Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Synthesis of Polysubstituted Fused Pyrrolidines via [2+2]/[2+3] Cycloaddition of Azomethine Ylides

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Contents

I. General Information

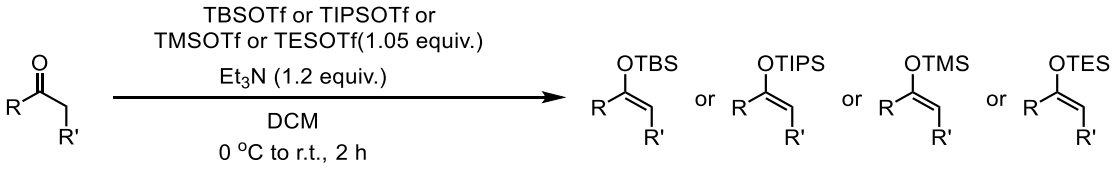
All commercial reagents were purchased from TCI, Leyan, Energy Chemical and used as received. Solvents used in catalytic reactions were dried and distilled in appropriate method. Solvent employed for column chromatography were purchased in technical grade quality without distillation before use. Column chromatography was performed using glass columns with Silica Gel (Haiyang, 300-400 mesh). Ethyl propiolate (CAS:623-47-2) was purchased from Energy Chemical. N-(Methoxymethyl)-N-(trimethylsilylmethyl)benzylamine（CAS:93102-05-7） was purchased from TCI with a purity of 98%.

All reactions were generally performed in dried glassware filled with dry argon. TLC plates were stained using potassium permanganate. Chromatographic purification of products (column chromatography) was performed on the glass column filled in (300 – 400 Mesh) silica gel. Concentration of reaction product solutions and chromatography fractions under reduced pressure was performed by rotary evaporation at 30 – 40 °C at the appropriate pressure and then at rt, ca. 0.1 mmHg (vacuum pump) unless otherwise indicated. For reactions that require heating, oil bath is used as the heat source.

All unknown compounds starting materials and products were characterized by ^{1}H NMR, ^{13}C NMR, high-resolution mass spectrometry (HRMS) and Infrared Spectroscopy (IR). The known desired products were characterized by ^{1}H NMR. NMR spectra were obtained on a Bruker 600 spectrometer, operating at 600 MHz for ^{1}H NMR, 151 MHz for ^{13}C NMR, 565 MHz for ^{19}F NMR or a Bruker 400 spectrometer, operating at 400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR. ^{1}H and ^{13}C positive chemical shifts (δ) are downfield from tetramethylsilane and are given in parts per million (ppm). Chemical shifts were reported in ppm relative to the central line of $CHCl_3$ (δ 7.26) for ^{1}H NMR, for ^{13}C NMR, the residual $CDCl_3$ (δ 77.16) were used as the internal standards. Coupling constants *(J)* are given in Hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplet, t = triplet, q =quadruple, m = multiplet. For the characterization of mixtures, * indicates the overlap of the signals of the two isomers. Electrospray ionization high-resolution mass spectra (ESI-HRMS) and atmospheric pressure chemical ionization

high-resolution mass spectra (APCI-HRMS) were operated in positive ion mode and carried out with a Waters Xevo G2-XS QTOF. IR were determined in Bruker Vertex 70 (KBr).

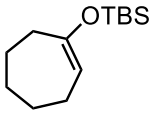
II. General Procedure of Silyl Enol Ethers



The reaction was carried out following the previously described procedure[1].

General Procedure: To a flame-dried two necked round bottom flask ketone (1.0 equiv.) was added under nitrogen atmosphere and dissolved with freshly distilled CH_2Cl_2. Subsequently, triethylamine (1.2 equiv.) was added at room temperature. The mixture was stirred for 5 minutes at room temperature. Then, the reaction mixture was cooled to 0 °C and TBSOTf or TIPSOTf or TMSOTf or TESOTf (1.05 equiv.) was added dropwise. The reaction was stirred for 2 h at room temperature and then quenched with a saturated $NaHCO_3$ aqueous solution. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The resulting crude mixture was purified by silica gel column chromatography (petroleum ether) to afford the corresponding product.

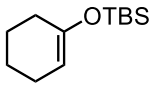
Tert-butyl(cyclohept-1-en-1-yloxy)dimethylsilane (1a)



1a

According to the general procedure, the silyl enol ethers **1a** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (0.90 g, 80% yield). Spectroscopic data match with those previously reported[1]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.03 – 4.99 (m, 1H), 2.28 – 2.16 (m, 2H), 2.03 – 1.89 (m, 2H), 1.75 – 1.63 (m, 2H), 1.60 – 1.48 (m, 4H), 0.91 (d, J = 1.1 Hz, 9H), 0.11 (d, J = 1.1 Hz, 6H).

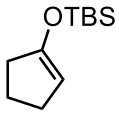
Tert-butyl(cyclohex-1-en-1-yloxy)dimethylsilane (1b)



1b

According to the general procedure, the silyl enol ethers **1b** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (0.99 g, 93.5% yield).Spectroscopic data match with those previously reported[1]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.88 – 4.86 (m, 1H), 2.05 – 1.96 (m, 4H), 1.70 – 1.62 (m, 2H), 1.55 – 1.46 (m, 2H), 0.92 (s, 9H), 0.12 (s, 6H).

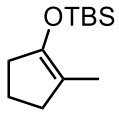
Tert-butyl(cyclopent-1-en-1-yloxy)dimethylsilane (1c)



1c

According to the general procedure, the silyl enol ethers **1c** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (0.66 g, 72% yield). Spectroscopic data match with those previously reported[1]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.65 – 4.58 (m, 1H), 2.27 – 2.22 (m, 4H), 1.90 – 1.80 (m, 2H), 0.92 (s, 9H), 0.14 (s, 6H).

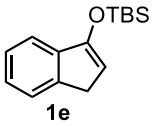
Tert-butyldimethyl((2-methylcyclopent-1-en-1-yl)oxy)silane (1d)



1d

According to the general procedure, the silyl enol ethers **1d** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (0.77 g, 74% yield). Spectroscopic data match with those previously reported[2]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.29 – 2.25 (m, 2H), 2.21 – 2.15 (m, 2H), 1.85 – 1.73 (m, 2H), 1.58 – 1.51 (m, 3H), 0.94 (s, 9H), 0.11 (s, 6H).

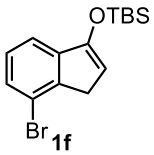
((1H-inden-3-yl)oxy)(tert-butyl)dimethylsilane (1e)



1e

According to the general procedure, the silyl enol ethers **1e** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (0.63 g, 51% yield). Spectroscopic data match with those previously reported[1]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41 – 7.37 (m, 2H), 7.34 – 7.27 (m, 1H), 7.24 – 7.22 (m, 1H), 5.42 (t, *J* = 2.4 Hz, 1H), 3.28 (d, *J* = 2.4 Hz, 2H), 1.04 (s, 9H), 0.26 (s, 6H).

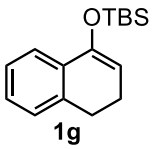
((7-Bromo-1H-inden-3-yl)oxy)(tert-butyl)dimethylsilane (1f)



1f

According to the general procedure, the silyl enol ethers **1f** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (1.41 g, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 2H), 7.22 – 7.15 (m, 1H), 5.57 – 5.26 (m, 1H), 3.28 – 3.17 (m, 2H), 1.03 (s, 9H), 0.25 (s, 6H). **^{13}C NMR** (151 MHz, CDCl3): δ 153.4, 143.8, 142.6, 128.3, 128.1, 118.9, 117.3, 106.6, 35.3, 25.7, 18.3, -4.7. **IR**(KBr): υ 2945, 1720, 1604, 1257, 877, 678. **HRMS(APCI)** *(m/z)*: $[M+H]^+$ Calcd for $C_{15}H_{22}BrOSi$ 325.0618; found: 325.0618.

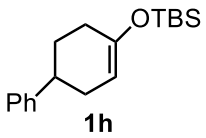
Tert-butyl((3,4-dihydronaphthalen-1-yl)oxy)dimethylsilane (1g)



1g

According to the general procedure, the silyl enol ethers **1g** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (1.05 g, 81% yield). Spectroscopic data match with those previously reported[2]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 7.2 Hz, 1H), 7.22 – 7.09 (m, 3H), 5.19 – 5.16 (m, 1H), 2.75 (t, *J* = 8.0 Hz, 2H), 2.36 – 2.27 (m, 2H), 1.01 (s, 9H), 0.20 (s, 6H).

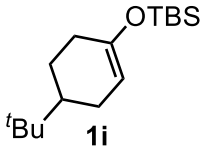
Tert-butyldimethyl((1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)oxy)silane (1h)



1h

According to the general procedure, the silyl enol ethers **1h** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (1.27 g, 88% yield). Spectroscopic data match with those previously reported[3]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36 – 7.16 (m, 5H), 4.96 – 4.94 (m, 1H), 2.84 – 2.68 (m, 1H), 2.34 – 2.14 (m, 3H), 2.07 (m, 1H), 2.01 – 1.79 (m, 2H), 0.94 (s, 9H), 0.16 (s, 6H).

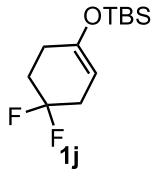
Tert-butyl((4-(tert-butyl)cyclohex-1-en-1-yl)oxy)dimethylsilane (1i)



1i

According to the general procedure, the silyl enol ethers **1i** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (1.16 g, 87% yield).Spectroscopic data match with those previously reported[4]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.89 – 4.79 (m, 1H), 2.05 – 1.94 (m, 2H), 1.86 – 1.72 (m, 2H), 1.53 (s, 1H), 1.31 – 1.14 (m, 2H), 0.93 – 0.90 (m, 9H), 0.86 (d, J = 0.6 Hz, 9H), 0.15 – 0.09 (m, 6H).

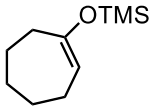
Tert-butyl((4,4-difluorocyclohex-1-en-1-yl)oxy)dimethylsilane (1j)



1j

According to the general procedure, the silyl enol ethers **1j** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (0.87 g, 70% yield). Spectroscopic data match with those previously reported[5]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.77 – 4.60 (m, 1H), 2.57 – 2.44 (m, 2H), 2.30 – 2.20 (m, 2H), 2.15 – 1.99 (m, 2H), 0.91 (s, 9H), 0.13 (s, 6H).

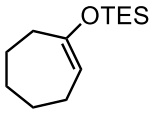
(Cyclohept-1-en-1-yloxy)trimethylsilane (1k)



1k

According to the general procedure, the silyl enol ethers **1k** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (0.52 g, 57% yield). Spectroscopic data match with those previously reported[6]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.02 (t, *J* = 6.6 Hz, 1H), 2.25 – 2.19 (m, 2H), 2.02 – 1.94 (m, 2H), 1.72 – 1.63 (m, 2H), 1.59 – 1.49 (m, 4H), 0.16 (s, 9H).

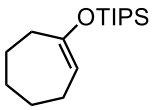
(Cyclohept-1-en-1-yloxy)triethylsilane (1l)



1l

According to the general procedure, the silyl enol ethers **1l** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (0.88 g, 78% yield). Spectroscopic data match with those previously reported[7]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.01 (t, *J* = 6.6 Hz, 1H), 2.29 – 2.20 (m, 2H), 2.03 – 1.93 (m, 2H), 1.74 – 1.63 (m, 2H), 1.62 – 1.47 (m, 4H), 0.97 (t, *J* = 8.0 Hz, 9H), 0.65 (m, 6H).

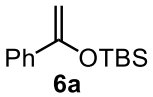
(Cyclohept-1-en-1-yloxy)triisopropylsilane (1m)



1m

According to the general procedure, the silyl enol ethers **1m** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (0.89 g, 66% yield). Spectroscopic data match with those previously reported[8]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.01 – 4.99 (m, 1H), 2.28 (dt, *J* = 8.2, 2.7 Hz, 2H), 1.98 – 1.96 (m,2H), 1.68 – 1.66 (m, 2H), 1.61 – 1.59 (m, 2H), 1.52 – 1.50 (m, 2H), 1.08 (dd, *J* = 6.2, 2.6 Hz, 18H).

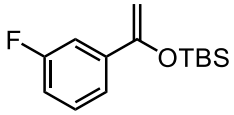
Tert-butyldimethyl((1-phenylvinyl)oxy)silane (6a)



6a

According to the general procedure, the silyl enol ethers **6a** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (0.5 g, 43% yield). Spectroscopic data match with those previously reported[1]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.65 – 7.57 (m, 2H), 7.36 – 7.24 (m, 3H), 4.89 (d, *J* = 1.7 Hz, 1H), 4.42 (d, *J* = 1.7 Hz, 1H), 1.01 (s, 9H), 0.22 (s, 6H).

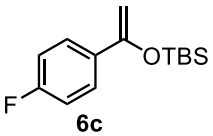
Tert-butyl((1-(3-fluorophenyl)vinyl)oxy)dimethylsilane (6b)



6b

According to the general procedure, the silyl enol ethers **6b** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (1.22 g, 97% yield). Spectroscopic data match with those previously reported[9]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 – 7.18 (m, 3H), 6.98 – 6.96 (m, 1H), 4.89 (d, *J* = 1.9 Hz, 1H), 4.45 (d, *J* = 1.9 Hz, 1H), 1.00 (s, 9H), 0.21 (s, 6H).

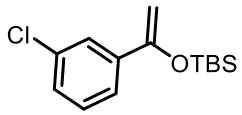
Tert-butyl((1-(4-fluorophenyl)vinyl)oxy)dimethylsilane (6c)



6c

According to the general procedure, the silyl enol ethers **6c** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (0.84 g, 67% yield). Spectroscopic data match with those previously reported[10]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62 – 7.51 (m, 2H), 7.05 – 6.94 (m, 2H), 4.81 (d, *J* = 1.9, 1H), 4.39 (d, *J* = 1.8, 1H), 1.00 (s, 9H), 0.21 (s, 6H).

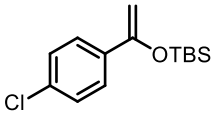
Tert-butyl((1-(3-chlorophenyl)vinyl)oxy)dimethylsilane (6d)



6d

According to the general procedure, the silyl enol ethers **6d** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (1.06 g, 79% yield).Spectroscopic data match with those previously reported[9]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.64 – 7.55 (m, 1H), 7.49 – 7.46 (m, 1H), 7.30 – 7.16 (m, 2H), 4.89 (d, *J* = 2.2 Hz, 1H), 4.45 (d, *J* = 2.0 Hz, 1H), 1.01 (s, 9H), 0.28 – 0.17 (s, 6H).

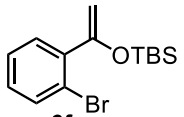
Tert-butyl((1-(4-chlorophenyl)vinyl)oxy)dimethylsilane (6e)



6e

According to the general procedure, the silyl enol ethers **6e** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (0.55 g, 41% yield). Spectroscopic data match with those previously reported[9]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 – 7.49 (m, 2H), 7.32 – 7.27 (m, 2H), 4.86 (d, *J* = 1.9 Hz, 1H), 4.42 (dd, *J* = 2.0, 1H), 0.99 (s, 9H), 0.20 (s, 6H).

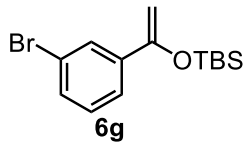
((1-(2-Bromophenyl)vinyl)oxy)(tert-butyl)dimethylsilane (6f)



6f

According to the general procedure, the silyl enol ethers **6f** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (1.21 g, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59 – 7.53 (m, 1H), 7.41 – 7.37 (m, 1H), 7.30 – 7.23 (m, 1H), 7.17 – 7.11 (m, 1H), 4.63 (d, *J* = 1.3 Hz, 1H), 4.54 (d, *J* = 1.3 Hz, 1H), 0.92 (s, 9H), 0.12 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 156.1, 140.3, 133.2, 130.5, 129.3, 126.94, 96.5, 25.7, -4.7. **IR**(KBr): υ 2949, 1722, 1615, 1262, 867, 678. **HRMS(APCI)** *(m/z)*: $[M+H]^+$ Calcd for $C_{14}H_{22}BrOSi$ 313.0618; found: 313.0632.

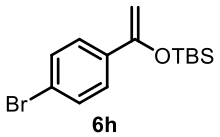
((1-(3-Bromophenyl)vinyl)oxy)(tert-butyl)dimethylsilane (6g)



6g

According to the general procedure, the silyl enol ethers **6g** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (1.42 g, 92% yield).Spectroscopic data match with those previously reported[7]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 – 7.73 (m, 1H), 7.53 – 7.51 (m, 1H), 7.42 – 7.40 (m, 1H), 7.19 (t, *J* = 7.9 Hz, 1H), 4.88 (t, *J* = 3.3 Hz, 1H), 4.45 (d, *J* = 1.9 Hz, 1H), 1.00 (s, 9H), 0.21 (s, 6H).

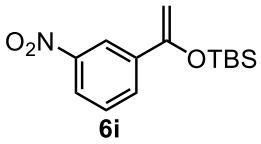
((1-(4-bromophenyl)vinyl)oxy)(tert-butyl)dimethylsilane (6h)



6h

According to the general procedure, the silyl enol ethers **6h** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (1.08 g, 69% yield). Spectroscopic data match with those previously reported[6]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54 – 7.35 (m, 4H), 4.88 – 4.86 (m, 1H), 4.44 – 4.42 (m, 1H), 0.99 (s, 9H), 0.20 (s, 6H).

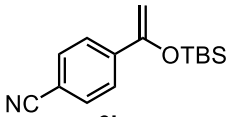
Tert-butyldimethyl((1-(3-nitrophenyl)vinyl)oxy)silane (6i)



6i

According to the general procedure, the silyl enol ethers **6i** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (1.28 g, 93% yield).Spectroscopic data match with those previously reported[9]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.47 – 8.45 (m, 1H), 8.15 – 8.13 (m, 1H), 7.94 – 7.88 (m, 1H), 7.50 – 7.48 (m, 1H), 5.05 – 4.99 (m, 1H), 4.56 (d, *J* = 2.3 Hz, 1H), 1.02 (s, 9H), 0.24 (s, 6H).

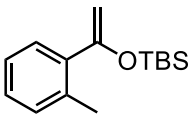
4-(1-((Tert-butyldimethylsilyl)oxy)vinyl)benzonitrile (6j)



6j

According to the general procedure, the silyl enol ethers **6j** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (0.58 g, 45% yield). Spectroscopic data match with those previously reported[11]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.72 – 7.66 (m, 2H), 7.64 – 7.57 (m, 2H), 5.00 (d, *J* = 2.2 Hz, 1H), 4.57 (d, *J* = 2.2 Hz, 1H), 1.00 (s, 9H), 0.22 (s, 6H).

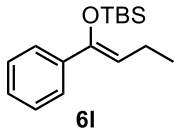
Tert-butyldimethyl((1-(o-tolyl)vinyl)oxy)silane (6k)



6k

According to the general procedure, the silyl enol ethers **6k** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (1.14 g, 92% yield).Spectroscopic data match with those previously reported[9]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.33 – 7.28 (m, 1H), 7.17 – 7.15 (m, 3H), 4.56 (s, 1H), 4.38 (s, 1H), 2.40 (s, 3H), 0.91 (s, 9H), 0.09 (s, 6H).

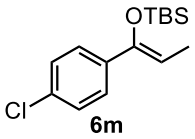
(Z)-Tert-butyldimethyl((1-phenylbut-1-en-1-yl)oxy)silane (6l)



6l

According to the general procedure, the silyl enol ethers **6l** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (1.00 g, 77% yield).Spectroscopic data match with those previously reported[12]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44 – 7.42 (m, 2H), 7.30 – 7.22 (m, 3H), 5.10 – 5.08 (m, 1H), 2.23 – 2.21 (m, 2H), 1.05 – 1.00 (m, 3H), 0.99 – 0.97 (s, 9H), -0.05 (s, 6H).

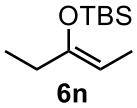
(Z)-Tert-butyl((1-(4-chlorophenyl)prop-1-en-1-yl)oxy)dimethylsilane (**6m**)



6m

According to the general procedure, the silyl enol ethers **6m** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (1.08 g, 77% yield). Spectroscopic data match with those previously reported[13]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 5.20 – 5.18 (m, 1H), 1.72 (s, *J* = 6.9 Hz, 3H), 0.98 (s, 9H), -0.06 (s, 6H)

(Z)-Tert-butyldimethyl(pent-2-en-3-yloxy)silane (6n)

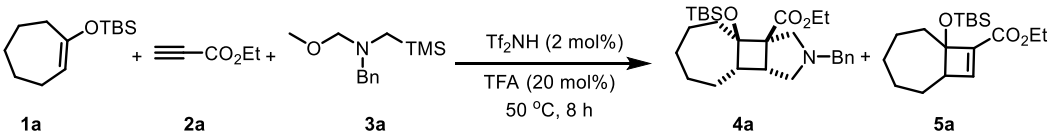


6n

According to the general procedure, the silyl enol ethers **6n** was isolated (petroleum ethe as the eluent solvent) as a colorless liquid (0.72 g, 72% yield).Spectroscopic data match with those previously reported[14]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.52 – 4.47 (m, 1H), 2.07 – 1.98 (m, 2H), 1.53 – 1.52 (m, 3H), 1.04 – 1.00 (m, 3H), 0.96 (s, 9H), 0.12 (s, 6H).

III. Optimization of Reaction Conditions

Table S1. Optimization of solvents

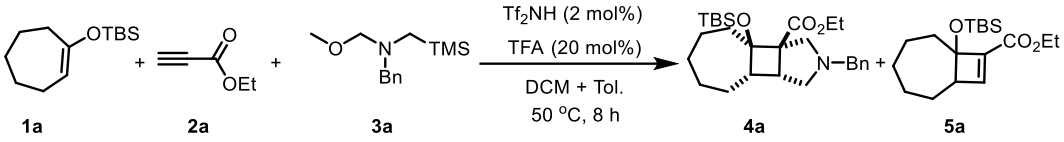


1a **2a** **3a** **4a** **5a**

entry	solvent	yield **4a/5a**
1	DCM	11% / 52%
2	DCE	9% / 69%
3	$CHCl_3$	ND
4	CCl_4	ND
5	MeCN	ND
6	THF	ND
7	Tol.	ND
8	CH_3OH	ND
9	DCM + MeCN	10% / 75%
10	DCM + THF	5% / 69%
11	DCM + Tol.	14% / 67%
12	DCM + CH_3OH	9% / 77%

Conditions: **1a** (0.165 mmol, 1.1 eq.), **2a** (0.15 mmol, 1.0 eq.),**3a** (0.15 mmol, 1.0 eq.), Tf_2NH (2 mol%, 0.08 mol in Tol.), TFA (20 mol%), the reaction stir for 8 h at 50 °C. Isolated yield. TFA=Trifluoroacetic acid; DCM= Dichloromethane; DCE=1,2-Dichloroethane; THF=Tetrahydrofuran.

Table S2. Optimization of 3a equivalents

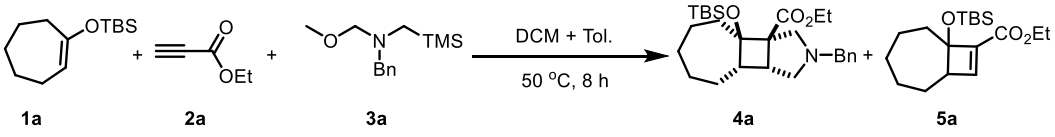


1a **2a** **3a** **4a** **5a**

entry	**3a** eq.	yield 4a/5a
1	1	14% / 67%
2	1.5	46% / 51%
3	2	37% / 36%
4	2.5	44% / 21%
5	3	82% / 11%

Conditions: **1a** (0.165 mmol, 1.1 eq.), **2a** (0.15 mmol, 1.0 eq.),Tf_2NH (2 mol%, 0.08 mol in Tol.),TFA (20 mol%), DCM(1mL) + Tol.(1mL), the reacti

Table S3. Optimization of catalysts

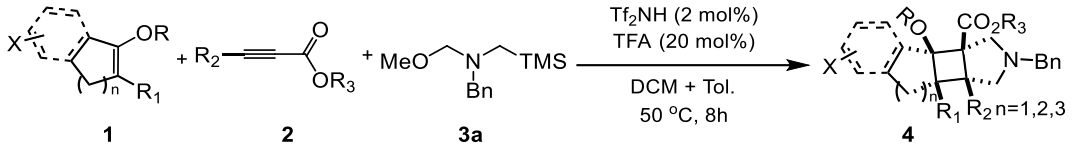


1a **2a** **3a** **4a** **5a**

entry	cat.1(2 mol%)	cat.2(20 mol%)	yield **4a/5a**
1	Tf_2NH	TFA	82% / 11%
2	$AlCl_3$	TFA	ND
3	$BF_3 \cdot Et_2O$	TFA	ND
4	Tf_2NH	AcOH	20% / 45%
5	Tf_2NH	TsOH	32% / 41%

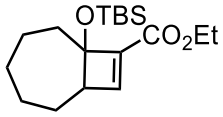
Conditions: **1a** (0.165 mmol, 1.1 eq.), **2a** (0.15 mmol, 1.0 eq.), **3a** (0.45 mmol, 3.0 eq.), DCM(1mL) + Tol.(1mL), the reaction stir for 8 h at 50 °C. Isolated yield

IV. General Procedure for Synthesis of 3-Azabicyclo[3.2.0]heptane



To the reaction tube was added **1** (0.275 mmol), pumped under a double row of tubes for gas exchange three times, under nitrogen atmosphere was added DCM (1 mL), **2** (0.25 mmol), Tf_2NH (62.5 μL, 0.08 M in Tol.), Tol. (1 mL), TFA (0.05 mmol), **3a** (0.75 mmol), The reaction was carried out at 50 ℃ for 8 h. The reaction was monitored by TLC until complete consumption of the starting material **1**. Then, the resulting mixture was filtered through celite, and concentrated in vacuo. The crude residue was analyzed by ^{1}H NMR to determine the diastereoselectivity and then purified via silica gel flash column chromatography to afford the product **4**.

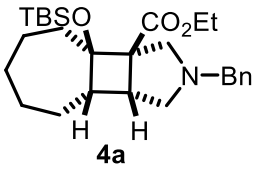
Ethyl 7-((tert-butyldimethylsilyl)oxy)bicyclo[5.2.0]non-8-ene-8-carboxylate (5a)



5a

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.91 (d, *J* = 6.8 Hz, 1H), 4.29 – 4.12 (m, 2H), 2.83 – 2.70 (m, 1H), 2.15 (dd, *J* = 14.0, 8.2 Hz, 1H), 1.89 – 1.50 (m, 6H), 1.33 – 1.27 (m, 6H), 0.92 – 0.85 (s, 9H), 0.12 – -0.03 (s, 6H).

Ethyl-2-benzyl-3b-((tert- -butyldimethylsilyl)oxy)decahydrocyclohepta[3,4] Cyclobuta[1,2-c]pyrrole-3a(1H)-carboxylate (4a)

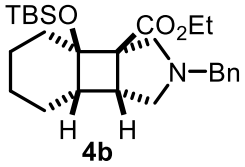


4a

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **4a** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (56.4 mg, >20:1 *dr*, 82% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.1 Hz, 2H), 7.31 – 7.29 (m, 2H), 7.21 – 4.08 (m, 1H), 4.21 – 4.08 (m, 2H), 3.73 (d, *J* = 12.9 Hz,

1H), 3.51 (t, *J* = 10.9 Hz, 2H), 2.67 (d, *J* = 9.1 Hz, 1H), 2.43 – 2.36 (m, 2H), 2.27 – 2.15 (m, 2H), 1.86 – 1.72 (m, 2H), 1.71 – 1.56 (m, 4H), 1.46 (s, 1H), 1.42 – 1.29 (m, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.92 (s, 9H), 0.16 (s, 3H), 0.09 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 174.0, 139.5, 128.8, 128.1, 126.7, 80.1, 60.3, 60.1, 59.7, 58.1, 57.9, 49.6, 31.9, 26.3, 26.1, 24.3, 18.7, 14.3, -1.9, -1.9. **IR** (KBr): υ 2933, 1724, 1460, 1363, 1251, 1093, 835 cm^{-1}. **HRMS(APCI)** *(m/z)*: $[M+H]^+$ Calcd for $C_{27}H_{44}NO_3Si$ 458.3085; found: 458.3104.

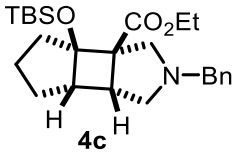
Ethyl-2-benzyl-3b-((tert-butyldimethylsilyl)oxy)decahydro-3aH-benzo[3,4]cyclobuta[1,2-c]pyrrole-3a-carboxylate (4b)



4b

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **4b** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (33.6 mg, >20:1 *dr*, 38% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.5 Hz, 2H), 7.31 – 7.28 (m, 2H), 7.24 – 7.22 (m, 1H), 4.19 – 4.14 (m, 1H), 4.12 – 4.06 (m, 1H), 3.65 (t, *J* = 10.2 Hz, 2H), 3.50 (d, *J* = 10.8 Hz, 1H), 2.70 (d, *J* = 9.0 Hz, 1H), 2.53 (t, *J* = 6.9 Hz, 1H), 2.43 (dd, *J* = 7.6, 4.6 Hz, 1H), 2.36 – 2.27 (m, 1H), 2.19 (d, *J* = 10.4 Hz, 1H), 1.81 (d, *J* = 16.1 Hz, 1H), 1.56 (dt, *J* = 14.2, 8.5 Hz, 2H), 1.51 – 1.44 (m, 2H), 1.38 (d, *J* = 10.1 Hz, 1H), 1.35 – 1.27 (m, 2H), 1.25 (t, *J* = 6.9 Hz, 3H), 0.87 (s, 9H), 0.14 (s, 3H), 0.07 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 174.4, 139.5, 128.6, 128.1, 126.7, 73.2, 62.3, 60.0, 59.7, 57.5, 56.8, 42.2, 37.8, 34.6, 25.8, 23.3, 21.2, 20.5, 18.3, 14.3, -2.5, -2.5. **IR** (KBr): υ 2933, 1720, 1458, 1379, 1213, 1091, 833 cm^{-1}. **HRMS(ESI)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{26}H_{41}NNaO_3Si$ 466.2748; found: 466.2753.

