Supporting Information

for

Bioinspired-Metalloporphyrin Magnetic Nanocomposite as a Reusable Catalyst for Synthesis of Diastereomeric (-)-isopulegol Epoxide. Anticancer Activity Against Human Osteosarcoma Cells (MG-63)

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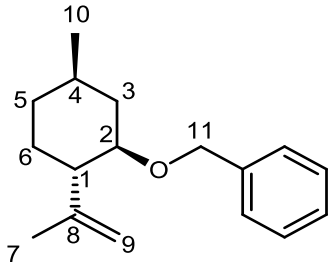
Characterization of (–)-isopulegol benzyl ether (1)



^{1}H-NMR (CDCl$_3$, 400 MHz) δ H (ppm): 7.32-7.19 (m, 5H, H*Ar*), 4.79-4.80 (m, 2H, H*9*), 4.59 (d, *J* = 16.0 Hz, 1H, H*11*), 4.41 (d, *J* = 16.0 Hz, 1H, H*11*), 3.28 (ddd, *J1* = 6.0 Hz, *J2* = 6.0 Hz, *J3* = 6.0 Hz, 1H, *H2*), 2.18-2.03 (m, 2H, C*H*), 1.68-1.67 (m, 3H, CH$_3$-*7*), 1.65-1.60 (m, 2H, C*H*), 1.41-1.25 (m, 2H, C*H*), 0.93 (s, *J* = 9.0 Hz, 3H, CH$_3$-*5*), 0.99-0.90 (m, 2H, C*H*).

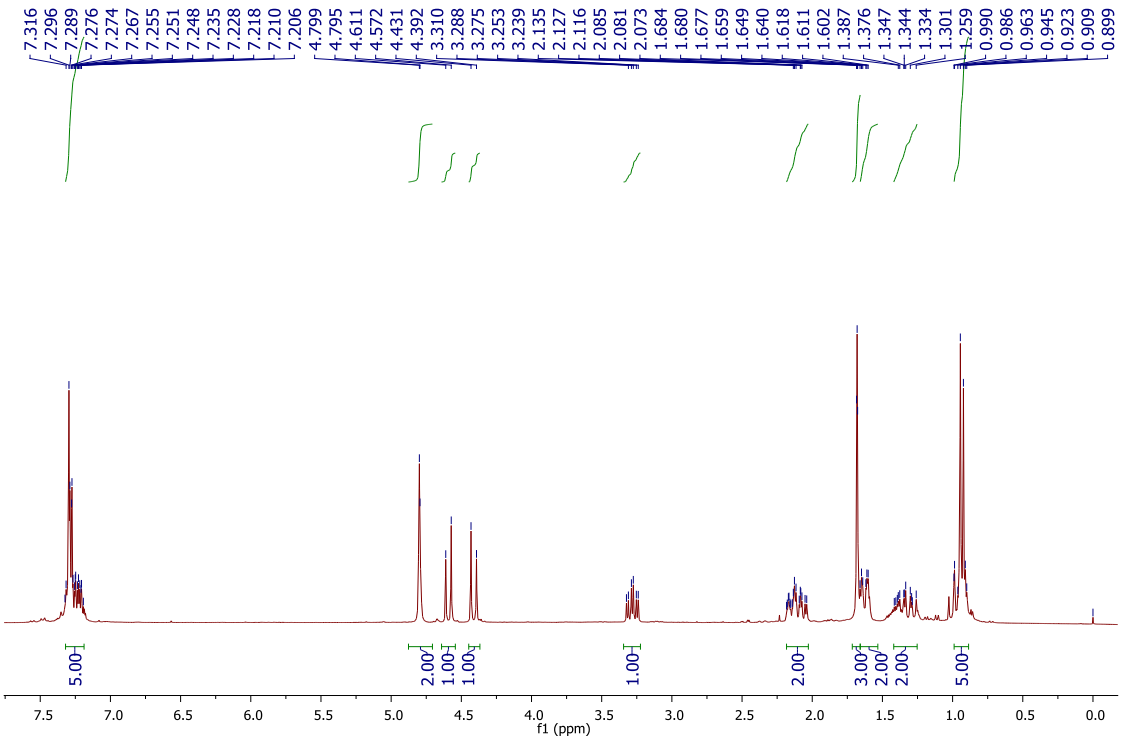


Figure S1. ^{1}H NMR spectrum of (–)-isopulegol benzyl ether (**1**).

^{13}C-NMR (101 MHz, $CDCl_3$) δ C (ppm): 20.1 (C-7), 22.20 (C-10), 31.1 (C-6), 31.6 (C-4), 34.5 (C-5), 40.3 (C-3), 51.8 (C-1), 70.4 (C-11), 79.2 (C-2), 111.1 (C-8), 127.3 ($C_{Ar.}$), 127.6 (C_{Ar}), 128.2 (C_{Ar}), 139.2 (C_{Ar}), 147.9 (C-9).

