Supplementary Information

Dearomative [4 + 3] Cycloaddition of Furans with Vinyl-*N*-Triftosylhydrazones by Silver Catalysis: Stereoselective Access to Oxa-Bridged Seven-Membered Bicycles

Zhaohong Liu,[a§] Yong Yang,[a§] Xinyu Jiang,[a§] Qingmin Song,[a] Giuseppe Zanoni,[b] Shaopeng Liu,[a] and Xihe Bi*[a,c]

[a]Department of Chemistry, Northeast Normal University, Changchun 130024, China.
[b]Department of Chemistry, Universi-ty of Pavia, Viale Taramelli 12, 27100, Pavia, Italy.
[c]State Key Laboratory of Elemento-Organic Chemistry, Nankai Uni-versity, Tianjin 300071, China

Table of Contents

1. General Information

1.1 Equipment and Methods

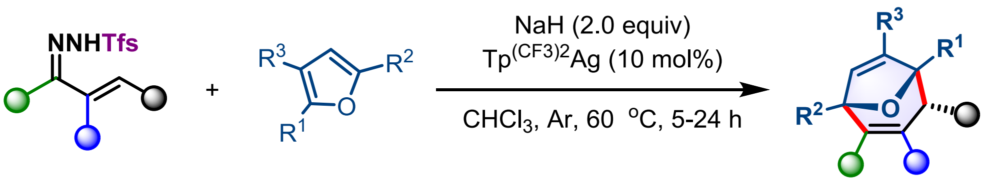
The products were purified by column chromatography over silica gel. NMR spectra were recorded on a Brüker Advance 600 (^{1}H: 600 MHz, ^{13}C:151 MHz) and Brüker Advance 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz) at ambient temperature. Data were reported as chemical shifts in ppm relative to TMS (0.00 ppm) for ^{1}H and $CDCl_3$ (77.0 ppm) for ^{13}C. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, qi = quintet, m = multiplet, br = broad. Thin layer chromatographic (TLC) analysis was performed with glass-backed silica gel plates, visualizing with UV light (254 nm) and/or staining with aqueous $KMnO_4$ stain. High-resolution mass spectra (HRMS) were recorded on Magnetic Sector High Resolution Gas Chromatography-Mass Spectra and Q Exactive Focus (Thermal) by using ESI method.

1.2 Solvents and Furan

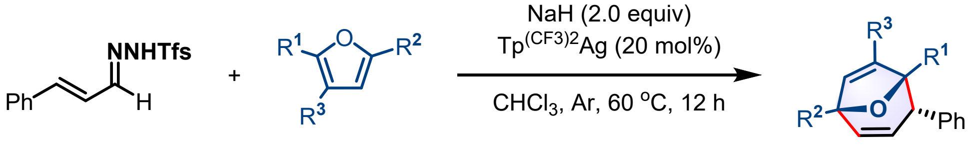
Trichlormethane ($CHCl_3$) was dried and degassed at reflux over CaH_2 in a 250 mL round bottom flask for 3 hours under argon atmosphere, distilled, then stored under argon atmosphere and was used directly. Superdry benzotrifluoride ($PhCF_3$, 99.5%, water ≤ 10 ppm, with molecular sieve) was purchased from J&K Scientific. Furan was dried and distilled before use. Furans with different substituents were commercially purchased from Tansoole or Energy Chemical and was purified by column chromatography or distilled before use.

2. Experimental Procedures and Characterization Data

2.1 Silver-Catalyzed Intermolecular [4 + 3] Reactions

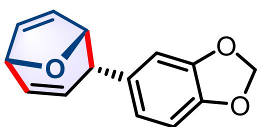


General procedure A: To an oven-dried screw-cap reaction tube was charged with vinyl-*N*-triftosylhydrazone (0.3 mmol), NaH (24.0 mg, 60 wt% dispersion in mineral oil, 0.6 mmol, 2.0 equiv) and dry $CHCl_3$ (3.0 mL) inside a glove box with argon atmosphere. Then, furan (0.6 mmol, 2.0 equiv) and $Tp^{(CF3)2}Ag$ (24.0 mg, 10 mol%) were added. The tube was sealed and stirred at 60 °C for 5-24 h in the dark. When the reaction was completed, the reaction mixture was cooled to room temperature, and filtered through a short pad of silica gel with CH_2Cl_2 as an eluent. After removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel (using petroleum ether / EtOAc as eluent) to obtain the desired products.



10 and **23**

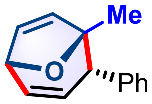
General procedure B: To an oven-dried screw-cap reaction tube was charged with vinyl-*N*-triftosylhydrazone (0.3 mmol), NaH (24.0 mg, 60 wt% dispersion in mineral oil, 0.6 mmol, 2.0 equiv) and dry $CHCl_3$ (3.0 mL) inside a glove box with argon atmosphere. Then, furan (0.6 mmol, 2.0 equiv) and $Tp^{(CF3)2}Ag$ (48.0 mg, 20 mol%) were added. The tube was sealed and stirred at 60 °C for 12 h in the dark. When the reaction was completed, the reaction mixture was cooled to room temperature, and filtered through a short pad of silica gel with CH_2Cl_2 as an eluent. After removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel (using petroleum ether / EtOAc as eluent) to obtain the desired products.



2

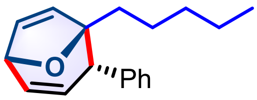
(**2**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)-3-(benzo[*d*][1,3]dioxol-5-yl)acrylaldehyde (120.0 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **2** (62.3 mg, 91% yield) as a yellow solid, m.p. 89-90 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.73 (d, *J* = 8.5 Hz, 1H), 6.64-6.60 (m, 3H), 6.33-6.29 (m, 1H), 5.93 (s, 2H), 5.53 (dd, *J* = 6.0 Hz, 2.0 Hz, 1H), 5.49 (dt, *J* = 10.0 Hz, 2.0 Hz, 1H), 5.06-5.03 (m, 1H), 4.69 (d, *J* = 4.0 Hz, 1H), 3.97-3.94 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 147.7, 146.4, 139.4, 132.0, 131.0, 127.9, 127.0, 121.0, 108.23, 108.16, 100.9, 83.3, 76.2, 42.9. **HRMS** (ESI) *m/z* calculated $C_{14}H_{13}O_3$

$[M+H]^+$ 229.0865, found 229.0861. The structure and configuration of 2 was unambiguously established by the X-ray crystallographic analysis.



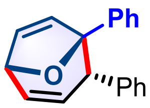
4

(**4**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and 2-methylfuran (49.2 mg, 0.6 mmol) afforded **4** (49.3 mg, 83% yield) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28-7.22 (m, 3H), 7.14-7.12 (m, 2H), 6.56 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 6.34 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.59 (dd, *J* = 9.5 Hz, 2.5 Hz, 1H), 5.39 (d, *J* = 6.0 Hz, 1H), 4.76 (d, *J* = 4.0 Hz, 1H), 3.67-3.64 (m, 1H), 1.47 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.1, 137.4, 131.3, 131.1, 130.4, 128.9, 128.1, 127.0, 87.3, 77.3, 50.5, 23.0. **HRMS** (ESI) *m/z* calculated $C_{14}H_{15}O$ $[M+H]^+$ 199.1123, found 199.1127. The relative configuration of **4** was confirmed by NOE, see Figure S10.



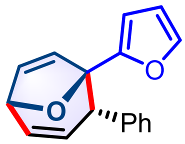
5

(**5**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and 2-pentylfuran (82.9 mg, 0.6 mmol) afforded **5** (57.2 mg, 75% yield) as a colourless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27-7.20 (m, 3H), 7.12 (d, *J* = 6.5 Hz, 2H), 6.54 (dd, *J* = 5.5 Hz, 1.5 Hz, 1H), 6.32 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.56 (dd, *J* = 9.5 Hz, 2.5 Hz, 1H), 5.38 (d, *J* = 5.5 Hz, 1H), 4.76 (d, *J* = 4.0 Hz, 1H), 3.72-3.69 (m, 1H), 1.78-1.74 (m, 2H), 1.60-1.52 (m, 1H), 1.33-1.22 (m, 5H), 0.87 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.0, 137.6, 131.1, 130.6, 130.3, 129.0, 128.0, 126.9, 90.1, 76.8, 49.0, 35.5, 32.3, 22.7, 22.6, 14.0. **HRMS** (ESI) *m/z* calculated $C_{18}H_{23}O$ $[M+H]^+$ 255.1749, found 255.1752.



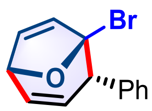
6

(**6**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and 2-phenylfuran (86.4 mg, 0.6 mmol) afforded **6** (59.3 mg, 76% yield) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32-7.26 (m, 3H), 7.21-7.12 (m, 5H), 6.77 (d, *J* = 7.0 Hz, 2H), 6.71 (dd, *J* = 6.0, 2.0 Hz, 1H), 6.44 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.88 (d, *J* = 6.0 Hz, 1H), 5.72 (dd, *J* = 9.5 Hz, 2.0 Hz, 1H), 4.94 (d, *J* = 4.0 Hz, 1H), 3.87-3.85 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.2, 138.7, 136.3, 131.1, 131.0, 129.2, 128.4, 128.0, 127.8, 127.5, 127.0, 126.0, 91.5, 77.4, 51.8. **HRMS** (ESI) *m/z* calculated $C_{19}H_{17}O$ $[M+H]^+$ 261.1279, found 261.1278.



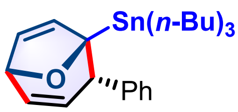
7

(**7**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and 2,2'-bifuran (80.4 mg, 0.6 mmol) afforded **7** (51.0 mg, 68% yield) as a yellow oil. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.52-7.48 (m, 1H), 7.18-7.14 (m, 3H), 6.93-6.90 (m, 2H), 6.74 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 6.40 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 6.36-6.33 (m, 1H), 6.28 (d, *J* = 3.0 Hz, 1H), 5.73 (dd, *J* = 9.5 Hz, 2.5 Hz, 1H), 5.63 (d, *J* = 6.0 Hz, 1H), 4.92 (d, *J* = 4.0 Hz, 1H), 4.48-4.44 (m, 1H); ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 152.9, 142.5, 139.8, 136.3, 130.8, 130.4, 128.6, 127.9, 127.1, 127.0, 110.3, 108.8, 86.9, 78.2, 46.6. **HRMS** (ESI) *m/z* calculated $C_{17}H_{15}O_2$ $[M+H]^+$ 251.1067, found 251.1065.



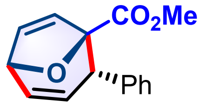
8

(**8**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and 2-bromofuran (87.6 mg, 0.6 mmol) afforded **8** (65.2 mg, 83% yield) as a yellow oil. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.31–7.28 (m, 3H), 7.26–7.24 (m, 2H), 6.60 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 6.35 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.74 (d, *J* = 6.0 Hz, 1H), 5.64 (dd, *J* = 9.5 Hz, 2.5 Hz, 1H), 4.96 (d, *J* = 4.0 Hz, 1H), 4.37–4.35 (m, 1H); ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 138.2, 134.7, 131.9, 130.5, 130.2, 129.4, 128.2, 127.8, 100.4, 80.1, 55.1. **HRMS** (ESI) *m/z* calculated $C_{13}H_{12}OBr$ $[M+H]^+$ 263.0072, found 263.0069.



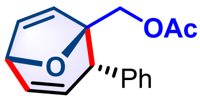
9

(**9**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and tributyl(furan-2-yl)stannane (214.8 mg, 0.6 mmol) afforded **9** (86.8 mg, 61% yield) as a yellow oil. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.0 Hz, 2H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.12 (d, *J* = 7.0 Hz, 2H), 6.56 (d, *J* = 6.0 Hz, 1H), 6.31-6.26 (m, 1H), 5.66 (d, *J* = 6.0 Hz, 1H), 5.43-5.36 (m, 1H), 4.57 (d, *J* = 3.0 Hz, 1H), 4.17-4.11 (m, 1H), 1.43-1.28 (m, 6H), 1.27-1.19 (m, 6H), 0.90-0.76 (m, 15H); ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 138.0, 136.5 (d, $J_{Sn-^{13}C}$ = 37.2 Hz), 132.1, 131.1, 128.8, 128.21, 128.20, 127.0, 90.4, 76.2, 48.7(d, $J_{Sn-^{13}C}$ = 20.0 Hz), 28.9 (d, $J_{Sn-^{13}C}$ = 19.9 Hz), 27.4 (d, $J_{Sn-^{13}C}$ = 57.2 Hz), 13.6, 9.2.



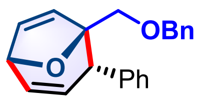
10

(**10**) Prepared according to **General Procedure B** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol), methyl furan-2-carboxylate (75.6 mg, 0.6 mmol) and $Tp^{(CF3)2}Ag$ (48.0 mg, 20 mol%) afforded **10** (51.0 mg, 68% yield) as a yellow solid, m.p. 94-96 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28-7.24 (m, 3H), 7.10-7.16 (m, 2H), 6.70 (dd, *J* = 6.0 Hz, 2.0 Hz, 1H), 6.35 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.69 (d, *J* = 6.0 Hz, 1H), 5.59 (dd, *J* = 9.5 Hz, 2.5 Hz, 1H), 4.87 (d, *J* = 4.0 Hz, 1H), 4.20-4.17 (m, 1H), 3.77 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.9, 139.6, 135.5, 130.4, 129.3, 128.7, 128.2, 127.5, 126.6, 90.9, 77.5, 52.3, 46.1. **HRMS** (ESI) *m/z* calculated $C_{15}H_{15}O_3$ $[M+H]^+$ 243.1021, found 243.1022.



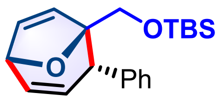
11

(**11**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and furan-2-ylmethyl acetate (84 mg, 0.6 mmol) afforded **11** (69.1 mg, 90% yield) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29-7.23 (m, 3H), 7.12-7.08 (m, 2H), 6.67 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 6.35 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.60 (dd, *J* = 9.5 Hz, 2.5 Hz, 1H), 5.39 (d, *J* = 6.0 Hz, 1H), 4.85 (d, *J* = 4.0 Hz, 1H), 4.34-4.29 (m, 2H), 3.99-3.96 (m, 1H), 2.13 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.9, 139.8, 136.2, 130.8, 130.0, 128.8, 128.4, 127.3, 127.0, 88.6, 77.7, 65.1, 44.5, 20.9. **HRMS** (ESI) *m/z* calculated $C_{16}H_{17}O_3$ $[M+H]^+$ 257.1178, found 257.1183.



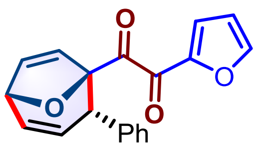
12

(**12**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and 2-((benzyloxy)methyl)furan (112.8 mg, 0.6 mmol) afforded **12** (70.2 mg, 77% yield) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.0 Hz, 2H), 7.35 (t, *J* = 7.0 Hz, 2H), 7.29 (t, *J* = 7.0 Hz, 1H), 7.22-7.18 (m, 3H), 7.09-7.06 (m, 2H), 6.63 (dd, *J* = 5.5 Hz, 2.0 Hz, 1H), 6.32 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.59 (dd, *J* = 9.5 Hz, 2.5 Hz, 1H), 5.32 (d, *J* = 5.5 Hz, 1H), 4.84 (d, *J* = 4.5 Hz, 1H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.19-4.16 (m, 1H), 3.74 (d, *J* = 11.0 Hz, 1H), 3.58 (d, *J* = 11.0 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.3, 138.1, 137.0, 130.7, 130.3, 128.9, 128.3, 128.1, 128.0, 127.7, 127.6, 126.9, 90.2, 77.8, 73.6, 70.9, 43.5. **HRMS** (ESI) *m/z* calculated $C_{21}H_{21}O_2$ $[M+H]^+$ 305.1542, found 305.1539.



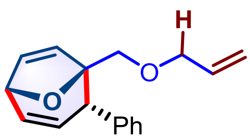
13

(**13**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and *tert*-butyl(furan-2yl-methoxy)dimethylsilane (127.2 mg, 0.6 mmol) afforded **13** (78.8 mg, 80% yield) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30-7.26 (m, 2H), 7.25-7.23 (m, 1H), 7.22-7.20 (m, 2H), 6.63 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 6.34 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.63 (dd, *J* = 9.5 Hz, 2.5 Hz, 1H), 5.33 (d, *J* = 6.0 Hz, 1H), 4.84 (d, *J* = 4.0 Hz, 1H), 4.25-4.22 (m, 1H), 3.87 (d, *J* = 11.5 Hz, 1H), 3.78 (d, *J* = 11.5 Hz, 1H), 0.97 (s, 9H), 0.14 (s, *3*H), 0.12 (s, *3*H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.2, 137.4, 130.8, 130.7, 129.0, 128.0, 127.9, 126.8, 91.0, 77.7, 64.8, 43.0, 26.0, 18.4, -5.2, -5.4. **HRMS** (ESI) *m/z* calculated $C_{20}H_{29}O_2Si$ $[M+H]^+$ 329.1937, found 329.1939.



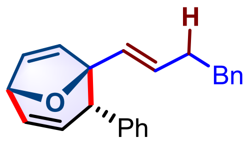
14

(**14**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and 1,2-di(furan-2-yl)ethane-1,2-dione (114 mg, 0.6 mmol) afforded **14** (47.8 mg, 52% yield) as a yellow solid, m.p. 130-132 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74-7.71 (m, 1H), 7.28-7.24 (m, 4H), 7.17-7.14 (m, 2H), 6.72 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 6.59 (dd, *J* = 3.5 Hz, 1.5 Hz, 1H), 6.35 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.81 (d, *J* = 5.5 Hz, 1H), 5.61 (dd, *J* = 9.5, 2.5 Hz, 1H), 4.86 (d, *J* = 3.5 Hz, 1H), 4.54-4.52 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.0, 180.4, 149.4, 149.0, 139.5, 134.9, 130.2, 129.5, 129.2, 128.2, 127.6, 126.1, 123.0, 112.9, 93.5, 77.6, 45.2. **HRMS** (ESI) *m/z* calculated $C_{19}H_{15}O_4$ $[M+H]^+$ 307.0970, found 307.0974.



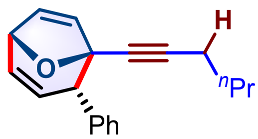
15

(**15**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and 2-((allyloxy)methyl)furan (82.9 mg, 0.6 mmol) afforded **15** (47.3 mg, 62% yield) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28-7.20 (m, 3H), 7.17-7.15 (m, 2H), 6.63 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 6.32 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 6.01– 5.93 (m, 1H), 5.59 (dd, *J* = 9.5 Hz, 2.5 Hz, 1H), 5.35 (d, *J* = 6.0 Hz, 1H), 5.31 (dd, *J* = 17.5 Hz, 1.5 Hz, 1H), 5.19 (dd, *J* = 10.5 Hz, 1.0 Hz, 1H), 4.83 (d, *J* = 4.0 Hz, 1H), 4.18-4.13 (m, 2H), 4.10-4.05 (m, 1H), 3.72 (d, *J* = 11.0 Hz, 1H), 3.57 (d, *J* = 11.0 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.4, 137.1, 134.7, 130.7, 130.3, 129.0, 128.2, 127.7, 127.0, 117.2, 90.2, 77.7, 72.6, 71.0, 43.7. **HRMS** (ESI) *m/z* calculated $C_{17}H_{19}O_2$ $[M+H]^+$ 255.1380, found 255.1347.



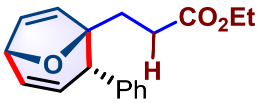
16

(**16**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and (*E*)-2-(4-phenylbut-1-en-1-yl)furan (118.9 mg, 0.6 mmol) afforded **16** (41.5 mg, 44% yield) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27-7.20 (m, 5H), 7.17-7.13 (m, 3H), 7.09-7.06 (m, 2H), 6.58 (dd, *J* = 6.0 Hz, 2.0 Hz, 1H), 6.33 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.63-5.60 (m, 2H), 5.56 (dd, *J* = 9.5 Hz, 2.5 Hz, 1H), 5.49 (d, *J* = 6.0 Hz, 1H), 4.81 (d, *J* = 4.0 Hz, 1H), 3.74-3.72 (m, 1H), 2.63 (t, *J* = 7.5 Hz, 2H), 2.58-2.50 (m, 1H), 2.44-2.37 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.9, 137.8, 136.9, 134.1, 131.0, 130.4, 130.2, 129.09, 129.07, 128.5, 128.2, 128.0, 127.0, 125.7, 89.1, 76.8, 49.8, 35.9, 30.3. **HRMS** (ESI) m/z calculated $C_{23}H_{21}O$ $[M-H]^-$ 313.1598, found 313.1601.



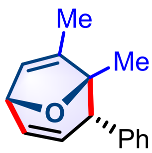
17

(**17**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and 2-(hex-1-yn-1-yl)furan (88.9 mg, 0.6 mmol) afforded **17** (56.3 mg, 71% yield) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29-7.22 (m, 5H), 6.60 (dd, *J* = 6.0 Hz, 2.0 Hz, 1H), 6.32 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.61 (dd, *J* = 9.5 Hz, 2.5 Hz, 1H), 5.38 (d, *J* = 6.0 Hz, 1H), 4.80 (d, *J* = 4.0 Hz, 1H), 4.00-3.98 (m, 1H), 2.30-2.22 (m, 2H), 1.55-1.49 (m, 2H), 1.45-1.37 (m, 2H), 0.91 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.5, 136.0, 130.9, 129.3, 129.2, 129.0, 127.9, 127.2, 87.9, 83.1, 78.8, 76.9, 49.6, 30.4, 21.9, 18.4, 13.5. **HRMS** (ESI) *m/z* calculated $C_{19}H_{21}O$ $[M+H]^+$ 265.1581, found 265.1581.



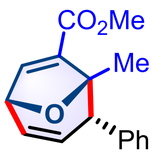
18

(**18**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and ethyl 3-(furan-2-yl)propanoate (100.9 mg, 0.6 mmol) afforded **18** (51.1 mg, 60% yield) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.27-7.21 (m, 3H), 7.14-7.12 (m, 2H), 6.57 (dd, J = 6.0 Hz, 1.8 Hz, 1H), 6.32 (ddd, J = 9.6 Hz, 4.2 Hz, 2.4 Hz, 1H), 5.57 (dd, J = 9.6 Hz, 2.4 Hz, 1H), 5.35 (d, J = 6.0 Hz, 1H), 4.76 (d, J = 4.2 Hz, 1H), 4.12-4.06 (m, 2H), 3.69-3.67 (m, 1H), 2.54-2.49 (m, 1H), 2.27-2.22 (m, 1H), 2.18-2.12 (m, 2H), 1.21 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.9, 139.1, 136.9, 131.0, 130.4, 129.1, 129.0, 128.2, 127.1, 89.3, 77.2, 60.2, 49.5, 30.4, 28.4, 14.2. **HRMS** (ESI) *m/z* calculated $C_{18}H_{21}O_3$ $[M+H]^+$ 285.1485, found 285.1484.



19

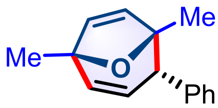
(**19**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and 2,3-dimethylfuran (57.7 mg, 0.6 mmol) afforded **19** (41.3 mg, 65% yield) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29-7.22 (m, 3H), 7.13-7.10 (m, 2H), 6.36 (ddd, J = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 6.16-6.12 (m, 1H), 5.62 (dd, J = 9.5 Hz, 2.5 Hz, 1H), 4.62 (d, J = 4.0 Hz, 1H), 3.66-3.62 (m, 1H), 1.45 (s, 3H), 1.04 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.9, 139.1, 132.1, 131.9, 129.3, 128.4, 128.0, 127.0, 88.1, 75.5, 50.2, 21.8, 13.8. **HRMS** (ESI) *m/z* calculated $C_{15}H_{15}O$ $[M-H]^-$ 211.1128, found 211.1336.



20

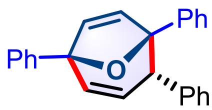
(**20**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and methyl 2-methylfuran-3-carboxylate (84 mg, 0.6 mmol) afforded **20** (58.4 mg, 76% yield) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 (d, J = 2.0 Hz, 1H), 7.25-7.21 (m, 3H), 7.08-7.05 (m, 2H), 6.32 (ddd, J = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.75 (dd, J = 9.5 Hz, 2.5 Hz, 1H), 4.80-4.77 (m, 1H), 3.71-3.69 (m, 1H), 3.22 (s, 3H), 1.69 (s, 3H); **^{13}C**

NMR (151 MHz, $CDCl_3$) δ 163.2, 148.9, 137.2, 134.5, 131.8, 128.69, 128.68, 128.1, 127.2, 87.5, 75.2, 51.0, 50.2, 22.7. **HRMS** (ESI) *m/z* calculated $C_{16}H_{17}O_3$ $[M+H]^+$ 257.1178, found 257.1173.



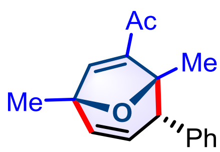
21

(**21**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and methyl- 2,5-dimethylfuran (57.7 mg, 0.6 mmol) afforded **21** (55.3 mg, 87% yield) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.27-7.21 (m, 3H), 7.12-7.10 (m, 2H), 6.34 (d, J = 6.0 Hz, 1H), 6.21 (dd, J = 9.6 Hz, 2.4 Hz, 1H), 5.58 (dd, J = 9.6 Hz, 2.4 Hz, 1H), 5.31 (d, J = 6.0 Hz, 1H), 3.58 (t, J = 2.4 Hz, 1H), 1.47 (s, 3H), 1.44 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.6, 137.4, 135.2, 131.0, 130.1, 128.9, 128.1, 126.9, 87.8, 82.5, 49.9, 23.3, 21.6. **HRMS** (ESI) *m/z* calculated $C_{15}H_{17}O$ $[M+H]^+$ 213.1279, found 213.1281.



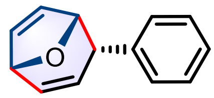
22

(**22**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and methyl 2,5-diphenylfuran (132.1 mg, 0.6 mmol) afforded **22** (83.7 mg, 83% yield) as a white solid, m.p. 141-142 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59-7.56 (m, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.34-7.27 (m, 4H), 7.25-7.16 (m, 5H), 6.84-6.82 (m, 2H), 6.77 (d, J = 6.0 Hz, 1H), 6.71 (dd, J = 9.5 Hz, 2.5 Hz, 1H), 5.93 (d, J = 6.0 Hz, 1H), 5.83 (dd, J = 9.5 Hz, 2.5 Hz, 1H), 3.90 (t, J = 3.0 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.9, 141.4, 140.2, 136.4, 134.2, 131.4, 129.3, 128.5, 128.3, 127.94, 127.86, 127.83, 127.4, 127.1, 126.1, 126.0, 92.2, 86.5, 51.3. **HRMS** (ESI) *m/z* calculated $C_{25}H_{21}O$ $[M+H]^+$ 337.1592, found 337.1595.



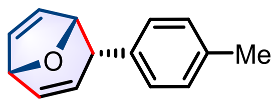
23

(**23**) Prepared according to **General Procedure B** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol), methyl-1-(2,5-dimethylfuran-3-yl)ethan-1-one (82.9 mg, 0.6 mmol) and $Tp^{(CF3)2}Ag$ (48.0 mg, 20 mol%) afforded **23** (41.9 mg, 55% yield) as a yellow solid, m.p. 114-116 °C. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.24-7.21 (m, 3H), 7.09 (s, 1H), 7.01-6.98 (m, 2H), 6.20 (dd, *J* = 9.5 Hz, 2.5 Hz, 1H), 5.75 (dd, *J* = 9.5 Hz, 2.5 Hz, 1H), 3.63 (t, *J* = 2.5 Hz, 1H), 2.00 (s, 3H), 1.71 (s, 3H), 1.50 (s, 3H); ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 192.7, 151.5, 141.6, 137.1, 132.6, 131.7, 128.5, 128.1, 127.3, 88.7, 80.0, 49.7, 26.9, 23.0, 21.3. **HRMS** (ESI) *m/z* calculated $C_{17}H_{19}O_2$ $[M+H]^+$ 253.1234, found 253.1234. The relative configuration of **23** was confirmed by NOE, see Figure S49.



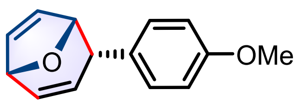
24

(**24**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **24** (46.9 mg, 85% yield) as a yellow solid, m.p. 72-74 °C. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.15-7.13 (m, 2H), 6.64 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 6.34 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.57 (dt, *J* = 9.5 Hz, 4.0 Hz, 1H), 5.49 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 5.10 (dt, *J* = 6.0 Hz, 1.5 Hz, 1H), 4.71 (d, *J* = 4.0 Hz, 1H), 4.06-4.03 (m, 1H); ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 139.4, 137.2, 131.9, 128.4, 128.0, 127.8, 127.0, 83.3, 76.3, 43.3. **HRMS** (ESI) *m/z* calculated $C_{13}H_{13}O$ $[M+H]^+$ 185.0966, found 185.0967.



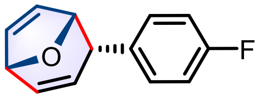
25

(**25**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)-3-(*p*-tolyl)acrylaldehyde (110.4 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **25** (47.5 mg, 80% yield) as a yellow oil. ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.62 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 6.31 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.54 (dt, *J* = 10.0 Hz, 2.0 Hz, 1H), 5.50 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 5.07 (dt, *J* = 6.0 Hz, 2.0 Hz 1H), 4.69 (d, *J* = 4.0 Hz, 1H), 4.02-3.98 (m, 1H), 2.32 (s, 3H); ^{13}**C NMR** (151 MHz, $CDCl_3$) δ 139.3, 136.5, 134.1, 131.8, 129.1, 128.0, 127.9, 127.0, 83.3, 76.2, 42.9, 21.0. **HRMS** (ESI) *m/z* calculated $C_{14}H_{15}O$ $[M+H]^+$ 199.1123, found 199.1123.



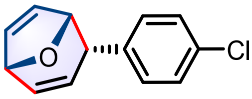
26

(**26**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)-3-(4-methoxyphenyl)acrylaldehyde (115.2 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **26** (47.5 mg, 74% yield) as a yellow solid, m.p. 77-79 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.63 (dd, *J* = 6.0 Hz, 1.2 Hz, 1H), 6.31 (ddd, *J* = 9.6 Hz, 4.2 Hz, 2.4 Hz, 1H), 5.53 (dt, *J* = 9.6 Hz, 2.4 Hz, 1H), 5.50 (dd, *J* = 6.0 Hz, 1.8 Hz, 1H), 5.06 (dt, *J* = 6.0 Hz, 1.8 Hz, 1H), 4.69 (d, *J* = 4.2 Hz, 1H), 4.02-3.96 (m, 1H), 3.79 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.6, 139.3, 131.8, 129.1, 129.0, 128.1, 127.0, 113.8, 83.3, 76.2, 55.2, 42.5. **HRMS** (ESI) *m/z* calculated $C_{14}H_{15}O_2$ [M+H]$^+$ 215.1072, found 215.1071.



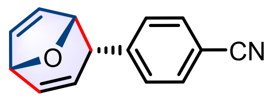
27

(**27**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)-3-(4-fluorophenyl)acrylaldehyde (111.6 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **27** (47.9 mg, 79% yield) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.11-7.08 (m, 2H), 6.99-6.95 (m, 2H), 6.64 (dd, *J* = 6.0 Hz, 2.0 Hz, 1H), 6.34 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.52 (dt, *J* = 9.5 Hz, 2.0 Hz, 1H), 5.47 (dd, *J* = 6.0 Hz, 2.0 Hz, 1H), 5.06 (dt, *J* = 6.0 Hz, 2.0 Hz, 1H), 4.71 (d, *J* = 4.0 Hz, 1H), 4.03-4.00 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.9 (d, *J* = 245.1 Hz), 139.6, 132.9 (d, *J* = 3.1 Hz), 132.1, 129.4 (d, *J* = 8.0 Hz), 127.5, 126.7, 115.2 (d, *J* = 21.6 Hz), 83.1, 76.2, 42.5. **^{19}F NMR** (565 MHz, $CDCl_3$) δ(-115.74)-(-115.82) (m).**HRMS** (ESI) *m/z* calculated $C_{13}H_{12}OF$ [M+H]$^+$ 203.0872, found 203.0873.



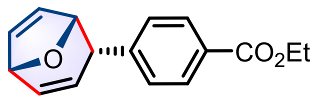
28

(**28**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)-3-(4-chlorophenyl)acrylaldehyde (116.4 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **28** (53.6 mg, 82% yield) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 2H), 6.64 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 6.35 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.51 (dt, *J* = 9.5 Hz, 2.0 Hz, 1H), 5.47 (dd, *J* = 6.0 Hz, 2.0 Hz, 1H), 5.06 (dt, *J* = 6.0 Hz, 2.0 Hz, 1H), 4.71 (d, *J* = 4.0 Hz, 1H), 4.02-3.99 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.6, 135.7, 132.7, 132.3, 129.3, 128.6, 127.2, 126.7, 83.0, 76.2, 42.6. **HRMS** (ESI) *m/z* calculated $C_{13}H_{12}OCl$ [M+H] 219.0577, found 219.0577.



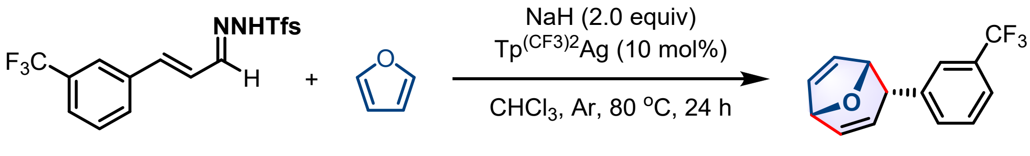
29

(**29**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (E)-4-(3-oxoprop-1-en-1-yl)benzonitrile (113.7 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **29** (48.9 mg, 78% yield) as a colorless oil.**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 6.67 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 6.40 (ddd, *J* = 10.0 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.52 (dt, *J* = 10.0 Hz, 2.0 Hz, 1H), 5.43 (dd, *J* = 6.0 Hz, 2.0 Hz, 1H), 5.09 (dt, *J* = 6.0 Hz, 1.8 Hz 1H), 4.75 (d, *J* = 4.0 Hz, 1H), 4.11-4.08 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 142.9, 140.1, 132.9, 132.3, 128.8, 126.24, 126.21, 118.8, 110.9, 82.7, 76.3, 43.2. **HRMS** (ESI) *m/z* calculated $C_{14}H_{10}NO$ [M-H]$^-$ 208.0768, found 208.0764.



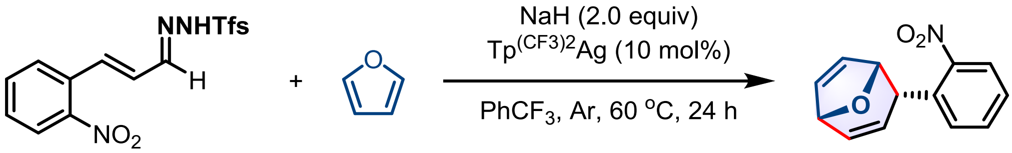
30

(**30**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from ethyl (*E*)-4-(3-oxoprop-en-1-yl)benzoate (127.8 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **30** (63.8 mg, 83% yield) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.64 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 6.38 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.0 Hz, 1H), 5.56 (dt, *J* = 9.5, 2.0 Hz, 1H), 5.43 (dd, *J* = 6.0, 1.5 Hz, 1H), 5.10 (dt, *J* = 6.0 Hz, 2.0 Hz, 1H), 4.73 (d, *J* = 4.0 Hz, 1H), 4.37 (q, *J* = 7.0 Hz, 2H), 4.12-4.08 (m, 1H), 1.39 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.4, 142.5, 139.6, 132.3, 129.7, 129.3, 127.9, 126.9, 126.6, 82.9, 76.3, 60.9, 43.2, 14.3. **HRMS** (ESI) *m/z* calculated $C_{16}H_{17}O_3$ [M+H]$^+$ 257.1172, found 257.1146.



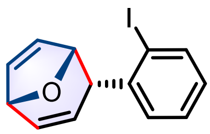
31, 82%

(31) Procedure: To an oven-dried screw-cap reaction tube was charged with vinyl-*N*-triftosylhydrazone derived from (*E*)-3-(3-(trifluoromethyl)phenyl)acrylaldehyde (126.6 mg, 0.3 mmol), NaH (24.0 mg, 60 wt% dispersion in mineral oil, 0.6 mmol, 2.0 equiv) and dry $CHCl_3$ (3.0 mL) inside a glove box with argon atmosphere. Then, furan (41.0 mg, 0.6 mmol) and $Tp^{(CF3)2}Ag$ (24.0 mg, 10 mol%) were added. The tube was sealed and stirred at 80 °C for 24 h in the dark. When the reaction was completed, the reaction mixture was cooled to room temperature, and filtered through a short pad of silica gel with CH_2Cl_2 as an eluent. After removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel (using petroleum ether / EtOAc as eluent) to obtain product **31** (62.0 mg, 82% yield) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.38 (s, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 6.67 (dd, *J* = 6.0 Hz, 1.0 Hz, 1H), 6.39 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.0 Hz, 1H), 5.54 (dt, *J* = 9.5 Hz, 2.0 Hz, 1H), 5.46 (dd, *J* = 6.0, 1.5 Hz, 1H), 5.10 (dt, *J* = 6.0 Hz, 2.0 Hz 1H), 4.74 (d, *J* = 4.0 Hz, 1H), 4.12-4.08 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.9, 138.3, 132.7, 131.5, 130.8 (q, *J* = 30.2 Hz), 128.9, 126.7, 126.3, 124.7 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 273.4 Hz), 123.84 (q, *J* = 3.8 Hz), 82.8, 76.3, 43.0. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.57. **HRMS** (ESI) *m/z* calculated $C_{14}H_{12}OF_3$ [M+H]$^+$ 253.0840, found 253.0845.



32, 68%

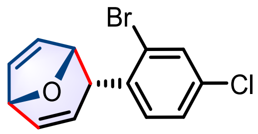
(**32**) **Procedure:** To an oven-dried screw-cap reaction tube was charged with vinyl-*N*-triftosylhydrazone derived from (*E*)-3-(2-nitrophenyl)acrylaldehyde (119.7 mg, 0.3 mmol), NaH (24.0 mg, 60 wt% dispersion in mineral oil, 0.6 mmol, 2.0 equiv) and dry $PhCF_3$ (3.0 mL) inside a glove box with argon atmosphere. Then, furan (41.0 mg, 0.6 mmol) and $Tp^{(CF3)2}Ag$ (24.0 mg, 10 mol%) were added. The tube was sealed and stirred at 60 °C for 24 h in the dark. When the reaction was completed, the reaction mixture was cooled to room temperature, and filtered through a short pad of silica gel with CH_2Cl_2 as an eluent. After removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel (using petroleum ether / EtOAc as eluent) to obtain product **32** (46.7 mg, 68% yield) as a yellow solid, m.p. 102-104 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.39 (td, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.24 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 6.67 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 6.39 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.54 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 5.46-5.41 (m, 2H), 4.76 (d, *J* = 4.0 Hz, 1H), 4.54-4.50 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.9, 139.1, 132.9, 132.2, 131.8, 130.4, 127.9, 127.3, 126.8, 124.3, 81.6, 76.0, 38.5. **HRMS** (ESI) *m/z* calculated $C_{13}H_{12}NO_3$ [M+H]$^+$ 230.0817, found 230.0818.



33

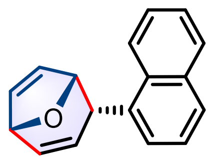
(**33**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)-3-(2-iodophenyl)acrylaldehyde (119.7 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **33** (74.4 mg, 80% yield) as a white oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.24 (td, *J* = 8.0 Hz, 1.0 Hz, 1H), 6.98 (dd, *J* = 7.5 Hz, 1.5 Hz, 1H), 6.91 (td, *J* = 7.5 Hz, 1.5 Hz, 1H), 6.61 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 6.35 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.50

(dt, *J* = 9.5 Hz, 2.0 Hz, 1H), 5.44 (dd, *J* = 6.0 Hz, 2.0 Hz, 1H), 5.30 (dt, *J* = 6.0 Hz, 2.0 Hz, 1H), 4.73 (d, *J* = 4.0 Hz, 1H), 4.37-4.34 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 139.5, 139.3, 138.9, 131.7, 128.8, 128.6, 128.4, 127.8, 126.7, 101.2, 80.3, 76.1, 46.9. **HRMS** (ESI) *m/z* calculated $C_{13}H_{12}OI$ $[M+H]^+$ 310.9933, found 310.9933.



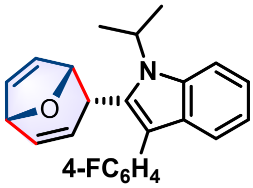
34

(**34**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)-3-(2-bromo-4-chlorophenyl)acrylaldehyde (139.8 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **34** (67.5 mg, 76% yield) as a white solid, m.p. 98-100 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 2.0 Hz, 1H), 7.19 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H), 6.95 (d, *J* = 8.5 Hz, 1H), 6.62 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 6.38 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.47-5.41 (m, 2H), 5.28 (dt, *J* = 6.0 Hz, 2.0 Hz 1H), 4.73 (d, *J* = 4.0 Hz, 1H), 4.46-4.43 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 139.2, 135.0, 133.4, 132.5, 132.2, 129.9, 127.8, 127.0, 126.7, 125.0, 80.1, 76.1, 41.7. **HRMS** (ESI) *m/z* calculated $C_{13}H_{11}OClBr$ $[M+H]^+$ 296.9682, found 296.9689.



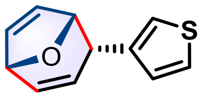
35

(**35**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)-3-(naphthalen-2-yl)acrylaldehyde (121.2 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **35** (59.0 mg, 84% yield) as a yellow solid, m.p. 107-109 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81-7.75 (m, 3H), 7.58 (s, 1H), 7.47-7.41 (m, 2H), 7.25 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H), 6.65 (dd, *J* = 6.0 Hz, 2.0 Hz, 1H), 6.39 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.66 (dt, *J* = 9.5 Hz, 2.5 Hz, 1H), 5.47 (dd, *J* = 6.0 Hz, 2.0 Hz, 1H), 5.18 (dt, *J* = 6.0 Hz, 2.0 Hz, 1H), 4.77 (d, *J* = 4.0 Hz, 1H), 4.22-4.19 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.4, 134.7, 133.4, 132.5, 132.2, 128.0, 127.7, 127.56, 127.55, 126.9, 126.4, 126.0, 125.6, 83.3, 76.3, 43.3; **HRMS** (ESI) *m/z* calculated $C_{17}H_{15}O$ $[M+H]^+$ 235.1123, found 235.1118.



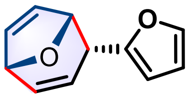
36

(**36**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)-3-(3-(4-fluorophenyl)-1-isopropyl-1-hindol-2-yl)acrylaldehyde (158.7 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **36** (101.1 mg, 81% yield) as a yellow solid, m.p. 161-163 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.5 Hz, 1H), 7.37-7.32 (m, 3H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 8.5 Hz, 2H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.62 (d, *J* = 5.5 Hz, 1H), 6.06-6.04 (m, 1H), 6.95 (d, *J* = 5.5 Hz, 1H), 5.60 (d, *J* = 9.5 Hz, 1H), 5.04 (d, *J* = 5.5 Hz, 1H), 4.70-4.62 (m, 2H), 4.52-4.50 (m, 1H), 1.72 (d, *J* = 7.0 Hz, 3H), 1.59 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.1 (d, *J* = 244.1 Hz), 138.4, 134.4, 132.3 (d, *J* = 7.8 Hz), 131.9, 131.2 (d, *J* = 3.4 Hz), 129.3, 128.8, 126.5, 126.4, 121.5, 119.6, 119.5, 116.2, 115.2 (d, *J* = 21.0 Hz), 112.3, 83.2, 76.3, 47.7, 36.6, 22.4, 22.1. **^{19}F NMR** (565 MHz, $CDCl_3$) δ (-116.08)-(-116.13) (m, 1F). **HRMS** (ESI) *m/z* calculated $C_{24}H_{23}NOF$ $[M+H]^+$ 360.1764, found 360.1761.



37

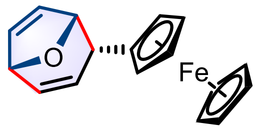
(**37**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)-3-(thiophen-2-yl)acrylaldehyde (108.0 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **37** (41.0 mg, 72% yield) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 5.4 Hz, 3.0 Hz, 1H), 7.00-6.98 (m, 1H), 6.91 (d, *J* = 5.4 Hz, 1H), 6.64 (dd, *J* = 6.0 Hz, 1.2 Hz, 1H), 6.30 (ddd, *J* = 9.6 Hz, 3.6 Hz, 2.4 Hz, 1H), 5.54-5.52 (m, 2H), 5.12 (dt, *J* = 6.0 Hz, 1.8 Hz, 1H), 4.68 (d, *J* = 3.6 Hz, 1H), 4.15-4.12 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 139.8, 138.0, 131.9, 127.5, 127.33, 127.25, 125.6, 121.3, 82.6, 76.2, 38.8. **HRMS** (ESI) *m/z* calculated $C_{11}H_{11}OS$ $[M+H]^+$ 191.0531, found 191.0532.



38

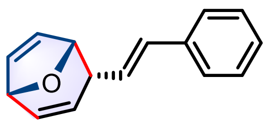
(**38**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)-3-(furan-2-yl)acrylaldehyde (103.2 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **38** (40.7 mg, 78% yield) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 1.0 Hz, 1H), 6.66 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 6.33 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 6.28 (dd, *J* = 3.0 Hz, 2.0

Hz, 1H), 6.02 (d, J = 3.0 Hz, 1H), 5.63 (dd, J = 6.0 Hz, 1.5 Hz, 1H), 5.50 (dt, J = 9.5 Hz, 2.0 Hz, 1H), 5.25 (dt, J = 6.0 Hz, 2.0 Hz, 1H), 4.69 (d, J = 3.5 Hz, 1H), 4.13-4.10 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.0, 141.5, 140.0, 132.8, 127.2, 124.7, 110.1, 105.7, 81.3, 76.2, 36.9. **HRMS** (ESI) *m/z* calculated $C_{11}H_{11}O_2$ [M+H]$^+$ 175.0759, found 175.0762.



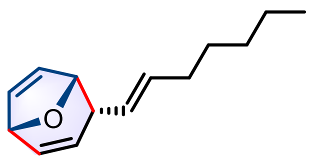
39

(**39**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from ferrocene cinnamaldehyde (138.6 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **39** (39.4 mg, 45% yield) as a red oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.57 (dd, J = 6.0 Hz, 1.0 Hz, 1H), 6.28 (ddd, J = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.72 (dt, J = 6.0 Hz, 2.0 Hz, 1H), 5.48 (dd, J = 6.0 Hz, 1.5 Hz, 1H), 4.94 (dt, J = 6.0 Hz, 1.8Hz, 1H), 4.62 (d, J = 4.0 Hz, 1H), 4.14-4.10 (m, 7H), 4.03-4.00 (m, 1H), 3.88-3.86 (m, 1H), 3.76-3.72 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.5, 132.1, 128.1, 127.3, 84.8, 83.2, 76.2, 68.4, 67.7, 67.6, 67.4, 66.6, 37.5. **HRMS** (ESI) *m/z* calculated $C_{17}H_{17}OFe$ [M+H]$^+$ 293.0629, found 293.0625.



40

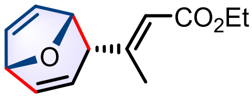
(**40**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (2*E*,4*E*)-5-phenylpenta-2,4-dienal (114.0 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **40** (51.0 mg, 81% yield) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 (d, J = 7.2 Hz, 2H), 7.30 (t, J = 7.2 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 6.67 (dd, J = 6.0 Hz, 1.2 Hz, 1H), 6.51 (d, J = 16.2 Hz, 1H), 6.25 (ddd, J = 9.6 Hz, 4.2 Hz, 2.4 Hz, 1H), 5.96-5.90 (m, 2H), 5.39 (dt, J = 9.6 Hz, 2.4 Hz, 1H), 5.03 (dt, J = 6.0 Hz, 1.8 Hz, 1H), 4.67 (d, J = 2.4 Hz, 1H), 3.57-3.52 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 140.3, 137.0, 132.3, 131.9, 128.5, 127.5, 127.0, 126.9, 126.1, 125.6, 82.1, 76.1, 41.4. **HRMS** (ESI) *m/z* calculated $C_{15}H_{15}O$ [M+H]$^+$ 211.1123, found 211.1123.



41

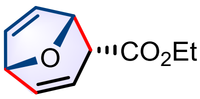
(**41**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (2*E*,4*E*)-deca-2,4-dienal (112.2 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **41** (44.7

mg, 73% yield) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.62 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 6.16 (ddd, *J* = 10.0 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.88 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 5.57 (dt, *J* = 15.5 Hz, 6.5 Hz, 1H), 5.29 (dt, *J* = 10.0 Hz, 2.0 Hz, 1H), 5.13 (dd, *J* = 15.5 Hz, 9.0 Hz, 1H), 4.92 (dt, *J* = 6.0 Hz, 1.8 Hz, 1H), 4.61 (d, *J* = 4.0 Hz, 1H), 3.34-3.29 (m, 1H), 1.98 (q, *J* = 7.0 Hz, 2H), 1.37-1.23 (m, 6H), 0.89 (q, *J* = 7.0 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.0, 133.7, 131.3, 127.8, 127.0, 125.2, 82.2, 76.0, 41.1, 32.5, 31.3, 28.9, 22.5, 14.0. **HRMS** (ESI) *m/z* calculated $C_{14}H_{19}O$ $[M-H]^-$ 203.1441, found 203.1436.



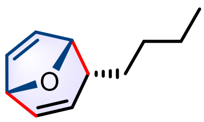
42

(**42**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from ethyl (2*E*,4*E*)-3-methyl-6-oxohexa-2,4-dienoate (117.0 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **42** (47.5 mg, 72% yield) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.61 (d, *J* = 5.5 Hz, 1H), 6.26 (ddd, *J* = 9.5 Hz, 3.5 Hz, 2.0 Hz, 1H), 5.73 (d, *J* = 5.5 Hz, 1H), 5.62 (s, 1H), 5.37 (d, *J* = 10.0 Hz, 1H), 5.14 (d, *J* = 5.5 Hz, 1H), 4.67 (d, *J* = 3.5 Hz, 1H), 4.18-4.11 (m, 2H), 3.49-3.45 (m, 1H), 2.18 (s, 3H), 1.28 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.6, 154.5, 139.5, 132.0, 126.4, 126.1, 116.4, 81.1, 76.4, 59.7, 46.4, 18.6, 14.2. **HRMS** (ESI) *m/z* calculated $C_{13}H_{17}O_3$ $[M+H]^+$ 221.1178, found 221.1178.



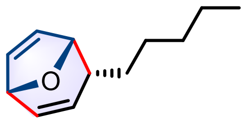
43

(**43**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from ethyl (*E*)-4-oxobut-2-enoate (105.0 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **43** (29.2 mg, 54% yield) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.69 (dd, *J* = 6.0 Hz, 1.8 Hz, 1H), 6.27 (ddd, *J* = 9.6 Hz, 4.2 Hz, 2.4 Hz, 1H), 5.92 (dd, *J* = 6.0 Hz, 1.8 Hz, 1H), 5.59 (dt, *J* = 9.6 Hz, 2.4 Hz, 1H), 5.30 (dt, *J* = 6.0 Hz, 1.8 Hz, 1H), 4.67 (d, *J* = 4.2 Hz, 1H), 4.20-4.10 (m, 2H), 3.73-3.70 (m, 1H), 1.27 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.7, 141.0, 132.9, 126.8, 122.1, 79.4, 76.4, 60.7, 42.2, 14.1. **HRMS** (ESI) *m/z* calculated $C_{10}H_{13}O_3$ $[M+H]^+$ 181.0859, found 181.0645.



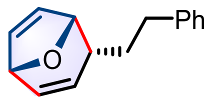
44

(**44**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)-hept-2-enal (100.2 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **44** (37.4 mg, 76% yield) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.62 (dd, *J* = 6.0 Hz, 1.8 Hz, 1H), 6.11 (ddd, *J* = 9.6 Hz, 3.6 Hz, 1.8 Hz, 1H), 5.89 (dd, *J* = 6.0 Hz, 1.8 Hz, 1H), 5.30 (dt, *J* = 9.6 Hz, 1.8 Hz, 1H), 4.96 (dt, *J* = 6.0 Hz, 1.8 Hz, 1H), 4.58 (d, *J* = 3.6 Hz, 1H), 2.66-2.61 (m, 1H), 1.36-1.28 (m, 4H), 1.25-1.20 (m, 1H), 1.16-1.10 (m, 1H), 0.91 (t, *J* = 6.6 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 140.2, 131.1, 128.4, 126.3, 81.9, 76.4, 37.3, 29.7, 28.0, 22.8, 13.9. **HRMS** (ESI) *m/z* calculated $C_{11}H_{17}O$ $[M+H]^+$ 165.1279, found 165.1281.



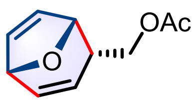
45

(**45**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)-oct-2-enal (104.4 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **45** (39.0 mg, 73% yield) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.62 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 6.11 (ddd, *J* = 10.0 Hz, 4.0 Hz, 2.0 Hz, 1H), 5.88 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 5.30 (dt, *J* = 10.0 Hz, 2.0 Hz, 1H), 4.96 (dt, *J* = 6.0 Hz, 1.8 Hz, 1H), 4.58 (d, *J* = 4.0 Hz, 1H), 2.67-2.61 (m, 1H), 1.38-1.25 (m, 6H), 1.23-1.18 (m, 1H), 1.16-1.08 (m, 1H), 0.89 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 140.2, 131.0, 128.4, 126.2, 81.9, 76.4, 37.3, 31.9, 28.3, 27.2, 22.5, 14.0. **HRMS** (ESI) *m/z* calculated $C_{12}H_{17}O$ $[M-H]^-$ 177.1285, found 177.1277.



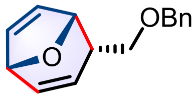
46

(**46**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)-5-phenylpent-2-enal (114.6 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **46** (54.1 mg, 85% yield) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.21-7.16 (m, 3H), 6.64 (dd, *J* = 6.0 H, 1.5 Hz, 1H), 6.14 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.0 Hz, 1H), 5.90 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 5.35 (dt, *J* = 9.5 Hz, 2.0 Hz, 1H), 4.99 (dt, *J* = 6.0 Hz, 1.8 Hz, 1H), 4.60 (d, *J* = 4.0 Hz, 1H), 2.72-2.62 (m, 3H), 1.60-1.52 (m, 1H), 1.50-1.42 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.7, 140.5, 131.4, 128.4, 128.3, 127.9, 126.1, 126.0, 81.7, 76.4, 36.8, 33.8, 30.2. **HRMS** (ESI) *m/z* calculated $C_{15}H_{17}O$ $[M+H]^+$ 213.1274, found 213.1272.



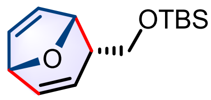
47

(**47**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)-4-oxobut-2-en-1-yl acetatel (105.0 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **47** (33.5 mg, 62% yield) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.67 (dd, *J* = 6.0 Hz, 2.0 Hz, 1H), 6.25 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.0 Hz, 1H), 5.92 (dd, *J* = 6.0 Hz, 2.0 Hz, 1H), 5.26 (dt, *J* = 9.5 Hz, 2.5 Hz, 1H), 5.04 (dt, *J* = 6.0 Hz, 2.0 Hz, 1H), 4.65 (d, *J* = 4.0 Hz, 1H), 3.94 (dd, *J* = 11.0 Hz, 7.0 Hz, 1H), 3.85 (dd, *J* = 11.0 Hz, 9.5 Hz, 1H), 3.08-3.02 (m, 1H), 2.08 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.9, 141.0, 133.6, 125.9, 123.6, 80.0, 76.3, 62.4, 36.5, 20.8. **HRMS** (ESI) *m/z* calculated $C_{10}H_{13}O_3$ $[M+H]^+$ 181.0859, found 181.1082.



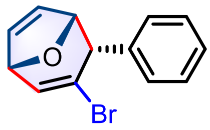
48

(**48**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)-4-(benzyloxy)but-2-enal (119.4 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **48** (57.5 mg, 84% yield) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38-7.28 (m, 5H), 6.60 (dd, *J* = 6.0, 1.5 Hz, 1H), 6.19 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.0 Hz, 1H), 5.83 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 5.24 (dt, *J* = 9.5 Hz, 2.0 Hz, 1H), 5.10 (dt, *J* = 6.0 Hz, 1.8 Hz, 1H), 4.62 (d, *J* = 4.0 Hz, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 3.30 (dd, *J* = 9.0 Hz, 6.5 Hz, 1H), 3.22 (t, *J* = 9.0 Hz, 1H), 3.11-3.05 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.3, 138.1, 132.9, 128.4, 127.72, 127.67, 126.3, 124.5, 80.5, 76.4, 73.1, 68.4, 37.6. **HRMS** (ESI) *m/z* calculated $C_{15}H_{15}O_2$ $[M-H]^-$ 227.1078, found 227.1050.



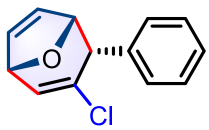
49

(**49**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)-4-((tertbutyldimethylsilyl)oxy)but-2-enal (126.6 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **49** (53.0 mg, 70% yield) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.61 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 6.18 (ddd, *J* = 10.0 Hz, 3.5 Hz, 2.0 Hz, 1H), 5.91 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 5.23 (dt, *J* = 10.0 Hz, 1.5 Hz, 1H), 5.07 (d, *J* = 6.0 Hz, 1H), 4.61 (d, *J* = 3.5 Hz, 1H), 3.45 (dd, *J* = 10.0 Hz, 6.5 Hz, 1H), 3.35 (t, *J* = 10.0 Hz, 1H), 2.95-2.88 (m, 1H), 0.89 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.3, 132.8, 126.5, 124.6, 80.6, 76.5, 61.5, 40.0, 25.8, 18.2, -5.5, -5.6. **HRMS** (ESI) *m/z* calculated $C_{14}H_{23}O_2Si$ $[M-H]^-$ 251.1473, found 251.1474.



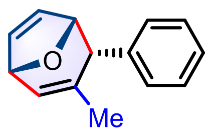
50

(**50**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*Z*)-2-bromo-3-phenylacrylaldehyde (129.6 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **50** (66.0 mg, 84% yield) as a white solid, m.p. 91-93 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34-7.27 (m, 3H), 7.09-7.07 (m, 2H), 6.79 (dd, *J* = 4.5 Hz, 1.5 Hz, 1H), 6.63 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 5.64 (dd, *J* = 6.0 Hz, 2.0 Hz, 1H), 5.07 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 4.83 (d, *J* = 4.5 Hz, 1H), 4.16 (d, *J* = 6.0 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.7, 134.6, 134.3, 128.9, 128.4, 127.8, 127.5, 124.4, 83.2, 77.8, 52.2. **HRMS** (ESI) *m/z* calculated $C_{13}H_{12}OBr$ $[M+H]^+$ 263.0072, found 263.0079.



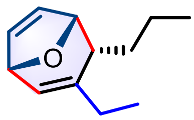
51

(**51**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*Z*)2-chloro-3-phenylacrylaldehyde (116.4 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **51** (52.3 mg, 80% yield) as a white solid, m.p. 95-97 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33-7.27 (m, 3H), 7.10-7.07 (m, 2H), 6.61 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 6.53 (dd, *J* = 4.5 Hz, 1.5 Hz, 1H), 5.62 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 5.06 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 4.88 (d, *J* = 4.5 Hz, 1H), 4.10 (d, *J* = 6.0 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.7, 134.1, 132.9, 130.3, 128.9, 128.4, 127.6, 127.4, 82.8, 76.97, 51.0. **HRMS** (ESI) *m/z* calculated $C_{13}H_{12}OCl$ $[M+H]^+$ 219.0577, found 219.0580.



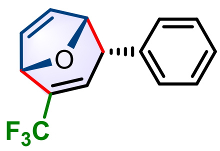
52

(**52**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)2-methyl-3-phenylacrylaldehyde (110.4 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **52** (39.8 mg, 67% yield) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.0 Hz, 2H), 7.23 (t, *J* = 7.0 Hz, 1H), 7.03 (d, *J* = 7.0 Hz, 2H), 6.57 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 6.11-6.06 (m, 1H), 5.58 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 4.93 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 4.75 (d, *J* = 4.0 Hz, 1H), 3.74 (d, *J* = 6.0 Hz, 1H), 1.47 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.7, 136.1, 134.2, 129.2, 128.2, 126.83, 126.76, 126.6, 82.2, 76.8, 48.2, 20.9. **HRMS** (ESI) *m/z* calculated $C_{14}H_{15}O$ [M+H]$^+$ 199.1123, found 199.1121.



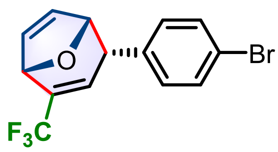
53

(**53**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)-2-ethylhex-2-enal (104.4 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **53** (32.1 mg, 60% yield) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.57 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 5.91 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 5.86-5.83 (m, 1H), 4.96 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 4.60 (d, *J* = 4.0 Hz, 1H), 2.62-2.58 (m, 1H), 1.97-1.84 (m, 2H), 1.53-1.42 (m, 2H), 1.38-1.30 (m, 1H), 1.13-1.04 (m, 1H), 0.98-0.93 (m, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.4, 140.2, 126.5, 123.5, 80.5, 76.6, 39.0, 28.7, 26.5, 20.5, 14.3, 11.7.



54

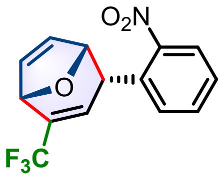
(**54**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-one (126.6 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **54** (57.5 mg, 76% yield) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34-7.25 (m, 3H), 7.10-7.08 (m, 2H), 6.65 (dd, *J* = 6.0 Hz, 1.0 Hz, 1H), 6.18-6.15 (m, 1H), 5.58 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 5.14 (dt, *J* = 6.0 Hz, 1.5 Hz, 1H), 4.92 (s, 1H), 4.07-4.01 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.9, 135.3, 134.8 (q, *J* = 31.5 Hz), 129.9 (q, *J* = 6.3 Hz), 128.8, 128.3, 127.9, 127.6, 121.7 (q, *J* = 252.0 Hz), 82.5, 74.4, 41.1. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -68.34. **HRMS** (ESI) *m/z* calculated $C_{14}H_{12}OF_3$ [M+H]$^+$ 253.0840, found 253.0845.



55

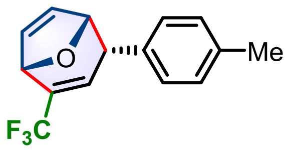
(**55**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)-4-(4-bromophenyl)-1,1,1-trifluorobut-3-en-2-one (150.0 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **55** (69.3 mg, 70% yield) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ

7.44 (d, J = 8.4 Hz, 2H), 6.97 (d, J =8.4 Hz, 2H), 6.67 (dd, J = 6.0 Hz, 1.8 Hz, 1H), 6.12-6.09 (m, 1H), 5.57 (dd, J = 6.0 Hz, 1.8 Hz, 1H), 5.11 (dt, J = 6.0 Hz, 1.8 Hz, 1H), 4.92 (s, 1H), 4.02-3.99 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.2, 135.2 (q, J = 31.3 Hz), 134.3, 131.9, 129.6, 129.2 (q, J = 6.3 Hz), 128.0, 122.6 (q, J = 268.8 Hz), 121.5, 82.2, 74.4, 40.5. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -68.41. **HRMS** (ESI) *m/z* calculated $C_{14}H_9BrF_3O$ $[M-H]^-$ 328.9794, found 328.9791.



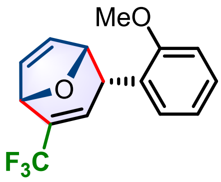
56

(**56**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-(4-nitrophenyl)but-3-en-2-one (140.1 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **56** (47.2 mg, 53% yield) as a yellow oil. **^{1}HNMR** (500 MHz, $CDCl_3$) δ 7.96 (d, J = 8.0 Hz, 1H), 7.56 (td, J = 7.5 Hz, 1.0 Hz, 1H), 7.47-7.43 (m, 1H), 7.06 (dd, J = 7.5 Hz, 1.0 Hz, 1H), 6.69 (dd, J = 6.0 Hz, 1.5 Hz, 1H), 6.05-6.03 (m, 1H), 5.64 (dd, J = 6.0 Hz, 1.5 Hz, 1H), 5.54-5.51 (m, 1H), 5.00-4.96 (m, 1H), 4.62-4.58 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.7, 138.8, 135.1 (q, J = 31.5 Hz), 133.4, 130.2, 130.1, 129.2 (q, J = 6.3 Hz), 128.6, 128.2, 124.9, 122.5 (q, J = 272.2 Hz), 81.0, 74.3, 36.6. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -68.46. **HRMS** (ESI) *m/z* calculated $C_{14}H_9F_3NO_3$ $[M-H]^-$ 296.0540, found 296.0540.



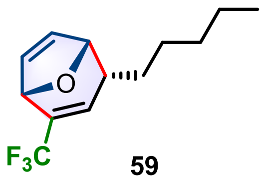
57

(**57**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)-1,1,1trifluoro-4-(ptolyl)but-3-en-2-one (130.8 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **57** (55.9 mg, 70% yield) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.12 (d, J = 7.5 Hz, 2H), 6.98 (d, J = 7.5 Hz, 2H), 6.65 (dd, J = 6.0 Hz, 1.5 Hz, 1H), 6.6-6.13 (m, 1H), 5.59 (dd, J = 6.0 Hz, 1.5 Hz, 1H), 5.12 (dt, J = 6.0 Hz, 1.5 Hz, 1H), 4.93-4.90 (m, 1H), 4.02-3.98 (m, 1H), 2.33 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.8, 137.3, 134.7 (q, J = 31.1 Hz), 132.2, 130.2 (q, J = 6.5 Hz), 129.4, 128.4, 127.8, 122.8 (q, J = 270.3 Hz), 82.6, 74.4, 40.7, 21.0. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -68.32. **HRMS** (ESI) *m/z* calculated $C_{15}H_{14}F_3O$ $[M+H]^+$ 267.0991, found 267.0988.



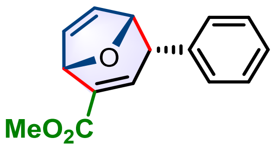
58

(**58**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (E)-1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-en-2-one (135.6 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **58** (62.6 mg, 74% yield) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 1H), 6.87 (t, J = 8.0 Hz, 2H), 6.82 (dd, J = 7.5, 1.5 Hz, 1H), 6.60 (dd, J = 6.0, 1.0 Hz, 1H), 6.12 (s, 1H), 5.52 (dd, J = 6.0, 1.5 Hz, 1H), 5.29 (d, J = 5.5 Hz, 1H), 4.91 (s, 1H), 4.51 – 4.46 (m, 1H), 3.87 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.2, 138.1, 134.7 (q, J = 31.5 Hz), 130.5 (q, J = 6.0 Hz), 128.8, 128.6, 127.8, 123.6, 120.7, 122.8 (q, J = 268.5 Hz), 110.2, 80.4, 74.2, 55.4, 34.5. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -68.26.**HRMS** (ESI) *m/z* calculated $C_{15}H_{12}F_3O_2$ $[M-H]^-$ 281.0795, found 281.0795.



59

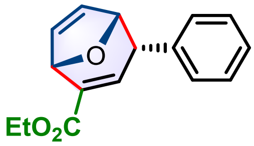
(**59**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)1,1,1-trifluoronon-3-en-2-one (124.8 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **59** (40.6 mg, 55% yield) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.62 (dd, J = 6.0 Hz, 1.5 Hz, 1H), 5.95 (dd, J = 6.0 Hz, 2.0 Hz, 1H), 5.89-5.86 (m, 1H), 5.01-4.98 (m, 1H), 4.80 (s, 1H), 2.70-2.61 (m, 1H), 1.43-1.36 (m, 2H), 1.31-1.15 (m, 6H), 0.90 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 139.7, 133.8 (q, J = 30.2 Hz), 130.5 (q, J = 6.0 Hz), 127.4, 122.8 (q, J = 270.3 Hz), 81.1, 74.5, 35.2, 31.8, 27.6, 27.0, 22.4, 14.0. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -68.29. **HRMS** (ESI) *m/z* calculated $C_{13}H_{16}F_3O$ $[M-H]^-$ 245.1159, found 245.1157.



60

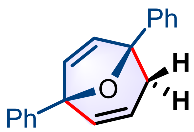
(**60**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from methyl (*E*)-2-oxo-4-phenylbut-3-enoate (123.6 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **60** (66.8 mg, 92% yield) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32-7.25 (m, 3H), 7.11-7.08 (m, 2H), 6.75-6.73 (m, 1H), 6.66 (dd, J = 6.0 Hz, 1.5 Hz, 1H), 5.53 (dd, J = 6.0 Hz, 1.5 Hz, 1H), 5.22 (s, 1H), 5.12 (dt, J = 6.0 Hz, 1.5 Hz, 1H), 4.10 (dd, J = 6.0 Hz, 2.0 Hz, 1H), 3.79

(s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.2, 139.4, 139.0, 136.2, 135.7, 128.6, 128.1, 127.7, 127.4, 82.4, 75.9, 51.8, 42.9. **HRMS** (ESI) *m/z* calculated $C_{15}H_{13}O_3$ $[M\text{-}H]^-$ 241.0870, found 241.0869.



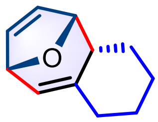
61

(**61**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from ethyl (*E*)-2-oxo-4-phenylbut-3-enoate (127.8 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **61** (72.2 mg, 94% yield) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.8 Hz, 2H), 7.27-7.25 (m, 1H), 7.11-7.08 (m, 2H), 6.74-6.72 (m, 1H), 6.66 (dd, *J* = 6.0 Hz, 1.8 Hz, 1H), 5.53 (dd, *J* = 6.0, 1.8 Hz, 1H), 5.23-5.21 (m, 1H), 5.12 (dt, *J* = 6.0 Hz, 1.8 Hz, 1H), 4.29-4.20 (m, 2H), 4.09 (dd, *J* = 6.0 Hz, 2.4 Hz, 1H), 1.32 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.8, 139.5, 138.7, 136.4, 135.8, 128.6, 128.1, 127.6, 127.3, 82.4, 75.9, 60.6, 42.9, 14.2. **HRMS** (ESI) *m/z* calculated $C_{16}H_{15}O_3$ $[M\text{-}H]^-$ 255.1027, found 255.1025.



62

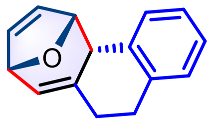
(**62**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from acrylaldehyde (83.4 mg, 0.3 mmol) and 2,5-diphenylfuran (132.1 mg, 0.6 mmol) afforded **62** (56.2 mg, 72% yield) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61-7.58 (m, 2H), 7.56-7.54 (m, 2H), 7.43-7.37 (m, 4H), 7.35-7.27 (m, 2H), 6.59 (d, *J* = 5.5 Hz, 1H), 6.52 (dt, *J* = 9.5 Hz, 2.0 Hz, 1H), 5.96 (d, *J* = 5.5 Hz, 1H), 5.73 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.0 Hz, 1H), 2.80 (dt, *J* = 18.0 Hz, 2.5 Hz, 1H), 2.36 (ddd, *J* = 18 Hz, 4.0 Hz, 2.0 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.2, 140.43, 140.35, 135.0, 130.6, 128.4, 128.3, 127.7, 127.4, 126.0, 125.1, 124.9, 86.9, 86.4, 33.2. **HRMS** (ESI) *m/z* calculated $C_{19}H_{15}O$ $[M\text{-}H]^-$ 259.1128, found 259.1127.



63

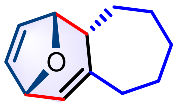
(**63**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cyclohex-1-ene-1-carbaldehyde (99.6 mg, 0.3 mmol) and furan (41 mg, 0.6 mmol) afforded **63**

(31.6 mg, 65% yield) as a white oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.59 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 5.93 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 5.78-5.75 (m, 1H), 4.78 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 4.63-4.60 (m, 1H), 2.51-2.45 (m, 1H), 2.14-2.08 (m, 1H), 1.97-1.89 (m, 1H), 1.77-1.69 (m, 2H), 1.64-1.60 (m, 1H), 1.33-1.24 (m, 1H), 1.19-1.09 (m, 1H), 1.02-0.94 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 140.0, 138.1, 126.5, 121.9, 81.2, 76.6, 40.2, 34.4, 27.3, 25.6, 25.5. **HRMS** (ESI) *m/z* calculated $C_{11}H_{15}O$ $[M+H]^+$ 163.1123, found 163.1119.



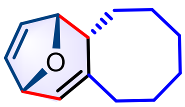
64

(**64**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from 3,4-dihydronaphthalene-2-carbaldehyde (114.0 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **64** (31.6 mg, 78% yield) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.2 Hz, 1H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.55 (dd, *J* = 6.0 Hz, 1.8 Hz, 1H), 6.00-5.98 (m, 1H), 5.62 (dd, *J* = 6.0 Hz, 1.8 Hz, 1H), 5.57 (dd, *J* = 6.0 Hz, 1.8 Hz, 1H), 4.71 (d, *J* = 4.2 Hz, 1H), 4.09 (d, *J* = 5.4 Hz, 1H), 2.85-2.81 (m, 1H), 2.77-2.71 (m, 1H), 2.34-2.31 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.8, 137.5, 135.1, 134.0, 129.2, 126.9, 126.0, 125.9, 123.8, 81.6, 76.7, 40.6, 31.8, 31.3. **HRMS** (ESI) *m/z* calculated $C_{15}H_{15}O$ $[M+H]^+$ 211.1117, found 211.1187.



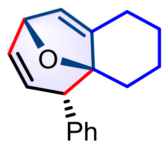
65

(**65**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cyclohept-1-ene-1-carbaldehyde (103.8 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **65** (28.0 mg, 53% yield) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.56 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 5.86 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 5.83-5.80 (m, 1H), 4.85 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 4.60 (d, *J* = 4.0 Hz, 1H), 2.75-2.70 (m, 1H), 2.22-2.15 (m, 1H), 2.12-2.07 (m, 1H), 1.67-1.60 (m, 1H), 1.56-1.51 (m, 2H), 1.50-1.41 (m, 3H), 1.40-1.35 (m, 1H), 1.34-1.27 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.6, 140.1, 125.7, 123.6, 82.7, 76.4, 41.5, 36.0, 31.0, 28.0, 27.9, 26.3. **HRMS** (ESI) *m/z* calculated $C_{12}H_{17}O$ $[M+H]^+$ 177.1274, found 177.1273.



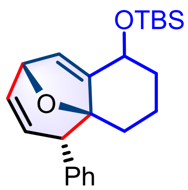
66

(**66**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from (*E*)-cyclooct-1-ene-1-carbaldehyde (108.0 mg, 0.3 mmol) and furan (41.0 mg, 0.6 mmol) afforded **66** (34.2 mg, 60% yield) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.60 (dd, *J* = 6.0, 1.8 Hz, 1H), 5.91 (dd, *J* = 6.0 Hz, 1.8 Hz, 1H), 5.84-5.82 (m, 1H), 4.85 (dd, *J* = 5.4 Hz, 1.8 Hz, 1H), 4.59-4.57 (m, 1H), 2.78-2.75 (m, 1H), 2.28-2.22 (m, 1H), 1.94-1.89 (m, 1H), 1.79-1.74 (m, 1H), 1.68-1.53 (m, 4H), 1.50-1.40 (m, 3H), 1.37-1.30 (m, 2H).; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.0, 139.8, 127.1, 124.8, 82.7, 76.6, 41.1, 33.3, 30.2, 27.3, 25.7, 25.6, 23.8. **HRMS** (ESI) *m/z* calculated $C_{13}H_{17}O$ [M-H]$^-$ 189.1285, found 189.1278.



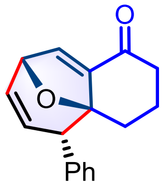
67

(**67**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and 4,5,6,7-tetrahydrobenzofuran (73.3 mg, 0.6 mmol) afforded **67** (37.1 mg, 52% yield) as a yellow oil. **^{1}H NMR** (500 MHz, CDCl3) δ 7.29-7.22 (m, 3H), 7.13 (d, *J* = 7.0 Hz, 2H), 6.31 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 6.22-6.19 (m, 1H), 5.54 (dd, *J* = 9.5 Hz, 2.5 Hz, 1H), 4.65-4.62 (m, 1H), 3.78-3.74 (m, 1H), 2.31-2.23 (m, 2H), 1.78 (td, *J* = 13.5 Hz, 5.0 Hz, 1H), 1.52-1.45 (m, 1H), 1.44-1.37 (m, 1H), 1.33-1.25 (m, 1H), 1.16-1.05 (m, 1H), 0.71-0.66 (m, 1H); **^{13}C NMR** (126 MHz, CDCl3) δ 142.0, 140.1, 131.4, 130.6, 129.7, 129.3, 128.1, 127.2, 86.0, 75.8, 51.8, 38.7, 28.2, 25.8, 23.1. **HRMS** (ESI) m/z calculated $C_{17}H_{17}O$ [M-H]$^-$ 237.1285, found 237.1282.



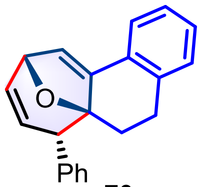
68

(**68**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and tertbutyldimethyl((4,5,6,7-tetrahydrobenzofuran-4-yl)oxy)silane (151.3 mg, 0.6 mmol) afforded **68** (58.9 mg, 54% yield) as a yellow oil. Another stereoisomer cannot be separated in analytical purity by column chromatography. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25-7.18 (m, 5H), 6.64 (d, *J* = 2.0 Hz, 1H), 6.27-6.22 (m, 1H), 5.58 (dd, *J* = 9.5 Hz, 2.0 Hz, 1H), 4.63-4.60 (m, 1H), 4.36 (t, *J* = 6.0 Hz, 1H), 3.85-3.81 (m, 1H), 2.23 (dt, *J* = 13.5 Hz, 6.5 Hz, 1H), 1.85 (q, *J* = 7.0 Hz, 1H), 1.37-1.31 (m, 1H), 1.20-1.14 (m, 2H), 0.89 (s, 9H), 0.63-0.56 (m, 1H), 0.05 (s, 3H), -0.07 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.6, 139.4, 138.4, 130.7, 130.4, 129.8, 127.8, 126.7, 88.6, 75.9, 66.5, 52.6, 35.8, 32.8, 26.1, 18.5, 18.1, -4.3, -4.6. **HRMS** (ESI) *m/z* calculated $C_{23}H_{33}O_2Si$ [M+H]$^+$ 369.2250, found 369.2251.



69

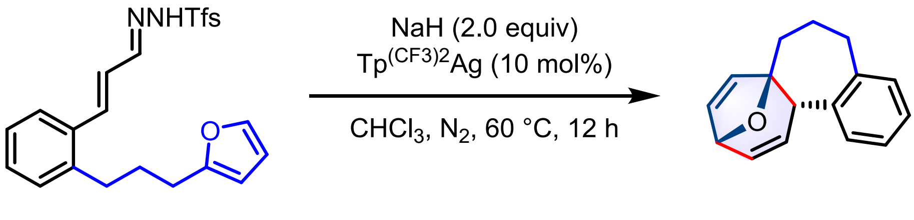
(**69**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and 6,7-dihydrobenzofuran-4(5*H*)-one (81.6 mg, 0.6 mmol) afforded **69** (37.1 mg, 49% yield) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 2.0 Hz, 1H), 7.25-7.21 (m, 3H), 7.12-7.09 (m, 2H), 6.27 (ddd, *J* = 9.5 Hz, 4.5 Hz, 2.5 Hz, 1H), 5.70 (dd, *J* = 9.5 Hz, 2.5 Hz, 1H), 4.84-4.81 (m, 1H), 3.84-3.80 (m, 1H), 2.22-2.12 (m, 2H), 1.99 (ddd, *J* = 17.0 Hz, 6.5 Hz, 4.0 Hz, 1H), 1.62-1.55 (m, 1H), 1.38-1.30 (m, 1H), 1.13-1.05 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.3, 144.6, 140.1, 136.5, 132.5, 129.2, 128.7, 127.9, 127.8, 87.6, 76.3, 51.1, 38.9, 33.2, 18.9. **HRMS** (ESI) *m/z* calculated $C_{17}H_{17}O_2$ $[M+H]^+$ 253.1229, found 253.1228.



70

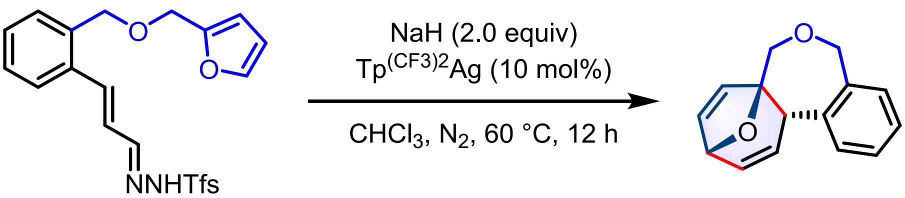
(70) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and 4,5-dihydronaphtho[2,1-*b*]furan (102.1 mg, 0.6 mmol) afforded **70** (37.1 mg, 49% yield) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 7.00-6.98 (m, 2H), 6.96-6.88 (m, 4H), 6.84 (d, *J* = 2.5 Hz, 1H), 6.68 (d, *J* = 7.5 Hz, 1H), 6.34 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.56 (dd, *J* = 9.5 Hz, 2.5 Hz, 1H), 4.90-4.87 (m, 1H), 3.89-3.86 (m, 1H), 2.60-2.54 (m, 1H), 2.40-2.35 (m, 1H), 2.30-2.17 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.2, 138.6, 136.3, 131.0, 130.9, 130.1, 129.4, 129.1, 128.0, 127.4, 127.3, 126.9, 125.8, 124.3, 86.1, 77.2, 51.9, 34.2, 27.6.

2.2 Silver-catalyzed Intramolecular [4 + 3] Reactions



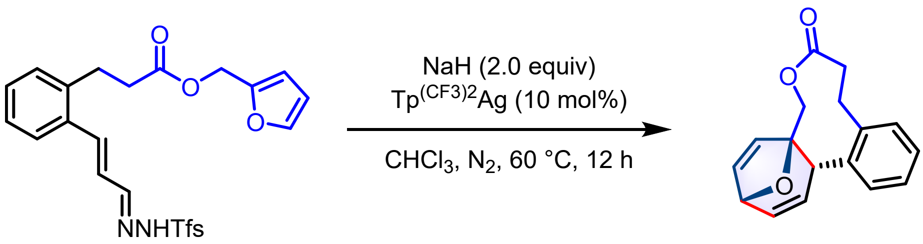
S-71 **71**

Synthesis of compound **71**: To an oven-dried screwcap reaction tube were added vinyl-*N*-triftosylhydrazone (138.6 mg, 0.3 mmol), NaH (24.0 mg, 60 wt% dispersion in mineral oil, 0.6 mmol, 2.0 equiv) and dry $CHCl_3$ (8.0 mL) inside a glove box with nitrogen atmosphere. Then, $Tp^{(CF3)2}Ag$ (24.0 mg, 10 mol%) were added and the vial was sealed. After transferred out of the glove box, the reaction heated at 60 °C in the dark for additional 12 h. When the reaction was completed, the reaction was allowed to cool to room temperature, and filtered through a short pad of silica gel with CH_2Cl_2 as an eluent. After removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel (using petroleum ether / EtOAc as eluent) to obtain **71** (51.1 mg, 76% yield) as a colorless oil. (**71**) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.16-7.08 (m, 4H), 6.46 (ddd, *J* = 9.5 Hz, 4.5 Hz, 2.5 Hz, 1H), 6.36 (d, *J* = 5.5 Hz, 2.0 Hz, 1H), 5.79 (dd, *J* = 9.5 Hz, 3.0 Hz, 1H), 5.30 (d, *J* = 5.5 Hz, 1H), 4.74 (d, *J* = 4.5 Hz, 1H), 4.03-4.00 (m, 1H), 2.97 (t, *J* = 13.0 Hz, 1H), 2.80 (dd, *J* = 14.0 Hz, 6.5 Hz, 1H), 2.24-2.10 (m, 3H), 1.52-1.42 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.5, 136.5, 136.1, 131.9, 129.9, 129.7, 128.6, 126.8, 126.3, 126.2, 86.8, 76.0, 45.1, 41.1, 35.2, 26.1. **HRMS** (ESI) *m/z* calculated $C_{16}H_{15}O$ [M-H]$^-$ 223.1128, found 223.1126.



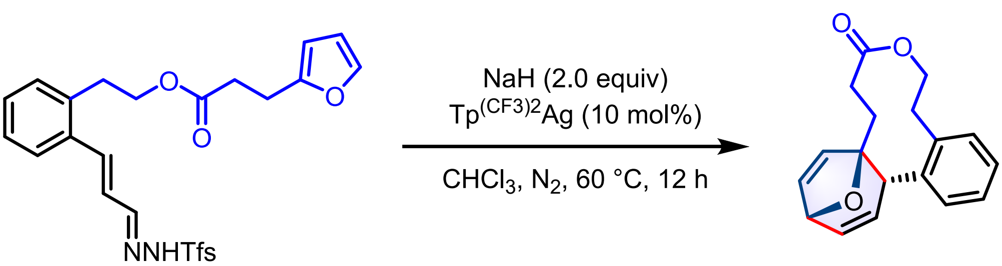
72

Synthesis of compound **72**: To an oven-dried screwcap reaction tube were added vinyl-*N*-triftosylhydrazone (139.2 mg, 0.3 mmol), NaH (24.0 mg, 60 wt% dispersion in mineral oil, 0.6 mmol, 2.0 equiv) and dry $CHCl_3$ (8.0 mL) inside a glove box with nitrogen atmosphere. Then, $Tp^{(CF3)2}Ag$ (24.0 mg, 10 mol%) were added and the vial was sealed. After transferred out of the glove box, the reaction heated at 60 °C in the dark for additional 12 h. When the reaction was completed, the reaction was allowed to cool to room temperature, and filtered through a short pad of silica gel with CH_2Cl_2 as an eluent. After removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel (using petroleum ether / EtOAc as eluent) to obtain **72** (48.8 mg, 72% yield) as a colorless oil. (**72**) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25-7.22 (m, 1H), 7.21-7.17 (m, 3H), 6.50 (ddd, *J* = 9.5 Hz, 4.5 Hz, 2.5 Hz, 1H), 6.42 (dd, *J* = 6.0 Hz, 1.0 Hz, 1H), 5.88 (dd, *J* = 9.5 Hz, 3.0 Hz, 1H), 5.46 (d, *J* = 6.0 Hz, 1H), 4.78-4.76 (m, 1H), 4.75 (d, *J* = 2.5 Hz, 2H), 4.18-4.15 (m, 2H), 4.06 (d, *J* = 11.5 Hz, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 139.5, 137.3, 136.8, 132.7, 129.4, 128.9, 128.5, 127.8, 126.8, 125.8, 84.8, 79.8, 76.5, 74.4, 44.6. **HRMS** (ESI) *m/z* calculated $C_{15}H_{13}O_2$ [M-H]$^-$ 225.0921, found 225.0920.



73

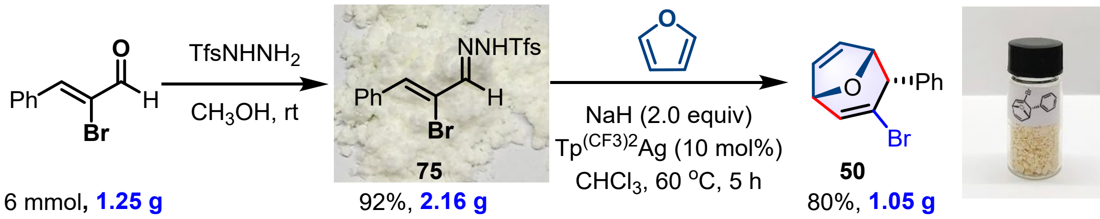
Synthesis of compound **73**: To an oven-dried screwcap reaction tube were added vinyl-*N*-triftosylhydrazone (151.8 mg, 0.3 mmol), NaH (24.0 mg, 60 wt% dispersion in mineral oil, 0.6 mmol, 2.0 equiv) and dry $CHCl_3$ (8.0 mL) inside a glove box with nitrogen atmosphere. Then, $Tp^{(CF3)2}Ag$ (24.0 mg, 10 mol%**)** were added and the vial was sealed. After transferred out of the glove box, the reaction heated at 60 °C in the dark for additional 12 h. When the reaction was completed, the reaction was allowed to cool to room temperature, and filtered through a short pad of silica gel with CH_2Cl_2 as an eluent. After removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel (using petroleum ether / EtOAc as eluent) to obtain **73** (48.2 mg, 60% yield) as a colorless oil. (**73**) ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.21-7.15 (m, 2H), 7.13-7.08 (m, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.70 (dd, *J* = 6.0, 2.0 Hz, 1H), 6.22-6.17 (m, 1H), 5.69 (d, *J* = 5.5 Hz, 1H), 5.43 (dd, *J* = 9.5, 2.0 Hz, 1H), 4.81 (d, *J* = 3.5 Hz, 1H), 4.72 (d, *J* = 13.0 Hz, 1H), 4.46 (s, 1H), 4.28 (d, *J* = 12.5 Hz, 1H), 3.39 (td, *J* = 13.0, 5.0 Hz, 1H), 2.93-2.87 (m, 1H), 2.86-2.80 (m, 1H), 2.47 (td, *J* = 12.5, 5.0 Hz, 1H); ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 173.1, 139.8, 138.3, 135.8, 131.8, 130.6, 129.4, 129.2, 128.5, 127.6, 126.8, 91.5, 78.0, 67.1, 40.1, 36.9, 29.9. **HRMS** (ESI) *m/z* calculated $C_{17}H_{17}O_3$ [M+H]$^+$ 267.1027, found 267.1027.



