Supporting Information

Palladium-catalyzed [5+2] cycloaddition of vinyloxiranes with photogenerated siloxyketenes: access to seven-membered lactones

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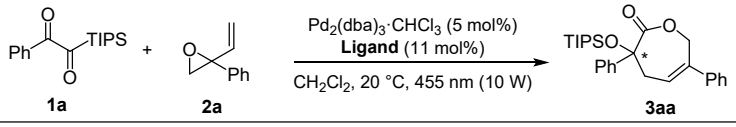
1. General information

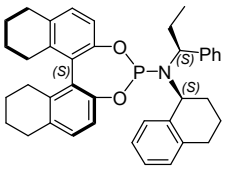
^{1}H NMR spectra were recorded on a Bruker DPX 400 MHz or 600 MHz spectrometer in $CDCl_3$. Chemical shifts were reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The spectra are interpreted as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, dtd = doublet of triplet of doublets, brs = broad signals, coupling constant (s) *J* are reported in Hz and relative integrations are reported. ^{13}C NMR spectra were recorded on a Bruker DPX 400 MHz or 600 MHz spectrometer in $CDCl_3$. Chemical shifts were reported in ppm with the internal chloroform signal at 77.16 ppm as a standard. ^{19}F NMR (377 MHz) spectra were recorded on a Bruker DPX 400 MHz spectrometer in $CDCl_3$ and referenced relative to $CFCl_3$. Optical rotations were measured on an AUTOPOL V. Enantiomeric excesses were determined by analysis of HPLC traces, obtained by using Chiralpak IA column with hexane and 2-propanol as solvents. (Chiralpak IA column were purchased from Daicel. *n*-Hexane and *i*-propanol were purchased from J&K.) High-resolution mass spectra (HRMS) were recorded on the Agilent 6500 Triple Quadrupole mass spectrometer using ESI (electrospray ionization). Anhydrous solvents (<30 ppm water, *Karl-Fischer* titration) were purchased from J&K and stored over molecular sieves under an argon atmosphere. Ligands and other ordinary organic reagents were purchased from Bidepharm. $Pd_2(dba)_3 \cdot CHCl_3$ was purchased from Laajoo. The photoreactors were manufactured by Beijing Roger Tech Ltd. The wavelength of blue LEDs' peak intensity was 453 nm, and the broadband source was 440-470 nm, and the light intensity is about 180 mW/cm^2 (15 W). The distance from the light source to the irradiation vessel is about 1.0 cm. Vinyl epoxides[1] and *α*-ketoacylsilanes[2] were synthesized according to the literature methods.

2. Asymmetric [5+2] cycloaddition

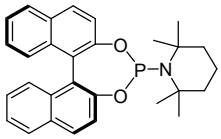
2.1. Chiral Ligand Screening



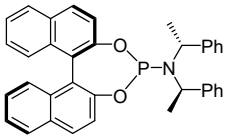
1a **2a** **3aa**



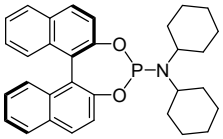
(*S,S,S*$_a$)-**L1**
31% yield, 43% ee



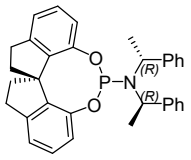
(*S*)-**L2**
35% yield, 0% ee



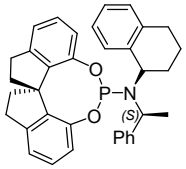
(*R,R,R*$_a$)-**L3**
trace



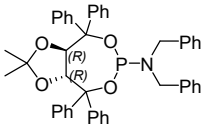
(*R*)-**L4**
50% yield, 14% ee



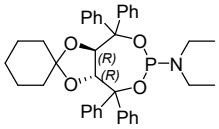
(*R,R,R*$_a$)-**L5**
63% yield, 0% ee



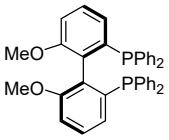
(*R,S,R*$_a$)-**L6**
62% yield, 0% ee



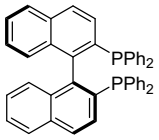
(*R,R*)-**L7**
25% yield, 9% ee



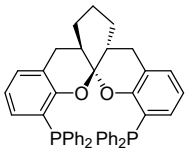
(*R,R*)-**L8**
60% yield, 0% ee



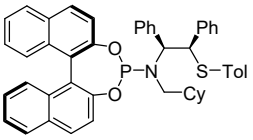
(*R*)-**L9**
14% yield, 34% ee



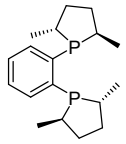
(*S*)-**L10**
trace



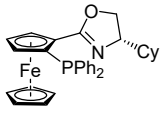
(*R,R,R*)-**L11**
trace



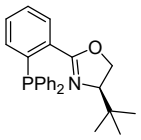
(*R*$_a$)-**L12**
49% yield, 3% ee



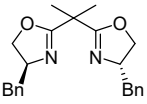
(*R,R*)-**L13**
72% yield, 0% ee



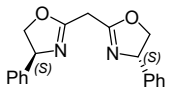
(*S,S*$_p$)-**L14**
52% yield, 3% ee



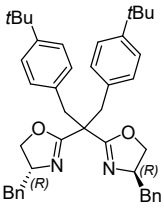
(*R*)-**L15**
68% yield, 2% ee



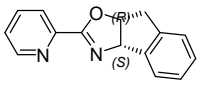
(*S,S*)-**L16**
56% yield, 3% ee



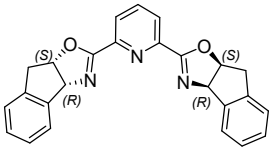
(*S,S*)-**L17**
45% yield, 0% ee



(*R,R*)-**L18**
79% yield, 0% ee

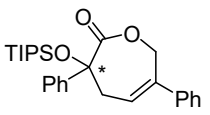


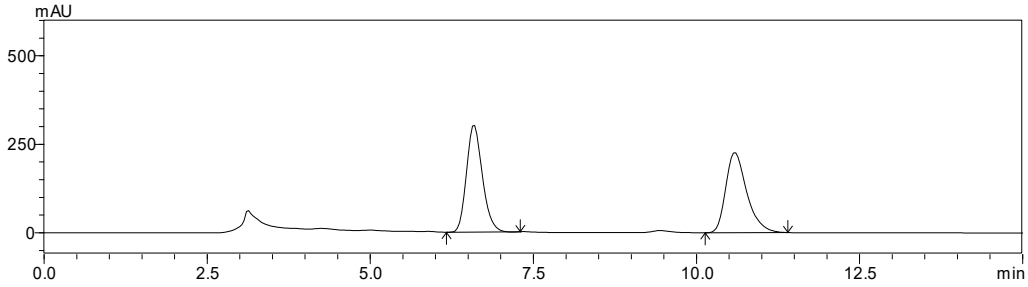
(*R,S*)-**L19**
49% yield, 0% ee



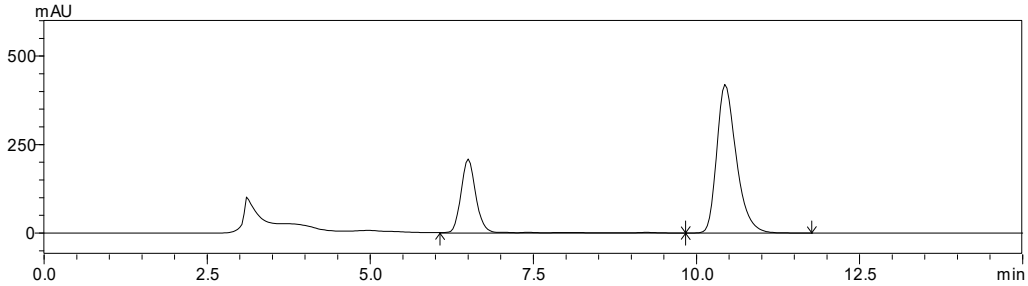
(*R,S*)-**L20**
46% yield, 0% ee

2.2. HPLC chromatogram of compound 3aa (43% ee)





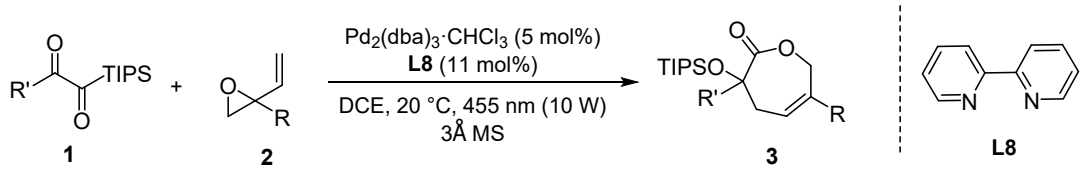
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.586	301686	5123248	50.202
2	10.585	225552	5082027	49.798
Total		527239	10205275	100.000



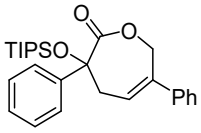
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.498	209402	3469063	28.434
2	10.438	419543	8731314	71.566
Total		628945	12200377	100.000

HPLC (Chiralcel IA, *n*-hexane/*i*-propanol = 97/3 v/v, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 6.498 min (minor), 10.438 min (major); $[\alpha]_D^{20}$ = +36.0 (*c* 0.20, CH_2Cl_2).

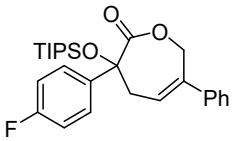
3. General procedure for [5+2] cycloaddition



General procedure A: Under a nitrogen atmosphere, $Pd_2(dba)_3 \cdot CHCl_3$ (0.005 mmol, 5 mol%), **L8** (0.011 mmol, 11 mol%) were added sequentially into a flame-dried Schlenk tube equipped with a magnetic stir bar. The tube was evacuated and back-filled with nitrogen for three times. Then the anhydrous DCE (<30 ppm water, *Karl-Fischer* titration) (1.0 mL) were added *via* syringe sequentially. The resulting mixture was stirred at room temperature for 30 minutes. Then, *α*-ketoacylsilanes **1** (0.4 mmol, 2.0 equiv.) and vinyl epoxides **2** (0.2 mmol, 1.0 equiv.) were added sequentially and the resulting solution was stirred under the irradiation of 10 W blue LEDs at 20 ºC for 4 h. The reaction mixture was concentrated *in vacuo* and the crude product was purified by column chromatography (petroleum ether/ethyl acetate = 20:1, v/v) to give the corresponding products **3**.

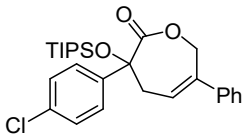


3,6-diphenyl-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one (3aa): Following the general procedure **A**, compound **3aa** was obtained as a yellow oil in 86% yield (74.9 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.35 (m, 2H), 7.27 (d, *J* = 6.8 Hz, 3H), 7.21 – 7.11 (m, 3H), 7.00 (d, *J* = 7.2 Hz, 2H), 5.93 (dt, *J* = 6.1, 2.8 Hz, 1H), 4.51 (d, *J* = 15.8 Hz, 1H), 4.23 – 4.11 (m, 1H), 3.21 (ddd, *J* = 18.7, 6.5, 2.6 Hz, 1H), 3.05 (dt, *J* = 18.7, 3.6 Hz, 1H), 1.00 – 0.87 (m, 12H), 0.84 (d, *J* = 6.8 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.8, 140.3, 139.5, 137.7, 129.1, 128.8(2C), 128.6(2C), 127.8, 126.2(2C), 126.2, 126.1(2C), 80.7, 69.1, 38.1, 18.5(3C), 18.4(3C), 13.6(3C); **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{36}O_3SiNa$ $[M+Na]^+$: 459.2326, found: 459.2322.

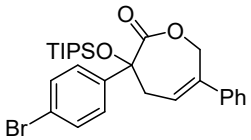


3-(4-fluorophenyl)-6-phenyl-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one (3ab) : Following the general procedure **A**, compound **3ab** was obtained as a yellow oil in 78% yield (70.8 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate =

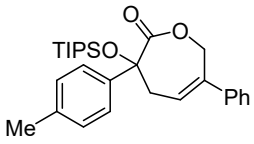
20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 8.3, 5.1 Hz, 2H), 7.30 – 7.24 (m, 3H), 7.15 – 6.99 (m, 4H), 6.02 (dt, *J* = 5.9, 2.7 Hz, 1H), 4.66 (d, *J* = 15.8 Hz, 1H), 4.35 – 4.17 (m, 1H), 3.32 – 3.06 (m, 2H), 1.08 – 1.00 (m, 3H), 0.97 (d, *J* = 6.7 Hz, 9H), 0.93 (d, *J* = 6.9 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.6, 162.9 (d, $^1J_{C\text{-}F}$ = 248.8 Hz), 140.2, 137.9, 135.9, 135.8, 128.8(2C), 128.1, 127.9, 126.2(2C), 126.0, 115.9, 115.8, 80.2, 69.2, 38.3, 18.5(3C), 18.4(3C), 13.6(3C); **^{19}F NMR** (377 MHz, $CDCl_3$) δ -112.19; **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{35}FO_3SiNa$ $[M+Na]^+$: 477.2232, found: 477.2240.



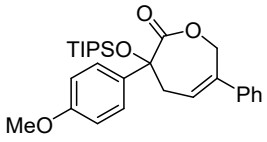
3-(4-chlorophenyl)-6-phenyl-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one (3ac): Following the general procedure **A**, compound **3ac** was obtained as a yellow oil in 83% yield (78.1 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.30 – 7.23 (m, 3H), 7.14 – 7.07 (m, 2H), 6.01 (ddd, *J* = 6.1, 3.7, 2.1 Hz, 1H), 4.67 (d, *J* = 15.8 Hz, 1H), 4.29 (dq, *J* = 15.8, 2.8 Hz, 1H), 3.29 – 3.08 (m, 2H), 1.08 – 1.00 (m, 3H), 0.97 (d, *J* = 6.8 Hz, 9H), 0.93 (d, *J* = 7.0 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.5, 140.1, 138.6, 138.1, 134.9, 129.1(2C), 128.8(2C), 128.0, 127.5(2C), 126.2(2C), 126.0, 80.3, 69.2, 38.2, 18.5(3C), 18.5(3C), 13.6(3C); **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{35}ClO_3SiNa$ $[M+Na]^+$: 493.1936, found: 493.1938.



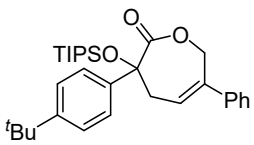
3-(4-bromophenyl)-6-phenyl-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one (3ad): Following the general procedure **A**, compound **3ad** was obtained as a yellow oil in 84% yield (87.0 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.24 (m, 3H), 7.11 (d, *J* = 7.1 Hz, 2H), 6.01 (dd, *J* = 6.4, 3.6 Hz, 1H), 4.68 (d, *J* = 15.8 Hz, 1H), 4.30 (dd, *J* = 15.7, 3.5 Hz, 1H), 3.29 – 3.08 (m, 2H), 1.05 (dt, *J* = 14.7, 7.2 Hz, 3H), 0.97 (d, *J* = 7.1 Hz, 9H), 0.93 (d, *J* = 7.1 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.4, 140.0, 139.1, 138.1 132.0(2C), 128.8(2C), 128.0, 127.8(2C), 126.2(2C), 125.9, 123.1, 80.4, 69.2, 38.1, 18.5(3C), 18.5(3C), 13.6(3C); **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{35}BrO_3SiNa$ $[M+Na]^+$:537.1431, found: 537.1431.



6-phenyl-3-(*p*-tolyl)-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one (3ae) : Following the general procedure **A**, compound **3ae** was obtained as a yellow oil in 53% yield (47.7 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.8 Hz, 2H), 7.29 – 7.21 (m, 3H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 6.2 Hz, 2H), 6.00 (dt, *J* = 6.0, 2.8 Hz, 1H), 4.57 (d, *J* = 15.8 Hz, 1H), 4.24 (dq, *J* = 15.8, 3.0 Hz, 1H), 3.27 (ddd, *J* = 18.9, 6.5, 2.7 Hz, 1H), 3.11 (dt, *J* = 18.8, 3.5 Hz, 1H), 2.33 (s, 3H), 1.04 – 0.94 (m, 12H), 0.92 (d, *J* = 6.6 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.0, 140.5, 138.9, 137.7, 136.5, 129.5(2C), 128.7(2C), 127.8, 126.3(2C), 126.2, 126.1(2C), 80.4, 69.2, 38.1, 21.3, 18.5(3C), 18.4(3C), 13.6(3C); **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{38}O_3SiNa$ $[M+Na]^+$: 473.2482, found: 473.2488.

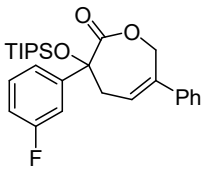


3-(4-methoxyphenyl)-6-phenyl-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one (3af) : Following the general procedure **A**, compound **3af** was obtained as a yellow oil in 54% yield (50.3 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.6 Hz, 2H), 7.31 – 7.18 (m, 3H), 7.16 – 7.05 (m, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.01 (dt, *J* = 6.1, 2.9 Hz, 1H), 4.59 (d, *J* = 15.8 Hz, 1H), 4.25 (dq, *J* = 15.8, 3.1 Hz, 1H), 3.79 (s, 3H), 3.27 (ddd, *J* = 18.9, 6.6, 2.7 Hz, 1H), 3.12 (dt, *J* = 18.9, 3.6 Hz, 1H), 1.05 – 0.96 (m, 12H), 0.94 (d, *J* = 6.4 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 159.9, 140.4, 137.6, 131.5, 128.6(2C), 127.7, 127.5(2C), 126.2(2C), 126.1, 114.0(2C), 80.0, 69.1, 55.3, 38.2, 18.5(3C), 18.4(3C), 13.5(3C); **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{38}O_4SiNa$ $[M+Na]^+$: 489.2432, found: 489.2427.

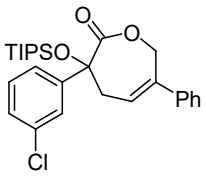


3-(4-(*tert*-butyl)phenyl)-6-phenyl-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one (3ag): Following the general procedure **A**, compound **3ag** was obtained as a yellow oil in 57% yield (56.1 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 4H), 7.31 – 7.23 (m, 3H), 7.14 – 7.10 (m,

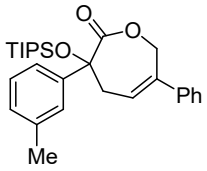
2H), 6.03 (dt, *J* = 6.0, 2.8 Hz, 1H), 4.60 (d, *J* = 15.7 Hz, 1H), 4.30 (dq, *J* = 15.7, 2.9 Hz, 1H), 3.30 (ddd, *J* = 18.8, 6.4, 2.7 Hz, 1H), 3.12 (dtd, *J* = 18.8, 3.6, 1.3 Hz, 1H), 1.29 (s, 9H), 1.02 – 0.94 (m, 12H), 0.91 (d, *J* = 6.3 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.0, 152.3, 140.6, 137.7, 136.6, 128.7(2C), 127.8, 126.4, 126.3(2C), 125.9(2C), 125.7(2C), 80.4, 69.1, 38.3, 34.8, 31.4(3C), 18.5(3C), 18.4(3C), 13.6(3C); **HRMS** (ESI-TOF, m/z): calcd for $C_{31}H_{44}O_3SiNa$ $[M+Na]^+$: 515.2952, found: 515.2961.



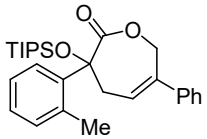
3-(3-fluorophenyl)-6-phenyl-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one (3ah) : Following the general procedure **A**, compound **3ah** was obtained as a yellow oil in 62% yield (56.0 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.22 (m, 5H), 7.19 (dt, *J* = 9.9, 2.2 Hz, 1H), 7.14 – 7.09 (m, 2H), 7.04 (td, *J* = 8.2, 2.5 Hz, 1H), 6.01 (ddd, *J* = 6.1, 3.7, 2.1 Hz, 1H), 4.69 (d, *J* = 15.8 Hz, 1H), 4.34 (dq, *J* = 15.8, 2.7 Hz, 1H), 3.28 – 3.06 (m, 2H), 1.08 – 1.01 (m, 3H), 0.97 (d, *J* = 6.9 Hz, 9H), 0.93 (d, *J* = 7.0 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.4, 162.9 (d, $^{1}J_{C\text{-}F}$ = 247.4 Hz), 142.6 (d, $^{3}J_{C\text{-}F}$ = 6.5 Hz), 140.1, 138.2, 130.5 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz), 128.8(2C), 128.0, 126.3(2C), 126.1, 121.9 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 116.1 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 113.2 (d, $^{2}J_{C\text{-}F}$ = 22.6 Hz), 80.5 (d, ^{4}J = 1.8 Hz), 69.2, 38.3, 18.5(3C), 18.4(3C), 13.6(3C); **^{19}F NMR** (377 MHz, $CDCl_3$) δ -111.44; **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{35}FO_3SiNa$ $[M+Na]^+$: 477.2232, found: 477.2239.



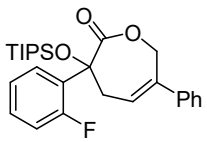
3-(3-chlorophenyl)-6-phenyl-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one (3ai) : Following the general procedure **A**, compound **3ai** was obtained as a yellow oil in 68% yield (64.1 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 2.1 Hz, 1H), 7.40 – 7.22 (m, 6H), 7.21 – 7.08 (m, 2H), 6.03 (ddd, *J* = 6.1, 3.8, 2.1 Hz, 1H), 4.72 (d, *J* = 15.8 Hz, 1H), 4.36 (dq, *J* = 15.8, 2.7 Hz, 1H), 3.29 – 3.10 (m, 2H), 1.05 – 0.97 (m, 12H), 0.95 (d, *J* = 6.9 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.3, 142.1, 140.1, 138.3, 134.8, 130.2, 129.2, 128.8(2C), 128.1, 126.4, 126.3(2C), 126.1, 124.3, 80.6, 69.3, 38.2, 18.5(3C), 18.4(3C), 13.6(3C); **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{35}ClO_3SiNa$ $[M+Na]^+$: 493.1936, found: 493.1943.



6-phenyl-3-(*m*-tolyl)-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one (3aj) : Following the general procedure **A**, compound **3aj** was obtained as a yellow oil in 70% yield (63.0 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.21 (m, 6H), 7.15 (d, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 7.3 Hz, 2H), 6.02 (dd, *J* = 6.3, 3.1 Hz, 1H), 4.60 (d, *J* = 15.8 Hz, 1H), 4.29 (dt, *J* = 15.8, 2.9 Hz, 1H), 3.29 (dd, *J* = 18.7, 6.6 Hz, 1H), 3.12 (dd, *J* = 18.7, 3.3 Hz, 1H), 2.34 (s, 3H), 1.04 – 0.90 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 140.5, 139.4, 138.6, 137.7, 129.8, 128.7(3C), 127.8, 127.1, 126.3(3C), 123.0, 80.7, 69.2, 38.1, 21.6, 18.5(3C), 18.4(3C), 13.6(3C); **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{38}O_3SiNa$ $[M+Na]^+$: 473.2482, found: 473.2488.

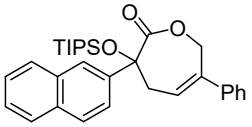


6-phenyl-3-(o-tolyl)-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H)*-one (3ak) : Following the general procedure **A**, compound **3ai** was obtained as a yellow oil in 58% yield (52.2 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.9 Hz, 1H), 7.31 – 7.20 (m, 5H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 2H), 6.07 (dt, *J* = 5.9, 2.8 Hz, 1H), 4.52 (d, *J* = 15.8 Hz, 1H), 4.14 (dq, *J* = 16.1, 3.3 Hz, 1H), 3.39 (ddd, *J* = 18.9, 6.4, 2.9 Hz, 1H), 3.10 (dt, *J* = 18.9, 3.5 Hz, 1H), 2.51 (s, 3H), 1.10 – 0.92 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.1, 140.8, 137.9, 137.4, 137.3, 132.7, 129.1, 128.7(2C), 127.8, 126.3(2C), 126.0, 125.6, 125.2, 79.2, 68.6, 38.7, 20.1, 18.2(3C), 18.1(3C), 13.9(3C). **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{38}O_3SiNa$ $[M+Na]^+$: 473.2482, found: 473.2490.

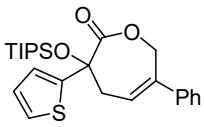


3-(2-fluorophenyl)-6-phenyl-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H)*-one (3al) : Following the general procedure **A**, compound **3ak** was obtained as a yellow oil in 58% yield (52.7 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1,

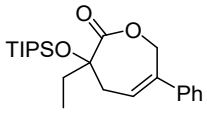
v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.47 (m, 1H), 7.38 – 7.30 (m, 1H), 7.30 – 7.24 (m, 3H), 7.18 – 7.14 (m, 1H), 7.10 (dd, *J* = 11.7, 8.0 Hz, 3H), 6.04 (dd, *J* = 6.7, 3.5 Hz, 1H), 4.77 (d, *J* = 16.0 Hz, 1H), 4.51 (d, *J* = 16.0 Hz, 1H), 3.32 (dd, *J* = 18.2, 6.7 Hz, 1H), 3.10 (dt, *J* = 18.2, 3.8 Hz, 1H), 1.12 – 1.05 (m, 3H), 0.97 (dd, *J* = 13.7, 7.2 Hz, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.2, 160.1 (d, $^1J_{C\text{-}F}$ = 249.3 Hz), 140.1, 138.1, 130.9 (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 128.7, 128.1 (d, $^2J_{C\text{-}F}$ = 12.8 Hz), 127.9, 127.8 (d, $^4J_{C\text{-}F}$ = 3.7 Hz), 126.3, 125.9, 124.3 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 116.7 (d, $^2J_{C\text{-}F}$ = 22.5 Hz), 78.1, 69.3, 38.7, 18.5, 18.4, 13.6; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -111.58; **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{35}FO_3SiNa$ $[M+Na]^+$: 477.2232, found: 477.2237.



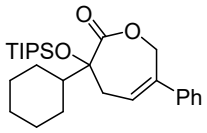
3-(naphthalen-2-yl)-6-phenyl-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one (3am) : Following the general procedure **A**, compound **3am** was obtained as a yellow oil in 90% yield (87.5 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.81 (m, 4H), 7.60 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.27 – 7.21 (m, 3H), 7.11 – 7.05 (m, 2H), 6.10 (dt, *J* = 6.1, 3.0 Hz, 1H), 4.61 (d, *J* = 15.8 Hz, 1H), 4.27 (dq, *J* = 15.8, 2.8 Hz, 1H), 3.43 (ddd, *J* = 18.7, 6.5, 2.6 Hz, 1H), 3.24 (dtd, *J* = 18.7, 3.5, 1.4 Hz, 1H), 1.05 (ddd, *J* = 9.7, 6.7, 5.4 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 9H), 0.92 (d, *J* = 7.0 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 140.3, 137.9, 136.9, 133.4, 133.1, 128.9, 128.7(2C), 128.5, 127.9, 127.8, 126.9, 126.7, 126.3(2C), 126.3, 125.1, 124.1, 80.9, 69.3, 38.2, 18.5(3C), 18.5(3C), 13.6(3C); **HRMS** (ESI-TOF, m/z): calcd for $C_{31}H_{38}O_3SiNa$ $[M+Na]^+$: 509.2482, found: 509.2489.



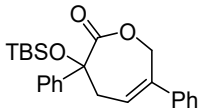
6-phenyl-3-(thiophen-2-yl)-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one (3an) : Following the general procedure **A**, compound **3an** was obtained as a yellow oil in 46% yield (40.1 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (ddd, *J* = 17.7, 9.5, 3.5 Hz, 4H), 7.17 (d, *J* = 6.6 Hz, 2H), 7.13 (d, *J* = 3.7 Hz, 1H), 6.95 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.00 (ddd, *J* = 6.1, 4.1, 2.0 Hz, 1H), 4.78 (d, *J* = 15.6 Hz, 1H), 4.59 (dq, *J* = 15.5, 2.6 Hz, 1H), 3.35 – 3.13 (m, 2H), 1.12 – 0.98 (m, 12H), 0.97 (d, *J* = 7.1 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.6, 144.4, 140.2, 138.1, 128.7(2C), 127.9, 126.6, 126.4, 126.3(2C), 126.1, 125.9, 77.8, 69.6, 40.9, 18.6(3C), 18.5(3C), 13.6(3C); **HRMS** (ESI-TOF, m/z): calcd for $C_{25}H_{34}O_3SSiNa$ $[M+Na]^+$: 465.1890, found: 465.1892.



3-ethyl-6-phenyl-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one (3ao) : Following the general procedure **A**, compound **3ao** was obtained as a yellow oil in 38% yield (29.5 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.18 (m, 5H), 6.06 (t, *J* = 5.5 Hz, 1H), 5.45 (d, *J* = 14.8 Hz, 1H), 4.93 (d, *J* = 14.7 Hz, 1H), 2.82 (dd, *J* = 17.6, 5.1 Hz, 1H), 2.69 (dd, *J* = 17.5, 5.6 Hz, 1H), 2.13 (dq, *J* = 14.5,7.2 Hz, 1H), 1.77 (dq, *J* = 14.5, 7.4 Hz, 1H), 1.27 (d, *J* = 11.3 Hz, 2H), 1.21 – 1.04 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.5, 140.4, 138.4, 128.8(2C), 127.8, 127.6, 126.3(2C), 81.6, 69.2, 37.2, 34.0, 18.5(6C), 13.9(3C), 9.4; **HRMS** (ESI-TOF, m/z): calcd for $C_{23}H_{36}O_3SiNa$ $[M+Na]^+$: 411.2326, found: 411.2327.

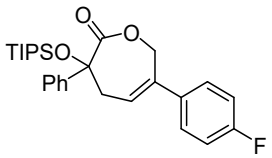


3-cyclohexyl-6-phenyl-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one (3ap) : Following the general procedure **A**, compound **3ap** was obtained as a yellow oil in 39% yield (33.3 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 5H), 6.23 (t, *J* = 6.3 Hz, 1H), 5.12 (d, *J* = 15.0 Hz, 1H), 4.97 (d, *J* = 14.9 Hz, 1H), 2.79 (dd, *J* = 16.1, 6.9 Hz, 1H), 2.70 (dd, *J* = 16.0, 5.5 Hz, 1H), 1.95 (t, *J* = 11.2 Hz, 1H), 1.82 (d, *J* = 10.4 Hz, 2H), 1.72 (q, *J* = 12.1 Hz, 3H), 1.31 – 1.17 (m, 8H), 1.05 (dd, *J* = 13.6, 7.3 Hz, 18H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.6, 139.6, 139.4, 128.8(2C), 128.7, 128.0, 125.9(2C), 85.3, 68.7, 46.3, 34.9, 27.6, 27.4, 26.8, 26.6(2), 26.6(1), 18.8(6C), 13.7(3C); **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{42}O_3SiNa$ $[M+Na]^+$: 465.2795, found: 465.2801.



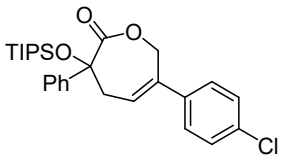
3-((*tert*-butyldimethylsilyl)oxy)-3,6-diphenyl-4,7-dihydrooxepin-2(3*H*)-one (3aq) : Following the general procedure **A**, compound **3aq** was obtained as a yellow oil in 35% yield (27.5 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 2H), 7.44 – 7.36 (m, 3H), 7.32 – 7.25 (m, 3H), 7.13 (dt, *J* = 5.9, 1.7 Hz, 2H), 6.05 (tt, *J* = 3.5, 2.0 Hz, 1H), 4.71 (d, *J* = 15.8 Hz, 1H), 4.37 (dq,

J = 16.0, 2.9 Hz, 1H), 3.31 (ddd, *J* = 18.7, 6.5, 2.6 Hz, 1H), 3.08 (ddd, *J* = 18.7, 6.3, 2.7 Hz, 1H), 0.83 (s, 9H), -0.04 (d, *J* = 5.9 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 140.5, 139.5, 137.8, 129.1, 128.9(2C), 128.7(2C), 127.9, 126.3, 126.3(2C), 126.3(2C), 80.8, 69.2, 38.2, 25.9(3C), 18.6, -2.8, -2.9. **HRMS** (ESI-TOF, m/z): calcd for $C_{24}H_{30}O_3SiNa$ $[M+Na]^+$: 417.1856, found: 417.1856.



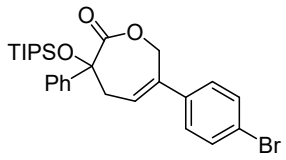
6-(4-fluorophenyl)-3-phenyl-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one

(3ba) : Following the general procedure **A**, compound **3ba** was obtained as a yellow oil in 71% yield (64.5 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 2H), 7.38 (d, *J* = 6.6 Hz, 3H), 7.07 (dd, *J* = 8.4, 5.3 Hz, 2H), 6.98 – 6.94 (m, 2H), 5.99 (dt, *J* = 6.1, 2.8 Hz, 1H), 4.56 (d, *J* = 15.8 Hz, 1H), 4.24 (dt, *J* = 16.0, 3.2 Hz, 1H), 3.30 (ddd, *J* = 18.7, 6.7, 2.6 Hz, 1H), 3.14 (dt, *J* = 18.6, 3.7 Hz, 1H), 1.06 – 0.95 (m, 12H), 0.93 (d, *J* = 6.8 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.8, 162.5 (d, $^{1}J_{C\text{-}F}$ = 247.3 Hz), 139.6, 136.9, 136.4 (d, $^{4}J_{C\text{-}F}$ = 3.4 Hz), 129.2, 128.9(2C), 128.0, 127.9, 126.3, 126.1(2C), 115.7, 115.5, 80.7, 69.1, 38.1, 18.5(3C), 18.4(3C), 13.6(3C); **^{19}F NMR** (377 MHz, $CDCl_3$) δ -114.27; **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{35}FO_3SiNa$ $[M+Na]^+$ 477.2232, found: 477.2242.

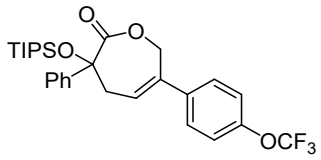


6-(4-chlorophenyl)-3-phenyl-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one

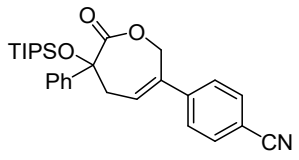
(3ca) : Following the general procedure **A**, compound **3ca** was obtained as a yellow solid in 65% yield (61.2 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 2H), 7.38 (d, *J* = 6.3 Hz, 3H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.03 (dt, *J* = 6.2, 2.8 Hz, 1H), 4.56 (d, *J* = 15.8 Hz, 1H), 4.26 (dq, *J* = 15.9, 3.0 Hz, 1H), 3.31 (ddd, *J* = 18.6, 6.6, 2.6 Hz, 1H), 3.14 (dt, *J* = 18.8, 3.6 Hz, 1H), 1.06 – 0.96 (m, 12H), 0.93 (d, *J* = 6.7 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.7, 139.5, 138.8, 136.8, 133.8, 129.2, 128.9(2C), 128.8(2C), 127.5(2C), 126.9, 126.1(2C), 80.7, 68.8, 38.1, 18.5(3C), 18.4(3C), 13.6(3C); **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{35}ClO_3SiNa$ $[M+Na]^+$: 493.1936, found: 493.1938.



6-(4-bromophenyl)-3-phenyl-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one (3da) : Following the general procedure **A**, compound **3da** was obtained as a yellow solid in 65% yield (66.9 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **1H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.41 – 7.36 (m, 5H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.04 (dt, *J* = 6.0, 2.7 Hz, 1H), 4.55 (d, *J* = 15.8 Hz, 1H), 4.25 (dd, *J* = 15.8, 3.2 Hz, 1H), 3.30 (ddd, *J* = 18.7, 6.6, 2.6 Hz, 1H), 3.13 (dt, *J* = 18.8, 3.6 Hz, 1H), 1.06 – 0.95 (m, 12H), 0.93 (d, *J* = 6.7 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.7, 139.5, 139.2, 136.9, 131.8(2C), 129.2, 128.9(2C), 127.9(2C), 126.9, 126.1(2C), 121.9, 80.7, 68.8, 38.1, 18.5(3C), 18.4(3C), 13.6(3C); **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{35}BrO_3SiNa$ $[M+Na]^+$: 537.1431, found: 537.1431.

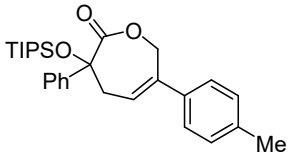


3-phenyl-6-(4-(trifluoromethoxy)phenyl)-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one (3ea) : Following the general procedure **A**, compound **3ea** was obtained as a yellow oil in 59% yield (61.3 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 6.0 Hz, 2H), 7.38 (d, *J* = 6.3 Hz, 3H), 7.12 (s, 4H), 6.04 (dt, *J* = 6.3, 2.8 Hz, 1H), 4.57 (d, *J* = 15.8 Hz, 1H), 4.27 (dd, *J* = 15.8, 3.4 Hz, 1H), 3.37 – 3.26 (m, 1H), 3.15 (dt, *J* = 18.8, 3.7 Hz, 1H), 1.06 – 0.96 (m, 12H), 0.93 (d, *J* = 6.7 Hz, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.7, 148.9, 139.5, 139.1, 136.8, 129.2, 128.9(2C), 127.7(2C), 127.2, 126.1(2C), 121.8 (q, $^1J_{C\text{-}F}$ = 257.5 Hz), 121.2(2C), 80.8, 68.9, 38.2, 18.5(3C), 18.4(3C), 13.6(3C). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -57.92. **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{35}F_3O_4SiNa$ $[M+Na]^+$: 543.2149, found: 543.2157.

