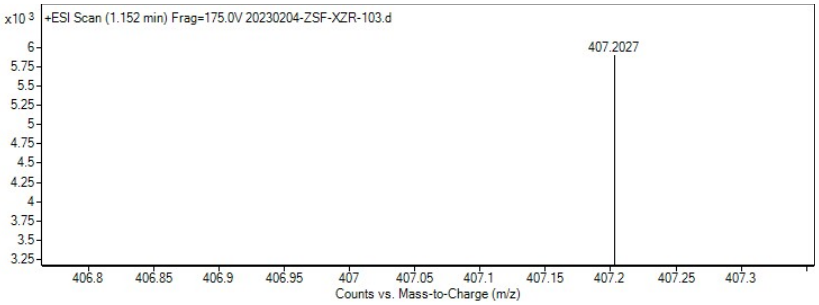
Colorless liquid, purified by chromatography (PE/EA = 10/1, Rf = 0.5); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.47 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.37 (td, *J* = 7.6, 1.4 Hz, 1H), 7.18 (dd, *J* = 7.5, 1.4 Hz, 1H), 5.10 (s, 1H), 4.86 (d, *J* = 1.3 Hz, 1H), 4.54 (s, 2H), 2.07 (d, *J* = 11.1 Hz, 1H), 1.85 (d, *J* = 10.3 Hz, 2H), 1.77 – 1.69 (m, 2H), 1.29 – 1.11 (m, 6H), 0.93 (s, 9H), 0.15 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 178.8, 156.0, 145.3, 135.2, 132.4, 132.1, 131.1, 126.9, 110.8, 91.9, 84.1, 51.8, 44.5, 32.4, 26.7, 26.4, 25.7, 18.3, -5.2. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{24}H_{34}O_2SiNa^+$: 405.222, found 405.2227.



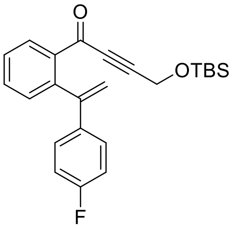
4-((tert-butyldimethylsilyl)oxy)-1-(2-(1-(4-methoxyphenyl)vinyl)phenyl)but-2-yn-1-one(3l)



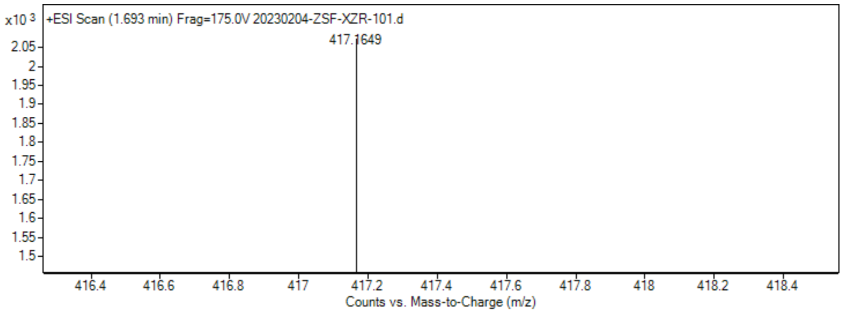
Yellow liquid, purified by chromatography (PE/EA = 10/1, Rf = 0.5); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.58 (td, *J* = 7.5, 1.4 Hz, 1H), 7.49 (td, *J* = 7.6, 1.3 Hz, 1H), 7.38 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.25 – 7.20 (m, 2H), 6.86 – 6.80 (m, 2H), 5.68 (d, *J* = 1.0 Hz, 1H), 5.15 (d, *J* = 1.0 Hz, 1H), 4.38 (s, 2H), 3.82 (s, 3H), 0.93 (s, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 178.7, 159.2, 148.3, 143.0, 137.1, 133.4, 132.5, 131.6, 131.1, 128.1, 127.7, 113.9, 113.6, 92.0, 84.1, 55.2, 51.6, 25.7, 18.3, -5.2. **HRMS** (ESI) [M+H]$^+$ calculated for $C_{25}H_{31}O_3Si^+$: 407.2037, found 407.2027.



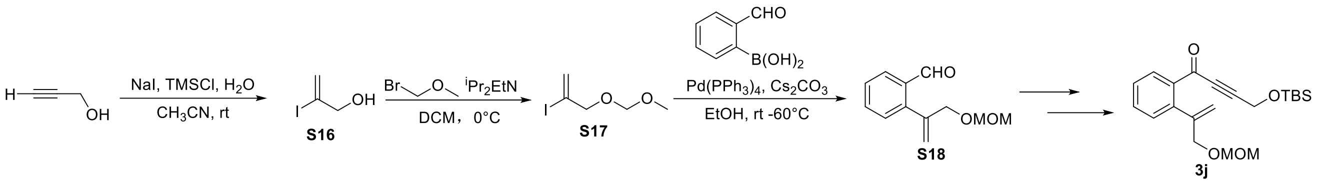
4-((tert-butyldimethylsilyl)oxy)-1-(2-(1-(4-fluorophenyl)vinyl)phenyl)but-2-yn-1-one (3m)



Yellow liquid, purified by chromatography (PE/EA = 21/1, Rf = 0.5); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.09 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.60 (td, *J* = 7.5, 1.4 Hz, 1H), 7.51 (td, *J* = 7.6, 1.3 Hz, 1H), 7.38 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.28 – 7.20 (m, 2H), 6.98 (t, *J* = 8.7 Hz, 2H), 5.68 (s, 1H), 5.23 (s, 1H), 4.41 (s, 2H), 0.92 (s, 9H), 0.12 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) ^{13}C NMR (126 MHz, Chloroform-*d*) δ 177.2, 164.9 (d, *J* = 256.3 Hz), 148.5 (d, *J* = 8.9 Hz), 145.1 (d, *J* = 1.0 Hz), 134.5 (d, *J* = 9.8 Hz), 131.9 (d, *J* = 2.8 Hz), 117.0 (d, *J* = 21.7 Hz), 115.5, 114.0 (d, *J* = 21.6 Hz), 92.0, 83.8, 51.7, 25.7, 23.6, 18.3, -5.2. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -114.81. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{24}H_{27}FO_2SiNa^+$: 417.1656, found 417.1649.



Typical procedure D:[1][3][4]



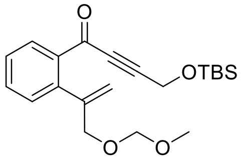
A solution of NaI (3.60 g, 24.0 mmol) in MeCN (40 mL) was allowed to cool to 0 °C and then charged with TMSCl (3.05 mL, 24.0 mmol). The mixture was allowed to stir for 30 min at 0 °C, after which H_2O (216 μL, 12.0 mmol) was added, immediately followed by propargyl alcohol (1.16 mL, 20.0 mmol). The solution was allowed to stir at 23 °C for 6 h, and then quenched by the addition of a saturated solution of aqueous $NaHCO_3$ (110 mL). The mixture was washed with Et_2O (3 × 70 mL). The combined organic layers were washed with a saturated solution of aqueous $Na_2S_2O_3$ (3 × 90 mL) and dried over Na_2SO_4 and then filtered. The resultant organic layer was evaporated in vacuo to afford dark oil, which was purified by silica gel chromatography (PE/EtOAc = 8/2) to furnish **S16** as colorless oil (2.4 g, 65% yield).

To a cooled (0 °C) solution of **S16** (5 mmol, 1.0 equiv), diisopropylethylamine (10 mmol, 2.0 equiv) in dichloromethane (25 mL) was added dropwise bromo(methoxy)methane (10 mmol, 2.0 equiv)). The reaction mixture was stirred for 3 days at rt before being diluted with 15 mL of water. The layers were separated and the aqueous layer was extracted with diethyl ether. Combined organic layer were dried over anhydrous magnesium sulfate, filtered and concentrated. The residue was finally purified by flash chromatography on silica gel (PE/EA = 9/1) to afford the desired product **S17**.

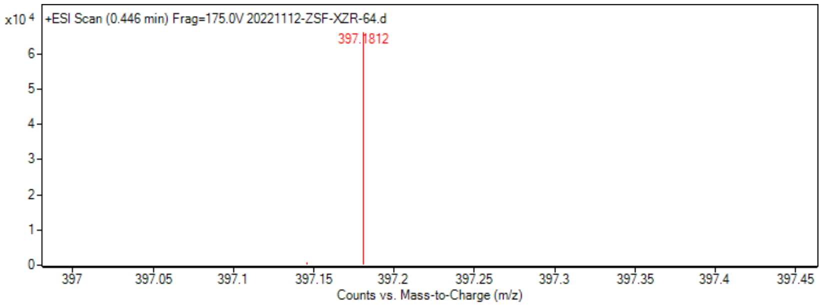
To an N_2-sparged solution of **S17** (3 mmol, 1.0 equiv), (2-formylphenyl)boronic acid (3.6 mmol, 1.2 equiv) and cesium carbonate (3 mmol, 1.0 equiv) in EtOH (15 mL) was added $Pd(PPh_3)_4$ (0.09 mmol, 3 mol%). The mixture was stirred at 60 °C for 12 h. After the reaction completed,it was diluted with water and extracted with EA. The combined organics were washed with brinem dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting residue was flash chromatographed (PE: EA = 30:1) on silica gel to afford the product **S18**.

The substrates such as **3j** were synthesized according to **General procedure D.**

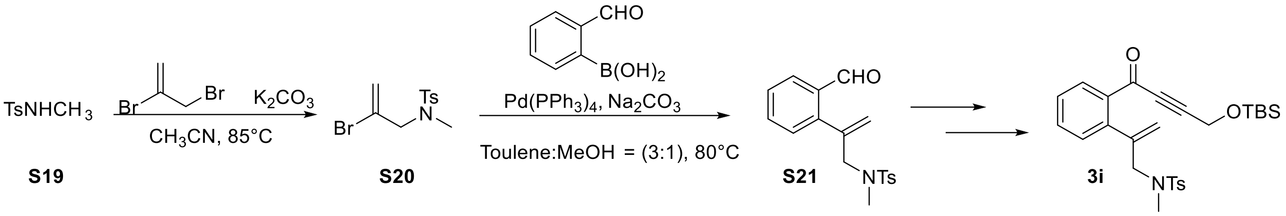
4-((tert-butyldimethylsilyl)oxy)-1-(2-(3-(methoxymethoxy)prop-1-en-2-yl)phenyl)but-2-yn-1-one (3j)



Yellow liquid, purified by chromatography (PE/EA = 10/1, Rf = 0.5); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.12 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.52 (d, *J* = 1.4 Hz, 1H), 7.42 (d, *J* = 1.4 Hz, 1H), 7.33 – 7.25 (m, 1H), 5.42 (d, *J* = 1.6 Hz, 1H), 5.08 (dt, *J* = 1.8, 0.9 Hz, 1H), 4.65 (s, 2H), 4.55 (s, 2H), 4.31 (t, *J* = 1.2 Hz, 2H), 3.31 (s, 3H), 0.93 (s, 9H), 0.15 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 178.4, 146.8, 141.6, 135.5, 132.9, 132.2, 131.3, 127.6, 115.2, 95.6, 92.2, 83.9, 69.9, 55.3, 51.7, 25.7, 18.3, -5.2. **HRMS** (ESI) $[M+Na]^+$ calculated for $C^{21}H^{30}O^{4}SiNa^{+}$: 397.1805, found 397.1812.



Typical procedure E:[1]

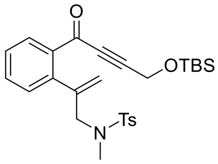


A solution of **S19** (5 mmol, 1.0 equiv) in MeCN (40 mL) charged with 2,3-dibromoprop-1-ene (7.5 mmol, 1.5 equiv) and potassium carbonate (7.5 mmol, 1.5 equiv). The mixture was stirred at 85 °C for 12 h. After the reaction completed,it was diluted with water and extracted with EA. The combined organics were washed with brine dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting residue was flash chromatographed (PE/EA = 3:1) on silica gel to afford the product **S20**.

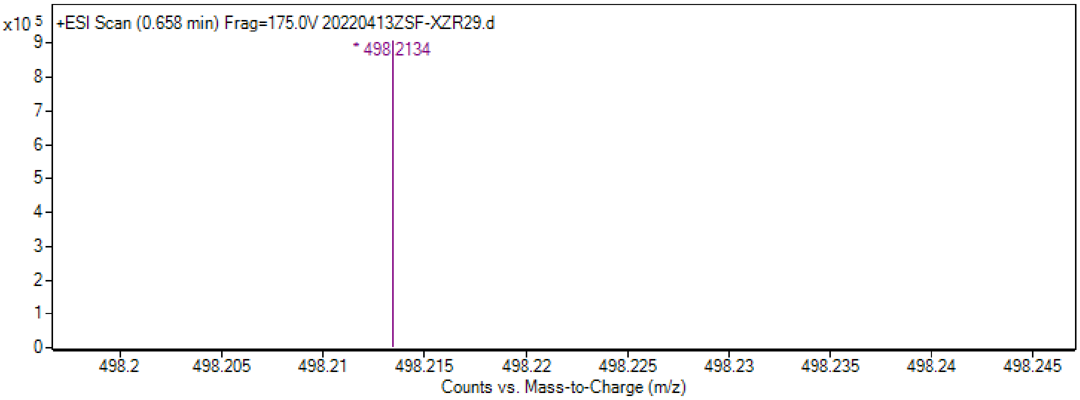
To an N_2-sparged solution of **S20** (3 mmol, 1.0 equiv), (2-formylphenyl)boronic acid (4.5 mmol, 1.5 equiv) and sodium carbonate (6 mmol, 2.0 equiv) in Toluene :MeOH (V:V = 3:1, 15 mL) was added $Pd(PPh_3)_4$ (0.09 mmol, 3 mol%). The mixture was stirred at 80 °C for 24 h. After the reaction completed, it was diluted with water and extracted with EA. The combined organics were washed with brine dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting residue was flash chromatographed (PE/EA = 5:1) on silica gel to afford the product **S21.**

The substrates such as **3i** were synthesized according to **General procedure E**

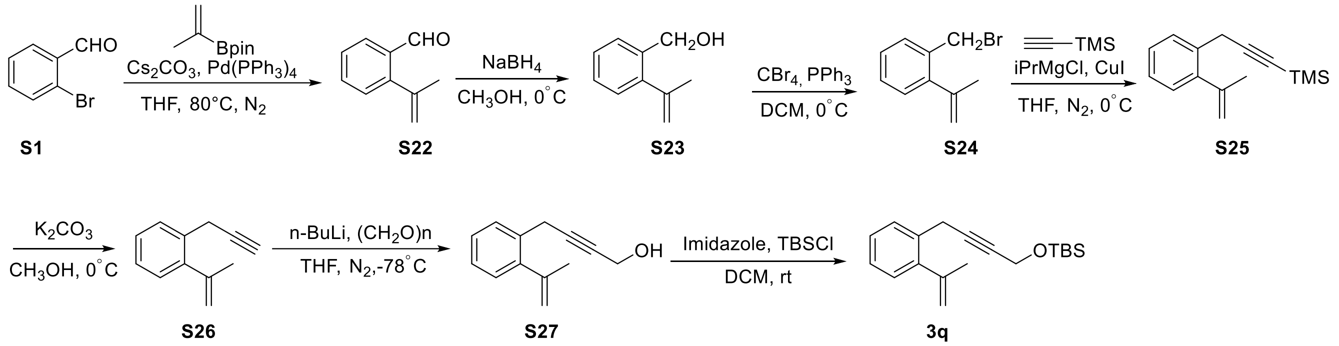
N-(2-(2-(4-((tert-butyldimethylsilyl)oxy)but-2-ynoyl)phenyl)allyl)-N,4-dimethylbenzenesulfonamide (3i)



Yellow liquid, purified by chromatography (PE/EA = 5/1, Rf = 0.5); ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 8.19 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.64 – 7.57 (m, 2H), 7.53 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.44 (td, *J* = 7.6, 1.3 Hz, 1H), 7.29 – 7.23 (m, 3H), 5.36 (d, *J* = 1.4 Hz, 1H), 5.06 (d, *J* = 1.2 Hz, 1H), 4.56 (s, 2H), 3.85 (s, 2H), 2.81 (s, 3H), 2.41 (s, 3H), 0.93 (s, 9H), 0.15 (s, 6H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 178.2, 145.1, 143.2, 141.5, 134.9, 134.8, 133.2, 133.0, 131.5, 129.6, 127.8, 127.4, 115.4, 92.4, 83.6, 55.0, 51.7, 34.6, 25.7, 21.5, 18.3, -5.2. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{27}H_{36}NO_4SSi^+$: 498.2129, found 498.2134.



Typical procedure F [1][5]:



To an N_2-sparged solution of corresponding bromide **S1** (10 mmol, 1.0 equiv), 2-isopropenylboronic acid pinacol ester (12.0 mmol, 1.2 equiv) and cesium carbonate (30 mmol, 3.0 equiv) in THF (50 mL) was added $Pd(PPh_3)_4$ (0.2 mmol, 2 mol%). The mixture was stirred at 80 °C for 12 h. After the reaction completed (monitored by GC-MS), it was diluted with water and extracted with EA. The combined organics were washed with brine dried over anhydrous Na_2SO_4 and concentrated in vacuo. Theresulting residue was flash chromatographed (PE/EA = 200:1) on silica gel to afford the product **S22** in a yield of 92%.

$NaBH_4$ (13.8 mmol, 1.5 equiv) was added into a solution of **S22** (9.2 mmol, 1.0 equiv) in methanol (CH_3OH, 40 mL). The reaction was stirred at 0 °C and monitored by TLC. After the **S22** was completely consumed, the reaction mixture was poured into water and extracted with EA (3×10 mL). The organic phase was washed with brine and dried with anhydrous Na_2SO_4. The solvent was distilled using rotary evaporator and the product **S23** was obtained by flash column chromatography eluted with PE/EA = 5/1.

To a solution of **S23** (9.2 mmol, 1.0 equiv) in DCM (35 mL) was added PPh_3 (13.8 mmol, 1.5 equiv). This reaction was cooled to 0 °C and CBr_4 (13.8 mmol, 1.5 equiv). was added. The reaction mixture was stirred for 30 min at room temperature, and monitored by TLC. After the **S23** was completely consumed, diluted with EtOAc and washed with brine and water. The organic layer was dried over Na_2SO_4 and concentrated. The crude product was purified using column chromatography on silica gel (PE/EA = 100:1) to give **S24.**

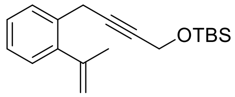
Under N_2 atmosphere, *i*PrMgCl (21.2 mmol, 4.0 equiv) was added dropwise into the suspension of (trimethylsilyl)acetylene (21.2 mmol, 4.0 equiv) in anhydrous THF (25 mL) at 0 °C. The reaction mixture was stirred for 30 min and **S24** (5.3 mmol, 1.0 equiv) dissolved in anhydrous THF (4 mL) was added into the reaction dropwise. Then the reaction mixture was stirred for 10 min at the reaction temperature and copper(I) iodide (2.12 mmol, 0.4 equiv) was added into the reaction.After the reaction temperature raised to 80 °C and maintained until the entire consumption of **S24**. And then the reaction was quenched using 5 mL saturated NH_4Cl (aq), and extracted with EtOAc (2×20 mL). The organic phase was washed with brine and dried with anhydrous Na_2SO_4, the solvent was removed by rotary evaporator. The resulting residue was purified by chromatography (SiO_2, PE) to yield **S25**

To a solution of **S25** (3.6 mmol, 1.0 equiv) in methanol (10 mL) was added dried potassium carbonate (10.8 mmol. 3.0 equiv) at 0 °C. After 2 h stirring the reaction was diluted with EtOAc washed with brine twice. The combined organic layers were dried over $MgSO_4$ and purified then by column chromatography on silica gel (PE) to give **S26**.

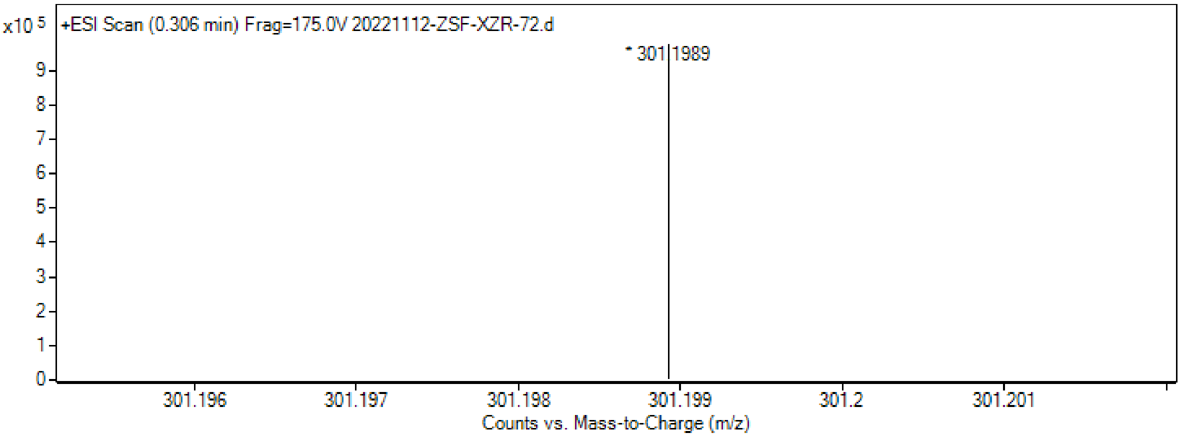
Under N_2 atmosphere, n-BuLi (3.12 mmol, 1.2 equiv, 1.6 M) in hexane was added dropwise into the suspension of **S26** (2.6 mmol, 1.0 equiv) in anhydrous THF (15 mL) at -78 °C. The reaction mixture was stirred for 1 h. After the $(CH_2O)n$ (4 mmol, 1.5 equiv) dissolved in anhydrous THF (4 mL) was added into the reaction dropwise, the reaction temperature was raised to room temperature and maintained until the entire consumption of **S26**. And then the reaction was quenched using 5 mL saturated NH_4Cl (aq), and extracted with EtOAc (2×20 mL). The organic phase was washed with brine and dried with anhydrous Na_2SO_4, the solvent was removed by rotary evaporator. The resulting residue was purified by chromatography (SiO_2, PE/EtA = 10:1) to yield **S27.**

To the solution of **S27** (2mmol, 1.0 equiv) in 10 mL DCM, 1H-imidazole (2.4 mmol, 1.2 equiv), TBSCl (2.4 mmol, 1.2 equiv) was added and the mixture was stirred at room temperature for about 1 h. After the complete consumption of **S27** determined by TLC. And then the reaction was quenched using 10 mL saturated NH_4Cl (aq), and extracted with DCM (2×20 mL). The organic phase was washed with brine and dried with anhydrous Na_2SO_4, the solvent was removed by rotary evaporator. The resulting residue was purified by chromatography (SiO_2, PE/EA = 50/1) to yield **3q.**

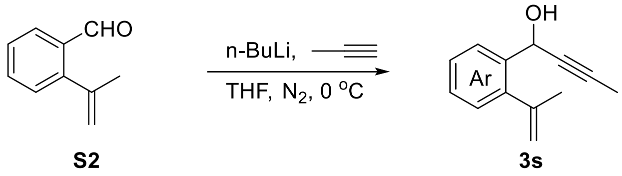
Tert-butyldimethyl((4-(2-(prop-1-en-2-yl)phenyl)but-2-yn-1-yl)oxy)silane (3q)



Colorless liquid, purified by chromatography (PE/EA = 50/1, Rf = 0.5); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.54 – 7.48 (m, 1H), 7.27 – 7.17 (m, 2H), 7.12 (dd, *J* = 7.2, 1.8 Hz, 1H), 5.23 (t, *J* = 1.8 Hz, 1H), 4.88 (dd, *J* = 2.1, 1.0 Hz, 1H), 4.35 (t, *J* = 2.3 Hz, 2H), 3.62 (t, *J* = 2.3 Hz, 2H), 2.05 (d, *J* = 1.3 Hz, 3H), 0.91 (s, 9H), 0.11 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.8, 143.1, 133.3, 128.9, 127.9, 127.1, 126.5, 115.4, 83.5, 80.6, 52.1, 25.9, 24.8, 22.9, 18.3, -5.1. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{19}H_{29}OSi^+$: 301.1982, found 301.1989.

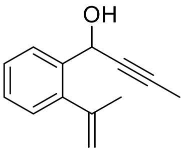


Typical procedure G[6]:



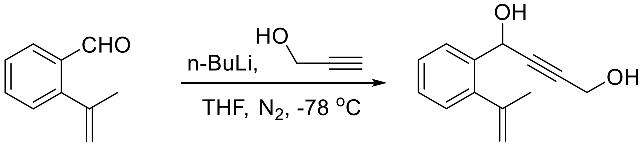
Under N_2 atmosphere, the solution of n-BuLi (2.4 mmol, 1.2 equiv) in hexane (1.6 mol/L) was added dropwise into the solution of prop-1-yne (2.4 mmol, 1.2 equiv) in anhydrous THF at -78℃. After the 30 min, aldehyde **S2** (2 mmol, 1.0 equiv) dissolved in anhydrous THF was added and the temperature was allowed to raise to room temperature. After the complete consumption of **S2** (determined by TLC), the reaction was quenched by saturated NH_4Cl (aq), and extracted with EtOAc. The organic phase was washed with brine and dried with anhydrous Na_2SO_4, the solvent was removed by rotary evaporator. The resulting residue was flash chromatography (PE:EA = 5:1) on silica gel to afford the product **3s**. .

1-(2-(prop-1-en-2-yl)phenyl)but-2-yn-1-ol (3s)



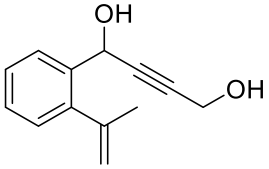
Yellow liquid, purified by chromatography (PE/EA = 5/1, Rf = 0.5); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.48 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.09 – 5.96 (m, 2H), 5.88 (dd, *J* = 7.4, 1.7 Hz, 1H), 4.37 (d, *J* = 2.3 Hz, 1H), 4.00 (s, 1H), 3.69 (dd, *J* = 2.2, 1.1 Hz, 1H), 1.08 (s, 1H), 0.83 (t, *J* = 1.3 Hz, 3H), 0.60 (d, *J* = 2.2 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.3, 142.5, 138.2, 128.0, 128.0, 127.5, 127.1, 116.1, 82.6, 80.1, 61.9, 25.5, 3.8.

Typical procedure H:

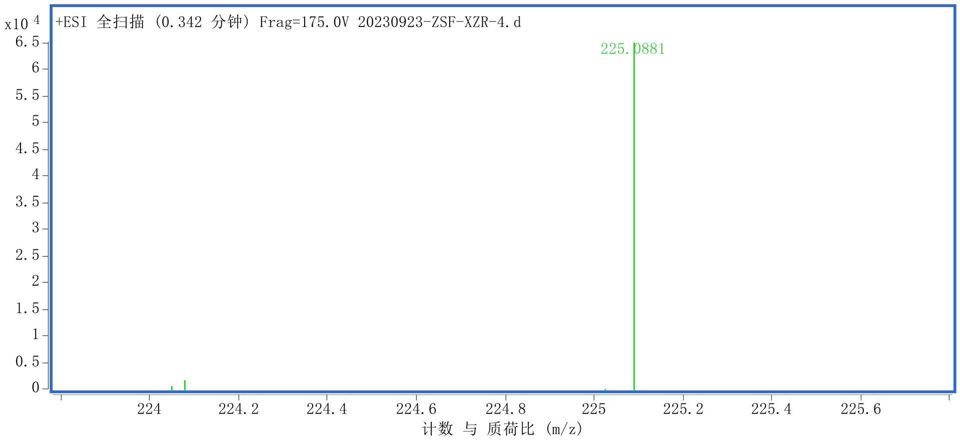


Under N_2 atmosphere, the solution of n-BuLi (4.2 mmol, 2.1 equiv) in hexane (1.6 mol/L) was added dropwise into the solution of prop-2-yn-1-ol (2.2 mmol, 1.1 equiv) in anhydrous THF at -78℃. After the 30 min, aldehyde **S22** (2 mmol, 1.0 equiv) dissolved in anhydrous THF was added and the temperature was allowed to raise to room temperature. After the complete consumption of **S22** (determined by TLC), the reaction was quenched by saturated NH_4Cl (aq) and extracted with EtOAc. The organic phase was washed with brine and dried with anhydrous Na_2SO_4, the solvent was removed by rotary evaporator. The resulting residue was flash chromatography (PE/EA = 2:1) on silica gel to afford the product **3t**.

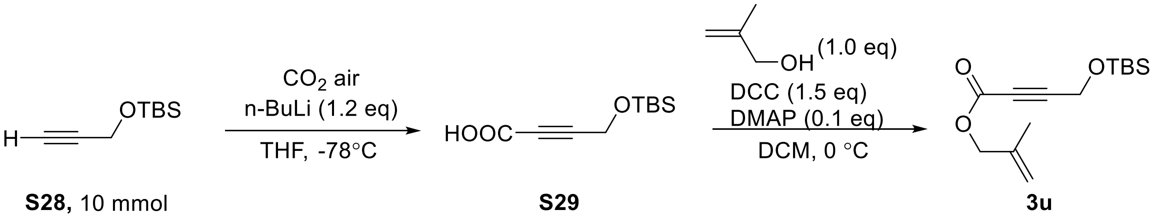
1-(2-(prop-1-en-2-yl)phenyl)but-2-yne-1,4-diol (3t)



Colorless solid, purified by chromatography (PE/EA = 2/1, Rf = 0.5); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.93 – 6.78 (m, 1H), 6.44 (t, *J* = 4.7 Hz, 2H), 6.35 – 6.20 (m, 1H), 4.86 (s, 1H), 4.41 (s, 1H), 4.09 (s, 1H), 3.42 (s, 2H), 2.16 (s, 1H), 1.79 (s, 2H), 1.23 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.0, 142.6, 137.3, 128.3, 128.0, 127.6, 127.2, 116.3, 86.3, 84.5, 61.5, 51.0, 25.4. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{13}H_{14}O_2Na^+$: 225.0886, found 225.0881.



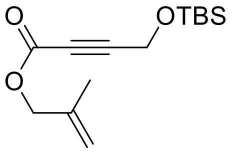
Typical procedure I:



Under N_2 atmosphere, the solution of n-BuLi (12 mmol, 1.2 equiv) in hexane (1.6 mol/L) was added dropwise into the solution of **S28** (10 mmol, 1.0 equiv) in anhydrous THF at -78 ℃. After the 30 min, dry CO_2 was passed through the reaction for 30 mim. Then, the mixture was stirred for 30 min at -78 ℃, and the temperature was allowed to raise to room temperature. After the complete consumption of **S28** (determined by TLC), the reaction was quenched by 1.0 M HCl and extracted with EtOAc. The organic phase was washed with brine and dried with anhydrous Na_2SO_4, the solvent was removed by rotary evaporator. The resulting residue was flash chromatography (PE/EA = 3:1) on silica gel to afford the product **S29**.

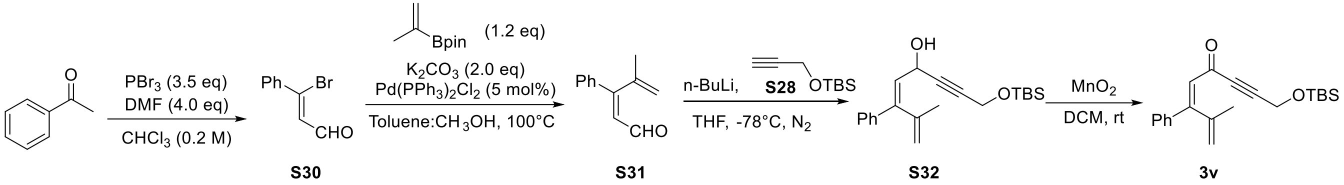
To a flame dried flask was added alcohol (2.0 mol) in DCM, then the reaction mixture was transferred to 0 °C, **S29** (1.0 eq) , DCC (1.5 eq) and DMAP (0.1 eq) was added successively and the mixture was stirred for 1 hours. The insoluble salts were removed via filtration and the mixture was evaporated under reduced pressure and purified by column chromatography (PE:EA = 5:1) to the compound **3u** in 80% yield as the colorless liquid.

2-methylallyl 4-((tert-butyldimethylsilyl)oxy)but-2-ynoate(3u)



Colorless liquid, purified by chromatography (PE/EA = 5/1, Rf = 0.5); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.03 (q, *J* = 1.2 Hz, 1H), 4.98 (q, *J* = 1.2 Hz, 1H), 4.61 (s, 2H), 4.46 (s, 2H), 1.79 (t, *J* = 1.1 Hz, 3H), 0.93 (s, 9H), 0.15 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.0, 138.9, 113.9, 86.2, 69.0, 55.8, 51.4, 34.9, 25.7, 19.4, -5.3.

Typical procedure J:



A solution of N,N-dimethylformamide (3 eq.) in anhydrous chloroform (0.5 M) was cooled to 0 °C in ice bath. Phosphorous tribromide (2.7 eq.) was added dropwise over a period of 10 min. The resulting white suspension was warmed to room temperature and stirred for an additional 30 min. A solution of carbonyl compound (100 mmol) in chloroform was added dropwise and the reaction mixture was stirred for 12 h at room temperature. The reaction mixture was then poured in ice water in ice bath. Solid NaOH was carefully added to neutralize the acids and the mixture was extracted three times with DCM. The organic part was then washed with cold water, dried with sodium sulfate and the solvents evaporated. Purification of the residue was done by silica gel by column chromatography. (PE: EA = 15: 1- 10: 1) to afford the product **S30**

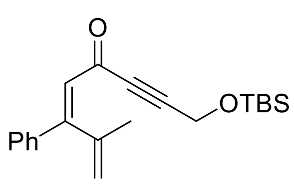
Note: make sure if ice bath is needed, be careful while neutralizing the mixture (every time NaOH added, wait for about 20mins before adding it for the next time and make sure to check PH value from time to time.)

To an N_2-sparged solution of **S30** (2 mmol, 1.0 equiv), alkenylboronic acid pinacol ester (2.2 mmol, 1.1 equiv) and K_2CO_3(3.3 mmol, 3.0 equiv) in Toluene (7 mL) and CH_3OH (1 mL) was added $Pd(PPh_3)_2Cl_2$ (0.1 mmol, 5 mol%). The mixture was stirred at 100 °C for 12 h. After the reaction completed (monitored by GC-MS), it was diluted with water and extracted with EtOAc. The combined organics were washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting residue was flash chromatographed (PE: EA = 25:1) on silica gel to afford the product **S31**.

