Supplementary Information for

Single-Step Assembly of Azabicyclo[3.3.0]octane Systems via Palladium-Photoredox Domino Cycloaddition/Transannular Cascades

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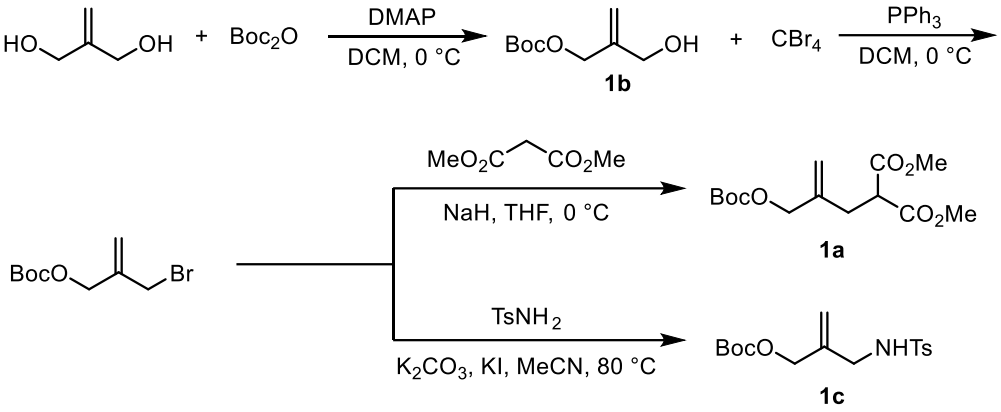
Contents

1. General information

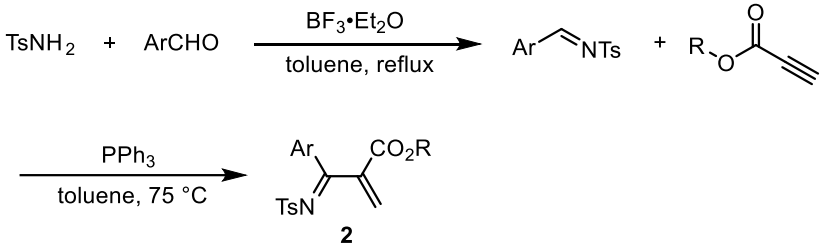
^{1}H NMR spectra were recorded on a Bruker DPX 400 MHz or 600 MHz spectrometer in $CDCl_3$. Chemical shifts were reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The spectra are interpreted as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, qt = quartet of triplet, 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. Melting points were obtained in open capillary tubes using SGW X-4 micro melting point apparatus which were uncorrected. High-resolution mass spectra (HRMS) were recorded on the Agilent 6500 Triple Quadrupole mass spectrometer using ESI (electrospray ionization). Anhydrous THF was distilled from calcium hydride. Anhydrous toluene was distilled from sodium/benzophenone. Other anhydrous solvents (<30 ppm water, *Karl-Fischer* titration) were purchased from J&K and stored over molecular sieves under an argon atmosphere. Ligands, photosensitizers and other ordinary organic reagents were purchased from Bide pharm and Leyan pharm. $Pd_2(dba)_3 \cdot CHCl_3$ was purchased from Laajoo. The photoreactors were manufactured by Beijing Roger Tech Ltd. The white 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.

2. Preparation of TMM-type 1,4-dipole precursor 1a-1c



Substrates **1a/1b/1c** were synthesized according to the literature procedure.[1, 2] Spectral data of compounds were in accordance with those reported in the literature.

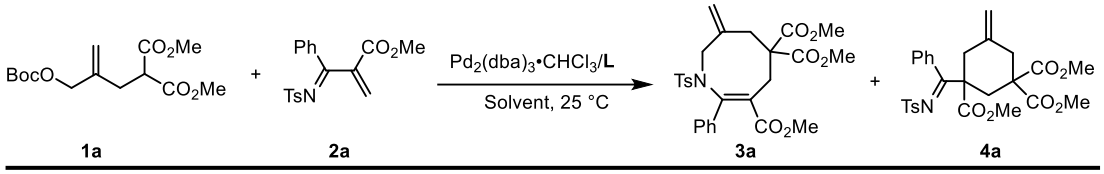
3. Preparation of azadiene 2



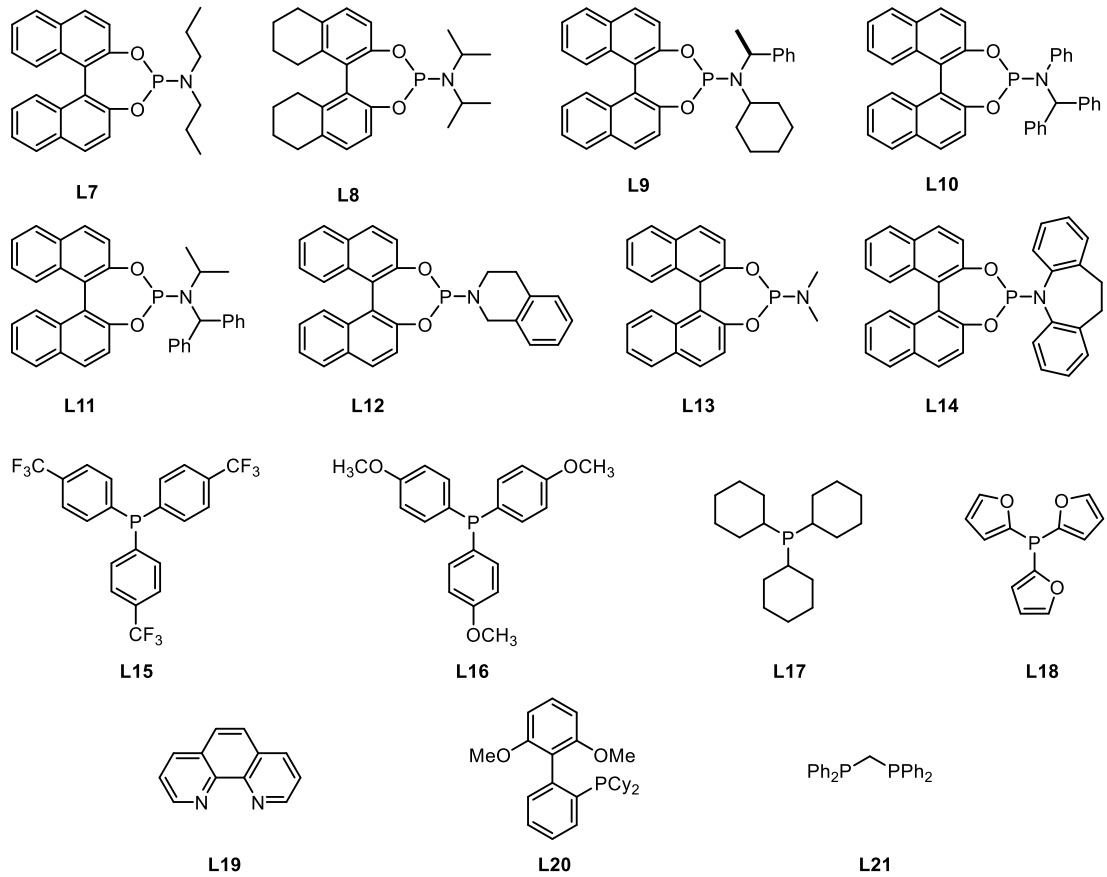
Substrates **2** were synthesized according to the literature procedure.[3] Spectral data of compounds were in accordance with those reported in the literature.

4. Optimization of reaction conditions

Table S1. Optimization of the reaction conditions for Pd-catalyzed [4+4] cycloaddition of TMM-type all-carbon-1,4-dipole precursor **1a** and azadiene **2a**.[a,b]



1a **2a** **3a** **4a**

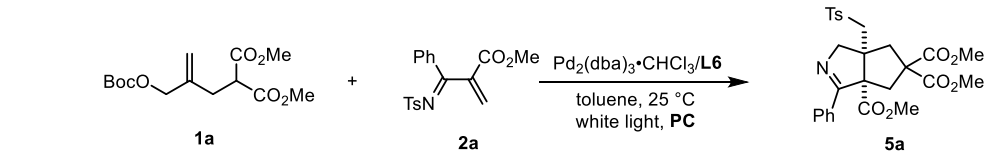


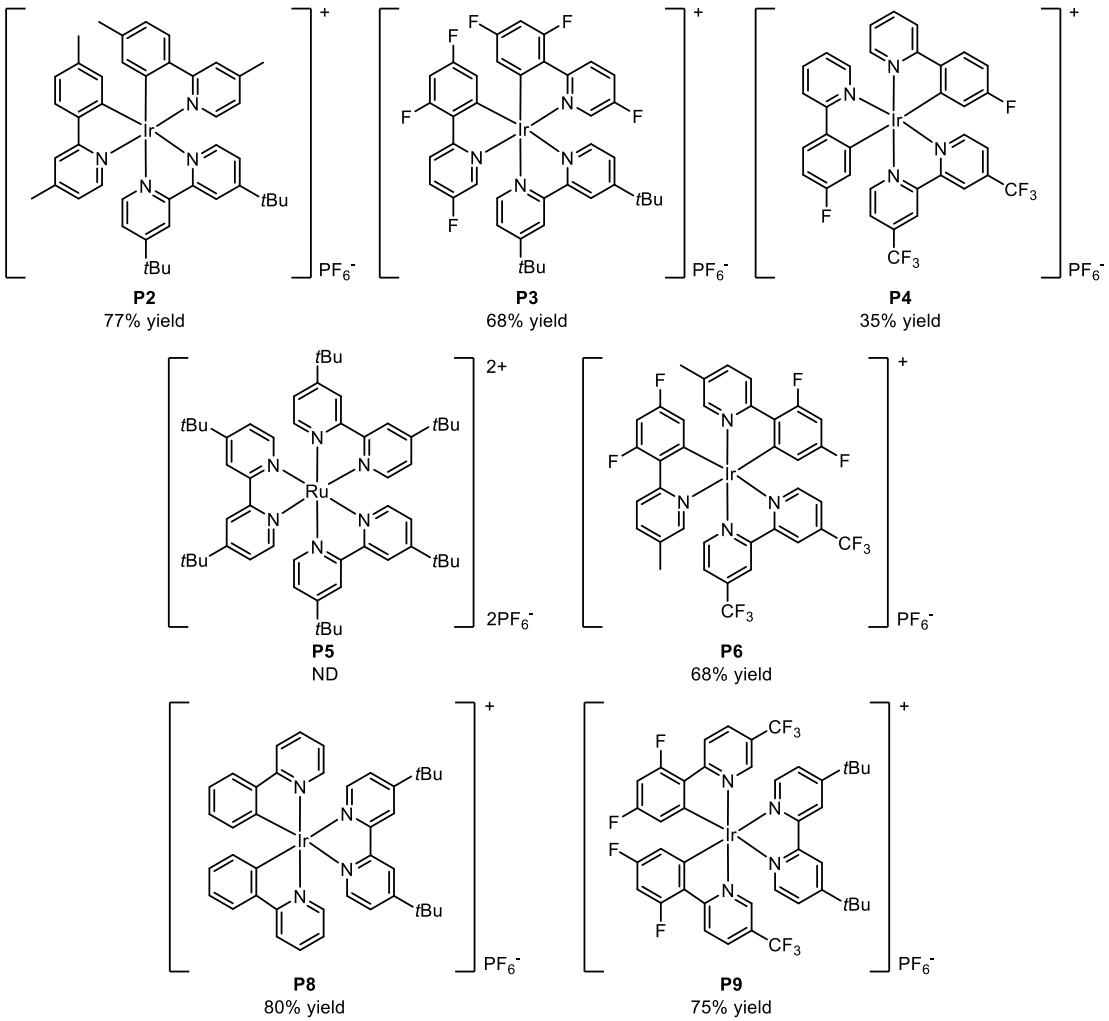
entry	**ligand**	solvent	**3a** yield (%)	**4a** yield (%)
1	**L7**	toluene	84	16
2	**L8**	toluene	63	27
3	**L9**	toluene	81	19
4	**L10**	toluene	ND	ND
5	**L11**	toluene	ND	ND
6	**L12**	toluene	ND	ND
7	**L13**	toluene	64	36
8	**L14**	toluene	5	95

9	**L15**	toluene	0	24
10	**L16**	toluene	0	12
11	**L17**	toluene	52	48
12	**L18**	toluene	55	20
13	**L19**	toluene	22	39
14	**L20**	toluene	16	20
15	**L21**	toluene	25	40
16	**L6**	1,4-Dioxane	25	40
17	**L6**	MTBE	92	8
18	**L6**	2-Me-THF	84	16
19	**L6**	Dibutyl ether	trace	trace
20	**L6**	Anisole	82	18
21	**L6**	Diethoxymethane	80	11
22	**L6**	Chlorobenzene	74	15
23	**L6**	CPME	80	10

[a] Reaction conditions: **1a** (0.12 mmol), **2a** (0.1 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (5 mol%) and **ligand** (11 mol%) in 1.0 mL of solvent under a N_2 atmosphere at 25 °C for 1 h. [b] Yield of **3a** and **4a** was determined by ^{1}H-NMR spectroscopic analysis of the crude product with 1,3,5-trimethoxybenzene as an internal standard.

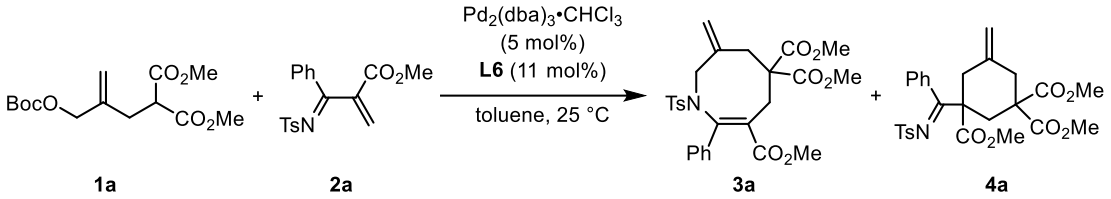
Table S2. Optimization of the reaction conditions for Pd-photoredox domino cycloaddition/transannular cascades of TMM-type all-carbon-1,4-dipole precursor **1a** and azadiene **2a**.[a,b]





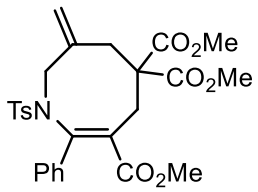
[a] Reaction conditions: **1a** (0.12 mmol), **2a** (0.1 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (5 mol%), ligand (11 mol%) and photosensitizer in 1.0 mL of solvent under a N_2 atmosphere at 25 °C for 48 h. [b] Yield of **5a** was determined by isolated yield

5. General procedure for the construction of azocane 3a and cyclohexane 4a

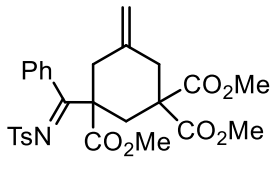


1a **2a** **3a** **4a**

General procedure: Under a nitrogen atmosphere, a flame-dried 10 mL Schlenk tube with a magnetic stir bar was charged with $Pd_2(dba)_3 \cdot CHCl_3$ (5.2 mg, 0.005 mmol, 5 mol%), **L6** (4.7 mg, 0.011 mmol, 11 mol%) and anhydrous toluene (1.0 mL). The reaction mixture was stirred for 30 min at 25 ℃. Then, TMM-type all-carbon-1,4-dipole precursor **1a** (36.3 mg, 0.12 mmol) and azadiene **2a** (34.3 mg, 0.1 mmol) were added sequentially at 25 ℃ for 1 h. Then, the reaction mixture was concentrated and the crude product was purified by column chromatography (petroleum ether/ethyl acetate = 4:1, v/v) to give the corresponding products **3a** and **4a**.

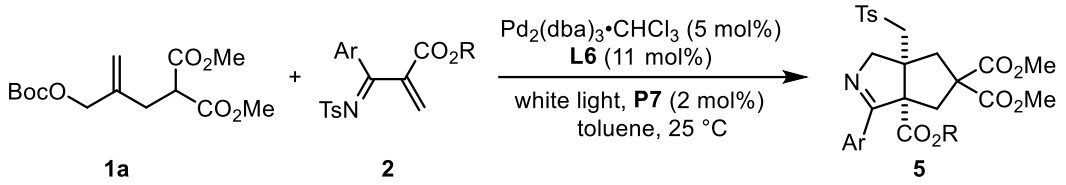


3a was obtained as white solid, 48.0 mg, 91% yield; m.p. = 120–121 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 1H), 7.14 – 7.05 (m, 4H), 7.04 – 6.95 (m, 4H), 5.25 (d, *J* = 1.2 Hz, 1H), 5.06 (d, *J* = 1.2 Hz, 1H), 4.70 – 3.99 (brs, 2H), 3.71 (s, 6H), 3.36 (s, 3H), 3.32 (s, 2H), 2.96 (s, 2H), 2.32 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7(2C), 169.4, 144.7, 143.0, 136.7, 136.67, 136.67 , 134.7, 129.1(2C), 128.7(2C), 128.5(2C), 127.9(2C), 127.1, 121.4, 59.9, 59.6, 52.7(2C), 51.6, 37.9, 34.5, 21.4; **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{29}NO_8SNa$ $[M+Na]^+$: 550.1506, found: 550.1504.



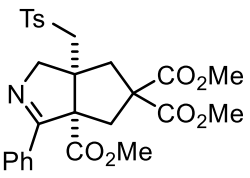
4a was obtained as white solid, 52.2 mg, 99% yield; m.p. = 100–100 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (m, 2H), 7.45 – 7.30 (m, 3H), 7.23 (m, 2H), 7.16 – 7.09 (m, 2H), 4.95 (s, 1H), 4.82 (s, 1H), 3.71 (s, 3H), 3.65 (s, 3H), 3.54 (s, 3H), 2.98 – 2.84 (m, 2H), 2.80 (d, *J* = 13.6 Hz, 1H), 2.58 (d, *J* = 14.9 Hz, 1H), 2.40 (s, 3H), 2.27 (t, *J* = 13.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.3, 171.6, 170.8, 170.6, 143.8, 138.2, 137.6, 134.2, 130.0, 129.4(2C), 127.9(2C), 127.4(2C), 126.6(2C), 114.9, 58.9, 54.2, 53.1, 52.6, 52.5, 39.4, 38.2, 34.4, 21.6; **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{29}NO_8SNa$ $[M+Na]^+$: 550.1506, found: 550.1507.

6. General procedure for the construction of azabicyclo[3.3.0]octanes 5

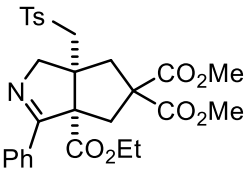


1a 2 5

General procedure: Under a nitrogen atmosphere, a flame-dried 10 mL Schlenk tube with a magnetic stir bar was charged with $Pd_2(dba)_3 \cdot CHCl_3$ (5.2 mg, 0.005 mmol, 5 mol%), **L6** (4.7 mg, 0.011 mmol, 11 mol%) and anhydrous toluene (1.0 mL). The reaction mixture was stirred for 30 min at 25 ℃. Then, TMM-type all-carbon-1,4-dipole precursor **1a** (36.3 mg, 0.12 mmol) , azadiene **2** (0.1 mmol) and photosensitizer **P7** (2.3 mg, 0.002 mmol, 2 mol%) were added under nitrogen atmosphere and stirred under 15W white light at 25 ℃ for 48 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) to give the corresponding product **5**.

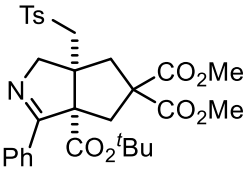


5a was obtained as white solid, 45.4 mg, 86% yield; m.p. = 195-196 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.75 (m, 2H), 7.65 – 7.56 (m, 2H), 7.45 – 7.31 (m, 5H), 4.38 (d, *J* = 17.7 Hz, 1H), 4.30 (d, *J* = 17.7 Hz, 1H), 3.72 (s, 3H), 3.64 (s, 3H), 3.39 – 3.36 (m, 4H), 3.27 (d, *J* = 14.5 Hz, 1H), 3.14 (d, *J* = 13.4 Hz, 1H), 2.97 (d, *J* = 14.7 Hz, 1H), 2.94 – 2.86 (m, 2H), 2.47 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.4, 171.3, 170.0, 169.4, 145.4, 137.7, 132.0, 130.7, 130.3(2C), 128.7(2C), 128.0(2C), 127.6(2C), 74.9, 71.9, 62.6, 60.2, 56.6, 53.4, 53.2, 52.7, 45.0, 38.8, 21.8; **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{29}NO_8SNa$ $[M+Na]^+$: 550.1506, found: 550.1503.

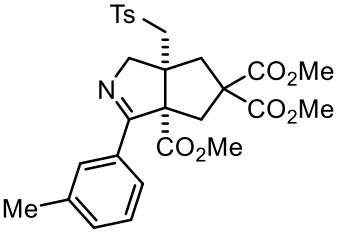


5b was obtained as white solid, 47.1 mg, 87% yield; m.p. = 176–177 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.73 (m, 2H), 7.62 – 7.47 (m, 2H), 7.45 – 7.22 (m, 5H), 4.31 (d, *J* = 17.6 Hz, 1H), 4.23 (d, *J* = 17.6 Hz, 1H), 4.06 (qt, *J* = 7.1, 3.5 Hz, 2H), 3.64 (s, 3H), 3.30 (d, *J* = 11.6 Hz, 4H), 3.19 (d, *J* = 14.4 Hz, 1H), 3.12 (d, *J* = 13.5 Hz, 1H), 2.90 (d, *J* = 14.7 Hz, 1H), 2.88 – 2.76 (m, 2H), 2.39 (s, 3H), 0.98 (t, *J* = 7.1 Hz, 3H).

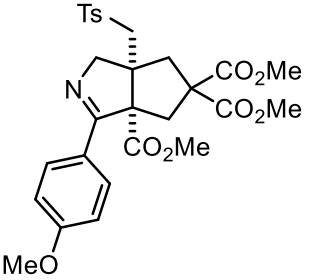
; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.4, 170.6, 170.1, 169.6, 145.3, 137.8, 132.0, 130.7, 130.2(2C), 128.6(2C), 127.9(2C), 127.7(2C), 74.9, 71.8, 62.6, 62.3, 60.2, 56.5, 53.3, 52.7, 45.0, 38.7, 21.8, 14.0; **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{31}NO_8SNa$ $[M+Na]^+$: 564.1663, found: 564.1659.



5c was obtained as white solid, 51.3 mg, 90% yield; m.p. = 187-188 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.73 (m, 2H), 7.63 – 7.53 (m, 2H), 7.39 – 7.24 (m, 5H), 4.29 (d, *J* = 17.4 Hz, 1H), 4.19 (d, *J* = 17.5 Hz, 1H), 3.64 (s, 3H), 3.31 (m, 4H), 3.23 (d, *J* = 13.5 Hz, 1H), 3.14 (d, *J* = 14.4 Hz, 1H), 2.92 (d, *J* = 14.7 Hz, 1H), 2.78 (m, 2H), 2.39 (s, 3H), 1.19 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.6, 170.3, 170.2, 169.5, 145.2, 138.0, 132.2, 130.6, 130.2(2C), 128.5(2C), 127.7(8)(2C), 127.7(7)(2C), 83.5, 75.7, 71.4, 62.6, 60.1, 56.5, 53.3, 52.7, 44.9, 38.6, 27.8(3C), 21.8; **HRMS** (ESI-TOF, m/z): calcd for $C_{30}H_{35}NO_8SNa$ $[M+Na]^+$: 592.1976, found: 592.1979.

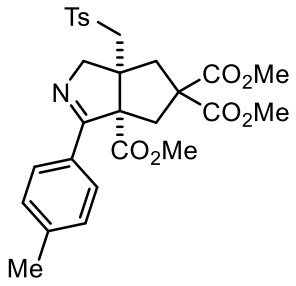


5d was obtained as white solid, 45.5 mg, 84% yield; m.p. = 200–201 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.67 (m, 2H), 7.44 (s, 1H), 7.33 – 7.30(m, 2H), 7.26 – 7.11 (m, 3H), 4.30 (d, *J* = 17.7 Hz, 1H), 4.21 (d, *J* = 17.7 Hz, 1H), 3.65 (s, 3H), 3.56 (s, 3H), 3.33 (s, 3H), 3.30 (d, *J* = 13.4 Hz, 1H), 3.20 (d, *J* = 14.4 Hz, 1H), 3.05 (d, *J* = 13.4 Hz, 1H), 2.90 (d, *J* = 14.6 Hz, 1H), 2.88 – 2.82 (m, 1H), 2.80 (d, *J* = 14.2 Hz, 1H), 2.40 (s, 3H), 2.27 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.4, 171.3, 170.0, 169.7, 145.4, 138.5, 137.7, 131.9, 131.6, 130.3(2C), 128.5, 128.3, 128.0(2C), 124.7, 74.9, 71.8, 62.6, 60.3, 56.6, 53.4, 53.1, 52.8, 45.0, 38.9, 21.8, 21.5; **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{31}NO_8SNa$ $[M+Na]^+$: 564.1663, found: 564.1664.

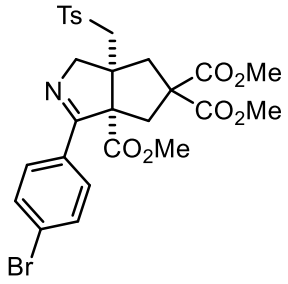


5e was obtained as white solid, 40.1 mg, 72% yield; m.p. = 199–200 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.55 – 7.45 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.84 – 6.73 (m, 2H), 4.25 (d, *J* = 17.5 Hz, 1H), 4.17 (d, *J* = 17.5 Hz, 1H), 3.75 (s, 3H), 3.65 (s, 3H), 3.56 (s, 3H), 3.34 (s, 3H), 3.29 (d, *J* = 13.4 Hz, 1H), 3.19 (d, *J* = 14.3 Hz, 1H), 3.07 (d, *J* = 13.5 Hz, 1H), 2.96 – 2.77 (m, 3H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.4(2C), 170.0, 168.8, 161.5, 145.3, 137.7, 130.3(2C), 129.3(2C), 128.0(2C), 124.7, 114.0(2C), 74.9, 71.8, 62.7, 60.2, 56.6, 55.4, 53.3, 53.1, 52.8, 45.0, 38.9, 21.8; **HRMS**

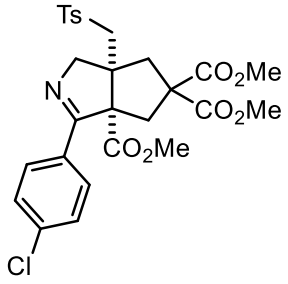
(ESI-TOF, m/z): calcd for $C_{28}H_{31}NO_9SNa$ $[M+Na]^+$: 580.1612, found: 580.1618.



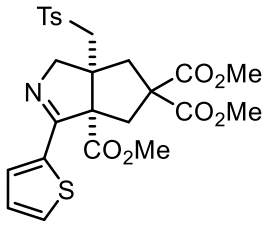
5f was obtained as white solid, 43.3 mg, 80% yield; m.p. = 207–208 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 4.27 (d, *J* = 17.6 Hz, 1H), 4.20 (d, *J* = 17.7 Hz, 1H), 3.64 (s, 3H), 3.55 (s, 3H), 3.33 (s, 3H), 3.29 (d, *J* = 13.4 Hz, 1H), 3.19 (d, *J* = 14.4 Hz, 1H), 3.06 (d, *J* = 13.5 Hz, 1H), 2.89 (d, *J* = 14.7 Hz, 1H), 2.82 (dd, *J* = 17.1, 14.6 Hz, 2H), 2.39 (s, 3H), 2.28 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.4, 171.3, 170.0, 169.4, 145.3, 141.0, 137.8, 130.2(2C), 129.4(2C), 129.2, 128.0(2C), 127.6(2C), 74.9, 71.9, 62.7, 60.2, 56.6, 53.3, 53.1, 52.7, 45.0, 38.9, 21.8, 21.5; **HRMS** (ESI-TOF, m/z): calcd for $C_{28}H_{31}NO_8SNa$ $[M+Na]^+$: 564.1663, found: 564.1664.



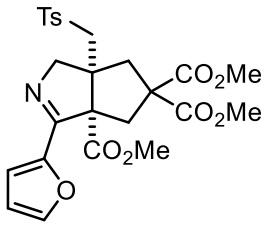
5g was obtained as white solid, 50.9 mg, 84% yield; m.p. = 189–190 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.73 (m, 2H), 7.57 – 7.46 (m, 4H), 7.43 – 7.34 (m, 2H), 4.37 (d, *J* = 17.9 Hz, 1H), 4.31 (d, *J* = 17.9 Hz, 1H), 3.72 (s, 3H), 3.64 (s, 3H), 3.44 (s, 3H), 3.36 (d, *J* = 13.4 Hz, 1H), 3.23 (d, *J* = 14.4 Hz, 1H), 3.12 (d, *J* = 13.4 Hz, 1H), 2.96 (d, *J* = 14.7 Hz, 1H), 2.88 (d, *J* = 14.7 Hz, 2H), 2.47 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.2, 171.1, 170.0, 168.6, 145.4, 137.8, 132.0(2C), 131.0, 130.3(2C), 129.1(2C), 128.0(2C), 125.4, 74.8, 72.0, 62.6, 60.3, 56.8, 53.4, 53.2, 52.8, 45.1, 38.8, 21.8; **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{28}BrNO_8SNa$ $[M+Na]^+$: 628.0611, found: 628.0618.



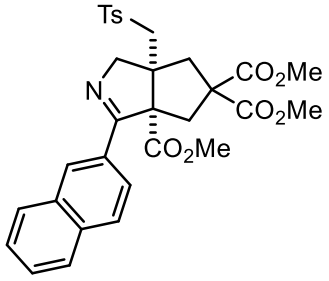
5h was obtained as white solid, 47.2 mg, 84% yield; m.p. = 187–188 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.65 (m, 2H), 7.54 – 7.43 (m, 2H), 7.41 – 7.22 (m, 4H), 4.31 (d, *J* = 17.9 Hz, 1H), 4.24 (d, *J* = 17.9 Hz, 1H), 3.65 (s, 3H), 3.56 (s, 3H), 3.36 (s, 3H), 3.29 (d, *J* = 13.4 Hz, 1H), 3.17 (d, *J* = 14.4 Hz, 1H), 3.05 (d, *J* = 13.3 Hz, 1H), 2.90 (d, *J* = 14.8 Hz, 1H), 2.80 (d, *J* = 14.6 Hz, 2H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 171.1, 170.0, 168.5, 145.4, 137.7, 136.9, 130.5, 130.3(2C), 129.0(2C), 128.9(2C), 128.0(2C), 74.8, 71.9, 62.6, 60.2, 56.8, 53.4, 53.2, 52.8, 45.1, 38.8, 21.8; **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{28}ClNO_8SNa$ $[M+Na]^+$: 584.1116, found: 584.1117.



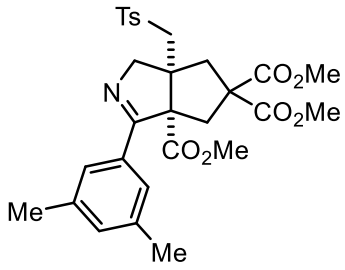
5i was obtained as white solid, 44.8 mg, 84% yield; m.p. = 224–225 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.72 (m, 2H), 7.46 – 7.32 (m, 3H), 7.15 – 7.07 (m, 1H), 7.06 – 6.98 (m, 1H), 4.31 (d, *J* = 17.7 Hz, 1H), 4.23 (d, *J* = 17.8 Hz, 1H), 3.73 (s, 3H), 3.65 (s, 3H), 3.48 (s, 3H), 3.35 (d, *J* = 13.5 Hz, 1H), 3.25 (d, *J* = 3.1 Hz, 1H), 3.22 (d, *J* = 2.3 Hz, 1H), 3.05 (d, *J* = 14.4 Hz, 1H), 2.93 (s, 2H), 2.47 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 170.7, 169.8, 164.5, 145.4, 137.6, 137.2, 130.3(2C), 129.6, 128.0(2C), 127.9, 127.7, 75.3, 72.5, 62.8, 60.2, 56.6, 53.4, 53.2, 52.9, 45.2, 39.0, 21.8; **HRMS** (ESI-TOF, m/z): calcd for $C_{25}H_{27}NO_8S_2Na$ $[M+Na]^+$: 556.1070, found: 556.1070.



5j was obtained as white solid, 41.4 mg, 80% yield; m.p. = 190–191 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.56 (m, 2H), 7.56 – 7.25 (m, 3H), 6.91 – 6.68 (m, 1H), 6.53 – 6.25 (m, 1H), 4.31 (d, *J* = 17.8 Hz, 1H), 4.25 (d, *J* = 17.8 Hz, 1H), 3.65 (s, 3H), 3.56 (s, 3H), 3.43 (s, 3H), 3.28 (d, *J* = 13.4 Hz, 1H), 3.10 (d, *J* = 5.1 Hz, 1H), 3.06 (d, *J* = 6.0 Hz, 1H), 2.96 (d, *J* = 14.5 Hz, 1H), 2.87 (d, *J* = 14.6 Hz, 1H), 2.80 (d, *J* = 14.5 Hz, 1H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 170.4, 169.9, 161.2, 148.5, 145.4, 144.6, 137.7, 130.3(2C), 128.0(2C), 112.6, 111.9, 75.1, 73.0, 63.0, 60.2, 55.7, 53.4, 53.1, 52.8, 45.5, 39.1, 21.8; **HRMS** (ESI-TOF, m/z): calcd for $C_{25}H_{27}NO_9SNa$ $[M+Na]^+$: 540.1299, found: 540.1306.

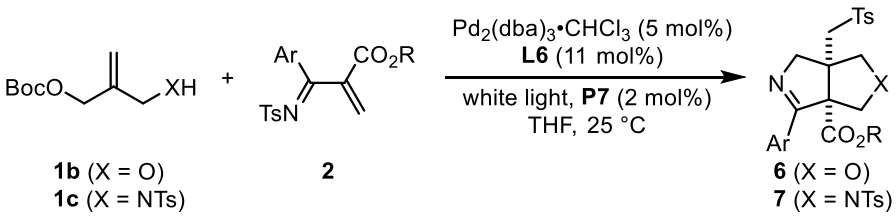


5k was obtained as white solid, 60.0 mg, 90% yield; m.p. = 203–204 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 – 7.72 (m, 7H), 7.60 – 7.31 (m, 4H), 4.44 (d, *J* = 17.8 Hz, 1H), 4.36 (d, *J* = 17.7 Hz, 1H), 3.72 (s, 3H), 3.64 (s, 3H), 3.52 – 3.29 (m, 5H), 3.19 (d, *J* = 13.5 Hz, 1H), 3.05 (d, *J* = 15.4 Hz, 1H), 2.98 (s, 1H), 2.93 (d, *J* = 14.7 Hz, 1H), 2.47 (s, 3H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.4, 171.3, 170.0, 169.4, 145.4, 137.7, 134.3, 132.8, 130.3(2C), 129.5, 129.0, 128.6, 128.0(2C), 127.8, 127.7, 127.6, 126.7, 124.8, 75.0, 72.1, 62.7, 60.3, 56.7, 53.4, 53.2, 52.8, 45.1, 39.0, 21.8. ; **HRMS** (ESI-TOF, m/z): calcd for $C_{31}H_{31}NO_8SNa$ $[M+Na]^+$: 600.1663, found: 600.1666.



5l was obtained as white solid, 46.7 mg, 84% yield; m.p. = 165–166 ℃; **^{1}H NMR**, $CDCl_3$) δ 7.89 – 7.62 (m, 2H), 7.45 – 7.26 (m, 2H), 7.13 (s, 2H), 6.97 (s, 1H), 4.28 (d, *J* = 17.6 Hz, 1H), 4.20 (d, *J* = 17.6 Hz, 1H), 3.65 (s, 3H), 3.56 (s, 3H), 3.34 (s, 3H), 3.30 (d, *J* = 13.4 Hz, 1H), 3.21 (d, *J* = 14.4 Hz, 1H), 3.05 (d, *J* = 13.4 Hz, 1H), 2.91 (d, *J* = 14.7 Hz, 1H), 2.84 (d, *J* = 14.5 Hz, 1H), 2.79 (d, *J* = 14.7 Hz, 1H), 2.39 (s, 3H), 2.22 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.4, 171.3, 170.0, 169.8, 145.3, 138.2(2C), 137.7, 132.5, 131.8, 130.2(2C), 128.0(2C), 125.4(2C), 74.9, 71.7, 62.5, 60.3, 56.6, 53.3, 53.1, 52.7, 44.9, 38.9, 21.8, 21.4(2C); **HRMS** (ESI-TOF, m/z): calcd for $C_{29}H_{33}NO_8SNa$ $[M+Na]^+$: 578.1819, found: 578.1823.

7. General procedure for construction of oxazabicyclo[3.3.0]octane 6 and diazabicyclo[3.3.0]octane 7

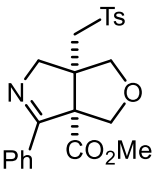


1b (X = O)
1c (X = NTs)

2

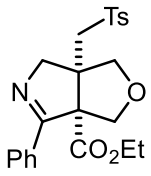
6 (X = O)
7 (X = NTs)

General procedure: Under a nitrogen atmosphere, a flame-dried 10 mL Schlenk tube with a magnetic stir bar was charged with $Pd_2(dba)_3{\cdot}CHCl_3$ (5.2 mg, 0.005 mmol, 5 mol%), **L6** (4.7 mg, 0.011 mmol, 11 mol%) and anhydrousTHF (1.0 mL). The reaction mixture was stirred for 30 min at 25 ℃. Then, TMM-type oxa/aza-1,4-dipole precursor **1b**/**1c** (22.6/41 mg, 0.12 mmol) , azadiene **2** (0.1 mmol) and photosensitizer **P7** (2.3 mg, 0.002 mmol, 2 mol%) were added under nitrogen atmosphere and stirred under 15W white light at 25 ℃ for 24 h. The reaction mixture was concentrated and purified by column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) to give the corresponding product **6**/**7**.

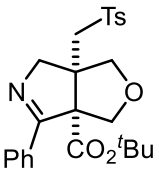


6a was obtained as white solid, 38.0 mg, 92% yield; m.p. = 140–141 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 – 7.72 (m, 2H), 7.67 – 7.54 (m, 2H), 7.53 – 7.28 (m, 5H), 4.58 (d, *J* = 9.6 Hz, 1H), 4.44 (d, *J* = 17.7 Hz, 1H), 4.37 (d, *J* = 5.0 Hz, 1H), 4.34 (d, *J* = 12.9 Hz, 1H), 4.03 (d, *J* = 9.5 Hz, 1H), 3.82 (d, *J* = 9.8 Hz, 1H), 3.65 (s, 3H), 3.40 (d, *J* = 13.6 Hz, 1H), 3.21 (d, *J* = 13.5

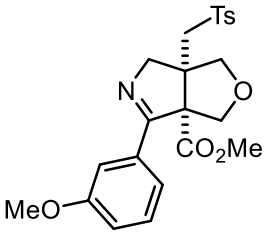
Hz, 1H), 2.47 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.9, 169.3, 145.5, 137.5, 131.7, 131.0, 130.3(2C), 128.8(2C), 127.8(2C), 127.7(2C), 75.8, 73.2, 68.2, 62.3, 59.9, 58.6, 21.8, 14.0; **HRMS** (ESI-TOF, m/z): calcd for $C_{22}H_{23}NO_5SNa$ $[M+Na]^+$: 436.1189, found: 436.1186.



