Supporting Information

Divergent Total Syntheses of Five Illudalane Sesquiterpenes and Assignment of the Absolute Configuration

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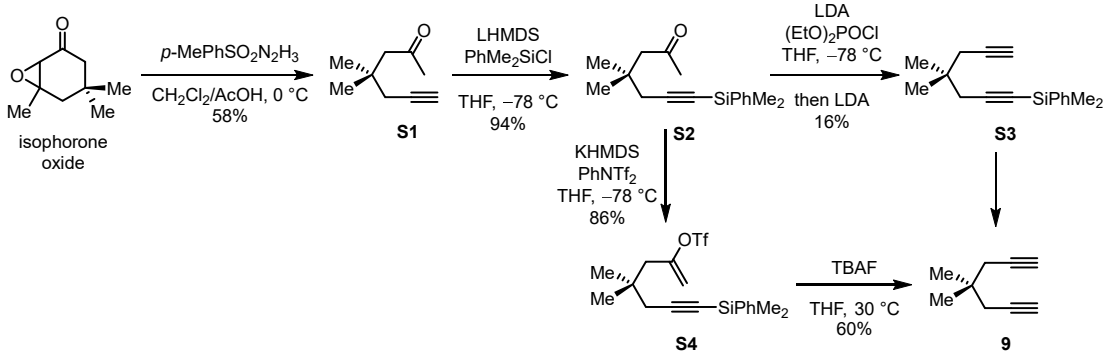
1. General Information

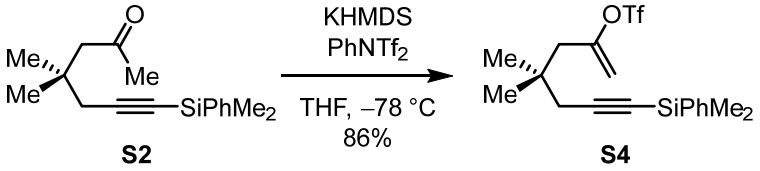
All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise stated. All the chemicals were purchased commercially and used without further purification, unless otherwise stated. The boiling point of petroleum ether (PE) is between 60-90 ºC. Tetrahydrofuran (THF) was distilled from sodium-benzophenone. Dichloromethane (CH_2Cl_2) and diethyl ether (Et_2O) were distilled from calcium hydride under argon atmosphere. Toluene was distilled from sodium under argon atmosphere. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm Qingdao silica gel plates (60F-254) using UV lights as the visualizing agent and $KMnO_4$. Flash column chromatography was performed over Qingdao silica gel (200-300 mesh). Infrared spectra were recorded on a Nicolet AVATER FTIR380 spectrometer as thin film and are reported in reciprocal centimeter (cm^{-1}). High resolution mass spectra (HRMS) were recorded on a Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer using electron spray ionization. HPLC analyses were performed on a Shimadzu LC-16A instrument using a Daicel Chiralcel IF Column. NMR spectra were recorded on Bruker AV-400, Bruker AV-500 and Bruker AV-600 instruments and were calibrated using residual undeuterated solvents ($CHCl_3$, $\delta_H = 7.26$; DMSO-*d*$_6$, $\delta_H = 2.50$) and deuterated solvents ($CDCl_3$, $\delta_C = 77.0$; DMSO-*d*$_6$, $\delta_C = 39.6$) as internal references. The data for ^1H NMR are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, brs = broad singlet), coupling constants (Hz) and integration.

2. Experimental Procedures

2.1. Synthesis of symmetrical terminal diyne 9[1, 2]

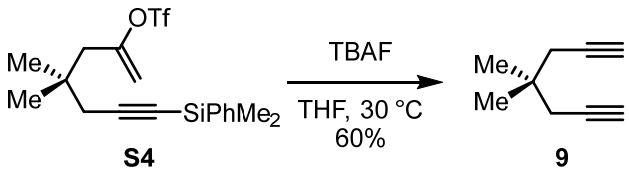


A modified synthetic route toward diyne 9



To a solution of **S2** (17.52 g, 64.3 mmol) in THF (100 mL) at −78 °C was added KHMDS (77.16 mL, 1 M in THF, 77.16 mmol). The reaction mixture was stirred at this temperature for 1.5 h before the addition of a solution of $PhNTf_2$ (29.86 g, 83.59 mmol) in THF (100 mL). The reaction mixture was stirred at −78 °C for 30 min, and at rt for 5 h, then quenched with saturated NH_4Cl solution and extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 150:1) afforded **S4** (22.37 g, 86% yield) as a colorless oil.

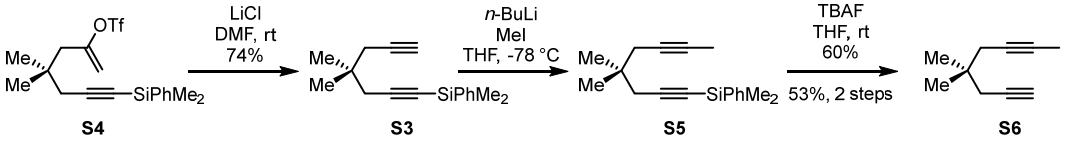
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.64 (m, 2H), 7.44 – 7.37 (m, 3H), 5.22 (d, *J* = 3.3 Hz, 1H), 5.01 (d, *J* = 3.3 Hz, 1H), 2.44 (s, 2H), 2.27 (s, 2H), 1.11 (s, 6H), 0.45 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.5, 137.4, 133.6, 129.3, 127.8, 118.5 (q, *J* = 318.1 Hz), 107.6, 106.0, 85.6, 44.8, 34.1, 32.9, 26.8, -0.8; **IR** (KBr, cm^{-1}) 2963, 2175, 1664, 1420, 1211, 703; **HRMS** (ESI, m/z) calcd for $C_{18}H_{23}F_3O_3SSi$ $[M+Na]^+$: 427.0981, found: 427.0977.

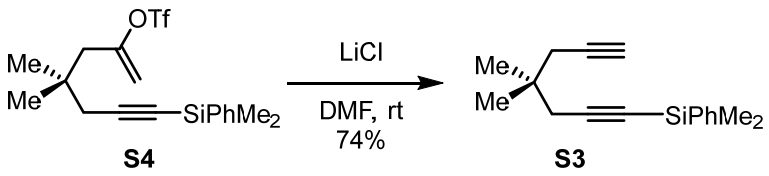


To a solution of **S4** (5.00 g, 12.36 mmol) in THF (10 mL) at 30 °C was added TBAF (37.08 mL, 1 M in THF, 37.08 mmol). The reaction mixture was stirred at this temperature for 13 h before being quenched with H_2O and extracted with Et_2O. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo* carefully at 10 °C. Purification of the residue by distillation afforded **9** (0.891 g, 60% yield) as a colorless oil. The spectroscopic data of **9** matched those reported.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.21 (d, *J* = 2.7 Hz, 4H), 2.01 (t, *J* = 2.7 Hz, 2H), 1.07 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 81.8, 70.2, 33.6, 30.8, 26.2.

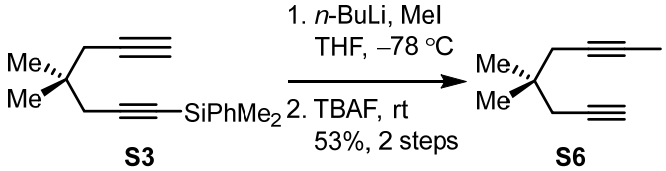
2.2. Synthesis of unsymmetrical diyne S6





To a solution of **S4** (0.505 g, 1.25 mmol) in DMF (4 mL) was added LiCl (0.212 g, 5.00 mmol). The reaction mixture was stirred at rt for 20 h, then diluted with EtOAc, washed with H_2O, extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 150:1) afforded **S3** (0.236 g, 74% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.63 (m, 2H), 7.43 – 7.37 (m, 3H), 2.33 (s, 2H), 2.25 (d, *J* = 2.7 Hz, 2H), 2.04 (t, *J* = 2.7 Hz, 1H), 1.12 (s, 6H), 0.43 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.6, 133.6, 129.2, 127.8, 106.7, 84.6, 81.9, 70.3, 33.9, 32.4, 31.0, 26.2, -0.6; **IR** (KBr, cm^{-1}) 3307, 2962, 2174, 1250, 817; **HRMS** (ESI, m/z) calcd for $C_{17}H_{22}Si$ $[M+Na]^+$: 277.1383, found: 277.1379.

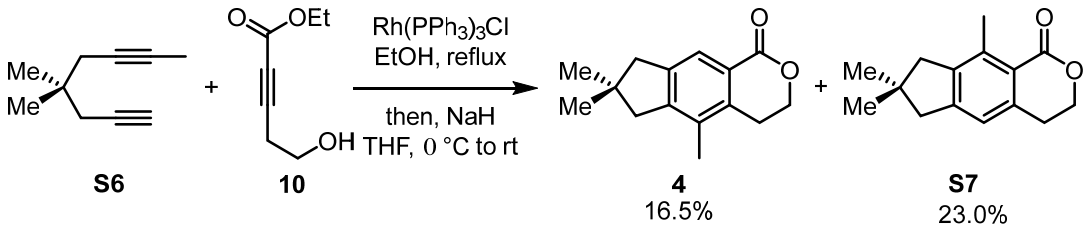


To a solution of **S3** (0.550 g, 2.346 mmol) in THF (20 mL) at −78 °C was added *n*-BuLi (1.10 mL, 2.5 M in hexane, 2.815 mmol). The reaction mixture was stirred at this temperature for 30 min before the addition of MeI (0.37 mL, 5.865 mmol). The reaction mixture was stirred at −78 °C for 1 h, then allowed to warm to rt and stirred overnight. The reaction was quenched with saturated NH_4Cl solution and extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo* to afford crude product.

To a solution of the crude product in THF (10 mL) was added TBAF (3.52 mL, 1 M in THF, 3.519 mmol). The reaction mixture was stirred at rt for 1 h before being quenched with H_2O and extracted with Et_2O. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo* carefully at 10 °C. Purification of the residue by flash chromatography (PE) afforded **S6** (0.167 g, 53% yield over 2 steps) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.18 (d, *J* = 2.7 Hz, 2H), 2.13 (q, *J* = 2.5 Hz, 2H), 1.99 (t, *J* = 2.7 Hz, 1H), 1.80 (t, *J* = 2.5 Hz, 3H), 1.04 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 82.3, 77.5, 76.4, 70.0, 33.8, 31.4, 30.8, 26.2, 3.5, **IR** (KBr, cm^{-1}) 2958, 1428, 1255, 1119, 791.

2.3. Intermolecular [2+2+2] cycloaddition with unsymmetrical diyne



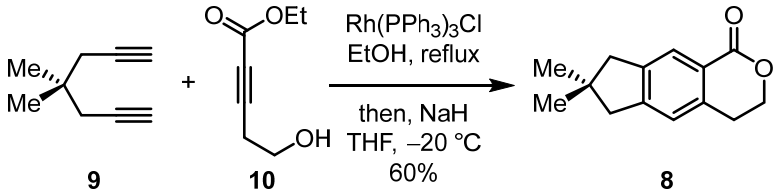
S6 **10** **4** 16.5% **S7** 23.0%

To a solution of diyne **S6** (0.134 g, 1.00 mmol) and ethyl 5-hydroxypent-2-ynoate **10** (0.569 g, 4.00 mmol) in EtOH (7 mL) was added $Rh(PPh_3)_3Cl$ (0.0463 g, 0.05 mmol). The reaction mixture was heated to reflux for 19 h. The reaction mixture was cooled to rt, then the solvent was removed *in vacuo*. To the residue in THF (10 mL) at 0 °C was added NaH (0.18 g, 60% dispersion in mineral oil, 4.50 mmol). The mixture was stirred at 0 °C for 15 min and at rt for 30 min, then quenched with 1 N HCl aqueous solution carefully and extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 20:1) afforded **4** (0.038 g, 16.5% yield) and S7 (0.053 g, 23.0% yield) as a white solid.

S7: Mp = 85-86 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.89 (s, 1H), 4.39 (t, *J* = 5.8 Hz, 2H), 2.96 (t, *J* = 5.8 Hz, 2H), 2.75 (s, 2H), 2.71 (s, 2H), 2.54 (s, 3H), 1.16 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.1, 148.8, 143.4, 139.3, 138.8, 121.9, 121.0, 66.7, 48.3, 46.6, 39.4, 29.4, 28.9, 18.0; **IR** (KBr, cm^{-1}) 2922, 1701, 1242, 1082, 793; **HRMS** (ESI, m/z) calcd for $C_{15}H_{18}O_2$ $[M+Na]^+$: 253.1199, found: 253.1201.

2.4. Synthesis of intermediate 12

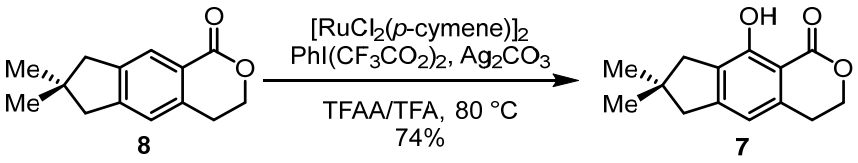
Synthesis of lactone 8



To a solution of diyne **9** (1.00 g, 8.32 mmol) and ethyl 5-hydroxypent-2-ynoate **10** (4.73 g, 33.28 mmol) in EtOH (40 mL) was added $Rh(PPh_3)_3Cl$ (0.385 g, 0.416 mmol). The reaction mixture was heated to reflux for 18 h. The reaction mixture was cooled to rt, then the solvent was removed *in vacuo.* To the residue in THF (40 mL) at −20 °C was added NaH (1.50 g, 60% dispersion in mineral oil, 37.44 mmol). The mixture was stirred at −20 °C for 15 min, then quenched with 1 N HCl aqueous solution carefully and extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 15:1) afforded **8** (1.08 g, 60% yield) as a white solid.

Mp = 86-88 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.03 (s, 1H), 4.46 (t, *J* = 6.0 Hz, 2H), 2.97 (t, *J* = 6.0 Hz, 2H), 2.72 (s, 4H), 1.12 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.7, 150.5, 143.3, 137.8, 126.3, 123.4, 123.2, 67.2, 47.7, 46.9, 40.4, 28.4, 27.9; **IR** (KBr, cm^{-1}) 2953, 1716, 1242, 1080, 786; **HRMS** (ESI, m/z) calcd for $C_{14}H_{16}O_2$ $[M+Na]^+$: 239.1043, found: 239.1039.

Synthesis of phenol 7 through C–H oxygenation

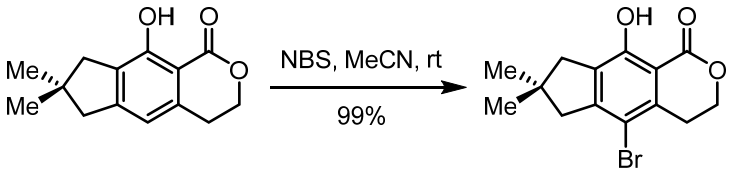


To a screw-capped tube were added **8** (0.533 g, 2.47 mmol), $[RuCl_2(p\text{-cymene})]_2$ (75.5 mg, 0.123 mmol), Ag_2CO_3 (0.680 g, 2.47 mmol), $PhI(CF_3CO_2)_2$ (2.121 g, 4.93 mmol)

and trifluoroacetic anhydride (35 mL). Trifluoroacetic acid (0.92 ml) was added to the mixture. The reaction mixture was heated to 80 °C and stirred for 20 h, then cooled to rt and diluted with Et_2O. To the mixture at 0 °C was added $NaHCO_3$ solid slowly. Then the mixture was acidified by 1 N HCl aqueous solution at 0 °C, and extracted with Et_2O. The combined organic layer was concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 20:1) afforded **7** (0.425 g, 74% yield) as a white solid.