Under N_2 atmosphere, the solution of n-BuLi (1.65 mmol, 1.1 equiv) in hexane (1.6 mol/L) was added dropwise into the solution of **S28** (1.8 mmol, 1.2 equiv) in anhydrous THF at -78℃. After the 30 min, aldehyde **S31** (1.5 mmol, 1.0 equiv) dissolved in anhydrous THF was added and the temperature was allowed to raise to room temperature. After the complete consumption of **S31** (determined by TLC, about 1 h), the reaction was quenched by saturated NH_4Cl (aq), and extracted with EtOAc. The organic phase was washed with brine and dried with anhydrous Na_2SO_4, the solvent was removed by rotary evaporator. The resulting residue was flash chromatography (PE: EA = 10:1) on silica gel to afford the product **S32**.

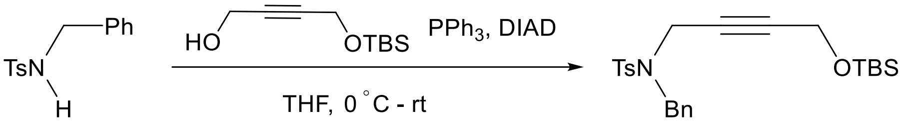
To the solution of **S32** (0.9 mmol, 1.0 equiv) in 10 mL DCM, activated MnO_2 (9 mmol, 10 equiv) was added and the mixture was stirred at room temperature for about 3 h. After the complete consumption of **S32** determined by TLC, the reaction mixture was filtered through silica gel and the filtrate was concentrated by rotary evaporator. The resulting residue was flash chromatographed (PE: EA = 20:1) on silica gel to afford the product **3v**.

(E)-1-((tert-butyldimethylsilyl)oxy)-7-methyl-6-phenylocta-5,7-dien-2-yn-4-one (3v)



Organic liquid, purified by chromatography (PE/EA = 20/1, Rf = 0.6); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.30 (td, *J* = 4.6, 2.3 Hz, 3H), 7.12 (dd, *J* = 7.4, 2.0 Hz, 2H), 6.30 (s, 1H), 5.40 (dd, *J* = 2.2, 1.2 Hz, 1H), 4.91 (d, *J* = 1.5 Hz, 1H), 3.94 (s, 2H), 2.01 (d, *J* = 1.3 Hz, 3H), 0.81 (s, 9H), 0.00 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 177.8, 157.2, 144.1, 137.3, 129.8, 128.2, 127.7, 126.8, 125.6, 92.7, 84.0, 51.3, 25.7, 20.5, 18.2, -5.2.

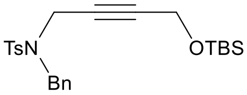
Procedure for formation of 6:



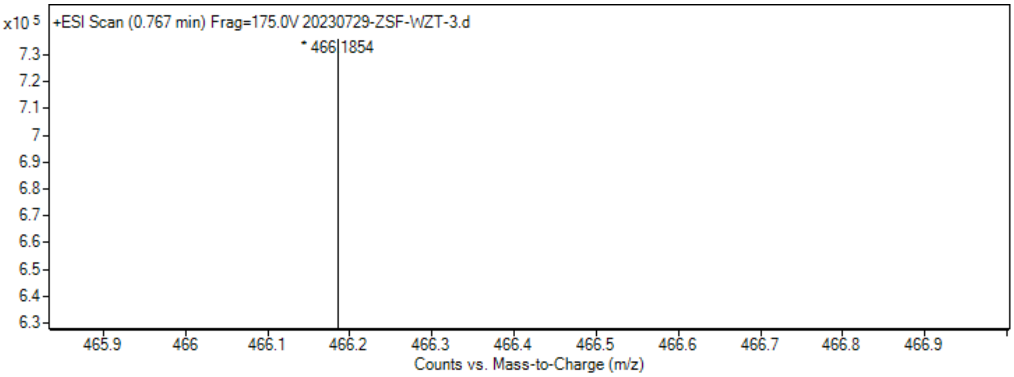
S6-1 **6**

To a flame dried flask was added PPh_3 (1.3 eq) in dry THF, 4-((tert-butyldimethylsilyl)oxy)but-2-yn-1-ol (1.0 eq) and **S6-1** (1.05 eq) under nitrogen, then the reaction mixture was transferred to 0 °C, DIAD (1.3 eq) was added dropwise and the mixture was moved to room temperature, stirred for 4 hours. The mixture was evaporated under reduced pressure and purified by column chromatography (PE:EA = 10:1) to the compound **6** in 94% yield as the yellow oil.

N-benzyl-N-(4-((tert-butyldimethylsilyl)oxy)but-2-yn-1-yl)-4-methylbenzenesulfonamide(6)



Yellow oil, 94%, purified by chromatography (PE/EA = 10/1, R_f = 0.7); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 1.9 Hz, 0H), 7.86 (d, *J* = 1.8 Hz, 0H), 4.41 (s, 0H), 4.10 (t, *J* = 1.9 Hz, 0H), 4.04 (t, *J* = 2.0 Hz, 0H), 2.50 (s, 0H), 0.96 (s, 2H), 0.12 (s, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 143.5, 136.2, 135.1, 129.5, 128.8, 128.7, 128.1, 127.9, 84.7, 77.1, 51.4, 49.9, 36.0, 25.8, 21.6, 18.2, -5.2. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{24}H_{33}NO_3SSiNa^+$: 446.1848, found 466.1854.



4. General procedure for Rh-catalyzed reactions

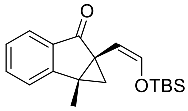
General procedure for 5-*exo*-cycloisomerization of 1,6-enynes

To a dichloromethane solution of **1** or **3** (0.1 mmol, 1.0 mL) in Schlenk tube with a magnetic bar was added $Rh_2(OPiv)_4$ (0.002 mmol, 2 mol%, 1.3 mg) at 30 °C under N_2. The sealed tube was then stirred at 30 °C under nitrogen atmosphere for 48 h. The mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to afford the desired product **2** or **4**.

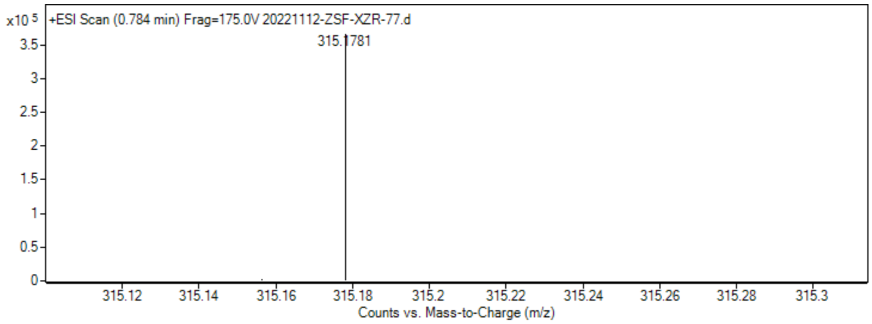
General procedure for asymmetric 5-*exo*-cycloisomerization of 1,6-enynes

To a dichloromethane solution of **1** or **3** (0.05 mmol, 0.5 mL) in Schlenk tube with a magnetic bar was added Rh_2(*S*-TCPTTL)$_4$ (0.001 mmol, 2 mol%, 2 mg), the catalyst was dissolved in dichloromethane) at 30 °C under N_2. The sealed tube was then stirred at 30 °C under nitrogen atmosphere for 48 h. The mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to afford the desired product **2** or **4**.

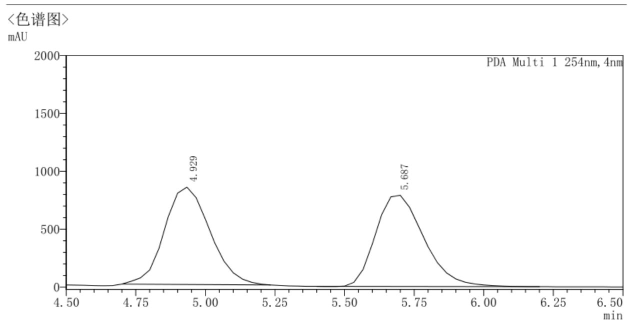
(1aR,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-1a-methyl-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (2d)



Yellow liquid, 13,2 mg, 84%, 93% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.4); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.24 (dd, *J* = 14.7, 7.3 Hz, 1H), 6.56 (d, *J* = 5.4 Hz, 1H), 4.62 (d, *J* = 5.5 Hz, 1H), 1.73 (d, *J* = 3.9 Hz, 1H), 1.67 (d, *J* = 4.0 Hz, 1H), 1.57 (s, 3H), 0.70 (s, 9H), 0.08 (s, 3H), 0.05 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 203.0, 157.4, 144.2, 133.4, 126.5, 124.5, 122.2, 101.0, 44.2, 40.4, 34.3, 25.2, 17.7, 13.1, -5.4, -5.5. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{19}H_{27}O_2Si^+$: 315.1775, found 315.1781.



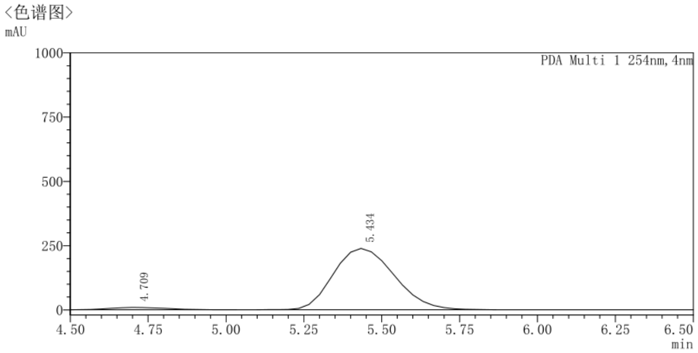
Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 1.0 mL/min, 254 nm, RT_1 = 4.7 min, RT_2 = 5.5 min. **$[\alpha]_D^{25}$** = +28.1 (c 0.5, CH_2Cl_2).



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.929	9552121	840476		51.604	50.057
2	5.687	9530300	788241		48.396	49.943
总计		19082421	1628717		100.000	100.000

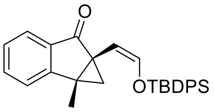


〈峰表〉

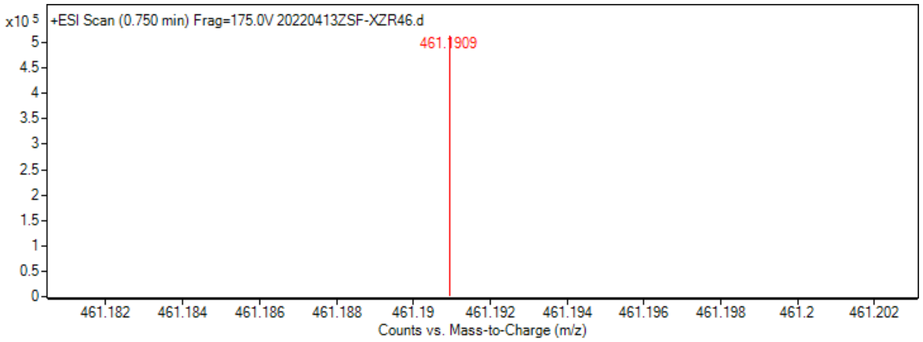
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.709	116472	9160		3.699	3.459
2	5.434	3250640	238503		96.301	96.541
总计		3367111	247664		100.000	100.000

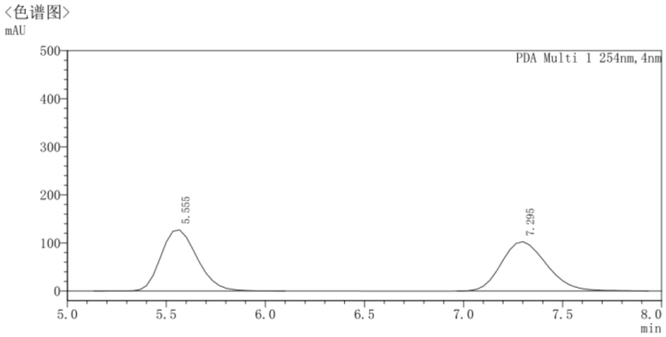
(1aR,6aS)-6a-((Z)-2-((tert-butyldiphenylsilyl)oxy)vinyl)-1a-methyl-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (2e)



Yellow liquid, 7.0 mg, 32%, 74% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.4); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.66 (dd, *J* = 15.4, 7.3 Hz, 3H), 7.56 (d, *J* = 7.3 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.35 (m, 5H), 7.34 – 7.24 (m, 3H), 6.52 (dd, *J* = 5.5, 1.5 Hz, 1H), 4.65 (d, *J* = 5.5 Hz, 1H), 1.83 (d, *J* = 4.0 Hz, 1H), 1.66 (s, 3H), 1.62 (d, *J* = 4.6 Hz, 1H), 0.88 – 0.73 (m, 9H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 202.7, 157.3, 145.0, 135.5, 135.3, 133.5, 132.5, 132.1, 130.0, 129.9, 127.9, 127.8, 126.7, 124.7, 122.4, 101.5, 44.4, 40.3, 34.4, 26.1, 18.9, 13.4. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{29}H_{30}O_2SiNa^+$: 461.1907, found 461.1909.



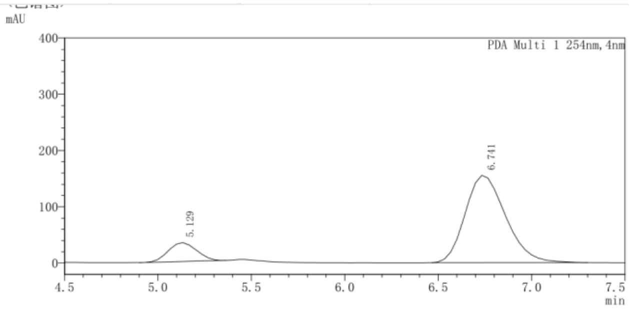
Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 1.0 mL/min, 254 nm, RT$_1$ = 5.1 min, RT$_2$ = 6.7 min. **[α]$_D$^{25}** = +32.1 (c 0.5, CH_2Cl_2)



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	5.555	1613470	127035		55.326	49.875
2	7.295	1621564	102575		44.674	50.125
总计		3235034	229610		100.000	100.000

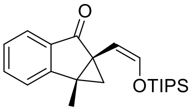


<峰表>

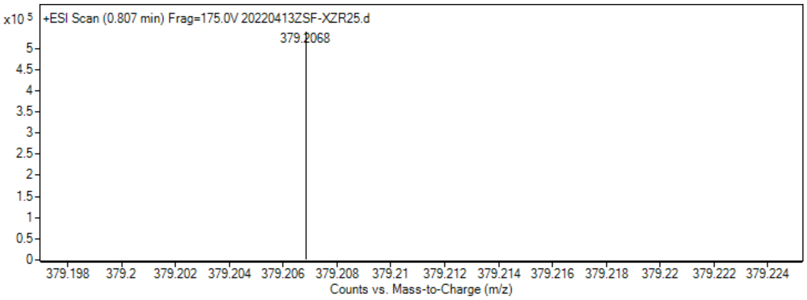
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	5.129	356294	33435		17.725	13.240
2	6.741	2334693	155200		82.275	86.760
总计		2690987	188635		100.000	100.000

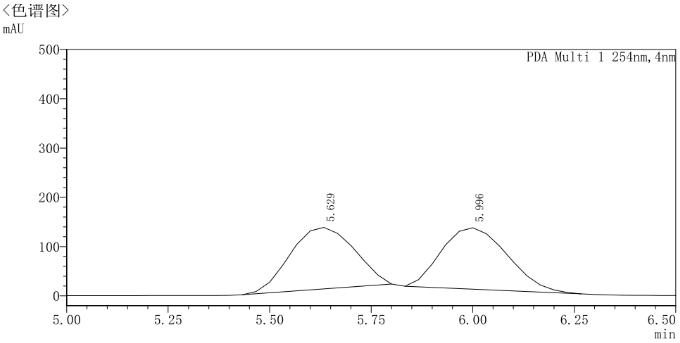
(1aR,6aS)-1a-methyl-6a-((Z)-2-((triisopropylsilyl)oxy)vinyl)-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (2f)



Yellow liquid, 9.3 mg, 52%, 83% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.4); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.62 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.50 – 7.35 (m, 2H), 7.29 – 7.17 (m, 1H), 6.65 (d, *J* = 5.6 Hz, 1H), 4.57 (d, *J* = 5.6 Hz, 1H), 1.73 (d, *J* = 4.0 Hz, 1H), 1.64 (d, *J* = 4.1 Hz, 1H), 1.59 (s, 3H), 1.09 – 1.01 (m, 3H), 0.94 (dd, *J* = 7.4, 2.5 Hz, 18H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 202.8, 157.4, 144.9, 133.5, 133.3, 126.5, 124.5, 122.2, 100.2, 44.2, 40.3, 34.3, 17.5, 13.2, 11.7. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{22}H_{32}O_2SiNa^+$: 379.2064, found 379.2068.

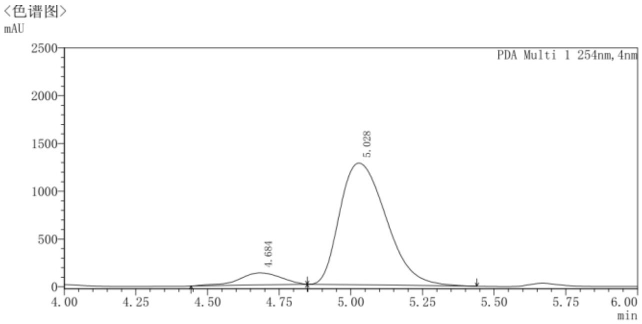


Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 1.0 mL/min, 254 nm, RT_1 = 4.6 min, RT_2 = 5.0 min. **$[\alpha]_D^{25}$** = -15.4 (c 0.5, CH_2Cl_2)



〈峰表〉
PDA Ch1 254nm

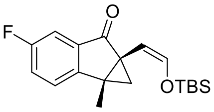
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	5.629	1393381	125007		50.072	49.931
2	5.996	1397213	124647		49.928	50.069
总计		2790594	249653		100.000	100.000



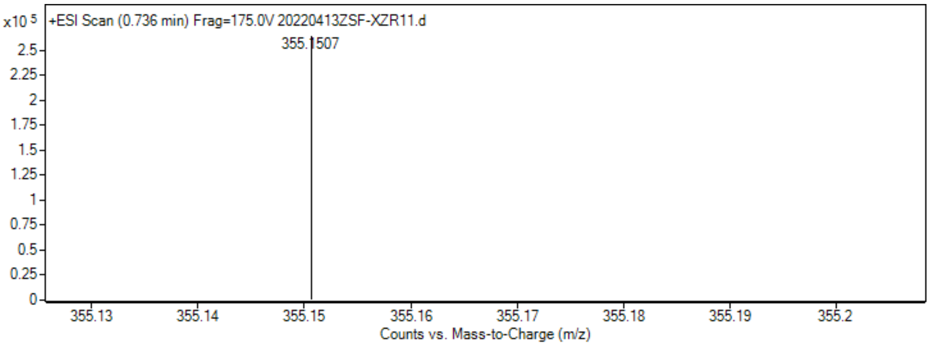
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.684	1271200	125491		8.962	8.141
2	5.028	14344112	1274700		91.038	91.859
总计		15615312	1400191		100.000	100.000

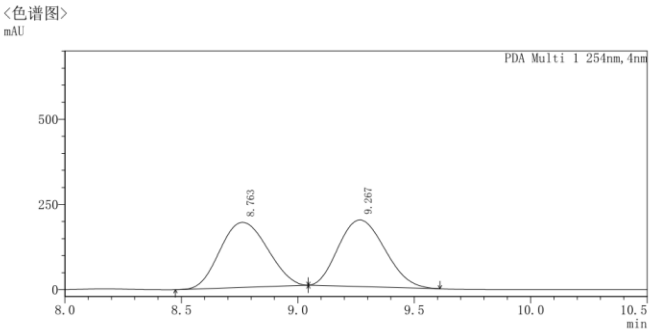
(1aR,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-4-fluoro-1a-methyl-1a,6a-dihydrocyclopropa[a]inden-6 (1H)-one (2g)



Yellow solid, M.P: 64-67°C, 16.2 mg, 98%, 94% ee, purified by chromatography (PE/EA = 15/1, Rf = 0.4); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.35 (dd, *J* = 8.3, 4.4 Hz, 1H), 7.28 (dd, *J* = 9.9, 2.2 Hz, 1H), 7.16 (td, *J* = 8.6, 2.6 Hz, 1H), 6.56 (d, *J* = 5.6 Hz, 1H), 4.61 (d, *J* = 5.6 Hz, 1H), 1.73 (d, *J* = 4.1 Hz, 1H), 1.62 (d, *J* = 4.0 Hz, 1H), 1.55 (s, 3H), 0.71 (s, 9H), 0.08 (s, 3H), 0.05 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 201.7, 161.9 (d, *J* = 246.1 Hz), 152.8 (d, *J* = 2.3 Hz), 144.4, 135.4 (d, *J* = 7.0 Hz), 123.5 (d, *J* = 7.9 Hz), 120.3 (d, *J* = 23.4 Hz), 110.9 (d, *J* = 22.5 Hz), 100.8, 44.3, 40.9, 33.9, 25.2, 17.7, 13.1, -5.4, -5.5. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -115.74. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{19}H_{25}FO_2SiNa^+$: 355.1500, found 355.1507.

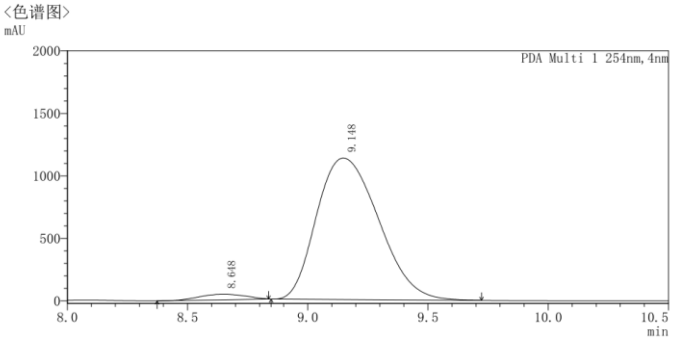


Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 0.5 mL/min, 254 nm, RT$_1$ = 8.6 min, RT$_2$ = 9.1min. **[α]$_D$^{25}** = -7.3 (c 0.5, CH$_2$Cl$_2$).



〈峰表〉
PDA Ch1 254nm

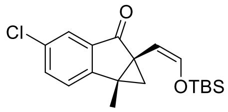
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	8.763	2708439	191010		49.420	49.972
2	9.267	2711513	195496		50.580	50.028
总计		5419952	386505		100.000	100.000



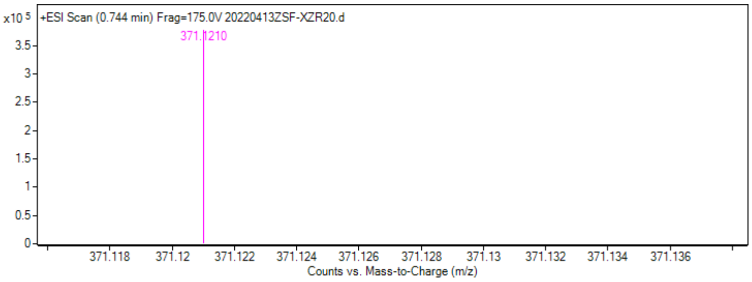
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	8.648	585149	44008		3.743	2.801
2	9.148	20303663	1131764		96.257	97.199
总计		20888812	1175772		100.000	100.000

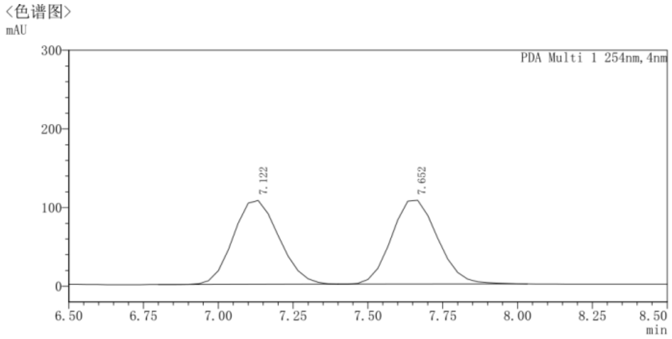
(1aR,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-4-chloro-1a-methyl-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (2h)

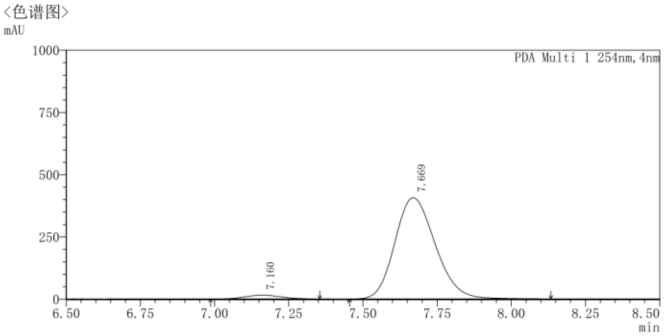


Yellow solid, M.P: 74-76 °C, 12.5 mg, 72%, 94% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.4); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 2.1 Hz, 1H), 7.42 (dd, *J* = 8.0, 2.1 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 5.5 Hz, 1H), 4.60 (d, *J* = 5.6 Hz, 1H), 1.72 (d, *J* = 4.2 Hz, 1H), 1.65 (d, *J* = 4.2 Hz, 1H), 1.55 (s, 3H), 0.71 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 201.5, 155.5, 144.5, 135.1, 133.2, 132.6, 124.5, 123.5, 100.6, 44.0, 40.9, 34.1, 25.2, 17.7, 13.0, -5.4, -5.5. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{19}H_{25}ClO_2SiNa^+$: 371.1204, found 371.1210.



Resolution of enantiomers: Phenomenex INC column, 2% IPA-Hexanes, 0.8 mL/min, 254 nm, RT$_1$ = 7.1 min, RT$_2$ = 7.6 min. **[α]$_D$^{25}** = +65.1 (c 0.5, CH$_2$Cl$_2$).





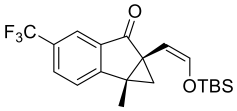
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	7.122	1141937	106786		50.042	49.892
2	7.652	1146877	106606		49.958	50.108
总计		2288814	213392		100.000	100.000

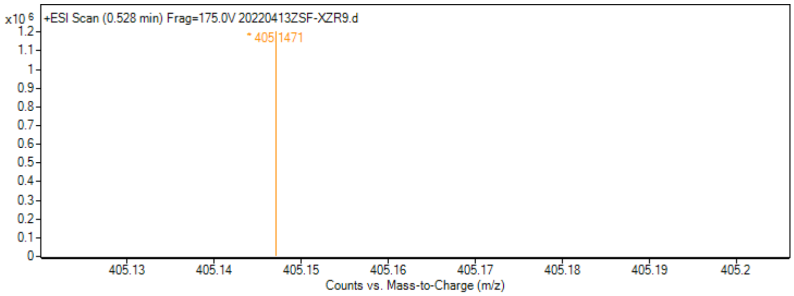
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	7.160	123455	14979		3.552	3.112
2	7.669	3843876	406690		96.448	96.888
总计		3967331	421669		100.000	100.000

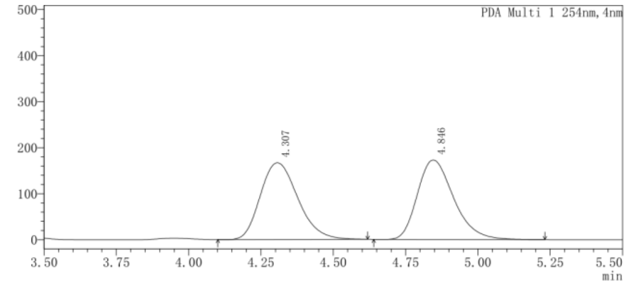
(1aR,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-1a-methyl-4-(trifluoromethyl)-1a,6a-dihydrocyclopropa [a]inden-6(1H)-one (2i)

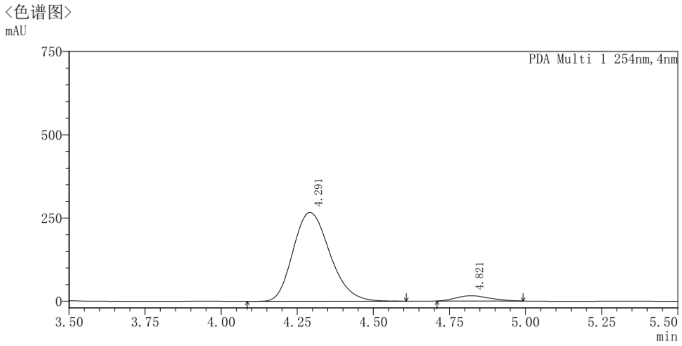


Yellow solid, M.P: 63-64°C, 11.8 mg, 62%, 90% ee, purified by chromatography (PE/EA = 10/1, Rf = 0.4); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 1.8 Hz, 1H), 7.72 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 6.58 (d, *J* = 5.5 Hz, 1H), 4.63 (d, *J* = 5.5 Hz, 1H), 1.78 (d, *J* = 4.3 Hz, 1H), 1.69 (d, *J* = 4.3 Hz, 1H), 1.59 (s, 3H), 0.68 (s, 9H), 0.08 (s, 3H), 0.05 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 201.30, 160.59, 144.78, 133.97, 130.10 (q, *J* = 3.7 Hz), 129.30 (q, *J* = 32.7 Hz), 122.83 (q, *J* = 272.5 Hz), 122.82, 121.70 (q, *J* = 3.8 Hz), 100.3, 43.8, 41.3, 34.4, 25.1, 17.6, 12.9, -5.4, -5.5. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -62.37. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{20}H_{25}F_3O_2SiNa^+$: 405.1468, found 405.1471.



Resolution of enantiomers: Phenomenex INA column, 2% IPA-Hexanes, 1.0 mL/min, 254 nm, RT$_1$ = 4.3 min, RT$_2$ = 4.8 min. **[α]$_D^{25}$** = + 64.0 (c 0.5, CH_2Cl_2).





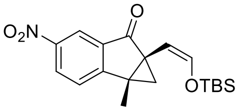
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.307	1505376	166547		49.119	49.959
2	4.846	1507853	172518		50.881	50.041
总计		3013229	339065		100.000	100.000

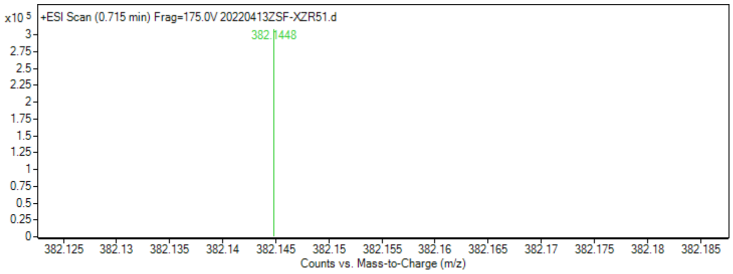
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.291	2250569	267081		94.400	94.818
2	4.821	122995	15844		5.600	5.182
总计		2373564	282925		100.000	100.000

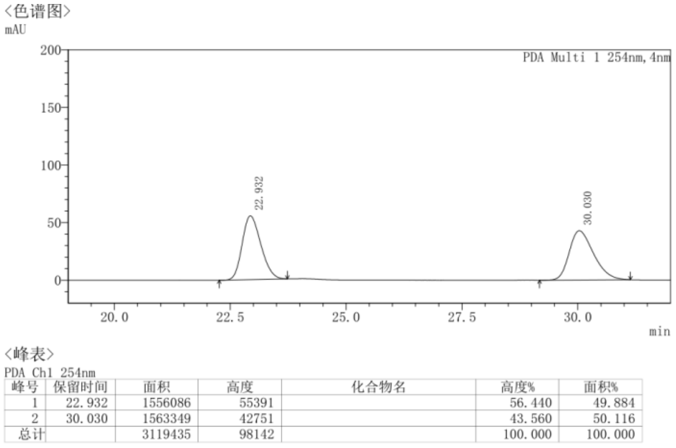
(1aR,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-1a-methyl-4-nitro-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (2j)



Yellow solid, M.P: 87-88°C, 11.5 mg, 64%, 96% ee, purified by chromatography (PE/EA = 5/1, Rf = 0.4); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.45 (d, *J* = 2.2 Hz, 1H), 8.36 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 6.60 (d, *J* = 5.5 Hz, 1H), 4.63 (d, *J* = 5.5 Hz, 1H), 1.81 (d, *J* = 4.3 Hz, 1H), 1.73 (d, *J* = 4.4 Hz, 1H), 1.61 (s, 3H), 0.69 (d, *J* = 1.9 Hz, 9H), 0.08 (s, 3H), 0.06 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 200.1, 163.4, 147.2, 145.2, 134.6, 128.3, 123.1, 119.9, 99.8, 43.7, 42.3, 34.8, 25.1, 17.7, 12.8, -5.4, -5.5. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{19}H_{25}NO_4SiNa^+$: 382.1445, found 382.1448.



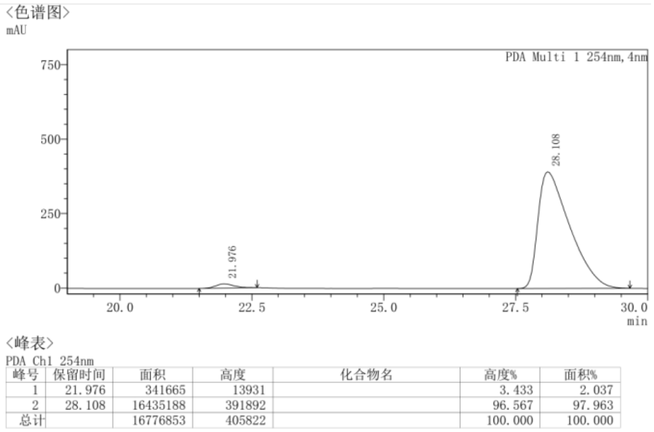
Resolution of enantiomers: Phenomenex INC column, 2% IPA-Hexanes, 0.8 mL/min, 254 nm, RT$_1$ = 22.0 min, RT$_2$ = 28.1 min. **[α]$_D^{25}$** = + 125.2 (c 0.5, CH_2Cl_2).