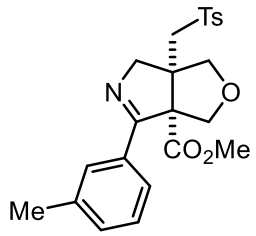
6b was obtained as white solid, 41.0mg, 96% yield; m.p. = 100–100 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.73 (m, 2H), 7.66 – 7.55 (m, 2H), 7.49 – 7.33 (m, 5H), 4.58 (d, *J* = 9.5 Hz, 1H), 4.43 (d, *J* = 17.7 Hz, 1H), 4.36 (s, 1H), 4.34 (d, *J* = 14.7 Hz, 1H), 4.15 (d, *J* = 7.1 Hz, 1H), 4.11 (d, *J* = 7.1 Hz, 1H), 4.04 (d, *J* = 9.5 Hz, 1H), 3.81 (d, *J* = 9.8 Hz, 1H), 3.40 (d, *J* = 13.6 Hz, 1H), 3.31 – 3.17 (m, 1H), 2.46 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.9, 169.3, 145.5, 137.5, 131.7, 131.0, 130.3(2C), 128.8(2C), 127.8(2C), 127.7(2C), 77.8, 75.8, 73.2, 68.2, 62.3, 59.9, 58.6, 21.8, 14.0; **HRMS** (ESI-TOF, m/z): calcd for $C_{23}H_{25}NO_6SNa$ $[M+Na]^+$: 450.1346, found: 450.1346.



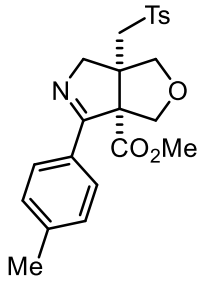
6c was obtained as white solid, 40.5mg, 89% yield; m.p. = 142–143 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 – 7.68 (m, 2H), 7.59 – 7.51 (m, 2H), 7.37 – 7.27 (m, 5H), 4.47 (d, *J* = 9.4 Hz, 1H), 4.36 – 4.20 (m, 3H), 3.92 (d, *J* = 9.4 Hz, 1H), 3.69 (d, *J* = 9.7 Hz, 1H), 3.36 (d, *J* = 13.6 Hz, 1H), 3.28 (d, *J* = 13.6 Hz, 1H), 2.39 (s, 3H), 1.18 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.8, 168.9, 145.4, 137.7, 131.9, 130.9, 130.3(2C), 128.7(2C), 127.8(2C), 127.7(2C), 83.6, 76.5, 73.0, 67.7, 60.0, 58.5, 27.9, 27.8, 21.8; **HRMS** (ESI-TOF, m/z): calcd for $C_{25}H_{29}NO_5SNa$ $[M+Na]^+$: 478.1659, found: 478.1670.



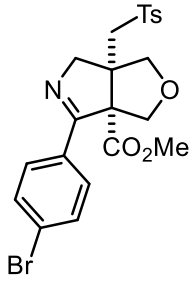
6d was obtained as white solid, 40.8 mg, 92 yield; m.p. = 148–149 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.62 (m, 2H), 7.36 – 7.28 (m, 2H), 7.28 – 7.23 (m, 1H), 7.22 – 7.16 (m, 1H), 6.94 – 6.85 (m, 2H), 4.50 (d, *J* = 9.5 Hz, 1H), 4.35 (d, *J* = 17.8 Hz, 1H), 4.31 – 4.14 (m, 2H), 3.96 (d, *J* = 9.5 Hz, 1H), 3.78 – 3.70 (m, 4H), 3.58 (s, 3H), 3.32 (d, *J* = 13.6 Hz, 1H), 3.12 (d, *J* = 13.6 Hz, 1H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 169.1, 160.0, 145.5, 137.5, 133.0, 130.4(2C), 129.8, 127.9(2C), 120.0, 117.7, 112.3, 77.8, 76.0, 73.3, 68.3, 59.9, 58.7, 55.5, 53.2, 21.8; **HRMS** (ESI-TOF, m/z): calcd for $C_{23}H_{25}NO_6SNa$ $[M+Na]^+$: 466.1295, found: 466.1303.



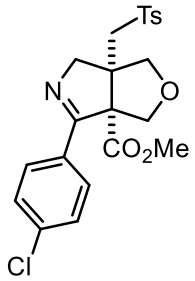
6e was obtained as white solid, 40.2 mg, 94% yield; m.p. = 136–137 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.66 (m, 2H), 7.48 (s, 1H), 7.41 – 7.27 (m, 2H), 7.24 – 7.11 (m, 3H), 4.50 (d, *J* = 9.5 Hz, 1H), 4.34 (d, *J* = 17.7 Hz, 1H), 4.32 – 4.17 (m, 2H), 3.95 (d, *J* = 9.5 Hz, 1H), 3.72 (d, *J* = 9.8 Hz, 1H), 3.57 (s, 3H), 3.32 (d, *J* = 13.5 Hz, 1H), 3.12 (d, *J* = 13.5 Hz, 1H), 2.39 (s, 3H), 2.28 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 169.2, 145.5, 138.8, 137.5, 131.9, 131.6, 130.3(2C), 128.7, 128.4, 127.9(2C), 124.7, 77.8, 75.9, 73.2, 68.2, 59.9, 58.7, 53.1, 21.8, 21.5; **HRMS** (ESI-TOF, m/z): calcd for $C_{23}H_{25}NO_5SNa$ $[M+Na]^+$: 450.1346, found: 450.1349.



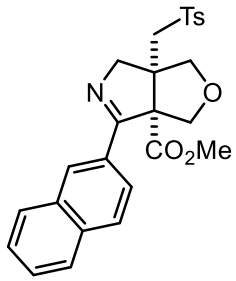
6f was obtained as white solid, 39.7 mg, 93 yield; m.p. = 207–208 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.9 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 4.50 (d, *J* = 9.5 Hz, 1H), 4.42 – 4.17 (m, 3H), 3.94 (d, *J* = 9.5 Hz, 1H), 3.71 (d, *J* = 9.8 Hz, 1H), 3.57 (s, 3H), 3.32 (d, *J* = 13.6 Hz, 1H), 3.12 (d, *J* = 13.5 Hz, 1H), 2.39 (s, 3H), 2.29 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 169.0, 145.5, 141.5, 137.5, 130.3(2C), 129.7(2C), 129.0, 127.9(2C), 127.7(2C), 77.8, 75.9, 73.3, 68.2, 59.9, 58.7, 53.1, 21.8, 21.5; **HRMS** (ESI-TOF, m/z): calcd for $C_{23}H_{25}NO_6SNa$ $[M+Na]^+$: 450.1346, found: 450.1346.



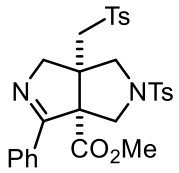
6g was obtained as white solid, 46.3 mg, 94% yield; m.p. = 189–190 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.66 (m, 2H), 7.49 – 7.42 (m, 2H), 7.39 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.47 (d, *J* = 9.6 Hz, 1H), 4.36 (d, *J* = 17.9 Hz, 1H), 4.28 (d, *J* = 3.4 Hz, 1H), 4.25 (d, *J* = 4.7 Hz, 1H), 3.93 (d, *J* = 9.5 Hz, 1H), 3.76 (d, *J* = 9.9 Hz, 1H), 3.58 (s, 3H), 3.30 (d, *J* = 13.5 Hz, 1H), 3.12 (d, *J* = 13.6 Hz, 1H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.4, 168.1, 145.6, 137.4, 132.2(2C), 130.7, 130.4(2C), 129.2(2C), 127.9(2C), 125.7, 78.0, 75.7, 73.1, 68.7, 59.9, 58.9, 53.3, 21.8; **HRMS** (ESI-TOF, m/z): calcd for $C_{22}H_{22}BrNO_5SNa$ $[M+Na]^+$: 514.0294, found: 514.0288.



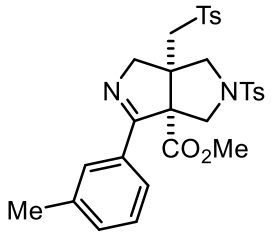
6h was obtained as white solid, 40.3 mg, 90% yield; m.p. = 115–116 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.9 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.30 (m, 4H), 4.47 (d, *J* = 9.5 Hz, 1H), 4.37 (d, *J* = 17.8 Hz, 1H), 4.29 (d, *J* = 5.2 Hz, 1H), 4.25 (d, *J* = 2.9 Hz, 1H), 3.93 (d, *J* = 9.6 Hz, 1H), 3.76 (d, *J* = 9.8 Hz, 1H), 3.58 (s, 3H), 3.30 (d, *J* = 13.6 Hz, 1H), 3.12 (d, *J* = 13.5 Hz, 1H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.4, 167.9, 145.6, 137.4, 137.3, 130.4(2C), 130.2, 129.2(2C), 129.0(2C), 127.9(2C), 78.0, 75.8, 73.1, 68.6, 59.9, 58.9, 53.3, 21.8; **HRMS** (ESI-TOF, m/z): calcd for $C_{22}H_{22}ClNO_5SNa$ $[M+Na]^+$: 470.0799, found: 470.0793.



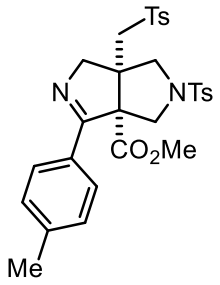
6i was obtained as white solid, 44.0mg mg, 95% yield; m.p. = 150–151 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 2H), 7.81 – 7.59 (m, 5H), 7.50 – 7.40 (m, 2H), 7.36 – 7.22 (m, 2H), 4.61 (d, *J* = 9.6 Hz, 1H), 4.42 (d, *J* = 17.8 Hz, 1H), 4.35 (d, *J* = 2.6 Hz, 1H), 4.32 (d, *J* = 5.4 Hz, 1H), 4.06 (d, *J* = 9.5 Hz, 1H), 3.77 (d, *J* = 9.8 Hz, 1H), 3.57 (s, 3H), 3.36 (d, *J* = 13.6 Hz, 1H), 3.16 (d, *J* = 13.5 Hz, 1H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 169.1, 145.6, 137.5, 134.5, 132.9, 130.4(2C), 129.2, 129.0, 128.9, 127.9(2C), 127.8(9), 127.8, 127.8, 126.9, 124.6, 77.9, 76.0, 73.4, 68.4, 59.9, 58.9, 53.2, 21.8; **HRMS** (ESI-TOF, m/z): calcd for $C_{26}H_{25}NO_5SNa$ $[M+Na]^+$: 486.1346, found: 486.1339.



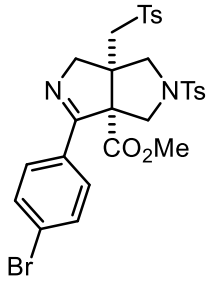
7a was obtained as white solid, 51.0 mg, 90 yield; m.p. = 79–80 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.66 (m, 2H), 7.55 – 7.49 (m, 2H), 7.43 – 7.38 (m, 2H), 7.37 – 7.25 (m, 5H), 7.18 (m, 2H), 4.32 (d, *J* = 17.5 Hz, 1H), 4.23 (d, *J* = 17.5 Hz, 1H), 3.92 (d, *J* = 10.5 Hz, 1H), 3.75 (d, *J* = 10.5 Hz, 1H), 3.55 (s, 3H), 3.45 (d, *J* = 10.5 Hz, 1H), 3.18 (d, *J* = 13.6 Hz, 1H), 3.11 (d, *J* = 10.6 Hz, 1H), 3.02 (d, *J* = 13.6 Hz, 1H), 2.41 (s, 3H), 2.34 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.8, 169.0, 145.7, 144.3, 137.3, 131.7, 131.3, 131.1(2C), 130.4, 129.9(2C), 128.9(2C), 128.0(2C), 127.9(2C), 127.6(2C), 73.5, 68.3, 59.5, 57.2, 56.8, 53.4, 52.5, 21.8, 21.7; **HRMS** (ESI-TOF, m/z): calcd for $C_{29}H_{30}N_2O_6S_2Na$ $[M+Na]^+$: 589.1437, found: 589.1439.



7b was obtained as white solid, 43.6 mg, 75% yield; m.p. = 40–41 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 – 7.63 (m, 2H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 5.1 Hz, 2H), 7.25 – 7.01 (m, 6H), 4.31 (d, *J* = 17.5 Hz, 1H), 4.21 (d, *J* = 17.5 Hz, 1H), 3.92 (d, *J* = 10.5 Hz, 1H), 3.75 (d, *J* = 10.6 Hz, 1H), 3.55 (s, 3H), 3.46 (d, *J* = 10.5 Hz, 1H), 3.17 (d, *J* = 13.6 Hz, 1H), 3.10 (d, *J* = 10.6 Hz, 1H), 3.01 (d, *J* = 13.6 Hz, 1H), 2.40 (s, 3H), 2.34 (s, 3H), 2.27 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.8, 169.1, 145.6, 144.2, 138.8, 137.3, 132.0, 131.8 , 131.2, 130.4(2C), 129.9(2C), 128.7, 128.3(2C), 128.0(2C), 127.9, 124.6, 73.5, 68.2, 59.5, 57.2, 56.7, 53.4, 52.5, 21.8, 21.7, 21.5; **HRMS** (ESI-TOF, m/z): calcd for $C_{30}H_{32}N_2O_6S_2Na$ $[M+Na]^+$: 603.1594, found: 603.1593.

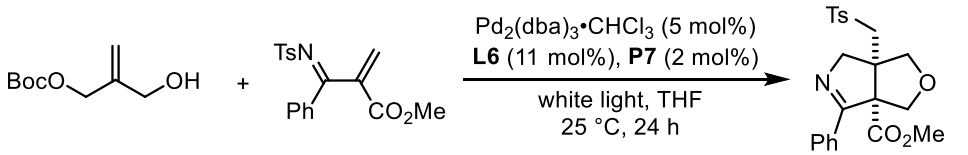


7c was obtained as white solid, 45.9 mg, 79% yield; m.p. = 194–195 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 7.9 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 4H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 4.30 (d, *J* = 17.5 Hz, 1H), 4.20 (d, *J* = 17.5 Hz, 1H), 3.92 (d, *J* = 10.5 Hz, 1H), 3.75 (d, *J* = 10.5 Hz, 1H), 3.54 (s, 3H), 3.44 (d, *J* = 10.5 Hz, 1H), 3.17 (d, *J* = 13.6 Hz, 1H), 3.10 (d, *J* = 10.6 Hz, 1H), 3.01 (d, *J* = 13.6 Hz, 1H), 2.40 (s, 3H), 2.33 (s, 3H), 2.29 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.8, 168.8, 145.6, 144.2, 141.6, 137.3, 131.7, 130.3(2C), 129.9(2C), 129.6(2C), 128.5, 128.0(2C), 127.9(2C), 127.6(2C), 73.5, 68.1, 59.4, 57.2, 56.7, 53.3, 52.5, 21.8, 21.7, 21.5; **HRMS** (ESI-TOF, m/z): calcd for $C_{30}H_{32}N_2O_6S_2Na$ $[M+Na]^+$: 603.1594, found: 603.1591.



7d was obtained as white solid, 57.5 mg, 89% yield; m.p. = 122–123 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 4.32 (d, *J* = 17.6 Hz, 1H), 4.23 (d, *J* = 17.7 Hz, 1H), 3.86 (d, *J* = 10.4 Hz, 1H), 3.70 (d, *J* = 10.5 Hz, 1H), 3.56 (s, 3H), 3.41 (d, *J* = 10.5 Hz, 1H), 3.24 – 3.09 (m, 2H), 3.02 (d, *J* = 13.6 Hz, 1H), 2.41 (s, 3H), 2.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.6, 168.0, 145.7, 144.4, 137.2, 132.2(2C), 131.6, 130.4(2C), 130.2, 129.9(2C), 129.1(2C), 128.0(2C), 128.0(2C), 125.9, 73.4, 68.6, 59.5, 57.4, 56.9, 53.5, 52.4, 21.8, 21.7; **HRMS** (ESI-TOF, m/z): calcd for $C_{29}H_{29}BrN_2O_6S_2Na$ $[M+Na]^+$: 667.0543, found: 667.0544.

8. Scale-up experiment



1b
0.79 g
(4.2 mmol)

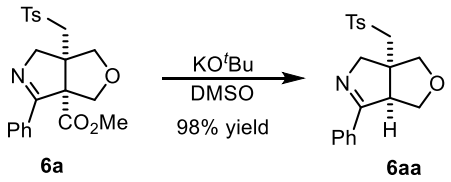
2a
1.20 g
(3.5 mmol)

6a
1.22 g, 85% yield

Under a nitrogen atmosphere, $Pd_2(dba)_3 \cdot CHCl_3$ (182 mg, 0.175 mmol, 5 mol%) and **L6** (164.5 mg, 0.385 mmol, 11 mol%) were added to a flame drying Schlenk tube with a magnetic stir bar. The vacuum tube is removed and pumped back with nitrogen three times. Then 50 mL of anhydrous THF was added through the syringe. The reaction mixture was stirred for 30 min at 25 ℃. Then, TMM type oxa-1,4-dipolar precursor **1b** (0.79 g, 4.2 mmol, 1.2 equiv), azadiene **2a** (1.2 g, 3.5 mmol, 1.0 equiv) and photosensitizer **P7** (80.5 mg, 0.07 mmol, 2 mol%) were added in sequence under nitrogen and stirred under 15W white light at 25℃ for 24 h. Then, the reaction mixture was concentrated and the crude product was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) to obtain the corresponding product **6a** (1.22 g, 85% yield).

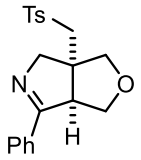
9. Procedure for the synthesis of 6aa-6ad and 7aa

Synthesis of compound 6aa



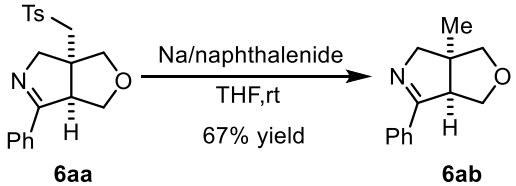
6a **6aa**

To a 10 mL reaction tube charged with a magnetic bar was added **6a** (41.3 mg, 0.10 mmol, 1.0 equiv), potassium *tert*-butanol (22.4 mg, 0.2 mmol, 2.0 equiv) and anhydrous DMSO (1.0 mL) at 25 ℃ under N_2 protection. The mixture was stirred at 25 ℃ for 30 min. The mixture was quenched with a saturated NH_4Cl solution (5 mL) and extracted with ethyl acetate (3×10 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2/1, v/v) to give the product **6aa** as a white solid (34.8 mg, 98% yield).



6aa was obtained as white solid, 34.8 mg, 98% yield; m.p. = 98-99 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 2H), 7.61 (d, *J* = 7.3 Hz, 2H), 7.47 – 7.21 (m, 5H), 4.36 (d, *J* = 17.5 Hz, 1H), 4.06 – 3.89 (m, 3H), 3.85 (d, *J* = 9.6 Hz, 1H), 3.82 – 3.70 (m, 2H), 3.42 (s, 2H), 2.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.8, 145.2, 137.6, 132.8, 130.9, 130.2(2C), 128.7(2C), 127.9(2C), 127.8(2C), 78.2, 71.3, 70.6, 62.1, 60.7, 53.0, 21.7; **HRMS** (ESI-TOF, m/z): calcd for $C_{20}H_{21}NO_3SNa$ $[M+Na]^+$: 378.1134, found: 378.1140.

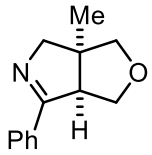
Synthesis of compound 6ab



6aa **6ab**

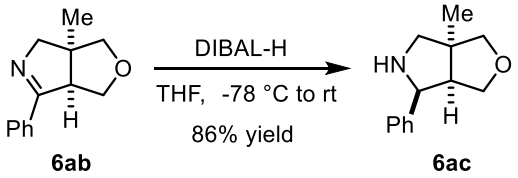
Sodium metal (4.6 mg, 0.2 mmol, 2.0 equiv) and naphthalene (25.6 mg, 0.2 mmol, 2.0 equiv) were added to anhydrous THF (1.0 mL) in a 10 mL reaction tube equipped with a magnetic stir bar. After half an hour, the solution was transferred into a separate dry round bottomed flask containing **6aa** (35.5 mg, 0.1 mmol, 1.00 equiv) and anhydrous THF (1.0 mL) at 25 ℃ and stirred for 24 hours. The reaction mixture was

diluted with 10% HCl (15 mL) and extracted with ethyl acetate (3×10 mL). The combined organic layer was then washed with brine (3×5 mL) and dried over $MgSO_4$. After filtration, the solution was concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (dichloromethane/methanol = 20/1, v/v) yielding **6ab** as a white solid (13.5 mg, 67% yield).

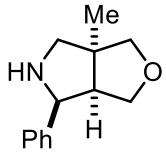


6ab was obtained as white solid, 13.5 mg, 67% yield; m.p. = 67-68 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 – 7.69 (m, 2H), 7.40 – 7.31 (m, 3H), 3.92 (d, *J* = 17.0 Hz, 1H), 3.84 (dd, *J* = 17.1, 2.3 Hz, 1H), 3.32 (dd, *J* = 8.6, 2.6 Hz, 1H), 3.16 (dd, *J* = 11.8, 8.5 Hz, 1H), 3.01 (dd, *J* = 11.7, 2.7 Hz, 1H), 2.91 (d, *J* = 11.4 Hz, 1H), 2.65 (d, *J* = 11.4 Hz, 1H), 1.26 (s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.9, 133.8, 130.5, 128.7(2C), 128.1(2C), 75.4, 62.3, 62.0, 52.7, 51.1, 24.6; **HRMS** (ESI-TOF, m/z): calcd for $C_{13}H_{16}NO$ $[M+H]^+$: 204.1383, found: 204.1386.

Synthesis of compound 6ac



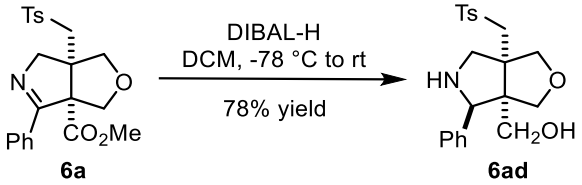
To a solution of **6ab** (20.1 mg, 0.1 mmol, 1.0 equiv) in THF (1 mL) was added DIBAL-H (0.5 mL, 0.6 mmol, 6.0 equiv) slowly at 0 °C. Then the resulting mixture was warmed to room temperature and stirred for 12 h. The reaction mixture was quenched with saturated potassium sodium tartrate and extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation to afford crude product. The residue was purified by column chromatography on silica gel (dichloromethane/methanol = 10/1, v/v) to give the product **6ac** as a white solid (17.5 mg, 86% yield).



6ac was obtained as white solid, 17.5 mg, 86% yield; m.p. = 56-57 °C; **^{1}H NMR** (600 MHz, CD_3OD) δ 7.24 – 7.20 (m, 4H), 7.15 – 7.10 (m, 1H), 4.28 (d, *J* = 6.7 Hz, 1H), 3.60 (d, *J* = 8.7 Hz, 1H), 3.53 (d, *J* = 8.7 Hz, 1H), 3.47 (dd, *J* = 9.6, 7.9 Hz, 1H), 3.12 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.03 (d, *J* = 11.2 Hz, 1H), 2.66 (d, *J* = 11.2 Hz, 1H), 2.54 (dt, *J* = 7.8, 6.3 Hz, 1H), 1.21 (s, 3H); **^{13}C NMR** (100

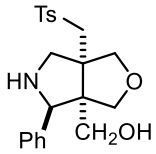
MHz, CD_3OD) δ 140.7, 129.4(2C), 127.9, 127.5(2C), 82.3, 71.7, 65.9, 59.4, 57.7, 53.4, 24.0; **HRMS** (ESI-TOF, m/z): calcd for $C_{13}H_{18}NO[M+H]^+$: 204.1383, found: 204.1386.

Synthesis of compound 6ad



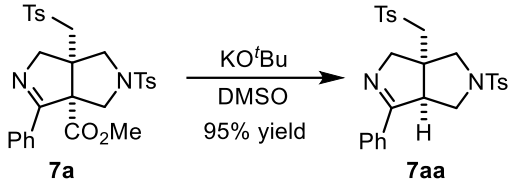
6a **6ad**

To a solution of **6a** (41.3 mg, 0.1 mmol, 1.0 equiv) in DCM (1 mL) was added DIBAL-H (0.5 mL, 0.6 mmol, 6.0 equiv) slowly at 0 °C. Then the resulting mixture was warmed to room temperature and stirred for 12 h. The reaction mixture was quenched with saturated potassium sodium tartrate and extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation to afford the crude product. The residue was purified by column chromatography on silica gel (dichloromethane/methanol = 10/1, v/v) to give the product **6ad** as a white solid (30.2 mg, 78% yield).



6ad was obtained as white solid, 30.2 mg, 78% yield; m.p. =145-146 °C; **^{1}H NMR** (600 MHz, CD_2Cl_2) δ 7.75 – 7.70 (m, 2H), 7.34 – 7.30 (m, 2H), 7.24 (m, 4H), 7.20 – 7.17 (m, 1H), 4.10 (d, *J* = 10.3 Hz, 2H), 3.85 (d, *J* = 9.4 Hz, 1H), 3.74 (d, *J* = 14.0 Hz, 1H), 3.60 – 3.45 (m, 4H), 3.39 – 3.30 (m, 2H), 3.08 (d, *J* = 10.9 Hz, 1H), 2.86 (d, *J* = 9.6 Hz, 1H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, DMSO) δ 144.5, 140.0, 138.2, 130.0(2C), 127.9(2C), 127.6(2C), 127.6(2C), 127.0, 78.3, 71.0, 64.4, 62.0, 60.4, 60.0, 55.8, 53.9, 21.1; **HRMS** (ESI-TOF, m/z): calcd for $C_{21}H_{25}NO_4Na$ $[M+Na]^+$: 410.1397, found: 410.1397.

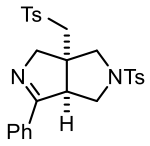
Synthesis of compound 7aa



7a **7aa**

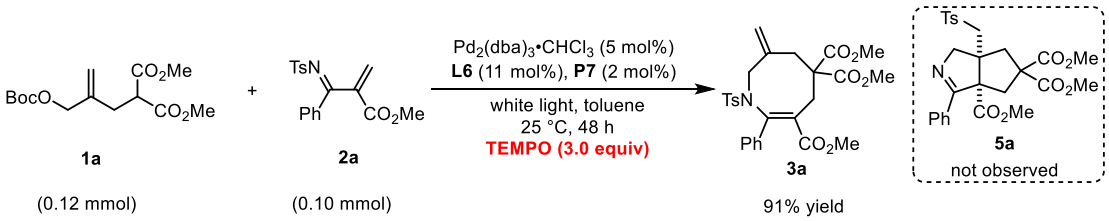
To a 10 mL reaction tube charged with a magnetic bar was added **7a** (56.7 mg, 0.10 mmol, 1.0 equiv) and potassium *tert*-butanol (22.4 mg, 0.2 mmol) in anhydrous DMSO (1.0 mL) at 25 °C under N_2 protection. The mixture was stirred at 25 °C for 30 min. The mixture was quenched with a saturated NH_4Cl solution (5 mL) and extracted with ethyl acetate (3×10 mL). The combined organic phase was washed with brine,

dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 2/1, v/v) to give the product **7aa** as a white solid (48.3 mg, 95% yield).



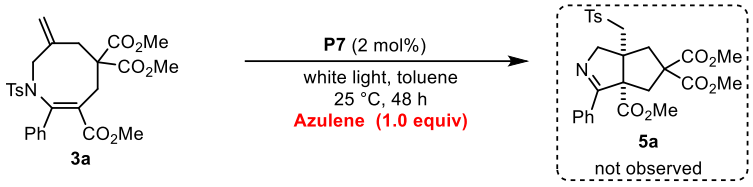
7aa was obtained as white solid, 48.3 mg, 95% yield; m.p. = 100-102℃; **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.79 – 7.71 (m, 2H), 7.63 (m, 4H), 7.49 – 7.25 (m, 7H), 4.40 (d, *J* = 17.5 Hz, 1H), 4.05 (dd, *J* = 17.6, 2.1 Hz, 1H), 3.90 – 3.69 (m, 1H), 3.46 (d, *J* = 10.2 Hz, 1H), 3.43 – 3.25 (m, 5H), 2.45 (s, 3H), 2.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.4, 145.4, 144.3, 137.5, 132.4, 131.6, 131.1, 130.3(2C), 129.9(2C), 128.9(2C), 128.1(2C), 128.0(2C), 127.9(2C), 70.7, 62.0, 57.9, 57.6, 51.5, 50.7, 21.8, 21.7; **HRMS** (ESI-TOF, m/z): calcd for $C_{27}H_{28}N_2O_4S_2Na$ $[M+Na]^+$: 531.1383, found: 531.1385.

10. Radical trapping experiment



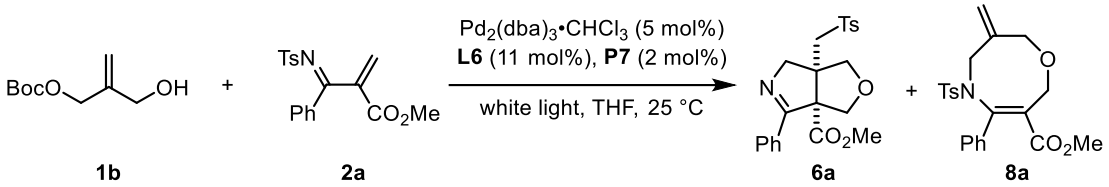
Under a nitrogen atmosphere, $Pd_2(dba)_3{\cdot}CHCl_3$ (5.2 mg, 0.005 mmol, 5 mol%) and **L6** (4.7 mg, 0.011 mmol, 11 mol%) were added to a flame-drying Schlenk tube with a magnetic stir bar. The vacuum tube was removed and pumped back with nitrogen three times. Then, 1 mL of anhydrous toluene was added through the syringe. The resulting mixture was stirred at room temperature for 30 minutes. Then, TMM-type all-carbon-1,4-dipole precursor **1a** (36.3 mg, 0.12 mmol, 1.2 equiv), azadiene **2a** (34.3 mg, 0.1 mmol, 1.0 equiv), photosensitizer **P7** (2.3 mg, 0.002 mmol, 2 mol%), and TEMPO (46.9 mg, 0.3 mmol, 3.0 equiv) were added in sequence under nitrogen and stirred under 15W white light at 25℃ for 48 h. The reaction mixture was then concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) to obtain the corresponding product **3a** (48.0 mg, 91% yield).

11. Control experiments with triplet state quenchers



Under a nitrogen atmosphere, **3a** (52.7 mg, 0.1 mmol, 1.0 equiv), photosensitizer **P7** (2.3 mg, 0.002 mmol, 2 mol%), azulene (12.8 mg, 1.0 equiv) were added to a flame-drying Schlenk tube with a magnetic stir bar. The vacuum tube was removed and pumped back with nitrogen three times. Then, 1 mL of anhydrous toluene was added through the syringe. Then stirred under 15W white light at 25℃ for 48 h. No product **5a** was generated through ^{1}H NMR analysis.

12. Successive light/dark experiments



The reactions were performed normally according to the general procedure described above, although at intermediate conversion, light irradiation was ceased. The yields of products **6a** and **8a** were determined by means of ^{1}H NMR analysis from an aliquot of the reaction mixture (1,3,5-trimethoxybenzene was used as the internal standard). The reaction mixture was then stirred in the dark for 4 h. After that time, in all cases, the reactions did not evolve further. The mixtures were then irradiated again for 4 h. Similar successive intervals of irradiation and dark periods were performed for 48 h.

Table S3. Successive light/dark experiments data.

light (on/off)	on	off	on	off	on	off	on	off	on	off	on	off
time/h	4	8	12	16	20	24	28	32	36	40	44	48
8a yield (%)	59	59	37	37	18	18	9	9	4	4	0	0
6a yield (%)	33	33	55	55	74	74	83	83	88	88	92	92

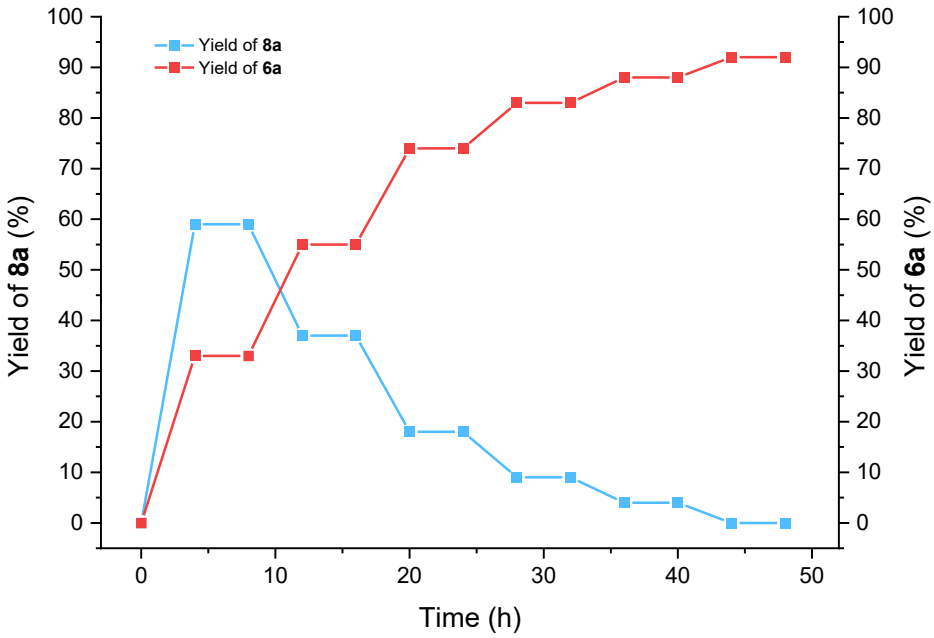
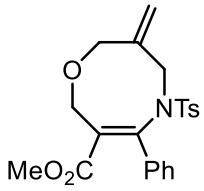


Figure S1. Successive light/dark experiments data plot



8a was obtained as white solid, 39.3 mg, 95% yield; m.p. = 170–171 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 1H), 7.18 – 7.13 (m, 4H), 7.07 – 7.00 (m, 4H), 5.43 (s, 1H), 5.35 (s, 1H), 4.53 (s, 2H), 4.37 (brs, 2H), 4.23 (s, 2H),3.44 (s, 3H), 2.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.6, 145.8, 143.4, 141.7, 136.8, 136.7, 135.4, 129.3(2C), 129.2, 128.6(2C), 128.2(2C), 127.4(2C), 124.0, 74.0, 68.1, 58.3, 52.1, 21.6; **HRMS** (ESI-TOF, m/z): calcd for $C_{22}H_{23}NO_5SNa$ $[M+Na]^+$: 436.1189, found: 436.1187.

13. Cyclic voltammetry experiments

Cyclic voltammetry experiments were recorded with a CHI660E potentiostation at room temperature in MeCN with the protection of Ar. Bu_4NPF_6 (0.1 M) was used as the supporting electrolyte, the scan rate is 0.1 V/s. The working electrode is a glassy carbon, the counter electrode is a Pt plate, and the reference electrode is Ag/AgCl.

The cyclic voltammetry (CV) experiments revealed the redox potential of **3a** and **8a** is -0.88 V and -0.87 (vs. SCE in CH_3CN), respectively.

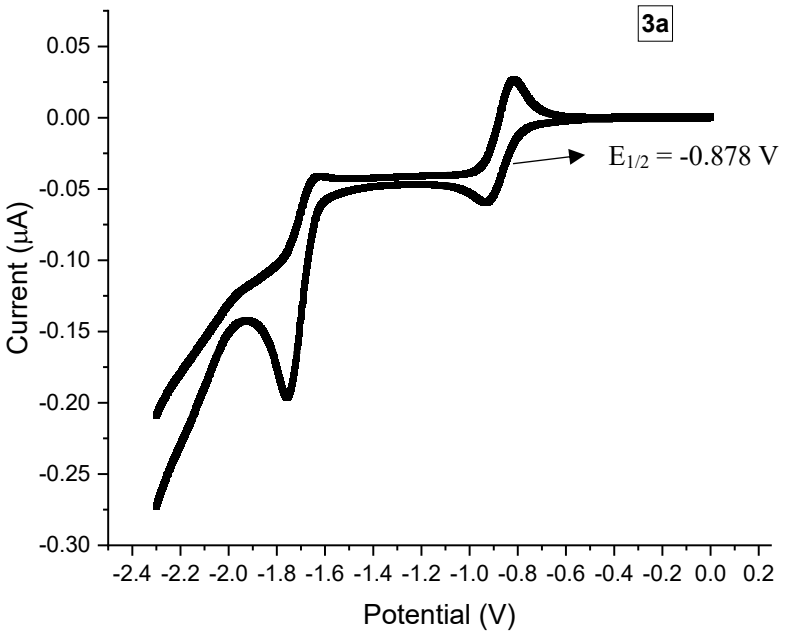


Figure S2. Cyclic voltammetry spectra of **3a**

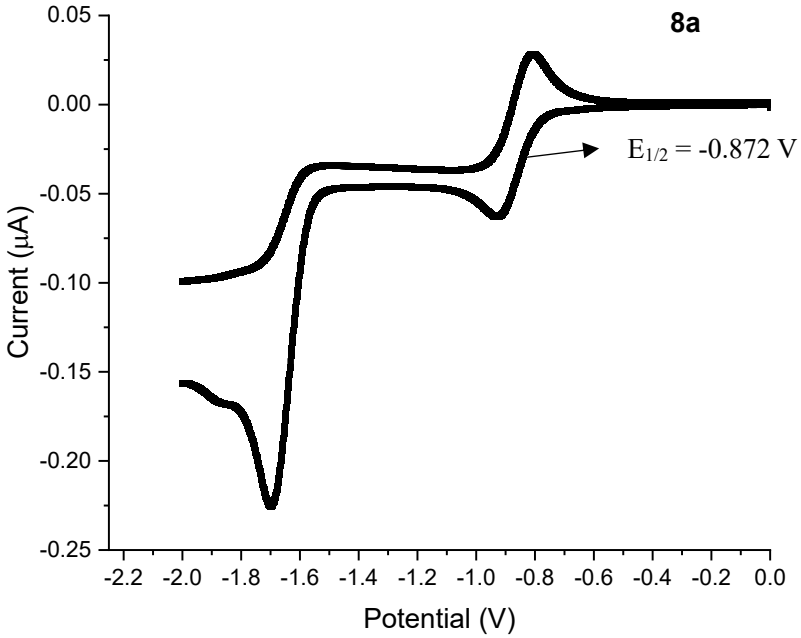


Figure S3. Cyclic voltammetry spectra of **8a**

14. Stern-Volmer quenching experiments.

Stern-Volmer quenching experiments were conducted on a Hitachi F4600 Fluorescence Spectrophotometer. Stern-Volmer luminescence quenching experiments

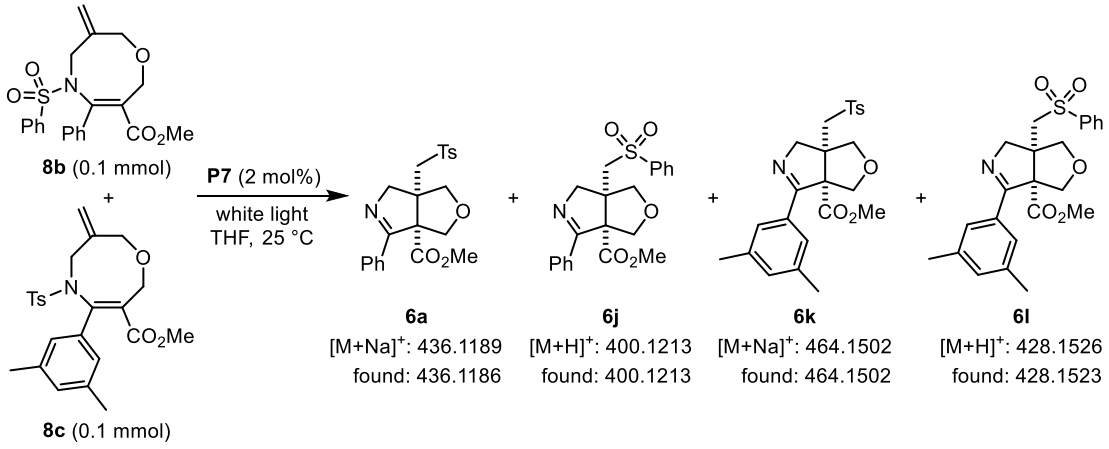
were run with freshly prepared solutions of 1.0×10^{-5} M $Ir(dtbppy)_2(dtbbpy)PF_6$ and the appropriate amount of quencher in THF at room temperature. After degassing with argon for 5 min, the emission spectra of the samples were collected. The solutions were irradiated at 475 nm and luminescence was measured at 591 nm.