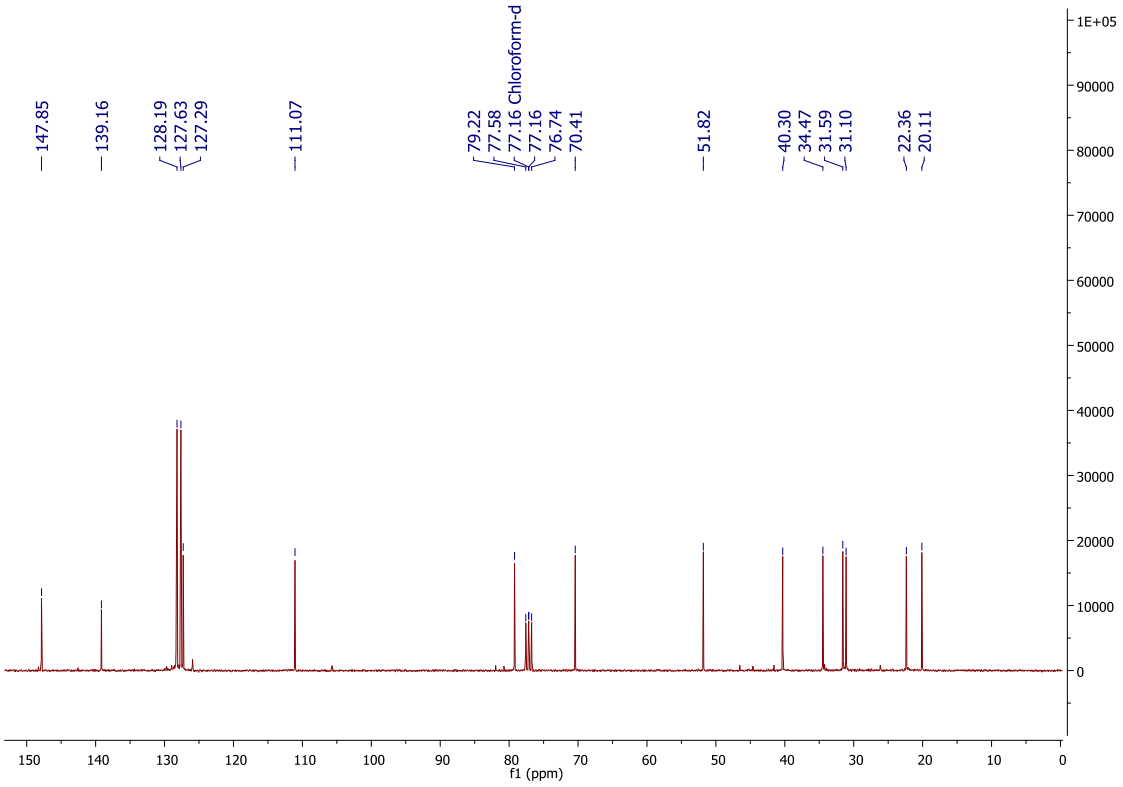


Figure S2. ^{13}C NMR spectrum of (–)-isopulegol benzyl ether (**1**).

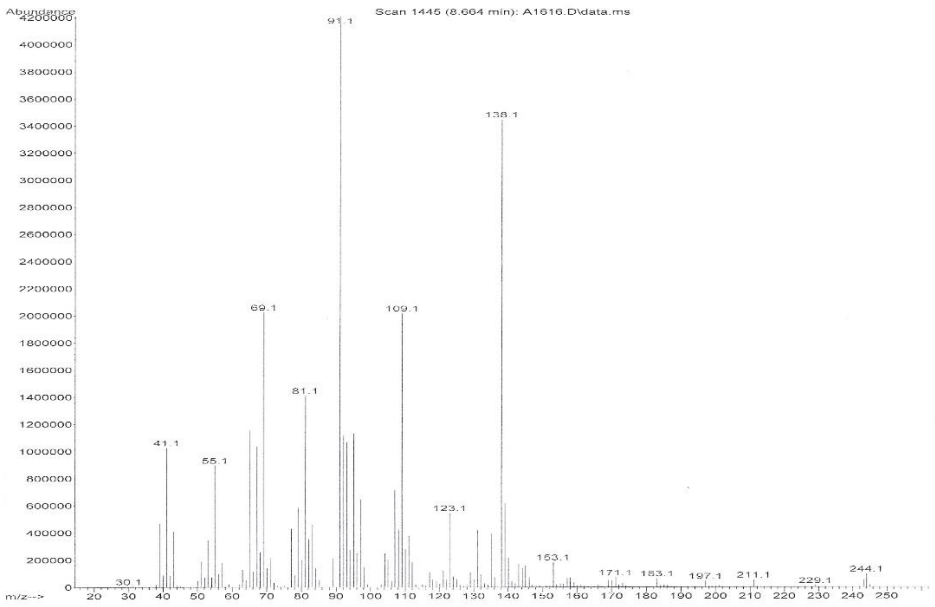
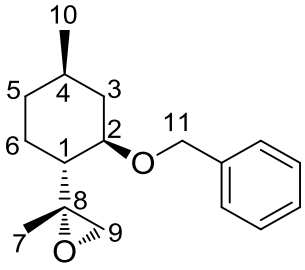


Figure S3. MS spectrum of (–)-isopulegol benzyl ether (**1**).

(-)-Isopulegol Benzyl Ether Epoxide –

(*R*)-2-((1*R*,2*R*,4*R*)-2-(benzyloxy)-4-methylcyclohexyl)-2-methyloxirane (**A**)



^{1}H-NMR (CDCl$_3$, 400 MHz) δ H (ppm): 7.36-7.25 (m, 5H, *HAr*), 4.68 (d, *J* = 12.0 Hz, 1H, *H11*), 4.40 (d, *J* = 12.0 Hz, 1H, *H11*), 3.26 (ddd, J_1 = 4.0 Hz, J_2 = 4.0 Hz, J_3 = 4.0 Hz, 1H, *H2*), 2.76 (d, *J* = 8.0 Hz, 1H, *H9*), 2.68 (d, *J* = 4.0 Hz, 1H, *H9*), 2.24-2.19 (m, 1H, *H3*), 1.90-1.86 (m, 1H, *H6*), 1.71-1.66 (m, 1H, *H5*), 1.43-1.39 (m, 1H, *H6*), 1.31-1.24 (m, 1H, *H4*), 1.13 (s, 3H, CH$_3$-*7*), 1.11-1.08 (m, 1H, *H1*), 0.95 (d, *J* = 8.0 Hz, 3H, CH$_3$-10), 0.92-0.86 (m, 2H, *H3*, *H5*).