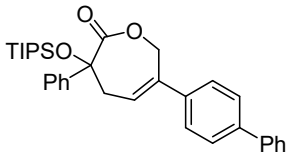


4-(7-oxo-6-phenyl-6-((triisopropylsilyl)oxy)-2,5,6,7-tetrahydrooxepin-3-yl)benzonitrile (3fa) : Following the general procedure **A**, compound **3fa** was obtained as a yellow oil in 33% yield (30.0 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 2H), 7.46 (dq, *J* = 5.3, 2.9 Hz, 2H),

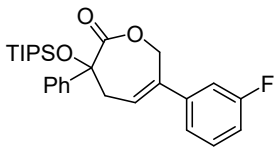
7.39 (dd, *J* = 5.1, 2.1 Hz, 3H), 7.22 – 7.17 (m, 2H), 6.15 (dt, *J* = 6.1, 2.9 Hz, 1H), 4.56 (d, *J* = 15.7 Hz, 1H), 4.29 (dq, *J* = 15.8, 2.8 Hz, 1H), 3.36 (ddd, *J* = 19.0, 6.5, 2.6 Hz, 1H), 3.16 (dtd, *J* = 19.0, 3.6, 1.2 Hz, 1H), 1.01 – 0.89 (m, 21H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.5, 144.8, 139.4, 136.6, 132.6(2C), 129.4, 129.3, 129.0(2C), 126.8(2C), 126.0(2C), 118.6, 111.6, 80.6, 68.3, 38.2, 18.5(3C), 18.4(3C), 13.6(3C). **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{35}NO_3SiNa$ $[M+Na]^+$: 484.2278, found: 484.2281.



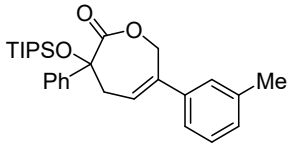
3-phenyl-6-(*p*-tolyl)-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one (3ga) : Following the general procedure **A**, compound **3ga** was obtained as a yellow solid in 88% yield (79.2 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.42 – 7.34 (m, 3H), 7.10 (d, *J* = 7.9 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 6.02 (dt, *J* = 6.1, 2.8 Hz, 1H), 4.62 (d, *J* = 15.8 Hz, 1H), 4.26 (dt, *J* = 16.0, 3.1 Hz, 1H), 3.31 (ddd, *J* = 18.7, 6.7, 2.6 Hz, 1H), 3.16 (dt, *J* = 18.7, 3.6 Hz, 1H), 2.32 (s, 3H), 1.11 – 0.98 (m, 12H), 0.95 (d, *J* = 6.8 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 139.6, 137.7, 137.6, 137.4, 129.3(2C), 129.0, 128.8(2C), 126.1(2C), 126.1(2C), 125.4, 80.7, 69.2, 38.1, 21.1, 18.5(3C), 18.4(3C), 13.6(3C); **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{38}O_3SiNa$ $[M+Na]^+$ 473.2482, found: 473.2491.



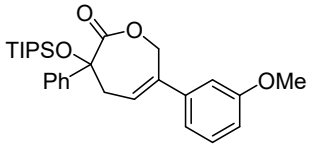
6-((1,1'-biphenyl)-4-yl)-3-phenyl-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one (3ha) : Following the general procedure **A**, compound **3ha** was obtained as a yellow solid in 78% yield (79.8 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 15.3, 7.7 Hz, 6H), 7.46 – 7.35 (m, 6H), 7.20 (d, *J* = 7.9 Hz, 2H), 6.12 (dd, *J* = 6.2, 3.1 Hz, 1H), 4.68 (d, *J* = 15.8 Hz, 1H), 4.32 (dt, *J* = 15.8, 2.7 Hz, 1H), 3.35 (dd, *J* = 18.7, 6.4 Hz, 1H), 3.19 (d, *J* = 18.1 Hz, 1H), 1.09 – 0.99 (m, 12H), 0.96 (d, *J* = 6.9 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.86, 140.76, 140.47, 139.62, 139.19, 137.36, 129.12, 128.95(2C), 128.89(2C), 127.61, 127.38(2C), 127.08(2C), 126.62(2C), 126.21, 126.14(2C), 80.74, 69.02, 38.18, 18.51(3C), 18.43(3C), 13.61(3C); **HRMS** (ESI-TOF, m/z): calcd for $C_{33}H_{40}O_3SiNa$ $[M+Na]^+$: 535.2639, found: 535.2646.



6-(3-fluorophenyl)-3-phenyl-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one (3ia) : Following the general procedure **A**, compound **3ia** was obtained as a yellow oil in 38% yield (34.5 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 2H), 7.38 (d, *J* = 6.2 Hz, 3H), 7.28 – 7.21 (m, 1H), 6.96 – 6.91 (m, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.80 (dd, *J* = 10.0, 2.2 Hz, 1H), 6.07 (dq, *J* = 5.1, 2.5 Hz, 1H), 4.57 (d, *J* = 15.8 Hz, 1H), 4.26 (dd, *J* = 16.1, 3.2 Hz, 1H), 3.32 (dd, *J* = 18.7, 6.5 Hz, 1H), 3.20 – 3.08 (m, 1H), 1.08 – 0.88 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.7, 162.9 (d, $^1J_{C\text{-}F}$ = 246.7 Hz), 142.6 (d, $^3J_{C\text{-}F}$ = 7.5 Hz), 139.5, 136.8 (d, $^4J_{C\text{-}F}$ = 2.2 Hz), 130.2 (d, $^3J_{C\text{-}F}$ = 8.4 Hz), 129.2, 128.9 (2C), 127.3, 126.1(2C), 121.8 (d, $^4J_{C\text{-}F}$ = 2.8 Hz), 114.7 (d, $^2J_{C\text{-}F}$ = 21.3 Hz), 113.3 (d, $^2J_{C\text{-}F}$ = 22.1 Hz), 80.7, 68.8, 38.1, 18.5(3C), 18.4(3C), 13.6(3C); **^{19}F NMR** (377 MHz, Chloroform-*d*) δ -112.60; **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{35}FO_3SiNa$ $[M+Na]^+$: 477.2232, found: 477.2242.

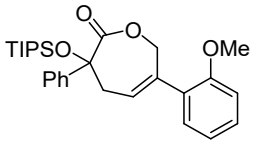


3-phenyl-6-(*m*-tolyl)-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3H)-one (3ja) : Following the general procedure **A**, compound **3ja** was obtained as a yellow solid in 78% yield (70.2 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.0 Hz, 2H), 7.38 (d, *J* = 6.9 Hz, 3H), 7.19 – 7.15 (m, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.92 (d, *J* = 9.2 Hz, 2H), 6.03 (dt, *J* = 5.4, 2.8 Hz, 1H), 4.62 (d, *J* = 15.8 Hz, 1H), 4.27 (dt, *J* = 15.8, 2.7 Hz, 1H), 3.31 (dd, *J* = 18.7, 6.4 Hz, 1H), 3.21 – 3.08 (m, 1H), 2.32 (s, 3H), 1.00 (td, *J* = 19.5, 19.0, 7.0 Hz, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 140.4, 139.6, 138.3, 137.8, 129.1, 128.9(2C), 128.6(2C), 126.9, 126.1(2C), 125.9, 123.3, 80.7, 69.2, 38.1, 21.5, 18.5(3C), 18.4(3C), 13.6(3C); **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{38}O_3SiNa$ $[M+Na]^+$: 473.2482, found: 473.2481.

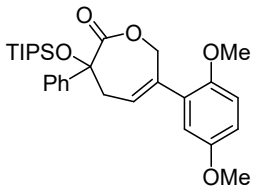


6-(3-methoxyphenyl)-3-phenyl-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one (3ka) : Following the general procedure **A**, compound **3ka** was obtained as a yellow solid in

77% yield (71.7 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.37 (d, *J* = 6.5 Hz, 3H), 7.22 – 7.15 (m, 1H), 6.82 – 6.76 (m, 1H), 6.68 (d, *J* = 7.7 Hz, 1H), 6.63 (d, *J* = 2.2 Hz, 1H), 6.04 (dt, *J* = 5.9, 2.8 Hz, 1H), 4.59 (d, *J* = 15.8 Hz, 1H), 4.25 (dd, *J* = 16.0, 3.2 Hz, 1H), 3.77 (s, 3H), 3.30 (dd, *J* = 18.8, 6.5 Hz, 1H), 3.14 (dt, *J* = 18.9, 3.8 Hz, 1H), 1.06 – 0.96 (m, 12H), 0.93 (d, *J* = 6.8 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 159.8, 141.9, 139.6, 137.7, 129.7, 129.1, 128.9(2C), 126.3, 126.1(2C), 118.7, 112.9, 112.3, 80.7, 69.1, 55.4, 38.1, 18.5(3C), 18.4(3C), 13.6(3C); **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{38}O_4SiNa$ $[M+Na]^+$: 489.2432, found: 489.2432.

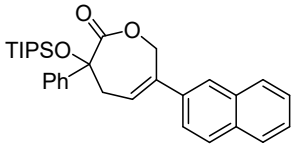


6-(2-methoxyphenyl)-3-phenyl-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one (3la) : Following the general procedure **A**, compound **3la** was obtained as a yellow solid in 79% yield (73.6 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.47 (m, 2H), 7.39 (d, *J* = 6.3 Hz, 3H), 7.27 – 7.19 (m, 1H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.89 – 6.86 (m, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 5.87 (dq, *J* = 6.0, 2.5 Hz, 1H), 4.43 (d, *J* = 15.7 Hz, 1H), 4.18 (dd, *J* = 15.7, 3.5 Hz, 1H), 3.64 (s, 3H), 3.27 (dd, *J* = 18.5, 6.0 Hz, 1H), 3.20 – 3.08 (m, 1H), 1.09 – 0.97 (m, 12H), 0.94 (d, *J* = 6.8 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.1, 156.5, 139.7, 137.2, 130.4, 129.6, 129.3, 128.9, 128.7(2C), 126.9, 126.3(2C), 120.9, 110.7, 80.6, 69.2, 55.3, 37.9, 18.5(3C), 18.4(3C), 13.6(3C); **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{38}O_4SiNa$ $[M+Na]^+$: 489.2432, found: 489.2436.

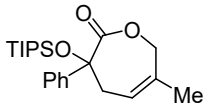


6-(2,5-dimethoxyphenyl)-3-phenyl-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one (3ma) : Following the general procedure **A**, compound **3ma** was obtained as a yellow oil in 83% yield (82.3 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.45 (m, 2H), 7.38 (d, *J* = 6.4 Hz, 3H), 6.74 (dt, *J* = 8.8, 2.3 Hz, 1H), 6.69 (d, *J* = 8.9 Hz, 1H), 6.58 (s, 1H), 5.88 (dt, *J* = 5.4, 2.8 Hz, 1H), 4.43 (d, *J* = 15.7 Hz, 1H), 4.19 (dt, *J* = 15.6, 2.7 Hz, 1H), 3.74 (s, 3H), 3.58 (s, 3H), 3.27 (dd, *J* = 18.6, 6.4 Hz, 1H), 3.19 – 3.05 (m, 1H), 1.06 – 0.90 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.1,

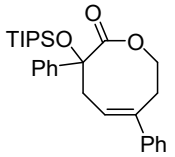
153.7, 150.7, 139.7, 137.1, 131.3, 128.9, 128.7(2C), 127.1, 126.3(2C), 115.8, 113.4, 111.9, 80.6, 69.1, 56.0, 55.8, 37.9, 18.5(3C), 18.4(3C), 13.6(3C); **HRMS** (ESI-TOF, m/z): calcd for $C_{29}H_{40}O_5SiNa$ $[M+Na]^+$: 519.2537, found: 519.2550.



6-(naphthalen-2-yl)-3-phenyl-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one (3na) : Following the general procedure **A**, compound **3na** was obtained as a yellow oil in 81% yield (78.7 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.68 (m, 3H), 7.50 (d, *J* = 7.3 Hz, 3H), 7.45 – 7.40 (m, 2H), 7.36 (d, *J* = 7.6 Hz, 3H), 7.25 (d, *J* = 8.6 Hz, 1H), 6.15 (dt, *J* = 6.1, 2.7 Hz, 1H), 4.73 (d, *J* = 15.7 Hz, 1H), 4.35 (dd, *J* = 15.8, 3.3 Hz, 1H), 3.34 (dt, *J* = 18.9, 4.0 Hz, 1H), 3.18 (dt, *J* = 18.7, 3.7 Hz, 1H), 1.06 – 0.90 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.9, 139.7, 137.7, 137.6, 133.3, 132.8, 129.1, 128.9(2C), 128.4, 128.1, 127.7, 126.8, 126.6, 126.3, 126.1(2C), 124.9, 124.4, 80.8, 69.1, 38.3, 18.5(3C), 18.4(3C), 13.6(3C); **HRMS** (ESI-TOF, m/z): calcd for $C_{31}H_{38}O_3SiNa$ $[M+Na]^+$: 509.2482, found: 509.2493.



6-methyl-3-phenyl-3-((triisopropylsilyl)oxy)-4,7-dihydrooxepin-2(3*H*)-one (3oa) : Following the general procedure **A**, compound **3oa** was obtained as a yellow oil in 80% yield (59.8 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 2H), 7.38 – 7.31 (m, 3H), 5.64 – 5.54 (m, 1H), 4.01 (d, *J* = 15.8 Hz, 1H), 3.85 (dd, *J* = 15.8, 3.2 Hz, 1H), 3.08 (dd, *J* = 18.3, 6.1 Hz, 1H), 2.97 – 2.86 (m, 1H), 1.55 (s, 3H), 0.94 (d, *J* = 6.2 Hz, 12H), 0.90 (d, *J* = 6.6 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.05, 139.36, 132.47, 128.89, 128.73(2C), 126.29(2C), 122.40, 80.71, 69.86, 37.32, 22.46, 18.46(3C), 18.39(3C), 13.58(3C); **HRMS** (ESI-TOF, m/z): calcd for $C_{22}H_{34}O_3SiNa$ $[M+Na]^+$: 397.2169, found: 397.2173.

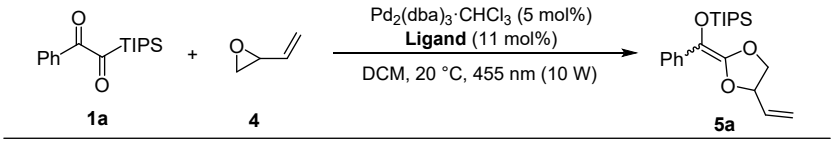


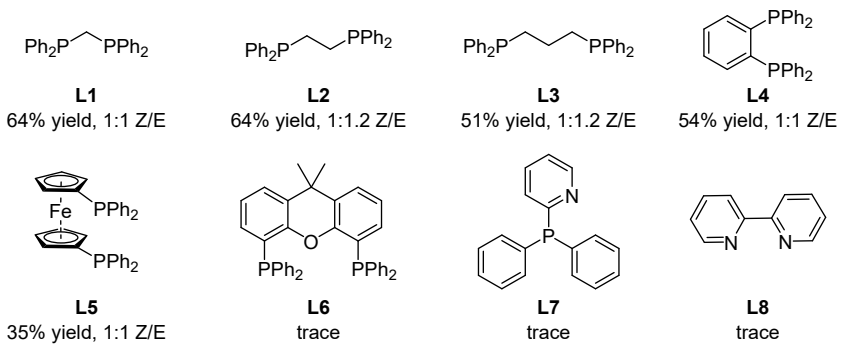
(E)-3,6-diphenyl-3-((triisopropylsilyl)oxy)-3,4,7,8-tetrahydro-2H-oxocin-2-one (3pa) : Following the general procedure **A**, compound **3pa** was obtained as a yellow oil in 60% yield

(54.0 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.35 – 7.31 (m, 1H), 7.31 – 7.27 (m, 2H), 7.25 (s, 3H), 7.23 – 7.17 (m, 2H), 6.14 (ddd, *J* = 10.0, 6.9, 1.4 Hz, 1H), 4.74 (td, *J* = 11.3, 10.9, 1.6 Hz, 1H), 4.06 (dt, *J* = 10.7, 3.4 Hz, 1H), 3.25 (dd, *J* = 12.2, 10.0 Hz, 1H), 3.00 (t, *J* = 13.2 Hz, 1H), 2.92 (dd, *J* = 12.3, 6.9 Hz, 1H), 2.52 – 2.40 (m, 1H), 0.93 – 0.80 (m, 21H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.5, 144.2, 141.9, 141.3, 128.6, 128.5(2C), 128.4(3C), 127.2, 127.0(2C), 126.6(2C), 88.0, 42.6, 34.0, 29.9, 18.4(3C), 18.4(3C), 13.6(3C); **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{38}O_3SiNa$ $[M+Na]^+$: 473.2482, found: 473.2489.

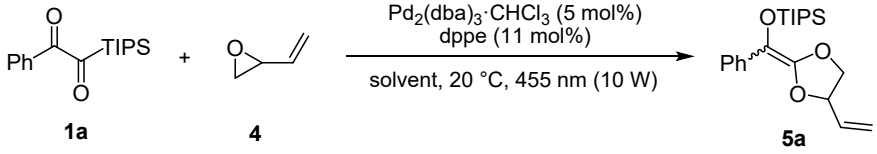
4. General procedure for [3+2] cycloaddition

4.1. Ligand Screening



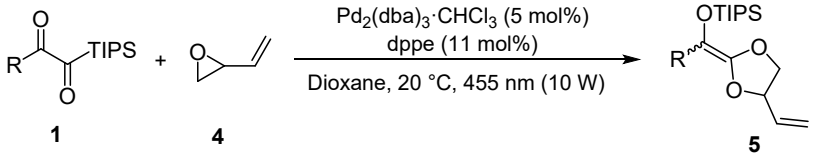


4.2. Solvent Screening



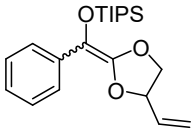
entry	solvent	yield (%)	Z/E
1	DCM	64	1:1.2
2	DCE	45	1:1
3	THF	63	1:1.2
4	CH_3CN	26	1:1.8
5	toluene	48	1:1.4
6	1,4-dioxane	70	1:1

5. General procedure for [3+2] cycloaddition

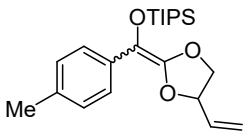


General procedure B: Under a nitrogen atmosphere, $Pd_2(dba)_3·CHCl_3$ (0.005 mmol, 5 mol%), dppe (0.011 mmol, 11 mol%) were added sequentially into a flame-dried Schlenk tube equipped with a magnetic stir bar. The tube was evacuated and back-filled with nitrogen for three times. Then the anhydrous dioxane (<30 ppm water, *Karl-Fischer* titration) (1.0 mL) were added *via* syringe sequentially. The resulting mixture was stirred at room temperature for 30 minutes. Then, *α*-ketoacylsilanes **1** (0.4 mmol, 2.0 equiv.) and vinyl epoxide **4** (0.2 mmol, 1.0 equiv.) were added sequentially and the resulting solution was stirred under the irradiation of 10 W blue LEDs at 20 ºC for 4 h. The reaction mixture was concentrated *in vacuo* and the crude

product was purified by column chromatography (petroleum ether/ethyl acetate = 20:1, v/v) to give the corresponding products **5**.

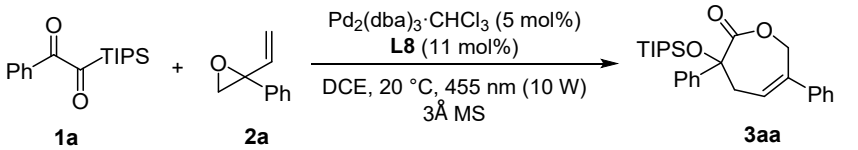


(*Z/E*)-triisopropyl(phenyl(4-vinyl-1,3-dioxolan-2-ylidene)methoxy)silane (5a) : Following the general procedure **B**, compound **5a** was obtained as a yellow oil in 70% yield (50.4 mg), 1:1 (*Z/E*); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 4H), 7.35 (d, *J* = 7.2 Hz, 6H), 5.91 (ddd, *J* = 17.5, 10.2, 7.6 Hz, 1H), 5.70 (ddd, *J* = 17.5, 10.1, 7.7 Hz, 1H), 5.34 (dd, *J* = 17.1, 3.9 Hz, 2H), 5.28 (d, *J* = 10.3 Hz, 1H), 5.20 (d, *J* = 10.2 Hz, 1H), 4.61 (q, *J* = 7.5 Hz, 1H), 4.47 (d, *J* = 7.5 Hz, 1H), 4.24 (t, *J* = 7.3 Hz, 1H), 4.11 (t, *J* = 7.3 Hz, 1H), 3.69 (t, *J* = 7.8 Hz, 1H), 3.59 (t, *J* = 8.1 Hz, 1H), 1.32 (dq, *J* = 18.4, 7.6 Hz, 6H), 1.03 (dt, *J* = 13.9, 5.1 Hz, 36H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.7, 135.3, 134.3, 128.9, 128.9, 128.3(3C), 128.2(2C), 126.9(6C), 119.8, 119.3, 110.6, 110.4, 79.4, 78.1, 69.9, 69.8, 18.9(3C), 18.8(3C), 18.8(3C), 18.7(3C), 11.8(3C), 11.7(3C); **HRMS** (ESI-TOF, m/z): calcd for $C_{21}H_{32}O_3SiNa$ $[M+Na]^+$: 383.2013, found: 383.2012.



(*Z/E*)-triisopropyl(p-tolyl(4-vinyl-1,3-dioxolan-2-ylidene)methoxy)silane (5b) : Following the general procedure **B**, compound **5b** was obtained as a yellow oil in 60% yield (47.6 mg) , 1.2:1 (*Z/E*); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1, v/v); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 8.1, 2.4 Hz, 2H, major + minor), 7.16 (dd, *J* = 8.0, 2.3 Hz, 2H, major + minor), 5.91 (ddd, *J* = 17.5, 10.3, 7.6 Hz, 1H, minor), 5.70 (ddd, *J* = 17.5, 10.2, 7.6 Hz, 1H, major), 5.33 (dd, *J* = 17.2, 3.0 Hz, 2H, major + minor), 5.27 (d, *J* = 10.3 Hz, 1H, minor), 5.19 (d, *J* = 10.2 Hz, 1H, major), 4.59 (q, *J* = 7.4 Hz, 1H, major), 4.46 (q, *J* = 7.5 Hz, 1H, minor), 4.23 (dd, *J* = 8.0, 6.5 Hz, 1H, major), 4.10 (t, *J* = 7.3 Hz, 1H, minor), 3.68 (t, *J* = 7.7 Hz, 1H, minor), 3.58 (t, *J* = 8.1 Hz, 1H, major), 2.34 (s, 3H, major + minor), 1.32 (dq, *J* = 18.4, 7.5 Hz, 3H, major + minor), 1.07 – 0.98 (m, 18H, major + minor); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.8, 138.7, 135.4, 134.4, 133.7, 133.7, 129.0(2C), 129.0(2C), 126.9(6C), 119.7, 119.2, 110.7, 110.5, 79.4, 78.1, 69.8, 69.7, 21.4, 21.4, 18.9(3C), 18.9(3C), 18.8(3C), 18.8(3C), 11.8(3C), 11.7(3C); **HRMS** (ESI-TOF, m/z): calcd for $C_{22}H_{34}O_3SiNa$ $[M+Na]^+$: 397.2169, found: 397.2163.

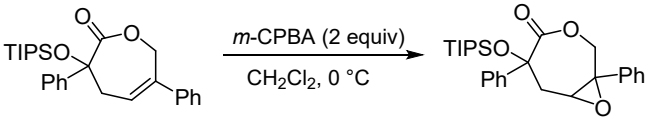
6. Scale-up experiment



1a 6 mmol | **2a** 3 mmol | **3aa** 827 mg, 64% yield

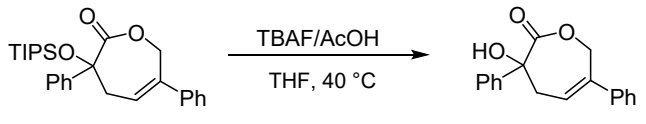
Under a nitrogen atmosphere, $Pd_2(dba)_3 \cdot CHCl_3$ (0.15 mmol, 5 mol%), **L8** (0.33 mmol, 11 mol%) were added sequentially into a flame-dried Schlenk tube equipped with a magnetic stir bar. The tube was evacuated and back-filled with nitrogen for three times. Then the anhydrous DCE (<30 ppm water, *Karl-Fischer* titration) (30.0 mL) were added *via* syringe sequentially. The resulting mixture was stirred at room temperature for 30 minutes. Then, *α*-ketoacylsilane **1a** (6.0 mmol, 2.0 equiv.) and **2a** (3.0 mmol, 1.0 equiv.) were added sequentially and the resulting solution was stirred under the irridation of 10 W blue LEDs at 20 ºC for 4 h. The reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography (petroleum ether/ethyl acetate = 20:1, v/v) to give the corresponding products **3aa** (827.0 mg, 64% yield).

7. Synthetic transformations of products



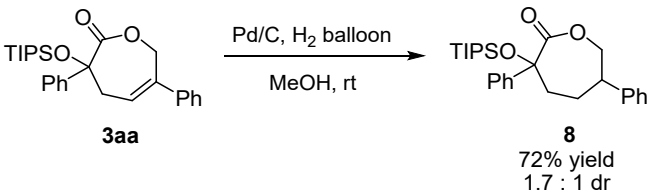
3aa **6**
62% yield

A flame-dried tube was charged with **3aa** (0.1 mmol, 1.0 equiv.), then CH_2Cl_2 (1 mL) was added to it and cooled to 0 ℃. After that *m*-CPBA (0.2 mmol, 2.0 equiv.) was added in one portion and continued to stir for 24 hours at room temperature. After complete conversion, the mixture was purified by column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) to afford the product **6** as a yellow oil in 62% yield (28.0 mg, >20:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (s, 5H), 7.27 – 7.22 (m, 3H), 6.93 – 6.79 (m, 2H), 4.15 (d, *J* = 14.4 Hz, 1H), 4.01 (d, *J* = 14.4 Hz, 1H), 3.24 (d, *J* = 6.8 Hz, 1H), 3.11 (dd, *J* = 16.0, 6.8 Hz, 1H), 2.77 (d, *J* = 16.0 Hz, 1H), 1.08 – 0.90 (m, 21H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.7, 138.9, 137.1, 129.5(3C), 128.7(2C), 128.5, 126.7(2C), 125.2(2C), 80.1, 66.8, 61.0, 59.5, 36.4, 18.5(3C), 18.4(3C), 13.6(3C). **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{36}O_4SiNa$ $[M+Na]^+$: 475.2275, found: 475.2275.



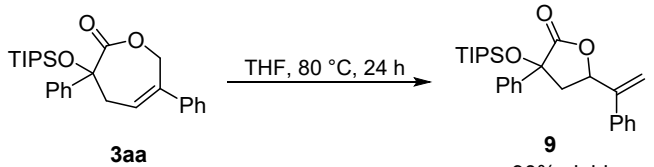
3aa **7**
71% yield

3aa (0.1 mmol, 1.0 equiv.) was dissolved in THF (1.0 mL), then AcOH (0.3 mmol, 3.0 equiv.) and TBAF (1.0 M in THF, 0.3 mmol, 3.0 equiv.) was added sequentially. The reaction mixture was stirred at room temperature for 18 hours. After complete conversion, the solvent was removed under reduced pressure, then the residue was purified by column chromatography (petroleum ether/ethyl acetate = 4/1, v/v) to afford the product **7** as a yellow solid in 71% yield (19.8 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.3 Hz, 2H), 7.42 (d, *J* = 7.1 Hz, 2H), 7.30 – 7.26 (m, 3H), 7.14 (d, *J* = 7.1 Hz, 2H), 6.12 (dt, *J* = 5.2, 2.7 Hz, 1H), 4.66 (d, *J* = 15.7 Hz, 1H), 4.40 (dd, *J* = 15.8, 3.4 Hz, 1H), 3.43 (dd, *J* = 19.5, 6.2 Hz, 1H), 2.96 (dt, *J* = 19.6, 3.9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.7, 140.4, 138.5, 137.3, 129.5, 129.4(2C), 128.8(2C), 128.0, 127.0, 126.3(2C), 125.7(2C), 76.9, 69.7, 36.8. **HRMS** (ESI-TOF, m/z): calcd for $C_{18}H_{16}O_3Na$ $[M+Na]^+$: 303.0992, found: 303.0999.



3aa **8**
72% yield
1.7 : 1 dr

3aa (0.1 mmol, 1.0 equiv.) was dissolved in MeOH (1.0 mL), then Pd/C (10% on carbon) was added. The reaction mixture was stirred at H_2 atmosphere (1 atm) at room temperature for 2 hours. After complete conversion, the crude reaction mixture was filtrated with celite and washed with MeOH. The solvent was removed under reduced pressure, then the residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) to afford the product **8** as a white solid in 72% yield (27.2 mg, 1.7:1 dr). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H, major + minor), 7.42 – 7.36 (m, 2H, major + minor), 7.33 (d, *J* = 4.4 Hz, 3H, major + minor), 7.28 – 7.16 (m, 2H, major + minor), 6.91 (dd, *J* = 7.3, 1.7 Hz, 1H, major + minor), 4.43 (dd, *J* = 12.6, 3.7 Hz, 1H, major), 4.34 (dd, *J* = 12.6, 3.6 Hz, 1H, major), 4.08 – 4.00 (m, 2H, minor), 2.98 (tt, *J* = 8.9, 3.3 Hz, 1H, minor), 2.94 – 2.88 (m, 1H, major), 2.73 (ddd, *J* = 15.0, 4.9, 3.1 Hz, 1H, minor), 2.60 (ddd, *J* = 14.9, 8.8, 2.2 Hz, 1H, major), 2.40 (dddd, *J* = 14.9, 9.8, 8.1, 2.6 Hz, 1H, major + minor), 2.16 – 1.96 (m, 2H, major + minor), 1.86 (qd, *J* = 14.1, 13.6, 3.1 Hz, 1H, minor), 1.06 – 1.01 (m, 3H, major + minor), 0.94 (dd, *J* = 14.9, 7.4 Hz, 9H, major + minor), 0.85 (dd, *J* = 7.4, 1.2 Hz, 9H, major + minor). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.5, 175.2, 142.1, 141.7, 141.6, 138.7, 129.0, 128.8(2C), 128.7(2C), 128.6, 128.4, 127.6(2C), 127.1, 127.0, 126.9, 126.8, 126.4(2C), 84.1, 83.1, 73.5, 71.6, 45.3, 44.3, 38.9, 37.7, 31.7, 30.2, 18.7(3C), 18.6(3C), 18.5(3C), 18.4(3C), 13.8(3C), 13.8(3C). **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{38}O_3SiNa$ $[M+Na]^+$: 461.2482, found: 461.2483.



3aa **9**
90% yield
2.9 : 1 dr

Under a nitrogen atmosphere, to a sealed tube added **3aa** (0.1 mmol, 1.0 equiv.) and THF (1 mL), the resulting solution was stirred at 80 ºC for 24 h. After complete conversion, the solvent was removed under reduced pressure, then the residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) to afford the product **9** as a yellow solid in 90% yield (39.0 mg, 2.9:1 dr). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 7.42 – 7.37 (m, 2H), 7.34 – 7.28 (m, 6H), 5.52 (s, 1H), 5.42 (s, 1H), 5.01 (dd, *J* = 11.2, 5.1 Hz, 1H), 2.87 (dd, *J* = 12.7, 5.1 Hz, 1H), 2.46 (dd, *J* = 12.7, 11.2 Hz, 1H), 1.05 (q, *J* = 7.4 Hz, 3H), 0.93 (d, *J* = 7.5 Hz, 9H), 0.90 (d, *J* = 7.4 Hz, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.0, 145.8, 140.7, 137.9, 128.9(2C), 128.7(2C), 128.4, 127.2(2C), 126.8, 126.0(2C), 115.1, 80.7, 76.5,

46.5, 18.4(3C), 18.3(3C), 13.4(3C). **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{36}O_3SiNa$ $[M+Na]^+$: 459.2326, found: 459.2324.

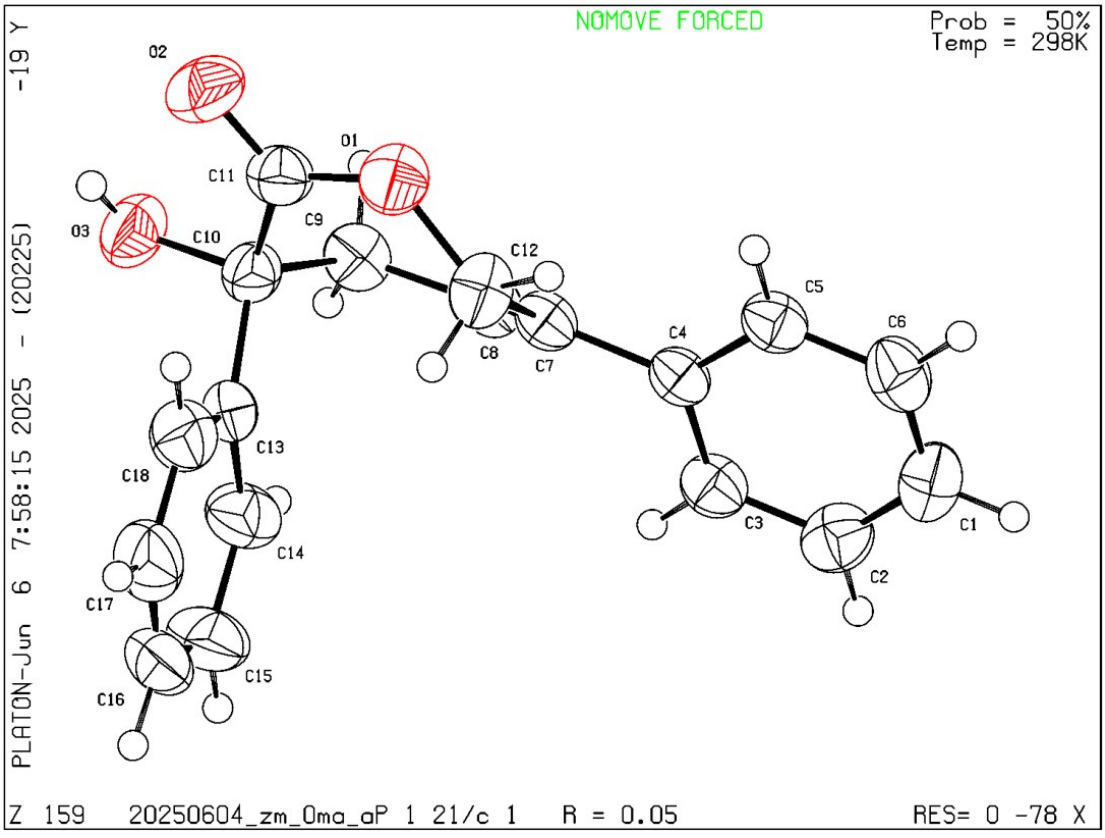
8. Crystallographic data for compound 7

Preparations:

The product **7** (10.0 mg) was dissolved in 1.0 mL DCM. The solution was filtered by millipore filter and transferred to a vial. Then, drops of hexane were added subsequently. A single crystal was obtained by natural volatilization at room temperature.

The data set was collected by a Bruker APEX-II CCD at 298 K equipped with micro-focus Cu radiation source (Kα = 0.71073 Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL program package.

Data of 7: Details of the X-ray experiments and crystal data are summarized below. CCDC 2542833 contains the supplementary crystallographic data, and can be obtained free of charge *via* https://www.ccdc.cam.ac.uk/conts/retrieving.html.



Crystal data and structure refinement for cu_20240314_yly_0m.

Identification code	20250604_zm_0ma_a
Empirical formula	C18 H16 O3
Formula weight	280.31
Temperature	298.00 K
Wavelength	0.71073 Å
Crystal system	Monoclinic

Space group	P 2_1 /c	
Unit cell dimensions	a = 13.3008(9) Å	α= 90°.
	b = 9.8645(5) Å	β= 97.685(2)°.
	c = 10.7668(6) Å	γ = 90°.
Volume	1399.98(14) Å^3	
Z	4	
Density (calculated)	1.330 Mg/m^3	
Absorption coefficient	0.090 mm^{-1}	
F(000)	592.0	
Crystal size	0.320 x 0.220 x 0.080 mm^3	
2Θ range for data collection	5.158 to 54.98	
Index ranges	-17≤h≤17, -12≤k≤12, -13≤l≤13	
Reflections collected	19285	
Independent reflections	3190 [R_{int} = 0.0684, R_{sigma} = 0.0425]	
Completeness to theta = 27.49°	99.60 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.746 and 0.622	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3190/0/191	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0501, wR_2 = 0.1079	
R indices (all data)	R1 = 0.0834, wR_2 = 0.1274	
Largest diff. peak and hole	0.15 and -0.18 e.Å^{-3}	

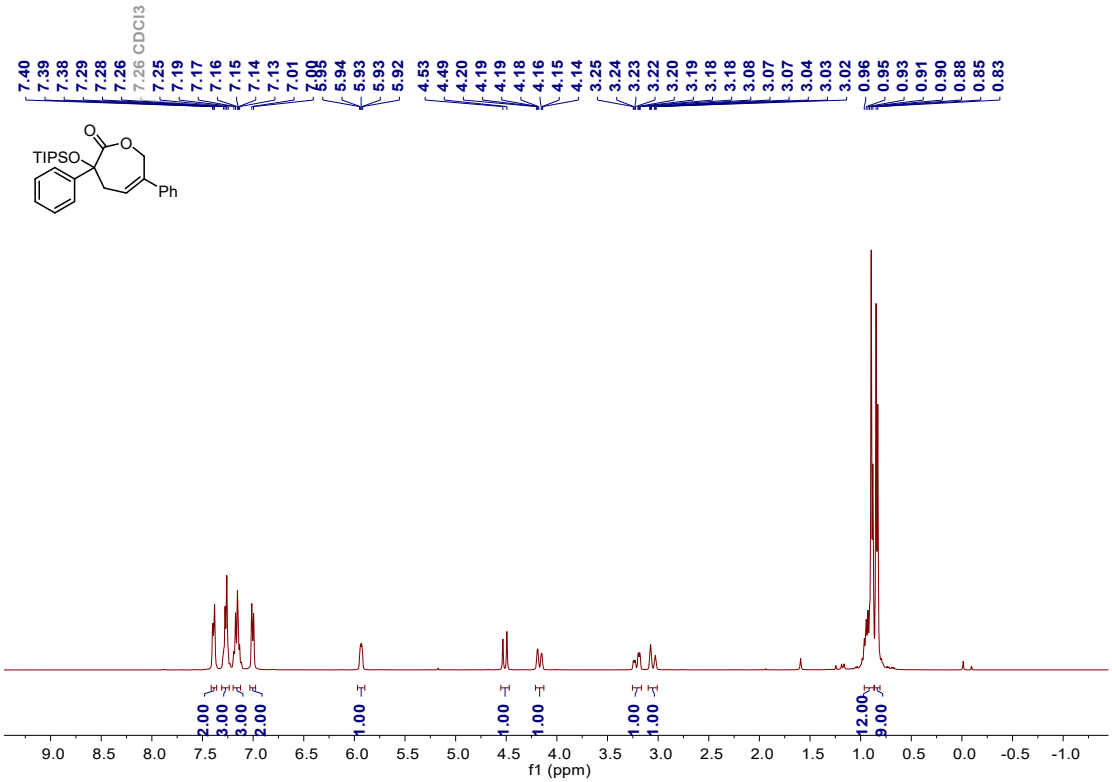
9. References

[1] J. Xu, Y. Song, J. He, S. Dong, L. Lin, and X. Feng, Asymmetric Catalytic Vinylogous Addition Reactions Initiated by Meinwald Rearrangement of Vinyl Epoxides, *Angew. Chem. Int. Ed*., 2021, **60**, 14521–14527.

