Supporting Information

Stereoselective Synthesis of trans-Decalin-based Spirocarbocycles via Photocyclization of 1,2-Diketones

Sijia Chen,[†] Zhongchao Zhang,[†] Chongguo Jiang,[†] Chunbo Zhao,[†] Haojie Luo,[†] Jun Huang,*[,†] Zhen Yang*[,†,‡,¶]

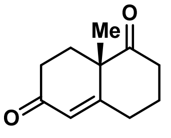
[†] State Key Laboratory of Chemical Oncogenomics and Key Laboratory of Chemical Genomics, Peking University Shenzhen Graduate School, Shenzhen 518055, China

[‡] Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education and Beijing National Laboratory for Molecular Science (BNLMS), and Peking-Tsinghua Center for Life Sciences, Peking University, Beijing 100871, China

[¶] Shenzhen Bay Laboratory, Shenzhen 518055, China

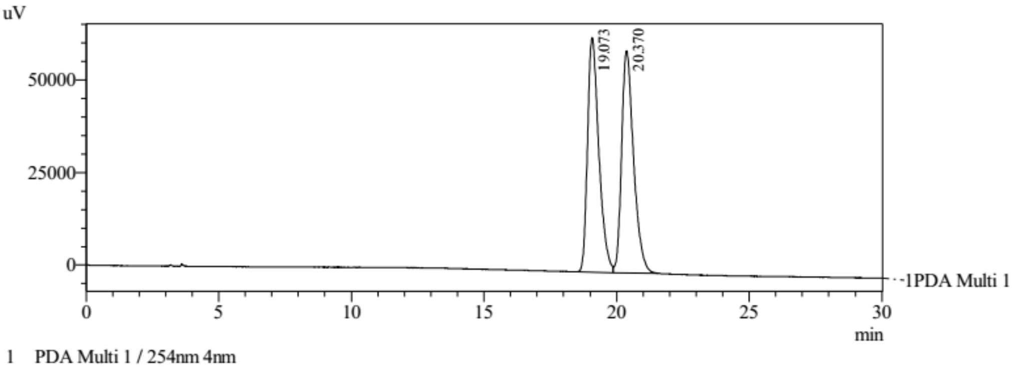
Table of Contents

Part I: Experimental Procedures



1

Conditions: Chiralcel OD-H, hexane/*i*-PrOH 40/1, 1 mL/min.



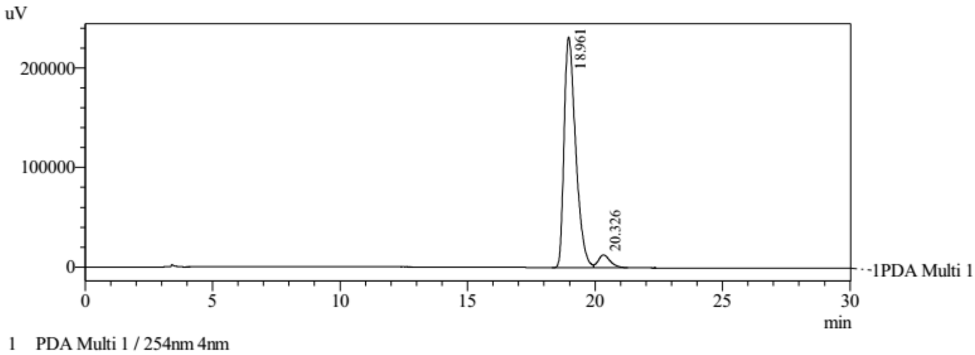
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.073	1876643	63385	49.877	51.384
2	20.370	1885915	59971	50.123	48.616
Total		3762558	123356	100.000	100.000

Figure S1. HPLC spectrum of (±) **1**

Conditions: Chiralcel OD-H, hexane/*i*-PrOH 40/1, 1 mL/min. (*ee* = 89%).

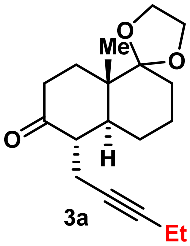


PeakTable

PDA Ch1 254nm 4nm

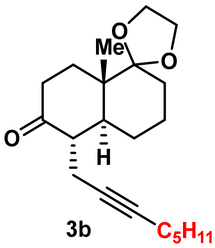
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.961	7311420	231915	94.608	94.760
2	20.326	416674	12824	5.392	5.240
Total		7728093	244739	100.000	100.000

Figure S2. HPLC spectrum of (+) **1**



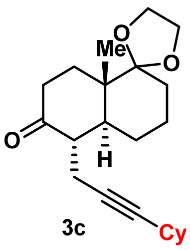
3a

*(4aS,5S,8aS)-8a-methyl-5-(pent-2-yn-1-yl)hexahydro-2H-spiro[naphthalene-1,2'-[1,3]dioxolan]-6(5H)-one (**3a**):* yellowish oil (4.05 g, 50%), R_f = 0.43 (silica gel, hexane/EtOAc = 5:1, $KMnO_4$); $[\alpha]_D^{25}$ = 8.00 (c = 1.0, in $CHCl_3$); IR (thin film) ν_{max} 2950, 1772, 1427, 1236, 1186, 1070, 969, 919 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.98 – 3.83 (m, 4H), 2.55 – 2.44 (m, 1H), 2.44 – 2.31 (m, 3H), 2.29 – 2.25 (m, 1H), 2.16 – 2.02 (m, 3H), 1.99 – 1.90 (m, 1H), 1.78 – 1.67 (m, 4H), 1.59 – 1.48 (m, 2H), 1.27 (dd, J = 9.1, 3.7 Hz, 1H), 1.23 (s, 3H), 1.08 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.3, 112.4, 82.4, 77.0, 65.2, 64.9, 49.7, 452, 42.2, 37.5, 30.2, 30.0, 25.1, 22.7, 15.9, 14.3, 14.3, 12.5; MS (ESI, *m/z*) calcd for $C_{18}H_{27}O_3^+$ $[M+H]^+$: 291.1955, found 291.1954.



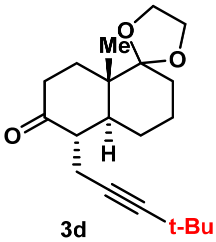
3b

*(4aS,5S,8aS)-8a-methyl-5-(oct-2-yn-1-yl)hexahydro-2H-spiro[naphthalene-1,2'-[1,3]dioxolan]-6(5H)-one (**3b**):* yellowish oil (3.25 g, 35%), R_f = 0.45 (silica gel, hexane/EtOAc = 5:1, $KMnO_4$); $[\alpha]_D^{24}$ = 11.47 (c = 1.0, in $CHCl_3$); IR (thin film) ν_{max} 2954, 2932, 2874, 1712, 1459, 1186, 1123, 1069 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.96 – 3.82 (m, 4H), 2.52 (dd, J = 16.7, 3.4 Hz, 1H), 2.40 – 2.29 (m, 3H), 2.24 (m, 1H), 2.12 – 2.04 (m, 3H), 1.97 – 1.88 (m, 1H), 1.76 – 1.64 (m, 4H), 1.58 – 1.49 (m, 2H), 1.46 – 1.38 (m, 2H), 1.36 – 1.22 (m, 5H), 1.20 (s, 3H), 0.90 – 0.83 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.4, 112.6, 81.3, 77.7, 65.2, 65.0, 49.7, 45.1, 42.3, 37.6, 31.1, 30.2, 30.1, 28.83 25.2, 22.8, 22.4, 18.9, 16.0, 14.4, 14.1; MS (ESI, *m/z*) calcd for $C_{21}H_{33}O_3^+$ $[M+H]^+$: 333.2424, found 333.2427.



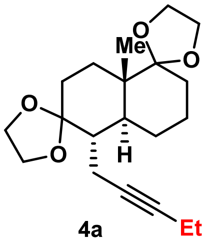
3c

*(4aS,5S,8aS)-5-(3-cyclohexylprop-2-yn-1-yl)-8a-methylhexahydro-2H-spiro[naphthalene-1,2'-[1,3]dioxolan]-6(5H)-one (**3c**):* yellowish oil (3.36 g, 35%), R_f = 0.47 (silica gel, hexane/EtOAc = 5:1, $KMnO_4$); $[\alpha]_D^{24}$ = 7.94 (c = 1.0, in $CHCl_3$); IR (thin film) ν_{max} 2930, 2855, 1711, 1447, 1187,1122, 1023, 949 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.98 – 3.81 (m, 4H), 2.52 (m, 1H), 2.42 – 2.25 (m, 4H), 2.26 – 2.17 (m, 1H), 2.12 (td, J = 12.2, 3.3 Hz, 1H), 1.92 (td, J = 12.6, 8.2 Hz, 1H), 1.75 – 1.63 (m, 8H), 1.58 – 1.47 (m, 2H), 1.37 (d, J = 9.5 Hz, 3H), 1.26 (dd, J = 10.9, 7.8 Hz, 4H), 1.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.4, 112.6, 85.7, 77.8, 65.3, 65.1, 49.8, 45.1, 42.3, 37.6, 33.0, 33.0, 30.2, 30.2, 29.0, 26.1, 25.3, 24.8, 22.8, 16.1, 14.5; MS (ESI, *m/z*) calcd for $C_{22}H_{33}O_3^+$ $[M+H]^+$: 345.2424, found 345.2422.



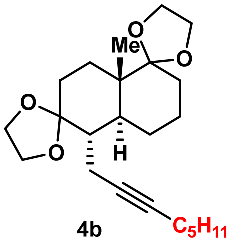
3d

*(4aS,5S,8aS)-5-(4,4-dimethylpent-2-yn-1-yl)-8a-methylhexahydro-2H-spiro[naphthalene-1,2'-[1,3]dioxolan]-6(5H)-one (**3d**):* yellowish oil (3.73 g, 42%), $R_f = 0.52$ (silica gel, hexane/EtOAc = 5:1, $KMnO_4$); $[\alpha]_D^{24}$ = -1.89 (c = 1.0, in $CHCl_3$); IR (thin film) ν_{max} 2964, 1713, 1446, 1264, 1186, 1080, 949, 876 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.01 – 3.83 (m, 4H), 2.49 (dd, J = 16.8, 4.0 Hz, 1H), 2.40 – 2.36 (m, 3H), 2.26 – 2.22 (m, 1H), 2.11 (td, J = 12.2, 3.3 Hz, 1H), 1.94 (td, J = 12.6, 7.7 Hz, 1H), 1.77 – 1.66 (m, 4H), 1.59 – 1.48 (m, 2H), 1.26 (dd, J = 13.2, 3.8 Hz, 1H), 1.22 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.6, 112.6, 90.2, 76.4, 65.3, 65.1, 50.0, 45.4, 42.3, 37.6, 31.4, 31.2, 30.2, 27.5, 25.4, 22.9, 16.2, 14.6; MS (ESI, m/z) calcd for $C_{20}H_{31}O_3^+$ $[M+H]^+$: 319.2268, found 319.2269.



4a

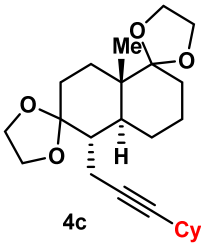
*(4a'S,5'S,8a'S)-8a'-methyl-5'-(pent-2-yn-1-yl)hexahydro-2'H,5'H-dispiro[[1,3]dioxolane-2,1'-naphthalene-6',2''-[1,3]dioxolane] (**4a**):* colorless oil (3.25 g, 62%), R_f = 0.45 (silica gel, hexane/EtOAc = 5:1, $KMnO_4$); $[\alpha]_D^{24}$ = 2.96 (c = 1.0, in $CHCl_3$); IR (thin film) ν_{max} 2876, 1445, 1379, 1291, 1189, 1128, 1075, 954 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.01 – 3.78 (m, 8H), 2.35 – 2.29 (m, 1H), 2.15 – 2.10 (m, 2H), 2.09 – 2.00 (m, 1H), 1.89 (td, J = 12.3, 3.3 Hz, 1H), 1.83 (dd, J = 13.0, 2.3 Hz, 1H), 1.76 – 1.64 (m, 5H), 1.57 – 1.48 (m, 3H), 1.37 – 1.30 (m, 1H), 1.22 – 1.16 (m, 1H), 1.08 (t, J = 7.5 Hz, 3H), 1.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 112.8, 110.7, 81.4, 79.8, 65.3, 65.1, 64.9, 64.8, 44.4, 44.2, 42.5, 30.6, 30.3, 27.5, 24.5, 23.1, 16.3, 14.5, 14.4, 12.7; MS (ESI, m/z) calcd for $C_{20}H_{31}O_4^+$ $[M+H]^+$: 335.2217, found 335.2222.



4b

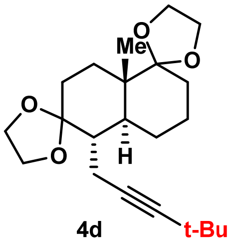
*(4a'S,5'S,8a'S)-8a'-methyl-5'-(oct-2-yn-1-yl)hexahydro-2'H,5'H-dispiro[[1,3]dioxolane-2,1'-naphthalene-6',2''-[1,3]dioxolane] (**4b**):* colorless oil (3.76 g, 60%), R_f = 0.47 (silica gel, hexane/EtOAc = 5:1, $KMnO_4$); $[\alpha]_D^{24}$ = 2.21 (c = 1.0, in $CHCl_3$); IR (thin film) ν_{max} 2954, 2874, 1436, 1343, 1264, 1189, 1043, 955 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.01 – 3.78 (m, 8H), 2.33 (dd, J = 17.1, 3.0 Hz, 1H), 2.15 – 2.01 (m, 3H), 1.91 (td, J = 12.3, 3.3 Hz, 1H), 1.87 – 1.80 (m, 1H), 1.80 – 1.64 (m, 5H), 1.58 – 1.42 (m, 5H), 1.39 – 1.25 (m, 5H), 1.18 (dd, J = 13.0, 3.8 Hz, 1H), 1.04 (s, 3H), 0.89 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 112.8, 110.7, 80.3, 80.1, 65.3, 65.0, 64.8, 64.8,

44.4, 44.1, 42.5, 31.2, 30.6, 30.3, 29.0, 27.4, 24.6, 23.1, 22.4, 18.9, 16.3, 14.3, 14.2; MS (ESI, *m/z*) calcd for $C_{23}H_{36}NaO_4^+$ $[M+Na]^+$: 399.2506, found 399.2514.



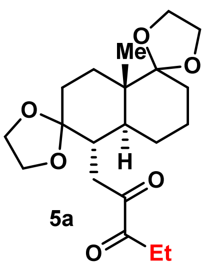
4c

(4a'S,5'S,8a'S)-5'-(3-cyclohexylprop-2-yn-1-yl)-8a'-methylhexahydro-2'H,5'H-dispiro[[1,3]dioxolane-2,1'-naphthalene-6',2''-[1,3]dioxolane] ***(4c)****:* colorless oil (4.01 g, 62%), R_f = 0.49 (silica gel, hexane/EtOAc = 5:1, $KMnO_4$); $[\alpha]_D^{24}$ = 2.67 (c = 1.0, in $CHCl_3$); IR (thin film) ν_{max} 2929, 2860, 1447, 1189, 1113, 1043, 995, 949 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.01 – 3.77 (m, 8H), 2.37 – 2.24 (m, 2H), 2.11 – 2.01 (m, 1H), 1.95 – 1.86 (m, 2H), 1.75 – 1.65 (m, 9H), 1.57 – 1.42 (m, 4H), 1.41 – 1.23 (m, 6H), 1.21 – 1.11 (m, 1H), 1.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 112.8, 110.7, 84.5, 80.3, 65.3, 65.1, 64.9, 64.8, 44.5, 44.1, 42.5, 33.2, 30.7, 30.3, 29.3, 27.5, 26.2, 25.0, 24.6, 23.2, 16.3, 14.3; MS (ESI, *m/z*) calcd for $C_{24}H_{37}O_4^+$ $[M+H]^+$: 389.2686, found 389.2685.



4d

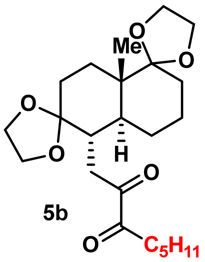
(4a'S,5'S,8a'S)-5'-(4,4-dimethylpent-2-yn-1-yl)-8a'-methylhexahydro-2'H,5'H-dispiro[[1,3]dioxolane-2,1'-naphthalene-6',2''-[1,3]dioxolane] ***(4d)****:* colorless oil (4.10 g, 68%), R_f = 0.55 (silica gel, hexane/EtOAc = 5:1, $KMnO_4$); $[\alpha]_D^{24}$ = 3.25 (c = 1.0, in $CHCl_3$); IR (thin film) ν_{max} 2957, 2876, 1461, 1360, 1265, 1128, 1040, 949 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.99 – 3.77 (m, 8H), 2.31 (dd, *J* = 17.2, 3.2 Hz, 1H), 2.02 (dd, *J* = 17.2, 6.5 Hz, 1H), 1.95 – 1.82 (m, 2H), 1.77 – 1.62 (m, 5H), 1.57 – 1.46 (m, 3H), 1.33 (m, 1H), 1.21 – 1.10 (m, 10H), 1.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 112.8, 110.7, 88.8, 79.0, 65.3, 65.1, 64.9, 64.8, 44.7, 44.3, 42.5, 31.4, 30.7, 30.3, 27.5, 27.5, 24.7, 23.2, 16.3, 14.3; MS (ESI, *m/z*) calcd for $C_{22}H_{35}O_4^+$ $[M+H]^+$: 363.2530, found 363.2533.



5a

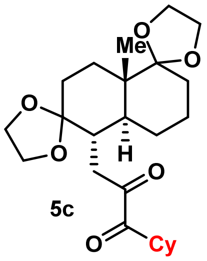
1-((4a'S,5'S,8a'S)-8a'-methylhexahydro-2'H,5'H-dispiro[[1,3]dioxolane-2,1'-naphthalene-6',2''-[1,3]dioxolan]-5'-yl)pentane-2,3-dione ***(5a)****:* yellowish oil (1.44 g, 63%), R_f = 0.39 (silica gel, hexane/EtOAc = 5:1, $KMnO_4$ & UV); $[\alpha]_D^{24}$ = -31.69 (c = 1.0, in $CHCl_3$); IR (thin film) ν_{max} 2939, 2882, 1706, 1457, 1381, 1265, 1117, 948 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.96 – 3.77 (m, 7H), 3.59 – 3.55 (m, 1H), 2.91 – 2.83 (m, 1H), 2.73 (dd, *J* = 14.0, 4.4 Hz, 1H), 2.58 – 2.47 (m, 1H), 2.46 – 2.41 (m, 1H), 2.26 (dd, *J* = 14.0, 10.1 Hz, 1H), 1.81 – 1.62 (m, 5H), 1.54 – 1.38 (m, 4H), 1.37 – 1.29

(m, 1H), 1.23 – 1.16 (m, 2H), 1.09 – 0.99 (m, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 200.9, 199.1, 112.7, 110.2, 65.3, 65.1, 64.4, 63.2, 43.4, 42.8, 42.7, 35.3, 30.0, 29.7, 29.2, 27.2, 24.4, 22.8, 14.3, 7.1; MS (ESI, *m/z*) calcd for $C_{20}H_{30}NaO_6^+$ [M+Na]$^+$: 389.1935, found 389.1936.



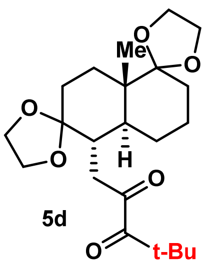
5b

*1-((4a'S,5'S,8a'S)-8a'-methylhexahydro-2'H,5'H-dispiro[[1,3]dioxolane-2,1'-naphthalene-6',2''-[1,3]dioxolan]-5'-yl)octane-2,3-dione (**5b**)*: yellowish oil (1.58 g, 62%), R_f = 0.35 (silica gel, hexane/EtOAc = 5:1, KMnO$_4$ & UV); $[\alpha]_D^{24}$ = -25.89 (c = 1.0, in CHCl$_3$); IR (thin film) ν_{max} 2955, 2934, 2874, 1699, 1451, 1116, 1081, 948 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.95 – 3.74 (m, 7H), 3.57 (dd, *J* = 13.5, 7.0 Hz, 1H), 2.83 – 2.76 (m, 1H), 2.70 (dd, *J* = 14.1, 4.4 Hz, 1H), 2.56 – 2.37 (m, 2H), 2.24 (dd, *J* = 14.1, 10.0 Hz, 1H), 1.79 – 1.59 (m, 5H), 1.59 – 1.51 (m, 2H), 1.51 – 1.36 (m, 4H), 1.34 – 1.22 (m, 5H), 1.16 (dd, *J* = 12.9, 4.3 Hz, 1H), 1.02 (s, 3H), 0.86 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 200.5, 199.1, 112.6, 110.2, 65.2, 65.0, 64.3, 63.2, 43.4, 42.7, 42.6, 35.7, 35.3, 31.4, 30.0, 29.7, 27.2, 24.4, 22.8, 22.7, 22.5, 14.2, 14.0; MS (ESI, *m/z*) Calcd for $C_{23}H_{36}NaO_6^+$ [M+Na]$^+$: 431.2404, found 431.2403.



5c

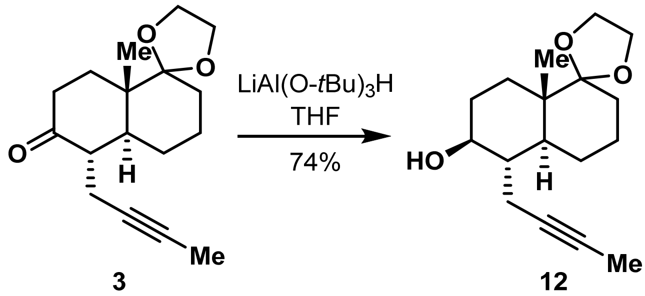
*1-cyclohexyl-3-((4a'S,5'S,8a'S)-8a'-methylhexahydro-2'H,5'H-dispiro[[1,3]dioxolane-2,1'-naphthalene-6',2''-[1,3]dioxolan]-5'-yl)propane-1,2-dione (**5c**):* yellowish oil (1.52 g, 58%), R_f = 0.45 (silica gel, hexane/EtOAc = 5:1, KMnO$_4$ & UV); $[\alpha]_D^{24}$ = -15.81 (c = 1.0, in CHCl$_3$); IR (thin film) ν_{max} 2932, 2862, 1708, 1446, 1189, 1117, 1044, 948 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.97 – 3.78 (m, 7H), 3.66 – 3.62 (m, 1H), 3.07 – 3.03 (m, 1H), 2.66 (dd, *J* = 14.7, 4.5 Hz, 1H), 2.49 – 2.41 (m, 1H), 2.37 (dd, *J* = 14.7, 8.8 Hz, 1H), 1.86 – 1.59 (m, 10H), 1.54 – 1.41 (m, 3H), 1.38 – 1.10 (m, 8H), 1.05 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 202.6, 199.0, 112.7, 110.3, 65.3, 65.1, 64.4, 63.6, 43.5, 43.4, 42.7, 42.2, 35.2, 30.0, 29.8, 29.0, 28.0, 27.3, 26.0, 25.8, 25.7, 24.6, 22.9, 14.3; MS (ESI, *m/z*) calcd for $C_{24}H_{37}O_6^+$ [M+H]$^+$: 421.2585, found 421.2586.



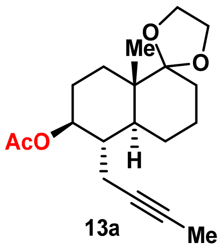
5d

4,4-dimethyl-1-((4a'S,5'S,8a'S)-8a'-methylhexahydro-2'H,5'H-dispiro[[1,3]dioxolane-2,1'-

*naphthalene-6',2''-[1,3]dioxolan]-5'-yl)pentane-2,3-dione (**5d**):* yellowish oil (1.55 g, 63%), R_f = 0.44 (silica gel, hexane/EtOAc = 5:1, $KMnO_4$ & UV); $[\alpha]_D^{24}$ = -10.5 (c = 1.0, in $CHCl_3$); IR (thin film) ν_{max} 2956, 1776, 1699, 1460, 1264, 1116, 1044, 948 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.99 – 3.73 (m, 8H), 2.57 (dd, J = 5.9, 1.9 Hz, 2H), 2.47 – 2.43 (m, 1H), 1.79 – 1.66 (m, 3H), 1.64 (d, J = 5.9 Hz, 2H), 1.55 – 1.43 (m, 3H), 1.39 – 1.32 (m, 1H), 1.27 (s, 1H), 1.25 (d, J = 17.5 Hz, 9H), 1.17 – 1.11 (m, 1H), 1.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.4, 200.6, 112.7, 110.3, 65.3, 65.1, 64.5, 64.1, 43.7, 42.7, 42.4, 40.5, 36.6, 30.1, 29.7, 27.4, 26.5, 24.7, 22.9, 14.3; MS (ESI, *m/z*) calcd for $C_{22}H_{34}NaO_6^+$ $[M+Na]^+$: 417.2248, found 417.2243.

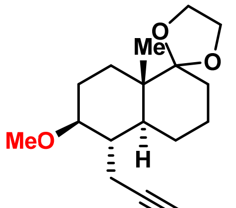


To a solution of **3** (2.00 g, 7.24 mmol) in THF (20 mL) was added lithium tri-tert-butoxyaluminum hydride (3.68 g, 14.47 mmol) at 0 ºC in a portion-wise manner under Ar, and the reaction mixture was then warmed up to room temperature, and stirred at room temperature for 4 h. The reaction mixture was carefully quenched by addition of a saturated aqueous solution of potassium sodium tartrate (20 mL) at 0 ºC, and the resulting mixture was stirred vigorously for another 4 hours. The mixture was extracted with ethyl acetate (3×30 mL), and the combined extracts were washed with brine (15 mL), and dried over Na_2SO_4. The solvent was removed under vacuum. The residue was purified by a flash column chromatography on silica gel (EtOAc: Hexane = 1:9) to give **12** (1.49 g, 74%) as a colorless oil. *(4aS,5S,6S,8aS)-5-(but-2-yn-1-yl)-8a-methyloctahydro-2H-spiro[naphthalene-1,2'-[1,3]dioxolan]-6-ol (**12**):* colorless oil (1.49 g, 74%), R_f = 0.34 (silica gel, hexane/EtOAc = 5:1, $KMnO_4$); $[\alpha]_D^{25}$ = -23.42 (c = 1.0, in $CHCl_3$); IR (thin film) ν_{max} 2943, 2873, 1437, 1371, 1289, 1187, 1085, 916 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.00 – 3.78 (m, 4H), 3.51 (td, J = 10.4, 5.1 Hz, 1H), 2.66 – 2.52 (m, 1H), 2.21 – 2.16 (m, 1H), 1.89 – 1.82 (m, 1H), 1.78 (t, J = 2.6 Hz, 3H), 1.74 – 1.39 (m, 10H), 1.35 (s, 1H), 1.12 – 1.02 (m, 1H), 1.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 113.1, 76.3, 72.7, 65.3, 65.0, 42.9, 42.4, 42.0, 30.4, 30.2, 28.2, 23.6, 23.0, 17.9, 15.0, 3.8; MS (ESI, *m/z*) calcd for $C_{17}H_{26}NaO_3^+$ $[M+Na]^+$: 301.1774, found 301.1775.



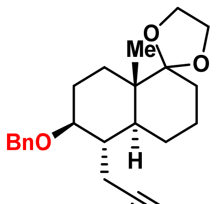
13a

To a solution of **12** (600mg, 2.16 mmol) in DCM (20 mL) was sequentially added Et_3N (0.9 mL, 6.48 mmol), Ac_2O (0.4 mL, 4.32 mmol) and DMAP (25 mg, 0.22 mmol) at room temperature, and the resultant reaction mixture was stirred at room temperature for 1 h. The reaction was quenched by saturated aqueous solution of $NaHCO_3$ (10 mL) at room temperature, and the resulting mixture was extracted with DCM (3×30 mL), and the combined extracts were washed with brine (15 mL), and dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (EtOAc: Hexane = 1: 20) to give **13a** (576 mg, 76%) as a colorless oil. *(4aS,5S,6S,8aS)-5-(but-2-yn-1-yl)-8a-methyloctahydro-2H-spiro[naphthalene-1,2'-[1,3]dioxolan]-6-yl acetate (**13a**):* colorless oil (576 mg, 76%), R_f = 0.41 (silica gel, hexane/EtOAc = 10:1, $KMnO_4$); $[\alpha]_D^{25}$ = 19.49 (c = 1.0, in $CHCl_3$); IR (thin film) ν_{max} 2982, 2875, 1733, 1440, 1378, 1244, 1188, 1080, 962 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.66 (td, J = 10.8, 5.1 Hz, 1H), 3.98 – 3.80 (m, 4H), 2.36 – 2.24 (m, 1H), 2.18 – 2.14 (m, 1H), 2.03 (s, 3H), 1.99 (dd, J = 9.4, 4.7 Hz, 1H), 1.76 (t, J = 2.6 Hz, 3H), 1.74 – 1.60 (m, 5H), 1.58 – 1.47 (m, 3H), 1.46 – 1.36 (m, 2H), 1.11 – 1.02 (m, 1H), 1.01 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 112.8, 77.3, 75.1, 65.4, 65.1, 42.3, 41.9, 39.8, 30.3, 27.9, 26.5, 23.6, 23.0, 21.5, 17.6, 14.9, 3.8; MS (ESI, *m/z*) calcd for $C_{19}H_{28}NaO_4^+$ $[M+Na]^+$: 343.1880, found 343.1881.



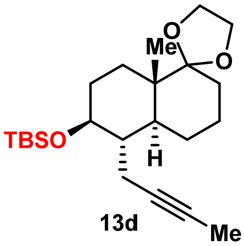
13b

To a solution of **12** (500 mg, 1.80 mmol) in THF (20 mL) was added *n*-BuLi (2.5M, 0.9 mL, 2.16 mmol) at 0 ºC under Ar, and the resultant mixture was stirred at 0 ºC for 20 min. To this solution was added MeI (0.2 mL, 3.60 mmol) at 0 ºC, and the resultant mixture was then slowly warmed up to room temperature, and stirred at room temperature for 8 h. The reaction was quenched with water (5 mL) at room temperature, and the resultant mixture was extracted with ethyl acetate (3×30 mL). The combined organic phases were washed with brine (15 mL), and dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (EtOAc: Hexane = 1:20) to give **13b** (455 mg, 87%) as a colorless oil. *(4aS,5S,6S,8aS)-5-(but-2-yn-1-yl)-6-methoxy-8a-methyloctahydro-2H-spiro[naphthalene-1,2'-[1,3]dioxolane] (**13b**)*: colorless oil (455 mg, 87%), R_f = 0.45 (silica gel, hexane/EtOAc = 10:1, $KMnO_4$); $[\alpha]_D^{26}$ = 35.50 (c = 1.0, in $CHCl_3$); IR (thin film) ν_{max} 2925, 2821, 1736, 1439, 1379, 1188, 1080, 949 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.01 – 3.81 (m, 4H), 3.37 (s, 3H), 3.04 (td, J = 10.8, 5.0 Hz, 1H), 2.65 – 2.53 (m, 1H), 2.23 – 2.13 (m, 1H), 2.08 – 1.97 (m, 1H), 1.79 (t, J = 2.6 Hz, 3H), 1.72 – 1.40 (m, 8H), 1.39 – 1.26 (m, 2H), 1.09 – 1.00 (m, 1H), 0.99 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 113.1, 80.7, 76.6, 76.3, 65.3, 65.0, 56.8, 42.4, 42.0, 41.4, 30.4, 28.0, 25.7, 23.7, 23.1, 17.2, 14.9, 3.8; MS (ESI, *m/z*) calcd for $C_{18}H_{28}NaO_3^+$ $[M+Na]^+$: 315.1931, found 315.1927.



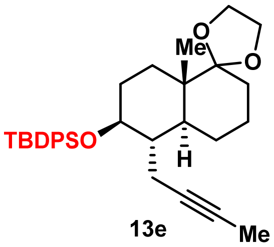
13c

To a solution of **12** (365 mg, 1.31 mmol) in THF (20 mL) was carefully added NaH (60%, 157 mg, 3.93 mmol) and imidazole (9 mg, 0.13 mmol) at 0 ºC under Ar, and the resultant mixture was stirred at 0 ºC for 30 min. To this solution was sequentially added BnBr (0.2 mL, 1.97 mmol) and TBAI (48 mg, 0.13 mmol) at 0 ºC, and the resultant reaction was then warmed up to room temperature, and stirred for 12 h. The reaction mixture was quenched by addition of a saturated aqueous solution of NH_4Cl (10 mL) at 0 ºC, and the mixture was extracted with ethyl acetate (3×20 mL). The combined organic phases were washed with brine (15 mL), and dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (EtOAc: Hexane = 1:20) to give **13c** (383 mg, 79%) as a colorless oil. *(4aS,5S,6S,8aS)-6-(benzyloxy)-5-(but-2-yn-1-yl)-8a-methyloctahydro-2H-spiro[naphthalene-1,2'-[1,3]dioxolane] (**13c**):* colorless oil (383 mg, 79%), R_f= 0.42 (silica gel, hexane/EtOAc = 15:1, $KMnO_4$); $[\alpha]_D^{26}$ = 52.08 (c = 1.0, in $CHCl_3$); IR (thin film) ν_{max} 2930, 2870, 1733, 1453, 1287, 1188, 1079, 949 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 5H), 4.65 (d, J = 11.3 Hz, 1H), 4.49 (d, J = 11.3 Hz, 1H), 3.98 – 3.76 (m, 4H), 3.38 – 3.21 (m, 1H), 2.79 – 2.61 (m, 1H), 2.23 – 2.14 (m, 1H), 2.11 – 1.97 (m, 1H), 1.77 (t, J = 2.5 Hz, 3H), 1.73 – 1.61 (m, 4H), 1.60 – 1.40 (m, 6H), 1.04 (dd, J = 13.3, 3.3 Hz, 1H), 1.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 128.4, 128.1, 127.6, 113.1, 79.2, 76.7, 76.2, 71.4, 65.3, 65.0, 42.3, 41.9, 41.4, 30.3, 28.1, 26.5, 23.7, 23.1, 17.3, 15.0, 3.9; MS (ESI, *m/z*) calcd for $C_{24}H_{32}NaO_3^+$ [M+Na]$^+$: 391.2242, found 391.2242.



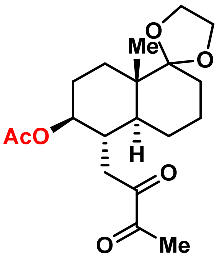
13d

To a solution of **12** (500 mg, 1.80 mmol) in DCM (20 mL) was added TBSCl (543 mg, 3.60 mmol) and imidazole (367 mg, 5.40 mmol) at room temperature under Ar, and the resultant mixture was stirred at the same temperature for 12 h. The reaction mixture was quenched by addition of a saturated aqueous solution of NH_4Cl (10 mL), and the resultant mixture was extracted with DCM (3×20 mL). The combined extracts were washed with brine (15 mL), and dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (EtOAc: Hexane = 1:20) to give **13d** (424 mg, 60%) as a colorless oil. *(((4aS,5S,6S,8aS)-5-(but-2-yn-1-yl)-8a-methyloctahydro-2H-spiro[naphthalene-1,2'-[1,3]dioxolan]-6-yl)oxy)(tert-butyl)dimethylsilane (**13d**):* colorless oil (424 mg, 60%), R_f = 0.35 (silica gel, hexane/EtOAc = 10:1, $KMnO_4$); $[\alpha]_D^{26}$ = 32.75 (c = 1.0, in $CHCl_3$); IR (thin film) ν_{max} 2929, 2857, 1460, 1257, 1187, 1089, 1016, 834 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.02 – 3.76 (m, 4H), 3.48 (td, J = 10.3, 4.9 Hz, 1H), 2.62 – 2.47 (m, 1H), 2.16 – 2.10 (m, 1H), 1.77 (t, J = 2.5 Hz, 4H), 1.71 – 1.41 (m, 9H), 1.37 (d, J = 12.3 Hz, 2H), 1.08 – 0.97 (m, 3H), 0.89 (s, 9H), 0.10 – 0.06 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 113.2, 76.4, 72.8, 65.4, 65.0, 43.0, 42.3, 41.6, 31.1, 30.3, 28.3, 26.1, 23.7, 23.1, 18.2, 17.3, 15.1, 3.8, -4.0, -4.7; MS (ESI, *m/z*) calcd for $C_{23}H_{41}O_3Si^+$ [M+H]$^+$: 393.2819, found 393.2816.



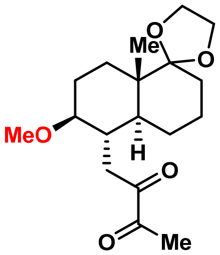
13e

To a solution of **12** (365 mg, 1.31 mmol) in DCM (20 mL) was added TBDPSCl (682 mL, 2.62 mmol) and imidazole (357 mg, 5.24 mmol) at room temperature under Ar, and the resultant mixture was stirred at the same temperature for 12 h. The reaction mixture was quenched by addition of a saturated aqueous solution of NH_4Cl (10 mL) at room temperature, and the resultant mixture was extracted with DCM (3×20 mL). The combined extracts were washed with brine (15 mL), and dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (EtOAc: Hexane = 1:30) to give **13e** (550 mg, 82%) as a colorless oil. *(((4aS,5S,6S,8aS)-5-(but-2-yn-1-yl)-8a-methyloctahydro-2H-spiro[naphthalene-1,2'-[1,3]dioxolan]-6-yl)oxy)(tert-butyl)diphenylsilane (**13e**):* colorless oil (550 mg, 82%), R_f = 0.55 (silica gel, hexane/EtOAc = 15:1, $KMnO_4$); $[\alpha]_D^{26}$ = 9.09 (c = 1.0, in $CHCl_3$); IR (thin film) v_{max} 2930, 2857, 1187, 1044, 916, 824, 702, 505 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 4H), 7.42 – 7.35 (m, 6H), 3.93 – 3.67 (m, 4H), 3.61 (dd, J = 9.9, 4.7 Hz, 1H), 2.93 – 2.68 (m, 1H), 2.34 – 2.12 (m, 1H), 1.76 (t, J = 2.5 Hz, 3H), 1.70 – 1.39 (m, 9H), 1.32 – 1.20 (m, 2H), 1.17 (dd, J = 10.3, 6.7 Hz, 1H), 1.05 (d, J = 11.8 Hz, 9H), 0.98 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.3, 136.1, 135.6, 134.1, 129.5, 129.4, 127.5, 127.4, 113.1, 76.8, 76.4, 74.3, 65.2, 64.9, 43.4, 42.2, 41.7, 30.9, 30.3, 28.1, 27.2, 23.7, 23.1, 19.6, 17.6, 15.1, 4.0; MS (ESI, *m/z*) calcd for $C_{33}H_{45}O_3Si^+$ $[M+H]^+$: 517.3132, found 517.3136.



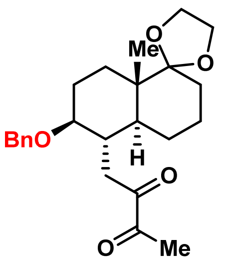
14a

(4aS,5S,6S,8aS)-5-(2,3-dioxobutyl)-8a-methyloctahydro-2H-spiro[naphthalene-1,2'-[1,3]dioxolan]-6-yl acetate (**14a**): yellowish oil (1.39 g, 63%), R_f = 0.43 (silica gel, hexane/EtOAc = 5:1, $KMnO_4$ & UV); $[\alpha]_D^{24}$ = 3.15 (c = 1.0, in $CHCl_3$); IR (thin film) v_{max} 2949, 2875, 1713, 1376, 1243, 1123, 1027, 952 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.45 (td, J = 10.8, 4.9 Hz, 1H), 4.06 – 3.75 (m, 4H), 2.84 (dd, J = 17.2, 5.7 Hz, 1H), 2.42 (dd, J = 17.2, 5.4 Hz, 1H), 2.33 (d, J = 4.2 Hz, 3H), 2.24 – 2.13 (m, 1H), 1.95 (s, 3H), 1.71 – 1.61 (m, 4H), 1.57 – 1.39 (m, 5H), 1.23 – 1.17 (m, 1H), 1.11 (dd, J = 12.8, 3.9 Hz, 1H), 1.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.8, 197.6, 170.5, 112.5, 77.3, 65.3, 65.1, 44.6, 42.7, 37.8, 36.9, 30.0, 27.9, 26.8, 24.6, 24.0, 22.8, 21.3, 14.7; MS (ESI, *m/z*) calcd for $C_{19}H_{28}NaO_6^+$ $[M+Na]^+$: 375.1778, found 375.1782.



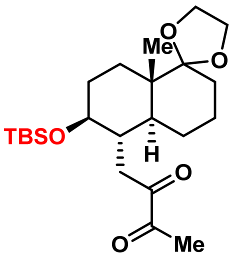
14b

*1-((4aS,5S,6S,8aS)-6-methoxy-8a-methyloctahydro-2H-spiro[naphthalene-1,2'-[1,3]dioxolan]-5-yl)butane-2,3-dione (**14b**):* yellowish oil (870 mg, 43%), R_f = 0.35 (silica gel, hexane/EtOAc = 5:1, $KMnO_4$ & UV); $[\alpha]_D^{24}$ = -18.33 (c = 1.0, in $CHCl_3$); IR (thin film) v_{max} 2927, 2871, 2354, 1702, 1188, 1083, 1044, 939; ^1H NMR (500 MHz, $CDCl_3$) δ 4.01 – 3.74 (m, 4H), 3.05 (s, 3H), 2.79 (dd, J = 12.9, 3.9 Hz, 1H), 2.66 (td, J = 10.8, 4.8 Hz, 1H), 2.24 (s, 3H), 2.11 (dd, J = 12.9, 10.8 Hz, 1H), 2.06 – 1.91 (m, 2H), 1.72 – 1.64 (m, 2H), 1.54 – 1.41 (m, 5H), 1.41 – 1.33 (m, 1H), 1.32 – 1.14 (m, 2H), 1.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.3, 198.0, 112.8, 84.4, 65.2, 65.1, 54.8, 45.1, 42.8, 42.7, 39.4, 30.0, 27.8, 25.3, 24.1, 23.4, 22.8, 14.9; MS (ESI, *m/z*) calcd for $C_{18}H_{28}NaO_5^+$ $[M+Na]^+$: 347.1829, found 347.1828.



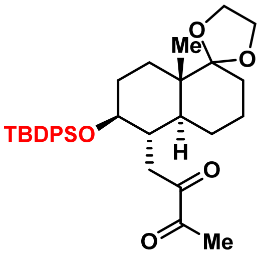
14c

*1-((4aS,5S,6S,8aS)-6-(benzyloxy)-8a-methyloctahydro-2H-spiro[naphthalene-1,2'-[1,3]dioxolan]-5-yl)butane-2,3-dione (**14c**):* yellowish oil (999 mg, 40%), R_f = 0.31 (silica gel, hexane/EtOAc = 10:1, $KMnO_4$ & UV); $[\alpha]_D^{25}$ = -9.33 (c = 1.0, in $CHCl_3$); IR (thin film) ν_{max} 2942, 2870, 1703, 1454, 1354, 1295, 1085, 901 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.18 (m, 5H), 4.45 (d, J = 11.6 Hz, 1H), 4.16 (d, J = 11.6 Hz, 1H), 4.01 – 3.75 (m, 4H), 3.03 – 2.88 (m, 1H), 2.81 (dd, J = 13.1, 3.1 Hz, 1H), 2.27 – 2.07 (m, 2H), 2.05 – 1.93 (m, 1H), 1.80 (s, 3H), 1.74 – 1.66 (m, 2H), 1.54 – 1.35 (m, 7H), 1.29 – 1.16 (m, 1H), 1.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.5, 198.1, 138.3, 128.4, 128.2, 127.7, 112.9, 83.2, 70.1, 65.2, 65.1, 45.0, 42.8, 41.9, 39.5, 30.0, 28.0, 26.1, 24.2, 23.3, 22.8, 15.0; MS (ESI, *m/z*) calcd for $C_{24}H_{32}NaO_5^+$ $[M+Na]^+$: 423.2142, found 423.2144.



14d

*1-((4aS,5S,6S,8aS)-6-((tert-butyldimethylsilyl)oxy)-8a-methyloctahydro-2H-spiro[naphthalene-1,2'-[1,3]dioxolan]-5-yl)butane-2,3-dione (**14d**):* yellowish oil (1.85 g, 70%), R_f = 0.40 (silica gel, hexane/EtOAc = 10:1, $KMnO_4$ & UV); $[\alpha]_D^{25}$ = 4.42 (c = 1.0, in $CHCl_3$); IR (thin film) ν_{max} 2927, 2856, 1713, 1256, 1043, 895, 836, 773 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.93 – 3.83 (m, 4H), 3.32 (dd, J = 12.6, 7.8 Hz, 1H), 2.85 (dd, J = 18.8, 3.3 Hz, 1H), 2.75 (dd, J = 18.9, 7.0 Hz, 1H), 2.32 (s, 3H), 2.07 – 1.95 (m, 1H), 1.79 (dd, J = 6.7, 3.5 Hz, 1H), 1.71 – 1.33 (m, 11H), 1.05 (s, 4H), 1.00 – 0.94 (m, 1H), 0.83 (s, 9H), 0.04 – -0.01 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.4, 198.1, 112.9, 75.2, 65.2, 65.1, 44.8, 42.7, 40.4, 36.5, 31.3, 30.1, 28.4, 26.0, 25.2, 24.1, 23.1, 18.2, 15.0, -3.6, -4.5; MS (ESI, *m/z*) calcd for $C_{23}H_{40}NaO_5^+$ $[M+Na]^+$: 447.2537, found 447.2538.



14e

*1-((4aS,5S,6S,8aS)-6-((tert-butyldiphenylsilyl)oxy)-8a-methyloctahydro-2H-spiro[naphthalene-1,2'-[1,3]dioxolan]-5-yl)butane-2,3-dione (**14e**):* yellowish oil (2.84 g, 83%), , R_f = 0.31 (silica gel, hexane/EtOAc = 15:1, $KMnO_4$ & UV; $[\alpha]_D^{25}$ = 3.90 (c = 1.0, in $CHCl_3$); IR (thin film) ν_{max} 2950, 1713, 1471, 1350, 1111, 1090, 966, 823 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 4H), 7.50 – 7.30 (m, 6H), 3.90 – 3.70 (m, 4H), 3.37 (td, J = 10.6, 5.0 Hz, 1H), 2.97 (dd, J = 19.4, 1.9 Hz, 1H), 2.70 (dd, J = 19.4, 7.8 Hz, 1H), 2.28 (s, 3H), 2.22 – 2.16 (m, 1H), 1.70 – 1.51 (m, 4H), 1.43 (d, J = 13.4 Hz, 1H), 1.36 – 1.20 (m, 4H), 1.06 – 0.99 (m, 4H), 0.97 (s, 9H), 0.89 – 0.82 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.3, 197.8, 136.1, 135.9, 134.7, 134.2, 129.7, 129.7, 127.8, 127.6, 112.8, 76.1, 65.2, 65.0, 45.2, 42.6, 39.9, 37.2, 31.0, 30.1, 28.2, 27.2, 25.1, 24.1, 23.1, 19.5, 14.9; MS (ESI, *m/z*) calcd for $C_{33}H_{44}NaO_5Si^+$ $[M+Na]^+$: 571.2850, found 571.2842.

Part II: Computational Details:

Computational Details:

The calculations were performed with the Gaussian 09 program package[1]. The geometry optimizations were performed using B3LYP functional[2] with def-SVP basis set[4] for all atoms. Frequency calculations were also performed at the same level of theory to identify all the stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency), and the free energies at 298.15 K. An IRC[3] analysis was performed to confirm that all the stationary points were smoothly connected to each other. Higher level of single point electronic energies for those structures were calculated at B3LYP/def2-TZVP level.[2,4] Dispersion correction using DFT-D3 method[5] and solvation effect using SMD method[6] were applied in all calculations. Vibrational harmonic frequencies and thermal corrections were calculated using the same level as the optimization at 298.15 K; the vibrational harmonic frequency calculations, combined with near-zero gradients, confirmed that the optimized transition state structures are indeed the first order saddle points.