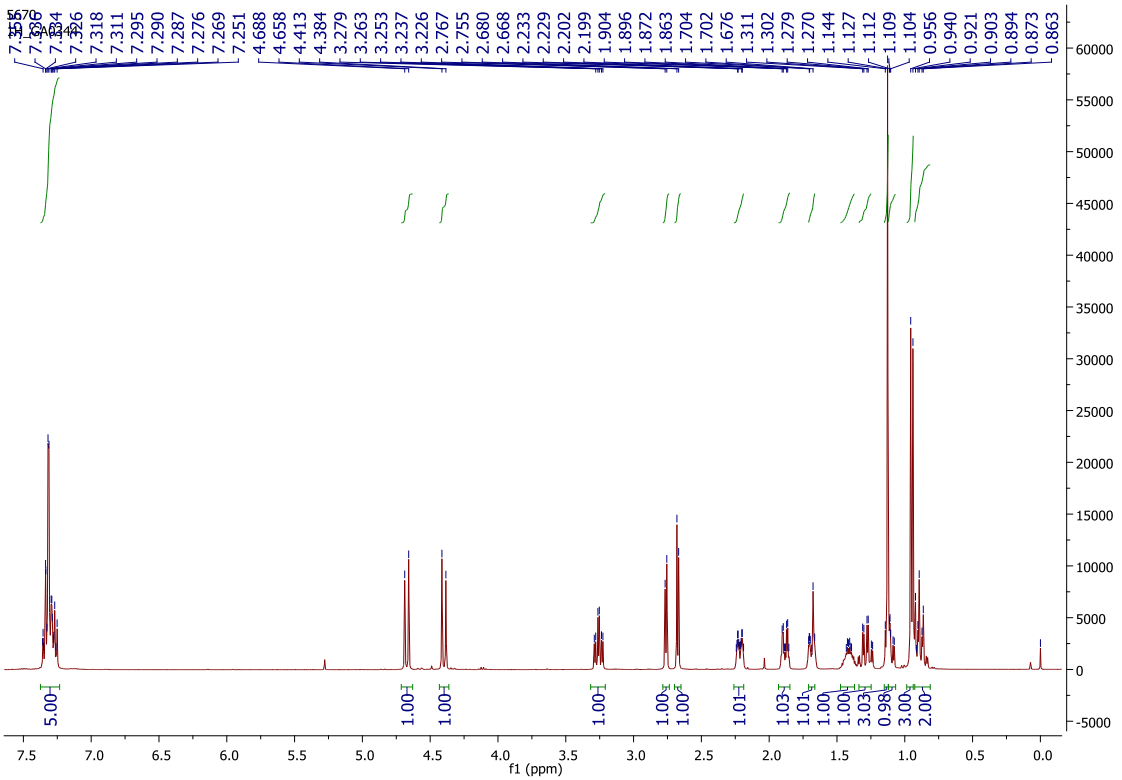


Figure S4. ^{1}H NMR of (*R*)-2-((1*R*,2*R*,4*R*)-2-(benzyloxy)-4-methylcyclohexyl)-2-methyloxirane (**A**).

^{13}C-NMR (101 MHz, $CDCl_3$) δ C (ppm): 16.7 (C-7), 22.3 (C-10), 26.4 (C-6), 31.5 (C-4), 33.9 (C-5), 39.9 (C-3), 50.8 (C-1), 56.8 (C-9), 57.9 (C-8), 70.2 (C-11), 78.8 (C-2), 127.6 (C-Ar), 128.4 (C-Ar), 139.0 (C-Ar).

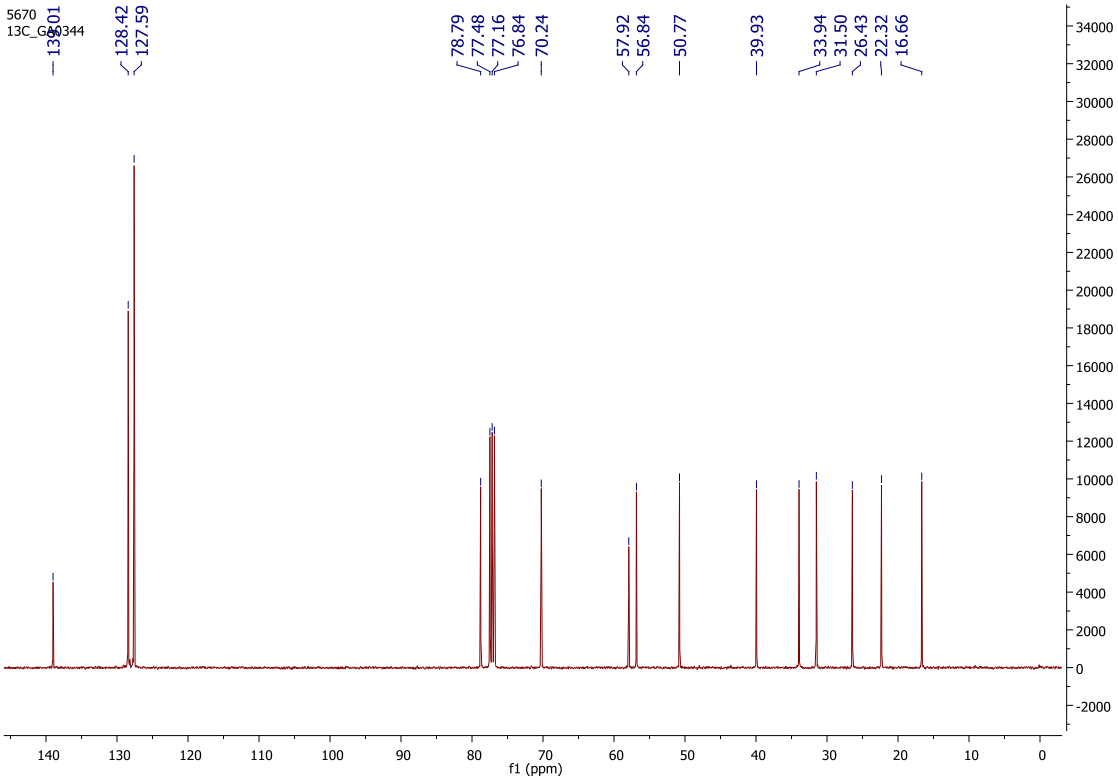


Figure S5. ^{13}C NMR of (*R*)-2-((1*R*,2*R*,4*R*)-2-(benzyloxy)-4-methylcyclohexyl)-2-methyloxirane (**A**).