Mp = 88-90 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.99 (s, 1H), 6.57 (s, 1H), 4.53 (t, *J* = 6.1 Hz, 2H), 3.00 (t, *J* = 6.1 Hz, 2H), 2.71 (s, 4H), 1.17 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.0, 158.7, 153.6, 138.2, 129.1, 114.6, 106.5, 68.1, 48.7, 43.4, 40.0, 28.8, 27.8; **IR** (KBr, cm^{-1}) 2952, 1673, 1256, 1143, 804; **HRMS** (ESI, m/z) calcd for $C_{14}H_{16}O_3$ $[M+Na]^+$: 255.0992, found: 255.0991.

Synthesis of phenyl bromide S8

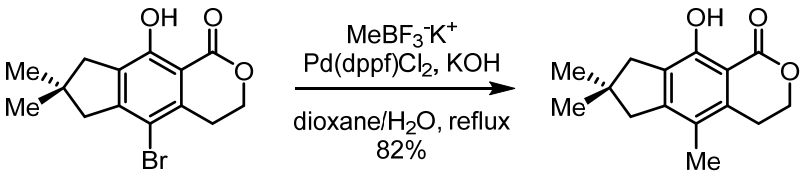


7 **S8**

To a solution of **7** (100 mg, 0.431 mmol) in MeCN (5 mL) was added NBS (84.4 mg, 0.474 mmol). The reaction mixture was stirred at rt for 1 h, then quenched with saturated Na_2SO_3 solution, extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 4:1) afforded S**8** (133 mg, 99 % yield) as a white solid.

Mp = 130-131 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 11.08 (s, 1H), 4.52 (t, *J* = 6.2 Hz, 2H), 3.07 (t, *J* = 6.2 Hz, 2H), 2.80 (s, 2H), 2.78 (s, 2H), 1.17 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.4, 157.9, 153.3, 136.9, 130.6, 109.1, 108.1, 67.4, 50.5, 44.5, 39.0, 28.9, 27.8; **IR** (KBr, cm^{-1}) 2954, 1678, 1432, 1154, 802; **HRMS** (ESI, m/z) calcd for $C_{14}H_{15}BrO_3$ $[M+Na]^+$: 333.0097, found: 333.0094.

Synthesis of compound 11

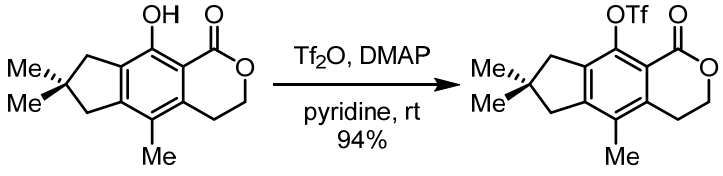


S8 **11**

To a solution of S**8** (105 mg, 0.337 mmol) in dioxane (7 mL) and H_2O (1.75 mL) were added $MeBF_3^-K^+$ (61.7 mg, 0.506 mmol), $Pd(dppf)Cl_2$ (12.3 mg, 0.0168 mmol) and KOH (56.7 mg, 1.01 mmol) in sequence. The reaction mixture was heated to reflux for 72 h. Then reaction mixture was cooled to rt, diluted with EtOAc and washed with H_2O. The aqueous layer was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 20:1) afforded **11** (67.8 mg, 82% yield) as a white solid.

Mp = 109-111 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.99 (s, 1H), 4.51 (t, *J* = 6.1 Hz, 2H), 2.93 (t, *J* = 6.1 Hz, 2H), 2.74 (s, 2H), 2.70 (s, 2H), 2.07 (s, 3H), 1.17 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.4, 156.9, 152.9, 135.6, 128.5, 121.3, 106.6, 67.6, 48.0, 43.8, 39.3, 29.2, 24.9, 14.6; **IR** (KBr, cm^{-1}) 2922, 1668, 1450, 1168, 803; **HRMS** (ESI, m/z) calcd for $C_{15}H_{18}O_3$ $[M+Na]^+$: 269.1148, found: 269.1145.

Synthesis of phenol triflate 12



11 **12**

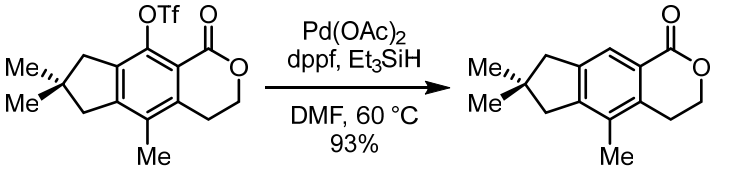
To a solution of **11** (0.500 g, 2.03 mmol) in pyridine (10 mL) at rt were added DMAP (0.125 g, 1.02 mmol) and Tf_2O (0.68 mL, 4.06 mmol) in sequence. The reaction mixture was stirred at rt for 12 h, then pyridine was removed *in vacuo*. The residue was diluted with EtOAc, washed with 1 N HCl aqueous solution and extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 5:1) afforded **12** (0.724 g, 94%) as a white solid.

Mp = 91-92 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.47 (t, *J* = 5.9 Hz, 2H), 2.94 (t, *J* = 5.9 Hz, 2H), 2.85 (s, 2H), 2.77 (s, 2H), 2.19 (s, 3H), 1.16 (s, 6H); **^{13}C NMR** (100 MHz,

$CDCl_3$) δ 162.1, 151.8, 143.9, 139.7, 135.5, 131.4, 118.5 (q, J = 318.6 Hz), 117.1, 66.3, 47.4, 44.6, 40.1, 28.3, 26.0, 15.5; **IR** (KBr, cm^{-1}) 2957, 1730, 1206, 875, 602; **HRMS** (ESI, m/z) calcd for $C_{16}H_{17}F_3O_5S$ $[M+Na]^+$: 401.0641, found: 401.0644.

2.5. Divergent total syntheses of five illudalane sesquiterpenes

Total synthesis of granulolactone (4)

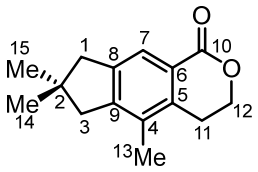


12 granulolactone (**4**)

To a solution of **12** (0.724 g, 1.91 mmol) in DMF (20 mL) were added $Pd(OAc)_2$ (21.4 mg, 0.0955 mmol), dppf (52.9 mg, 0.0955 mmol) and Et_3SiH (0.556 g, 4.78 mmol) in sequence. The reaction mixture was heated at 60 °C for 3 h. Then reaction mixture was cooled to rt, diluted with EtOAc and washed with H_2O. The aqueous layer was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 10:1) afforded granulolactone (**4**) (0.410 g, 93% yield) as a white solid.

Mp = 117-119 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 4.49 (t, J = 6.0 Hz, 2H), 2.94 (t, J = 6.0 Hz, 2H), 2.77 (s, 2H), 2.72 (s, 2H), 2.18 (s, 3H), 1.16 (s, 3H), 1.16 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.2, 149.3, 142.4, 136.1, 130.7, 124.1, 123.5, 66.7, 47.5, 47.2, 39.6, 28.8, 28.8, 25.1, 15.2; **IR** (KBr, cm^{-1}) 2922, 1718, 1644, 1158, 1087, 775; **HRMS** (ESI, m/z) calcd for $C_{15}H_{18}O_2$ $[M+Na]^+$: 253.1199, found: 253.1198.

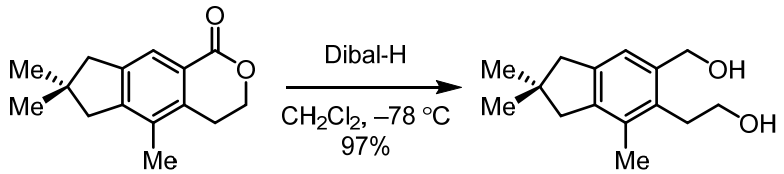
Table S1. NMR spectroscopic data comparison of natural and synthetic granulolactone.



granulolactone (**4**)

position	Natural Kokubun, 2016[3] (400 MHz, $CDCl_3$)		Synthetic This Report (400 MHz, $CDCl_3$)	
	δH (mult, *J* in Hz)	δC	δH (mult, *J* in Hz)	δC
1	2.77 (s, 2H)	47.6	2.77 (s, 2H)	47.5
2		39.7		39.6
3	2.72 (s, 2H)	47.3	2.72 (s, 2H)	47.2
4		130.7		130.7
5		136.2		136.1
6		123.6		123.5
7	7.79 (s, 1H)	124.2	7.79 (s, 1H)	124.1
8		142.5		142.4
9		149.3		149.3
10		166.2		166.2
11	2.94 (t, *J* = 6.0 Hz, 2H)	25.2	2.94 (t, *J* = 6.0 Hz, 2H)	25.1
12	4.48 (t, *J* = 6.1 Hz, 2H)	66.7	4.49 (t, *J* = 6.0 Hz, 2H)	66.7
13	2.18 (s, 3H)	15.3	2.18 (s, 3H)	15.2
14	1.16 (s, 3H)	28.9	1.16 (s, 3H)	28.8
15	1.16 (s, 3H)	28.9	1.16 (s, 3H)	28.8

Total Synthesis of riparol (5)



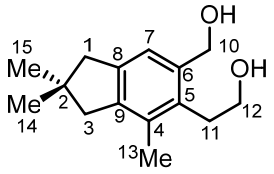
granulolactone (**4**) riparol B (**5**)

To a solution of granulolactone (**4**) (26.2 mg, 0.114 mmol) in CH_2Cl_2 (5 mL) at −78 °C was added Dibal-H (0.34 mL, 1 M in hexane, 0.342 mmol). The reaction mixture was stirred at −78 °C for 3 h, then allowed to warm to 0 °C and stirred for additional 2 h. Then the mixture was quenched with saturated Rochelle salt solution carefully, and

extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 1:1) afforded riparol (**5**) (25.8 g, 97% yield) as a white solid.

Mp = 112-114 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.99 (s, 1H), 4.58 (s, 2H), 3.82 (t, *J* = 5.9 Hz, 2H), 3.40 (brs, 2H), 2.99 (t, *J* = 5.9 Hz, 2H), 2.72 (s, 2H), 2.67 (s, 2H), 2.19 (s, 3H), 1.15 (s, 3H), 1.15 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.4, 141.5, 137.8, 133.4, 133.0, 124.0, 64.2, 61.5, 47.8, 47.3, 39.3, 31.6, 29.2, 29.2, 16.0; **IR** (KBr, cm^{-1}) 2921, 1433, 1258, 1038, 801; **HRMS** (ESI, m/z) calcd for $C_{15}H_{22}O_2$ $[M+Na]^+$: 6257.1512, found: 257.1515.

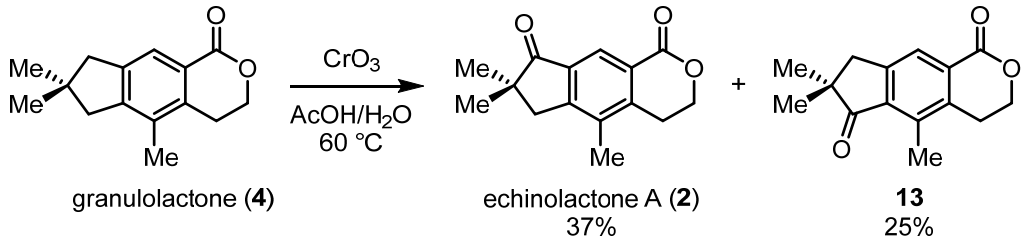
Table S2. NMR spectroscopic data comparison of natural and synthetic riparol B.



riparol B (**5**)

position	Natural Anke, 2006[4] (500 MHz, $CDCl_3$)		Synthetic This Report (400 MHz, $CDCl_3$)	
	δH (mult, *J* in Hz)	δC	δH (mult, *J* in Hz)	δC
1	2.73 (s, 2H)	47.8	2.72 (s, 2H)	47.8
2		39.3		39.3
3	2.68 (s, 2H)	47.3	2.67 (s, 2H)	47.3
4		133.1		133.0
5		133.3		133.4
6		137.9		137.8
7	7.01 (s, 1H)	124.0	6.99 (s, 1H)	124.0
8		141.6		141.5
9		143.4		143.4
10	4.62 (s, 2H)	64.3	4.58 (s, 2H)	64.2
11	3.03 (t, *J* = 5.9 Hz, 2H)	31.6	2.99 (t, *J* = 5.9 Hz, 2H)	31.6
12	3.86 (t, *J* = 5.9 Hz, 2H)	61.7	3.82 (t, *J* = 5.9 Hz, 2H)	61.5
13	2.21 (s, 3H)	16.0	2.19 (s, 3H)	16.0
14	1.16 (s, 3H)	29.2	1.15 (s, 3H)	29.2
15	1.16 (s, 3H)	29.2	1.15 (s, 3H)	29.2

Total synthesis of echinolactone A (2) and compound 13



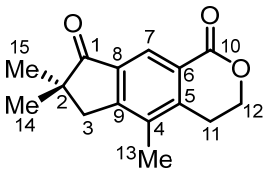
granulolactone (**4**) | echinolactone A (**2**) 37% | **13** 25%

To a solution of granulolactone (**4**) (0.41 g, 1.78 mmol) in acetic acid (20 mL) and H_2O (5 mL) was added CrO_3 (0.71 g, 7.12 mmol). The resultant mixture was heated at 60 °C for 40 h and then cooled to rt, quenched with saturated Na_2SO_3 solution and extracted with EtOAc. The combined organic layer was washed with saturated $NaHCO_3$ solution, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 5:1 to 1:1) afforded echinolactone A (**2**) (0.16 g, 37% yield) as a white solid and **13** (0.11 g, 25% yield) as a white solid.

Echinolactone A (2): Mp = 208-210 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 4.53 (t, *J* = 5.9 Hz, 2H), 3.08 (t, *J* = 5.9 Hz, 2H), 2.96 (s, 2H), 2.30 (s, 3H), 1.25 (s, 3H), 1.25 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.1, 164.8, 155.8, 143.9, 134.3, 133.1, 125.4, 124.9, 66.3, 45.6, 42.5, 25.8, 25.3, 25.3, 14.2; **IR** (KBr, cm^{-1}) 2917, 1719, 1637, 1263, 1090, 769; **HRMS** (ESI, m/z) calcd for $C_{15}H_{16}O_3$ $[M+Na]^+$: 267.0992, found: 267.0998.

Compound 13: Mp = 121-122 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 4.54 (t, *J* = 6.0 Hz, 2H), 3.03 (t, *J* = 6.0 Hz, 2H), 2.97 (s, 2H), 2.63 (s, 3H), 1.22 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 212.2, 165.0, 150.8, 137.6, 136.6, 136.0, 129.7, 126.1, 66.8, 46.1, 41.8, 25.3, 24.4, 13.2; **IR** (KBr, cm^{-1}) 2919, 1720, 1444, 1293, 775; **HRMS** (ESI, m/z) calcd for $C_{15}H_{16}O_3$ $[M+Na]^+$: 267.0992, found: 267.0997.