74

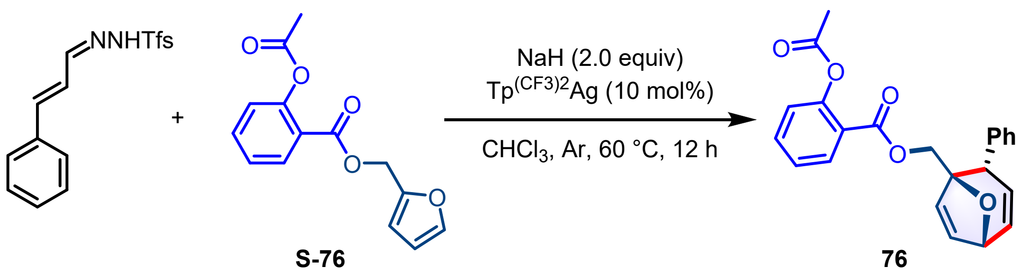
Synthesis of compound **74:** To an ovendried screwcap reaction tube equipped with a Tefloncoated magnetic stir bar were added vinyl-*N*-triftosylhydrazone (0.3 mmol, 156 mg), NaH (24.0 mg, 60 wt% dispersion in mineral oil, 0.6 mmol, 2.0 equiv) and dry $CHCl_3$ (8.0 mL) inside a glove box with nitrogen atmosphere. Then, $Tp^{(CF3)2}Ag$ (24.0 mg, 10 mol%**)** were added and the vial was sealed. After transferred out of the glove box, the reaction heated at 60 °C in the dark for additional 12 h. When the reaction was completed, the reaction was allowed to cool to room temperature, and filtered through a short pad of silica gel with CH_2Cl_2 as an eluent. After removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel (using petroleum ether / EtOAc as eluent) to obtain **74** (57.5 mg, 68% yield) as a colorless oil. (**74**) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.22-7.19 (m, 2H), 7.18-7.16 (m, 1H), 7.15-7.10 (m, 1H), 6.66 (dd, *J* = 6.0 Hz, 2.0 Hz, 1H), 6.14 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.89 (d, *J* = 6.0 Hz, 1H), 5.32 (dd, *J* = 9.5 Hz, 2.5 Hz, 1H), 5.15-5.04 (m, 1H), 4.80-4.75 (m, 1H), 3.94-3.80 (m, 2H), 3.40-3.32 (m, 1H), 2.82-2.75 (m, 1H), 2.51 (dt, *J* = 14.5 Hz, 2.0 Hz, 1H), 2.45 (ddd, *J* = 16.0 Hz, 6.5 Hz, 2.0 Hz, 1H), 2.35 (td, *J* = 14.5 Hz, 2.0 Hz, 1H), 1.89-1.78 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.1, 138.4, 138.3, 137.6, 132.1, 132.0, 130.7, 128.8, 128.3, 127.4, 126.7, 89.7, 77.9, 65.2, 41.9, 32.0, 31.6, 29.0. **HRMS** (ESI) *m/z* calculated $C_{18}H_{17}O_3$ $[M-H]^-$ 281.1183, found 281.1183.

2.3 Gram-Scale Experiments



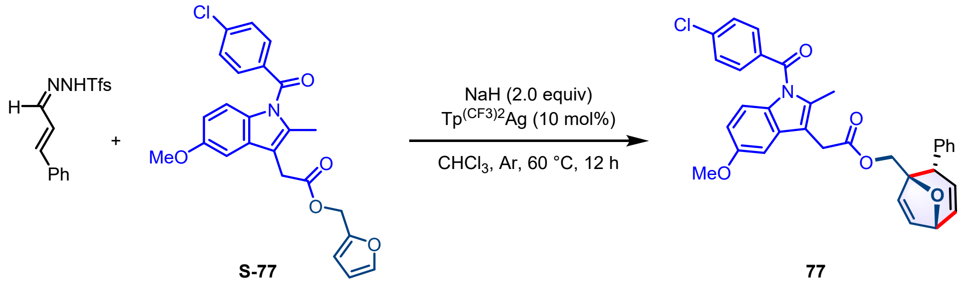
To an ovendried screwcap reaction tube equipped with a Tefloncoated magnetic stir bar were added vinyl-*N*-triftosylhydrazone (2.16 g, 5 mmol), NaH (400.0 mg, 60 wt% dispersion in mineral oil, 0.6 mmol, 2.0 equiv) and dry $CHCl_3$ (50.0 mL) inside a glove box with nitrogen atmosphere. Then, furan (1.40 g, 10.0 mmol, 2.0 equiv) and $Tp^{(CF3)2}Ag$ (400.0 mg, 10 mol%) were added and the vial was sealed. After transferred out of the glove box, the reaction heated at 60 °C in the dark for additional 12 h. When the reaction was completed, the reaction was allowed to cool to room temperature, and filtered through a short pad of silica gel with CH_2Cl_2 as an eluent. After removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel (using petroleum ether / EtOAc as eluent) to obtain **50** (1.05 g, 80% yield) as a white solid.

2.4 Late-Stage Modification of Pharmaceutical Molecules



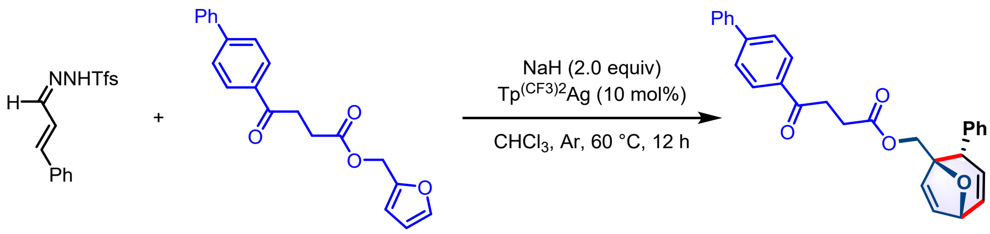
(**76**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and furan (from Aspirin, 156 mg, 0.6 mmol) afforded **76** (65.4 mg, 58% yield) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.56 (td, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.30 (td, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.28-7.21 (m, 3H), 7.13-7.08 (m, 3H), 6.69 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 6.36 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.61

(dd, *J* = 9.5 Hz, 2.5 Hz, 1H), 5.44 (d, *J* = 6.0 Hz, 1H), 4.86 (d, *J* = 4.0 Hz, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.05-4.02 (m, 1H), 2.37 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.8, 164.2, 150.8, 140.0, 136.2, 134.0, 132.0, 130.8, 130.1, 128.9, 128.4, 127.3, 127.0, 126.0, 123.8, 123.0, 88.7, 77.7, 65.7, 44.7, 21.1. **HRMS** (ESI) *m/z* calculated $C_{23}H_{19}O_5$ $[M-H]^-$ 375.1238, found 375.1238.



S-77 **77**

(**77**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and furan (from Indometacin, 262.2 mg, 0.6 mmol) afforded **77** (104.6 mg, 63% yield) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.20-7.12 (m, 3H), 7.02 (d, *J* = 2.5 Hz, 1H), 6.89-6.86 (m, 2H), 6.84 (d, *J* = 9.0 Hz, 1H), 6.66 (dd, *J* = 9.0 Hz, 2.5 Hz, 1H), 6.62 (dd, *J* = 9.0 Hz, 2.5 Hz, 1H), 6.32 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.50 (dd, *J* = 9.5 Hz, 2.5 Hz, 1H), 5.30 (d, *J* = 6.0 Hz, 1H), 4.81 (d, *J* = 4.0 Hz, 1H), 4.31 (ABq, *J* = 12.5 Hz, 2H), 3.84 (s, 3H), 3.82-3.80 (m, 1H), 3.75 (ABq, *J* = 15.5 Hz, 2H), 2.41 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.6, 168.2, 156.1, 139.9, 139.2, 136.1, 136.0, 133.8, 131.2, 130.7, 130.5, 129.9, 129.1, 128.7, 128.3, 127.3, 126.7, 114.9, 112.5, 112.0, 101.2, 88.7, 77.7, 65.4, 55.7, 44.2, 30.3, 13.3. **HRMS** (ESI) *m/z* calculated $C_{33}H_{27}ClNO_5$ $[M-H]^-$ 552.1583, found 552.1591.

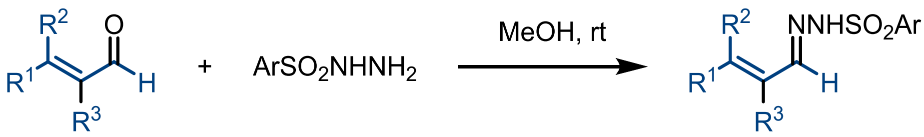


S-78 **78**

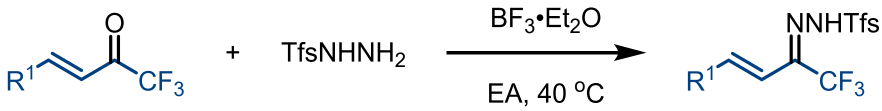
(**78**) Prepared according to **General Procedure A** using vinyl-*N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and furan (from Fenbufen, 200.5 mg, 0.6 mmol) afforded **78** (74.3 mg, 55% yield) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.64-7.62 (m, 2H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.42-7.38 (m, 1H), 7.29-7.23 (m, 3H), 7.16-7.11 (m, 2H), 6.64 (dd, *J* = 6.0 Hz, 1.5 Hz, 1H), 6.34 (ddd, *J* = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.59 (dd, *J* = 9.5 Hz, 2.5 Hz, 1H), 5.39 (d, *J* = 6.0 Hz, 1H), 4.84 (d, *J* = 4.0 Hz, 1H), 4.36 (ABq, *J* = 17.0 Hz, 2H), 4.02-3.98 (m, 1H), 3.41-3.32 (m, 2H), 2.95-2.81 (m, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 197.5, 172.8, 145.9, 139.84, 138.76, 136.2, 135.3, 130.7, 130.1, 128.9, 128.6, 128.4, 128.2, 127.3, 127.24, 127.22, 127.0, 88.7, 77.7, 65.2, 44.5, 33.4, 28.2. **HRMS** (ESI) *m/z* calculated $C_{30}H_{25}O_4$ $[M-H]^-$ 449.1758, found 449.1761.

3. The Synthesis of Substrates.

General procedures for synthesis of vinyl-*N*-sulfonylhydrazones

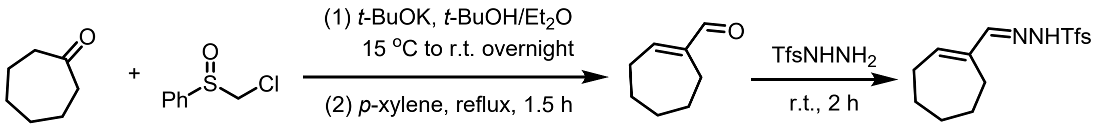


Vinyl-*N*-sulfonylhydrazones were prepared according to literature procedure[6]. To a stirred solution of $ArSO_2NHNH_2$ (2.0 mmol, 1.0 equiv) in methanol (2 mL) were added carbonyl compounds (2.2 mmol, 1.1 equiv) and the mixture was stirred for 1-12 h at room temperature. If the hydrazone precipitated, the mixture was filtered and the resulting solid was washed with ice cold diethyl ether and dried under reduced pressure to give pure Vinyl-*N*-sulfonylhydrazones. If not, the solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel to obtain the vinyl-*N*-sulfonylhydrazones. The yields were around 80% in general.



To a stirred solution of $TfsNHNH_2$ (2.2 mmol, 1.1 equiv) in ethyl acetate (2 mL) were added carbonyl compounds (2.2 mmol, 1.1 equiv) and boron trifluoride etherate. The mixture was stirred for 5 h at 40 °C. When the ketones were consumed, the solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel to obtain the vinyl-*N*-sulfonylhydrazones.

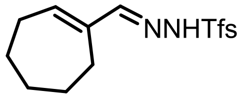
General Procedures for synthesis of vinyl-*N*-triftosylhydrazones



Cyclic cinnamaldehyde **S-65'**[7,8]: A two necked-flask was equipped with a thermometer, addition funnel and then flushed with argon. The flask was charged with cycloheptanone (676.2 mg, 6 mmol) and chloromethyl phenyl sulfoxide (1.1 g, 6.3 mmol). The solids were dissolved in a mixture of *tert*-butanol and Et_2O (2:1). The clear solution was cooled to 10 °C. The addition funnel was charged with potassium-tert-butoxide (706.9 mg, 6.3 mmol) dissolved in tert-butanol (0.63 mol L^{-1}). The resulting suspension was slowly added to the reaction mixture ensuring that the inside temperature did not rise above 15 °C. The solution turned turbid and after a while yellow. After addition was complete the cooling bath was removed and the solution stirred at room temperature overnight. The orange coloured reaction was poured into distilled water and the aqueous phase was back-extracted with Et_2O. The combined organic layers were dried over Na_2SO_4, filtered and concentrated to yield a light yellow oil. The crude oil was transferred into a roundbottomed flask and dissolved in p-xylene (0.89 mol L^{-1}). The flask was heated at reflux for

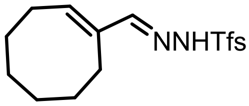
1.5 h, during which time the reaction mixture turned dark brown. The solution was cooled to rt and the solvent was evaporated in vacuo. The resulting dark brown crude oil was purified by flash column chromatography on silica gel (PE/Et_2O) to obtain **S-65' (**305.3 mg, 41%**)** as a dark orange oil.

vinyl-*N*-sulfonylhydrazone **S-65:** To a stirred solution of $TfsNHNH_2$ (2.0 mmol, 1.0 equiv) in MeOH was added **S-65'**. The mixture was stirred for 2 h at room temperature and purified by flash chromatography on silica gel to give vinyl-*N*-sulfonylhydrazone **S-65** as a white solid.



S-65

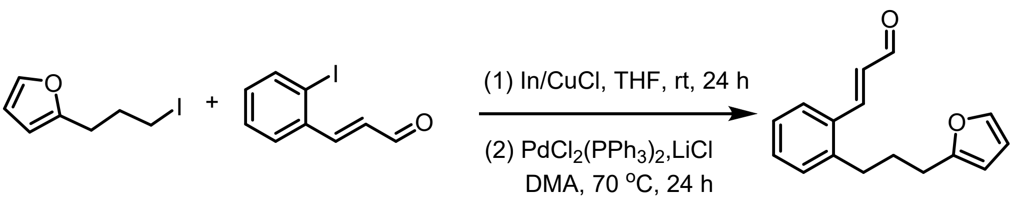
(**S-65**) White solid; **^{1}H NMR** (500 MHz, DMSO) δ 11.58 (s, 1H), 8.02 (d, *J* = 7.5 Hz, 1H), 8.00-7.96 (m, 1H), 7.89 (dt, *J* = 7.9, 3.9 Hz, 1H), 7.84 (t, *J* = 7.6 Hz, 1H), 7.57 (s, 1H), 6.17 (t, *J* = 6.7 Hz, 1H), 2.30-2.25 (m, 2H), 2.22 (dd, *J* = 11.0 Hz, 6.5 Hz, 2H), 1.66 (dt, *J* = 11.7, 6.0 Hz, 2H), 1.45-1.38 (m, 2H), 1.34-1.27 (m, 2H); **^{13}C NMR** (126 MHz, DMSO) δ 151.8, 142.7, 141.5, 138.5, 133.8, 133.6, 131.7, 128.8 (q, *J* = 6.3 Hz), 126.9 (q, *J* = 32.5 Hz), 123.2 (q, *J* = 272.5 Hz), 31.9, 28.9, 26.5, 26.1, 25.4.



S-66

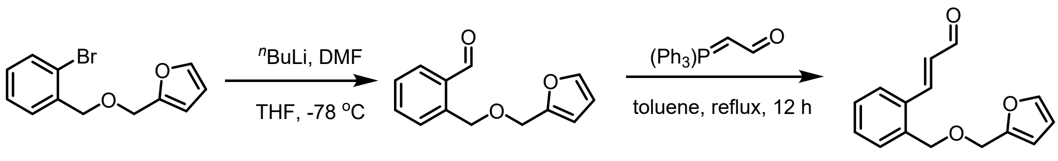
(**S-66**) White solid; **^{1}H NMR** (500 MHz, DMSO) δ 11.53 (s, 1H), 8.02 (d, *J* = 7.5 Hz, 1H), 7.98 (dd, *J* = 7.5, 0.5 Hz, 1H), 7.90-7.81 (m, 2H), 7.57 (s, 1H), 6.00 (t, *J* = 8.5 Hz, 1H), 2.29-2.24 (m, 2H), 2.24-2.16 (m, 2H), 1.50-1.43 (m, 2H), 1.37-1.31 (m, 2H), 1.29-1.18 (m, 4H); **^{13}C NMR** (126 MHz, DMSO) δ 151.0, 140.3, 138.5, 138.2, 133.8, 133.5, 131.8, 128.7 (q, *J* = 6.3 Hz), 126.9 (q, *J* = 32.5 Hz), 123.2 (q, *J* = 272.5 Hz), 29.7, 28.4, 27.0, 26.6, 25.9, 23.1.

Synthesis of substrate S-71 for product 71



Synthesis of compound **S-71**[2]: To a 100 mL sample vial was added alkyl iodide (1.18 g, 5 mmol), indium (1.15 g, 10 mmol), CuCl (0.99 g, 10 mmol), and analytical grade THF (20 mL) sequentially. The reaction was stirred vigorously at room temperature for 24 h. After reaction, it was stood for around 10 minutes. Then the upper clear solution was carefully separated from the bottom black precipitate by syringe. The residual black precipitate was washed with 20 mL THF and the THF layer was carefully separated by syringe. The combined organic layers were concentrated under vacuo. Then the residue was dissolved in 15 mL DMA and transferred to another 100 mL sample vial. Aryl halide (903.0 mg, 3.5 mmol), LiCl (423.9 mg, 10 mmol), and $PdCl_2(PPh_3)_2$ (175.5 mg, 0.25 mmol, 0.05 equiv) was added to the sample vial sequentially. The reaction mixture was stirred at 100 °C for 24 h. After reaction, it was directly purified by silica gel column chromatography using EtOAc/hexane as eluant to afford the desired product **S-71** (722.4 mg) as a yellow oil. (**S-71**) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.66 (d, J = 7.5 Hz, 1H), 7.68 (d, J = 16.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.36 (td, J = 7.5 Hz, 1.5 Hz, 1H), 7.33 (dd, J = 2.0 Hz, 1.0 Hz, 1H), 7.29-7.23 (m, 2H), 6.66 (dd, J = 15.5 Hz, 7.5 Hz, 1H), 6.31 (dd, J = 3.0, 2.0 Hz, 1H), 6.04 (dd, J = 3.0 Hz, 0.5 Hz, 1H), 2.83-2.79 (m, 2H), 2.70 (t, J = 7.0 Hz, 2H), 1.98-1.90 (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 193.8, 155.3, 149.9, 142.0, 141.0, 132.3, 131.0, 130.3, 129.7, 126.9, 126.8, 110.2, 105.4, 32.3, 29.9, 27.4.

Synthesis of substrate S-72 for product 72

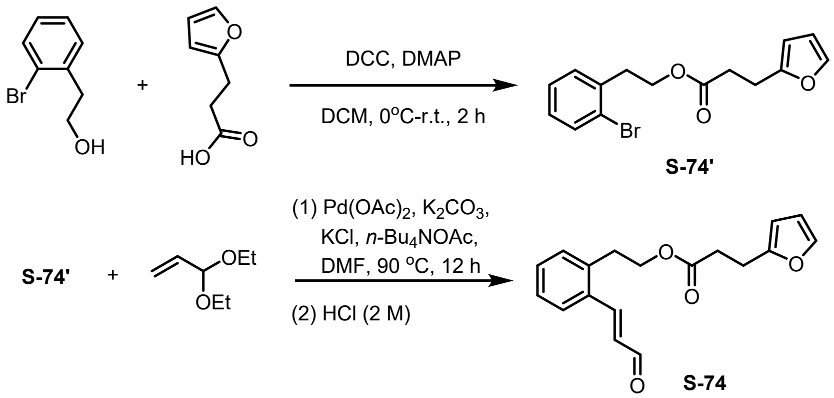


S-72' **S-72**

Synthesis of compound **S-72'**[3]: A solution of n-BuLi (6 mL, 15 mmol, 2.5 M) was added dropwise to a solution of 2-(((2-bromobenzyl)oxy)methyl)furan (2.66 g, 10 mmol) in THF (40 mL) at -78 °C under a N_2 atmosphere. The reaction mixture was stirred at -78 °C for 1 h. DMF (3.66 g, 50 mmol) was added dropwise to the resulting mixture. The reaction was stirred at room temperature overnight and quenched by saturated NH_4Cl solution (40 mL). The reaction was extracted by EtOAc (40 mL × 3) and dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography to afford **S-72'** (1.51 g, 70%).

Synthesis of compound **S-72**[4]: To a flask equipped with a stir bar and a condenser was added **S-72'** (1.62 g, 7.5 mmol), (triphenylphosphoranylidene) acetaldehyde (1.52 g, 5.0 mmol), and toluene (20 mL). The reaction mixture was refluxed overnight. After evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography to afford **S-72** (665.8 mg, 55%) as a yellow oil. **(S-72) ^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.66 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 16.0 Hz, 1H), 7.65 (d, J = 7.0 Hz, 1H), 7.45 (dd, J = 1.5, 1.0 Hz, 1H), 7.41 – 7.38 (m, 3H), 6.66 (dd, J = 16.0, 8.0 Hz, 1H), 6.40 – 6.36 (m, 2H), 4.65 (s, 2H), 4.53 (s, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 194.1, 151.3, 149.9, 143.0, 136.8, 133.6, 130.8, 130.5, 130.0, 128.8, 127.0, 110.4, 109.9, 69.8, 63.9.

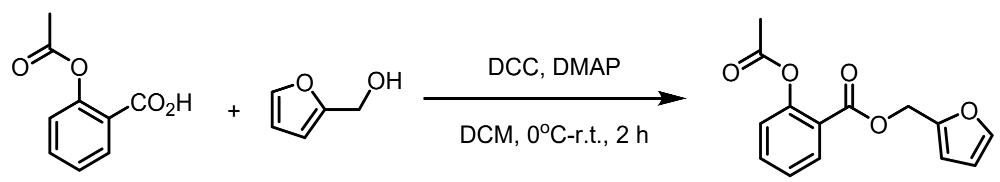
Synthesis of substrate S-74 for product 74



Synthesis of compound **S-74'[1]:** To an oven-dried flask 2-(2-bromophenyl)ethan-1-ol (1.60 g, 8 mmol) and dry dichloromethane (50 mL) were charged under nitrogen atmosphere. To the above solution, 3-(furan-2-yl)propanoic acid (1.12 g, 8 mmol) was added and the reaction mixture cooled to 0 °C. To this cooled reaction mixture, DCC (1.98 g, 9.6 mmol) and a catalytic amount of DMAP (48.8 mg, 0.4 mmol) were added. Initially, the reaction mixture was homogeneous. The white solid separates out from the reaction mixture after 2 h duration. Progress of the reaction was monitored using TLC. After completion of the reaction mixture was filtered and concentrated in vacuo. The residue was subjected to column chromatography (hexane/EtOAc) to give S-**74'** (2.20 g, 85% yield) as a yellow oil.

Synthesis of compound **S-74[5]:** To a stirred solution of S-**74'** (1.61 g, 5 mmol) in 50 mL of DMF were added acrolein diethyl acetal (2.3 mL, 15 mmol), n-Bu_4NOAc (3.10 g, 10 mmol), K_2CO_3 (1.10 g, 7.5 mmol), KCl (372.8 mg, 5 mmol), and $Pd(OAc)_2$ (33.7 mg, 0.15 mmol). The mixture was stirred for 12 h at 90 °C. After cooling, 2 M HCl was slowly added and the reaction mixture was stirred at room temperature for 10 min. Then, it was diluted with ether and washed with water. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by chromatography to obtain **S-74** (834.7 mg, 50% yield) as a yellow oil.

Synthesis of substrate S-76 for product 76

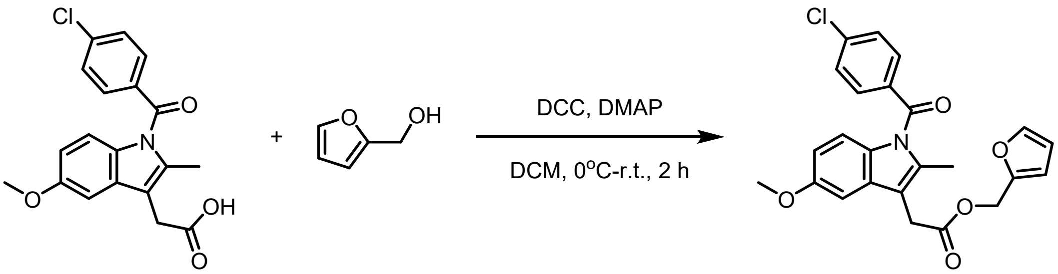


Acetylsalicylic acid **S-76**

Synthesis of compound **S-76**[1]: To an oven-dried flask acetylsalicylic acid (322.2 mg, 1.79 mmol) in dichloromethane (25 mL) was charged under nitrogen atmosphere. To the above solution, furan-2-ylmethanl (175.4 mg, 1.79 mmol) was added and the reaction mixture cooled to 0 °C. To this cooled reaction mixture, DCC (443.6 mg, 2.15 mmol) and a catalytic amount of DMAP (10.9 mg, 0.09 mmol) were added. Initially, the reaction mixture was homogeneous. The white solid separates out from the reaction mixture after 2 h duration. Progress of the reaction was monitored using TLC. After completion of the reaction mixture was filtered and concentrated in vacuo. The residue was subjected to column chromatography (hexane/EtOAc) to furnish the corresponding ester **S-76** as a yellow oil. (395.6 mg, 85% yield) .

(**S-76**) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 7.57-7.52 (m, 1H), 7.45 (dd, *J* = 1.5 Hz, 0.5 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.08 (dd, *J* = 8.5 Hz, 1.0 Hz, 1H), 6.47 (d, *J* = 3.5 Hz, 1H), 6.38 (dd, *J* = 3.0, 2.0 Hz, 1H), 5.25 (s, 2H), 2.19 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.6, 164.2, 150.5, 149.0, 143.3, 134.0, 132.0, 126.0, 123.8, 122.9, 111.1, 110.6, 58.6, 20.6.

Synthesis of substrate S-77 for product 77

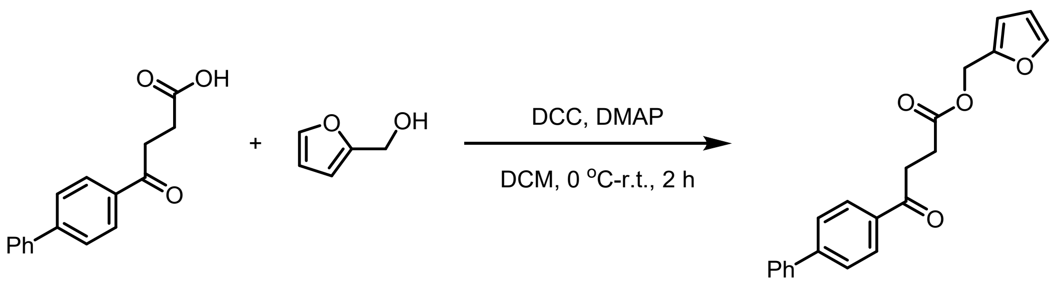


Indometacin **S-77**

Synthesis of compound **S-77**[1]: To an oven-dried flask indometacin (639.2 mg, 1.79 mmol,) in (25 mL) was charged under nitrogen atmosphere. To the above solution, furan-2-ylmethanl (175.4 mg, 1.79 mmol) was added and the reaction mixture cooled to 0 °C. To this cooled reaction mixture, DCC (443.6 mg, 2.15 mmol) and a catalytic amount of DMAP (10.9 mg, 0.09 mmol) were added. Initially, the reaction mixture was homogeneous. The white solid separates out from the reaction mixture after 2 h duration. Progress of the reaction was monitored using TLC. After completion of the reaction mixture was filtered and concentrated in vacuo. The residue was subjected to column chromatography (hexane/EtOAc) to furnish the corresponding ester **S-77** as a yellow solid. (380.3 mg, 87% yield).

(**S-77**) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.67-7.63 (m, 2H), 7.48-7.44 (m, 2H), 7.41 (dd, *J* = 1.5, 0.5 Hz, 1H), 6.93 (d, *J* = 2.5 Hz, 1H), 6.88 (d, *J* = 9.0 Hz, 1H), 6.66 (dd, *J* = 9.0 Hz, 2.5 Hz, 1H), 6.39 (d, *J* = 3.5 Hz, 1H), 6.36 (dd, *J* = 3.5 Hz, 2.0 Hz, 1H), 5.09 (s, 2H), 3.80 (s, 3H), 3.69 (s, 2H), 2.35 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.4, 168.2, 156.0, 149.2, 143.3, 139.2, 135.9, 133.8, 131.1, 130.7, 130.5, 129.1, 114.9, 112.3, 111.8, 110.8, 110.6, 101.1, 58.5, 55.6, 30.1, 13.3..

Synthesis of substrate S-78 for product 78



Fenbufen **S-78**

Synthesis of compound **S-78**[1]: To an oven-dried flask fenbufen (454.8 mg, 1.79 mmol) in dry dichloromethane (25 mL) was charged under inert atmosphere. To the above solution, furan-2-

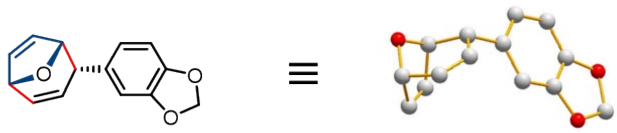
ylmethanl (175.4 mg, 1.79 mmol) was added and the reaction mixture cooled to 0 ℃. To this cooled reaction mixture, DCC (443.6 mg, 2.15 mmol) and a catalytic amount of DMAP (10.9 mg ,0.9 mmol) were added. Initially, the reaction mixture was homogeneous. The white solid separates out from the reaction mixture after 2 h duration. Progress of the reaction was monitored using TLC. After completion of the reaction mixture was filtered and concentrated in vacuo. The residue was subjected to column chromatography (hexane/EtOAc) to furnish the corresponding ester **S-78** (508.4 mg, 85% yield) as a white solid..

(**S-78**) ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.07-8.03 (m, 2H), 7.71-7.67 (m, 2H), 7.65-7.61 (m, 2H), 7.50-7.45 (m, 2H), 7.43-7.38 (m, 1H), 6.42 (d, J = 3.5 Hz, 1H), 6.37 (dd, J = 3.0 Hz, 1.5 Hz, 1H), 5.11 (s, 2H), 3.35 (t, J = 6.5 Hz, 2H), 2.82 (t, J = 6.5 Hz, 2H); ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 197.5, 172.6, 149.4, 145.9, 143.3, 139.8, 135.2, 128.9, 128.6, 128.2, 127.2, 110.7, 110.6, 58.3, 33.3, 28.2, 111.8, 110.8, 110.6, 101.1, 58.5, 55.6, 30.1, 13.3.

----

4. X-Ray Crystal Data of Compound 2

Single-crystal X-ray diffraction data for the reported complex was recorded at a temperature of 293(2) K on a Oxford Diffraction Gemini R Ultra diffractometer, using a ω scan technique with Mo-Kα radiation (λ = 0.71073 Å). Non-hydrogen atoms were refined with anisotropic temperature parameters, and hydrogen atoms of the ligands were refined as rigid groups. The single crystals of compound **2** suitable for X-ray diffraction analysis were obtained by evaporation of a solution of **2** in PE / ethyl acetate. CCDC 2089005 for compound **2** contains the crystal structure information of this compound and can be obtained free of charge via http://www.ccdc.cam.ac.uk.



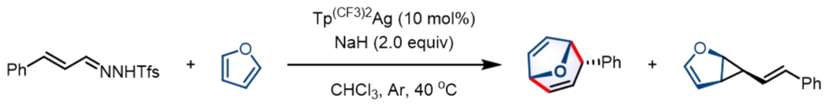
X-Ray structure of **2**
CCDC: 2089005

Empirical formula	$C_{14}H_{12}O_3$
Formula weight	228.24
Temperature	293(2)
Wavelengt	0.71073 Å
Space group	P-1
Unit cell dimensions	a = 5.6312 (6) Å b = 9.3841 (11) Å c = 11.0292 (13) Å alpha = 74.196 (10) deg. beta = 78.153 (10) deg gamma = 80.784 (11) deg.
Volume	545.41 (11)
Z	2
Calculated density	1.390 Mg/m3
Absorption coefficient	0.098 mm^{-1}
F(000)	240.0
Crystal size	0.21 x 0.19 x 0.24 mm^3
Theta range for data collection	MoKα (λ = 0.71073)
Reflections collected	3904
Completeness to theta = 25.242 deg	99.4%
Data / restraints / parameters	2489 [R_{int} = 0.0207, R_{sigma} = 0.0389]
Goodness-of-fit on F^2	1.055
Final R indices [I>2sigma(I)]	R_1 = 0.0517, wR_2 = 0.1065
R indices (all data)	R_1 = 0.0813, wR_2 = 0.1302
Largest diff. peak and hole	0.17/-0.23

5. Mechanistic Studies

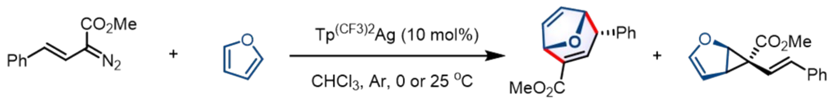
5.1 Control Experiments

We tried to capture the furanocyclopropane intermediate by shortening the reaction time or performing the reaction at low temperature, but all failed. Selected experiments are shown in below.



3 24 cp

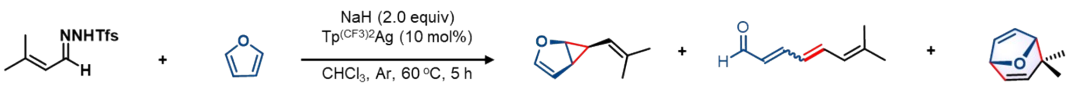
entry	Reaction time	NMR yield		
		3	24	cp
1	10 min	76%	15%	N.D.
2	30 min	38%	52%	N.D.
3	60 min	10%	78%	N.D.



S-61 61 cp

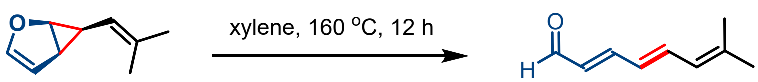
entry	T (°C)	Reaction time	NMR yield		
			S-61	61	cp
1	25	5 min	12%	50%	N.D.
2	25	30 min	trace	56%	N.D.
3	0	10 min	65%	15%	N.D.

Figure S1 control experiments



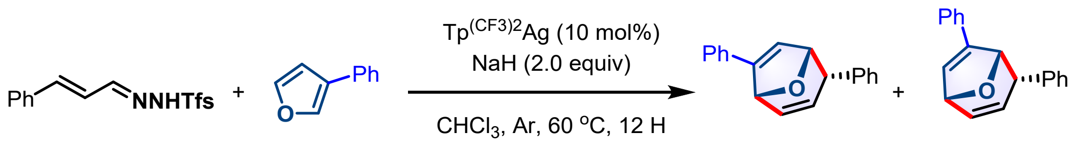
79 80, 57% 81, 12% NMR yield 82, trace

Prepared according to General Procedure **A** using vinyl-*N*-triftosylhydrazone **79** (183.6 mg, 0.6 mmol) and furan (81.0 mg, 1.2 mmol) afforded **80** (46.6 mg, 57% yield) as a colorless oil. **(80)** ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 6.28 (d, J = 2.5 Hz, 1H), 5.11 (t, J = 2.5 Hz, 1H), 4.75-4.72 (m, 1H), 4.62 (t, J = 5.5 Hz, 1H), 2.42-2.38 (m, 1H), 1.75 (s, 3H), 1.71 (s, 3H), 1.31-1.25 (m, 1H). ^{13}**C NMR** (126 MHz, CDCl3) δ 146.1, 135.8, 115.1, 101.7, 65.1, 26.5, 25.7, 18.7, 11.3. HRMS (ESI) m/z calcd for $C_9H_{13}O$ $[M+H]^+$ 137.0966, Found: 137.0972.



80 **81**, 90%

To an oven-dried screwcap reaction tube equipped with a tefloncoated magnetic stir bar were added **80** (40.8 mg, 0.3 mmol), and dry xylene (2.0 mL) inside a glove box with nitrogen atmosphere. After transferred out of the glove box, the reaction heated at 160 °C in the dark for additional 12 h. When the reaction was completed, the reaction was allowed to cool to room temperature, and filtered through a short pad of silica gel with CH_2Cl_2 as an eluent. After removal of the solvent under vacuum, the residue was purified by flash chromatography on silica gel (using petroleum ether / EtOAc as eluent) to obtain **81** (36.8 mg, 90% yield) as a colorless oil. **(81)** **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.57 (d, J = 8.4 Hz, 1H), 7.19 (dd, J = 15.0 Hz, 11.4 Hz, 1H), 6.93 (dd, J = 14.4 Hz, 11.4 Hz, 1H), 6.36 (dd, J = 15.0 Hz, 11.4 Hz, 1H), 6.15 (dd, J = 15.0 Hz, 8.4 Hz, 1H), 6.03 (d, J = 11.4 Hz, 1H), 1.91 (s, 3H), 1.90 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 193.6, 153.0, 144.2, 139.5, 130.1, 127.4, 125.2, 26.6, 18.9. **HRMS** (ESI) *m/z* calculated $C_9H_{13}O$ $[M+H]^+$ 257.0961, found 257.0949.



3 **83 + 83'** : 80% (1:1 r.r.)

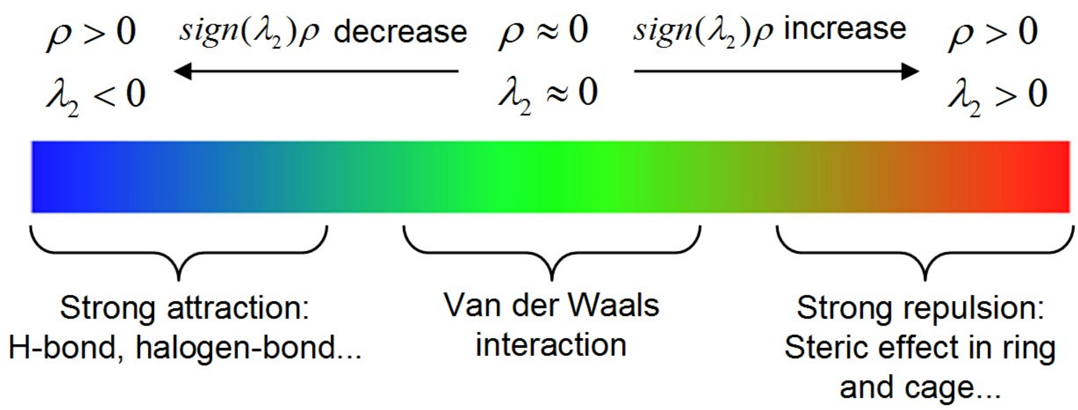
Prepared according to **General Procedure A** using *N*-triftosylhydrazone derived from cinnamaldehyde (106.2 mg, 0.3 mmol) and 3-phenylfuran (86.4 mg, 0.6 mmol) afforded **83 + 83'** (62.4 mg, 80% yield).

(**83**) Yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39-7.35 (m, 4H), 7.31-7.24 (m, 4H), 7.16-7.13 (m, 2H), 6.55 (ddd, J = 10.0 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.79 (d, J = 2.0 Hz, 1H), 5.67 (dt, J = 10.0 Hz, 2.0 Hz, 1H), 5.22 (dt, J = 6.0 Hz, 2.0 Hz, 1H), 5.11 (d, J = 4.0 Hz, 1H), 4.15-4.10 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.5, 137.5, 132.2, 131.9, 128.7, 128.5, 128.4, 128.2, 128.1, 127.0, 125.9, 120.9, 84.6, 77.1, 43.4. **HRMS** (ESI) *m/z* calculated $C_{19}H_{15}O$ $[M-H]^-$ 259.1128, found 259.1130. The relative configuration of **83** was confirmed by NOE, see Figure S169.

(**83'**) White oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.99-6.89 (m, 9H), 6.80-6.75 (m, 2H), 6.40 (ddd, J = 9.5 Hz, 4.0 Hz, 2.5 Hz, 1H), 5.67 (dt, J = 9.5 Hz, 2.0 Hz, 1H), 5.52 (dd, J = 6.0 Hz, 1.5 Hz, 1H), 4.86-4.82 (m, 1H), 4.24-4.21 (m, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 140.1, 138.3, 133.4, 132.1, 131.6, 128.7, 128.1, 127.7, 127.6, 126.8, 126.7, 125.7, 83.6, 77.2, 44.3. **HRMS** (ESI) *m/z* calculated $C_{19}H_{15}O$ $[M-H]^-$ 259.1128, found 259.1128.

5.2 DFT Caculations

All quantum mechanical calculations were performed using the Gaussian 16 suite of program[9] with the B3LYP functional[10,11] and GD3BJ empirical dispersion.[12] The Ag atom was represented with the Stuttgart-Dresden relativistic effective core potential associated with their adapted basis set.[13,14] All the other atoms H, B, C, N, O and F atoms were described with the standard 6-31G(d,p)[15-18] basis set. Frequency calculations at the same level were used to confirm the presence of local minima (no imaginary frequencies) and transition states (one imaginary frequency). Geometry optimizations were carried out without any symmetry constrained in solvent (chloroform) using the SMD solvation model.[19] Intrinsic reaction coordinate (IRC)[20,21] were traced from the various transition structures to obtain the connected intermediates. Three-dimensional diagrams of the computed species were generated using CYLview visualization software.[22] The Reduced density gradient surface was generated for the transition states using Multiwfn.[23] The isosurface was visualized using VMD, with the surface contour set at 0.5 and the color range fixed from -0.035 to 0.02.[24]



5.2.1 Frontier molecular orbital theory analysis of the *endo*- and *exo*-TS

It can be seen that the frontier MO's of reacting partners are properly matched with each other, this primary orbital overlap will lead directly to the formation of both sigma bonds. The *endo*-transition state **TS2-4** was suggested to be favored owing to a stabilizing secondary (transient) orbital interaction in the paticipating $HOMO_{furan}$-$LUMO_{carbene}$ frontier molecular orbitals to produce the *endo*-cycloadducts.

As for another *endo*-transition state **TS2-4'**, there exists the same secondary (transient) orbital interactions. However, owing to the stabilizing C-H⋯π interactions (2.94 Å, within the typical distance range for C-H⋯π interactions)[25] between the 2-methyl and phenyl groups in **TS2-4**, the distance betwwen the two reacting fragments is longer than that in **TS2-4'**, thus resulting in a weaker secondary orbital interactions in **TS2-4'**. Moreover, the steric effect between the methyl group and the bulkyl $Tp^{(CF3)2}$ ligand in **TS2-4'** would also account for this regioselectivity.

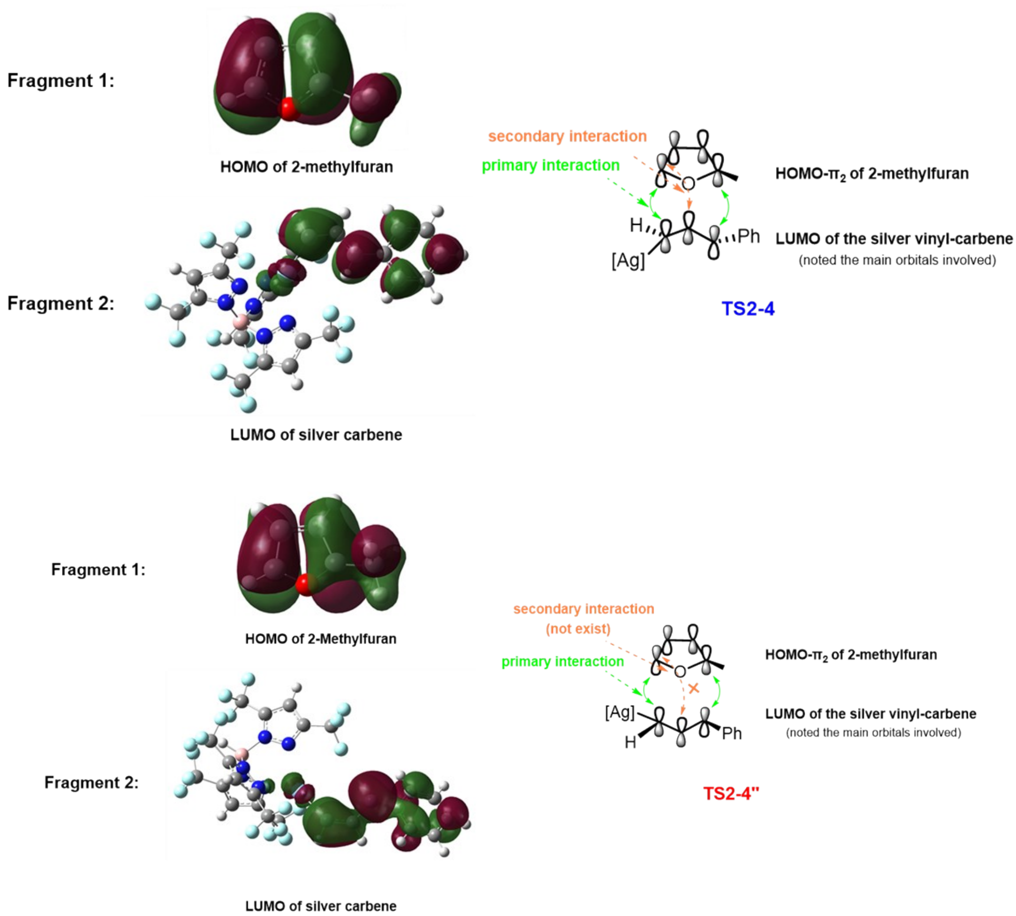


Figure S2. The frontier MO's of reacting partners and stabilizing secondary orbital interactions in the paticipating $HOMO_{furan}$-$LUMO_{carbene}$ orbitals of **TS2-4** and **TS2-4"**.

5.2.3 Carbene formation process

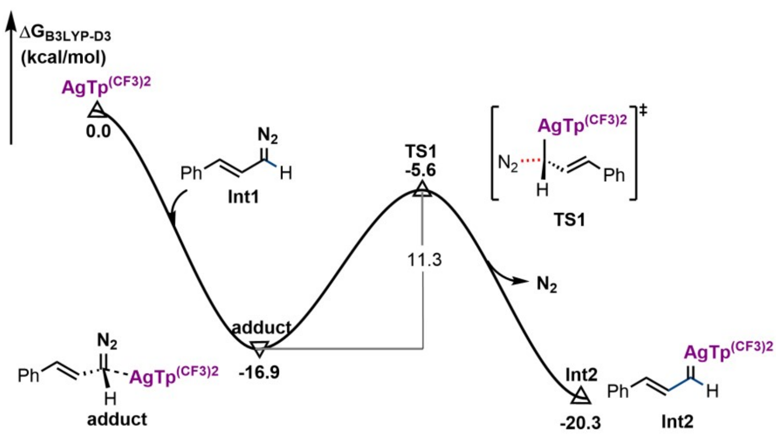


Figure S3. The silver carbene formation process

5.2.4 Three plausible concerted [4+3]-cycloaddtion pathways

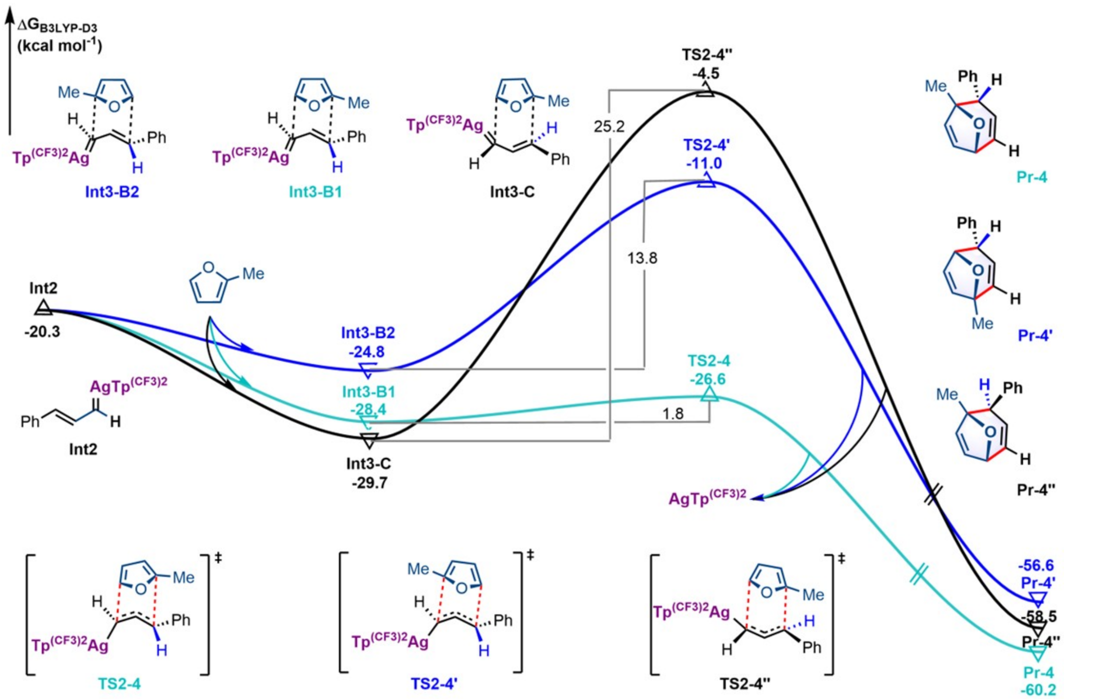


Figure S4. Three plausible Ag-catalyzed concerted [4+3]-cycloaddition pathways which are *endo*-face attack (methyl and phenyl groups on the same (blueviolet) or different sides (blue)) and *exo*-face attack (black) on 2-methyl furan respectively.

5.2.5 Concerted cyclopropanation and cope rearrangement pathway:

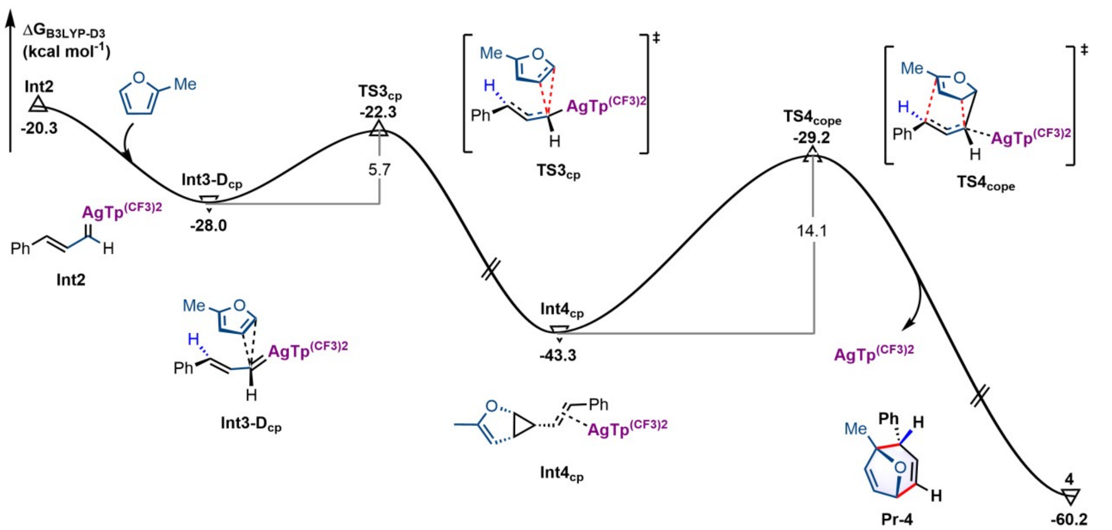


Figure S5. Silver-catalyzed tandem concerted-cyclopropanation and cope rearrangement processes.

5.2.6 Cartesian coordinates of all optimized geometries

AgTp$^{(CF3)2}$

Zero-point correction=	0.228373 (Hartree/Particle)
Thermal correction to Energy=	0.265075

Thermal correction to Enthalpy= 0.266019
Thermal correction to Gibbs Free Energy= 0.150718
Sum of electronic and zero-point Energies= -2871.492086
Sum of electronic and thermal Energies= -2871.455384
Sum of electronic and thermal Enthalpies= -2871.454440
Sum of electronic and thermal Free Energies= -2871.569741

Ag	-2.18464300	0.11213300	-0.02642200
N	-0.49901200	1.63225500	-0.79370000
N	0.77093800	1.37753700	-0.43000800
N	-0.63364400	-0.11225500	1.73957000
N	0.65152100	-0.35814700	1.41666600
N	-0.66694800	-1.42150400	-1.01292900
N	0.63781000	-1.08645700	-1.00848300
B	1.20806300	-0.04961400	-0.00115400
C	-0.58236000	2.94157900	-1.02838900
C	0.65431300	3.57144400	-0.82213600
C	1.49046200	2.53383100	-0.44112200
C	-0.80789500	-0.53265800	2.99279900
C	0.37869800	-1.06854300	3.51460100
C	1.28386400	-0.93766100	2.47407100
C	-0.84281400	-2.28524100	-2.01384800
C	0.36289000	-2.53257900	-2.68575500
C	1.28183100	-1.74487400	-2.01061800
H	2.38680100	-0.11631300	0.01419800
C	2.74168000	-1.58989800	-2.29792600
C	-2.20555500	-2.82903300	-2.28113500
C	2.71750000	-1.36529300	2.45174300
C	-2.16581400	-0.48103500	3.60858000
C	2.93862000	2.61101000	-0.07601000
C	-1.90744700	3.53408900	-1.36906100
H	0.54456500	-3.18116300	-3.52671600
H	0.55776400	-1.48206600	4.49339700
H	0.90914400	4.61211400	-0.93726800
F	3.06692400	-2.31371800	-3.38834900
F	3.51309400	-2.01307900	-1.27875500
F	3.06687800	-0.30323200	-2.54504700
F	-2.70473800	-3.50066800	-1.22028900
F	-2.19612400	-3.66163000	-3.33536100
F	-3.09603200	-1.83359900	-2.55197700
F	-1.77867200	4.78780000	-1.83204500
F	-2.56846700	2.80340400	-2.29628200
F	-2.72532500	3.58489100	-0.27998100
F	3.71506400	1.87956700	-0.89751100

F	3.35566300	3.89166300	-0.14654900
F	3.15765400	2.17536800	1.18280000
F	3.56171600	-0.33092600	2.28001500
F	3.02882500	-1.96027200	3.62139900
F	2.95615300	-2.25191800	1.46225500
F	-2.83113600	0.65270400	3.27297200
F	-2.09344700	-0.54097100	4.94978500

Int1

Zero-point correction=	0.147889 (Hartree/Particle)
Thermal correction to Energy=	0.157583
Thermal correction to Enthalpy=	0.158527
Thermal correction to Gibbs Free Energy=	0.111279
Sum of electronic and zero-point Energies=	-457.099739
Sum of electronic and thermal Energies=	-457.090046
Sum of electronic and thermal Enthalpies=	-457.089101
Sum of electronic and thermal Free Energies=	-457.136350

C	-2.88398500	1.27267500	-0.13153600
C	-1.49187900	1.27253200	-0.16434200
C	-0.76413400	0.07882100	-0.00999700
C	-1.48023100	-1.11587200	0.19292900
C	-2.87017800	-1.11413900	0.22395500
C	-3.58025100	0.07908800	0.06181700
H	-3.42530200	2.20535600	-0.25874200
H	-0.95302000	2.19957700	-0.33454400
H	-0.94626200	-2.04894300	0.33902300
H	-3.40414900	-2.04631500	0.38260800
H	-4.66547200	0.07670500	0.09058900
C	0.69409600	0.13364400	-0.07958600
C	1.51899300	-0.92297100	-0.23729800
H	1.12370600	1.13279900	-0.05787400
H	1.12525700	-1.92726900	-0.34861900
C	2.98564900	-0.87398500	-0.36554800
H	3.58480500	-1.77643100	-0.29878900
N	3.64634800	0.19675700	0.08034800
N	4.18107400	1.13549400	0.42593600

adduct

Zero-point correction=	0.378091 (Hartree/Particle)
Thermal correction to Energy=	0.425984
Thermal correction to Enthalpy=	0.426929

Thermal correction to Gibbs Free Energy= 0.287437
Sum of electronic and zero-point Energies= -3328.629516
Sum of electronic and thermal Energies= -3328.581623
Sum of electronic and thermal Enthalpies= -3328.580679
Sum of electronic and thermal Free Energies= -3328.720170

Ag	0.86495800	0.99789300	-0.25331700
N	-1.40624700	1.76047100	-0.28397500
N	-2.36960000	0.82273100	-0.33417600
N	-0.11788500	-0.77385700	-1.46558600
N	-1.21789600	-1.35364100	-0.94577400
N	-0.02071300	-0.27760700	1.54037200
N	-1.32360800	-0.61324800	1.47344400
B	-2.08963000	-0.63524900	0.12153000
C	-1.91888500	2.87459400	-0.80578600
C	-3.24893000	2.67877800	-1.20736600
C	-3.49572100	1.35315900	-0.88676100
C	0.43086900	-1.65719100	-2.30001700
C	-0.31334300	-2.84555600	-2.33732000
C	-1.35634600	-2.60791400	-1.45707600
C	0.32240200	-0.30732400	2.82885900
C	-0.76681800	-0.67087800	3.63371100
C	-1.79773100	-0.85558800	2.72605300
H	-3.11062800	-1.21374400	0.25197200
C	-3.21459700	-1.23896600	3.01455500
C	1.71838600	0.03891600	3.22326900
C	-2.46071700	-3.54279100	-1.07622100
C	1.72775100	-1.33967900	-2.96565700
C	-4.75624600	0.57780400	-1.10199600
C	-1.04325100	4.07105200	-0.96305500
H	-0.80457800	-0.78545800	4.70437800
H	-0.13036000	-3.73709700	-2.91418900
H	-3.93038200	3.38489600	-1.65257300
F	-3.39242700	-1.34180300	4.34741700
F	-3.54896700	-2.42086000	2.46301600
F	-4.08438800	-0.31574900	2.55253100
F	2.62833800	-0.78338200	2.65627100
F	1.87394800	-0.02231300	4.55621700
F	2.05039500	1.30034300	2.82859700
F	-1.76161700	5.16983200	-1.24476500
F	-0.31004100	4.31468900	0.14763500
F	-0.14545800	3.90191900	-1.97447000
F	-5.28662000	0.12933400	0.05139800
F	-5.67475000	1.36383600	-1.69988900

F	-4.55099300	-0.49366900	-1.89709400
F	-3.67514100	-3.07266900	-1.41720000
F	-2.28683100	-4.72479200	-1.70204400
F	-2.47583700	-3.77867700	0.25279200
F	1.78995500	-0.04328500	-3.36080800
F	1.92144400	-2.11524500	-4.04669400
F	2.77733900	-1.53331600	-2.13127100
C	6.46673900	-2.09465500	1.21253000
C	5.61355600	-0.99631300	1.28150700
C	5.20716900	-0.32089900	0.11658300
C	5.69723000	-0.77597200	-1.12197000
C	6.54783700	-1.87364000	-1.18914000
C	6.93745000	-2.53950800	-0.02333400
H	6.76275900	-2.60440000	2.12446900
H	5.23307500	-0.66428000	2.24262000
H	5.42066000	-0.26087200	-2.03590000
H	6.91575200	-2.20863400	-2.15436800
H	7.60490800	-3.39382000	-0.07980200
C	4.28976600	0.80866600	0.24595500
C	3.58714500	1.37623600	-0.75701600
H	4.13366400	1.16739800	1.26098700
H	3.64980300	0.99290500	-1.76952100
C	2.61731300	2.47760300	-0.62917600
H	2.24103500	2.99779600	-1.50420100
N	2.66927000	3.27475500	0.44025600
N	2.70498400	3.91086200	1.37870300

TS1

Zero-point correction=	0.376137 (Hartree/Particle)
Thermal correction to Energy=	0.424173
Thermal correction to Enthalpy=	0.425117
Thermal correction to Gibbs Free Energy=	0.284754
Sum of electronic and zero-point Energies=	-3328.610883
Sum of electronic and thermal Energies=	-3328.562848
Sum of electronic and thermal Enthalpies=	-3328.561903
Sum of electronic and thermal Free Energies=	-3328.702266

Ag	0.89830400	0.92118800	-0.24717800
N	-1.38110000	1.79793300	-0.05402500
N	-2.41354300	0.94905400	-0.20274200
N	-0.29342800	-0.65608200	-1.55260300
N	-1.43442100	-1.20986100	-1.10042000
N	-0.10697300	-0.54697700	1.42873500

N	-1.43472800	-0.76078900	1.37965900
B	-2.23516700	-0.56644700	0.06275200
C	-1.82300100	3.00619700	-0.40491600
C	-3.17164400	2.96174500	-0.79106100
C	-3.50897500	1.62577300	-0.64619200
C	0.19440300	-1.47636600	-2.48401500
C	-0.63388600	-2.59558700	-2.65452400
C	-1.66177900	-2.38449200	-1.74979200
C	0.27292900	-0.78592800	2.68551100
C	-0.81689800	-1.16180700	3.48467200
C	-1.88956300	-1.13003800	2.60797400
H	-3.29186400	-1.08618500	0.15483000
C	-3.32438300	-1.43202200	2.90140600
C	1.70978500	-0.65749600	3.05610400
C	-2.83171100	-3.27311300	-1.47076500
C	1.50994400	-1.17430700	-3.12111900
C	-4.82648700	0.97614000	-0.92180800
C	-0.88030200	4.16102100	-0.40494000
H	-0.82875800	-1.42068900	4.53049700
H	-0.51259800	-3.42585200	-3.33044100
H	-3.80687900	3.76895300	-1.11656100
F	-3.47404000	-1.68110100	4.21900400
F	-3.77043400	-2.50971800	2.22781300
F	-4.12842000	-0.39532500	2.58403200
F	2.49284900	-1.48363800	2.31159800
F	1.90885400	-0.96124300	4.34917300
F	2.18550500	0.59684800	2.84986200
F	-1.53749100	5.32307300	-0.56820500
F	-0.16991300	4.23806300	0.74478500
F	0.03330300	4.06719800	-1.40752200
F	-5.36846900	0.42484900	0.18145300
F	-5.69613600	1.89447000	-1.39155700
F	-4.71810400	0.00054800	-1.84877300
F	-4.00890500	-2.67618700	-1.73591600
F	-2.75089600	-4.38080600	-2.23700100
F	-2.86061300	-3.66849400	-0.17976000
F	1.60417600	0.11618500	-3.51062200
F	1.71000500	-1.95365100	-4.20075500
F	2.53837500	-1.39525100	-2.26420000
C	6.79653700	-2.28460000	0.86199800
C	5.61918700	-1.54403700	0.80310700
C	5.51915300	-0.41839800	-0.03578400
C	6.63073000	-0.06153400	-0.82369200
C	7.80207000	-0.80636300	-0.76807500

C	7.88999400	-1.91863500	0.07617300
H	6.86025500	-3.14739400	1.51751200
H	4.76738400	-1.82036900	1.41616600
H	6.56969600	0.79207300	-1.49054400
H	8.65010000	-0.52505200	-1.38465800
H	8.80756900	-2.49754000	0.11641300
C	4.26459900	0.32055000	-0.04792500
C	4.00325900	1.50524800	-0.64761500
H	3.44651000	-0.14133900	0.49946000
H	4.78371400	2.03160900	-1.19478600
C	2.66240700	2.08917500	-0.58427300
H	2.50416100	2.90225800	-1.29403700
N	2.70310100	3.12392700	0.81902300
N	2.65554900	3.42519200	1.88899900

Int2

Zero-point correction=	0.368773 (Hartree/Particle)
Thermal correction to Energy=	0.414396
Thermal correction to Enthalpy=	0.415340
Thermal correction to Gibbs Free Energy=	0.280827
Sum of electronic and zero-point Energies=	-3219.116597
Sum of electronic and thermal Energies=	-3219.070975
Sum of electronic and thermal Enthalpies=	-3219.070031
Sum of electronic and thermal Free Energies=	-3219.204544

Ag	-1.00776300	0.98305200	0.17606200
N	1.16872000	1.75285200	-0.65703800
N	2.28132100	1.03789400	-0.41708200
N	0.44591900	0.01360500	1.73639000
N	1.58767200	-0.60744800	1.38387800
N	-0.10186900	-1.03235900	-0.96255700
N	1.23294600	-1.18435700	-1.03887900
B	2.18300600	-0.45845000	-0.04339300
C	1.56056500	2.99591400	-0.93548600
C	2.95849200	3.11017000	-0.88051200
C	3.37963900	1.83394400	-0.54496500
C	0.16040400	-0.37101900	2.98133900
C	1.12648200	-1.26471800	3.46540000
C	2.01790700	-1.38876400	2.41198800
C	-0.62979700	-1.81567700	-1.90540700
C	0.36673900	-2.49536100	-2.62115600
C	1.54360700	-2.05873000	-2.03571100
H	3.25445700	-0.95352100	-0.08091800

C	2.94304700	-2.42490500	-2.41319900
C	-2.10796300	-1.89120000	-2.06579400
C	3.24193900	-2.24577800	2.34900400
C	-1.08958200	0.10766700	3.64332500
C	4.77932400	1.36245400	-0.31737800
C	0.54106600	4.04904700	-1.21420900
H	0.25567200	-3.19077200	-3.43651500
H	1.17582300	-1.74396800	4.42899500
H	3.57054800	3.97866000	-1.05943000
F	2.92188800	-3.23234000	-3.49482600
F	3.59004100	-3.07879400	-1.42918300
F	3.67380200	-1.33559500	-2.72623600
F	-2.71218100	-2.27713200	-0.90333300
F	-2.44968200	-2.78347700	-3.01162200
F	-2.66108600	-0.70396600	-2.39937200
F	1.12700000	5.17184700	-1.67348800
F	-0.36700900	3.64615900	-2.13049500
F	-0.15874400	4.38327500	-0.10052600
F	5.14731000	0.39480300	-1.17899700
F	5.63585800	2.39409900	-0.46998100
F	4.94368100	0.87376100	0.93074100
F	4.36579000	-1.52953100	2.15994700
F	3.37733000	-2.92461300	3.50757800
F	3.16612400	-3.15150600	1.35029500
F	-1.21134700	1.45052100	3.59807900
F	-1.11606700	-0.27112500	4.93612900
F	-2.19697600	-0.40357600	3.04767200
C	-7.13741200	-2.05699500	-0.40828900
C	-5.88209400	-1.47247400	-0.29166800
C	-5.75436400	-0.07837100	-0.10225300
C	-6.92482200	0.71111800	-0.02942600
C	-8.17483500	0.12111400	-0.13927600
C	-8.28357700	-1.26244100	-0.33007400
H	-7.22564300	-3.12778200	-0.55935400
H	-4.98468000	-2.07642300	-0.36492400
H	-6.84596100	1.78138900	0.12441800
H	-9.06978600	0.73150900	-0.07666000
H	-9.26502200	-1.71844100	-0.41725800
C	-4.42994200	0.47494700	0.00425900
C	-4.06576200	1.80606700	0.06028600
H	-3.60891800	-0.23660800	0.02711400
H	-4.83946000	2.57377400	0.02777800
C	-2.70471500	2.14887500	0.11759900
H	-2.55779200	3.23507800	0.11402700

Int3-B2

Zero-point correction= 0.467984 (Hartree/Particle)
Thermal correction to Energy= 0.520694
Thermal correction to Enthalpy= 0.521638
Thermal correction to Gibbs Free Energy= 0.369985
Sum of electronic and zero-point Energies= -3488.400452
Sum of electronic and thermal Energies= -3488.347742
Sum of electronic and thermal Enthalpies= -3488.346797
Sum of electronic and thermal Free Energies= -3488.498451

Ag	0.68674600	0.53844200	-0.47495600
N	-0.90682500	-0.96847800	-1.51905700
N	-2.09172900	-1.25346200	-0.95012800
N	-0.47526300	-0.55011100	1.42445400
N	-1.82172000	-0.55362700	1.45766300
N	-1.42308300	1.79603300	-0.22961100
N	-2.59302900	1.13196100	-0.25030100
B	-2.66921000	-0.35473600	0.17156500
C	-0.64405000	-1.95391100	-2.37859900
C	-1.67099300	-2.91060100	-2.38046500
C	-2.57576600	-2.42354100	-1.45179400
C	-0.06659800	-0.75735100	2.67892300
C	-1.15206300	-0.88992700	3.55698000
C	-2.25581200	-0.75016100	2.73247800
C	-1.68064900	3.03497000	-0.65241400
C	-3.04055500	3.19695700	-0.95894300
C	-3.58699700	1.95370900	-0.68708300
H	-3.79148500	-0.65634000	0.38394700
C	-5.01127800	1.52568900	-0.83148500
C	-0.57353100	4.02607900	-0.76928600
C	-3.69845000	-0.78266400	3.12571100
C	1.38568400	-0.81207900	2.99658300
C	-3.86111200	-3.04831800	-1.01433400
C	0.64784000	-1.97675000	-3.12522300
H	-3.55082500	4.07721000	-1.31343100
H	-1.14164800	-1.06354700	4.62019800
H	-1.75072100	-3.81086500	-2.96702100
F	-5.73948500	2.53753200	-1.34842900
F	-5.56806900	1.18233000	0.34673400
F	-5.13450500	0.46620300	-1.65927900
F	0.17395400	4.08847900	0.35376400
F	-1.05713800	5.25875300	-1.01819100

F	0.28100500	3.71805800	-1.78191600
F	0.61024200	-2.89346900	-4.11314700
F	0.94590600	-0.78103900	-3.67714800
F	1.68781300	-2.30140200	-2.31554800
F	-4.92885900	-2.26615000	-1.26134200
F	-4.04507400	-4.21290100	-1.67177300
F	-3.85840100	-3.32173300	0.30839400
F	-4.36009200	-1.82176300	2.58184200
F	-3.79684900	-0.89350500	4.46759000
F	-4.34270700	0.34479900	2.75823800
F	2.04821200	-1.68327000	2.18418500
F	1.59178400	-1.20870900	4.26517200
F	1.99472900	0.38700300	2.84054100
C	4.61662900	1.41120200	1.65348800
C	4.24683700	3.10330600	0.28881100
O	3.68756800	2.33056600	1.27007300
C	5.77602000	1.59618200	0.95393700
C	5.53513500	2.68850100	0.06692700
H	6.22398300	3.12123400	-0.64403900
H	6.67697900	1.00762400	1.04394800
C	2.48323700	1.05309300	-1.37904100
C	3.71196300	0.38487700	-1.34872600
C	3.92005700	-0.60606400	-0.40718900
H	3.08824300	-0.79321700	0.26641000
C	5.08188700	-1.44684300	-0.23902400
C	5.09616400	-2.36017300	0.83566900
C	6.19904400	-1.39040100	-1.09927100
C	6.19488800	-3.18501200	1.04932200
H	4.24016200	-2.40082900	1.50106400
C	7.29241700	-2.21759400	-0.88403900
H	6.20163400	-0.69854700	-1.93386000
C	7.29445300	-3.11497900	0.19092700
H	6.19638300	-3.88193900	1.88116100
H	8.14685700	-2.16998300	-1.55159200
H	8.15275900	-3.75919000	0.35521100
H	4.52255700	0.65922400	-2.02214300
H	2.46873300	1.84724400	-2.13469700
C	3.43037000	4.22495200	-0.24473200
H	3.20109000	4.95034400	0.54400500
H	3.98779800	4.73901900	-1.03110900
H	2.48040700	3.87990400	-0.65469600
H	4.30625900	0.72695800	2.42415800

Int3-B1

Zero-point correction=	0.468380 (Hartree/Particle)
Thermal correction to Energy=	0.520832
Thermal correction to Enthalpy=	0.521776
Thermal correction to Gibbs Free Energy=	0.372387
Sum of electronic and zero-point Energies=	-3488.405185
Sum of electronic and thermal Energies=	-3488.352733
Sum of electronic and thermal Enthalpies=	-3488.351789
Sum of electronic and thermal Free Energies=	-3488.501178

Ag	0.64151100	0.57455600	-0.57116400
N	-1.05197100	-0.75793800	-1.66299100
N	-2.18862300	-1.11285800	-1.03740800
N	-0.40959700	-0.76063000	1.27227900
N	-1.74809800	-0.71051600	1.41038500
N	-1.42803700	1.82887500	-0.01812200
N	-2.60392800	1.17515000	-0.03446100
B	-2.67452900	-0.34963500	0.21899900
C	-0.85888000	-1.64148400	-2.64350300
C	-1.88316300	-2.60063600	-2.66889200
C	-2.71103100	-2.22509100	-1.62383100
C	0.07718000	-1.13208900	2.45946000
C	-0.94761100	-1.32096200	3.39858100
C	-2.09940900	-1.03738900	2.68397300
C	-1.70091000	3.10551100	-0.29811000
C	-3.07516100	3.30223200	-0.50211000
C	-3.61503900	2.03937300	-0.32473500
H	-3.78572100	-0.66272400	0.47006300
C	-5.04977800	1.63330900	-0.42547100
C	-0.60083000	4.10720300	-0.37058900
C	-3.51081200	-1.06020900	3.17714400
C	1.54139500	-1.32284900	2.64446700
C	-3.95974600	-2.90038200	-1.15676400
C	0.36970100	-1.56870900	-3.48798100
H	-3.59757900	4.21539100	-0.73448100
H	-0.86917900	-1.62081300	4.43039000
H	-2.00948000	-3.43214500	-3.34234500
F	-5.79721800	2.69653300	-0.78961800
F	-5.53761900	1.17218900	0.74282600
F	-5.23389000	0.66632700	-1.34935900
F	0.15061400	4.11670600	0.76020100
F	-1.09014200	5.34819300	-0.54723400
F	0.25848000	3.85962900	-1.39103900
F	0.25406000	-2.37115200	-4.56549100

F	0.61858700	-0.31572700	-3.92562700
F	1.47118500	-1.96807500	-2.80462600
F	-5.04335000	-2.10596400	-1.24726300
F	-4.19111400	-3.99656900	-1.90956500
F	-3.85986200	-3.30094500	0.12950100
F	-4.25145700	-2.01434000	2.58137800
F	-3.52091300	-1.30562700	4.50463700
F	-4.13205100	0.12061200	2.97259900
F	2.04987200	-2.20883300	1.74296600
F	1.81911300	-1.79447100	3.87373400
F	2.24343300	-0.17692900	2.47852800
C	4.87625600	1.80553500	1.25045000
C	3.24219000	2.99325600	0.36541900
O	3.54872400	2.10709000	1.35284600
C	5.42978800	2.53438200	0.22548600
C	4.37968100	3.30894800	-0.33999300
H	4.44060700	3.99576000	-1.17158600
H	6.46377100	2.49997400	-0.08520400
H	2.23284800	3.36490100	0.35578800
C	2.43269000	1.18719100	-1.44599600
C	3.67267700	0.51742600	-1.47977400
C	3.94721400	-0.46758100	-0.56226300
H	3.13584400	-0.72487300	0.11233200
C	5.18073200	-1.20424300	-0.38733600
C	5.21523000	-2.23026600	0.57892600
C	6.35493200	-0.92180900	-1.11717700
C	6.38164300	-2.95543200	0.80380800
H	4.31672300	-2.44727600	1.14615700
C	7.51677200	-1.64556300	-0.88818900
H	6.35299200	-0.12493600	-1.85240800
C	7.53410900	-2.66473200	0.07248800
H	6.39319900	-3.74402600	1.54935800
H	8.41526000	-1.41889300	-1.45354400
H	8.44639000	-3.22619500	0.24906300
H	4.45170900	0.82435700	-2.17684200
H	2.38906600	2.00391000	-2.17385300
C	5.43620500	0.87423600	2.26367900
H	5.64988700	1.39527200	3.20461100
H	4.72701900	0.07317700	2.48012400
H	6.36456400	0.43280100	1.89563300

Int3-C

Zero-point correction= 0.470037 (Hartree/Particle)

Thermal correction to Energy= 0.515101
Thermal correction to Enthalpy= 0.516045
Thermal correction to Gibbs Free Energy= 0.386191
Sum of electronic and zero-point Energies= -3488.398893
Sum of electronic and thermal Energies= -3488.353829
Sum of electronic and thermal Enthalpies= -3488.352885
Sum of electronic and thermal Free Energies= -3488.482738

Ag	-0.68970700	0.32605000	-0.60398500
N	1.01887000	-1.30842700	-1.28002500
N	2.30603400	-1.12318700	-0.98634600
N	1.42309700	1.67671700	-0.63403900
N	2.54059300	1.22557100	-0.06518100
N	0.54222600	-0.27583400	1.52923700
N	1.81650500	-0.66761200	1.44185600
B	2.73201800	-0.28118600	0.24429000
C	0.98117100	-2.03243600	-2.39003100
C	2.26882100	-2.33966500	-2.84770000
C	3.08213400	-1.73323400	-1.91213800
C	1.54322300	2.99463200	-0.71172300
C	2.76360000	3.43465600	-0.18266300
C	3.36604100	2.26060900	0.21955000
C	0.06332700	-0.82126700	2.64196500
C	1.02682400	-1.58834800	3.30528900
C	2.13362500	-1.45804800	2.49285300
H	3.86739400	-0.49836900	0.51664600
C	3.48184600	-2.07990800	2.67439200
C	-1.35025400	-0.58202400	3.04109400
C	4.69222500	2.08579400	0.88679100
C	0.40608500	3.80240600	-1.23694100
C	4.57537800	-1.69903000	-1.86600300
C	-0.34108900	-2.33967100	-3.01051900
H	0.93831800	-2.14455000	4.22393100
H	3.15073400	4.43774100	-0.10856200
H	2.56442700	-2.91269700	-3.71128000
F	3.45851000	-2.88192100	3.74670200
F	4.44199500	-1.17167800	2.86559500
F	3.83020500	-2.82065600	1.61547000
F	-2.22191700	-1.02946500	2.10895300
F	-1.62151000	0.72060300	3.21094000
F	-1.63713600	-1.21127500	4.18363700
F	-0.23666000	-3.35381400	-3.87637500
F	-1.25909200	-2.66670200	-2.08996200
F	-0.83028500	-1.28460800	-3.68469300

F	5.06643100	-2.32979300	-0.79534000
F	5.07159600	-2.29652700	-2.95613200
F	5.03676800	-0.44217200	-1.83867600
F	5.54741300	1.37534600	0.14686700
F	5.24192100	3.28629000	1.10885400
F	4.57009500	1.46551900	2.06769800
F	-0.18464900	3.22472100	-2.29127700
F	0.81030700	5.02329100	-1.59885600
F	-0.55781300	3.96369600	-0.30482600
C	-6.63789000	-2.51810900	1.33614500
C	-5.44862100	-1.89572100	0.97921500
C	-5.33130900	-1.23879800	-0.25629600
C	-6.42407000	-1.23987200	-1.13900500
C	-7.60698300	-1.87299700	-0.78449600
C	-7.71781200	-2.50564700	0.45459500
H	-6.72327600	-3.01702100	2.29546400
H	-4.59864300	-1.89484200	1.65635300
H	-6.33730200	-0.75524100	-2.10629700
H	-8.44559400	-1.87694400	-1.47249700
H	-8.64617000	-2.99580500	0.72926800
C	-4.07908500	-0.56690900	-0.55590600
C	-3.81200700	0.31836500	-1.56988600
H	-3.24650400	-0.78540300	0.11158000
H	-4.61482300	0.63426600	-2.23660500
C	-2.52338500	0.88506300	-1.63075100
H	-2.45746800	1.65889700	-2.40634300
C	-5.10605200	1.95884400	0.76515200
C	-3.41578400	3.01172300	-0.14235400
O	-4.74719200	2.76588600	-0.26155600
C	-4.01866700	1.70456100	1.55705800
C	-2.92255000	2.39949300	0.97426700
H	-1.89991600	2.43009800	1.31887400
H	-4.01053700	1.09779100	2.44961000
H	-2.97960200	3.67605000	-0.87087300
C	-6.54191000	1.58865900	0.85021900
H	-7.14556400	2.43864400	1.18262300
H	-6.91454000	1.26934800	-0.12712800
H	-6.67512800	0.76551600	1.55475700

TS2-4´

Zero-point correction= 0.469285 (Hartree/Particle)
Thermal correction to Energy= 0.519765
Thermal correction to Enthalpy= 0.520709

Thermal correction to Gibbs Free Energy= 0.376808
Sum of electronic and zero-point Energies= -3488.384050
Sum of electronic and thermal Energies= -3488.333569
Sum of electronic and thermal Enthalpies= -3488.332625
Sum of electronic and thermal Free Energies= -3488.476527

Ag	-0.71669300	-0.61591100	-0.17764200
N	0.58658100	1.39918700	-0.91983800
N	1.80764200	1.58662500	-0.38697700
N	0.69800000	-0.27083400	1.63105100
N	2.02623900	-0.11073300	1.46552900
N	1.58908700	-1.69787900	-0.86278200
N	2.56101200	-0.76899600	-0.91298900
B	2.63306400	0.37999700	0.12166600
C	0.09096600	2.61255200	-1.17061200
C	0.99758500	3.61990200	-0.80183400
C	2.08286600	2.91809500	-0.30497900
C	0.51191200	-0.66043400	2.89513400
C	1.73254200	-0.77266800	3.57483300
C	2.67214000	-0.41344800	2.62265700
C	1.77697200	-2.49241700	-1.91970200
C	2.88310100	-2.08347700	-2.68287400
C	3.35434000	-0.97395300	-2.00130400
H	3.75716700	0.70930900	0.29152700
C	4.52586900	-0.11232700	-2.33872400
C	0.84656700	-3.62750300	-2.17339500
C	4.15891500	-0.36720500	2.78397700
C	-0.85359800	-0.98195600	3.40041300
C	3.34786900	3.47181400	0.26421200
C	-1.30290000	2.76793700	-1.67825800
H	3.28671000	-2.52688500	-3.57825000
H	1.90904900	-1.06192700	4.59753000
H	0.88934200	4.68835700	-0.88995500
F	5.05898500	-0.50384600	-3.51487200
F	5.49853500	-0.17937800	-1.40732700
F	4.17676500	1.18767200	-2.45835800
F	0.58844400	-4.33869400	-1.05228300
F	1.35468200	-4.47145600	-3.09299200
F	-0.36261600	-3.21251200	-2.64279700
F	-1.50011500	4.01298500	-2.15919800
F	-1.60086000	1.88923600	-2.65395700
F	-2.21678000	2.57872600	-0.68711300
F	4.44223200	3.07827600	-0.41433300
F	3.30887900	4.82106900	0.23106000

F	3.51867300	3.10075500	1.55288300
F	4.65323300	0.88117400	2.69291200
F	4.49320200	-0.85006200	3.99997500
F	4.78567700	-1.12059500	1.85645700
F	-1.78514600	-0.10797700	2.95607200
F	-0.88036900	-0.96566400	4.74747600
F	-1.25617400	-2.21777500	3.01031500
C	-4.72348800	-1.10749300	0.97946900
C	-3.41790900	-2.72961800	0.22074100
O	-3.53972300	-1.87028300	1.22212800
C	-5.56365500	-2.02081700	0.17706500
C	-4.72994900	-2.93222300	-0.37474100
H	-4.94704600	-3.68514400	-1.11961900
H	-6.60809800	-1.85543800	-0.04413100
C	-2.46579200	-1.06710700	-1.27959700
C	-3.63547000	-0.36805300	-1.19699700
C	-4.17228900	0.16745600	0.07565900
H	-3.35869700	0.53372300	0.70248400
C	-5.26131300	1.20355800	-0.03478600
C	-5.16073900	2.38709000	0.70517200
C	-6.38091700	1.01438100	-0.85473300
C	-6.15542200	3.36136000	0.62767500
H	-4.28896000	2.54949600	1.33227000
C	-7.37702100	1.98695500	-0.93448700
H	-6.47291800	0.10742400	-1.44591300
C	-7.26768600	3.16314100	-0.19110700
H	-6.05830100	4.27675500	1.20325300
H	-8.23667700	1.82708100	-1.57826800
H	-8.04244500	3.92103600	-0.25287800
H	-4.30863200	-0.28569400	-2.05484400
H	-2.31892700	-1.53872100	-2.25609600
C	-2.28169800	-3.68510200	0.22454900
H	-2.61697500	-4.61699300	0.70178700
H	-1.96551300	-3.91326700	-0.79231400
H	-1.43964200	-3.27420300	0.77572400
H	-5.10836500	-0.71441600	1.91772400

TS2-4

Zero-point correction=	0.468387 (Hartree/Particle)
Thermal correction to Energy=	0.519930
Thermal correction to Enthalpy=	0.520874
Thermal correction to Gibbs Free Energy=	0.373704
Sum of electronic and zero-point Energies=	-3488.403546

Sum of electronic and thermal Energies= -3488.352002
Sum of electronic and thermal Enthalpies= -3488.351058
Sum of electronic and thermal Free Energies= -3488.498229

Ag	0.66108800	0.62862400	-0.43834100
N	-0.95773500	-0.69978600	-1.66216000
N	-2.09149000	-1.12018300	-1.07226700
N	-0.41366600	-0.75310700	1.31739600
N	-1.75790700	-0.74573100	1.39987200
N	-1.48150600	1.82788500	0.03862500
N	-2.62831900	1.13119100	-0.04820700
B	-2.65064100	-0.39975700	0.17812300
C	-0.69854500	-1.55539900	-2.65193400
C	-1.67446400	-2.56202000	-2.72011900
C	-2.54527200	-2.24529800	-1.69066200
C	0.03554400	-1.11244200	2.52347100
C	-1.02108700	-1.33701700	3.41824200
C	-2.15066300	-1.08823700	2.65686600
C	-1.78517200	3.09439500	-0.25397800
C	-3.15185400	3.24120300	-0.53799300
C	-3.65312300	1.95808600	-0.39489200
H	-3.75777900	-0.75829000	0.38250300
C	-5.06301400	1.49735200	-0.57581100
C	-0.71418100	4.12811800	-0.27785800
C	-3.58009500	-1.16101400	3.08986200
C	1.49615600	-1.25333100	2.77500000
C	-3.77275200	-2.98530200	-1.26809900
C	0.54741900	-1.40871400	-3.46043300
H	-3.69446300	4.13512500	-0.79762600
H	-0.97606100	-1.63848100	4.45157500
H	-1.74389200	-3.38633300	-3.41051600
F	-5.83084900	2.53240900	-0.97707700
F	-5.59511600	1.01135300	0.56284600
F	-5.15864100	0.52851000	-1.51117700
F	0.03213200	4.11423100	0.85726600
F	-1.23263200	5.36178900	-0.41339800
F	0.16084700	3.94130200	-1.30027400
F	0.48747100	-2.17268900	-4.57040400
F	0.76179700	-0.13159100	-3.84371900
F	1.64411900	-1.79530300	-2.76383500
F	-4.89093500	-2.24344400	-1.38402100
F	-3.92829800	-4.08337300	-2.03746800
F	-3.69239400	-3.39413400	0.01716100
F	-4.26142000	-2.13804300	2.46141400

F	-3.63765300	-1.41118900	4.41532500
F	-4.23294900	-0.00157300	2.86195300
F	2.08128200	-2.10273600	1.88956300
F	1.73044900	-1.73129300	4.01126300
F	2.16209400	-0.07691000	2.66240800
C	4.77264400	1.90662800	1.21269100
C	3.03175200	2.84998400	0.23450900
O	3.43624300	2.08448800	1.30329400
C	5.27926900	2.67508600	0.17549800
C	4.18163800	3.31593000	-0.41994200
H	4.18722300	3.98579800	-1.26759300
H	6.31643000	2.72428200	-0.12138500
H	2.05640000	3.29441200	0.32475800
C	2.48903700	1.37613100	-1.23247500
C	3.65985600	0.56144700	-1.35525100
C	3.97804000	-0.36974400	-0.40928200
H	3.24678400	-0.52877200	0.37704100
C	5.17351700	-1.19680800	-0.34064500
C	5.23635000	-2.20499700	0.64099600
C	6.28328000	-1.01808400	-1.19081800
C	6.36140800	-3.01701700	0.75889500
H	4.38728600	-2.34772200	1.30103800
C	7.40443400	-1.83018600	-1.07114200
H	6.26753600	-0.23198600	-1.93821300
C	7.44838200	-2.83340900	-0.09667100
H	6.38998500	-3.79266000	1.51790000
H	8.25141000	-1.68092000	-1.73389900
H	8.32778200	-3.46335800	-0.00472100
H	4.35752900	0.73376200	-2.17602100
H	2.40098300	2.09472100	-2.05203500
C	5.41096900	1.04415100	2.23958600
H	5.78332200	1.64647500	3.07657100
H	4.68345400	0.33015700	2.62820200
H	6.25196400	0.49664200	1.80856600

TS2-4′′

Zero-point correction= 0.471763 (Hartree/Particle)
Thermal correction to Energy= 0.514742
Thermal correction to Enthalpy= 0.515687
Thermal correction to Gibbs Free Energy= 0.393562
Sum of electronic and zero-point Energies= -3488.364304
Sum of electronic and thermal Energies= -3488.321325
Sum of electronic and thermal Enthalpies= -3488.320380

Sum of electronic and thermal Free Energies= -3488.442504

Ag	-0.68970700	0.32605000	-0.60398500
N	1.01887000	-1.30842700	-1.28002500
N	2.30603400	-1.12318700	-0.98634600
N	1.42309700	1.67671700	-0.63403900
N	2.54059300	1.22557100	-0.06518100
N	0.54222600	-0.27583400	1.52923700
N	1.81650500	-0.66761200	1.44185600
B	2.73201800	-0.28118600	0.24429000
C	0.98117100	-2.03243600	-2.39003100
C	2.26882100	-2.33966500	-2.84770000
C	3.08213400	-1.73323400	-1.91213800
C	1.54322300	2.99463200	-0.71172300
C	2.76360000	3.43465600	-0.18266300
C	3.36604100	2.26060900	0.21955000
C	0.06332700	-0.82126700	2.64196500
C	1.02682400	-1.58834800	3.30528900
C	2.13362500	-1.45804800	2.49285300
H	3.86739400	-0.49836900	0.51664600
C	3.48184600	-2.07990800	2.67439200
C	-1.35025400	-0.58202400	3.04109400
C	4.69222500	2.08579400	0.88679100
C	0.40608500	3.80240600	-1.23694100
C	4.57537800	-1.69903000	-1.86600300
C	-0.34108900	-2.33967100	-3.01051900
H	0.93831800	-2.14455000	4.22393100
H	3.15073400	4.43774100	-0.10856200
H	2.56442700	-2.91269700	-3.71128000
F	3.45851000	-2.88192100	3.74670200
F	4.44199500	-1.17167800	2.86559500
F	3.83020500	-2.82065600	1.61547000
F	-2.22191700	-1.02946500	2.10895300
F	-1.62151000	0.72060300	3.21094000
F	-1.63713600	-1.21127500	4.18363700
F	-0.23666000	-3.35381400	-3.87637500
F	-1.25909200	-2.66670200	-2.08996200
F	-0.83028500	-1.28460800	-3.68469300
F	5.06643100	-2.32979300	-0.79534000
F	5.07159600	-2.29652700	-2.95613200
F	5.03676800	-0.44217200	-1.83867600
F	5.54741300	1.37534600	0.14686700
F	5.24192100	3.28629000	1.10885400
F	4.57009500	1.46551900	2.06769800