Table S1. Calculated imaginary frequencies of all transition states species:

Species	Frequencies
A-TS-T	-1349.71
B-TS-T	-1354.58

Table S2. energy values**:**

Species	Zero-point correction (Hartree)	Thermal correction to Energy (Hartree)	Thermal correction to Enthalpy (Hartree)	Thermal correction to Gibbs Free Energy (Hartree)	Sum of electronic and zero-point Energie (Hartree)	Sum of electronic and thermal Energies (Hartree)	Sum of electronic and thermal Enthalpies (Hartree)	Sum of electronic and thermal Free Energies (Hartree)	Solvated Electronic Energy (Hartree)	Solvated Gibbs Free Energy (Hartree)
A-T	0.453419	0.476673	0.477617	0.400505	-1190.894576	-1190.871322	-1190.870378	-1190.947490	-1192.6701431	-1192.2696381
A-TS-T	0.448119	0.470812	0.471756	0.396525	-1190.883888	-1190.861195	-1190.860251	-1190.935482	-1192.6563538	-1192.2598288
A-H-T	0.453936	0.476948	0.477892	0.401775	-1190.900937	-1190.877925	-1190.876981	-1190.953098	-1192.6744827	-1192.2727077
B-T	0.453580	0.476838	0.477782	0.400181	-1190.896556	-1190.873298	-1190.872354	-1190.949956	-1192.6715559	-1192.2713749
B-TS-T	0.448206	0.470843	0.471787	0.396602	-1190.884088	-1190.861452	-1190.860508	-1190.935692	-1192.6555022	-1192.2589002
B-H-T	0.452793	0.476026	0.476970	0.400586	-1190.893709	-1190.870476	-1190.869532	-1190.945916	-1192.6679921	-1192.2674061

Table S3. Data for calculated geometries

A-T

C	2.695429	-0.754778	0.120014
C	1.087830	-0.771778	2.065054
C	1.563602	1.383302	0.839429
C	0.272364	2.104800	1.215191
C	-0.856026	1.803209	0.227054
C	-1.085490	0.278164	0.078523
C	1.378218	-0.141865	0.687328
C	0.235850	-0.407283	-0.350716
C	0.095089	-1.902772	-0.681161
C	1.419117	-2.507019	-1.164505
C	2.564546	-2.249823	-0.186119
C	-2.277991	0.046563	-0.867417
C	-2.982591	-1.301952	-0.741710
O	-3.039363	-2.108639	-1.683149
C	-3.644383	-1.593409	0.551230
O	-3.630361	-0.767654	1.482596
O	3.753268	-0.515661	1.037256
C	4.341239	0.525439	-0.922288
C	4.917252	-0.206102	0.285773
O	-0.574941	2.343737	-1.058576
H	1.957538	-0.639774	2.725324
H	0.223903	-0.301740	2.554752
H	0.874612	-1.847649	2.004549
H	2.348121	1.587496	1.583634
H	1.912203	1.785833	-0.122724
H	0.427761	3.195245	1.231948
H	-0.079853	1.820517	2.218144
H	0.554007	0.092932	-1.280969
H	-0.279272	-2.453014	0.199638
H	-0.653857	-2.043214	-1.470703
H	1.301272	-3.589252	-1.339322
H	3.524001	-2.596808	-0.601153
H	2.401766	-2.790182	0.758703
H	-3.050455	0.789784	-0.615560
H	-1.984339	0.180692	-1.916325
H	4.941599	0.396844	-1.836717
H	4.225933	1.606317	-0.718831
H	5.455932	-1.124279	-0.016495
H	5.585854	0.413707	0.901300
H	1.683247	-2.052724	-2.134349
O	3.071799	-0.089848	-1.095900
C	-1.147971	3.642459	-1.102871
C	-4.338996	-2.926827	0.708867
H	-5.403356	-2.766962	0.946748
H	-4.240378	-3.498353	-0.225239
H	-3.885710	-3.483193	1.545666
O	-2.039271	2.462237	0.679452
C	-2.406413	3.472927	-0.254985
H	-1.379262	-0.065818	1.080903
H	-1.352488	3.906383	-2.150663
H	-3.262469	3.137346	-0.869592
H	-2.694239	4.389740	0.283383
H	-0.465173	4.397227	-0.669621

A-TS-T

C	2.691184	-0.629915	0.044431
C	1.011154	-0.935109	1.905333
C	1.381422	1.354611	0.915649
C	0.025955	1.935514	1.314883
C	-1.027106	1.698807	0.234665
C	-1.104467	0.227271	-0.194764
C	1.316464	-0.156924	0.609646
C	0.252394	-0.396648	-0.510820
C	0.197530	-1.868742	-0.954230
C	1.571445	-2.347893	-1.438586
C	2.668466	-2.096557	-0.401858
C	-2.242318	-0.097318	-1.127065
C	-3.072196	-1.344417	-0.739469
O	-3.782112	-1.911049	-1.579595
C	-3.028496	-1.763502	0.645045
O	-2.242934	-1.194432	1.522606
O	3.695198	-0.411713	1.023121
C	4.275495	0.854454	-0.802121
C	4.859568	0.051728	0.356022
O	-0.740467	2.451775	-0.941173
H	1.836097	-0.798128	2.619673
H	0.087784	-0.585627	2.384148
H	0.888908	-2.013024	1.737765
H	2.124011	1.536195	1.706745
H	1.727275	1.879805	0.013169
H	0.101253	3.020908	1.485274
H	-0.349599	1.493857	2.250091
H	0.612162	0.185545	-1.383232
H	-0.156996	-2.497944	-0.121182
H	-0.531449	-1.995809	-1.768021

H	1.531133	-3.418611	-1.696981
H	3.660132	-2.339514	-0.814577
H	2.520250	-2.730314	0.485351
H	-2.961549	0.734729	-1.151406
H	-1.898224	-0.266351	-2.158757
H	4.916262	0.857968	-1.697934
H	4.070959	1.899566	-0.504235
H	5.476235	-0.792349	-0.006932
H	5.456307	0.653939	1.056961
H	1.832871	-1.804128	-2.361888
O	3.064083	0.168460	-1.088396
C	-1.449193	3.679625	-0.833068
C	-3.878532	-2.890183	1.140420
H	-4.539533	-2.545113	1.954110
H	-4.484842	-3.281988	0.313007
H	-3.246359	-3.695908	1.552164
O	-2.292180	2.157635	0.699810
C	-2.716742	3.268873	-0.085663
H	-1.551313	-0.364925	0.861498
H	-1.638539	4.070096	-1.843443
H	-3.517340	2.962516	-0.783496
H	-3.105627	4.061308	0.573107
H	-0.865148	4.425838	-0.262651

A-H-T

C	-2.710471	-0.398081	-0.131476
C	-0.641907	-1.482900	-1.102914
C	-0.929292	1.023534	-1.239277
C	0.553743	1.367577	-1.392687
C	1.250097	1.482060	-0.033112
C	0.969755	0.287212	0.841291
C	-1.181990	-0.236080	-0.379564
C	-0.492339	-0.014262	1.019779
C	-0.815492	-1.126358	2.029048
C	-2.327902	-1.305493	2.197279
C	-3.025838	-1.529313	0.853716
C	2.078753	-0.580655	1.352327
C	2.337619	-1.846261	0.502467
O	1.825086	-2.931910	0.836457
C	3.150940	-1.754195	-0.680022
O	3.681080	-0.618886	-1.135582
O	-3.363592	-0.606904	-1.375328
C	-4.235697	1.325934	-0.497640
C	-4.588787	0.110299	-1.347991
O	0.830669	2.668254	0.658779
H	-1.227921	-1.671011	-2.014535
H	0.407594	-1.346830	-1.397292
H	-0.674697	-2.385859	-0.479884
H	-1.388157	0.887923	-2.230387
H	-1.432301	1.876519	-0.760597
H	0.682144	2.323460	-1.925508
H	1.089808	0.599223	-1.970891
H	-0.957041	0.914852	1.403008
H	-0.344454	-2.070191	1.714098
H	-0.365161	-0.869427	3.002224
H	-2.538928	-2.146222	2.878526
H	-4.119138	-1.571517	0.980345
H	-2.709621	-2.483613	0.405584
H	3.009183	0.002930	1.433079
H	1.840264	-0.960206	2.355924
H	-5.090862	1.723810	0.071061
H	-3.807795	2.137154	-1.115639
H	-5.394191	-0.488694	-0.882150
H	-4.879896	0.359773	-2.379007
H	-2.752465	-0.399819	2.662394
O	-3.262299	0.814990	0.403429
C	1.855783	3.643841	0.531361
C	3.441162	-2.946708	-1.523339
H	4.524211	-3.017916	-1.722836
H	3.090133	-3.862884	-1.034168
H	2.940966	-2.851389	-2.504820
O	2.658373	1.663843	-0.274188
C	3.115094	2.793183	0.476759
H	3.373161	0.206366	-0.679930
H	1.819282	4.320074	1.398101
H	3.442123	2.483606	1.485388
H	3.952752	3.260041	-0.060060
H	1.737090	4.234738	-0.396602

B-T

C	3.051989	-0.391340	0.097405
C	1.492673	-0.926246	2.008895
C	1.372597	1.326591	0.876949
C	-0.066337	1.637618	1.275592
C	-1.071087	1.089687	0.257738
C	-0.874286	-0.416007	0.001879
C	1.612583	-0.183012	0.663022
C	0.598243	-0.702908	-0.409830

C	0.868767	-2.170461	-0.786500
C	2.309645	-2.376261	-1.269449
C	3.336342	-1.852043	-0.265784
C	-1.855843	-0.946668	-1.060661
C	-3.331463	-0.722083	-0.758037
O	-4.045585	0.016260	-1.454752
C	-3.884997	-1.470192	0.391393
O	-3.173848	-2.257712	1.045749
O	3.996974	0.088376	1.042702
C	4.289060	1.334616	-0.863124
C	5.035679	0.739349	0.326085
O	-0.984057	1.776864	-0.980060
H	2.273960	-0.574045	2.698453
H	0.520046	-0.749284	2.487870
H	1.604693	-2.013933	1.906378
H	2.074085	1.708217	1.634009
H	1.590187	1.850332	-0.065461
H	-0.218946	2.725029	1.364080
H	-0.320239	1.204891	2.254696
H	0.786059	-0.099645	-1.314207
H	0.653932	-2.826134	0.075277
H	0.188041	-2.486076	-1.590434
H	2.491556	-3.443224	-1.479211
H	4.355577	-1.906031	-0.679615
H	3.325215	-2.453128	0.655876
H	-1.640081	-0.493357	-2.036766
H	-1.745145	-2.038556	-1.135677
H	4.908628	1.416124	-1.770100
H	3.876863	2.331473	-0.619878
H	5.809077	0.019006	-0.001811
H	5.502291	1.492435	0.978093
H	2.445990	-1.834389	-2.220477
O	3.241495	0.399828	-1.085297
C	-1.821411	2.919920	-0.891142
C	-5.315473	-1.187039	0.785572
H	-5.818600	-2.116795	1.091064
H	-5.322934	-0.491391	1.643151
H	-5.838607	-0.720271	-0.061886
O	-2.392286	1.335062	0.736612
C	-2.926360	2.486173	0.088997
H	-1.088520	-0.927454	0.951693
H	-2.203919	3.152439	-1.895935
H	-3.851090	2.197872	-0.435062
H	-3.159215	3.272003	0.827440
H	-1.262382	3.796296	-0.515197

B-TS-T

C	2.920074	-0.450207	0.062782
C	1.190037	-1.168808	1.756384
C	1.290329	1.237962	1.007679
C	-0.149947	1.580279	1.381401
C	-1.107737	1.294404	0.230571
C	-0.943296	-0.122533	-0.347042
C	1.458991	-0.230503	0.562336
C	0.505502	-0.504102	-0.649410
C	0.701294	-1.914139	-1.230616
C	2.158667	-2.148012	-1.646650
C	3.139988	-1.854292	-0.511048
C	-2.029569	-0.466382	-1.333509
C	-3.356637	-0.920645	-0.685316
O	-4.429279	-0.798196	-1.290045
C	-3.264508	-1.546627	0.615977
O	-2.137794	-1.603902	1.280969
O	3.818736	-0.191788	1.129904
C	4.321711	1.314971	-0.528181
C	4.942701	0.491553	0.595895
O	-0.902203	2.207143	-0.847286
H	1.936440	-0.987011	2.543317
H	0.196315	-1.002992	2.192498
H	1.242806	-2.231274	1.485715
H	1.964092	1.442538	1.852786
H	1.595604	1.892189	0.177674
H	-0.246652	2.645874	1.641545
H	-0.494519	1.005194	2.253677
H	0.816752	0.214753	-1.434359
H	0.381551	-2.669288	-0.492524
H	0.058975	-2.054094	-2.112293
H	2.289228	-3.182121	-2.004988
H	4.180399	-1.914885	-0.867035
H	3.030340	-2.587425	0.302126
H	-2.271189	0.398814	-1.967981
H	-1.724099	-1.281921	-2.005051
H	5.009675	1.493686	-1.369520
H	3.950753	2.287969	-0.156274
H	5.696700	-0.219437	0.208033
H	5.401011	1.099331	1.390003
H	2.397065	-1.482336	-2.493057
O	3.241489	0.500087	-0.963447

C	-1.887675	3.228721	-0.742688
C	-4.468728	-2.127216	1.285468
H	-4.296583	-3.184608	1.550085
H	-4.680916	-1.584712	2.223656
H	-5.333721	-2.048293	0.613475
O	-2.443870	1.501969	0.680809
C	-3.073144	2.488333	-0.131831
H	-1.326329	-0.887728	0.616777
H	-2.086400	3.634150	-1.745591
H	-3.705725	2.009426	-0.900729
H	-3.706188	3.128332	0.501663
H	-1.540337	4.046824	-0.084069

B-H-T

C	2.950205	-0.435837	0.075718
C	1.140549	-1.246983	1.640062
C	1.282234	1.202502	1.041443
C	-0.170727	1.525756	1.379735
C	-1.105121	1.266304	0.200567
C	-0.881509	-0.083004	-0.457946
C	1.469504	-0.238627	0.521918
C	0.560866	-0.432419	-0.742933
C	0.790514	-1.790543	-1.428330
C	2.266950	-1.998824	-1.785077
C	3.187768	-1.799824	-0.580676
C	-2.010466	-0.579223	-1.318594
C	-3.359051	-0.857868	-0.633120
O	-4.420213	-0.501920	-1.172583
C	-3.359162	-1.602157	0.598053
O	-2.217065	-1.949607	1.210853
O	3.799670	-0.257210	1.198569
C	4.383644	1.356585	-0.326456
C	4.950278	0.453606	0.763956
O	-0.919521	2.250023	-0.831536
H	1.870927	-1.151123	2.456578
H	0.145464	-1.065823	2.069349
H	1.158791	-2.289261	1.294473
H	1.922928	1.359817	1.921961
H	1.621053	1.899824	0.260940
H	-0.281942	2.582931	1.667950
H	-0.533549	0.924593	2.226857
H	0.909113	0.343536	-1.457872
H	0.431389	-2.605664	-0.776416
H	0.195372	-1.846564	-2.351934
H	2.414250	-3.002537	-2.216044
H	4.245525	-1.850364	-0.882936
H	3.024530	-2.586227	0.171697
H	-2.225241	0.167391	-2.105113
H	-1.724031	-1.506715	-1.837340
H	5.110315	1.590555	-1.120131
H	3.996356	2.302174	0.095809
H	5.717460	-0.234526	0.361255
H	5.374632	1.002279	1.617581
H	2.550768	-1.270027	-2.562661
O	3.323857	0.578038	-0.868121
C	-1.946670	3.223858	-0.690102
C	-4.604268	-2.011900	1.295936
H	-4.602014	-3.098466	1.492824
H	-4.677759	-1.507492	2.276968
H	-5.479925	-1.748485	0.690007
O	-2.447895	1.423113	0.655370
C	-3.108164	2.404889	-0.139729
H	-1.462563	-1.486889	0.775778
H	-2.150200	3.673288	-1.673335
H	-3.693527	1.920216	-0.940972
H	-3.788207	2.986464	0.501079
H	-1.644826	4.019841	0.016671

Part III: References

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian 09, Revision E.01. Gaussian Inc: Wallingford, CT, 2009.
2. (a) Head-Gordon, M.; Pople, J. A.; Frisch, M. J. MP2 energy evaluation by direct methods. *Chem. Phys. Lett.* **1988**, *153*, 503-506. (b) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys*. **1993**, *98*, 5648-5652. (c) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785-789. (d) Vosko, S. H.; Wilk, L.; Nusair, M. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. *Can. J. Phys*. **1980**, *58*, 1200-1211. (e) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* **1994**, *98*, 11623-11627.
3. (a) Fukui, K. Formulation of the reaction coordinate. *J. Phys. Chem.* **1970**, *74*, 4161-4163. (b) Fukui, K. The path of chemical reactions-the IRC approach. *Acc. Chem. Res.*, **1981**, *14*, 363-368.
4. Weigend, F.; Ahlrichs, R., Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.
5. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H., A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104-154104.
6. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G., Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009**, *113*, 6378-6396.

Part IV: NMR Spectra

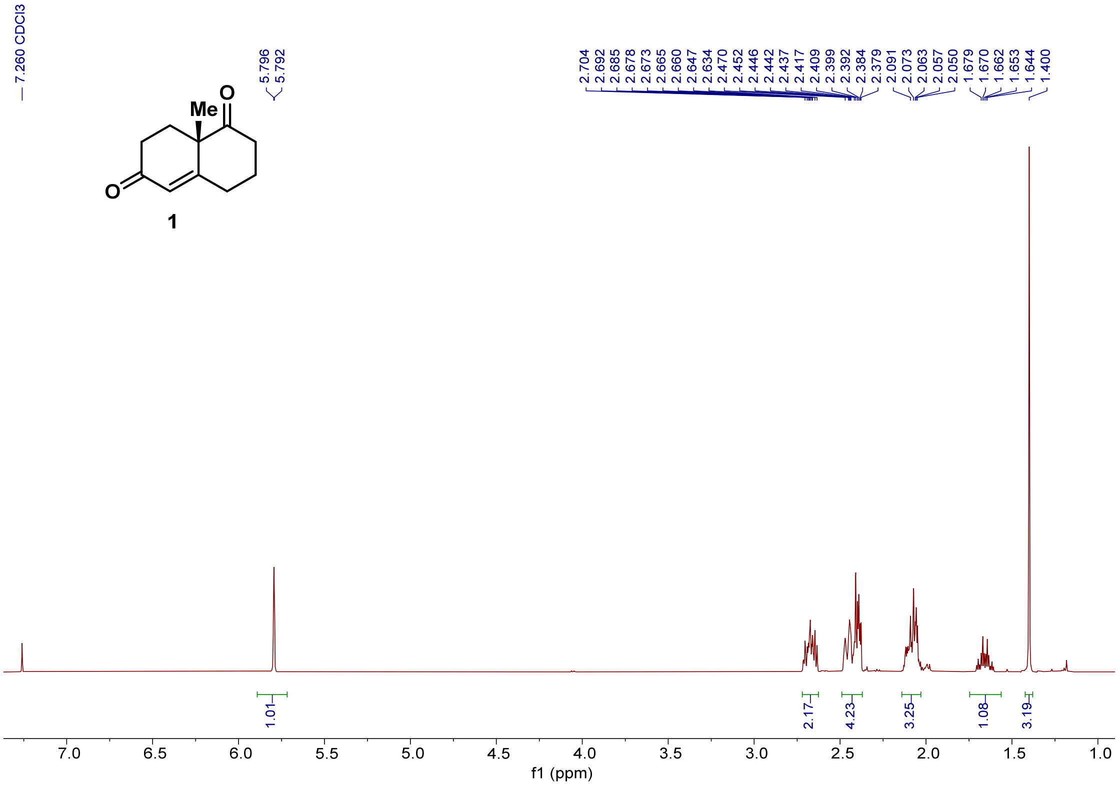


Figure S3. ^{1}H NMR Spectra of **1** ($CDCl_3$, 500 MHz)

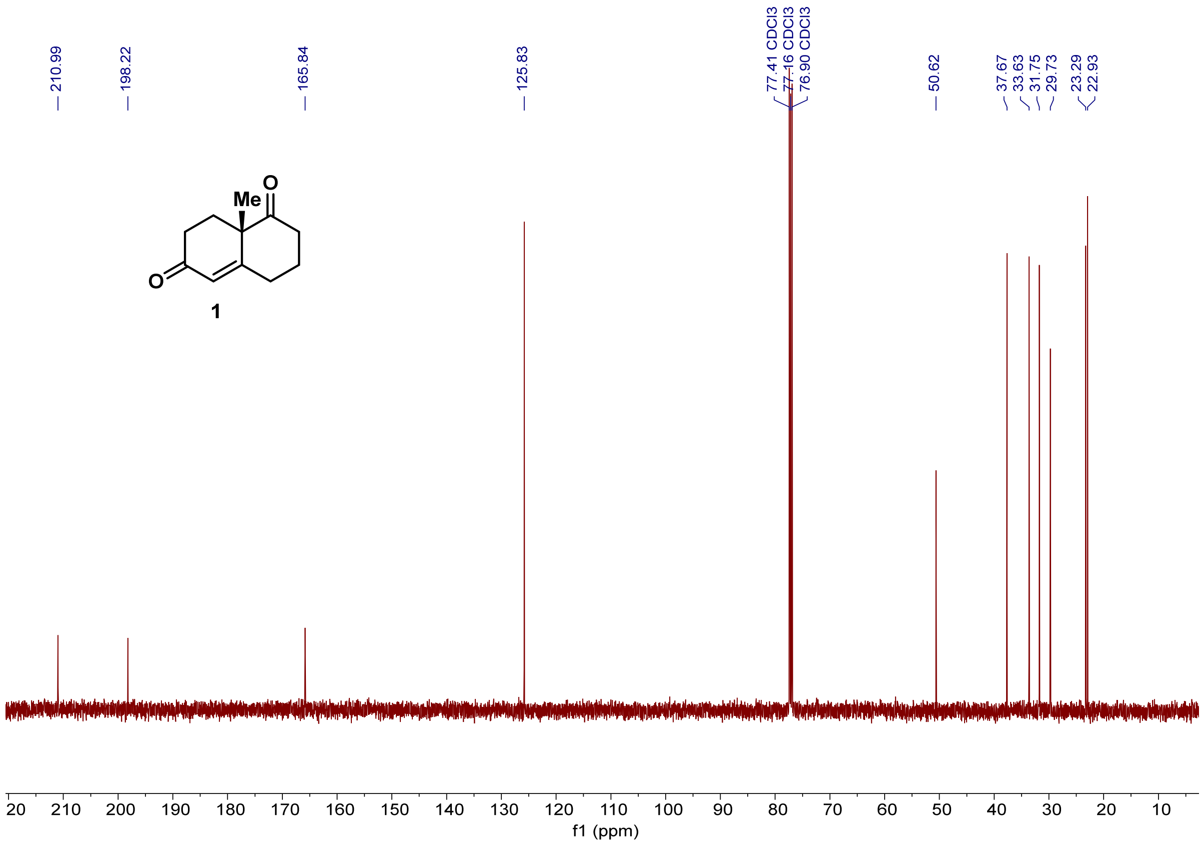


Figure S4. ^{13}C NMR Spectra of **1** ($CDCl_3$, 125 MHz)

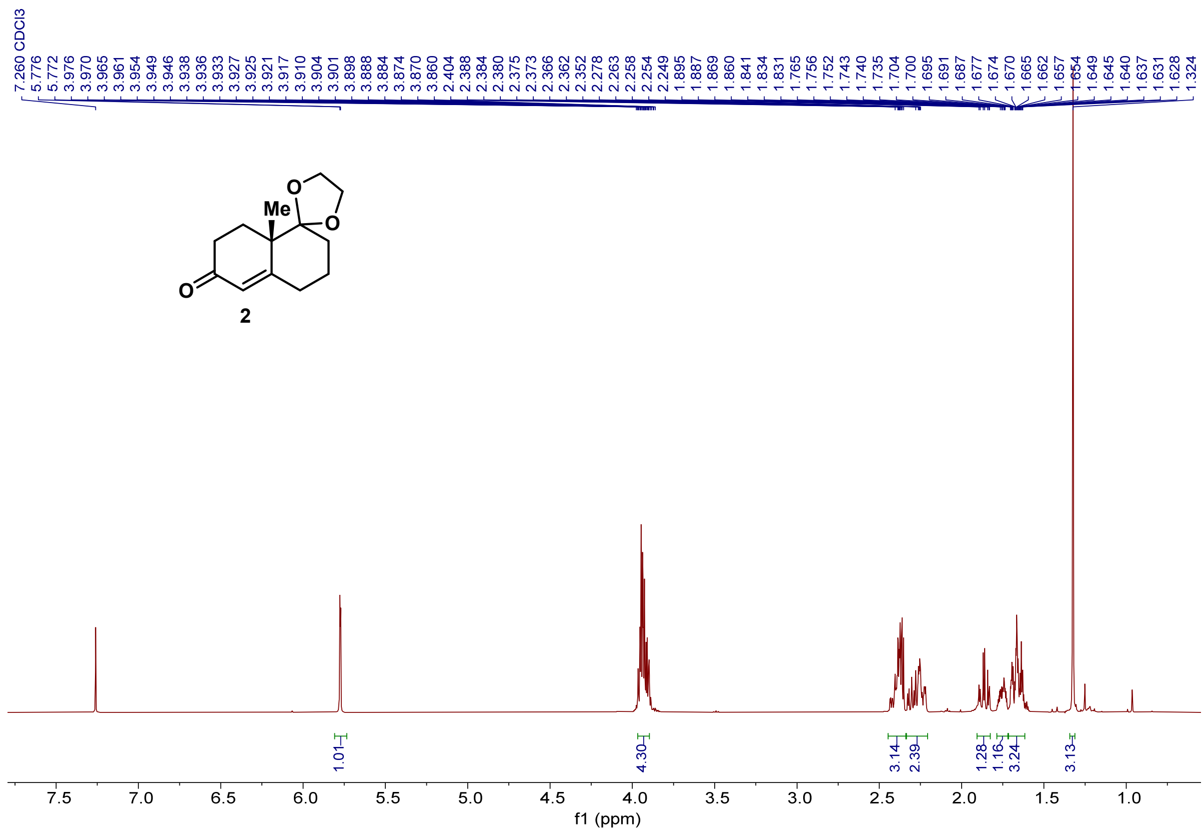


Figure S5. ^{1}H NMR Spectra of **2** ($CDCl_3$, 500 MHz)

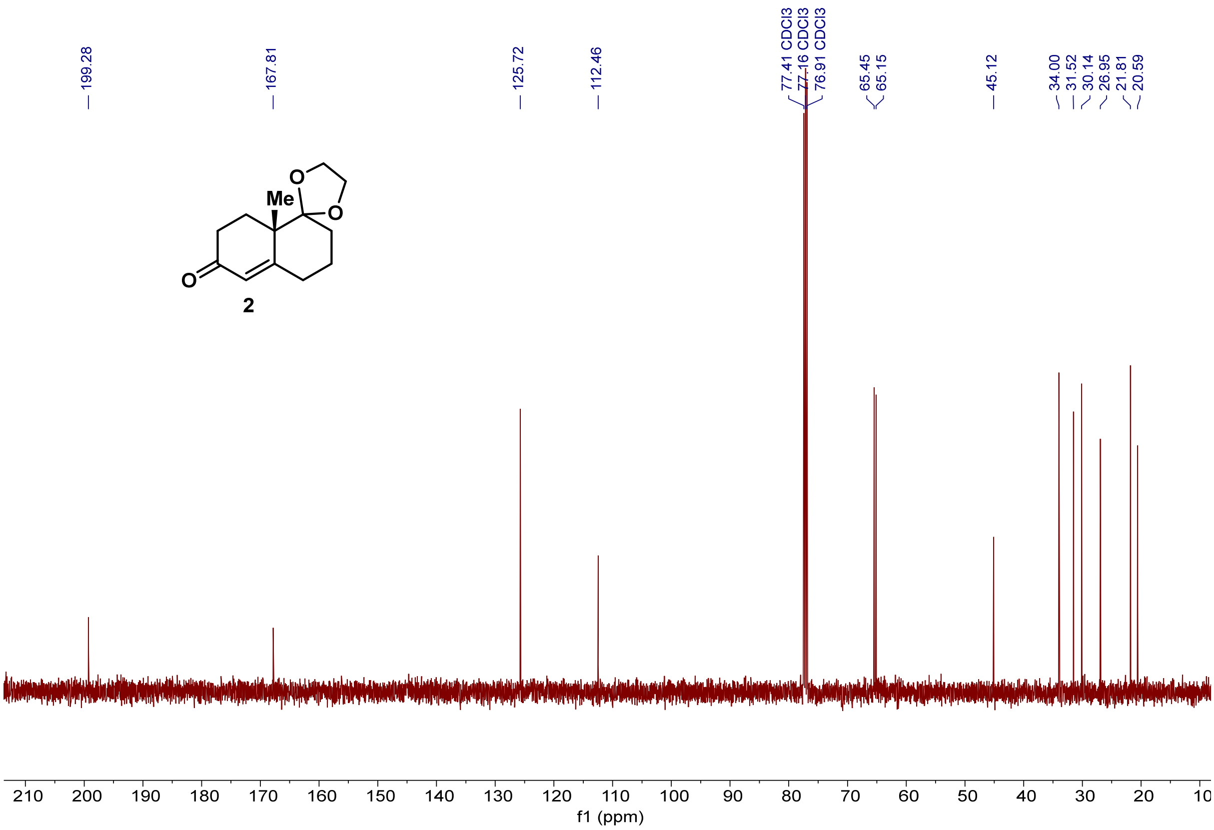


Figure S6. ^{13}C NMR Spectra of **2** ($CDCl_3$, 125 MHz)

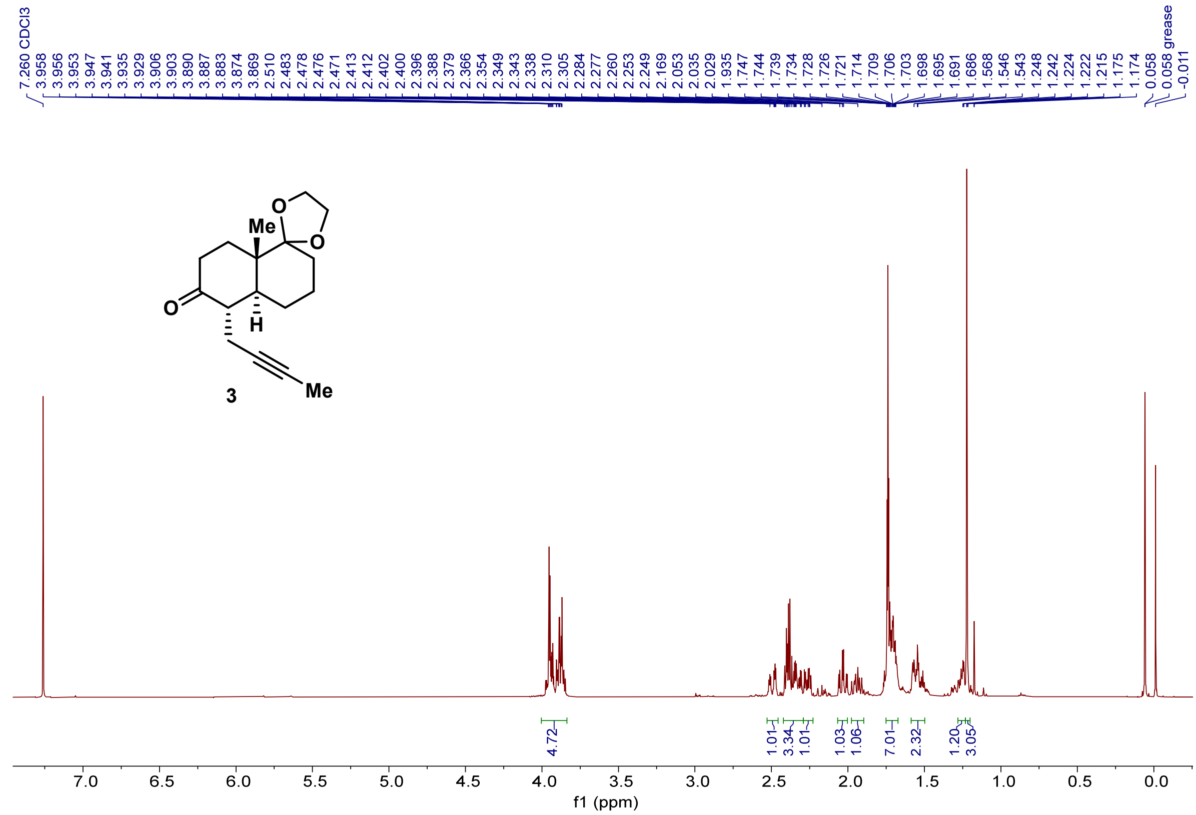


Figure S7. ^{1}H NMR Spectra of **3** ($CDCl_3$, 500 MHz)

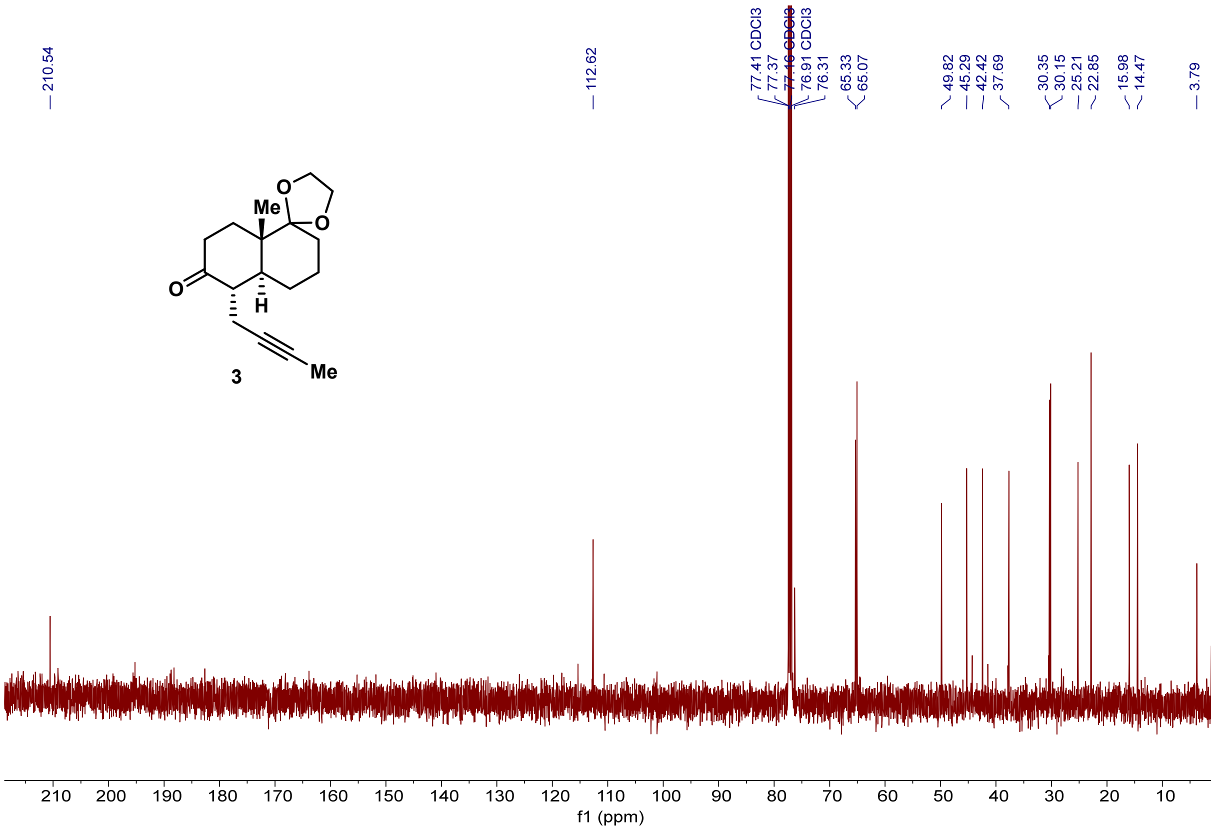


Figure S8. ^{13}C NMR Spectra of **3** ($CDCl_3$, 125 MHz)

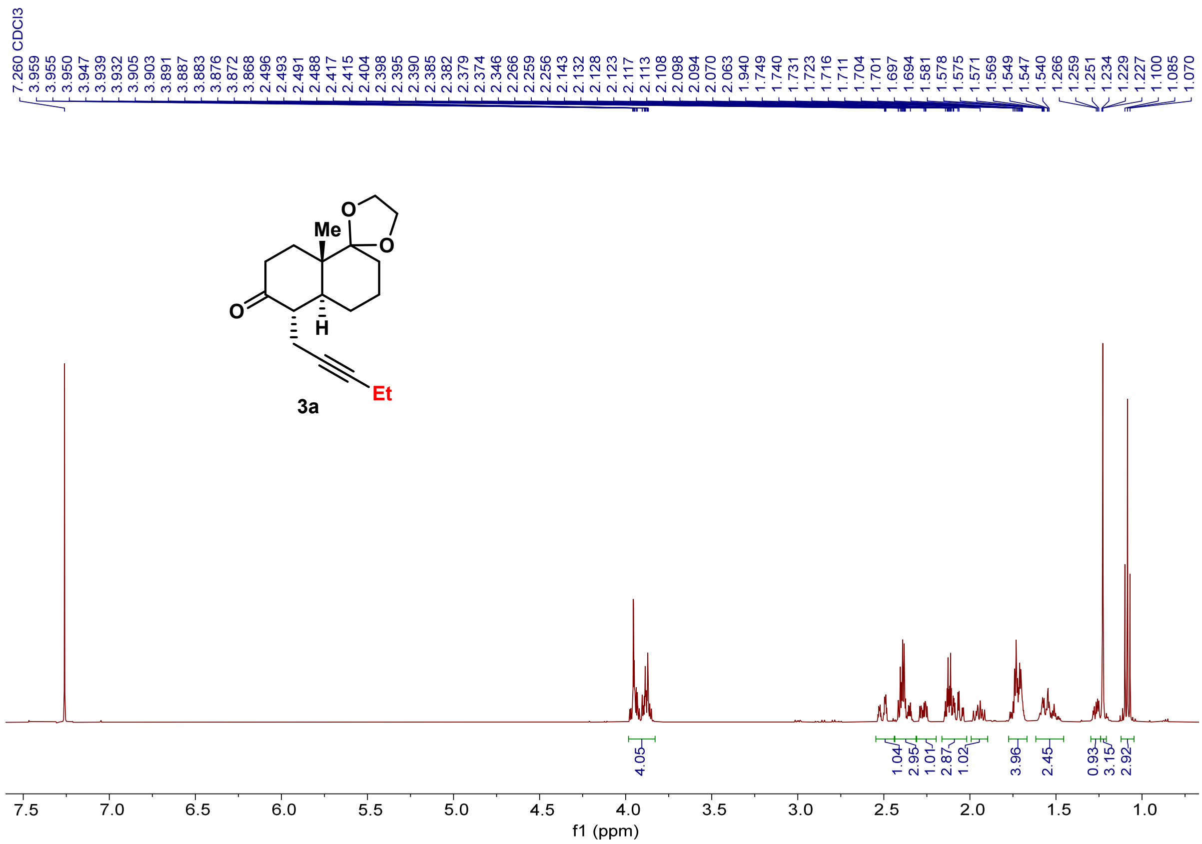


Figure S9. ^{1}H NMR Spectra of **3a** ($CDCl_3$, 500 MHz)

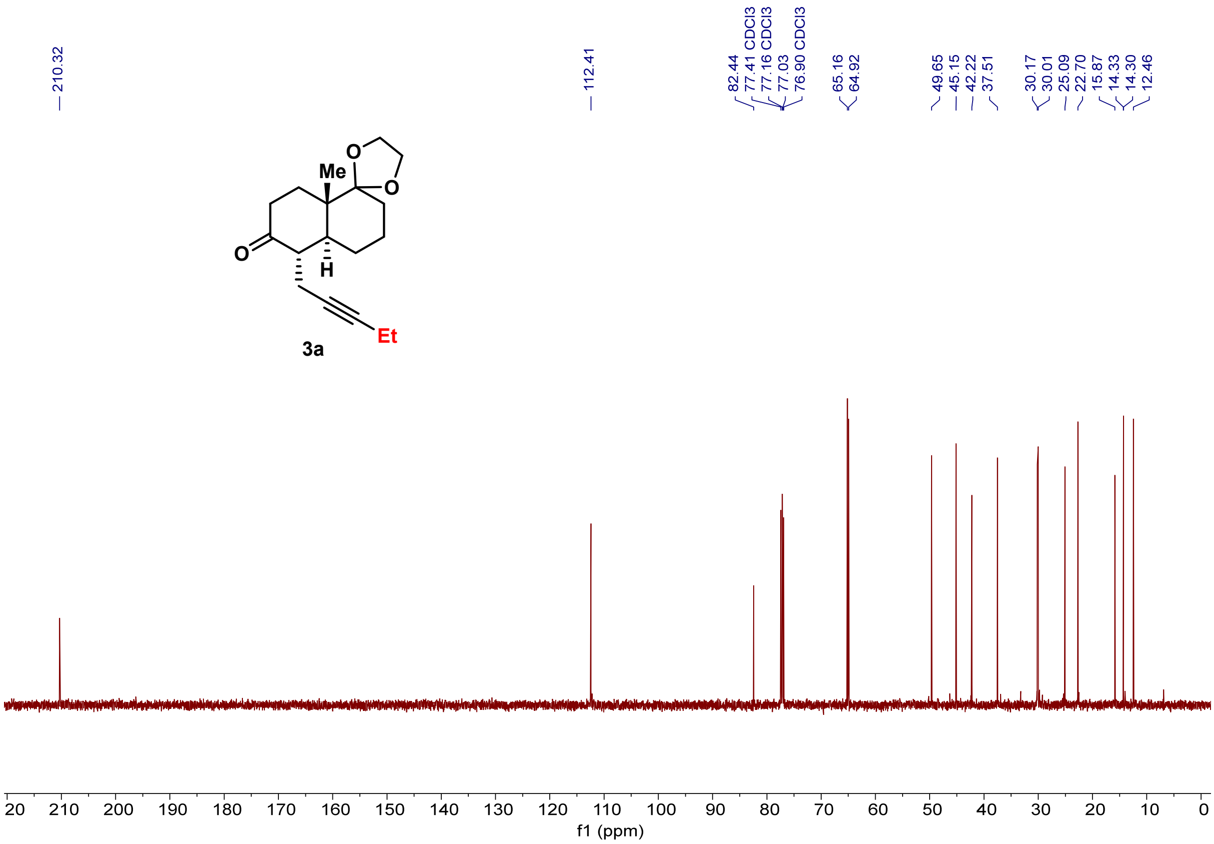


Figure S10. ^{13}C NMR Spectra of **3a** ($CDCl_3$, 125 MHz)

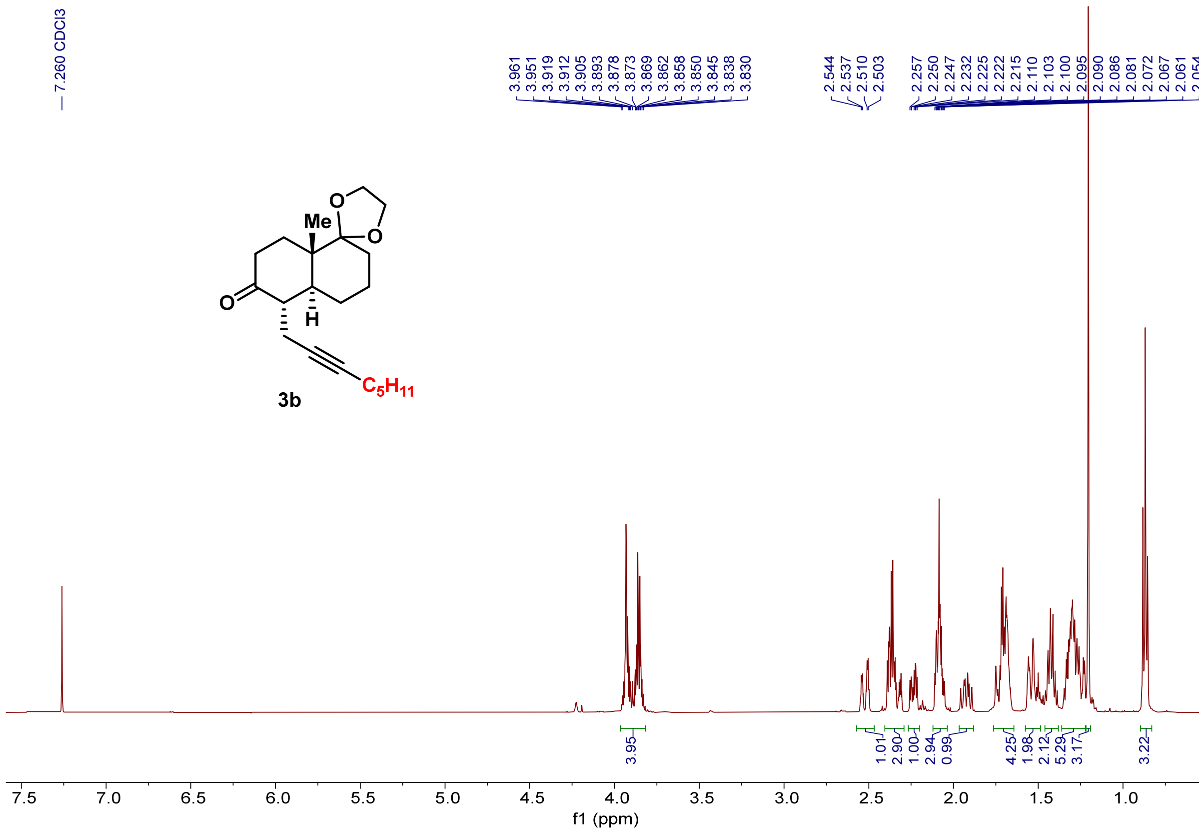


Figure S11. ^{1}H NMR Spectra of **3b** ($CDCl_3$, 500 MHz)

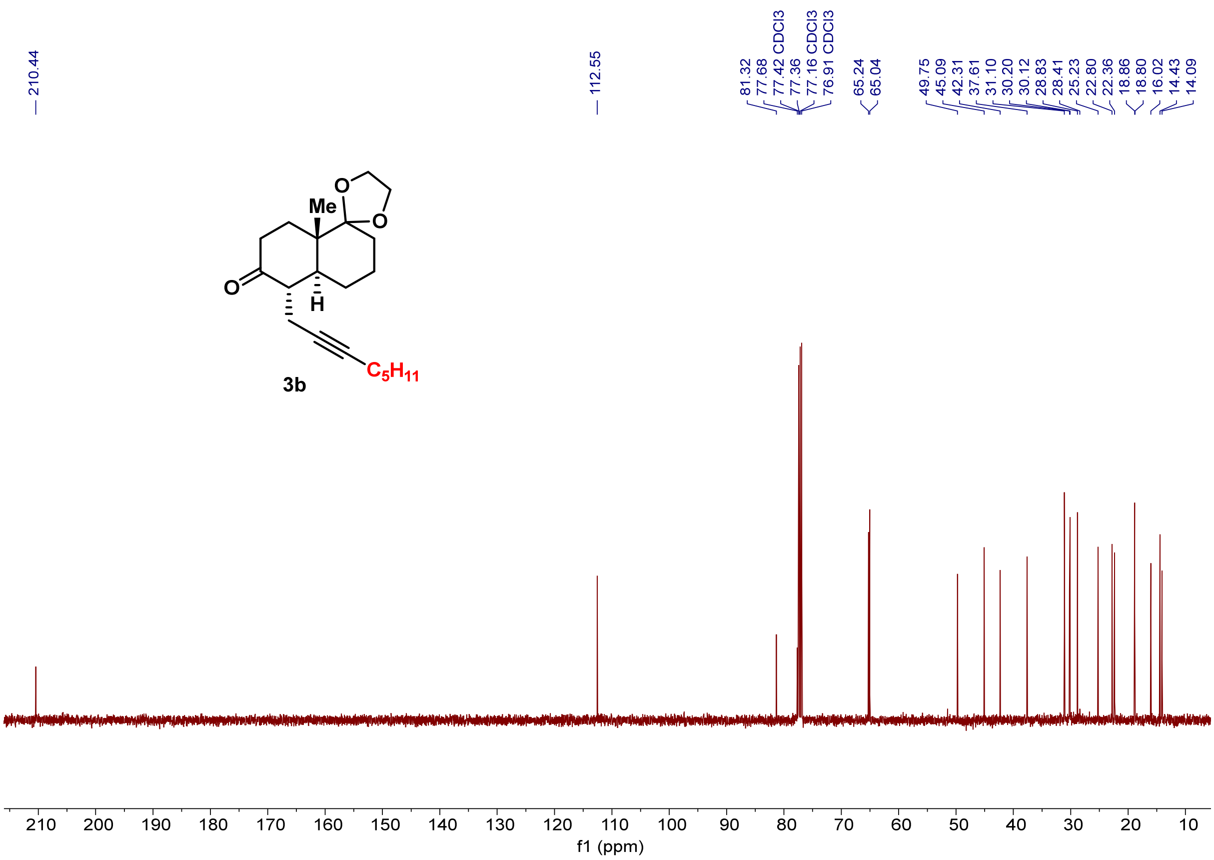


Figure S12. ^{13}C NMR Spectra of **3b** ($CDCl_3$, 125 MHz)

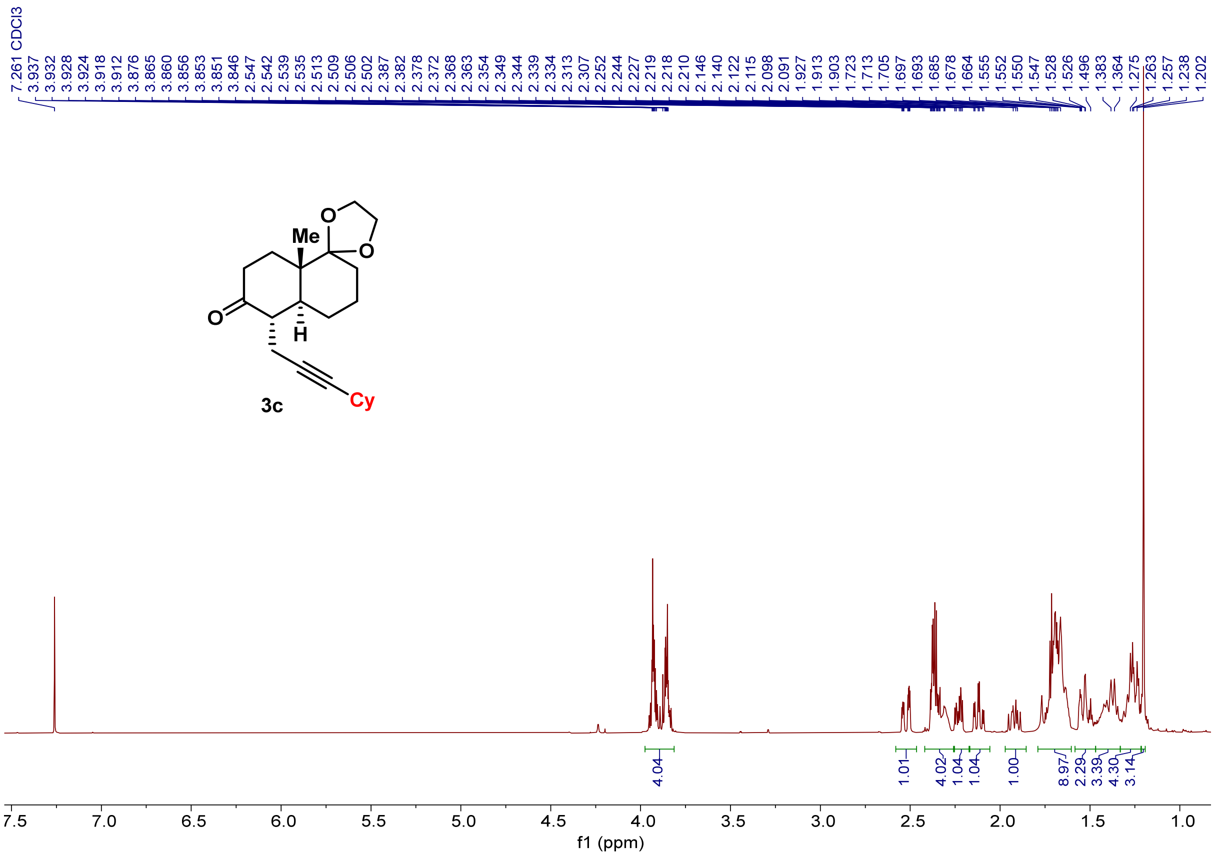


Figure S13. ^{1}H NMR Spectra of **3c** ($CDCl_3$, 500 MHz)