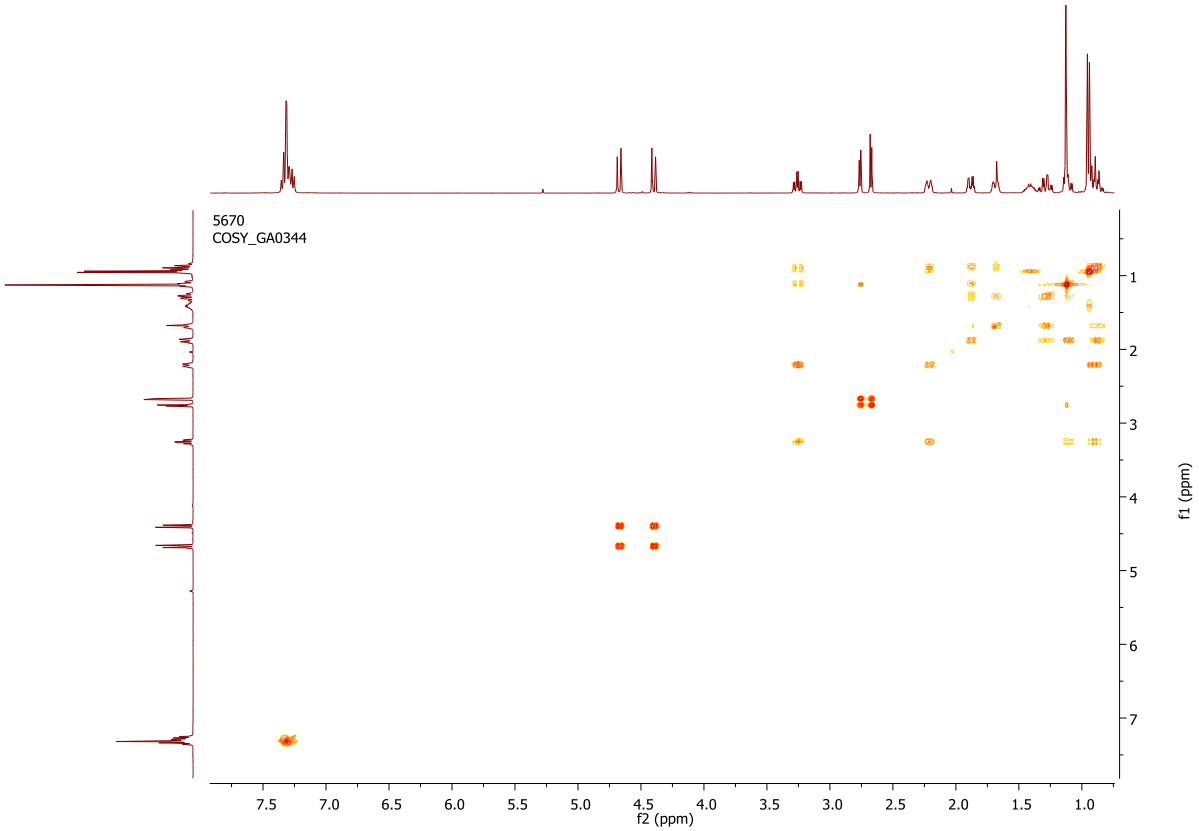


Figure S6. ^{1}H-^{1}H Cosy NMR spectrum of (*R*)-2-((1*R*,2*R*,4*R*)-2-(benzyloxy)-4-methylcyclohexyl)-2-methyloxirane (**A**).

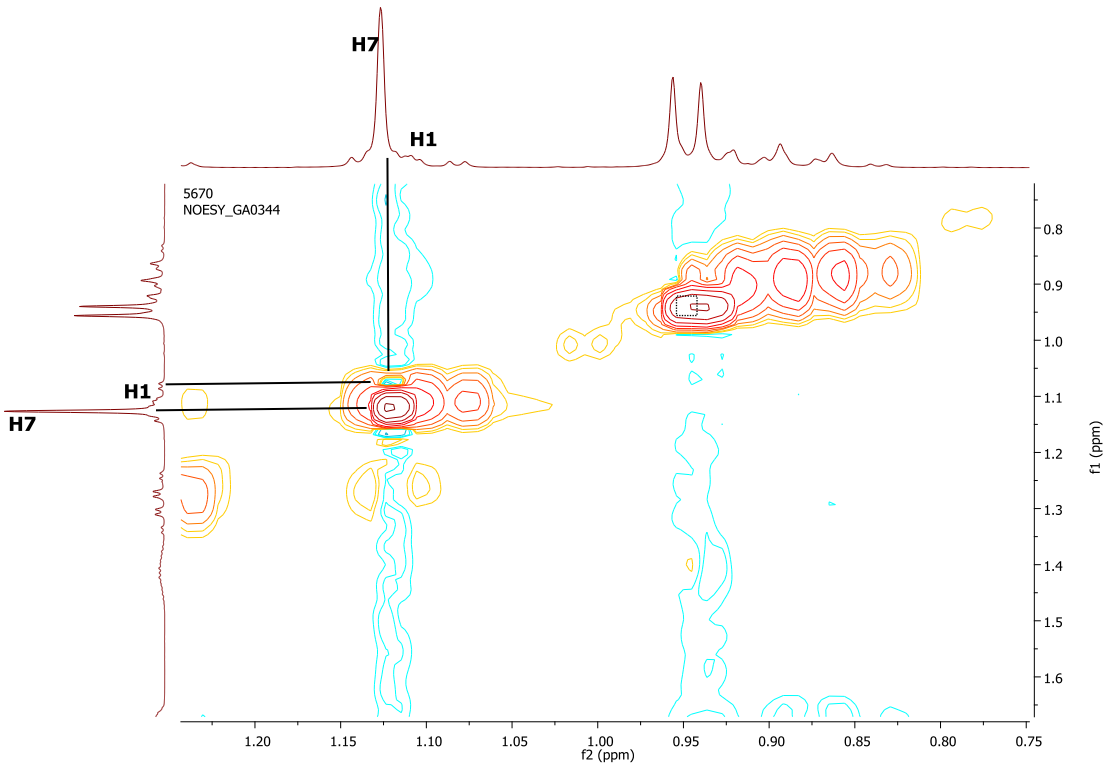


Figure S7. Noesy NMR spectrum of (*R*)-2-((1*R*,2*R*,4*R*)-2-(benzyloxy)-4-methylcyclohexyl)-2-methyloxirane (**A**).

