

Supporting Information

Total Synthesis of (+)-Mutilin: A Transannular [2+2] Cycloaddition/Fragmentation Approach

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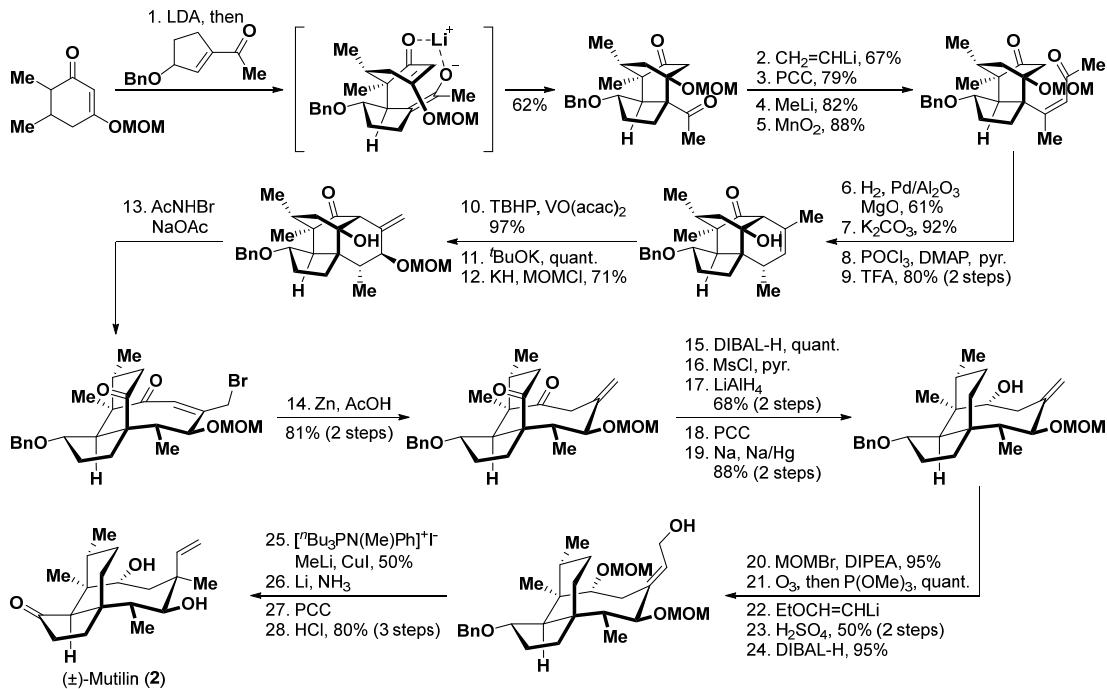
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I. Supplementary Figures and Tables

Gibbons (1982): (\pm)-mutilin (28 steps, 0.64% yield)



Boeckman (1989): (\pm)-pleuromutilin (27 steps, 0.42% yield)

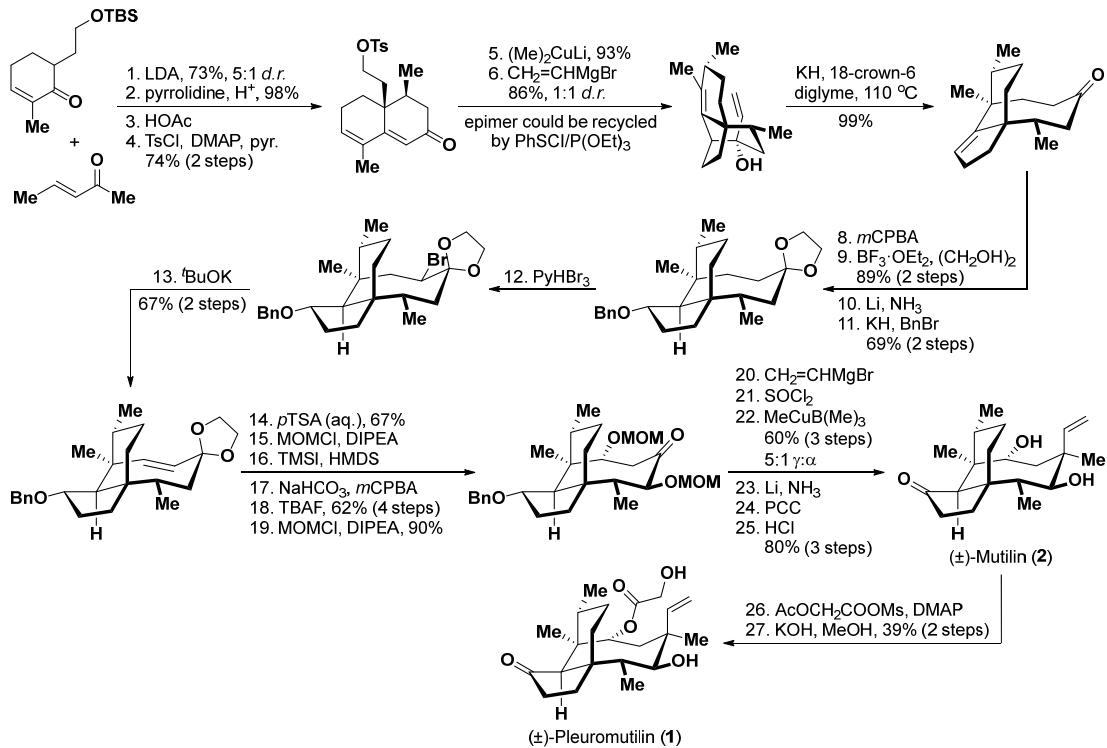
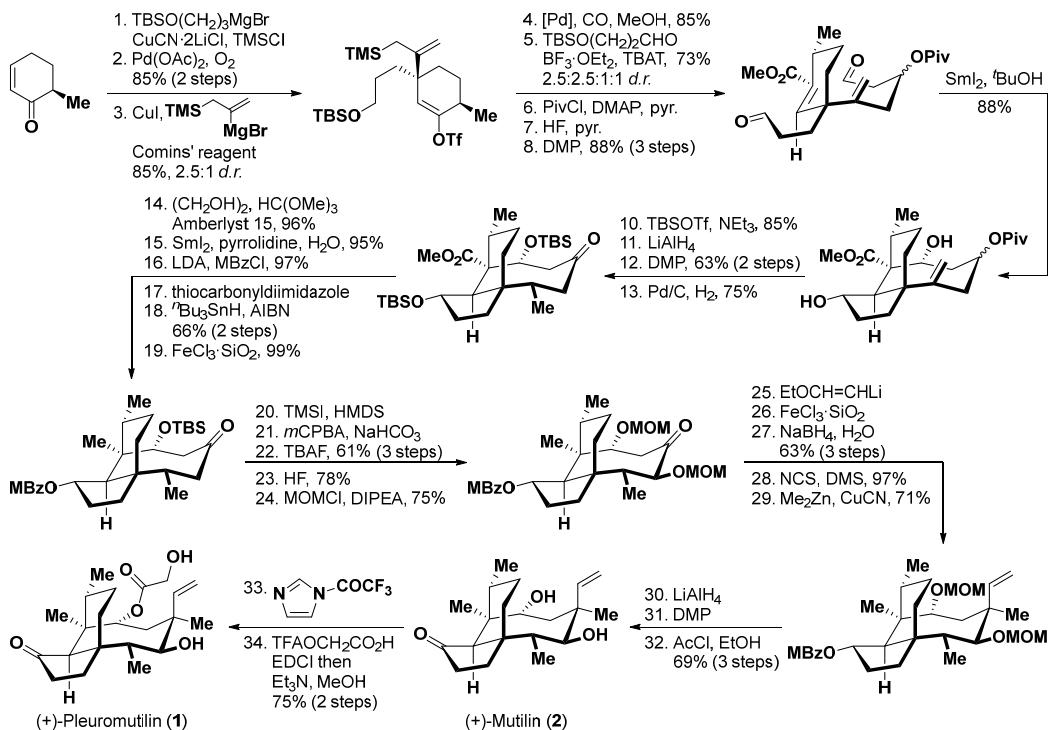


Figure S1. Reported Total Syntheses of Pleuromutilin^[1]

Procter (2013): (+)-pleuromutilin (34 steps, 0.46% yield)



Herzon (2017): (+)-pleuromutilin (20 steps, 0.30% yield)

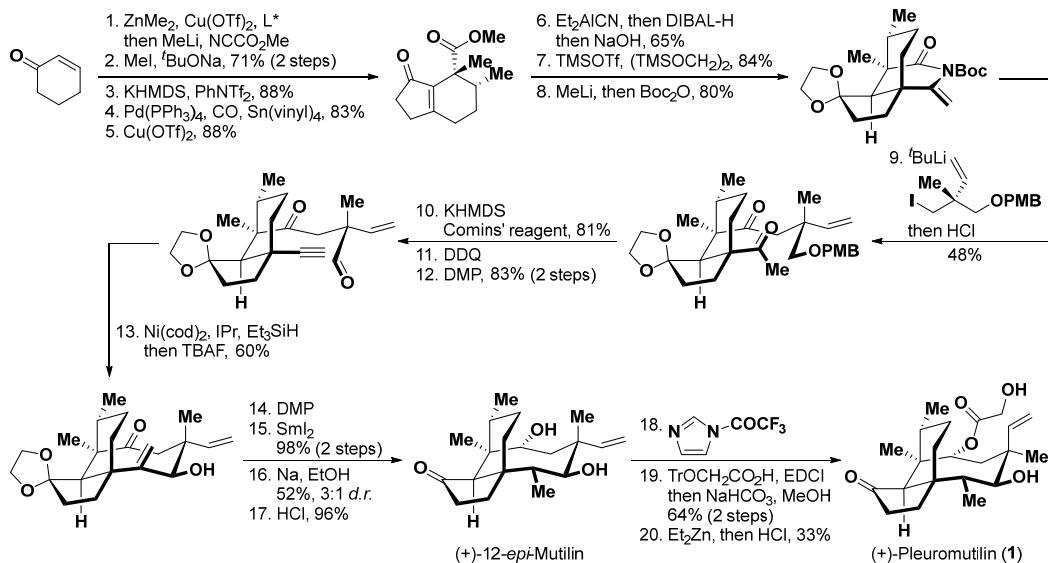
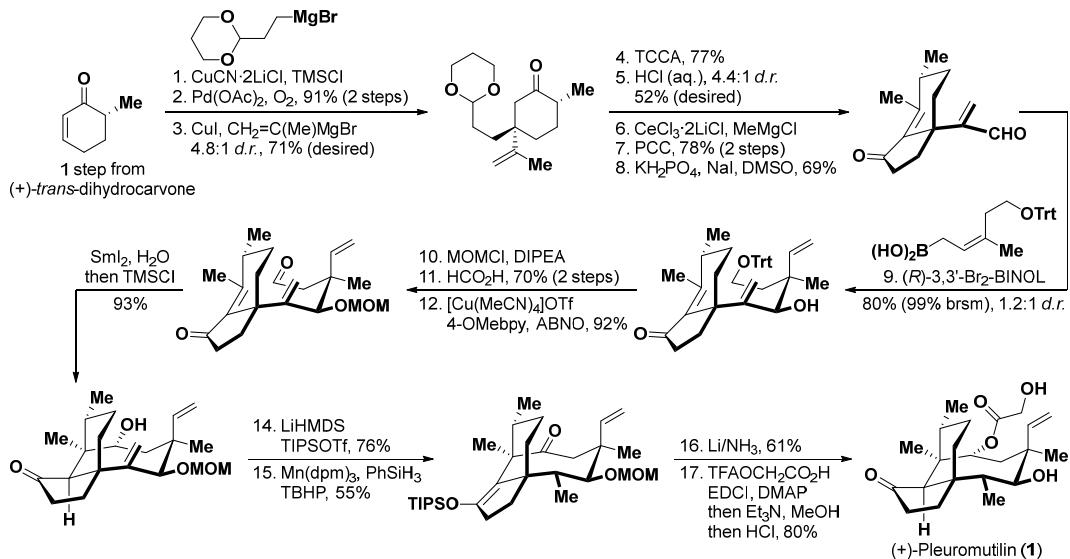


Figure S1. Reported Total Syntheses of Pleuromutilin (continued)^[1]

Reisman (2018): (+)-pleuromutilin (17 steps, 0.74% yield)



Pronin (2022): (±)-pleuromutilin (15 steps, 0.49% yield)

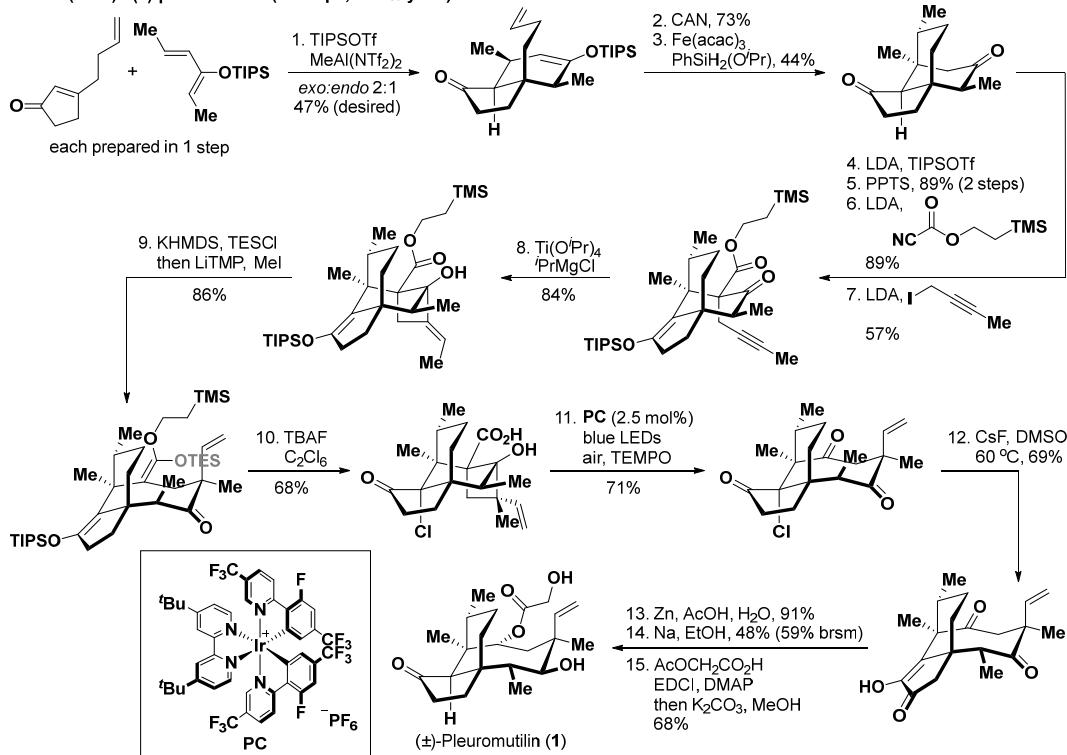


Figure S1. Reported Total Syntheses of Pleuromutilin (continued)^[1]

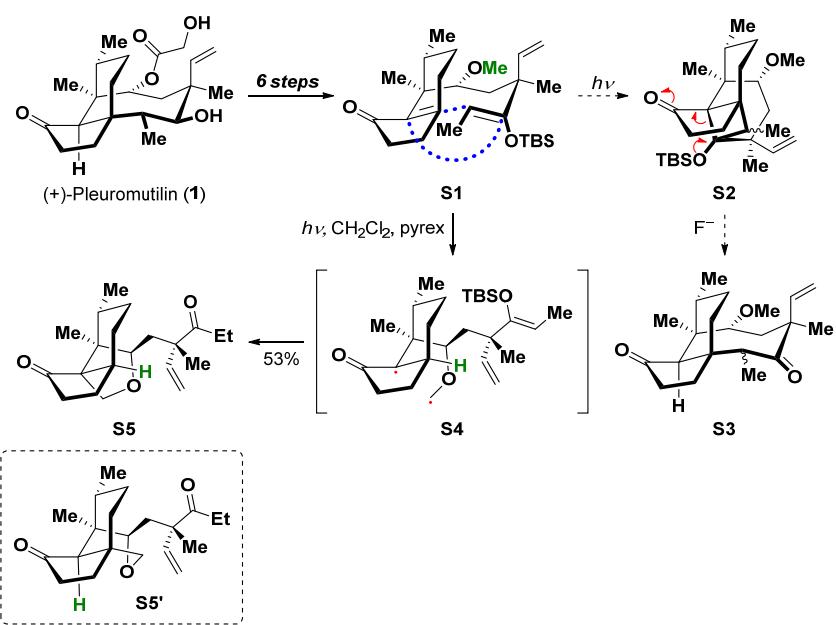
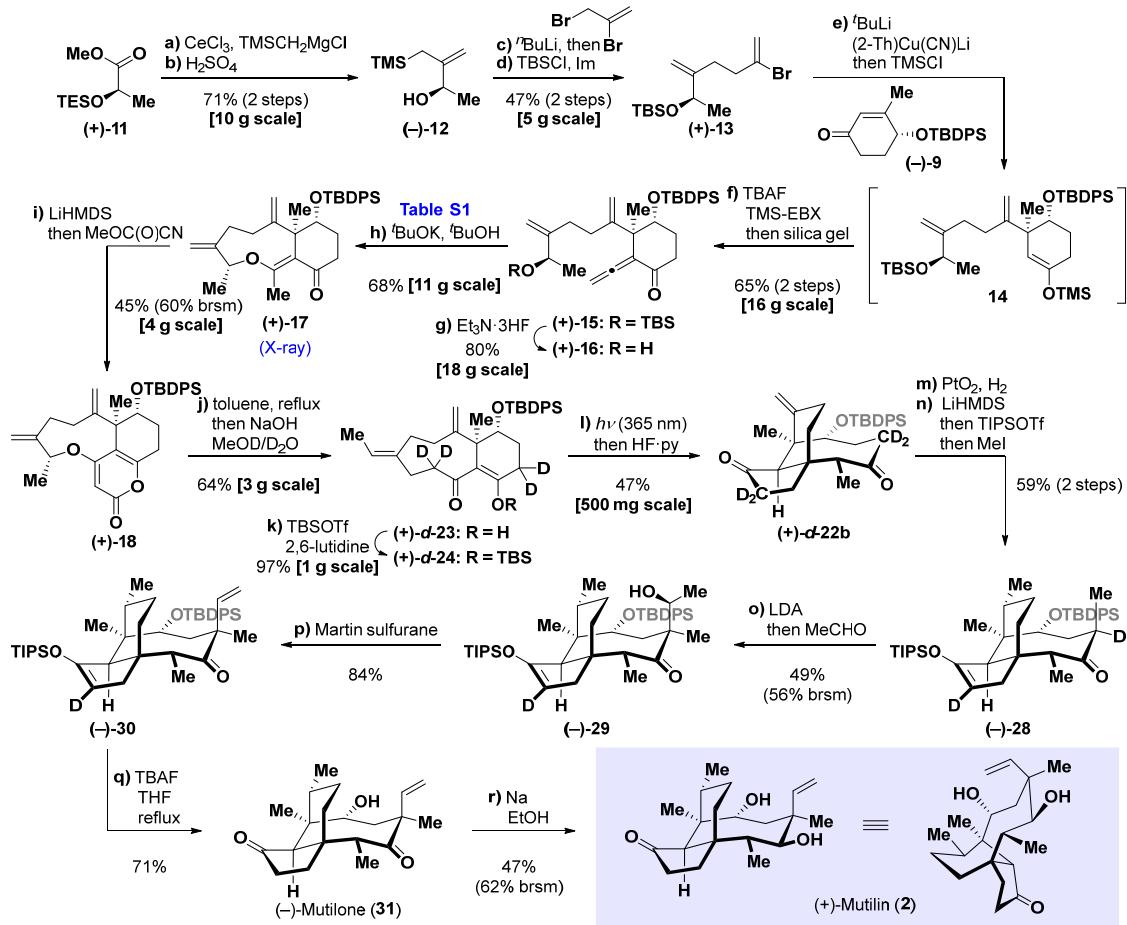


Figure S2. A Relay Approach to Pleuromutilin Proposed by Paquette and Co-workers^[2]

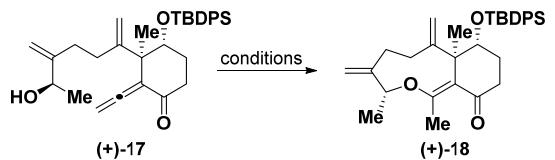
Paquette group has reported their efforts in developing a relay approach to pleuromutilin (**1**), in which enone **S1** was successfully prepared from **1** via 6 transformations. In the attempt to obtain intermediate **S2** via the intramolecular [2+2] cycloaddition, **S5** was the only reported product (53% isolated yield; the structure was originally assigned as **S5'**,^[2a] but revised by the subsequent publication^[2b]). A plausible mechanism involved the excitation of the enone moiety, intramolecular hydrogen atom abstraction to give biradical **S4**, and the collapse of biradical to afford **S5**.

Scheme S1. Total Synthesis of (+)-Mutilin (2)^a



^aReagents and conditions: (a) CeCl₃ (3.0 equiv), TMSCH₂MgCl (3.0 equiv), THF, -78 °C, 1 h, then (+)-11, -78 °C to rt, 12 h; (b) H₂SO₄ (1 M), THF, rt, 1 h, 71% (2 steps); (c) ⁷BuLi (2.5 equiv), THF, -78 °C, 30 min, then HMPA (5.0 equiv), 2,3-dibromoprop-1-ene (3.0 equiv), -78 °C to rt, 12 h, then H₂SO₄ (1 M), rt, 1 h, 48%; (d) TBSCl (1.2 equiv), imidazole (1.5 equiv), DCM, 0 °C to rt, 2 h, 97%; (e) ⁷BuLi (3.0 equiv), (2-Th)Cu(CN)Li (1.5 equiv), Et₂O, -78 °C, 20 min, then (+)-13 (1.5 equiv), 30 min, then (-)-9 (1.0 equiv), TMSCl (1.5 equiv), -78 °C to rt, 1 h; (f) TMS-EBX (1.3 equiv), TBAF (1.3 equiv), THF, -78 °C, 2 h, then silica gel, rt, 12 h, 65% (2 steps); (g) Et₃N·3HF (5.0 equiv), THF, 35 °C, 24 h, 80%; (h) ⁷BuOK (2.0 equiv), ⁷BuOH/THF, 80 °C, 40 min, 68%; (i) LiHMDS (1.1 equiv), THF, 0 °C, 30 min, then MeOC(O)CN (1.5 equiv), rt, 2 h, 45% (60% brsm); (j) toluene, reflux, 2 h; NaOH (1.2 equiv, 0.5 M in D₂O), MeOD, 65 °C, 9.5 h, 64%; (k) TBSOTf (1.4 equiv), 2,6-lutidine (2.1 equiv), DCM, 0 °C, 30 min, 97%; (l) hν (365 nm, 10 W), toluene, rt, 24 h; HF·py (30 equiv), py (7.5 equiv), THF, 30 °C, 32 h, 47%; (m) PtO₂ (10 mol%), H₂ (1 atm), EtOH, 30 °C, 24 h; (n) LiHMDS (5.0 equiv), THF, 0 °C, 30 min, then TIPSOTf (1.3 equiv), 0 °C to rt, 40 min, then 0 °C, MeI (3.0 equiv), 1 h, 59% (2 steps); (o) LDA (10 equiv), rt, 1.5 h, then -15 °C, MeCHO (30 equiv), 30 min, 49% (56% brsm); (p) Martin sulfurane (2.0 equiv), toluene, 50 °C, 4 h, 84%; (q) TBAF (10 equiv), THF, reflux, 2 h, 71%; (r) Na (excess), EtOH, -20 °C, 3 h, 3 cycles, 47% (62% brsm).

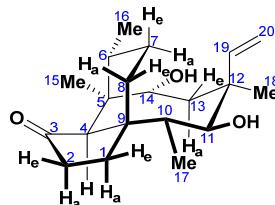
Table S1. Optimization of the Cyclization^a

					
entry	base	equiv	solvent	temp.	yield ^b
1	DABCO	0.1	THF	rt	no reaction
2	DABCO	1.0	DMSO	80 °C	decomposed
3	Cs ₂ CO ₃	1.0	DMSO	rt	decomposed
4	Cs ₂ CO ₃	1.0	THF	80 °C	decomposed
5	DBU	1.0	DMSO	rt	decomposed
6	^t BuOK	1.5	^t BuOH	rt	decomposed
7	^t BuOK	1.5	^t BuOH	65 °C	38%
8	^t BuOK	1.5	^t BuOH	80 °C	40%
9	^t BuOK	0.5	^t BuOH	65 °C	18%
10	^t BuOK	3.0	^t BuOH	65 °C	42%
11 ^c	^t BuOK	2.0	^t BuOH	80 °C	51%
12 ^{c,d}	^t BuOK	2.0	^t BuOH	80 °C	62%

^a[17] = 0.01 M (0.04 mmol). ^b Isolated yield after flash chromatography.

^c Substrate 17 was added dropwise to ^tBuOK in ^tBuOH. ^d 1 g scale.

Table S2. Comparison of the ^1H and ^{13}C NMR Data of Synthesized Mutilin with the Reported Values



Position	Mutilin (2) synthesized by Pronin ^a		Mutilin (2) synthesized by us ^d		$\Delta\delta_{\text{H}}^e$	$\Delta\delta_{\text{C}}^f$
	δ_{H} (m, J [Hz]) ^b	δ_{C}^c	δ_{H} (m, J [Hz]) ^b	δ_{C}^c		
1a	1.63-1.56 (m, 1H)	25.3	1.63-1.59 (m, 1H)	25.2	0.02	-0.1
1e	1.53-1.43 (m, 1H)		1.50-1.44 (m, 1H)		-0.01	
2a	2.29-2.13 (m, 1H)	34.6	2.28-2.14 (m, 1H)	34.6	0	0
2e	2.29-2.13 (m, 1H)		2.28-2.14 (m, 1H)		0	
3	-	217.7	-	217.8	-	0.1
4	2.05 (s, 1H)	59.3	2.08-2.03 (m, 1H)	59.2	0	-0.1
5	-	42.5	-	42.5	-	0
6	1.67 (ddt, 14.2, 7.1, 3.7, 1H)	37.0	1.68 (ddt, 14.3, 7.2, 3.8, 1H)	37.0	0.01	0
7a	1.53-1.43 (m, 1H)	27.3	1.50-1.44 (m, 1H)	27.3	-0.01	0
7e	1.36 (m, 1H)		1.40-1.37 (m, 1H)		0.03	
8a	1.16-1.08 (m, 1H)	30.5	1.14-1.09 (m, 1H)	30.5	-0.01	0
8e	1.74 (dq, 14.5, 3.1, 1H)		1.74 (dq, 14.5, 3.2, 1H)		0	
9	-	45.4	-	45.4	-	0
10	2.29-2.13 (m, 1H)	36.6	2.28-2.14 (m, 1H)	36.6	0	0
11	3.41 (t, 6.6, 1H)	75.3	3.41 (d, 6.4, 1H)	75.3	0	0
12	-	45.2	-	45.2	-	0
13a	1.91 (dd, 15.9, 7.7, 1H)	45.5	1.91 (dd, 15.9, 7.7, 1H)	45.5	0	0
13e	1.63-1.56 (m, 1H)		1.63-1.59 (m, 1H)		0.02	
14	4.35 (dd, 7.7, 5.5, 1H)	66.9	4.35 (d, 7.7, 1H)	66.9	0	0
15	1.36 (s, 3H)	13.6	1.36 (s, 3H)	13.6	0	0
16	0.96 (d, 7.1, 3H)	18.3	0.96 (d, 7.1, 3H)	18.3	0	0
17	0.92 (d, 7.1, 3H)	11.4	0.92 (d, 7.1, 3H)	11.4	0	0
18	1.15 (s, 3H)	28.7	1.15 (s, 3H)	28.7	0	0
19	6.15 (ddd, 17.9, 11.2, 0.9, 1H)	139.5	6.15 (ddd, 17.8, 11.1, 0.8, 1H)	139.5	0	0
20 cis	5.29 (dd, 1H)	116.2	5.29 (dd, 11.2, 1.4, 1H)	116.1	0	-0.1
20 trans	5.37 (dd, 1H)		5.36 (dd, 17.8, 1.4, 1H)		-0.01	

^aChemical shifts and coupling constants are reported by Nicholas J. Foy and Sergey V. Pronin (600 MHz in CDCl_3)^[1]

^bTMS was used as the internal standard (0.00 ppm), and solvent signal was used as reference (CDCl_3 at 7.26 ppm): δ_{H} in ppm, J values (Hz) in parentheses.

^cSolvent signal was used as reference (CDCl_3 at 77.16 ppm): δ_{C} in ppm.

^d600 MHz NMR spectrometer (CDCl_3).

^eThe difference in the ^1H chemical shift of the product synthesized by us and that reported by Pronin group.

^fThe difference in the ^{13}C chemical shift of the product synthesized by us and that reported by Pronin group.

II. Experimental Procedures and Spectroscopic Data

General Information

Unless otherwise mentioned, all reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Anhydrous tetrahydrofuran and diethyl ether were distilled over sodium-benzophenone. Anhydrous toluene and dichloromethane were obtained from the solvent purification system operated by active aluminum (Innovative Technology). Tert-butyl alcohol (Mreda), ethanol (Mreda) and ethyl acetate (Energy) were stored over molecular sieves under inert atmosphere in a sealed flask. Hexamethylphosphoramide was distilled over calcium hydride and stored over molecular sieves under inert atmosphere in a sealed flask.

Photochemical reactions were performed in a SSSTECH-AL1 photoreactor (purchased from 3S Tech.), light source: 365-370 nm, setting temperature: 30 °C, setting power: 5 or 10 W.

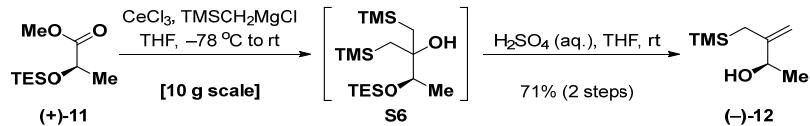
Reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm E. Merck silica plates (60F-254), using UV light as the visualizing agent and an ethanolic solution of phosphomolybdic acid or KMnO₄, and heat as developing agents. If not specially mentioned, flash column chromatography uses silica gel (200-300 mesh) supplied by Tsingtao Haiyang Chemicals (China) or SiliaFlash® P60 supplied by SiliCycle® Inc. (Canada). Yields refer to chromatographically.

NMR spectra were recorded on Brüker Advance 600 (¹H 600 MHz, ¹³C 150 MHz), Brüker Advance 500 (¹H 500 MHz, ¹³C 125 MHz) and Brüker Advance 400 (¹H 400 MHz, ¹³C 100 MHz, ¹⁹F 377 MHz). TMS was used as the internal standard for ¹H NMR (0.00 ppm), and solvent signal was used as reference for ¹H NMR (CDCl₃ at 7.26 ppm, pyridine-*d*₅ at 8.74 ppm), ¹³C NMR (CDCl₃ at 77.16 ppm, pyridine-*d*₅ at 150.35 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet.

Mass spectrometric data were obtained using Brüker Apex IV FTMS using ESI (electrospray ionization) or EI (electron ionization). Infrared spectra were recorded on a

Thermo Nicolet iS5 spectrometer. Optical rotations were measured on an InsMark IP-digi300 digital polarimeter with a LED light source at ambient temperature and are reported as follows: $[\alpha]_\lambda$ (c g/100 mL). Enantioselectivities were measured with HPLC (Agilent Technologies 1200 series) with Daicel chiral column, eluted with *n*-hexane and isopropanol. Low-temperature diffraction data were collected on a XtaLAB PRO 007HF(Mo): Kappa single diffractometer at 100 or 180 K.

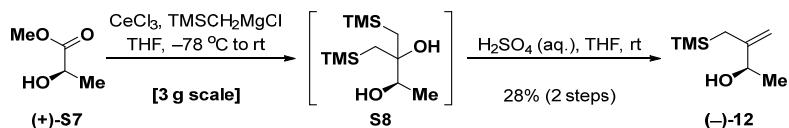
Synthesis of compound (-)-12



A 500 mL round-bottom flask equipped with a magnetic stir bar was charged with anhydrous CeCl₃ (3.0 equiv, 137 mmol, 33.9 g). The flask was dried at 160 °C under vacuum (*ca.* 1.5 torr) for 2 h and then cooled under a balloon of N₂. After the flask was cooled to room temperature, THF (200 mL) was added, and the mixture was stirred for 4 h. Then TMSCH₂MgCl (3.0 equiv, 137 mmol, 106 mL of a 1.3 M solution in THF) was added at –78 °C. After being stirred at –78 °C for 1 h, (+)-**11** (1.0 equiv, 45.8 mmol, 10.0 g) was added dropwise. The resulting mixture was warmed to room temperature over 12 h. Then the reaction was quenched with saturated NH₄Cl solution at 0 °C, and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The crude product **S6** (yellow oil) was used immediately in the next step without further purification.

Intermediate **S6** was dissolved in THF (100 mL) and then H₂SO₄ solution (aq., 1 M, 30 mL) was added. After being stirred for 1 h, the reaction was quenched with saturated NaHCO₃ solution at 0 °C, and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give compound (*-*)-**12** (8.30 g, contaminated with 38 wt.% triethylsilanol that has a similar polarity with the desired product, 71% yield for 2 steps) as a colorless oil. The mixture was used in the next step without further purification.

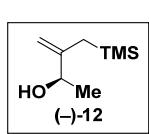
The pure sample of **(-)-12** could be prepared from commercially available methyl *(R)*-
(+)-lactate (S7**)** without the use of TES protecting group.



A 500 mL round-bottom flask equipped with a magnetic stir bar was charged with anhydrous CeCl₃ (4.0 equiv, 115 mmol, 28.4 g). The flask was dried at 160 °C under vacuum (*ca.* 1.5 torr) for 2 h and then cooled under a balloon of N₂. After the flask was

cooled to room temperature, THF (200 mL) was added, and the mixture was stirred for 4 h. Then TMSCH₂MgCl (4.0 equiv, 115 mmol, 88.7 mL of a 1.3 M solution in THF) was added at -78 °C. After being stirred at -78 °C for 1 h, (+)-S7 (1.0 equiv, 28.8 mmol, 3.00 g) was added dropwise. The resulting mixture was warmed to room temperature over 12 h. Then the reaction was quenched with saturated NH₄Cl solution at 0 °C, and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The crude product S8 (yellow oil) was used immediately in the next step without further purification.

S8 was dissolved in THF (100 mL) and then H₂SO₄ solution (aq., 1 M, 30 mL) was added. After being stirred for 1 h, the reaction was quenched with saturated NaHCO₃ solution at 0 °C, and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give compound (-)-12 (1.27 g, 8.02 mmol, 28% yield over 2 steps) as a colorless oil.



*R*_f = 0.4 (petroleum ether: ethyl acetate = 5:1)

[α]_D²¹ = -12.5 (c = 1.0, CHCl₃)

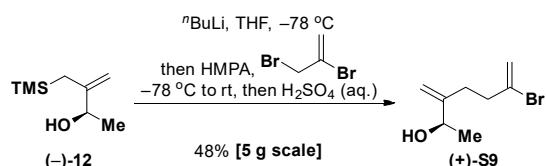
HRMS-EI calc. for C₈H₁₈OSi [M⁺]: 158.1121; Found: 158.1122.

IR (neat, cm⁻¹): 3675, 2987, 2900, 1393, 1249, 1066.

¹H NMR (400 MHz, CDCl₃) δ 4.92 (t, *J* = 1.3 Hz, 1H), 4.62 (s, 1H), 4.11 (q, *J* = 6.4 Hz, 1H), 1.64 (d, *J* = 14.0 Hz, 1H), 1.43 (d, *J* = 14.0 Hz, 1H), 1.27 (d, *J* = 6.4 Hz, 3H), 0.03 (s, 9H).

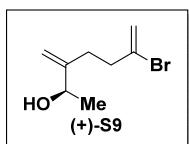
¹³C NMR (100 MHz, CDCl₃) δ 151.5, 106.2, 71.6, 22.7, 22.4, -1.1.

Synthesis of compound (+)-S9



To a solution of compound (-)-12 (1.0 equiv, 32.5 mmol, 8.30 g, contaminated by 38 wt.% triethylsilanol) in THF (100 mL) was added ⁿBuLi (2.5 equiv, 81.3 mmol, 50.8 mL of a 1.6 M solution in hexane) dropwise at -78 °C. The mixture was stirred for 30 min at

the same temperature, and then HMPA (5.0 equiv, 163 mmol, 28.3 mL) and 2,3-dibromopropene (3.0 equiv, 97.5 mmol, 10.1 mL) were added. The resulting mixture was warmed to room temperature over 12 h before it was quenched with H_2SO_4 solution (aq., 1 M, 40 mL). After being stirred at room temperature for another 1 h, the mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give compound (+)-S9 (3.20 g, 15.6 mmol, 48% yield) as a colorless oil.



R_f = 0.3 (petroleum ether: ethyl acetate = 5:1)

$[\alpha]_D^{25} = +7.2$ ($c = 1.0$, CHCl_3)

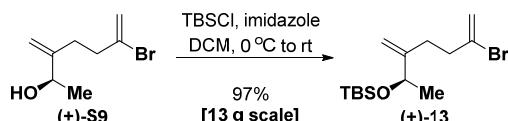
HRMS-ESI calc. for $\text{C}_8\text{H}_{17}\text{BrNO}$ [$\text{M}+\text{NH}_4^+$]: 222.0488; Found: 222.0484.

IR (neat, cm^{-1}): 2974, 2930, 2856, 1628, 1099, 1073.

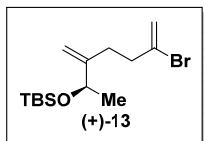
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.59 (dd, $J = 1.4, 1.4$ Hz, 1H), 5.42 (d, $J = 1.7$ Hz, 1H), 5.09 (s, 1H), 4.84 (s, 1H), 4.27 (q, $J = 6.5$ Hz, 1H), 2.63-2.59 (m, 2H), 2.42-2.25 (m, 2H), 1.31 (d, $J = 6.5$ Hz, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 151.3, 134.1, 117.0, 109.6, 71.1, 40.2, 30.2, 22.3.

Synthesis of compound (+)-13



To a solution of compound (+)-S9 (1.0 equiv, 64.8 mmol, 13.3 g) and imidazole (1.5 equiv, 97.3 mmol, 6.62 g) in DCM (150 mL) was added TBSCl (1.2 equiv, 77.8 mmol, 11.7 g) at 0 °C. After being stirred at room temperature for 2 h, the reaction was diluted with water, and extracted with DCM. The combined organic layers were washed with brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give compound (+)-13 (20.1 g, 62.9 mmol, 97% yield) as a colorless oil.



$R_f = 0.4$ (petroleum ether)

$[\alpha]_D^{25} = +3.5$ ($c = 1.0$, CHCl₃)

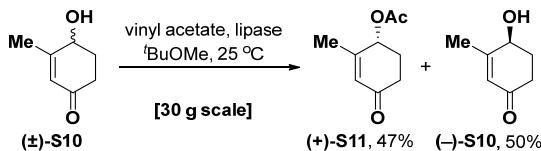
HRMS-ESI calc. for C₁₄H₂₈BrOSi [M+H⁺]: 319.1087; Found: 319.1087.

IR (neat, cm⁻¹): 2955, 2929, 2856, 1116, 1087.

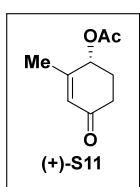
¹H NMR (400 MHz, CDCl₃) δ 5.58 (dd, $J = 1.7, 1.7$ Hz, 1H), 5.41 (d, $J = 1.7$ Hz, 1H), 5.03 (s, 1H), 4.75 (dt, $J = 1.7, 1.3$ Hz, 1H), 4.24 (q, $J = 6.4$ Hz, 1H), 2.61-2.57 (m, 2H), 2.39-2.21 (m, 2H), 1.23 (d, $J = 6.4$ Hz, 3H), 0.89 (s, 9H), 0.05 (s, 3H), 0.03 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 151.5, 134.4, 116.7, 108.9, 72.0, 40.4, 29.7, 26.0, 23.7, 18.4, -4.7, -4.8.

Synthesis of compound (+)-S11^[3]



Enantio-enriched enone (+)-S11 was prepared according to the reported literature.^[3] To a solution of compound (±)-S10 (245 mmol, 30.9 g, prepared from commercially available 3-methylanisole through a four-step sequence according to the reported literature^[4]) in 'BuOMe (150 mL) was added vinyl acetate (67 mL) and lipase acrylic resin from *Candida antarctica* (1.9 g). After being stirred at 25 °C for 8.5 h, the reaction was filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give compound (+)-S11 (19.4 g, 115 mmol, 47% yield) as a pale-yellow oil and compound (-)-S10 (15.3 g, 121 mmol, 50% yield) as a brown oil.



$R_f = 0.65$ (petroleum ether: ethyl acetate = 1:1)

HPLC (Daicel chiral column AD-H, *n*-hexane: isopropanol = 100:1, flow rate 1.0 mL/min, $\lambda = 240$ nm): t_R (major) = 17.832 min, t_R (minor) = 19.757 min; 95% ee.

$[\alpha]_D^{30} = +28.6$ ($c = 1.0$, CHCl₃) [lit.^[5]: $[\alpha]_D^{25} = +43.4$ ($c = 1.03$, CHCl₃, 95% ee)]

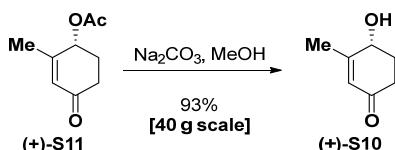
¹H NMR (400 MHz, CDCl₃) δ 5.93 (s, 1H), 5.55 (dd, $J = 7.8, 4.8$ Hz, 1H), 2.54 (ddd, $J = 16.9, 6.8, 4.9$ Hz, 1H), 2.39 (ddd, $J = 17.0, 10.3, 4.9$ Hz, 1H), 2.26 (ddt, $J = 13.3, 6.8, 4.8$

Hz, 1H), 2.13 (s, 3H), 2.07 (dddd, J = 13.1, 10.3, 8.0, 5.1 Hz, 1H), 1.93 (t, J = 1.3 Hz, 3H).

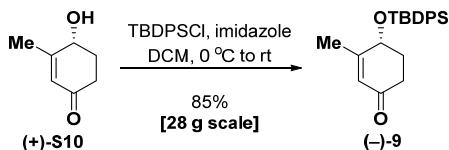
^{13}C NMR (100 MHz, CDCl_3) δ 198.0, 170.5, 158.4, 128.9, 70.0, 34.5, 28.6, 21.1, 20.6.

The characterization data were in agreement with literature values.^[5]

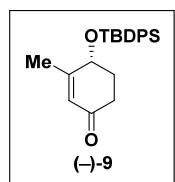
Synthesis of compound (-)-9



The procedure was adapted from the reported protocol.^[4] To a solution of compound (+)-S11 (1.0 equiv, 243 mmol, 40.9 g) in MeOH (600 mL) was added Na_2CO_3 (5.0 equiv, 1.22 mmol, 129 g). After being stirred at room temperature for 2 h, the mixture was filtered through a short pad of Celite and the filtrate was concentrated *in vacuo*. The residue was purified by flash column chromatography to give compound (+)-S10 (28.6 g, 227 mmol, 93% yield) as a brown oil.



To a solution of compound (+)-S10 (1.0 equiv, 227 mmol, 28.6 g) and imidazole (2.0 equiv, 453 mmol, 30.9 g) in DCM (350 mL) was added TBDPSCl (1.1 equiv, 249 mmol, 64.8 mL) at 0 °C. After being stirred at room temperature for 2.5 h, the reaction was diluted with water, and extracted with DCM. The combined organic layers were washed with brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give compound (-)-9 (70.5 g, 193 mmol, 85% yield) as a pale-yellow oil.



R_f = 0.5 (petroleum ether: ethyl acetate = 5:1)

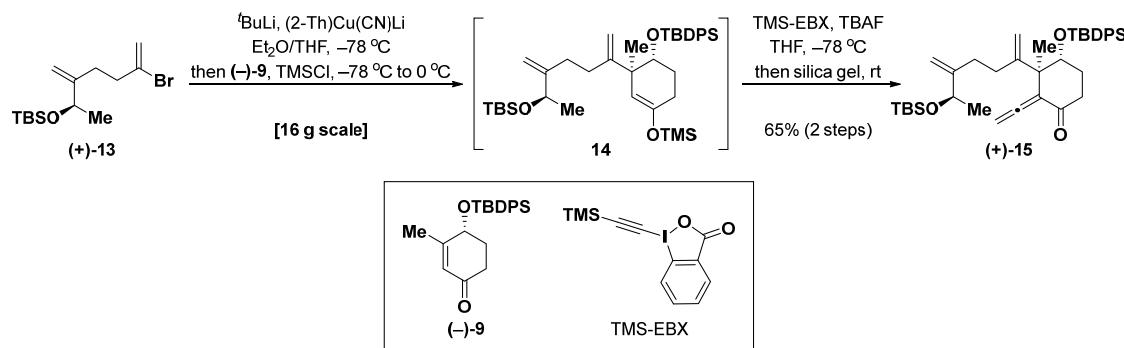
$[\alpha]_D^{33} = -2.3$ (c = 1.0, CHCl_3); [lit.^[6]: $[\alpha]_D^{25} = +4.7$ (c = 1.03, CHCl_3 , enantiomer, >99% ee)]

^1H NMR (400 MHz, CDCl_3) δ 7.75-7.65 (m, 4H), 7.51-7.36 (m, 6H), 5.80 (s, 1H), 4.35 (dd, J = 7.5, 4.7 Hz, 1H), 2.50 (ddd, J = 16.6, 6.4, 4.4 Hz, 1H), 2.13 (ddd, J = 16.2, 10.0, 5.1 Hz, 1H), 2.06-1.88 (m, 5H), 1.09 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 198.9, 163.8, 136.1, 133.8, 133.1, 130.2, 130.1, 128.0, 127.8, 126.9, 70.7, 34.9, 32.4, 27.1, 21.7, 19.6.

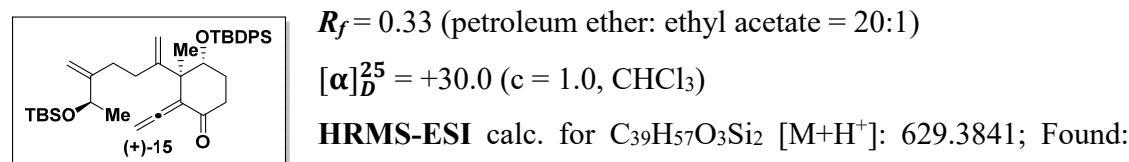
The characterization data were in agreement with literature values.^[6]

Synthesis of compound (+)-15



To a solution of compound (+)-13 (1.5 equiv, 66.6 mmol, 21.3 g) in Et₂O (80 mL) was added 'BuLi (3.0 equiv, 133 mmol, 103 mL of a 1.3 M solution in pentane) dropwise at -78 °C. After 20 min, (2-Th)Cu(CN)Li (1.5 equiv, 66.6 mmol, 267 mL of a 0.25 M solution in THF) was added dropwise. After 30 min, a solution of compound (-)-9 (1.0 equiv, 44.4 mmol, 16.2 g) in Et₂O (80 mL) and TMSCl (1.5 equiv, 66.6 mmol, 8.45 mL) were added dropwise. The resulting mixture was warmed to 0 °C over 1 h. Then NEt₃ (20 mL) and a mixture of ammonia and saturated NH₄Cl solution (1:1, 1 L) were added sequentially. The mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The crude product **14** (yellow oil) was used immediately in the next step without further purification.

To a solution of intermediate **14** and TMS-EBX^[7] (1.3 equiv, 57.8 mmol, 19.9 g) in THF (400 mL) at -78 °C was added TBAF (1.3 equiv, 57.8 mmol, 57.8 mL of a 1 M solution in THF). After being stirred at -78 °C for 2 h, the reaction was quenched with silica (200 g) and warmed to room temperature for 12 h. Then the solvent was removed *in vacuo* and the residue was purified by flash column chromatography to give compound (+)-**15** (18.1 g, 28.8 mmol, 65% yield for 2 steps) as a yellow oil.



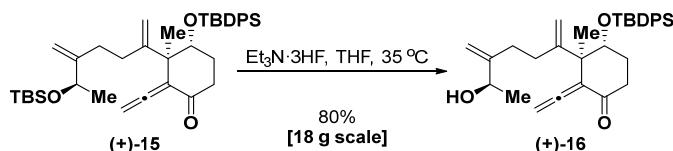
629.3828.

IR (neat, cm^{-1}): 2955, 2928, 2855, 1684, 1109, 1082.

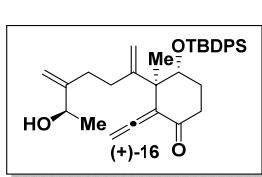
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.71-7.65 (m, 4H), 7.47-7.35 (m, 6H), 5.26 (d, $J = 13.9$ Hz, 1H), 5.19 (d, $J = 14.0$ Hz, 1H), 4.95 (s, 1H), 4.93 (s, 1H), 4.87 (s, 1H), 4.57 (s, 1H), 4.24 (dd, $J = 4.4, 2.2$ Hz, 1H), 4.17 (q, $J = 6.4$ Hz, 1H), 2.66 (ddd, $J = 18.3, 10.7, 8.0$ Hz, 1H), 2.28 (ddd, $J = 17.7, 6.0, 3.1$ Hz, 1H), 2.16-1.72 (m, 6H), 1.17 (d, $J = 6.3$ Hz, 3H), 1.10 (s, 3H), 1.07 (s, 9H), 0.86 (s, 9H), 0.02 (s, 3H), -0.01 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 212.2, 200.8, 153.1, 152.9, 136.2, 136.1, 134.0, 133.6, 130.1, 130.0, 127.8, 127.8, 112.5, 112.4, 108.2, 80.2, 72.2, 71.9, 51.8, 34.4, 29.7, 29.6, 27.2, 26.3, 26.0, 23.8, 23.3, 19.8, 18.4, -4.7, -4.8.

Synthesis of compound (+)-16



To a solution of compound (+)-15 (1.0 equiv, 28.8 mmol, 18.1 g) in THF (150 mL) was added $\text{Et}_3\text{N}\cdot 3\text{HF}$ (5.0 equiv, 144 mmol, 23.5 mL). After being stirred at 35 °C for 24 h, the reaction was quenched with saturated NaHCO_3 solution at 0 °C. The mixture was extracted with EtOAc . The combined organic layers were washed with brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give compound (+)-16 (11.8 g, 22.9 mmol, 80% yield) as a pale-yellow oil.



$R_f = 0.3$ (petroleum ether: ethyl acetate = 2:1)

$[\alpha]_D^{25} = +30.1$ ($c = 1.0$, CHCl_3)

HRMS-ESI calc. for $\text{C}_{33}\text{H}_{43}\text{O}_3\text{Si}$ [$\text{M}+\text{H}^+$]: 515.2976; Found: 515.2971.

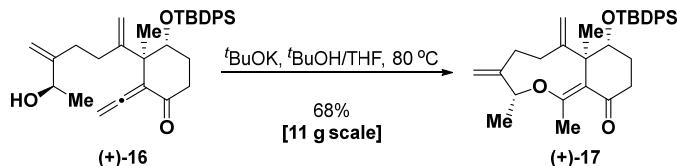
IR (neat, cm^{-1}): 2928, 2855, 1675, 1105, 1079.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.72-7.65 (m, 4H), 7.48-7.36 (m, 6H), 5.26 (d, $J = 13.9$ Hz, 1H), 5.19 (d, $J = 14.0$ Hz, 1H), 5.01 (s, 1H), 4.94 (s, 1H), 4.87 (s, 1H), 4.66 (s, 1H), 4.22 (dd, $J = 4.3, 2.4$ Hz, 1H), 4.19-4.15 (m, 1H), 2.67 (ddd, $J = 18.3, 10.5, 8.2$ Hz, 1H), 2.29 (ddd, $J = 17.7, 5.8, 3.6$ Hz, 1H), 2.15-2.01 (m, 2H), 1.97-1.77 (m, 4H), 1.40 (d, $J = 4.2$ Hz,

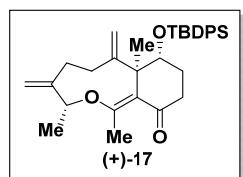
1H), 1.24 (d, J = 6.4 Hz, 3H), 1.10 (s, 3H), 1.07 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 212.2, 200.8, 152.9, 152.8, 136.2, 136.2, 134.0, 133.6, 130.1, 130.0, 127.8, 127.8, 112.7, 112.3, 108.8, 80.2, 71.9, 71.1, 51.7, 34.5, 30.6, 29.8, 27.2, 26.3, 23.3, 22.4, 19.8.

Synthesis of compound (+)-17



To a solution of *t*BuOK (2.0 equiv, 45.8 mmol, 5.14 g) in *t*BuOH (750 mL) at 80 °C was added a solution of compound (+)-**16** (1.0 equiv, 22.9 mmol, 11.8 g) in THF (60 mL) over 30 min. After being stirred at 80 °C for another 10 min, the reaction was cooled to room temperature and filtered through a short silica column. The filtrate was concentrated *in vacuo*. The residue was purified by flash column chromatography to give compound (+)-**17** (8.00 g, 15.5 mmol, 68% yield) as a white solid.



$R_f = 0.5$ (petroleum ether: ethyl acetate = 5:1)

$$[\alpha]_D^{25} = +51.6 \text{ (c = 1.0, CHCl}_3\text{)}$$

Melting point: 64-65 °C

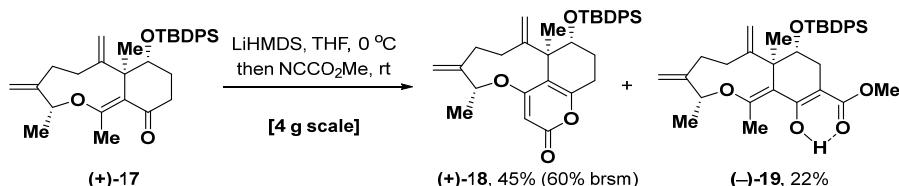
HRMS-ESI calc. for C₃₃H₄₃O₃Si [M+H⁺]: 515.2976; Found:

IR (neat, cm⁻¹): 2930, 2855, 1663, 1109, 1065.

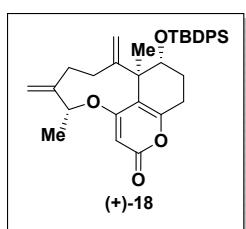
¹H NMR (400 MHz, CDCl₃) δ 7.71-7.66 (m, 4H), 7.42-7.34 (m, 6H), 5.17 (s, 1H), 5.02 (s, 1H), 4.86-4.80 (m, 3H), 3.62 (dd, *J* = 10.7, 3.6 Hz, 1H), 2.53 (t, *J* = 12.9, 1H), 2.32-2.22 (m, 2H), 2.17 (s, 3H), 2.13-2.08 (m, 1H), 2.00 (ddd, *J* = 16.8, 11.1, 7.1 Hz, 1H), 1.86 (dtd, *J* = 13.1, 10.9, 6.0 Hz, 1H), 1.70 (t, *J* = 13.1 Hz, 1H), 1.62 (ddt, *J* = 13.0, 7.3, 3.6 Hz, 1H), 1.45 (s, 3H), 1.37 (d, *J* = 6.4 Hz, 3H), 1.02 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 201.7, 165.8, 154.3, 151.1, 136.1, 136.1, 135.1, 133.5, 129.8, 129.6, 127.7, 127.4, 124.8, 116.1, 110.5, 78.2, 73.0, 51.9, 38.6, 33.8, 31.5, 27.7, 27.1, 19.7, 19.6, 18.2, 17.6.

Synthesis of compounds (+)-18 and (-)-19



To a solution of compound (+)-17 (1.0 equiv, 7.77 mmol, 4.0 g) in THF (80 mL) at 0 °C was added LiHMDS (1.1 equiv, 8.55 mmol, 8.55 mL of a 1 M solution in THF). The mixture was stirred at the same temperature for 30 min. Then NCCO₂Me (1.5 equiv, 11.7 mmol, 925 µL) was added dropwise. After being stirred at room temperature for 2 h, the reaction was quenched with saturated NaHCO₃ solution at 0 °C, and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give compound (+)-18 (1.88 g, 3.48 mmol, 45% yield, 60% brsm) as a white solid, and compound (-)-19 (1.00 g, 1.75 mmol, 22% yield) as a white solid. Compound (+)-17 (1.03 g, 2.00 mmol, 26% yield) was recovered.



R_f = 0.2 (petroleum ether: ethyl acetate = 5:1)

[α]_D²⁵ = +56.2 (c = 1.0, CHCl₃)

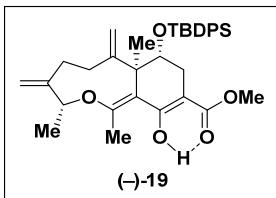
Melting point: 156-158 °C

HRMS-ESI (m/z) calc. for C₃₄H₄₁O₄Si [M+H⁺]: 541.2769; Found: 541.2766.

IR (neat, cm⁻¹): 3070, 2931, 2856, 1718, 1557, 1427, 1110, 1062.

¹H NMR (400 MHz, CDCl₃) δ 7.68-7.65 (m, 4H), 7.44-7.34 (m, 6H), 5.45 (s, 1H), 5.28 (s, 1H), 5.09 (s, 1H), 4.88 (s, 1H), 4.83-4.80 (m, 2H), 3.44 (dd, *J* = 11.9, 3.6 Hz, 1H), 2.49 (t, *J* = 13.0 Hz, 1H), 2.38 (dd, *J* = 18.9, 6.1 Hz, 1H), 2.28-2.12 (m, 2H), 1.96-1.81 (m, 2H), 1.68-1.62 (m, 1H), 1.51 (s, 3H), 1.46 (d, *J* = 6.4 Hz, 3H), 1.25-1.15 (m, 1H), 1.02 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 169.6, 164.4, 159.5, 151.6, 146.5, 136.1, 134.8, 133.1, 129.9, 129.7, 127.7, 127.5, 118.7, 116.2, 112.0, 96.4, 81.9, 71.4, 47.2, 33.5, 30.3, 27.1, 27.0, 26.5, 19.7, 19.1, 18.9.



Enol form: keto form ~ 3:1 in pyridine-*d*₅

*R*_f = 0.7 (petroleum ether: ethyl acetate = 5:1)

[α]_D²⁷ = -88.8 (c = 1.0, CHCl₃)

Melting point: 120-124 °C

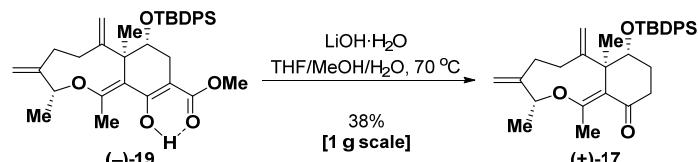
HRMS-ESI (m/z) calc. for C₃₅H₄₅O₅Si [M+H⁺]: 573.3031; Found: 573.3027.

IR (neat, cm⁻¹): 2943, 2857, 1637, 1605, 1439, 1371, 1277, 1226, 1110, 1064, 1024.

Enol form: ¹**H NMR** (400 MHz, Pyridine-*d*₅) δ 13.44 (s, 1H), 7.96-7.82 (m, 4H), 7.54-7.45 (m, 6H), 5.34 (s, 1H), 5.10 (s, 1H), 4.92 (s, 1H), 4.90-4.81 (m, 2H), 3.78 (dd, *J* = 10.7, 4.9 Hz, 1H), 3.50 (s, 3H), 2.69-2.57 (m, 2H), 2.43-2.37 (m, 4H), 2.33-2.22 (m, 2H), 2.16-2.11 (m, 1H), 1.77 (t, *J* = 13.5 Hz, 1H), 1.65-1.60 (m, 4H), 1.40 (d, *J* = 6.4 Hz, 3H), 1.17 (s, 9H).

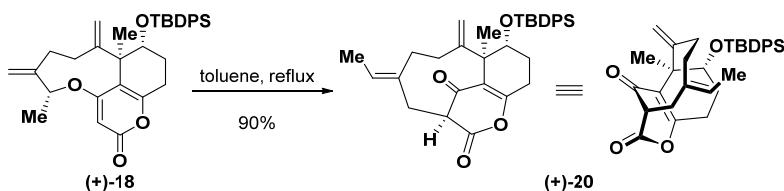
Enol form: ¹³**C NMR** (100 MHz, Pyridine-*d*₅) δ 173.8, 168.8, 161.7, 154.4, 151.8, 137.0, 135.9, 134.7, 130.6, 130.5, 128.5, 128.4, 119.9, 116.9, 110.7, 94.2, 78.8, 71.1, 51.9, 51.2, 34.0, 31.7, 29.3, 27.7, 20.2, 19.9, 19.7, 16.7.

Hydrolytic decarboxylation of compound (-)-19

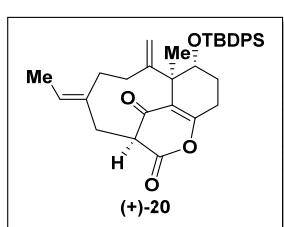


To a solution of compound (-)-19 (1.0 equiv, 1.73 mmol, 991 mg) in THF/MeOH/H₂O (2:2:1, 62.5 mL) was added LiOH·H₂O (10.0 equiv, 17.3 mmol, 727 mg). After being stirred at 70 °C for 2.5 h, the reaction was cooled to room temperature, diluted with water, and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give compound (+)-17 (337 mg, 0.655 mmol, 38% yield).

Synthesis of compound (+)-20



Compound (+)-**18** (1.0 equiv, 38.8 μmol , 21.0 mg) was dissolved in toluene (2 mL). The solution was then heated to reflux and stirred for 0.5 h. After cooling to room temperature, toluene was removed *in vacuo*. The residue was purified by flash column chromatography to give compound (+)-**20** (18.9 mg, 34.9 μmol , 90% yield) as a white solid.



$R_f = 0.5$ (petroleum ether: ethyl acetate = 5:1)

$$[\alpha]_D^{22} = +5.1 \text{ (c = 1.0, CHCl}_3\text{)}$$

Melting point: 44-46 °C

HRMS-ESI (m/z) calc. for C₃₄H₄₁O₄Si [M+H⁺]: 541.2769;

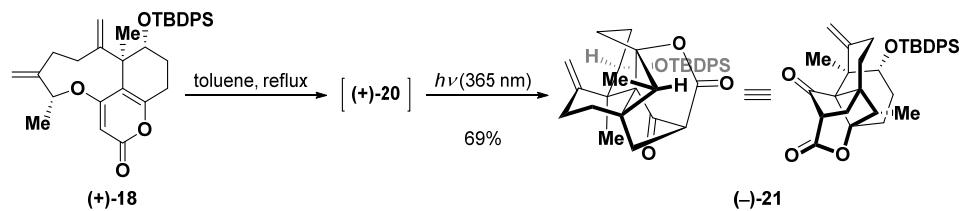
Found: 541.2768.

IR (neat, cm⁻¹): 2929, 2856, 1781, 1682, 1641, 1383, 1105.

¹H NMR (500 MHz, CDCl₃) δ 7.67-7.63 (m, 4H), 7.45-7.41 (m, 2H), 7.39-7.35 (m, 4H), 5.27 (q, *J* = 6.4 Hz, 1H), 5.22 (s, 1H), 5.05 (s, 1H), 3.62 (dd, *J* = 11.8, 3.4 Hz, 1H), 3.43 (dd, *J* = 7.0, 3.5 Hz, 1H), 2.68-2.63 (m, 2H), 2.55 (dd, *J* = 13.0, 7.0 Hz, 1H), 2.24 (ddd, *J* = 19.3, 5.3, 1.9 Hz, 1H), 2.04-1.97 (m, 2H), 1.81 (qd, *J* = 12.1, 5.3 Hz, 1H), 1.67-1.62 (m, 4H), 1.43-1.37 (m, 5H), 1.02 (s, 9H).

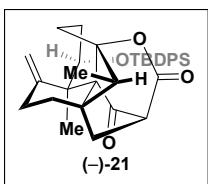
¹³C NMR (125 MHz, CDCl₃) δ 192.9, 169.4, 164.0, 151.4, 136.5, 136.3, 136.1, 134.8, 132.9, 130.0, 129.7, 127.7, 127.5, 125.5, 118.9, 115.8, 72.2, 55.5, 46.8, 44.9, 35.0, 32.2, 27.7, 27.1, 26.2, 19.6, 17.2, 14.5.

Synthesis of compound (-)-21



Compound (+)-**18** (1.0 equiv, 0.801 mmol, 433 mg) was dissolved in toluene (45 mL). The solution was then heated to reflux and stirred for 2 h. After cooling to room temperature,

the solution was bubbled by N₂ balloon for 25 min. Then the solution was stirred and irradiated at 365 nm (5 W) for 2 h. After the completion of the reaction, toluene was removed *in vacuo* and the residue was purified by flash column chromatography to give compound (-)-21 (299 mg, 0.553 mmol, 69% yield) as a white solid.