F	-0.18464900	3.22472100	-2.29127700
F	0.81030700	5.02329100	-1.59885600
F	-0.55781300	3.96369600	-0.30482600
C	-6.63789000	-2.51810900	1.33614500
C	-5.44862100	-1.89572100	0.97921500
C	-5.33130900	-1.23879800	-0.25629600
C	-6.42407000	-1.23987200	-1.13900500
C	-7.60698300	-1.87299700	-0.78449600
C	-7.71781200	-2.50564700	0.45459500
H	-6.72327600	-3.01702100	2.29546400
H	-4.59864300	-1.89484200	1.65635300
H	-6.33730200	-0.75524100	-2.10629700
H	-8.44559400	-1.87694400	-1.47249700
H	-8.64617000	-2.99580500	0.72926800
C	-4.07908500	-0.56690900	-0.55590600
C	-3.81200700	0.31836500	-1.56988600
H	-3.24650400	-0.78540300	0.11158000
H	-4.61482300	0.63426600	-2.23660500
C	-2.52338500	0.88506300	-1.63075100
H	-2.45746800	1.65889700	-2.40634300
C	-5.10605200	1.95884400	0.76515200
C	-3.41578400	3.01172300	-0.14235400
O	-4.74719200	2.76588600	-0.26155600
C	-4.01866700	1.70456100	1.55705800
C	-2.92255000	2.39949300	0.97426700
H	-1.89991600	2.43009800	1.31887400
H	-4.01053700	1.09779100	2.44961000
H	-2.97960200	3.67605000	-0.87087300
C	-6.54191000	1.58865900	0.85021900
H	-7.14556400	2.43864400	1.18262300
H	-6.91454000	1.26934800	-0.12712800
H	-6.67512800	0.76551600	1.55475700

4´

Zero-point correction= 0.242596 (Hartree/Particle)
Thermal correction to Energy= 0.254365
Thermal correction to Enthalpy= 0.255309
Thermal correction to Gibbs Free Energy= 0.204783
Sum of electronic and zero-point Energies= -616.921482
Sum of electronic and thermal Energies= -616.909713
Sum of electronic and thermal Enthalpies= -616.908769
Sum of electronic and thermal Free Energies= -616.959295

C	0.81153100	-0.84824000	-0.83227200
C	2.65363000	0.13931100	0.01954400
O	2.16362100	-1.12115300	-0.45427900
C	0.90984500	0.53394300	-1.45161400
C	2.00110600	1.12266200	-0.96099200
H	2.34848100	2.13554000	-1.12595600
H	0.16626200	0.96218200	-2.11077700
C	1.97146500	0.41378500	1.35910300
C	0.70654200	-0.06900100	1.55612500
C	-0.03204900	-0.86440100	0.48289900
H	-0.08461900	-1.91239300	0.79102400
C	-1.44619300	-0.36345000	0.27959000
C	-2.48108300	-1.27292900	0.03641600
C	-1.74098400	1.00616200	0.28815200
C	-3.78205500	-0.82774100	-0.19566200
H	-2.26436200	-2.33792900	0.03818000
C	-3.04139300	1.45458100	0.05978000
H	-0.94543100	1.72274300	0.47063600
C	-4.06609300	0.53852300	-0.18376400
H	-4.57427400	-1.54765100	-0.37799000
H	-3.25471700	2.51932500	0.07325100
H	-5.07935100	0.88698700	-0.35888200
H	0.11064400	0.29153000	2.38955800
H	2.38694700	1.17225600	2.01510200
C	4.16699700	0.10711500	0.06303900
H	4.55933400	-0.06859000	-0.94124200
H	4.56159900	1.05238300	0.44397400
H	4.50492600	-0.69896500	0.71843400
H	0.46800900	-1.63011000	-1.51313700

4

Zero-point correction= 0.242749 (Hartree/Particle)
Thermal correction to Energy= 0.254420
Thermal correction to Enthalpy= 0.255364
Thermal correction to Gibbs Free Energy= 0.205299
Sum of electronic and zero-point Energies= -616.921940
Sum of electronic and thermal Energies= -616.910269
Sum of electronic and thermal Enthalpies= -616.909325
Sum of electronic and thermal Free Energies= -616.959390

C	1.18396800	0.90583700	0.24322200
C	2.90776600	-0.53363100	-0.03315500
O	2.53643500	0.82660800	-0.26038300

C	1.24702400	0.00311300	1.46712000
C	2.27464800	-0.83311200	1.32355500
H	2.57393400	-1.64546500	1.97461200
H	0.52010000	0.02752000	2.26854900
H	3.98999300	-0.62720300	-0.08894500
C	2.17511600	-1.39164800	-1.05685400
C	0.92803500	-0.97688300	-1.44292700
C	0.27874600	0.28371700	-0.87893700
H	0.23658300	1.03513600	-1.66673500
C	-1.14616200	0.01906000	-0.43811700
C	-2.15458300	0.93511400	-0.76033700
C	-1.48203400	-1.11910800	0.30735200
C	-3.46711000	0.72904100	-0.33488000
H	-1.90622700	1.80628000	-1.35991500
C	-2.79336300	-1.32825900	0.73195500
H	-0.70942900	-1.84042100	0.55634800
C	-3.78941300	-0.40246700	0.41521200
H	-4.23785000	1.44823800	-0.59549900
H	-3.03856400	-2.21552100	1.30819900
H	-4.81098100	-0.56642700	0.74441100
H	0.27629700	-1.65074600	-1.98986500
H	2.51715600	-2.40215900	-1.26163900
C	0.84168400	2.35514700	0.52531200
H	1.51440800	2.75631400	1.28721700
H	0.94606200	2.94854500	-0.38605300
H	-0.18887900	2.43752300	0.88125000

4′′

Zero-point correction= 0.243111 (Hartree/Particle)
Thermal correction to Energy= 0.254843
Thermal correction to Enthalpy= 0.255787
Thermal correction to Gibbs Free Energy= 0.204943
Sum of electronic and zero-point Energies= -616.923286
Sum of electronic and thermal Energies= -616.911555
Sum of electronic and thermal Enthalpies= -616.910611
Sum of electronic and thermal Free Energies= -616.961454

C	-3.49813800	0.59010400	0.66056400
C	-2.17043100	0.71115300	1.06450400
C	-1.16397400	-0.01332000	0.42576100
C	-1.50561100	-0.86650800	-0.62895100
C	-2.83057700	-0.98441300	-1.03536300
C	-3.83065700	-0.25817100	-0.39088000

H	-4.27074900	1.15831100	1.16851600
H	-1.91191000	1.37595400	1.88500500
H	-0.72078300	-1.42006200	-1.13580000
H	-3.08429500	-1.64671500	-1.85693500
H	-4.86419600	-0.35518700	-0.70694000
C	0.28396700	0.14167600	0.85657500
C	0.84816600	-1.23220200	1.18800600
H	0.29764800	0.76246700	1.76047100
H	0.28329100	-1.83224100	1.89790700
C	1.90037700	-1.75759200	0.52447000
H	2.21408300	-2.78770300	0.67517800
C	1.16533500	0.84451400	-0.22517500
C	2.56378000	-0.88426500	-0.53798400
O	1.53228300	-0.15110500	-1.18480600
C	2.51468700	1.22083200	0.37879200
C	3.36456300	0.21960300	0.15882200
H	4.40690600	0.14147400	0.44457600
H	2.69716800	2.14223400	0.91725500
H	3.11268600	-1.46748800	-1.27780500
C	0.47155000	1.98871100	-0.93403000
H	1.17335200	2.47248100	-1.61672600
H	-0.38516300	1.62134100	-1.50165600
H	0.11547400	2.72324500	-0.20525300

Int3-D$_{cp}$

Zero-point correction=	0.469020 (Hartree/Particle)
Thermal correction to Energy=	0.514618
Thermal correction to Enthalpy=	0.515562
Thermal correction to Gibbs Free Energy=	0.383412
Sum of electronic and zero-point Energies=	-3488.401249
Sum of electronic and thermal Energies=	-3488.355652
Sum of electronic and thermal Enthalpies=	-3488.354707
Sum of electronic and thermal Free Energies=	-3488.486857

Ag	0.62917200	0.56581300	-0.53519700
N	-1.06709800	-0.75986100	-1.65429200
N	-2.19666900	-1.11268000	-1.03259700
N	-0.42875200	-0.73263600	1.27518000
N	-1.75923500	-0.68402900	1.41919200
N	-1.44069400	1.82909800	-0.05510900
N	-2.61760300	1.18427200	-0.05221800
B	-2.68741700	-0.33840200	0.21765900
C	-0.88209200	-1.63761100	-2.63044900

C	-1.90252900	-2.59399500	-2.66534800
C	-2.72213800	-2.21441100	-1.62107900
C	0.05551100	-1.11795900	2.45192300
C	-0.95534900	-1.31597300	3.39013900
C	-2.10900300	-1.01821300	2.68156300
C	-1.70176300	3.10218800	-0.34029000
C	-3.07485200	3.30814400	-0.52716200
C	-3.61784000	2.05506400	-0.33837000
H	-3.80513600	-0.65107700	0.47517600
C	-5.06229800	1.66882300	-0.40180300
C	-0.59001100	4.09222500	-0.42951300
C	-3.51491300	-1.05820200	3.18734800
C	1.52432400	-1.32570300	2.61811600
C	-3.97285100	-2.90250900	-1.16086200
C	0.34904800	-1.56940300	-3.47878100
H	-3.59256200	4.22421200	-0.76224500
H	-0.88160500	-1.62341400	4.41936400
H	-2.03388400	-3.41733900	-3.34415200
F	-5.78394900	2.71551700	-0.83153400
F	-5.54506000	1.32270200	0.80473300
F	-5.28627800	0.65060400	-1.24063400
F	0.16853000	4.09588000	0.68581000
F	-1.07288900	5.33116300	-0.59957000
F	0.23755400	3.83290200	-1.46012600
F	0.22371100	-2.33853800	-4.56470000
F	0.61741200	-0.31608100	-3.89050900
F	1.43481700	-2.00053400	-2.80652100
F	-5.05864600	-2.12841500	-1.27038300
F	-4.17714100	-3.99565000	-1.90680000
F	-3.87881700	-3.29683200	0.11886700
F	-4.22196600	-2.06064600	2.64084300
F	-3.50589200	-1.23994200	4.51094700
F	-4.17019100	0.08763700	2.93355700
F	2.00611300	-2.20949900	1.72337200
F	1.80084000	-1.80352100	3.84224000
F	2.22930900	-0.19854400	2.44647200
C	4.98259000	1.79007400	1.26543600
C	3.36079800	3.03651900	0.48256600
O	3.67410500	2.11623300	1.42295900
C	5.51652400	2.52712000	0.23740800
C	4.45987300	3.33987100	-0.26019900
H	4.50662800	4.05032500	-1.07583300
H	6.53536100	2.48041100	-0.10463800
H	2.34567400	3.40624400	0.50284400

C	2.41531400	1.16562100	-1.42782000
C	3.66361400	0.51433900	-1.48423700
C	3.92969100	-0.49392400	-0.59419800
H	3.11367000	-0.77549200	0.06859100
C	5.17010900	-1.22458100	-0.41830000
C	5.19812300	-2.26447200	0.52505700
C	6.35034700	-0.91368300	-1.12514500
C	6.36558600	-2.98335400	0.74996100
H	4.29357300	-2.49633200	1.08033100
C	7.50916100	-1.63488500	-0.89613400
H	6.35225000	-0.10327600	-1.84576500
C	7.52111200	-2.67109500	0.04091400
H	6.37101300	-3.78624300	1.48003900
H	8.40975800	-1.39403700	-1.44727700
H	8.43371000	-3.23407000	0.21470500
H	4.43920400	0.85501800	-2.16195200
H	2.38159400	2.01855500	-2.11334400
C	5.55340800	0.81195300	2.22855500
H	5.79549800	1.28871700	3.18032600
H	4.83892600	0.01422500	2.42095700
H	6.46575900	0.37770300	1.81372200

TS3$_{cp}$

Zero-point correction= 0.468967 (Hartree/Particle)
Thermal correction to Energy= 0.513047
Thermal correction to Enthalpy= 0.513991
Thermal correction to Gibbs Free Energy= 0.388564
Sum of electronic and zero-point Energies= -3488.397352
Sum of electronic and thermal Energies= -3488.353272
Sum of electronic and thermal Enthalpies= -3488.352328
Sum of electronic and thermal Free Energies= -3488.477756

Ag	-0.62692800	0.55008700	0.45784400
N	1.12398800	-0.56134200	1.75514100
N	2.16497900	-1.05613600	1.07869400
N	0.40551700	-0.90891100	-1.22531000
N	1.73641100	-0.82488200	-1.38531900
N	1.47013300	1.81697300	-0.24100200
N	2.61271600	1.14167400	-0.06602700
B	2.66039400	-0.39663100	-0.21549400
C	0.93682900	-1.35539500	2.80159100
C	1.85084700	-2.41220100	2.82087900
C	2.62925000	-2.18006100	1.69866600

C	-0.08536700	-1.33859000	-2.37934300
C	0.92081900	-1.51350100	-3.33042100
C	2.06305300	-1.17489100	-2.65090200
C	1.76098100	3.09577100	-0.02747200
C	3.11347400	3.27161400	0.29729400
C	3.61493000	1.99017700	0.25390200
H	3.77026300	-0.74747800	-0.45097400
C	5.00889500	1.53326500	0.59934800
C	0.68620600	4.12100600	-0.11519500
C	3.46521000	-1.12118600	-3.18437600
C	-1.55224500	-1.56335000	-2.55191400
C	3.74574900	-3.00798100	1.15341800
C	-0.20700900	-1.11427900	3.73462600
H	3.63903500	4.18454700	0.51859200
H	0.83522200	-1.84031600	-4.35324100
H	1.95806800	-3.21342700	3.53180600
F	5.77439000	2.61547100	0.84181100
F	5.60770500	0.83180800	-0.39552500
F	5.00890100	0.74978200	1.70585900
F	-0.03774200	3.99591100	-1.23780200
F	1.20279400	5.35915400	-0.09542800
F	-0.18544100	4.04115300	0.91606400
F	-0.03924900	-1.78829700	4.88670800
F	-0.35760800	0.18312500	4.02995000
F	-1.38912500	-1.52252200	3.20610900
F	4.91056700	-2.35698900	1.10100500
F	3.92270600	-4.09030500	1.92325900
F	3.46599500	-3.43118100	-0.09341200
F	4.31918400	-1.93533300	-2.53513300
F	3.46125300	-1.47547600	-4.48144900
F	3.97072200	0.13736100	-3.10652500
F	-2.04043800	-2.36022400	-1.57798700
F	-1.81680700	-2.15064000	-3.71903600
F	-2.26015700	-0.41385000	-2.49390400
C	-4.82005800	1.88157200	-1.14452900
C	-3.01091500	2.78232000	-0.29302500
O	-3.49098900	1.99346500	-1.30302900
C	-5.23644600	2.69032000	-0.10789700
C	-4.08555100	3.29221400	0.42198200
H	-4.01000900	3.99141400	1.24216400
H	-6.26167500	2.78991500	0.23986900
H	-2.00626700	3.13615100	-0.41535600
C	-2.45123000	1.27941500	1.27554700
C	-3.65708200	0.53311700	1.41940700

C	-3.99982700	-0.40996800	0.49650600
H	-3.24599100	-0.62083000	-0.27073900
C	-5.23942600	-1.17566900	0.39358200
C	-5.30385700	-2.22768400	-0.51272200
C	-6.38605100	-0.85099000	1.13762000
C	-6.47309400	-2.96167300	-0.68066100
H	-4.41655800	-2.48672600	-1.08909100
C	-7.56809000	-1.57838600	0.96750100
H	-6.37604600	-0.01058500	1.82803800
C	-7.61452500	-2.62914000	0.06425400
H	-6.50283500	-3.78425800	-1.38620000
H	-8.45509800	-1.30936800	1.53520500
H	-8.52947600	-3.20225000	-0.06713400
H	-4.36515000	0.76977000	2.21288000
H	-2.35167200	2.04254300	2.05505000
C	-5.54518600	1.02591500	-2.11445400
H	-5.78086200	1.59779500	-3.02389800
H	-4.94078100	0.16574800	-2.39001400
H	-6.48539600	0.67596100	-1.67749800

Int4$_{cp}$

Zero-point correction=	0.473233 (Hartree/Particle)
Thermal correction to Energy=	0.517576
Thermal correction to Enthalpy=	0.518520
Thermal correction to Gibbs Free Energy=	0.391676
Sum of electronic and zero-point Energies=	-3488.440932
Sum of electronic and thermal Energies=	-3488.396589
Sum of electronic and thermal Enthalpies=	-3488.395645
Sum of electronic and thermal Free Energies=	-3488.522489

Ag	-0.86468600	0.54757500	-0.27523600
N	0.87879800	0.37118300	2.05770300
N	1.46106600	-0.58627600	1.32116100
N	0.51090900	-0.90324900	-1.44898500
N	1.81935000	-0.90085400	-1.16667400
N	1.00207700	1.87910800	-0.42360300
N	2.18357700	1.35294300	-0.07592200
B	2.34818100	-0.17942500	0.10560500
C	0.26406700	-0.25143500	3.05594700
C	0.44314000	-1.63646600	2.99549100
C	1.21156800	-1.80752800	1.86523400
C	0.36714900	-1.51048900	-2.62082000
C	1.60037000	-1.92582500	-3.12670700

C	2.49852900	-1.51369300	-2.16391100
C	1.13546600	3.19831600	-0.37748100
C	2.42501500	3.56139000	0.01516100
C	3.05507300	2.34787500	0.20267700
H	3.49381600	-0.45543700	0.27050300
C	4.46033000	2.11762500	0.66875900
C	-0.04595200	4.07009200	-0.64601400
C	3.99180800	-1.62963900	-2.21650900
C	-0.98135100	-1.60082400	-3.25717900
C	1.64792600	-3.10102900	1.26356700
C	-0.49475700	0.55005600	4.06002600
H	2.83845900	4.54778800	0.14298000
H	1.81068700	-2.43905700	-4.05003200
H	0.05008800	-2.39694900	3.64813800
F	5.04926400	3.29923200	0.90469800
F	5.19824400	1.46852600	-0.23900100
F	4.49523100	1.40879400	1.80486400
F	-0.75470600	3.64364700	-1.70653700
F	0.32900100	5.33207000	-0.87490600
F	-0.89584900	4.08300600	0.40244400
F	0.29462400	1.38087600	4.75144200
F	-1.44353500	1.31657900	3.47693500
F	-1.11422200	-0.25156700	4.94053000
F	2.95032100	-3.10473900	0.95120400
F	1.42343700	-4.10512200	2.12235100
F	0.97443300	-3.39279800	0.13202900
F	4.49834400	-2.31528800	-1.18834200
F	4.34592700	-2.26368800	-3.34457300
F	4.57201300	-0.42142700	-2.22825300
F	-1.85941500	-2.29671900	-2.50425000
F	-0.90443300	-2.20469200	-4.44673700
F	-1.51702800	-0.38327400	-3.44037300
C	-5.31229300	0.20097600	-1.74509400
C	-3.97326200	2.00252100	-1.80978600
O	-4.22888700	0.74564400	-2.38962800
C	-5.82902200	1.00992700	-0.81057200
C	-5.02346500	2.24918000	-0.75092000
H	-5.48785700	3.21355400	-0.57562600
H	-6.69189700	0.79013900	-0.19947800
H	-3.61491700	2.72712300	-2.53107800
C	-3.52731600	2.09819200	-0.37599800
C	-3.01182000	1.01623100	0.48992500
C	-2.93573900	-0.32161300	0.18523500
H	-3.16437200	-0.64686000	-0.82523700

C	-2.75353700	-1.40515900	1.18273300
C	-2.17793700	-2.61839400	0.78448500
C	-3.18566200	-1.26638100	2.50551900
C	-2.03449500	-3.66461500	1.68654400
H	-1.82590000	-2.73070300	-0.23470300
C	-3.04183700	-2.31477700	3.40817900
H	-3.65597300	-0.34346200	2.82759200
C	-2.47138100	-3.51756200	3.00116000
H	-1.56977500	-4.59050600	1.36460500
H	-3.38192400	-2.19052000	4.43083400
H	-2.36627200	-4.33682000	3.70558700
H	-2.84641700	1.31115500	1.52540300
H	-3.07143700	3.06044000	-0.16675400
C	-5.67651100	-1.16872200	-2.19259600
H	-5.87346400	-1.17571400	-3.26880300
H	-4.85761600	-1.87079900	-2.00457300
H	-6.56474500	-1.51751900	-1.66408100

TS4$_{cope}$

Zero-point correction=	0.469684 (Hartree/Particle)
Thermal correction to Energy=	0.520734
Thermal correction to Enthalpy=	0.521678
Thermal correction to Gibbs Free Energy=	0.376301
Sum of electronic and zero-point Energies=	-3488.419959
Sum of electronic and thermal Energies=	-3488.368909
Sum of electronic and thermal Enthalpies=	-3488.367965
Sum of electronic and thermal Free Energies=	-3488.513342

Ag	-0.77056300	-0.51287400	-0.36374000
N	0.66947100	1.11047900	-1.38632600
N	1.83563700	1.37139600	-0.76406600
N	0.37496200	0.25404700	1.58975100
N	1.72040800	0.31073300	1.53962700
N	1.31886900	-1.80377000	-0.46891000
N	2.44803200	-1.06909300	-0.44892800
B	2.48957200	0.34343400	0.19310000
C	0.37623800	2.18488700	-2.12084700
C	1.35851100	3.17673900	-1.98270100
C	2.27168300	2.61494400	-1.10622800
C	0.04166900	0.17901700	2.88004900
C	1.17910300	0.18624300	3.69944400
C	2.22998200	0.26923400	2.80095800
C	1.62035100	-2.94825900	-1.08664900

C	2.96481300	-2.97437700	-1.48530700
C	3.45599600	-1.75212900	-1.05790100
H	3.61207600	0.65202000	0.39082300
C	4.84286200	-1.21741600	-1.22256400
C	0.57199700	-3.98598300	-1.29512600
C	3.69376600	0.28670800	3.10832800
C	-1.39317700	0.10091000	3.27654700
C	3.52670900	3.23178000	-0.57572900
C	-0.90422800	2.24471000	-2.88297000
H	3.50117500	-3.75776900	-1.99472500
H	1.23373800	0.14047600	4.77441300
H	1.40498200	4.14720700	-2.44856200
F	5.58164000	-2.09148700	-1.93727300
F	5.46560000	-1.02366300	-0.04454400
F	4.84748800	-0.03947500	-1.88200100
F	-0.13181000	-4.22828100	-0.16299500
F	1.11553500	-5.14638700	-1.70237600
F	-0.33659500	-3.61532800	-2.23612300
F	-0.84641900	3.17984400	-3.84960500
F	-1.20355200	1.05824300	-3.46526800
F	-1.95011400	2.55476200	-2.08090400
F	4.63255500	2.56211800	-0.95220400
F	3.63743000	4.49561900	-1.03472400
F	3.52430300	3.28274800	0.77339000
F	4.29120800	1.42659000	2.71317200
F	3.87601500	0.16837900	4.43996200
F	4.34124700	-0.73768300	2.51285600
F	-2.08677000	1.19526800	2.88522100
F	-1.51710700	-0.00859100	4.61220800
F	-2.01488500	-0.96670600	2.71646900
C	-5.02990200	-2.19192200	0.67523300
C	-3.13126800	-2.90617900	-0.31468800
O	-3.73682700	-2.54579900	0.93370000
C	-5.39611500	-2.51290200	-0.61232800
C	-4.26818300	-3.04808500	-1.25782900
H	-4.21191800	-3.50897100	-2.23165900
H	-6.37262200	-2.34051900	-1.04083000
H	-2.39681300	-3.69179400	-0.16557100
C	-2.69655000	-1.73550900	-1.18406400
C	-3.16861200	-0.38934500	-1.09217500
C	-3.76791600	0.20062300	0.00635100
H	-3.62927800	-0.24985100	0.97620600
C	-4.44260600	1.48805300	-0.00065000
C	-4.70232000	2.12956700	1.22788700

C	-4.88431300	2.11841700	-1.18197400
C	-5.35733900	3.35659700	1.27282800
H	-4.35489300	1.66606500	2.14545100
C	-5.53149100	3.34760400	-1.13439100
H	-4.73263100	1.63193400	-2.13962200
C	-5.77294200	3.97453500	0.09183900
H	-5.53933000	3.83483800	2.23080800
H	-5.86086700	3.81646300	-2.05705700
H	-6.28438000	4.93159500	0.12488000
H	-3.13816300	0.17315400	-2.02234400
H	-2.23727500	-2.04834600	-2.11373900
C	-5.82672100	-1.70891600	1.83054100
H	-6.84398200	-1.47244800	1.51449000
H	-5.86522500	-2.48240100	2.60675100
H	-5.38489700	-0.81488000	2.28028400

6. References

1. Z. Wei, J. Tan, X. Cui, M. Zhou, Y. Huang, N. Zang, Z. Chen and W. Wei, Design, synthesis and bioactive evaluation of oxime derivatives of dehydrocholic acid as anti-hepatitis B virus agents, *Molecules* 2020, **25**, 3359.
2. Z. L. Shen, K. K. K. Goh, Y. S. Yang, Y. C. Lai, C. H. A. Wong, H. L. Cheong and T. P. Loh, Direct synthesis of water-tolerant alkyl indium reagents and their application in palladium-catalyzed couplings with aryl halides, *Angew. Chem. Int. Ed.* 2011, **123**, 531-534.
3. B. Yu, S. Zou and H. Huang, Palladium-catalyzed ring-closing reaction for the synthesis of saturated N-H eterocycles with aminodienes and N,O-Acetals, *J. Org. Chem.* **2021**, **86**, 7849-7863.
4. Le, P. Q.; Nguyen, T. S.; May, J. A. A general method for the enantioselective synthesis of α-chiral heterocycles. *Org. Lett.* 2012, **14**, 6104-6107.
5. G. Battistuzzi, S. Cacchi, and G. Fabrizi, An efficient palladium-catalyzed synthesis of cinnamaldehydes from acrolein diethyl acetal and aryl iodides and bromides, *Org. Lett.* 2003, **5**, 777-780.
6. Z. Liu, K. Raveendra Babu, F. Wang, Y. Yang, and X. Bi, Influence of sulfonyl substituents on the decomposition of *N*-sulfonylhydrazones at room temperature, *Org. Chem. Front.* 2019, **6**, 121-124.
7. DesMarteau, D. D.; Petrov, V. A.; Montanari, V.; Pregnolato, M.; Resnati, G. Mild and selective oxygenation of sulfides to sulfoxides and sulfones by perfluoro-cis-2,3-dialkyloxaziridines, *J. Org. Chem.* 1994, **59**, 2762-2765.
8. I. G. Molnár, E. M. Tanzer, C. Daniliuc and R. Gilmour, Enantioselective aziridination of cyclic enals facilitated by the fluorine-iminium ion gauche effect. *Chem. Eur. J.* 2014, **20**, 794-800.
9. Gaussian 16 Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.
10. A. D. Becke, Density-functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.*, 1993, **98**, 5648-5652.
11. J. P. Perdew and Y. Wang, Accurate and simple analytic representation of the electron-gas correlation energy, *Phys. Rev. B,* 1992, **45**, 13244-13249.
12. S. Grimme, S. Ehrlich and L. Goerigk, Effect of the damping function in dispersion corrected density Functional theory, *J. Comp. Chem.,* 2011, **32**, 1456-1465.
13. W. Küchle, M. Dolg, H. Stoll, and H. Preuss, Energy-adjusted pseudopotentials for the actinides. Parameter sets and test calculations for thorium and thorium monoxide, *J. Chem. Phys.*, **1994**, *100*, 7535-7542.
14. X. Cao, M. Dolg, and H. Stoll, Valence basis sets for relativistic energy-consistent small-core actinide Pseudopotentials, *J. Chem. Phys.*, 2003, **118**, 487-496.

15. W. J. Hehre, R. Ditchfield, and J. A. Pople, Self-consistent molecular orbital methods. XII. Further extensions of Gaussian-type basis sets for use in molecular orbital studies of organic molecules, *J. Chem. Phys*. 1972, **56**, 2257-2261.

16. J. D. Dill and J. A. Pople, Self-consistent molecular orbital methods. XV. Extended Gaussian-type basis sets for lithium, beryllium, and boron, *J. Chem. Phys.* 1975, **62**, 2921-2923.

17. M. M. Francl, W. J. Petro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, and Pople, J. A. Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements, *J. Chem. Phys*. 1982 , **77**, 3654-3665.

18. P. Xiao, H. Yuan, J. Liu, Y. Zheng, X. Bi, and J. Zhang, Radical mechanism of isocyanide-alkyne cycloaddition by multicatalysis of Ag_2CO_3, solvent, and substrate, *ACS Catal*. 2015, **5**, 6177-6184.

19. A. V. Marenich, C. J. Cramer, and D. G. Truhlar, 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.

20. K. Fukui, Formulation of the reaction coordinate, *J. Phys. Chem.,* 1970, **74**, 4161-4163.

21. K. Fukui, The path of chemical reactions-the IRC approach, *Acc. Chem. Res.*, 1981, **14**, 363-368.

22. C. Y. Legault, CYLview, 1.0b; Université de Sherbrooke: Canada, 2009. Available at: http://www.cylview.org (accessed September, **2014**).

23. Lu, T.; Chen, F. Multiwfn: A multifunctional wavefunction analyzer, *J. Comput. Chem*. 2012, **33**, 580-592.

24. T. Lu, and Q. Chen, Interaction region indicator (IRI): A simple real space function clearly revealing both chemical bonds and weak interactions, *Chemistry-Methods*, 2021, **1**, 231-239.

25. M. Nishio, The CH/π hydrogen bond in chemistry. Conformation, supramolecules, optical resolution and interactions involving carbohydrates, *Phys. Chem. Chem. Phys*. 2011, **13**, 13873-13900.

7. NMR Spectra of Products

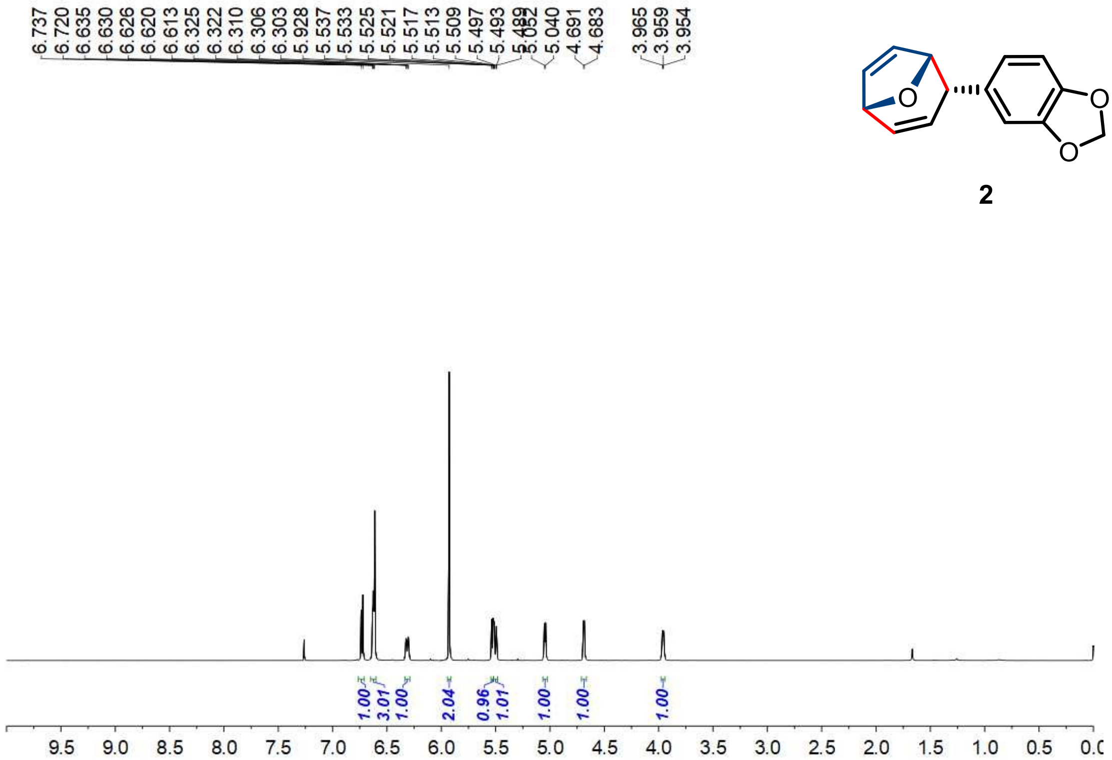


Figure S6. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **2**.

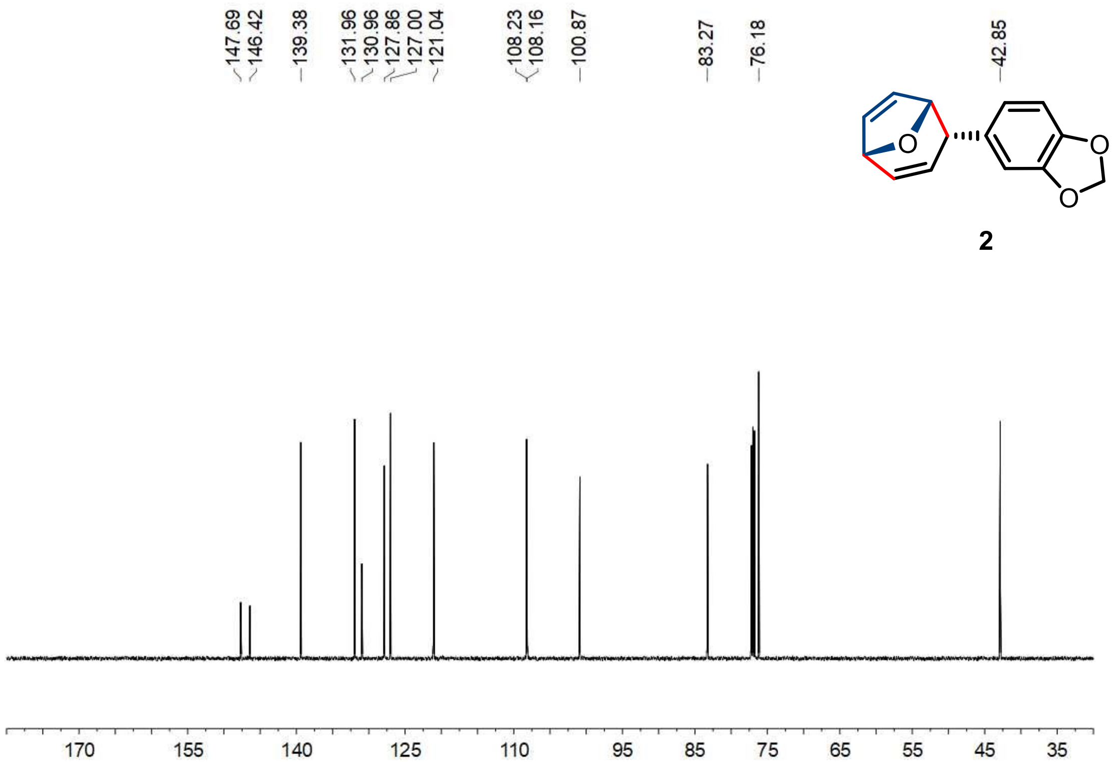


Figure S7. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **2**.

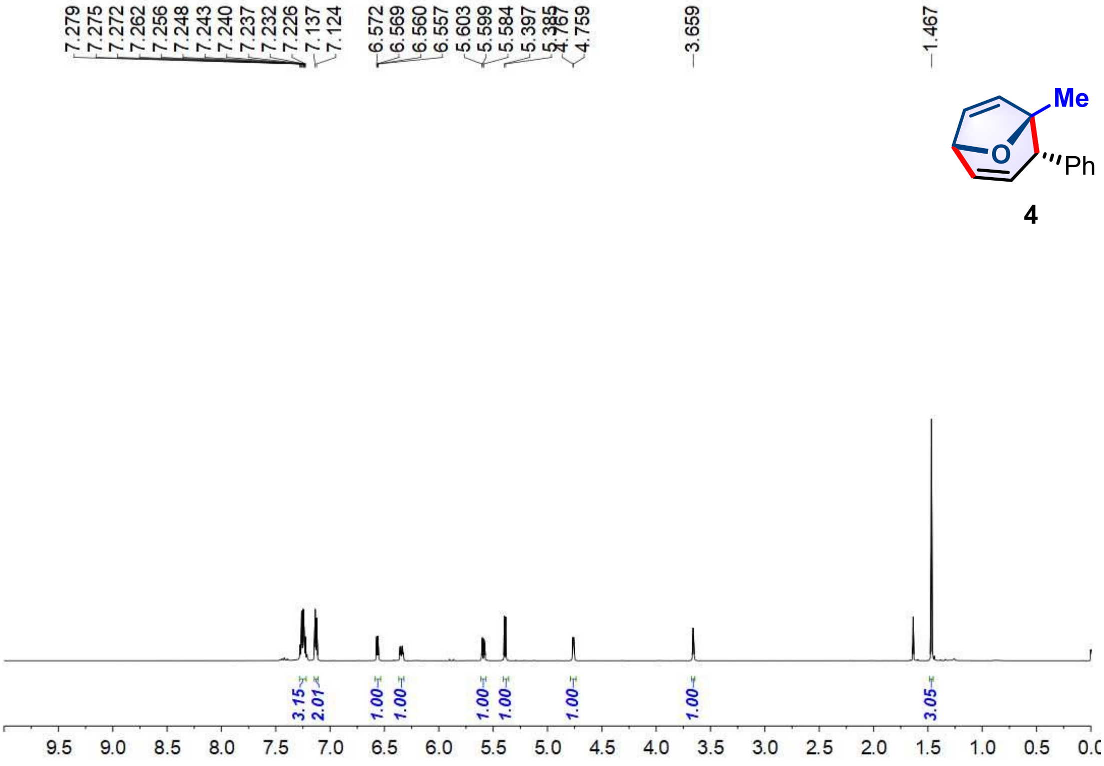


Figure S8. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **4**.

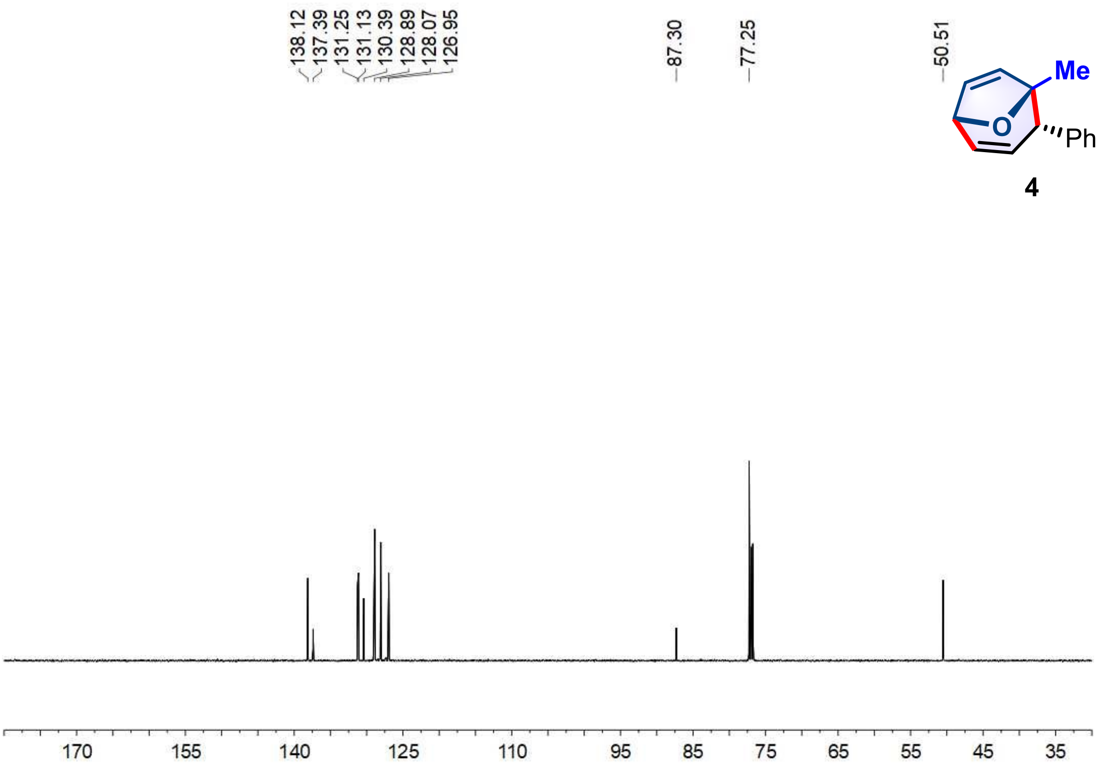


Figure S9. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **4**.

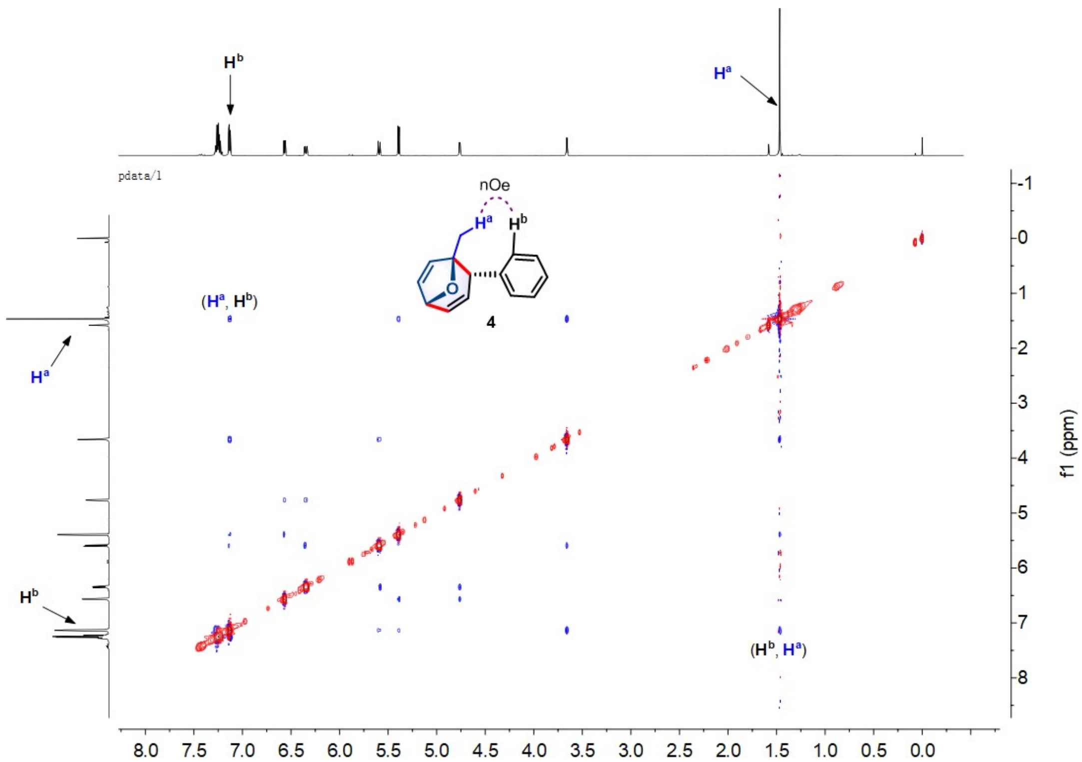


Figure S10. NOE of **4**.

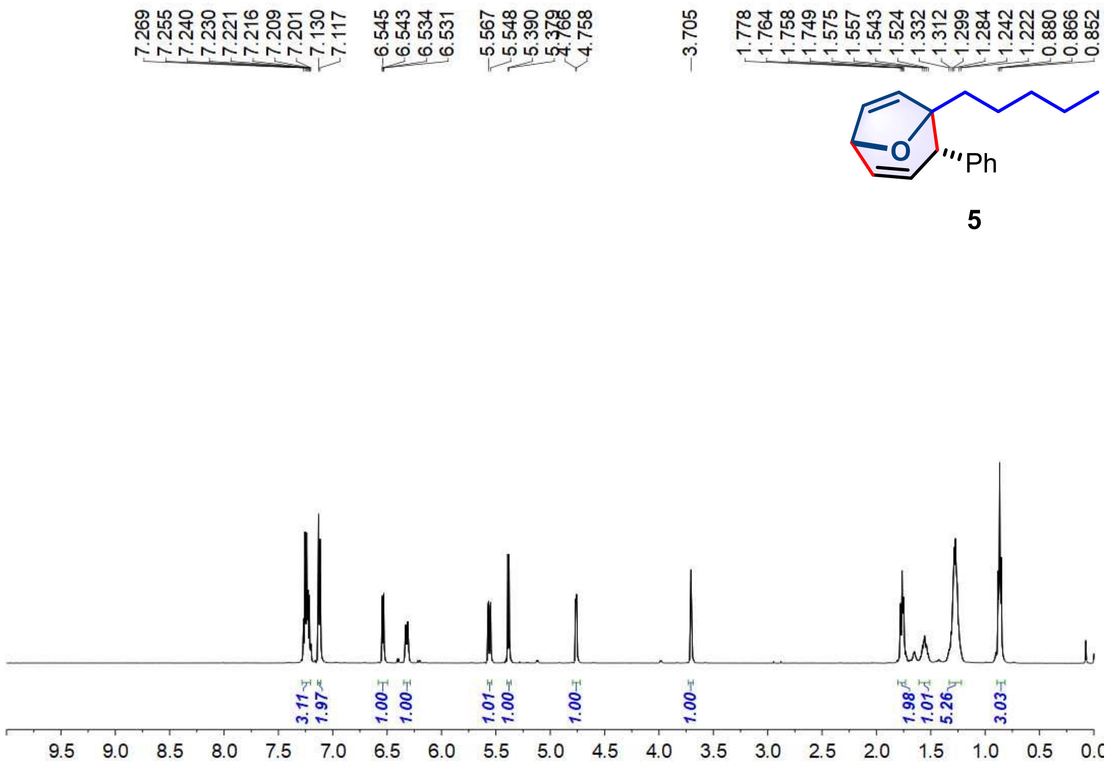


Figure S11. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **5**.

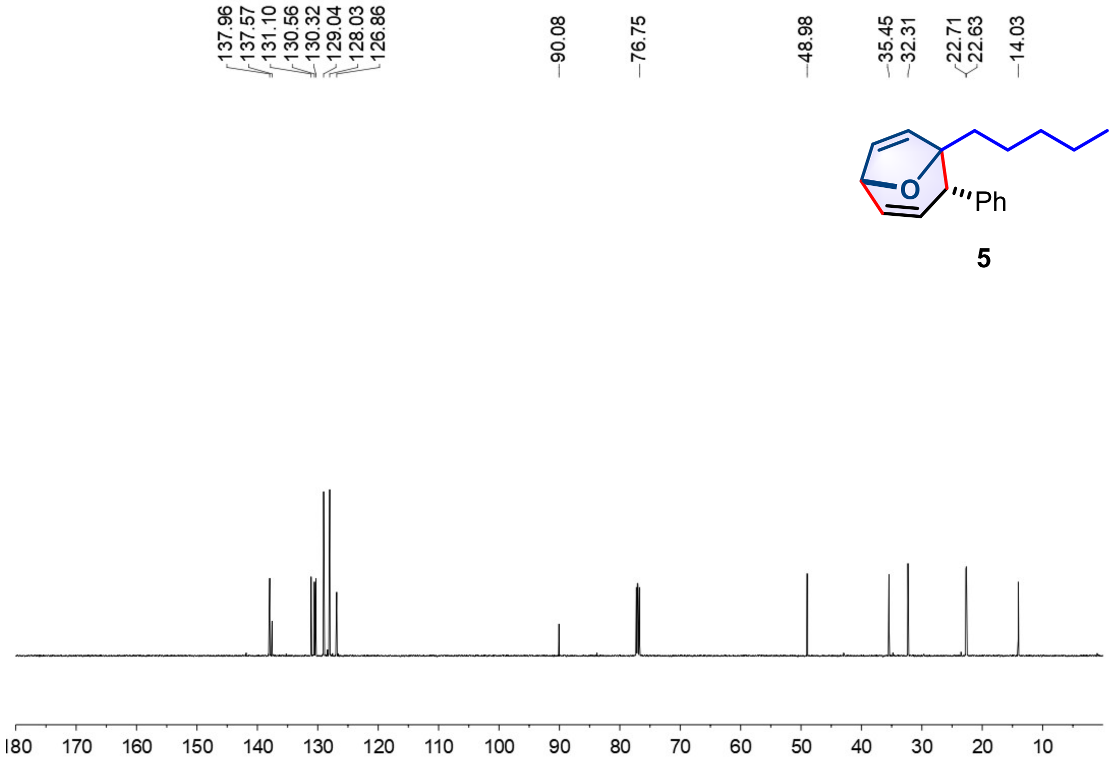


Figure S12. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **5**.

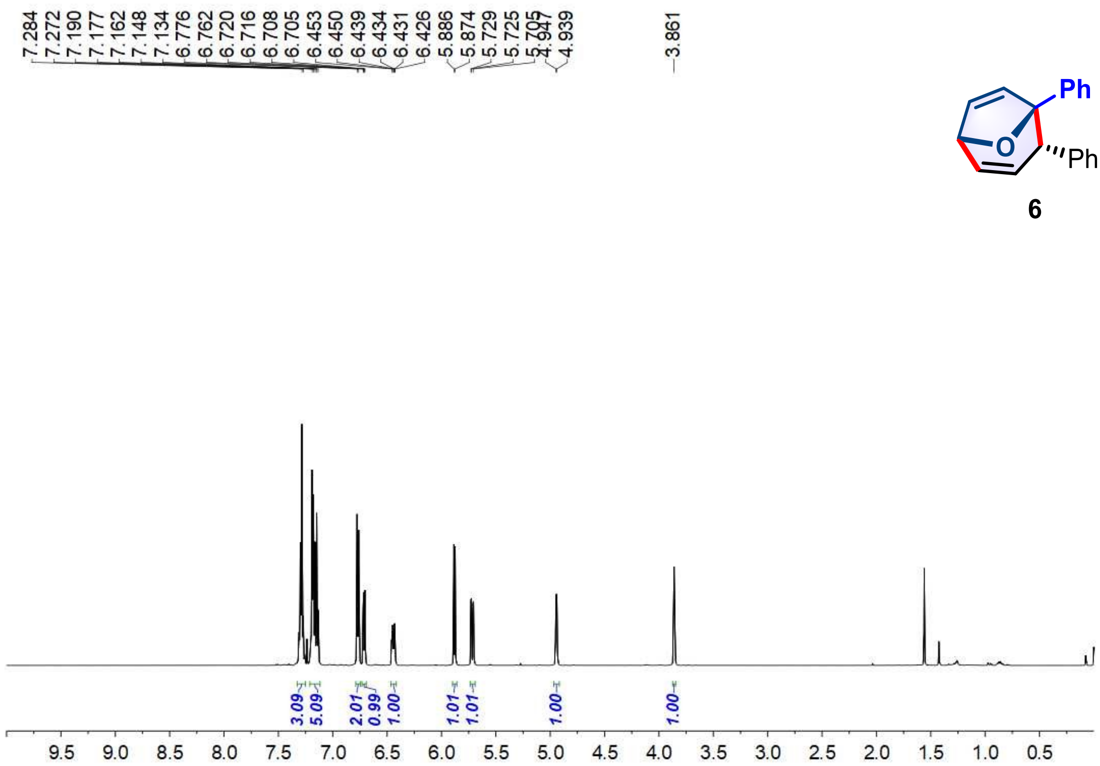


Figure S13. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **6**.

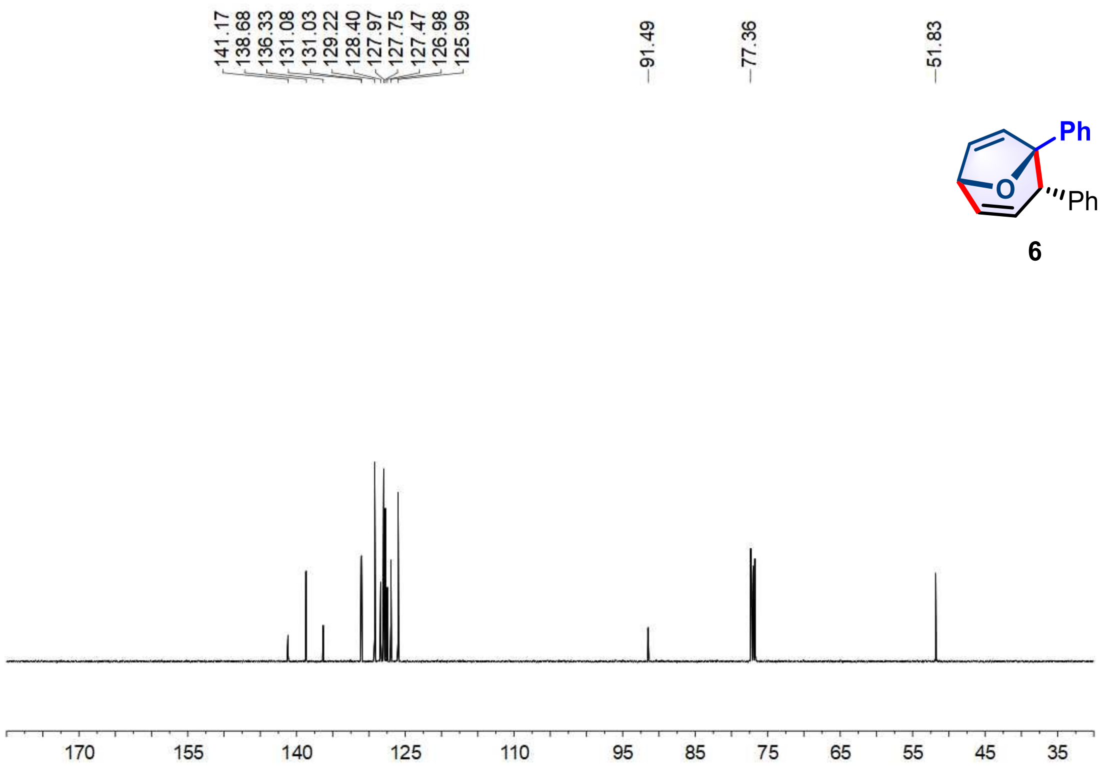


Figure S14. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **6**.

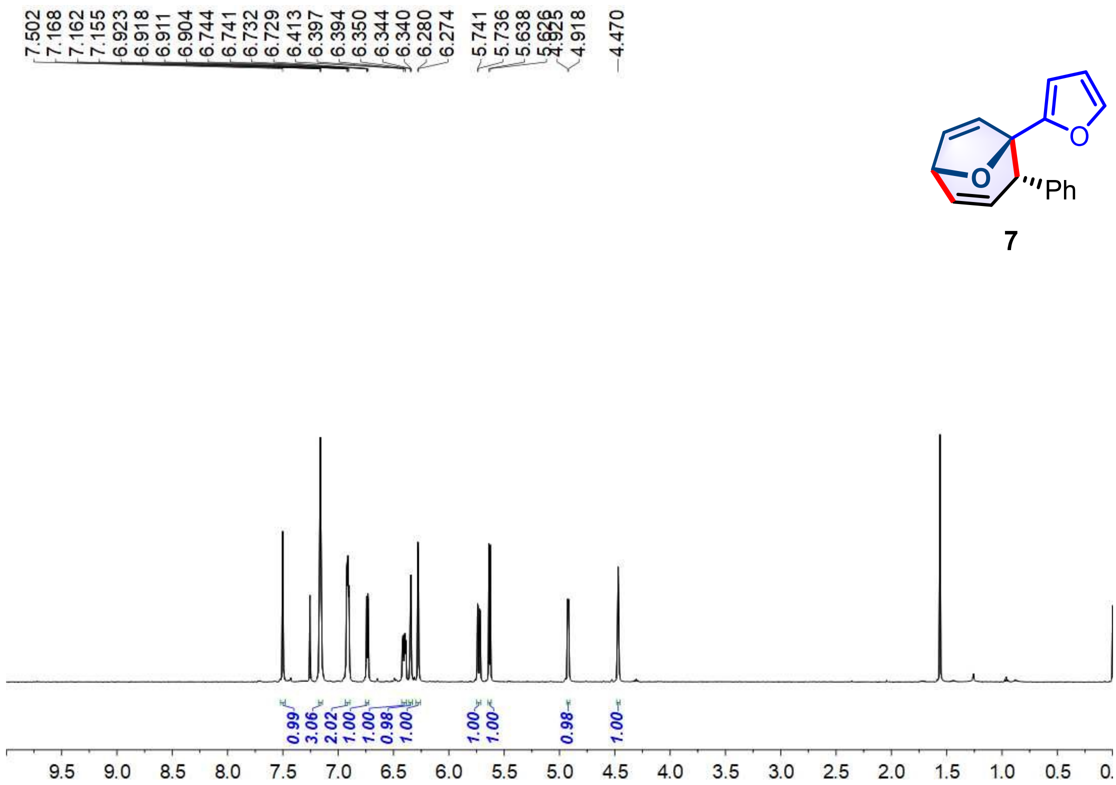


Figure S15. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **7**.

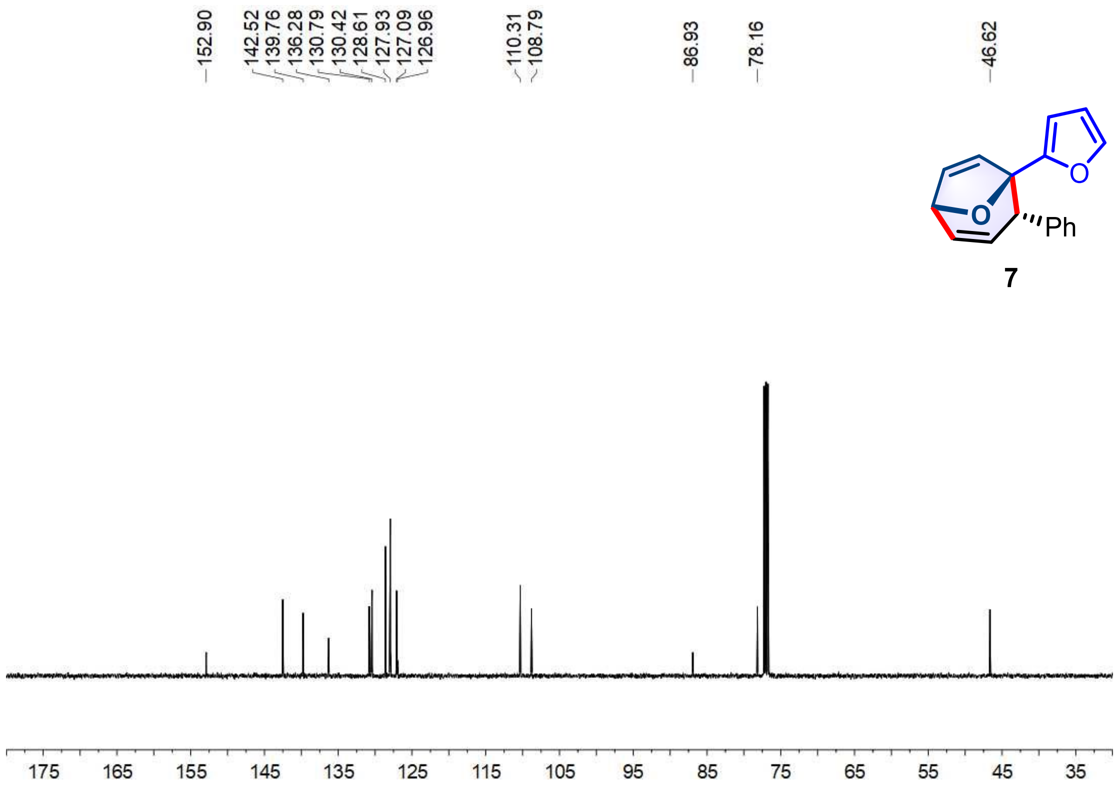


Figure S16. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **7**.

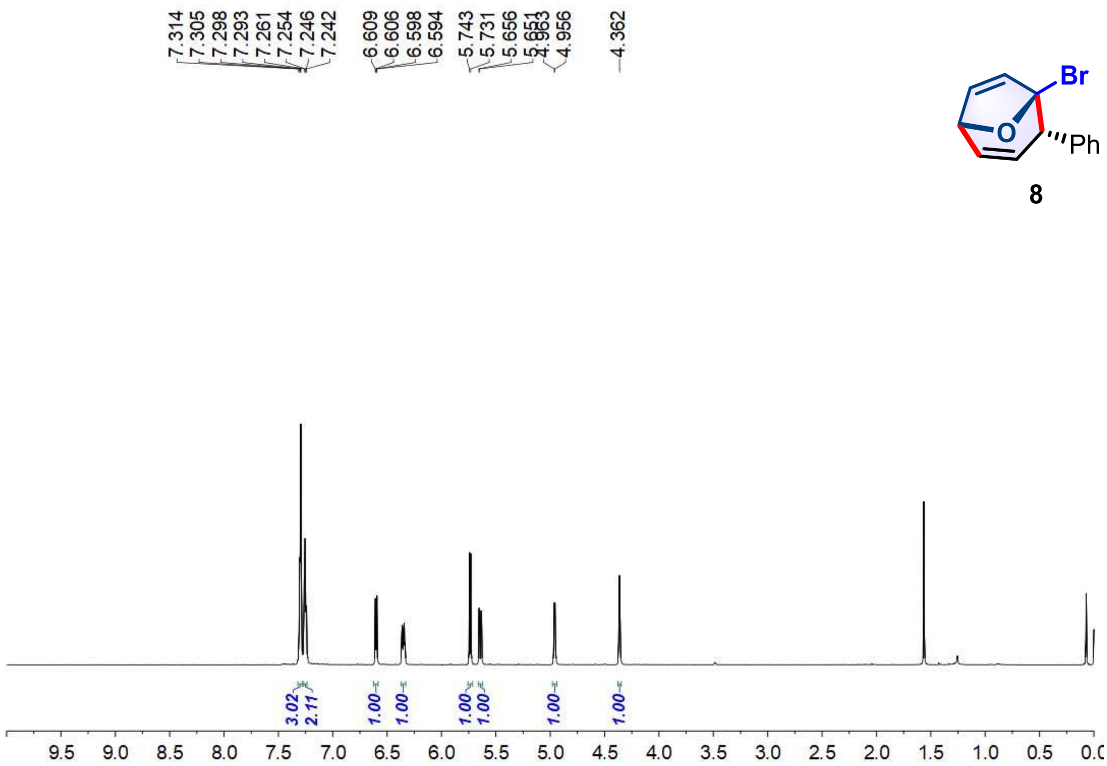


Figure S17. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **8**.

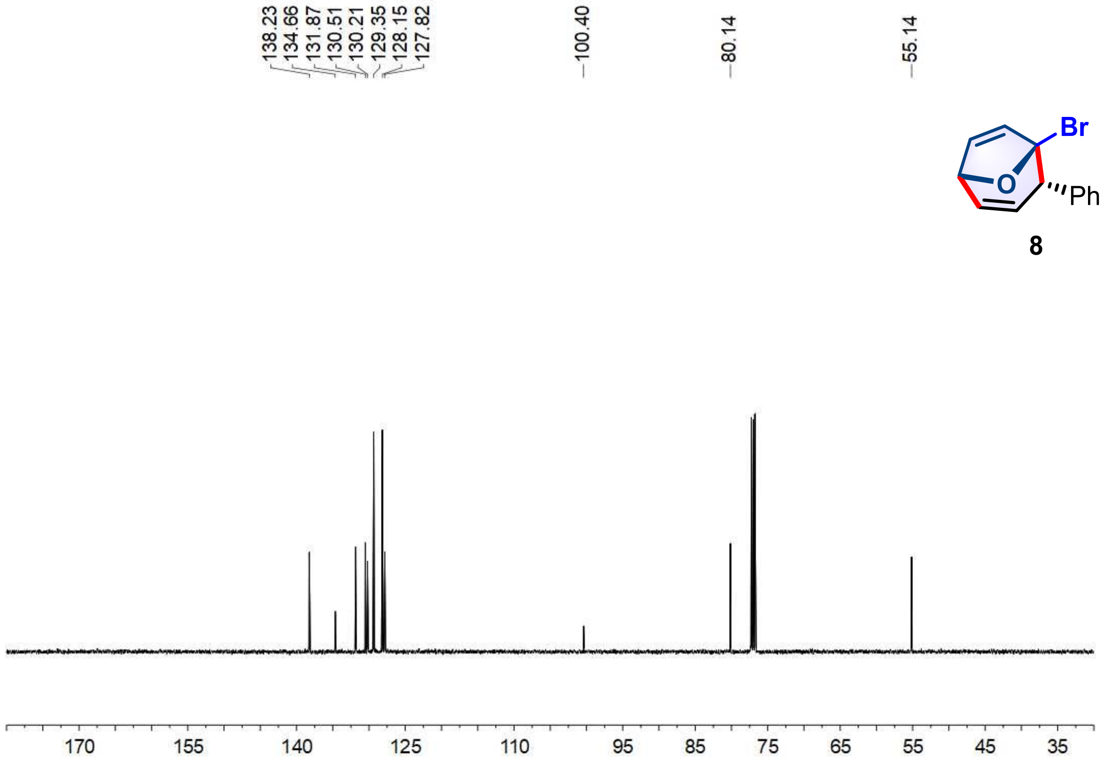


Figure S18. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **8**.

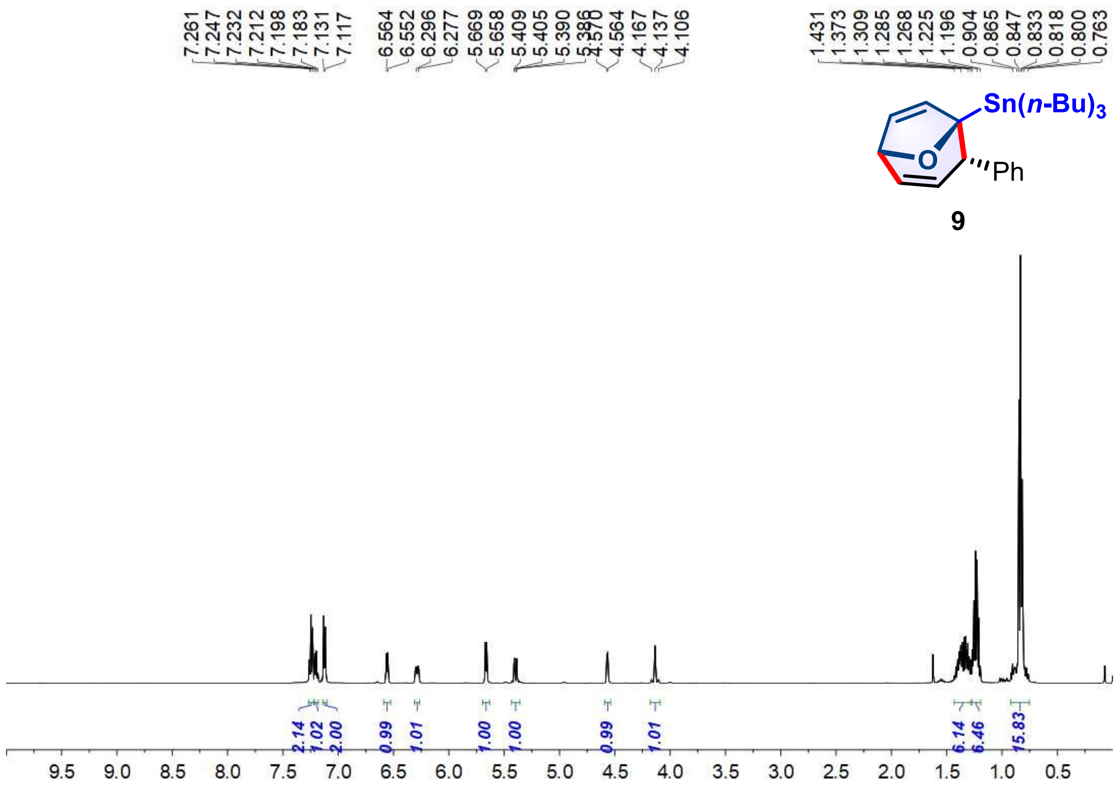


Figure S19. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **9**.

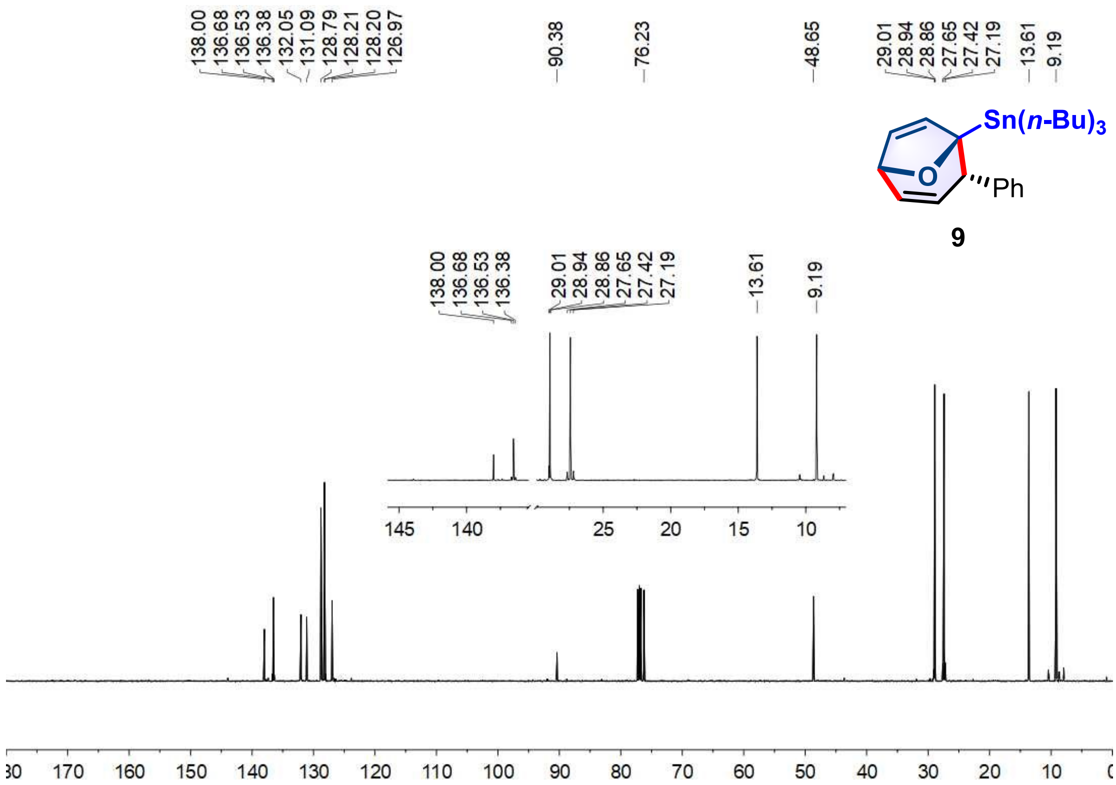


Figure S20. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **9**.

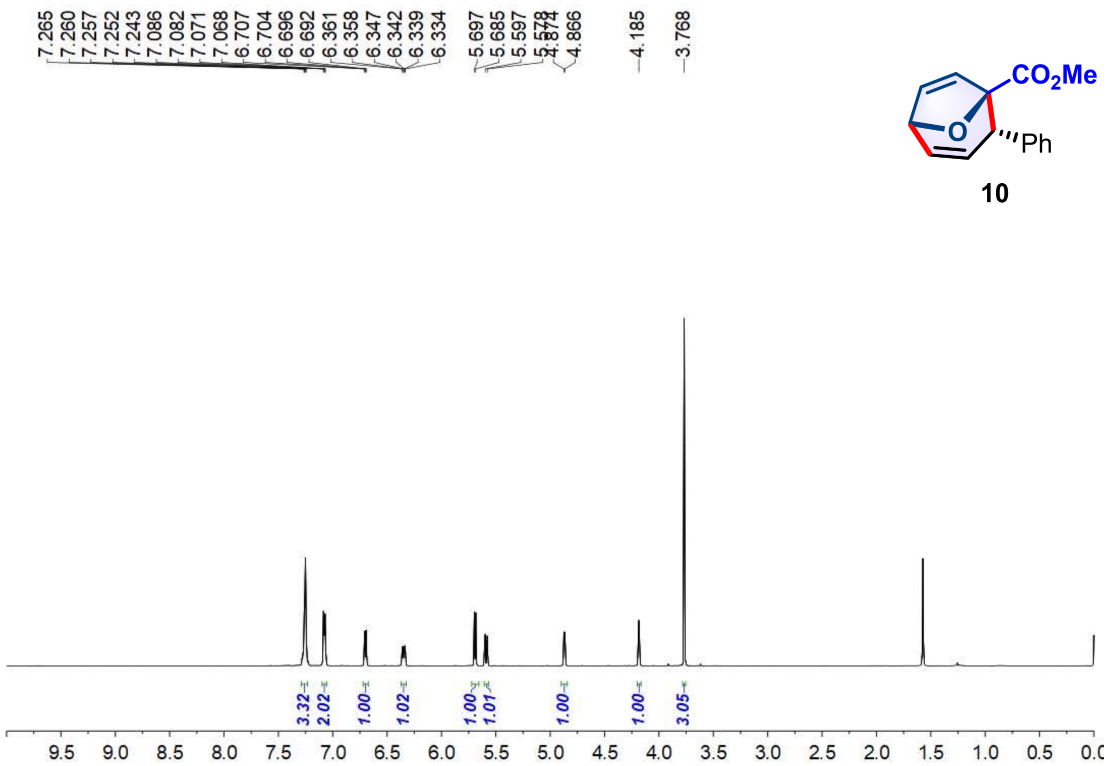


Figure S21. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **10**.

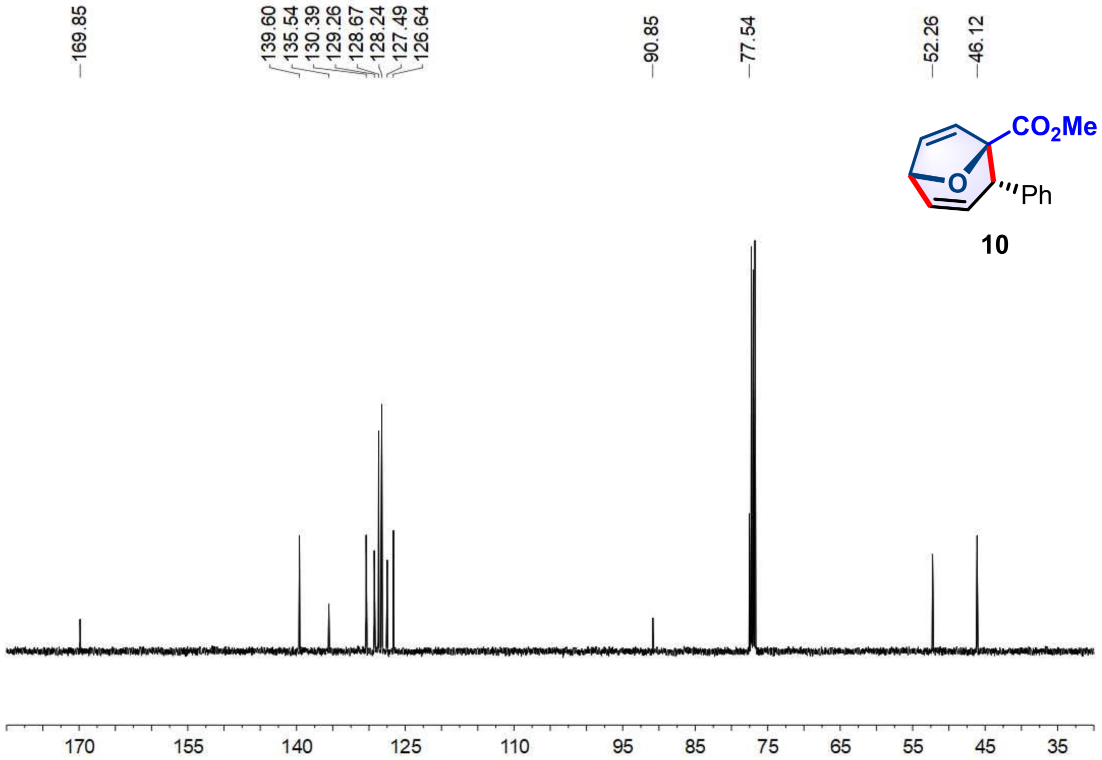


Figure S22. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **10**.

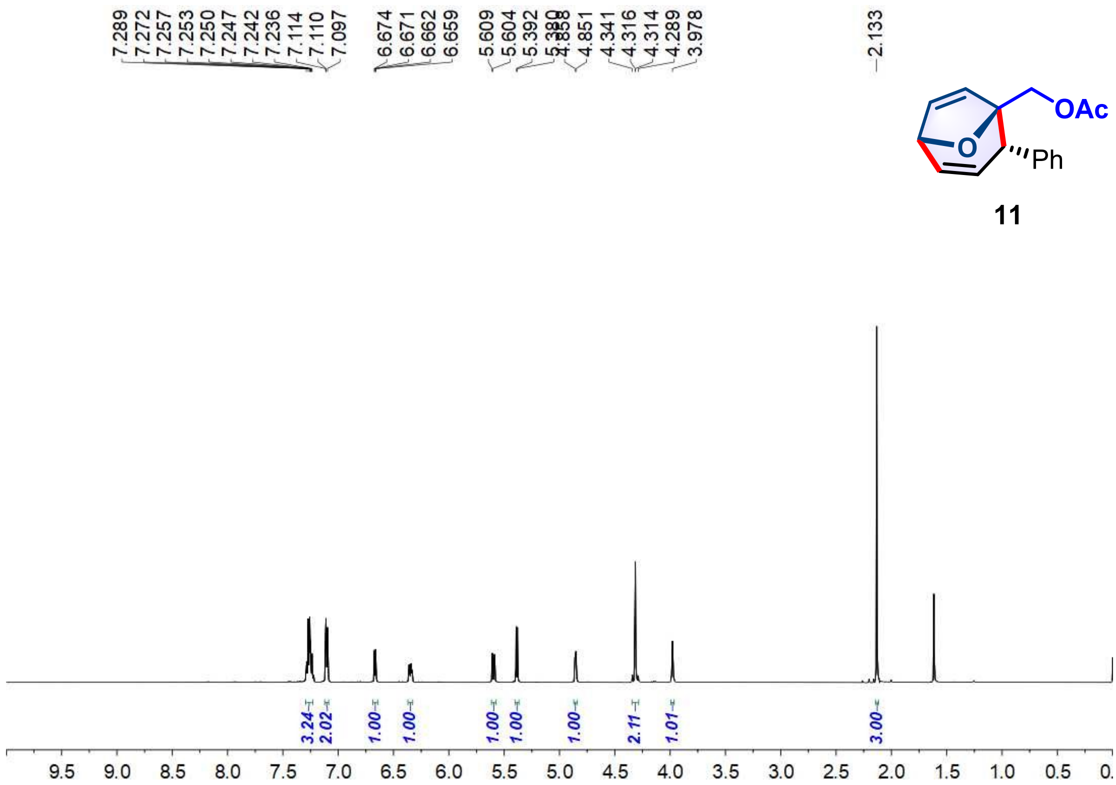


Figure S23. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **11**.

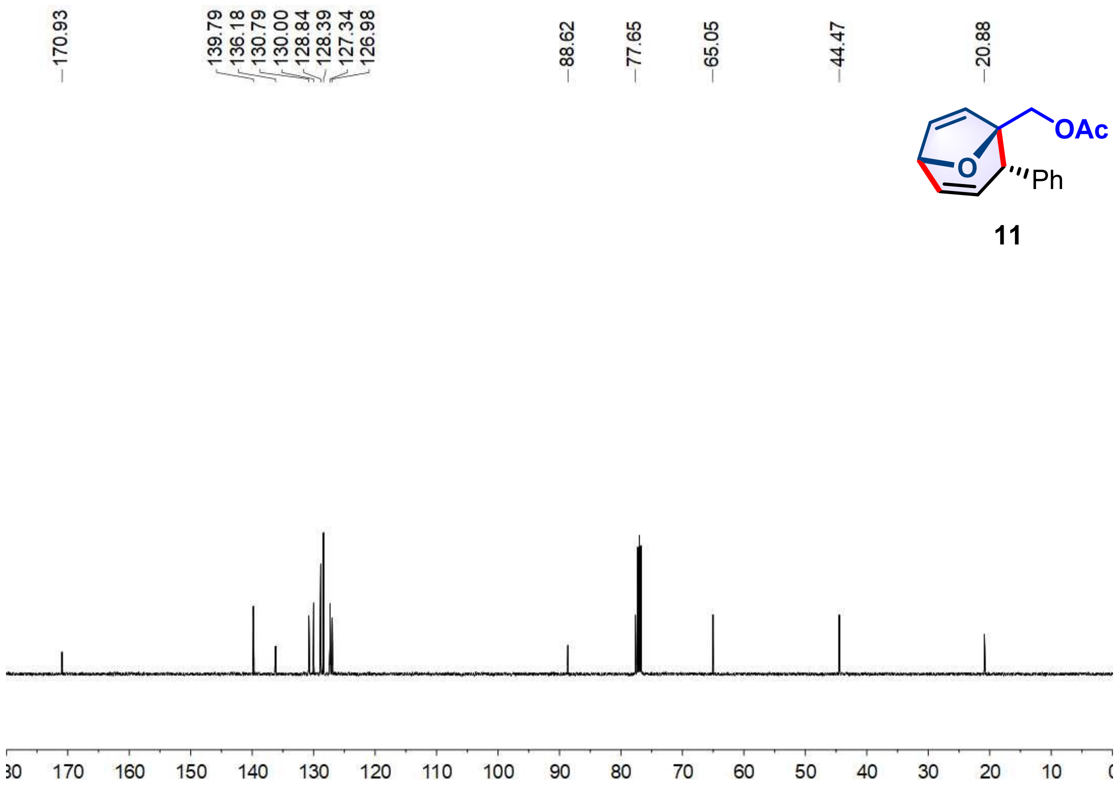


Figure S24. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **11**.

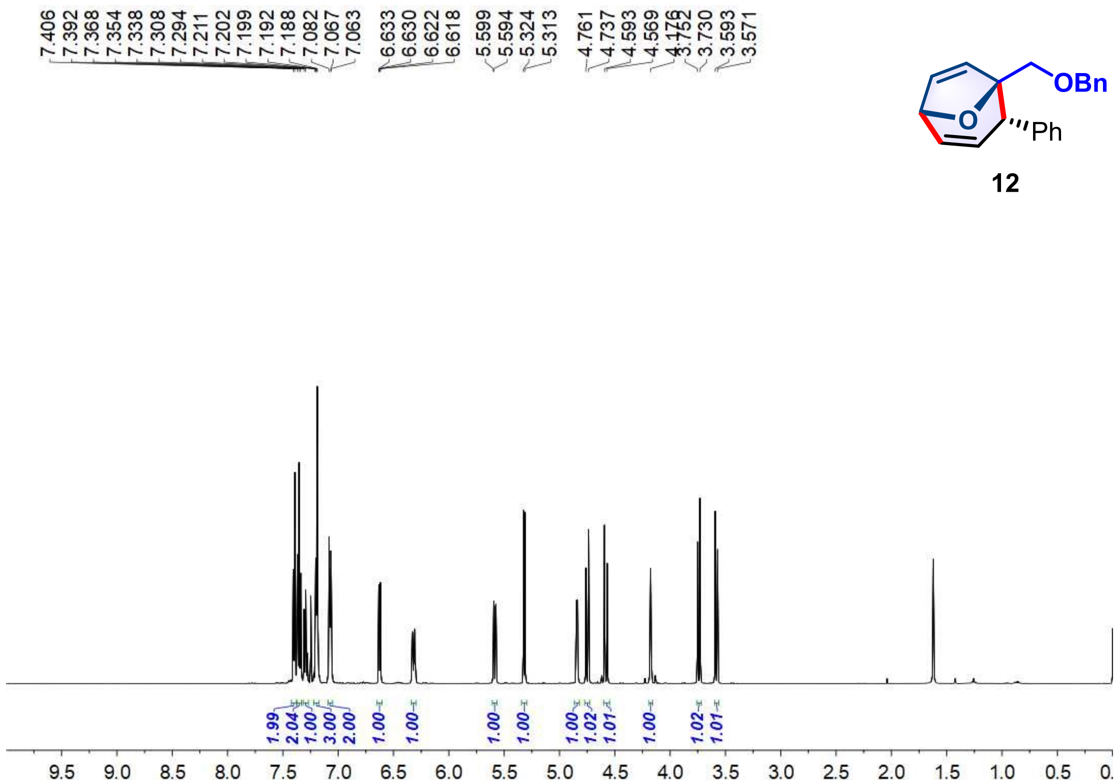


Figure S25. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **12**.

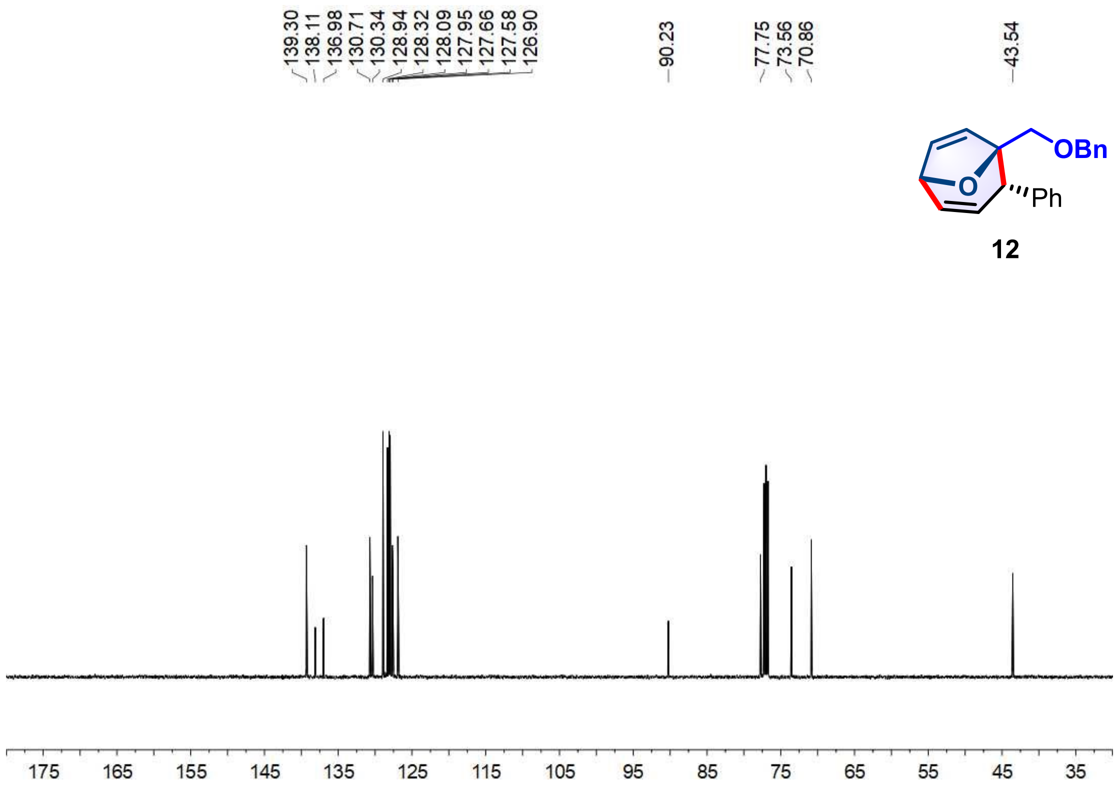


Figure S26. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **12**.

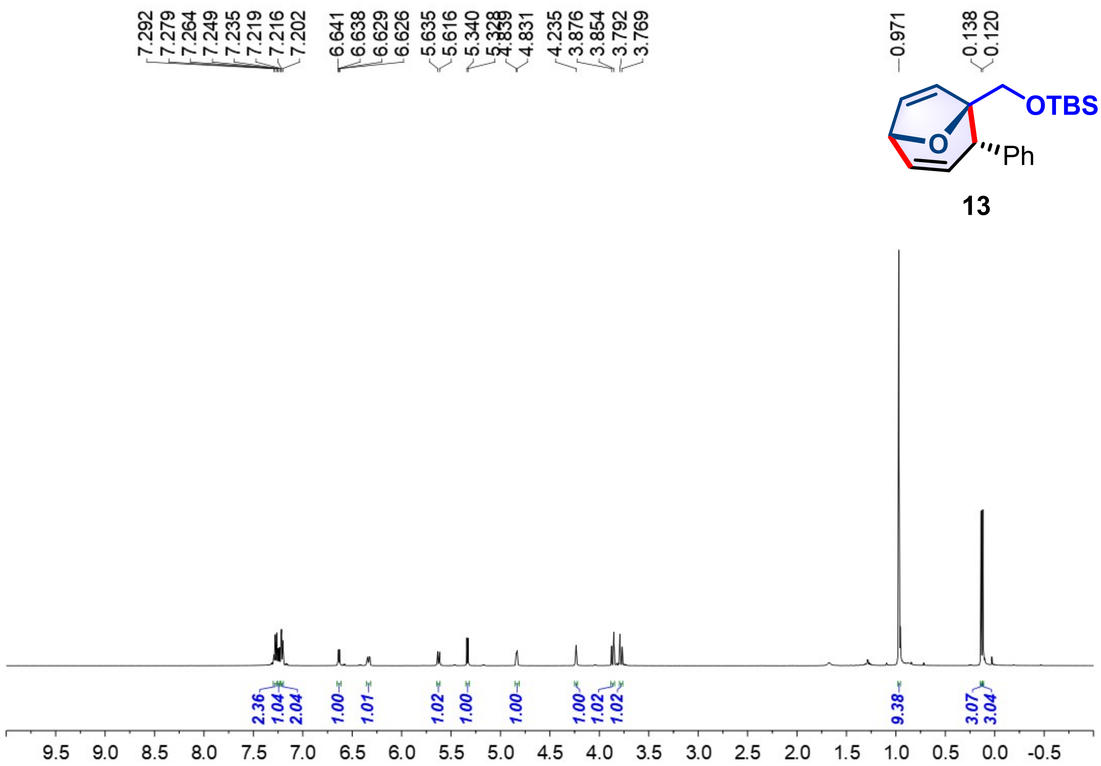


Figure S27. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **13**.