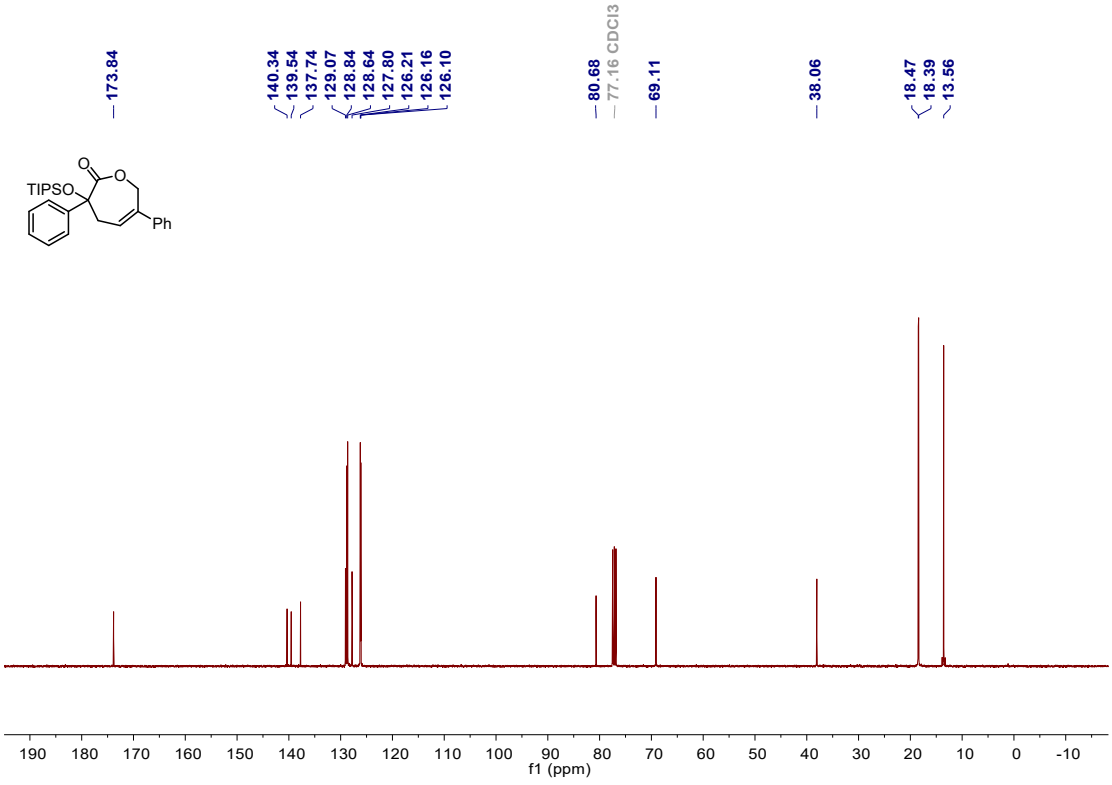
[2] L. Yao, X. Zou, J. Zhang, Y.-Z. Liu, Q. Wang, H. Zheng, X. Shao, W.-P. Deng, Asymmetric Trapping of Siloxyketenes In Situ Generated from [1,3]-Silyl Migration of *α*-Ketoacylsilanes: A Visible-Light-Driven Palladium-Catalyzed [4+2] Cycloaddition, *ACS Catal*., 2025, **15**, 5796–5805.

10. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra

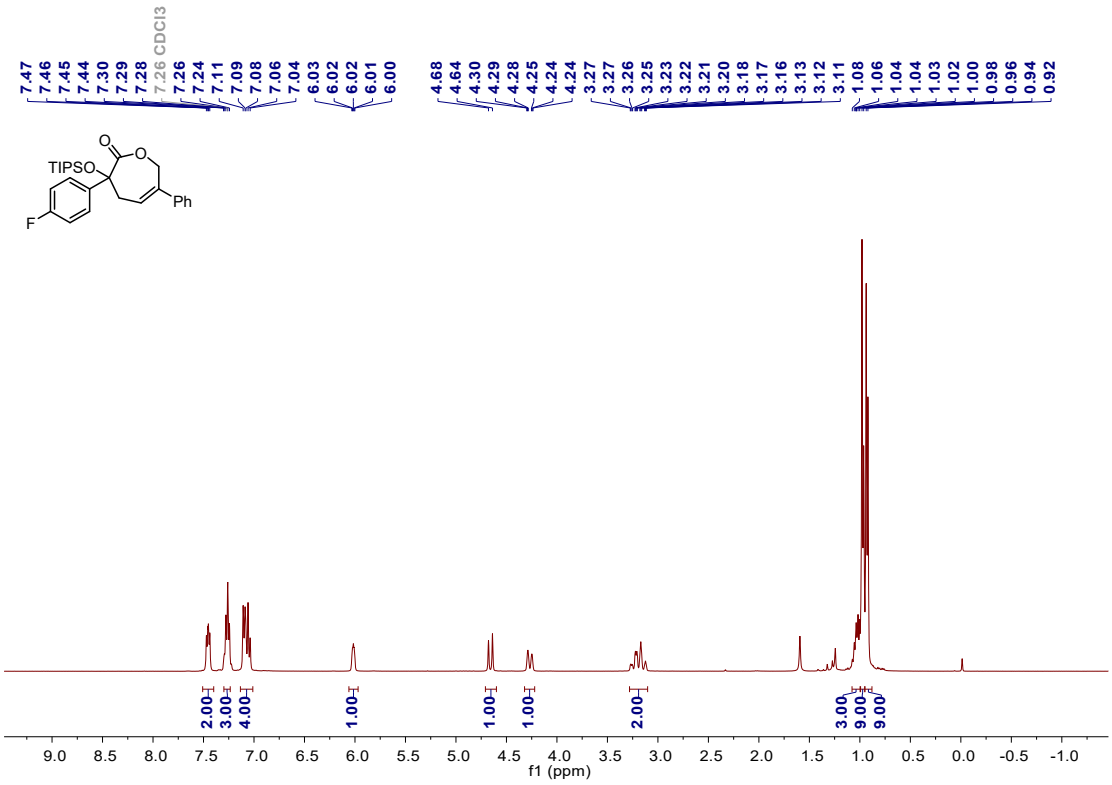
^{1}H NMR of **3aa** in $CDCl_3$ (400 MHz)



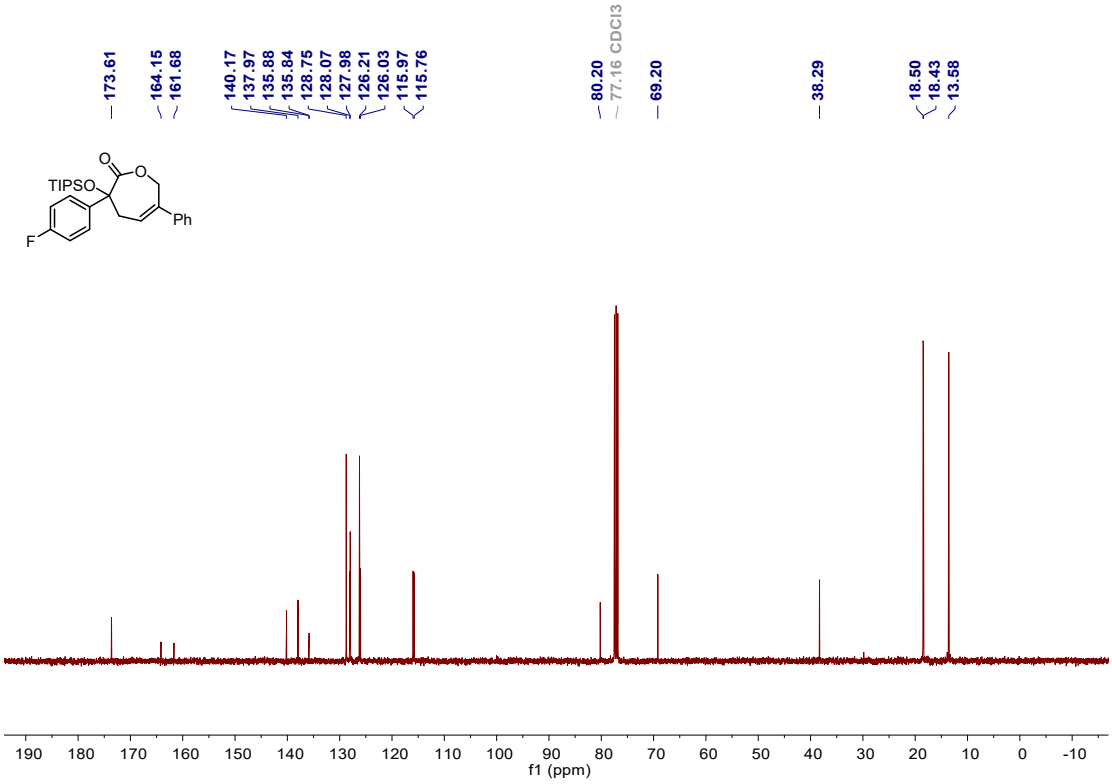
^{13}C NMR of **3aa** in $CDCl_3$ (101 MHz)



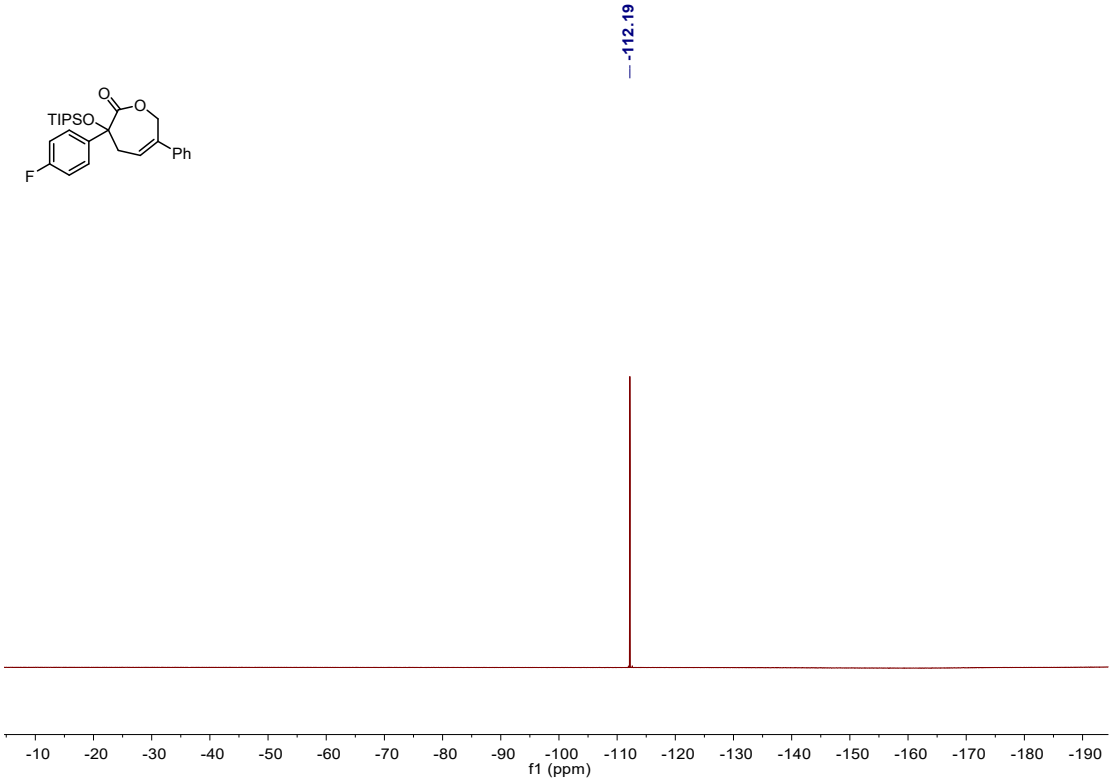
^{1}H NMR of **3ab** in $CDCl_3$ (400 MHz)



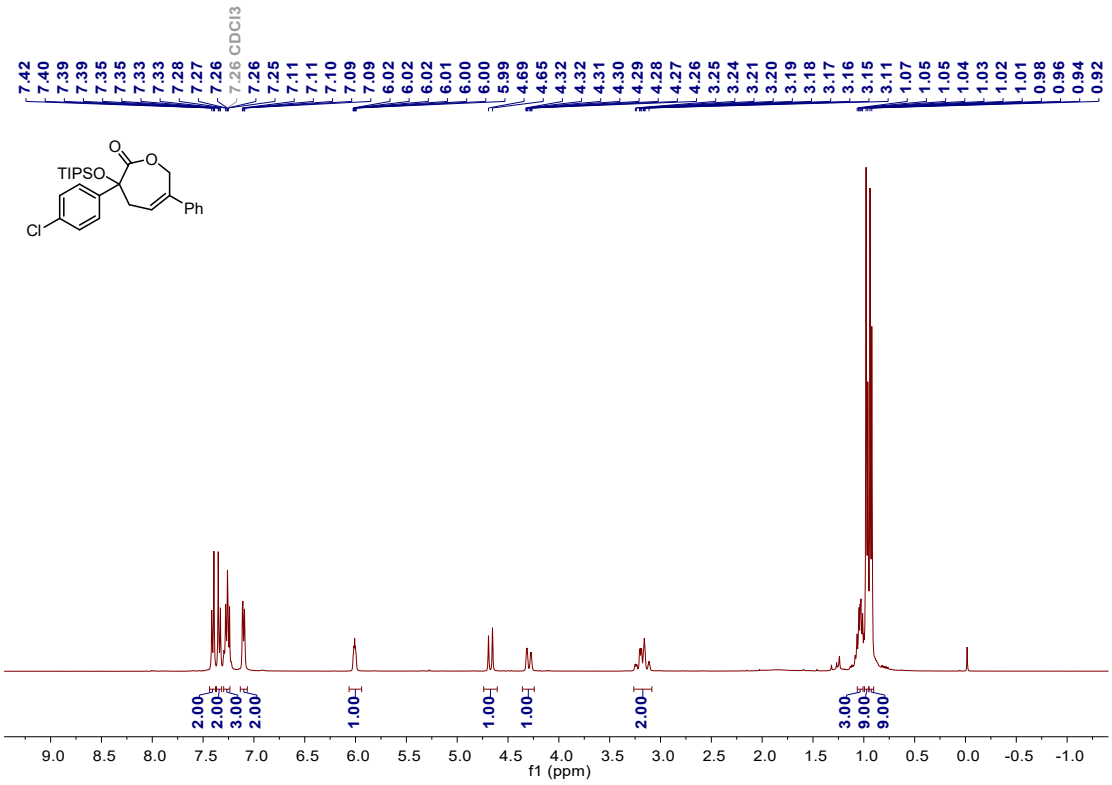
^{13}C NMR of **3ab** in $CDCl_3$ (101 MHz)



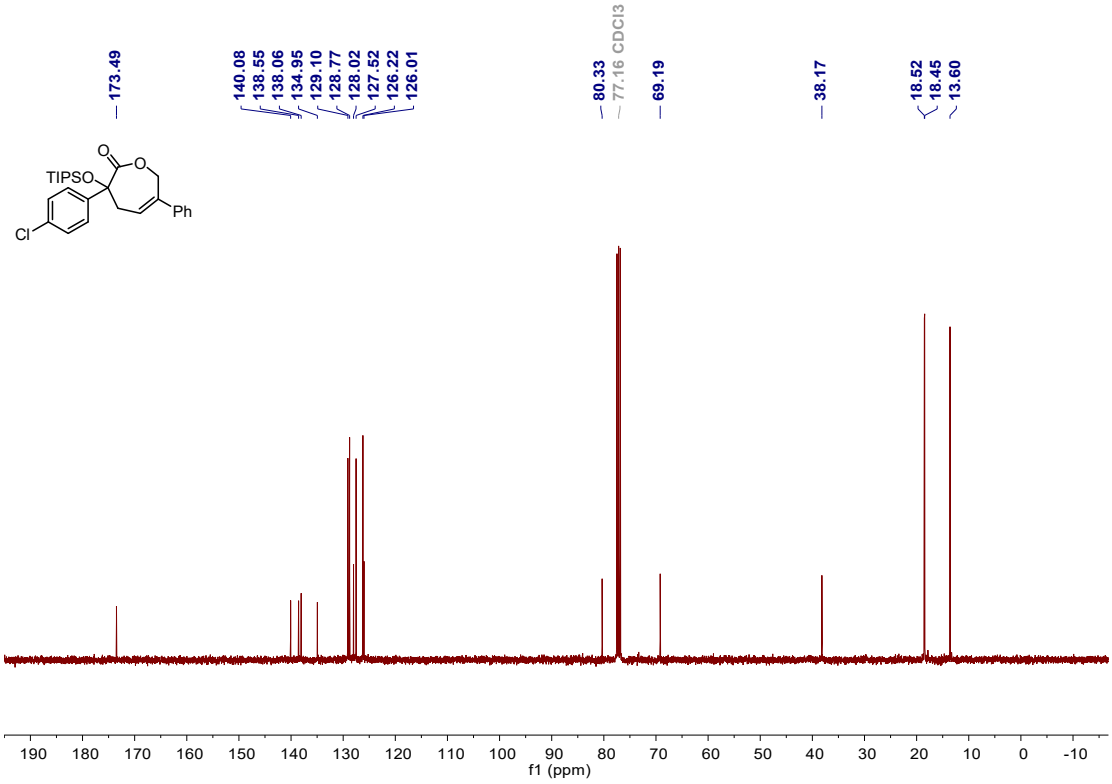
^{19}F NMR of **3ab** in $CDCl_3$ (377 MHz)



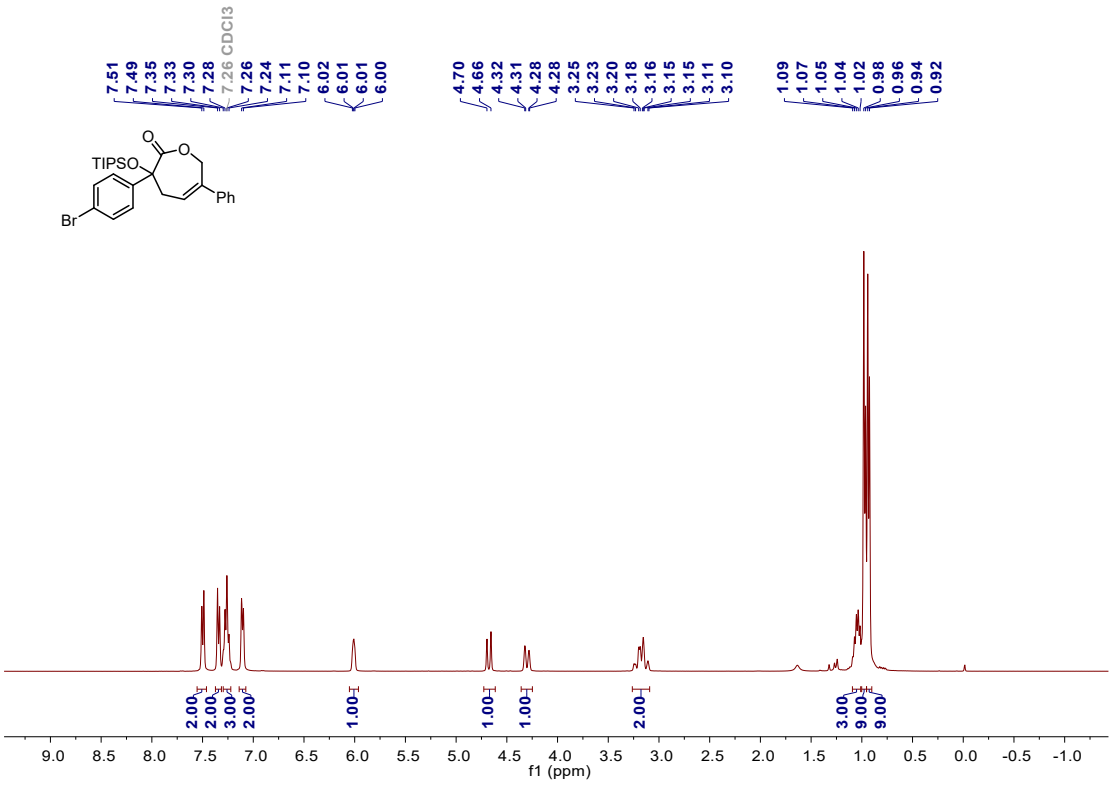
^{1}H NMR of **3ac** in $CDCl_3$ (400 MHz)



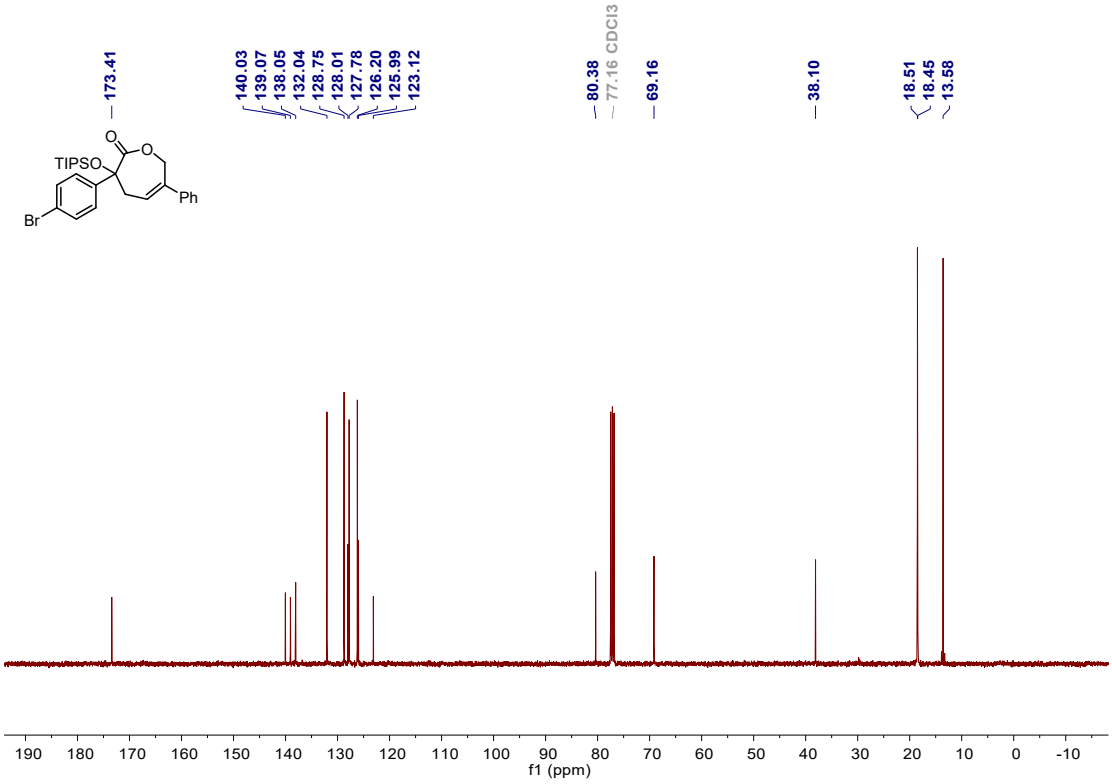
^{13}C NMR of **3ac** in $CDCl_3$ (101 MHz)



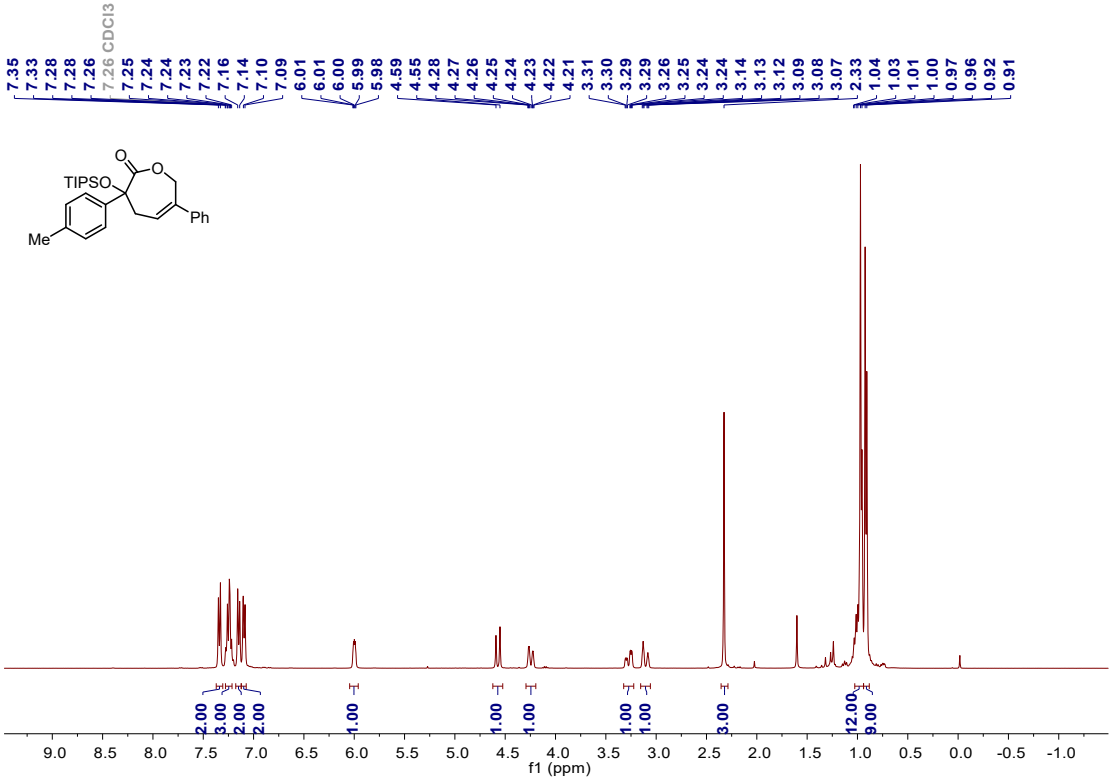
^{1}H NMR of **3ad** in $CDCl_3$ (400 MHz)



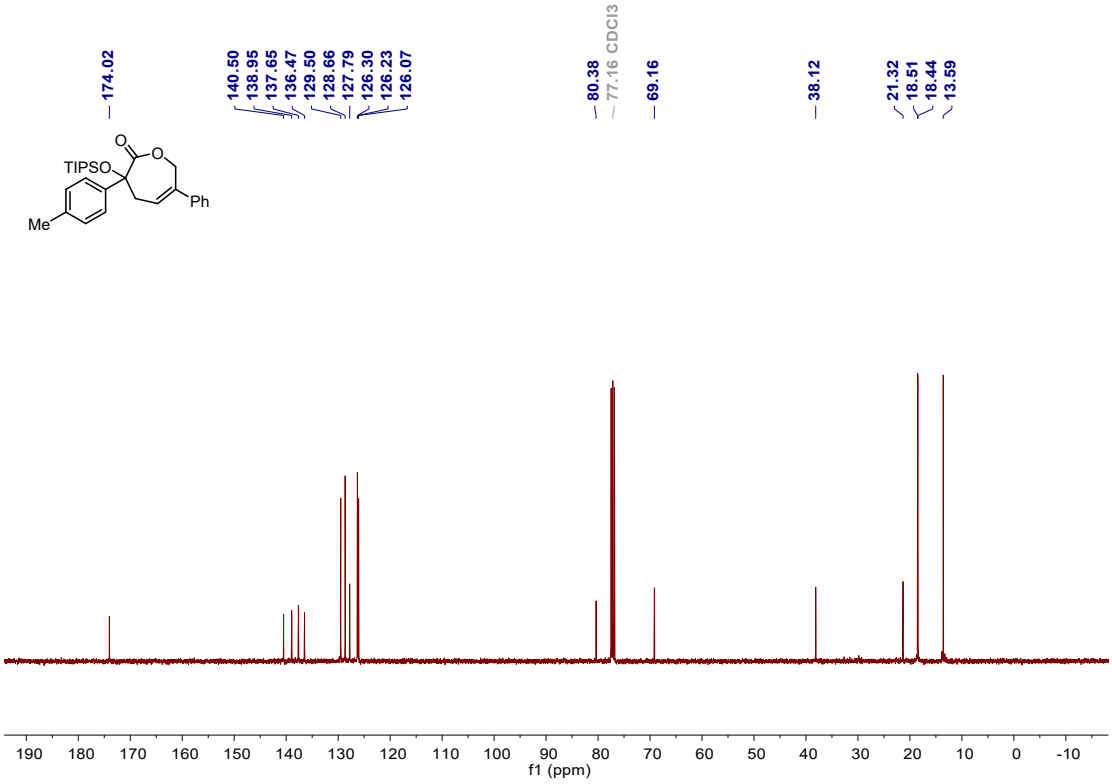
^{13}C NMR of **3ad** in $CDCl_3$ (101 MHz)



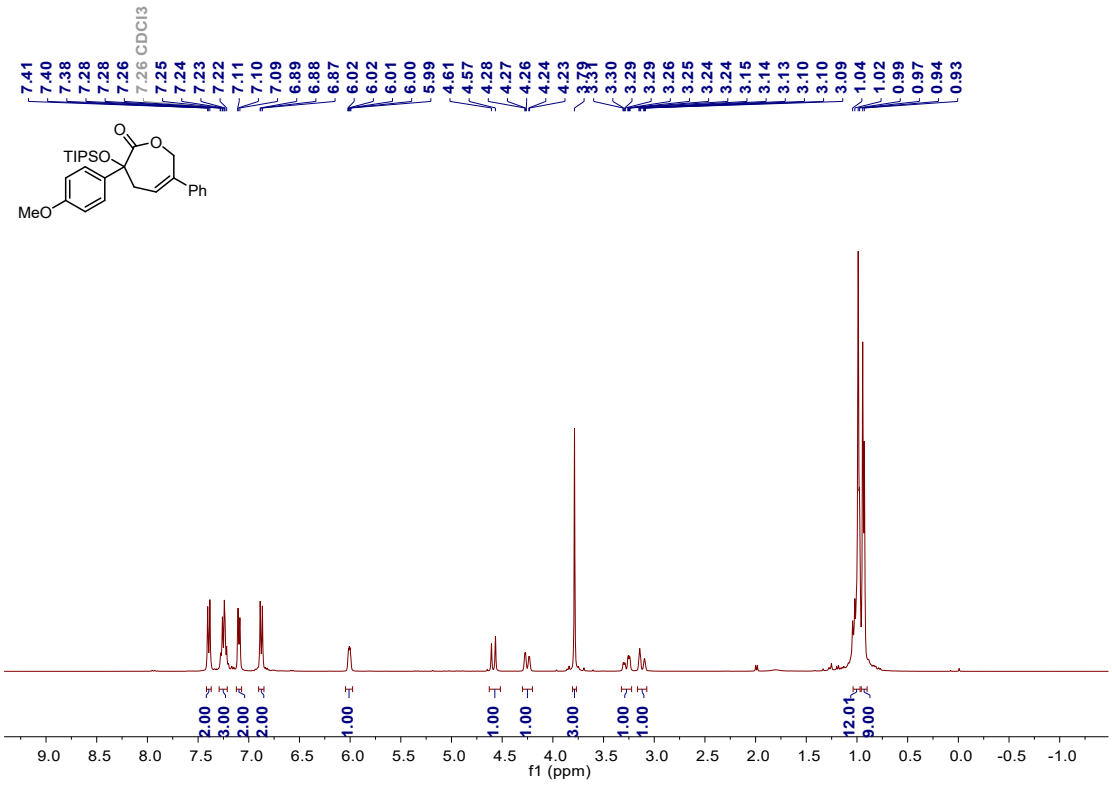
^{1}H NMR of **3ae** in $CDCl_3$ (400 MHz)



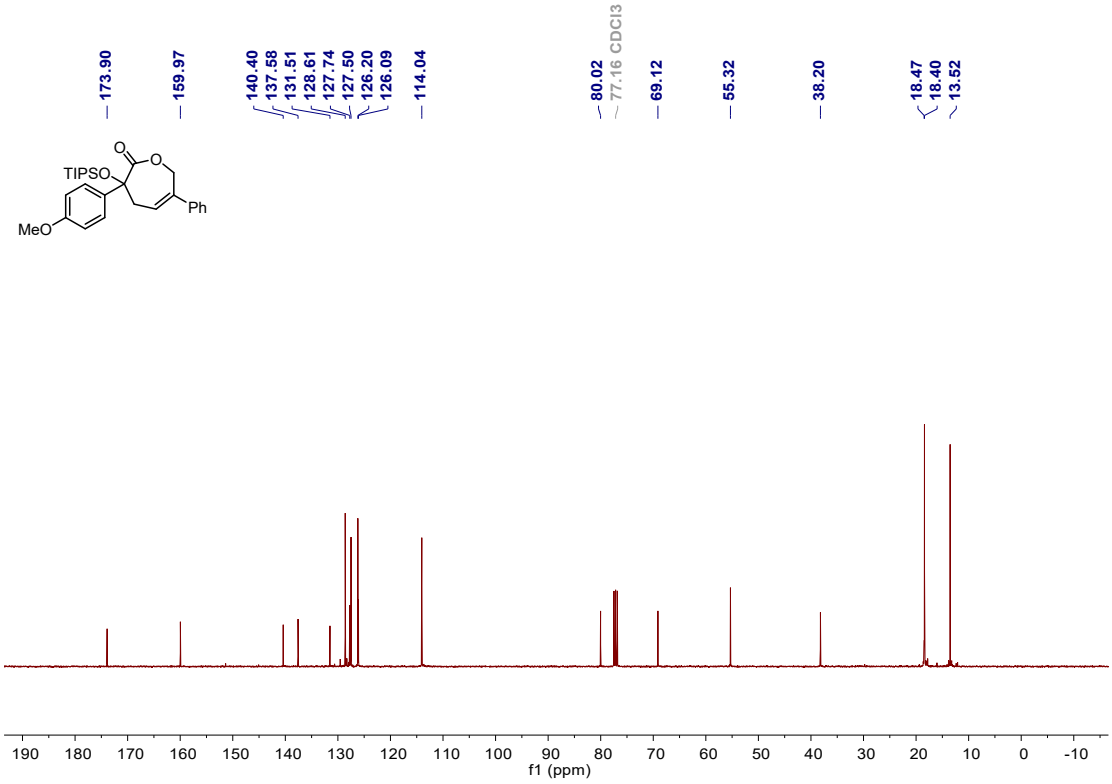
^{13}C NMR of **3ae** in $CDCl_3$ (101 MHz)



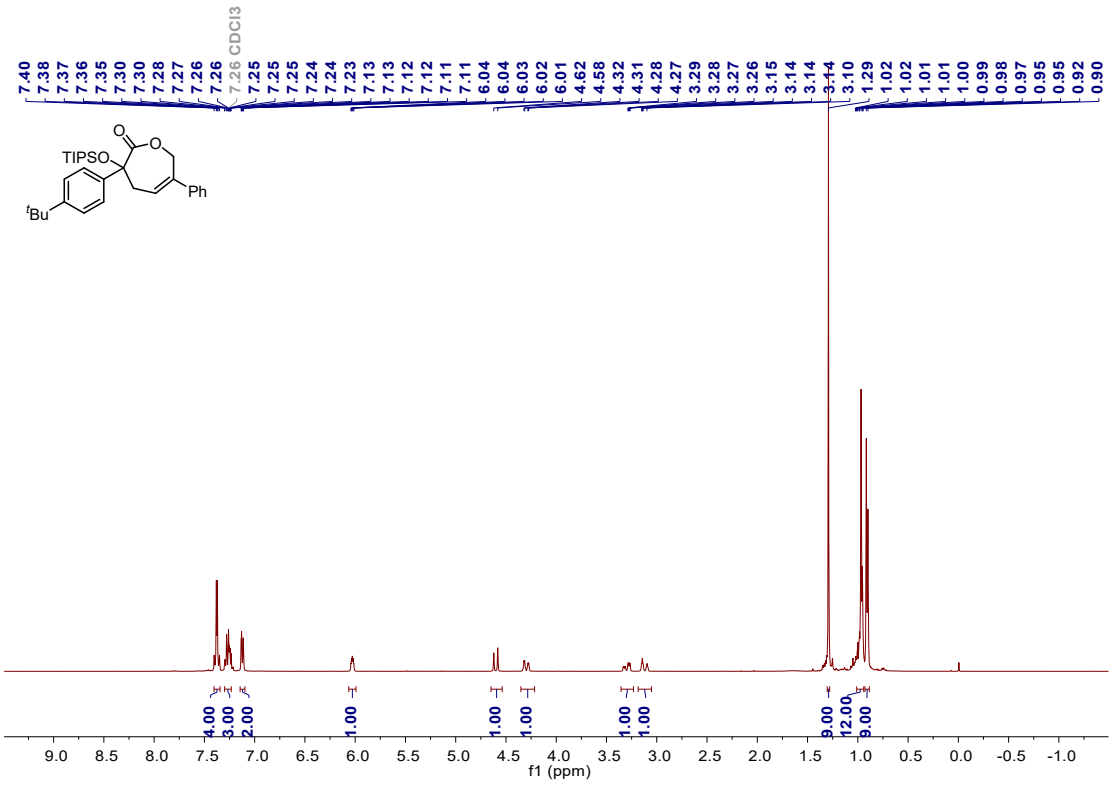
^{1}H NMR of **3af** in $CDCl_3$ (400 MHz)