The results revealed that both **8a** and the photocatalyst **P7** exhibit intrinsic fluorescence. This dual fluorescence emission phenomenon led to a systematic enhancement of the overall fluorescence intensity with increasing concentrations of **8a**, which prevented us from accurately characterizing the direct quenching interaction between **P7** and **8a**.

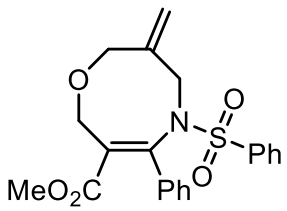
Table S4. Luminescence quenching data for $Ir(dtbppy)_2(dtbbpy)PF_6$ (**P7**) and **8a**.

Vial	Intensity	I_0/I	**8a** (mol/L)	**P7** (mol/L)
1	1571		$1*10^{-4}$	0
2	8929	1.00	0	$1*10^{-5}$
3	9246	0.97	$2*10^{-4}$	$1*10^{-5}$
4	9562	0.93	$4*10^{-4}$	$1*10^{-5}$
5	10223	0.89	$6*10^{-4}$	$1*10^{-5}$
6	10494	0.85	$8*10^{-4}$	$1*10^{-5}$

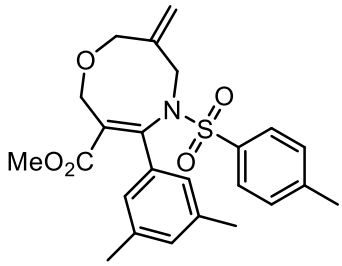
15. Crossover reactions with two different azocane



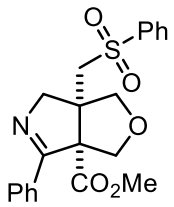
Under a nitrogen atmosphere, photosensitizer **P7** (2.3 mg, 0.002 mmol, 2 mol%), **8b** and **8c** were added to a flame-drying Schlenk tube with a magnetic stir bar. The vacuum tube was removed and pumped back with nitrogen three times. Then, 2 mL of anhydrous THF was added through the syringe. The stirred under 15W white light at 25℃ for 12 h. Determine the transannular cyclization products by high-resolution mass spectrometry.



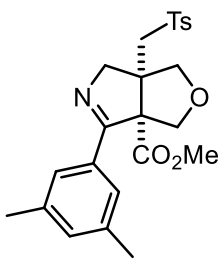
8b was obtained as white solid, 39.5 mg, 99% yield; m.p. = 168–169 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 1H), 7.30 – 7.18 (m, 5H), 7.17 – 7.08 (m, 2H), 7.05 – 6.98 (m, 2H), 5.43 (s, 1H), 5.36 (s, 1H), 4.54 (s, 2H), 4.44 (bs, 2H), 4.24 (s, 2H), 3.43 (s, 3H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.5, 145.4, 141.6, 139.6, 136.6, 135.5, 132.5(2C), 128.7(2C), 128.5(2C), 128.1(2C), 127.1(2C), 124.0, 73.9, 68.1, 58.3, 52.1.; **HRMS** (ESI-TOF, m/z): calcd for $C_{21}H_{21}NO_5SNa$ $[M+Na]^+$: 422.1033, found: 422.1033.



8c was obtained as white solid, 43.7 mg, 99% yield; m.p. = 188–189 ℃;**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.87 (s, 1H), 6.56 (s, 2H), 5.42 (s, 1H), 5.36 (s, 1H), 4.53 (s, 2H), 4.38(bs, 2H) 4.24 (s, 2H), 3.46 (s, 3H), 2.36 (s, 3H), 2.11 (s, 6H).;**^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.0, 146.1, 143.2, 141.9, 137.6(2C), 136.9, 136.1, 134.6, 131.0, 129.1(2C), 127.3(2C), 126.4(2C), 123.9, 73.8, 68.2, 58.6, 52.1, 21.5, 21.2(2C).; **HRMS** (ESI-TOF, m/z): calcd for $C_{24}H_{27}NO_5SNa$ $[M+Na]^+$: 464.1502, found: 464.1502.



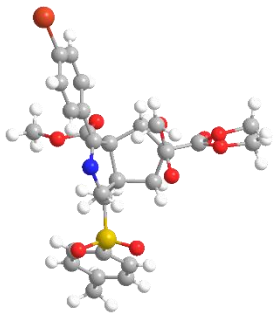
6j was obtained as white solid, 39.5mg, 99% yield; m.p. = 201–202 ℃; **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.97 – 7.91 (m, 2H), 7.74 – 7.66 (m, 1H), 7.65 – 7.56 (m, 4H), 7.50 – 7.32 (m, 3H), 4.59 (d, *J* = 9.5 Hz, 1H), 4.46 (d, *J* = 17.7 Hz, 1H), 4.43 – 4.33 (m, 2H), 4.04 (d, *J* = 9.6 Hz, 1H), 3.83 (d, *J* = 9.7 Hz, 1H), 3.65 (s, 3H), 3.42 (d, J = 13.5 Hz, 1H), 3.21 (d, *J* = 13.5 Hz, 1H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 169.1, 140.5, 134.4, 131.7, 131.0, 129.8(2C), 129.0(2C), 127.9(2C), 127.7(2C), 77.8, 75.9, 73.2, 68.3, 59.8, 58.8, 53.2.; **HRMS** (ESI-TOF, m/z): calcd for $C_{21}H_{22}NO_5S$ $[M+H]^+$: 400.1213, found: 400.1213.



6k was obtained as white solid, 43.7 mg, 99% yield; m.p. = 221–222 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.11 (s, 2H), 6.99 (s, 1H), 4.50 (d, *J* = 9.6 Hz, 1H), 4.37 – 4.27 (m, 2H), 4.25 (d, *J* = 17.7 Hz, 1H), 3.94 (d, *J* = 9.5 Hz, 1H), 3.70 (d, *J* = 9.8 Hz, 1H), 3.57 (s, 3H), 3.32 (d, *J* = 13.6 Hz, 1H), 3.11 (d, *J* = 13.6 Hz, 1H), 2.39 (s, 3H), 2.23 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 169.4, 145.5, 138.6(2C), 137.5, 132.8(2C), 131.6, 130.3(2C), 127.9(2C), 125.5(2C), 75.9, 73.3, 68.1, 59.9, 58.7, 53.1, 21.8, 21.4(2C). **HRMS** (ESI-TOF, m/z): calcd for $C_{24}H_{27}NO_5S[M+Na]^+$: 464.1502, found: 464.1502.

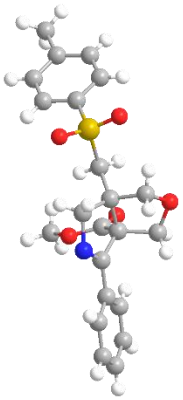
16. Crystallographic data for compound 5g and 6a



The X-ray crystal structure of **5g** with thermal ellipsoids at the 30% probability level (CCDC: 2425567).

Identification code	data_20240402xll_98_0m	
Empirical formula	$C_{27}H_{28}BrNO_8S$	
Formula weight	606.47	
Temperature	175	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	P 1 - 1	
Unit cell dimensions	a = 9.2452(3) Å	α = 84.233(2)°
	b = 10.0380(3) Å	β = 78.354(2)°
	c = 15.7587(6) Å	γ = 73.787(2)°
Volume	1373.87(8) Å^3	
Z	2	
Density (calculated)	1.466 Mg/m^3	
Absorption coefficient	3.177 mm^{-1}	
F(000)	624	
Crystal size	0.100×0.100×0.100 mm^3	
Theta range for data collection	2.866 to 68.452°	
Index ranges	-11<=h<=10, -12<=k<=12,	
	-18<=l<=18	

Reflections collected	18787
Independent reflections	3531 [R(int) = 0.0589]
Completeness to theta = 68.452°	99.5 %
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5018 / 48 / 367
Goodness-of-fit on F^2	1.028
Final R indices [I>2sigma(I)]	R_1 = 0.0589, wR_2 = 0.1389
R indices (all data)	R_1 = 0.0856, wR_2 = 0.1613
Largest diff. peak and hole	0.531 and -0.674 e.Å^{-3}



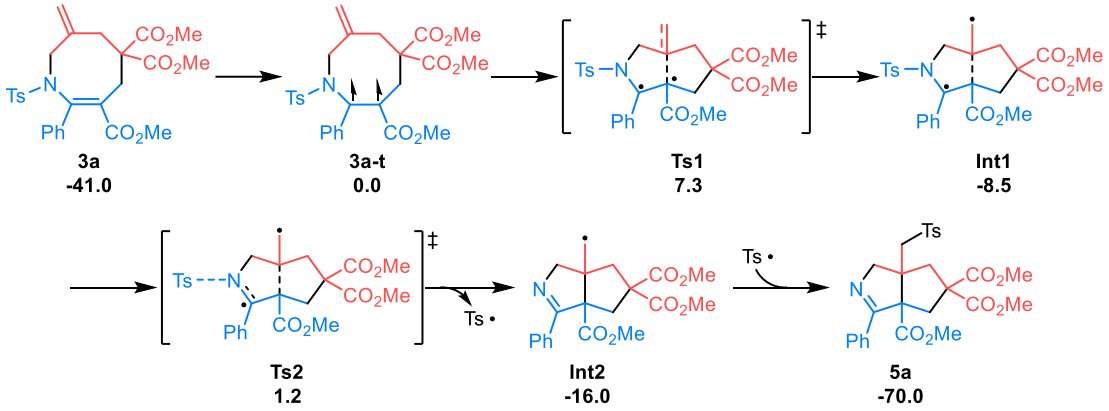
The X-ray crystal structure of **6a** with thermal ellipsoids at the 30% probability level (CCDC: 2425568).

Identification code	data_cu_20240607_xcl_e_79_0m	
Empirical formula	$C_{22}H_{23}NO_5S$	
Formula weight	413.47	
Temperature	294,00	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 12.461(4) Å	α = 90°
	b = 9.433(3) Å	β = 93.239(12)°
	c = 17.709(5) Å	γ = 90°

Volume	2078.2(10) $Å^3$
Z	4
Density (calculated)	1.321 Mg/m^3
Absorption coefficient	0.166 mm^{-1}
F(000)	872
Crystal size	0.180×0.150×0.130 mm^3
Theta range for data collection	4.228 to 69.696°
Index ranges	-9<=h<=9, -6<=k<=7, -13<=l<=14
Reflections collected	4100
Independent reflections	1082 [R(int) = 0.0301]
Completeness to theta = 69.696°	99.5 %
Absorption correction	multi-scan
Max. and min. transmission	0.8389
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1152 / 81 / 265
Goodness-of-fit on F^2	1.058
Final R indices [I>2sigma(I)]	R_1 = 0.0301, wR_2 = 0.0808
R indices (all data)	R_1 = 0.0327, wR_2 = 0.0837
Largest diff. peak and hole	0.143 and -0.129 $e.Å^{-3}$

17. DFT calculations

Computational details: All density functional theory (DFT) calculations were performed using Gaussian 16.[4] Geometry optimizations and frequencies were calculated at the M06-2X-D3/def2-SVP-SMD(Toluene) level of theory.[5,6] Frequency calculations confirmed that optimized structures are minima (no imaginary frequency) or transition structures (one imaginary frequency). To obtain more accurate electronic energies, single-point energy calculations were performed at the M06-2X-D3/def2-TZVP-SMD(Toluene) level of theory with the optimized structures. Structures were generated using CYLview.[7] Grimme's quasi-RRHO correction[8] for the frequencies that are below 100 cm^{-1} and concentration correction for all species (from 1 atm to 1 mol/L) are implemented by the GoodVibes program.[9]



18. The calculated Cartesian coordinates and energies of structures.

3a

N	0.9382	-0.35127	-0.36662
O	-0.92928	2.97733	1.60246
C	0.81386	2.07688	-0.60598
O	-2.71568	1.67145	1.86648
C	0.25015	0.84271	-0.00635
C	2.19951	2.24603	-0.71865
C	-0.5612	-1.52094	-1.96268
C	-0.90009	0.7389	0.70588
C	2.72395	3.37503	-1.34455
C	0.7905	-0.8805	-1.72712
C	-0.03905	3.02984	-1.18363
C	-1.77072	-0.61675	-1.84616
C	0.48628	4.15116	-1.81669
C	1.86904	4.33169	-1.89033
C	-1.48184	1.92865	1.40054
C	-1.65691	-0.56557	0.75855
H	2.86913	1.48714	-0.31102
H	3.80547	3.50292	-1.4117
H	1.59913	-1.596	-1.92514
H	0.92494	-0.02876	-2.41453
H	-1.11986	2.87212	-1.14837
H	-1.48175	0.4333	-1.98375
H	-2.48933	-0.85624	-2.6425
H	-0.18686	4.88318	-2.26538
H	-0.99184	-1.43347	0.7958
H	-2.29634	-0.61942	1.64483
H	2.27963	5.21164	-2.38848
C	-3.32265	2.71678	2.61008
H	-4.26853	2.3175	2.99144
H	-3.50429	3.59253	1.97074
S	1.58281	-1.36985	0.80378
O	1.29276	-2.73471	0.39259
O	1.17161	-0.8694	2.10238
C	3.3375	-1.13681	0.66781
C	4.07039	-1.93032	-0.2126
C	5.43955	-1.70994	-0.33357
C	6.08312	-0.71949	0.42019
C	5.31985	0.04927	1.31003
C	3.94978	-0.15405	1.44421
H	3.57411	-2.72012	-0.77841
H	6.02328	-2.32494	-1.02164
H	5.80896	0.81776	1.91217
H	3.35537	0.43708	2.14299
C	7.5684	-0.51403	0.30661
H	7.84947	0.51704	0.55876
H	8.10174	-1.18292	1.00035
H	7.92581	-0.73711	-0.70761
C	-2.54337	-0.72988	-0.51115
C	-3.60346	0.37206	-0.49613
O	-3.49723	1.42623	-1.06466
O	-4.64325	0.0426	0.26253
C	-3.273	-2.07771	-0.51186
O	-3.95424	-2.45213	-1.42982
O	-3.06203	-2.79341	0.58408
C	-0.66619	-2.81464	-2.27537
H	-1.63708	-3.26656	-2.49693
H	0.21613	-3.45736	-2.32052
C	-3.69245	-4.06764	0.63065
H	-4.78237	-3.95949	0.55135
H	-3.33473	-4.70178	-0.19176
C	-5.6555	1.03108	0.39903
H	-6.1723	1.18282	-0.55865
H	-5.21837	1.98497	0.72095
H	-3.42043	-4.50869	1.59454
H	-6.35755	0.65416	1.14974
H	-2.67782	3.02052	3.44557

M06-2X-D3/def-TZVP-SMD(toluene): E = -2101.04937337 hartree

Corrected G = -2100.583718 hartree

3a-t

N	0.71502	-1.0464	-0.51399
O	0.73985	1.91781	2.04796
C	0.94545	1.32245	-1.10496
O	-1.39894	1.65855	2.66809
C	0.37727	0.3037	-0.28423
C	2.07984	1.04983	-1.91547
C	-1.24462	-1.85097	-1.81866
C	-0.68177	0.55514	0.7329
C	2.64626	2.04514	-2.69616
C	0.2612	-1.72155	-1.73842

C	0.41413	2.63826	-1.11889
C	-2.05154	-0.56607	-1.85051
C	0.98367	3.61964	-1.91598
C	2.10189	3.33454	-2.70645
C	-0.35188	1.4232	1.86263
C	-1.88944	-0.321	0.74012
H	2.52405	0.05254	-1.89107
H	3.52654	1.81946	-3.30037
H	0.73428	-2.70958	-1.77247
H	0.62013	-1.13473	-2.60071
H	-0.46627	2.87009	-0.51823
H	-1.41926	0.29138	-2.11344
H	-2.82914	-0.63379	-2.62486
H	0.5542	4.62264	-1.9212
H	-1.53497	-1.3623	0.84182
H	-2.50484	-0.10573	1.61905
H	2.55021	4.1142	-3.32385
C	-1.13918	2.49229	3.78646
H	-2.08372	2.57694	4.33388
H	-0.79854	3.48522	3.4612
S	1.44309	-1.89537	0.73106
O	1.42027	-3.30094	0.36153
O	0.84038	-1.43977	1.97562
C	3.11146	-1.30196	0.68825
C	4.08317	-2.05846	0.04012
C	5.37037	-1.53663	-0.07444
C	5.68579	-0.27417	0.44176
C	4.68133	0.45842	1.09221
C	3.39232	-0.04469	1.22749
H	3.8315	-3.04142	-0.36072
H	6.14488	-2.12149	-0.57466
H	4.91381	1.44493	1.49909
H	2.60859	0.53465	1.72259
C	7.07272	0.294	0.31698
H	7.04671	1.28917	-0.15046
H	7.53487	0.4119	1.30876
H	7.72031	-0.355	-0.28642
C	-2.77703	-0.24917	-0.52379
C	-3.32471	1.1767	-0.57423
O	-2.86969	2.06547	-1.24143
O	-4.32639	1.3357	0.28721
C	-3.97652	-1.19826	-0.4145
O	-4.79142	-1.31887	-1.29047
O	-4.01423	-1.87881	0.72258
C	-1.82253	-3.05361	-1.8869
H	-2.90422	-3.15886	-2.01157
H	-1.22862	-3.96978	-1.83823
C	-5.10321	-2.7821	0.87512
H	-6.05828	-2.24348	0.81614
H	-5.07718	-3.55069	0.0908
C	-4.84502	2.65494	0.4166
H	-5.20418	3.02447	-0.55275
H	-4.06772	3.33202	0.79662
H	-4.98352	-3.24214	1.86084
H	-5.6724	2.59051	1.12999
H	-0.36718	2.04877	4.43017

M06-2X-D3/def-TZVP-SMD(toluene): E = -2100.97851807 hartree

Corrected G = -2100.518468 hartree

5a

S	2.74571	1.15011	0.77195
O	0.21669	-2.57949	-0.77224
O	-0.1059	-1.37062	-2.62121
O	-3.77795	0.96376	0.56273
O	2.5098	1.05643	2.21225
O	-2.40758	2.06203	1.9418
O	2.70431	2.452	0.1093
N	-1.32755	-0.99971	1.7921
C	-0.9093	-0.52657	-0.4971
C	-2.84151	-2.14232	0.30408
C	0.13067	0.31909	0.35364
C	-1.6985	-1.24314	0.60175
C	-1.73681	1.74767	-0.3604
C	-2.66082	1.62601	0.85223
C	-0.26757	1.79091	0.08395
O	-3.04168	3.72366	-0.59266
O	-1.5706	3.2755	-2.21149
C	-1.7506	0.50619	-1.26111
C	-0.24064	-1.51791	-1.43573
C	-0.1619	-0.14425	1.81325
C	1.58062	0.04659	-0.05499
C	4.32354	0.40796	0.41599
C	-2.09438	2.99117	-1.16977
C	-3.19293	-2.48731	-1.00732
C	-5.00096	-3.86353	-0.18489

C	-3.57998	-2.67883	1.36933
C	-4.26662	-3.34469	-1.2489
C	5.01112	0.79915	-0.72991
C	4.84285	-0.54288	1.29244
C	6.23994	0.20657	-1.00826
C	-4.65297	-3.52912	1.12628
C	0.87538	-3.5736	-1.54981
C	6.78476	-0.76257	-0.15561
C	6.07248	-1.12281	0.99769
C	-4.6482	0.71227	1.65888
C	8.09965	-1.41808	-0.47603
C	-3.41981	4.91525	-1.27458
H	0.32359	2.19738	-0.74754
H	-0.10821	2.43105	0.96144
H	-2.76568	0.15779	-1.48557
H	-1.24304	0.75783	-2.20222
H	0.68117	-0.71044	2.23771
H	-0.33033	0.70825	2.48542
H	1.74667	0.20708	-1.13134
H	1.88862	-0.97345	0.21318
H	-2.6386	-2.08899	-1.8593
H	-3.28599	-2.41829	2.38688
H	-4.52867	-3.60432	-2.27562
H	4.59197	1.56938	-1.37944
H	4.29436	-0.80464	2.19899
H	6.79262	0.50902	-1.90002
H	-5.22049	-3.93897	1.96344
H	1.15835	-4.36902	-0.85358
H	1.76741	-3.1541	-2.03525
H	0.19845	-3.96528	-2.32074
H	6.49568	-1.86235	1.68072
H	-5.46486	0.09539	1.2698
H	-5.03909	1.65611	2.06331
H	-4.1057	0.17951	2.45284
H	7.93529	-2.36919	-1.00668
H	8.66456	-1.64464	0.43828
H	8.71811	-0.78001	-1.12074
H	-4.19409	5.386	-0.66106
H	-2.55651	5.58546	-1.38014
H	-3.81344	4.67754	-2.27181
H	-5.84259	-4.53159	-0.37522

M06-2X-D3/def-TZVP-SMD(toluene): E = -2101.09610176 hartree

Corrected G = -2100.630073 hartree

Int1

S	-2.21039	1.41918	-0.29896
O	0.12713	3.22468	0.36872
O	1.92048	3.06548	1.70183
O	2.43063	-2.24456	0.65744
O	-2.34749	2.4572	-1.31091
O	1.23921	-2.01046	-1.22187
O	-2.26999	1.74146	1.11551
N	-0.73165	0.59112	-0.59777
C	1.42619	1.28737	0.12757
C	-0.09277	-0.28434	1.62408
C	1.3925	1.37983	-1.46867
C	0.18898	0.47015	0.44184
C	2.95842	-0.38039	-0.66774
C	2.09529	-1.62553	-0.47117
C	2.52588	0.40937	-1.91285
O	4.51624	-1.89718	-1.5695
O	5.34528	-0.27275	-0.27736
C	2.75834	0.62536	0.46747
C	1.22919	2.6294	0.82007
C	-0.02879	0.87401	-1.85446
C	1.65098	2.74768	-2.00506
C	-3.44094	0.18613	-0.63713
C	4.40869	-0.82568	-0.78303
C	0.59358	-0.06425	2.84258
C	-0.67617	-1.82828	3.91271
C	-1.08542	-1.29414	1.5899
C	0.3033	-0.83202	3.96335
C	-4.14611	-0.37445	0.42159
C	-3.68834	-0.18567	-1.95908
C	-5.10856	-1.34562	0.14719
C	-1.37059	-2.04914	2.71917
C	-0.33527	4.37125	1.06737
C	-5.3678	-1.75565	-1.16462
C	-4.64564	-1.15992	-2.21129
C	1.72038	-3.43839	0.96562
C	-6.39776	-2.80968	-1.46407
C	5.83308	-2.39541	-1.77654
H	3.38583	0.99717	-2.26468
H	2.20987	-0.25524	-2.72626
H	2.78837	0.15186	1.45527

H	3.56554	1.36987	0.42546
H	-0.57798	1.62526	-2.43187
H	0.0402	-0.05761	-2.43098
H	2.67068	3.13854	-2.01943
H	0.82656	3.43694	-2.18525
H	1.3282	0.73962	2.91413
H	-1.59938	-1.49477	0.64819
H	0.83825	-0.64062	4.89512
H	-3.93533	-0.05304	1.44258
H	-3.14318	0.28709	-2.77809
H	-5.67009	-1.79121	0.97069
H	-2.13509	-2.82712	2.66641
H	0.38385	5.1966	0.97317
H	-0.48215	4.1356	2.12974
H	-1.29015	4.63893	0.60442
H	-4.84574	-1.4631	-3.24128
H	2.04072	-3.73626	1.96922
H	1.9666	-4.22432	0.23771
H	0.63878	-3.25511	0.95043
H	-5.93151	-3.68434	-1.94195
H	-7.15923	-2.4259	-2.15892
H	-6.90385	-3.14704	-0.55062
H	5.73224	-3.26801	-2.42943
H	6.46254	-1.63294	-2.25475
H	6.28858	-2.68533	-0.82018
H	-0.90104	-2.42321	4.79905

M06-2X-D3/def-TZVP-SMD(toluene): E = -2100.99158115 hartree

Corrected G = -2100.532015 hartree

Int2

O	-2.4522	-2.21764	-0.04014
O	-1.17506	-2.45853	-1.85655
O	1.08601	1.9334	0.24976
O	2.20396	1.03679	1.96135
N	-0.9591	0.01962	2.00568
C	-0.40453	-1.06041	-0.03687
C	-2.00292	1.03722	0.08621
C	0.37145	-1.83717	1.13176
C	-1.1437	0.02315	0.74799
C	1.89457	-0.28631	-0.03455
C	1.76022	0.9567	0.84714
C	1.86218	-1.55783	0.82178
O	3.73651	1.00156	-0.81069
O	3.62652	-1.1251	-1.48156
C	0.68733	-0.50441	-0.96119
C	-1.3646	-1.9785	-0.77071
C	-0.13451	-1.09866	2.40649
C	0.10874	-3.30159	1.19533
C	3.17905	-0.20538	-0.85333
C	-2.28345	0.98703	-1.28523
C	-3.64954	2.97179	-1.10113
C	-2.56615	2.06389	0.85852
C	-3.10374	1.9495	-1.87425
C	-3.37955	3.02514	0.26868
C	-3.39896	-3.11816	-0.60076
C	0.82453	3.0822	1.04529
C	4.93467	1.16925	-1.56162
H	2.27483	-2.37299	0.21139
H	2.46448	-1.45968	1.73443
H	0.39092	0.41131	-1.48685
H	0.94862	-1.27366	-1.70106
H	-0.74216	-1.76633	3.03881
H	0.69999	-0.73939	3.02676
H	0.63294	-3.9809	0.52065
H	-0.71	-3.69561	1.79823
H	-1.86396	0.19834	-1.91287
H	-2.35637	2.08266	1.92873
H	-3.31413	1.89743	-2.9435
H	-3.81147	3.81948	0.87979
H	-3.76647	-2.73986	-1.56418
H	-4.22159	-3.18675	0.11793
H	-2.94305	-4.10609	-0.7549
H	0.20946	3.74871	0.43197
H	1.76454	3.57702	1.32586
H	0.2859	2.79032	1.95827
H	5.24926	2.20611	-1.40834
H	5.71007	0.47832	-1.20509
H	4.74859	0.98008	-2.6272
H	-4.28905	3.72565	-1.56331

M06-2X-D3/def-TZVP-SMD(toluene): E = -1281.44202863 hartree

Corrected G = -1281.098422 hartree

TS1

S	-2.25189	1.24608	0.17932

O	-0.02901	2.92453	1.21339
O	2.13335	3.45963	0.97339
O	2.67265	-2.12018	0.42416
O	-2.31313	2.4979	-0.56817
O	1.2888	-1.99172	-1.32596
O	-2.37057	1.22644	1.62368
N	-0.80426	0.42597	-0.22829
C	1.3858	1.23606	0.48878
C	0.10342	-0.54944	1.84014
C	0.99963	1.38802	-1.65881
C	0.22219	0.33869	0.7242
C	2.86528	-0.18255	-0.8837
C	2.16051	-1.51963	-0.6467
C	2.24685	0.60802	-2.05349
O	4.40413	-1.49366	-2.09711
O	5.27329	0.07515	-0.76358
C	2.78216	0.71497	0.3523
C	1.24532	2.6435	0.93711
C	-0.32616	0.62062	-1.59982
C	0.93813	2.73836	-1.92993
C	-3.50678	0.18595	-0.50023
C	4.32199	-0.50285	-1.20913
C	0.97541	-0.46439	2.95262
C	-0.09922	-2.37192	3.98647
C	-0.87496	-1.57516	1.83856
C	0.87041	-1.36505	4.00479
C	-4.07401	-0.79475	0.31399
C	-3.92815	0.37028	-1.81402
C	-5.05496	-1.62318	-0.21856
C	-0.97117	-2.46742	2.89602
C	-0.35993	4.27207	1.49286
C	-5.48025	-1.4829	-1.54826
C	-4.90883	-0.47376	-2.33137
C	2.10935	-3.3768	0.78375
C	-6.53287	-2.40042	-2.10628
C	5.71647	-1.86882	-2.50173
H	3.00238	1.32223	-2.41209
H	2.01127	-0.08011	-2.87878
H	3.10904	0.15443	1.24291
H	3.46802	1.56262	0.22315
H	-1.08356	1.17211	-2.16816
H	-0.19161	-0.36796	-2.05525
H	1.83712	3.31322	-2.16091
H	-0.00841	3.27456	-1.82251
H	1.72112	0.33144	2.99514
H	-1.52845	-1.67192	0.97058
H	1.54826	-1.27698	4.85558
H	-3.75661	-0.88646	1.35412
H	-3.50794	1.17761	-2.41564
H	-5.50969	-2.39073	0.41163
H	-1.72659	-3.25526	2.8692
H	0.15272	4.61808	2.40122
H	-1.44507	4.29158	1.63467
H	-0.07451	4.92183	0.65326
H	-5.24516	-0.33768	-3.36102
H	2.605	-3.68049	1.71142
H	2.2926	-4.11677	-0.00766
H	1.0281	-3.27676	0.94534
H	-6.83944	-2.09308	-3.11425
H	-7.42378	-2.41371	-1.46182
H	-6.15575	-3.43279	-2.1639
H	5.59458	-2.68847	-3.21667
H	6.22915	-1.0219	-2.97708
H	6.30404	-2.20201	-1.63582
H	-0.17665	-3.07539	4.81666

M06-2X-D3/def-TZVP-SMD(toluene): E = -2100.96677077 hartree

Corrected G = -2100.50726 hartree

TS2

S	-2.38668	1.50509	-0.04224
O	0.02965	3.09781	0.74947
O	1.63045	2.65659	2.2529
O	2.83773	-2.21831	0.65876
O	-2.59926	2.74629	-0.80025
O	1.61078	-2.16779	-1.20675
O	-2.31425	1.52193	1.42066
N	-0.62356	0.60054	-0.74783
C	1.40705	1.25032	0.29454
C	-0.14663	-0.6813	1.25151
C	1.48876	1.6381	-1.23202
C	0.18968	0.33405	0.26424
C	3.02227	-0.26119	-0.63292
C	2.39421	-1.64924	-0.46043
C	2.37447	0.49784	-1.81994
O	4.74354	-1.47682	-1.6853

O	5.38051	0.2533	-0.42393
C	2.75477	0.61528	0.59626
C	1.07268	2.41295	1.21677
C	0.01704	1.53093	-1.68639
C	2.08606	2.97863	-1.47614
C	-3.62184	0.33184	-0.53577
C	4.5152	-0.44904	-0.86806
C	0.4001	-0.6731	2.54829
C	-0.86085	-2.66055	3.10998
C	-1.04861	-1.70395	0.89846
C	0.04427	-1.6582	3.46517
C	-4.15625	-0.53127	0.41471
C	-3.99185	0.26986	-1.87891
C	-5.0899	-1.48047	0.00307
C	-1.40622	-2.67858	1.82333
C	-0.53739	4.08882	1.59878
C	-5.47967	-1.57733	-1.33792
C	-4.91883	-0.68893	-2.2692
C	2.27994	-3.48615	0.98377
C	-6.47876	-2.60761	-1.78721
C	6.10475	-1.72953	-2.01445
H	3.13934	0.92156	-2.48521
H	1.77749	-0.20901	-2.40927
H	2.80007	0.05063	1.5337
H	3.51566	1.40709	0.64286
H	-0.48446	2.50751	-1.65219
H	-0.06812	1.13354	-2.70826
H	3.15862	3.08353	-1.6474
H	1.48777	3.87942	-1.33536
H	1.0762	0.12902	2.84974
H	-1.44535	-1.72543	-0.11804
H	0.46668	-1.63417	4.47088
H	-3.83946	-0.45482	1.45599
H	-3.56548	0.9697	-2.59971
H	-5.52459	-2.15933	0.73961
H	-2.10729	-3.46452	1.53587
H	0.15836	4.9305	1.72017
H	-0.76864	3.65803	2.58102
H	-1.45694	4.41414	1.10212
H	-5.22035	-0.75051	-3.31719
H	2.72714	-3.78315	1.93789
H	2.51945	-4.22232	0.20419
H	1.1883	-3.40554	1.08231
H	-7.33915	-2.12936	-2.27814
H	-6.85093	-3.20127	-0.94258
H	-6.02718	-3.29523	-2.51796
H	6.10367	-2.60104	-2.67656
H	6.54436	-0.86311	-2.52671
H	6.68629	-1.94081	-1.1071
H	-1.13946	-3.42753	3.83448

M06-2X-D3/def-TZVP-SMD(toluene): E = -2100.97553811 hartree

Corrected G = -2100.516594 hartree

Ts

S	2.15071	-0.00022	0.24136
O	2.64451	-1.2864	-0.28025
O	2.64511	1.28588	-0.27989
C	0.36397	0.00016	0.09718
C	-0.30819	-1.21909	0.07234
C	-1.69745	-1.20582	-0.00085
C	-2.41101	0.00072	-0.03441
C	-1.69718	1.20676	-0.00109
C	-0.30762	1.21943	0.07214
H	0.25059	-2.1557	0.09
H	-2.24056	-2.15236	-0.03775
H	-2.23978	2.15354	-0.03813
H	0.25143	2.15589	0.08972
C	-3.91377	-0.00039	-0.07913
H	-4.2996	0.90403	-0.56763
H	-4.29596	-0.87918	-0.61534
H	-4.32697	-0.02924	0.94151

M06-2X-D3/def-TZVP-SMD(toluene: E = -819.539157838 hartree

Corrected G = -819.445588 hartree

19. References

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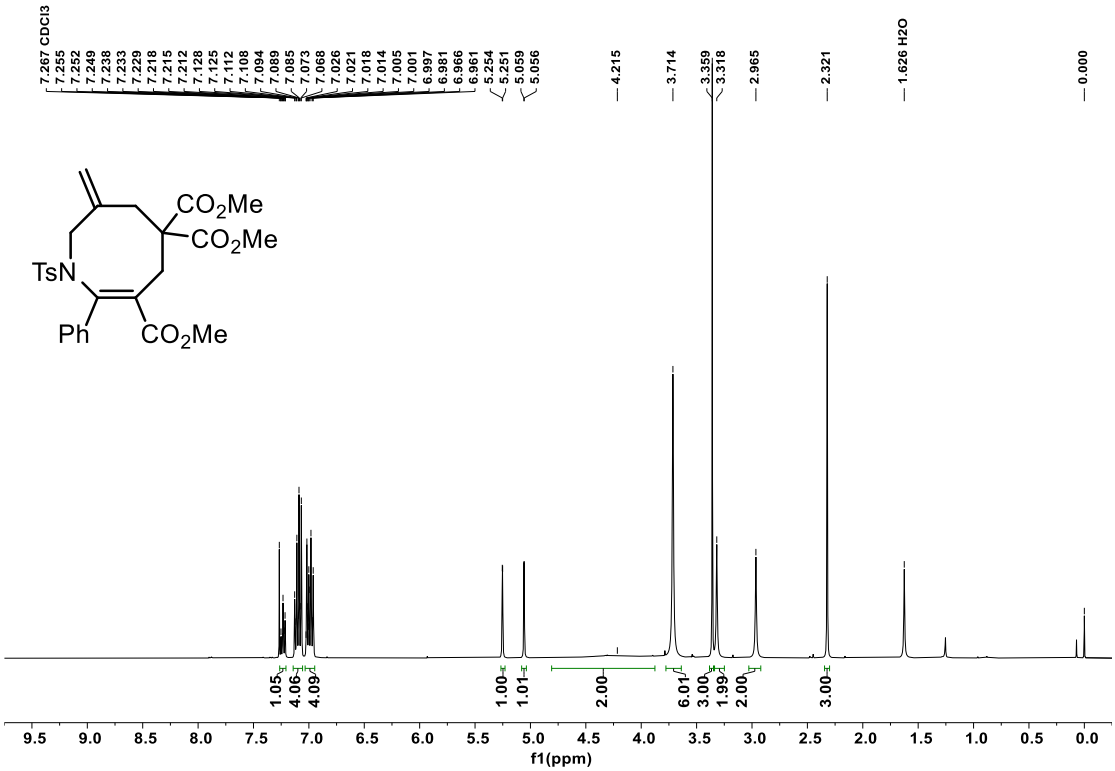
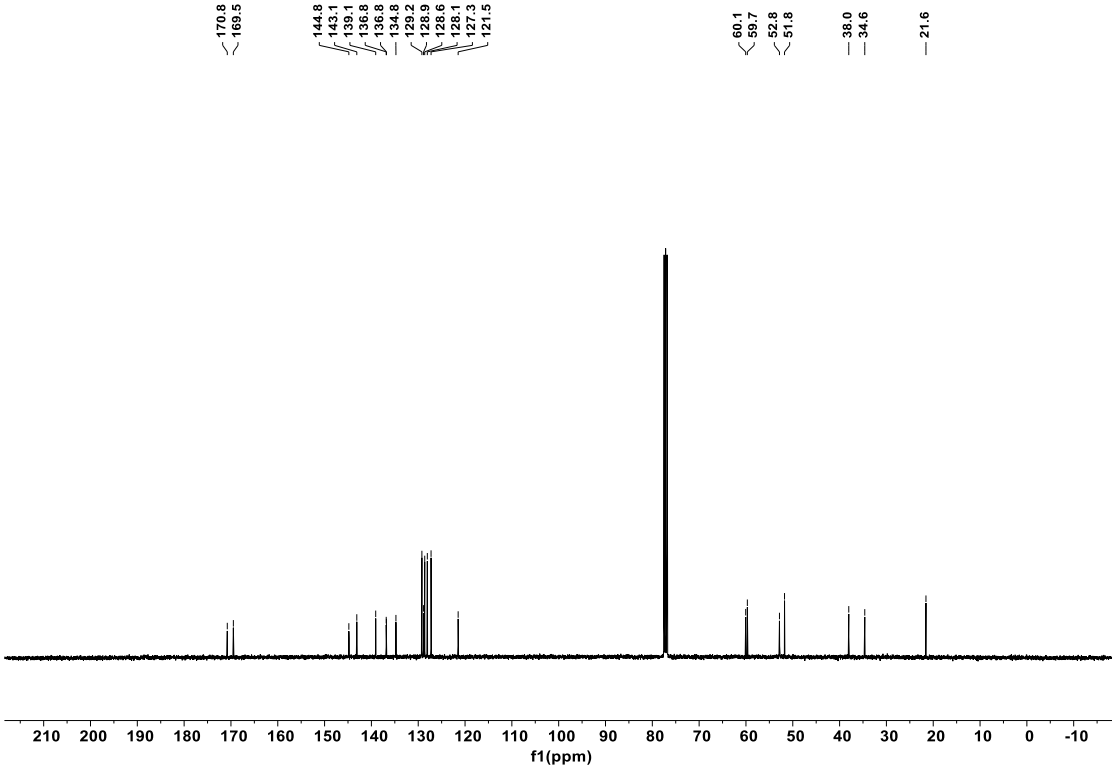
20. ^{1}H NMR and ^{13}C NMR spectra