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	22.932	1556086	55391		56.440	49.884
2	30.030	1563349	42751		43.560	50.116
总计		3119435	98142		100.000	100.000

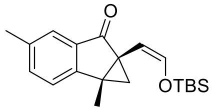


〈峰表〉

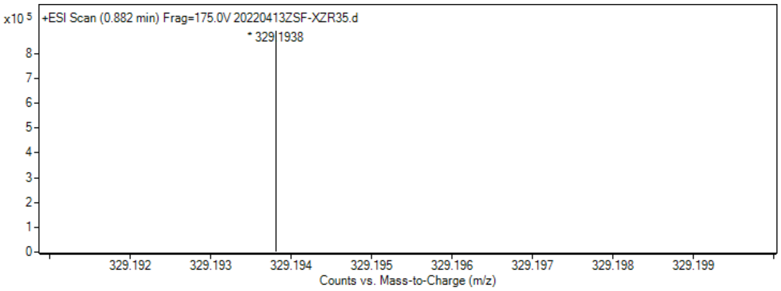
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	21.976	341665	13931		3.433	2.037
2	28.108	16435188	391892		96.567	97.963
总计		16776853	405822		100.000	100.000

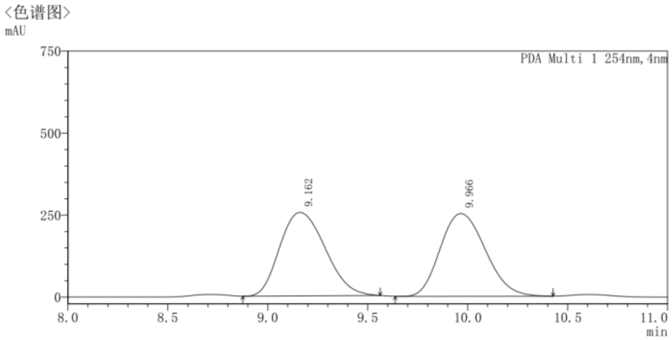
(1aR,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-1a,4-dimethyl-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one(2k)



Yellow liquid, 14.0 mg, 85%, 91% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.4); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 0.9 Hz, 2H), 6.55 (d, *J* = 5.6 Hz, 1H), 4.61 (d, *J* = 5.7 Hz, 1H), 2.34 (s, 3H), 1.69 (q, *J* = 4.0 Hz, 2H), 1.55 (s, 3H), 0.72 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 203.3, 154.7, 144.0, 136.3, 134.2, 133.5, 124.7, 121.9, 101.1, 44.3, 40.5, 34.1, 25.2, 21.0, 17.7, 13.2, -5.4, -5.5. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{20}H_{29}O_2Si^+$: 329.1932, found 329.1938.

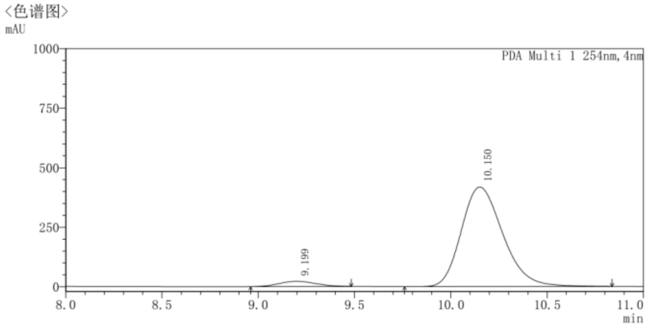


Resolution of enantiomers: DAICEL Chiralcel® ODHcolumn, 2% IPA-Hexanes, 0.5 mL/min, 254 nm, RT_1 = 9.1 min, RT_2 = 10.1min. **$[\alpha]_D^{25}$** = + 48.8 (c 0.5, CH_2Cl_2).



〈峰表〉
PDA Ch1 254nm

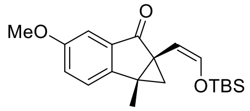
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	9.162	4035256	254550		50.228	50.467
2	9.966	3960616	252235		49.772	49.533
总计		7995873	506785		100.000	100.000



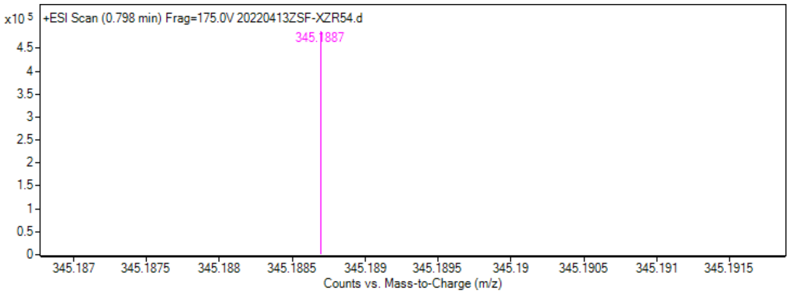
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	9.199	297179	22306		5.063	4.511
2	10.150	6290638	418258		94.937	95.489
总计		6587818	440564		100.000	100.000

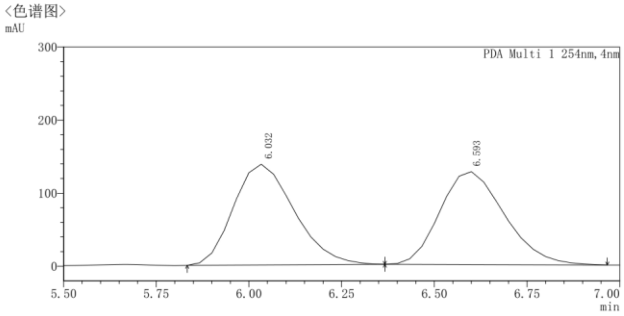
(1aR,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-4-methoxy-1a-methyl-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (2l)



Yellow liquid, 14,1 mg, 82%, 80% ee, purified by chromatography (PE/EA = 15/1, Rf = 0.4); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.3 Hz, 1H), 7.13 (d, *J* = 2.5 Hz, 1H), 7.03 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.55 (d, *J* = 5.6 Hz, 1H), 4.61 (d, *J* = 5.6 Hz, 1H), 3.79 (s, 3H), 1.72 (d, *J* = 4.0 Hz, 1H), 1.65 (d, *J* = 3.9 Hz, 1H), 1.54 (s, 3H), 0.72 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 203.1, 158.8, 150.1, 144.1, 134.7, 123.0, 121.4, 107.2, 101.2, 55.9, 44.8, 40.6, 33.8, 25.2, 17.7, 13.3, -5.4, -5.5. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{20}H_{29}O_3Si^+$: 345.1881, found 345.1887.

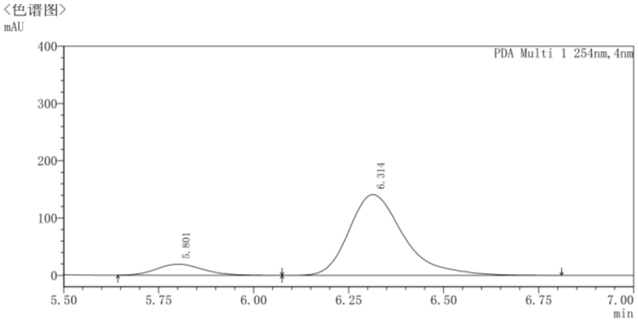


Resolution of enantiomers: DAICEL Chiralcel® ODHcolumn, 2% IPA-Hexanes, 1.0 mL/min, 254 nm, RT_1 = 5.8 min, RT_2 = 6.3 min. **$[\alpha]_D^{25}$** = +23.6 (c 0.5, CH_2Cl_2).



〈峰表〉
PDA Ch1 254nm

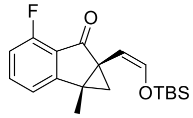
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	6.032	1570662	137988		52.041	50.478
2	6.593	1540935	127162		47.959	49.522
总计		3111597	265150		100.000	100.000



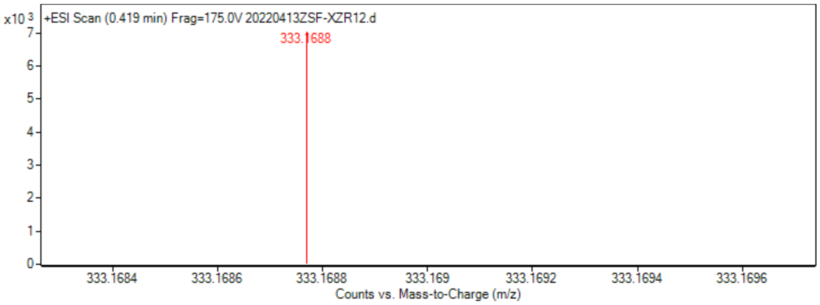
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	5.801	162764	19261		12.014	10.372
2	6.314	1406541	141057		87.986	89.628
总计		1569305	160318		100.000	100.000

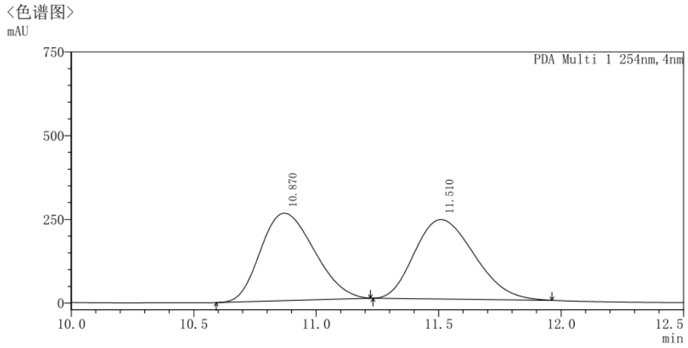
(1aR,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-5-fluoro-1a-methyl-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (2m)



Yellow liquid, 9.1 mg, 55%, 90% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.4); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.42 (dd, *J* = 7.9, 5.0 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 6.86 (t, *J* = 8.8 Hz, 1H), 6.56 (d, *J* = 5.6 Hz, 1H), 4.60 (d, *J* = 5.6 Hz, 1H), 1.74 (d, *J* = 4.1 Hz, 1H), 1.64 (d, *J* = 4.1 Hz, 1H), 1.55 (s, 3H), 0.72 (s, 9H), 0.09 (s, 3H), 0.06 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 199.2, 159.6 (d, *J* = 2.8 Hz), 159.4 (d, *J* = 262.6 Hz), 135.4 (d, *J* = 8.6 Hz), 120.3 (d, *J* = 12.4 Hz), 118.2 (d, *J* = 3.6 Hz), 114.1 (d, *J* = 19.8 Hz), 100.7, 43.2, 40.9, 34.1 (d, *J* = 2.0 Hz), 25.2, 17.7, 13.2, -5.4, -5.5. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -114.82. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{19}H_{26}FO_2Si^+$: 333.1681, found 333.1688.



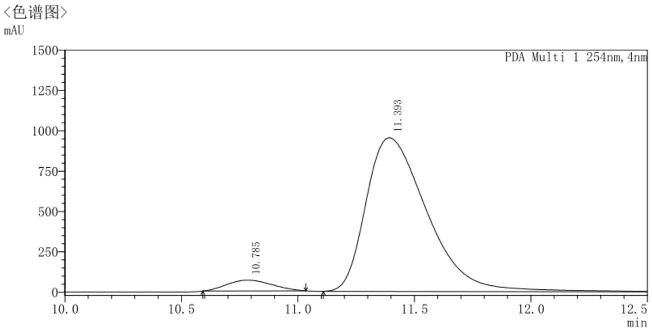
Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 0.5 mL/min, 254 nm, RT$_1$ = 10.8 min, RT$_2$ = 11.4 min. **$[\alpha]_D^{25}$** = + 65.6 (c 0.5, CH_2Cl_2).



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	10.870	3985240	261303		52.408	49.687
2	11.510	4035371	237286		47.592	50.313
总计		8020611	498589		100.000	100.000

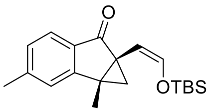


〈峰表〉

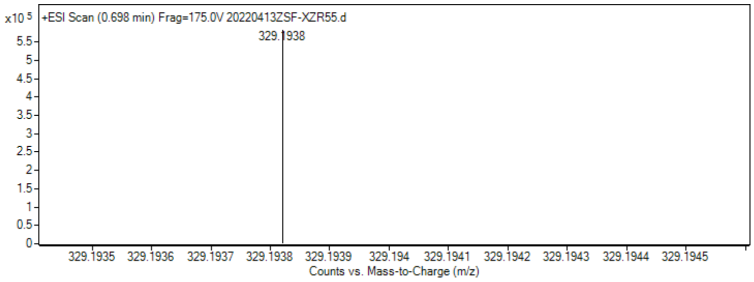
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	10.785	903061	67203		6.595	4.927
2	11.393	17424778	951812		93.405	95.073
总计		18327839	1019015		100.000	100.000

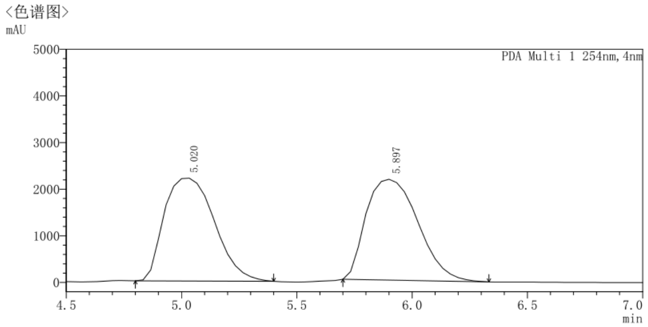
(1aR,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-1a,3-dimethyl-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (2n)



Yellow liquid, 13.3 mg, 81%, 91% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.4); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.7 Hz, 1H), 7.19 (s, 1H), 7.04 (d, *J* = 7.7 Hz, 1H), 6.55 (d, *J* = 5.7 Hz, 1H), 4.61 (d, *J* = 5.7 Hz, 1H), 2.40 (s, 3H), 1.68 (q, *J* = 4.1 Hz, 2H), 1.55 (s, 3H), 0.72 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 202.7, 157.8, 144.3, 144.0, 131.0, 127.5, 124.4, 122.9, 101.1, 44.0, 40.5, 34.0, 25.2, 22.1, 17.7, 13.1, -5.4, -5.5. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{20}H_{29}O_2Si^+$: 329.1932, found 329.1938.



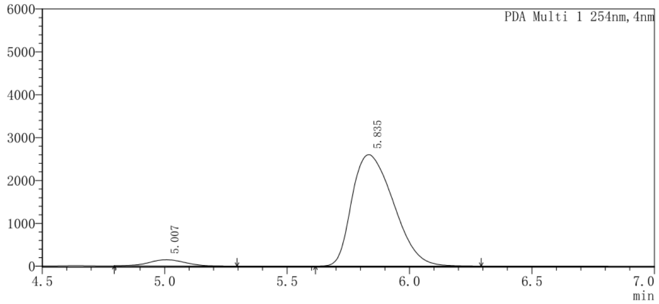
Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 1.0 mL/min, 254 nm, RT_1 = 5.0 min, RT_2 = 5.8 min. **$[\alpha]_D^{25}$** = + 8.7 (c 0.5, CH_2Cl_2).



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	5.020	33546266	2207215		50.511	49.732
2	5.897	33907893	2162571		49.489	50.268
总计		67454159	4369786		100.000	100.000

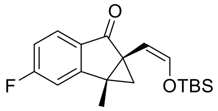


<峰表>

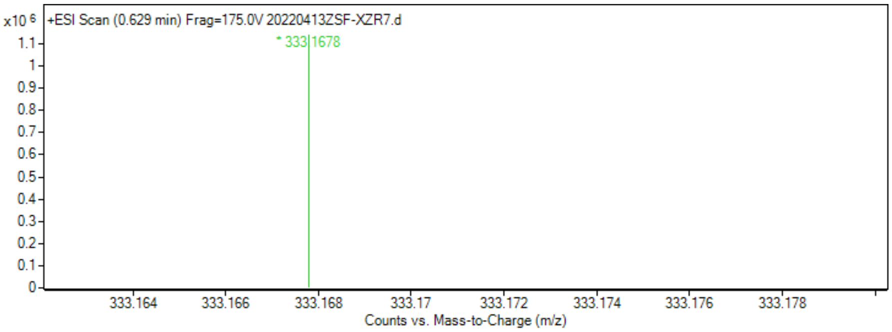
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	5.007	1495691	145331		5.293	4.634
2	5.835	30781254	2600503		94.707	95.366
总计		32276945	2745834		100.000	100.000

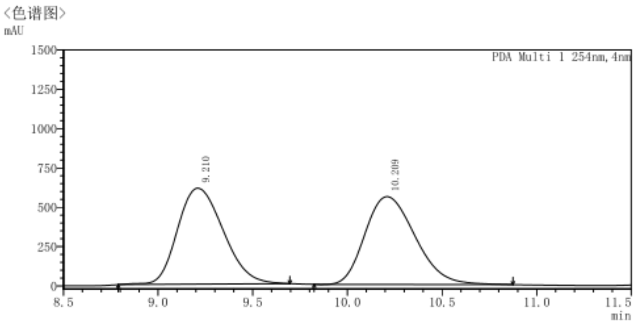
(1aR,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-3-fluoro-1a-methyl-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (2o)



Yellow liquid, 11.3 mg, 68%, 93% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.4); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.61 (dd, *J* = 8.3, 5.3 Hz, 1H), 7.07 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.92 (td, *J* = 8.7, 2.3 Hz, 1H), 6.56 (d, *J* = 5.6 Hz, 1H), 4.61 (d, *J* = 5.6 Hz, 1H), 1.72 (d, *J* = 4.1 Hz, 1H), 1.64 (d, *J* = 4.1 Hz, 1H), 1.54 (s, 3H), 0.71 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 201.1, 166.5 (d, *J* = 254.1 Hz), 160.3 (d, *J* = 9.6 Hz), 144.5, 129.56 (d, *J* = 2.2 Hz), 114.0 (d, *J* = 23.4 Hz), 109.9 (d, *J* = 23.0 Hz), 100.7, 43.7, 40.8, 33.7 (d, *J* = 2.4 Hz), 25.2, 17.7, 13.0, -5.4, -5.5. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -104.74. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{19}H_{26}FO_2Si^+$: 333.1681, found 333.1678.



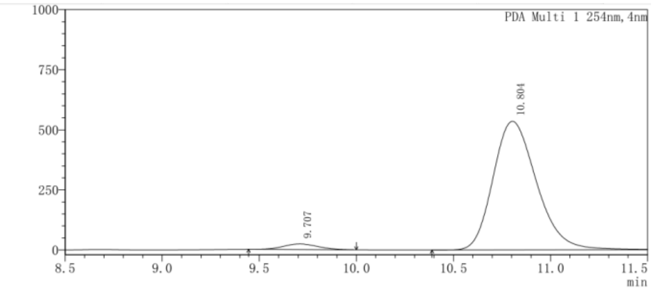
Resolution of enantiomers: DAICEL Chiralcel® ODHcolumn, 2% IPA-Hexanes, 0.5 mL/min, 254 nm, RT_1 = 9.7 min, RT_2 = 10.8 min. **$[\alpha]_D^{25}$** = + 21.1 (c 0.5, CH_2Cl_2).



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	9.210	10265027	609754		52.180	49.880
2	10.209	10314338	558815		47.820	50.120
总计		20579365	1168569		100.000	100.000

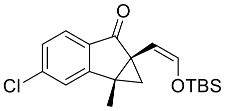


〈峰表〉

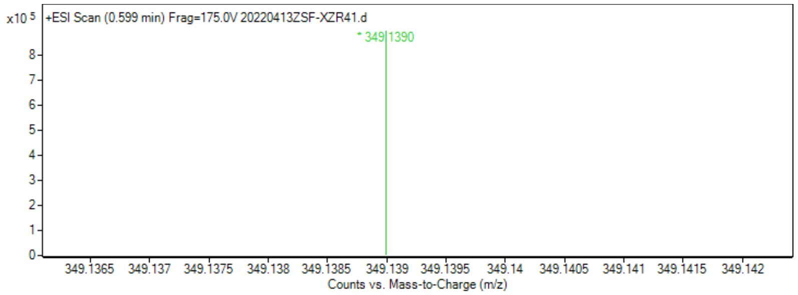
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	9.707	288882	23299		4.172	3.342
2	10.804	8355491	535219		95.828	96.658
总计		8644373	558517		100.000	100.000

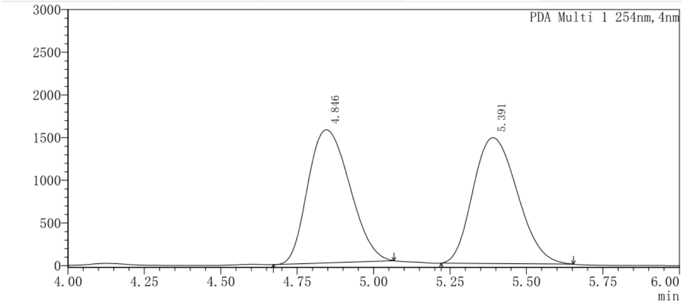
(1aR,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-3-chloro-1a-methyl-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (2p)



Yellow solid, M.P: 84-85°C, 12.5 mg, 72%, 92% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.4); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 8.1 Hz, 1H), 7.38 (d, *J* = 1.8 Hz, 1H), 7.22 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.56 (d, *J* = 5.6 Hz, 1H), 4.60 (d, *J* = 5.6 Hz, 1H), 1.72 (d, *J* = 4.2 Hz, 1H), 1.65 (d, *J* = 4.1 Hz, 1H), 1.55 (s, 3H), 0.71 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 201.4, 158.9, 144.6, 139.8, 131.9, 127.1, 125.7, 122.9, 100.6, 43.6, 40.7, 34.0, 25.2, 17.7, 13.0, -5.4, -5.5. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{19}H_{26}ClO_2Si^+$: 349.1385, found 349.1390.



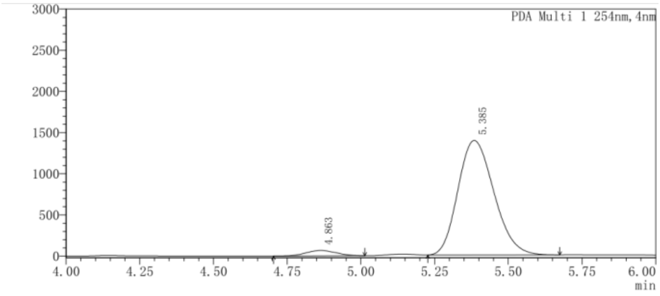
Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 1.0 mL/min, 254 nm, RT_1 = 4.8 min, RT_2 = 5.4 min. **$[\alpha]_D^{25}$** = + 4.1 (c 0.5, CH_2Cl_2).



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.846	14903388	1559363		51.395	49.987
2	5.391	14910856	1474695		48.605	50.013
总计		29814244	3034057		100.000	100.000

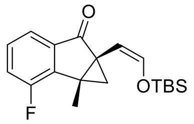


〈峰表〉

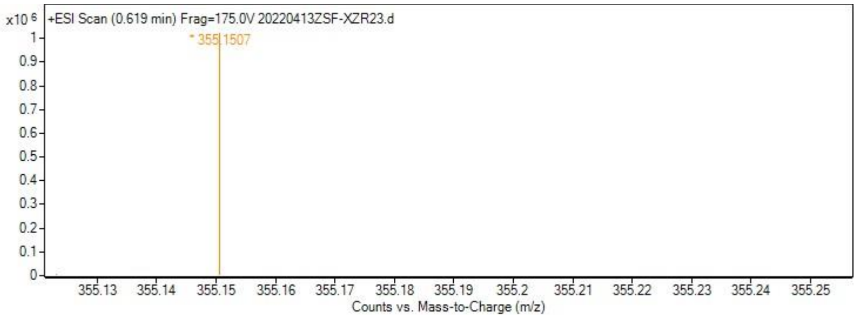
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.863	476820	65808		4.519	3.878
2	5.385	11818770	1390482		95.481	96.122
总计		12295590	1456290		100.000	100.000

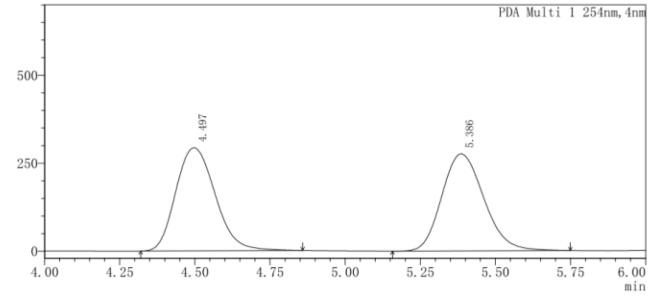
(1aS,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-2-fluoro-1a-methyl-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (2q)



Yellow liquid, 10.3 mg, 62%, 95% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.4); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 7.3 Hz, 1H), 7.21 (dd, *J* = 7.6, 4.4 Hz, 1H), 7.14 (ddd, *J* = 9.3, 8.1, 1.0 Hz, 1H), 6.58 (d, *J* = 5.6 Hz, 1H), 4.59 (d, *J* = 5.6 Hz, 1H), 1.81 (d, *J* = 4.3 Hz, 1H), 1.68 – 1.64 (m, 4H), 0.72 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 201.6, 159.3 (d, *J* = 249.7 Hz), 144.6, 141.9 (d, *J* = 15.7 Hz), 136.9, 128.3, 128.3, 120.7 (d, *J* = 21.0 Hz), 120.3 (d, *J* = 3.6 Hz), 100.6, 44.0, 40.2, 32.8, 32.8, 25.2, 17.7, 13.8, 13.8, -5.4, -5.5. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -121.38. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{19}H_{25}FO_2SiNa^+$: 355.1500, found 355.1508.

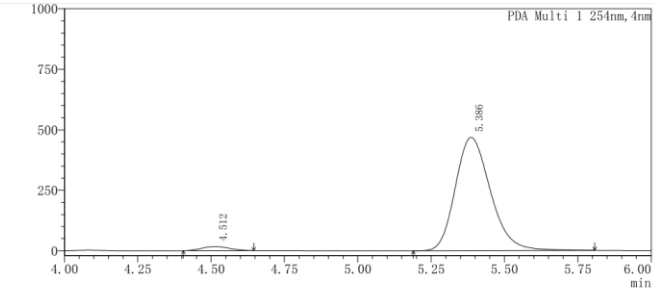


Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 1.0 mL/min, 254 nm, RT_1 = 4.5 min, RT_2 = 5.3 min. **$[\alpha]_D^{25}$** = + 54.8 (c 0.5, CH_2Cl_2).



<峰表>
PDA Ch1 254nm

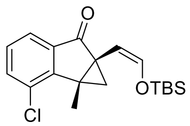
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.497	2676591	293225		51.528	49.913
2	5.386	2685942	275839		48.472	50.087
总计		5362533	569064		100.000	100.000



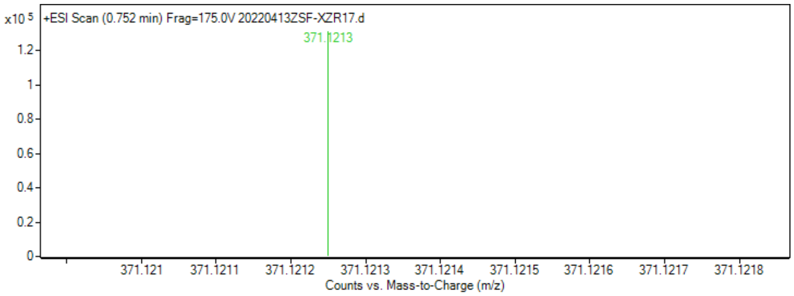
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.512	110782	17001		3.504	2.759
2	5.386	3904712	468193		96.496	97.241
总计		4015495	485194		100.000	100.000

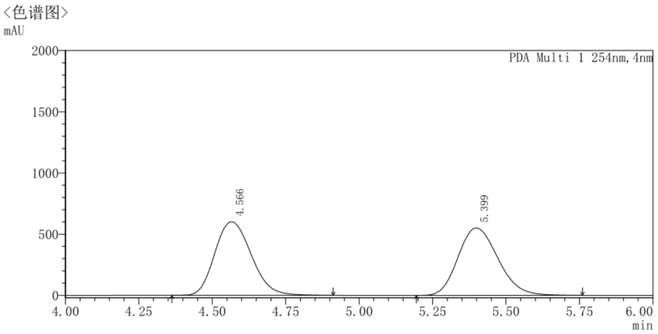
(1aS,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-2-chloro-1a-methyl-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (2r)



Yellow liquid,15.8 mg, 91%, 96% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.4); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.54 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.42 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 1H), 6.58 (d, *J* = 5.6 Hz, 1H), 4.57 (d, *J* = 5.6 Hz, 1H), 1.82 (d, *J* = 4.3 Hz, 1H), 1.73 (s, 3H), 1.71 (d, *J* = 4.4 Hz, 1H), 0.73 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 201.6, 152.7, 144.7, 136.4, 134.7, 130.7, 128.0, 122.9, 100.8, 43.9, 40.5, 35.1, 25.2, 17.7, 13.9, -5.4, -5.5. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{19}H_{25}ClO_2SiNa^+$: 371.1204, found 371.1213.



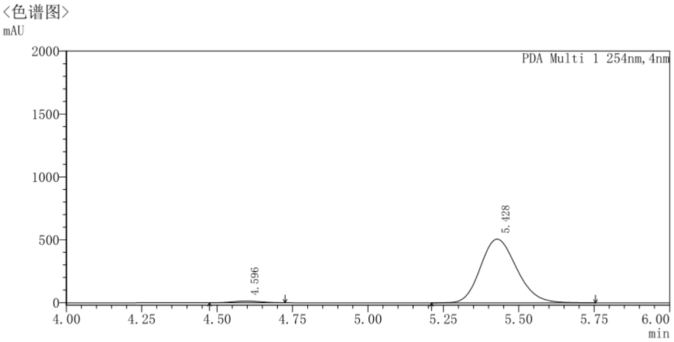
Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 1.0 mL/min, 254 nm, RT_1 = 4.5 min, RT_2 = 5.4min. **[α]$_D$^{25}** = + 9.0 (c 0.5, CH_2Cl_2).



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.566	5191355	601336		52.159	49.791
2	5.399	5234928	551554		47.841	50.209
总计		10426283	1152890		100.000	100.000

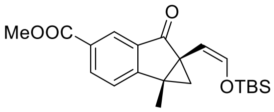


〈峰表〉

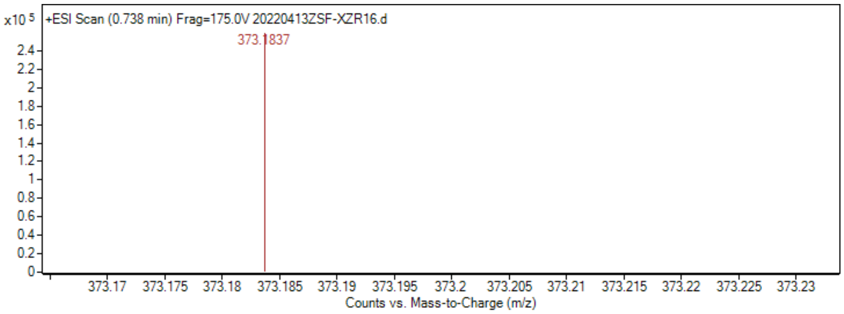
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.596	92715	13936		2.674	2.131
2	5.428	4257094	507166		97.326	97.869
总计		4349809	521101		100.000	100.000

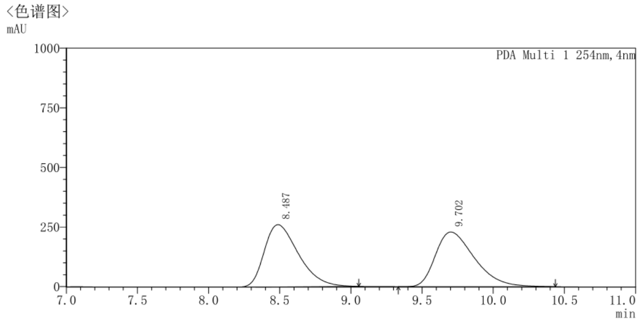
Methyl-(1aR,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-1a-methyl-6-oxo-1,1a,6,6a-tetrahydrocyclopropa[a]indene-4-carboxylate (2s)



Yellow liquid, 8.9 mg, 48%, 88% ee, purified by chromatography (PE/EA = 10/1, Rf = 0.4); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.29 (d, *J* = 1.6 Hz, 1H), 8.17 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 6.58 (d, *J* = 5.6 Hz, 1H), 4.63 (d, *J* = 5.6 Hz, 1H), 3.91 (s, 3H), 1.75 (d, *J* = 4.2 Hz, 1H), 1.69 (d, *J* = 4.2 Hz, 1H), 1.59 (s, 3H), 0.69 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 201.7, 166.4, 161.9, 144.7, 134.7, 133.6, 128.9, 125.9, 122.3, 100.4, 52.2, 43.8, 41.4, 34.56, 25.2, 17.7, 12.9, -5.4, -5.5. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{21}H_{28}O_4SiNa^+$: 373.1830, found 373.1837.

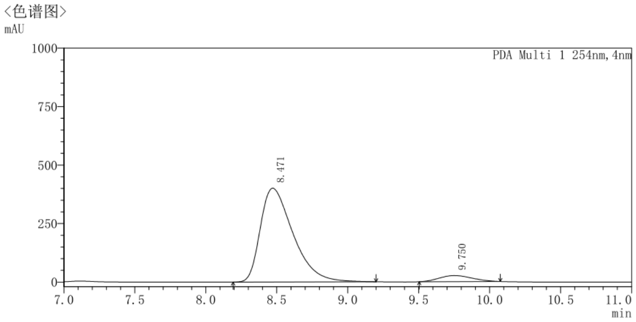


Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 1.0 mL/min, 254 nm, RT_1 = 8.5 min, RT_2 = 9.7 min. **[α]$_D$^{25}** = +120.6 (c 0.5, CH_2Cl_2).



〈峰表〉
PDA Ch1 254nm

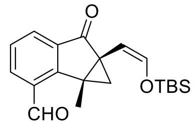
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	8.487	4381210	261423		53.255	49.963
2	9.702	4387711	229469		46.745	50.037
总计		8768921	490892		100.000	100.000



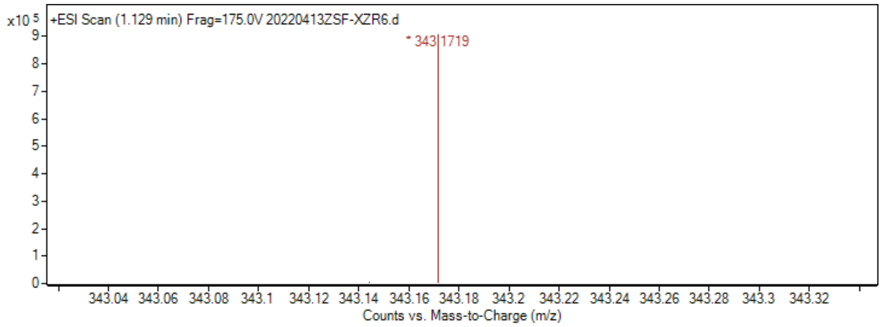
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	8.471	6440512	401145		93.914	93.855
2	9.750	421685	25996		6.086	6.145
总计		6862196	427141		100.000	100.000

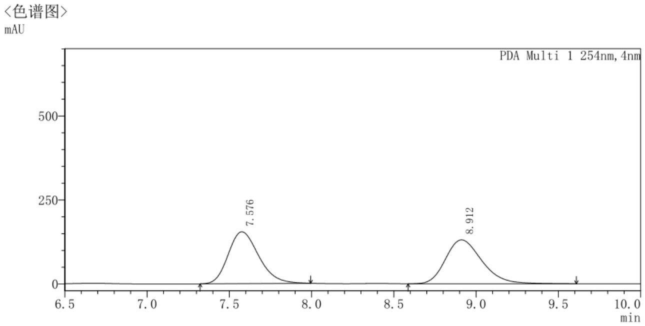
(1aR,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-1a-methyl-6-oxo-1,1a,6,6a-tetrahydrocyclopropa[a]indene-2-carbaldehyde (2t)



Yellow solid, M,P: 51-53 °C, 10.3 mg, 60%, 93% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.4); ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 10.57 (s, 1H), 8.01 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.87 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 6.62 (d, *J* = 5.5 Hz, 1H), 4.61 (d, *J* = 5.6 Hz, 1H), 1.95 (d, *J* = 4.4 Hz, 1H), 1.82 (d, *J* = 4.5 Hz, 1H), 1.74 (s, 3H), 0.70 (s, 9H), 0.09 (s, 3H), 0.06 (s, 3H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 201.3, 190.5, 158.0, 145.0, 135.7, 133.9, 133.1, 129.9, 127.3, 100.7, 43.9, 41.6, 34.9, 25.16, 17.7, 16.1, -5.4, -5.5. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{20}H_{27}O_3Si^+$: 343.1724, found 343.1719.