R_f = 0.4 (petroleum ether: ethyl acetate = 5:1)

$[\alpha]_D^{25} = -75.8$ (c = 1.0, CHCl₃)

Melting point: 83-85 °C

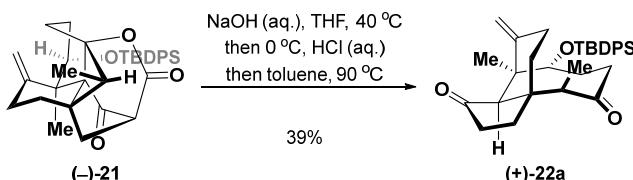
HRMS-ESI (m/z) calc. for C₃₄H₄₁O₄Si [M+H⁺]: 541.2769; Found: 541.2768.

IR (neat, cm⁻¹): 3071, 2930, 2856, 1766, 1737, 1472, 1427, 1110, 1085.

¹H NMR (400 MHz, CDCl₃) δ 7.75-7.68 (m, 4H), 7.45-7.36 (m, 6H), 5.06 (d, *J* = 1.9 Hz, 1H), 5.02 (t, *J* = 1.2 Hz, 1H), 3.89 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.36 (dd, *J* = 5.1, 2.1 Hz, 1H), 2.26-2.18 (m, 2H), 2.13-2.01 (m, 3H), 1.96-1.87 (m, 1H), 1.83-1.63 (m, 6H), 1.34-1.26 (m, 1H), 1.13-1.06 (m, 1H), 1.03 (s, 9H), 0.68 (d, *J* = 7.9 Hz, 3H).

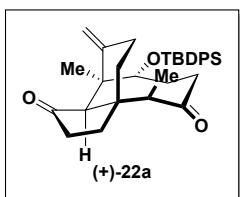
¹³C NMR (100 MHz, CDCl₃) δ 204.5, 172.0, 144.6, 136.4, 136.3, 134.5, 133.5, 130.0, 129.8, 127.8, 127.6, 115.1, 82.4, 70.8, 56.4, 54.4, 52.5, 41.8, 41.5, 40.4, 27.3, 27.3, 26.1, 24.5, 24.2, 19.7, 16.6, 9.6.

Synthesis of compound (+)-22a



To a solution of compound (-)-21 (1.0 equiv, 1.18 mmol, 637 mg) in THF (12 mL) was added NaOH solution (2.0 equiv, 2.36 mmol, 4.71 mL of a 0.5 M solution in water). The mixture was stirred at 40 °C for 10 min. After cooling to 0 °C, HCl solution (2.0 equiv, 2.36 mmol, 2.36 mL of a 1 M solution in water) and toluene (12 mL) were added. Then the mixture was stirred at 90 °C for 1 h. After cooling to room temperature, the mixture was diluted with water and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give compound (+)-22a (234 mg, 0.455 mmol, 39%

yield) as a white solid.



R_f = 0.3 (petroleum ether: ethyl acetate = 5:1)

$[\alpha]_D^{25} = +149.6$ ($c = 1.0$, CHCl₃)

Melting point: 131-133 °C

HRMS-ESI (m/z) calc. for C₃₃H₄₃O₃Si [M+H⁺]: 515.2976; Found:

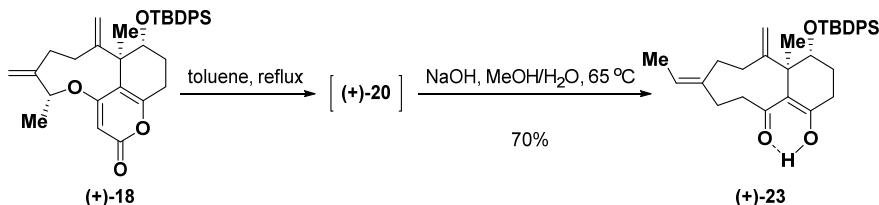
515.2967.

IR (neat, cm⁻¹): 3069, 2931, 2856, 1735, 1697, 1471, 1426, 1104, 1056.

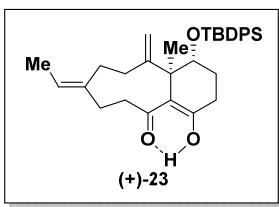
¹H NMR (600 MHz, CDCl₃) δ 7.72-7.69 (m, 2H), 7.64-7.61 (m, 2H), 7.47-7.39 (m, 4H), 7.37-7.34 (m, 2H), 4.74 (s, 1H), 4.68 (s, 1H), 3.90 (dd, $J = 9.3, 2.5$ Hz, 1H), 2.65-2.59 (m, 2H), 2.55 (q, $J = 6.8$ Hz, 1H), 2.36-2.28 (m, 1H), 2.18-1.91 (m, 7H), 1.70-1.62 (m, 1H), 1.57-1.51 (m, 1H), 1.48 (s, 3H), 1.33-1.29 (m, 1H), 1.04 (s, 9H), 0.93 (d, $J = 6.8$ Hz, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 217.5, 214.7, 147.9, 136.4, 136.3, 134.9, 133.2, 129.9, 129.6, 127.8, 127.5, 111.3, 74.1, 59.8, 57.2, 47.6, 44.2, 39.0, 38.9, 38.2, 30.4, 29.4, 28.2, 27.2, 19.7, 10.7.

Synthesis of compound (+)-23



Compound (+)-18 (1.0 equiv, 0.386 mmol, 209 mg) was dissolved in toluene (25 mL). The solution was then heated to reflux and stirred for 1.5 h. After the solution was cooled to room temperature, toluene was removed *in vacuo*. The residue was dissolved in MeOH (10 mL), and then NaOH solution (1.2 equiv, 0.464 mmol, 928 μL of a 0.5 M solution in water) was added. The reaction was stirred at 65 °C for 12 h. Then the reaction was cooled to 0 °C, and HCl solution (1.2 equiv, 0.464 mmol, 464 μL of a 1 M solution in water) was added. The mixture was diluted with saturated NaCl solution, and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give compound (+)-23 (139 mg, 0.270 mmol, 70% yield) as a white solid.



R_f = 0.6 (petroleum ether: ethyl acetate = 5:1)

$[\alpha]_D^{23} = +191.3$ ($c = 1.0$, CHCl₃)

Melting point: 38-39 °C

HRMS-ESI (m/z) calc. for C₃₃H₄₃O₃Si [M+H⁺]: 515.2976;

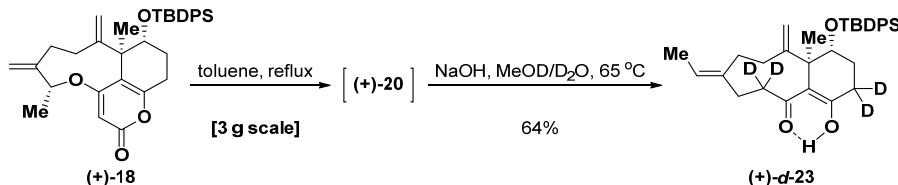
Found: 515.2973.

IR (neat, cm⁻¹): 2932, 2856, 1544, 1427, 1110.

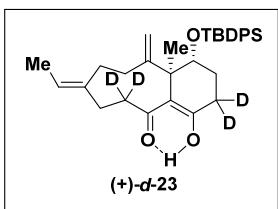
¹H NMR (400 MHz, CDCl₃) δ 17.88 (s, 1H), 7.70-7.66 (m, 4H), 7.46-7.41 (m, 2H), 7.40-7.35 (m, 4H), 5.34 (s, 1H), 5.25 (q, $J = 6.8$ Hz, 1H), 5.07 (s, 1H), 3.61 (dd, $J = 11.9, 3.6$ Hz, 1H), 3.38 (td, $J = 12.4, 4.0$ Hz, 1H), 2.48 (td, $J = 12.8, 4.7$ Hz, 1H), 2.33 (ddd, $J = 13.4, 9.7, 3.3$ Hz, 1H), 2.24-2.17 (m, 2H), 2.16-1.94 (m, 4H), 1.78 (qd, $J = 12.5, 5.9$ Hz, 1H), 1.62-1.52 (m, 2H), 1.51-1.49 (m, 6H), 1.01 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 202.0, 187.7, 153.3, 138.2, 136.1, 136.1, 135.0, 133.2, 129.9, 129.6, 127.7, 127.5, 122.0, 116.3, 114.3, 72.6, 47.7, 38.4, 34.1, 32.3, 31.8, 31.7, 27.0, 25.9, 21.1, 19.7, 13.4.

Synthesis of compound (+)-d-23



Compound (+)-18 (1.0 equiv, 5.55 mmol, 3.0 g) was dissolved in toluene (140 mL). The solution was then heated to reflux and stirred for 2 h. After cooling to room temperature, toluene was removed *in vacuo*. Then the residue was dissolved in MeOD (100 mL) and NaOH solution (1.2 equiv, 6.66 mmol, 13.3 mL of a 0.5 M solution in D₂O) was added. The reaction was stirred at 65 °C for 9.5 h. Then the reaction was cooled to 0 °C, and HCl solution (1.2 equiv, 6.66 mmol, 6.7 mL of a 1 M solution in D₂O) was added. The mixture was diluted with saturated NaCl solution, and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography to give compound (+)-d-23 (1.84 g, 3.55 mmol, 64% yield) as a white solid.



R_f = 0.6 (petroleum ether: ethyl acetate = 5:1)

$[\alpha]_D^{21} = +170.0$ ($c = 1.0$, CHCl₃)

Melting point: 40-42 °C

HRMS-ESI (m/z) calc. for C₃₃H₃₉D₄O₃Si [M+H⁺]: 519.3227;

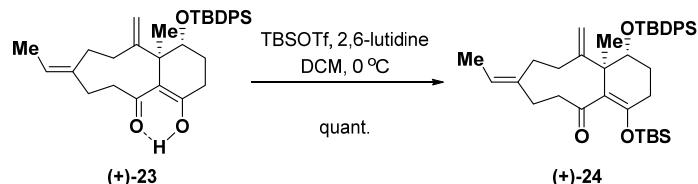
Found: 519.3237.

IR (neat, cm⁻¹): 2932, 2856, 1534, 1427, 1111, 1066.

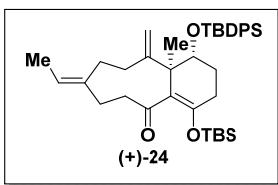
¹H NMR (400 MHz, CDCl₃) δ 17.87 (s, 1H), 7.70-7.66 (m, 4H), 7.47-7.33 (m, 6H), 5.34 (s, 1H), 5.25 (q, $J = 6.8$ Hz, 1H), 5.07 (s, 1H), 3.62 (dd, $J = 12.0, 3.6$ Hz, 1H), 2.48 (d, $J = 13.2$ Hz, 1H), 2.33 (ddd, $J = 13.4, 9.6, 3.4$ Hz, 1H), 2.20 (d, $J = 13.2$ Hz, 1H), 2.12 (ddd, $J = 13.4, 9.5, 3.9$ Hz, 1H), 1.99 (ddd, $J = 13.6, 7.6, 4.0$ Hz, 1H), 1.77 (t, $J = 12.5$ Hz, 1H), 1.62-1.53 (m, 2H), 1.51-1.50 (m, 6H), 1.02 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 202.1, 187.6, 153.3, 138.2, 136.1, 136.1, 135.0, 133.2, 129.9, 129.6, 127.7, 127.5, 122.0, 116.3, 114.3, 72.6, 47.7, 38.3, 32.3, 31.7, 27.0, 25.7, 21.1, 19.7, 13.4. The carbon atoms ($\delta = 34.1, 31.8$ ppm in **23**) directly attached to the deuterium atoms were not detected.

Synthesis of compound (+)-24



To a solution of compound (+)-23 (1.0 equiv, 0.503 mmol, 259 mg) and 2,6-lutidine (2.1 equiv, 1.06 mmol, 123 μL) in DCM (20 mL) at 0 °C was added TBSOTf (1.4 equiv, 0.704 mmol, 162 μL). After being stirred at 0 °C for 30 min, the reaction was quenched with saturated NaHCO₃ solution, and extracted with DCM. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give compound (+)-24 (316 mg, 0.502 mmol, quant.) as a white solid.



R_f = 0.62 (petroleum ether: ethyl acetate = 5:1)

$[\alpha]_D^{24} = +77.0$ ($c = 1.0$, CHCl₃)

Melting point: 98-99 °C

HRMS-ESI (m/z) calc. for C₃₉H₅₇O₃Si₂ [M+H⁺]: 629.3841;

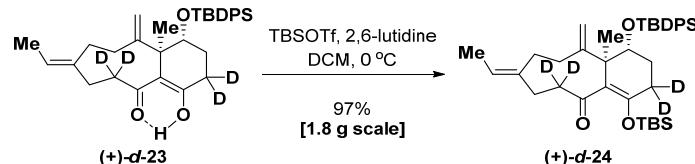
Found: 629.3843.

IR (neat, cm⁻¹): 2953, 2930, 2857, 1676, 1642, 1472, 1427, 1372, 1255, 1110, 1052.

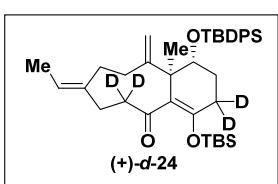
¹H NMR (400 MHz, CDCl₃) δ 7.70-7.64 (m, 4H), 7.46-7.33 (m, 6H), 5.22 (q, $J = 6.7$ Hz, 1H), 5.08 (s, 1H), 4.94 (s, 1H), 3.77 (dd, $J = 11.4, 3.7$ Hz, 1H), 2.93-2.83 (m, 1H), 2.36 (ddd, $J = 13.9, 8.3, 5.7$ Hz, 1H), 2.30-2.20 (m, 3H), 2.08-1.79 (m, 6H), 1.59-1.55 (m, 4H), 1.51 (d, $J = 6.7$ Hz, 3H), 1.01 (s, 9H), 0.84 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 208.4, 151.3, 150.7, 139.4, 136.2, 136.1, 135.3, 133.7, 129.8, 129.6, 127.6, 127.5, 125.2, 120.9, 114.4, 72.1, 49.5, 45.9, 32.8, 30.1, 29.8, 29.5, 27.3, 27.0, 25.8, 20.3, 19.6, 18.3, 13.6, -3.2, -3.5.

Synthesis of compound (+)-d-24



To a solution of compound (+)-d-23 (1.0 equiv, 3.55 mmol, 1.84 g) and 2,6-lutidine (2.1 equiv, 7.45 mmol, 868 μL) in DCM (50 mL) at 0 °C was added TBSOTf (1.4 equiv, 4.97 mmol, 1.14 mL). After being stirred at 0 °C for 30 min, the reaction was quenched with saturated NaHCO₃ solution, and extracted with DCM. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography to give compound (+)-d-24 (2.18 g, 3.44 mmol, 97% yield) as a white solid.



R_f = 0.62 (petroleum ether: ethyl acetate = 5:1)

$[\alpha]_D^{22} = +73.6$ ($c = 1.0$, CHCl₃)

Melting point: 107-109 °C

HRMS-ESI (m/z) calc. for C₃₉H₅₃D₄O₃Si₂ [M+H⁺]: 633.4092;

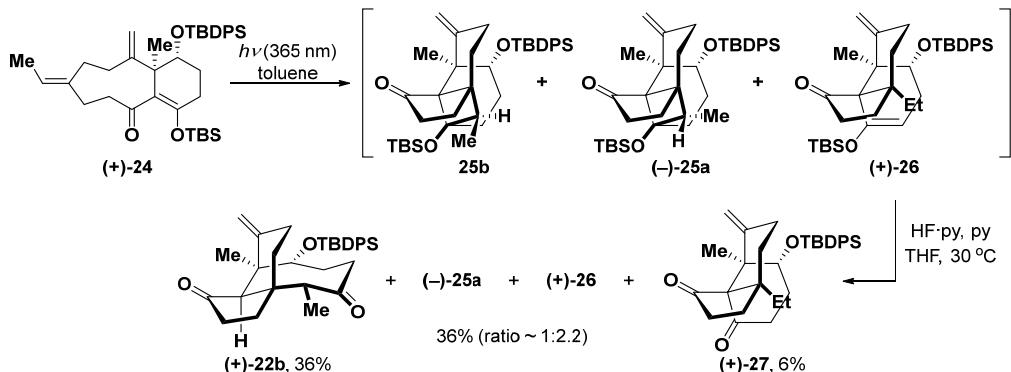
Found: 633.4090.

IR (neat, cm⁻¹): 2954, 2930, 2857, 1675, 1314, 1255, 1111, 1062.

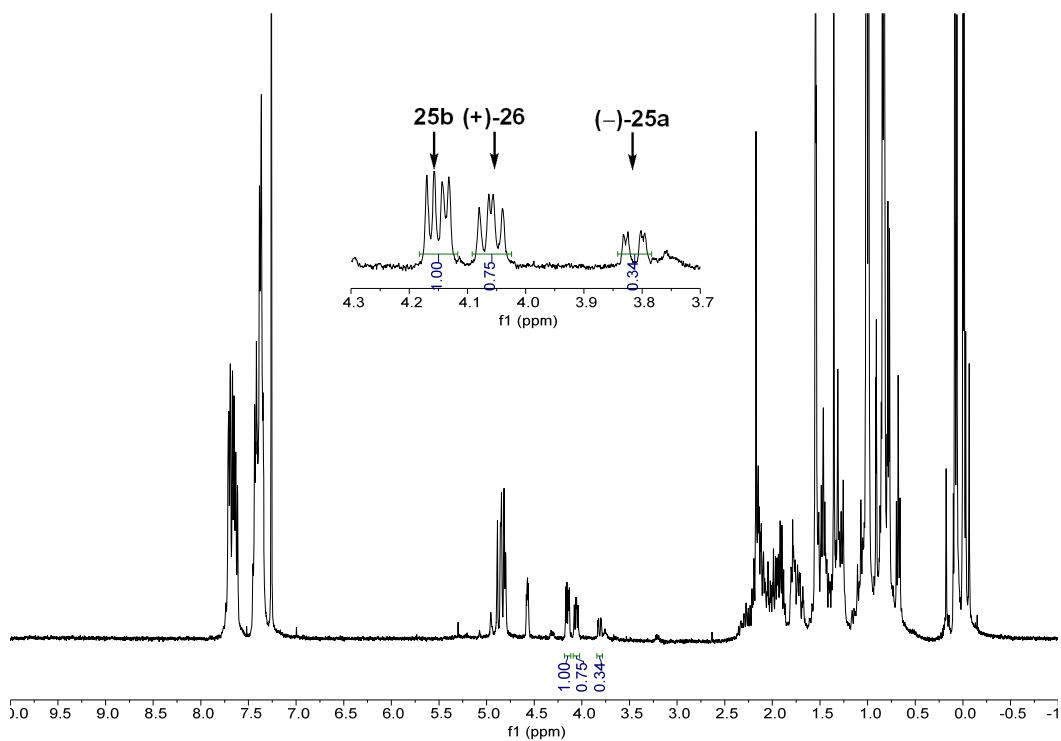
¹H NMR (400 MHz, CDCl₃) δ 7.70-7.64 (m, 4H), 7.48-7.34 (m, 6H), 5.22 (q, *J* = 6.7 Hz, 1H), 5.08 (s, 1H), 4.95 (s, 1H), 3.77 (dd, *J* = 11.7, 3.8 Hz, 1H), 2.33-2.20 (m, 3H), 2.04 (ddd, *J* = 13.9, 8.3, 4.2 Hz, 1H), 1.99-1.79 (m, 3H), 1.58-1.53 (m, 4H), 1.51 (d, *J* = 6.7 Hz, 3H), 1.01 (s, 9H), 0.84 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 208.4, 151.3, 150.7, 139.3, 136.2, 136.1, 135.3, 133.7, 129.8, 129.6, 127.6, 127.5, 125.3, 120.9, 114.4, 72.1, 49.5, 32.6, 30.1, 29.8, 27.1, 27.0, 25.8, 20.3, 19.6, 18.3, 13.6, -3.3, -3.6. The carbon atoms (δ = 45.9, 29.5 ppm in **24**) directly attached to the deuterium atoms were not detected.

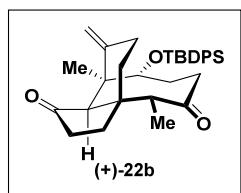
Syntheses of compounds (+)-22b, (-)-25a, (+)-26 and (+)-27



Compound **(+)-24** (1.0 equiv, 0.318 mmol, 200 mg) was dissolved in toluene (8 mL). The solution was bubbled by N₂ balloon for 25 min, and then was stirred and irradiated at 365 nm (10 W) for 24 h. After the completion of the reaction, toluene was removed *in vacuo* and the residue was dissolved in THF (6 mL). Pyridine (7.5 equiv, 2.38 mmol, 193 μ L) was added, followed by HF·py (30 equiv, 9.54 mmol, 859 μ L) at 0 °C. The reaction was stirred at 30 °C for 33 h before it was quenched with saturated NaHCO₃ solution at 0 °C, which was then extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give compound **(+)-22b** (58.7 mg, 0.114 mmol, 36% yield) as a white solid, **(+)-27** (9.2 mg, 0.0179 mmol, 6% yield) as a colorless oil, and a mixture of **(-)-25a** and **(+)-26** (71.1 mg, ~1:2.2, 36% combined). The pure samples of **(-)-25a** and **(+)-26** could be obtained by prep-TLC.



^1H NMR spectrum of the crude products after irradiation for 24 h



$R_f = 0.3$ (petroleum ether: ethyl acetate = 5:1)

$[\alpha]_D^{31} = +52.9$ ($c = 1.0$, CHCl_3)

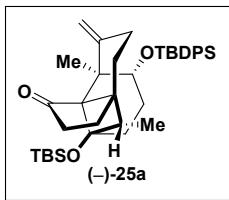
Melting point: 54-56 °C

HRMS-ESI (m/z) calc. for $\text{C}_{33}\text{H}_{43}\text{O}_3\text{Si}$ [$\text{M}+\text{H}^+$]: 515.2976; Found: 515.2974.

IR (neat, cm^{-1}): 2920, 2847, 1734, 1695, 1211, 1098.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.75-7.70 (m, 4H), 7.48-7.36 (m, 6H), 5.04-4.99 (m, 2H), 4.59 (d, $J = 7.7$ Hz, 1H), 2.79 (q, $J = 6.7$ Hz, 1H), 2.31 (td, $J = 14.3, 4.7$ Hz, 1H), 2.10 (q, $J = 3.4, 2.7$ Hz, 1H), 2.08-2.00 (m, 3H), 1.95-1.84 (m, 1H), 1.76 (dt, $J = 11.8, 3.8$ Hz, 1H), 1.65 (s, 3H), 1.62-1.55 (m, 3H), 1.40-1.34 (m, 1H), 1.25-1.13 (m, 2H), 1.01 (s, 9H), 0.91 (d, $J = 6.7$ Hz, 3H).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 216.1, 215.6, 147.8, 136.4, 136.2, 134.8, 133.7, 130.1, 129.9, 127.8, 127.8, 113.0, 73.4, 59.2, 47.3, 46.9, 45.3, 44.7, 34.4, 31.1, 30.3, 28.8, 26.9, 24.7, 19.8, 13.1, 11.7.



R_f = 0.64 (petroleum ether: ethyl acetate = 5:1)

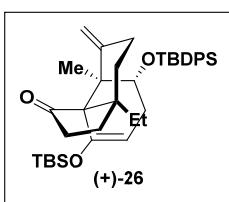
$[\alpha]_D^{31} = -9.6$ (c = 1.0, CHCl₃)

HRMS-ESI (m/z) calc. for C₃₉H₅₇O₃Si₂ [M+H⁺]: 629.3841; Found: 629.3844.

IR (neat, cm⁻¹): 2952, 2930, 2856, 1734, 1472, 1256, 1217, 1111, 1078.

¹H NMR (400 MHz, CDCl₃) δ 7.71-7.62 (m, 4H), 7.47-7.33 (m, 6H), 4.81-4.80 (m, 2H), 3.82 (dd, *J* = 11.6, 2.9 Hz, 1H), 2.36-2.26 (m, 2H), 2.17 (ddd, *J* = 19.6, 10.4, 2.5 Hz, 1H), 2.11-2.02 (m, 1H), 1.95 (q, *J* = 7.1 Hz, 1H), 1.79 (qd, *J* = 12.5, 3.3 Hz, 1H), 1.62-1.36 (m, 5H), 1.32 (s, 3H), 1.30-1.24 (m, 2H), 1.01 (s, 9H), 0.85 (s, 9H), 0.79 (d, *J* = 7.1 Hz, 3H), -0.06 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 216.8, 149.6, 136.2, 136.1, 135.4, 133.8, 129.8, 129.6, 127.6, 127.5, 111.5, 75.6, 75.2, 64.5, 46.9, 43.8, 42.6, 39.1, 33.8, 29.1, 27.3, 27.0, 25.9, 25.8, 23.4, 19.5, 18.0, 14.9, 8.3, -2.4, -2.6.



R_f = 0.66 (petroleum ether: ethyl acetate = 5:1)

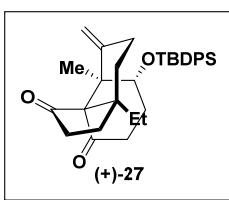
$[\alpha]_D^{22} = +130.0$ (c = 1.0, CHCl₃)

HRMS-ESI (m/z) calc. for C₃₉H₅₇O₃Si₂ [M+H⁺]: 629.3841; Found: 629.3839.

IR (neat, cm⁻¹): 2931, 2857, 1742, 1662, 1472, 1427, 1254, 1216, 1208, 1172, 1096, 1077.

¹H NMR (400 MHz, CDCl₃) δ 7.75-7.67 (m, 2H), 7.66-7.60 (m, 2H), 7.48-7.32 (m, 6H), 4.90 (d, *J* = 1.2 Hz, 1H), 4.86 (s, 1H), 4.58 (dd, *J* = 5.1, 2.8 Hz, 1H), 4.07 (dd, *J* = 9.6, 6.5 Hz, 1H), 2.23-2.04 (m, 3H), 1.91 (ddd, *J* = 16.8, 6.5, 5.1 Hz, 1H), 1.83-1.66 (m, 4H), 1.55 (s, 3H), 1.35-1.24 (m, 2H), 1.17-1.04 (m, 2H), 1.00 (s, 9H), 0.83 (s, 9H), 0.69 (t, *J* = 7.3 Hz, 3H), 0.09 (s, 3H), 0.07 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 218.7, 150.6, 149.5, 136.4, 136.2, 135.3, 133.7, 129.8, 129.5, 127.6, 127.4, 111.4, 102.8, 68.5, 66.7, 47.7, 47.3, 37.8, 33.5, 31.1, 31.0, 29.0, 28.6, 27.0, 26.1, 19.5, 18.4, 13.4, 8.7, -4.2, -4.5.



R_f = 0.45 (petroleum ether: ethyl acetate = 5:1)

$[\alpha]_D^{30} = +100.5$ (c = 1.0, CHCl₃)

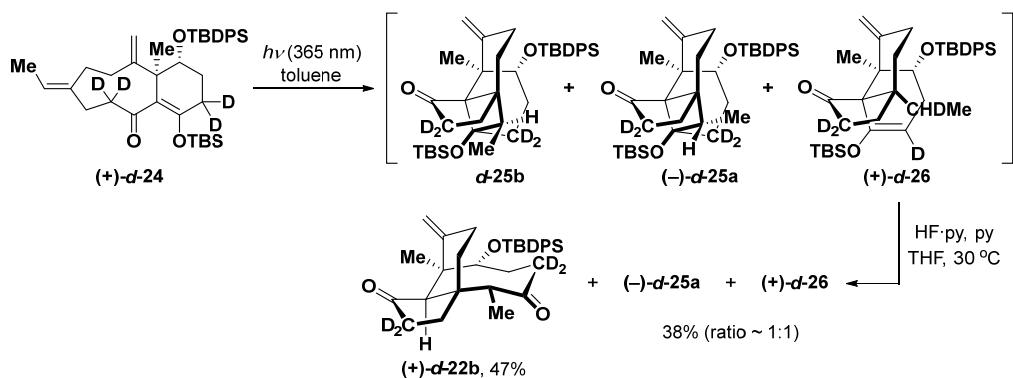
HRMS-ESI (m/z) calc. for C₃₃H₄₃O₃Si [M+H⁺]: 515.2976; Found: 515.2977.

IR (neat, cm⁻¹): 2932, 1355, 1188, 1173, 1096.

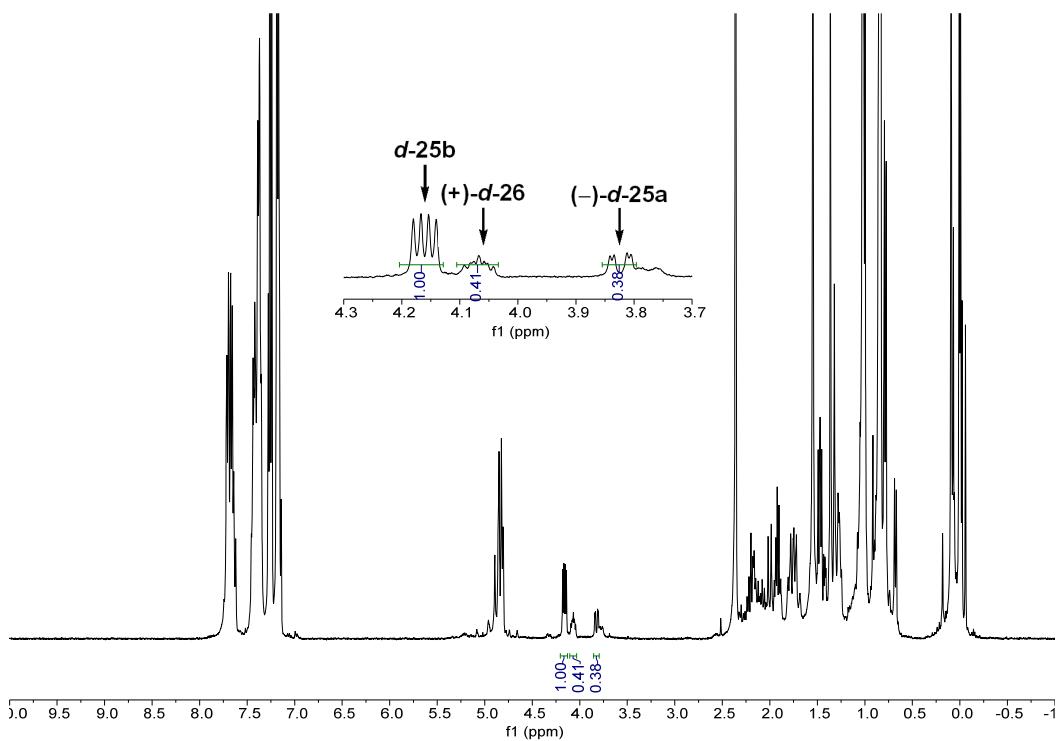
¹H NMR (400 MHz, CDCl₃) δ 7.79-7.72 (m, 2H), 7.68-7.60 (m, 2H), 7.50-7.35 (m, 6H), 4.93 (s, 1H), 4.92 (s, 1H), 4.36 (dd, *J* = 11.3, 5.1 Hz, 1H), 2.43-2.27 (m, 2H), 2.18-1.94 (m, 3H), 1.93-1.78 (m, 2H), 1.77-1.68 (m, 2H), 1.61 (s, 3H), 1.56-1.31 (m, 3H), 1.07-0.97 (m, 11H), 0.71 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 215.3, 211.4, 147.9, 136.4, 136.1, 135.0, 133.4, 130.1, 129.7, 127.8, 127.5, 112.5, 75.3, 69.0, 48.7, 48.3, 40.3, 36.1, 31.4, 30.3, 29.6, 28.6, 28.3, 27.0, 19.5, 15.4, 8.7.

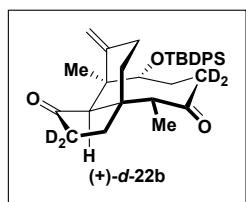
Synthesis of compounds (+)-d-22b, (-)-d-25a and (+)-d-26



Compound (+)-d-24 (1.0 equiv, 0.790 mmol, 500 mg) was dissolved in toluene (20 mL). The solution was bubbled by N₂ balloon for 25 min, and then was stirred and irradiated at 365 nm (10 W) for 24 h. After the completion of the reaction, toluene was removed *in vacuo* and the residue was dissolved in THF (15 mL). Pyridine (7.5 equiv, 5.92 mmol, 479 µL) was added, followed by HF·py (30.0 equiv, 23.7 mmol, 2.13 mL) at 0 °C. The reaction was stirred at 30 °C for 32 h before it was quenched with saturated NaHCO₃ solution at 0 °C, which was then extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give compound (+)-d-22b (192 mg, 0.370 mmol, 47% yield) as a white solid, combined with a mixture of (-)-d-25a and (+)-d-26 (189 mg, ~1:1, 38% combined). The pure samples of (-)-d-25a and (+)-d-26 could be obtained by prep-TLC.



^1H NMR spectrum of the crude products after irradiation for 24 h



$R_f = 0.3$ (petroleum ether: ethyl acetate = 5:1)

$[\alpha]_D^{21} = +57.2$ ($c = 1.0$, CHCl_3)

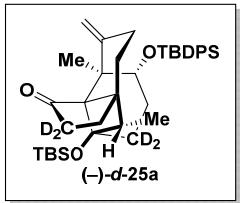
Melting point: 61-64 °C

HRMS-ESI (m/z) calc. for $\text{C}_{33}\text{H}_{39}\text{D}_4\text{O}_3\text{Si} [\text{M}+\text{H}^+]$: 519.3227; Found: 519.3213.

IR (neat, cm^{-1}): 2930, 2856, 1741, 1697, 1097, 1060.

^1H NMR (400 MHz, CDCl_3) δ 7.76-7.69 (m, 4H), 7.47-4.38 (m, 6H), 5.04-5.00 (m, 2H), 4.59 (d, $J = 7.8$ Hz, 1H), 2.79 (q, $J = 6.8$ Hz, 1H), 2.31 (td, $J = 14.1, 4.4$ Hz, 1H), 2.13-1.98 (m, 2H), 1.88 (dd, $J = 15.4, 7.8$ Hz, 1H), 1.65 (s, 3H), 1.60-1.56 (m, 3H), 1.36 (d, $J = 13.2$ Hz, 1H), 1.24-1.15 (m, 1H), 1.01 (s, 9H), 0.90 (d, $J = 6.7$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 216.3, 215.7, 147.8, 136.4, 136.2, 134.8, 133.7, 130.1, 129.9, 127.8, 127.8, 113.0, 73.4, 59.3, 47.2, 46.9, 45.2, 31.1, 30.1, 28.8, 26.9, 24.5, 19.8, 13.1, 11.7. The carbon atoms ($\delta = 44.7, 34.4$ ppm in **22b**) directly attached to the deuterium atoms were not detected.



R_f = 0.64 (petroleum ether: ethyl acetate = 5:1)

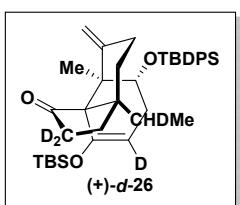
$[\alpha]_D^{21} = -9.9$ (c = 1.0, CHCl₃)

HRMS-ESI (m/z) calc. for C₃₉H₅₃D₄O₃Si₂ [M+H⁺]: 633.4092; Found: 633.4090.

IR (neat, cm⁻¹): 2953, 2929, 2856, 1732, 1472, 1427, 1255, 1103.

¹H NMR (400 MHz, CDCl₃) δ 7.69-7.63 (m, 4H), 7.46-7.33 (m, 6H), 4.82-4.78 (m, 2H), 3.81 (dd, *J* = 11.7, 3.0 Hz, 1H), 2.32 (dt, *J* = 16.7, 9.7 Hz, 1H), 2.06 (dd, *J* = 16.9, 9.3 Hz, 1H), 1.94 (q, *J* = 7.1 Hz, 1H), 1.77 (t, *J* = 12.1 Hz, 1H), 1.57-1.54 (m, 1H), 1.53-1.47 (m, 2H), 1.39 (d, *J* = 13.0 Hz, 1H), 1.31 (s, 3H), 1.28-1.23 (m, 2H), 1.01 (s, 9H), 0.85 (s, 9H), 0.79 (d, *J* = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 216.9, 149.6, 136.2, 136.1, 135.4, 133.9, 129.8, 129.6, 127.6, 127.5, 111.5, 75.5, 75.2, 64.5, 46.9, 43.8, 42.6, 28.9, 27.3, 27.0, 25.8, 25.7, 23.4, 19.5, 18.0, 14.8, 8.3, -2.4, -2.6. The carbon atoms (δ = 39.1, 33.8 ppm in **25a**) directly attached to the deuterium atoms were not detected.



R_f = 0.66 (petroleum ether: ethyl acetate = 5:1)

$[\alpha]_D^{21} = +118.4$ (c = 1.0, CHCl₃)

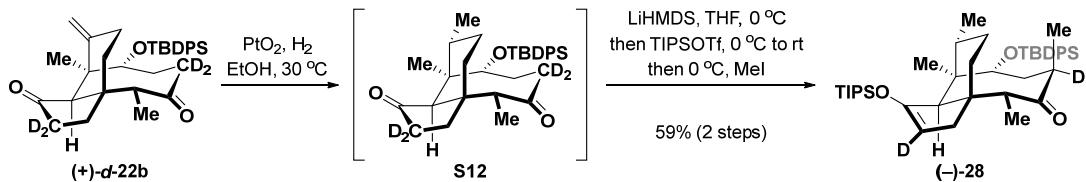
HRMS-ESI (m/z) calc. for C₃₉H₅₃D₄O₃Si₂ [M+H⁺]: 633.4092; Found: 633.4075.

IR (neat, cm⁻¹): 2930, 2856, 1742, 1646, 1472, 1427, 1253, 1224, 1110, 1075.

¹H NMR (400 MHz, CDCl₃) δ 7.72-7.69 (m, 2H), 7.64-7.61 (m, 2H), 7.47-7.33 (m, 6H), 4.89 (d, *J* = 1.7 Hz, 1H), 4.86 (s, 1H), 4.06 (ddd, *J* = 10.0, 6.4, 4.0 Hz, 1H), 2.12-2.03 (m, 1H), 1.90 (dd, *J* = 16.8, 6.5 Hz, 1H), 1.83-1.65 (m, 4H), 1.54 (s, 3H), 1.29 (d, *J* = 12.2 Hz, 2H), 1.15-1.04 (m, 2H), 0.99 (s, 9H), 0.82 (s, 9H), 0.67 (d, *J* = 7.3 Hz, 3H).

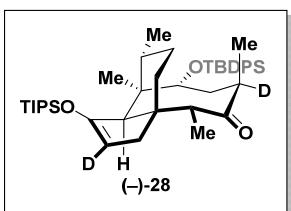
¹³C NMR (100 MHz, CDCl₃) δ 218.8, 150.6, 149.5, 136.4, 136.2, 135.4, 133.8, 129.8, 129.5, 127.6, 127.4, 111.4, 68.5, 66.7, 47.7, 47.2, 33.5, 30.9, 29.0, 27.0, 26.0, 19.5, 18.4, 18.3, 13.3, 8.6, -4.2, -4.5. The carbon atoms (δ = 102.8, 37.8, 31.1 ppm in **26**) directly attached to the deuterium atoms were not detected.

Synthesis of compound (-)-28



To a solution of compound $(+)-d\text{-}22b$ (1.0 equiv, 0.384 mmol, 199 mg) in ethanol (15 mL) was added PtO_2 (0.1 equiv, 0.0384 mmol, 8.7 mg). The reaction system was fully pumped three times with a hydrogen balloon. After being stirred at 30°C for 24 h, the mixture was filtered through a short pad of Celite and concentrated *in vacuo*. The crude product **S12** (white solid) was used immediately in the next step without further purification.

To a solution of intermediate **S12** in THF (4 mL) at 0°C was added LiHMDS (5.0 equiv, 1.92 mmol, 1.92 mL of a 1.0 M solution in THF). After being stirred at 0°C for 30 min, TIPSOTf (1.3 equiv, 0.499 mmol, 134 μL) was added dropwise at the same temperature. 10 min later, the cooling bath was removed, and the reaction was stirred at room temperature for 30 min. Then the reaction was recooled to 0°C and MeI (3.0 equiv, 1.15 mmol, 71.6 μL) was added. The reaction was stirred at 0°C for another 1 h before it was quenched with saturated NaHCO_3 solution at 0°C , and extracted with EtOAc . The combined organic layers were washed with brine, dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give compound $(-)\text{-}28$ (156 mg, 0.226 mmol, 59% yield for 2 steps) as a white solid.



Found: 689.4756.

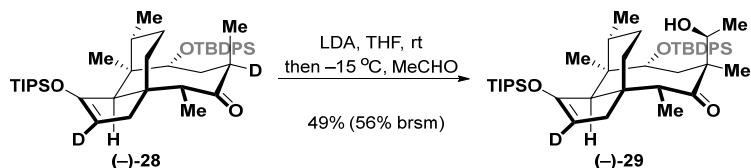
IR (neat, cm^{-1}): 2931, 2864, 1670, 1619, 1463, 1253, 1108, 1059.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.90-7.79 (m, 4H), 7.47-7.39 (m, 6H), 4.99 (d, $J = 9.1$ Hz, 1H), 2.80 (q, $J = 6.6$ Hz, 1H), 2.40 (dd, $J = 14.1, 3.4$ Hz, 1H), 2.21 (s, 1H), 2.06 (dd, $J = 15.5, 9.2$ Hz, 1H), 1.78-1.54 (m, 4H), 1.52 (s, 3H), 1.48-1.44 (m, 1H), 1.40-1.35 (m, 2H), 1.27-1.20 (m, 3H), 1.17 (d, $J = 7.2$ Hz, 3H), 1.14-1.07 (m, 18H), 0.98 (s, 9H), 0.86 (d, $J =$

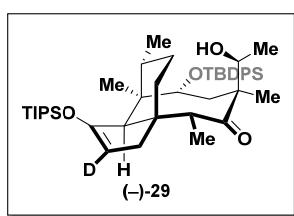
6.5 Hz, 3H), 0.27 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 219.2, 156.3, 136.4, 136.2, 135.9, 134.2, 129.9, 129.5, 127.9, 127.5, 70.4, 53.8, 46.9, 43.8, 42.5, 38.9, 36.8, 34.4, 31.6, 27.7, 27.3, 20.0, 19.7, 18.3, 18.3, 15.3, 13.2, 13.0. The carbon atoms (C2 and C12) directly attached to the deuterium atoms were not detected.

Synthesis of compound (-)-29



To a solution of compound (-)-28 (1.0 equiv, 0.226 mmol, 156 mg) in THF (2 mL) at room temperature was added LDA (10.0 equiv, 2.26 mmol, 513 μL of a 2.0 M solution in THF/heptane/ethylbenzene 22%/35%/14%). After being stirred at room temperature for 1.5 h, the mixture was cooled to -15 °C, at which temperature MeCHO (30.0 equiv, 6.79 mmol, 1.36 mL of a 5.0 M solution in THF) was added dropwise. 30 min later, the reaction was quenched with saturated NaHCO₃ solution, and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give compound (-)-29 (81.5 mg, 0.111 mmol, 49% yield, 56% brsm) as a white solid, alongside with recovered (-)-28 (18.8 mg, 0.0273 mmol, 12% yield).



*R*_f = 0.4 (petroleum ether: ethyl acetate = 4:1)

[α]_D³¹ = -43.8 (c = 1.0, CHCl₃)

Melting point: 60-64 °C

HRMS-ESI (m/z) calc. for C₄₅H₇₀DO₄Si₂ [M+H⁺]: 732.4948;

Found: 732.4961.

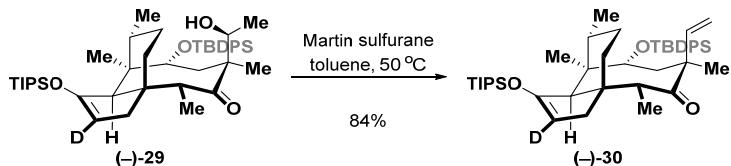
IR (neat, cm⁻¹): 3477, 2930, 2863, 1700, 1622, 1463, 1252, 1108, 1047.

¹H NMR (600 MHz, CDCl₃) δ 7.96-7.90 (m, 2H), 7.89-7.84 (m, 2H), 7.52-7.50 (m, 3H), 7.44-7.36 (m, 3H), 5.40 (d, *J* = 9.3 Hz, 1H), 3.40 (p, *J* = 6.2 Hz, 1H), 3.08 (q, *J* = 6.5 Hz, 1H), 2.51 (dd, *J* = 14.2, 3.4 Hz, 1H), 2.06 (d, *J* = 3.3 Hz, 1H), 1.77-1.66 (m, 3H), 1.60 (d, *J* = 16.2 Hz, 1H), 1.56-1.51 (m, 2H), 1.49 (s, 3H), 1.43 (dt, *J* = 10.8, 3.4 Hz, 1H), 1.40-1.35 (m, 1H), 1.27-1.19 (m, 6H), 1.12-1.09 (m, 18H), 0.95 (d, *J* = 6.54 Hz, 3H), 0.93 (s,

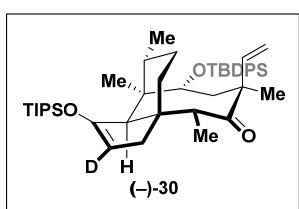
9H), 0.71 (d, J = 6.9 Hz, 1H), 0.44 (s, 3H), 0.33 (d, J = 6.2 Hz, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 217.9, 156.0, 136.9, 135.9, 135.8, 134.6, 130.0, 129.7, 128.0, 127.6, 72.2, 71.8, 56.3, 54.0, 47.2, 44.7, 44.1, 42.9, 38.6, 34.6, 31.8, 27.9, 27.1, 20.3, 19.9, 19.2, 18.6, 18.3, 16.8, 13.2. The carbon atom (C2) directly attached to the deuterium atom was not detected.

Synthesis of compound (-)-30



In an nitrogen-filled glove box, a 4.0 mL vial equipped with a magnetic stir bar was charged compound (*-*)-**29** (1.0 equiv, 71.7 μ mol, 52.5 mg), Martin sulfurane (2.0 equiv, 143 μ mol, 96.4 mg) and toluene (1.5 mL). After being stirred at 50 °C for 4 h, the reaction was cooled to room temperature and transferred out of the glove box. The mixture was concentrated *in vacuo*. The residue was purified by flash column chromatography to give compound (*-*)-**30** (43.2 mg, 60.5 μ mol, 84% yield) as a colorless oil.



$R_f = 0.5$ (petroleum ether: ethyl acetate = 10:1)

$$[\alpha]_D^{27} = -38.0 \text{ (c = 1.0, CHCl}_3\text{)}$$

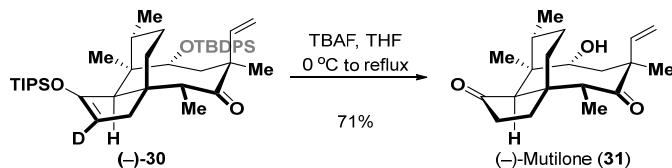
HRMS-ESI (m/z) calc. for C₄₅H₆₈DO₃Si₂ [M+H⁺]: 714.4843;
Found: 714.4852.

IR (neat, cm⁻¹): 2942, 2864, 1701, 1622, 1464, 1273, 1253, 1107, 1050.

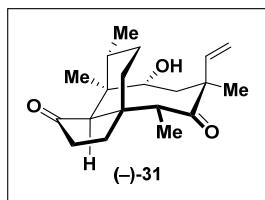
¹H NMR (400 MHz, CDCl₃) δ 7.86-7.83 (m, 2H), 7.80-7.78 (m, 2H), 7.51-7.34 (m, 6H), 5.22 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.10 (d, *J* = 8.1 Hz, 1H), 4.62-4.52 (m, 2H), 2.79 (q, *J* = 6.5 Hz, 1H), 2.43 (dd, *J* = 14.1, 3.4 Hz, 1H), 2.09 (d, *J* = 3.2 Hz, 1H), 1.83-1.61 (m, 4H), 1.59-1.52 (m, 1H), 1.48-1.42 (m, 4H), 1.39-1.30 (m, 2H), 1.28-1.16 (m, 3H), 1.15-1.07 (m, 2H), 1.02 (s, 9H), 0.87 (d, *J* = 6.4 Hz, 3H), 0.67 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 215.7, 156.3, 140.9, 136.5, 136.2, 136.1, 134.6, 129.7, 129.7, 127.9, 127.7, 116.4, 71.7, 54.3, 47.2, 46.1, 44.9, 44.0, 38.6, 34.7, 31.6, 27.6, 24.4, 20.0, 19.8, 18.3, 16.9, 14.3, 13.2. The carbon atom (C2) directly attached to the deuterium atom was not detected.

Synthesis of (-)-mutilone (31)



To a solution of compound **(-)-30** (1.0 equiv, 42.3 μmol , 30.2 mg) in THF (2 mL) at 0 °C was added TBAF (10.0 equiv, 423 μmol , 423 μL of a 1.0 M solution in THF). The mixture was then heated to reflux and stirred for 2 h. After being cooled to room temperature, the mixture was quenched with silica. Then the solvent was removed *in vacuo* and the residue was purified by flash column chromatography to give **(-)-mutilone (31)** (9.6 mg, 30.1 μmol , 71% yield) as a white solid.



$R_f = 0.3$ (petroleum ether: ethyl acetate = 4:1)

$[\alpha]_D^{22} = -45.9$ ($c = 0.5$, CHCl₃) [lit.^[8]: $[\alpha]_D^{22} = -51.3$ ($c = 4.065$, CHCl₃, prepared from (+)-pleuromutilin)]

Melting point: 149-152 °C [lit.^[8]: m.p. = 157-158 °C]

HRMS-ESI (m/z) calc. for C₂₀H₃₀NaO₃ [M+Na⁺]: 341.2087; Found: 341.2082.

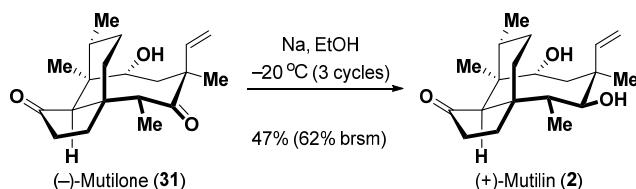
IR (neat, cm⁻¹): 3675, 3519, 2972, 2928, 1735, 1697, 1453, 1374, 1057.

¹H NMR (400 MHz, CDCl₃) δ 6.09 (dd, $J = 17.7, 10.8$ Hz, 1H), 5.37-5.28 (m, 2H), 4.70 (t, $J = 6.3$ Hz, 1H), 3.26 (q, $J = 6.7$ Hz, 1H), 2.31-2.12 (m, 3H), 1.91 (dd, $J = 15.5, 7.8$ Hz, 1H), 1.71 (d, $J = 15.5$ Hz, 1H), 1.65-1.61 (m, 4H), 1.46-1.41 (m, 3H), 1.37 (s, 3H), 1.12 (s, 3H), 1.06 (d, $J = 6.7$ Hz, 3H), 1.02 (d, $J = 6.5$ Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 217.4, 216.0, 140.2, 117.3, 67.8, 60.0, 54.6, 45.5, 45.0, 44.2, 42.6, 37.5, 34.8, 30.1, 27.2, 25.4, 24.9, 18.4, 13.6, 13.6.

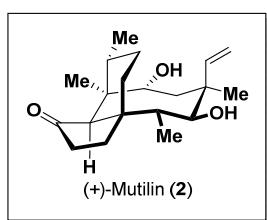
The characterization data were in agreement with literature values.^[8]

Synthesis of (+)-mutilin (2)



The procedure was adapted from that reported by Pronin's group.^[1h] To a solution of

(*-*)-mutilone (**31**) (1.0 equiv, 65.3 μ mol, 20.8 mg) in EtOH (1.2 mL) at -20 °C was added freshly cut sodium metal (\sim 160 mg, excess) in one portion. After 3 h, the sodium metal was completely consumed. The mixture was quenched with 1/2-saturated NH₄Cl solution, and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was partially purified by flash column chromatography to give (*+*)-mutilin (**2**, impure) and recovered (*-*)-**31** (impure). The recovered (*-*)-**31** was resubjected to the above reaction conditions two additional times. Following the last cycle, the crude product was combined with the (*+*)-mutilin (**2**, impure) isolated from the first two cycles. The mixture was purified by flash column chromatography to give (*+*)-mutilin (**2**) (9.8 mg, 30.6 μ mol, 47% yield, 62% brsm) as a white solid, alongside with recovered (*-*)-**31** (5.0 mg, 15.7 μ mol, 24% yield).



R_f = 0.3 (petroleum ether: ethyl acetate = 2:1)

$[\alpha]_D^{24} = +33.0$ (c = 0.2, CHCl₃) [lit.^[1d]: $[\alpha]_D^{24} = +69$ (c = 0.07, CHCl₃, synthetic (*+*)-mutilin); lit.^[1d]: $[\alpha]_D^{24} = +66$ (c = 0.07, CHCl₃, natural (*+*)-mutilin); lit.^[9]: $[\alpha]_D^{25} = +69$ (c = 1.0, CHCl₃, prepared from (*+*)-pleuromutilin)]

Melting point: 178-179 °C [lit.^[1d]: m.p. = 186-188 °C]

HRMS-ESI (m/z) calc. for C₂₀H₃₃O₃ [M+H⁺]: 321.2424; Found: 321.2430.

IR (neat, cm⁻¹): 3480, 2928, 2863, 1726, 1457, 1119, 1013.

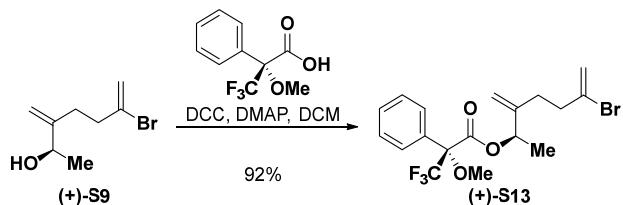
¹H NMR (600 MHz, CDCl₃) δ 6.15 (ddd, *J* = 17.8, 11.1, 0.8 Hz, 1H), 5.36 (dd, *J* = 17.8, 1.4 Hz, 1H), 5.29 (dd, *J* = 11.2, 1.4 Hz, 1H), 4.35 (d, *J* = 7.7 Hz, 1H), 3.41 (d, *J* = 6.4 Hz, 1H), 2.28-2.14 (m, 3H), 2.08-2.03 (m, 1H), 1.91 (dd, *J* = 15.9, 7.7 Hz, 1H), 1.74 (dq, *J* = 14.5, 3.2 Hz, 1H), 1.68 (dtd, *J* = 14.3, 7.2, 3.8 Hz, 1H), 1.63-1.59 (m, 2H), 1.50-1.44 (m, 2H), 1.40-1.36 (m, 4H), 1.17-1.09 (m, 4H), 0.96 (d, *J* = 7.1 Hz, 3H), 0.92 (d, *J* = 7.1 Hz, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 217.8, 139.5, 116.1, 75.3, 66.9, 59.2, 45.5, 45.4, 45.2, 42.5, 37.0, 36.6, 34.6, 30.5, 28.7, 27.3, 25.2, 18.3, 13.6, 11.4.

To our surprise, the specific rotation of our synthetic (*+*)-mutilin (**2**) was not consistent with those reported in the literature.^[1d,9] We were confident in the absolute stereochemistry and high enantiopurity of compounds provided by our route because: 1) the specific

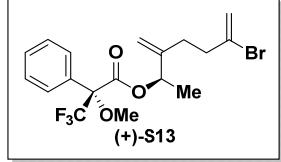
rotation of the synthesized mutilone (*-*)-**31** (vide supra) was in agreement with the literature,^[8] 2) the Mosher's esters^[10] of compound (+)-**S9** were prepared to determine its absolute stereochemistry, which also indicated the excellent enantiopurity (vide infra), 3) the enantiomeric excess of compound (+)-**S11** was confirmed by HPLC using a chiral column (vide infra), and 4) the X-ray crystallography analysis of synthesized (+)-**17** and (+)-**22a** were consistent with current assignment (vide infra). Consequently, we prepared (+)-mutilin from commercially available (+)-pleuromutilin by following the reported protocol,^[9] and its specific rotation, $[\alpha]_D^{24} = +35.7$ ($c = 1.0$, CHCl_3), accorded with the synthesized sample in our hands. In order to further validate the enantiopurity of the synthesized (+)-mutilin (**2**), we undertook the synthesis of (+)-pleuromutilin (**1**); the specific rotations of the synthesized **1** and the intermediate (**S15**) were both in agreement with those reported in the literature (vide infra).

Synthesis of compound (+)-S13



To a solution of (+)-**S9** (1.0 equiv, 0.10 mmol, 20.5 mg), DCC (2.1 equiv, 0.21 mmol, 43.3 mg) and DMAP (0.10 equiv, 0.010 mmol, 1.2 mg) in DCM (4 mL) was added (*R*)-(+)-alpha-methoxy-alpha-trifluoromethylphenylacetic acid (2.1 equiv, 0.21 mmol, 49.2 mg). After being stirred at room temperature for 1 h, the mixture was filtered through a short pad of silica gel and concentrated *in vacuo*. The residue was purified by flash column chromatography to give compound (+)-**S13** (38.9 mg, 0.092 mmol, 92% yield) as a colorless oil.

$R_f = 0.7$ (petroleum ether: ethyl acetate = 5:1)



$$[\alpha]_D^{29} = +34.4 \text{ (c = 1.0, CHCl}_3\text{)}$$

HRMS-ESI (m/z) calc. for C₁₈H₂₀BrF₃NaO₃ [M+Na⁺]: 443.0440;
Found: 443.0440.

IR (neat, cm⁻¹): 2986, 2949, 1746, 1630, 1451, 1271, 1169, 1122, 1081, 1015.

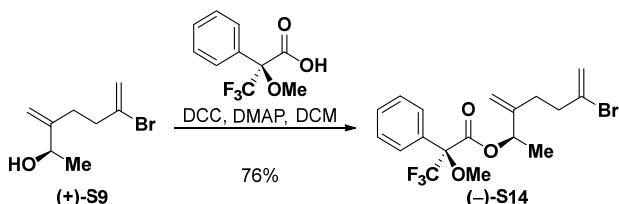
¹H NMR (400 MHz, CDCl₃) δ 7.54-7.49 (m, 2H), 7.42-7.38 (m, 3H), 5.59-5.51 (m, 2H),

5.41 (d, $J = 1.8$ Hz, 1H), 5.17 (s, 1H), 4.97 (s, 1H), 3.53 (s, 3H), 2.63-2.52 (m, 2H), 2.35-2.29 (m, 2H), 1.39 (d, $J = 6.5$ Hz, 3H).

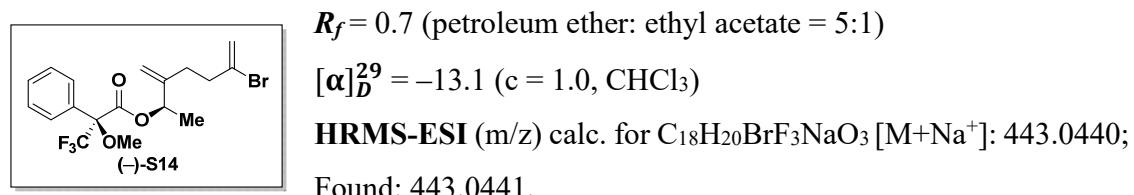
^{13}C NMR (100 MHz, CDCl_3) δ 166.0, 145.8, 133.5, 132.3, 129.8, 128.6, 127.6 (q, $J = 1.4$ Hz), 123.5 (q, $J = 288.4$ Hz), 117.3, 113.2, 84.8 (q, $J = 27.6$ Hz), 75.6, 55.5 (q, $J = 1.6$ Hz), 39.8, 30.4, 19.2.

^{19}F NMR (377 MHz, CDCl_3) δ -71.3.

Synthesis of compound (-)-S14



To a solution of (+)-S9 (1.0 equiv, 0.10 mmol, 20.5 mg), DCC (2.1 equiv, 0.21 mmol, 43.3 mg) and DMAP (0.10 equiv, 0.010 mmol, 1.2 mg) in DCM (4 mL) was added (*S*)-(-)-alpha-methoxy-alpha-trifluoromethylphenylacetic acid (2.1 equiv, 0.21 mmol, 49.2 mg). After being stirred at room temperature for 1 h, the mixture was filtered through a short pad of silica gel and concentrated *in vacuo*. The residue was purified by flash column chromatography to give compound (-)-S14 (32.0 mg, 0.076 mmol, 76% yield) as a colorless oil.



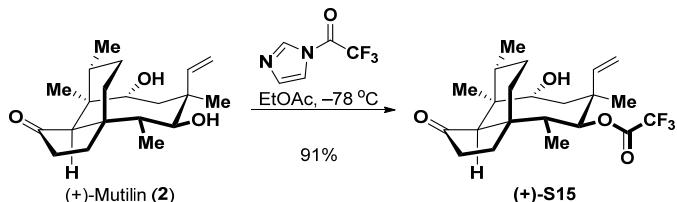
IR (neat, cm^{-1}): 2985, 2925, 2849, 1747, 1628, 1451, 1270, 1169, 1123, 1081, 1018.

^1H NMR (400 MHz, CDCl_3) δ 7.56-7.49 (m, 2H), 7.43-7.35 (m, 3H), 5.54 (q, $J = 6.6$ Hz, 1H), 5.49 (q, $J = 1.4$ Hz, 1H), 5.38 (d, $J = 1.8$ Hz, 1H), 5.05 (s, 1H), 4.91 (t, $J = 1.6$ Hz, 1H), 3.58 (q, $J = 1.3$ Hz, 3H), 2.52-2.48 (m, 2H), 2.28-2.15 (m, 2H), 1.46 (d, $J = 6.5$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 165.8, 145.7, 133.5, 132.5, 129.7, 128.5, 127.3, 123.5 (q, $J = 288.7$ Hz), 117.2, 113.0, 84.5 (q, $J = 27.6$ Hz), 75.3, 55.6 (q, $J = 1.8$ Hz), 39.7, 30.3, 19.4.

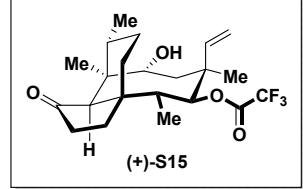
¹⁹F NMR (377 MHz, CDCl₃) δ -71.4.

Synthesis of compound (+)-S15



The procedure was adapted from the method reported by Procter and co-workers.^[1d] To a solution of (+)-mutilin (2) (1.0 equiv, 31.2 μmol, 10.0 mg) in EtOAc (0.6 mL) was added trifluoroacetyl imidazole (5.0 equiv, 156 μmol, 17.8 μL) dropwise at -78 °C. After being stirred at the same temperature for 70 min, the reaction was quenched with HCl solution (aq., 1 M, 3 mL). The resulting mixture was warmed to room temperature over 1 h. Then the mixture was diluted with HCl solution (aq., 1 M), and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give compound (+)-S15 (11.8 mg, 28.3 μmol, 91% yield) as a white solid.

$R_f = 0.5$ (petroleum ether: ethyl acetate = 4:1)



$[\alpha]_D^{33} = +44.4$ (c = 1.0, CHCl₃) [lit.^[1d]: $[\alpha]_D^{24} = +46$ (c = 0.3, CHCl₃)]

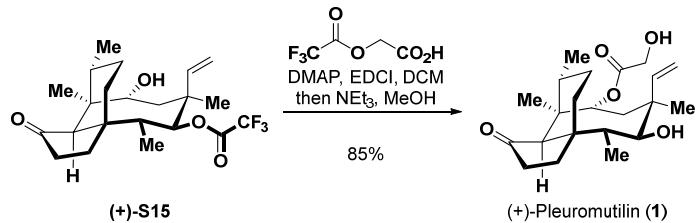
¹H NMR (400 MHz, CDCl₃) δ 6.07 (ddd, $J = 17.9, 11.2, 1.2$ Hz, 1H), 5.48 (dd, $J = 17.9, 1.0$ Hz, 1H), 5.34 (dd, $J = 11.2, 1.0$ Hz, 1H), 4.97 (d, $J = 6.9$ Hz, 1H), 4.30 (d, $J = 7.4$ Hz, 1H), 2.43-2.27 (m, 2H), 2.19 (dt, $J = 19.4, 9.5$ Hz, 1H), 2.07 (s, 1H), 1.97 (dd, $J = 16.1, 7.4$ Hz, 1H), 1.84-1.67 (m, 4H), 1.49-1.38 (m, 6H), 1.15 (ddd, $J = 14.4, 12.8, 5.1$ Hz, 1H), 1.02 (s, 3H), 0.97 (d, $J = 7.1$ Hz, 3H), 0.83 (d, $J = 7.1$ Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 216.9, 138.5, 116.9, 82.4, 66.9, 59.3, 45.1, 44.6, 44.0, 42.4, 36.8, 36.8, 34.5, 30.3, 28.7, 27.3, 25.3, 18.3, 13.5, 11.6. CF₃ and C(O)CF₃ were not detected.

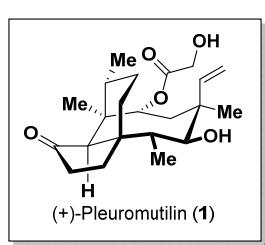
¹⁹F NMR (377 MHz, CDCl₃) δ -74.8.