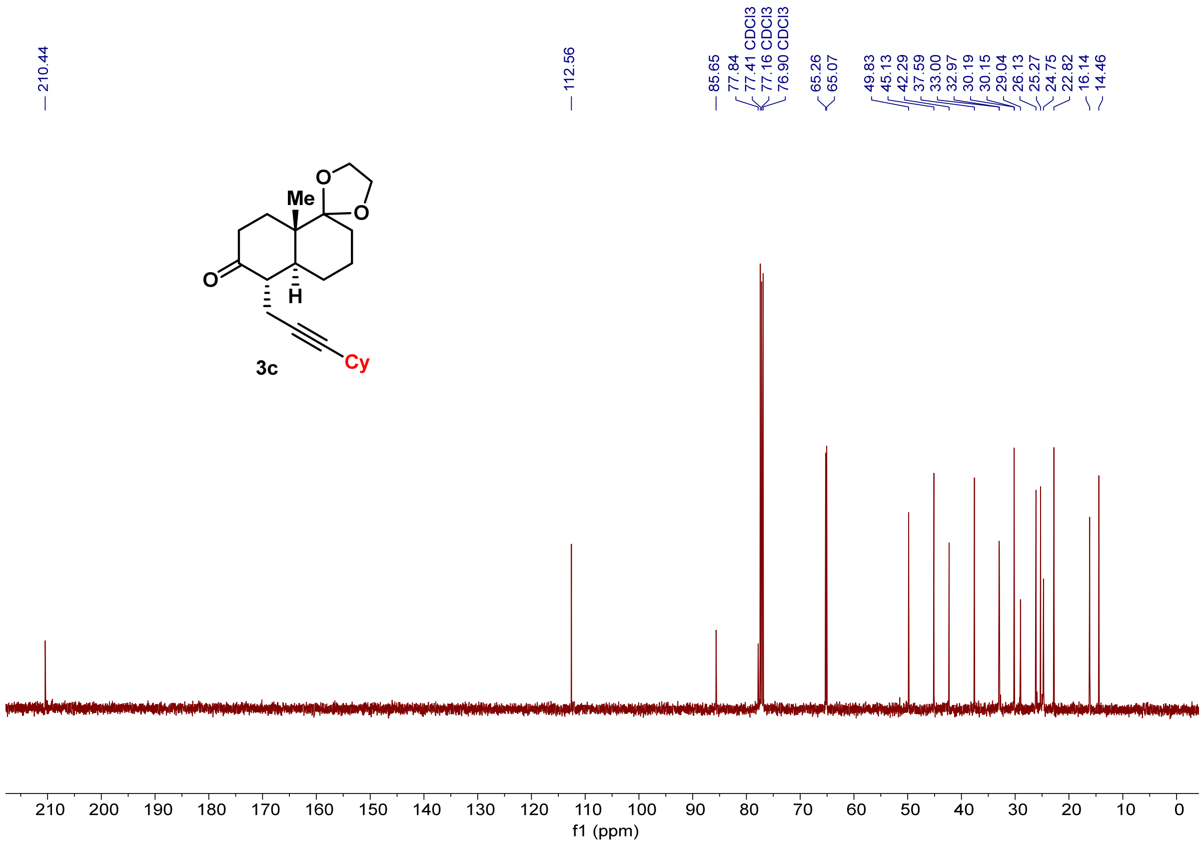


Figure S14. ^{13}C NMR Spectra of **3c** ($CDCl_3$, 125 MHz)

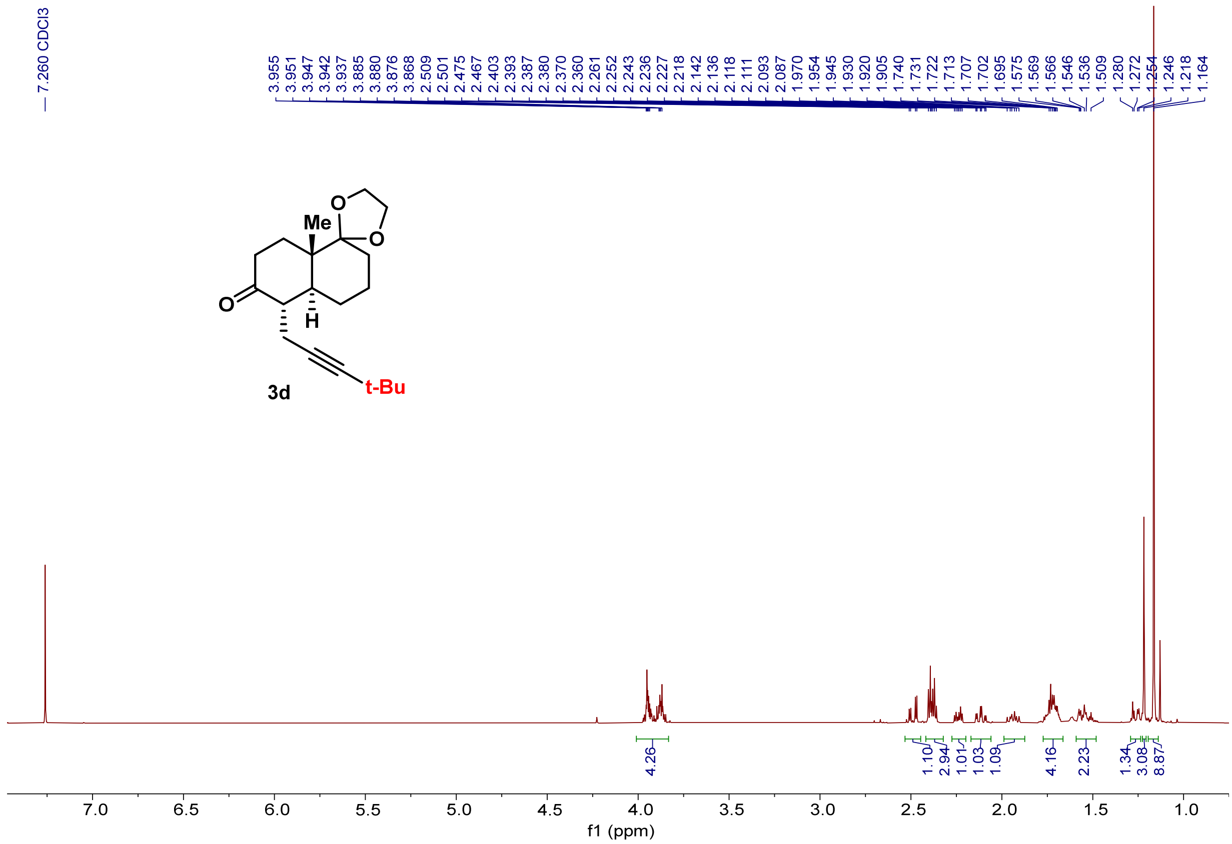


Figure S15. ^{1}H NMR Spectra of **3d** ($CDCl_3$, 500 MHz)

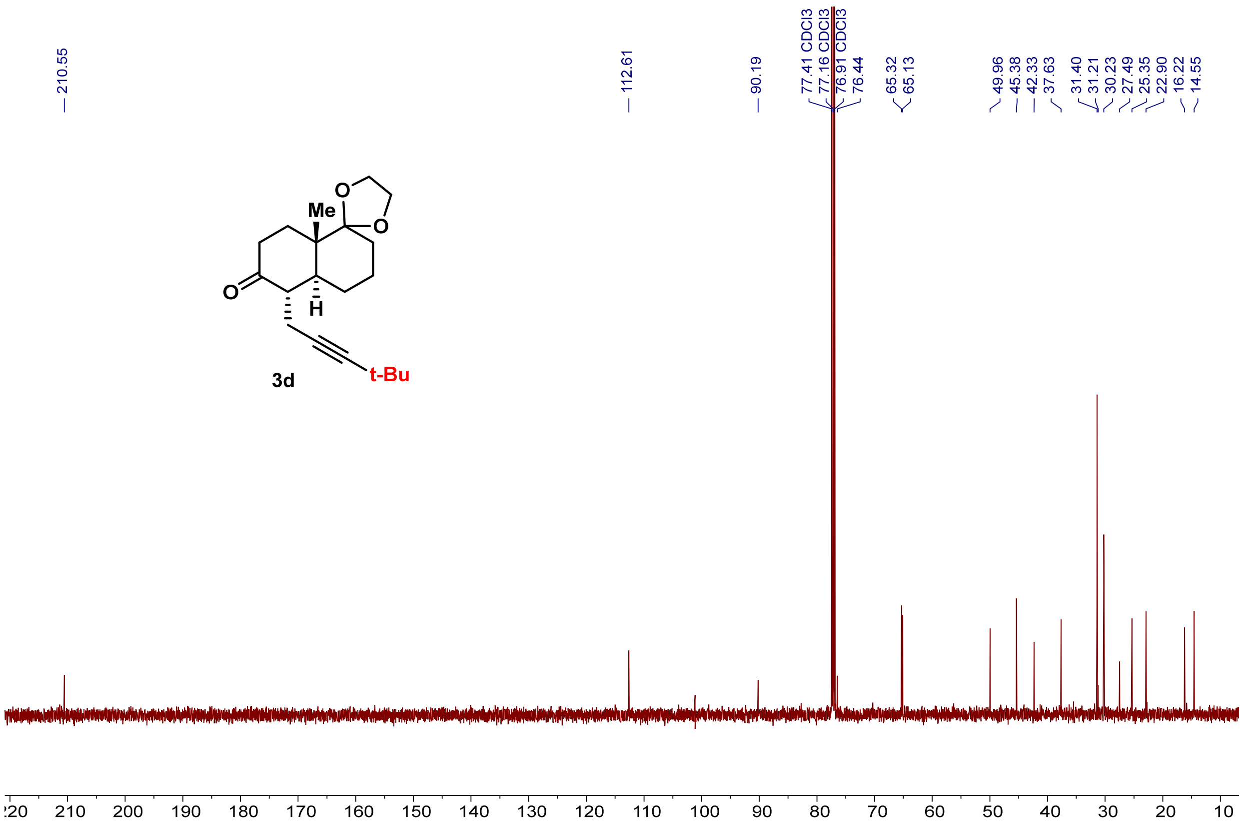


Figure S16. ^{13}C NMR Spectra of **3d** ($CDCl_3$, 125 MHz)

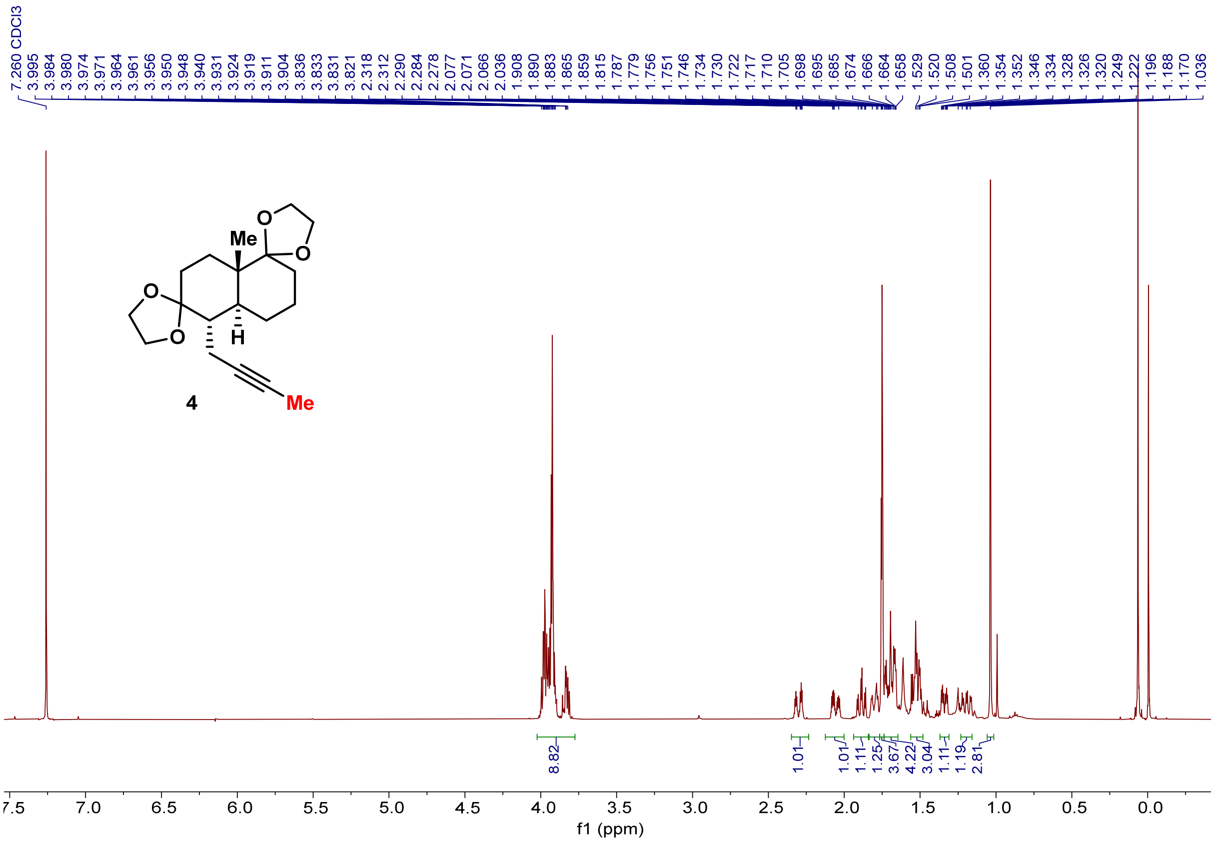


Figure S17. ^{1}H NMR Spectra of **4** ($CDCl_3$, 500 MHz)

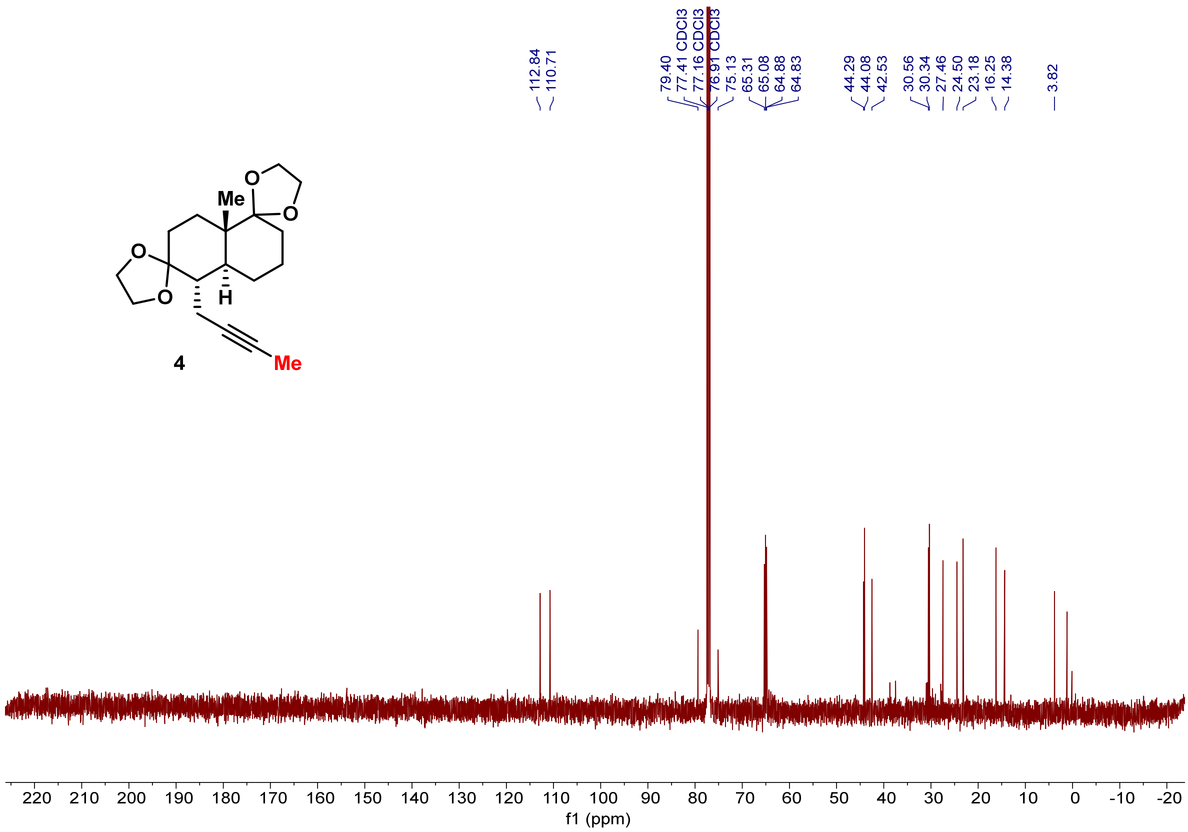


Figure S18. ^{13}C NMR Spectra of **4** ($CDCl_3$, 125 MHz)

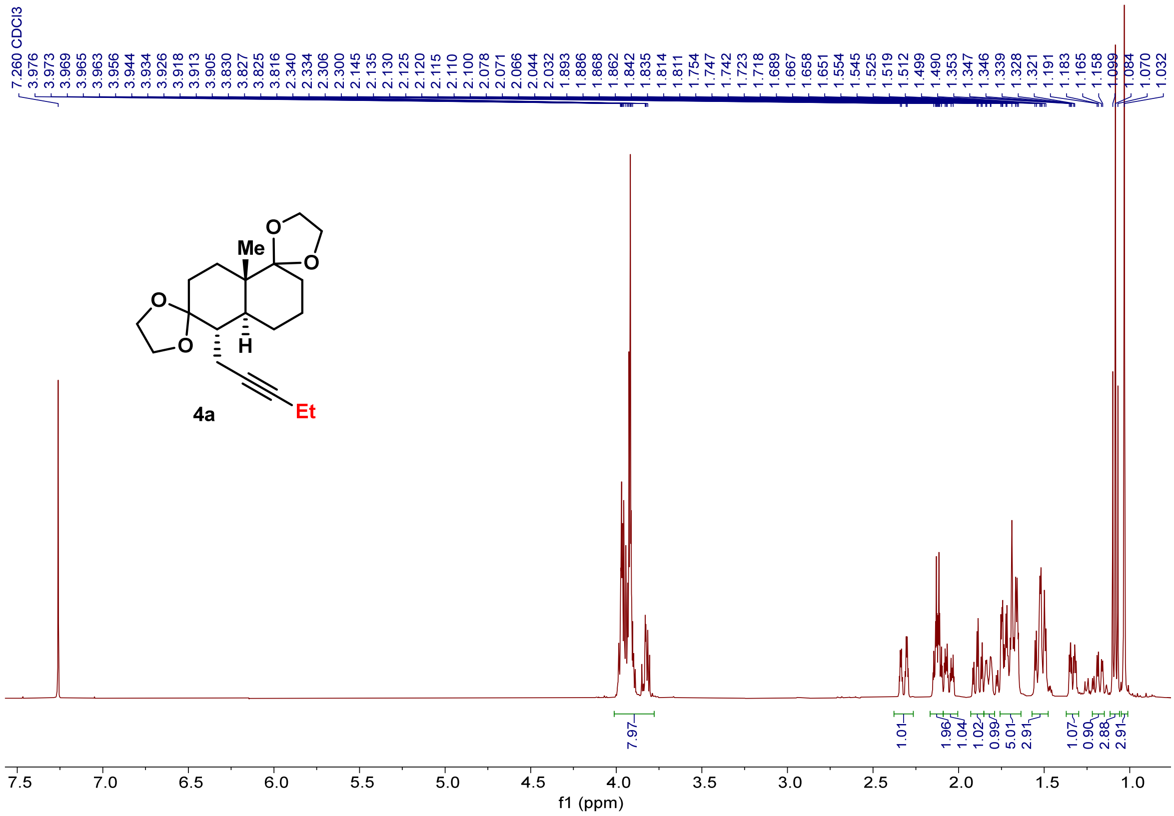


Figure S19. ^{1}H NMR Spectra of **4a** ($CDCl_3$, 500 MHz)

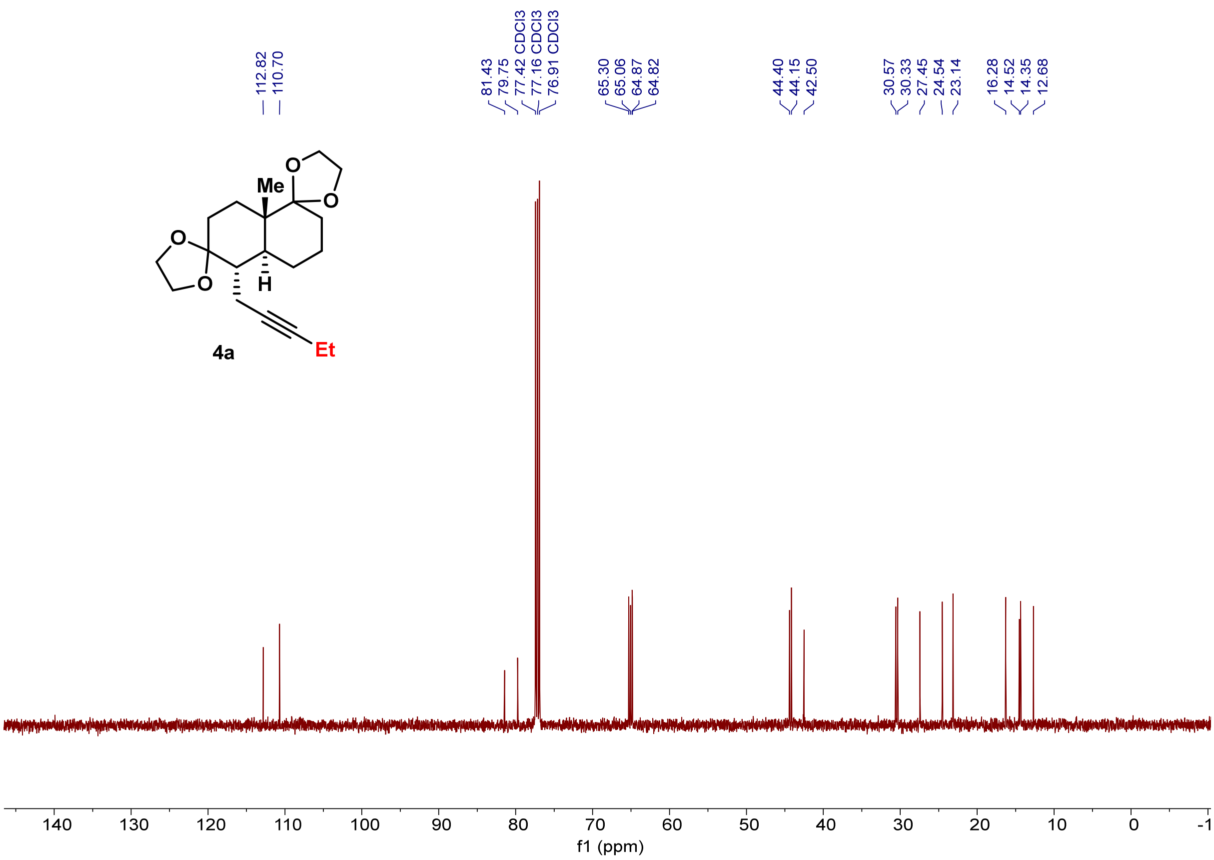


Figure S20. ^{13}C NMR Spectra of **4a** ($CDCl_3$, 125 MHz)

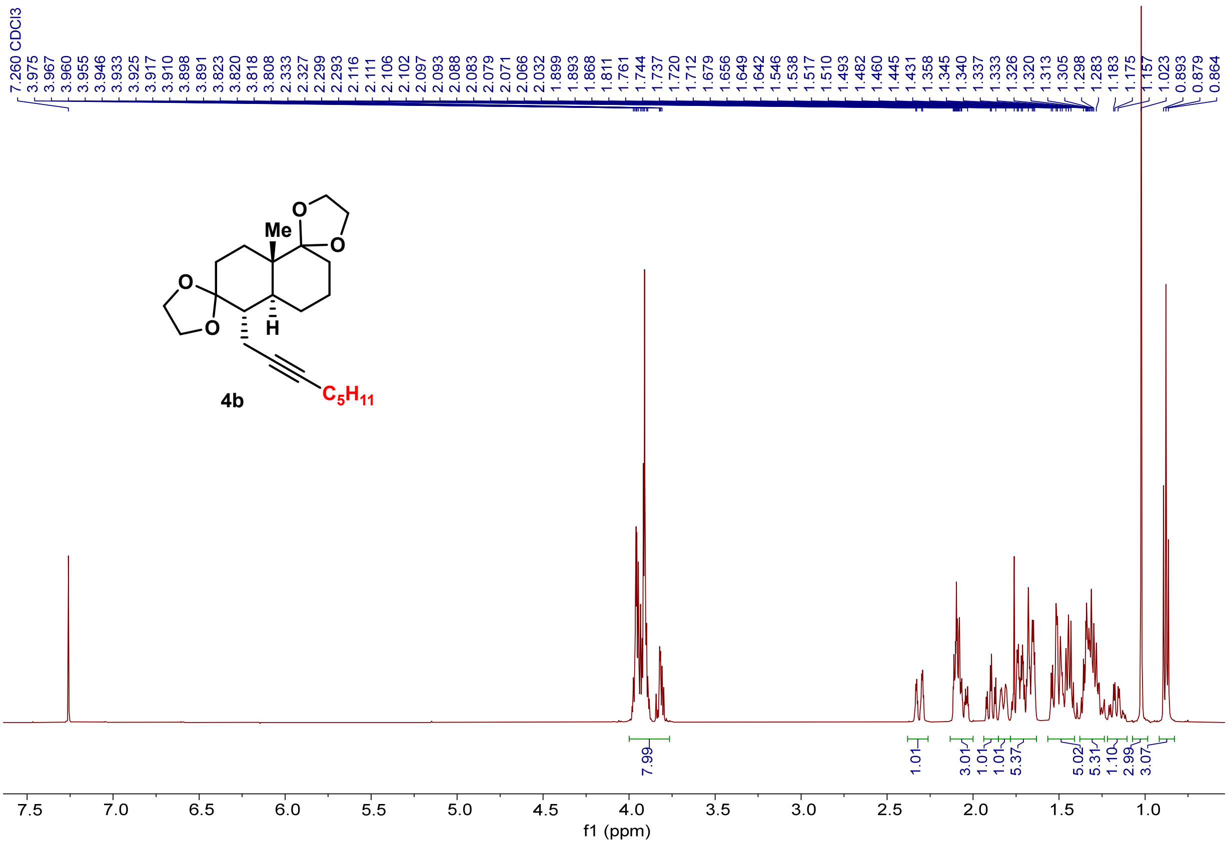


Figure S21. ^{1}H NMR Spectra of **4b** ($CDCl_3$, 500 MHz)

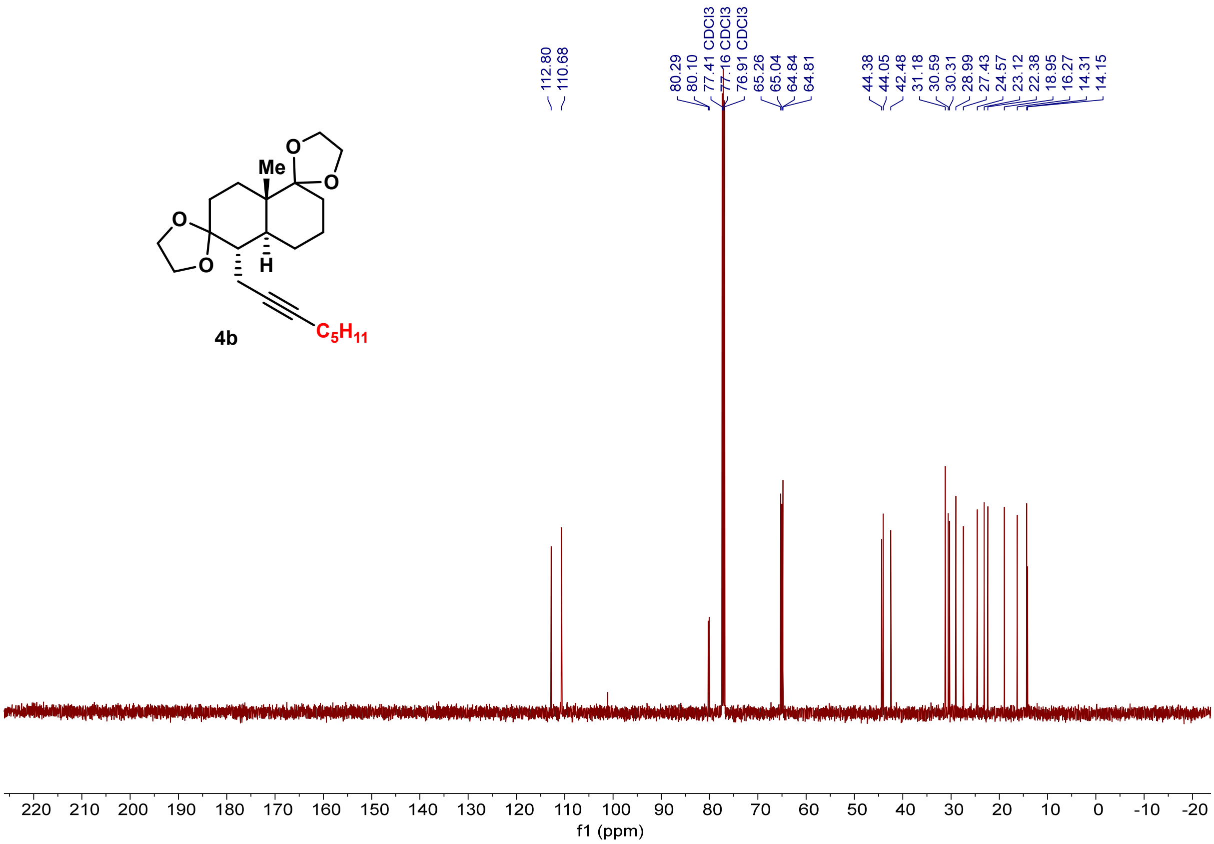


Figure S22. ^{13}C NMR Spectra of **4b** ($CDCl_3$, 125 MHz)

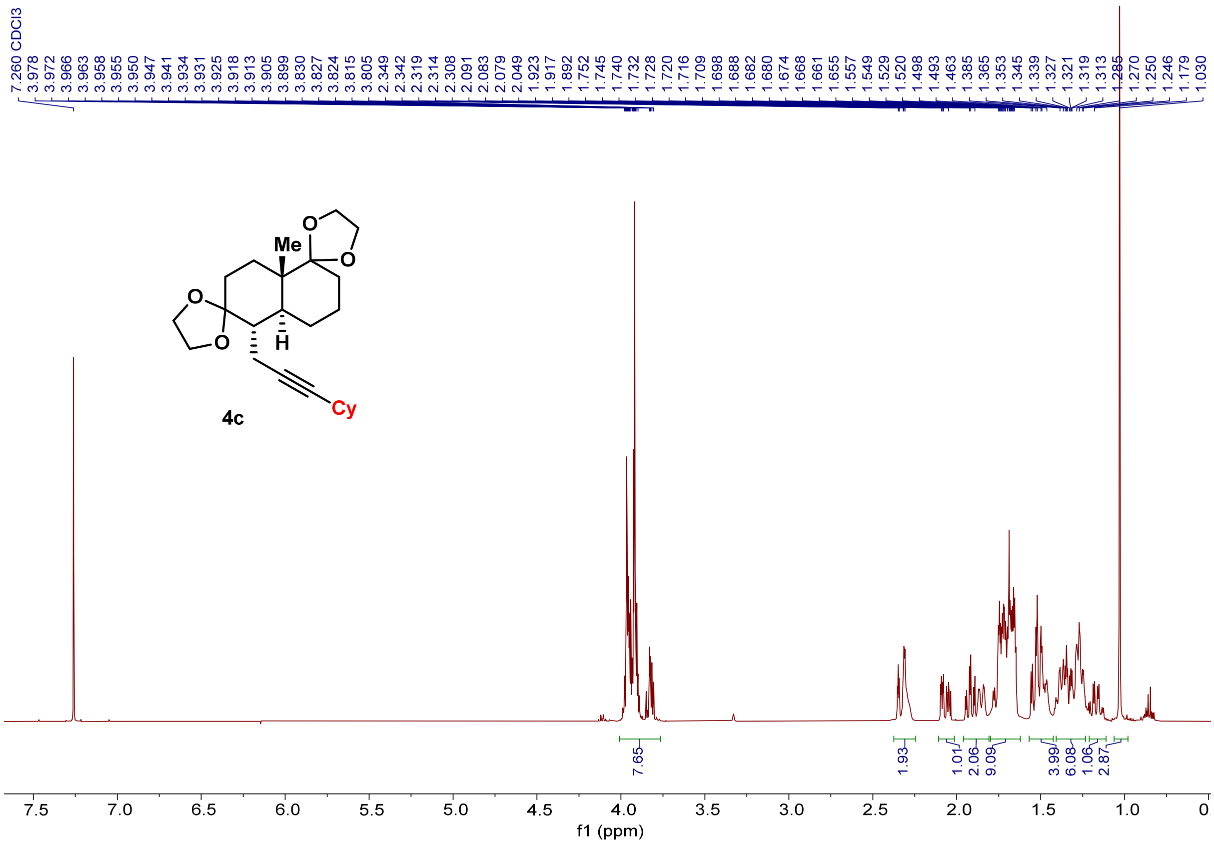


Figure S23. ^{1}H NMR Spectra of **4c** ($CDCl_3$, 500 MHz)

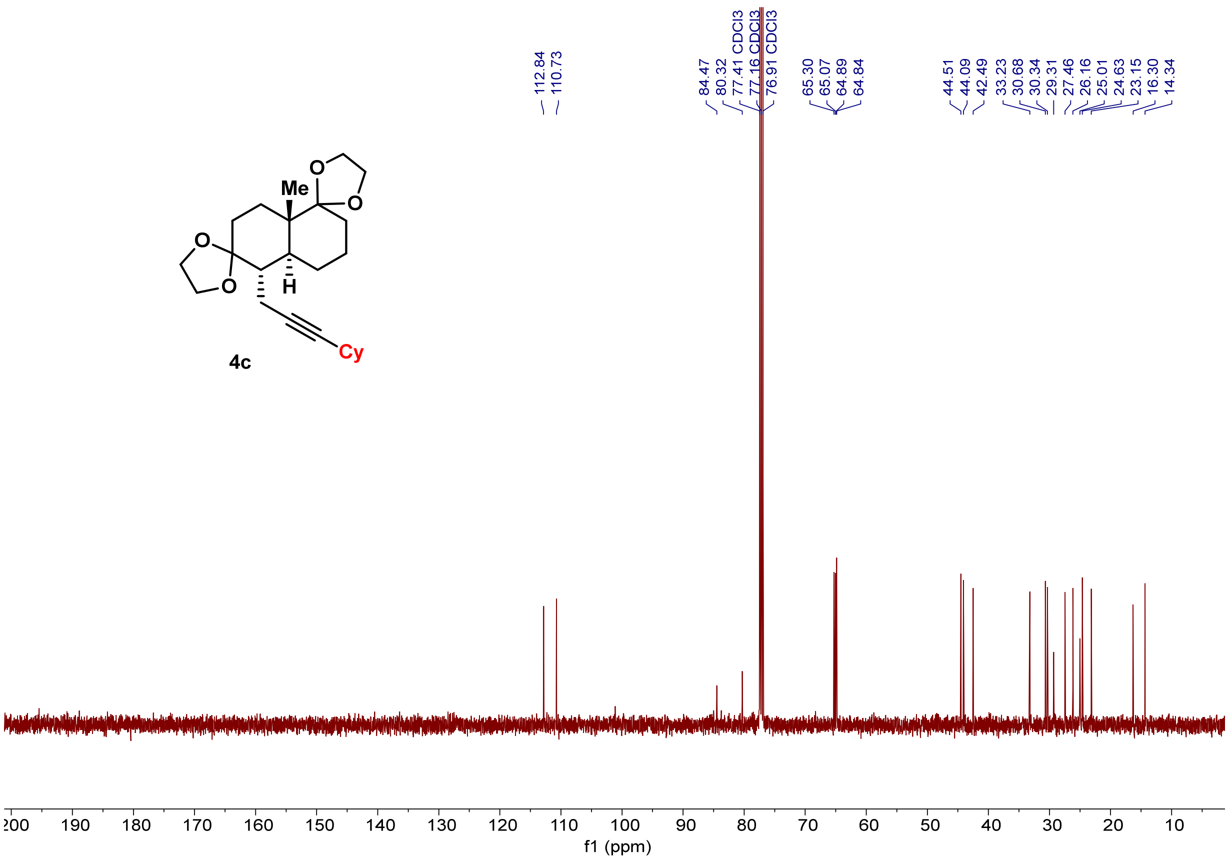


Figure S24. ^{13}C NMR Spectra of **4c** ($CDCl_3$, 125 MHz)

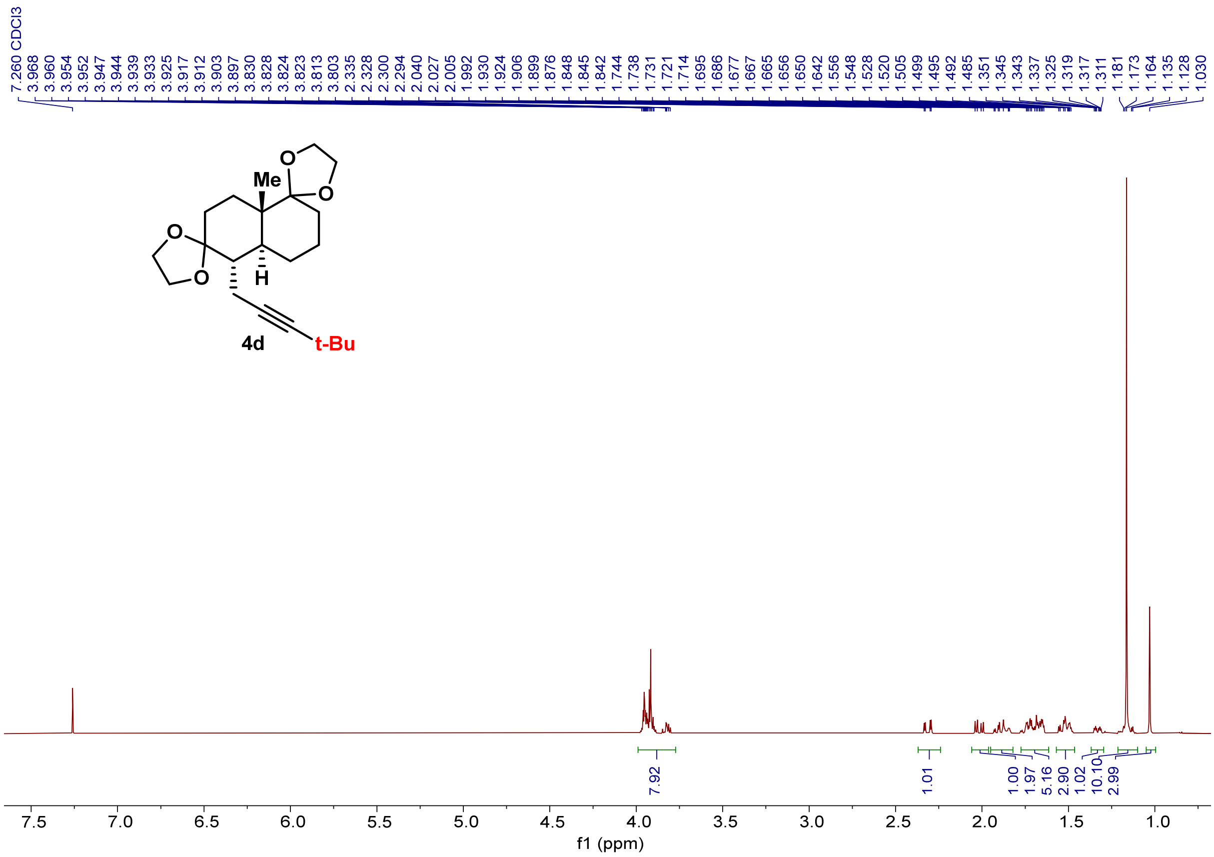


Figure S25. ^{1}H NMR Spectra of **4d** ($CDCl_3$, 500 MHz)

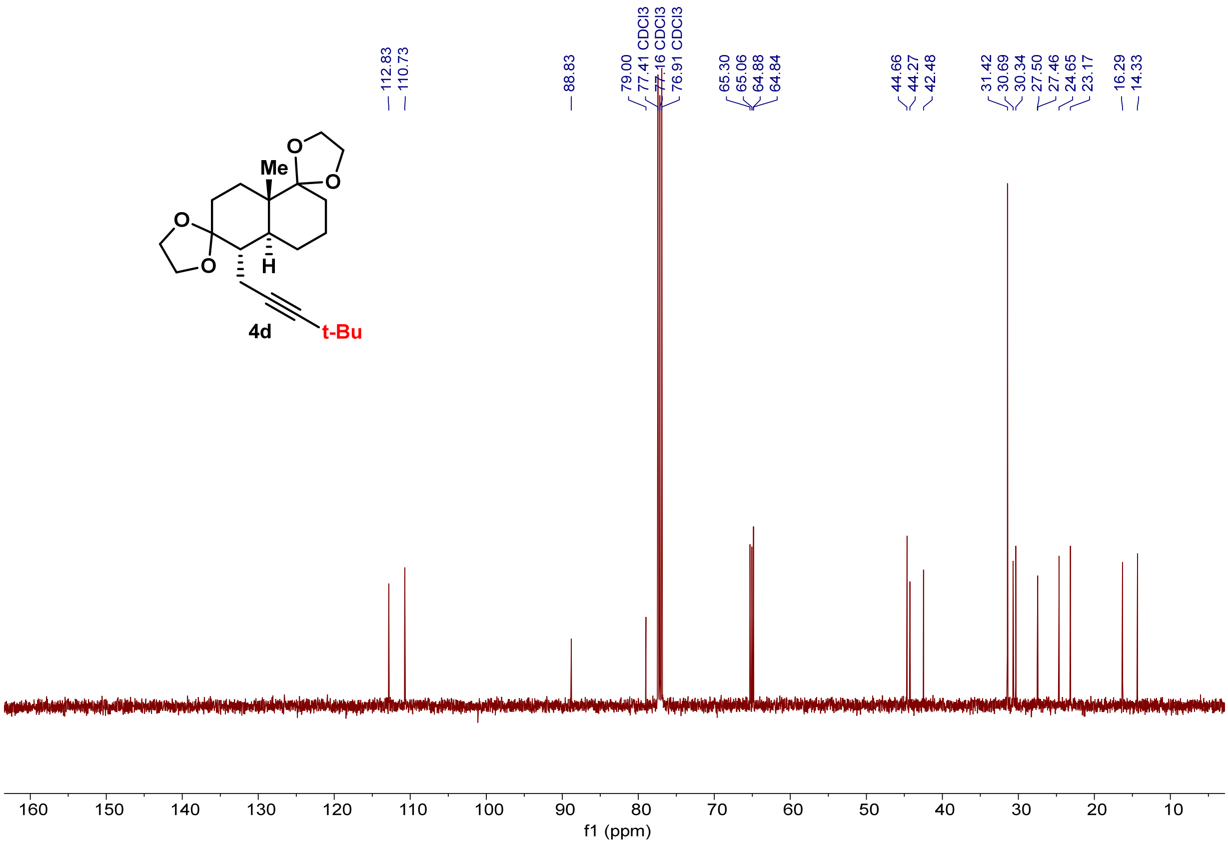


Figure S26. ^{13}C NMR Spectra of **4d** ($CDCl_3$, 125 MHz)

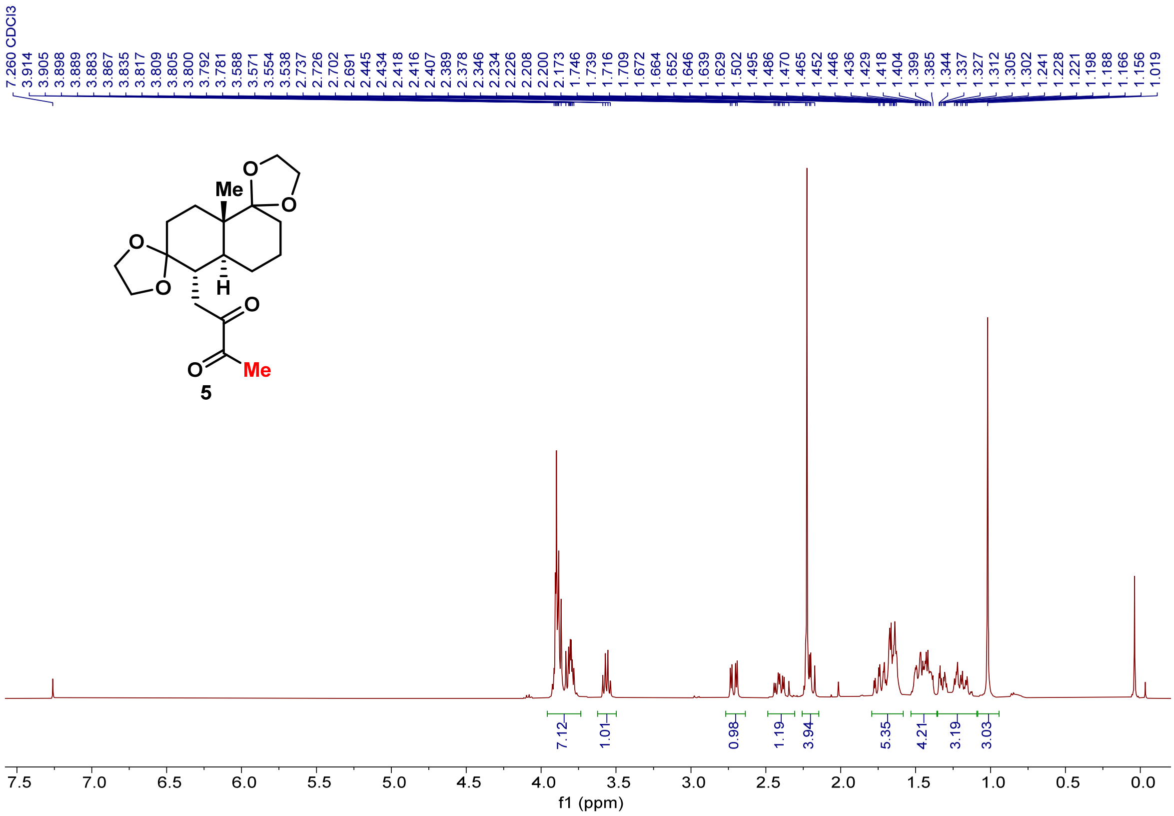


Figure S27. ^{1}H NMR Spectra of **5** ($CDCl_3$, 400 MHz)