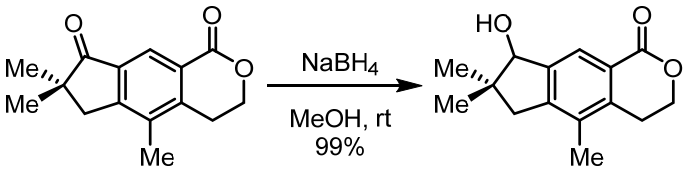
Table S3. NMR spectroscopic data comparison of natural and synthetic echinolactone A.



echinolactone A (**2**)

position	Natural Shiono, 2005[5] (400 MHz, $CDCl_3$)		Synthetic This Report (400 MHz, $CDCl_3$)	
	δH (mult, *J* in Hz)	δC	δH (mult, *J* in Hz)	δC
1		209.8		210.1
2		45.2		45.6
3	2.96 (s, 2H)	42.6	2.96 (s, 2H)	42.5
4		133.1		133.1
5		143.7		143.9
6		125.5		125.4
7	8.42 (s, 1H)	125.1	8.41 (s, 1H)	124.9
8		134.2		134.3
9		155.8		155.8
10		165.0		164.8
11	3.08 (t, *J* = 5.9 Hz, 2H)	25.3	3.08 (t, *J* = 5.9 Hz, 2H)	25.8
12	4.52 (t, *J* = 5.9 Hz, 2H)	66.2	4.53 (t, *J* = 5.9 Hz, 2H)	66.3
13	2.30 (s, 3H)	14.8	2.30 (s, 3H)	14.2
14	1.25 (s, 3H)	25.1	1.25 (s, 3H)	25.3
15	1.25 (s, 3H)	25.1	1.25 (s, 3H)	25.3

Total synthesis of (±)-radulactone (1)



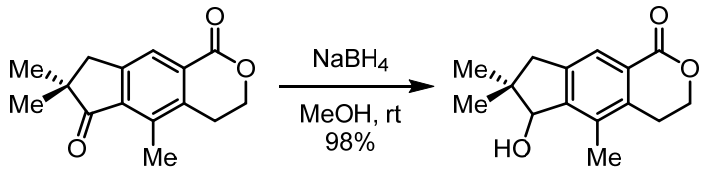
echinolactone A (**2**) radulactone (**1**)

To a solution of echinolactone A (**2**) (20 mg, 0.0819 mmol) in MeOH (5 mL) at rt was added $NaBH_4$ (1.6 mg, 0.041 mmol). The reaction mixture was stirred at rt for 20 min then the solvent was removed *in vacuo.* The residue was diluted with EtOAc and H_2O,

and extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 2:1) afforded (±)-radulactone (**1**) (20 mg, 99% yield) as a white solid.

Mp = 146-148 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 4.69 (s, 1H), 4.48 (t, *J* = 5.9 Hz, 2H), 2.96 (t, *J* = 5.9 Hz, 2H), 2.79 (d, *J* = 16.3 Hz, 1H), 2.61 (d, *J* = 16.3 Hz, 1H), 2.19 (s, 3H), 2.13 (brs, 1H), 1.17 (s, 3H), 1.05 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.9, 147.4, 143.8, 138.1, 131.2, 124.2, 124.1, 82.9, 66.6, 44.2, 44.1, 26.8, 25.2, 21.5, 14.9; **IR** (KBr, cm^{-1}) 2923, 1704, 1161, 1085, 787; **HRMS** (ESI, m/z) calcd for $C_{15}H_{18}O_3$ $[M+Na]^+$: 269.1148, found: 269.1150.

Total synthesis of (±)-calomelanolactone (3)

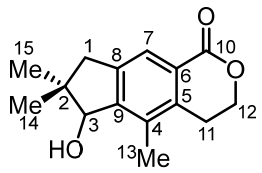


13 (±)-calomelanolactone (**3**)

To a solution of **13** (20 mg, 0.0819 mmol) in MeOH (5 mL) at rt was added $NaBH_4$ (1.6 mg, 0.041 mmol). The reaction mixture was stirred at rt for 15 min then the solvent was removed *in vacuo*. The residue was diluted with EtOAc and H_2O, and extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 2:1) afforded (±)-calomelanolactone (**3**) (19.8 mg, 98% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 4.64 (s, 1H), 4.55 – 4.43 (m, 2H), 2.99 – 2.92 (m, 2H), 2.93 (d, *J* = 15.8 Hz, 1H), 2.61 (d, *J* = 15.8 Hz, 1H), 2.37 (s, 3H), 1.77 (brs, 1H), 1.21 (s, 3H), 1.01 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.9, 148.5, 142.4, 137.0, 132.9, 125.4, 124.8, 82.4, 66.7, 44.5, 43.0, 27.3, 25.0, 22.0, 14.6; **IR** (KBr, cm^{-1}) 2925, 1705, 1165, 1045, 786; **HRMS** (ESI, m/z) calcd for $C_{15}H_{18}O_3$ $[M+Na]^+$: 269.1148, found: 269.1151.

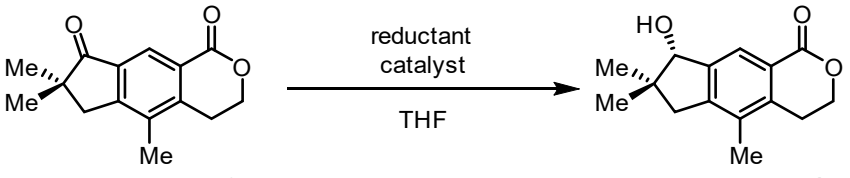
Table S4. NMR spectroscopic data comparison of natural and synthetic calomelanolactone.

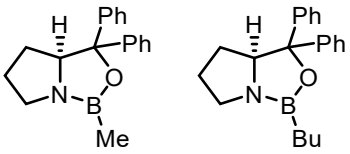


(±)-calomelanolactone (**3**)

position	Natural Bardouille, 1978[6]	Synthetic This Report (400 MHz, $CDCl_3$)
	δH (mult, *J* in Hz)	δH (mult, *J* in Hz)
1a	2.83 (s, 1H)	2.93 (d, *J* = 15.8 Hz, 1H)
1b	2.68 (s, 1H)	2.61 (d, *J* = 15.8 Hz, 1H)
2		
3	4.62 (s, 1H)	4.64 (s, 1H)
4		
5		
6		
7	7.73 (s, 1H)	7.80 (s, 1H)
8		
9		
10		
11	2.93 (t, *J* = 6.0 Hz, 2H)	2.95 (m, 2H)
12	4.47 (t, *J* = 6.0 Hz, 2H)	4.48 (m, 2H)
13	2.37 (s, 3H)	2.37 (s, 3H)
14	1.22 (s, 3H)	1.21 (s, 3H)
15	1.02 (s, 3H)	1.05 (s, 3H)
OH	2.0 (s, 1H)	1.77 (brs, 1H)

2.6. Asymmetric synthesis of (+)-radulactone (1) and assignment of absolute configuration



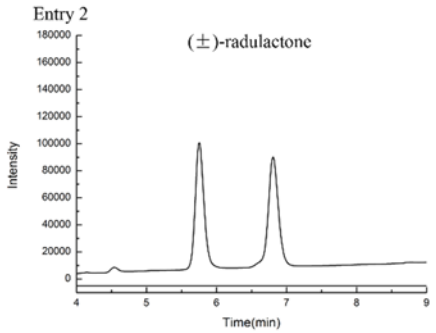


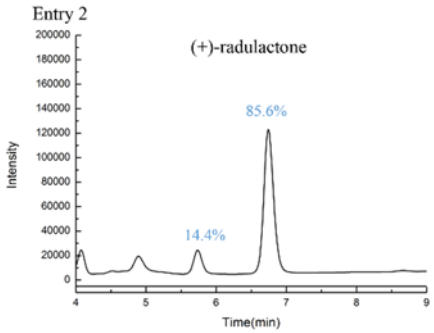
(*S*)-CBS-Me (*S*)-CBS-Bu

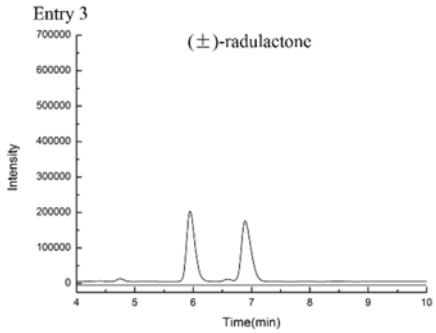
Table S5. Optimization of the asymmetric reduction condition

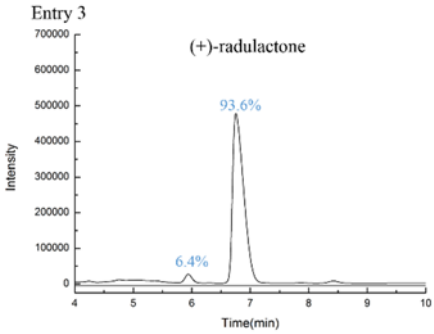
entry	reductant	catalyst	t/°C	yield/%	*ee*/%
1	BH_3•THF (1.3 eq.)	(*S*)-CBS-Me (0.3 eq.)	−78 °C	no reaction	-
2	BH_3•THF (1.3 eq.)	(*S*)-CBS-Me (0.3 eq.)	0 °C to rt	27	71.2
3	BH_3•SMe_2 (1.3 eq.)	(*S*)-CBS-Me (0.3 eq.)	0 °C to rt	38	87.2
4	BH_3•SMe_2 (1.3 eq.)	(*S*)-CBS-Bu (0.3 eq.)	0 °C to rt	35	56.6

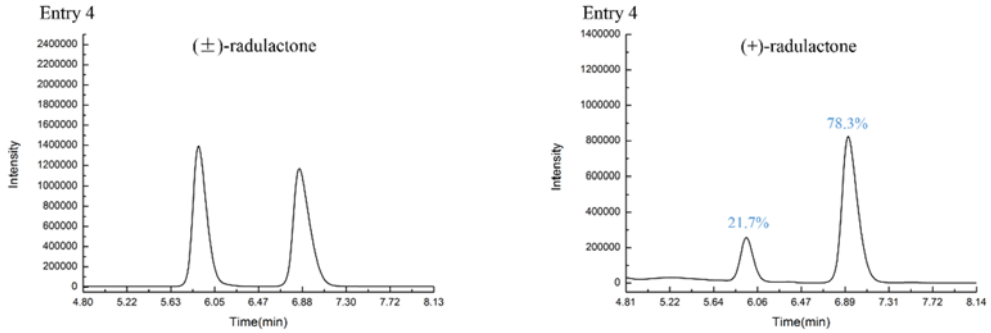
(HPLC analyses were performed on a Shimadzu LC-16A instrument using a Daicel Chiralcel IF Column. Flow rate: 1.1 mL/min, eluent: EtOAc/hexane = 65/35)

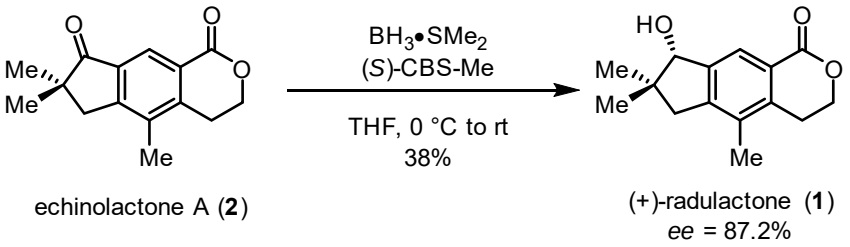








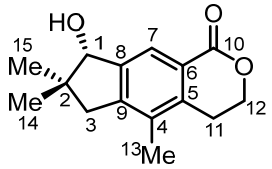




To a solution of BH_3•SMe_2 (0.13 mL, 2 M in THF, 0.267 mmol) and (*S*)-CBS-Me (0.06 ml, 1 M in toluene, 0.062 mmol) in THF (2 mL) at 0 °C was added echinolactone A (**2**) (50 mg, 0.205 mmol) in THF (3 mL). The reaction mixture was allowed to warm to rt and stirred overnight. The reaction was quenched with H_2O carefully, then diluted with EtOAc, washed with 1 N HCl aqueous solution, and extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 2:1) afforded (+)-radulactone (**1**) (19 mg, 38% yield) as a colorless oil.

$[\alpha]_D^{25}$ = +15.5 (c 0.5, $CHCl_3$); *ee* = 87.2%.

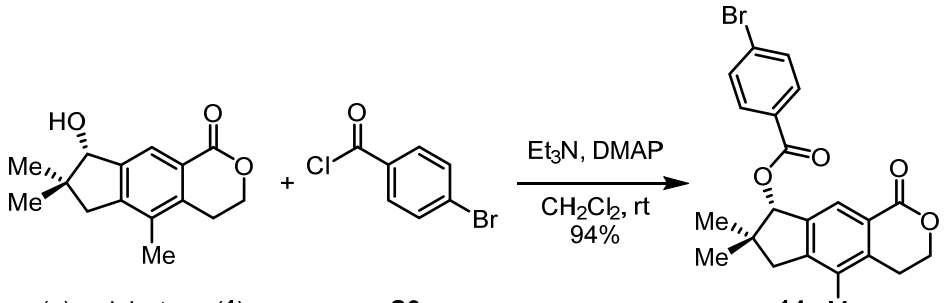
Table S6. NMR spectroscopic data comparison of natural and synthetic (+)-radulactone.



(+)-radulactone (**1**)

position	Natural Anke, 1998[7] (500 MHz, $CDCl_3$)		Synthetic This Report (400 MHz, $CDCl_3$)	
	δH (mult, *J* in Hz)	δC	δH (mult, *J* in Hz)	δC
1	4.69 (s, 1H)	83.0	4.69 (s, 1H)	82.9
2		44.1		44.1
3α	2.62 (d, *J* = 16.3 Hz, 1H)	44.2	2.61 (d, *J* = 16.3 Hz, 1H)	44.2
3β	2.79 (d, *J* = 16.3 Hz, 1H)		2.79 (d, *J* = 16.3 Hz, 1H)	
4		131.3		131.2
5		138.2		138.1
6		124.2		124.1
7	7.99 (s, 1H)	124.2	7.99 (s, 1H)	124.2
8		143.8		143.8
9		147.4		147.4
10		165.9		165.9
11	2.96 (t, *J* = 5.9 Hz, 2H)	25.2	2.96 (t, *J* = 5.9 Hz, 2H)	25.2
12	4.48 (t, *J* = 5.9 Hz, 2H)	66.6	4.48 (t, *J* = 5.9 Hz, 2H)	66.6
13	2.18 (s, 3H)	14.9	2.19 (s, 3H)	14.9
14	1.17 (s, 3H)	26.8	1.17 (s, 3H)	26.8
15	1.05 (s, 3H)	21.5	1.05 (s, 3H)	21.5

Synthesis of *p*-bromobenzoate derivative of (+)-radulactone

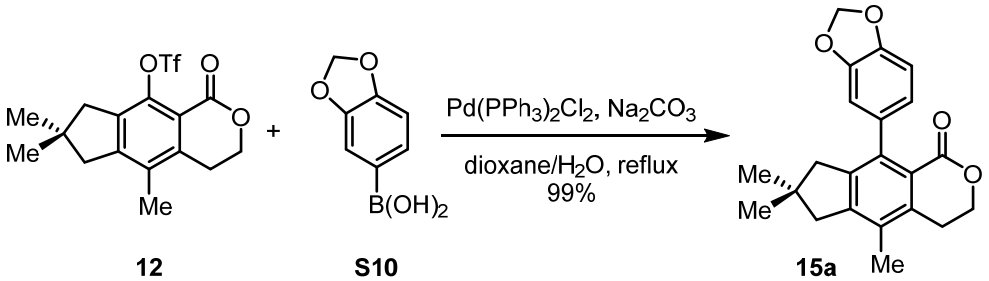


(+)-radulactone (**1**) **S9** **14**

To a solution of (+)-radulactone (**1**) (15.1 mg, 0.0613 mmol) in CH_2Cl_2 (5 mL) were added *p*-bromobenzoyl chloride **S9** (20.2 mg, 0.092 mmol) and DMAP (3.8 mg, 0.031 mmol). The reaction mixture was stirred at rt for 2 h, then quenched with H_2O, and extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 4:1) afforded **14** (24.8 mg, 94% yield) as a white solid.

