

Supporting Information

**Pd-Catalyzed exclusively regioselective [5+4]
cycloaddition for the construction of 1,5-di/ox-azonanes**

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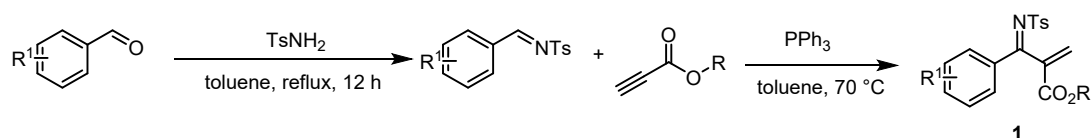
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1. General materials and methods

^1H NMR spectrum were recorded on Bruker DPX 400 MHz spectrometer or Bruker Ascend 600 MHz spectrometer in CDCl_3 . Chemical shifts were reported in ppm with the internal TMS signal at 0.00 ppm as a standard. The spectrum is interpreted as: s = singlet, d = doublet, t = triplet, m = multiplet, brs = broad singlet, dd = doublet of doublets, dt = doublet of triplets, coupling constant(s) J are reported in Hz and relative integrations are reported. ^{13}C NMR spectrum were recorded on Bruker DPX 400 MHz spectrometer or Bruker Ascend 600 MHz spectrometer in CDCl_3 . ^{13}C NMR spectra were referenced to the solvent resonance (CDCl_3 at 77.16 ppm). ^{19}F NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer in CDCl_3 . Melting points were obtained in open capillary tubes using SGW X-4 micro melting point apparatus which were uncorrected. Mass spectrum were recorded on TOF mass spectrometer. Commercially available materials purchased from Adamas-beta, TCI or Energy Chemical and were used as received. Tetrahydrofuran was distilled over sodium, dichloromethane was distilled over calcium hydride.

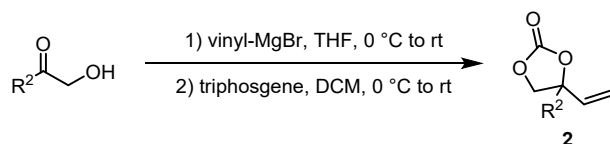
2. Experimental procedure

Preparation of 1-azadienes 1



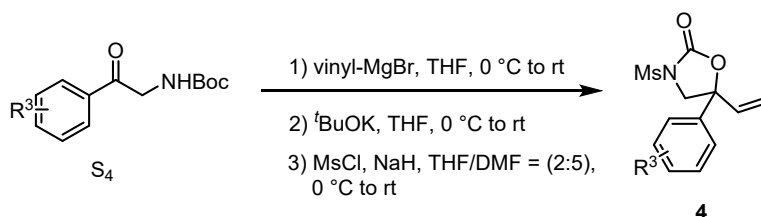
Substrates **1** were synthesized according to the literature procedure.¹ Spectral data of compounds were in accordance with those reported in the literature.

Preparation of vinylethylene carbonates 2



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

Preparation of oxazolidinones 4



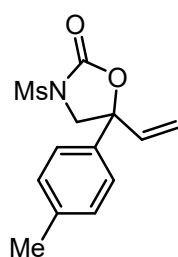
Substrates **4** were synthesized according to the literature procedure.³

References:

[1] (a) B.-Y. Cheng, Y.-N. Wang, T.-R. Li, L.-Q. Lu and W.-J. Xiao, Synthesis of polysubstituted pyrroles through a formal [4 + 1] cycloaddition/E1cb elimination/aromatization sequence of sulfur ylides and α,β -unsaturated imines, *J. Org. Chem.*, 2017, **82**, 12134-12140; (b) P. Zheng, Q. Ouyang, S. Niu, L. Shuai, Y. Yuan, K. Jiang, T. Liu and Y. Chen, Enantioselective [4 + 1] annulation reactions of α -substituted ammonium ylides to construct spirocyclic oxindoles, *J. Am. Chem. Soc.*, 2015, **137**, 9390-9399.

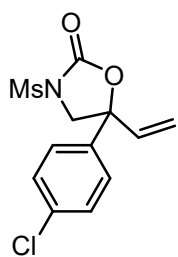
[2] A. Khan, R. Zheng, Y. Kan, J. Ye, J. Xing and Y. Zhang, Palladium-catalyzed decarboxylative cycloaddition of vinyl ethylene carbonates with formaldehyde: enantioselective construction of tertiary vinylglycols, *Angew. Chem. Int. Ed.*, 2014, **53**, 6439-6442.

[3] (a) K. Ohmatsu, N. Imagawa and T. Ooi, Ligand-enabled multiple absolute stereocontrol in metal-catalysed cycloaddition for construction of contiguous all-carbon quaternary stereocentres, *Nat. Chem.*, 2014, **6**, 47-51; (b) Y. Yang and W. Yang, Divergent synthesis of N-heterocycles by Pd-catalyzed controllable cyclization of vinyl ethylene carbonates, *Chem. Commun. (Camb)*, 2018, **54**, 12182-12185.