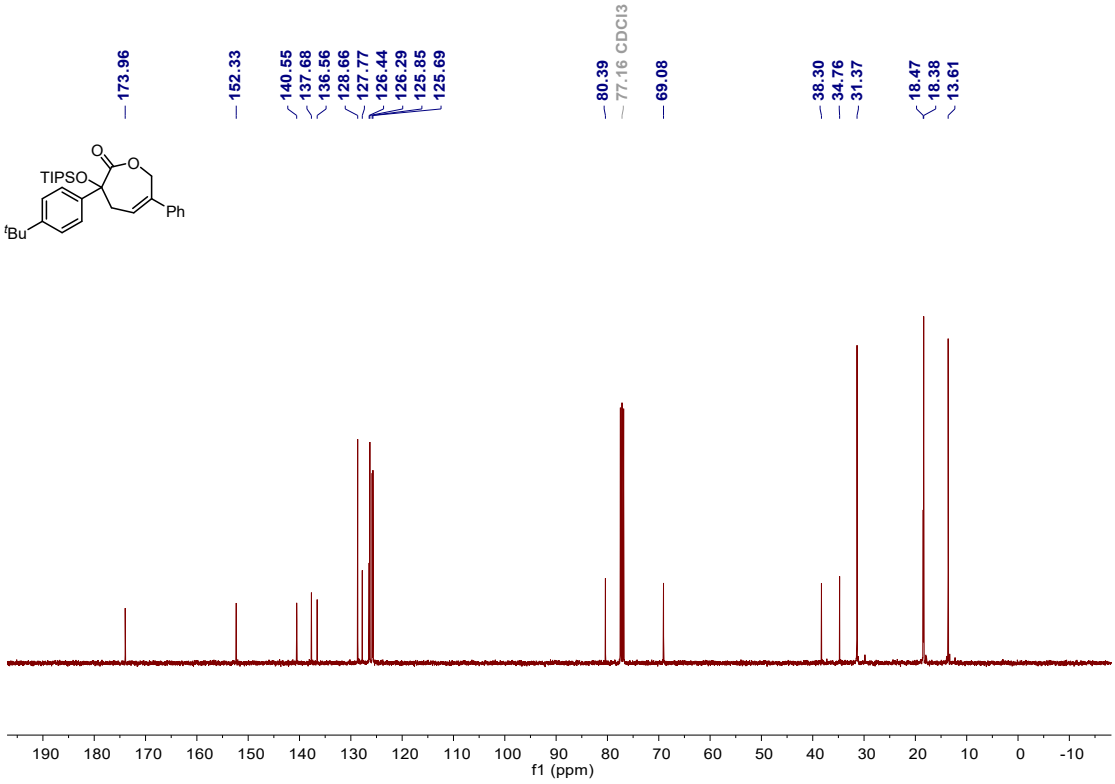
^{13}C NMR of **3af** in $CDCl_3$ (101 MHz)



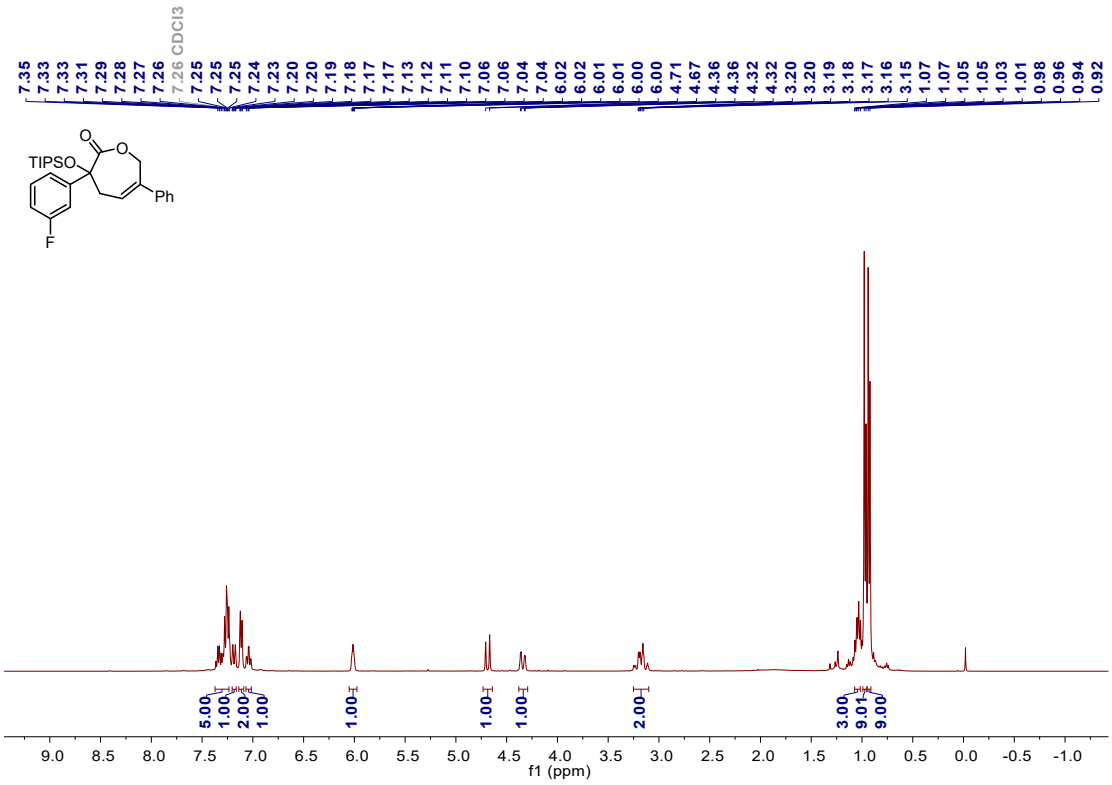
^{1}H NMR of **3ag** in $CDCl_3$ (400 MHz)



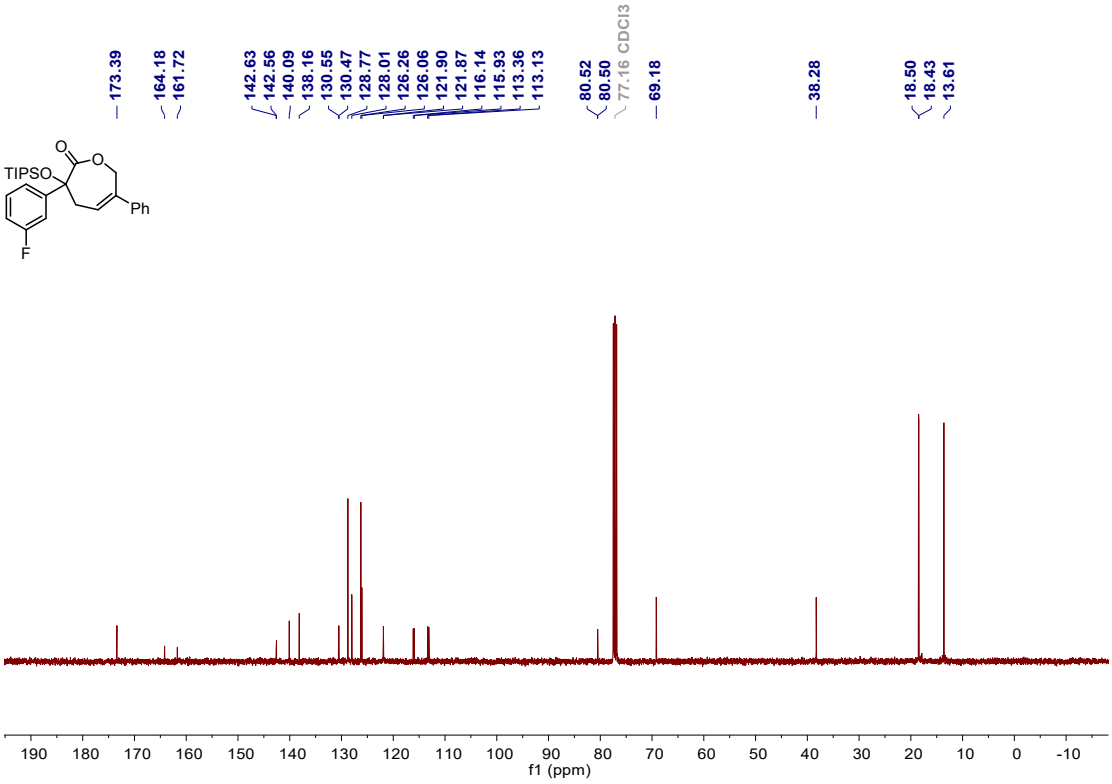
^{13}C NMR of **3ag** in $CDCl_3$ (101 MHz)



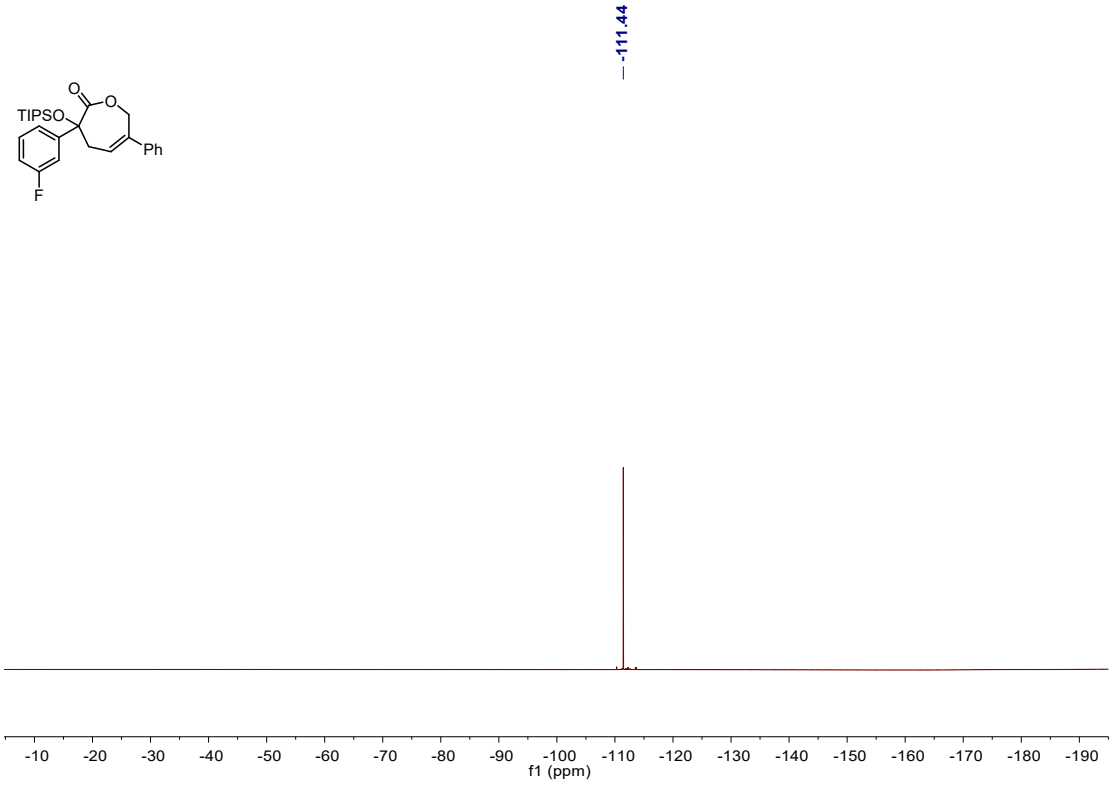
^{1}H NMR of **3ah** in $CDCl_3$ (400 MHz)



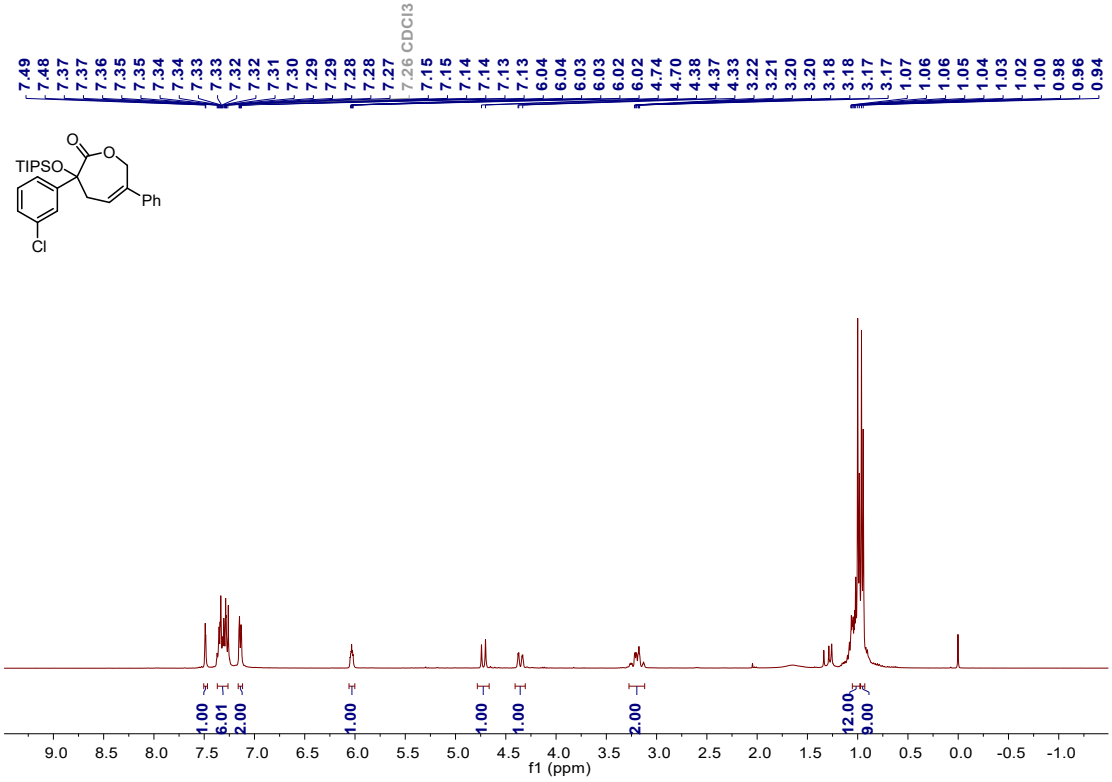
^{13}C NMR of **3ah** in $CDCl_3$ (101 MHz)



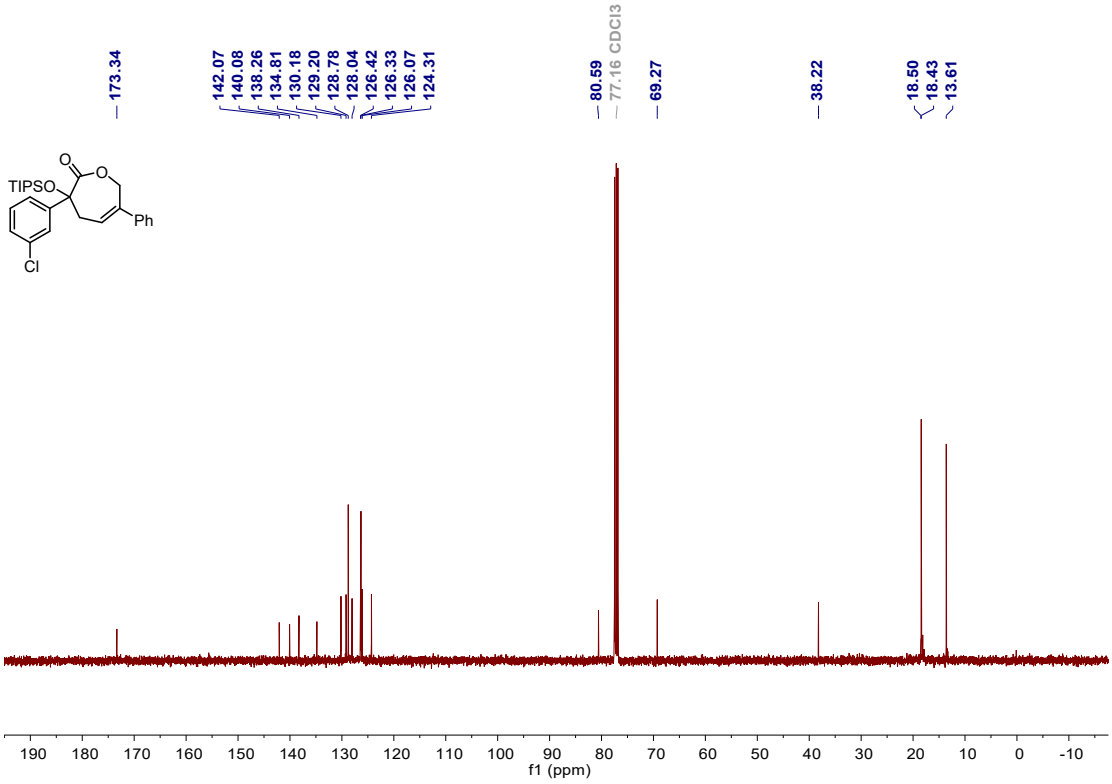
^{19}F NMR of **3ah** in $CDCl_3$ (377 MHz)



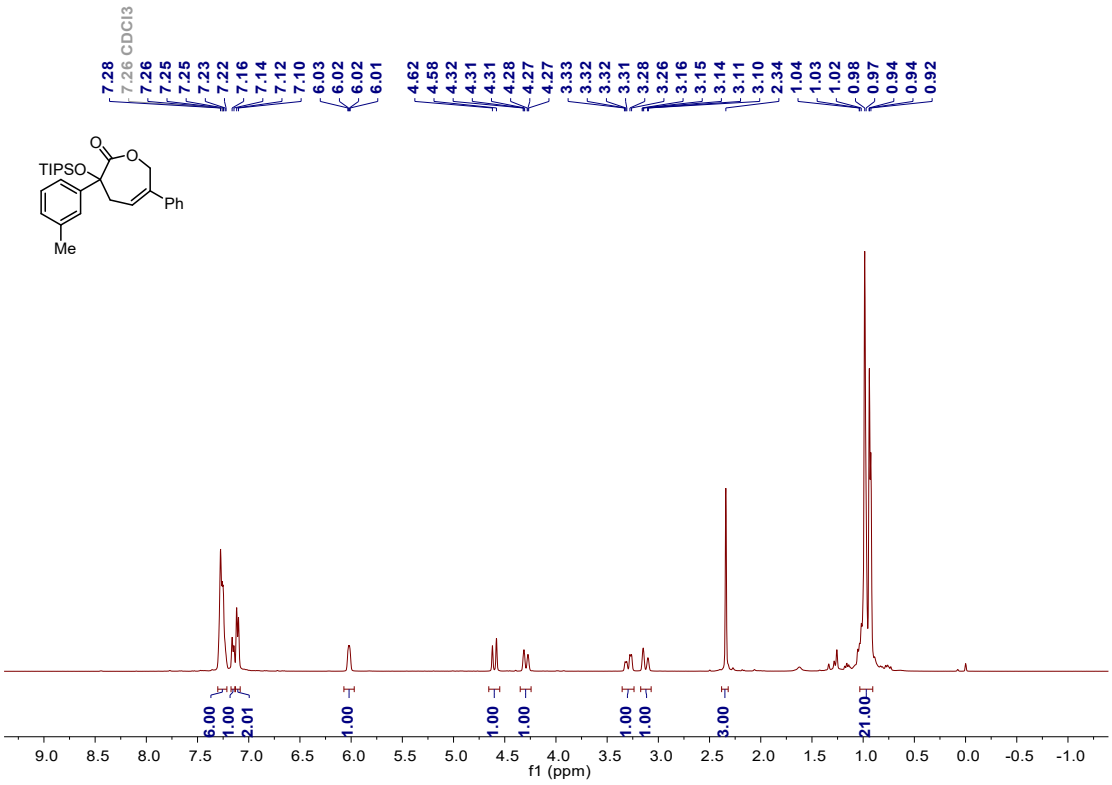
^{1}H NMR of **3ai** in $CDCl_3$ (400 MHz)



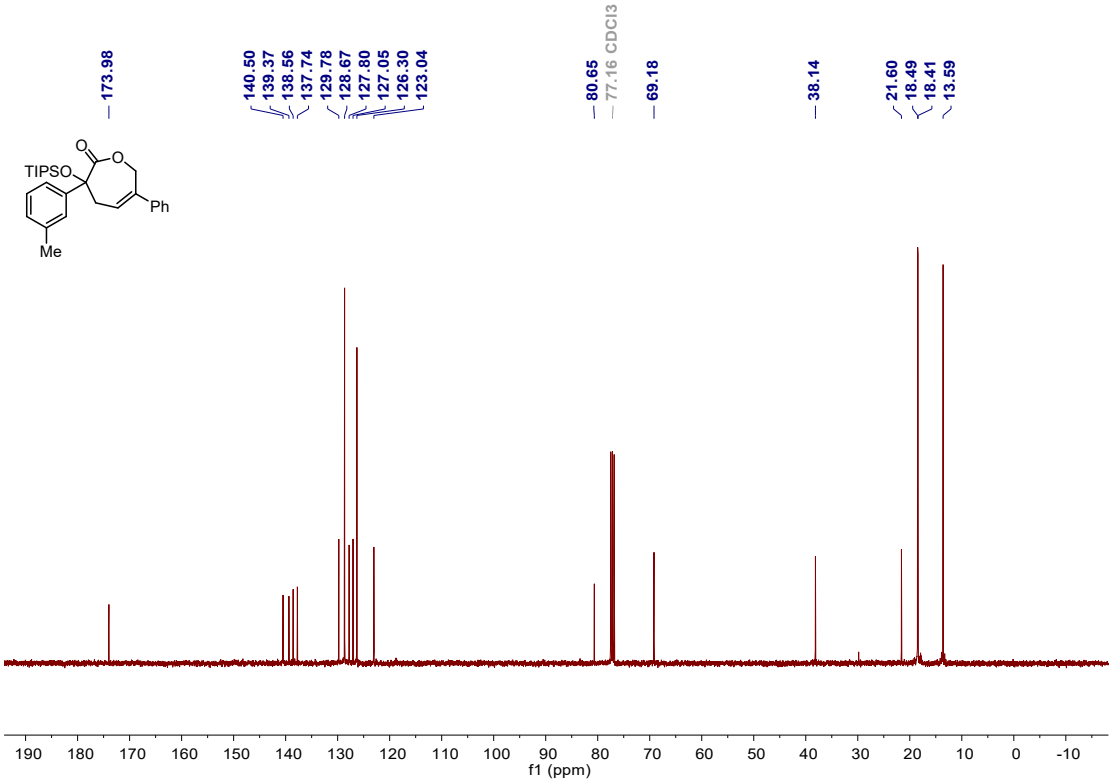
^{13}C NMR of **3ai** in $CDCl_3$ (101 MHz)



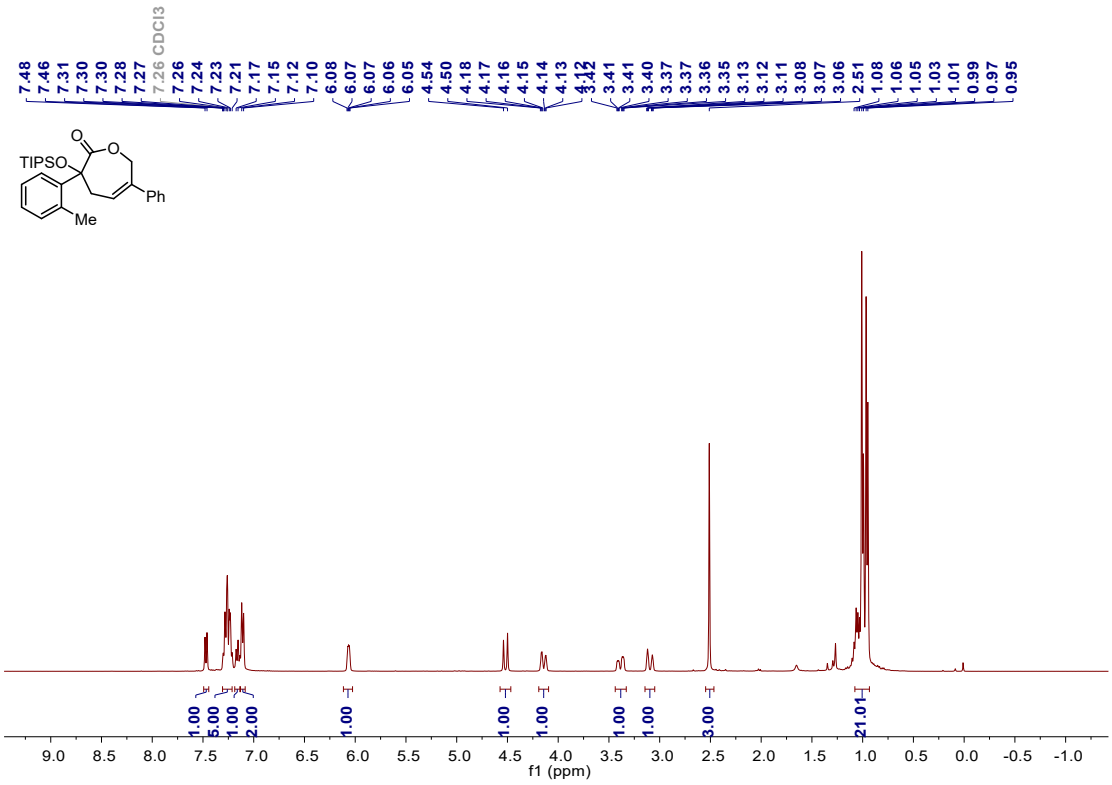
^{1}H NMR of **3aj** in $CDCl_3$ (400 MHz)



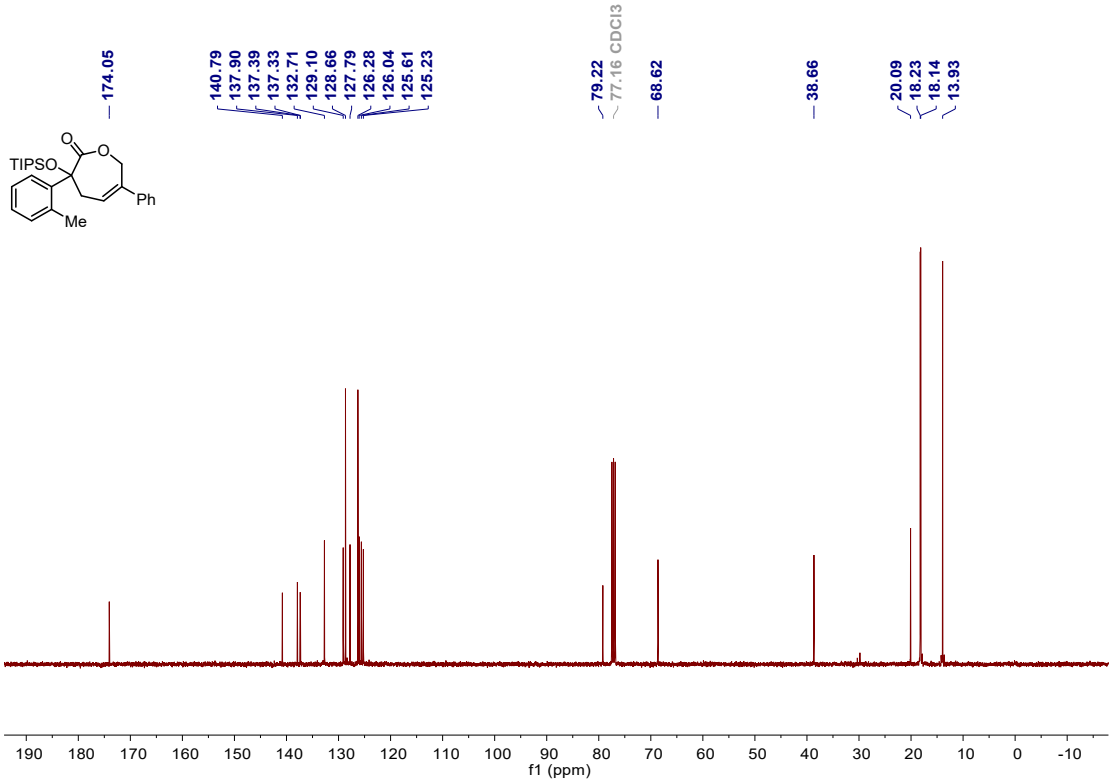
^{13}C NMR of **3aj** in $CDCl_3$ (101 MHz)



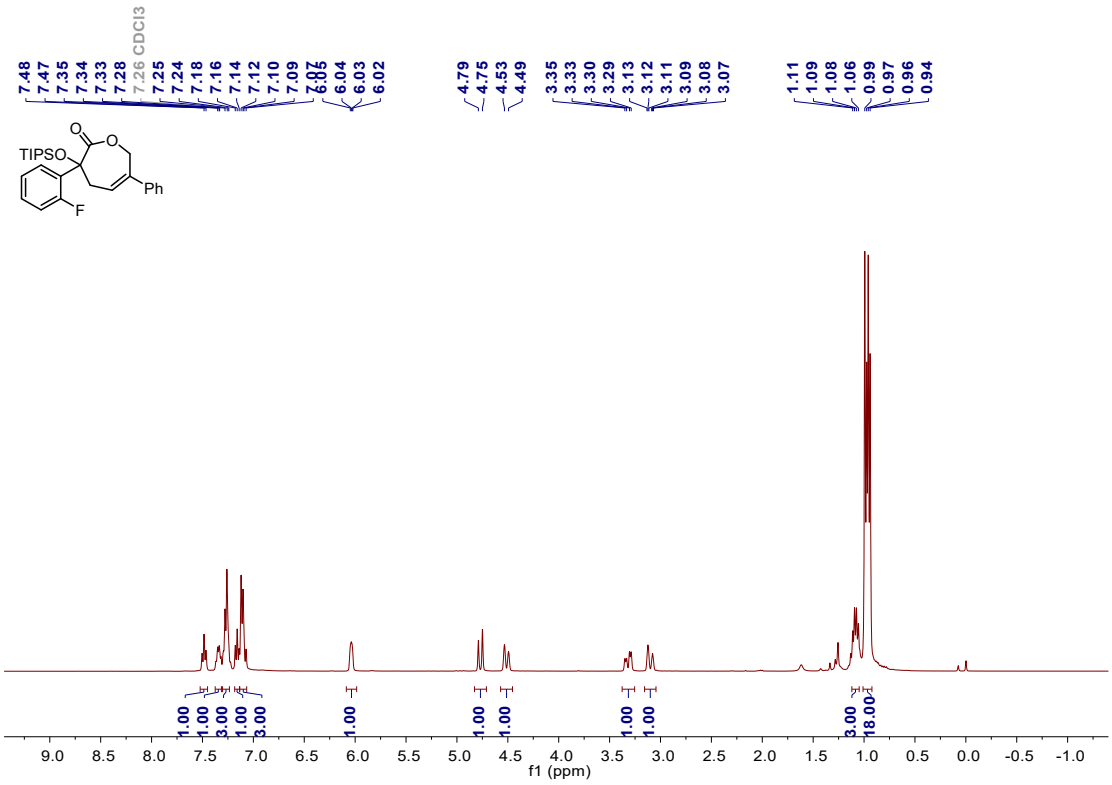
^{1}H NMR of **3ak** in $CDCl_3$ (400 MHz)



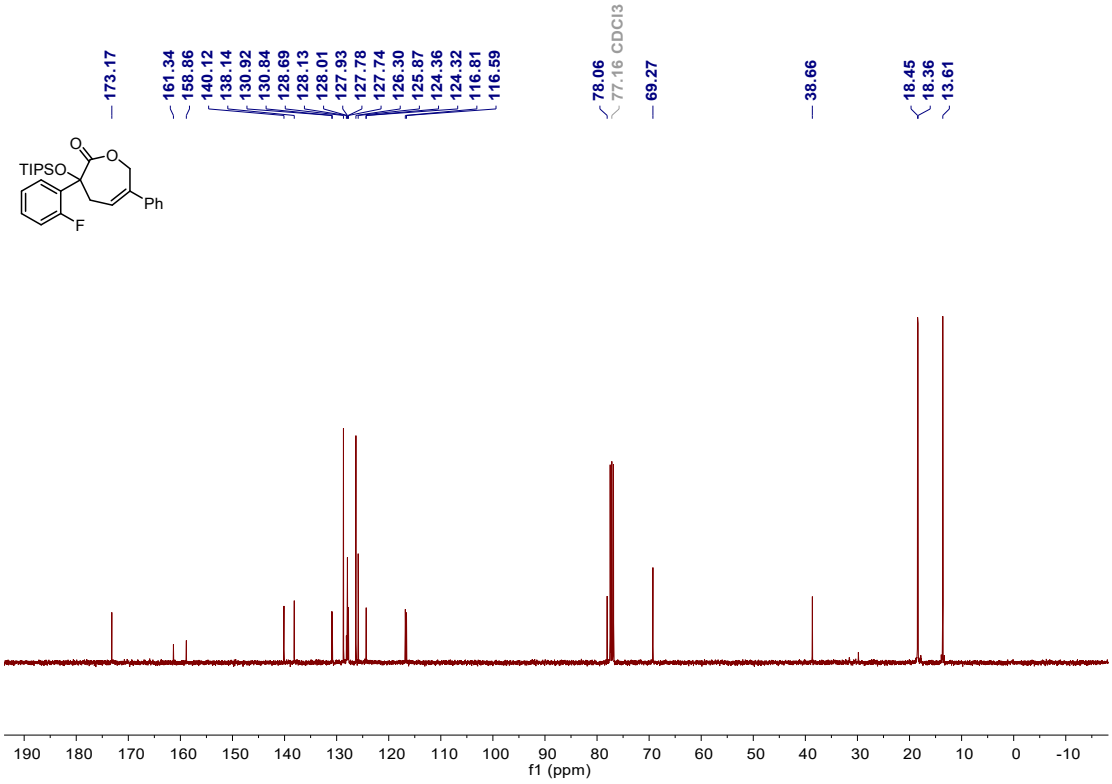
^{13}C NMR of **3ak** in $CDCl_3$ (101 MHz)



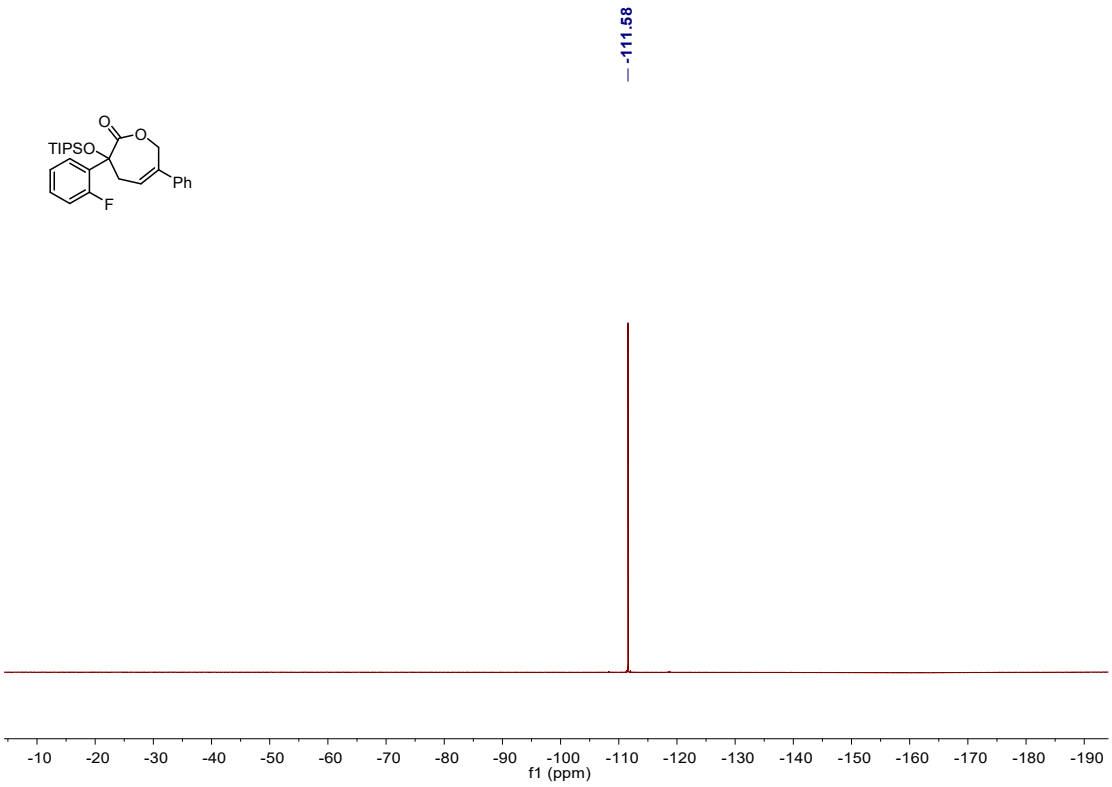
^{1}H NMR of **3al** in $CDCl_3$ (400 MHz)