The characterization data were in agreement with literature values.^[1d]

Synthesis of (+)-pleuromutilin (1)



(+)-Pleuromutilin (**1**) was prepared according to the procedure reported by Procter and co-workers.^[1d] A 10 mL round-bottom flask equipped with a magnetic stir bar was charged with compound (+)-**S15** (1.0 equiv, 24.0 µmol, 10.0 mg), 2-(2,2,2-trifluoroacetoxy)acetic acid^[11] (3.0 equiv, 72.0 µmol, 12.4 mg), DMAP (3.0 equiv, 72.0 µmol, 8.8 mg) and EDCI (3.0 equiv, 72.0 µmol, 13.8 mg). The reaction system was fully pumped three times with a nitrogen balloon, and then DCM (1 mL) was added. After 45 min, compound (+)-**S15** was completely consumed (new spot: $R_f = 0.55$, petroleum ether: ethyl acetate = 4:1), and then MeOH (1 mL) and NEt₃ (1 mL) were added sequentially. After being stirred at room temperature for 25 h, the reaction was quenched with saturated NH₄Cl solution, and extracted with CHCl₃. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give (+)-pleuromutilin (**1**) (7.7 mg, 20.3 µmol, 85% yield) as a white solid.



$R_f = 0.3$ (petroleum ether: ethyl acetate = 1:1)
 $[\alpha]_D^{20} = +32.5$ ($c = 0.2$, CHCl_3) [lit.^[1d]: $[\alpha]_D^{23} = +33$ ($c = 0.2$, CDCl_3);
 lit.^[1e]: $[\alpha]_D^{20} = +32$ ($c = 0.25$, CHCl_3); lit.^[1g]: $[\alpha]_D^{23} = +33.4$ ($c = 0.252$, CHCl_3)]

(+)-Pleuromutilin (1) **¹H NMR** (600 MHz, CDCl₃) δ 6.50 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.84 (d, *J* = 8.5 Hz, 1H), 5.36 (dd, *J* = 11.0, 1.5 Hz, 1H), 5.22 (dd, *J* = 17.4, 1.5 Hz, 1H), 4.07 (d, *J* = 17.1 Hz, 1H), 4.01 (d, *J* = 17.1 Hz, 1H), 3.37 (s, 1H), 2.41 (brs, 1H), 2.34 (*p*, *J* = 7.0 Hz, 1H), 2.30-2.16 (m, 2H), 2.13-2.06 (m, 2H), 1.78 (dq, *J* = 14.6, 3.2 Hz, 1H), 1.70-1.62 (m, 3H), 1.54 (qd, *J* = 14.0, 3.7 Hz, 1H), 1.49-1.43 (m, 4H), 1.39 (dq, *J* = 14.6, 3.7 Hz, 1H), 1.32 (d, *J* = 16.1 Hz, 1H), 1.17 (s, 3H), 1.14 (td, *J* = 14.1, 4.5 Hz, 1H), 0.89 (d, *J* = 7.1 Hz, 3H), 0.70 (d, *J* = 7.1 Hz, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 217.0, 172.3, 139.0, 117.6, 74.7, 70.0, 61.5, 58.2, 45.6, 44.9, 44.2, 42.0, 36.8, 36.2, 34.6, 30.5, 27.0, 26.5, 25.0, 16.8, 14.9, 11.7.

The characterization data were in agreement with literature values.^[1d,e,g]

III. DFT Calculation of Transannular [2+2] Photocycloadditions

The [2+2] photocycloaddition of α,β -enones to alkenes has found numerous applications in organic synthesis^[12]. The mechanism involves the excitation of enone to its triplet excited state after intersystem crossing, attack of the photoexcited enone by an olefin, and subsequent cyclization of the 1,4-biradical intermediate on the singlet hypersurface to generate cyclobutane. It's worth noting that rotation around the C=C bond could be possible during the process given the breakage of π bond, which might determine the stereochemistry of the final product. In addition, fragmentation of the 1,4-biradical intermediate could lead to a new olefin-containing molecule with the geometry different from the original one, further complicating the reaction process. To investigate the origin of the C10 stereocenter established in photocycloaddition, preliminary density functional theory (DFT) calculations were carried out and summarised as following.

Geometry optimizations were performed using Orca 5.0 software package^[13]. The geometries of intermediates and transition states were optimized under B3LYP^[14]-D3(BJ)^[15]/def2-SVP^[16] in the gas phase. Vibrational frequency calculations were performed under the same level of theory to confirm if each optimized structure is a local minimum or a transition state structure.

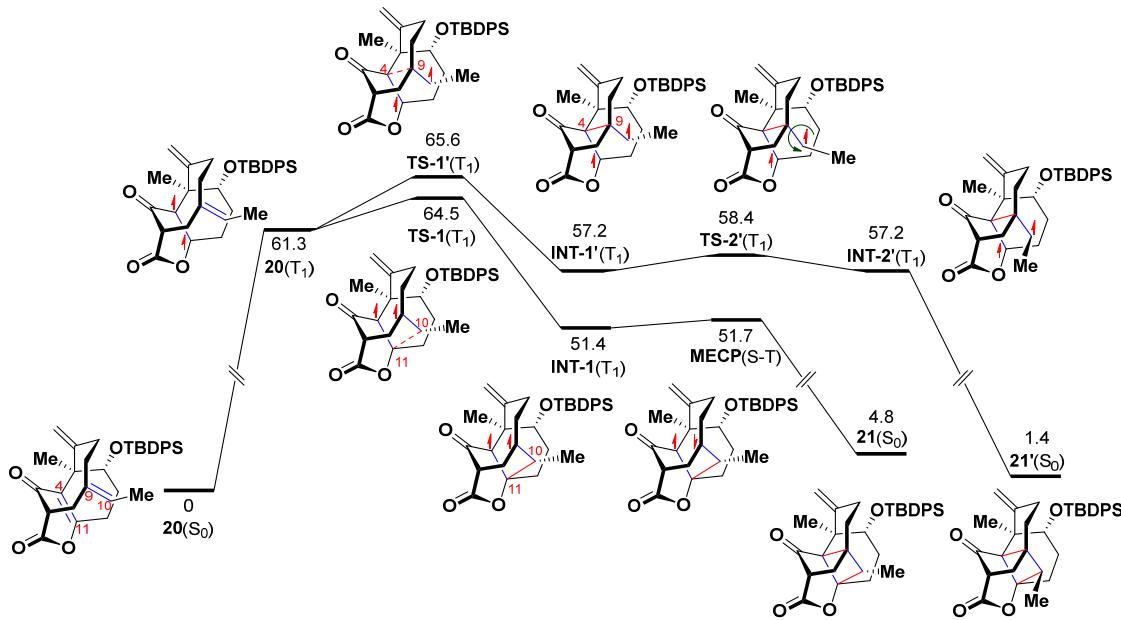


Figure S3. DFT-calculated energy profiles of related intermediates and transition states in the generation of **21** (unit in kcal/mol)

For substrate **20** (S_0) (Figure S3), irradiation at 365 nm gives its triplet intermediate **20** (T_1). Because of the constraint imposed by the lactone moiety, C9–C10 double bond aligns close to the enone moiety (C4–C11), and two radical addition pathways (via **TS-1** and **TS-1'**) were considered:^[17] bonding of C10 to the β -position (C11) of the enone produces **INT-1** (T_1), while attack of alkene (C9) at the α -position (C4) gives **INT-1'** (T_1). Conformational rigidity allows the construction of the larger ring (formation of C10–C11 bond) via a lower barrier (64.5 vs 65.6 kcal/mol) to form the more stable intermediate, **INT-1** (T_1) (51.4 vs 57.2 kcal/mol). After intersystem crossing of **INT-1** (T_1) via the singlet-triplet minimum energy crossing point (MECP), the singlet intermediate directly reaches the product **21** with no barrier on the potential energy surface. The rotation of C9–C10 bond is prevented in this pathway, suggesting that **21** should be obtained as the only product, which nicely agrees with our experimental result.

Similarly, photoexcitation of compound **24** (S_0) gives its triplet intermediate **24** (T_1) (Figure S4), but the radical addition sequence is opposite to that of **20** (T_1). The looser and more flexible structure of **24** (T_1) than that of **20** (T_1) makes **24** (T_1) easier to form C4–C9 instead of C10–C11 bonds (63.2 vs 65.1 kcal/mol). Furthermore, the better stability of

triplet intermediate **INT-3** (T_1) than **INT-3'** (T_1) (45.8 vs 53.0 kcal/mol) implies a longer lifetime of the former for subsequent transformations.

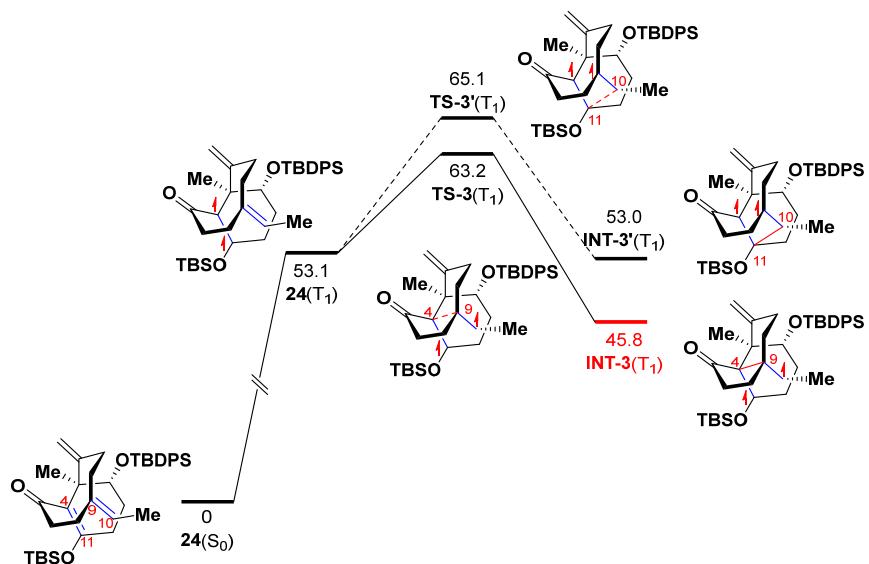


Figure S4. DFT-calculated energy profiles of related intermediates and transition states in the generation of 1,4-biradicals from compound **24** (unit in kcal/mol)

Starting from **INT-3** (T_1) (Figure S5), a rapid equilibrium occurs between **INT-3** (T_1) and **INT-4** (T_1), via a single-bond rotation transition state **TS-4** (T_1) with a low barrier. Both biradicals **INT-3** (T_1) and **INT-4** (T_1) could undergo an irreversible intersystem crossing process, affording **INT-3** (S_0) and **INT-4** (S_0) respectively. The competition between biradical recombination and fragmentation (**TS-5** vs **TS-6**, and **TS-5'** vs **TS-6'**) determines the ratio of [2+2] cycloaddition product and alkene product with *E* or *Z* configuration (**25a** vs **24**, and **25b** vs **24'**). In both pathways fragmentation is more favorable than cyclization. However, the barrier for **INT-4** (S_0) cyclization lies only 0.92 kcal/mol higher in energy than fragmentation, whereas the gap for **INT-3** (S_0) is 1.94 kcal/mol, indicating that **INT-4** (S_0) has more opportunities to realize irreversible biradical recombination, affording product **25b**.

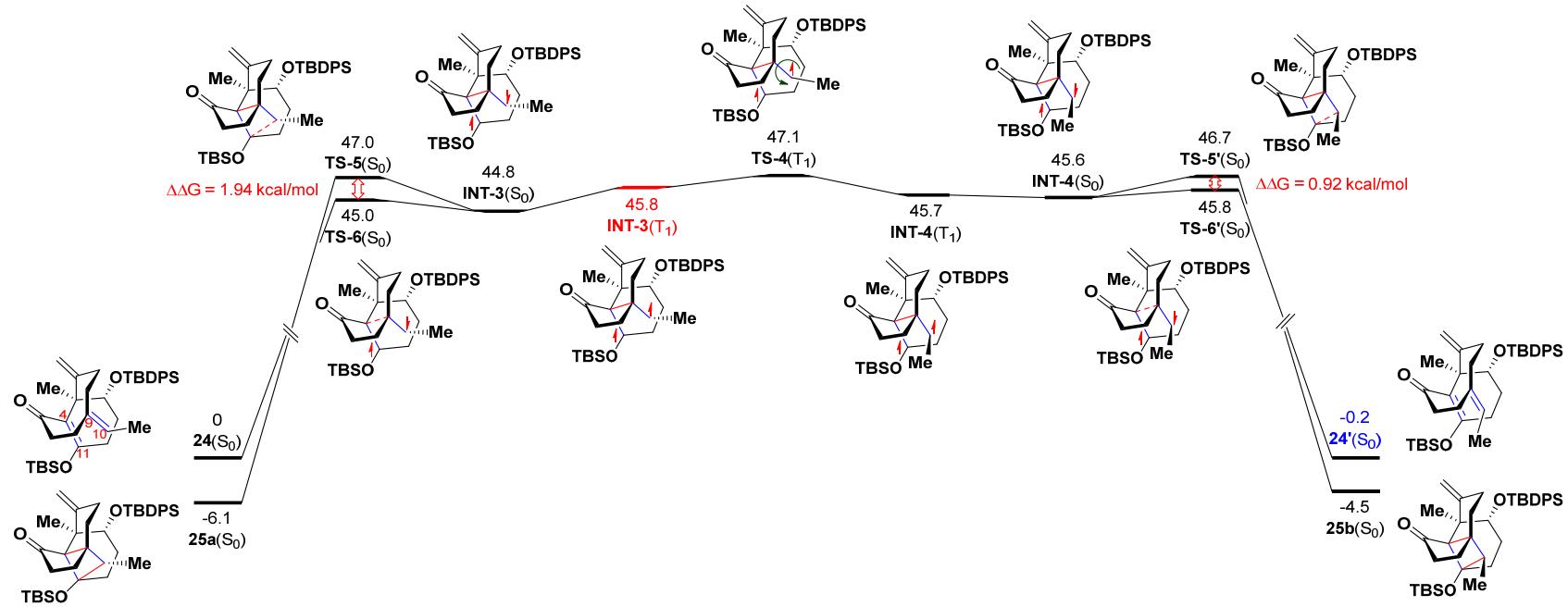


Figure S5. DFT-calculated energy profiles of related intermediates and transition states in the generation of compounds **25a** and **25b** from 1,4-biradical **INT-3** (T_1) (unit in kcal/mol)

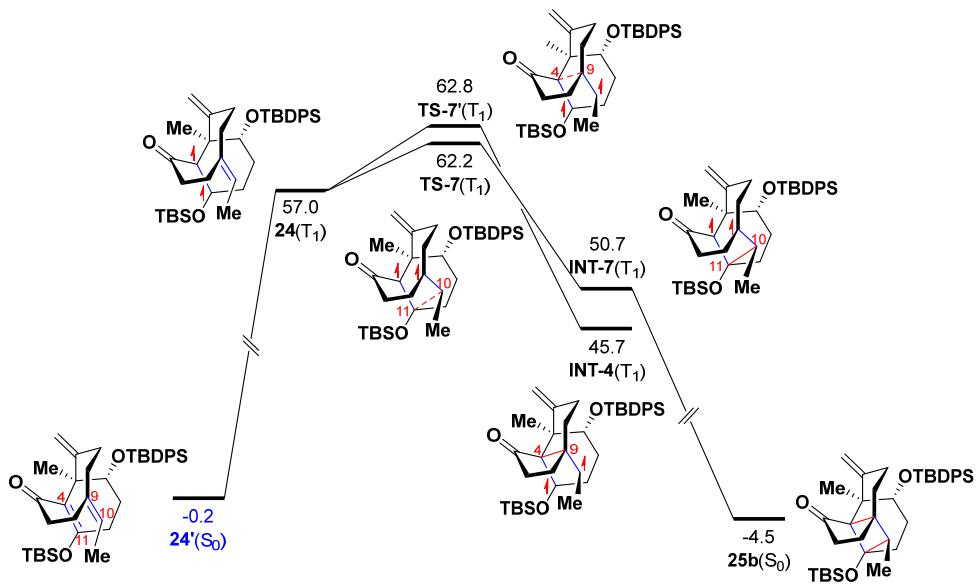


Figure S6. DFT-calculated energy profiles of related intermediates and transition states in the generation of compound **25b** from **24'** (unit in kcal/mol)

Another plausible way to yield compound **25b** from **24'** has also been taken into consideration (Figure S6). Interestingly, following the photoexcitation, the formation of C10–C11 bond (via **TS-7**) is slightly preferred over that of C4–C9 bond (via **TS-7'**) to give **INT-7 (T₁)**, which could be responsible for the formation of product **25b**.

These preliminary DFT calculations are consistent with our experimental observations that the major and minor products of the transannular [2+2] photocycloaddition reaction of **24** were **25b** and **25a**, respectively.

Compound 20 (S_0)						
Gibbs Free Energy = -1907.416245						
Hartree						
C	-1.079148	0.566868	1.353312	H	-0.115429	3.115945
C	-2.417481	1.034882	0.782587	H	0.030799	0.318800
C	-2.506728	1.845148	-0.299312	H	-0.861187	-2.555345
C	-1.341803	2.488847	-0.980469	H	-1.307397	-1.044523
C	-0.075059	2.403719	-0.134843	H	-2.976364	-3.176425
C	0.082911	0.981501	0.390902	H	-3.374753	-2.307490
C	-1.101653	-0.970490	1.376238	H	-6.026670	-0.649918
C	-1.513466	-1.679889	0.096682	H	-5.461771	-1.409977
C	-4.914624	0.661939	0.561075	H	-4.593754	-0.501870
C	-3.664574	0.582844	1.421530	H	-0.718569	-2.779658
C	-2.990470	-2.169756	0.015362	H	-0.466677	-1.229420
C	-3.967517	-1.326515	-0.793529	H	-1.643101	0.874774
C	-5.165742	-0.748681	-0.067476	H	0.127858	0.906953
C	-3.826305	-1.107280	-2.113632	H	-0.879548	2.290970
O	-3.726470	0.090997	2.534001	H	2.192071	-3.085804
O	-3.679518	2.212372	-0.901346	H	1.309593	-4.941534
C	-0.738118	-1.686425	2.445888	H	-0.576912	-4.542626
C	-4.900957	1.696614	-0.538728	H	0.772726	-2.256537
O	-5.873183	2.072540	-1.126011	H	1.711018	-0.405393
H	-5.775065	0.893334	1.205878	H	-0.278525	-2.962313
C	-0.853826	1.193487	2.739668	H	5.943146	0.749637
O	1.322166	0.808417	1.040171	H	-3.208384	-1.246422
C	2.021778	-1.591458	-0.488265	H	4.527136	-0.680306
Si	2.630591	-0.103465	0.502856	H	5.879654	3.231194
C	3.648963	0.969412	-0.666455	H	4.521197	-1.347828
C	1.898456	-2.888670	0.042773	H	1.940905	-0.556023
C	1.390781	-3.943182	-0.721290	H	4.395569	4.268169
C	0.980019	-3.720342	-2.038925	H	2.405230	-1.571162
C	1.090094	-2.440382	-2.589034	H	5.486054	2.831705
C	1.612838	-1.394883	-1.823001	H	3.411987	-0.903642
C	3.632638	2.371644	-0.541668	H	5.479489	0.909679
C	4.425679	3.181099	-1.359656	H	1.909679	3.431771
C	5.258452	2.600263	-2.321083	H	4.531564	-2.362964
C	5.293693	1.209413	-2.458621	H	5.486054	1.281296
C	4.495267	0.405641	-1.639606	H	4.548605	-1.571162
C	3.652093	-0.495709	2.062361	H	5.479489	2.557830
C	2.801140	-1.178471	3.147574	H	5.479489	-0.903642
C	4.848733	-1.384286	1.675115	H	5.479489	0.909679
C	4.173748	0.842030	2.626123	H	1.909679	3.431771
C	-2.725192	-1.612455	-2.999911	H	4.829775	1.362803
H	-1.616371	3.530093	-1.214347	H	3.345499	1.520762
H	-1.199993	1.991190	-1.958323	H	-2.132201	2.885008
H	0.803698	2.663626	-0.741801	H	-3.135273	-2.411691
				H	-2.022453	-2.533541
				H	-0.803277	-3.948699
				H	-2.022453	-3.271436

Compound 20 (T_1)						
Gibbs Free Energy = -1907.318587						
Hartree						
C	-1.054237	0.585028	1.347531	C	-2.412933	1.026107
C	-2.531674	1.906622	0.805881	C	-1.394998	2.549122
C	-0.099561	2.424173	-0.254819	C	-0.970933	-0.970933
C	0.072335	0.996787	-0.164757	C	0.349845	0.349845

C	-1.166201	-0.937243	1.413560	H	-1.223663	-2.702444	2.598353
C	-1.465949	-1.685917	0.127347	H	-0.870043	-1.131803	3.530382
C	-4.869587	0.522476	0.659763	H	-1.629605	1.009562	3.407184
C	-3.546412	0.454289	1.394396	H	0.141978	0.906632	3.150769
C	-2.909863	-2.233753	-0.078284	H	-0.763101	2.333153	2.604116
C	-3.903392	-1.341583	-0.814401	H	2.271670	-3.097317	1.064950
C	-5.121307	-0.844865	-0.058161	H	1.373464	-4.970038	-0.258668
C	-3.743993	-0.993277	-2.103983	H	0.564058	-4.590545	-2.588370
O	-3.532292	-0.426374	2.361524	H	0.702823	-2.307100	-3.587161
O	-3.769995	2.237978	-0.763989	H	1.649006	-0.436034	-2.281709
C	-1.076510	-1.618767	2.578282	H	3.009660	2.826952	0.099770
C	-4.925292	1.660673	-0.355554	H	4.432149	4.210347	-1.390128
O	-5.967379	2.023215	-0.834796	H	5.923133	3.116517	-3.063865
H	-5.706262	0.700346	1.355009	H	5.976151	0.628945	-3.238143
C	-0.808305	1.241213	2.715899	H	4.543567	-0.752283	-1.765050
O	1.326358	0.824946	0.975161	H	2.363136	-2.128942	2.811865
C	2.023265	-1.608700	-0.493970	H	3.319328	-1.291548	4.051457
Si	2.633842	-0.101753	0.466163	H	1.863664	-0.524001	3.370757
C	3.669740	0.933816	-0.716798	H	4.539815	-2.339061	1.327502
C	1.938582	-2.906245	0.043945	H	5.446119	-1.519996	2.621239
C	1.424551	-3.971802	-0.701062	H	5.482667	-0.874891	0.964498
C	0.971995	-3.760073	-2.006530	H	4.677248	0.717045	3.548977
C	1.049756	-2.481150	-2.565560	H	4.778814	1.399896	1.907906
C	1.576916	-1.424448	-1.818858	H	3.270825	1.554517	2.843997
C	3.657264	2.338959	-0.633185	H	-2.017281	-2.214020	-2.630297
C	4.459227	3.120277	-1.469644	H	-2.958877	-1.605981	-4.016811
C	5.295542	2.507462	-2.407913	H	-1.897790	-0.513132	-3.118064
C	5.325123	1.113017	-2.505240				
C	4.518004	0.337081	-1.668374				
C	3.618434	-0.468748	2.055013				
C	2.738447	-1.142989	3.123396				
C	4.833996	-1.351605	1.717227				
C	4.112113	0.881588	2.614159				
C	-2.600112	-1.359870	-3.003650				
H	-1.637181	3.607034	-1.171968				
H	-1.266059	2.080794	-1.969158				
H	0.766065	2.673167	-0.795871				
H	-0.096737	3.128966	0.681657				
H	-0.000084	0.337114	-0.529342				
H	-0.780265	-2.544066	0.088607				
H	-1.209065	-1.064190	-0.735588				
H	-2.806102	-3.165338	-0.660161				
H	-3.325580	-2.524762	0.896363				
H	-5.979399	-0.709204	-0.733336				
H	-5.414659	-1.573794	0.712047				
H	-4.517742	-0.361770	-2.557934				

TS-1 (T₁)

Gibbs Free Energy = -1907.313507

Hartree

C	-1.330137	0.711698	1.257472
C	-2.617658	0.847165	0.481090
C	-2.612351	1.226397	-0.932682
C	-1.433589	1.840176	-1.605480
C	-0.133140	1.700256	-0.796669
C	-0.148363	0.577189	0.245129
C	-1.341590	-0.534082	2.175289
C	-2.270367	-1.716959	1.936263
C	-4.996562	0.281256	0.176005
C	-3.892404	0.710721	1.138761
C	-2.422296	-2.295048	0.513344
C	-3.255253	-1.503648	-0.461393
C	-4.715653	-1.217425	-0.129880
C	-2.790823	-1.100694	-1.698967
O	-4.075489	0.759851	2.358385

O	-3.808828	1.632000	-1.492930	H	1.195534	-2.751539	0.934005
C	-0.527850	-0.584645	3.238974	H	4.879458	-0.211678	-1.478172
C	-5.022260	1.167382	-1.057557	H	6.221144	1.538734	-2.586172
O	-6.017012	1.499490	-1.639785	H	5.664050	3.947931	-2.255998
H	-5.979623	0.385540	0.652975	H	3.743011	4.584146	-0.796310
C	-1.168883	2.014362	2.088346	H	2.386933	2.827458	0.308154
O	1.075557	0.569590	0.952016	H	3.382767	-1.865599	3.759709
C	2.090053	-1.591831	-0.668180	H	1.804700	-1.572569	2.990046
Si	2.521715	-0.122026	0.438373	H	2.978105	-2.689196	2.241428
C	3.510523	1.171772	-0.512707	H	4.979971	-1.800748	0.945132
C	2.331867	-1.581807	-2.054892	H	5.514570	-1.220596	2.538578
C	1.970632	-2.663388	-2.865182	H	5.478133	-0.101804	1.156555
C	1.350415	-3.782268	-2.304222	H	2.494057	0.965891	3.224235
C	1.078283	-3.805530	-0.932728	H	4.106493	0.495855	3.824166
C	1.439427	-2.721470	-0.128869	H	3.957916	1.554376	2.400556
C	4.608661	0.837126	-1.329116	H	-0.734235	-1.836931	-1.663325
C	5.375697	1.824031	-1.954527	H	-1.679466	-2.268126	-3.096321
C	5.064560	3.174433	-1.768892	H	-1.077579	-0.622578	-2.917912
C	3.987140	3.530006	-0.952758				
C	3.222307	2.537930	-0.333053				
C	3.502291	-0.567290	2.015942				
C	2.872559	-1.739626	2.787795				
C	4.946947	-0.939216	1.633657				
C	3.512030	0.686667	2.912903				
C	-1.499771	-1.469162	-2.353890				
H	-1.653977	2.908329	-1.792290				
H	-1.319995	1.399574	-2.613093				
H	0.713592	1.528037	-1.476914				
H	0.088392	2.639617	-0.270425				
H	-0.273680	-0.385012	-0.272967				
H	-1.911286	-2.533826	2.580619				
H	-3.266089	-1.456485	2.328014				
H	-1.429680	-2.499786	0.090123				
H	-2.907532	-3.284440	0.629921				
H	-5.367131	-1.552178	-0.956344				
H	-5.011935	-1.787740	0.763208				
H	-3.529590	-0.667878	-2.381554				
H	-0.505707	-1.467080	3.884682				
H	0.129055	0.238058	3.516860				
H	-1.920948	2.028479	2.886143				
H	-0.159817	2.071023	2.517503				
H	-1.317324	2.901962	1.455578				
H	2.804207	-0.711902	-2.516536				
H	2.172777	-2.629455	-3.938958				
H	1.069904	-4.629897	-2.934736				
H	0.576747	-4.668976	-0.488031				

INT-1 (T₁)

Gibbs Free Energy = -1907.334312

Hartree

C	-1.309268	0.711243	1.235033
C	-2.602302	0.811129	0.466229
C	-2.638969	0.806209	-1.040523
C	-1.504932	1.665867	-1.603541
C	-0.126204	1.401311	-0.971210
C	-0.133778	0.465723	0.244316
C	-1.349415	-0.499588	2.194079
C	-2.251648	-1.697061	1.915288
C	-4.991991	0.246257	0.239676
C	-3.878433	0.740593	1.152563
C	-2.396208	-2.282874	0.476574
C	-3.283989	-1.555415	-0.494772
C	-4.710450	-1.266259	-0.116413
C	-2.730743	-0.699329	-1.599204
O	-4.043135	0.948787	2.350837
O	-3.843756	1.474679	-1.508223
C	-0.583796	-0.521236	3.292585
C	-5.048723	1.119008	-1.001751
O	-6.061220	1.512621	-1.511592
H	-5.961717	0.329162	0.744240
C	-1.100014	2.053001	1.980678
O	1.092230	0.555272	0.939433
C	2.133917	-1.584262	-0.674670
Si	2.554098	-0.125696	0.449554

C	3.536416	1.184579	-0.481203	H	4.980821	-1.837759	1.001068
C	2.382305	-1.552678	-2.060117	H	5.502405	-1.251468	2.596776
C	1.984650	-2.601787	-2.895213	H	5.498525	-0.143591	1.205728
C	1.319733	-3.708238	-2.361406	H	2.499345	0.978755	3.223096
C	1.047523	-3.755247	-0.990751	H	4.091426	0.485379	3.856846
C	1.447648	-2.704898	-0.161382	H	3.988988	1.540138	2.426126
C	4.657094	0.870186	-1.274550	H	-0.628236	-1.415776	-1.681206
C	5.410367	1.870897	-1.894686	H	-1.760373	-2.237910	-2.749890
C	5.061705	3.214512	-1.726756	H	-1.195172	-0.607170	-3.151867
C	3.960725	3.549842	-0.933765				
C	3.209832	2.544055	-0.318944				
C	3.505822	-0.575464	2.041063				
C	2.841100	-1.733262	2.805432				
C	4.950071	-0.970407	1.682296				
C	3.518807	0.682032	2.932907				
C	-1.502196	-1.257884	-2.321065				
H	-1.812528	2.703474	-1.408933				
H	-1.482512	1.555153	-2.696720				
H	0.566065	0.972294	-1.711403				
H	0.319710	2.354780	-0.657850				
H	-0.251031	-0.563320	-0.116638				
H	-1.892539	-2.515892	2.557260				
H	-3.259665	-1.460128	2.292575				
H	-1.401846	-2.452561	0.040289				
H	-2.828843	-3.290843	0.628287				
H	-5.392433	-1.532790	-0.944584				
H	-5.010716	-1.867689	0.754865				
H	-3.509095	-0.605802	-2.374899	O	-4.041067	0.950782	2.356445
H	-0.571118	-1.395896	3.949261	O	-3.843188	1.468355	-1.508086
H	0.041997	0.319821	3.588720	C	-0.583770	-0.542429	3.281257
H	-1.877632	2.179473	2.743566	C	-5.046758	1.121215	-0.993556
H	-0.106081	2.075258	2.445299	O	-6.060199	1.519750	-1.497632
H	-1.157843	2.894720	1.273696	H	-5.953274	0.320377	0.751316
H	2.885414	-0.689400	-2.501277	C	-1.094669	2.048254	1.997784
H	2.190840	-2.551066	-3.967509	O	1.093706	0.559398	0.942294
H	1.006528	-4.528524	-3.012292	C	2.131916	-1.583962	-0.670230
H	0.514410	-4.610119	-0.566880	Si	2.554236	-0.123203	0.450111
H	1.200767	-2.751161	0.900540	C	3.535119	1.185171	-0.484843
H	4.954998	-0.173149	-1.410905	C	2.380493	-1.557640	-2.055695
H	6.273891	1.601909	-2.508782	C	1.983235	-2.610047	-2.886837
H	5.650264	3.998727	-2.210011	C	1.318536	-3.714590	-2.348890
H	3.687342	4.598810	-0.791664	C	1.045927	-3.756311	-0.978122
H	2.356900	2.816876	0.306938	C	1.445614	-2.702708	-0.152700
H	3.334959	-1.869714	3.784374	C	4.654100	0.869354	-1.280014
H	1.774305	-1.541288	2.993300	C	5.406072	1.868954	-1.903520
H	2.932919	-2.685563	2.261175	C	5.057815	3.212870	-1.737213

C	3.958559	3.549631	-0.942439	
C	3.208948	2.544962	-0.324272	Compound 21 (S_0)
C	3.508951	-0.570965	2.040563	Gibbs Free Energy = -1907.408522
C	2.848365	-1.730245	2.806220	Hartree
C	4.953484	-0.962940	1.679500	C -1.353704 0.598795 1.193894
C	3.520773	0.686677	2.932205	C -2.665181 0.393587 0.398033
C	-1.489367	-1.256507	-2.313993	C -2.668743 0.833352 -1.119960
H	-1.816091	2.702123	-1.430553	C -1.537282 1.745203 -1.548477
H	-1.478666	1.531918	-2.695677	C -0.157754 1.384608 -0.962999
H	0.577244	0.998821	-1.699973	C -0.156269 0.398964 0.217577
H	0.303868	2.372022	-0.640916	C -1.281752 -0.484219 2.281209
H	-0.249999	-0.554394	-0.118350	C -2.017977 -1.797516 2.044893
H	-1.923194	-2.512206	2.548465	C -5.057074 0.254034 0.224777
H	-3.276327	-1.443791	2.273426	C -3.945006 0.838954 1.087686
H	-1.412621	-2.462465	0.036073	C -2.210899 -2.173127 0.570455
H	-2.842406	-3.293596	0.626925	C -3.003812 -1.070063 -0.117795
H	-5.403294	-1.509588	-0.961663	C -4.538984 -1.194346 0.077401
H	-5.020232	-1.878489	0.730218	C -2.717058 -0.650657 -1.593338
H	-3.493526	-0.590580	-2.383104	O -4.093667 1.440503 2.120121
H	-0.573843	-1.423715	3.929108	O -3.883758 1.500818 -1.522995
H	0.048808	0.291698	3.582632	C -0.601597 -0.303687 3.418988
H	-1.872421	2.169325	2.761400	C -5.090366 1.066922 -1.073040
H	-0.100772	2.062545	2.462767	O -6.099392 1.383847 -1.636743
H	-1.150099	2.897349	1.299438	H -6.047914 0.329523 0.685559
H	2.883532	-0.695972	-2.500088	C -1.255825 2.023150 1.779063
H	2.189613	-2.563356	-3.959280	O 1.064050 0.505107 0.926075
H	1.005692	-4.537501	-2.996628	C 2.132880 -1.597828 -0.721096
H	0.512817	-4.609653	-0.551189	Si 2.531972 -0.166319 0.448105
H	1.198267	-2.744837	0.909257	C 3.534188 1.152121 -0.449922
H	4.951787	-0.174196	-1.415112	C 2.343350 -1.491620 -2.109596
H	6.268290	1.598834	-2.518950	C 1.952285 -2.508603 -2.986281
H	5.645373	3.996217	-2.223087	C 1.331756 -3.658483 -2.492387
H	3.685541	4.598858	-0.801553	C 1.099449 -3.781479 -1.119296
H	2.357320	2.818859	0.302857	C 1.493876 -2.762865 -0.248433
H	3.344081	-1.865114	3.784432	C 4.660068 0.837547 -1.235721
H	1.781353	-1.541199	2.995620	C 5.428485 1.838998 -1.835680
H	2.941672	-2.682462	2.262079	C 5.089173 3.183386 -1.655236
H	4.984862	-1.830201	0.998183	C 3.982172 3.518570 -0.870580
H	5.507795	-1.242974	2.593090	C 3.216414 2.511989 -0.275583
H	5.499521	-0.135022	1.202115	C 3.456592 -0.643022 2.046914
H	2.501230	0.981035	3.224548	C 2.747443 -1.777146 2.807390
H	4.095895	0.491626	3.854922	C 4.893005 -1.078362 1.704640
H	3.987676	1.545891	2.424263	C 3.493552 0.615424 2.937146
H	-0.623583	-1.424733	-1.665940	C -1.559173 -1.260303 -2.371027
H	-1.744559	-2.230128	-2.758632	H -1.829125 2.757564 -1.232330
H	-1.171258	-0.596344	-3.132773	H -1.508672 1.766365 -2.648765

H	0.497293	0.968462	-1.743807	C	-0.161105	0.533507	0.227549
H	0.334249	2.304100	-0.620730	C	-1.329129	-0.566126	2.195038
H	-0.226460	-0.620539	-0.176567	C	-2.236398	-1.760823	1.964880
H	-1.500993	-2.605449	2.585421	C	-5.039712	0.269486	0.166060
H	-3.017078	-1.719787	2.514314	C	-3.932875	0.666479	1.133564
H	-1.236294	-2.325235	0.087289	C	-2.368947	-2.250424	0.517469
H	-2.745759	-3.134771	0.491505	C	-3.151905	-1.338455	-0.399726
H	-5.011979	-1.747578	-0.747965	C	-4.662356	-1.198822	-0.144141
H	-4.769749	-1.726158	1.013846	C	-2.759815	-1.164821	-1.750865
H	-3.611738	-0.791305	-2.220062	O	-4.101594	0.770928	2.337778
H	-0.542927	-1.098688	4.168652	O	-3.841760	1.670166	-1.463233
H	-0.087981	0.628839	3.652931	C	-0.522232	-0.570580	3.264211
H	-1.921196	2.143625	2.638647	C	-5.052017	1.168466	-1.061523
H	-0.220531	2.226688	2.083137	O	-6.040272	1.470991	-1.669935
H	-1.539872	2.776400	1.029761	H	-6.031289	0.342991	0.629227
H	2.812536	-0.594249	-2.518942	C	-1.250422	1.969584	2.022138
H	2.128162	-2.398706	-4.059547	O	1.059873	0.526432	0.940752
H	1.023531	-4.454038	-3.175609	C	2.094604	-1.637102	-0.665927
H	0.603322	-4.672049	-0.724811	Si	2.511178	-0.155379	0.431518
H	1.280656	-2.871827	0.816181	C	3.492859	1.139970	-0.525753
H	4.947605	-0.207166	-1.384193	C	2.343832	-1.638936	-2.051361
H	6.295689	1.570027	-2.444619	C	1.998473	-2.732606	-2.852373
H	5.689142	3.968323	-2.123081	C	1.386253	-3.851898	-2.283513
H	3.715437	4.568055	-0.719992	C	1.105889	-3.863469	-0.913502
H	2.358219	2.784530	0.343295	C	1.451768	-2.767547	-0.119028
H	3.219460	-1.918303	3.796467	C	4.592053	0.809157	-1.342303
H	1.682734	-1.553714	2.973677	C	5.353090	1.798467	-1.971353
H	2.826880	-2.736522	2.273662	C	5.035045	3.147690	-1.789138
H	4.907668	-1.949384	1.027618	C	3.956963	3.499686	-0.972330
H	5.429954	-1.368544	2.625500	C	3.198203	2.505226	-0.349075
H	5.467252	-0.268402	1.229060	C	3.495081	-0.585271	2.011406
H	2.478659	0.941385	3.211383	C	2.867931	-1.750975	2.795341
H	4.045965	0.402422	3.869827	C	4.939315	-0.958930	1.629319
H	3.997336	1.458082	2.436951	C	3.505159	0.676674	2.897162
H	-0.587680	-1.209065	-1.869312	C	-1.484481	-1.571130	-2.399465
H	-1.761076	-2.324728	-2.567523	H	-1.596643	2.867542	-1.914692
H	-1.453854	-0.762050	-3.347489	H	-1.363446	1.256471	-2.553053
				H	0.696929	1.544399	-1.468346
				H	0.044847	2.613307	-0.235785
				H	-0.270972	-0.417879	-0.314412
				H	-1.863357	-2.592657	2.581564
				H	-3.236802	-1.522805	2.361964
				H	-1.368787	-2.440424	0.105883
				H	-2.881589	-3.232962	0.529676
				H	-5.239265	-1.585397	-1.001678
				H	-4.944829	-1.799308	0.733862

TS-1' (T₁)

Gibbs Free Energy = -1907.311693

Hartree

C	-1.354198	0.637853	1.232355
C	-2.645667	0.672813	0.424785
C	-2.647075	1.359329	-0.854302
C	-1.448820	1.817634	-1.601369
C	-0.154800	1.683174	-0.786446

H	-3.502424	-0.722230	-2.422949	O	-4.091228	1.029987	2.322861
H	-0.495150	-1.430606	3.939579	O	-3.879021	1.760729	-1.376005
H	0.124228	0.268954	3.516025	C	-0.524551	-0.577472	3.294976
H	-1.979319	1.967795	2.840533	C	-5.089260	1.256838	-0.988472
H	-0.236512	2.096349	2.425487	O	-6.076814	1.547868	-1.600327
H	-1.466710	2.829597	1.371572	H	-6.066628	0.329545	0.670114
H	2.809949	-0.769204	-2.519519	C	-1.308391	1.911639	1.968732
H	2.206555	-2.707696	-3.925273	O	1.052135	0.492203	0.941431
H	1.118115	-4.708837	-2.906800	C	2.114492	-1.645434	-0.676579
H	0.610148	-4.727097	-0.462643	Si	2.513636	-0.167561	0.431185
H	1.203433	-2.789492	0.943038	C	3.484821	1.145060	-0.513089
H	4.868818	-0.238455	-1.488514	C	2.382216	-1.645011	-2.058633
H	6.199310	1.515904	-2.603200	C	2.040959	-2.734764	-2.866680
H	5.629675	3.923045	-2.279255	C	1.414448	-3.851440	-2.308766
H	3.707457	4.552903	-0.818131	C	1.116541	-3.865244	-0.942719
H	2.362333	2.792303	0.292464	C	1.458916	-2.774248	-0.140943
H	3.380549	-1.867484	3.767193	C	4.593440	0.831720	-1.323922
H	1.800409	-1.582364	2.998406	C	5.344694	1.833141	-1.945523
H	2.973218	-2.705528	2.257664	C	5.007213	3.177379	-1.761503
H	4.971910	-1.827034	0.949098	C	3.919825	3.512208	-0.949875
H	5.509699	-1.230471	2.535526	C	3.171218	2.505661	-0.333746
H	5.468045	-0.125406	1.142712	C	3.493468	-0.599252	2.012671
H	2.487299	0.958060	3.206881	C	2.865237	-1.769590	2.788609
H	4.100686	0.494123	3.809440	C	4.939772	-0.967539	1.633677
H	3.950181	1.539858	2.376571	C	3.496717	0.658953	2.903670
H	-0.732850	-1.966640	-1.708732	C	-1.552900	-1.810832	-2.409783
H	-1.676134	-2.351291	-3.159988	H	-1.584463	2.860099	-1.932972
H	-1.029324	-0.729190	-2.951623	H	-1.481996	1.173933	-2.417776
				H	0.654192	1.565101	-1.465146
				H	0.034274	2.594460	-0.181465
INT-1' (T₁)				H	-0.247583	-0.435852	-0.353393
Gibbs Free Energy = -1907.325021				H	-1.825438	-2.668851	2.506183
Hartree				H	-3.212210	-1.595549	2.355374
C	-1.369529	0.560581	1.216361	H	-1.290502	-2.283749	0.071385
C	-2.674062	0.464631	0.366481	H	-2.856101	-3.054644	0.296290
C	-2.691766	1.517736	-0.708096	H	-5.038454	-1.462169	-1.091783
C	-1.490843	1.837055	-1.529876	H	-4.829321	-1.777795	0.641681
C	-0.178238	1.681781	-0.755171	H	-3.337482	-0.492896	-2.459569
C	-0.164575	0.498996	0.220288	H	-0.499617	-1.424843	3.986592
C	-1.313729	-0.603096	2.214588	H	0.111739	0.273418	3.536185
C	-2.203718	-1.797613	1.950131	H	-1.952835	1.890819	2.852398
C	-5.070311	0.320423	0.214063	H	-0.274316	2.113801	2.279380
C	-3.961653	0.704991	1.171847	H	-1.641354	2.741582	1.328985
C	-2.302851	-2.114533	0.462101	H	2.858023	-0.776375	-2.518849
C	-2.999947	-0.990201	-0.324922	H	2.262065	-2.708112	-3.936915
C	-4.566404	-1.086248	-0.173351	H	1.148169	-4.704449	-2.938207

H	0.609456	-4.726998	-0.500924	Si	2.503536	-0.164078	0.425405
H	1.197208	-2.797345	0.918053	C	3.478572	1.144389	-0.521638
H	4.885390	-0.211506	-1.471763	C	2.370581	-1.650006	-2.061236
H	6.198306	1.563862	-2.573216	C	2.046140	-2.750734	-2.861359
H	5.593863	3.962170	-2.246187	C	1.434160	-3.871842	-2.295952
H	3.654962	4.561444	-0.794130	C	1.131899	-3.878036	-0.930934
H	2.328482	2.779659	0.304300	C	1.458415	-2.776387	-0.136972
H	3.377301	-1.893177	3.759937	C	4.577368	0.824567	-1.343266
H	1.797774	-1.600564	2.992244	C	5.334129	1.821724	-1.965064
H	2.969384	-2.720690	2.244568	C	5.012546	3.168300	-1.770368
H	4.976669	-1.833254	0.950659	C	3.935835	3.509639	-0.947323
H	5.508772	-1.240211	2.540448	C	3.181683	2.507314	-0.331135
H	5.467204	-0.130667	1.151287	C	3.489199	-0.597576	2.003384
H	2.476630	0.937114	3.209093	C	2.861740	-1.764403	2.785285
H	4.087706	0.473888	3.818446	C	4.932335	-0.971578	1.617712
H	3.942792	1.525110	2.388948	C	3.501539	0.661837	2.892652
H	-0.562331	-1.543609	-2.000214	C	-1.644953	-1.975687	-2.421449
H	-1.642680	-2.902964	-2.253758	H	-1.598960	2.979422	-1.817877
H	-1.514326	-1.639051	-3.495388	H	-1.473088	1.325296	-2.395957
				H	0.648410	1.656871	-1.420225
				H	0.035487	2.641597	-0.098998
TS-2' (T₁)				H	-0.261633	-0.379646	-0.380451
Gibbs Free Energy = -1907.323189				H	-1.827540	-2.662595	2.500259
Hartree				H	-3.214596	-1.590763	2.335656
C	-1.375031	0.573903	1.227397	H	-1.252321	-2.253342	0.080878
C	-2.673202	0.474241	0.368337	H	-2.815873	-3.039052	0.270367
C	-2.698648	1.554752	-0.679522	H	-4.983061	-1.460389	-1.152421
C	-1.495107	1.936281	-1.472115	H	-4.799252	-1.812620	0.579251
C	-0.181890	1.751286	-0.704830	H	-3.032803	-0.246719	-2.438947
C	-0.170333	0.534579	0.227608	H	-0.498222	-1.427408	3.984259
C	-1.314113	-0.596157	2.217945	H	0.112463	0.273506	3.543353
C	-2.200493	-1.789699	1.943288	H	-1.979736	1.876069	2.876498
C	-5.065015	0.292953	0.189954	H	-0.299938	2.122976	2.317668
C	-3.973129	0.687531	1.164151	H	-1.667297	2.752431	1.368616
C	-2.273518	-2.095969	0.452459	H	2.835931	-0.778921	-2.527390
C	-2.963441	-0.968416	-0.338878	H	-2.268793	-2.729218	-3.931381
C	-4.534872	-1.099231	-0.216387	H	1.180925	-4.733326	-2.919175
C	-2.604884	-1.021012	-1.799798	H	0.634309	-4.742425	-0.483553
O	-4.119399	1.011127	2.313313	H	1.195908	-2.795324	0.921852
O	-3.880429	1.779665	-1.364323	H	4.857688	-0.220576	-1.499247
C	-0.524094	-0.575935	3.297774	H	6.179715	1.547112	-2.601241
C	-5.086586	1.245524	-1.000064	H	5.603421	3.949758	-2.255300
O	-6.070622	1.526248	-1.621521	H	3.683748	4.560643	-0.782577
H	-6.066247	0.280513	0.635286	H	2.347997	2.786996	0.316170
C	-1.330161	1.915929	1.997210	H	3.377283	-1.885593	3.755058
O	1.047530	0.499840	0.944719	H	1.795364	-1.593065	2.992417

H	2.962335	-2.717432	2.244050	C	5.112525	3.150389	-1.622763	
H	4.962685	-1.838364	0.935739	C	4.045868	3.503630	-0.791147	
H	5.504727	-1.245078	2.522083	C	3.260875	2.509354	-0.200519	
H	5.460430	-0.137440	1.131409	C	3.436855	-0.726331	2.018977	
H	2.484022	0.944381	3.202572	C	2.688959	-1.834099	2.782611	
H	4.096229	0.475557	3.804770	C	4.839712	-1.227321	1.629722	
H	3.948575	1.525587	2.374782	C	3.563446	0.513453	2.927521	
H	-0.591956	-1.766652	-2.147918	C	-3.094242	-1.389928	-2.827793	
H	-1.820265	-3.023851	-2.122097	H	-1.552975	2.551395	-2.187713	
H	-1.702226	-1.926393	-3.519028	H	-1.326941	0.833869	-2.484116	
				H	0.723456	1.414426	-1.489615	
				H	0.016768	2.554873	-0.354374	
INT-2' (T₁)				H	-0.233963	-0.480350	-0.237939	
Gibbs Free Energy = -1907.325025				H	-1.785254	-2.360875	2.957794	
Hartree				H	-3.190366	-1.366367	2.592051	
C	-1.375877	0.653955	1.209428	H	-1.149049	-2.320113	0.507747	
C	-2.637877	0.385334	0.333032	H	-2.698045	-3.109720	0.786194	
C	-2.645607	1.277698	-0.878586	H	-4.860702	-1.862552	-0.904539	
C	-1.423002	1.583340	-1.673822	H	-4.695998	-1.877522	0.854338	
C	-0.142983	1.578651	-0.832363	H	-1.287776	-1.688380	-1.605631	
C	-0.148086	0.499089	0.254125	H	-0.486300	-0.893261	4.238936	
C	-1.306873	-0.353758	2.364471	H	0.096151	0.732734	3.545611	
C	-2.160781	-1.596012	2.261137	H	-2.069700	2.165474	2.629889	
C	-5.014471	0.105513	0.093479	H	-3.973238	0.680535	1.033355	
C	-3.973238	0.680535	1.033355	H	-1.731112	2.818622	1.016810	
C	-2.182750	-2.135881	0.835970	H	-2.875052	-1.171048	-0.153327	
C	-2.875052	-1.171048	-0.153327	H	-4.432311	-1.316793	-0.054596	
C	-4.432311	-1.316793	-0.054596	H	-2.355995	-1.461787	-1.535530	
C	-2.355995	-1.461787	-1.535530	H	O	-4.175487	1.168338	2.114312
O	-4.175487	1.168338	2.114312	H	O	-3.805595	1.364419	-1.628557
O	-3.805595	1.364419	-1.628557	H	C	-0.525044	-0.155403	3.432142
C	-0.525044	-0.155403	3.432142	H	C	-5.008177	0.850758	-1.235115
C	-5.008177	0.850758	-1.235115	H	O	-5.969787	0.984866	-1.937076
O	-5.969787	0.984866	-1.937076	H	H	-6.032601	0.132357	0.497830
H	-6.032601	0.132357	0.497830	H	C	-1.393752	2.095044	1.772482
C	-1.393752	2.095044	1.772482	H	O	1.062162	0.540569	0.983258
O	1.062162	0.540569	0.983258	H	C	2.013318	-1.518814	-0.774306
C	2.013318	-1.518814	-0.774306	H	Si	2.499101	-0.167369	0.456469
Si	2.499101	-0.167369	0.456469	H	C	3.522234	1.145105	-0.425364
C	3.522234	1.145105	-0.425364	H	C	2.021887	-1.250495	-2.157471
C	2.021887	-1.250495	-2.157471	H	C	1.514284	-2.168643	-3.081889
C	1.514284	-2.168643	-3.081889	H	C	0.986872	-3.385926	-2.642390
C	0.986872	-3.385926	-2.642390	H	C	0.967997	-3.675635	-1.275099
C	0.967997	-3.675635	-1.275099	H	C	1.471220	-2.750707	-0.356175
C	1.471220	-2.750707	-0.356175	H	C	4.602858	0.810999	-1.263933
C	4.602858	0.810999	-1.263933	H	C	5.390376	1.800438	-1.859022
C	5.390376	1.800438	-1.859022	H				

H	-2.847563	-2.259113	-3.463565	H	-1.486120	1.835053	-2.605290
Compound 21' (S_0)				H	0.513281	1.042525	-1.683855
Gibbs Free Energy	=	-1907.408522		H	0.328452	2.367840	-0.551041
Hartree				H	-0.228845	-0.568394	-0.150249
C	-1.371581	0.636789	1.227658	H	-1.608975	-2.517266	2.747741
C	-2.664837	0.398740	0.409019	H	-3.088793	-1.588647	2.542375
C	-2.617467	0.813019	-1.116414	H	-1.191109	-2.327163	0.242333
C	-1.530018	1.790631	-1.505612	H	-2.720990	-3.125549	0.604617
C	-0.153069	1.447620	-0.907134	H	-4.910785	-1.784016	-0.845087
C	-0.160653	0.445485	0.261574	H	-4.741972	-1.788008	0.917900
C	-1.299457	-0.426924	2.335591	H	-1.405247	-0.914931	-1.625781
C	-2.067594	-1.724393	2.137175	H	-0.537041	-1.016840	4.221164
C	-5.045299	0.198303	0.150742	H	-0.050566	0.687149	3.656576
C	-3.975852	0.822504	1.043954	H	-1.994284	2.181429	2.647307
C	-2.189148	-2.161627	0.673000	H	-0.284044	2.289766	2.127006
C	-2.942416	-1.081202	-0.097407	H	-1.588982	2.812287	1.043127
C	-4.483307	-1.232097	0.003735	H	2.485536	-0.427384	-2.510519
C	-2.473558	-0.678528	-1.524971	H	1.607639	-2.116899	-4.083626
O	-4.174368	1.440597	2.058576	H	0.629537	-4.246139	-3.223746
O	-3.845587	1.374247	-1.616084	H	0.542596	-4.657898	-0.763019
C	-0.592246	-0.237125	3.455449	H	1.393849	-2.963988	0.810037
C	-5.060977	0.977367	-1.161385	H	4.819841	-0.270358	-1.474017
O	-6.058065	1.276283	-1.755795	H	6.189712	1.472196	-2.568737
H	-6.050349	0.247851	0.583229	H	5.695877	3.885914	-2.179497
C	-1.309275	2.067338	1.801782	H	3.815727	4.538430	-0.675417
O	1.058023	0.537183	0.974592	H	2.438455	2.790572	0.422969
C	2.030926	-1.563863	-0.720655	H	3.198487	-1.923863	3.814445
Si	2.502833	-0.169852	0.468360	H	1.662225	-1.545390	2.996284
C	3.515169	1.128361	-0.446348	H	2.783029	-2.756468	2.307476
C	2.068190	-1.355798	-2.113745	H	4.838378	-2.024454	0.998675
C	1.569029	-2.307918	-3.007943	H	5.414443	-1.449787	2.580459
C	1.020625	-3.499977	-2.527228	H	5.444671	-0.357800	1.176978
C	0.974451	-3.730986	-1.149335	H	2.538159	0.937583	3.227200
C	1.470043	-2.772600	-0.261031	H	4.102266	0.353897	3.854057
C	4.586677	0.782837	-1.292101	H	4.055246	1.408838	2.420909
C	5.364898	1.763769	-1.913082	H	-3.079609	-2.276948	-2.851504
C	5.088401	3.116980	-1.694990	H	-4.251532	-0.936837	-2.798854
C	4.033930	3.481982	-0.853112	H	-2.725953	-0.740352	-3.672873
C	3.258015	2.496022	-0.237160	Compound 24 (S_0)			
C	3.445967	-0.676671	2.045789	Gibbs Free Energy	=	-2321.423477	
C	2.722202	-1.787875	2.826725	Hartree			
C	4.862234	-1.150522	1.671598	C	0.377808	-2.521089	-0.534228
C	3.537291	0.581927	2.932510	C	1.227752	-1.252911	-0.360717
C	-3.180376	-1.182196	-2.771912	C	1.079645	-0.423948	0.704947
H	-1.862688	2.785106	-1.172002	C	0.043503	-0.610820	1.782180

C	-0.716022	-1.933617	1.707717	H	-1.460173	-3.338030	0.249146
C	-0.961052	-2.352422	0.264292	H	1.913433	-4.544309	1.807549
C	1.105832	-3.777997	-0.006067	H	1.888546	-2.782197	1.758547
C	2.085352	-3.674664	1.153347	H	3.753295	-4.380453	-0.052867
C	3.175771	-2.019972	-1.888888	H	4.142718	-4.083386	1.637352
C	2.232556	-0.921639	-1.413544	H	5.138142	-2.790303	-1.440713
C	3.593494	-3.670886	0.775085	H	4.957386	-1.052035	-1.125960
C	4.190719	-2.320179	0.431061	H	4.872851	-0.440550	1.029426
C	4.454619	-2.026445	-1.026045	H	1.354732	-5.881458	-0.121872
C	4.466541	-1.399323	1.369373	H	0.201997	-5.151077	-1.379714
O	2.345429	0.205093	-1.868338	H	-0.373611	-1.740702	-2.434494
O	1.911214	0.611093	0.919999	H	0.813017	-3.054086	-2.630174
C	0.870242	-4.990132	-0.532775	H	-0.850788	-3.409571	-2.123553
H	2.703222	-3.009918	-1.838864	H	-4.252370	-1.826240	1.870525
H	0.534240	-0.492261	2.761721	H	-4.868781	-1.260475	4.188954
H	-0.659879	0.236085	1.707584	H	-4.458978	1.036618	5.074592
H	3.438159	-1.807712	-2.936256	H	-3.429470	2.764314	3.594937
C	-0.023562	-2.692332	-2.019629	H	-2.813322	2.202419	1.272230
O	-1.768601	-1.433746	-0.426793	H	-3.963859	2.538576	-0.927801
C	-3.492960	0.147379	1.374979	H	-2.991500	4.451791	-2.145021
Si	-2.975199	-0.293609	-0.388163	H	-0.736239	4.264045	-3.194079
C	-2.267722	1.217710	-1.257733	H	0.548451	2.114551	-2.986442
C	-4.075854	-0.809950	2.230191	H	-0.406105	0.230874	-1.739743
C	-4.421404	-0.497129	3.546854	H	-5.544127	-2.879491	-1.561757
C	-4.191354	0.789861	4.043818	H	-3.943001	-3.078760	-0.809094
C	-3.616501	1.756285	3.215235	H	-5.286185	-2.342136	0.107830
C	-3.273399	1.435937	1.897872	H	-4.694686	-1.616619	-3.503990
C	-2.974715	2.430174	-1.381335	H	-3.023606	-1.830002	-2.920873
C	-2.428079	3.517932	-2.068270	H	-3.625724	-0.203396	-3.309758
C	-1.162649	3.412994	-2.656313	H	-6.457286	-0.504507	-1.985898
C	-0.445662	2.218928	-2.546432	H	-5.999211	0.079454	-0.366344
C	-0.994538	1.139148	-1.850349	H	-5.392203	0.906245	-1.824295
C	-4.411459	-1.019266	-1.421550	H	5.049488	-1.070896	3.423172
C	-4.811815	-2.404923	-0.883696	H	4.108211	-2.564394	3.172784
C	-3.906199	-1.172928	-2.869525	H	3.308300	-0.979768	3.134373
C	-5.627919	-0.079074	-1.392053	H	-0.519824	2.498688	0.315538
C	4.226351	-1.521053	2.844100	H	0.052679	4.004018	1.059699
Si	1.855626	2.307545	1.017615	H	-0.392197	2.620387	2.091722
C	2.815528	2.751823	2.608476	H	2.070605	2.849434	-1.383252
C	0.080927	2.905251	1.139962	H	2.888661	4.085819	-0.379777
C	2.700348	3.006011	-0.497424	H	3.656609	2.495212	-0.684034
C	4.297647	2.369081	2.454628	H	4.858395	2.607841	3.376874
C	2.213845	2.002066	3.809263	H	4.416839	1.293692	2.260934
C	2.701967	4.269929	2.844666	H	4.777957	2.914511	1.626369
H	-0.153201	-2.734408	2.207425	H	1.147523	2.241188	3.954154
H	-1.673260	-1.848971	2.239776	H	2.742120	2.273966	4.741088

H	2.299049	0.911691	3.686114	C	-6.151371	-0.733801	-0.178185
H	3.269315	4.561901	3.746990	C	-4.590353	-2.160848	-1.567481
H	3.110825	4.850479	2.001190	C	3.164150	-1.461962	2.698384
H	1.657540	4.587295	2.996459	Si	4.555814	1.302585	-0.397677
				C	4.778617	2.745447	0.840454
Compound 24 (T_1)				C	4.617132	1.891635	-2.177025
Gibbs Free Energy = -2321.338923 Hartree				C	5.838719	-0.025896	-0.081785
				C	3.807240	3.892255	0.512592
C	0.019472	-1.139253	-1.394389	C	6.226574	3.262269	0.742890
C	1.511631	-0.821643	-1.306922	C	4.504124	2.249608	2.271167
C	1.920934	0.542164	-0.868218	H	-0.969855	2.223862	-1.510649
C	1.125867	1.755589	-1.210797	H	-0.291528	1.225225	-2.795991
C	-0.278183	1.394353	-1.708488	H	-0.649619	0.296429	0.091267
C	-0.794172	0.145020	-0.993405	H	-0.663609	-2.283826	1.688274
C	-0.389226	-2.252596	-0.423934	H	0.649272	-1.229710	1.176384
C	0.174548	-2.203038	0.982620	H	0.795154	-4.281727	0.926198
C	2.355485	-3.227655	-1.704814	H	1.198411	-3.436607	2.417802
C	2.547051	-1.720999	-1.759988	H	2.841035	-4.876082	-0.383903
C	1.185504	-3.329665	1.321045	H	4.132800	-3.668362	-0.555187
C	2.604105	-3.109274	0.837236	H	4.451678	-2.167998	1.056677
C	3.045221	-3.791285	-0.438560	H	-1.575240	-3.955486	-0.016810
C	3.452062	-2.290301	1.483924	H	-1.682642	-3.313822	-1.756236
O	3.670435	-1.265573	-2.066312	H	0.128727	-2.456487	-3.147898
O	2.994212	0.669978	-0.070263	H	-1.393044	-1.526810	-3.008166
C	-1.257697	-3.216060	-0.758165	H	0.101259	-0.730717	-3.548290
H	1.296026	-3.508599	-1.702501	H	-3.982692	-2.542240	1.243801
H	1.050252	2.364803	-0.289474	H	-3.291005	-3.407937	3.444075
H	1.643763	2.406891	-1.945292	H	-1.892956	-2.008001	4.964769
H	2.828139	-3.665324	-2.598317	H	-1.214359	0.286846	4.254313
C	-0.305449	-1.489329	-2.865570	H	-1.944652	1.176227	2.069946
O	-2.161148	-0.059524	-1.278368	H	-3.144779	2.499874	-1.954146
C	-3.019296	-0.612383	1.473298	H	-3.721493	4.895996	-1.707777
Si	-3.460033	0.097161	-0.220515	H	-4.764667	5.721182	0.402703
C	-3.833729	1.931536	0.018998	H	-5.227707	4.123412	2.261646
C	-3.385146	-1.903861	1.895966	H	-4.634291	1.732890	2.024637
C	-2.990111	-2.401917	3.140469	H	-6.078966	-0.367867	-2.930517
C	-2.207021	-1.617699	3.993268	H	-5.569580	1.129538	-2.113801
C	-1.827754	-0.333250	3.595469	H	-4.386177	0.175425	-3.044019
C	-2.236306	0.161368	2.353598	H	-6.406506	0.283457	0.161399
C	-3.592406	2.850079	-1.020921	H	-5.989526	-1.353747	0.717410
C	-3.921439	4.201436	-0.887440	H	-7.034162	-1.136567	-0.706444
C	-4.508033	4.664031	0.294594	H	-3.741755	-2.163998	-2.266488
C	-4.766317	3.768513	1.336200	H	-4.329303	-2.827215	-0.732374
C	-4.431481	2.418093	1.196919	H	-5.458708	-2.605375	-2.086590
C	-4.928189	-0.729572	-1.114275	H	3.032533	-0.406569	2.403111
C	-5.254306	0.106580	-2.369108	H	4.003929	-1.490339	3.413301