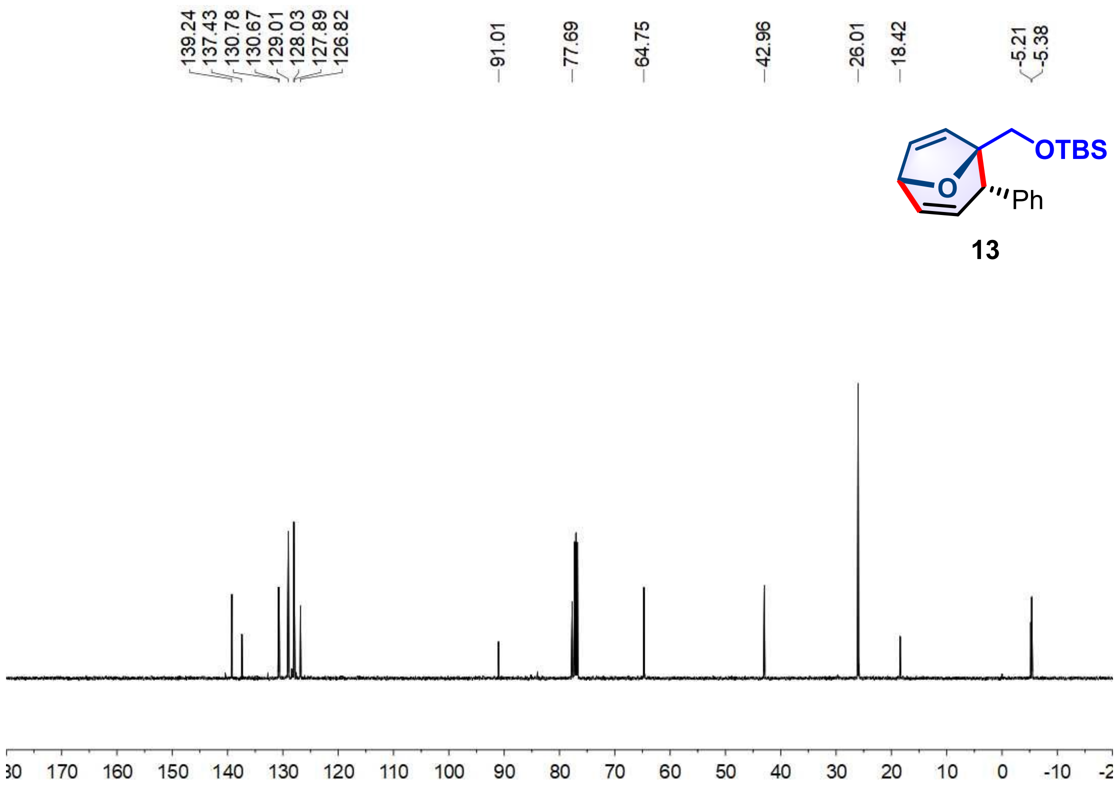


Figure S28. ^{13}C NMR (126 MHz, CDCl$_3$) Spectrum of **13**.

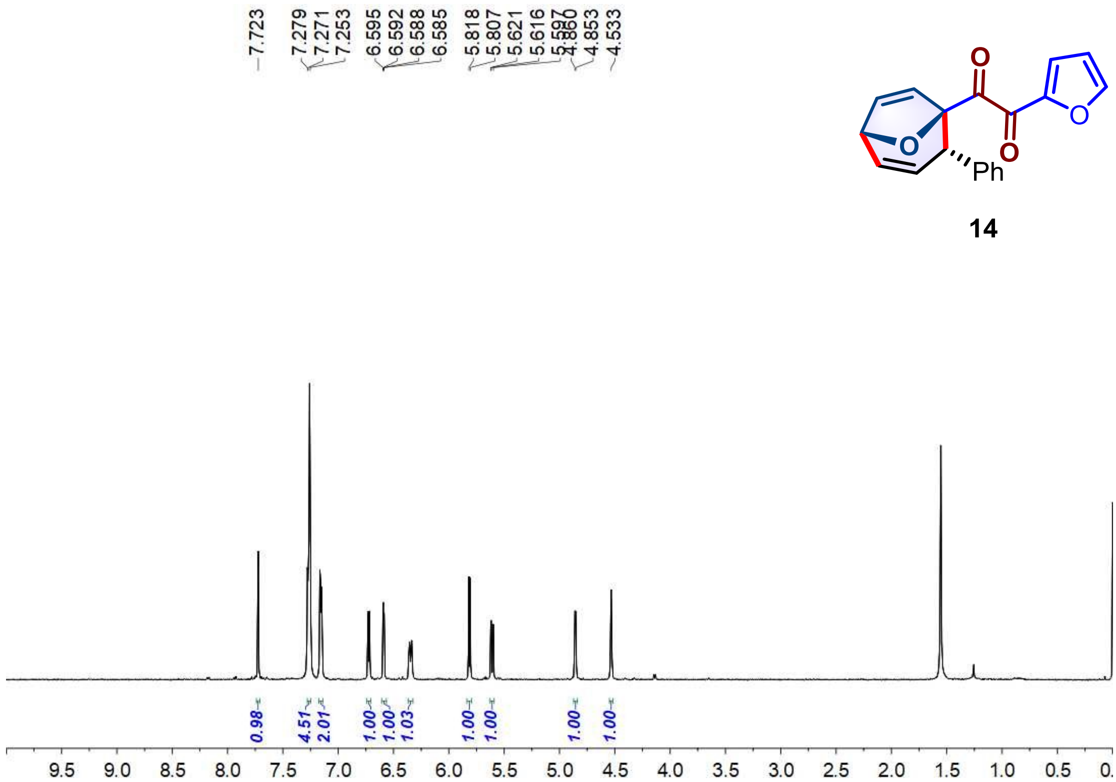


Figure S29. ^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of **14**.

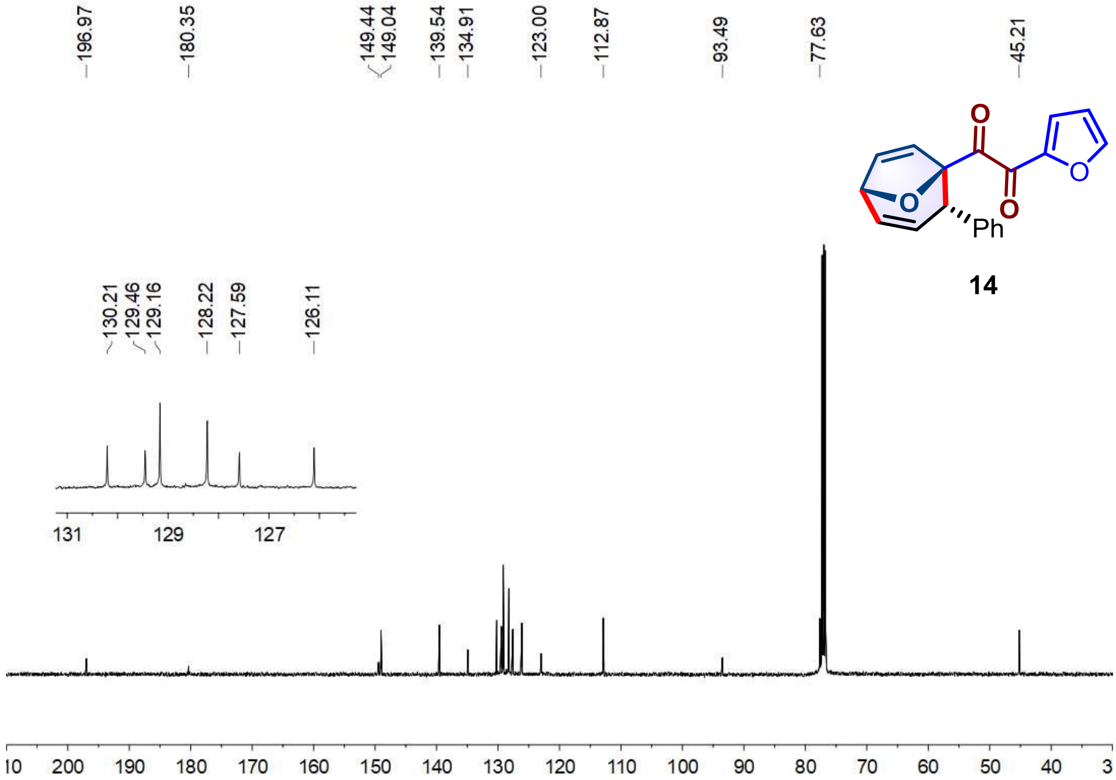


Figure S30. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **14**.

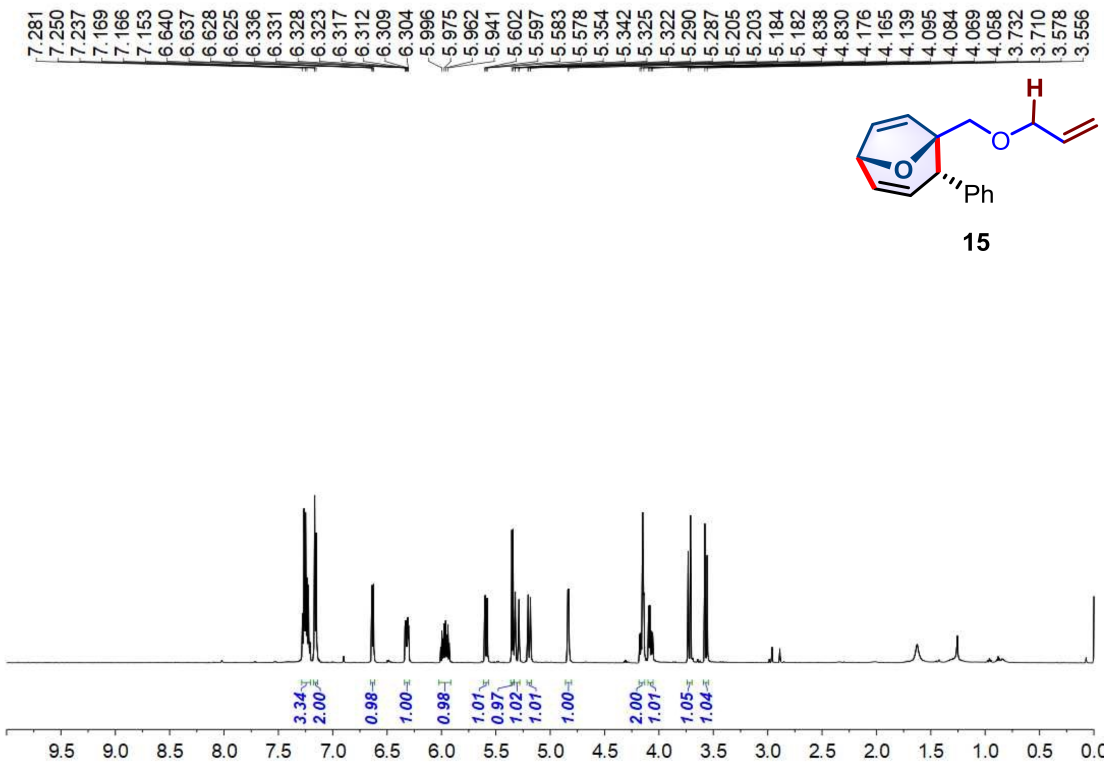


Figure S31. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **15**.

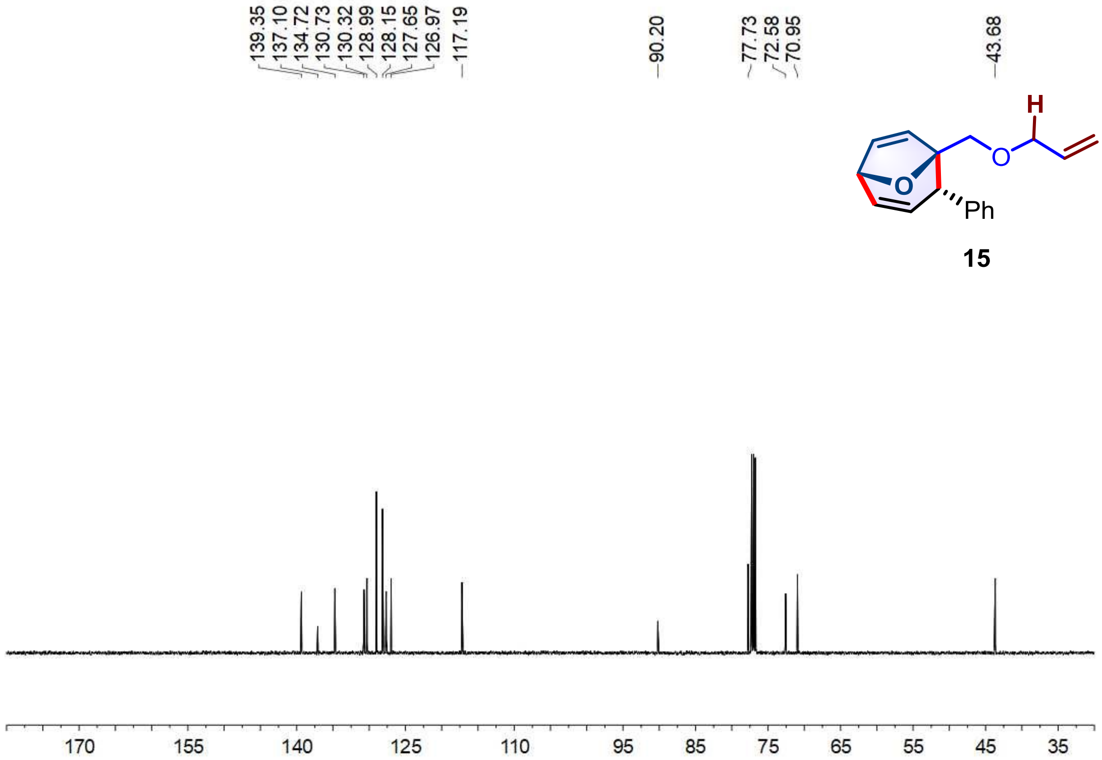


Figure S32. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **15**.

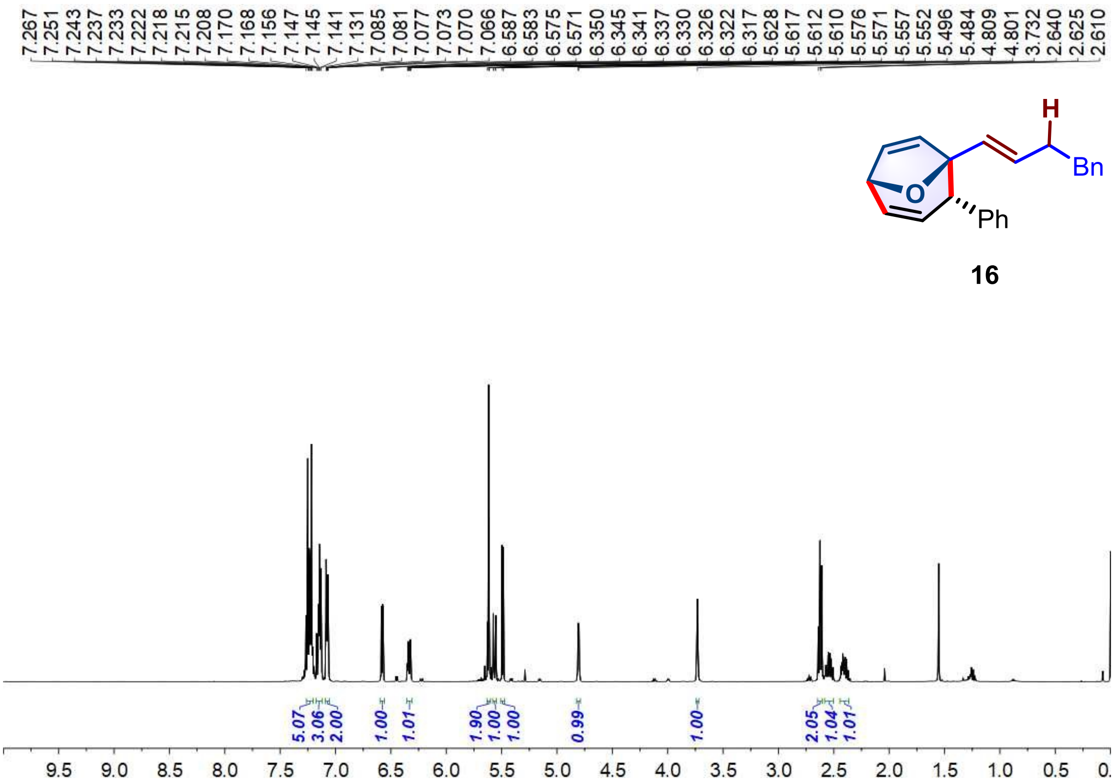


Figure S33. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **16**.

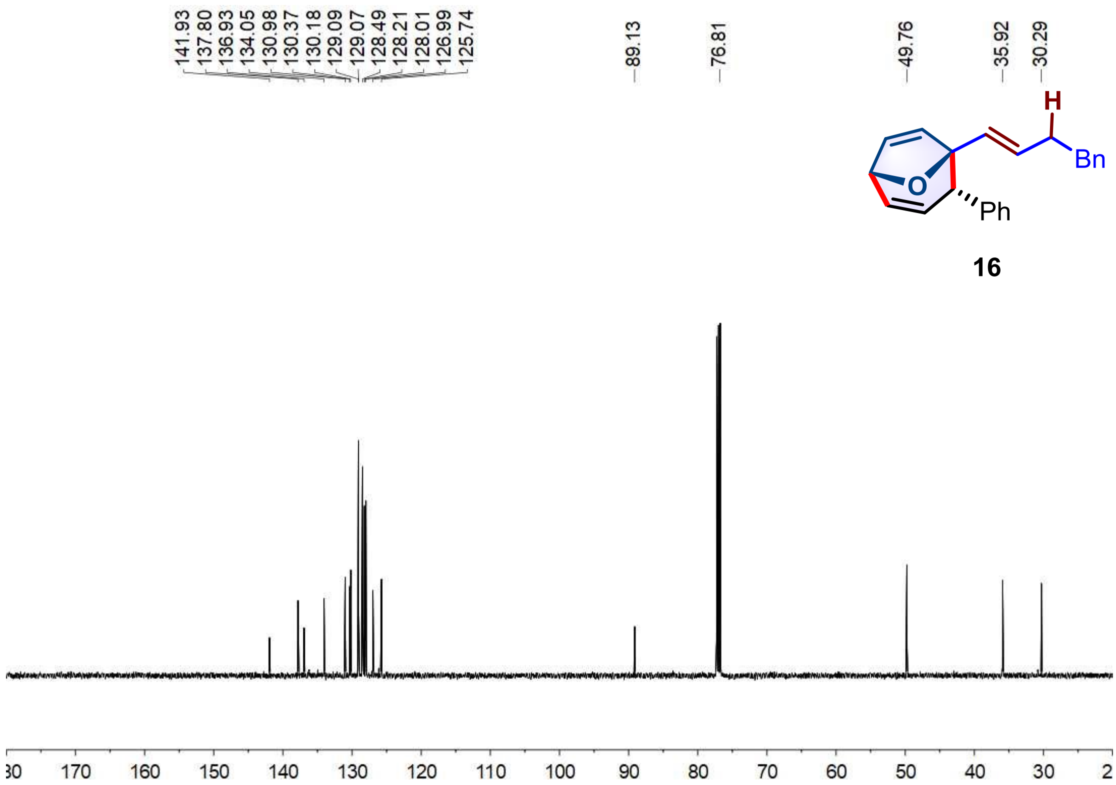


Figure S34. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **16**.

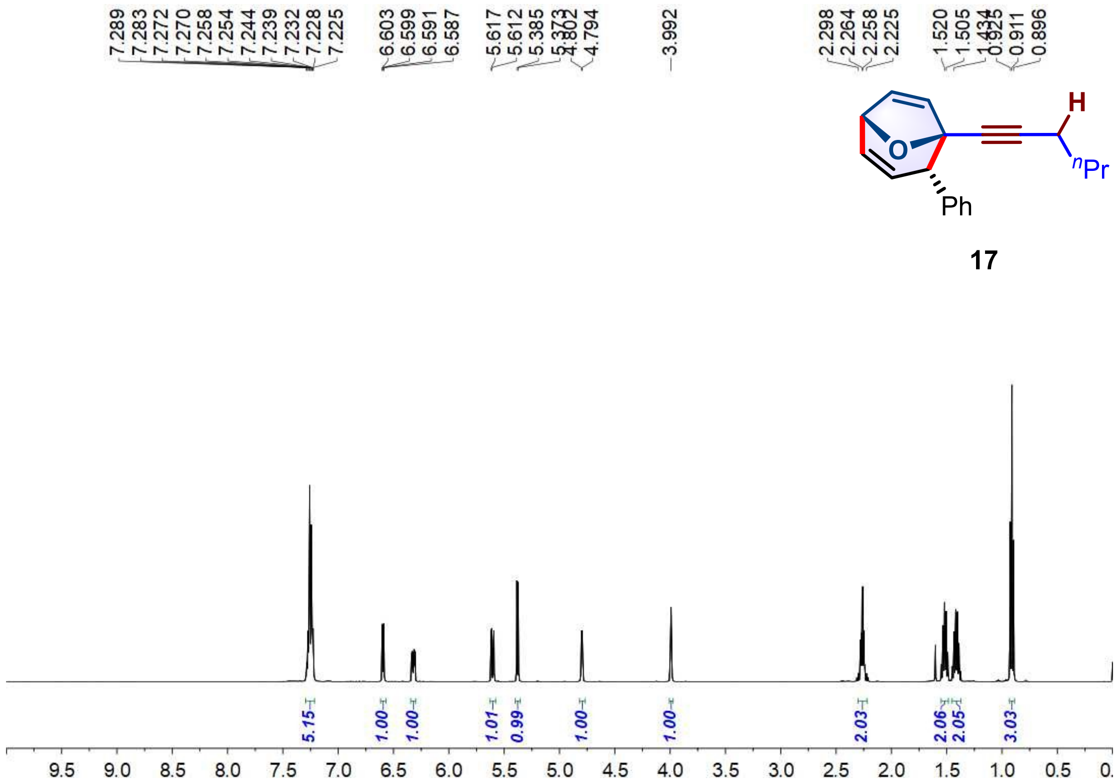


Figure S35. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **17**.

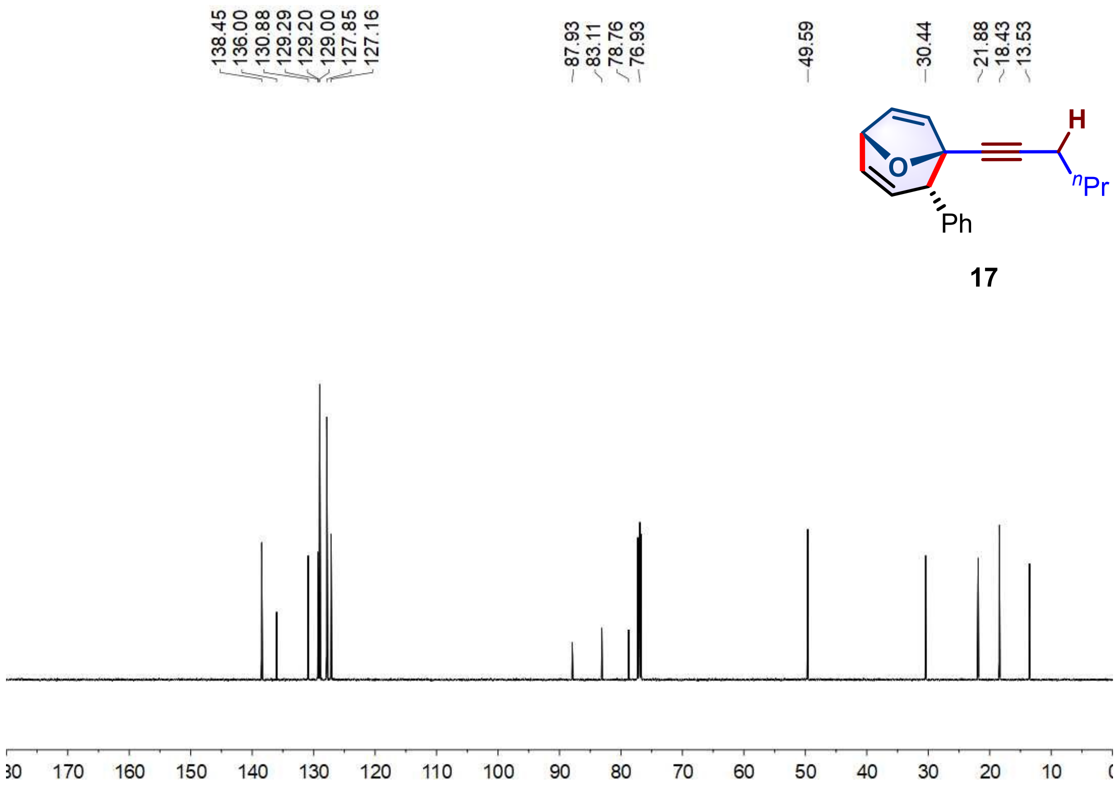


Figure S36. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **17**.

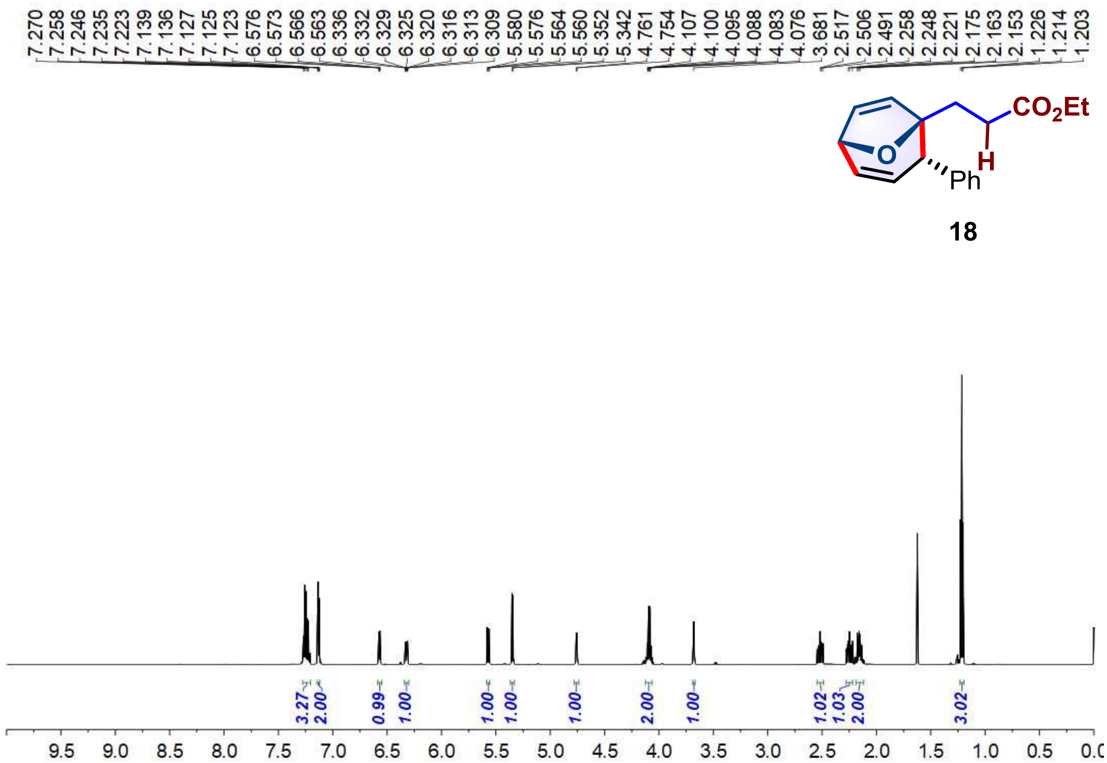


Figure S37. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **18**.

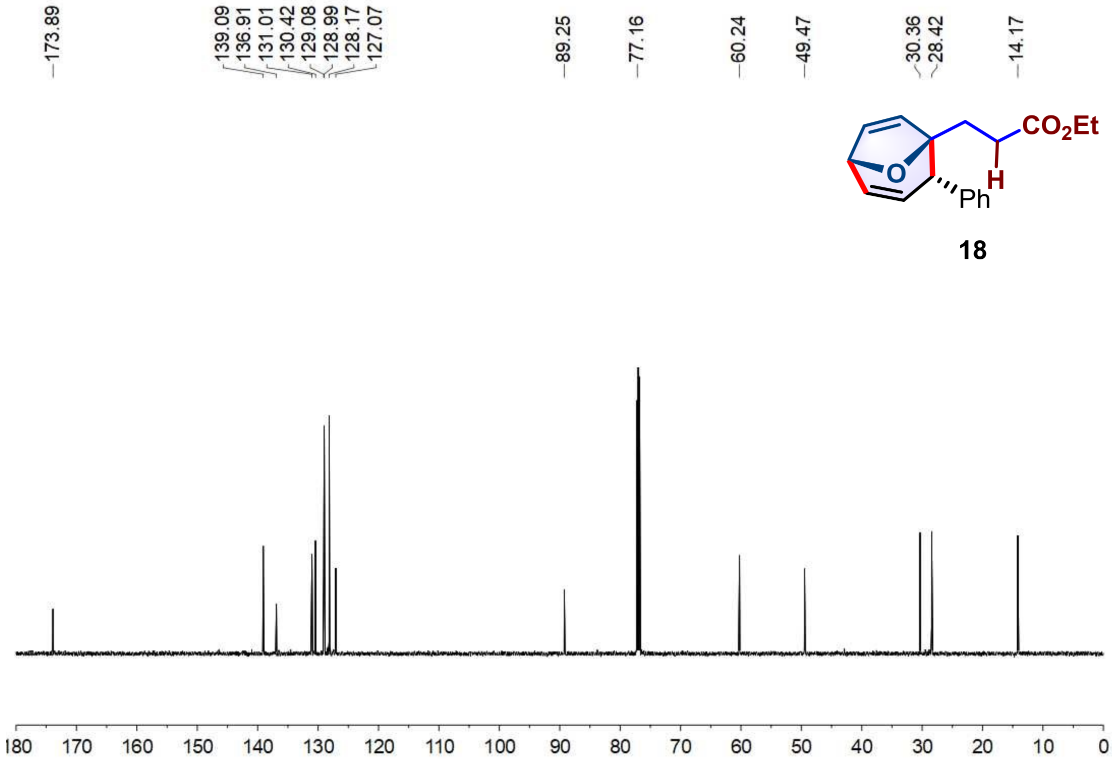


Figure S38. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **18**.

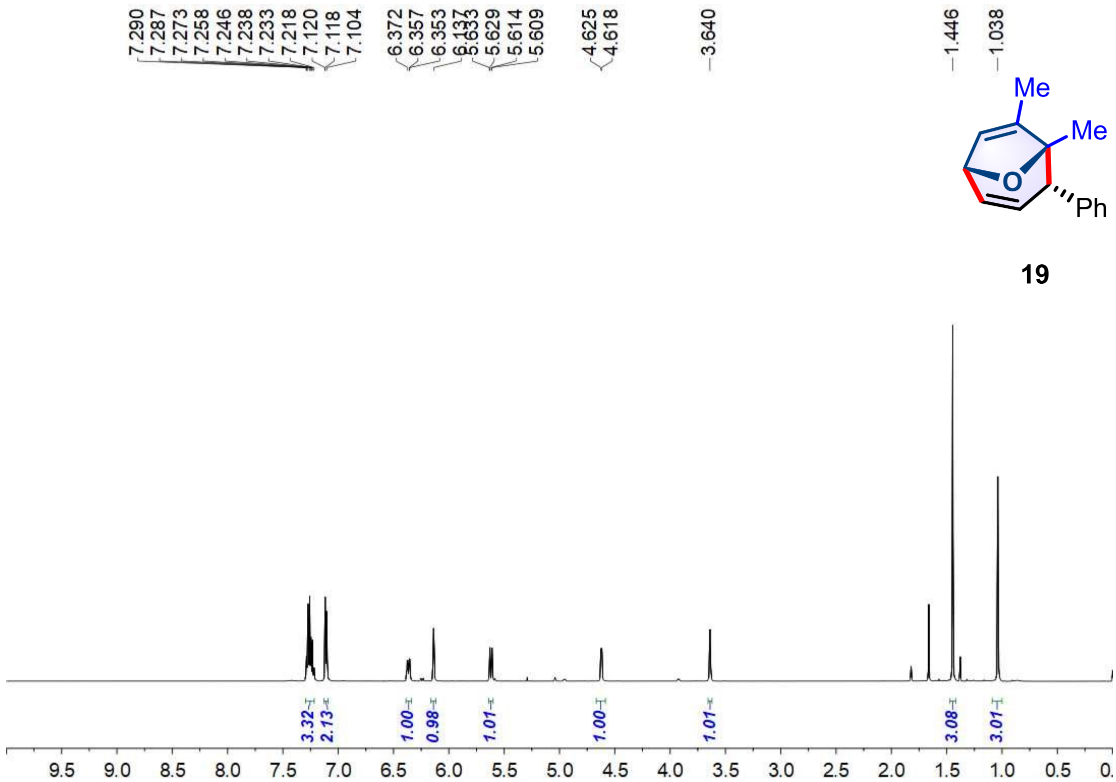


Figure S39. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **19**.

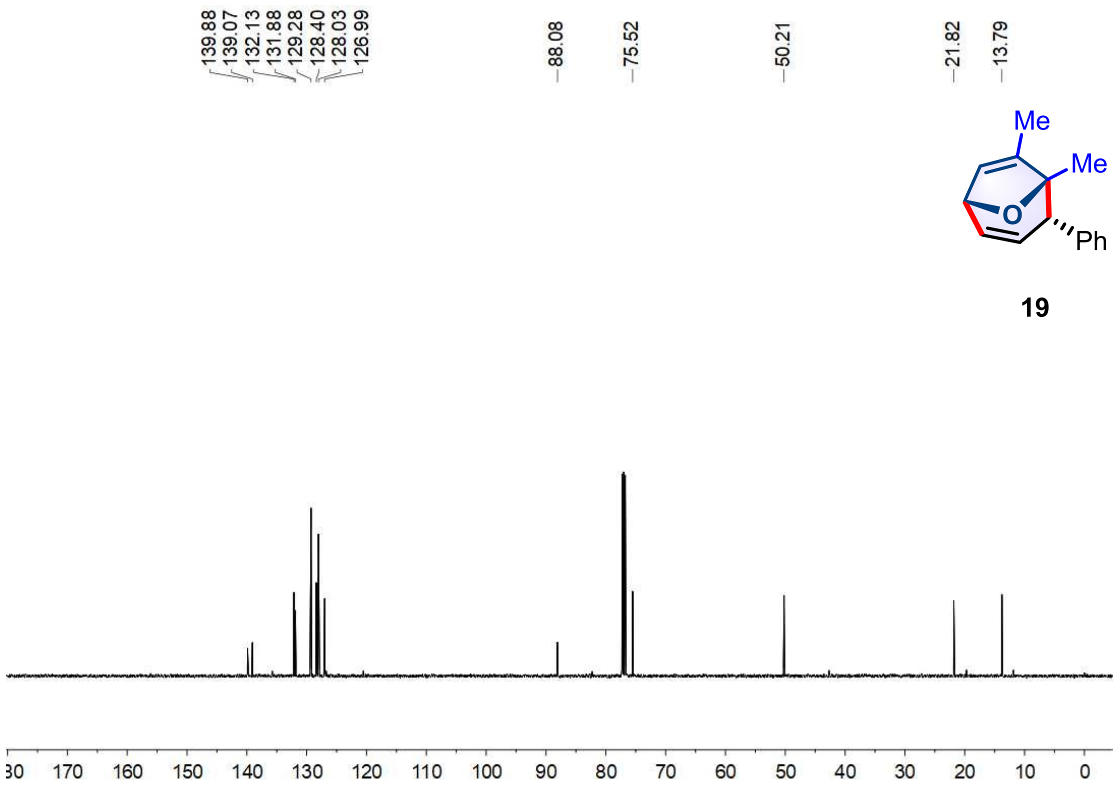


Figure S40. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **19**.

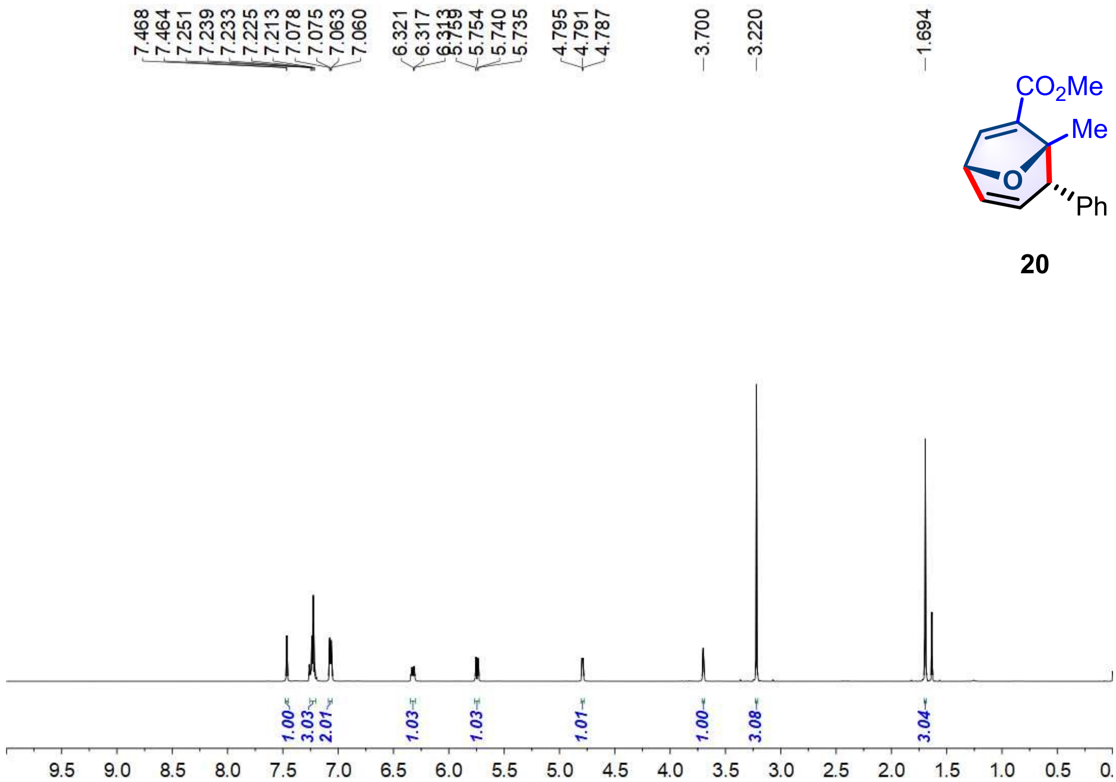


Figure S41. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **20**.

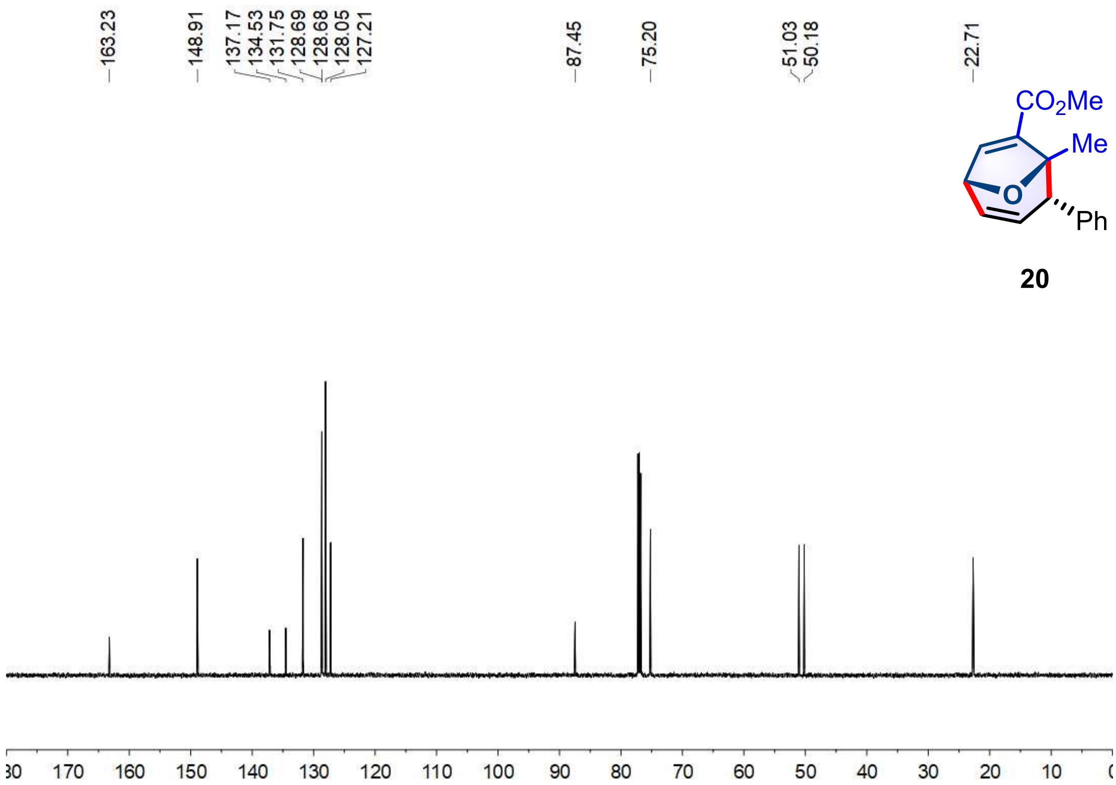


Figure S42. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **20**.

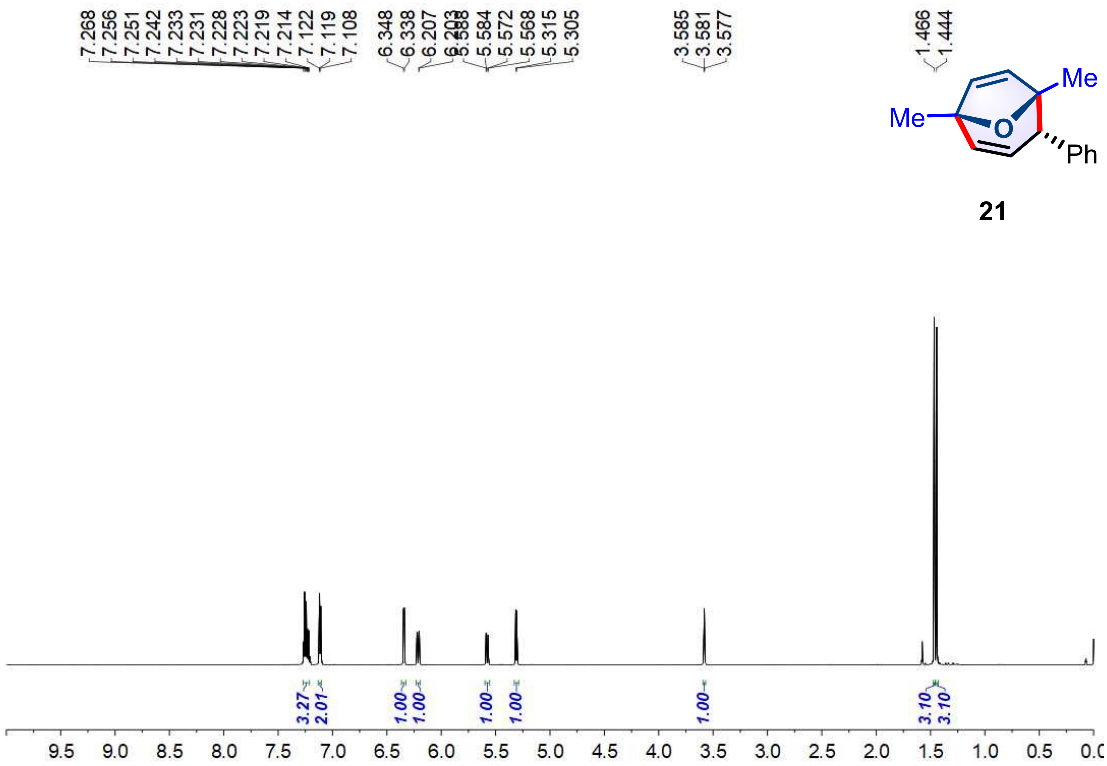


Figure S43. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **21**.

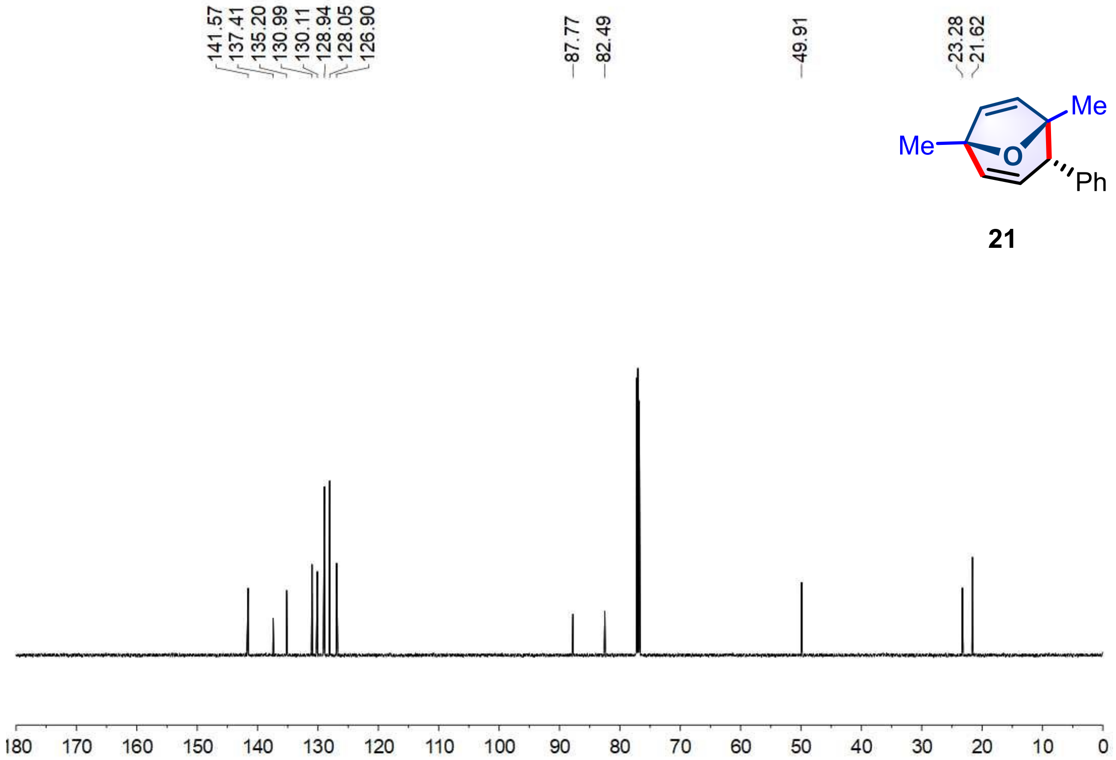


Figure S44. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **22**.

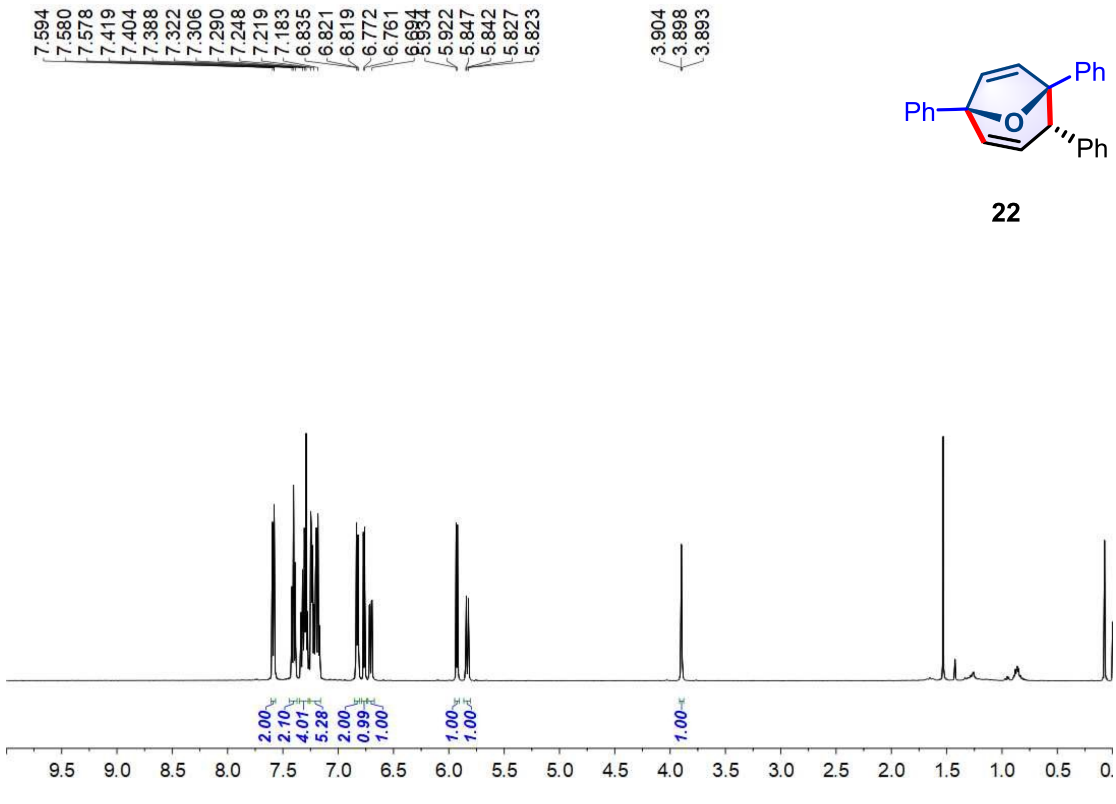


Figure S45. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **22**.

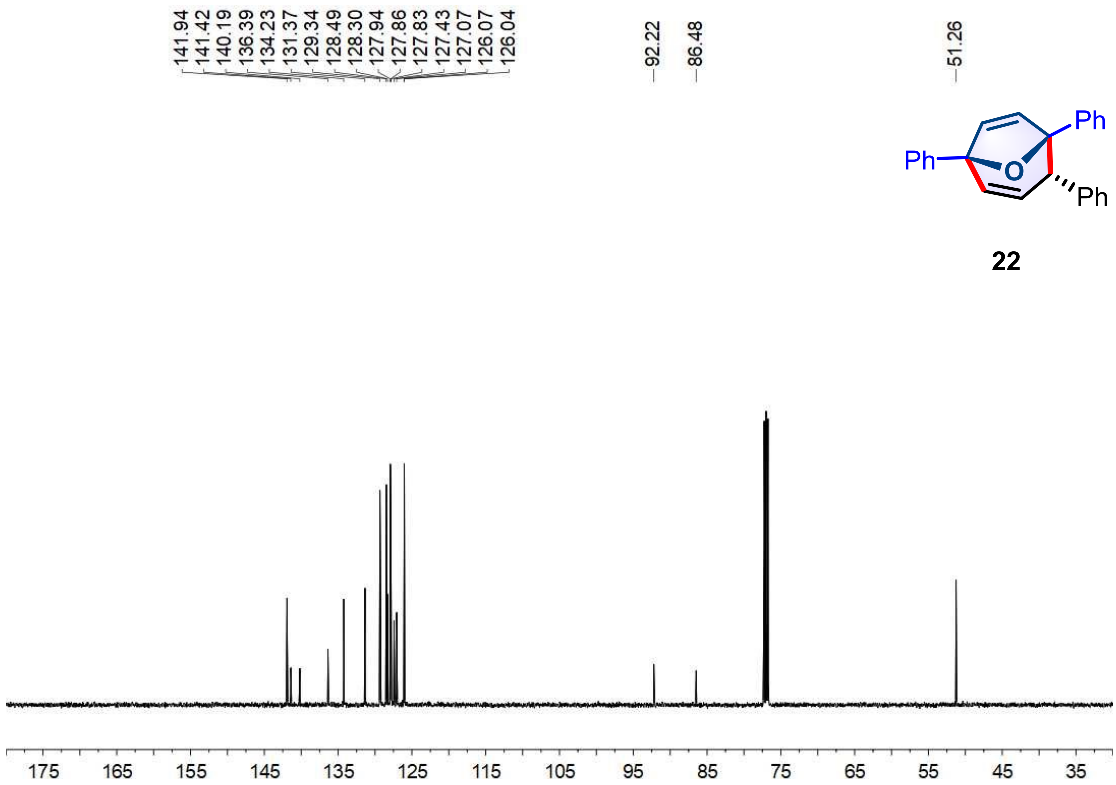


Figure S46. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **22**.

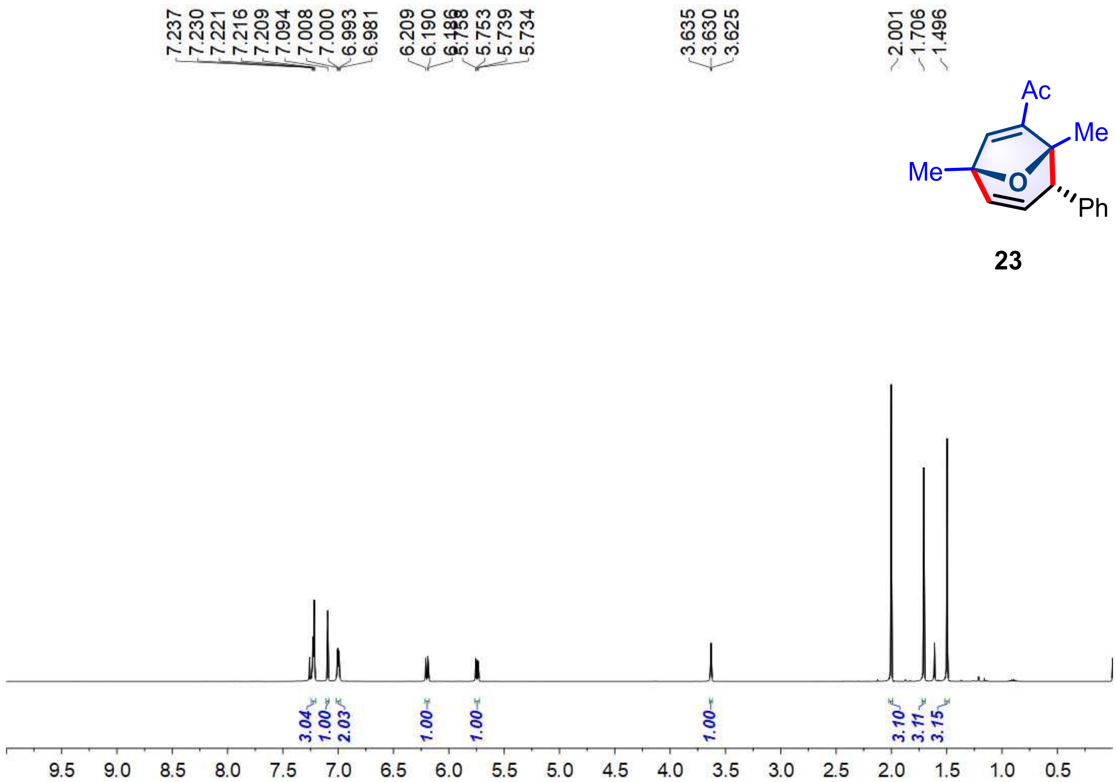


Figure S47. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **23**.

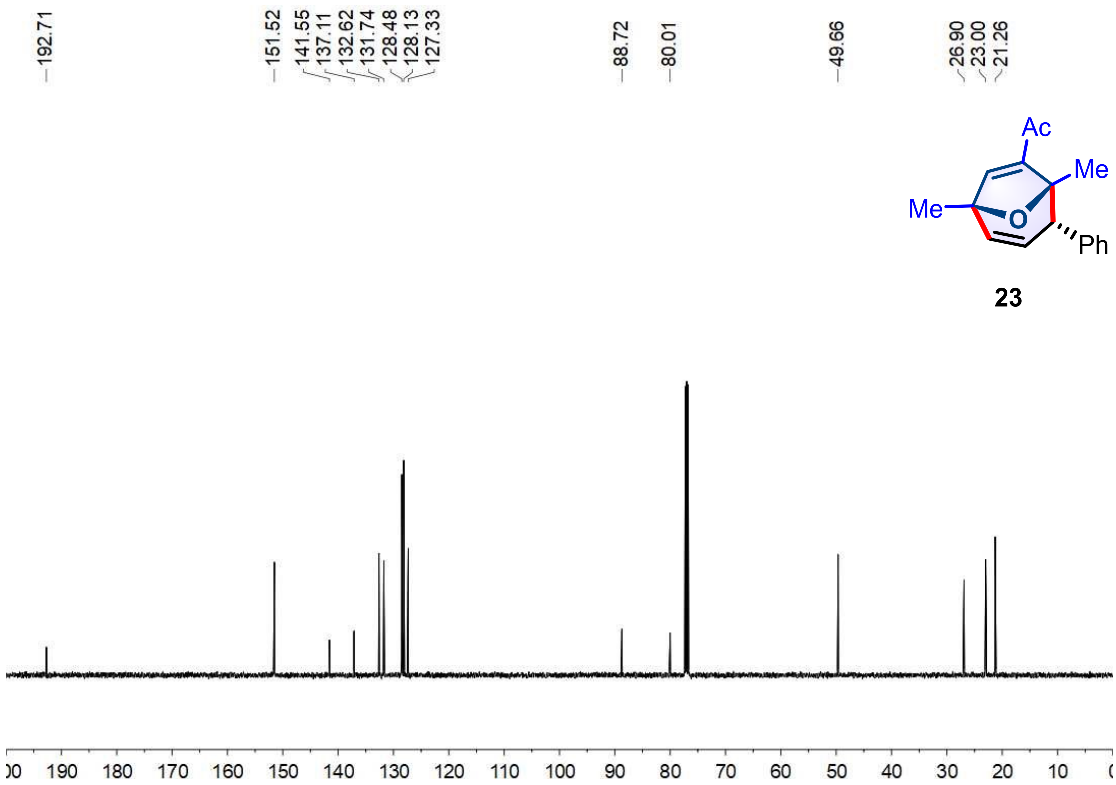


Figure S48. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **23**.

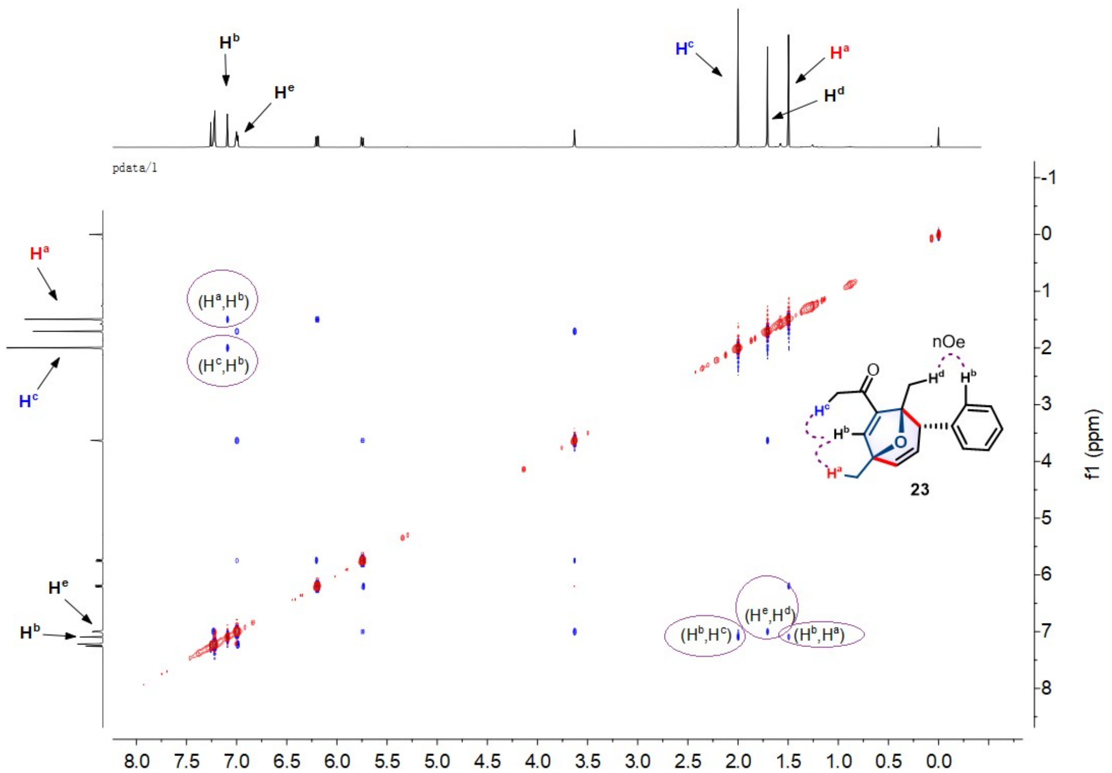


Figure S49. NOE of **23**.

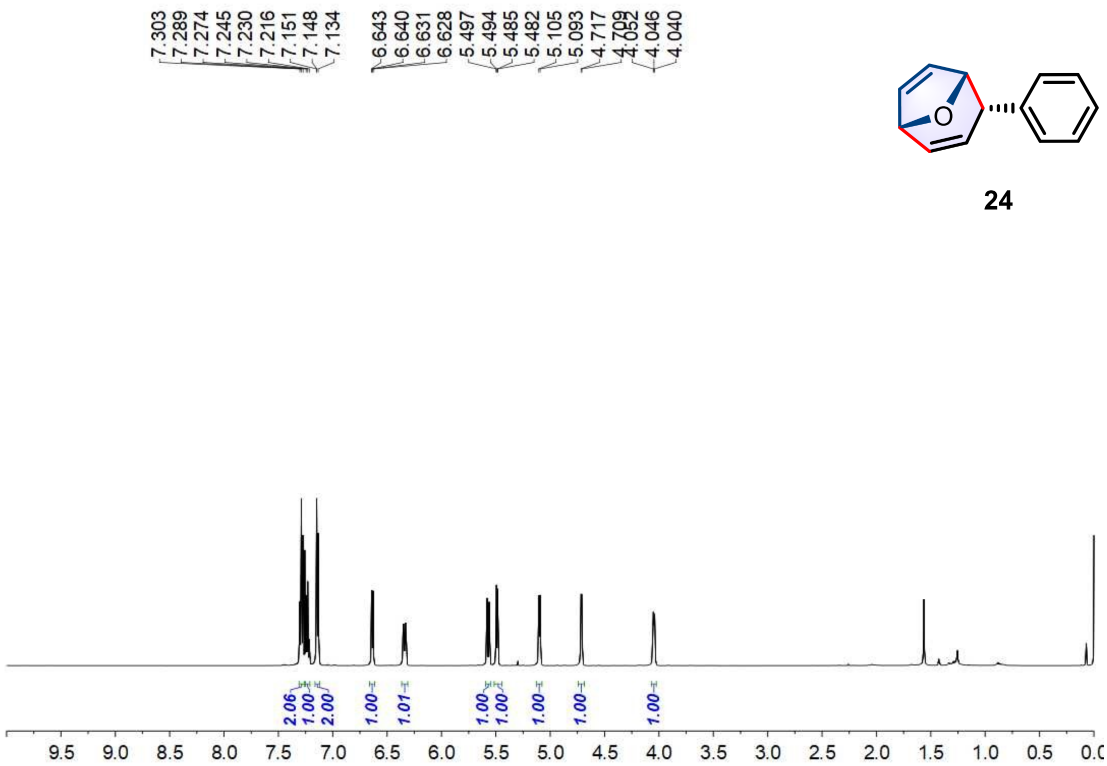


Figure S50. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **24**.

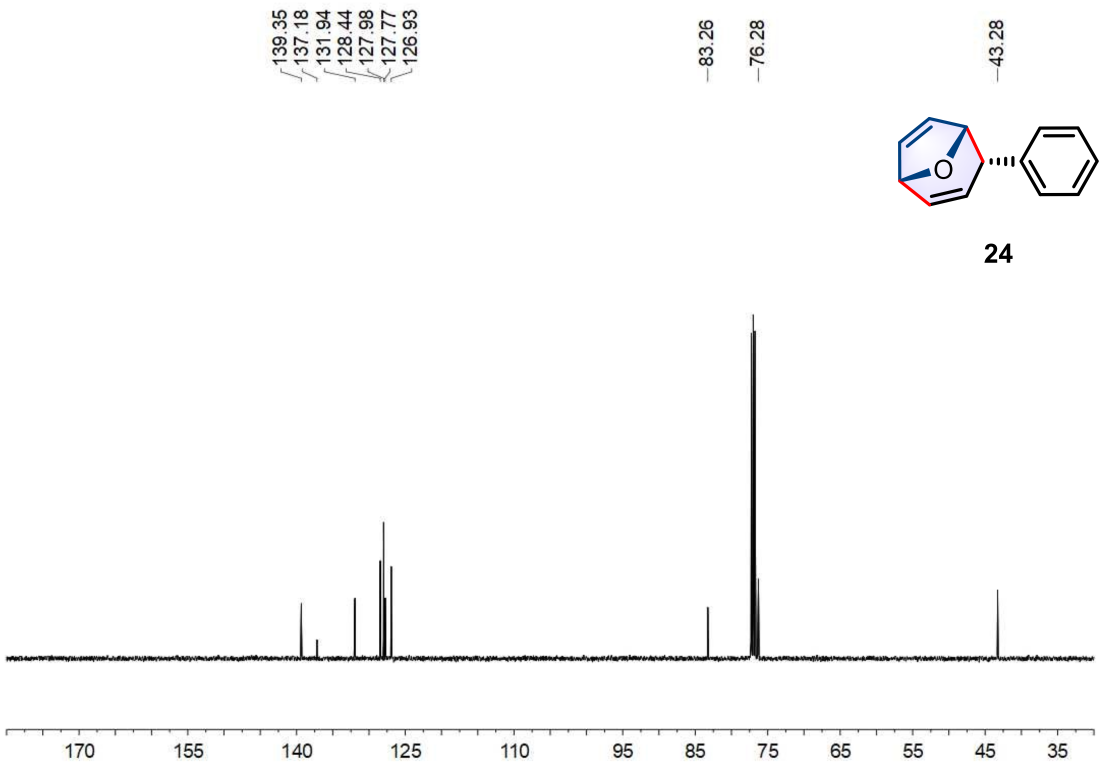


Figure S51. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **24**.

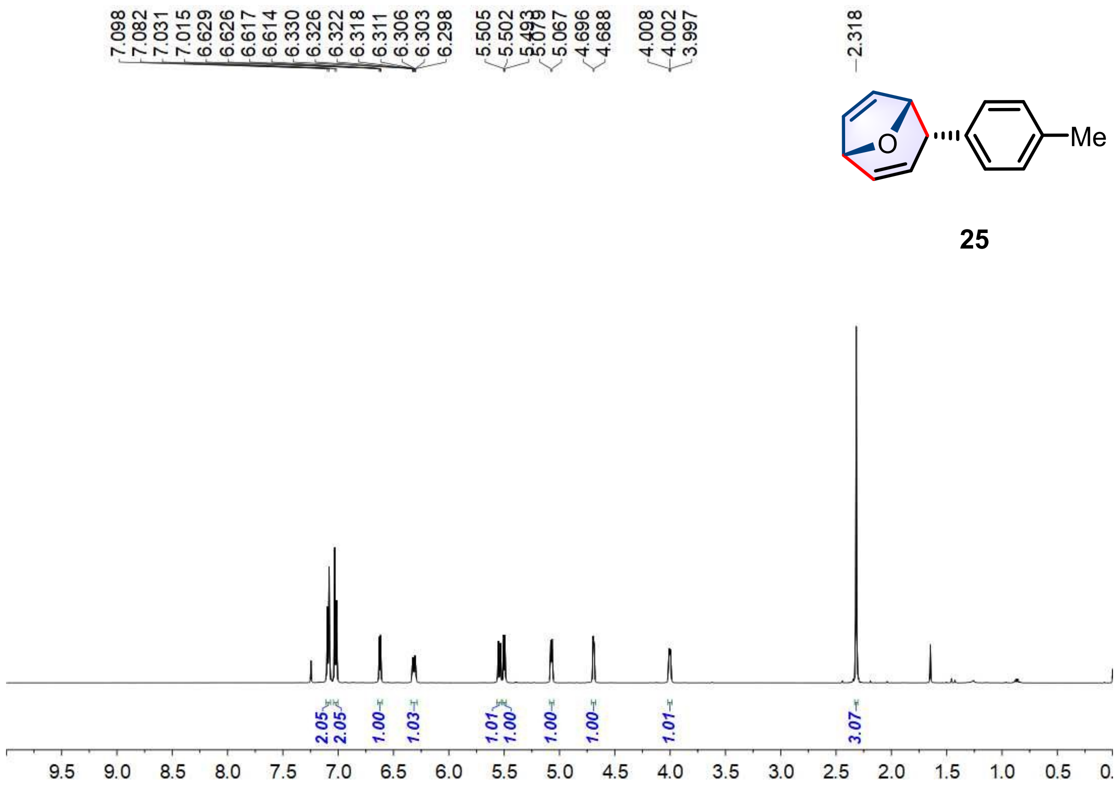


Figure S52. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **25**.

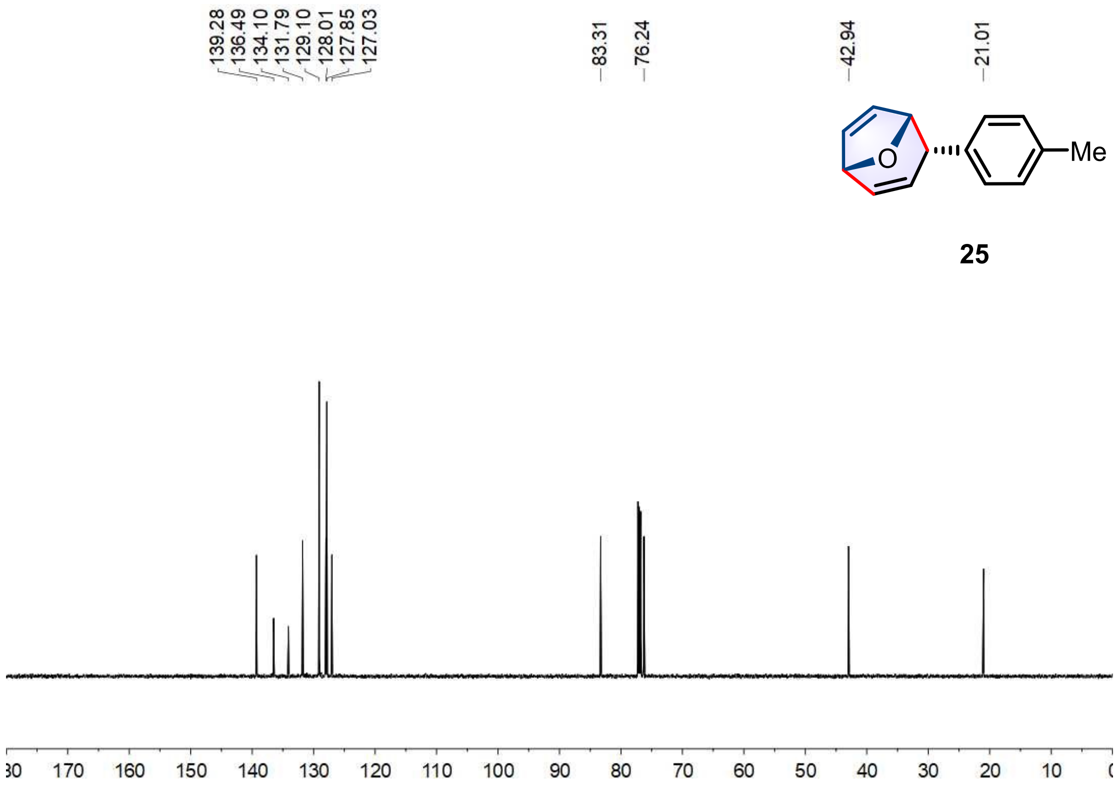


Figure S53. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **25**.

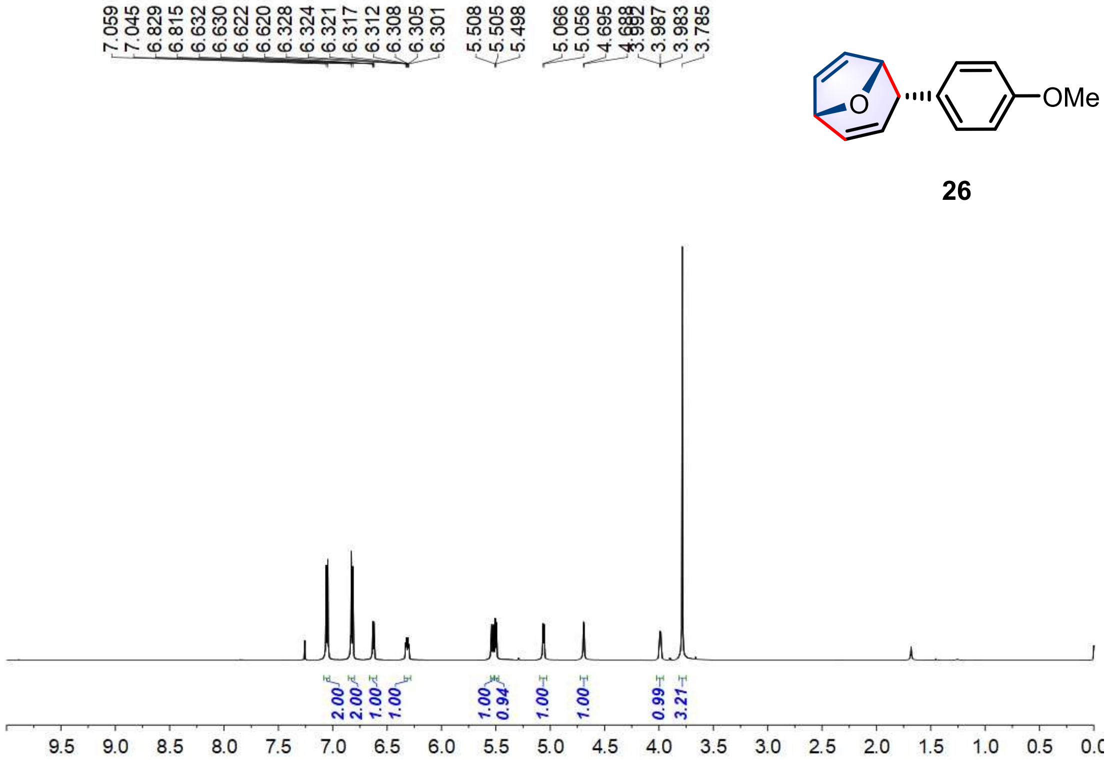


Figure S54. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **26**.

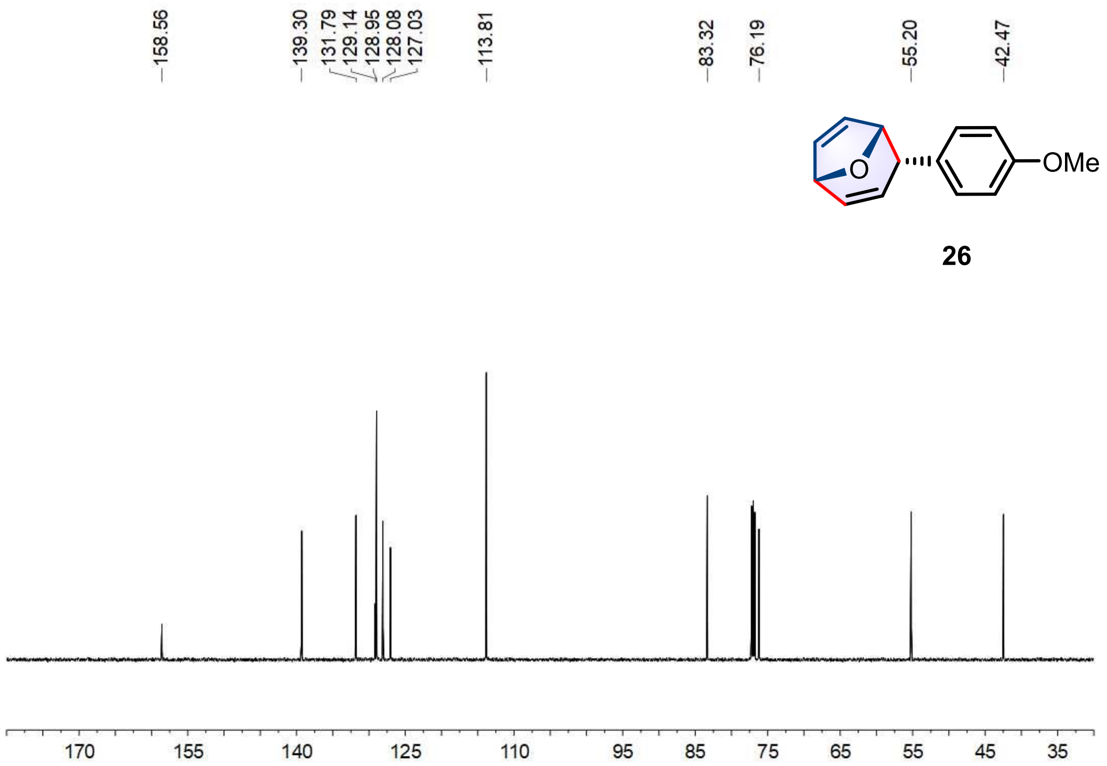
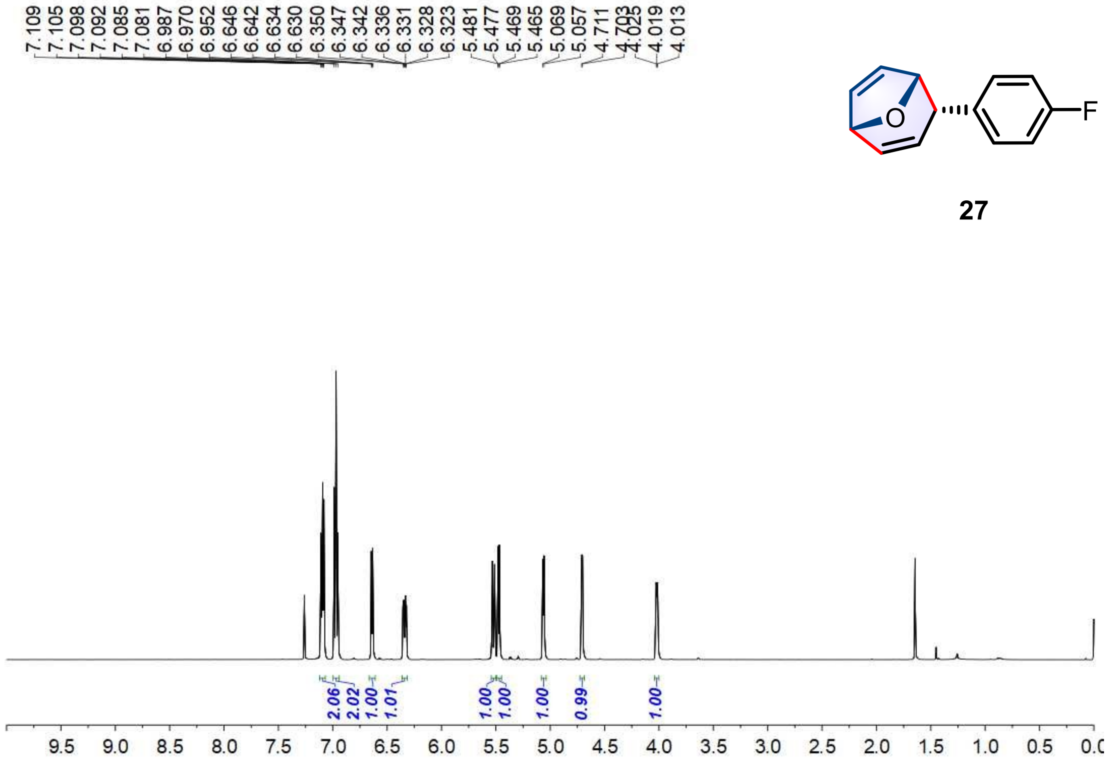
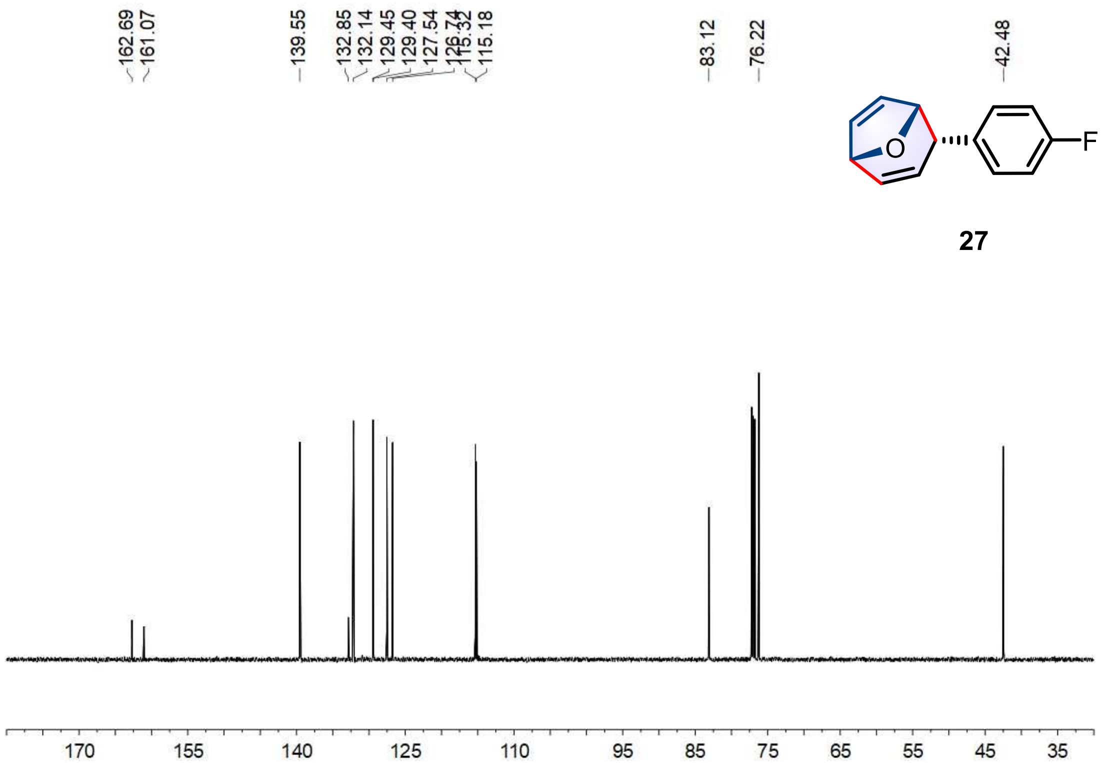


Figure S55. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **26**.



27

Figure S56. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **27**.



27

Figure S57. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **27**.

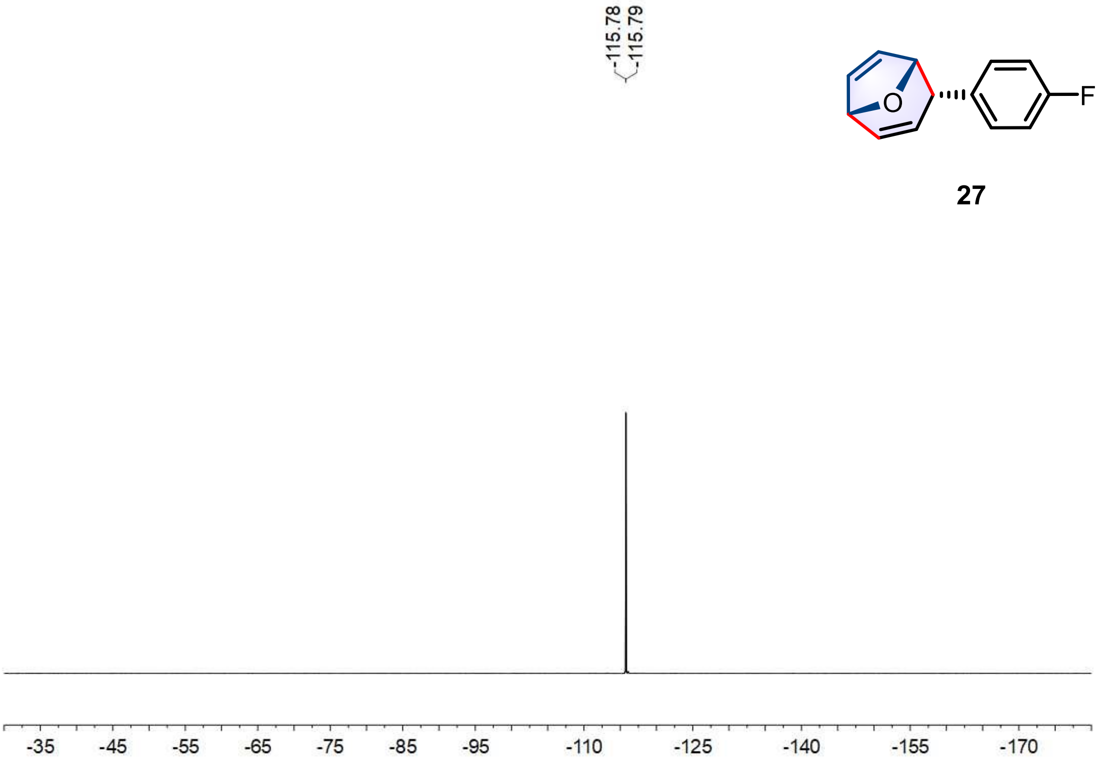


Figure S58. ^{19}F NMR (565 MHz, CDCl$_3$) Spectrum of **27**.

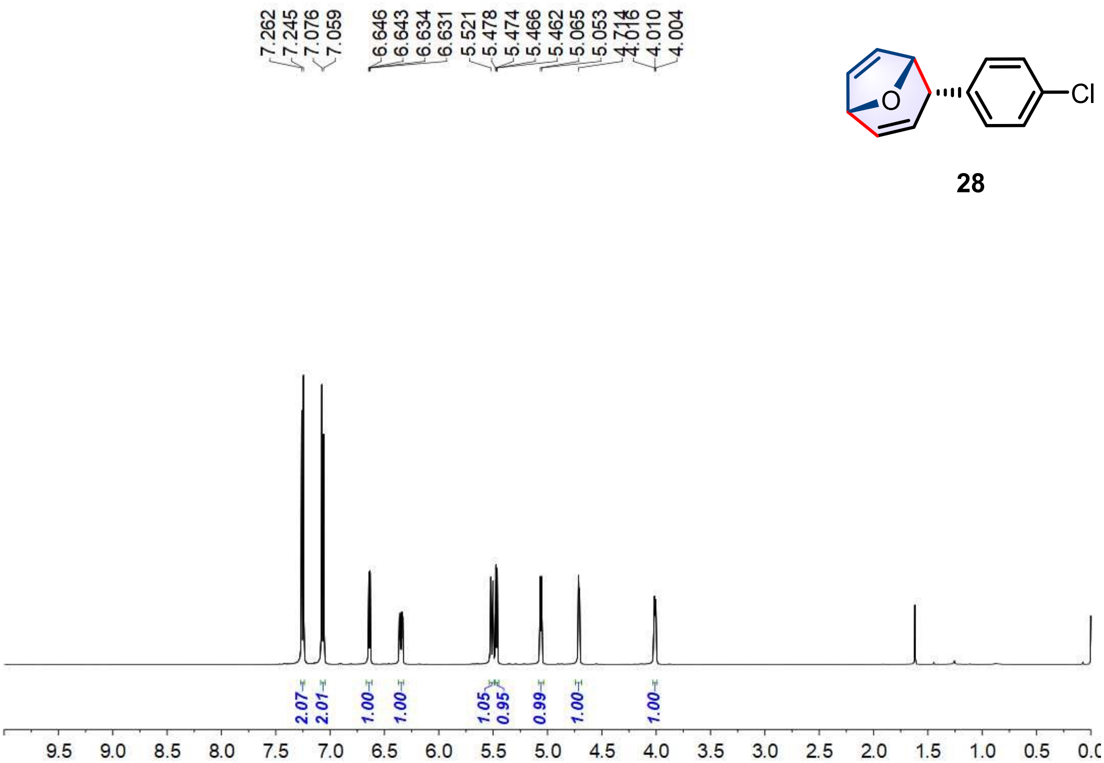


Figure S59. ^{1}H NMR (500 MHz, CDCl$_3$) Spectrum of **28**.