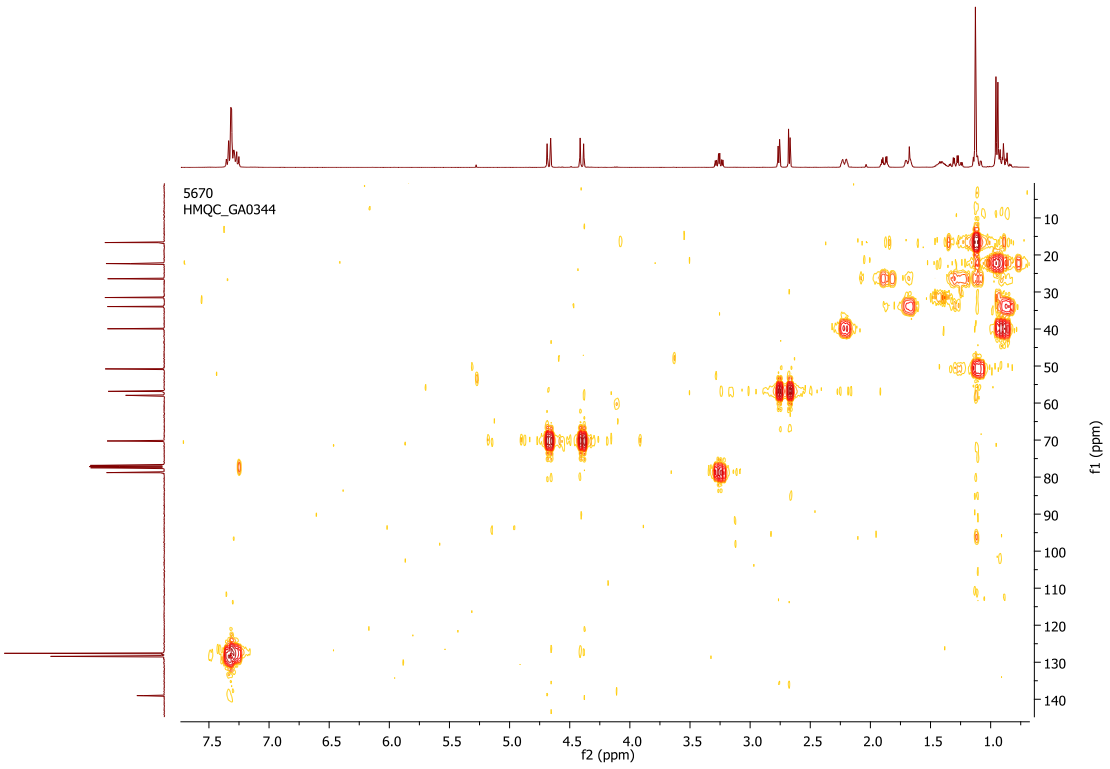


Figure S8. HMQC spectrum of (*R*)-2-((1*R*,2*R*,4*R*)-2-(benzyloxy)-4-methylcyclohexyl)-2-methyloxirane (**A**).

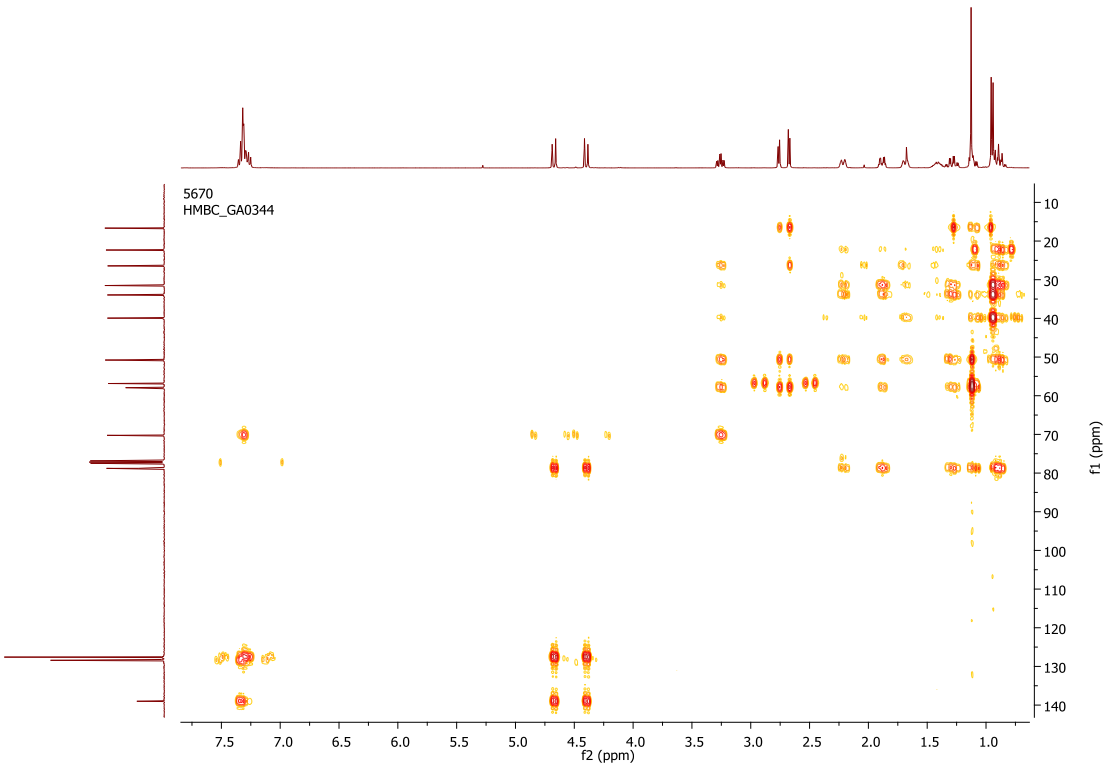
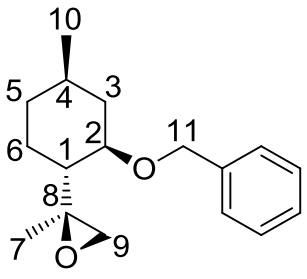


Figure S9. HMBC spectrum of (*R*)-2-((1*R*,2*R*,4*R*)-2-(benzyloxy)-4-methylcyclohexyl)-2-methyloxirane (**A**).

Characterization of (*S*)-2-((*1R,2R,4R*)-2-(benzyloxy)-4-methylcyclohexyl)-2-methyloxirane (**B**)



^{1}H-NMR (CDCl$_3$, 400 MHz) δ H (ppm): 7.42-7.40 (m, 2H, *HAr*), 7.35-7.31 (m, 2H, *HAr*), 7.26-7.23 (m, 1H, *HAr*), 4.72 (d, *J* = 12.0 Hz, 1H, *H11*), 4.44 (d, *J* = 12.0 Hz, 1H, *H11*), 3.32-3.26 (m, 1H, *H2*), 2.51-2.48 (m, 2H, *H9*), 2.23-2.20 (m, 1H, *H3*), 1.75-1.70 (m, 1H, *H6*), 1.69-1.64 (m, 1H, H5), 1.45-1.35 (m, 1H, *H4*), 1.34-1.30 (m, 1H, *H1*), 1.25 (s, 3H, *H7*), 1.21-1.11 (m, 1H, *H6*), 0.95 (d, *J* = 6Hz, 3H, *H10*), 0.92-0.85 (m, 2H, *H3* and *H5*).