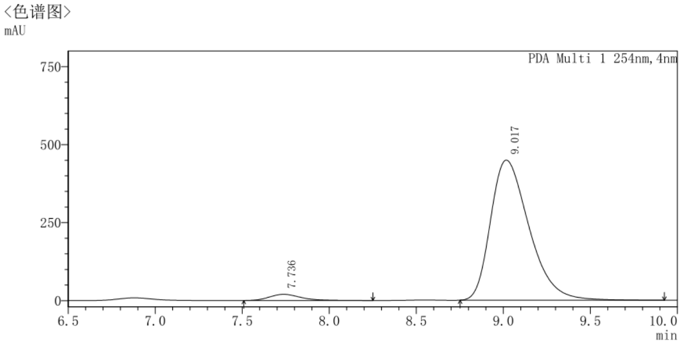


Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 1.0 mL/min, 254 nm, RT_1 = 7.7min, RT_2 = 9.0 min. **[α]$_D$^{25}** = -34.0 (c 0.5, CH_2Cl_2).



〈峰表〉
PDA Ch1 254nm

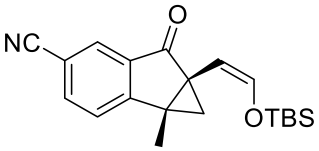
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	7.576	2001976	154356		54.131	49.787
2	8.912	2019123	130795		45.869	50.213
总计		4021099	285151		100.000	100.000



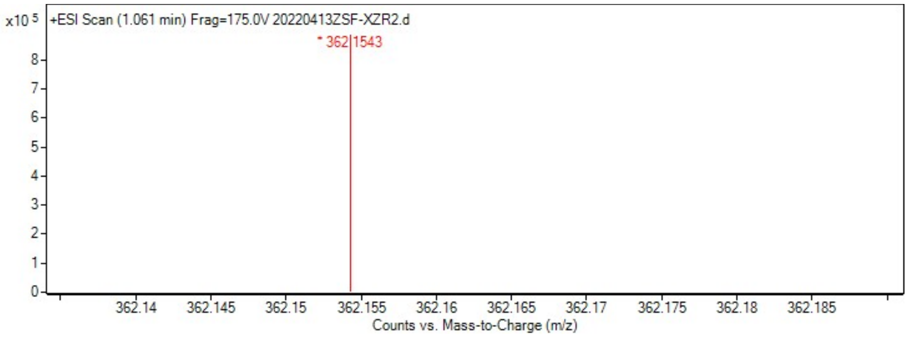
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	7.736	250477	19738		4.212	3.497
2	9.017	6912192	448932		95.788	96.503
总计		7162668	468670		100.000	100.000

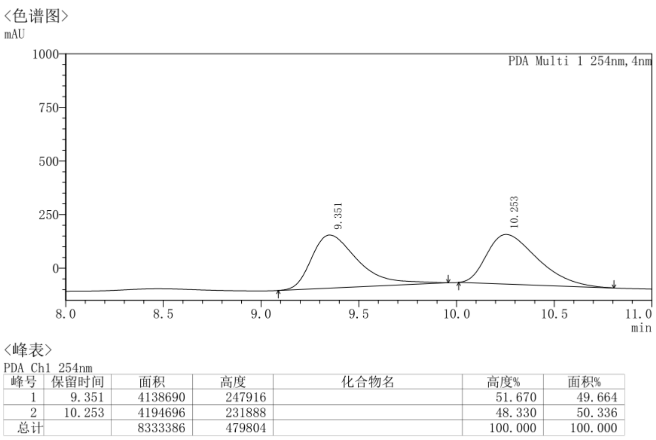
(1aR,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-1a-methyl-6-oxo-1,1a,6,6a-tetrahydrocyclopropa[a]indene-4-carbonitrile (2u)



Yellow liquid, 5.1 mg, 30%, 94% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.5); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.90 (s, 1H), 7.78 – 7.71 (m, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 6.60 (d, *J* = 5.5 Hz, 1H), 4.62 (d, *J* = 5.5 Hz, 1H), 1.78 (d, *J* = 4.4 Hz, 1H), 1.71 (d, *J* = 4.4 Hz, 1H), 1.60 (s, 3H), 0.70 (s, 9H), 0.09 (s, 4H), 0.06 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 200.3, 161.6, 145.1, 136.7, 134.2, 128.3, 123.4, 118.4, 110.6, 99.9, 43.7, 41.5, 34.8, 25.1, 17.6, 12.7, -5.4, -5.5. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{20}H_{25}NO_2SiNa^+$: 362.1547, found 362.1543.



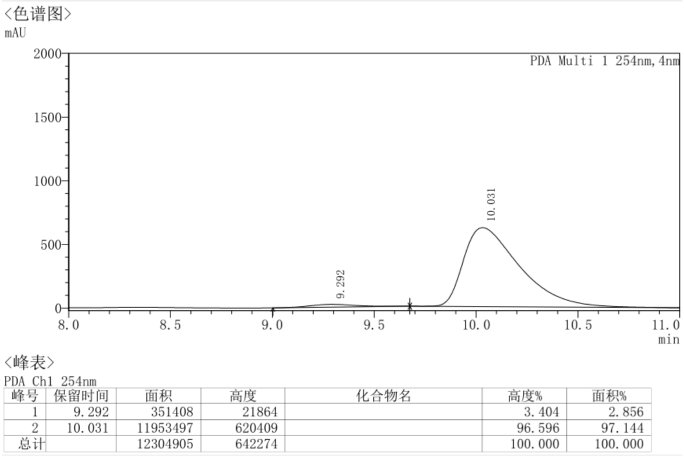
Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 1.0 mL/min, 254 nm, RT_1 = 9.2 min, RT_2 = 10.0 min. **$[\alpha]_D^{25}$** = +62 (c 0.5, CH_2Cl_2).



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	9.351	4138690	247916		51.670	49.664
2	10.253	4194696	231888		48.330	50.336
总计		8333386	479804		100.000	100.000

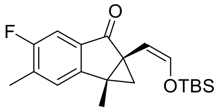


〈峰表〉

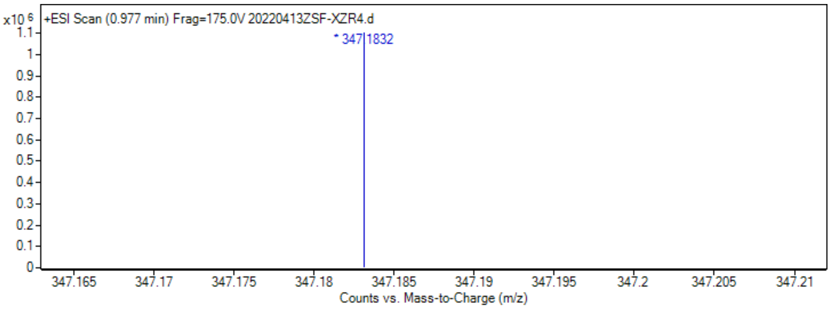
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	9.292	351408	21864		3.404	2.856
2	10.031	11953497	620409		96.596	97.144
总计		12304905	642274		100.000	100.000

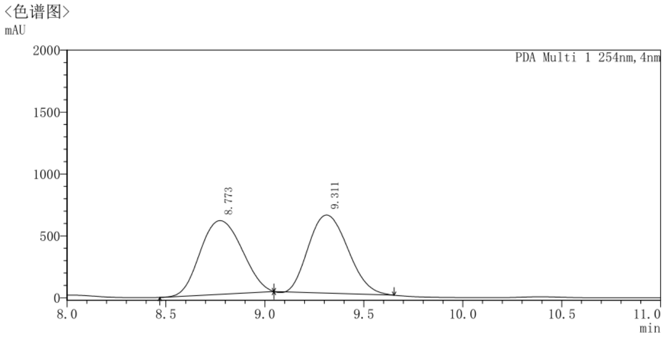
(1aR,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-4-fluoro-1a,3-dimethyl-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (2v)



Yellow solid, M,P = 60-61 °C, 10.4 mg, 60%, 94% ee, purified by chromatography (PE/EA = 5/1, Rf = 0.4); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.21 (dd, *J* = 9.6, 7.4 Hz, 2H), 6.55 (d, *J* = 5.6 Hz, 1H), 4.59 (d, *J* = 5.6 Hz, 1H), 2.32 (d, *J* = 2.3 Hz, 3H), 1.69 (d, *J* = 4.1 Hz, 1H), 1.62 (d, *J* = 4.1 Hz, 1H), 1.54 (s, 3H), 0.72 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 201.8, 160.4 (d, *J* = 245.0 Hz), 152.7, 144.3, 133.0 (d, *J* = 7.1 Hz), 131.1 (d, *J* = 18.9 Hz), 124.9 (d, *J* = 4.7 Hz), 110.4 (d, *J* = 23.4 Hz), 100.9, 44.2, 40.7, 33.7, 25.2, 17.7, 15.5 (d, J = 4.1 Hz), 13.2, -5.4, -5.5. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -119.55. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{20}H_{28}FO_2Si^+$: 347.1837, found 347.1832.



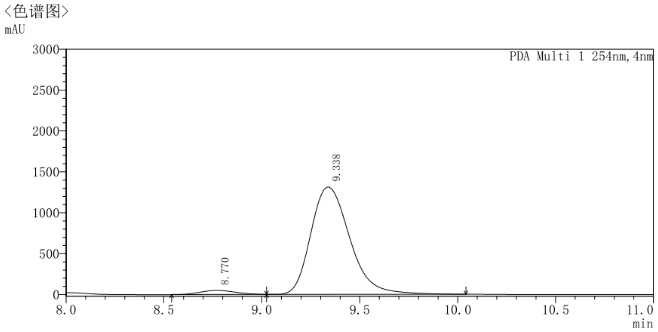
Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 0.5 mL/min, 254 nm, RT$_1$ = 8.7 min, RT$_2$ = 9.3 min. **$[\alpha]_D^{25}$** = - 28.0 (c 0.5, CH_2Cl_2).



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	8.773	8772710	595113		48.548	50.044
2	9.311	8757354	630716		51.452	49.956
总计		17530064	1225829		100.000	100.000

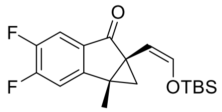


〈峰表〉

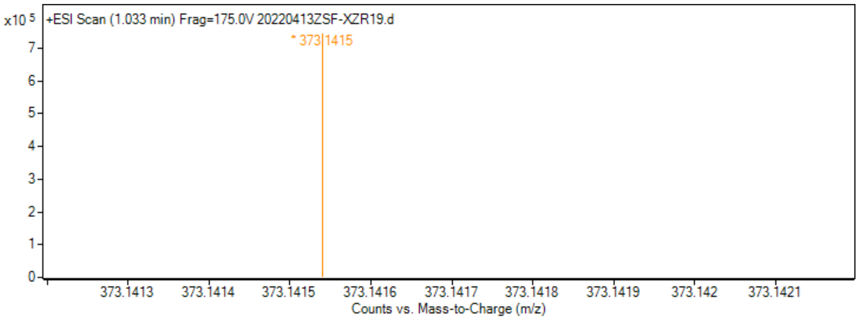
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	8.770	623006	49951		3.668	3.312
2	9.338	18185524	1311753		96.332	96.688
总计		18808530	1361704		100.000	100.000

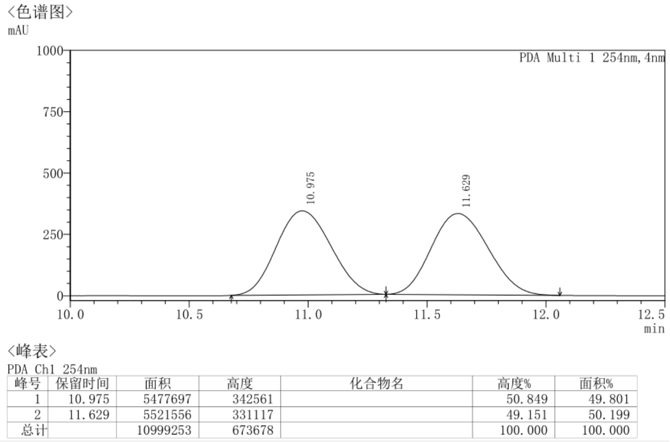
(1aR,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-3,4-difluoro-1a-methyl-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (2w)



Yellow solid, M,P: 79-80 °C, 14.9 mg, 85%, 95% ee, purified by chromatography (PE/EA = 5/1, Rf = 0.4); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.41 (dd, J = 8.9, 7.5 Hz, 1H), 7.19 (dd, J = 9.6, 6.6 Hz, 1H), 6.56 (d, J = 5.5 Hz, 1H), 4.59 (d, J = 5.6 Hz, 1H), 1.72 (d, J = 4.2 Hz, 1H), 1.62 (d, J = 4.2 Hz, 1H), 1.53 (s, 3H), 0.71 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) 200.5, 154.1 (dd, J = 7.6, 2.4 Hz), 154.1 (dd, J = 257.0, 14.0 Hz), 149.9 (dd, J = 249.4, 14.0 Hz), 144.7, 129.6 (dd, J = 4.8, 2.7 Hz), 113.1 (dd, J = 17.9, 2.2 Hz), 111.5 (d, J = 18.9 Hz), 100.5, 44.0, 40.6, 33.56 (d, J = 1.8 Hz), 25.2, 17.7, 13.0, -5.4, -5.5. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -128.02 (d, J = 19.2 Hz), -139.03 (d, J = 19.3 Hz). **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{19}H_{24}F_2O_2SiNa^+$: 373.1406, found 373.1415.

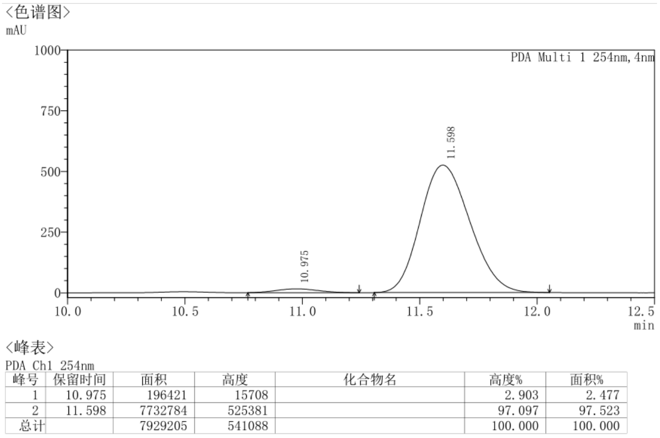


Resolution of enantiomers: Phenomenex INC column, 2% IPA-Hexanes, 0.5 mL/min, 254 nm, RT_1 = 10.9 min, RT_2 = 11.6 min. **$[\alpha]_D^{25}$** = -5.6 (c 0.5, CH_2Cl_2).



<峰表>
PDA Ch1 254nm

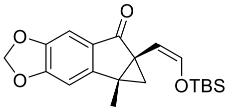
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	10.975	5477697	342561		50.849	49.801
2	11.629	5521556	331117		49.151	50.199
总计		10999253	673678		100.000	100.000



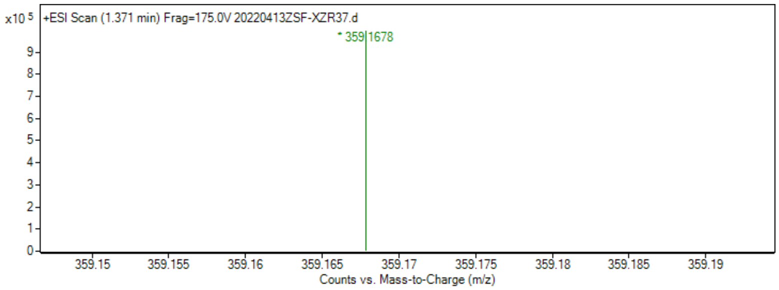
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	10.975	196421	15708		2.903	2.477
2	11.598	7732784	525381		97.097	97.523
总计		7929205	541088		100.000	100.000

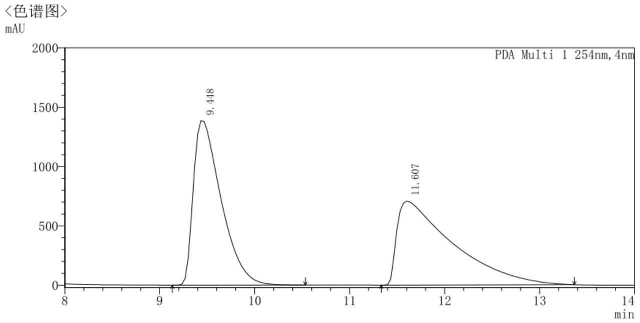
(4bR,5aS)-5a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-4b-methyl-5,5a-dihydrocyclopropa[1,2]indeno-[5,6-d][1,3]dioxol-6(4bH)-one (2x)



Yellow liquid, 15.8 mg, 88%, 86% ee, purified by chromatography (PE/EA = 15/1, Rf = 0.4); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.02 (s, 1H), 6.84 (s, 1H), 6.54 (d, *J* = 5.6 Hz, 1H), 6.13 – 5.81 (m, 2H), 4.59 (d, *J* = 5.7 Hz, 1H), 1.67 (d, *J* = 3.9 Hz, 1H), 1.62 (d, *J* = 3.9 Hz, 1H), 1.51 (s, 3H), 0.75 (s, 9H), 0.08 (d, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 201.4, 154.7, 152.7, 147.0, 144.0, 127.4, 104.0, 103.0, 101.8, 101.2, 44.8, 40.2, 33.3, 25.3, 17.8, 13.2, -5.4, -5.5. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{20}H_{27}O_4Si^+$: 359.1673, found 359.1678.

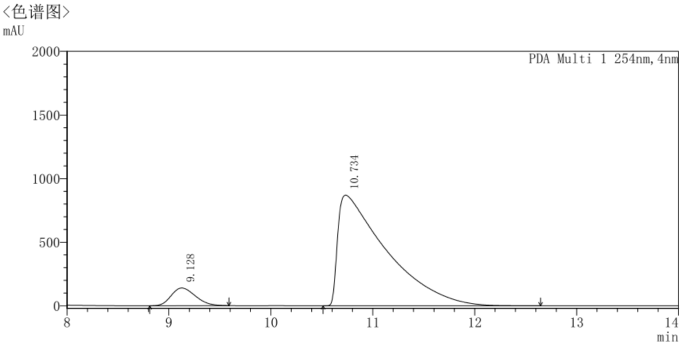


Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 1.0 mL/min, 254 nm, RT_1 = 9.1 min, RT_2 = 10.7 min. **$[\alpha]_D^{25}$** = -47 (c 0.5, CH_2Cl_2).



〈峰表〉
PDA Ch1 254nm

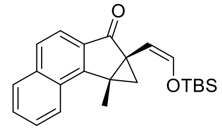
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	9.448	28243687	1386611		66.222	49.501
2	11.607	28813663	707280		33.778	50.499
总计		57057351	2093890		100.000	100.000



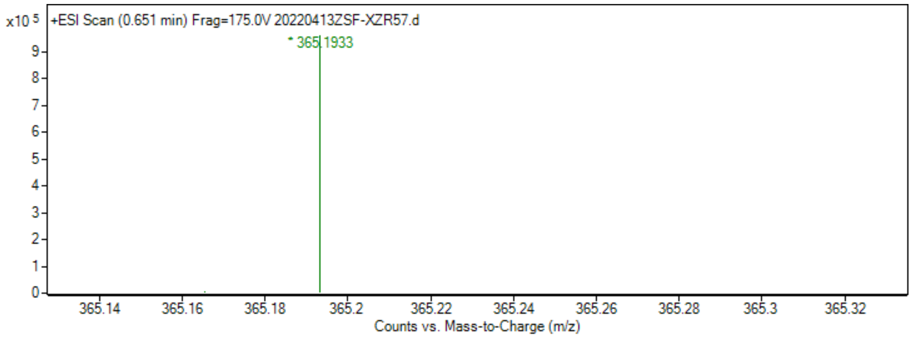
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	9.128	2302719	138879		13.772	7.373
2	10.734	28929660	869541		86.228	92.627
总计		31232378	1008420		100.000	100.000

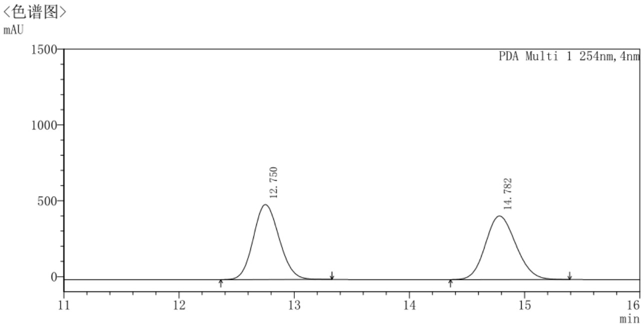
(7aS,8aR)-7a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-8a-methyl-8,8a-dihydrocyclopropa[4,5]cyclopenta[1,2-a]naphthalen-7(7aH)-one (2y)



Yellow liquid, 14.8 mg, 81%, 95% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.4); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.44 – 8.32 (m, 1H), 7.96 – 7.79 (m, 1H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.63 – 7.53 (m, 2H), 6.63 (d, *J* = 5.7 Hz, 1H), 4.65 (d, *J* = 5.7 Hz, 1H), 1.96 (d, *J* = 4.0 Hz, 1H), 1.90 (s, 3H), 1.87 (d, *J* = 4.1 Hz, 1H), 0.71 (s, 9H), 0.10 (s, 3H), 0.06 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 203.1, 157.3, 144.5, 137.0, 131.2, 129.9, 129.3, 128.0, 127.8, 126.4, 125.7, 120.4, 46.3, 40.6, 34.7, 25.3, 17.8, 15.6, -5.38, -5.43. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{23}H_{29}O_2Si^+$: 365.1932, found 365.1933.

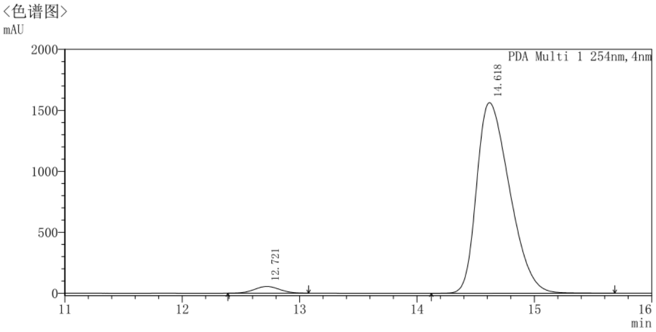


Resolution of enantiomers: Phenomenex INC column, 2% IPA-Hexanes, 1.0 mL/min, 254 nm, RT_1 = 12.7 min, RT_2 = 14.6 min. **$[\alpha]_D^{25}$** = + 11.7 (c 0.5, CH_2Cl_2)



〈峰表〉
PDA Ch1 254nm

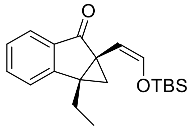
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	12.750	7735772	494475		54.107	50.035
2	14.782	7725043	419400		45.893	49.965
总计		15460815	913875		100.000	100.000



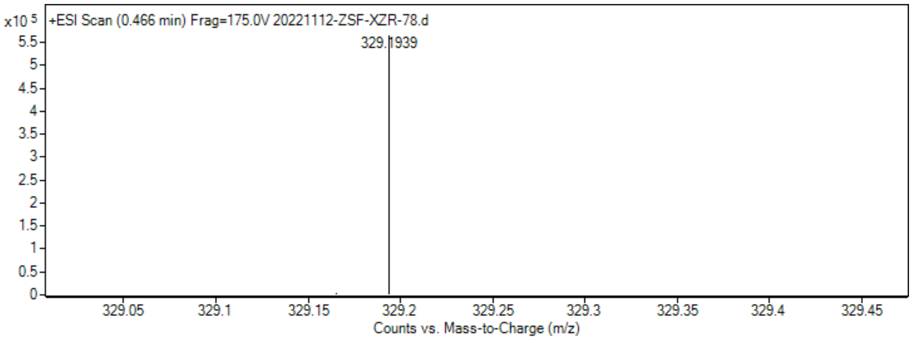
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	12.721	839808	55384		3.420	2.677
2	14.618	30530582	1564213		96.580	97.323
总计		31370391	1619597		100.000	100.000

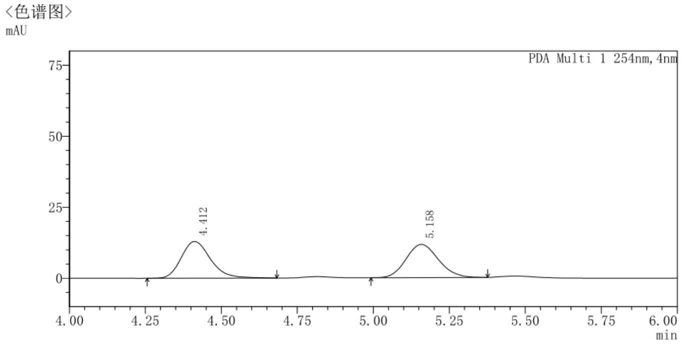
(1aR,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-1a-ethyl-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (4a)



Yellow liquid, 14.2 mg, 86%, 96% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.4); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 7.5 Hz, 1H), 7.51 – 7.42 (m, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.26 – 7.20 (m, 1H), 6.52 (d, *J* = 5.8 Hz, 1H), 4.60 (d, *J* = 5.8 Hz, 1H), 2.28 (dq, *J* = 14.9, 7.5 Hz, 1H), 1.81 (d, *J* = 4.0 Hz, 1H), 1.71 (d, *J* = 3.7 Hz, 1H), 1.02 (t, *J* = 7.4 Hz, 3H), 0.77 (s, 9H), 0.12 (s, 3H), 0.08 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 202.7, 155.8, 143.8, 134.0, 133.2, 126.4, 124.7, 122.6, 101.0, 43.9, 40.4, 40.26, 25.3, 21.4, 17.8, 11.9, -5.38, -5.42. **HRMS** (ESI) [M+H]$^+$ calculated for $C_{20}H_{29}O_2Si^+$: 329.1932, found 329.1939.

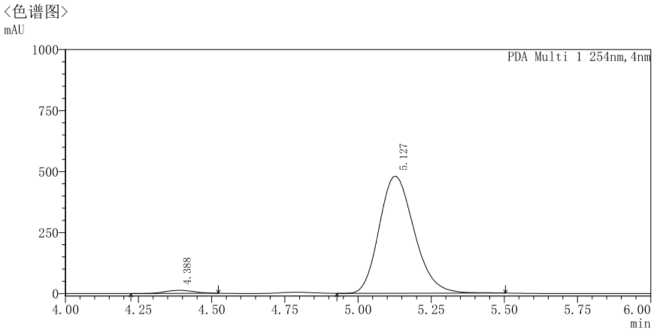


Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 1.0 mL/min, 254 nm, RT$_1$ = 4.4 min,RT$_2$ = 5.1 min. **[α]$_D^{25}$** = + 21.0 (c 0.5, CH_2Cl_2).



〈峰表〉
PDA Ch1 254nm

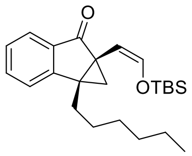
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.412	87089	12957		52.563	50.153
2	5.158	86557	11693		47.437	49.847
总计		173646	24651		100.000	100.000



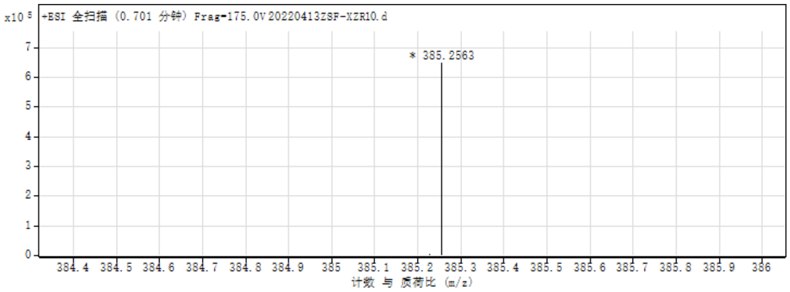
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.388	89895	12710		2.580	2.201
2	5.127	3995096	479910		97.420	97.799
总计		4084991	492621		100.000	100.000

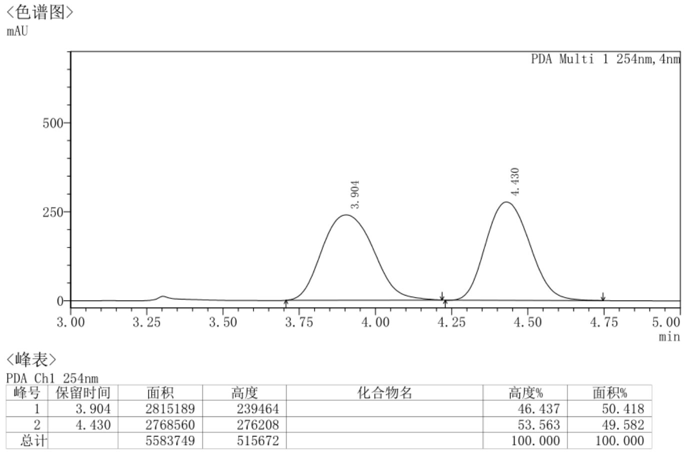
(1aR,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-1a-hexyl-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (4b)



Yellow liquid, 16.2 mg, 84%, 94% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.4); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 7.5 Hz, 1H), 7.49 (td, *J* = 7.4, 1.3 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.27 (td, *J* = 7.4, 1.1 Hz, 1H), 6.55 (d, *J* = 5.8 Hz, 1H), 4.63 (d, *J* = 5.9 Hz, 1H), 2.23 (ddd, *J* = 14.5, 9.9, 6.5 Hz, 1H), 1.88 (d, *J* = 4.0 Hz, 1H), 1.74 (d, *J* = 3.9 Hz, 2H), 1.45 (tdd, *J* = 9.5, 6.3, 2.7 Hz, 2H), 1.39 – 1.28 (m, 6H), 0.91 (t, *J* = 6.8 Hz, 3H), 0.82 (s, 9H), 0.16 (s, 3H), 0.12 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 202.8, 156.2, 143.7, 133.8, 133.2, 126.4, 124.6, 122.7, 101.0, 44.0, 40.5, 39.5, 31.7, 29.8, 28.5, 27.5, 25.4, 22.7, 17.8, 14.1, -5.35, -5.41. **HRMS** (ESI) [M+H]$^+$ calculated for $C_{24}H_{37}O_2Si^+$: 385.2558, found 385.2563.

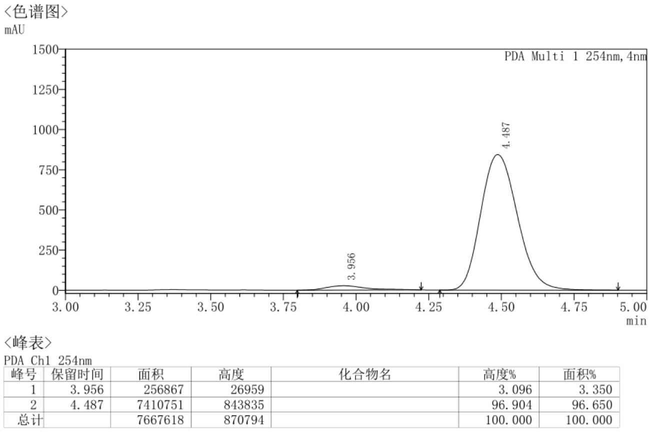


Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 1.0 mL/min, 254 nm, RT_1 = 3.9 min, RT_2 = 4.4 min. **$[\alpha]_D^{25}$** = + 22.2(c 0.5, CH_2Cl_2).



<峰表>
PDA Ch1 254nm

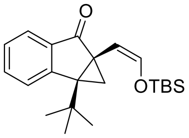
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	3.904	2815189	239464		46.437	50.418
2	4.430	2768560	276208		53.563	49.582
总计		5583749	515672		100.000	100.000



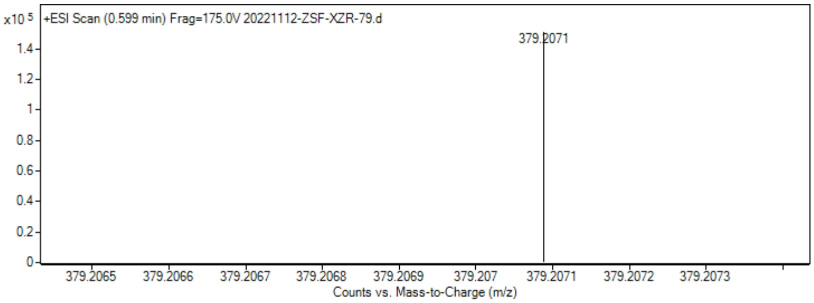
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	3.956	256867	26959		3.096	3.350
2	4.487	7410751	843835		96.904	96.650
总计		7667618	870794		100.000	100.000

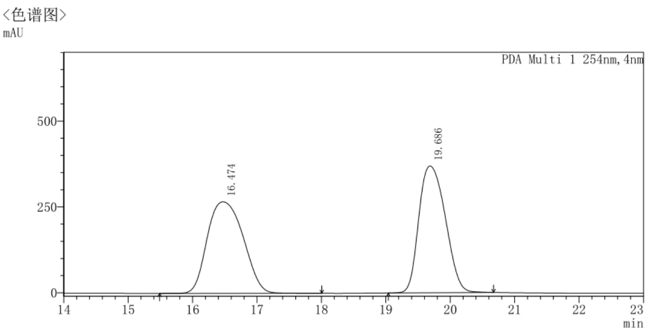
(1aS,6aS)-1a-(tert-butyl)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (4c)

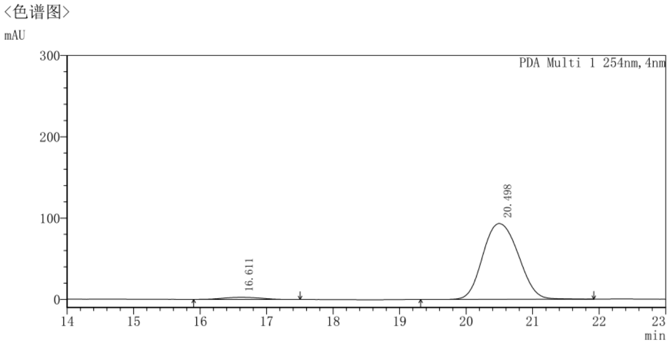


Yellow liquid,15.1 mg, 85%, 94% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.4); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.8 Hz, 1H), 7.70 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.47 (td, *J* = 7.6, 1.4 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 1H), 6.50 (d, *J* = 5.6 Hz, 1H), 4.78 (d, *J* = 5.6 Hz, 1H), 1.57 (d, *J* = 4.4 Hz, 1H), 1.31 (s, 11H), 0.80 (s, 9H), 0.17 (s, 3H), 0.12 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 202.1, 156.1, 142.9, 134.1, 132.9, 126.3, 125.1, 124.8, 47.5, 40.8, 40.1, 32.6, 29.4, 25.3, 17.8, -5.28, -5.30. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{22}H_{32}O_2SiNa^+$: 379.2064, found 379.2071.