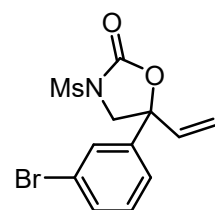
4b: Following the literature procedure³, compound **4b** was obtained as a white solid; purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 82-83 °C ; ¹H NMR (600 MHz, CDCl₃) δ 7.27 – 7.20 (m, 4H), 6.11 (dd, J = 17.1, 10.7 Hz, 1H), 5.43 – 5.35 (m, 2H), 4.30 (d, J = 9.4 Hz, 1H), 4.21 (d, J = 9.4 Hz, 1H), 3.29 (s, 3H), 2.37 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 151.9, 139.0, 137.2, 135.7, 129.7(2C), 124.9(2C), 117.1, 83.8, 54.7, 40.2, 21.2. **HRMS**

(ESI-TOF, m/z): calcd for C₁₃H₁₅NNaO₄S [M+Na]⁺: 304.0619, found: 304.0619.



4c: Following the literature procedure³, compound **4c** was obtained as a white solid; purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 91-93 °C ; ¹H NMR (600 MHz, CDCl₃) δ 7.43 – 7.39 (m, 2H), 7.34 – 7.29 (m, 2H), 6.10 (dd, J = 17.1, 10.7 Hz, 1H), 5.45 – 5.38 (m, 2H), 4.32 (d, J = 9.4 Hz, 1H), 4.18 (d, J = 9.4 Hz, 1H), 3.31 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 151.6, 137.2, 136.6, 135.1, 129.3(2C), 126.5(2C), 117.8, 83.2, 54.5, 40.3. **HRMS** (ESI-

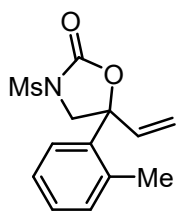
TOF, m/z): calcd for C₁₂H₁₂ClNNaO₄S [M+Na]⁺: 324.0073, found: 324.0053.



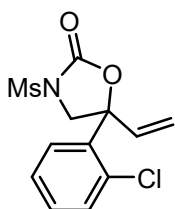
4e: Following the literature procedure³, compound **4e** was obtained as a white solid; purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 99-101 °C ; ¹H NMR (400 MHz, CDCl₃) δ 7.55 – 7.50 (m, 2H), 7.36 – 7.27 (m, 2H), 6.10 (dd, J = 17.1, 10.7 Hz, 1H), 5.49 – 5.40 (m, 2H), 4.33 (d, J = 9.4 Hz, 1H), 4.18 (d, J = 9.4 Hz, 1H), 3.32 (s, 3H). ¹³C NMR (100

MHz, CDCl₃) δ 151.6, 141.0, 136.5, 132.3, 130.8, 128.2, 123.5, 123.4, 117.9, 82.9, 54.5, 40.4. **HRMS**

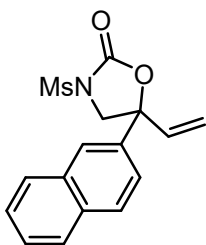
(ESI-TOF, m/z): calcd for C₁₂H₁₂BrNNaO₄S [M+Na]⁺: 367.9568, found: 367.9552.



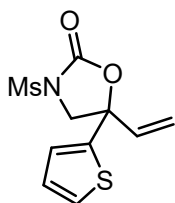
4f: Following the literature procedure³, compound **4f** was obtained as a white solid; purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 75-76 °C ; **¹H NMR** (400 MHz, CDCl₃) δ 7.48 – 7.42 (m, 1H), 7.34 – 7.21 (m, 3H), 6.14 (dd, *J* = 17.1, 10.5 Hz, 1H), 5.41 (d, *J* = 10.5 Hz, 1H), 5.31 (d, *J* = 17.1 Hz, 1H), 4.45 (d, *J* = 9.4 Hz, 1H), 4.24 (d, *J* = 9.4 Hz, 1H), 3.31 (s, 3H), 2.31 (s, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 151.6, 136.4, 136.0, 134.6, 132.5, 129.1, 126.5, 125.2, 118.4, 84.3, 54.1, 40.2, 21.1. **HRMS** (ESI-TOF, m/z): calcd for C₁₃H₁₅NNaO₄S [M+Na]⁺: 304.0619, found: 304.0621.