$[\alpha]_D^{25}$ = +6.0 (c 0.2, $CHCl_3$); **Mp =** 155-157 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.88 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 6.10 (s, 1H), 4.49 (t, *J* = 6.0 Hz, 2H), 2.98 (t, *J* = 6.0 Hz, 2H), 2.96 (d, *J* = 16.5 Hz, 1H), 2.76 (d, *J* = 16.5 Hz, 1H), 2.24 (s, 3H), 1.22 (s, 3H), 1.19 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.6, 165.4, 148.6, 140.0, 138.8, 131.7, 131.4, 131.2, 129.0, 128.2, 125.7, 124.4, 84.1, 66.5, 45.1, 43.5, 27.3, 25.3, 22.7, 15.1; **IR** (KBr, cm^{-1}) 2959, 1717, 1267, 1101, 756; **HRMS** (ESI, m/z) calcd for $C_{22}H_{21}BrO_4$ $[M+Na]^+$: 451.0515, found: 451.0521.

2.7. Synthesis of illudalane analogues

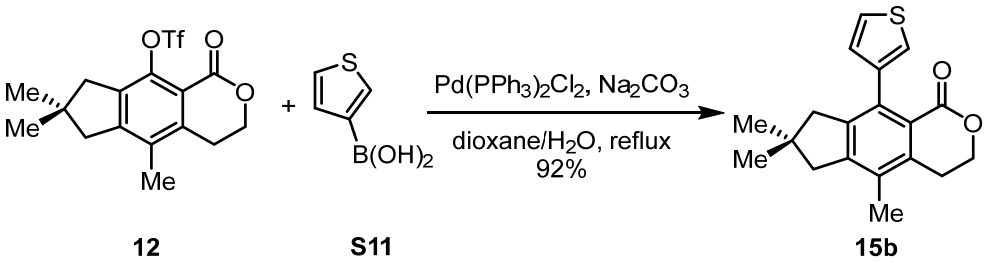


12 **S10** **15a**

To a tube were added **12** (25 mg, 0.066 mmol), aryl boronic acid **S10** (16.4 mg, 0.099 mmol) and $Pd(PPh_3)_2Cl_2$ (2.3 mg, 0.0033 mmol). The tube was degassed with argon for three times, then Na_2CO_3 (0.08 mL, 2 M aqueous solution, 0.16 mmol) and dioxane (4 mL) were added to the tube. The reaction mixture was degassed with argon again, then heated to reflux for 22 h. The reaction mixture was cooled to rt, diluted with EtOAc, and washed with H_2O. The aqueous layer was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 5:1) afforded **15a** (23 mg, 99% yield) as a white solid.

Mp = 165-167 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.82 (d, *J* = 7.9 Hz, 1H), 6.66 (d, *J* = 1.7 Hz, 1H), 6.60 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.98 (s, 2H), 4.45 (t, *J* = 5.8 Hz, 2H), 2.96 (t, *J* = 5.8 Hz, 2H), 2.78 (s, 2H), 2.56 (s, 2H), 2.22 (s, 3H), 1.11 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 147.9, 147.2, 146.3, 142.6, 139.0, 137.7, 134.4, 129.7, 122.5,

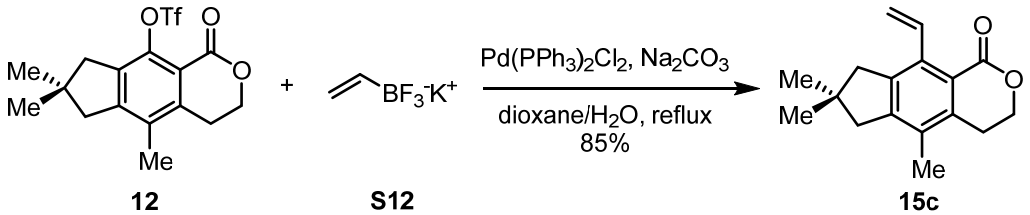
121.4, 109.1, 108.0, 100.9, 66.0, 47.6, 47.4, 39.1, 28.9, 26.3, 15.5; **IR** (KBr, cm^{-1}) 2924, 1723, 1457, 1227, 798; **HRMS** (ESI, m/z) calcd for $C_{22}H_{22}O_4$ $[M+Na]^+$: 373.1410, found: 373.1413.



12 **S11** **15b**

To a tube were added **12** (25 mg, 0.066 mmol), thiophene boronic acid **S11** (12.7 mg, 0.099 mmol) and $Pd(PPh_3)_2Cl_2$ (2.3 mg, 0.0033 mmol). The tube was degassed with argon for three times, then Na_2CO_3 (0.08 mL, 2 M aqueous solution, 0.16 mmol) and dioxane (4 mL) were added to the tube. The reaction mixture was degassed with argon again, then heated to reflux for 17 h. The mixture was cooled to rt, diluted with EtOAc, and washed with H_2O. The aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 4:1) afforded **15b** (19 mg, 92% yield) as a white solid.

Mp = 151-152 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.04 (dd, *J* = 3.0, 1.3 Hz, 1H), 6.98 (dd, *J* = 4.9, 1.3 Hz, 1H), 4.45 (t, *J* = 5.8 Hz, 2H), 2.96 (t, *J* = 5.8 Hz, 2H), 2.78 (s, 2H), 2.60 (s, 2H), 2.22 (s, 3H), 1.12 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3, 148.0, 143.0, 140.0, 137.9, 134.2, 129.9, 128.8, 124.3, 122.8, 121.5, 66.0, 47.6, 47.6, 39.0, 28.9, 26.3, 15.6; **IR** (KBr, cm^{-1}) 2951, 1722, 1149, 1088, 773; **HRMS** (ESI, m/z) calcd for $C_{19}H_{20}O_2S$ $[M+Na]^+$: 335.1076, found: 335.1083.

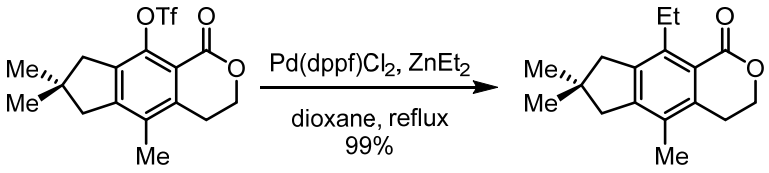


12 **S12** **15c**

To a tube were added **12** (25 mg, 0.066 mmol), potassium vinyltrifluoroborate **S12** (17.7 mg, 0.132 mmol) and $Pd(PPh_3)_2Cl_2$ (2.3 mg, 0.0033 mmol). The tube was degassed with argon for three times, then Na_2CO_3 (0.10 mL, 2 M aqueous solution, 0.20 mmol) and dioxane (4 mL) were added to the tube. The reaction mixture was degassed with

argon again, then heated to reflux for 18 h. The reaction mixture was cooled to rt, diluted with EtOAc, and washed with H_2O. The aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 5:1) afforded **15c** (14.3 mg, 85% yield) as a white solid.

Mp = 93-95 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 17.9, 11.5 Hz, 1H), 5.47 (dd, *J* = 11.5, 1.7 Hz, 1H), 5.27 (dd, *J* = 17.9, 1.7 Hz, 1H), 4.40 (t, *J* = 5.9 Hz, 2H), 2.92 (t, *J* = 5.9 Hz, 2H), 2.87 (s, 2H), 2.74 (s, 2H), 2.18 (s, 3H), 1.14 (s, 7H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.1, 148.9, 141.2, 137.6, 136.1, 135.9, 129.4, 121.7, 117.6, 66.0, 48.6, 47.4, 39.3, 28.8, 26.0, 15.6; **IR** (KBr, cm^{-1}) 2949, 1706, 1156, 1090, 918; **HRMS** (ESI, m/z) calcd for $C_{17}H_{20}O_2$ $[M+Na]^+$: 279.1356, found: 279.1361.



12 **15d**

To a solution of **12** (26.5 mg, 0.07 mmol) in dioxane (4 mL) was added $Pd(dppf)Cl_2$ (2.6 mg, 0.0035 mmol). The reaction mixture was degassed with argon, and $ZnEt_2$ (0.04 mL, 2 M in hexane, 0.084) was added dropwise. The reaction mixture was heated to reflux for 6 h before being cooled to rt, diluted with EtOAc and washed with H_2O. The aqueous layer was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (PE/EtOAc = 5:1) afforded **15d** (17.9 mg, 99% yield) as a white solid.

Mp = 84-86 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.37 (t, *J* = 5.9 Hz, 2H), 2.95 (q, *J* = 7.4 Hz, 2H), 2.91 (t, *J* = 5.9 Hz, 2H), 2.78 (s, 2H), 2.73 (s, 2H), 2.15 (s, 3H), 1.19 (t, *J* = 7.4 Hz, 3H), 1.17 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.1, 148.1, 142.2, 142.1, 137.8, 127.9, 121.8, 66.0, 47.5, 46.4, 38.8, 29.2, 26.2, 24.6, 15.4, 14.4; **IR** (KBr, cm^{-1}) 2925, 1716, 1151, 1097, 799; **HRMS** (ESI, m/z) calcd for $C_{17}H_{22}O_2$ $[M+Na]^+$: 281.1512, found: 281.1520.

3. X-Ray Crystallographic Data

Fig. S1 X-ray Crystallographic Structure of **14** （CCDC 1894774）

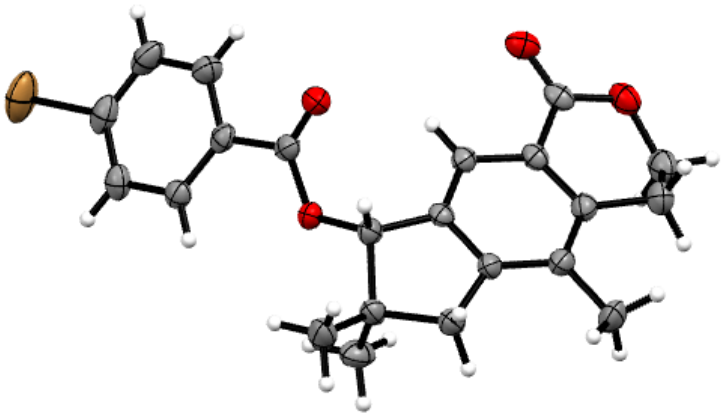


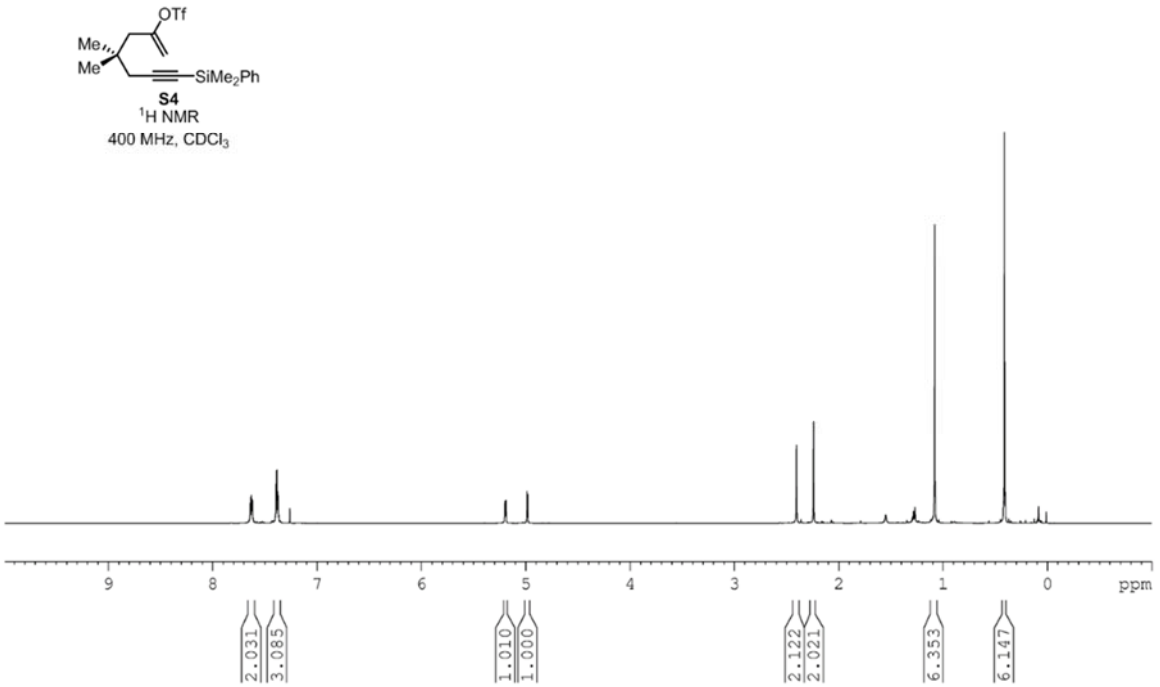
Table S6. Crystal data and structure refinement for **14**.