Resolution of enantiomers: Phenomenex INC column, 1% IPA-Hexanes, 0.5 mL/min, 254 nm, RT_1 = 16.6 min, RT_2 = 20.4 min. **$[\alpha]_D^{25}$** = -8.5 (c 0.5, CH_2Cl_2).





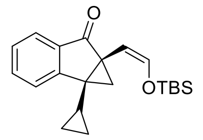
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	16.474	10378064	266629		41.938	49.504
2	19.686	10585923	369136		58.062	50.496
总计		20963987	635765		100.000	100.000

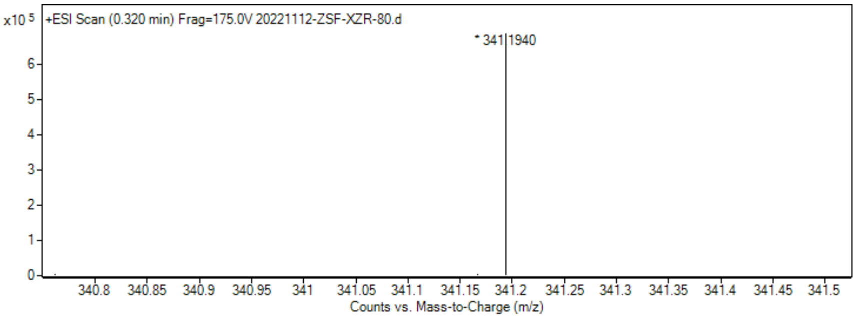
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	16.611	101596	2584		2.696	2.849
2	20.498	3464410	93263		97.304	97.151
总计		3566005	95847		100.000	100.000

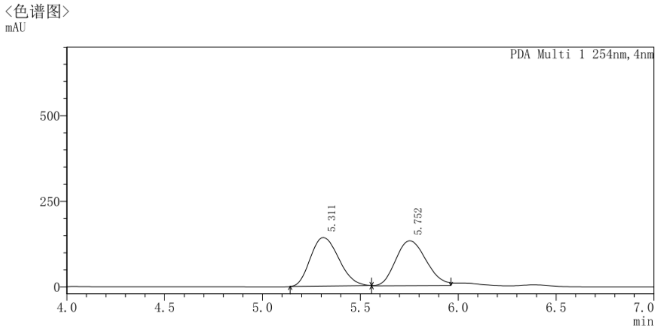
(1aS,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-1a-cyclopropyl-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (4d)

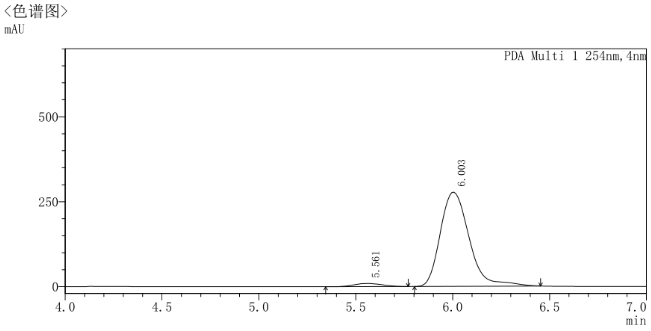


Yellow liquid, 10.9 mg, 64%, 94% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.4); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.8 Hz, 2H), 7.60 – 7.54 (m, 1H), 7.38 – 7.32 (m, 1H), 6.62 (d, *J* = 5.6 Hz, 1H), 4.73 (d, *J* = 5.5 Hz, 1H), 1.58 (d, *J* = 4.4 Hz, 1H), 1.52 (d, *J* = 4.4 Hz, 1H), 1.39 (td, *J* = 8.1, 4.2 Hz, 1H), 0.96 – 0.89 (m, 1H), 0.81 (s, 9H), 0.60 (ddt, *J* = 7.3, 5.4, 2.9 Hz, 2H), 0.32 (tt, *J* = 9.4, 4.8 Hz, 1H), 0.18 (s, 3H), 0.15 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 202.5, 157.2, 144.0, 133.5, 133.4, 126.7, 124.4, 122.9, 101.9, 40.7, 40.3, 39.2, 25.2, 17.7, 7.9, 3.4, 1.5, -5.4, -5.5. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{21}H_{29}O_2Si^+$: 341.1932, found 341.1940.



Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 0.8 mL/min, 254 nm, RT_1 = 5.5 min, RT_2 = 6.0 min. **$[\alpha]_D^{25}$** = + 220 (c 0.5, CH_2Cl_2).





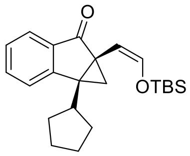
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	5.311	1436127	142036		52.023	50.224
2	5.752	1423328	130991		47.977	49.776
总计		2859456	273028		100.000	100.000

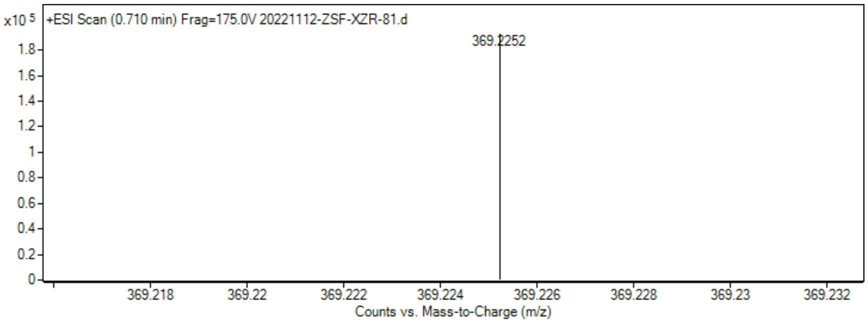
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	5.561	94862	9186		3.204	3.194
2	6.003	2875600	277507		96.796	96.806
总计		2970462	286693		100.000	100.000

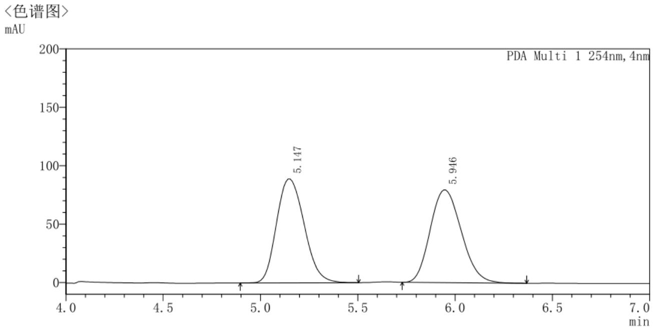
(1aS,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-1a-cyclopentyl-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (4e)



Yellow solid, M.P: 59-60°C, 14.9 mg, 81%, 96% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.4); ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 7.5 Hz, 1H), 7.51 – 7.40 (m, 2H), 7.35 – 7.13 (m, 1H), 6.53 (d, *J* = 5.8 Hz, 1H), 4.61 (d, *J* = 5.7 Hz, 1H), 2.39 – 2.24 (m, 1H), 2.04 – 1.86 (m, 2H), 1.83 (d, *J* = 4.1 Hz, 1H), 1.79 – 1.57 (m, 6H), 1.54 – 1.33 (m, 1H), 0.79 (s, 9H), 0.13 (s, 3H), 0.09 (s, 3H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 202.5, 155.6, 143.8, 134.3, 133.0, 126.3, 124.8, 123.5, 101.8, 43.6, 41.3, 40.5, 39.8, 30.8, 29.0, 26.3, 25.9, 25.3, 17.8, -5.35, -5.39. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{23}H_{33}O_2Si^+$: 369.2245, found 369.2252.



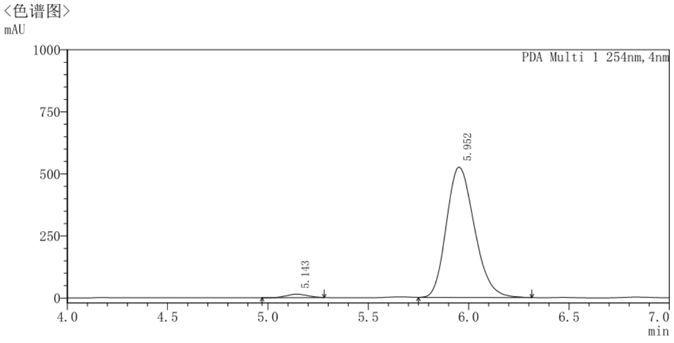
Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 0.8 mL/min, 254 nm, RT_1 = 5.1 min, RT_2 = 5.9 min. $[\alpha]_D^{25}$ = + 25.0 (c 0.5, CH_2Cl_2).



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	5.147	880848	88927		52.844	49.906
2	5.946	884169	79354		47.156	50.094
总计		1765017	168281		100.000	100.000

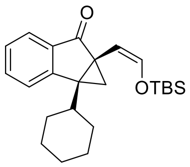


〈峰表〉

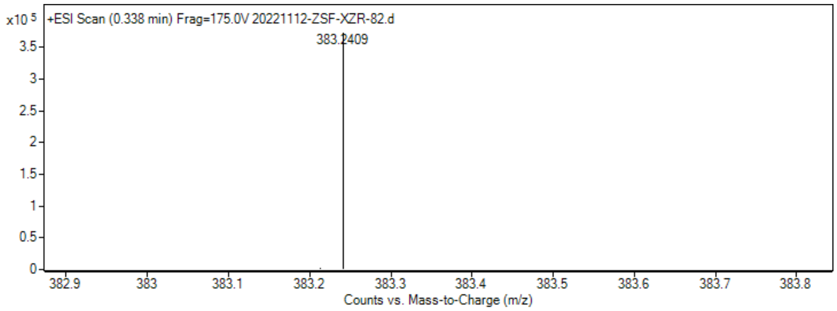
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	5.143	102183	13827		2.561	1.960
2	5.952	5111680	526117		97.439	98.040
总计		5213863	539944		100.000	100.000

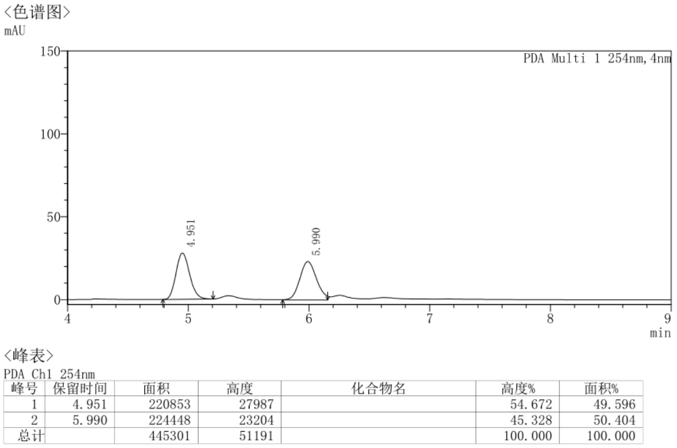
(1aS,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-1a-cyclohexyl-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (4f)



Yellow solid, M.P: 59-60°C, 15.8 mg, 83%, 96% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.4); ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.53 – 7.46 (m, 1H), 7.29 (t, *J* = 7.4 Hz, 1H), 6.59 (d, *J* = 5.9 Hz, 1H), 4.62 (d, *J* = 5.9 Hz, 1H), 2.02 – 1.83 (m, 4H), 1.78 (dd, *J* = 11.1, 4.2 Hz, 3H), 1.71 – 1.59 (m, 2H), 1.31 (m, 4H), 0.86 (s, 9H), 0.20 (s, 3H), 0.15 (s, 3H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 202.6, 155.3, 143.8, 134.4, 133.0, 126.3, 124.7, 124.2, 101.3, 43.6, 43.2, 40.7, 39.1, 32.0, 30.2, 27.3, 26.7, 26.5, 25.3, 17.8, -5.36, -5.39. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{24}H_{35}O_2Si^+$: 383.2401, found 383.2409.

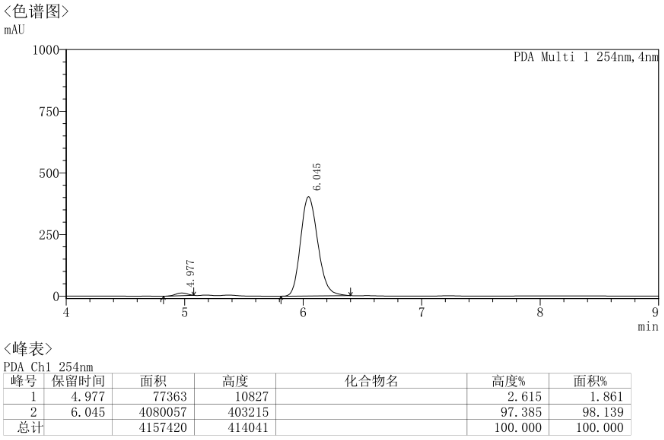


Resolution of enantiomers: DAICEL Chiralcel® ODH zcolumn, 2% IPA-Hexanes, 0.8 mL/min, 254 nm, RT$_1$ = 4.9 min, RT$_2$ = 6.0 min. **[α]$_D$^{25}** = +39.0 (c 0.5, CH$_2$Cl$_2$).



<峰表>
PDA Ch1 254nm

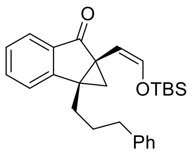
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.951	220853	27987		54.672	49.596
2	5.990	224448	23204		45.328	50.404
总计		445301	51191		100.000	100.000



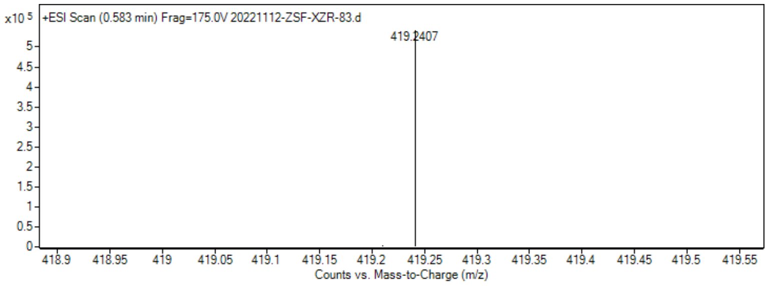
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.977	77363	10827		2.615	1.861
2	6.045	4080057	403215		97.385	98.139
总计		4157420	414041		100.000	100.000

(1aR,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-1a-(3-phenylpropyl)-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (4g)



Yellow liquid, 17.8 mg, 85%, 92% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.4); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 1.3 Hz, 1H), 7.37 – 7.15 (m, 8H), 6.53 (d, *J* = 5.9 Hz, 1H), 4.60 (d, *J* = 5.8 Hz, 1H), 2.67 (t, *J* = 7.3 Hz, 2H), 2.34 – 2.23 (m, 1H), 1.78 (dd, *J* = 50.3, 4.0 Hz, 6H), 0.79 (s, 9H), 0.14 (s, 3H), 0.08 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 202.5, 155.9, 143.9, 142.1, 133.8, 133.3, 128.8, 128.3, 126.5, 125.8, 124.7, 122.6, 101.0, 43.9, 40.4, 39.2, 36.3, 29.1, 28.1, 25.3, 17.8, -5.4, -5.5. **HRMS** (ESI) [M+H]$^+$ calculated for $C_{27}H_{35}O_2Si^+$: 419.2401, found 419.2407.



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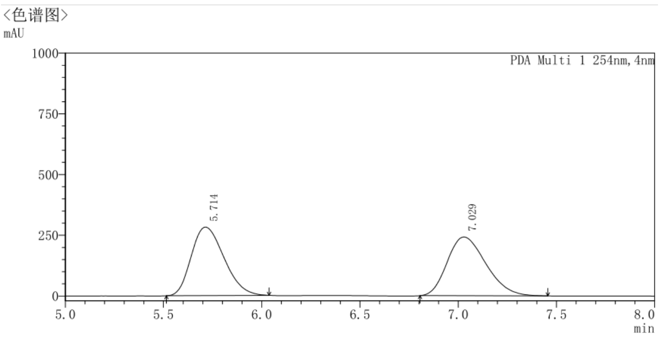
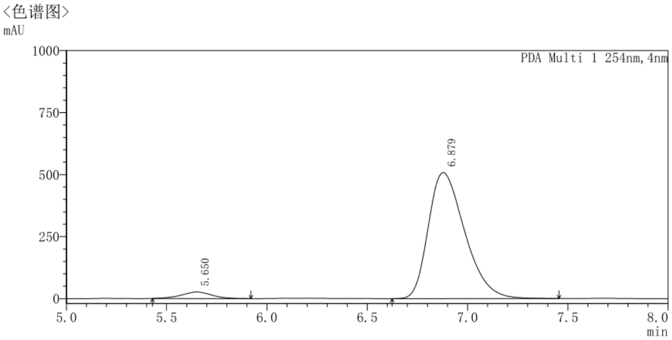
Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 1.0 mL/min, 254 nm, RT$_1$ = 5.7 min, RT$_2$ = 6.9 min. **[α]$_D$^{25}** = +20.0 (c 0.5, CH$_2$Cl$_2$).





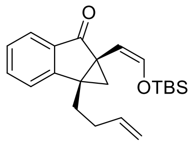
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	5.714	3284999	282515		53.868	49.743
2	7.029	3318890	241946		46.132	50.257
总计		6603889	524461		100.000	100.000

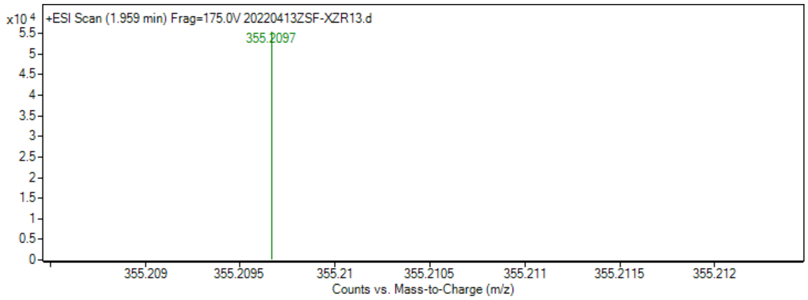
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	5.650	277148	26178		4.890	4.130
2	6.879	6433164	509185		95.110	95.870
总计		6710312	535363		100.000	100.000

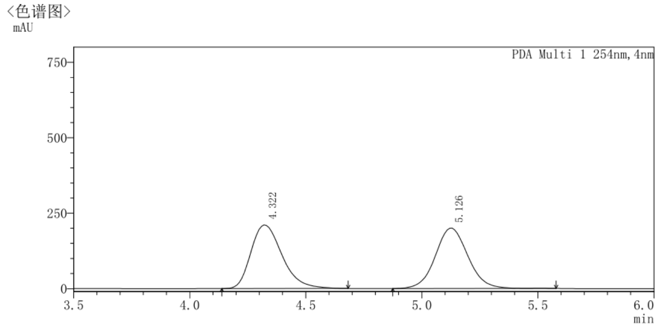
(1aR,6aS)-1a-(but-3-en-1-yl)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (4h)

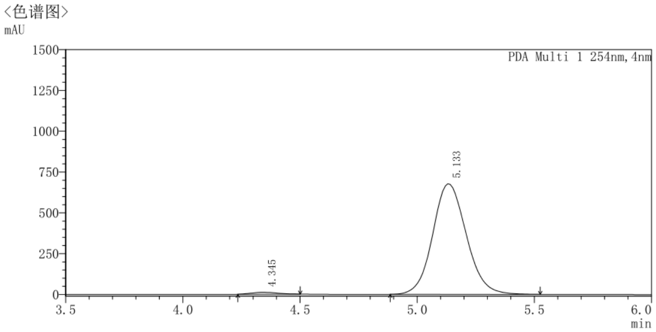


Yellow liquid, 15 mg, 85%, 98% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.4); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.75 – 7.54 (m, 1H), 7.46 (td, *J* = 7.4, 1.2 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.24 (dd, *J* = 7.3, 1.2 Hz, 1H), 6.53 (d, *J* = 5.9 Hz, 1H), 5.91 – 5.76 (m, 1H), 5.02 – 4.88 (m, 2H), 4.61 (d, *J* = 5.9 Hz, 1H), 2.35 (ddd, *J* = 14.1, 9.7, 6.6 Hz, 1H), 2.18 (dddt, *J* = 9.4, 7.8, 6.3, 3.3 Hz, 2H), 1.85 (d, *J* = 4.0 Hz, 1H), 1.82 – 1.74 (m, 1H), 1.72 (d, *J* = 4.0 Hz, 1H), 0.78 (s, 9H), 0.12 (s, 3H), 0.08 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 202.4, 155.7, 143.9, 138.5, 133.8, 133.3, 126.6, 124.7, 122.7, 114.5, 101.0, 43.83, 40.4, 39.0, 31.6, 27.9, 25.3, 17.8, -5.36, -5.40. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{22}H_{31}O_2Si^+$: 355.2088, found 355.2097.



Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 1.0 mL/min, 254 nm, RT_1 = 4.3 min, RT_2 = 5.1 min. **$[\alpha]_D^{25}$** = + 24.2 (c 0.5, CH_2Cl_2).





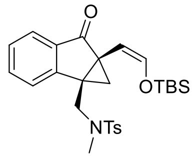
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.322	1969433	210915		51.343	50.125
2	5.126	1959600	199884		48.657	49.875
总计		3929033	410799		100.000	100.000

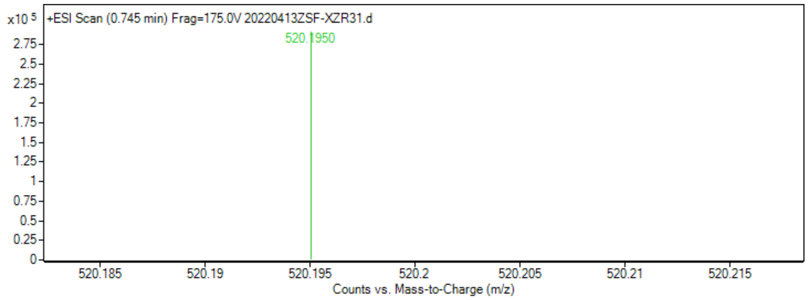
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.345	92868	11496		1.668	1.350
2	5.133	6784705	677864		98.332	98.650
总计		6877572	689360		100.000	100.000

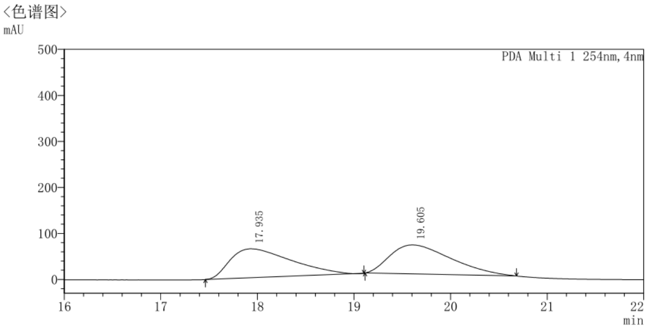
N-(((1aS,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-6-oxo-6,6a-dihydrocyclopropa[a]inden-1a(1H)-yl)methyl)-N,4-dimethylbenzenesulfonamide (4i)



Colorless solid, M.P: 92-93 °C, 22.0 mg, 88%, >99% ee, purified by chromatography (PE/EA = 5/1, Rf = 0.4); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 7.7 Hz, 1H), 7.66 (dd, *J* = 10.7, 7.9 Hz, 3H), 7.53 (td, *J* = 7.5, 1.3 Hz, 1H), 7.38 – 7.26 (m, 4H), 6.45 (d, *J* = 5.9 Hz, 1H), 4.54 (d, *J* = 5.9 Hz, 1H), 3.67 (d, *J* = 13.6 Hz, 1H), 3.48 (d, *J* = 13.6 Hz, 1H), 2.70 (s, 3H), 2.44 (s, 3H), 1.90 (d, *J* = 4.4 Hz, 1H), 1.81 (d, *J* = 4.4 Hz, 1H), 0.74 (s, 9H), 0.06 (s, 3H), 0.02 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 201.5, 153.6, 144.2, 143.5, 134.1, 132.9, 129.8, 127.5, 127.2, 124.6, 124.5, 100.0, 48.9, 41.3, 39.7, 35.5, 34.5, 25.3, 21.5, 17.7, -5.48, -5.50. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{27}H_{35}NO_4SSiNa^+$: 520.1948, found 520.1950.



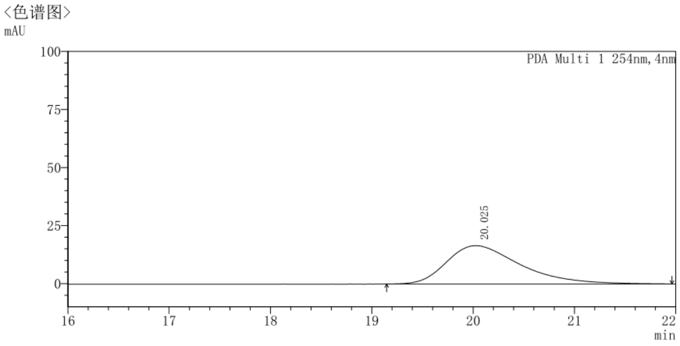
Resolution of enantiomers: DAICEL Chiralcel® ODH column, 4% IPA-Hexanes, 0.8 mL/min, 254 nm, RT_1 = 18.0 min, RT_2 = 19.6 min. **$[\alpha]_D^{25}$** = + 11.3 (c 0.5, CH_2Cl_2).



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	17.935	2752179	62732		49.870	49.604
2	19.605	2796076	63058		50.130	50.396
总计		5548255	125789		100.000	100.000

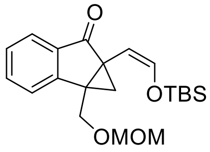


〈峰表〉

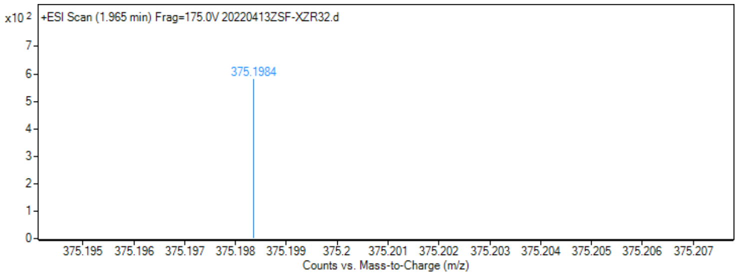
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	20.025	838548	16505		100.000	100.000
总计		838548	16505		100.000	100.000

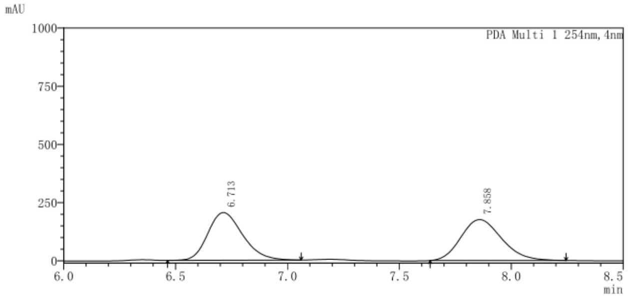
(1aS,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-1a-((methoxymethoxy)methyl)-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one(4j)



Yellow liquid, 10.9 mg, 58%, 82% ee, purified by chromatography (PE/EA = 5/1, Rf = 0.4); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.76 – 7.54 (m, 2H), 7.48 (td, *J* = 7.5, 1.2 Hz, 1H), 7.29 – 7.25 (m, 2H), 6.54 (d, *J* = 5.7 Hz, 1H), 4.73 (s, 2H), 4.67 (d, *J* = 5.7 Hz, 1H), 4.11 (dd, *J* = 11.0, 0.7 Hz, 1H), 3.94 (d, *J* = 11.0 Hz, 1H), 3.40 (s, 3H), 2.01 (d, *J* = 4.3 Hz, 1H), 1.82 (d, *J* = 4.3 Hz, 1H), 0.74 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 202.2, 155.0, 144.7, 133.7, 133.4, 126.9, 124.7, 123.4, 100.6, 96.5, 67.0, 55.4, 41.8, 39.6, 37.7, 25.2, 17.8, -5.4, -5.5. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{21}H_{31}O_4Si^+$: 375.1985, found 375.1984.



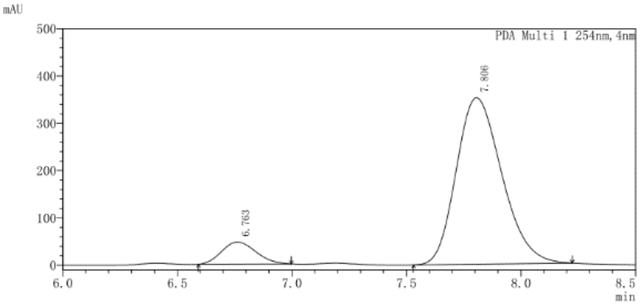
Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 0.8 mL/min, 254 nm, RT$_1$ = 6.7 min, RT$_2$ = 7.8 min. **[α]$_D$^{25}** = + 10.9 (c 0.5, CH$_2$Cl$_2$).



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	6.713	2218867	204966		53.834	49.912
2	7.858	2226732	175770		46.166	50.088
总计		4445599	380736		100.000	100.000

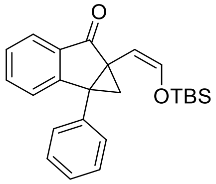


<峰表>

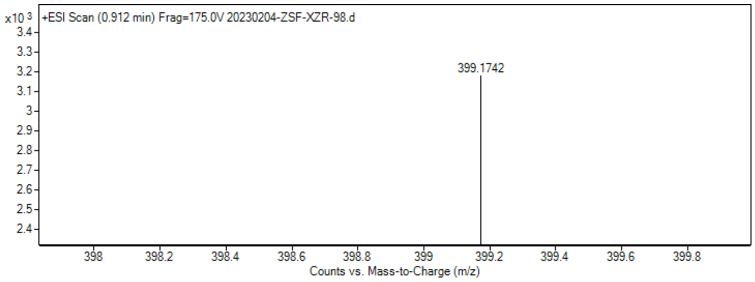
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	6.763	484931	46701		11.708	9.051
2	7.806	4872654	352171		88.292	90.949
总计		5357585	398872		100.000	100.000

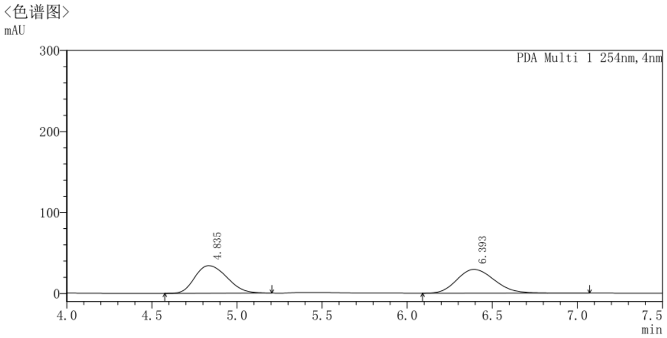
(Z)-6a-(2-((tert-butyldimethylsilyl)oxy)vinyl)-1a-phenyl-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one(4k)



Yellow solid, M.P: 84-85 °C, 10.0 mg, 54%, 90% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.5); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 5.7 Hz, 0H), 7.66 – 7.59 (m, 6H), 7.58 – 7.52 (m, 4H), 7.32 (d, *J* = 7.7 Hz, 1H), 6.58 (d, *J* = 5.6 Hz, 1H), 4.60 (d, *J* = 5.6 Hz, 1H), 2.60 (d, *J* = 4.4 Hz, 1H), 2.30 (d, *J* = 4.4 Hz, 1H), 1.00 (s, 9H), 0.29 (s, 3H), 0.27 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 156.9, 144.4, 135.9, 133.7, 133.4, 130.1, 128.3, 127.4, 126.9, 124.7, 124.0, 100.8, 44.1, 42.8, 42.0, 25.3, 17.8, -5.37, -5.4. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{24}H_{28}O_2SiNa^+$: 399.1751, found 399.1742.

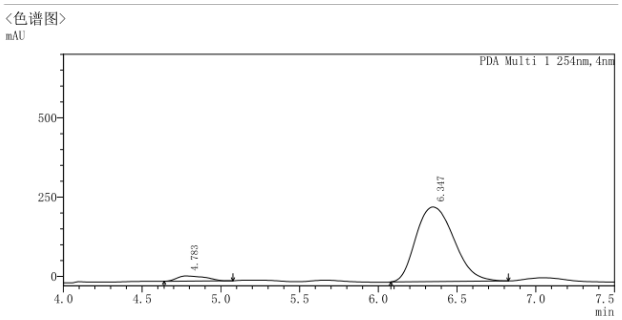


Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 1.0 mL/min, 254 nm, RT$_1$ = 4.8 min, RT$_2$ = 6.4 min. **[α]$_D$^{25}** = -2.0 (c 0.5, CH$_2$Cl$_2$).