H	2.252353	-1.774494	3.228833	C	3.490215	-2.453428	-2.613369
H	5.632891	2.232235	-2.436077	C	3.524422	-1.277229	-1.858402
H	3.920575	2.720845	-2.373920	C	5.248994	1.519073	-1.480221
H	4.355186	1.042385	-2.825774	C	5.753512	2.583786	-2.232910
H	6.843553	0.349706	-0.335748	C	5.202212	3.860603	-2.094622
H	5.852345	-0.345548	0.971164	C	4.152893	4.066349	-1.193965
H	5.615773	-0.893644	-0.718802	C	3.656230	2.997721	-0.442719
H	2.757401	3.565129	0.573641	C	4.685589	0.318598	2.108853
H	3.935070	4.723785	1.229427	C	4.774026	1.773352	2.614264
H	3.974184	4.300601	-0.497223	C	4.118198	-0.547159	3.245315
H	6.960075	2.486580	1.015557	C	6.093200	-0.173578	1.722391
H	6.378637	4.114409	1.430154	C	-0.970063	1.695578	-0.997313
H	6.472027	3.614355	-0.273129	H	-0.745443	1.621532	-2.078260
H	4.667677	3.063605	3.001132	H	-1.505732	2.655451	-0.897138
H	3.464414	1.904033	2.381726	O	-3.208359	0.786496	-0.888604
H	5.165297	1.415075	2.555928	Si	-4.444865	1.594161	-0.032208
				C	-5.330733	2.630236	-1.362083
				C	-3.682252	2.646397	1.324108
TS-3 (T₁)				C	-5.586586	0.319535	0.739417
Gibbs Free Energy	=	-2321.322759		C	-6.520491	3.376501	-0.732518
Hartree				C	-5.831350	1.694387	-2.477759
C	0.362648	-1.768311	1.472734	C	-4.340193	3.645380	-1.960310
C	0.197629	-2.973409	0.563089	C	-0.028936	-0.626993	-3.218310
C	0.143052	-2.737712	-0.951095	C	-0.585005	0.423511	2.354605
C	-1.148237	-2.125071	-1.431890	H	-0.722559	-3.497981	0.872456
C	-1.503501	-0.545939	0.245368	H	1.019758	-3.671408	0.777751
C	-0.229686	-0.401476	1.092046	H	1.011676	-2.154638	-1.276947
C	1.026558	-1.939962	2.622354	H	0.253256	-3.722408	-1.447844
C	-2.551438	-1.464396	0.746583	H	1.133130	-1.153326	3.366249
C	-2.421393	-2.930146	-1.166890	H	1.476054	-2.906731	2.868445
O	-2.613449	-1.824343	1.918842	H	-2.874910	-3.238246	-2.125538
C	-1.195954	-1.210280	-2.492645	H	-2.161508	-3.855610	-0.631124
C	0.843468	0.390541	0.266788	H	0.212378	2.382246	0.695380
C	-1.895361	0.598290	-0.581274	H	1.119637	2.224985	-0.807105
C	0.335691	1.753413	-0.198965	H	3.777409	-2.638698	1.250196
H	1.092249	-0.218613	-0.614617	H	3.741145	-4.714856	-0.076224
H	-2.186176	-0.980316	-2.898794	H	3.542115	-4.616533	-2.561942
C	-3.413210	-2.119400	-0.323594	H	3.396219	-2.399536	-3.701135
H	-4.177327	-2.747311	0.155397	H	3.459021	-0.317355	-2.376076
H	-3.902640	-1.359482	-0.945297	H	5.694824	0.528488	-1.603992
O	2.012528	0.593188	1.046758	H	6.578886	2.415660	-2.929923
C	3.635796	-1.306324	-0.453956	H	5.592051	4.694435	-2.684425
Si	3.588320	0.298120	0.544324	H	3.722611	5.064276	-1.074006
C	4.184966	1.699526	-0.575469	H	2.848093	3.177807	0.269646
C	3.711329	-2.568972	0.163807	H	5.376958	1.812510	3.539253
C	3.681742	-3.748517	-0.583733	H	5.246635	2.440455	1.878181

H	3.777163	2.180073	2.850665	H	1.023086	-0.387674	-0.416099
H	4.020343	-1.607034	2.969182	H	-3.221451	-1.956998	-1.604634
H	3.125429	-0.194940	3.556272	C	-3.317062	-2.204714	1.263750
H	4.788518	-0.496541	4.122493	H	-3.709189	-2.588002	2.217049
H	6.083853	-1.221061	1.381537	H	-4.179177	-2.073083	0.585220
H	6.534423	0.437566	0.918395	O	2.135356	0.364344	1.136084
H	6.770852	-0.110397	2.592726	C	3.497131	-0.768297	-1.157347
H	-2.926983	3.351179	0.944050	Si	3.653768	0.273540	0.414266
H	-3.201549	2.001200	2.075652	C	4.191272	2.002985	-0.097387
H	-4.463677	3.230475	1.837367	C	3.825156	-2.134082	-1.237784
H	-6.031567	-0.346717	-0.015342	C	3.548881	-2.884350	-2.384901
H	-5.036719	-0.303915	1.462129	C	2.929700	-2.282358	-3.483265
H	-6.408567	0.818081	1.279264	C	2.607659	-0.922682	-3.435166
H	-7.046217	3.978926	-1.495388	C	2.896521	-0.178192	-2.288974
H	-7.259227	2.683954	-0.296935	C	5.140855	2.207921	-1.115182
H	-6.198024	4.067982	0.063534	C	5.572631	3.494175	-1.452196
H	-6.312024	2.278306	-3.283558	C	5.057108	4.603302	-0.774929
H	-6.576388	0.971647	-2.106884	C	4.110312	4.420711	0.238082
H	-5.000980	1.124559	-2.924066	C	3.683847	3.132715	0.571376
H	-3.472915	3.141112	-2.414516	C	4.808392	-0.399783	1.769571
H	-4.831040	4.243561	-2.749114	C	4.858544	0.655675	2.893097
H	-3.962506	4.350181	-1.201381	C	4.262880	-1.712943	2.360511
H	0.841116	-0.451207	-2.570229	C	6.221276	-0.603649	1.194763
H	-0.290678	0.323857	-3.707508	C	-0.775769	1.452658	-0.975135
H	0.316927	-1.309999	-4.019285	H	-0.479713	1.030764	-1.962264
H	0.327755	0.739100	2.878269	H	-1.229946	2.429032	-1.208831
H	-1.139090	1.331087	2.079796	O	-3.060242	0.621077	-0.835461
H	-1.215302	-0.178764	3.018385	Si	-4.328030	1.728717	-0.578544
				C	-4.787838	2.379254	-2.313352
				C	-3.733121	3.066269	0.593701
				C	-5.754863	0.766654	0.171470
				C	-5.943751	3.388602	-2.191853
				C	-5.222292	1.191496	-3.192223
				C	-3.570814	3.063865	-2.958308
				C	-1.450798	-1.635358	-2.909692
				C	-0.429523	0.623019	2.544782
				H	0.833474	-3.670079	1.209269
				H	1.880488	-2.418574	0.568547
				H	0.536129	-1.971040	-1.246800
				H	-0.070146	-3.579155	-0.943806
				H	0.137847	-1.385209	3.986769
				H	0.788403	-3.043506	3.455159
				H	-2.582626	-3.877188	0.030210
				H	-1.554931	-3.424056	1.403682
				H	0.296154	2.341638	0.701743
				H	1.296558	2.043476	-0.717230

H	4.298151	-2.632435	-0.389969	C	0.206549	-2.871800	-0.966614
H	3.813529	-3.944357	-2.417992	C	-1.094166	-2.357501	-1.516949
H	2.703105	-2.869514	-4.376961	C	-1.503977	-0.577643	0.290862
H	2.129689	-0.441231	-4.292180	C	-0.225020	-0.451646	1.115833
H	2.643664	0.885322	-2.273393	C	1.029848	-1.999673	2.631148
H	5.543006	1.349764	-1.661960	C	-2.481982	-1.581160	0.718772
H	6.309786	3.632353	-2.247701	C	-2.361289	-3.122015	-1.184812
H	5.390872	5.610595	-1.037948	O	-2.511341	-1.995292	1.881196
H	3.702612	5.285730	0.768073	C	-1.192379	-1.268591	-2.388055
H	2.939659	2.998205	1.360753	C	0.858535	0.326471	0.296611
H	5.502886	0.297427	3.715919	C	-1.800002	0.382883	-0.773876
H	5.268054	1.614842	2.540045	C	0.351244	1.668133	-0.217952
H	3.856866	0.844916	3.310591	H	1.130626	-0.306138	-0.561773
H	4.261267	-2.536349	1.630256	H	-2.182010	-1.082655	-2.817177
H	3.233500	-1.589795	2.728895	C	-3.330213	-2.261237	-0.351104
H	4.893491	-2.035627	3.208729	H	-4.095543	-2.873828	0.146318
H	6.238893	-1.361884	0.395472	H	-3.820417	-1.525759	-0.999039
H	6.629168	0.331448	0.777130	O	2.007912	0.553001	1.097913
H	6.913312	-0.940219	1.987561	C	3.667434	-1.297086	-0.420794
H	-2.903130	3.656222	0.175190	Si	3.595298	0.280432	0.617548
H	-3.384204	2.575566	1.516053	C	4.192782	1.716667	-0.455781
H	-4.549569	3.758918	0.854629	C	3.755391	-2.574739	0.163607
H	-5.992435	-0.124487	-0.431449	C	3.749056	-3.733942	-0.615732
H	-5.483189	0.437613	1.186099	C	3.646767	-3.643243	-2.007020
H	-6.665948	1.383529	0.237829	C	3.552451	-2.387139	-2.611107
H	-6.238250	3.762742	-3.189321	C	3.564689	-1.231292	-1.824586
H	-6.839585	2.937071	-1.734717	C	5.274435	1.574104	-1.346021
H	-5.662695	4.264649	-1.583867	C	5.777733	2.665447	-2.060482
H	-5.455942	1.532457	-4.217471	C	5.206889	3.930743	-1.897440
H	-6.124410	0.697104	-2.797046	C	4.138012	4.098095	-1.011885
H	-4.425779	0.432920	-3.262764	C	3.642293	3.003059	-0.299126
H	-2.735803	2.358250	-3.087781	C	4.673888	0.268462	2.195797
H	-3.833210	3.457807	-3.957086	C	4.744097	1.709690	2.741095
H	-3.207293	3.912947	-2.356123	C	4.104485	-0.632642	3.303182
H	-0.707528	-0.821501	-2.825665	C	6.090045	-0.200798	1.811322
H	-2.178028	-1.342849	-3.682312	C	-0.915709	1.564770	-1.071107
H	-0.884943	-2.504143	-3.302827	H	-0.653467	1.568647	-2.141617
H	0.535449	0.919241	2.980522	H	-1.519049	2.476756	-0.937648
H	-0.957680	1.517816	2.195535	O	-3.110742	0.592272	-1.116203
H	-1.052521	0.185256	3.331448	Si	-4.361034	1.410364	-0.291169
				C	-5.520718	1.938954	-1.704748
				C	-3.663762	2.881670	0.653482
TS-3' (T₁)				C	-5.221669	0.271500	0.928965
Gibbs Free Energy =	-2321.319701			C	-6.757831	2.645956	-1.122193
Hartree				C	-5.957500	0.689413	-2.491937
C	0.372018	-1.826490	1.478050	C	-4.767223	2.895681	-2.645797
C	0.239070	-3.040110	0.565777				

C	-0.042907	-0.683594	-3.152271	H	0.276413	-1.380240	-3.950247
C	-0.582502	0.364189	2.385593	H	0.844682	-0.497624	-2.531877
H	-0.671620	-3.579112	0.875346	H	-0.321354	0.258538	-3.645331
H	1.072769	-3.714999	0.808542	H	0.326877	0.681251	2.914163
H	1.053794	-2.263715	-1.303891	H	-1.144109	1.271128	2.116931
H	0.385805	-3.878536	-1.393977	H	-1.212174	-0.248118	3.041269
H	1.112709	-1.220852	3.386084				
H	1.494901	-2.960363	2.871483				
H	-2.857057	-3.451672	-2.116708				
H	-2.108365	-4.034014	-0.623515				
H	0.178439	2.314332	0.655975				
H	1.153575	2.141563	-0.800000				
H	3.814797	-2.672542	1.248287				
H	3.818630	-4.712711	-0.134020				
H	3.636924	-4.549770	-2.617665				
H	3.464488	-2.305359	-3.697634				
H	3.490183	-0.258548	-2.316727				
H	5.734993	0.592738	-1.488529				
H	6.617438	2.527298	-2.746875				
H	5.596311	4.785541	-2.456701				
H	3.691625	5.086557	-0.873792				
H	2.816858	3.151808	0.400748				
H	5.336997	1.729035	3.673189				
H	5.218406	2.400507	2.028358				
H	3.741432	2.101628	2.977939				
H	4.019104	-1.685747	2.998462				
H	3.106047	-0.298161	3.615193				
H	4.766811	-0.599468	4.187271				
H	6.093705	-1.238676	1.442218				
H	6.534987	0.435696	1.029406				
H	6.757368	-0.155757	2.690703				
H	-3.241818	3.654395	-0.006860				
H	-2.873381	2.556301	1.349231				
H	-4.460076	3.348570	1.256173				
H	-5.685697	-0.594966	0.434543				
H	-4.521586	-0.112854	1.686277				
H	-6.016325	0.826665	1.454817				
H	-7.435550	2.968135	-1.933352				
H	-7.335463	1.983116	-0.457409				
H	-6.486975	3.546726	-0.546300				
H	-6.629128	0.972063	-3.322871				
H	-6.504468	-0.026933	-1.857225				
H	-5.090901	0.163905	-2.923046				
H	-3.855475	2.426036	-3.047611				
H	-5.405872	3.181497	-3.501111				
H	-4.470435	3.825860	-2.134149				

INT-3' (T₁)

Gibbs Free Energy = -2321.319701

Hartree

C	0.116899	-1.673207	1.800429
C	0.857906	-2.679973	0.935095
C	0.328688	-3.029358	-0.500760
C	-1.089925	-2.666408	-0.805108
C	-1.632372	-0.437227	0.531348
C	-0.278224	-0.293710	1.218004
C	-0.166525	-2.005535	3.068027
C	-2.704076	-1.173390	1.240855
C	-2.181899	-3.328495	-0.008514
O	-3.080515	-0.860370	2.362506
C	-1.466223	-1.547550	-1.738222
C	0.791028	0.140586	0.183909
C	-1.813134	-0.169829	-0.938830
C	0.347274	1.318258	-0.671308
H	0.970375	-0.699911	-0.498061
H	-2.454294	-1.794330	-2.155454
C	-3.283588	-2.373143	0.508224
H	-3.966755	-2.889769	1.197687
H	-3.872408	-1.996058	-0.339882
O	1.988547	0.426103	0.879747
C	3.639167	-0.969118	-1.074792
Si	3.570445	0.292016	0.332069
C	4.099277	1.956921	-0.366607
C	3.967397	-2.326902	-0.900136
C	3.912487	-3.232648	-1.962841
C	3.526406	-2.798277	-3.233968
C	3.209694	-1.452348	-3.437104
C	3.270213	-0.552529	-2.369746
C	5.191482	2.075414	-1.246096
C	5.603832	3.323332	-1.721938
C	4.925272	4.480313	-1.326607
C	3.836653	4.383358	-0.454442
C	3.430720	3.133246	0.019981
C	4.586796	-0.131520	1.886668
C	4.518349	1.093675	2.821823
C	3.989383	-1.341738	2.628756

C	6.051749	-0.399414	1.499516	H	-6.071477	-0.624839	-0.572652
C	-0.999051	1.075414	-1.379709	H	-5.398362	-0.308539	1.051460
H	-0.879579	1.053400	-2.469360	H	-6.588847	0.809956	0.347997
H	-1.646998	1.934197	-1.177193	H	-6.460922	3.701372	-2.565968
O	-3.182032	0.087120	-1.249526	H	-6.923911	2.613512	-1.239954
Si	-4.330004	1.175362	-0.640087	H	-5.693350	3.871715	-0.972160
C	-4.969196	2.157181	-2.151732	H	-5.888017	1.702114	-4.084523
C	-3.631522	2.306514	0.694681	H	-6.407030	0.612380	-2.777938
C	-5.726654	0.164764	0.113541	H	-4.785629	0.430304	-3.491828
C	-6.069716	3.135178	-1.701177	H	-3.030147	2.281063	-3.173888
C	-5.543812	1.166470	-3.180955	H	-4.197424	3.530677	-3.664215
C	-3.822243	2.948805	-2.802629	H	-3.361687	3.664904	-2.101637
C	-0.512600	-1.368058	-2.920946	H	0.472082	-0.977098	-2.630770
C	-0.395810	0.781243	2.324895	H	-0.937698	-0.685398	-3.671134
H	0.930243	-3.605318	1.524408	H	-0.342514	-2.337868	-3.413837
H	1.894397	-2.331427	0.817572	H	0.548791	0.854296	2.880358
H	1.001470	-2.588505	-1.247305	H	-0.619889	1.760328	1.878243
H	0.453318	-4.123138	-0.617266	H	-1.218448	0.537556	3.005424
H	-0.665924	-1.328718	3.760344				
H	0.087846	-2.998124	3.451131				
H	-2.680193	-4.104972	-0.626153				
H	-1.739442	-3.863594	0.847074				
H	0.282286	2.208752	-0.028901	C	0.407759	-1.732728	1.794501
H	1.140262	1.532391	-1.403257	C	0.763413	-2.646501	0.642149
H	4.267100	-2.693901	0.082641	C	-0.184998	-2.529457	-0.566455
H	4.168663	-4.282128	-1.796710	C	-1.590970	-2.026547	-0.198384
H	3.477057	-3.506139	-4.065369	C	-1.496948	-0.542526	0.577234
H	2.911333	-1.102366	-4.428648	C	-0.136009	-0.364729	1.397532
H	3.027569	0.498335	-2.549396	C	0.595594	-2.126988	3.060684
H	5.723493	1.177798	-1.575329	C	-2.711187	-0.653904	1.548147
H	6.453646	3.393628	-2.406184	C	-2.252084	-2.935349	0.879969
H	5.243935	5.457362	-1.699421	O	-3.199401	0.283824	2.135752
H	3.302417	5.285440	-0.144257	C	-2.475648	-1.995436	-1.394391
H	2.579525	3.063851	0.701819	C	0.931233	0.290164	0.459565
H	5.068748	0.884766	3.756581	C	-1.754670	0.629170	-0.299309
H	4.965077	1.988891	2.362196	C	0.515018	1.662159	-0.047955
H	3.478114	1.334705	3.093422	H	1.038424	-0.350535	-0.426008
H	4.063789	-2.273835	2.048057	H	-3.546340	-2.154663	-1.245414
H	2.927690	-1.183371	2.870719	C	-3.267345	-2.060842	1.600522
H	4.533281	-1.509313	3.575897	H	-3.482256	-2.345223	2.641791
H	6.154203	-1.281210	0.847096	H	-4.237794	-2.024994	1.074760
H	6.496689	0.460574	0.972556	O	2.170266	0.335272	1.144410
H	6.660099	-0.581417	2.403634	C	3.538579	-0.704684	-1.190359
H	-2.824982	2.967989	0.343972	Si	3.689550	0.270253	0.422818
H	-3.251230	1.706476	1.535397	C	4.230424	2.019939	-0.011999
H	-4.442075	2.945498	1.082995	C	3.888984	-2.059717	-1.334135

INT-3 (S₀)

Gibbs Free Energy = -2321.352037

Hartree

C	0.407759	-1.732728	1.794501
C	0.763413	-2.646501	0.642149
C	-0.184998	-2.529457	-0.566455
C	-1.590970	-2.026547	-0.198384
C	-1.496948	-0.542526	0.577234
C	-0.136009	-0.364729	1.397532
C	0.595594	-2.126988	3.060684
C	-2.711187	-0.653904	1.548147
C	-2.252084	-2.935349	0.879969
O	-3.199401	0.283824	2.135752
C	-2.475648	-1.995436	-1.394391
C	0.931233	0.290164	0.459565
C	-1.754670	0.629170	-0.299309
C	0.515018	1.662159	-0.047955
H	1.038424	-0.350535	-0.426008
H	-3.546340	-2.154663	-1.245414
C	-3.267345	-2.060842	1.600522
H	-3.482256	-2.345223	2.641791
H	-4.237794	-2.024994	1.074760
O	2.170266	0.335272	1.144410
C	3.538579	-0.704684	-1.190359
Si	3.689550	0.270253	0.422818
C	4.230424	2.019939	-0.011999
C	3.888984	-2.059717	-1.334135

C	3.631682	-2.758006	-2.517850	H	5.522293	0.145482	3.732834
C	3.007631	-2.114139	-3.589320	H	5.269426	1.520065	2.628948
C	2.660418	-0.764511	-3.476687	H	3.868733	0.687418	3.351158
C	2.931811	-0.071099	-2.294786	H	4.327665	-2.593173	1.498618
C	5.175752	2.268544	-1.024079	H	3.282380	-1.717841	2.637146
C	5.611233	3.567477	-1.302781	H	4.946504	-2.163694	3.103565
C	5.103956	4.645763	-0.571600	H	6.295754	-1.325696	0.333813
C	4.161268	4.419811	0.436485	H	6.661308	0.348989	0.810471
C	3.730882	3.119293	0.711147	H	6.954091	-0.983433	1.951344
C	4.844169	-0.458260	1.749758	H	-3.002566	3.741405	-0.018559
C	4.874459	0.536693	2.927922	H	-3.430778	2.693223	1.366738
C	4.315159	-1.807662	2.269364	H	-4.657413	3.776187	0.645511
C	6.262853	-0.612595	1.173302	H	-5.865627	-0.226982	-0.487677
C	-0.721234	1.508021	-0.925727	H	-5.484194	0.487573	1.105118
H	-0.412050	1.096471	-1.911653	H	-6.663885	1.282914	0.023522
H	-1.169838	2.489284	-1.152198	H	-6.163976	3.612780	-3.432769
O	-2.986892	0.640588	-0.868743	H	-6.784684	2.876468	-1.938960
Si	-4.305564	1.704899	-0.696458	H	-5.594970	4.198730	-1.853393
C	-4.734231	2.266999	-2.468701	H	-5.382041	1.337657	-4.340790
C	-3.799215	3.121935	0.421906	H	-6.084169	0.579937	-2.892973
C	-5.716547	0.720404	0.054764	H	-4.382296	0.274125	-3.317911
C	-5.880666	3.292959	-2.413427	H	-2.667421	2.189858	-3.200307
C	-5.169688	1.044032	-3.296464	H	-3.738354	3.253417	-4.146159
C	-3.498794	2.907639	-3.124116	H	-3.139300	3.782862	-2.558104
C	-2.001575	-1.627226	-2.758560	H	-1.424602	-0.685015	-2.756756
C	-0.331862	0.549335	2.616231	H	-2.843921	-1.494884	-3.453436
H	0.798265	-3.682655	1.010768	H	-1.330031	-2.391978	-3.196797
H	1.788003	-2.414565	0.310881	H	0.651048	0.809601	3.033181
H	0.247267	-1.871805	-1.333696	H	-0.866032	1.467080	2.343675
H	-0.284188	-3.514825	-1.050456	H	-0.927571	0.067221	3.400294
H	0.394583	-1.485953	3.918982				
H	0.976206	-3.129893	3.276500				
H	-2.701217	-3.822690	0.410681				
H	-1.502214	-3.287081	1.597681				
H	0.323056	2.340337	0.796013				
H	1.343075	2.102351	-0.622691				
H	4.366346	-2.590496	-0.508986				
H	3.915497	-3.810315	-2.601032				
H	2.796851	-2.660740	-4.512189				
H	2.178426	-0.250227	-4.312212				
H	2.663194	0.986869	-2.231056				
H	5.571529	1.435283	-1.612388				
H	6.344948	3.739809	-2.094808				
H	5.440976	5.662841	-0.788825				
H	3.759798	5.260644	1.008489				
H	2.989655	2.950806	1.496752				

TS-5 (S₀)

Gibbs Free Energy = -2321.348644

Hartree

C	0.310369	-1.710047	1.829873
C	0.844052	-2.691132	0.809146
C	0.104544	-2.660415	-0.541362
C	-1.331327	-2.118753	-0.447796
C	-1.492846	-0.744651	0.386059
C	-0.217584	-0.393265	1.268881
C	0.297125	-2.028158	3.131284
C	-2.740235	-1.007456	1.276632
C	-2.198847	-3.151305	0.340300
O	-3.211053	-0.216996	2.061043
C	-1.916512	-1.898070	-1.825077
C	0.858121	0.229999	0.323531

C	-1.855861	0.420792	-0.514503	H	0.177027	2.280453	0.437873
C	0.394165	1.525530	-0.331517	H	1.214769	1.930080	-0.943230
H	1.047137	-0.477047	-0.491778	H	4.359315	-2.633896	-0.167754
H	-2.981592	-1.666813	-1.878477	H	4.034198	-4.070633	-2.143030
C	-3.337940	-2.361160	0.963878	H	3.030968	-3.136989	-4.227544
H	-3.798929	-2.803359	1.858756	H	2.397963	-0.723374	-4.319792
H	-4.148008	-2.168417	0.236902	H	2.748578	0.726867	-2.351575
O	2.060422	0.414309	1.051866	H	5.629039	1.278522	-1.588973
C	3.566072	-0.838113	-1.090687	H	6.382227	3.531871	-2.292414
Si	3.614446	0.304892	0.416120	H	5.324031	5.567545	-1.313620
C	4.145586	2.007384	-0.185059	H	3.510181	5.329900	0.380367
C	3.929969	-2.197087	-1.070873	H	2.762629	3.071283	1.094322
C	3.744423	-3.017624	-2.187848	H	5.279524	0.586384	3.801148
C	3.184753	-2.494787	-3.356496	H	5.080073	1.816978	2.528496
C	2.828951	-1.143694	-3.407471	H	3.646662	1.063741	3.273445
C	3.025611	-0.329003	-2.289893	H	4.209104	-2.407383	1.839651
C	5.165111	2.163096	-1.142349	H	3.105554	-1.418046	2.819909
C	5.589612	3.432298	-1.545970	H	4.745466	-1.794426	3.413718
C	4.995976	4.573509	-0.998191	H	6.233633	-1.272545	0.646852
C	3.978883	4.439769	-0.047838	H	6.566445	0.452007	0.931951
C	3.560543	3.168384	0.353496	H	6.806734	-0.727944	2.240648
C	4.707377	-0.254243	1.870384	H	-2.635801	3.473907	0.346316
C	4.673388	0.872802	2.922941	H	-3.196789	2.417219	1.672747
C	4.155565	-1.539490	2.514594	H	-4.228919	3.757678	1.097348
C	6.154274	-0.462270	1.389474	H	-6.119230	0.057199	-0.270705
C	-0.837531	1.266235	-1.204003	H	-5.437392	0.429718	1.336642
H	-0.507690	0.785761	-2.151997	H	-6.601360	1.551883	0.571650
H	-1.299166	2.217664	-1.507786	H	-6.276647	4.125881	-2.688724
O	-3.170688	0.577178	-0.832421	H	-6.817615	3.217647	-1.259885
Si	-4.314190	1.768756	-0.412672	H	-5.545151	4.453098	-1.102197
C	-4.858111	2.587884	-2.051768	H	-5.725940	1.950141	-3.956392
C	-3.517682	2.977765	0.781131	H	-6.339118	1.038109	-2.558369
C	-5.757581	0.869385	0.380296	H	-4.702410	0.712402	-3.181062
C	-5.931700	3.650753	-1.752349	H	-2.891124	2.517952	-3.021205
C	-5.438449	1.508757	-2.984586	H	-3.982702	3.760094	-3.674588
C	-3.658971	3.256890	-2.745400	H	-3.183488	4.020347	-2.107503
C	-1.132680	-1.902677	-3.091906	H	-0.327480	-1.139540	-3.094606
C	-0.520138	0.628055	2.373731	H	-1.779404	-1.696678	-3.957860
H	0.829184	-3.700729	1.246391	H	-0.616989	-2.864126	-3.280738
H	1.905697	-2.462604	0.629110	H	0.430004	0.954614	2.819757
H	0.685580	-2.089570	-1.275246	H	-1.043939	1.503035	1.971555
H	0.051716	-3.680442	-0.956876	H	-1.160855	0.218326	3.159598
H	-0.041506	-1.341148	3.906759				
H	0.647473	-3.010034	3.463941				
H	-2.534562	-3.960749	-0.325547				
H	-1.594386	-3.605246	1.139895				

Compound **25a** (S_0)
Gibbs Free Energy = -2321.433268
Hartree

C	0.310369	-1.710047	1.829873	C	-5.438449	1.508757	-2.984586
C	0.844052	-2.691132	0.809146	C	-3.658971	3.256890	-2.745400
C	0.104544	-2.660415	-0.541362	C	-1.132680	-1.902677	-3.091906
C	-1.331327	-2.118753	-0.447796	C	-0.520138	0.628055	2.373731
C	-1.492846	-0.744651	0.386059	H	0.829184	-3.700729	1.246391
C	-0.217584	-0.393265	1.268881	H	1.905697	-2.462604	0.629110
C	0.297125	-2.028158	3.131284	H	0.685580	-2.089570	-1.275246
C	-2.740235	-1.007456	1.276632	H	0.051716	-3.680442	-0.956876
C	-2.198847	-3.151305	0.340300	H	-0.041506	-1.341148	3.906759
O	-3.211053	-0.216996	2.061043	H	0.647473	-3.010034	3.463941
C	-1.916512	-1.898070	-1.825077	H	-2.534562	-3.960749	-0.325547
C	0.858121	0.229999	0.323531	H	-1.594386	-3.605246	1.139895
C	-1.855861	0.420792	-0.514503	H	0.177027	2.280453	0.437873
C	0.394165	1.525530	-0.331517	H	1.214769	1.930080	-0.943230
H	1.047137	-0.477047	-0.491778	H	4.359315	-2.633896	-0.167754
H	-2.981592	-1.666813	-1.878477	H	4.034198	-4.070633	-2.143030
C	-3.337940	-2.361160	0.963878	H	3.030968	-3.136989	-4.227544
H	-3.798929	-2.803359	1.858756	H	2.397963	-0.723374	-4.319792
H	-4.148008	-2.168417	0.236902	H	2.748578	0.726867	-2.351575
O	2.060422	0.414309	1.051866	H	5.629039	1.278522	-1.588973
C	3.566072	-0.838113	-1.090687	H	6.382227	3.531871	-2.292414
Si	3.614446	0.304892	0.416120	H	5.324031	5.567545	-1.313620
C	4.145586	2.007384	-0.185059	H	3.510181	5.329900	0.380367
C	3.929969	-2.197087	-1.070873	H	2.762629	3.071283	1.094322
C	3.744423	-3.017624	-2.187848	H	5.279524	0.586384	3.801148
C	3.184753	-2.494787	-3.356496	H	5.080073	1.816978	2.528496
C	2.828951	-1.143694	-3.407471	H	3.646662	1.063741	3.273445
C	3.025611	-0.329003	-2.289893	H	4.209104	-2.407383	1.839651
C	5.165111	2.163096	-1.142349	H	3.105554	-1.418046	2.819909
C	5.589612	3.432298	-1.545970	H	4.745466	-1.794426	3.413718
C	4.995976	4.573509	-0.998191	H	6.233633	-1.272545	0.646852
C	3.978883	4.439769	-0.047838	H	6.566445	0.452007	0.931951
C	3.560543	3.168384	0.353496	H	6.806734	-0.727944	2.240648
C	4.707377	-0.254243	1.870384	H	-2.635801	3.473907	0.346316
C	4.673388	0.872802	2.922941	H	-3.196789	2.417219	1.672747
C	4.155565	-1.539490	2.514594	H	-4.228919	3.757678	1.097348
C	6.154274	-0.462270	1.389474	H	-6.119230	0.057199	-0.270705
C	-0.837531	1.266235	-1.204003	H	-5.437392	0.429718	1.336642
H	-0.507690	0.785761	-2.151997	H	-6.601360	1.551883	0.571650
H	-1.299166	2.217664	-1.507786	H	-6.276647	4.125881	-2.688724
O	-3.170688	0.577178	-0.832421	H	-6.817615	3.217647	-1.259885
Si	-4.314190	1.768756	-0.412672	H	-5.545151	4.453098	-1.102197
C	-4.858111	2.587884	-2.051768	H	-5.725940	1.950141	-3.956392
C	-3.517682	2.977765	0.781131	H	-6.339118	1.038109	-2.558369
C	-5.757581	0.869385	0.380296	H	-4.702410	0.712402	-3.181062
C	-5.931700	3.650753	-1.752349	H	-2.891124	2.517952	-3.021205

H	-3.982702	3.760094	-3.674588	C	4.888127	0.530455	2.927102
H	-3.183488	4.020347	-2.107503	C	4.311800	-1.808916	2.264160
H	-0.327480	-1.139540	-3.094606	C	6.264030	-0.623451	1.165856
H	-1.779404	-1.696678	-3.957860	C	-0.716723	1.534415	-0.908250
H	-0.616989	-2.864126	-3.280738	H	-0.410054	1.138523	-1.899409
H	0.430004	0.954614	2.819757	H	-1.173151	2.515766	-1.118618
H	-1.043939	1.503035	1.971555	O	-2.970223	0.634575	-0.863528
H	-1.160855	0.218326	3.159598	Si	-4.304878	1.683225	-0.704935
				C	-4.725947	2.243955	-2.479160
				C	-3.822877	3.103800	0.419655
TS-6 (S₀)				C	-5.709604	0.682589	0.035460
Gibbs Free Energy	=	-2321.351737		C	-5.873098	3.269422	-2.427239
Hartree				C	-5.158434	1.021388	-3.308974
C	0.400167	-1.722700	1.787157	C	-3.488464	2.885782	-3.129466
C	0.746650	-2.633879	0.629678	C	-2.023565	-1.639660	-2.757696
C	-0.195283	-2.518616	-0.583134	C	-0.310076	0.555407	2.643955
C	-1.621001	-2.078117	-0.231646	H	0.776173	-3.670590	0.997650
C	-1.493208	-0.481097	0.605947	H	1.772796	-2.408577	0.298071
C	-0.130474	-0.343219	1.409373	H	0.221083	-1.827703	-1.329571
C	0.590560	-2.129906	3.049109	H	-0.245296	-3.495985	-1.092165
C	-2.711068	-0.635435	1.556381	H	0.399829	-1.495497	3.914512
C	-2.266497	-2.933338	0.887793	H	0.962266	-3.138440	3.253973
O	-3.204993	0.291640	2.158748	H	-2.726137	-3.838659	0.464639
C	-2.497547	-2.011542	-1.393379	H	-1.507122	-3.258727	1.607550
C	0.936418	0.311534	0.472420	H	0.327067	2.359715	0.817602
C	-1.743271	0.639589	-0.287816	H	1.347322	2.129370	-0.602214
C	0.519669	1.685677	-0.029647	H	4.356111	-2.583516	-0.518789
H	1.037991	-0.327363	-0.415144	H	3.889460	-3.795213	-2.612091
H	-3.569925	-2.159272	-1.244053	H	2.762576	-2.636363	-4.512770
C	-3.273822	-2.039105	1.594370	H	2.153560	-0.224409	-4.301934
H	-3.506991	-2.321936	2.632261	H	2.655297	1.004872	-2.220071
H	-4.237185	-1.995371	1.056302	H	5.575227	1.433706	-1.615257
O	2.177669	0.351530	1.152707	H	6.362795	3.733862	-2.095851
C	3.530593	-0.692915	-1.189500	H	5.477219	5.660331	-0.782373
Si	3.693806	0.277370	0.425246	H	3.799893	5.266080	1.020261
C	4.244278	2.024287	-0.008614	H	3.015519	2.960566	1.506664
C	3.875862	-2.048520	-1.339550	H	5.536054	0.133313	3.729038
C	3.609460	-2.742291	-2.523953	H	5.288448	1.511981	2.629163
C	2.980898	-2.093224	-3.589620	H	3.884754	0.686682	3.353902
C	2.638821	-0.742771	-3.470826	H	4.317649	-2.592477	1.491317
C	2.919624	-0.053907	-2.288520	H	3.280369	-1.713927	2.634480
C	5.187421	2.268483	-1.023791	H	4.942880	-2.170957	3.095962
C	5.630838	3.564950	-1.301462	H	6.290349	-1.335998	0.325677
C	5.133866	4.645173	-0.566079	H	6.667021	0.336117	0.802678
C	4.193317	4.423662	0.445007	H	6.955379	-0.999023	1.941516
C	3.754932	3.125571	0.718579	H	-3.034610	3.737619	-0.015473

H	-3.451728	2.677442	1.364579	C	4.175627	1.994659	-0.165069
H	-4.692139	3.743576	0.642316	C	4.041987	-2.193095	-1.087503
H	-5.844284	-0.266851	-0.506911	C	3.899625	-3.001124	-2.219673
H	-5.483648	0.454451	1.088265	C	3.329082	-2.481366	-3.384361
H	-6.662328	1.235384	-0.004350	C	2.914135	-1.146651	-3.414188
H	-6.154353	3.587628	-3.447620	C	3.068820	-0.343579	-2.281762
H	-6.777993	2.853129	-1.954217	C	5.184447	2.163757	-1.131371
H	-5.589005	4.175992	-1.867742	C	5.601191	3.438482	-1.525548
H	-5.365882	1.315290	-4.354159	C	5.010234	4.571972	-0.959206
H	-6.074989	0.557969	-2.909499	C	4.003579	4.424996	0.000281
H	-4.371745	0.250856	-3.327108	C	3.593140	3.148146	0.392171
H	-2.656088	2.169035	-3.203328	C	4.755766	-0.275216	1.875516
H	-3.724854	3.232281	-4.151974	C	4.696264	0.834380	2.945245
H	-3.131829	3.760861	-2.561405	C	4.224985	-1.580238	2.497119
H	-1.426714	-0.710039	-2.744989	C	6.208557	-0.448100	1.398452
H	-2.864490	-1.481946	-3.448739	C	-0.814417	1.259076	-1.132206
H	-1.368633	-2.413242	-3.205719	H	-0.530381	0.707443	-2.057336
H	0.676400	0.790278	3.067634	H	-1.250983	2.208266	-1.478551
H	-0.825675	1.487367	2.383966	O	-3.133878	0.578491	-0.790358
H	-0.918242	0.072246	3.417859	Si	-4.327085	1.748656	-0.458593
				C	-4.855755	2.458214	-2.151748
				C	-3.593173	3.044354	0.682176

TS-4 (T₁)

Gibbs Free Energy = -2321.348384

Hartree

C	0.370700	-1.743472	1.815002	C	-5.395393	1.317909	-3.034197
C	0.841822	-2.694723	0.736759	C	-3.652499	3.109347	-2.854955
C	-0.002452	-2.639732	-0.551552	C	-3.523356	-2.244306	-2.000032
C	-1.436294	-2.116287	-0.337007	C	-0.411393	0.589735	2.453821
C	-1.502150	-0.703053	0.481194	H	0.866894	-3.714860	1.148067
C	-0.169797	-0.408999	1.313404	H	1.885280	-2.451474	0.483072
C	0.427225	-2.092125	3.107040	H	0.498917	-2.034818	-1.320800
C	-2.708965	-0.916283	1.438196	H	-0.079749	-3.648486	-0.989206
C	-2.199997	-3.115261	0.585394	H	0.133894	-1.421547	3.914979
O	-3.189202	-0.053697	2.136563	H	0.792483	-3.081923	3.397300
C	-2.087625	-1.994709	-1.689913	H	-2.602449	-3.957038	0.003308
C	0.894257	0.213792	0.350343	H	-1.503061	-3.539398	1.320307
C	-1.841698	0.491824	-0.369755	H	0.238464	2.272953	0.478674
C	0.436712	1.515184	-0.293508	H	1.249591	1.910377	-0.921483
H	1.065212	-0.490391	-0.472321	H	4.482540	-2.627593	-0.188746
H	-1.429791	-1.689123	-2.509687	H	4.233564	-4.041555	-2.190655
C	-3.265996	-2.317654	1.319086	H	3.212529	-3.113432	-4.268567
H	-3.547904	-2.703178	2.310101	H	2.472519	-0.728682	-4.322685
H	-4.196598	-2.223718	0.732978	H	2.751060	0.701545	-2.329061
O	2.105739	0.379460	1.066411	H	5.646042	1.285338	-1.592224
C	3.624591	-0.849345	-1.088225	H	6.385623	3.548406	-2.279159
Si	3.657603	0.284140	0.425205	H	5.332158	5.570327	-1.267239

H	3.536892	5.309042	0.443044	C	-2.139531	-1.961790	-1.659914
H	2.803254	3.041021	1.140163	C	0.900004	0.218601	0.363800
H	5.307282	0.547358	3.819863	C	-1.834097	0.510828	-0.351352
H	5.083358	1.793077	2.566309	C	0.445853	1.533501	-0.254412
H	3.665264	0.997854	3.296729	H	1.060994	-0.474028	-0.471246
H	4.296529	-2.436431	1.809112	H	-1.574340	-1.397333	-2.408352
H	3.171393	-1.482474	2.798157	C	-3.276447	-2.283455	1.349163
H	4.814916	-1.838303	3.395363	H	-3.556892	-2.661153	2.343673
H	6.307207	-1.243380	0.642109	H	-4.208722	-2.187100	0.765825
H	6.605653	0.481619	0.959136	O	2.116207	0.366503	1.075074
H	6.861544	-0.716576	2.248345	C	3.629226	-0.847042	-1.091405
H	-2.724881	3.549997	0.231329	Si	3.665800	0.277865	0.427884
H	-3.261658	2.539733	1.603077	C	4.180294	1.992272	-0.154810
H	-4.337018	3.811541	0.950742	C	4.060639	-2.186290	-1.103274
H	-6.086199	-0.008517	-0.254175	C	3.916244	-2.988365	-2.239423
H	-5.439633	0.469459	1.340595	C	3.329184	-2.467140	-3.395175
H	-6.624205	1.512734	0.500952	C	2.899527	-1.136880	-3.412263
H	-6.292196	3.926795	-2.902766	C	3.056438	-0.339531	-2.276141
H	-6.841546	3.091417	-1.433071	C	5.177195	2.166533	-1.132491
H	-5.597242	4.360716	-1.325249	C	5.592730	3.443284	-1.521458
H	-5.676599	1.701000	-4.032276	C	5.012565	4.573760	-0.938277
H	-6.292582	0.849076	-2.598387	C	4.017961	4.421760	0.032959
H	-4.639583	0.529238	-3.177334	C	3.608696	3.142921	0.419451
H	-2.862525	2.371387	-3.062265	C	4.769148	-0.287457	1.871880
H	-3.960722	3.547105	-3.821852	C	4.707794	0.813489	2.950373
H	-3.210683	3.920796	-2.253282	C	4.245039	-1.599314	2.484677
H	-3.871061	-3.234352	-1.649195	C	6.221525	-0.450418	1.390010
H	-3.706703	-2.197528	-3.084065	C	-0.808077	1.298466	-1.094375
H	-4.179472	-1.491050	-1.527291	H	-0.524831	0.773159	-2.035244
H	0.558387	0.883528	2.878650	H	-1.246000	2.255929	-1.416175
H	-0.929759	1.484266	2.088496	O	-3.121645	0.585197	-0.789363
H	-1.035461	0.173259	3.250798	Si	-4.327579	1.748027	-0.478621
				C	-4.848596	2.432620	-2.183832
				C	-3.612399	3.062690	0.652347
				C	-5.755956	0.845326	0.339129
				C	-5.945208	3.495605	-1.985872
				C	-5.389437	1.281335	-3.051030
				C	-3.639604	3.067835	-2.891649
				C	-3.555647	-2.292926	-1.979831
				C	-0.391055	0.569036	2.481434
				H	0.859487	-3.721151	1.104585
				H	1.869000	-2.452523	0.435246
				H	0.447824	-2.011858	-1.339145
				H	-0.126294	-3.629203	-1.014956
				H	0.176484	-1.457493	3.908830
				H	0.820830	-3.114041	3.362014

INT-4 (T₁)

Gibbs Free Energy = -2321.350683

Hartree

C	0.379262	-1.756317	1.801801	C	-5.389437	1.281335	-3.051030
C	0.829628	-2.696432	0.705130	C	-3.639604	3.067835	-2.891649
C	-0.038318	-2.626011	-0.567271	C	-3.555647	-2.292926	-1.979831
C	-1.467343	-2.100176	-0.318446	C	-0.391055	0.569036	2.481434
C	-1.500528	-0.687402	0.497184	H	0.859487	-3.721151	1.104585
C	-0.161481	-0.413058	1.324009	H	1.869000	-2.452523	0.435246
C	0.454708	-2.119741	3.088757	H	0.447824	-2.011858	-1.339145
C	-2.709301	-0.884891	1.458093	H	-0.126294	-3.629203	-1.014956
C	-2.218096	-3.091474	0.615228	H	0.176484	-1.457493	3.908830
O	-3.182832	-0.013824	2.150317	H	0.820830	-3.114041	3.362014

H	-2.626576	-3.937484	0.043781	Gibbs Free Energy = -2321.350763
H	-1.515893	-3.510849	1.347486	Hartree
H	0.253578	2.277405	0.532543	C 0.396282 -1.777185 1.758681
H	1.258348	1.937115	-0.877403	C 0.780260 -2.687991 0.612939
H	4.514124	-2.621903	-0.211508	C -0.149945 -2.574051 -0.612037
H	4.261436	-4.025344	-2.220431	C -1.564838 -2.058775 -0.275622
H	3.210843	-3.094671	-4.282359	C -1.508449 -0.615652 0.543811
H	2.444423	-0.718049	-4.313676	C -0.141663 -0.411704 1.346930
H	2.727133	0.702462	-2.313633	C 0.536599 -2.176744 3.029273
H	5.630266	1.290600	-1.606293	C -2.703960 -0.777008 1.527721
H	6.367753	3.557127	-2.284168	C -2.250411 -3.019286 0.736324
H	5.333487	5.573698	-1.242199	O -3.183634 0.129593 2.168605
H	3.559791	5.303451	0.489110	C -2.335894 -1.948250 -1.553517
H	2.828045	3.032337	1.176597	C 0.920575 0.233215 0.394840
H	5.322267	0.522038	3.821090	C -1.807818 0.584866 -0.290854
H	5.090125	1.776741	2.578190	C 0.483648 1.573440 -0.177122
H	3.677043	0.969848	3.305712	H 1.060256 -0.436917 -0.463078
H	4.316395	-2.449517	1.789295	H -1.845459 -1.383428 -2.352761
H	3.192261	-1.507317	2.790348	C -3.254755 -2.186767 1.518720
H	4.839139	-1.862711	3.378620	H -3.445439 -2.525026 2.548493
H	6.321762	-1.238536	0.626425	H -4.235194 -2.127977 1.015295
H	6.613727	0.484705	0.957824	O 2.144952 0.335977 1.099285
H	6.877601	-0.723702	2.235977	C 3.630631 -0.806160 -1.120611
H	-2.756826	3.583895	0.195118	Si 3.687483 0.268508 0.433404
H	-3.266855	2.567872	1.573466	C 4.197809 2.001746 -0.095388
H	-4.369954	3.815961	0.921994	C 4.054976 -2.146563 -1.176737
H	-6.070124	-0.024012	-0.260652	C 3.891731 -2.914961 -2.333399
H	-5.442809	0.487174	1.331489	C 3.291789 -2.357730 -3.465429
H	-6.630931	1.503610	0.464473	C 2.868772 -1.025478 -3.438405
H	-6.279589	3.892999	-2.961457	C 3.044797 -0.261672 -2.282187
H	-6.833212	3.083778	-1.478792	C 5.171862 2.210438 -1.089101
H	-5.585123	4.350848	-1.390361	C 5.584004 3.499958 -1.437731
H	-5.666301	1.650703	-4.055488	C 5.023497 4.608943 -0.796960
H	-6.289455	0.821662	-2.611276	C 4.051918 4.422768 0.191562
H	-4.636098	0.487934	-3.181006	C 3.645797 3.131386 0.537122
H	-2.851016	2.323804	-3.082195	C 4.809377 -0.341993 1.845201
H	-3.941312	3.490967	-3.867080	C 4.760075 0.720693 2.961925
H	-3.198033	3.887565	-2.301102	C 4.299288 -1.675515 2.421898
H	-3.877288	-3.260963	-1.558825	C 6.255116 -0.482765 1.336832
H	-3.715354	-2.333607	-3.068734	C -0.772172 1.372594 -1.018674
H	-4.249458	-1.524182	-1.585568	H -0.502290 0.854492 -1.968194
H	0.582601	0.853848	2.903470	H -1.198857 2.340046 -1.327349
H	-0.910614	1.470517	2.135373	O -3.066575 0.615989 -0.806499
H	-1.009586	0.141434	3.277096	Si -4.318629 1.747641 -0.561523
			C -4.809433 2.348231 -2.305736	
			C -3.671902 3.119876 0.540895	

INT-4 (S_0)

C	-5.744493	0.841900	0.258270	H	-4.501290	0.372991	-3.214092
C	-5.945267	3.380587	-2.186168	H	-2.776165	2.270896	-3.124843
C	-5.284020	1.144678	-3.140361	H	-3.876271	3.361282	-4.002659
C	-3.597116	2.993472	-2.998471	H	-3.207256	3.854456	-2.430796
C	-3.760082	-2.333032	-1.768093	H	-4.005908	-3.324487	-1.349464
C	-0.331005	0.524793	2.549141	H	-4.002642	-2.357452	-2.841768
H	0.815650	-3.724485	0.980464	H	-4.459961	-1.611146	-1.303060
H	1.808777	-2.449788	0.298593	H	0.653839	0.779440	2.964003
H	0.293373	-1.930052	-1.386209	H	-0.848710	1.445705	2.254524
H	-0.254968	-3.562520	-1.087211	H	-0.937596	0.068406	3.339260
H	0.308087	-1.535608	3.880843				
H	0.905623	-3.181638	3.255851				
H	-2.704483	-3.876713	0.219443				
H	-1.503313	-3.425972	1.428187				
H	0.299475	2.293017	0.634176				
H	1.298974	1.988546	-0.788355				
H	4.518090	-2.609297	-0.303820				
H	4.232134	-3.953570	-2.348997				
H	3.158398	-2.958709	-4.368721				
H	2.403780	-0.579024	-4.321312				
H	2.720209	0.782490	-2.285304				
H	5.609230	1.351954	-1.607481				
H	6.340923	3.640688	-2.214017				
H	5.341743	5.618790	-1.069282				
H	3.609131	5.287555	0.693019				
H	2.882572	2.994290	1.307575				
H	5.386949	0.400101	3.813308				
H	5.134997	1.697697	2.619330				
H	3.733869	0.861184	3.336537				
H	4.362339	-2.502192	1.698040				
H	3.251044	-1.597367	2.746434				
H	4.908150	-1.965591	3.297441				
H	6.345235	-1.238613	0.540041				
H	6.639712	0.469996	0.937631				
H	6.923675	-0.789128	2.161418				
H	-2.837371	3.668944	0.077947				
H	-3.312991	2.661029	1.475574				
H	-4.465330	3.843802	0.787240				
H	-6.042947	-0.045684	-0.321939				
H	-5.441797	0.515418	1.264774				
H	-6.627464	1.494553	0.355412				
H	-6.258091	3.730078	-3.186963				
H	-6.836706	2.958313	-1.693906				
H	-5.634158	4.269082	-1.611921				
H	-5.541677	1.462873	-4.167164				
H	-6.181310	0.672240	-2.708597				

TS-5 (S_0)

Gibbs Free Energy = -2321.350763

Hartree

C	0.346435	-1.736088	1.848694
C	0.866223	-2.724587	0.827849
C	0.074673	-2.727403	-0.494179
C	-1.365012	-2.194433	-0.359962
C	-1.492225	-0.794584	0.426564
C	-0.197019	-0.428475	1.280269
C	0.358850	-2.037943	3.153914
C	-2.717986	-1.015108	1.356214
C	-2.193057	-3.199077	0.491040
O	-3.187938	-0.178263	2.091809
C	-1.919830	-2.011707	-1.757816
C	0.868509	0.182749	0.314900
C	-1.856473	0.338708	-0.516813
C	0.389985	1.458360	-0.367302
H	1.066078	-0.541501	-0.484093
H	-1.224044	-1.589398	-2.488467
C	-3.301227	-2.396451	1.154992
H	-3.682911	-2.799066	2.104517
H	-4.167980	-2.255807	0.485561
O	2.067488	0.397128	1.040130
C	3.617098	-0.877003	-1.063056
Si	3.627193	0.298049	0.418526
C	4.133952	1.996858	-0.214248
C	4.018412	-2.224661	-1.013352
C	3.886130	-3.065875	-2.122310
C	3.342761	-2.576052	-3.312745
C	2.944980	-1.238094	-3.391366
C	3.088674	-0.402161	-2.281472
C	5.158115	2.150416	-1.166964
C	5.562692	3.418031	-1.595229
C	4.944024	4.559936	-1.077383
C	3.922177	4.428328	-0.131843

C	3.523954	3.158540	0.294341	H	6.820053	-0.637753	2.293916
C	4.716246	-0.212500	1.893440	H	-2.588657	3.443340	0.318436
C	4.655128	0.935100	2.922395	H	-3.140233	2.410283	1.668072
C	4.178316	-1.492871	2.558605	H	-4.167618	3.752650	1.088242
C	6.170854	-0.406831	1.430228	H	-6.110181	0.047777	-0.198392
C	-0.838482	1.165696	-1.232995	H	-5.414029	0.448557	1.395620
H	-0.503913	0.657063	-2.163453	H	-6.576738	1.562480	0.615879
H	-1.304017	2.105366	-1.565206	H	-6.256912	4.089657	-2.669991
O	-3.172839	0.525619	-0.796642	H	-6.788328	3.205626	-1.222626
Si	-4.293996	1.741943	-0.388538	H	-5.499487	4.427770	-1.098005
C	-4.848013	2.542377	-2.034228	H	-5.757582	1.897535	-3.916184
C	-3.468335	2.961436	0.773454	H	-6.352071	1.000712	-2.500609
C	-5.738696	0.870772	0.433092	H	-4.731122	0.656565	-3.152009
C	-5.904433	3.622102	-1.732653	H	-2.900219	2.435673	-3.038313
C	-5.455503	1.460860	-2.946685	H	-3.984961	3.688192	-3.681880
C	-3.651781	3.188167	-2.754351	H	-3.153106	3.949725	-2.132146
C	-3.328470	-2.227365	-2.182945	H	-3.770828	-3.145631	-1.758768
C	-0.480813	0.607650	2.376646	H	-3.407119	-2.296588	-3.279348
H	0.885015	-3.727093	1.280826	H	-3.973537	-1.382597	-1.865940
H	1.916103	-2.478796	0.605260	H	0.476296	0.937679	2.803964
H	0.610485	-2.155391	-1.264968	H	-1.008925	1.478858	1.972090
H	0.013123	-3.752318	-0.895748	H	-1.109379	0.208921	3.178034
H	0.030103	-1.343125	3.926807				
H	0.722611	-3.012894	3.492361				
H	-2.557397	-4.033970	-0.125789				
H	-1.547874	-3.629952	1.269722				
H	0.163159	2.226355	0.386336				
H	1.205523	1.859520	-0.988108				
H	4.437908	-2.635962	-0.093806				
H	4.206250	-4.108861	-2.054921				
H	3.233569	-3.234105	-4.178720				
H	2.524758	-0.843493	-4.320233				
H	2.783539	0.644422	-2.366333				
H	5.641387	1.265020	-1.590784				
H	6.359214	3.515690	-2.337771				
H	5.256268	5.552659	-1.412401				
H	3.433885	5.318856	0.273022				
H	2.722306	3.063024	1.031300				
H	5.258488	0.676816	3.811180				
H	5.049797	1.877571	2.511967				
H	3.622603	1.116609	3.260655				
H	4.248562	-2.373021	1.901237				
H	3.124223	-1.380835	2.852962				
H	4.764685	-1.721929	3.466987				
H	6.271602	-1.234712	0.710121				
H	6.570601	0.502515	0.952258				

Compound **25b** (S_0)

Gibbs Free Energy = -2321.350763

Hartree

C	0.480562	-2.405181	0.986657
C	0.778051	-3.060658	-0.357501
C	-0.246659	-2.753076	-1.470290
C	-1.628223	-2.468541	-0.889397
C	-1.622482	-1.366057	0.215685
C	-0.261177	-1.065782	0.951242
C	0.855026	-3.009288	2.121917
C	-2.705487	-1.848367	1.203992
C	-2.271368	-3.745767	-0.297744
O	-3.233121	-1.182075	2.060013
C	-2.547091	-1.553591	-1.771854
C	0.602615	-0.048777	0.131145
C	-2.236030	-0.344927	-0.817726
C	-0.209823	1.135182	-0.382473
H	0.996700	-0.568379	-0.754015
H	-2.130846	-1.403227	-2.781705
C	-3.042852	-3.317079	0.953377
H	-2.746440	-3.878825	1.854371
H	-4.136716	-3.414644	0.873671
O	1.691009	0.375412	0.927569

C	3.731602	-0.845470	-0.746103	H	5.740675	3.746099	-2.485520
Si	3.311157	0.497242	0.511773	H	4.263467	5.675760	-1.924377
C	3.599356	2.161600	-0.323251	H	2.362094	5.361870	-0.340628
C	4.386129	-2.049670	-0.429062	H	1.945188	3.137138	0.675822
C	4.572676	-3.050351	-1.387306	H	4.332015	1.649446	3.973286
C	4.094925	-2.872410	-2.688535	H	4.100175	2.602934	2.487577
C	3.447314	-1.681414	-3.030713	H	2.740761	1.677030	3.172862
C	3.278771	-0.679652	-2.071517	H	4.183444	-1.766224	2.467238
C	4.666233	2.360790	-1.218998	H	2.786511	-0.905004	3.128134
C	4.906996	3.613811	-1.790618	H	4.364185	-0.816565	3.956541
C	4.079073	4.695608	-1.476593	H	6.120323	-0.399016	1.348148
C	3.013017	4.519195	-0.588832	H	6.050022	1.378551	1.350314
C	2.779601	3.264989	-0.018450	H	6.310918	0.497025	2.873172
C	4.245732	0.425559	2.169614	H	-5.520620	1.057203	-2.559710
C	3.827041	1.662512	2.990793	H	-3.956391	1.766682	-3.026953
C	3.871802	-0.837261	2.967532	H	-5.292867	2.823451	-2.514312
C	5.762905	0.475917	1.914165	H	-2.660595	3.138646	0.844613
C	-1.202504	0.620220	-1.414383	H	-2.393079	3.452378	-0.889254
H	-0.636915	0.105290	-2.205514	H	-3.804542	4.153723	-0.067068
H	-1.737261	1.439892	-1.917187	H	-7.524551	2.634914	1.126626
O	-3.343328	0.325501	-0.303791	H	-6.257046	3.696920	0.477556
Si	-4.207891	1.740904	-0.535328	H	-7.137241	2.592107	-0.608019
C	-5.663104	1.581983	0.682843	H	-5.953992	1.575924	2.847054
C	-4.800102	1.856116	-2.322930	H	-4.701108	2.715341	2.308852
C	-3.164026	3.258019	-0.127340	H	-4.362265	0.958588	2.335127
C	-6.695641	2.687748	0.397776	H	-5.621391	-0.602338	0.788324
C	-5.130821	1.717178	2.122746	H	-7.200216	0.117783	1.192169
C	-6.324114	0.200448	0.523510	H	-6.678761	0.023386	-0.505912
C	-4.017237	-1.918214	-1.904728	H	-4.141490	-2.869944	-2.444778
C	-0.480887	-0.463063	2.347573	H	-4.548777	-1.141132	-2.474118
H	0.859808	-4.146491	-0.197491	H	-4.524487	-2.002152	-0.934784
H	1.774590	-2.741979	-0.699539	H	0.483372	-0.179700	2.784265
H	0.094556	-1.893457	-2.065094	H	-1.116042	0.430500	2.288307
H	-0.300287	-3.596611	-2.179421	H	-0.986047	-1.161436	3.022982
H	0.695122	-2.565113	3.104734				
H	1.355253	-3.982521	2.098917				
H	-2.909708	-4.246473	-1.040471				
H	-1.481491	-4.462047	-0.030197				
H	-0.716638	1.648357	0.448812				
H	0.476861	1.861798	-0.842418				
H	4.750669	-2.222624	0.584514				
H	5.086164	-3.975822	-1.114141				
H	4.230972	-3.658104	-3.436212				
H	3.076776	-1.531173	-4.048130				
H	2.786535	0.253180	-2.361533				
H	5.316466	1.521484	-1.482782				

TS-6 (S₀)

Gibbs Free Energy = -2321.350501
Hartree

C	0.391137	-1.784659	1.752800
C	0.658921	-2.696307	0.575058
C	-0.380604	-2.579594	-0.557738
C	-1.767095	-2.117713	-0.084937
C	-1.535197	-0.509907	0.659761
C	-0.126889	-0.396950	1.393655
C	0.626256	-2.195431	3.005544
C	-2.663513	-0.607488	1.703309

C	-2.299282	-2.961784	1.115575	H	0.488187	-1.553182	3.875733
O	-3.321328	0.337130	2.079314	H	0.986984	-3.210154	3.198568
C	-2.717979	-2.065563	-1.189016	H	-3.056649	-3.674669	0.763763
C	0.931349	0.226593	0.423295	H	-1.488205	-3.561191	1.541939
C	-1.790305	0.582712	-0.269171	H	0.301888	2.287986	0.648877
C	0.501657	1.564471	-0.155835	H	1.321922	1.979001	-0.760068
H	1.052183	-0.453037	-0.432462	H	4.094802	-2.570181	-0.609382
H	-2.328329	-1.782304	-2.171727	H	3.689920	-3.648688	-2.787807
C	-2.879611	-2.025663	2.181257	H	2.905107	-2.297398	-4.733241
H	-2.352082	-2.127348	3.145060	H	2.561311	0.160910	-4.470876
H	-3.951009	-2.169868	2.385781	H	2.985795	1.249158	-2.293885
O	2.164943	0.311796	1.113348	H	5.735561	1.593268	-1.385240
C	3.560451	-0.573655	-1.268108	H	6.496765	3.930725	-1.681777
Si	3.691449	0.295357	0.404896	H	5.423577	5.771965	-0.386077
C	4.229060	2.073504	0.100517	H	3.584313	5.252126	1.215992
C	3.758410	-1.955995	-1.445945	H	2.828192	2.905304	1.522621
C	3.528404	-2.573089	-2.679077	H	5.540063	-0.010255	3.694812
C	3.090901	-1.816437	-3.769372	H	5.286038	1.417485	2.660021
C	2.896972	-0.439950	-3.621613	H	3.887135	0.558587	3.351637
C	3.134655	0.170304	-2.387429	H	4.334334	-2.636314	1.343745
C	5.262800	2.388519	-0.801044	H	3.272017	-1.810061	2.505843
C	5.692658	3.707096	-0.975553	H	4.931738	-2.272893	2.971063
C	5.090440	4.739638	-0.250024	H	6.273168	-1.321204	0.218094
C	4.059420	4.447557	0.648237	H	6.671493	0.317132	0.789506
C	3.635475	3.127050	0.819962	H	6.945503	-1.083271	1.849460
C	4.843947	-0.513680	1.688762	H	-2.819319	3.690821	-0.294491
C	4.888999	0.422519	2.914069	H	-3.419912	2.872848	1.175881
C	4.308730	-1.882987	2.145815	H	-4.497156	3.957742	0.246706
C	6.257520	-0.656803	1.097434	H	-6.139875	0.055678	-0.520588
C	-0.740799	1.344595	-1.008567	H	-5.494424	0.616504	1.049373
H	-0.463403	0.797326	-1.938651	H	-6.591636	1.662723	0.105792
H	-1.159631	2.304441	-1.350189	H	-6.103903	3.290341	-3.760930
O	-3.017420	0.556709	-0.840794	H	-6.773418	2.590354	-2.270424
Si	-4.278490	1.706255	-0.801983	H	-5.684302	3.996974	-2.184845
C	-4.656041	2.100448	-2.633313	H	-5.175899	0.994983	-4.447466
C	-3.695413	3.206064	0.163054	H	-5.853256	0.282645	-2.965634
C	-5.769410	0.932052	0.032008	H	-4.120017	0.091336	-3.329181
C	-5.870116	3.044578	-2.708966	H	-2.553358	2.124708	-3.265757
C	-4.968449	0.791664	-3.381015	H	-3.653516	3.004980	-4.351750
C	-3.440759	2.775994	-3.291572	H	-3.178675	3.726028	-2.797631
C	-4.187901	-2.292130	-1.060879	H	-4.452273	-3.369382	-1.019003
C	-0.254113	0.516037	2.624307	H	-4.730251	-1.864988	-1.916647
H	0.720254	-3.732814	0.939087	H	-4.607892	-1.837267	-0.147970
H	1.656577	-2.469142	0.165699	H	0.742501	0.729331	3.033447
H	-0.032159	-1.889856	-1.342149	H	-0.745802	1.460548	2.358892
H	-0.483330	-3.558940	-1.052760	H	-0.861718	0.057561	3.415529