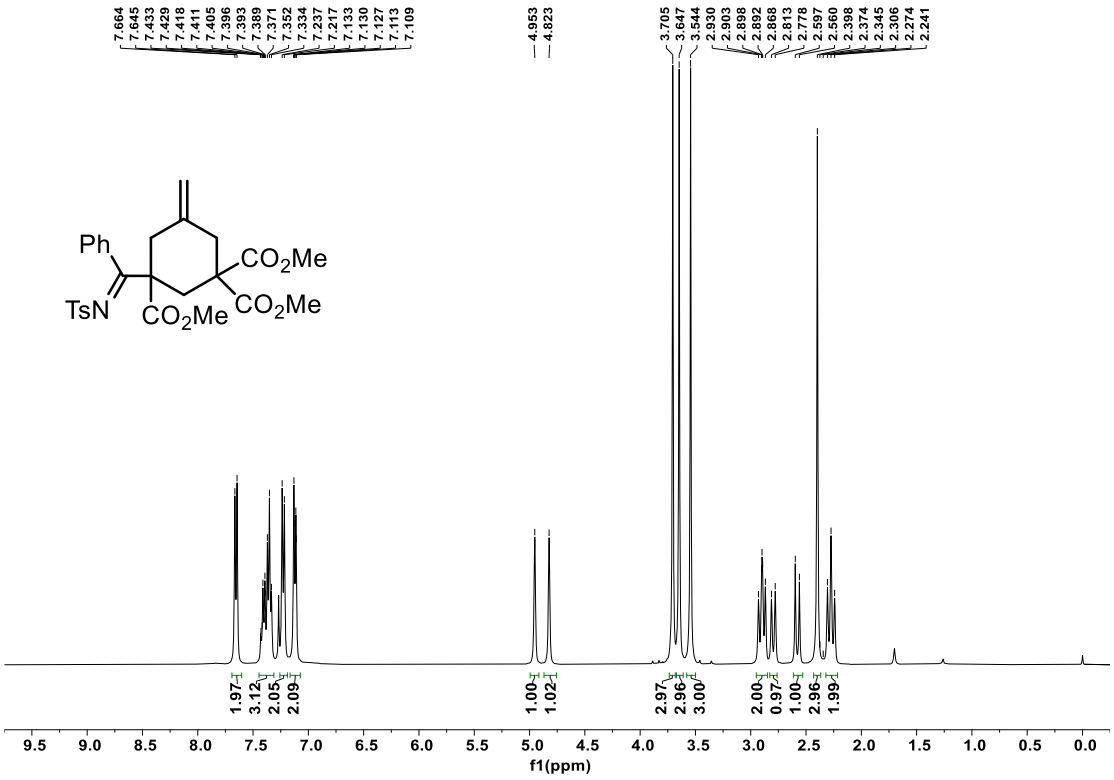
^{1}H NMR of **3a** in $CDCl_3$ (400 MHz)



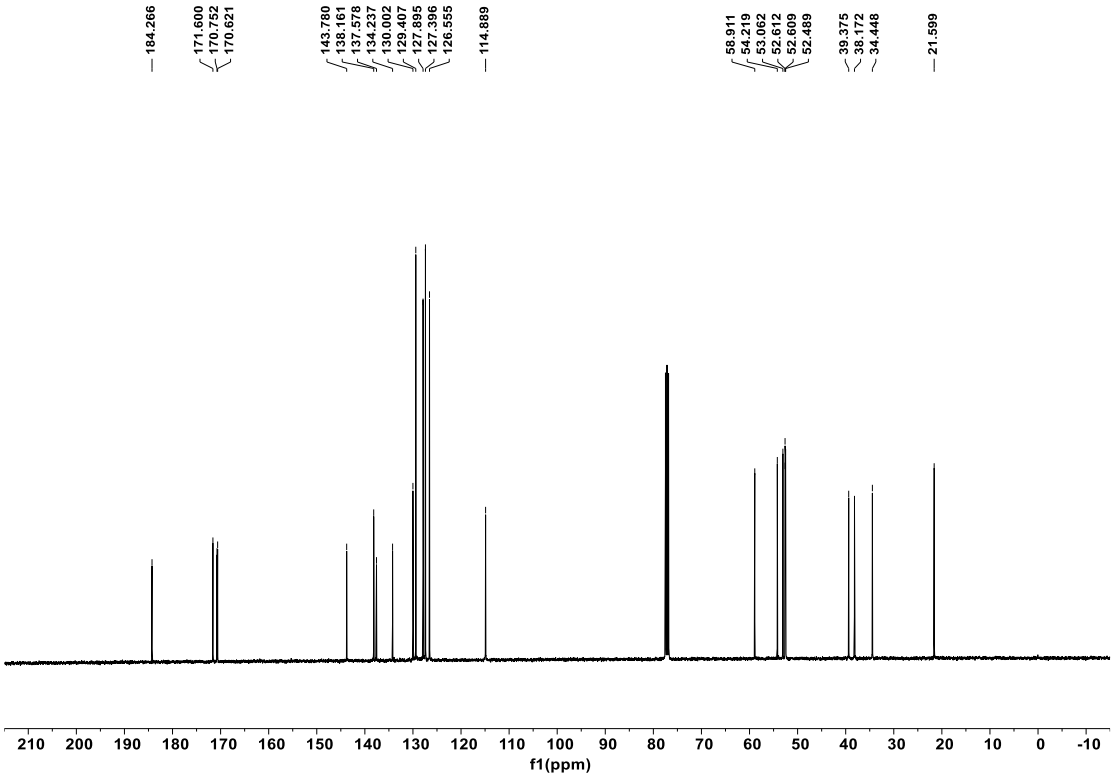
^{13}C NMR of **3a** in $CDCl_3$ (100 MHz)



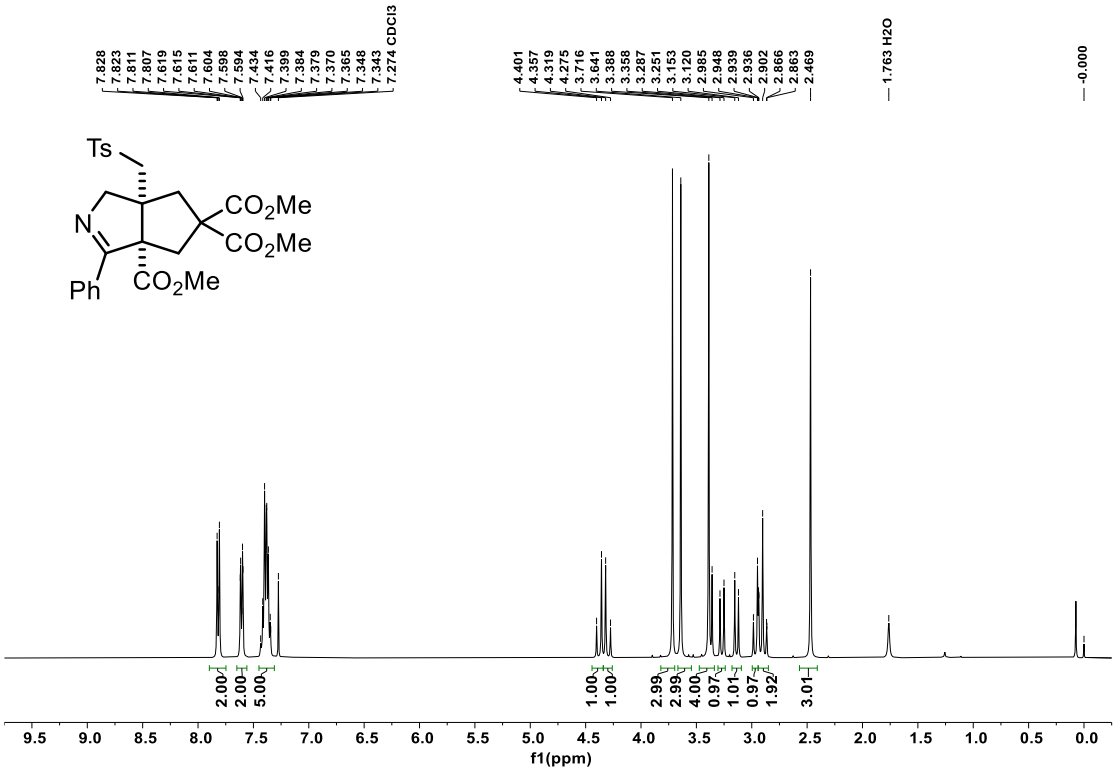
^{1}H NMR of **4a** in $CDCl_3$ (400 MHz)



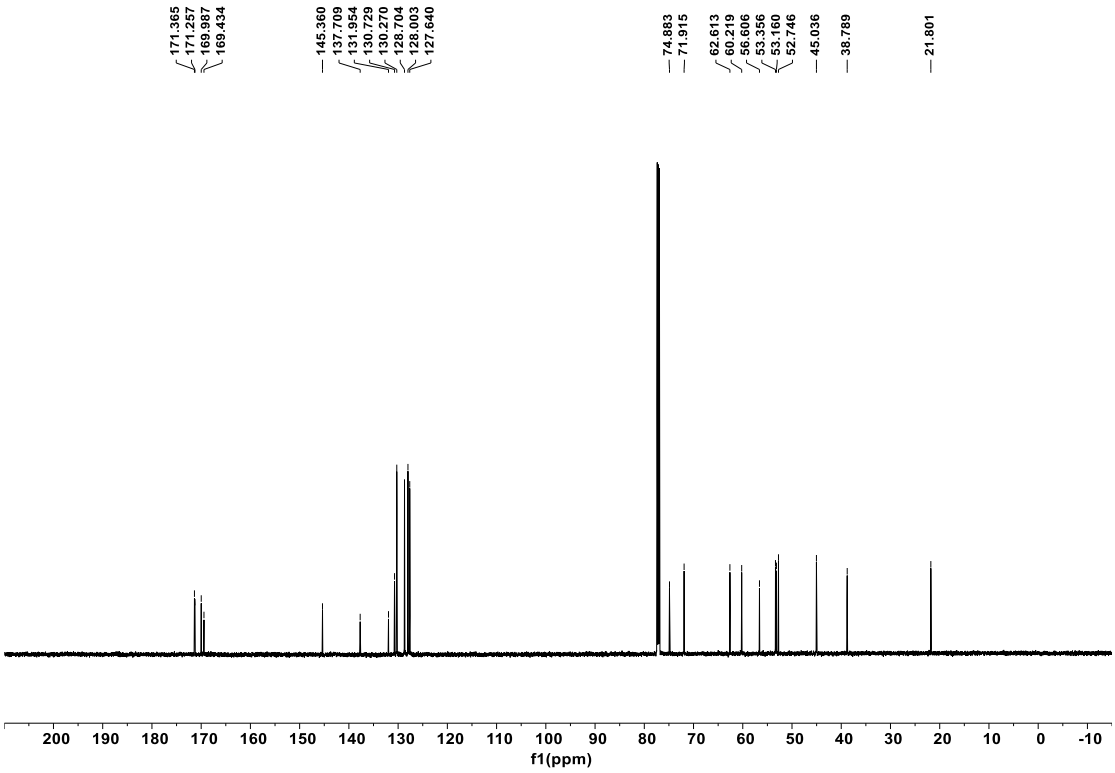
^{13}C NMR of **4a** in $CDCl_3$ (100 MHz)



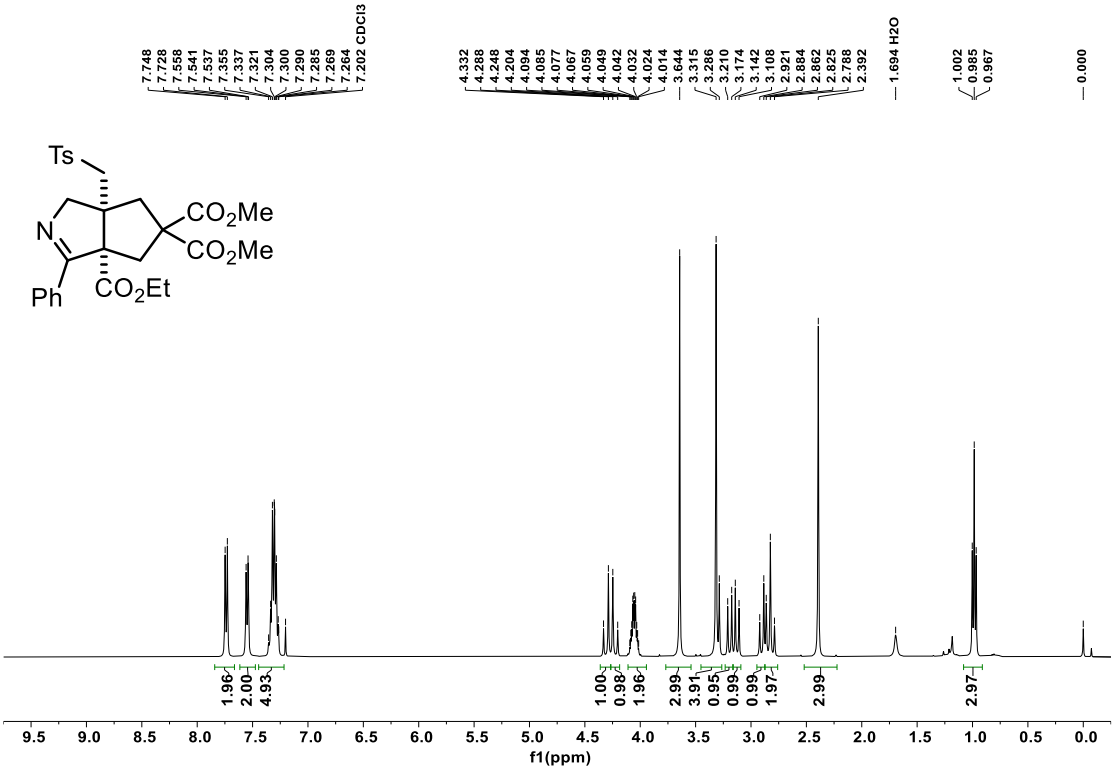
^{1}H NMR of **5a** in $CDCl_3$ (400 MHz)



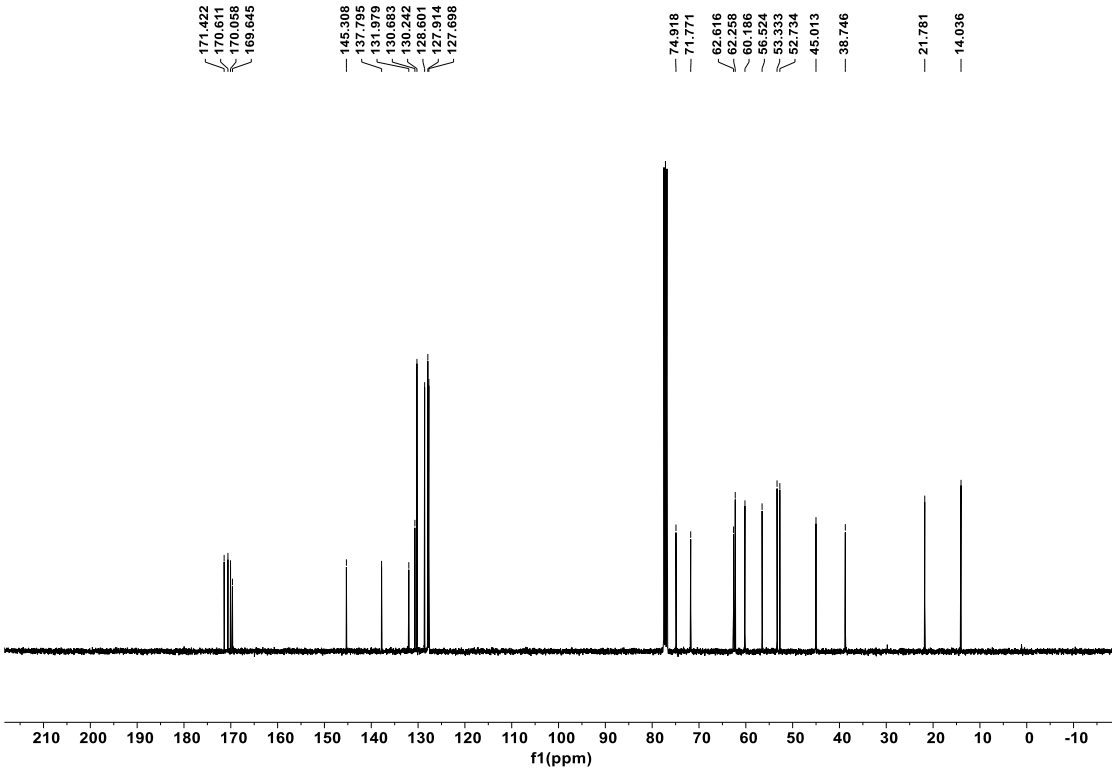
^{13}C NMR of **5a** in $CDCl_3$ (100 MHz)



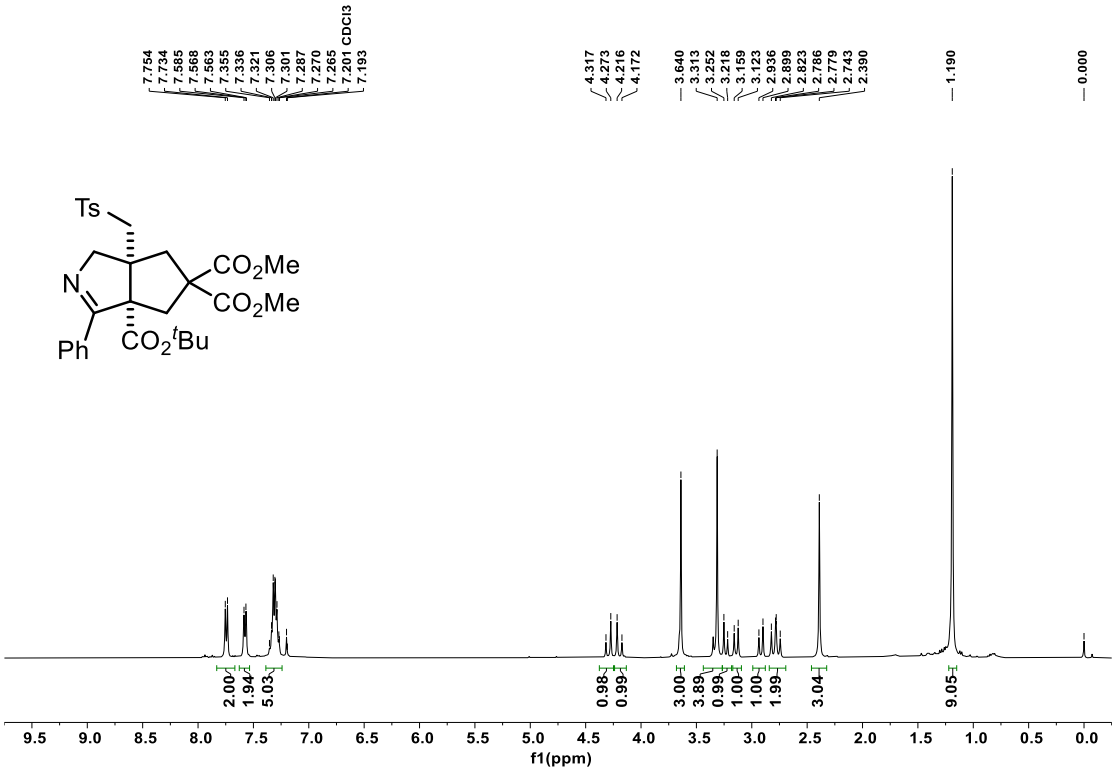
^{1}H NMR of **5b** in $CDCl_3$ (400 MHz)



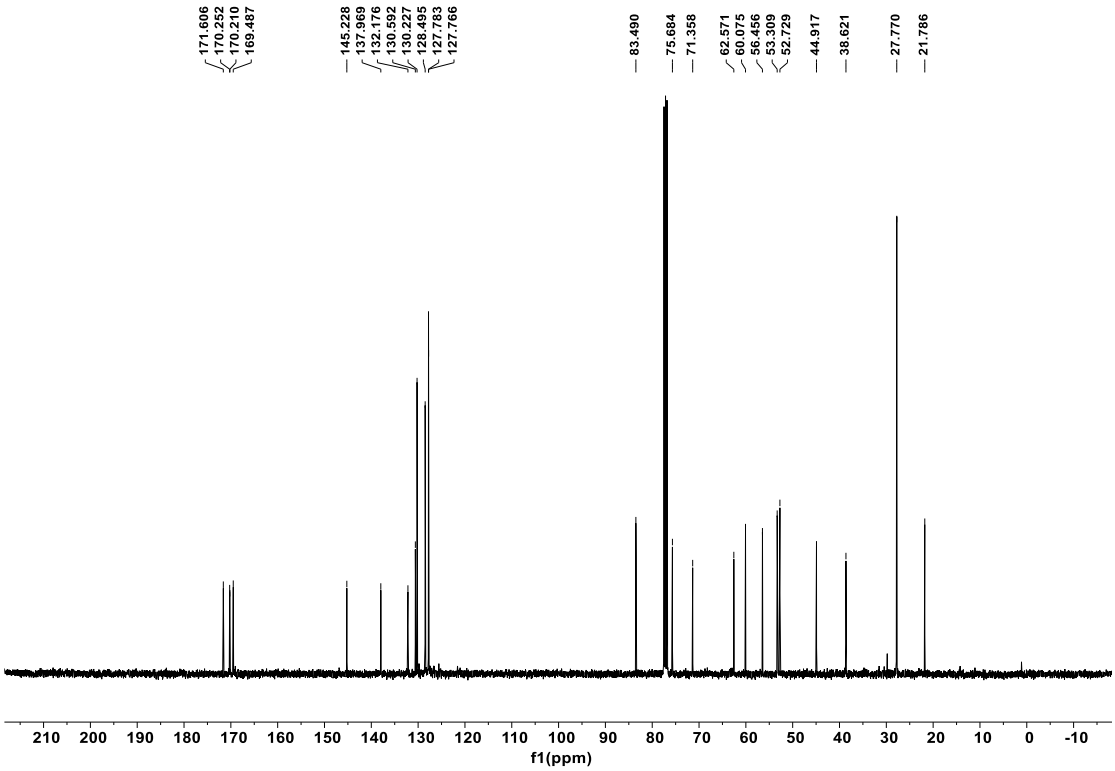
^{13}C NMR of **5b** in $CDCl_3$ (100 MHz)



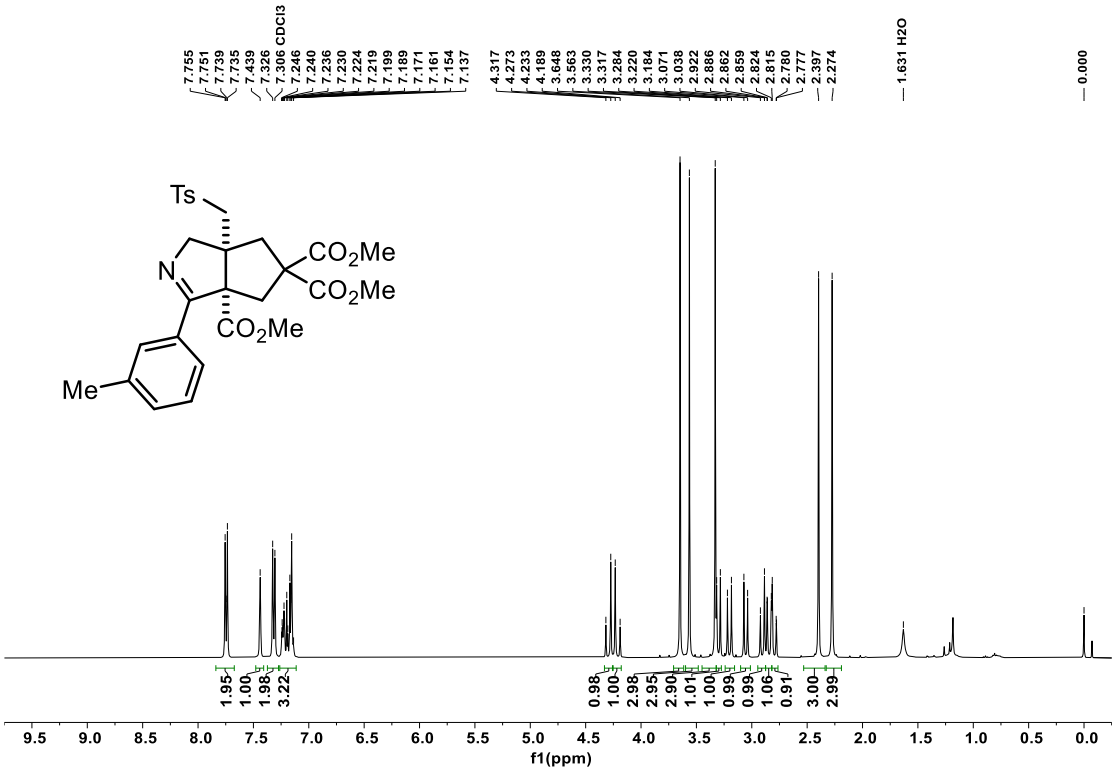
^{1}H NMR of **5c** in $CDCl_3$ (400 MHz)



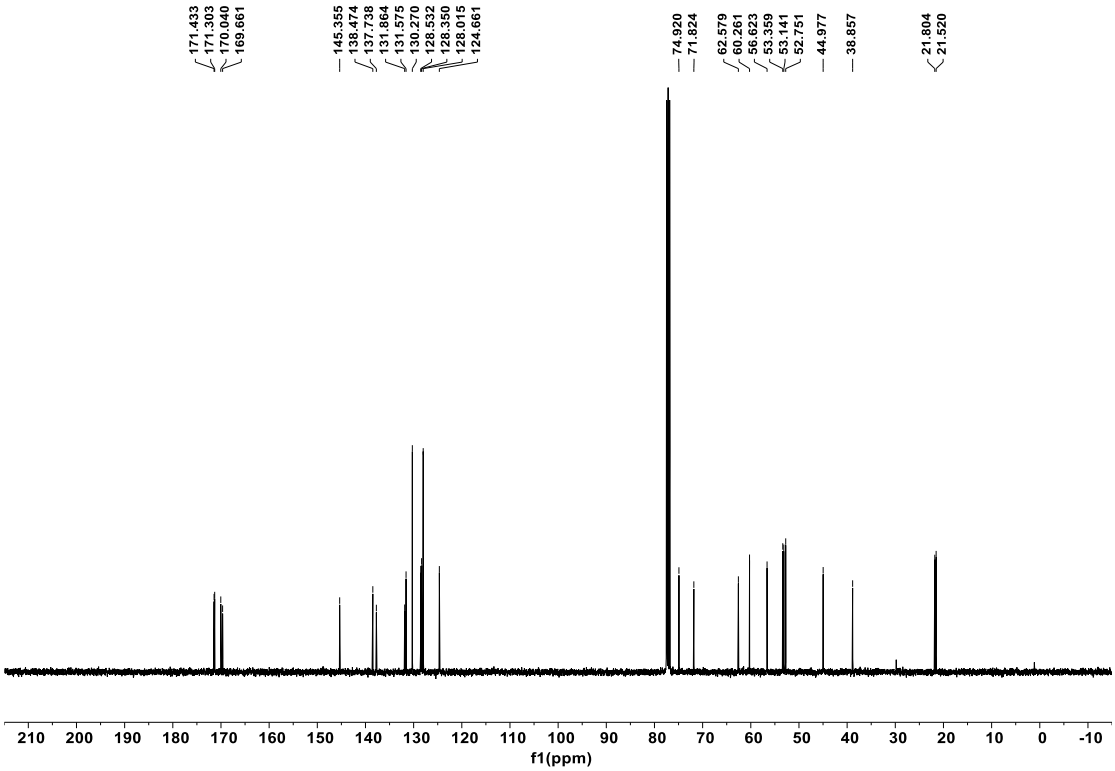
^{13}C NMR of **5c** in $CDCl_3$ (100 MHz)



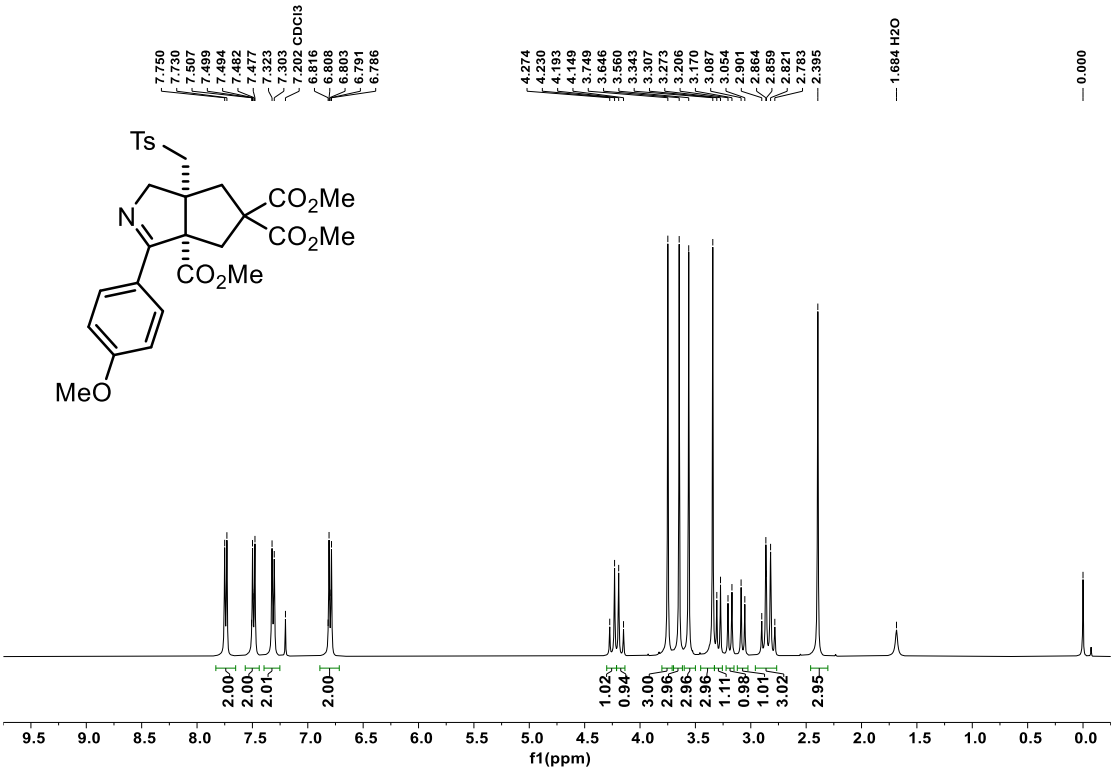
^{1}H NMR of **5d** in $CDCl_3$ (400 MHz)



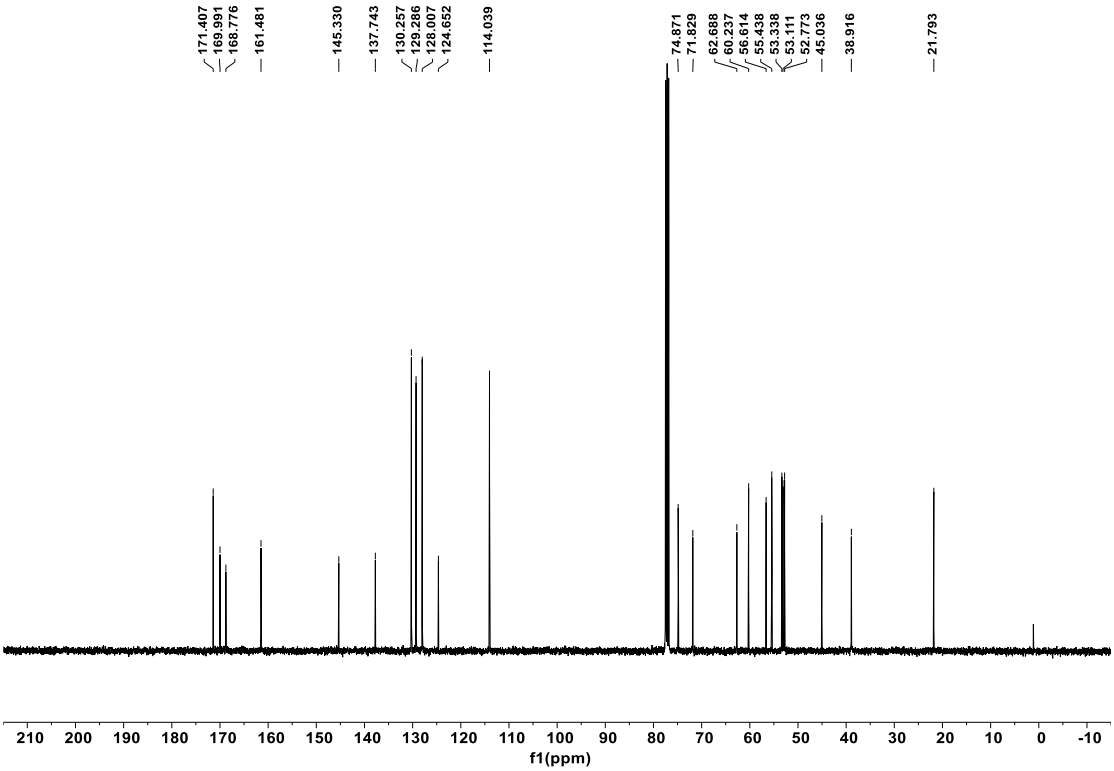
^{13}C NMR of 5**d** in $CDCl_3$ (100 MHz)



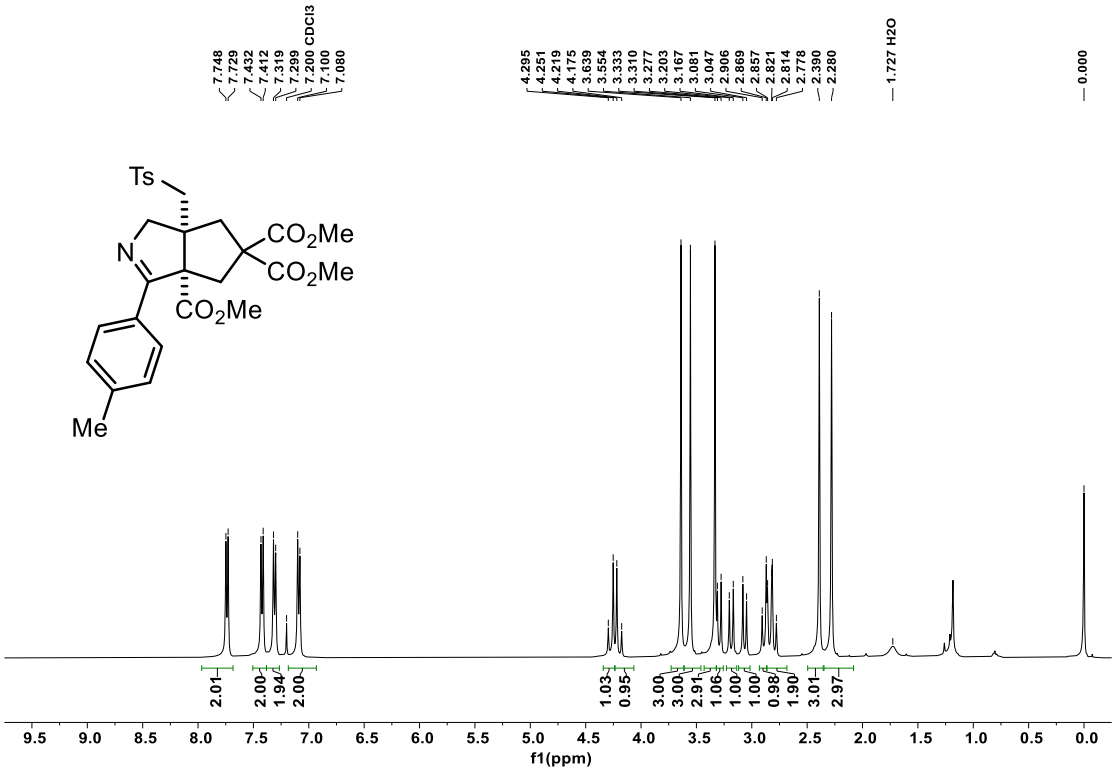
^{1}H NMR of **5e** in $CDCl_3$ (400 MHz)



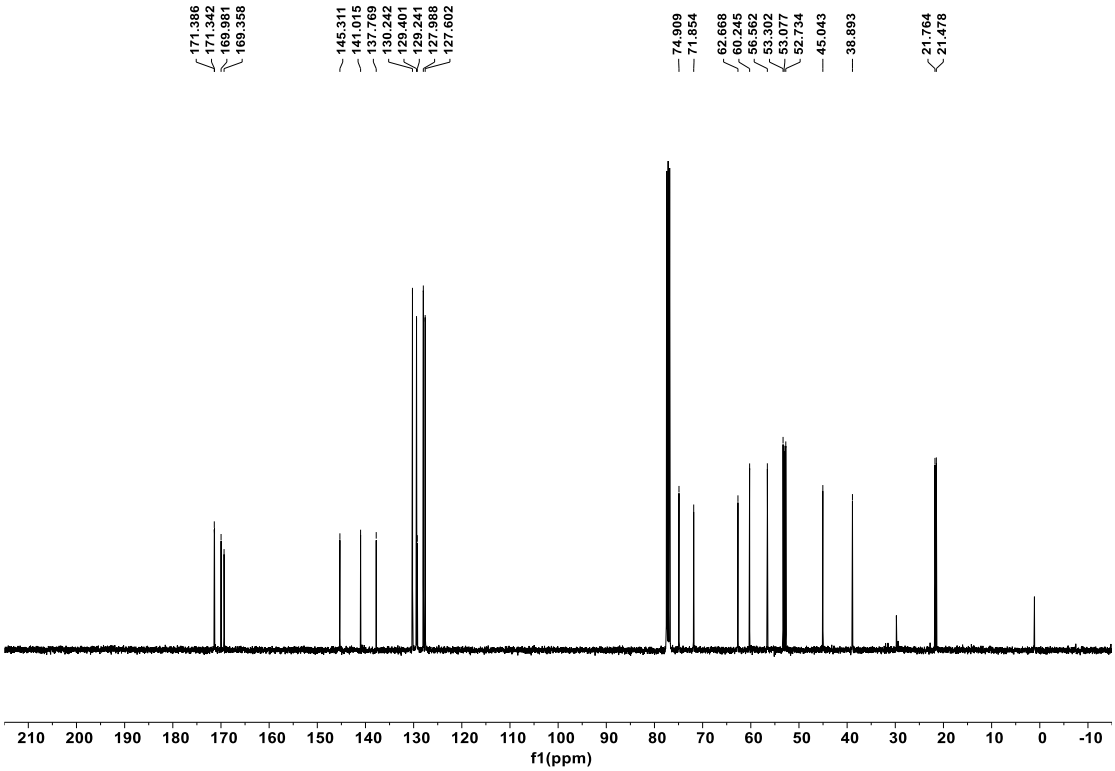
^{13}C NMR of **5e** in $CDCl_3$ (100 MHz)