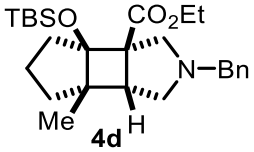
Ethyl-2-benzyl-3b-((tert-butyldimethylsilyl)oxy)octahydrocyclopenta[3,4] cyclobuta[1,2-c]pyrrole-3a(1H)-carboxylate (4c)



4c

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **4c** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (62.4 mg, >20:1 *dr*, 73% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.36 (d, *J* = 7.1 Hz, 2H), 7.31 – 7.29 (m, 2H), 7.25 – 7.22 (m, 1H), 4.20 – 4.09 (m, 2H), 3.83 (d, *J* = 12.9 Hz, 1H), 3.63 (d, *J* = 9.6 Hz, 1H), 3.39 (d, *J* = 12.9 Hz, 1H), 2.73 (d, *J* = 9.0 Hz, 1H), 2.29 – 2.24 (m, 1H), 2.17 (t, *J* = 4.7 Hz, 1H), 2.14 (d, *J* = 9.6 Hz, 1H), 2.10 (dt, *J* = 9.1, 5.0 Hz, 1H), 1.79 (dd, *J* = 13.9, 4.2 Hz, 1H), 1.75 – 1.66 (m, 3H), 1.64 – 1.58 (m, 1H), 1.51 – 1.48 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.90 (s, 9H), 0.15 (s, 3H), 0.06 (s, 3H). **^{13}C NMR** (151 MHz, CDCl3): δ 173.3, 139.4, 128.9, 128.1, 126.7, 82.7, 60.1, 59.9, 59.8, 58.6, 57.9, 48.9, 38.5, 38.3, 31.1, 25.8, 24.3, 18.2, 14.3, -2.5, -2.6. **IR** (KBr): υ 2950, 1726, 1460, 1361, 1255, 1103, 837 cm^{-1}. **HRMS(ESI)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{25}H_{39}NNaO_3Si$ 452.2591; found: 452.2611.

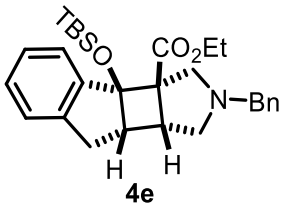
Ethyl-2-benzyl-3b-((tert-butyldimethylsilyl)oxy)-6a-methyloctahydrocyclopenta[3,4]cyclobuta[1,2-c]pyrrole-3a(1H)-carboxylate (4d)



4d

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **4d** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (82.2 mg, >20:1 *dr*, 74% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.31 – 7.28 (m, 2H), 7.24 – 7.22 (m, 1H), 4.21 – 4.07 (m, 2H), 3.62 (d, *J* = 12.8 Hz, 1H), 3.54 – 3.46 (m, 2H), 2.83 (d, *J* = 9.7 Hz, 1H), 2.28 (d, *J* = 5.7 Hz, 1H), 2.13 (dd, *J* = 9.7, 5.8 Hz, 1H), 2.04 (d, *J* = 9.7 Hz, 1H), 1.89 (s, 1H), 1.65 – 1.60 (m, 3H), 1.59 – 1.54 (m, 1H), 1.41 – 1.34 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.12 (s, 3H), 0.91 (s, 9H), 0.09 (s, 3H), 0.05 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 173.7, 139.7, 128.7, 128.1, 126.7, 84.2, 60.4, 60.1, 60.0, 58.4, 55.4, 47.1, 42.8, 41.0, 38.2, 25.9, 22.4, 18.6, 15.1, 14.3, -1.94, -2.7. **IR** (KBr): υ 2952, 1726, 1458, 1361, 1255, 1195, 889 cm^{-1}. **HRMS(APCI)** *(m/z)*: $[M+H]^+$ Calcd for $C_{26}H_{42}NO_3Si$ 444.2928; found: 444.2922.

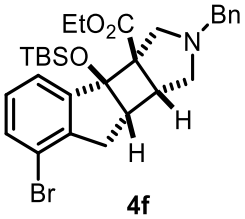
Ethyl-2-benzyl-3b-((tert-butyldimethylsilyl)oxy)-2,3,3b,8,8a,8b hexahydroindeno[1',2':3,4]cyclobuta[1,2-c]pyrrole-3a(1H)-carboxylate (4e)



4e

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **4e** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (41.7 mg, >20:1 *dr*, 35% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.5 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.18 (m, 4H), 7.14 (t, *J* = 7.3 Hz, 1H), 3.92 – 3.81 (m, 4H), 3.51 (d, *J* = 12.7 Hz, 1H), 3.21 (dd, *J* = 16.8, 8.0 Hz, 1H), 2.86 (d, *J* = 9.0 Hz, 1H), 2.77 (d, *J* = 16.8 Hz, 1H), 2.71 (dd, *J* = 7.9, 4.7 Hz, 1H), 2.27 – 2.21 (m, 2H), 2.16 (dd, *J* = 9.1, 4.7 Hz, 1H), 1.08 (t, *J* = 7.1 Hz, 3H), 0.87 (s, 9H), -0.10 (s, 3H), -0.41 (s, 3H). **^{13}C NMR** (151 MHz, CDCl3): δ 172.9, 144.6, 143.3, 139.4, 128.9, 128.6, 128.1, 126.7, 126.3, 125.7, 125.1, 84.1, 63.9, 60.1, 59.9, 58.7, 57.1, 46.7, 41.1, 37.8, 29.7, 25.8, 18.1, 14.0, -3.7, -3.8. **IR** (KBr): υ 2924, 1724, 1460, 1369, 1255, 1109, 873 cm^{-1}. **HRMS(ESI)** *(m/z)*: $[M+H]^+$ Calcd for $C_{29}H_{40}NO_3Si$ 478.2772; found: 478.2775.

Ethyl-2-benzyl-7-bromo-3b-((tert-butyldimethylsilyl)oxy)-2,3,3b,8,8a,8b-hexahydroindeno[1',2':3,4]cyclobuta[1,2-c]pyrrole-3a(1H)-carboxylate (4f)

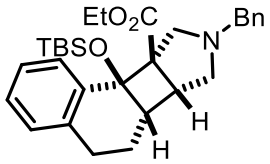


4f

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **4f** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (58.6 mg, >20:1 *dr*, 42% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 – 7.35 (m, 3H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.27 (d, *J* = 6.1 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 7.7 Hz, 1H), 3.96 – 3.75 (m, 4H), 3.51 (d, *J* = 12.7 Hz, 1H), 3.15 (dd, *J* = 17.5, 8.0 Hz, 1H), 2.88 – 2.84 (m, 1H), 2.76 – 2.69 (m, 1H), 2.29 (t, *J* = 4.6 Hz, 1H), 2.22 (d, *J* = 10.0 Hz, 1H), 2.17 (dd, *J* = 9.2, 4.6 Hz, 1H), 1.59 (s, 1H), 1.09 (t, *J* = 7.1 Hz, 3H), 0.86 (s, 9H), -0.07 (s, 3H), -0.41 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 172.6, 146.9, 143.9, 139.3, 131.7, 128.9, 128.4, 128.2, 126.9, 124.7, 120.5, 85.2, 64.0, 60.2, 59.9, 58.7, 57.0, 45.9,

41.2, 39.67, 25.7, 14.1 -3.6, -3.8. **IR** (KBr): υ 2945, 1728, 1454, 1365, 1261, 1109, 877, 777, 466 cm^{-1}. **HRMS(ESI)** *(m/z)*: $[M+H]^+$ Calcd for $C_{29}H_{39}BrNO_3Si$ 556.1877; found: 556.1869.

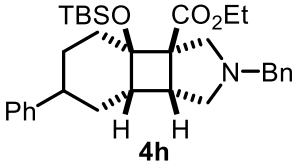
Ethyl-8-benzyl-9b-((tert-butyldimethylsilyl)oxy)-5,6,6a,6b,7,8,9,9b-octahydro-9aH-naphtho[1',2':3,4]cyclobuta[1,2-c]pyrrole-9a-carboxylate (4g)



4g

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **4g** isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (69.5 mg, >20:1 *dr*, 71% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.43 – 7.40 (m, 1H), 7.39 – 7.35 (m, 2H), 7.31 – 7.28 (m, 2H), 7.24 – 7.21 (m, 1H), 7.10 – 7.05 (m, 2H), 7.04 – 6.99 (m, 1H), 3.85 (dd, *J* = 21.8, 11.4 Hz, 2H), 3.52 – 3.43 (m, 3H), 2.95 – 2.82 (m, 2H), 2.75 (d, *J* = 9.1 Hz, 1H), 2.69 – 2.62 (m, 2H), 2.30 (d, *J* = 10.1 Hz, 1H), 2.11 – 2.08 (m, 1H), 1.71 – 1.65 (m, 1H), 1.64 – 1.53 (m, 1H), 0.91 (d, *J* = 7.0 Hz, 9H), 0.89 (d, *J* = 7.2 Hz, 3H), 0.04 (s, 3H), -0.37 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 172.4, 139.4, 138.8, 136.9, 128.9, 128.6, 128.1, 127.7, 126.8, 126.7, 125.3, 72.6, 64.2, 60.0, 59.9, 58.2, 57.1, 43.9, 39.1, 34.4, 29.7, 26.0, 23.2, 21.0, 18.4, 13.7, -2.5, -3.3. **IR** (KBr): υ 2933, 1724, 1460, 1367, 1255, 1176, 1091, 833 cm^{-1}. **HRMS(ESI)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{30}H_{41}NNaO_3Si$ 514.2748; found: 514.2756.

Ethyl-2-benzyl-3b-((tert-butyldimethylsilyl)oxy)-6-phenyldecahydro-3aH-benzo[3,4]cyclobuta[1,2-c]pyrrole-3a-carboxylate (4h)

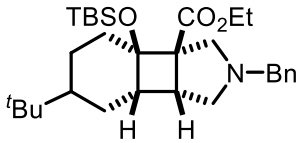


4h

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **4h** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (35.5 mg,

1.1:1 *dr*, 27% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.19* (dd, *J* = 16.0, 8.3 Hz, 2H), 7.16 – 7.09* (m, 4H), 7.09 – 7.04* (m, 1H), 7.04 – 6.98* (m, 3H), 4.06 – 3.91* (m, 2H), 3.51 – 3.47* (m, 2H), 3.36* (dd, *J* = 10.4, 6.0 Hz, 1H), 2.65 – 2.57* (m, 2H), 2.41* (dd, *J* = 8.1, 4.2 Hz, 1H), 2.31 – 2.11* (m, 2H), 2.04* (dd, *J* = 43.0, 10.3 Hz, 1H), 1.91 – 1.81* (m, 1H), 1.76 – 1.24* (m, 5H), 1.13 – 1.07* (m, 3H), 0.76* (d, *J* = 35.1 Hz, 9H), 0.01* (d, *J* = 10.7 Hz, 3H), -0.03* (s, 1H), -0.09* (s, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 174.4, 173.8, 148.2, 147.3, 139.5, 139.4, 128.6, 128.6, 128.4, 128.4, 128.1, 126.8, 126.8, 126.7, 125.9, 125.7, 74.3, 72.3, 62.3, 60.2, 60.1, 59.6, 59.6, 58.4, 57.3, 57.3, 56.4, 45.6, 42.7, 41.8, 40.3, 37.8, 36.5, 36.1, 32.3, 31.7, 28.5, 28.5, 27.5, 25.9, 25.8, 18.5, 18.3, 14.4, 14.3, -2.4, -2.4, -2.5. **IR** (KBr): υ 2935, 1726, 1458, 1367, 1257, 1126, 835 cm^{-1}. **HRMS(ESI)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{32}H_{45}NNaO_3Si$ 542.3061; found: 542.3088.

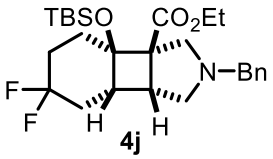
Ethyl-2-benzyl-6-(tert-butyl)-3b-((tert-butyldimethylsilyl)oxy)decahydro-3aH-benzo[3,4]cyclobuta[1,2-c]pyrrole-3a-carboxylate (4i)



4i

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **4i** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (61.1 mg, 1.3:1 *dr*, 49% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.40 – 7.20* (m, 5H), 4.21 – 4.05* (m, 2H), 3.71 – 3.58* (m, 2H), 3.49* (dd, *J* = 17.2, 10.3 Hz, 1H), 2.80 – 2.63* (m, 1H), 2.47 – 1.84* (m, 4H), 1.82 – 1.46* (m, 4H), 1.46 – 1.21* (m, 5H), 1.12 – 0.98* (m, 1H), 0.96 – 0.78* (m, 18H), 0.14* (d, *J* = 9.4 Hz, 3H), 0.08* (s, 1H), 0.02* (s, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 174.5, 173.9, 139.6, 128.6, 128.6, 128.1, 126.7, 74.5, 72.8, 62.2, 61.9, 60.1, 60.0, 59.7, 59.7, 58.5, 57.4, 56.6, 46.0, 43.5, 42.7, 41.7, 40.1, 37.9, 32.6, 32.4, 28.7, 27.2, 26.9, 26.1, 25.9, 25.8, 24.7, 22.2, 20.0, 18.5, 18.3, -2.4. **IR** (KBr): υ 2950, 1728, 1467, 1373, 1255, 1128, 839 cm^{-1}. **HRMS(ESI)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{30}H_{49}NNaO_3Si$ 522.3374; found: 522.3368.

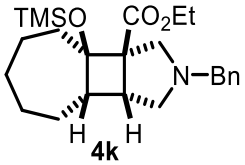
Ethyl-2-benzyl-3b-((tert-butyldimethylsilyl)oxy)-6,6-difluorodecahydro-3aH-benzo[3,4]cyclobuta[1,2-c]pyrrole-3a-carboxylate (4j)



4j

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **4j** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (44.6 mg, >20:1 *dr*, 37% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.33 – 7.29 (m, 4H), 7.27 – 7.22 (m, 1H), 4.21 – 4.08 (m, 2H), 3.67 – 3.61 (m, 2H), 3.50 (d, *J* = 10.5 Hz, 1H), 2.75 (dd, *J* = 8.8, 5.2 Hz, 2H), 2.57 – 2.45 (m, 1H), 2.30 (dd, *J* = 9.2, 4.3 Hz, 1H), 2.19 (d, *J* = 10.5 Hz, 1H), 1.92 (s, 6H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.87 (s, 9H), 0.14 (s, 3H), 0.07 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 173.7, 139.2, 128.7, 128.2, 126.9, 72.2, 61.6, 60.4, 59.5, 57.3 (d, *J* = 83.1 Hz), 41.2 (d, *J* = 8.5 Hz), 39.3, 32.5 (t, *J* = 24.3 Hz), 31.2, 29.6 (t, *J* = 24.5 Hz), 25.7, 18.3, 14.3, -2.5 (d, *J* = 37.4 Hz). **^{19}F NMR** (565 MHz, $CDCl_3$): δ -86.06 (d, *J* = 246.7 Hz), -92.84 (d, *J* = 235.6 Hz). **IR** (KBr): υ 2945, 1728, 1461, 1371, 1255, 1101,1039, 846 cm^{-1}. **HRMS(APCI)** *(m/z)*: $[M+H]^+$ Calcd for $C_{26}H_{40}F_2NO_3Si$ 480.2740; found: 480.2748.

Ethyl-2-benzyl-3b-((trimethylsilyl)oxy)decahydrocyclohepta[3,4]cyclobuta[1,2-c]pyrrole-3a(1H)-carboxylate (4k)

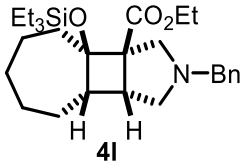


4k

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **4k** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (72.0 mg, >20:1 *dr*, 69% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.32 – 7.30 (m, 2H), 7.25 – 7.23 (m, 1H), 4.16 – 4.11 (m, 2H), 3.71 (d, *J* = 13.0 Hz, 1H), 3.57 (d, *J* = 13.1 Hz, 1H), 3.41 (d, *J* = 10.2 Hz, 1H), 2.70 (d, *J* = 9.1 Hz, 1H), 2.31 (s, 2H), 2.22 – 2.18 (m, 2H), 1.85 – 1.78 (m, 1H), 1.77 – 1.65 (m, 4H), 1.65 – 1.52 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 6H), 0.15 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 172.1, 137.6, 127.0, 126.4, 124.9, 79.1, 58.4, 57.9, 56.6, 56.2, 48.3, 37.6, 33.4, 29.9, 25.3, 22.9 12.6.

IR (KBr): υ 2927, 1724, 1450, 1361, 1251, 1087, 839 cm^{-1}. **HRMS(ESI)** *(m/z)*: $[M+H]^+$ Calcd for $C_{24}H_{38}NO_3Si$ 416.2615; found: 416.2619.

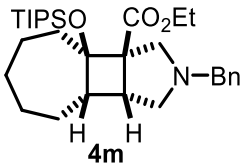
Ethyl-2-benzyl-3b-((triethylsilyl)oxy)decahydrocyclohepta[3,4]cyclobuta[1,2-c]pyrrole-3a(1H)-carboxylate (4l)



4l

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **4l** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (71.2 mg, >20:1 *dr*, 62% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.29 (d, *J* = 8.5 Hz, 2H), 7.25 – 7.23 (m, 2H), 7.18 – 7.16 (m, 1H), 4.13 – 4.00 (m, 2H), 3.69 (d, *J* = 12.9 Hz, 1H), 3.42 (t, *J* = 11.1 Hz, 2H), 2.61 (d, *J* = 9.1 Hz, 1H), 2.31 (s, 2H), 2.11 (d, *J* = 9.7 Hz, 2H), 1.76 – 1.67 (m, 2H), 1.61 – 1.49 (m, 4H), 1.42 (s, 1H), 1.26 (d, *J* = 10.0 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.9 Hz, 9H), 0.58 (q, *J* = 7.9 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 173.9, 139.5, 128.7, 128.1, 126.7, 80.4, 60.1, 60.1, 59.7, 58.1, 58.0, 50.0, 38.6, 35.9, 31.9, 26.6, 24.3, 14.3, 7.2, 6.8. **IR** (KBr): υ 2925, 1724, 1452, 1365, 1218, 1087, 732 cm^{-1}. **HRMS(APCI)** *(m/z)*: $[M+H]^+$ Calcd for $C_{27}H_{44}NO_3Si$ 458.3085; found: 458.3104.

Ethyl-2-benzyl-3b-((triisopropylsilyl)oxy)decahydrocyclohepta[3,4]cyclobuta[1,2-c]pyrrole-3a(1H)-carboxylate (4m)

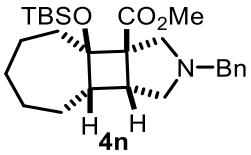


4m

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **4m** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (91.0 mg, >20:1 *dr*, 73% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.40 – 6.94 (m, 5H), 4.14 – 3.98 (m, 2H), 3.73 (d, *J* = 12.8 Hz, 1H), 3.57 (d, *J* = 9.9 Hz, 1H), 3.34 (d, *J* = 12.8 Hz, 1H), 2.66 – 2.42 (m, 3H), 2.14 – 1.88 (m, 3H), 1.59 (dq, *J* = 15.9, 7.3, 5.9 Hz, 3H), 1.53 – 1.35 (m, 4H), 1.29 – 1.14 (m, 6H), 1.06 – 0.96 (m, 20H). **^{13}C NMR** (151 MHz, $CDCl_3$):

δ 174.4, 139.5, 128.8, 128.0, 126.7, 80.6, 60.1, 59.9, 59.6, 58.7, 57.7, 49.5, 38.0, 36.9, 32.2, 25.7, 23.6, 18.4, 14.3, 13.9. **IR** (KBr): υ 2929, 1726, 1498, 1379, 1255, 1126, 887, 676cm^{-1}. **HRMS(ESI)** *(m/z)*: [M+Na]$^{+}$ Calcd for $C_{30}H_{49}NNaO_3Si$ 522.3374; found: 522.3368.

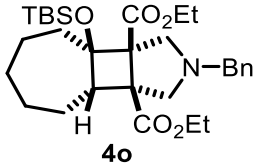
Methyl-2-benzyl-3b-((tert-butyldimethylsilyl)oxy)decahydrocyclohepta[3,4] cyclobuta[1,2-c]pyrrole-3a(1H)-carboxylate (4n)



4n

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **4n** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (89.9 mg, >20:1 *dr*, 81% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.29 (m, 2H), 7.25 – 7.23 (m, 1H), 3.74 (d, *J* = 12.9 Hz, 1H), 3.68 (s, 3H), 3.52 (dd, *J* = 15.0, 12.4 Hz, 2H), 2.68 (d, *J* = 9.0 Hz, 1H), 2.41 (d, *J* = 11.9 Hz, 2H), 2.22 (d, *J* = 10.5 Hz, 2H), 1.81 – 1.76 (m, 2H), 1.65 (dd, *J* = 13.8, 9.5 Hz, 4H), 1.45 – 1.29 (m, 4H), 0.93 (s, 9H), 0.17 (s, 3H), 0.10 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 174.4, 139.3, 128.8, 128.1, 126.7, 80.0, 60.3, 59.7, 57.9, 57.8, 51.3, 49.5, 38.9, 35.9, 31.8, 26.2, 26.1, 24.1, 18.6, -1.9, -2.0. **IR** (KBr): υ 2927, 1730, 1461, 1355, 1257, 1120, 833 cm^{-1}. **HRMS(ESI)** *(m/z)*: [M+H]$^{+}$ Calcd for $C_{26}H_{42}NO_3Si$ 444.2928; found: 444.2922.

Diethyl-2-benzyl-3b-((tert-butyldimethylsilyl)oxy)octahydrocyclohepta [3,4]cyclobuta[1,2-c]pyrrole-3a,8b(1H,3bH)-dicarboxylate (4o)

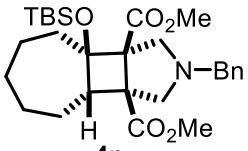


4o

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **4o** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (61.0 mg, >20:1 *dr*, 46% yield). **^{1}H NMR** (600 MHz,$CDCl_3$): δ 7.38 – 7.29 (m, 4H), 7.27 – 7.22 (m, 1H), 4.23 – 4.03 (m, 4H), 3.74 (d, *J* = 12.7 Hz, 1H), 3.63 (d, *J* = 9.7 Hz, 1H), 3.49 (d, *J* = 12.7 Hz, 1H), 2.92 (d, *J* = 9.4 Hz, 1H), 2.81 (dd, *J* = 12.2, 7.2 Hz, 1H), 2.53

(d, *J* = 9.4 Hz, 1H), 2.32 (d, *J* = 9.7 Hz, 1H), 2.30 – 2.24 (m, 2H), 1.93 – 1.77 (m, 1H), 1.73 – 1.64 (m, 3H), 1.60 (s, 2H), 1.23 (dt, *J* = 11.4, 7.0 Hz, 8H), 0.94 (s, 9H), 0.16 (s, 3H), 0.00 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 174.1, 173.7, 141.0, 130.7, 130.2, 128.8, 82.4, 63.6, 62.4, 62.2, 61.9, 61.5, 61.4, 56.9, 54.6, 35.2, 33.9, 30.5, 28.7, 28.1, 27.5, 20.8, 16.2, 16.0. **IR** (KBr): υ 2923, 1624, 1498, 1258, 1078, 833 cm^{-1}. **HRMS(APCI)** *(m/z)*: $[M+H]^+$ Calcd for $C_{30}H_{48}NO_5Si$ 530.3296; found: 530.3334.

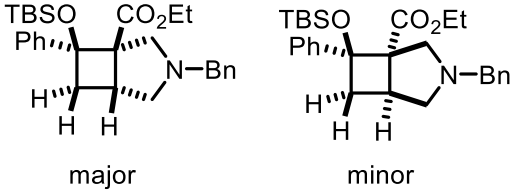
Dimethyl-2-benzyl-3b-((tert-butyldimethylsilyl)oxy)octahydrocyclohepta [3,4]cyclobuta[1,2-c]pyrrole-3a,8b(1H,3bH)-dicarboxylate (4p)



4p

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **4p** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (51.6 mg, >20:1 *dr*, 41% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.21 – 7.15 (m, 4H), 7.11 (d, *J* = 6.6 Hz, 1H), 3.59 (s, 3H), 3.45 (d, *J* = 1.3 Hz, 2H), 3.43 (s, 3H), 3.08 (dd, *J* = 12.8, 5.4 Hz, 1H), 3.03 (d, *J* = 10.4 Hz, 1H), 2.74 (d, *J* = 9.8 Hz, 1H), 2.56 (d, *J* = 9.8 Hz, 1H), 2.16 – 2.10 (m, 2H), 1.76 – 1.61 (m, 3H), 1.44 (d, *J* = 1.8 Hz, 3H), 1.42 – 1.37 (m, 1H), 1.11 (s, 2H), 0.66 (s, 9H), 0.10 (s, 3H), -0.00 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 173.4, 169.9, 138.8, 128.7, 128.3, 127.2, 82.2, 66.8, 59.9, 57.8, 57.7, 52.1, 51.5, 50.4, 49.5, 32.9, 31.9, 29.7, 27.5, 26.5, 25.9, 24.1, 18.7, -2.5. **IR** (KBr): υ 2929, 1724, 1498, 1263, 1091, 833 cm^{-1}. **HRMS(APCI)** *(m/z)*: $[M+H]^+$ Calcd for $C_{28}H_{44}NO_5Si$ 502.2983; found: 502.2993.

Ethyl-3-benzyl-7-((tert-butyldimethylsilyl)oxy)-7-phenyl-3-azabicyclo[3.2.0]heptane-1-carboxylate (7a)

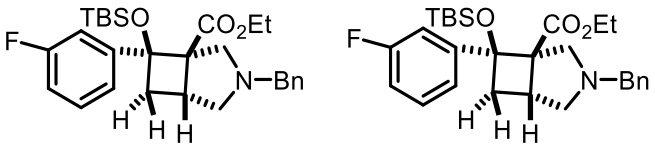


7a

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **7a** was isolated

(petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (44 mg, 1.3:1 *dr*, 63% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): (major) δ 7.59 (d, *J* = 7.0 Hz, 2H), 7.37 – 7.34 (m, 2H), 7.33 – 7.29 (m, 1H), 7.12 – 7.10 (m, 3H), 6.92 – 6.90 (m, 2H), 4.26 – 4.14 (m, 2H), 3.64 (d, *J* = 13.8 Hz, 1H), 3.39 – 3.33 (m, 1H), 3.24 (d, *J* = 13.8 Hz, 1H), 2.89 (dd, *J* = 12.7, 6.2 Hz, 1H), 2.82 (d, *J* = 9.1 Hz, 1H), 2.69 (d, *J* = 10.6 Hz, 1H), 2.35 (dd, *J* = 12.7, 9.5 Hz, 1H), 2.24 (dd, *J* = 9.2, 5.1 Hz, 1H), 1.86 (d, *J* = 10.6 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.83 (s, 9H), -0.08 (s, 3H), -0.45 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): (major) δ 172.1, 141.4, 139.3, 127.9, 127.9, 127.7, 127.6, 127.3, 126.4, 80.5, 64.4, 60.3, 59.3, 59.0, 58.1, 35.0, 33.7, 25.6, 17.9, 14.3, -3.1, -3.4. **^{1}H NMR** (600 MHz, $CDCl_3$): (minor) δ 7.44 – 7.41 (m, 2H), 7.35 (d, *J* = 6.5 Hz, 2H), 7.30 – 7.27 (m, 2H), 7.26 – 7.21 (m, 3H), 7.18 – 7.13 (t, 1H), 3.80 (dd, *J* = 14.4, 11.5 Hz, 2H), 3.55 – 3.43 (m, 3H), 2.87 – 2.83 (m, 1H), 2.78 – 2.70 (m, 2H), 2.50 (dd, *J* = 12.3, 7.4 Hz, 1H), 2.25 (d, *J* = 10.3 Hz, 1H), 2.11 (dd, *J* = 9.1, 4.5 Hz, 1H), 0.92 (s, 9H), 0.82 (t, *J* = 7.1 Hz, 3H), 0.00 (s, 3H), -0.25 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): (minor) δ 172.6, 144.1, 139.2, 129.0, 128.1, 127.4 127.0, 126.8, 126.4, 76.3, 65.5, 59.9, 59.9, 58.2, 56.7, 36.7, 33.3, 26.1, 18.5, 13.7, -2.6, -2.8. **IR** (KBr): υ 2949, 1732, 1454, 1369, 1265, 1199, 999, 833 cm^{-1}. **HRMS(ESI)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{28}H_{39}NNaO_3Si$ 488.2591; found: 488.2603.