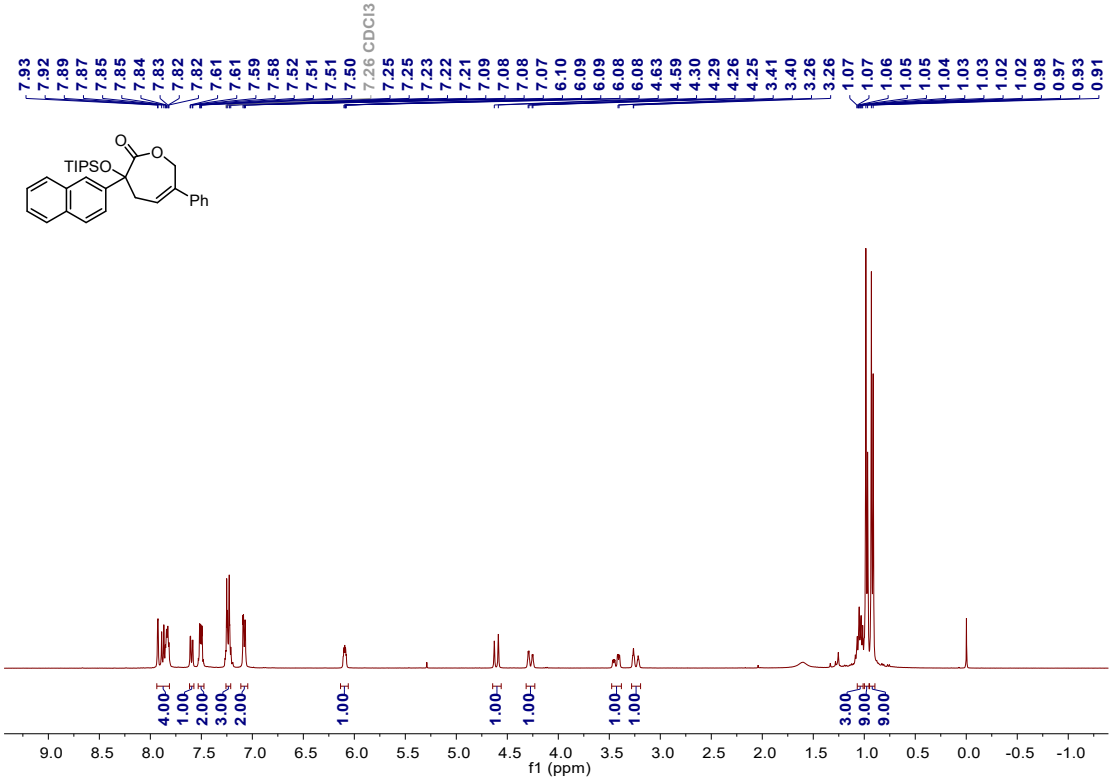
^{13}C NMR of **3al** in $CDCl_3$ (101 MHz)



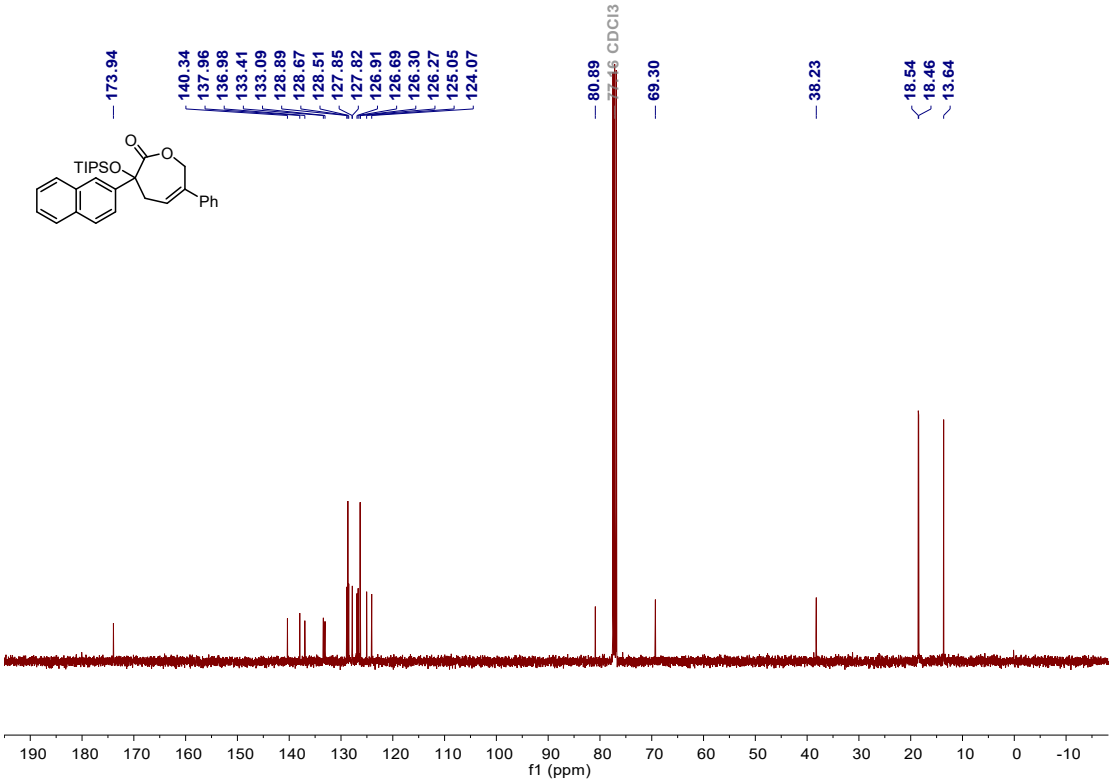
^{19}F NMR of **3al** in $CDCl_3$ (377 MHz)



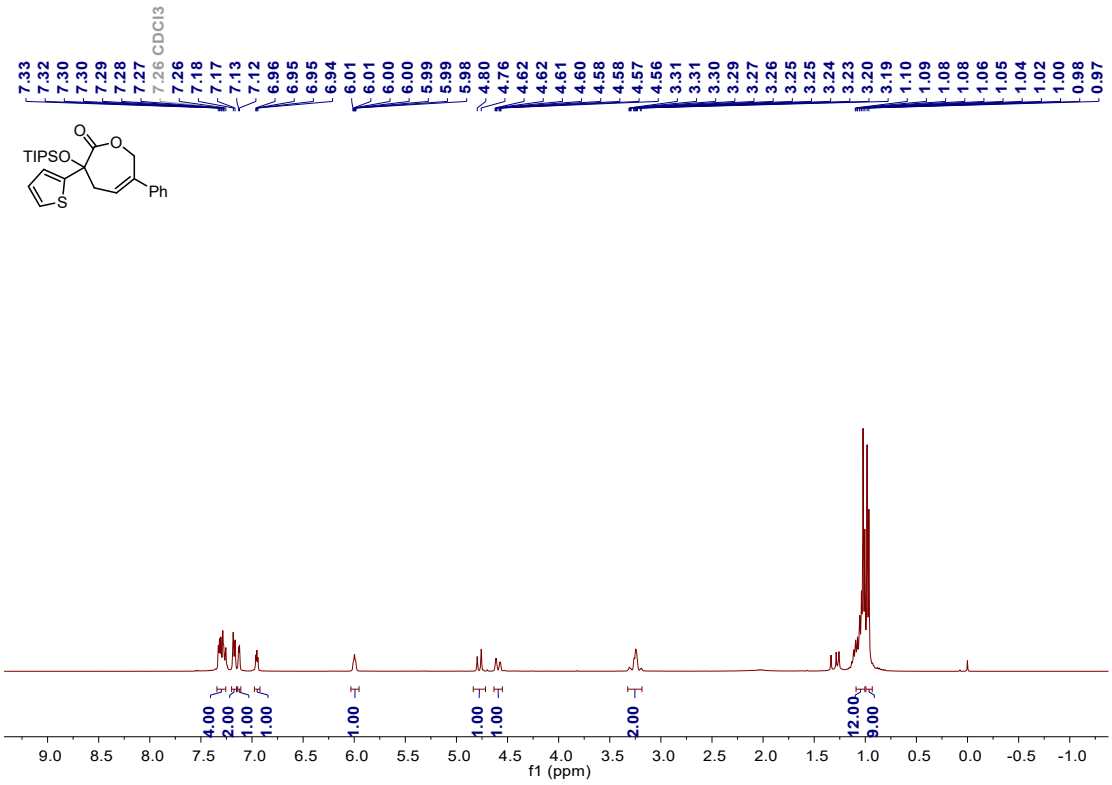
^{1}H NMR of **3am** in $CDCl_3$ (400 MHz)



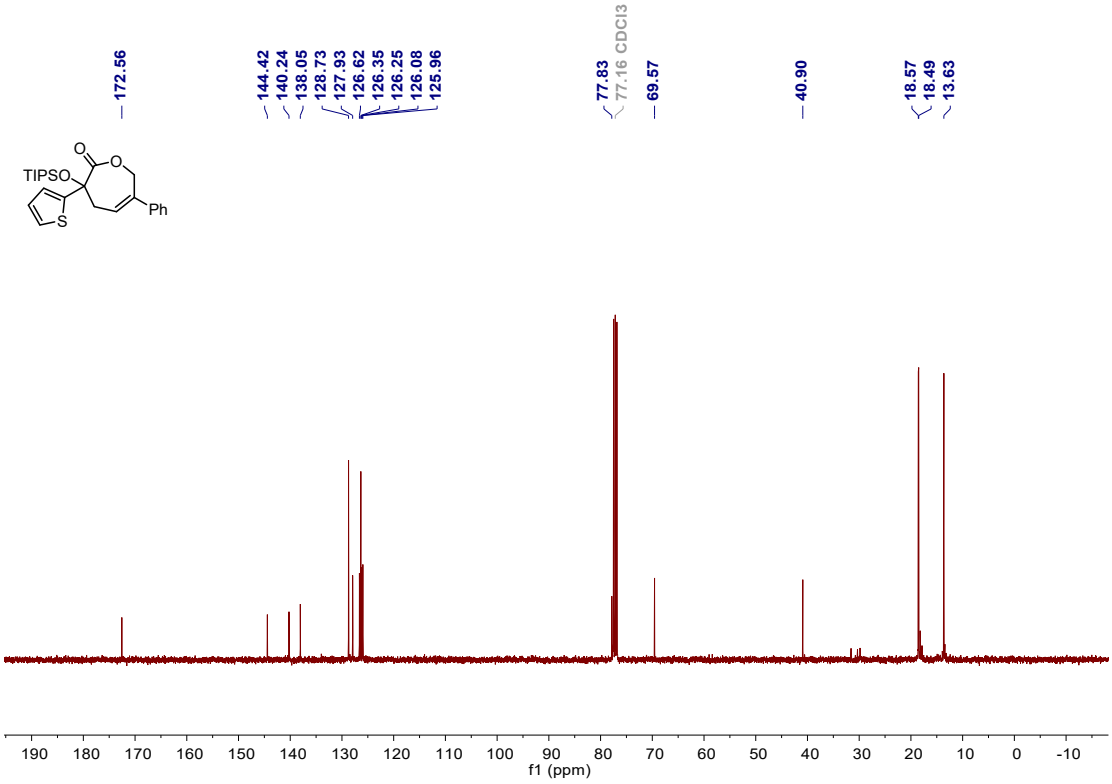
^{13}C NMR of **3am** in $CDCl_3$ (101 MHz)



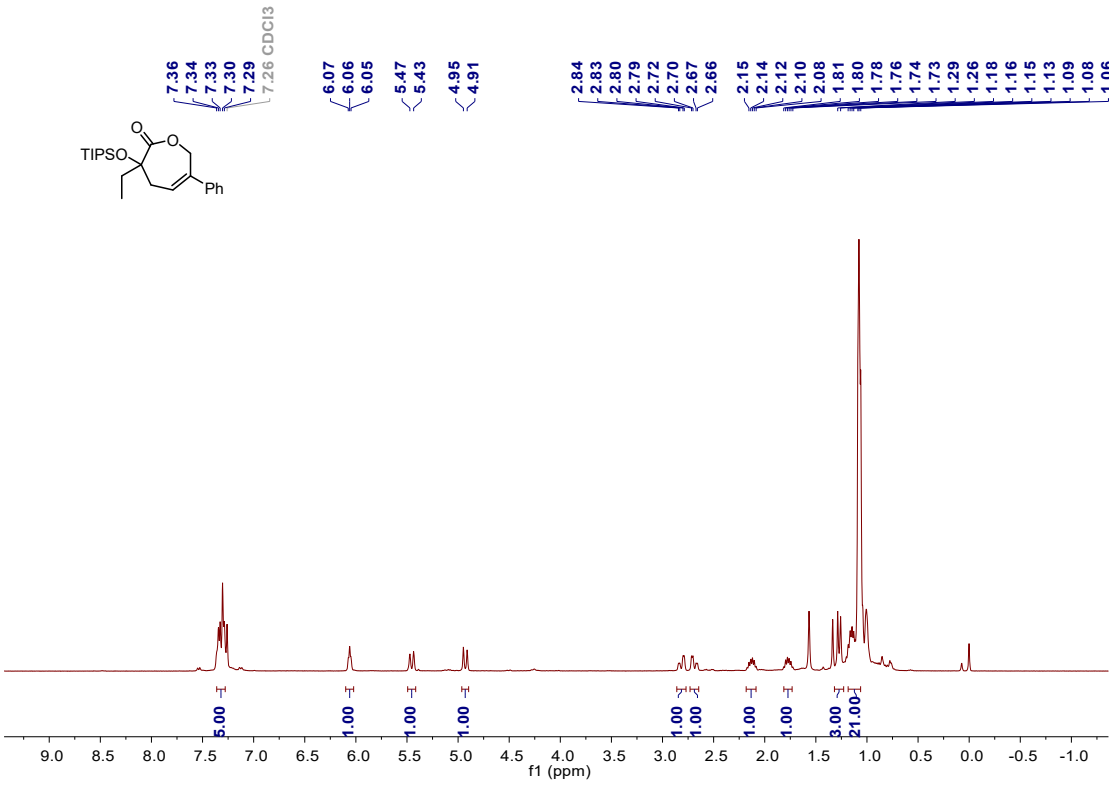
^{1}H NMR of **3an** in $CDCl_3$ (400 MHz)



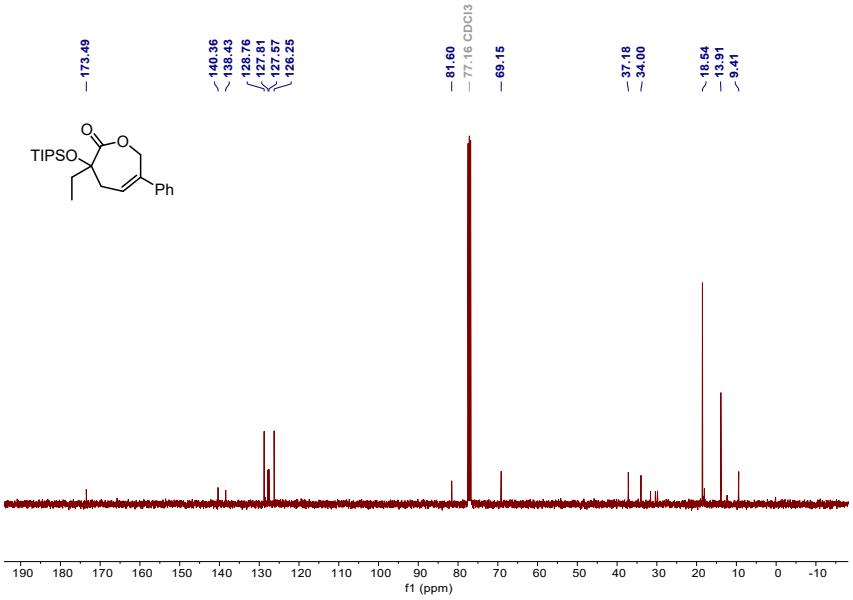
^{13}C NMR of **3an** in $CDCl_3$ (101 MHz)



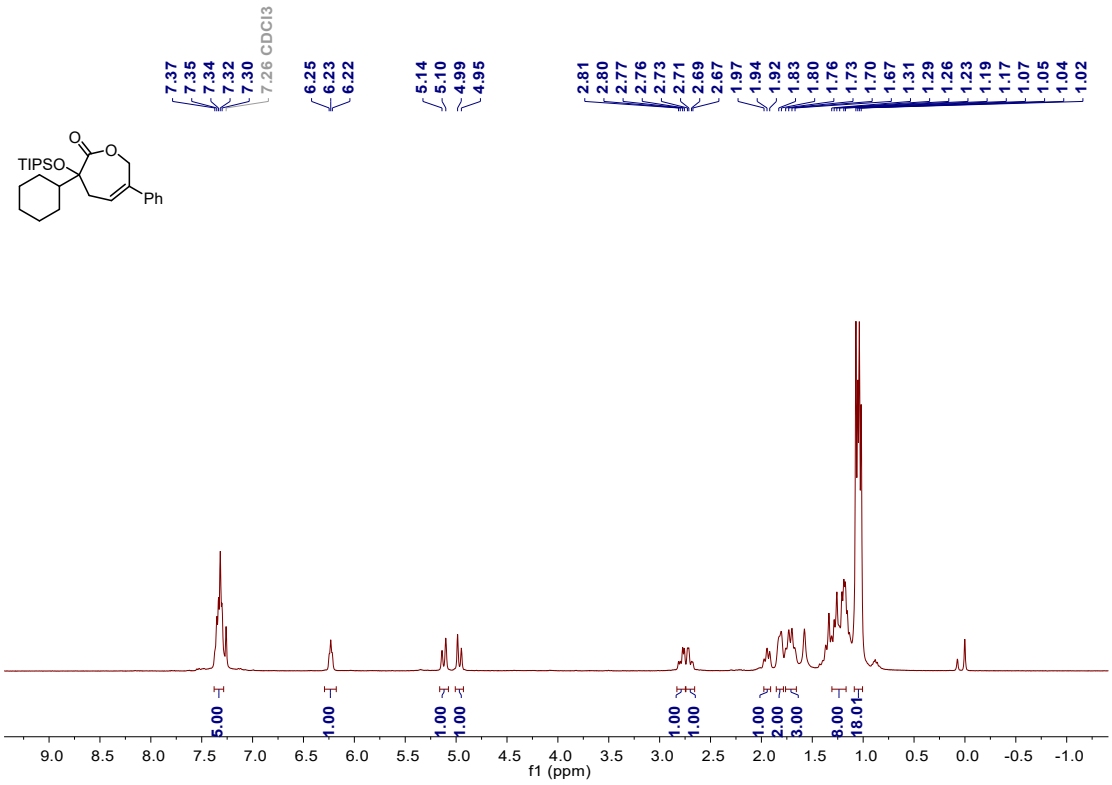
^{1}H NMR of **3ao** in $CDCl_3$ (400 MHz)



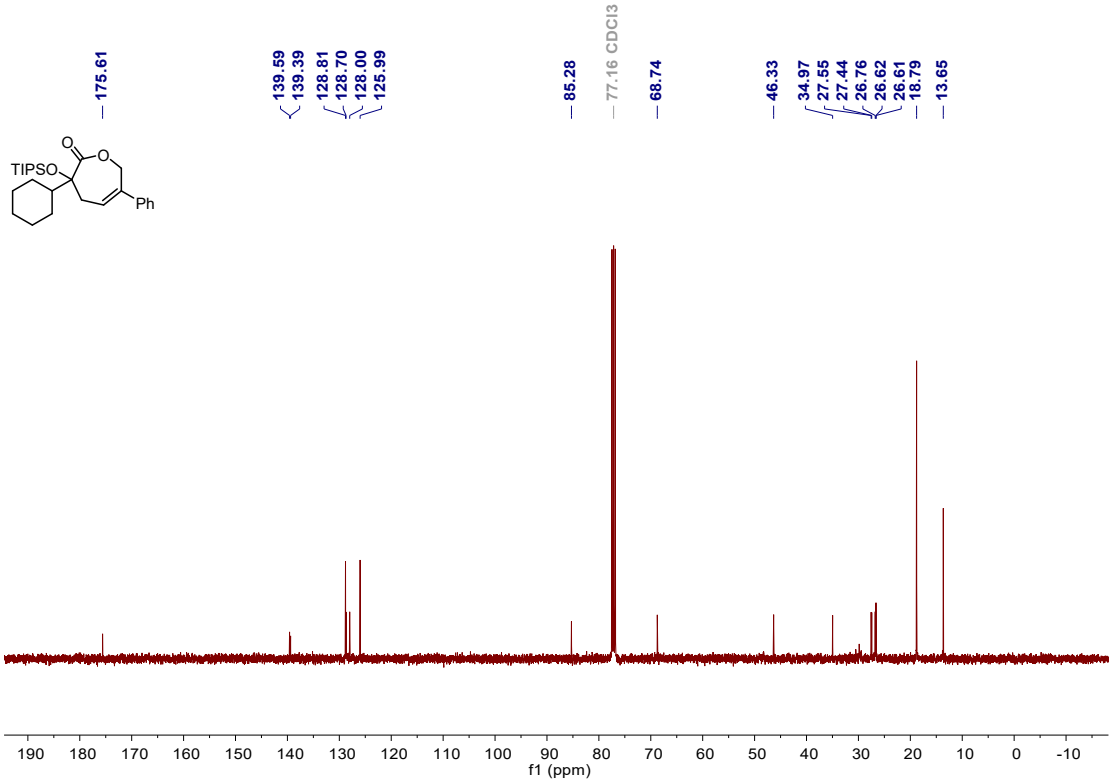
^{13}C NMR of **3ao** in $CDCl_3$ (101 MHz)



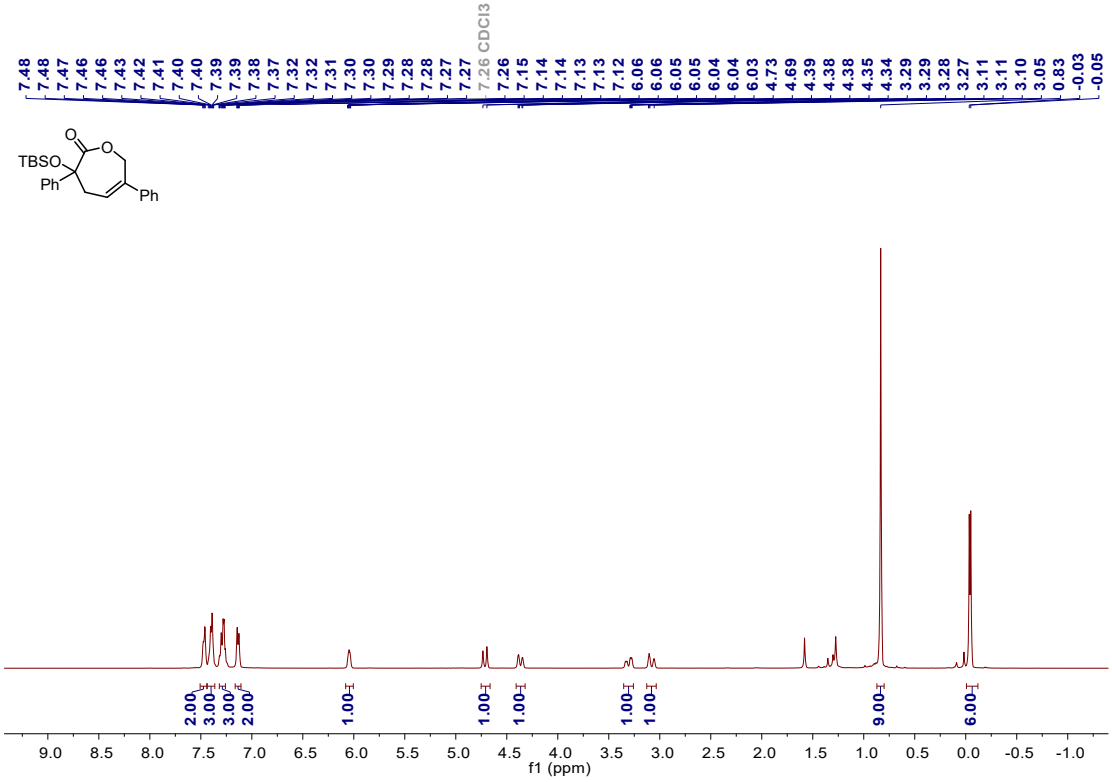
^{1}H NMR of **3ap** in $CDCl_3$ (400 MHz)



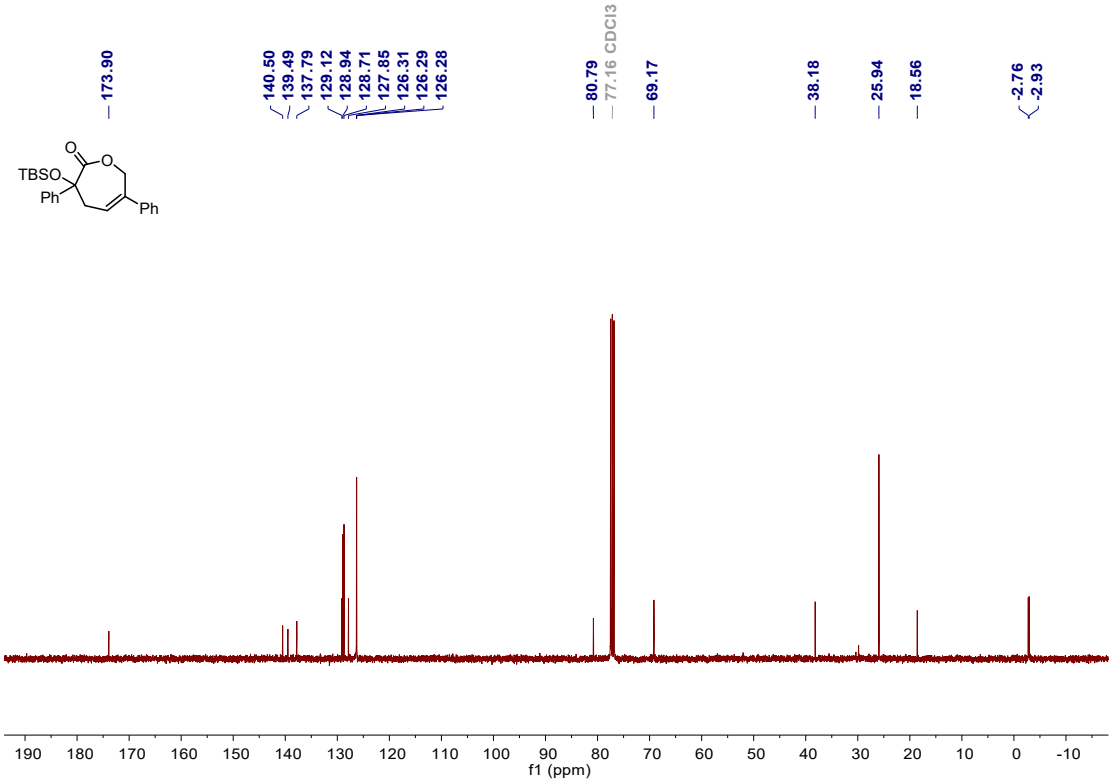
^{13}C NMR of **3ap** in $CDCl_3$ (101 MHz)



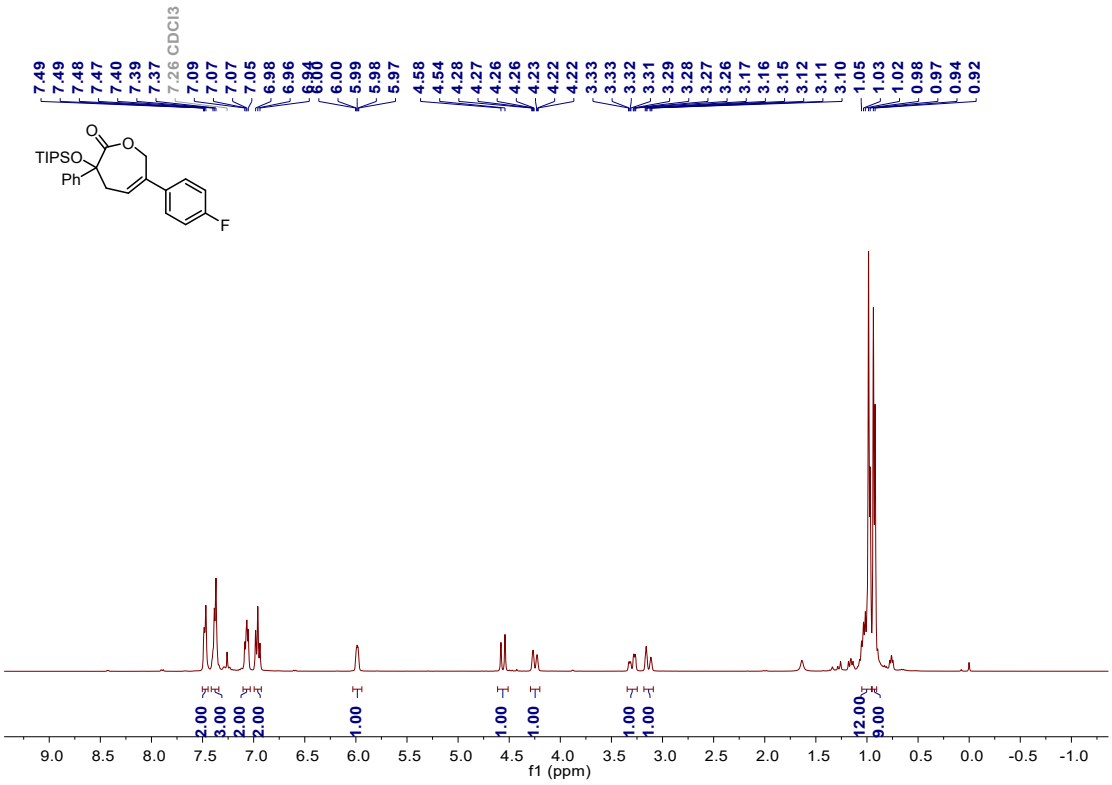
^{1}H NMR of **3aq** in $CDCl_3$ (400 MHz)



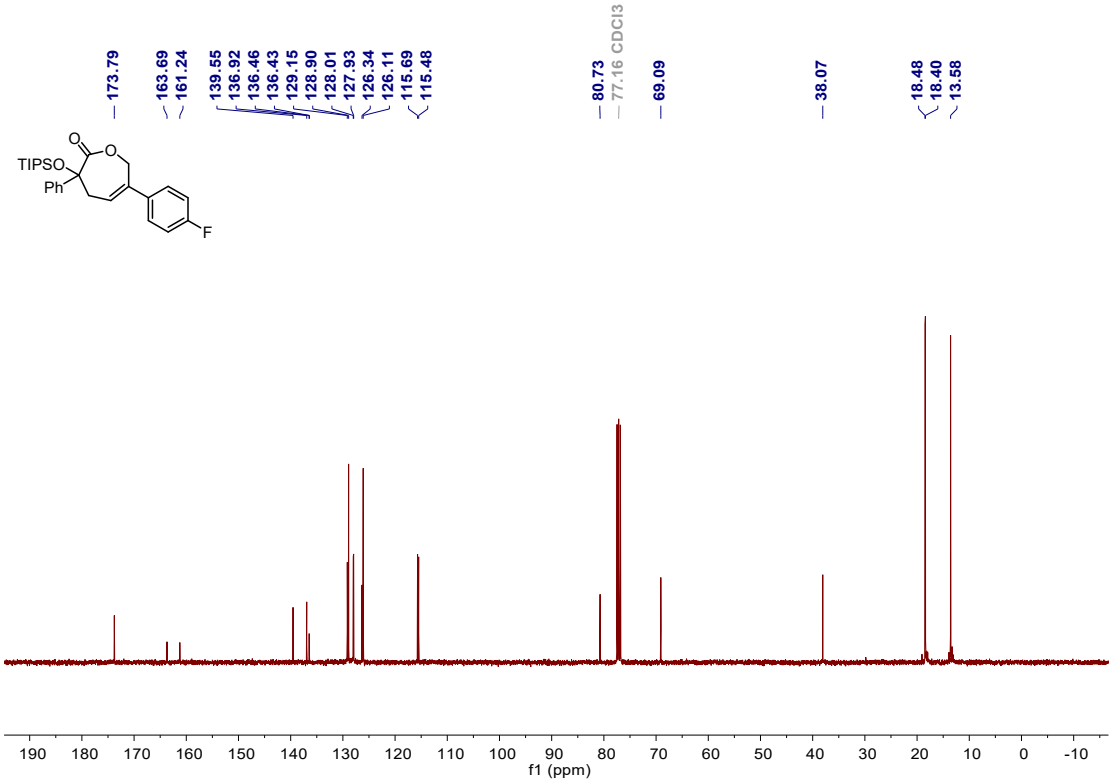
^{13}C NMR of **3aq** in $CDCl_3$ (101 MHz)



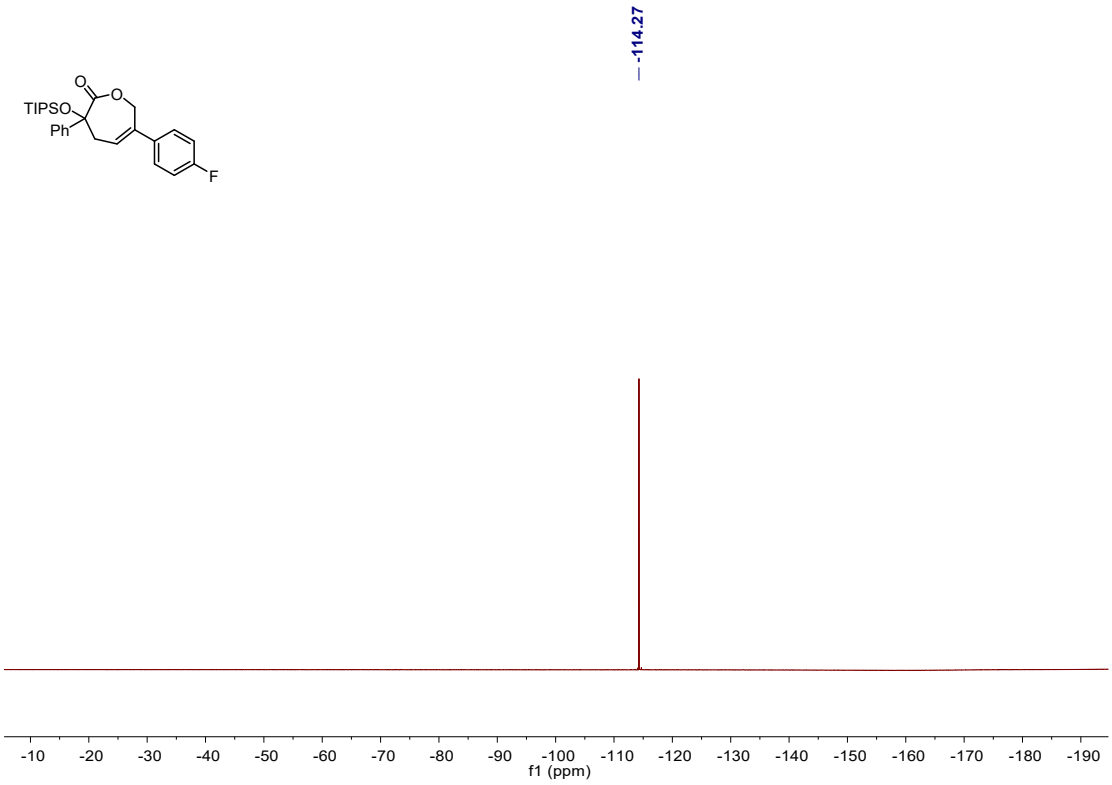
^{1}H NMR of **3ba** in $CDCl_3$ (400 MHz)



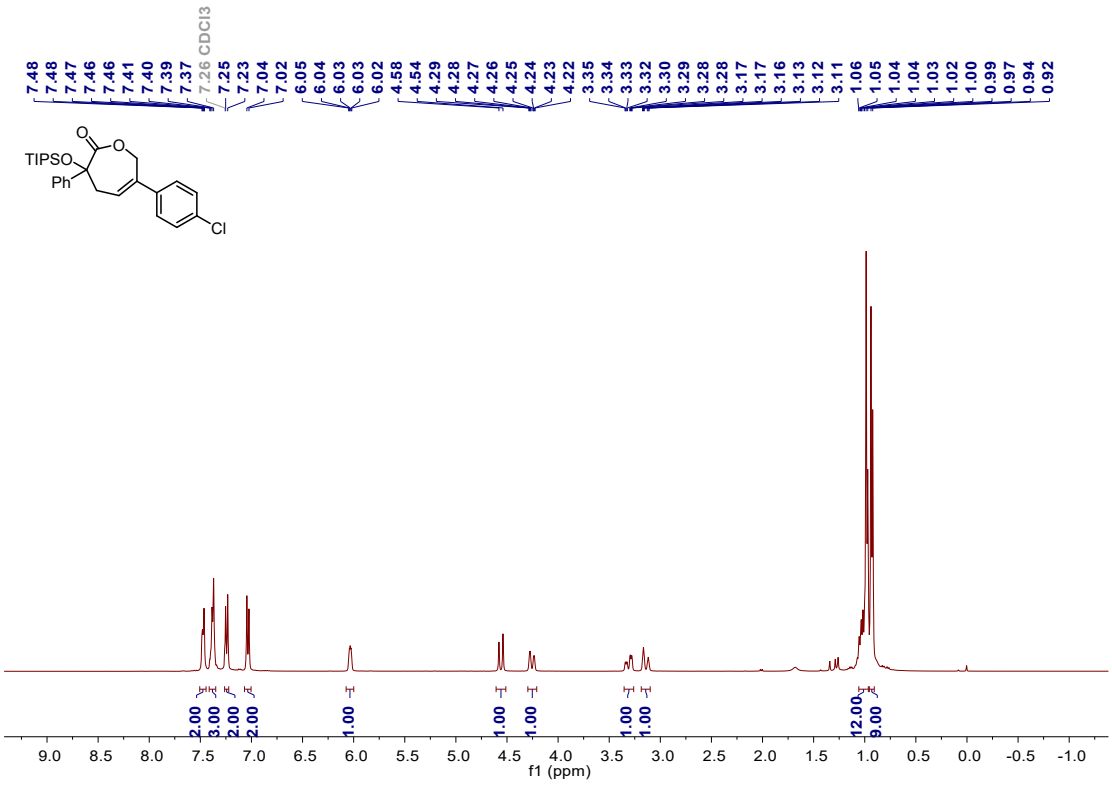
^{13}C NMR of **3ba** in $CDCl_3$ (101 MHz)