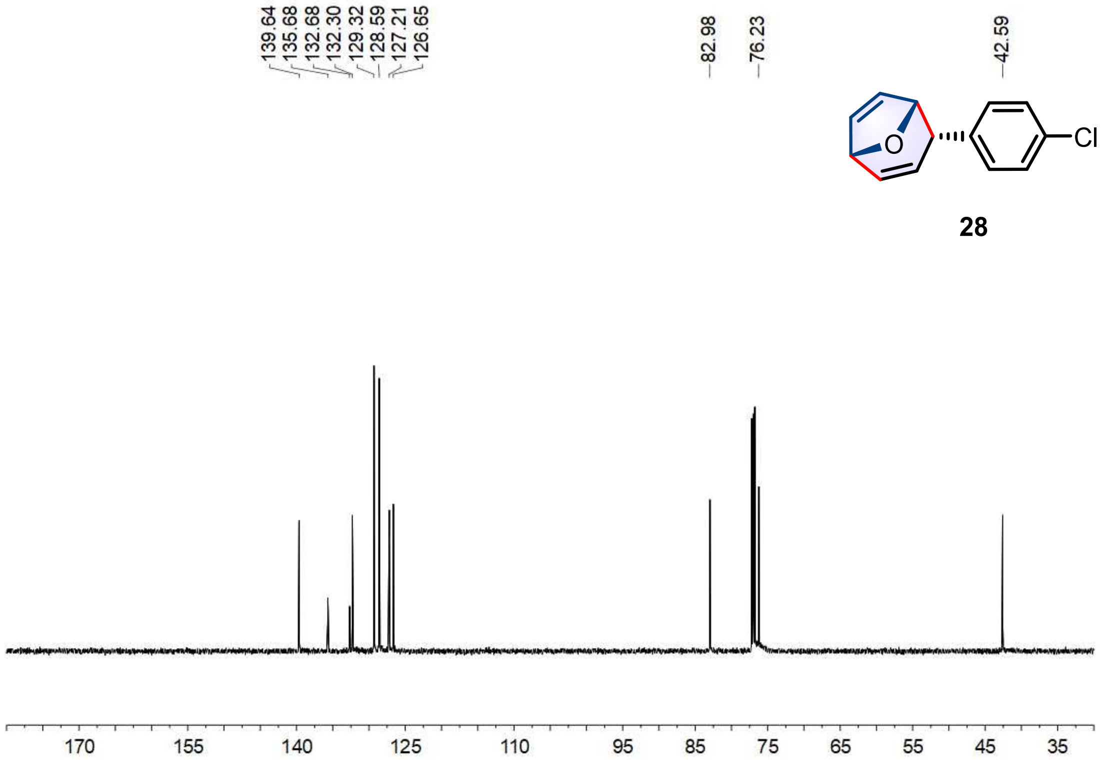


Figure S60. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **28**.

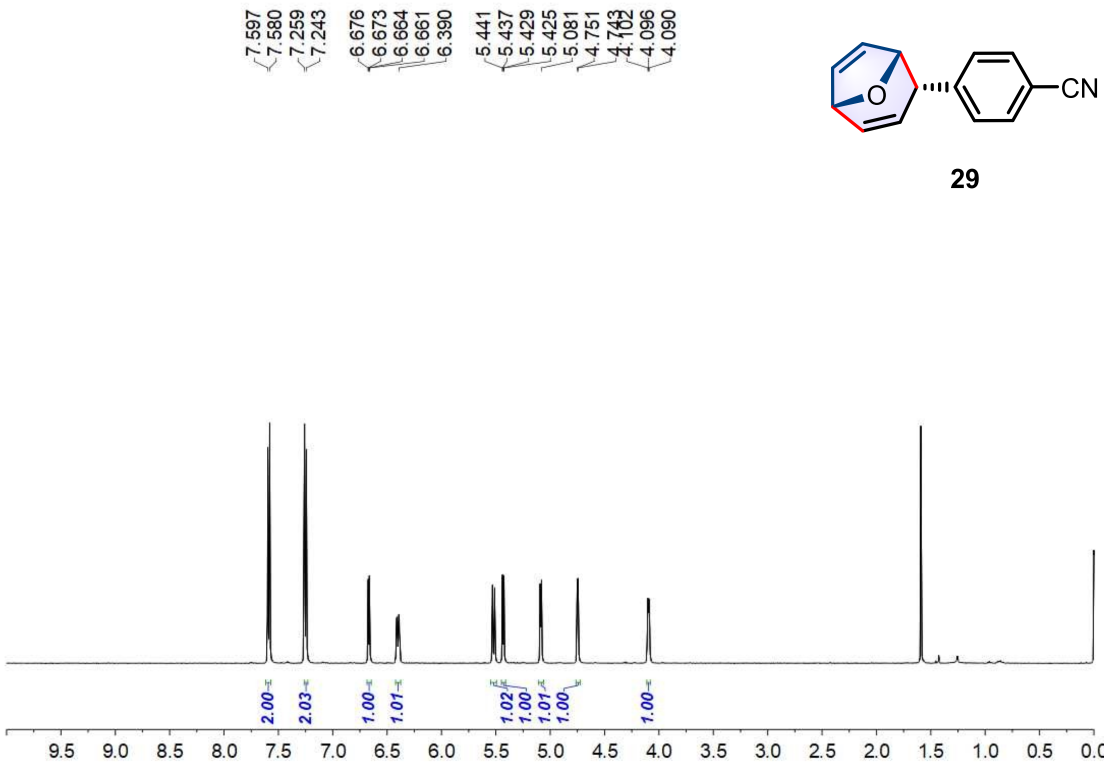


Figure S61. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **29**.

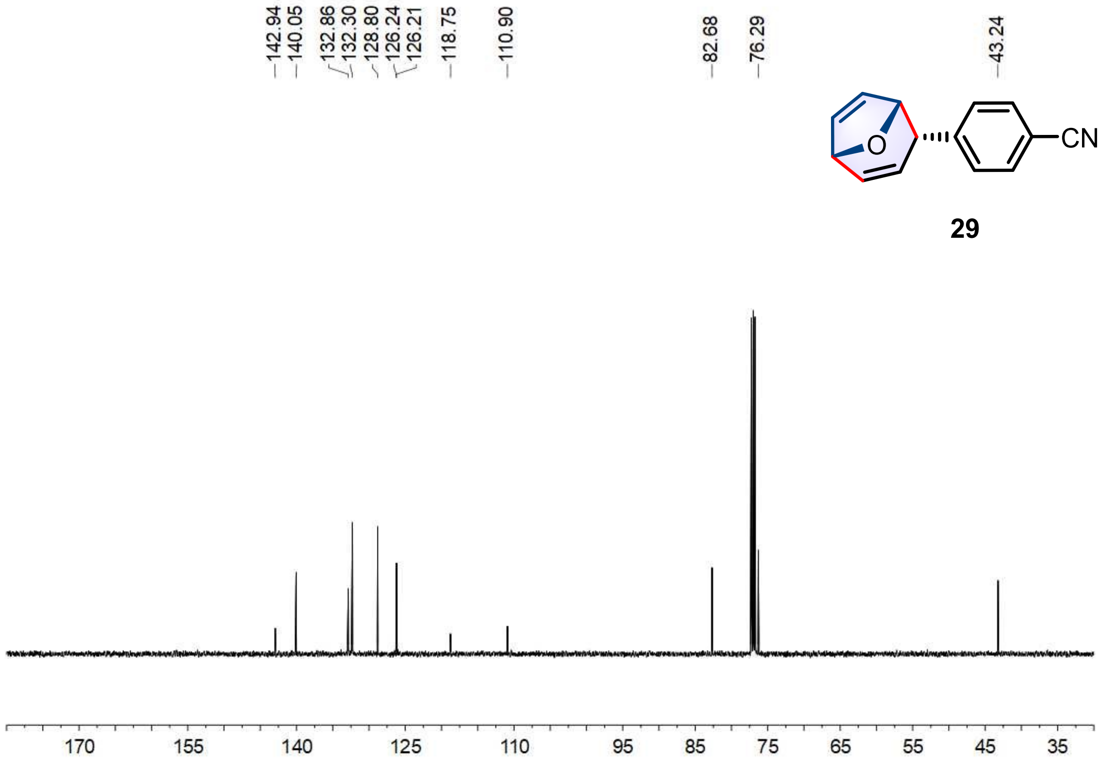


Figure S62. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **29**.

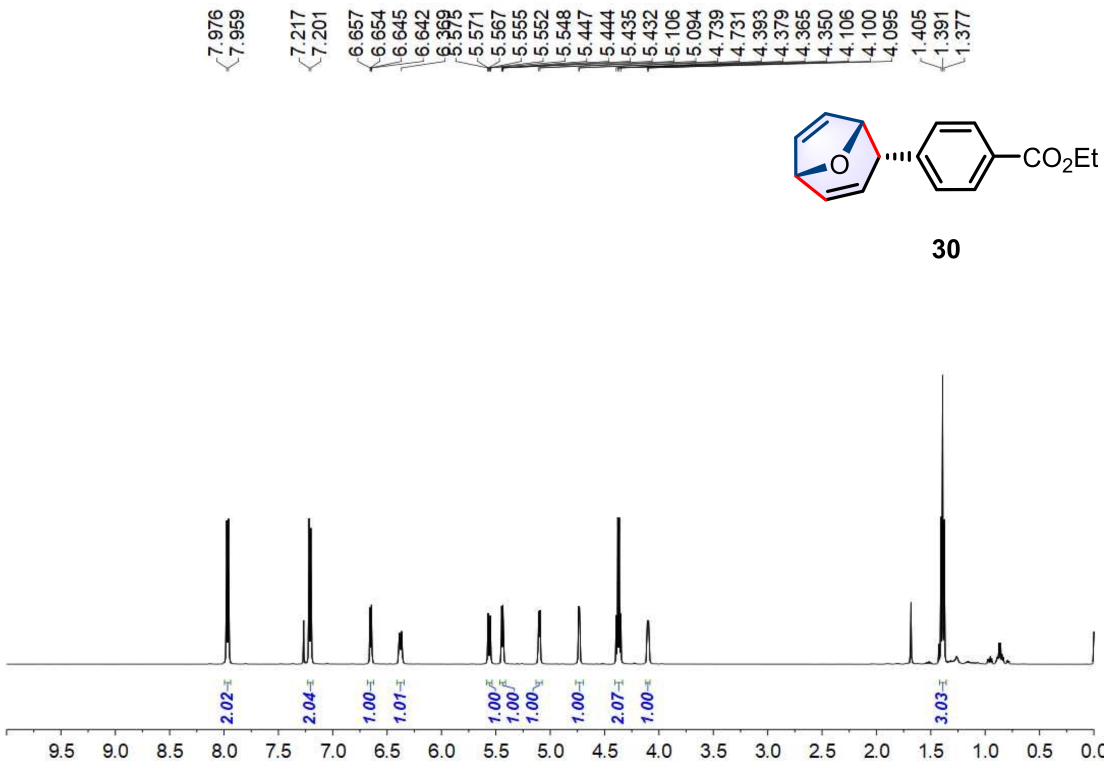
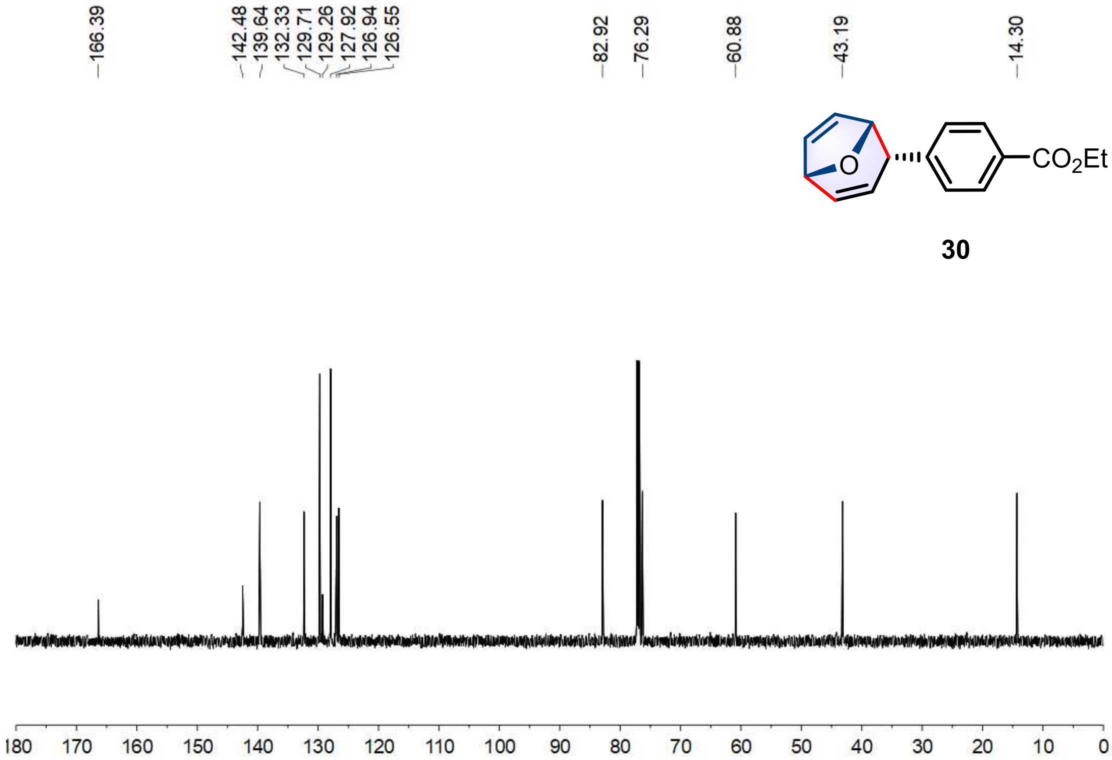
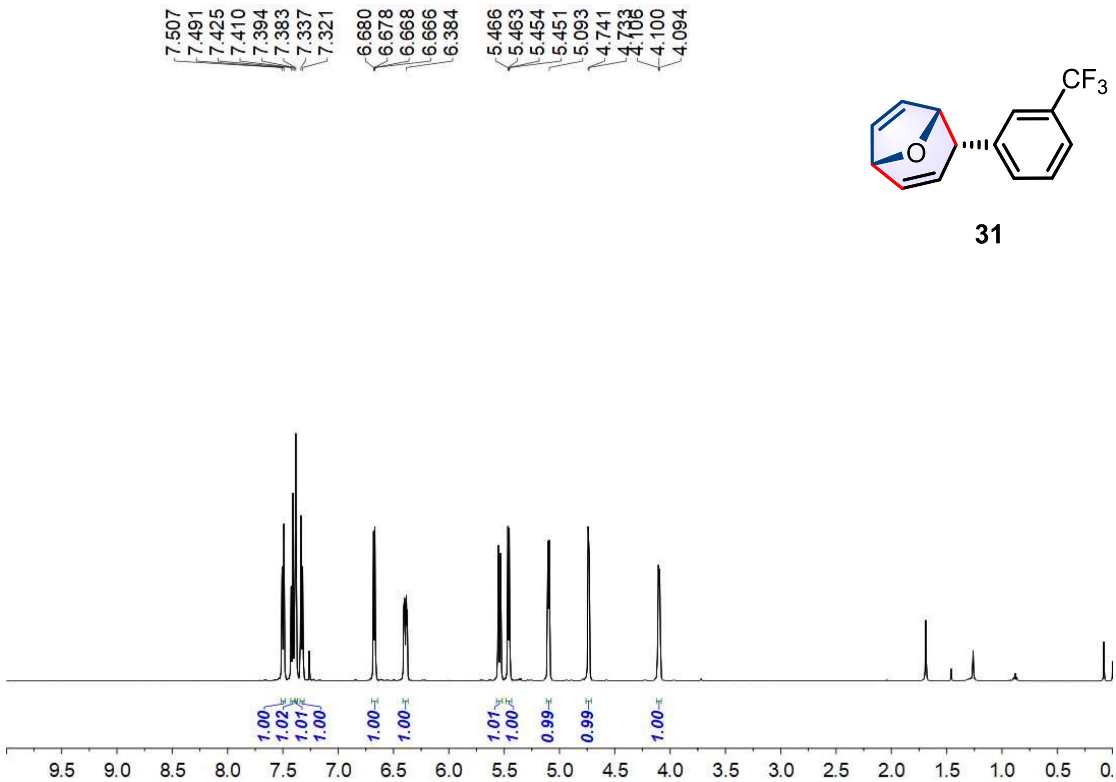


Figure S63. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **30**.



30

Figure S64. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **30**.



31

Figure S65. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **31**.

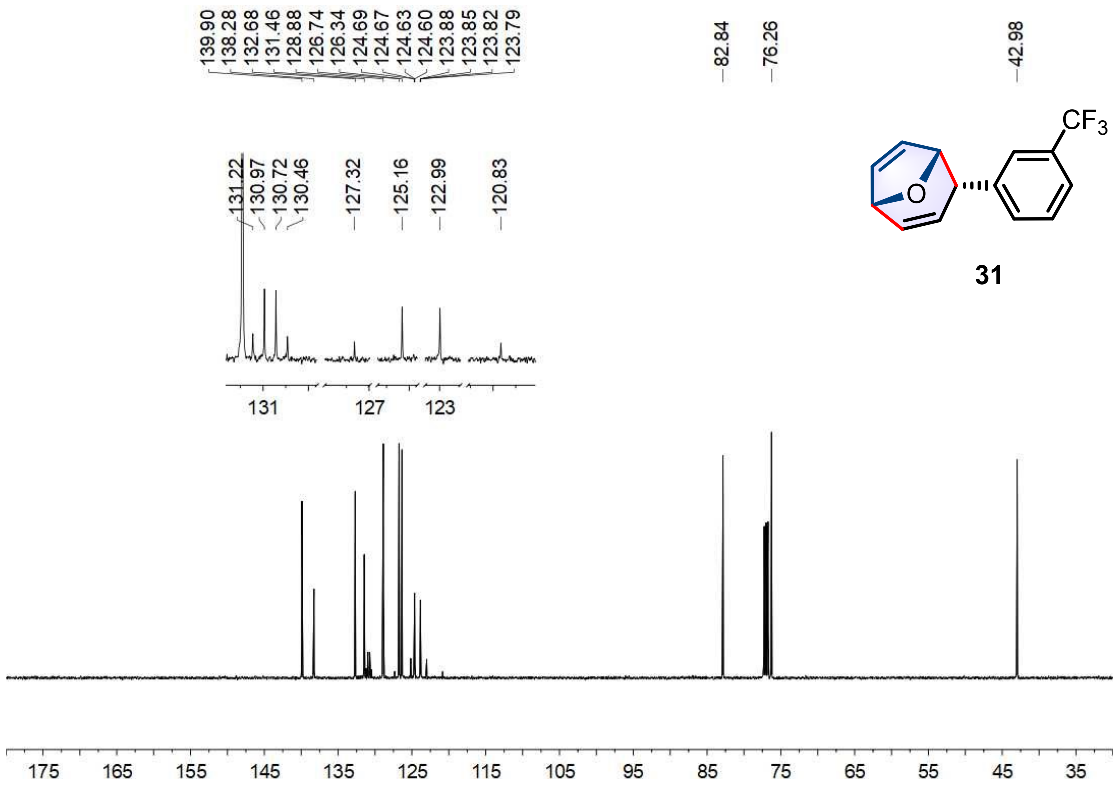


Figure S66. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **31**.

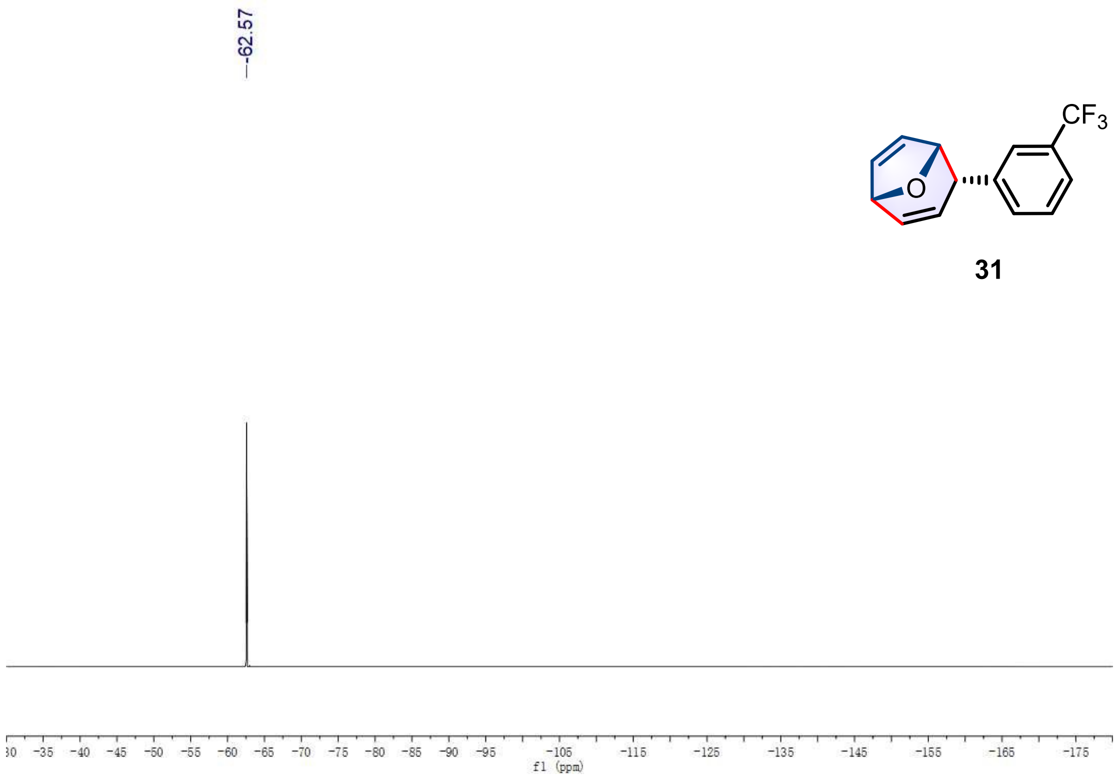


Figure S67. ^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of **31**.

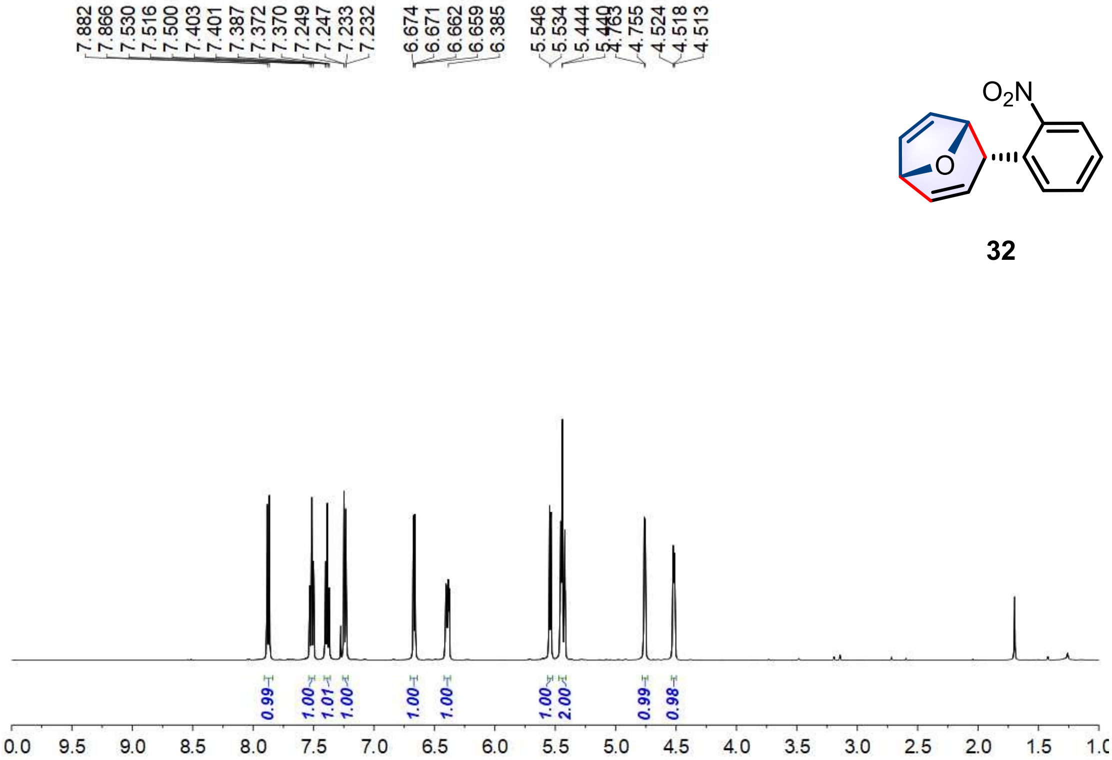


Figure S68. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **32**.

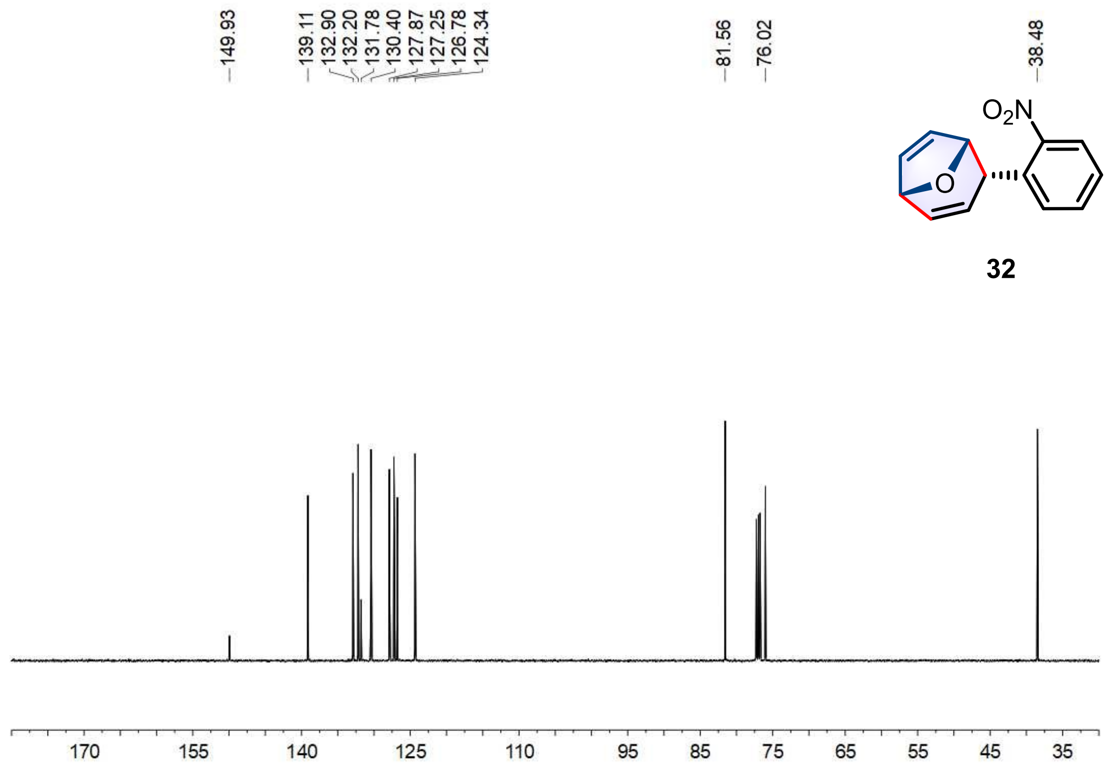


Figure S69. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **32**.

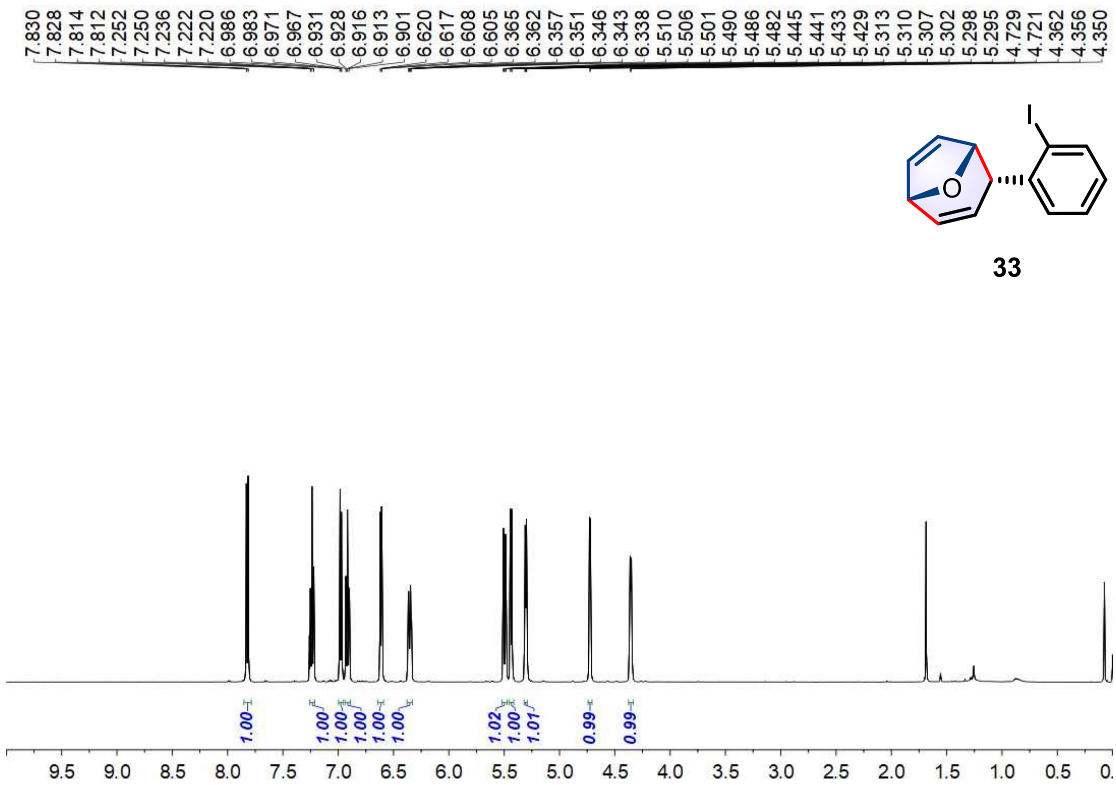


Figure S70. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **33**.

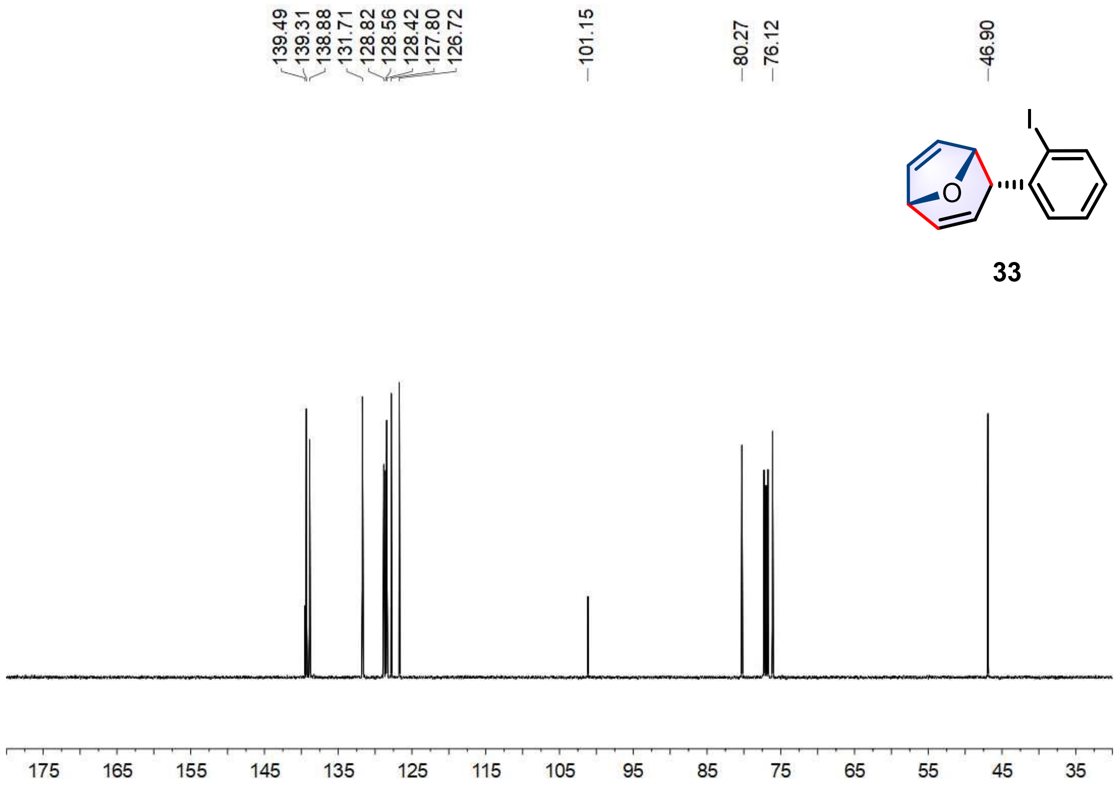


Figure S71. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **33**.

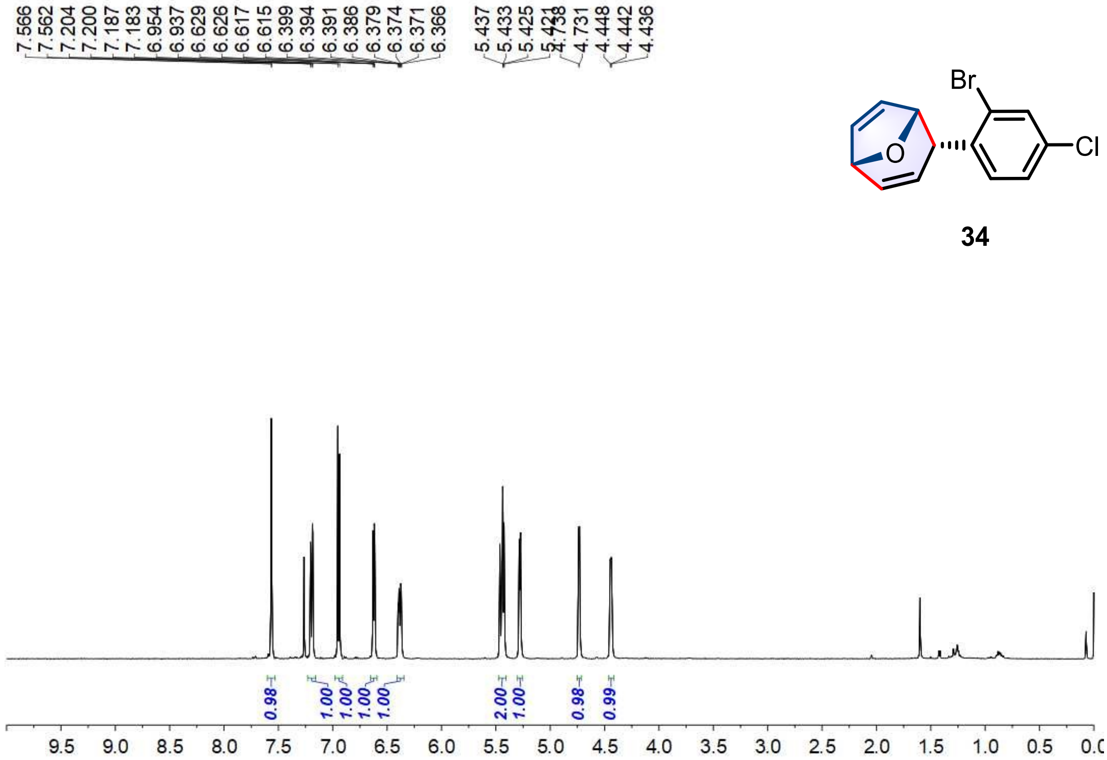


Figure S72. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **34**.

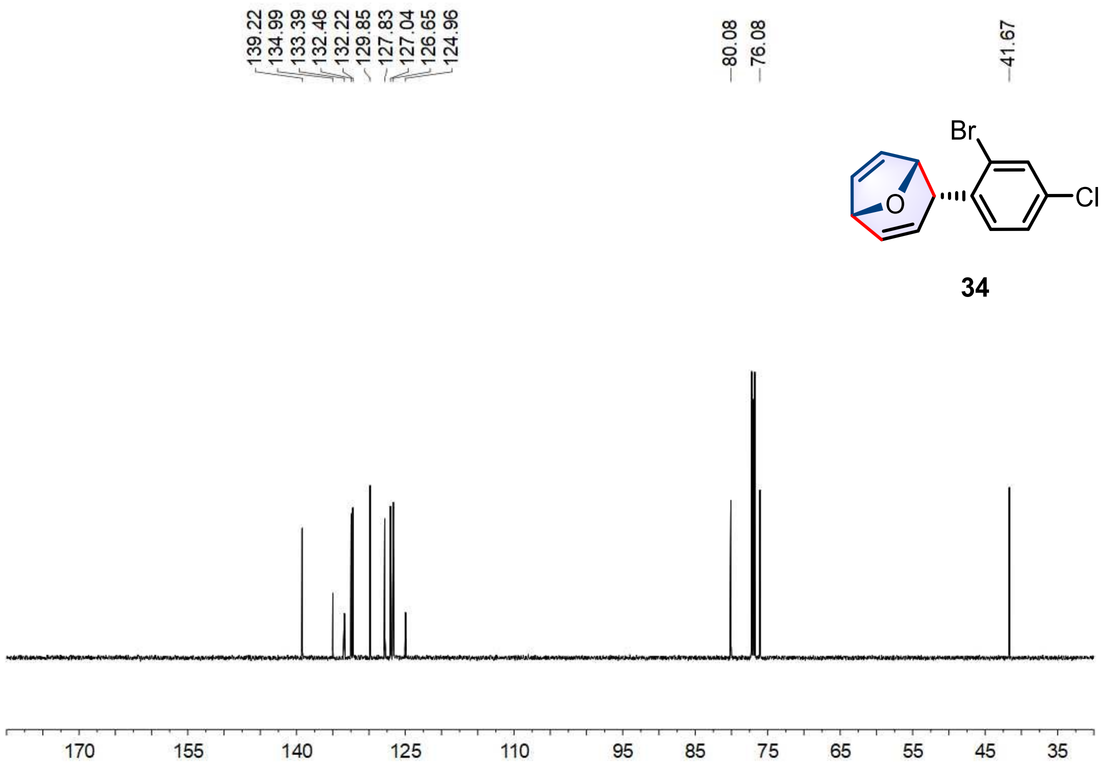


Figure S73. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **34**.

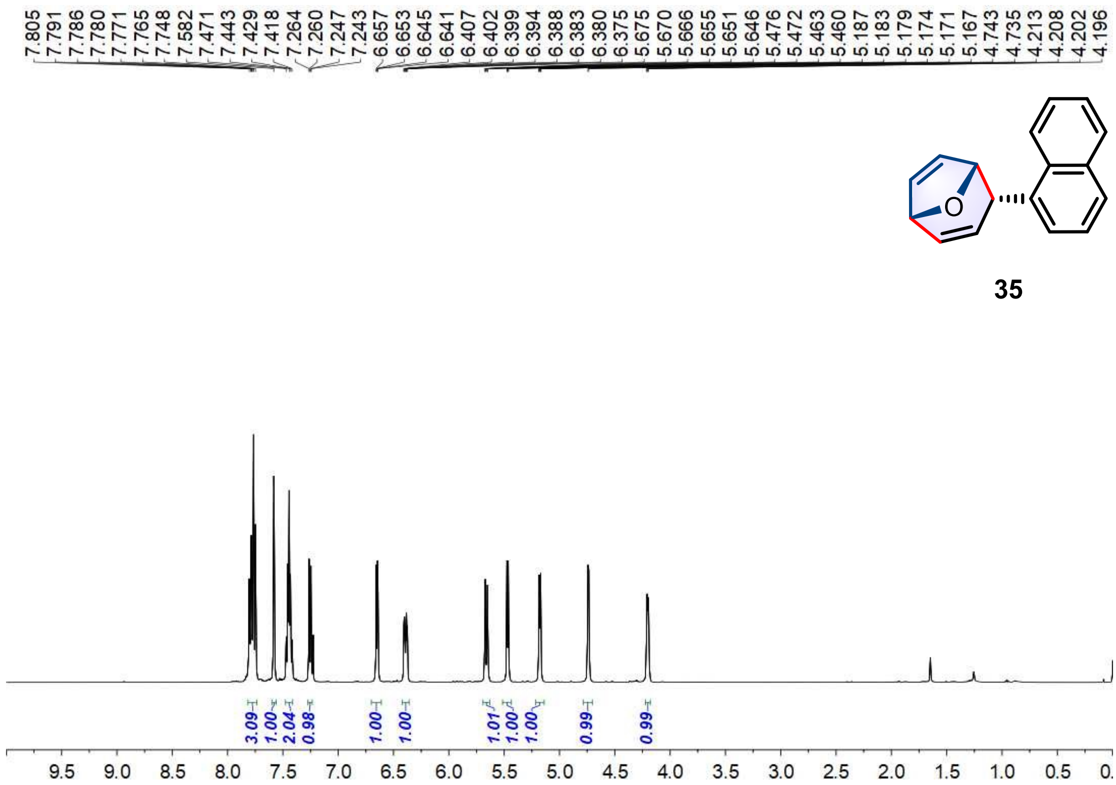


Figure S74 ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **35**.

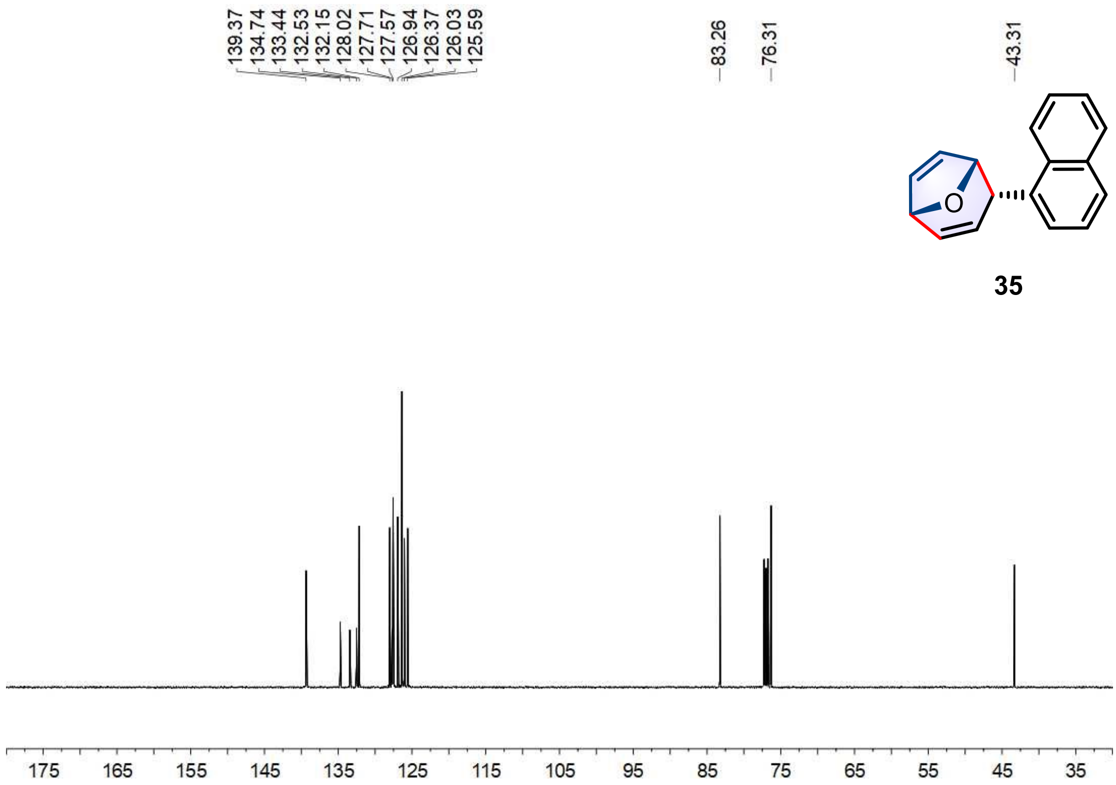


Figure S75. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **35**.

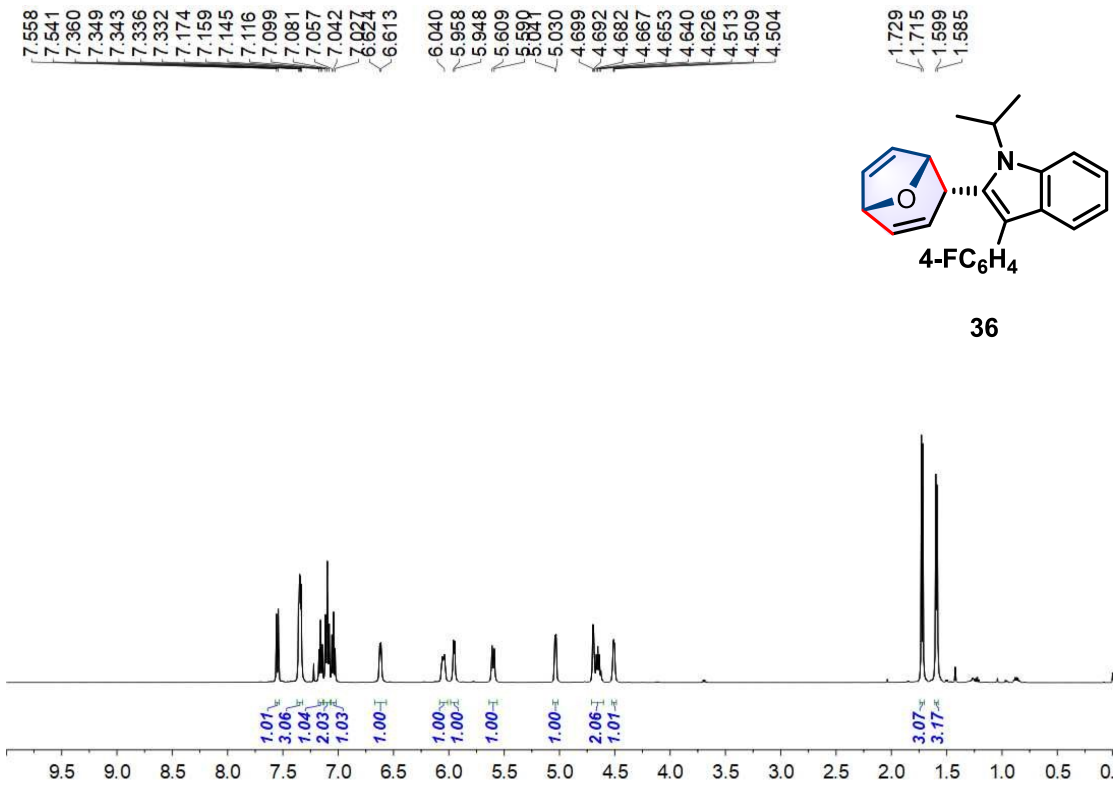


Figure S76. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **36**.

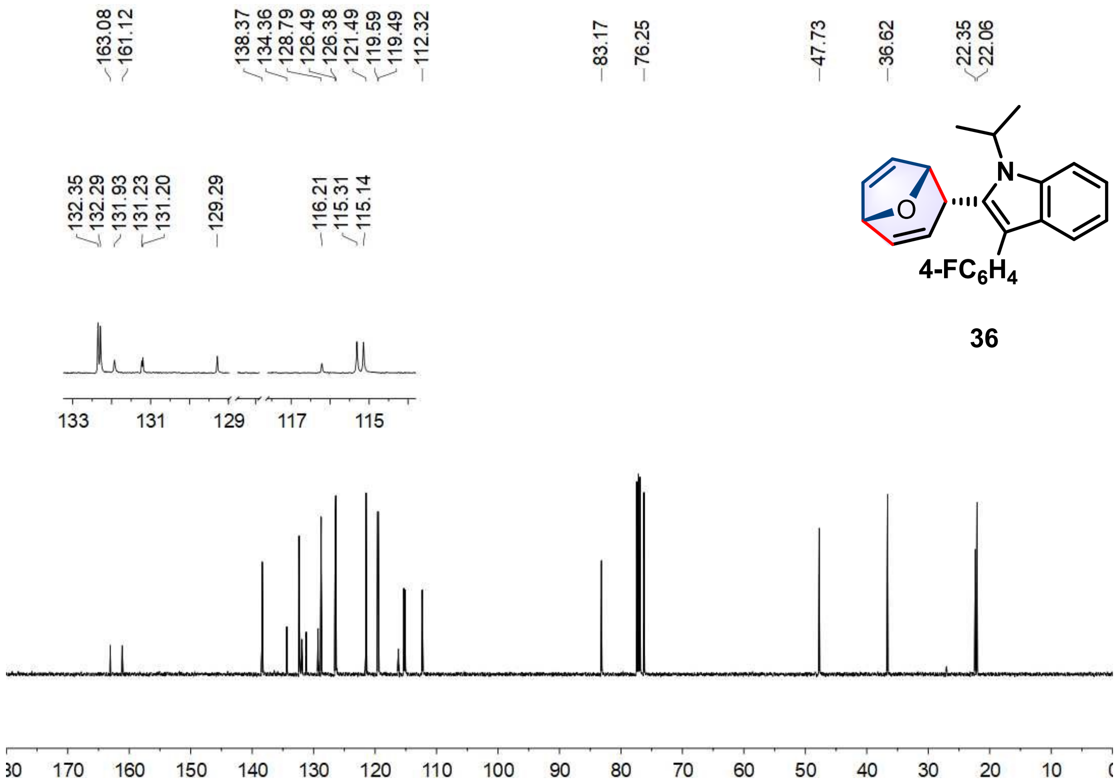


Figure S77. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **36**.

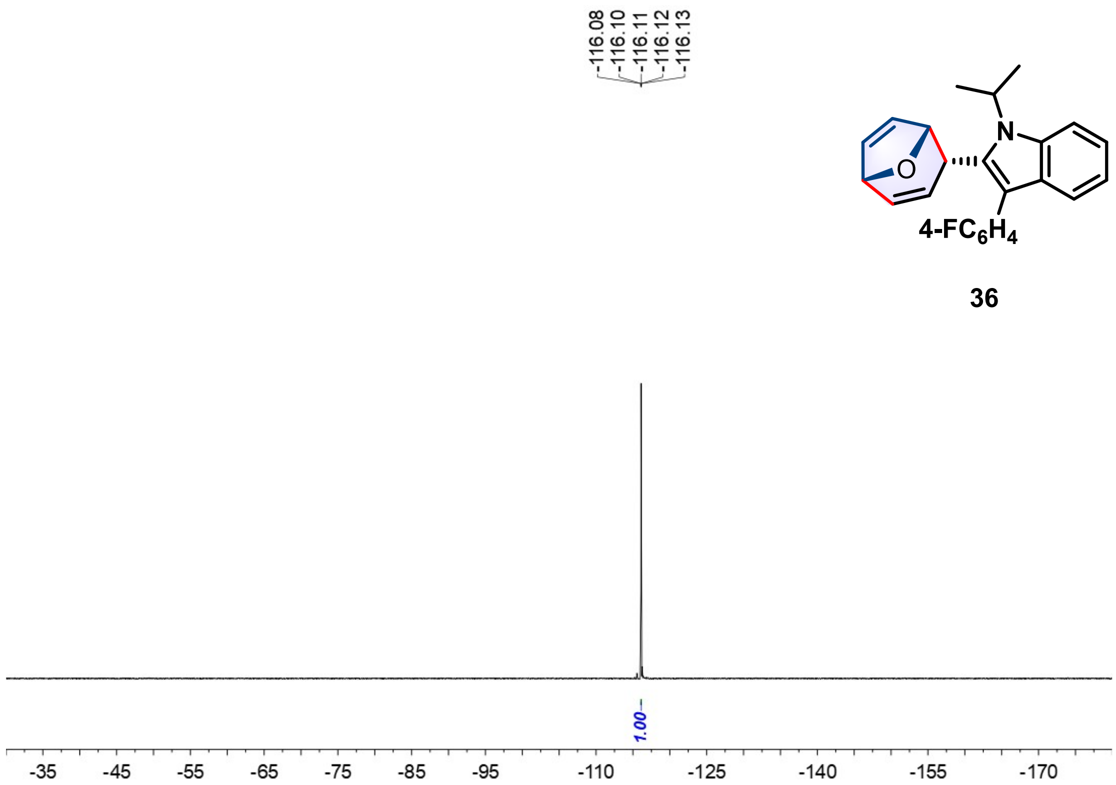


Figure S78. ^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of **36**.

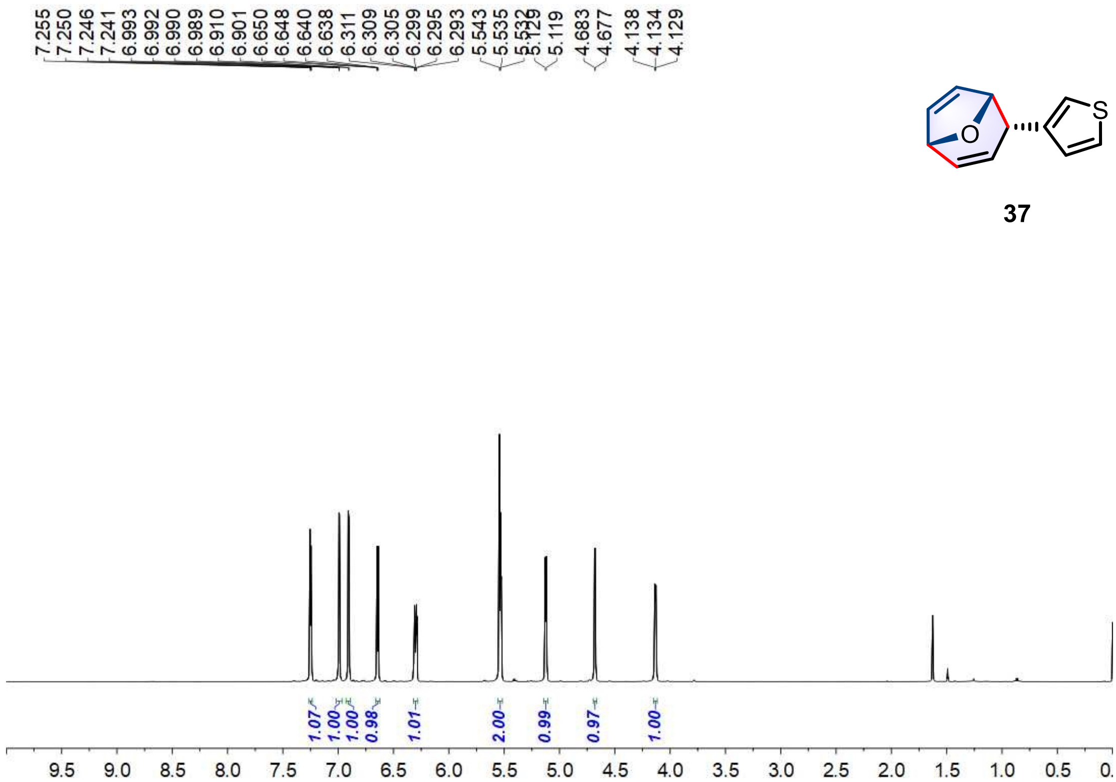
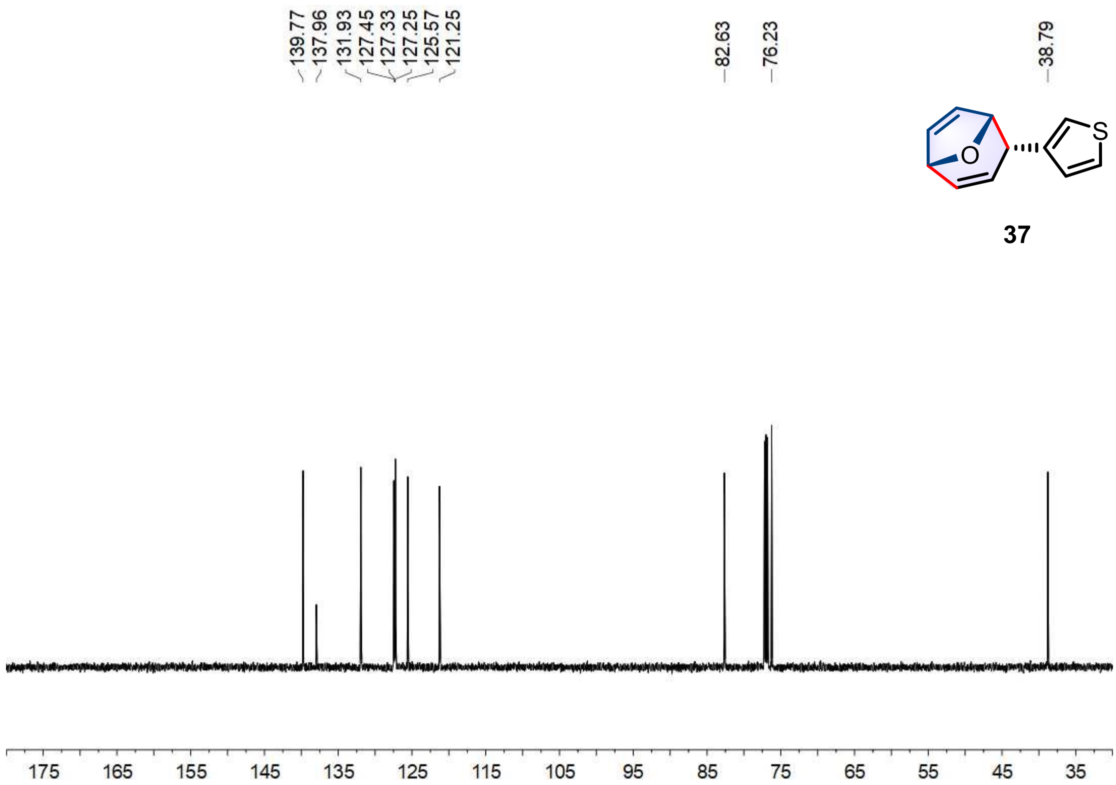
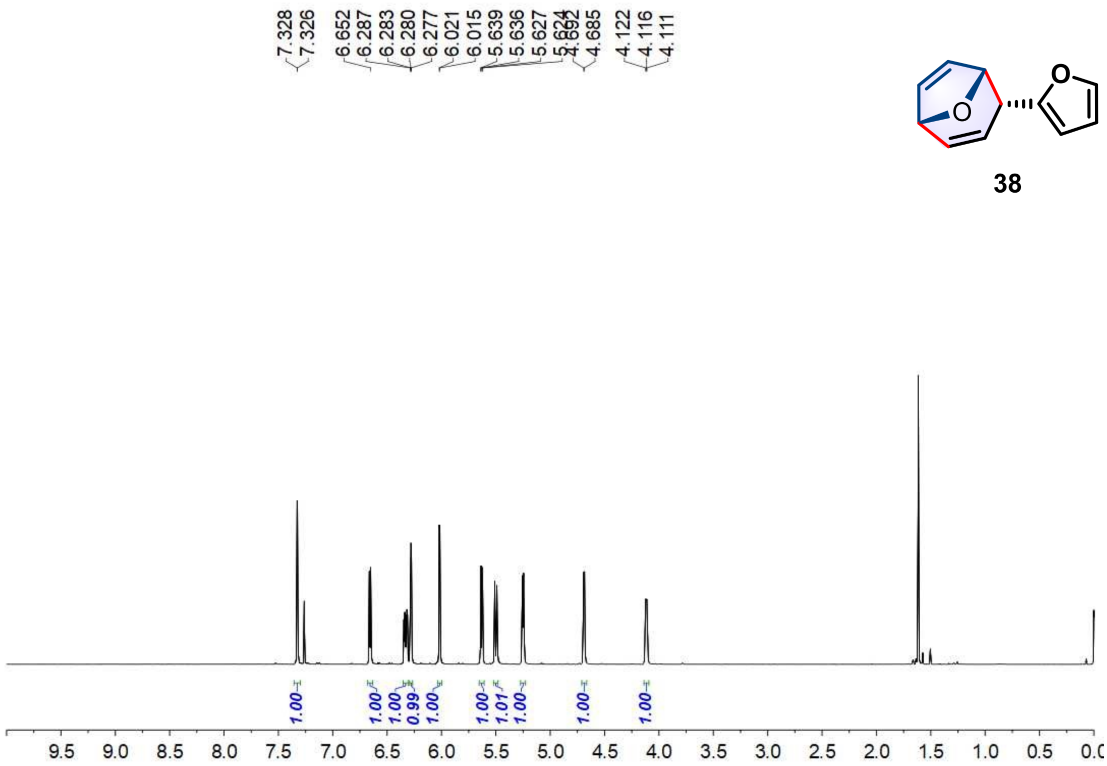


Figure S79. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **37**.



37

Figure S80. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **37**.



38

Figure S81. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **38**.

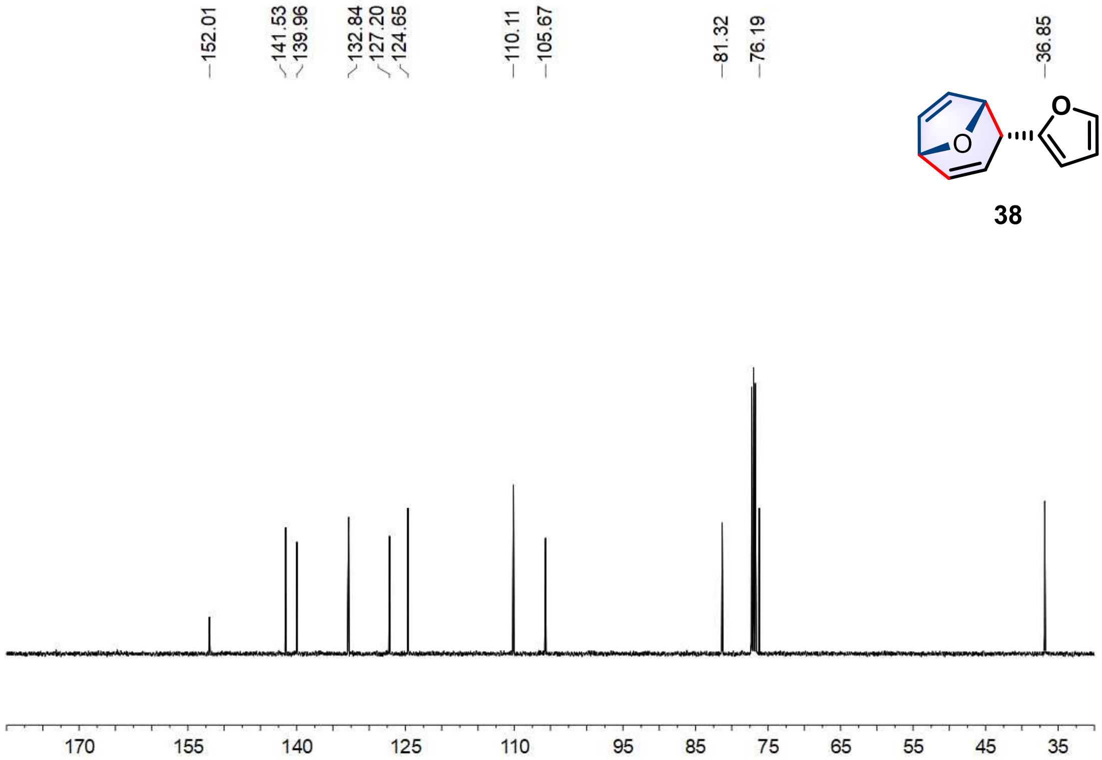


Figure S82. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **38**.

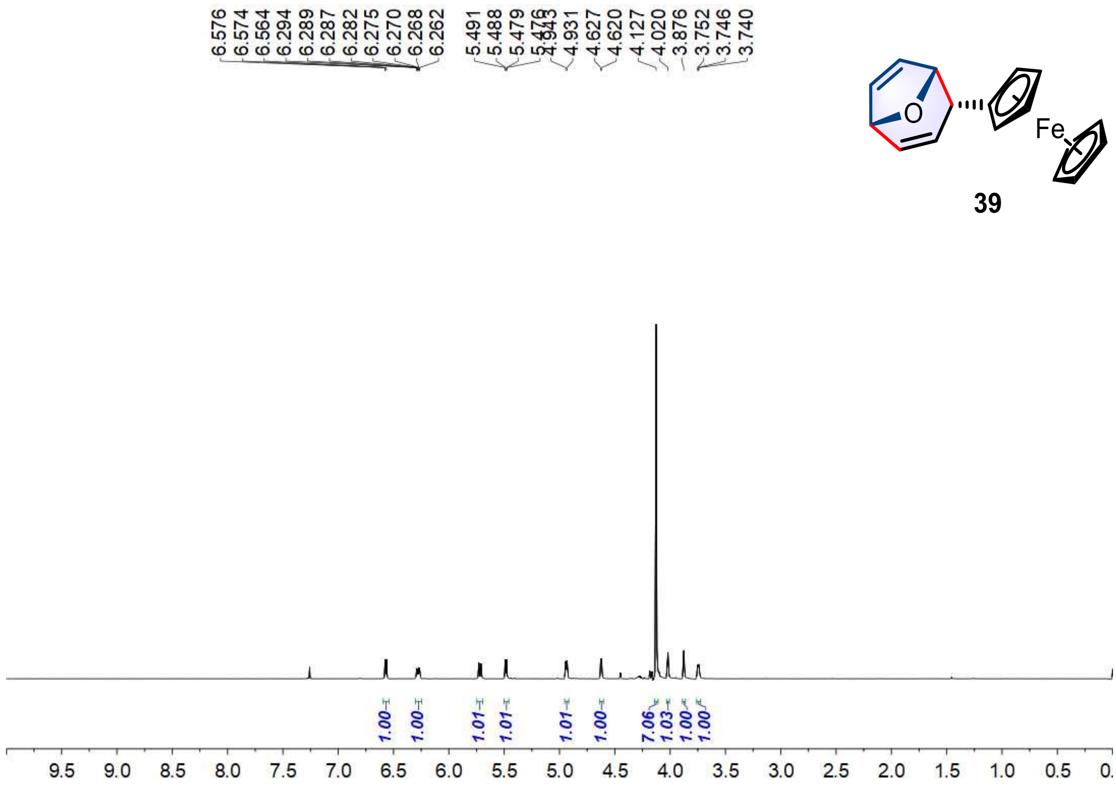


Figure S83. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **39**.

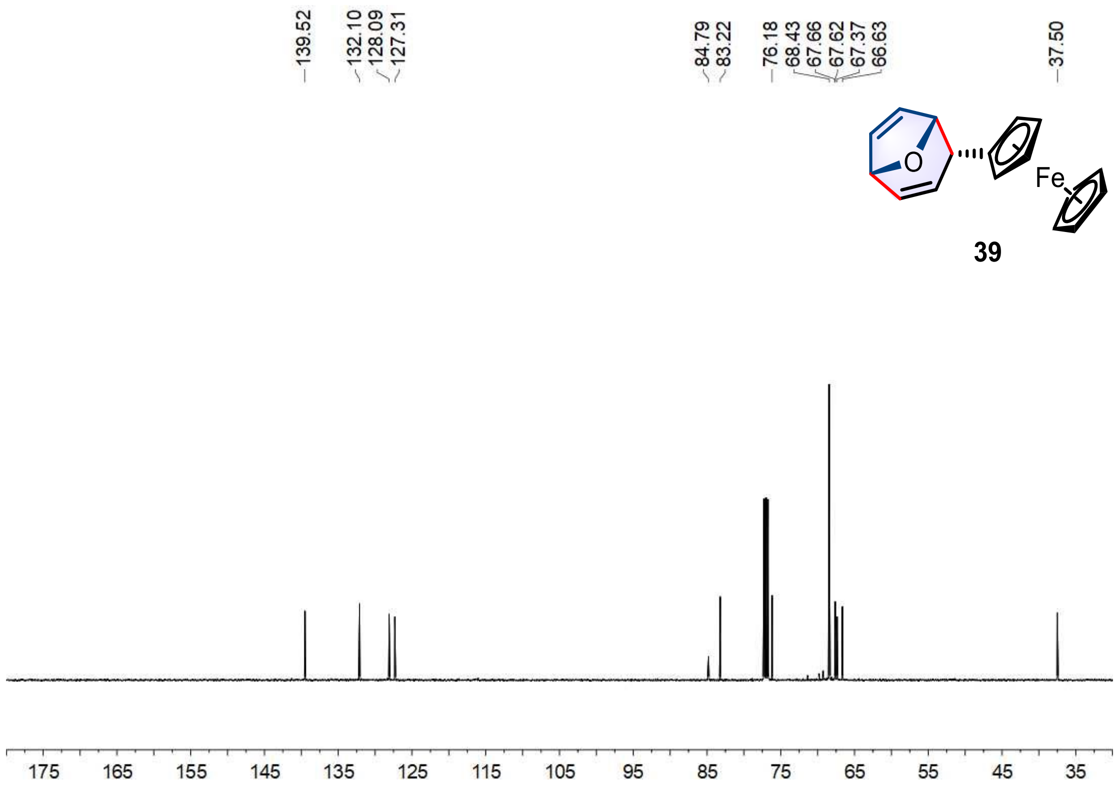


Figure S84. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **39**.

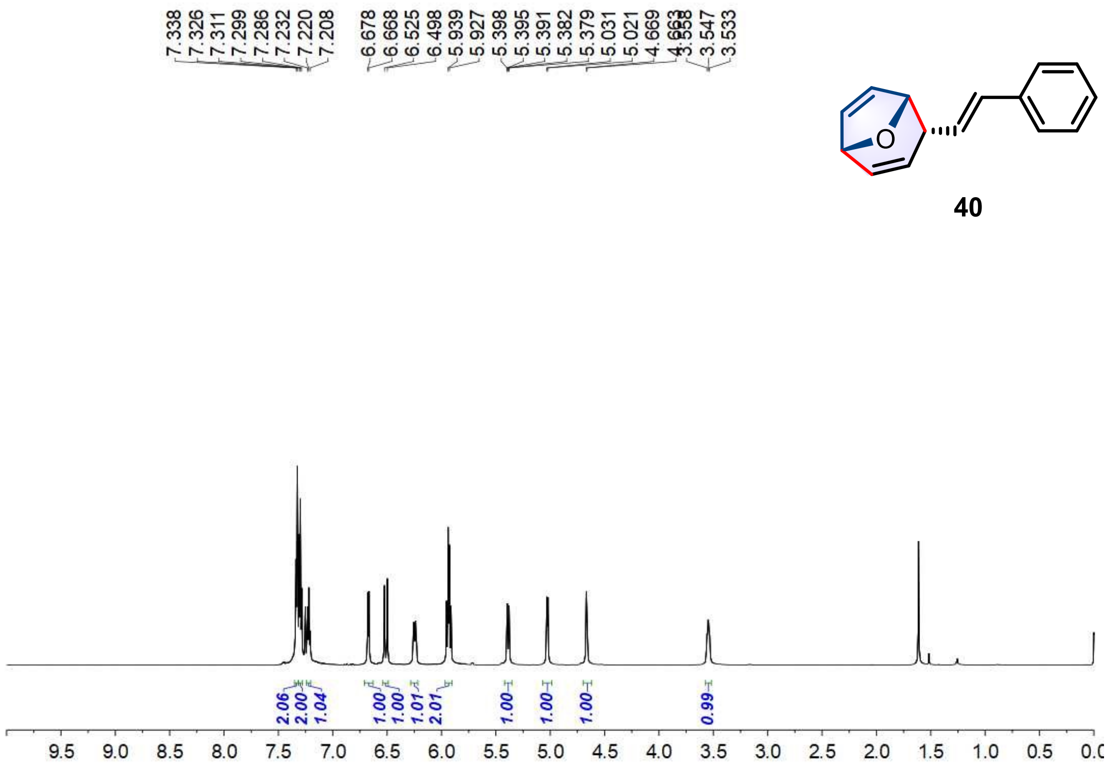


Figure S85. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **40**.

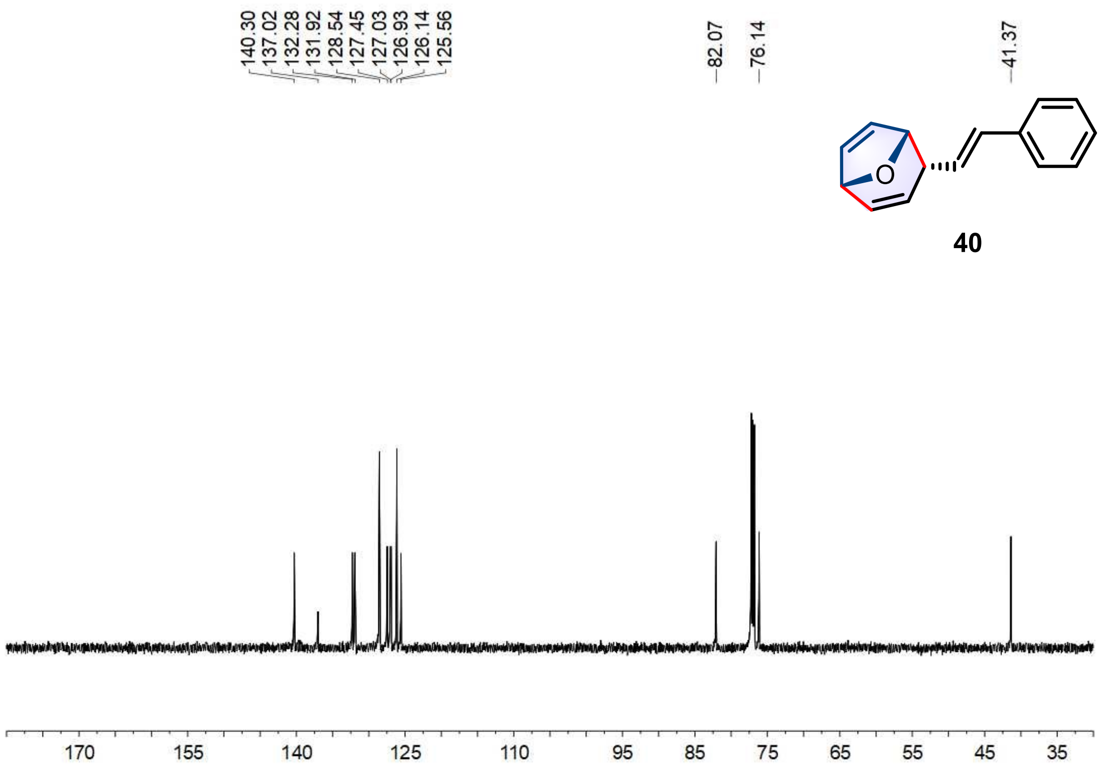


Figure S86. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **40**.

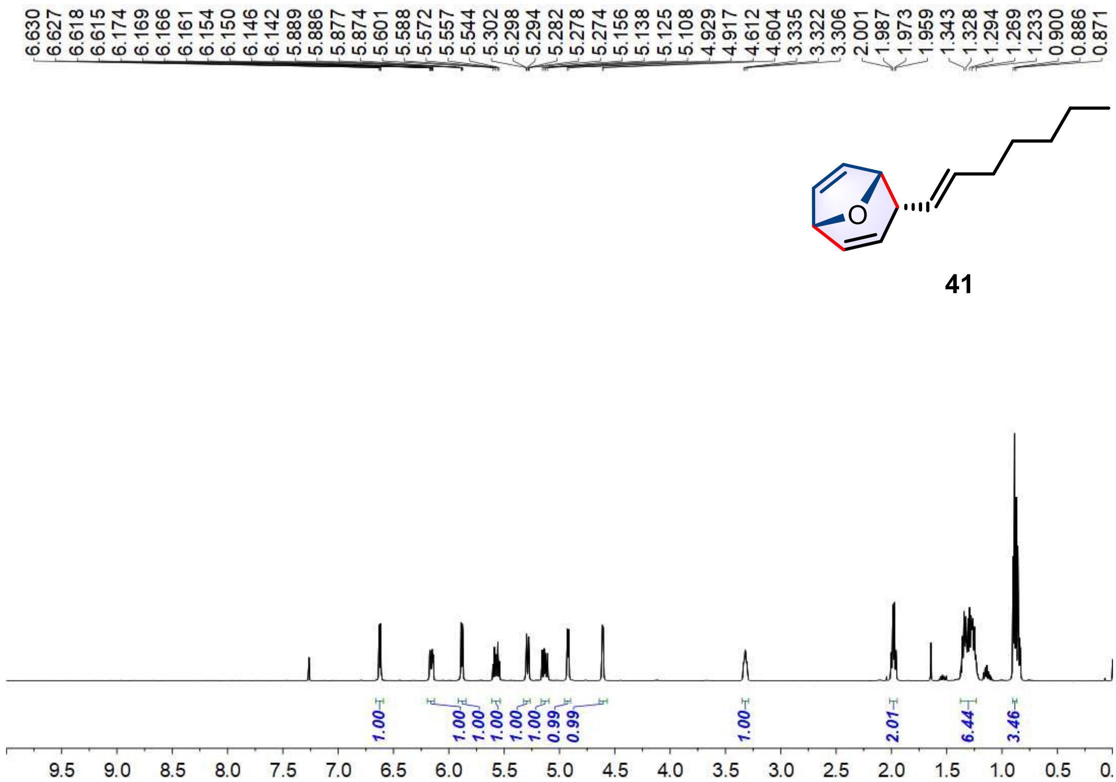


Figure S87. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **41**.

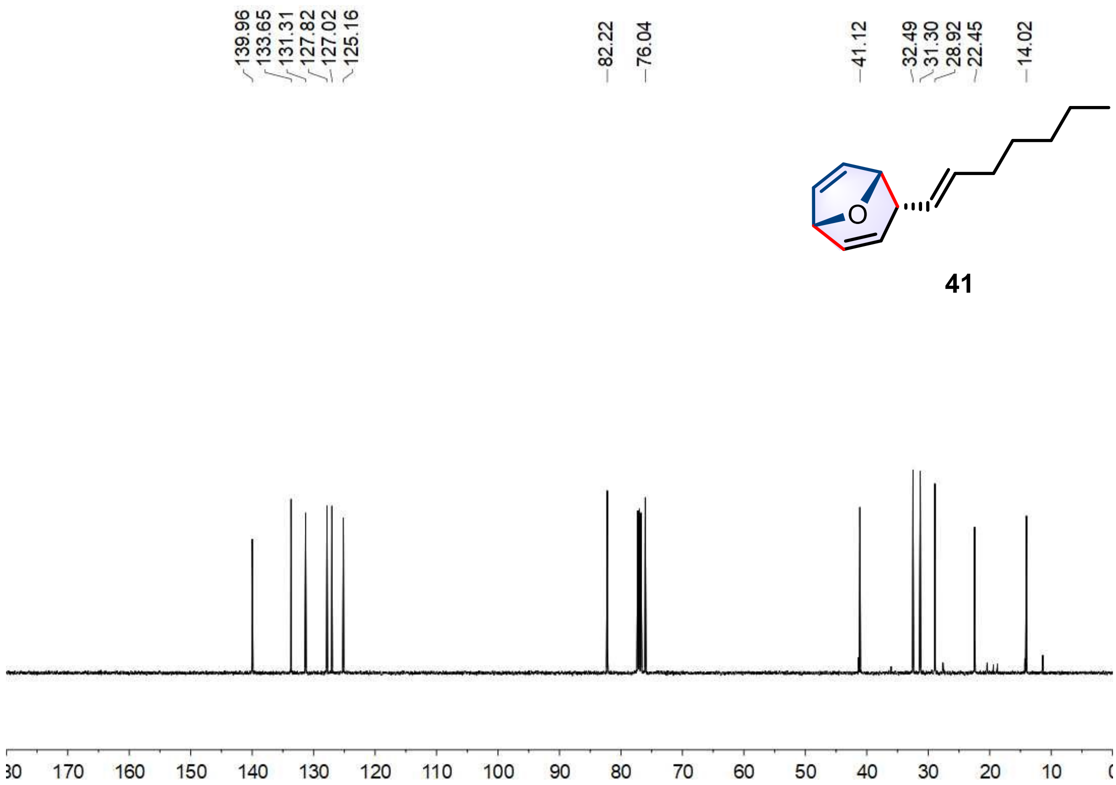


Figure S88. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **41**.

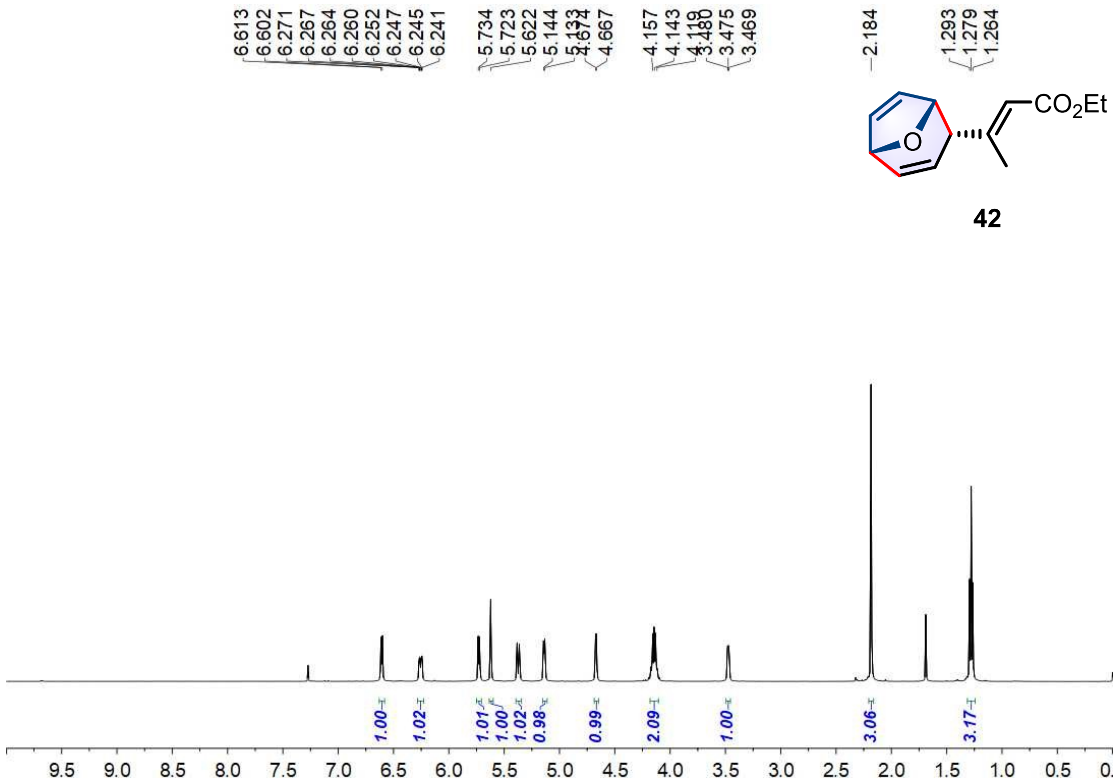


Figure S89. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **42**.

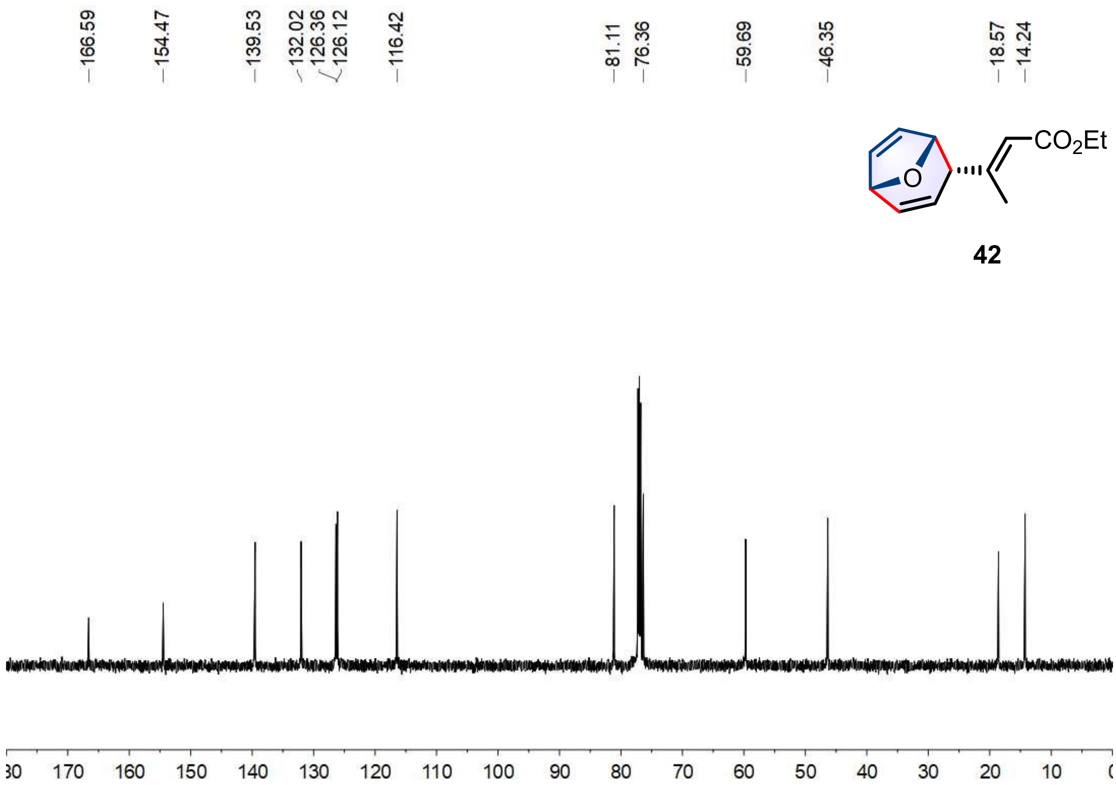


Figure S90. ^{13}C NMR (151 MHz, CDCl$_3$) Spectrum of **42**.

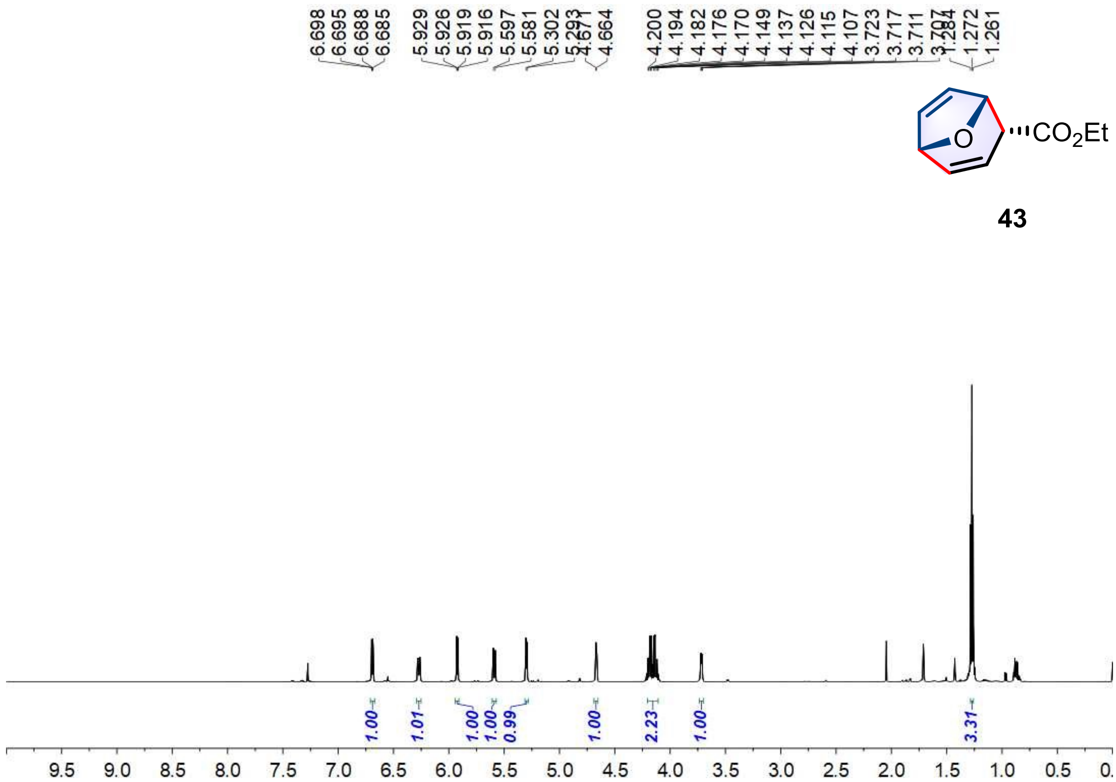


Figure S91. ^{1}H NMR (600 MHz, CDCl$_3$) Spectrum of **43**.

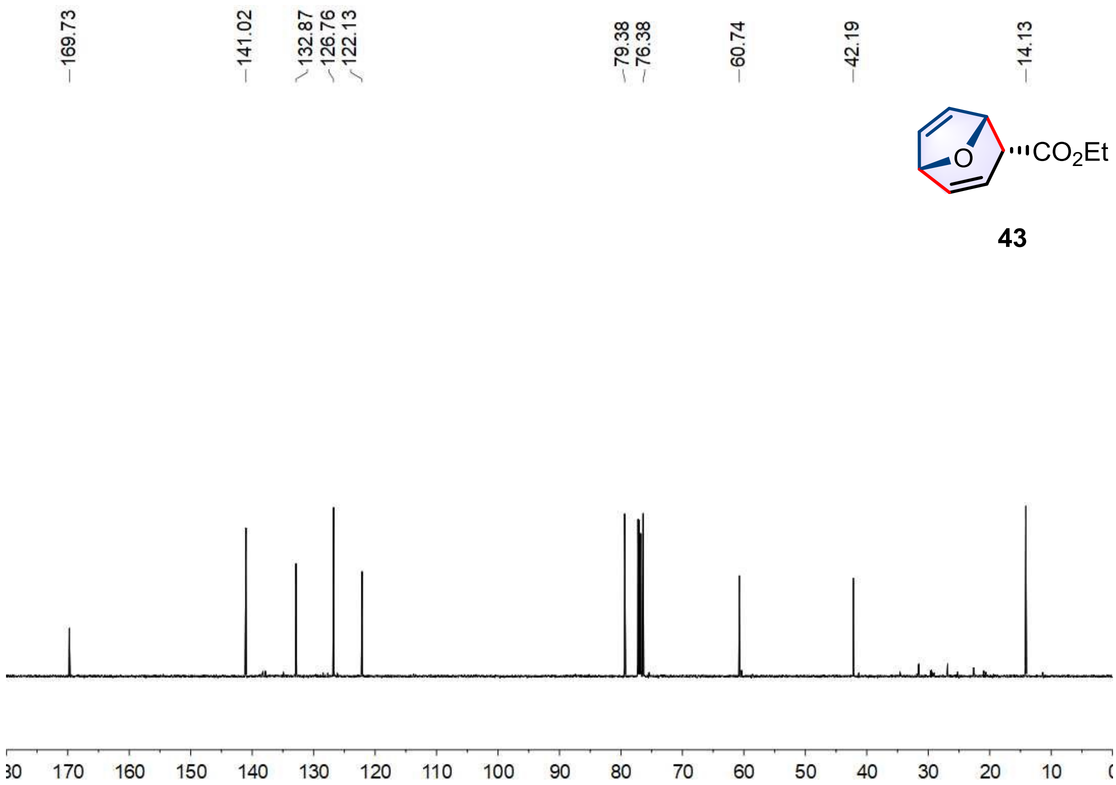


Figure S92. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **43**.

