Evolution of a Strategy for the Enantioselective Synthesis of (-)-Cajanusine

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Supplementary Information – Table of Contents

General:

^{1}H NMR spectra were recorded at room temperature on a Varian I400 (400 MHz), Varian VXR400 (400 MHz), Varian I500 (500 MHz), or a Varian I600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the residual solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. ^{13}C NMR spectra were recorded on a Varian I400 (101 MHz) and a Varian I500 (126 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: 77.16 ppm). Infrared (IR) spectra were recorded on a Bruker Tensor II FT-IR Spectrometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). Melting points were obtained on a Thomas Hoover capillary melting point apparatus without correction. High Resolution Mass Spectrometry (HRMS) analysis was obtained using Electron Impact Ionization (EI), Chemical Ionization (CI), Atmospheric Pressure Chemical Ionization (APCI) or Electrospray Ionization (ESI) and reported as m/z (relative intensity). ESI was acquired using a Waters/Micromass LCT Classic (ESI-TOF). Optical rotations were measured on a Perkin-Elmer 241 polarimeter at 589 nm wavelength (sodium D-line) using a standard 10 cm cell (1 mL). Specific rotations, $[\alpha]_D^{20}$, are reported in degree mL/(g·dm) at the specific temperature. Concentrations (c) are given in grams per 100 mL of the specific solvent. The diastereomeric and regioisomeric ratios were determined using NMR or GC-MS analysis of unpurified reaction mixtures. Unless otherwise noted, all reactions have been carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (150 °C) and flame-dried glassware with standard vacuum-line techniques. Dichloromethane (DCM), Tetrahydrofuran (THF), Diethyl ether (Et_2O), dioxane and Dimethylformamide (DMF) were purified under a positive pressure of dry argon by passage through two columns of activated alumina. Toluene (PhMe) was purified under a positive pressure of dry argon by passage through columns of activated alumina and Q5 (Grubbs apparatus). Benzene (PhH) and Nitromethane ($MeNO_2$) was distilled over CaH_2. All work-up and purification procedures were carried out with reagent grade solvents in air. Standard flah column chromatography (FCC) techniques using ZEOprep 60/40-63 µm silica gel were used for purification. For difficult separations medium pressure liquid chromatography (MPLC) was performed using a Teledyne ISCO CombiFlash Rf 150 instrument. Chiral HPLC analysis was performed on an Agilent 1220 Infinity LC system using chiral column eluted with a mixture of hexane and isopropyl alcohol.

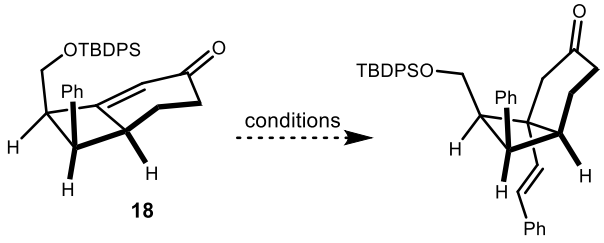
Reagents and Catalysts:

Allyl acetate was purchased from Sigma-Aldrich and used as received.
Allylpalladium(II) chloride dimer [Pd(allyl)Cl]$_2$ was purchased from Sigma-Aldrich and used as received.
Ammonium acetate was purchased from Mallinckrodt and used as received.
2,2′-Bipyridyl (bpy) was purchased from Combi-Blocks and used as received.
Bismuth(III) trifluoromethanesulfonate was purchased from Matrix Scientific and used as received.
Bis(pinacolato)diboron was purchased from Oakwood Chemical and used as received.
1-(3,5-Bis(trifluoromethyl)phenyl)-3-((S)-(6-methoxyquinolin-4-yl)((1S,2S,4S,5R)-5-vinylquinuclidin-2-yl)methyl)thiourea was synthesized via known literature.[1]
Boron tribromide solution (1 M in DCM) was purchased from Alfa-Aesar and used as received.
Boron trifluoride diethyl etherate was purchased from Sigma-Aldrich and used as received.
Bromotrichloromethane was purchased from Oakwood Chemical and used as received.
1-Bromo-3,5-dimethoxybenzene was purchased from Combi-Blocks and used as received.
***tert*-Butanol** was purchased from Alfa-Aesar and used as received.
***tert*-Butyldimethylsilyl chloride (TBSCl)** was purchased from Oakwood Chemical and used as received.
***n*-Butyllithium solution** was purchased from Sigma-Aldrich and titrated before every use.
***t*-Butyllithium solution** was purchased from Sigma-Aldrich and titrated before every use.
Chloro(1,5-cyclooctadiene)rhodium(I) dimer was purchased from Strem and used as received.
Chromic acid (Jones' reagent) was prepared via known literature.[2]
Copper(I) chloride was purchased from Strem and used as received.
Copper(I) iodide was purchased from Strem and used as received.
1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU) was purchased from Oakwood Chemical and used as received.
Dibromobis(triphenylphosphine)nickel(II) was purchased from Strem and used as received.
Dibromomethane was purchased from Oakwood Chemical and used as received.
Dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](2-isopropoxyphenylmethylene)ruthenium(II) (Hoveyda-Grubbs II) was purchased from Sigma-Aldrich and used as received.
Dichlorobis(triphenylphosphine)nickel(II) was prepared via known literature.[3]
Dicyclohexylcarbodiimide (DCC) was purchased from Oakwood Chemical and used as received.
3,4-Dihydro-2*H*-pyran was purchased from Sigma-Aldrich and used as received.
3,5-Dimethoxybenzaldehyde was purchased from Shaoyuan Chemical and used as received.

4,7-Dimethoxy-1,10-phenanthroline (4,7-diOMeBPhen) was purchased from Strem and used as received.
4-(Dimethylamino)pyridine (DMAP) was purchased from Oakwood Chemical and used as received.
4,7-Diphenyl-1,10-phenanthroline (BPhen) was purchased from Strem and used as received.
4,4′-Di-*tert*-butyl-2,2′-dipyridyl (dtbbpy) was purchased from Combi-Blocks and used as received.
Ethanethiol was purchased from Alfa-Aesar and used as received.
Ethylenebis(diphenylphosphine) (dppe) was purchased from Sigma-Aldrich and used as received.
Imidazole was purchased from Oakwood Chemical and used as received.
Iodine was purchased from Alfa-Aesar and used as received.
2-Iodoxybenzoic acid (IBX) was prepared via known literature.[4]
Iodoform was purchased from TCI and used as received.
$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ was purchased from Strem and used as received.
2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (pinB-OiPr) was purchased from Oakwood Chemical and used as received.
Lithium chloride was purchased from VWR. It was heated with heat gun under high-vac for 10 min and stored in glovebox before use.
Lithium hydroxide monohydrate was purchased from Oakwood Chemical and used as received.
Magnesium turning was purchased from Strem and used as received.
2-Mercaptopyridine *N*-oxide was purchased from Chem-Inpex and used as received.
4-Methoxypyridine *N*-oxide (MPO) was purchased from Sigma-Aldrich and used as received.
2-Methyl-2-butene was purchased from Oakwood Chemical and used as received.
2-Methylpropene (isobutylene) was purchased from Sigma-Aldrich and used as received.
***N*-Hydroxytetrachlorophthalimide (TCNHPI)** was purchased from Sigma-Aldrich and used as received.
***N*-Hydroxyphthalimide (NHPI)** was purchased from Sigma-Aldrich and used as received.
***N*-Methylimidazole (NMI)** was purchased from Alfa-Aesar and used as received.
Nickel chloride ethylene glycol dimethyl ether complex ($NiCl_2$·DME) was purchased from Strem and used as received.
(Oxydi-2,1-phenylene)bis(diphenylphosphine) (DPEPhos) was purchased from Strem and used as received.
1,2,2,6,6-Pentamethylpiperidine (*N*-MePMP) was purchased from Sigma-Aldrich and distilled over CaH_2 before use.
***E*-Phenylethenylboronic acid** was purchased from Combi-Blocks and used as received.
Phenylmagnesium bromide solution (3.0 M in diethyl ether) was purchased form Sigma-Aldrich and used as received.
Potassium carbonate was purchased from VWR and used received.
Sodium carbonate was purchased from VWR and used received.

Sodium chlorite was purchased from VWR and used as received.
Sodiom hydride (60 % dispersion in mineral oil) was purchased from Sigma-Aldrich and used as received.
Sodium perborate tetrahydrate was purchased from Merck KGaA and used as received.
Sodium periodate was purchased from Sigma-Aldrich and used as received.
Sodium phosphate mono-basic monohydrate was purchased from Macron Chemical and used as received.
Sodium *tert*-butoxide was purchased from Strem and used as received.
Tetrabromomethane was purchased form Oakwood chemical and dried over anhydrous $MgSO_4$ before use.
Tetrabutylammonium fluoride (TBAF, 1M in THF) was purchased from Sigma-Aldrich and used as received.
2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) was purchased from Sigma-Aldrich and used as received.
1,1,1-Triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1H)-one (DMP) was purchased from Chem-Impex and used as received.
Triethylaluminum solution (1 M in hexanes) was purchased from Sigma-Aldrich and used as received.
Trimethylsilyldiazomethane ($TMSCHN_2$) was purchased from Sigma-Aldrich and used as received.
Trimethylsilyl trifluoromethanesulfonate (TMSOTf) was purchased from Oakwood Chemical and distilled over K_2CO_3 before use.
Triphenylphosphine was purchased from Oakwood chemical and used as received.
Tris(trimethylsilyl)silane was purchased from Alfa-Aesar and used as received.
Zinc (II) chloride was purchased from Alfa-Aesar. It was heated with heat gun under high-vac for 10 min and stored in glovebox before use.

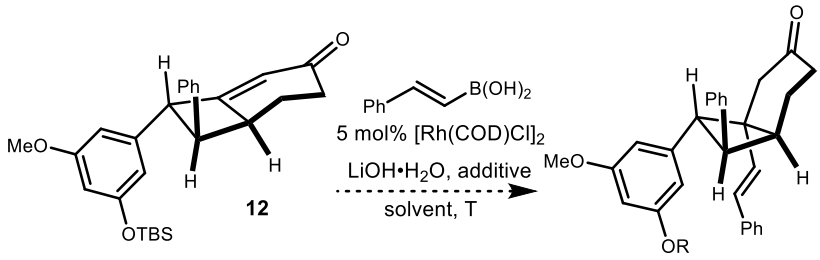
Attempts for conjugate addition:



18 **SI-9**

Nu	[M]/L	LA[a]/base[b]	solvent	T(°C)	pdt:SM:bypdts[c]
ref: 5 Ph—≡	10 mol% $Ni(COD)_2$ 20 mol% PBu_3	BEt_3	THF/MeOH	50	SM only
ref: 6 Ph / $Al(iBu)_2$	5 mol% CuCN	-	THF	rt	comlex mixture
ref: 7 Ph / $Cu(Th)CN{\cdot}2Li^+$		BF_3OEt_2	THF	-78	comlex mixture
		$EtAlCl_2$	THF	-78	comlex mixture
		$Zn(OTf)_2$	THF	-78	comlex mixture
		$Bi(OTf)_3$	THF	-78 - rt	SM only
Ph / $B(OH)_2$	5 mmol% $[Rh(COD)Cl]_2$	K_2CO_3	$PhMe/H_2O$	rt	SM only
		K_2CO_3	THF/H_2O	rt	SM only
		K_2CO_3	$dioxane/H_2O$	rt	1:2:0
		K_2CO_3	$dioxane/H_2O$	60	2:1:0
		Cs_2CO_3	$dioxane/H_2O$	60	1.5:1:0
		LiOH	$dioxane/H_2O$	60	pdt only
		KOH	$dioxane/H_2O$	60	1:1:0.5
		CsOH	$dioxane/H_2O$	60	2.5:1:0.8
		Et_3N	$dioxane/H_2O$	60	SM only

Reactions were run on 0.1 mmol scale.
a: 50 mol%; b: 3 eq. c: Crude NMR



12

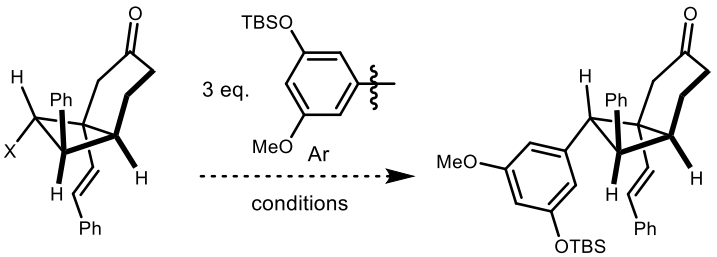
1:1 mixture with cyclobutene **11**

R=H **SI-20** or TBS **4**

additive	solvent	T(°C)	yield[a]
20 mol% DBU	$PhMe/H_2O$	60	nd
20 mol% DBU	$dioxane/H_2O$	60	trace
20 mol% DBU	$PhMe/dioxane/H_2O$	60	nd
-	$PhMe/dioxane/H_2O$	60	trace
-	$dioxane/H_2O$	80	9% **SI-20**
-	$dioxane/H_2O$	100	nd

Reactions were run on 0.1 mmol scale.
a: Isolated yield
No SM could be recycled from above conditions

Sp^2-Sp^3 cross coupling with alkyl halides:

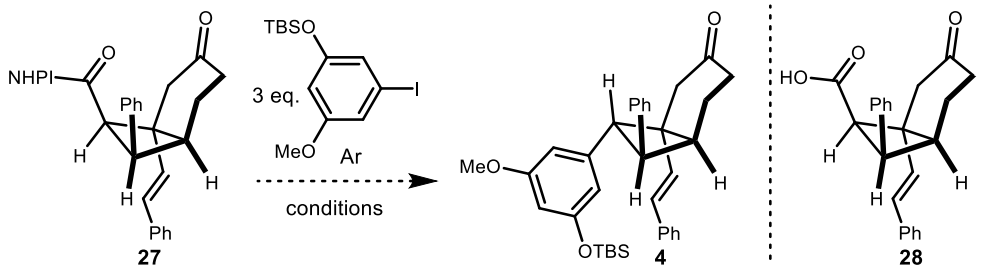


X=Br **(SI-11)** or I **(SI-12)** **4**

	X	[M]	L	Ar	base	solvent	T(°C)	result[a]
Ref: 8	Br	-	-	Ar_2Zn (s)	-	PhMe	rt	SM
Ref: 9	Br	5 mol% $Ni(COD)_2$	10 mol% Bpen	$ArB(OH)_2$	*t*BuOK	2-butanol	60	complex mixture
Ref: 10	Br[b]	10 mol% $Ni(dtbbpy)Cl_2$ 1 mol% $[Ir(dFCF_3ppy)dtbbpy]PF_6$		ArBr	Na_2CO_3	DME	rt	26%[c] Z-styryl
Ref: 11	Br	11 mol% $NiI_2 \cdot xH_2O$ 3 eq. Mn	5 mol% dtbbpy 5 mol% dppbz	ArBr	pyridine	DMPU	80	SM
	I	11 mol% $NiI_2 \cdot xH_2O$ 3 eq. Mn	5 mol% dtbbpy 5 mol% dppbz	ArI	pyridine	DMPU	80	complex mixture

Reactions were run on 0.05 mmol scale.
a: Crude NMR; b: With blue LED irradiation; c: Isolated yield, see text

Sp^2-Sp^3 reductive cross coupling with isolated NHPI ester:



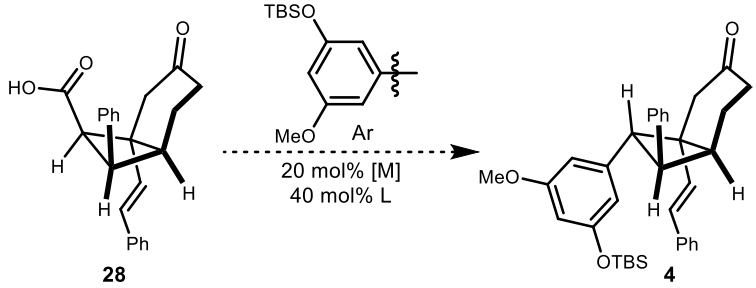
27 **4** **28**

NHPI =*N*-hydoxylphthalimide hydrolysis

	[M]/L		reductant[a]	additive	T	result[b]
Ref: 12	10 mol% $Ni(dtbbpy)Br_2$		Zn	-	rt	SM
	10 mol% $Ni(dtbbpy)Br_2$		Zn	-	50 - 80	hydrolysis
	10 mol% $Ni(dtbbpy)Br_2$		Mn	-	rt	SM
Ref: 13	10 mol% $Ni(dtbbpy)Br_2$		TDAE	-	rt	complex mixture
Ref: 14	10 mol% $Ni(dtbbpy)Br_2$		TDAE	TMSBr	rt	complex mixture
	10 mol% $Ni(BPhen)Br_2$		Zn	-	rt	SM
	10 mol% $Ni(dtbbpy)Br_2$		Zn	-	rt	hydrolysis[c]
Ref: 15	10 mol% CuCl	10 mol% DavePhos	Zn	-	60	hydrolysis

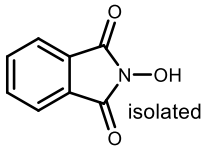
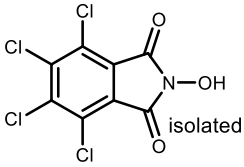
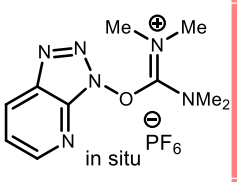
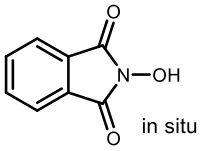
Reactions were run on 0.05 mmol scale in 1 mL DMA
a: 2 eq. b: Crude NMR c: TCNHPI ester as SM

Sp^2-Sp^3 decarboxylative cross coupling with different catalyst systems:



28 **4**

[activation] [arylation]

	[Ni]/Bphen $ArB(OH)_2$	[Ni]/dtbbpy $ArZnCl$	[Fe]/dppbz Ar_2Zn	[Fe]/DMPU $ArMgBr$
 isolated	<1	3	4	<1
 isolated	<1	20	11	<1
 in situ	<1	<1	<1	<1
 in situ	<1	<1	1	<1

See Ref 16 for detailed reaction conditions.

Ref: 17

isolated NHPI ester (**27**)

3 eq. $ArZnCl$
10 mol% $CoBr_2$
DMI/THF, rt, 12 h

<1

Ref: 18

isolated TCNHPI ester (**20**)

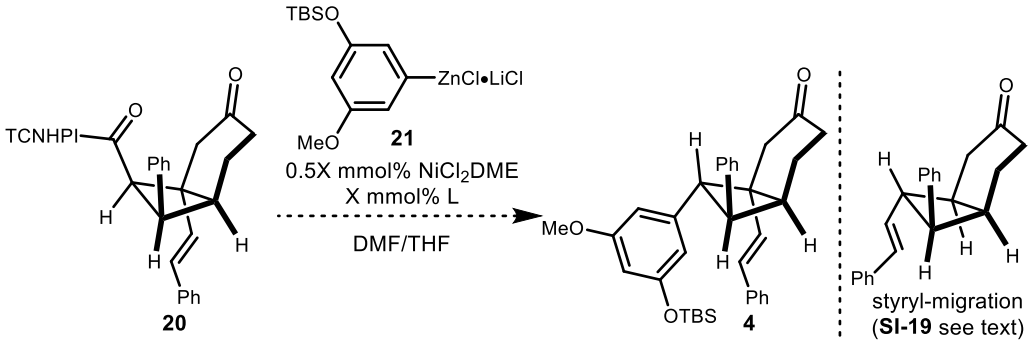
2 eq. Ar_2Zn
10 mol% $Ni(dpm)_2 \cdot 2H_2O$
DMI/THF, rt, 12 h

<1

color code (%)	<1	1-5	5-15	>15

Reactions were run on 0.05 mmol scale.
Yields were determined by NMR after semi-pufication by FCC, using CH_2Br_2 as internal standard.
For all above reaction conditions, hydrolysis of TCNHPI or NHPI esters were observed.

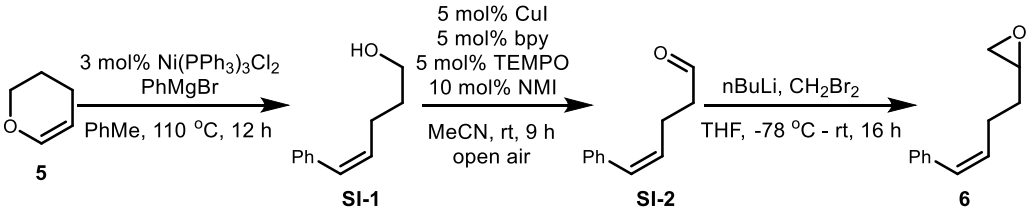
Optimizations of decarboxylative Negishi coupling with isolated TCNHPI ester:



L	[Zn] (0.25 M)	T	yield (%)[a]
40 mol% dtbbpy	3 eq.	rt	20
40 mol% bpy	3 eq.	rt	<1
40 mol% 4,7-diOMebpy	3 eq.	rt	16
40 mol% Phen	3 eq.	rt	8
40 mol% 4,7-diOMePhen	3 eq.	rt	14 + 28 migration
40 mol% BPhen	3 eq.	rt	37
40 mol% 2,9-diMeBphen	3 eq.	rt	25 + 13 migration
40 mol% BPhen	3 eq.	0	<1
40 mol% BPhen	3 eq.	60	26
40 mol% BPhen	6 eq.[b]	rt	14
80 mol% BPhen	3 eq.	rt	40
200 mol% BPhen	3 eq.	rt	40

Reactions were run on 0.025 mmol scale
a: After semi-purification by FCC, using CH_2Br_2 as internal standard
b: 0.5 M
All reactions delivered complex mixtures. TCNHPI ester hydrolysis and styryl migration are the only two products we could identify and isolate.

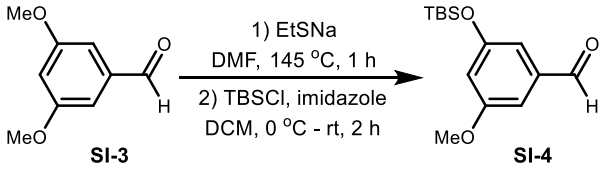
Experimental Procedures:



(*Z*)-2-(4-Phenylbut-3-en-1-yl)oxirane (6): Prepared according to a modified procedure of known literature.[19] A flame-dried 1 L round bottom flask equipped with a stir bar was cooled under vacuum. After backfilled with N_2, dichlorobis(triphenylphosphine)nickel(II) (2.9 g, 4.5 mmol, 0.030 eq.) was added. The flask was evacuated/backfilled with N_2 (x 3) and capped with a septum. Then PhMe (300 mL) was added. To the stirring suspension was added phenylmagnesium bromide (3.00 M in Et_2O, 50.0 mL, 150 mmol, 1.00 eq.) and 3,4-dihydro-2H-pyran **5** (41.0 mL, 450 mmol, 3.00 eq.) sequentially at room temperature. Then the septum was replaced with a reflux condenser and the reaction was heated to 110 °C in an oil bath for 12 h. After cooled down to room temperature, the reaction was quenched with saturated NH_4Cl solution (150 mL). The aqueous layer was extracted with Et_2O (3 x 100 mL). The combined organic layers were washed with brine (300 mL), dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The residue was purified by FCC (Hex : EtOAc = 9 : 1 to 4 : 1) to afford alcohol **SI-1** (19.7 g, 81% yield) as pale yellow oil. All spectral data matched that reported in the literature.[20]

To a 1 L round bottom flask charged with alcohol **SI-1** (16.7 g, 100 mmol, 1.00 eq.) was added MeCN (400 mL). Copper iodide (0.95 g, 5.0 mmol, 0.050 eq.), bpy (0.78 g, 5.0 mmol, 0.050 eq.), TEMPO (0.78 g, 5.0 mmol, 0.050 eq.) and NMI (0.80 mL, 10 mmol, 0.10 eq.) were added sequentially to the solution at room temperature. The reaction was stirred at the same temperature for 9 h without capping, with color changed from dark red to green. Then the mixture was concentrated by rotary evaporation. The residue was filtered through a pad of silica and washed with 9 : 1 Hex : EtOAc (300 mL). The filtrate was concentrated by rotary evaporation to afford crude aldehyde **SI-2** (15.4 g, 92% yield), which was used directly in next reaction without further purification.

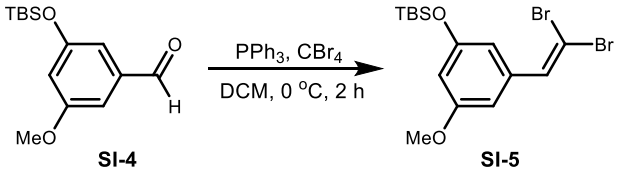
A flame-dried 1 L round bottom flask equipped with a stir bar was cooled under vacuum. After evacuated/backfilled with N_2 (x 3) and capped with a septum, aldehyde **SI-2** (15.4 g, 95.0 mmol, 1.00 eq.) was added followed by THF (300 mL). To the stirring solution was added dibromomethane (8.00 mL, 114 mmol, 1.20 eq.) at room temperature. Then the solution was cooled to -78 °C in a dry ice/acetone and *n*-butyllithium (2.50 M in hexanes, 40.0 mL, 100 mmol, 1.05 eq.) was added slowly over 5 minutes. The reaction was naturally warmed to room temperature over 16 h and quenched with saturated NH_4Cl solution (150 mL). The aqueous layer was extracted with Et_2O (3 x 100 mL). The combined organic layers were washed with brine (200 mL), dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The residue was purified by FCC (Hex : EtOAc = 30 : 1) to afford epoxide **6** (10.8 g, 65% yield) as pale yellow oil. All spectral data matched that reported in the literature.[19]



SI-3 SI-4

3-((*tert*-Butyldimethylsilyl)oxy)-5-methoxybenzaldehyde (SI-4): Demethylation was adapted from the literature procedure:[21] A flame-dried 1 L round bottom flask equipped with a stir bar was cooled under vacuum. After evacuated/backfilled with N_2 (x 3) and capped with a septum, ethanethiol (20.0 mL, 280 mmol, 3.50 eq.) was added followed by DMF (240 mL). To the stirring solution was added sodium hydride (9.60 g, 240 mmol, 3.00 eq.) at 0 °C in an ice/water bath. When hydrogen bubble evolution ceased (~ 15 min), a solution of 3,5-dimethoxybezaldehyde **SI-3** (13.3 g, 80.0 mmol, 1.00 eq.) in DMF (40 mL) was added at the same temperature. Then the septum was replaced with a reflux condenser and the reaction was heated to 145 °C for 1 h. After cooled down to room temperature, brine (200 mL), formaldehyde (40% v/v in H_2O, 40 mL), acetic acid (60 mL) were added sequentially. The mixture was extracted with EtOAc (3 x 150 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The resulting crude phenol was used directly into next reaction without further purification.

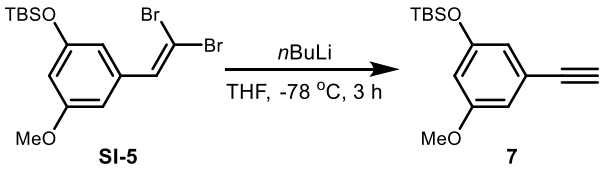
A flame-dried 500 mL round bottom flask equipped with a stir bar was cooled under vacuum. After evacuated/backfilled with N_2 (x 3) and capped with a septum, above crude phenol (assuming 80 mmol, 1.0 eq.) was added followed by DCM (160 mL). To the stirring solution was added imidazole (8.12 g, 120 mmol, 1.50 eq.) and TBSCl (13.6 g, 90.0 mmol, 1.10 eq.) sequentially at 0 °C in an ice/water bath. Then ice bath was removed and the reaction was stirred at room temperature for 2 h and quenched with saturated NH_4Cl solution (50 mL). The aqueous layer was extracted with DCM (3 x 50 mL). The organic layers were washed with brine (100 mL), dried over anhydrous MgSO4, filtered and concentrated by rotary evaporation. The residue was purified by FCC (Hex : EtOAc = 19 : 1) to afford aldehyde **SI-4** (10.7 g, 50 % yield for 2 steps) as pale yellow oil. All spectral data matched that reported in the literature.[22]



SI-4 SI-5

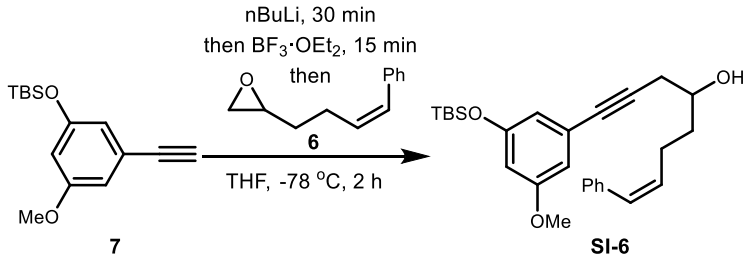
***tert*-Butyl(3-(2,2-dibromovinyl)-5-methoxyphenoxy)dimethylsilane (SI-5):** A flame-dried 500 mL round bottom flask equipped with a stir bar was cooled under vacuum. After evacuated/backfilled with N_2 (x 3) and capped with a septum, aldehyde **SI-4** (10.7 g, 40.0 mmol, 1.00 eq.) and tetrabromomethane (27 g, 80 mmol, 2.0 eq.) were added followed by DCM (135 mL). To the stirring solution was added triphenylphosphine (4 x 10.5 g, 160 mmol, 4.00 eq.) every 5 min at 0 °C in an ice/water bath. The mixture was stirred at the same temperature for 2 h and quenched with H_2O (50 mL). The aqueous layer was extracted with DCM (3 x 50 mL). The combined organic layers were washed with brine (100 mL), dried over anhydrous $MgSO_4$, filtered

and concentrated by rotary evaporation. The residue was purified by FCC (Hex : EtOAc = 19 : 1) to afford vinyl bromide **SI-5** (15.2 g, 91% yield) as colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (s, 1H), 6.68 (s, 1H), 6.65 (s, 1H), 6.39 (s, 1H) 3.78 (s, 3H), 0.98 (s, 9H), 0.21 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 160.6, 156.8, 136.9, 112.7, 107.2, 106.8, 89.8, 55.5, 25.8, 18.3, -4.2. (Vinyl carbon attached to two bromine atoms was not detected).
IR: 2955 (m), 2885 (m), 1560 (s), 1461 (m), 1161 (s), 837 (s).
HRMS (EI): Calculated for $C_{15}H_{22}Br_2O_2Si$ [M+]: 419.9756. Found: 419.9713.



SI-5 **7**

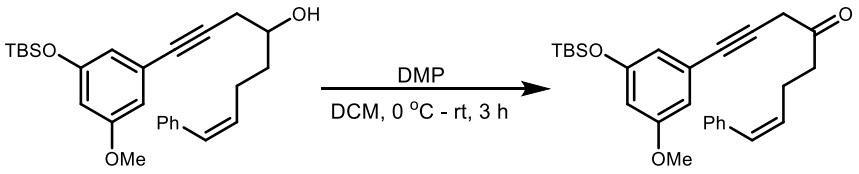
***tert*-Butyl(3-ethynyl-5-methoxyphenoxy)dimethylsilane (7):** A flame-dried 250 mL round bottom flask equipped with a stir bar was cooled under vacuum. After evacuated/backfilled with N_2 (x 3) and capped with a septum, vinyl bromide **SI-5** (15.2 g, 36.0 mmol, 1.00 eq.) was added followed by THF (120 mL). To the stirring solution was added *n*BuLi (2.40 M in hexanes, 37.5 mL, 90.0 mmol, 2.50 eq.) slowly (~ 5 min) at -78 °C in a dry ice/acetone bath. The reaction was stirred at the same temperature for 3 h and quenched with saturated NH_4Cl solution (50 mL). After warmed to room temperature, the aqueous layer was extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with brine (100 mL), dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The residue was purified by FCC (Hex : EtOAc = 19 : 1) to afford alkyne **7** (7.54 g, 80% yield) as pale yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.65 (s, 1H), 6.59 (s, 1H), 6.41 (s, 1H), 3.77 (s, 3H), 3.02 (s, 1H), 0.98 (s, 9H), 0.20 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 160.5, 156.7, 123.3, 116.7, 110.5, 108.2, 83.7, 76.8, 55.5, 25.8, 18.3, -4.3.
IR: 3293 (m), 2955 (m), 2858 (m), 1585 (s), 1462 (m), 1161 (s), 835 (s).
HRMS (EI): Calculated for $C_{15}H_{22}O_2Si$ [M+]: 262.1389. Found: 262.1362.



7 **SI-6**

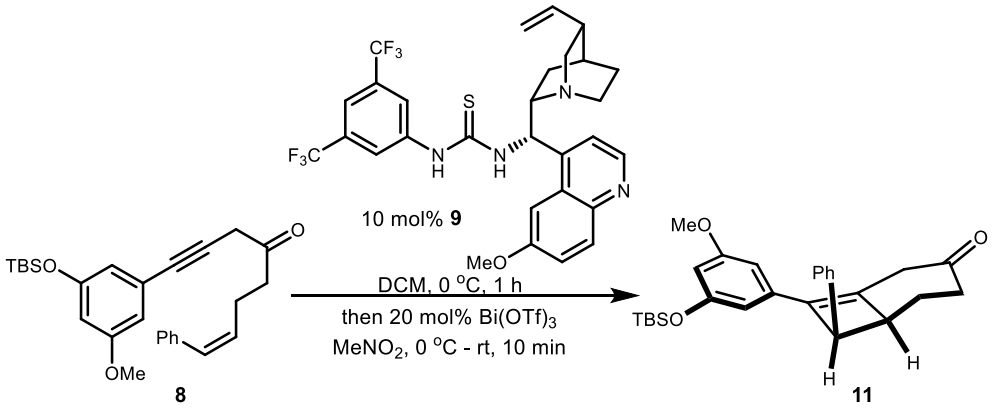
(*Z*)-1-(3-((*tert*-Butyldimethylsilyl)oxy)-5-methoxyphenyl)-8-phenyloct-7-en-1-yn-4-ol (SI-6): A flame-dried 100 mL round bottom flask equipped with a stir bar was cooled under vacuum. After evacuated/backfilled with N_2 (x 3) and capped with a septum, alkyne **7** (682 mg, 2.60 mmol, 1.20 eq.) was added followed by THF (13 mL). To the stirring solution was added *n*-butyllithium (2.28 M in hexanes, 1.14 mL, 2.60 mmol, 1.20 eq.) dropwise at -78 °C in a dry ice/acetone bath and the reaction was stirred for 30 min before boron trifluoride diethyl etherate (0.32 mL, 2.6 mmol, 1.2 eq.) was

added. After 15 min, a solution of epoxide **6** (374 mg, 2.14 mmol, 1.00 eq.) in THF (2 mL) was added and the reaction was stirred for another 2 h at the same temperature. Then the reaction was warmed up to room temperature and quenched with saturated NH_4Cl solution (10 mL). The aqueous layer was extracted with Et_2O (3 x 10ml). The combined organic layers were washed with brine (20 mL), dried over anhydrous $MgSO_4$ and concentrated by rotary evaporation. The residue was purified by FCC (Hex : EtOAc = 30 : 1 to 4 : 1) to afford alcohol **SI-6** (700 mg, 75% yield) as pale yellow oil.
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 – 7.30 (m, 4H), 7.24 (t, *J* = 6.7 Hz, 1H), 6.62 (s, 1H), 6.57 (s, 1H), 6.49 (d, *J* = 11.6 Hz, 1H), 6.41 (s, 1H), 3.88 (s, 1H), 3.76 (s, 3H), 2.64 (dd, *J* = 16.8, 5.0 Hz, 1H), 2.60 – 2.48 (m, 3H), 2.25 (s, 1H), 1.84 – 1.73 (m, 2H), 1.02 (s, 9H), 0.24 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 160.4, 156.5, 137.5, 132.0, 129.6, 128.8, 128.2, 126.7, 124.6, 116.2, 110.0, 107.3, 85.8, 83.1, 69.7, 55.3, 36.5, 28.4, 25.7, 24.9, 18.2, -4.4.
IR: 3402 (br), 3008 (m), 2857 (m), 1582 (s), 1462 (m), 1156 (s), 831 (s).
HRMS (EI): Calculated for $C_{27}H_{37}O_3Si$ [M+H]: 437.2506. Found: 437.2509.

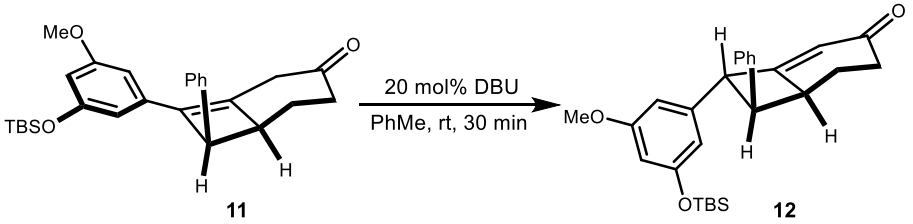


SI-6 **8**

(*Z*)-1-(3-((*tert*-Butyldimethylsilyl)oxy)-5-methoxyphenyl)-8-phenyloct-7-en-1-yn-4-one (8): A 25 mL round bottom flask equipped with a stir bar was charged with alcohol **SI-6** (262 mg, 0.600 mmol, 1.00 eq.). After evacuated/backfilled with N_2 (x 3) and capped with a septum, DCM (6 mL) was added. To the stirring solution was added Dess-Martin periodinane (417 mg, 0.900 mmol, 1.50 eq.) at 0 °C in an ice/water bath. Then ice bath was removed and the reaction was stirred at room temperature for 3 h before quenched with 1 M NaOH solution (6 mL). The aqueous layer was extracted with Et_2O (3 x 5 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation to afford crude ketone **8** (255 mg, 98% yield), which was used directly into next reaction without further purification.
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 – 7.18 (m, 5H), 6.59 (s, 1H), 6.53 (s, 1H), 6.47 (d, *J* = 11.6 Hz, 1H), 6.39 (s, 1H), 5.63 (dt, *J* = 11.6, 7.2 Hz, 1H), 3.76 (s, 3H), 3.45 (s, 2H), 2.83 (t, *J* = 7.3 Hz, 2H), 2.67 (q, *J* = 7.3 Hz, 2H), 0.99 (s, 9H), 0.21 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 203.8, 160.5, 156.7, 137.3, 130.5, 130.3, 128.8, 128.4, 128.0, 126.9, 124.2, 116.2, 110.1, 107.6, 84.8, 81.6, 77.5, 77.2, 76.8, 55.5, 41.6, 34.9, 25.8, 22.9, 18.3, -4.3.
IR: 3008 (m), 2857 (m), 1725 (s), 1586 (s), 1447 (m), 1159 (s), 835 (s).
HRMS (EI): Calculated for $C_{27}H_{35}O_3Si$ [M+H]: 435.2350. Found: 435.2355.



(6*S*,7*S*)-8-(3-((*tert*-Butyldimethylsilyl)oxy)-5-methoxyphenyl)-7-phenylbicyclo-[4.2.0]oct-1(8)-en-3-one (11): A flame-dried 25 mL round bottom flask equipped with a stir bar was cooled under vacuum. After evacuated/backfilled with N_2 (x 3) and capped with a septum, ketone **8** (217 mg, 0.500 mmol, 1.00 eq.) was added followed by DCM (1 mL). To the stirring solution was added thiourea catalyst **9** (29.7 mg, 0.0500 mmol, 0.100 eq.) at 0 °C in an ice/water bath and the reaction was stirred for 1 h at the same temperature. Then the mixture was diluted with $MeNO_2$ (2.5 mL) and bismuth triflate (656 mg, 1.00 mmol, 0.200 eq.) was added also at 0 °C. After addition, the ice bath was immediately replaced with a room temperature water bath and the reaction was stirred vigorously for 10 min before it was quenched with saturated NH_4Cl solution (2 mL). The aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The residue was purified by FCC (Hex : EtOAc = 15:1 to 9:1) to afford cyclobutene **11** (75 mg, 35% yield, >20:1 dr) as yellow solid.
(Note: ~50 % of Cyclobutene decomposition product was observed left in -20 °C freezer for 5 days. It should be used directly after preparation.)
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.26 – 7.22 (m, 2H), 7.18 (t, *J* = 6.9 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 6.42 (s, 1H), 6.27 (s, 1H), 6.25 (s, 1H), 4.43 (t, *J* = 3.9 Hz, 2H), 3.74 – 3.66 (m, 4H), 3.36 (d, *J* = 17.6 Hz, 1H), 3.20 – 3.11 (m, 1H), 2.51 – 2.35 (m, 1H), 1.64 – 1.51 (m, 1H), 1.21 (qd, *J* = 13.1, 4.3 Hz, 1H), 0.90 (s, 9H), 0.05 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 207.6, 160.8, 156.9, 140.5, 139.7, 136.7, 135.6, 128.5, 128.2, 126.5, 110.9, 105.6, 105.2, 55.3, 47.8, 44.5, 42.3, 40.7, 25.8, 25.1, 18.3, -4.3, -4.4.
IR： 3025 (m), 2885 (m), 1718 (s), 1665 (w), 1587 (s), 1158 (s), 728 (s).
HRMS (ESI): Calculated for $C_{27}H_{35}O_3Si$ $[M + H]^+$: 435.2350. Found: 435.2349.
Optical rotation: $[\alpha]_D^{20}$: -96.6 (c = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 98 : 2 er.
Racemic sample was obtained following the same procedure except for using 0.1 eq. Et_3N instead of thiourea catalyst **9**. The enantiomeric purity was established by HPLC analysis using a chiral column (Chiralpak IA PG024, 22 °C, 0.5 mL/min, 99 : 1 Hexane : Isopropanol, 254 nm, t_{major} = 17.986 min, t_{minor} = 13.555 min). Absolute stereochemistry was determined according to published literature.[14] Relative stereochemistry was determined by analysis of relevant NOE interactions (see Supporting Information Spectrums).
Melting point: 98 °C – 100 °C.



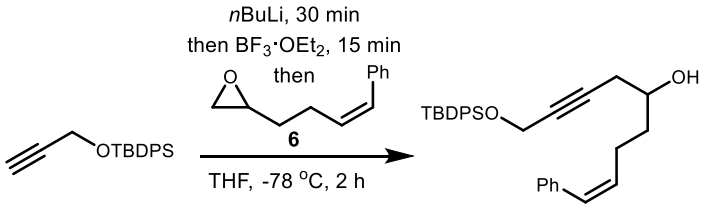
11 12

(6*S*,7*R*,8*R*)-8-(3-((*tert*-Butyldimethylsilyl)oxy)-5-methoxyphenyl)-7-phenyl-bicyclo[4.2.0]oct-1-en-3-one (12): A flame-dried 4 mL vial equipped with a stir bar was cooled under vacuum. After evacuated/backfilled with N_2 (x 3) and capped with a septum, a solution of cyclobutene **11** (60 mg, 0.14 mmol, 1.0 eq.) in PhMe (1.5 mL) was added followed by DBU (3.7 μL, 0.028, 0.20 eq.) at room temperature. The reaction was stirred at the same temperature for 30 min and quenched with saturated NH_4Cl (1 mL). The aqueous layer was extracted with Et_2O (3 x 1 mL). The combined organic layers were washed with brine (2 mL), dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The residue was purified by FCC (Hex : EtOAc = 9 : 1) to afford enone **12** (60 mg, quant. yield, >20:1 dr) as 1 : 1 inseparable mixture with **11**.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.25 (m, 3H), 6.46 (s, 1H), 6.38 (s, 1H), 6.32 (s, 1H), 6.12 (s, 1H), 4.48 (s, 1H), 3.88 (dd, *J* = 10.5, 3.2 Hz, 1H), 3.89 – 3.87 (m, 4H), 2.44 – 2.33 (m, 2H), 1.64 (dd, *J* = 12.7, 6.3 Hz, 1H), 1.53 – 1.41 (m, 1H), 0.99 (s, 9H), 0.21 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 199.0, 172.5, 161.2, 157.4, 142.8, 139.4, 128.8, 128.0, 127.1, 122.3, 111.2, 105.8, 104.5, 55.5, 54.5, 49.9, 45.4, 37.6, 25.8, 25.6, 18.4, -4.2, -4.2.

IR, HRMS and optical rotation were not collected due to the compound is a mixture. Relative stereochemistry was determined by analysis of relevant NOE interactions (See Supporting Information Spectrums).



SI-7 SI-8

(*Z*)-9-((*tert*-Butyldiphenylsilyl)oxy)-1-phenylnon-1-en-7-yn-5-ol (SI-8): A flame-dried 250 mL round bottom flask equipped with a stir bar was cooled under vacuum. After backfilled with N_2, *tert*-butyldiphenyl(prop-2-yn-1-yloxy)silane **SI-7** (17.7 g, 1.50 eq, 60.0 mmol.) was added. The flask was evacuated/backfilled with N_2 (x 3) and capped with a septum. Then THF (120 mL) was added. To the stirring solution was added *n*-butyllithium (2.5 M in hexane, 24 mL, 60 mmol, 1.5 eq.) dropwise at -78 °C in a dry ice/acetone bath and the reaction was stirred for 30 min before boron trifluoride diethyl etherate (7.4 mL, 60 mmol, 1.5 eq.) was added. After 15 min, a solution of epoxide **6** (6.77 g, 39.0 mmol, 1.0 eq.) in THF (40 mL) was added and the reaction was stirred for another 2 h at the same temperature. Then the reaction was warmed up to

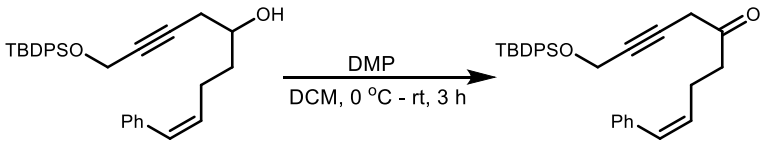
room temperature and quenched with saturated NH_4Cl solution (50 mL). The aqueous layer was extracted with Et_2O (3 x 100 mL). The combined organic layers were washed with brine (250 mL), dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The residue was purified by FCC (Hex : EtOAc = 30 : 1 to 4 : 1) to afford alcohol **SI-8** (15 g, 82% yield) as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.71 (d, *J* = 6.7 Hz, 4H), 7.45 – 7.27 (m, 10H), 6.45 (d, *J* = 11.6 Hz, 1H), 5.64 (dt, *J* = 11.7, 7.3 Hz, 1H), 4.34 (s, 2H), 3.66 (h, *J* = 6.0 Hz, 1H), 2.50 – 2.33 (m, 4H), 2.26 (dd, *J* = 16.6, 6.7 Hz, 1H), 1.70 (d, *J* = 5.3 Hz, 1H), 1.61 (d, *J* = 7.5 Hz, 2H), 1.06 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 137.6, 135.7, 133.4, 133.4, 132.1, 129.9, 129.6, 128.9, 128.3, 127.8, 127.8, 126.8, 81.8, 81.4, 69.6, 53.0, 36.4, 27.9, 26.9, 25.0, 19.3.

IR (neat): 3435 (br), 3012 (m), 2857 (m), 2362 (w), 1497 (m), 1111 (s)

HRMS (EI): Calculated for $C_{27}H_{27}O_2Si$ $[M - C_4H_9]^+$: 411.1780. Found: 411.1776.



SI-8 **17**

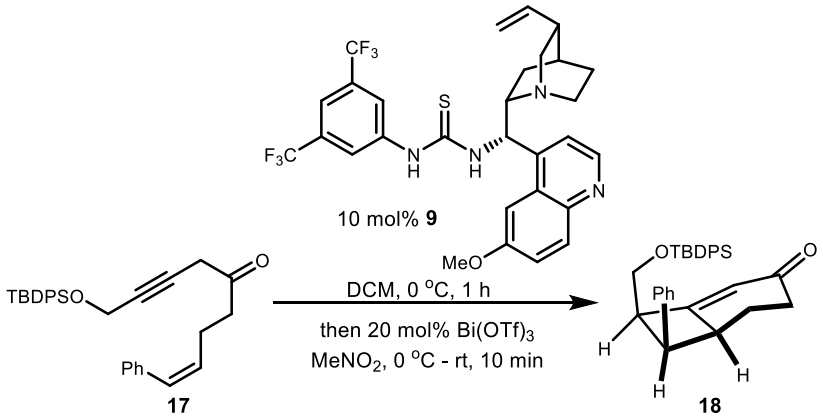
(*Z*)-9-((*tert*-Butyldiphenylsilyl)oxy)-1-phenylnon-1-en-7-yn-5-one (17): A 250 mL round bottom flask equipped with a stir bar was charged with alcohol **SI-8** (14.1 g, 30.0 mmol, 1.00 eq.). After evacuated/backfilled with N_2 (x 3) and capped with a septum, DCM (150 mL) was added. To the stirring solution was added Dess-Martin periodinane (20.8 g, 45.0 mmol, 1.50 eq.) at 0 °C in an ice/water bath. Then ice bath was removed and the reaction was stirred for 3 h before quenched with 1 M NaOH solution (200 mL). The aqueous layer was extracted with Et_2O (3 x 150 mL). The combined organic layers were washed with brine (300 mL), dried over anhydrous $MgSO_4$ and concentrated by rotary evaporation to afford crude ketone **17** (13.8 g, 98% yield), which was directly used to next reaction without further purification.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.71 (d, *J* = 6.6 Hz, 4H), 7.43 (t, *J* = 7.3 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 4H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 7.4 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 6.46 (d, *J* = 11.6 Hz, 1H), 5.58 (dt, *J* = 11.6, 7.2 Hz, 1H), 4.36 (s, 2H), 3.19 (s, 2H), 2.68 (t, *J* = 7.3 Hz, 2H), 2.60 (q, *J* = 7.3 Hz, 2H), 1.07 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 203.9, 137.3, 135.7, 133.3, 130.5, 130.2, 129.9, 128.8, 128.4, 127.8, 126.9, 83.1, 77.9, 53.0, 41.3, 34.3, 26.8, 22.8, 19.3.

IR (neat): 3070 (m), 2857 (m), 1725 (s), 1427 (m), 1112 (s)

HRMS (EI): Calculated for $C_{27}H_{25}O_2Si$ $[M - C_4H_9]^+$: 409.1618. Found: 409.1622



(6*S*,7*R*,8*R*)-8-(((*tert*-Butyldiphenylsilyl)oxy)methyl)-7-phenylbicyclo[4.2.0]oct-1-en-3-one (18): A flame-dried 250 mL round bottom flask equipped with a stir bar was cooled under vacuum. After evacuated/backfilled with N_2 (x 3) and capped with a septum, ketone **17** (4.66 g, 10.0 mmol, 1.00 eq.) was added followed by DCM (20 mL). To the stirring solution was added thiourea catalyst **9** (594 mg, 1.00 mmol, 0.100 eq.) at 0 °C in an ice/water bath and stirred for 1 h at the same temperature. Then the reaction was diluted with $MeNO_2$ (50 mL) and bismuth triflate (1.32 g, 2.00 mmol, 0.200 eq.) was added also at 0 °C. After addition, the ice bath was immediately transferred into a room temperature water bath and the reaction was vigorously stirred for 10 min before it was quenched with saturated NH_4Cl solution (40 mL). The aqueous layer was extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with brine (100 mL), dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The residue was purified by FCC (Hex : EtOAc = 9:1 to 4:1) to afford bicyclic enone **18** (3.03 g, 65% yield, >20:1 dr) as yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.0 Hz, 1H), 7.37 - 7.27 (d, *J* = 7.1 Hz, 10H), 7.19 – 7.15 (m, 2H), 5.87 (s, 1H), 3.95 (d, *J* = 5.3 Hz, 2H), 3.87 (dd, *J* = 10.8, 5.2 Hz, 1H), 3.68 (dd, *J* = 10.4, 6.9 Hz, 1H), 3.62 – 3.50 (m, 1H), 2.42 (dd, *J* = 13.7, 4.5 Hz, 2H), 1.92 (ddt, *J* = 18.5, 12.9, 5.8 Hz, 1H), 1.70 – 1.60 (m, 1H), 0.93 (s, 9H).

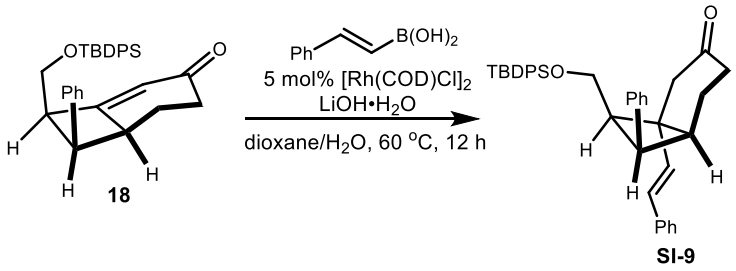
^{13}C NMR (126 MHz, $CDCl_3$): δ 199.0, 174.3, 137.0, 135.6, 135.5, 133.4, 133.2, 129.9, 129.8, 129.7, 128.2, 127.8, 127.7, 127.0, 117.3, 60.3, 50.2, 44.6, 43.8, 37.6, 26.8, 24.3, 19.1.

IR: 3070 (w), 2857 (m), 1659 (s), 1427 (m), 1025 (s)

HRMS (ESI): Calculated for $C_{31}H_{42}O_2SiNa$ $[M + Na]^+$: 489.2220. Found: 489.2219.

Optical rotation: $[\alpha]_D^{20}$: +61.7 (c = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 95.5 : 4.5 er.