			C	2.101083	3.058943	2.489589	
Compound 24' (S_0)			C	1.026119	2.596268	-0.410574	
Gibbs Free Energy =	-2321.423815		C	4.101233	2.559715	0.188576	
Hartree			C	2.990252	2.412736	3.566814	
C	0.544951	-2.279747	-0.727780	C	0.628590	2.954405	2.919880
C	1.528090	-1.157474	-0.368845	C	2.475547	4.545054	2.334088
C	1.420141	-0.461859	0.793530	H	-0.100912	-2.852510	1.946556
C	0.367297	-0.724357	1.837463	H	-1.498554	-1.792799	2.086731
C	-0.540140	-1.921522	1.563367	H	-1.405471	-2.961350	-0.121534
C	-0.784942	-2.069589	0.068187	H	1.695159	-4.779612	1.342278
C	1.104520	-3.677113	-0.377887	H	1.907079	-3.040229	1.542395
C	2.018734	-3.861902	0.825168	H	3.676839	-4.652221	-0.347057
C	3.426496	-2.012876	-1.905563	H	3.966661	-4.564190	1.390135
C	2.635040	-0.854771	-1.313081	H	5.248065	-3.092573	-1.503058
C	3.539186	-4.010005	0.538810	H	5.296057	-1.391597	-1.018189
C	4.318253	-2.713528	0.385233	H	4.360052	-2.446653	2.450489
C	4.662163	-2.288461	-1.021570	H	1.138020	-5.752581	-0.815835
C	4.652310	-2.013267	1.483332	H	0.141088	-4.712484	-1.986455
O	2.988681	0.287448	-1.567600	H	-0.065998	-1.135316	-2.475886
O	2.285323	0.499933	1.167645	H	0.990809	-2.512519	-2.875309
C	0.772868	-4.760156	-1.098539	H	-0.713753	-2.781061	-2.458537
H	2.825553	-2.926556	-1.991133	H	-4.627406	-1.448600	2.005016
H	0.874416	-0.815572	2.812518	H	-4.890189	-0.874377	4.385122
H	-0.238599	0.193501	1.908261	H	-3.694525	1.094274	5.344948
H	3.757712	-1.713380	-2.911356	H	-2.241263	2.494773	3.872703
C	0.173990	-2.174679	-2.225110	H	-1.990706	1.933796	1.482949
O	-1.424586	-0.916086	-0.444297	H	-4.377241	2.417171	-0.150259
C	-3.278822	0.190589	1.548391	H	-4.186874	4.524100	-1.433840
Si	-2.932816	-0.209721	-0.265780	H	-2.445304	4.760071	-3.204883
C	-2.757201	1.415392	-1.190734	H	-0.894622	2.862984	-3.677272
C	-4.097436	-0.578507	2.396554	H	-1.086771	0.752247	-2.390614
C	-4.248383	-0.259004	3.749154	H	-5.112147	-3.294993	-1.072411
C	-3.579485	0.844030	4.287075	H	-3.365884	-3.254650	-0.763209
C	-2.766525	1.628340	3.463779	H	-4.505127	-2.777679	0.512162
C	-2.624159	1.304366	2.112420	H	-4.675088	-1.968216	-3.143224
C	-3.618487	2.498888	-0.934153	H	-2.941107	-1.756631	-2.791429
C	-3.510909	3.693060	-1.652278	H	-3.967636	-0.334345	-3.074029
C	-2.534482	3.825520	-2.644642	H	-6.429630	-1.182673	-1.458569
C	-1.668522	2.761478	-2.912073	H	-5.949272	-0.569639	0.142489
C	-1.780571	1.570613	-2.190424	H	-5.661453	0.413930	-1.310920
C	-4.276411	-1.281272	-1.108440	H	4.733751	0.024257	2.133141
C	-4.310518	-2.724021	-0.569613	H	5.588945	-0.250495	0.606755
C	-3.942508	-1.333491	-2.612929	H	6.306279	-0.797485	2.145277
C	-5.651670	-0.614848	-0.916774	H	1.273697	2.160674	-1.388380
C	5.360117	-0.696559	1.583615	H	0.909546	3.685897	-0.525776
Si	2.377490	2.171224	0.811855	H	0.053694	2.185313	-0.100703

H	4.329363	1.921989	-0.675868	C	-2.460314	-0.059457	2.444287
H	4.161293	3.614331	-0.126644	C	-3.554005	2.893337	-0.796558
H	4.862169	2.393935	0.966768	C	-3.910352	4.227588	-0.583357
H	2.854234	2.920389	4.539443	C	-4.611216	4.587419	0.571876
H	2.744681	1.347899	3.702876	C	-4.953971	3.607412	1.507676
H	4.060462	2.477682	3.310259	C	-4.590087	2.275110	1.290157
H	-0.046582	3.435936	2.193717	C	-4.874960	-0.668335	-1.276509
H	0.472478	3.451464	3.895212	C	-5.102287	0.260450	-2.486951
H	0.308346	1.908266	3.032520	C	-6.166382	-0.732957	-0.439325
H	2.295145	5.090037	3.278810	C	-4.507625	-2.065061	-1.808046
H	3.538224	4.677483	2.076423	C	4.589917	-1.865368	1.799745
H	1.876223	5.041844	1.552231	Si	4.681911	1.341479	-0.701785
				C	5.058350	2.801238	0.478045
				C	4.382639	1.908098	-2.466218
Compound 24' (T ₁)				C	6.093095	0.108789	-0.652607
Gibbs Free Energy = -2321.423815				C	3.996051	3.903913	0.333947
Hartree				C	6.441850	3.381623	0.129355
C	0.069529	-1.093271	-1.246783	C	5.061279	2.291343	1.930650
C	1.567354	-0.821954	-1.099920	H	-0.882126	2.282717	-1.149035
C	2.026980	0.535783	-0.667592	H	-0.167624	1.377625	-2.485746
C	1.190762	1.759959	-0.819167	H	-0.673988	0.239684	0.302412
C	-0.194585	1.460491	-1.388228	H	-0.875621	-2.442343	1.686218
C	-0.753203	0.169140	-0.797260	H	0.457195	-1.335494	1.368131
C	-0.417658	-2.261371	-0.383480	H	0.696082	-4.359295	0.948765
C	0.019688	-2.299078	1.066186	H	0.951121	-3.583175	2.513333
C	2.388677	-3.235812	-1.481916	H	2.909845	-4.840580	-0.126162
C	2.570053	-1.733850	-1.593514	H	4.122740	-3.557235	-0.238396
C	1.024829	-3.421191	1.425694	H	2.649648	-1.978624	2.811808
C	2.475253	-3.128654	1.084203	H	-1.648673	-3.968874	-0.176577
C	3.041954	-3.743984	-0.174571	H	-1.599211	-3.231682	-1.879602
C	3.177552	-2.339451	1.917587	H	0.247444	-2.288285	-3.079339
O	3.666105	-1.284960	-2.003254	H	-1.263057	-1.334274	-2.959278
O	3.229679	0.650773	-0.084447	H	0.276530	-0.539577	-3.360099
C	-1.262676	-3.192980	-0.844546	H	-4.120585	-2.656136	0.998958
H	1.331974	-3.527808	-1.507247	H	-3.611762	-3.690266	3.175266
H	1.087170	2.220860	0.185624	H	-2.336826	-2.420472	4.904864
H	1.699690	2.531244	-1.430148	H	-1.596826	-0.085369	4.425895
H	2.898058	-3.700127	-2.340556	H	-2.142305	0.970525	2.260708
C	-0.184627	-1.332789	-2.755625	H	-3.019308	2.623711	-1.710584
O	-2.102680	0.003181	-1.179332	H	-3.643629	4.988798	-1.321409
C	-3.171364	-0.758142	1.447879	H	-4.891126	5.630498	0.741377
Si	-3.478198	0.081303	-0.215219	H	-5.504545	3.881828	2.411468
C	-3.880133	1.890835	0.136901	H	-4.860212	1.522268	2.035844
C	-3.575125	-2.073739	1.742556	H	-5.882432	-0.163844	-3.144128
C	-3.283805	-2.667236	2.973605	H	-5.433968	1.264355	-2.181562
C	-2.569900	-1.956159	3.943188	H	-4.185046	0.372138	-3.087142

H	-6.447768	0.258853	-0.049339	H	-3.844762	-1.517197	-1.164932
H	-6.072576	-1.414963	0.420062	O	1.960245	0.541527	1.079246
H	-7.005473	-1.093910	-1.060736	C	3.666777	-1.296952	-0.396499
H	-3.610126	-2.023933	-2.441626	Si	3.564356	0.271027	0.652481
H	-4.310026	-2.792867	-1.007495	C	4.190493	1.718719	-0.388519
H	-5.336555	-2.463312	-2.420657	C	3.762504	-2.578993	0.176314
H	5.196380	-2.210264	2.656675	C	3.771211	-3.730898	-0.613977
H	4.615896	-0.764490	1.813120	C	3.677757	-3.627666	-2.004945
H	5.080278	-2.195827	0.876024	C	3.575229	-2.366758	-2.597786
H	5.317811	2.289660	-2.907427	C	3.570517	-1.218414	-1.800338
H	3.622531	2.699849	-2.545462	C	5.289192	1.584814	-1.258680
H	4.052106	1.035644	-3.049830	C	5.811927	2.685106	-1.945048
H	6.946248	0.525418	-1.213828	C	5.243403	3.950329	-1.773532
H	6.436025	-0.112441	0.367959	C	4.156463	4.108665	-0.908448
H	5.775646	-0.822792	-1.140340	C	3.641316	3.004764	-0.223806
H	2.991211	3.536608	0.592763	C	4.595595	0.250613	2.263025
H	4.221550	4.749149	1.009634	C	4.638255	1.685613	2.827332
H	3.954649	4.305943	-0.691449	C	4.007892	-0.668138	3.346023
H	7.243745	2.634980	0.245163	C	6.026385	-0.200741	1.911518
H	6.683832	4.230326	0.794925	C	-0.798347	1.439651	-1.312681
H	6.480736	3.758665	-0.906508	H	-0.349766	1.238077	-2.303129
H	5.265323	3.120357	2.632927	H	-1.364072	2.373671	-1.444447
H	4.088527	1.850802	2.201269	O	-3.079548	0.634516	-1.222784
H	5.835171	1.524333	2.096982	Si	-4.208325	1.536754	-0.314966

TS-7 (T₁)

Gibbs Free Energy = -2321.350501

Hartree

C	0.332187	-1.881553	1.347706	C	-6.189390	0.474651	-2.013224
C	0.181959	-3.081214	0.420667	C	-5.048326	2.573282	-2.791151
C	0.161143	-2.890320	-1.108051	C	-2.221776	-0.939967	-3.524479
C	-1.127480	-2.394448	-1.711286	C	-0.651149	0.283964	2.282807
C	-1.509617	-0.614310	0.143389	H	-0.736594	-3.613265	0.719573
C	-0.254819	-0.498948	1.002027	H	1.006581	-3.769910	0.656204
C	0.991187	-2.071369	2.497390	H	0.997747	-2.255657	-1.430471
C	-2.495201	-1.623518	0.535118	H	0.369276	-3.886753	-1.546205
C	-2.409809	-3.141633	-1.416947	H	1.082317	-1.299315	3.258101
O	-2.540494	-2.057573	1.690561	H	1.447134	-3.038662	2.728533
C	-1.147634	-1.274182	-2.534195	H	-2.920215	-3.429005	-2.353485
C	0.846354	0.309759	0.232822	H	-2.180709	-4.077203	-0.884815
C	-1.770600	0.345774	-0.940159	H	-0.019746	2.249032	0.557230
C	0.322475	1.640259	-0.294076	H	1.153995	2.186281	-0.759972
H	1.158246	-0.302459	-0.630192	H	3.816122	-2.686565	1.260308
H	-0.175087	-0.809182	-2.725365	H	3.847016	-4.713545	-0.141121
C	-3.351104	-2.276071	-0.546550	H	3.680978	-4.528276	-2.624368
H	-4.117500	-2.889813	-0.052081	H	3.494683	-2.276137	-3.684205

H	3.488237	-0.241493	-2.283342	C	-0.194301	-2.068114	3.194784
H	5.747637	0.603310	-1.407240	C	-2.701898	-1.149945	1.382794
H	6.665100	2.554127	-2.616069	C	-2.246988	-3.321799	0.114472
H	5.648439	4.812212	-2.310387	O	-3.075328	-0.838494	2.506322
H	3.711417	5.096865	-0.764236	C	-1.300827	-1.536671	-1.555636
H	2.801875	3.145804	0.461148	C	0.791144	0.162907	0.356271
H	5.205549	1.697863	3.775340	C	-1.771026	-0.190176	-0.795000
H	5.126025	2.389298	2.136701	C	0.303670	1.359044	-0.451756
H	3.626234	2.066222	3.041721	H	0.960895	-0.657110	-0.354771
H	3.936104	-1.718057	3.027141	H	-0.311381	-1.296878	-1.970684
H	3.001130	-0.343139	3.641406	C	-3.311138	-2.330394	0.640963
H	4.650398	-0.641362	4.244838	H	-4.008613	-2.829575	1.328840
H	6.050837	-1.235022	1.533244	H	-3.886920	-1.930626	-0.204037
H	6.485238	0.447593	1.147594	O	2.004663	0.435282	1.029267
H	6.669697	-0.157224	2.808683	C	3.510408	-0.969057	-1.026307
H	-3.111600	3.791409	-0.576617	Si	3.549314	0.301087	0.374869
H	-2.518659	2.934346	0.869871	C	4.028389	1.956856	-0.378975
H	-4.116413	3.708243	0.893178	C	3.947143	-2.300953	-0.903461
H	-5.210551	-0.400728	0.930026	C	3.801191	-3.215774	-1.950568
H	-3.953216	0.394865	1.891448	C	3.206115	-2.818349	-3.150801
H	-5.555676	1.155122	1.728401	C	2.770865	-1.498371	-3.301702
H	-7.535956	2.862608	-1.625258	C	2.930542	-0.587904	-2.254051
H	-7.159996	2.166096	-0.034180	C	5.022957	2.050639	-1.370073
H	-6.343975	3.655296	-0.571593	C	5.403666	3.288247	-1.896666
H	-7.016039	0.625935	-2.730890	C	4.790097	4.459018	-1.441031
H	-6.591015	-0.102705	-1.164789	C	3.797874	4.386572	-0.458202
H	-5.426032	-0.143853	-2.510426	C	3.423420	3.146782	0.066590
H	-4.235720	2.002055	-3.266114	C	4.667707	-0.112341	1.858363
H	-5.839930	2.730718	-3.545937	C	4.631910	1.104048	2.806834
H	-4.650151	3.565442	-2.522153	C	4.140361	-1.341773	2.622028
H	-3.231029	-1.136372	-3.140012	C	6.112409	-0.343408	1.380895
H	-2.091309	-1.536479	-4.447390	C	-0.927669	1.013028	-1.302950
H	-2.181651	0.121694	-3.811095	H	-0.638388	0.806140	-2.345145
H	0.243523	0.610128	2.830518	H	-1.585352	1.887322	-1.345842
H	-1.231031	1.182617	2.024948	O	-3.133797	0.044008	-1.120555
H	-1.274711	-0.357591	2.915629	Si	-4.262373	1.179670	-0.567050
				C	-4.913968	2.066993	-2.130829
				C	-3.515310	2.378316	0.679315
				C	-5.663980	0.244396	0.270025
				C	-5.974296	3.108055	-1.727292
C	0.126516	-1.699380	1.945847	C	-5.543866	1.018939	-3.067458
C	0.902651	-2.672272	1.078124	C	-3.765961	2.774381	-2.871106
C	0.295365	-3.143812	-0.297235	C	-2.221619	-1.850849	-2.743255
C	-1.096139	-2.700218	-0.626690	C	-0.375293	0.735708	2.528901
C	-1.612956	-0.426988	0.685905	H	1.100210	-3.558997	1.697017
C	-0.264941	-0.304836	1.388192	H	1.889983	-2.238429	0.869457

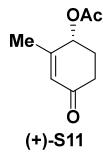
INT-7 (T₁)

Gibbs Free Energy = -2321.342725
Hartree

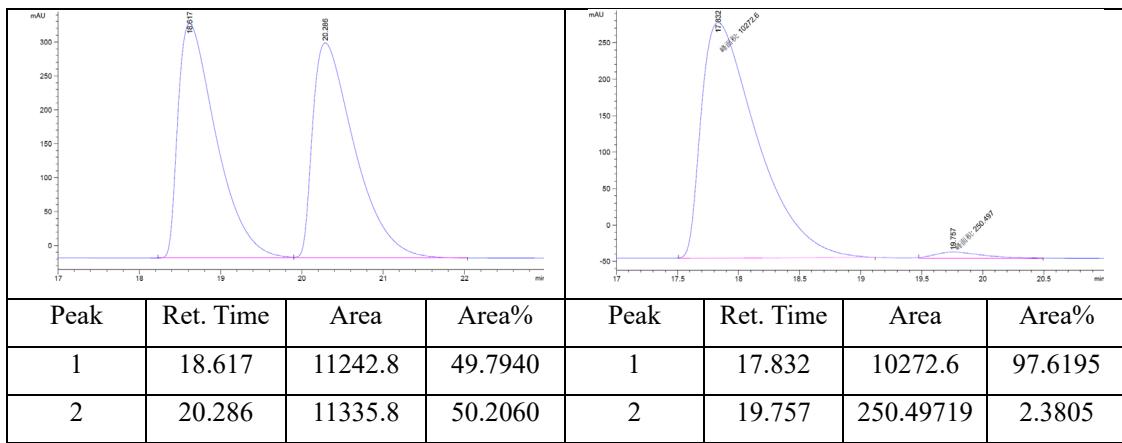
H	0.974678	-2.828361	-1.103015	H	-0.596674	1.730967	2.119446	
H	0.327259	-4.248703	-0.293494	H	-1.196481	0.474796	3.204148	
H	-0.731335	-1.419721	3.886001					
H	0.066036	-3.065656	3.560558	TS-7' (T₁)				
H	-2.770442	-4.054984	-0.533386	Gibbs Free Energy =	-2321.323332			
H	-1.849055	-3.904012	0.961229	Hartree				
H	0.075004	2.184568	0.238455	C	0.205273	-1.507281	1.937518	
H	1.122840	1.719404	-1.090333	C	0.753049	-2.632288	1.071764	
H	4.403113	-2.642501	0.027173	C	0.267721	-2.824182	-0.381738	
H	4.148392	-4.244598	-1.825806	C	-1.166396	-2.510173	-0.730991	
H	3.083943	-3.534567	-3.967380	C	-1.517908	-0.442559	0.515061	
H	2.308875	-1.175788	-4.238443	C	-0.227666	-0.180280	1.295702	
H	2.598155	0.443727	-2.397785	C	0.124009	-1.721659	3.257570	
H	5.501518	1.141495	-1.746330	C	-2.635320	-1.114495	1.225287	
H	6.177021	3.339535	-2.667764	C	-2.281674	-3.216603	0.014636	
H	5.083128	5.428009	-1.853760	O	-2.908249	-0.879518	2.397880	
H	3.313802	5.299804	-0.101848	C	-1.416842	-1.916740	-1.963439	
H	2.644444	3.097238	0.831919	C	0.860043	0.301871	0.295731	
H	5.250457	0.903099	3.699791	C	-1.824987	0.384499	-0.661176	
H	5.024355	2.013312	2.325546	C	0.428177	1.534911	-0.492357	
H	3.607086	1.316554	3.150543	H	1.023456	-0.499077	-0.436713	
H	4.185946	-2.264644	2.023872	H	-0.551366	-1.488901	-2.479156	
H	3.095411	-1.201885	2.937985	C	-3.355129	-2.213994	0.461118	
H	4.749804	-1.512893	3.527671	H	-4.107362	-2.666669	1.122606	
H	6.198784	-1.221306	0.721046	H	-3.869933	-1.781280	-0.408730	
H	6.501986	0.528357	0.829992	O	2.064075	0.530309	1.005101	
H	6.779002	-0.511129	2.245812	C	3.568160	-0.999876	-0.957130	
H	-2.681982	2.974237	0.277420	Si	3.620860	0.300424	0.414775	
H	-3.154473	1.824382	1.559857	C	4.211237	1.911337	-0.360874	
H	-4.294349	3.078786	1.023208	C	3.910733	-2.353077	-0.782015	
H	-6.039361	-0.575521	-0.362241	C	3.749086	-3.285410	-1.811329	
H	-5.330091	-0.181175	1.228431	C	3.234246	-2.883152	-3.046302	
H	-6.506993	0.922958	0.478583	C	2.894676	-1.542081	-3.249455	
H	-6.382895	3.610436	-2.622958	C	3.067405	-0.615381	-2.218338	
H	-6.823922	2.651266	-1.194135	C	5.241991	1.932472	-1.318601	
H	-5.553353	3.892472	-1.076898	C	5.701209	3.136691	-1.859961	
H	-5.894063	1.494885	-4.001607	C	5.132434	4.347157	-1.452331	
H	-6.413650	0.524850	-2.604971	C	4.106056	4.347351	-0.502530	
H	-4.817876	0.236427	-3.339737	C	3.652436	3.140454	0.036362	
H	-3.002830	2.058015	-3.211436	C	4.668254	-0.130008	1.944424	
H	-4.150910	3.299477	-3.764161	C	4.654778	1.107504	2.865693	
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H	-3.227473	-2.144927	-2.414170	C	6.116182	-0.438181	1.524682	
H	-1.791876	-2.676899	-3.331640	C	-0.800814	1.229612	-1.359852	
H	-2.335927	-0.975372	-3.400017	H	-0.463279	0.745528	-2.298260	
H	0.572380	0.783919	3.081949	H	-1.282965	2.167805	-1.678648	

O	-3.128127	0.592289	-0.991382	H	5.228557	0.897524	3.786111
Si	-4.344393	1.568732	-0.286705	H	5.108514	1.986537	2.381789
C	-5.064768	2.579498	-1.734980	H	3.628758	1.374954	3.164518
C	-3.544821	2.634199	1.031815	H	4.097627	-2.256255	2.141290
C	-5.647079	0.449732	0.469164	H	3.002639	-1.128926	2.970087
C	-6.167542	3.514523	-1.204979	H	4.612811	-1.485957	3.651883
C	-5.660930	1.618482	-2.780198	H	6.183101	-1.331362	0.883086
C	-3.951886	3.414867	-2.390769	H	6.567371	0.403597	0.974136
C	-2.702071	-1.926890	-2.725966	H	6.742258	-0.622062	2.416272
C	-0.455347	0.921934	2.355745	H	-2.700616	3.217889	0.632547
H	0.600549	-3.567681	1.631141	H	-3.168273	1.988183	1.839431
H	1.847362	-2.510482	1.013602	H	-4.272604	3.337006	1.468377
H	0.918001	-2.270845	-1.072209	H	-5.990495	-0.313984	-0.246093
H	0.446992	-3.887642	-0.636631	H	-5.244484	-0.061569	1.356775
H	-0.218469	-0.965987	3.962626	H	-6.525140	1.037034	0.784253
H	0.399485	-2.692787	3.679965	H	-6.605879	4.100508	-2.032940
H	-2.726654	-4.010223	-0.615971	H	-6.990095	2.954961	-0.730483
H	-1.870734	-3.718298	0.904273	H	-5.779673	4.233951	-0.465039
H	0.224238	2.364181	0.201046	H	-6.051458	2.184585	-3.645327
H	1.263590	1.863465	-1.128849	H	-6.496734	1.030674	-2.367443
H	4.306204	-2.696486	0.175142	H	-4.904920	0.911639	-3.158039
H	4.022399	-4.330690	-1.645734	H	-3.162569	2.771160	-2.808448
H	3.100832	-3.611996	-3.849876	H	-4.360902	4.021409	-3.218911
H	2.496317	-1.216600	-4.214065	H	-3.479731	4.109839	-1.676680
H	2.806990	0.431095	-2.399554	H	-3.332852	-2.795343	-2.480161
H	5.687388	0.992140	-1.656994	H	-2.505583	-1.948179	-3.809689
H	6.501469	3.131061	-2.604905	H	-3.300478	-1.018030	-2.522436
H	5.487199	5.290243	-1.876517	H	0.488227	1.133897	2.878395
H	3.656924	5.291720	-0.183320	H	-0.803841	1.847317	1.880296
H	2.846682	3.147698	0.775032	H	-1.225188	0.610921	3.068272

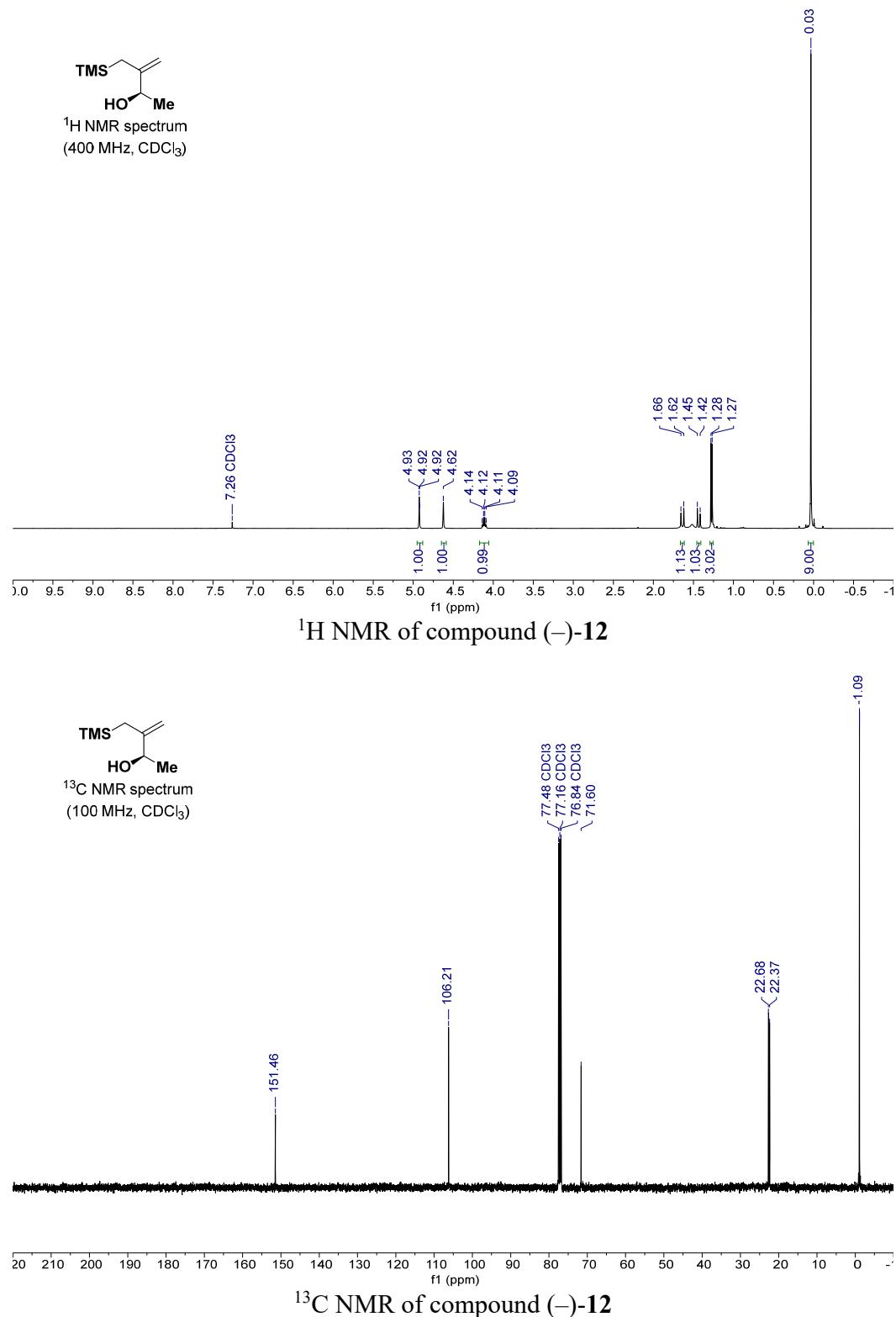
IV. HPLC Chromatograms

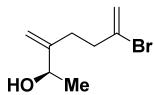


The racemic and optically active **S11** were analyzed with chiral HPLC (Daicel chiral column AD-H, *n*-hexane: isopropanol = 100:1, flow rate 1.0 mL/min, λ = 240 nm). For (+)-**S11**, *ee* = 95%.

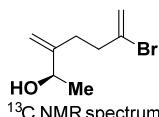
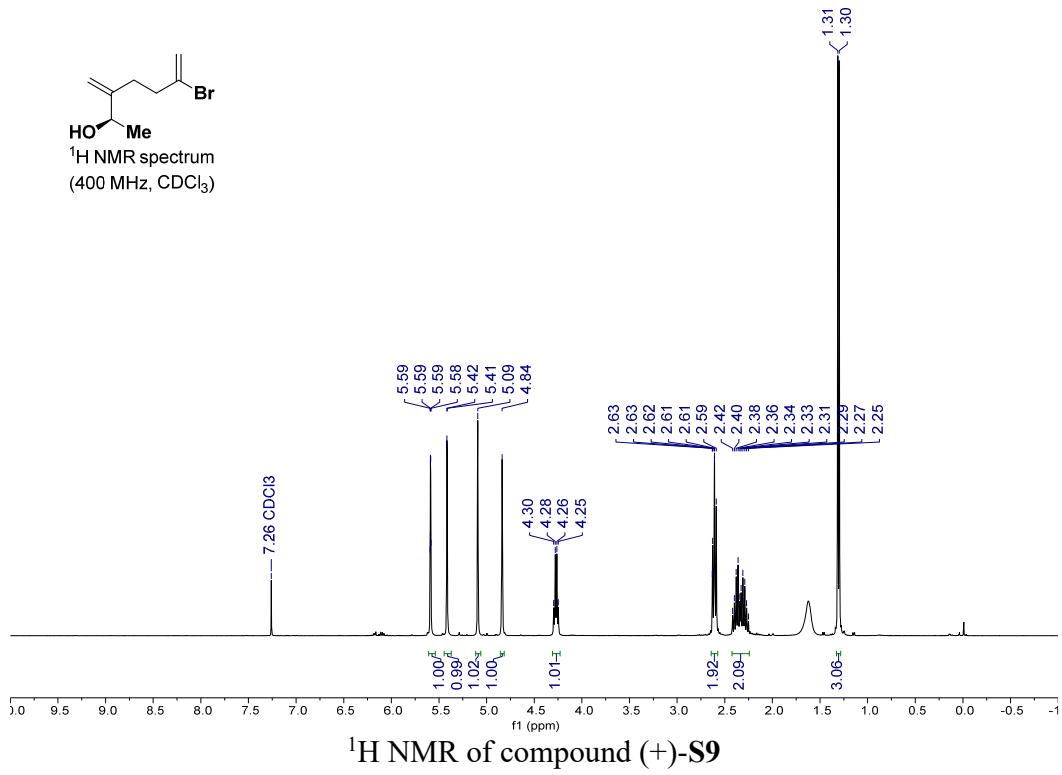


V. NMR Spectra

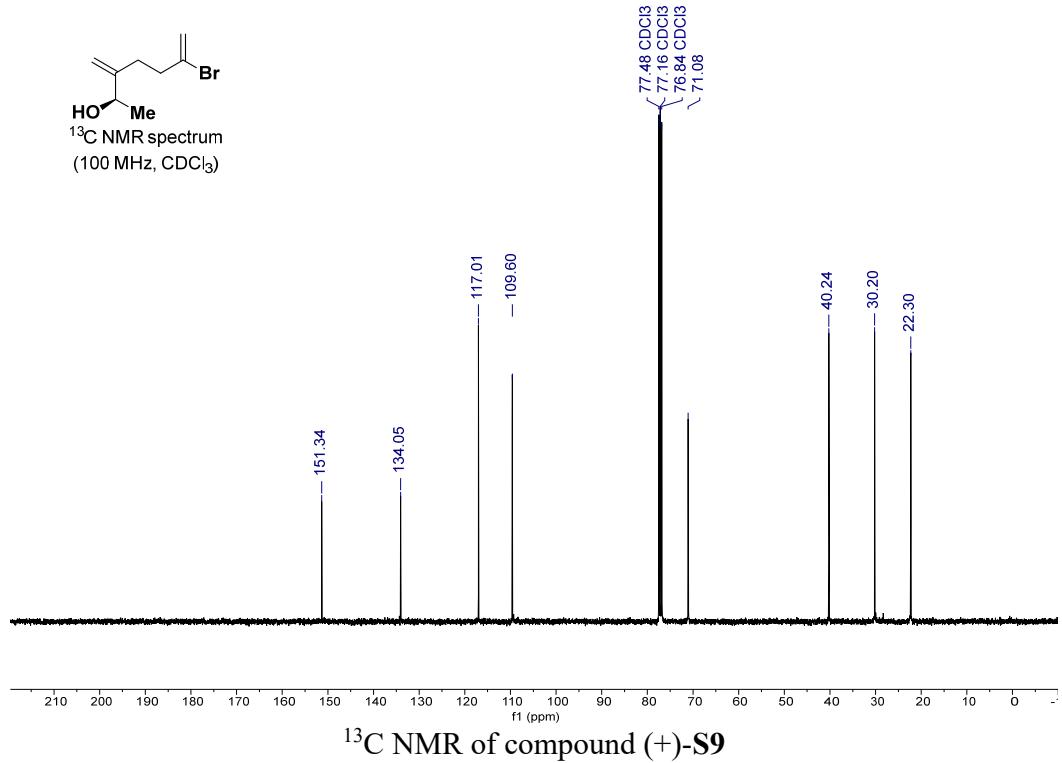


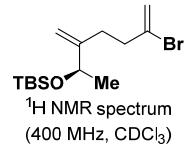


¹H NMR spectrum
(400 MHz, CDCl₃)

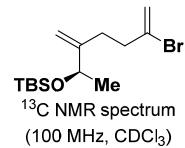
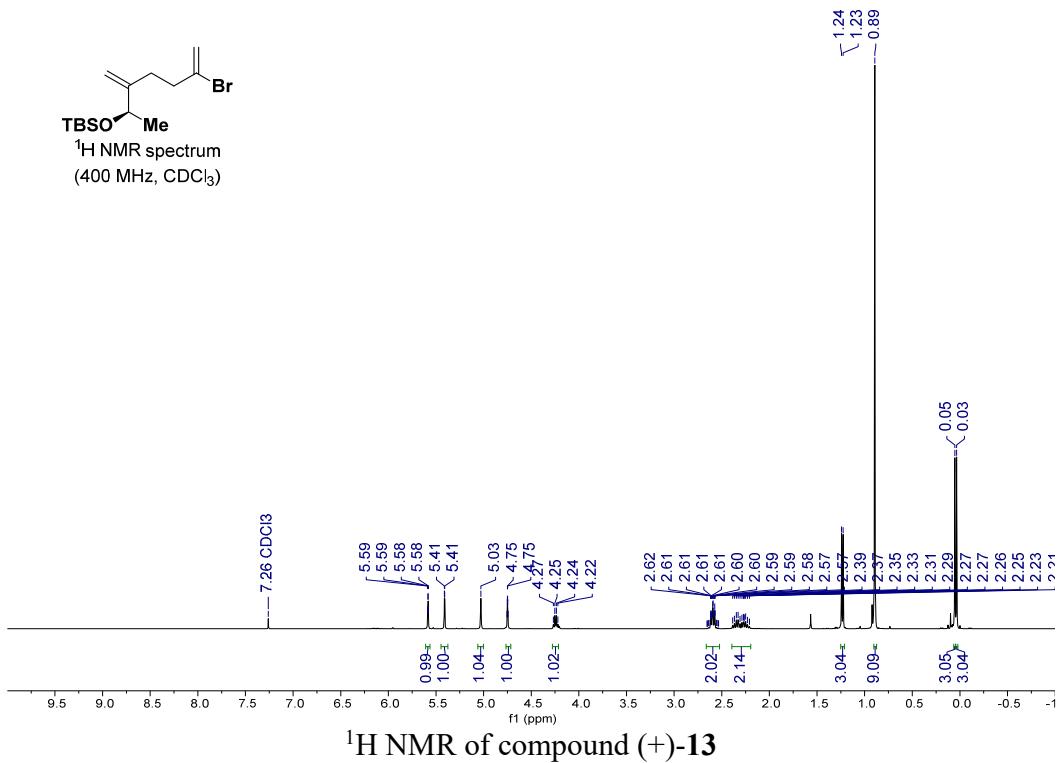


¹³C NMR spectrum
(100 MHz, CDCl₃)

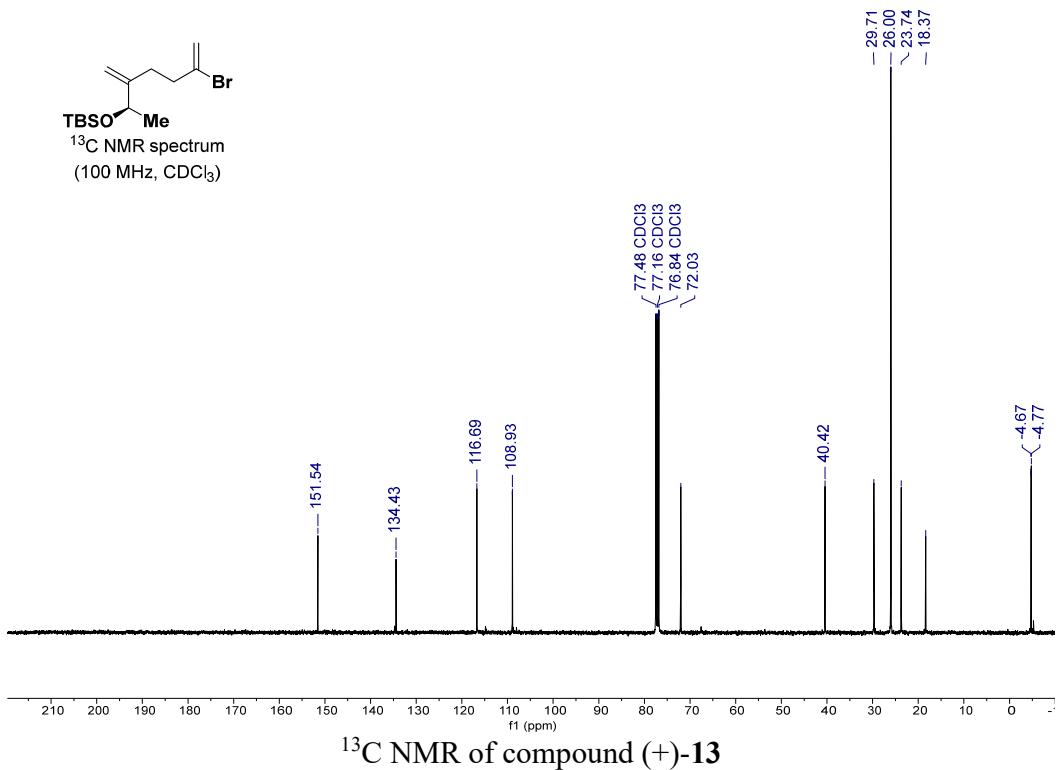


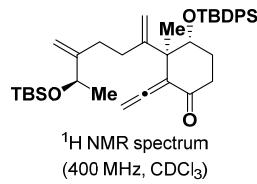


¹H NMR spectrum
(400 MHz, CDCl₃)

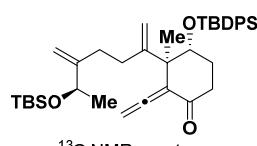
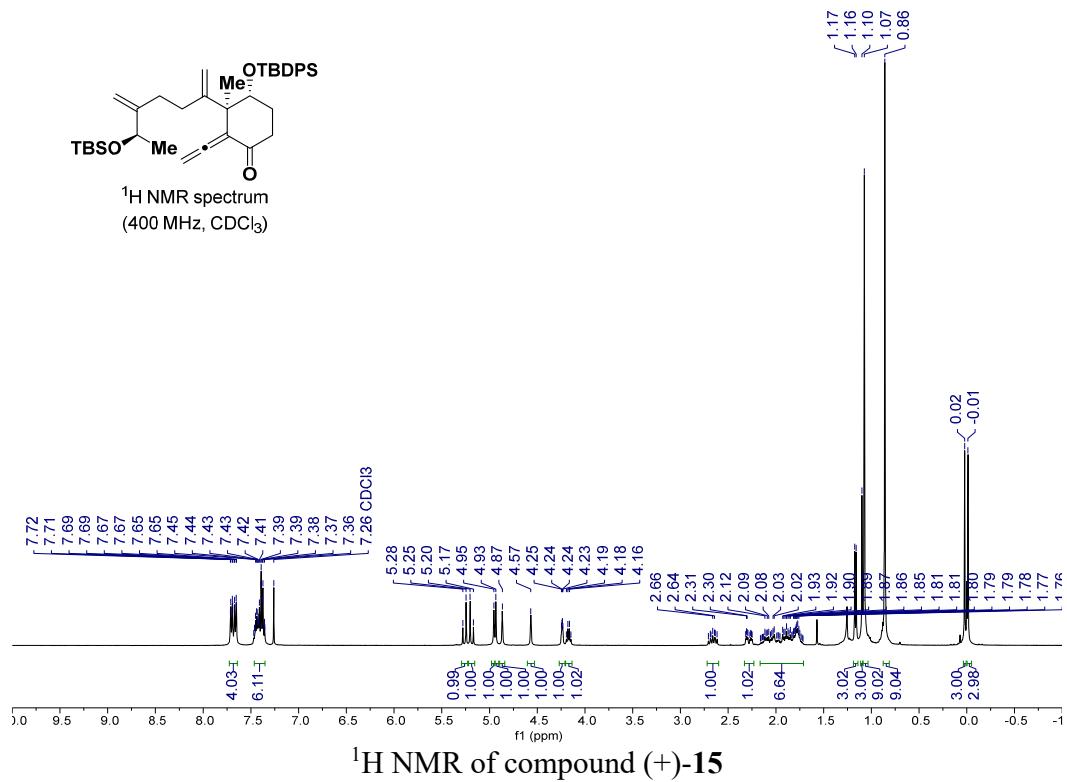


¹³C NMR spectrum
(100 MHz, CDCl₃)

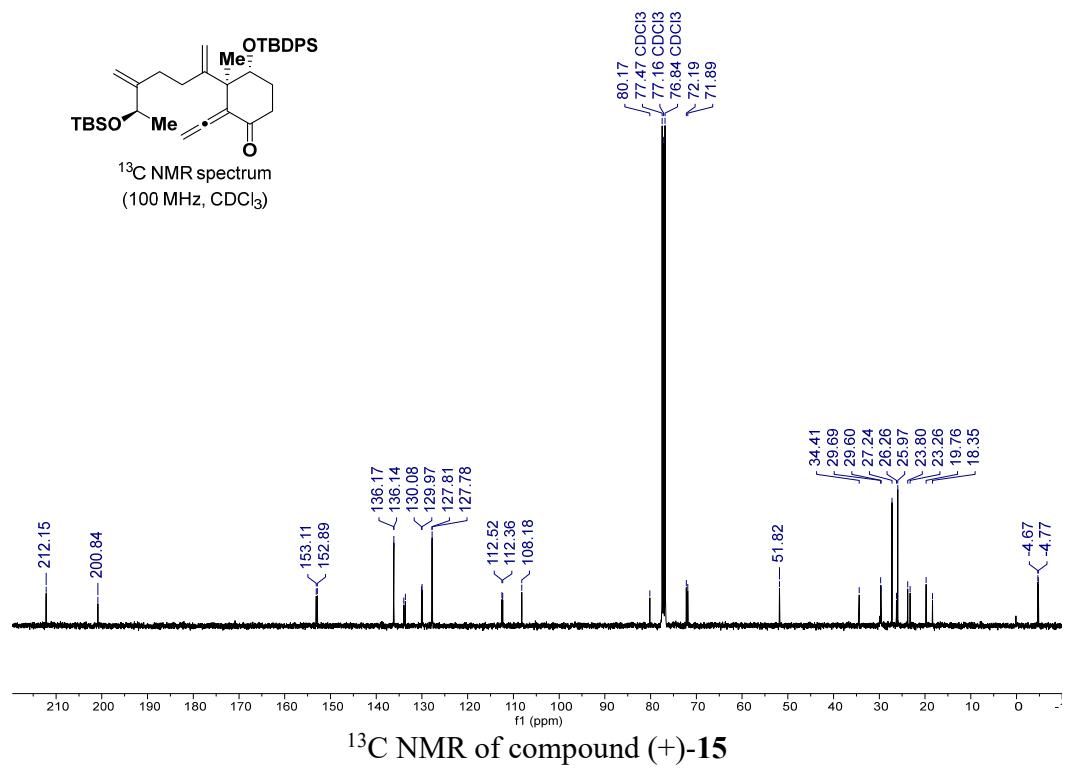


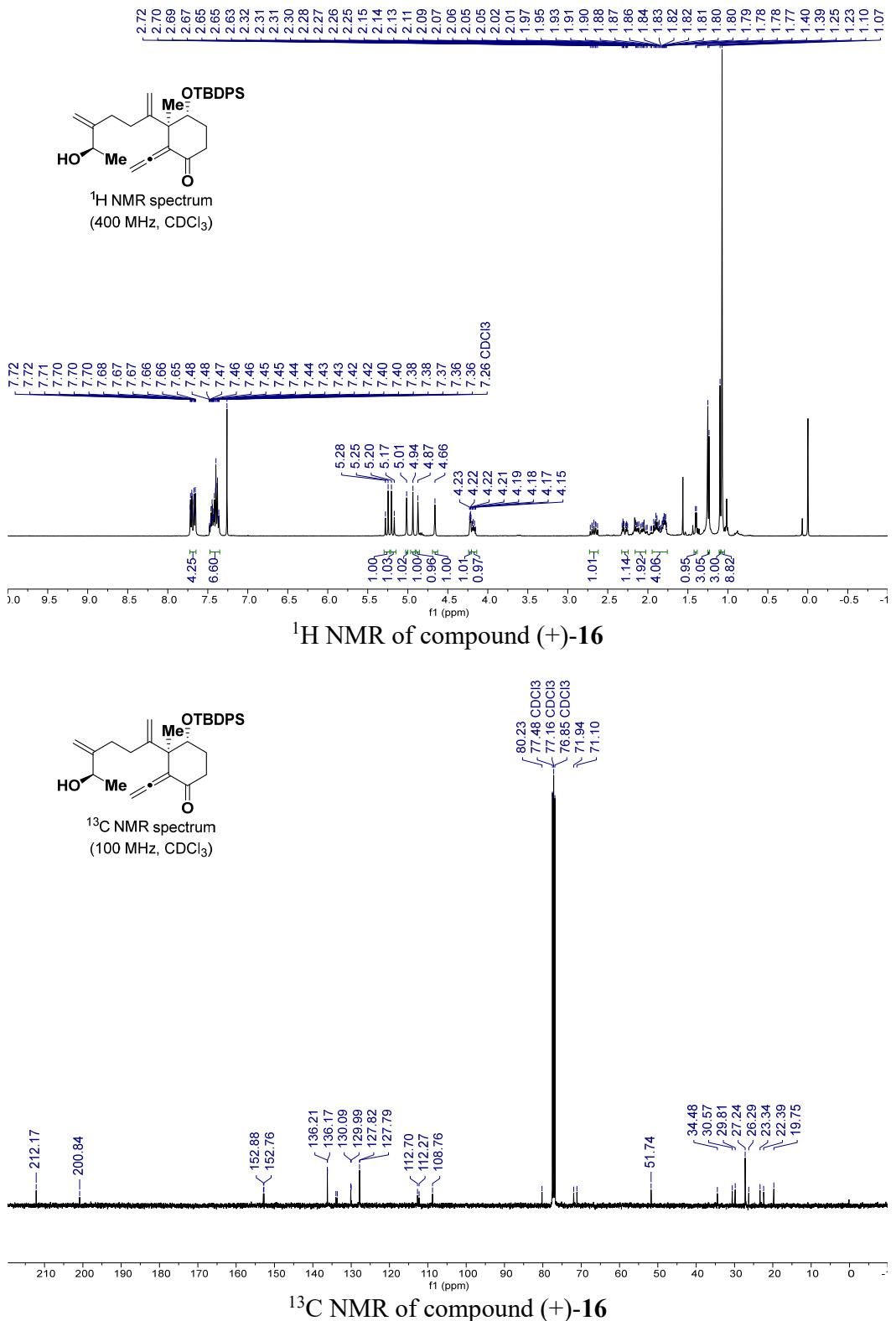


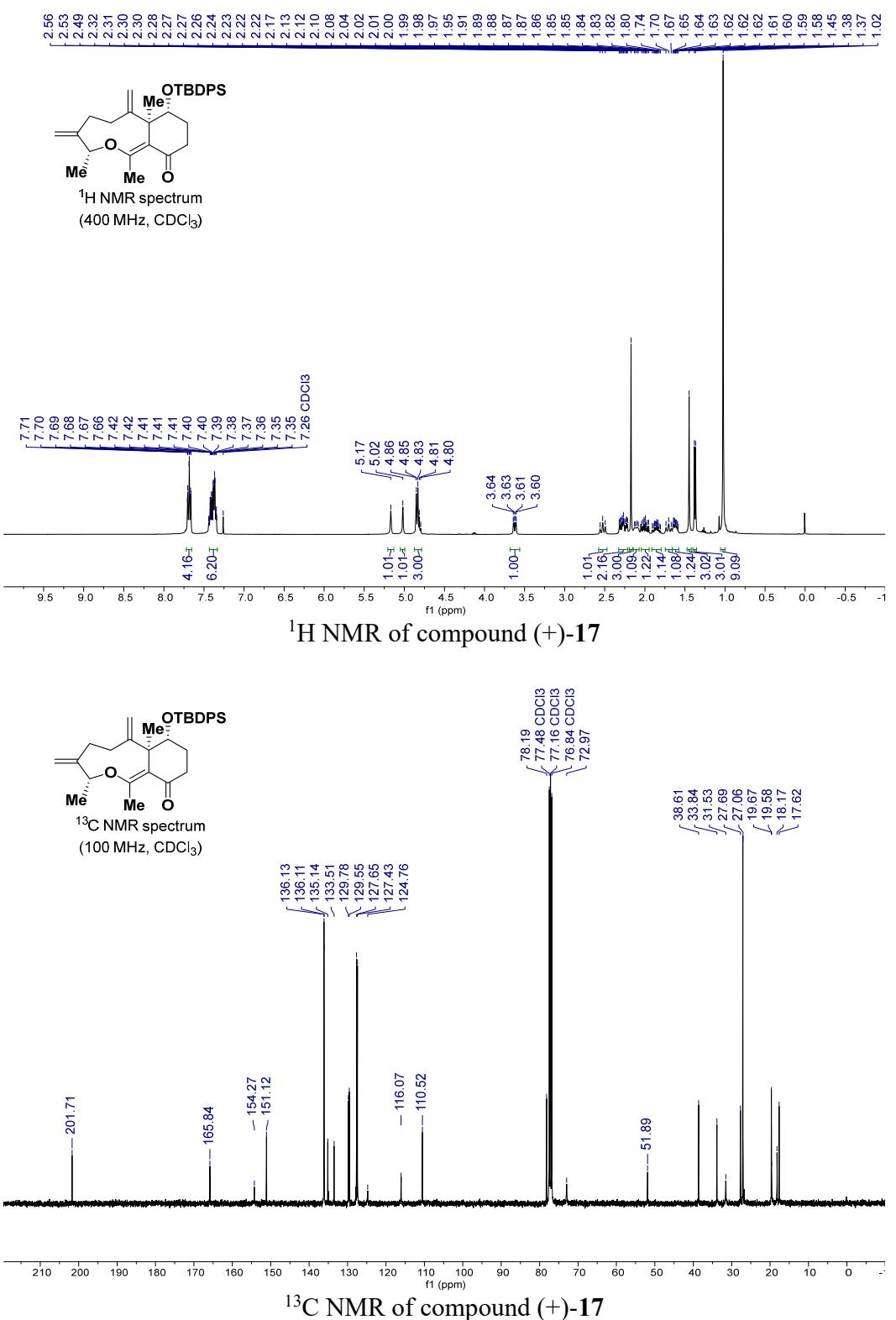
¹H NMR spectrum
(400 MHz, CDCl₃)

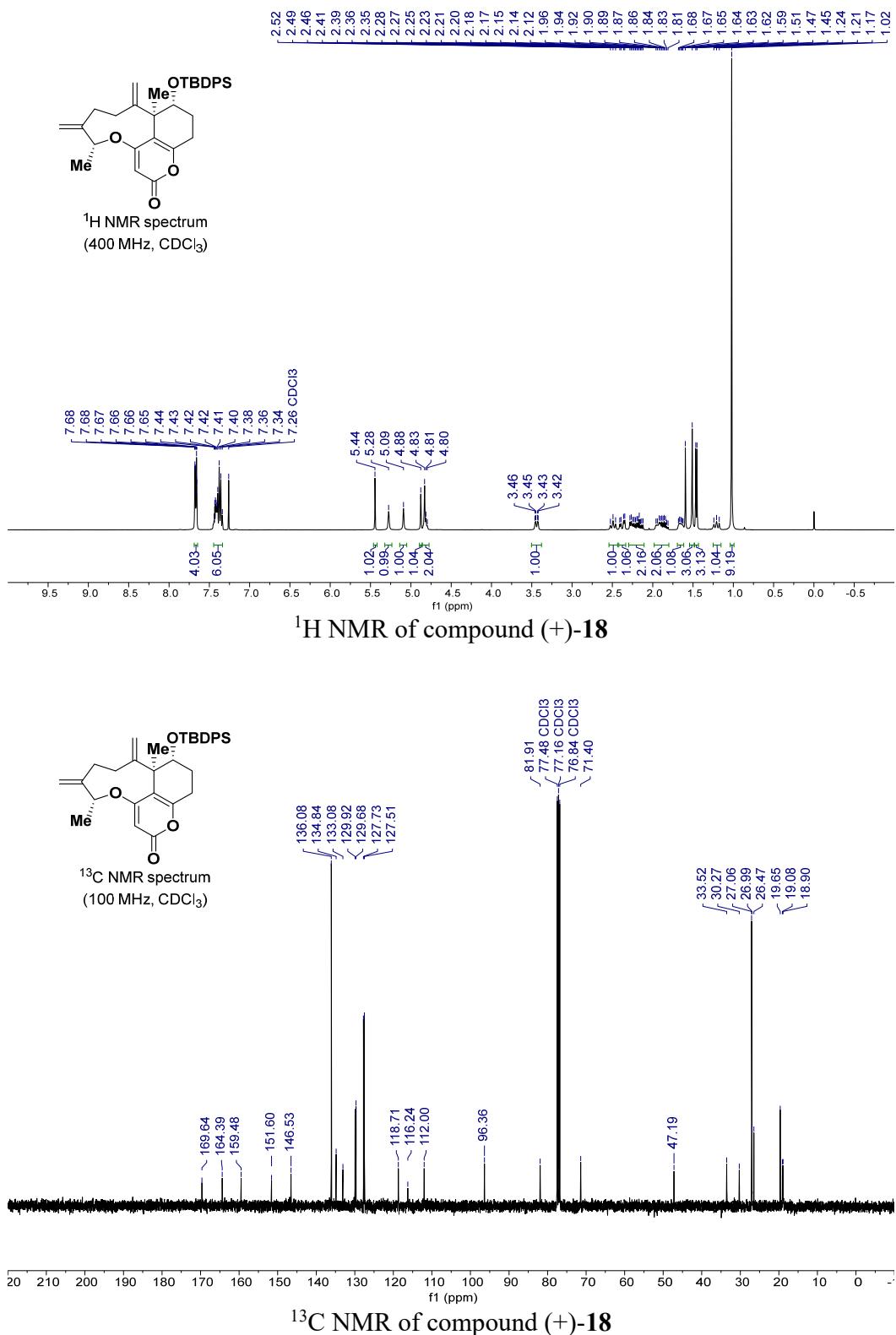


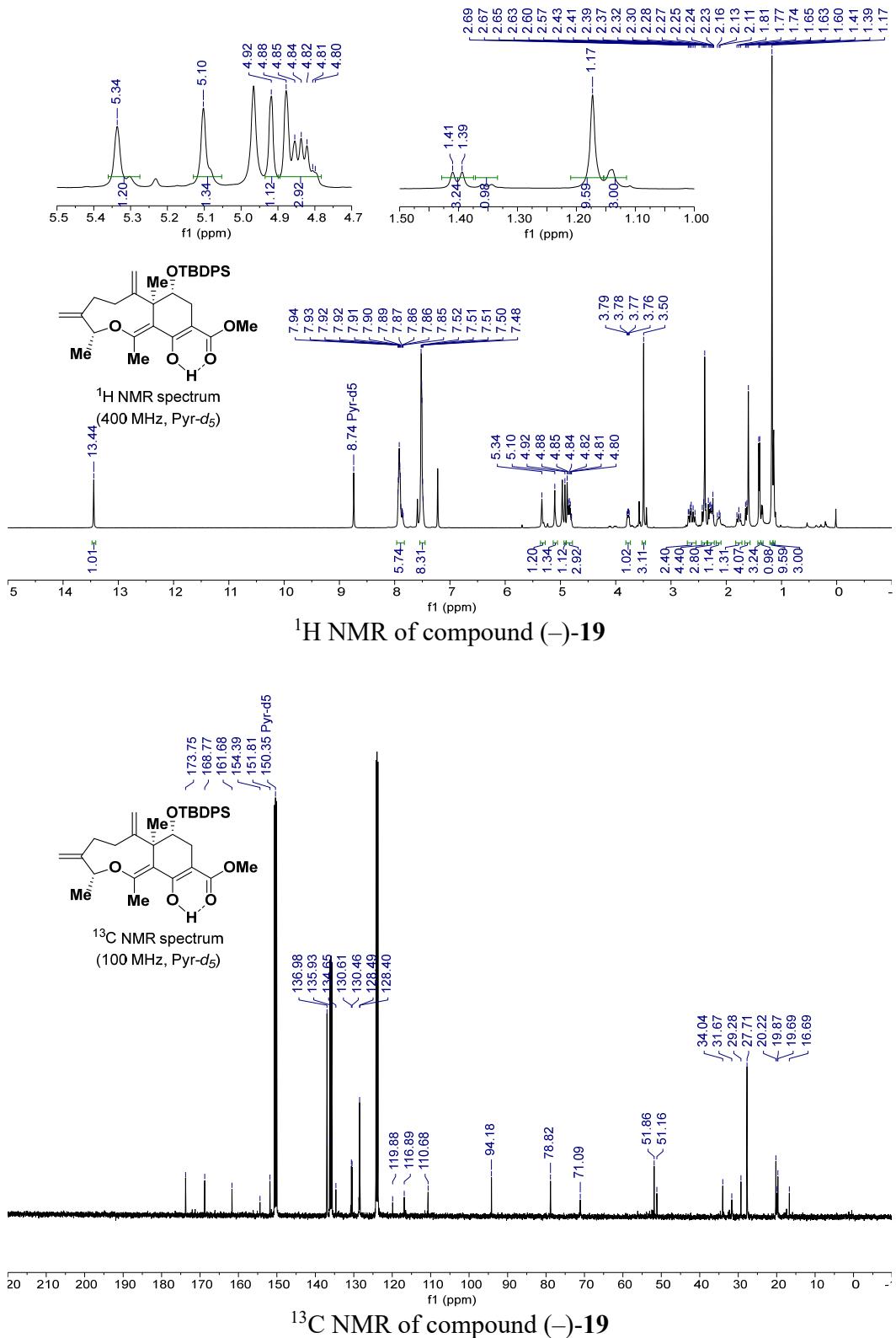
¹³C NMR spectrum
(100 MHz, CDCl₃)

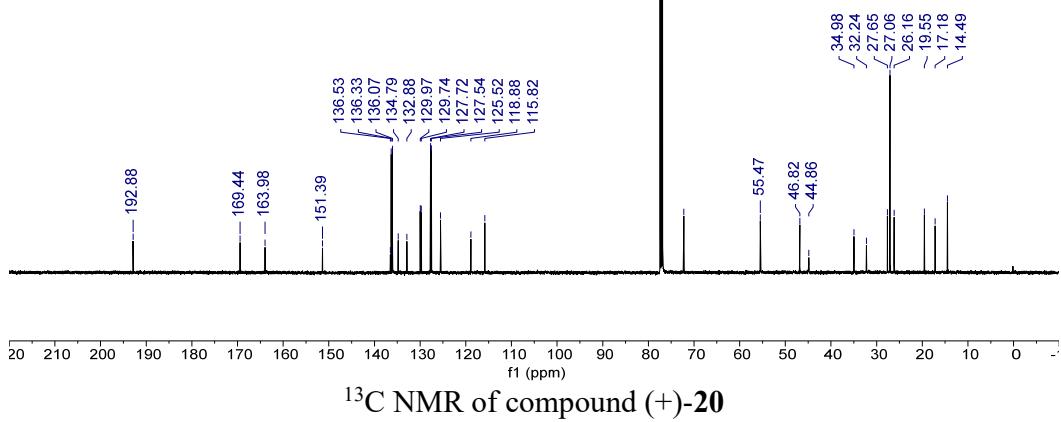
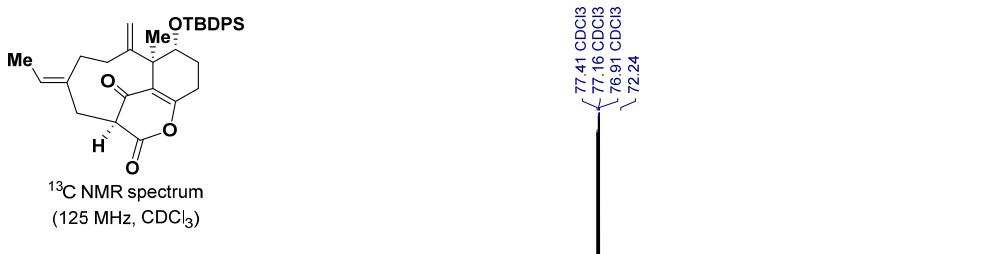
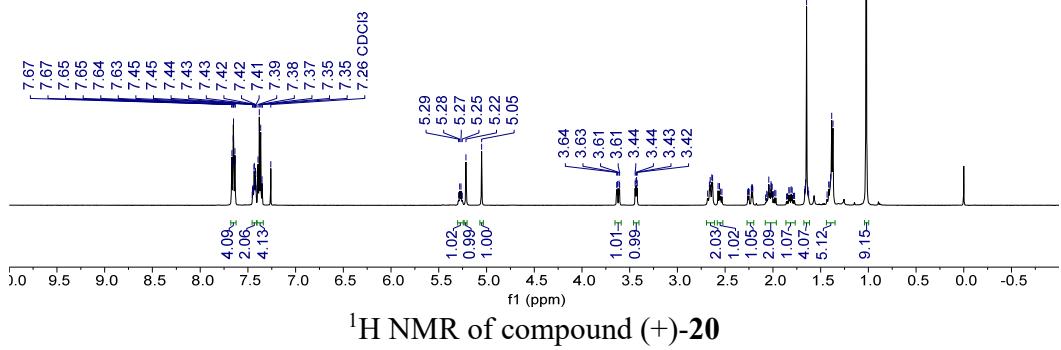
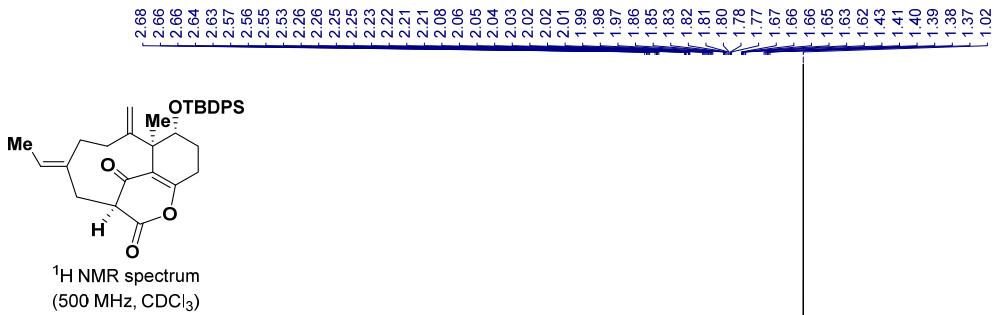