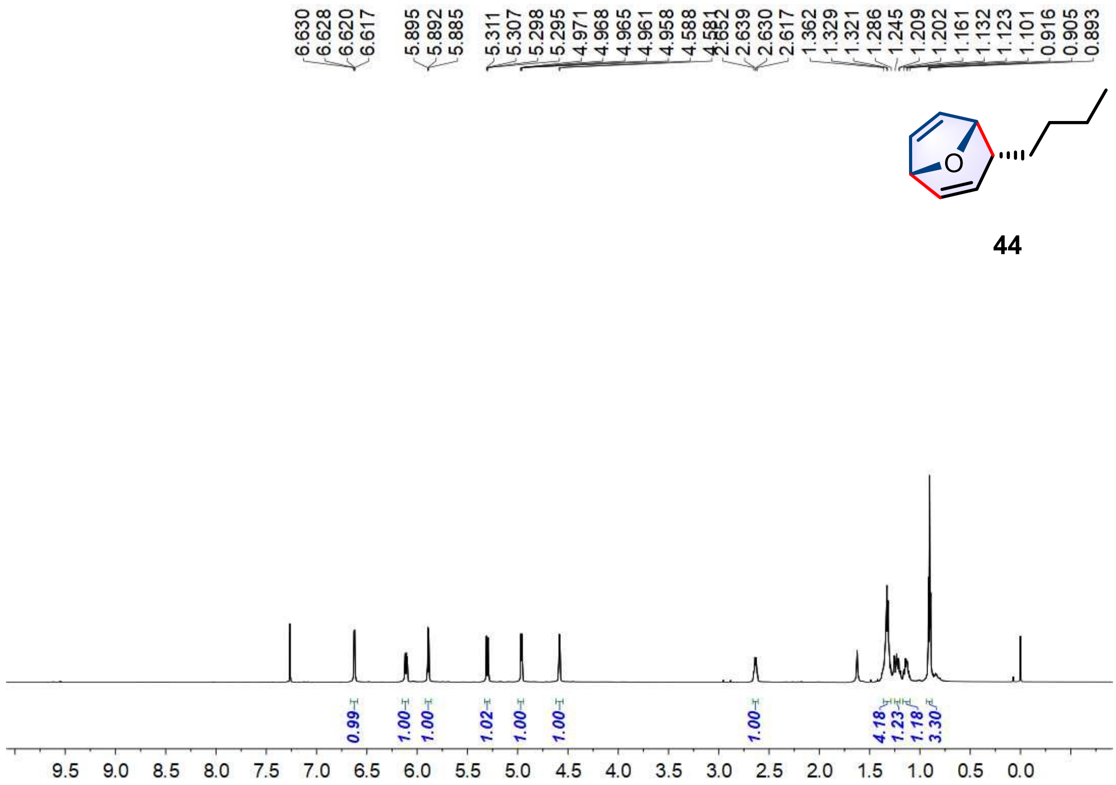


Figure S93. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **44**.

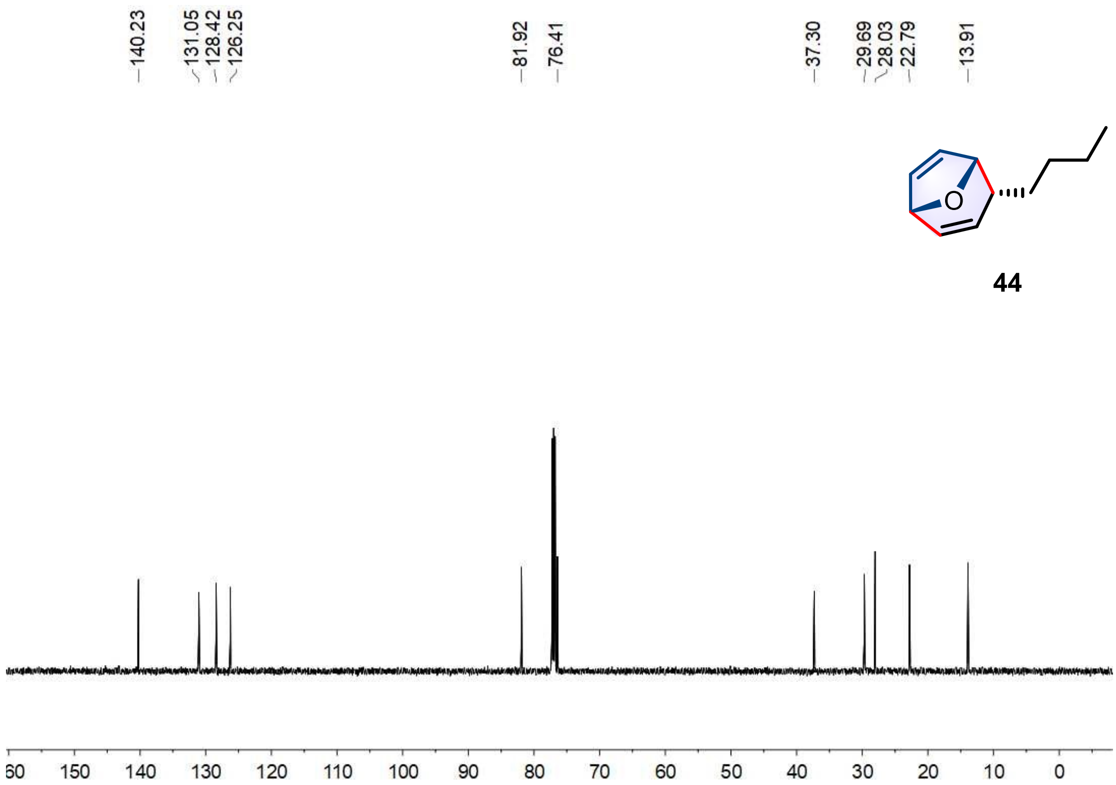


Figure S94. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **44**.

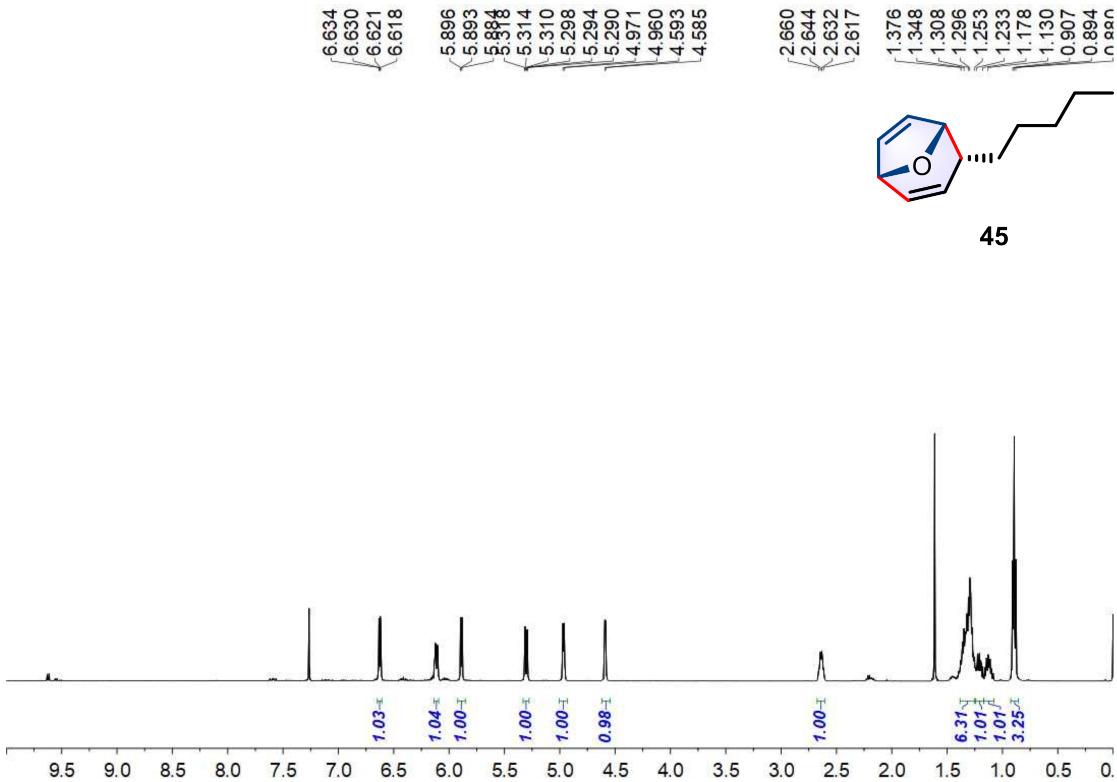


Figure S95. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **45**.

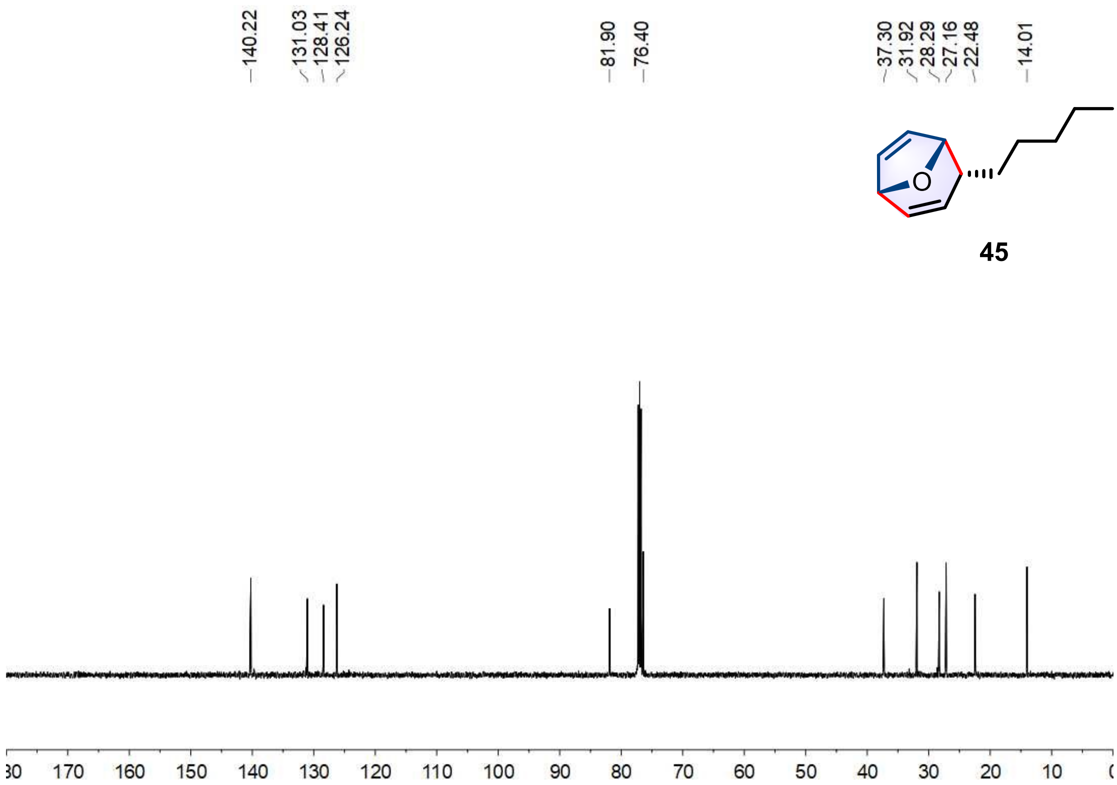


Figure S96. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **45**.

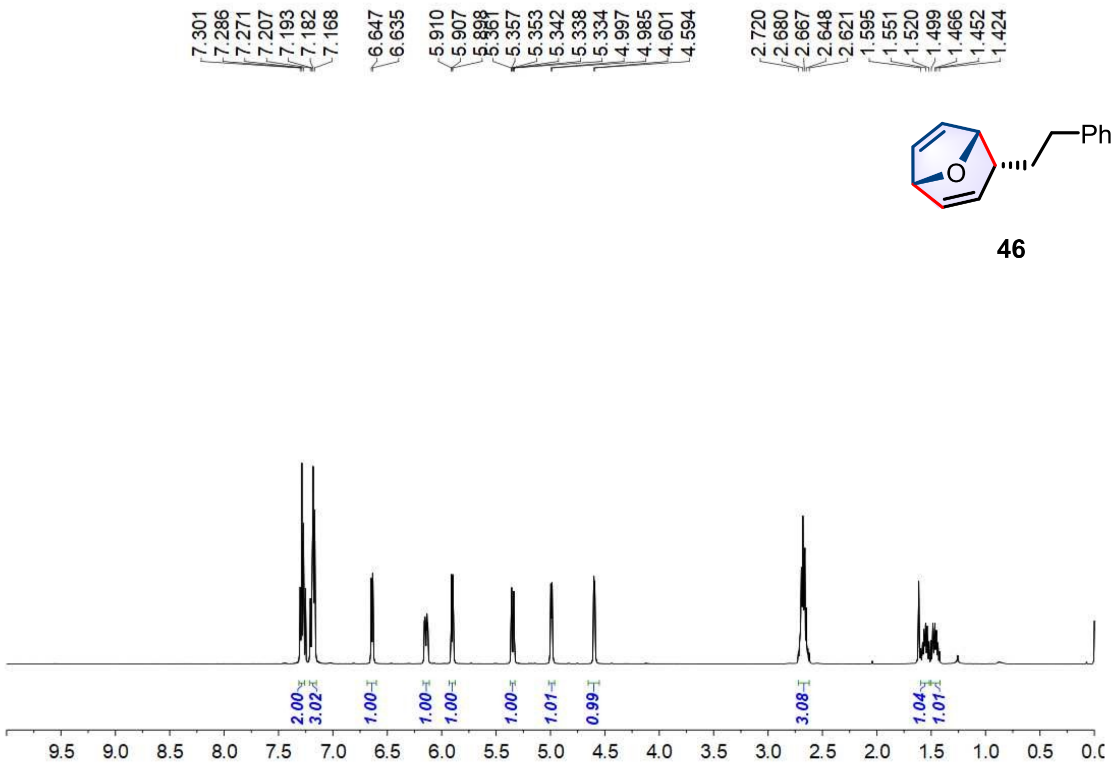
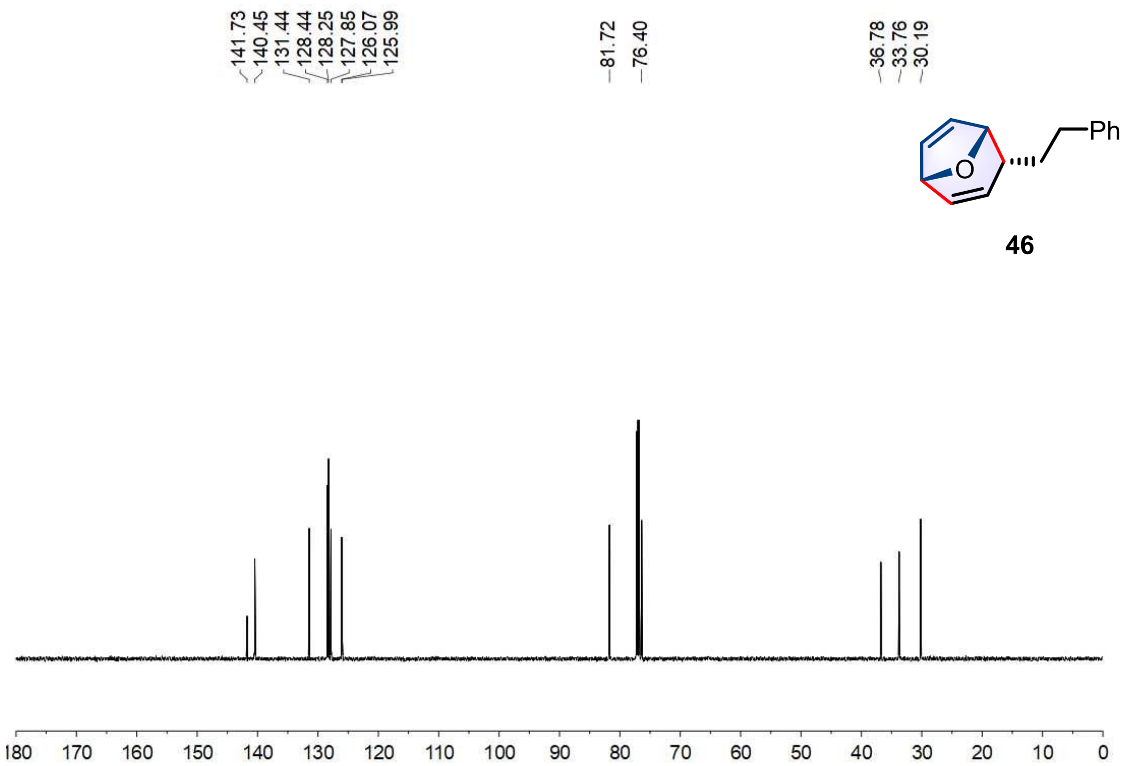
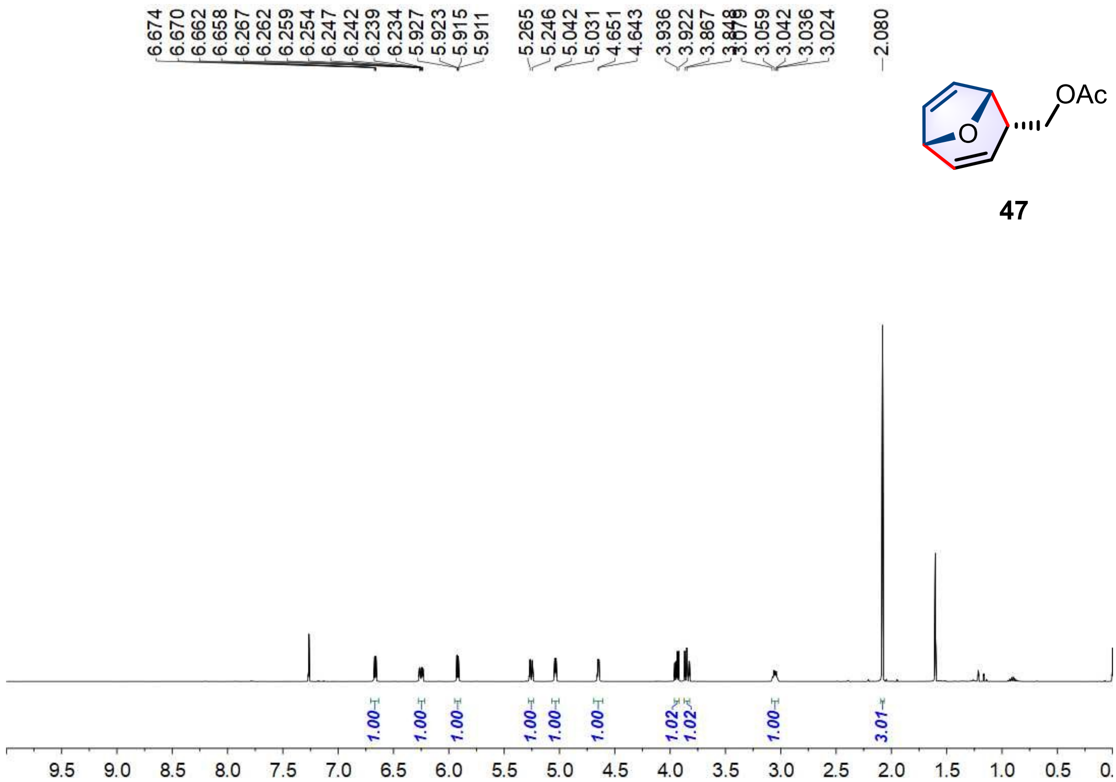


Figure S97. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **46**.



46

Figure S98. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **46**.



47

Figure S99. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **47**.

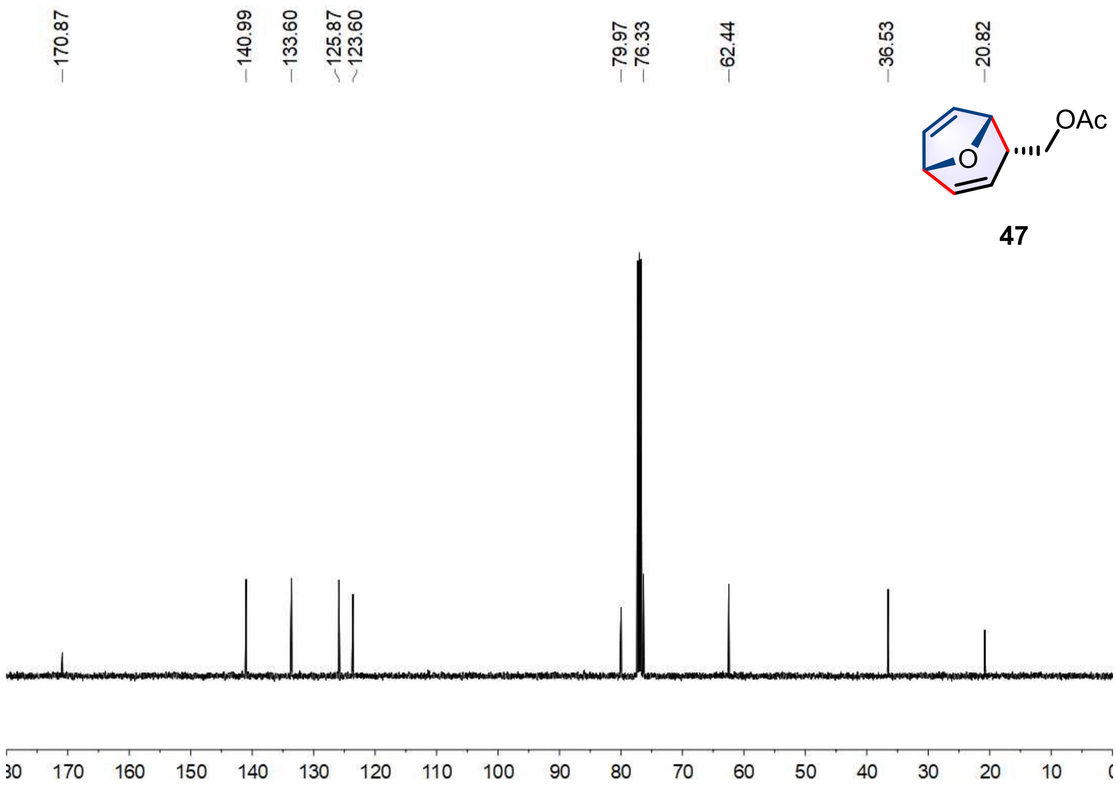


Figure S100. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **47**.

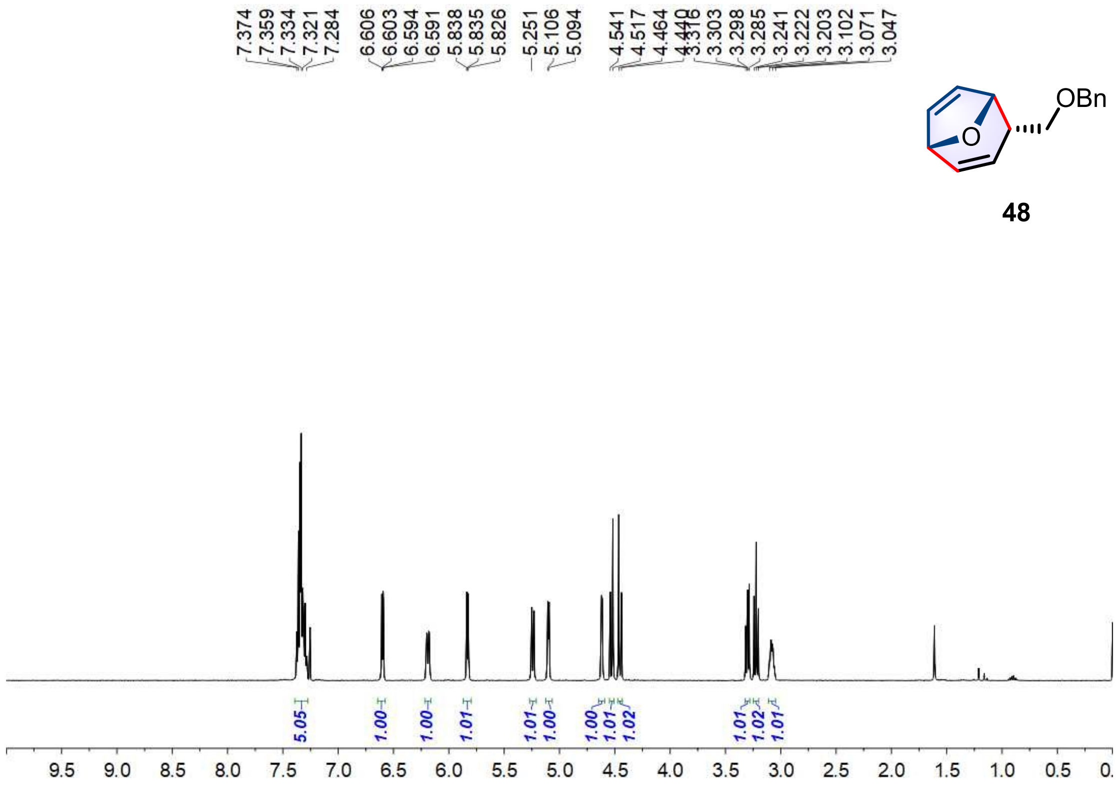


Figure S101. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **48**.

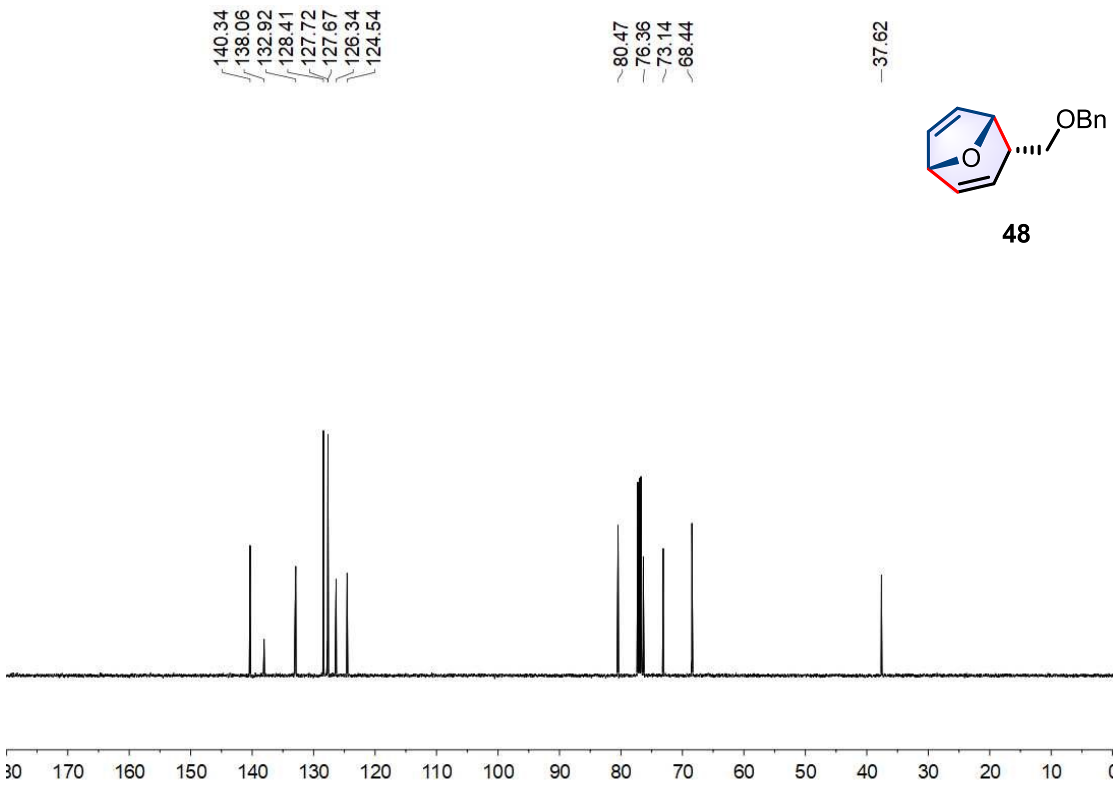


Figure S102. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **48**.

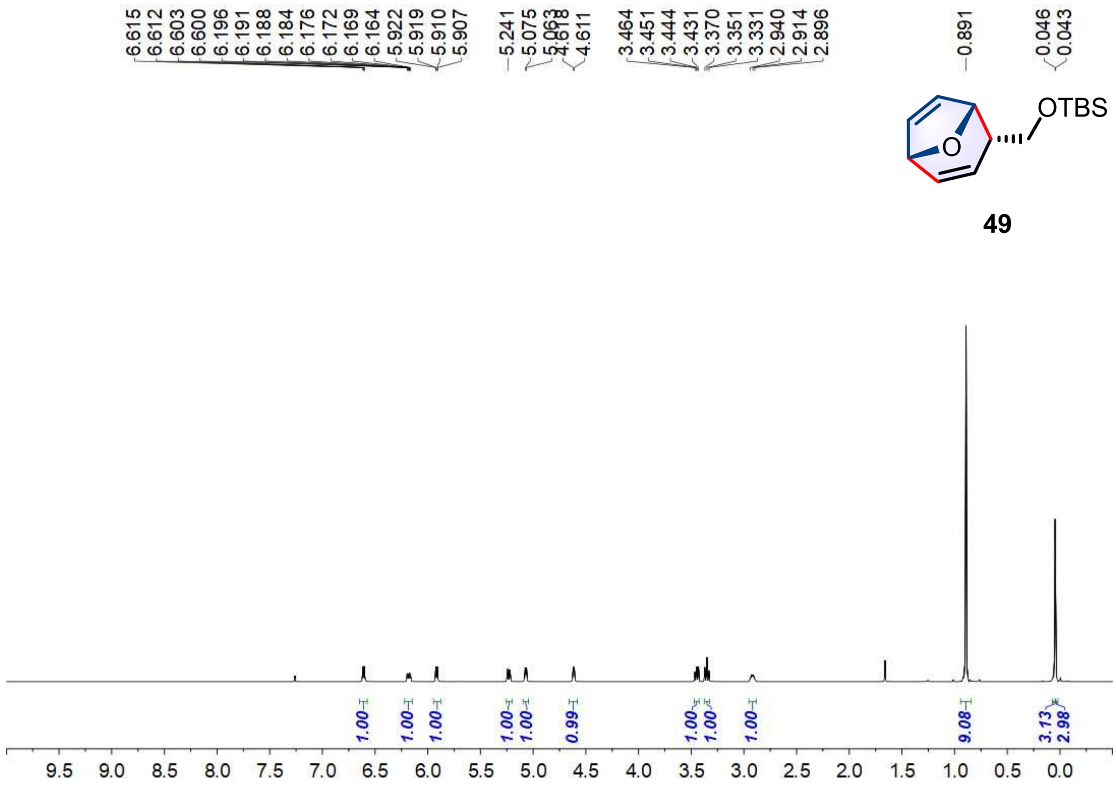


Figure S103. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **49**.

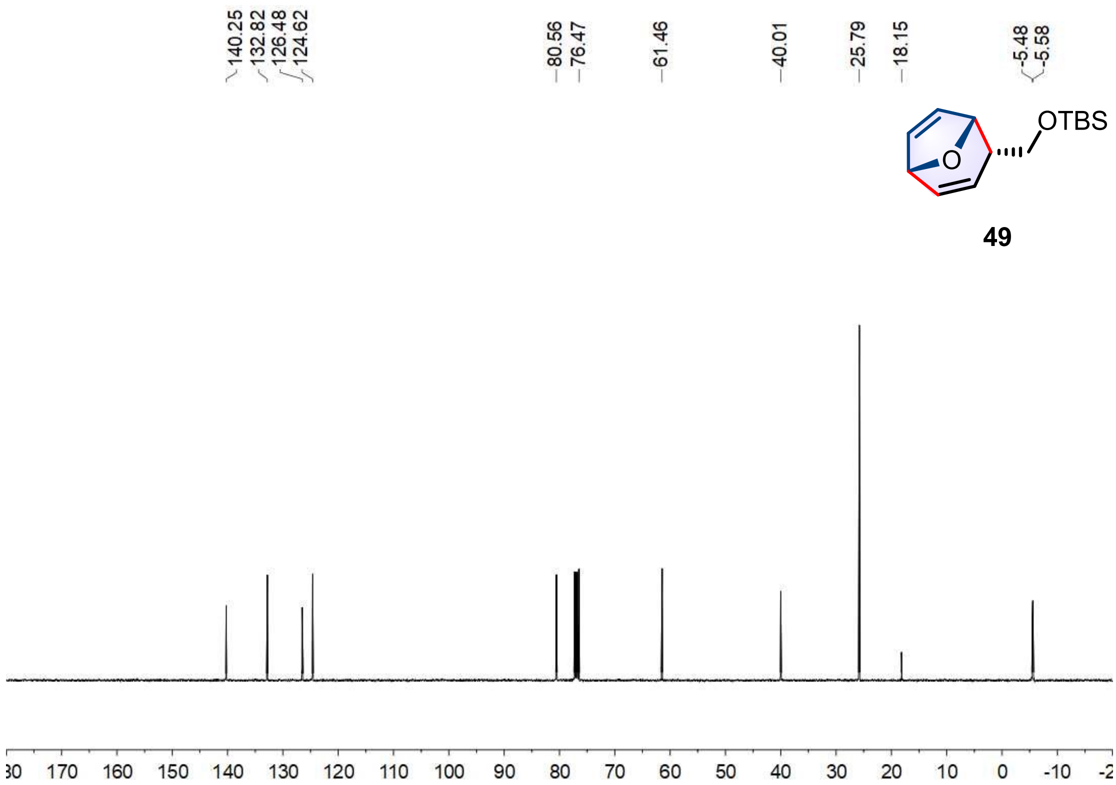


Figure S104. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **49**.

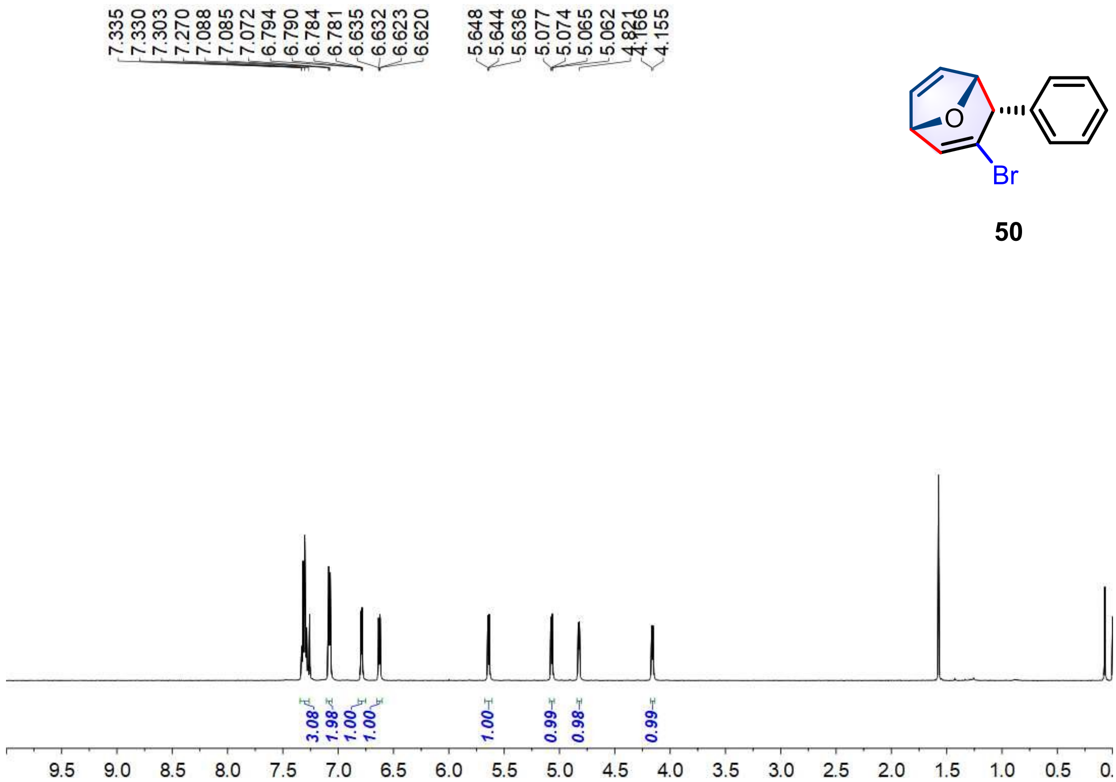


Figure S105. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **50**.

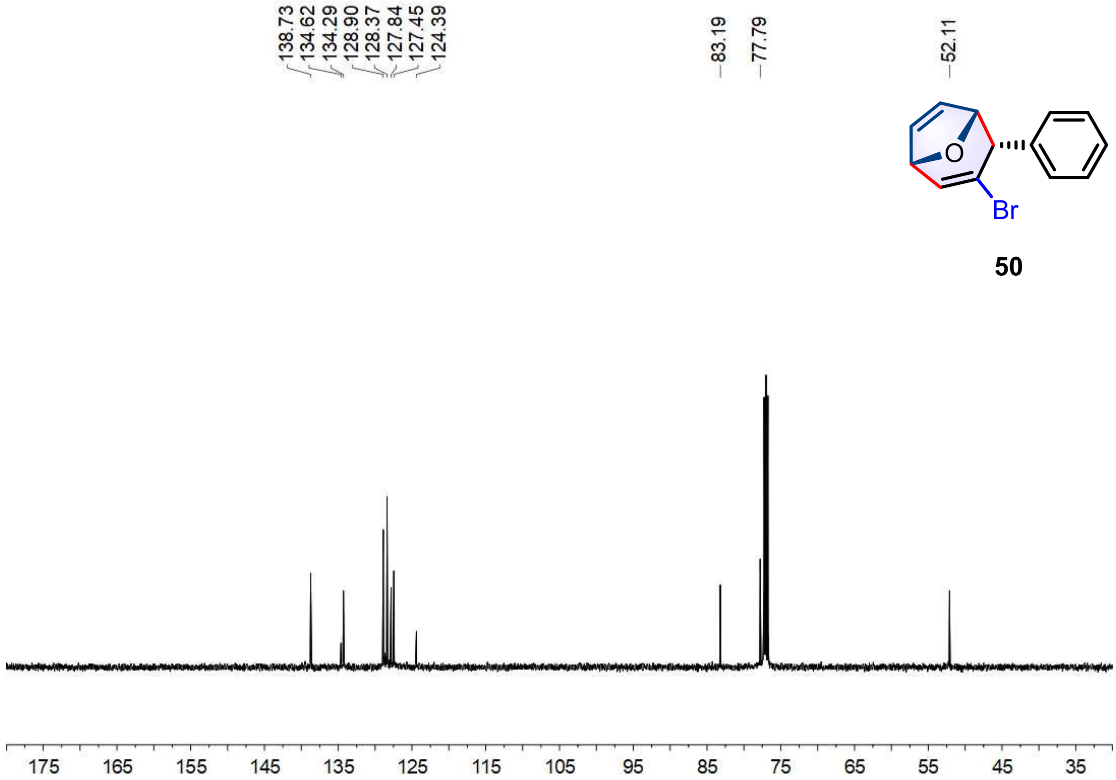


Figure S106. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **50**.

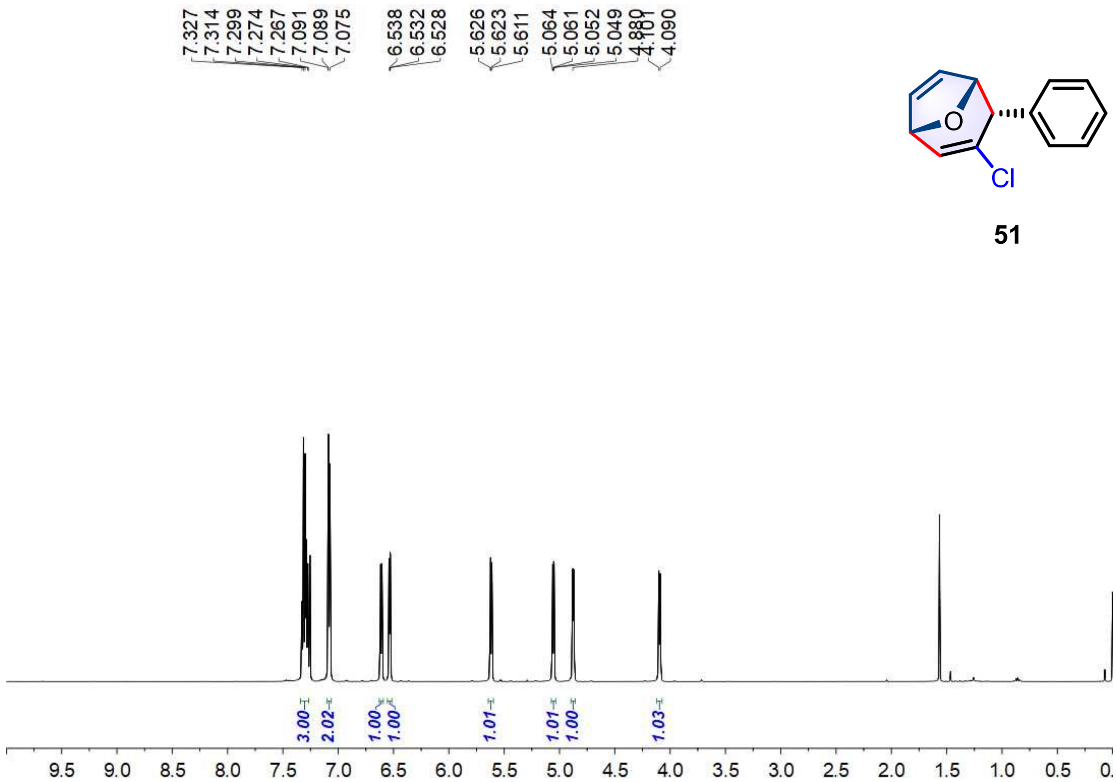


Figure S107. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **51**.

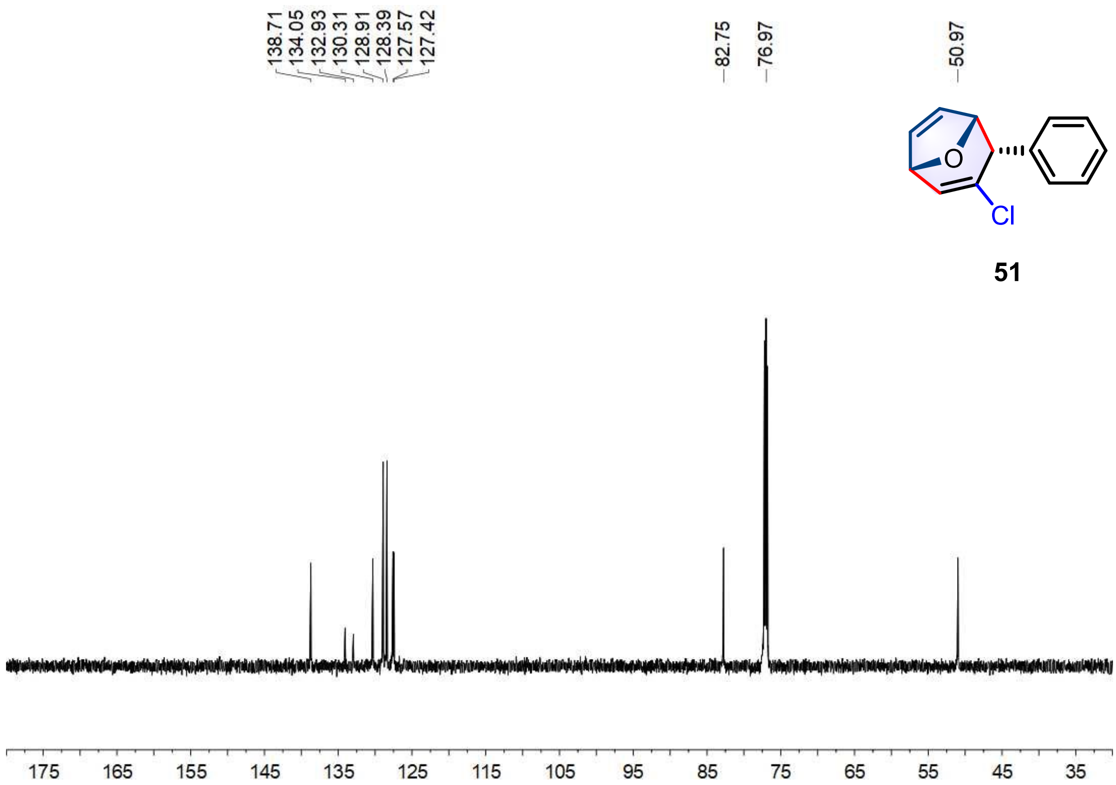


Figure S108. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **51**.

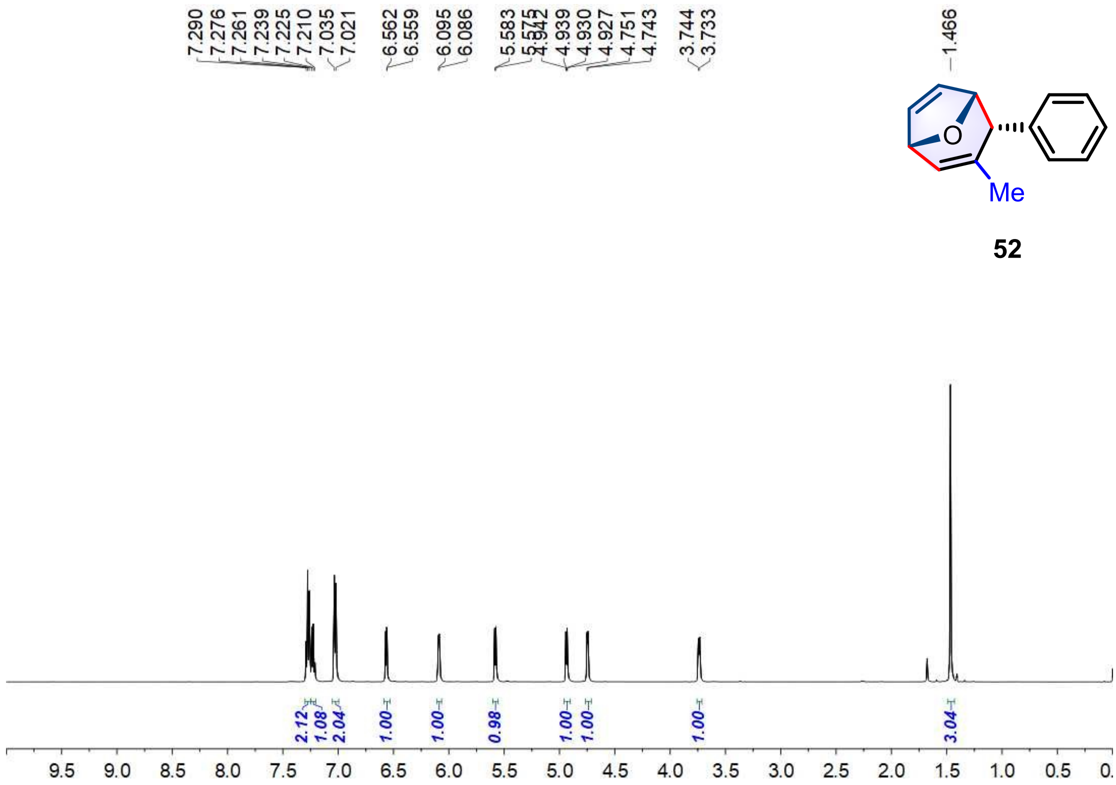


Figure S109. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **52**.

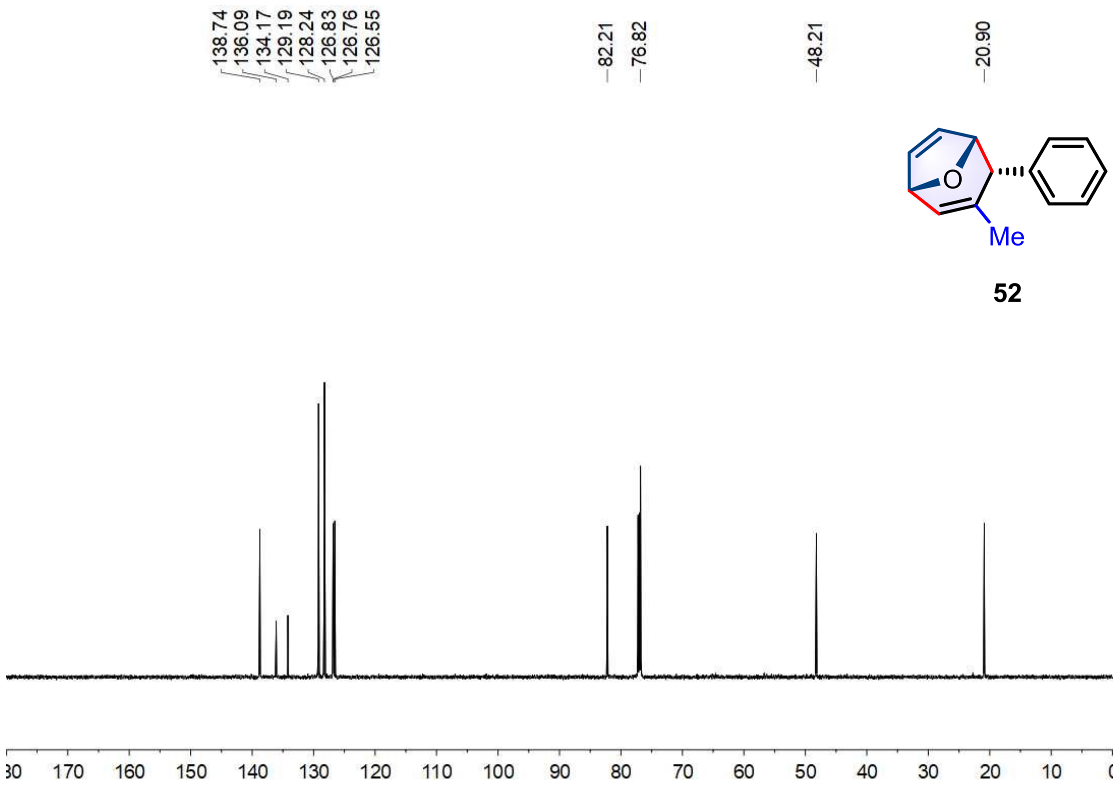


Figure S110. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **52**.

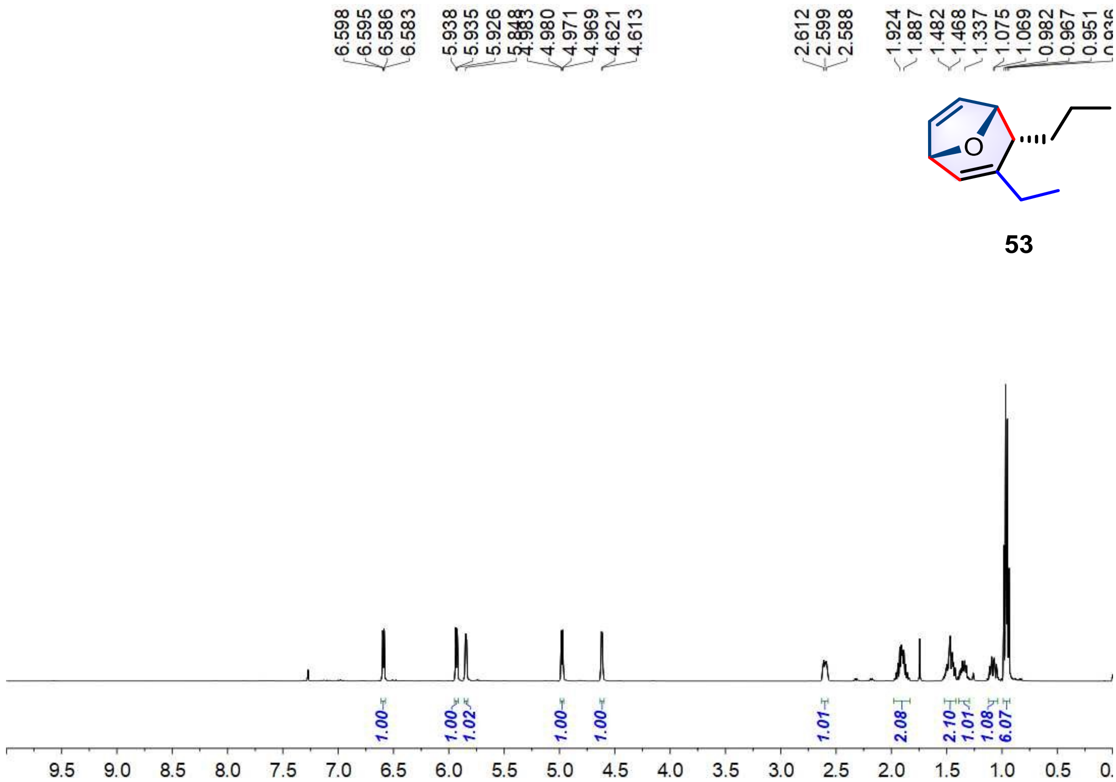


Figure S111. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **53**.

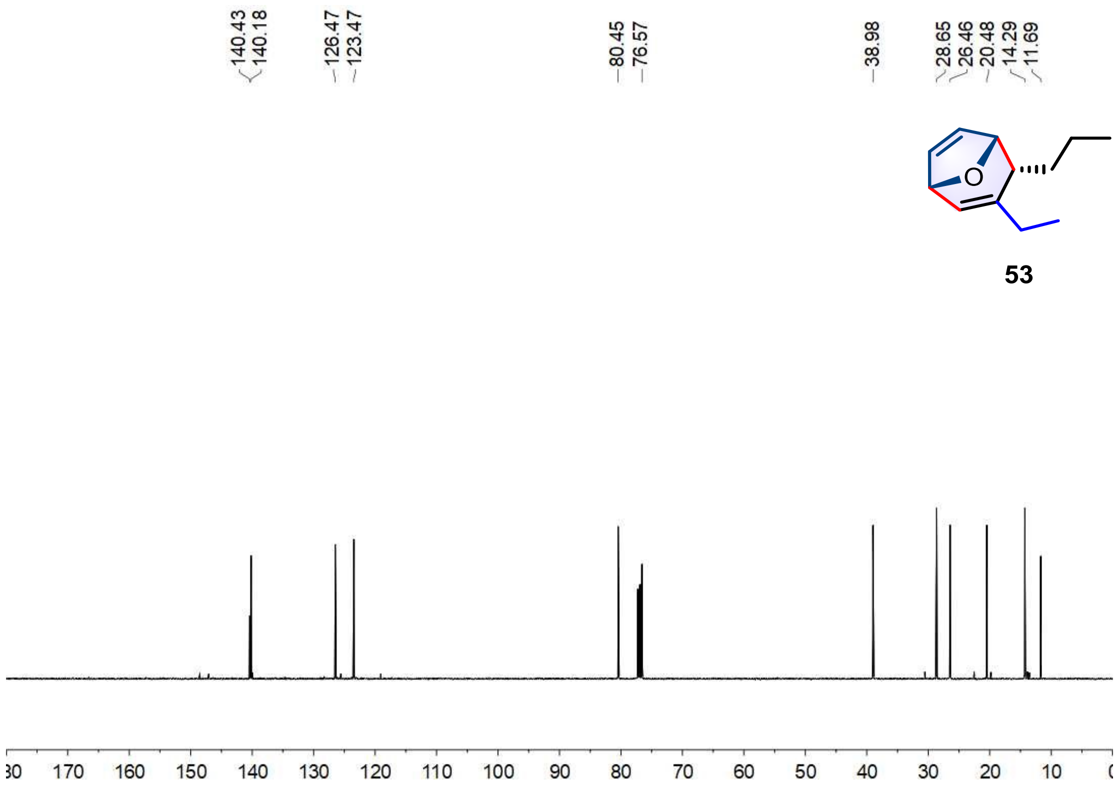


Figure S112. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **53**.

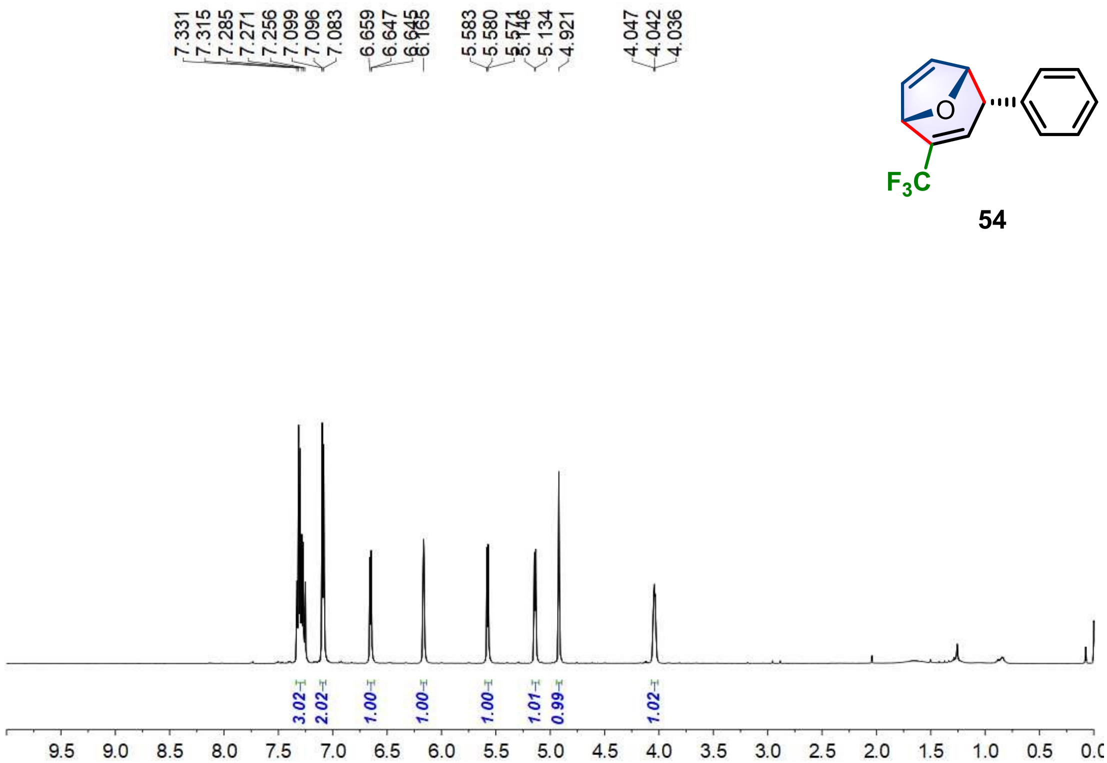


Figure S113. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **54**.

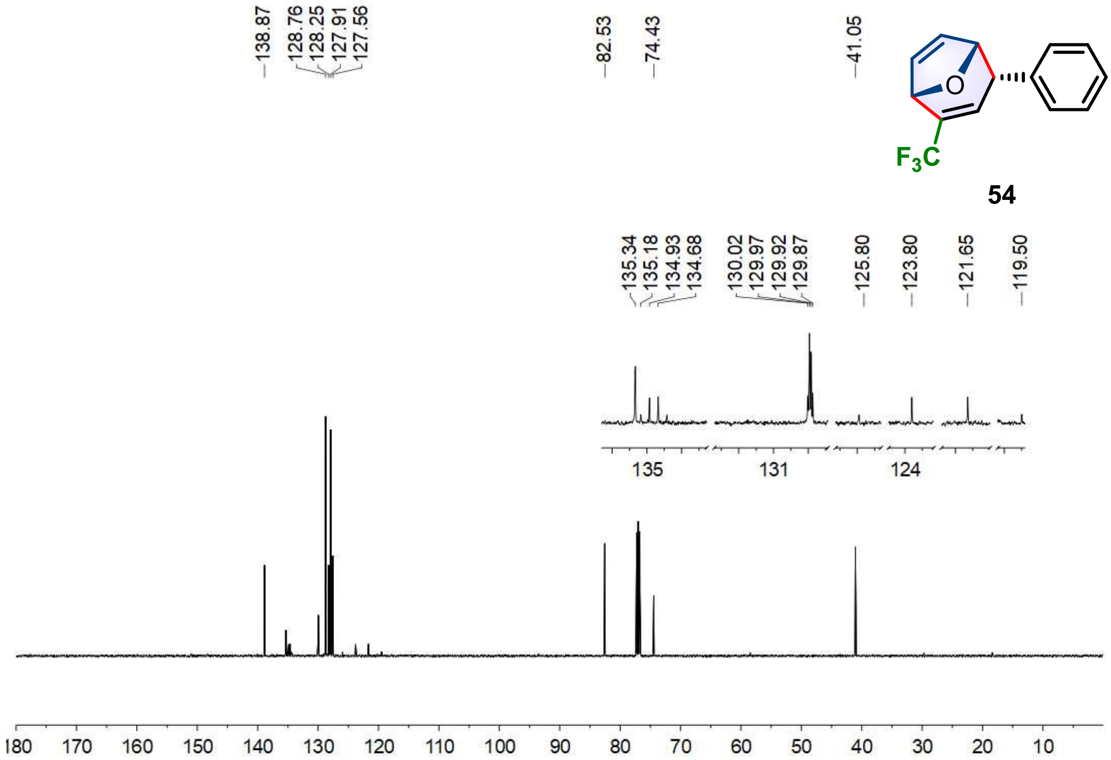


Figure S114. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **54**.

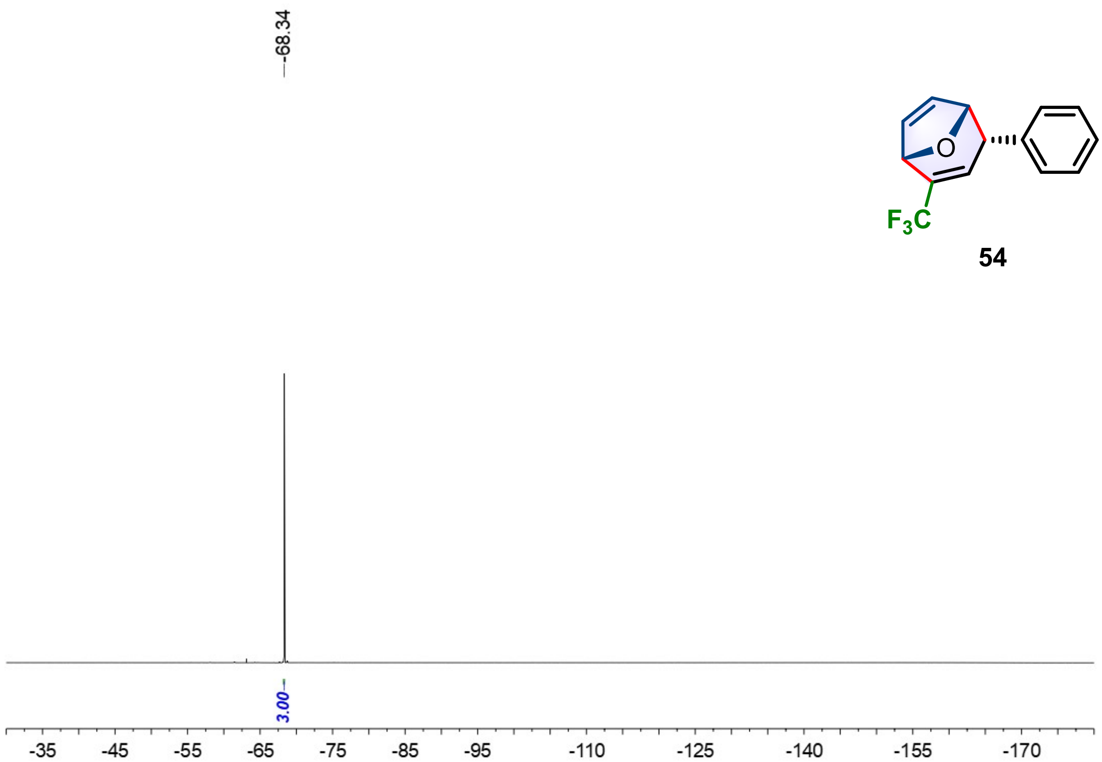


Figure S115. ^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of **54**.

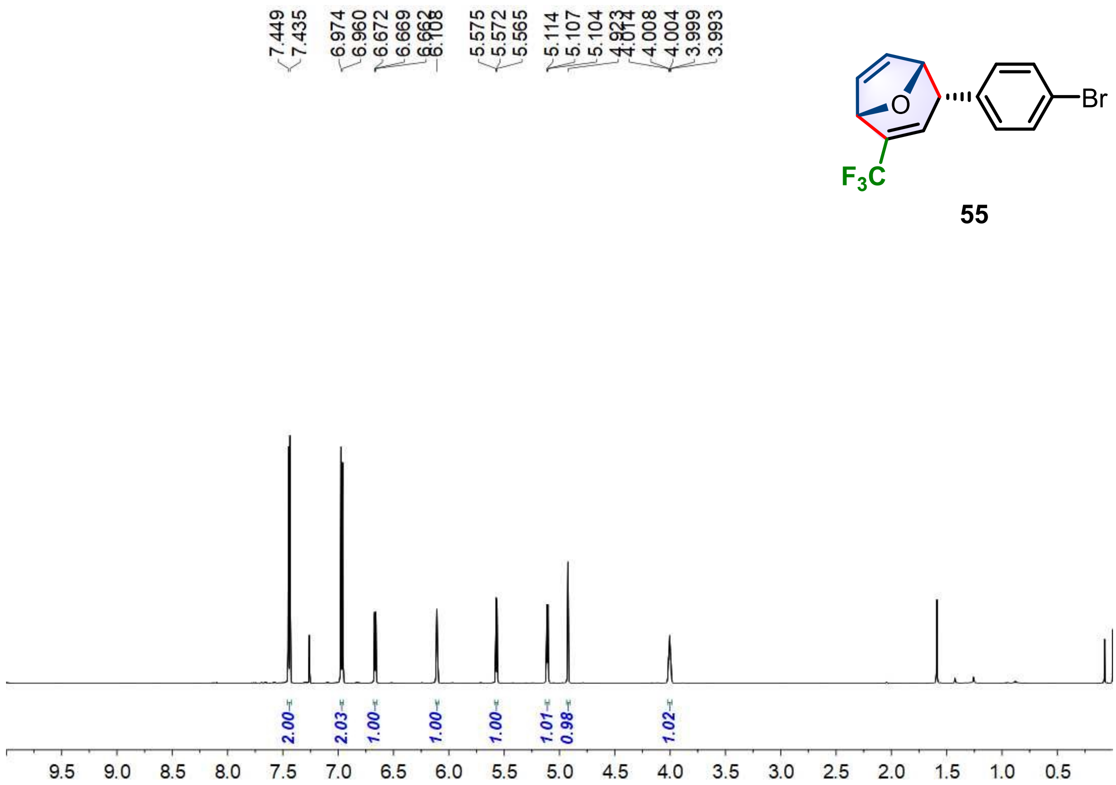


Figure S116. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **55**.

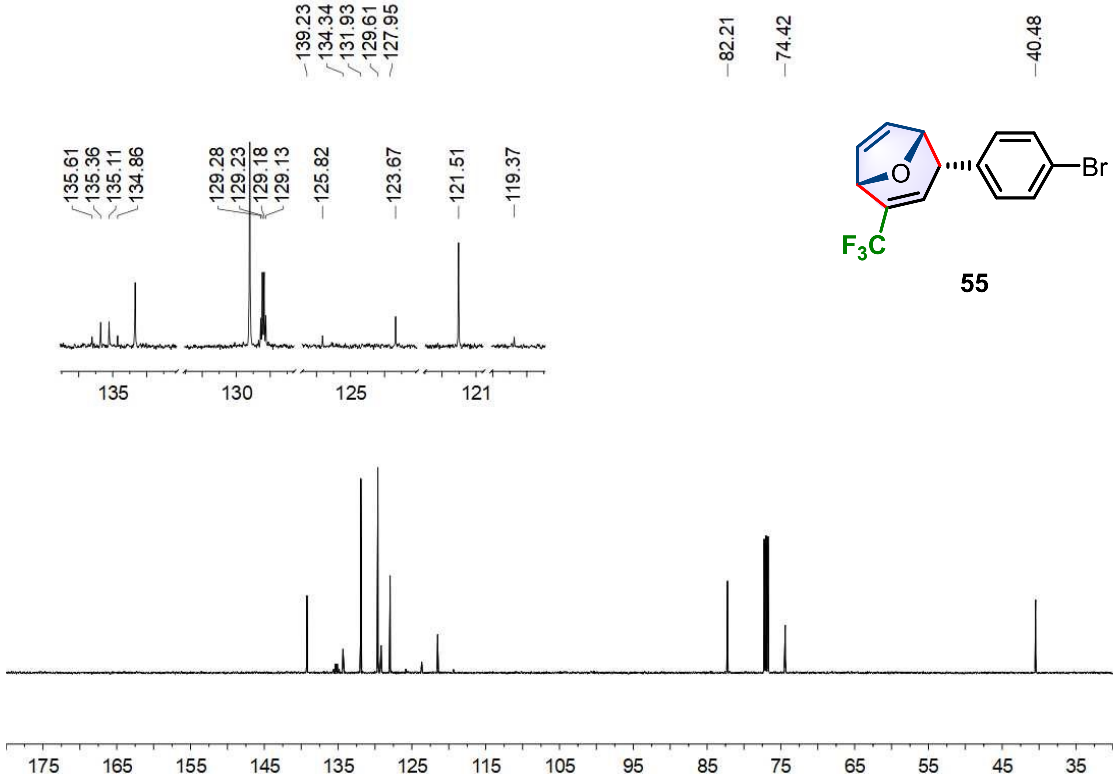


Figure S117. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **55**.

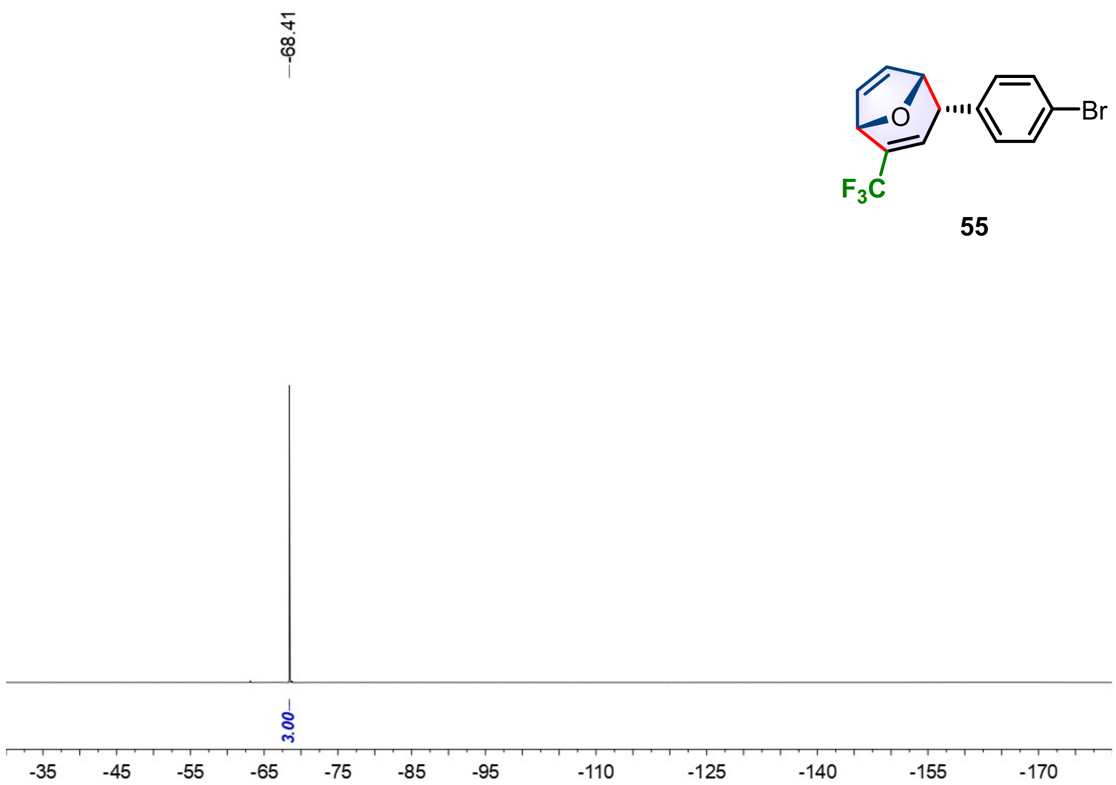


Figure S118. ^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of **55**.

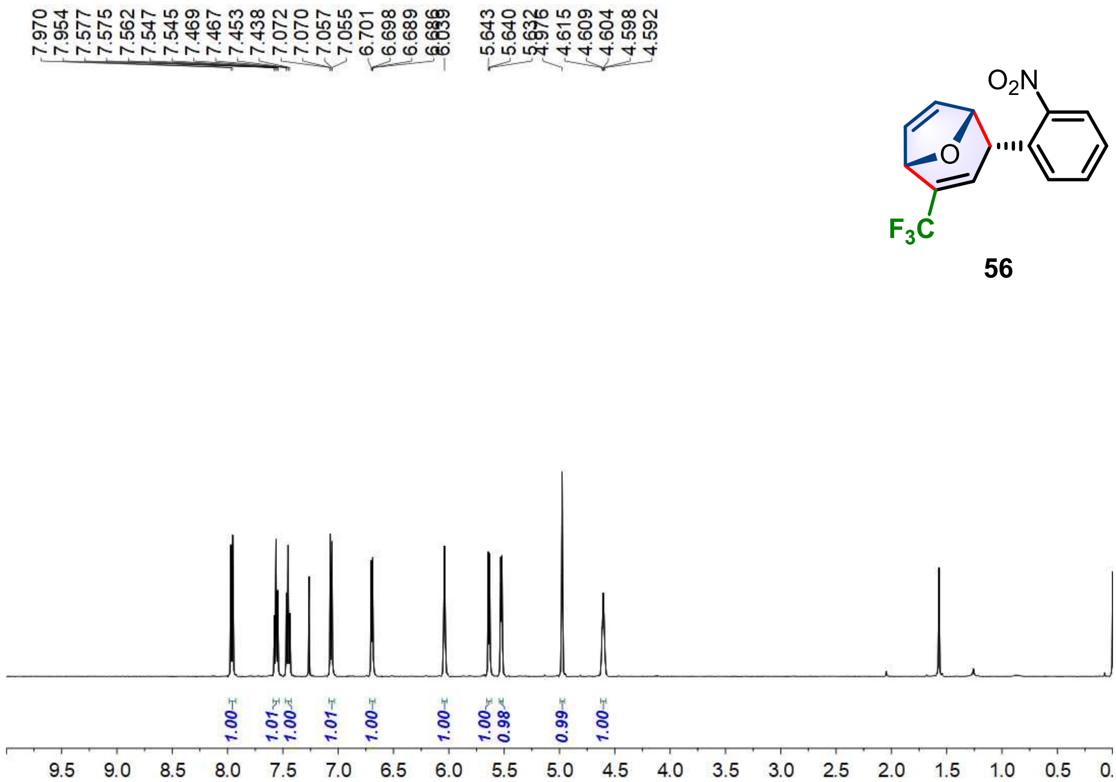


Figure S119. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **56**.

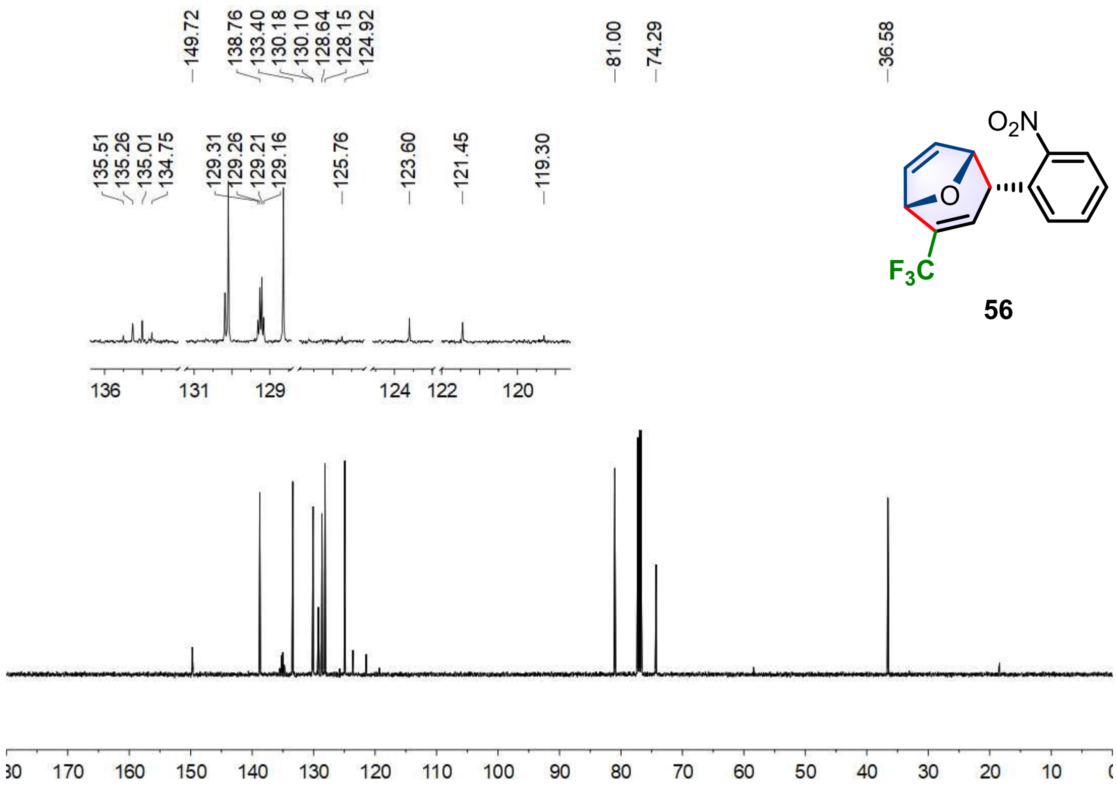


Figure S120. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **56**.

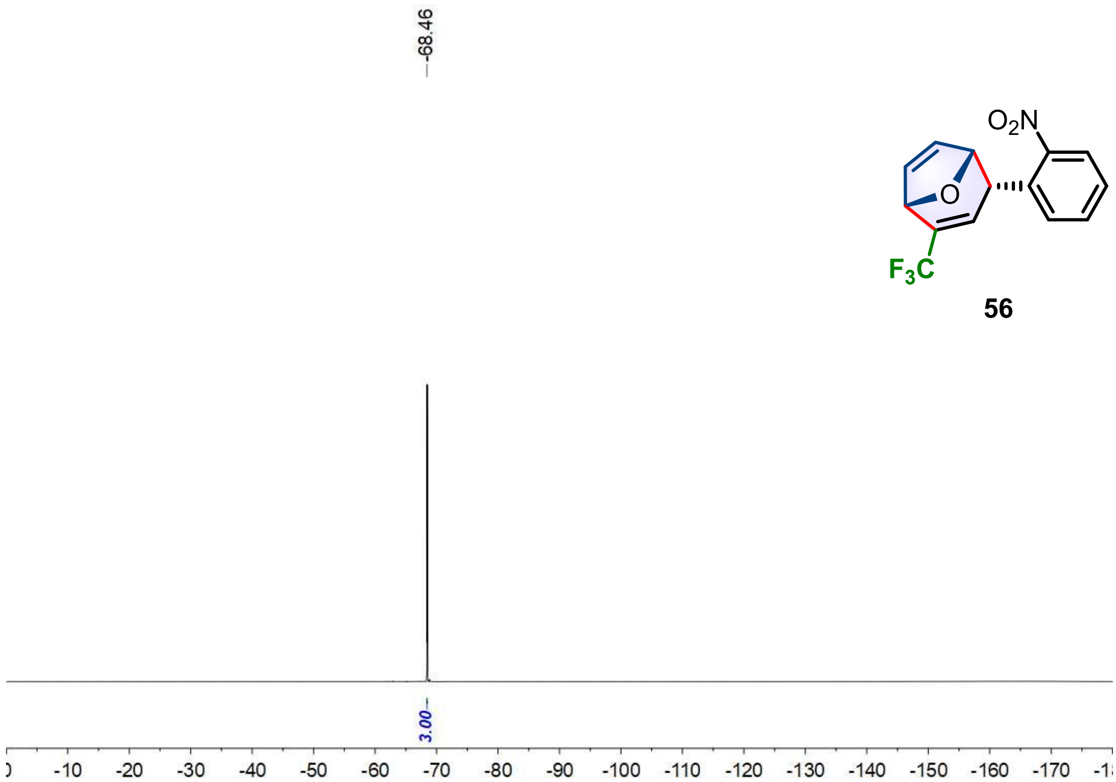


Figure S121. ^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of **56**.

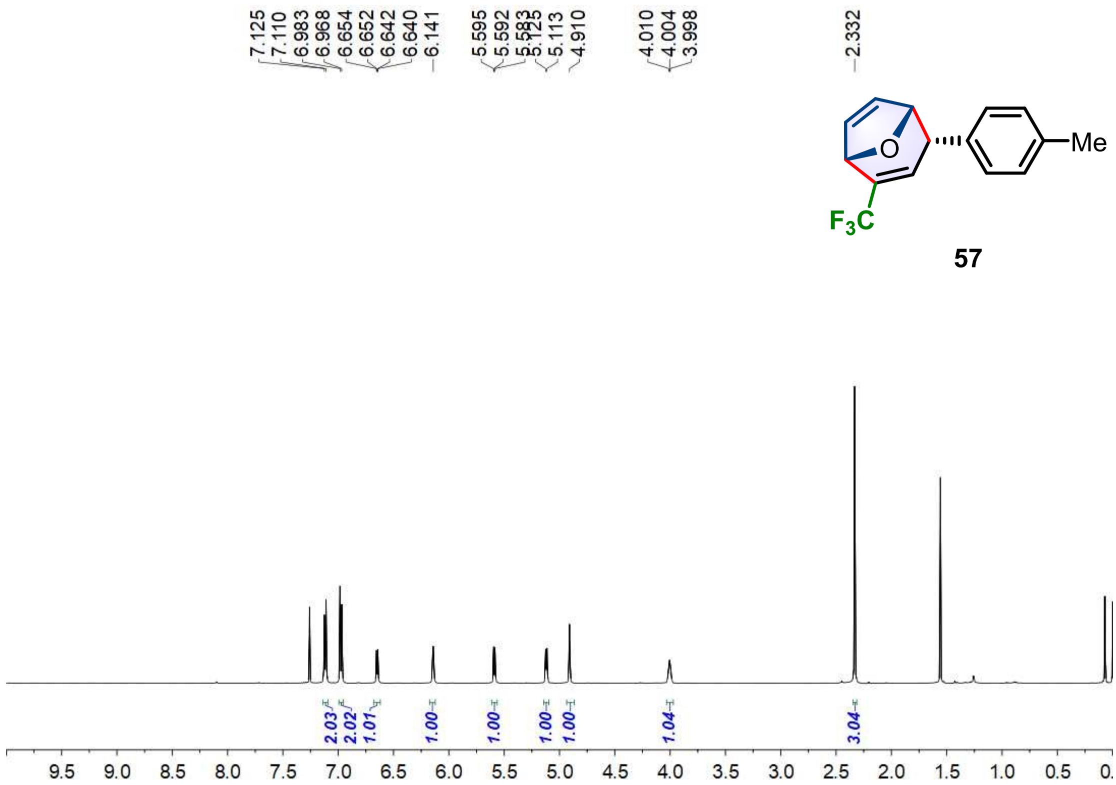


Figure S122. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **57**.

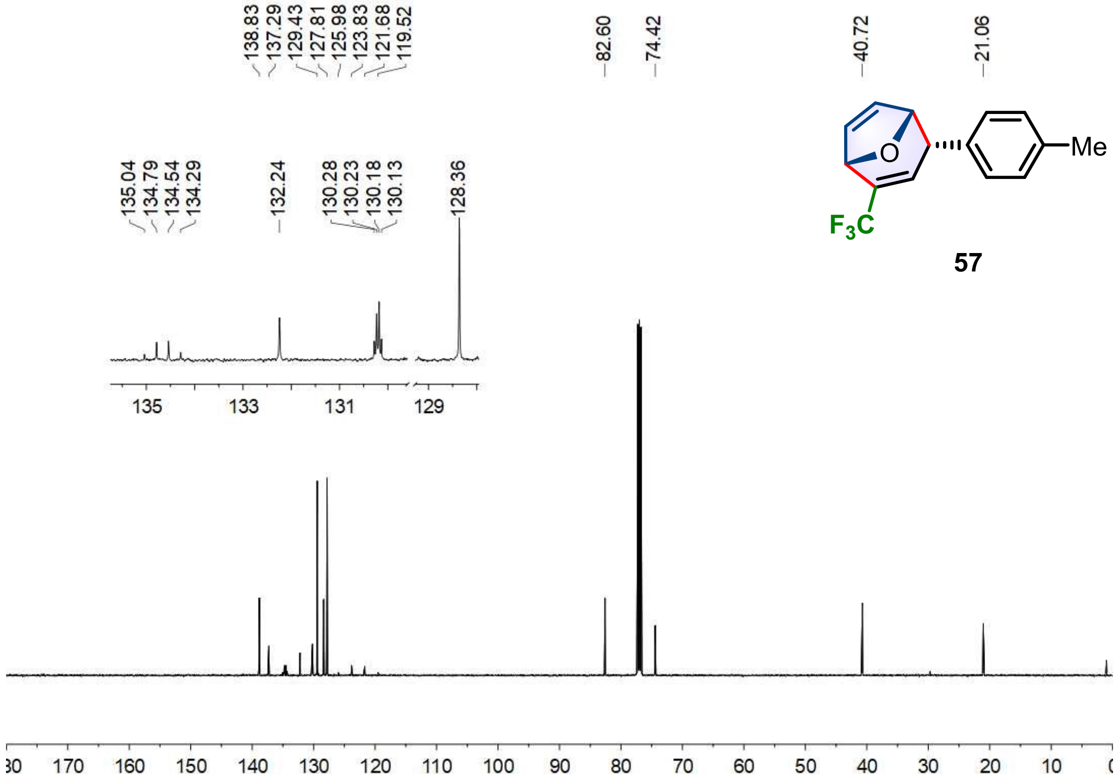


Figure S123 ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **57**.

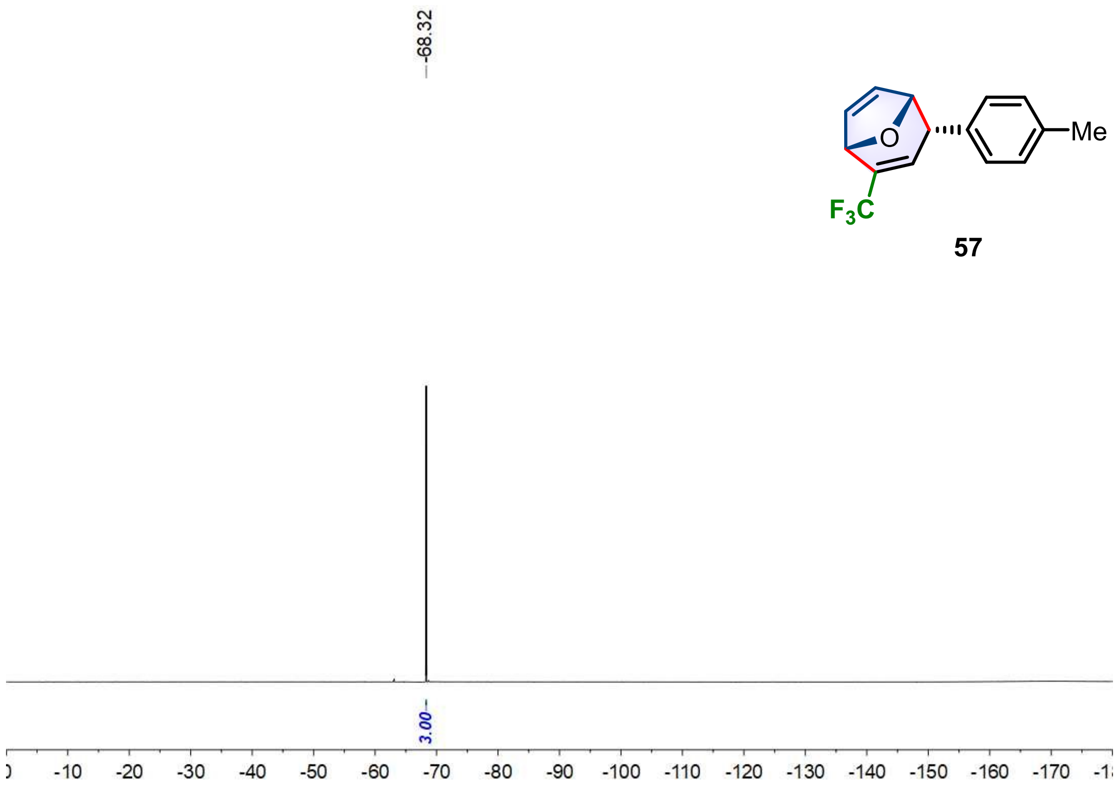


Figure S124. ^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of ^{13}C.

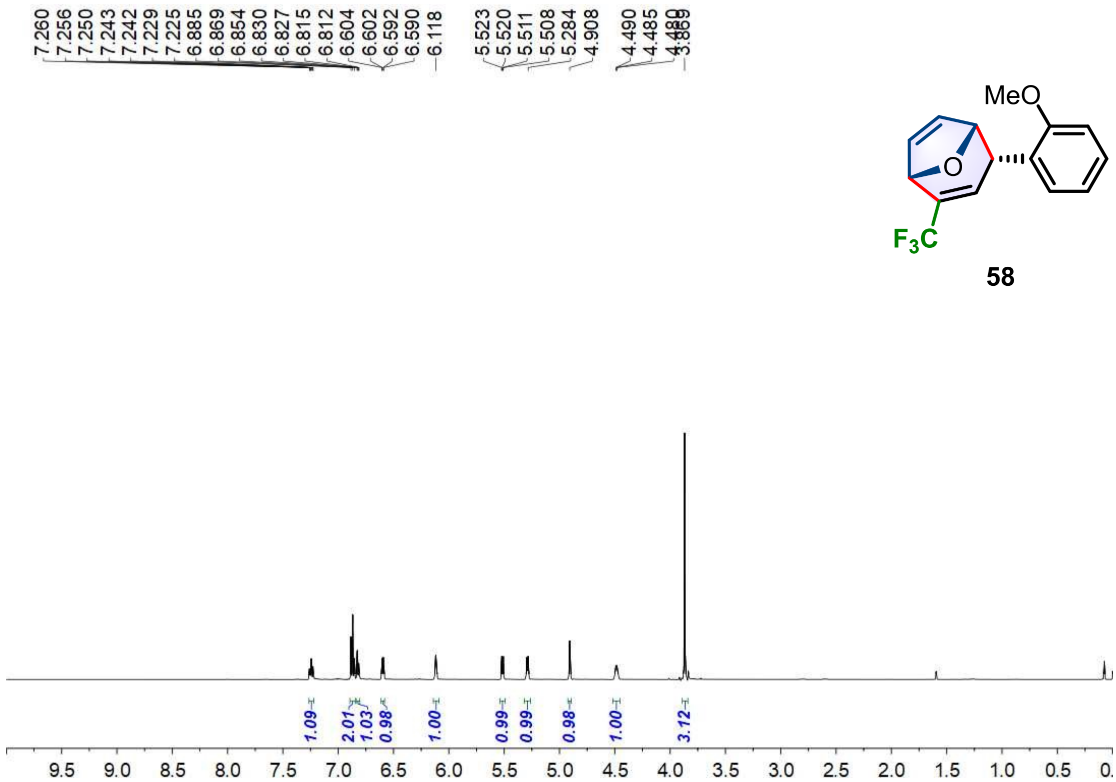


Figure S125. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **58**.