Racemic sample was obtained following the same procedure except for using 0.1 eq. Et_3N instead of thiourea catalyst **9**. The enantiomeric purity was established by HPLC analysis using a chiral column (Chiralpak IA PG024, 22 °C, 0.5 mL/min, 98 : 2 Hexane : Isopropanol, 254 nm, t_{major} = 23.799 min, t_{minor} = 16.252 min). Absolute stereochemistry was determined according to published literature.[14] Relative stereochemistry was determined by analysis of relevant NOE interactions (see Supporting Information Spectrums).



(1*R*,6*S*,7*R*,8*R*)-8-(((*tert*-Butyldiphenylsilyl)oxy)methyl)-7-phenyl-1-((*E*)-styryl) bicyclo[4.2.0] octan-3-one (SI-9): A flame-dried 100 mL round bottom flask equipped with a stir bar was cooled under vacuum. After backfilled with N_2, enone **18** (4.6 g, 10 mmol, 1.0 eq.), *E*-phenylethenylboronic acid (1.8 g, 12 mmol, 1.2 eq.) and lithium hydroxide monohydrate (1.2 g, 30 mmol, 3.0 eq.) were added. The flask was then evacuated/backfilled N_2 (x 3), capped with a stopper and transferred into glovebox. Chloro(1,5-cyclooctadiene)rhodium(I) dimer (0.12 g, 0.25 mmol, 0.025 eq.) was added in glovebox. Then the flask was moved out and the stopper was quickly replaced with a septum. Dioxane (50 mL) and degassed H_2O (5 mL) were added. The reaction was stirred at 60 °C in an oil bath for 12 h. After cooled down to room temperature, it was quenched with 1 M HCl solution (30 mL). The aqueous layer was extracted with Et_2O (3 x 30 mL). The combined organic layers were washed with H_2O (30 mL), saturated $NaHCO_3$ (30 mL) and brine (50 mL) successively, dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The crude ketone **SI-9** was used directly into next reaction without further purification. A small amount of product (~50 mg) was purified by FCC (Hex : EtOAc = 20:1 to 4:1) for characterization.

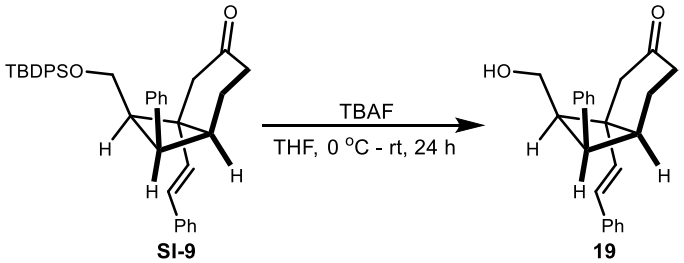
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62 (dd, *J* = 23.6, 7.2 Hz, 4H), 7.47 – 7.16 (m, 14H), 7.12 (d, *J* = 6.9 Hz, 2H), δ 6.53 (d, *J* = 16.1 Hz, 1H), 6.49 (d, *J* = 16.1 Hz, 1H).4.14 (q, *J* = 9.9, 9.0 Hz, 2H), 3.88 (dd, *J* = 10.9, 5.1 Hz, 1H), 3.24 – 3.14 (m, 1H), 3.12 (d, *J* = 15.5 Hz, 1H), 2.99 (q, *J* = 10.4, 9.7 Hz, 1H), 2.60 (d, *J* = 15.4 Hz, 1H), 2.40 (d, *J* = 18.4 Hz, 1H), 2.16 – 2.05 (m, 1H), 1.97 (q, *J* = 13.7, 12.1 Hz, 1H), 1.87 – 1.78 (m, 1H), 1.03 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 212.2, 138.9, 138.8, 137.2, 135.7, 133.6, 133.5, 129.9, 129.8, 129.4, 128.7, 128.3, 127.8, 127.8, 127.4, 126.8, 126.4, 126.3, 62.3, 48.6, 42.7, 42.2, 41.3, 40.6, 37.6, 26.9, 22.0, 19.2.

IR: 3069 (w), 2857 (m), 1714 (s), 1427 (m), 1027 (s)

HRMS (EI): Calculated for $C_{35}H_{33}O_2Si$ $[M - C_4H_9]^+$: 513.2244. Found: 513.2246.

Optical rotation: $[\alpha]_D^{20}$: +44.0 (c = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 95.5 : 4.5 er.



(1*R*,6*S*,7*R*,8*R*)-8-(Hydroxymethyl)-7-phenyl-1-((*E*)-styryl)bicyclo[4.2.0]octan-3-one (19): A 250 mL round bottom flask equipped with a stir bar was charged with above crude ketone **SI-9** (assuming 30 mmol for three combined batches, 1.0 eq.). After evacuated/backfilled with N_2 (x 3) and capped with a septum, THF (150 mL) was added followed by TBAF (1.0 M in THF, 36 mL, 36 mmol, 1.2 eq) at 0 °C in an ice bath. Then ice bath was removed and the mixture was stirred at room temperature for 24 h. The reaction was quenched with saturated NH_4Cl solution (100 mL). The aqueous layer was extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with brine (100 mL), dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The residue was purified by FCC (Hex : EtOAc = 4 : 1 to 2 : 1) to afford alcohol **19** (8 g, 73% yield for 2 steps, >20 : 1 dr) as yellow oil (with ~ 10% inseparable impurity).

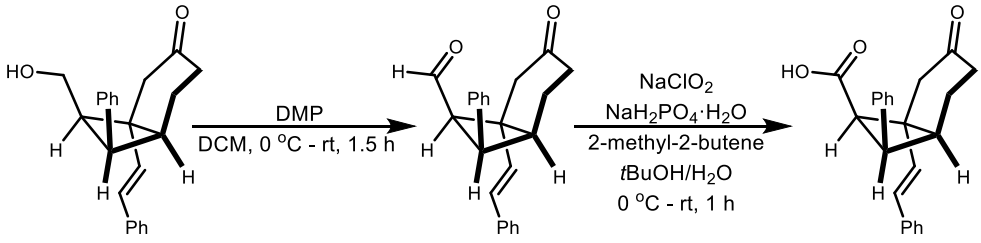
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43 – 7.20 (m, 10H), 6.49 (d, *J* = 16.0 Hz, 1H), 6.45 (d, *J* = 15.9 Hz, 1H), 4.21 (t, *J* = 10.0 Hz, 1H), 4.05 (t, *J* = 10.2 Hz, 1H), 3.94 (dd, *J* = 10.6, 6.1 Hz, 1H), 3.13 (m, 2H), 3.03 – 2.90 (m, 1H), 2.53 (d, *J* = 15.2 Hz, 1H), 2.42 (d, *J* = 17.7 Hz, 1H), 2.12 (dq, *J* = 43.4, 14.5, 14.1 Hz, 2H), 1.93 – 1.84 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 212.0, 139.0, 138.3, 137.0, 129.3, 128.7, 128.6, 127.5, 126.7, 126.6, 126.4, 61.1, 48.6, 42.3, 41.9, 41.8, 40.3, 37.6, 22.0.

IR： 3411 (br), 2937 (m), 1709 (s), 1494 (m), 1076 (s)

HRMS (ESI): Calculated for $C_{23}H_{24}O_2Na$ $[M+Na]^+$: 355.1669. Found: 355.1671.

Optical rotation: $[\alpha]_D^{20}$: +10.6 (c = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 95.5 : 4.5 er.



19 **SI-10** **28**

(1*S*,6*R*,7*R*,8*R*)-4-Oxo-8-phenyl-6-((*E*)-styryl)bicyclo[4.2.0]octane-7-carboxylic acid (28): A 100 mL round bottom flask equipped with a stir bar was charged with alcohol **19** (1.66 g, assuming 5.00 mmol, 1.00 eq., ~10 % impurity). After evacuated/backfilled with N_2 (x 3) and capped with a septum, DCM (50 mL) was added. To the stirring solution was added Dess-Martine Periodinane (2.90 g, 6.25 mmol, 1.25 eq) at 0 °C in an ice/water bath. Then ice bath was removed and the mixture was stirred at room temperature for 1.5 h. The reaction was quenched with 1M NaOH solution (30 mL). The aqueous layer was extracted with Et_2O (3 x 30 mL). The combined organic layers were washed with brine (50 mL), dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The crude aldehyde **SI-10** was used directly into next reaction without further purification.

(Note: Aldehyde decomposed upon silica gel purification.)

A 250 mL round bottom flask equipped with a stir bar was charged with above aldehyde **SI-10** (assuming 5 mmol, 1 eq.). Then *t*BuOH (50 mL) and 2-methyl-2-butene (10 mL) were added. The mixture was cooled to 0 °C in an ice/water bath and a solution of

sodium chloride (2.26 g, 25.0 mmol, 5.00 eq.) and sodium phosphate mono-basic monohydrate (3.45 g, 25.0 mmol, 5.00 eq.) in H_2O (25 mL) was added in one portion via syringe. Then ice bath was removed and the reaction was stirred at room temperature for 1 h. Brine (50 mL) was added to the solution. The aqueous layer was extracted with EtOAc (3 x 30 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The crude acid **28** was used directly into all following reactions without further purification. A small amount of product (~50 mg) was purified by FCC (Hex : EtOAc = 2 : 1) for characterization.

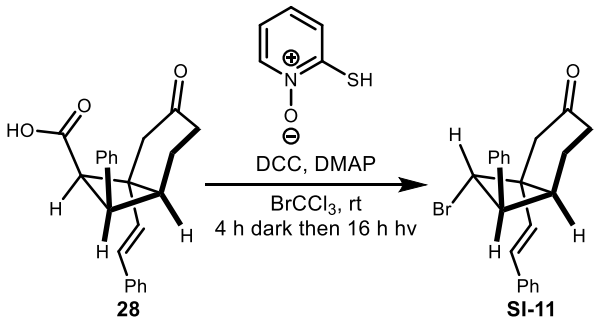
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 4H), 7.28 (dd, *J* = 6.4, 3.6 Hz, 2H), 7.21 (d, *J* = 7.5 Hz, 2H), 6.53 (d, *J* = 16.1 Hz, 1H), 6.45 (d, *J* = 16.1 Hz, 1H), 4.42 (t, *J* = 10.2 Hz, 1H), 3.91 (d, *J* = 10.7 Hz, 1H), 3.25 (d, *J* = 15.8 Hz, 1H), 3.08 (q, *J* = 10.2 Hz, 1H), 2.84 (d, *J* = 15.8 Hz, 1H), 2.35 (d, *J* = 18.1 Hz, 1H), 2.10 (ddd, *J* = 18.4, 14.1, 5.0 Hz, 1H), 1.94 (qd, *J* = 14.2, 3.8 Hz, 1H), 1.88 – 1.79 (m, 1H).

13C NMR (126 MHz, $CDCl_3$) δ 211.3, 177.1, 138.2, 136.6, 136.5, 128.8, 128.5, 128.3, 128.1, 127.9, 126.7, 126.6, 49.4, 43.7, 42.8, 41.6, 41.1, 37.2, 21.2.

IR: 3173 (br), 3025 (m), 2938 (m), 1698 (s), 1601 (w), 1225 (m), 731 (s).

HRMS: Calculated for $C_{23}H_{22}O_3Na$ $[M+Na]^+$: 369.1461. Found: 369.1462.

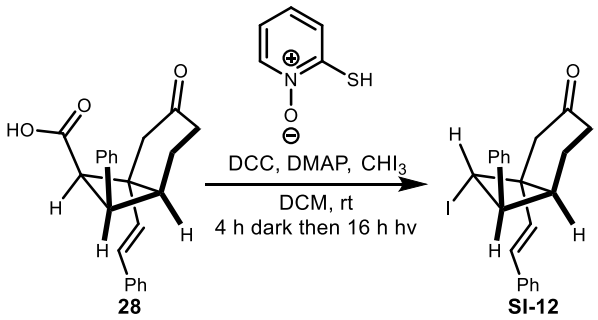
Optical rotation: $[\alpha]_D^{20}$: +22.8 (c = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 95.5 : 4.5 er.



(1*R*,6*S*,7*S*,8*S*)-8-Bromo-7-phenyl-1-((*E*)-styryl)bicyclo[4.2.0]octan-3-one (SI-11): A flame-dried 10 mL round bottom flask equipped with a stir bar was cooled under vacuum. After evacuated/backfilled with N_2 (x 3), wrapped with aluminum foil, and capped with a septum, a solution of crude acid **28** (assuming 0.4 mmol, 1 eq.) in bromotrichloromethane (4 mL) was added. Then 2-Mercaptopyridine *N*-oxide (76 mg, 0.60 mmol, 1.5 eq.), DCC (165 mg, 0.800 mmol, 2.00 eq.) and DMAP (49 mg, 0.40 mmol, 1.0 eq.) were added sequentially to the solution at room temperature. After 4 h, the aluminum foil was removed and the reaction was stirred for another 12 h in the presence of hood light. Then the mixture was filtered through a pad of Celite. The filtrate was concentrated by rotary evaporation and purified by FCC (Hex : EtOAc = 19 :1 to 9 : 1) to afford bromide **SI-11** (76 mg, 55% for three steps, >20 : 1 dr) as pale yellow oil.

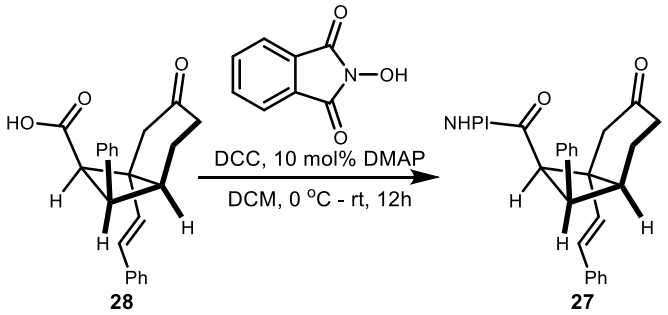
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.4 Hz, 2H), 7.38 (dt, *J* = 11.7, 7.6 Hz, 4H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 2H), 6.71 (d, *J* = 16.1 Hz, 1H), 6.53 (d, *J* = 16.1 Hz, 1H), 4.83 (d, *J* = 10.2 Hz, 1H), 4.24 (t, *J* = 10.3 Hz, 1H), 3.15 (ddd, *J*

= 10.3, 7.9, 6.0 Hz, 1H), 2.72 (d, *J* = 16.4 Hz, 1H), 2.68 (d, *J* = 16.4 Hz, 1H), 2.24 – 2.14 (m, 2H), 1.87 (dq, *J* = 12.8, 6.1 Hz, 1H), 1.78 (dq, *J* = 14.3, 7.7 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 210.2, 137.1, 136.8, 133.3, 129.2, 128.9, 128.8, 128.0, 127.0, 126.7, 126.6, 54.8, 48.8, 47.2, 45.8, 41.5, 37.4, 21.5.
IR: 3081 (m), 2919 (m), 1713 (s), 1600 (w), 1448 (m), 966 (m).
HRMS (ESI): Calculated for $C_{22}H_{22}OBr$ $[M + H]^+$: 381.0849. Found: 381.0841.
Optical rotation: $[\alpha]_D^{20}$: -43.8 (c = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 95.5 : 4.5 er. Relative stereochemistry was determined by analysis of relevant NOE interactions (see Supporting Information Spectrums).



28 **SI-12**

(1*R*,6*S*,7*S*,8*S*)-8-Iodo-7-phenyl-1-((*E*)-styryl)bicyclo[4.2.0]octan-3-one (SI-12): A flame-dried 10 mL round bottom flask equipped with a stir bar was cooled under vacuum. After evacuated/backfilled with N_2 (x 3), wrapped with aluminum foil, and capped with a septum, a solution of crude acid **28** (assuming 0.4 mmol, 1 eq.) in DCM (4 mL) was added. Then Iodoform (315 mg, 0.800 mmol, 2.00 eq.), 2-mercaptopyridine *N*-oxide (76 mg, 0.60 mmol, 1.5 eq.), DCC (165 mg, 0.800 mmol, 2.00 eq.) and DMAP (49 mg, 0.40 mmol, 1.0 eq.) were added sequentially to the solution at room temperature. After 4 h, the aluminum foil was removed and the reaction was stirred for another 12 h in the presence of hood light. Then the mixture was filtered through a pad of Celite. The filtrate was concentrated by rotary evaporation and purified by FCC (Hex : EtOAc = 19 : 1 to 9 : 1) to afford iodide **SI-12** (72 mg, 46% for three steps, >20 : 1 dr) as pale yellow oil.
(Note: Product was not very stable at room temperature. It should be used directly after preparation.)
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.5 Hz, 2H), 7.38 (q, *J* = 7.5 Hz, 4H), 7.29 (t, *J* = 7.3 Hz, 2H), 7.20 (d, *J* = 7.4 Hz, 2H), 6.62 (d, *J* = 16.1 Hz, 1H), 6.49 (d, *J* = 16.0 Hz, 1H), 4.89 (d, *J* = 10.6 Hz, 1H), 4.27 (t, *J* = 10.4 Hz, 1H), 3.10 (q, *J* = 8.2, 7.8 Hz, 1H), 2.63 (s, 2H), 2.20 (dtd, *J* = 32.0, 19.0, 16.0, 7.2 Hz, 2H), 1.82 (tq, *J* = 14.9, 7.7, 7.1 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 210.1, 137.1, 136.7, 136.5, 128.8, 128.8, 128.6, 128.0, 127.0, 126.7, 126.5, 48.9, 46.7, 44.8, 43.1, 37.3, 32.2, 21.6.
IR: 3082 (m), 2929 (m), 1710 (s), 1601 (w), 1448 (m), 965 (m).
HRMS (ESI): Calculated for $C_{22}H_{22}OI$ $[M + H]^+$: 381.0710. Found: 381.0707.
Optical rotation: $[\alpha]_D^{20}$: -76.0 (c = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 95.5 : 4.5 er. Relative stereochemistry was determined by analysis of relevant NOE interactions (see Supporting Information Spectrums).



1,3-Dioxoisoindolin-2-yl (1*S*,6*R*,7*R*,8*R*)-4-oxo-8-phenyl-6-((*E*)-styryl)bicyclo-[4.2.0]octane-7-carboxylate (27): A flame-dried 10 mL round bottom flask equipped with a stir bar was cooled under vacuum. After evacuated/backfilled with N_2 (x 3) and capped with a septum, a solution of crude acid **28** (assuming 0.4 mmol, 1 eq.) in DCM (2 mL) was added. Then NHPI (33 mg, 0.20 mmol, 1.0 eq.), DCC (41 mg, 1.0 mmol, 1.0 eq.) and DMAP (2.5 mg, 0.020 mmol, 0.10 eq.) were sequentially at 0 °C in an ice/water bath. After addition, the ice bath was removed and the reaction was stirred at room temperature for 12 h. The mixture was filtered though a pad of Celite. The filtrate was concentrated by rotary evaporation. The residue was purified by FCC (Hex : EtOAc = 9 : 1 to 4 : 1) to afford redox active ester **27** (61 mg, 68 yield for 3 steps, with ~10% inseparable impurity.

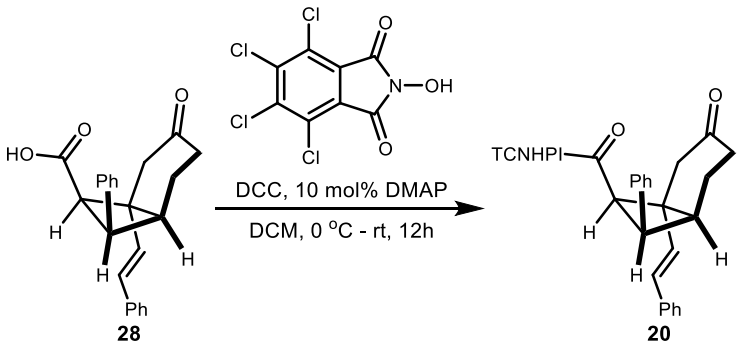
(Note: Various ratio of diastereomers of redox-active ester were observed after silica gel purification for different batches but would result in the same yield for following cross coupling.)

^{1}H NMR (600 MHz, $CDCl_3$): For 2:1 dr mixture: Aromatic region overlaps for major and minor. δ 7.86 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.76 (dd, *J* = 6.1, 3.0 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.49 – 7.15 (m, 9H), 6.77 (d, *J* = 16.1 Hz, 0.66H, major), 6.66 (d, *J* = 16.1 Hz, 0.66H, major), 6.60 (d, *J* = 16.0 Hz, 0.33H, minor), 6.51 (d, *J* = 16.1 Hz, 0.33H, minor), 4.55 (t, *J* = 9.8 Hz, 0.33H, minor), 4.38 (t, *J* = 10.1 Hz, 0.66H, major), 4.21 (d, *J* = 10.1 Hz, 0.33H, minor), 3.86 (d, *J* = 10.6 Hz, 0.66H, major), 3.14 (m, 1H), 3.10 – 3.02 (m, 0.33H, minor), 2.96 (d, *J* = 16.5 Hz, 0.66H, major), 2.77 (m, 1H), 2.40 (d, *J* = 16.1 Hz, 0.33H, minor), 2.31 – 1.84 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): For 2:1 dr mixture: Aromatic region is hard to differentiate for major and minor. δ 210.2 (major), 210.0 (minor), 168.7 (minor), 167.6 (major), 137.7, 137.0, 136.5, 136.3, 135.4, 134.9, 134.8, 130.8, 130.4, 129.0, 128.8, 128.7, 128.5, 128.1, 128.0, 127.9, 127.0, 126.9, 126.8, 126.7, 126.7, 124.1, 49.0 (major), 48.7 (major), 47.7 (minor), 44.2 (major), 43.7 (minor), 43.2 (minor), 42.0 (minor), 40.3 (minor), 39.4 (major), 38.4 (major), 37.4 (minor), 37.1 (major), 21.8 (major), 21.5 (minor).

HRMS: Calculated for $C_{31}H_{25}O_5NNa$ $[M + Na]^+$: 514.1625. Found: 514.1625.

Melting point, IR, optical rotation were not collected due to product is a mixture.



28 **20**

4,5,6,7-Tetrachloro-1,3-dioxoisoindolin-2-yl (1*S*,6*R*,7*R*,8*R*)-4-oxo-8-phenyl-6-((*E*)-styryl)bicyclo[4.2.0]octane-7-carboxylate (20): A flame-dried 50 mL round bottom flask equipped with a stir bar was cooled under vacuum. After evacuated/backfilled with N_2 (x 3) and capped with a septum, a solution of crude acid **28** (assuming 0.4 mmol, 1 eq.) in DCM (50 mL) was added. Then TCNHPI (1.65 g, 5.50 mmol, 1.10 eq), DCC (1.24 g, 6.00 mmol, 1.20 eq) and DMAP (61 mg, 0.50 mmol, 0.10 eq) were added sequentially at 0 °C. After addition, ice bath was removed and the reaction was stirred at room temperature for 12 h. The mixture was filtered through a pad of Celite. The filtrate was concentrated by rotary evaporation. The residue was purified by FCC (Hex : EtOAc = 9 : 1 to pure DCM) to afford redox active ester **20** (1.99 g, 72% yield for 3 steps) as pale yellow solid.

(Note: Various ratio of diastereomers of redox-active ester were observed after silica gel purification for different batches but would result in the same yield for following cross coupling.)

^{1}H NMR (600 MHz, $CDCl_3$): For >20:1 dr product: δ 7.43 – 7.37 (m, 4H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.20 (d, *J* = 7.7 Hz, 2H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.50 (d, *J* = 16.0 Hz, 1H), 4.57 (t, *J* = 9.8 Hz, 1H), 4.21 (d, *J* = 10.0 Hz, 1H), 3.11 (d, *J* = 15.4 Hz, 1H), 3.07 (q, *J* = 9.6 Hz, 1H), 2.76 (d, *J* = 15.5 Hz, 1H), 2.41 (dd, *J* = 14.3, 2.2 Hz, 1H), 2.13 – 2.07 (m, 2H), 2.06 – 1.98 (m, 1H).

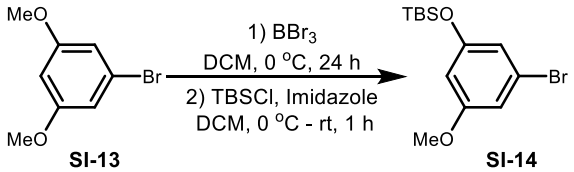
^{13}C NMR (126 MHz, $CDCl_3$): For >20:1 dr product: δ 209.7, 168.2, 141.2, 136.8, 136.2, 135.1, 130.6, 128.8, 128.8, 128.6, 128.2, 127.9, 126.8, 126.7, 47.7, 43.7, 43.3, 42.0, 40.4, 37.4, 21.5.

IR： 3026 (w), 2951 (w), 1812 (w), 1787 (m), 1747 (s), 1716 (m), 1038 (m).

HRMS (ESI): Calculated for $C_{31}H_{21}O_5NCl_4Na$ $[M+Na]^+$: 650.0066. Found: 650.0066.

Optical rotation: $[\alpha]_D^{20}$: -4.4 (c = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 95.5 : 4.5 er.

Melting point: 173 °C – 174 °C (Decompose).



SI-13 **SI-14**

(3-Bromo-5-methoxyphenoxy)(*tert*-butyl)dimethylsilane (SI-14): A flame-dried 200 mL round bottom flask equipped with a stir bar was cooled under vacuum. After backfilled with N_2, 1-bromo-3,5-dimethoxybenzene **SI-13** (13 g, 60 mmol, 1.0 eq.) was added. The flask was evacuated/backfilled with N_2 (x 3) and capped with a septum.

DCM (60 mL) was then added. To the stirring solution was added boron tribromide (1.0 M in DCM, 20 mL, 20 mmol, 0.33 eq.) at 0 °C. The reaction was stirred at the same temperature for 24 h (cryocooler was used to keep the temperature) and quenched with MeOH (5 mL) dropwise. After concentrated by rotary evaporation, the residue was purified by FCC (Hex : EtOAc = 9 :1 to 4 : 1) to afford phenol as white solid.

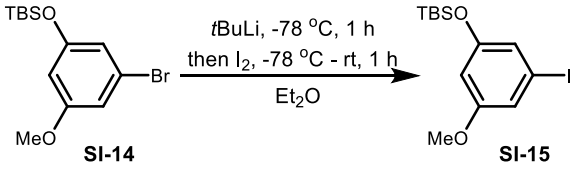
A flame-dried 500 mL round bottom flask equipped with a stir bar was cooled under vacuum. After backfilled with N_2, above crude phenol (assuming 60 mmol, 1.0 eq.) was added. The flask was evacuated/backfilled with N_2 (x 3) and capped with a septum and DCM (200 mL) was added. To the stirring solution was added imidazole (6.1 g, 90 mmol, 1.5 eq.) and TBSCl (9.0 g, 60 mmol, 1.0 eq.) at 0 °C sequentially in an ice/water bath. Then ice bath was removed and the mixture was stirred at room temperature for 1 h. The reaction was quenched with saturated NH_4Cl solution (100 mL). The aqueous layer was extracted with DCM (3 x 50 mL). The combined organic layers were washed with brine (100 mL), dried over anhydrous $MgSO_4$ and concentrated by rotary evaporation. The residue was purified by FCC (Hex : EtOAc = 30 : 1) to afford silylether **SI-14** (13.3 g, 70% yield for 2 steps) as colorless oil. All spectral data matched that reported in the literature.[23]

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.65 (s, 1H), 6.59 (s, 1H), 6.30 (s, 1H), 3.73 (s, 3H), 0.95 (s, 9H), 0.18 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 161.2, 157.4, 122.7, 116.3, 110.5, 105.7, 55.6, 25.9, 25.7, 18.3, -4.3.

IR: 2956 (m), 1595 (s), 1569 (m), 1442 (m), 1195 (s).

HRMS (ESI): Calculated for $C_{13}H_{22}O_2BrSi$ $[M+H]^+$: 317.0567. Found: 317.0569.

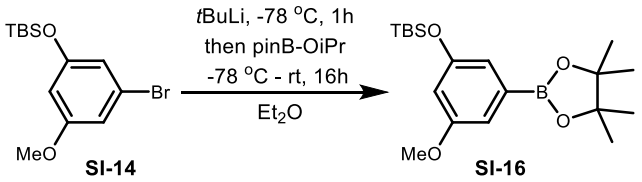


***tert*-Butyl(3-iodo-5-methoxyphenoxy)dimethylsilane (SI-15):** A flame-dried 50 mL round bottom flask equipped with a stir bar was cooled under vacuum. After evacuated/backfilled with N_2 (x 3) and capped with a septum, bromide **SI-14** (317 mg, 1.00 mmol, 1.00 eq.) was added followed by Et_2O (10 mL). To the stirring solution was added *t*-butyllithium solution (1.7 M in pentane, 2.2 mmol, 2.2 eq.) dropwise at -78 °C in a dry ice/acetone bath. After stirred at the same temperature for 1 h, a solution of iodine (760 mg, 3.00 mmol, 3.00 eq.) in Et_2O (3 mL) was added dropwise. Then the dry ice bath was removed. The reaction was naturally warmed to room temperature for 1 h and quenched with saturated $Na_2S_2O_3$ solution (5 mL). The aqueous layer was extracted with Et_2O (3 x 5 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The residue was purified by FCC (Hex : Et_2O = 100 : 1) to afford iodide **SI-15** (246 mg, 67%) as colorless oil.

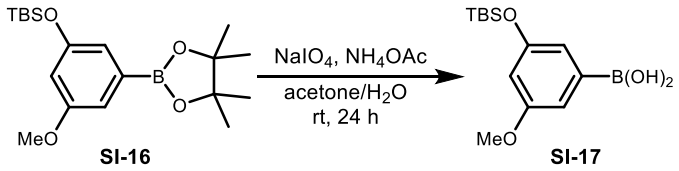
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (s, 1H), 6.81 (s, 1H), 6.34 (s, 1H), 3.74 (s, 3H), 0.97 (s, 9H), 0.20 (s, 5H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 161.1, 157.3, 122.4, 116.4, 106.6, 93.9, 55.6, 25.8, 18.3, -4.3.

IR: 2955 (m), 2858 (m), 1589 (s), 1562 (m), 1442 (m), 1195 (s).
HRMS (ESI): Calculated for $C_{13}H_{22}O_2ISi$ $[M+H]^+$: 365.0428. Found: 365.0430.

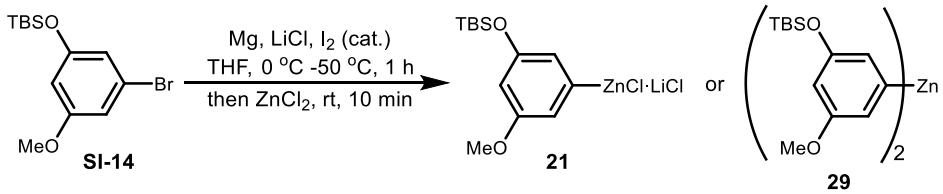


***tert*-Butyl(3-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)dimethylsilane (SI-16):** A flame-dried 50 mL round bottom flask equipped with a stir bar was cooled under vacuum. After evacuated/backfilled with N_2 (x 3) and capped with a septum, bromide **SI-14** (634 mg, 2.00 mmol, 1.00 eq.) was added followed by Et_2O (20 mL). To the stirring solution was added *t*-butyllithium solution (1.1 M in pentane, 4.4 mmol, 2.2 eq.) dropwise at -78 °C in a dry ice/acetone bath. After stirred at the same temperature for 1 h, pinB-OiPr (0.82 mL, 4.0 mmol, 2.0 eq.) was added dropwise. The reaction was naturally warmed to room temperature over 16 h and quenched with saturated NH_4Cl solution (10 mL). The aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The residue was purified by FCC (Hex : Et_2O = 100 : 1) to afford boronic ester **SI-16** (352 mg, 48%) as colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.94 (s, 1H), 6.89 (s, 1H), 6.50 (s, 1H), 3.80 (s, 3H), 1.33 (s, 12H), 0.98 (s, 9H), 0.20 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 160.3, 156.5, 119.2, 111.7, 110.1, 83.9, 55.5, 25.0, 18.3, -4.3. (Carbon attached to boron atom was not detected due to quadrupolar relaxation).
IR: 2977 (m), 2858 (m), 1580 (s), 1421 (s), 833 (s)
HRMS: Calculated for $C_{19}H_{34}O_4BSi$ $[M+H]^+$: 365.2314. Found: 365.2316.



(3-((*tert*-Butyldimethylsilyl)oxy)-5-methoxyphenyl)boronic acid (SI-17): A 25 mL round bottom flask equipped with a stir bar was charged with boronic ester **SI-16** (291 mg, 0.800 mmol, 1.00 eq.). Then acetone (4 mL) and H_2O (4 mL) were added. To the stirring solution was added sodium periodate (600 mg, 2.80 mmol, 3.50 eq.) and ammonium acetate (215 mg, 2.80 mmol, 3.50 eq.) at room temperature. The suspension was stirred at the same temperature for 24 h and diluted with H_2O (10 mL). The aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layer was washed with brine (15 mL), dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The residue was purified by FCC (Hex : EtOAc) = 3 : 1 to afford boronic acid **SI-17** (160 mg, 71% yield) as white solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (s, 1H), 7.30 (s, 1H), 6.65 (s, 1H), 3.89 (s, 3H), 1.04 (s, 9H), 0.28 (s, 6H).

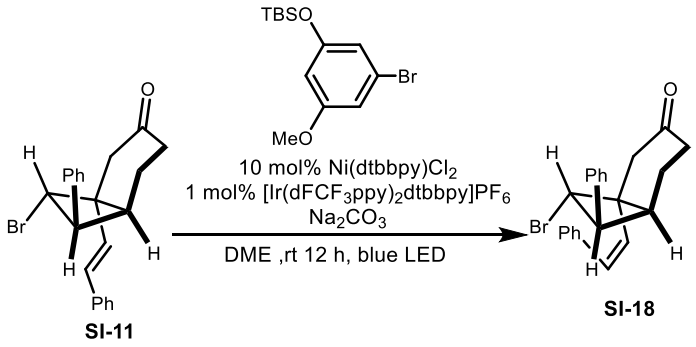
^{13}C NMR (101 MHz, $CDCl_3$): δ 160.6, 156.8, 119.5, 113.2, 111.2, 55.4, 25.9, 18.4, -4.1. (Carbon attached to boron atom was not detected due to quadrupolar relaxation).
IR: 3471 (br), 2954 (m), 1584 (m), 1447 (s), 1332 (s), 1193 (s), 832 (s).
HRMS: Calculated for $C_{13}H_{22}O_4BSi$ $[M-H]^+$: 281.1386. Found: 281.1381.
Melting point: 135 °C – 137 °C.



A flame-dried 15 mL round bottom flask equipped with a stir bar was cooled under vacuum. After backfilled with N_2 and capped with a septum, the flask was transferred into glovebox and magnesium (364 mg, 15.0 mmol, 1.50 eq), lithium chloride (528 mg, 12.5 mmol, 1.25 eq) and iodine (1 small piece, ~0.05 eq.) were added. Then the flask was moved out and THF (5 mL) was added. To the stirring suspension was added bromide **SI-14** (3.17 g, 10.0 mmol, 1.00 eq) dropwise via syringe at 0 °C in an ice/water bath. Then the ice bath was removed and the reaction was stirred at room temperature until yellow color disappeared (~10 min). Upon initiation, the septum was quickly replaced with a stopper and the mixture was heated to 50 °C for 1 h. After cooled down to room temperature, the Grignard reagent was titrated according to Knochel's procedure.[24] (Usually from 0.9 M – 1.0 M)

(3-((*tert*-Butyldimethylsilyl)oxy)-5-methoxyphenyl)zinc(II) bromide lithium chloride complex (21): A flame-dried 20 mL vial equipped with a stir bar was cooled under vacuum. After backfilled with N_2 and capped with a septum, the vial was transferred into glovebox and $ZnCl_2$ (912 mg, 6.69 mmol, 1.00 eq. based on Grignard) was added. Then the vial was moved out and THF (7.6 mL) was added followed by addition of above Grignard reagent (0.956 M in THF, 3.00 mL, 6.69 mmol, 1.00 eq.) dropwise via syringe at room temperature. After 10 min, the solution became homogenous and the Zinc reagent **21** (cal. 0.25 M) was used directly into next reaction without further titration.

Bis(3-((*tert*-butyldimethylsilyl)oxy)-5-methoxyphenyl)zinc (29): A flame-dried 20 mL vial equipped with a stir bar was cooled under vacuum. After backfilled with N_2 and capped with a septum, the vial was transferred into glovebox and $ZnCl_2$ (182 mg, 1.34 mmol, 0.500 eq. based on Grignard) was added. Then the vial was moved out and THF (5 mL) was added followed by addition of above Grignard reagent (0.890 M in THF, 3.00 mL, 2.67 mmol, 1.00 eq.) dropwise via syringe at room temperature. After 10 min, the solution became homogenous and the Zinc reagent **29** (cal. 0.33 M) was used directly into next reaction without further titration.



(1*R*,6*S*,7*S*,8*S*)-8-Bromo-7-phenyl-1-((*Z*)-styryl)bicyclo[4.2.0]octan-3-one (SI-18): [Ni pre-catalyst]: A flame-dried 4 mL vial equipped with a stir bar was cooled under vacuum. After backfilled with N_2 and capped with a septum, the vial was transferred into glovebox and charged with $NiCl_2$·DME (2.2 mg, 0.010 mmol) and dtbbpy (2.7 mg, 0.010 mmol) in glovebox. After moved out, DME (1 mL) was added. The vial was sonicated until all solids dissolved (~ 10 min) to afford Ni(dtbbpy)Cl_2 (0.01 M in DME) [Cross coupling]: Another flame-dried 4 mL vial equipped with a stir bar was cooled under vacuum. After backfilled with N_2 and capped with a septum, the vial was transferred into glovebox and charged with [Ir(dFCF_3ppy)$_2$(dtbbpy)]PF_6 (0.7 mg, 0.0006 mmol, 0.01 eq.) and Na_2CO_3 (13 mg, 0.12 mmol, 2.0 eq.) in glove box. After moved out, a solution of alkyl bromide (22.8 mg, 0.0600 mmol, 1.00 eq.) and aryl bromide **SI-11** (28.6 mg, 0.0900 mmol, 1.50 eq.) in DME (1 mL) was added followed by addition of Ni(dtbbpy)Cl_2 (0.010 M in DME, 0.12 mL 0.0012 mmol, 0.10 eq.) and tris(trimethylsilyl)silane (19 μL, 0.060 mmol, 1.0 eq.) via syringe. The suspension was sparged with N_2 while stirring for 10 min. Then the vent needle was removed and the reaction was irradiated with a blue LED strip (7 cm away , with cooling fan to keep the reaction at room temperature). After 12 h, the mixture was filtered though a pad of Celite and the filtrate was concentrated by rotary evaporation. The residue was purified by FCC (Hex : EtOAc = 9 : 1) to afford *Z*-styryl **SI-18** (6 mg, 26% yield) as pale yellow oil.

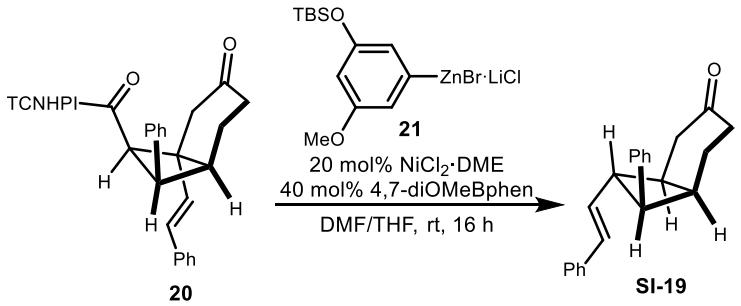
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43 – 7.22 (m, 8H), 7.11 (d, *J* = 7.3 Hz, 2H), 6.83 (d, *J* = 12.4 Hz, 1H), 6.32 (d, *J* = 12.4 Hz, 1H), 4.71 (d, *J* = 10.5 Hz, 1H), 4.03 (t, *J* = 10.6 Hz, 1H), 3.06 (dt, *J* = 10.9, 5.8 Hz, 1H), 2.60 (d, *J* = 17.9 Hz, 1H), 2.53 (d, *J* = 17.9 Hz, 1H), 2.09 – 2.01 (m, 1H), 2.01 – 1.93 (m, 1H), 1.72 (tt, *J* = 10.8, 5.4 Hz, 1H), 1.57 (tt, *J* = 10.8, 5.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 210.6, 137.4, 137.0, 135.0, 131.9, 128.8, 128.7, 128.5, 127.6, 126.9, 126.5, 55.6, 49.2, 47.8, 45.5, 40.7, 37.0, 21.1.

IR: 3025 (m), 2927 (m), 1711 (s), 1601 (w), 1448 (m), 966 (m).

HRMS (ESI): Calculated for $C_{22}H_{22}OBr$ $[M + H]^+$: 381.0849. Found: 381.0841.

Optical rotation: $[\alpha]_D^{20}$: -55.2 (c = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 95.5 : 4.5 er.



(1S,6R,7R)-7-phenyl-8-((E)-styryl)bicyclo[4.2.0]octan-3-one (SI-19): A flame-dried 4 mL vial equipped with a stir bar was cooled under vacuum. After backfilled with N_2 and capped with a septum, the vial was transferred into glovebox and with redox active ester **20** (16 mg, 0.025 mmol, 1.0 eq), $NiCl_2$·DME (1.1 mg, 0.0050 mmol, 0.20 eq.), 4,7-diMeOBPhen (2.4 mg, 0.010 mmol, 0.40 eq.) in glovebox. After moved out, DMF (0.2 mL) was added at room temperature. After stirred for 5 min, freshly made zinc reagent (0.25 M, 0.30 mL, 0.075 mmol, 3.0 eq.) was added dropwise via syringe. The mixture was stirred at the same temperature for 16 h. The reaction was quenched with 1M HCl solution (1 mL). The aqueous layer was extracted with Et_2O (3 x 1 mL). The combined organic layers were sequentially washed with H_2O (2 mL), saturated $NaHCO_3$ solution (2 mL), brine (2 mL), dried over anhydrous $MgSO_4$ and concentrated by rotary evaporation. The residue was semi-purified by FCC (Hex : EtOAc = 9 : 1 to 4 : 1) to afford styryl migration product **SI-19** (28% yield, determined by ^{1}H-NMR using CH_2Br_2 as internal standard, >20 : 1 dr) as yellow oil. The product was further purified by prep-TLC (Hex : EtOAc = 3 : 1) for characterization (with ~5% inseparable impurity).

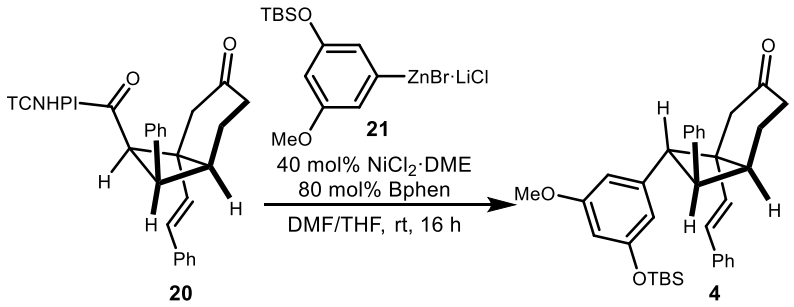
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 – 7.12 (m, 10H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.36 (dd, *J* = 15.8, 7.1 Hz, 1H), 3.69 (t, *J* = 9.2 Hz, 1H), 3.21 (q, *J* = 8.9 Hz, 1H), 2.91 (p, *J* = 8.3 Hz, 1H), 2.79 (ddt, *J* = 11.4, 8.5, 3.3 Hz, 1H), 2.57 (dd, *J* = 16.8, 7.8 Hz, 1H), 2.45 (dd, *J* = 16.8, 3.1 Hz, 1H), 2.23 (dtd, *J* = 27.8, 16.6, 14.2, 5.2 Hz, 2H), 1.81 (dq, *J* = 11.3, 5.8 Hz, 1H), 1.72 (dq, *J* = 11.3, 5.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 212.9, 140.4, 137.2, 131.7, 130.0, 128.7, 128.5, 127.5, 127.1, 126.3, 126.3, 47.7, 44.8, 41.9, 38.6, 36.8, 34.4, 23.2.

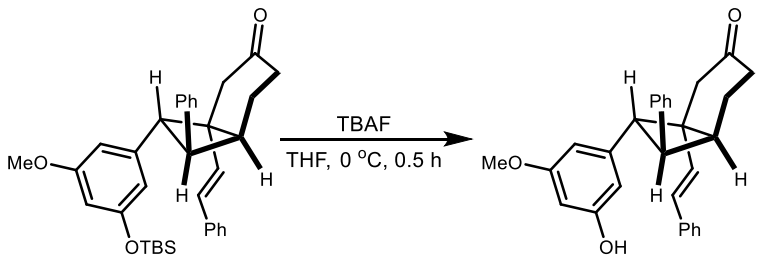
IR: 3024 (w), 2932 (m), 1739 (m), 1711 (s), 1600 (m), 749 (s)

HRMS (EI): Calculated for $C_{22}H_{22}O$ $[M]^+$: 302.1665. Found: 302.1669.

Optical rotation: $[\alpha]_D^{20}$: -132 (c = 0.10, $CHCl_3$) for an enantiomerically enriched sample of 95.5 : 4.5 er. Relative stereochemistry was determined by analysis of relevant NOE interactions (see Supporting Information Spectrums).



(1*R*,6*S*,7*R*,8*R*)-8-(3-((*tert*-Butyldimethylsilyl)oxy)-5-methoxyphenyl)-7-phenyl -1-((E)-styryl)bicyclo[4.2.0]octan-3-one (4): A flame-dried 25 mL test tube equipped with a stir bar was cooled under vacuum. After backfilled with N_2 and capped with a septum, the test tube was transferred into glovebox and charged with redox active ester **20** (315 mg, 0.500 mmol, 1.00 eq), $NiCl_2$·DME (44 mg, 0.20 mmol, 0.40 eq.), BPhen (133 mg, 0.400 mmol, 0.800 eq.) in glovebox. After moved out, DMF (4 mL) was added at room temperature. After stirred for 5 min, freshly made zinc reagent (0.25 M, 6.0 mL, 1.5 mmol, 3.0 eq.) was added dropwise via syringe. The mixture was stirred at the same temperature for 16 h. The reaction was quenched with 1M HCl solution (10 mL) and vacuum filtered though a filter paper. The aqueous layer of filtrate was extracted with Et_2O (3 x 10 mL). The combined organic layers were sequentially washed with H_2O (20 mL), saturated $NaHCO_3$ solution (20 mL), brine (20 mL), dried over anhydrous $MgSO_4$ and concentrated by rotary evaporation. The residue was purified by FCC (Hex : EtOAc = 9 : 1 to 4 : 1) to afford decarboxylative cross coupling product **4** (40% yield, determined by ^{1}H-NMR using CH_2Br_2 as internal standard, >20 : 1 dr) as yellow oil with inseparable impurity (~20% – 30%).



4 **SI-20**

(1*R*,6*S*,7*R*,8*R*)-8-(3-Hydroxy-5-methoxyphenyl)-7-phenyl-1-((*E*)-styryl)bicyclo-[4.2.0] octan-3-one (SI-20): A 4 mL vial equipped with a stir bar was charged with above crude semi-purified silyl ether **4** (with inseparable impurity ~20-30%) (48 mg, assuming 0.090 mmol, 1.0 eq.) After evacuated/backfilled with N_2 (x 3) and capped with a septum, THF (2 mL) was added followed by TBAF (1.0 M in THF, 0.18 mL, 0.18 mmol, 2.0 eq.) at 0 °C in an ice/water bath and the reaction was stirred for 0.5 h at the same temperature. The reaction was quenched with saturated NH_4Cl solution (1 mL). The aqueous layer was extracted with Et_2O (1 mL x 3). The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The residue was purified by FCC (Hex : EtOAc = 4 : 1 to 2 : 1) to afford phonol **SI-20** (20 mg, 53% yield) as yellow solid.

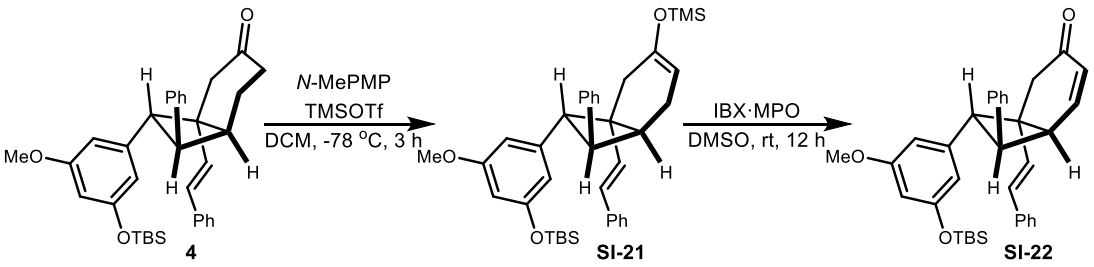
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.14 (m, 8H), 6.41 (d, *J* = 16.2 Hz, 1H), 6.29 (s, 1H), 6.28 (s, 1H), 6.25 (s, 1H), 6.18 (d, *J* = 16.2 Hz, 1H), 5.44 (s, 1H), 4.23 (t, *J* = 10.3 Hz, 1H), 3.89 (d, *J* = 11.2 Hz, 1H), 3.68 (s, 3H), 2.96 (q, *J* = 7.9 Hz, 1H), 2.84 (d, *J* = 16.0 Hz, 1H), 2.72 (d, *J* = 16.0 Hz, 1H), 2.29 (dt, *J* = 18.7, 6.2 Hz, 1H), 2.19 (ddd, *J* = 18.7, 8.6, 5.6 Hz, 1H), 1.89 (dt, *J* = 14.5, 7.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 212.8, 161.1, 157.0, 141.8, 139.7, 137.3, 133.8, 128.6, 128.6, 128.2, 127.5, 127.2, 126.4, 126.4, 107.1, 106.0, 99.9, 55.4, 52.9, 49.4, 44.9, 40.7, 39.8, 37.6, 22.1.

IR: 3368 (br), 3024 (w), 2927 (w), 1697 (s), 1787 (m), 1598 (s), 1152 (s), 753 (s).

HRMS (ESI): Calculated for $C_{29}H_{28}O_3Na$ $[M+Na]^+$: 447.1931. Found: 447.1932.

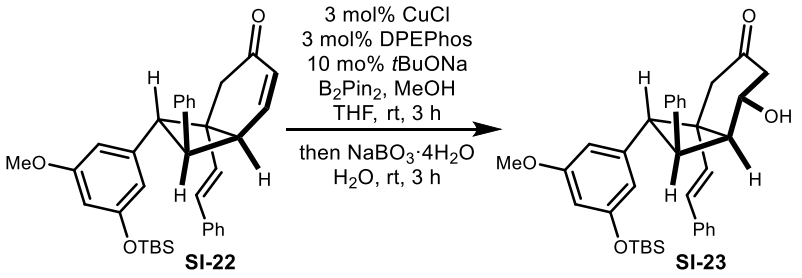
Optical rotation: $[\alpha]_D^{20}$: -18.8 (c = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 95.5 : 4.5 er. Relative stereochemistry was determined by analysis of relevant NOE interactions (see Supporting Information Spectrums).
Melting point: 78 ºC – 81 ºC.



(1*R*,6*S*,7*R*,8*R*)-8-(3-((*tert*-Butyldimethylsilyl)oxy)-5-methoxyphenyl)-7-phenyl-1-((*E*)-styryl)bicyclo[4.2.0]oct-4-en-3-one (SI-22): A flame-dried 50 mL round bottom flask equipped with a stir bar was cooled under vacuum. After evacuated/backfilled with N_2 (x 3) and capped with a septum, ketone **2** (2 mmol based on ^{1}H-NMR using CH_2Br_2 as internal standard, 1 eq.) and *N*-MePMP (0.73 mL, 4.0 mmol, 2.0 eq.) were added followed by DCM (20 mL) at room temperature. Then the reaction was cooled down to -78 ºC in a dry ice/acetone bath and TMSOTf (0.54 mL, 3.0 mmol, 1.5 eq.) was added dropwise. The reaction was stirred at the same temperature for 3 h and quenched with saturated $NaHCO_3$ solution (10 mL). After warmed to room temperature, the aqueous layer was extracted with DCM (3 x 10 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The crude silylether **SI-21** (>20 : 1 rr) was used directly into next reaction without further purification.
(Note: Silylether went back to ketone upon silica gel or basic Al_2O_3 purification.)