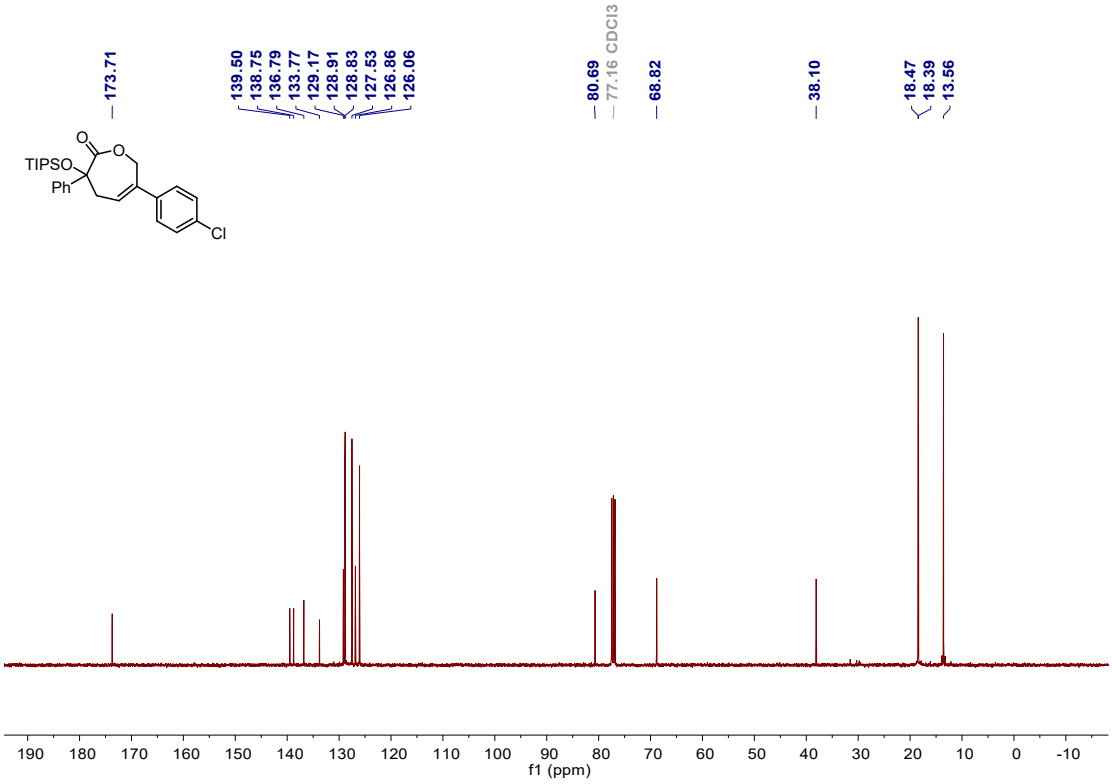
^{19}F NMR of **3ba** in $CDCl_3$ (377 MHz)



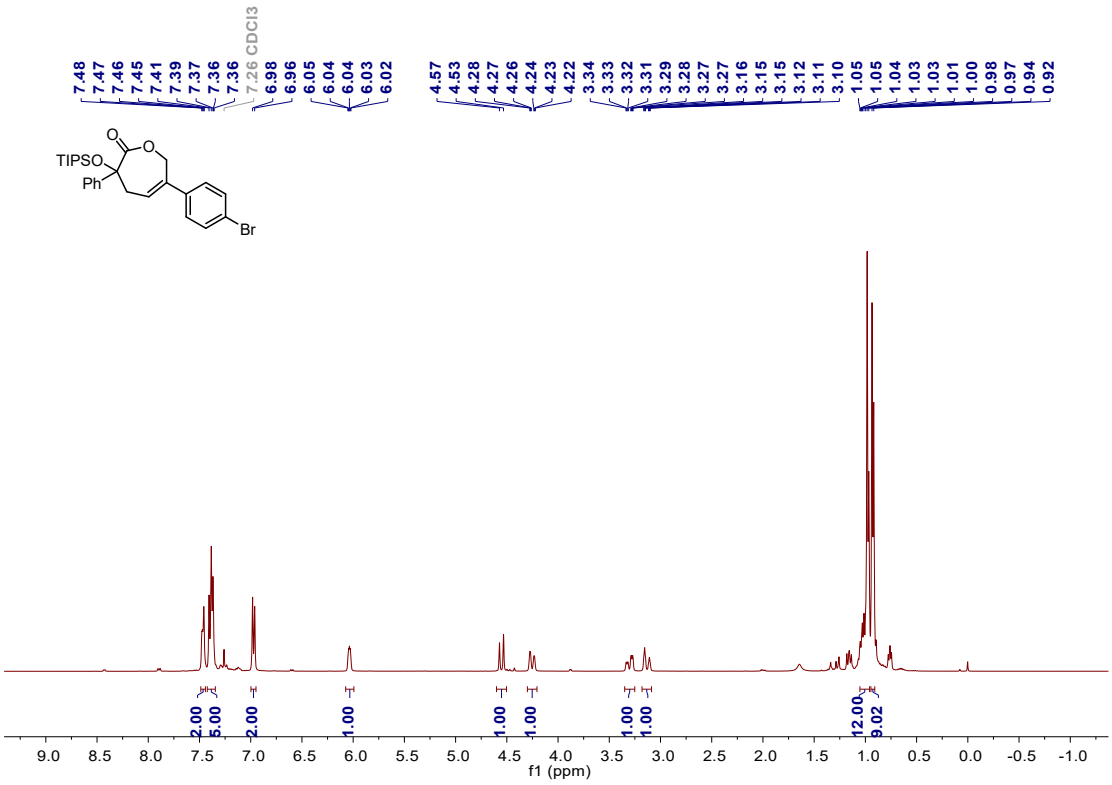
^{1}H NMR of **3ca** in $CDCl_3$ (400 MHz)



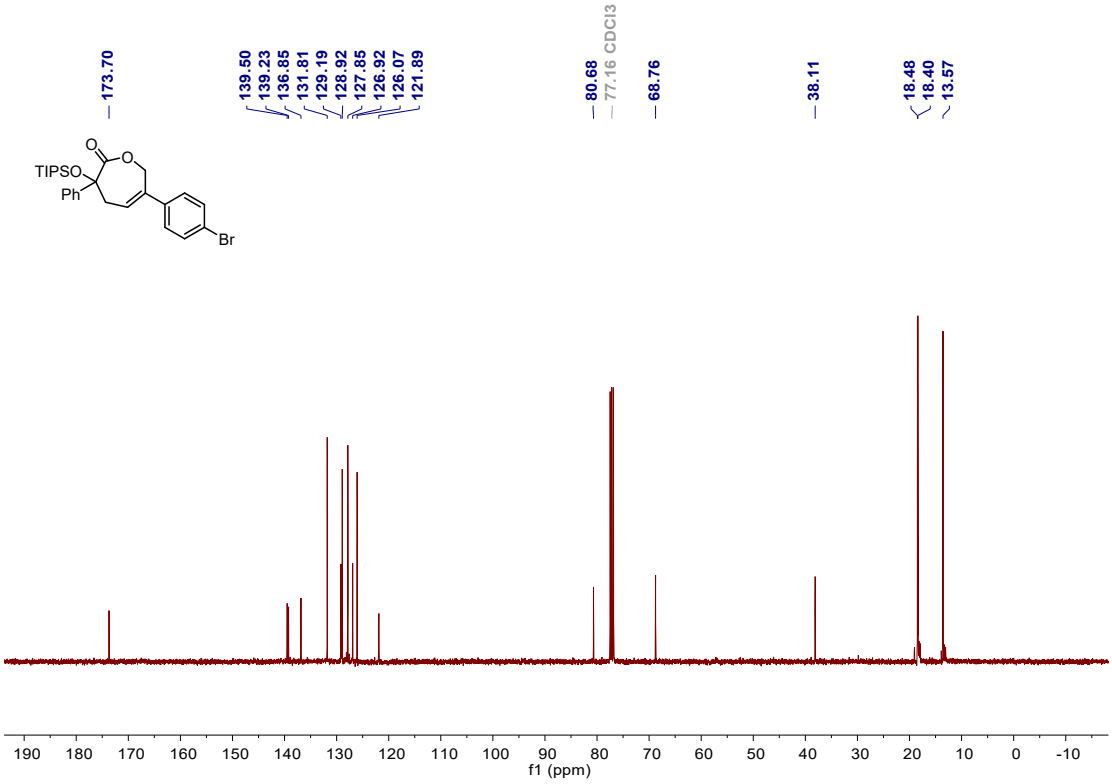
^{13}C NMR of **3ca** in $CDCl_3$ (101 MHz)



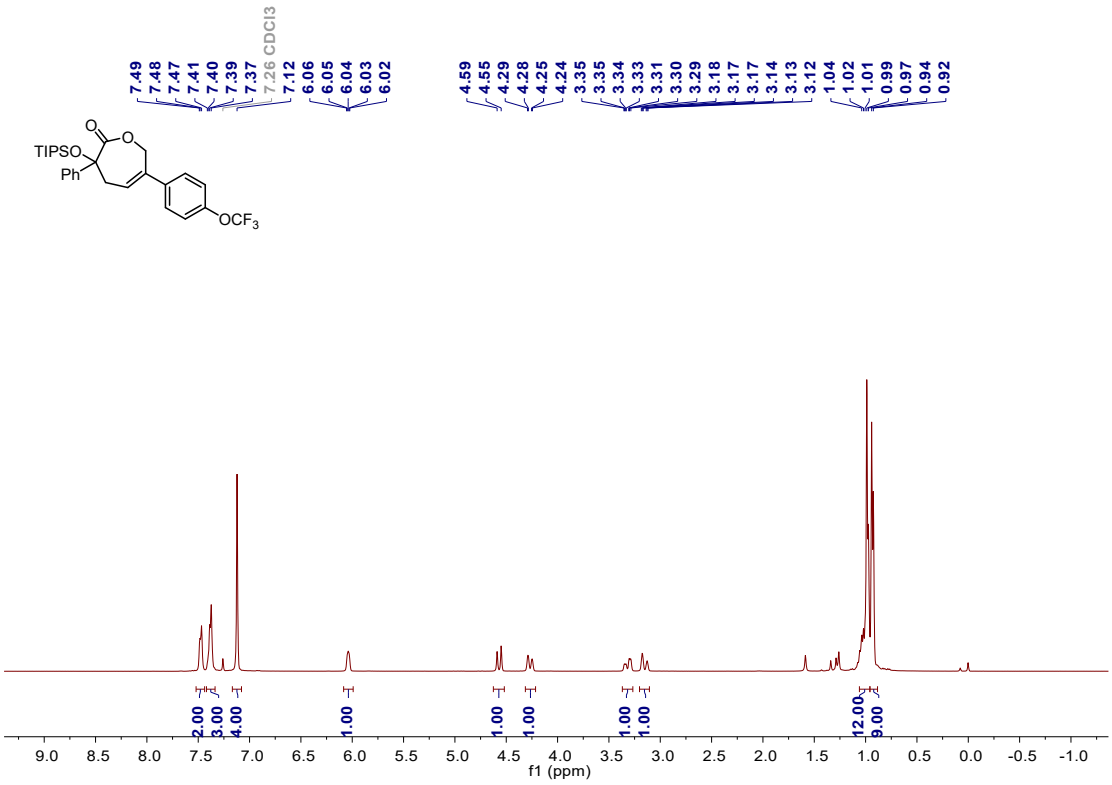
^{1}H NMR of **3da** in $CDCl_3$ (400 MHz)



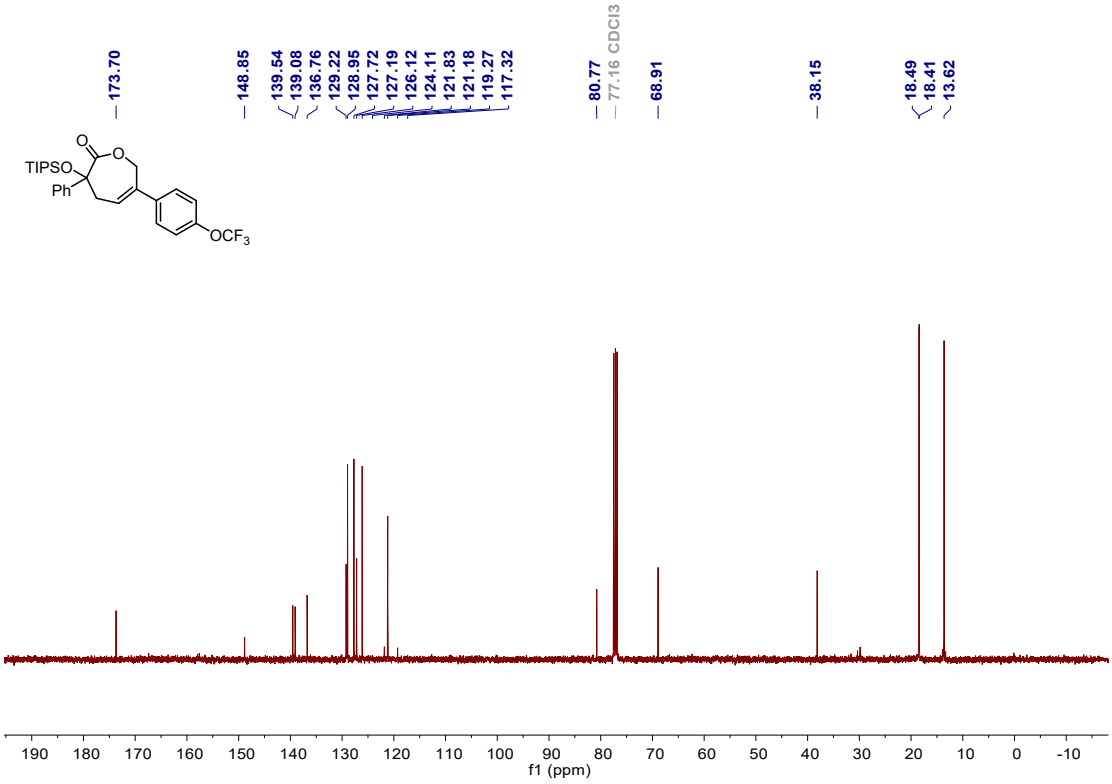
^{13}C NMR of **3da** in $CDCl_3$ (101 MHz)



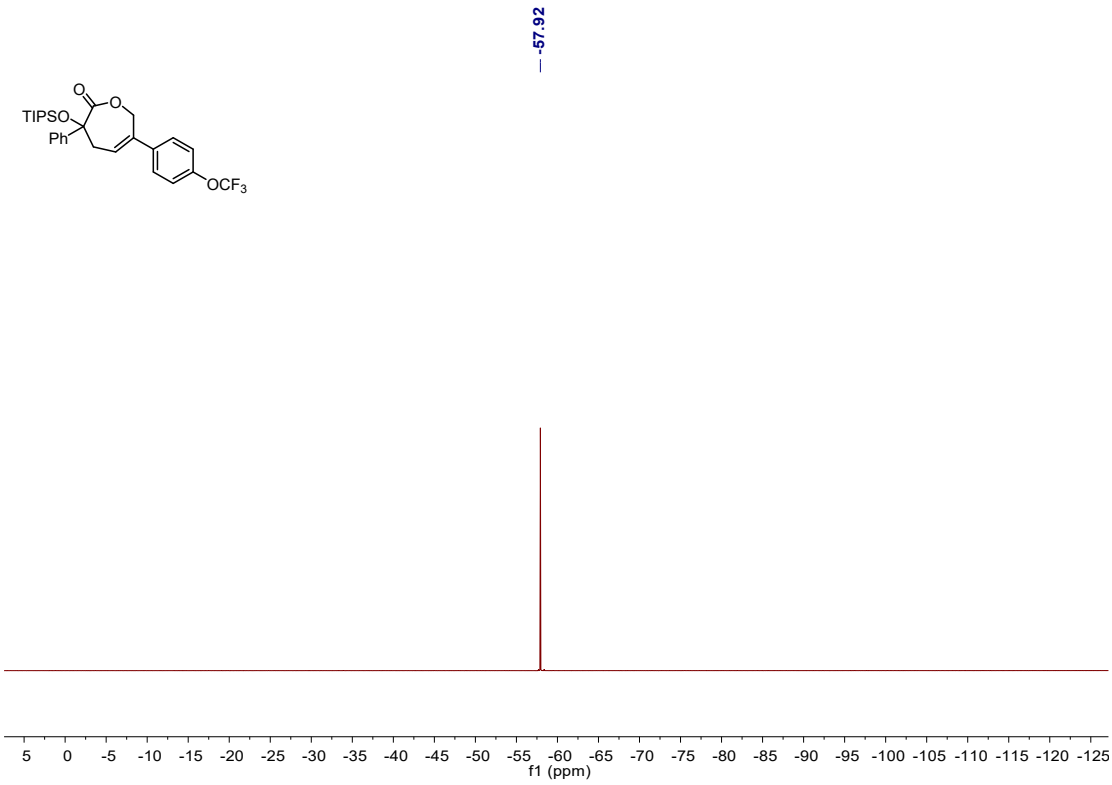
^{1}H NMR of **3ea** in $CDCl_3$ (400 MHz)



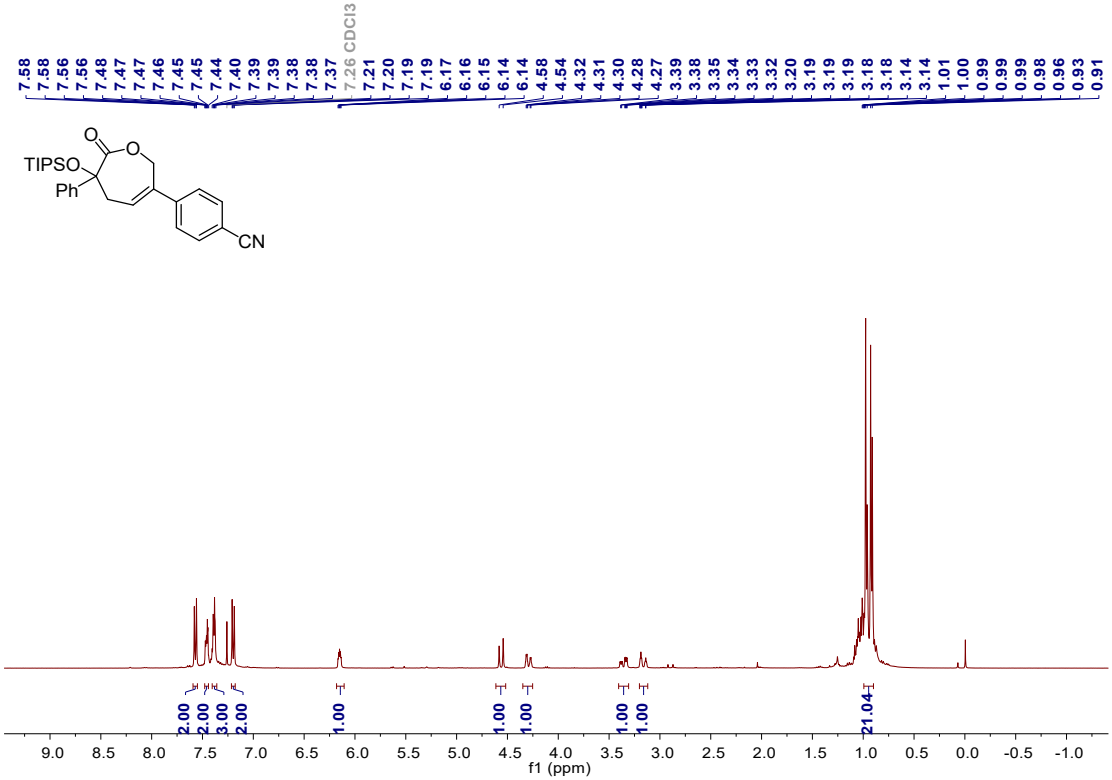
^{13}C NMR of **3ea** in $CDCl_3$ (101 MHz)



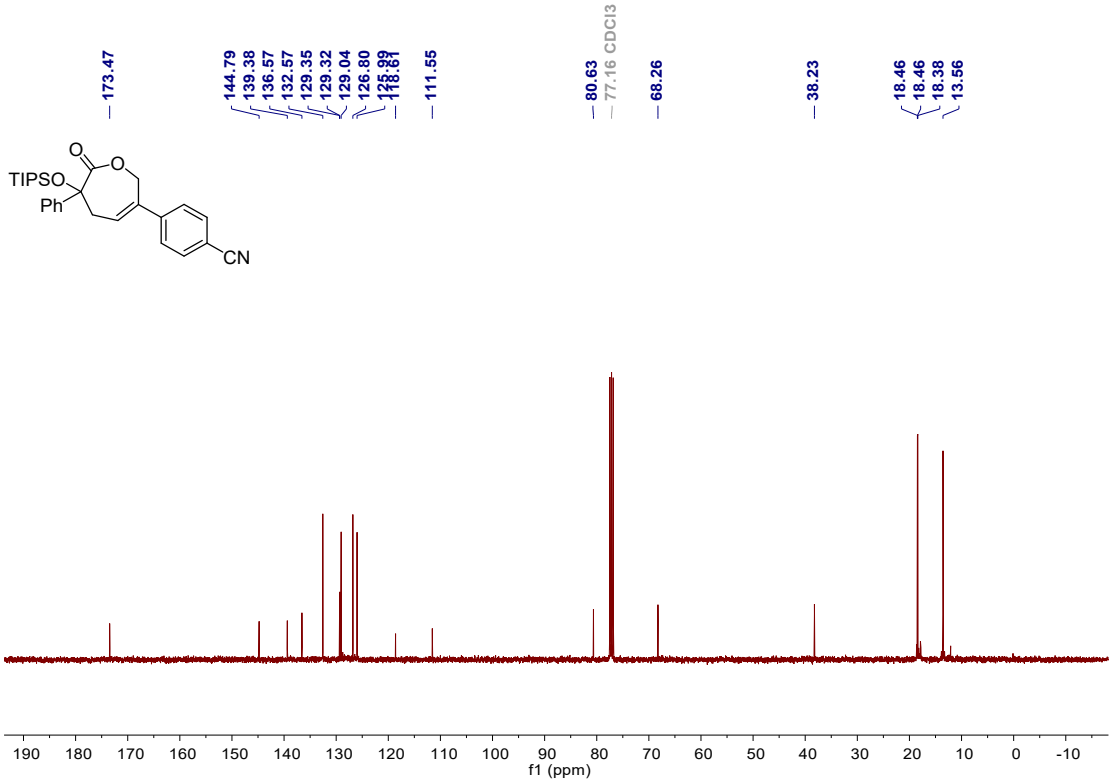
^{19}F NMR of **3ea** in $CDCl_3$ (377 MHz)



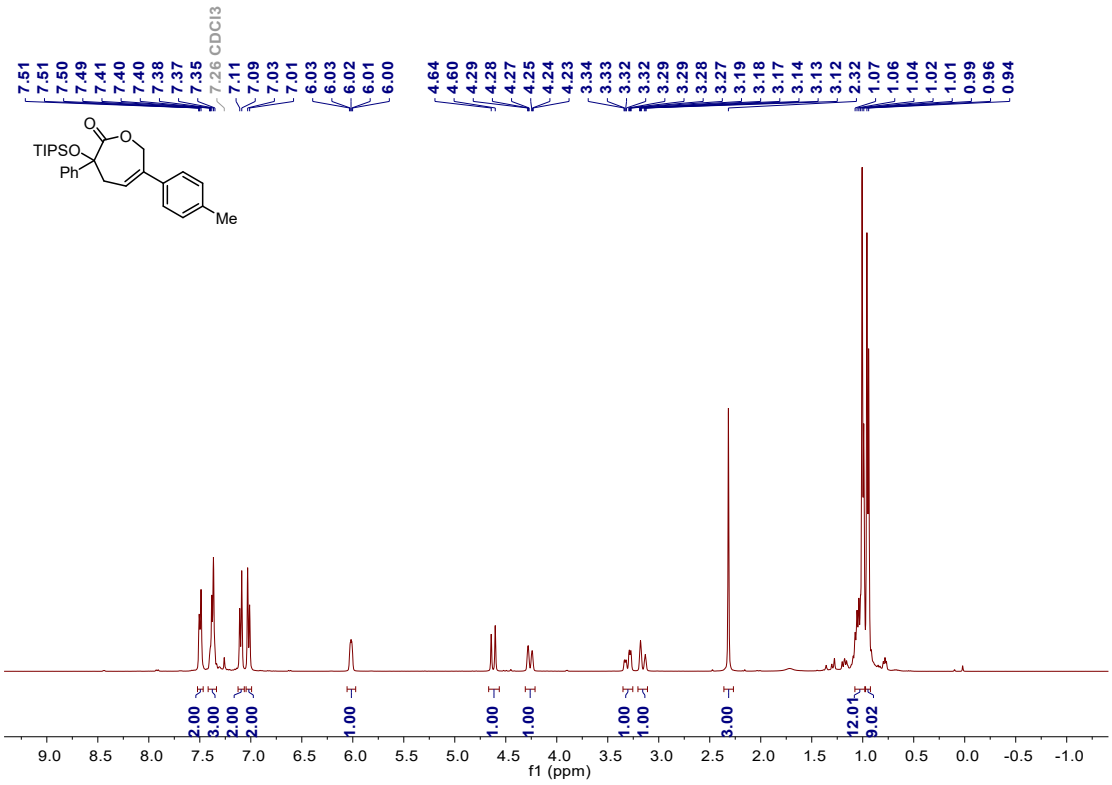
^{1}H NMR of **3fa** in $CDCl_3$ (400 MHz)



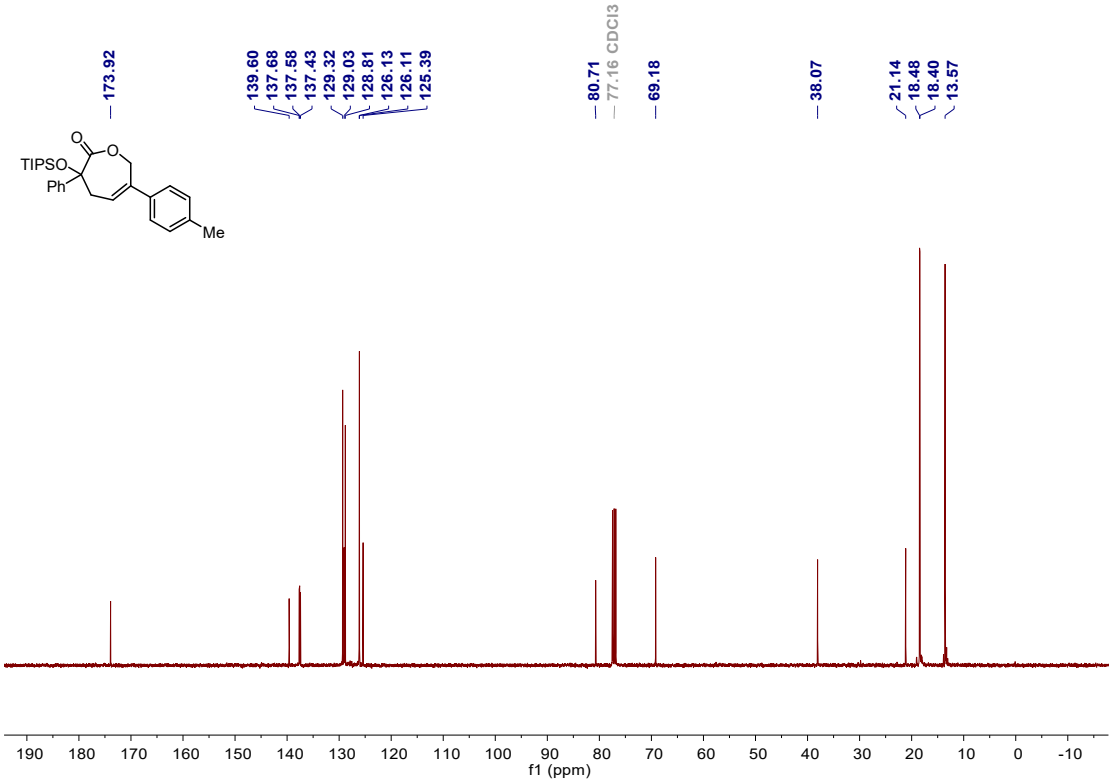
^{13}C NMR of **3fa** in $CDCl_3$ (101 MHz)



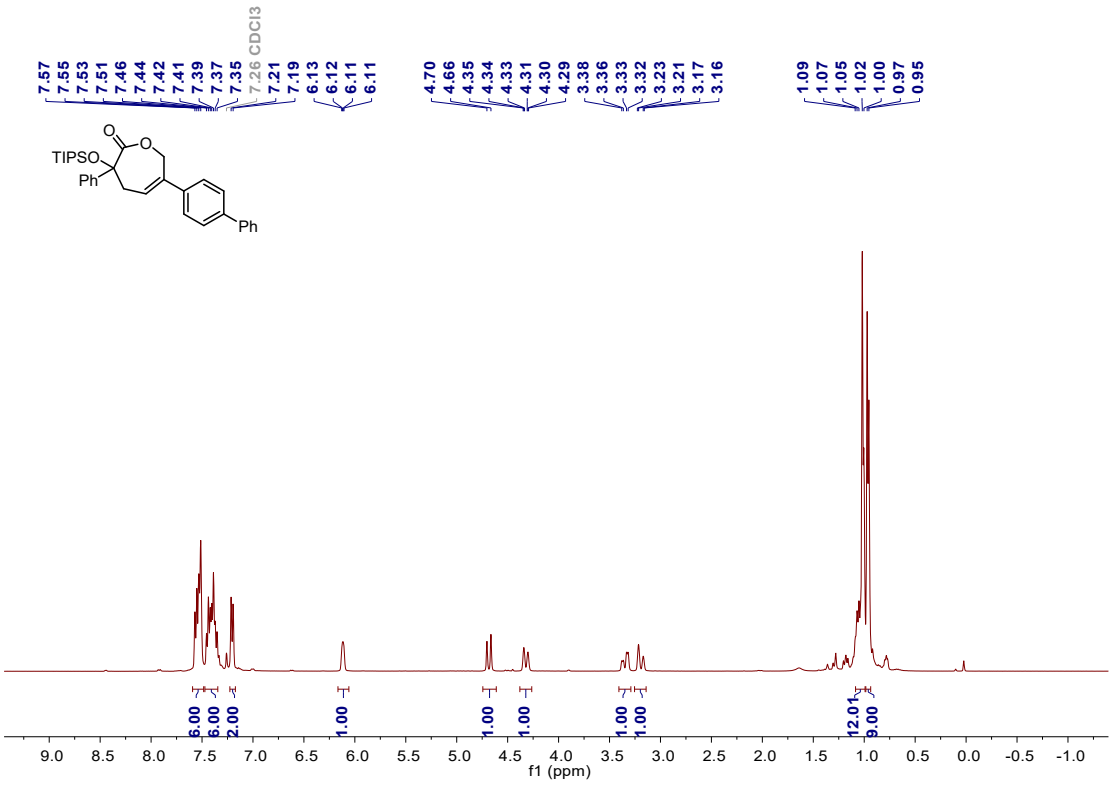
^{1}H NMR of **3ga** in $CDCl_3$ (400 MHz)



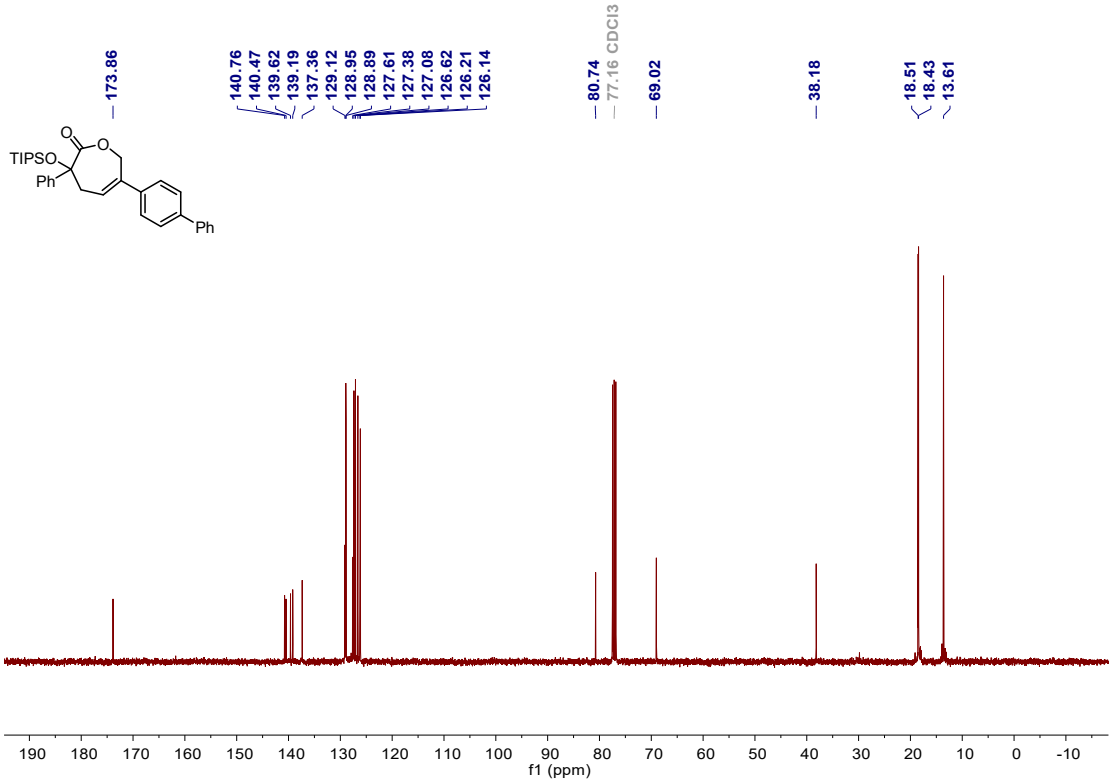
^{13}C NMR of **3ga** in $CDCl_3$ (101 MHz)



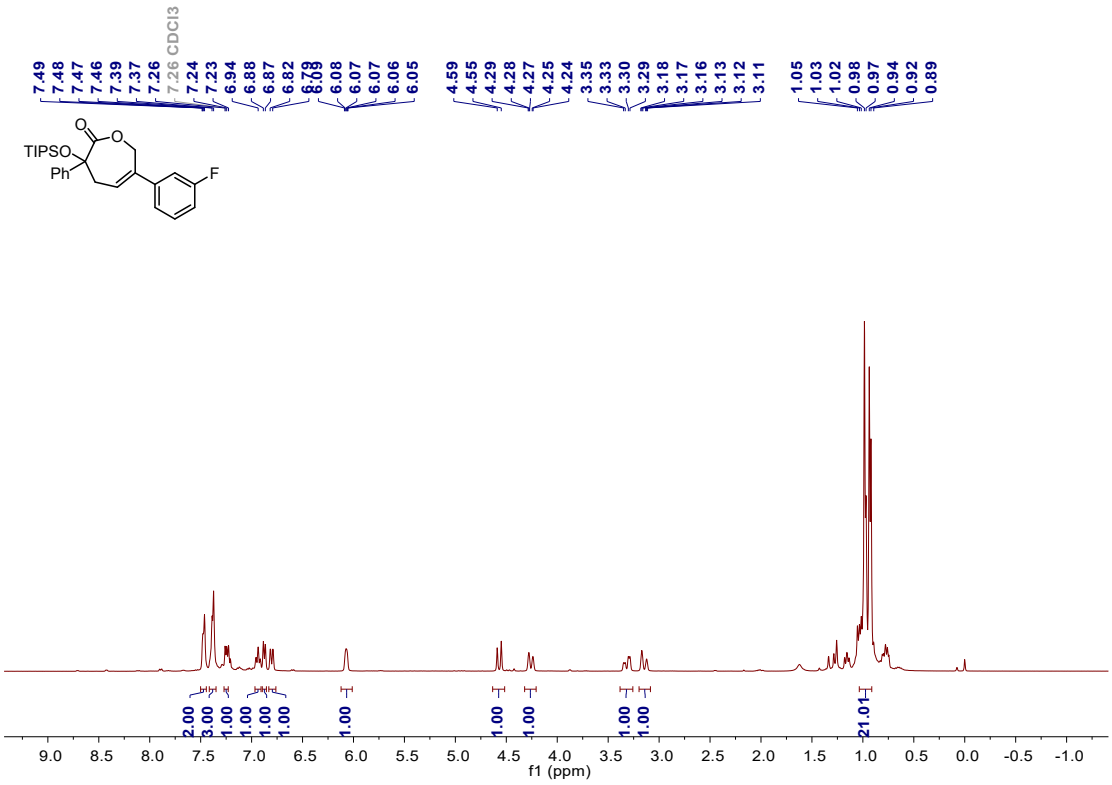
^{1}H NMR of **3ha** in $CDCl_3$ (400 MHz)