Ethyl-3-benzyl-7-((tert-butyldimethylsilyl)oxy)-7-(3-fluorophenyl)-3-azabicyclo[3.2.0]heptane-1-carboxylate (7b)

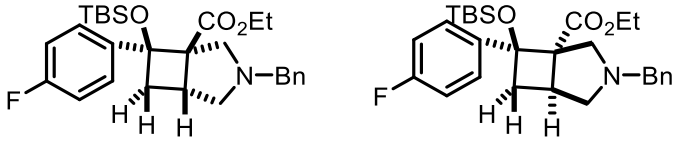


7b

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **7b** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (52.6 mg, 2.3:1 *dr*, 44% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): (major) δ 7.39 – 7.27 (m, 3H), 7.19 – 7.11 (m, 3H),7.00 –6.98 (m, 3H), 4.27 – 4.13 (m, 2H), 3.64 (d, *J* = 13.5 Hz, 1H), 3.35 –3.33 (m, 1H), 3.24 (d, *J* = 13.5 Hz, 1H), 2.83 (dd, *J* = 8.0, 3.8 Hz, 1H), 2.59 (d, *J* =

10.7 Hz, 1H), 2.34 (dd, *J* = 12.8, 9.4 Hz, 1H), 2.23 (dd, *J* = 9.2, 5.0 Hz, 1H), 1.87 (d, *J* = 10.6 Hz, 1H), 1.60 (d, *J* = 3.6 Hz, 1H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.84 (s, 9H), -0.06 (s, 3H), -0.39 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): (major) δ 171.7, 163.3 (d, *J* = 244.6 Hz), 144.3 (d, *J* = 6.0 Hz) 139.1, 129.0 (d, *J* = 7.6 Hz), 127.9 (d, *J* = 12.0 Hz), 126.6, 123.4, 114.9 (d, *J* = 21.1 Hz), 114.2 (d, *J* = 21.1 Hz), 64.4, 60.4, 59.2, 59.1, 57.9, 35.0, 33.7, 29.7, 25.6, 18.0, 14.2, -3.1, -3.4. **^{19}F NMR** (565 MHz, $CDCl_3$): (major) δ -113.9. **^{1}H NMR** (400 MHz, $CDCl_3$): (minor) δ 7.40 – 7.29 (m, 4H), 7.28 – 7.17 (m, 4H), 6.96 – 6.84 (m, 1H), 3.85 – 3.77 (m, 2H), 3.66 – 3.49 (m, 3H), 2.92 – 2.84 (m, 1H), 2.79 (d, *J* = 9.2 Hz, 1H), 2.70 (dd, *J* = 12.3, 8.4 Hz, 1H), 2.56 (dd, *J* = 12.3, 7.5 Hz, 1H), 2.27 (d, *J* = 10.4 Hz, 1H), 2.15 (dd, *J* = 9.2, 4.5 Hz, 1H), 0.95 (s, 9H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.06 (s, 3H), -0.20 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): (minor) δ 172.4, 163.2 (d, *J* = 244.6 Hz), 147.3(d, *J* = 6.0 Hz), 139.1, 129.1, 128.9 (d, *J* = 7.55 Hz), 128.1, 126.9, 121.7 (d, *J* = 15.1 Hz), 113.9(d, *J* = 22.6 Hz, 1H), 65.3, 60.1, 59.9, 58.1, 56.7, 36.7, 33.3, 29.7, 26.1, 18.4, 13.7, -2.6, -2.9. **^{19}F NMR** (565 MHz, $CDCl_3$): (minor) δ -114.1. **IR** (KBr): υ 2929, 1728, 1627, 1454,1365, 1261, 1047, 688, 459 cm^{-1}. **HRMS(ESI)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{28}H_{38}FNNaO_3Si$ 506.2497; found: 506.2496.

Ethyl-3-benzyl-7-((tert-butyldimethylsilyl)oxy)-7-(4-fluorophenyl)-3-azabicyclo[3.2.0]heptane-1-carboxylate (7c)

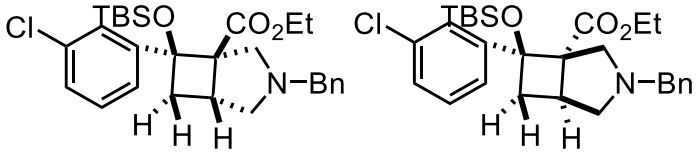


7c

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **7c** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (37.3 mg, 1.2:1 *dr*, 31% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): (major) δ 7.56 – 7.54 (m, 2H), 7.18 – 7.11 (m, 3H), 7.05 – 7.02 (m, 2H), 6.94 – 6.88 (m, 2H), 4.28 – 4.10 (m, 2H), 3.64 (d, *J* = 13.6 Hz, 1H), 3.33 (dt, *J* = 10.3, 5.6 Hz, 1H), 3.22 (d, *J* = 13.6 Hz, 1H), 2.82 (q, *J* = 5.3 Hz, 2H), 2.60 (d, *J* = 10.6 Hz, 1H), 2.35 (dd, *J* = 12.7, 9.5 Hz, 1H), 2.23 (dd, *J* = 9.2, 5.1 Hz, 1H), 1.85 (d, *J* = 10.6 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 0.83 (s, 9H), -0.07

(s, 3H), -0.43 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): (major) δ 171.9, 163.0 (d, *J* = 246.1 Hz), 139.2, 137.5(d, *J* = 3.0 Hz), 129.6, 127.9 (d, *J* = 19.63 Hz), 126.6, 114.4(d, *J* = 21.1 Hz), 64.4, 60.4, 59.4, 59.1, 58.1, 35.3, 33.6, 29.7, 25.6, 17.9, 14.3, -3.1, -3.4. **^{19}F NMR** (565 MHz, $CDCl_3$): (major) δ -115.6. **^{1}H NMR** (600 MHz, $CDCl_3$): (minor) δ 7.41 – 7.37 (m, 2H), 7.34 – 7.32 (m, 2H), 7.29 – 7.26 (m, 2H), 7.23 – 7.19 (m, 1H), 6.94 – 6.91 (m, 2H), 3.81 – 3.71 (m, 2H), 3.57 (dd, *J* = 10.8, 7.1 Hz, 1H), 3.53 – 3.46 (m, 2H), 2.86 – 2.79 (m, 1H), 2.74 (d, *J* = 9.1 Hz, 1H), 2.68 (dd, *J* = 12.3, 8.4 Hz, 1H), 2.50 (dd, *J* = 12.4, 7.5 Hz, 1H), 2.23 (d, *J* = 10.3 Hz, 1H), 2.10 (dd, *J* = 9.2, 4.5 Hz, 1H), 0.90 (s, 9H), 0.86 (t, *J* = 7.1 Hz, 3H), 0.00 (s, 3H), -0.27 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): (minor) δ 172.6, 162.8 (d, *J* = 246.1 Hz), 140.1 (d, *J* = 3.0 Hz), 139.2, 129.1, 128.2, 128.1, 126.9, 114.2 (d, *J* = 21.1 Hz), 65.5, 60.1, 59.9, 58.2, 56.7, 36.8, 33.2, 26.1, 18.5, 13.8, -2.6, -2.8. **^{19}F NMR** (565 MHz, $CDCl_3$): (minor) δ-116.1. **IR** (KBr): υ 2943, 1732, 1620, 1508, 1454, 1263, 1097, 835, 582 cm^{-1}. **HRMS(ESI)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{28}H_{38}FNNaO_3Si$ 506.2497; found: 506.2496.

Ethyl-3-benzyl-7-((tert-butyldimethylsilyl)oxy)-7-(3-chlorophenyl)-3-azabicyclo[3.2.0]heptane-1-carboxylate (7d)

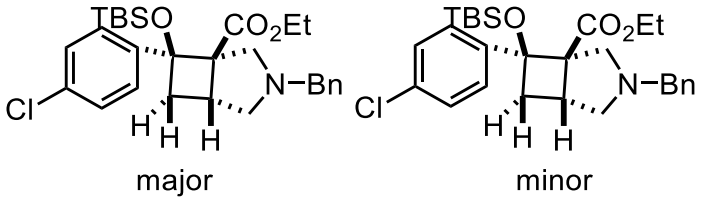


7d

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **7d** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (97.6 mg, 1.2:1 *dr*, 78% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): (major) δ 7.66 (d, *J* = 2.2 Hz, 1H), 7.53 (d, *J* = 6.8 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.26 – 7.19 (m, 3H), 7.06 (d, *J* = 6.3 Hz, 2H), 4.32 – 4.25 (m, 1H), 4.25 – 4.18 (m, 1H), 3.70 (d, *J* = 13.4 Hz, 1H), 3.42 – 3.36 (m, 1H), 3.30 (d, *J* = 13.4 Hz, 1H), 2.93 – 2.81 (m, 2H), 2.61 (d, *J* = 10.7 Hz, 1H), 2.39 (dd, *J* = 12.8, 9.4 Hz, 1H), 2.29 (dd, *J* = 9.2, 5.1 Hz, 1H), 1.93 (d, *J* = 10.7 Hz, 1H), 1.38 (t, *J* = 7.2 Hz, 3H), 0.90 (s, 9H), 0.00 (s, 3H), -0.32 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): (major) δ 171.7, 143.7, 139.1, 133.6, 128.9, 128.4, 128.1, 127.9, 127.4, 126.6, 126.1, 80.0, 64.4, 60.4, 59.3, 59.2, 58.0, 34.9, 33.7, 25.6, 18.0, 14.3, -3.0, -3.3. **^{1}H NMR**

(400 MHz, $CDCl_3$): (minor) δ 7.50 (t, *J* = 1.9 Hz, 1H), 7.41 – 7.30 (m, 5H), 7.29 – 7.17 (m, 3H), 3.84 (s, 1H), 3.81 (d, *J* = 3.2 Hz, 1H), 3.69 – 3.49 (m, 3H), 2.93 – 2.84 (m, 1H), 2.80 (d, *J* = 9.2 Hz, 1H), 2.71 (dd, *J* = 12.4, 8.4 Hz, 1H), 2.56 (dd, *J* = 12.4, 7.5 Hz, 1H), 2.28 (d, *J* = 10.4 Hz, 1H), 2.16 (dd, *J* = 9.2, 4.5 Hz, 1H), 0.96 (s, 9H), 0.93 (t, *J* = 7.1 Hz, 3H), 0.07 (s, 3H), -0.19 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): (minor) δ 172.4, 146.6, 139.1, 133.6, 129. 1, 128.8, 128.2, 127.2, 127.1, 126.9, 124.2, 65.4, 60.2, 59.9, 58.2, 56.73, 36.7, 33.30, 26.1, 18.5, 13.73, -2.55, -2.8. **IR** (KBr): υ 2947, 1733, 1631, 1465, 1413, 1261, 1103, 833, 466 cm^{-1}. **HRMS(ESI)** *(m/z)*: $[M+H]^+$ Calcd for $C_{28}H_{39}ClNO_3Si$ 500.2382; found: 500.2384.

Ethyl-3-benzyl-7-((tert-butyldimethylsilyl)oxy)-7-(4-chlorophenyl)-3-azabicyclo[3.2.0]heptane-1-carboxylate (7e)

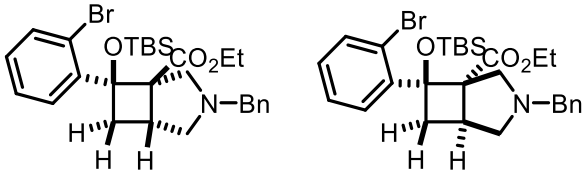


7e

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **7e** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (32.5 mg, 1:1 *dr*, 26% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): (major) δ 7.51 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 3.8 Hz, 3H), 6.90 (s, 2H), 4.26 – 4.09 (m, 2H), 3.65 (d, *J* = 13.5 Hz, 1H), 3.32 (s, 1H), 3.21 (d, *J* = 13.5 Hz, 1H), 2.86 – 2.67 (m, 2H), 2.58 (d, *J* = 10.6 Hz, 1H), 2.35 (dd, *J* = 12.8, 9.6 Hz, 1H), 2.26 – 2.15 (m, 1H), 1.83 (d, *J* = 10.7 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.82 (s, 9H), -0.07 (s, 3H), -0.42 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): (major) δ 171.8, 140.1, 139.1, 133.2, 129.4, 128.0, 127.8, 127.8, 126.6, 64.4, 60.4, 59.4, 59.1, 58.5, 58.0, 53.5, 35.1, 33.5, 29.7, 25.6, 18.5, 17.9, 14.3, -3.0, -3.3. **^{1}H NMR** (400 MHz, $CDCl_3$): (minor) δ 7.44 – 7.36 (m, 4H), 7.35 – 7.31 (m, 2H), 7.28 – 7.25 (m, 3H), 3.85 (s, 1H), 3.82 (d, *J* = 3.1 Hz, 1H), 3.66 – 3.61 (m, 1H), 3.60 – 3.51 (m, 2H), 2.91 – 2.85 (m, 1H), 2.80 (d, *J* = 9.2 Hz, 1H), 2.72 (dd, *J* = 12.3, 8.4 Hz, 1H), 2.56 (dd, *J* = 12.3, 7.5 Hz, 1H), 2.28 (d, *J* = 10.4 Hz, 1H), 2.16 (dd, *J* = 9.2, 4.5 Hz, 1H), 0.96 (s, 9H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.07 (s, 3H), -0.20 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): (minor) δ 129.1, 128.2, 127.9, 127. 6, 126.9, 65.4, 60.1,

59.9, 58.5, 58.2, 56.7, 53.5, 36.7, 33.3, 29.7, 26.1, 18.5, 13.78, -2.6, -2.7. **IR** (KBr): υ 2935, 1732, 1629, 1467, 1263, 1095, 833, 576 cm^{-1}. **HRMS(ESI)** *(m/z)*: $[M+H]^+$ Calcd for $C_{28}H_{39}ClNO_3Si$ 500.2382; found: 500.2384.

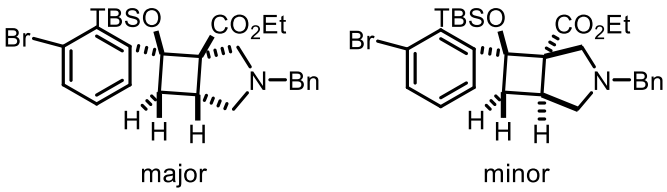
Ethyl-3-benzyl-7-(2-bromophenyl)-7-((tert-butyldimethylsilyl)oxy)-3-azabicyclo[3.2.0]heptane-1-carboxylate (7f)



7f

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **7f** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (56.5 mg, 3:1 *dr*, 42% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.04* (d, *J* = 7.9 Hz, 1H), 7.53* (d, *J* = 8.0 Hz, 1H), 7.25 – 7.18* (m, 2H), 7.06* (d, *J* = 3.4 Hz, 3H), 6.96 – 6.94* (m, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.59* (d, *J* = 13.8 Hz, 1H), 3.37 – 3.31* (m, 2H), 3.31 – 3.26* (m, 1H), 2.85* (d, *J* = 10.7 Hz, 1H), 2.68* (d, *J* = 9.1 Hz, 1H), 2.48* (dd, *J* = 12.7, 8.6 Hz, 1H), 2.28* (dd, *J* = 9.2, 5.0 Hz, 1H), 2.09* (d, *J* = 10.8 Hz, 1H), 1.27* (t, *J* = 7.2 Hz, 3H), 0.75 *(s, 9H), 0.00* (s, 3H), -0.53* (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 172.4, 172.0 140.1, 139.3, 135.0, 134.5, 133.3, 130.0, 129.0, 128.8, 128.0, 127.9, 127.8, 127.7, 127.1, 126.4, 121.6, 83.5, 65.8, 64.3, 60.7, 60.4, 59.5, 59.2, 59.1, 58.5, 58.4, 39.1, 38.2, 35.1, 34.2, 31.5, 30.2, 29.7, 25.6, 25.5, 18.1, 18.0, 14.3, 14.1, -3.0, -4.0. **IR** (KBr): υ 2937, 1728, 1463,1375, 1261, 1101, 833, 468 cm^{-1}. **HRMS(APCI)** *(m/z)*: $[M+H]^+$ Calcd for $C_{28}H_{39}BrNO_3Si$ 544.1877; found: 544.1872.

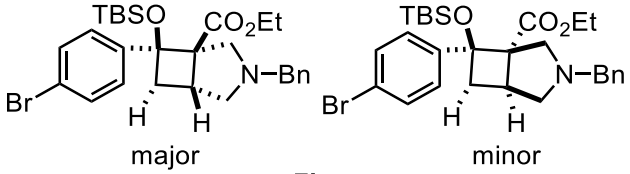
Ethyl-3-benzyl-7-(3-bromophenyl)-7-((tert-butyldimethylsilyl)oxy)-3-azabicyclo[3.2.0]heptane-1-carboxylate (7g)



7g

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **7g** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (72.0 mg, 1:1 *dr*, 53% yield).**^{1}H NMR** (600 MHz, $CDCl_3$): (major) δ 7.76 (s, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.45 – 7.37 (m, 1H), 7.30 – 7.11 (m, 4H), 7.01 (d, *J* = 7.0 Hz, 2H), 4.28 – 4.11 (m, 2H), 3.63 (d, *J* = 13.5 Hz, 1H), 3.37 – 3.15 (m, 2H), 2.82 (t, *J* = 12.4 Hz, 2H), 2.55 (d, *J* = 10.8 Hz, 1H), 2.45 – 2.29 (m, 1H), 2.22 (s, 1H), 1.87 (d, *J* = 10.8 Hz, 1H), 1.32 (td, *J* = 6.9, 2.7 Hz, 3H), 0.84 (s, 9H), -0.06 (s, 3H), -0.38 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): (major) δ 171.6, 143.9, 139.09, 130.1, 130.3, 129.2, 128.0, 127.9, 126.6, 126.5, 121.8, 79.9, 64.4, 60.4, 59.2, 59.1, 58.0, 34.9, 33.7, 29.7, 25.6, 17.9, 14.2, -3.1, -3.3. **^{1}H NMR** (600 MHz, $CDCl_3$): (minor) δ 7.60 – 7.59 (m, 1H), 7.33 – 7.25 (m, 6H), 7.22 – 7.17 (m, 1H), 7.12 – 7.10 (m, 1H), 3.77 (s, 1H), 3.75 (d, *J* = 2.4 Hz, 1H), 3.61 – 3.49 (m, 2H), 3.48 (d, *J* = 12.7 Hz, 1H), 2.84 – 2.81 (m, 1H), 2.74 (d, *J* = 9.2 Hz, 1H), 2.64 (dd, *J* = 12.4, 8.4 Hz, 1H), 2.49 (dd, *J* = 12.4, 7.5 Hz, 1H), 2.21 (d, *J* = 10.4 Hz, 1H), 2.10 (dd, *J* = 9.2, 4.5 Hz, 1H), 0.90 (s, 9H), 0.87 (t, *J* = 7.1 Hz, 3H), 0.00 (s, 3H), -0.25 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): (minor) δ 172.4, 146.8, 139.1, 130.1, 130.0, 129.1, 129.1, 128.2, 126.9, 124.6, 121.9, 75.9, 65.4, 60.2, 59.9, 58.2, 56.7, 36.7, 33.3, 26.1, 18.5, 13.8, -2.6, -2.8. **IR** (KBr): υ 2941, 1732, 1463,1363, 1265, 1103, 829, 468 cm^{-1}.**HRMS(APCI)** *(m/z)*: $[M+H]^+$ Calcd for $C_{28}H_{39}BrNO_3Si$ 544.1877; found: 544.1872.

Ethyl-3-benzyl-7-(4-bromophenyl)-7-((tert-butyldimethylsilyl)oxy)-3-azabicyclo[3.2.0]heptane-1-carboxylate (7h)

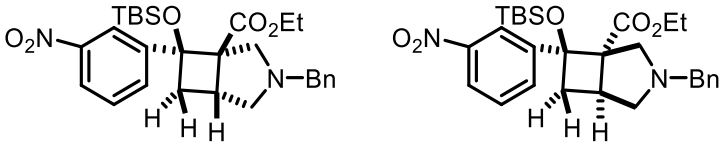


7h

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **7h** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (42.1 mg, 1:1 *dr*, 31% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): (major) δ 7.49 – 7.44 (m, 4H), 7.17 (d, *J* = 4.9 Hz, 3H), 6.91 – 6.90 (m, 2H), 4.30 – 4.09 (m, 2H), 3.65 (d, *J* = 13.4 Hz, 1H), 3.32 (s, 1H), 3.21 (d, *J* = 13.4 Hz, 1H), 2.86 – 2.76 (m, 2H), 2.57 (d, *J* = 10.4 Hz, 1H), 2.35 (dd, *J* = 12.8, 9.5 Hz, 1H), 2.29 – 2.18 (m, 1H), 1.83 (d, *J* = 10.6 Hz, 1H), 1.28 (d,

J = 7.4 Hz, 3H), 0.82 (s, 9H), -0.07 (s, 3H), -0.42 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): (major) δ 171.8, 140.6, 139.1, 130.8, 129.7, 128.0, 127.8, 126.6, 121.5, 64.3, 60.4, 59.4, 59.1, 58.0, 35.1, 33.5, 29.7, 25.6, 17.9, 14.3, -3.1, -3.3. **^{1}H NMR** (600 MHz, $CDCl_3$): (minor) δ 7.38 – 7.34 (m, 2H), 7.33 – 7.24 (m, 6H), 7.23 – 7.17 (m, 1H), 3.76 (d, *J* = 10.8 Hz, 2H), 3.60 – 3.54 (m, 1H), 3.53 – 3.45 (m, 2H), 2.83 – 2.79 (m, 1H), 2.73 (d, *J* = 9.2 Hz, 1H), 2.64 (dd, *J* = 12.4, 8.4 Hz, 1H), 2.49 (dd, *J* = 12.4, 7.5 Hz, 1H), 2.21 (d, *J* = 10.4 Hz, 1H), 2.09 (dd, *J* = 9.2, 4.5 Hz, 1H), 0.89 (s, 9H), 0.85 (t, *J* = 7.1 Hz, 3H), 0.00 (s, 3H), -0.27 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): (minor) δ 172.4, 143.5, 139.1, 130.5, 129.1, 128.2, 128.2, 126.9, 121.1, 76.0, 65.4, 60.1, 59.9, 58.2, 56.7, 36.6, 33.3, 26.1, 18.5, 13.8, -2.5, -2.7. **IR** (KBr): υ 2927, 1733, 1631, 1463, 1269, 1049, 831, 590 cm^{-1}. **HRMS(ESI)** *(m/z)*: $[M+H]^+$ Calcd for $C_{28}H_{39}BrNO_3Si$ 544.1877; found: 544.1872.

Ethyl-3-benzyl-7-((tert-butyldimethylsilyl)oxy)-7-(3-nitrophenyl)-3-azabicyclo[3.2.0]heptane-1-carboxylate (7i)

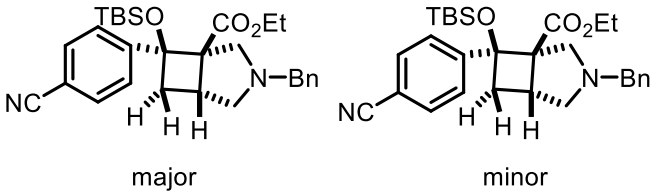


7i

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **7i** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (17.5 mg, 1:1 *dr*, 14% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): (major) δ 8.48 – 8.45(m, 1H), 8.13 (d, *J* = 8.8 Hz, 1H), 7.93 – 7.89 (m, 1H), 7.49 – 7.42 (m, 1H), 7.13 – 7.09 (m, 3H), 6.98 (d, *J* = 4.2 Hz, 2H), 4.27 – 4.22 (m, 1H), 4.17 – 4.13 (m, 1H), 3.60 (dd, *J* = 13.3, 4.5 Hz, 1H), 3.37 – 3.33 (m, 1H), 3.19 (dd, *J* = 13.3, 4.6 Hz, 1H), 2.87 (dd, *J* = 9.8, 4.3 Hz, 2H), 2.43 – 2.37 (m, 1H), 2.34 (dd, *J* = 11.1, 4.4 Hz, 1H), 2.25 – 2.20 (m, 1H), 1.89 – 1.82 (m, 1H), 1.25 (d, *J* = 4.5 Hz, 3H), 0.84 (s, 9H), -0.04 (s, 3H), -0.39 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): (major) δ 171.3, 147.8, 143.8, 138.8, 133.9, 128.5, 128.1, 128.1, 128.1, 126.8, 122.4, 64.3, 60.6, 59.2, 59.2, 57.9, 34.8, 33.7, 29.7, 25.6, 25.6, 18.0, 14.2, -2.9, -3.2. **^{1}H NMR** (600 MHz, $CDCl_3$): (minor) δ 8.30 – 8.29 (m, *J* = 2.1 Hz, 1H), 8.00 – 7.99 (m, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.36 (m, 1H), 7.27 (d, *J* = 6.6

Hz, 2H), 7.24 – 7.22 (m, 2H), 7.18 – 7.15 (m, 1H), 3.72 (dd, *J* = 11.5, 4.4 Hz, 2H), 3.52 – 3.37 (m, 3H), 2.86 – 2.83 (m, 1H), 2.73 (d, *J* = 9.2 Hz, 1H), 2.64 (dd, *J* = 12.6, 8.4 Hz, 1H), 2.55 (dd, *J* = 12.6, 7.5 Hz, 1H), 2.18 (d, *J* = 10.5 Hz, 1H), 2.08 (dd, *J* = 9.2, 4.5 Hz, 1H), 0.86 (s, 9H), 0.75 (t, *J* = 7.1 Hz, 3H), 0.00 (s, 3H), -0.32 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): (minor) δ 174.5, 150.2, 149.5, 141.3, 134.7, 131.6, 131.0, 130.7, 129.4, 124.5, 124.1, 67.7, 62.7, 62.3, 60.6, 59.1, 39.2, 35.7, 32.1, 28.5, 20.9, 16.2. **IR** (KBr): υ 2931, 1726, 1531, 1461, 1348, 1251, 1087, 837, 684 cm^{-1}. **HRMS(ESI)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{28}H_{38}N_2NaO_5Si$ 533.2442; found: 533.2438.

Ethyl-3-benzyl-7-((tert-butyldimethylsilyl)oxy)-7-(4-cyanophenyl)-3-azabicyclo[3.2.0]heptane-1-carboxylate (7j)

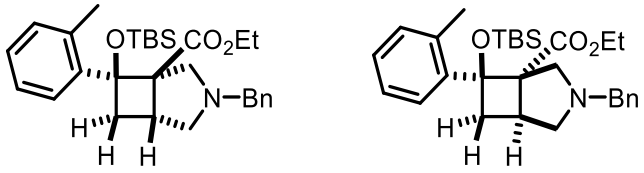


7j

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **7j** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (53.0 mg, 6:1 *dr*, 43% yield). **^{1}H NMR** (600 MHz,$CDCl_3$): (major) δ7.69 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.20 – 7.13 (m, 3H), 6.91 (d, *J* = 7.5 Hz, 2H), 4.26 – 4.13 (m, 2H), 3.63 (d, *J* = 13.3 Hz, 1H), 3.35 – 3.32 (m, 1H), 3.18 (d, *J* = 13.3 Hz, 1H), 2.87 – 2.79 (m, 2H), 2.45 – 2.35 (m, 2H), 2.24 (dd, *J* = 9.3, 5.1 Hz, 1H), 1.85 (d, *J* = 10.8 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.82 (s, 9H), -0.05 (s, 3H), -0.42 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): (major) δ 171.4, 146.9, 138.8, 131.4, 128.5, 128.0, 127.9, 126.8, 119.0, 111.0, 79.8, 64.35, 60.5, 59.3, 59.1, 57.8, 34.7, 33.5, 25.5, 18.0, 14.2, -2.9, -3.2. **^{1}H NMR** (600 MHz, $CDCl_3$): (minor) δ 7.51 (s, 4H), 7.30 – 7.26 (m, 2H), 7.25 – 7.23 (m, 2H), 7.19 – 7.17 (m, 1H), 3.73 (dd, *J* = 11.5, 3.8 Hz, 2H), 3.54 – 3.48 (m, 1H), 3.48 – 3.39 (m, 2H), 2.83 – 2.80 (m, 1H), 2.73 (d, *J* = 9.2 Hz, 1H), 2.62 (dd, *J* = 12.5, 8.4 Hz, 1H), 2.52 (dd, *J* = 12.6, 7.5 Hz, 1H), 2.19 (d, *J* = 10.5 Hz, 1H), 2.08 (dd, *J* = 9.2, 4.5 Hz, 1H), 0.86 (s, 9H), 0.79 (t, *J* = 7.1 Hz, 3H), 0.01 (s, 3H), -0.31 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): (minor) δ 174.5, 152.5, 141.3, 133.8, 131.6, 130.6, 129.5, 129.4, 121.3, 113.3, 78.6, 67.8, 62.7, 62.3, 60.6, 59.2, 39.0, 35.8, 28.5, 20.9, 16.2. **IR** (KBr): υ 2941, 2227, 1722,

1633, 1460, 1361, 1253, 1097, 835, 582 cm^{-1}. **HRMS(APCI)** *(m/z)*: $[M+H]^+$ Calcd for $C_{29}H_{39}N_2O_3Si$ 491.2724; found: 491.2706.

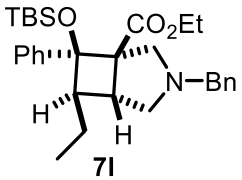
Ethyl-3-benzyl-7-((tert-butyldimethylsilyl)oxy)-7-(o-tolyl)-3-azabicyclo[3.2.0]heptane-1-carboxylate (7k)



7k

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **7k** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (29.0 mg, 3.8:1 *dr*, 24% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.60 – 7.51* (m, 1H), 7.31 – 7.24* (m, 2H), 7.13 – 7.04* (m, 4H), 6.67* (d, *J* = 7.0 Hz, 2H), 4.31 – 4.08* (m, 2H), 3.57* (d, *J* = 13.5 Hz, 1H), 3.31 – 3.19* (m, 1H), 3.19 – 3.04* (m, 2H), 2.73* (dd, *J* = 23.8, 9.8 Hz, 2H), 2.64 – 2.52* (m, 1H), 2.38* (d, *J* = 2.5 Hz, 3H), 2.30 – 2.20* (m, 1H), 2.06* (d, *J* = 9.7 Hz, 1H), 1.33 – 1.29 (m, 3H), 0.84 (d, *J* = 2.5 Hz, 9H), -0.06 (s, 3H), -0.58 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 172.6, 172.3, 139.3, 138.8, 131.9, 128.3, 127.9, 127.7, 127.6, 127. 6, 126.2, 124.8, 83.0, 82.0, 64. 9, 60.6, 59.7, 59.4, 58.0, 39.9, 37.9, 35.3, 33.5, 29.7, 25.6, 22.5, 21.5, 18.0, 14.1, -2.9, -3.4, -3.8, -4.3. **IR** (KBr): υ 2941, 1724, 1631, 1460, 1377, 1261, 1099, 831, 460 cm^{-1}. **HRMS(APCI)** *(m/z)*: $[M+H]^+$ Calcd for $C_{29}H_{42}NO_3Si$ 480.2928; found: 480.2927.