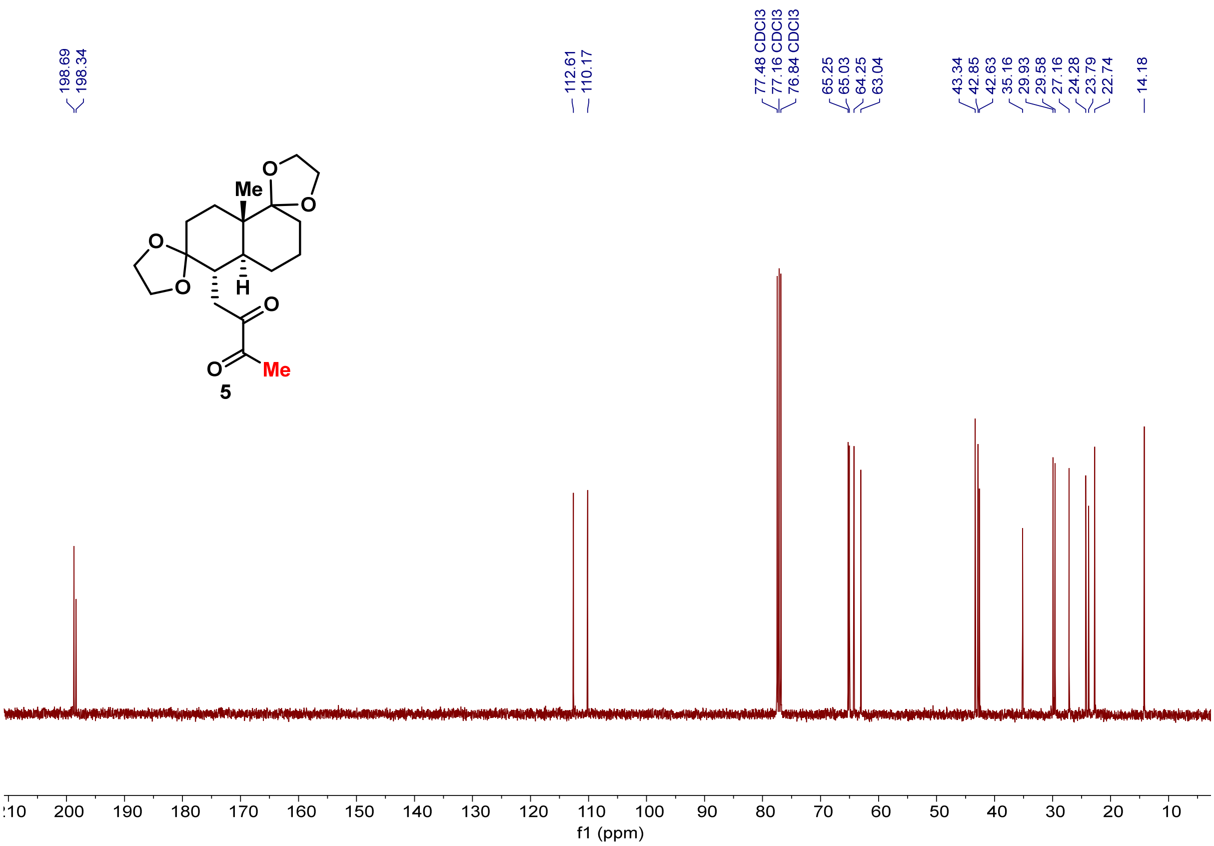


Figure S28. ^{13}C NMR Spectra of **5** ($CDCl_3$, 100 MHz)

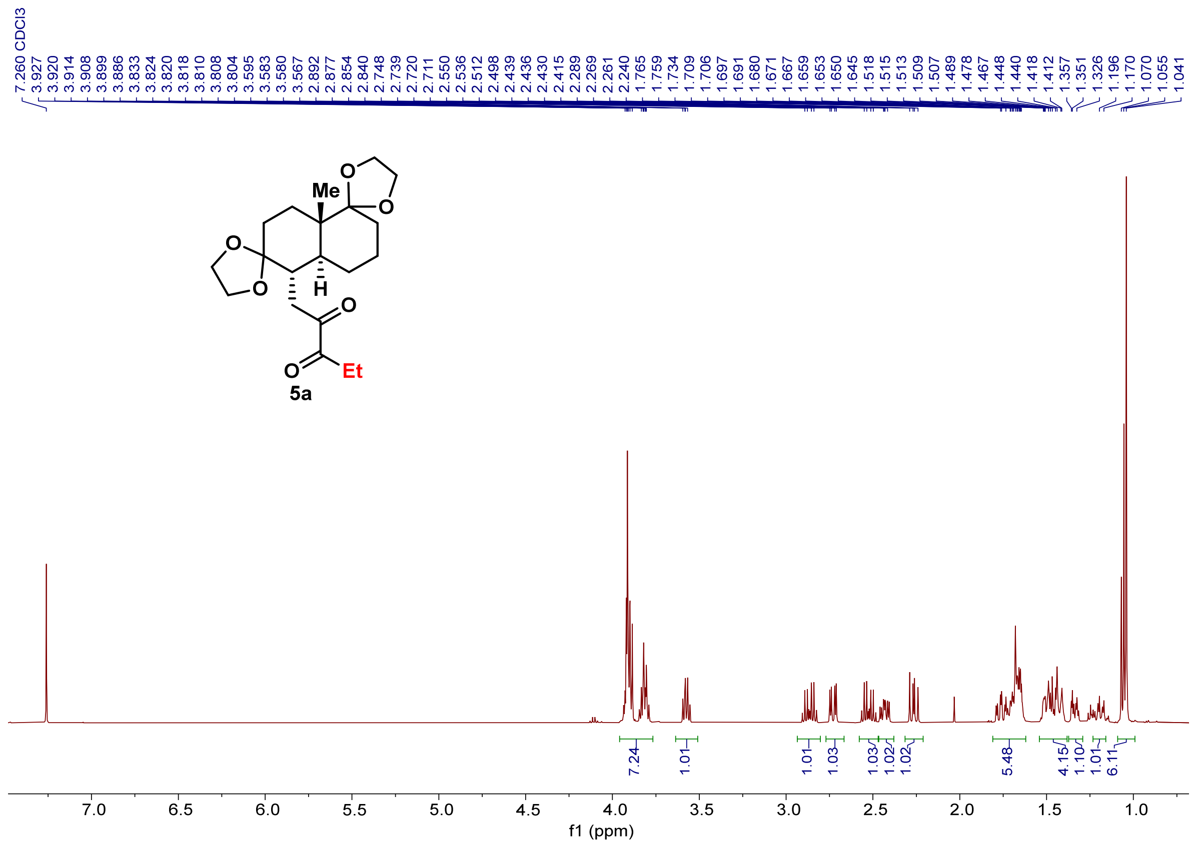


Figure S29. ^{1}H NMR Spectra of **5a** ($CDCl_3$, 500 MHz)

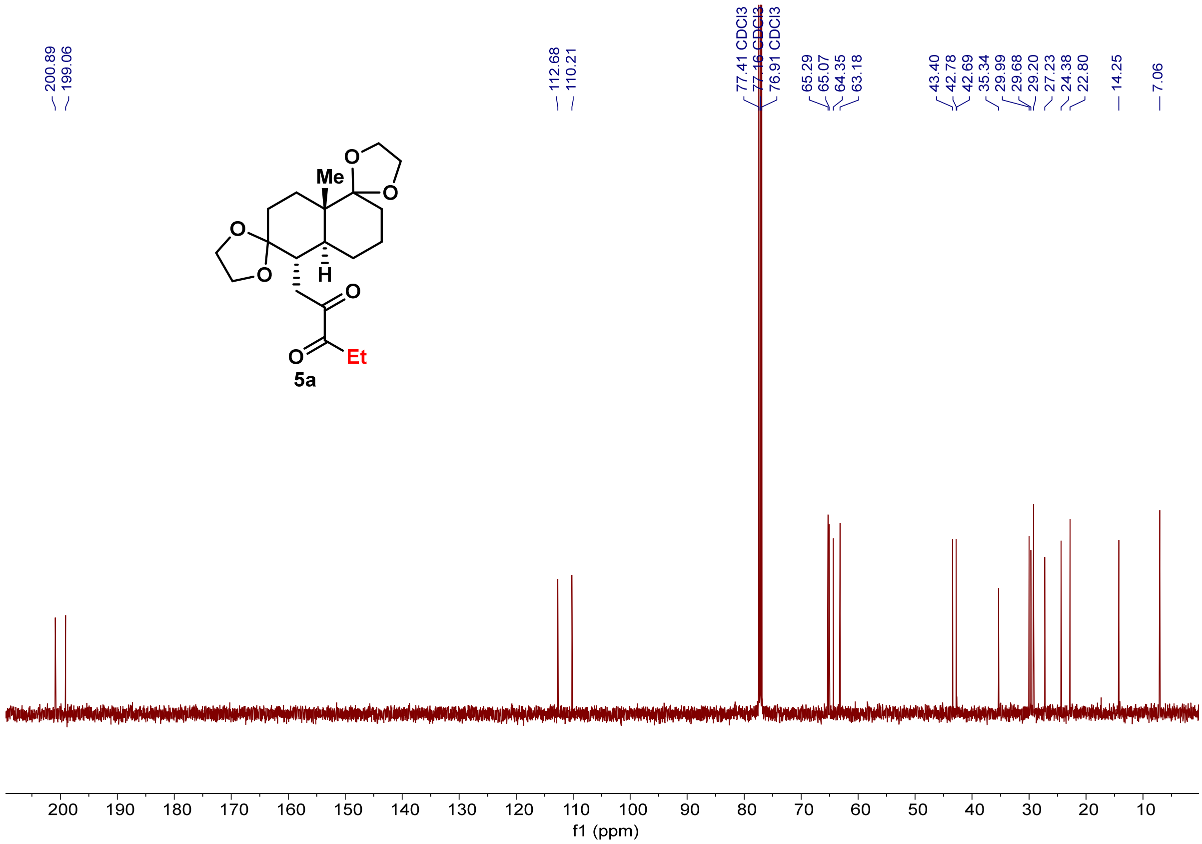


Figure S30. ^{13}C NMR Spectra of **5a** ($CDCl_3$, 125 MHz)

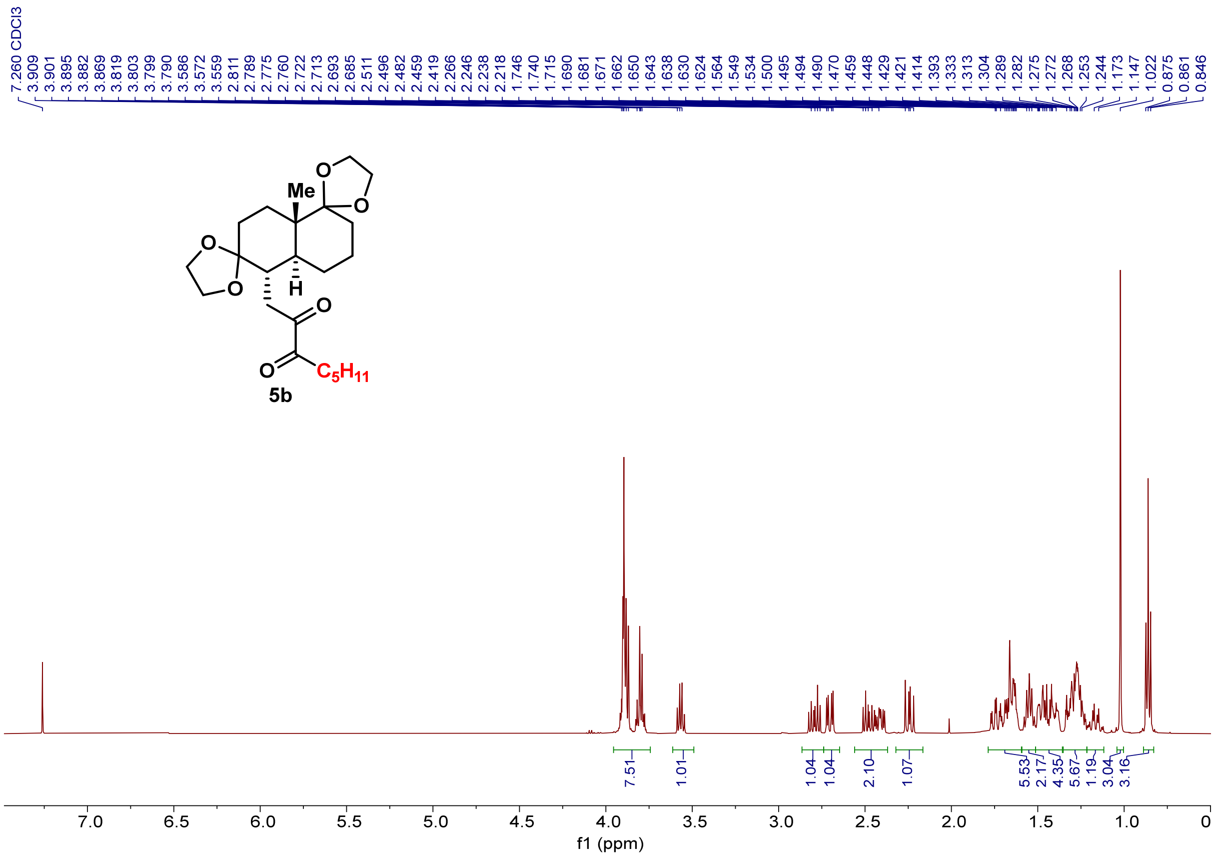


Figure S31. ^{1}H NMR Spectra of **5b** ($CDCl_3$, 500 MHz)

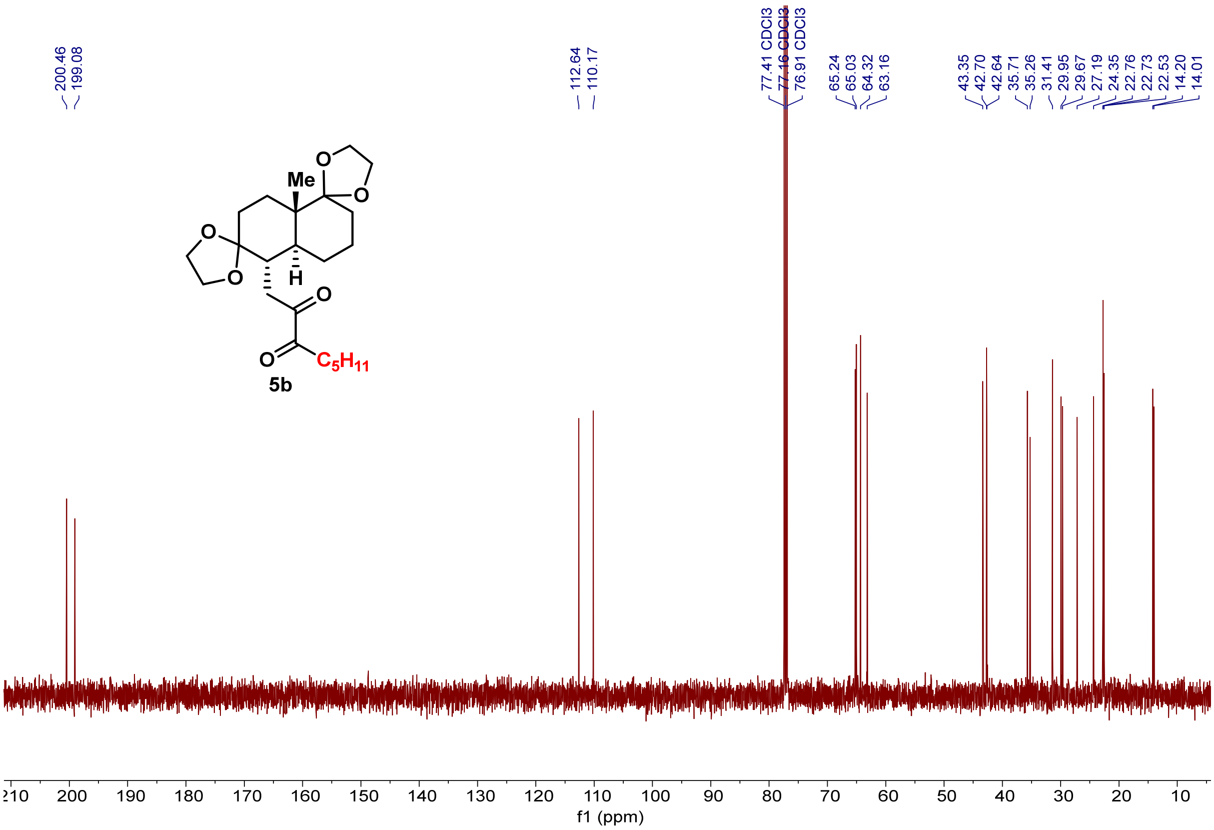


Figure S32. ^{13}C NMR Spectra of **5b** ($CDCl_3$, 125 MHz)

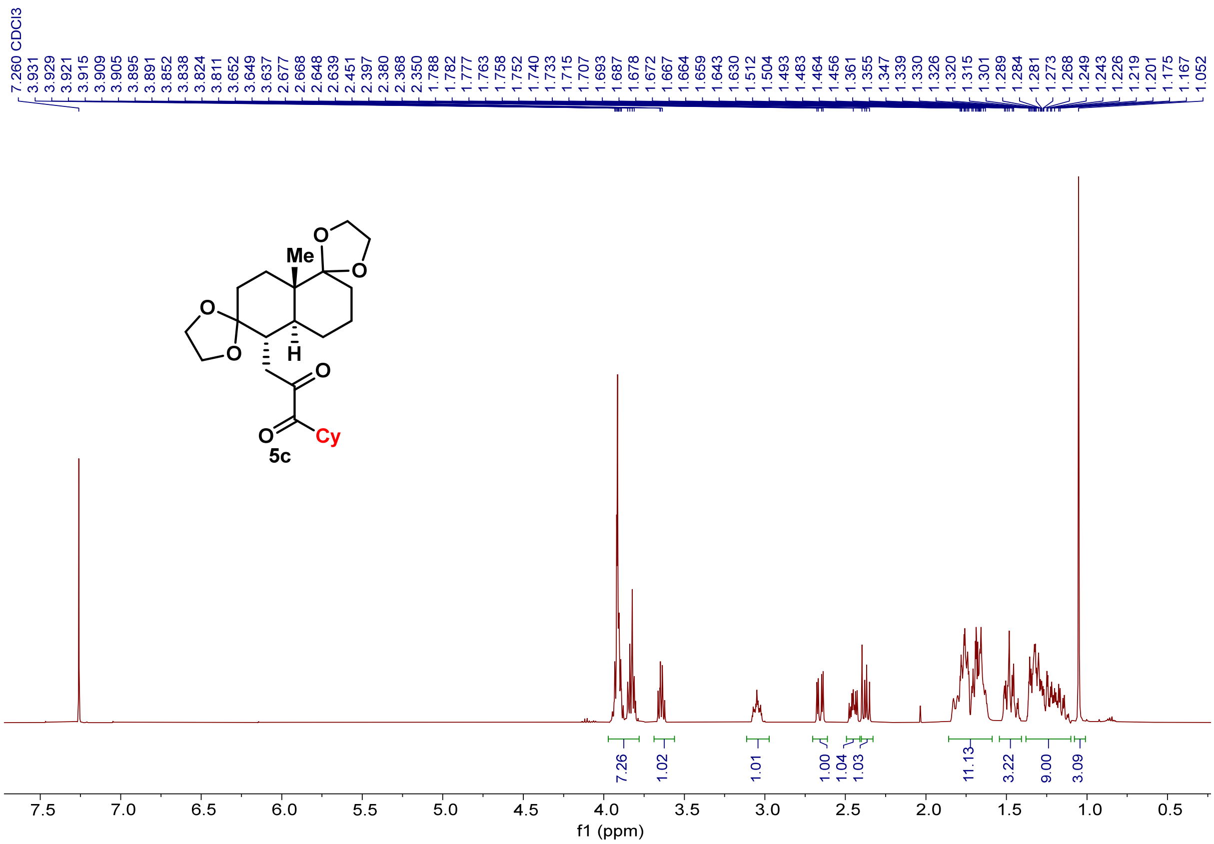


Figure S33. ^{1}H NMR Spectra of **5c** ($CDCl_3$, 500 MHz)

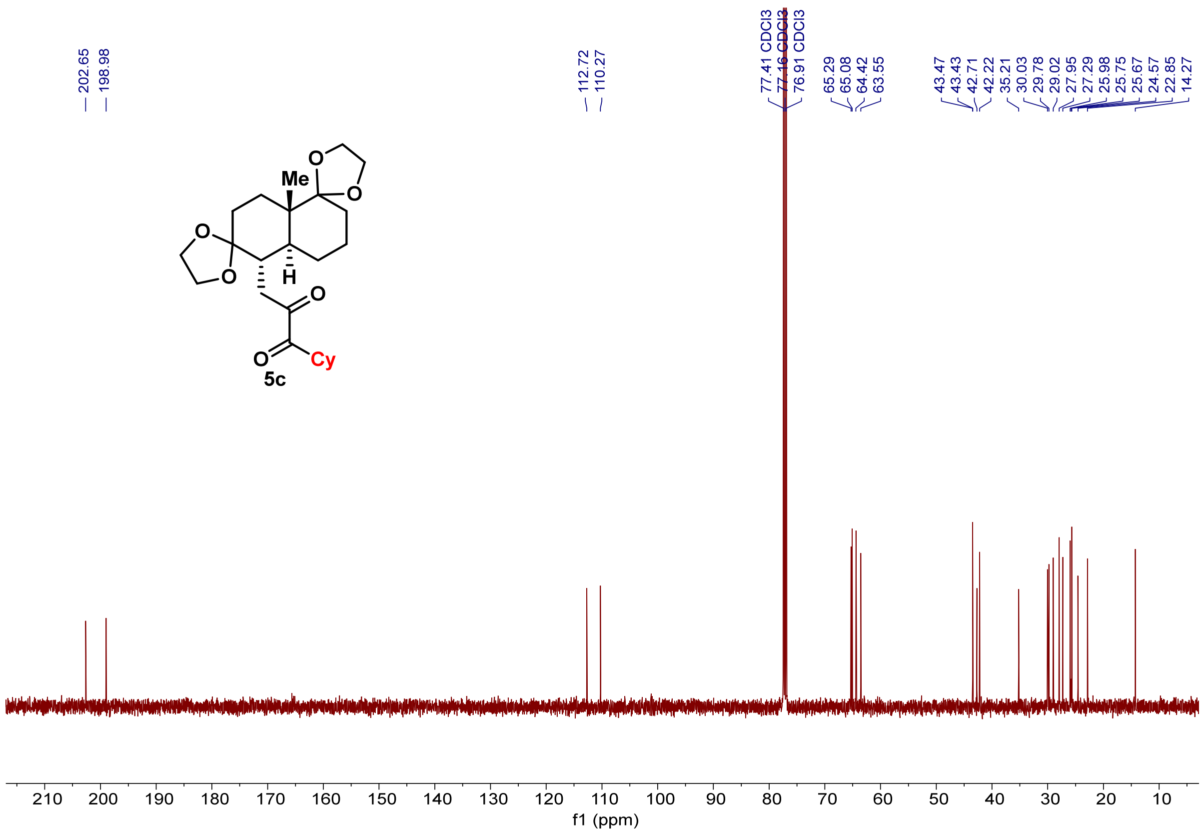


Figure S34. ^{13}C NMR Spectra of **5c** ($CDCl_3$, 125 MHz)

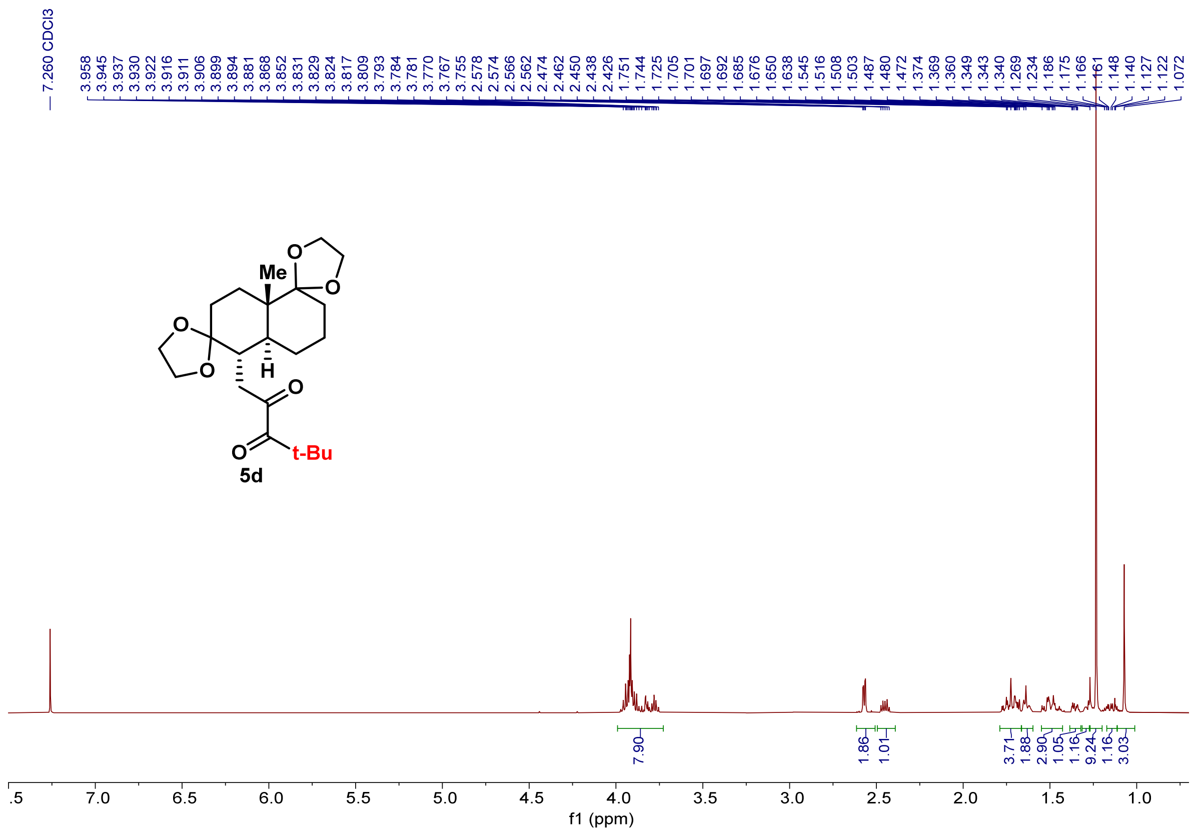


Figure S35. ^{1}H NMR Spectra of **5d** ($CDCl_3$, 500 MHz)

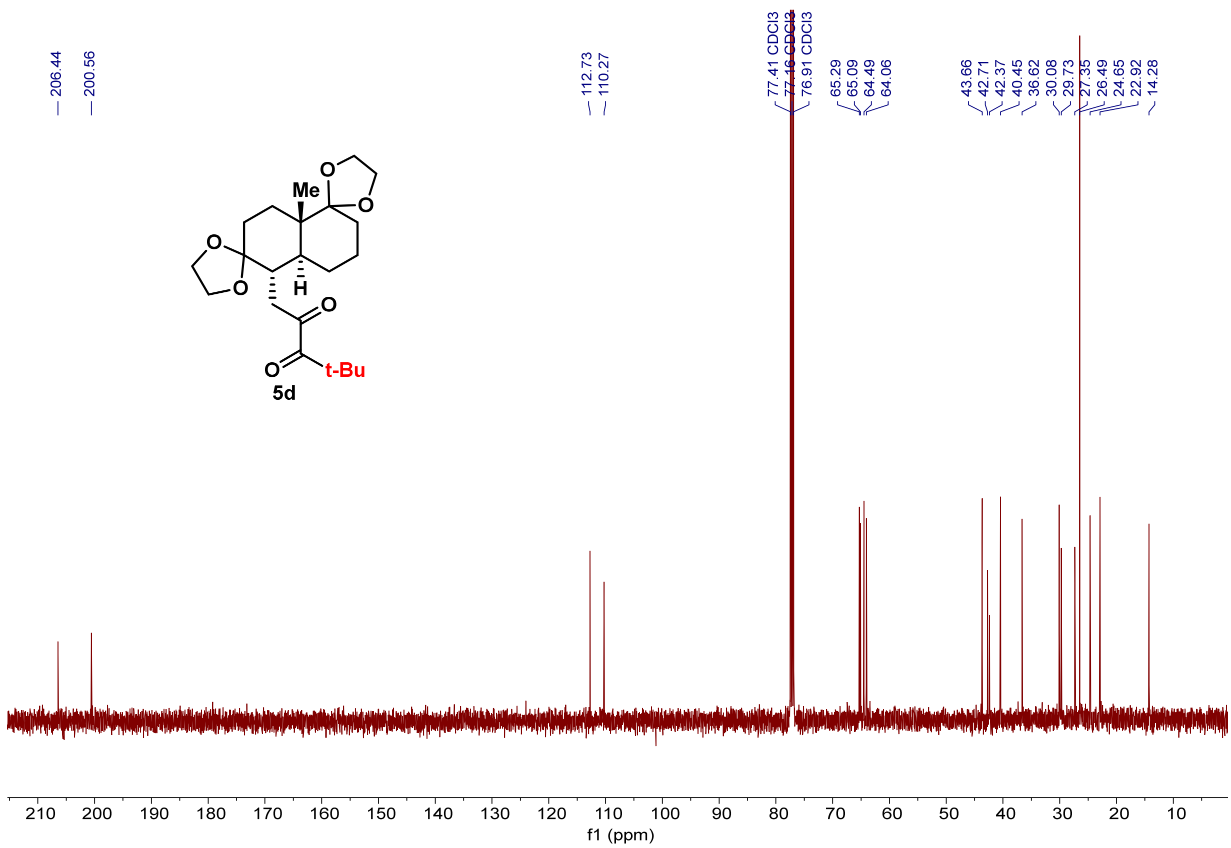


Figure S36. ^{13}C NMR Spectra of **5d** ($CDCl_3$, 125 MHz)

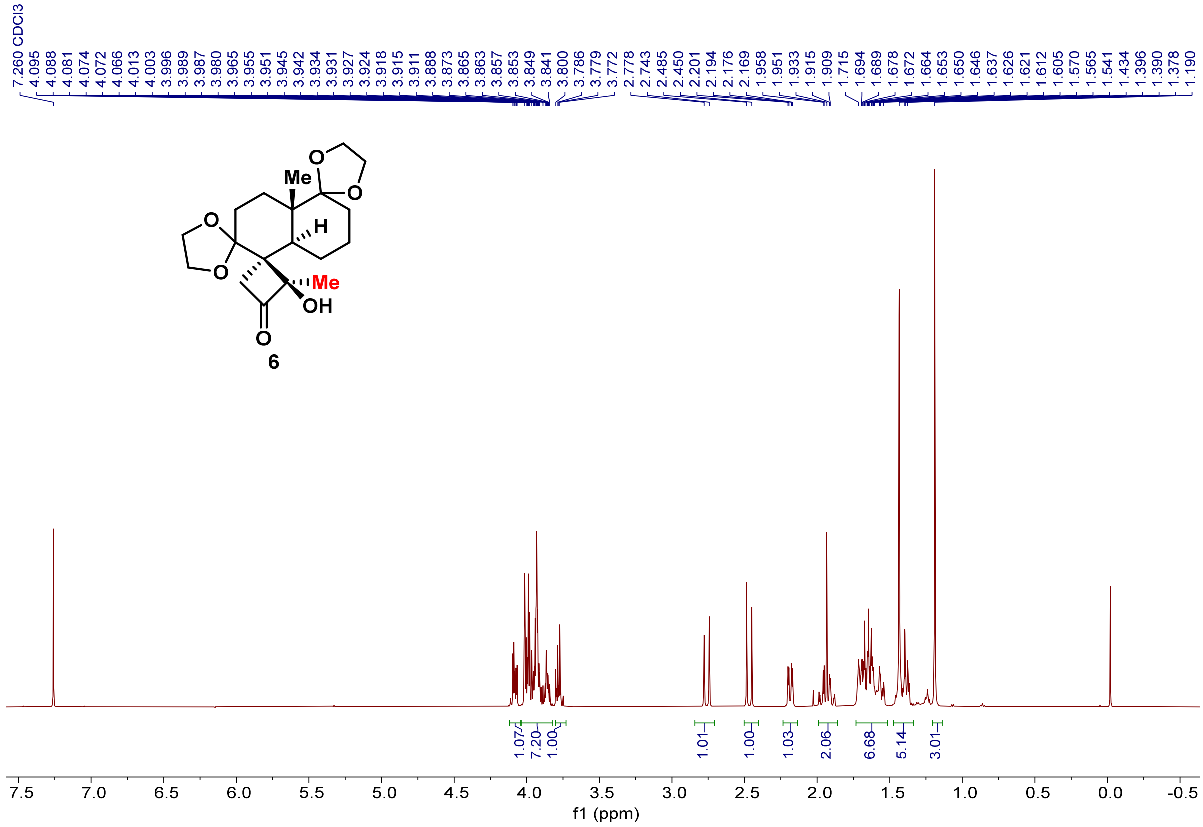


Figure S37. ^{1}H NMR Spectra of Compound **6** ($CDCl_3$, 500 MHz)

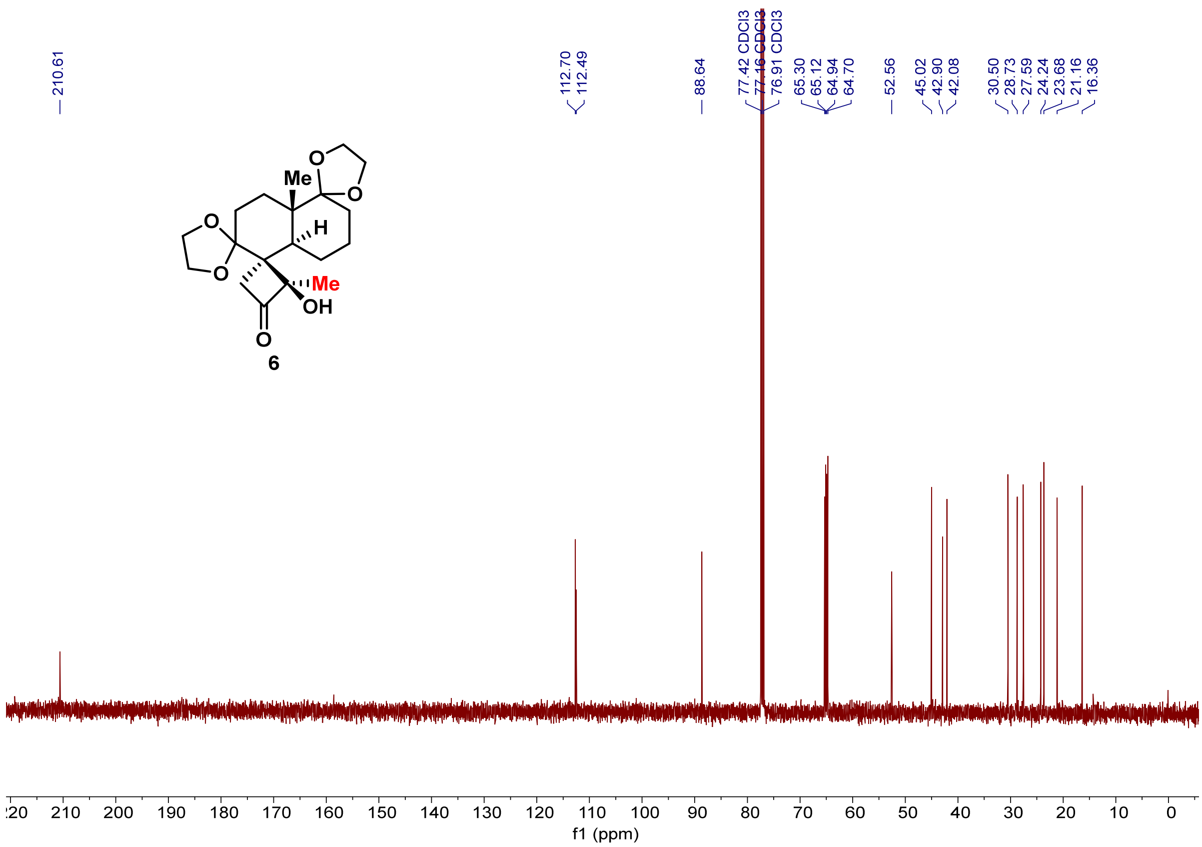


Figure S38. ^{13}C NMR Spectra of Compound **6** ($CDCl_3$, 125 MHz)

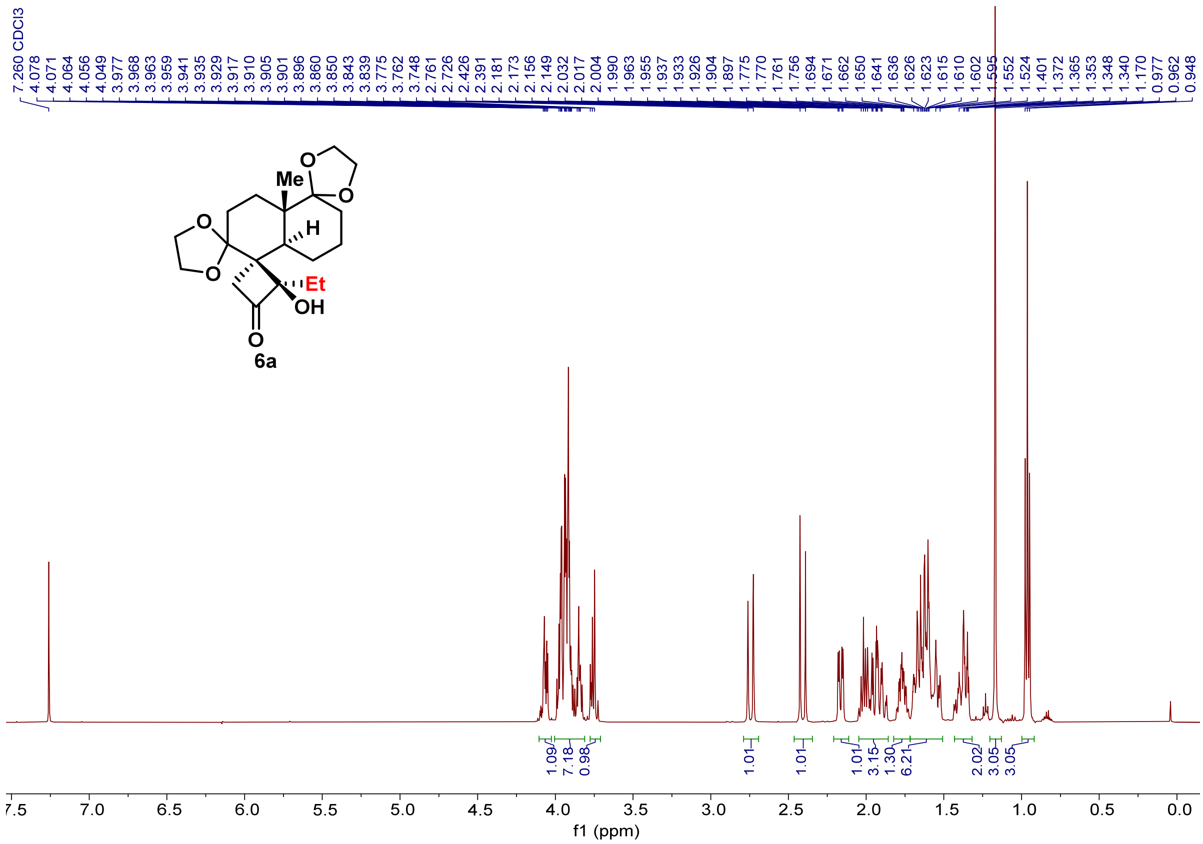


Figure S39. ^{1}H NMR Spectra of Compound **6a** ($CDCl_3$, 500 MHz)

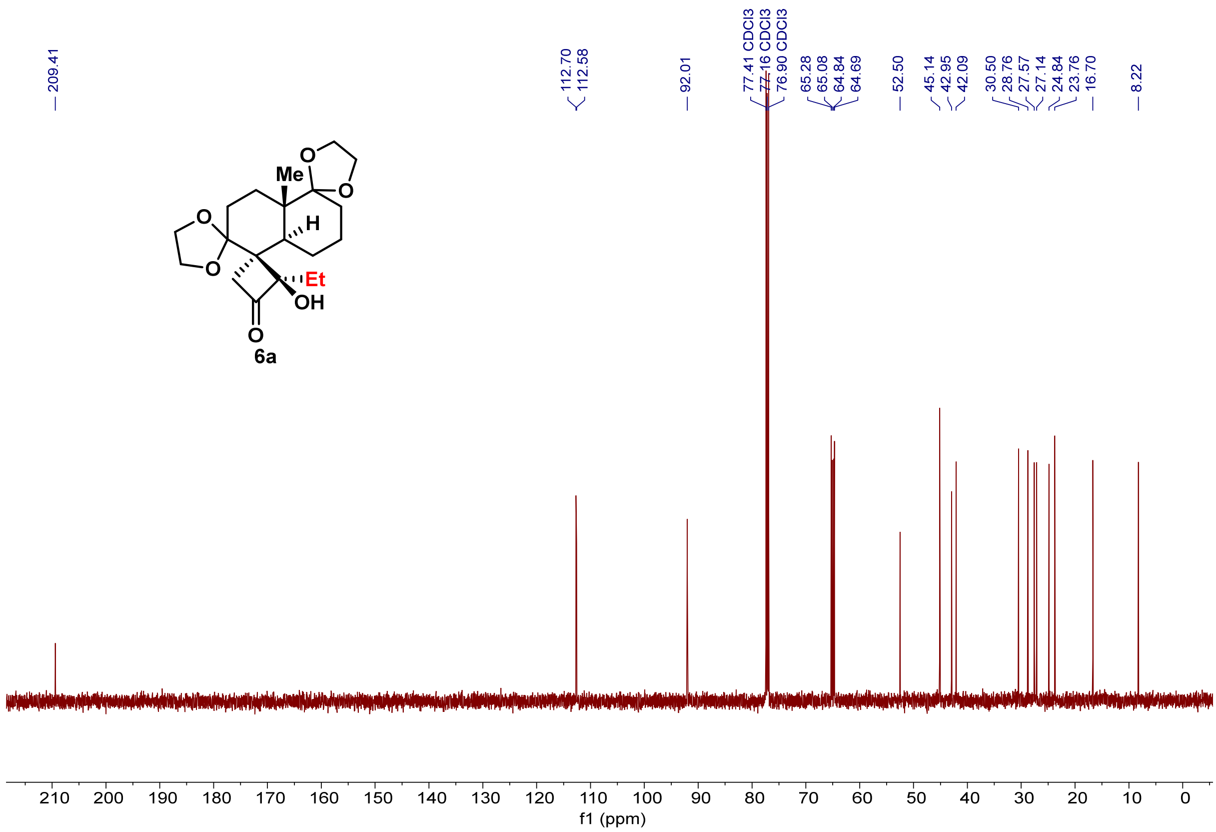


Figure S40. ^{13}C NMR Spectra of Compound **6a** ($CDCl_3$, 125 MHz)

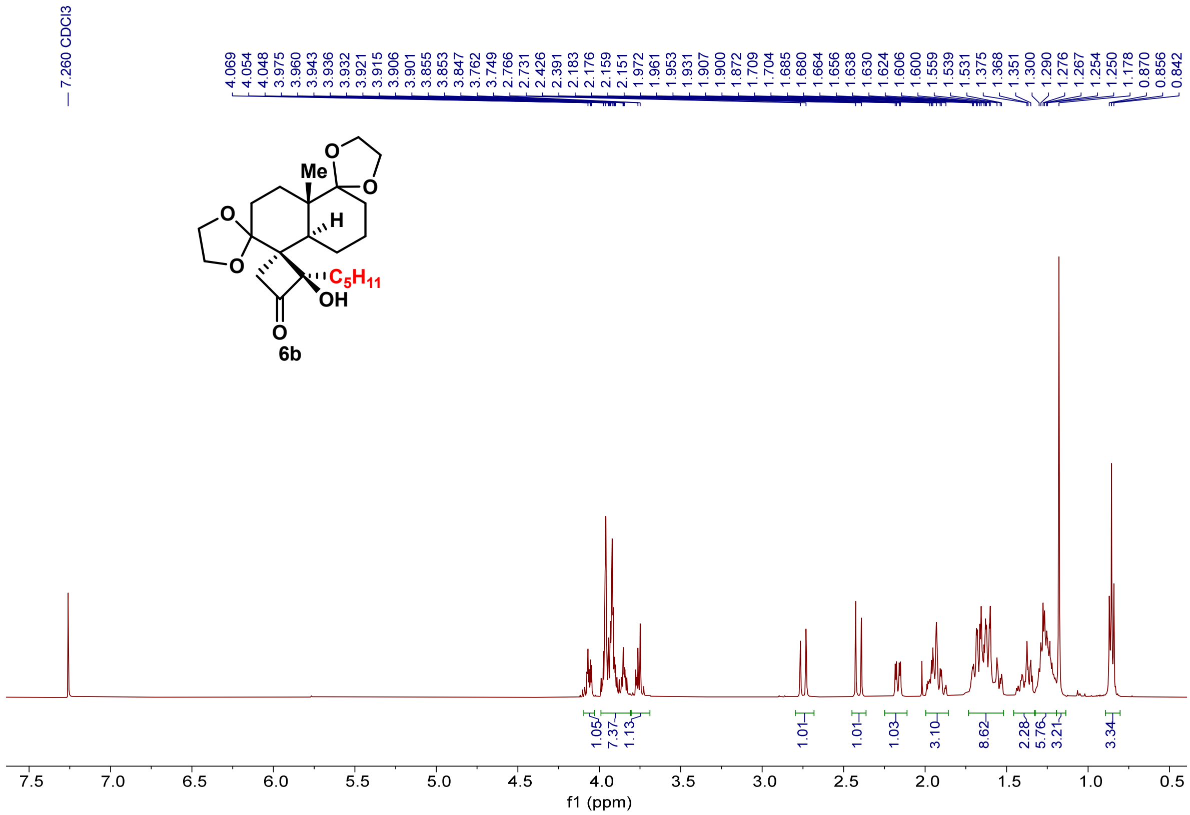


Figure S41. ^{1}H NMR Spectra of Compound **6b** ($CDCl_3$, 500 MHz)

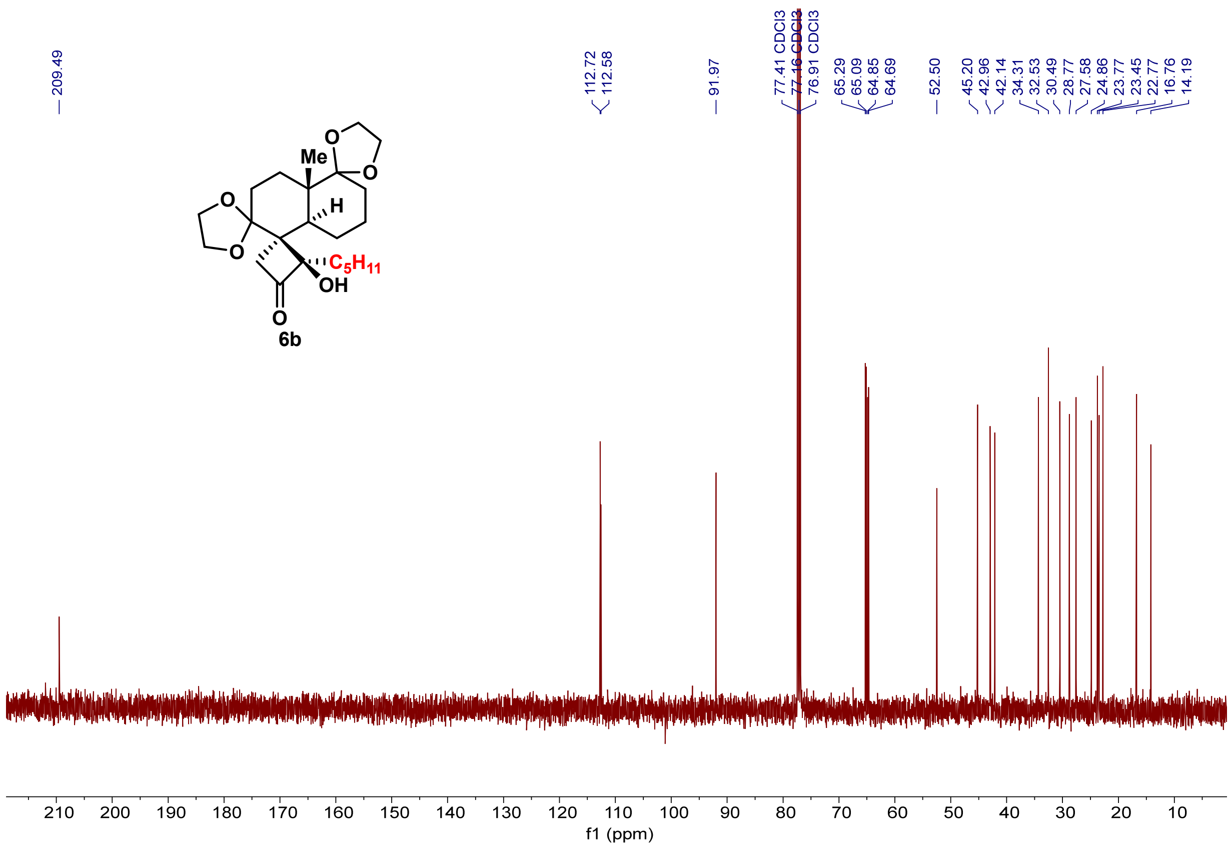


Figure S42. ^{13}C NMR Spectra of Compound **6b** ($CDCl_3$, 125 MHz)