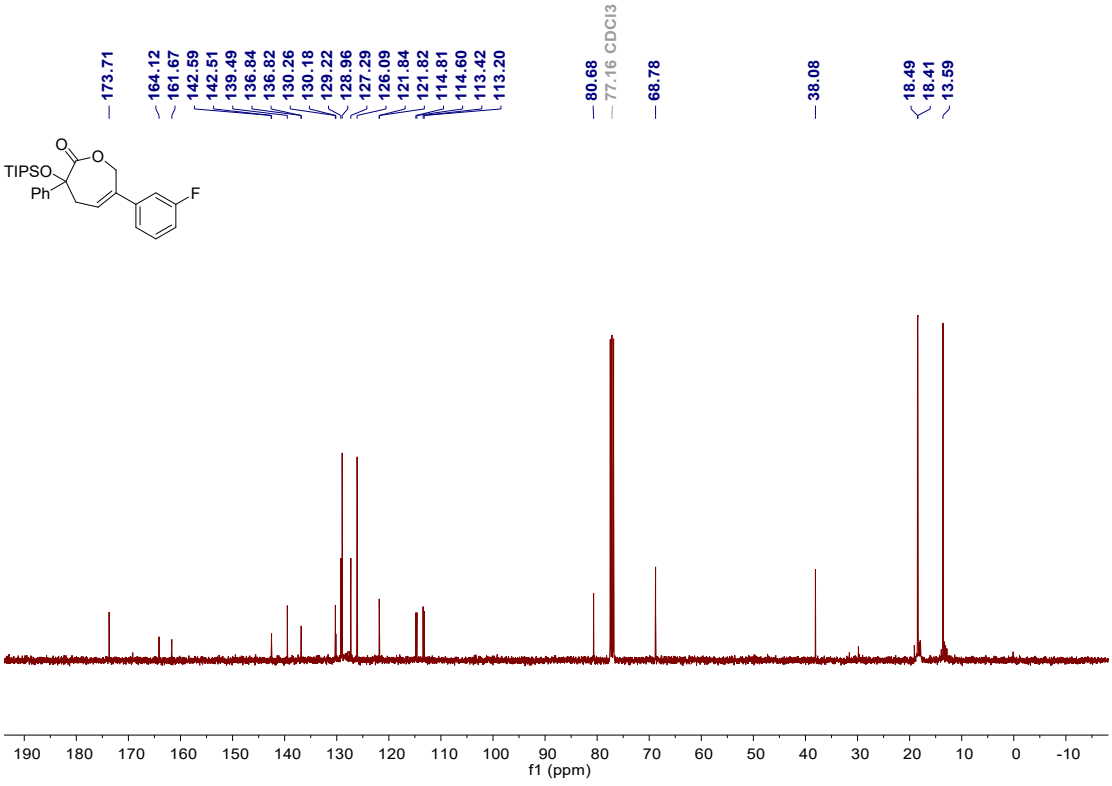
^{13}C NMR of **3ha** in $CDCl_3$ (101 MHz)



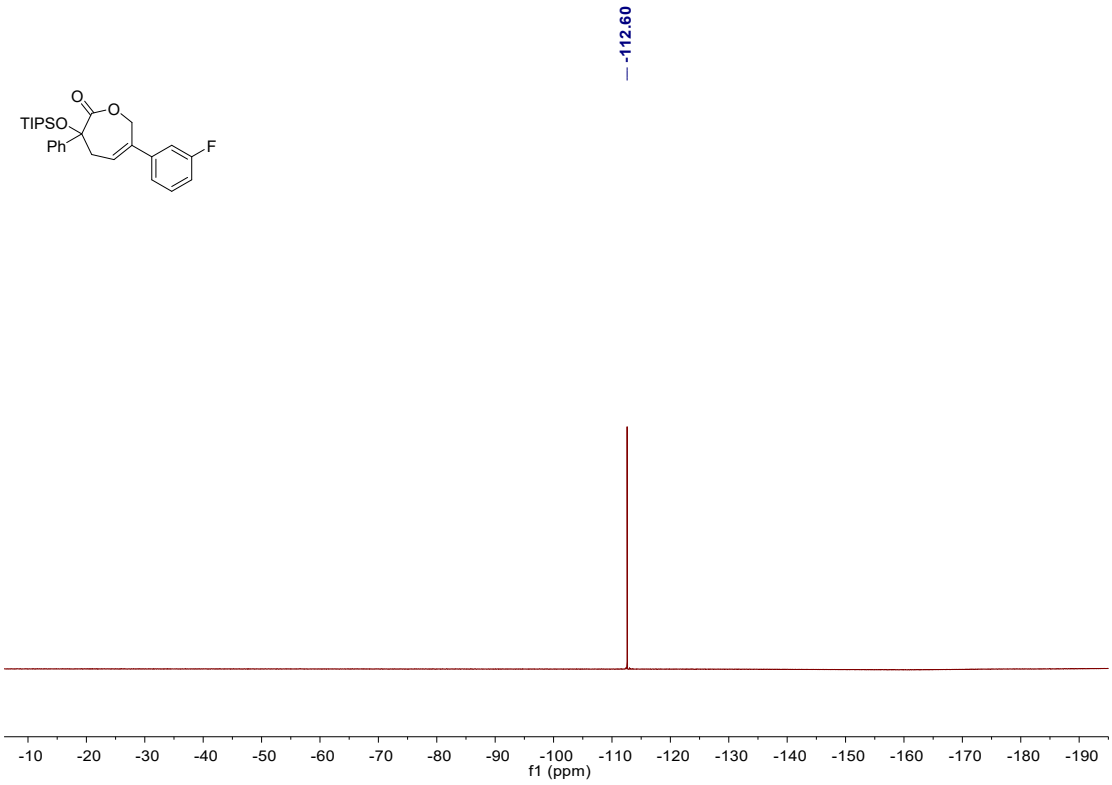
^{1}H NMR of **3ia** in $CDCl_3$ (400 MHz)



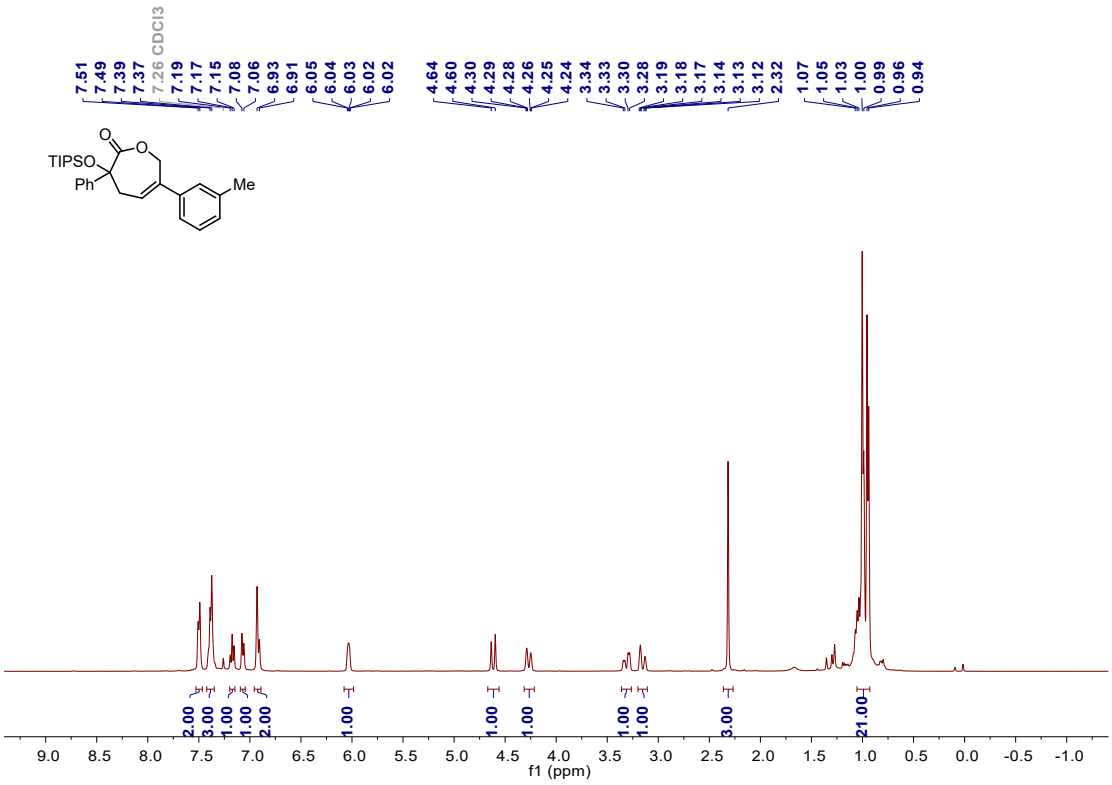
^{13}C NMR of **3ia** in $CDCl_3$ (101 MHz)



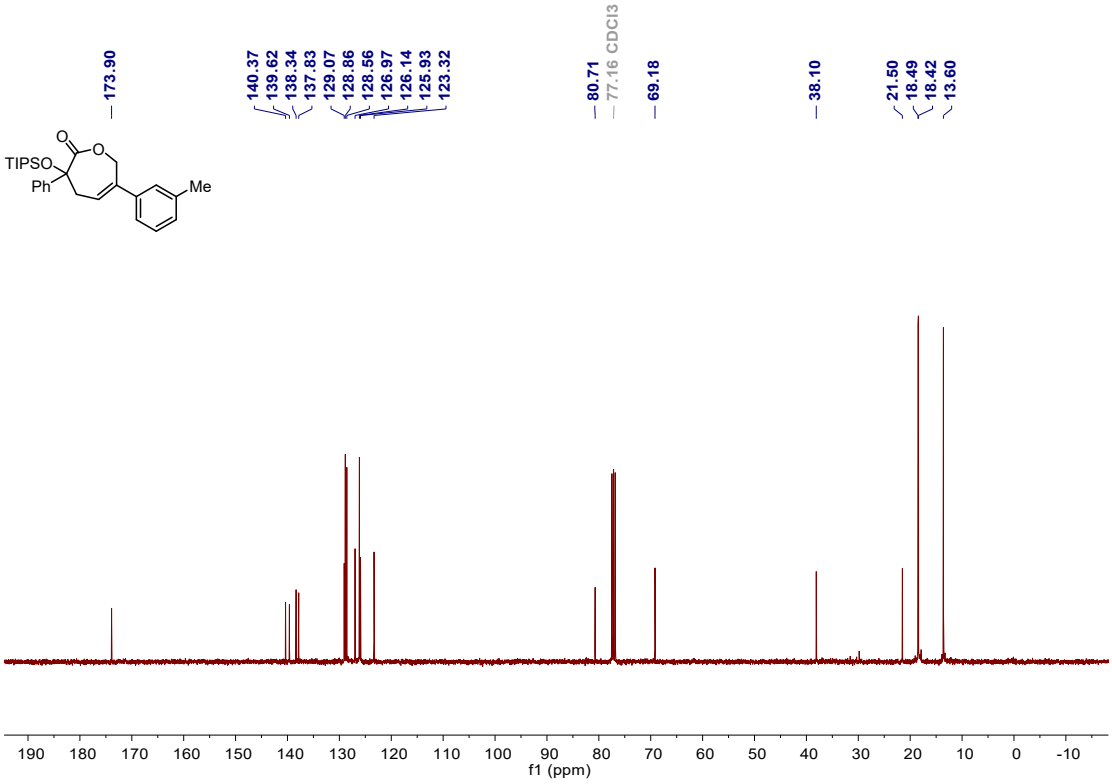
^{19}F NMR of **3ia** in $CDCl_3$ (377 MHz)



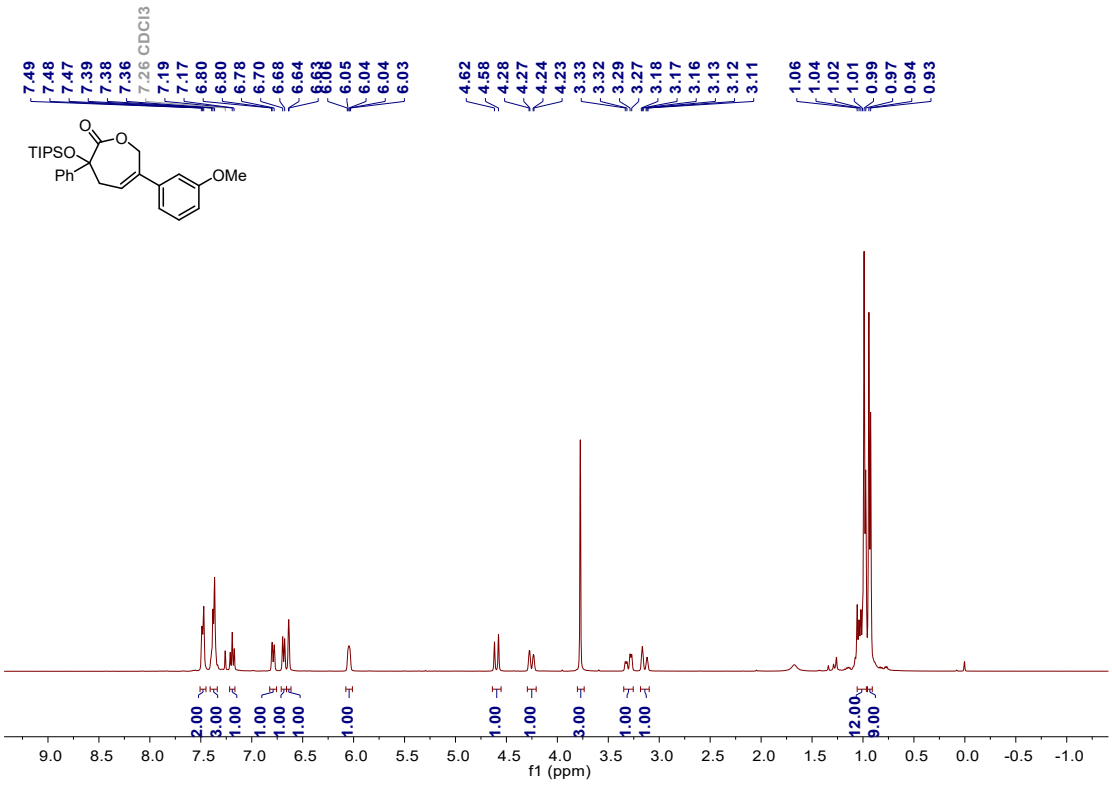
^{1}H NMR of **3ja** in $CDCl_3$ (400 MHz)



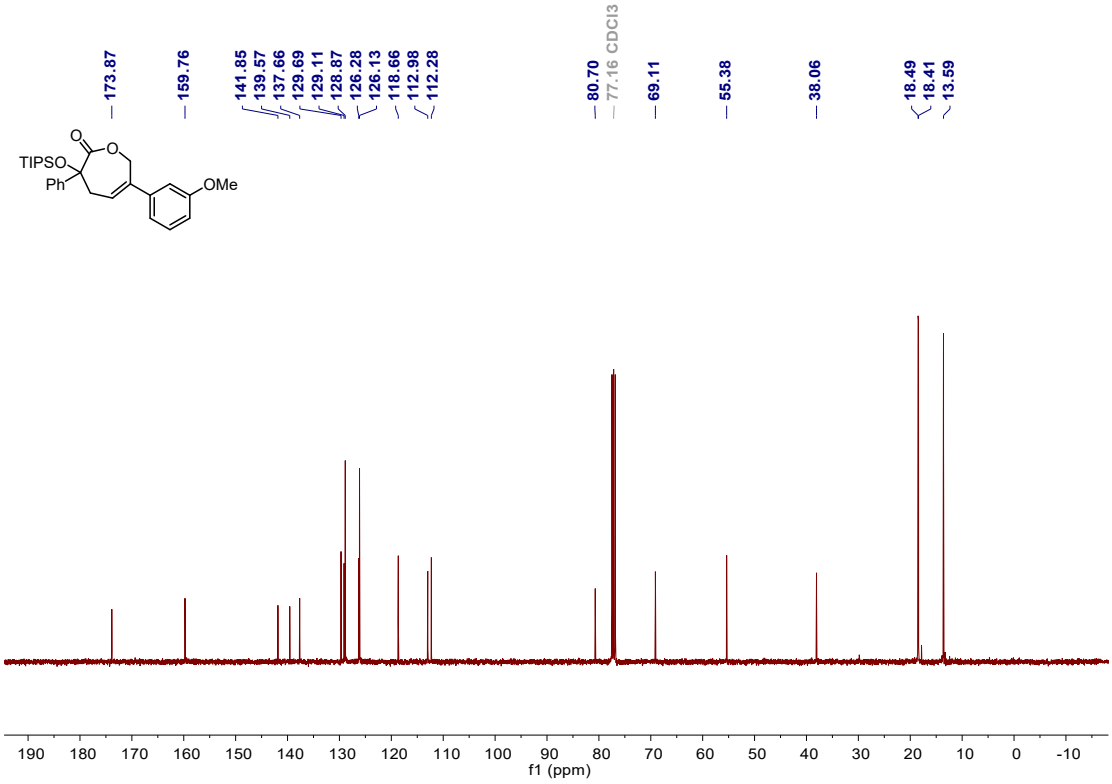
^{13}C NMR of **3ja** in $CDCl_3$ (101 MHz)



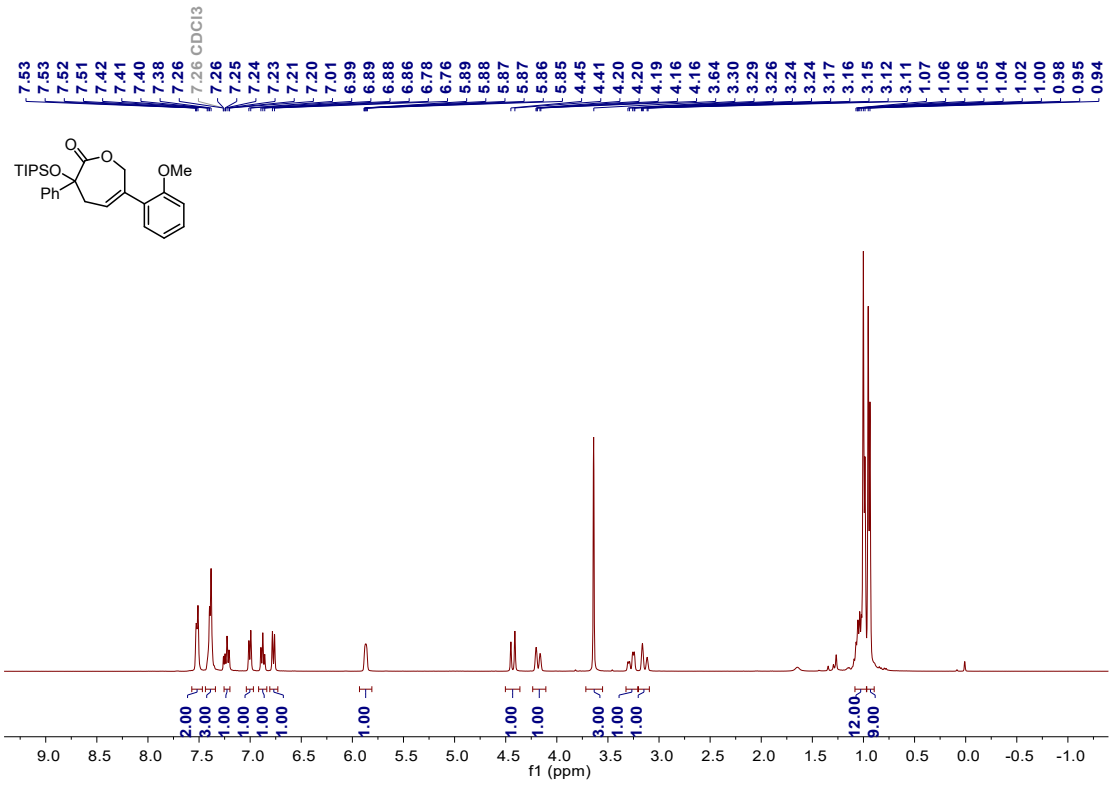
^{1}H NMR of **3ka** in $CDCl_3$ (400 MHz)



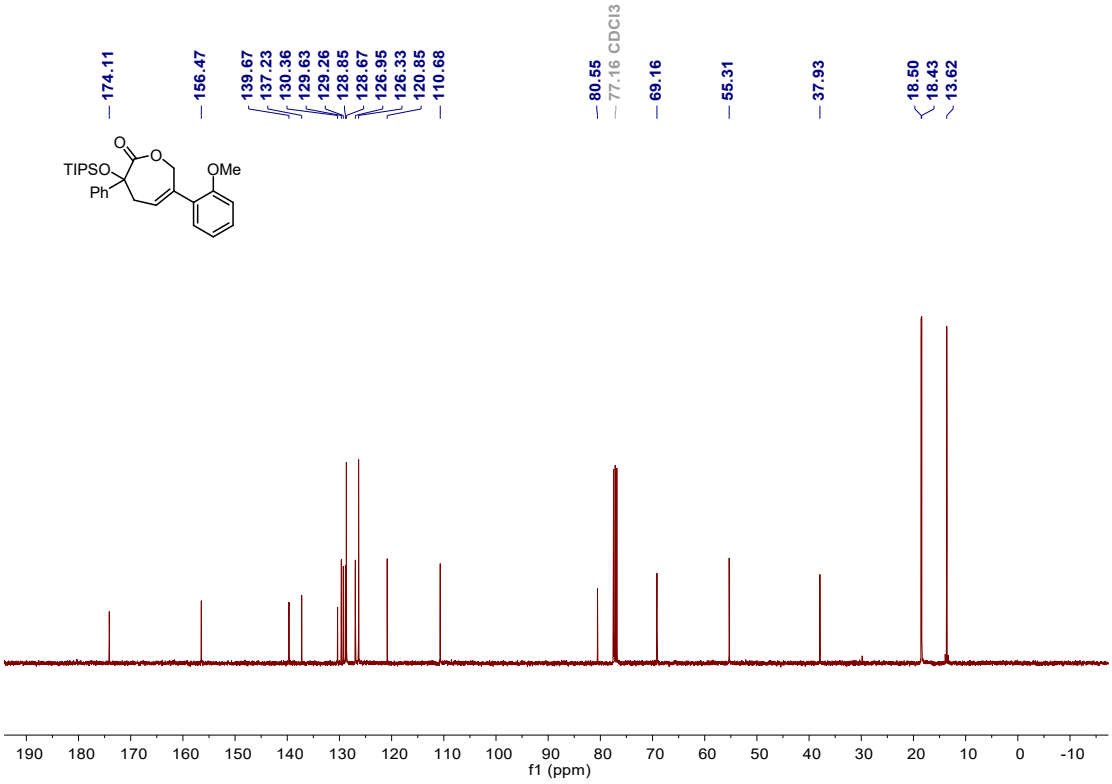
^{13}C NMR of **3ka** in $CDCl_3$ (101 MHz)



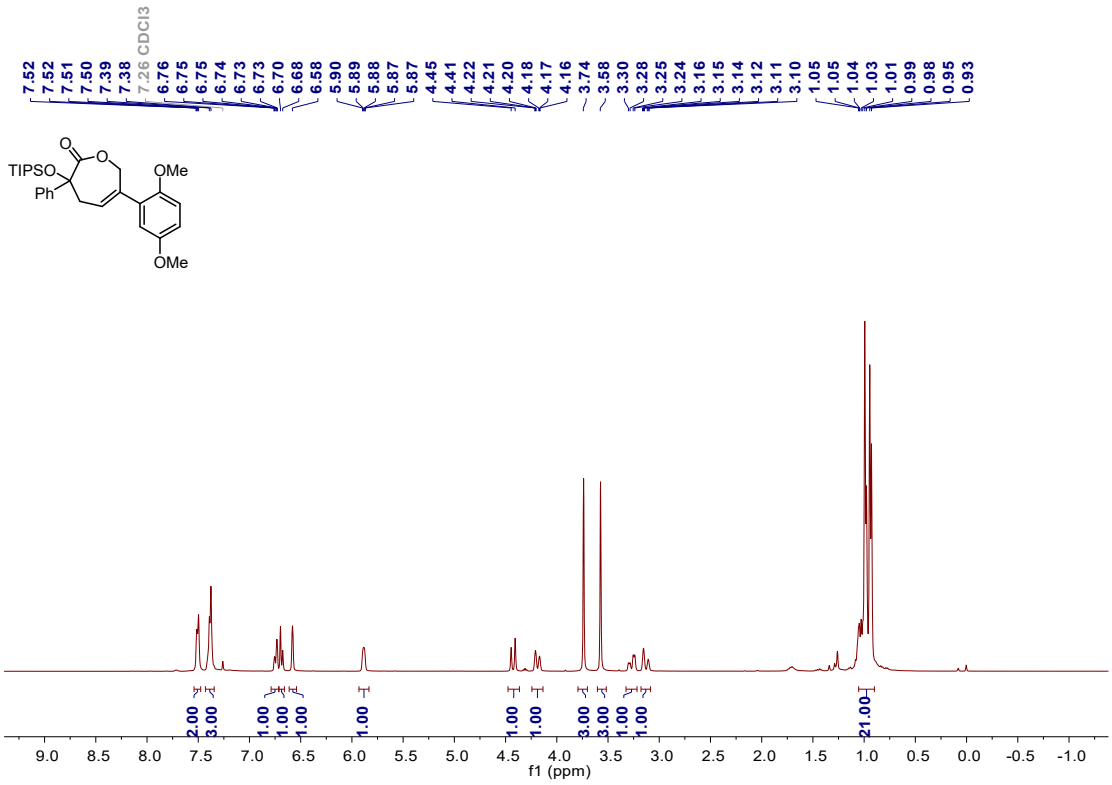
^{1}H NMR of **3la** in $CDCl_3$ (400 MHz)



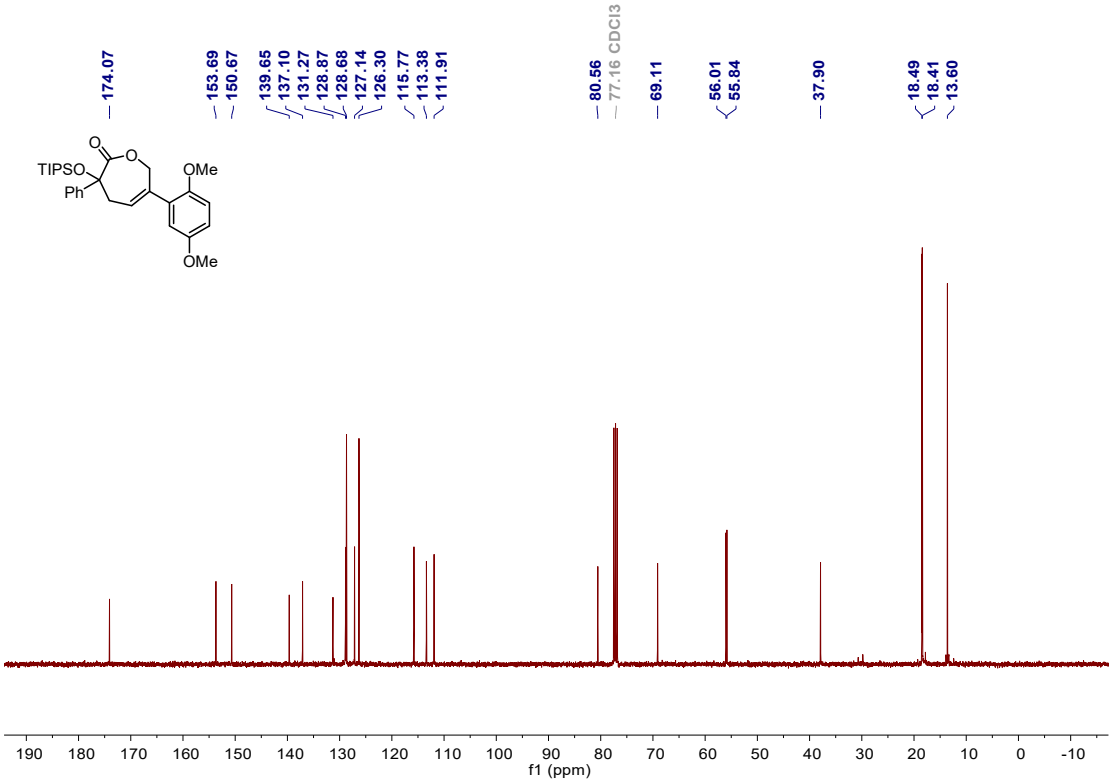
^{13}C NMR of **3la** in $CDCl_3$ (101 MHz)



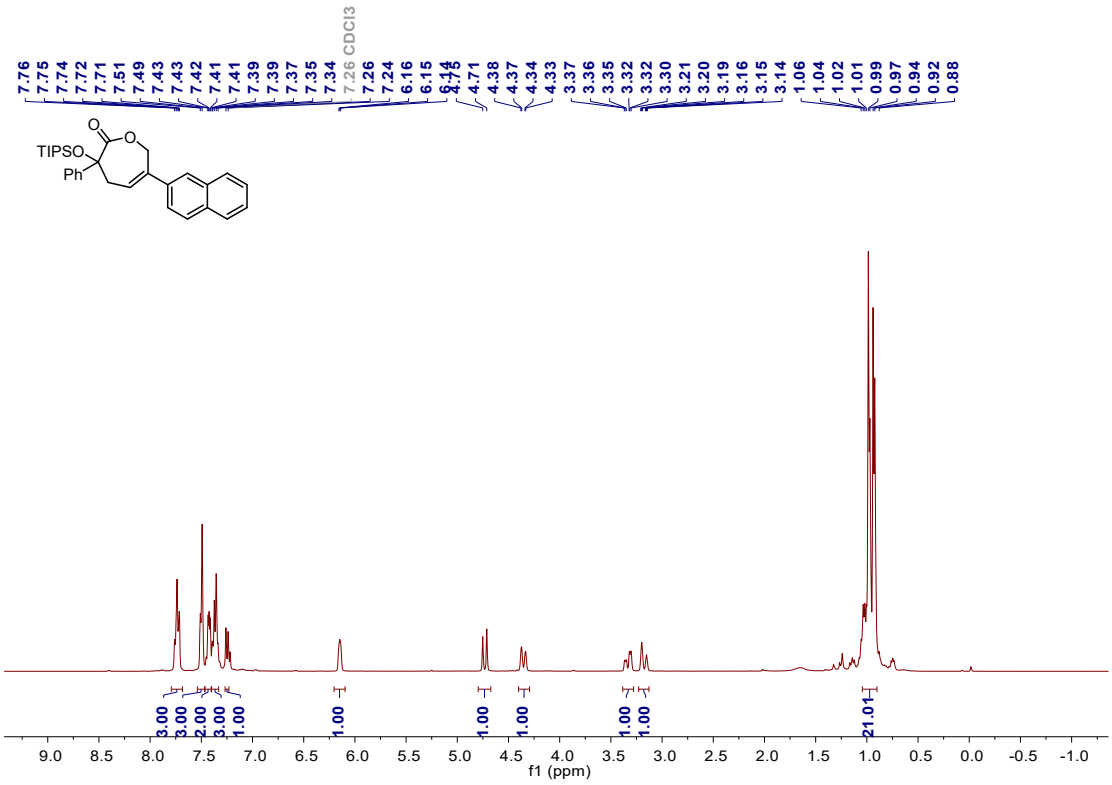
^{1}H NMR of **3ma** in $CDCl_3$ (400 MHz)



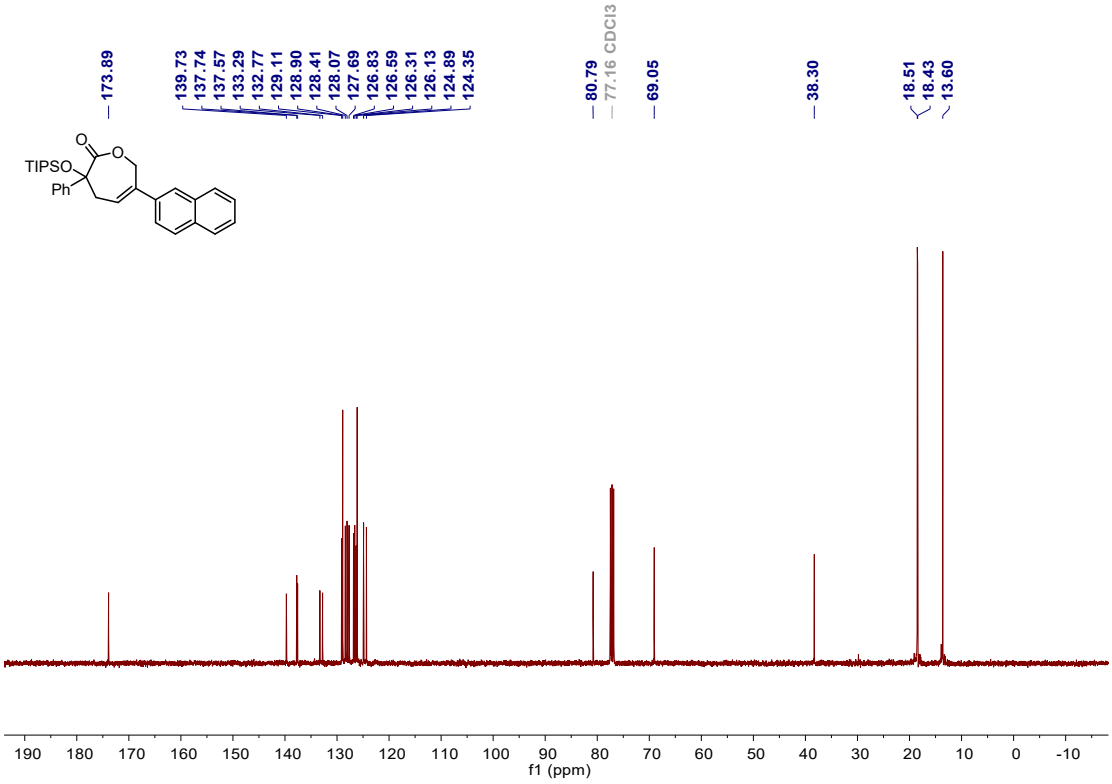
^{13}C NMR of **3ma** in $CDCl_3$ (101 MHz)



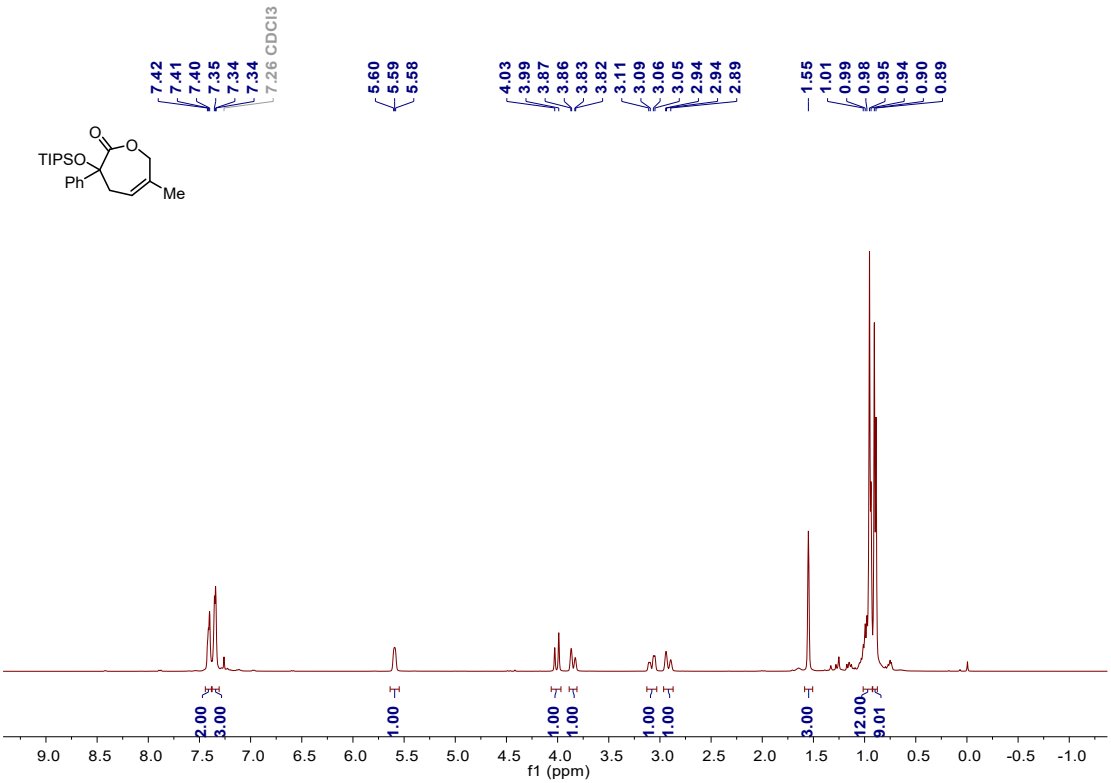
^{1}H NMR of **3na** in $CDCl_3$ (400 MHz)



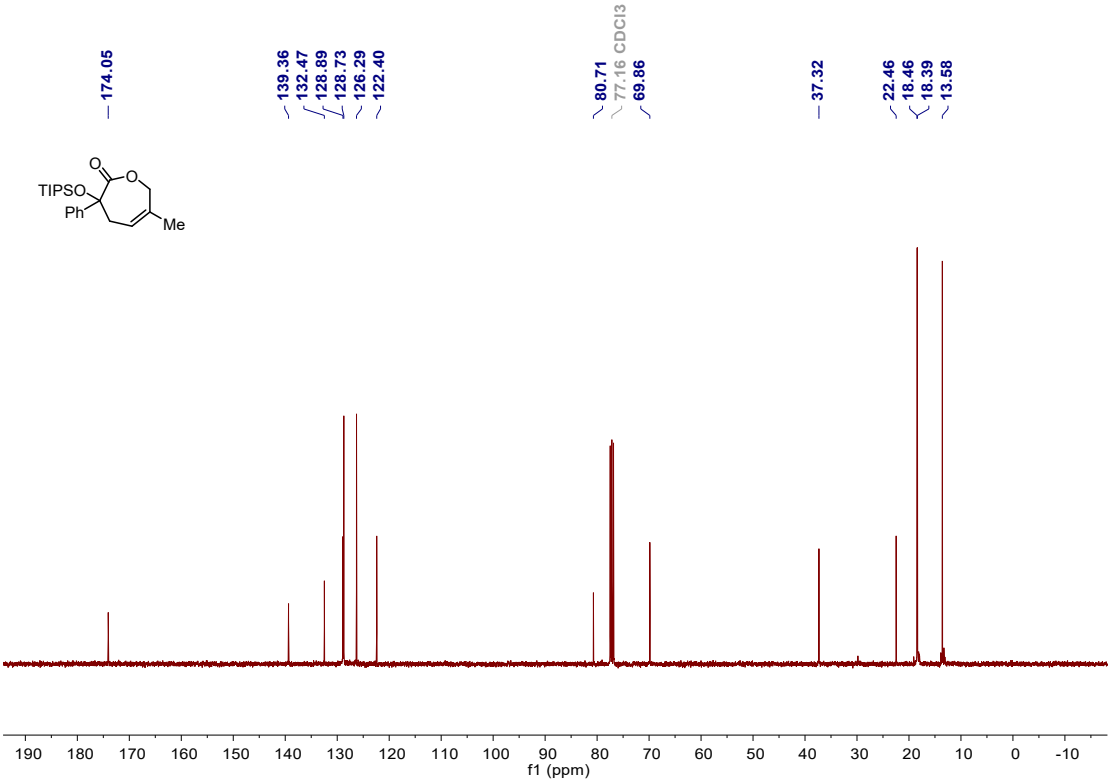
^{13}C NMR of **3na** in $CDCl_3$ (101 MHz)