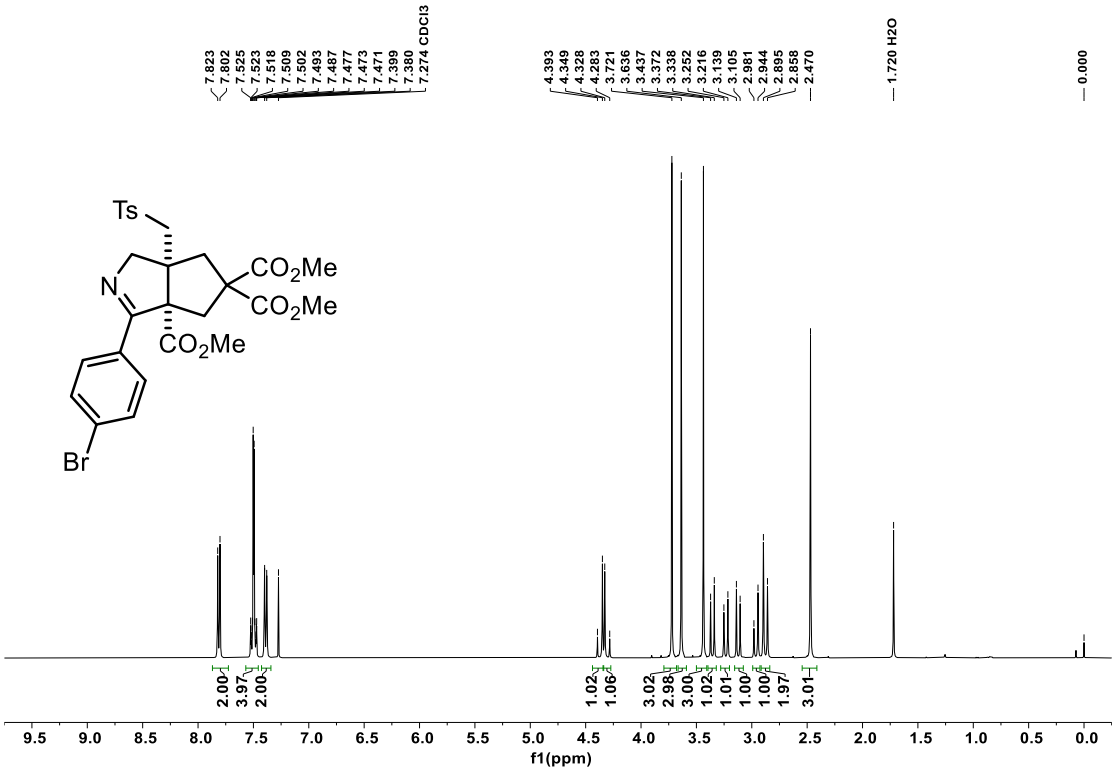
^{1}H NMR of **5f** in $CDCl_3$ (400 MHz)



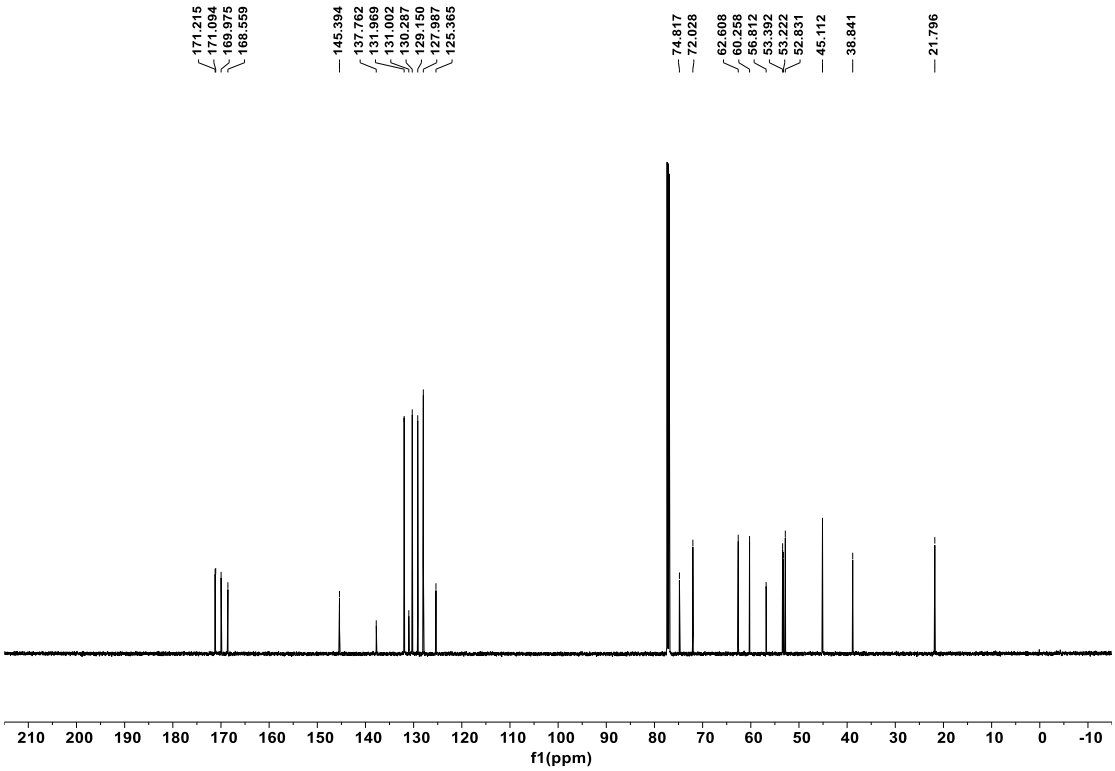
^{13}C NMR of **5f** in $CDCl_3$ (100 MHz)



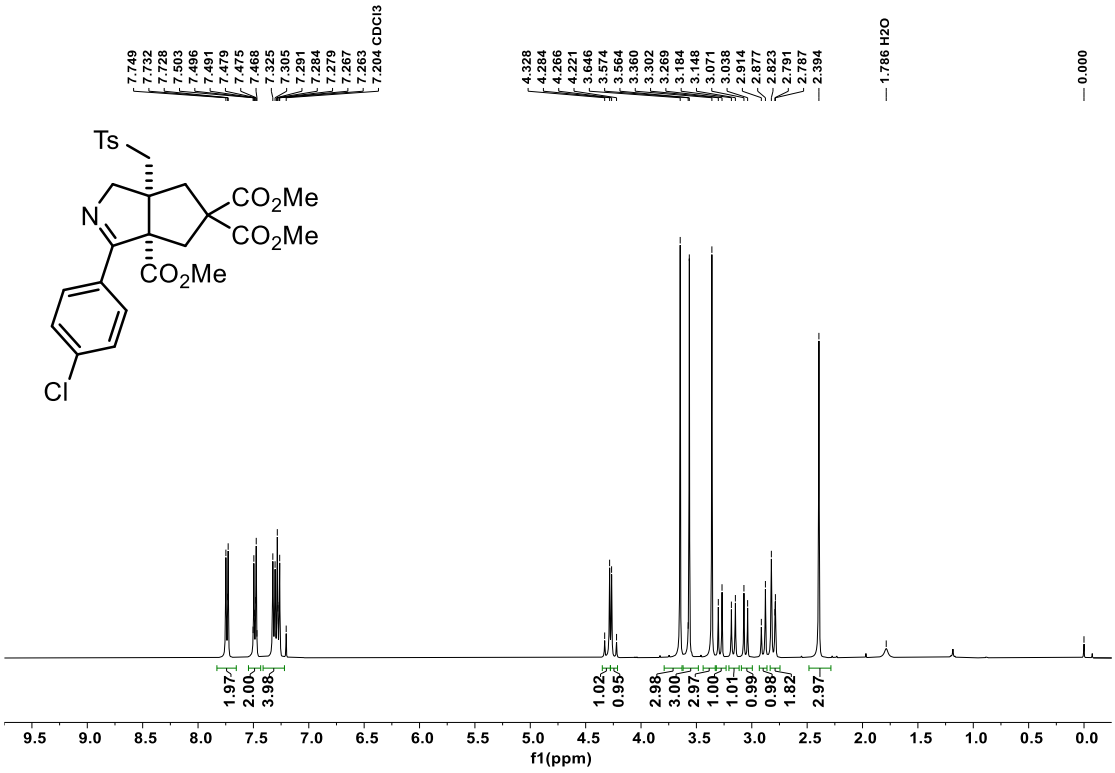
^{1}H NMR of **5g** in $CDCl_3$ (400 MHz)



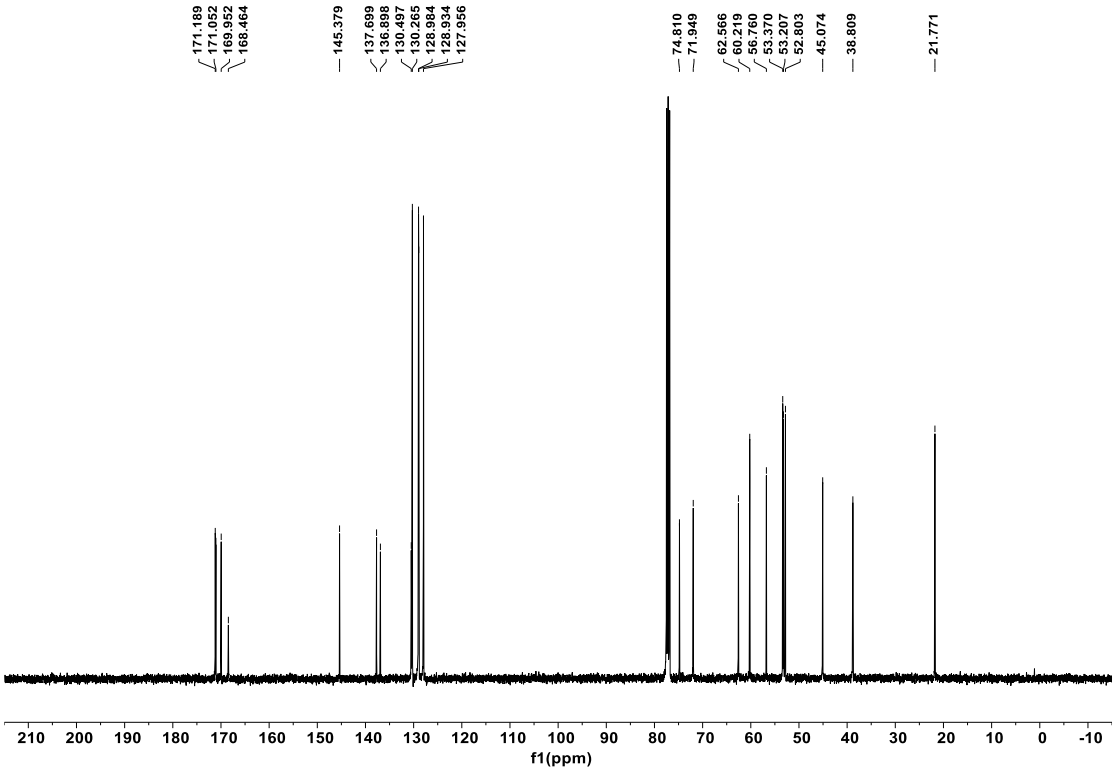
^{13}C NMR of **5g** in $CDCl_3$ (100 MHz)



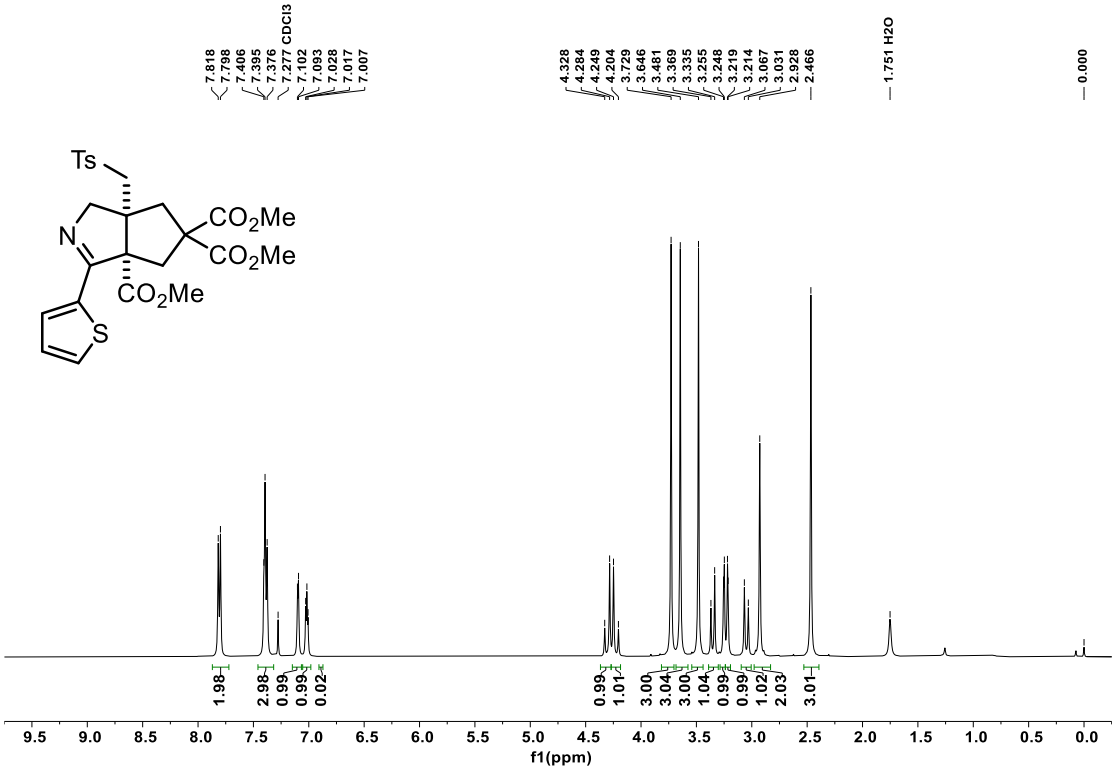
^{1}H NMR of **5h** in $CDCl_3$ (400 MHz)



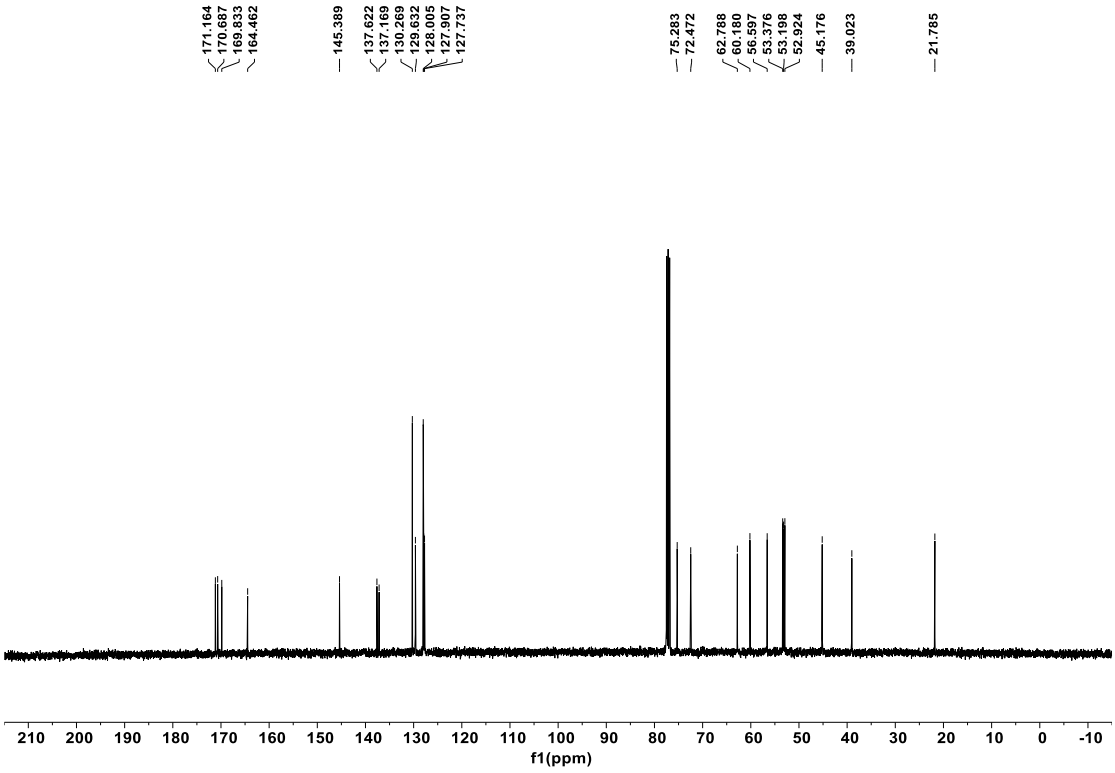
^{13}C NMR of **5h** in $CDCl_3$ (100 MHz)



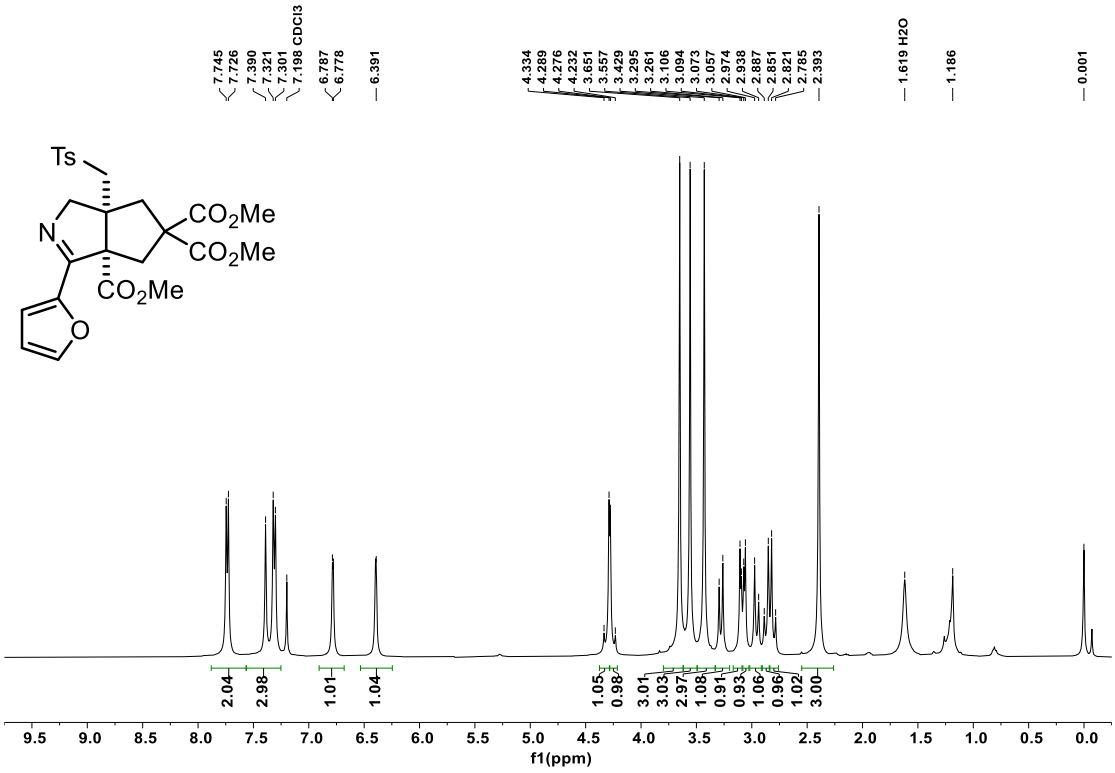
^{1}H NMR of **5i** in $CDCl_3$ (400 MHz)



^{13}C NMR of **5i** in $CDCl_3$ (100 MHz)



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



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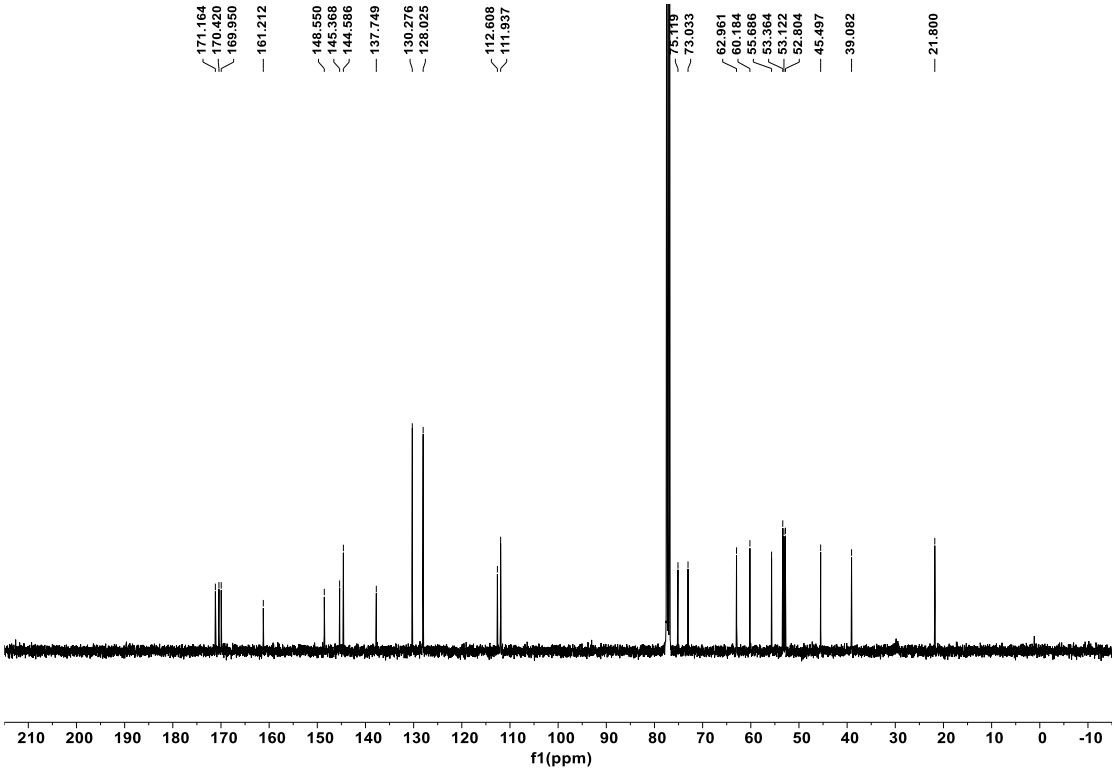
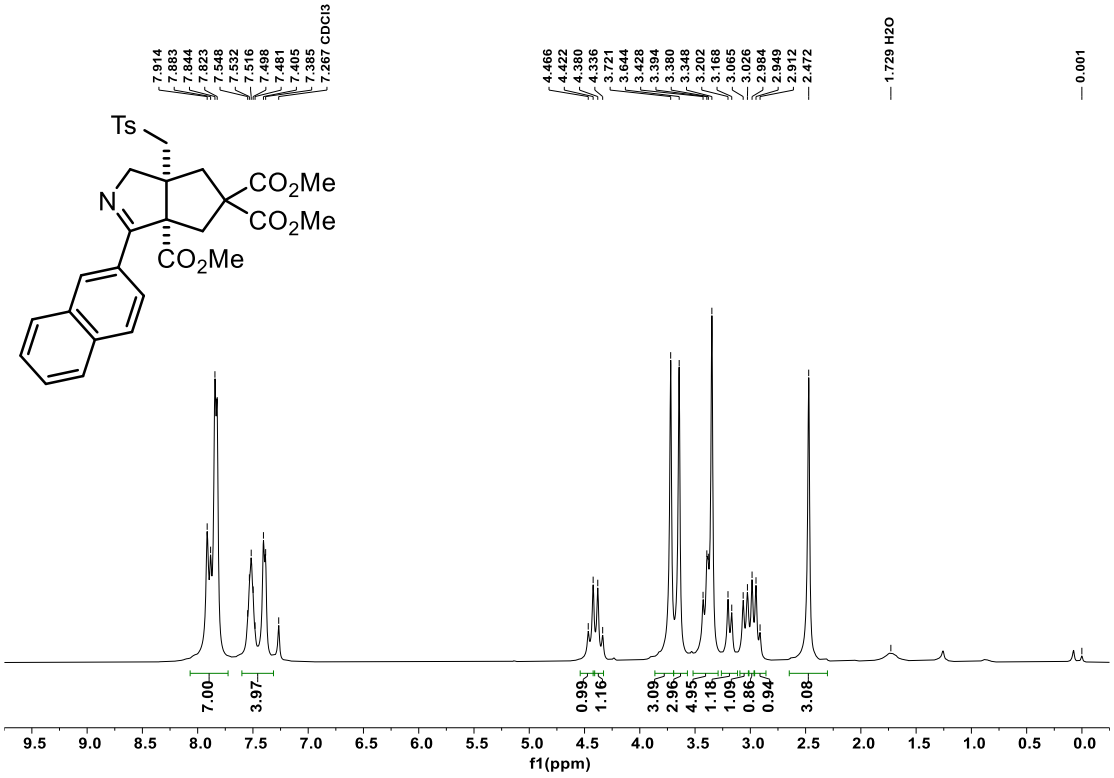
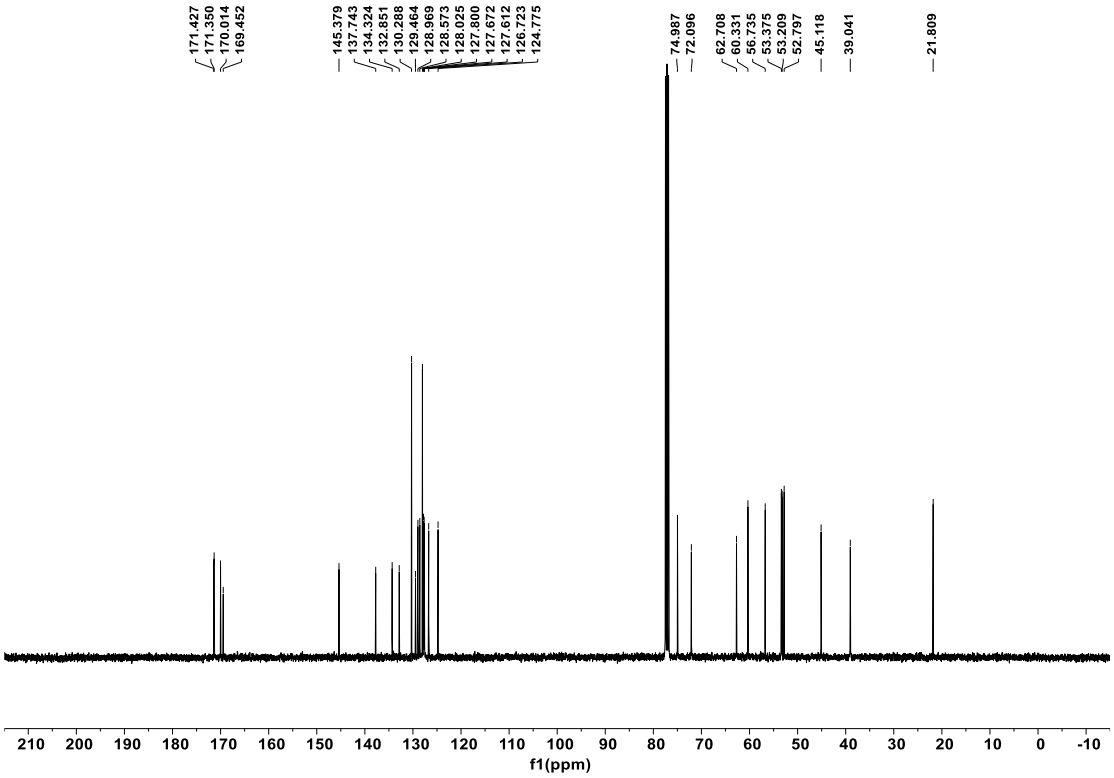


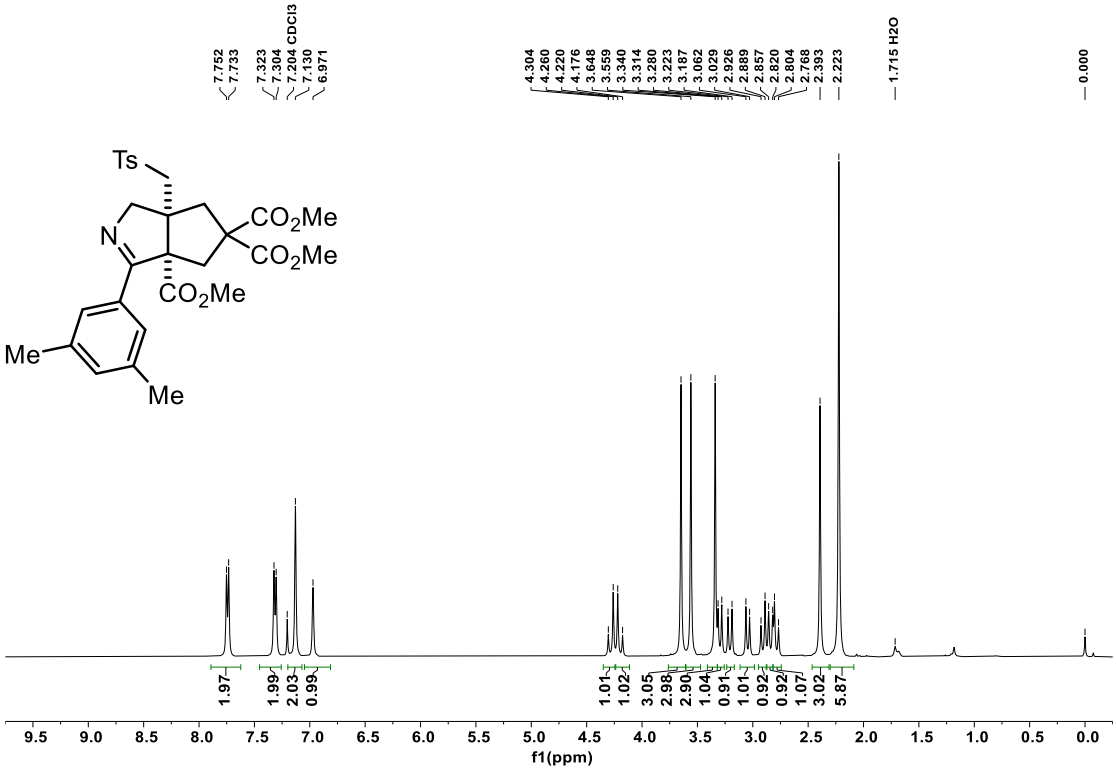
^{1}H NMR of **5k** in $CDCl_3$ (400 MHz)



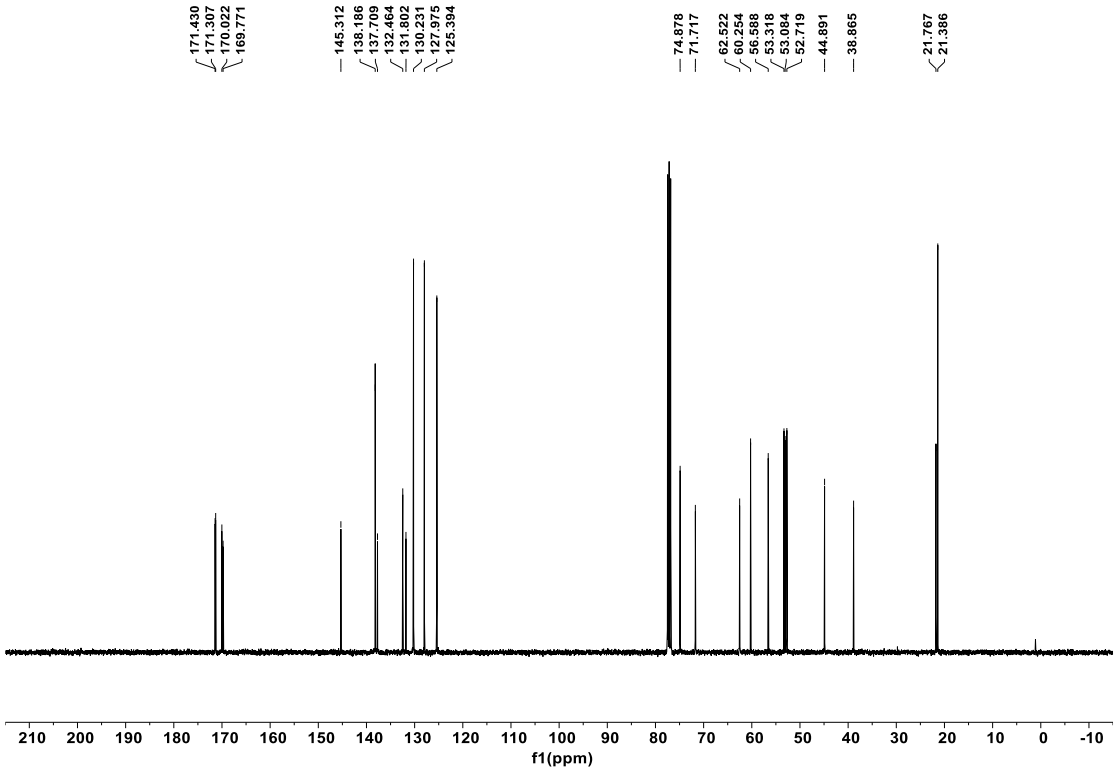
^{13}C NMR of **5k** in $CDCl_3$ (100 MHz)



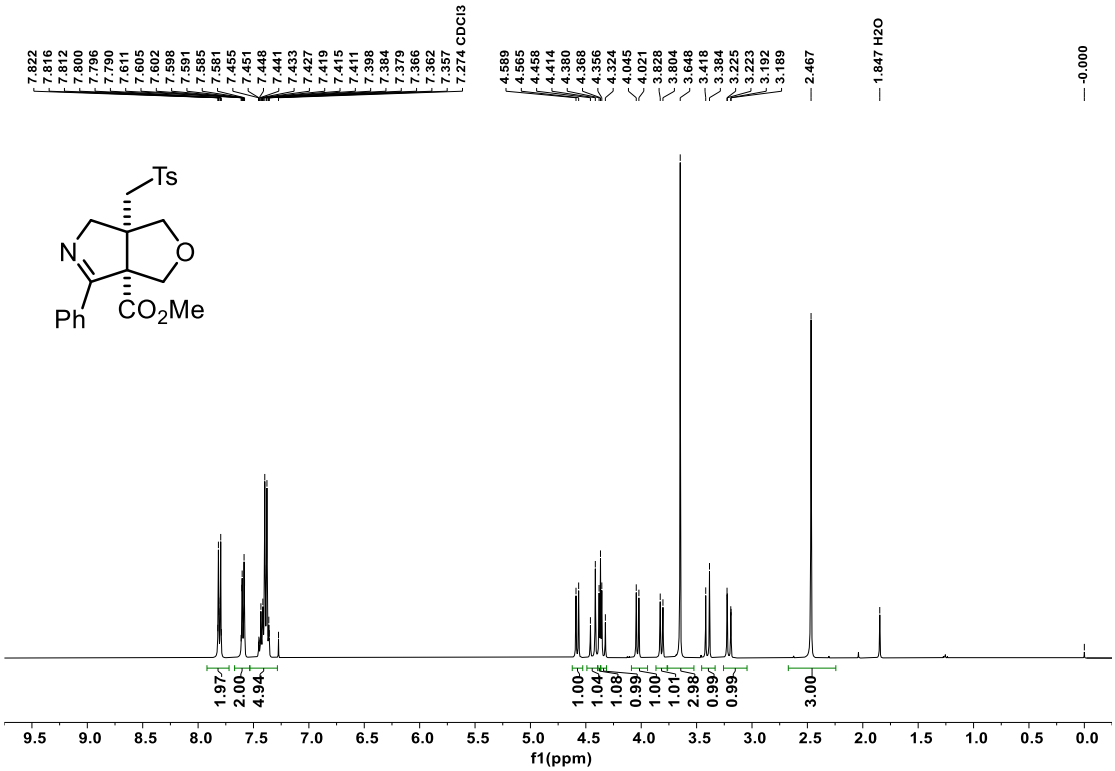
^{1}H NMR of **5l** in $CDCl_3$ (400 MHz)



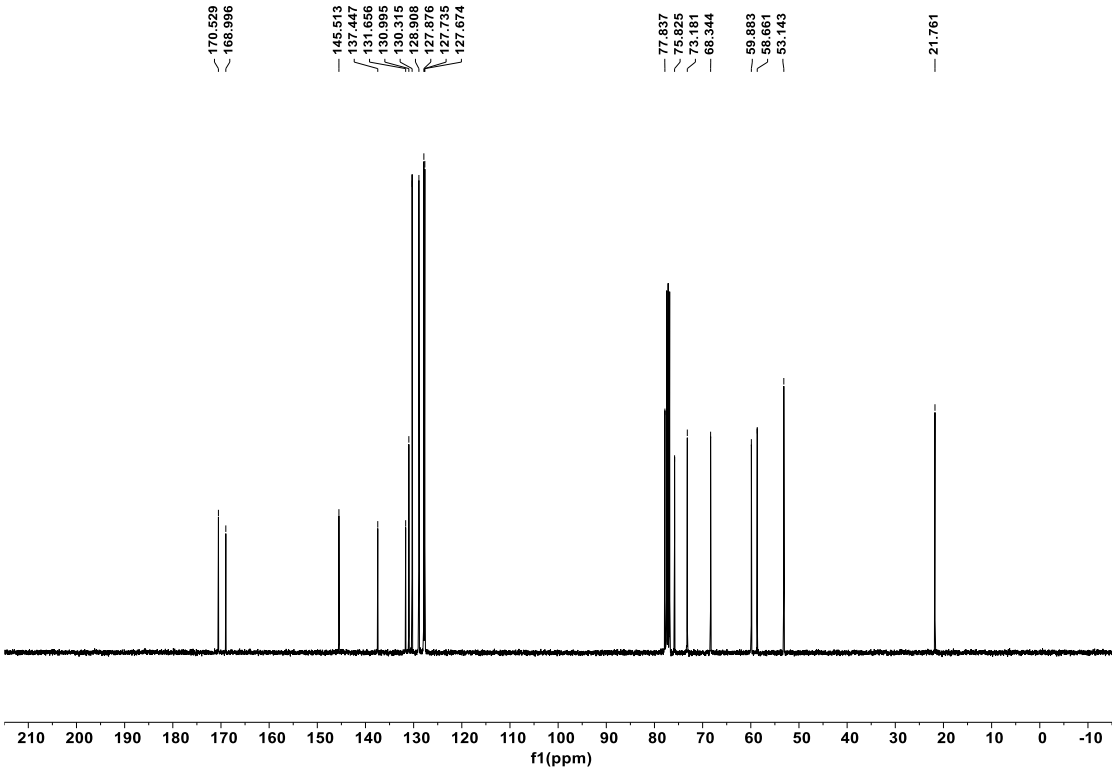
^{13}C NMR of **5l** in $CDCl_3$ (100 MHz)