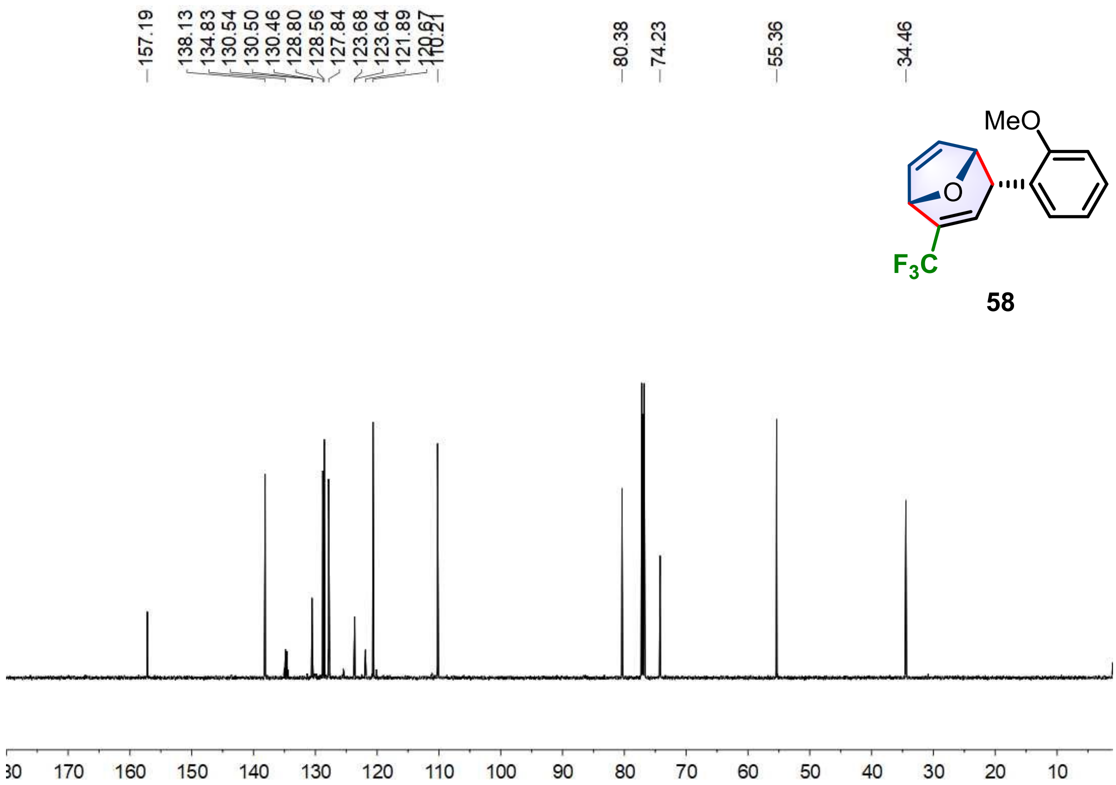


Figure S126. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **58**.

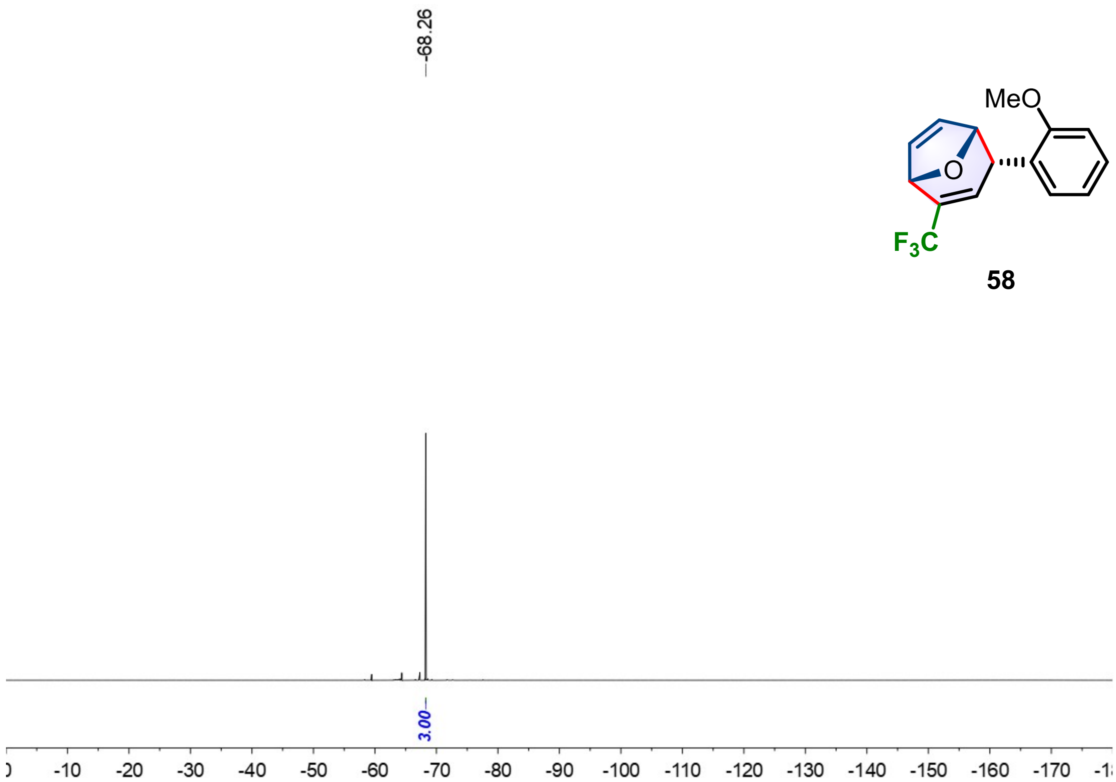


Figure S127. ^{19}F NMR (600 MHz, $CDCl_3$) Spectrum of **58**.

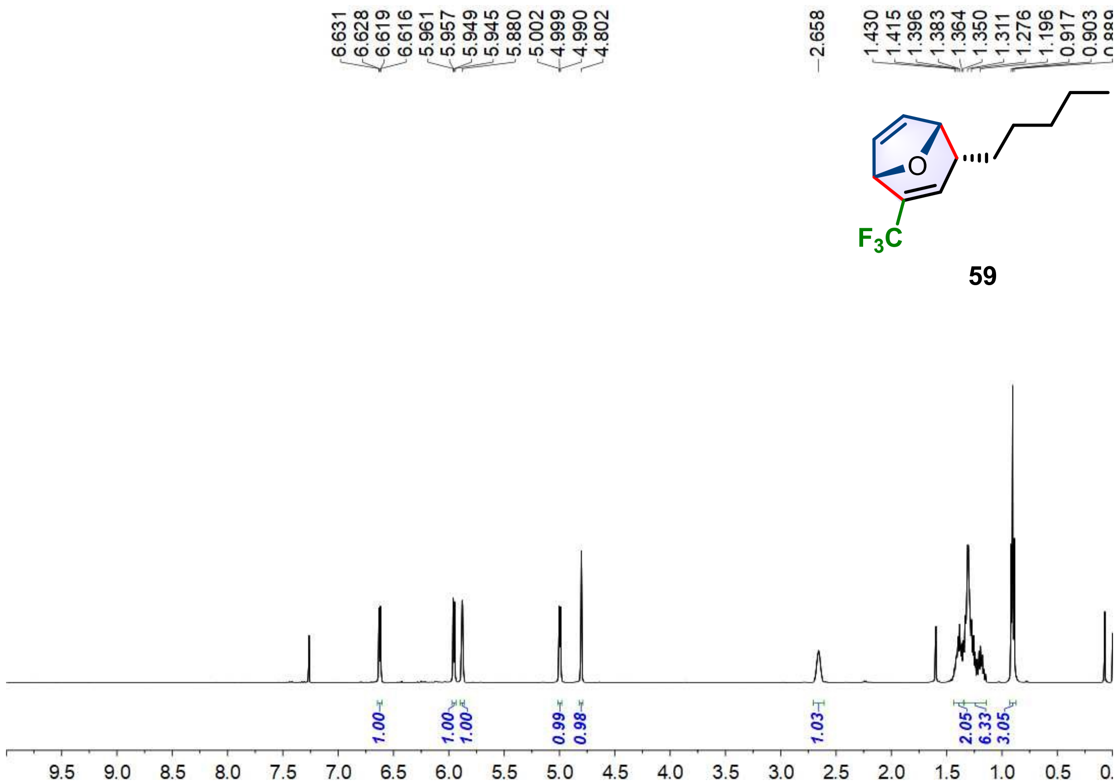


Figure S128. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **59**.

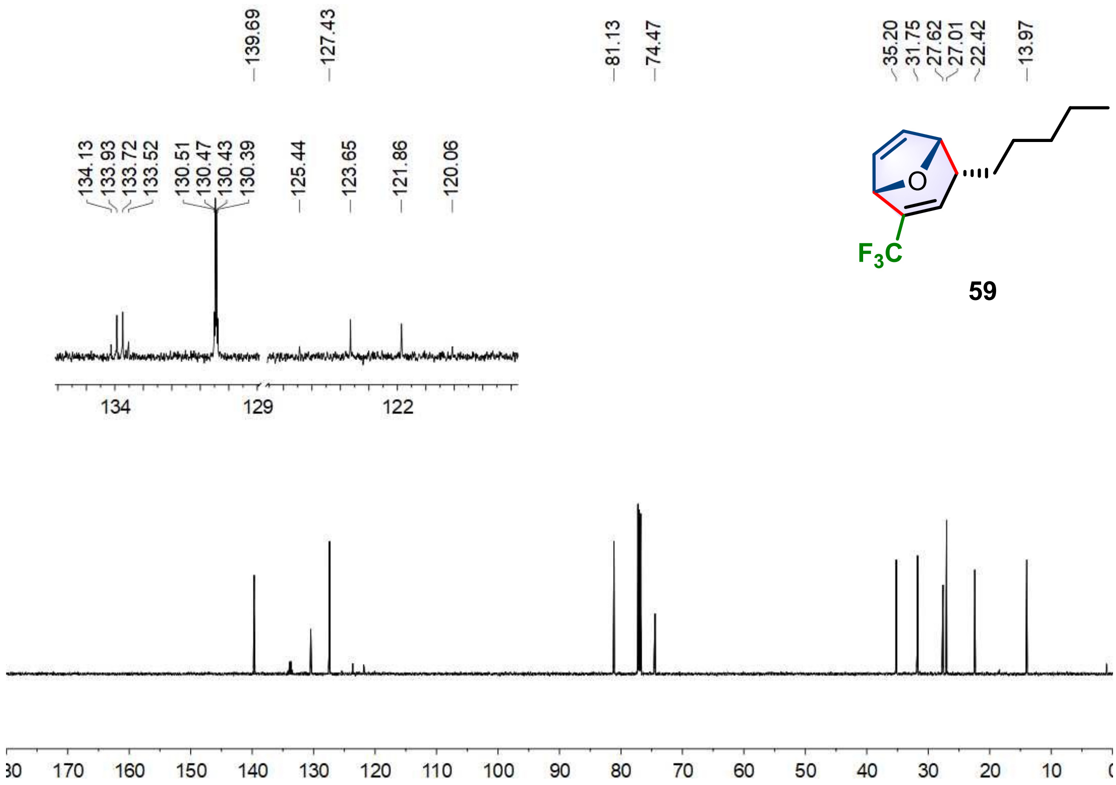


Figure S129. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **59**.

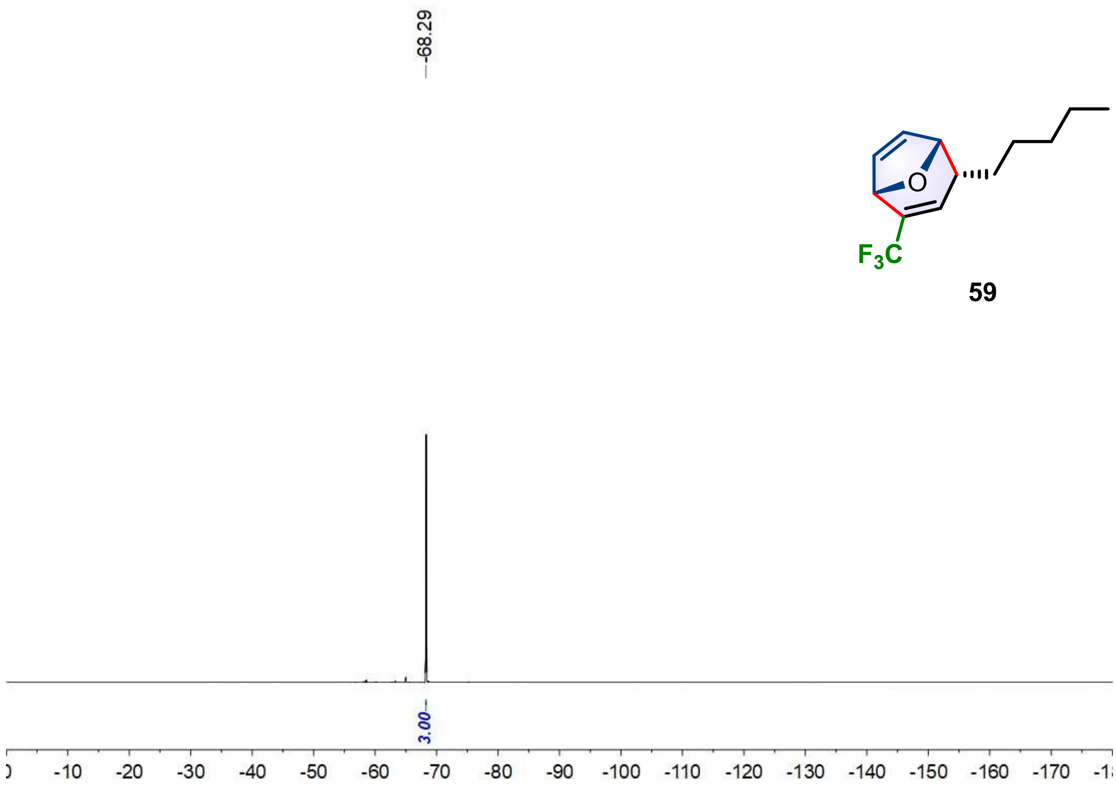


Figure S130. ^{19}F NMR (565 MHz, $CDCl_3$) Spectrum of **59**.

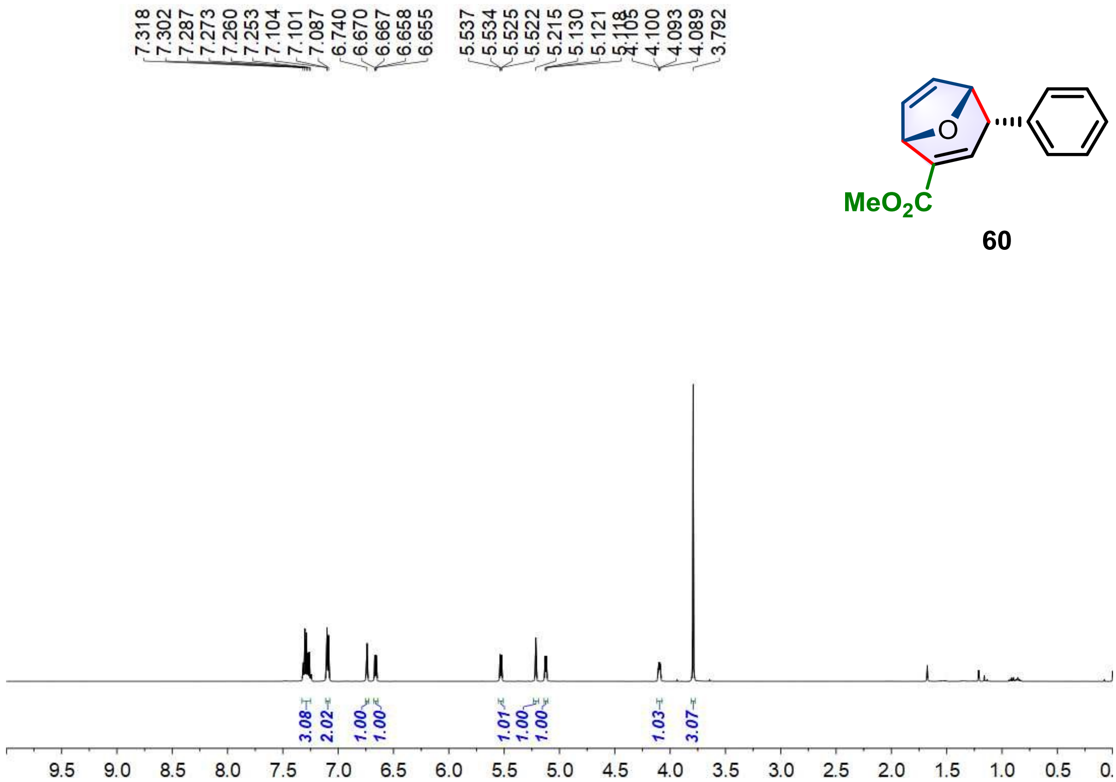


Figure S131. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **60**.

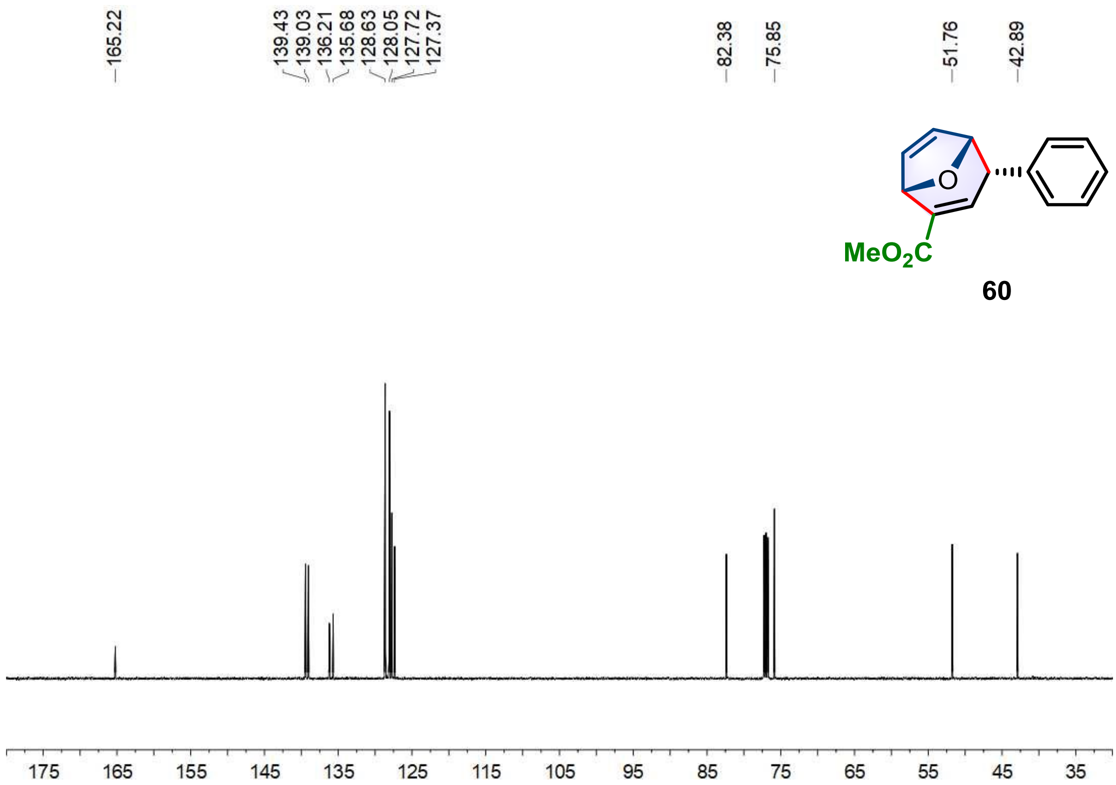


Figure S132. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **60**.

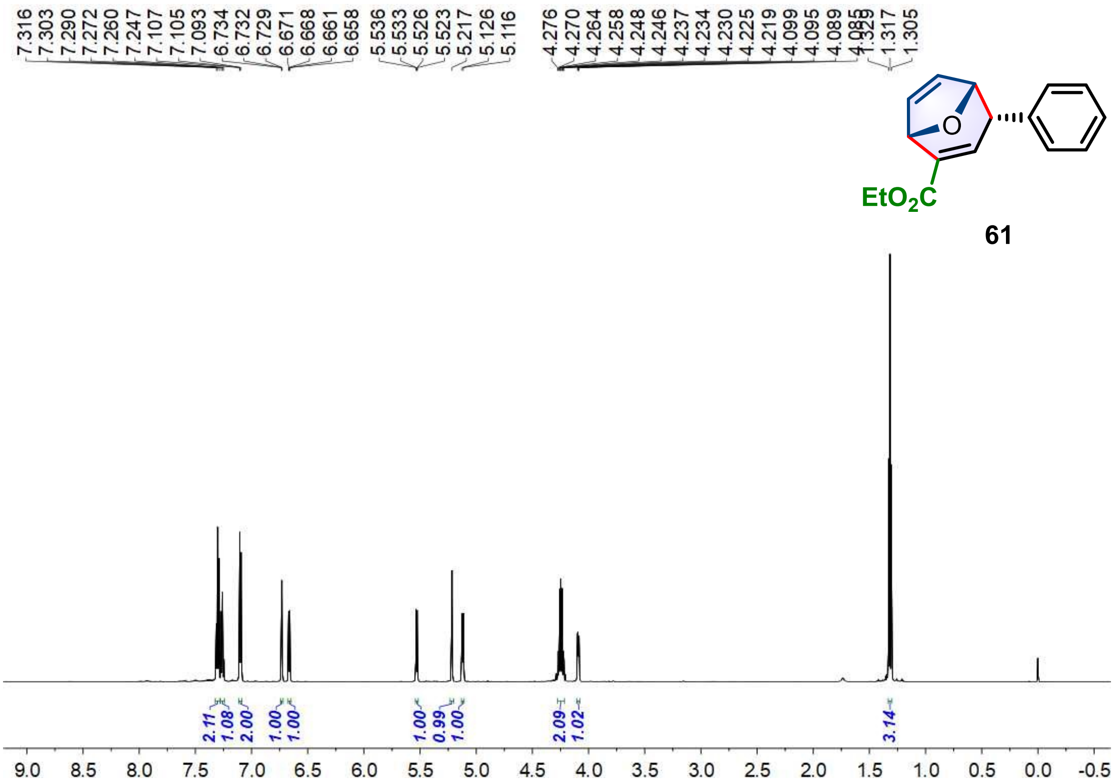


Figure S133. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **61**.

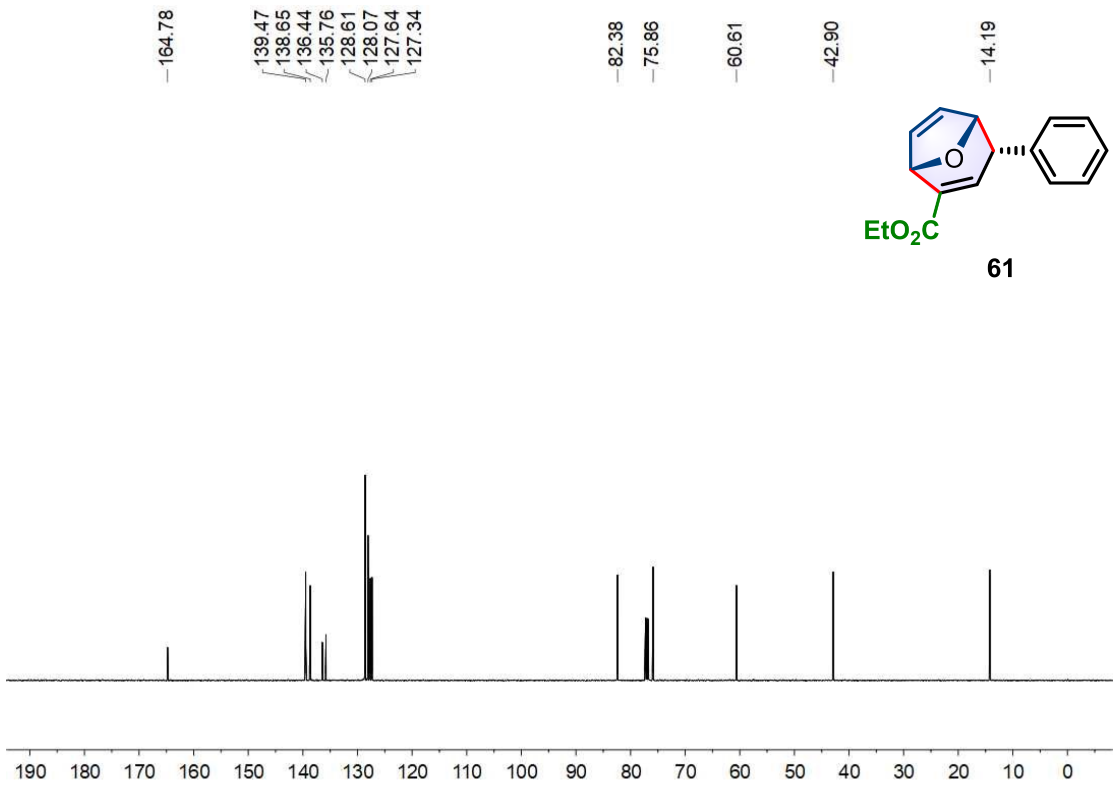


Figure S134. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **61**.

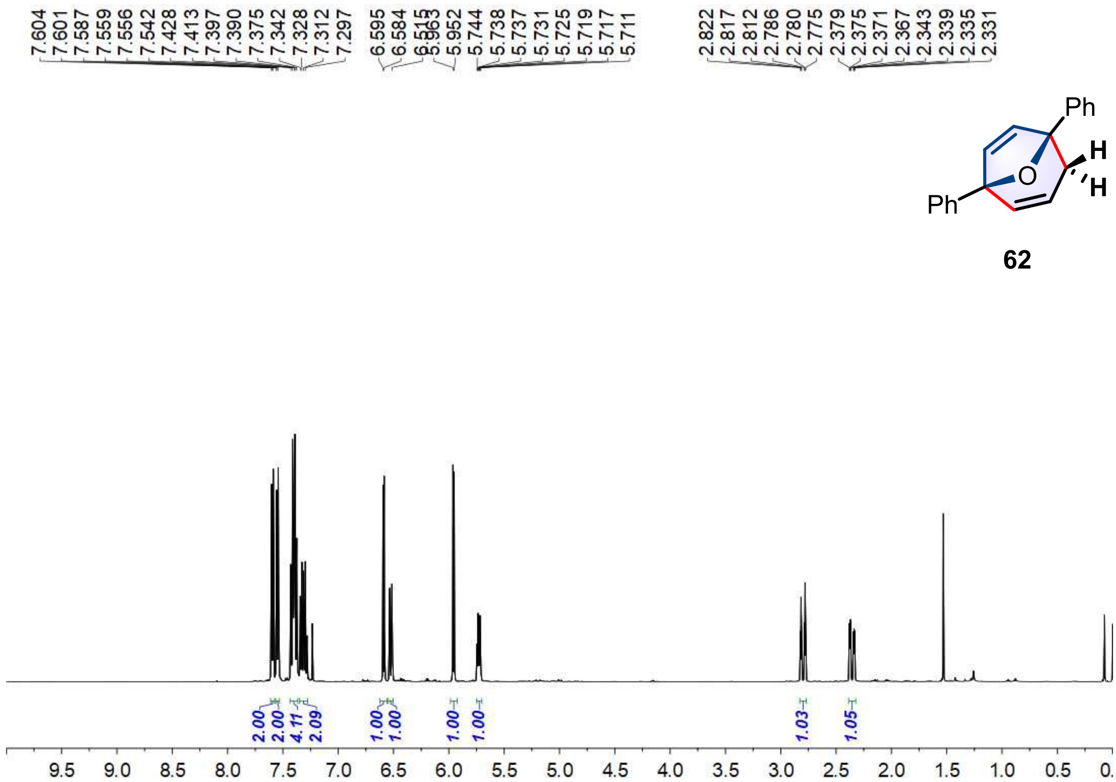


Figure S135. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **62**.

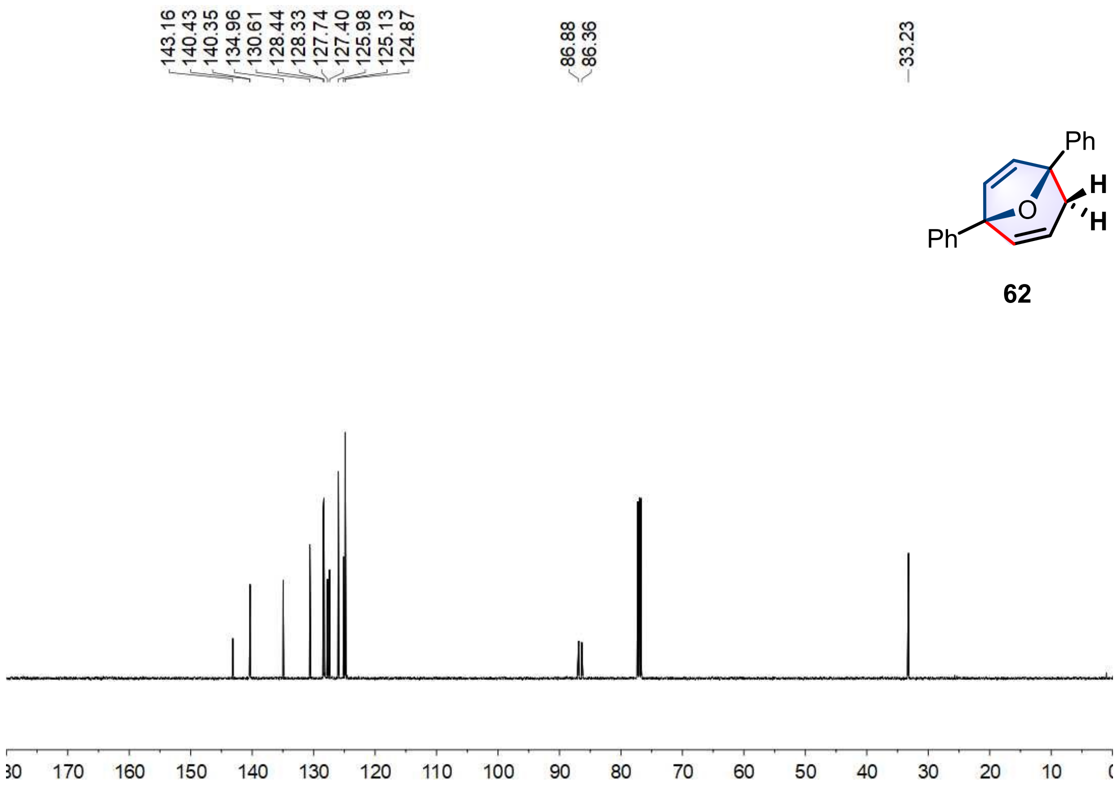


Figure S136. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **62**.

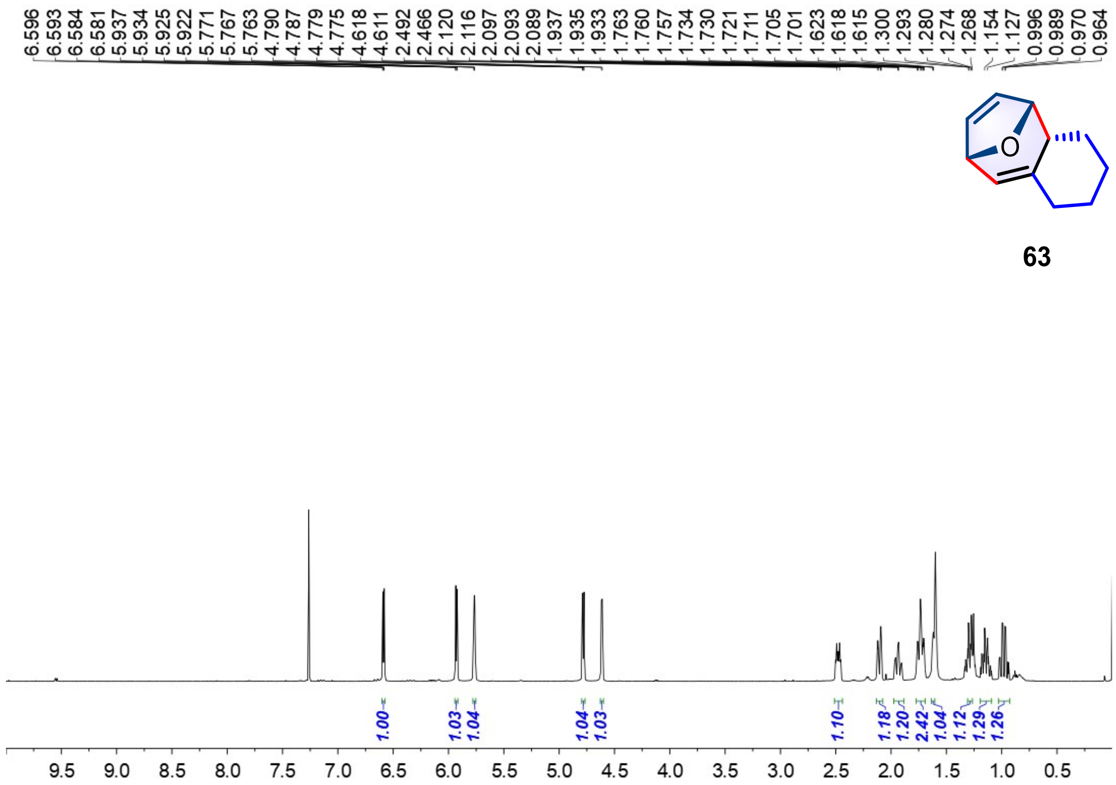


Figure S137. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **63**.

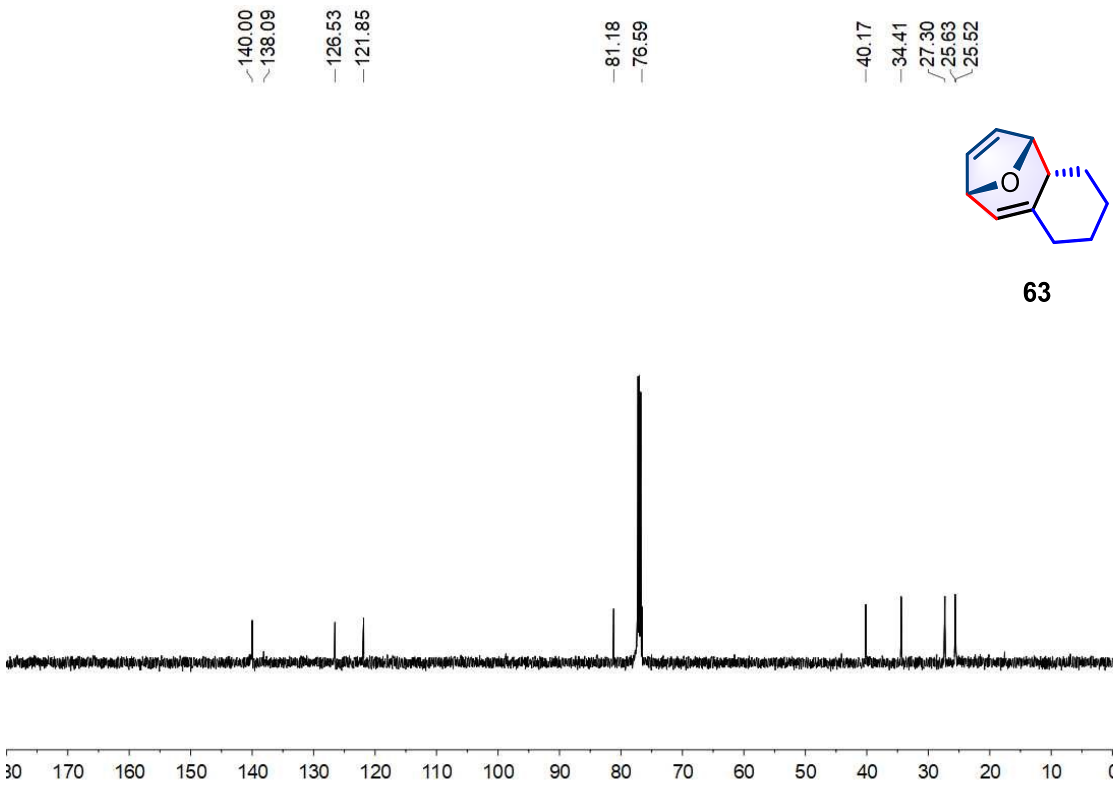


Figure S138. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **63**.

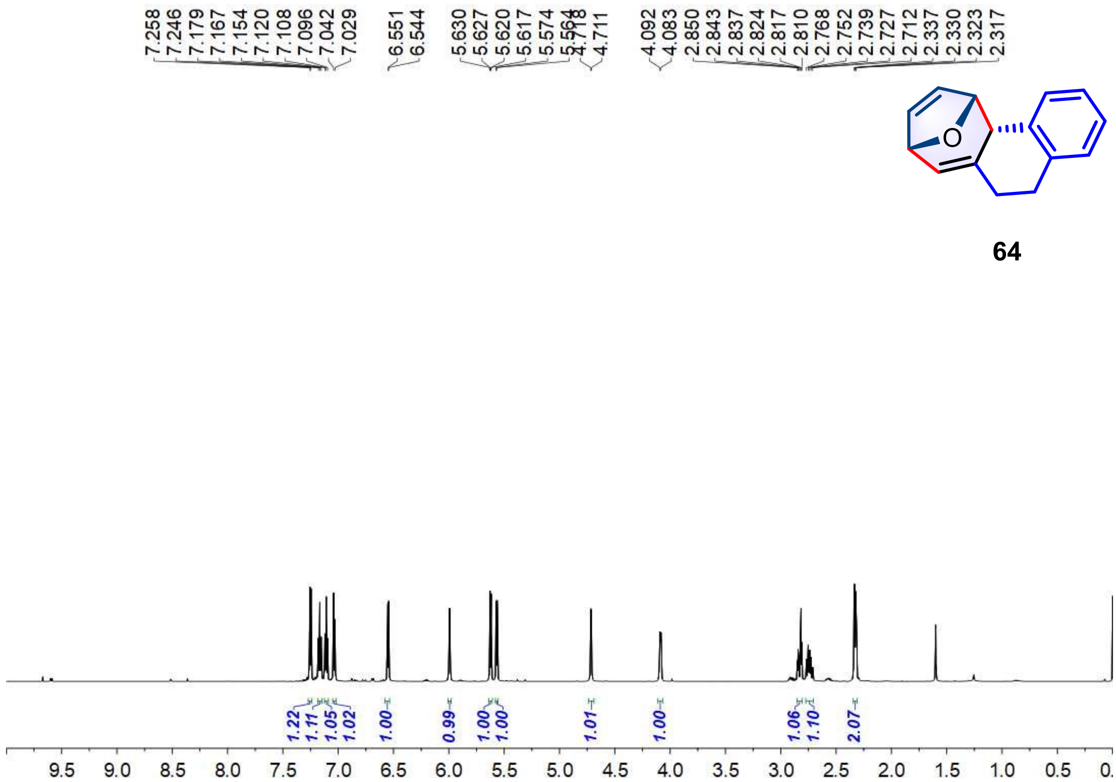


Figure S139. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **64**.

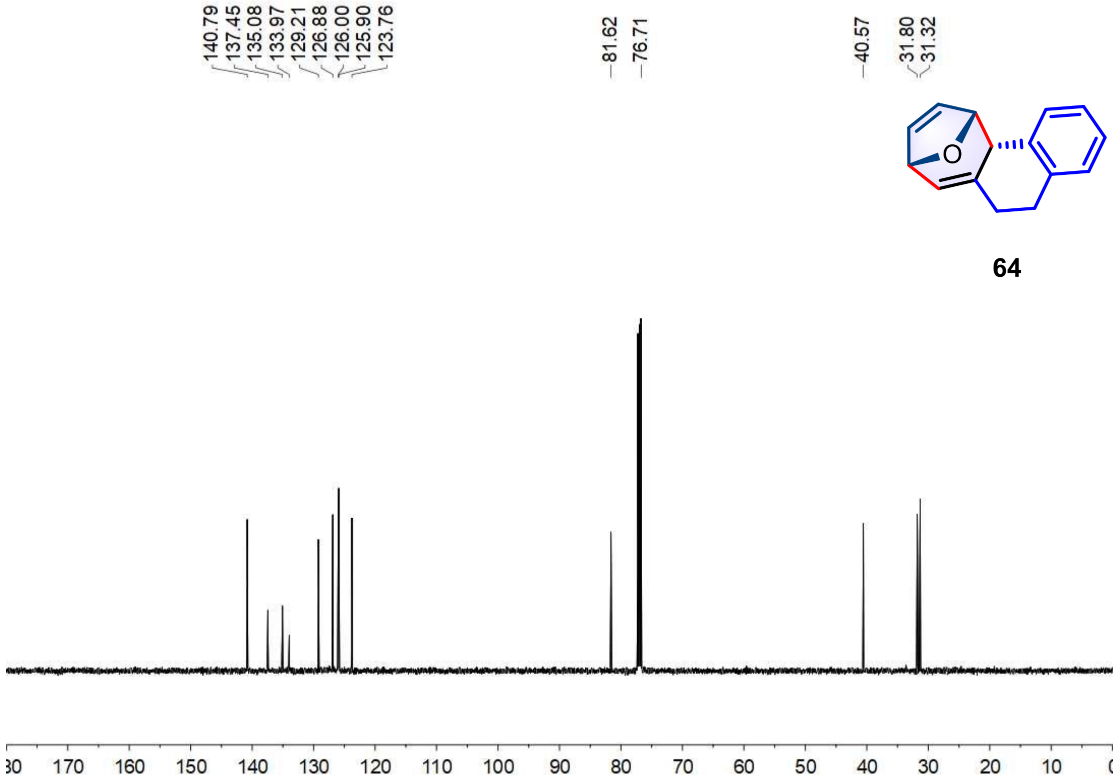


Figure S140. ^{13}C NMR 126 MHz, $CDCl_3$) Spectrum of **64**.

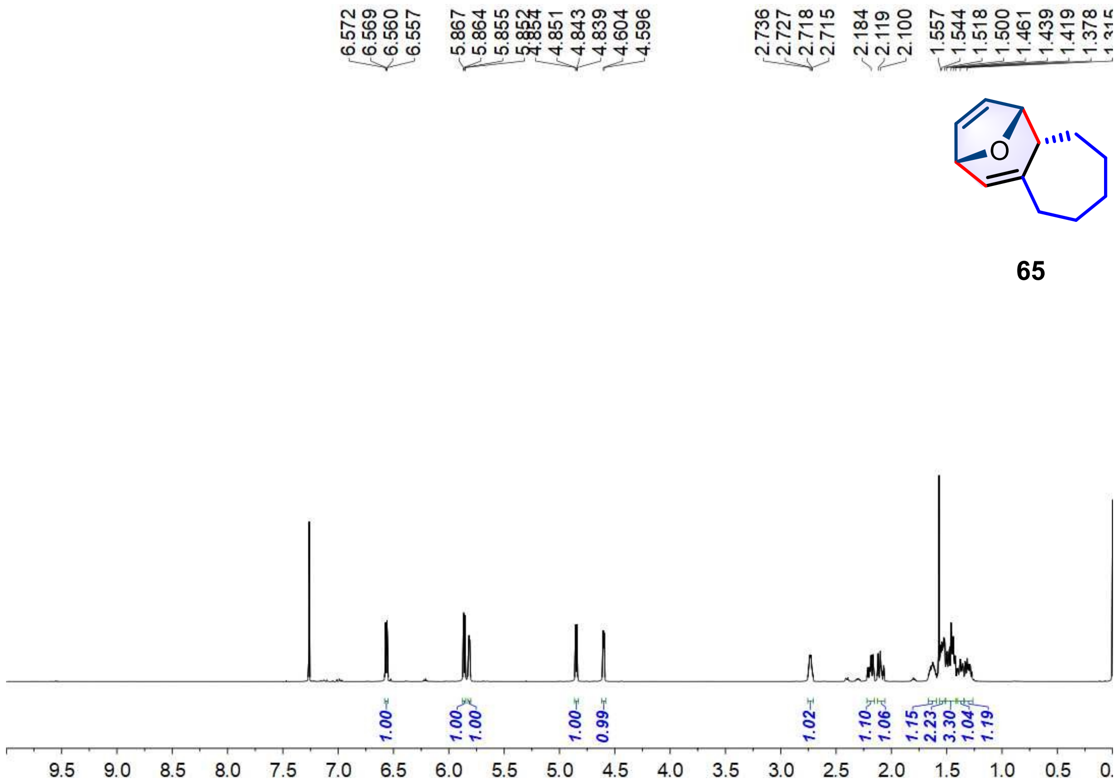


Figure S141. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **65**.

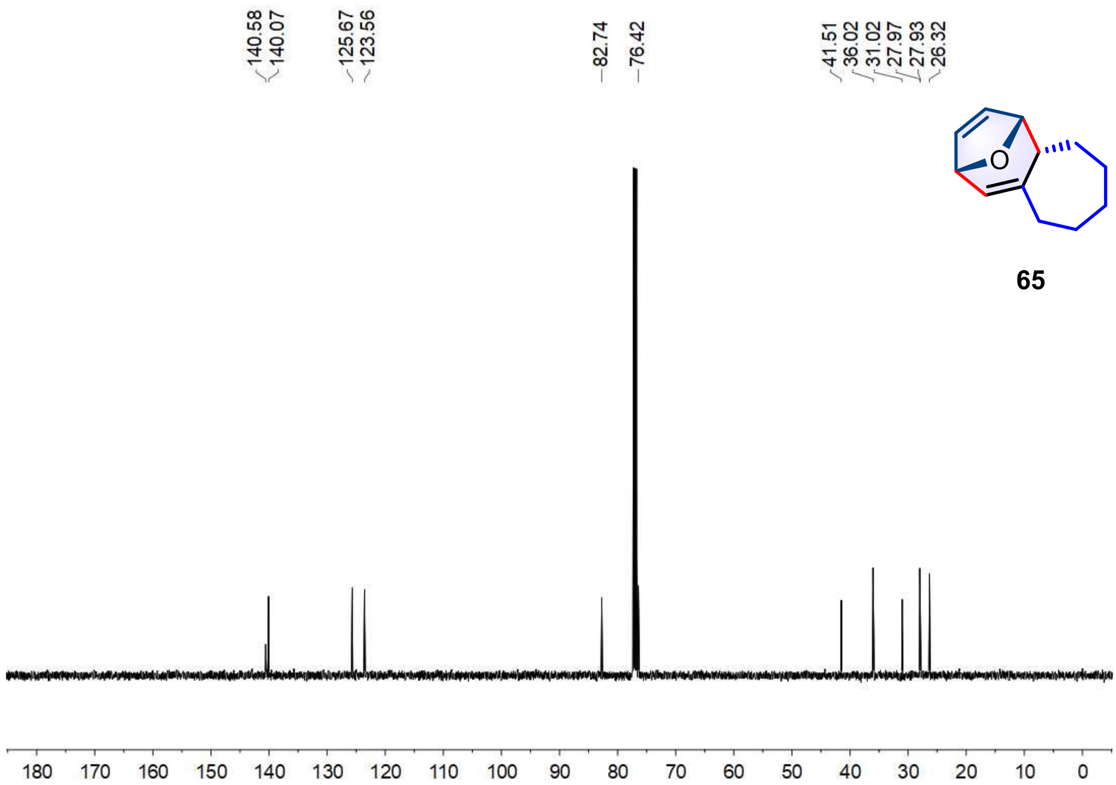


Figure S142. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **65**.

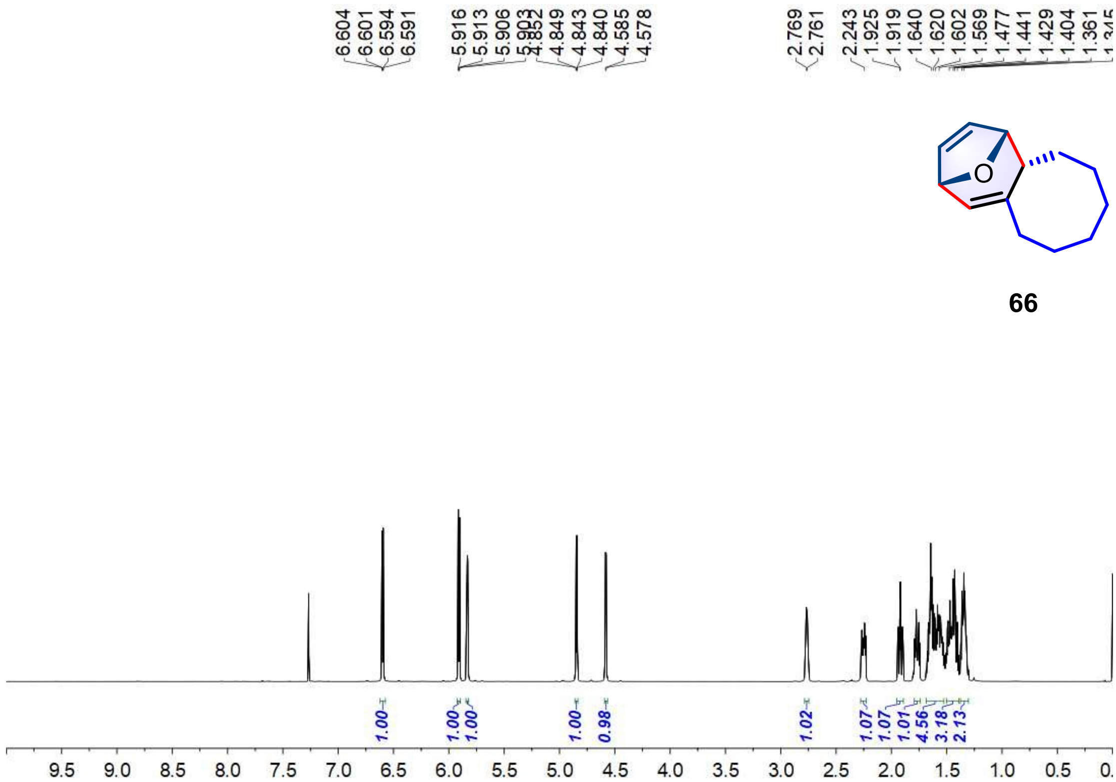


Figure S143. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **66**.

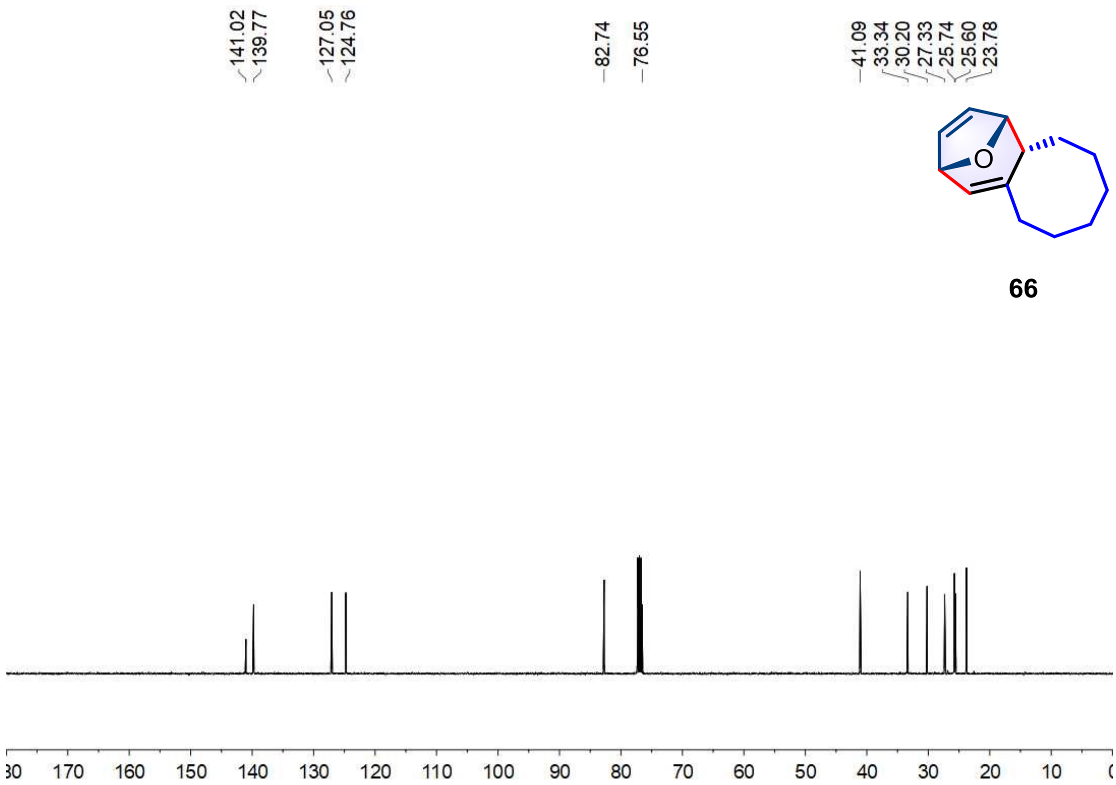


Figure S144. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **66**.

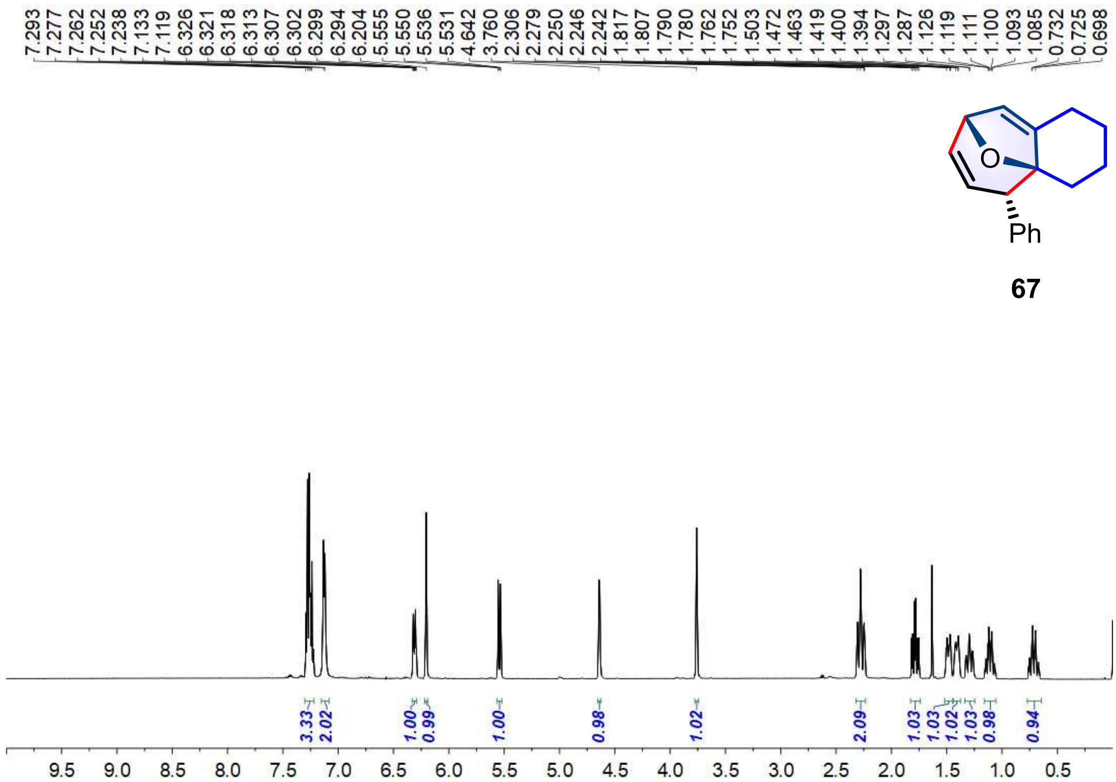


Figure S145. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **67**.

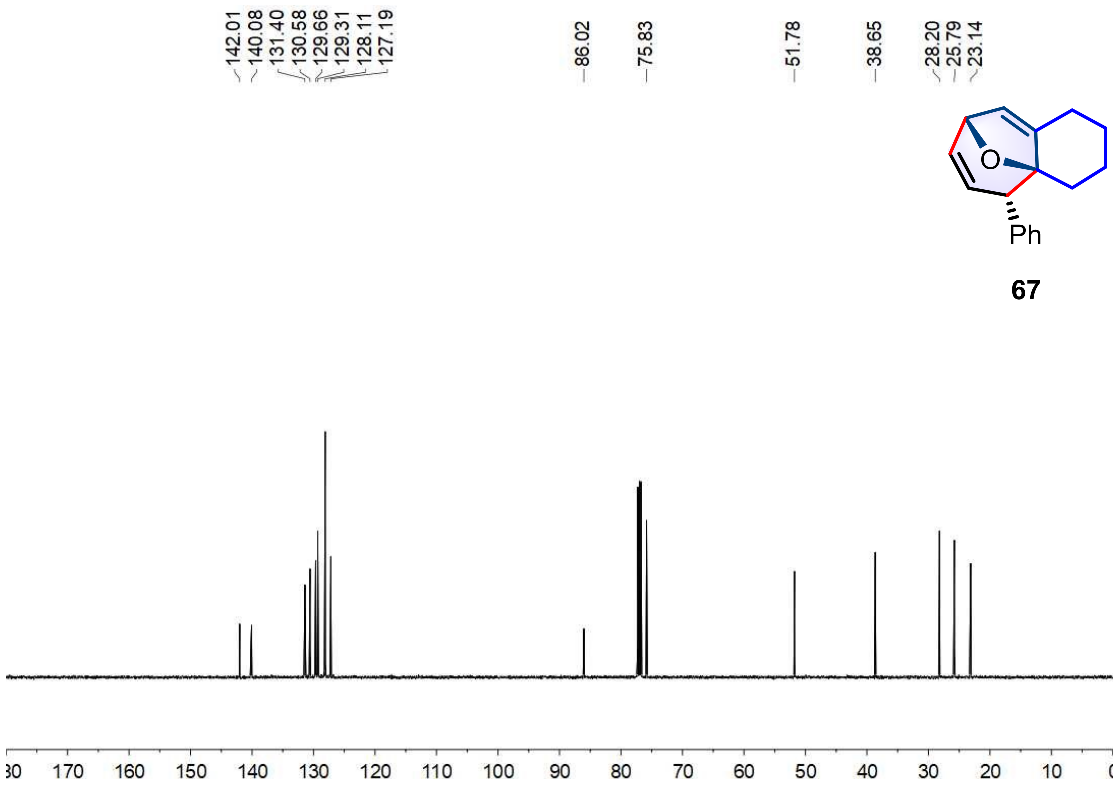


Figure S146. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **67**.

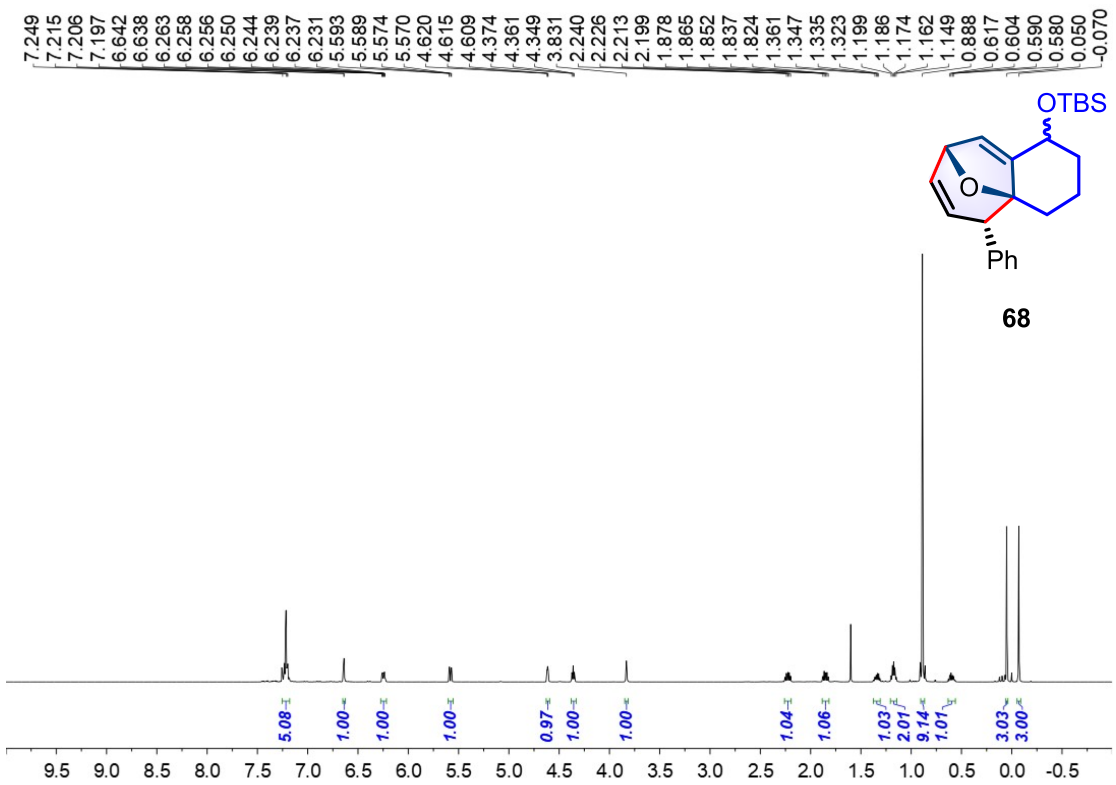


Figure S147. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **68**.

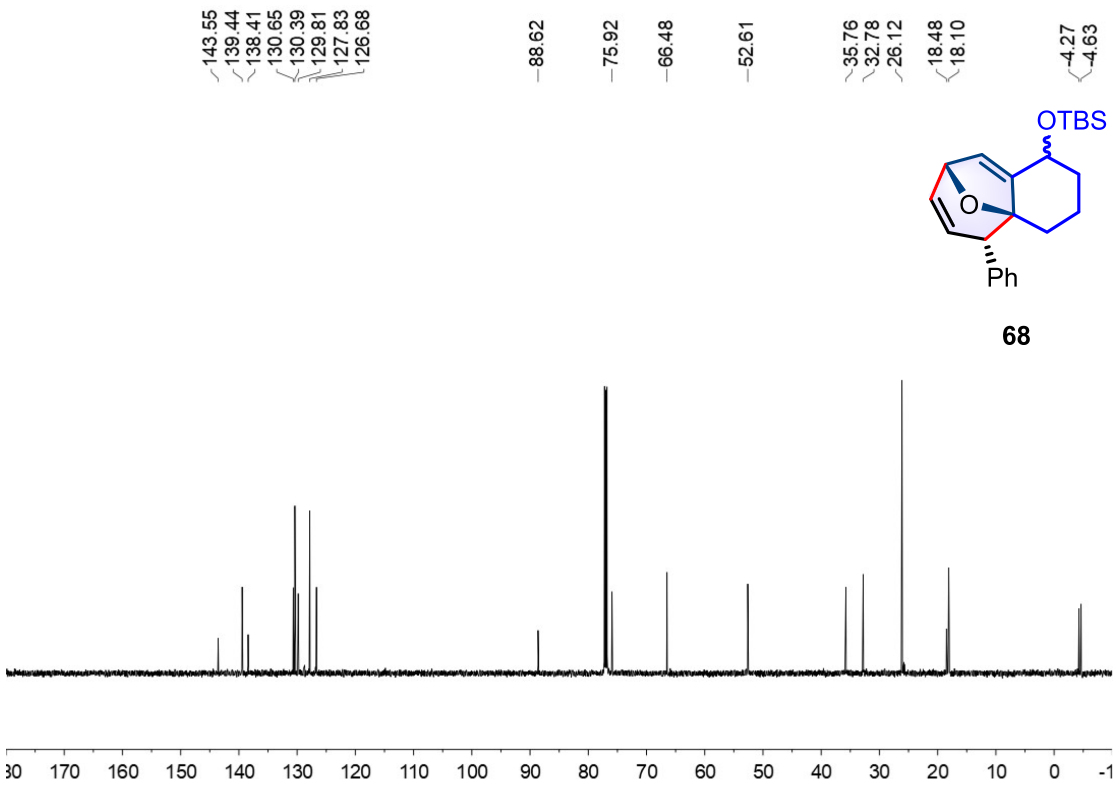


Figure S148. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **68**.

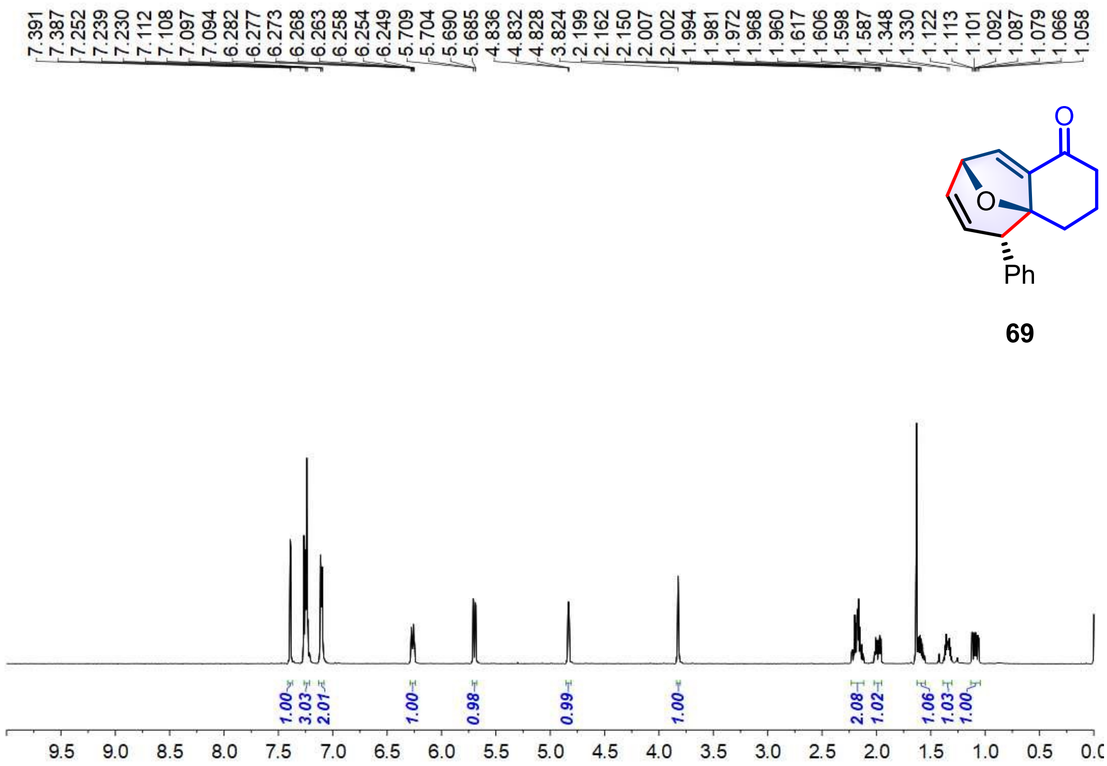


Figure S149. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **69**.

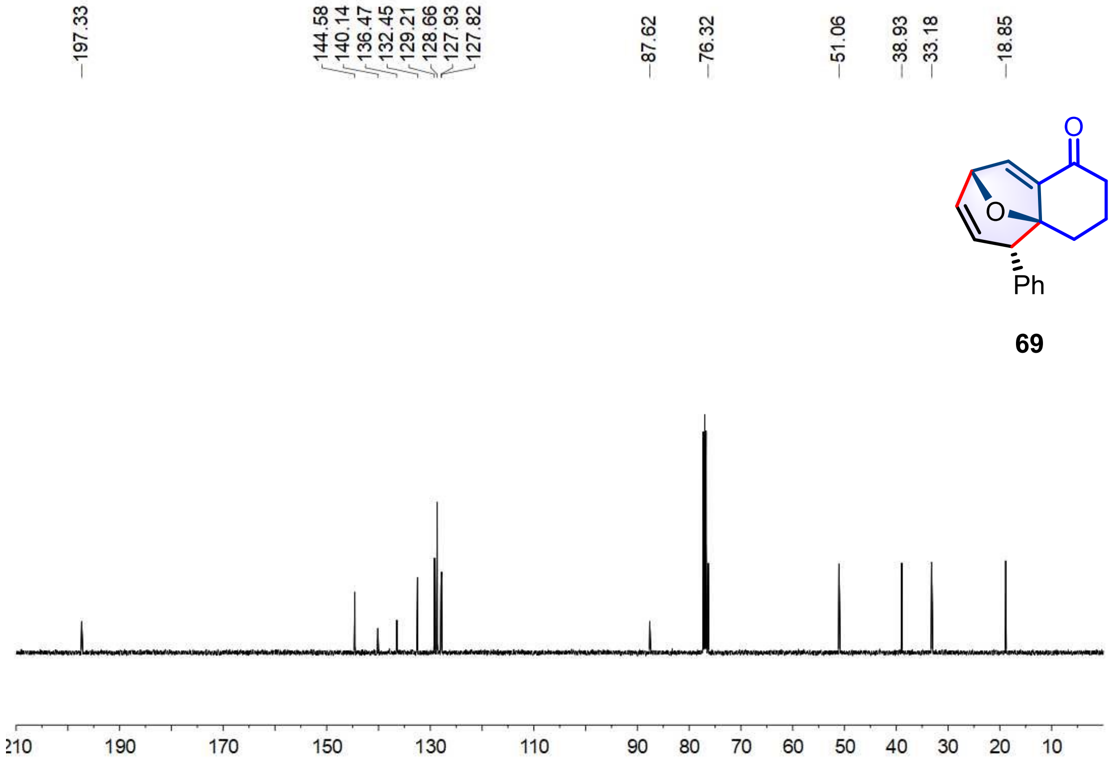


Figure S150. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **69**.

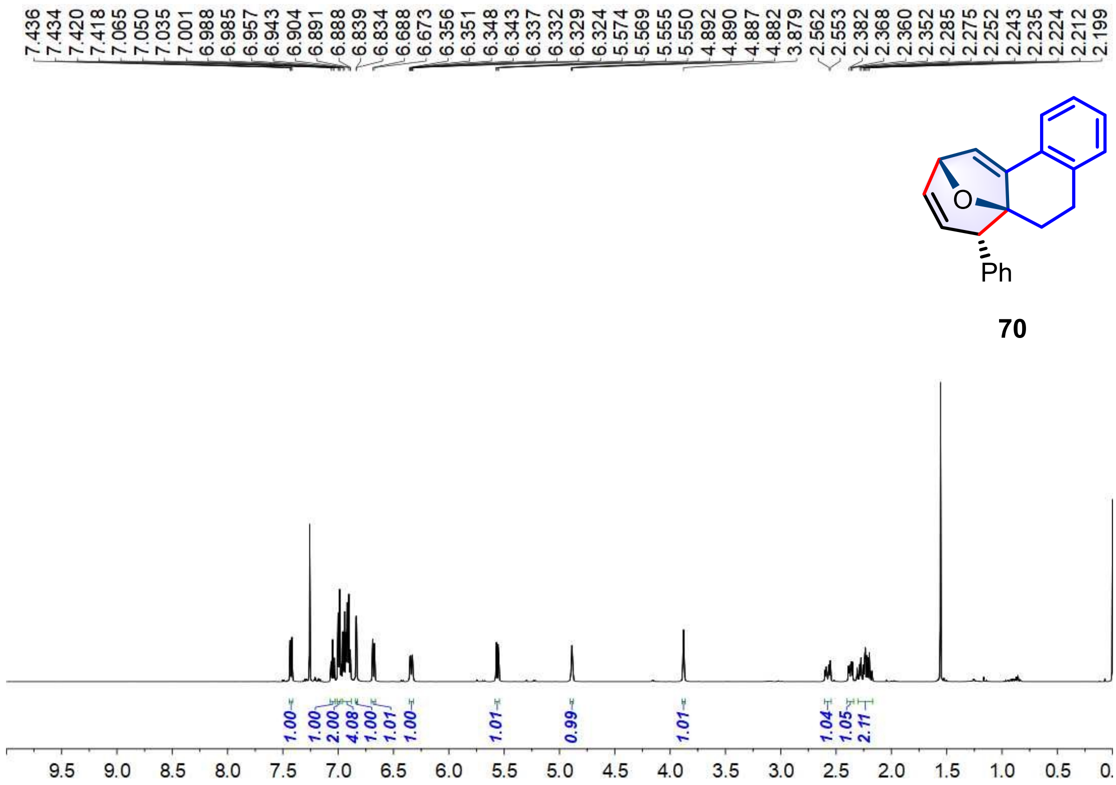


Figure S151. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **70**.

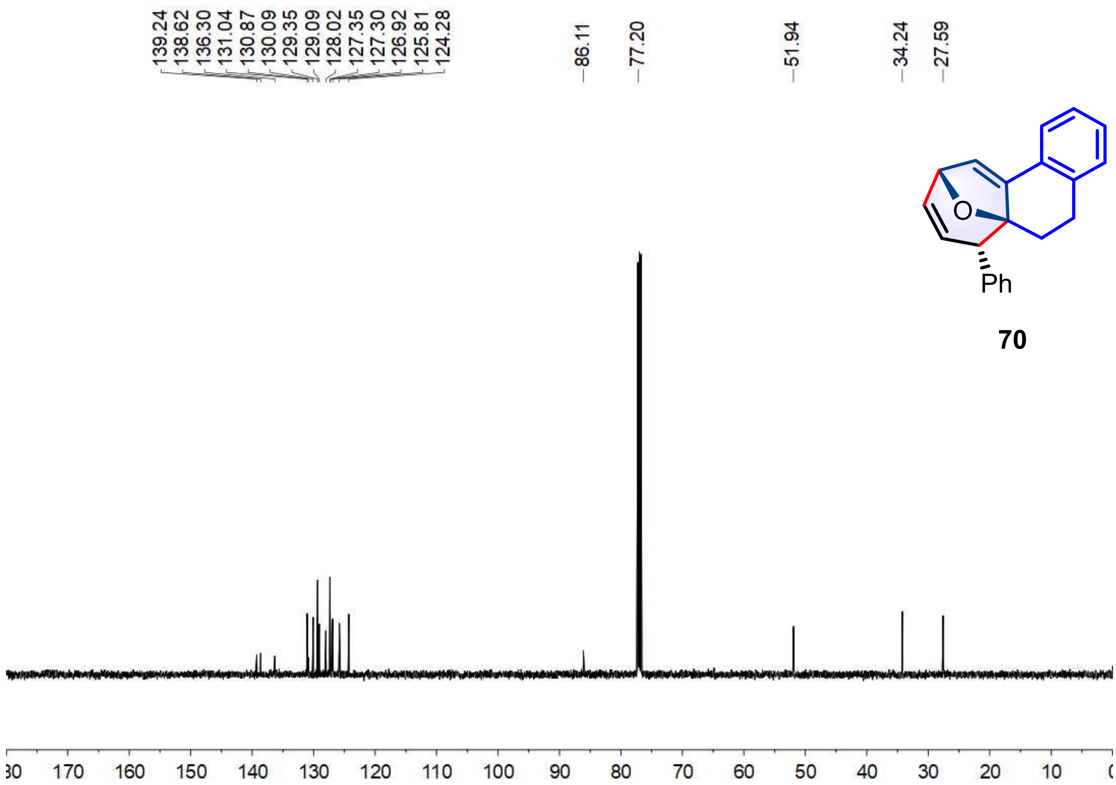


Figure S152. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **70**.

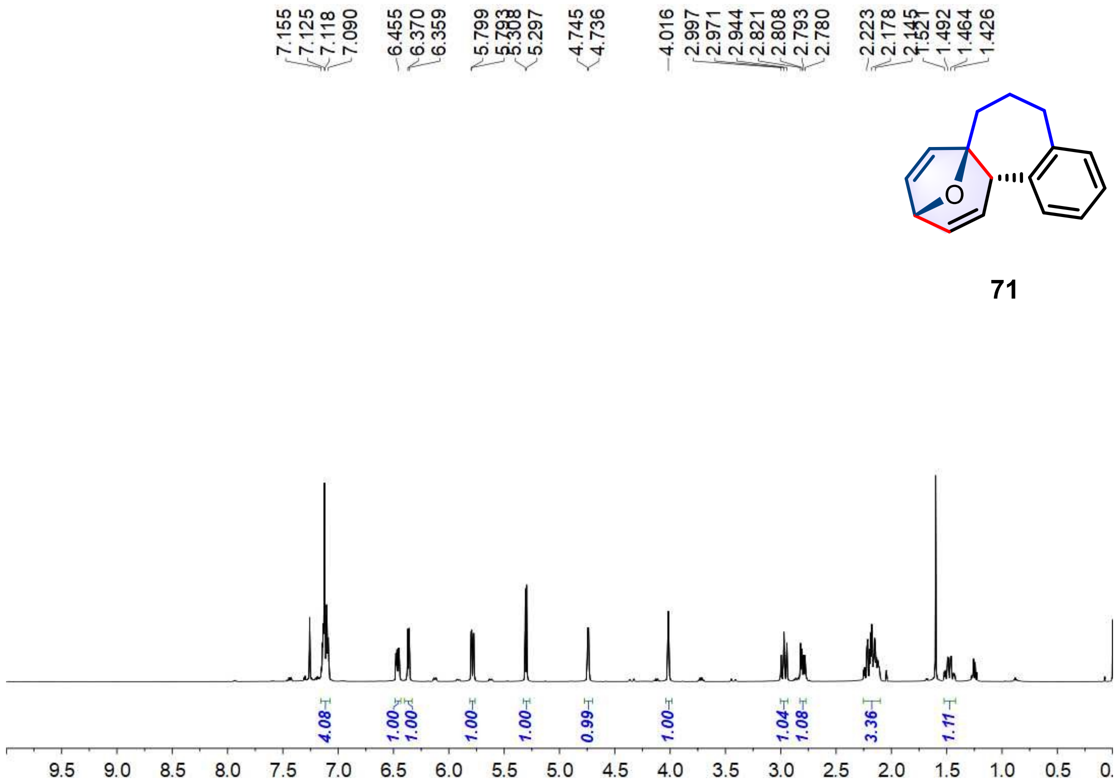


Figure S153. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **71**.

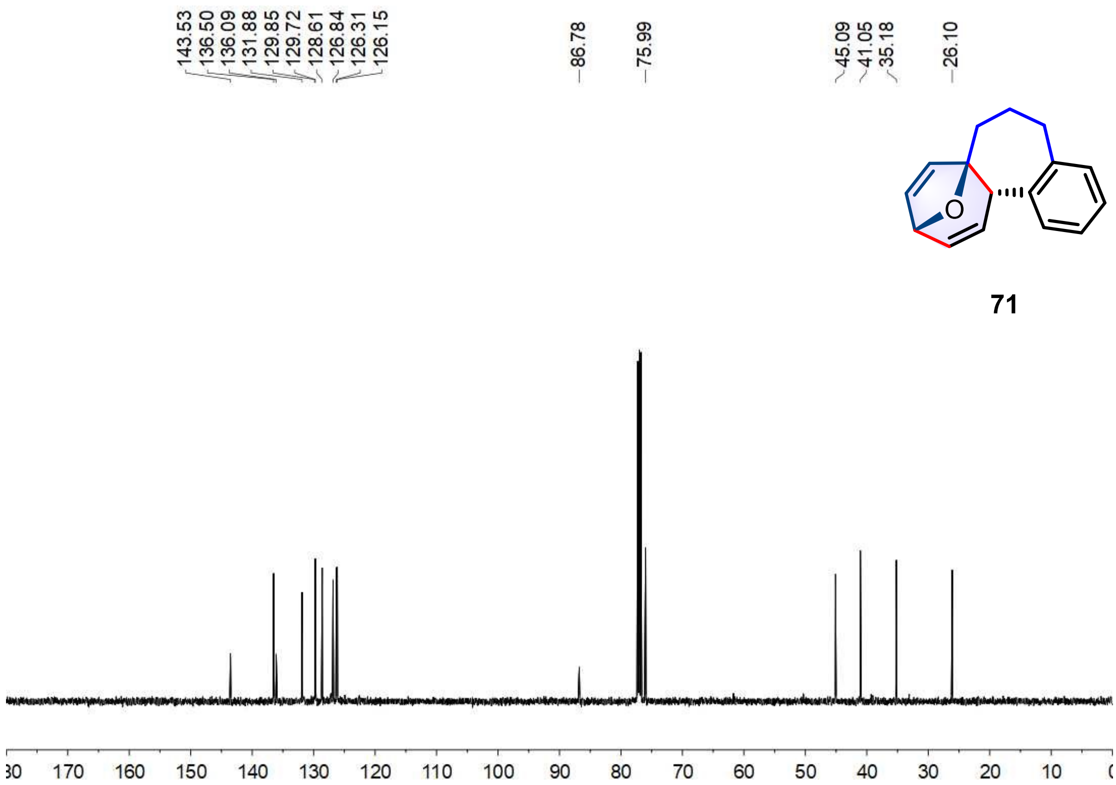


Figure S154. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **71**.

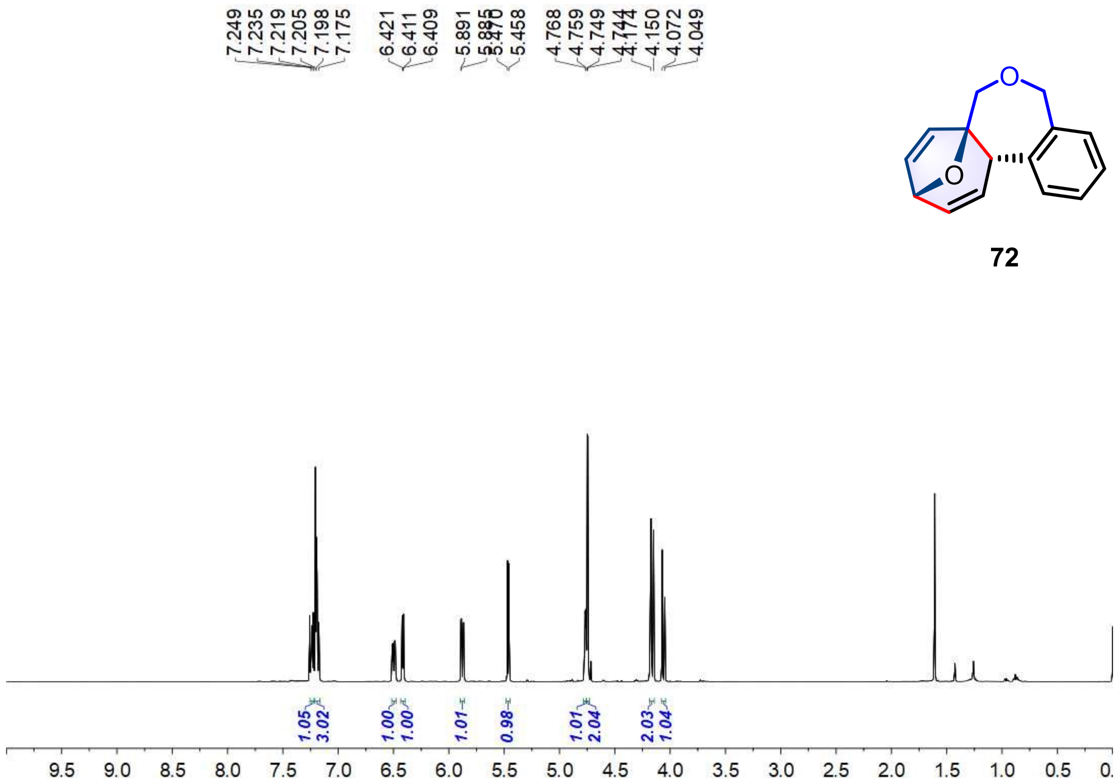


Figure S155. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **72**.

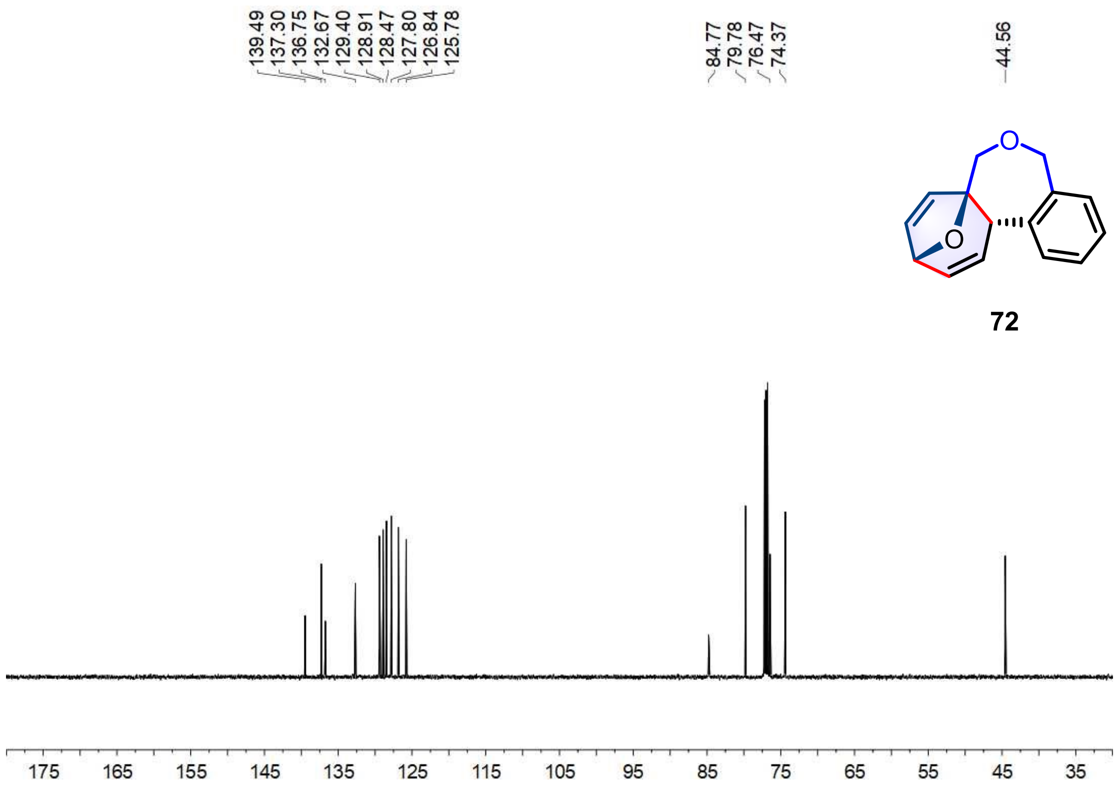


Figure S156. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **72**.

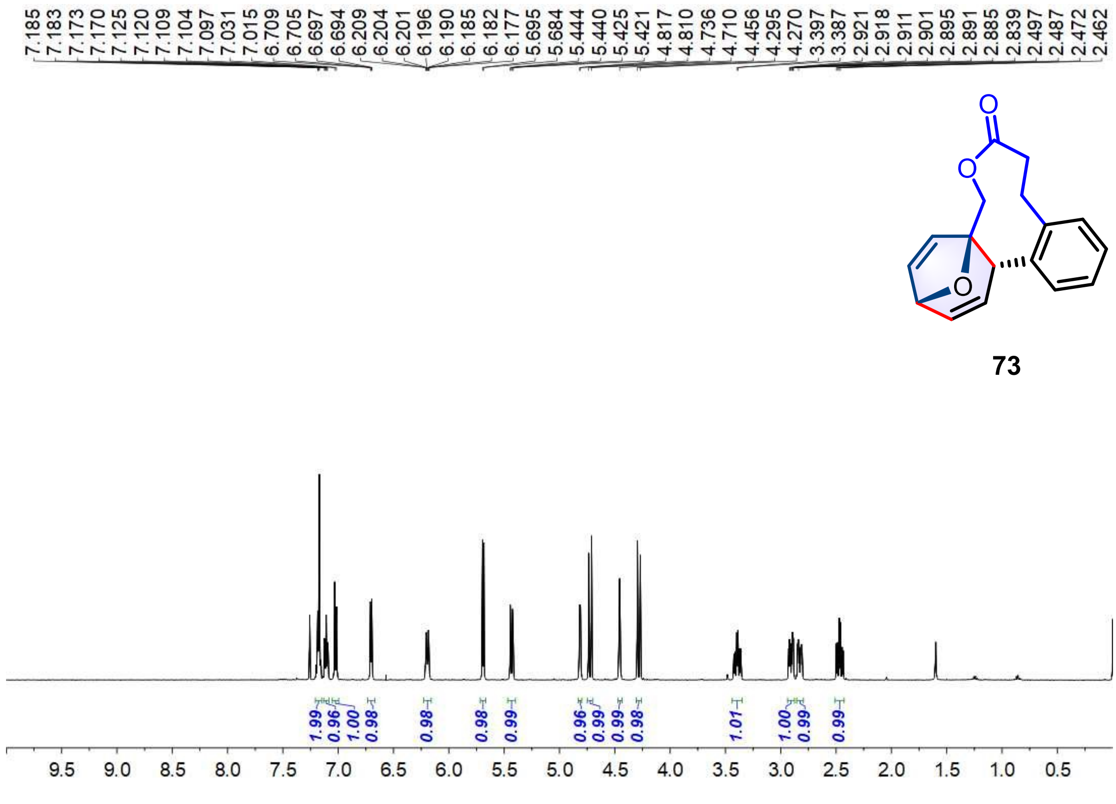


Figure S157. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **73**.