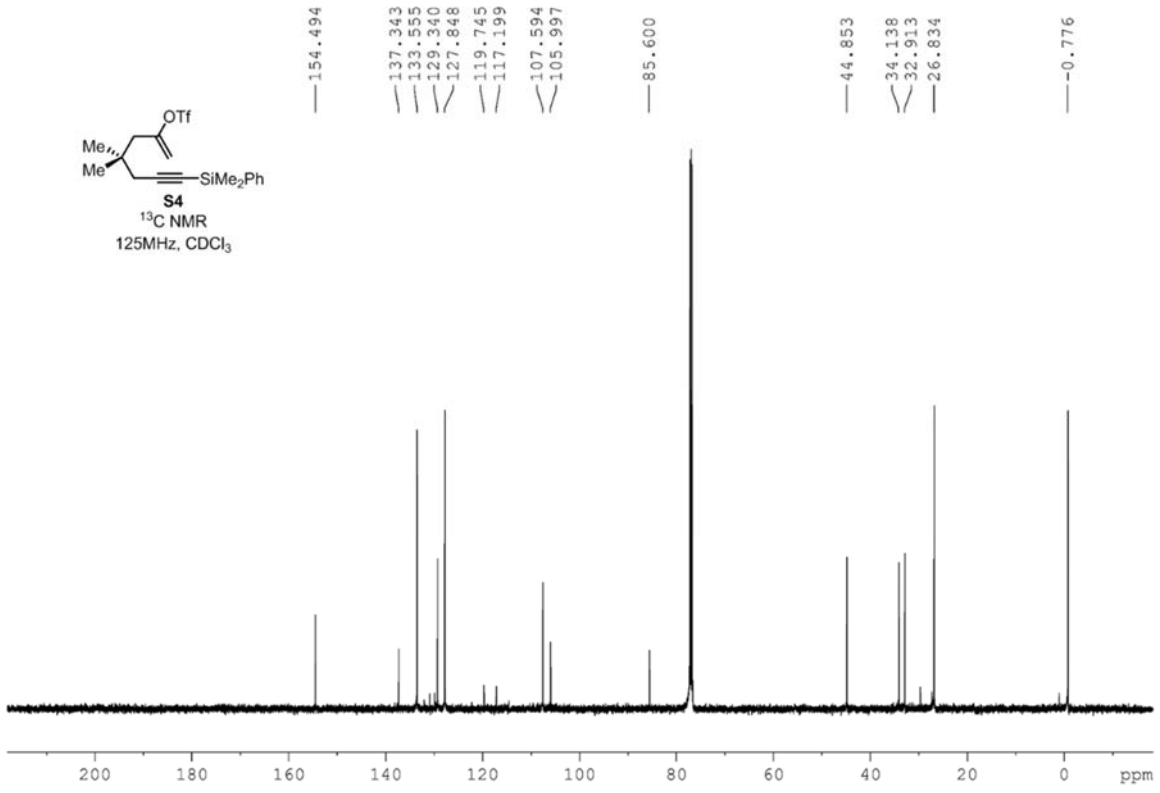
Identification code	exp_20218
Empirical formula	$C_{22}H_{21}BrO_4$
Formula weight	429.30
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.35275(17)
b/Å	12.5835(2)
c/Å	15.0399(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1959.31(6)
Z	4
ρ_{calc}g/cm^3	1.455
μ/mm^{-1}	3.064
F(000)	880.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.164 to 124.38
Index ranges	$-11 \le h \le 11$, $-14 \le k \le 14$, $-17 \le l \le 17$
Reflections collected	26160
Independent reflections	3093 [R_{int} = 0.0731, R_{sigma} = 0.0318]
Data/restraints/parameters	3093/0/247
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0313, wR_2 = 0.0834
Final R indexes [all data]	R_1 = 0.0321, wR_2 = 0.0848
Largest diff. peak/hole / e Å^{-3}	0.40/-0.54
Flack parameter	-0.020(11)

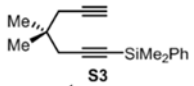
4. References

1. D. Felix, J. Schreiber, G. Ohloff and A. Eschenmoser, *Helv. Chim. Acta*, 1971, **54**, 2896-2912.
2. I. Fleming and E. Martínez de Marigorta, *Journal of the Chemical Society, Perkin Transactions 1*, 1999, 889-900.
3. T. Kokubun, A. Scott-Brown, G. C. Kite and M. S. J. Simmonds, *J. Nat. Prod.*, 2016, **79**, 1698-1701.
4. D. Weber, G. Erosa, O. Sterner and T. Anke, in *Zeitschrift für Naturforschung C*, 2006, vol. 61, p. 663.
5. S. Suzuki, T. Murayama and Y. Shiono, *Phytochemistry*, 2005, **66**, 2329-2333.
6. V. Bardouille, B. S. Mootoo, K. Hirotsu and J. Clardy, *Phytochemistry*, 1978, **17**, 275-277.
7. K. Fabian, T. J. M. Anke, O. Sterner and K. Lorenzen, *Zeitschrift Fur Naturforschung C A Journal of Biosciences*, 1998, **53**, 939-945.