Ethyl-3-benzyl-7-((tert-butyldimethylsilyl)oxy)-6-ethyl-7-phenyl-3-azabicyclo[3.2.0]heptane-1-carboxylate (7l)

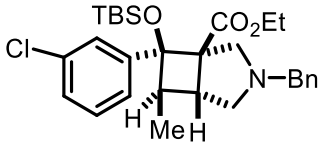


7l

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **7l** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (43.3

mg, >20:1 *dr*, 35% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.58 (s, 2H), 7.41 – 7.31 (m, 3H), 7.13 – 7.00 (m, 3H), 6.78 (d, *J* = 7.0 Hz, 2H), 4.29 – 4.24 (m, 1H), 4.17 – 4.15 (m, 1H), 3.71 (d, *J* = 14.2 Hz, 1H), 3.25 (d, *J* = 14.2 Hz, 1H), 3.01 (d, *J* = 10.7 Hz, 1H), 2.99 – 2.91 (m, 1H), 2.84 – 2.80 (m, 1H), 2.37 (dd, *J* = 9.0, 5.0 Hz, 1H), 2.00 (d, *J* = 10.7 Hz, 1H), 1.86 – 1.77 (m, 1H), 1.77 – 1.70 (m, 1H), 1.66 (d, *J* = 4.7 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 0.99 (t, *J* = 7.4 Hz, 3H), 0.83 (s, 9H), -0.39 (s, 3H), -0.42 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 172.5, 141.4, 139.3, 127.9, 127.8, 127.7, 127.3, 126.2, 82.5, 62.2, 60.4, 59.6, 58.6, 58.4, 47.6, 41.4, 26.2, 22.9, 18.8, 14.1, 11.2, -2.4, -2.9. **IR** (KBr): υ 2956, 1730, 1458, 1373, 1257, 1118, 837, 700 cm^{-1}. **HRMS(ESI)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{30}H_{43}NNaO_3Si$ 516.2904; found: 516.2909.

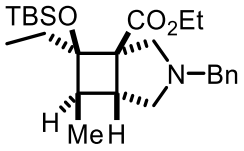
Ethyl-3-benzyl-7-((tert-butyldimethylsilyl)oxy)-7-(3-chlorophenyl)-6-methyl-3-azabicyclo[3.2.0]heptane-1-carboxylate (7m)



7m

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **7m** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (64.3 mg, >20:1 *dr*, 50% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.50 (s, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.16 – 7.07 (m, 3H), 6.78 (d, *J* = 7.1 Hz, 2H), 4.30 – 4.20 (m, 1H), 4.19 – 4.10 (m, 1H), 3.68 (d, *J* = 13.9 Hz, 1H), 3.24 (d, *J* = 13.9 Hz, 1H), 3.00 – 2.94 (m, 1H), 2.91 (d, *J* = 10.7 Hz, 1H), 2.83 (dd, *J* = 7.0, 4.7 Hz, 1H), 2.75 (d, *J* = 9.2 Hz, 1H), 2.26 (dd, *J* = 9.2, 4.9 Hz, 1H), 1.94 (d, *J* = 10.8 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.25 (d, *J* = 7.2 Hz, 3H), 0.83 (s, 9H), -0.31 (s, 3H), -0.43 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 172.2, 140.1, 139.2, 133.6, 127.9, 127.4, 126.5, 81.9, 62.4, 60.5, 58.5, 58.4, 58.4, 42.8, 40.2, 26.2, 18.9, 14.9, 14.1, -2.3, -2.6. **IR** (KBr): υ 2972, 1735, 1456, 1375, 1257, 1041, 867, 690 cm^{-1}. **HRMS(ESI)** *(m/z)*: $[M+Na]^+$ Calcd for $C_{29}H_{40}ClNNaO_3Si$ 536.2358; found: 536.2830.

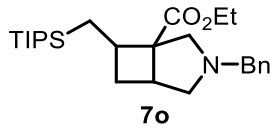
Ethyl-3-benzyl-7-((tert-butyldimethylsilyl)oxy)-7-ethyl-6-methyl-3-azabicyclo[3.2.0]heptane-1-carboxylate (7n)



7n

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **7n** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (24.6 mg, >20:1 *dr*, 23% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.24 (d, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 2H), 7.16 – 7.11 (m, 1H), 4.11 – 3.97 (m, 2H), 3.66 (d, *J* = 12.7 Hz, 1H), 3.35 (d, *J* = 10.2 Hz, 1H), 3.24 (d, *J* = 12.9 Hz, 1H), 2.72 – 2.63 (m, 2H), 2.27 (dd, *J* = 9.7, 7.4 Hz, 1H), 2.17 – 1.97 (m, 2H), 1.55 (dq, *J* = 14.1, 7.0 Hz, 1H), 1.47 (dt, *J* = 14.0, 7.3 Hz, 1H), 1.17 (t, *J* = 7.2 Hz, 3H), 0.93 (d, *J* = 7.5 Hz, 3H), 0.85 (s, 9H), 0.75 (t, *J* = 7.2 Hz, 3H), -0.00 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 174.2, 128.8, 128.1, 126.8, 63.2, 60.3, 58.5, 53.9, 37.5, 36.3, 31.9, 26.1, 19.2, 14.3, 9.7, 7.1, -1.8, -2.4. **IR** (KBr): υ 2933, 1724, 1458, 1375, 1253, 1182, 1039, 835, 775, 690 cm^{-1}. **HRMS(APCI)** *(m/z)*: $[M+H]^+$ Calcd for $C_{25}H_{42}NO_3Si$ 432.2928; found: 432.2932.

Ethyl-3-benzyl-7-((triisopropylsilyl)methyl)-3-azabicyclo[3.2.0]heptane-1-carboxylate (7o)



7o

According to the general procedure, the 3-azabicyclo[3.2.0]heptane **7o** was isolated (petroleum ether/EtOAc = 60:1 v/v as the eluent solvent) as a colorless oil (61.0 mg, >20:1 *dr*, 57% yield). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.21 (m, 1H), 4.25 – 4.08 (m, 2H), 3.75 (d, *J* = 13.4 Hz, 1H), 3.58 (d, *J* = 13.4 Hz, 1H), 2.93 (dd, *J* = 9.8, 6.9 Hz, 2H), 2.83 (d, *J* = 9.3 Hz, 1H), 2.78 – 2.70 (m, 1H), 2.26 (dd, *J* = 9.3, 6.3 Hz, 1H), 2.14 (d, *J* = 9.5 Hz, 1H), 2.06 – 1.95 (m, 1H), 1.93 – 1.81 (m, 1H), 1.63 (d, *J* = 5.1 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.02 (dd, *J* = 5.5, 2.6 Hz, 20H), 0.78 – 0.66 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 173.6, 139.7, 128.4, 128.2, 126.8, 61.1, 60.0, 59.9, 59.3, 58.8, 37.7, 35.4, 32.6, 18.8, 18.8, 14.7, 12.3, 11.2. **IR** (KBr): υ 2933, 1724, 1460, 1371, 1271, 1201, 740 cm^{-1}. **HRMS(ESI)** *(m/z)*: $[M+H]^+$ Calcd for $C_{26}H_{44}NO_2Si$ 430.3136; found: 430.3135.

V. Determination of the Relative Configuration of 7m by NMR Spectroscopy

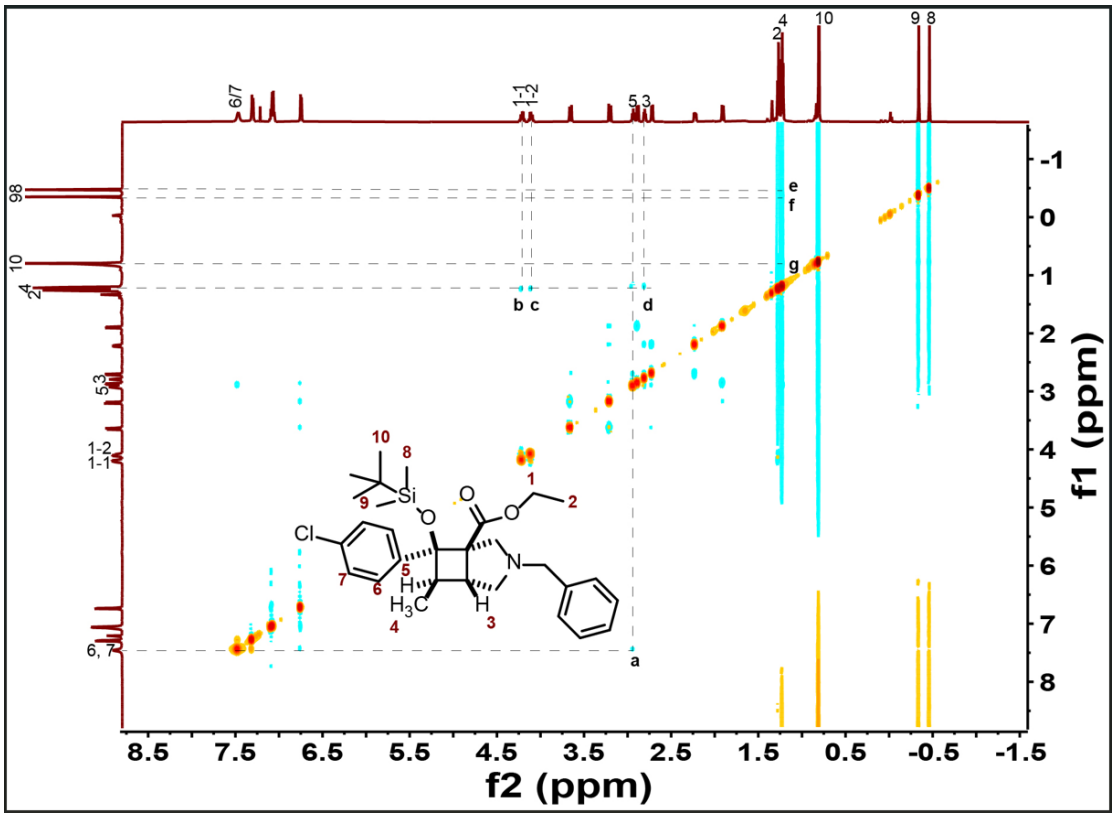
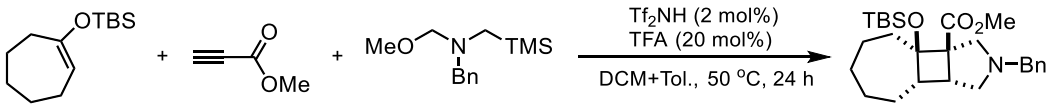


Figure.2D NOESY spectrum of **7m** at 600 MHz in $CDCl_3$.

Proton 5 and proton 6 or 7 have NOE contact (a), proving that 5 and 4-chlorobenzene are on the same side. 4 and 1 have NOE contact (b,c), indicating that -Me and -CO_2Et are on the same side. 4 and 3 have NOE contact (d), proving that proton 3 and -Me are on the same side. 4 and 8,9,10 both have NOE contact (e,f,g), proving that -Me and -OTBS are on the same side.

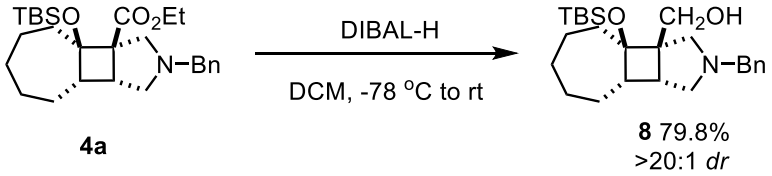
VI. Gram-scale Reaction and Product Transformation



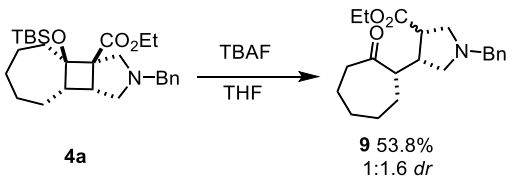
1a 5.5 mmol | **2a** 5 mmol | **3a** 15 mmol | **4n** 75%, >20:1 dr

To a stirred mixture of **1a** (1.24g, 5.5 mmol) in DCM (5 mL) was added methyl propiolate **2a** (0.42g, 5 mmol) and 0.08 M Tf_2NH of toluene solution (1.25 mL), and the mixture gave a light yellow solution. The mixture stirred until the substrate disappeared via TLC detection, then 5 mL toluene, N-benzyl-1-methoxy-N-((trimethylsilyl) methyl) methanamine **3a** (3.55g, 15 mmol) and TFA (0.2 eq. 1.0 mmol)

were added sequentially, and the reaction mixture was stirred at 50 °C for 24 h. The mixture was quenched with saturated $NaHCO_3$ solution, extracted with DCM. The combined organic layer was dried over Na_2SO_4 and the solvent was evaporated in vacuo. The crude material was purified by column chromatography (petroleum ether/ethyl acetate = 60:1) on silica gel to provide the desired compound **4n** (1.65g, 75%, >20:1 *dr*) as a colorless oil.



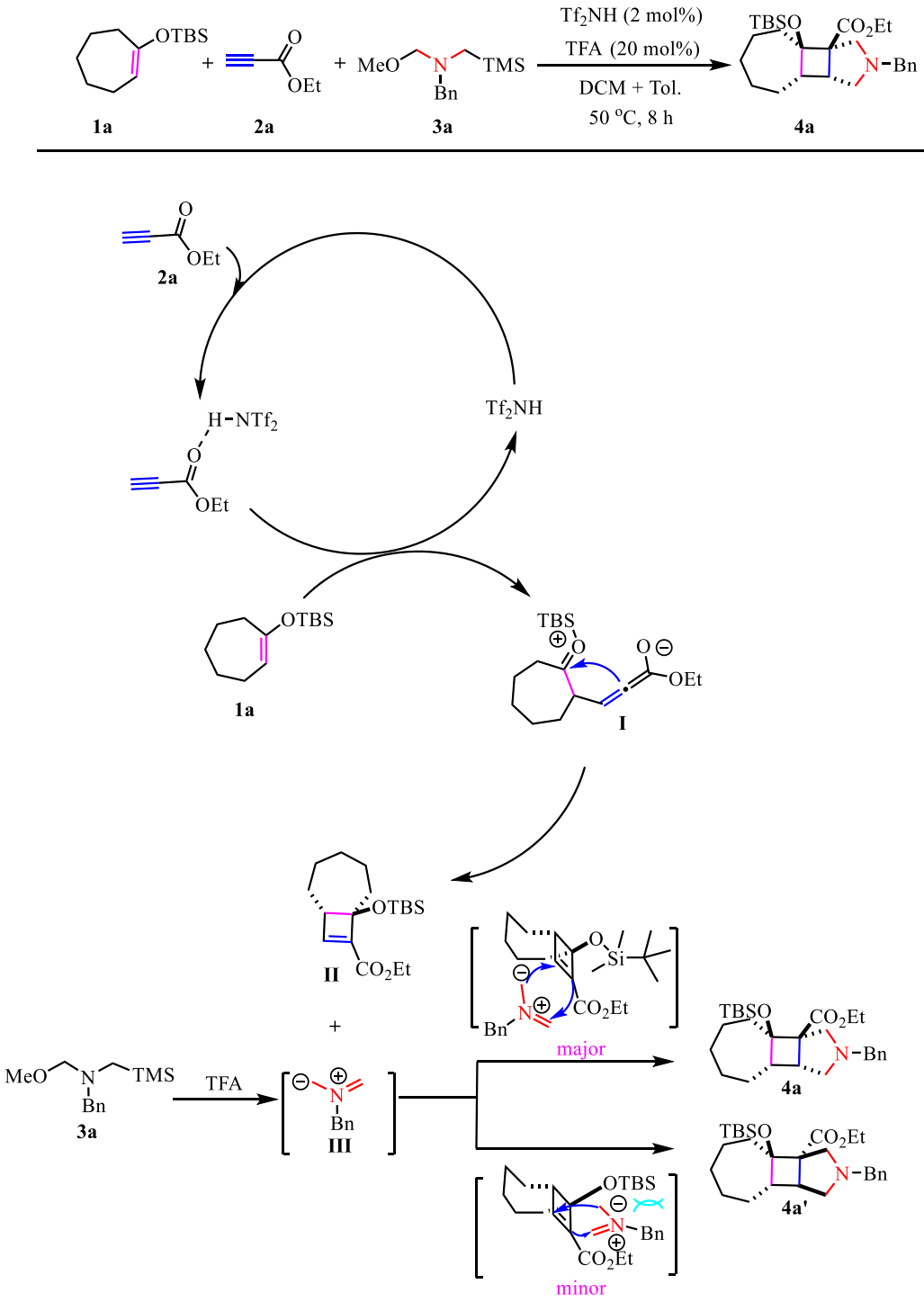
In a schlenk tube **4a** (0.2 mmol, 91.4 mg) was added in anhydrous DCM (2 mL) and then stirred at -78 °C under N_2. When the reaction temperature was cooled to -78 °C, the Diisobutylaluminium hydride (DIBALH: 0.40 mL, 1.5 M in Hexane, 0.6 mmol, 3.0 equiv) was added by drop. The resulting mixture was stirred at 78 °C for 0.5 h. The reaction mixture was then quenched by MeOH (3 mL) at -78 °C, then was raised to room temperature. And a solution of Na_2CO_3 (5 mL, 1.0 M) was added and extracted with DCM (10 mL×3). The combined organic layers were washed with brine and dried over with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography with (petroleum ether/ethyl acetate=1:1)as the eluent to give the colorless oil **8** (67.9mg, 79.8 % >20:1 *dr*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.33 – 7.21 (m, 5H), 3.78 – 3.57 (m, 4H), 3.17 – 3.08 (m, 1H), 3.03 (d, *J* = 9.4 Hz, 1H), 2.82 (d, *J* = 9.4 Hz, 1H), 2.14 (dd, *J* = 9.3, 3.5 Hz, 2H), 1.92 (dd, *J* = 13.9, 7.1 Hz, 1H), 1.80 – 1.58 (m, 6H), 1.54 (s, 1H), 1.32 – 1.16 (m, 4H), 0.90 (s, 9H), 0.06 (s, 3H), -0.01 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 140.3, 130.7, 130.4, 129.2, 80.1, 68.1, 62.6, 62.4, 61.4, 57.8, 56.8, 34.0, 28.3, 28.1, 26.4, 20.6. **IR** (KBr): υ 3450, 2924, 1458, 1375, 1257, 1072, 837 cm^{-1}. **HRMS(APCI)** *(m/z)*: $[M+H]^+$ Calcd for $C_{25}H_{42}NO_2Si$ 416.2979; found: 416.2995.



To a solution of **4a** (91.4 mg, 0.2 mmol, 1.0 equiv) in THF at 0 °C was added TBAF

(1.0 M in THF, 3 mL, 1.5 equiv) slowly dropwise. The reaction mixture was then warmed to room temperature and stirred for a further 8 h. Following this, the reaction was quenched by addition of H_2O (1.5 mL) and the aqueous phase was extracted with EA (3 × 4 mL). The combined organic phases were washed with brine (4 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue obtained was purified by column chromatography (petroleum ether/ethyl acetate = 5:1) on silica gel to provide the title compound as a colorless oil **9**. (68.4 mg, 53.8%, 1:1.6 *dr*) (the diastereoselectivity was determined by ^{13}C NMR analysis). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.32 – 7.22 (m, 5H), 4.17 – 4.08 (m, 2H), 3.64 – 3.51 (m, 2H), 2.89 – 2.69 (m, 4H), 2.69 – 2.54 (m, 1H), 2.54 – 2.45 (m, 1H), 2.45 – 2.35 (m, 1H), 2.35 – 2.26 (m, 1H), 1.99 – 1.77 (m, 5H), 1.65 – 1.47 (m, 1H), 1.33 – 1.28 (m, 3H), 1.26 – 1.21 (m, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 215.6, 215.4, 174.7, 174.4, 138.6, 128.6, 128.6, 128.2, 128.2, 126.9, 60.7, 60.7, 59.8, 59.6, 58.6, 57.8, 57.1, 57.1, 56.8, 56.5, 46.9, 46.8, 43.2, 43.1, 42.4, 29.9, 29.3, 29.2, 29.1, 28.6, 28.0, 25.0, 24.4, 18.4, 14.2. **IR** (KBr): υ 2927, 1730, 1450, 1371, 1170, 1039, 744 cm^{-1}. **HRMS(APCI)** *(m/z)*: $[M+H]^+$ Calcd for $C_{21}H_{30}NO_3$ 344.2220; found: 344.2223.

VII. Proposed reaction mechanism



A proposed reaction mechanism is depicted in part VII in SI. Initially, ethyl propiolate **2a** was activated by Tf_2NH, and this Lewis acid promoted a Mukaiyama - Michael addition reaction of **1a** and activated **2a** to give the intermediate **I**. Intermediate **I** underwent an intramolecular aldol reaction to give intermediate **II**. **3a** in the presence

of trifluoroacetic acid generated methylenimine ylide **III**, which undergoes a [3+2] cycloaddition reaction with **II** to give the final product **4a** as diastereomeric mixtures. Due to the steric hindrance of TBS, **4a** as the major product was obtained, and the minor product was **4a´**.

VIII. References

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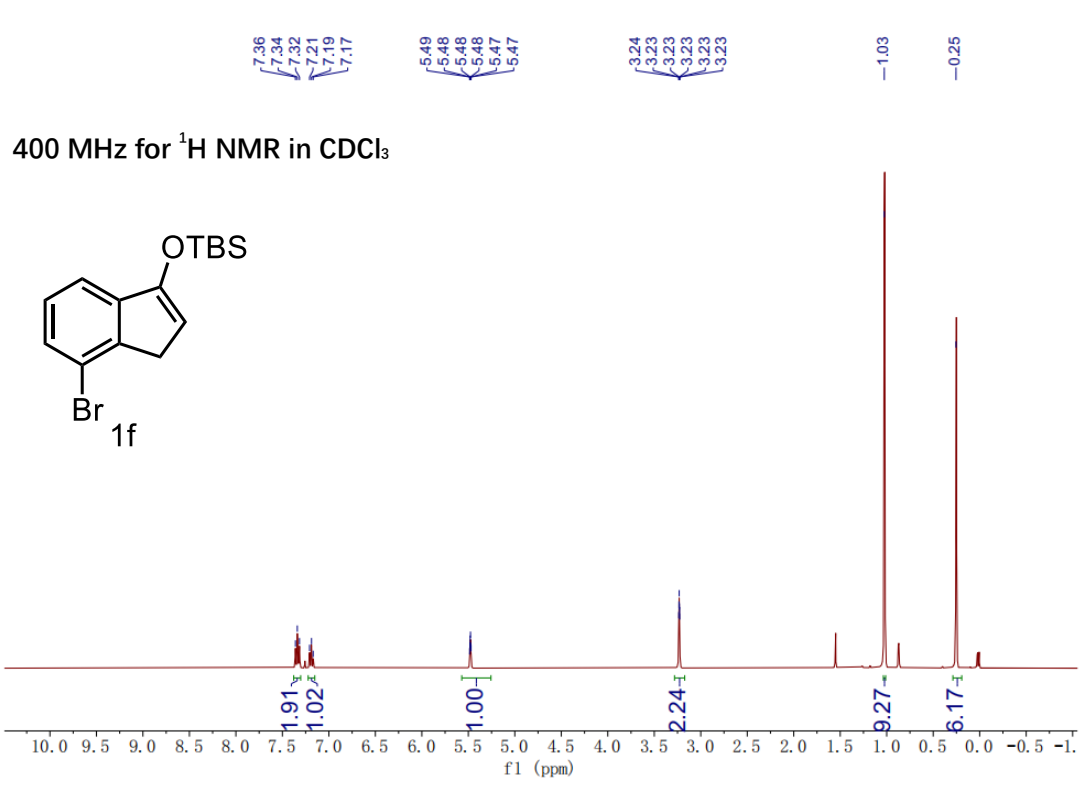
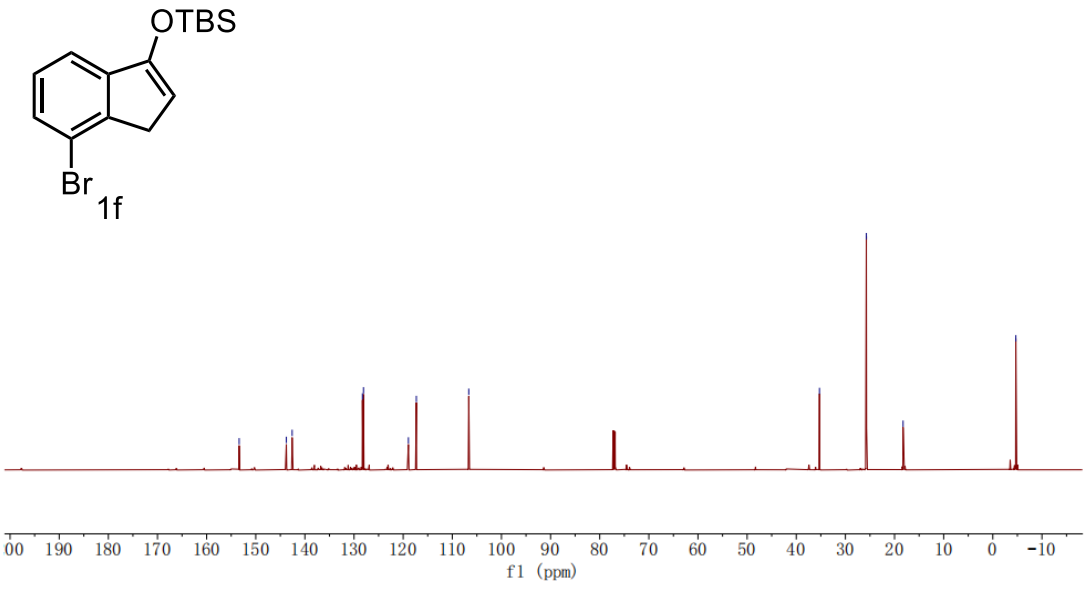
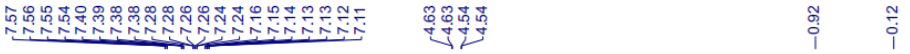
IX. NMR Spectral Data

400 MHz for ^{1}H NMR in $CDCl_3$

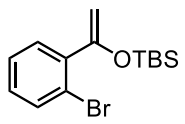


151 MHz for ^{13}C NMR in $CDCl_3$



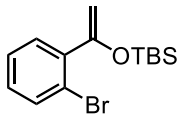


400 MHz for ^{1}H NMR in $CDCl_3$



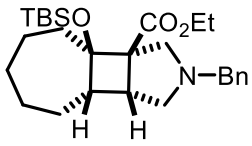
6f

101 MHz for ^{13}C NMR in $CDCl_3$



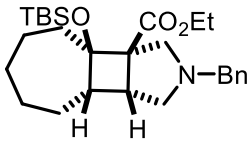
6f

600 MHz for ^{1}H NMR in $CDCl_3$



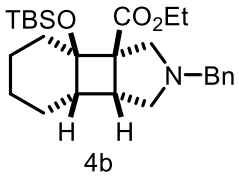
4a

151 MHz for ^{13}C NMR in $CDCl_3$



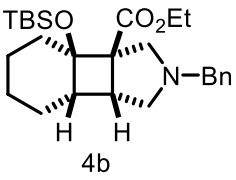
4a

600 MHz for ^{1}H NMR in $CDCl_3$



4b

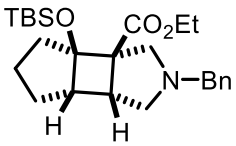
151 MHz for ^{13}C NMR in $CDCl_3$



4b

7.36 7.35 7.31 7.30 7.29 7.26 7.25 7.23 7.22 4.17 4.16 4.16 4.15 4.13 4.13 4.12 3.84 3.82 3.63 3.62 3.40 3.38 2.74 2.72 2.27 2.26 2.25 2.18 2.17 2.16 2.14 2.13 2.11 2.10 2.09 2.09 1.81 1.80 1.78 1.78 1.73 1.72 1.72 1.71 1.71 1.70 1.70 1.69 1.68 1.61 1.61 1.59 1.51 1.50 1.49 1.27 1.26 1.25 0.90 0.15 0.06

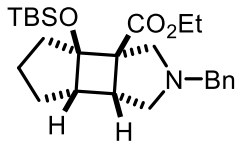
600 MHz for ^{1}H NMR in $CDCl_3$



4c

173.28 139.42 128.87 128.07 126.71 82.66 60.06 59.98 59.81 58.66 57.98 48.98 38.50 38.36 31.12 25.83 24.30 18.22 14.34 2.52 2.65