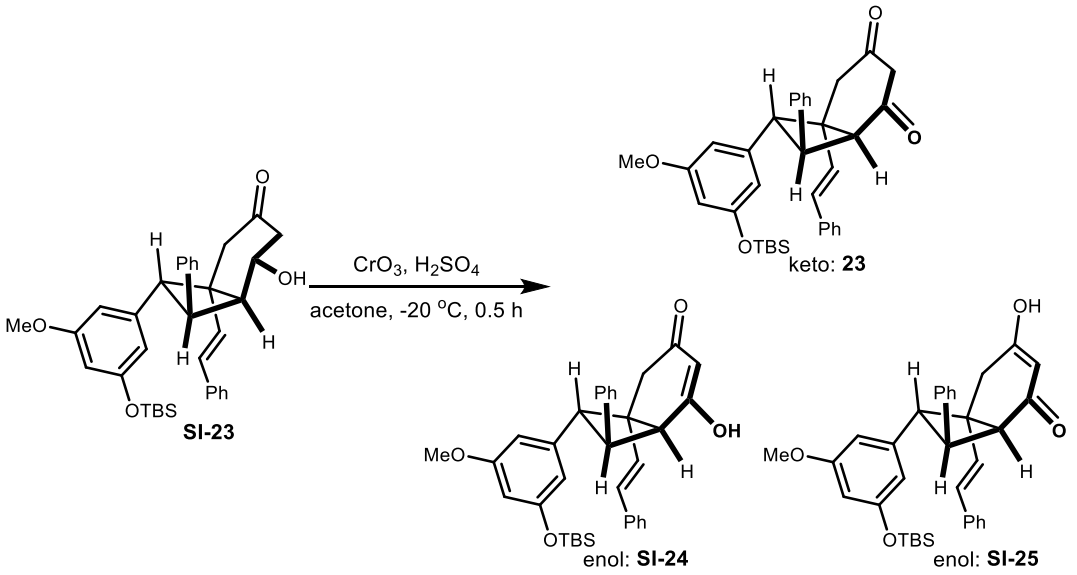
[IBX·MPO]:To a 25 mL round bottom flask charged with IBX (1.68 g, 6.00 mmol, 3.00 eq.) and MPO (0.75 g, 6.0 mmol, 3.0 eq.) was added DMSO (15 mL). The mixture was stirred at room temperature for 30 min until all solids had dissolved to afford IBX·MPO solution.
[Oxidation]: Another 50 mL round bottom flask equipped with a stir bar was charged with above silylether **SI-21** (assuming 2 mmol, 1 eq.). After evacuated/backfilled with N_2 (x 3) and capped with a septum, DMSO (5 mL) was added followed by the IBX·MPO solution via syringe. The reaction was stirred at room temperature for 12 h and quenched with saturated $NaHCO_3$ (20 mL) slowly in an ice/water bath. The aqueous layer was extracted with Et_2O (3 x 15 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous $MgSO_4$ and filtered though a pad of Celite. The filtrate was concentrated by rotary evaporation and purified by FCC (Hex : EtOAc = 9 : 1 to 4 : 1) to afford enone **SI-22** (850 mg, 80% yield for two steps) as yellow oil.
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.79 – 6.88 (m, 10H), 6.58 (dd, *J* = 10.3, 4.0 Hz, 1H), 6.53 (d, *J* = 16.2 Hz, 1H), 6.30 (s, 1H), 6.24 (s, 1H), 6.20 (d, *J* = 10.0 Hz, 1H), 6.19 (d, *J* = 16.2 Hz, 1H), 4.36 (t, *J* = 10.6 Hz, 1H), 3.95 (d, *J* = 11.5 Hz, 1H), 3.67 (s, 3H), 3.61 (dd, *J* = 10.0, 3.9 Hz, 1H), 2.79 (d, *J* = 17.5 Hz, 1H), 2.57 (d, *J* = 17.5 Hz, 1H), 0.90 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 198.1, 160.7, 156.9, 149.1, 139.7, 137.5, 137.1, 132.1, 130.1, 129.1, 128.7, 128.6, 128.5, 128.5, 127.8, 127.6, 127.2, 127.0, 126.4, 126.4, 112.3, 106.9, 104.8, 55.3, 49.0, 45.1, 44.6, 43.7, 41.8, 25.8, 18.3, -4.3, -4.4.
IR: 3060 (w), 2930 (m), 1713 (s), 1591 (s), 1196 (s), 839 (s).
HRMS (ESI): Calculated for $C_{35}H_{41}O_3Si$ $[M+H]^+$: 537.2819. Found: 537.2818.
Optical rotation: $[\alpha]_D^{20}$: -114.0 (c = 0.20, $CHCl_3$) for an enantiomerically enriched sample of 95.5 : 4.5 er.

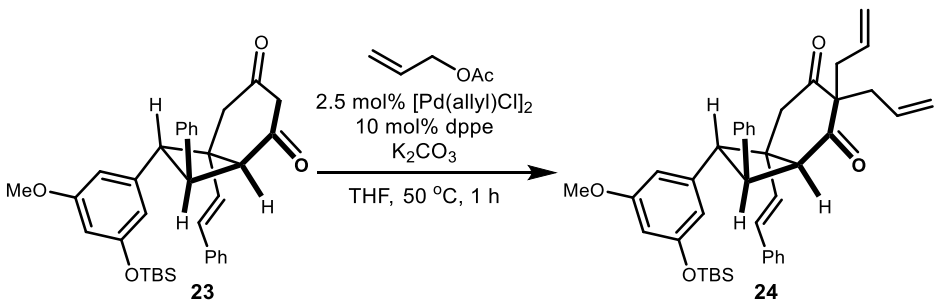


(1S,5S,6S,7S,8R)-8-(3-((*tert*-Butyldimethylsilyl)oxy)-5-methoxyphenyl)-5-hydroxy-7-phenyl-1-((E)-styryl)bicyclo[4.2.0]octan-3-one (SI-23):
[Cu pre-catalyst]: A flame-dried 10 mL round bottom flask equipped with a stir bar was cooled under vacuum. After backfilled with N_2 and capped with a septum, the flask was transferred into glovebox and charged with copper(I) chloride (4.5 mg, 0.045 mmol, 0.030 eq.), DPEPhos (24 mg, 0.045 mmol, 0.030 eq.) and sodium *tert*-butoxide (14 mg, 0.15 mmol, 0.10 eq.) Then the flask was moved out and THF (3 mL) was added. The mixture was stirred at room temperature for 0.5 h to afford (DPEPhos)Cu-O*t*Bu pre-catalyst solution.
[Conjugate addition and oxidation]: Another flame-dried 50 mL round bottom flask equipped with a stir bar was cooled under vacuum. After backfilled with N_2 and capped with a septum, enone **SI-22** (800 mg, 1.50 mmol, 1.00 eq.) and bis(pinacolato)diboron (570 g, 2.25 mmol, 1.50 eq.) were added followed by THF (12 mL). To the stirring solution was added (DPEPhos)Cu-O*t*Bu solution and methanol (0.12 mL, 3.0 mmol, 2.0 eq.) via syringe at room temperature. After stirred for 3 h at the same temperature, the solution was diluted with H_2O (15 mL) and sodium perborate tetrahydrate (1.15 g, 7.50 mmol, 5.00 eq.) was added. After another 3 h, the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The residue was purified by FCC (Hex : EtOAc = 3 : 1) to afford β-hydroxyl ketone **SI-23** (740 mg, 89% yield) as pale yellow oil.
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.14 (m, 8H), 6.46 (d, *J* = 16.2 Hz, 1H), 6.28 (s, 1H), 6.24 (s, 1H), 6.22 (s, 1H), 6.16 (d, *J* = 16.2 Hz, 1H), 4.35 (dq, *J* = 6.4, 3.3 Hz, 1H), 4.31 (t, *J* = 10.6 Hz, 1H), 3.85 (d, *J* = 11.4 Hz, 1H), 3.67 (s, 3H), 3.01 (dd, *J* = 9.6, 5.9 Hz, 1H), 2.85 (d, *J* = 16.5 Hz, 1H), 2.78 (d, *J* = 16.5 Hz, 1H), 2.51 (dd, *J* = 18.1, 3.8 Hz, 1H), 2.37 (dd, *J* = 18.0, 7.1 Hz, 1H), 0.89 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 209.5, 160.8, 157.0, 140.6, 138.4, 137.1, 133.1, 129.0, 128.9, 128.7, 128.7, 128.6, 127.5, 127.3, 127.0, 126.9, 126.6, 126.4, 111.9, 106.6, 104.7, 66.9, 55.4, 51.7, 49.2, 47.4, 45.3, 44.1, 39.7, 25.8, 18.3, -4.3, -4.4.
IR: 3436 (br), 3058 (w), 2929 (m), 1710 (s), 1591 (s), 1196 (s), 840 (s).

HRMS (ESI): Calculated for $C_{35}H_{43}O_4Si$ $[M+H]^+$: 555.2925. Found: 555.2925.
Optical rotation: $[\alpha]_D^{20}$: -49.5 (c = 0.20, $CHCl_3$) for an enantiomerically enriched sample of 95.5 : 4.5 er.



(1*S*,6*S*,7*R*,8*S*)-7-(3-((*tert*-Butyldimethylsilyl)oxy)-5-methoxyphenyl)-8-phenyl-6-((*E*)-styryl)bicyclo[4.2.0]octane-2,4-dione (keto 23): A 100 mL round bottom flask equipped with a stir bar was charged with β-hydroxyl ketone **SI-23** (660 mg, 1.20 mmol, 1.00 eq.). The flask was evacuated and backfilled with N_2 (3x) and capped with septum. Acetone (24 mL) was added and the flask was cooled to -20 °C (cryocooler). Jones' reagent (2.5 M, 1.4 mL, 3.0 eq.) was then added dropwise via syringe. The reaction was stirred at the same temperature for 0.5 h and quenched with saturated $NaHCO_3$ solution (20 mL) slowly. Then brine (20 mL) was added and the aqueous layer was extracted with EtOAc (3 x 30 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The residue was purified by FCC (Hex : EtOAc = 1 : 3) to afford diketone **23** (454 mg, 69% yield) as 1:2:1 (keto : enol : enol) tautomers.
^{1}H-NMR and ^{13}C-NMR are reported as a mixture of tautomers.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 – 7.01 (m, 10H), 6.54 (m, 1H), 6.41 – 6.11 (m, 4H), 5.67 (m, 0.66H), 4.53 (t, *J* = 11.1 Hz, 0.29H), 4.29 (t, *J* = 10.9 Hz, 0.69H), 4.14 – 3.95 (m, 1H), 3.84 (d, *J* = 10.8 Hz, 0.29H), 3.85 – 3.63 (m, 3H), 3.56 (t, *J* = 10.4 Hz, 0.85H), 3.29 (d, *J* = 19.9 Hz, 0.34H), 3.16 – 2.96 (m, 0.58H), 2.78 – 2.62 (m, 1H), 2.52 (m, 0.76H), 0.94 (m, 9H), 0.12 (m, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 205.4, 204.6, 161.0, 160.7, 157.2, 156.9, 139.8, 139.6, 137.9, 137.6, 137.0, 136.5, 131.7, 130.5, 129.8, 129.4, 129.3, 128.9, 128.7, 128.7, 128.4, 128.2, 128.0, 127.7, 127.3, 127.3, 126.8, 126.5, 126.5, 112.2, 111.9, 107.0, 106.7, 106.6, 105.1, 104.7, 77.4, 77.2, 76.9, 55.8, 55.4, 55.3, 54.9, 51.3, 50.1, 50.0, 46.6, 44.1, 43.8, 43.1, 42.2, 40.1, 25.8, 25.8, 18.3, -4.2, -4.3, -4.3, -4.3.
IR: 3028 (m), 2857 (m), 1591 (s), 1234 (s), 1157(s), 838 (s).
HRMS: Calculated for $C_{35}H_{41}O_4Si$ $[M+H]^+$: 553.2769. Found: 553.2765.
Optical rotation: $[\alpha]_D^{20}$: -52.2 (c = 0.25, $CHCl_3$) for an enantiomerically enriched sample of 95.5 : 4.5 er.



(1*S*,6*S*,7*R*,8*S*)-3,3-Diallyl-7-(3-((*tert*-butyldimethylsilyl)oxy)-5-methoxyphenyl)-8-phenyl-6-((E)-styryl)bicyclo[4.2.0]octane-2,4-dione (24):

[Pd pre-catalyst]: A flame-dried 4 mL vial equipped with a stir bar was cooled under vacuum. After backfilled with N_2 and capped with a septum, the vial was transferred into glovebox and charged with $[Pd(allyl)Cl]_2$ (7.3 mg, 0.020 mmol, 0.025 eq.) and dppe (31.9 mg, 0.0800 mmol, 0.100 eq.). Then the vial was moved out and THF (1 mL) was added. The mixture was stirred at room temperature for 10 min to afford (dppe)Pd(allyl) pre-catalyst solution.

[Allylation]: A flame-dried 25 mL round bottom flask equipped with a stir bar was cooled under vacuum. After backfilled with N_2 (x 3) and capped with a septum, diketone **23** (442 mg, 0.800 mmol, 1.00 eq.), allyl acetate (0.26 mL, 2.4 mmol, 3.0 eq.) and potassium carbonate (548 mg, 4.00 mmol, 5.00 eq.) were added followed by THF (7 mL). To the stirring suspension was added (dppe)Pd(allyl) pre-catalyst solution via syringe. The septum was replaced with a stopper and the reaction was heated to 50 °C for 1 h. After cooled down to room temperature, the mixture was filtered through a pad of silica gel. The filtrate was concentrated by rotary evaporation to afford bisallylated diketone **24** (500 mg, 98% yield) as colorless oil without further purification.

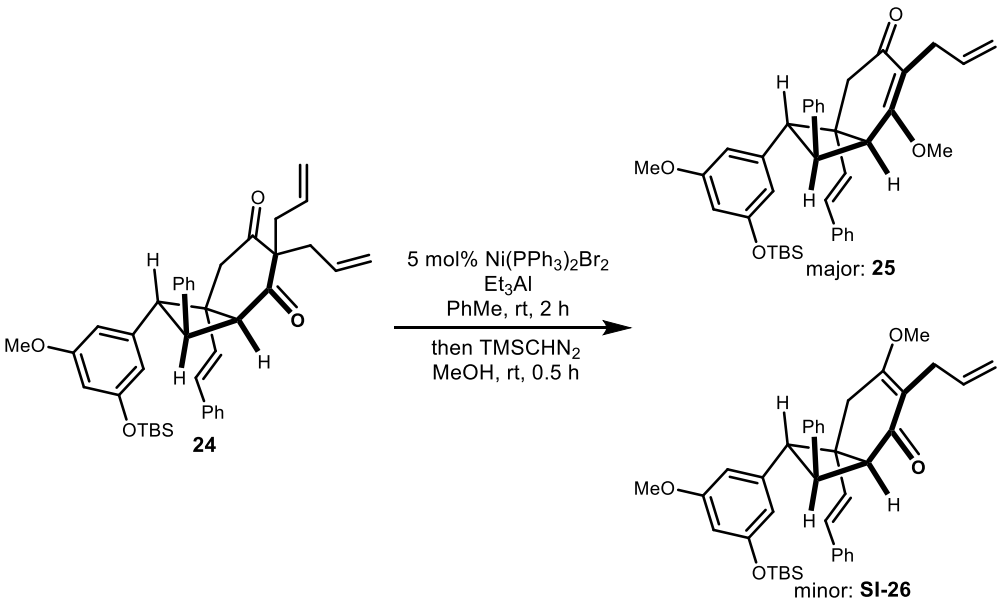
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34 – 7.01 (m, 10H), 6.51 (d, *J* = 16.2 Hz, 1H), 6.32 (s, 1H), 6.27 (s, 1H), 6.25 (s, 1H), 6.11 (d, *J* = 16.2 Hz, 1H), 5.54 (ddt, *J* = 17.4, 10.1, 7.4 Hz, 1H), 5.18 (ddt, *J* = 17.4, 10.1, 7.4 Hz, 1H), 5.07 (d, *J* = 10.0 Hz, 1H), 5.04 (d, *J* = 16.9 Hz, 1H), 4.84 (d, *J* = 10.6 Hz, 1H), 4.82 (d, *J* = 17.7 Hz, 1H). 4.42 (t, *J* = 11.2 Hz, 1H), 3.77 (d, *J* = 11.8 Hz, 1H), 3.74 (d, *J* = 10.6 Hz, 1H), 3.69 (s, 3H), 2.95 (d, *J* = 14.7 Hz, 1H), 2.84 (d, *J* = 14.7 Hz, 1H), 2.53 (dd, *J* = 13.9, 7.3 Hz, 1H), 2.44 (dd, *J* = 13.9, 7.4 Hz, 1H), 2.33 (dd, *J* = 13.9, 7.5 Hz, 1H), 2.26 (dd, *J* = 13.9, 7.4 Hz, 1H), 0.91 (s, 9H), 0.10 (s, 3H), 0.08 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 209.2, 208.4, 160.9, 157.1, 139.6, 137.8, 136.6, 132.8, 132.0, 131.1, 129.7, 128.7, 128.2, 127.9, 127.9, 127.0, 126.5, 119.8, 119.2, 111.9, 106.7, 105.0, 67.0, 55.4, 52.9, 52.6, 49.5, 43.3, 43.0, 42.2, 36.2, 25.8, 18.4, -4.2, -4.3.

IR: 3028 (m), 2858 (m), 1686 (m), 1639 (s), 1157 (s), 782 (s)

HRMS: Calculated for $C_{41}H_{48}O_4NaSi$ $[M+Na]^+$: 655.3214. Found: 655.3212.

Optical rotation: $[\alpha]_D^{20}$: -57.6 (c = 0.25, $CHCl_3$) for an enantiomerically enriched sample of 95.5 : 4.5 er.



(1*S*,6*S*,7*S*,8*R*)-4-Allyl-8-(3-((*tert*-butyldimethylsilyl)oxy)-5-methoxyphenyl)-5-methoxy-7-phenyl-1-((*E*)-styryl)bicyclo[4.2.0]oct-4-en-3-one (25): A flame-dried 25 mL round bottom flask equipped with a stir bar was cooled under vacuum. After backfilled with N_2 and capped with a septum, the vial was transferred into glovebox and charged with $Ni(PPh_3)_2Br_2$ (19 mg, 0.025 mmol, 0.050 eq.). Then the flask was moved out and a solution of diketone **24** (326 mg, 0.500 mmol, 1.00 eq.) in PhMe (10 mL) was added via syringe at room temperature followed by addition of triethylaluminum (1 M in hexanes, 1 mL, 1 mmol, 2 eq.). The reaction was stirred at the same temperature for 2 h. MeOH (2 mL) was slowly added to the solution. When bubble evolution ceased, $TMSCHN_2$ (2.0 M in hexanes, 0.36 mL, 0.75 mmol, 1.5 eq.) was added and the reaction was stirred for another 0.5 h before it was quenched with AcOH (5 drops). The mixture was concentrated by rotary evaporation and purified by FCC (Hex : EtOAc = 15 : 1 to 6 : 1) to afford methoxyl ether **25** (220 mg, 73% yield) and methoxyl ether **SI-26** (58 mg, 19% yield) as pale yellow oils.

Major **25**: **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.35 – 7.30 (m, 2H), 7.29 – 7.17 (m, 8H), 6.51 (d, *J* = 16.2 Hz, 1H), 6.28 (d, *J* = 16.2 Hz, 1H), 6.27 (s, 1H), 6.21 (s, 1H), 6.20 (s, 1H), 5.89 (ddt, *J* = 16.8, 10.0, 6.7 Hz, 1H), 5.08 (d, *J* = 17.1 Hz, 1H), 4.99 (d, *J* = 10.0 Hz, 1H), 4.22 (dd, *J* = 11.5, 9.5 Hz, 1H), 4.03 (d, *J* = 11.7 Hz, 1H), 3.85 (d, *J* = 9.3 Hz, 1H), 3.66 (s, 3H), 3.26 (dd, *J* = 13.9, 6.7 Hz, 1H), 3.25 (s, 3H), 3.11 (dd, *J* = 13.9, 6.7 Hz, 1H), 2.82 (d, *J* = 16.8 Hz, 1H), 2.60 (d, *J* = 16.8 Hz, 1H), 0.90 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 195.3, 168.2, 160.7, 156.9, 140.2, 137.8, 137.0, 136.5, 132.3, 129.5, 128.7, 128.4, 128.1, 127.7, 126.9, 126.4, 120.1, 114.4, 112.3, 107.3, 104.5, 55.5, 55.3, 50.4, 50.0, 43.9, 41.9, 33.3, 27.1, 25.8, 18.3, -4.3, -4.3.

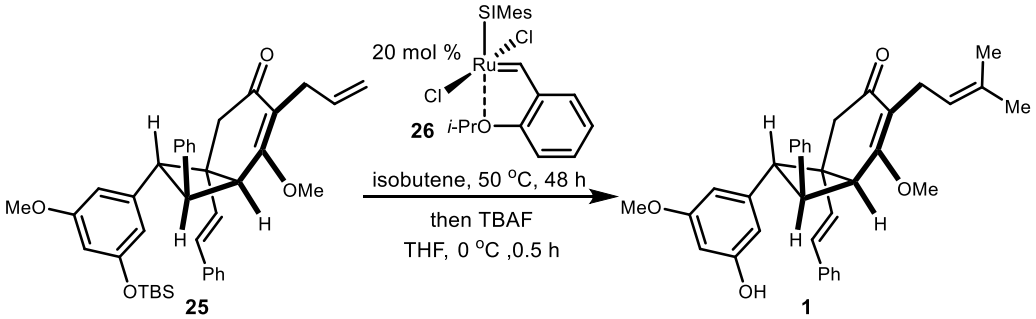
IR: 3027 (m), 2856 (m), 1638 (m), 1600 (s), 1365 (m), 1157 (s), 781 (s)

HRMS: Calculated for $C_{39}H_{47}O_4Si$ $[M+H]^+$: 607.3238. Found: 607.3239.

Optical rotation: $[\alpha]_D^{20}$: -112.8 (c = 0.25, $CHCl_3$) for an enantiomerically enriched sample of 95.5 : 4.5 er.

Regioselectivity was determined by analysis of relevant NOE interactions (see Supporting Information Spectrums).

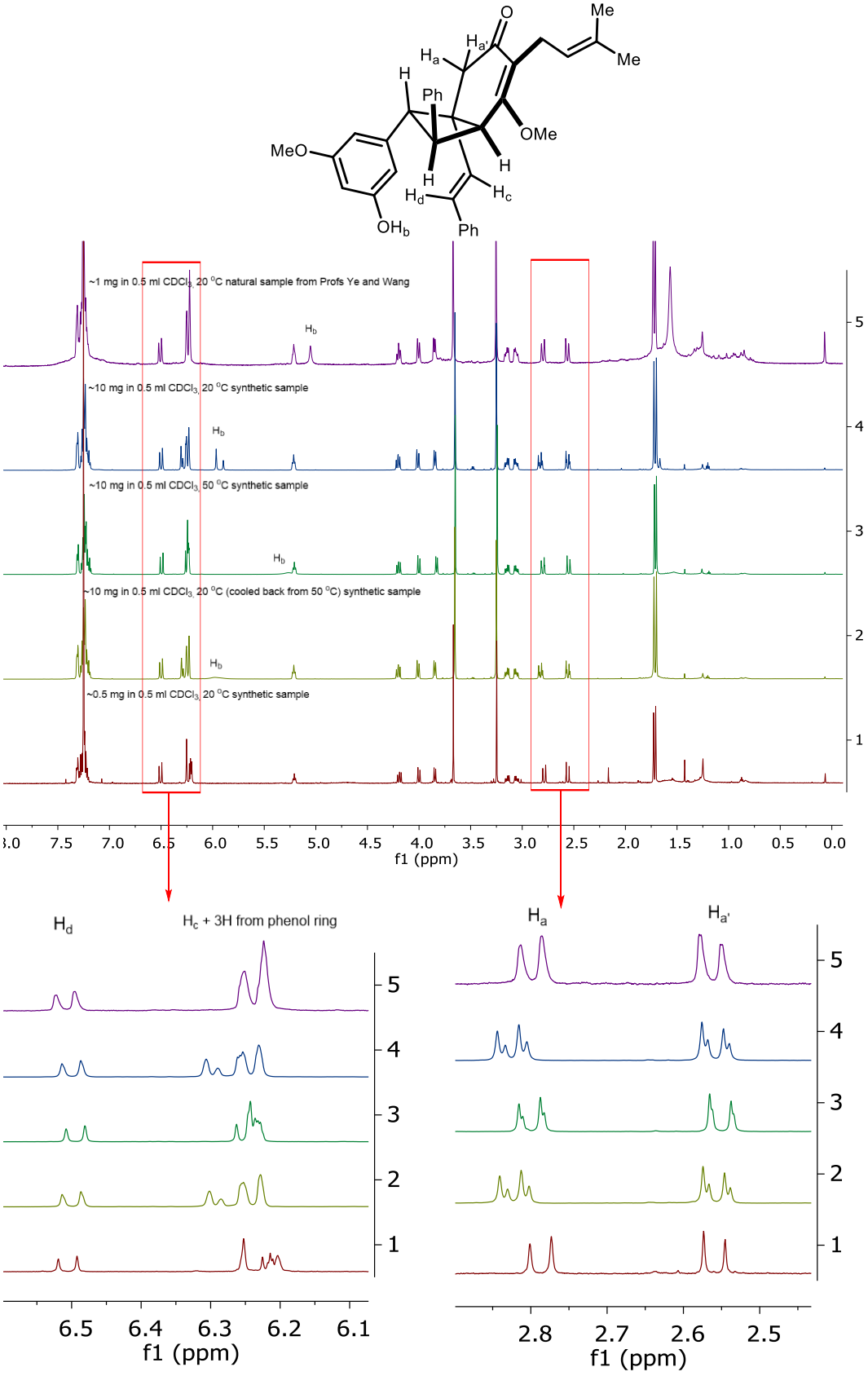
Minor **SI-26**: **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.32 – 7.11 (m, 10H), 6.57 (d, *J* = 16.2 Hz, 1H), 6.35 (s, 1H), 6.28 (s, 2H), 6.16 (d, *J* = 16.2 Hz, 1H), 5.65 (ddt, *J* = 16.5, 9.4, 6.3 Hz, 1H), 4.97 (d, *J* = 17.1 Hz, 1H), 4.86 (d, *J* = 9.9 Hz, 2H), 4.19 (s, 1H), 3.90 (s, 3H), 3.69 (m, 4H), 3.53 (d, *J* = 6.2 Hz, 1H), 3.12 (dd, *J* = 13.6, 6.0 Hz, 1H), 2.98 (dd, *J* = 13.6, 6.0 Hz, 1H), 2.95 (d, *J* = 17.7 Hz, 1H), 2.60 (d, *J* = 17.9 Hz, 1H), 0.92 (s, 9H), 0.10 (s, 3H), 0.10 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 195.3, 168.2, 160.7, 156.9, 140.2, 137.8, 137.0, 136.5, 132.3, 129.5, 128.7, 128.4, 128.1, 127.7, 126.9, 126.4, 120.1, 114.4, 112.3, 107.3, 104.5, 55.5, 55.3, 50.4, 50.0, 43.9, 41.9, 33.3, 27.1, 25.8, 18.3, -4.3, -4.3.
IR: 3027 (m), 2856 (m), 1636 (m), 1604 (s), 1592 (s), 1365 (m), 1157 (s), 781 (s)
HRMS: Calculated for $C_{39}H_{47}O_4Si$ $[M+H]^+$: 607.3238. Found: 607.3238.
Optical rotation: $[\alpha]_D^{20}$: -70.8 (c = 0.50, $CHCl_3$) for an enantiomerically enriched sample of 95.5 : 4.5 er.
Regioselectivity was determined by analysis of relevant NOE interactions (see Supporting Information Spectrums).



(1*S*,6*S*,7*S*,8*R*)-8-(3-Hydroxy-5-methoxyphenyl)-5-methoxy-4-(3-methylbut-2-en-1-yl)-7-phenyl-1-((*E*)-styryl)bicyclo[4.2.0]oct-4-en-3-one (1): A flame-dried 25 mL sealed tube equipped with a stir bar was cooled under vacuum. After backfilled with N_2, alkene **25** (150 mg, 0.250 mmol, 1.00 eq.) was added. The flask was evacuated/backfilled with N_2 (x 3) and capped with a dry ice/acetone condenser. The sealed tube was cooled to -78 °C in a dry ice/acetone and isobutene (5 mL) was added via the dry ice/acetone condenser. Then a solution of Hoveyda-Grubbs II catalyst **26** (15 mg, 0.025 mmol, 0.10 eq.) in DCM (0.2 mL) was added. The tube was sealed and heated to 50 °C in an oil bath for 24 h. After cooled back down to -78 °C in a dry ice/acetone bath, the seal was open and another portion of Hoveyda-Grubbs II catalyst **26** (15 mg, 0.025 mmol, 0.10 eq.) in DCM (0.2 mL) was added. The reaction was heated to 50 °C in an oil bath for another 24 h. After again cooled back down to -78 °C in a dry ice/acetone bath, the seal was open, and the sealed tube was placed into an ice bath to vent all the isobutene. When bubble evolution ceased, THF (5 mL) was added followed by addition of TBAF (1 M in THF, 0.5 mL, 0.5 mmol, 2 eq.) at the same temperature. After 0.5 h, the reaction was quenched with saturated NH_4Cl solution (5 mL). The aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layer was washed with brine (10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated by rotary evaporation. The residue was purified by quick FCC (pentane : Et_2O = 1 : 1.5) to afford cajanusine **1** (98 mg, 82% yield) as pale yellow solid
(Note: Natural product was not very stable on silica gel. We observed decomposition when long time standing on column or prepTLC.)

^{1}H NMR (600 MHz, $CDCl_3$): Spectrums vary due to potential aggregation at different temperatures and concentrations (see following discussion). For 10 mg / 0.5 mL $CDCl_3$ at 20 ºC: δ 7.44 – 7.09 (m, 10H), 6.50 (d, *J* = 16.2 Hz, 1H), δ 6.33 – 6.18 (m, 3H), 5.97 (s, 0.66H), 5.90 (s, 0.33H), 5.22 (t, *J* = 7.2 Hz, 1H), 4.20 (dd, *J* = 11.7, 9.3 Hz, 1H), 4.01 (d, *J* = 11.7 Hz, 1H), 3.85 (d, *J* = 9.2 Hz, 1H), 3.65 (s, 3H), 3.25 (s, 3H), 3.15 (dd, *J* = 13.8, 7.6 Hz, 1H), 3.06 (dd, *J* = 13.8, 7.3 Hz, 1H), 2.83 (d, *J* = 16.9 Hz, 0.66H), 2.82 (d, *J* = 16.9 Hz, 0.33H), 2.56 (d, *J* = 16.9 Hz, 0.66H). 2.55 (d, *J* = 16.9 Hz, 0.33H).1.72 (s, 3H), 1.70 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): No minor peaks were detected at different temperatures and concentrations. δ 197.0, 168.9, 161.0, 157.2, 140.0, 137.6, 137.0, 132.2, 131.7, 129.3, 128.9, 128.8, 128.6, 128.0, 127.7, 126.4, 122.4, 120.7, 107.7, 106.1, 100.1, 55.4, 55.1, 51.0, 45.0, 44.0, 42.4, 42.3, 26.0, 22.3, 17.9.
IR: 3390 (br), 2926 (m), 2852 (m), 1596 (s), 1453 (s), 1370 (m), 1154 (m), 697 (m)
HRMS: Calculated for $C_{35}H_{37}O_4$ $[M+H]^+$: 521.2686. Found: 521.2688.
Optical rotation: $[\alpha]_D^{20}$: -201.0 (c = 0.30, MeOH) for an enantiomerically enriched sample of 95.5 : 4.5 er. {Literature: $[\alpha]_D^{25}$: -222.0 (c = 0.30, MeOH)}[20]
Melting point: 163 ºC – 165 ºC (Literature: 164 ºC – 165 ºC)[20]

^{1}H-NMR (600 MHz, $CDCl_3$) Comparison for Temperatures and Concentrations:



Comparison of ^{1}H NMR ($CDCl_3$) Spectroscopic Data Natural[25] and Synthetic Ca*janusine* (10 mg in 0.5 mL $CDCl_3$):

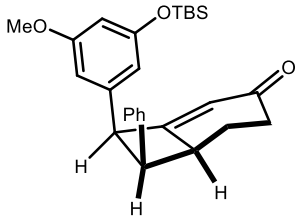
A: Natural δH [ppm, mult, *J* (Hz)], 300 MHz	B: Our Synthetic δH [ppm, mult, *J* (Hz)], 600 MHz	Error (B – A) $\Delta\delta$/ppm
7.31-7.24 (m, 10H)	7.32-7.20 (m, 10H)	-
6.50 (d, *J* = 16.2 Hz, 1H)	6.50 (d, *J* = 16.2 Hz, 1H)	0.00
6.32-6.22 (m, *J* = 4H)	δ 6.33 – 6.18 (m, 4H)	-
5.22 (dd, *J* = 7.2, 7.2 Hz, 1H)	5.22 (t, *J* = 7.2 Hz, 1H)	0.00
-	5.97 (s, 0.66H)	-
-	5.88 (s, 0.33H)	-
4.21 (dd, *J* = 11.7, 9.3 Hz, 1H)	4.20 (dd, *J* = 11.7, 9.3 Hz, 1H)	-0.01
4.01 (d, *J* = 11.7 Hz, 1H)	4.01 (d, *J* = 11.7 Hz, 1H),	0.00
3.85 (d, *J* = 9.3 Hz)	3.85 (d, *J* = 9.2 Hz, 1H)	0.00
3.64 (s, 3H)	3.65 (s, 3H)	0.01
3.25 (s, 3H)	3.25 (s, 3H)	0.00
3.16 (dd, *J*= 13.8, 7.2 Hz, 1H)	3.15 (dd, *J* = 13.8, 7.6 Hz, 1H)	-0.01
3.06 (dd, *J*= 13.8, 7.2 Hz, 1H)	3.15 (dd, *J* = 13.8, 7.6 Hz, 1H)	0.00
2.84 (d, *J* = 17.1 Hz, 1H)	2.83 (d, *J* = 16.9 Hz, 0.66H)	-0.01
	2.82 (d, *J* = 16.9 Hz, 0.33H)	-0.02
2.55 (d, *J* = 17.1 Hz, 1H)	2.56 (d, *J* = 16.9 Hz, 0.66H).	0.01
	2.55 (d, *J* = 16.9 Hz, 0.33H)	0.00
1.73 (s, 3H)	1.72 (s, 3H)	-0.01
1.70 (s, 3H)	1.70 (s, 3H)	0.00

Comparison of ^{13}C NMR ($CDCl_3$) Spectroscopic Data Natural[25] and Synthetic Cajanusine:

Natural[6] δ (ppm) 75 MHz	our Synthetic δ (ppm) 100 MHz	Error (B – A) $\Delta\delta$/ppm
197.3	197.0	-0.3
169.2	168.9	-0.3
160.9	161.0	0.1
157.4	157.2	-0.2
139.8	140.0	0.2
137.5	137.6	0.1
137.0	137.0	0.0
132.1	132.2	0.1
131.7	131.7	0.0
129.2	129.3	0.1
128.8	128.9	0.1
128.7	128.8	0.1
128.6	128.6	0.0
128.0	128.0	0.0
127.7	127.7	0.0
126.4	126.4	0.0
122.3	122.4	0.1
120.6	120.7	0.1
107.7	107.7	0.0
105.8	106.0	0.2
100.0	100.0	0.0
55.4	55.4	0.0
55.1	55.1	0.0
50.1	50.1	0.0
45.0	45.0	0.0
43.9	44.0	0.1
42.4	42.4	0.0
42.2	42.3	0.1
26.0	26.1	0.1
22.2	22.3	0.1
17.9	18.0	0.1

Coordinates and Energies for Computed Structures:

Geometries optimized with M06-2X[26]/6-311g(d,p) and characterized by frequency analysis using Gaussian09.[27]



Zero-point correction= 0.550307 (Hartree/Particle)
Thermal correction to Energy= 0.582316
Thermal correction to Enthalpy= 0.583260
Thermal correction to Gibbs Free Energy= 0.484738
Sum of electronic and zero-point Energies= -1563.795055
Sum of electronic and thermal Energies= -1563.763046
Sum of electronic and thermal Enthalpies= -1563.762102
Sum of electronic and thermal Free Energies= -1563.860624

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.973949	1.815423	0.855973
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3	6	0	2.428026	3.775424	-0.480450
4	6	0	3.839672	3.784001	0.099177
5	6	0	4.382151	2.379085	0.398186
6	6	0	3.395832	1.700272	1.332637
7	1	0	3.796628	4.368968	1.026655
8	1	0	4.472596	4.330856	-0.600480
9	1	0	5.383080	2.436199	0.831300
10	1	0	4.457208	1.813585	-0.534581
11	1	0	3.493785	2.087594	2.352581
12	1	0	0.536886	2.652221	-0.498604
13	8	0	2.064911	4.627733	-1.261084
14	6	0	1.612807	0.465726	1.433860
15	6	0	3.156847	0.142644	1.408068
16	1	0	3.523597	-0.312155	2.328058
17	1	0	1.359916	0.622591	2.489942
18	6	0	3.692450	-0.632777	0.231888
19	6	0	3.169058	-0.513081	-1.060769
20	6	0	4.772794	-1.494087	0.431458
21	6	0	3.715478	-1.233489	-2.115778
22	1	0	2.320334	0.135423	-1.245529
23	6	0	5.320861	-2.218038	-0.623680

24	1	0	5.188324	-1.601033	1.428544
25	6	0	4.792724	-2.089616	-1.902407
26	1	0	3.292705	-1.129922	-3.108256
27	1	0	6.158388	-2.882086	-0.443392
28	1	0	5.213786	-2.652449	-2.727145
29	6	0	0.566704	-0.422092	0.815780
30	6	0	0.796070	-1.795416	0.698176
31	6	0	-0.644984	0.123015	0.407587
32	6	0	-0.184951	-2.611975	0.138862
33	1	0	1.743302	-2.206042	1.017409
34	6	0	-1.627175	-0.708371	-0.137621
35	1	0	-0.855211	1.180336	0.514538
36	6	0	-1.402514	-2.069732	-0.279107
37	1	0	-2.152120	-2.712116	-0.724413
38	8	0	-0.039834	-3.945850	-0.047410
39	6	0	1.218535	-4.517532	0.262927
40	1	0	2.021900	-4.044687	-0.311506
41	1	0	1.146250	-5.567824	-0.012374
42	1	0	1.438251	-4.440918	1.332454
43	8	0	-2.802758	-0.162161	-0.557093
44	14	0	-4.218137	-0.140409	0.367298
45	6	0	-4.828813	-1.892936	0.597740
46	1	0	-4.138579	-2.467409	1.222350
47	1	0	-4.933525	-2.415148	-0.356723
48	1	0	-5.803460	-1.903086	1.095472
49	6	0	-3.829951	0.615725	2.032938
50	1	0	-3.035329	0.053279	2.532820
51	1	0	-4.707509	0.589120	2.685668
52	1	0	-3.501836	1.655229	1.949731
53	6	0	-5.410073	0.908818	-0.647009
54	6	0	-6.676594	1.184799	0.176252
55	1	0	-7.390760	1.766524	-0.418431
56	1	0	-6.455819	1.761484	1.079721
57	1	0	-7.180937	0.261162	0.478567
58	6	0	-5.789467	0.161117	-1.932973
59	1	0	-6.328184	-0.766591	-1.717666
60	1	0	-4.906854	-0.088385	-2.529225
61	1	0	-6.443879	0.786326	-2.552085
62	6	0	-4.741320	2.240894	-1.013499
63	1	0	-4.457506	2.812596	-0.124307
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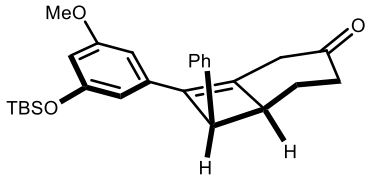

Zero-point correction= 0.549495 (Hartree/Particle)
Thermal correction to Energy= 0.581907
Thermal correction to Enthalpy= 0.582852
Thermal correction to Gibbs Free Energy= 0.482375
Sum of electronic and zero-point Energies= -1563.796663
Sum of electronic and thermal Energies= -1563.764250
Sum of electronic and thermal Enthalpies= -1563.763306
Sum of electronic and thermal Free Energies= -1563.863782

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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2	6	0	3.205193	1.727967	1.241530
3	6	0	4.188919	2.411054	0.300471
4	6	0	3.687220	3.848252	0.059371
5	6	0	2.284749	3.892372	-0.529491
6	6	0	1.202241	3.073943	0.184803
7	6	0	1.601389	0.482375	0.688825
8	6	0	2.991070	0.161724	1.230806
9	8	0	2.017308	4.552749	-1.500142
10	6	0	0.502682	-0.407365	0.313635
11	6	0	-0.763521	0.096733	0.013945
12	6	0	-1.784872	-0.780998	-0.347296
13	6	0	-1.555743	-2.149518	-0.411773
14	6	0	-0.289021	-2.651789	-0.106755
15	6	0	0.739332	-1.788089	0.264468
16	6	0	3.940989	-0.633393	0.370372
17	6	0	5.075186	-1.207978	0.949193
18	6	0	5.992339	-1.913150	0.177842
19	6	0	5.785691	-2.060104	-1.190025
20	6	0	4.657647	-1.496494	-1.777607
21	6	0	3.742772	-0.789124	-1.003932
22	8	0	-3.017339	-0.288882	-0.658399
23	14	0	-4.253950	-0.069849	0.473957
24	6	0	-5.679868	0.632141	-0.537376
25	6	0	-4.662557	-1.722970	1.246111
26	6	0	-3.664586	1.112740	1.797697
27	6	0	-6.198530	-0.437424	-1.508740
28	6	0	-6.814104	1.059668	0.405229
29	6	0	-5.195091	1.849887	-1.336236
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31	6	0	1.130695	-4.542436	0.057916
32	1	0	3.314466	2.125758	2.256768
33	1	0	5.203025	2.430649	0.706888
34	1	0	4.229955	1.877481	-0.653544
35	1	0	4.341563	4.404187	-0.612185
36	1	0	3.652068	4.381159	1.018507
37	1	0	0.854134	3.691040	1.025417
38	1	0	0.368469	2.928578	-0.501595
39	1	0	2.986464	-0.255845	2.242178
40	1	0	-0.976685	1.157217	0.066275
41	1	0	-2.348220	-2.828313	-0.701507
42	1	0	1.725202	-2.162392	0.502128
43	1	0	5.237592	-1.100828	2.017276
44	1	0	6.866198	-2.351780	0.645856
45	1	0	6.496395	-2.612964	-1.792975
46	1	0	4.485601	-1.609687	-2.841813
47	1	0	2.860759	-0.361800	-1.469629
48	1	0	-3.814631	-2.099962	1.825628
49	1	0	-5.511714	-1.635176	1.930785
50	1	0	-4.913779	-2.474360	0.493229
51	1	0	-4.424750	1.231826	2.575497
52	1	0	-3.435086	2.103116	1.395543
53	1	0	-2.761497	0.729001	2.281892
54	1	0	-5.406322	-0.797144	-2.171821
55	1	0	-6.995158	-0.020533	-2.136426
56	1	0	-6.615214	-1.298591	-0.977794
57	1	0	-6.499374	1.859340	1.082728
58	1	0	-7.663063	1.437316	-0.176790
59	1	0	-7.180606	0.225555	1.012533
60	1	0	-4.394067	1.580085	-2.028927
61	1	0	-4.823062	2.644316	-0.681713
62	1	0	-6.022819	2.267898	-1.921600
63	1	0	1.036682	-5.614487	-0.102790
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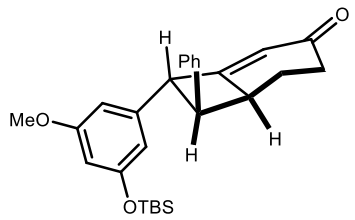

Zero-point correction= 0.549952 (Hartree/Particle)
Thermal correction to Energy= 0.582171
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Thermal correction to Gibbs Free Energy= 0.482228
Sum of electronic and zero-point Energies= -1563.796002
Sum of electronic and thermal Energies= -1563.763783
Sum of electronic and thermal Enthalpies= -1563.762839
Sum of electronic and thermal Free Energies= -1563.863726

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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4	6	0	2.548259	-3.560125	-1.065471
5	6	0	2.011307	-3.633024	0.362166
6	6	0	1.613642	-2.356089	1.001847
7	6	0	1.726488	0.251342	0.529201
8	6	0	2.792092	0.341800	-0.630853
9	8	0	1.910690	-4.691642	0.942224
10	6	0	0.443472	0.988372	0.213687
11	6	0	-0.733948	0.314139	-0.069355
12	6	0	-1.893888	1.043636	-0.361395
13	6	0	-1.873935	2.427479	-0.370378
14	6	0	-0.681015	3.102350	-0.086620
15	6	0	0.477812	2.389188	0.206180
16	6	0	4.230901	0.468697	-0.208136
17	6	0	5.136411	1.099137	-1.064974
18	6	0	6.484167	1.198759	-0.737822
19	6	0	6.952202	0.665762	0.458037
20	6	0	6.062165	0.033885	1.320111
21	6	0	4.714309	-0.064147	0.991199
22	8	0	-3.046854	0.383281	-0.659803
23	14	0	-4.131200	-0.189464	0.506603
24	6	0	-5.504667	-0.989518	-0.505185
25	6	0	-3.249451	-1.412333	1.613579
26	6	0	-4.733942	1.258376	1.523718
27	6	0	-4.960976	-2.235908	-1.217611
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29	6	0	-6.022792	0.006996	-1.551388
30	8	0	-0.756413	4.453978	-0.118674
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33	1	0	3.633705	-2.244866	-2.416785
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59	1	0	-6.331023	-2.097129	1.200555
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63	1	0	0.148968	6.236768	0.077525
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Renference:

[1]: Vakulya, B.; Varga, S.; Csámpai, A.; Soós, T. *Org. Lett.* **2005**, *7*, 1967-1969.
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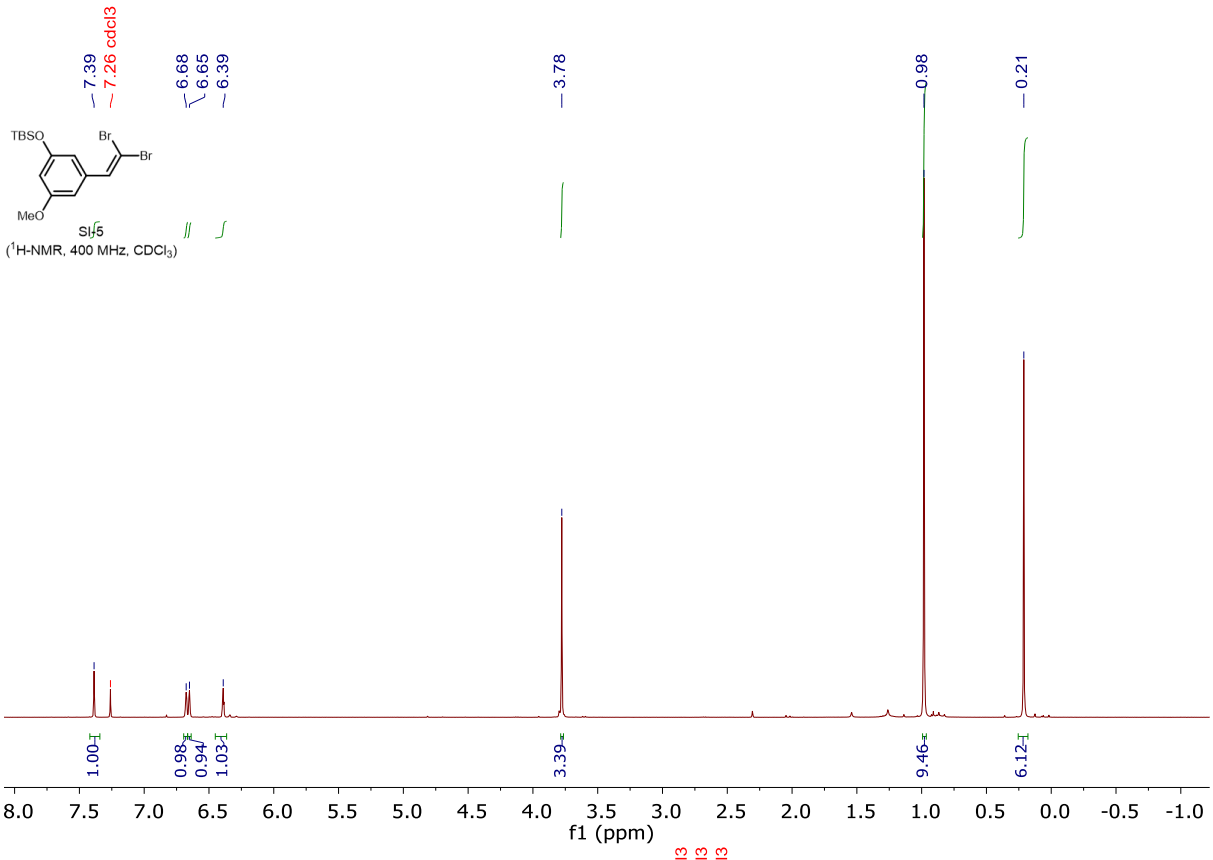
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0.21
TBSO
Br
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MeO
SI-5
(1H-NMR, 400 MHz, CDCl3)
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0.98
0.94
1.03
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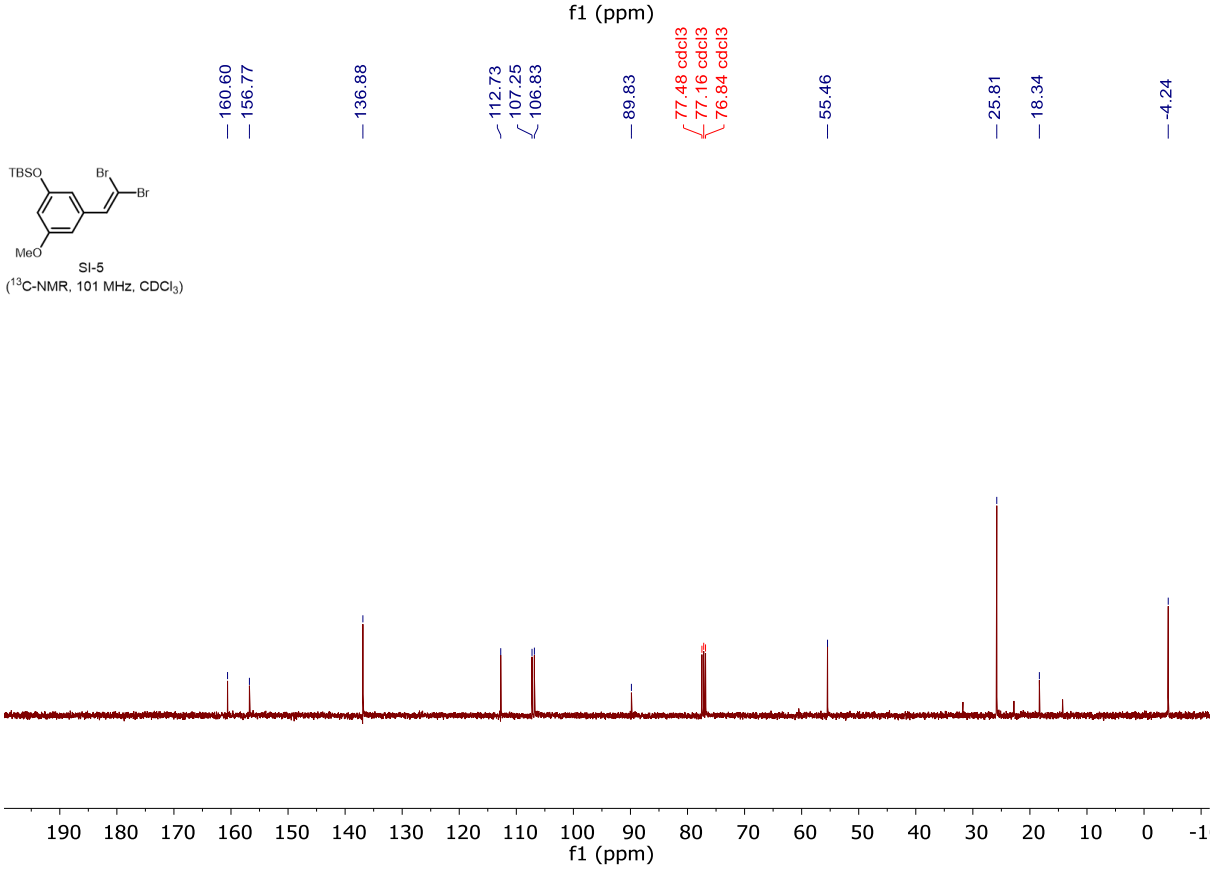
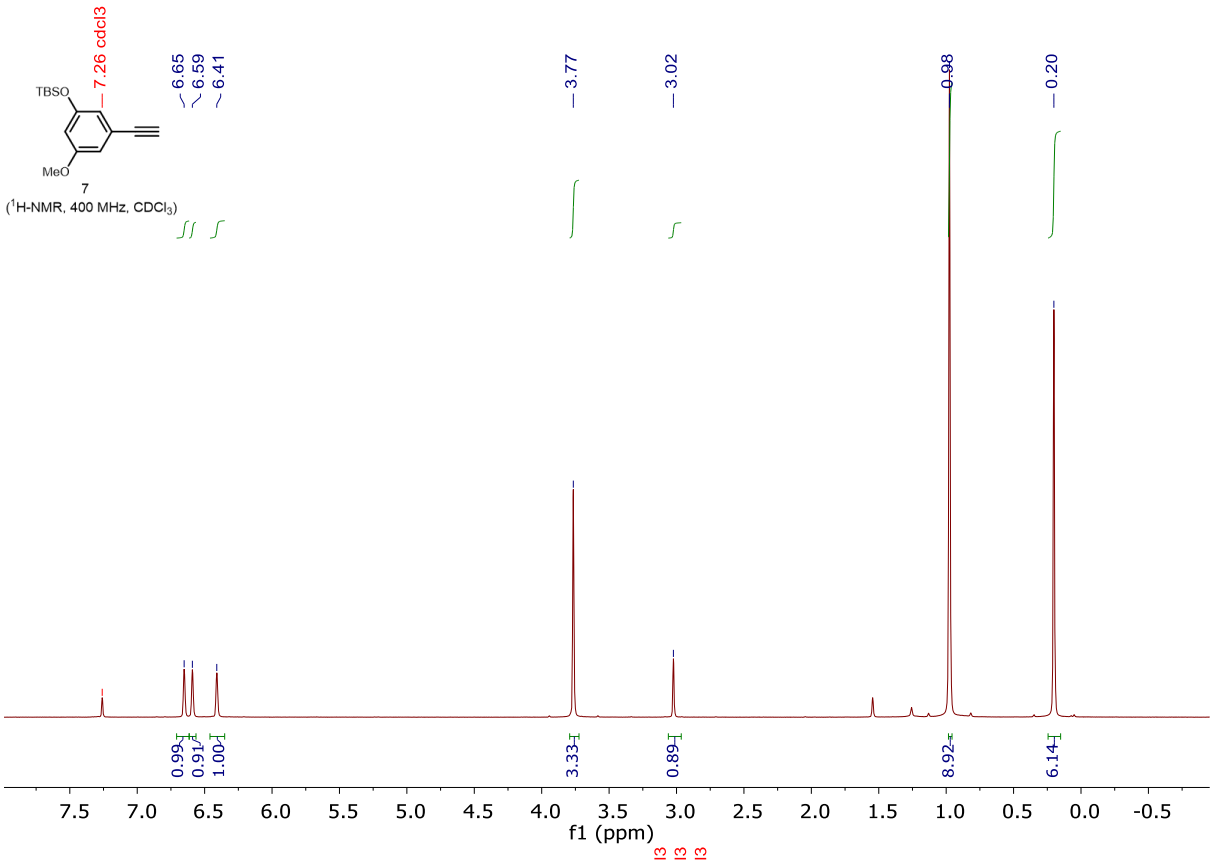
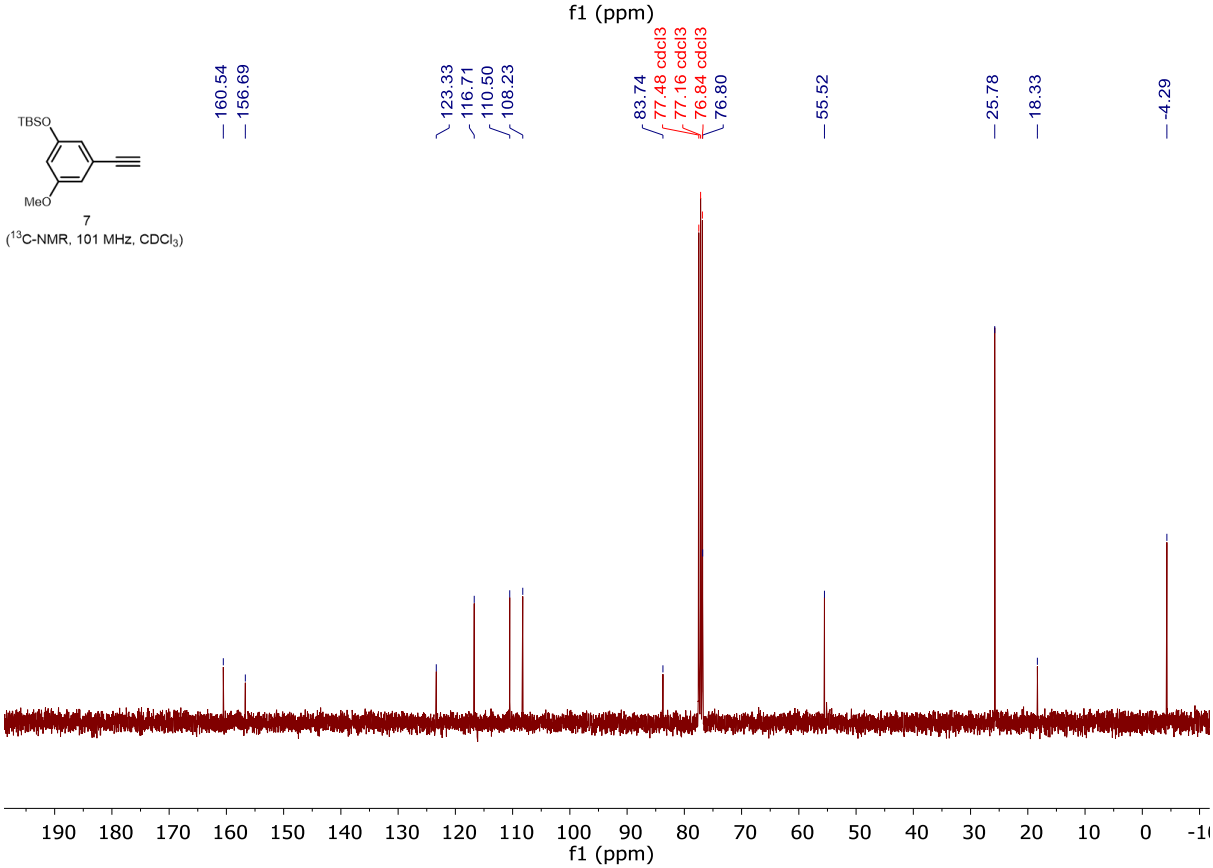
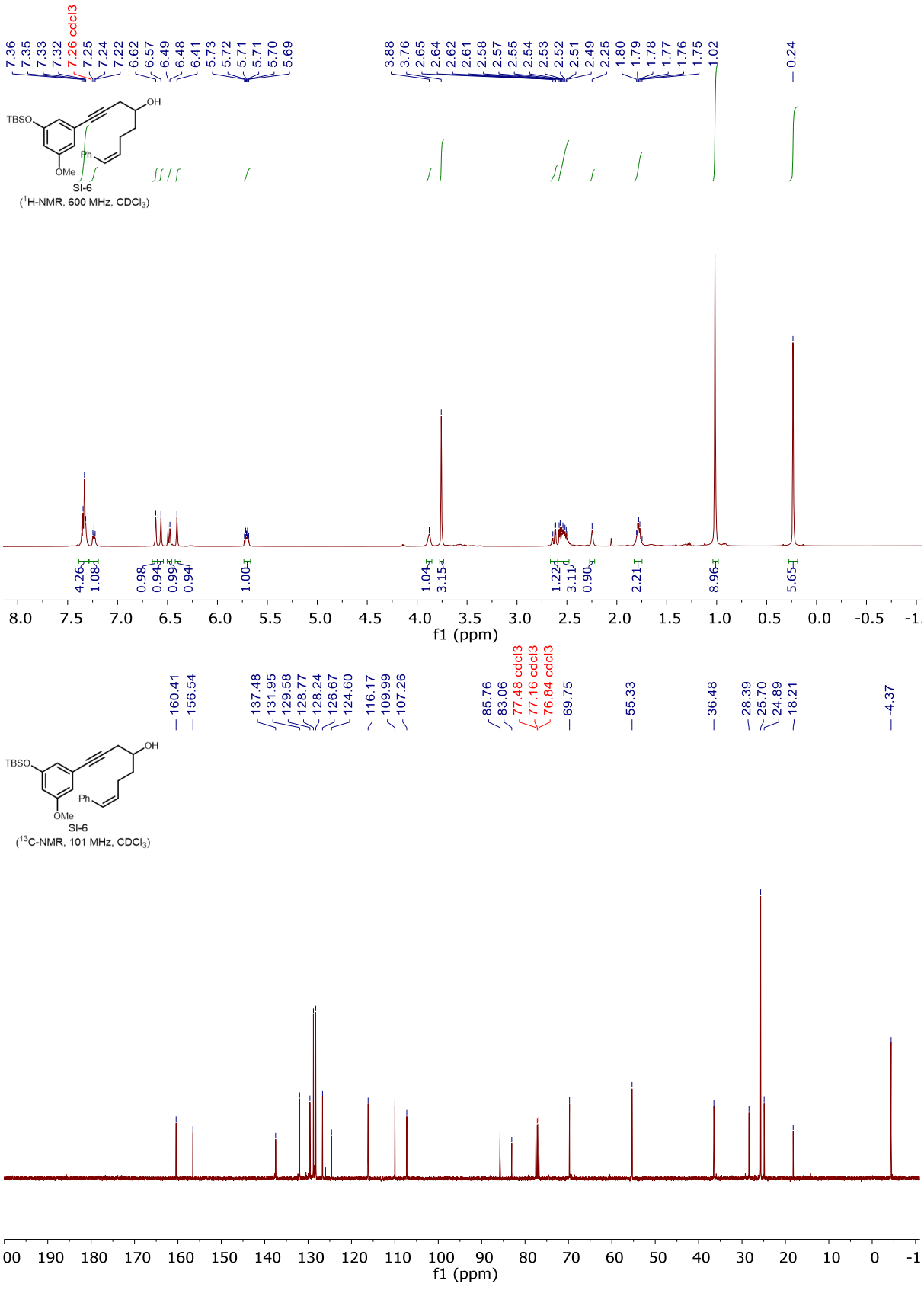
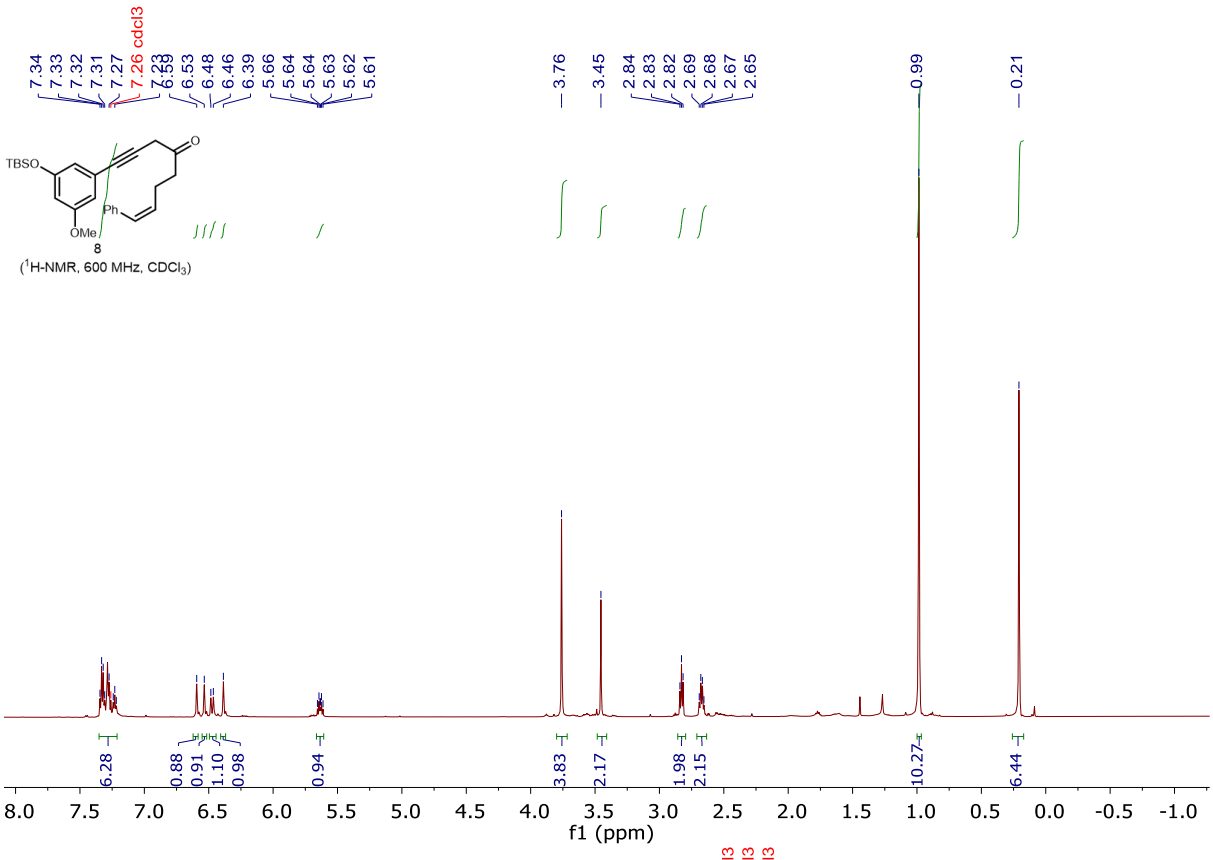
9.46
6.12
f1 (ppm)

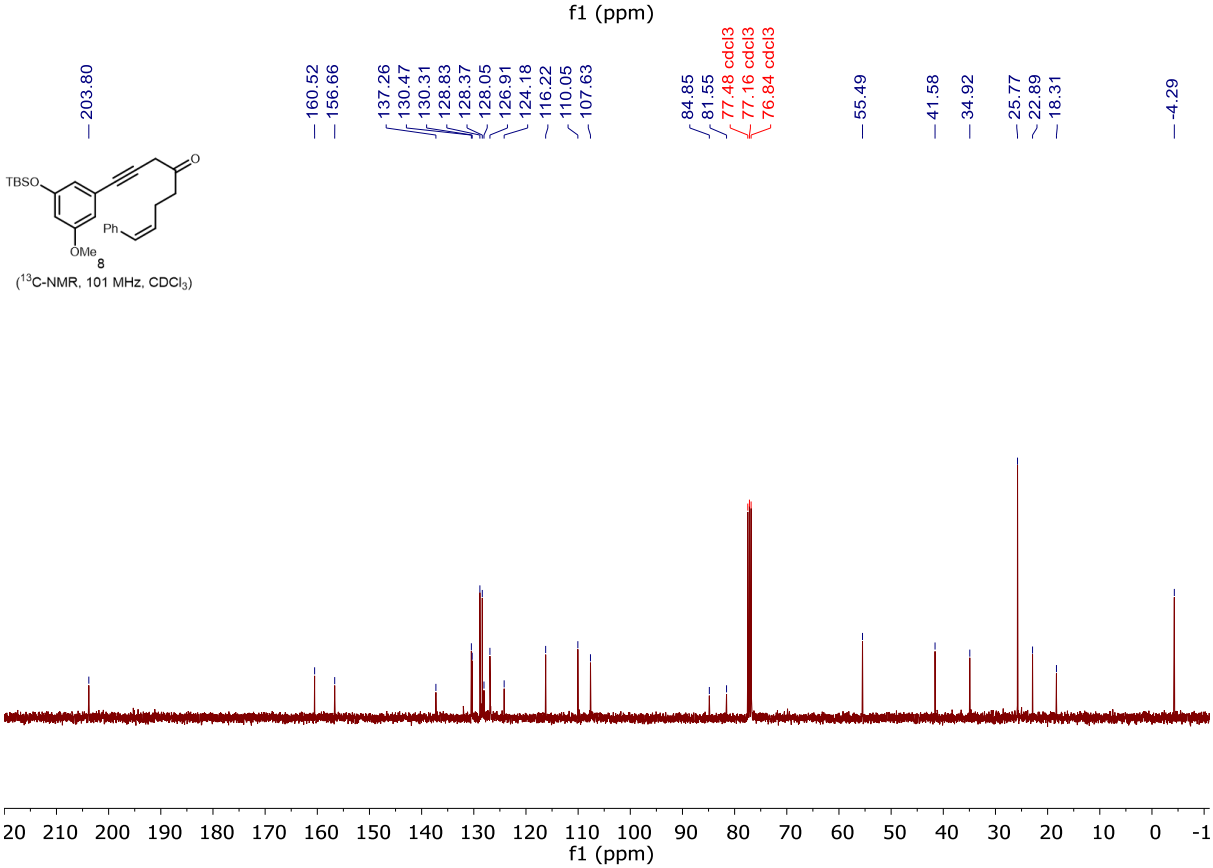

160.60
156.77
136.88
112.73
107.25
106.83
89.83
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
55.46
25.81
18.34
-4.24
TBSO
Br
Br
MeO
SI-5
(13C-NMR, 101 MHz, CDCl3)
f1 (ppm)

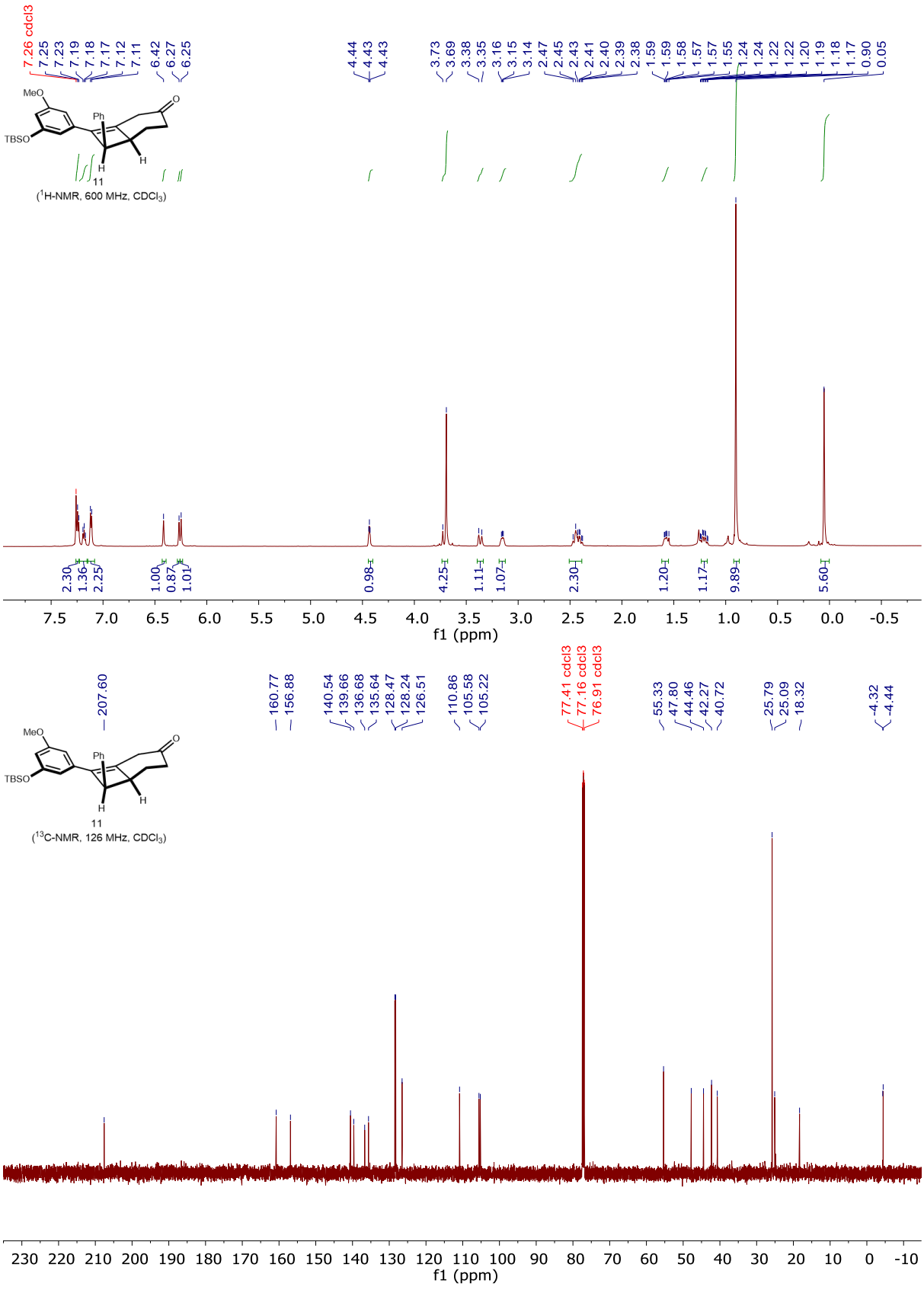

TBSO
MeO
7
(1H-NMR, 400 MHz, CDCl3)
7.26 cdcl3
6.65
6.59
6.41
3.77
3.02
0.98
0.20
0.99
0.91
1.00
3.33
0.89
8.92
6.14
f1 (ppm)

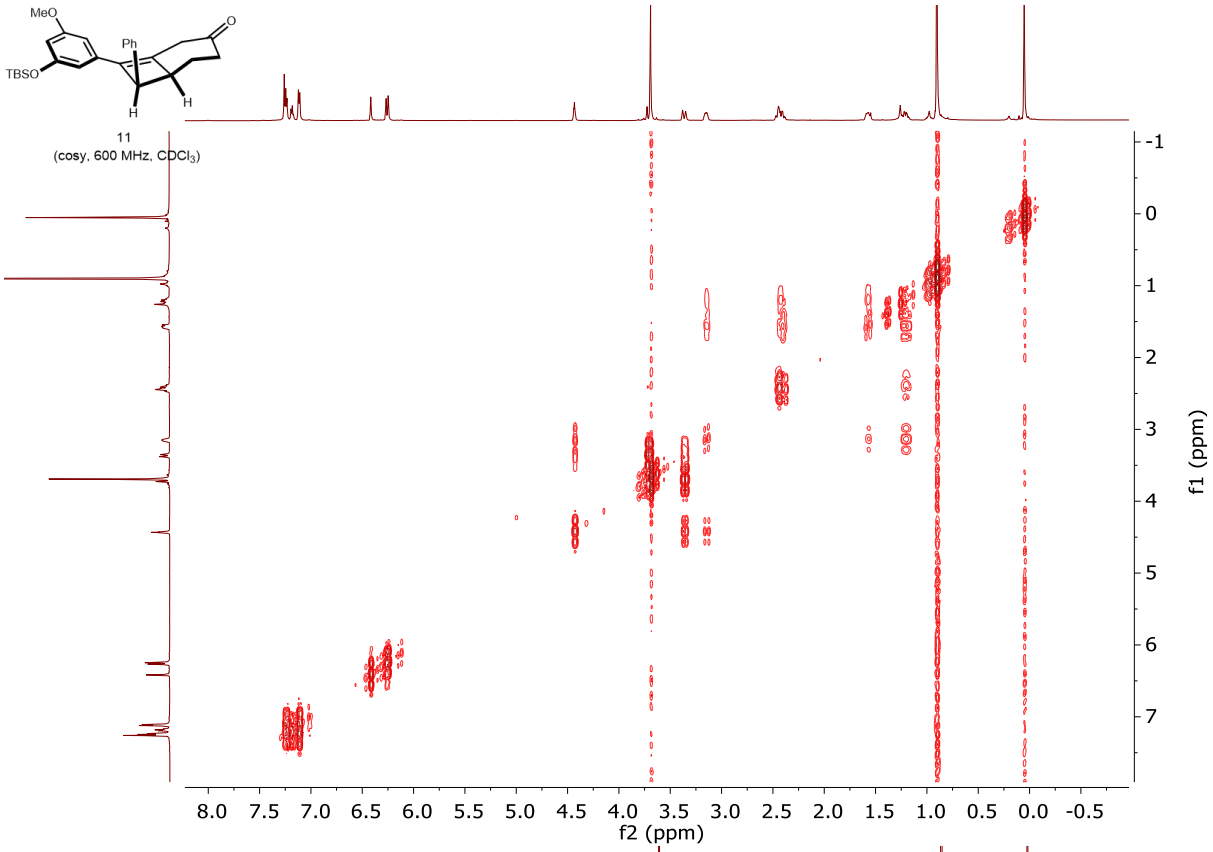

TBSO
MeO
7
(13C-NMR, 101 MHz, CDCl3)
160.54
156.69
123.33
116.71
110.50
108.23
83.74
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
76.80
55.52
25.78
18.33
-4.29
f1 (ppm)

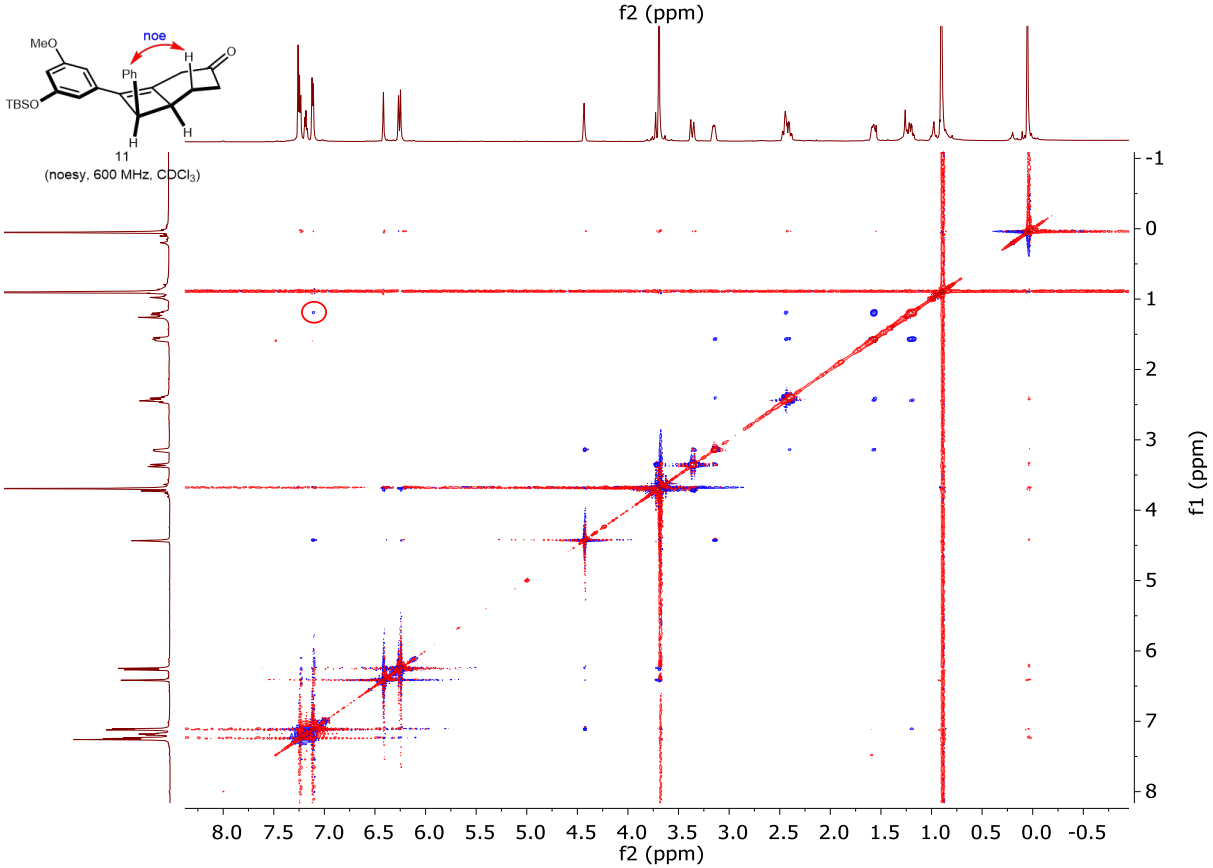

7.36
7.35
7.33
7.32
7.26 cdcl3
7.25
7.24
7.22
6.62
6.57
6.49
6.48
6.41
5.73
5.72
5.71
5.71
5.70
5.69
3.88
3.76
2.65
2.64
2.62
2.61
2.58
2.57
2.55
2.54
2.53
2.52
2.51
2.49
2.25
1.80
1.79
1.78
1.77
1.76
1.75
1.02
0.24
TBSO
OH
Ph
OMe
SI-6
(1H-NMR, 600 MHz, CDCl3)
4.26
1.08
0.98
0.94
0.99
0.94
1.00
1.04
3.15
1.22
3.11
0.90
2.21
8.96
5.65
f1 (ppm)
160.41
156.54
137.48
131.95
129.58
128.77
128.24
126.67
124.60
116.17
109.99
107.26
85.76
83.06
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
69.75
55.33
36.48
28.39
25.70
24.89
18.21
-4.37
TBSO
OH
Ph
OMe
SI-6
(13C-NMR, 101 MHz, CDCl3)
f1 (ppm)

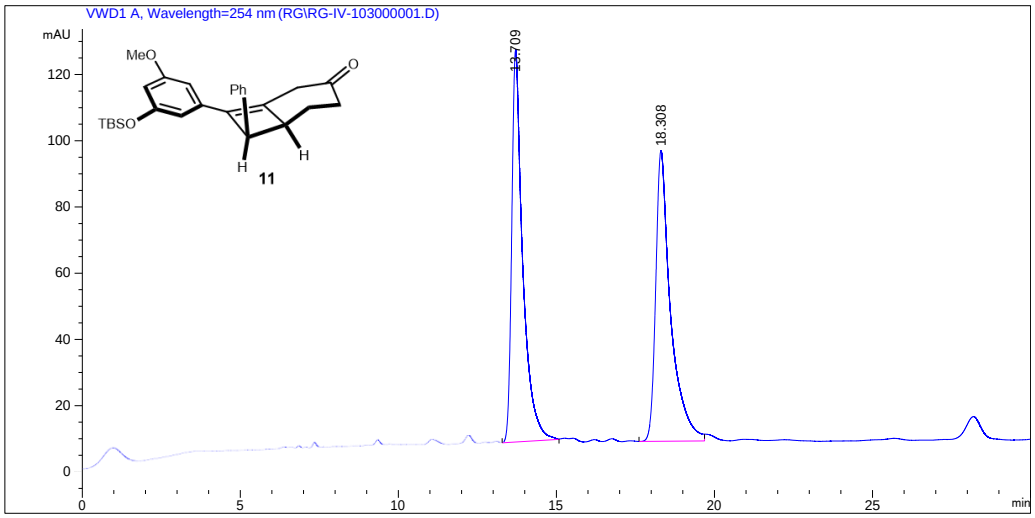

7.34
7.33
7.32
7.31
7.27
7.26 cdcl3
6.53
6.48
6.46
6.39
5.66
5.64
5.64
5.63
5.62
5.61
3.76
3.45
2.84
2.83
2.82
2.69
2.68
2.67
2.65
0.99
0.21
TBSO
OMe
Ph
O
8
(1H-NMR, 600 MHz, CDCl3)
6.28
0.88
0.91
1.10
0.98
0.94
3.83
2.17
1.98
2.15
10.27
6.44
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


203.80
160.52
156.66
137.26
130.47
130.31
128.83
128.37
128.05
126.91
124.18
116.22
110.05
107.63
84.85
81.55
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
55.49
41.58
34.92
25.77
22.89
18.31
-4.29
TBSO
OMe
Ph
O
8
(13C-NMR, 101 MHz, CDCl3)
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

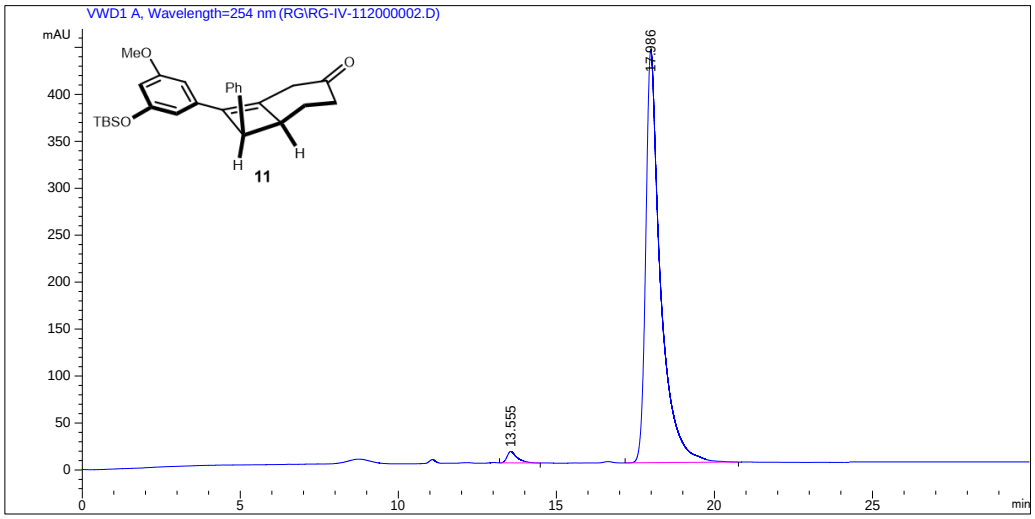

7.26 cdcl3
7.25
7.23
7.19
7.18
7.17
7.12
7.11
6.42
6.27
6.25
4.44
4.43
4.43
3.73
3.69
3.38
3.35
3.16
3.15
3.14
2.47
2.45
2.43
2.41
2.40
2.39
2.38
1.59
1.59
1.58
1.57
1.57
1.55
1.24
1.24
1.22
1.22
1.20
1.19
1.18
1.17
0.90
0.05
MeO
Ph
O
TBSO
H
H
11
(1H-NMR, 600 MHz, CDCl3)
2.30
1.36
2.25
1.00
0.87
1.01
0.98
4.25
1.11
1.07
2.30
1.20
1.17
9.89
5.60
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
207.60
160.77
156.88
140.54
139.66
136.68
135.64
128.47
128.24
126.51
110.86
105.58
105.22
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
55.33
47.80
44.46
42.27
40.72
25.79
25.09
18.32
-4.32
-4.44
MeO
Ph
O
TBSO
H
H
11
(13C-NMR, 126 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO
TBSO
Ph
O
H
H
11
(cosy, 600 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

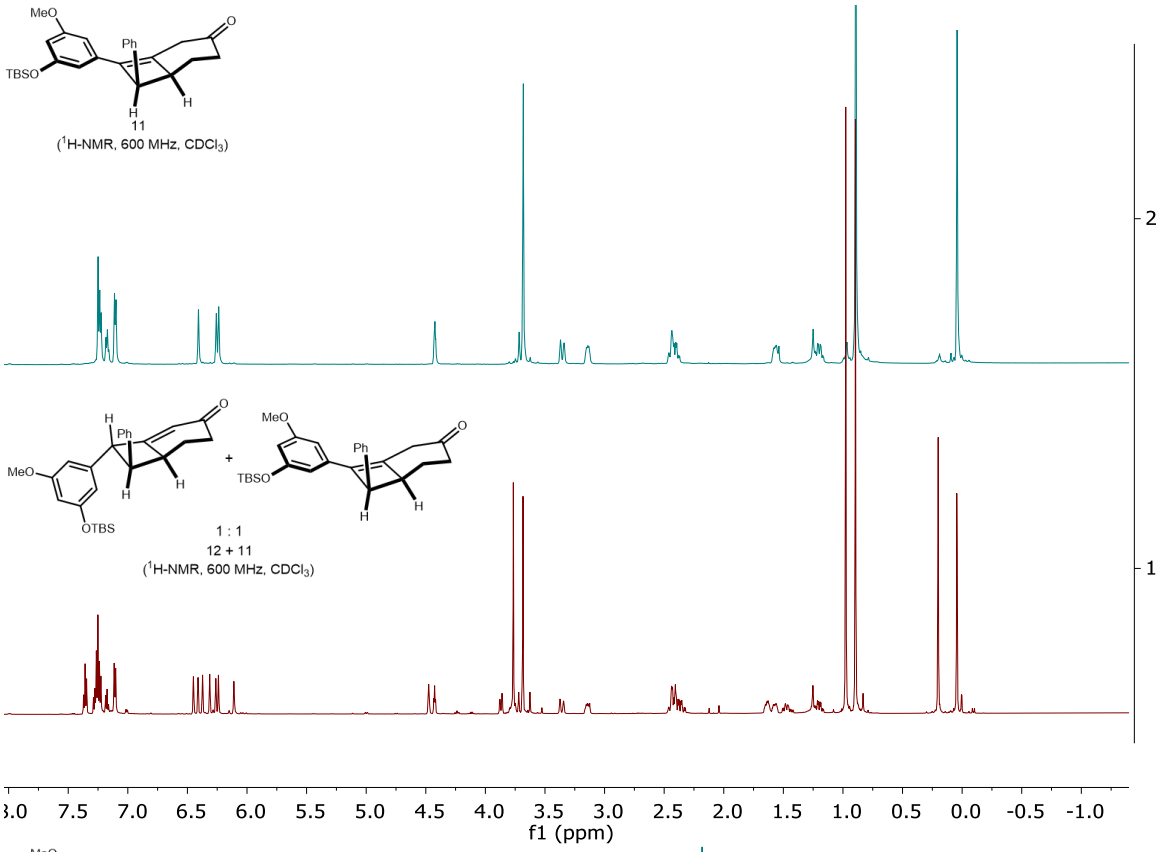

noe
MeO
TBSO
Ph
O
H
H
H
11
(noesy, 600 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

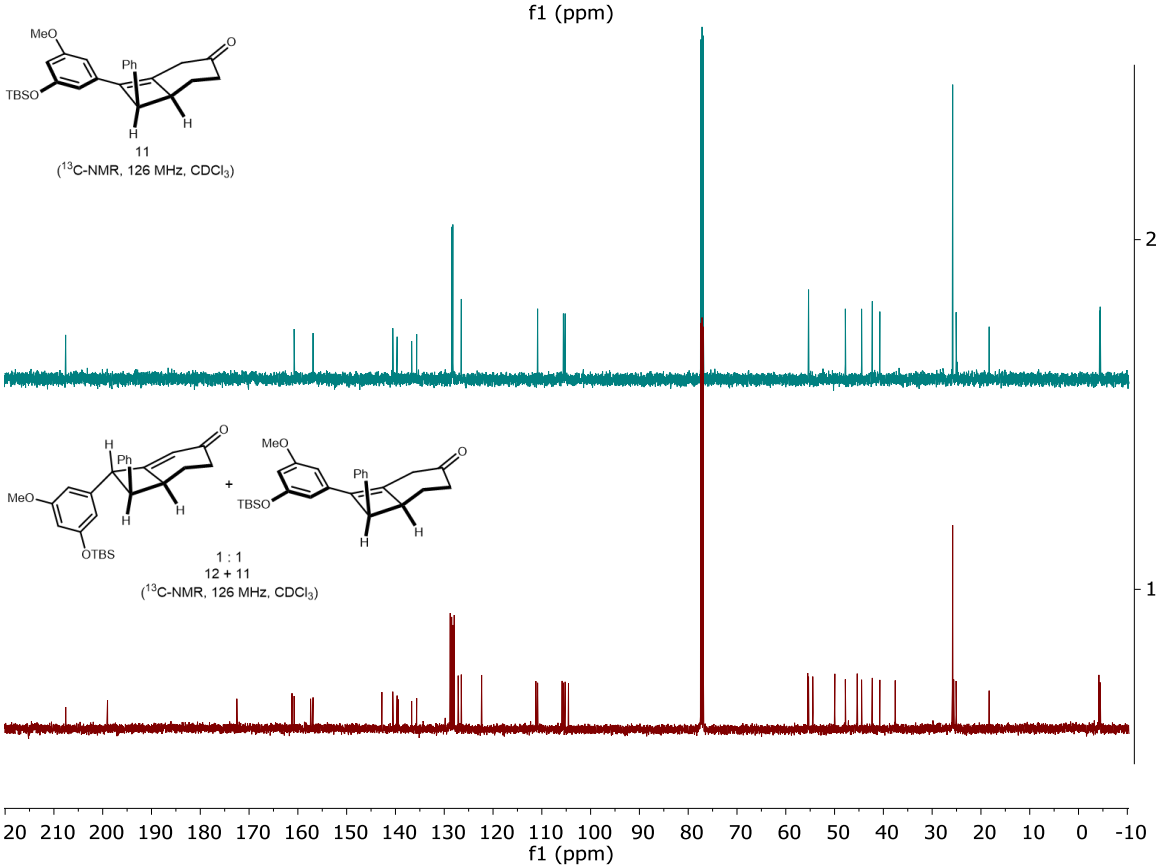


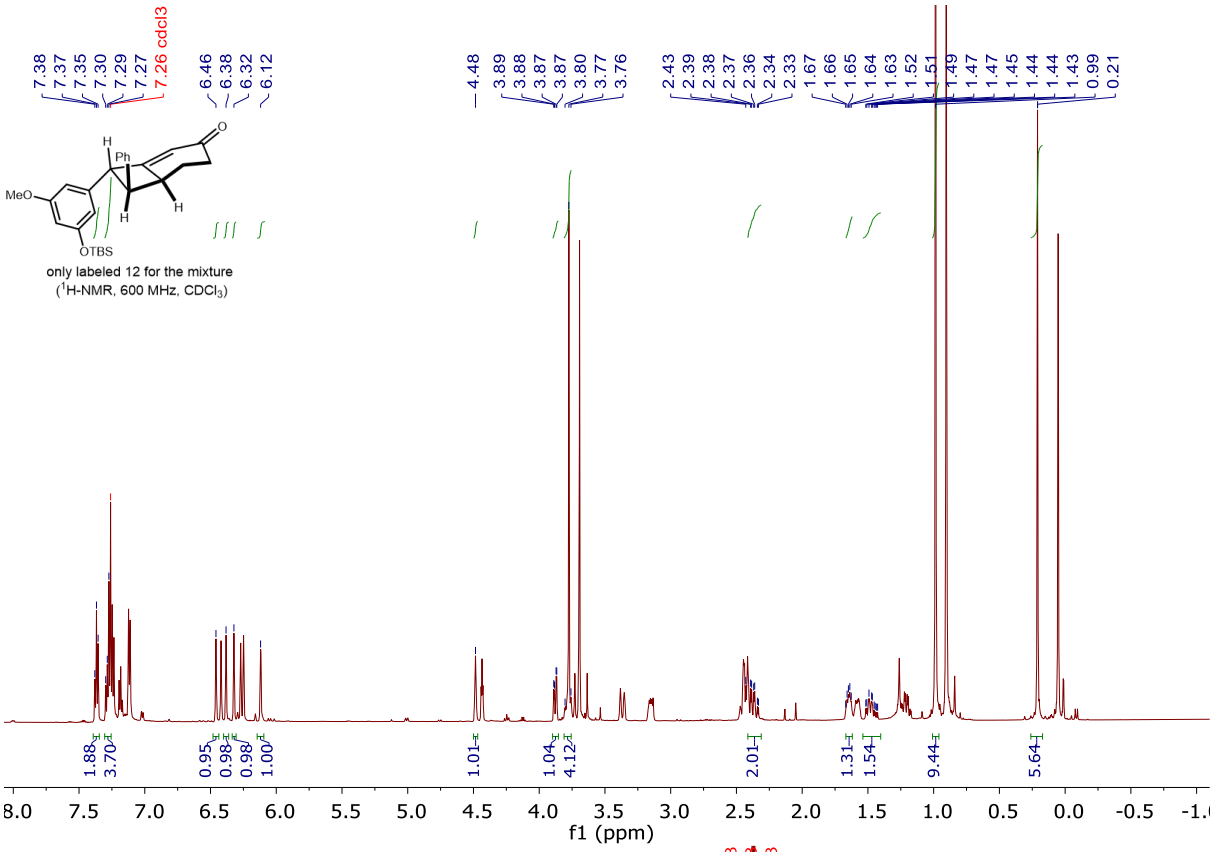
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.709	BV	0.3470	2867.04419	118.42130	49.8892
2	18.308	BV	0.4591	2879.77759	87.80560	50.1108

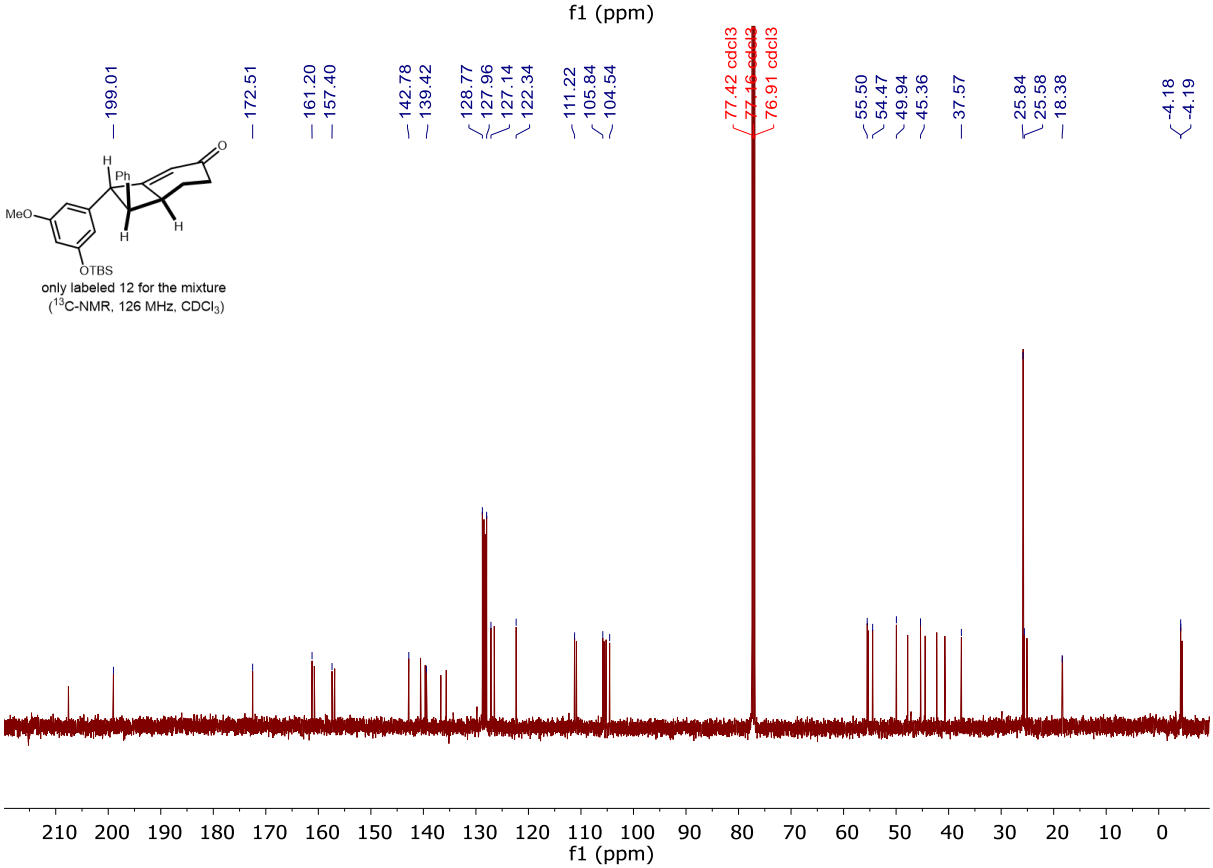


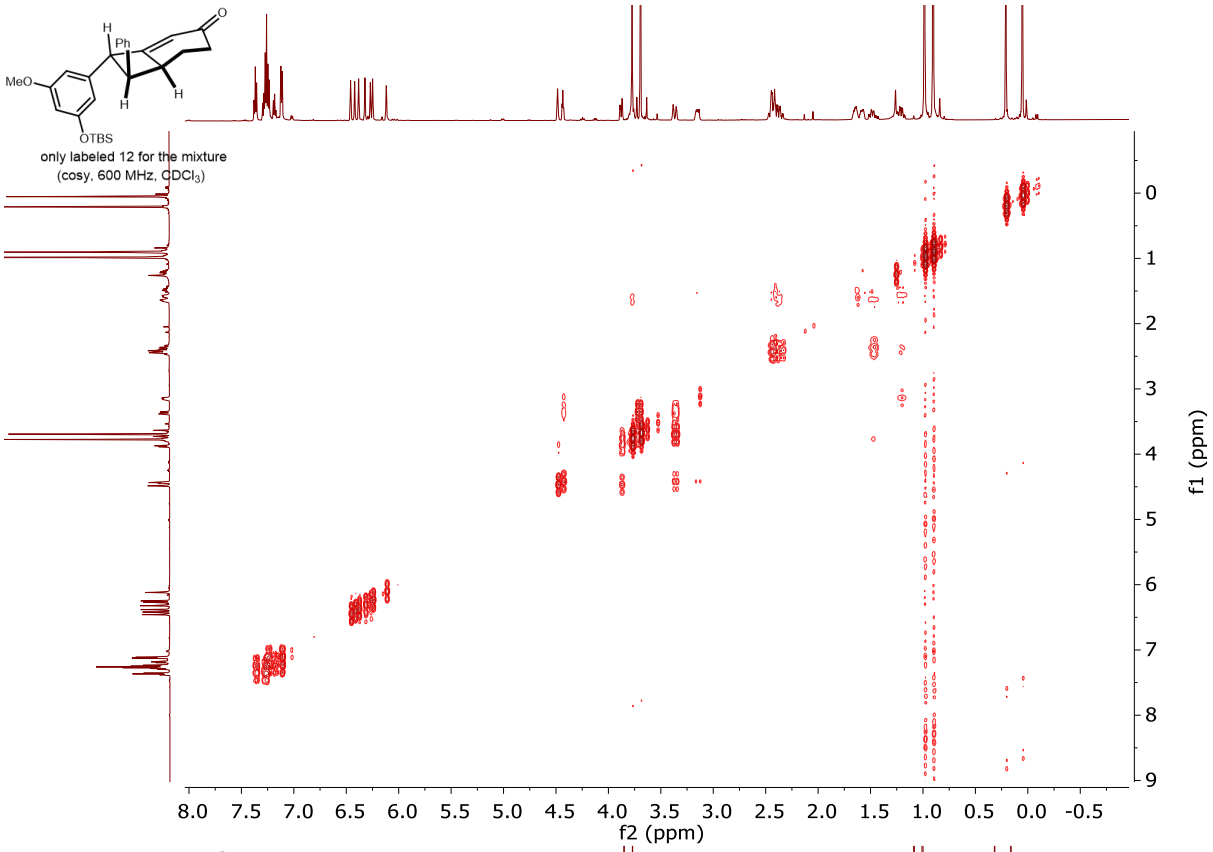
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.555	BB	0.2857	272.16254	12.22817	1.8755
2	17.986	BB	0.4579	1.42391e4	439.64291	98.1245

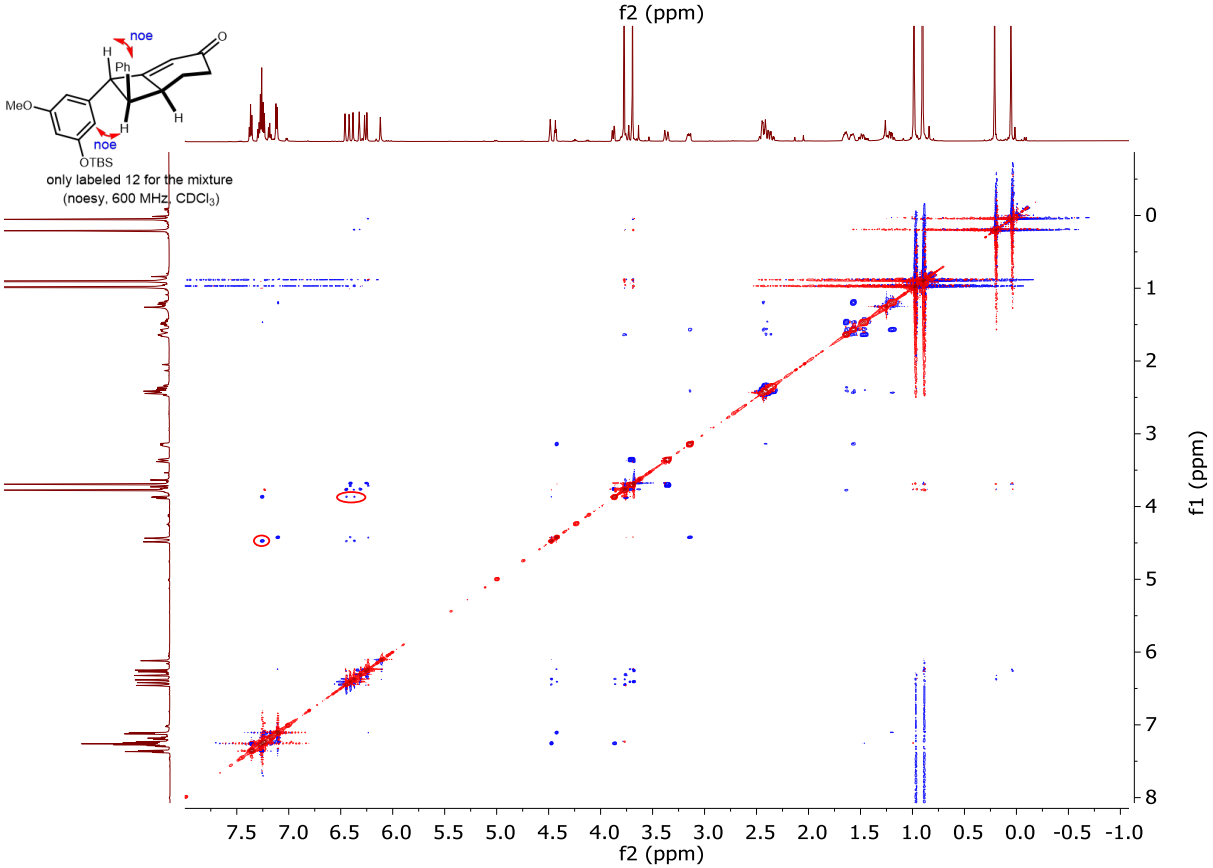

MeO
Ph
TBSO
O
H
H
11
(1H-NMR, 600 MHz, CDCl3)
2
1
MeO
OTBS
TBSO
1 : 1
12 + 11
(1H-NMR, 600 MHz, CDCl3)
f1 (ppm)