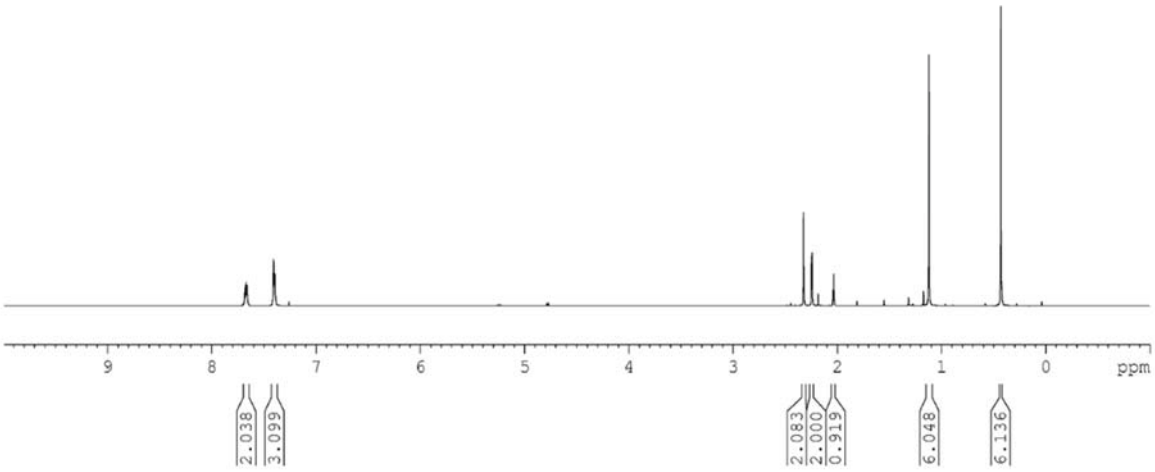
5. NMR Spectra Data

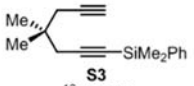




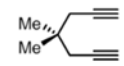


S3
^{1}H NMR
400 MHz, $CDCl_3$





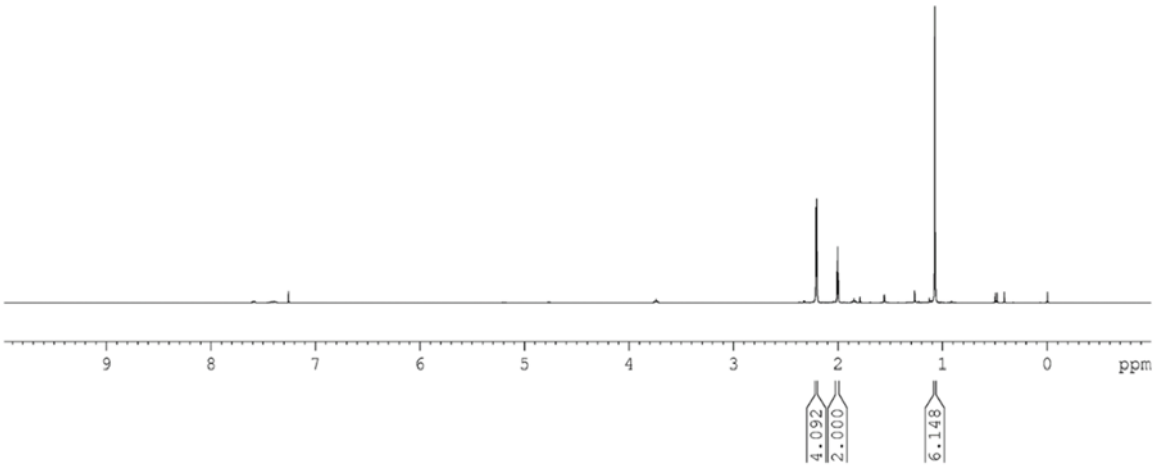
S3
^{13}C NMR
100 MHz, $CDCl_3$

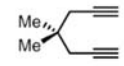


9

^{1}H NMR

400 MHz, $CDCl_3$

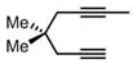




9

^{13}C NMR

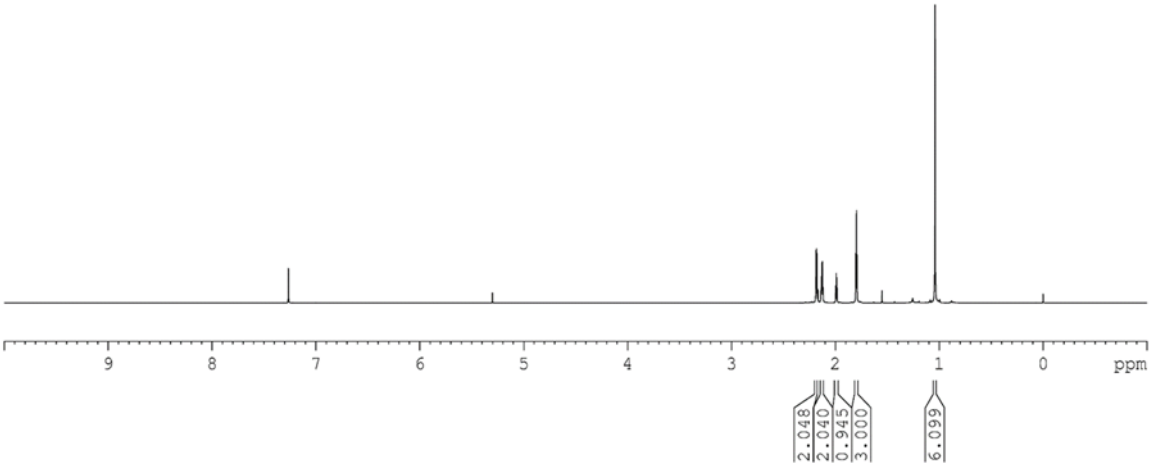
100 MHz, $CDCl_3$

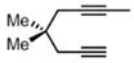


S6

^{1}H NMR

400 MHz, $CDCl_3$

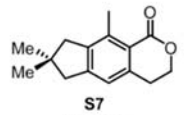




S6

^{13}C NMR

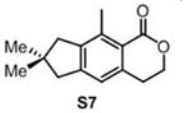
100 MHz, $CDCl_3$



S7

^{1}H NMR

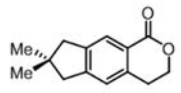
400 MHz, $CDCl_3$



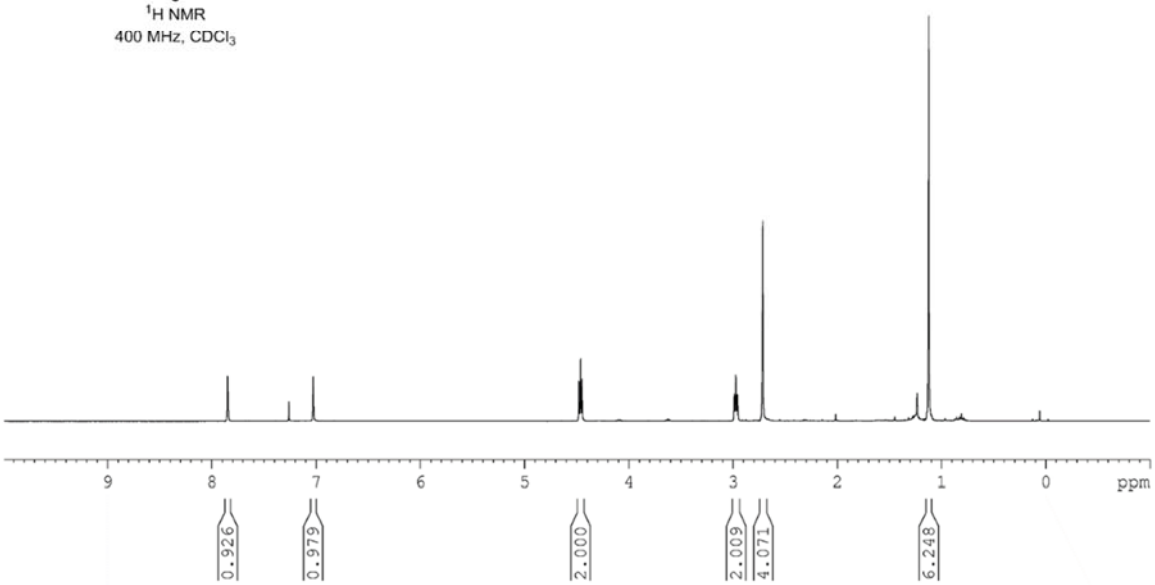
S7

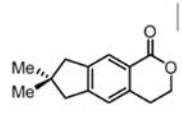
^{13}C NMR

100 MHz, $CDCl_3$

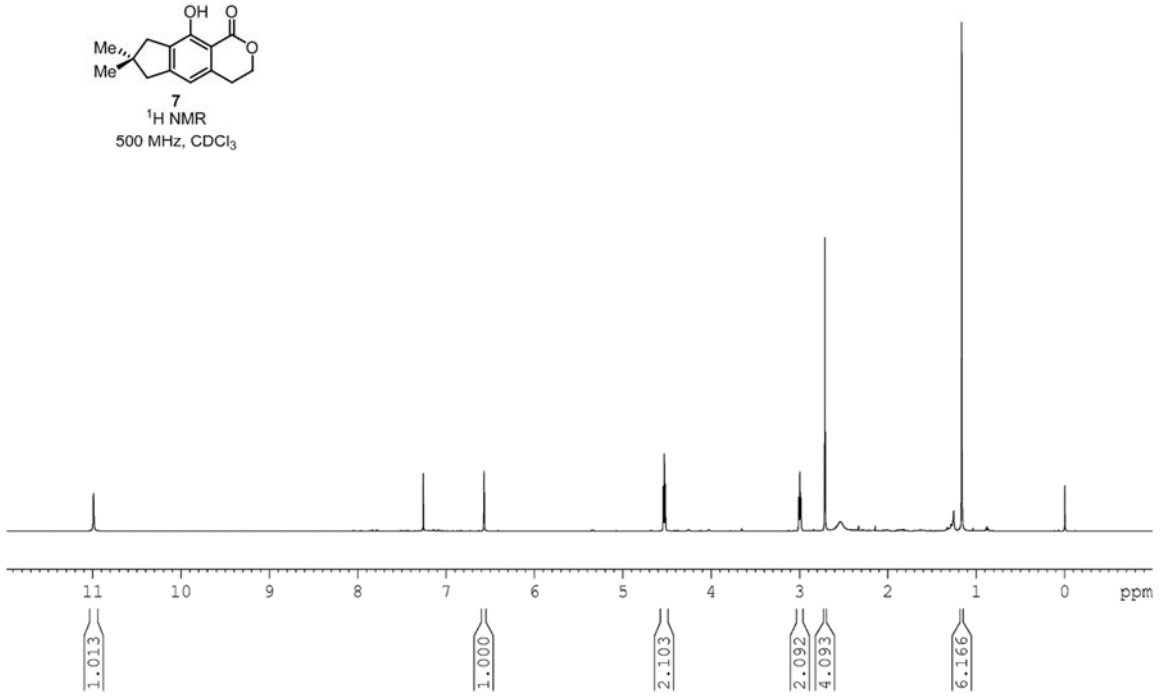


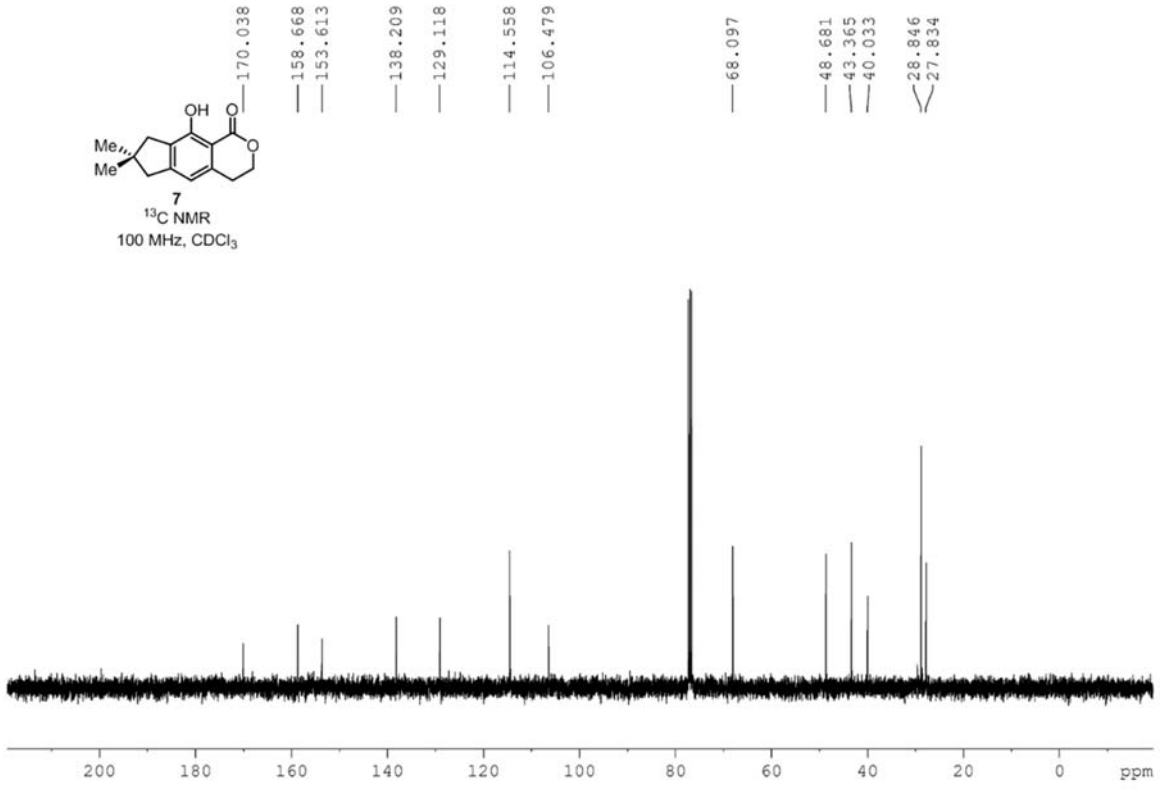
8
^{1}H NMR
400 MHz, $CDCl_3$





8
^{13}C NMR
100 MHz, $CDCl_3$


OH
O
Me
Me
O
7
1H NMR
500 MHz, CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.013
1.000
2.103
2.092
4.093
6.166


170.038
158.668
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129.118
114.558
106.479
68.097
48.681
43.365
40.033
28.846
27.834
OH
O
Me
Me
O
7
13C NMR
100 MHz, CDCl3
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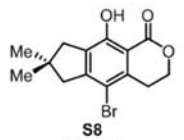
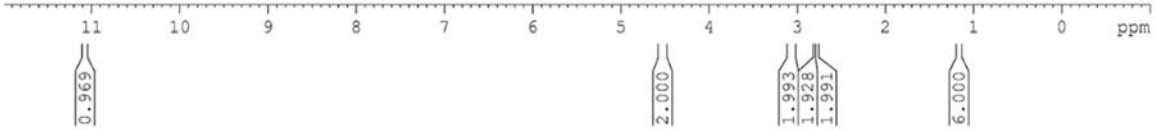
180
160
140
120
100
80
60
40
20
0
ppm

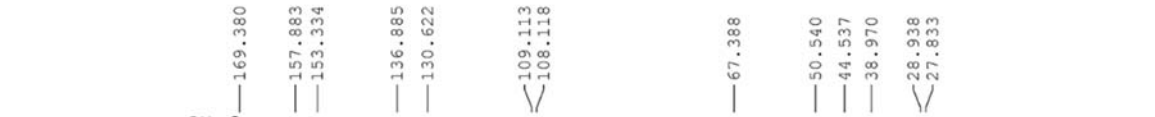


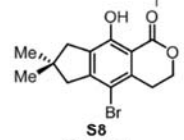
S8

^{1}H NMR

500 MHz, $CDCl_3$



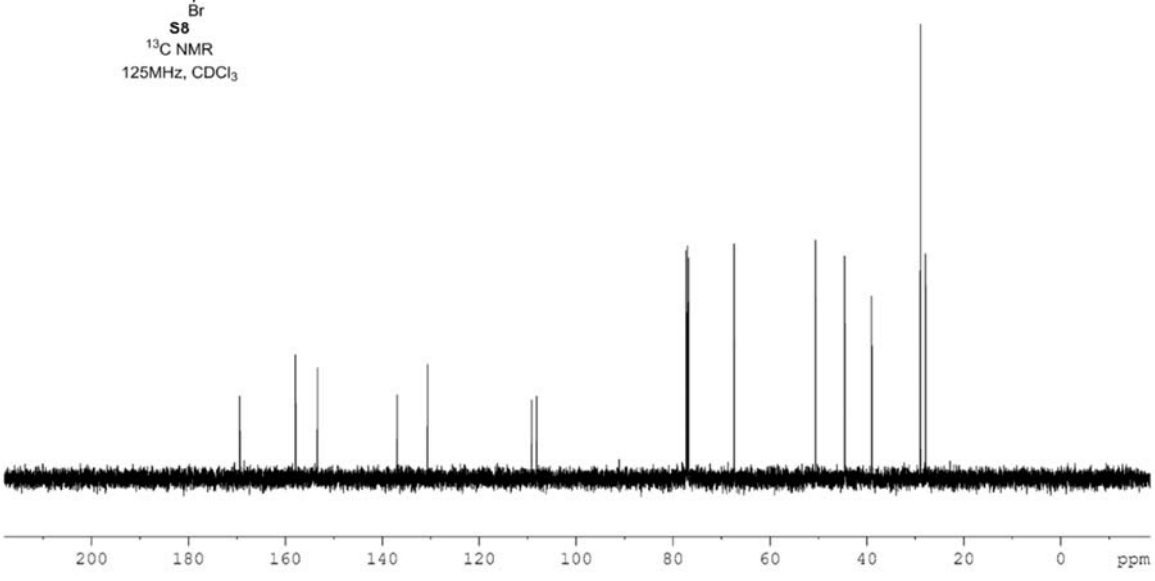


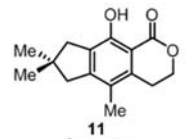


S8

^{13}C NMR

125MHz, $CDCl_3$

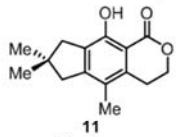




11

^{1}H NMR

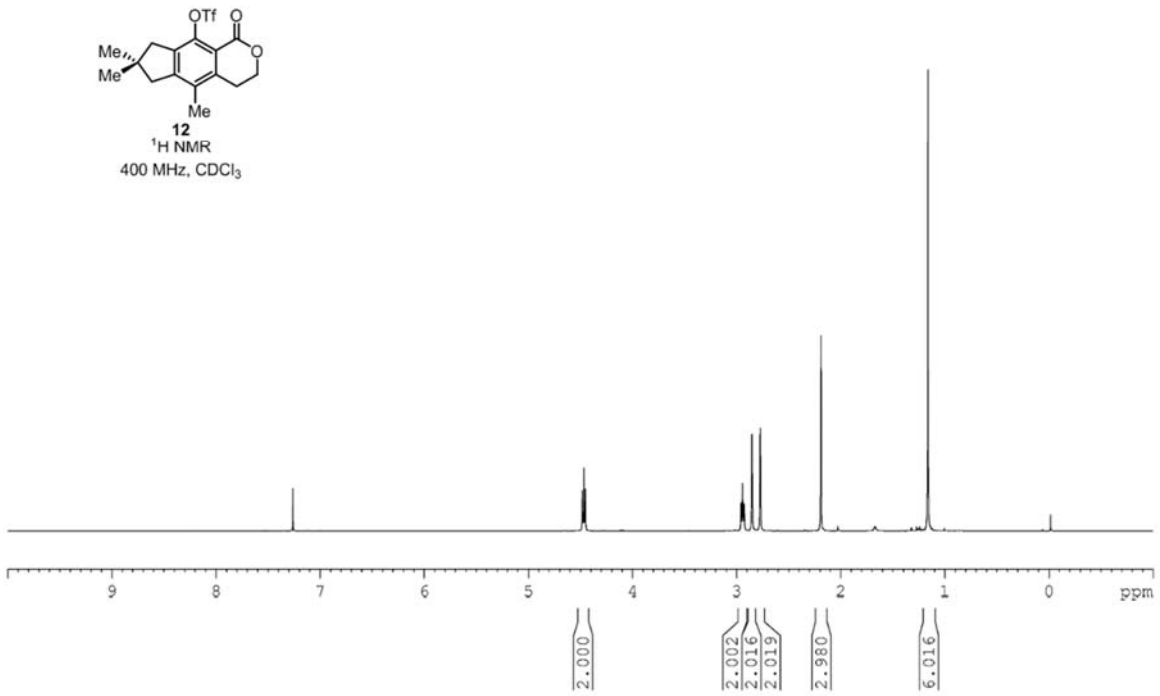
400 MHz, $CDCl_3$

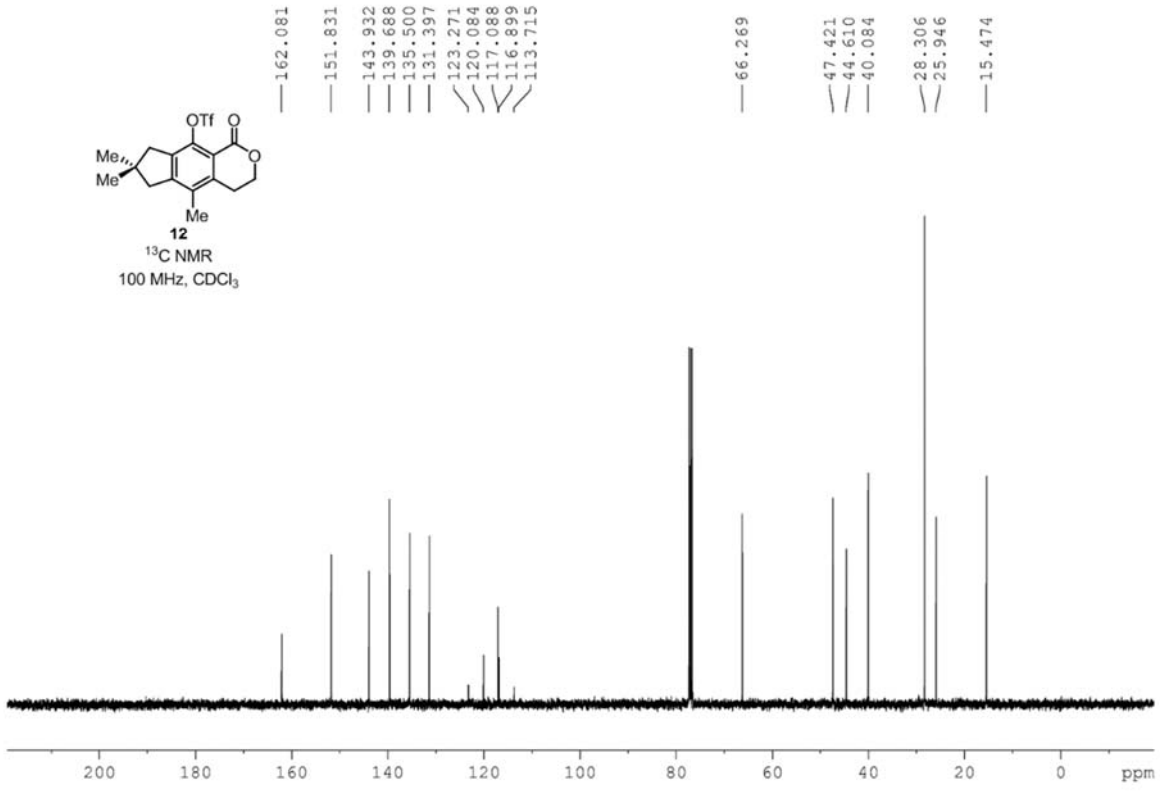


11

^{13}C NMR

100 MHz, $CDCl_3$


OTf
O
Me
Me
Me
O
12
^{1}H NMR
400 MHz, CDCl$_3$
9
8
7
6
5
4
3
2
1
0
ppm
2.000
2.002
2.016
2.019
2.980
6.016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143.932
139.688
135.500
131.397
123.271
120.084
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116.899
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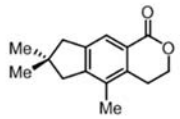
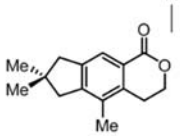
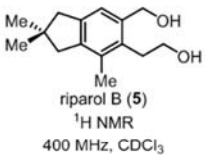
66.269
47.421
44.610
40.084
28.306
25.946
15.474
OTf
O
Me
Me
Me
O
12
^{13}C NMR
100 MHz, CDCl$_3$
200
180
160
140
120
100
80
60
40
20
0
ppm



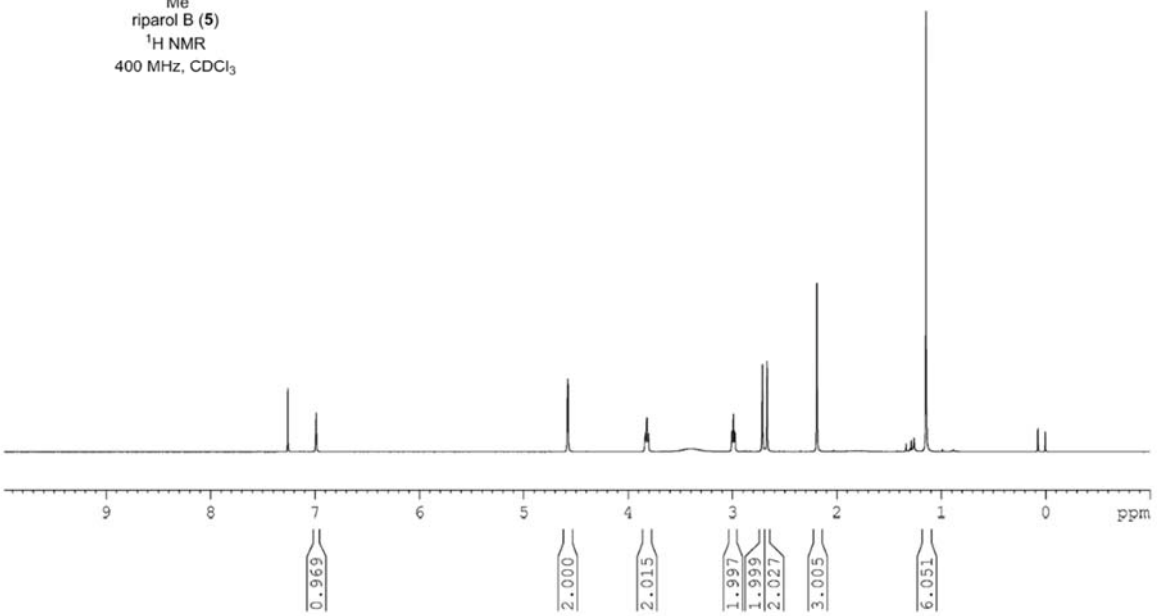
granulolactone (**4**)
^{1}H NMR
400 MHz, $CDCl_3$