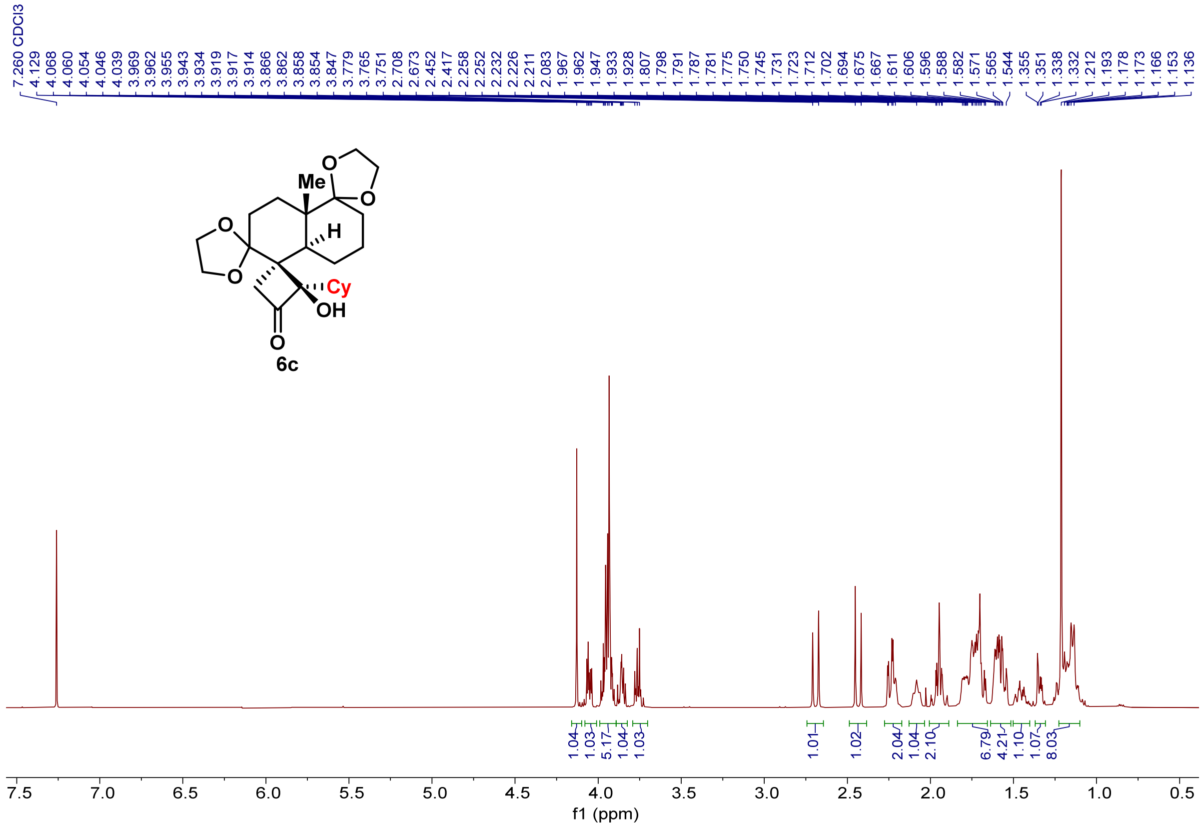


Figure S43. ^{1}H NMR Spectra of Compound **6c** ($CDCl_3$, 500 MHz)

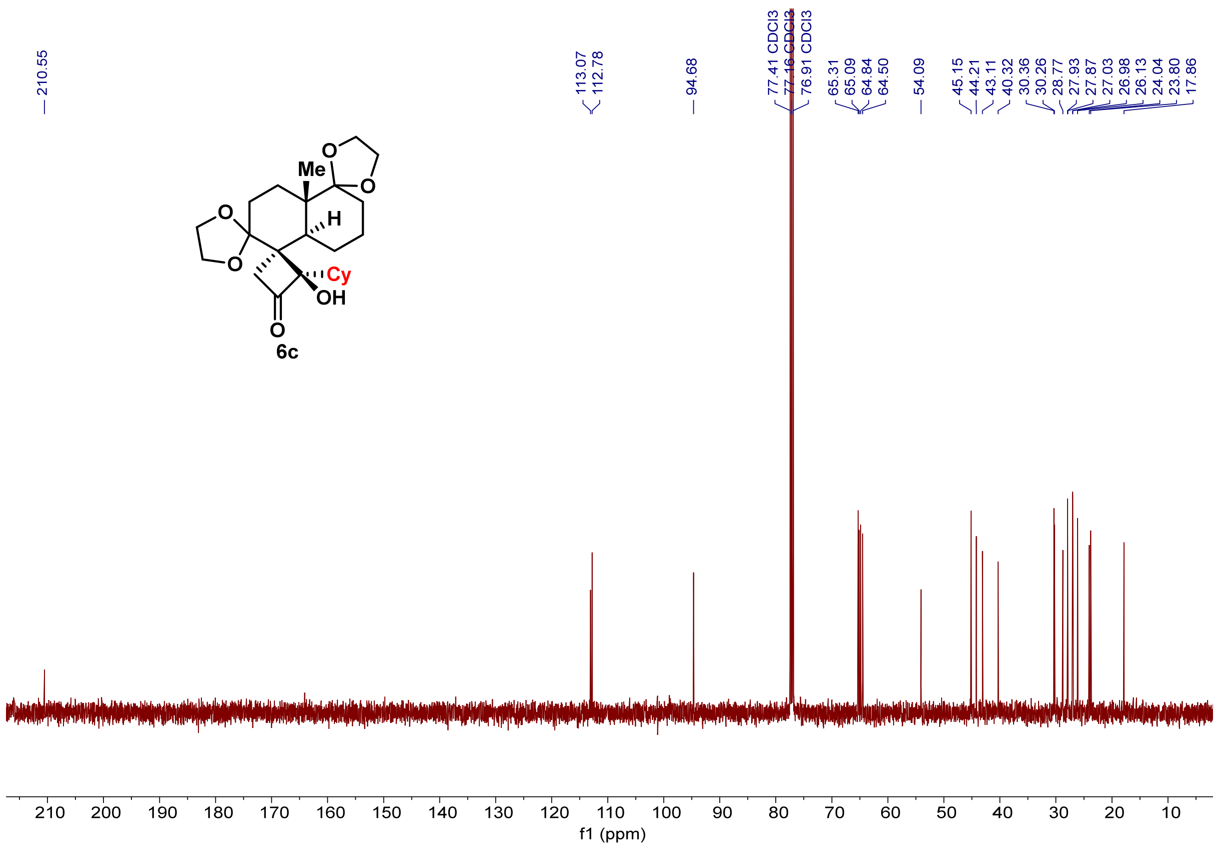


Figure S44. ^{13}C NMR Spectra of Compound **6c** ($CDCl_3$, 125 MHz)

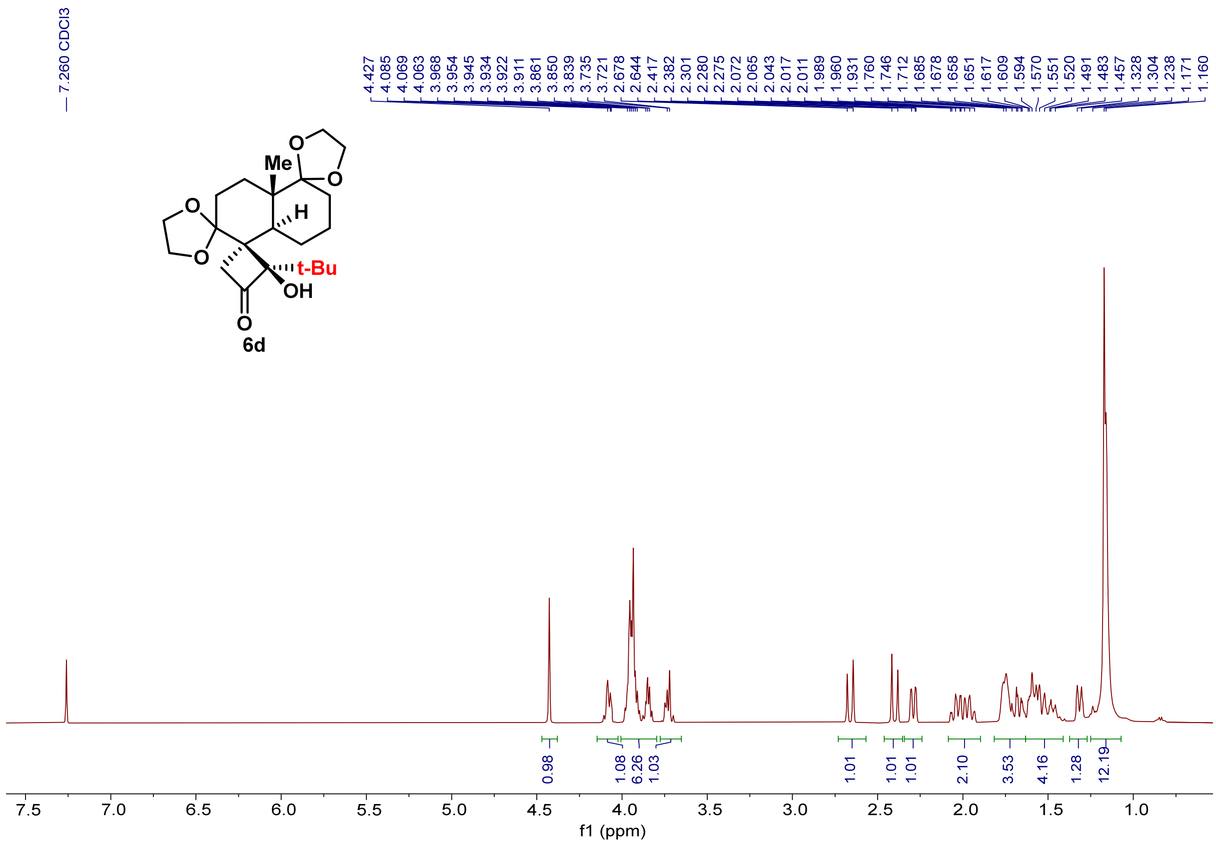


Figure S45. ^{1}H NMR Spectra of Compound **6d** ($CDCl_3$, 500 MHz)

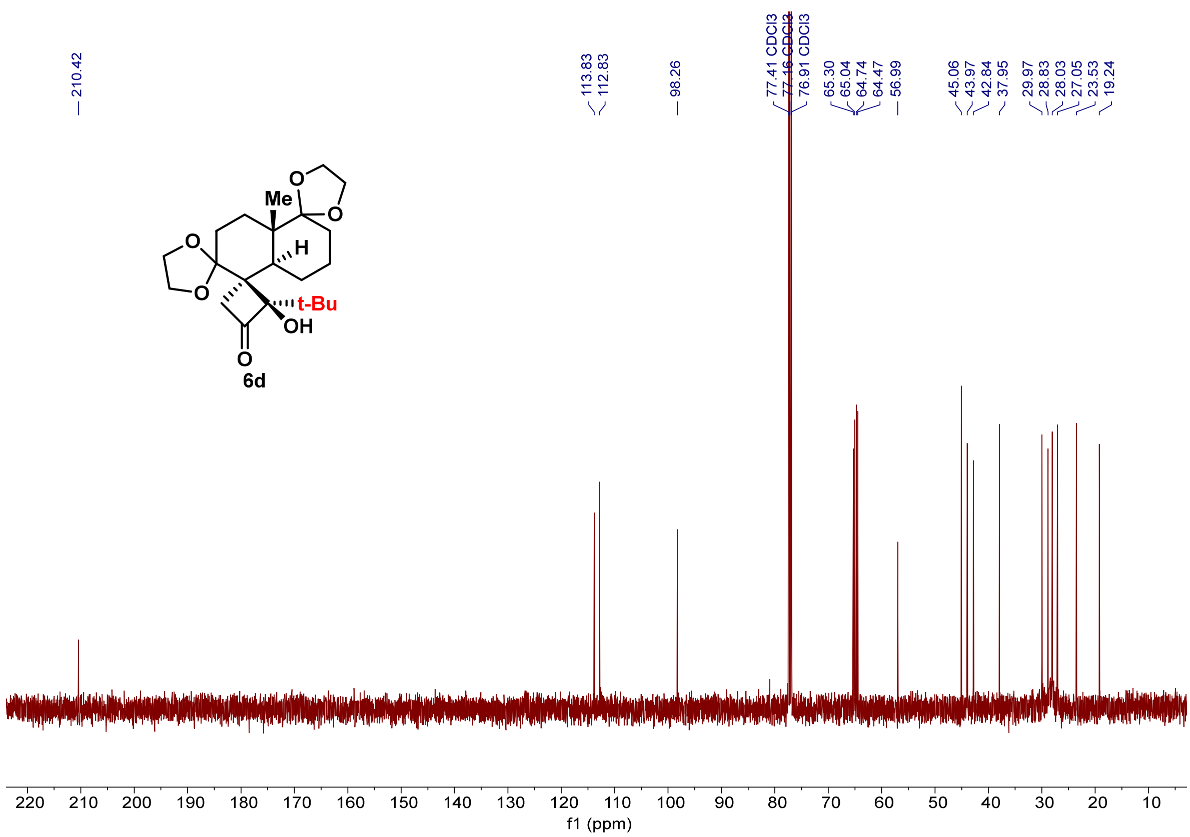


Figure S46. ^{13}C NMR Spectra of Compound **6d** ($CDCl_3$, 125 MHz)

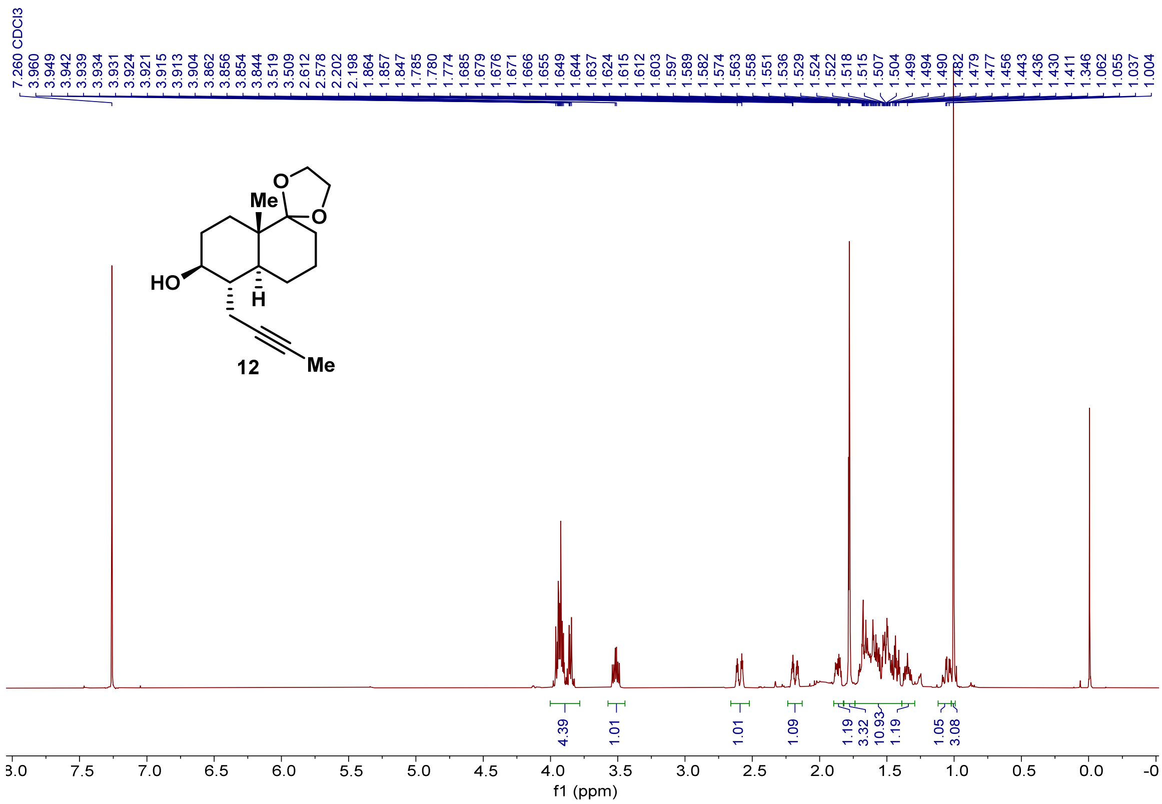


Figure S47. ^{1}H NMR Spectra of Compound **12** ($CDCl_3$, 500 MHz)

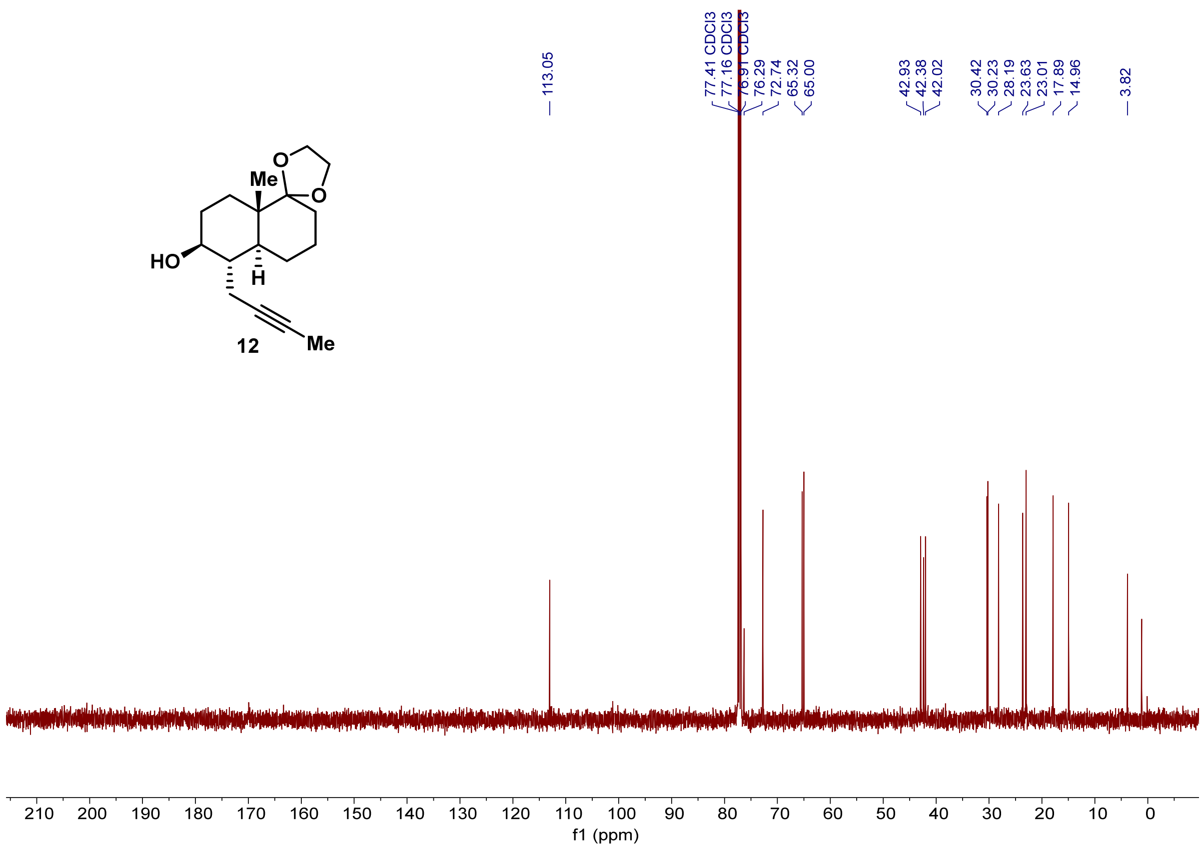


Figure S48. ^{13}C NMR Spectra of Compound **12** ($CDCl_3$, 125 MHz)

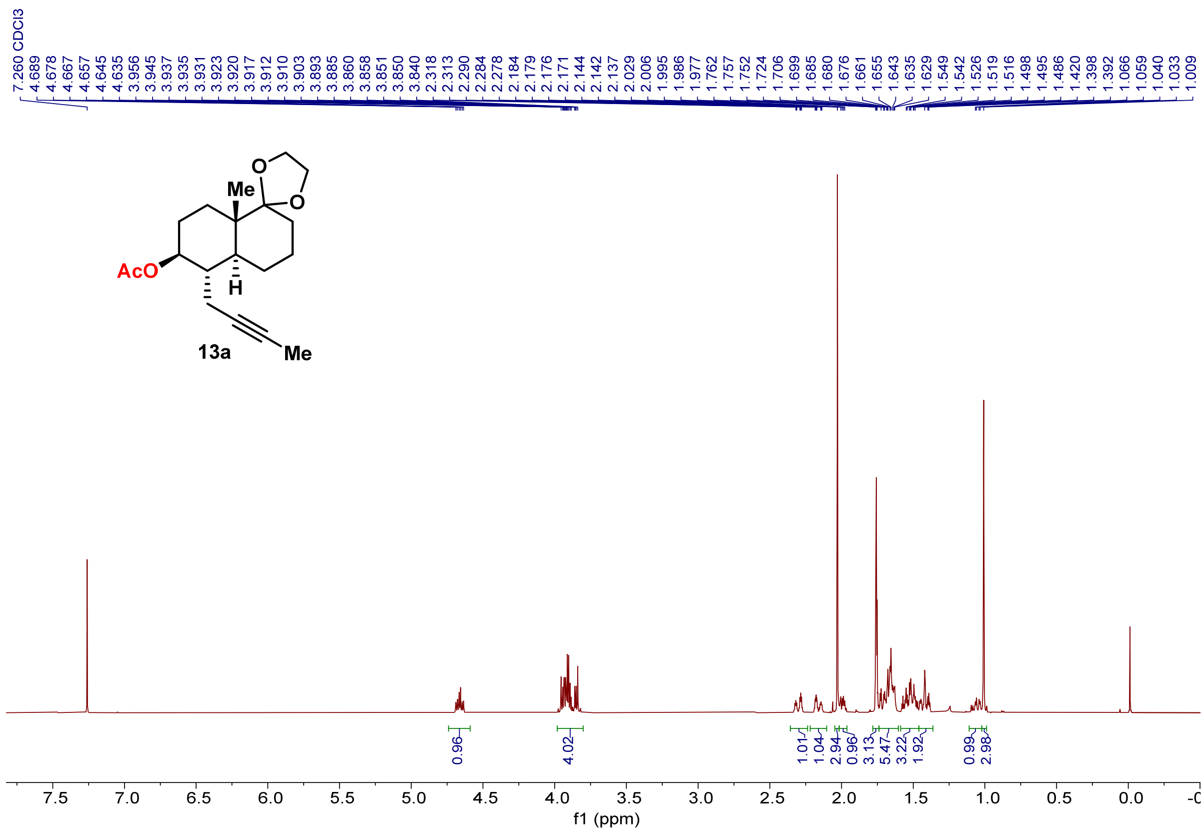


Figure S49. ^{1}H NMR Spectra of Compound **13a** ($CDCl_3$, 500 MHz)

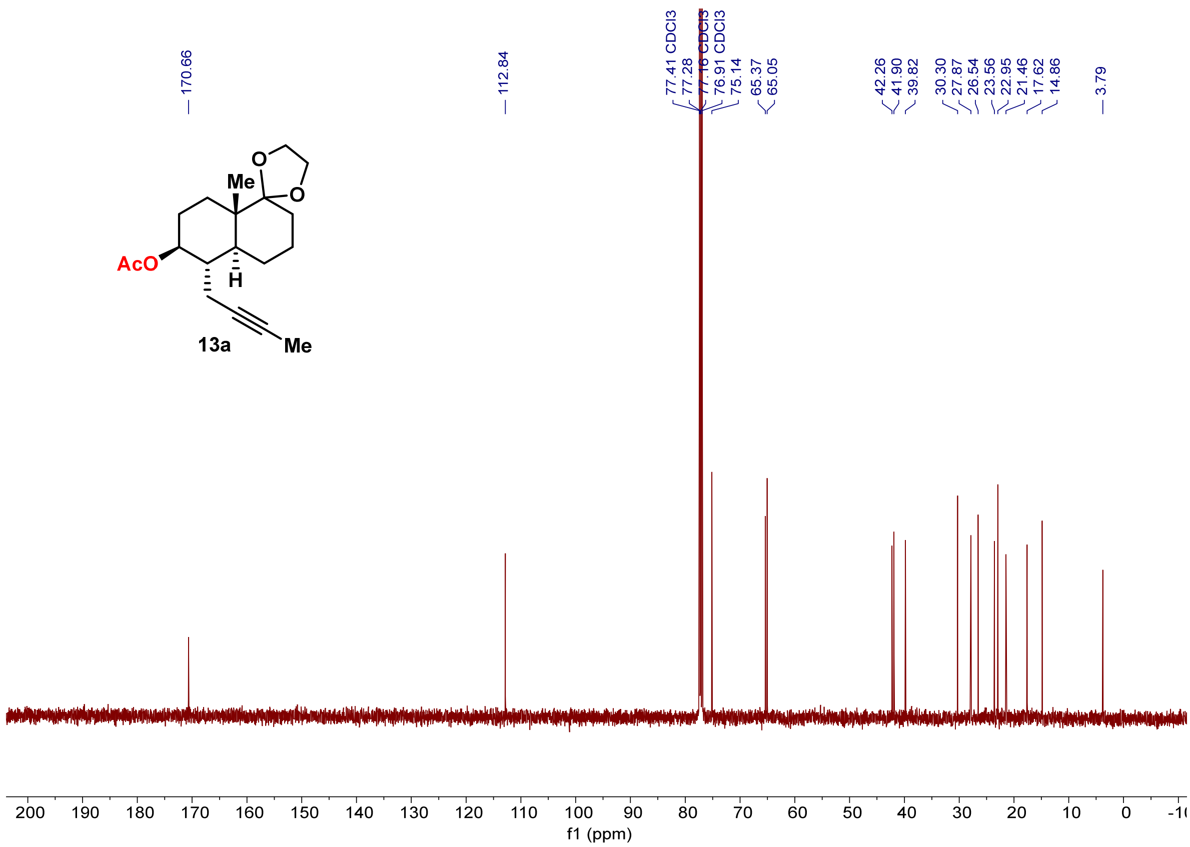


Figure S50. ^{13}C NMR Spectra of Compound **13a** ($CDCl_3$, 125 MHz)

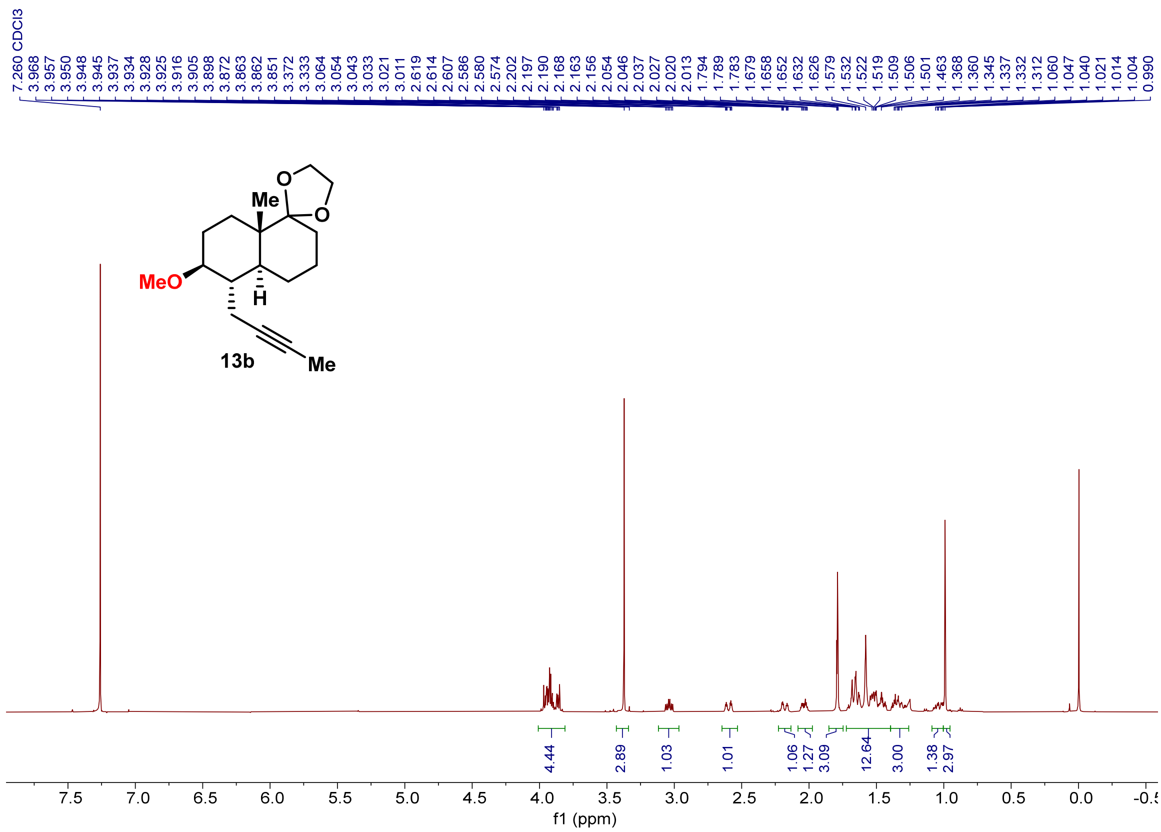


Figure S51. ^{1}H NMR Spectra of Compound **13b** ($CDCl_3$, 500 MHz)

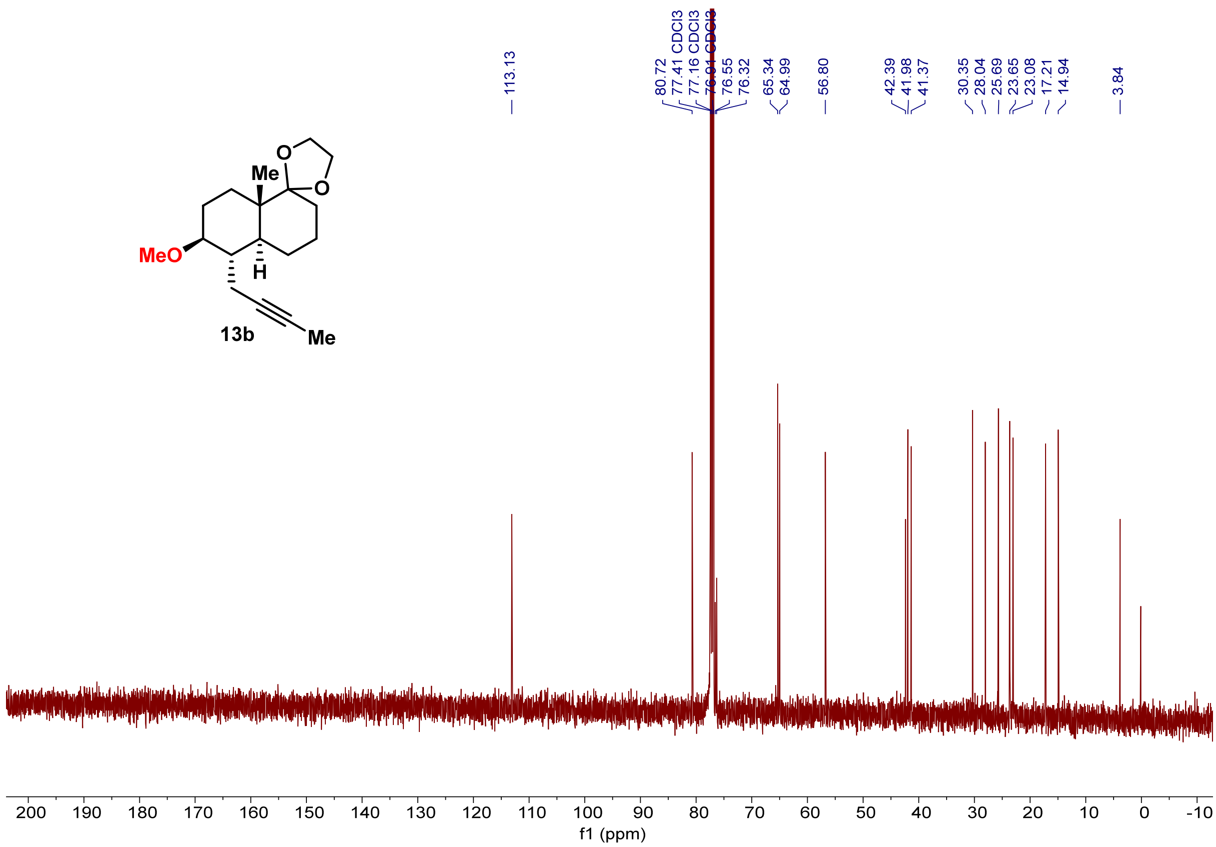


Figure S52. ^{13}C NMR Spectra of Compound **13b** ($CDCl_3$, 125 MHz)

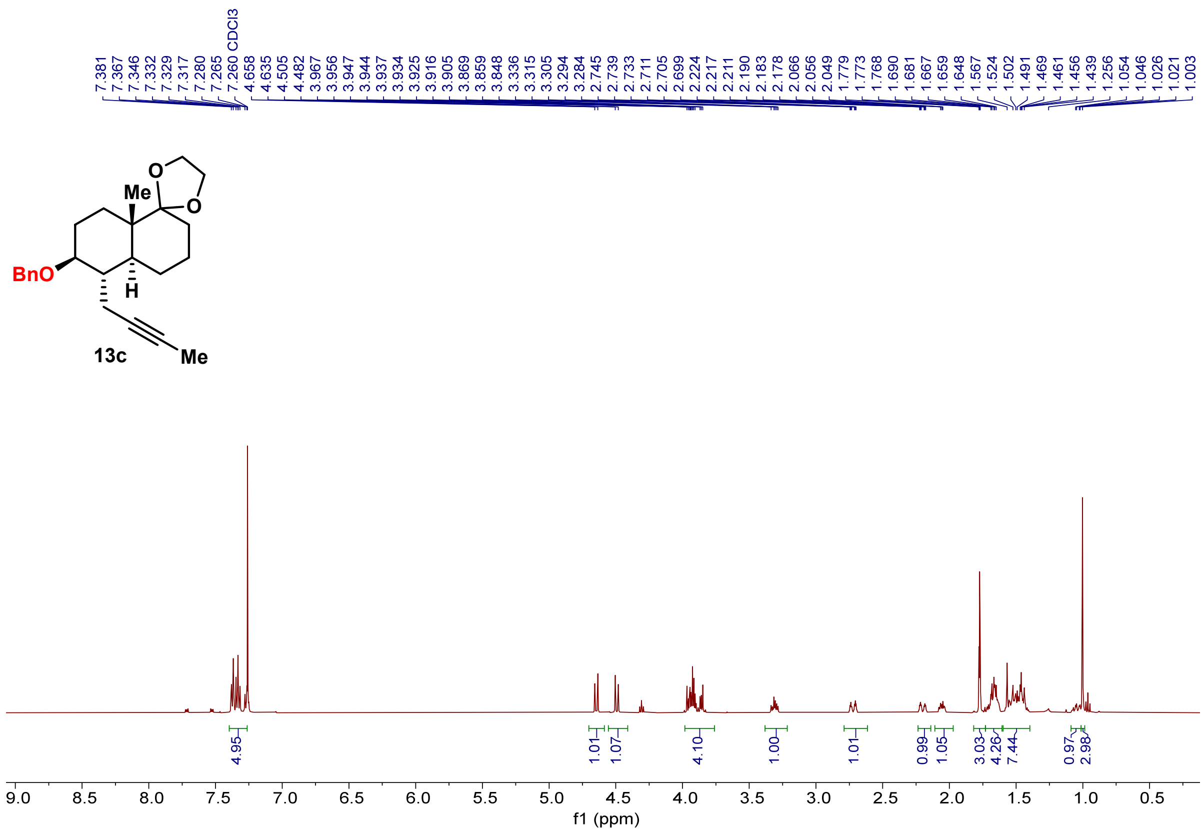


Figure S53. ^{1}H NMR Spectra of Compound **13c** ($CDCl_3$, 500 MHz)

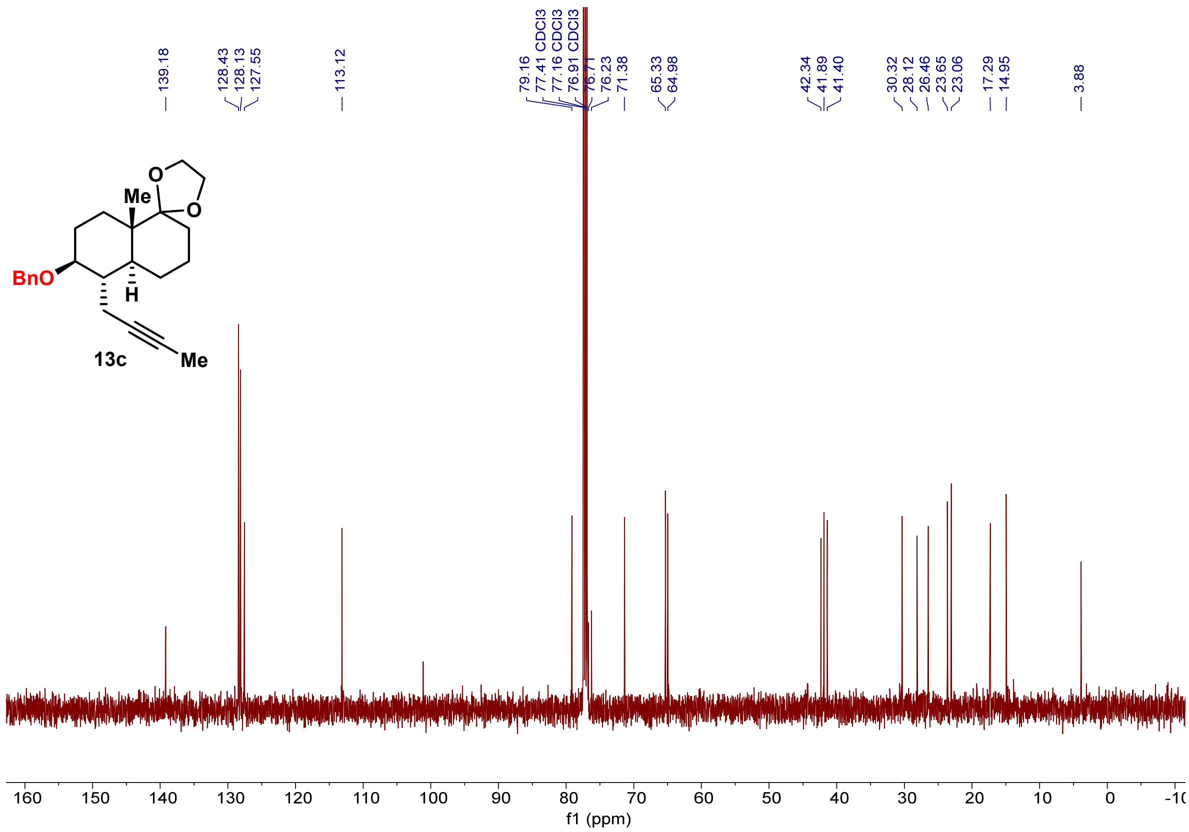


Figure S54. ^{13}C NMR Spectra of Compound **13c** ($CDCl_3$, 125 MHz)

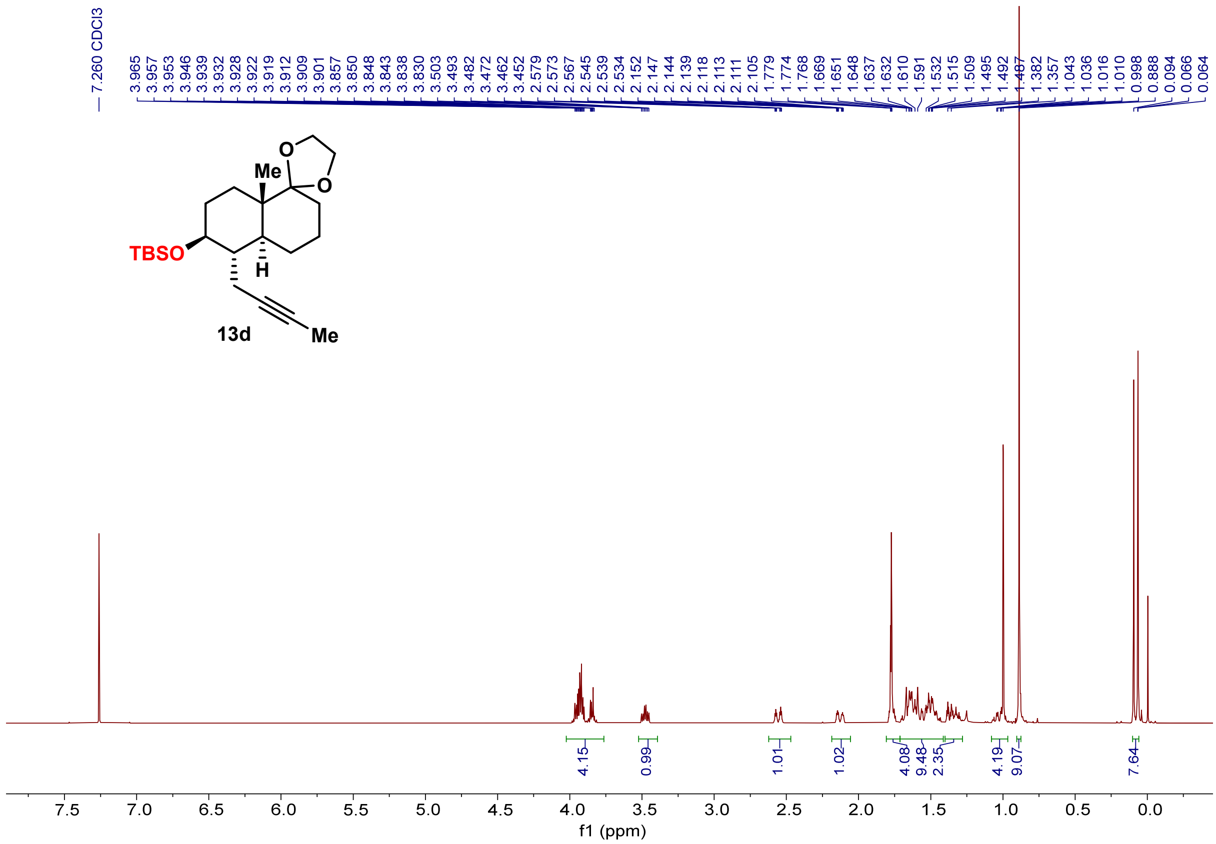


Figure S55. ^{1}H NMR Spectra of Compound **13d** ($CDCl_3$, 500 MHz)

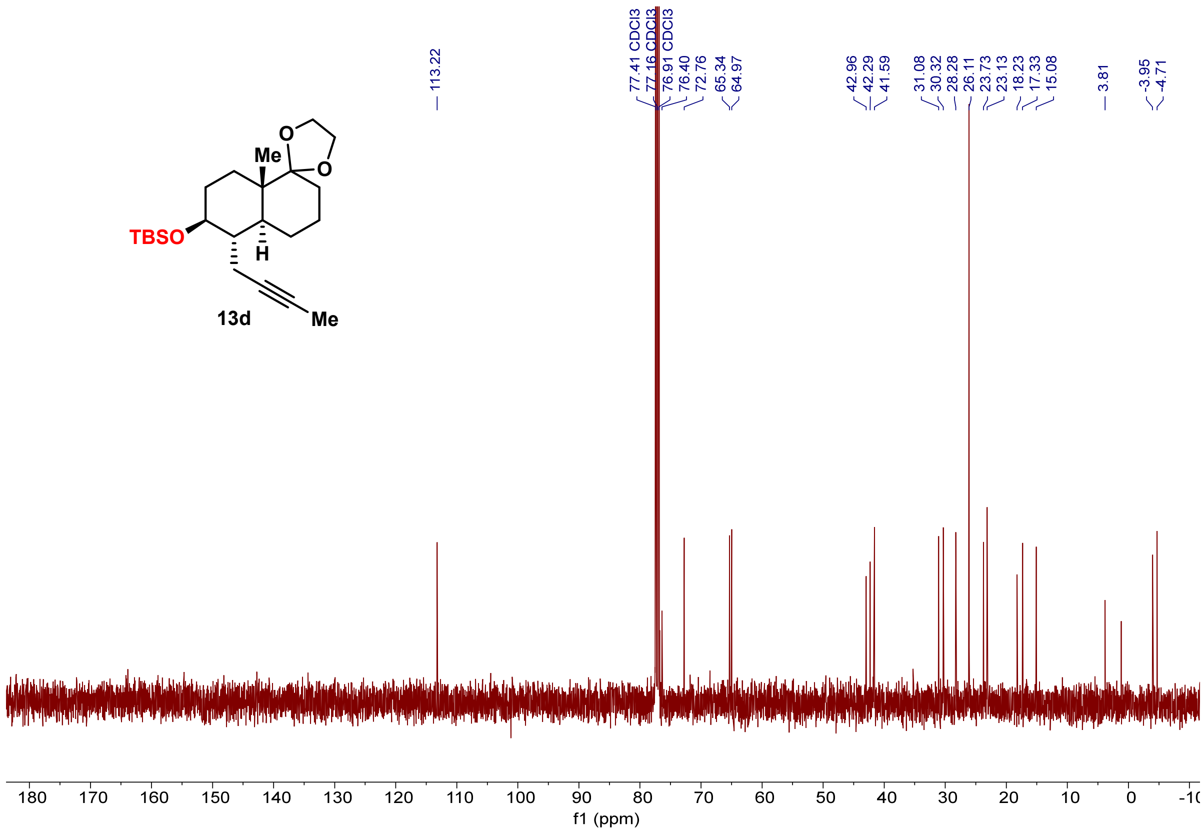


Figure S56. ^{13}C NMR Spectra of Compound **13d** ($CDCl_3$, 125 MHz)

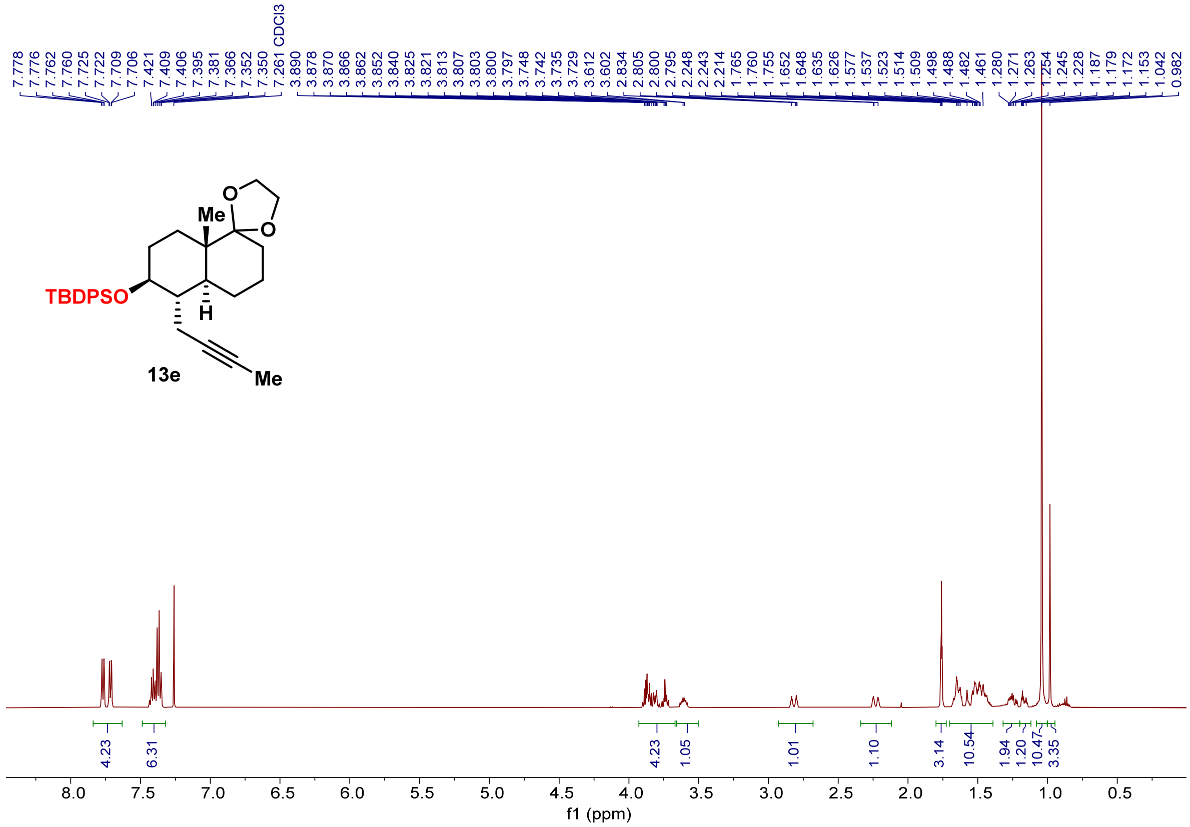


Figure S57. ^{1}H NMR Spectra of Compound **13e** ($CDCl_3$, 500 MHz)

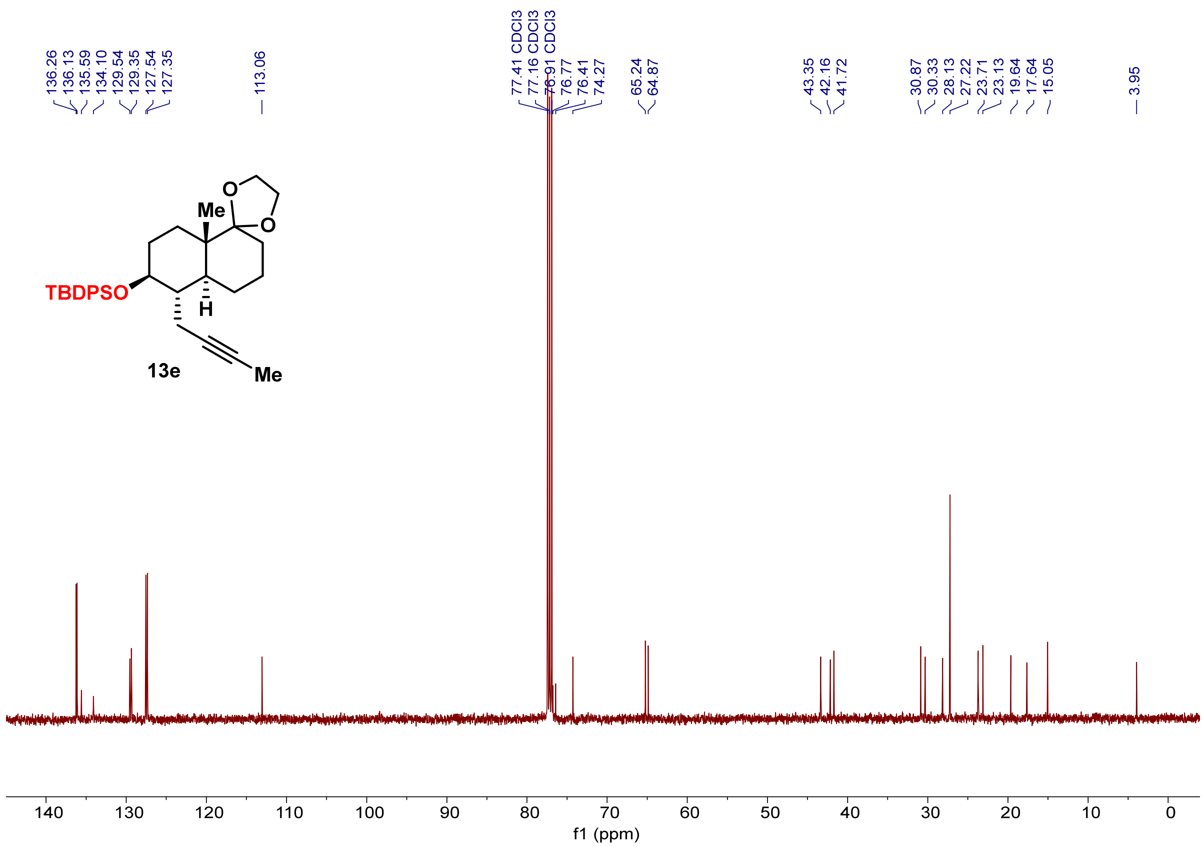


Figure S58. ^{13}C NMR Spectra of Compound **13e** ($CDCl_3$, 125 MHz)