151 MHz for ^{13}C NMR in $CDCl_3$



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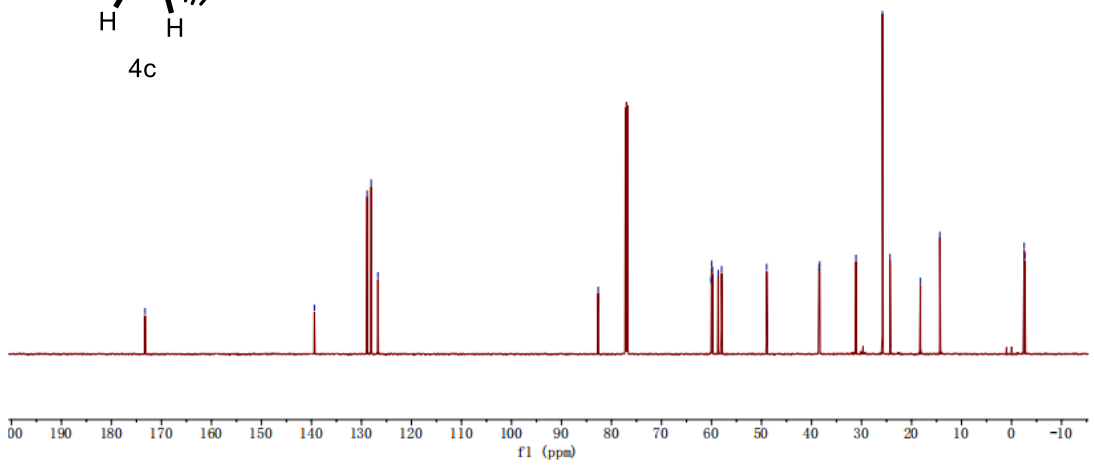
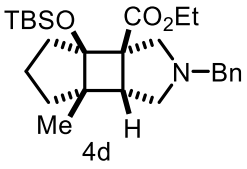
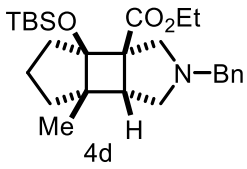


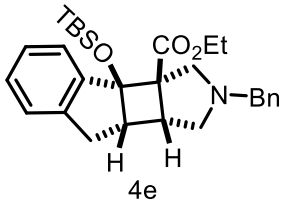
600 MHz for ^{1}H NMR in $CDCl_3$



151 MHz for ^{13}C NMR in $CDCl_3$

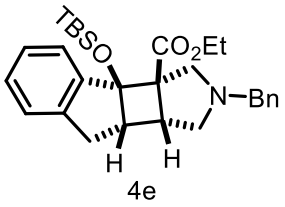


600 MHz for ^{1}H NMR in $CDCl_3$

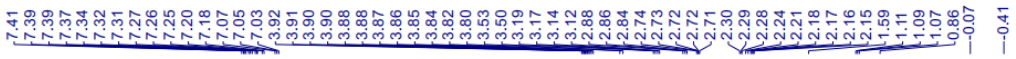


4e

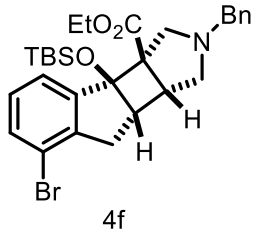
151 MHz for ^{13}C NMR in $CDCl_3$



4e

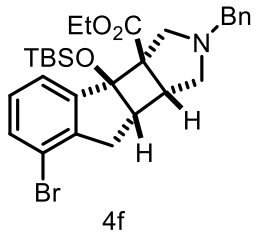


400 MHz for ^{1}H NMR in $CDCl_3$



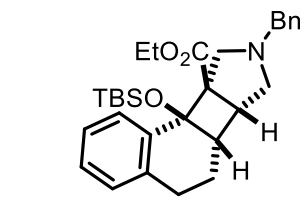
4f

151 MHz for ^{13}C NMR in $CDCl_3$



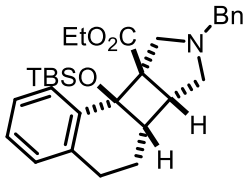
4f

600 MHz for ^{1}H NMR in $CDCl_3$

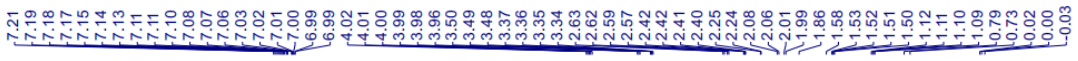


4g

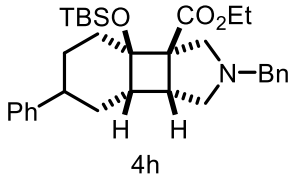
151 MHz for ^{13}C NMR in $CDCl_3$



4g

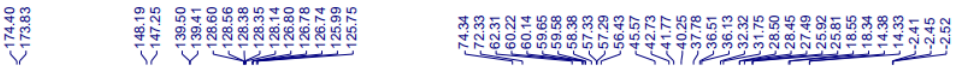


600 MHz for ^{1}H NMR in $CDCl_3$

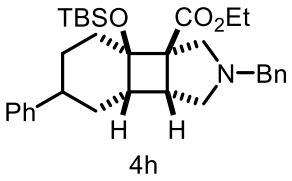


4h

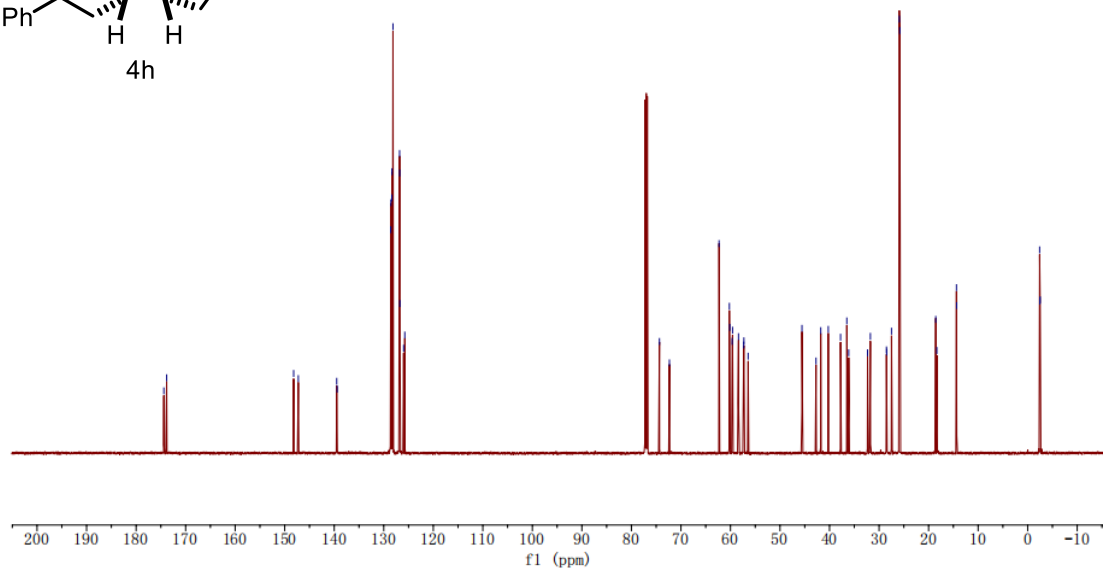
4h was a 1.1:1 diastereoisomeric mixture



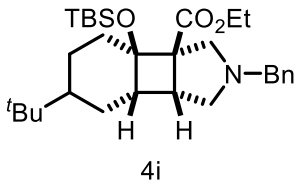
151 MHz for ^{13}C NMR in $CDCl_3$



4h

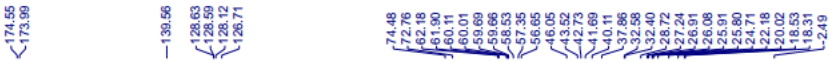


600 MHz for ^{1}H NMR in $CDCl_3$

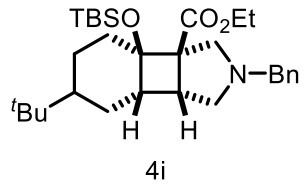


4i

4i was a 1.3:1 diastereoisomeric mixture

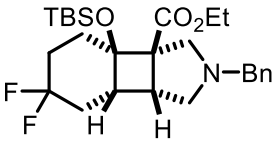


151 MHz for ^{13}C NMR in $CDCl_3$



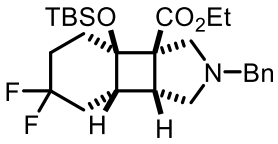
4i

600 MHz for ^{1}H NMR in $CDCl_3$

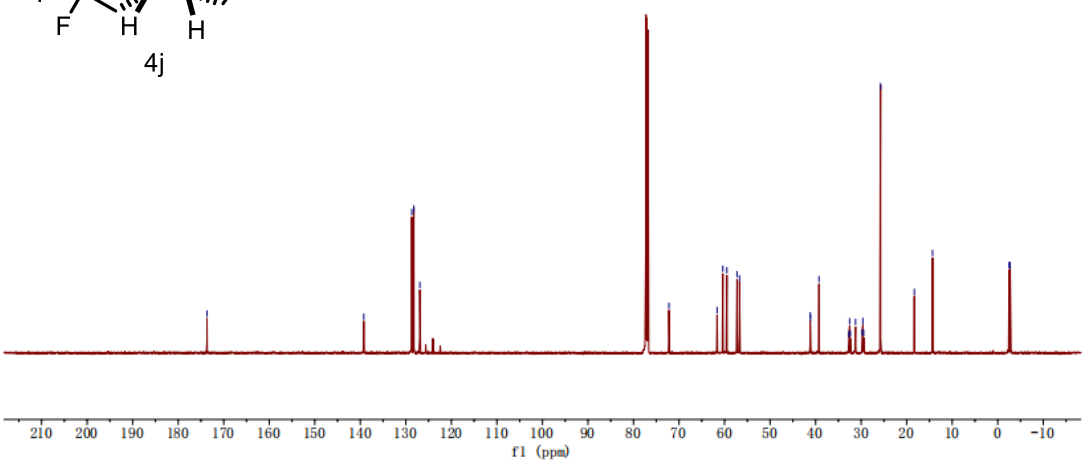


4j

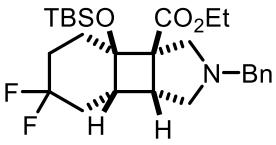
151 MHz for ^{13}C NMR in $CDCl_3$



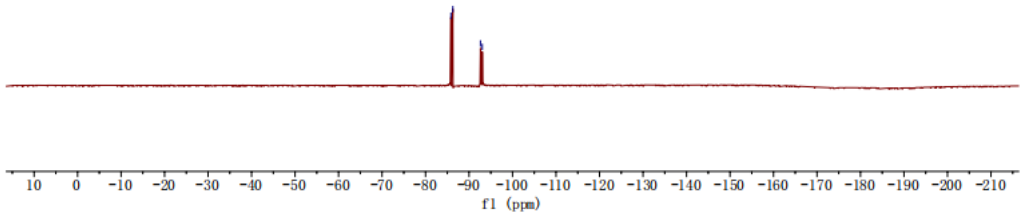
4j



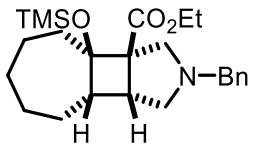
565 MHz for ^{19}F NMR in $CDCl_3$



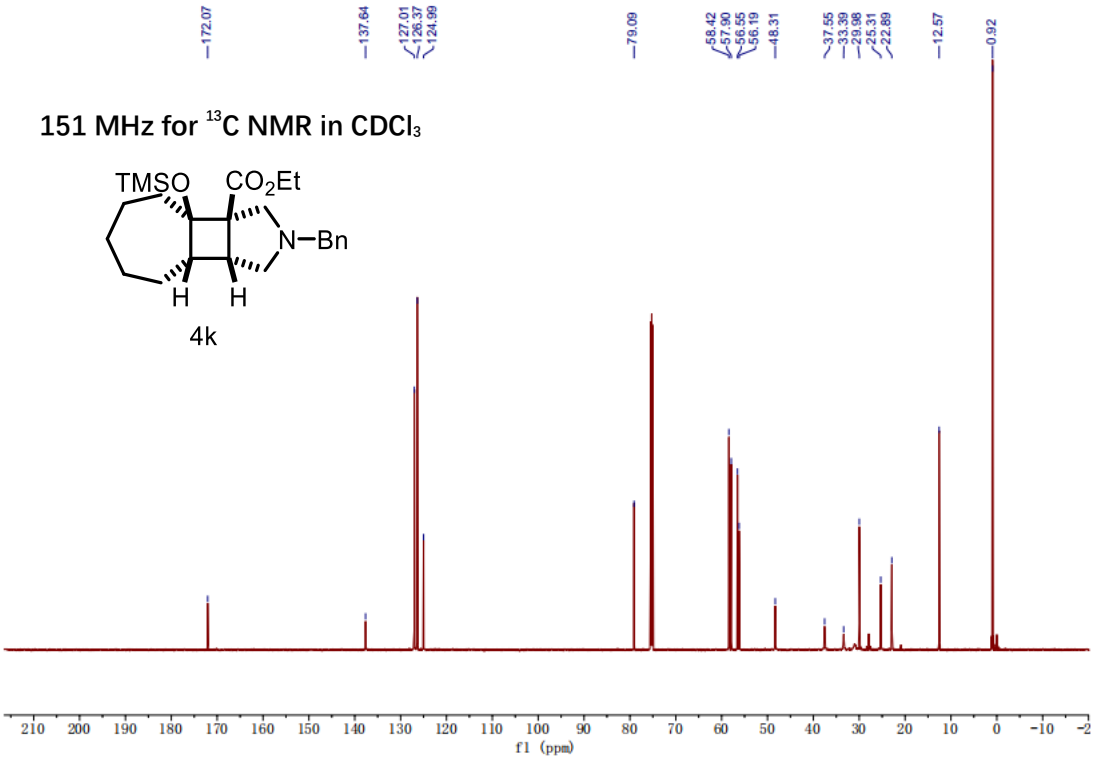
4j

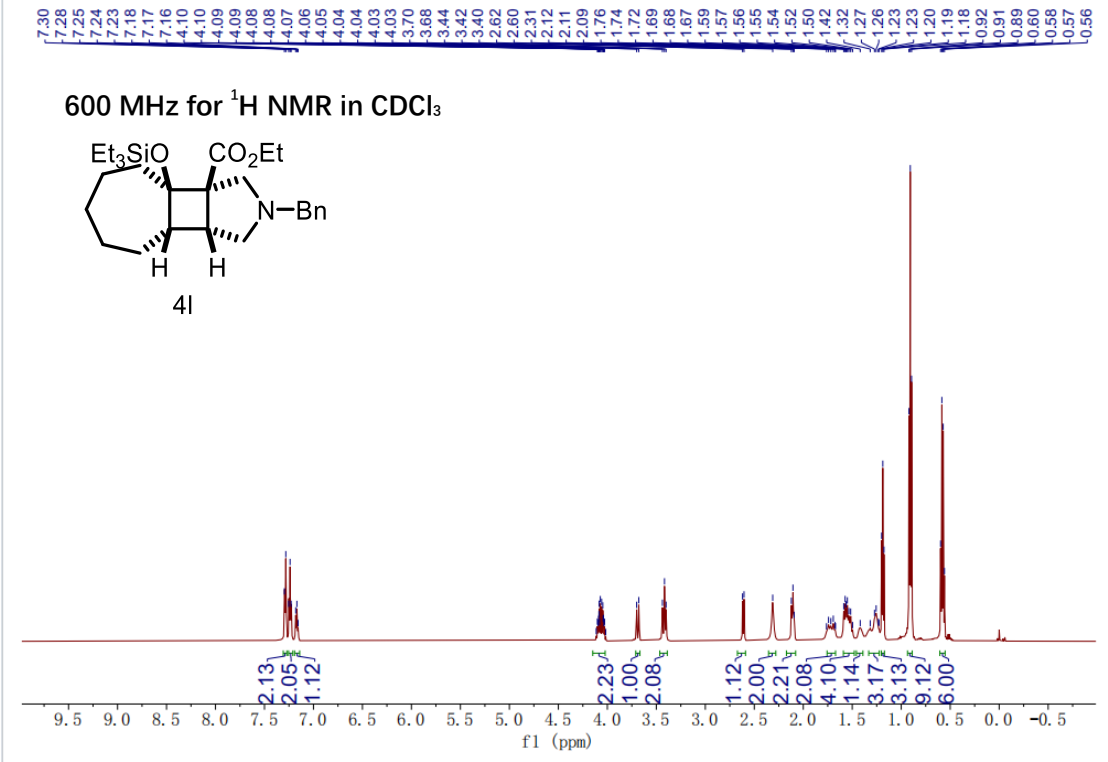


600 MHz for ^{1}H NMR in $CDCl_3$

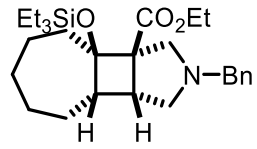


4k

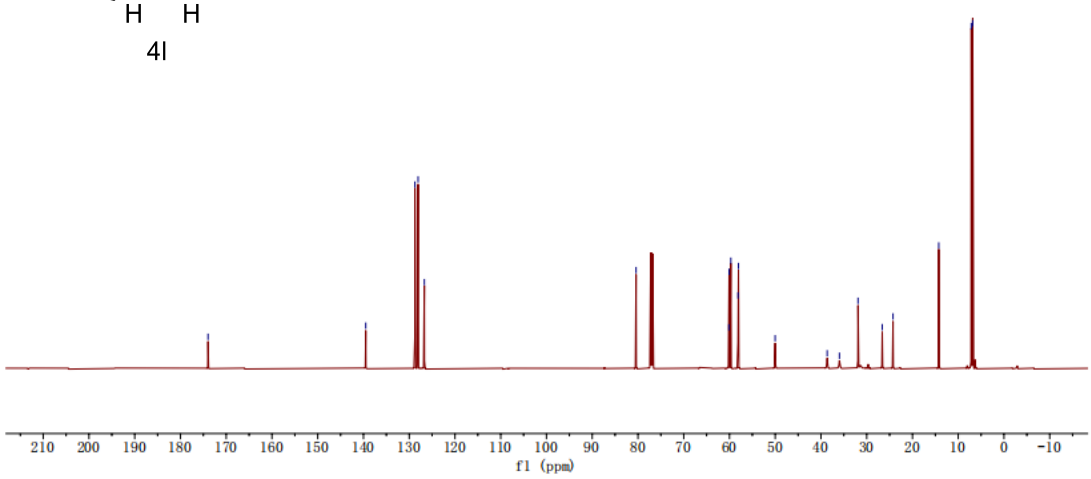

151 MHz for ^{13}C NMR in CDCl$_3$
TMSO
CO$_2$Et
N–Bn
H
H
4k
172.07
137.64
127.01
126.37
124.99
79.09
58.42
57.90
56.55
56.19
48.31
37.55
33.39
29.98
25.31
22.89
12.57
0.92
f1 (ppm)


600 MHz for ^{1}H NMR in CDCl$_3$
Et$_3$SiO
CO$_2$Et
N–Bn
H
H
4l
2.13
2.05
1.12
2.23
1.00
2.08
1.12
2.00
2.21
2.08
4.10
1.14
3.17
3.13
9.12
6.00
f1 (ppm)