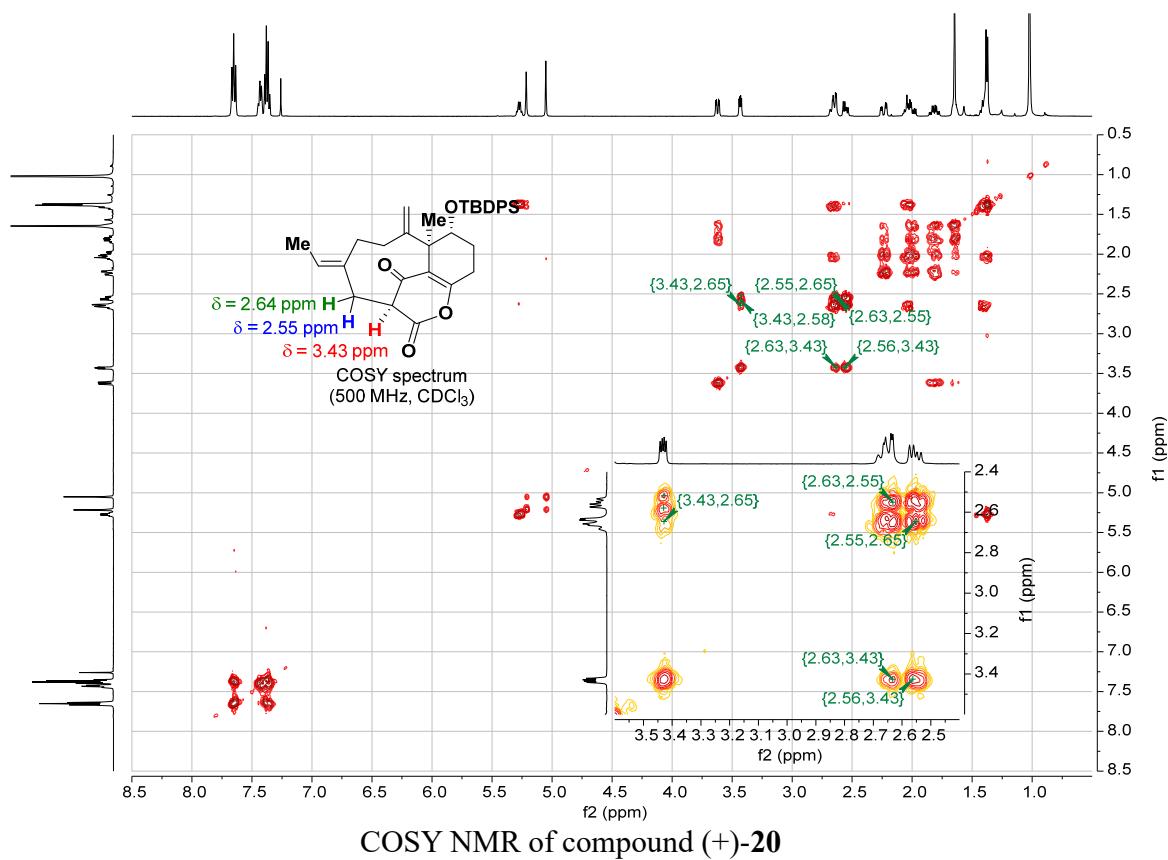


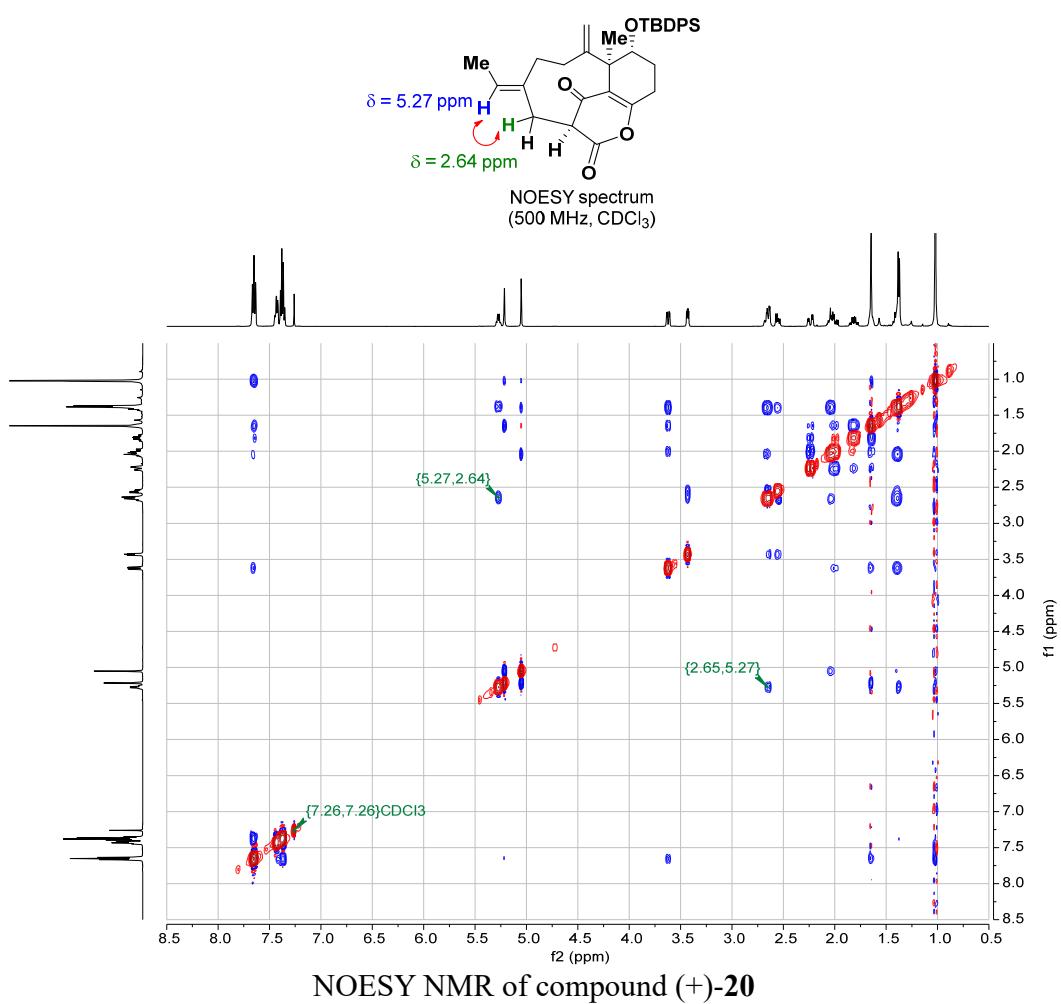


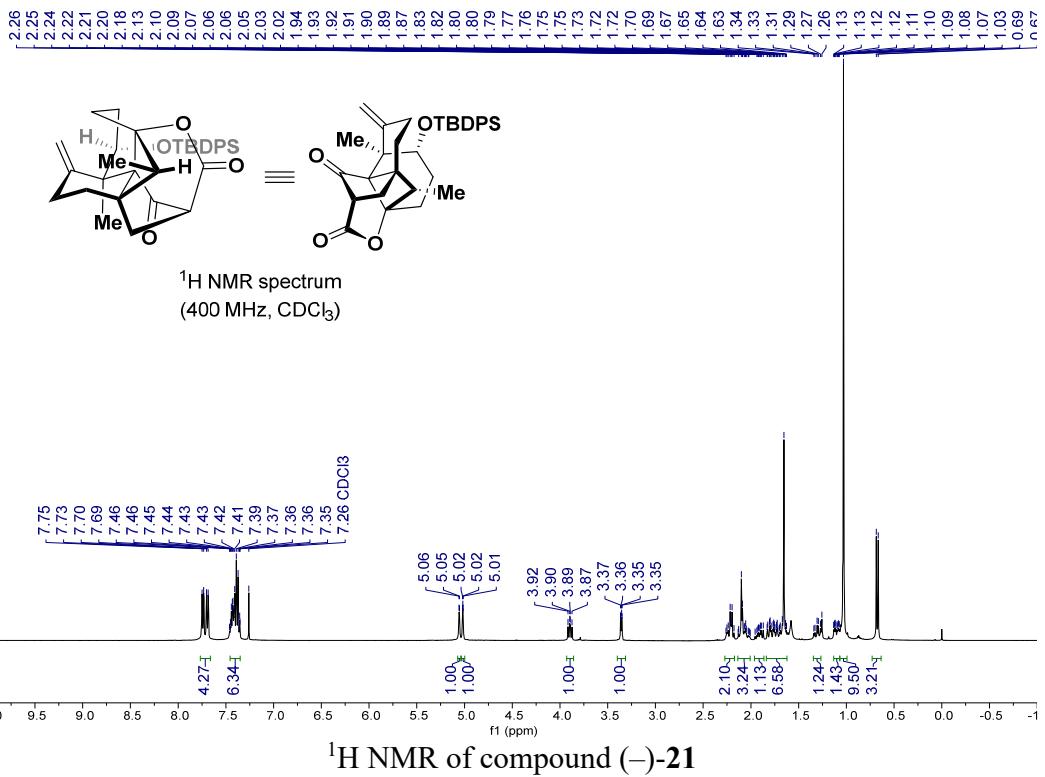


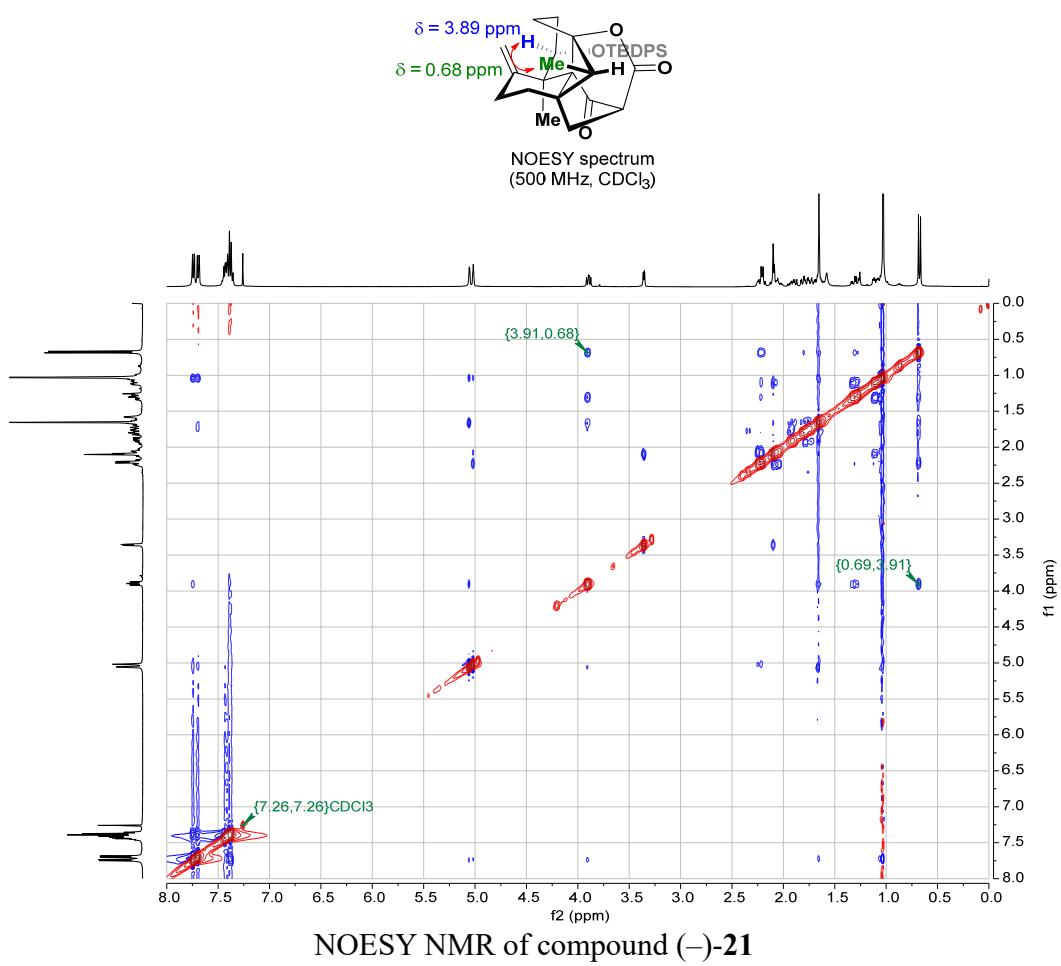


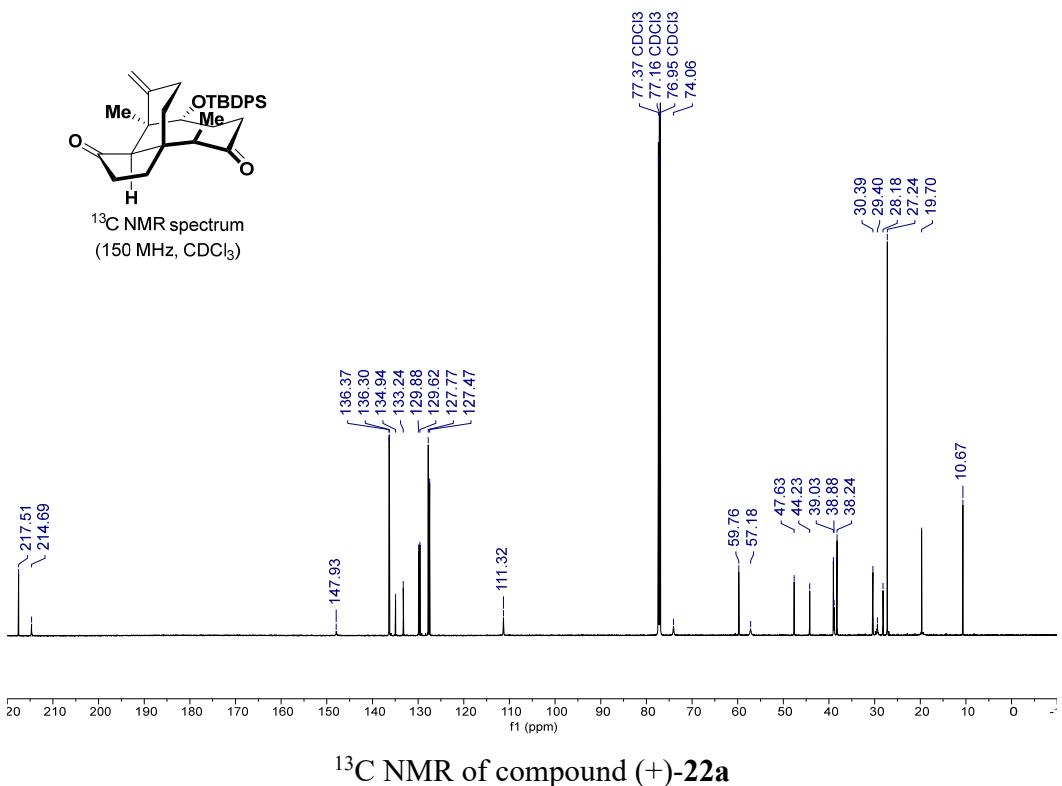
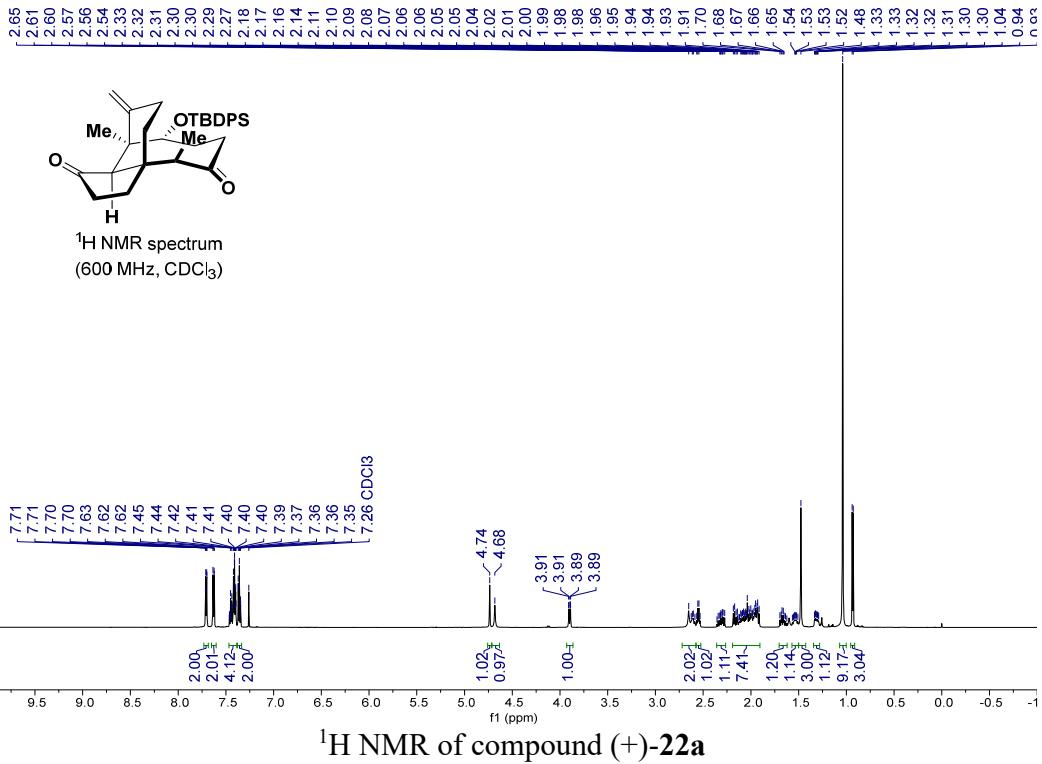


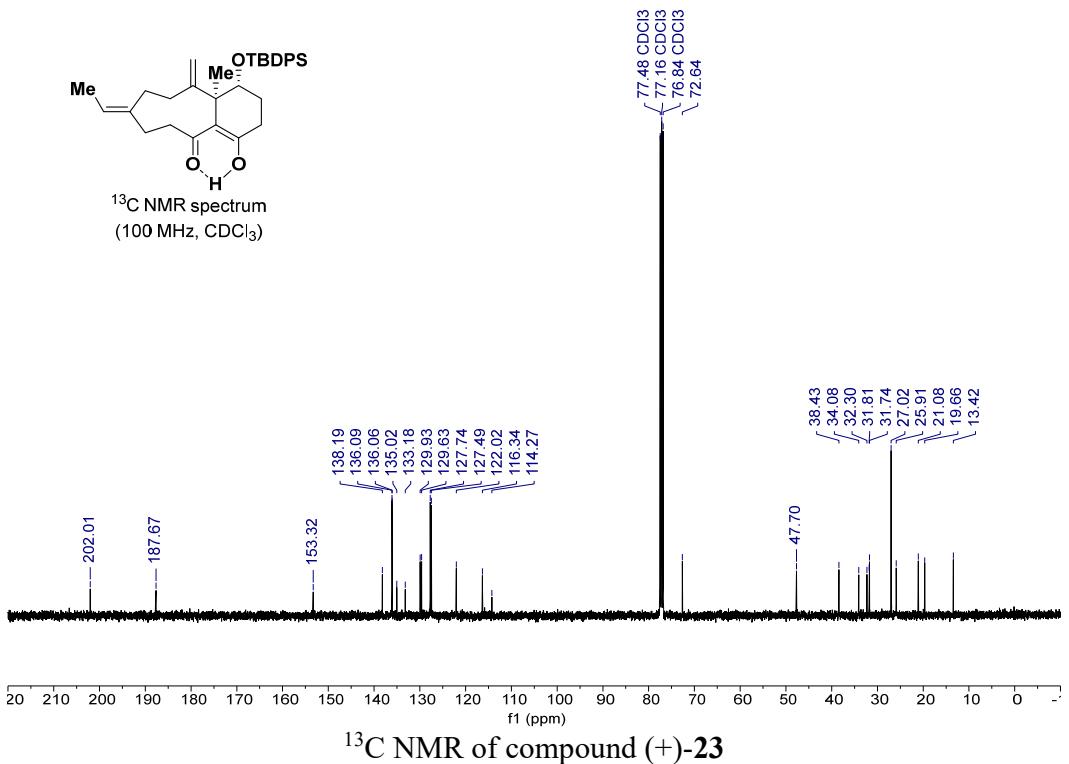
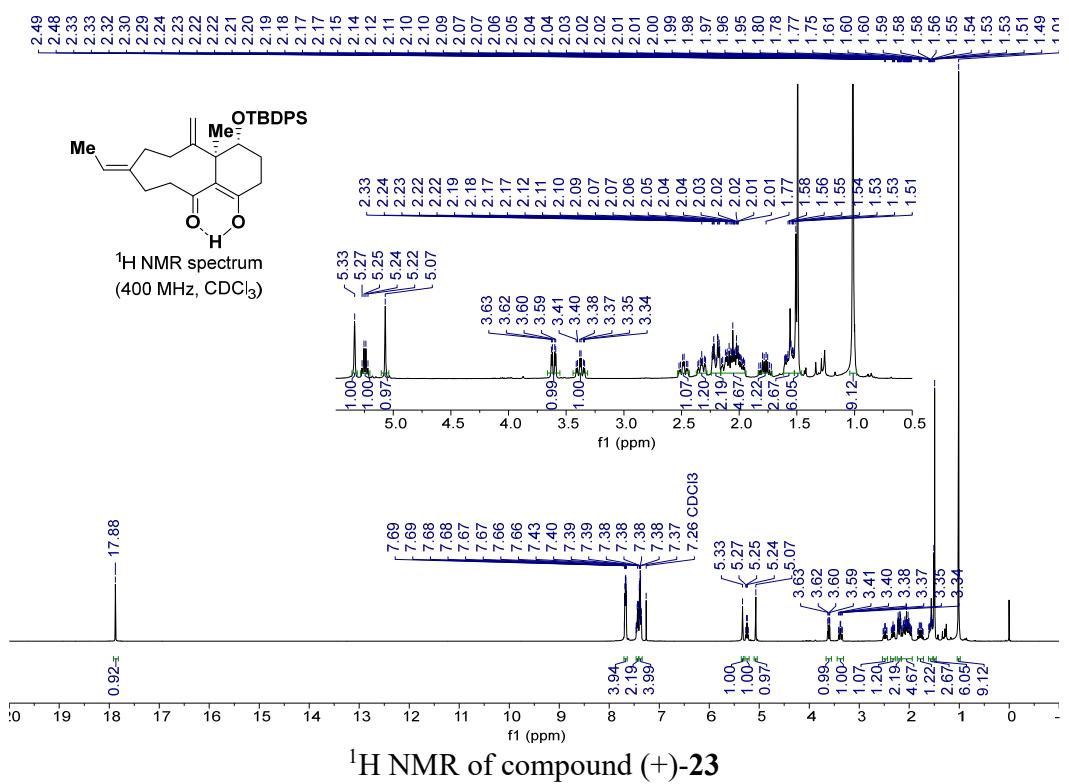


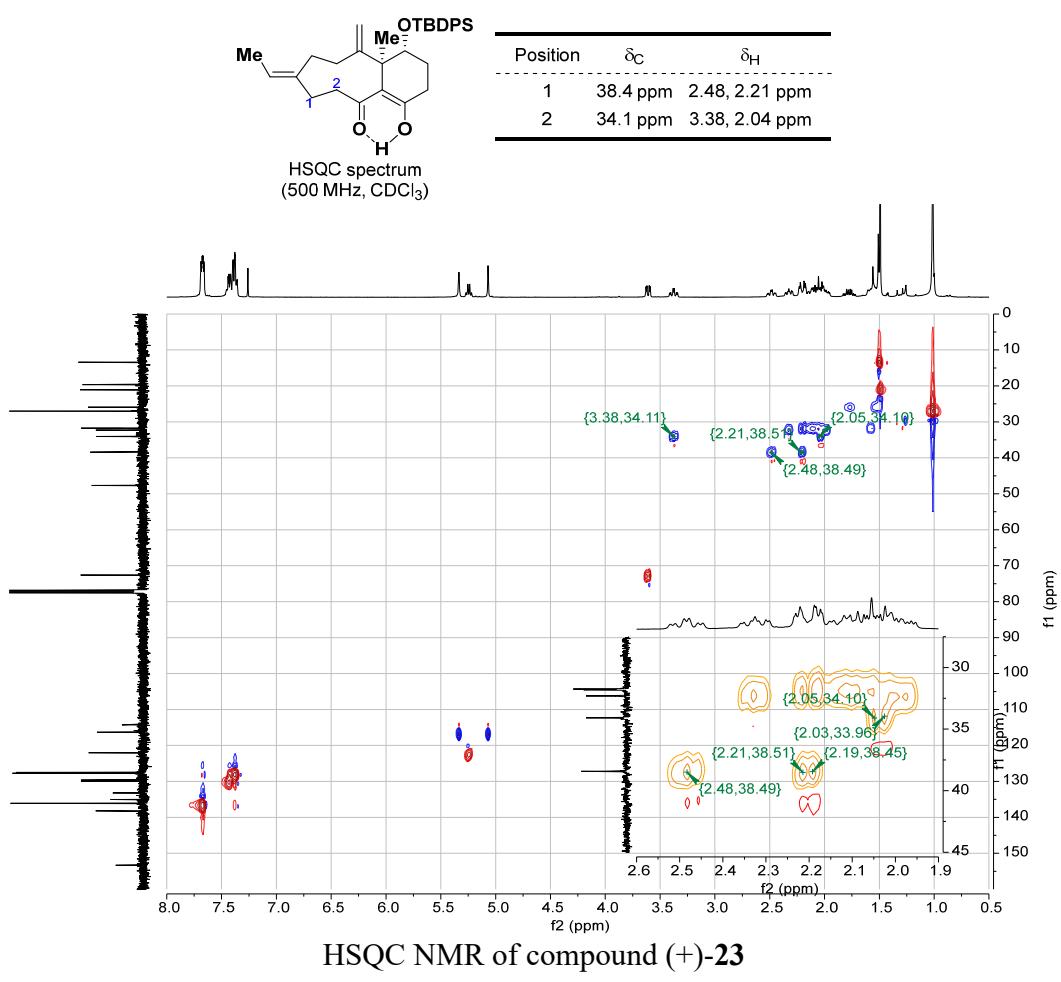


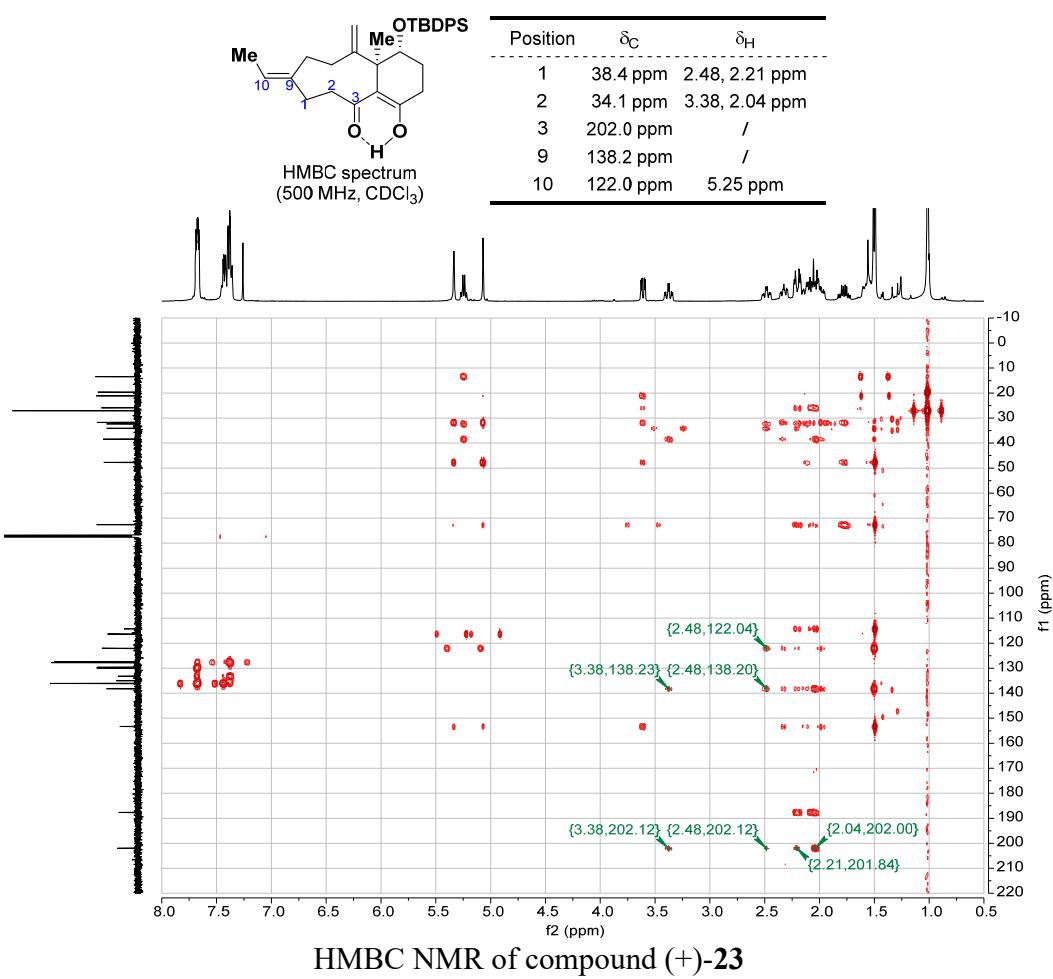


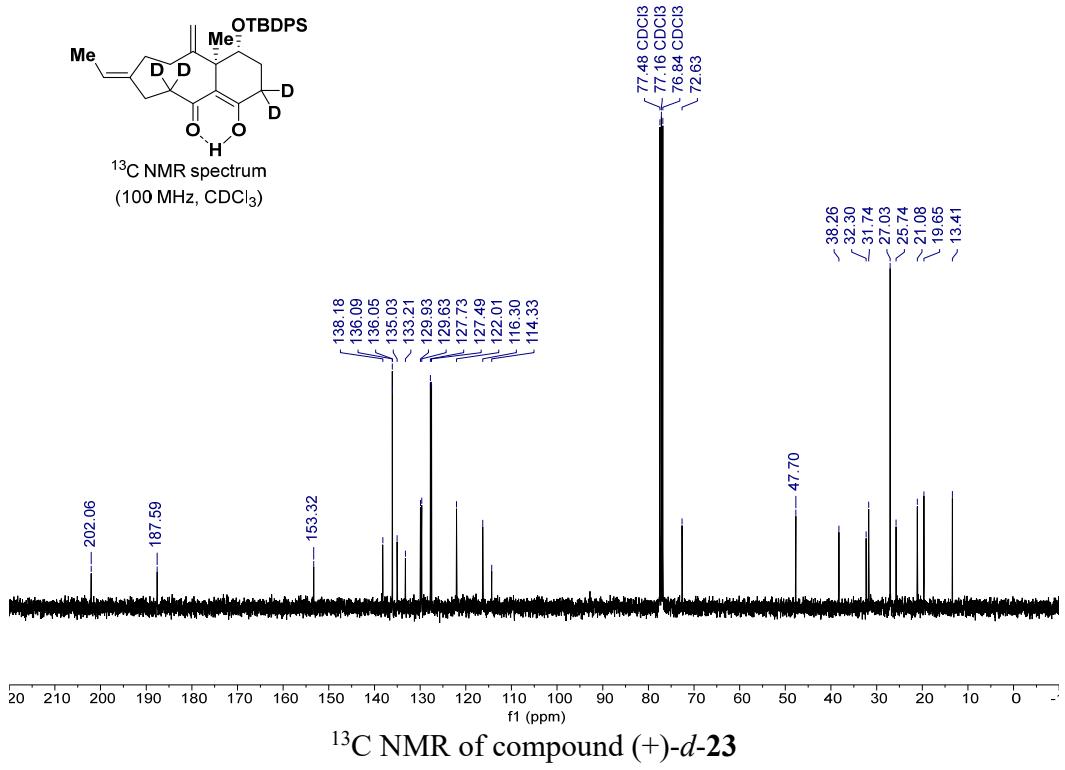
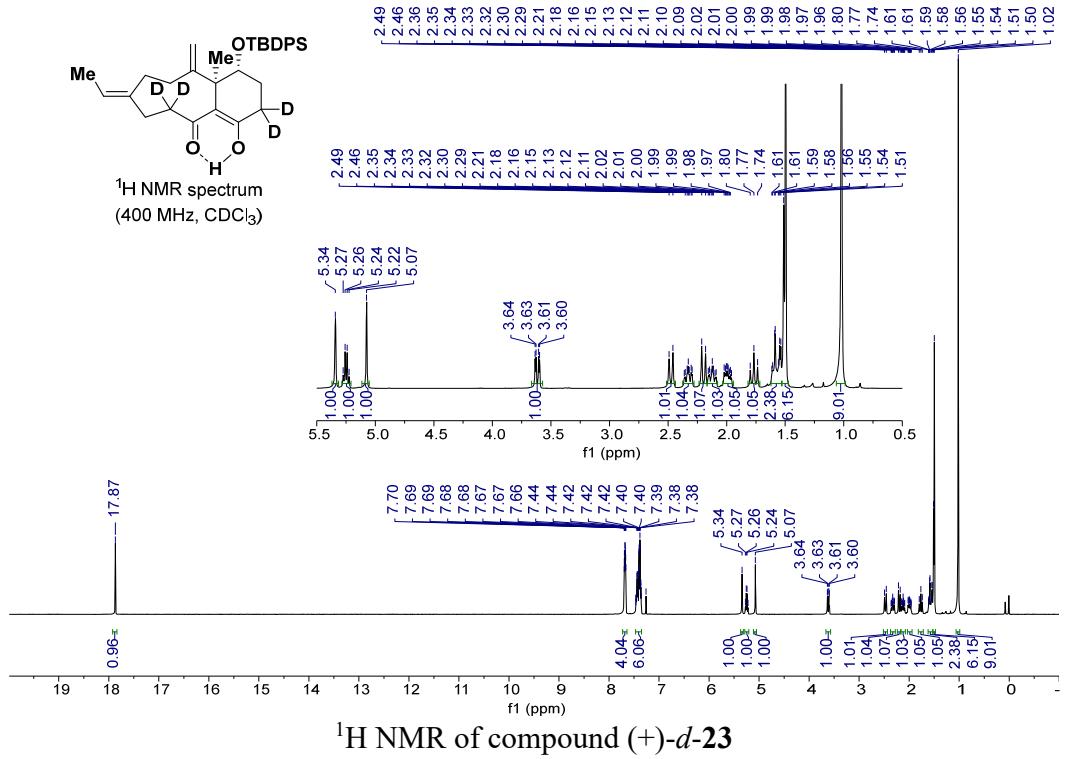


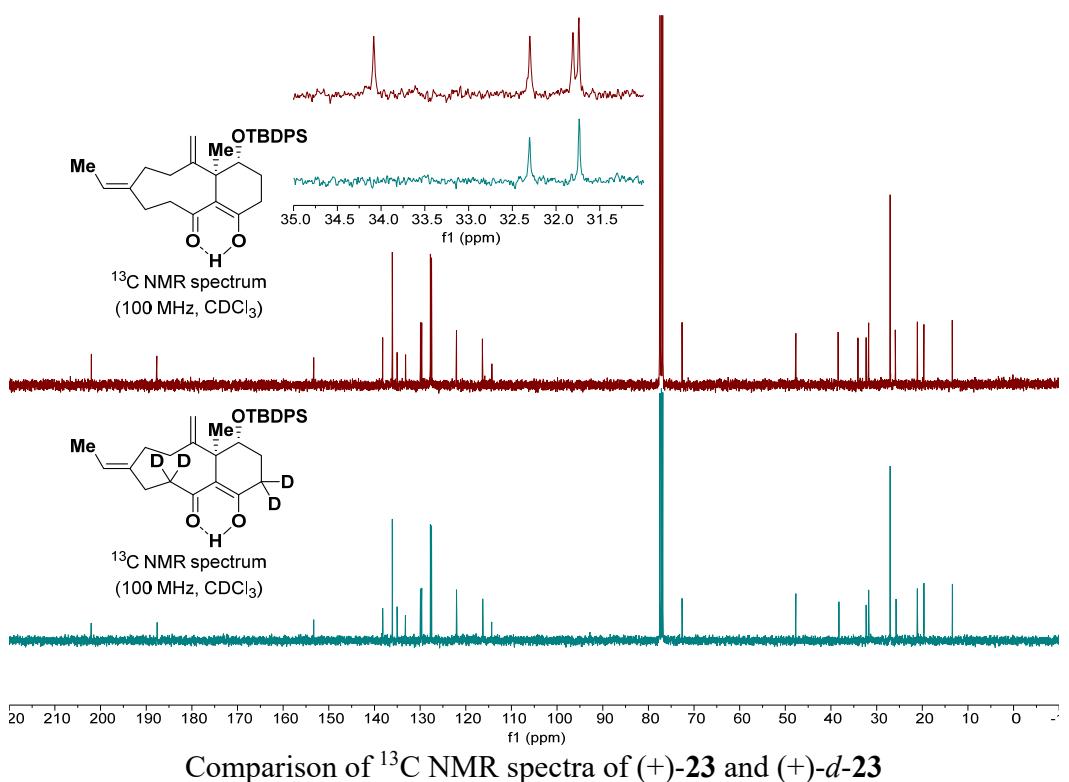
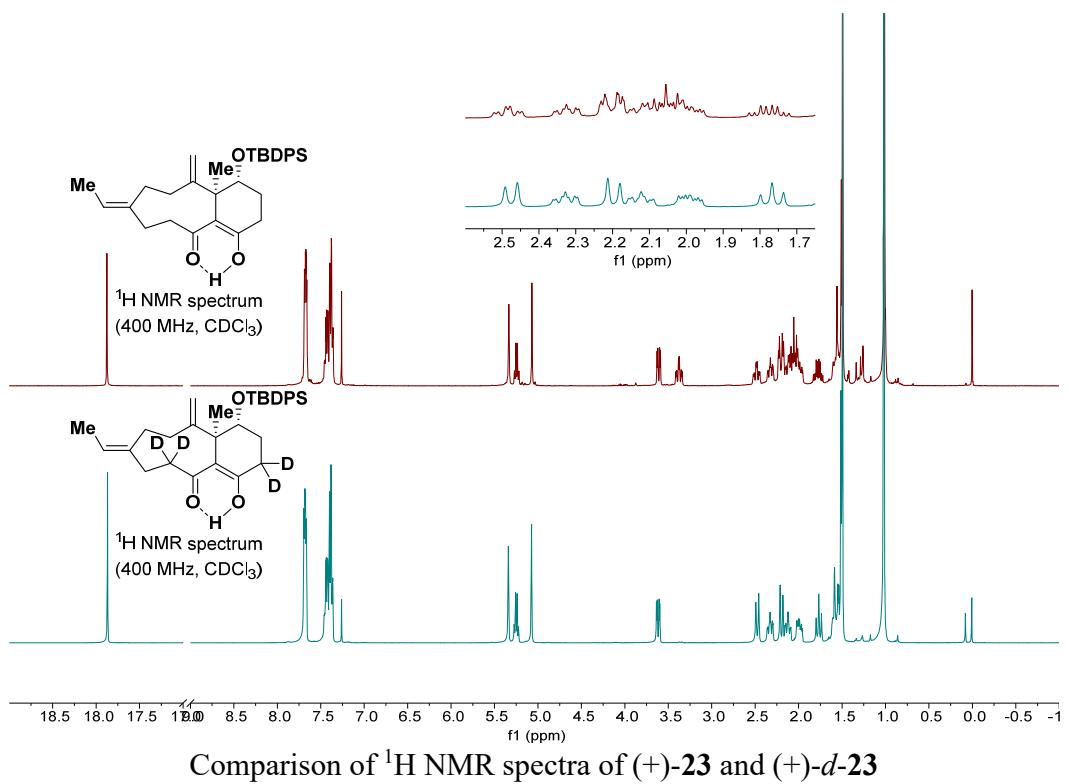


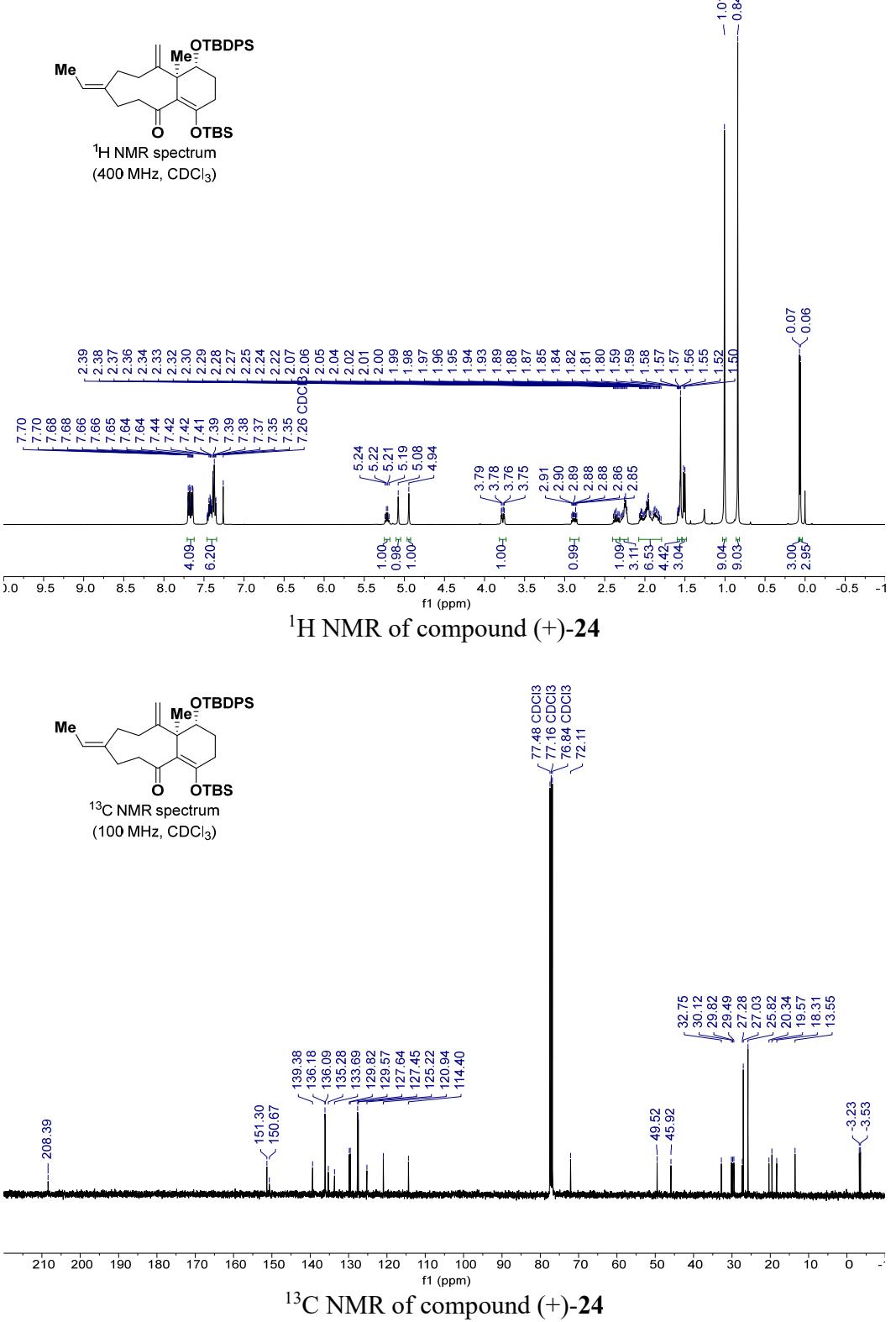


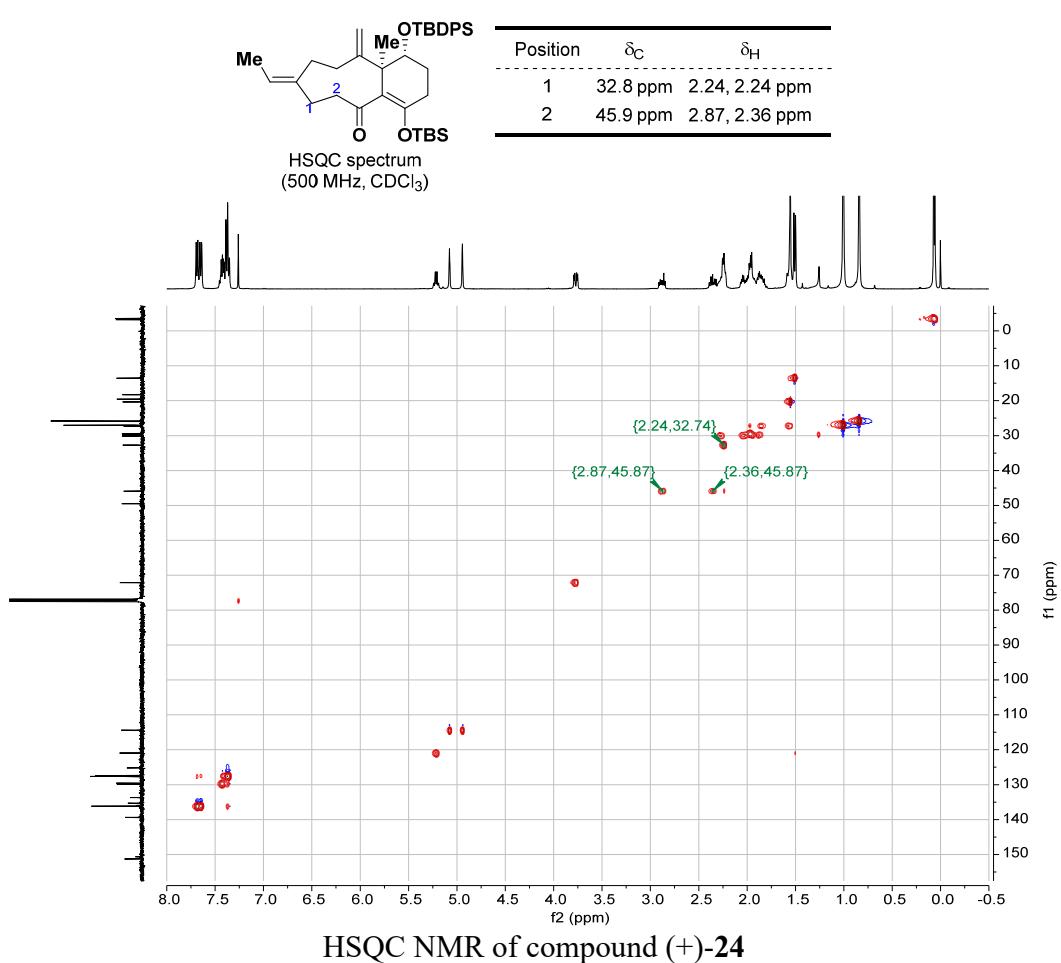


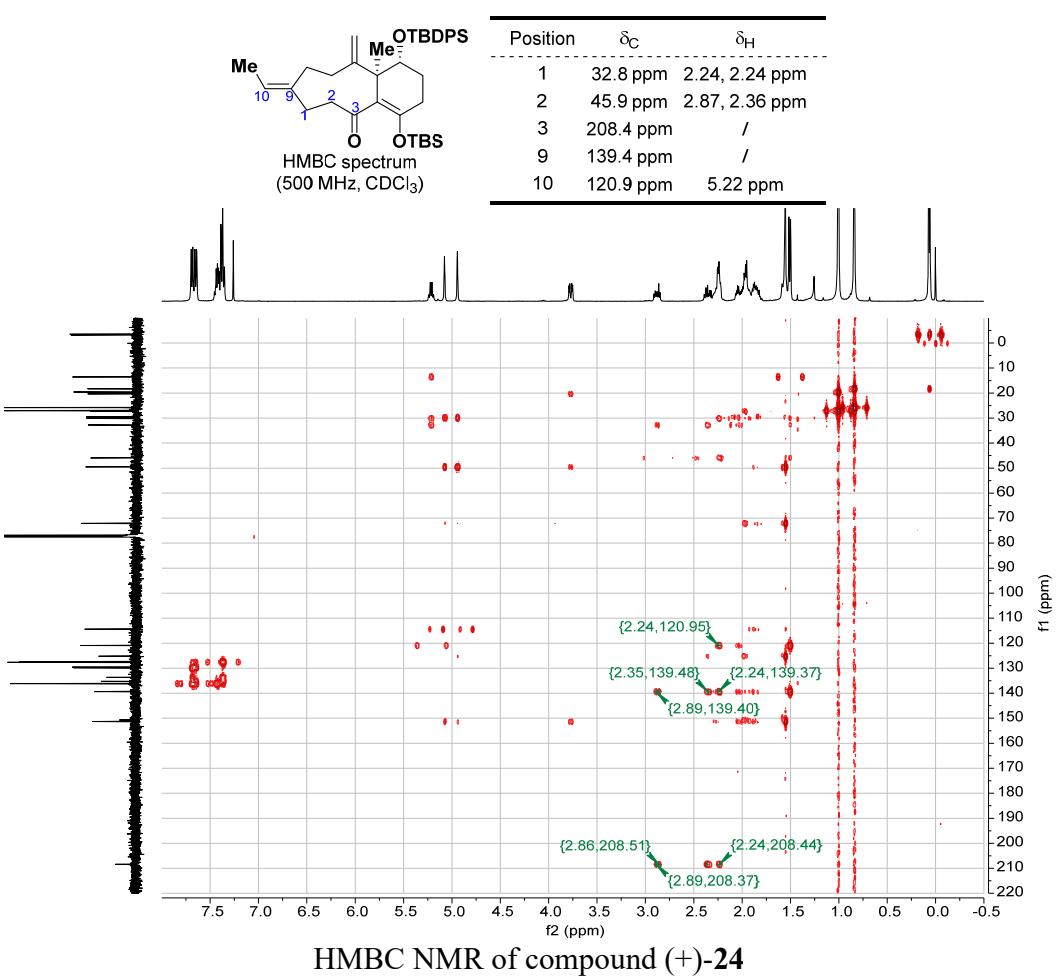


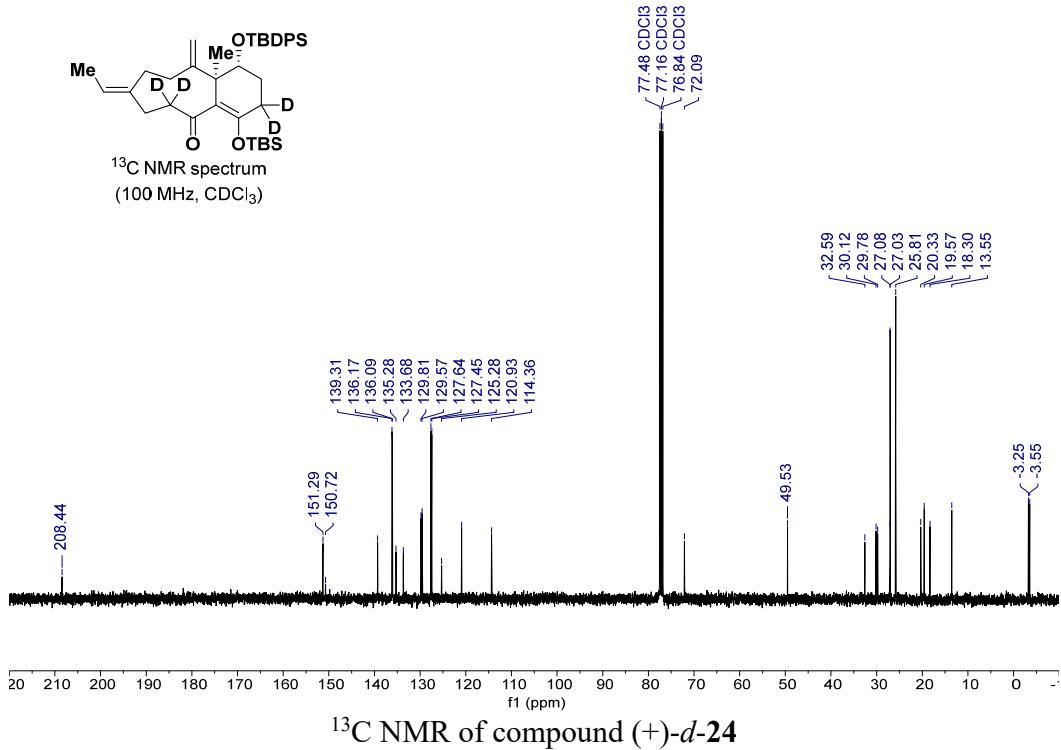
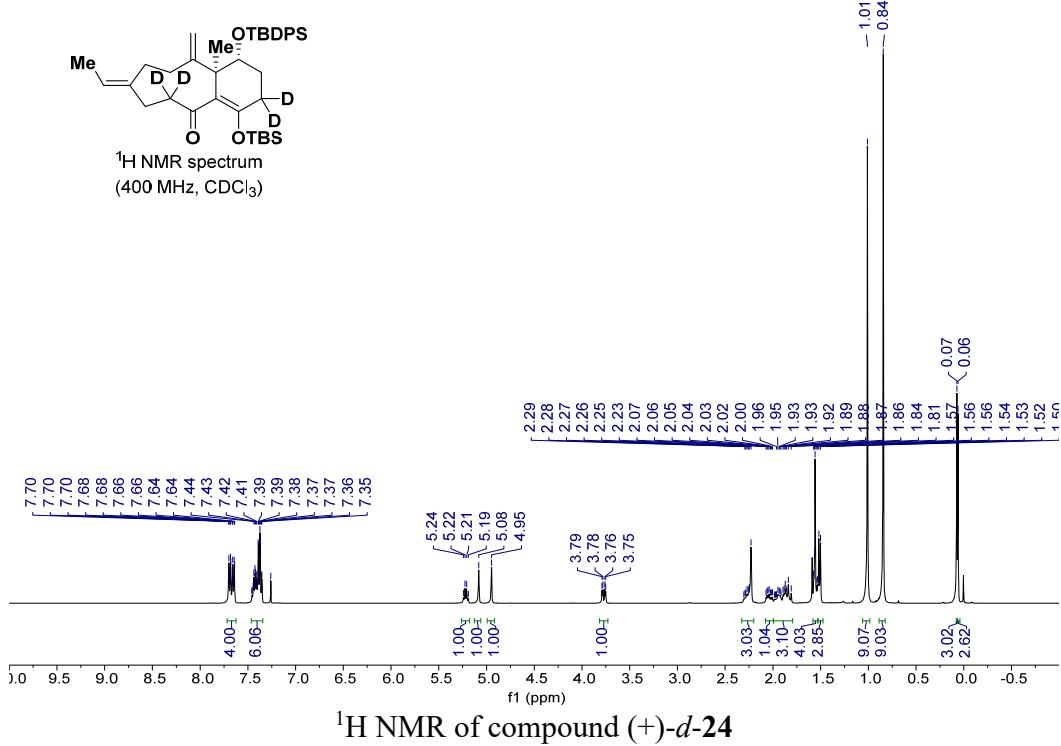


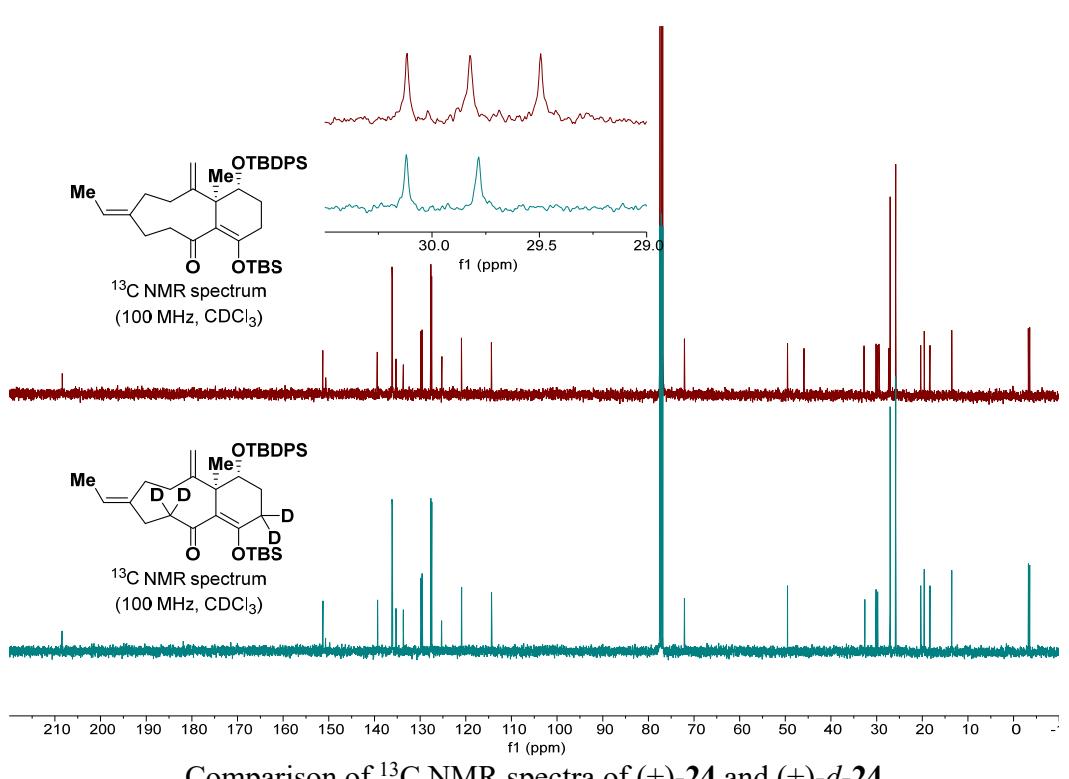
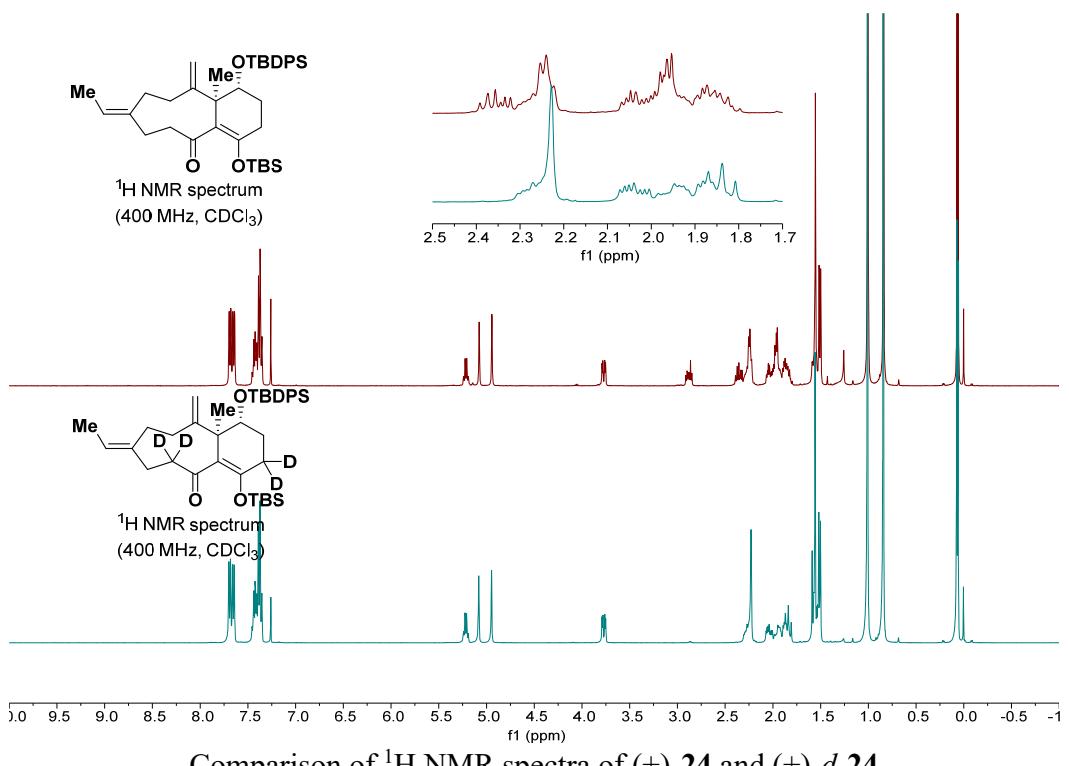


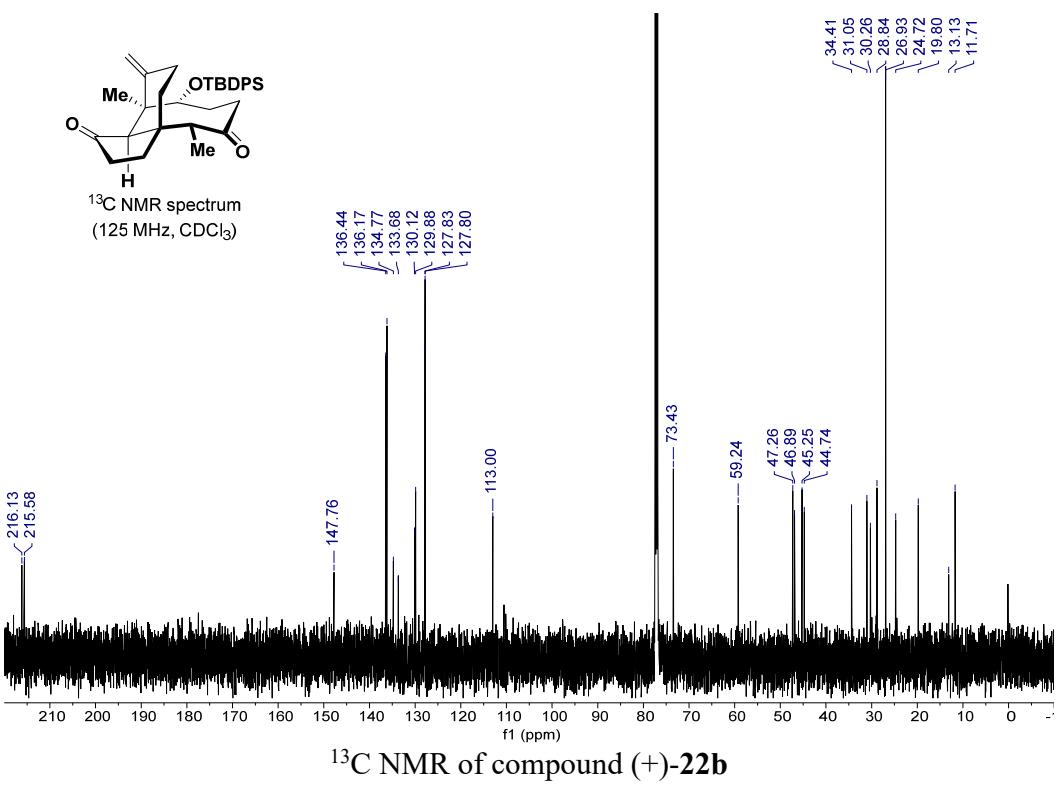
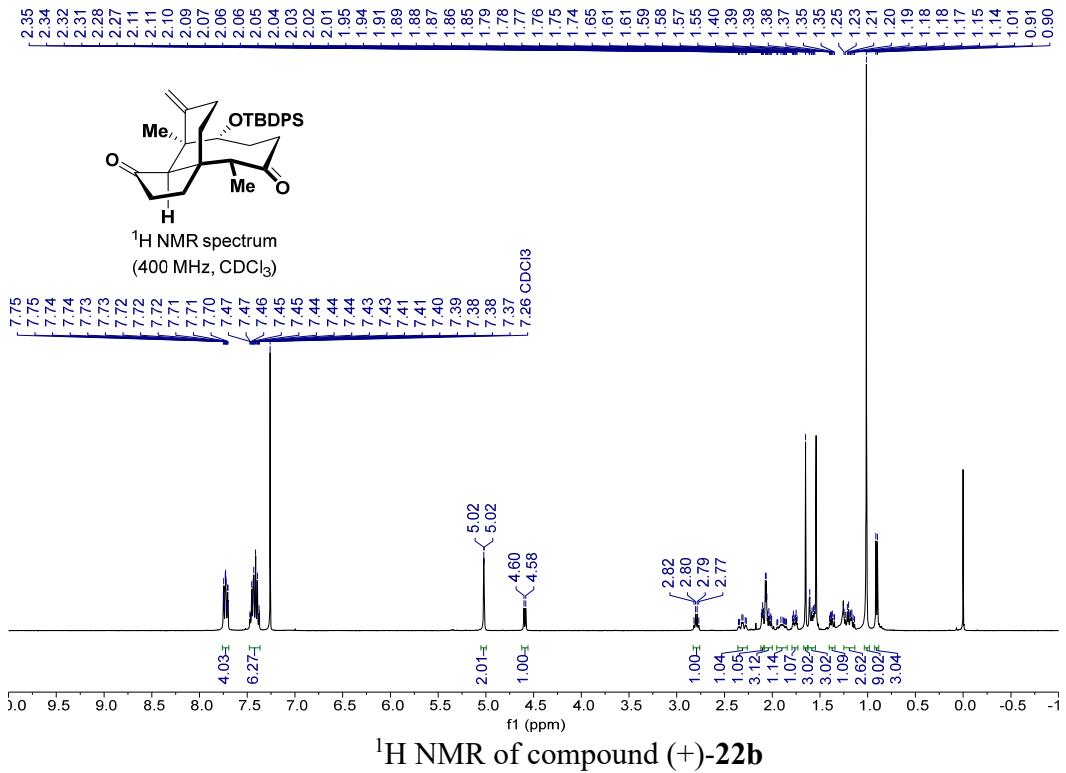