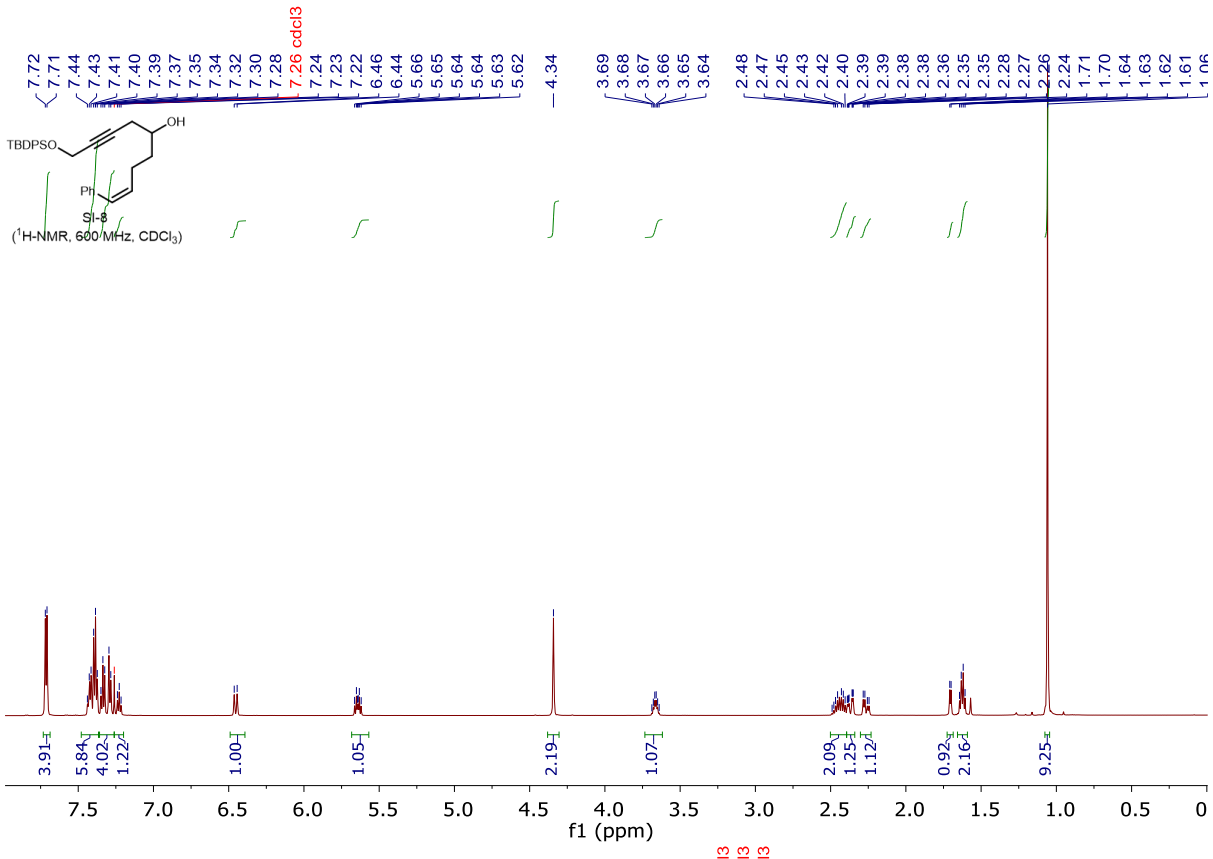

MeO
Ph
TBSO
O
H
H
11
(13C-NMR, 126 MHz, CDCl3)
2
1
MeO
OTBS
TBSO
1 : 1
12 + 11
(13C-NMR, 126 MHz, CDCl3)
f1 (ppm)

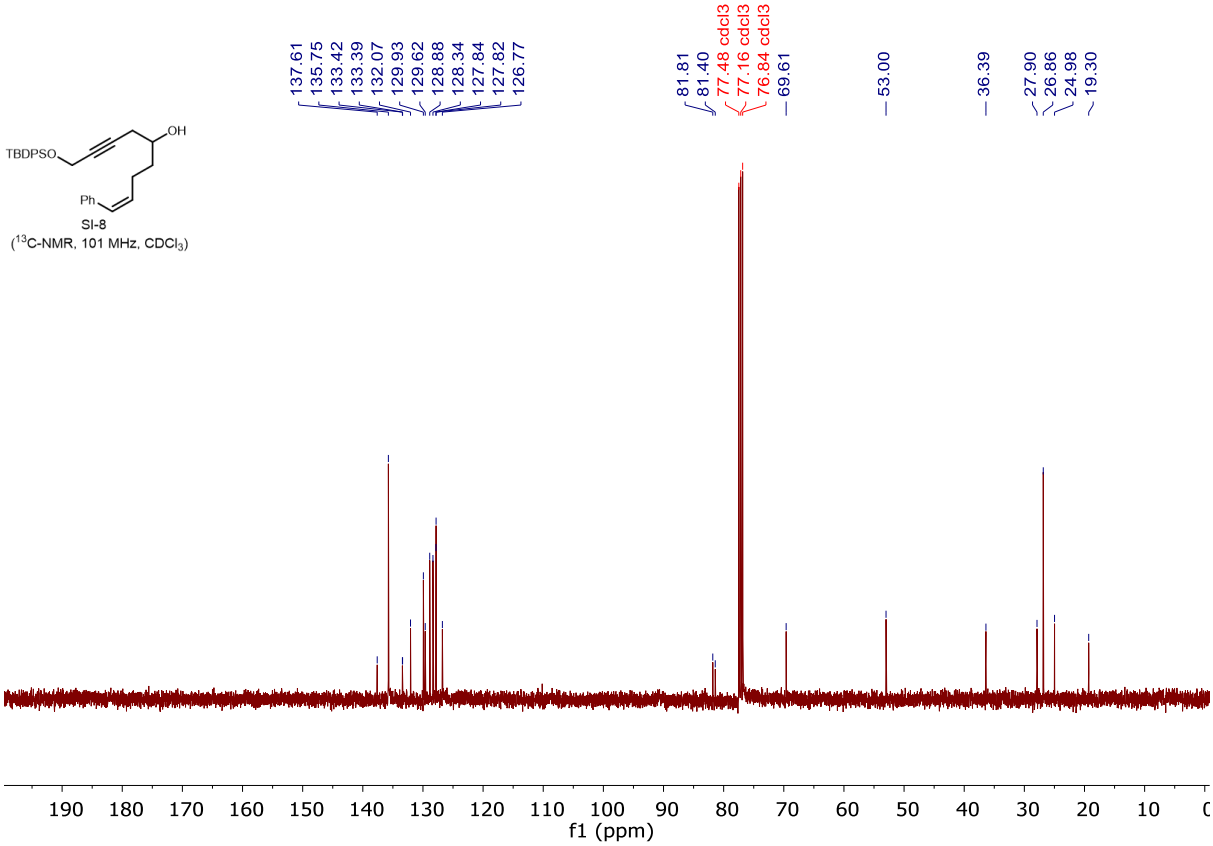

7.38
7.37
7.35
7.30
7.29
7.27
7.26 cdcl3
6.46
6.38
6.32
6.12
4.48
3.89
3.88
3.87
3.87
3.80
3.77
3.76
2.43
2.39
2.38
2.37
2.36
2.34
2.33
1.67
1.66
1.65
1.64
1.63
1.52
1.51
1.49
1.47
1.47
1.45
1.44
1.44
1.43
0.99
0.21
H
Ph
O
MeO
H
H
OTBS
only labeled 12 for the mixture
(1H-NMR, 600 MHz, CDCl3)
1.88
3.70
0.95
0.98
0.98
1.00
1.01
1.04
4.12
2.01
1.31
1.54
9.44
5.64
f1 (ppm)

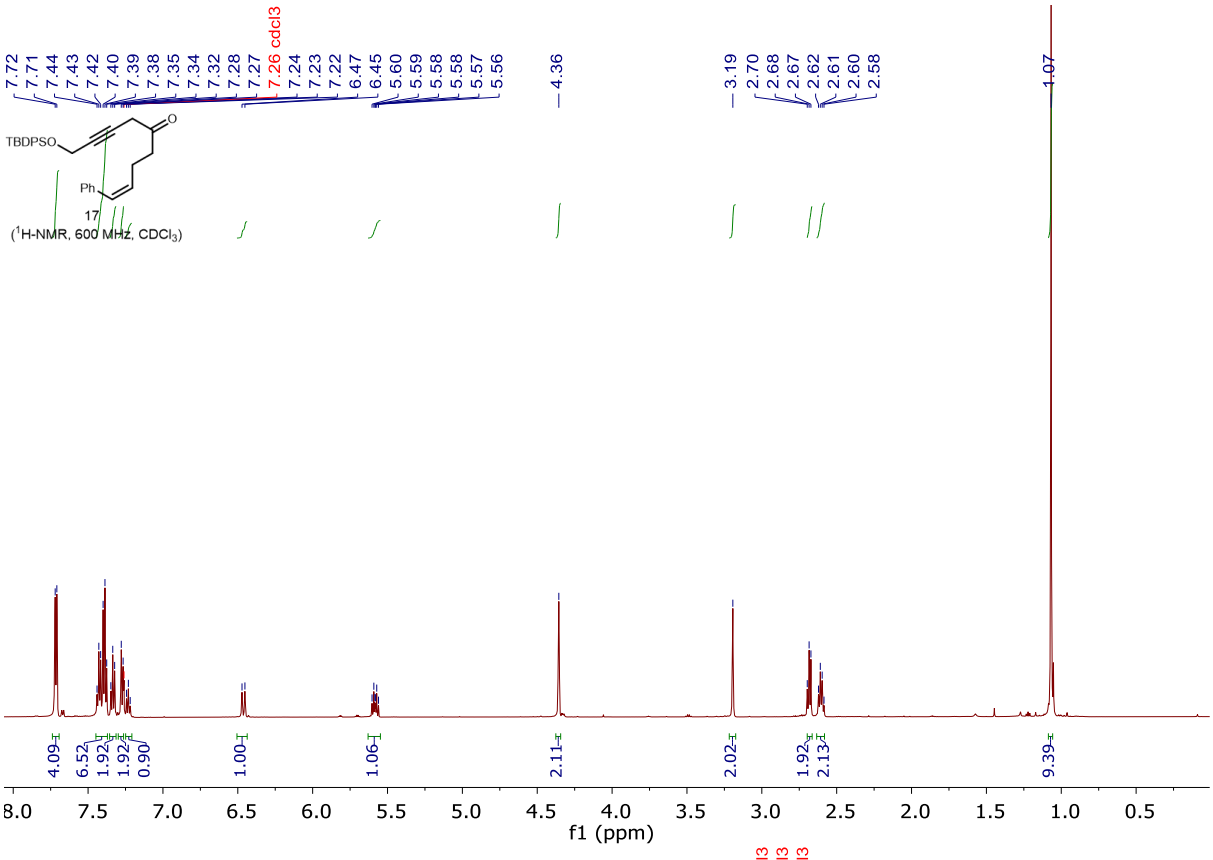

199.01
172.51
161.20
157.40
142.78
139.42
128.77
127.96
127.14
122.34
111.22
105.84
104.54
77.42 cdcl3
77.16 cdcl3
76.91 cdcl3
55.50
54.47
49.94
45.36
37.57
25.84
25.58
18.38
-4.18
-4.19
H
Ph
O
MeO
H
H
OTBS
only labeled 12 for the mixture
(13C-NMR, 126 MHz, CDCl3)
f1 (ppm)

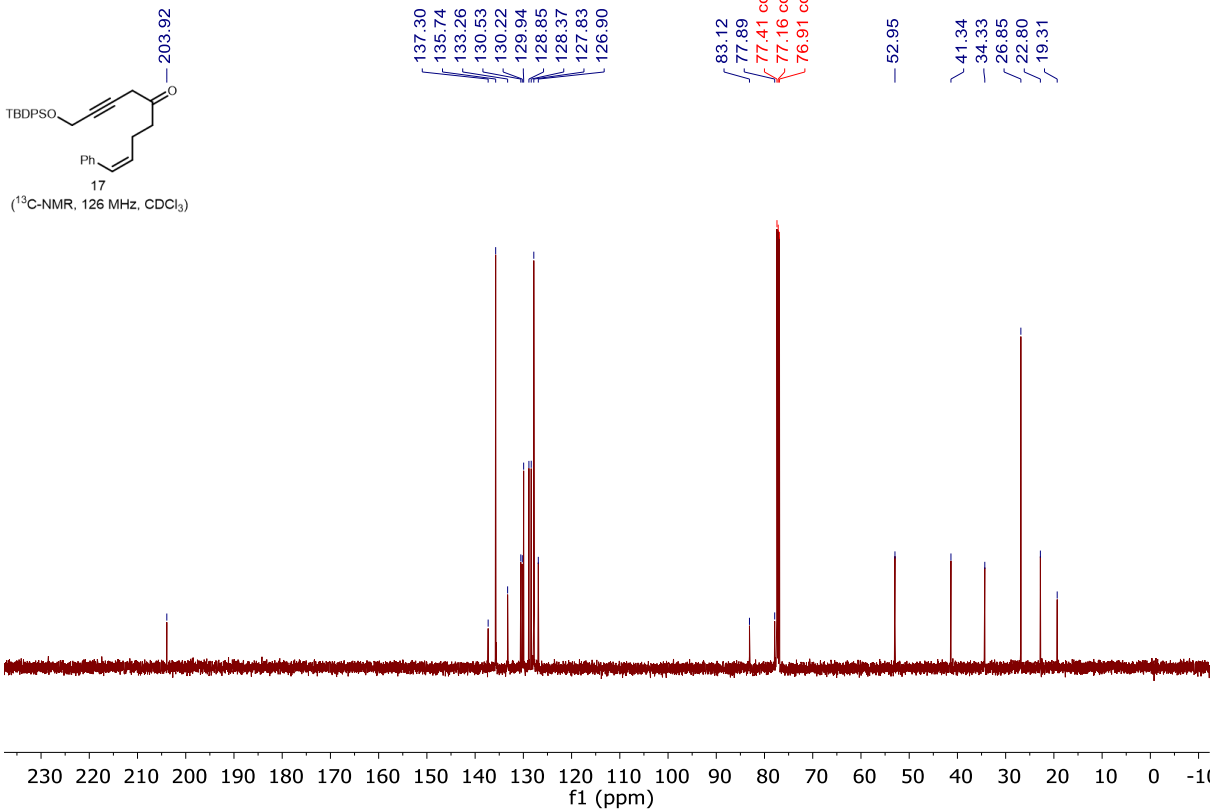

MeO
H
Ph
O
H
H
OTBS
only labeled 12 for the mixture
(cosy, 600 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

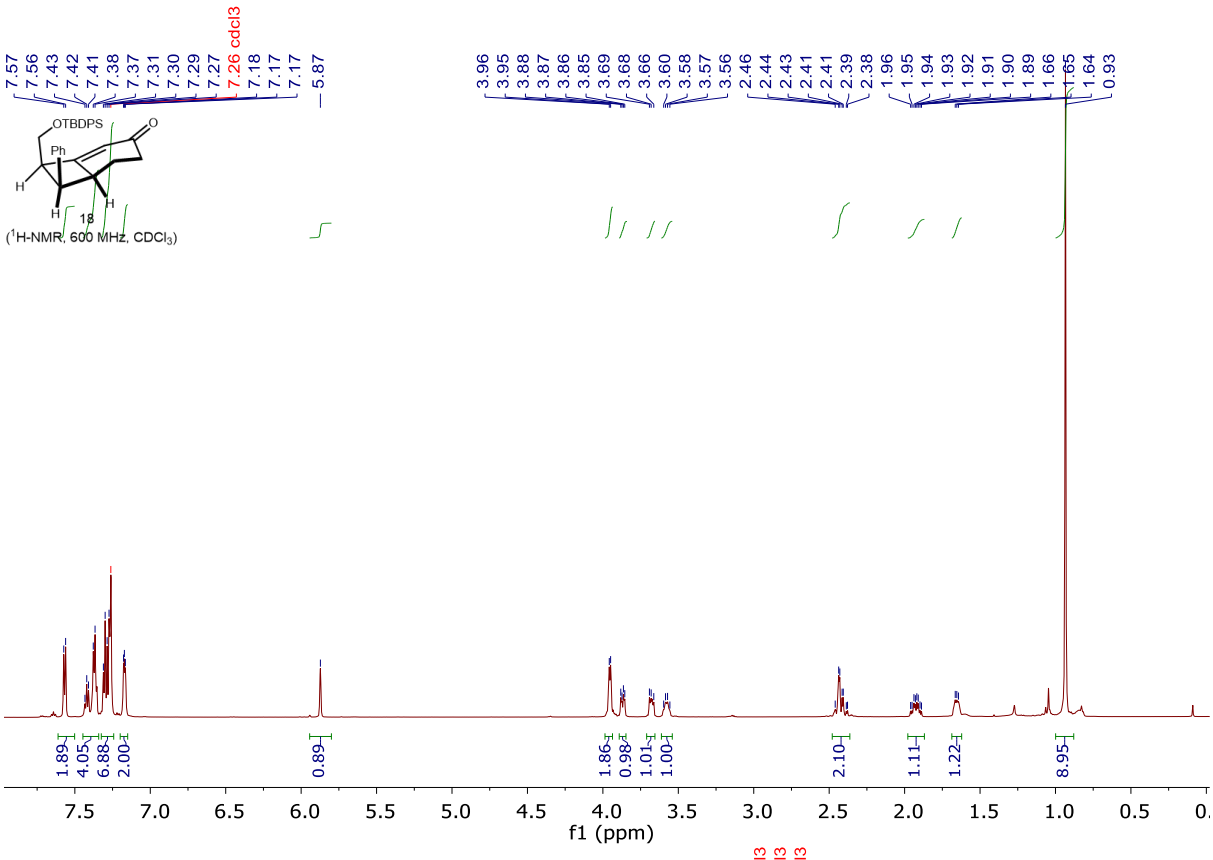

noe
MeO
H
Ph
O
H
H
noe
OTBS
only labeled 12 for the mixture
(noesy, 600 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

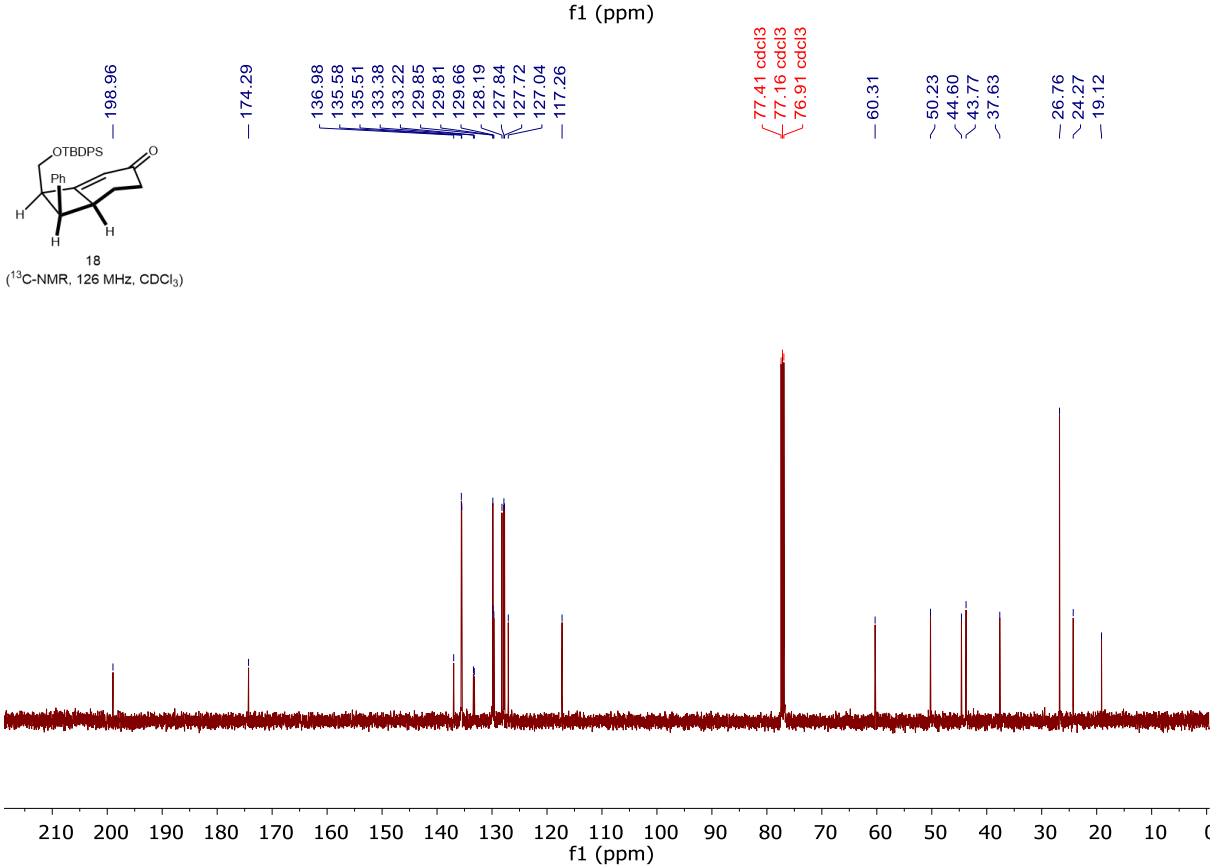

TBDPSO
OH
Ph
SI-8
(^{1}H-NMR, 600 MHz, CDCl$_3$)
f1 (ppm)

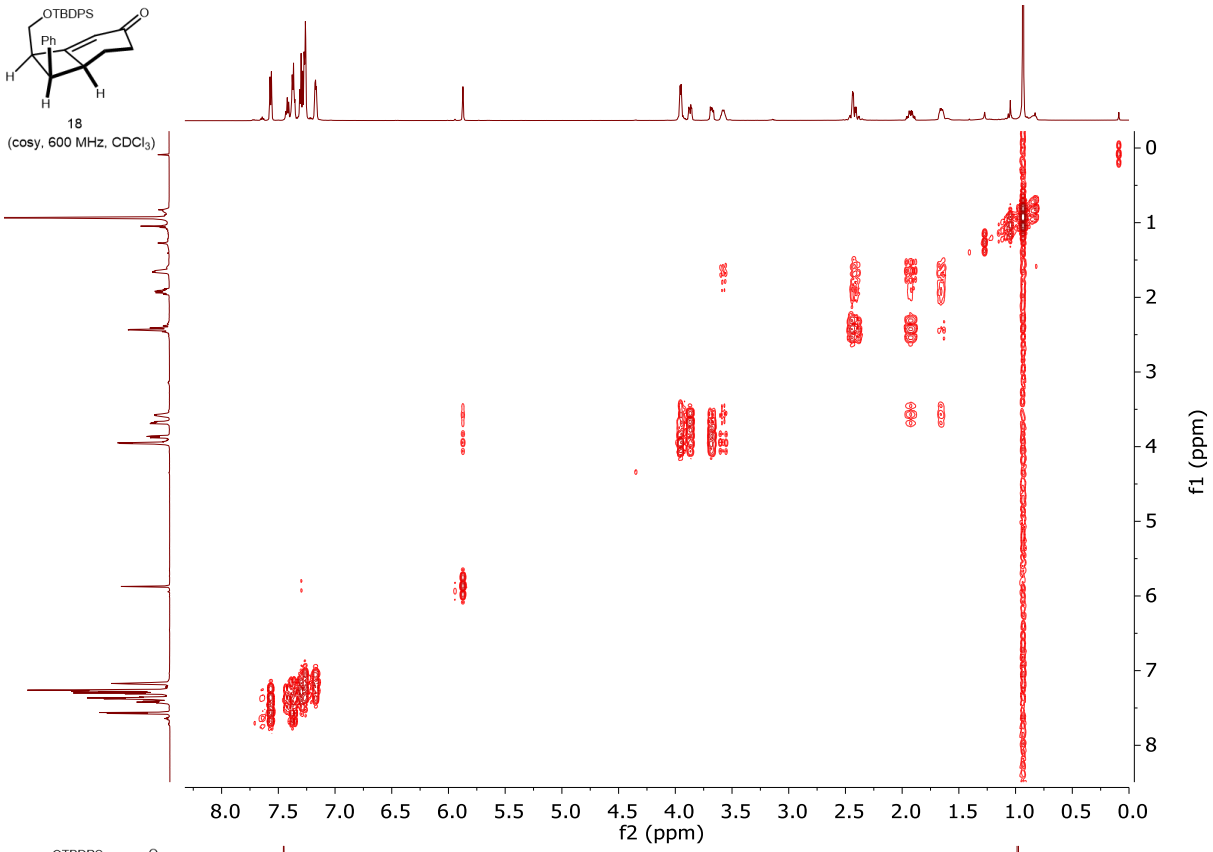

TBDPSO
OH
Ph
SI-8
(^{13}C-NMR, 101 MHz, CDCl$_3$)
f1 (ppm)

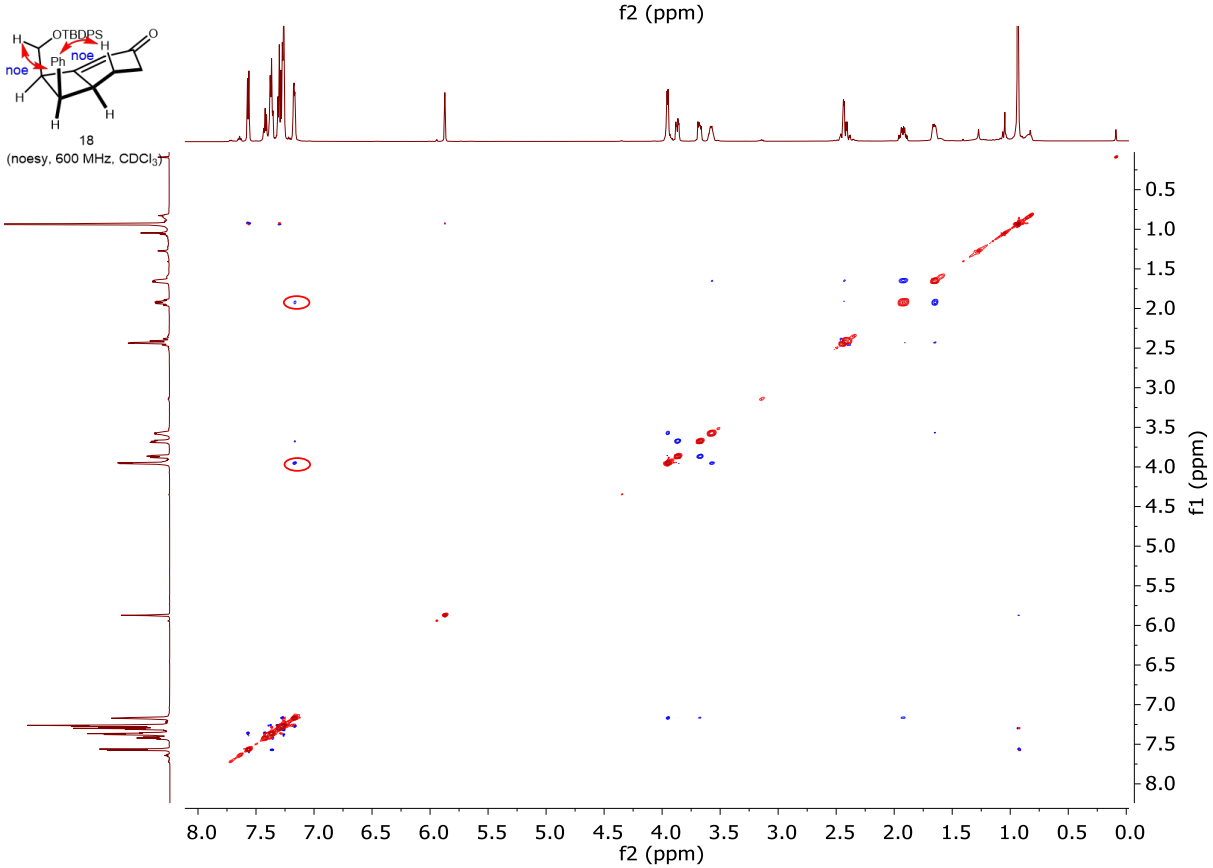

7.72
7.71
7.44
7.43
7.42
7.40
7.39
7.38
7.35
7.34
7.32
7.28
7.27
7.26 cdcl3
7.24
7.23
7.22
6.47
6.45
5.60
5.59
5.58
5.58
5.57
5.56
4.36
3.19
2.70
2.68
2.67
2.62
2.61
2.60
2.58
1.07
TBDPSO
O
Ph
17
(1H-NMR, 600 MHz, CDCl3)
4.09
6.52
1.92
1.92
0.90
1.00
1.06
2.11
2.02
1.92
2.13
9.39
f1 (ppm)


203.92
137.30
135.74
133.26
130.53
130.22
129.94
128.85
128.37
127.83
126.90
83.12
77.89
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
52.95
41.34
34.33
26.85
22.80
19.31
TBDPSO
O
Ph
17
(13C-NMR, 126 MHz, CDCl3)
f1 (ppm)

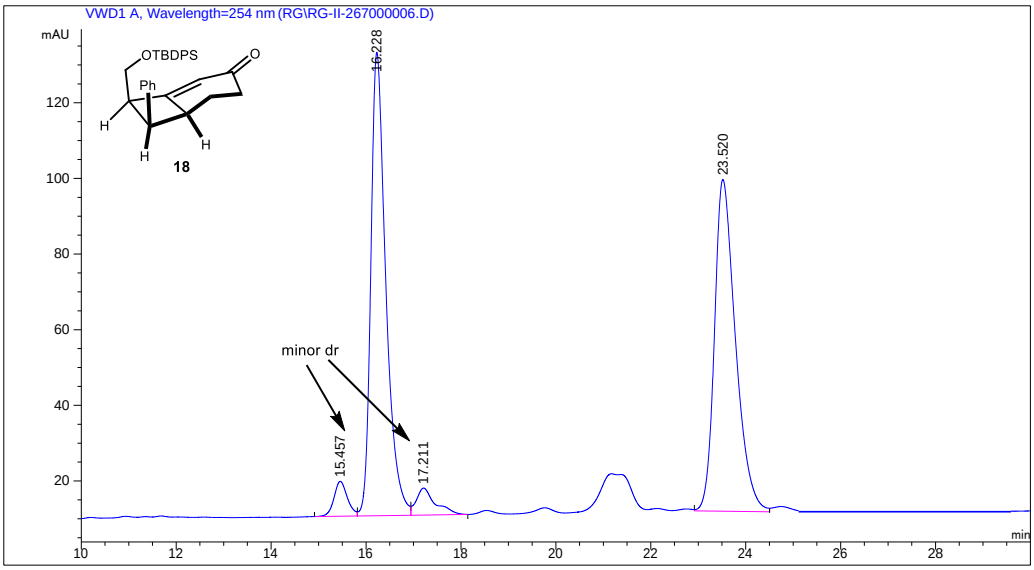

7.57 7.56 7.43 7.42 7.41 7.38 7.37 7.31 7.30 7.29 7.27 7.26 cdcl3 7.18 7.17 7.17 5.87
3.96 3.95 3.88 3.87 3.86 3.85 3.69 3.68 3.66 3.60 3.58 3.57 3.56 2.46 2.44 2.43 2.41 2.41 2.39 2.38 1.96 1.95 1.94 1.93 1.92 1.91 1.90 1.89 1.66 1.65 1.64 0.93
OTBDPS
Ph
O
H
H
H
18
(1H-NMR, 600 MHz, CDCl3)
1.89 4.05 6.88 2.00 0.89 1.86 0.98 1.01 1.00 2.10 1.11 1.22 8.95
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


198.96 174.29 136.98 135.58 135.51 133.38 133.22 129.85 129.81 129.66 128.19 127.84 127.72 127.04 117.26
77.41 cdcl3 77.16 cdcl3 76.91 cdcl3
60.31 50.23 44.60 43.77 37.63 26.76 24.27 19.12
OTBDPS
Ph
O
H
H
H
18
(13C-NMR, 126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

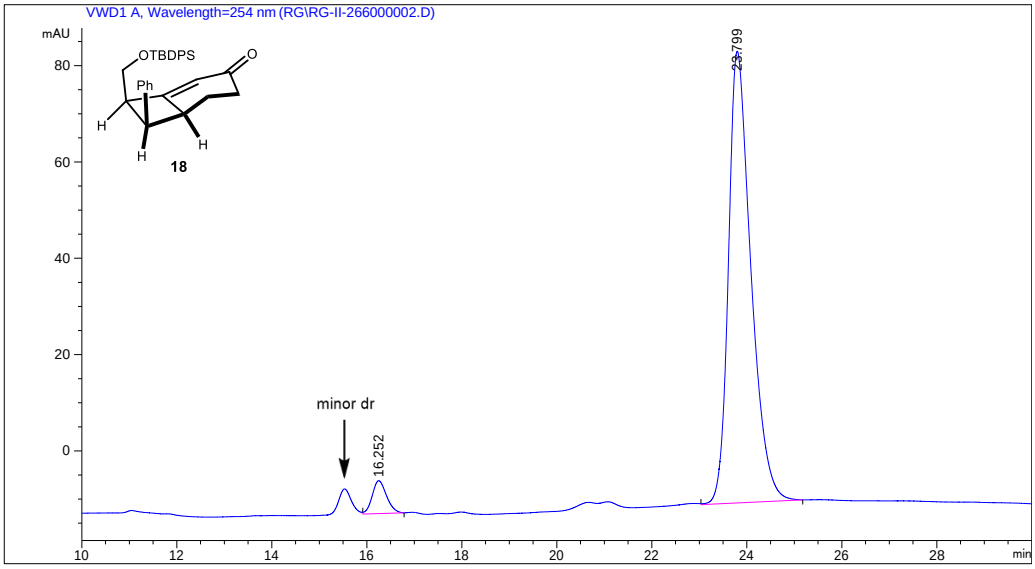

OTBDPS
Ph
O
H
H
H
18
(cosy, 600 MHz, CDCl3)
f2 (ppm)
f1 (ppm)


H
OTBDPS
noe
H
noe
Ph
O
H
H
H
18
(noesy, 600 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

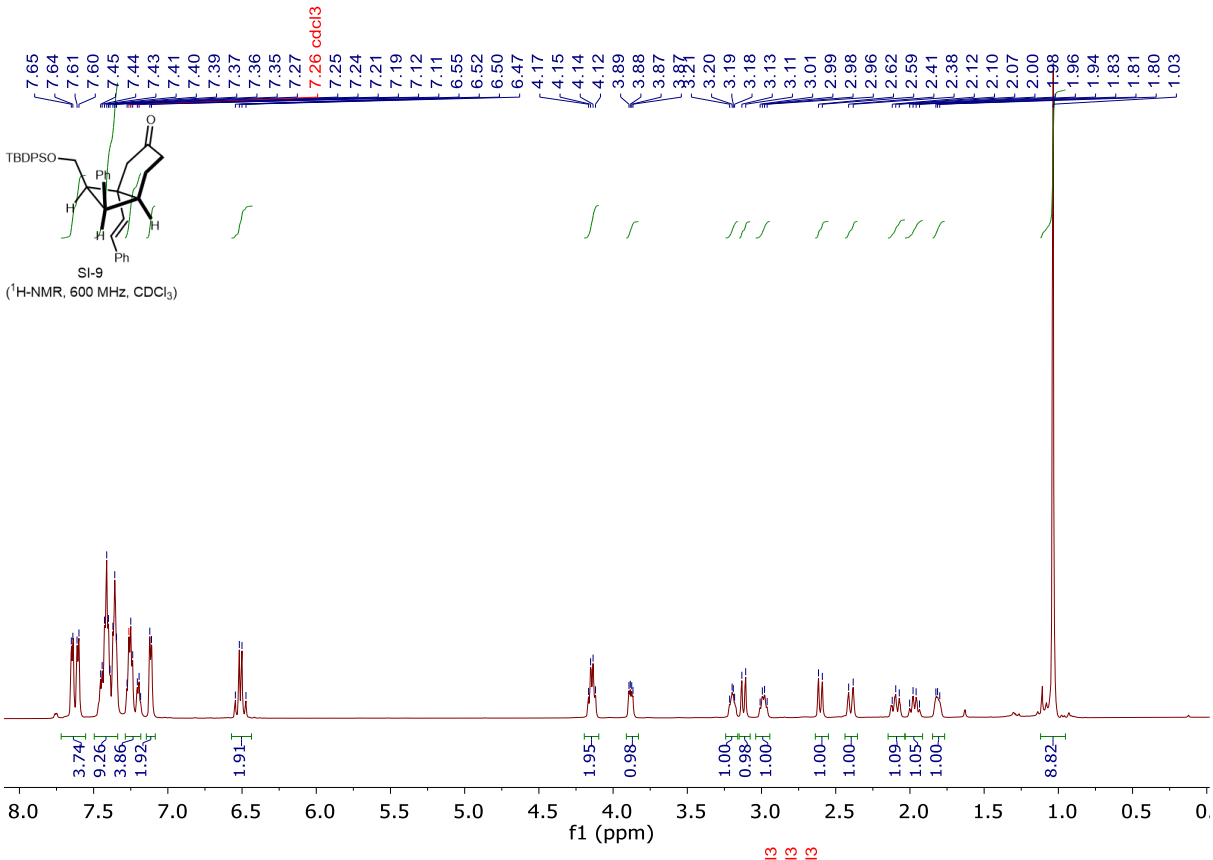
a

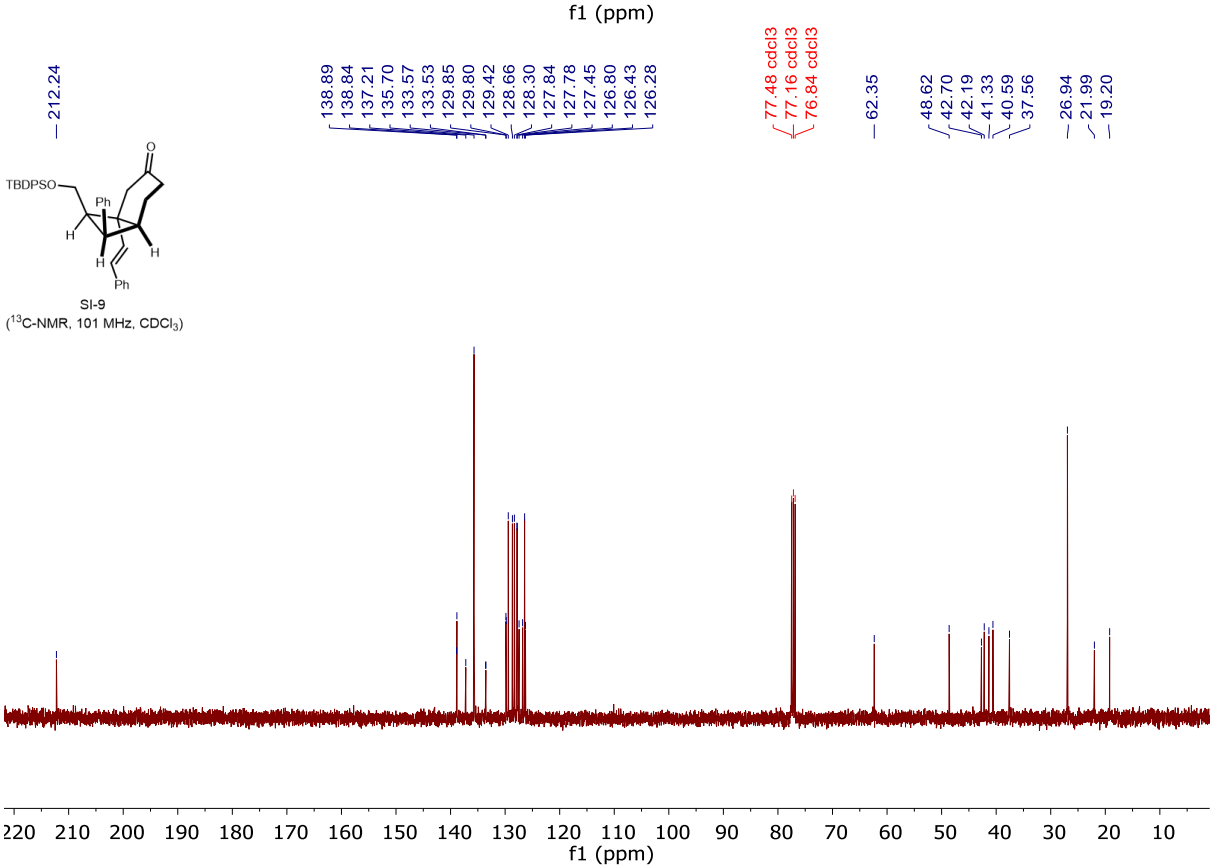


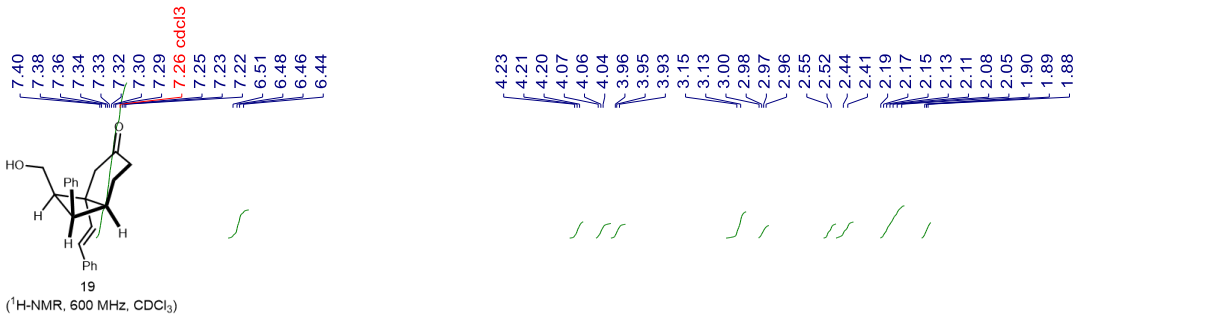
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.457	BV	0.2478	181.12306	9.23700	3.1405
2	16.228	VV	0.3249	2692.02563	122.50545	46.6778
3	17.211	VB	0.3256	197.93320	7.13658	3.4320
4	23.520	VV	0.4436	2696.16748	87.71323	46.7496

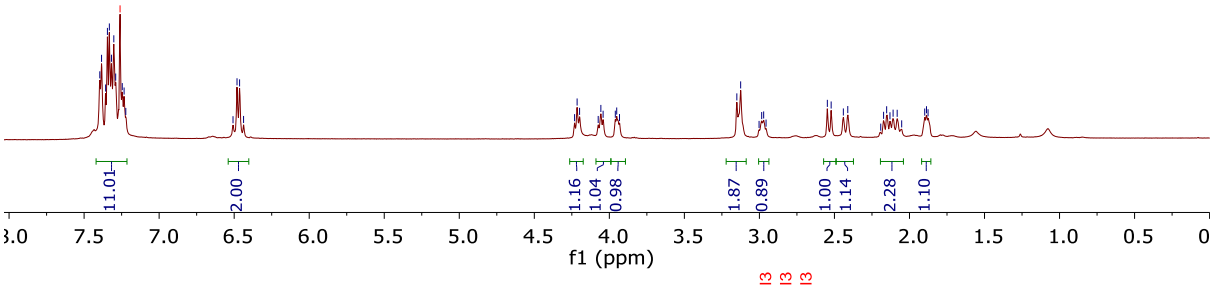


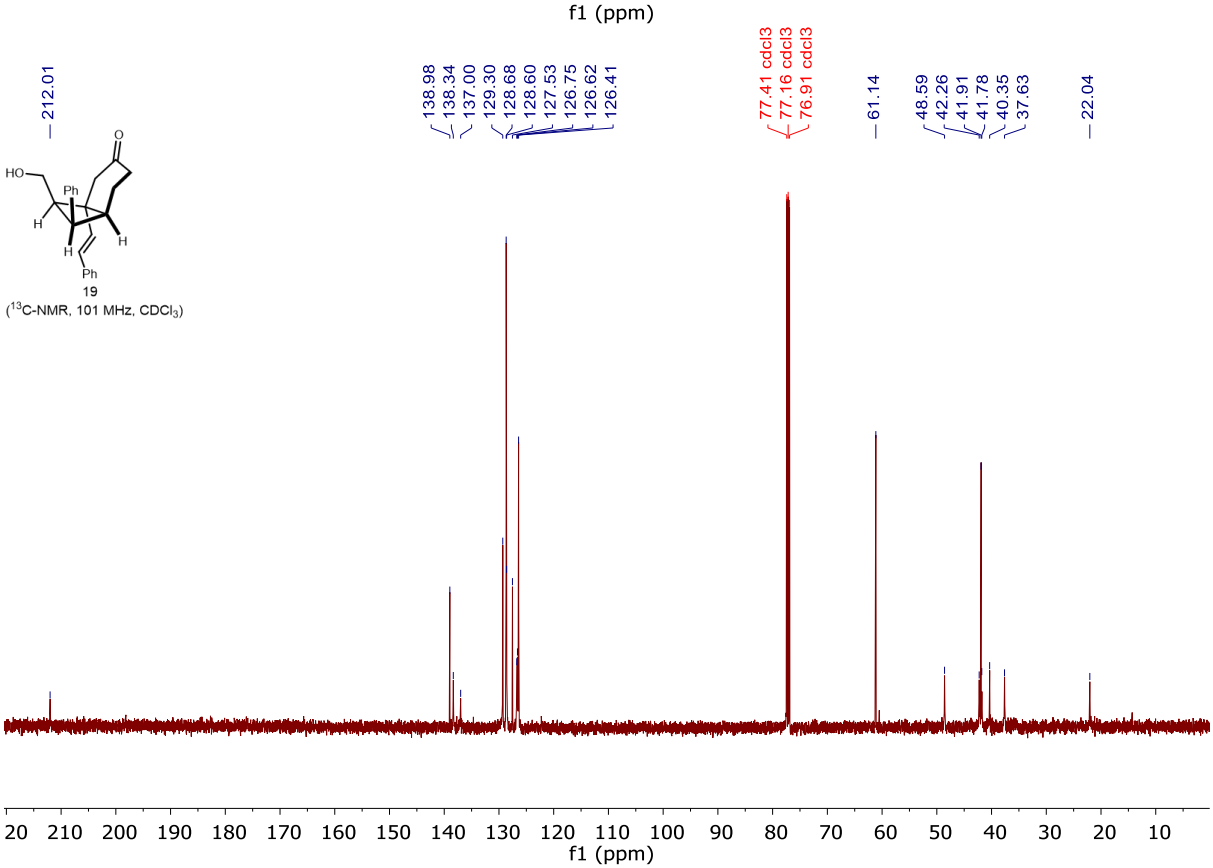
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.252	VB	0.2521	143.03381	6.83679	4.4385
2	23.799	VB	0.4591	3079.55078	93.77850	95.5615

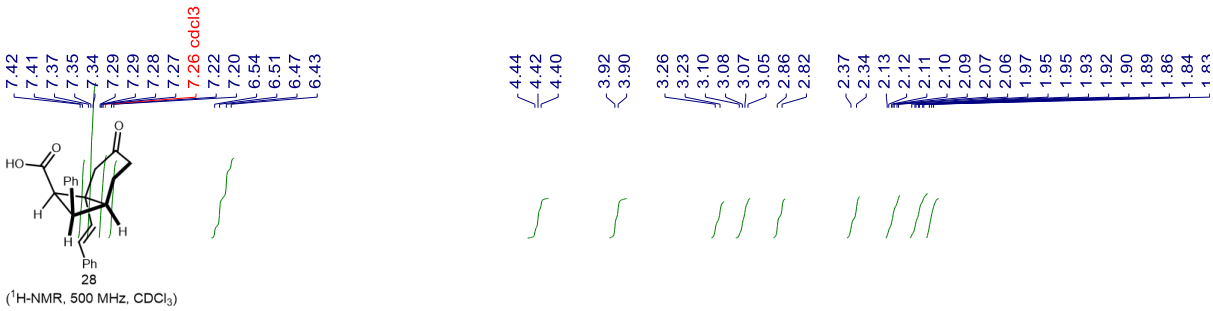

7.65 7.64 7.61 7.60 7.45 7.44 7.43 7.41 7.40 7.39 7.37 7.36 7.35 7.27 7.26 cdcl3 7.25 7.24 7.21 7.19 7.12 7.11 6.55 6.52 6.50 6.47 4.17 4.15 4.14 4.12 3.89 3.88 3.87 3.20 3.19 3.18 3.13 3.11 3.01 2.99 2.98 2.96 2.62 2.59 2.41 2.38 2.12 2.10 2.07 2.00 1.98 1.96 1.94 1.83 1.81 1.80 1.03
TBDPSO
Ph
H
O
H
H
Ph
SI-9
(1H-NMR, 600 MHz, CDCl3)
3.74 9.26 3.86 1.92 1.91 1.95 0.98 1.00 0.98 1.00 1.00 1.00 1.09 1.05 1.00 8.82
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


212.24
138.89 138.84 137.21 135.70 133.57 133.53 129.85 129.80 129.42 128.66 128.30 127.84 127.78 127.45 126.80 126.43 126.28
77.48 cdcl3 77.16 cdcl3 76.84 cdcl3
62.35
48.62 42.70 42.19 41.33 40.59 37.56
26.94 21.99 19.20
TBDPSO
Ph
H
O
H
H
Ph
SI-9
(13C-NMR, 101 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

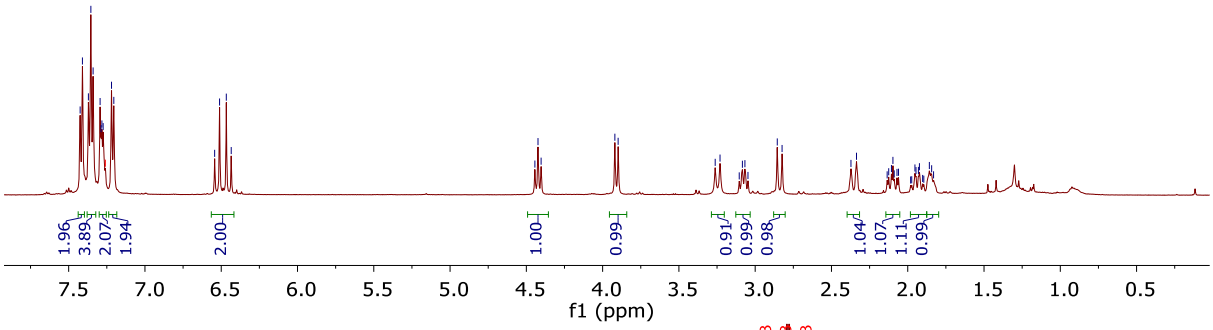

7.40
7.38
7.36
7.34
7.33
7.32
7.30
7.29
7.26 cdcl3
7.25
7.23
7.22
6.51
6.48
6.46
6.44
4.23
4.21
4.20
4.07
4.06
4.04
3.96
3.95
3.93
3.15
3.13
3.00
2.98
2.97
2.96
2.55
2.52
2.44
2.41
2.19
2.17
2.15
2.13
2.11
2.08
2.05
1.90
1.89
1.88
HO
Ph
H
H
H
Ph
O
19
(1H-NMR, 600 MHz, CDCl3)

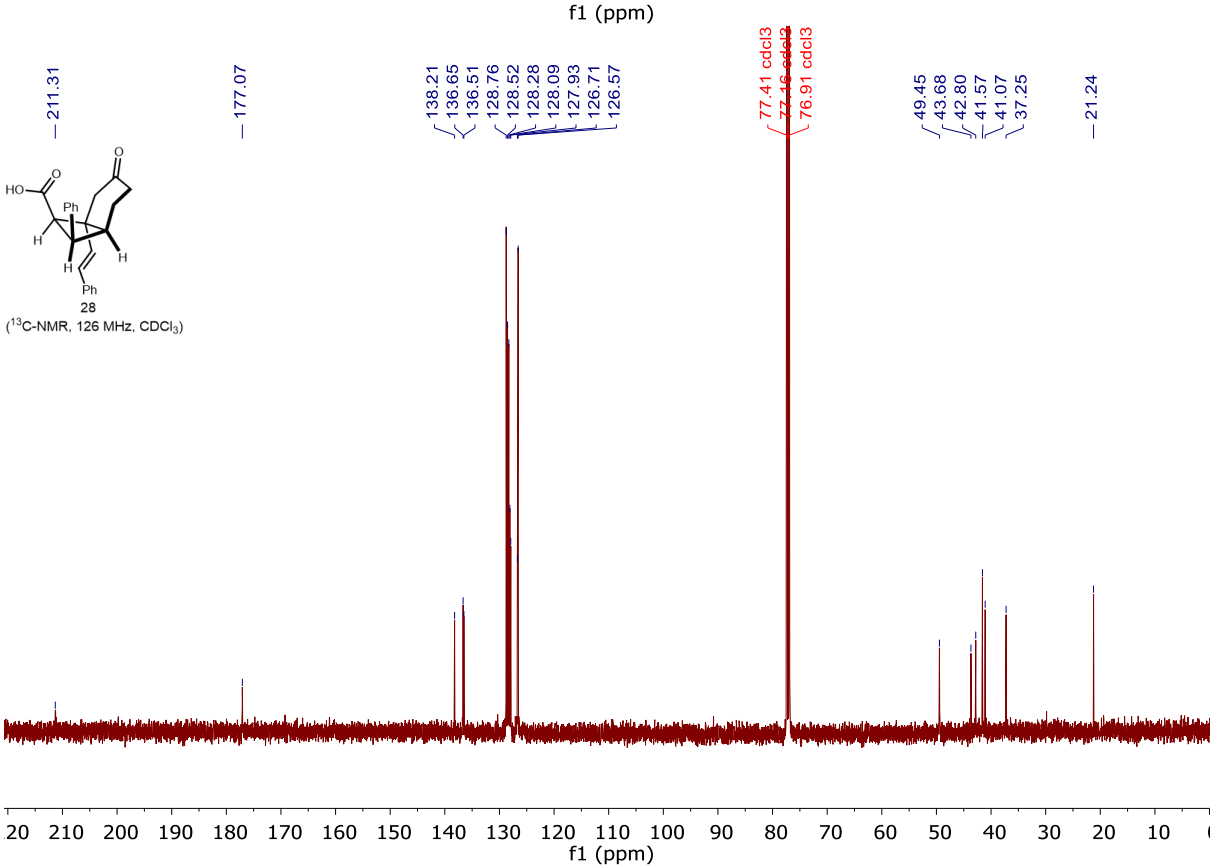

11.01
2.00
1.16
1.04
0.98
1.87
0.89
1.00
1.14
2.28
1.10
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