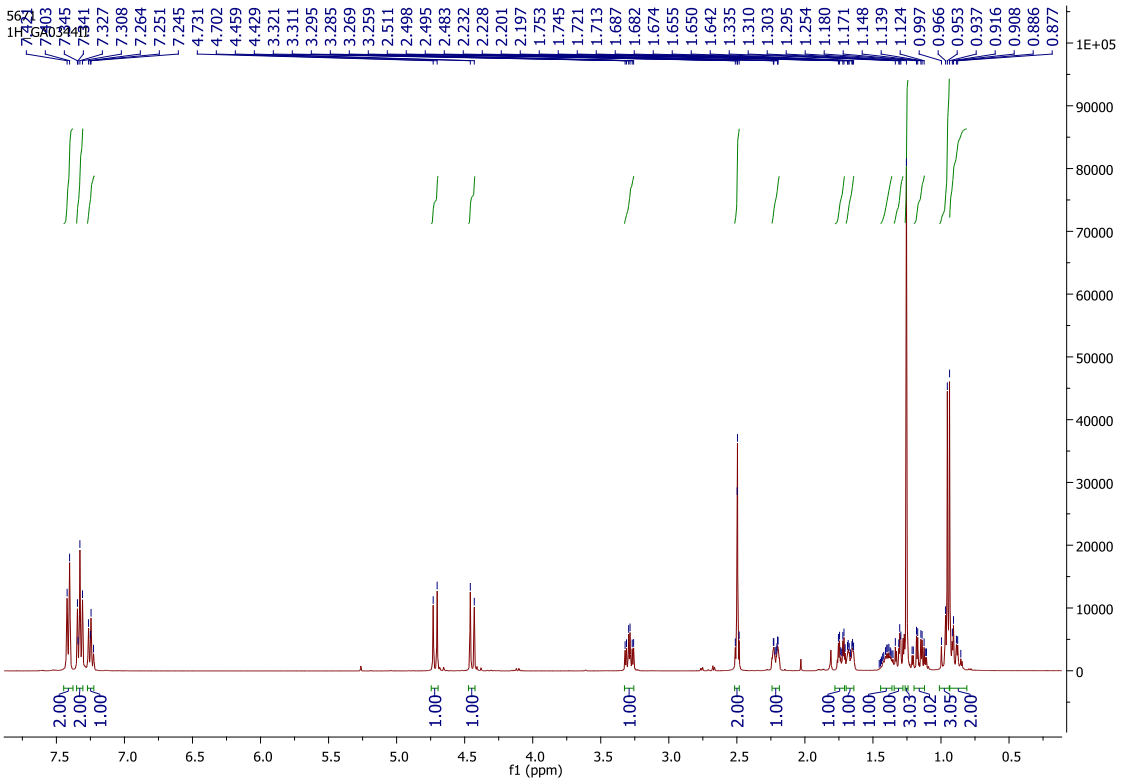


Figure S10. ^{1}H NMR of (*S*)-2-((*1R,2R,4R*)-2-(benzyloxy)-4-methylcyclohexyl)-2-methyloxirane (**B**).

^{13}C-NMR (101 MHz, $CDCl_3$) δ C (ppm): 18.9 (C-7), 22.2 (C-10), 27.8 (C-4), 31.3 (C-6), 34.2 (C-5), 39.6 (C-3), 49.2 (C-1), 52.0 (C-9), 58.3 (C-8), 69.7 (C-11), 78.3 (C-2), 127.4 (C-Ar), 127.7 (C-Ar), 128.3 (C-Ar), 138.9 (C-Ar).

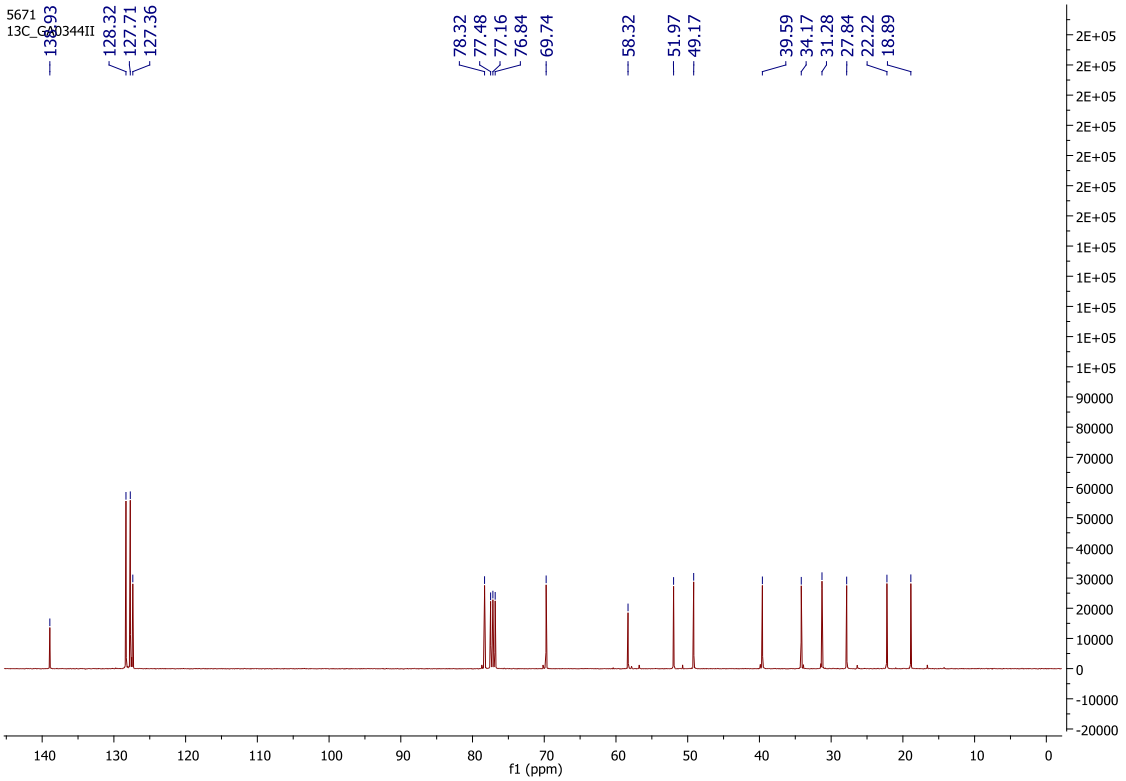


Figure S11. ^{13}C NMR of (*S*)-2-((*1R,2R,4R*)-2-(benzyloxy)-4-methylcyclohexyl)-2-methyloxirane (**B**).