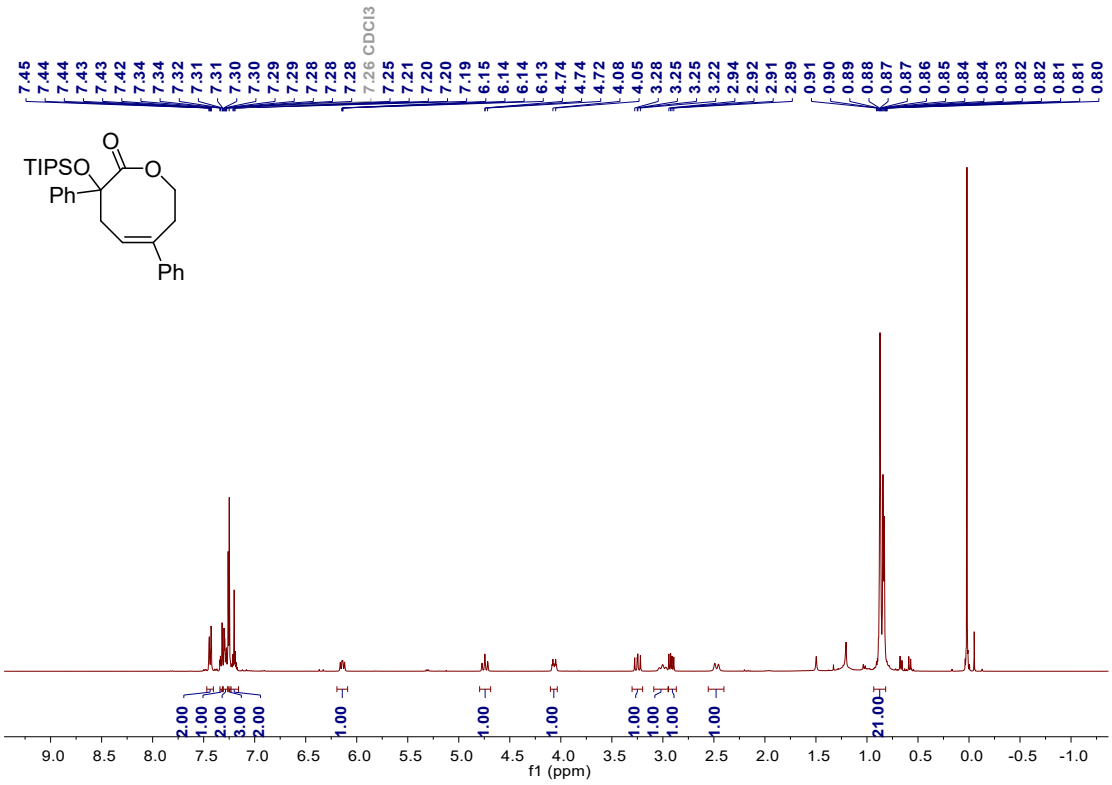
^{1}H NMR of **3oa** in $CDCl_3$ (400 MHz)



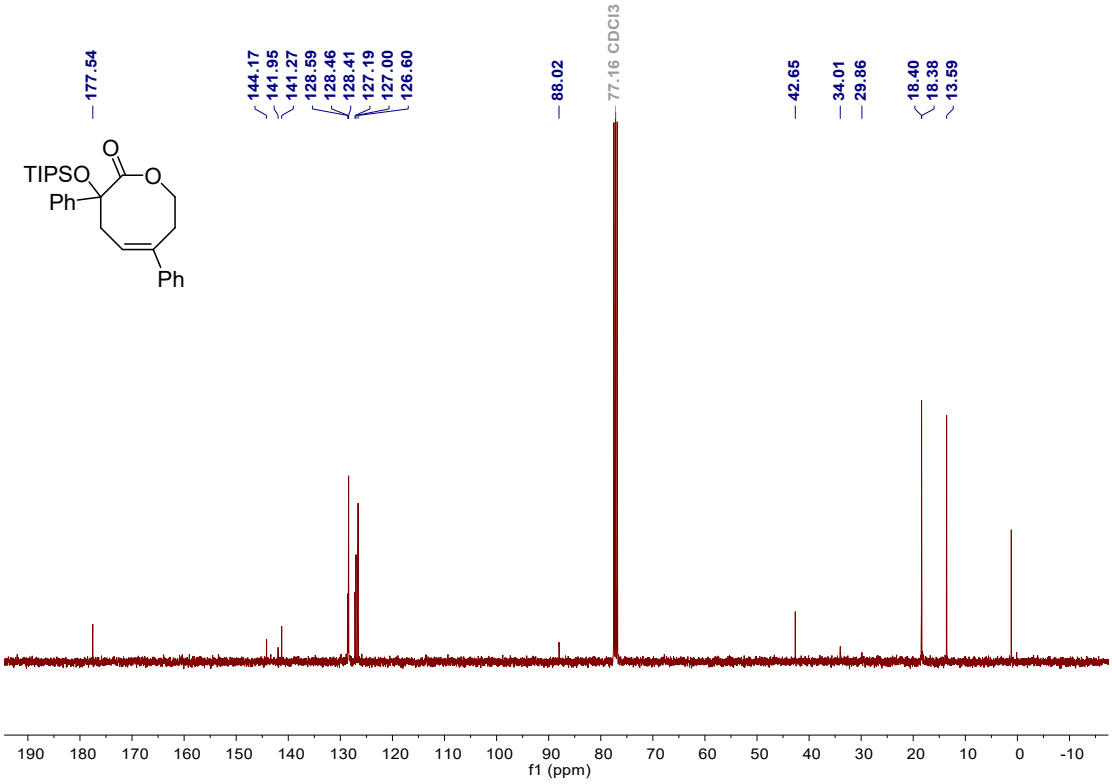
^{13}C NMR of **3oa** in $CDCl_3$ (101 MHz)



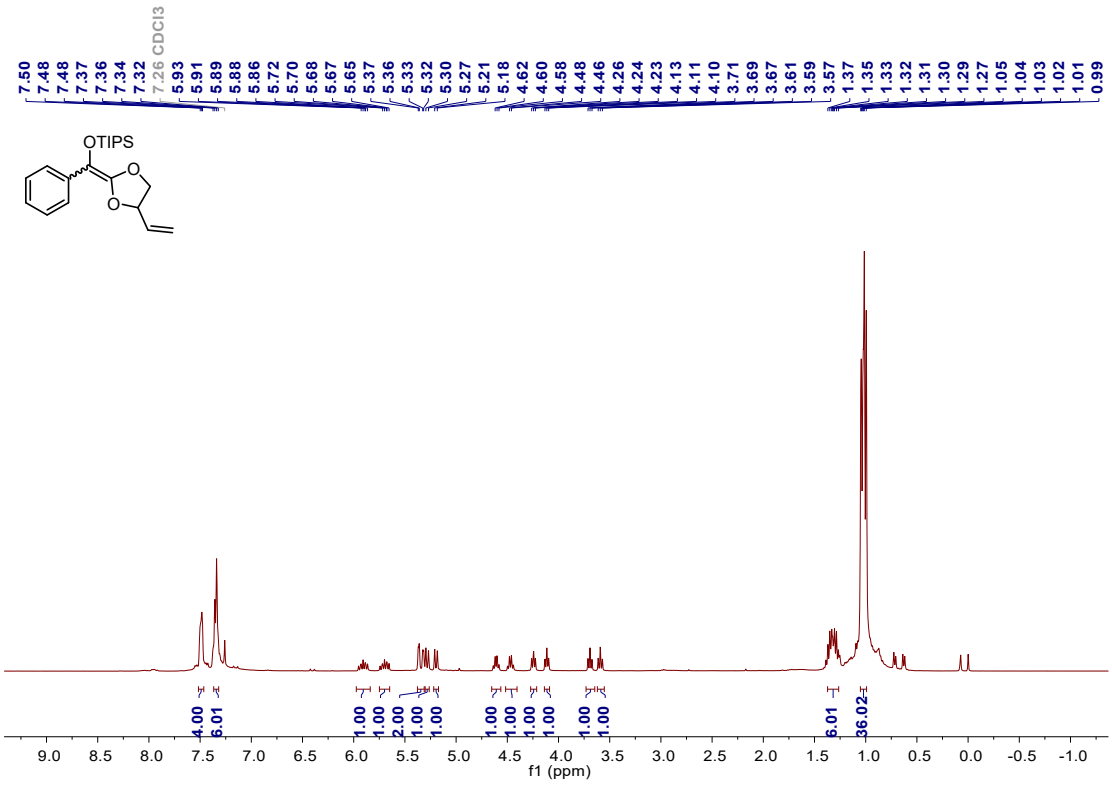
^{1}H NMR of **3pa** in $CDCl_3$ (400 MHz)



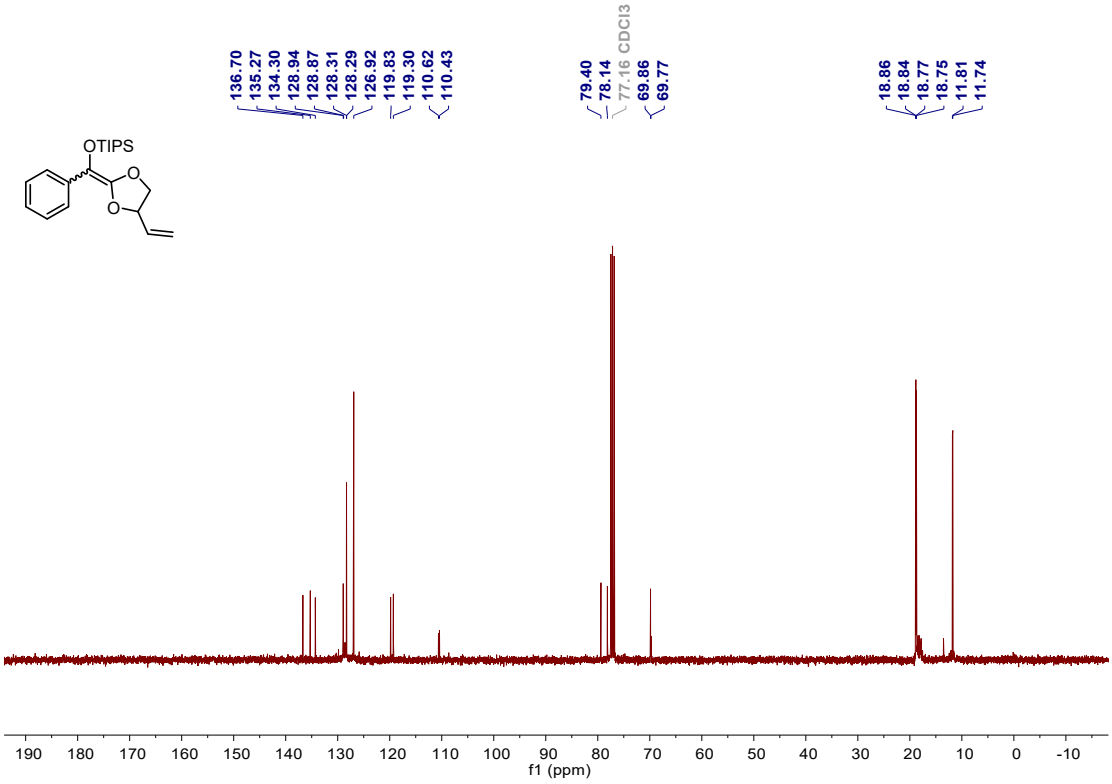
^{13}C NMR of **3pa** in $CDCl_3$ (101 MHz)



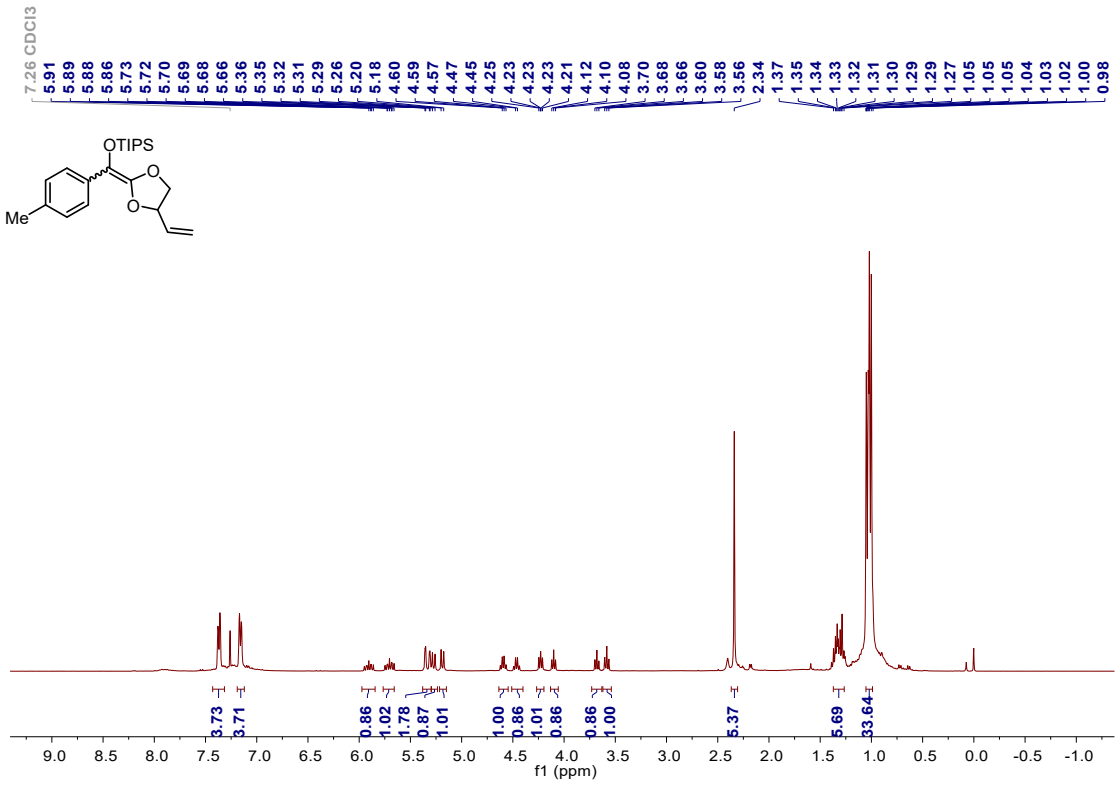
^{1}H NMR of **5a** in $CDCl_3$ (400 MHz)



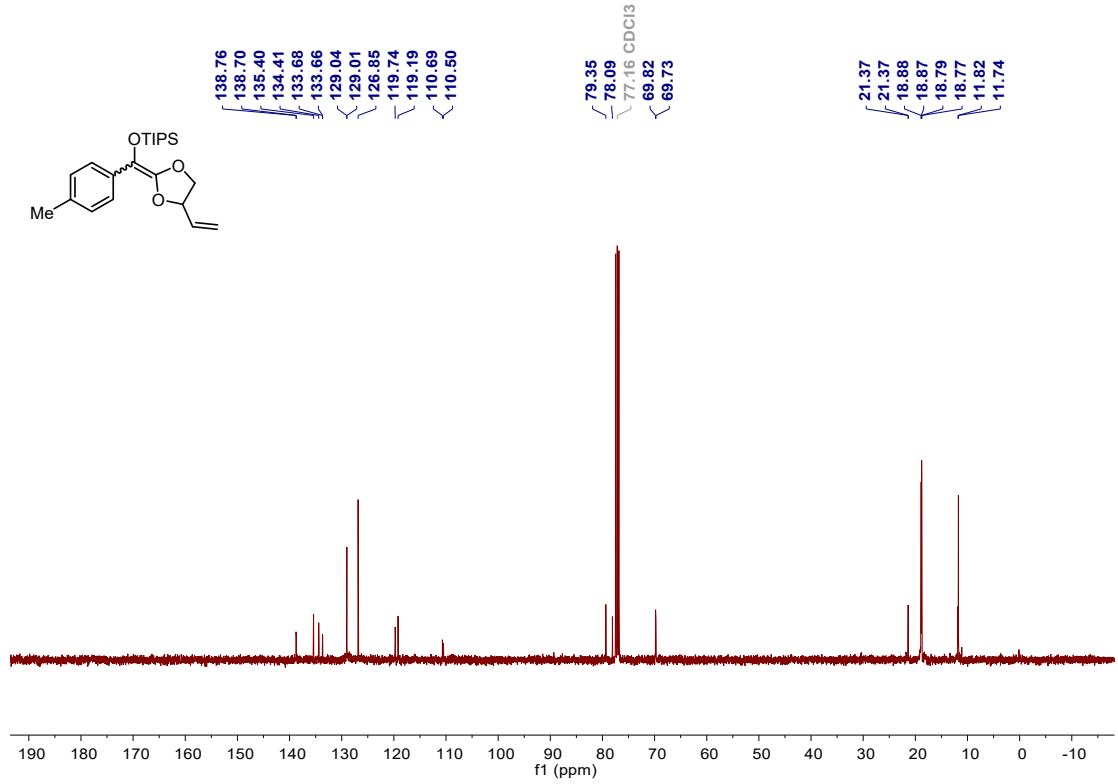
^{13}C NMR of **5a** in $CDCl_3$ (101 MHz)



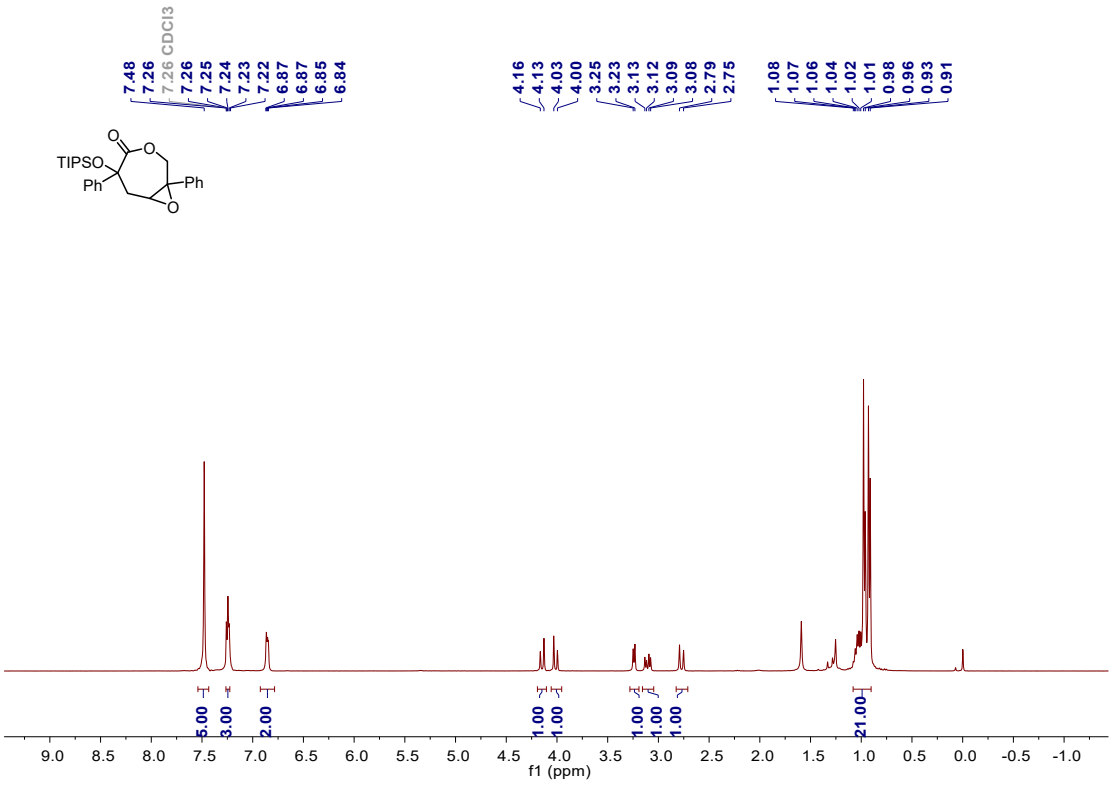
^{1}H NMR of **5b** in $CDCl_3$ (400 MHz)



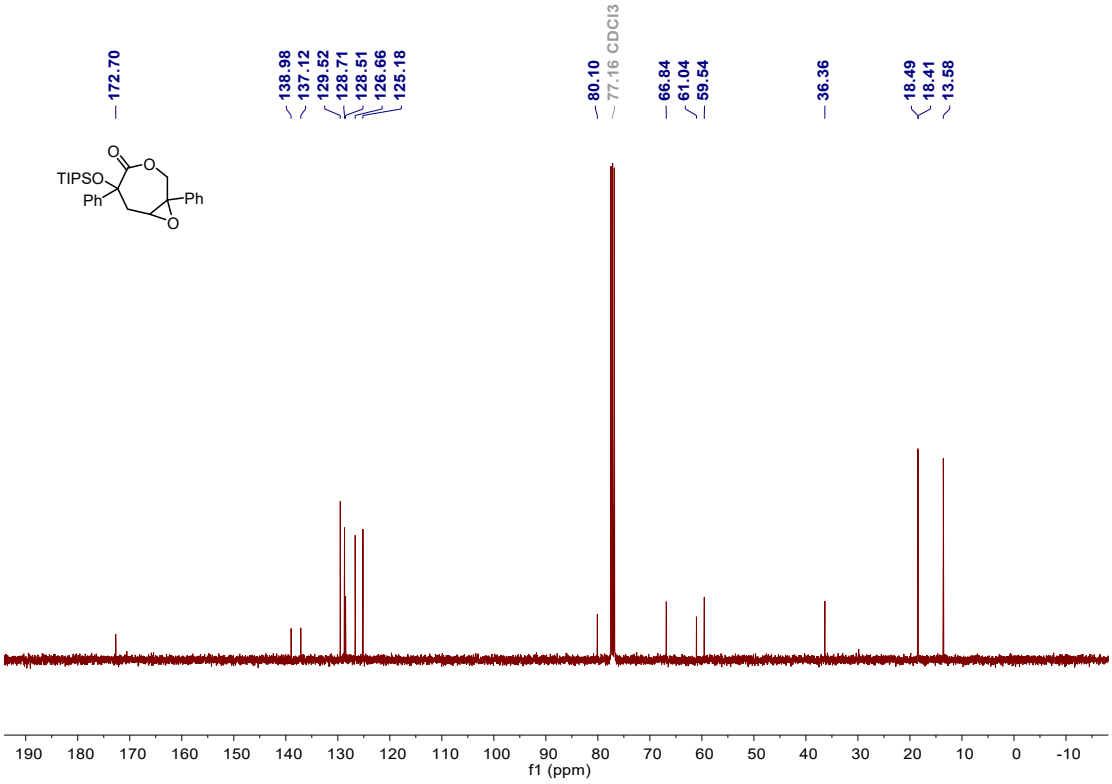
^{13}C NMR of **5b** in $CDCl_3$ (101 MHz)



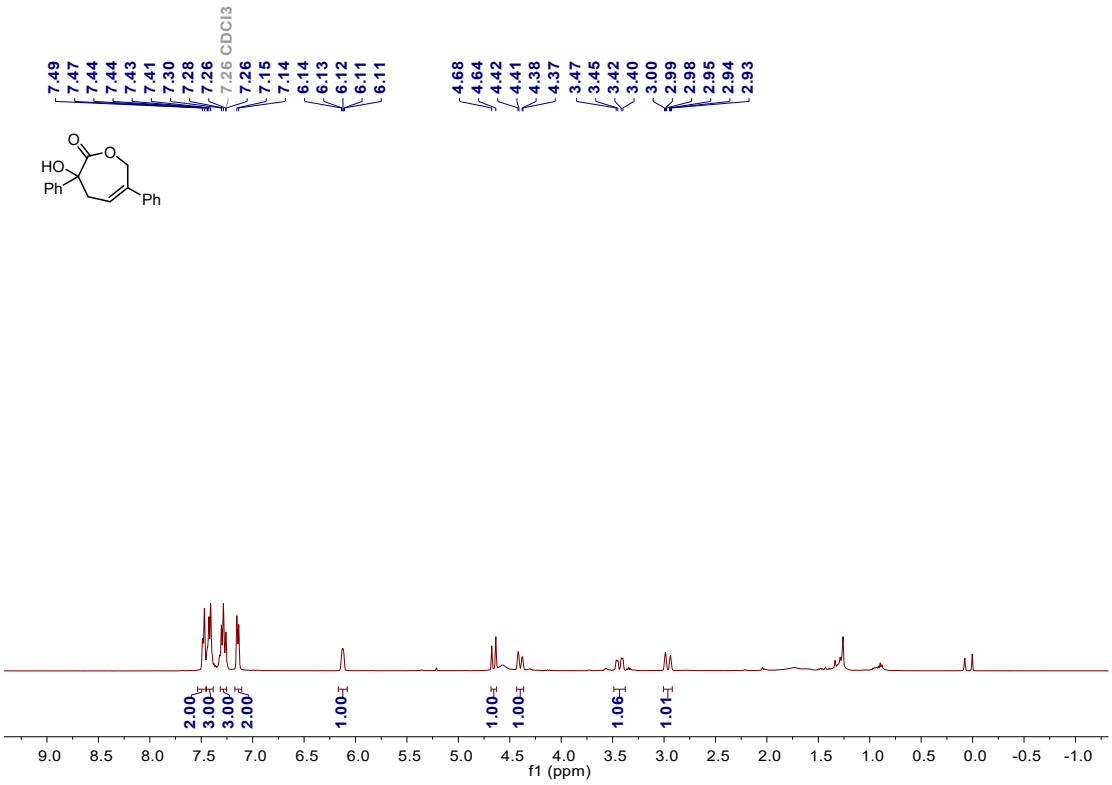
^{1}H NMR of **6** in $CDCl_3$ (400 MHz)



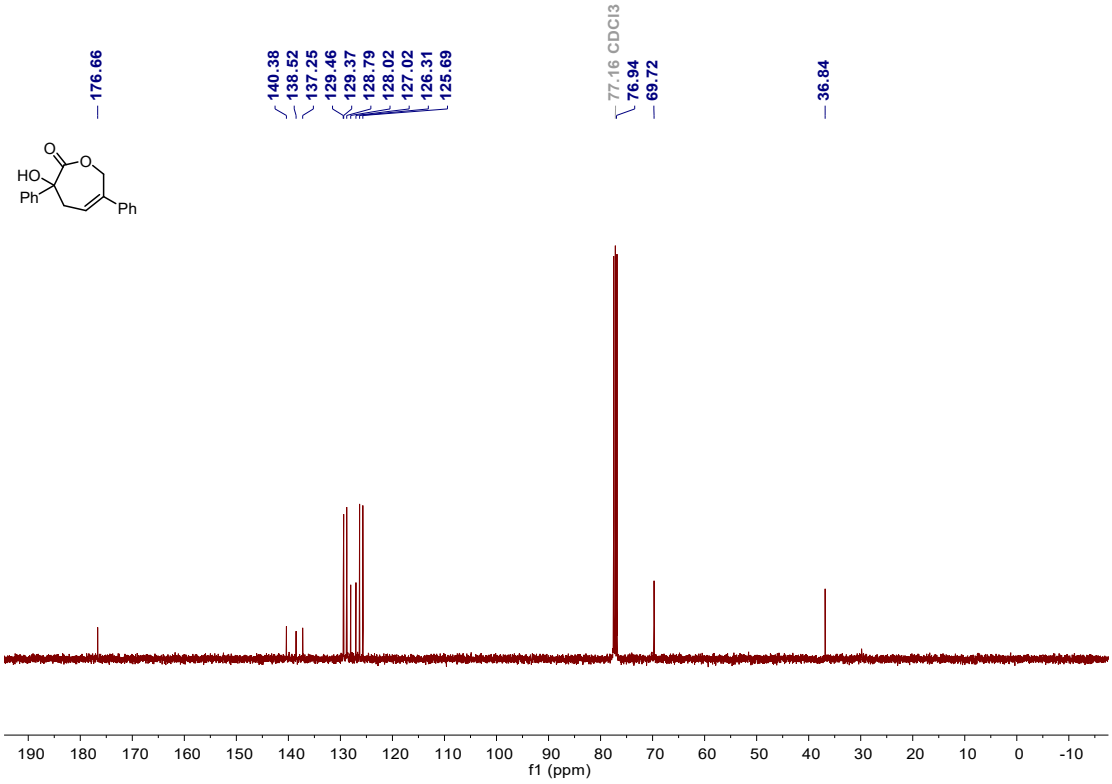
^{13}C NMR of **6** in $CDCl_3$ (101 MHz)



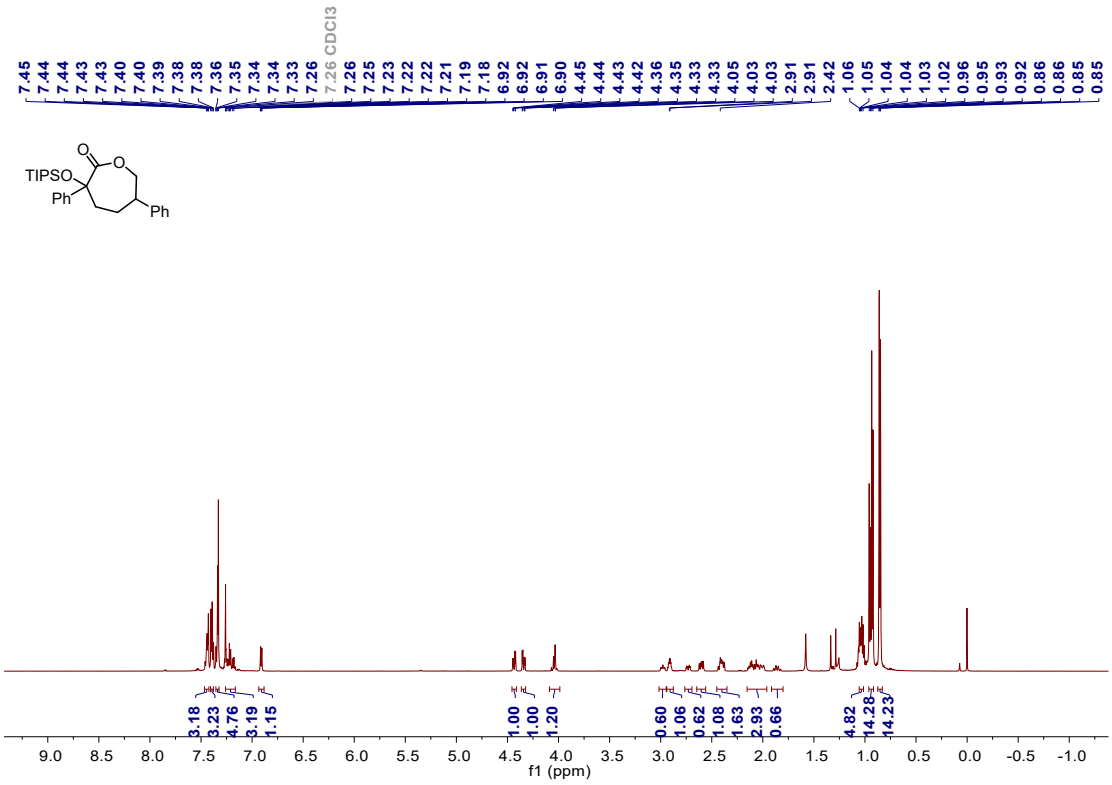
^{1}H NMR of **7** in $CDCl_3$ (400 MHz)



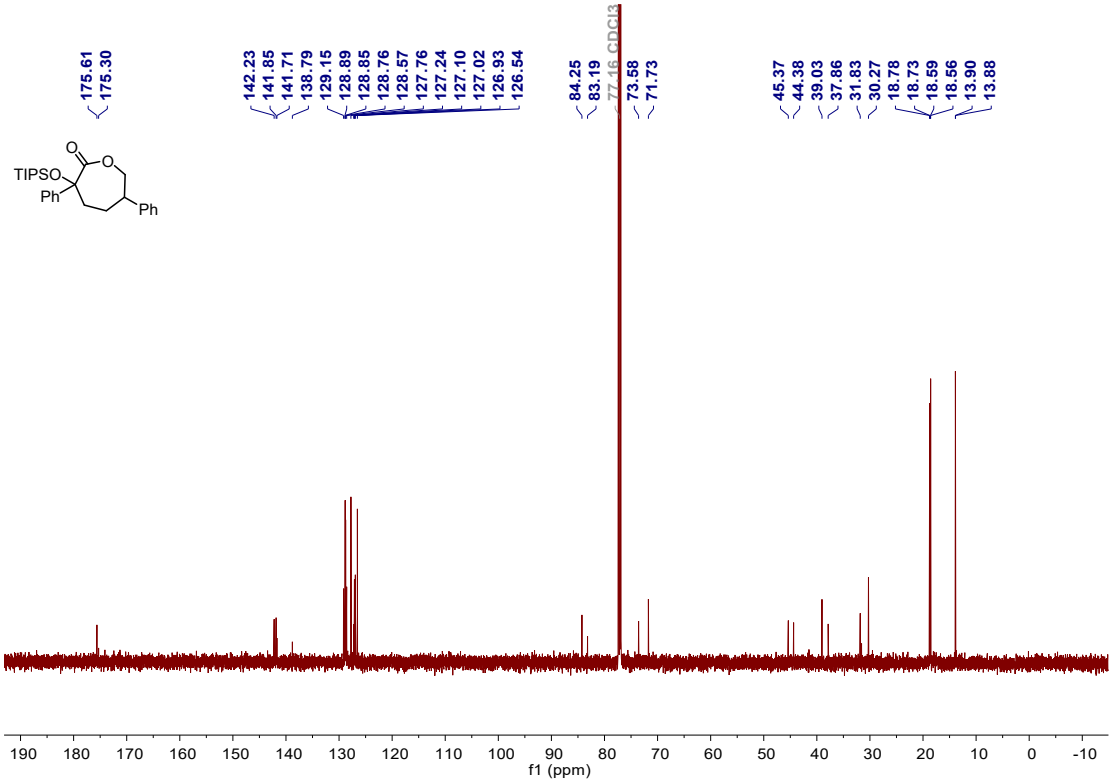
^{13}C NMR of **7** in $CDCl_3$ (101 MHz)



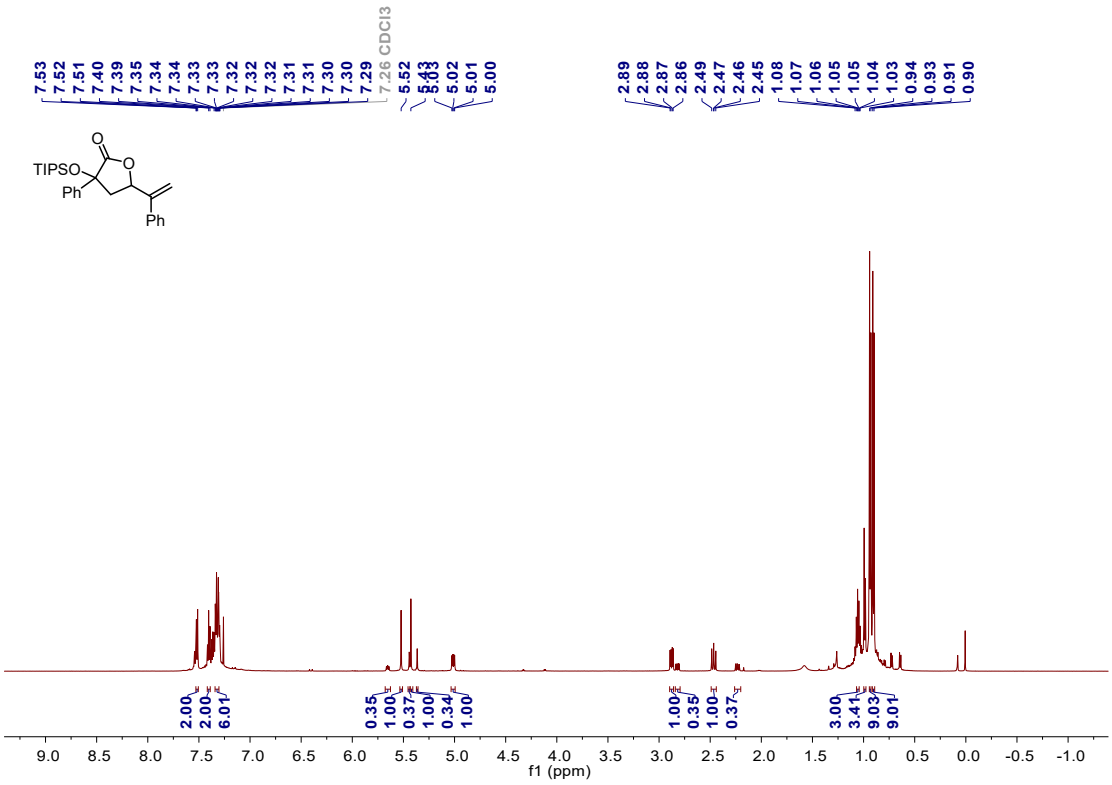
^{1}H NMR of **8** in $CDCl_3$ (600 MHz)



^{13}C NMR of **8** in $CDCl_3$ (151 MHz)



^{1}H NMR of **9** in $CDCl_3$ (400 MHz)



^{13}C NMR of **9** in $CDCl_3$ (101 MHz)