212.01
138.98
138.34
137.00
129.30
128.68
128.60
127.53
126.75
126.62
126.41
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
61.14
48.59
42.26
41.91
41.78
40.35
37.63
22.04
HO
Ph
H
H
H
Ph
O
19
(13C-NMR, 101 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

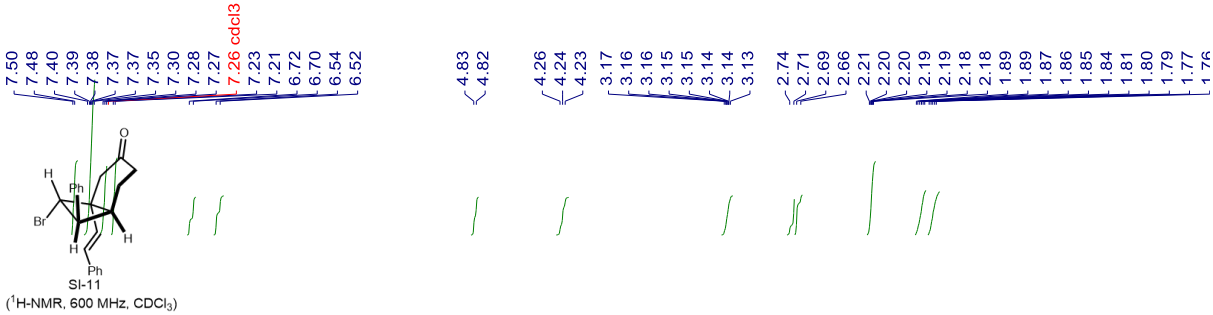


(^{1}H-NMR, 500 MHz, $CDCl_3$)



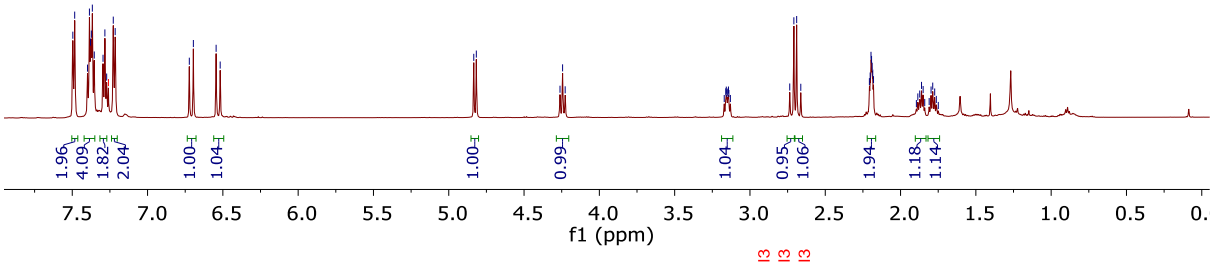


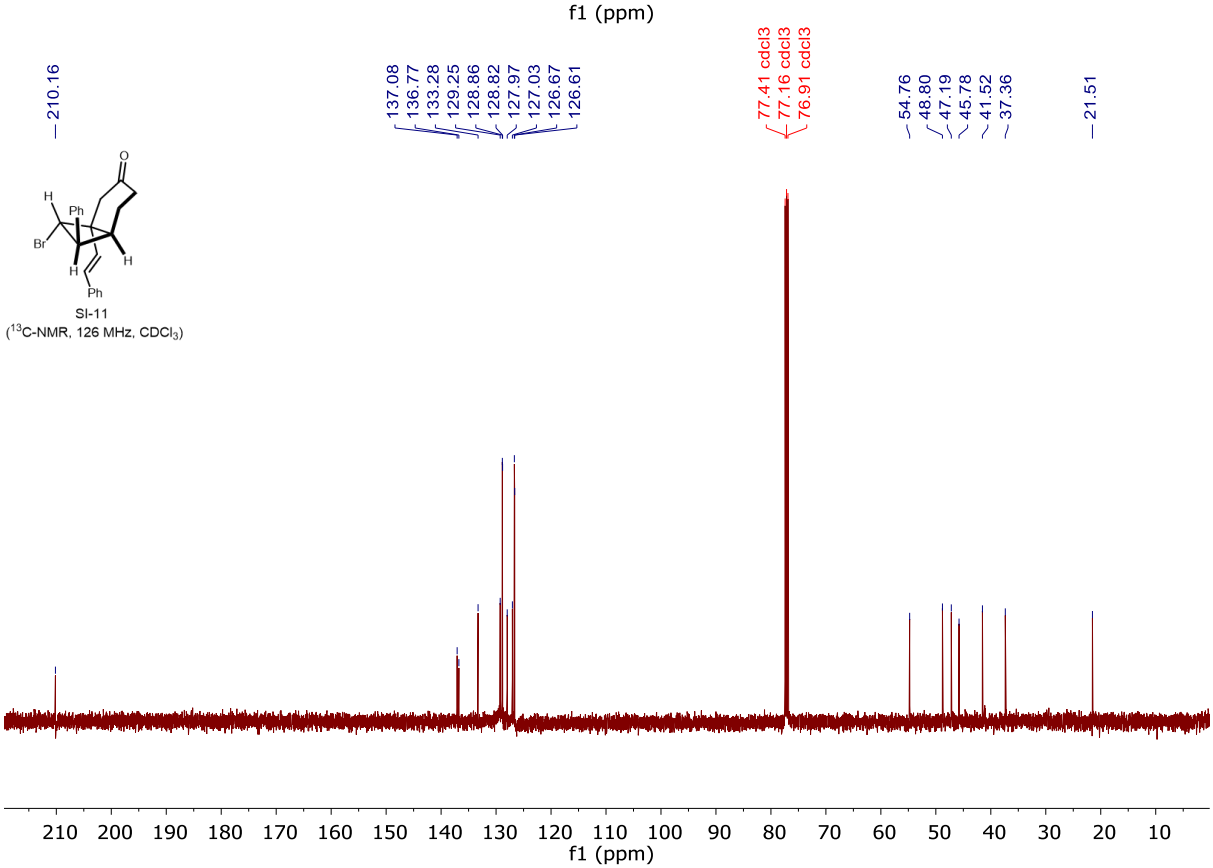
(^{13}C-NMR, 126 MHz, $CDCl_3$)



SI-11

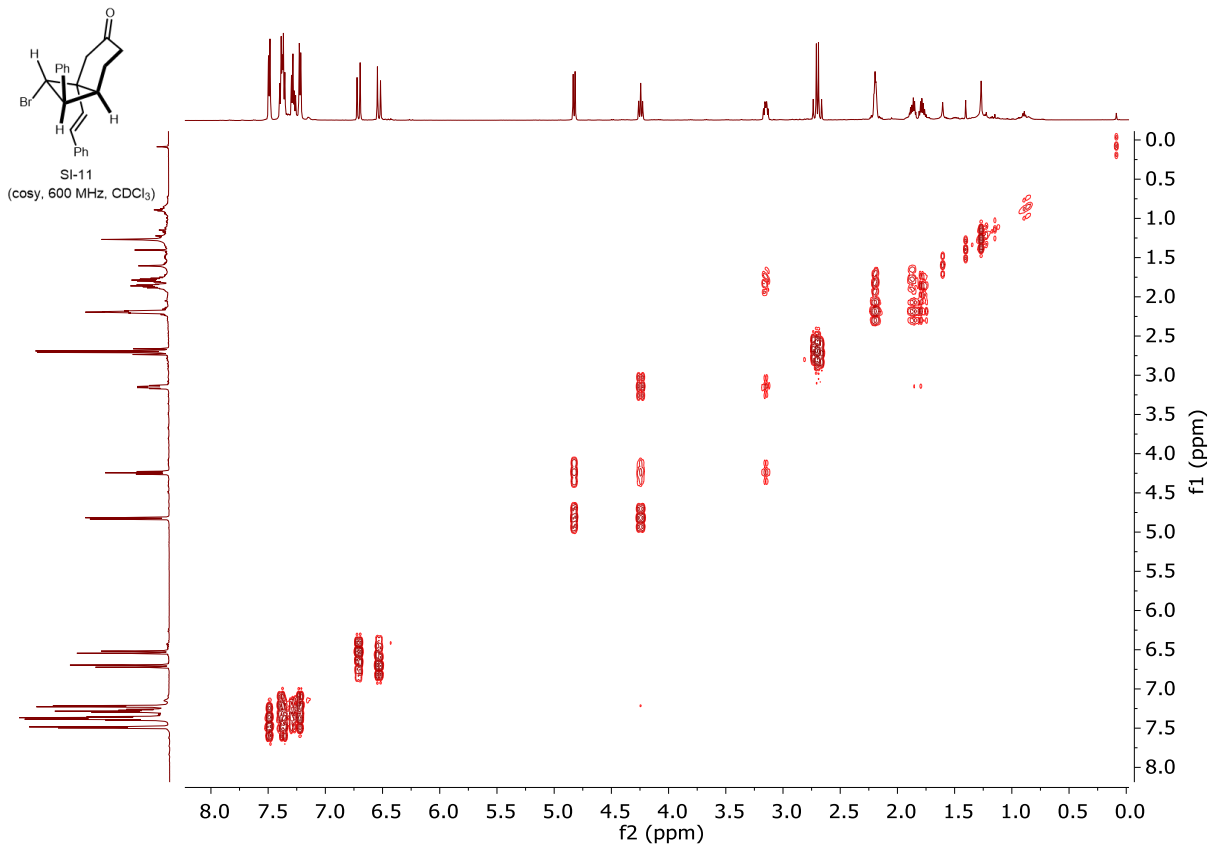
(^{1}H-NMR, 600 MHz, $CDCl_3$)

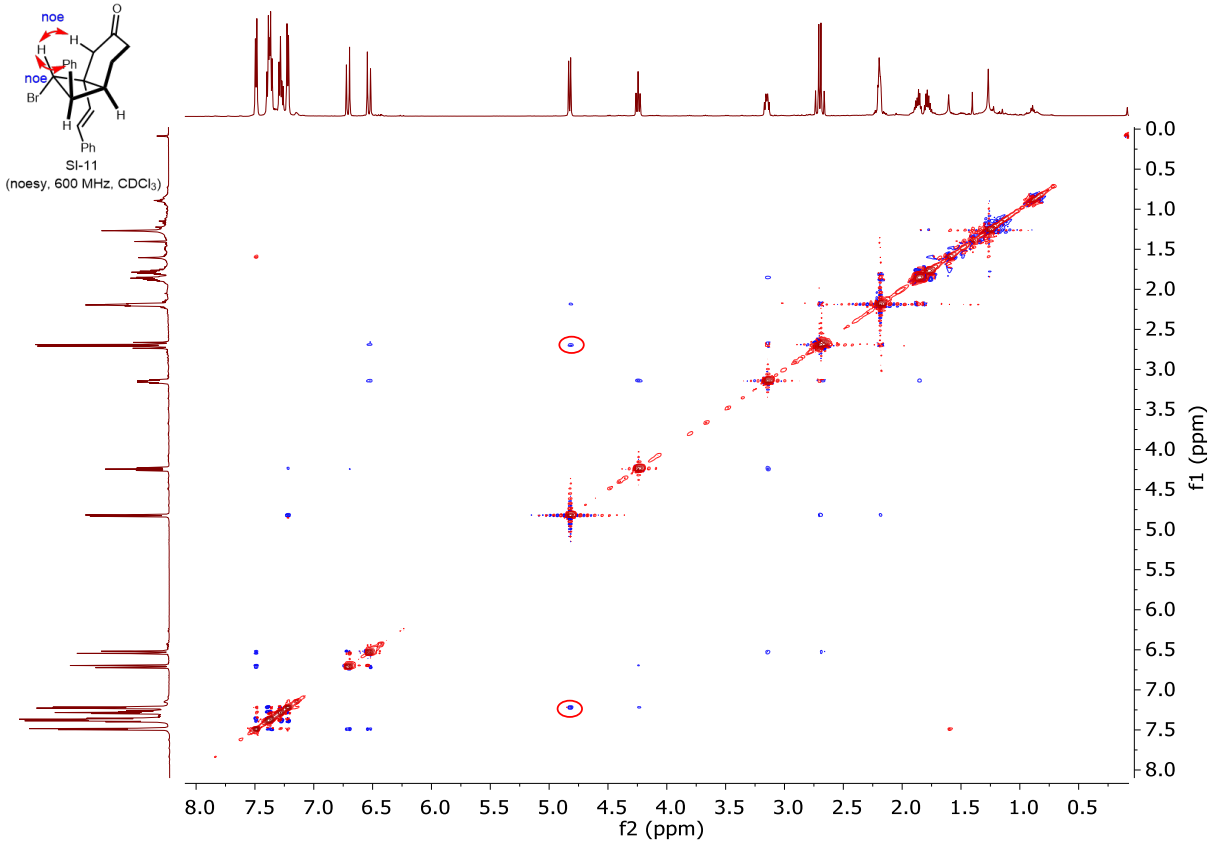


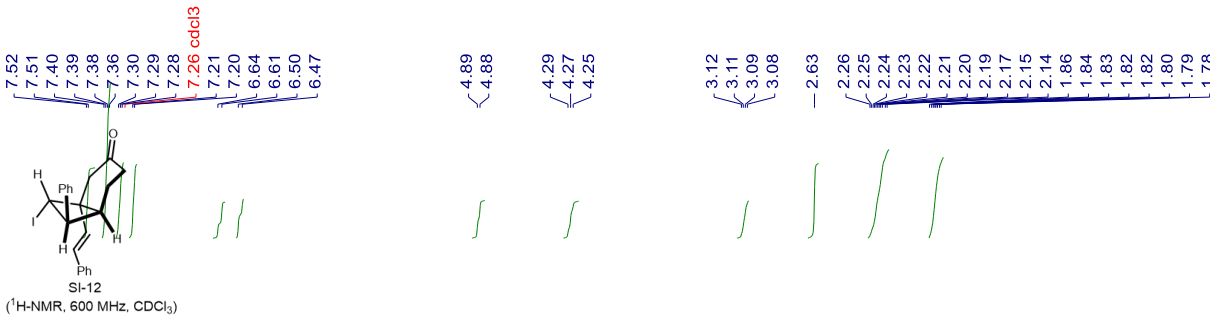


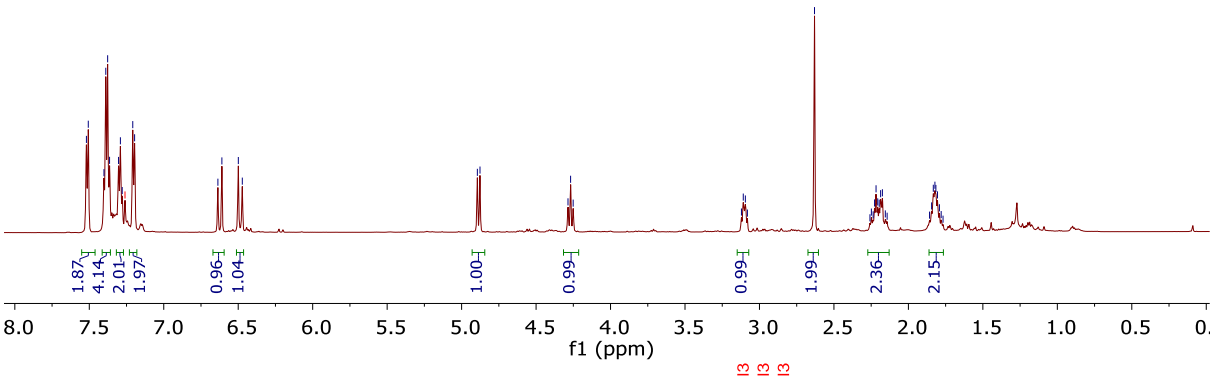
SI-11

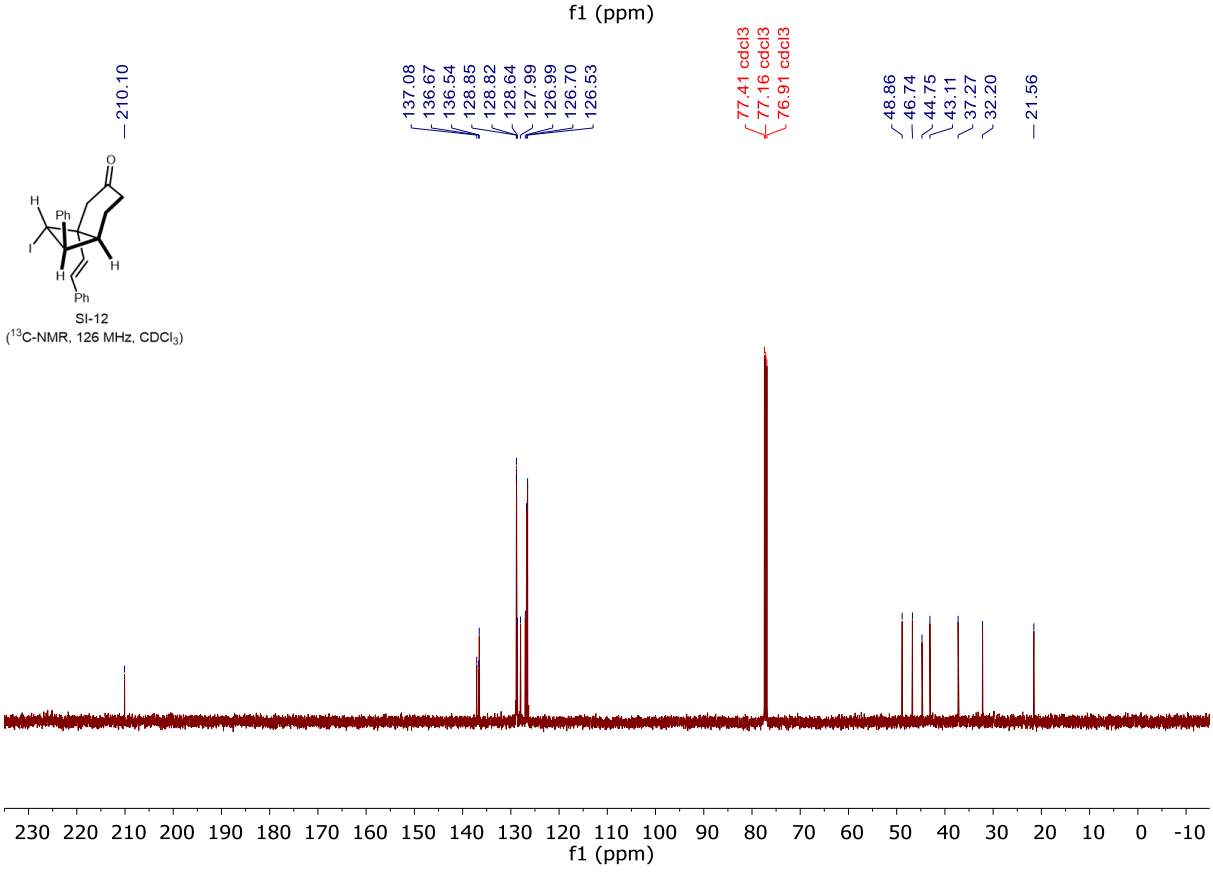
(^{13}C-NMR, 126 MHz, $CDCl_3$)

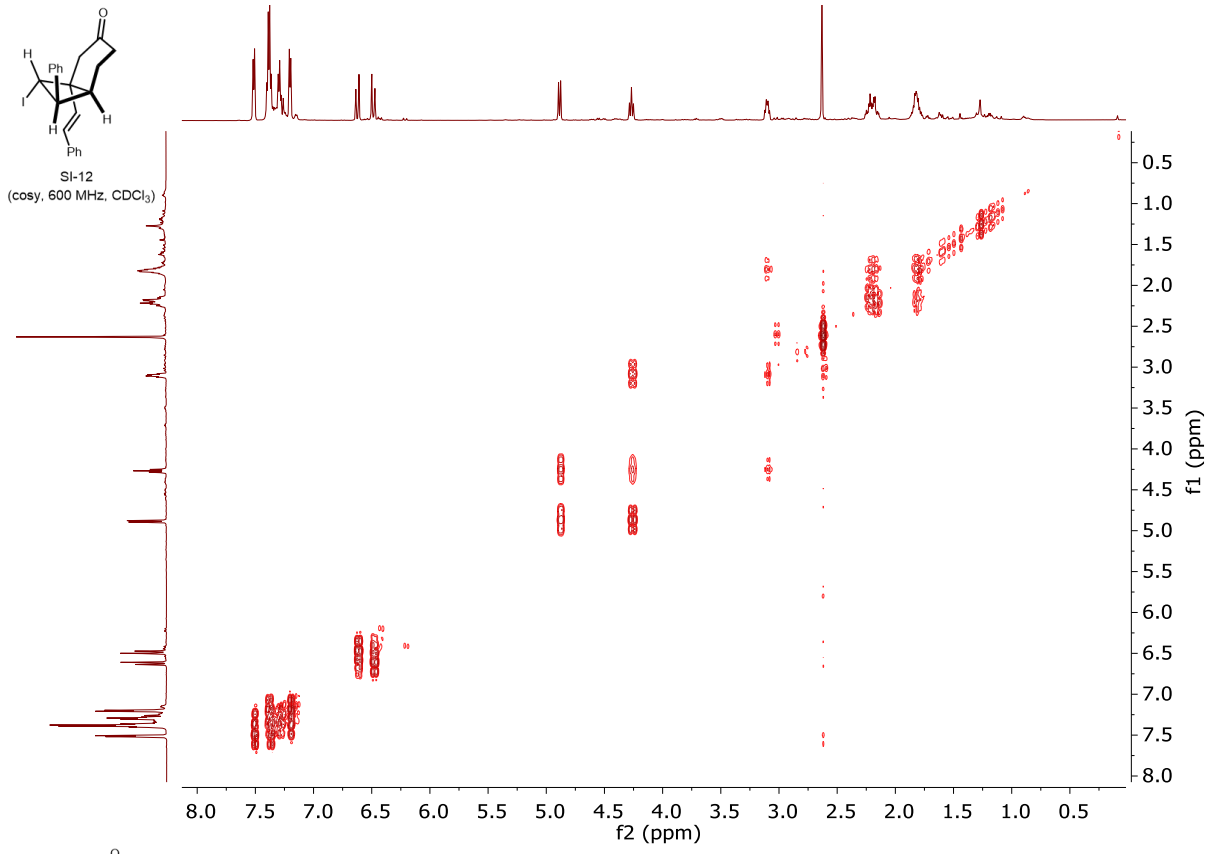

SI-11
(cosy, 600 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

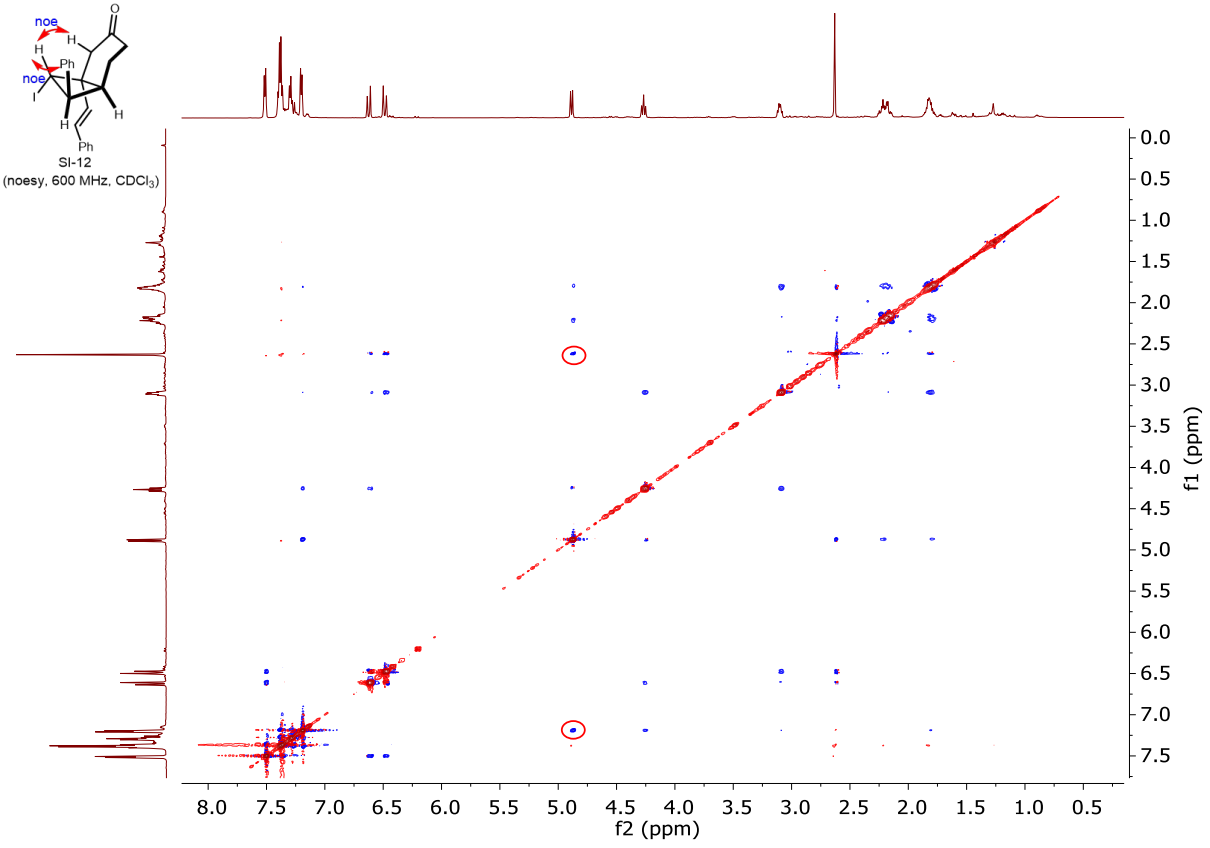

noe
noe
SI-11
(noesy, 600 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

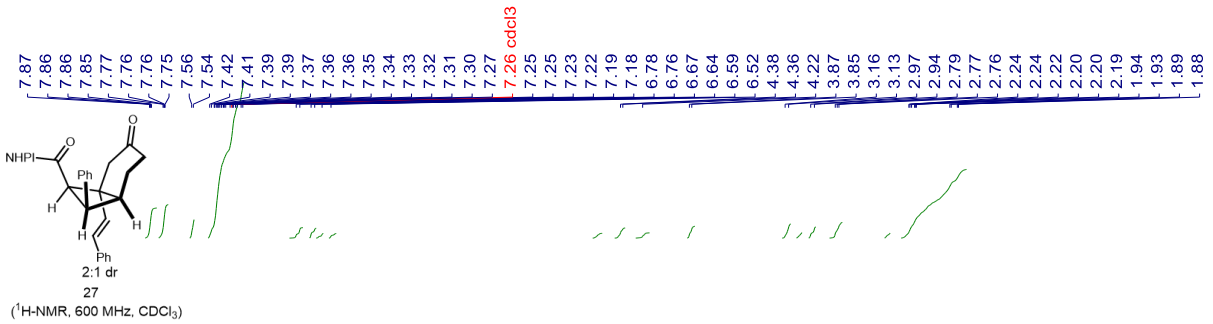

7.52
7.51
7.40
7.39
7.38
7.36
7.30
7.29
7.28
7.26 cdcl3
7.21
7.20
6.64
6.61
6.50
6.47
4.89
4.88
4.29
4.27
4.25
3.12
3.11
3.09
3.08
2.63
2.26
2.25
2.24
2.23
2.22
2.21
2.20
2.19
2.17
2.15
2.14
1.86
1.84
1.83
1.82
1.82
1.80
1.79
O
H
Ph
H
H
Ph
SI-12
(1H-NMR, 600 MHz, CDCl3)

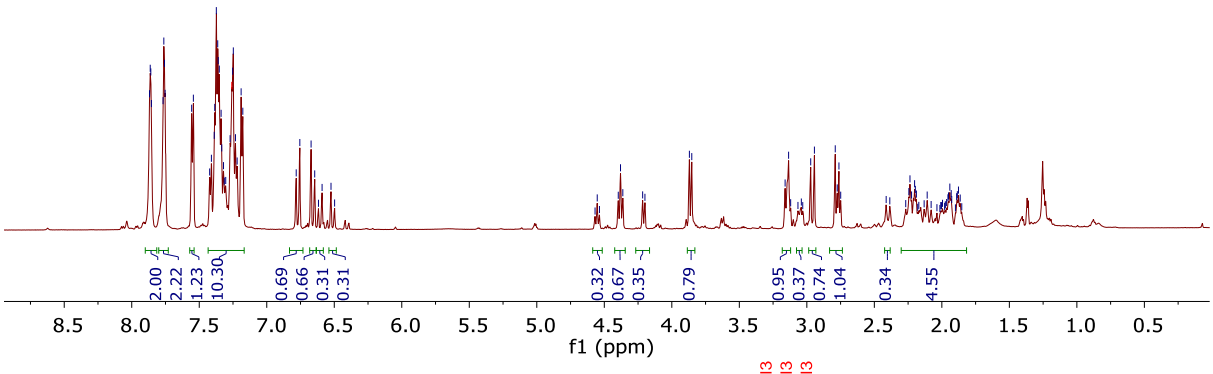

1.87
4.14
2.01
1.97
0.96
1.04
1.00
0.99
0.99
1.99
2.36
2.15
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

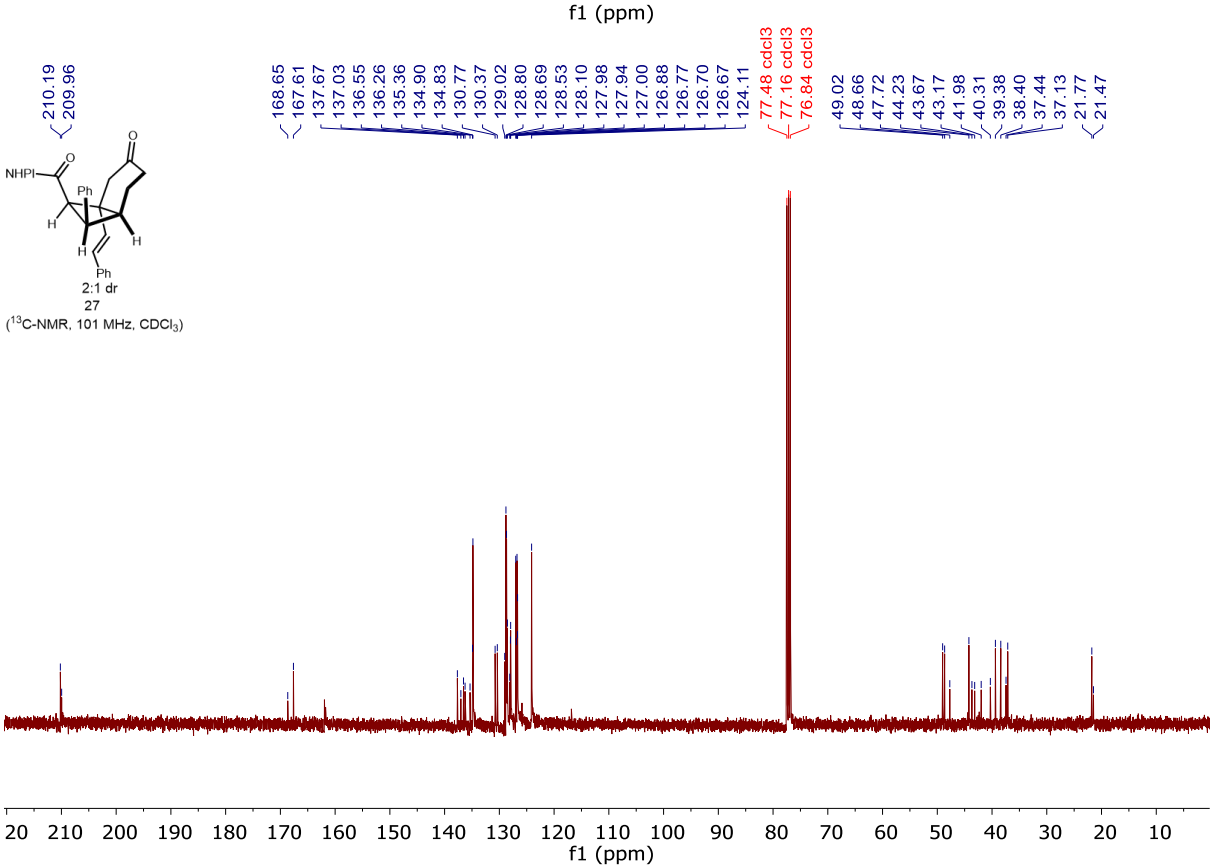

210.10
137.08
136.67
136.54
128.85
128.82
128.64
127.99
126.99
126.70
126.53
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
48.86
46.74
44.75
43.11
37.27
32.20
21.56
O
H
Ph
H
H
Ph
SI-12
(13C-NMR, 126 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

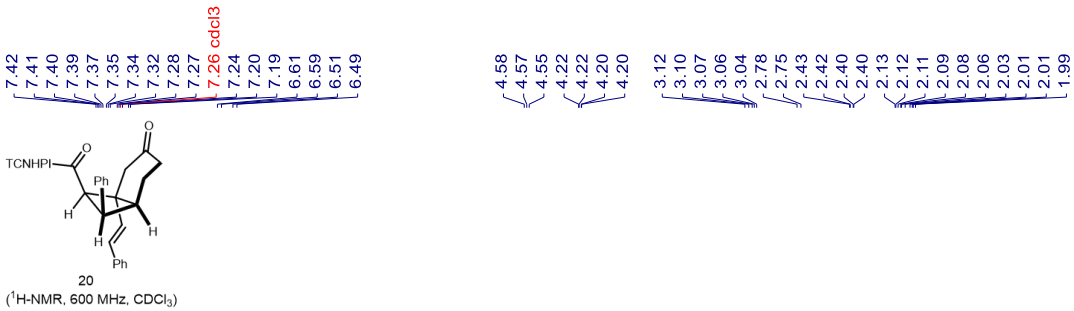

SI-12
(cosy, 600 MHz, CDCl3)
f2 (ppm)
f1 (ppm)


noe
noe
SI-12
(noesy, 600 MHz, CDCl3)
f2 (ppm)
f1 (ppm)


7.87 7.86 7.86 7.85 7.77 7.76 7.76 7.75 7.56 7.54 7.42 7.41 7.39 7.39 7.37 7.36 7.36 7.35 7.34 7.33 7.32 7.31 7.30 7.27 7.26 cdcl3 7.25 7.25 7.23 7.22 7.19 7.18 6.78 6.76 6.67 6.64 6.59 6.52 4.38 4.36 4.22 3.87 3.85 3.16 3.13 2.97 2.94 2.79 2.77 2.76 2.24 2.24 2.22 2.20 2.20 2.19 1.94 1.93 1.89 1.88
NHPI
Ph
Ph
2:1 dr
27
(1H-NMR, 600 MHz, CDCl3)

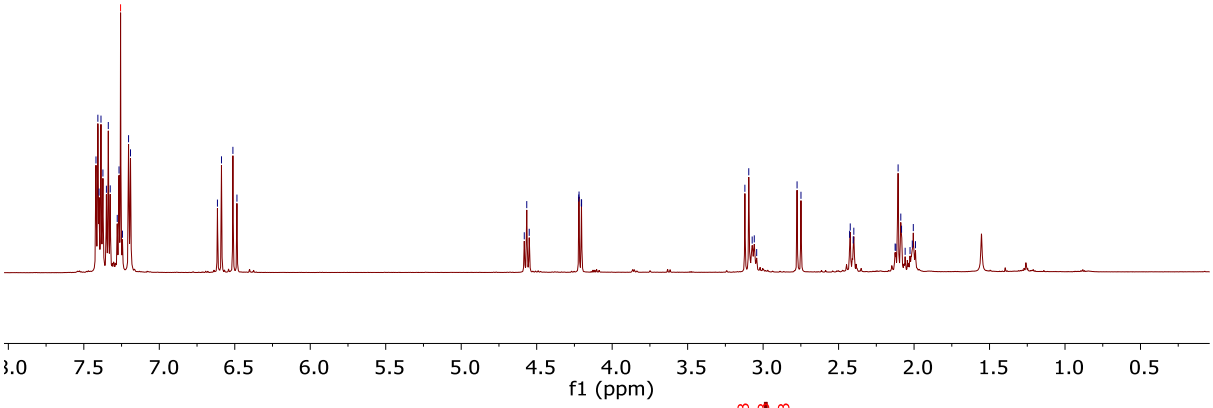

2.00 2.22 1.23 10.30 0.69 0.66 0.31 0.31 0.32 0.67 0.35 0.79 0.95 0.37 0.74 1.04 0.34 4.55
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

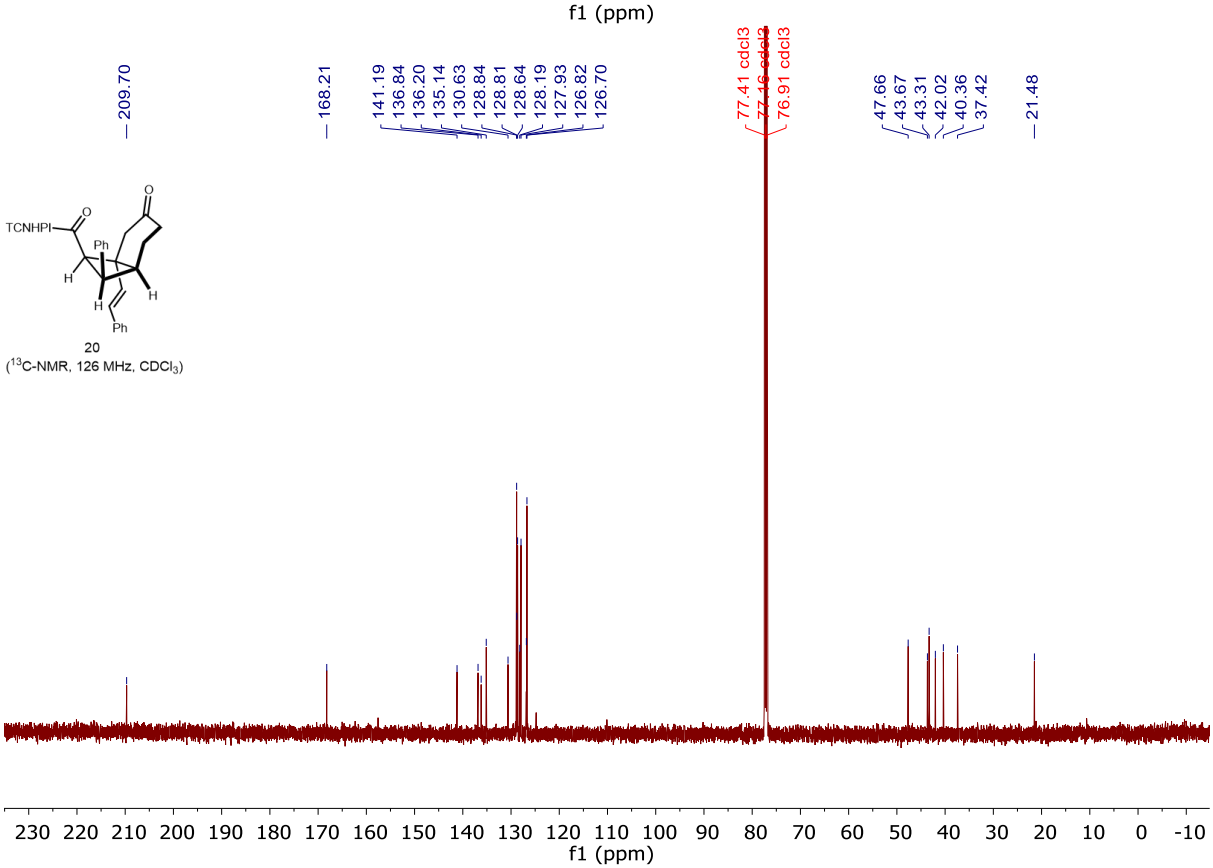

210.19 209.96 168.65 167.61 137.67 137.03 136.55 136.26 135.36 134.90 134.83 130.77 130.37 129.02 128.80 128.69 128.53 128.10 127.98 127.94 127.00 126.88 126.77 126.70 126.67 124.11 77.48 cdcl3 77.16 cdcl3 76.84 cdcl3 49.02 48.66 47.72 44.23 43.67 43.17 41.98 40.31 39.38 38.40 37.44 37.13 21.77 21.47
NHPI
Ph
Ph
2:1 dr
27
(13C-NMR, 101 MHz, CDCl3)
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



20

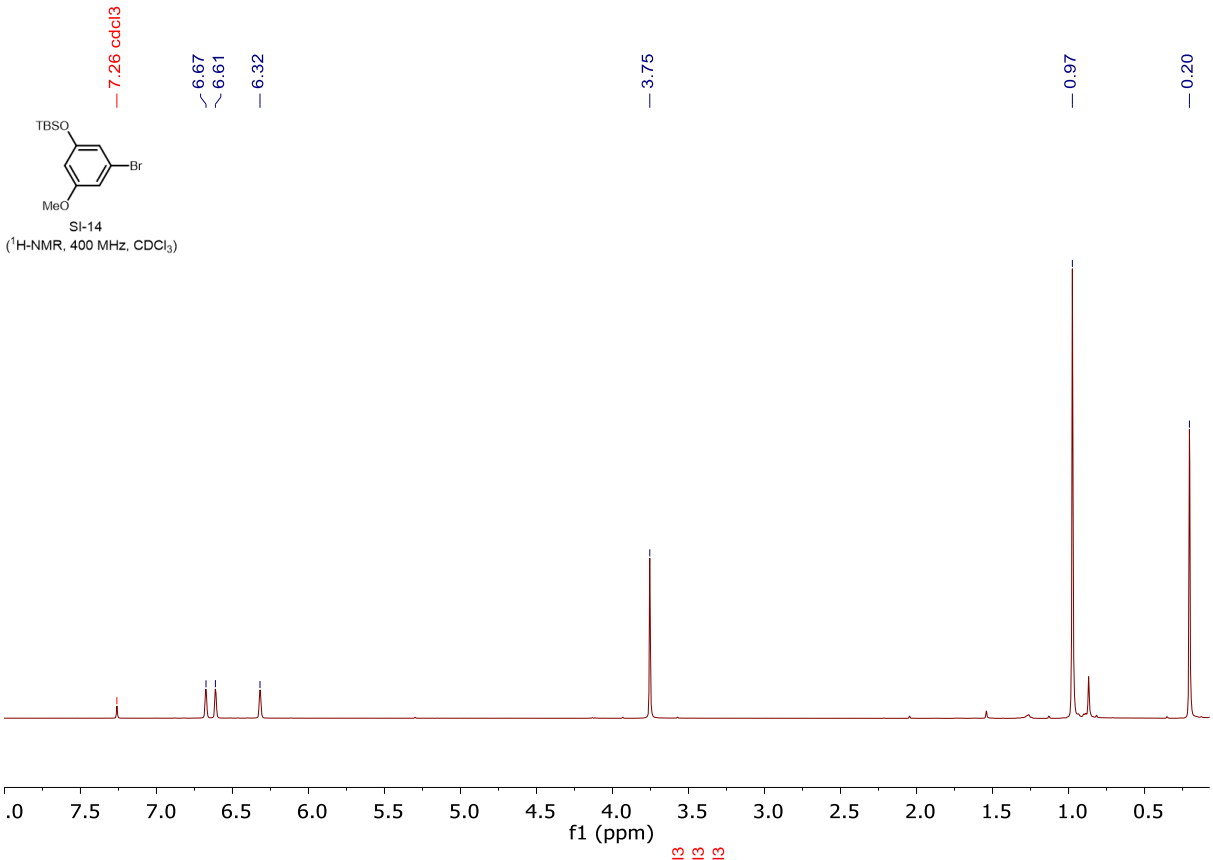
(^{1}H-NMR, 600 MHz, $CDCl_3$)

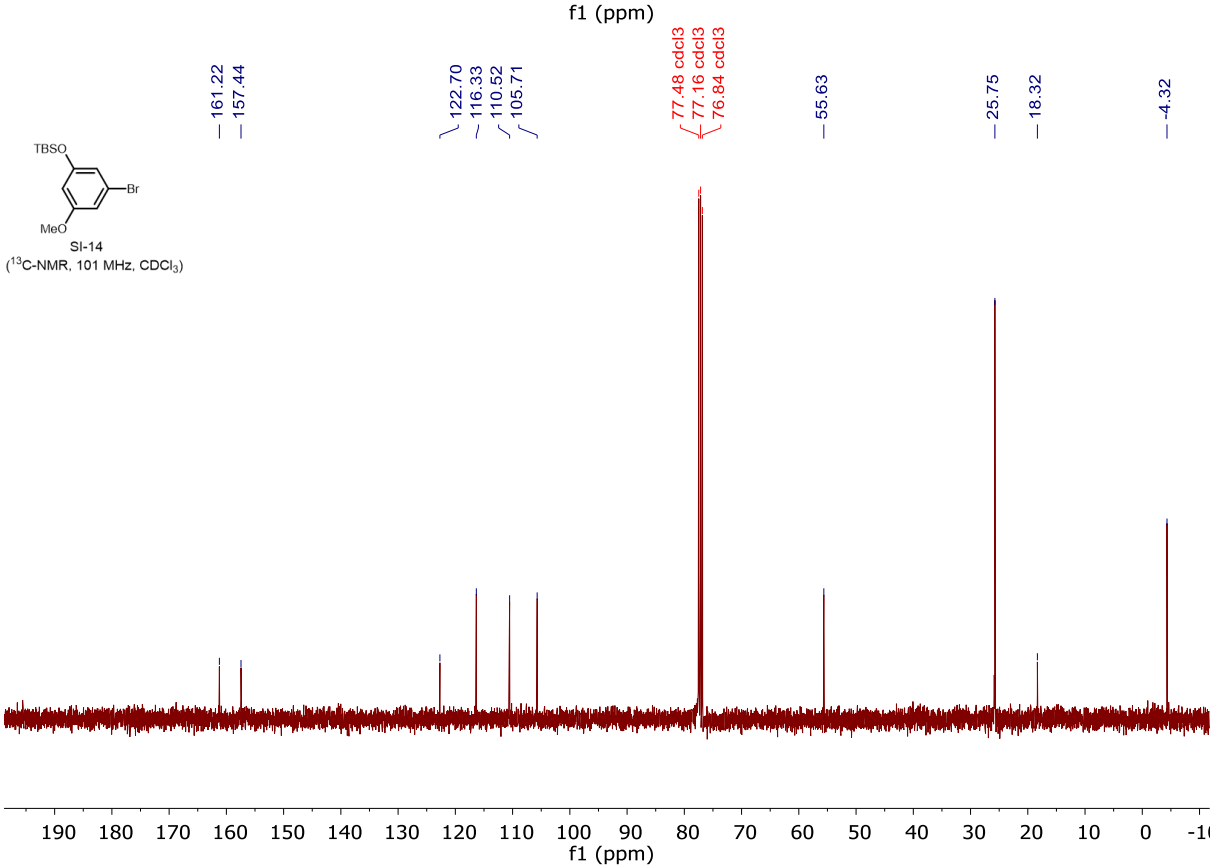


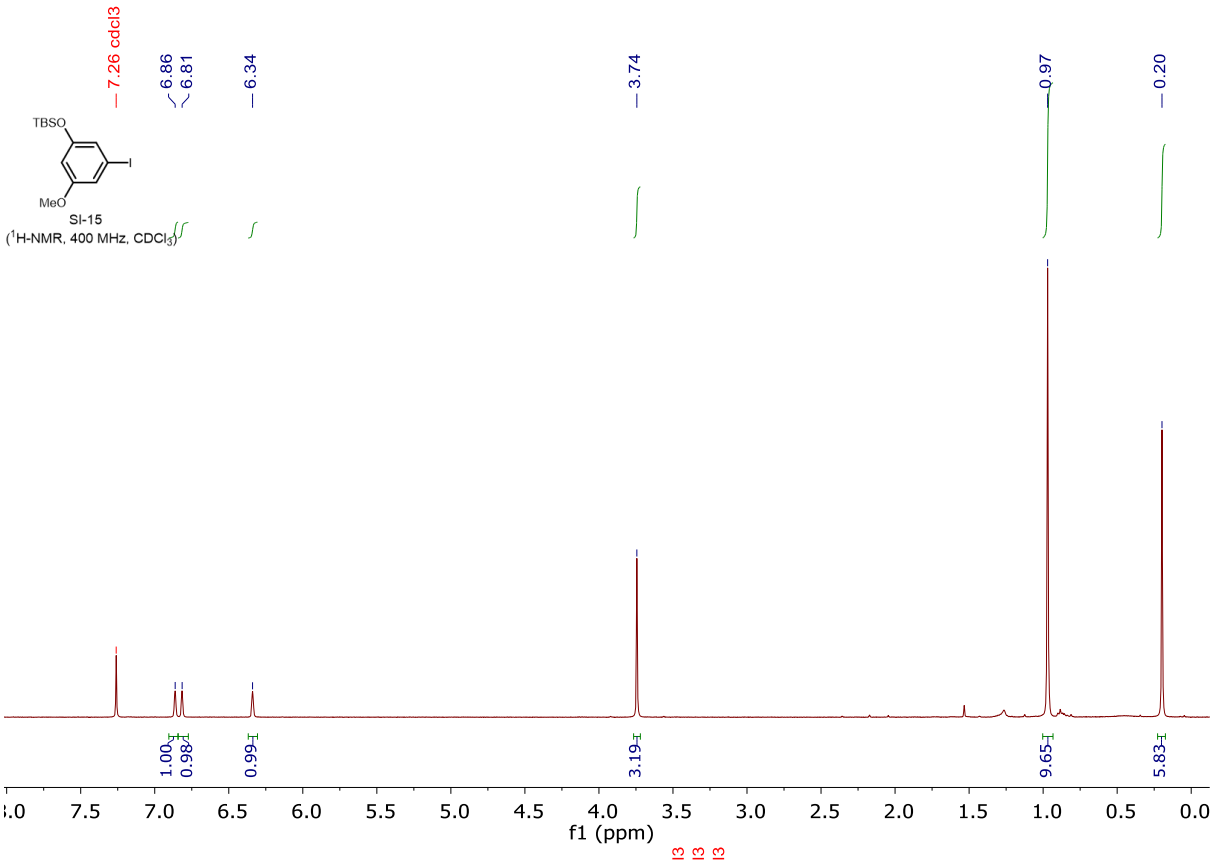


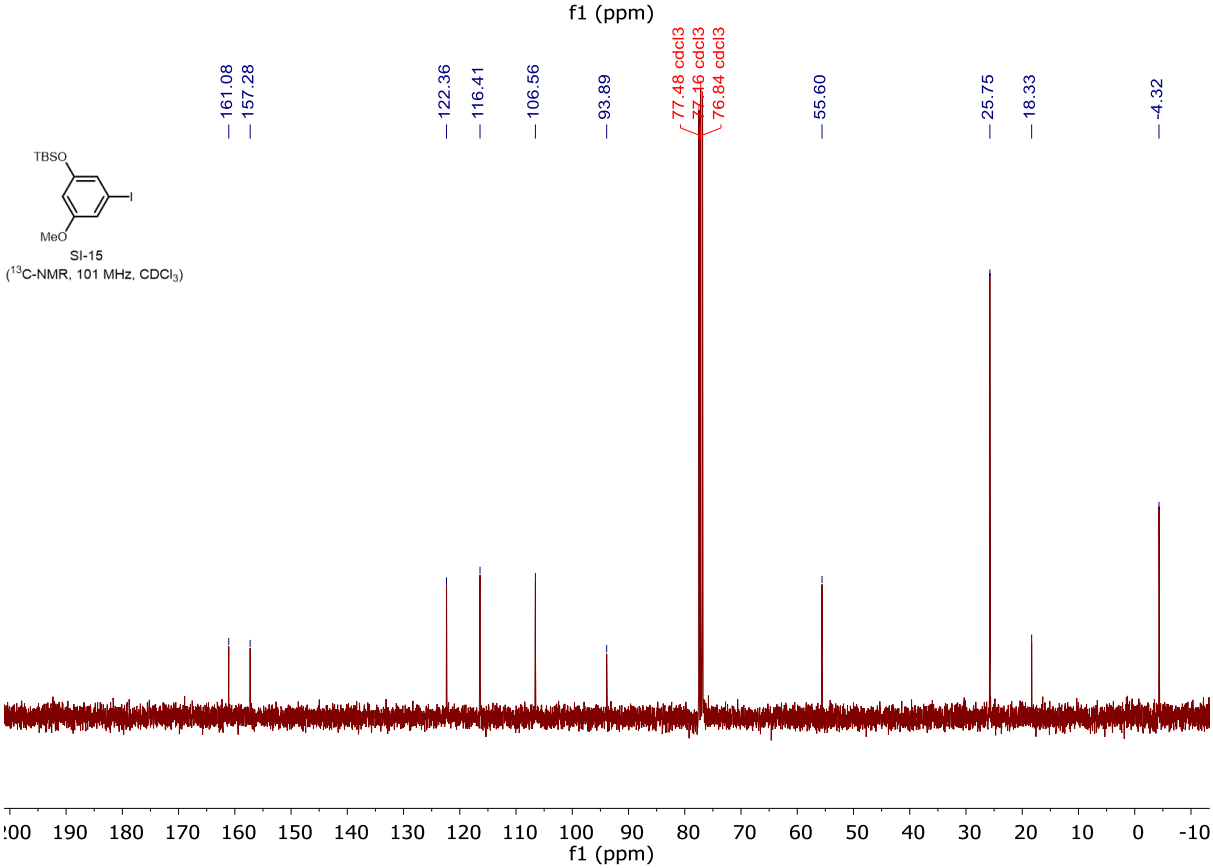
20

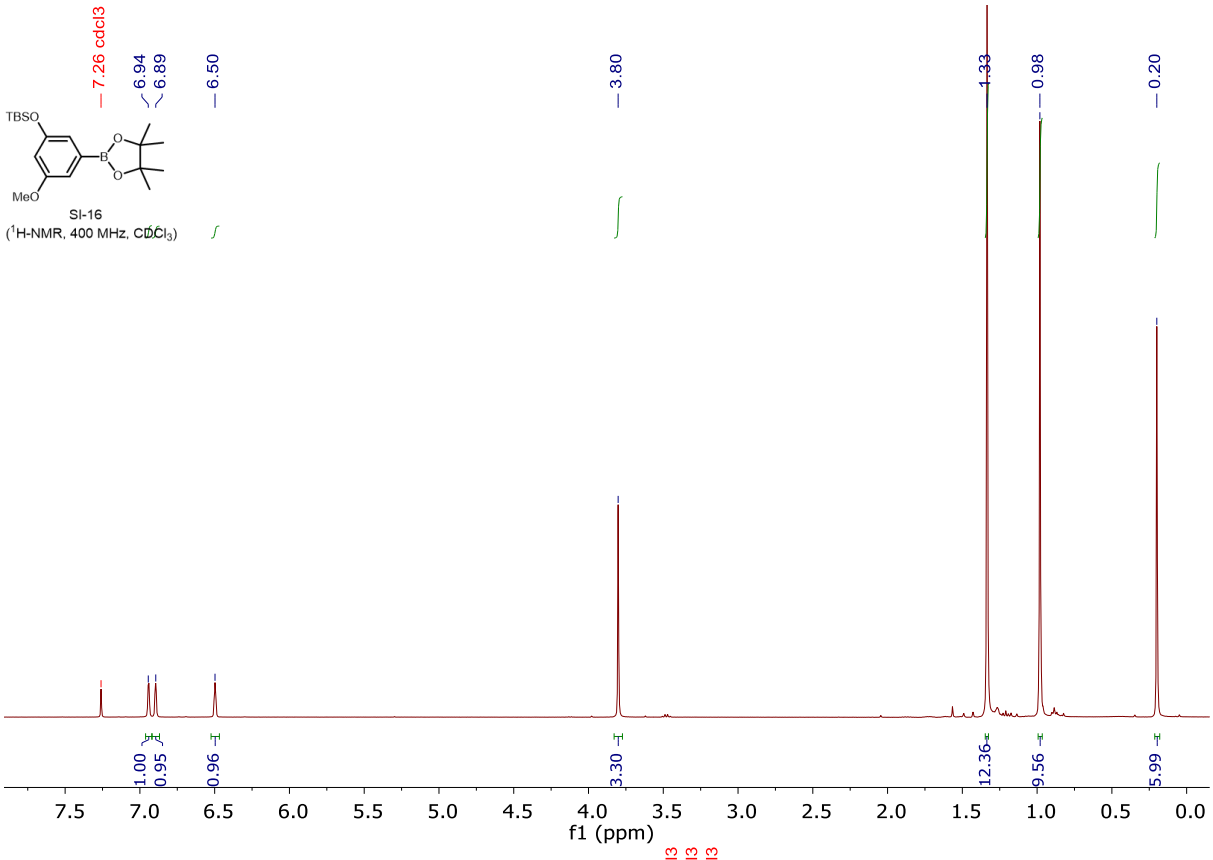
(^{13}C-NMR, 126 MHz, $CDCl_3$)