〈峰表〉
PDA Ch1 254nm

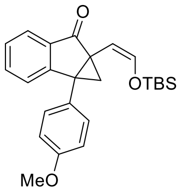
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.835	449820	34130		53.780	49.937
2	6.393	450964	29333		46.220	50.063
总计		900784	63463		100.000	100.000



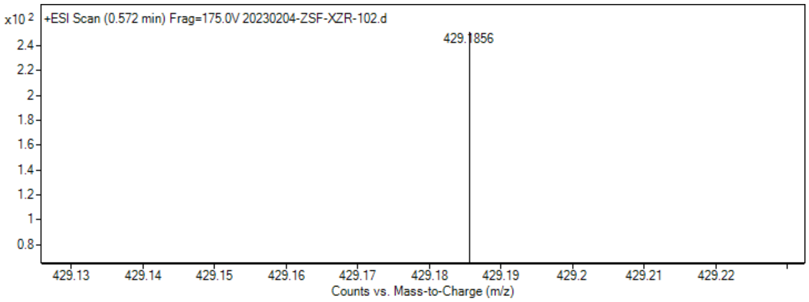
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.783	205622	16259		6.467	4.931
2	6.347	3964346	235139		93.533	95.069
总计		4169969	251398		100.000	100.000

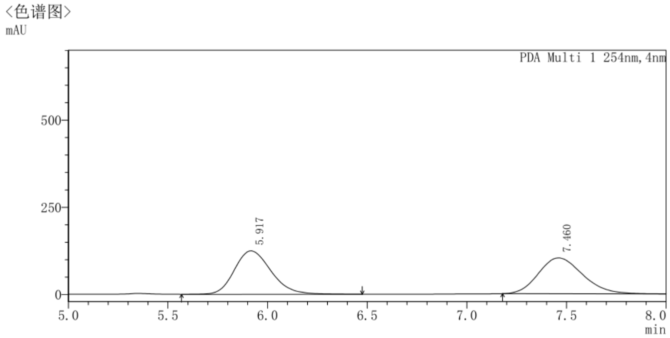
(Z)-6a-(2-((tert-butyldimethylsilyl)oxy)vinyl)-1a-(4-methoxyphenyl)-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (4l)



Yellow liquid, 7.1 mg, 35%, 76% ee, purified by chromatography (PE/EA = 10/1, Rf = 0.5); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.5 Hz, 1H), 7.56 – 7.46 (m, 1H), 7.37 (dd, *J* = 6.9, 1.8 Hz, 3H), 7.18 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.48 (d, *J* = 5.6 Hz, 1H), 4.49 (d, *J* = 5.6 Hz, 1H), 3.93 (s, 1H), 2.40 (d, *J* = 4.4 Hz, 1H), 2.16 (d, *J* = 4.4 Hz, 1H), 0.88 (s, 9H), 0.19 (s, 3H), 0.17 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 201.5, 162.2 (d, *J* = 245.9 Hz), 156.6, 144.4, 133.7, 133.3, 131.7 (d, *J* = 8.2 Hz), 127.0, 124.7, 123.9, 115.2 (d, *J* = 21.5 Hz), 100.8, 43.4, 42.6, 42.0, 25.3, 17.8, -5.4, -5.4. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{25}H_{30}O_3Si\ Na^+$: 429.1856, found 429.1856.

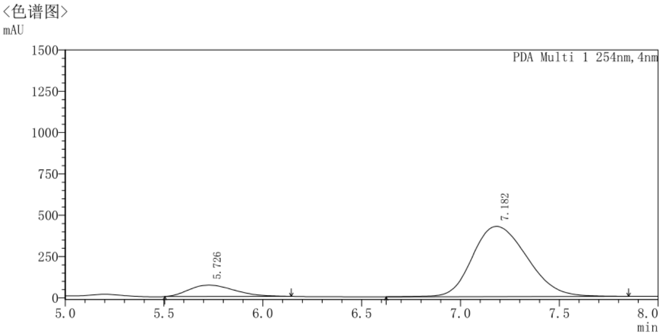


Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 1.0 mL/min, 254 nm, RT_1 = 5.7 min, RT_2 = 7.2 min. **$[\alpha]_D^{25}$** = 4.0 (c 0.5, CH_2Cl_2).



〈峰表〉
PDA Ch1 254nm

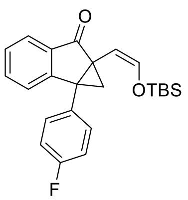
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	5.917	1601352	124437		54.804	50.266
2	7.460	1584400	102624		45.196	49.734
总计		3185752	227061		100.000	100.000



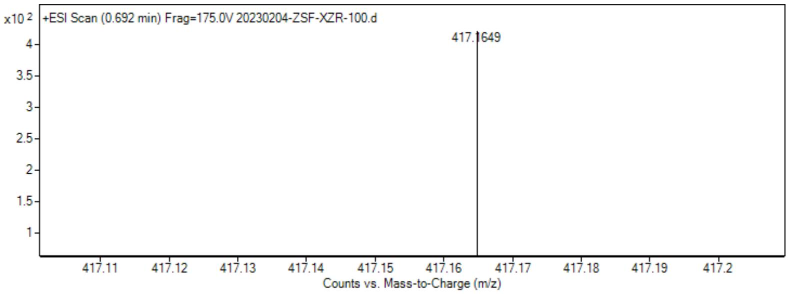
〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	5.726	1112847	69161		13.990	11.968
2	7.182	8185310	425190		86.010	88.032
总计		9298157	494351		100.000	100.000

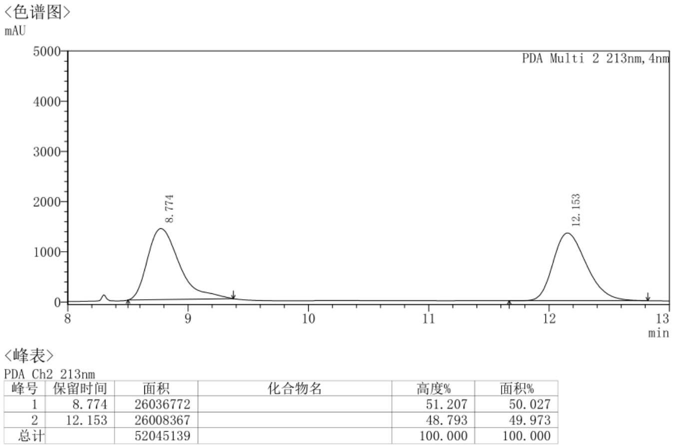
(Z)-6a-(2-((tert-butyldimethylsilyl)oxy)vinyl)-1a-(4-fluorophenyl)-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (4m)



Yellow liquid, 5.4 mg, 27%, 75% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.5); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 7.5 Hz, 1H), 7.73 – 7.59 (m, 1H), 7.54 (ddd, *J* = 9.5, 5.6, 3.0 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 8.6 Hz, 2H), 6.59 (d, *J* = 5.7 Hz, 1H), 4.60 (d, *J* = 5.6 Hz, 1H), 2.54 (d, *J* = 4.4 Hz, 1H), 2.29 (d, *J* = 4.4 Hz, 1H), 0.99 (s, 9H), 0.30 (s, 3H), 0.28 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 201.5, 162.2 (d, *J* = 245.9 Hz), 156.6, 144.4, 133.7, 133.3, 131.7 (d, *J* = 8.2 Hz), 127.0, 124.7, 123.9, 115.2 (d, *J* = 21.5 Hz), 100.8, 43.4, 42.6, 42.0, 25.3, 17.8, -5.4, -5.4. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -114.95. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{24}H_{27}FO_2SiNa^+$: 417.1656, found 417.1649.

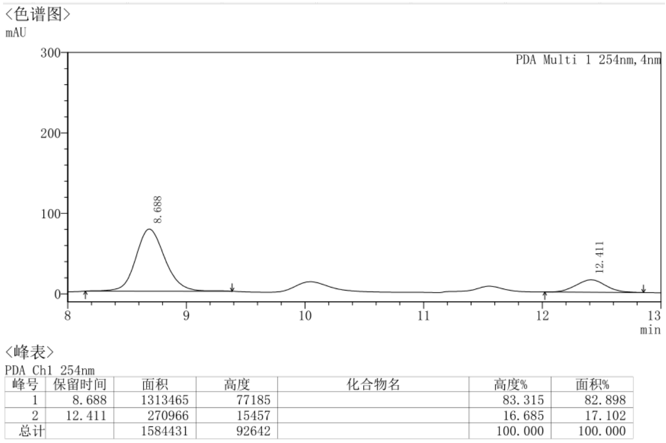


Resolution of enantiomers: DAICEL Chiralcel® ODH column, 1% IPA-Hexanes, 0.8 mL/min, 254 nm, RT_1 = 8.7 min, RT_2 = 12.4 min. **$[\alpha]_D^{25}$** = 3.0 (c 0.5, CH_2Cl_2).



<峰表>
PDA Ch2 213nm

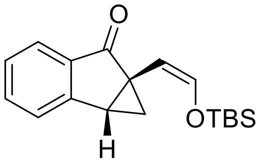
峰号	保留时间	面积	化合物名	高度%	面积%
1	8.774	26036772		51.207	50.027
2	12.153	26008367		48.793	49.973
总计		52045139		100.000	100.000



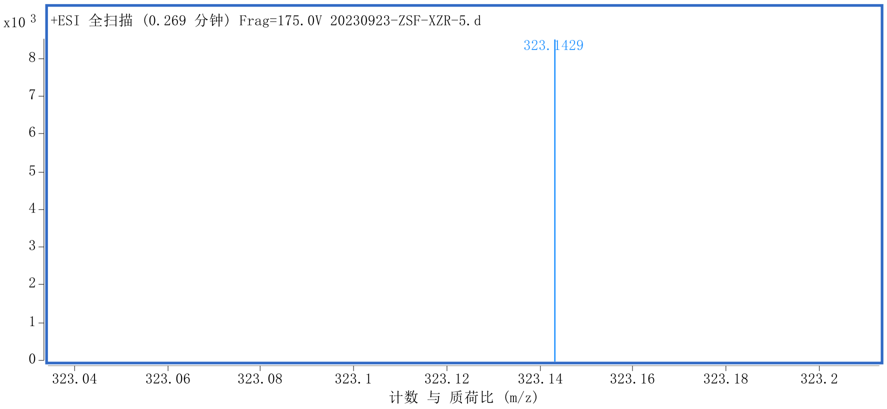
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	8.688	1313465	77185		83.315	82.898
2	12.411	270966	15457		16.685	17.102
总计		1584431	92642		100.000	100.000

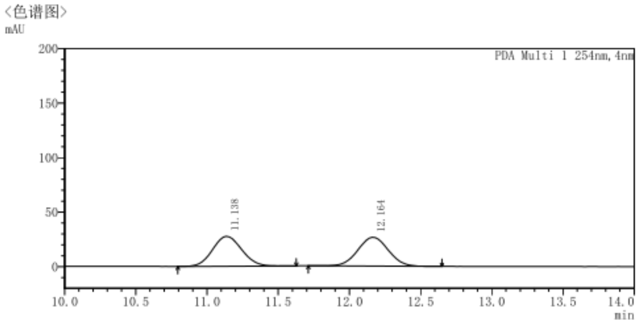
(1aR,6aR)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (4n)



Yellow liquid, 2.6 mg, 17%, 81% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.5); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 7.6 Hz, 1H), 7.47 (td, *J* = 7.4, 1.2 Hz, 1H), 7.41 (d, *J* = 7.4 Hz, 1H), 7.27 (td, *J* = 7.4, 1.1 Hz, 1H), 6.36 (d, *J* = 5.9 Hz, 1H), 5.01 (d, *J* = 6.0 Hz, 1H), 3.28 (dd, *J* = 7.0, 3.8 Hz, 1H), 2.02 (dd, *J* = 7.0, 3.7 Hz, 1H), 1.58 (t, *J* = 3.7 Hz, 1H), 0.85 (s, 9H), 0.12 (d, *J* = 1.7 Hz, 6H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 202.8, 154.5, 141.5, 133.5, 133.3, 126.6, 125.0, 124.0, 102.3, 40.2, 35.7, 30.0, 25.7, 25.4, 18.0, -5.45, -5.52. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{18}H_{24}O_2SiNa^+$: 301.1982, found 301.1983.



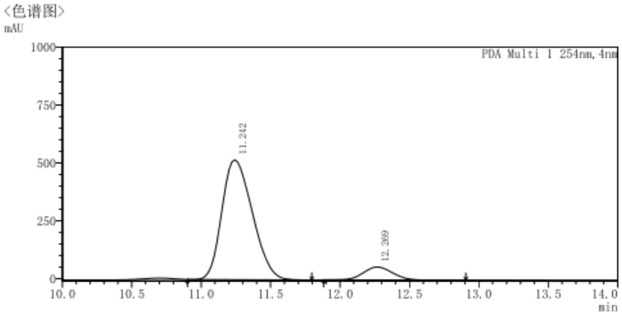
Resolution of enantiomers: Phenomenex INC column, 2% IPA-Hexanes, 0.8 mL/min, 254 nm, RT_1 = 11.0 min, RT_2 = 12.0 min. **$[\alpha]_D^{25}$** = + 13 (c 0.5, CH_2Cl_2).



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	面积%	峰结束
1	11.138	389075	27413		49.726	11.627
2	12.164	393364	26504		50.274	12.651
总计		782439	53918		100.000	

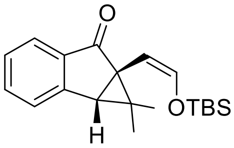


〈峰表〉

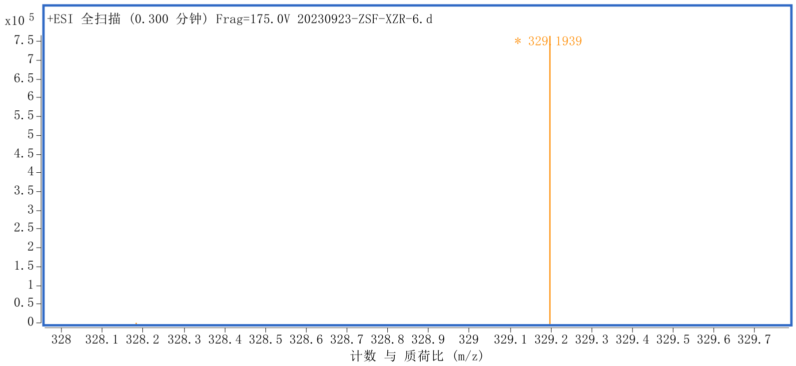
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	11.242	7914177	517911		90.258	90.680
2	12.269	813388	55903		9.742	9.320
总计		8727565	573813		100.000	100.000

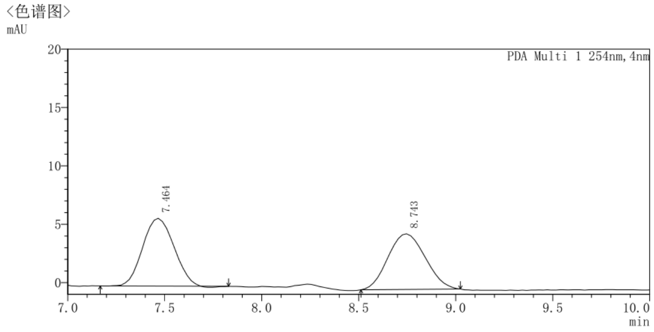
(1aR,6aR)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-1,1-dimethyl-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one(4o)



Yellow solid, 9.5 mg, 58%, 55% ee, purified by chromatography (PE/EA = 20/1, Rf = 0.4); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 7.5 Hz, 1H), 8.01 (td, *J* = 7.4, 1.2 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.80 (td, *J* = 7.4, 1.1 Hz, 2H), 6.95 (d, *J* = 5.6 Hz, 1H), 5.46 (d, *J* = 5.6 Hz, 1H), 3.41 (s, 1H), 1.84 (s, 3H), 1.41 (s, 3H), 1.25 (s, 9H), 0.58 (s, 3H), 0.55 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 202.8, 151.5, 143.0, 137.5, 133.4, 126.5, 125.4, 123.3, 102.2, 47.8, 44.8, 41.5, 25.3, 24.7, 17.8, 16.2, -5.46, -5.52. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{20}H_{29}O_2Si^+$: 329.1932, found 329.1939.

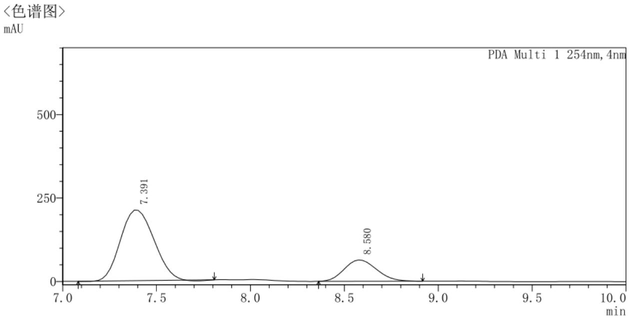


Resolution of enantiomers: Phenomenex INC column, 2% IPA-Hexanes, 0.8 mL/min, 254 nm, RT_1 = 7.4 min, RT_2 = 8.6 min. $[\boldsymbol{\alpha}]_D^{25}$ = + 15.0 (c 0.5, CH_2Cl_2).



〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	7.464	64907	5803		54.907	50.491
2	8.743	63644	4766		45.093	49.509
总计		128550	10568		100.000	100.000



〈峰表〉
PDA Ch1 254nm

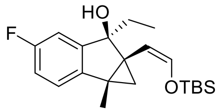
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	7.391	2624809	211542		76.836	77.419
2	8.580	765575	63775		23.164	22.581
总计		3390384	275317		100.000	100.000

5. Gram-scale reaction and synthetic applications

Procedure for gram-scale reaction: To a dichloromethane solution of **1g** (3.3 mmol, 30 mL) in Schlenk tube with a magnetic bar was added $Rh_2(S\text{-TCPTTL})_4$ (1 mol%, 33.0 mg) at 30 °C under N_2. The sealed tube was then stirred at 30 °C under nitrogen atmosphere for 72 h. The mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 30:1) to afford the desired product **2g** (0.94 g, 86%, 94% ee).

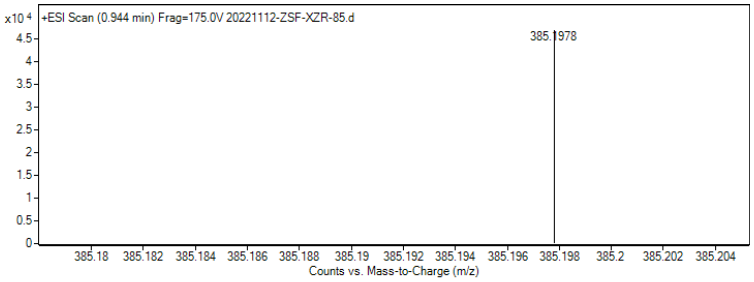
5.1 The derivatization of cis-alkenyl substituted cyclopropane-fused indanone:

1aR,6R,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-6-ethyl-4-fluoro-1a-methyl-1,1a,6,6a-tetrahydrocyclopropa [a]-inden-6-ol (5a)

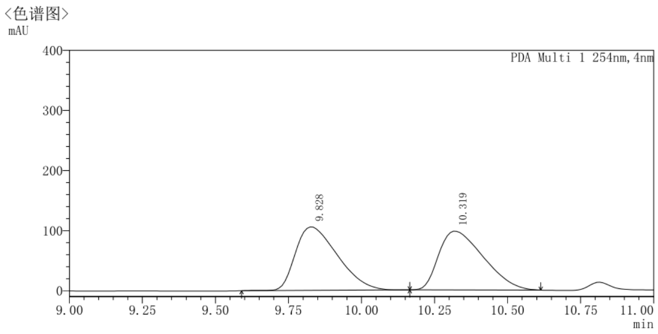


The substrates **2g** (33.2 mg, 94% ee, 0.1 mmol) was dissolved in THF (1 mL) at 0 °C, EtMgBr (3.0 equiv,0.3 mmol, 1.0 mol/L) was added into the solution. After 2 h, the solvent was removed. Then the reaction mixture was purified by silica gel column chromatography to obtain the product **5a** (Yellow oil, 21.7 mg, dr > 20:1, 60%, 94 % ee, PE/EA = 5/1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.06 (dd, *J* = 8.3, 4.9 Hz, 1H), 6.89 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.87 – 6.80 (m, 1H), 6.46 (dd, *J* = 5.7, 1.0 Hz, 1H), 4.69 (d, *J* = 5.7 Hz, 1H), 3.62 (s, 1H), 1.93 (dq, *J* = 14.3, 7.3 Hz, 1H), 1.86 – 1.73 (m, 1H), 1.45 – 1.40 (m, 3H), 1.29 – 1.24 (m, 1H), 1.10 (d, *J* = 3.9 Hz, 1H), 0.96 (d, *J* = 1.1 Hz, 9H), 0.72 (d, *J* = 3.9 Hz, 1H), 0.51 – 0.38 (m, 3H), 0.26 – 0.17 (m, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 162.1 (d, *J* = 242.8 Hz), 145.0 (d, *J* = 7.1 Hz), 144.7 (d, *J* = 2.4 Hz), 143.5, 121.6 (d, *J* = 8.3 Hz), 114.1 (d, *J* = 22.5 Hz), 111.3 (d, *J* = 22.4 Hz), 105.6, 86.8 (d, *J* = 1.9 Hz), 34.2, 33.8, 32.6, 31.7, 25.6, 18.3, 13.4, 9.0, -5.2, -5.5. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -117.22. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{21}H_{31}FO_2SiNa^+$: 385.1969, found 385.1978.

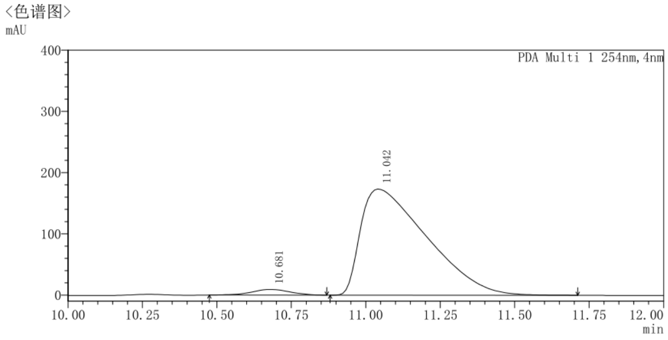


Resolution of enantiomers: Phenomenex INC column, 0.5% IPA-Hexanes, 0.5 mL/min, 254 nm, RT_1 = 10.6 min, RT_2 = 11.0 min. **$[\alpha]_D^{25}$** = + 16.7 (c 0.5, CH_2Cl_2).



<峰表>
PDA Ch1 254nm

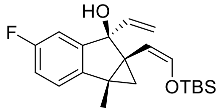
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	9.828	1059058	105753		51.952	50.377
2	10.319	1043188	97806		48.048	49.623
总计		2102246	203560		100.000	100.000



<峰表>
PDA Ch1 254nm

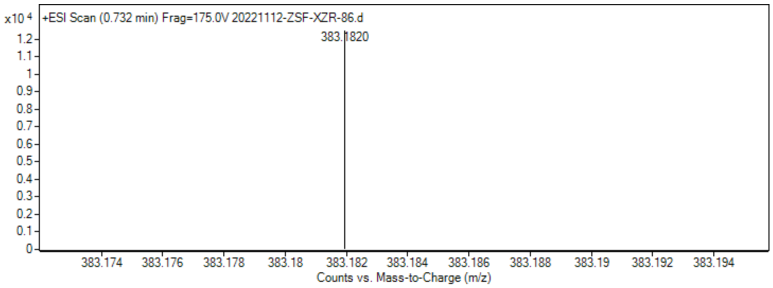
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	10.681	83059	9215		5.048	2.999
2	11.042	2686619	173322		94.952	97.001
总计		2769677	182536		100.000	100.000

(1aR,6R,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-4-fluoro-1a-methyl-6-vinyl-1,1a,6,6a-tetrahydrocyclopropa[a]inden-6-ol (5b)

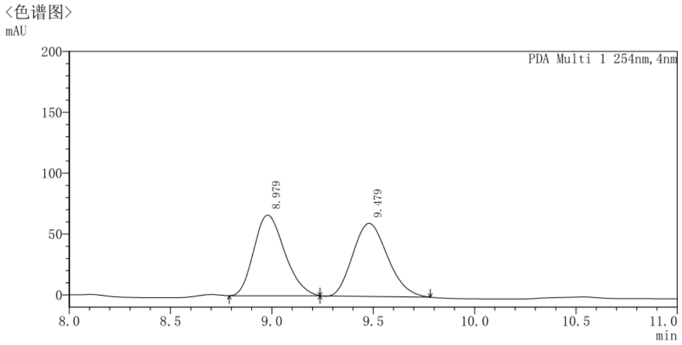


The substrates **2g** (33.2 mg, 94% ee, 0.1 mmol) was dissolved in THF (1 mL) at 0 °C, VinylMgBr (3.0 equiv,0.3 mmol) was added into the solution. After 2 h, the solvent was removed. Then the reaction mixture was purified by silica gel column chromatography to obtain the product **5b** (Yellow oil, 32.8mg, dr > 20:1, 91%, 95 % ee, PE/EA = 5/1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.11 (dd, *J* = 8.3, 5.0 Hz, 1H), 6.86 (td, *J* = 8.7, 2.4 Hz, 1H), 6.80 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.39 (d, *J* = 5.7 Hz, 1H), 5.91 (dd, *J* = 17.0, 10.5 Hz, 1H), 5.32 (d, *J* = 17.1 Hz, 1H), 5.02 (d, *J* = 10.5 Hz, 1H), 4.68 (d, *J* = 5.7 Hz, 1H), 3.65 (s, 1H), 1.47 (s, 3H), 1.22 (d, *J* = 4.0 Hz, 1H), 0.96 (s, 9H), 0.84 (d, *J* = 4.1 Hz, 1H), 0.21 (d, *J* = 7.9 Hz, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 161.9 (d, *J* = 243.3 Hz), 145.2 (d, *J* = 7.2 Hz), 144.3 (d, *J* = 2.3 Hz), 143.3 (d, *J* = 9.6 Hz), 122.2 (d, *J* = 8.3 Hz), 114.4 (d, *J* = 22.6 Hz), 112.5 (d, *J* = 22.5 Hz), 110.9, 105.9, 86.4 (d, *J* = 2.1 Hz), 36.4, 32.7, 31.6, 29.7, 25.6, 18.3, 13.8, -5.1, -5.5. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -117.29. **HRMS** (ESI) [M+Na]$^{+}$ calculated for C21H29FO2SiNa^{+}: 383.1813, found 383.1820.



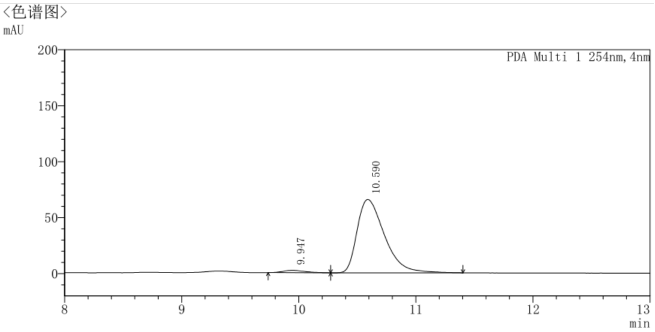
Resolution of enantiomers: Phenomenex INA column, 0.5% IPA-Hexanes, 0.5 mL/min, 254 nm, RT$_{1}$ = 9.9 min, RT$_{2}$ = 10.6 min. **[α]$_{D}^{25}$** = - 80.3 (c 0.5, CH$_{2}$Cl$_{2}$).



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	8.979	702256	66352		52.516	49.558
2	9.479	714770	59995		47.484	50.442
总计		1417027	126347		100.000	100.000

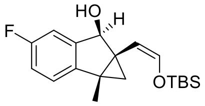


〈峰表〉

PDA Ch1 254nm

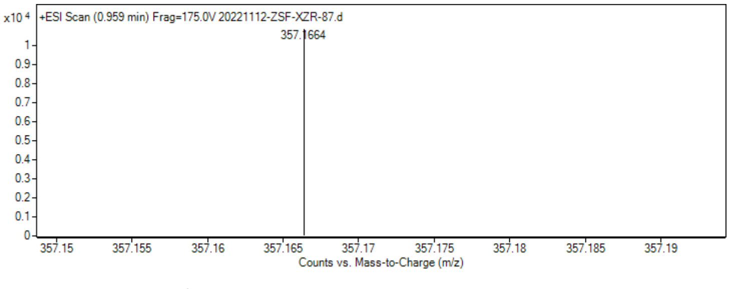
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	9.947	26152	2019		2.985	2.397
2	10.590	1065068	65606		97.015	97.603
总计		1091220	67625		100.000	100.000

(1aR,6S,6aS)-6a-((Z)-2-((tert-butyldimethylsilyl)oxy)vinyl)-4-fluoro-1a-methyl-1,1a,6,6a-tetrahydrocyclopropa[a]inden-6-ol (5c)[7]

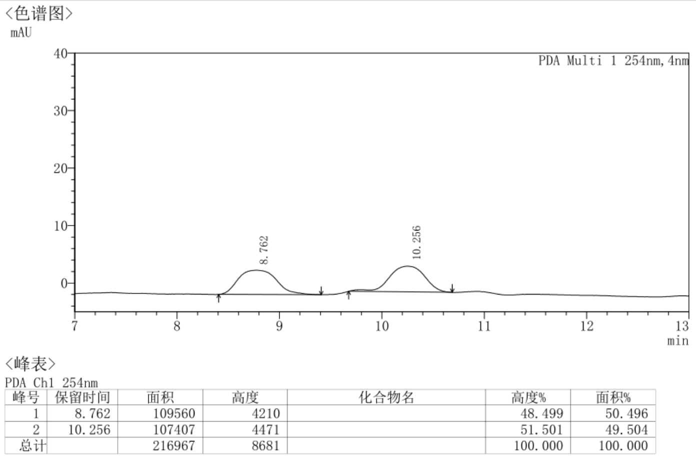


The substrates **2g** (33.2 mg, 94% ee, 0.1 mmol) and $NaBH_4$ (3.0 equiv, 1.0 mmol) were taken in 1mL MeOH at 0 °C. The reaction was monitored by TLC until disappearance of the starting material. Then the reaction mixture was purified by silica gel column chromatography to obtain the product **5c** (Yellow oil, 27.8 mg, dr = 3:1, 83%, 92% ee, PE/EA = 5/1).

^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.24 – 7.14 (m, 0.6H), 7.12 (dd, *J* = 8.2, 5.0 Hz, 1H), 6.99 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.95 (dd, *J* = 8.7, 2.6 Hz, 0.3H), 6.89 (td, *J* = 8.7, 2.5 Hz, 1H), 6.51 (d, *J* = 6.0 Hz, 0.3H), 6.43 (d, *J* = 6.0 Hz, 1H), 5.58 (s, 1H), 4.92 (s, 0.3H), 4.65 (d, *J* = 5.9 Hz, 0.3H), 4.55 (d, *J* = 6.1 Hz, 1H), 3.37 (s, 0.3H), 3.11 (s, 1H), 1.51 (s, 1H), 1.47 (s, 3H), 1.08 (d, *J* = 4.3 Hz, 1H), 1.05 (d, *J* = 4.3 Hz, 0.3H), 0.95 (s, 9H), 0.90 (s, 3H), 0.81 (d, *J* = 4.3 Hz, 1H), 0.56 (d, *J* = 4.3 Hz, 0.3H), 0.22 (d, *J* = 2.7 Hz, 6H), 0.19 (d, *J* = 7.2 Hz, 2H). ^{13}**C NMR** (126 MHz, Chloroform-*d*) δ 162.0 (d, *J* = 242.8 Hz), 161.5 (d, *J* = 242.1 Hz), 145.0 (d, *J* = 7.4 Hz), 144.6 (d, J = 2.1 Hz), 144.6 (d, *J* = 2.5 Hz), 143.3 (d, *J* = 7.4 Hz), 142.0, 141.7, 122.3 (d, *J* = 8.5 Hz), 122.2 (d, *J* = 8.3 Hz), 114.9 (d, *J* = 22.6 Hz), 114.3 (d, *J* = 22.5 Hz), 112.9 (d, *J* = 22.1 Hz), 112.6 (d, *J* = 22.5 Hz), 107.9, 105.5, 80.0 (d, *J* = 2.1 Hz), 77.7 (d, *J* = 2.3 Hz), 38.3, 34.6, 33.8, 33.6, 33.5, 29.2, 25.6, 25.5, 18.3, 18.0, 14.9, 14.0, -5.2, -5.41, -5.42. ^{19}**F NMR** (471 MHz, Chloroform-*d*) δ -117.18, -117.76. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{19}H_{27}FO_2SiNa^+$: 357.1656, found 357.1664.

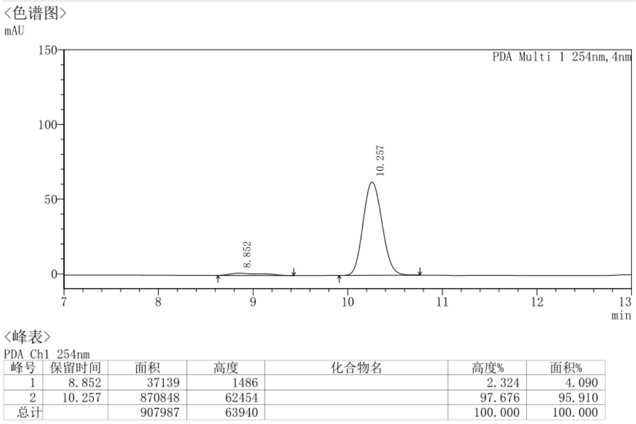


Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 1.0 mL/min, 254 nm, RT_1 = 8.9 min, RT_2 = 10.2 min. **[α]$_D$^{25}** = - 5.8 (c 0.5, CH_2Cl_2).