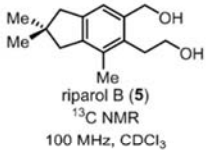


granulolactone (**4**)
^{13}C NMR
100 MHz, $CDCl_3$

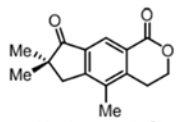


riparol B (**5**)
^{1}H NMR
400 MHz, $CDCl_3$

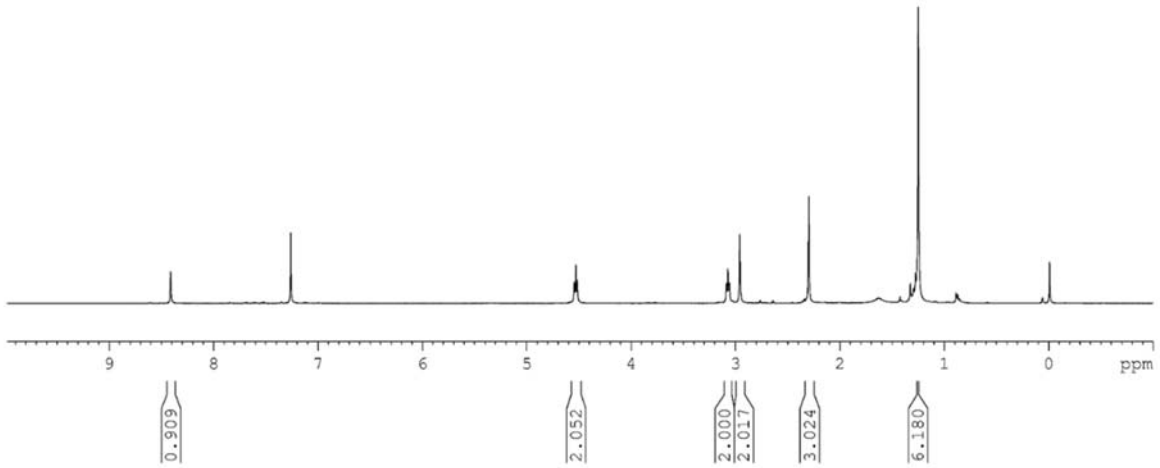


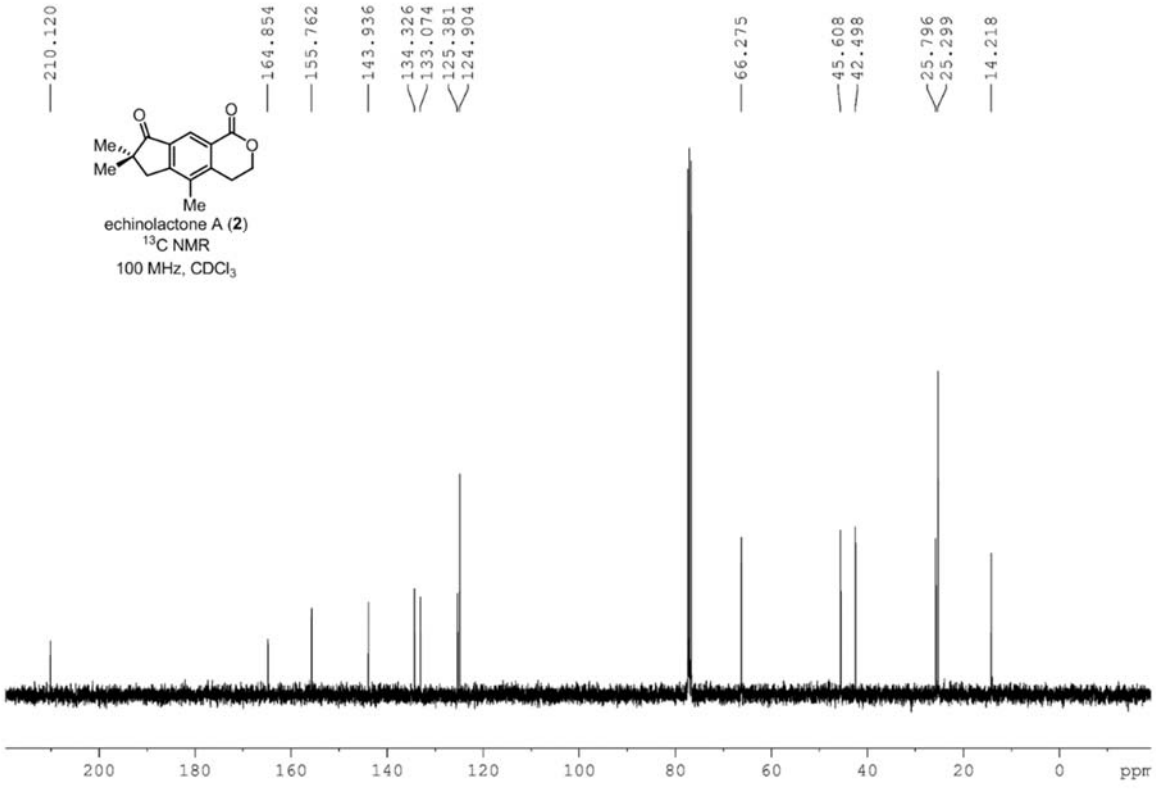


riparol B (**5**)
^{13}C NMR
100 MHz, $CDCl_3$

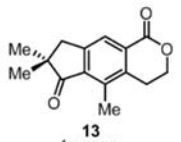


echinolactone A (**2**)
^{1}H NMR
400 MHz, $CDCl_3$

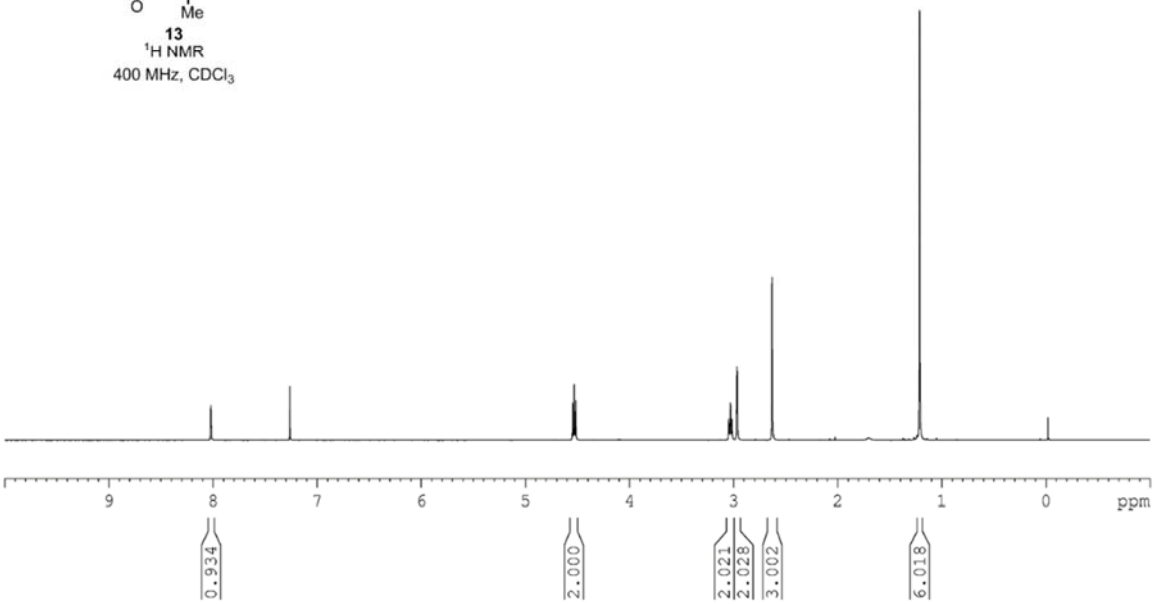


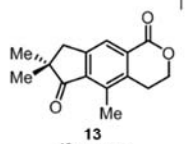


echinolactone A (**2**)
^{13}C NMR
100 MHz, $CDCl_3$

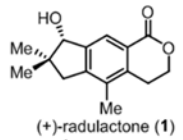


13
^{1}H NMR
400 MHz, $CDCl_3$

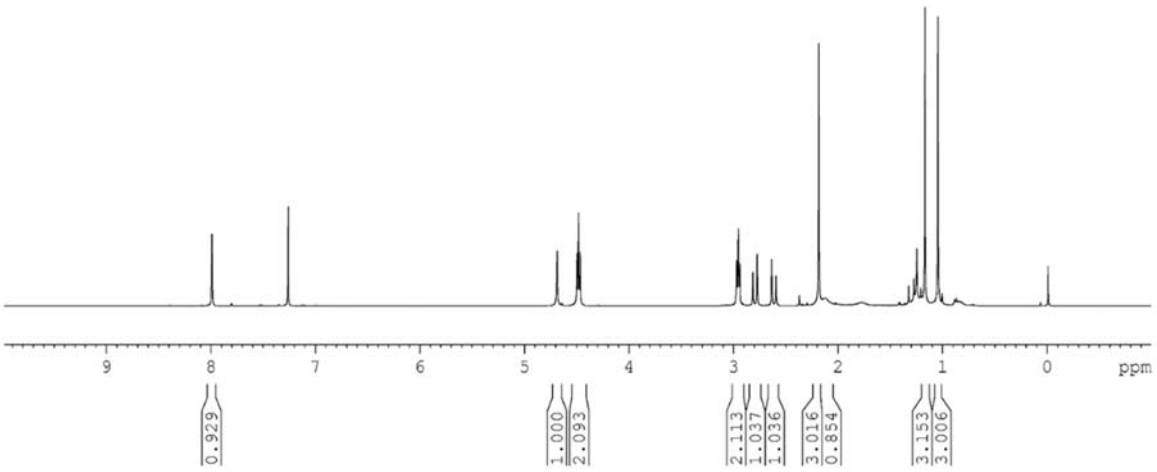


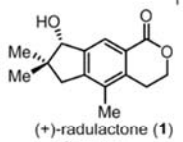


13
^{13}C NMR
100 MHz, $CDCl_3$

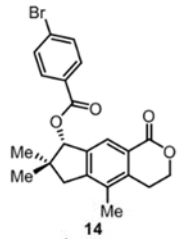


(+)-radulactone (**1**)
^{1}H NMR
400 MHz, $CDCl_3$





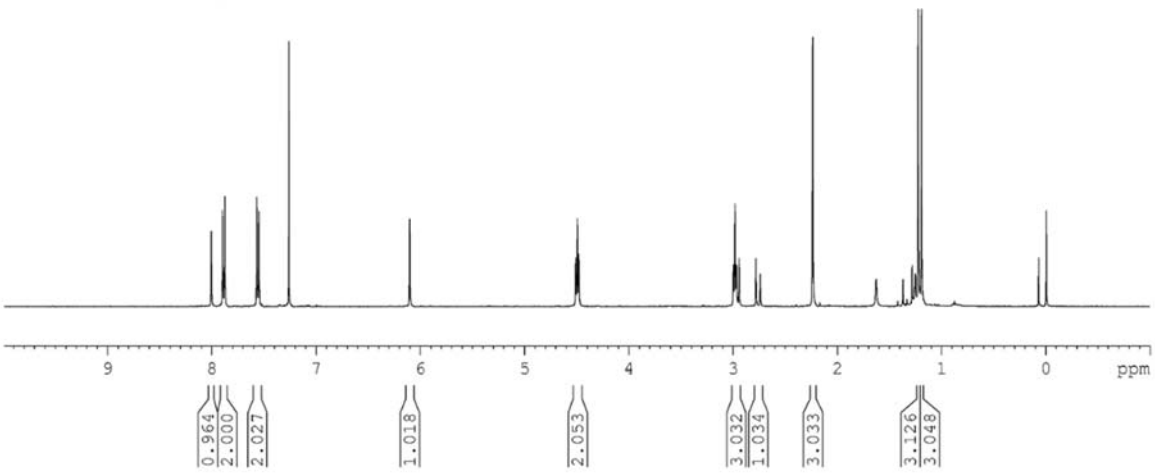
(+)-radulactone (**1**)
^{13}C NMR
100 MHz, $CDCl_3$