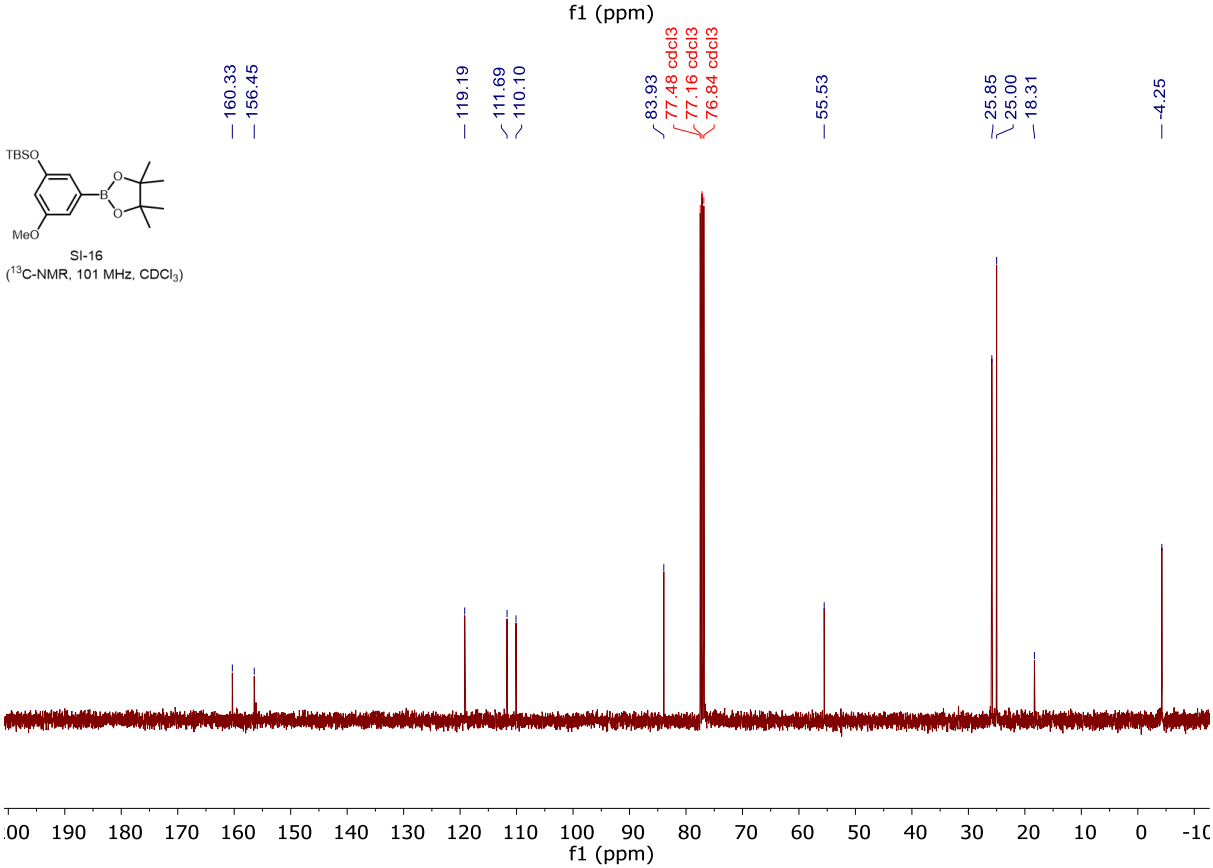

7.26 cdcl3
6.67
6.61
6.32
3.75
0.97
0.20
TBSO
Br
MeO
SI-14
(1H-NMR, 400 MHz, CDCl3)
f1 (ppm)

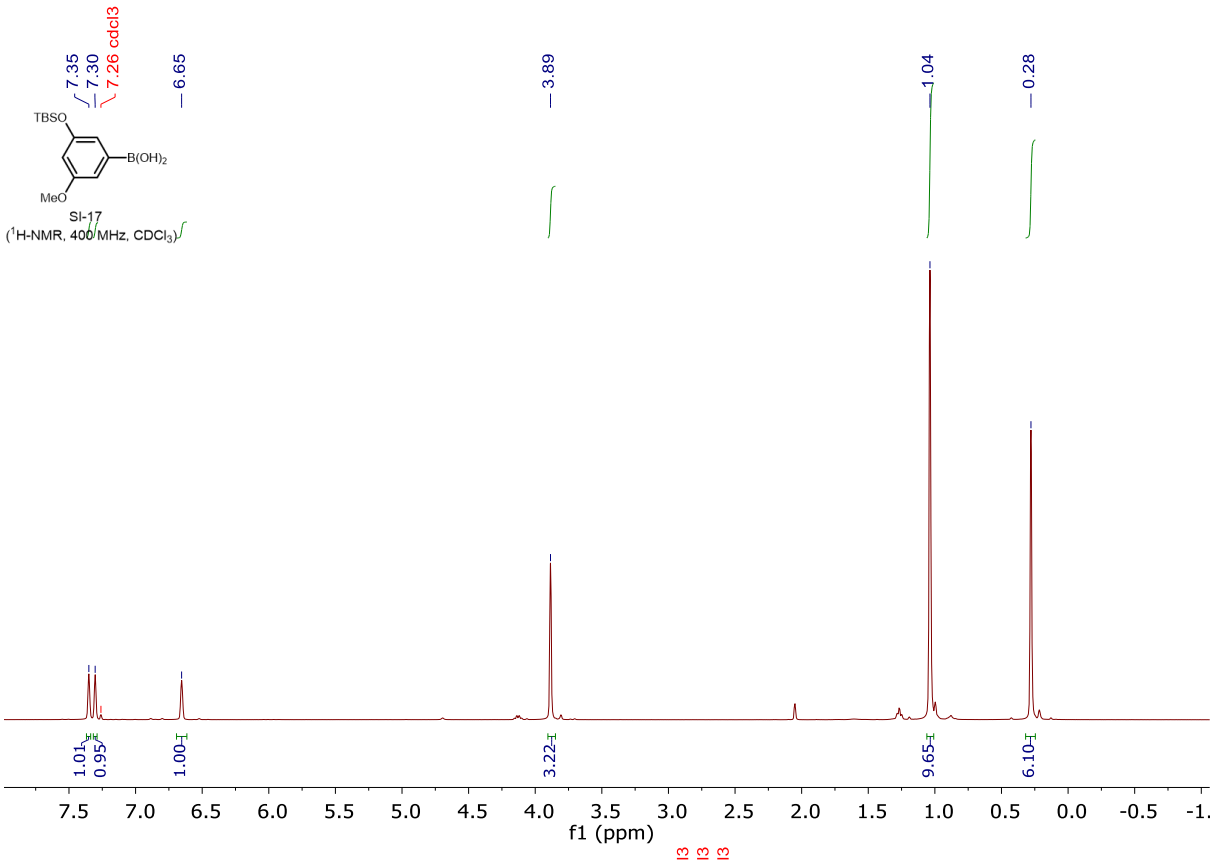

161.22
157.44
122.70
116.33
110.52
105.71
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
55.63
25.75
18.32
-4.32
TBSO
Br
MeO
SI-14
(13C-NMR, 101 MHz, CDCl3)
f1 (ppm)

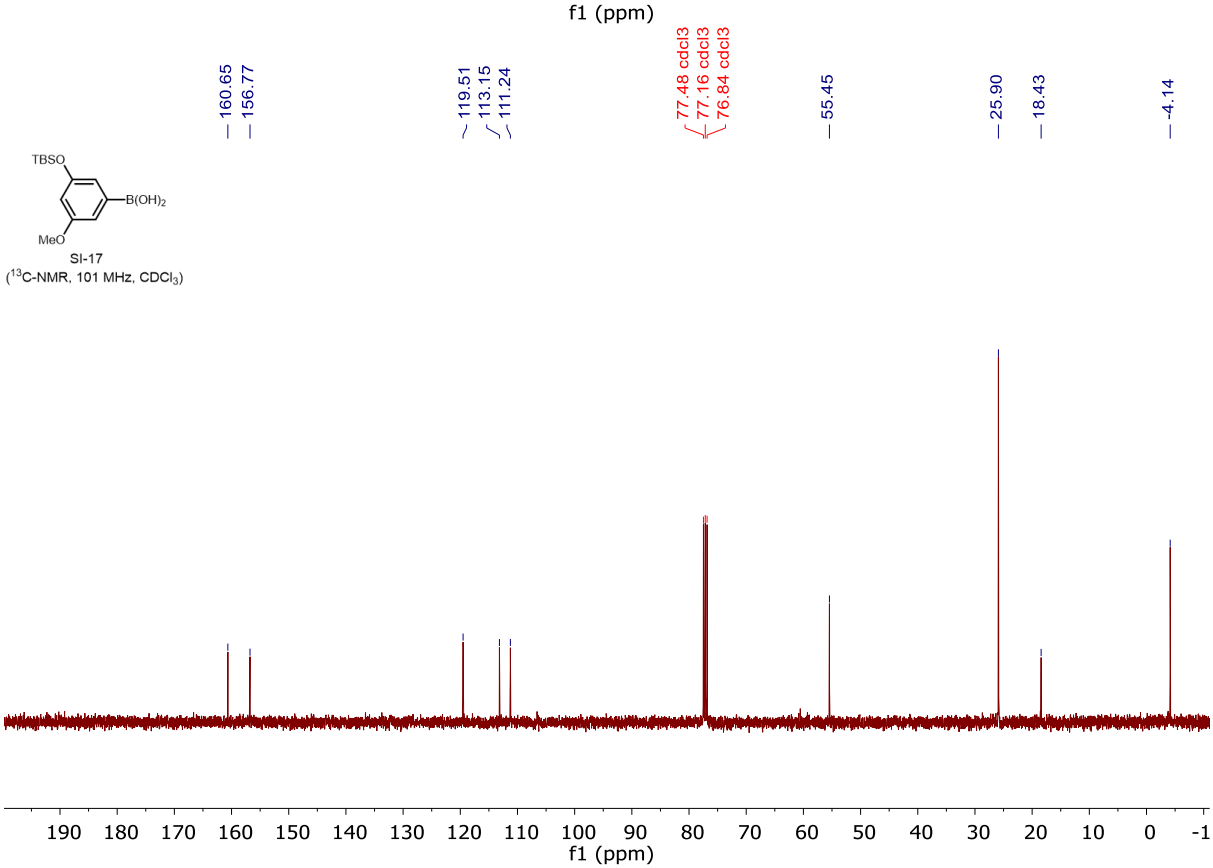

7.26 cdcl3
6.86
6.81
6.34
3.74
0.97
0.20
TBSO
I
MeO
SI-15
(1H-NMR, 400 MHz, CDCl3)
1.00
0.98
0.99
3.19
9.65
5.83
f1 (ppm)

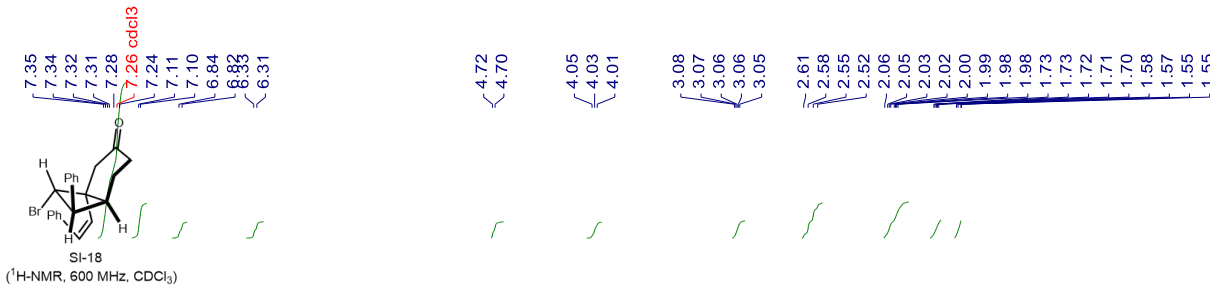

161.08
157.28
122.36
116.41
106.56
93.89
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
55.60
25.75
18.33
-4.32
TBSO
I
MeO
SI-15
(13C-NMR, 101 MHz, CDCl3)
f1 (ppm)


7.26 cdcl3
6.94
6.89
6.50
3.80
1.33
0.98
0.20
TBSO
MeO
SI-16
(1H-NMR, 400 MHz, CDCl3)
1.00
0.95
0.96
3.30
12.36
9.56
5.99
f1 (ppm)


160.33
156.45
119.19
111.69
110.10
83.93
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
55.53
25.85
25.00
18.31
-4.25
TBSO
MeO
SI-16
(13C-NMR, 101 MHz, CDCl3)
f1 (ppm)

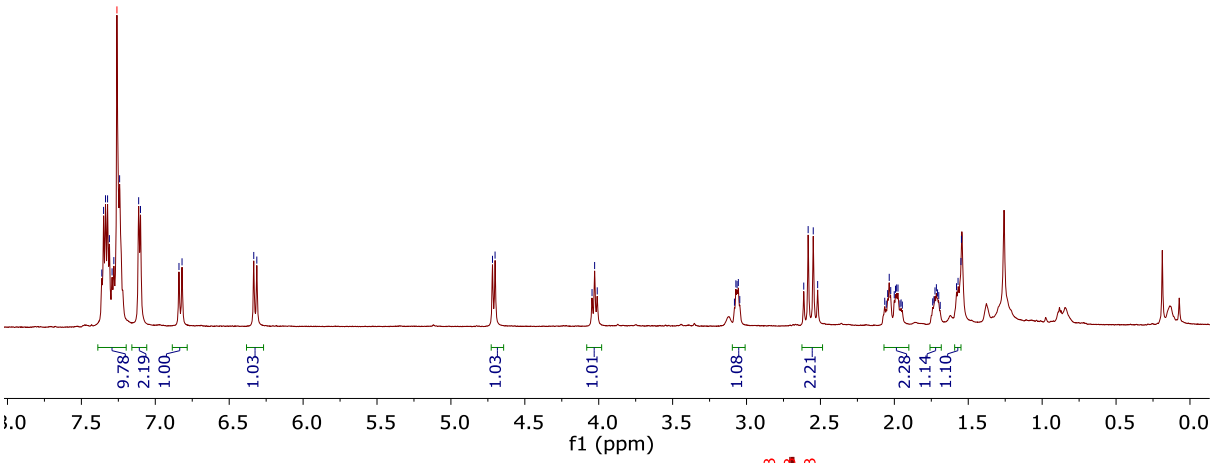

7.35
7.30
7.26 cdcl3
6.65
3.89
1.04
0.28
TBSO
B(OH)2
MeO
SI-17
(1H-NMR, 400 MHz, CDCl3)
1.01
0.95
1.00
3.22
9.65
6.10
f1 (ppm)

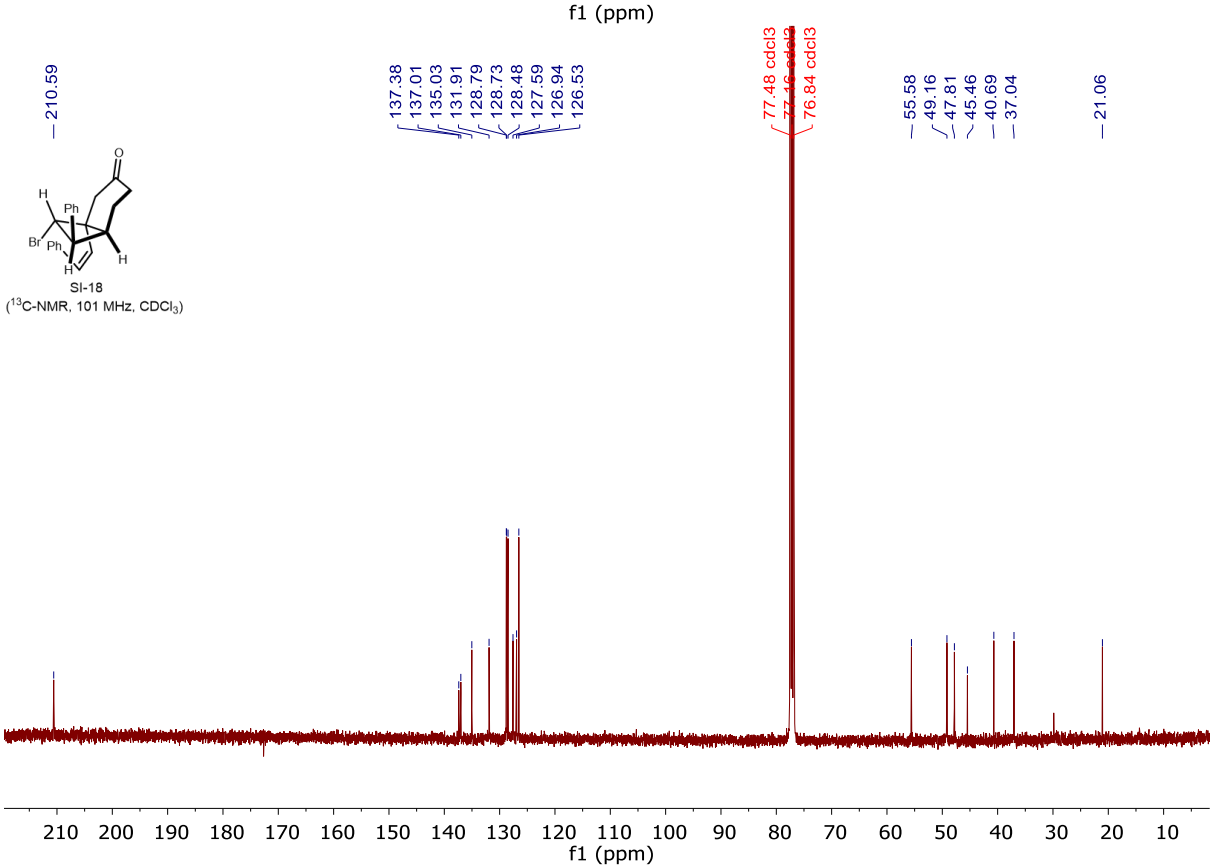

160.65
156.77
119.51
113.15
111.24
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
55.45
25.90
18.43
-4.14
TBSO
B(OH)2
MeO
SI-17
(13C-NMR, 101 MHz, CDCl3)
f1 (ppm)



SI-18

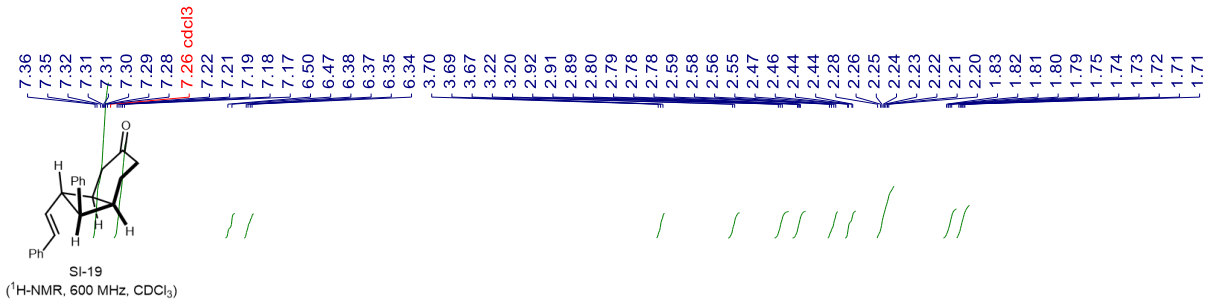
(^{1}H-NMR, 600 MHz, $CDCl_3$)



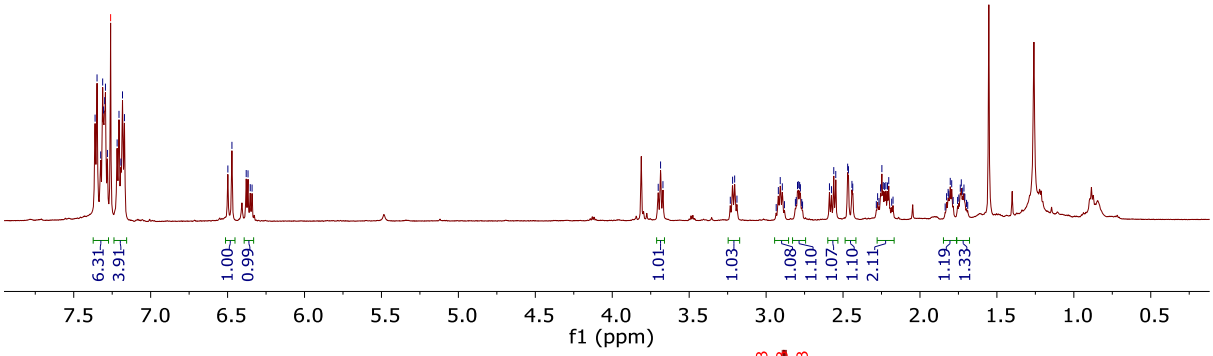


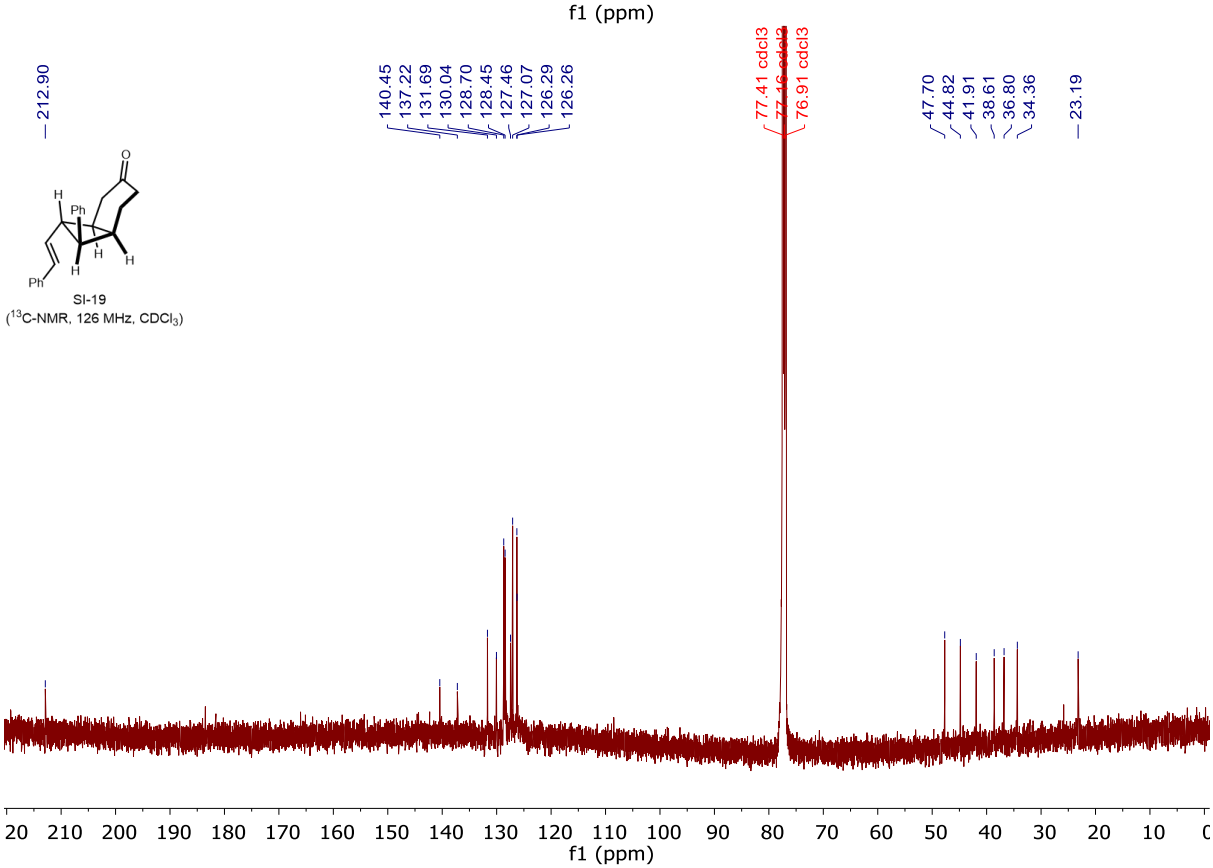
SI-18

(^{13}C-NMR, 101 MHz, $CDCl_3$)

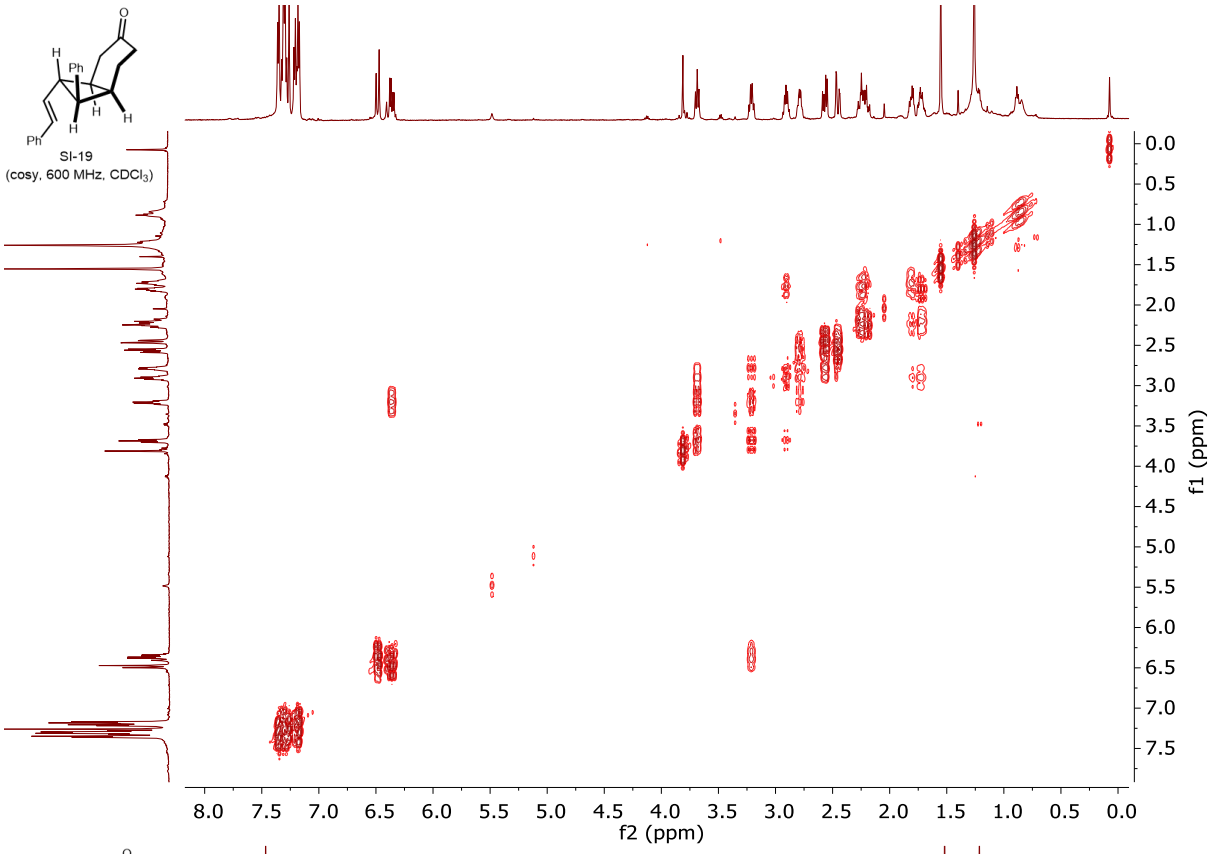


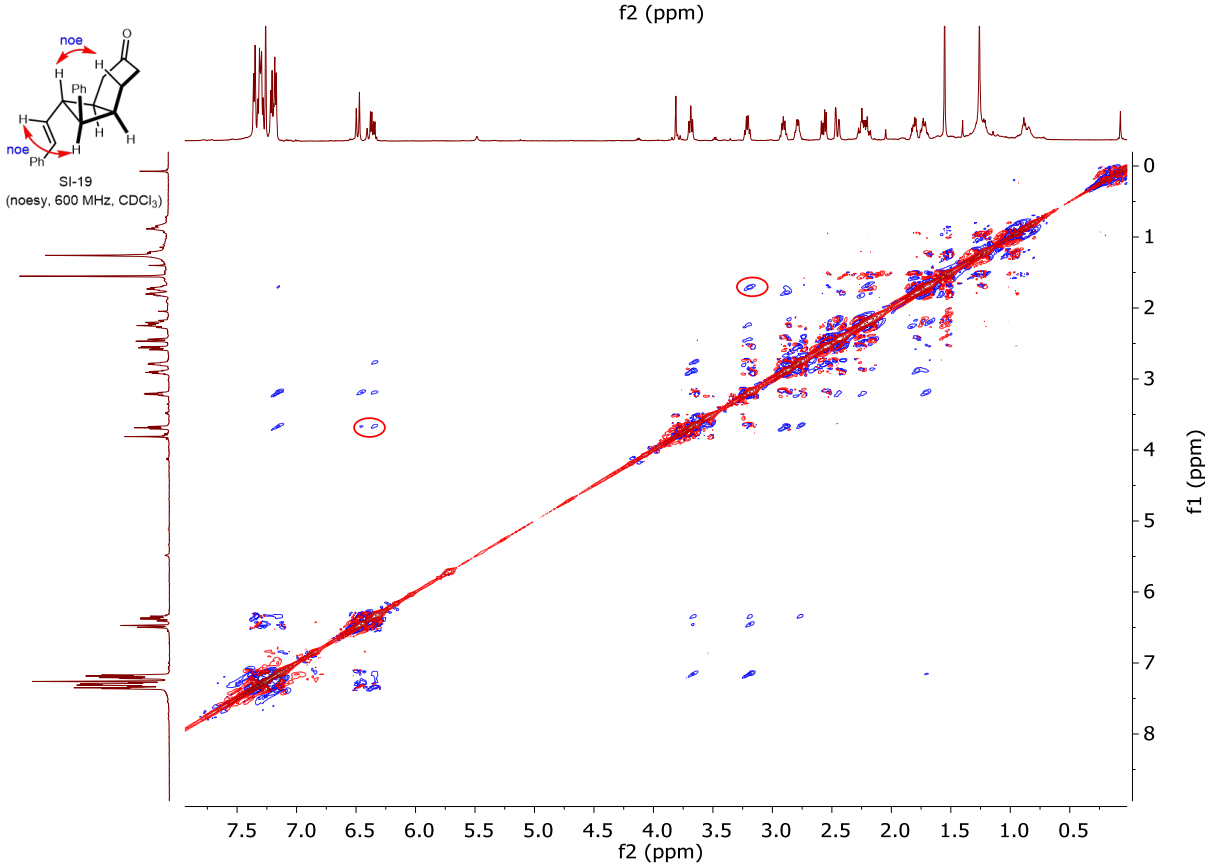
SI-19
(^{1}H-NMR, 600 MHz, $CDCl_3$)

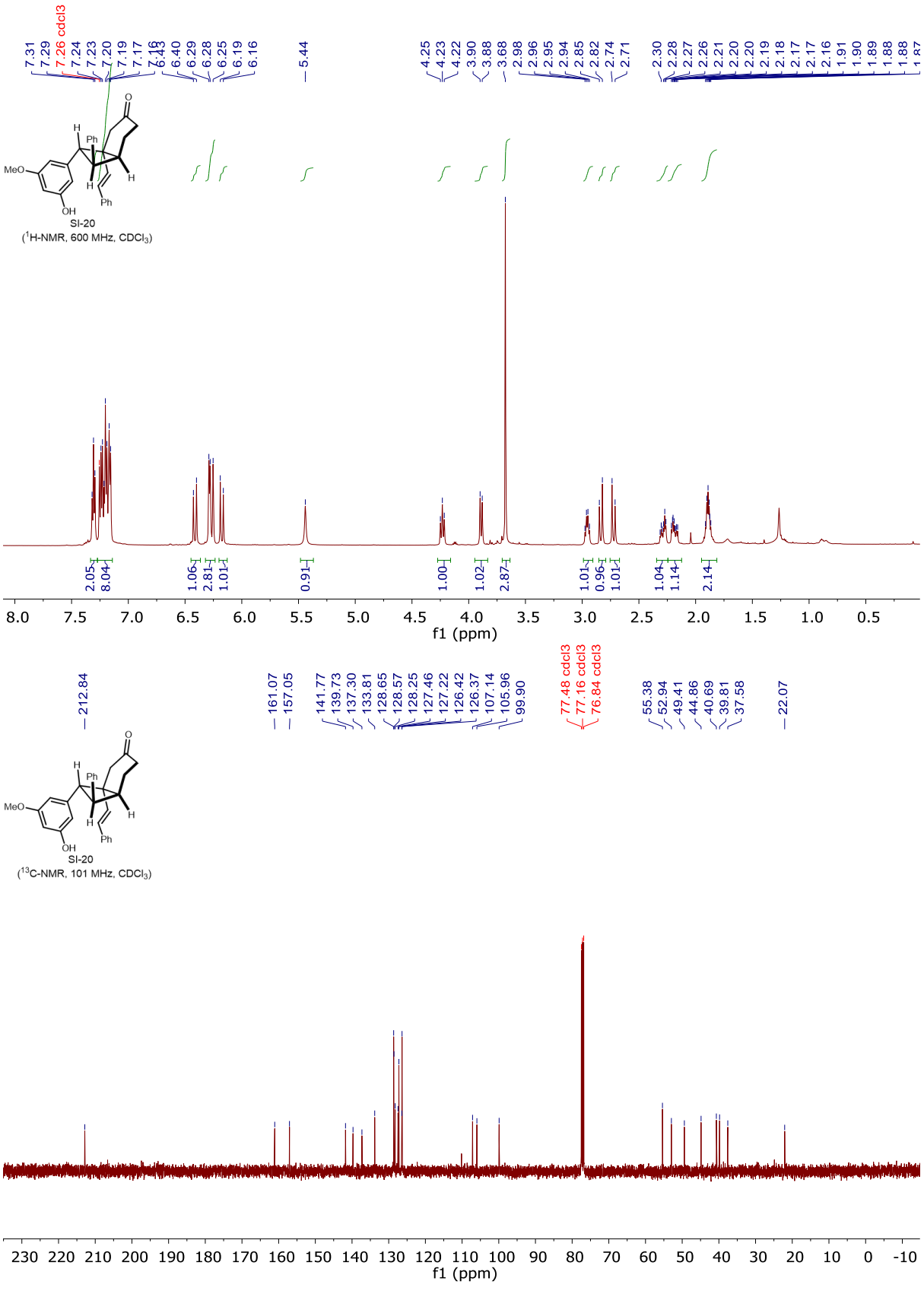


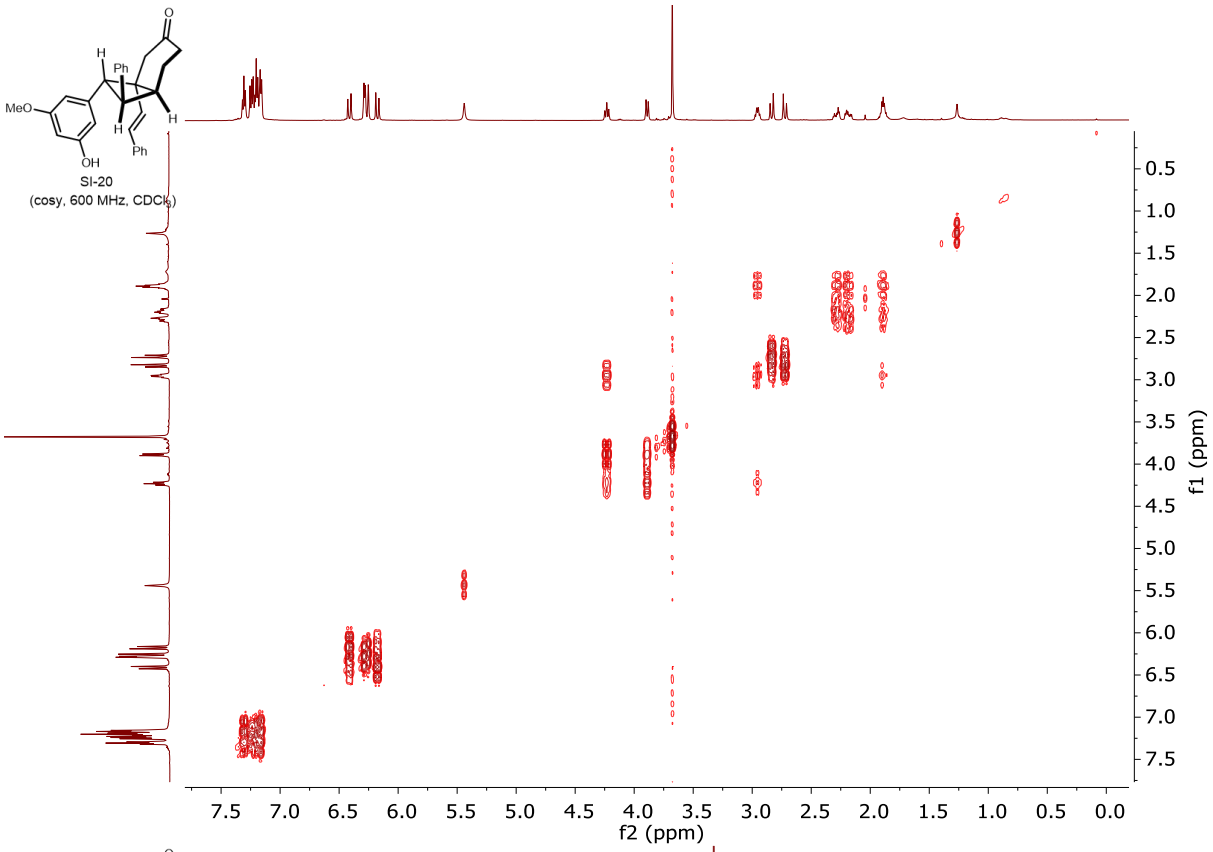


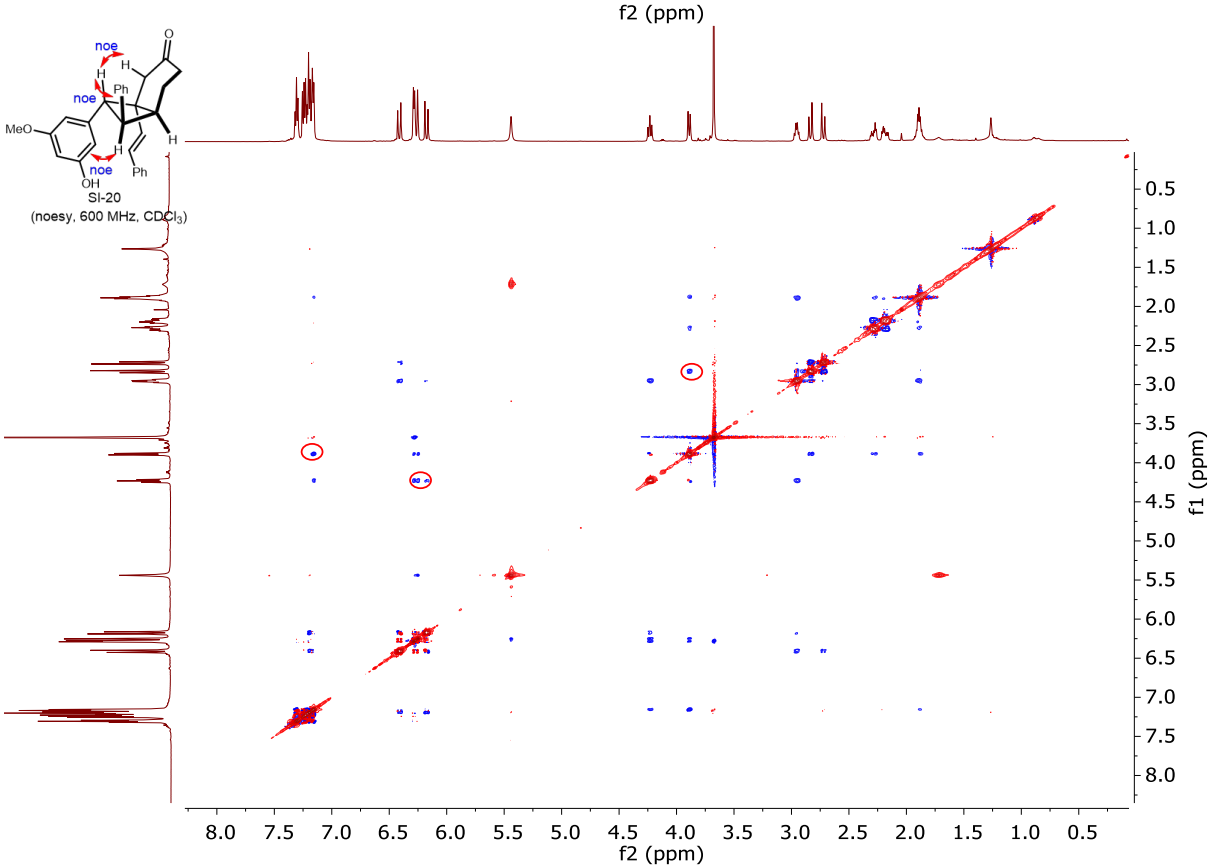
SI-19
(^{13}C-NMR, 126 MHz, $CDCl_3$)

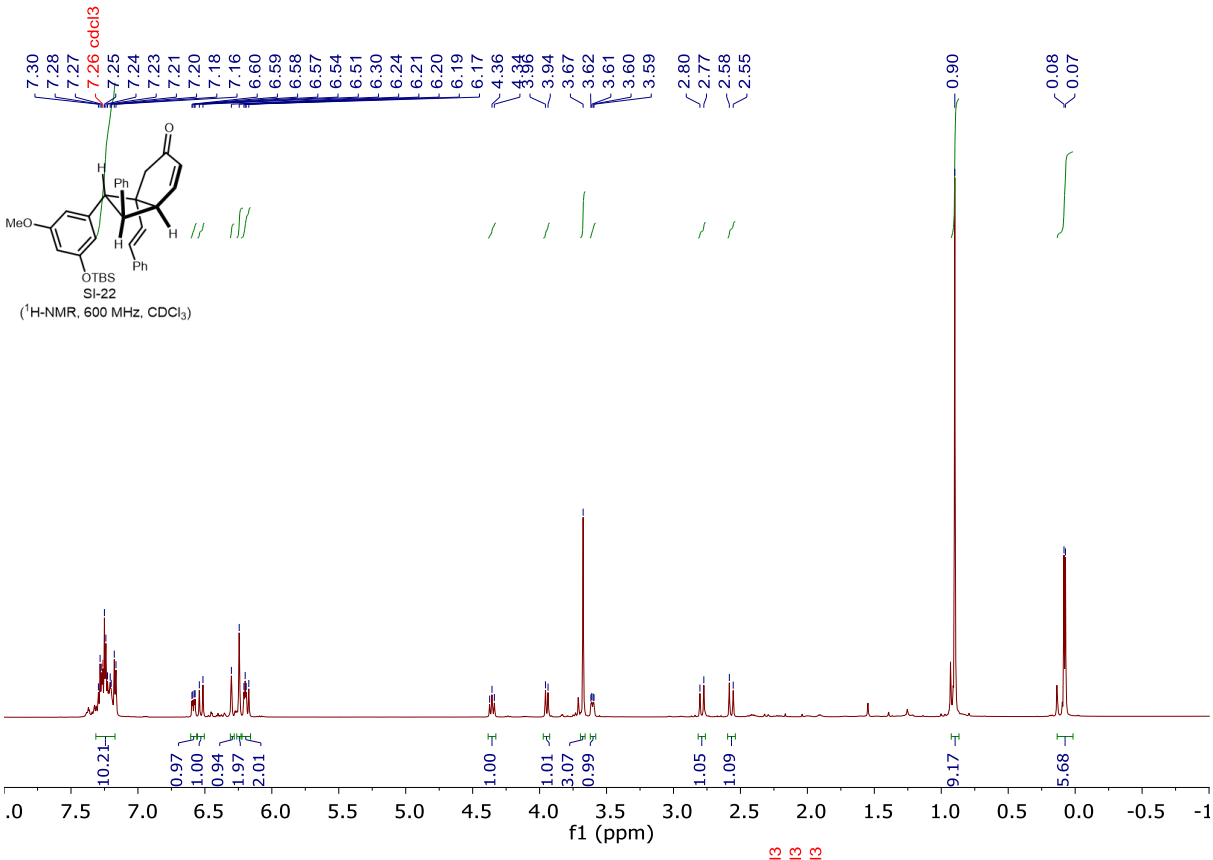

SI-19
(cosy, 600 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

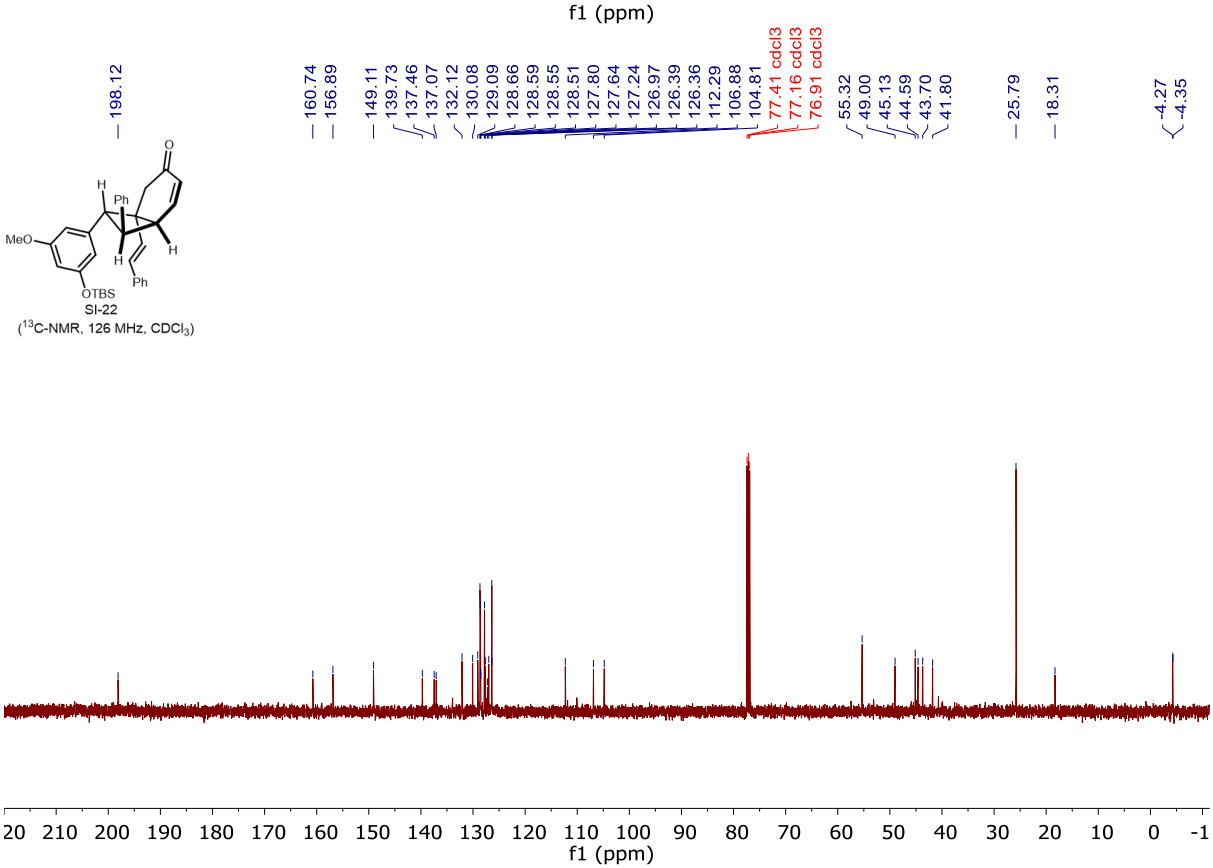

noe
noe
SI-19
(noesy, 600 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

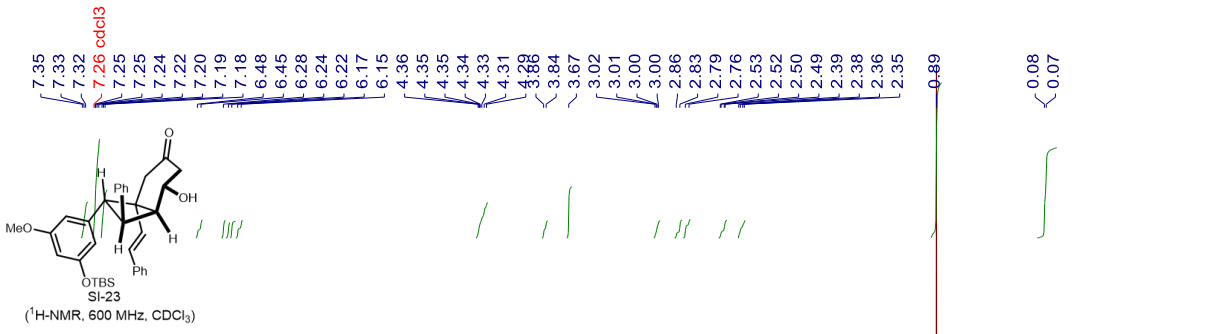

7.31
7.29
7.26 cdcl3
7.24
7.23
7.20
7.19
7.17
6.40
6.29
6.28
6.25
6.19
6.16
5.44
4.25
4.23
4.22
3.90
3.88
3.68
2.98
2.96
2.95
2.94
2.85
2.82
2.74
2.71
2.30
2.28
2.27
2.26
2.21
2.20
2.20
2.19
2.18
2.17
2.17
2.16
1.91
1.90
1.89
1.88
1.88
MeO
OH
Ph
Ph
H
H
H
O
SI-20
(1H-NMR, 600 MHz, CDCl3)
2.05
8.04
1.06
2.81
1.01
0.91
1.00
1.02
2.87
1.01
0.96
1.01
1.04
1.14
2.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
212.84
161.07
157.05
141.77
139.73
137.30
133.81
128.65
128.57
128.25
127.46
127.22
126.42
126.37
107.14
105.96
99.90
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
55.38
52.94
49.41
44.86
40.69
39.81
37.58
22.07
MeO
OH
Ph
Ph
H
H
H
O
SI-20
(13C-NMR, 101 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