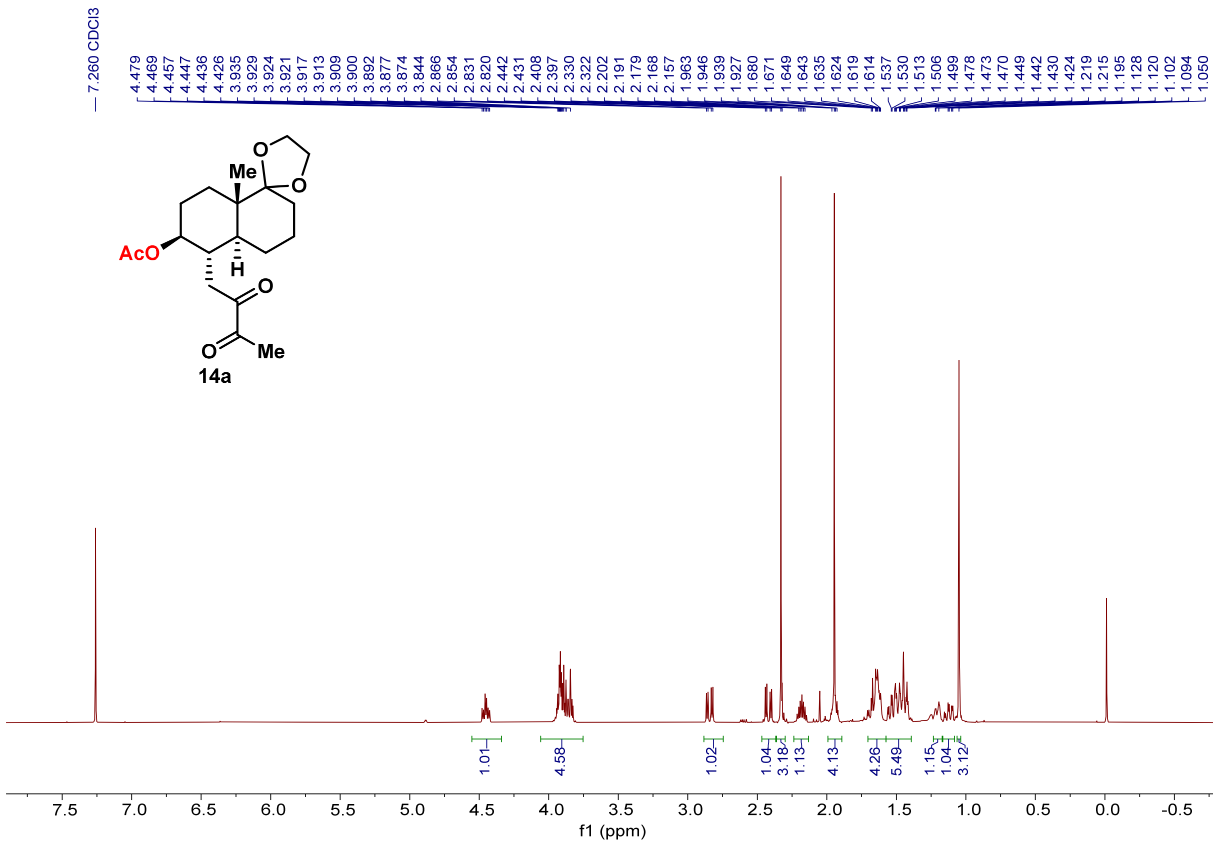


Figure S59. ^{1}H NMR Spectra of Compound **14a** ($CDCl_3$, 500 MHz)

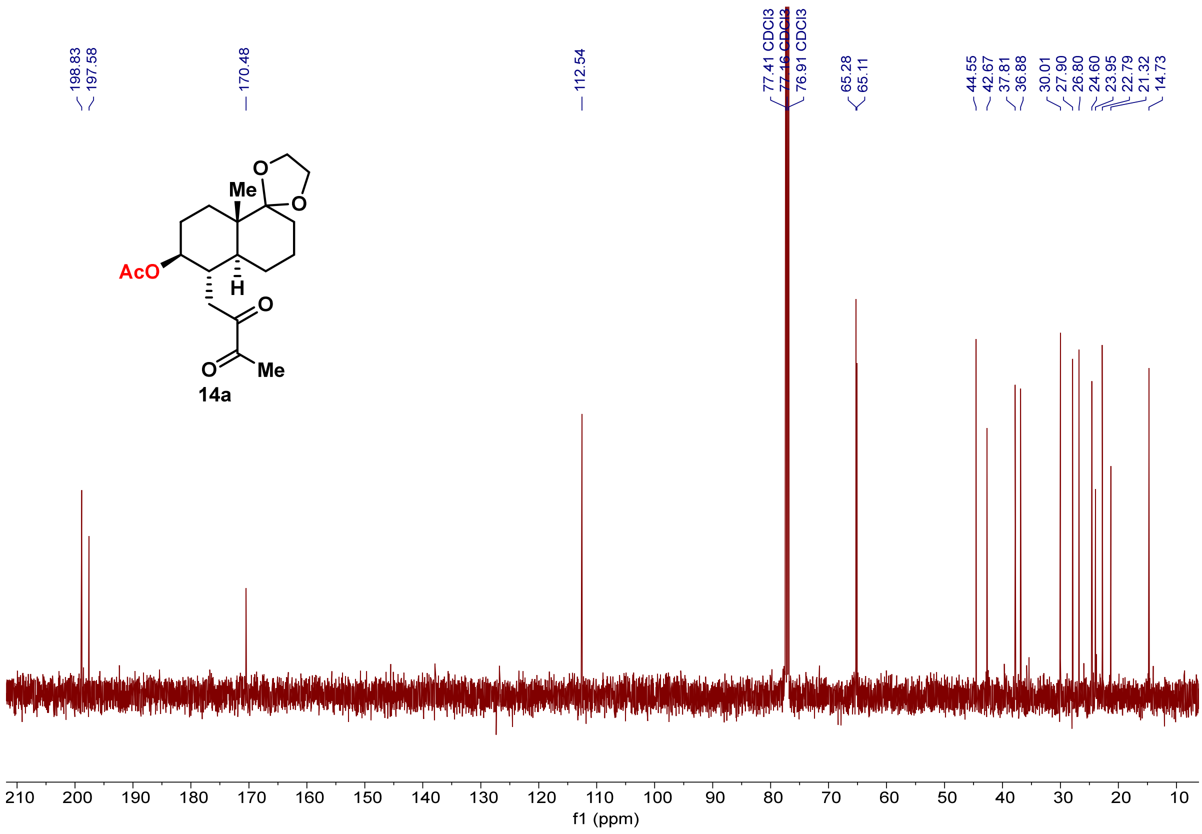


Figure S60. ^{13}C NMR Spectra of Compound **14a** ($CDCl_3$, 125 MHz)

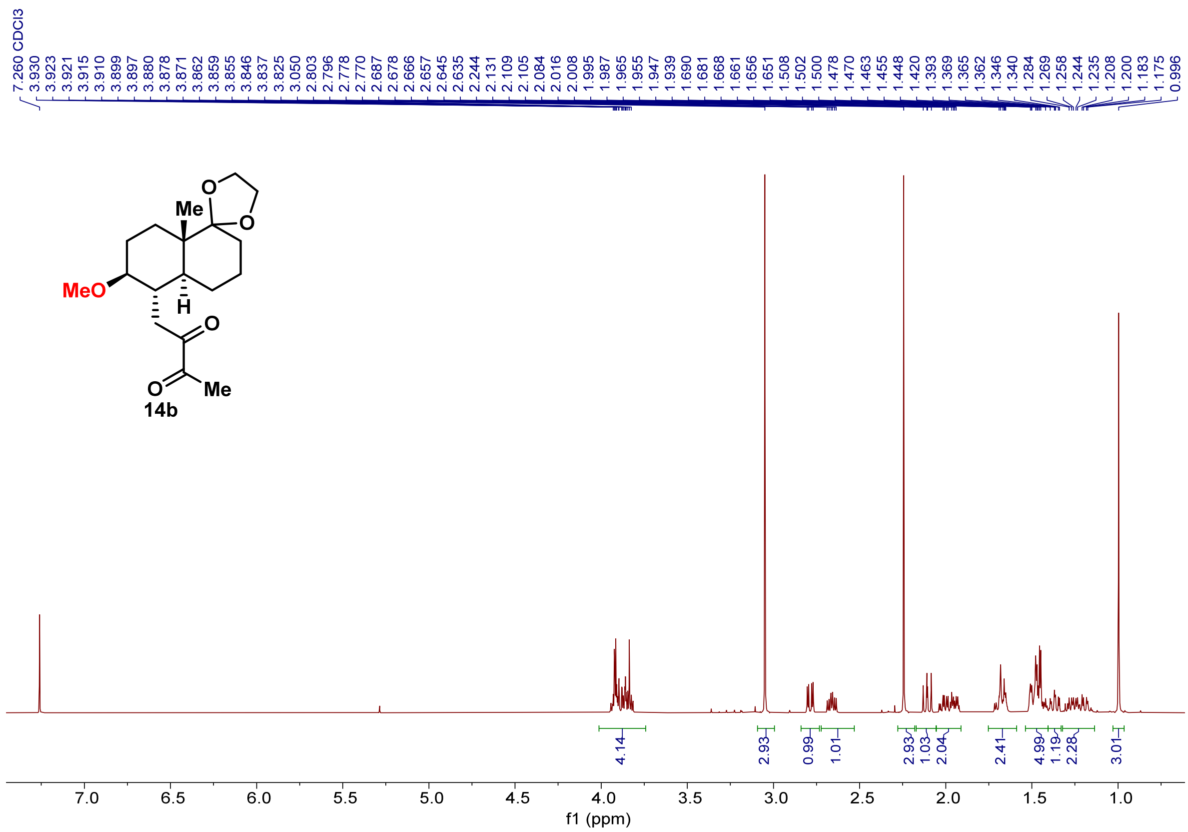


Figure S61. ^{1}H NMR Spectra of Compound **14b** ($CDCl_3$, 500 MHz)

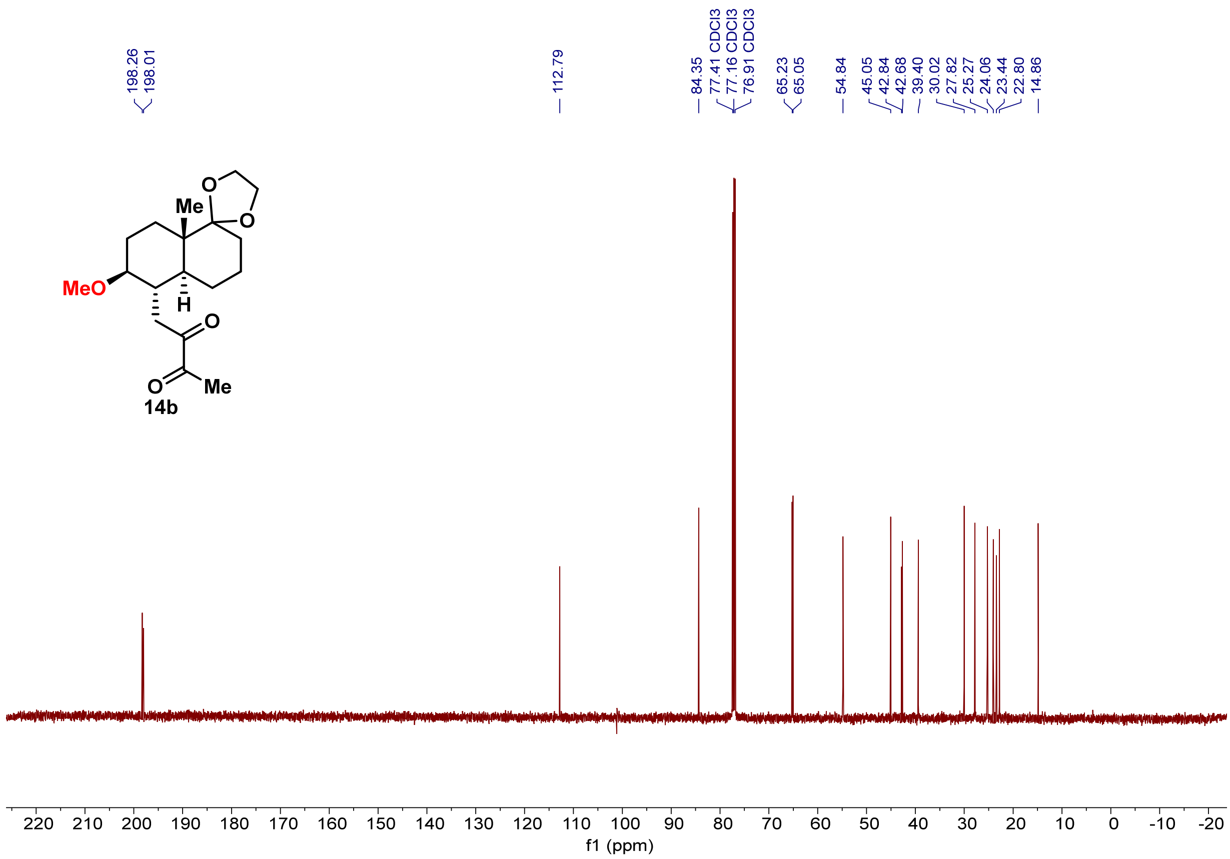


Figure S62. ^{13}C NMR Spectra of Compound **14b** ($CDCl_3$, 125 MHz)

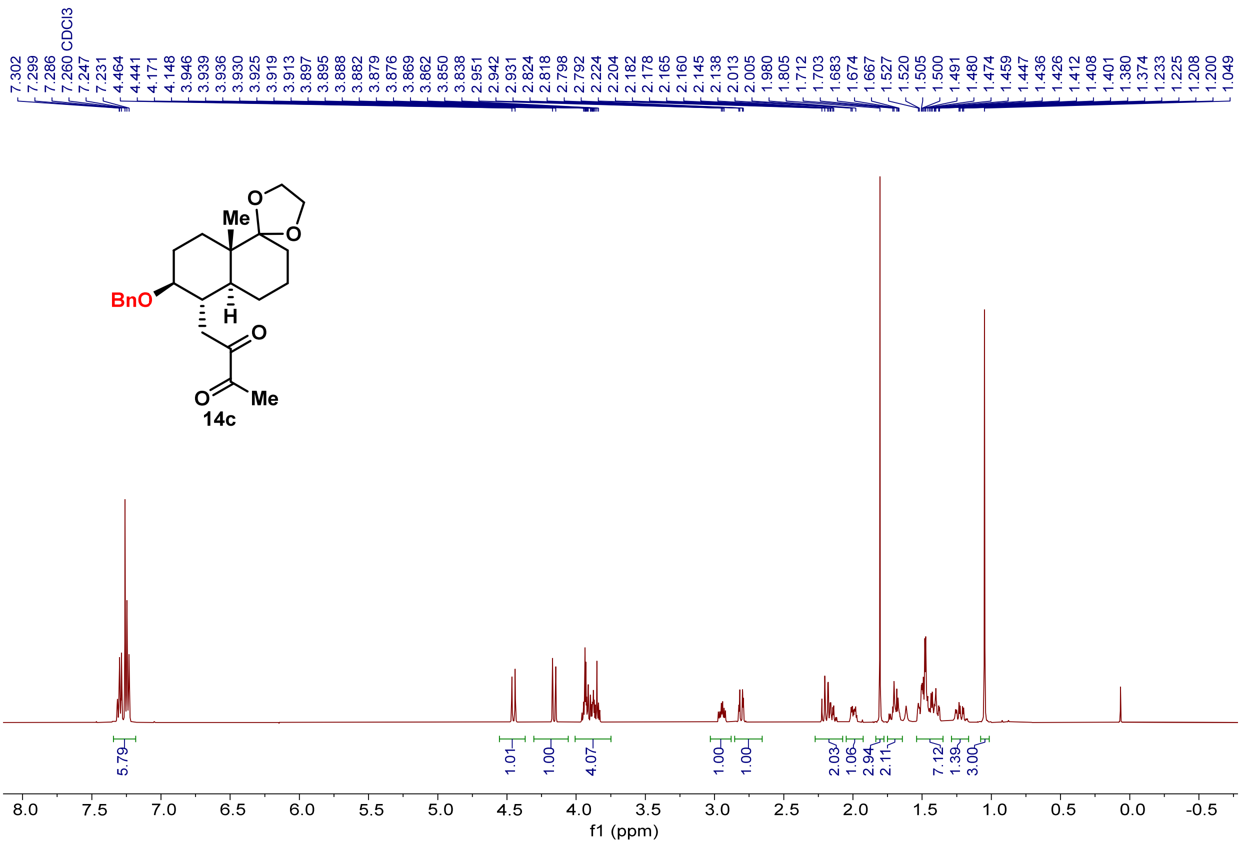


Figure S63. ^{1}H NMR Spectra of Compound **14c** ($CDCl_3$, 500 MHz)

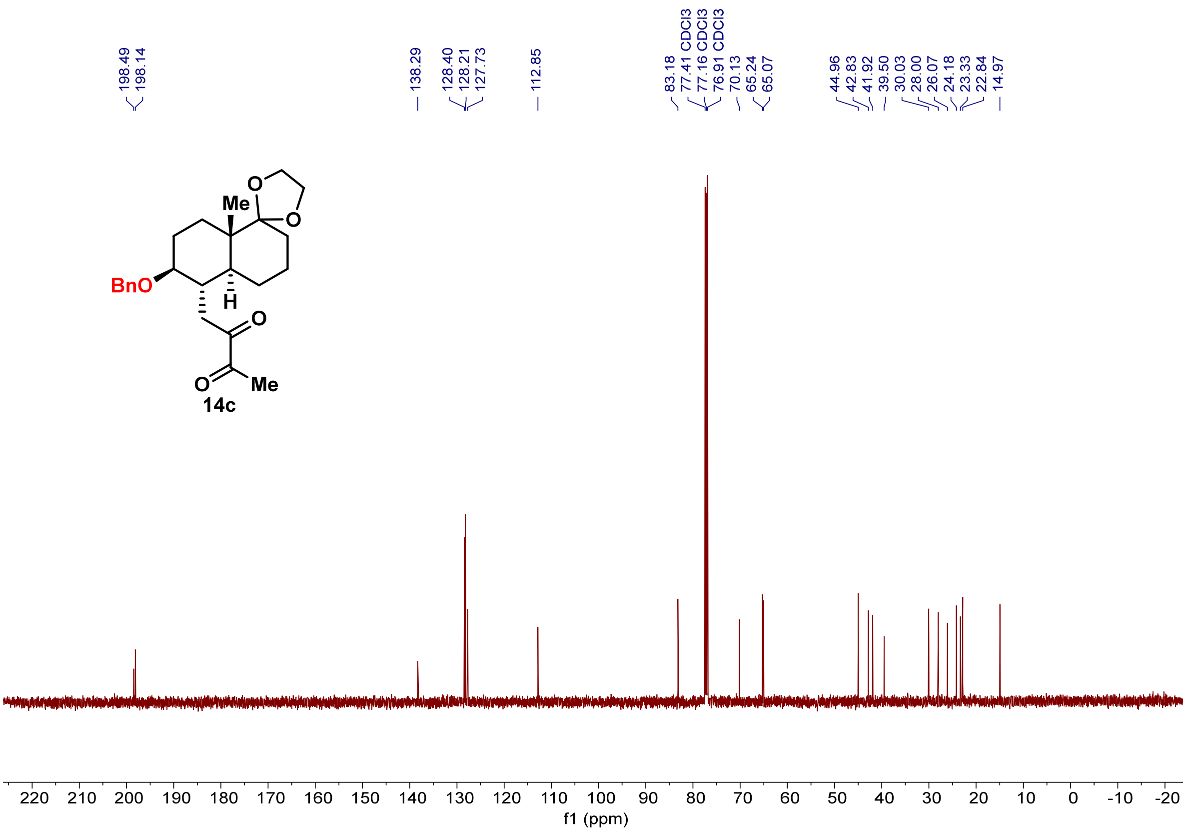


Figure S64. ^{13}C NMR Spectra of Compound **14c** ($CDCl_3$, 125 MHz)

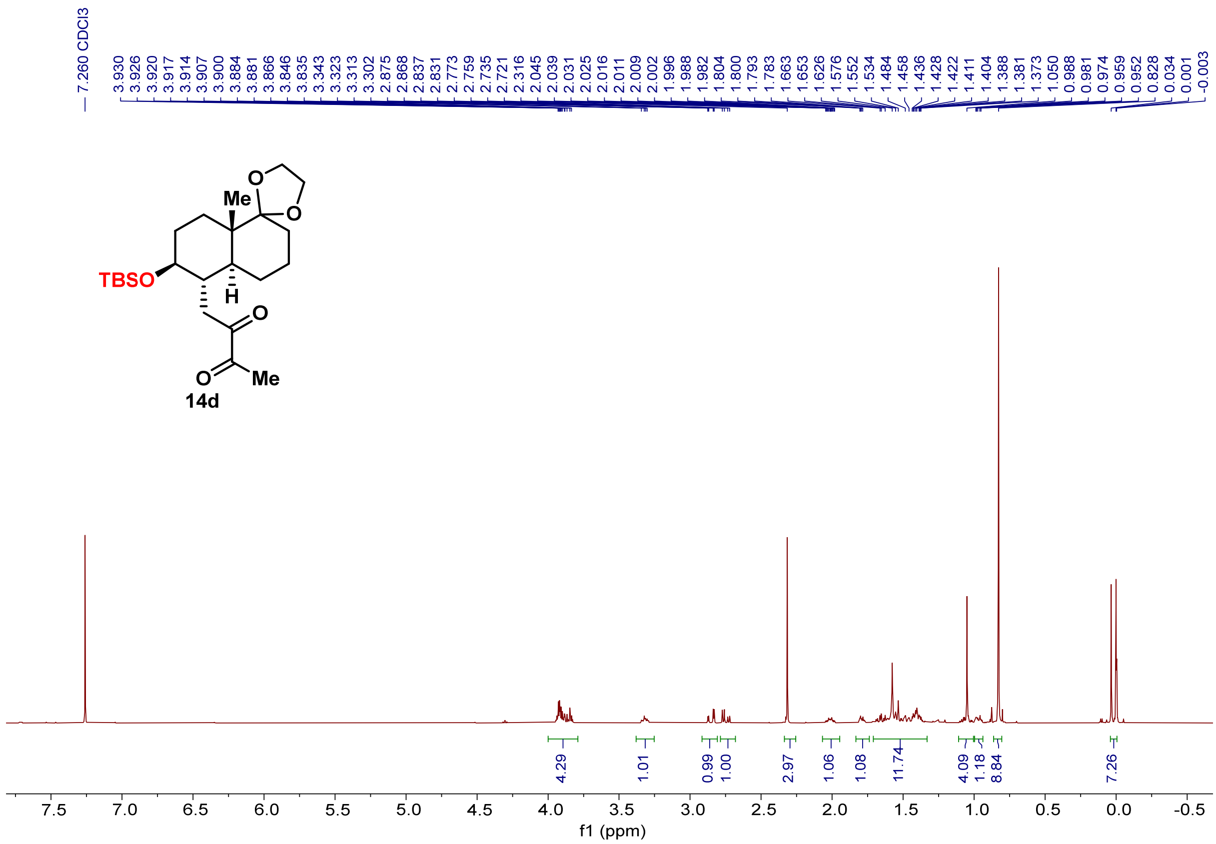


Figure S65. ^{1}H NMR Spectra of Compound **14d** ($CDCl_3$, 500 MHz)

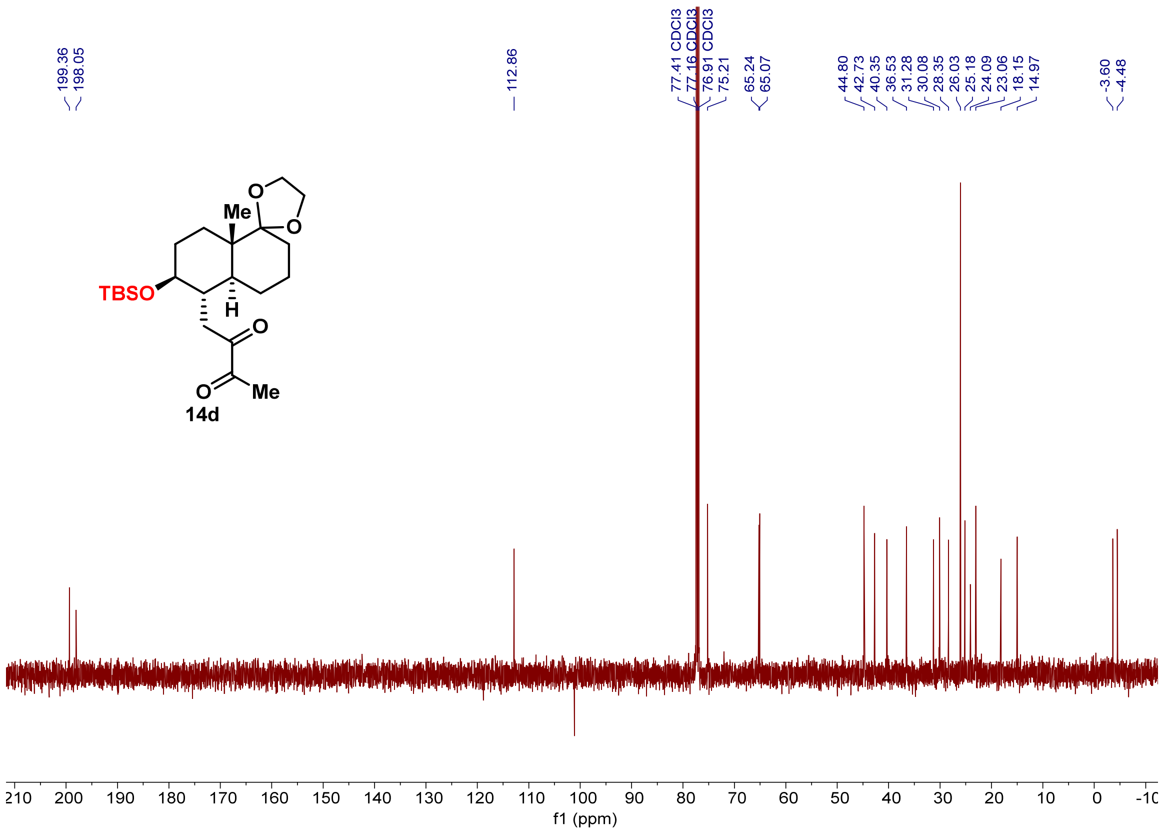


Figure S66. ^{13}C NMR Spectra of Compound **14d** ($CDCl_3$, 125 MHz)

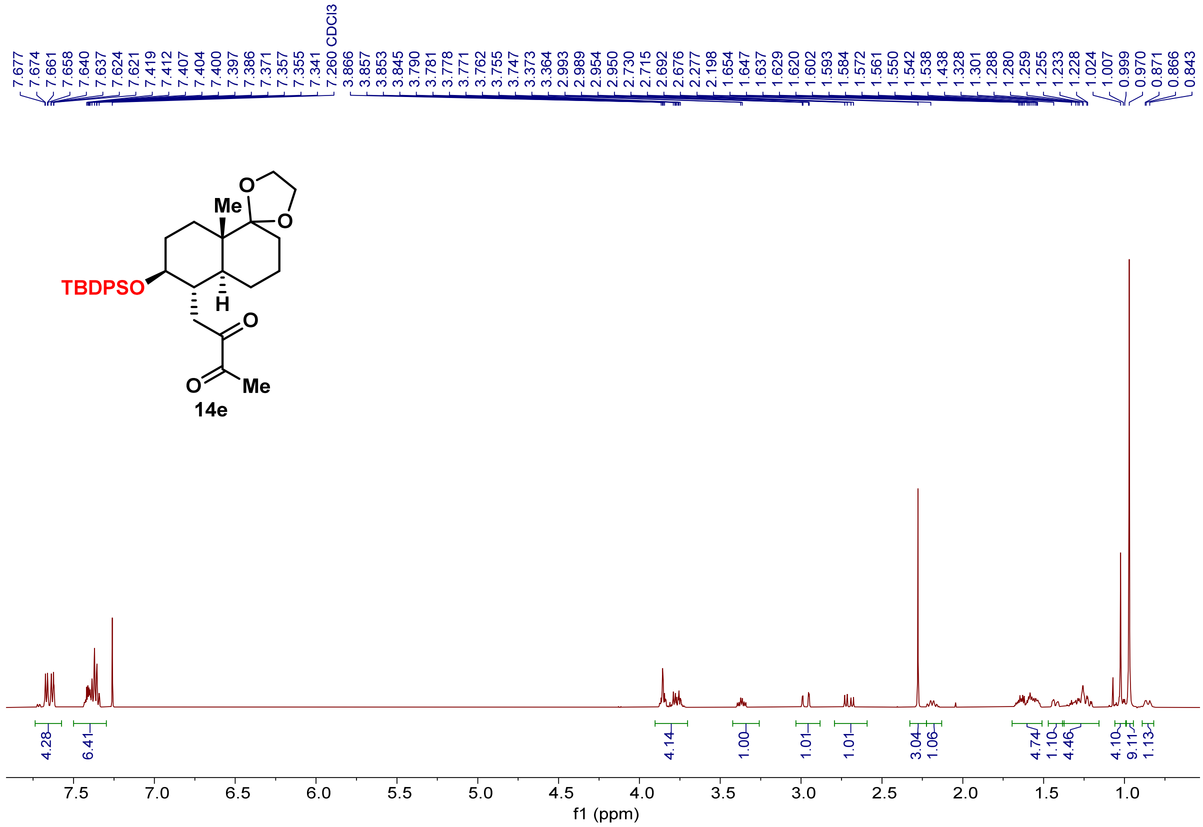


Figure S67. ^{1}H NMR Spectra of Compound **14e** ($CDCl_3$, 500 MHz)

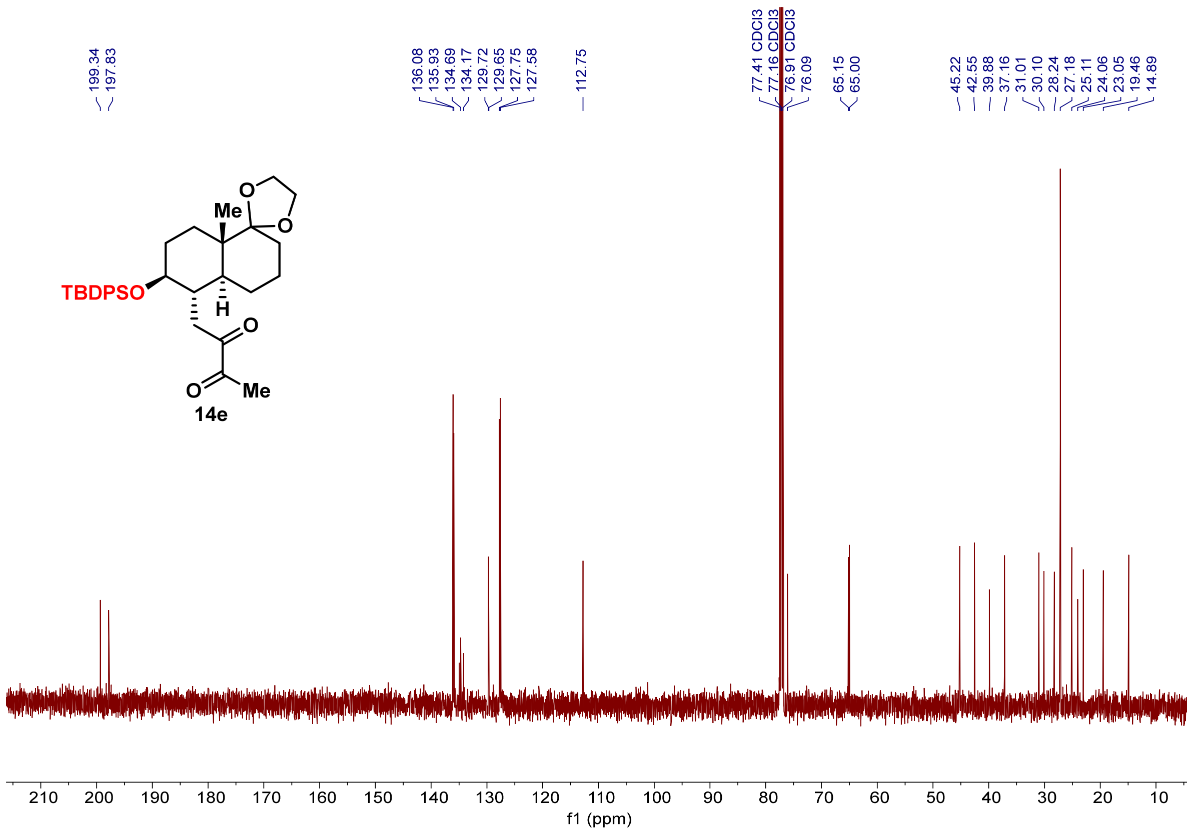


Figure S68. ^{13}C NMR Spectra of Compound **14e** ($CDCl_3$, 125 MHz)

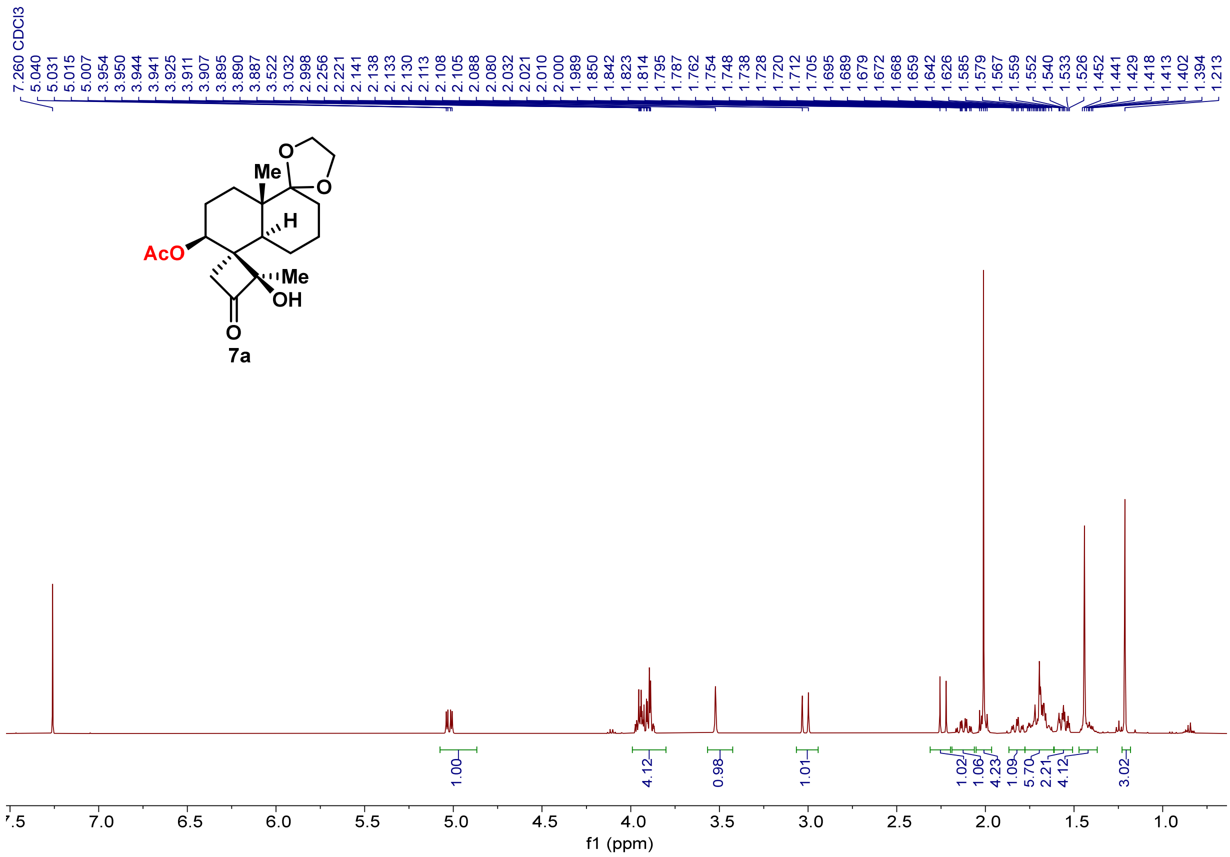


Figure S69. [1]H NMR Spectra of Compound **7a** ($CDCl_3$, 500 MHz)

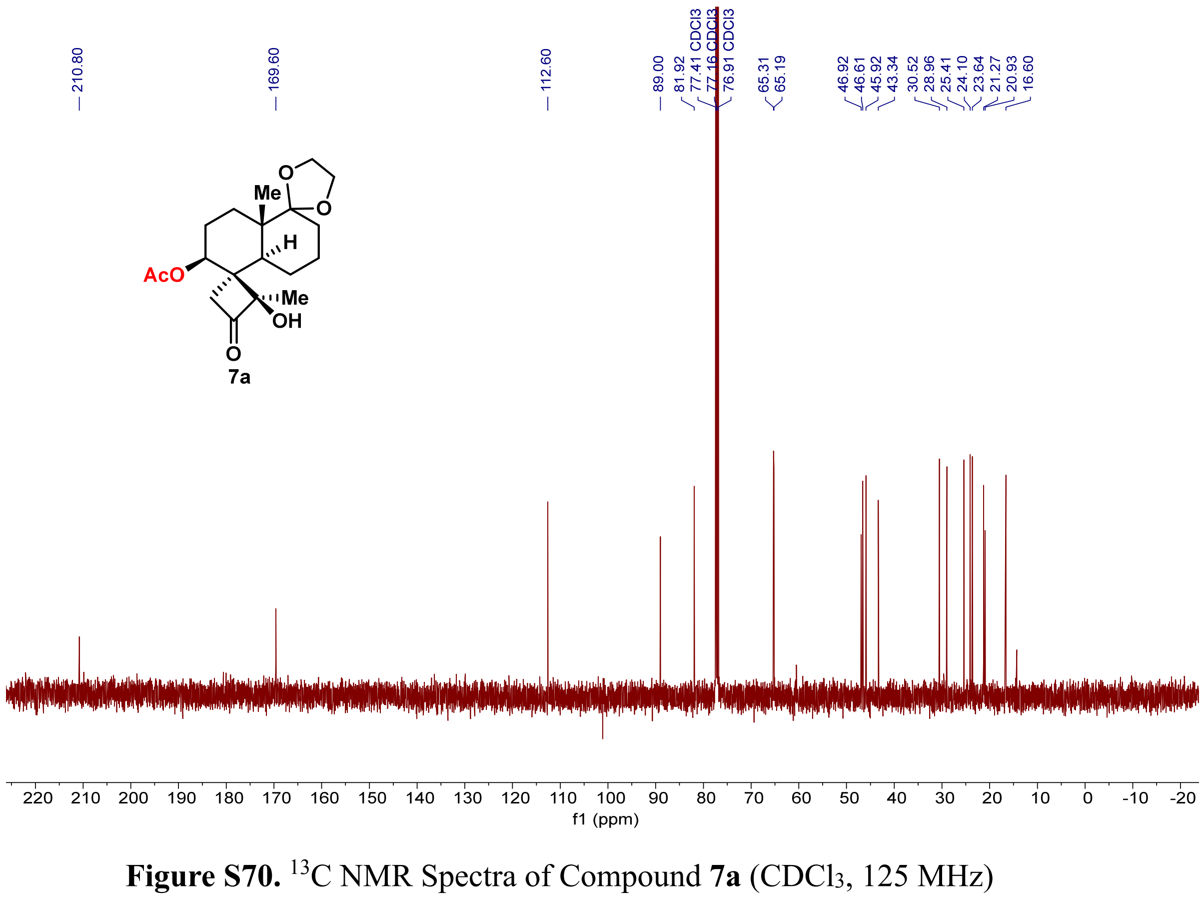


Figure S70. [13]C NMR Spectra of Compound **7a** ($CDCl_3$, 125 MHz)

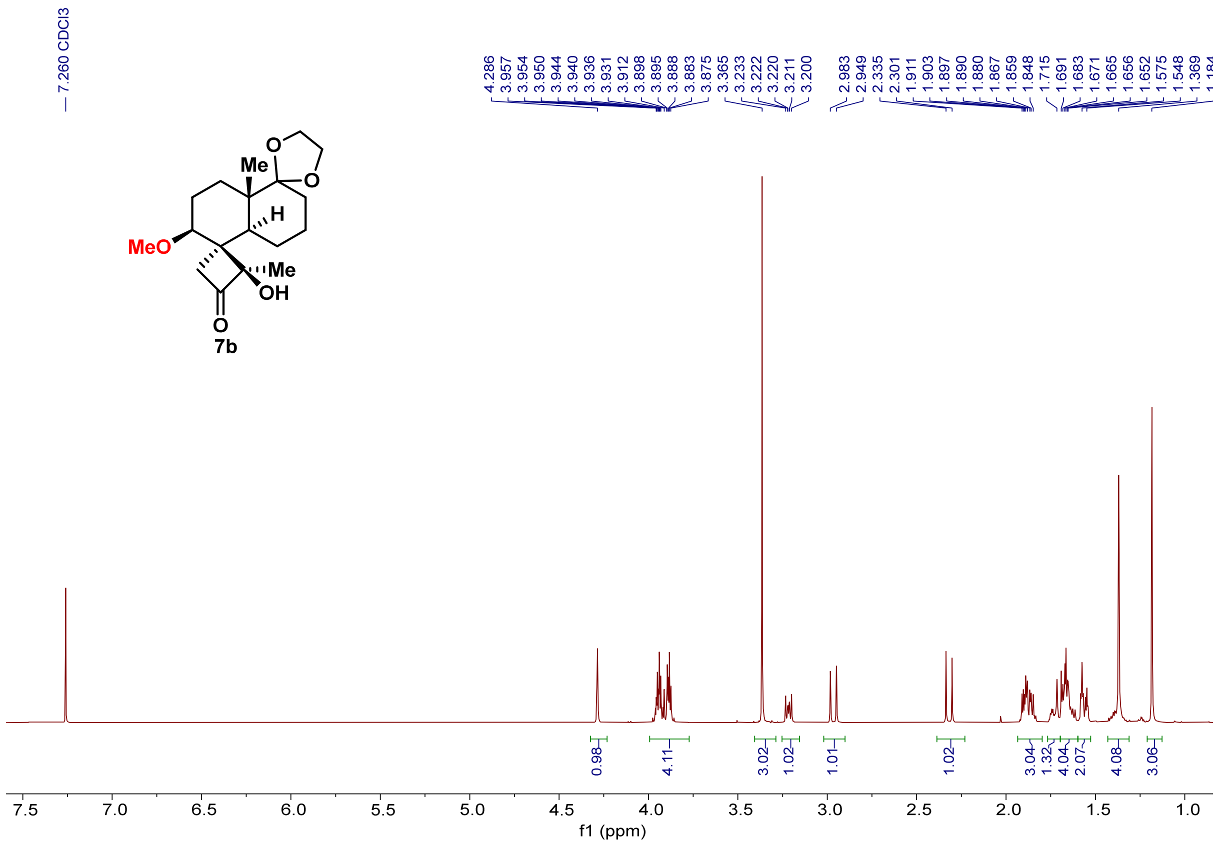


Figure S71. ^{1}H NMR Spectra of Compound **7b** ($CDCl_3$, 500 MHz)

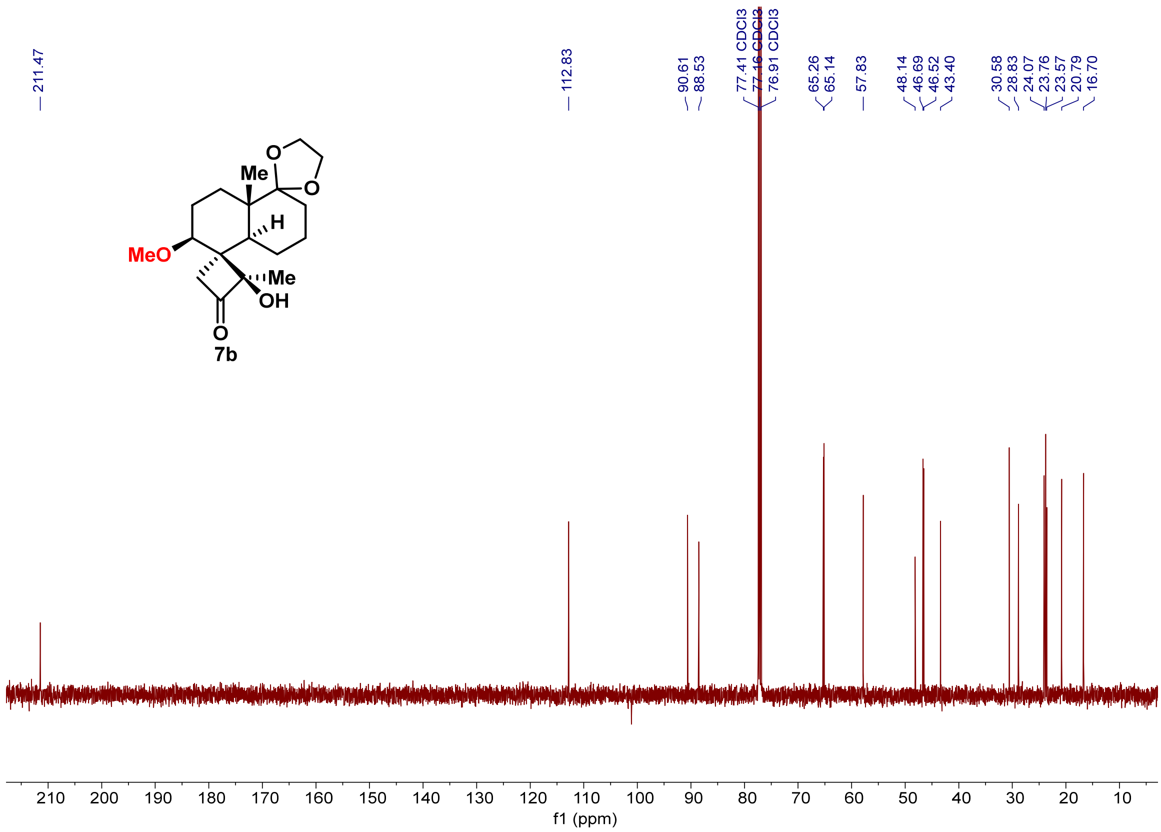


Figure S72. ^{13}C NMR Spectra of Compound **7b** ($CDCl_3$, 125 MHz)

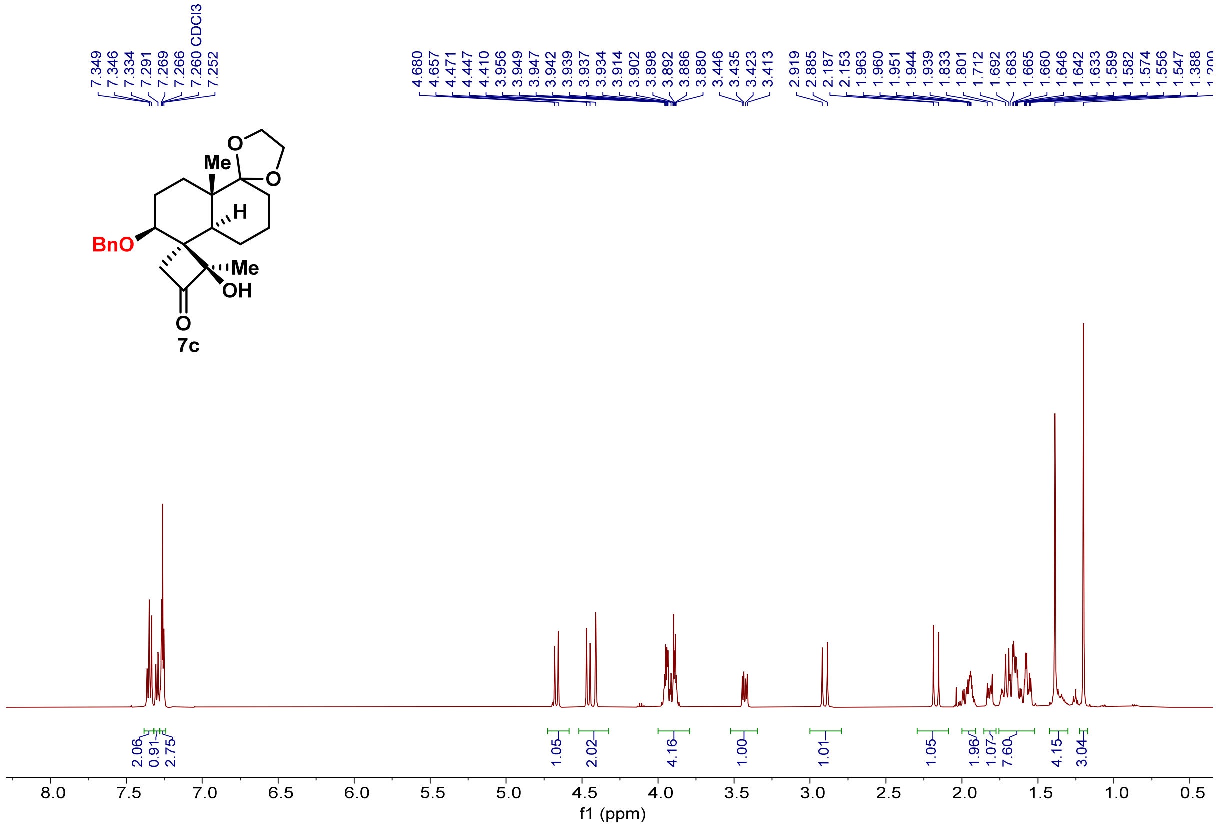


Figure S73. ^{1}H NMR Spectra of Compound **7c** ($CDCl_3$, 500 MHz)