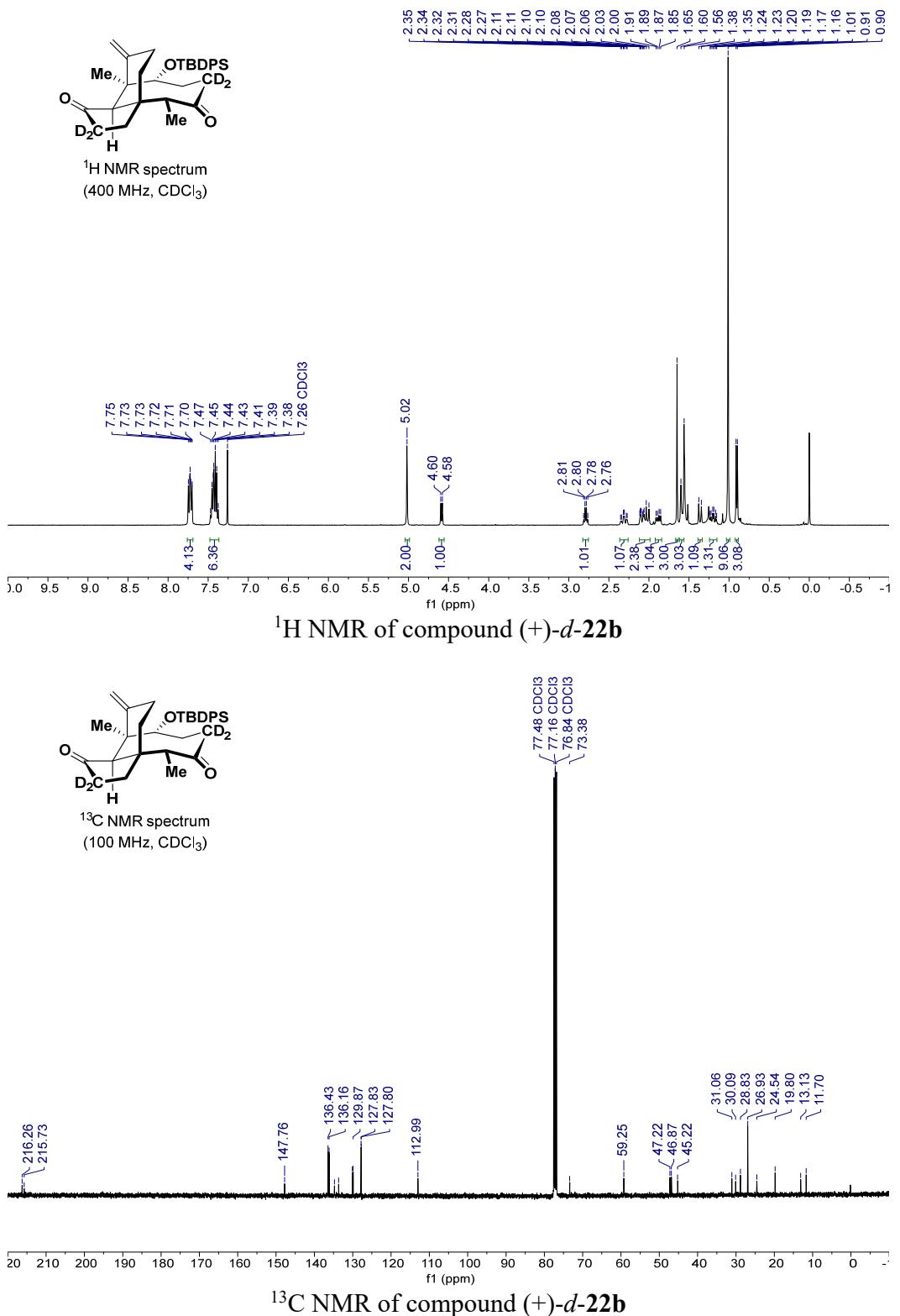


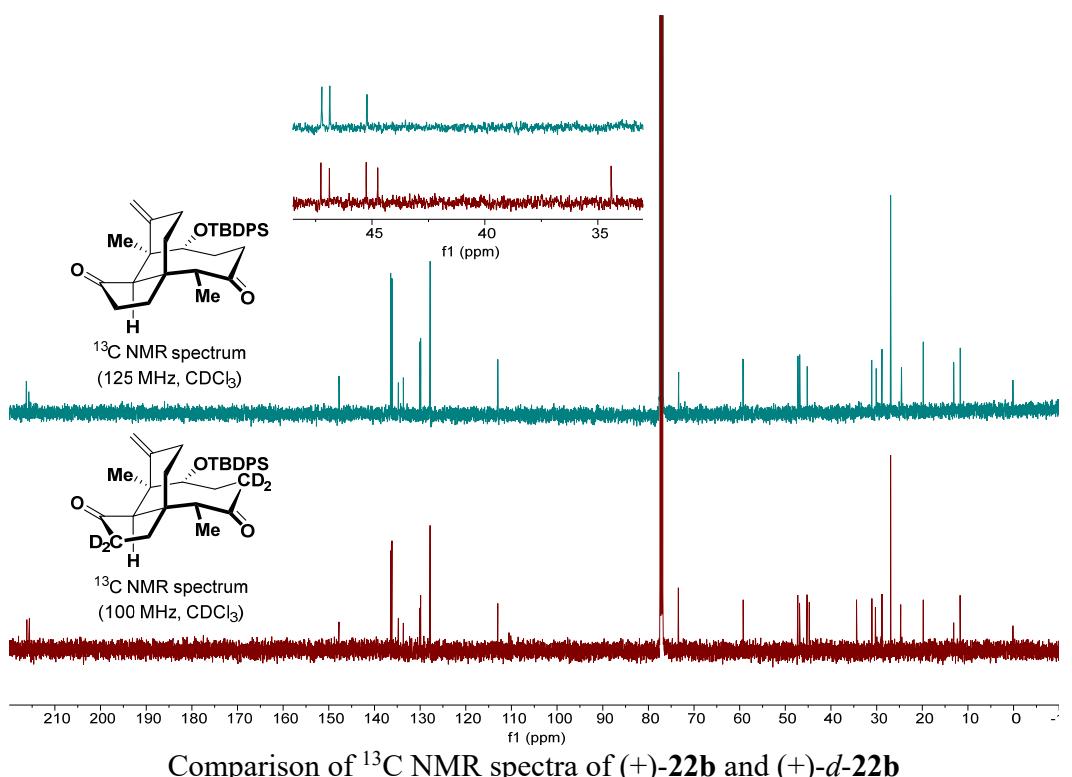
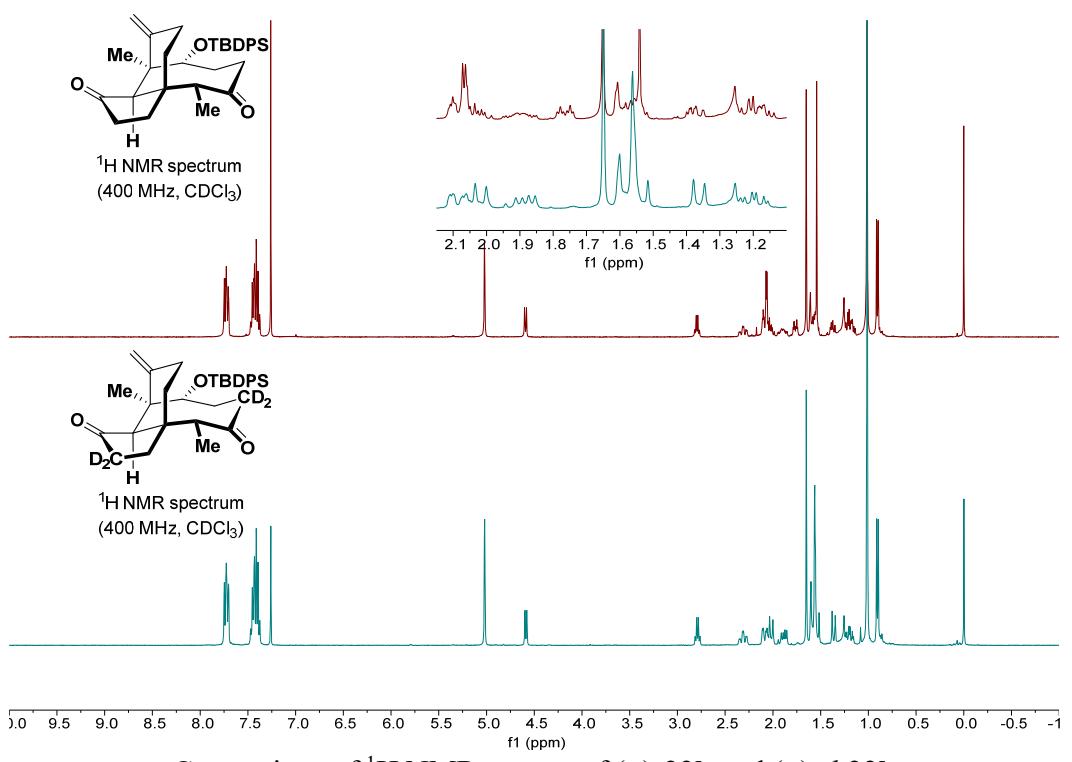


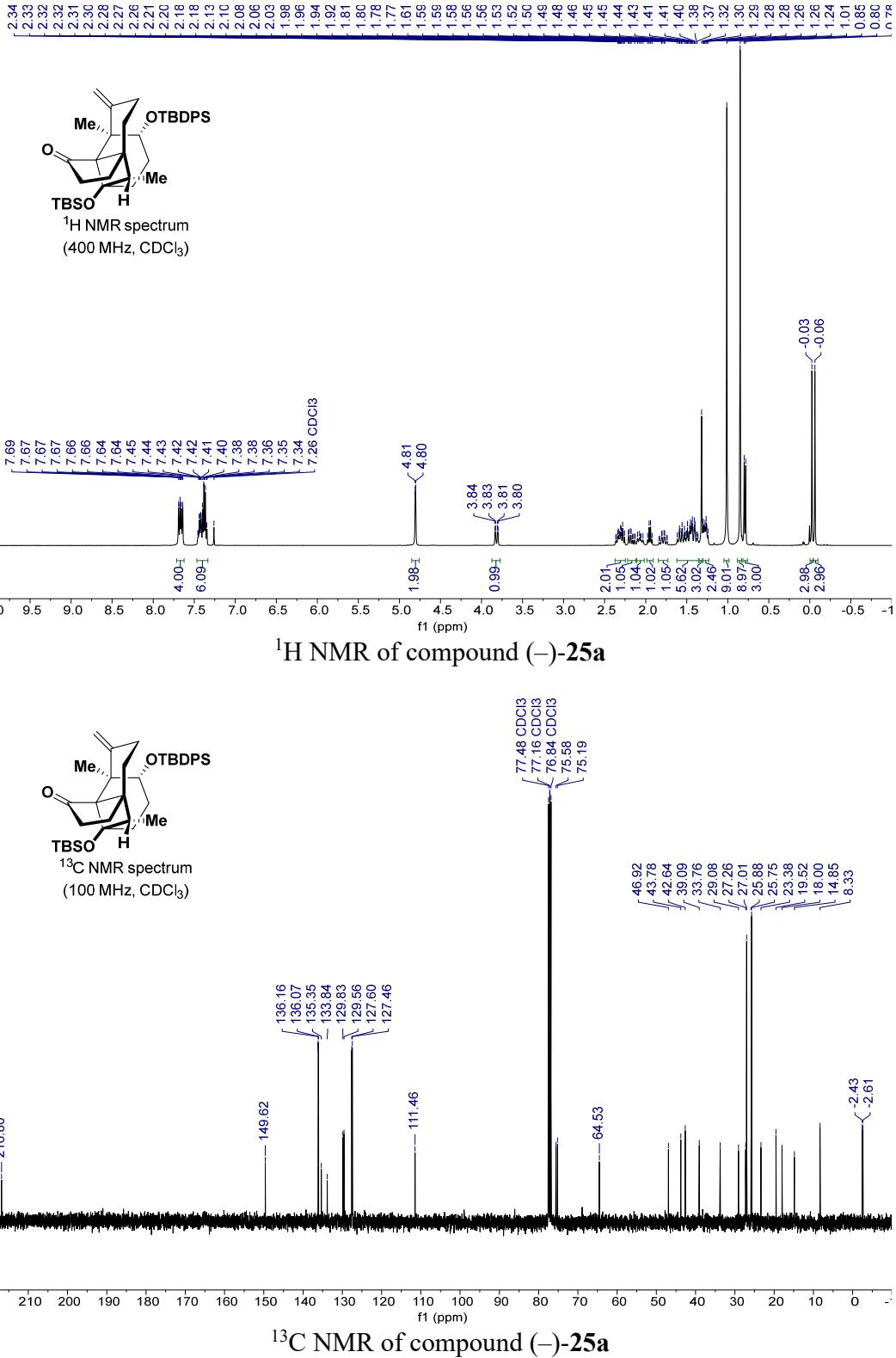


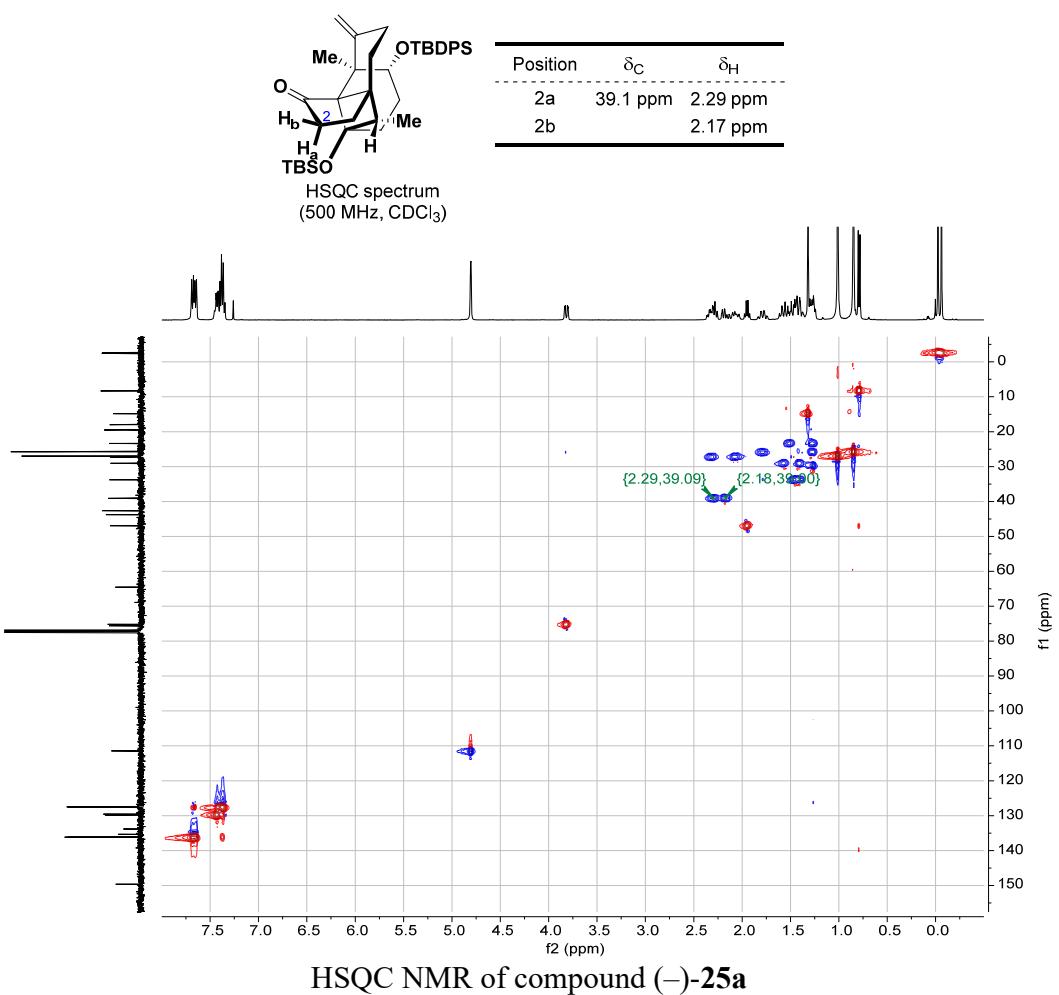


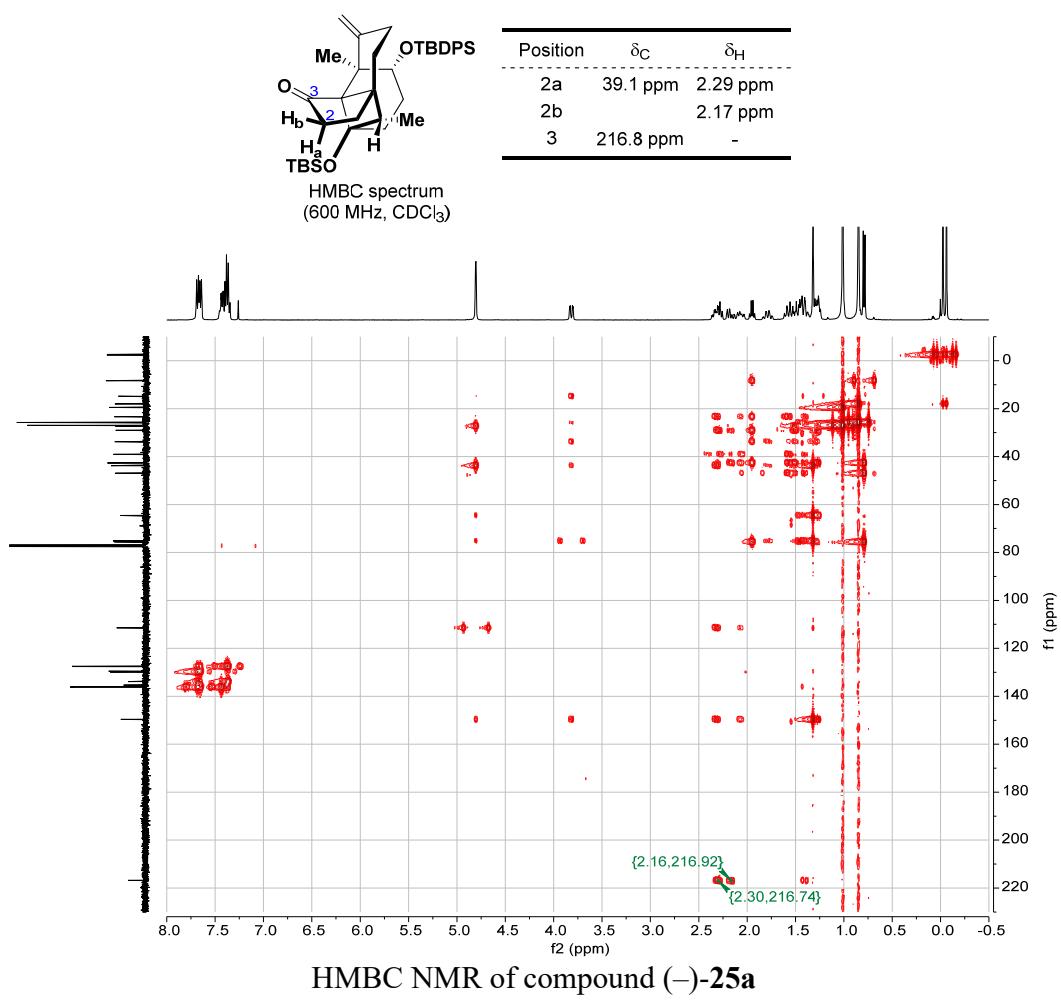


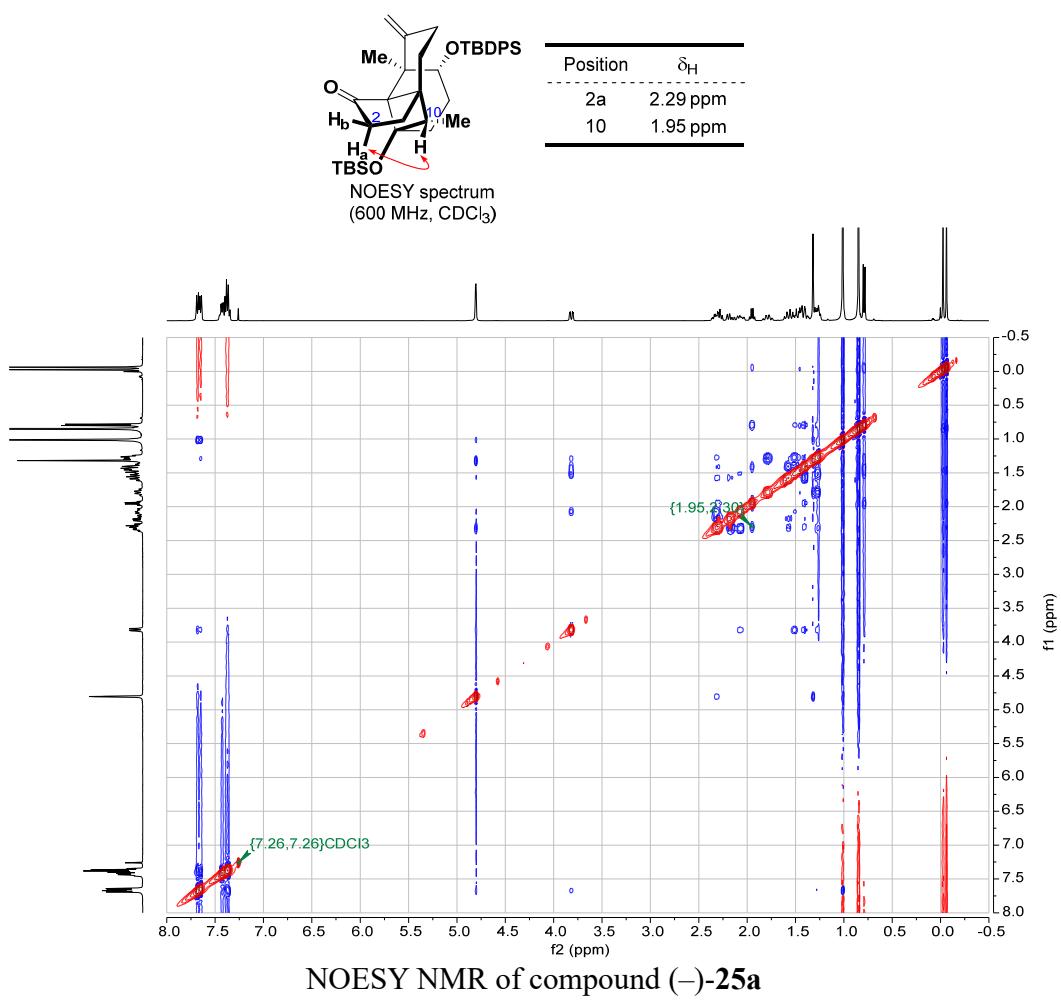


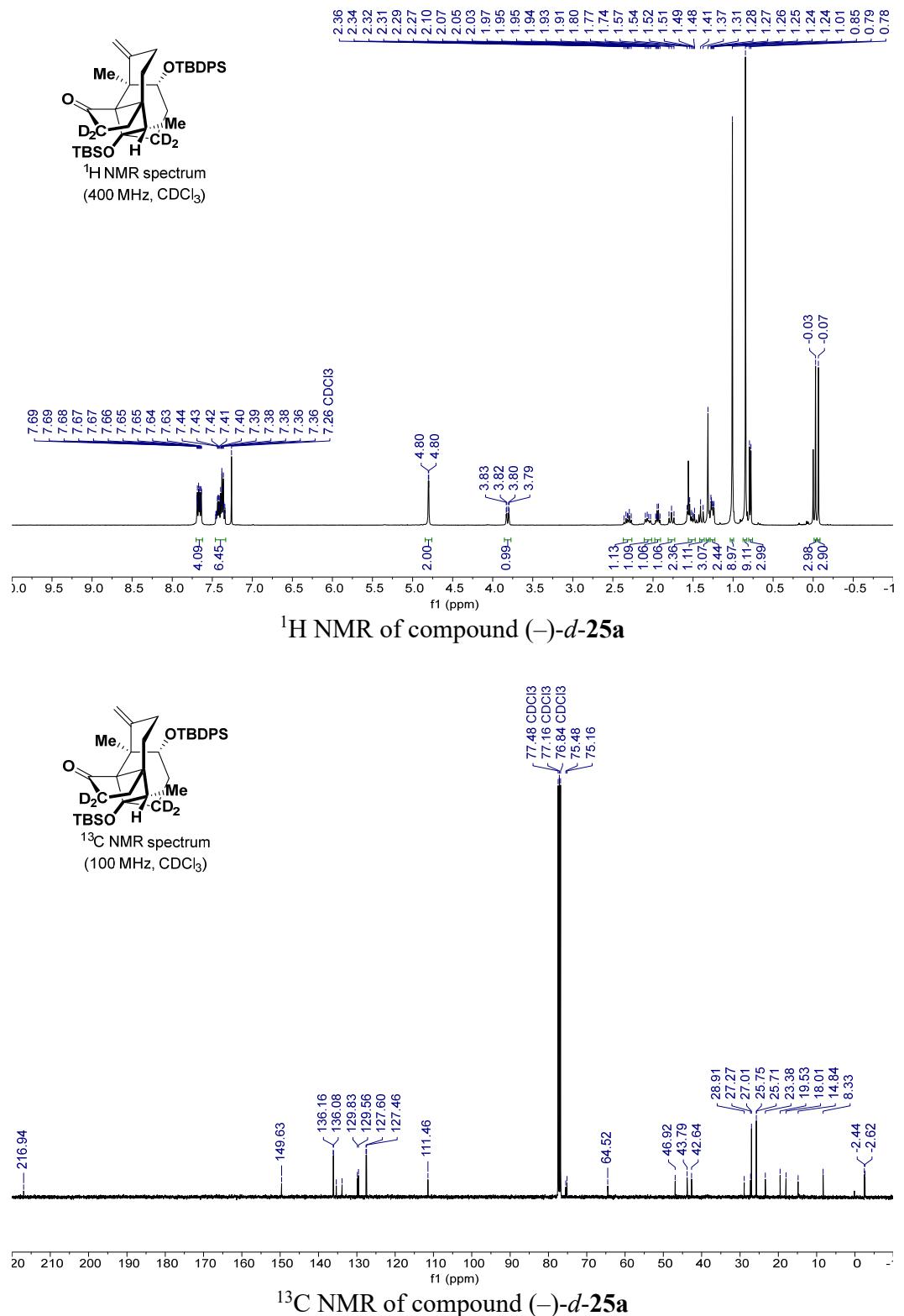


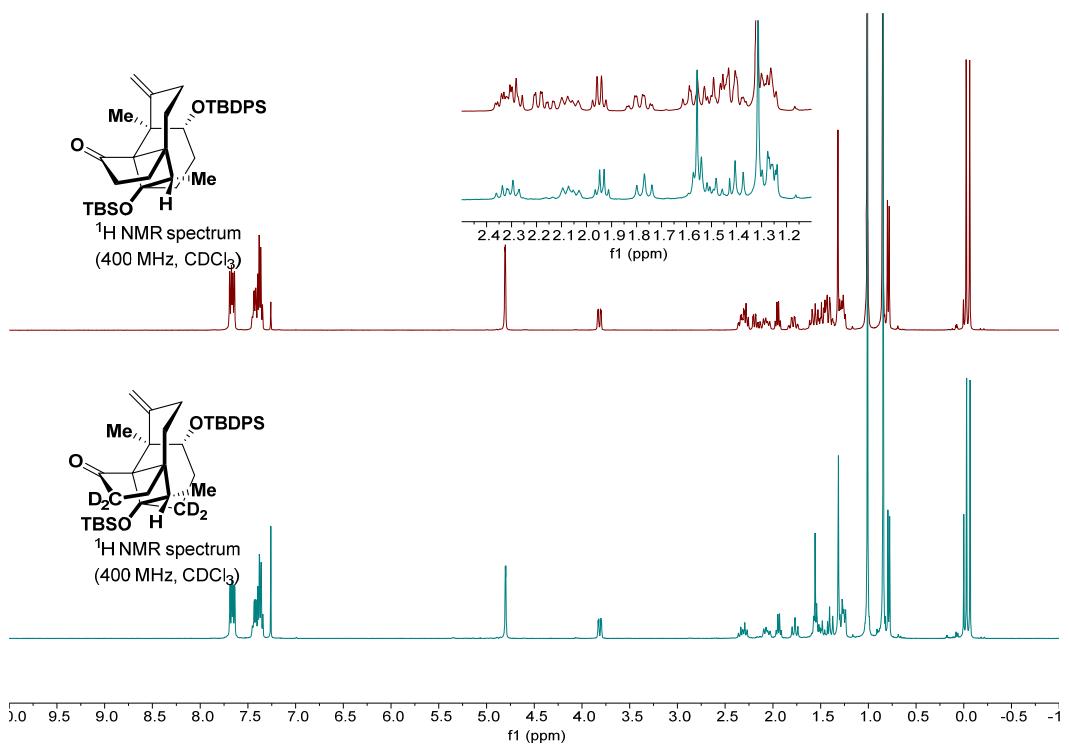




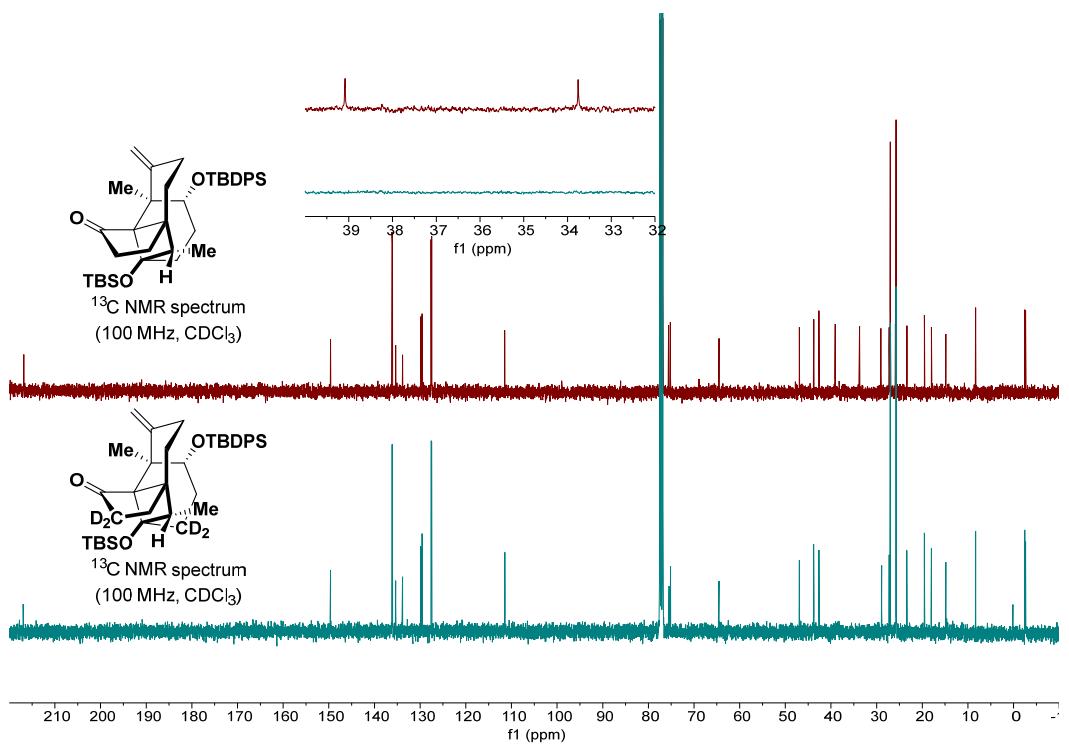




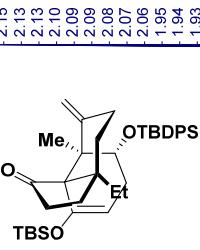




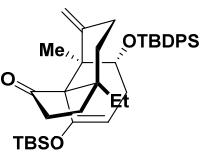
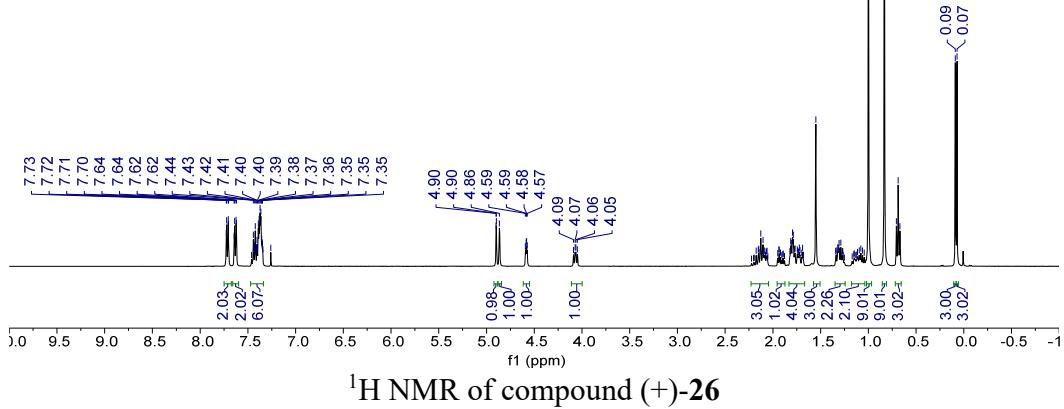
Comparison of ^1H NMR spectra of (-)-25a and (-)-d-25a



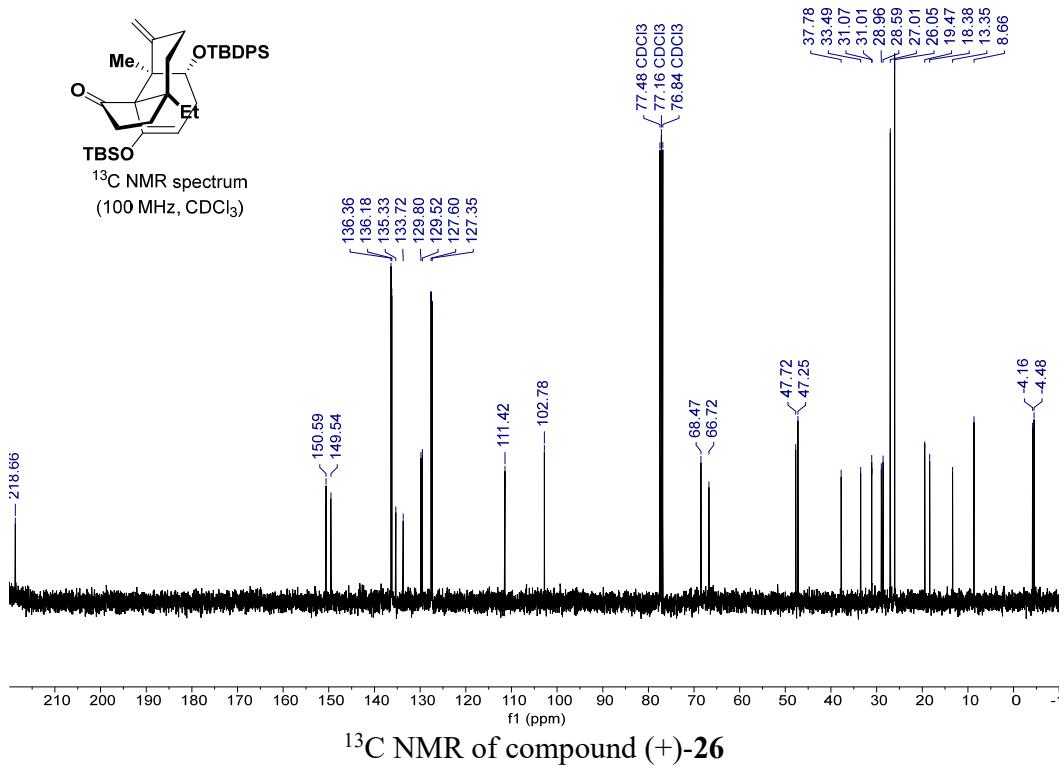
Comparison of ^{13}C NMR spectra of (-)-25a and (-)-d-25a

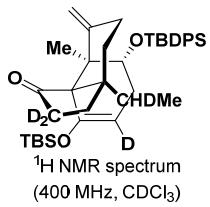


¹H NMR spectrum
(400 MHz, CDCl₃)

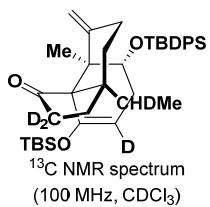
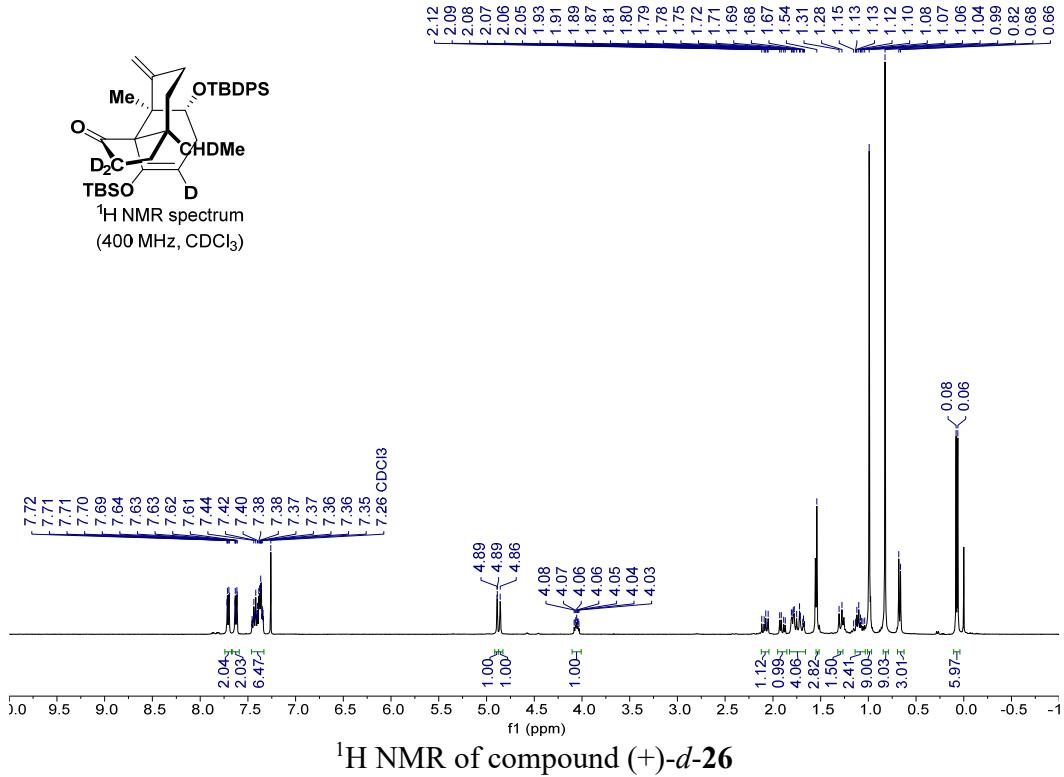


¹³C NMR spectrum
(100 MHz, CDCl₃)

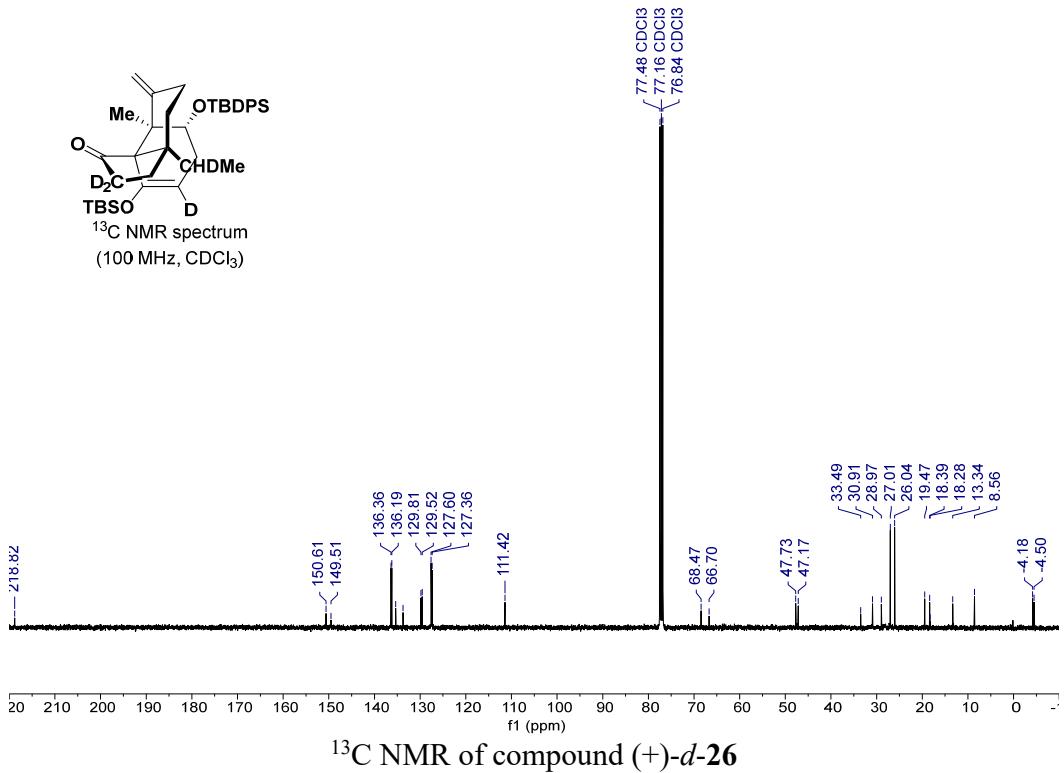


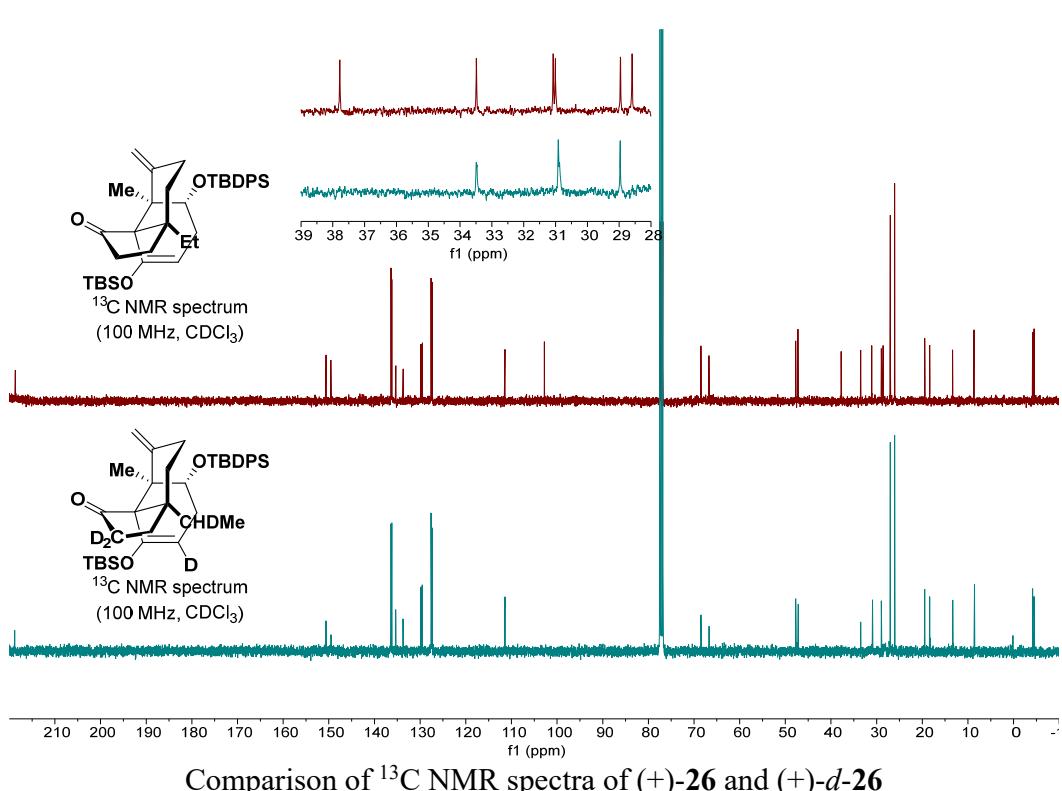
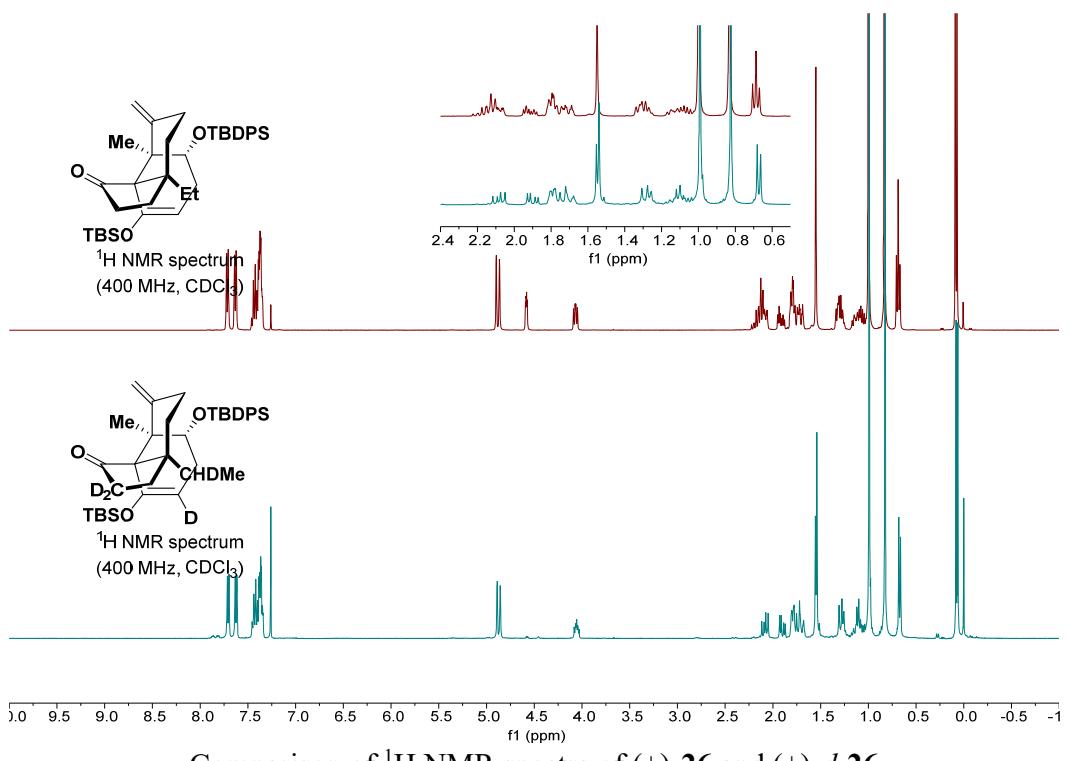


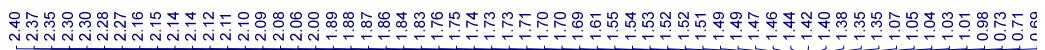
¹H NMR spectrum
(400 MHz, CDCl₃)



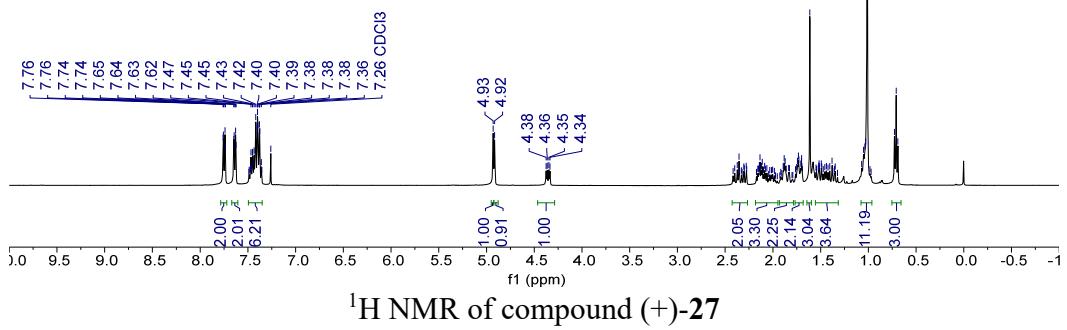
¹³C NMR spectrum
(100 MHz, CDCl₃)



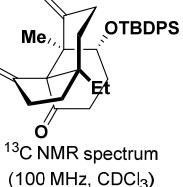




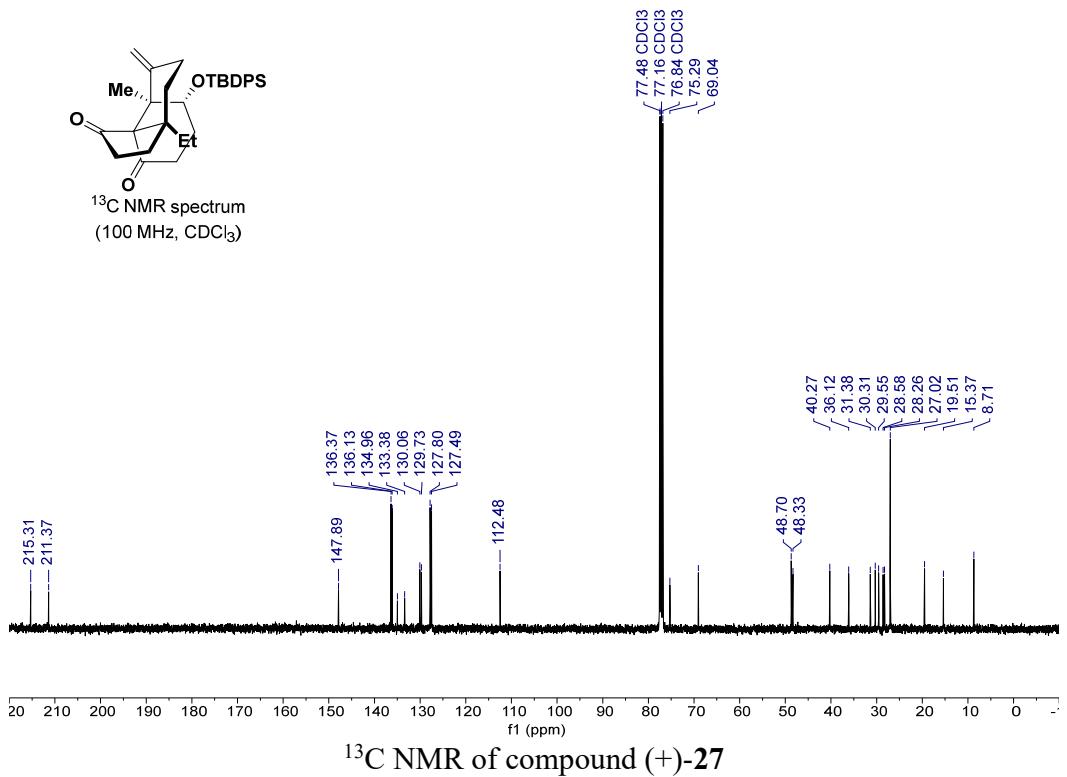
¹H NMR spectrum
(400 MHz, CDCl₃)



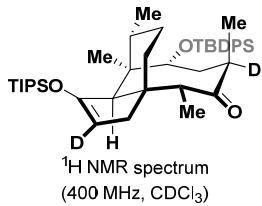
¹H NMR of compound (+)-27



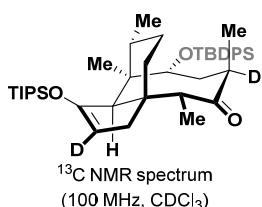
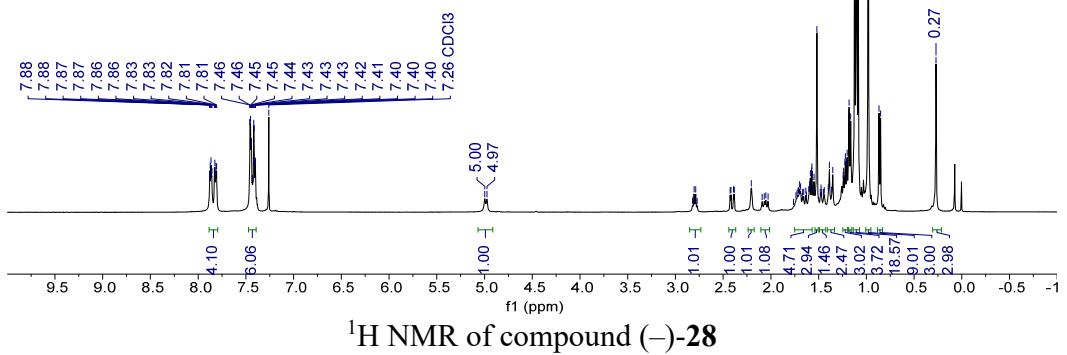
¹³C NMR spectrum
(100 MHz, CDCl₃)



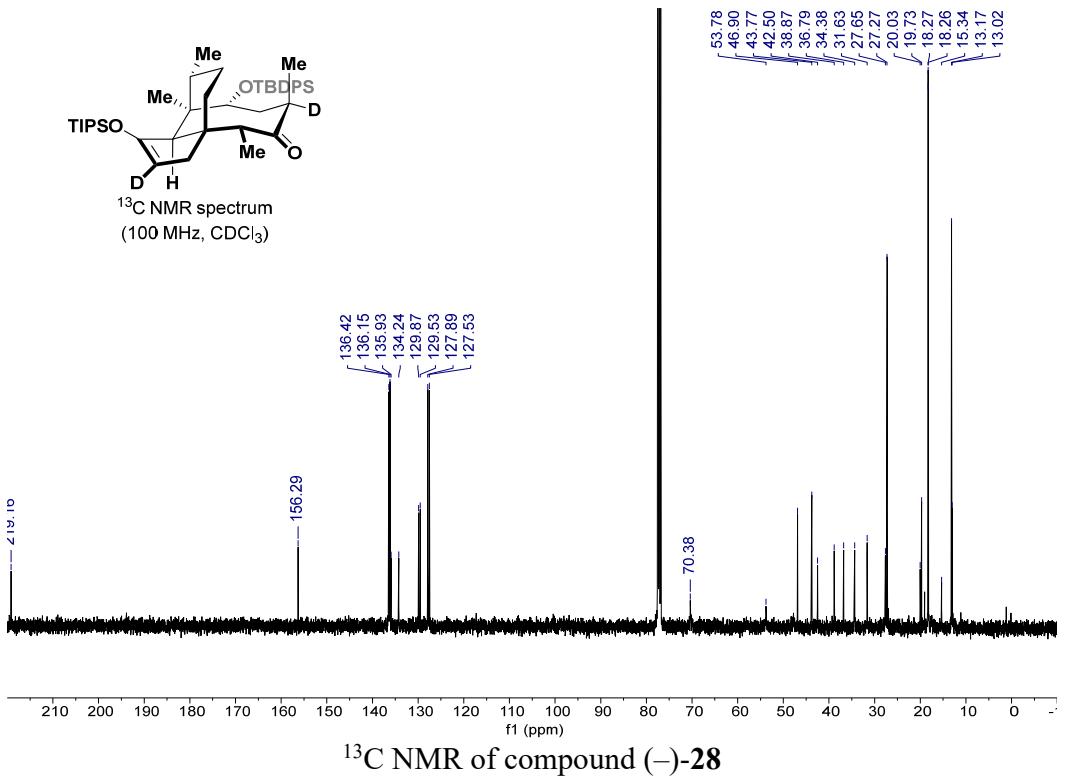
¹³C NMR of compound (+)-27

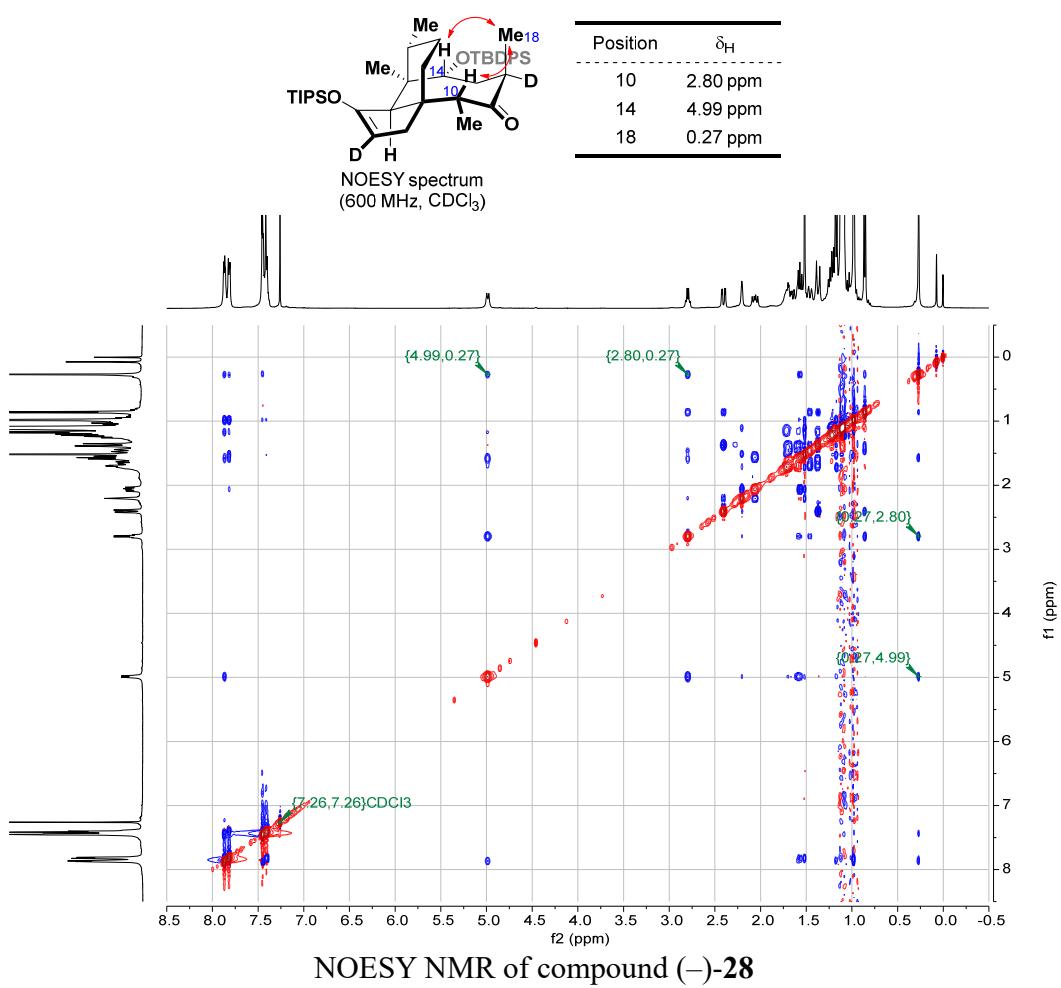


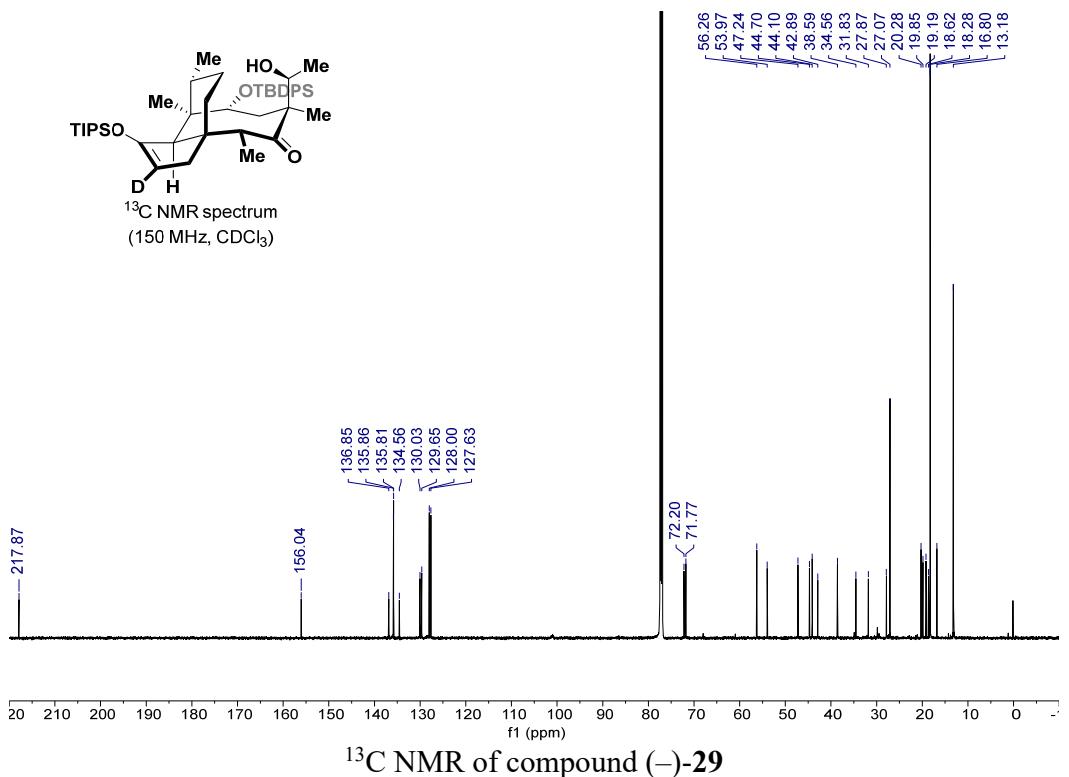
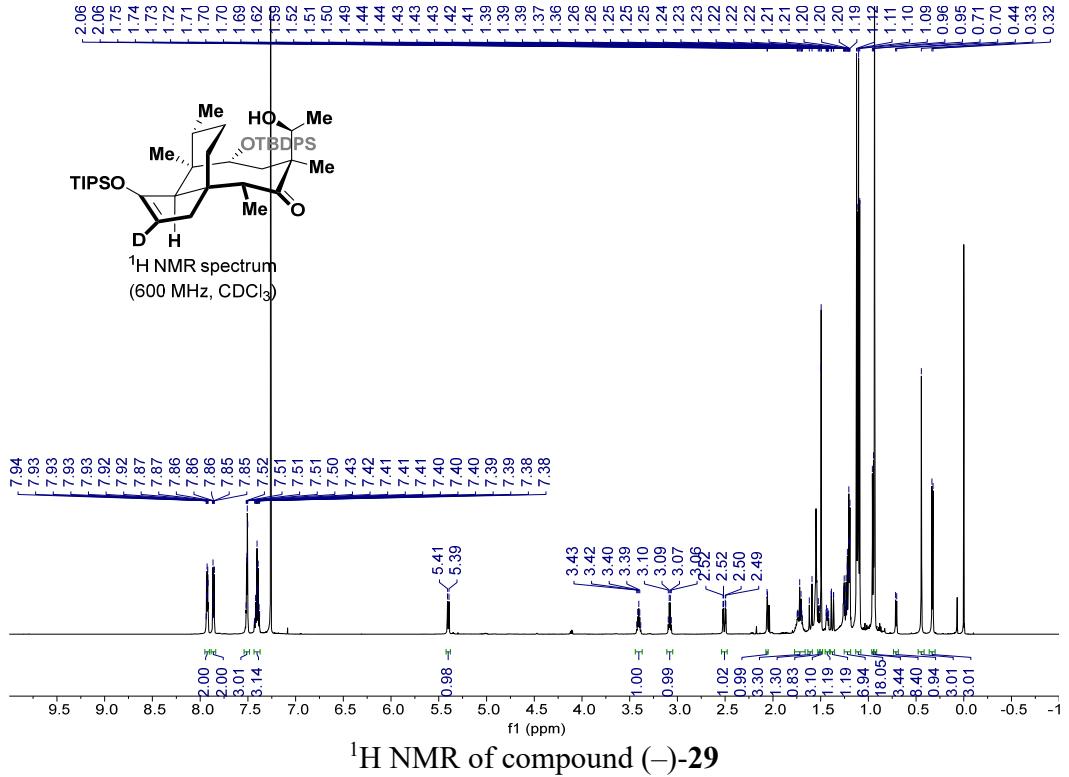
¹H NMR spectrum
(400 MHz, CDCl₃)