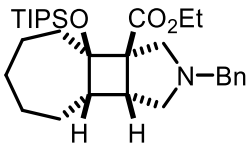
151 MHz for ^{13}C NMR in $CDCl_3$



4l

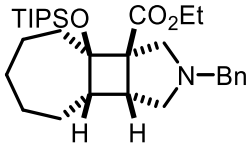


600 MHz for ^{1}H NMR in $CDCl_3$

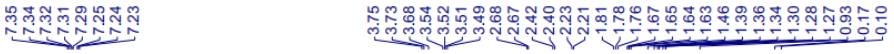


4m

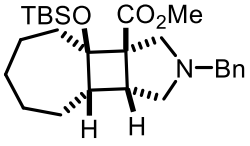
151 MHz for ^{13}C NMR in $CDCl_3$



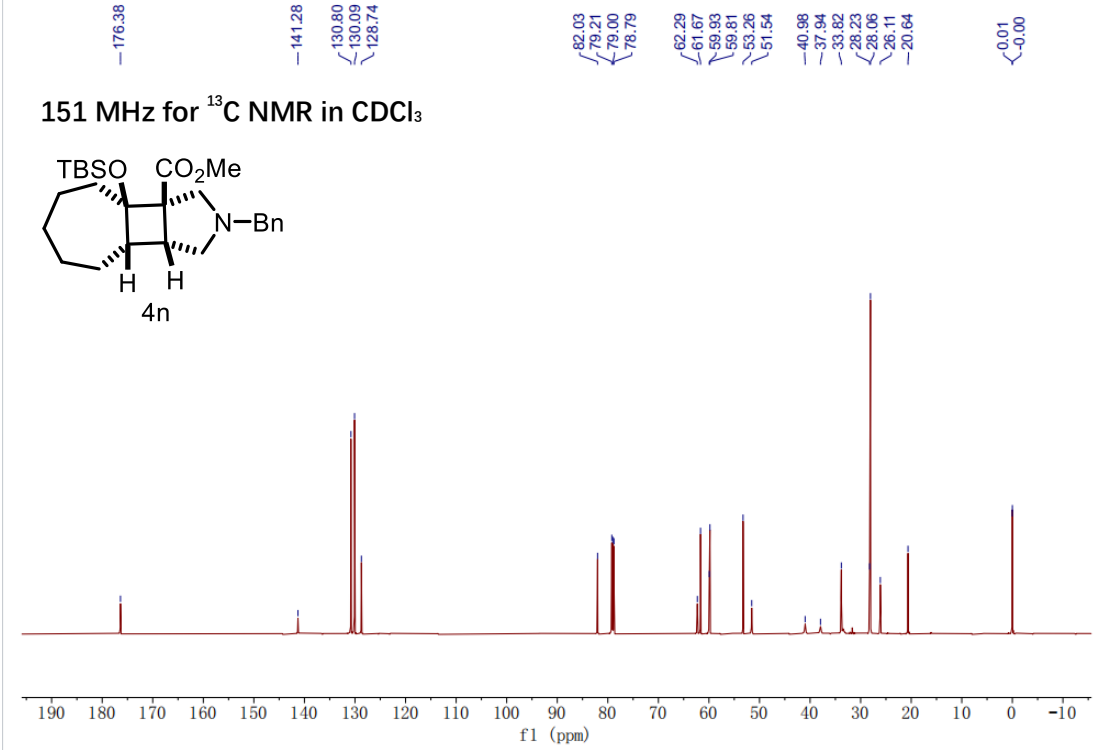
4m



600 MHz for ^{1}H NMR in $CDCl_3$



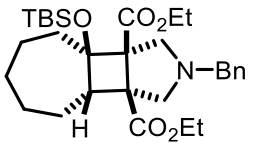
4n



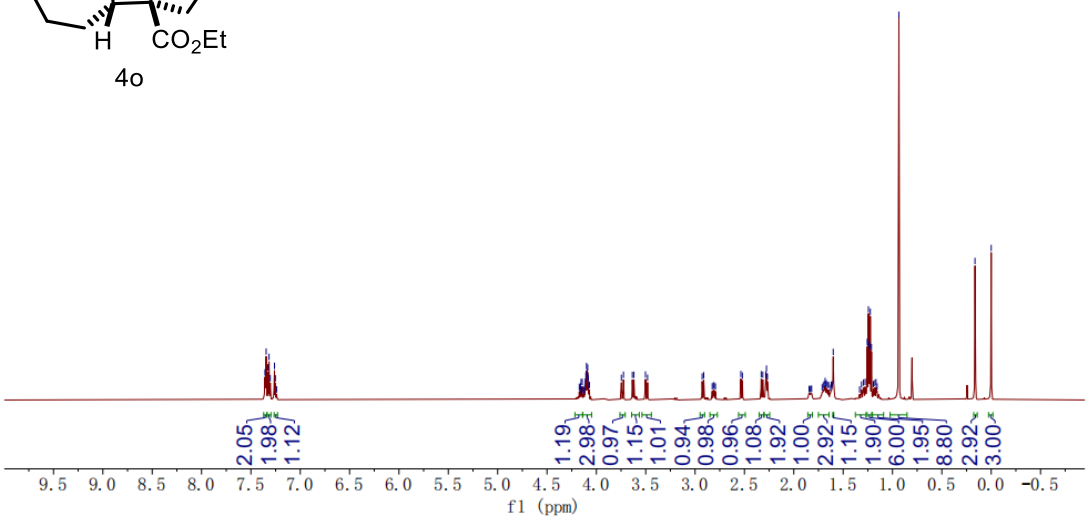
151 MHz for ^{13}C NMR in $CDCl_3$

4n

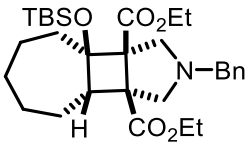
600 MHz for ^{1}H NMR in $CDCl_3$



4o

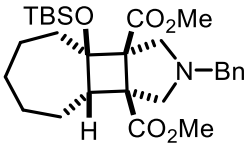


151 MHz for ^{13}C NMR in $CDCl_3$

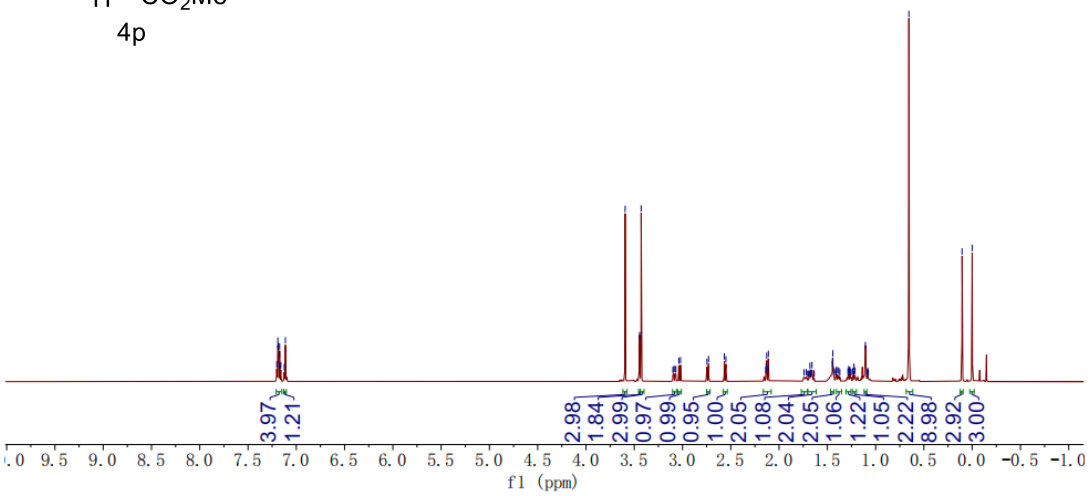


4o

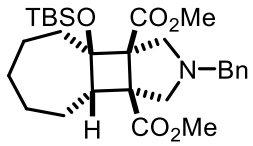
600 MHz for ^{1}H NMR in $CDCl_3$



4p

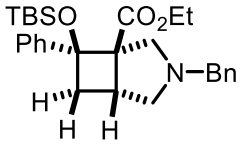


151 MHz for ^{13}C NMR in $CDCl_3$

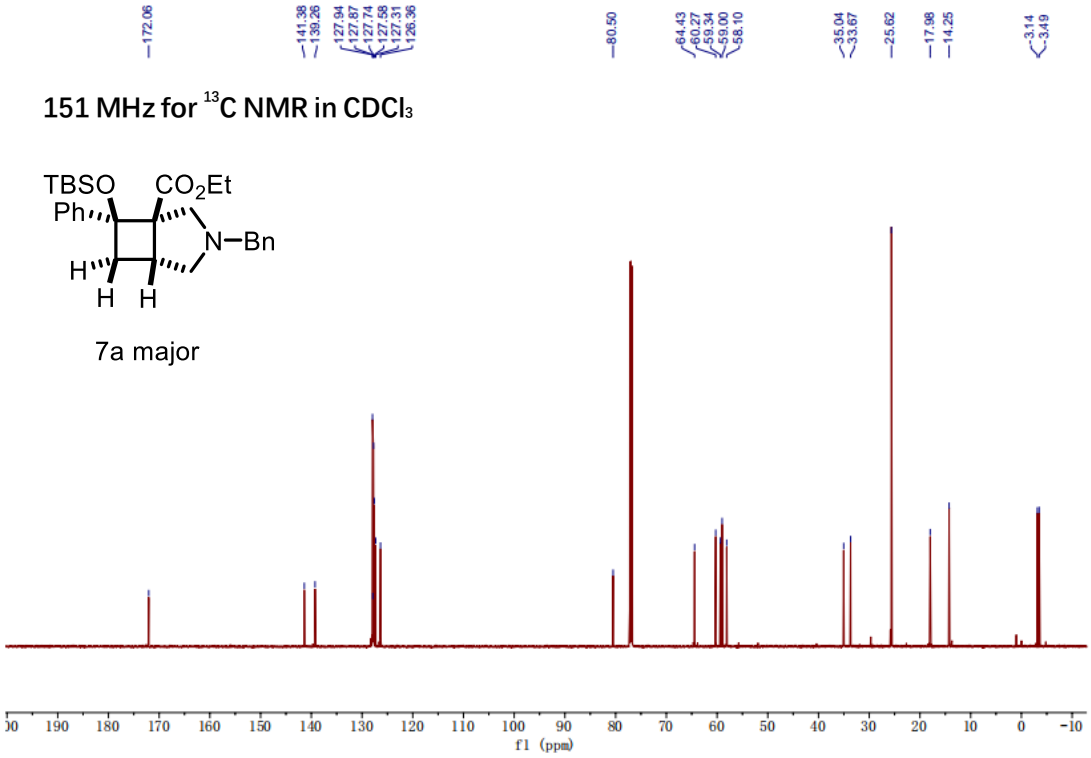


4p

600 MHz for ^{1}H NMR in $CDCl_3$

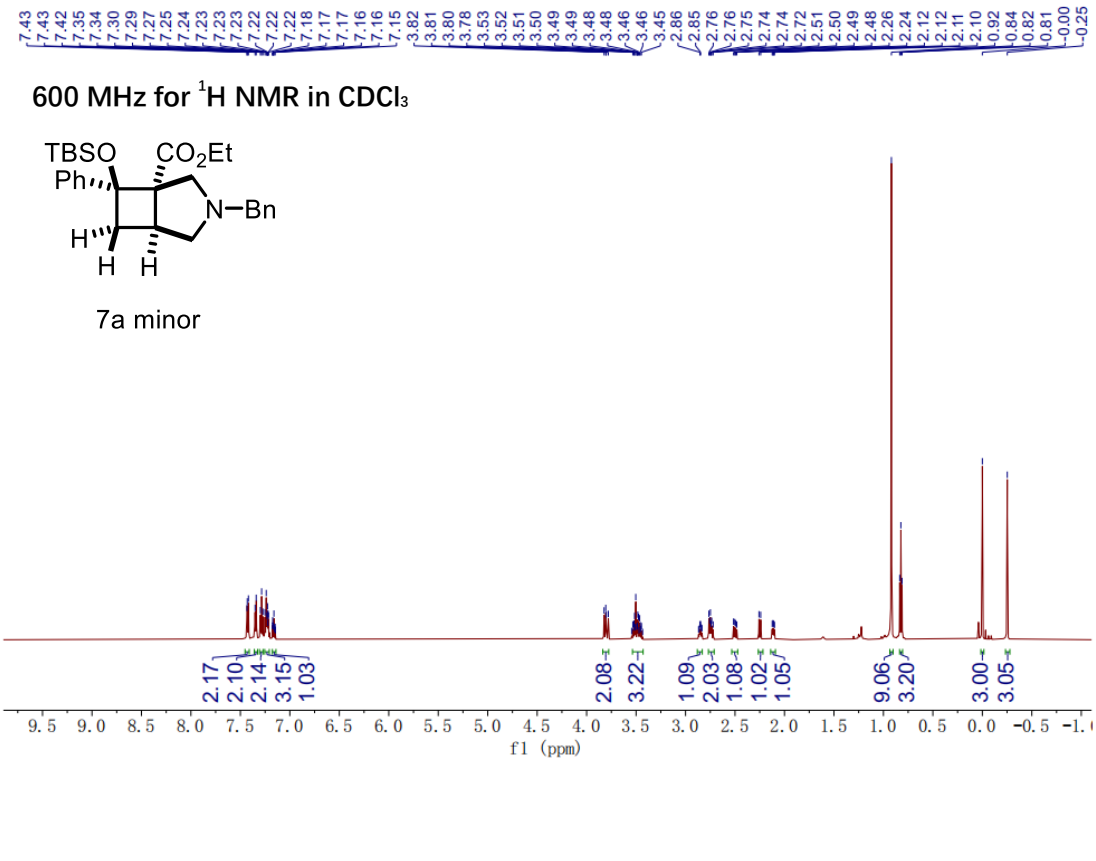


7a major



151 MHz for ^{13}C NMR in $CDCl_3$

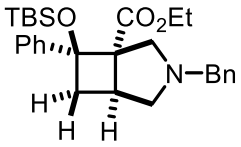
7a major



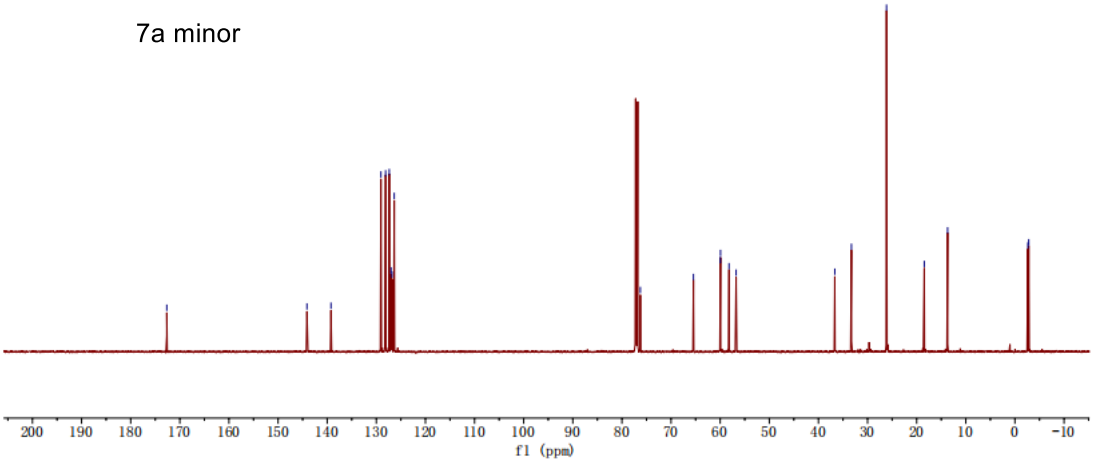
600 MHz for ^{1}H NMR in $CDCl_3$

7a minor

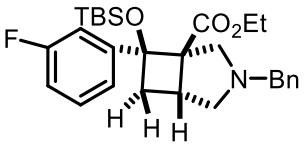
151 MHz for ^{13}C NMR in $CDCl_3$



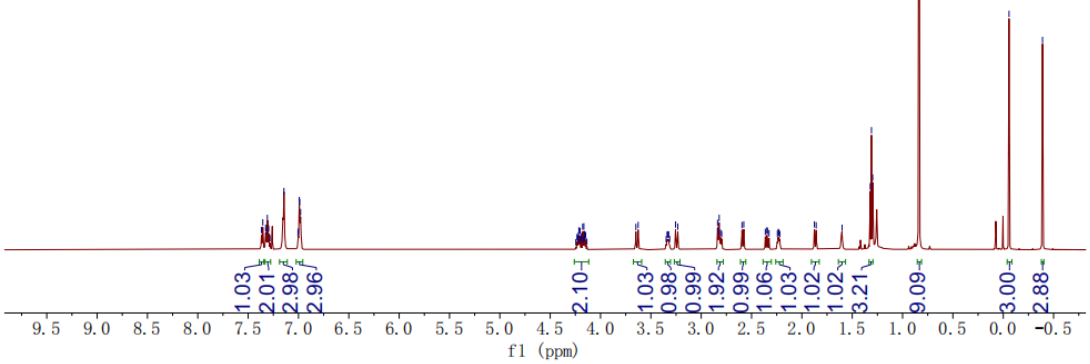
7a minor



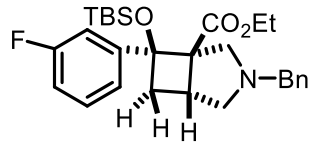
600 MHz for ^{1}H NMR in $CDCl_3$



7b major

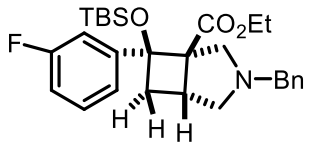


151 MHz for ^{13}C NMR in $CDCl_3$



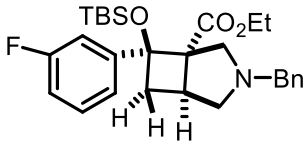
7b major

565 MHz for ^{19}F NMR in $CDCl_3$

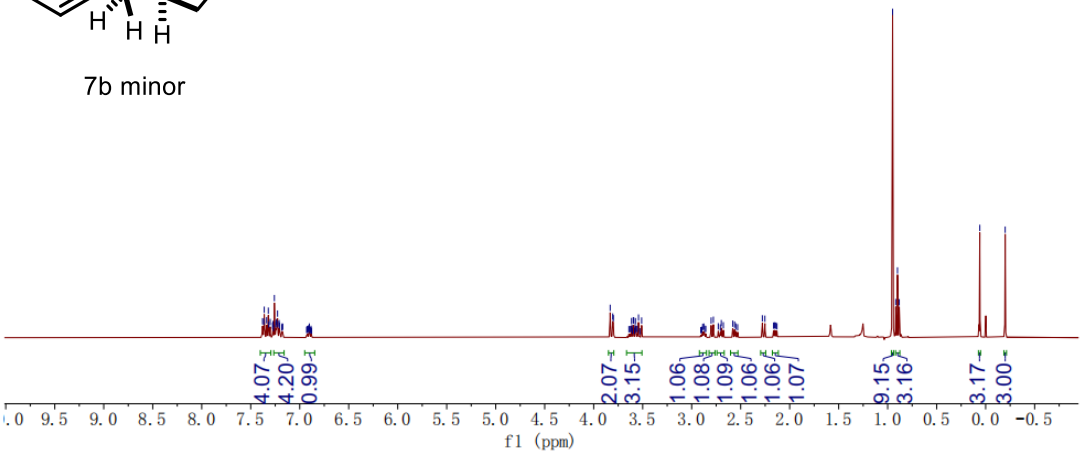


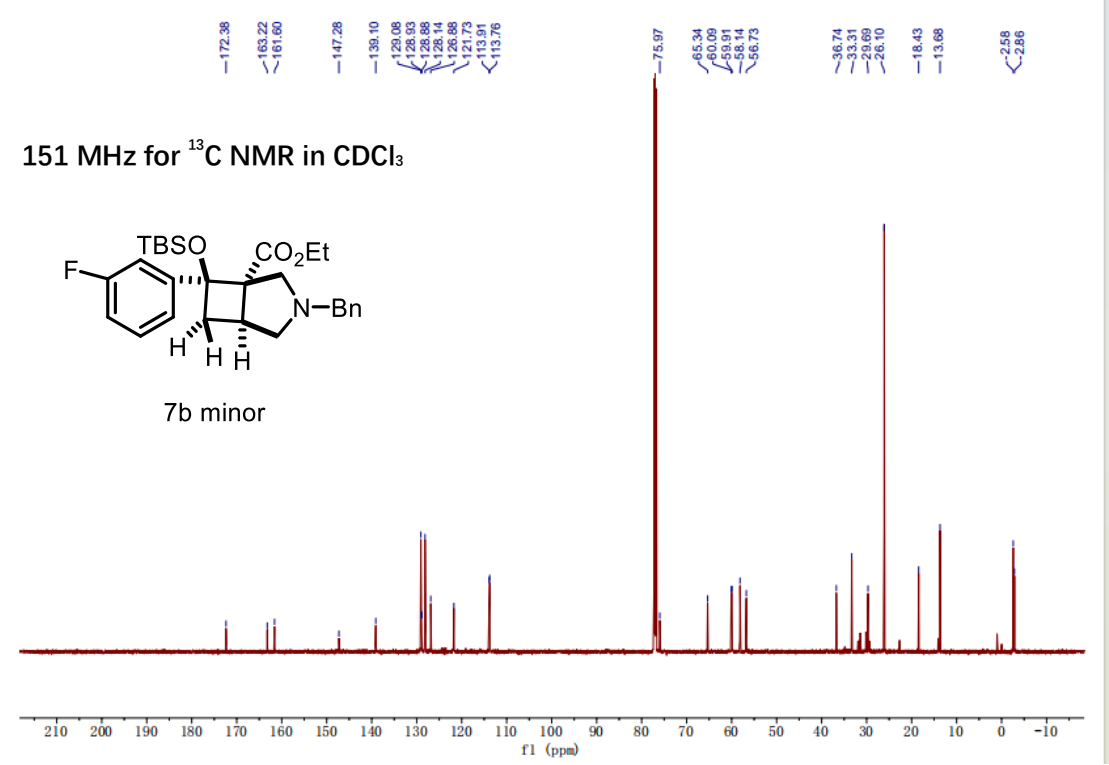
7b major

400 MHz for ^{1}H NMR in $CDCl_3$



7b minor

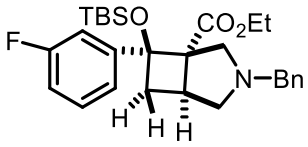




151 MHz for ^{13}C NMR in $CDCl_3$

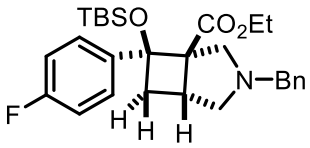
7b minor

565 MHz for ^{19}F NMR in $CDCl_3$

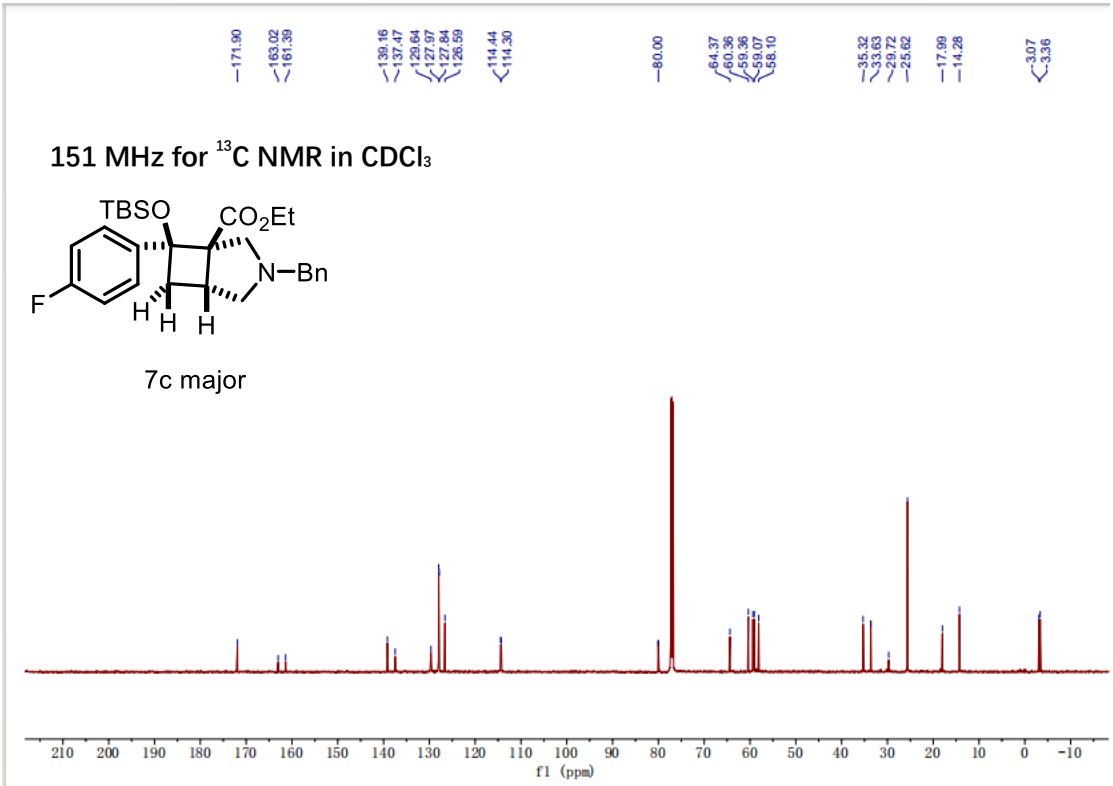


7b minor

600 MHz for ^{1}H NMR in $CDCl_3$



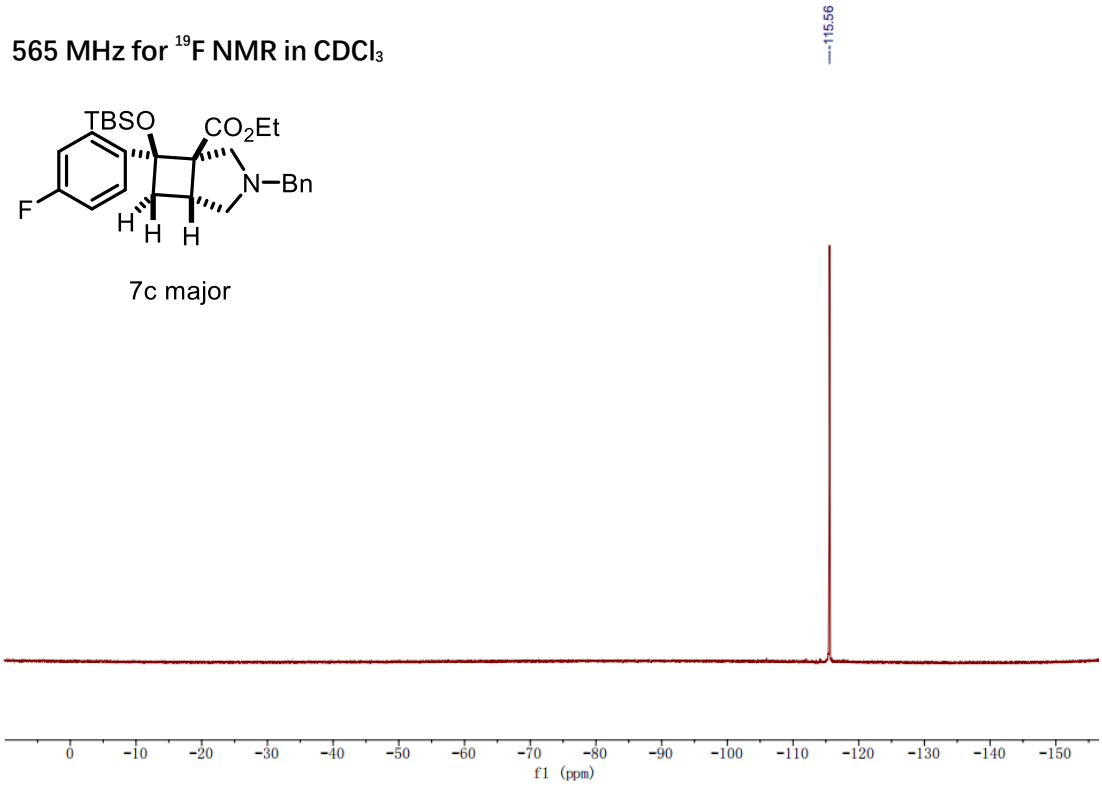
7c major



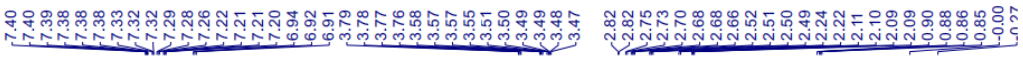
151 MHz for ^{13}C NMR in $CDCl_3$

7c major

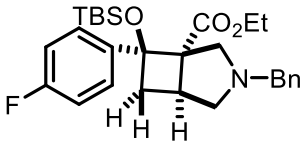
565 MHz for ^{19}F NMR in $CDCl_3$



7c major