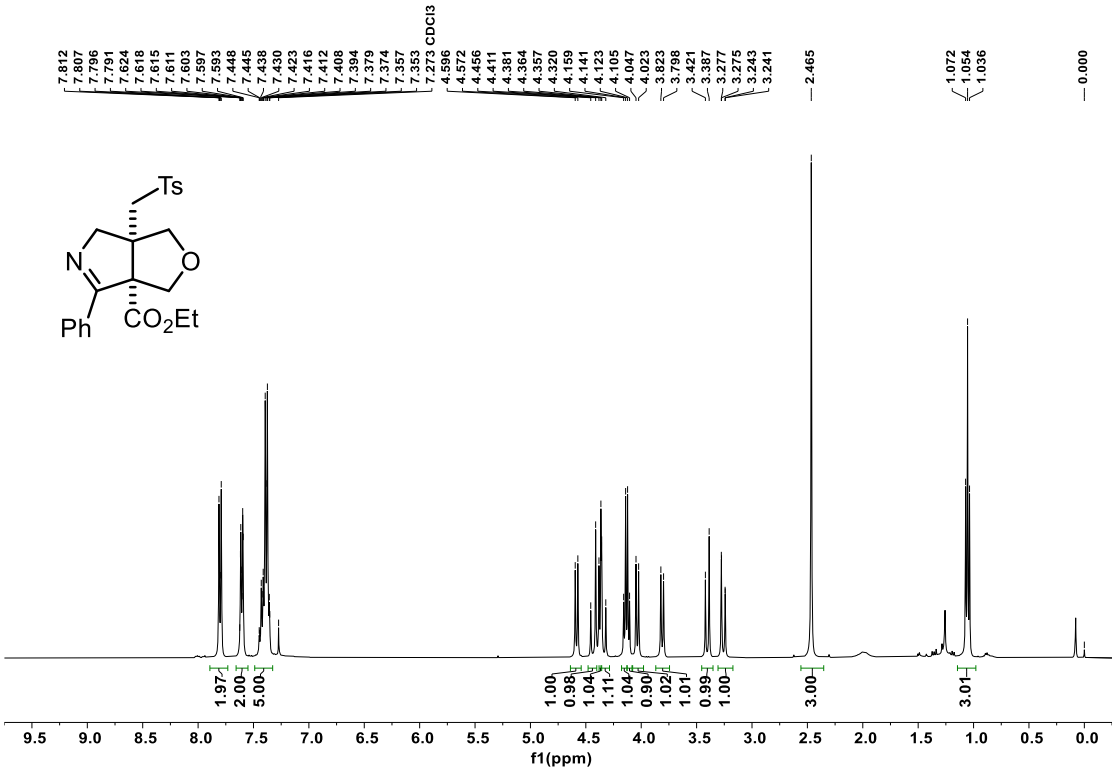
^{1}H NMR of **6a** in $CDCl_3$ (400 MHz)



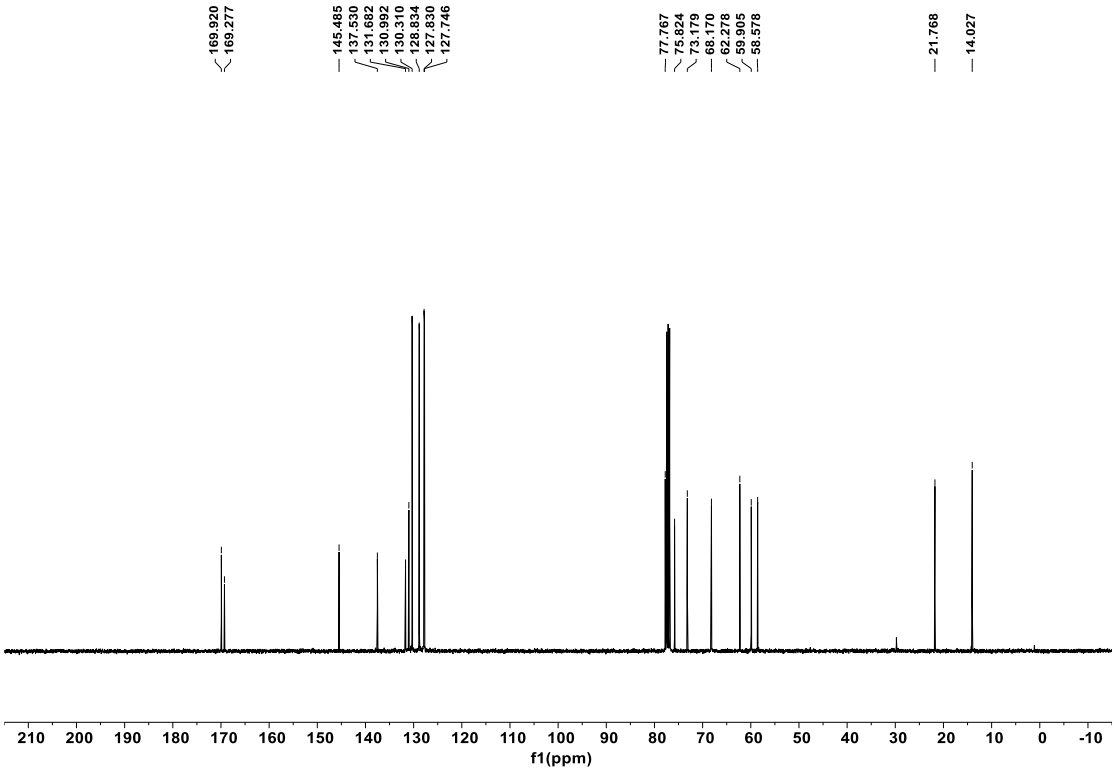
^{13}C NMR of **6a** in $CDCl_3$ (100 MHz)



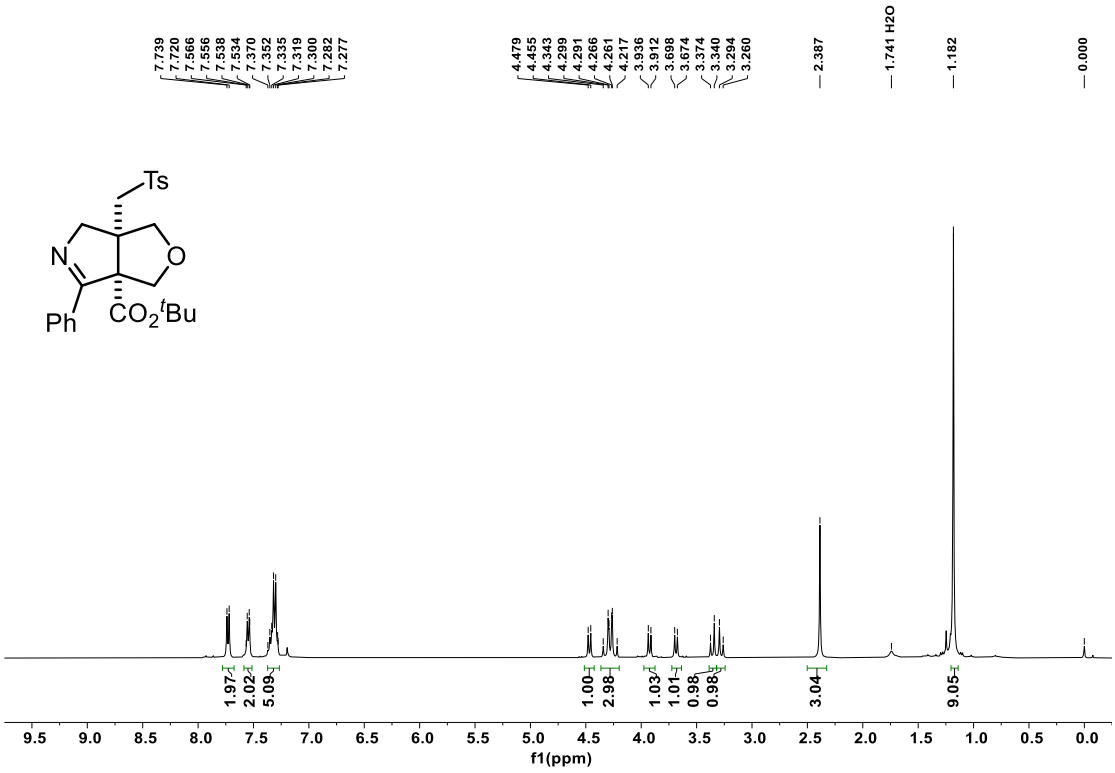
^{1}H NMR of **6b** in $CDCl_3$ (400 MHz)



^{13}C NMR of **6b** in $CDCl_3$ (100 MHz)



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



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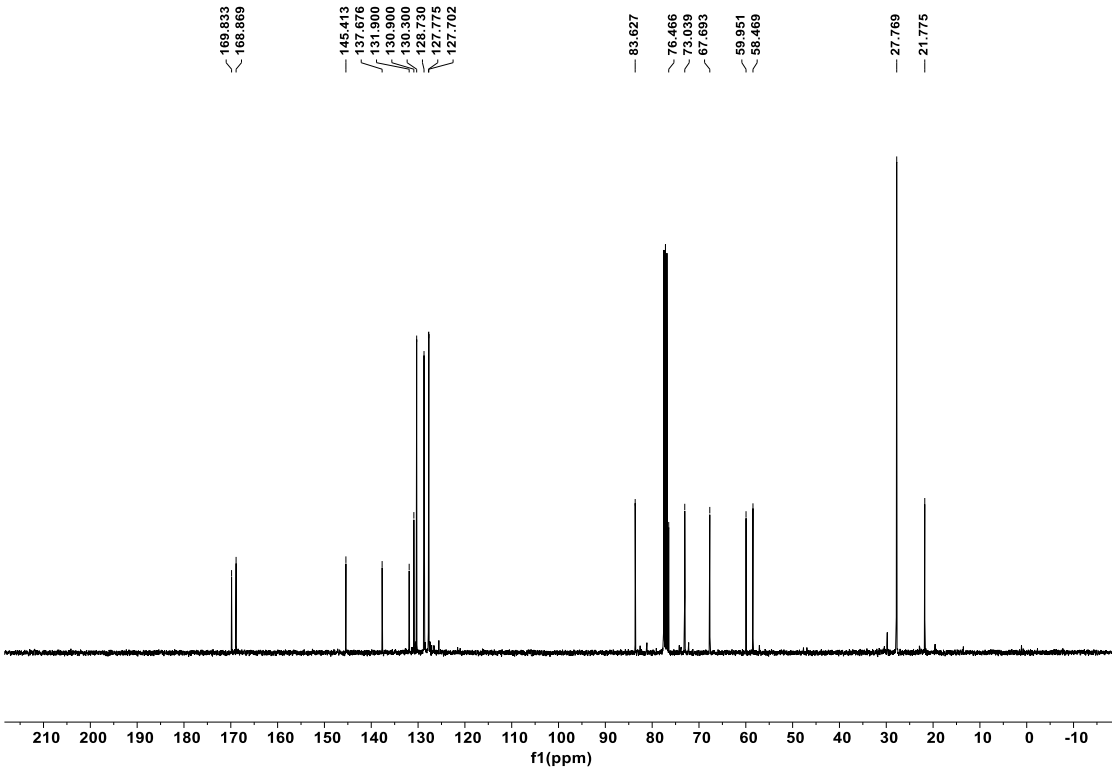
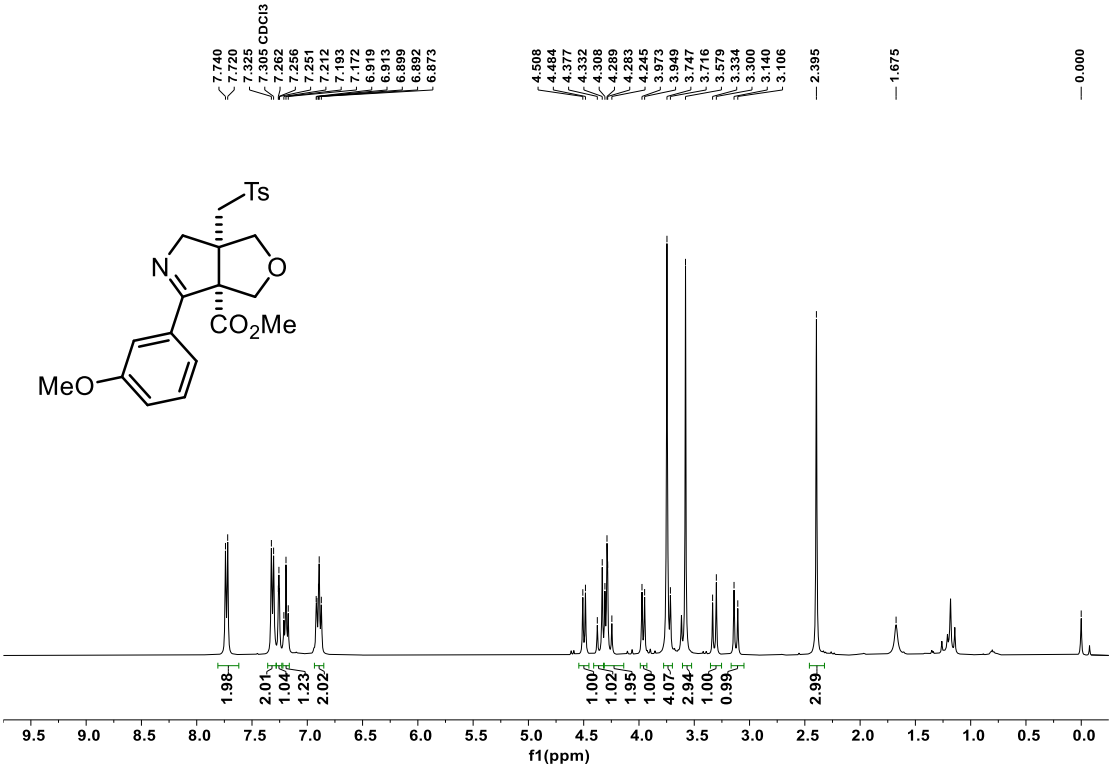


^{1}H NMR of **6d** in $CDCl_3$ (400 MHz)



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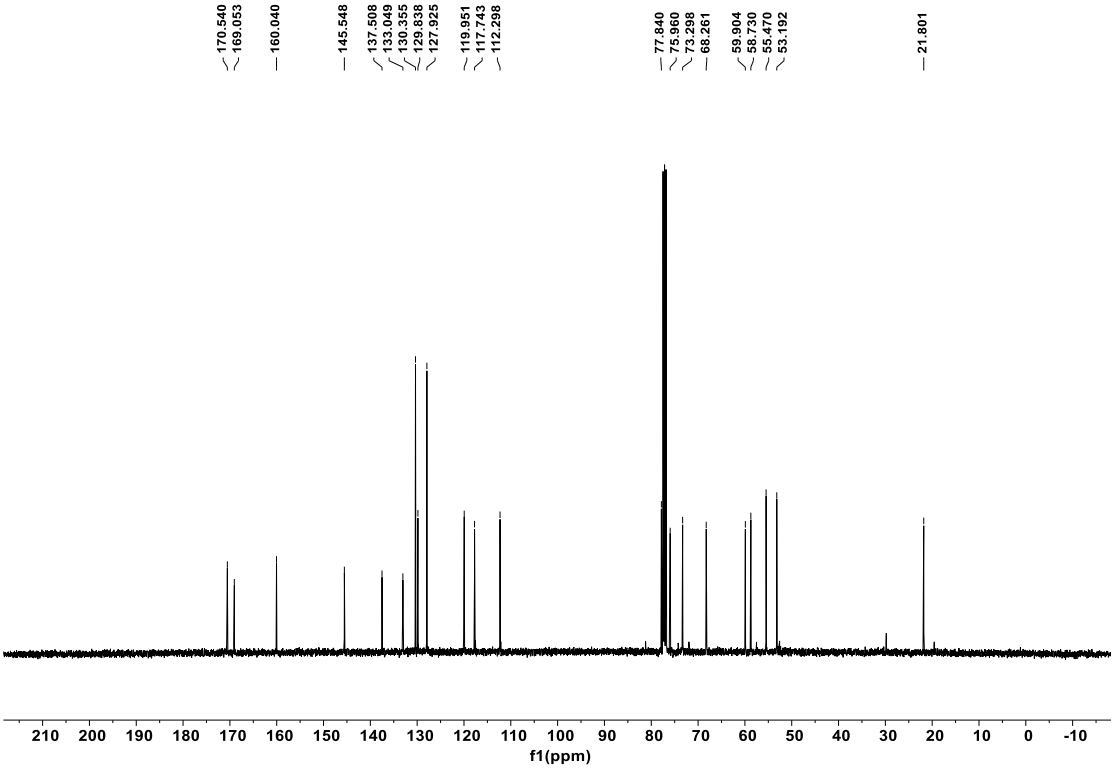
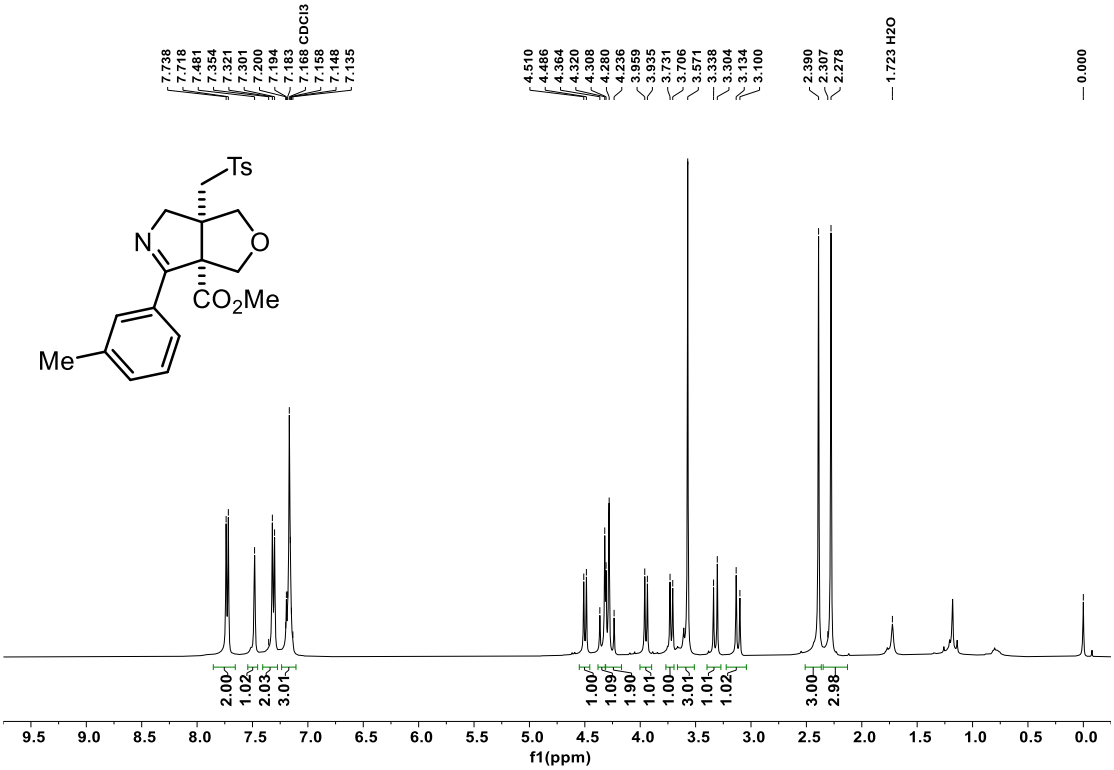
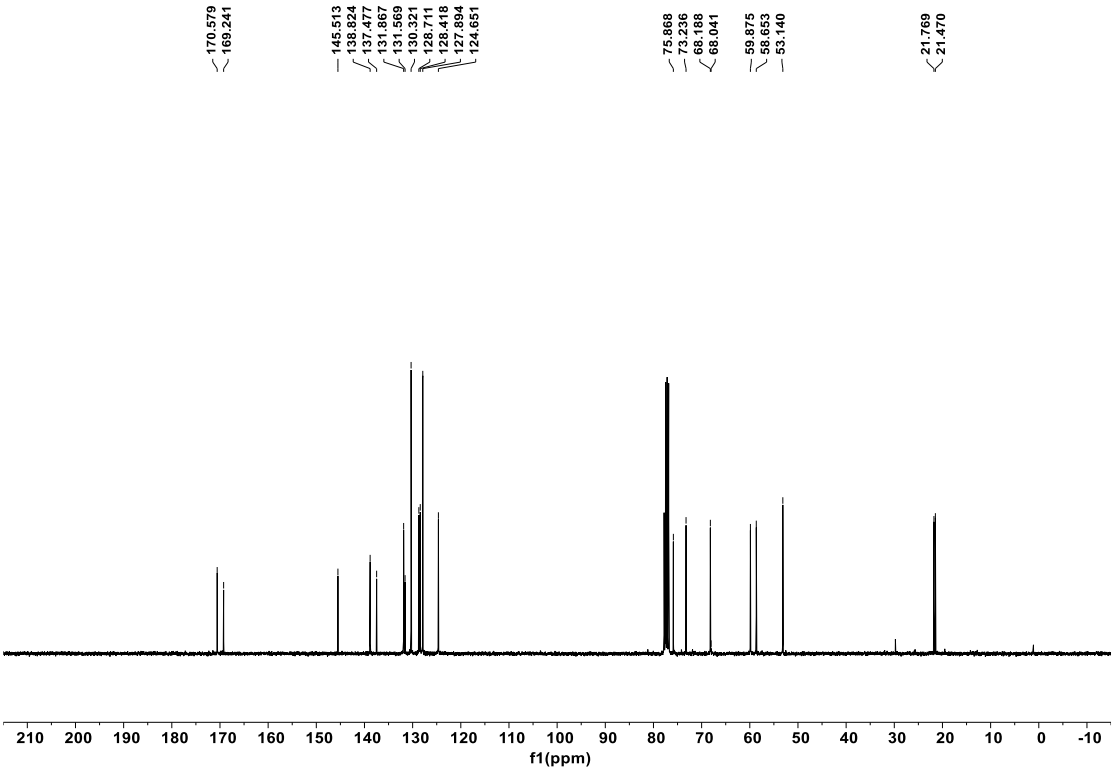


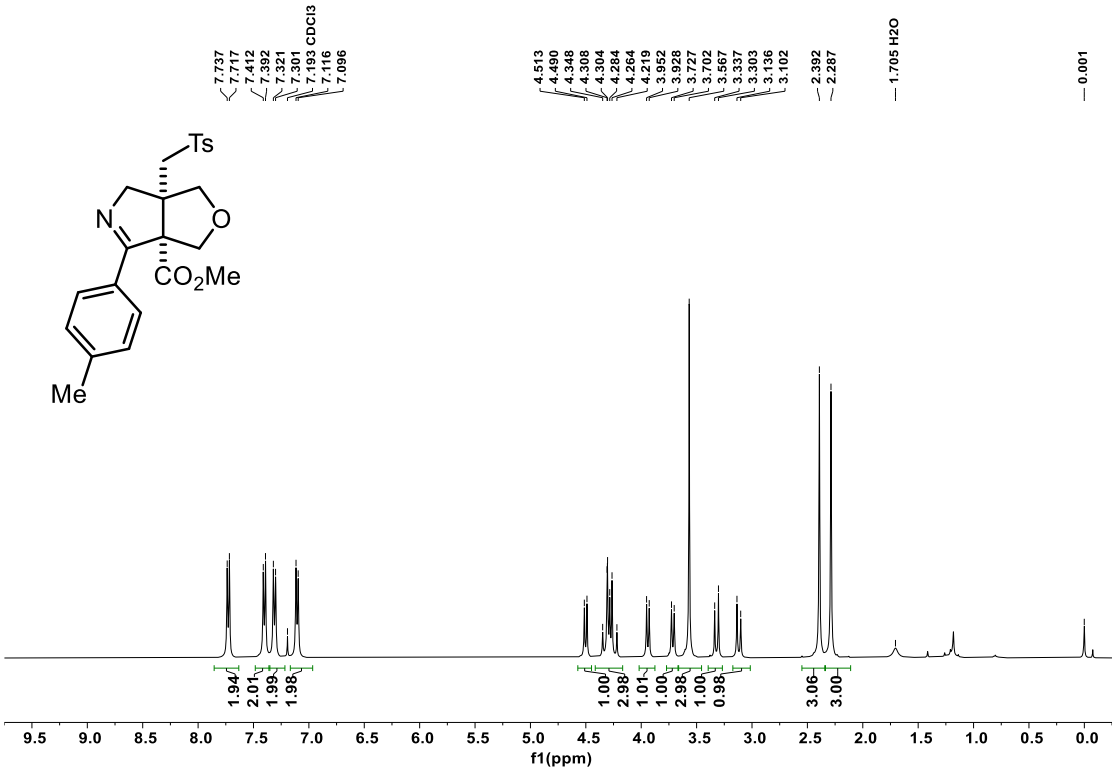
^{1}H NMR of **6e** in $CDCl_3$ (400 MHz)



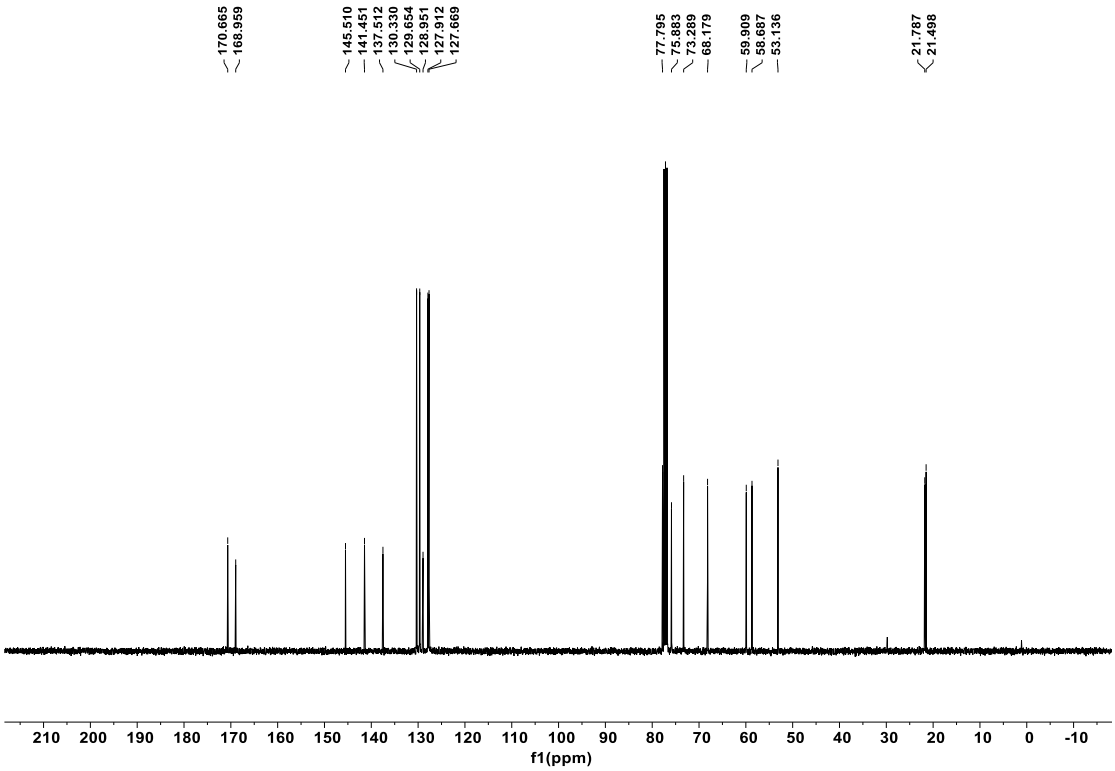
^{13}C NMR of **6e** in $CDCl_3$ (100 MHz)



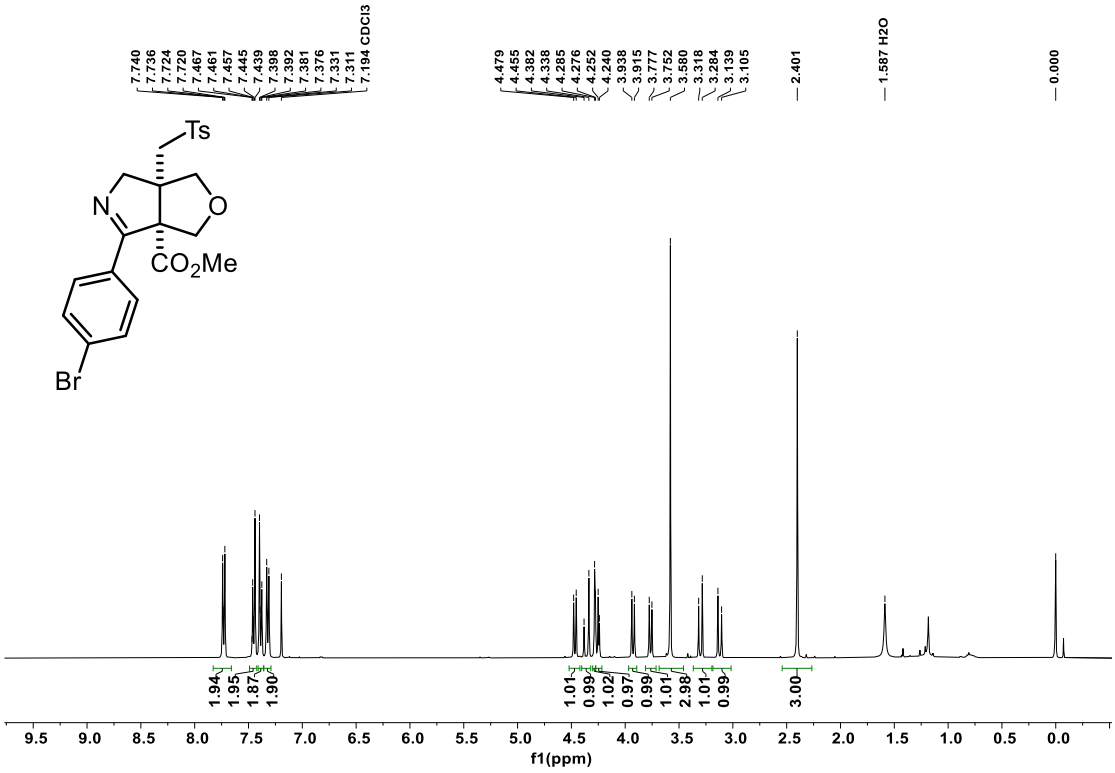
^{1}H NMR of **6f** in $CDCl_3$ (400 MHz)



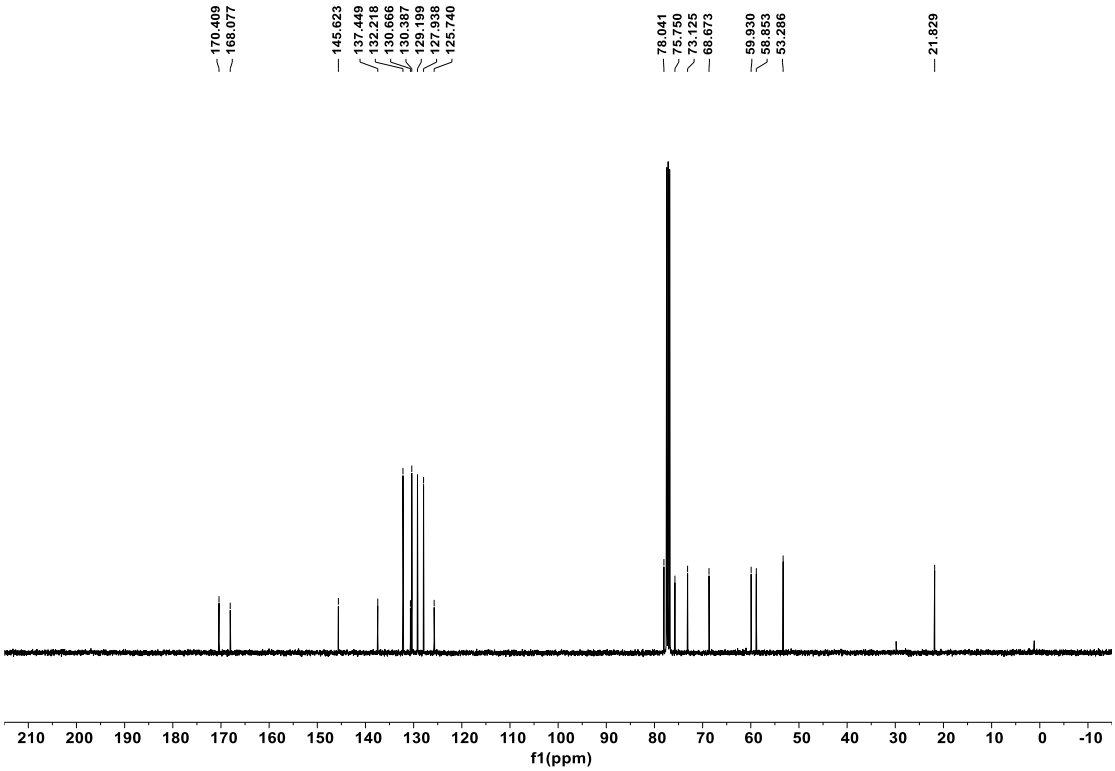
^{13}C NMR of **6f** in $CDCl_3$ (100 MHz)



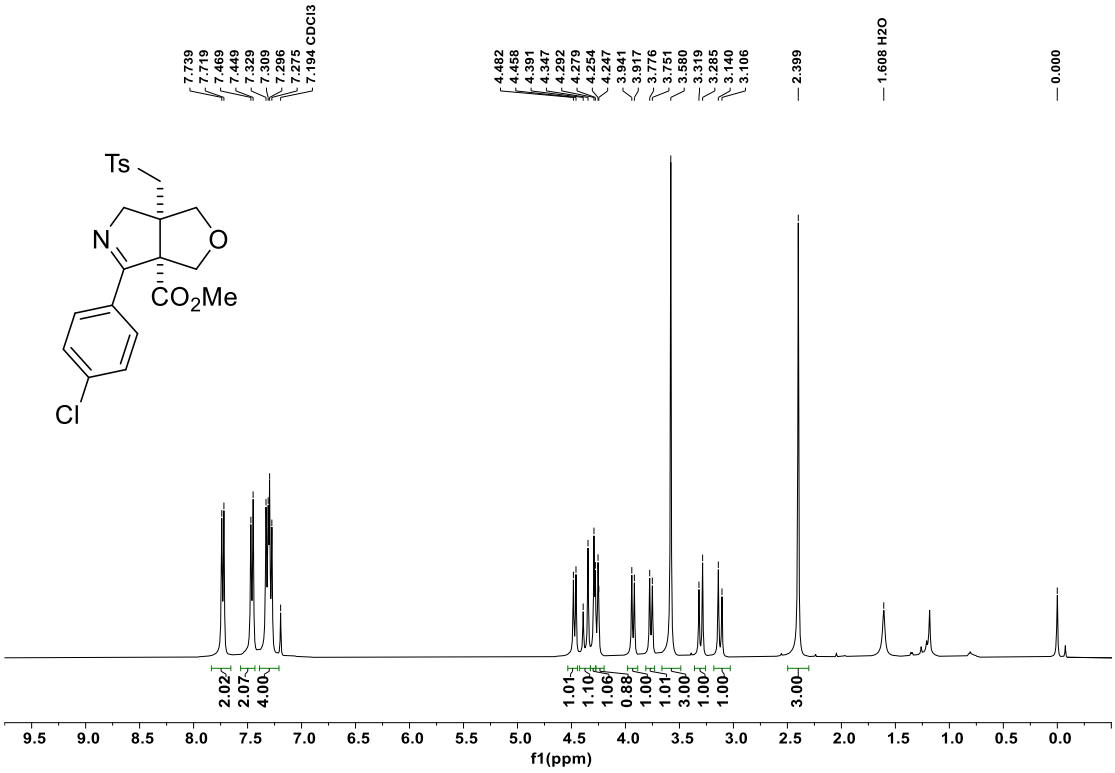
^{1}H NMR of **6g** in $CDCl_3$ (400 MHz)



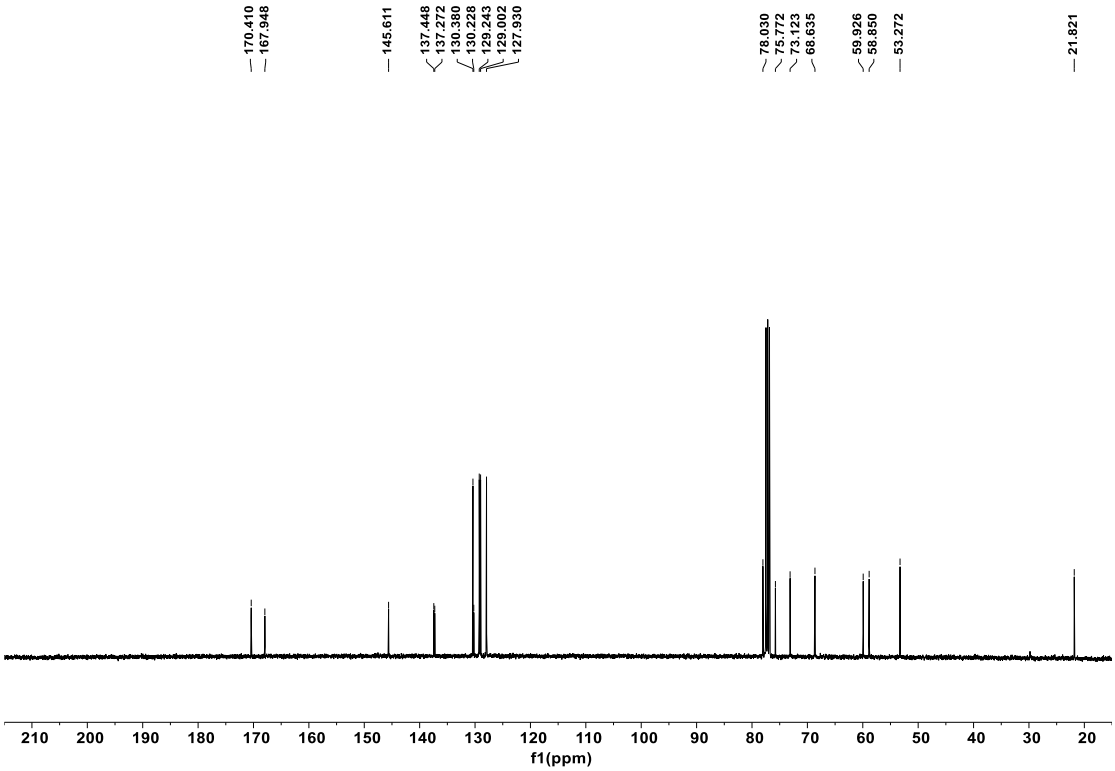
^{13}C NMR of **6g** in $CDCl_3$ (100 MHz)



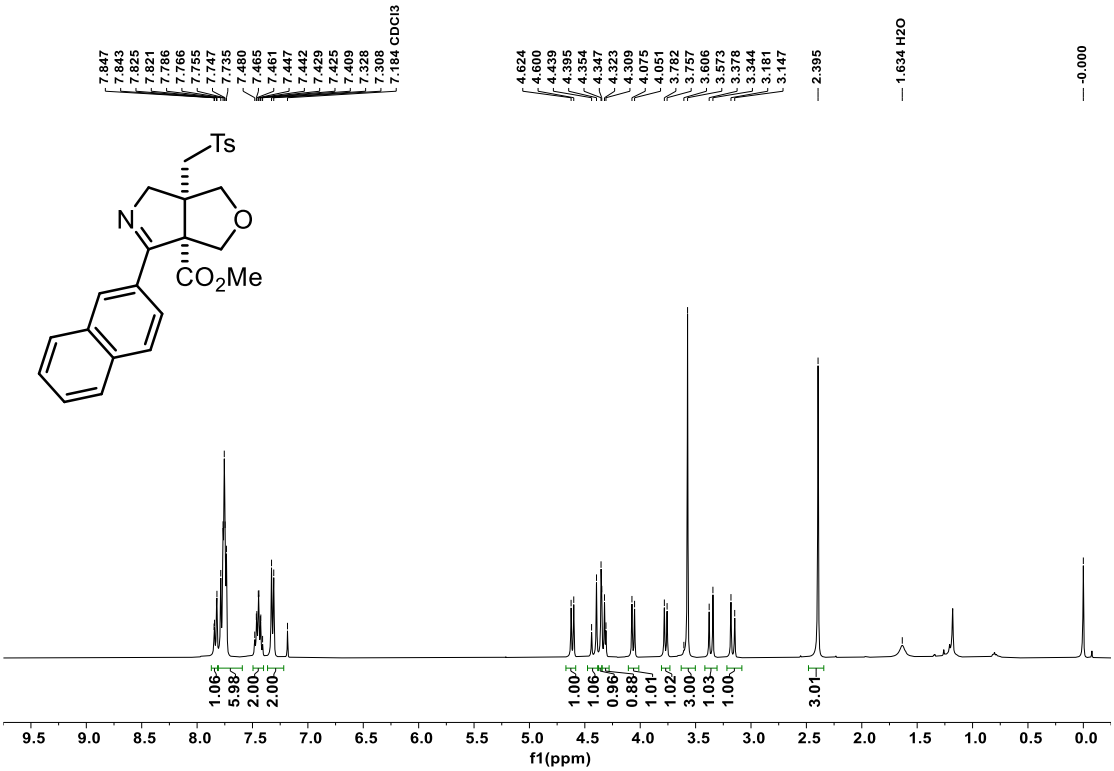
^{1}H NMR of **6h** in $CDCl_3$ (400 MHz)