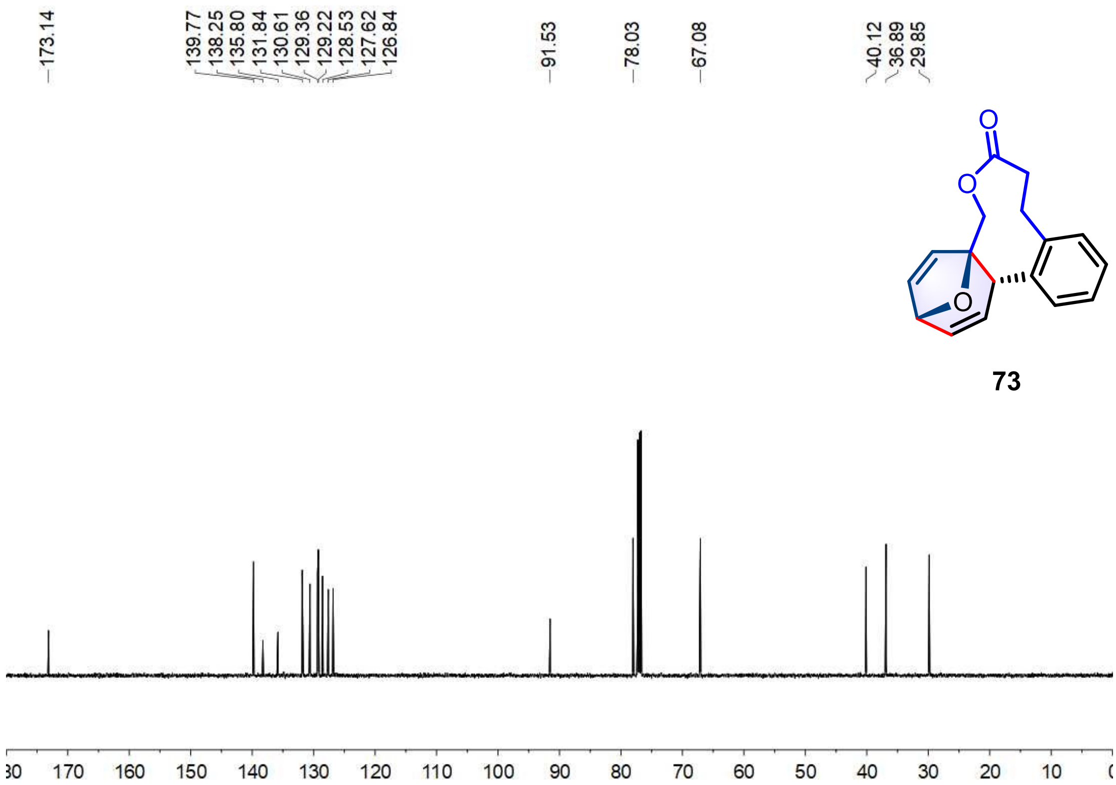


Figure S158. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **73**.

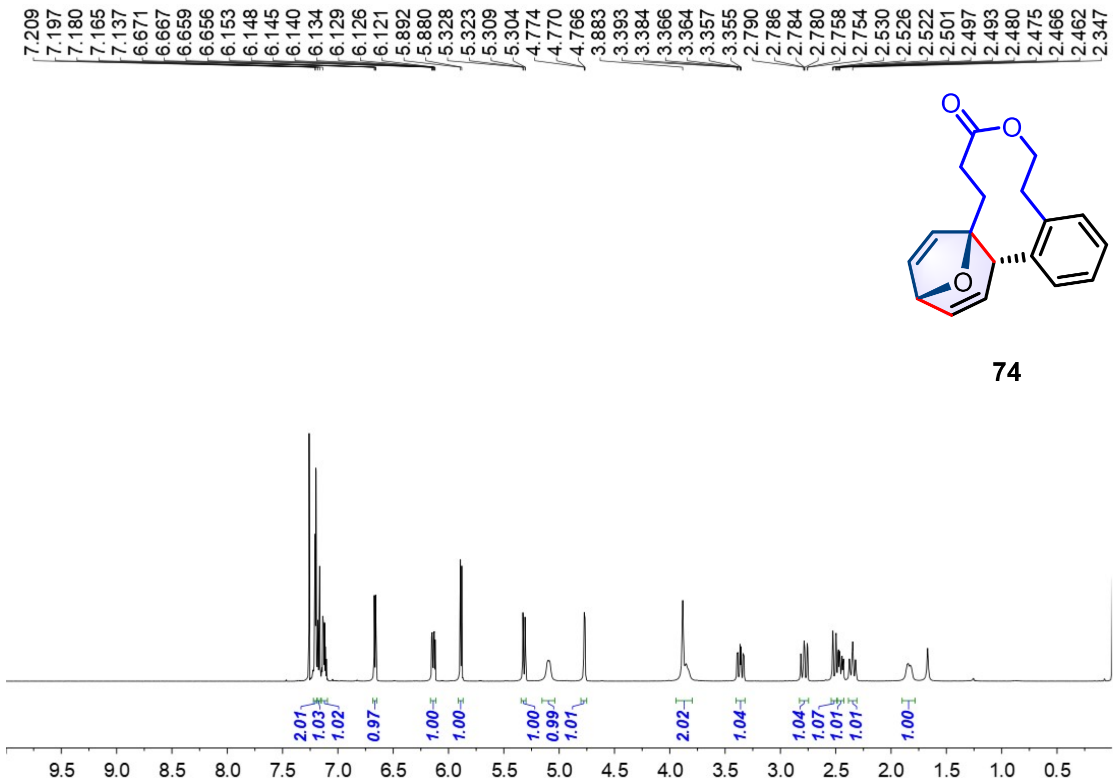


Figure S159. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **74**.

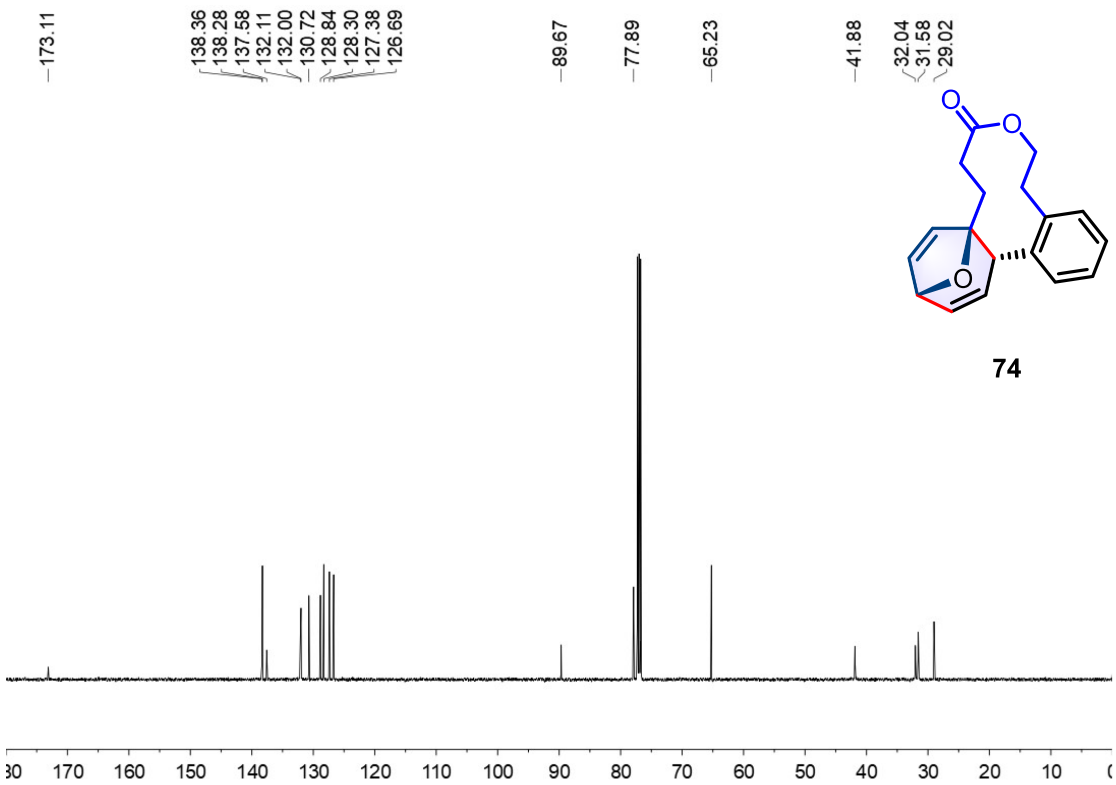


Figure S160. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **74**.

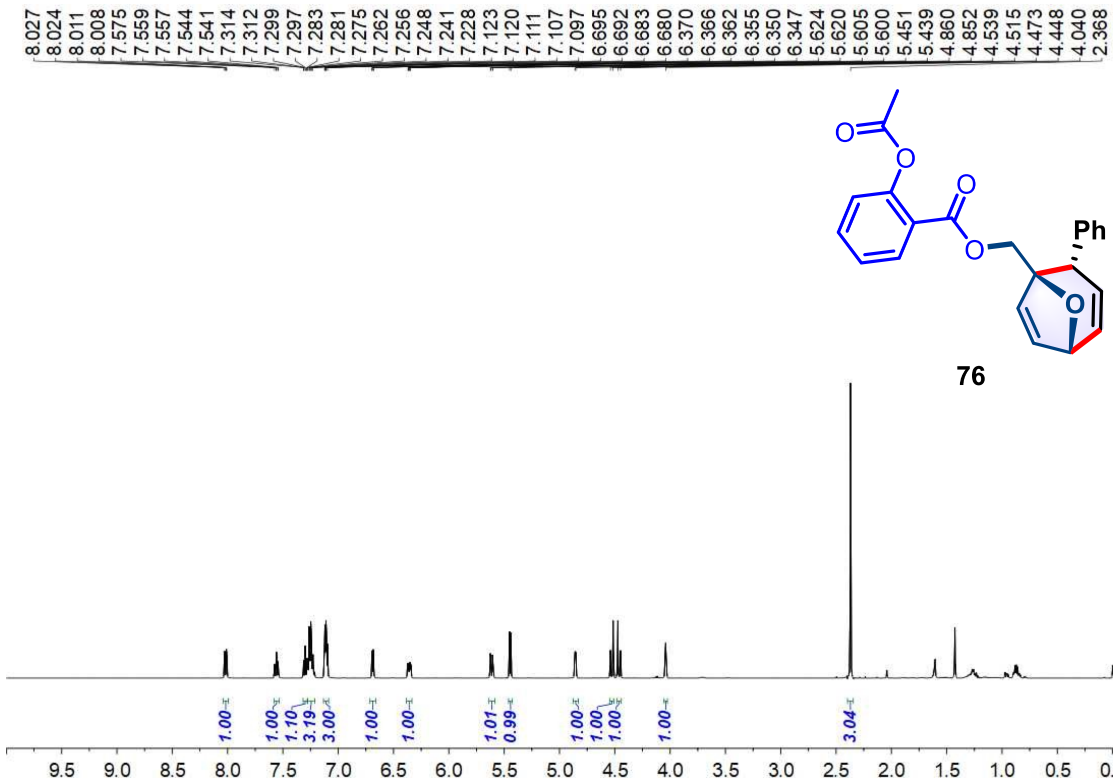


Figure S161. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **76**.

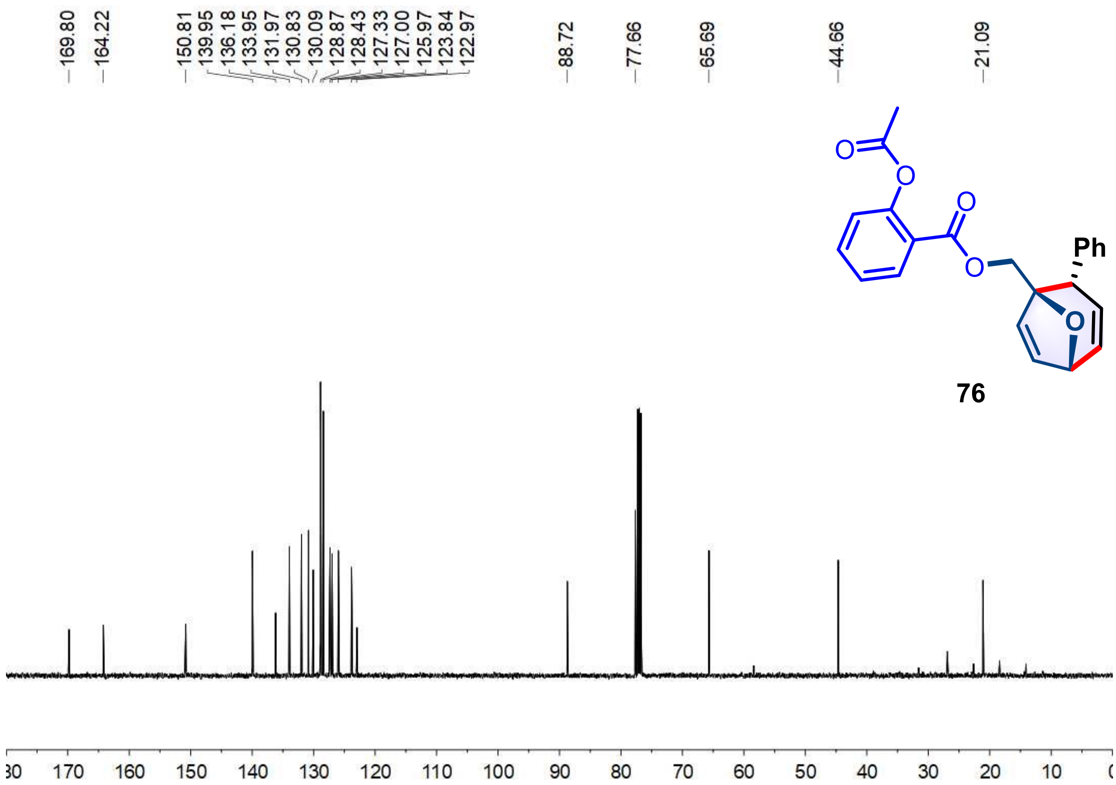


Figure S162. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **76**.

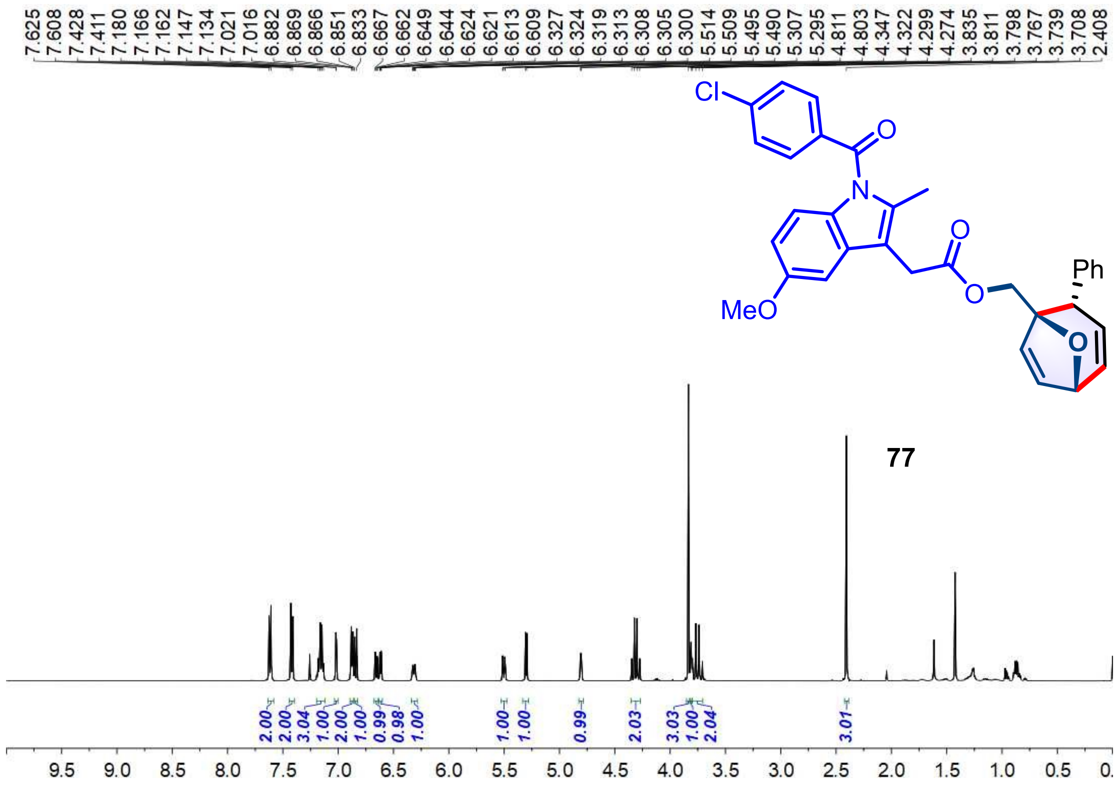


Figure S163. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **77**.

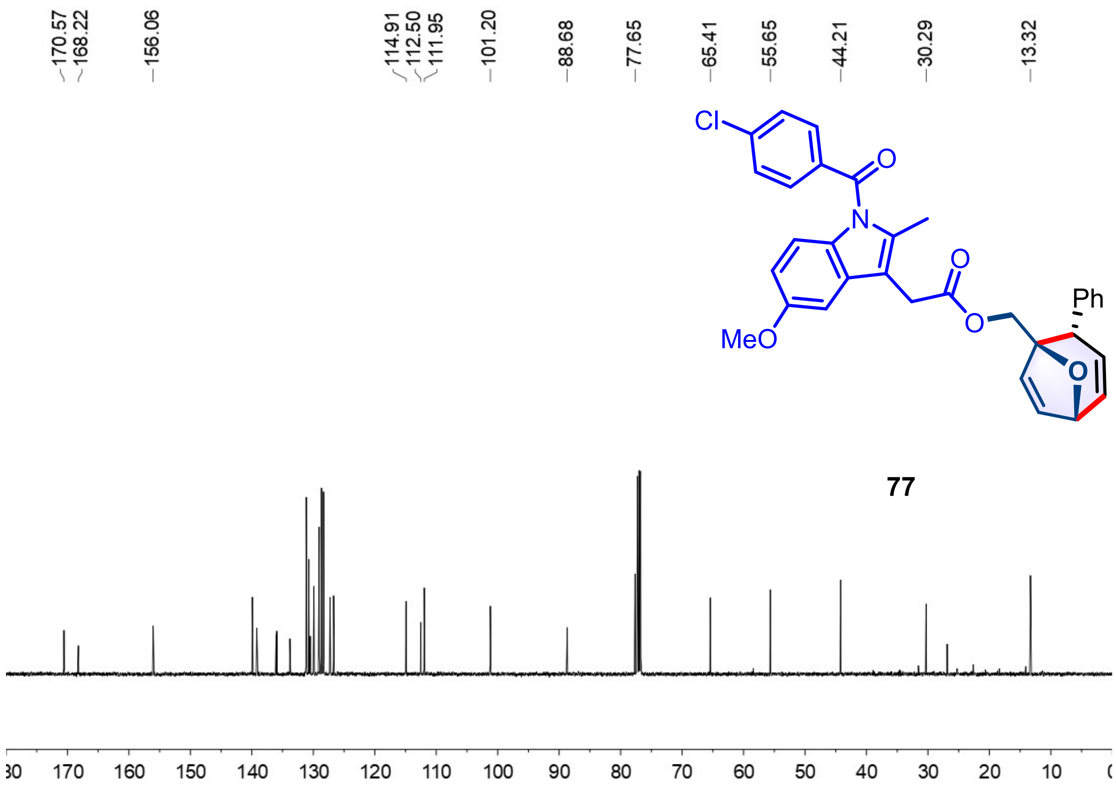


Figure S164. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **77**.

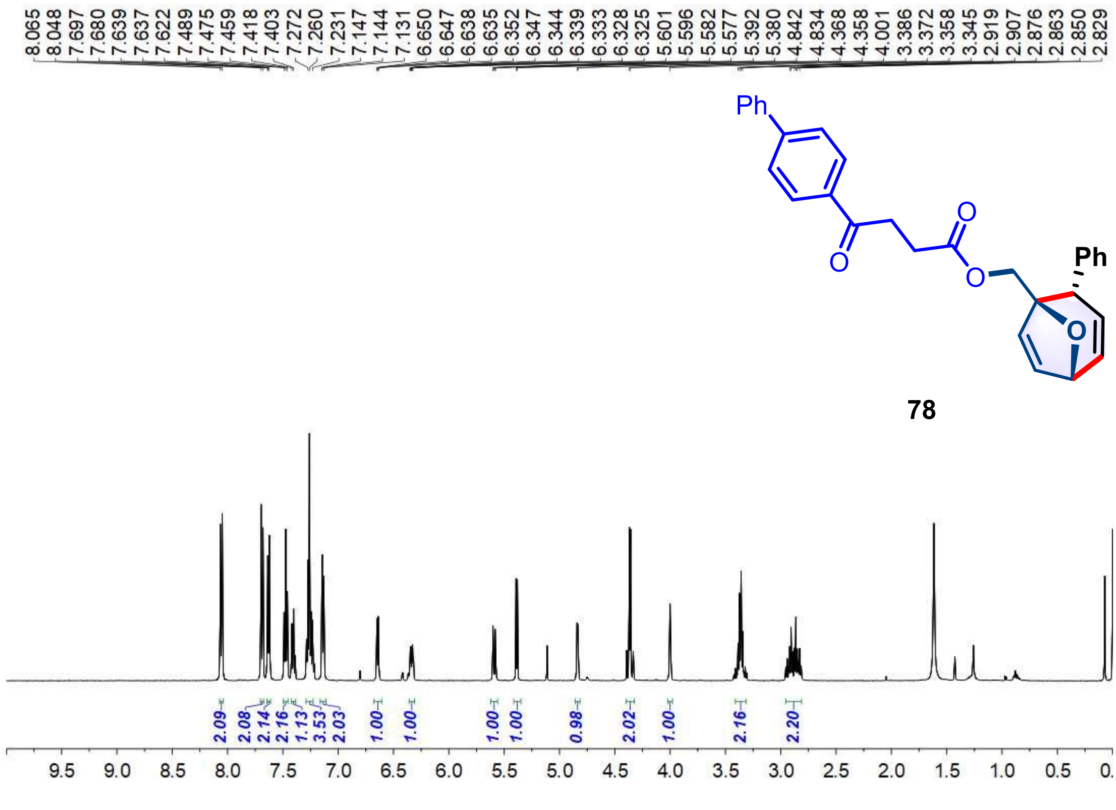
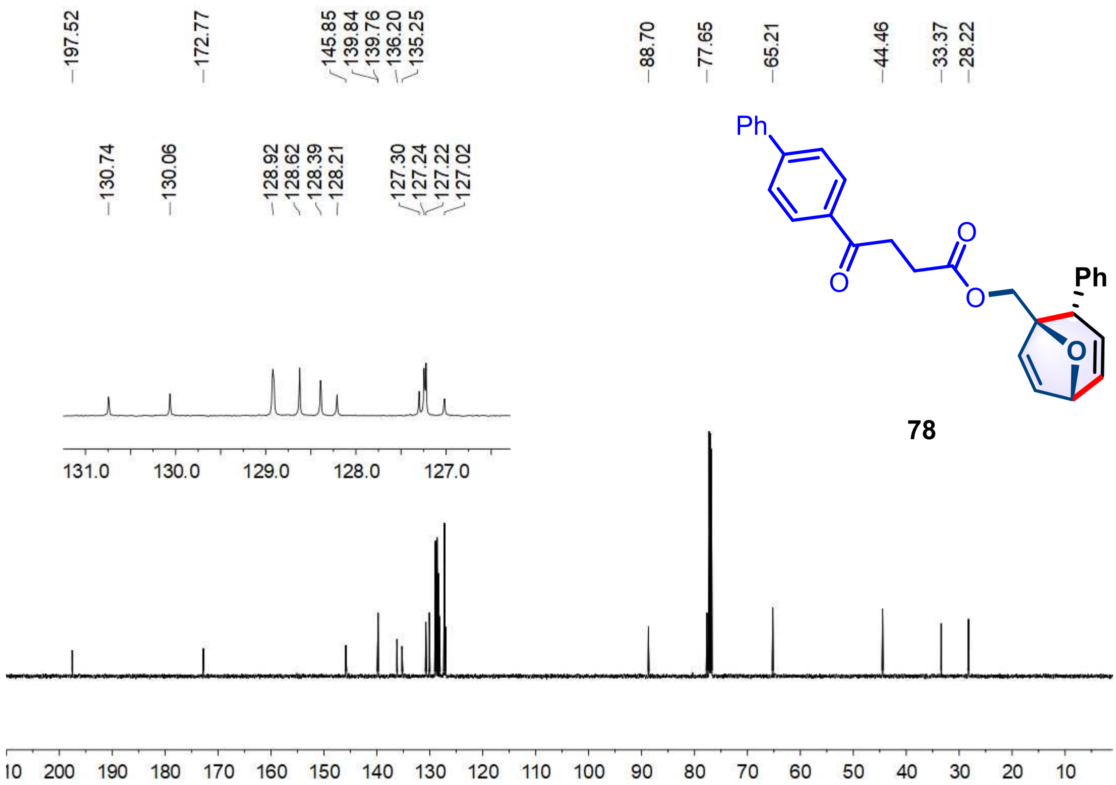
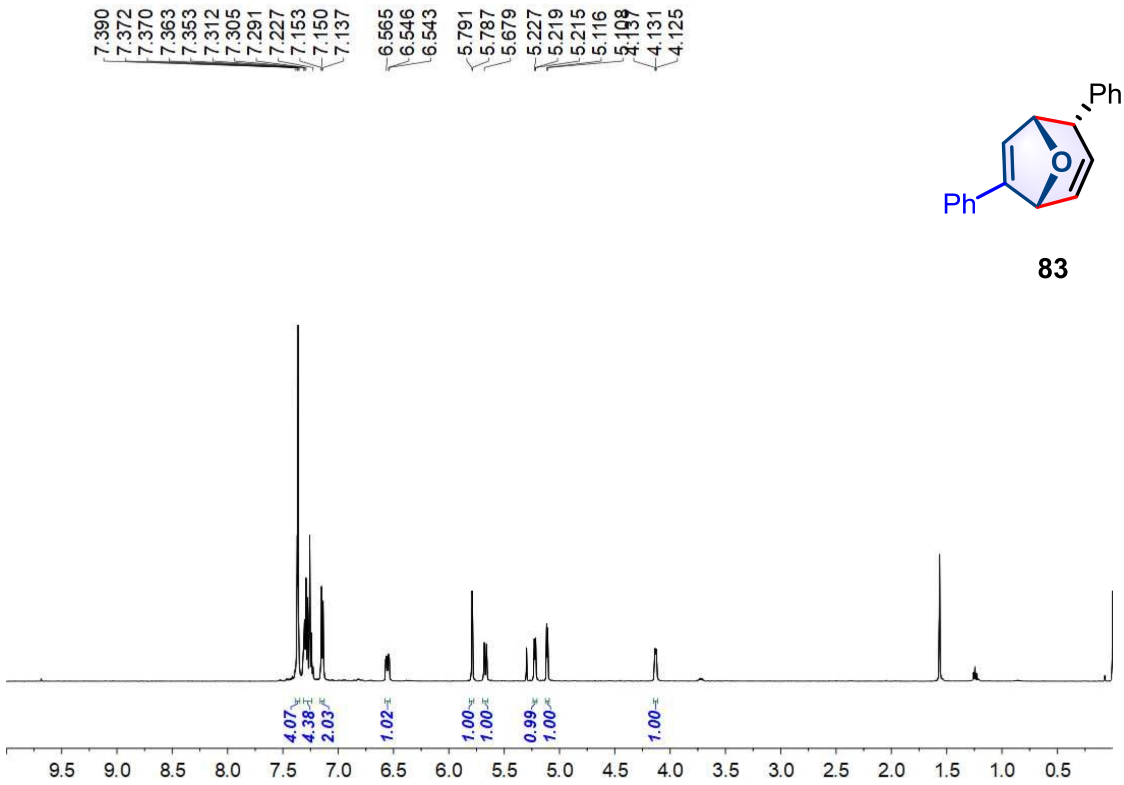


Figure S165. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **78**.



78

Figure S166. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **78**.



83

Figure S167. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **83**.

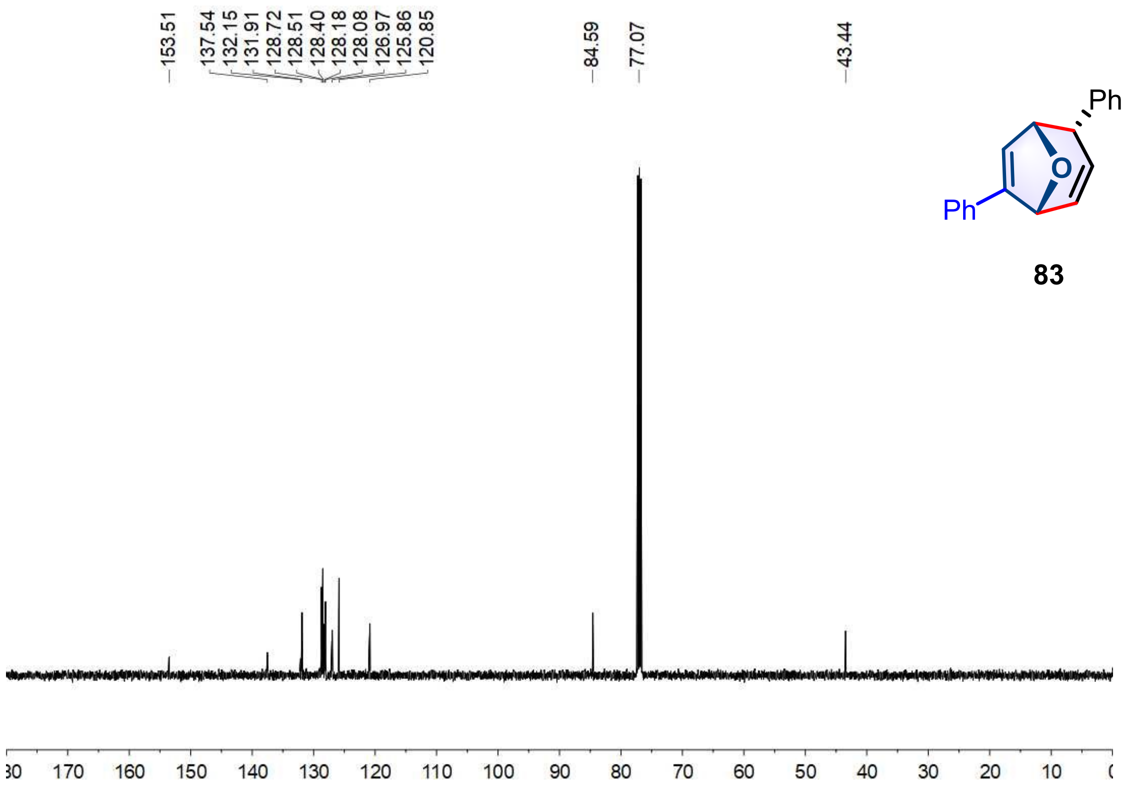


Figure S168. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **83**.

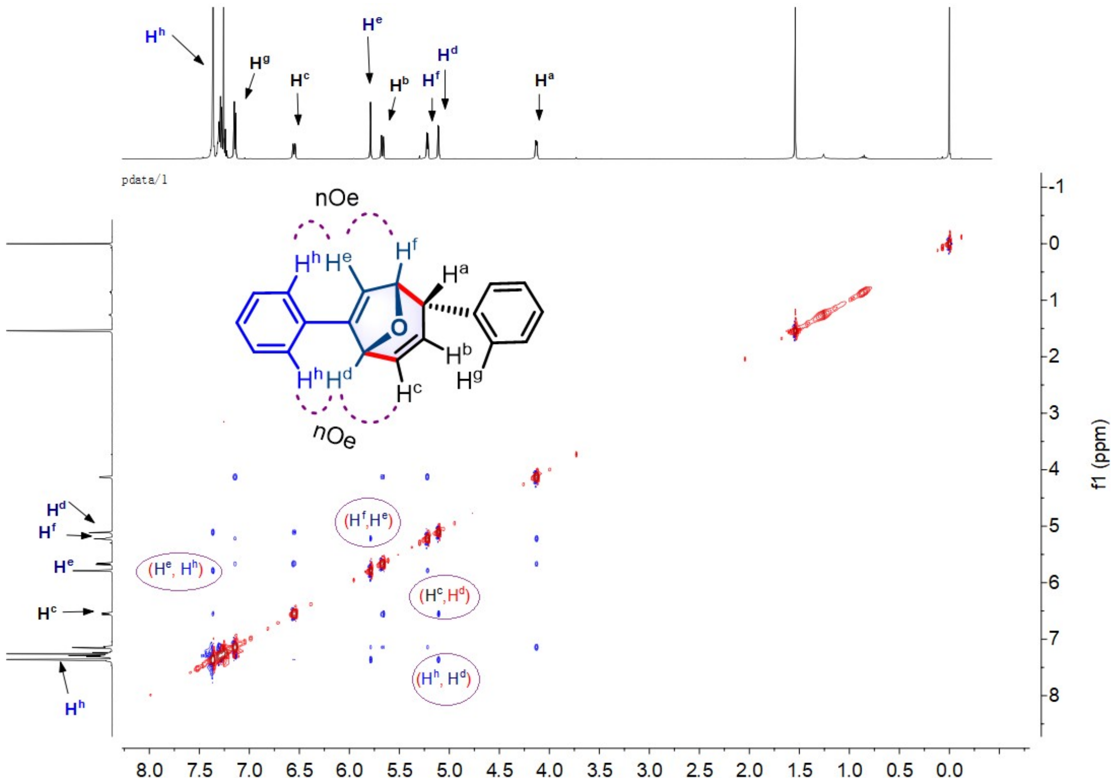


Figure S169. NOE of **83**.

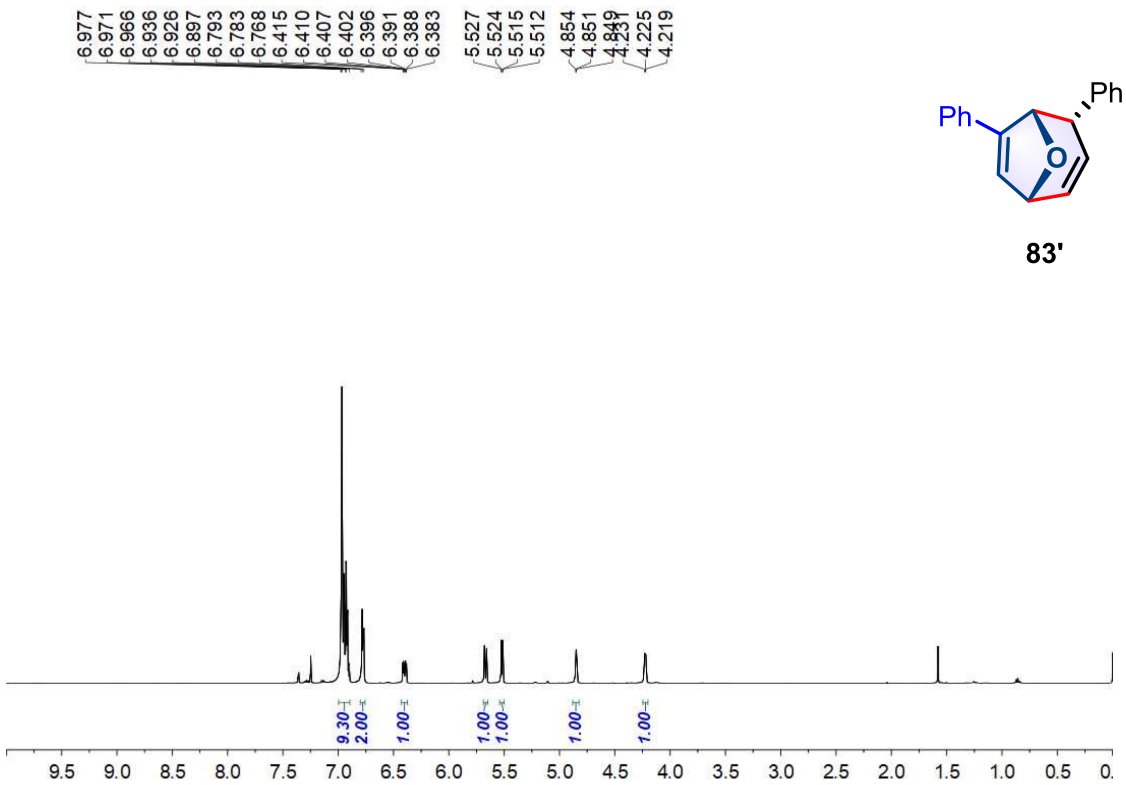


Figure S170. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **83'**.

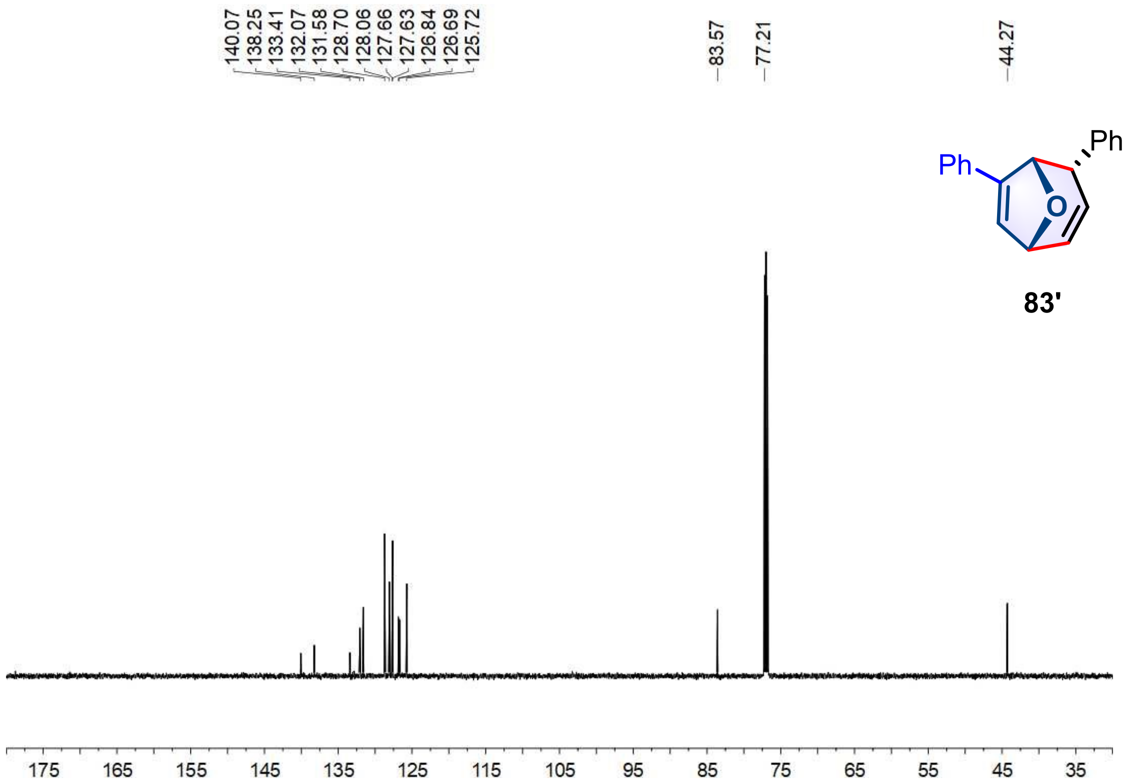


Figure S171. ^{13}C NMR (151 MHz, $CDCl_3$) Spectrum of **83'**.

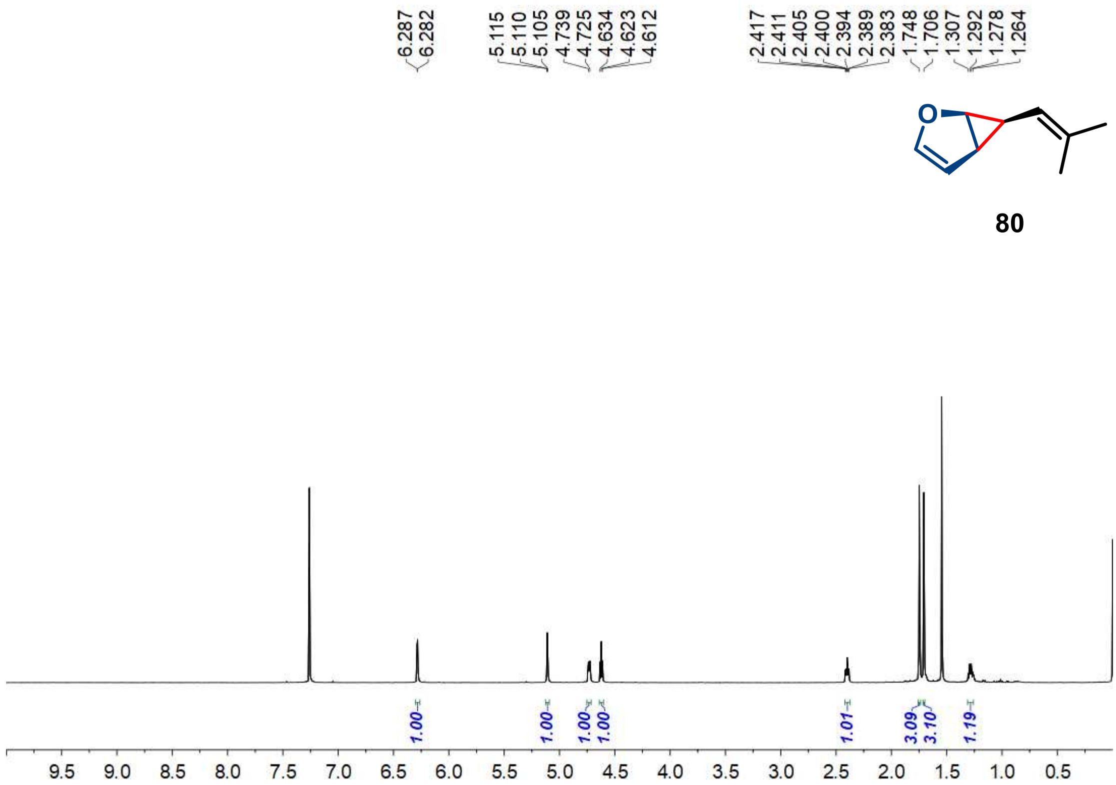


Figure S172. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **80**.

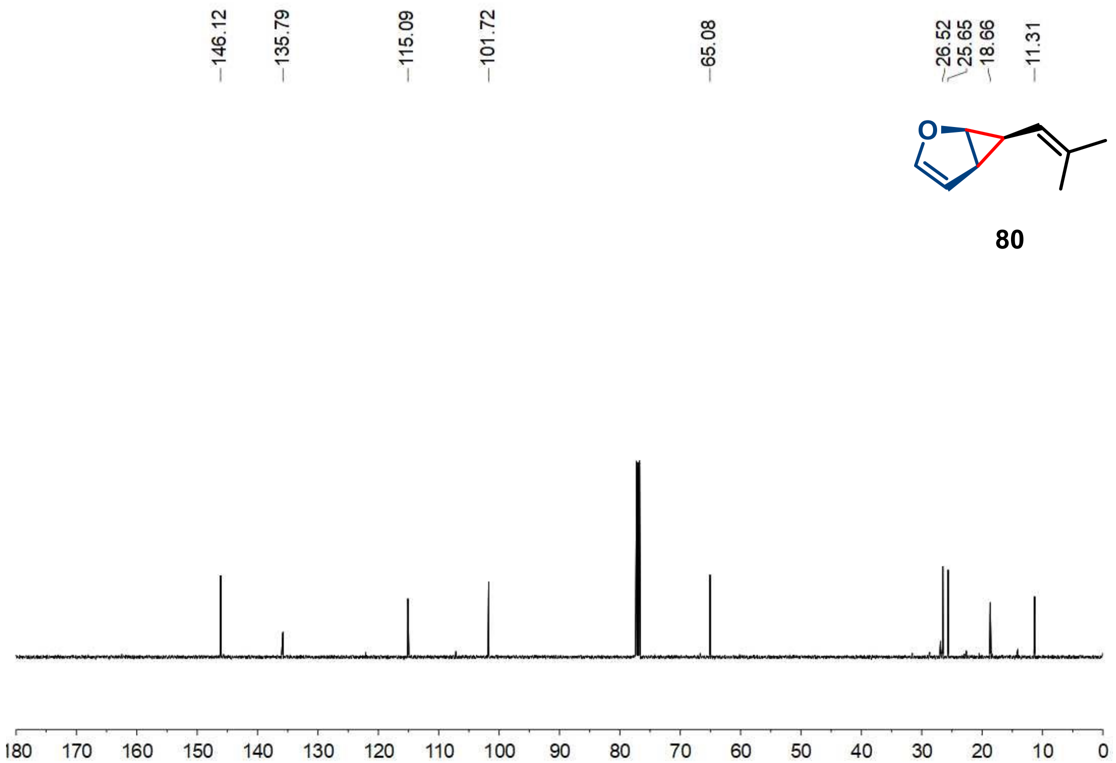


Figure S173. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **80**.

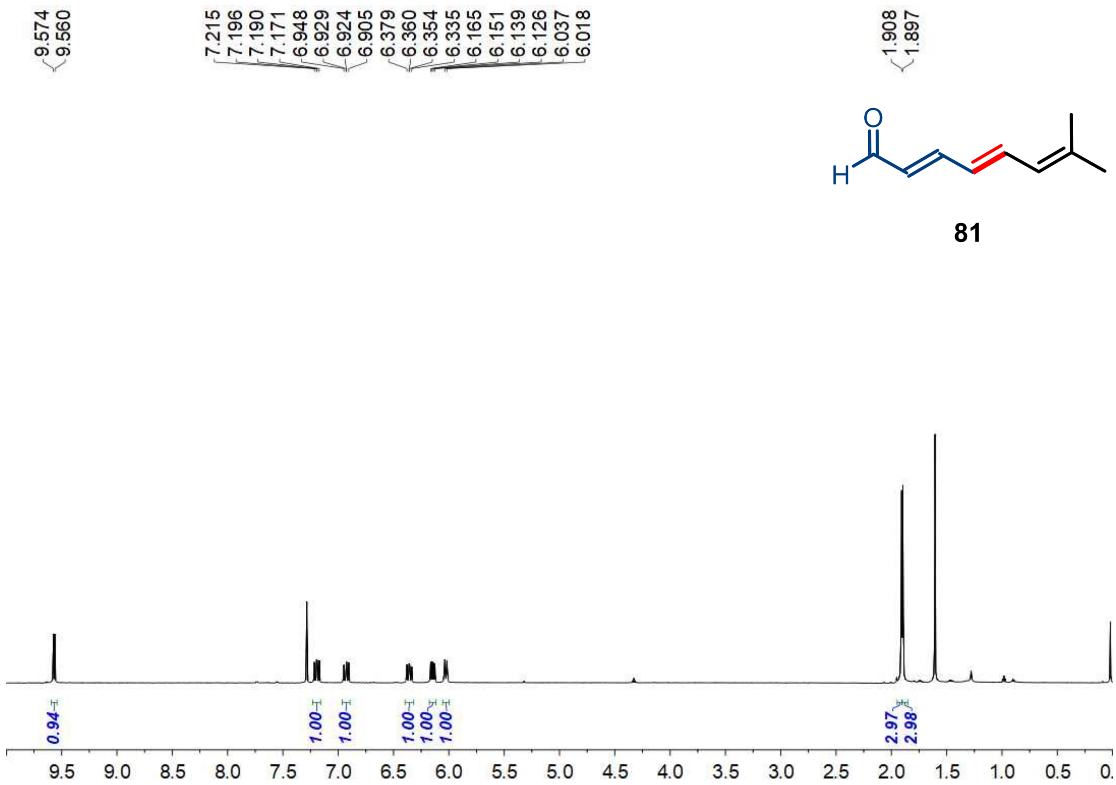


Figure S174. ^{1}H NMR (600 MHz, $CDCl_3$) Spectrum of **81**.

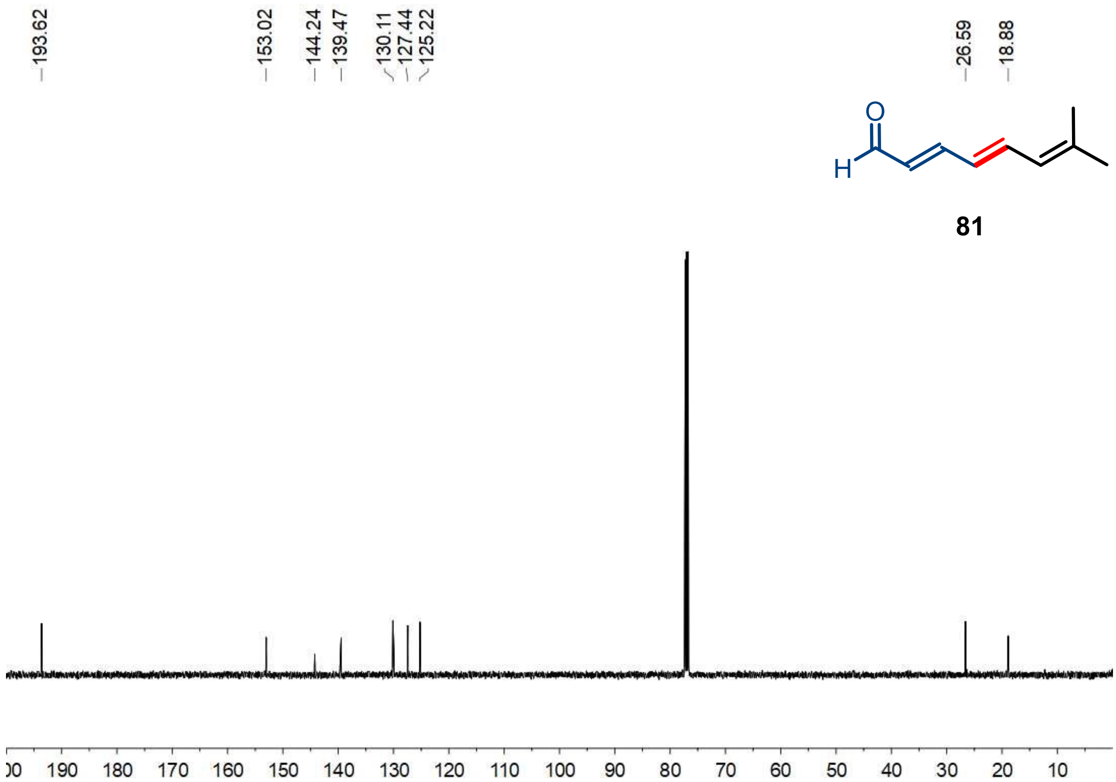


Figure S175. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **81**.

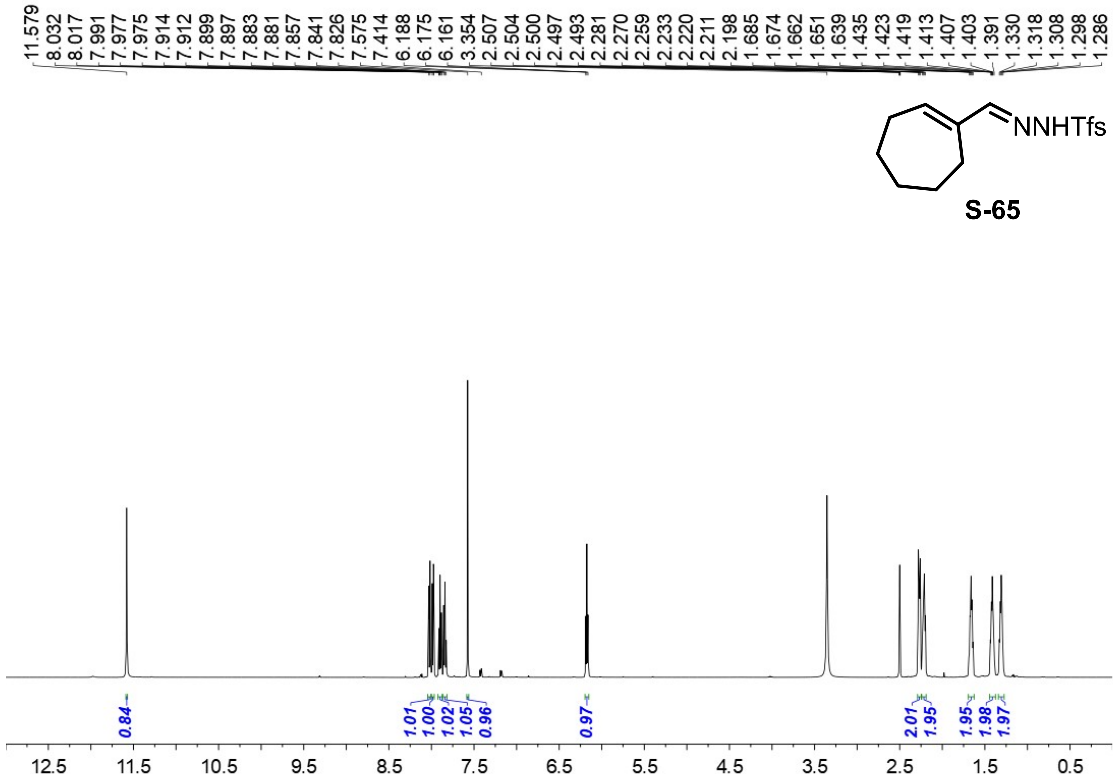


Figure S176. ^{1}H NMR (500 MHz, DMSO) Spectrum of **S-65**.

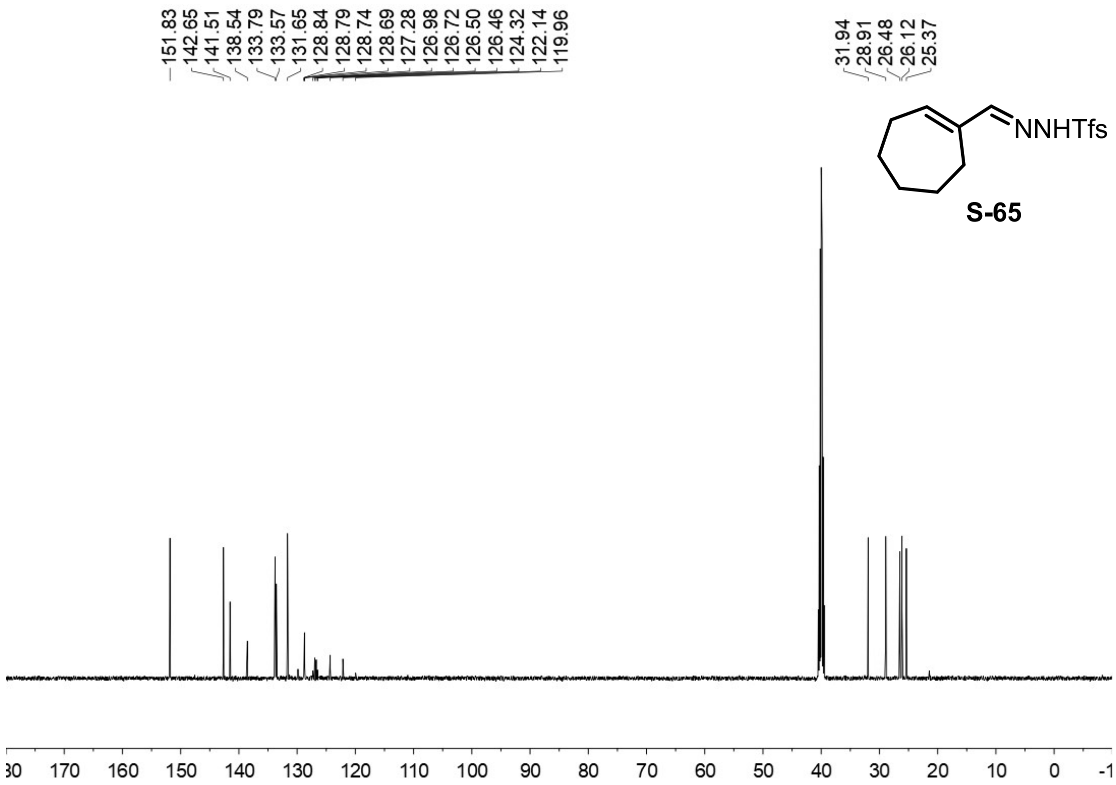


Figure S177. ^{13}C NMR (126 MHz, DMSO) Spectrum of **S-65**.

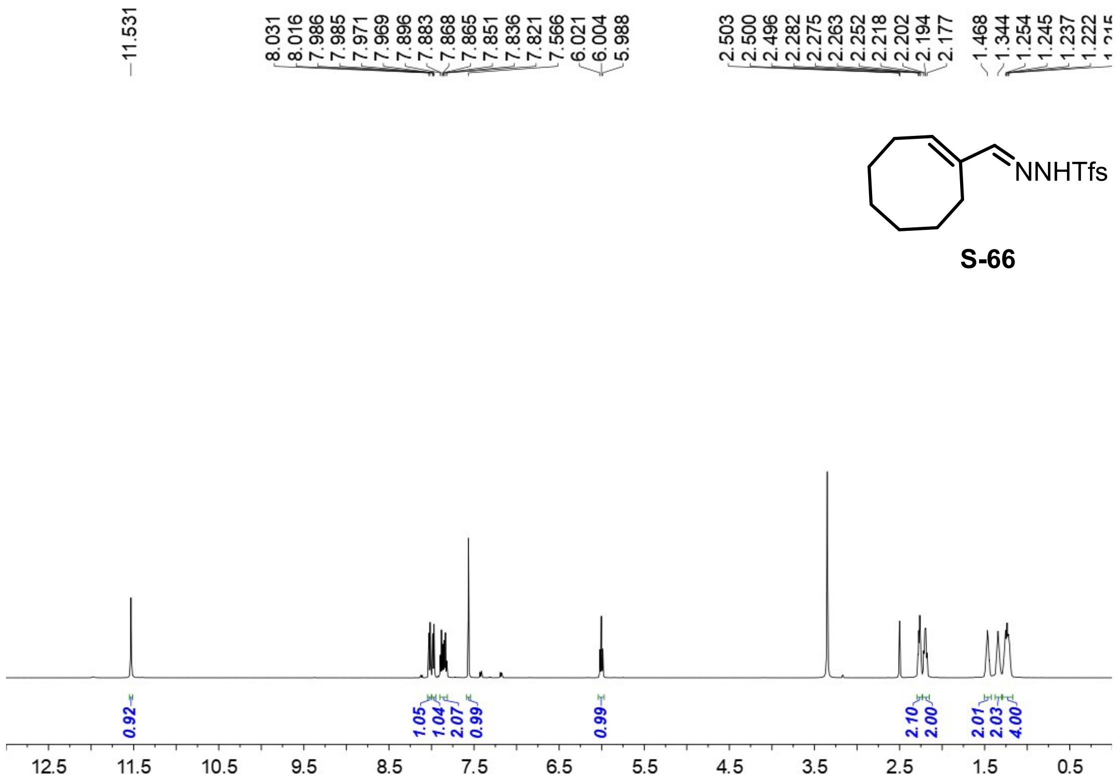


Figure S178. ^{1}H NMR (500 MHz, DMSO) Spectrum of **S-66**.

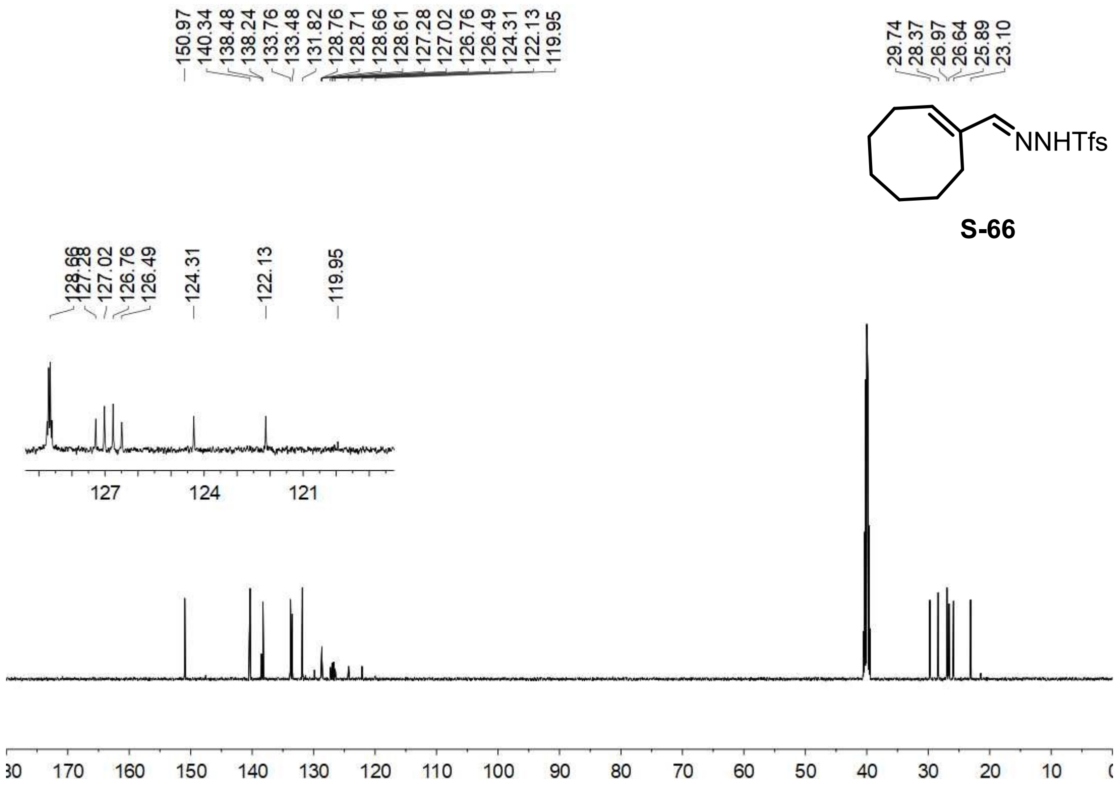


Figure S179. ^{13}C NMR (126 MHz, DMSO) Spectrum of **S-66**.

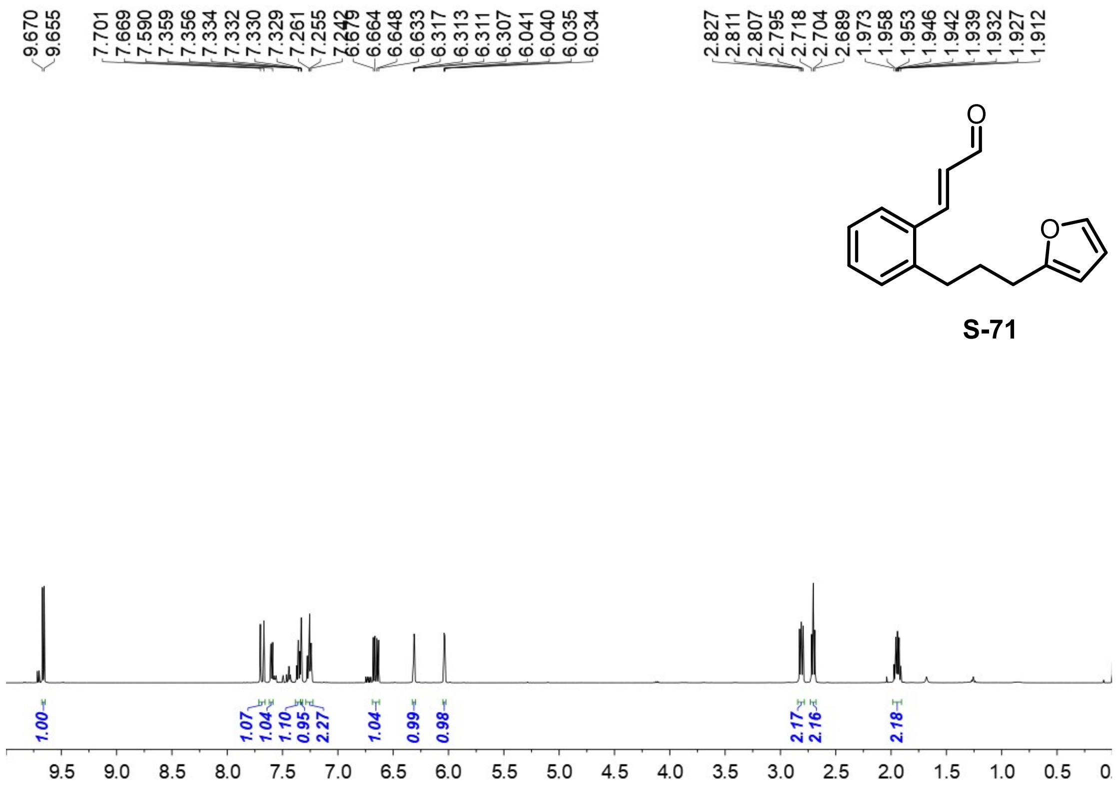


Figure S180. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **S-71**.

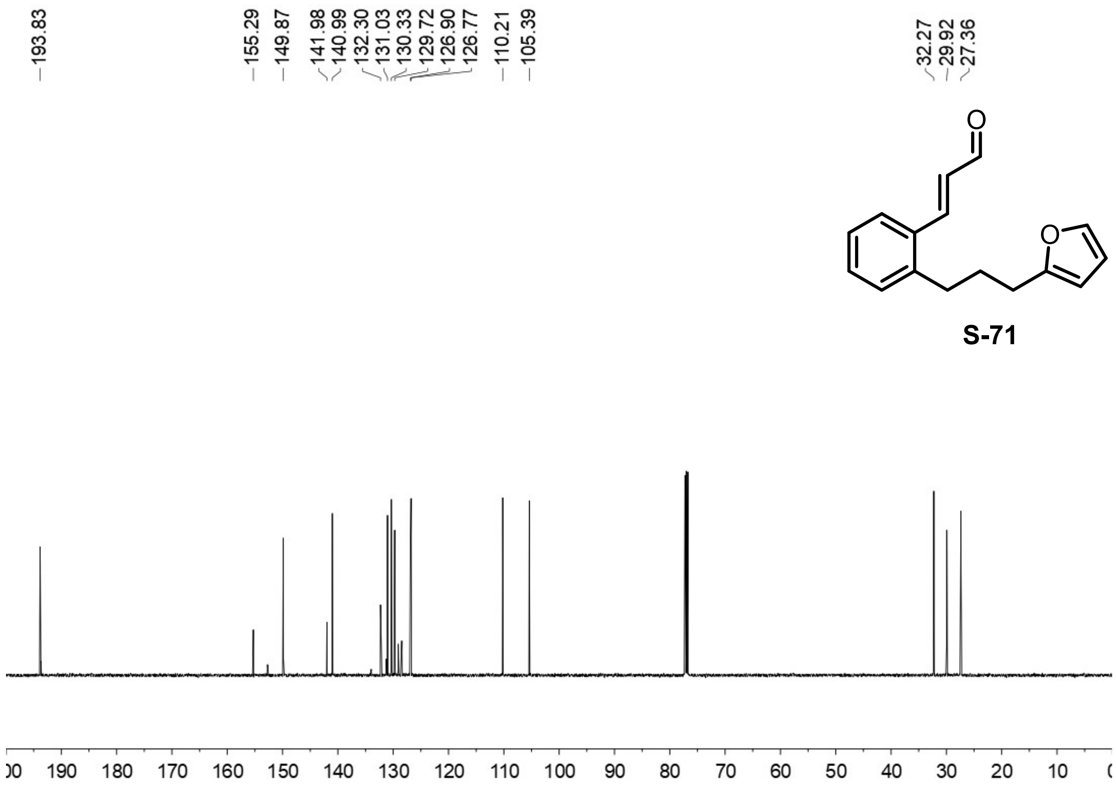


Figure S181. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **S-71**.

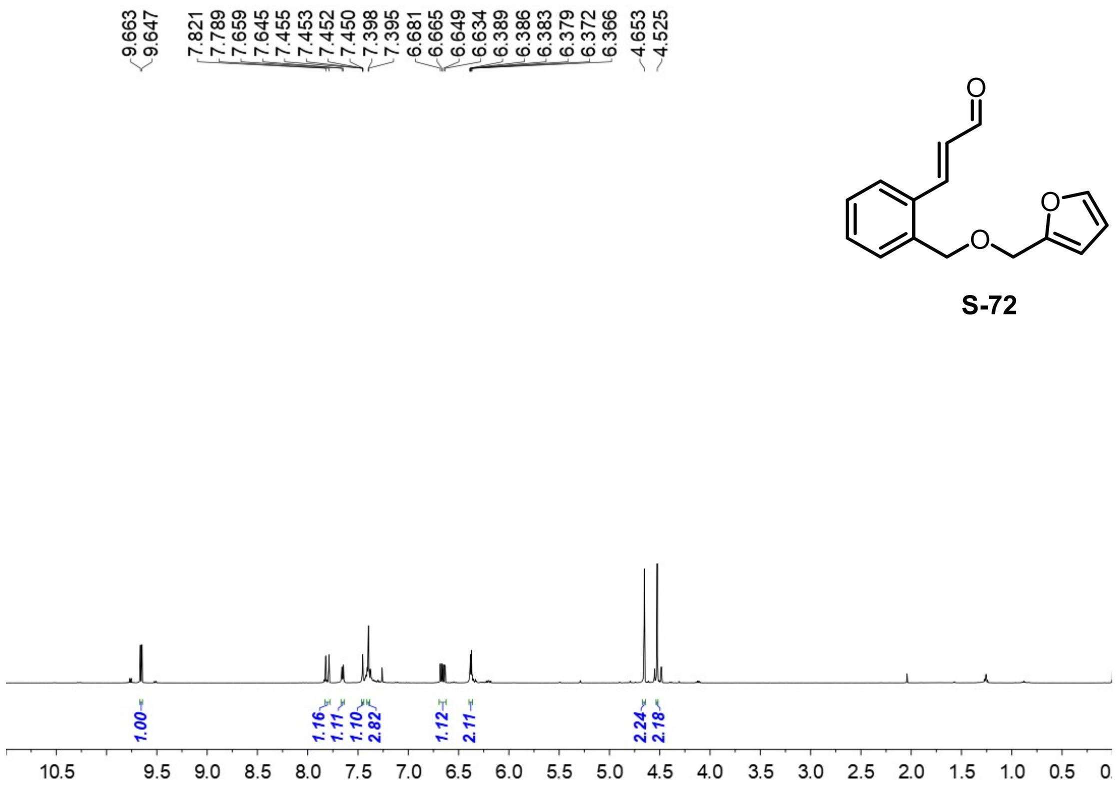


Figure S182. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **S-72**.

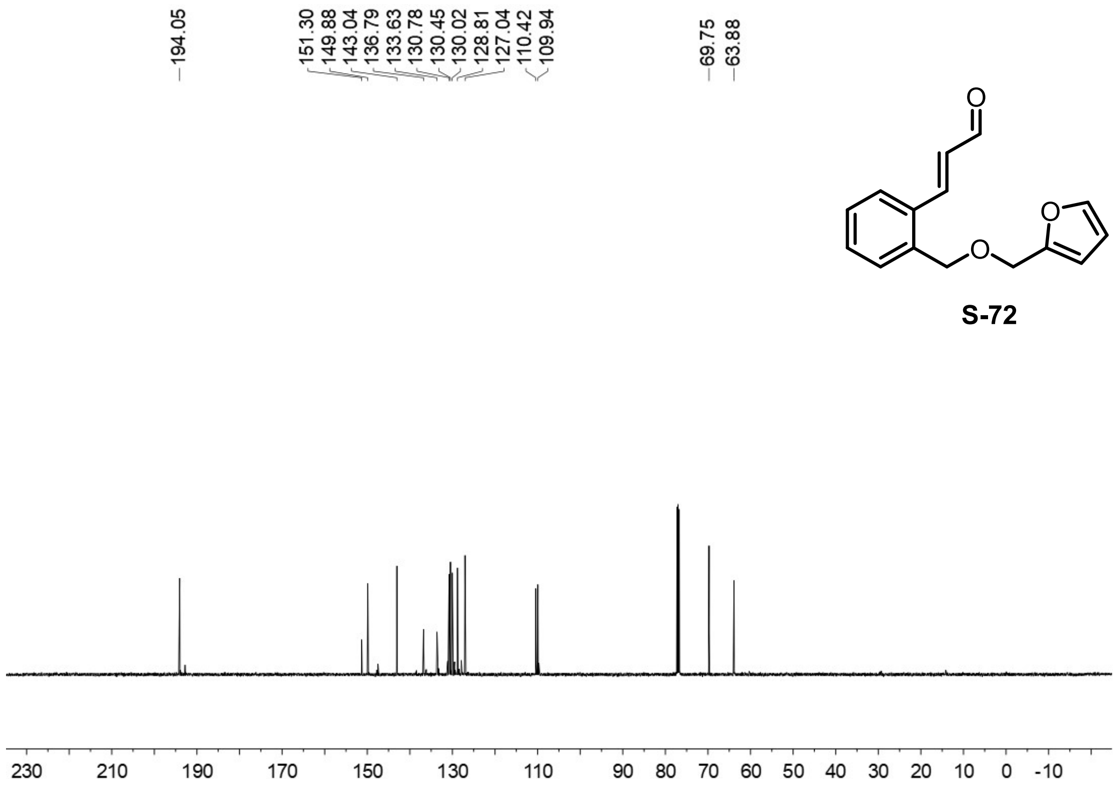


Figure S183. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **S-72**.

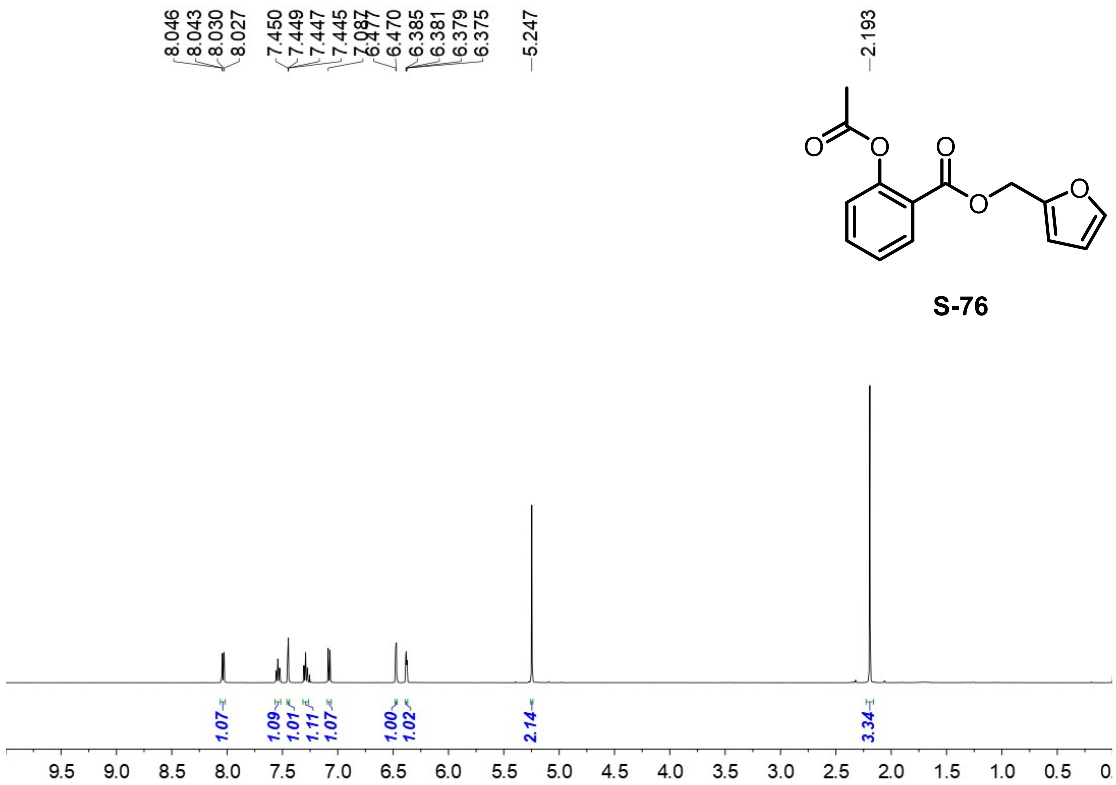


Figure S184. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **S-76**.

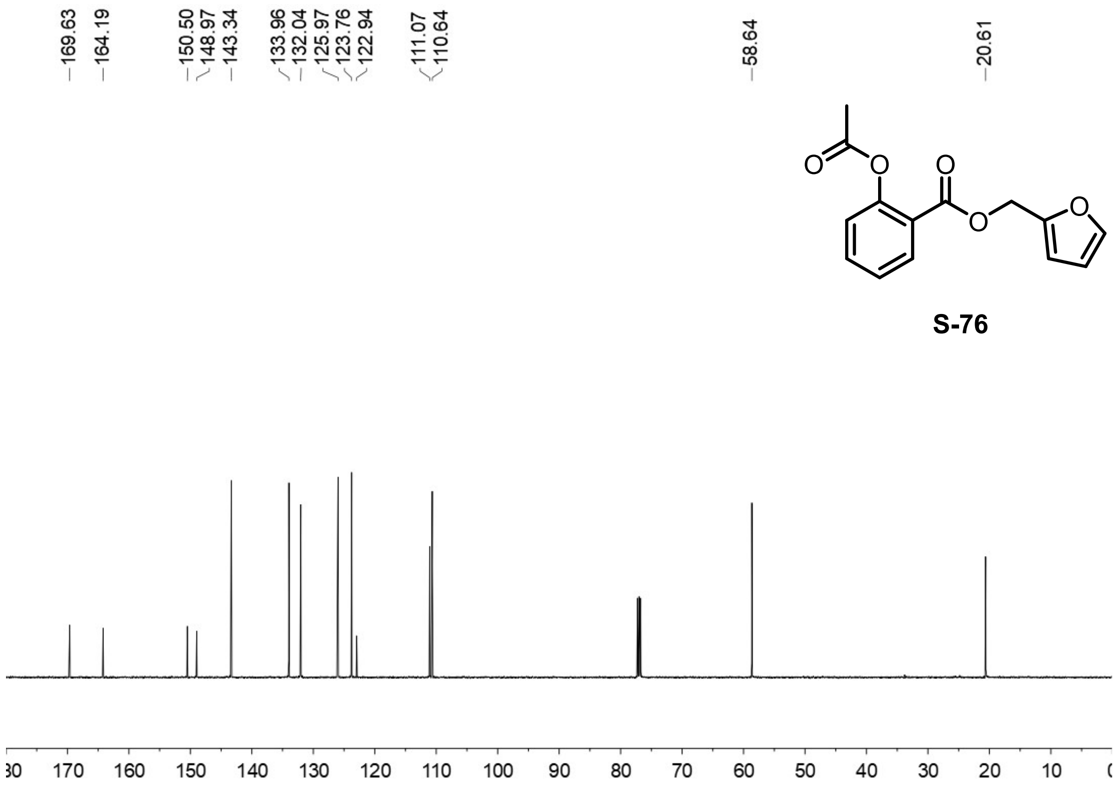


Figure S185. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **S-76**.

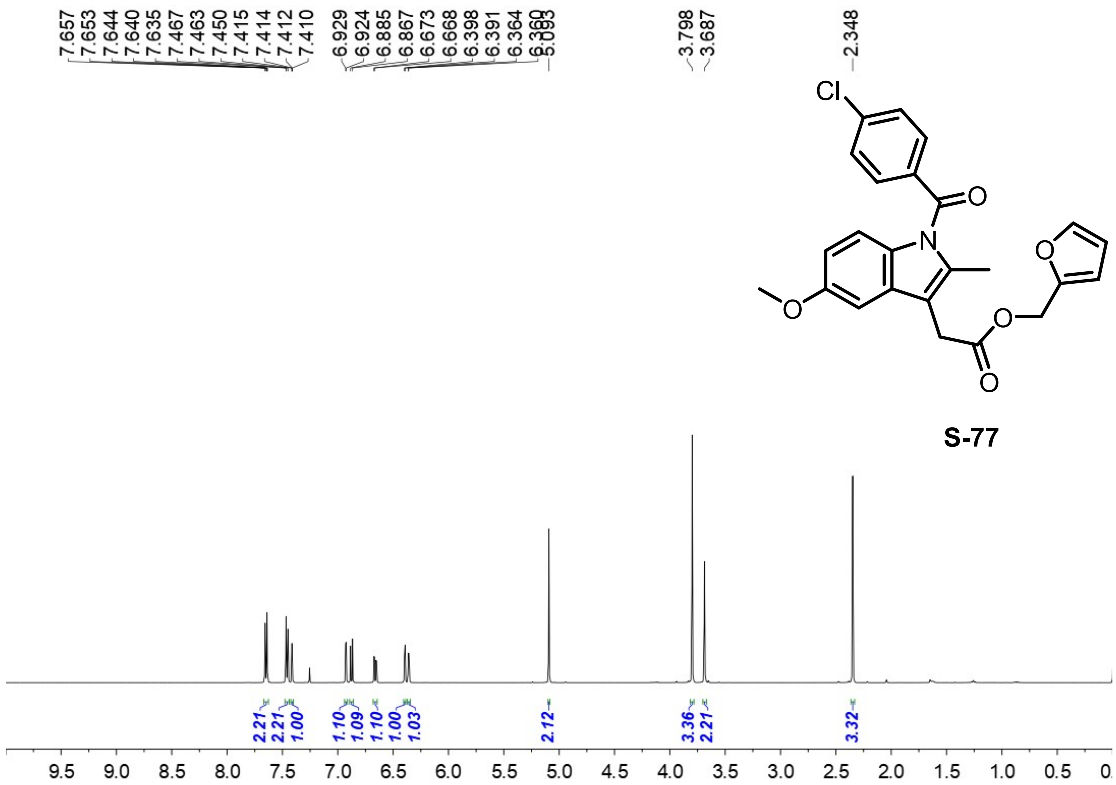


Figure S186. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **S-77**.

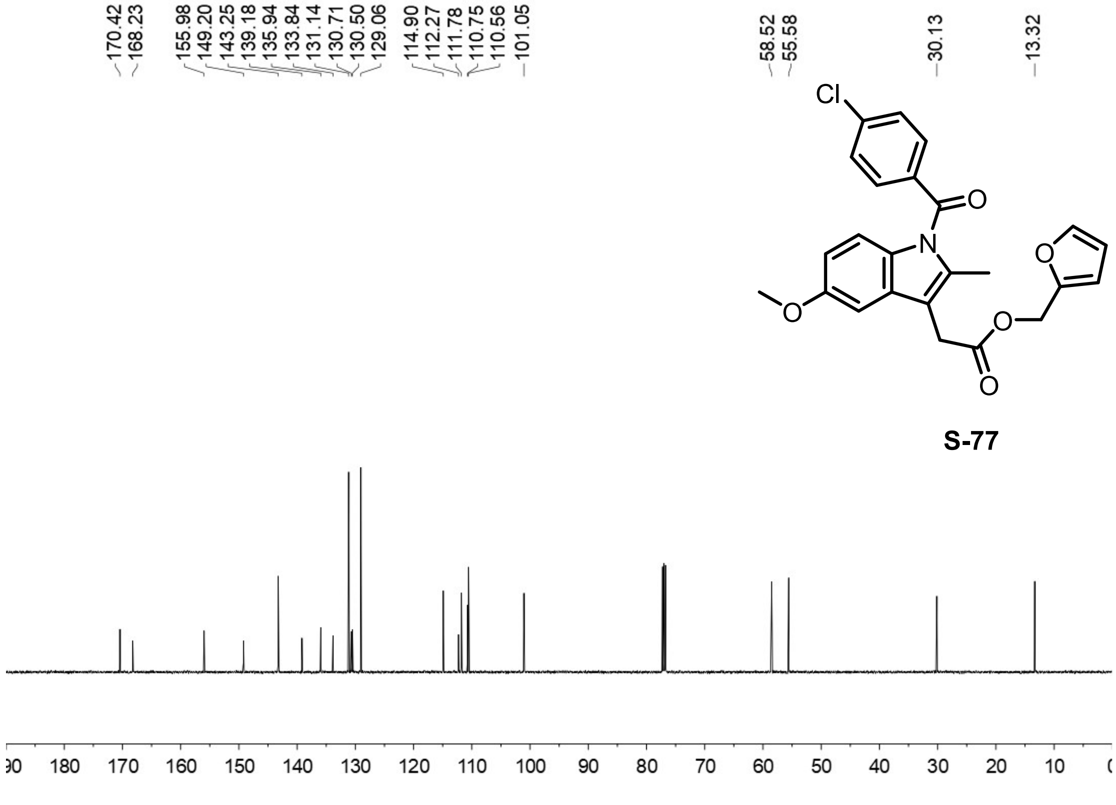


Figure S187. ^{13}C NMR 126 MHz, $CDCl_3$) Spectrum of **S-77**.

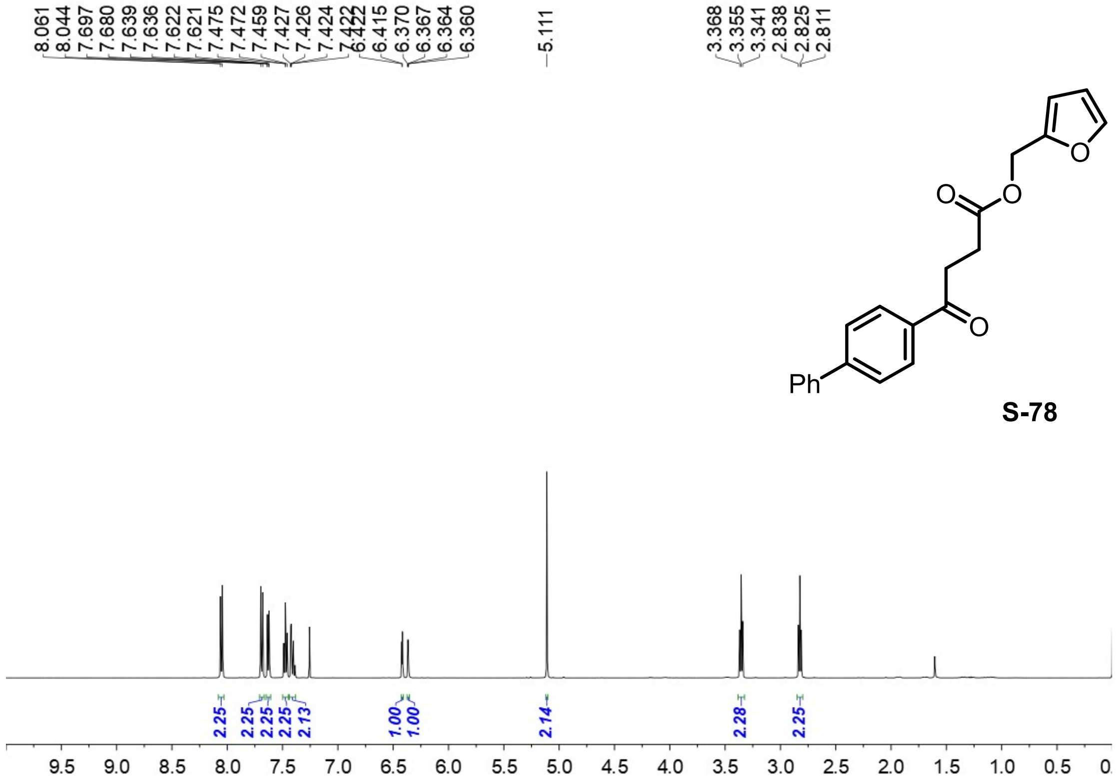


Figure S188. ^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of **S-78**.

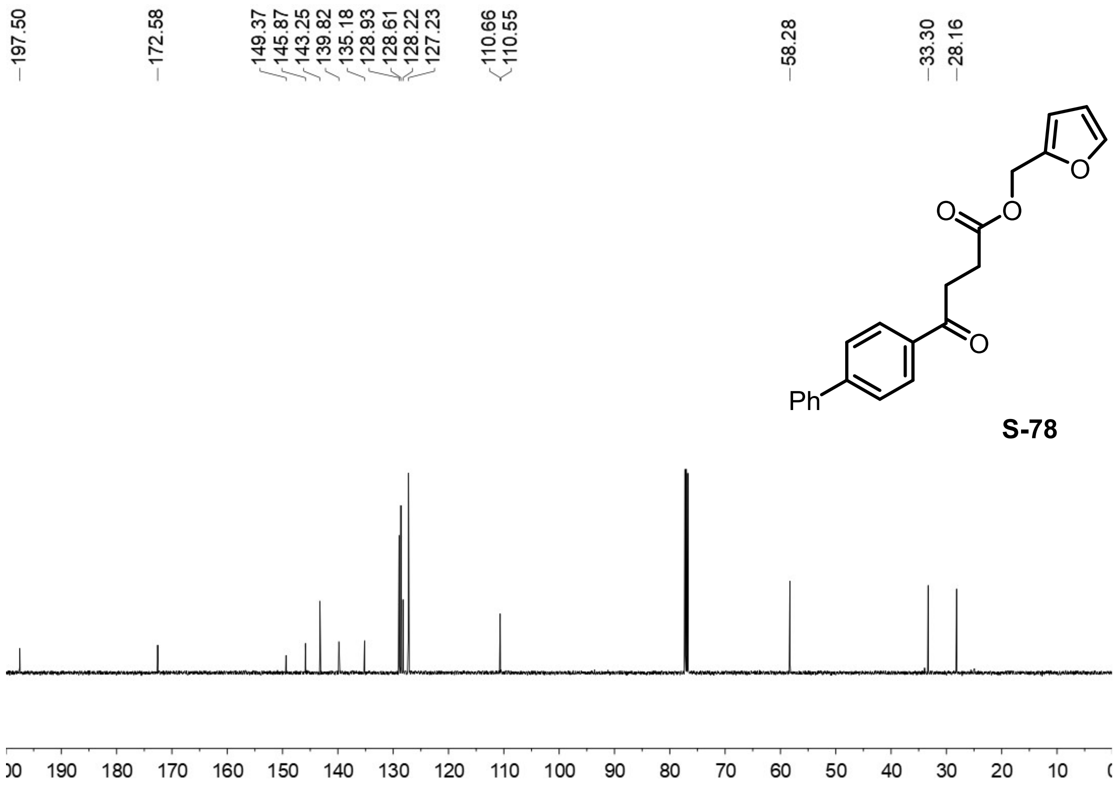


Figure S189. ^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of **S-78**.