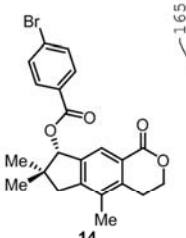


14

^{1}H NMR

400 MHz, $CDCl_3$

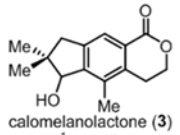




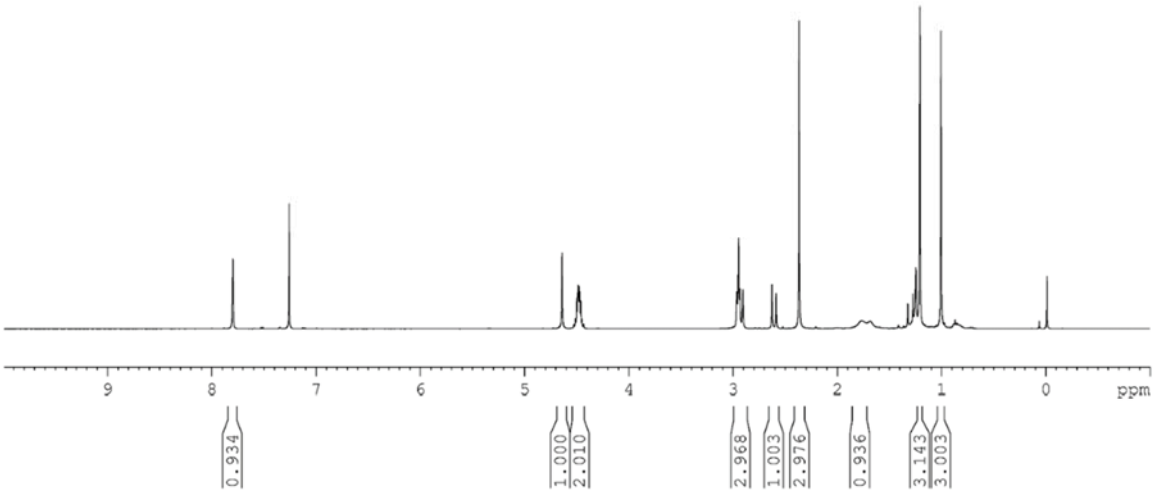
14

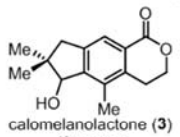
^{13}C NMR

100 MHz, $CDCl_3$

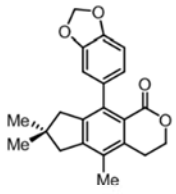


calomelanolactone (**3**)
^{1}H NMR
400 MHz, $CDCl_3$

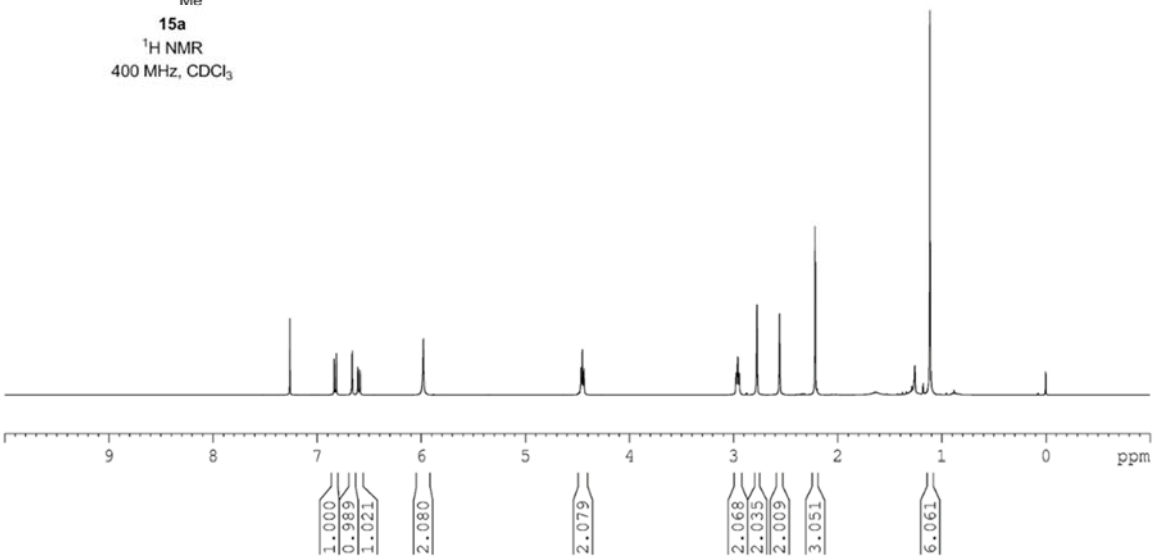


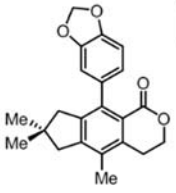


calomelanolactone (**3**)
^{13}C NMR
100 MHz, $CDCl_3$

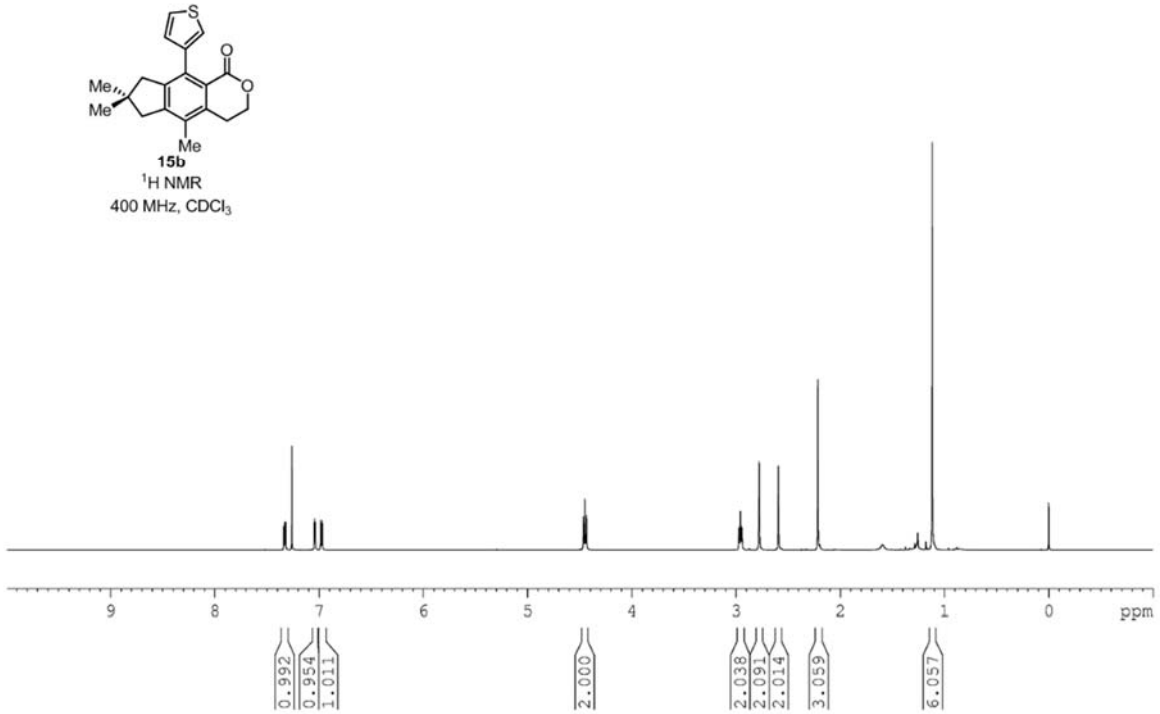


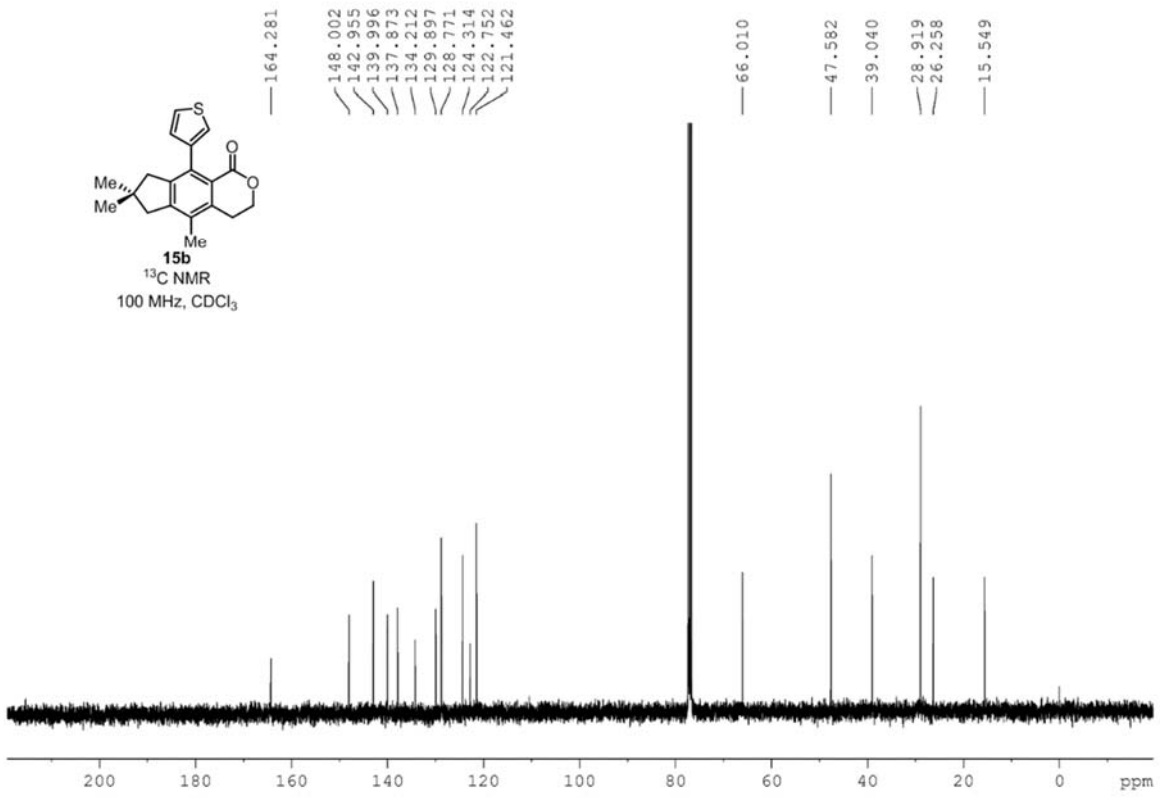
15a
^{1}H NMR
400 MHz, $CDCl_3$

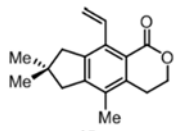




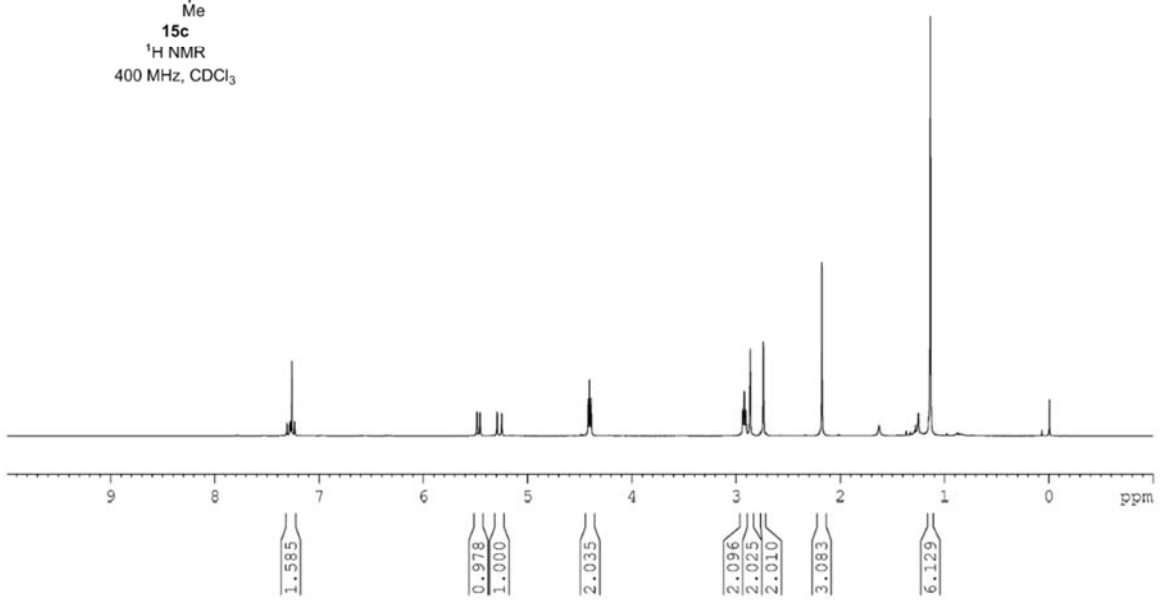
15a
^{13}C NMR
100 MHz, $CDCl_3$

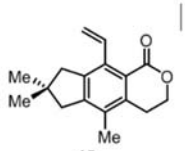

Me
Me
Me
15b
1H NMR
400 MHz, CDCl3
9
8
7
6
5
4
3
2
1
0
ppm
0.992
0.954
1.011
2.000
2.038
2.091
2.014
3.059
6.057


164.281
148.002
142.955
139.996
137.873
134.212
129.897
128.771
124.314
122.752
121.462
66.010
47.582
39.040
28.919
26.258
15.549
Me
Me
Me
15b
13C NMR
100 MHz, CDCl3
200
180
160
140
120
100
80
60
40
20
0
ppm

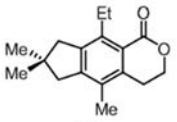


15c
^{1}H NMR
400 MHz, $CDCl_3$





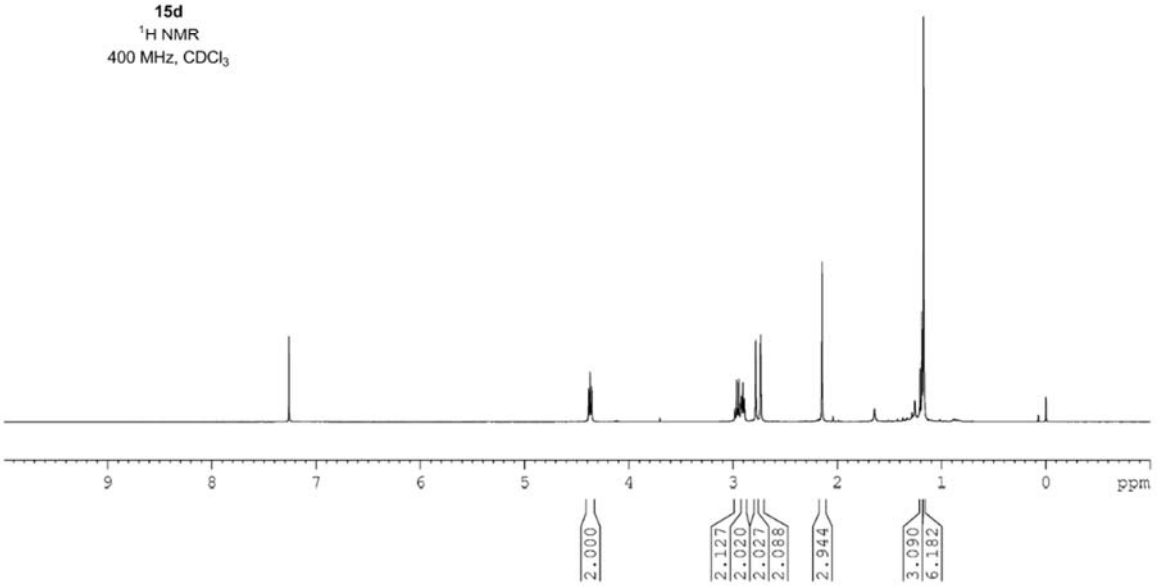
15c
^{13}C NMR
100 MHz, $CDCl_3$

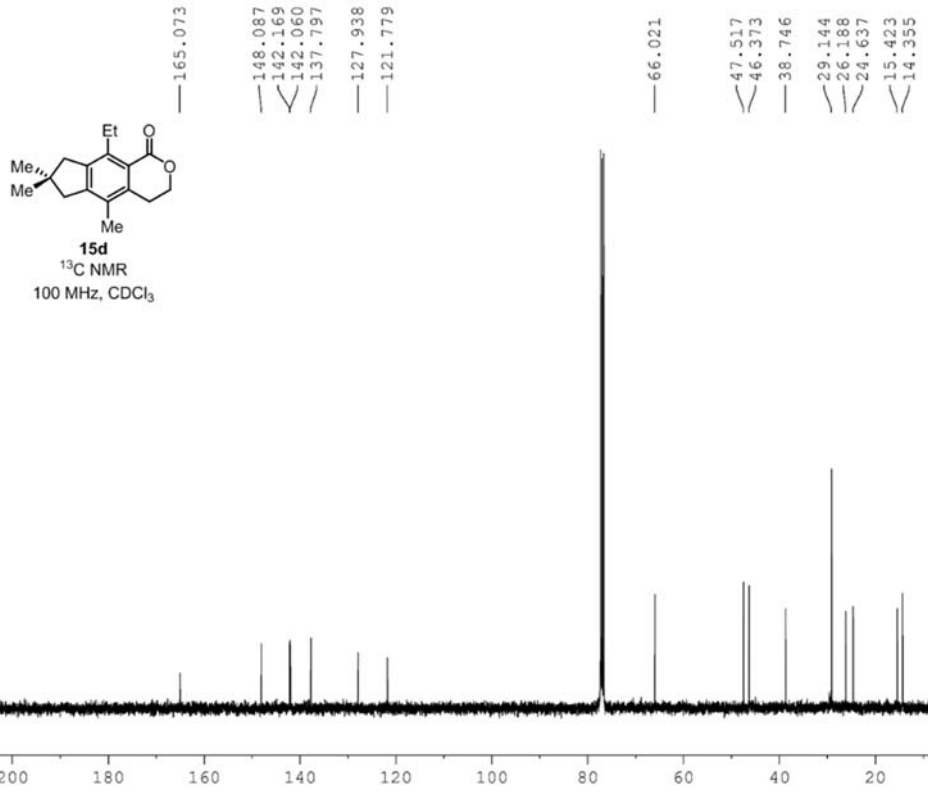


15d

^{1}H NMR

400 MHz, $CDCl_3$





15d

^{13}C NMR

100 MHz, $CDCl_3$