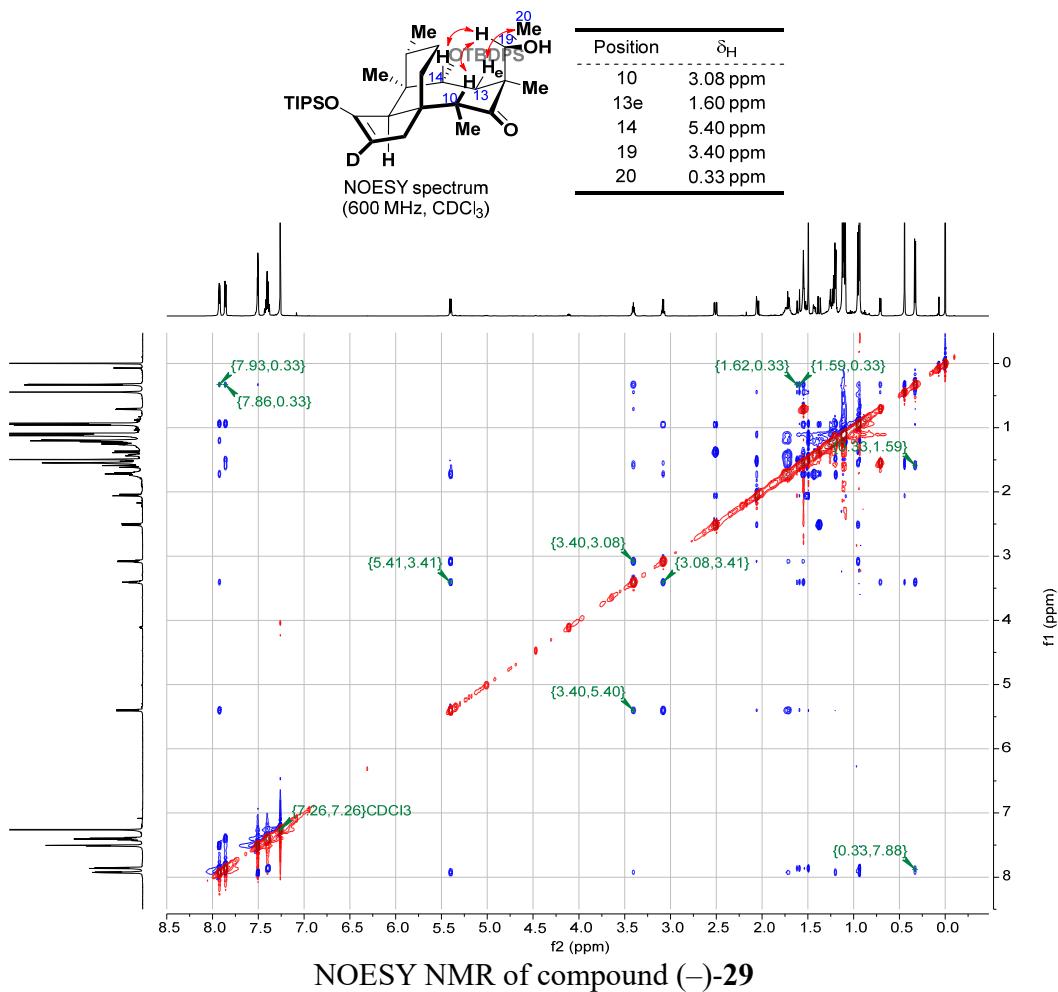


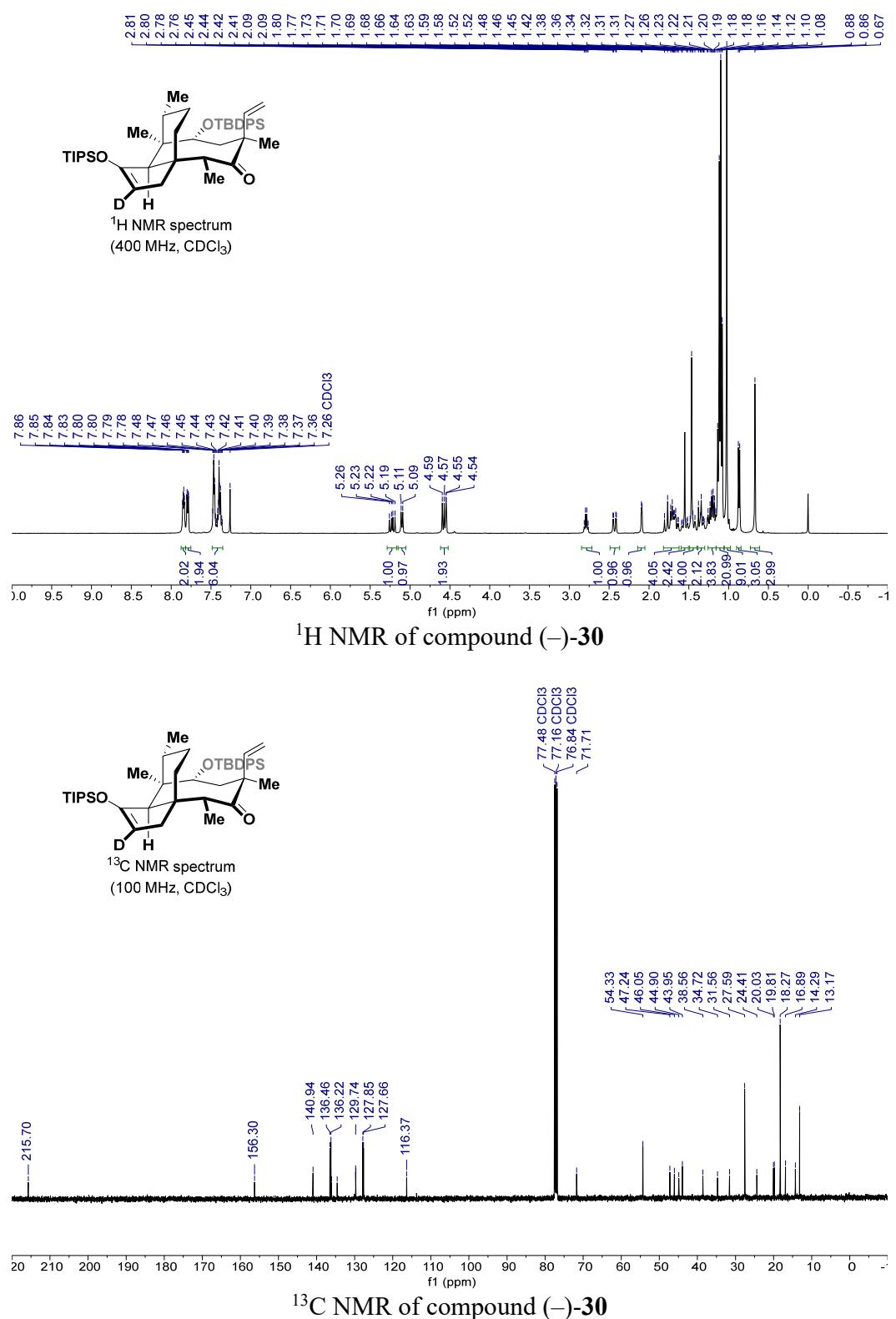
¹³C NMR spectrum
(100 MHz, CDCl₃)

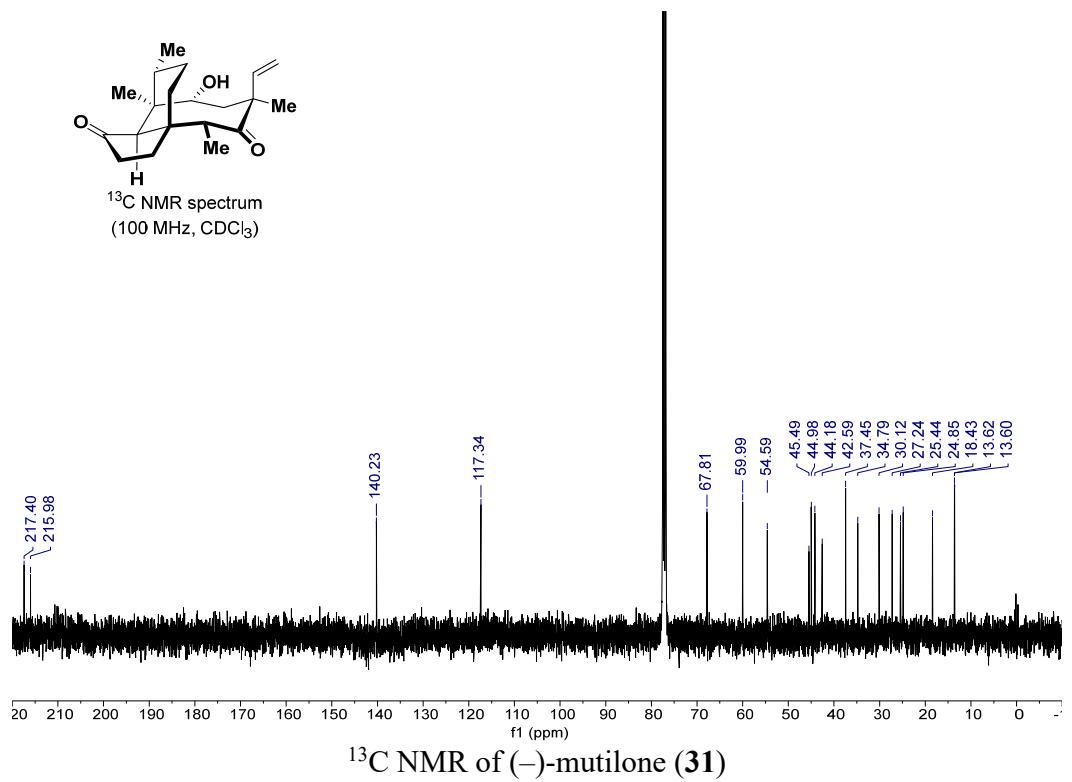
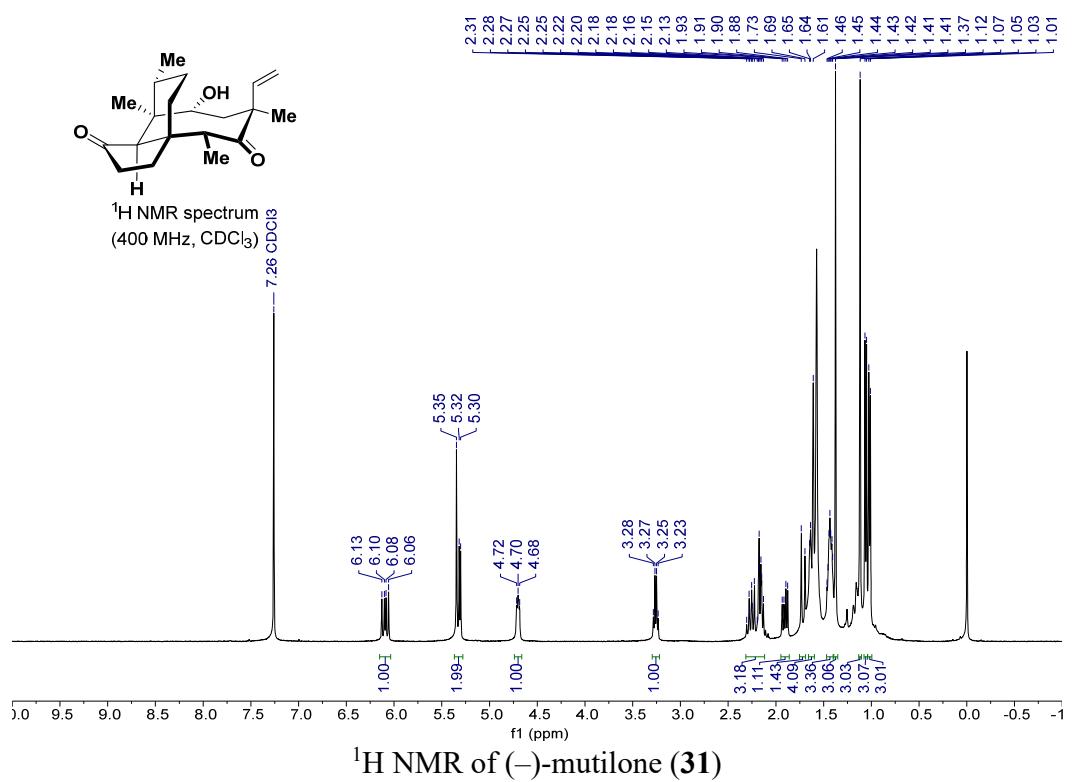


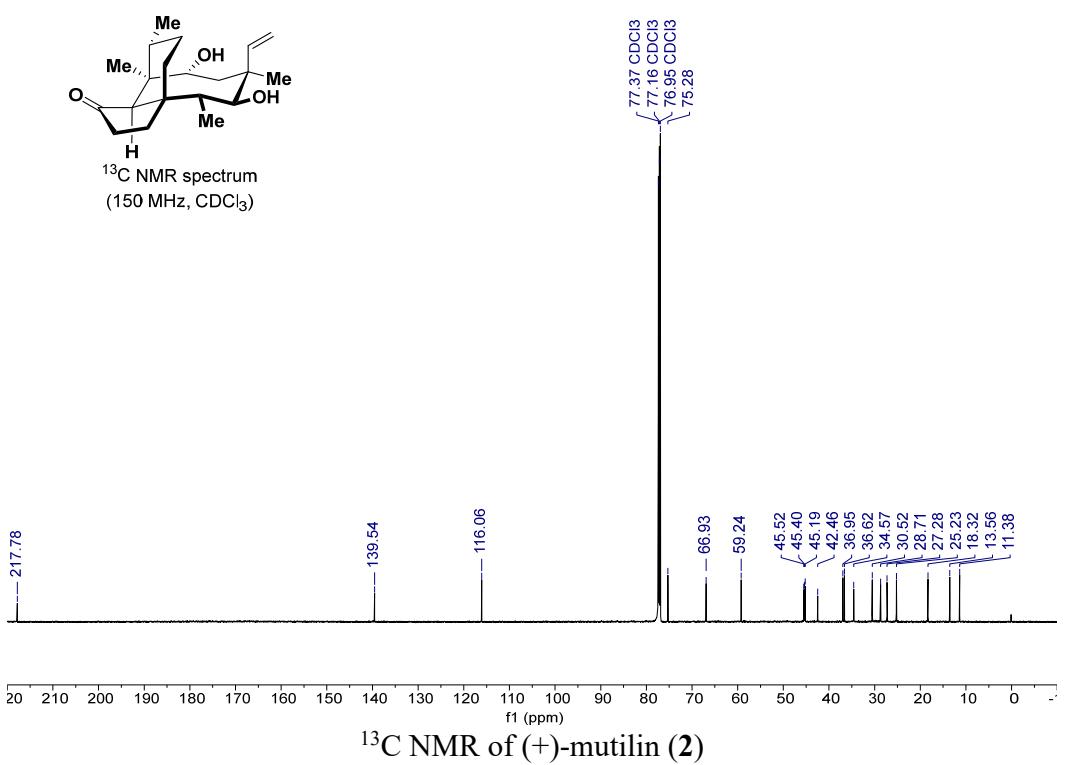
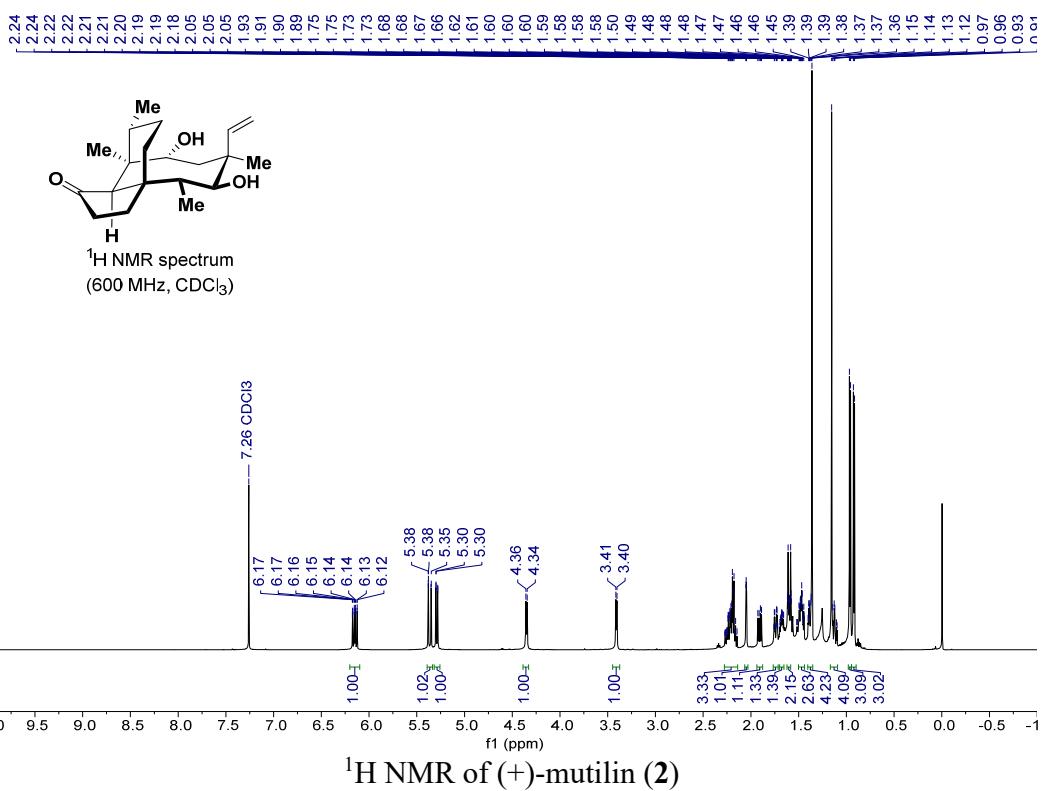


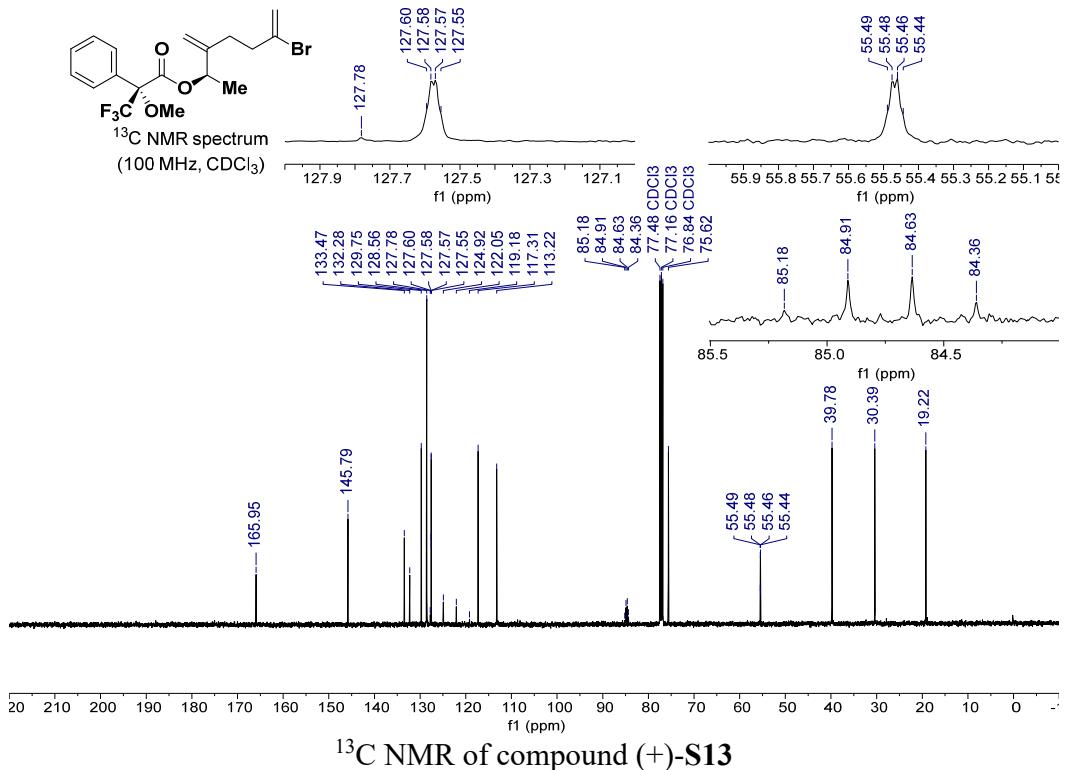
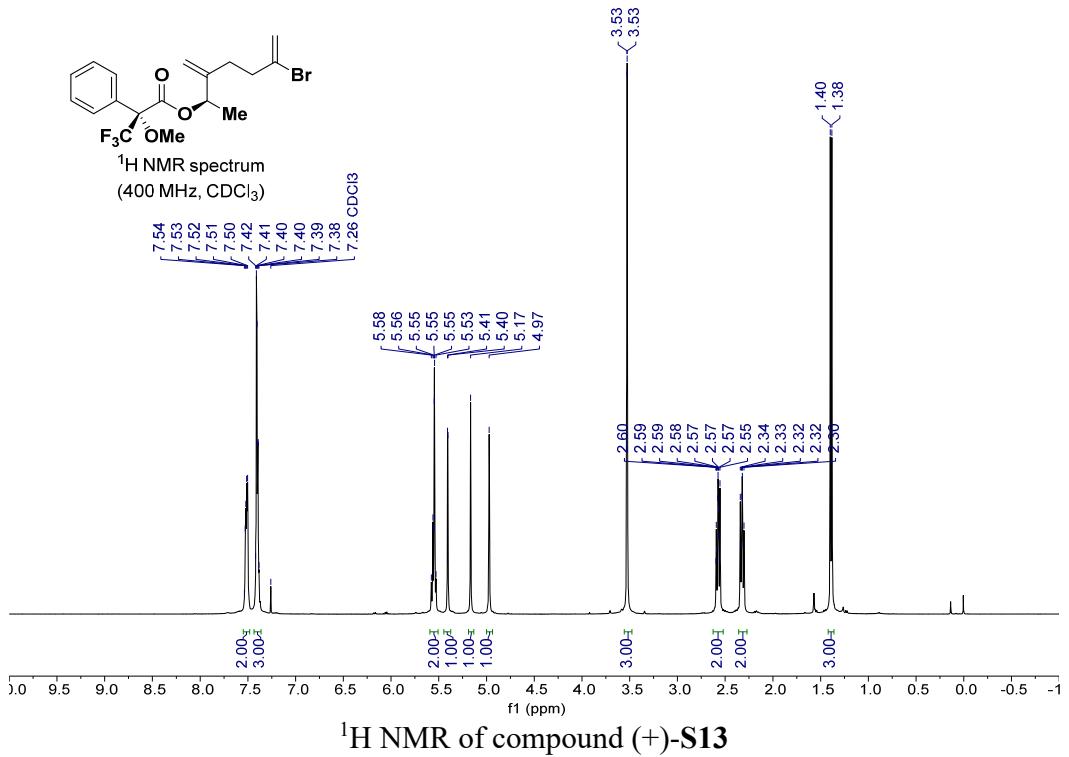


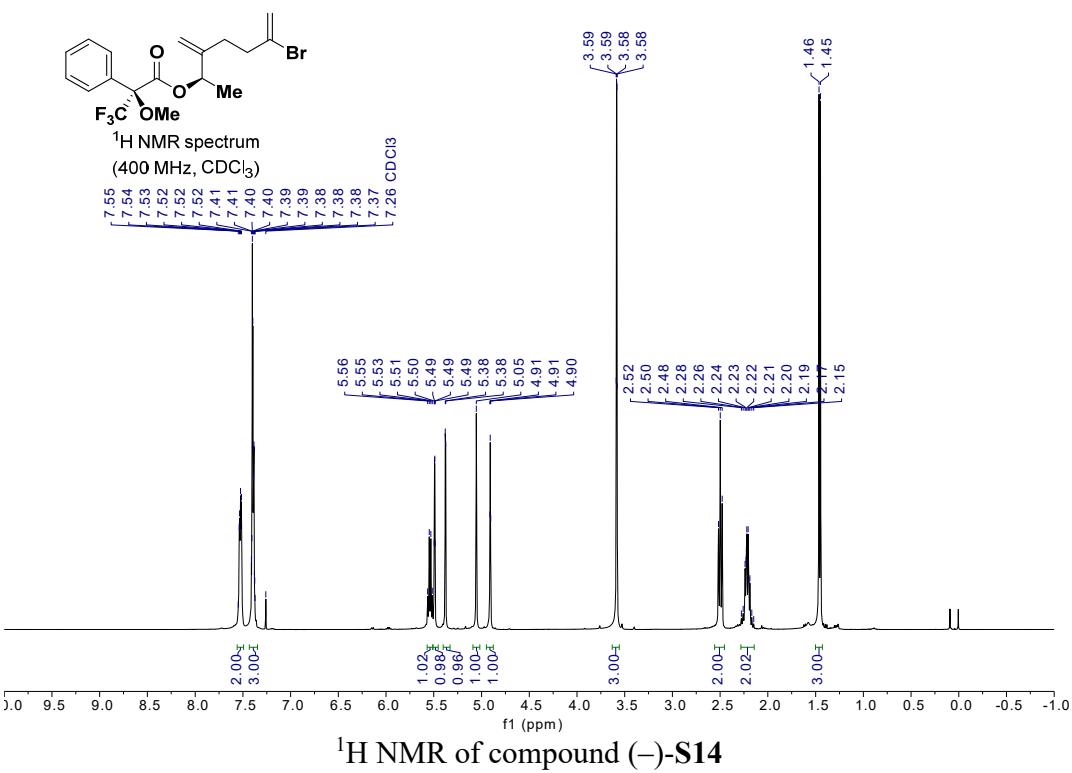
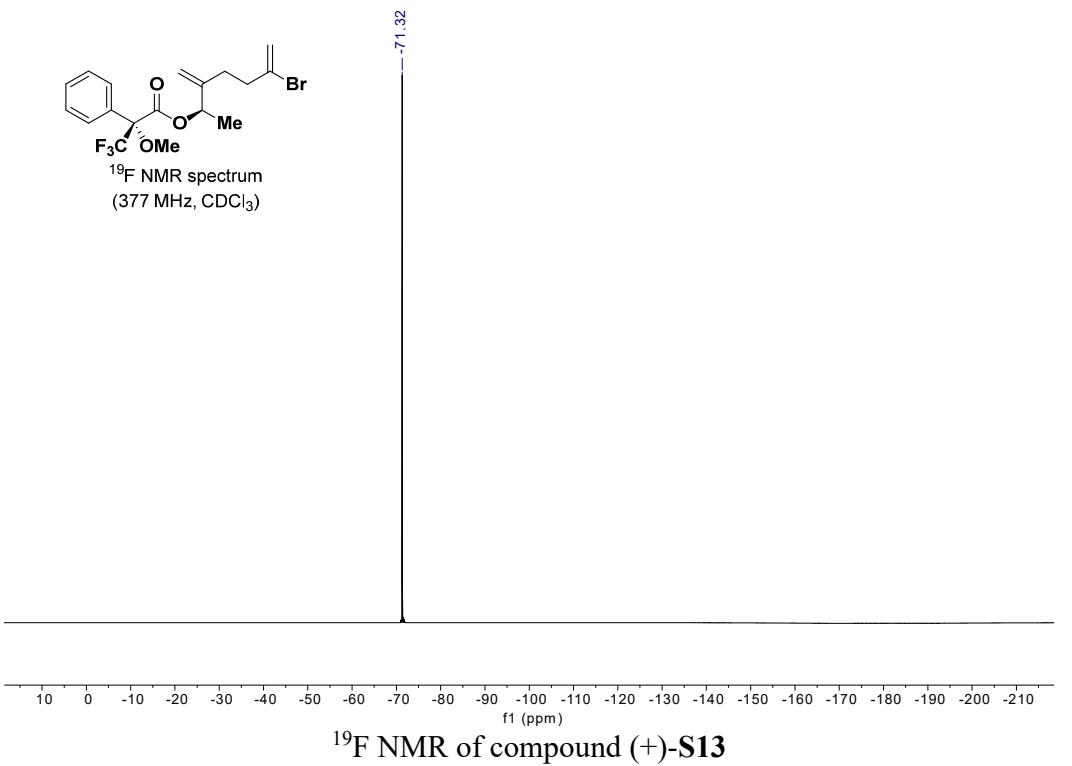


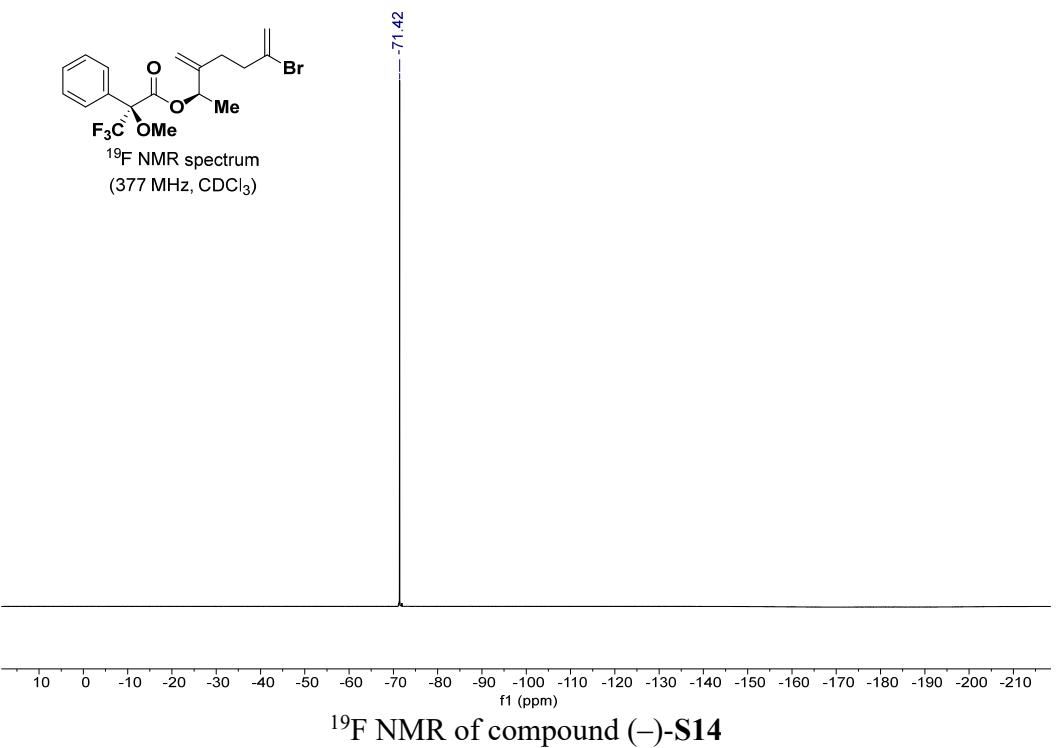
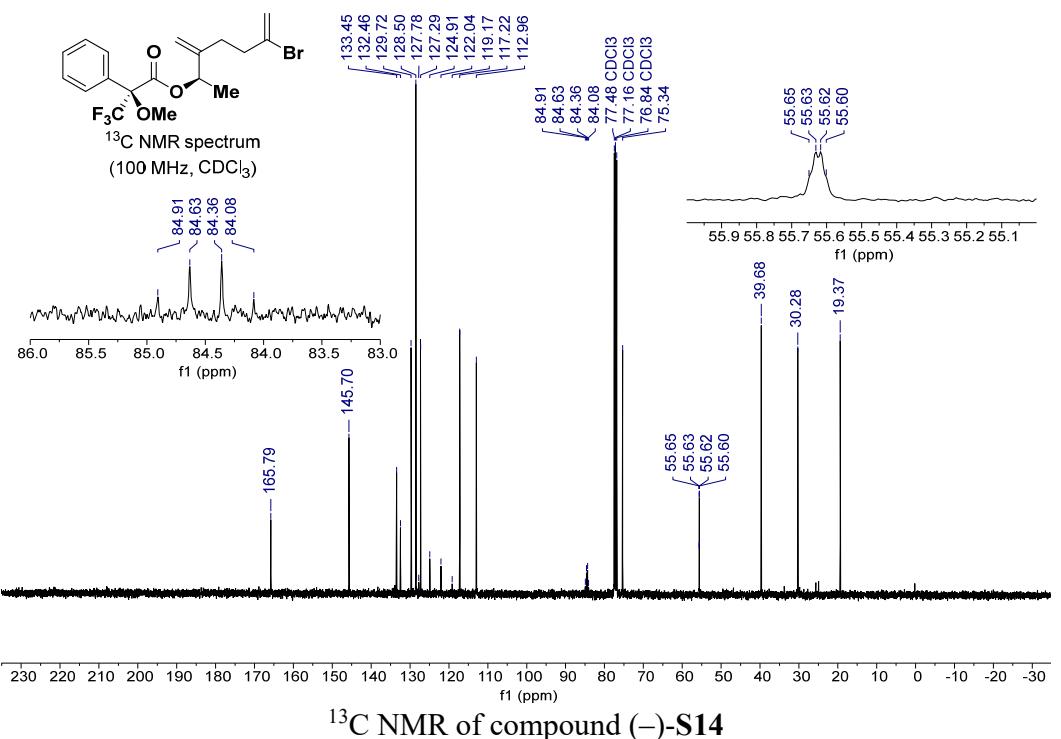


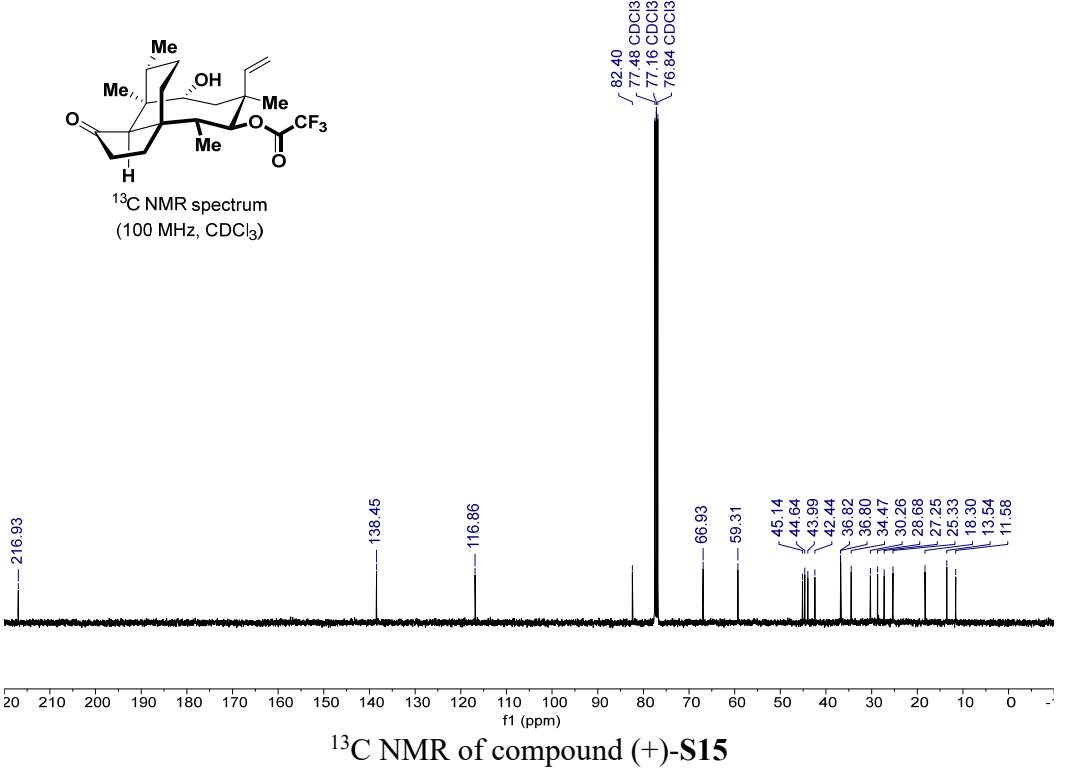
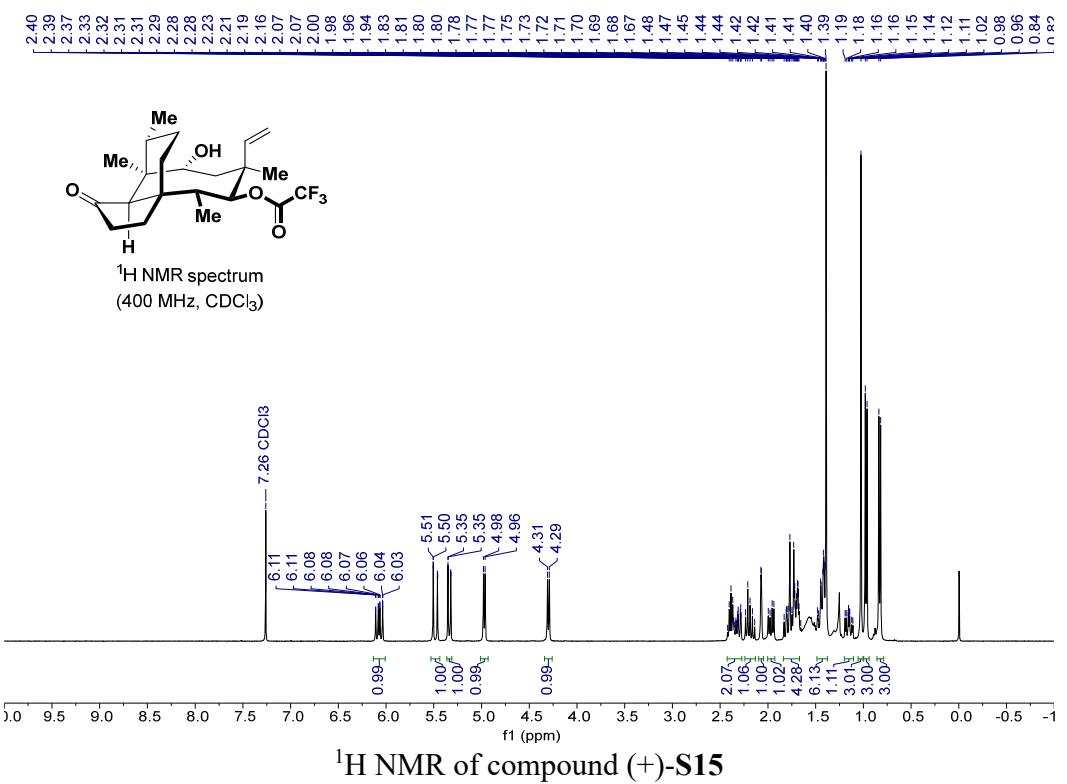


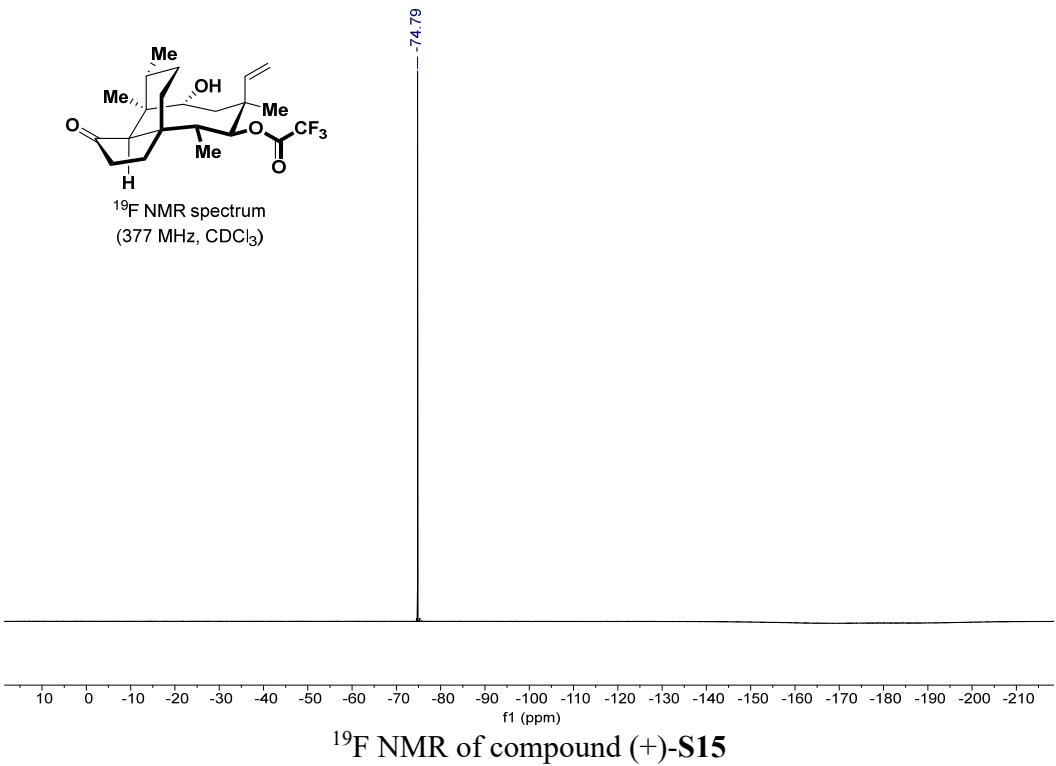


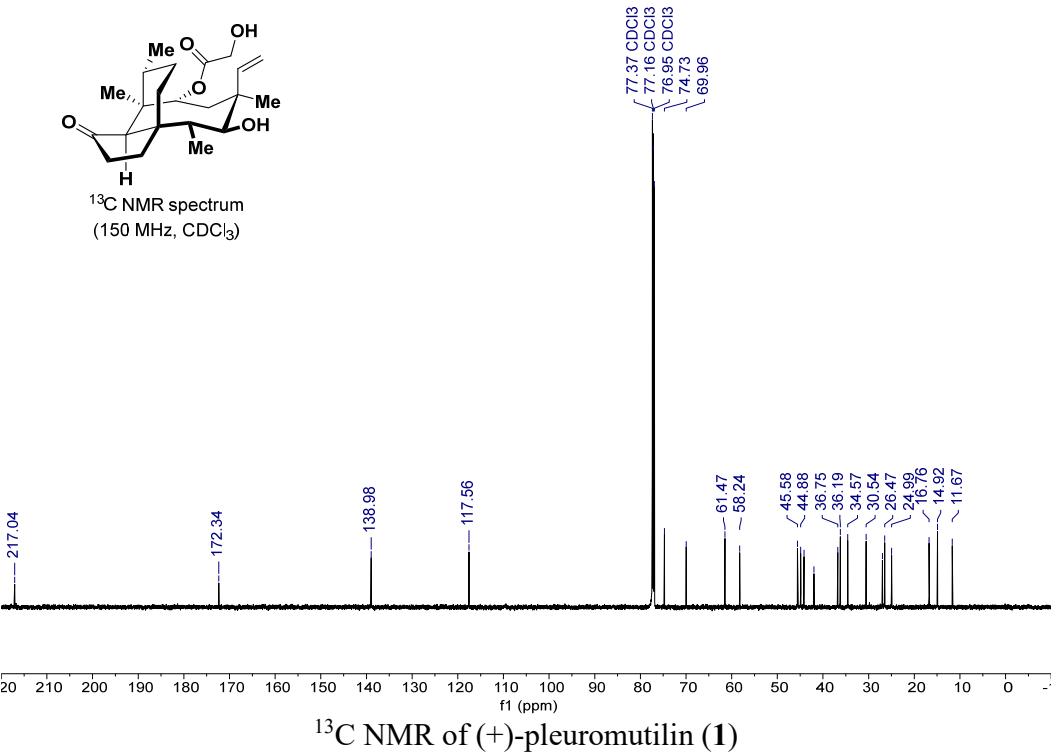
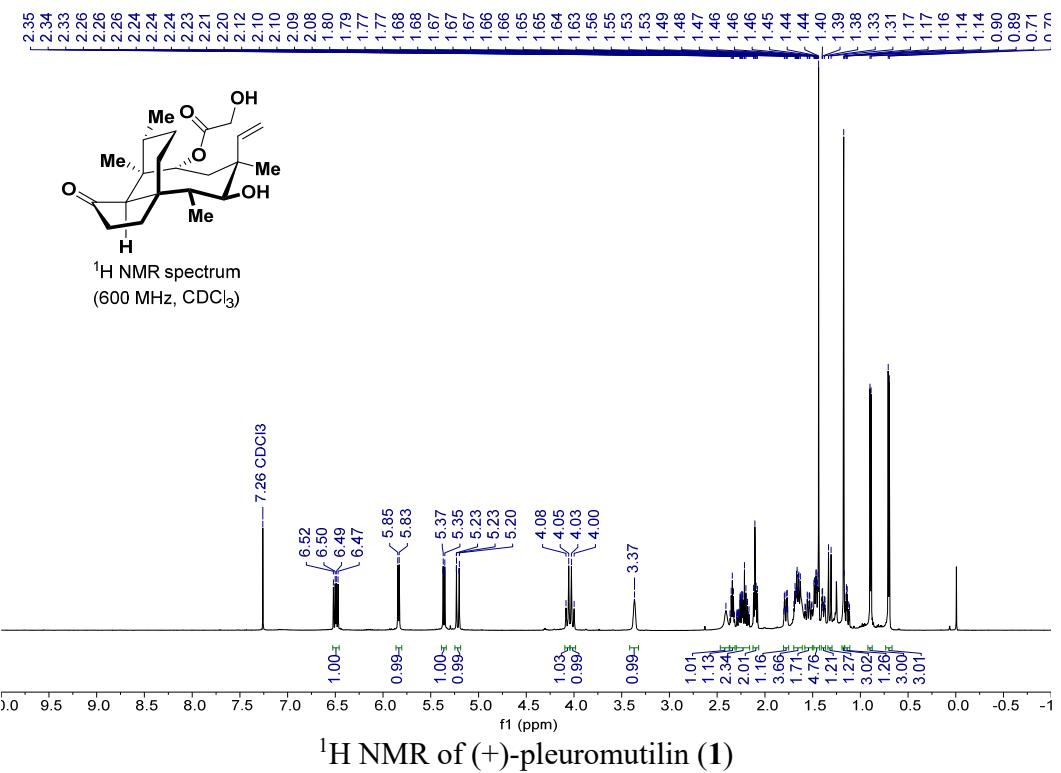












VI. X-Ray Crystallographic Data

Crystal structures were provided by Dr. Jie Su (Peking University). Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre with supplementary publication numbers: CCDC 2179634 (**17**), CCDC 2179635 (**22a**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing da-ta_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

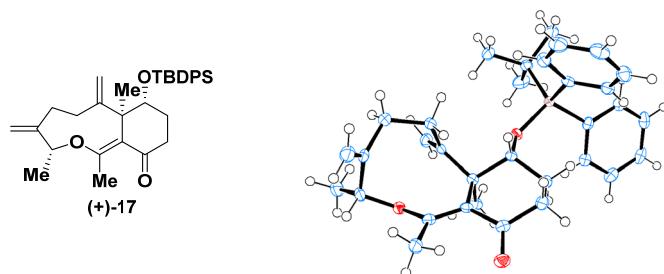


Figure S7. Structure of (+)-17 with 50% thermal ellipsoids

Table S3. Crystal data and structure refinement for (+)-17

Identification code	(+)-17
Empirical formula	C ₃₃ H ₄₂ O ₃ Si
Formula weight	514.75
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	8.5866(3)
b/Å	17.0719(5)
c/Å	20.0057(7)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	2932.63(17)
Z	4
ρ _{calcg} /cm ³	1.166
μ/mm ⁻¹	0.111
F(000)	1112.0
Crystal size/mm ³	0.5 × 0.1 × 0.08

Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^{\circ}$	5.162 to 52.738
Index ranges	-8 \leq h \leq 10, -19 \leq k \leq 21, -25 \leq l \leq 23
Reflections collected	16960
Independent reflections	5745 [R _{int} = 0.0361, R _{sigma} = 0.0436]
Data/restraints/parameters	5745/0/340
Goodness-of-fit on F ²	1.059
Final R indexes [I $>=$ 2 σ (I)]	R ₁ = 0.0331, wR ₂ = 0.0751
Final R indexes [all data]	R ₁ = 0.0387, wR ₂ = 0.0768
Largest diff. peak/hole / e Å ⁻³	0.21/-0.21
Flack parameter	-0.04(6)

Table S4. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å² $\times 10^3$) for (+)-17. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor

Atom	x	y	z	U(eq)
Si1	5651.9(6)	3671.2(3)	1771.7(3)	15.11(13)
O1	4907.8(16)	4085.7(8)	2445.5(7)	16.7(3)
O2	-84.3(17)	6024.3(9)	2816.3(8)	25.2(4)
O3	1282.3(16)	4609.5(8)	4402.6(7)	19.5(3)
C1	6868(2)	4420.5(12)	1318.5(11)	18.4(5)
C2	7657(2)	4260.7(14)	719.6(12)	23.1(5)
C3	8604(3)	4815.6(14)	418.5(12)	27.2(5)
C4	8759(2)	5555.5(14)	697.4(12)	25.9(5)
C5	7985(2)	5732.0(14)	1284.9(12)	26.0(5)
C6	7067(2)	5168.4(12)	1594.4(11)	20.6(5)
C7	4038(2)	3327.1(12)	1206.5(11)	18.2(5)
C8	3774(2)	3675.1(13)	585.0(10)	21.3(5)
C9	2539(3)	3449.1(14)	179.3(13)	29.1(6)
C10	1532(3)	2870.3(14)	385.7(13)	31.5(6)
C11	1747(3)	2515.4(14)	1000.3(13)	29.8(5)
C12	2986(2)	2742.4(13)	1404.0(12)	23.5(5)
C13	6938(2)	2845.7(12)	2075.3(11)	19.5(5)
C14	6099(3)	2336.3(13)	2598.8(12)	27.1(5)
C15	7414(3)	2332.6(13)	1481.2(12)	26.1(5)
C16	8406(3)	3190.5(14)	2405.6(14)	32.6(6)
C17	3360(2)	4388.2(12)	2498.4(11)	15.6(4)
C18	3118(2)	5072.6(12)	2028.0(11)	19.6(5)
C19	1413(3)	5305.7(13)	2039.0(11)	22.0(5)
C20	830(2)	5480.6(12)	2730.0(11)	18.5(5)

Atom	x	y	z	U(eq)
C21	1408(2)	4985.4(11)	3293.9(11)	16.6(4)
C22	3048(2)	4600.5(11)	3244.0(11)	16.0(4)
C23	4253(2)	5198.8(12)	3491.6(11)	20.5(5)
C24	3152(2)	3820.4(12)	3624.3(10)	16.8(4)
C25	1873(2)	3225.3(12)	3484.9(11)	19.0(5)
C26	1103(3)	2852.8(13)	4102.9(11)	22.5(5)
C27	-85(3)	3357.3(12)	4462.1(11)	21.3(5)
C28	446(3)	4075.8(12)	4842.7(11)	22.1(5)
C29	551(2)	4933.1(11)	3859.1(11)	18.0(5)
C30	-1090(3)	5206.4(13)	3964.5(12)	24.8(5)
C31	1587(3)	3903.3(14)	5403.3(12)	30.2(6)
C32	-1580(3)	3170.5(14)	4457.0(12)	29.3(6)
C33	4369(3)	3627.3(13)	3995.8(11)	22.8(5)

Table S5. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for (+)-17. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^*{}^2U_{11} + 2hka^*b^*U_{12} + \dots]$

Atom	U₁₁	U₂₂	U₃₃	U₂₃	U₁₃	U₁₂
Si1	16.4(3)	14.6(2)	14.3(3)	-0.1(2)	0.6(2)	-0.1(2)
O1	16.7(7)	18.6(7)	14.8(8)	-0.7(6)	0.3(6)	2.2(6)
O2	25.1(8)	22.7(8)	27.8(10)	0.4(7)	-1.8(7)	7.5(7)
O3	22.5(7)	19.3(7)	16.6(8)	0.3(6)	0.5(6)	3.5(6)
C1	15.1(9)	21.2(10)	19.0(12)	4.2(9)	-1.3(9)	1.4(8)
C2	23.2(11)	26.2(12)	19.9(12)	2.4(10)	0.9(10)	1.2(9)
C3	20.2(11)	41.3(14)	19.9(13)	7.4(11)	2.4(10)	1.6(10)
C4	17.3(10)	34.1(13)	26.4(13)	14.3(11)	-5.5(10)	-6.9(10)
C5	22.1(11)	24.1(11)	31.8(14)	5.2(10)	-6.5(11)	-6.1(9)
C6	18.1(10)	23.1(11)	20.5(13)	2.1(9)	-1.3(9)	-1.8(9)
C7	17.1(10)	17.4(10)	20.2(12)	-4.9(9)	1.5(9)	2.8(8)
C8	22.8(10)	19.9(10)	21.1(12)	-3.0(10)	-0.3(9)	2.0(9)
C9	33.8(13)	30.5(13)	23.0(14)	-2.7(10)	-7.4(11)	1.7(10)
C10	27.7(12)	32.5(13)	34.3(15)	-12.6(12)	-9.5(11)	-1.5(10)
C11	25.7(11)	26.2(12)	37.5(15)	-7.5(11)	3.5(11)	-7.3(10)
C12	23.2(11)	24.7(11)	22.7(13)	-0.8(10)	0.5(10)	-1.3(9)
C13	20.3(10)	17.8(10)	20.4(12)	-0.5(9)	-0.4(9)	4.0(9)
C14	34.3(12)	21.9(11)	25.0(13)	5.9(10)	2.0(11)	7.7(10)
C15	27.2(11)	21.3(11)	29.7(14)	0.1(10)	3.3(10)	7.6(9)
C16	29.8(12)	26.3(12)	41.6(16)	2.1(11)	-14.6(12)	5.4(10)
C17	14.6(9)	15.4(10)	16.6(11)	-1.2(8)	-0.1(9)	0.7(8)
C18	23.8(11)	19.9(10)	15.2(11)	1.8(9)	1.4(9)	3.1(9)

Atom	U₁₁	U₂₂	U₃₃	U₂₃	U₁₃	U₁₂
C19	24.4(11)	22.8(11)	18.9(12)	2.3(9)	-3.8(9)	3.1(9)
C20	15.6(10)	17.2(10)	22.6(12)	-0.5(9)	-3.9(9)	-1.1(8)
C21	18.2(10)	13.6(9)	18.0(11)	-3.7(9)	-2.9(9)	1.4(8)
C22	15.4(9)	16.8(9)	16.0(11)	-0.7(9)	-0.6(9)	0.5(8)
C23	20.7(10)	21.1(10)	19.6(12)	-3.7(9)	-3.4(10)	0.3(9)
C24	19.2(10)	19.2(10)	11.9(11)	-2.0(8)	4.4(9)	3.4(9)
C25	23.5(10)	16.9(10)	16.6(11)	-0.6(9)	2.6(9)	4.3(9)
C26	28.1(11)	18.4(10)	20.9(12)	2.1(9)	3.0(10)	2.2(9)
C27	27.7(11)	19.8(10)	16.4(12)	7.0(9)	5.0(9)	3.2(9)
C28	26.3(11)	23.9(11)	16.1(12)	1.9(9)	7.2(10)	5.6(9)
C29	20.0(10)	14.4(9)	19.6(12)	-2.2(8)	-2.4(10)	1.8(8)
C30	26.0(12)	24.9(12)	23.5(12)	3.7(10)	5.4(10)	6.3(9)
C31	41.1(13)	31.5(13)	17.9(12)	1.1(10)	1.5(11)	5.7(11)
C32	30.2(12)	27.3(12)	30.4(15)	5.8(10)	6.8(11)	1.1(10)
C33	23.6(10)	24.3(11)	20.4(12)	3.4(10)	0.7(10)	4.5(10)

Table S6. Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for (+)-17

Atom	x	y	z	U(eq)
H2	7543	3772	521	28
H3	9137	4691	28	33
H4	9380	5931	491	31
H5	8079	6228	1473	31
H6	6573	5291	1995	25
H8	4442	4068	439	26
H9	2393	3690	-233	35
H10	710	2718	113	38
H11	1066	2126	1143	36
H12	3122	2500	1816	28
H14A	5748	2661	2961	41
H14B	6806	1948	2767	41
H14C	5221	2083	2395	41
H15A	6499	2116	1276	39
H15B	8073	1916	1635	39
H15C	7968	2645	1161	39
H16A	8988	3482	2080	49
H16B	9038	2773	2578	49
H16C	8106	3532	2765	49
H17	2634	3972	2370	19

Atom	x	y	z	U(eq)
H18A	3421	4926	1578	24
H18B	3758	5512	2167	24
H19A	1270	5765	1760	26
H19B	797	4884	1849	26
H23A	4098	5688	3265	31
H23B	5283	5008	3400	31
H23C	4132	5274	3964	31
H25A	2309	2809	3213	23
H25B	1069	3480	3223	23
H26A	596	2371	3965	27
H26B	1915	2714	4418	27
H28	-466	4345	5027	27
H30A	-1699	4787	4148	37
H30B	-1528	5366	3545	37
H30C	-1095	5641	4269	37
H31A	2484	3641	5225	45
H31B	1095	3574	5730	45
H31C	1902	4386	5609	45
H32A	-1913	2725	4231	35
H32B	-2297	3485	4679	35
H33A	4446	3125	4173	27
H33B	5147	3994	4079	27

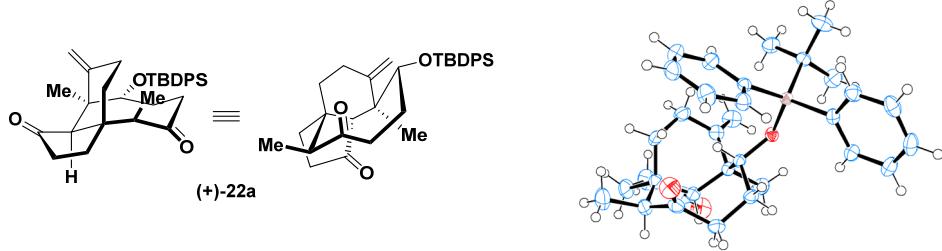


Figure S8. Structure of (+)-22a with 50% thermal ellipsoids

Table S7. Crystal data and structure refinement for (+)-22a

Identification code	(+)-22a
Empirical formula	C ₃₃ H ₄₂ O ₃ Si
Formula weight	514.75
Temperature/K	180.00(10)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	8.51640(10)
b/Å	18.3328(3)
c/Å	18.3508(3)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	2865.10(7)
Z	4
ρ _{calc} g/cm ³	1.193
μ/mm ⁻¹	0.114
F(000)	1112.0
Crystal size/mm ³	0.12 × 0.09 × 0.07
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.964 to 54.968
Index ranges	-11 ≤ h ≤ 11, -23 ≤ k ≤ 23, -23 ≤ l ≤ 23
Reflections collected	67329
Independent reflections	6572 [R _{int} = 0.0385, R _{sigma} = 0.0214]
Data/restraints/parameters	6572/0/339
Goodness-of-fit on F ²	1.061
Final R indexes [I>=2σ (I)]	R ₁ = 0.0309, wR ₂ = 0.0830
Final R indexes [all data]	R ₁ = 0.0338, wR ₂ = 0.0844
Largest diff. peak/hole / e Å ⁻³	0.25/-0.18
Flack parameter	0.02(2)

Table S8. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for (+)-**22a**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor

Atom	x	y	z	U(eq)
Si1	3159.1(5)	5303.2(2)	5661.1(2)	19.63(11)
O1	2571.0(13)	4450.6(6)	5621.4(6)	22.8(2)
O2	5765.5(17)	3574.5(9)	7410.8(8)	42.4(4)
O3	-499(2)	1913.5(10)	6124.3(10)	55.5(5)
C1	1388(2)	5869.4(10)	5397.7(10)	26.2(4)
C2	0(2)	5780.2(12)	5924.2(11)	36.6(5)
C3	873(2)	5588.9(14)	4645.0(11)	40.7(5)
C4	1807(3)	6678.2(11)	5349.0(13)	42.4(5)
C5	4699.6(19)	5446.6(9)	4948.0(9)	23.6(3)
C6	4932(2)	4918.9(10)	4409.9(9)	28.4(4)
C7	5997(2)	5030.8(13)	3850.2(10)	35.5(4)
C8	6845(2)	5670.8(12)	3807.1(10)	36.3(4)
C9	6634(2)	6202.1(11)	4332.5(11)	34.9(4)
C10	5574(2)	6089.4(10)	4895.4(11)	30.0(4)
C11	4033(2)	5488.1(9)	6583.2(9)	22.8(3)
C12	3138(2)	5607.6(11)	7207.8(10)	31.7(4)
C13	3808(3)	5680.2(12)	7891.5(11)	38.3(5)
C14	5415(3)	5622.4(12)	7966.5(11)	38.0(5)
C15	6334(2)	5504.3(12)	7363.7(11)	37.4(5)
C16	5658(2)	5443.3(10)	6678.9(10)	29.5(4)
C17	2966.7(19)	3849.7(9)	6085.1(9)	20.3(3)
C18	1505(2)	3338.5(9)	6074.5(9)	23.0(3)
C19	1655(2)	2664.7(9)	6593.2(10)	27.1(4)
C20	2066(2)	2829.5(10)	7404.5(10)	29.1(4)
C21	1643(2)	3621.4(10)	7632.6(10)	31.2(4)
C22	354(2)	4001.5(12)	7182.6(11)	35.8(4)
C23	139(2)	3760.7(10)	6398.7(10)	28.2(4)
C24	-1198(2)	3891.0(13)	6055.4(13)	40.9(5)
C25	1228(2)	3086.4(11)	5288.9(10)	33.2(4)
C26	993(3)	2287.5(13)	7829.5(13)	43.2(5)
C27	-524(3)	2255.0(14)	7391.1(14)	49.5(6)
C28	81(3)	2246.5(11)	6624.3(12)	39.1(5)
C29	3820(2)	2647.4(11)	7578.2(10)	32.4(4)
C30	4203(3)	2702.8(15)	8391.8(12)	49.9(6)
C31	4989(2)	3094.2(10)	7133.8(10)	29.4(4)
C32	5199(2)	2921.5(10)	6334.1(11)	29.1(4)
C33	4535(2)	3524.9(10)	5836.1(10)	25.6(4)

Table S9. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for (+)-**22a**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^*{}^2U_{11} + 2hka^*b^*U_{12} + \dots]$

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Si1	19.2(2)	20.1(2)	19.6(2)	-0.38(17)	0.86(17)	-0.07(17)
O1	24.0(5)	22.1(6)	22.3(6)	1.1(5)	0.0(5)	-2.3(5)
O2	41.6(8)	42.1(8)	43.6(9)	-4.5(7)	-11.2(7)	-8.0(7)
O3	61.1(11)	43.2(9)	62.2(11)	-6.0(8)	-4.2(9)	-29.8(8)
C1	24.4(8)	26.6(9)	27.7(9)	1.8(7)	-2.1(7)	5.2(7)
C2	26.7(9)	41.9(11)	41.3(11)	-0.4(9)	3.5(8)	9.8(8)
C3	34.4(10)	53.6(13)	33.9(11)	-1.4(9)	-11.3(8)	8.9(10)
C4	38.1(11)	28.2(10)	60.7(14)	5.2(9)	-4.2(10)	7.7(9)
C5	21.4(8)	27.9(9)	21.5(8)	4.1(7)	0.5(6)	-0.2(6)
C6	27.1(8)	31.4(9)	26.8(9)	-0.4(7)	2.8(7)	-1.8(7)
C7	32.5(10)	48.4(12)	25.5(9)	-1.8(9)	6.4(7)	2.4(9)
C8	23.9(9)	56.6(13)	28.4(9)	12.7(9)	4.5(8)	0.1(9)
C9	26.1(9)	37.8(10)	40.9(11)	15.1(9)	-0.5(8)	-5.2(8)
C10	29.0(9)	27.2(9)	33.8(10)	1.1(8)	1.4(7)	-2.3(7)
C11	27.4(8)	18.0(8)	23.1(8)	0.4(6)	-2.3(7)	-0.7(6)
C12	30.4(9)	35.4(10)	29.1(9)	-3.5(7)	-0.2(8)	2.4(8)
C13	49.2(12)	40.6(12)	25.2(10)	-3.4(8)	2.7(8)	3.9(10)
C14	49.1(12)	38.2(11)	26.6(9)	0.4(8)	-12.5(9)	0.6(9)
C15	32.2(10)	44.6(12)	35.4(11)	5.7(9)	-11.4(8)	0.2(8)
C16	27.9(9)	33.5(10)	27.1(9)	2.0(7)	-1.2(7)	0.3(7)
C17	21.8(8)	19.9(7)	19.3(7)	-1.1(6)	2.3(6)	-2.0(6)
C18	24.1(8)	22.6(8)	22.4(8)	-1.6(6)	0.9(6)	-5.1(6)
C19	31.9(9)	21.1(8)	28.4(9)	-1.4(7)	2.7(7)	-5.4(7)
C20	36.9(10)	25.2(9)	25.2(9)	3.1(7)	4.6(7)	-5.0(8)
C21	41.3(11)	30.5(9)	21.7(8)	-2.5(7)	8.1(8)	-0.9(8)
C22	36.3(10)	34.5(10)	36.7(10)	-4.1(8)	10.4(8)	3.4(8)
C23	22.5(8)	26.6(9)	35.6(10)	1.9(7)	5.9(7)	-5.9(7)
C24	24.4(9)	44.0(12)	54.1(13)	-1.7(10)	-0.3(9)	-3.2(8)
C25	37.3(10)	33.5(10)	28.9(10)	-6.2(8)	-4.6(8)	-9.1(8)
C26	52.7(13)	37.6(11)	39.4(12)	11.9(9)	10.0(10)	-9.5(10)
C27	47.8(13)	46.6(13)	54.3(14)	11.7(11)	11.7(11)	-20.6(11)
C28	41.2(11)	27.2(9)	48.8(12)	4.8(9)	1.8(10)	-11.9(9)
C29	43.3(10)	27.2(9)	26.7(10)	2.3(8)	-1.3(8)	1.1(8)
C30	66.4(15)	54.2(14)	29.2(11)	7.1(10)	-8.1(11)	2.7(12)
C31	29.2(9)	26.3(9)	32.8(9)	0.6(7)	-5.3(8)	4.9(7)
C32	25.5(9)	26.7(9)	35.0(10)	-1.4(7)	2.5(8)	3.9(7)
C33	23.4(8)	25.8(8)	27.7(9)	-1.1(7)	4.7(7)	0.3(7)

Table S10. Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for (+)-22a

Atom	x	y	z	U(eq)
H2A	-223	5271	5989	55
H2B	-908	6020	5727	55
H2C	262	5994	6386	55
H3A	1709	5659	4302	61
H3B	-38	5854	4487	61
H3C	625	5079	4677	61
H4A	2177	6845	5814	64
H4B	893	6952	5212	64
H4C	2615	6746	4991	64
H6	4364	4486	4428	34
H7	6142	4671	3500	43
H8	7553	5744	3428	44
H9	7201	6635	4309	42
H10	5443	6450	5246	36
H12	2052	5640	7164	38
H13	3180	5767	8297	46
H14	5874	5663	8424	46
H15	7417	5465	7415	45
H16	6300	5371	6275	35
H17	3099	4036	6582	24
H19	2459	2337	6396	33
H21A	1313	3614	8138	37
H21B	2589	3915	7605	37
H22A	-638	3933	7433	43
H22B	573	4521	7182	43
H24A	-2010	4131	6295	49
H24B	-1326	3743	5574	49
H25A	2067	2769	5141	50
H25B	1195	3503	4973	50
H25C	249	2829	5261	50
H26A	1477	1809	7859	52
H26B	794	2463	8319	52
H27A	-1117	1817	7500	59
H27B	-1176	2679	7481	59
H29	3980	2136	7441	39
H30A	4036	3194	8554	75
H30B	5280	2570	8470	75
H30C	3533	2379	8661	75

Atom	x	y	z	U(eq)
H32A	4674	2465	6225	35
H32B	6308	2859	6232	35
H33A	5301	3915	5804	31
H33B	4401	3326	5350	31

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