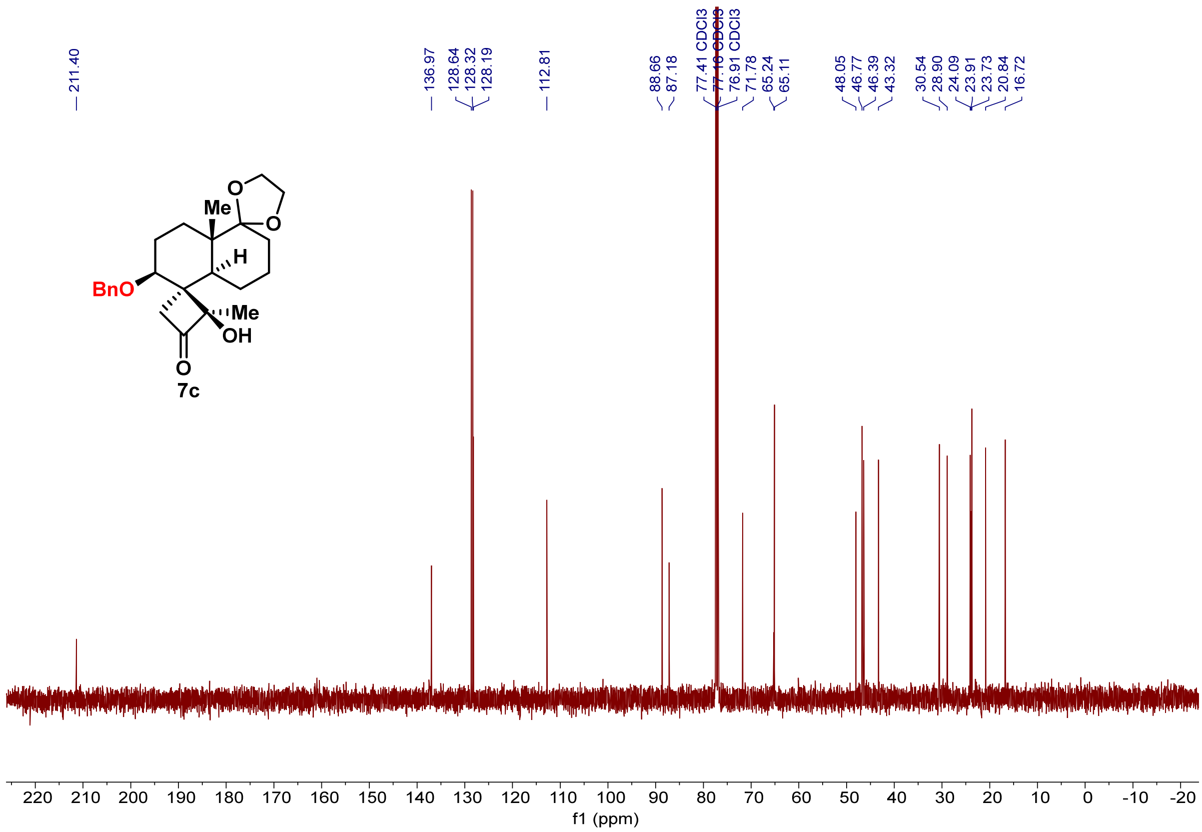


Figure S74. ^{13}C NMR Spectra of Compound **7c** ($CDCl_3$, 125 MHz)

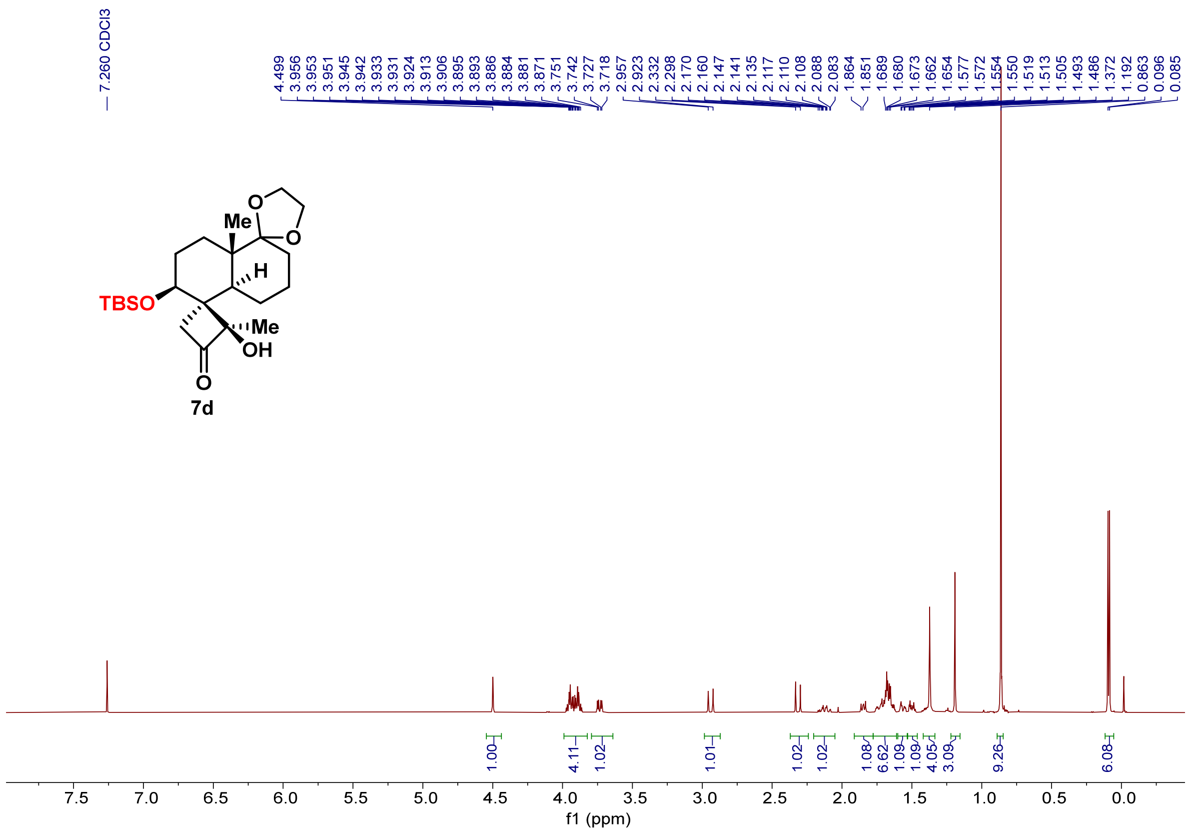


Figure S75. ^{1}H NMR Spectra of Compound **7d** ($CDCl_3$, 500 MHz)

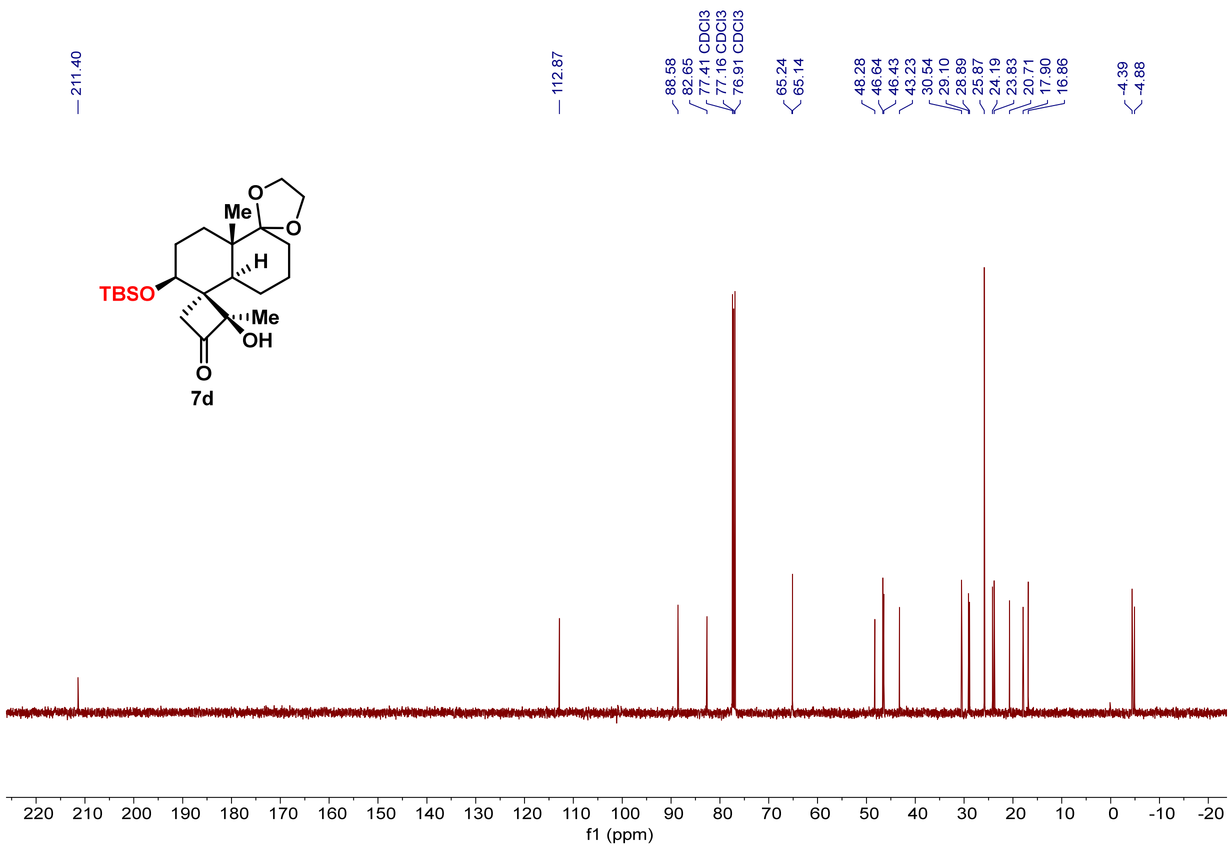


Figure S76. ^{13}C NMR Spectra of Compound **7d** ($CDCl_3$, 125 MHz)

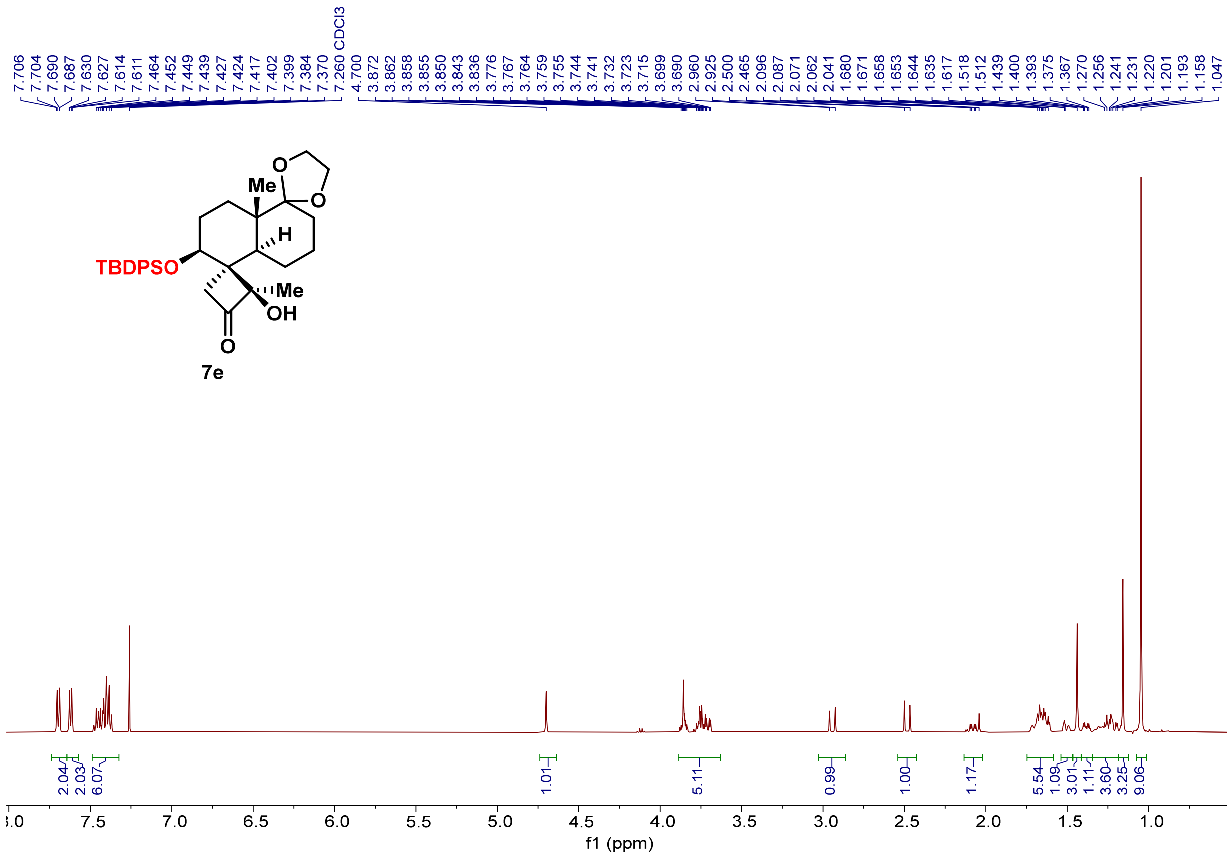


Figure S77. ^{1}H NMR Spectra of Compound **7e** ($CDCl_3$, 500 MHz)

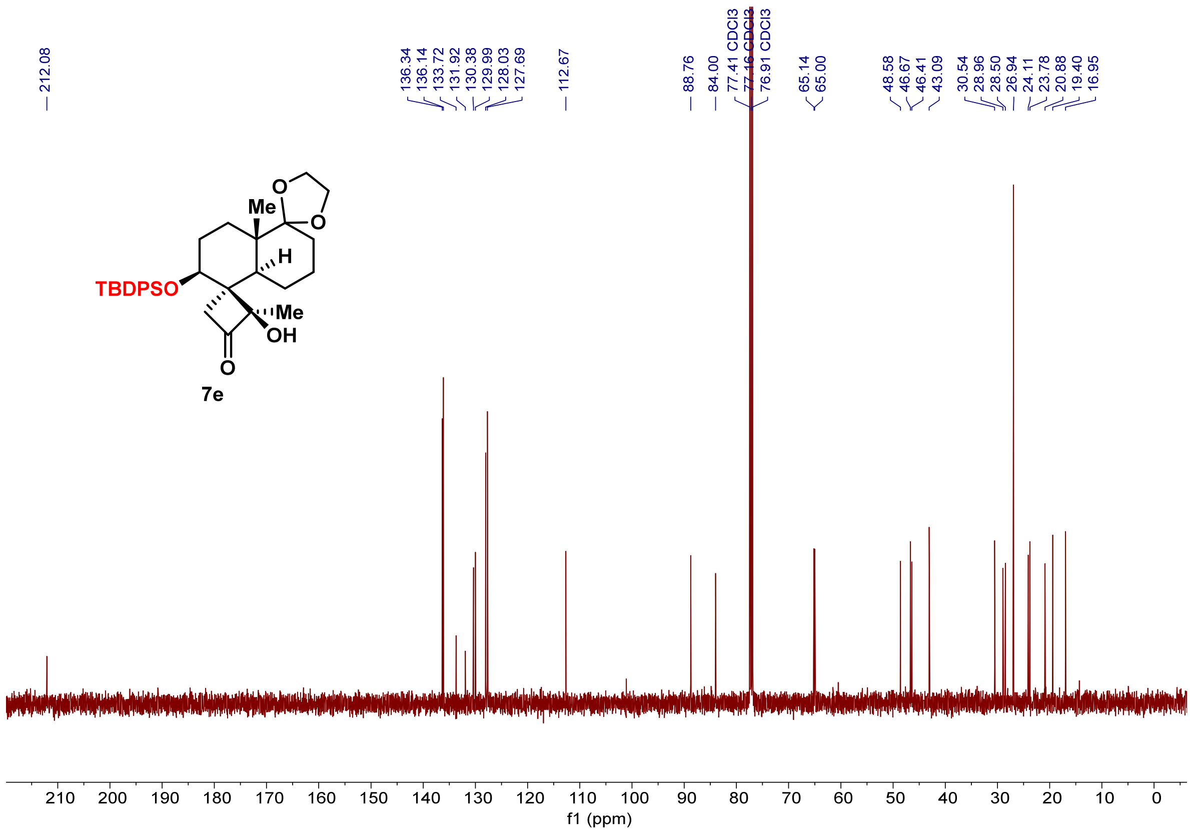


Figure S78. ^{13}C NMR Spectra of Compound **7e** ($CDCl_3$, 125 MHz)

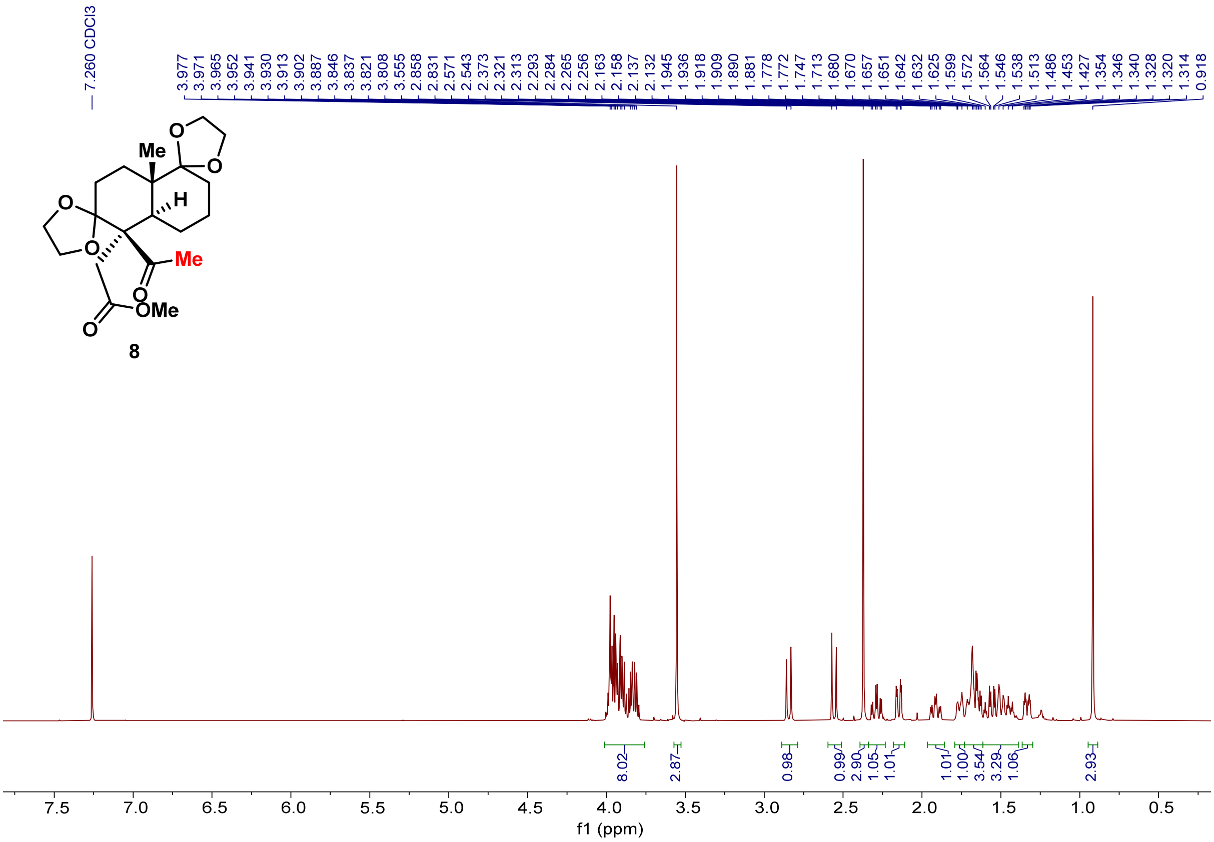


Figure S79. ^{1}H NMR Spectra of Compound **8** ($CDCl_3$, 500 MHz)

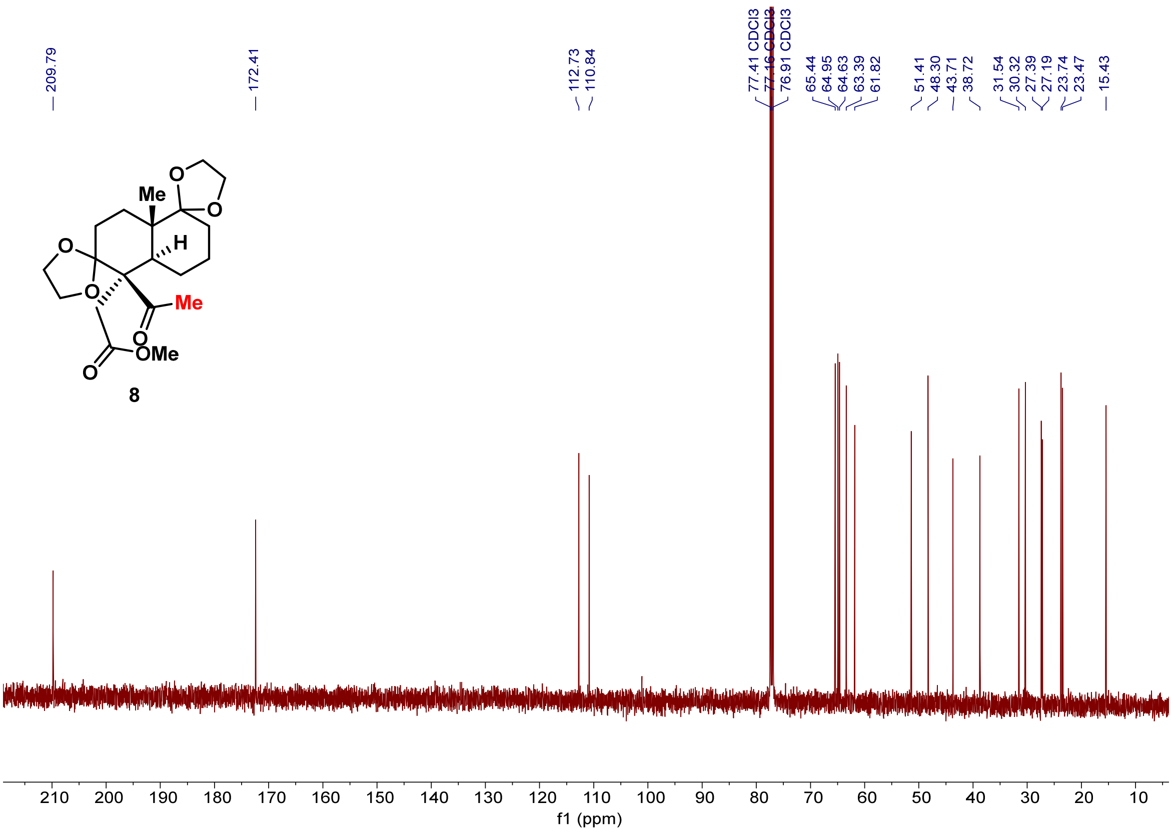


Figure S80. ^{13}C NMR Spectra of Compound **8** ($CDCl_3$, 125 MHz)

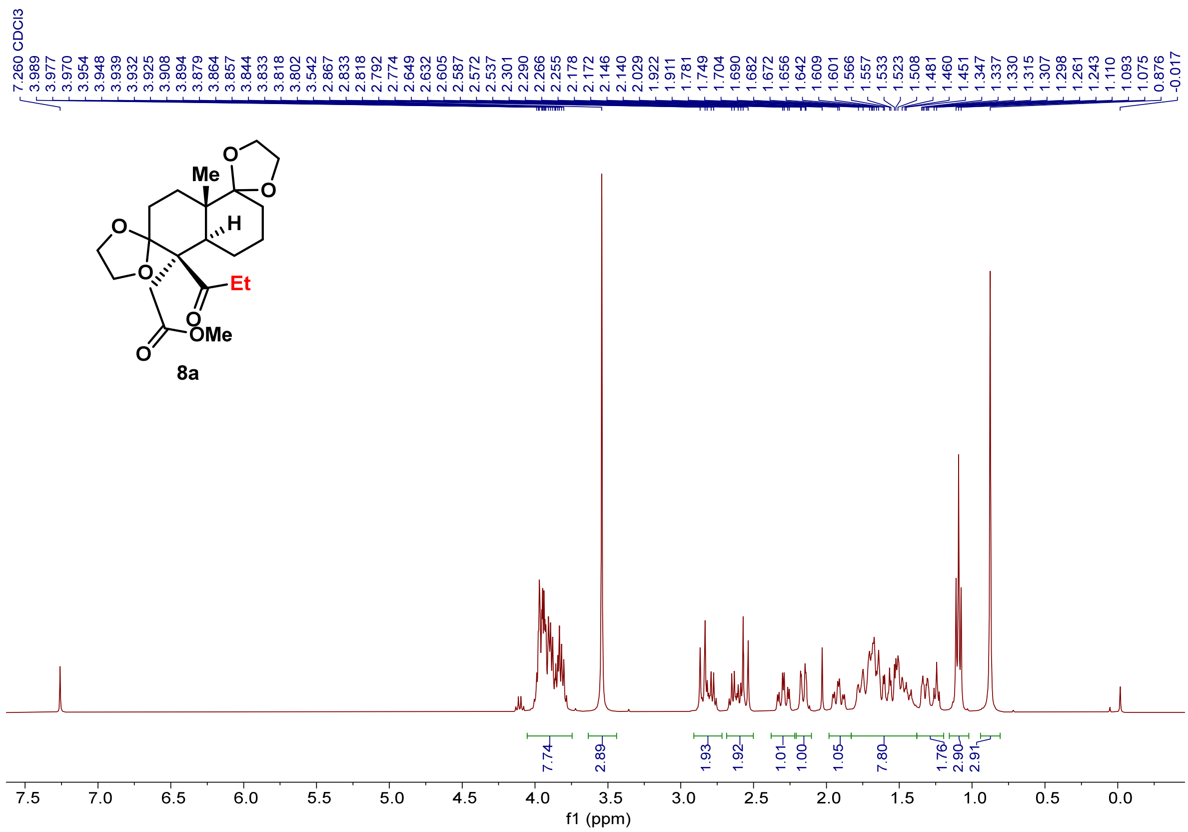


Figure S81. ^{1}H NMR Spectra of Compound **8a** ($CDCl_3$, 400 MHz)

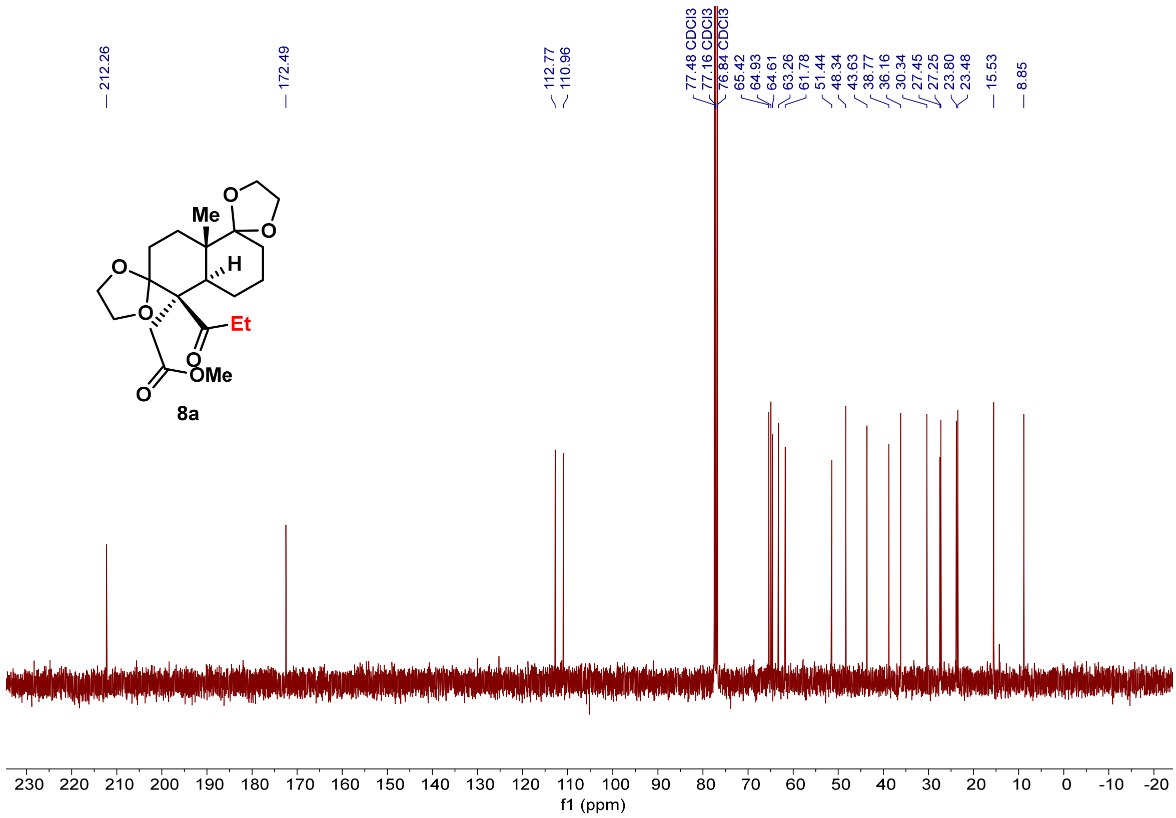


Figure S82. ^{13}C NMR Spectra of Compound **8a** ($CDCl_3$, 100 MHz)

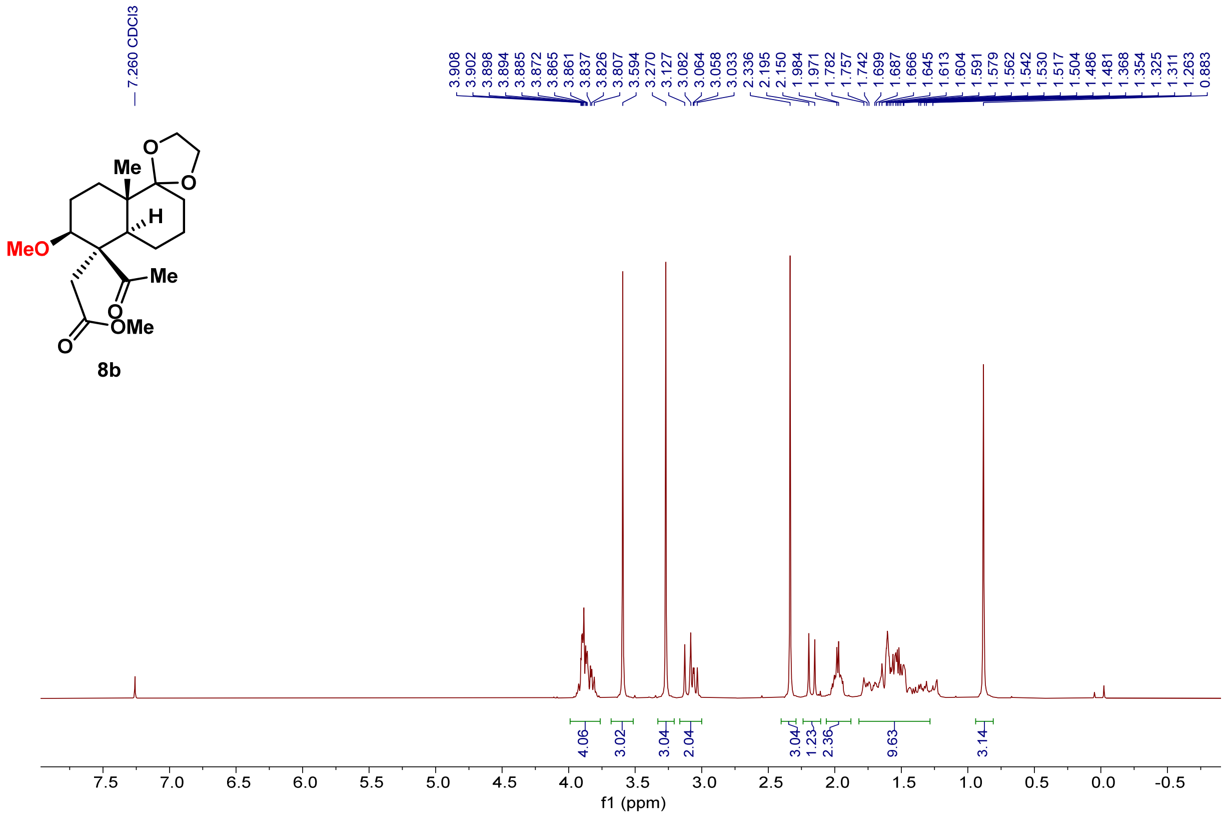


Figure S83. ^{1}H NMR Spectra of Compound **8b** ($CDCl_3$, 300 MHz)

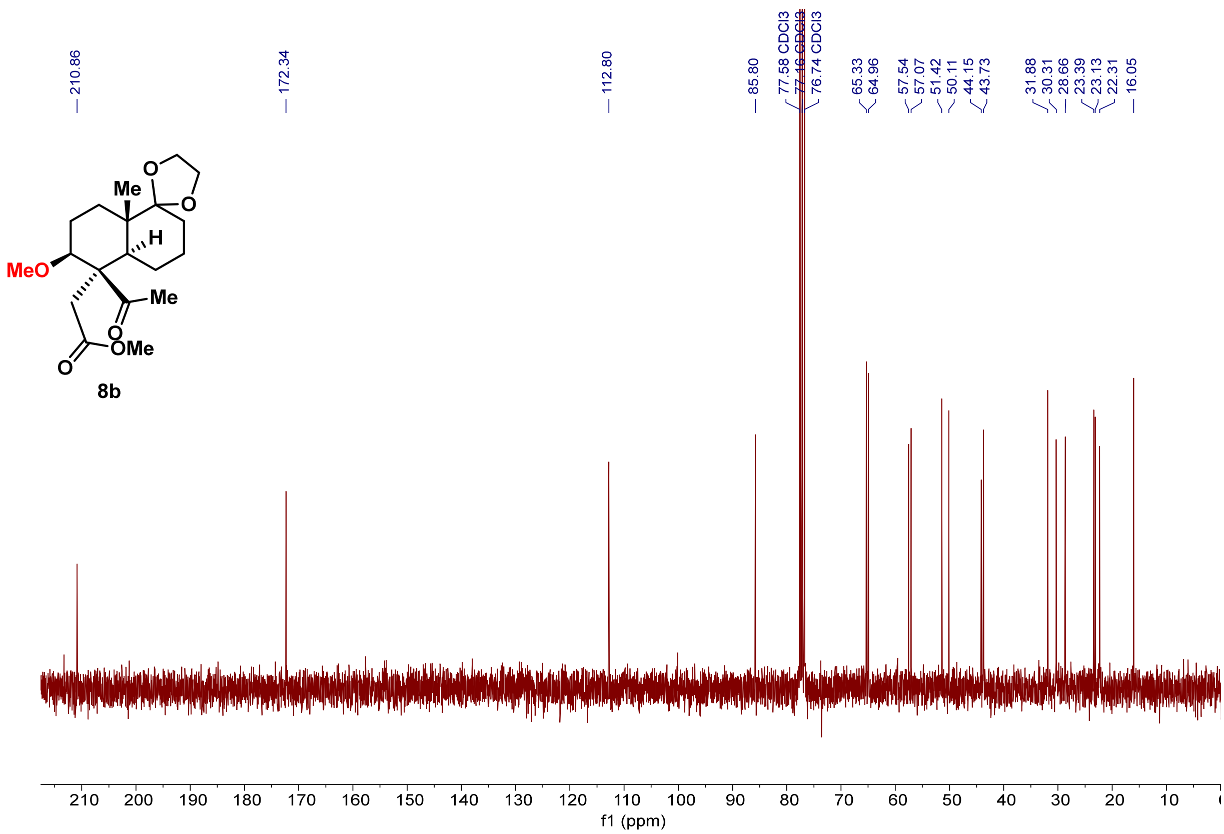


Figure S84. ^{13}C NMR Spectra of Compound **8b** ($CDCl_3$, 75 MHz)

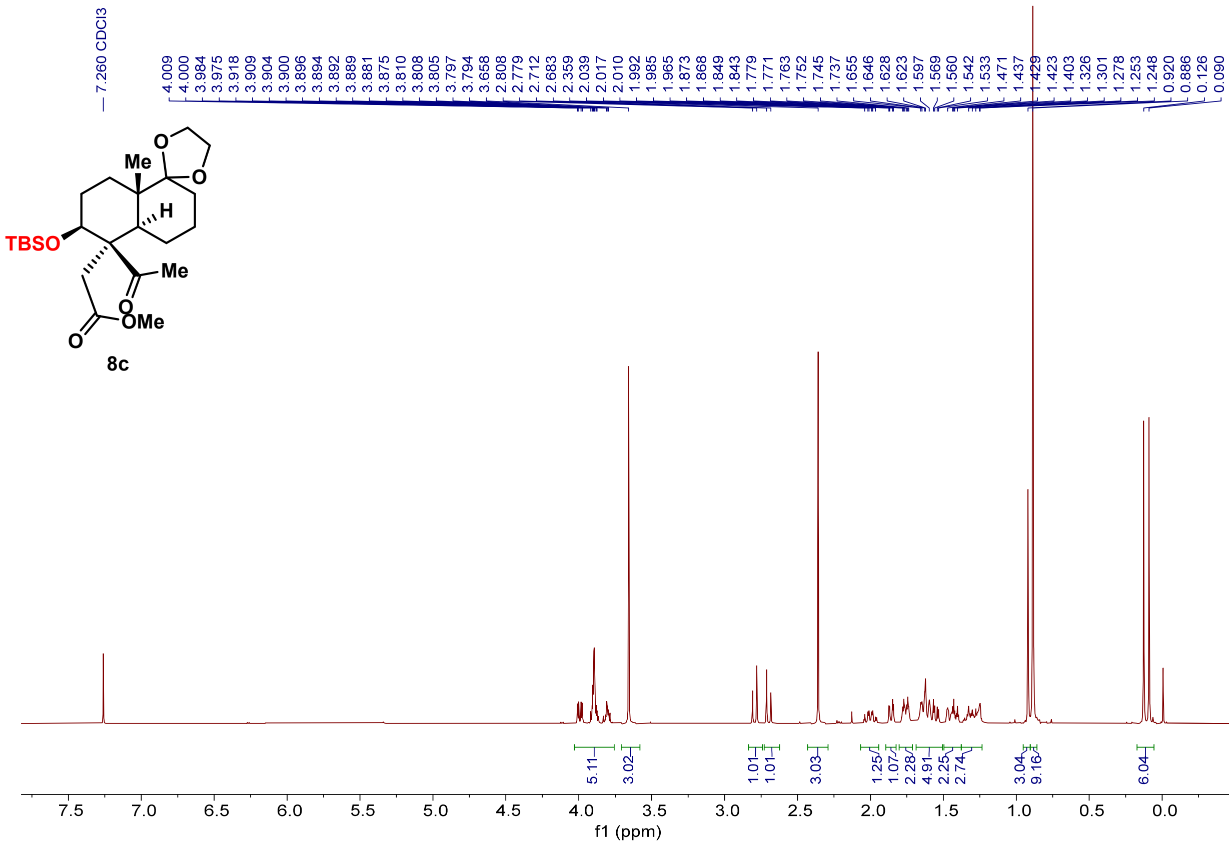


Figure S85. ^{1}H NMR Spectra of Compound **8c** ($CDCl_3$, 500 MHz)

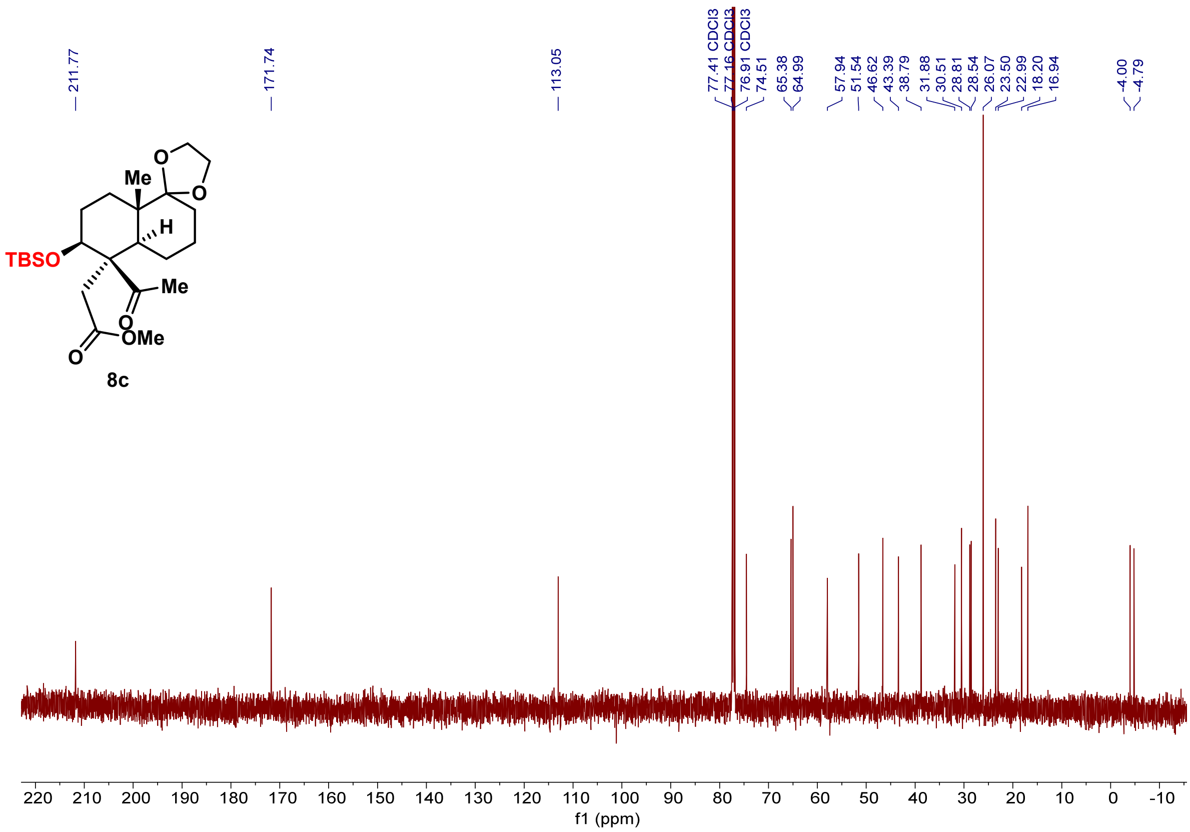


Figure S86. ^{13}C NMR Spectra of Compound **8c** ($CDCl_3$, 125 MHz)

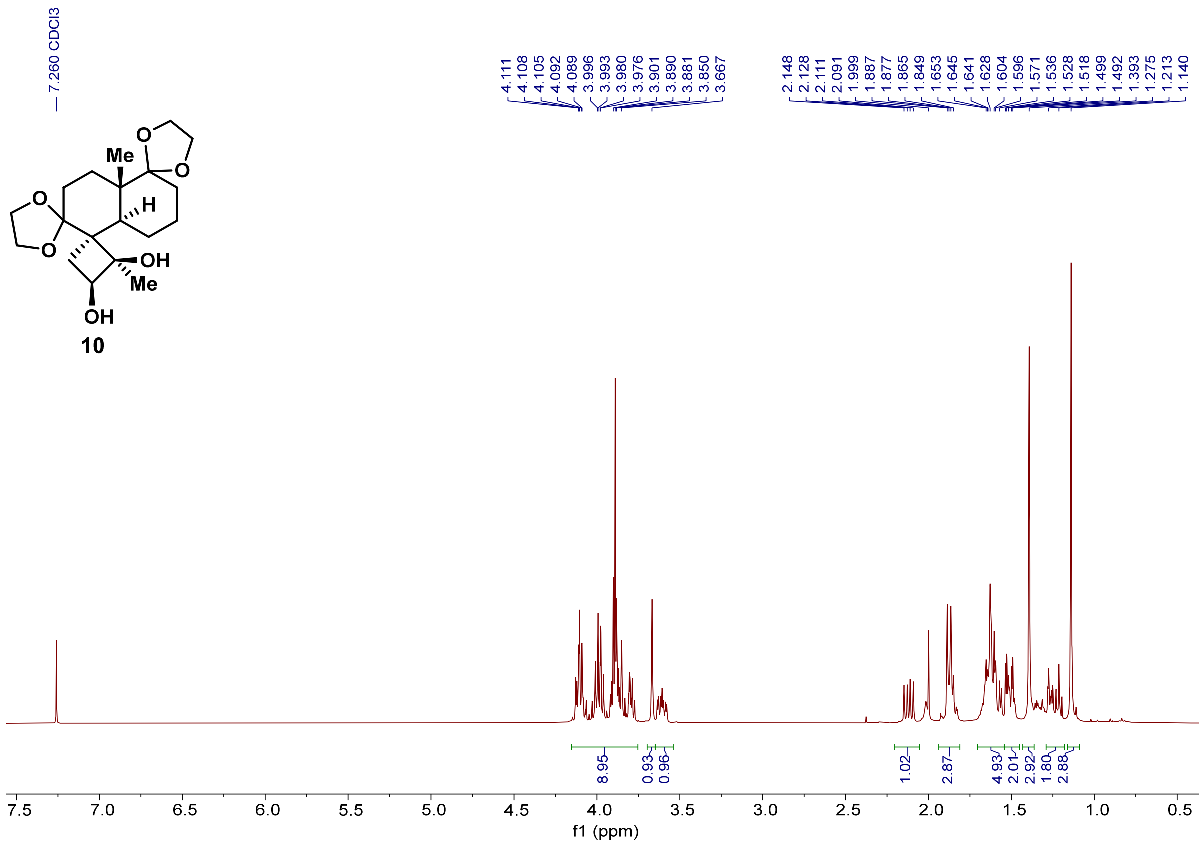


Figure S87. ^1H NMR Spectra of Compound **10** ($CDCl_3$, 300 MHz)

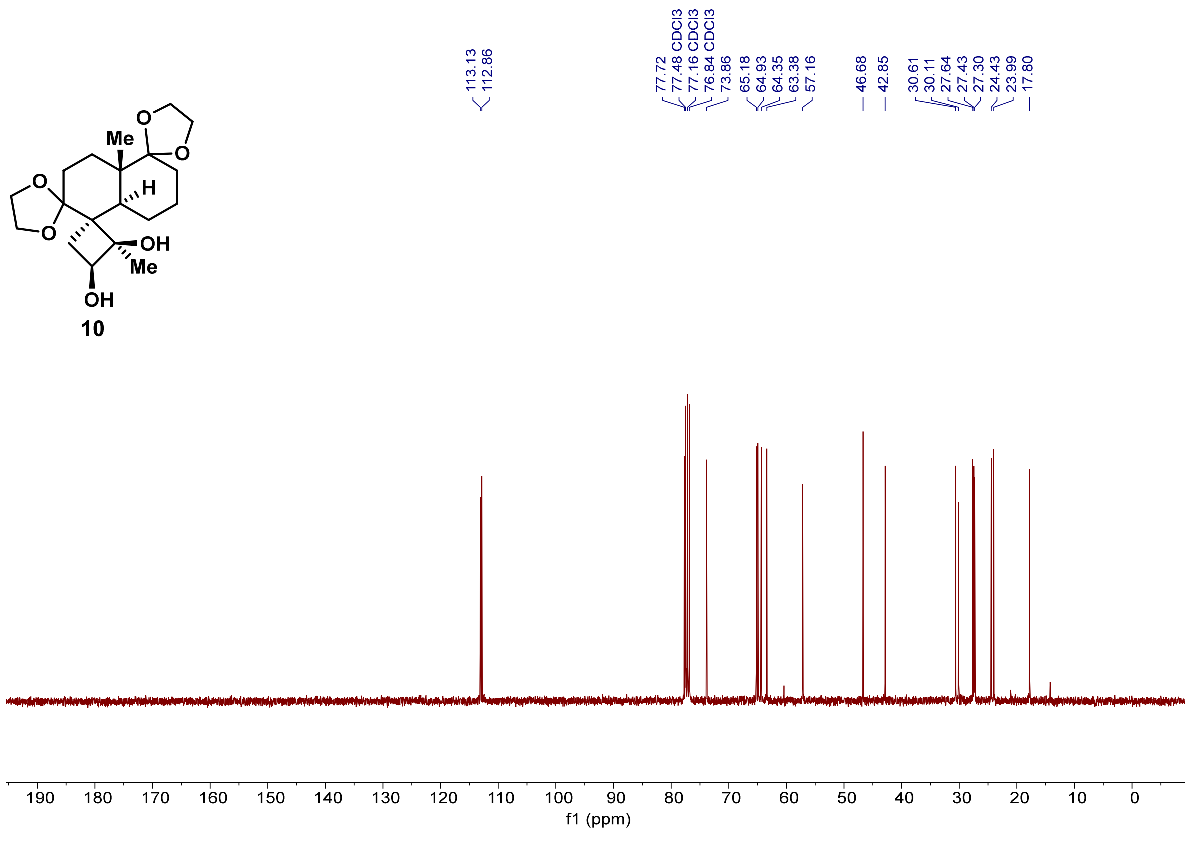


Figure S88. ^{13}C NMR Spectra of Compound **10** ($CDCl_3$, 100 MHz)