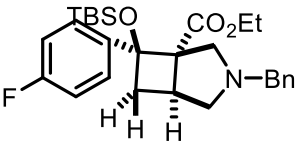


600 MHz for ^{1}H NMR in $CDCl_3$



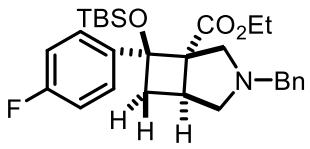
7c minor

151 MHz for ^{13}C NMR in $CDCl_3$



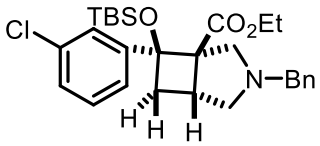
7c minor

565 MHz for ^{19}F NMR in $CDCl_3$

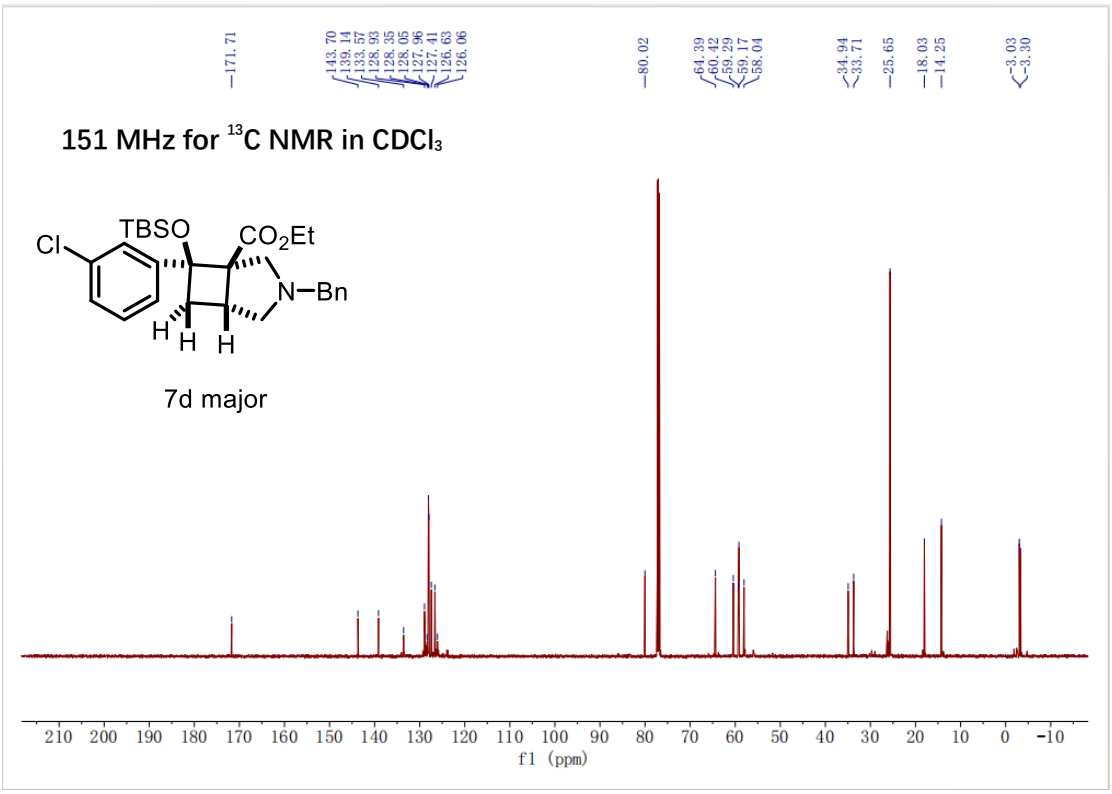


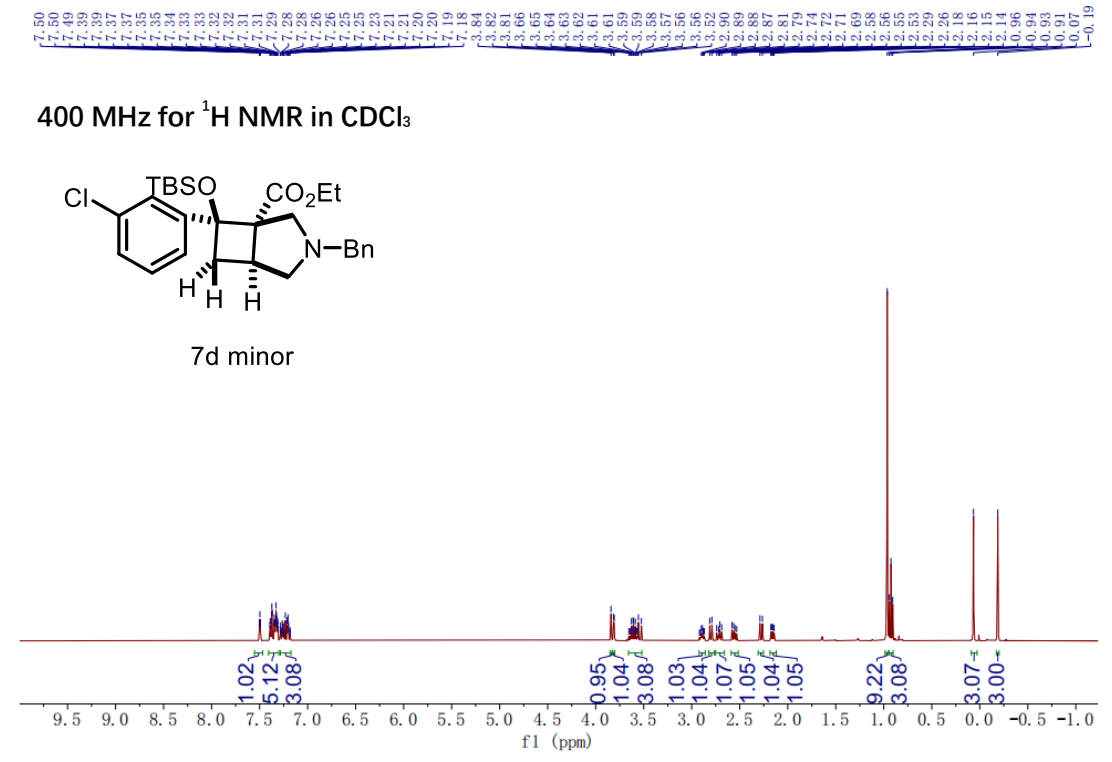
7c minor

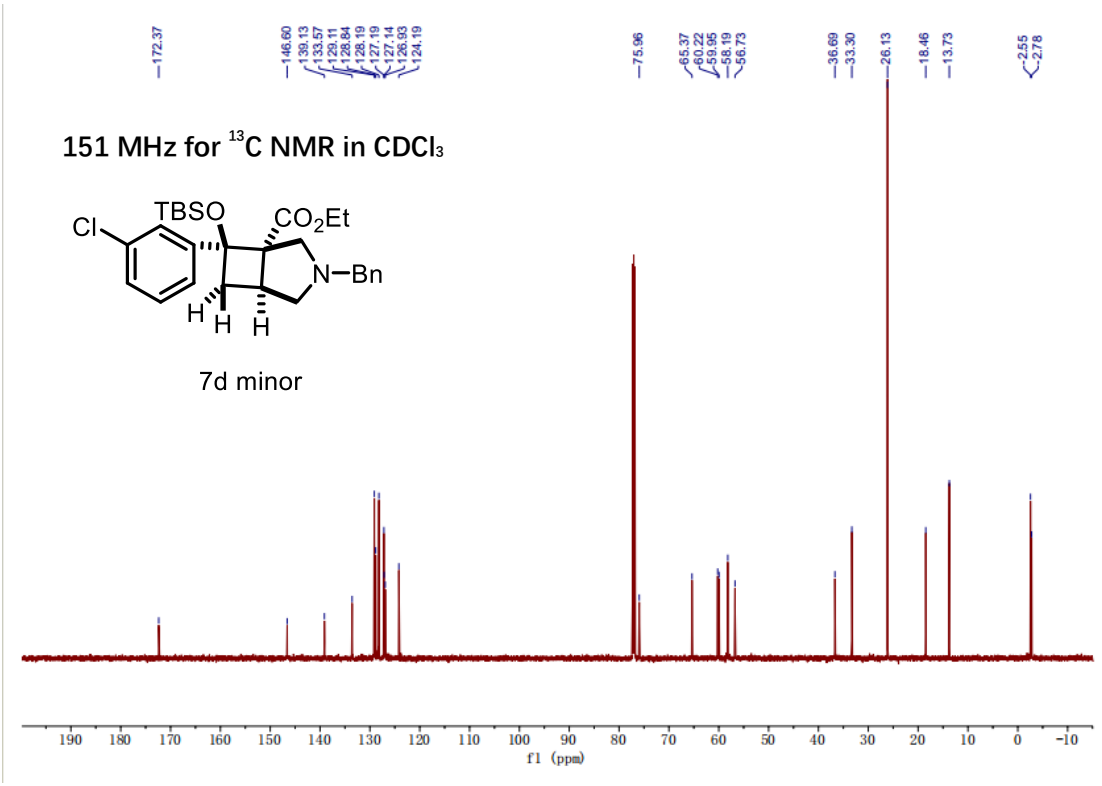
600 MHz for ^{1}H NMR in $CDCl_3$

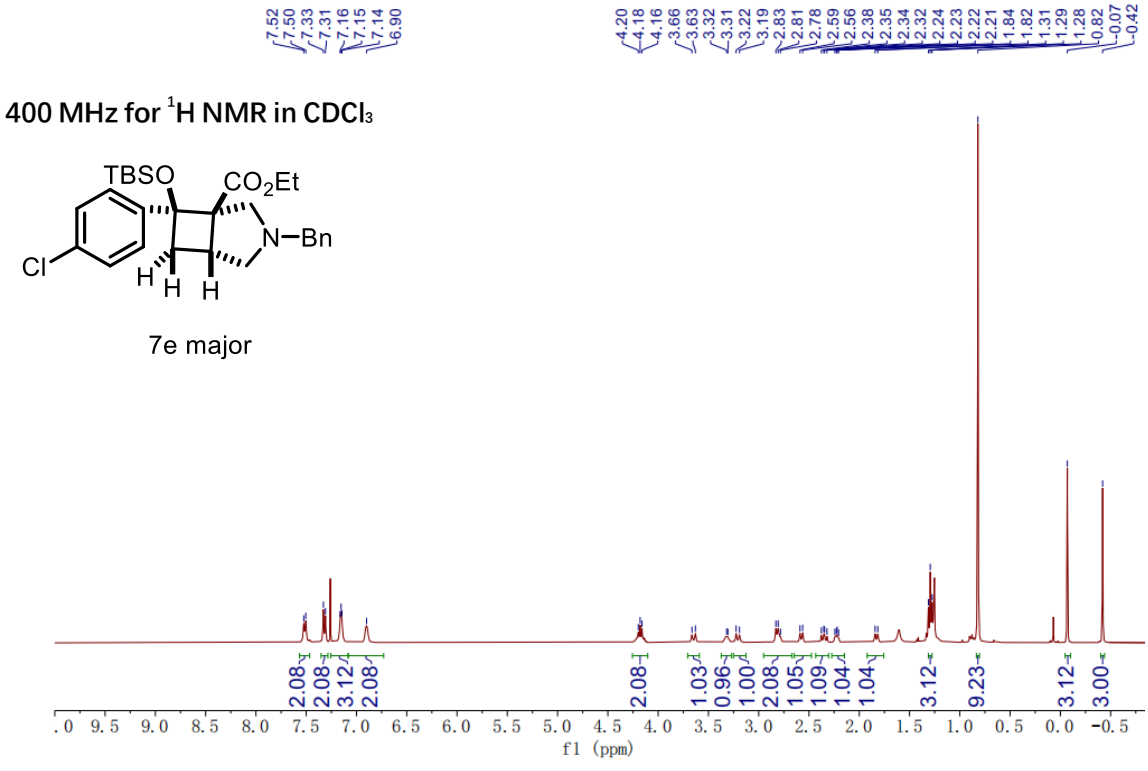


7d major

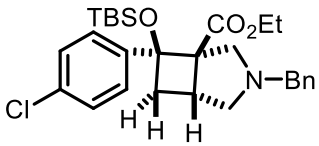

151 MHz for ^{13}C NMR in CDCl$_3$
TBSO
CO$_2$Et
Cl
N–Bn
H
H
H
7d major
f1 (ppm)


400 MHz for ^{1}H NMR in CDCl$_3$
TBSO
CO$_2$Et
Cl
N–Bn
H
H
H
7d minor
f1 (ppm)


151 MHz for ^{13}C NMR in CDCl$_3$
TBSO
CO$_2$Et
Cl
N–Bn
H
H
H
7d minor
f1 (ppm)

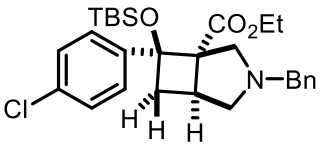

400 MHz for ^{1}H NMR in CDCl$_3$
TBSO
CO$_2$Et
Cl
N–Bn
H
H
H
7e major
f1 (ppm)

151 MHz for ^{13}C NMR in $CDCl_3$



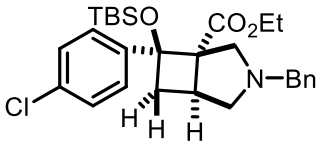
7e major

400 MHz for ^{1}H NMR in $CDCl_3$



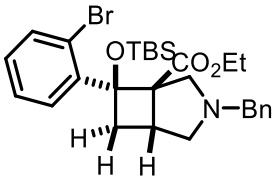
7e minor

151 MHz for ^{13}C NMR in $CDCl_3$



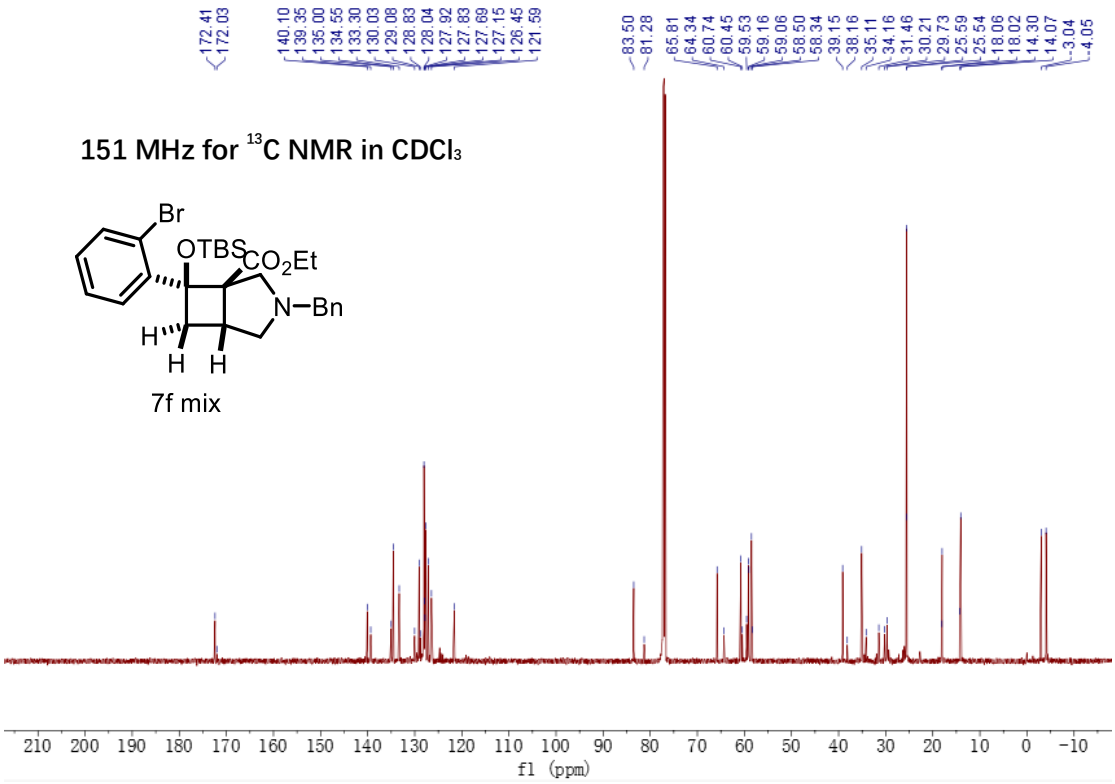
7e minor

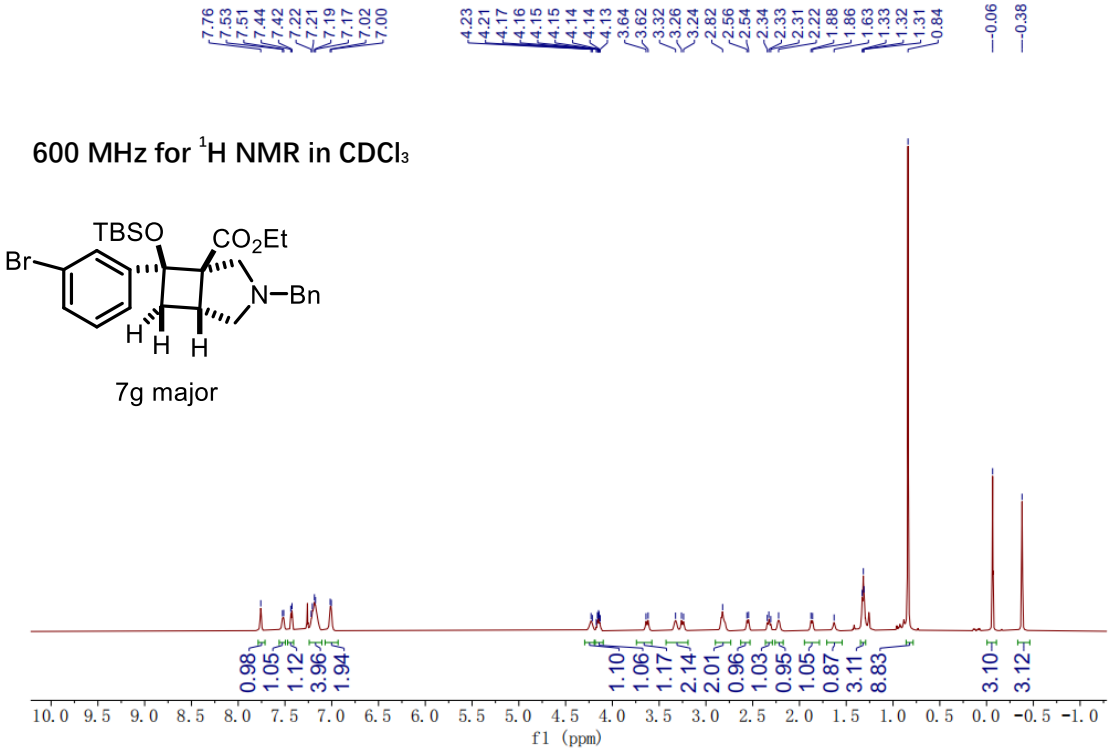
600 MHz for ^{1}H NMR in $CDCl_3$

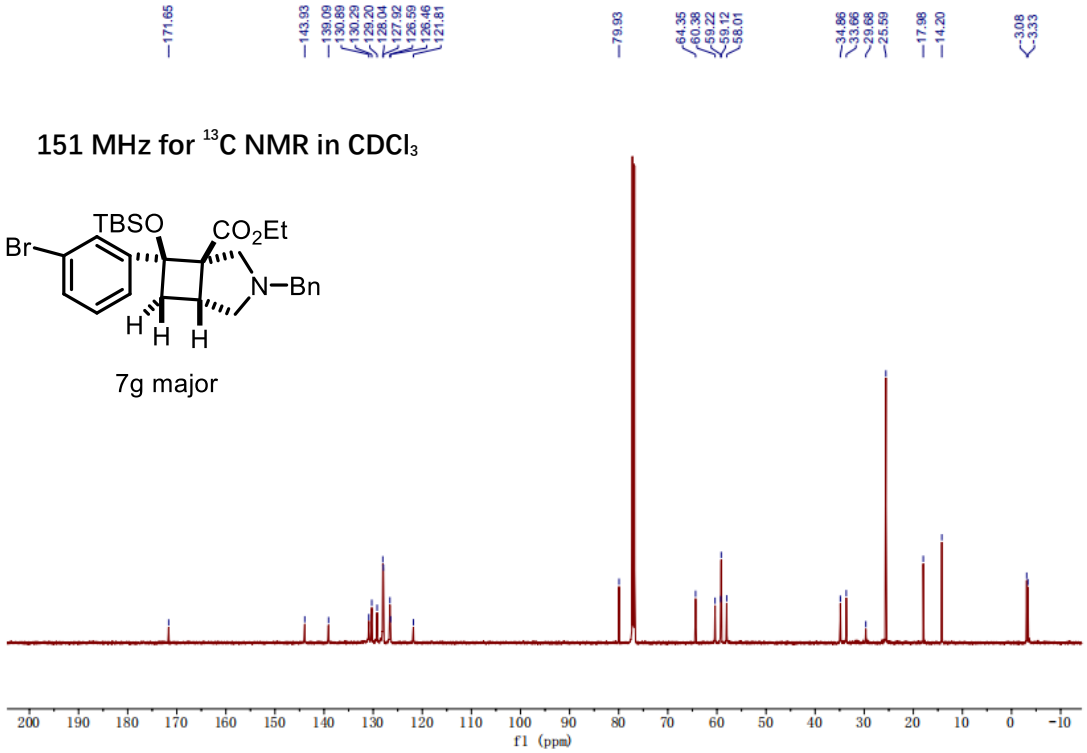


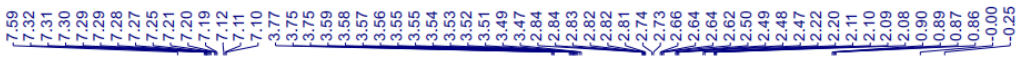
7f mix

7f was a 3:1 diastereoisomeric mixture

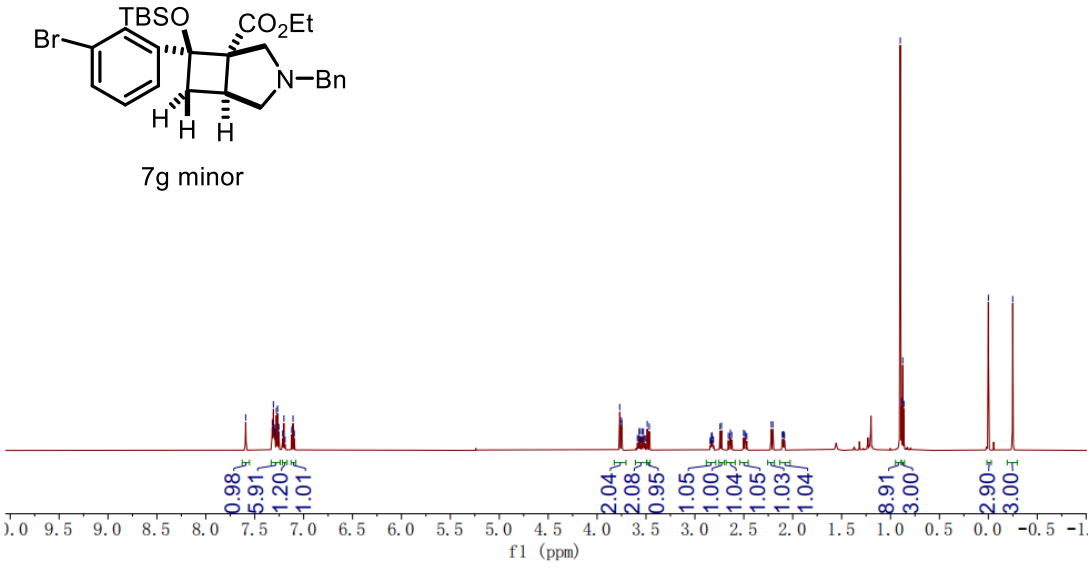

172.41
172.03
140.10
139.35
135.00
134.55
133.30
130.03
129.08
128.83
128.04
127.92
127.83
127.69
127.15
126.45
121.59
83.50
81.28
65.81
64.34
60.74
60.45
59.53
59.16
59.06
58.50
58.34
39.15
38.16
35.11
34.16
31.46
30.21
29.73
25.59
25.54
18.06
18.02
14.30
14.07
-3.04
-4.05
151 MHz for 13C NMR in CDCl3
Br
OTBS
CO2Et
N–Bn
H
H H
7f mix
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.76
7.53
7.51
7.44
7.42
7.22
7.21
7.19
7.17
7.02
7.00
4.23
4.21
4.17
4.16
4.15
4.15
4.14
4.14
4.13
3.64
3.62
3.32
3.26
3.24
2.82
2.56
2.54
2.34
2.33
2.31
2.22
1.88
1.86
1.63
1.33
1.32
1.31
0.84
0.06
0.38
600 MHz for 1H NMR in CDCl3
TBSO
CO2Et
Br
N–Bn
H
H H
7g major
0.98
1.05
1.12
3.96
1.94
1.10
1.06
1.17
2.14
2.01
0.96
1.03
0.95
1.05
0.87
3.11
8.83
3.10
3.12
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
f1 (ppm)