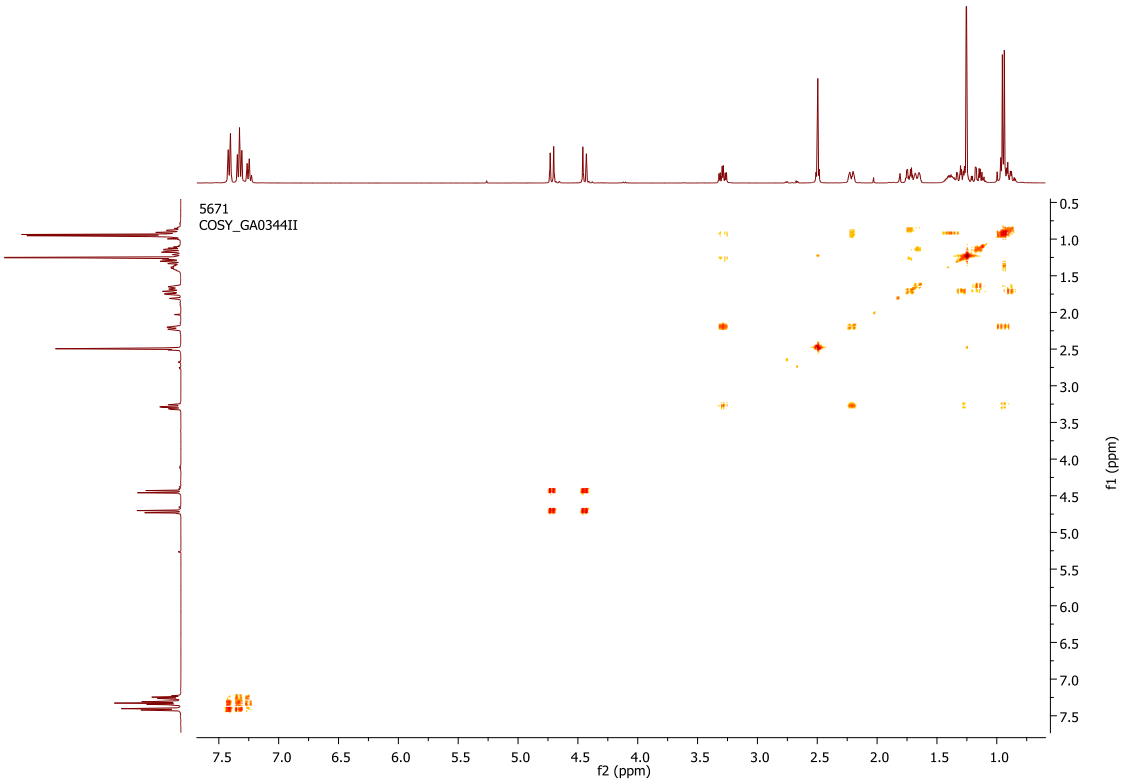


Figure S12. ^{1}H-^{1}H Cosy NMR spectrum of (*S*)-2-((*1R,2R,4R*)-2-(benzyloxy)-4-methylcyclohexyl)-2-methyloxirane (**B**).

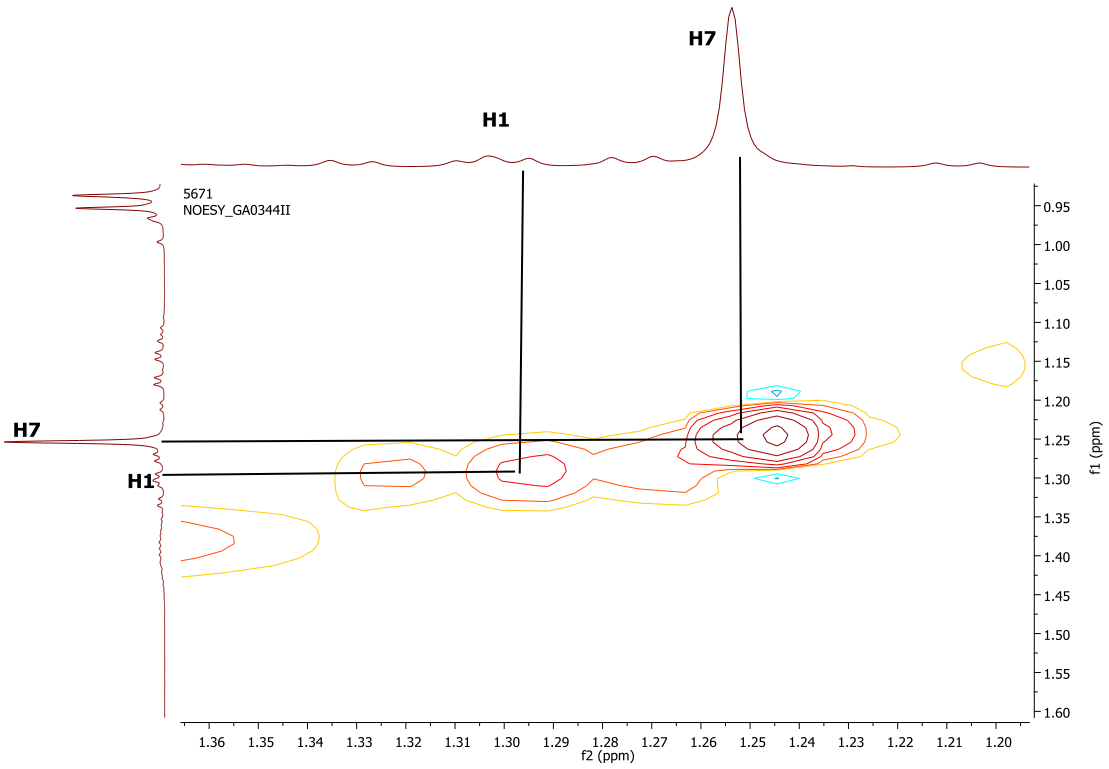


Figure S13. Noesy NMR spectrum of (*S*)-2-((*1R,2R,4R*)-2-(benzyloxy)-4-methylcyclohexyl)-2-methyloxirane (**B**).