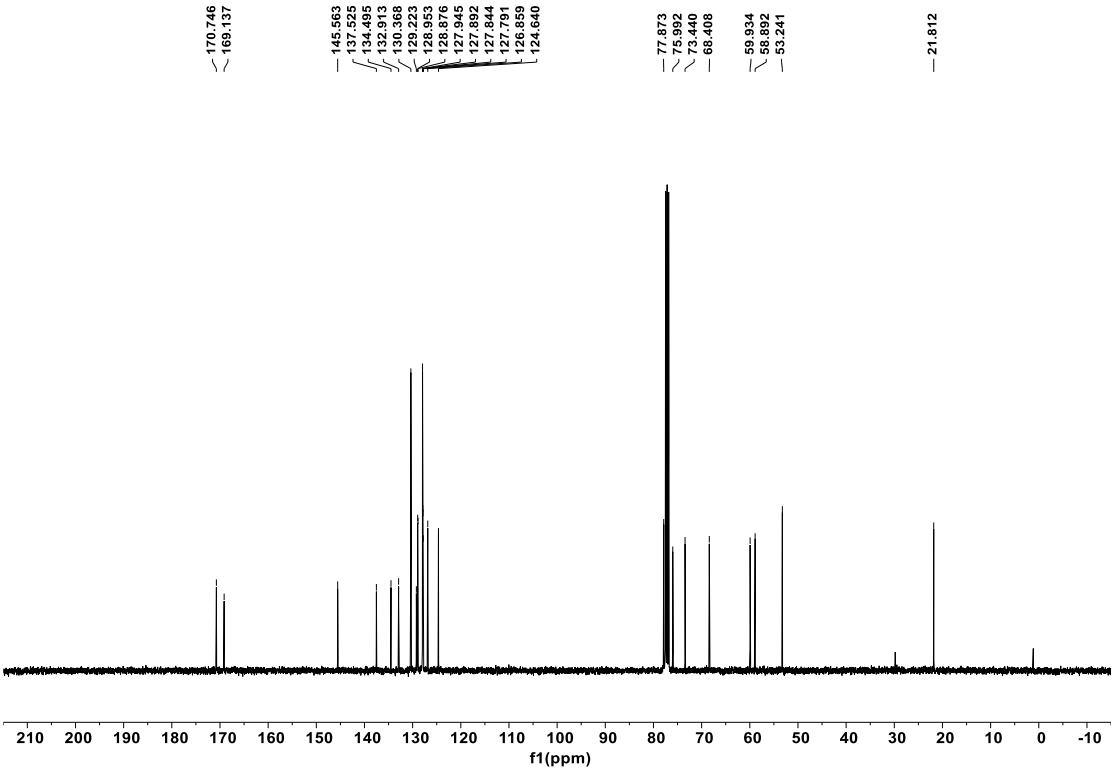
^{13}C NMR of **6h** in $CDCl_3$ (100 MHz)



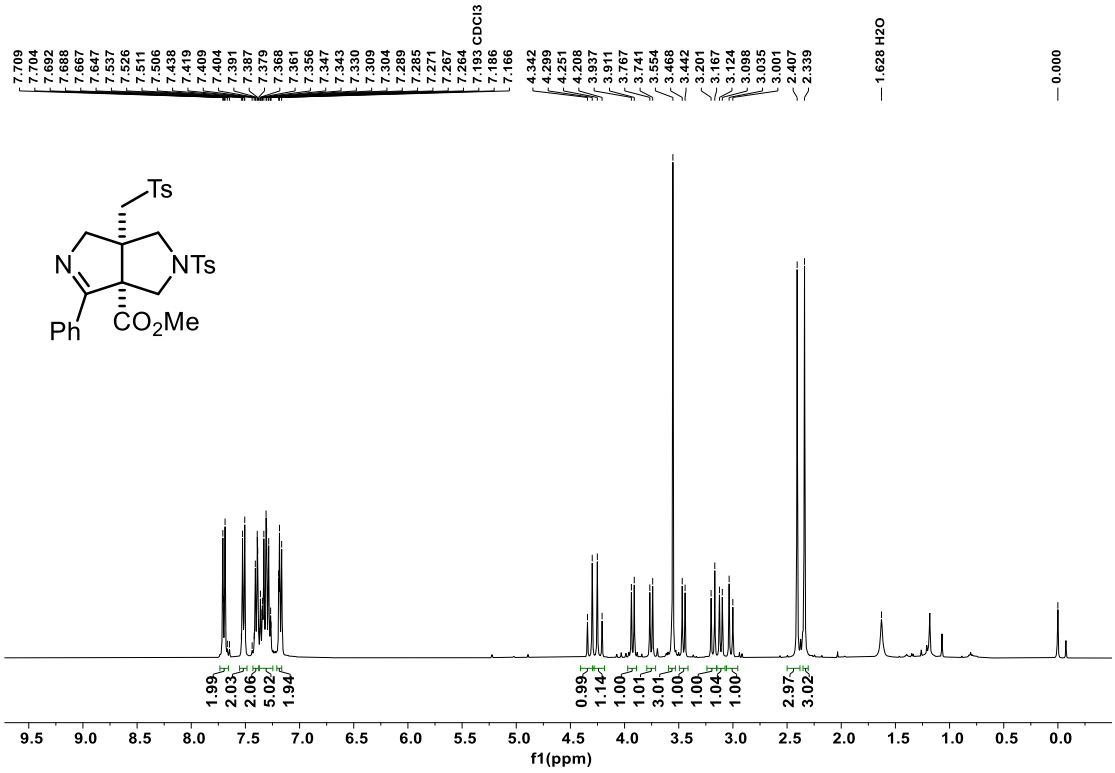
^{1}H NMR of **6i** in $CDCl_3$ (400 MHz)



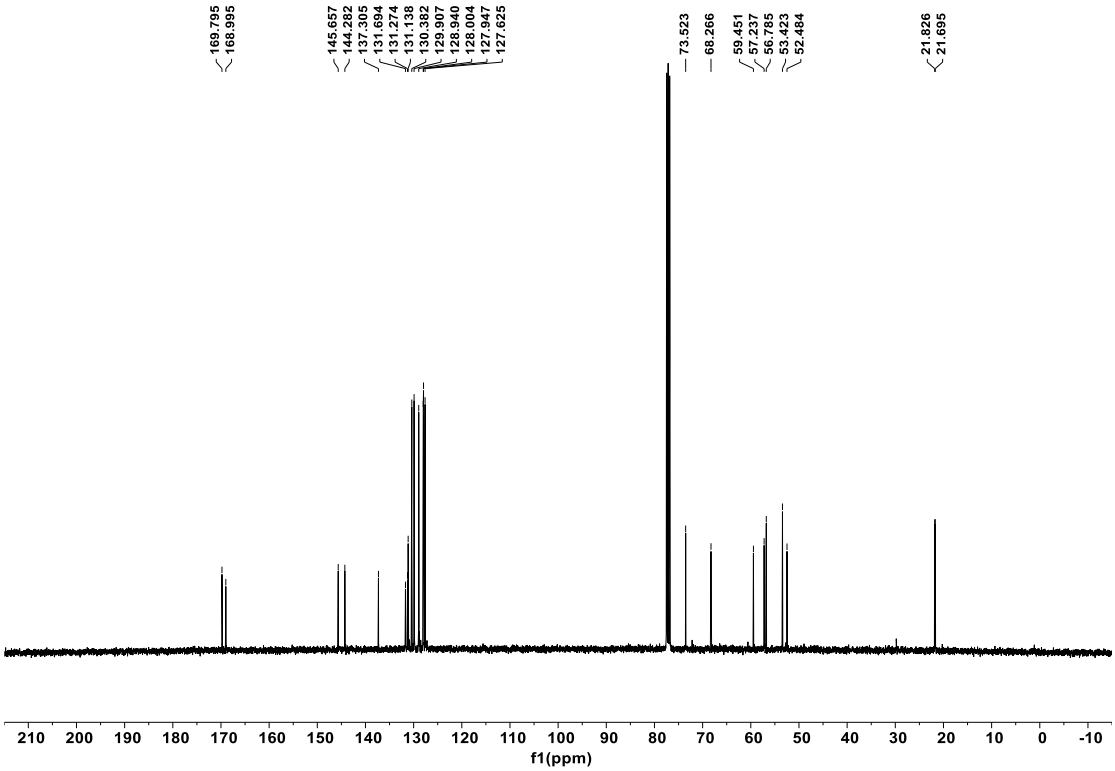
^{13}C NMR of **6i** in $CDCl_3$ (100 MHz)



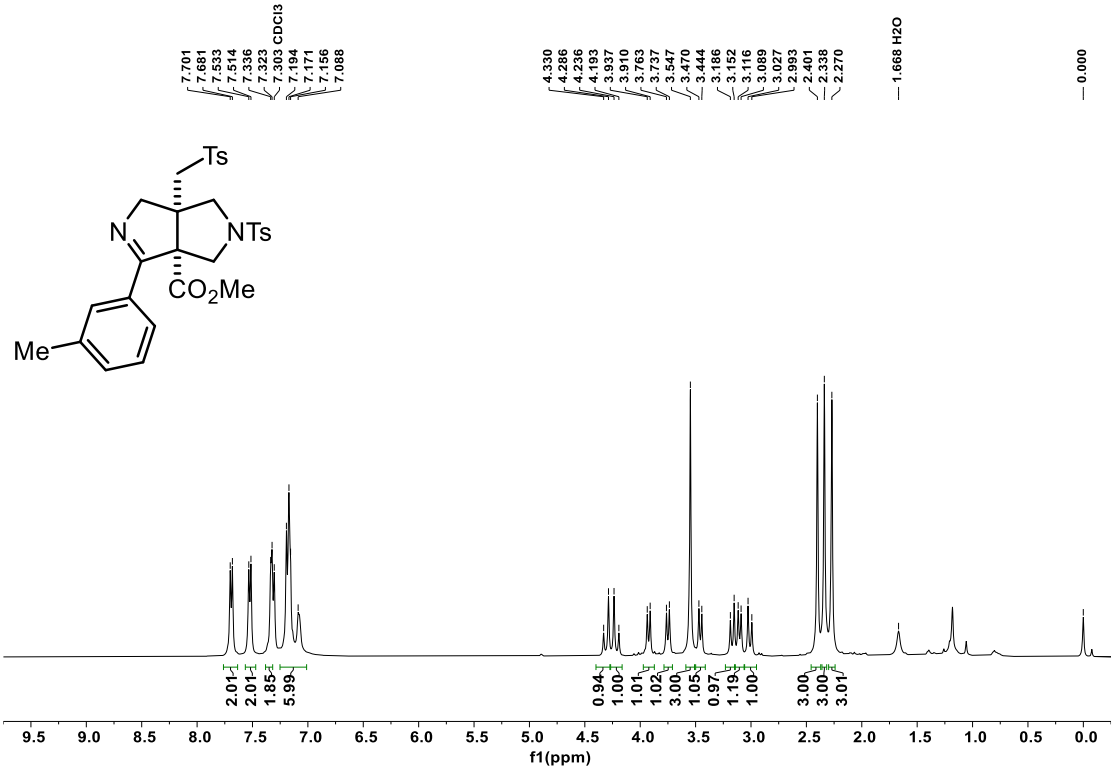
^{1}H NMR of **7a** in $CDCl_3$ (400 MHz)



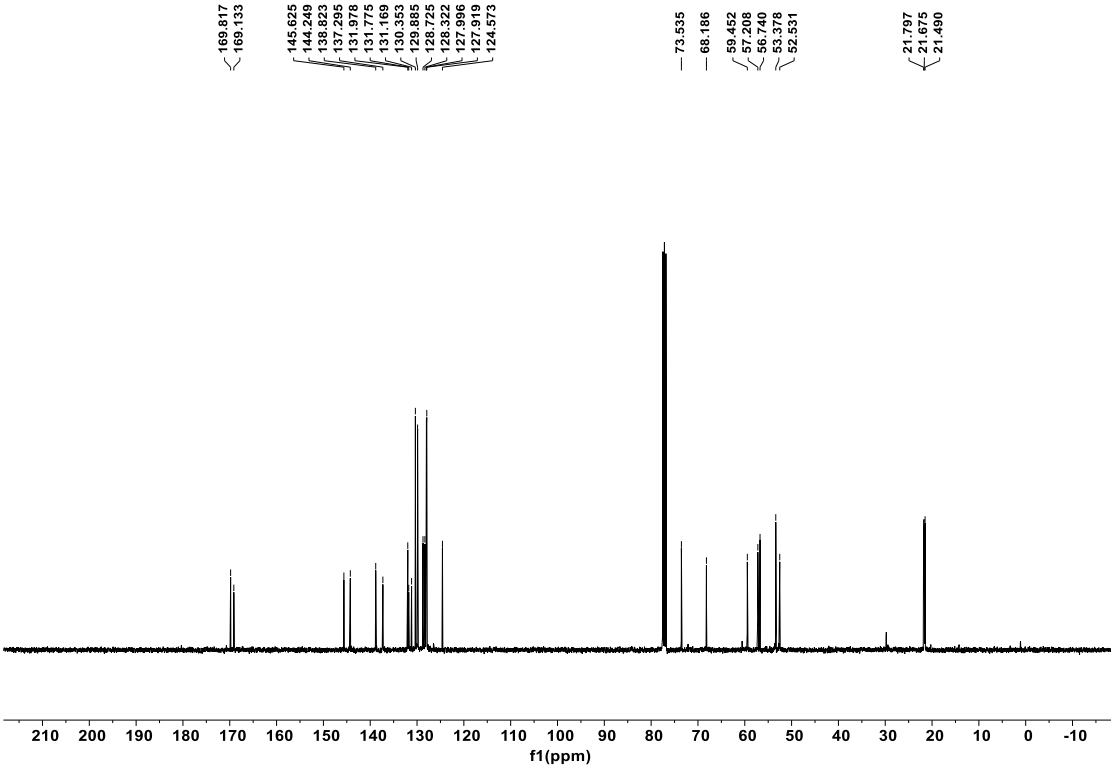
^{13}C NMR of **7a** in $CDCl_3$ (100 MHz)



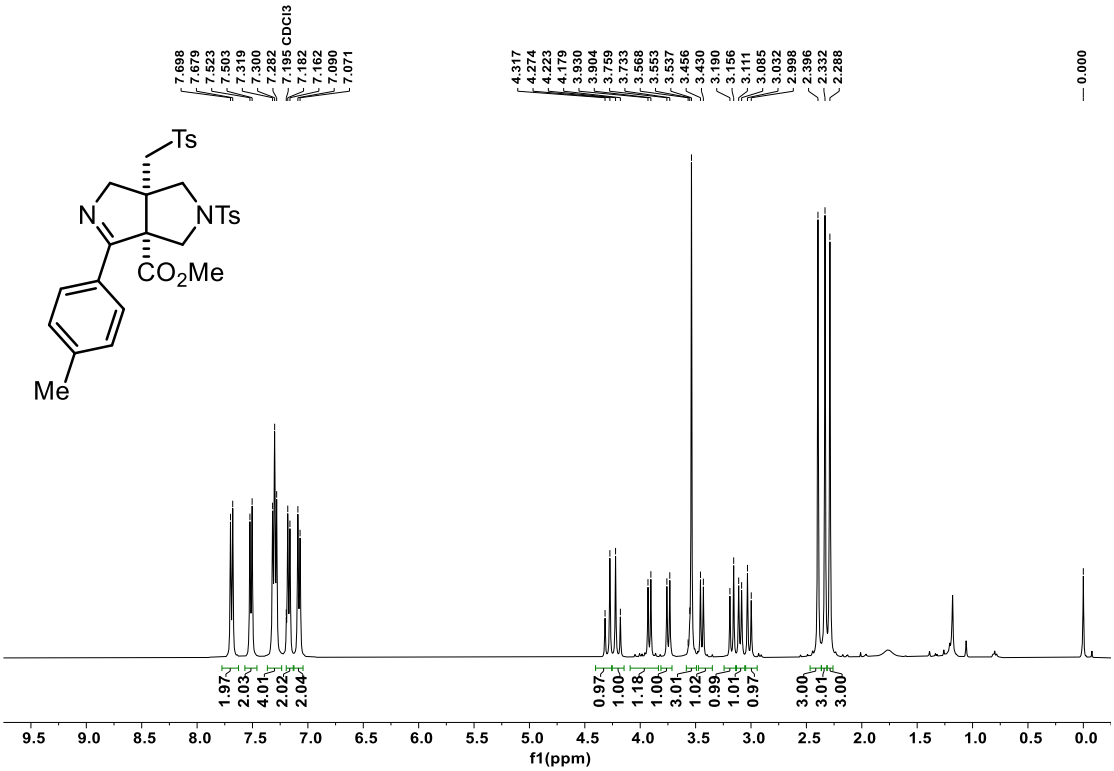
^{1}H NMR of **7b** in $CDCl_3$ (400 MHz)



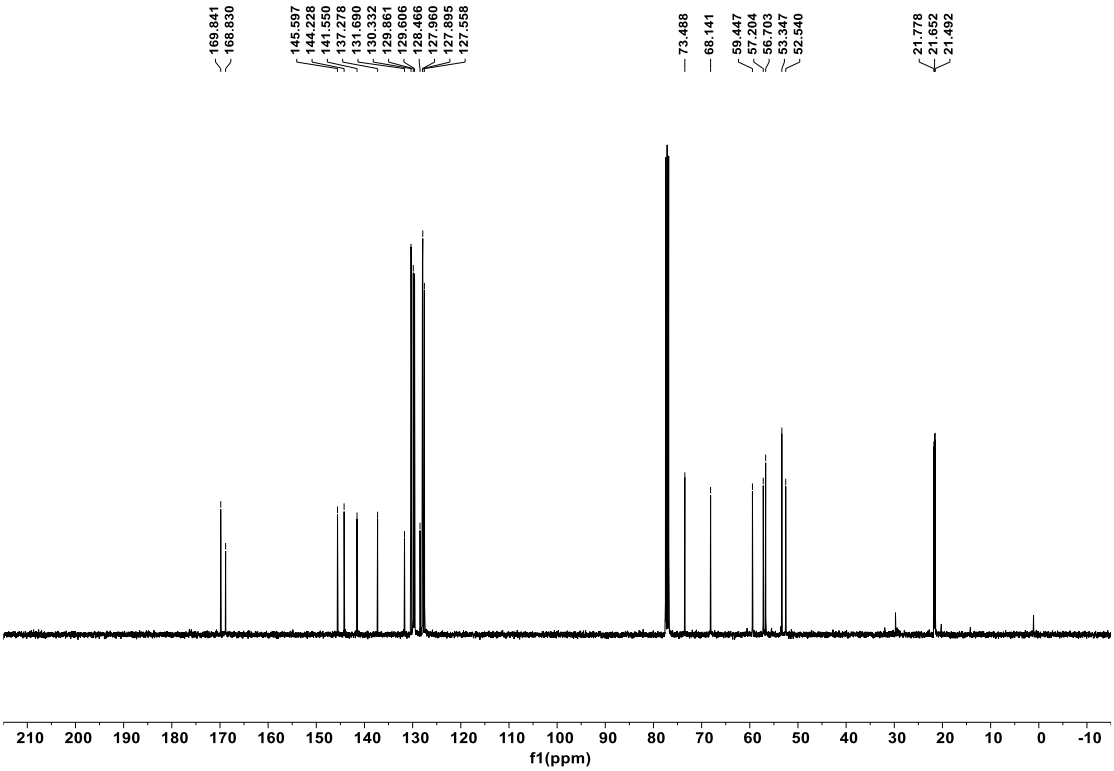
^{13}C NMR of **7b** in $CDCl_3$ (100 MHz)



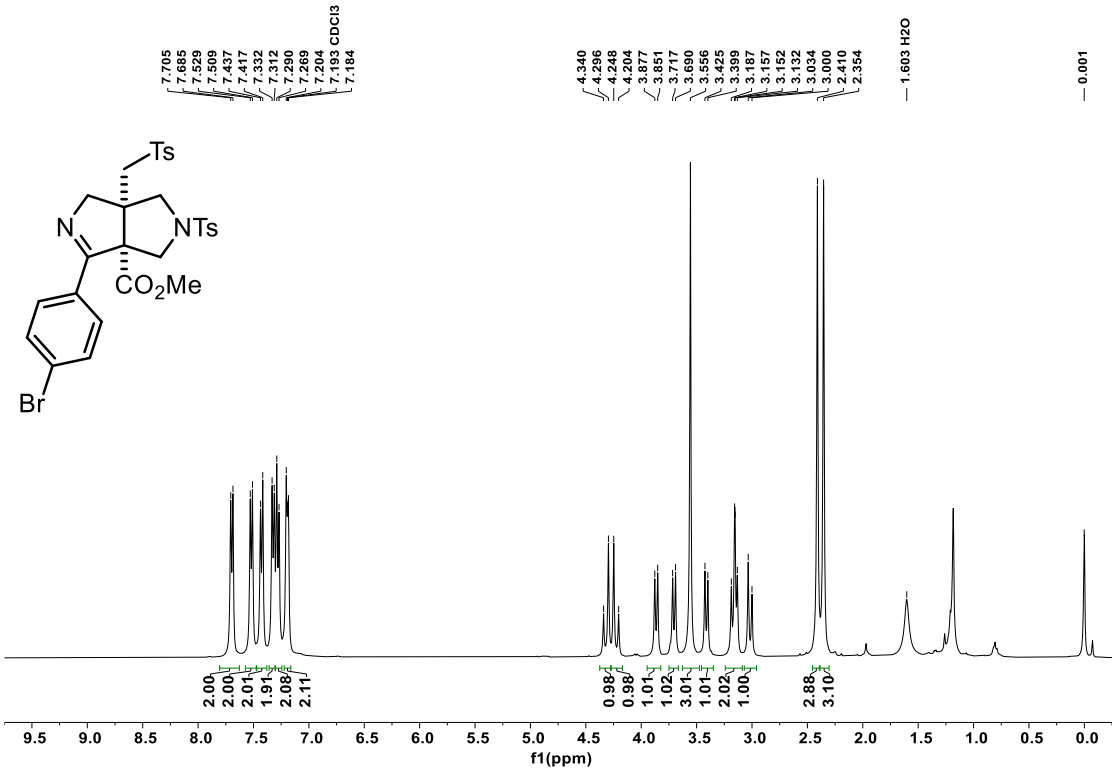
^{1}H NMR of **7c** in $CDCl_3$ (400 MHz)



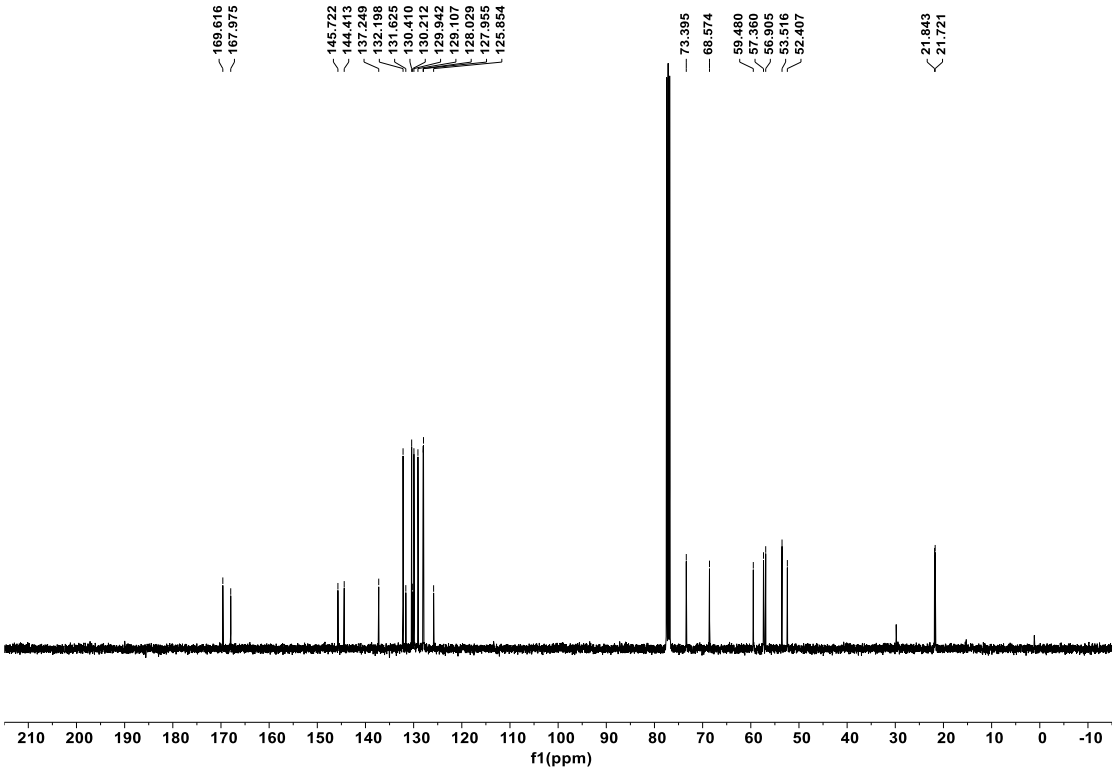
^{13}C NMR of **7c** in $CDCl_3$ (100 MHz)



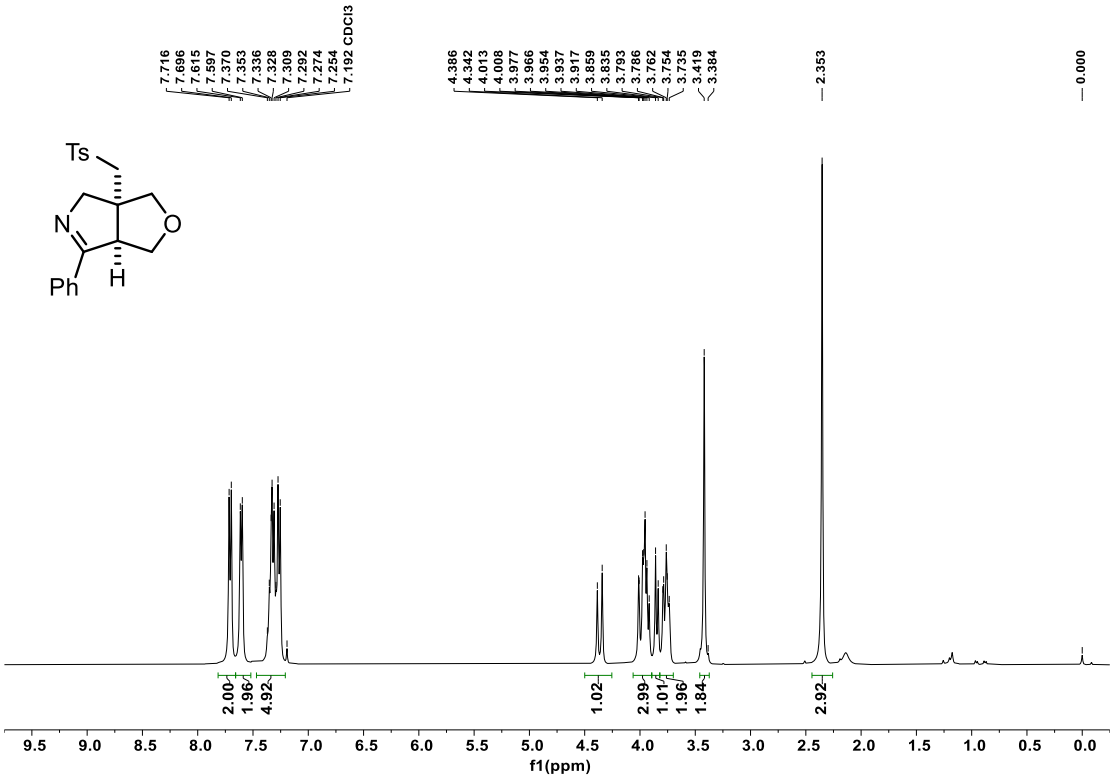
^{1}H NMR of **7d** in $CDCl_3$ (400 MHz)



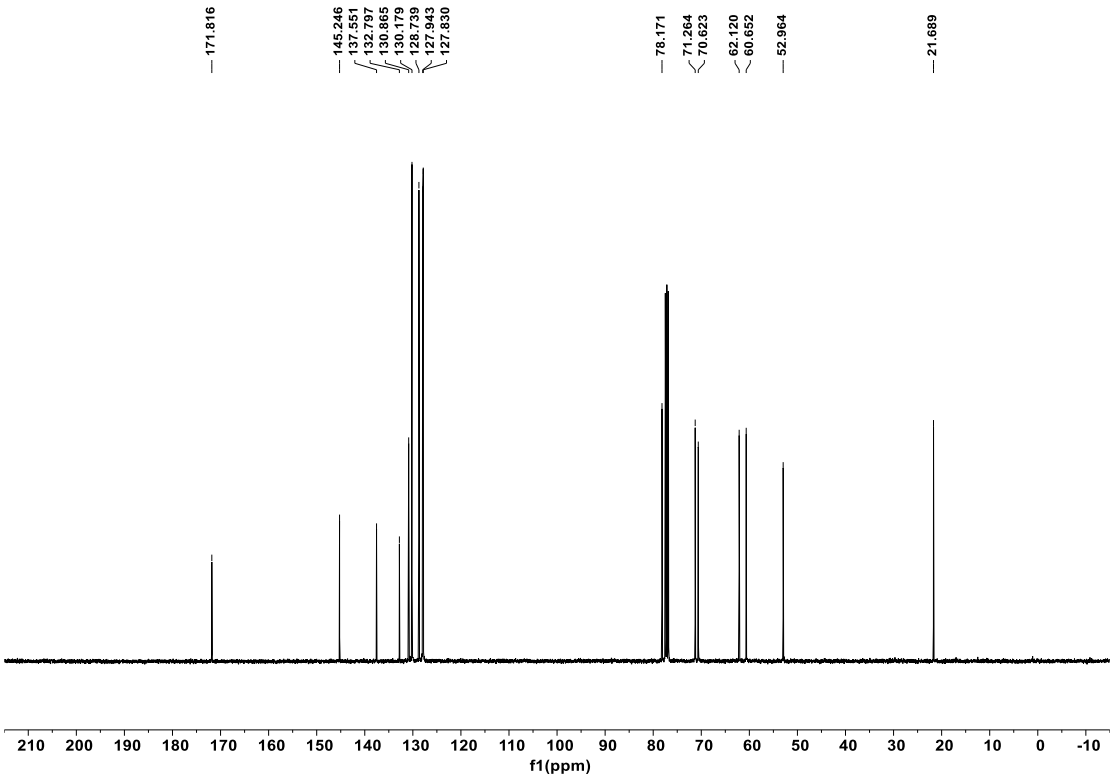
^{13}C NMR of **7d** in $CDCl_3$ (100 MHz)



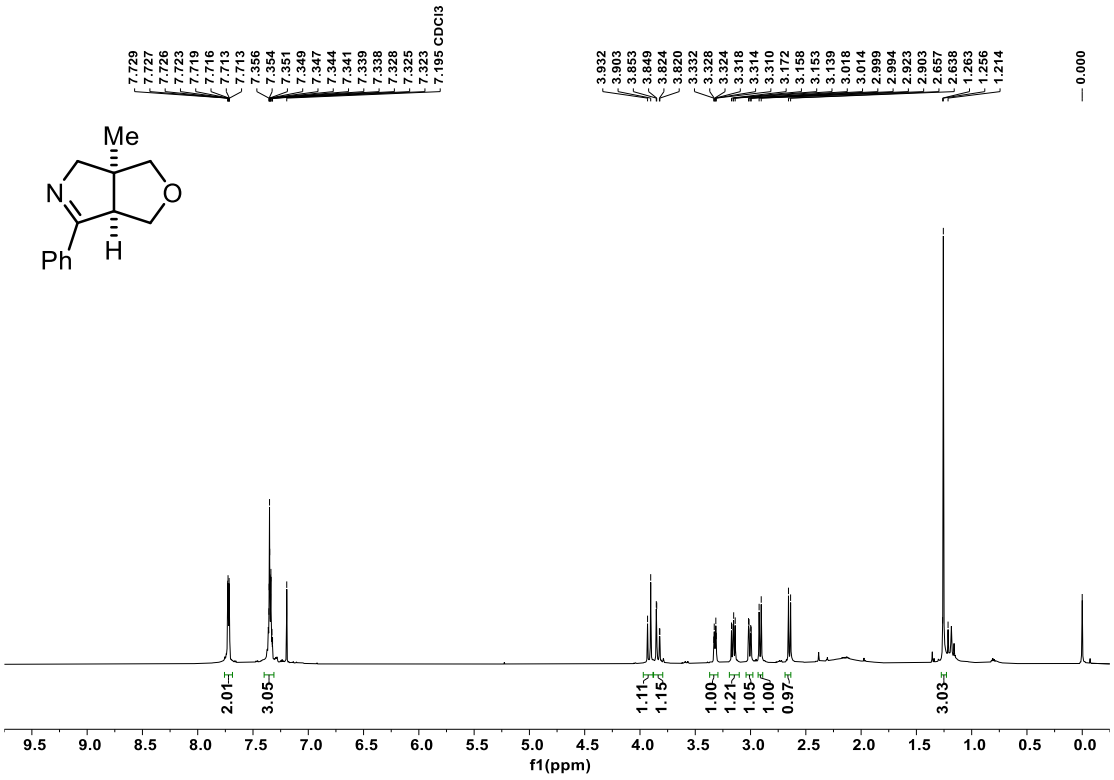
^{1}H NMR of **6aa** in $CDCl_3$ (400 MHz)



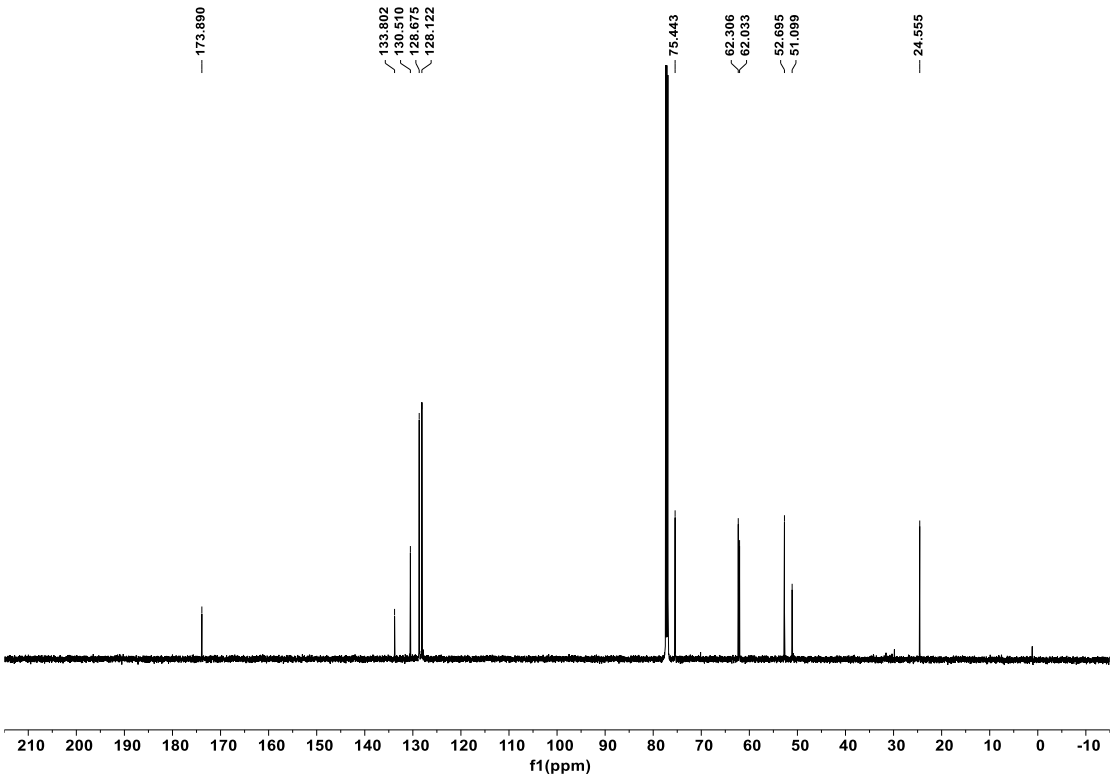
^{13}C NMR of **6aa** in $CDCl_3$ (100 MHz)



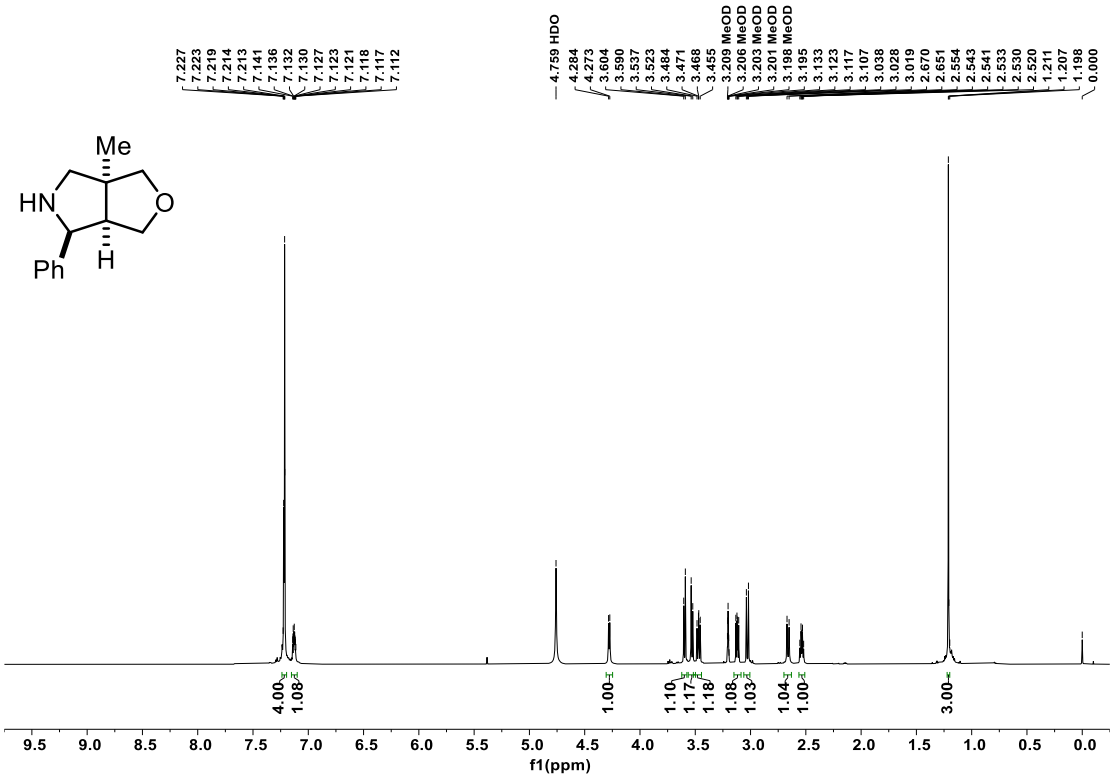
^{1}H NMR of **6ab** in $CDCl_3$ (600 MHz)