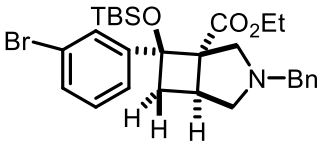




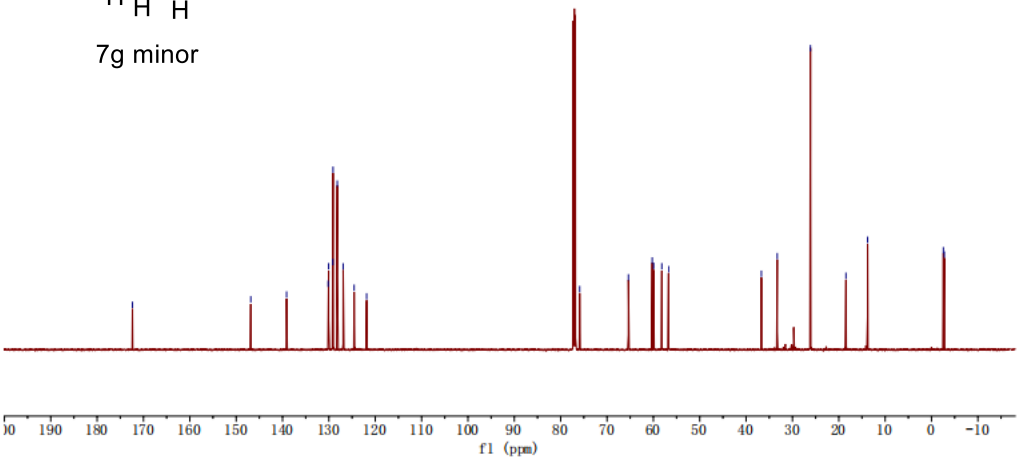
600 MHz for ^{1}H NMR in CDCl$_3$



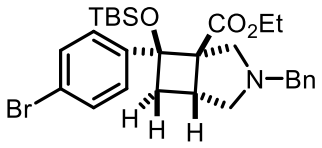
151 MHz for ^{13}C NMR in $CDCl_3$



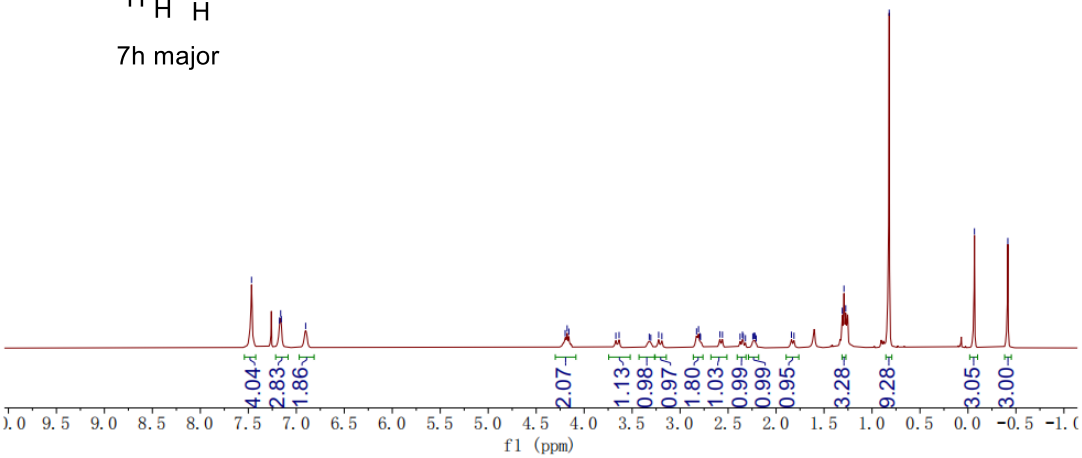
7g minor

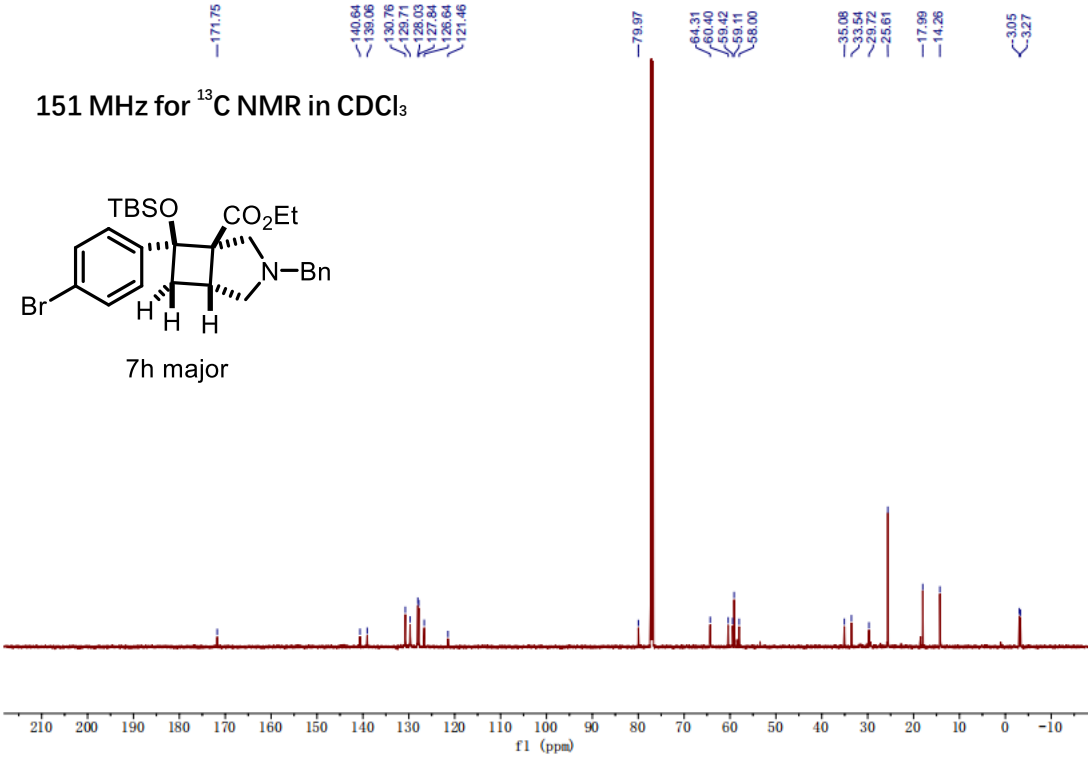


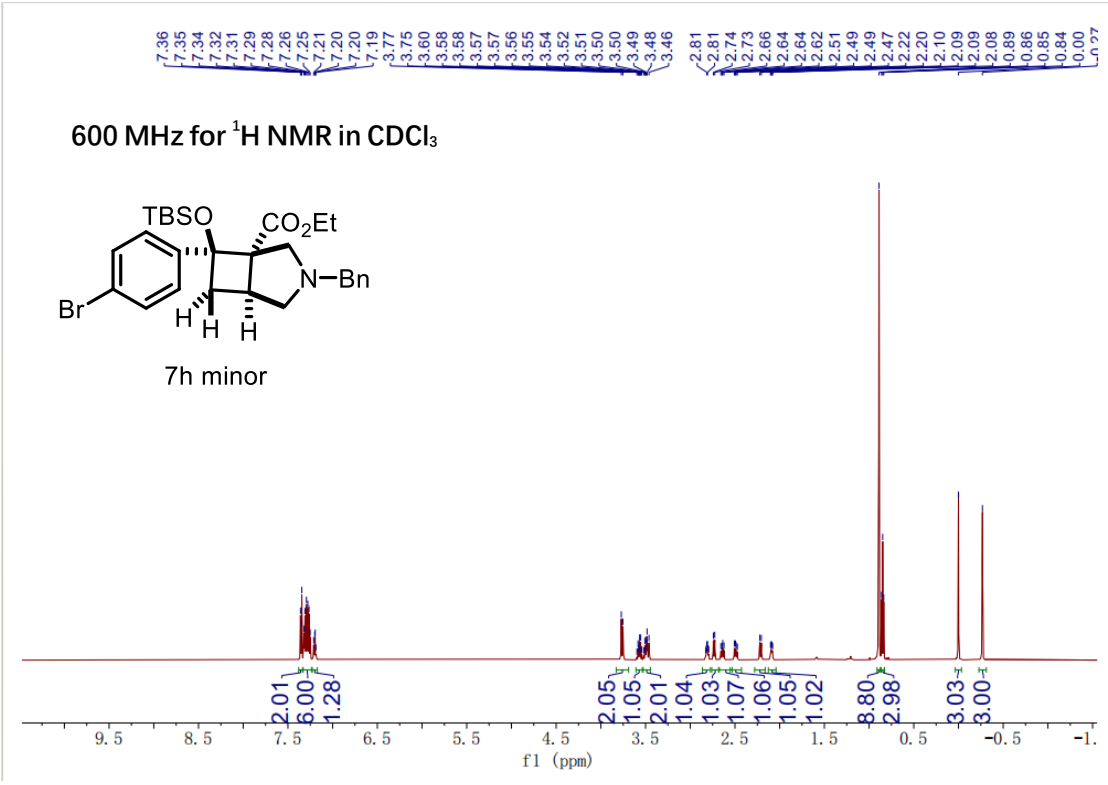
400 MHz for ^{1}H NMR in $CDCl_3$

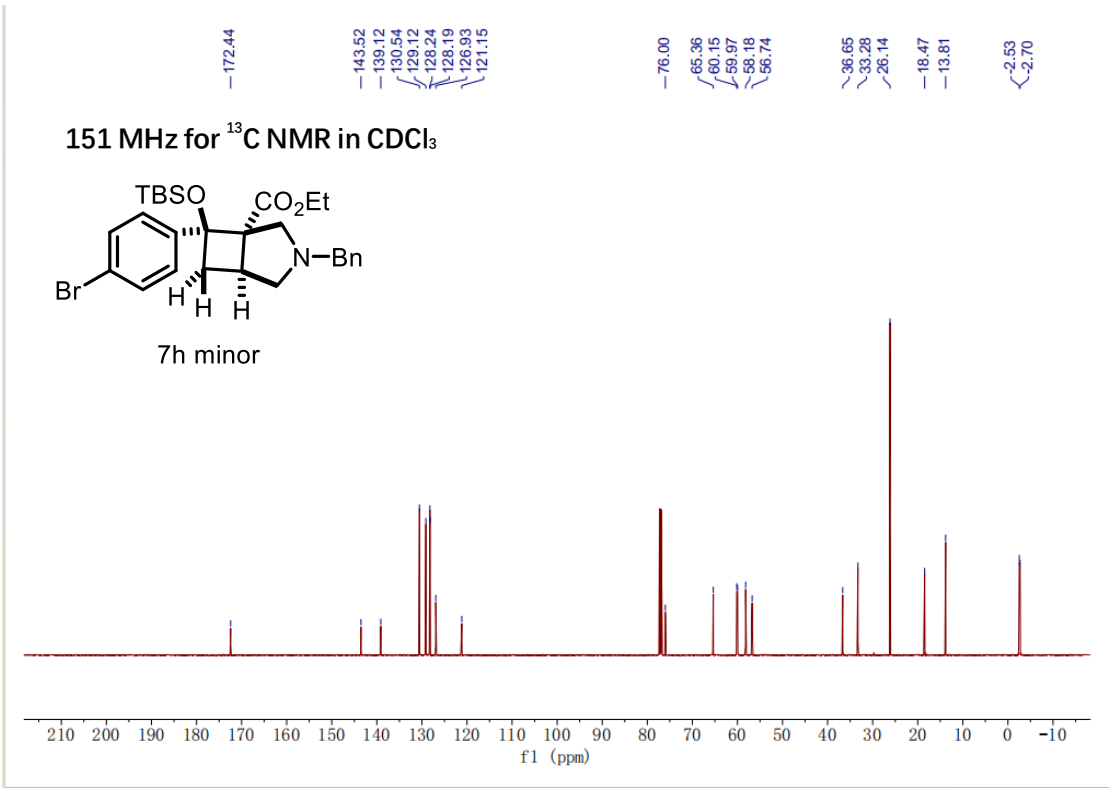


7h major

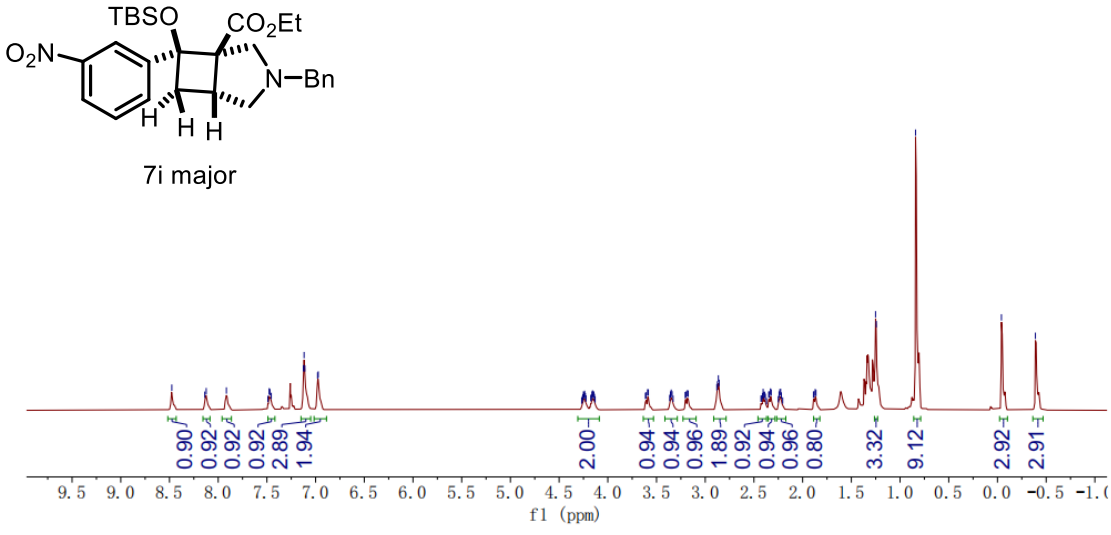



151 MHz for ^{13}C NMR in CDCl$_3$
TBSO
CO$_2$Et
N–Bn
Br
H
H
H
7h major
f1 (ppm)

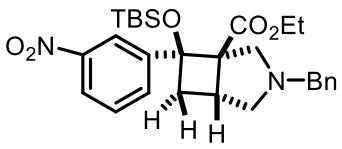

600 MHz for ^{1}H NMR in CDCl$_3$
TBSO
CO$_2$Et
N–Bn
Br
H
H
H
7h minor
f1 (ppm)



600 MHz for ^{1}H NMR in CDCl$_3$

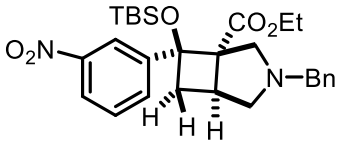


151 MHz for ^{13}C NMR in $CDCl_3$



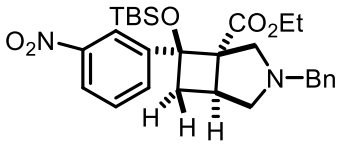
7i major

600 MHz for ^{1}H NMR in $CDCl_3$



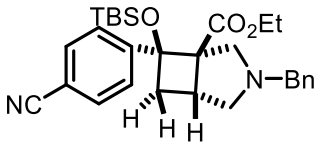
7i minor

151 MHz for ^{13}C NMR in $CDCl_3$

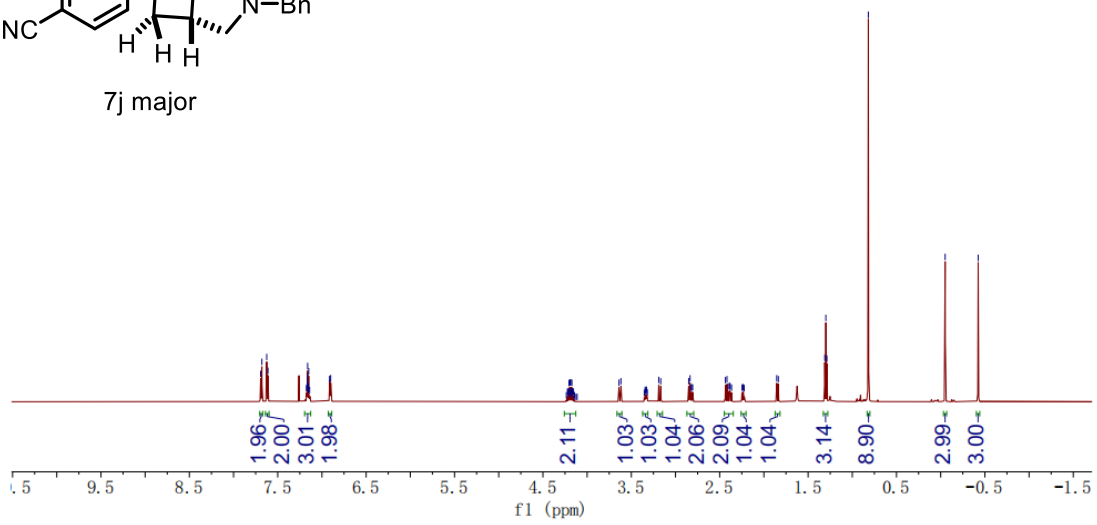


7i minor

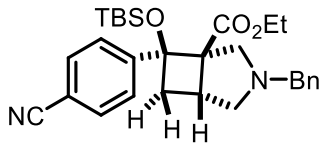
600 MHz for ^{1}H NMR in $CDCl_3$



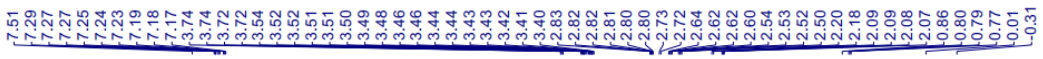
7j major



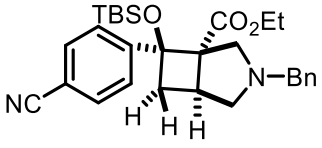
151 MHz for ^{13}C NMR in $CDCl_3$



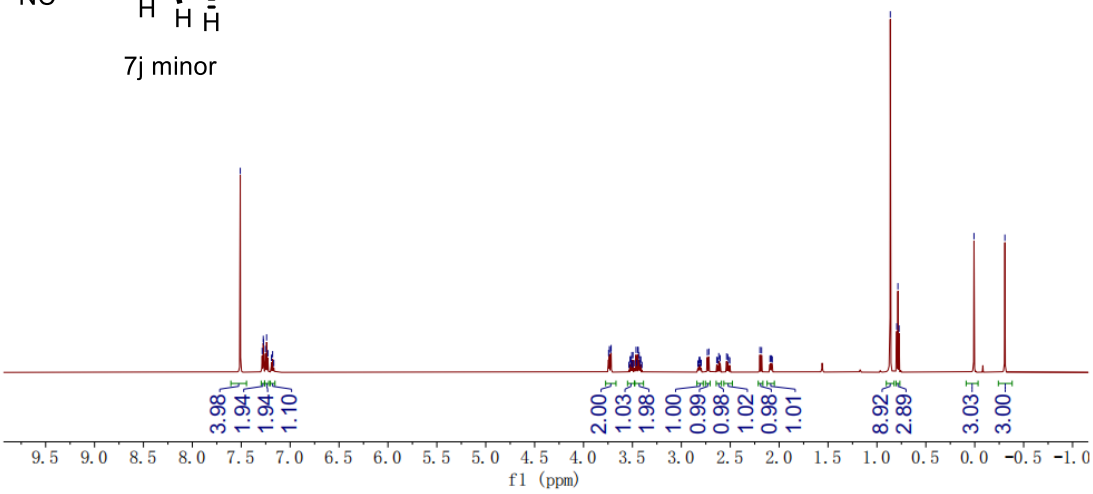
7j major

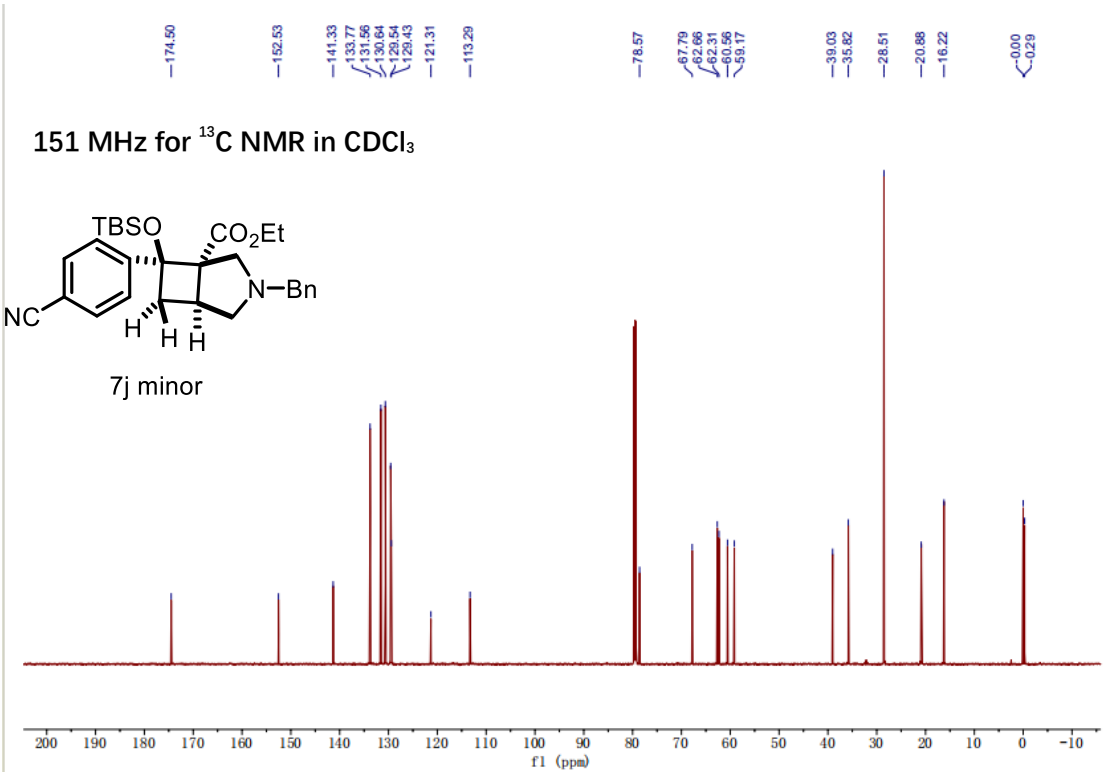


600 MHz for ^{1}H NMR in $CDCl_3$

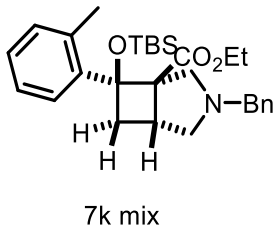


7j minor



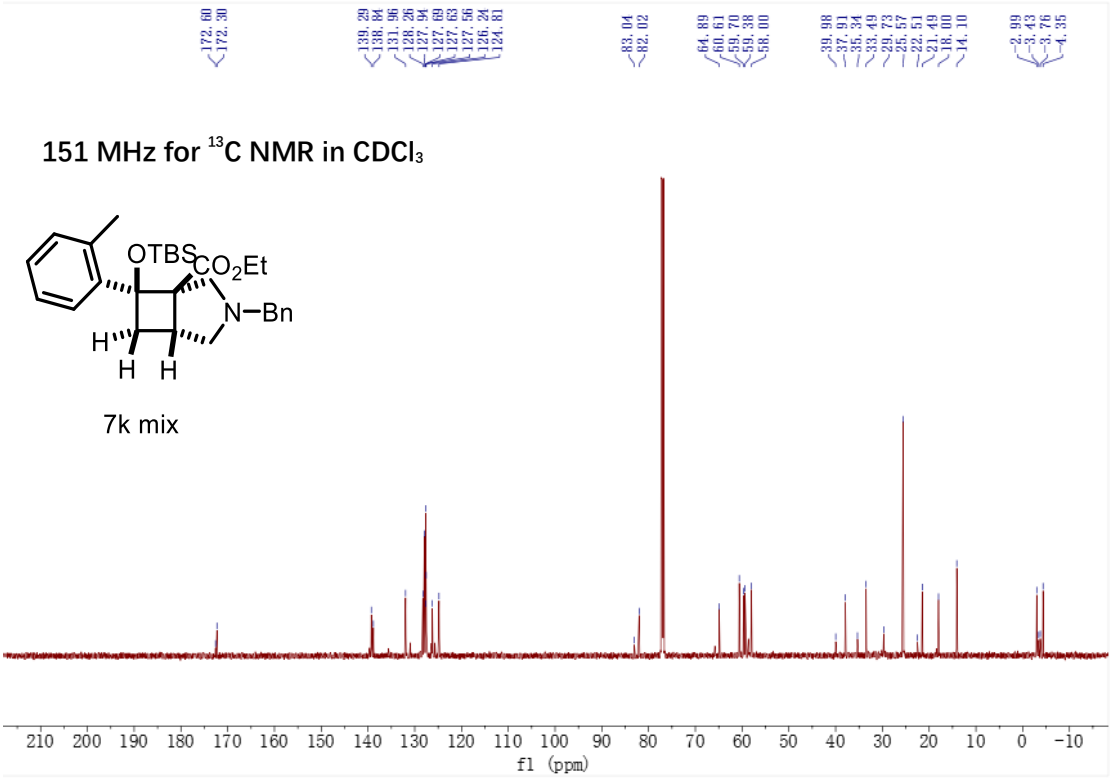


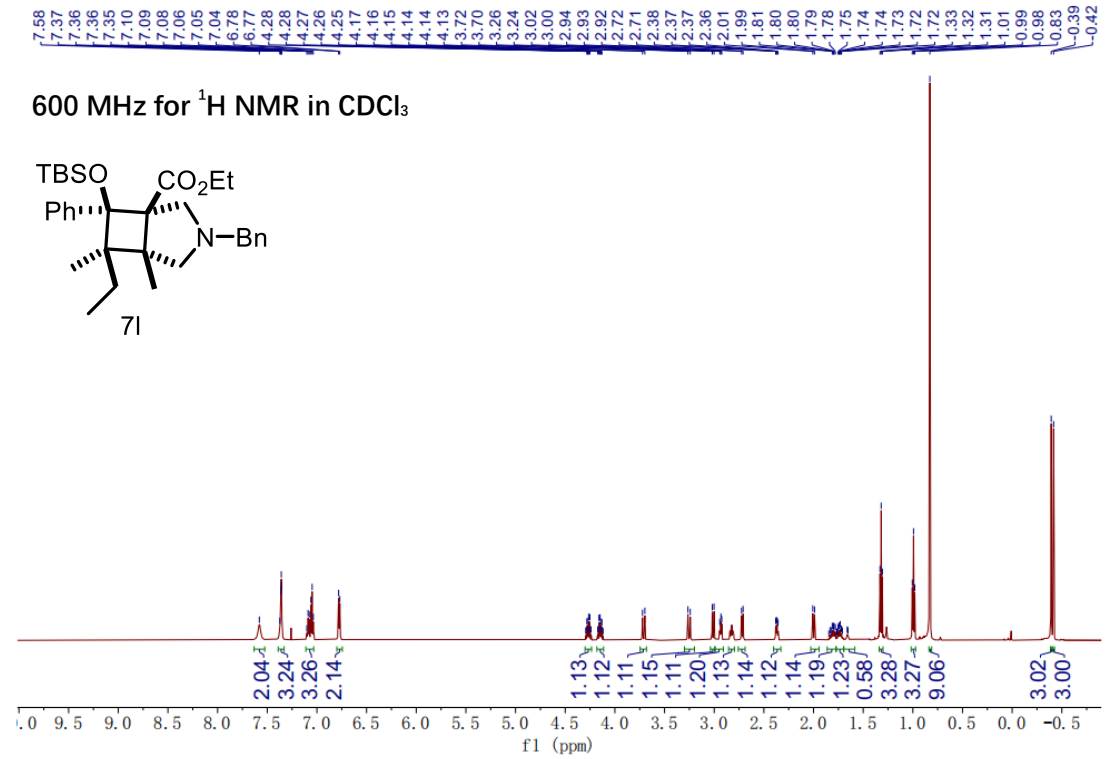
400 MHz for ^{1}H NMR in $CDCl_3$

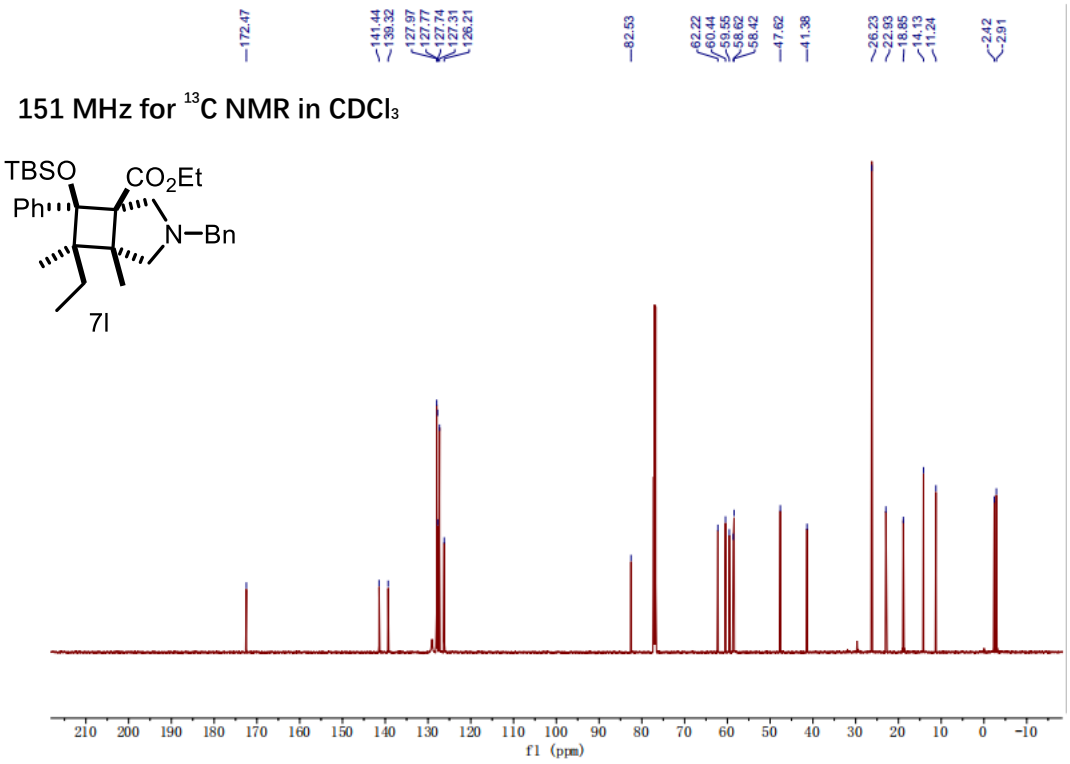


7k mix

7k was a 3.8:1 diastereoisomeric mixture


172.60
172.30
139.29
138.84
131.96
128.26
127.94
127.69
127.63
127.56
126.24
124.81
83.04
82.02
64.89
60.61
59.70
59.38
58.00
39.98
37.91
35.54
33.49
29.73
25.57
22.51
21.49
18.00
14.10
-2.99
-3.43
-3.76
-4.35
151 MHz for 13C NMR in CDCl3
OTBS
CO2Et
N–Bn
H
H H
7k mix
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

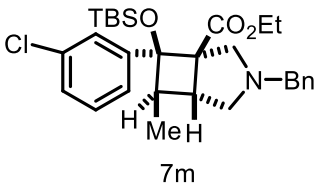

7.58
7.37
7.36
7.36
7.35
7.10
7.09
7.08
7.06
7.05
7.04
6.78
6.77
4.28
4.28
4.27
4.26
4.25
4.17
4.16
4.15
4.14
4.14
4.13
3.72
3.70
3.26
3.24
3.02
3.00
2.94
2.93
2.92
2.72
2.71
2.38
2.37
2.37
2.36
2.01
1.99
1.81
1.80
1.80
1.79
1.78
1.75
1.74
1.74
1.73
1.72
1.72
1.33
1.32
1.31
1.01
0.99
0.98
0.83
0.39
0.42
600 MHz for 1H NMR in CDCl3
TBSO
CO2Et
Ph
N–Bn
7l
2.04
3.24
3.26
2.14
1.13
1.12
1.11
1.15
1.11
1.20
1.13
1.14
1.12
1.14
1.19
1.23
0.58
3.28
3.27
9.06
3.02
3.00
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
f1 (ppm)



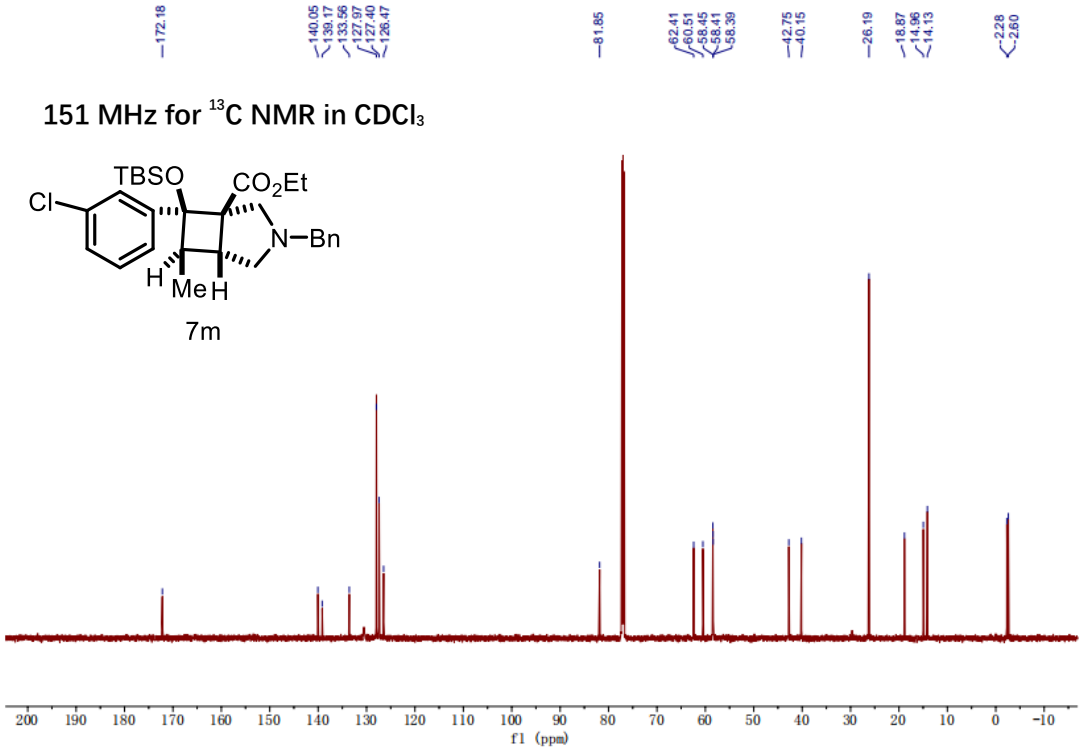
151 MHz for ^{13}C NMR in $CDCl_3$

7l

600 MHz for ^{1}H NMR in $CDCl_3$



7m


172.18
140.05
139.17
133.56
127.97
127.40
126.47
81.85
62.41
60.51
58.45
58.41
58.39
42.75
40.15
26.19
18.87
14.96
14.13
-2.28
-2.60
151 MHz for 13C NMR in CDCl3
TBSO
CO2Et
Cl
N–Bn
H
Me H
7m
f1 (ppm)


7.35
7.34
7.31
7.30
7.29
7.25
7.24
7.22
4.20
4.19
4.18
4.18
4.17
4.16
4.15
4.14
4.13
4.13
4.12
4.11
3.79
3.77
3.47
3.46
3.36
3.34
2.80
2.79
2.78
2.76
2.74
2.40
2.39
2.38
2.36
2.35
2.18
1.69
1.68
1.67
1.66
1.65
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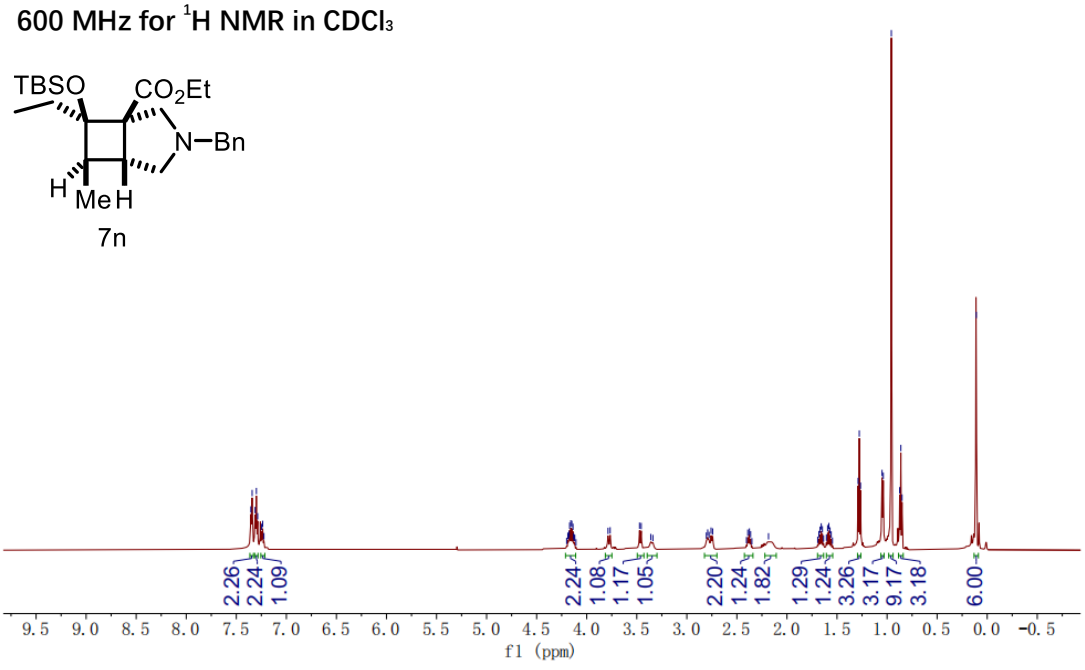
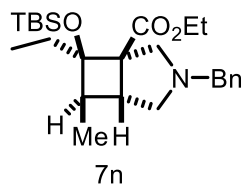
1.61
1.59
1.58
1.57
1.56
1.55
1.29
1.28
1.27
1.05
1.04
0.96
0.87
0.86
0.85
0.11

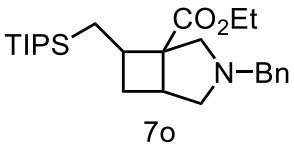

600 MHz for 1H NMR in CDCl3
TBSO
CO2Et
N–Bn
H
Me H
7n
2.26
2.24
1.09
2.24
1.08
1.17
1.05
2.20
1.24
1.82
1.29
1.24
3.26
3.17
9.17
3.18
6.00
f1 (ppm)

151 MHz for ^{13}C NMR in $CDCl_3$



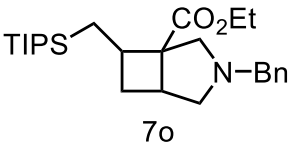
7n

600 MHz for ^{1}H NMR in $CDCl_3$

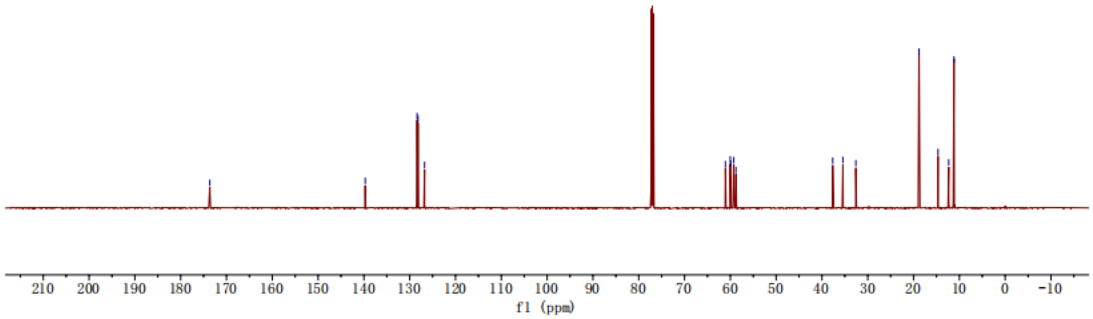


7o

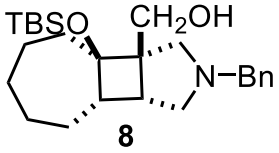
151 MHz for ^{13}C NMR in $CDCl_3$



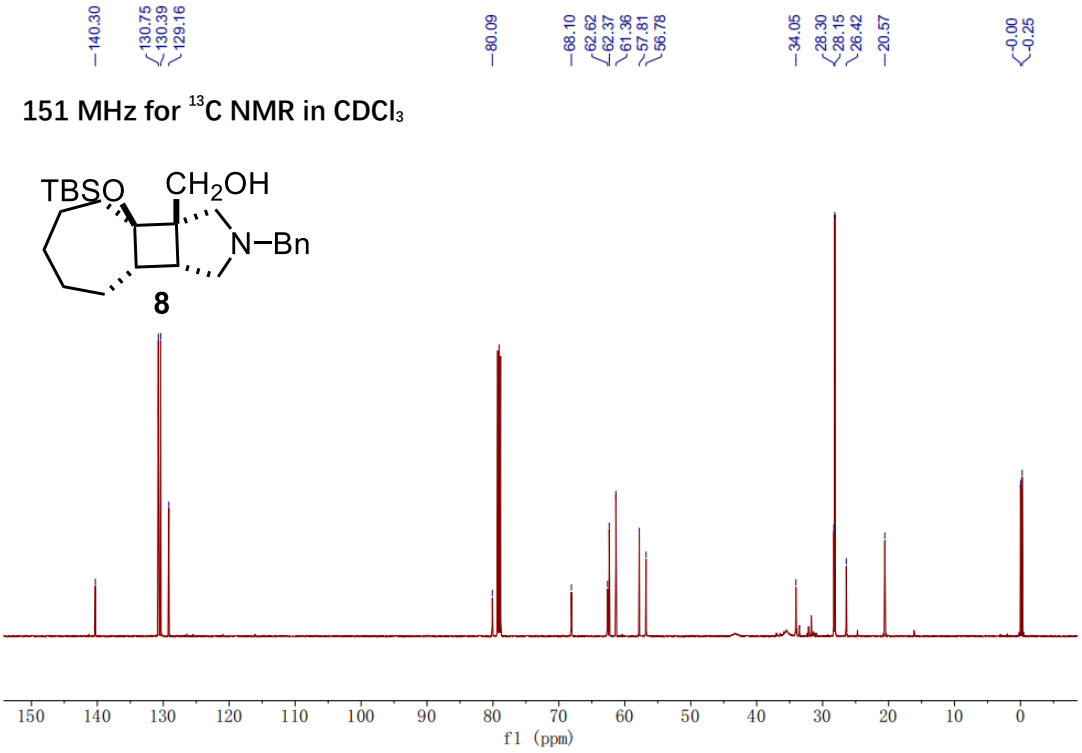
7o



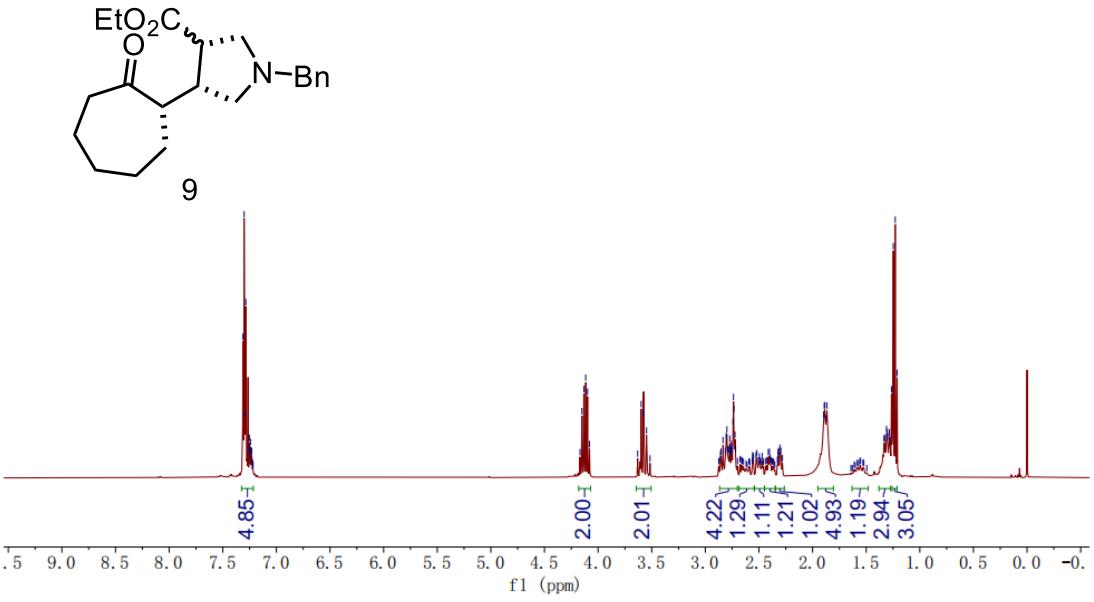
400 MHz for ^{1}H NMR in $CDCl_3$



8

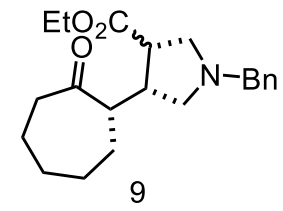


151 MHz for ^{13}C NMR in $CDCl_3$



400 MHz for ^{1}H NMR in $CDCl_3$

151 MHz for ^{13}C NMR in $CDCl_3$



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