<峰表>
PDA Ch1 254nm

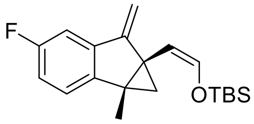
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	8.762	109560	4210		48.499	50.496
2	10.256	107407	4471		51.501	49.504
总计		216967	8681		100.000	100.000



<峰表>
PDA Ch1 254nm

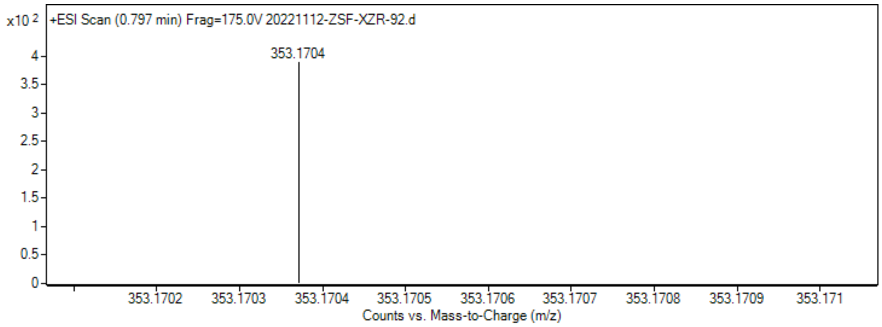
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	8.852	37139	1486		2.324	4.090
2	10.257	870848	62454		97.676	95.910
总计		907987	63940		100.000	100.000

Tert-butyl(((Z)-2-((1aR,6aR)-4-fluoro-1a-methyl-6-methylene-1a,6-dihydrocyclopropa[a]inden-6a(1H)-yl)vinyl)oxy)dimethylsilane (5d)[8]

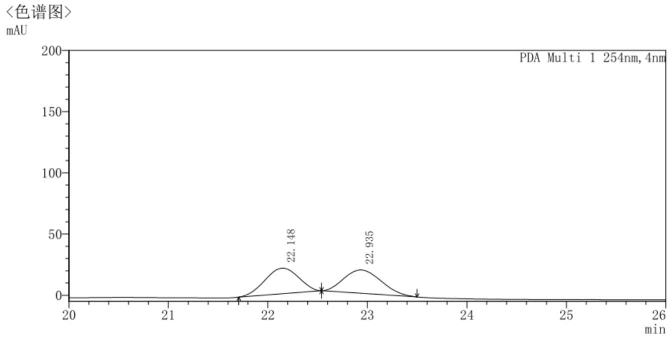


The $MePh_3PBr$ (1.5 equiv, 1.0 mmol) was dissolved in THF (1 mL) at -78 °C, then n-BuLi (1.5 equiv,0.15 mmmol, 1.6 mol/L) was added dropwise. After 2 h, the substrates **2g** (33.2mg, 94% ee, 0.1 mmol) in THF (1 mL) was added into the mixture. The reaction was monitored by TLC until disappearance of the starting material. Then the reaction mixture was purified by silica gel column chromatography to obtain the product **5d** (Colorless oil, 23.8 mg, 92%, 92%ee, PE/EA = 30/1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.15 (dd, *J* = 8.3, 5.1 Hz, 1H), 7.06 (dd, *J* = 9.1, 2.5 Hz, 1H), 6.86 (td, *J* = 8.7, 2.5 Hz, 1H), 6.45 (d, *J* = 6.0 Hz, 1H), 5.44 (s, 1H), 5.15 (s, 1H), 4.56 (d, *J* = 5.9 Hz, 1H), 1.56 (d, *J* = 4.1 Hz, 1H), 1.45 (s, 3H), 0.92 (d, *J* = 4.0 Hz, 1H), 0.84 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 161.7 (d, *J* = 241.6 Hz), 152.7 (d, *J* = 3.3 Hz), 146.8 (d, *J* = 2.2 Hz), 142.7, 140.0 (d, *J* = 7.9 Hz), 122.8 (d, *J* = 8.7 Hz), 114.4 (d, *J* = 22.9 Hz), 107.8 (d, *J* = 22.8 Hz), 105.5, 104.7, -5.4, -5.5. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -118.26. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{20}H_{27}FOSiNa^+$: 353.1707, found 353.1704.



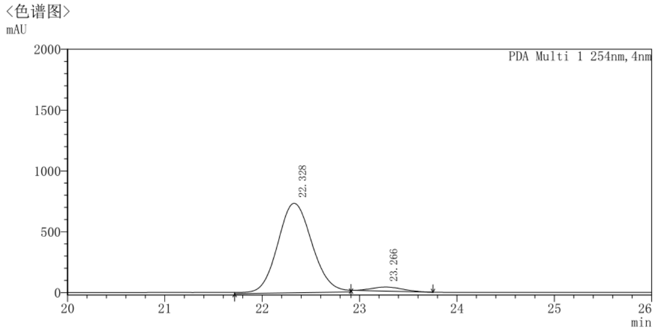
Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 1.0 mL/min, 254 nm, RT_1 = 22.2 min, RT_2 = 23.2 min. **$[\alpha]_D^{25}$** = - 11.3 (c 0.5, CH_2Cl_2).



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	22.148	493064	20888		52.317	49.932
2	22.935	494402	19038		47.683	50.068
总计		987467	39926		100.000	100.000

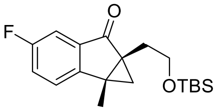


〈峰表〉

PDA Ch1 254nm

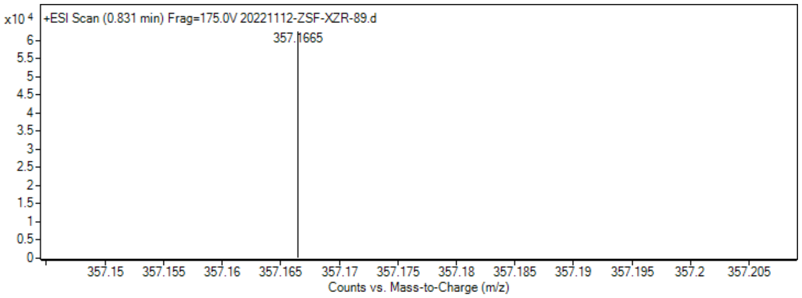
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	22.328	18176476	735634		95.710	96.135
2	23.266	730707	32975		4.290	3.865
总计		18907184	768608		100.000	100.000

(1aR,6aS)-6a-(2-((tert-butyldimethylsilyl)oxy)ethyl)-4-fluoro-1a-methyl-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (5e) [9]

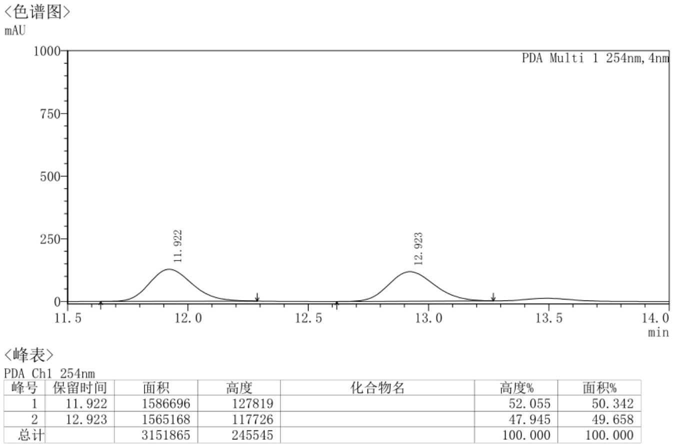


A flame dried reaction vessel was charged with 10% Pd/C (10 mol%), degassed and backfilled with hydrogen (1 atm). 1 mL EA were added and **2g** (33.2 mg, 94% ee, 0.1mmol) was introduced dropwise via syringe. The reaction was stirred at room temperature overnight. The reaction was monitored by TLC until disappearance of the starting material.The mixture was purified by silica gel column chromatography to obtain the product **5e** (Colorless oil, 24.1 mg, 72%, 94% ee, PE/EA = 20/1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.49 (dd, *J* = 8.3, 4.4 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.30 (td, *J* = 8.6, 2.6 Hz, 1H), 4.06 (dt, *J* = 10.1, 7.2 Hz, 1H), 3.91 (ddd, *J* = 10.0, 7.8, 5.7 Hz, 1H), 2.46 (ddd, *J* = 13.7, 7.6, 5.7 Hz, 1H), 2.02 (dt, *J* = 14.4, 7.2 Hz, 1H), 1.78 (s, 3H), 1.64 (d, *J* = 4.1 Hz, 1H), 1.39 (d, *J* = 4.9 Hz, 2H), 0.96 (d, *J* = 0.9 Hz, 8H), 0.14 (s, 3H), 0.12 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 202.9 (d, *J* = 2.7 Hz), 161.9 (d, *J* = 246.4 Hz), 152.9 (d, *J* = 2.3 Hz), 135.1 (d, *J* = 7.0 Hz), 123.5 (d, *J* = 7.9 Hz), 120.5 (d, *J* = 23.4 Hz), 110.7 (d, *J* = 22.4 Hz), 60.8, 44.0, 39.7, 29.6, 25.9, 18.6, 13.0, -5.45, -5.46. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -115.55. **HRMS** (ESI) [M+Na]$^+$ calculated for $C_{19}H_{27}FO_2SiNa^+$: 357.1656, found 357.1665.



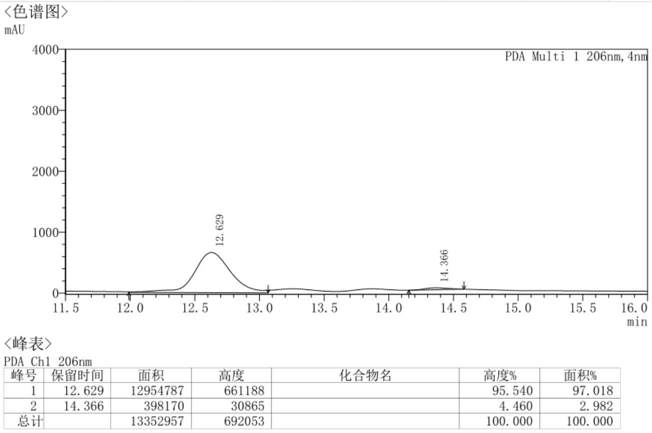
Resolution of enantiomers: DAICEL Chiralcel® ODH column, 0.5% IPA-Hexanes, 0.5 mL/min, 254 nm, RT$_1$ = 12.6 min, RT$_2$ = 14.3 min. **[α]$_D^{25}$** = + 14.0 (c 0.5, CH_2Cl_2).



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	11.922	1586696	127819		52.055	50.342
2	12.923	1565168	117726		47.945	49.658
总计		3151865	245545		100.000	100.000

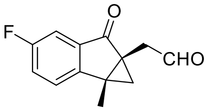


〈峰表〉

PDA Ch1 206nm

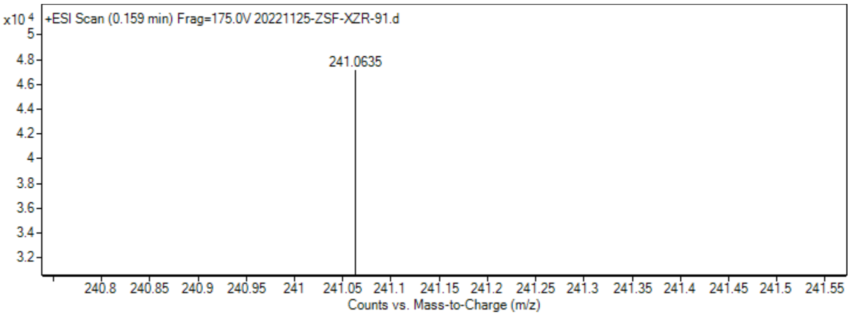
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	12.629	12954787	661188		95.540	97.018
2	14.366	398170	30865		4.460	2.982
总计		13352957	692053		100.000	100.000

2-((1aR,6aS)-4-fluoro-1a-methyl-6-oxo-1a,6-dihydrocyclopropa[a]inden-6a(1H)-yl)acetaldehyde (5f) [10]

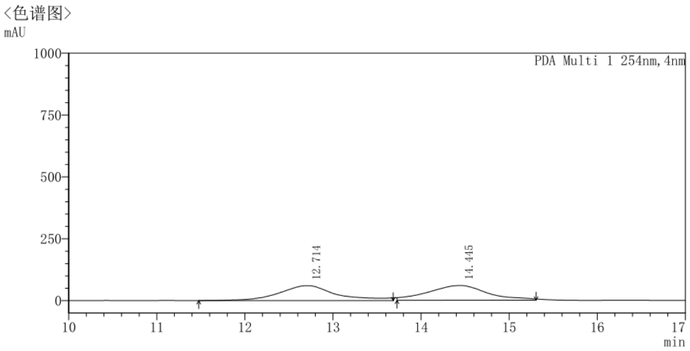


To an acetonitrile solution of **2g** (33.2mg, 94% ee, 0.1 mmol) in Schlenk tube with a magnetic bar was added $CuCl_2$ (0.5 mmol, 5.0 equiv) and H_2O (0.5 mmol, 5.0 equiv) at 40 °C under N_2. The sealed tube was then stirred at 40 °C under nitrogen atmosphere overnight. After the reaction completed (monitored by TLC), it was diluted with water and extracted with EA. The combined organics were washed with brinem dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting residue was flash chromatographed on silica gel to afford the product **5f** (Yellow solid, MP: 98-100°C, 21.0 mg, 96%, 94% ee, PE/EA = 5/1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.85 (s, 1H), 7.41 (dd, *J* = 8.3, 4.4 Hz, 1H), 7.31 (dd, *J* = 7.6, 2.5 Hz, 1H), 7.22 (td, *J* = 8.6, 2.6 Hz, 1H), 3.37 (d, *J* = 18.5 Hz, 1H), 2.68 (d, *J* = 18.5 Hz, 1H), 1.64 (d, *J* = 4.4 Hz, 1H), 1.58 (s, 3H), 1.27 (d, *J* = 4.5 Hz, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 201.6 (d, *J* = 2.5 Hz), 199.1, 162.1 (d, *J* = 247.1 Hz), 152.4, 134.5 (d, *J* = 7.0 Hz), 123.8 (d, *J* = 7.9 Hz), 120.9 (d, *J* = 23.4 Hz), 111.2 (d, *J* = 22.5 Hz), 42.9, 41.3, 37.2, 31.3, 12.8. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -114.84. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{13}H_{11}FO_2Na^+$: 241.0635, found 241.0635.

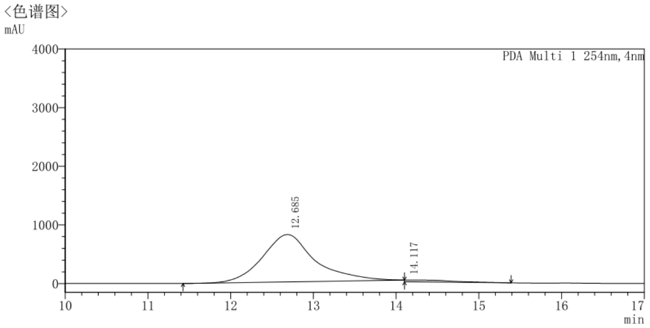


Resolution of enantiomers: DAICEL Chiralcel® NC column, 60% (W = 0.1%) Trisodium phosphate anhydrous-Acetonitrile, 0.5 mL/min, 254 nm, RT_1 = 12.7 min, RT_2 = 14.2 min. **$[\alpha]_D^{25}$** = -66.3(c 0.5, CH_2Cl_2).



〈峰表〉
PDA Ch1 254nm

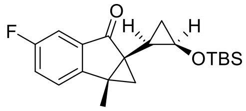
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	12.714	2749392	60464		49.708	50.503
2	14.445	2781694	59259		50.292	49.497
总计		5531086	119722		100.000	100.000



〈峰表〉
PDA Ch1 254nm

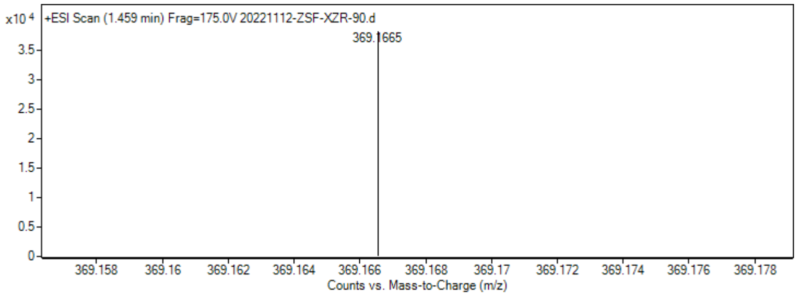
峰号	保留时间	面积	高度	化合物名	面积%	高度%
1	12.685	35616708	806421		96.777	96.550
2	14.117	1185996	28815		3.223	3.450
总计		36802704	835236		100.000	100.000

(1aR,6aS)-6a-((1S,2R)-2-((tert-butyldimethylsilyl)oxy)cyclopropyl)-4-fluoro-1a-methyl-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one (5g) [11]

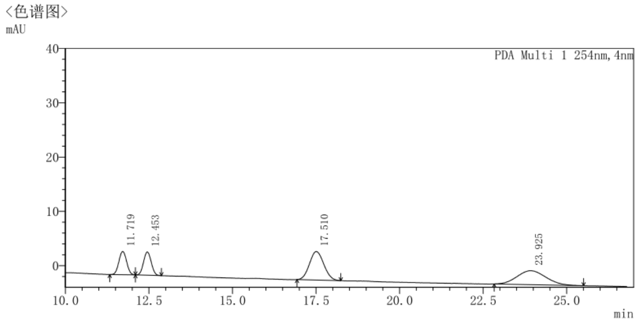


To a hexane solution of **2g** (33.2mg, 94% ee, 0.1 mmol) in Schlenk tube with a magnetic bar was added $ZnEt_2$ (0.22 mmol, 2.2 equiv) and CH_2I_2 (0.22 mmol, 2.2 equiv) at 0 °C under N_2. The sealed tube was then stirred at 0 °C under nitrogen atmosphere overnight. After the reaction completed (monitored by TLC), it was diluted with water and extracted with Et_2O. The combined organics were washed with brinem dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting residue was flash chromatographed on silica gel to afford the product **5f** (Yellow oil, 31.8 mg, 92%, dr = 2:1, major: 94% ee, minor: 92% ee, PE/EA = 20/1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (ddd, *J* = 8.2, 4.5, 1.1 Hz, 1.5H), 7.40 – 7.35 (m, 1H), 7.33 (dd, *J* = 7.7, 2.5 Hz, 0.5H), 7.25 (ddt, *J* = 11.0, 5.3, 2.5 Hz, 1.5H), 3.65 (tt, *J* = 6.5, 3.5 Hz, 1.5H), 1.93 (d, *J* = 3.8 Hz, 1H), 1.83 (s, 3H), 1.77 (s, 1.5H), 1.71 (d, *J* = 4.6 Hz, 1.5H), 1.47 (d, *J* = 3.5 Hz, 1H), 1.45 (d, *J* = 4.7 Hz, 0.5H), 1.35 – 1.27 (m, 1.5H), 1.08 – 0.94 (m, 3H), 0.85 (s, 9H), 0.74 (s, 4.5H), 0.15 (s, 3H), 0.15 (s, 3H), 0.12 (s, 1.5H), 0.09 (s, 1.5H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 203.8 (d, *J* = 2.6 Hz), 201.8 (d, *J* = 2.7 Hz), 161.8 (d, *J* = 246.0 Hz), 161.8 (d, *J* = 245.7 Hz), 152.9, 145.4, 135.9 (d, *J* = 7.1 Hz), 135.0 (d, *J* = 6.9 Hz), 123.2 (d, *J* = 6.1 Hz), 123.2 (d, *J* = 6.0 Hz), 120.2 (d, *J* = 23.4 Hz), 120.1 (d, *J* = 23.3 Hz), 50.0, 48.7, 44.7, 42.3, 41.2 (d, *J* = 1.4 Hz), 38.0 (d, *J* = 1.1 Hz), 33.5, 31.5, 25.5, 25.3, 17.8, 17.6, 14.6, 13.2, 12.9, 12.8, 11.3, 9.8, -5.06, -5.11, -5.4, -5.5. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -115.94, -116.18. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{20}H_{27}FO_2SiNa^+$: 369.1656, found 369.1665.



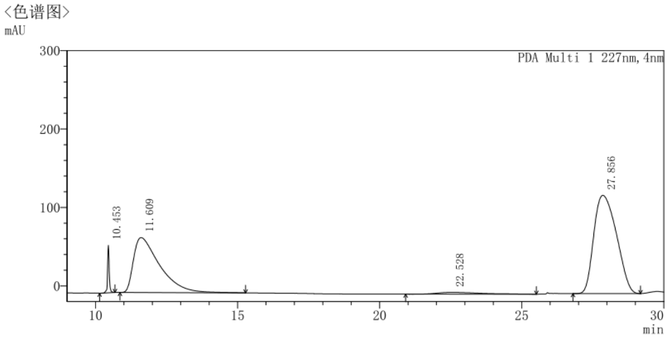
Resolution of enantiomers: DAICEL Chiralcel® IC column, 0.5% IPA-Hexanes, 0.5 mL/min, 254 nm, RT_1 = 10.4 min, RT_2 = 11.6 min, RT_2 = 22.5 min, RT_2 = 27.8 min. **$[\alpha]_D^{25}$** = + 5.3. (c 0.5, CH_2Cl_2).



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	11.719	68695	4262		26.051	15.300
2	12.453	68373	4273		26.116	15.229
3	17.510	156878	5239		32.017	34.941
4	23.925	155032	2588		15.817	34.530
总计		448978	16362		100.000	100.000

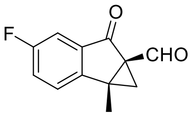


〈峰表〉

PDA Ch1 227nm

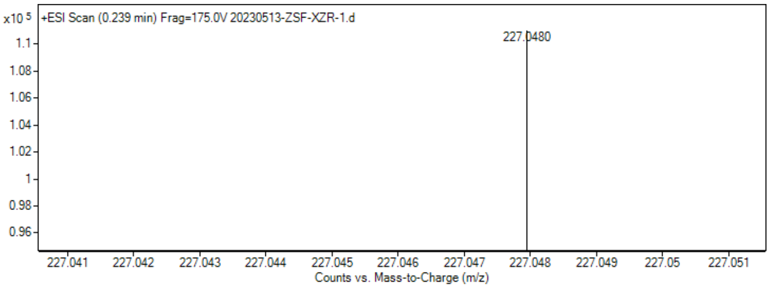
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	10.453	241653	60501		23.442	2.022
2	11.609	4513272	70116		27.168	37.757
3	22.528	238974	2259		0.875	1.999
4	27.856	6959695	125210		48.515	58.223
总计		11953594	258086		100.000	100.000

(1aR,6aR)-4-fluoro-1a-methyl-6-oxo-1a,6-dihydrocyclopropa[a]indene-6a(1H)-carbaldehyde(5h) [12]



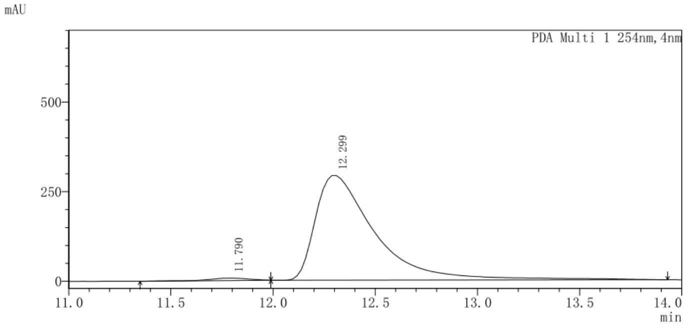
To a solution of **2g** (33.2mg, 94% ee, 0.1 mmol) in 1,2-dichloromethane(1 mL) was cooled to -78°C and ozone was bubbled into the reaction mixture until a pale color was observed. The excess ozone was discharged by nitrogen stream for 5 min, and then dimethyl sulfide (30 uL, 0.4 mmol) and CH_2Cl_2 were added. The mixture was stirred at room temperature for 6 h, and then saturated NaCl solution was added. The mixture was extracted with CH_2Cl_2 and the organic phase was dried over anhydrous $NaSO_4$, filtered, and the solvent was removed by rotary evaporator. The resulting residue was flash chromatography (PE: EA = 5:1) on silica gel to afford the product **5h**. (Yellow solid, 15.1 mg, 74%, 97% ee, PE/EA = 5/1, M.P: 80-81°C).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.29 (s, 1H), 7.43 (dd, *J* = 8.9, 4.3 Hz, 1H), 7.38 (dt, *J* = 7.5, 2.0 Hz, 1H), 7.28 (tt, *J* = 8.6, 2.0 Hz, 1H), 2.35 (d, *J* = 4.1 Hz, 1H), 2.08 (d, *J* = 4.1 Hz, 1H), 1.75 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 197.8 (d, *J* = 2.8 Hz), 195.3, 162.6 (d, *J* = 248.9 Hz), 150.1 (d, *J* = 2.5 Hz), 134.4 (d, *J* = 7.4 Hz), 124.3 (d, *J* = 8.0 Hz), 121.7 (d, *J* = 23.5 Hz), 111.3 (d, *J* = 22.7 Hz), 49.9, 47.8, 44.6, 12.0. **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -112.77. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{12}H_9FO_2Na^+$: 227.0479, found 227.0480.



Resolution of enantiomers: DAICEL Chiralcel® ODH column, 2% IPA-Hexanes, 0.8 mL/min, 254 nm, RT_1 = 11.8 min, RT_2 = 12.4 min. **$[\alpha]_D^{25}$** = + 16.5. (c 0.5, CH_2Cl_2).

〈色谱图〉

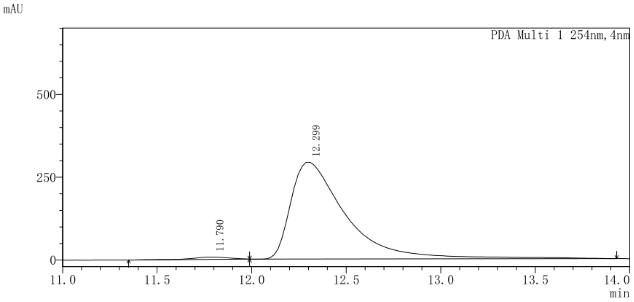


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	11.790	95341	6931		2.320	1.579
2	12.299	5941547	291834		97.680	98.421
总计		6036887	298765		100.000	100.000

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

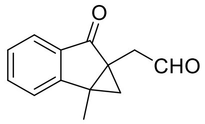
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	11.790	95341	6931		2.320	1.579
2	12.299	5941547	291834		97.680	98.421
总计		6036887	298765		100.000	100.000

6. Rh-catalyzed preliminary experiments

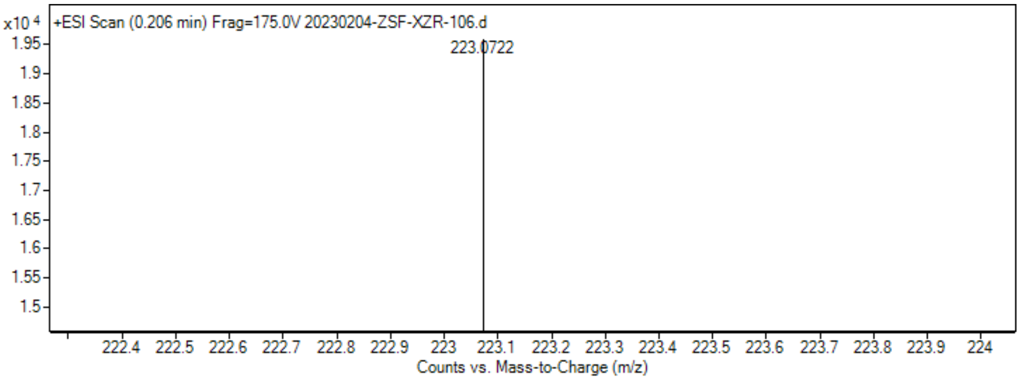
General procedure for $Rh_2(OPiv)_4$-catalyzed preliminary experiments:

To 1,2-dichloroethane solution of **1** (0.1 mmol, 1 mL) in Schlenk tube with a magnetic bar was added $Rh_2(OPiv)_4$ (0.002 mmol, 2 mol%, 1.3 mg) at room temperature under N_2. The sealed tube was then stirred at 30 °C under nitrogen atmosphere for 48 h. The mixture was then concentrated and the residue was purified by chromatography on silica gel to afford the desired product **2**.

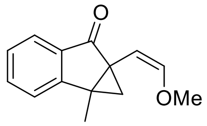
2-(1a-methyl-6-oxo-1a,6-dihydrocyclopropa[a]inden-6a(1H)-yl)acetaldehyde(2b)



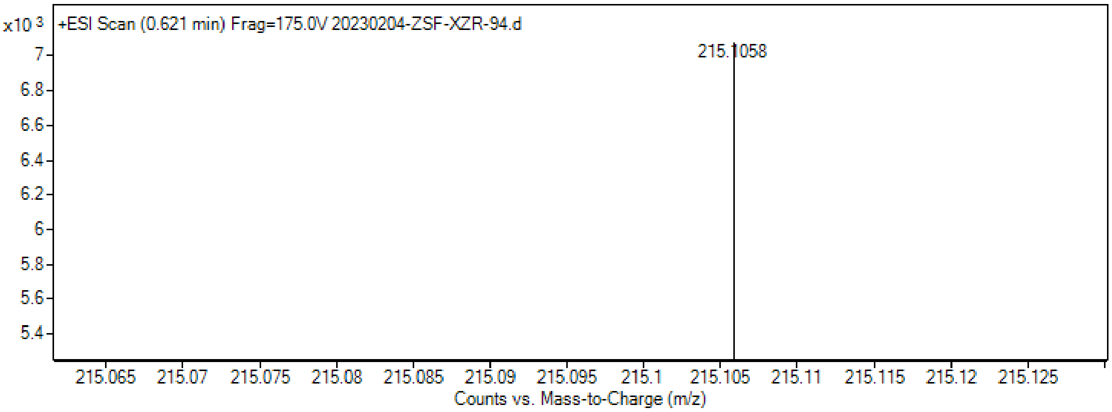
Colorless liquid, 7.0 mg, 35%, purified by chromatography (PE/EA = 5/1, Rf = 0.6); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.87 (s, 1H), 7.66 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.52 (td, *J* = 7.4, 1.2 Hz, 1H), 7.45 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.30 (td, *J* = 7.4, 1.1 Hz, 1H), 3.30 (dd, *J* = 18.2, 1.2 Hz, 1H), 2.70 (dd, *J* = 18.2, 1.4 Hz, 1H), 1.64 (d, *J* = 4.3 Hz, 1H), 1.60 (s, 3H), 1.27 (d, *J* = 4.3 Hz, 1H).). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 202.8, 199.5, 156.9, 134.0, 132.5, 127.1, 124.7, 122.5, 42.8, 41.1, 36.6, 31.6, 12.7. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{13}H_{12}O_2Na^+$:223.0729, found 223.0722.



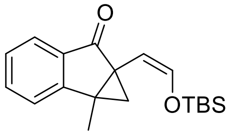
(Z)-6a-(2-methoxyvinyl)-1a-methyl-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one(2c)



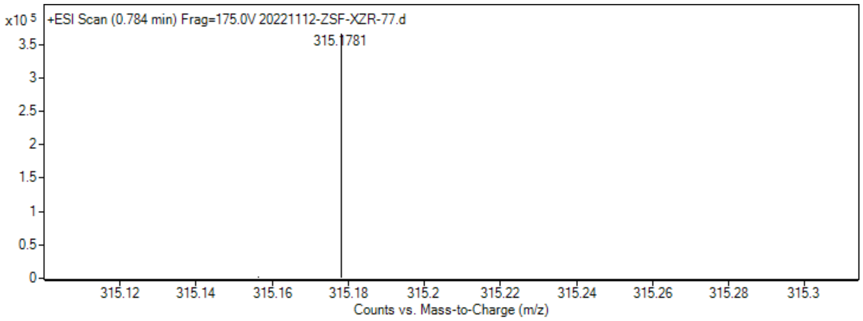
Colorless liquid, 10.1 mg, 47%, purified by chromatography (PE/EA = 2/1, Rf = 0.5); **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 6.3 Hz, 1H), 6.27 (d, *J* = 6.2 Hz, 1H), 4.49 (d, *J* = 6.2 Hz, 1H), 3.57 (s, 3H), 1.73 (d, *J* = 4.0 Hz, 1H), 1.68 (d, *J* = 4.0 Hz, 1H), 1.59 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 203.1, 157.3, 151.7, 133.5, 133.0, 126.6, 124.7, 122.3, 97.3, 60.0, 44.9, 40.3, 34.7, 12.9. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{14}H_{14}O_2Si^+$: 215.1067, found 215.1058.



(Z)-6a-(2-((tert-butyldimethylsilyl)oxy)vinyl)-1a-methyl-1a,6a-dihydrocyclopropa[a]inden-6(1H)-one(2d)

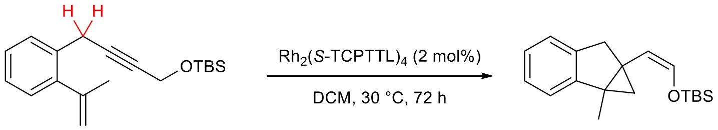


Yellow liquid, 23.6 mg, 75%, purified by chromatography (PE/EA = 20/1, Rf = 0.4); ^{1}**H NMR** (500 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.24 (dd, *J* = 14.7, 7.3 Hz, 1H), 6.56 (d, *J* = 5.4 Hz, 1H), 4.62 (d, *J* = 5.5 Hz, 1H), 1.73 (d, *J* = 3.9 Hz, 1H), 1.67 (d, *J* = 4.0 Hz, 1H), 1.57 (s, 3H), 0.70 (s, 9H), 0.08 (s, 3H), 0.05 (s, 3H). ^{13}**C NMR** (126 MHz, Chloroform-*d*) δ 203.0, 157.4, 144.2, 133.4, 126.5, 124.5, 122.2, 101.0, 44.2, 40.4, 34.3, 25.2, 17.7, 13.1, -5.4, -5.5. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{19}H_{27}O_2Si^+$: 315.1775, found 315.1781.



7. General procedure for mechanism experiments:

A) Control experiments

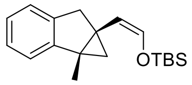


3q

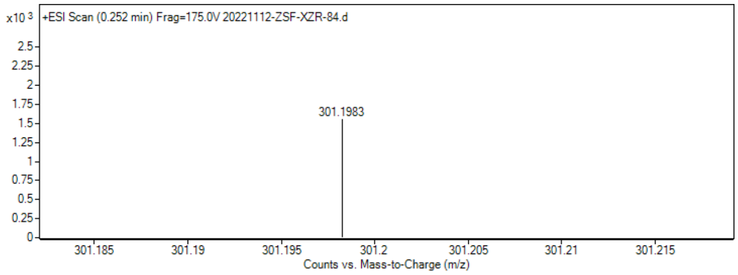
4q, 67%, 94% ee

To 1,2-dichloromethane solution of substrate **3q** (0.05 mmol, 0.5 mL) in Schlenk tube with a magnetic bar was added Rh_2(*S*-TCPTTL)$_4$ (0.01 mmol, 2 mol%, 2 mg), the catalyst was dissolved in dichloromethane) at 30 °C under N_2. The sealed tube was then stirred at 30 °C under nitrogen atmosphere for 48-72 h. The mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to afford the desired product **4q**.

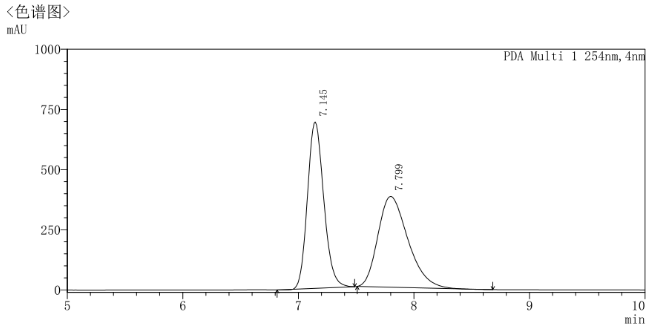
Tert-butyldimethyl(((Z)-2-((1aS,6aS)-1a-methyl-1a,6-dihydrocyclopropa[a]inden-6a(1H)-yl)vinyl)oxy)silane (4q)



Yellow liquid, 10.1 mg, 67%, 94% ee, purified by chromatography (PE/EA = 50/1, Rf = 0.5); ^{1}**H NMR** (400 MHz, Chloroform-d) δ 7.16 – 6.88 (m, 4H), 6.24 (d, *J* = 6.1 Hz, 1H), 4.39 (d, *J* = 6.1 Hz, 1H), 3.21 (d, *J* = 17.1 Hz, 1H), 3.05 (d, *J* = 17.1 Hz, 1H), 1.37 (s, 3H), 1.16 (d, *J* = 4.1 Hz, 1H), 0.81 (s, 9H), 0.46 (d, *J* = 4.1 Hz, 1H), 0.06 (s, 3H), 0.05 (s, 3H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 150.2, 141.7, 140.7, 125.6, 125.2, 124.8, 121.7, 109.4, 41.4, 35.7, 30.3, 30.0, 25.6, 18.1, 14.9, -5.38, -5.40. **HRMS** (ESI) $[M+H]^+$ calculated for $C_{19}H_{29}OSi^+$: 301.1982, found 301.1983.