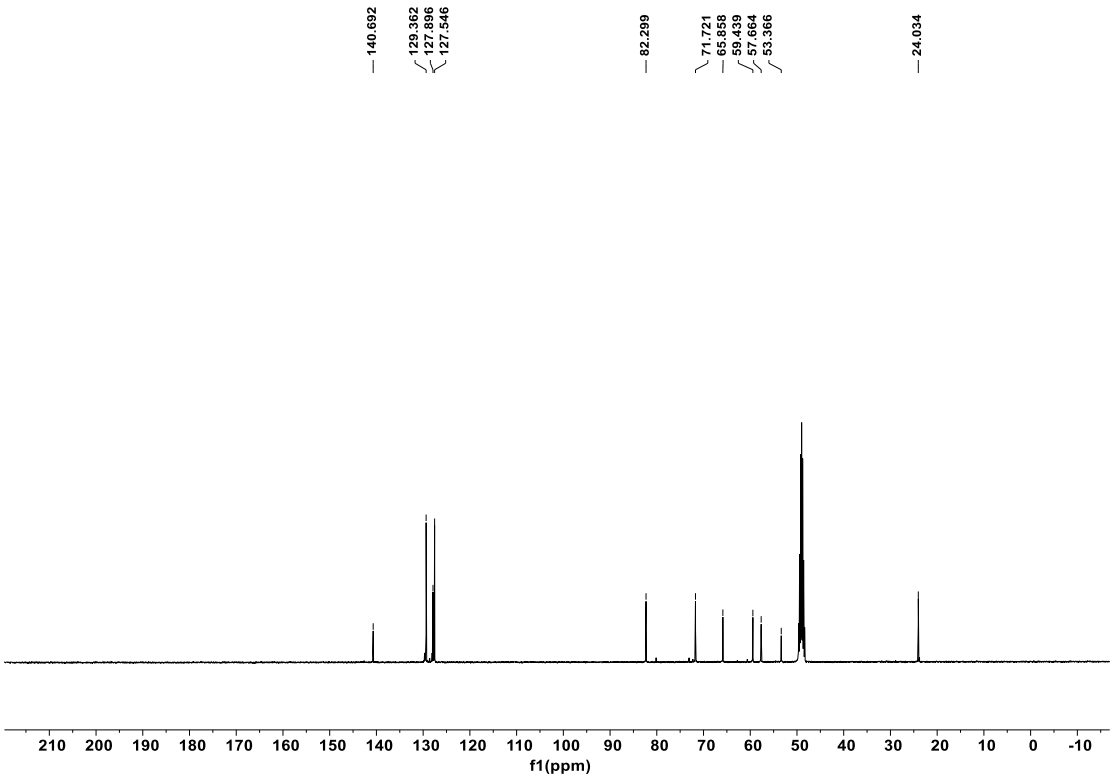
^{13}C NMR of **6ab** in $CDCl_3$ (151 MHz)



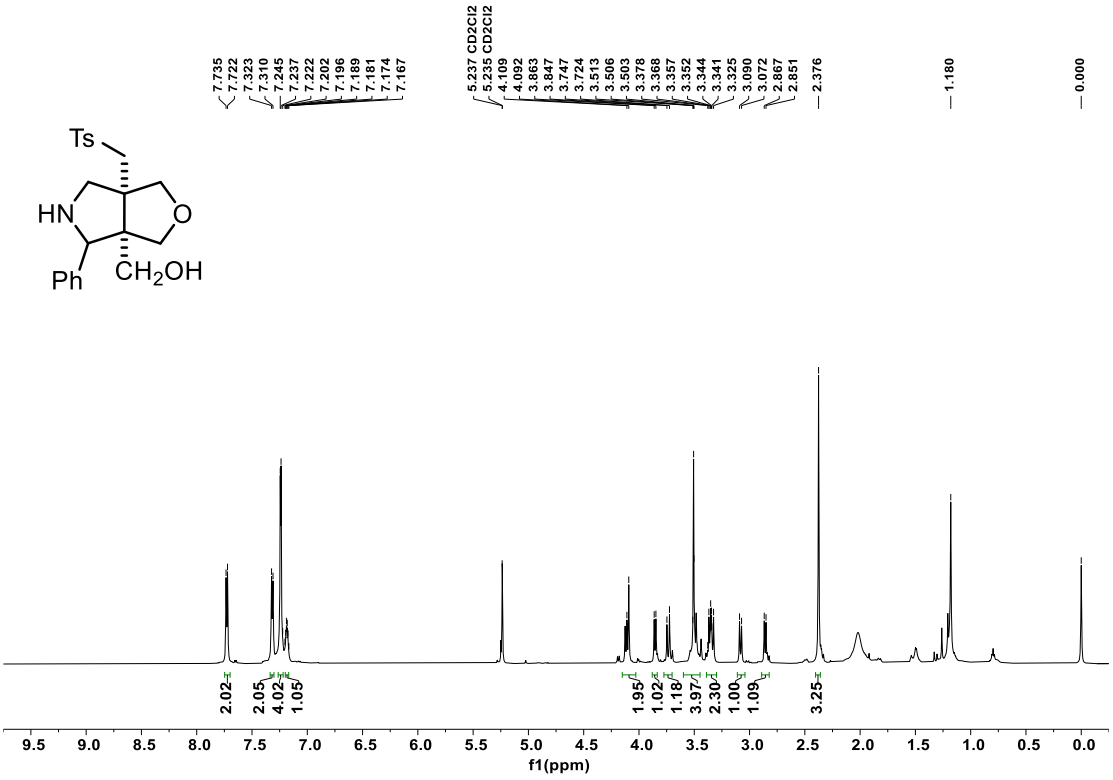
^{1}H NMR of **6ac** in CD_3OD (600 MHz)



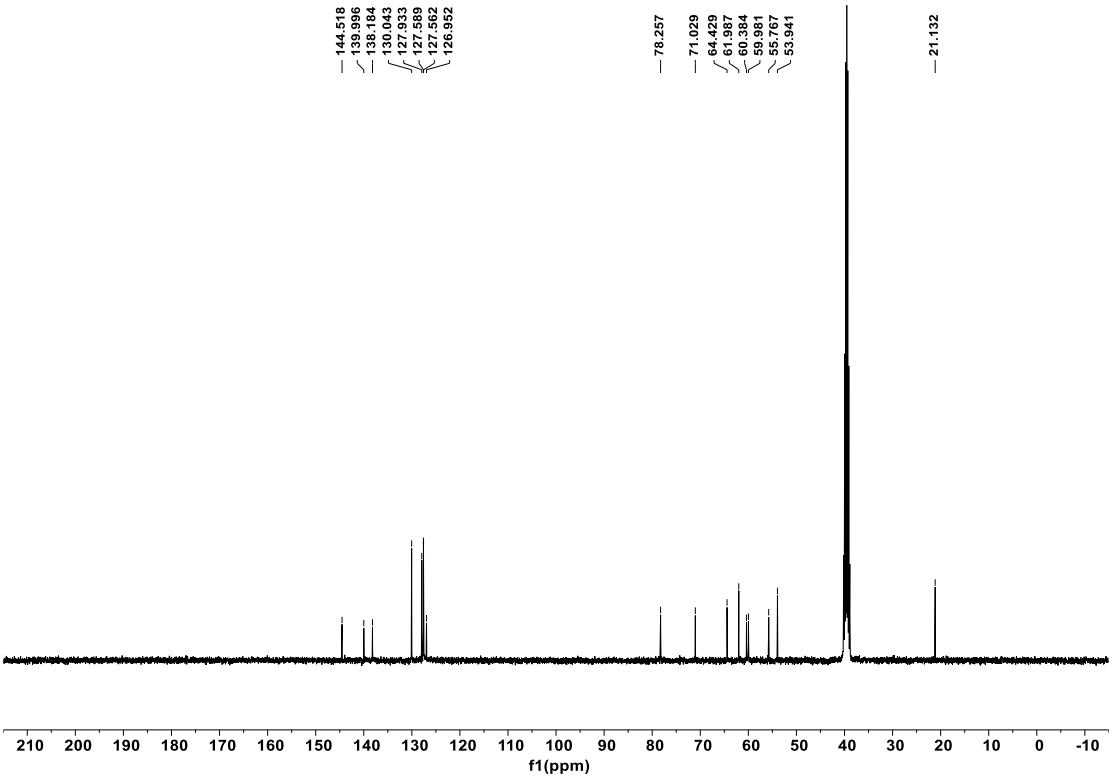
^{13}C NMR of **6ac** in CD_3OD (151 MHz)



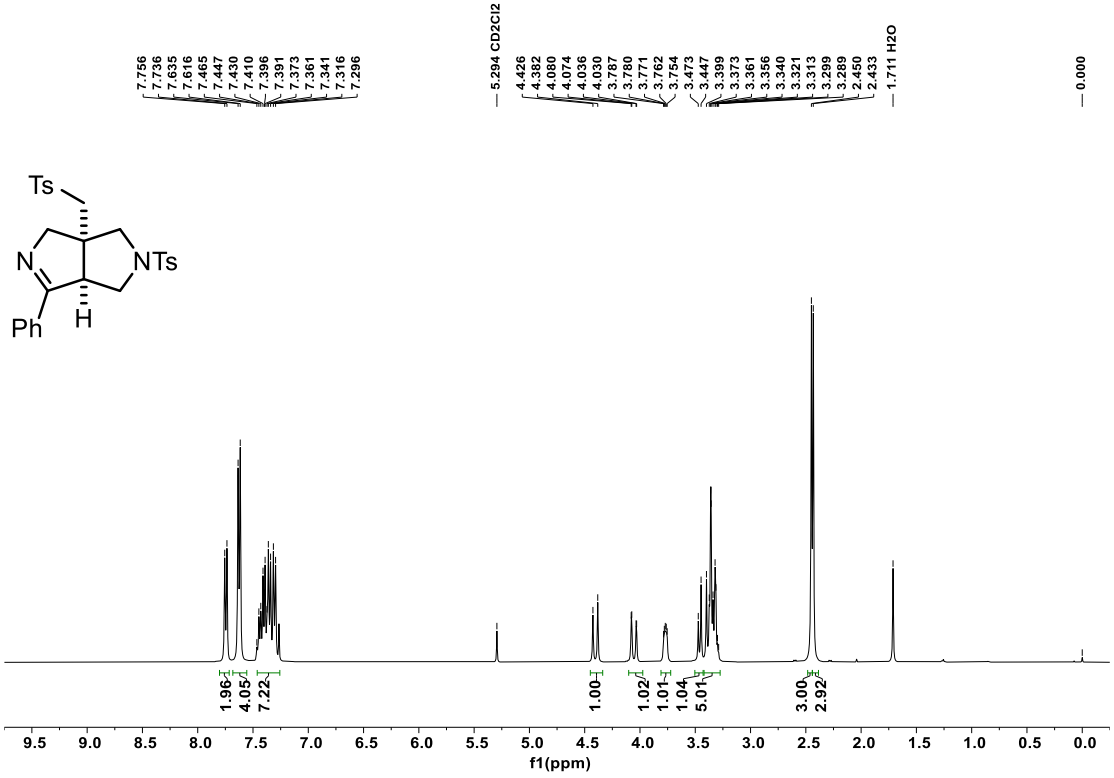
^{1}H NMR of **6ad** in CD_2Cl_2 (600 MHz)



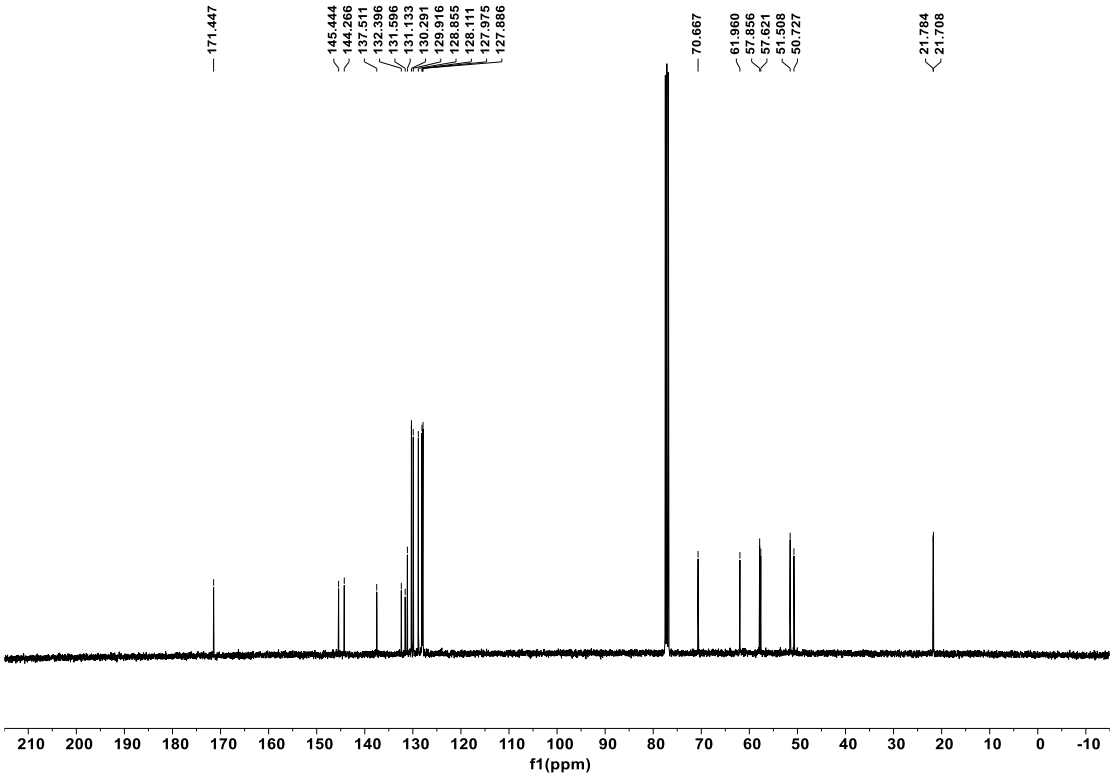
^{13}C NMR of **6ad** in DMSO (151 MHz)



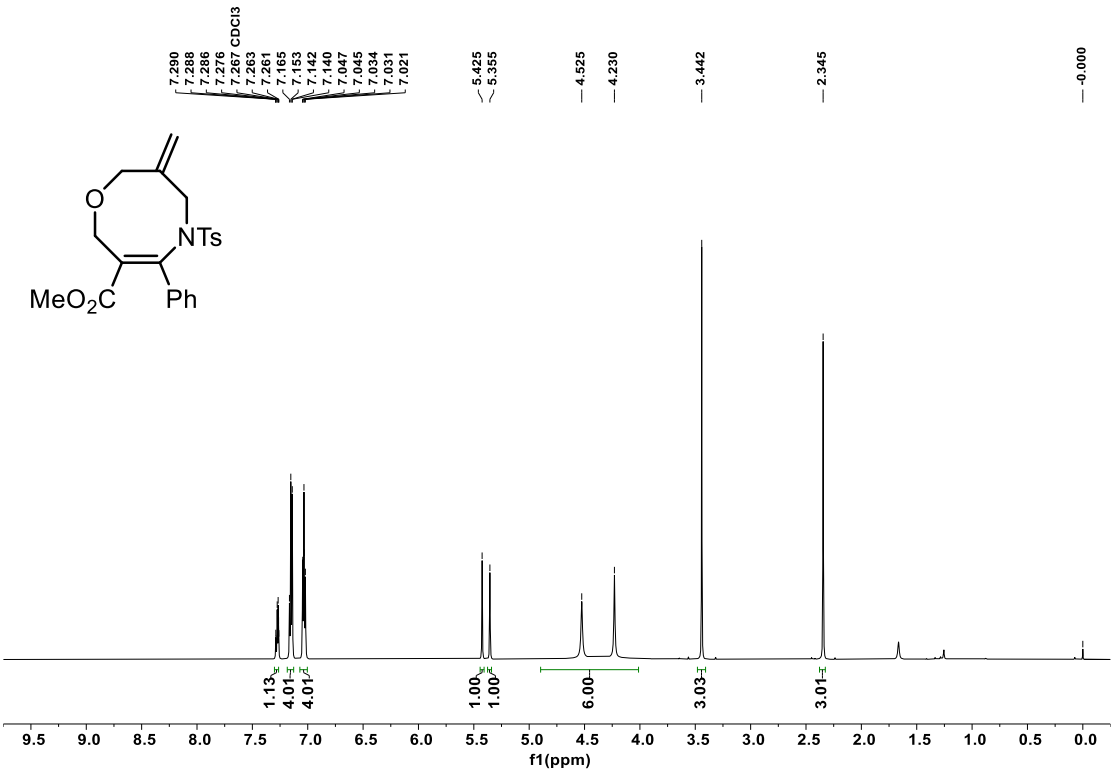
^{1}H NMR of **7aa** in CD_2Cl_2 (400 MHz)



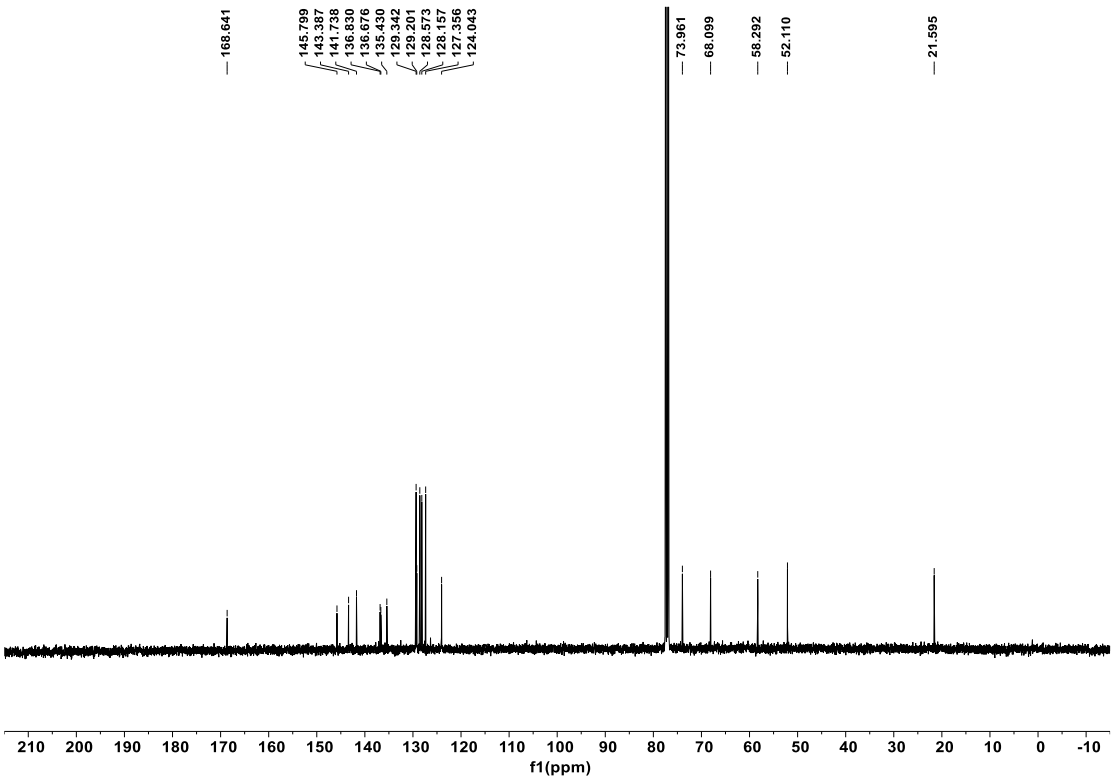
^{13}C NMR of **7aa** in $CDCl_3$ (100 MHz)



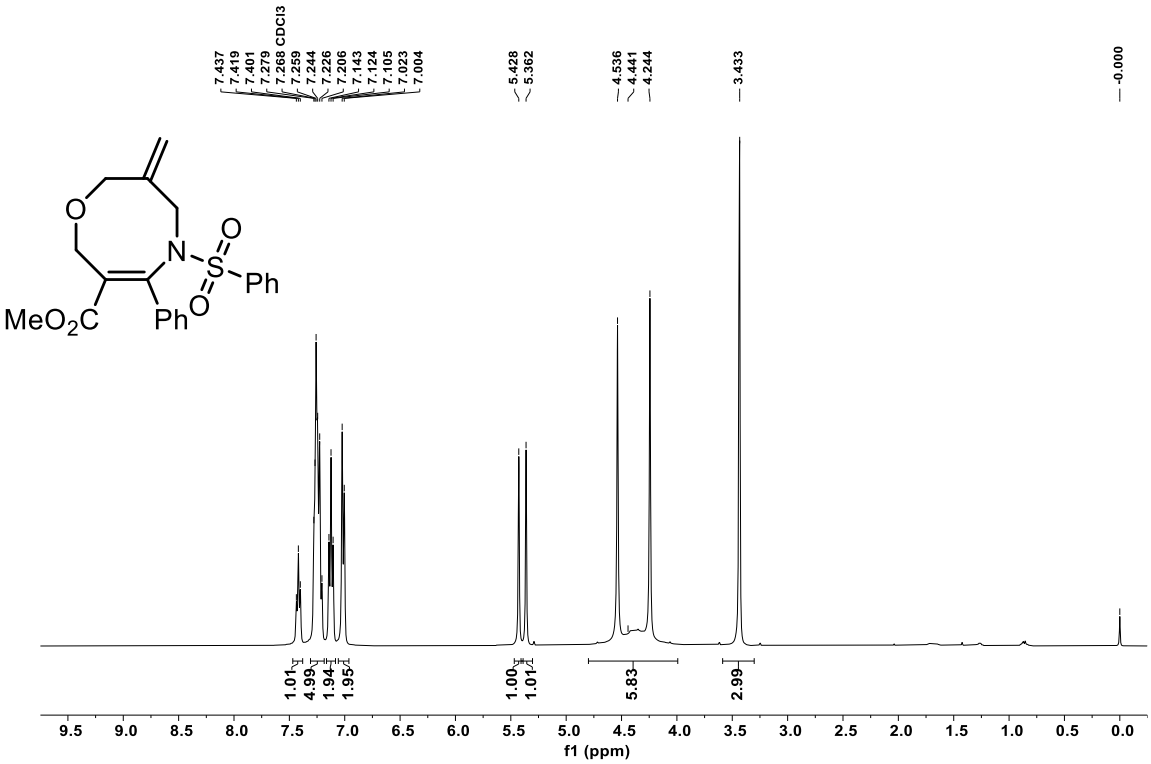
^{1}H NMR of **8a** in $CDCl_3$ (400 MHz)



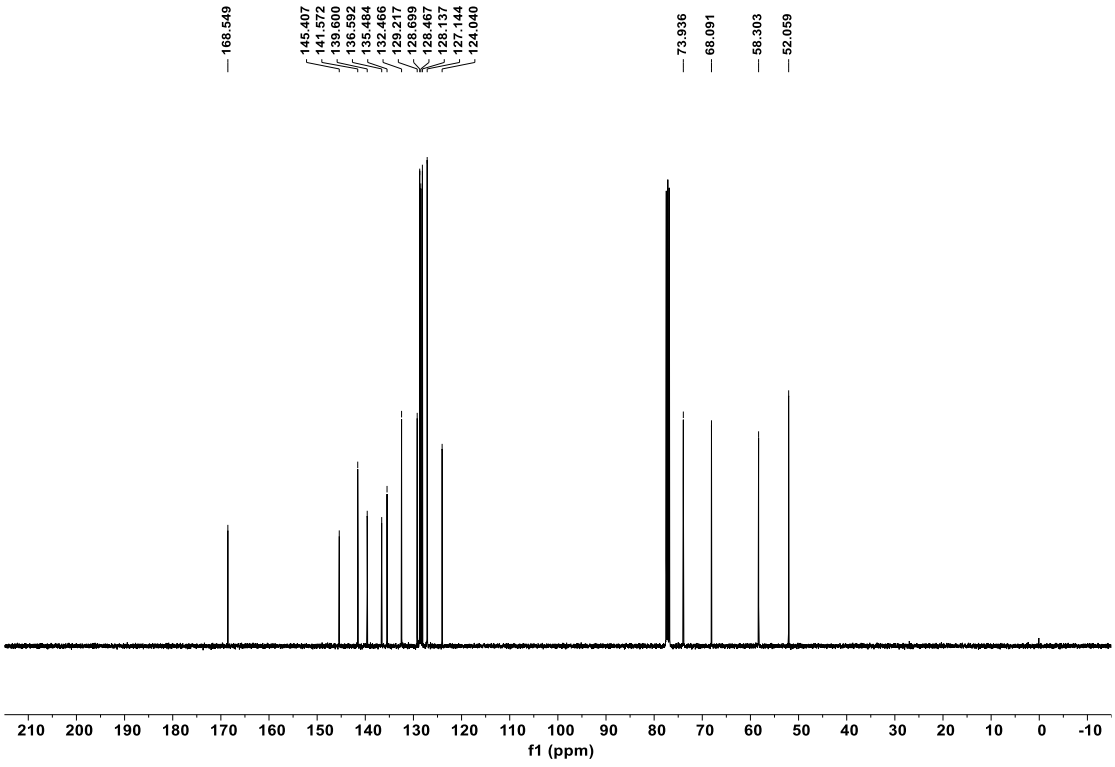
^{13}C NMR of **8a** in $CDCl_3$ (100 MHz)



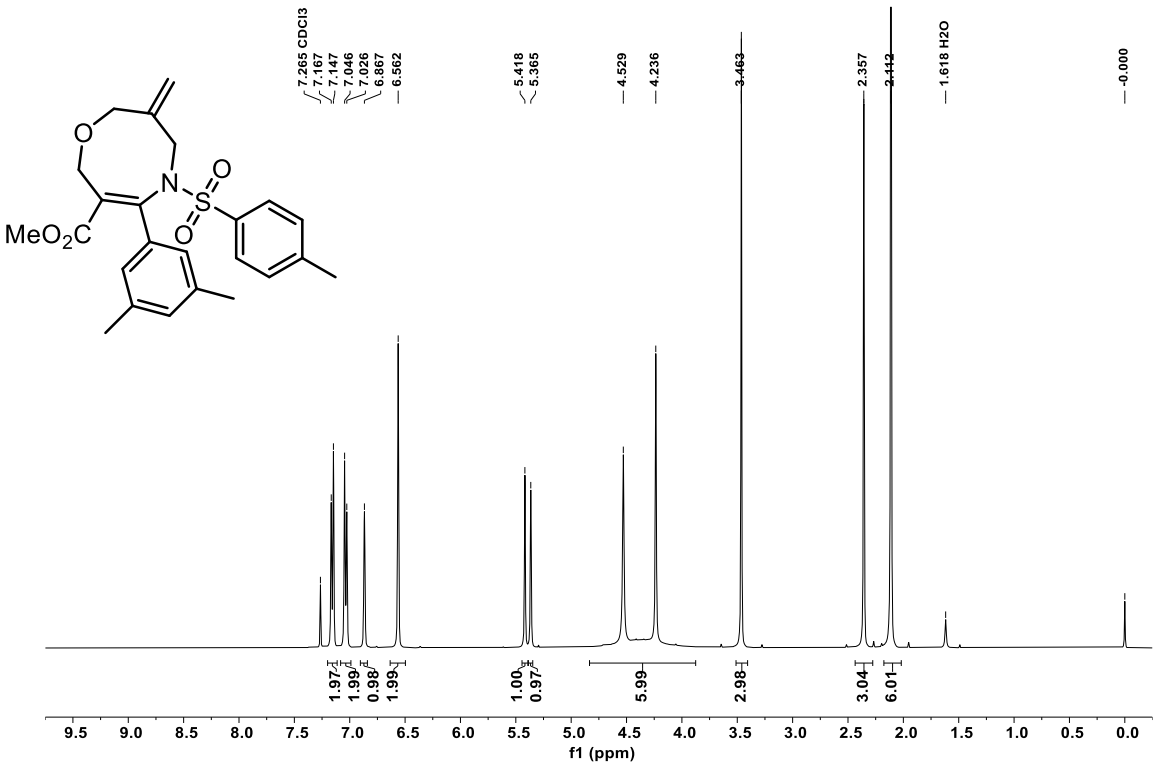
^{1}H NMR of **8b** in $CDCl_3$ (400 MHz)



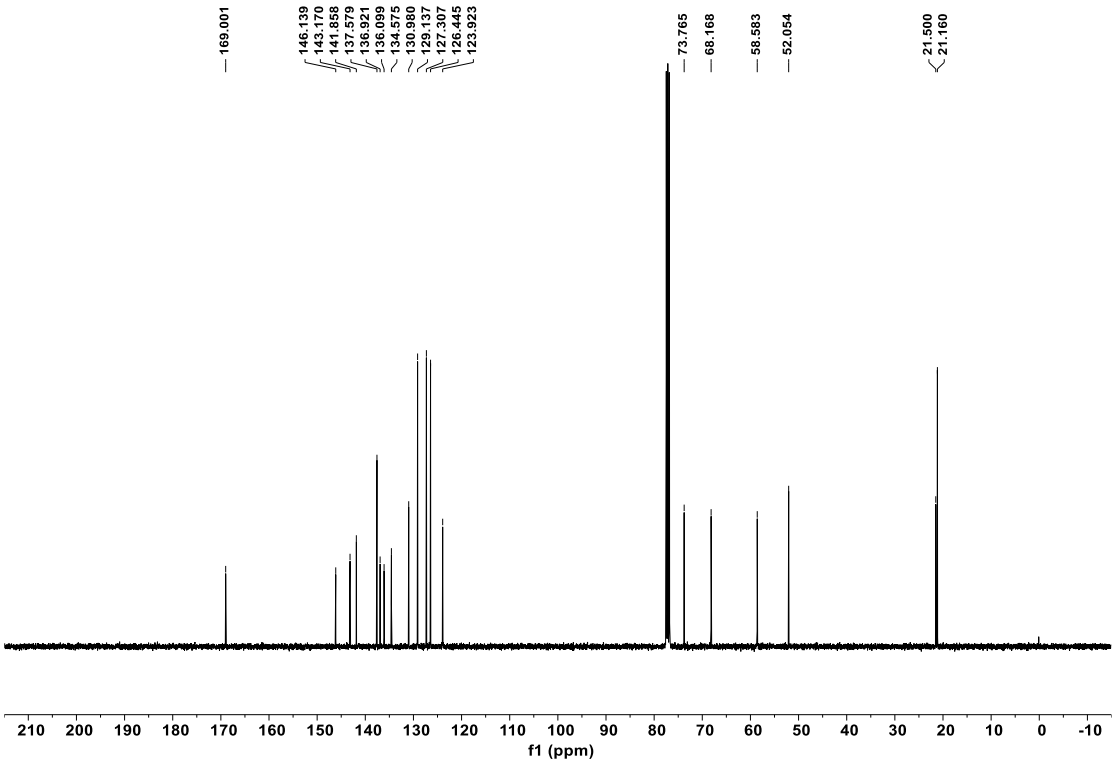
^{13}C NMR of **8b** in $CDCl_3$ (100 MHz)



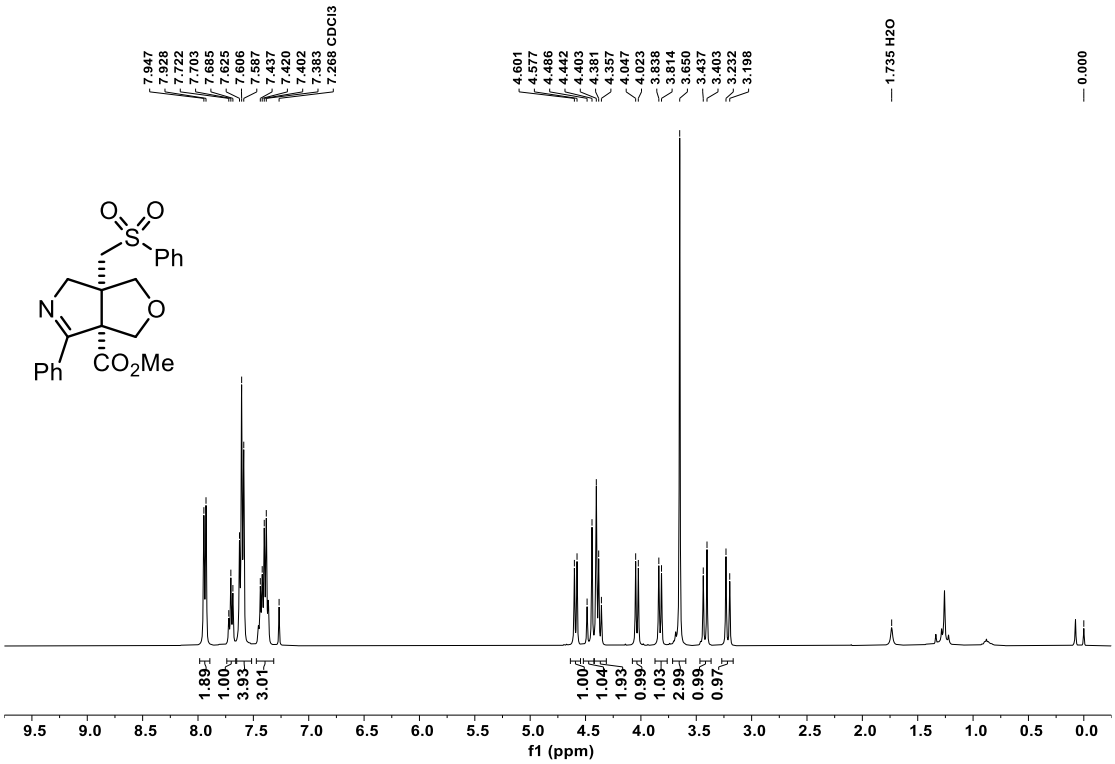
^{1}H NMR of **8c** in $CDCl_3$ (400 MHz)



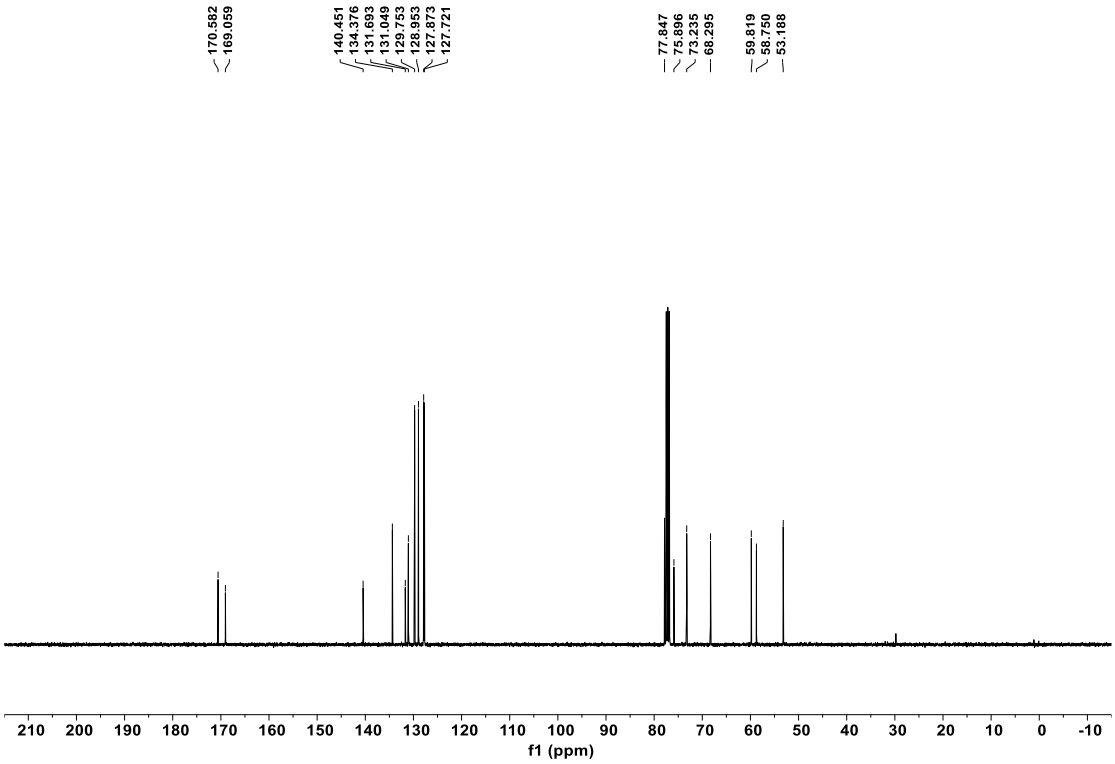
^{13}C NMR of **8c** in $CDCl_3$ (100 MHz)



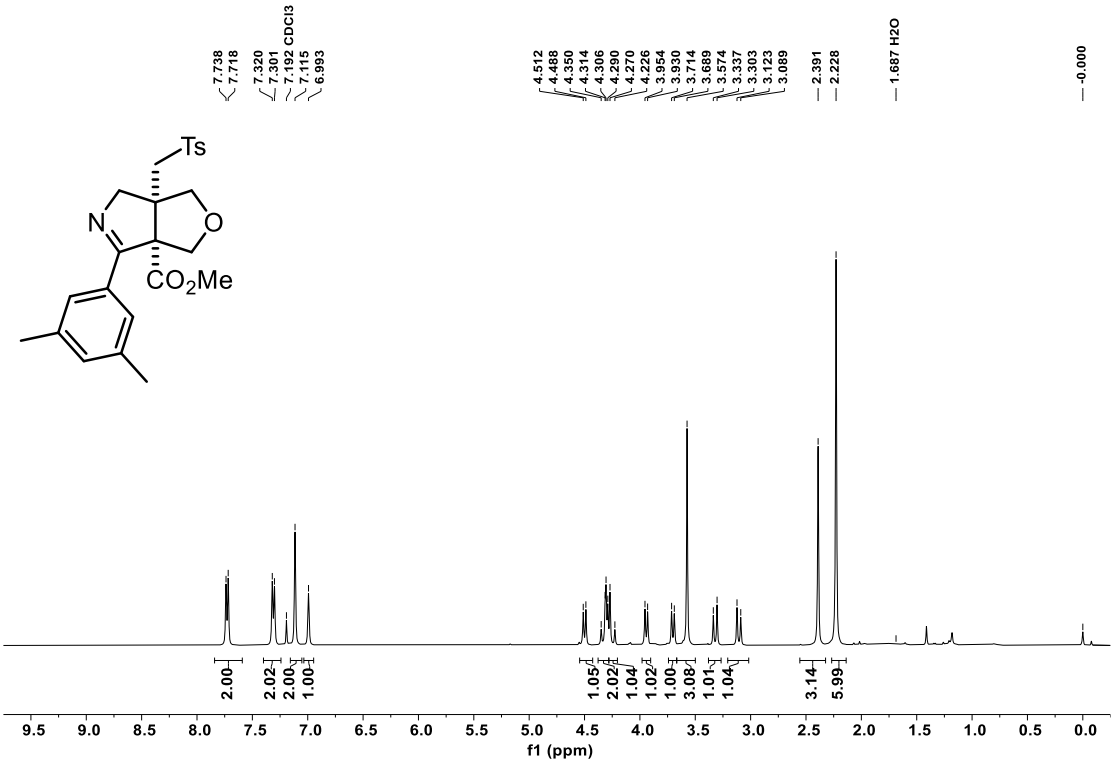
^{1}H NMR of **6j** in $CDCl_3$ (400 MHz)



^{13}C NMR of **6j** in $CDCl_3$ (100 MHz)



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



^{13}C NMR of **6k** in $CDCl_3$ (100 MHz)