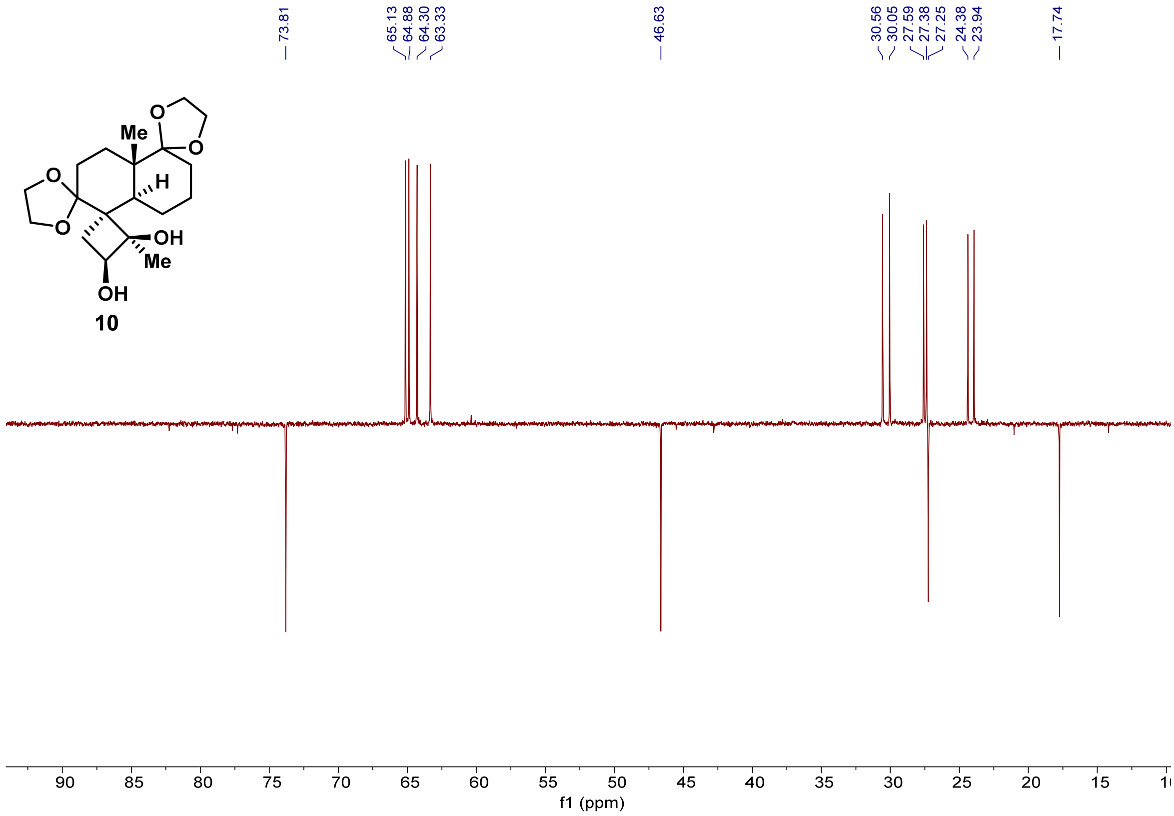


Figure S89. DEPT NMR Spectra of Compound **10** ($CDCl_3$, 100 MHz)

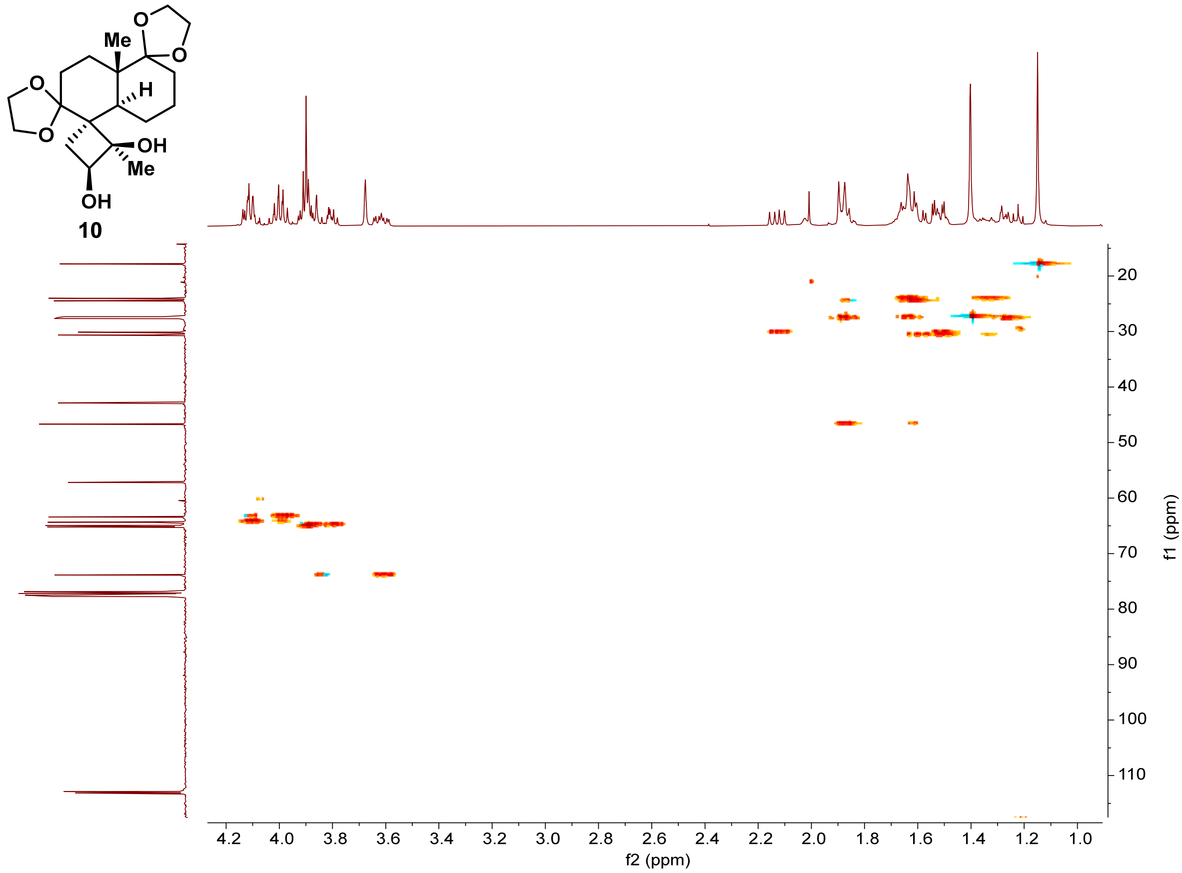


Figure S90. HSQC Spectra of Compound **10** ($CDCl_3$, 400 MHz)

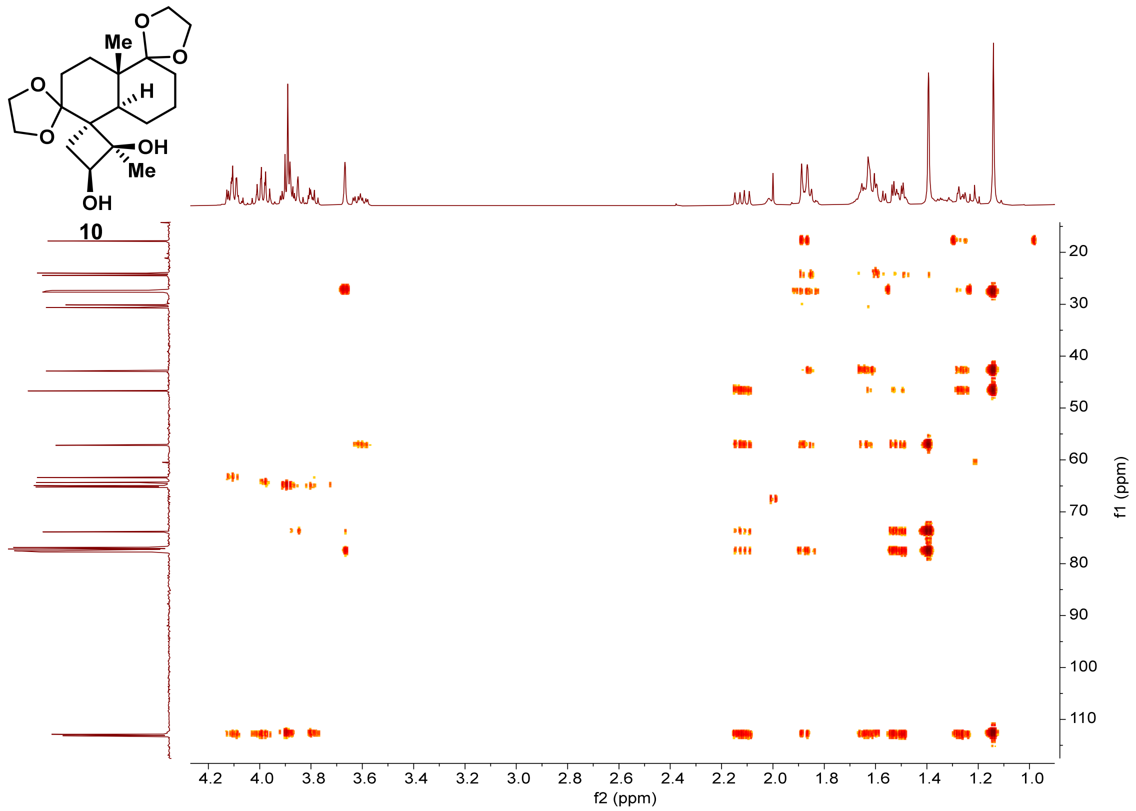


Figure S91. HMBC Spectra of Compound **10** ($CDCl_3$, 400 MHz)

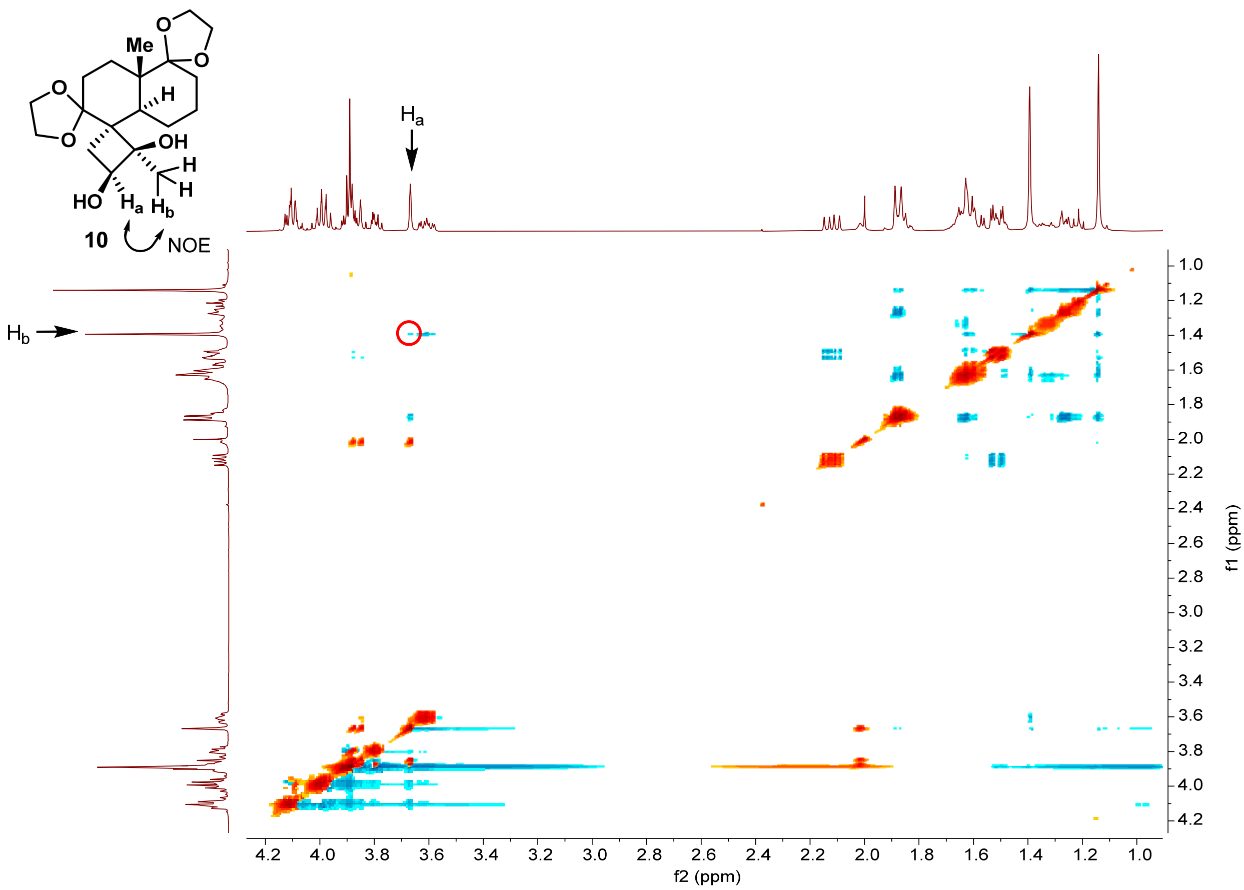


Figure S92. NOESY Spectra of Compound **10** ($CDCl_3$, 400 MHz)

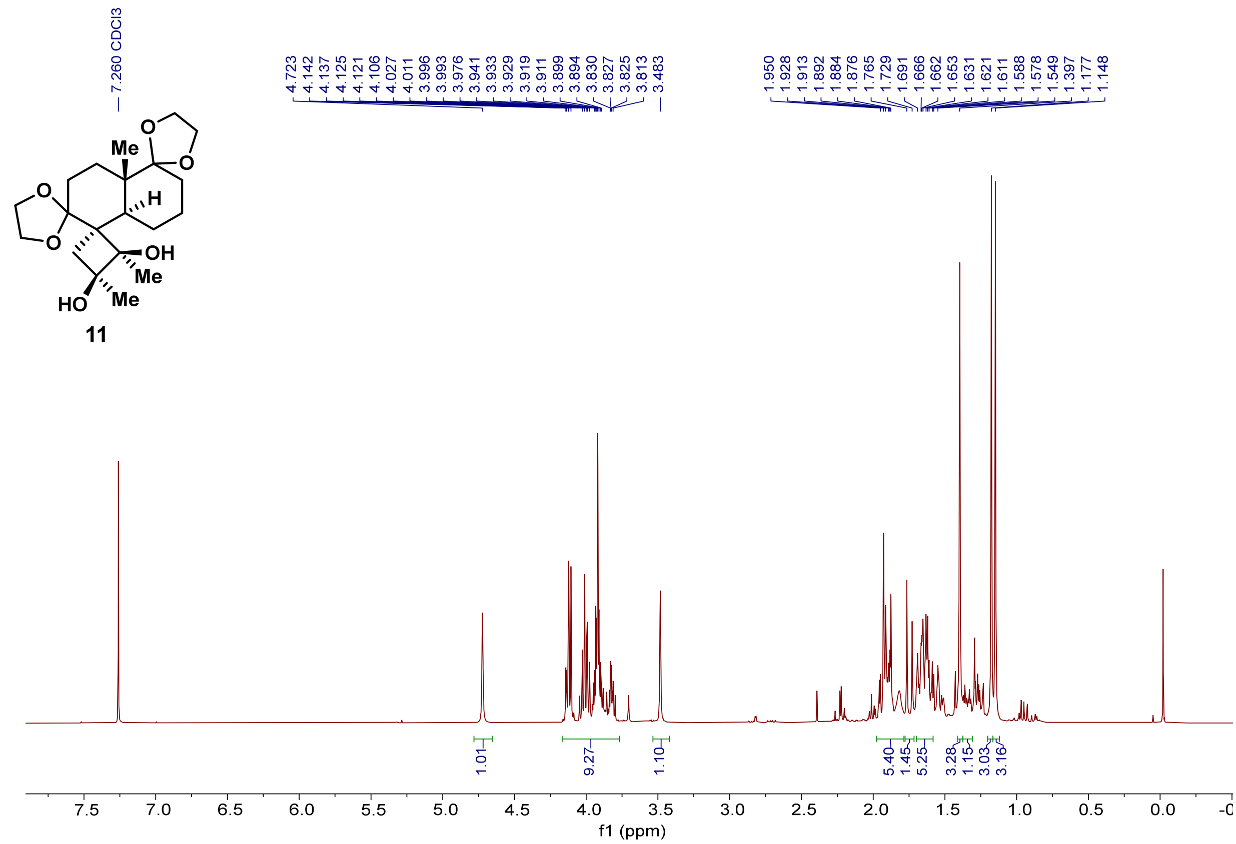


Figure S93. ^{1}H NMR Spectra of Compound **11** ($CDCl_3$, 400 MHz)

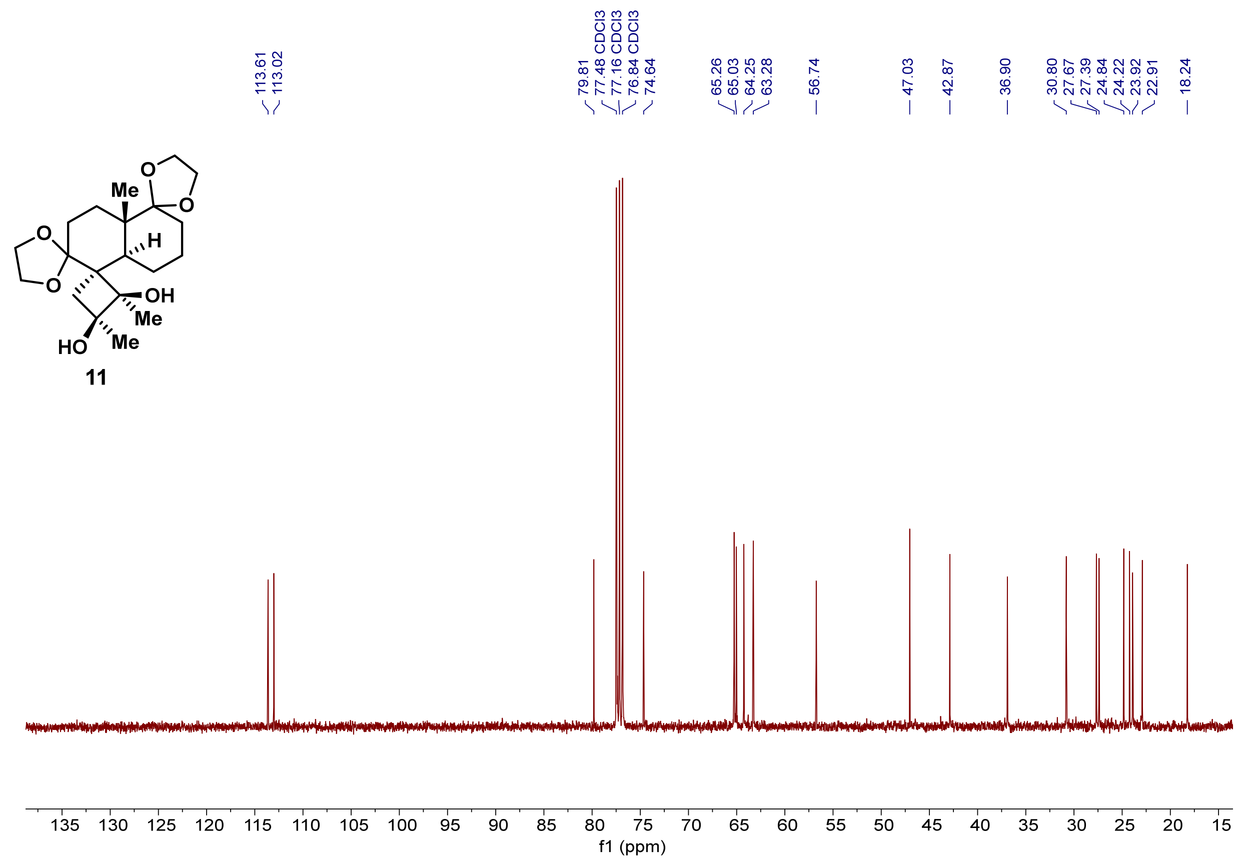


Figure S94. ^{13}C NMR Spectra of Compound **11** ($CDCl_3$, 100 MHz)

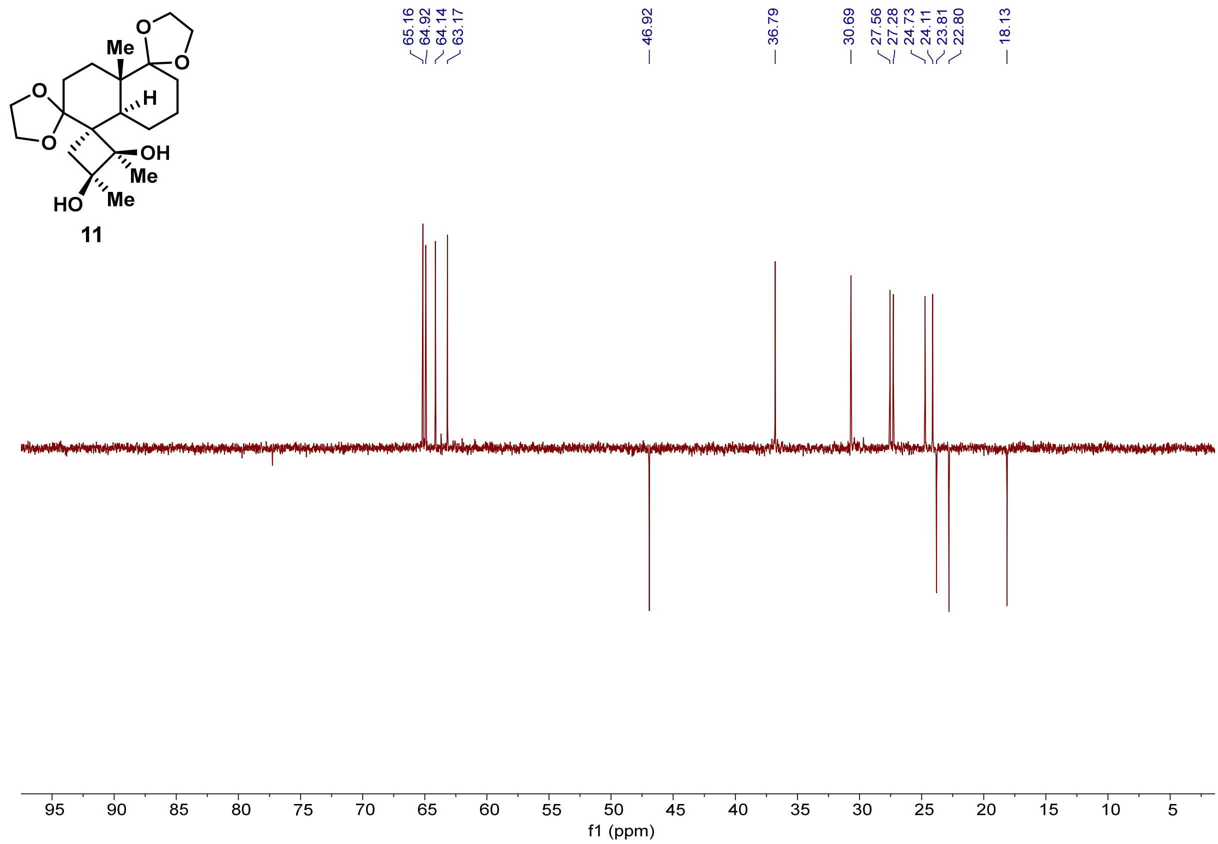


Figure S95. DEPT Spectra of Compound **11** ($CDCl_3$, 100 MHz)

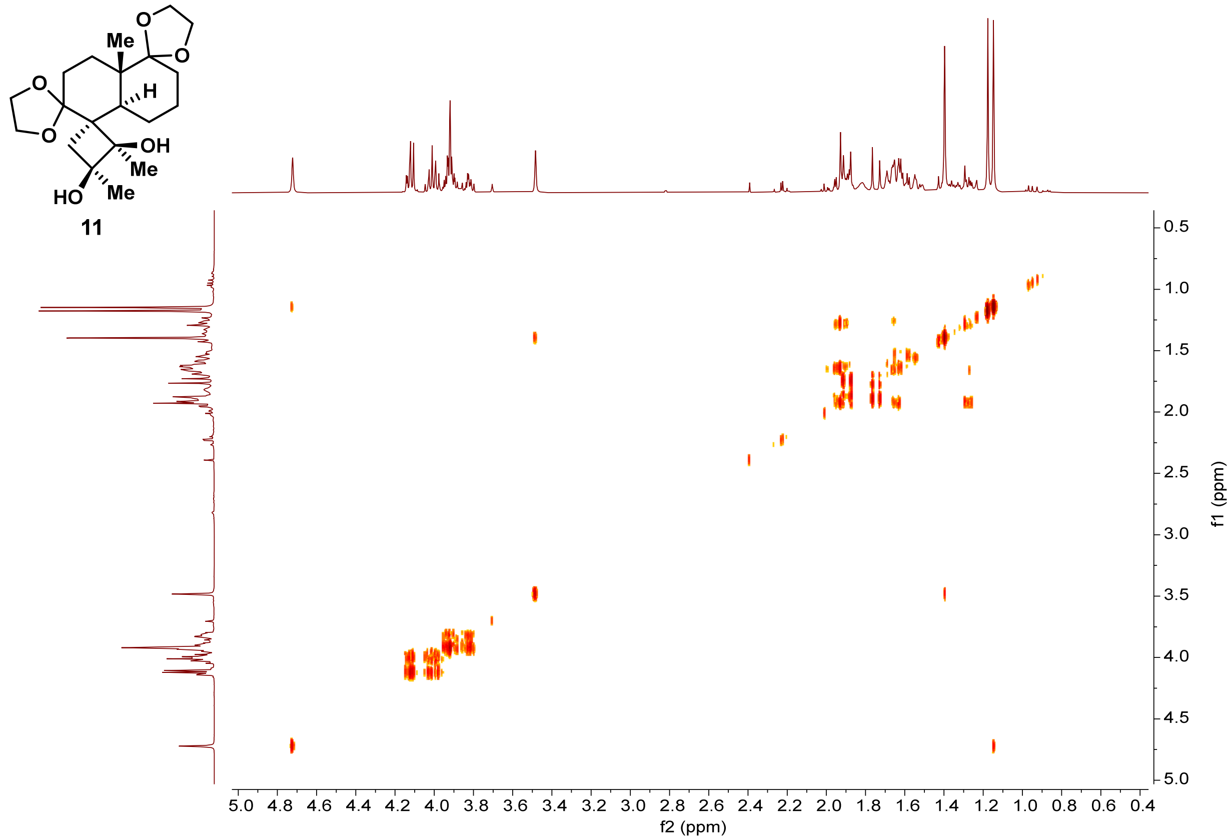


Figure S96. COSY Spectra of Compound **11** ($CDCl_3$, 400 MHz)

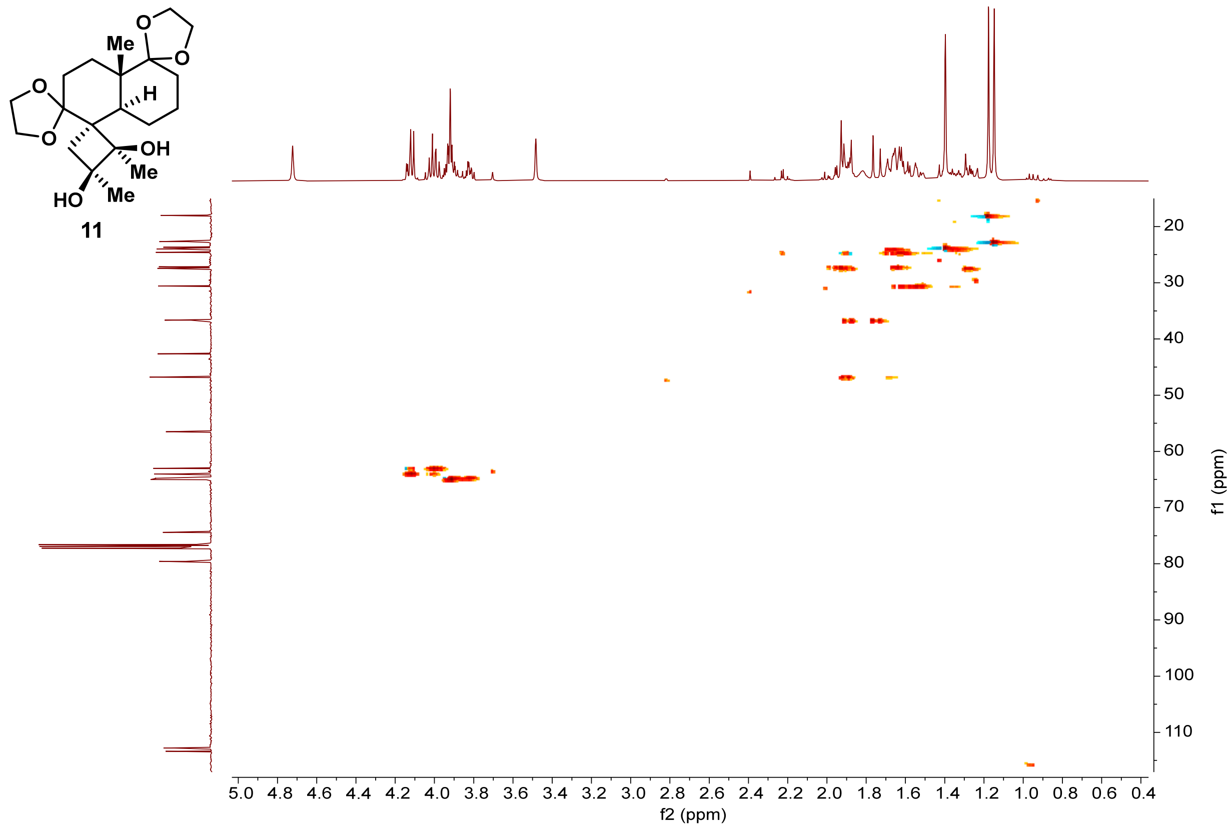


Figure S97. HSQC Spectra of Compound **11** ($CDCl_3$, 400 MHz)

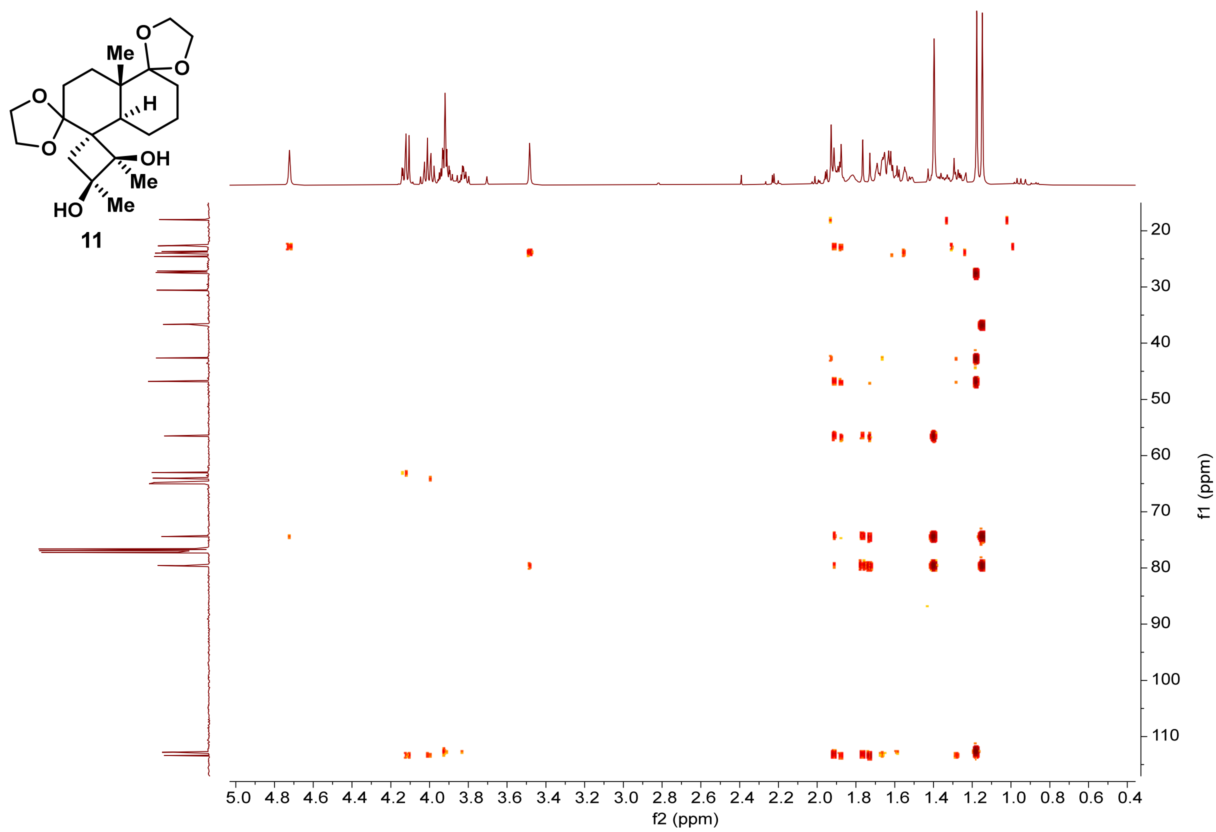
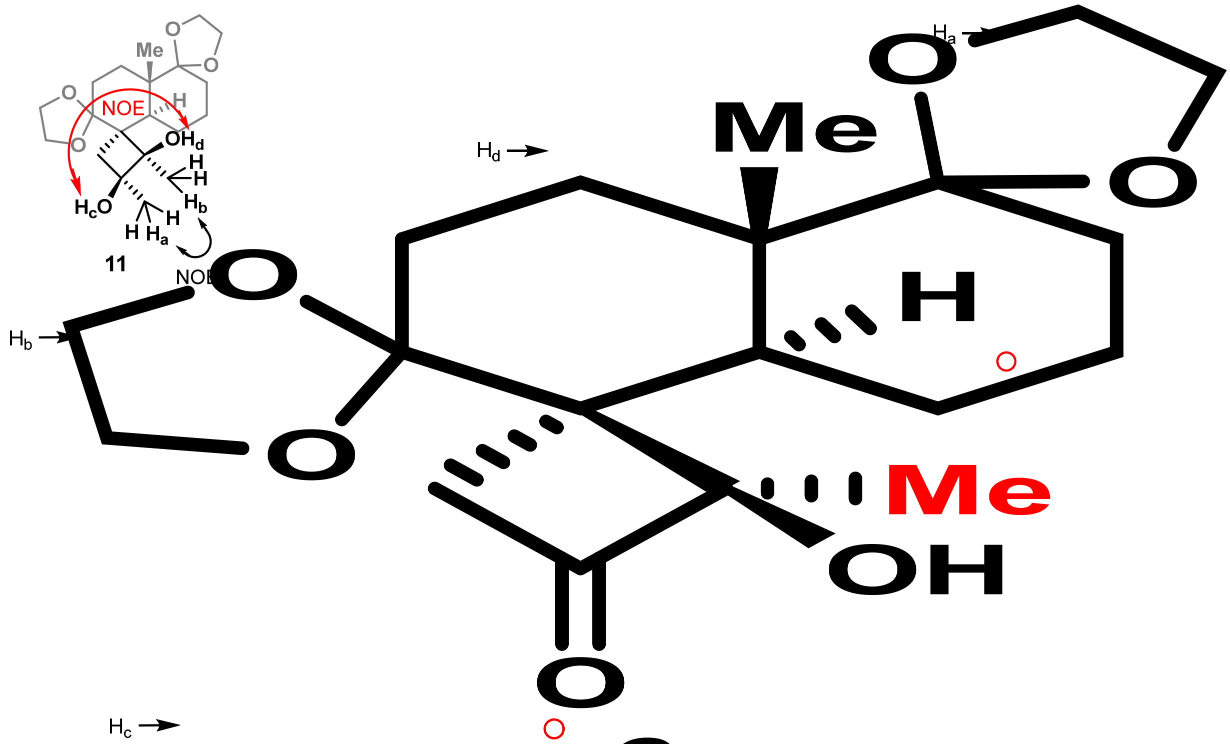
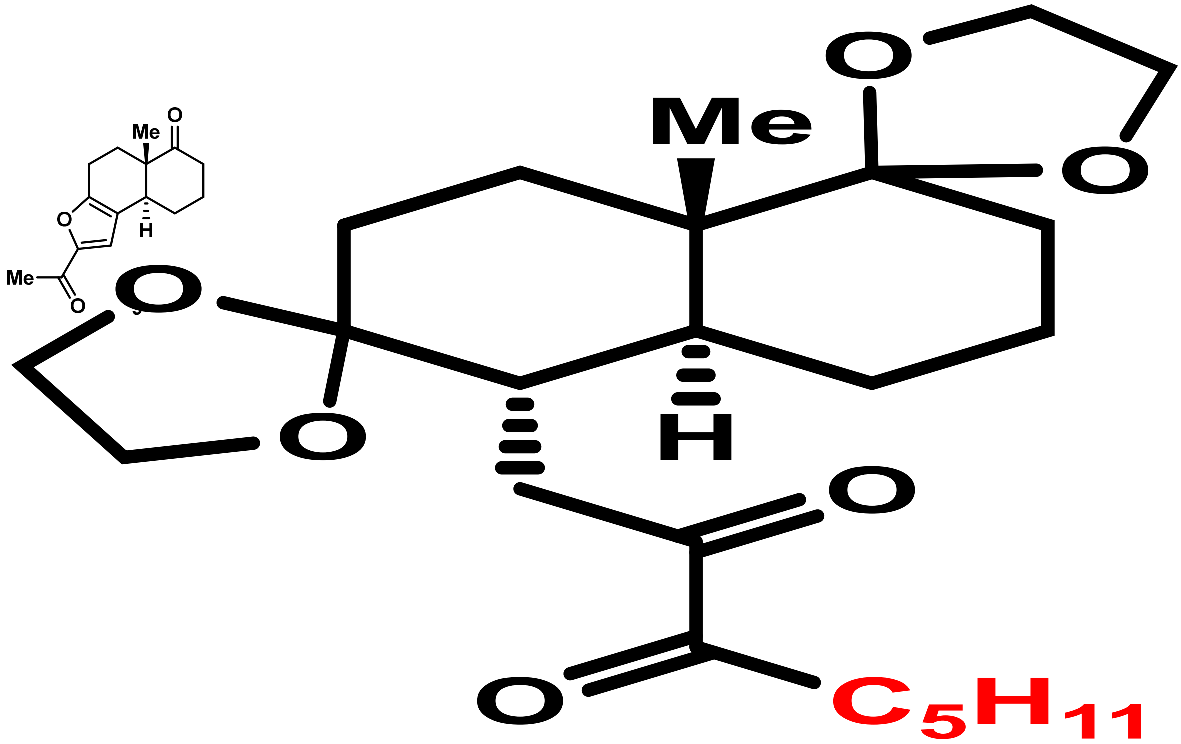


Figure S98. HMBC Spectra of Compound **11** ($CDCl_3$, 400 MHz)



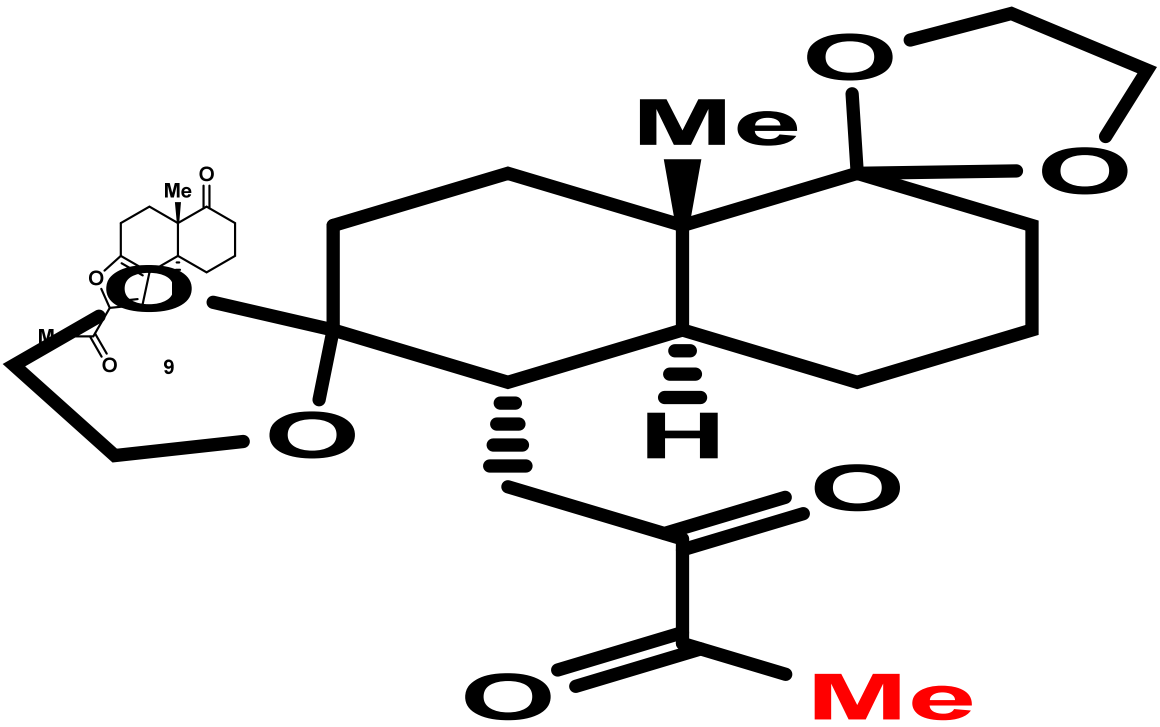
6

Figure S99. NOESY Spectra of Compound **11** (CDCl3, 400 MHz)



5b

Figure S100. ^{1}H NMR Spectra of Compound **9** (CDCl3, 500 MHz)



5

Figure S101. ^{13}C NMR Spectra of Compound **9** ($CDCl_3$, 125 MHz)

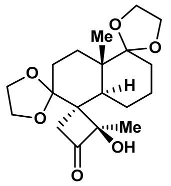
Part V: X-ray Crystal Images

X-ray Crystallography Data of **6**

CCDC 2002822 contains the supplementary crystallographic data for **6**. The XRD sample of **6** was prepared by slow evaporation from a CH_2Cl_2/hexane (1:3) solution at room temperature. The absolute and relative configurations of **6** was unambiguously assigned from the XRD analysis. The crystal parameters are depicted in **Table S4**.

Table S4. Crystal data and structure refinement for **6**.

Identification code	**6**
Empirical formula	$C_{19}H_{28}O_6$
Formula weight	352.41
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.17106 (13)
b/Å	34.8703 (6)
c/Å	9.23924 (15)
α/°	90
β/°	91.1734(15)
γ/°	90
Volume/Å^3	2631.96(8)
Z	6
ρ_{calc}g/cm^3	1.334
μ/mm^{-1}	0.809
F(000)	1140.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.068 to 147.102
Index ranges	$-10 \leq h \leq 9$, $-42 \leq k \leq 36$, $-11 \leq l \leq 8$
Reflections collected	10571
Independent reflections	7622 [R_{int} = 0.0191, R_{sigma} = 0.0307]
Data/restraints/parameters	7622/1/691
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0346, wR_2 = 0.0905
Final R indexes [all data]	R_1 = 0.0350, wR_2 = 0.0908
Largest diff. peak/hole / e Å^{-3}	0.26/-0.43
Flack/Hooft parameter	0.01(6)



6

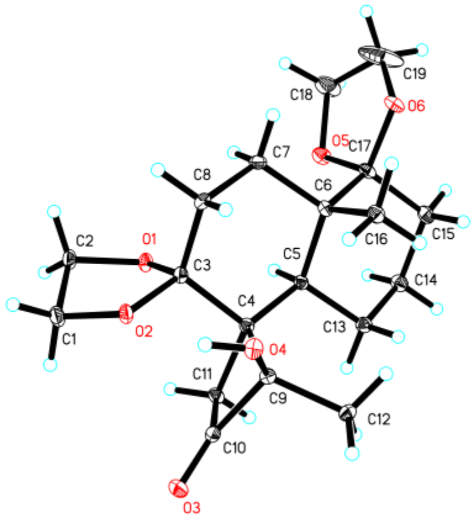


Figure S102. X-ray crystallographic structure of **6**.

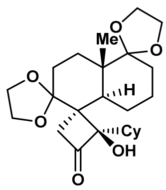
X-ray Crystallography Data of **6c**

CCDC 2002823 contains the supplementary crystallographic data for **6c**. The XRD sample of **6c** was prepared by slow evaporation from a CH_2Cl_2/hexane (1:3) solution at room temperature. The absolute and relative configurations of **6c** was unambiguously assigned from the XRD analysis. The crystal parameters are depicted in **Table S5**.

Table S5. Crystal data and structure refinement for **6c**.

Identification code	**6c**
Empirical formula	$C_{24}H_{36}O_6$
Formula weight	420.53
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.08181(13)
b/Å	10.73068(14)
c/Å	24.3476(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2111.51(5)
Z	4
ρ_{calc}g/cm^3	1.323
μ/mm^{-1}	0.759
F(000)	912.0
Crystal size/mm^3	0.13 × 0.11 × 0.08
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.262 to 146.832

Index ranges	-10 ≤ h ≤ 6, -12 ≤ k ≤ 13, -29 ≤ l ≤ 29
Reflections collected	9823
Independent reflections	4020 [R_{int} = 0.0209, R_{sigma} = 0.0210]
Data/restraints/parameters	4020/0/277
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0281, wR_2 = 0.0731
Final R indexes [all data]	R_1 = 0.0283, wR_2 = 0.0734
Largest diff. peak/hole / e Å^{-3}	0.23/-0.14
Flack/Hooft parameter	-0.04(5)/-0.04(5)



6c

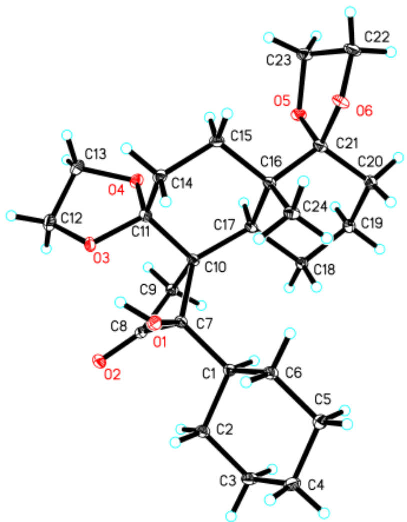


Figure S103. X-ray crystallographic structure of **6c**.

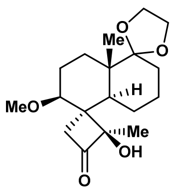
X-ray Crystallography Data of **7b**

CCDC 2002824 contains the supplementary crystallographic data for **7b**. The XRD sample of **7b** was prepared by slow evaporation from a CH_2Cl_2/hexane (1:3) solution at room temperature. The absolute and relative configurations of **7b** was unambiguously assigned from the XRD analysis. The crystal parameters are depicted in **Table S6**.

Table S6. Crystal data and structure refinement for **7b.**

Identification code	**7b**
Empirical formula	$C_{18}H_{28}O_5$
Formula weight	324.40
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.5133(10)
b/Å	10.7778(10)
c/Å	16.2346(19)

α/°	90
β/°	90
γ/°	90
Volume/Å^3	1664.6(3)
Z	4
ρ_{calc}g/cm^3	1.294
μ/mm^{-1}	0.759
F(000)	704.0
Crystal size/mm^3	0.12 × 0.11 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.85 to 149.132
Index ranges	$-11 \le h \le 11$, $-13 \le k \le 13$, $-16 \le l \le 19$
Reflections collected	9482
Independent reflections	3321 [R_{int} = 0.0423, R_{sigma} = 0.0357]
Data/restraints/parameters	3321/14/212
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0847, wR_2 = 0.2104
Final R indexes [all data]	R_1 = 0.1023, wR_2 = 0.2374
Largest diff. peak/hole / e Å^{-3}	0.56/-0.59
Flack/Hooft parameter	-0.05(16)/0.01(10)



7b

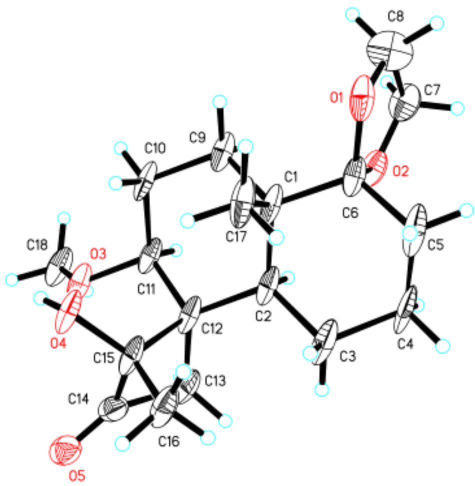


Figure S104. X-ray crystallographic structure of **7b**.