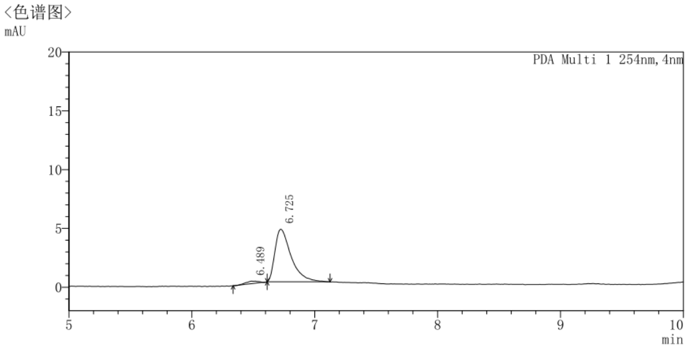


Resolution of enantiomers: DAICEL Chiralcel® OJH column, 0% IPA-Hexanes, 0.5 mL/min, 254 nm, RT_1 = 6.5 min, RT_2 = 6.8 min. **$[\alpha]_D^{25}$** = + 46.0 (c 0.5, CH_2Cl_2).



〈峰表〉
PDA Ch1 254nm

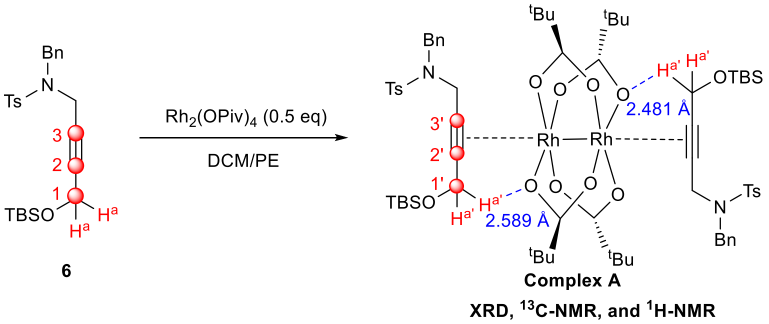
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	7.145	6781669	691835		64.710	49.862
2	7.799	6819239	377295		35.290	50.138
总计		13600908	1069129		100.000	100.000



〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	6.489	1361	200		4.280	3.223
2	6.725	40859	4464		95.720	96.777
总计		42220	4664		100.000	100.000

B) Cooperative weak hydrogen bonding



The substrate **6** (11.08 mg, 0.025 mmol) was mixed up with $Rh_2(OPiv)_4$ (15.6 mg, 0.0125 mmol), the mixture was dissolved in DCM/PE (0.5mL: 0.5 mL) as mixed solvent. The resulting solution was subjected to sonication and Pasteur pipette filtration followed by slow evaporation of the solvent to yield the crystal of **complex A**, green prism.

The NMR spectrum of compound 6 and complex A

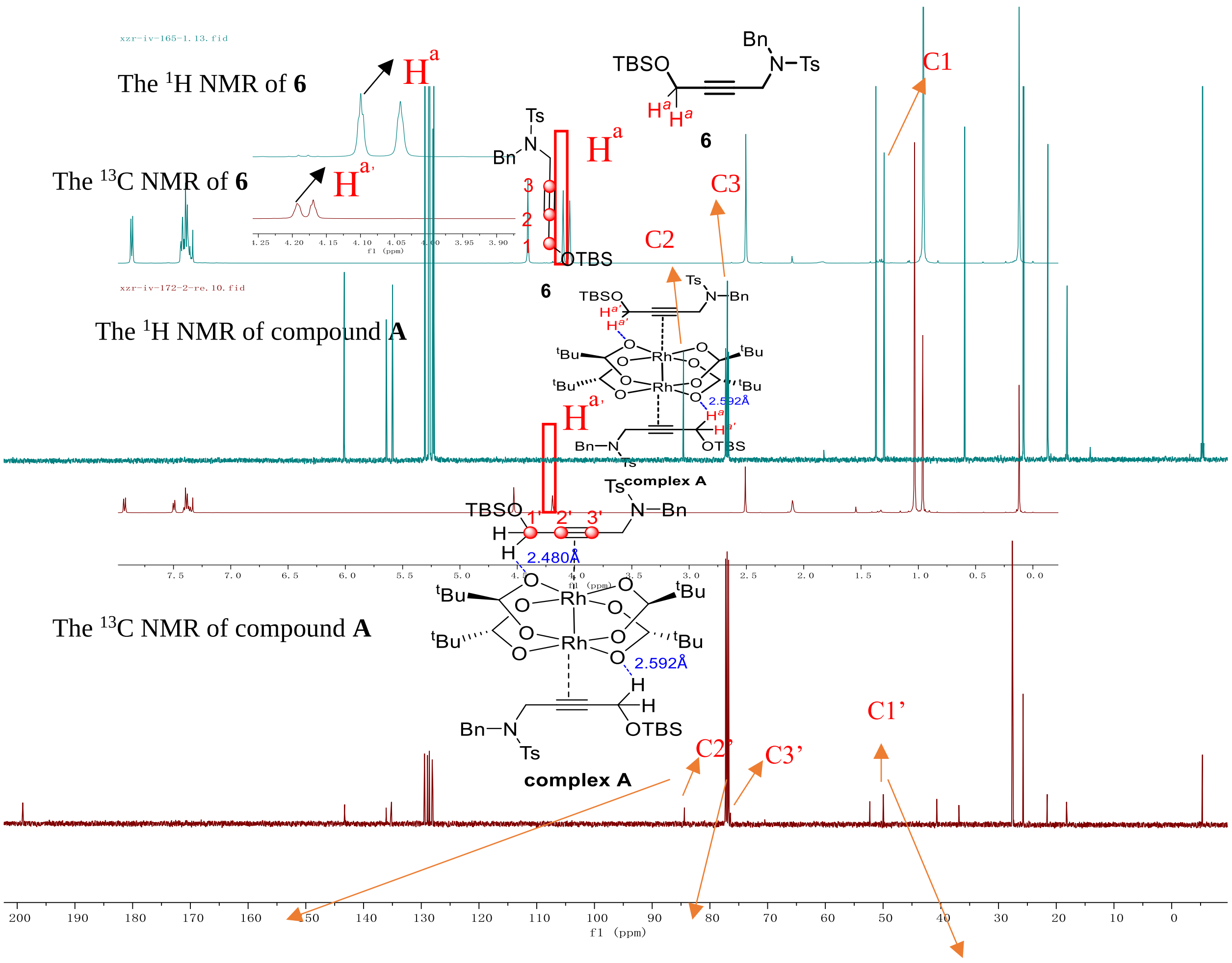
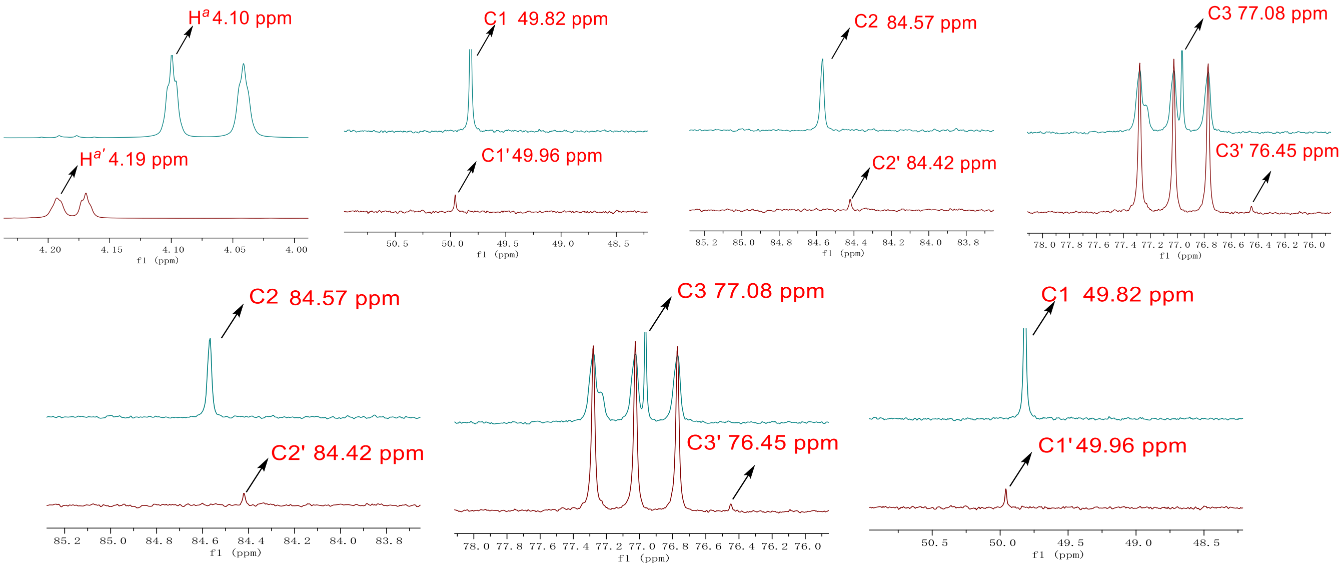
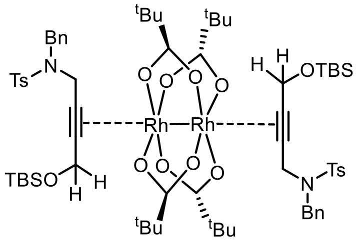


Figure S1. The NMR comparison between **Compound 6** and **complex A**.



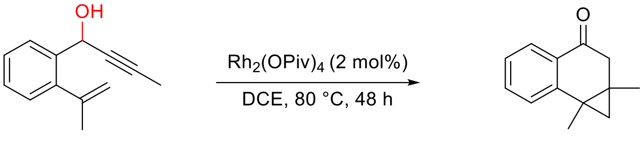


Complex A

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 – 7.90 (m, 2H), 7.55 – 7.47 (m, 2H), 7.43 – 7.34 (m, 4H), 4.53 (s, 2H), 4.19 (d, *J* = 2.0 Hz, 2H), 4.17 (t, *J* = 1.9 Hz, 2H), 2.51 (s, 3H), 1.03 (s, 18H), 0.96 (s, 9H), 0.12 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 199.03, 136.08, 135.17, 129.44, 128.93, 128.60, 128.11, 127.99, 84.42, 76.45, 52.30, 49.96, 40.69, 36.86, 27.60, 25.74, 21.56, 18.23, -5.32.

C) The origin of regioselectivity

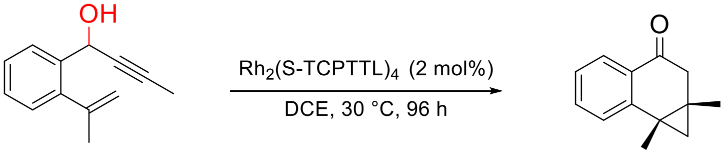
(*Z*)-tert-butyldimethyl((2-(1a-methyl-1a,6-dihydrocyclopropa[a]inden-6a(1H)-yl)vinyl)oxy)silane (4s)



3s

4s, 50%

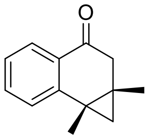
To 1,2-dichloroethane solution of substrate **3s** (0.1 mmol, 1 mL) in Schlenk tube with a magnetic bar was added Rh$_2$(OPiv)$_4$ (0.002 mmol, 2 mol%, 1.3 mg) at 30 °C under N$_2$, the catalyst was dissolved in dichloroethane), no product was observed. Then, elevating temperature to 80 °C for 48 h, the reaction proceeded smoothly. After the reaction completed, the mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to afford the desired product **4s**.



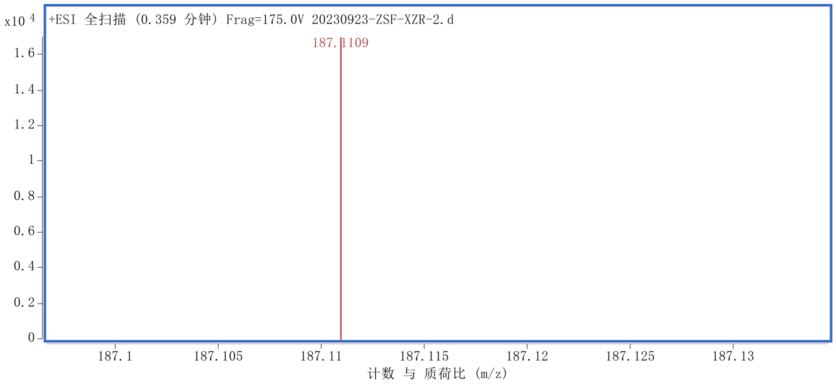
3s

4s, 43% , 34% ee

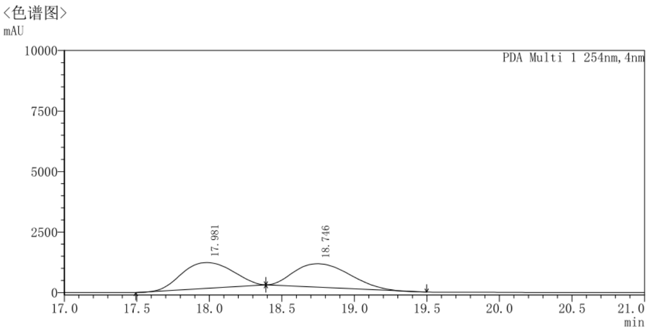
To 1,2-dichloromethane solution of substrate **3s** (0.1 mmol, 1 mL) in Schlenk tube with a magnetic bar was added Rh$_2$(S-TCPTTL)$_4$ (0.002 mmol, 2 mol%, 4.0 mg) at 30 °C under N$_2$, the catalyst was dissolved in dichloromethane), the reaction proceeded smoothly. After the reaction completed, the mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to afford the desired product **4s**.



Yellow liquid, 8.0 mg, 43%, 34% ee, purified by chromatography (PE/EA = 10/1, Rf = 0.6); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.59 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.52 (td, *J* = 7.6, 1.6 Hz, 1H), 7.30 – 7.20 (m, 1H), 2.96 (d, *J* = 17.4 Hz, 1H), 2.71 (dd, *J* = 17.4, 1.2 Hz, 1H), 1.61 (s, 3H), 1.40 (s, 3H), 0.95 (dd, *J* = 4.7, 1.2 Hz, 1H), 0.44 (d, *J* = 4.7 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 197.7, 149.9, 133.3, 130.5, 127.1, 125.8, 125.1, 44.4, 33.9, 23.2, 21.0, 21.0, 16.7. **HRMS** (ESI) [M+H]$^+$ calculated for $C_{13}H_{15}O^+$: 187.1118, found 187.1109.



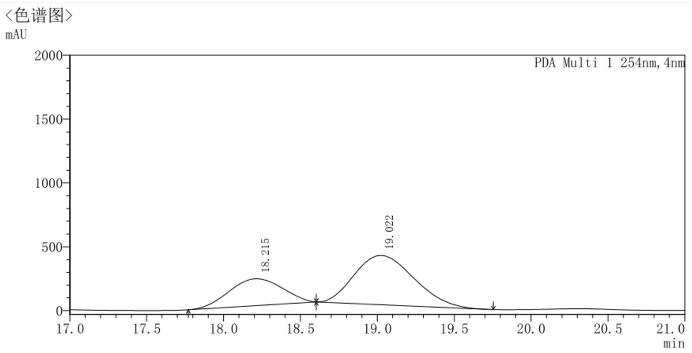
Resolution of enantiomers: Phenomenex INA column, 2% IPA-Hexanes, 0.3 mL/min, 254 nm, RT$_1$ = 18.2 min, RT$_2$ = 19.0 min.



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	17.981	26180828	1063958		52.347	50.364
2	18.746	25801877	968567		47.653	49.636
总计		51982705	2032525		100.000	100.000

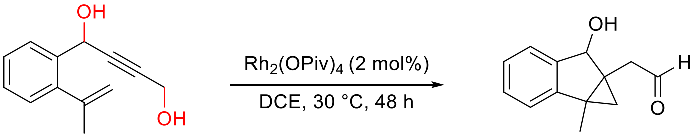


<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	18.215	5095661	210444		35.282	32.917
2	19.022	10384794	386012		64.718	67.083
总计		15480455	596457		100.000	100.000

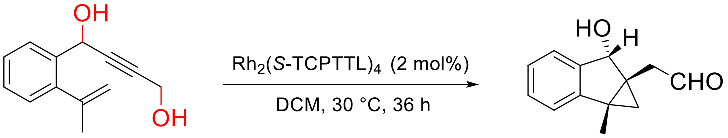
2-(6-hydroxy-1a-methyl-1a,6-dihydrocyclopropa[a]inden-6a(1H)-yl)acetaldehyde (4t)



3t

4t, 80%, dr > 20:1

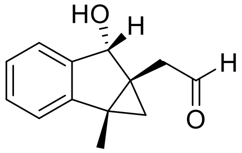
To 1,2-dichloroethane solution of substrate **3t** (0.1 mmol, 1 mL) in Schlenk tube with a magnetic bar was added Rh$_2$(OPiv)$_4$ (0.002 mmol, 2 mol%, 1.3 mg) at 30 °C for 48 h under N$_2$, the catalyst was dissolved in dichloroethane). After the reaction completed, the mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to afford the desired product **4t**.



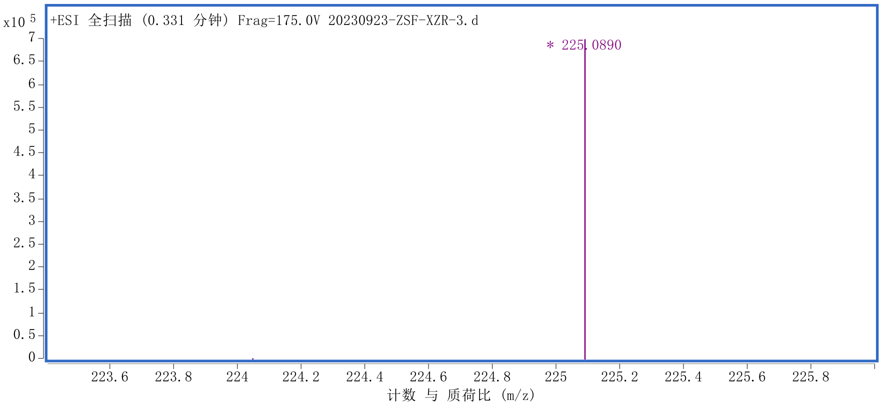
3t

4t, 86%, *dr* > 20:1, rac

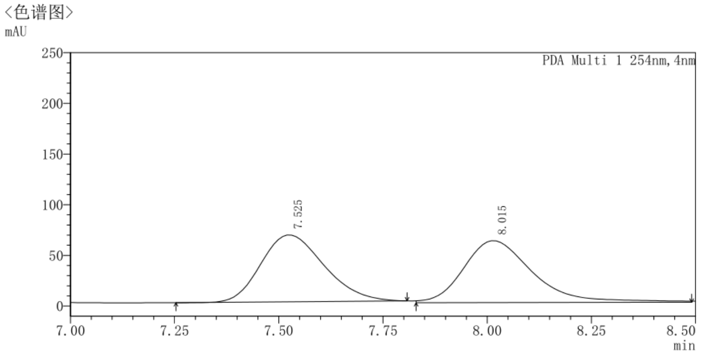
To 1,2-dichloromethane solution of substrate **3t** (0.1 mmol, 1 mL) in Schlenk tube with a magnetic bar was added $Rh_2(OPiv)_4$ (0.002 mmol, 2 mol%, 1.3 mg) at 30 °C for 36 h under N_2, the catalyst was dissolved in dichloromethane). After the reaction completed, the mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to afford the desired product **4t**.



Yellow liquid, 17.4 mg, 86%, dr > 20:1, 0% ee purified by chromatography (PE/EA = 5/1, Rf = 0.5); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.98 (d, *J* = 1.1 Hz, 1H), 7.32 – 7.17 (m, 5H), 5.33 (s, 1H), 2.94 (d, *J* = 18.6 Hz, 1H), 2.79 (dd, *J* = 18.7, 1.3 Hz, 1H), 1.50 (s, 3H), 1.07 (d, *J* = 4.8 Hz, 1H), 0.66 (d, *J* = 4.7 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 203.1, 148.4, 141.3, 128.7, 126.6, 125.5, 121.8, 80.1, 47.0, 32.4, 30.6, 27.5, 13.9. **HRMS** (ESI) $[M+Na]^+$ calculated for $C_{13}H_{14}ONa^+$: 225.0886, found 225.0890.

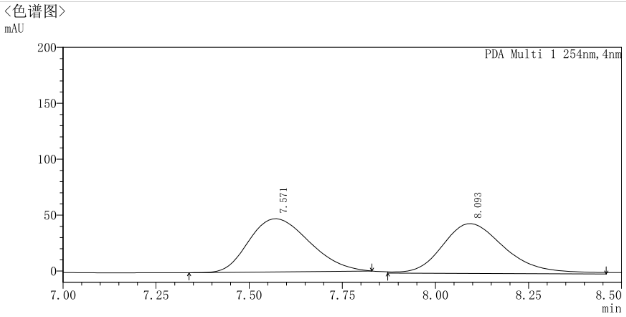


Resolution of enantiomers: Phenomenex INA column, 15% IPA-Hexanes, 0.5 mL/min, 254 nm, RT_1 = 7.6 min, RT_2 = 8.1 min.



〈峰表〉
PDA Ch1 254nm

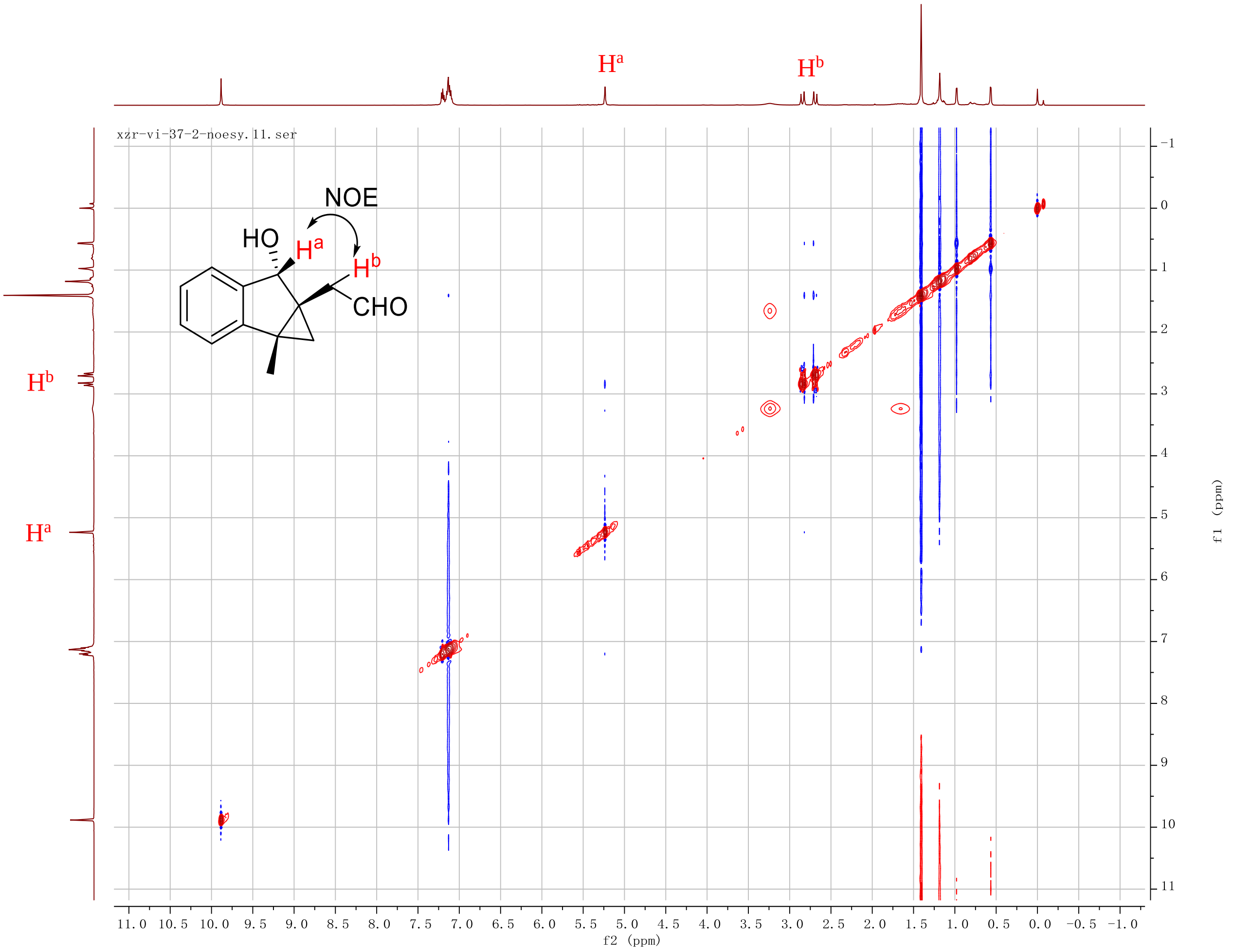
峰号	保留时间	面积	高度	浓度	高度%	面积%
1	7.525	697123	65966	0.000	51.927	49.656
2	8.015	706785	61070	0.000	48.073	50.344
总计		1403907	127036		100.000	100.000



〈峰表〉
PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	高度%	面积%
1	7.571	538331	47554	0.000		51.599	50.467
2	8.093	528359	44606	0.000		48.401	49.533
总计		1066689	92160			100.000	100.000

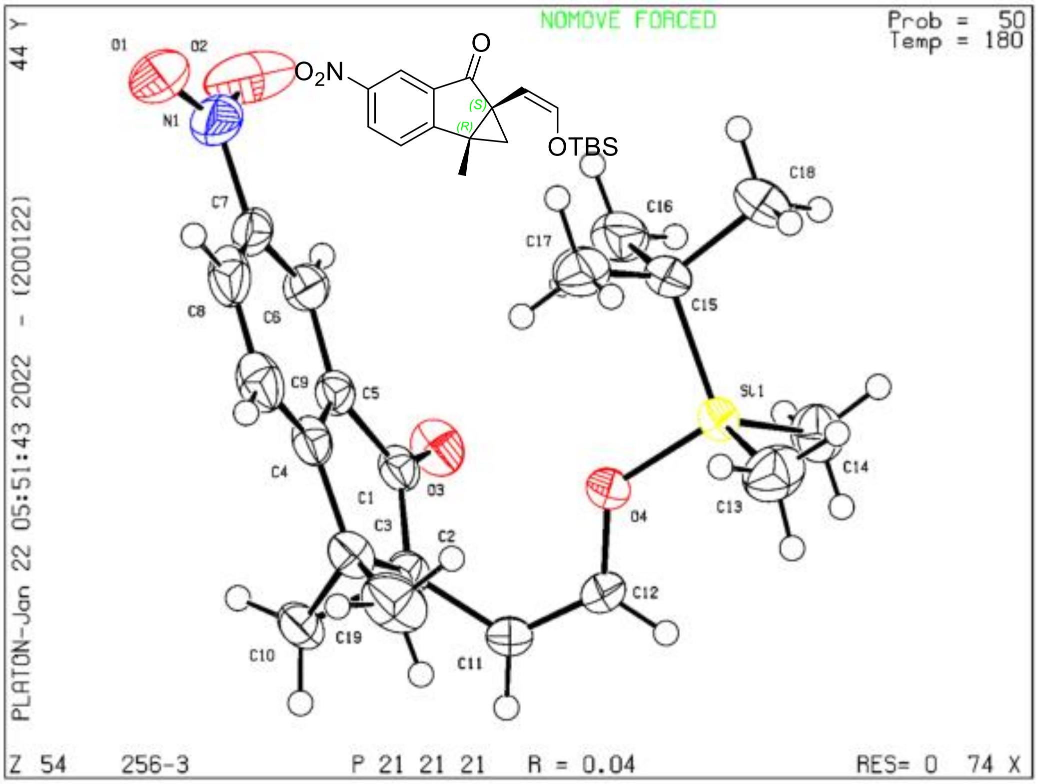
The NOE of 4t


H^a
H^b
xzr-vi-37-2-noesy.11.ser
NOE
HO
H^a
H^b
CHO
H^b
H^a
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f2 (ppm)
-1 0 1 2 3 4 5 6 7 8 9 10 11
f1 (ppm)

8. The X-ray diffraction analysis

Crystal data and structure refinement for 2j (CCDC 2220784).

Single crystal of **2j** was grown from slow evaporation of EA/PE solvent. A suitable crystal was selected and measured on aSuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 179.99(10) K during data collection.



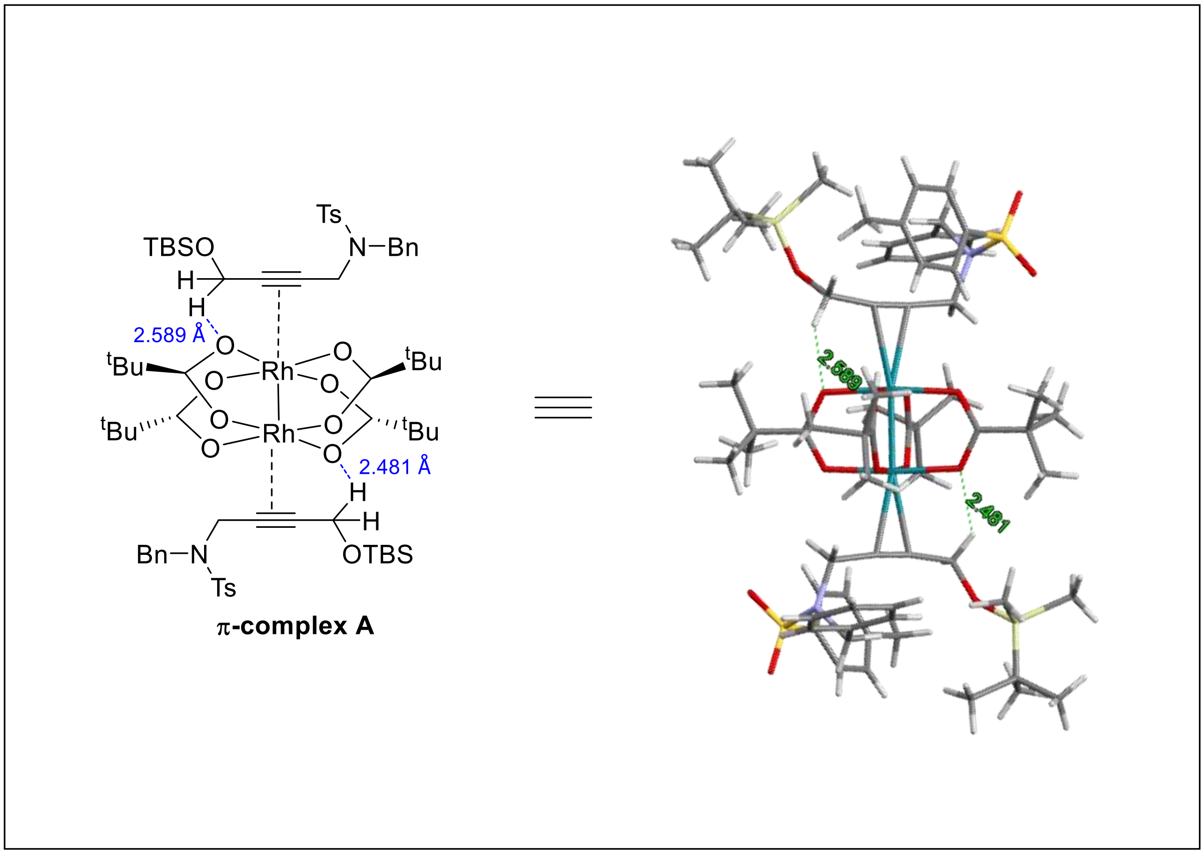
Ellipsoid plot of the crystal structure of **2j** (Prob = 50, Temp = 180 K)

Identification code	**256-3**
Empirical formula	$C_{19}H_{25}NO_4Si$
Formula weight	359.49
Temperature/K	179.99(10)
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	8.1571(2)
b/Å	8.3394(2)
c/Å	29.2782(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1991.66(7)
Z	4
ρ_{calc}g/cm^3	1.199
μ/mm^{-1}	1.222

F(000)	768.0
Crystal size/mm^3	0.12 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.038 to 147.51
Index ranges	$-9 \le h \le 9$, $-10 \le k \le 9$, $-35 \le l \le 36$
Reflections collected	18375
Independent reflections	3937 [R_{int} = 0.0473, R_{sigma} = 0.0254]
Data/restraints/parameters	3937/0/233
Goodness-of-fit on F^2	1.018
Final R indexes [I>=2σ (I)]	R_1 = 0.0355, wR_2 = 0.0989
Final R indexes [all data]	R_1 = 0.0364, wR_2 = 0.0998
Largest diff. peak/hole / e Å^{-3}	0.25/-0.17
Flack/Hooft parameter	0.019(13)/0.004(10)

Crystal data and structure refinement for complex A (CCDC 2283357)

Single crystal of **complex A** was grown from slow evaporation of DCM/PE solvent. A suitable crystal was selected and measured on aSuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 293(10) K during data collection.



Ellipsoid plot of the crystal structure of **complex A** (Prob = 50, Temp = 293 K)

Table 1 Crystal data and structure refinement for complex A.

Identification code	XZR-0626
Empirical formula	$C_{68}H_{102}N_2O_{14}Rh_2S_2Si_2$
Formula weight	1497.63
Temperature/K	293.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.1225(7)
b/Å	20.8129(16)
c/Å	27.9242(16)
α/°	90
β/°	103.361(6)
γ/°	90
Volume/Å^3	7985.6(9)
Z	4
ρ_{calc}g/cm^3	1.246
μ/mm^{-1}	0.551
F(000)	3144.0
Crystal size/mm^3	0.17 × 0.15 × 0.12
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.114 to 49.996
Index ranges	$-16 \leq h \leq 16, -21 \leq k \leq 24, -27 \leq l \leq 33$
Reflections collected	37141
Independent reflections	14065 [R_{int} = 0.0540, R_{sigma} = 0.0804]
Data/restraints/parameters	14065/1087/967
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0800, wR_2 = 0.1973
Final R indexes [all data]	R_1 = 0.1335, wR_2 = 0.2435
Largest diff. peak/hole / e Å^{-3}	0.88/-0.84

9. References

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