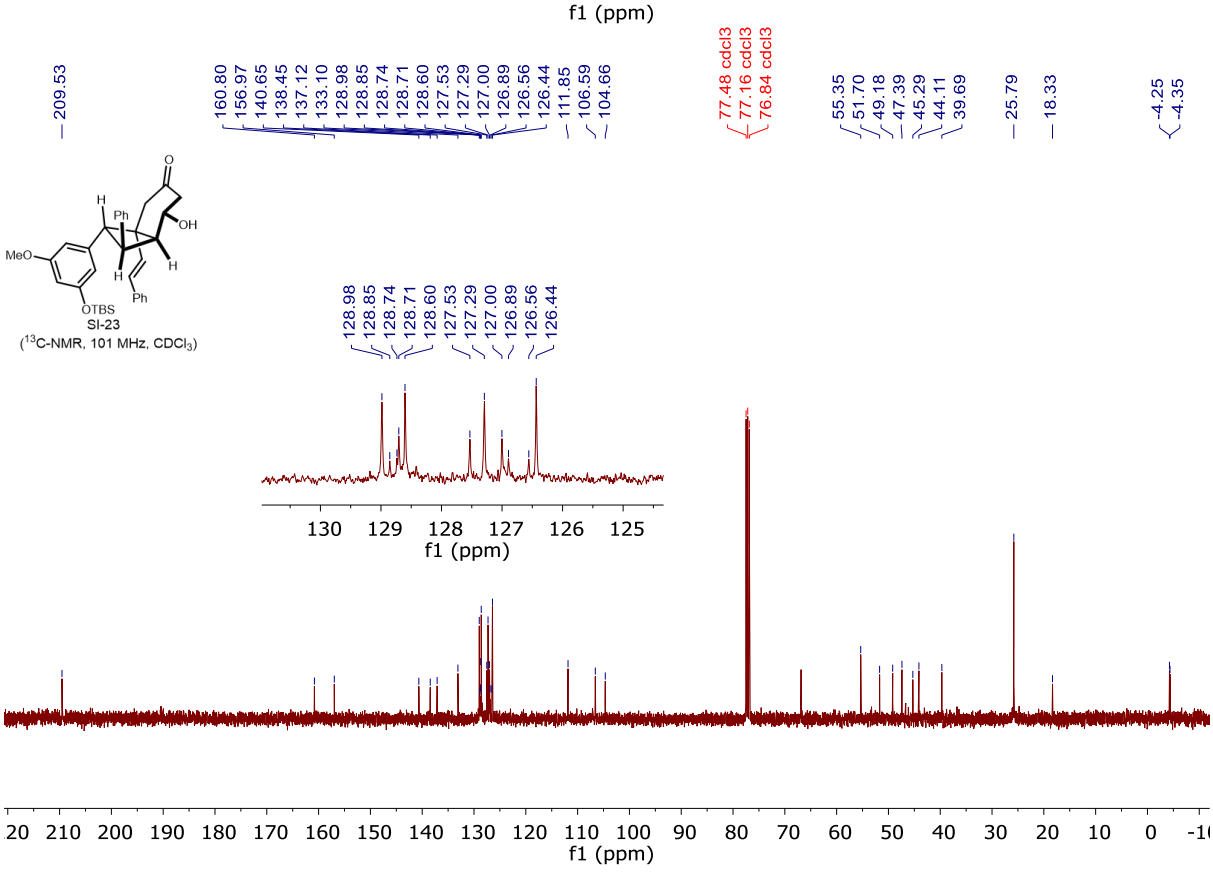

MeO
OH
H
Ph
H
H
Ph
O
SI-20
(cosy, 600 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

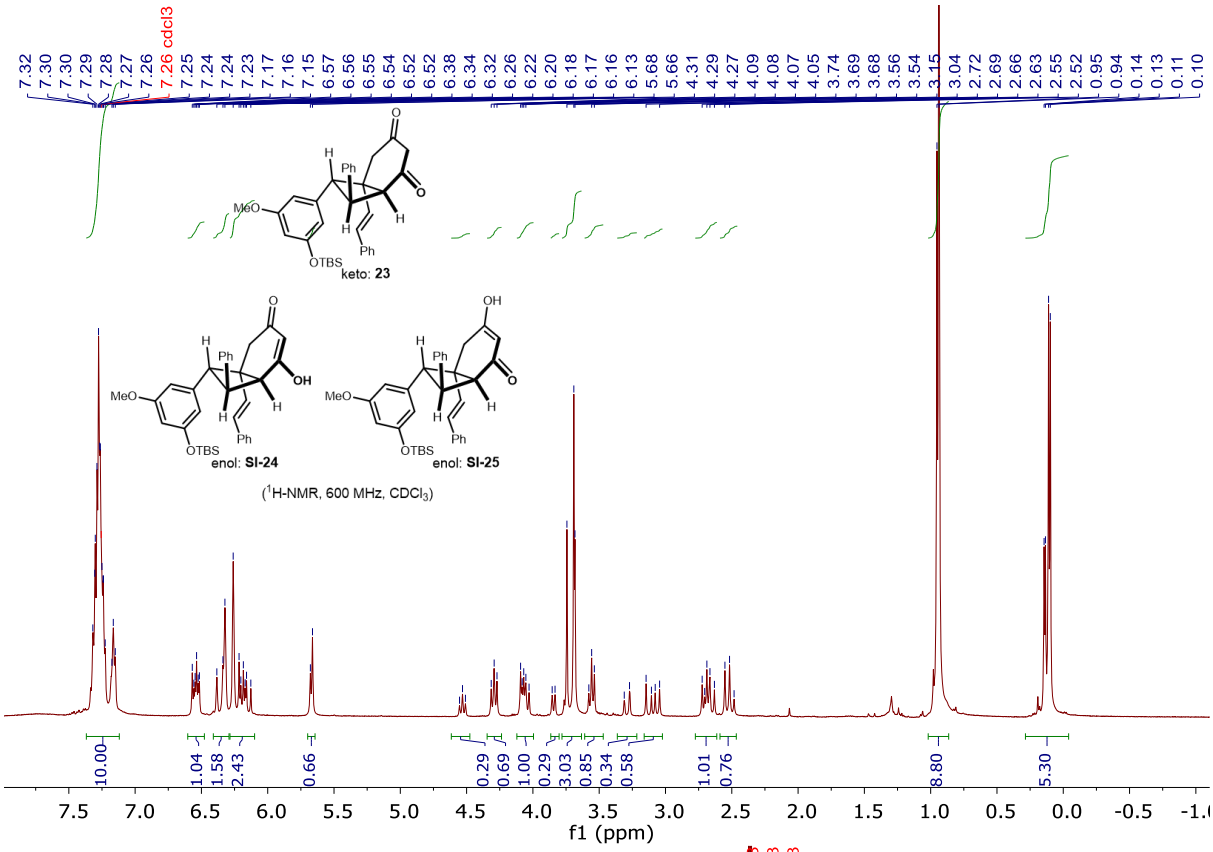

noe
noe
noe
MeO
OH
H
Ph
H
H
Ph
O
SI-20
(noesy, 600 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

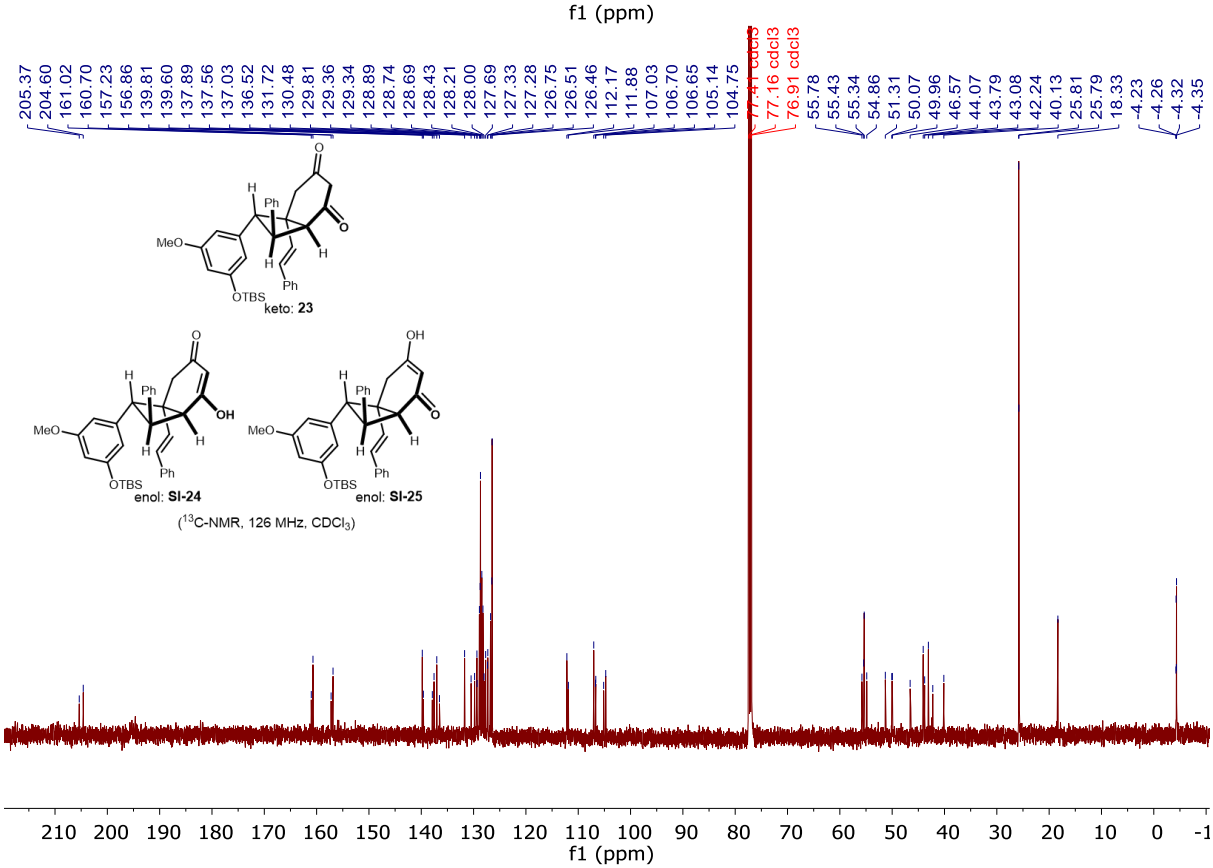

7.30
7.28
7.27
7.26 cdcl3
7.25
7.24
7.23
7.21
7.20
7.18
7.16
6.60
6.59
6.58
6.57
6.54
6.51
6.30
6.24
6.21
6.20
6.19
6.17
4.36
4.34
3.96
3.94
3.67
3.62
3.61
3.60
3.59
2.80
2.77
2.58
2.55
0.90
0.08
0.07
MeO
OTBS
Ph
Ph
H
H
H
O
SI-22
(1H-NMR, 600 MHz, CDCl3)
10.21
0.97
1.00
0.94
1.97
2.01
1.00
1.01
3.07
0.99
1.05
1.09
9.17
5.68
f1 (ppm)

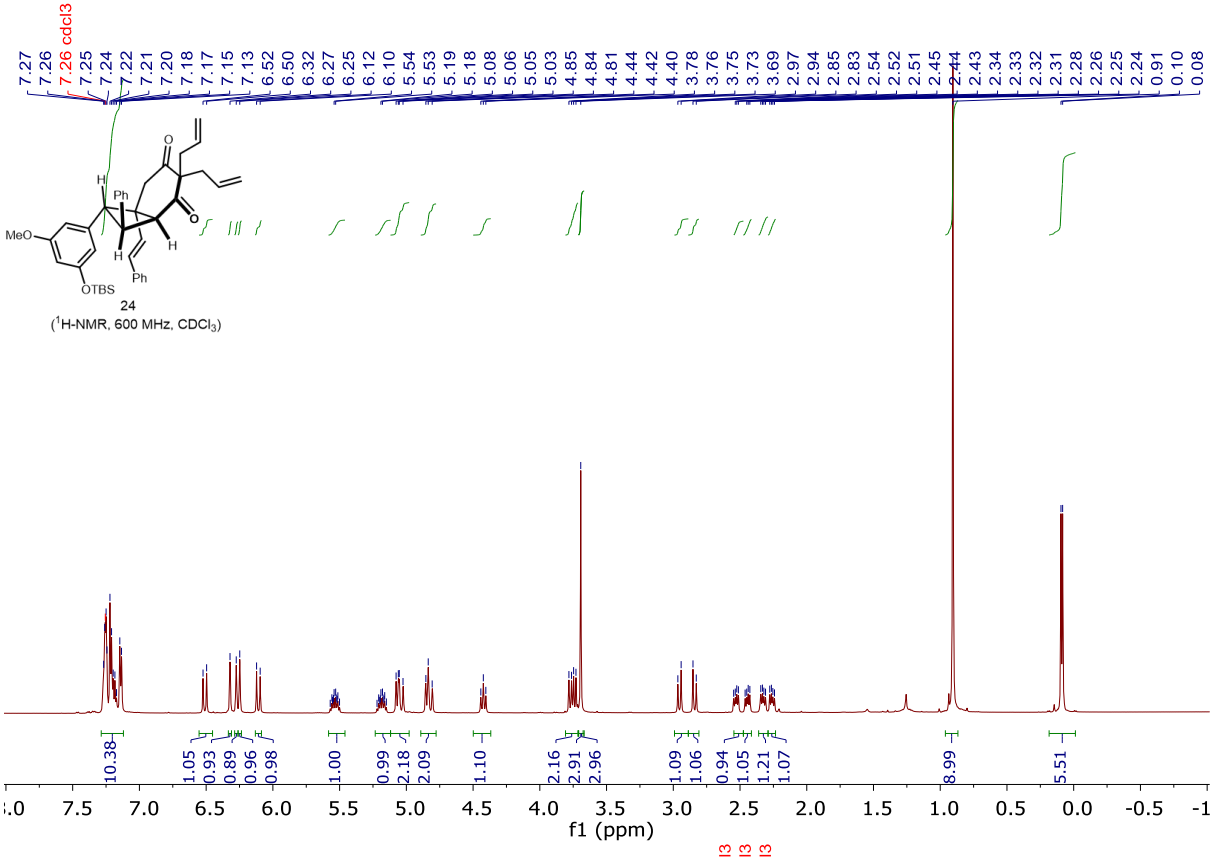

198.12
160.74
156.89
149.11
139.73
137.46
137.07
132.12
130.08
129.09
128.66
128.59
128.55
128.51
127.80
127.64
127.24
126.97
126.39
126.36
112.29
106.88
104.81
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
55.32
49.00
45.13
44.59
43.70
41.80
25.79
18.31
-4.27
-4.35
MeO
OTBS
Ph
Ph
H
H
H
O
SI-22
(13C-NMR, 126 MHz, CDCl3)
f1 (ppm)

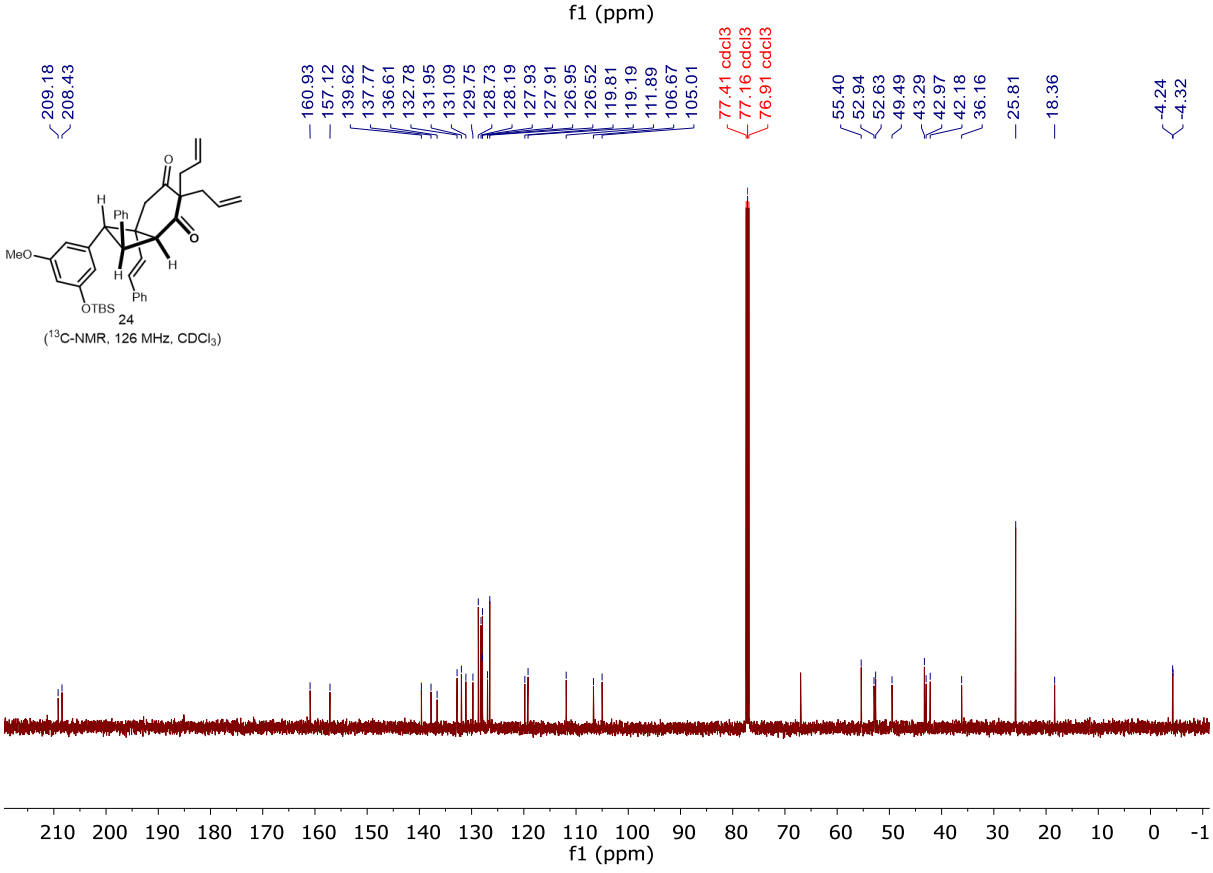

SI-23
(1H-NMR, 600 MHz, CDCl3)

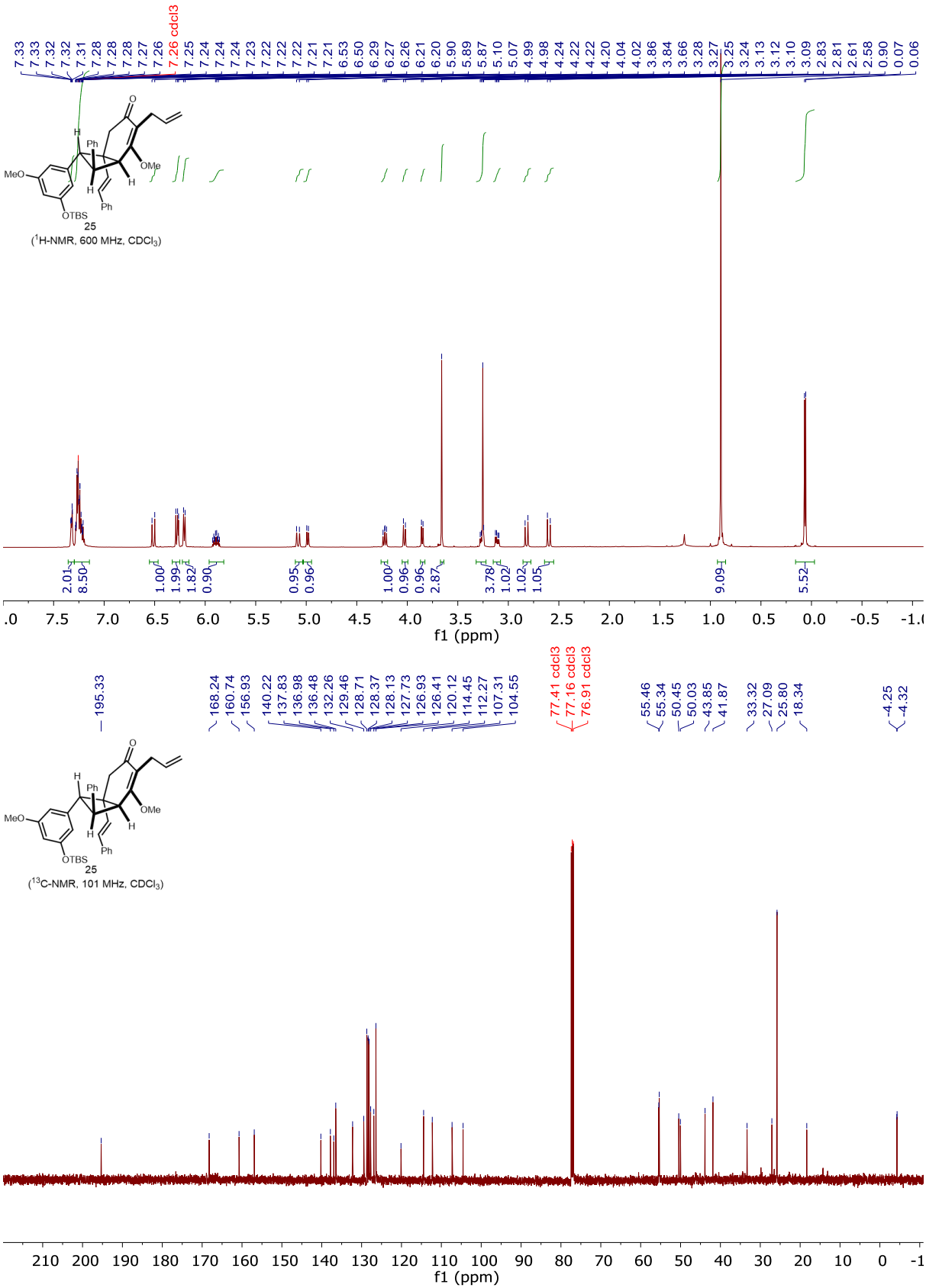

SI-23
(13C-NMR, 101 MHz, CDCl3)

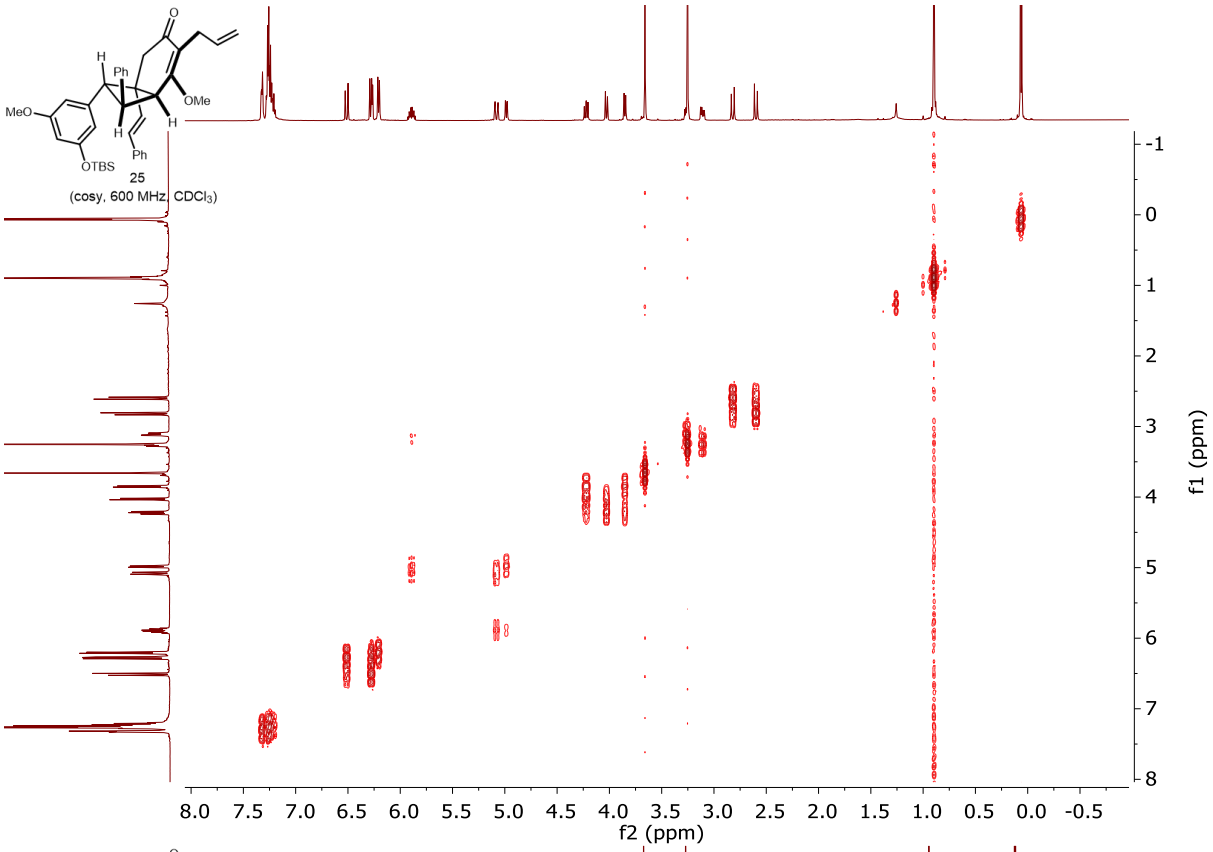

keto: 23
enol: SI-24
enol: SI-25
(1H-NMR, 600 MHz, CDCl3)
f1 (ppm)

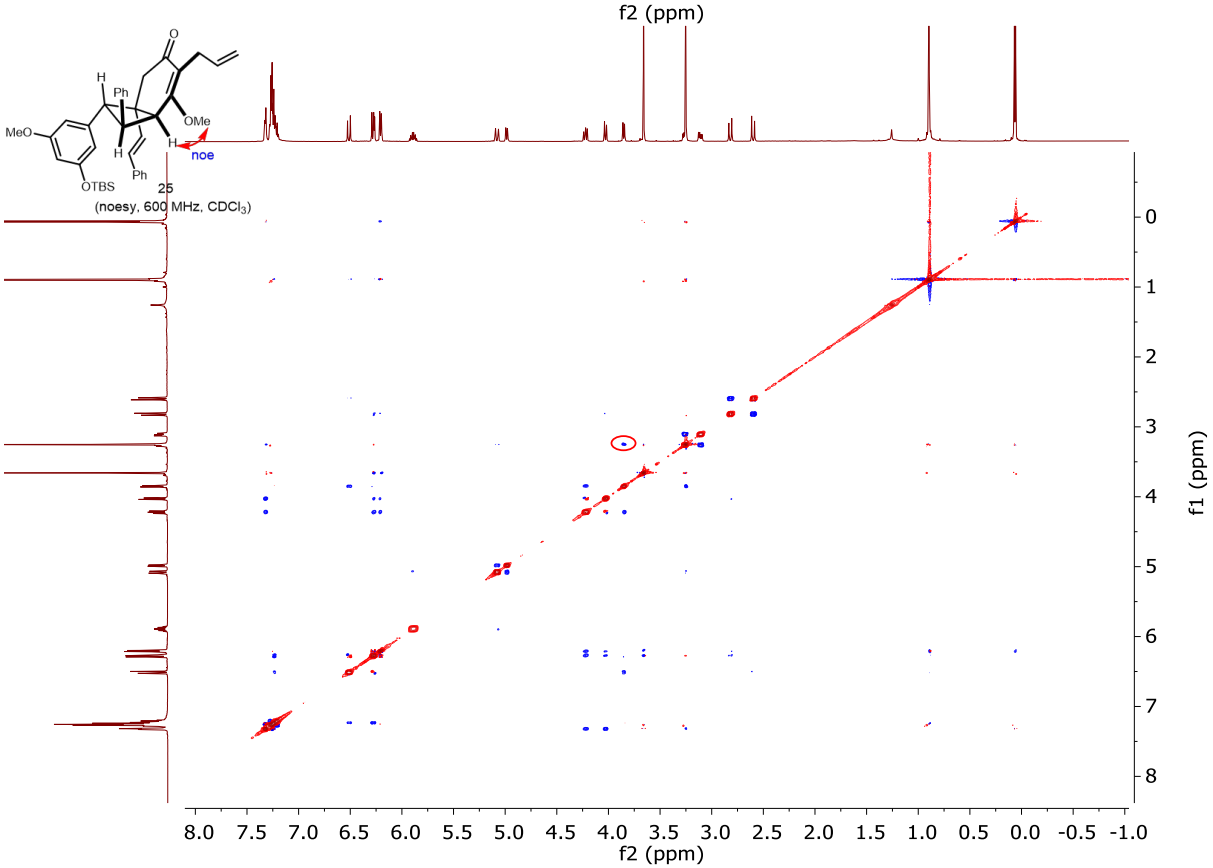

keto: 23
enol: SI-24
enol: SI-25
(13C-NMR, 126 MHz, CDCl3)
f1 (ppm)

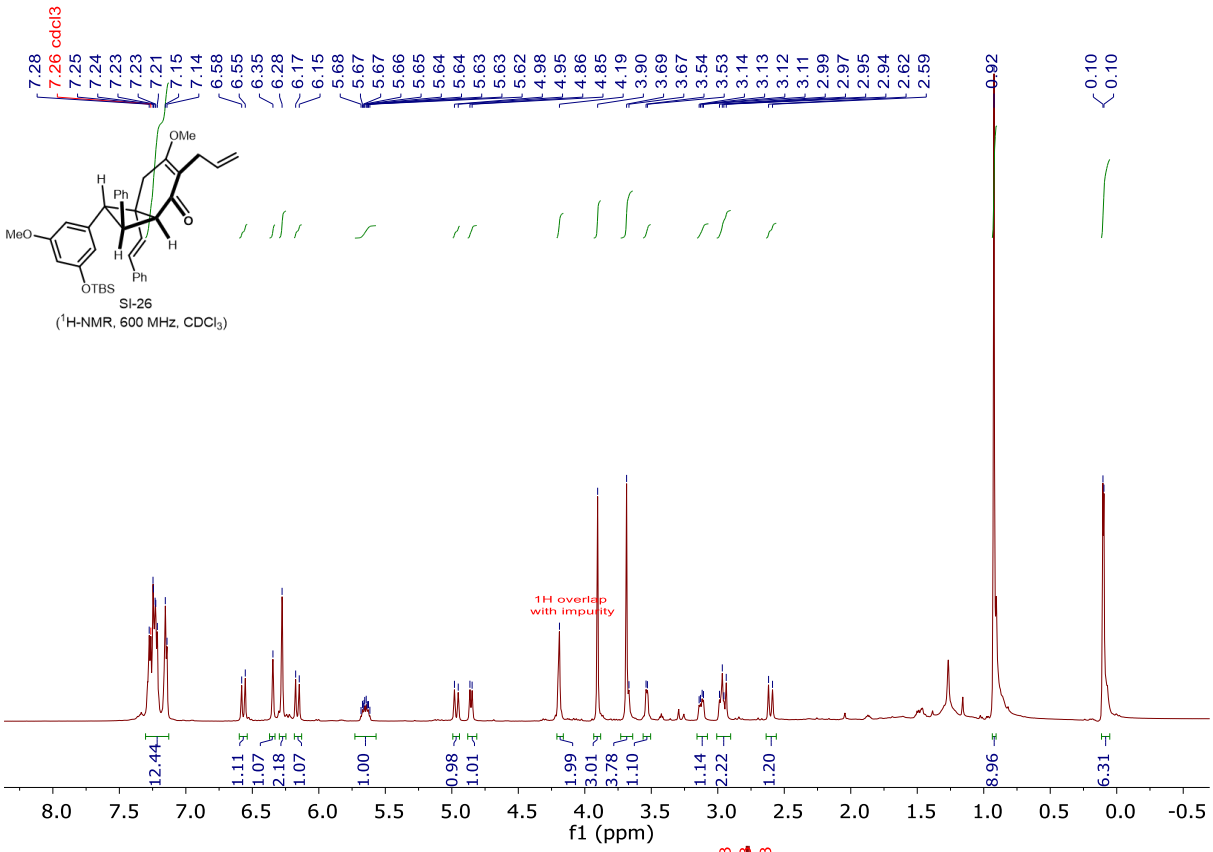

7.27 7.26 7.26 cdcl3 7.25 7.24 7.22 7.21 7.20 7.18 7.17 7.15 7.13 6.52 6.50 6.32 6.27 6.25 6.12 6.10 5.54 5.53 5.19 5.18 5.08 5.06 5.05 5.03 4.85 4.84 4.81 4.44 4.42 4.40 3.78 3.76 3.75 3.73 3.69 2.97 2.94 2.85 2.83 2.54 2.52 2.51 2.45 2.44 2.43 2.34 2.33 2.32 2.31 2.28 2.26 2.25 2.24 0.91 0.10 0.08
MeO
OTBS
Ph
H
O
24
(1H-NMR, 600 MHz, CDCl3)
10.38 1.05 0.93 0.89 0.96 0.98 1.00 0.99 2.18 2.09 1.10 2.16 2.91 2.96 1.09 1.06 0.94 1.05 1.21 1.07 8.99 5.51
f1 (ppm)

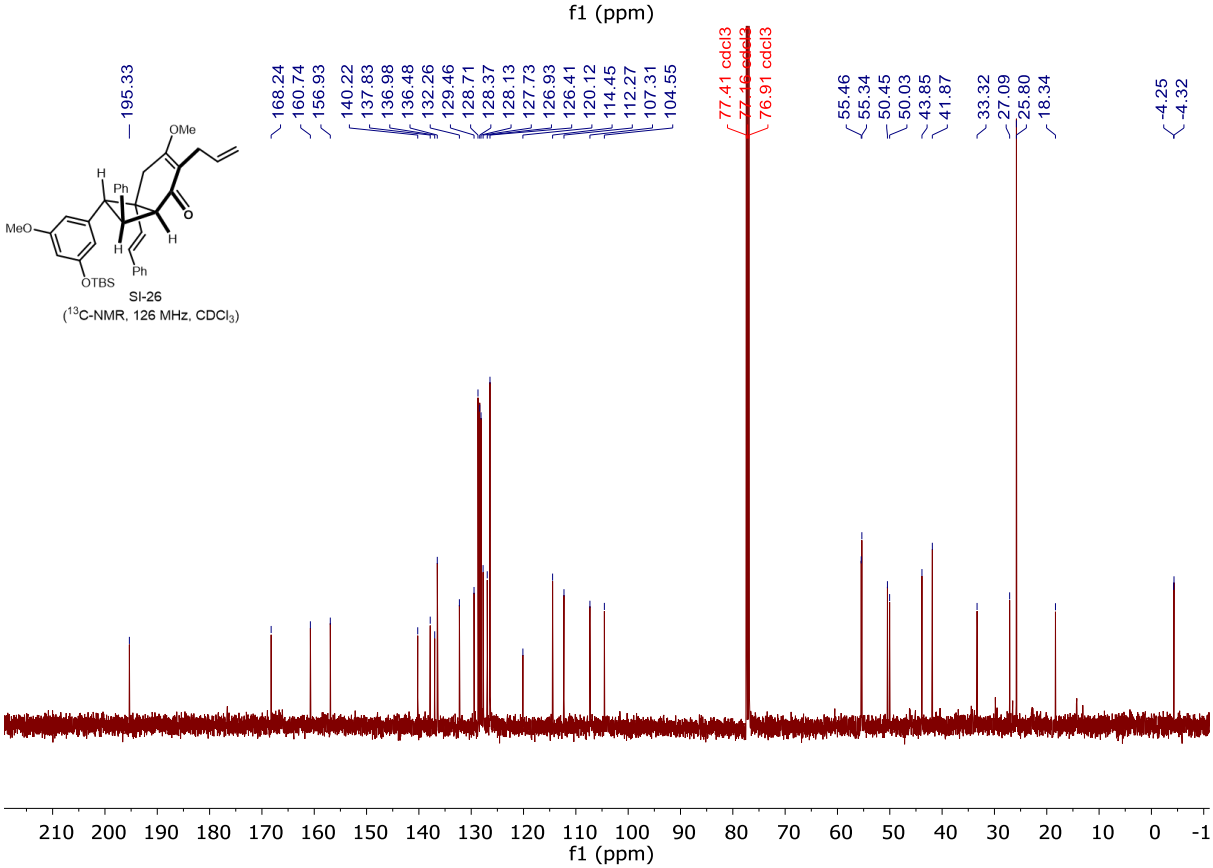

209.18 208.43 160.93 157.12 139.62 137.77 136.61 132.78 131.95 131.09 129.75 128.73 128.19 127.93 127.91 126.95 126.52 119.81 119.19 111.89 106.67 105.01 77.41 cdcl3 77.16 cdcl3 76.91 cdcl3 55.40 52.94 52.63 49.49 43.29 42.97 42.18 36.16 25.81 18.36 -4.24 -4.32
MeO
OTBS
Ph
H
O
24
(13C-NMR, 126 MHz, CDCl3)
f1 (ppm)

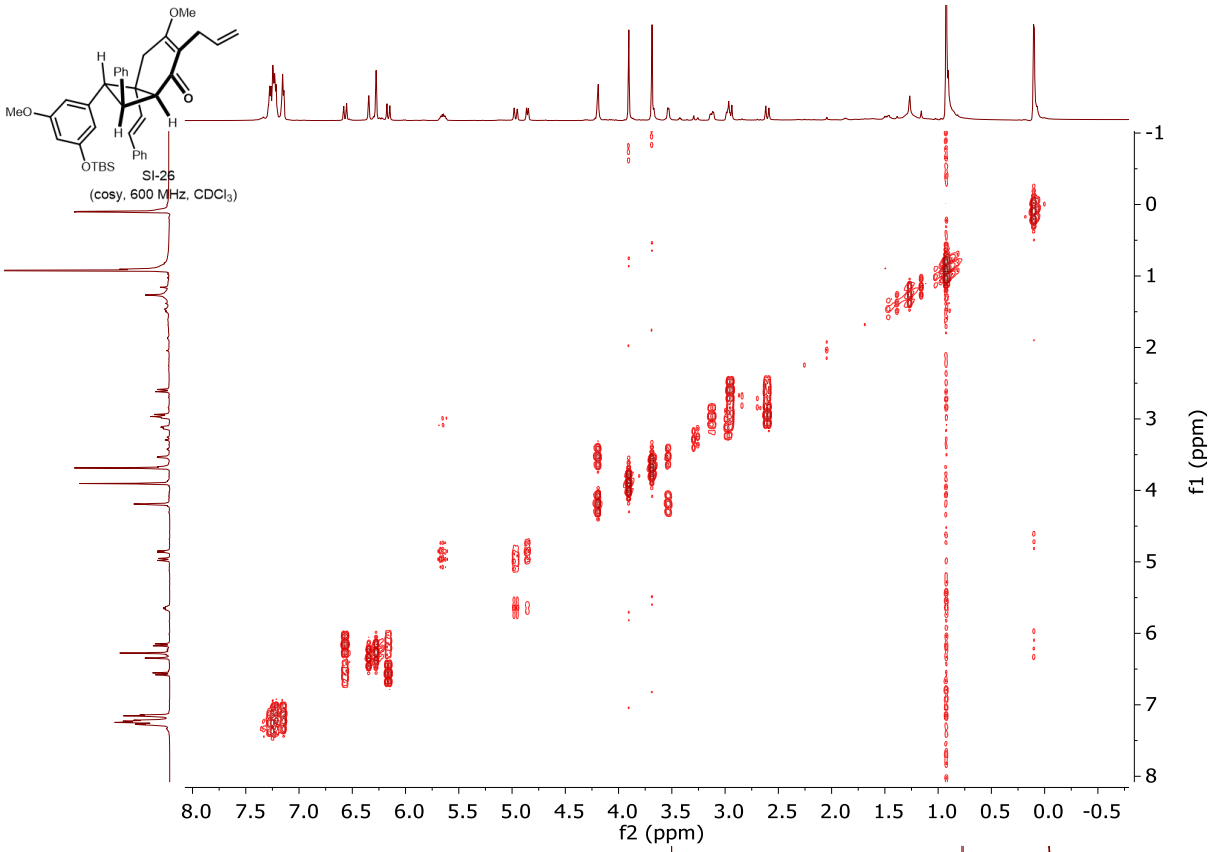

7.33 7.33 7.32 7.32 7.31 7.28 7.28 7.28 7.27 7.26 7.26 cdcl3 7.25 7.24 7.24 7.24 7.23 7.22 7.22 7.22 7.21 7.21 6.53 6.50 6.29 6.27 6.26 6.21 6.20 5.90 5.89 5.87 5.10 5.07 4.99 4.98 4.24 4.22 4.22 4.20 4.04 4.02 3.86 3.84 3.66 3.28 3.27 3.25 3.24 3.13 3.12 3.10 3.09 2.83 2.81 2.61 2.58 0.90 0.07 0.06
O
H
Ph
OMe
MeO
H
H
Ph
OTBS
25
(1H-NMR, 600 MHz, CDCl3)
2.01 8.50 1.00 1.99 1.82 0.90 0.95 0.96 1.00 0.96 0.96 2.87 3.78 1.02 1.02 1.05 9.09 5.52
f1 (ppm)
195.33
168.24 160.74 156.93 140.22 137.83 136.98 136.48 132.26 129.46 128.71 128.37 128.13 127.73 126.93 126.41 120.12 114.45 112.27 107.31 104.55
77.41 cdcl3 77.16 cdcl3 76.91 cdcl3
55.46 55.34 50.45 50.03 43.85 41.87 33.32 27.09 25.80 18.34 -4.25 -4.32
O
H
Ph
OMe
MeO
H
H
Ph
OTBS
25
(13C-NMR, 101 MHz, CDCl3)
f1 (ppm)

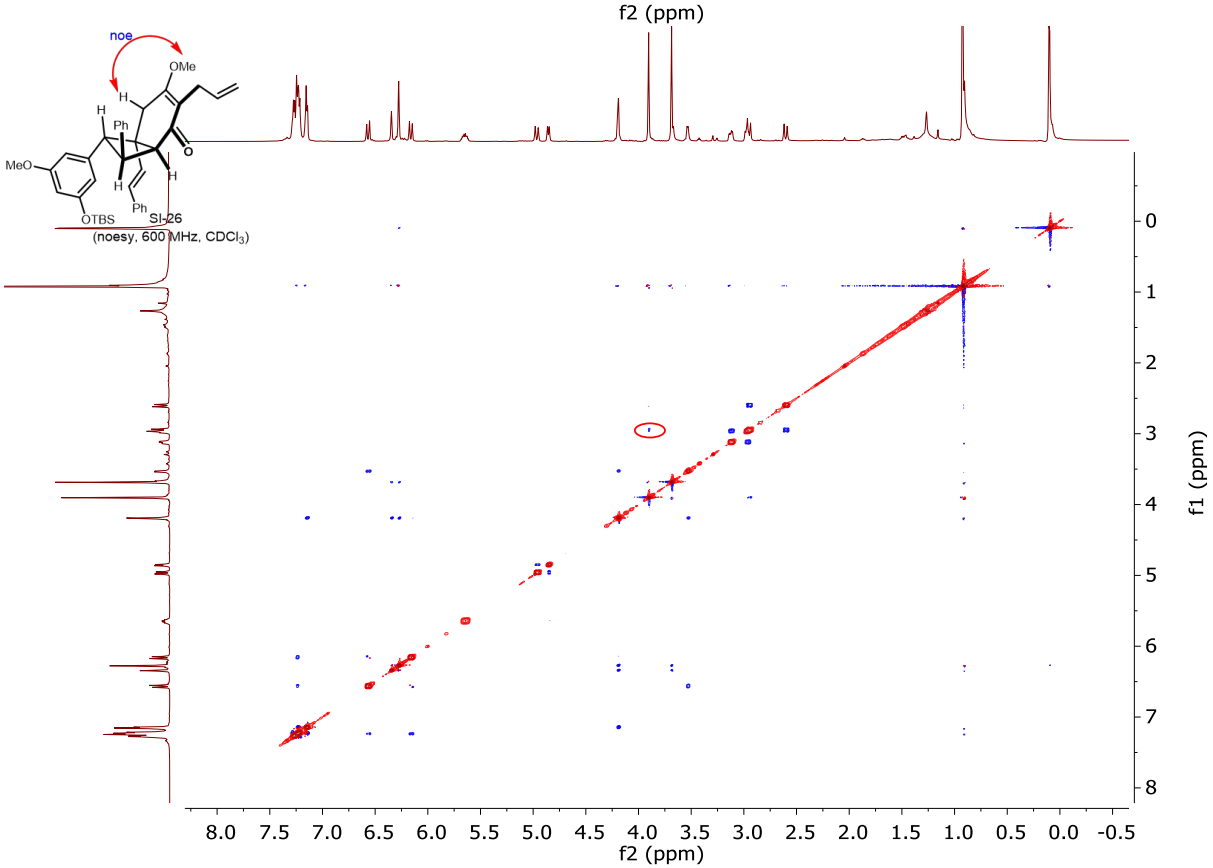

MeO
OTBS
H
Ph
H
OMe
H
Ph
O
25
(cosy, 600 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

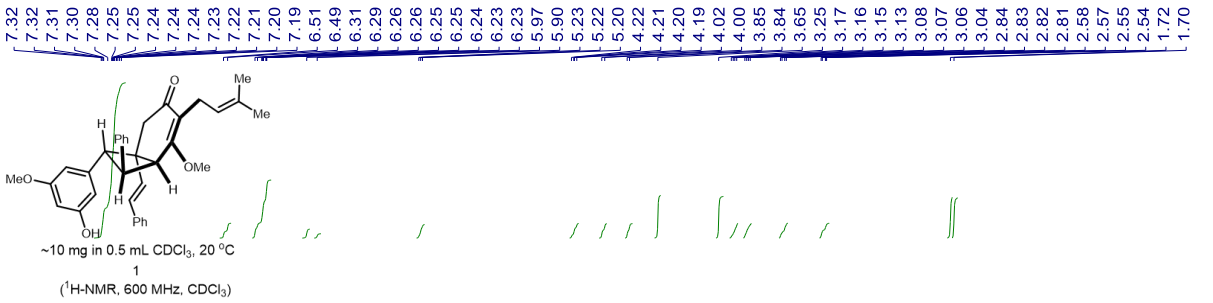

MeO
OTBS
H
Ph
H
OMe
H
noe
Ph
O
25
(noesy, 600 MHz, CDCl3)
f2 (ppm)
f1 (ppm)

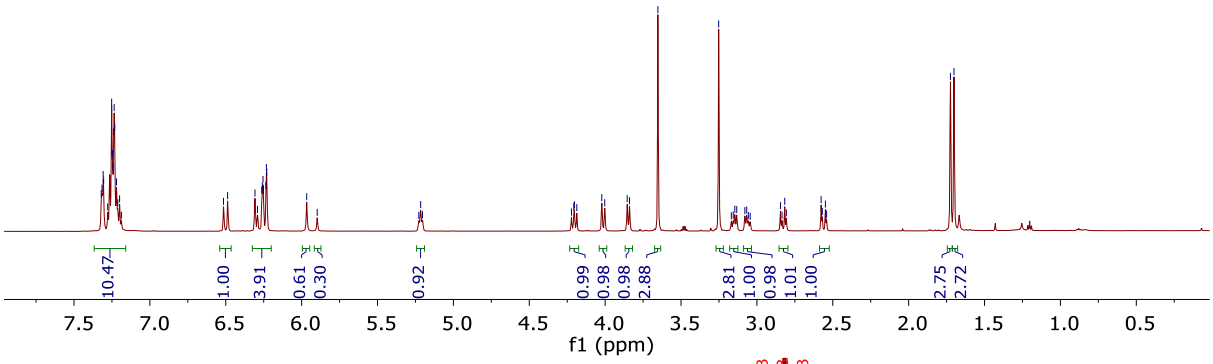

SI-26
(1H-NMR, 600 MHz, CDCl3)
1H overlap with impurity
f1 (ppm)

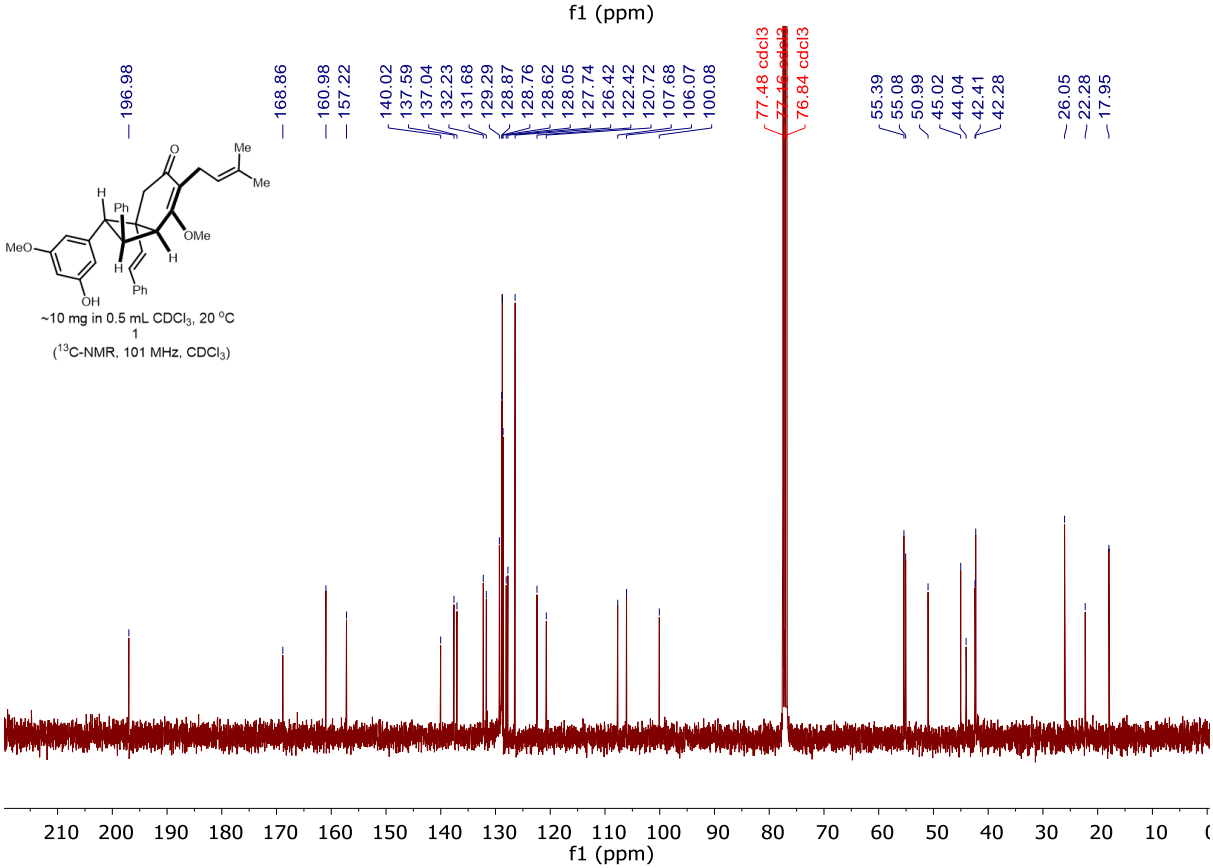

SI-26
(13C-NMR, 126 MHz, CDCl3)
f1 (ppm)


OMe
H
Ph
MeO
O
H
H
Ph
OTBS
SI-26
(cosy, 600 MHz, CDCl3)
f2 (ppm)
f1 (ppm)


noe
OMe
H
Ph
MeO
O
H
H
Ph
OTBS
SI-26
(noesy, 600 MHz, CDCl3)
f2 (ppm)
f1 (ppm)


~10 mg in 0.5 mL CDCl3, 20 °C
1
(1H-NMR, 600 MHz, CDCl3)


f1 (ppm)


~10 mg in 0.5 mL CDCl3, 20 °C
1
(13C-NMR, 101 MHz, CDCl3)
f1 (ppm)