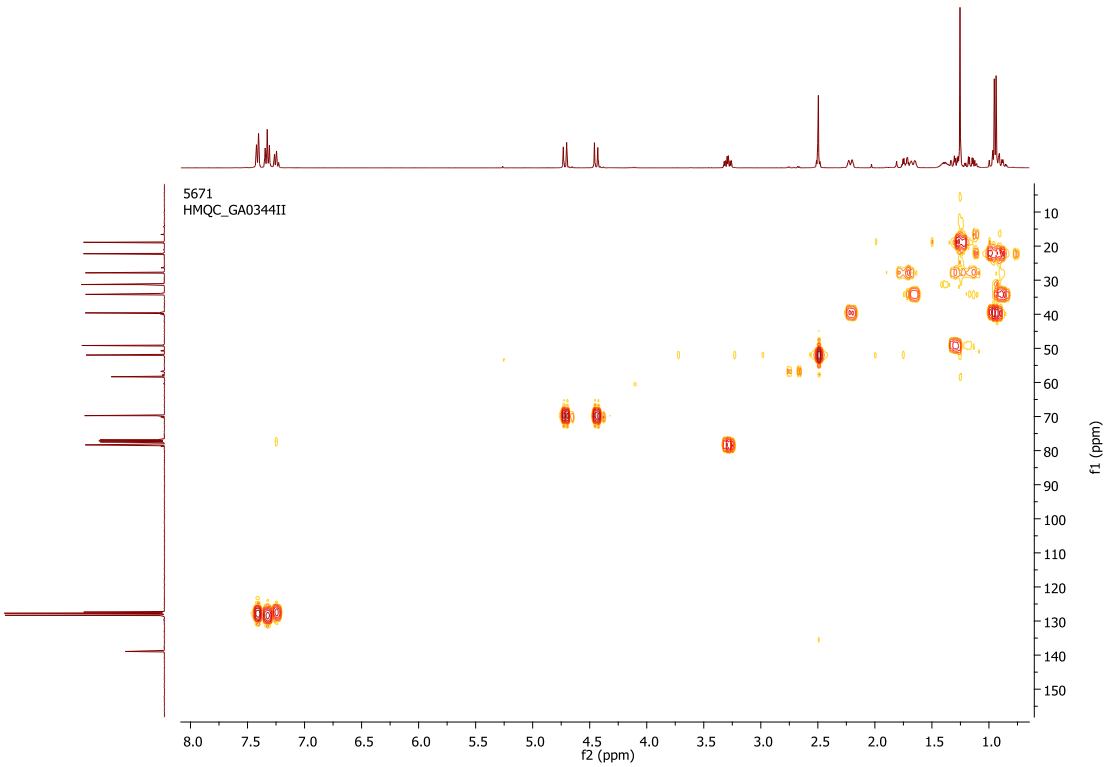


Figure S14. HMQC spectrum of (*S*)-2-((*1R,2R,4R*)-2-(benzyloxy)-4-methylcyclohexyl)-2-methyloxirane (**B**).

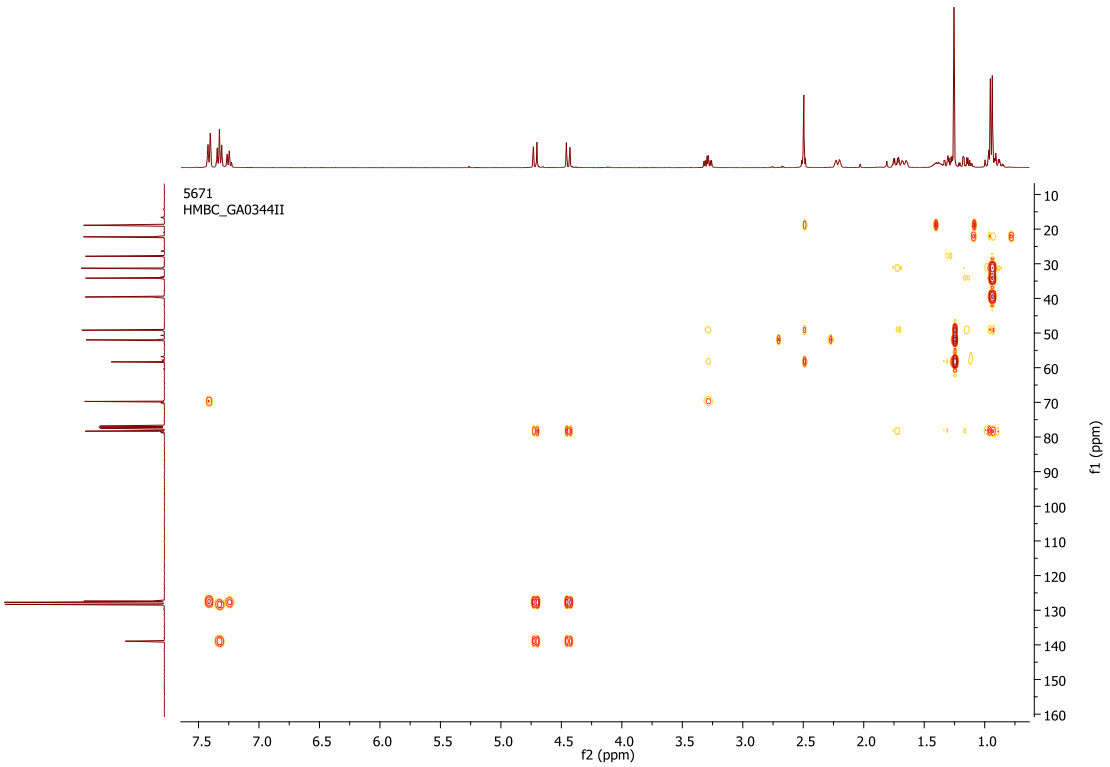


Figure S15. HMBC spectrum of (*S*)-2-((*1R,2R,4R*)-2-(benzyloxy)-4-methylcyclohexyl)-2-methyloxirane (**B**).