4g: Following the literature procedure³, compound **4g** was obtained as a white solid; purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 107-109 °C ; **¹H NMR** (400 MHz, CDCl₃) δ 7.71 – 7.64 (m, 1H), 7.48 – 7.30 (m, 3H), 6.39 – 6.28 (m, 1H), 5.48 – 5.36 (m, 2H), 4.60 (dd, *J* = 9.9, 1.3 Hz, 1H), 4.31 (dd, *J* = 9.9, 1.3 Hz, 1H), 3.32 (d, *J* = 1.3 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 151.1, 136.8, 135.0, 131.1, 130.3, 130.1, 127.6, 126.9, 117.9, 82.8, 54.2, 40.3. **HRMS** (ESI-TOF, m/z): calcd for C₁₂H₁₂ClNNaO₄S [M+Na]⁺: 324.0073, found: 324.0075.

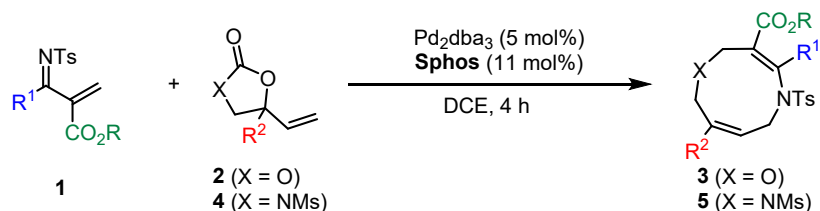


4h: Following the literature procedure³, compound **4h** was obtained as a white solid; purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 109-110 °C ; **¹H NMR** (400 MHz, CDCl₃) δ 7.94 – 7.83 (m, 4H), 7.58 – 7.51 (m, 2H), 7.43 – 7.36 (m, 1H), 6.21 (dd, *J* = 17.1, 10.7 Hz, 1H), 5.51 – 5.41 (m, 2H), 4.41 (d, *J* = 9.4 Hz, 1H), 4.33 (d, *J* = 9.4 Hz, 1H), 3.30 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 152.0, 137.0, 135.9, 133.2, 133.0, 129.3, 128.4, 127.8, 127.2, 127.1, 124.2, 122.4, 117.7, 83.9, 54.6, 40.4. **HRMS** (ESI-TOF, m/z): calcd for C₁₆H₁₅NNaO₄S [M+Na]⁺: 340.0619, found: 340.0615.

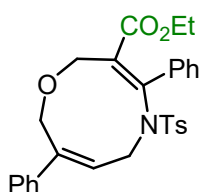


4i: Following the literature procedure³, compound **4i** was obtained as a white solid; purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 97-98 °C ; **¹H NMR** (600 MHz, CDCl₃) δ 7.43 – 7.39 (m, 1H), 7.16 – 7.12 (m, 1H), 7.07 – 7.02 (m, 1H), 6.18 (dd, *J* = 17.0, 10.7 Hz, 1H), 5.55 (d, *J* = 17.0 Hz, 1H), 5.49 (d, *J* = 10.7 Hz, 1H), 4.36 (d, *J* = 9.6 Hz, 1H), 4.24 (d, *J* = 9.6 Hz, 1H), 3.32 (s, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 151.4, 141.2, 135.9, 127.5, 127.4, 126.6, 117.9, 81.5, 55.2, 40.2. **HRMS** (ESI-TOF, m/z): calcd for C₁₀H₁₁NNaO₄S₂ [M+Na]⁺: 296.0027, found: 296.0020.

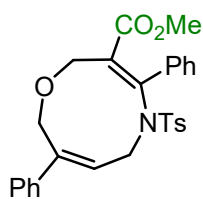
General procedure A for the [5 + 4] cyclization of 1-azadienes **1 with vinylolethylene carbonates **2** or oxazolidinones **4****



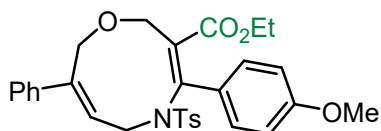
Under a nitrogen atmosphere, $\text{Pd}_2(\text{dba})_3$ (9.2 mg, 0.01 mmol) and **Sphos** (9.1 mg, 0.022 mmol) were dissolved in 1, 2-dichloroethane (2.0 mL), and stirred at room temperature for approximately 30 min. Then, 1-azadienes **1** (0.2 mmol) and vinylolethylene carbonates **2** or oxazolidinone **4** (0.3 mmol) were added sequentially. The reaction mixture was allowed to stir at 25 °C or 70 °C for 4 h and then directly purified by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, v/v) to provide the desired products **3a-3y**, **5a-5l**.



3a: Following the general procedure **A**, compound **3a** was obtained as a white solid in 93% yield (93.6 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 123-124 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.57 – 7.51 (m, 2H), 7.38 – 7.21 (m, 6H), 7.20 – 7.13 (m, 2H), 7.11 – 7.02 (m, 4H), 6.61 (t, $J = 8.2$ Hz, 1H), 4.64 (d, $J = 12.7$ Hz, 1H), 4.55 – 4.45 (m, 2H), 4.40 (d, $J = 12.4$ Hz, 1H), 4.27 – 4.16 (m, 2H), 3.95 (q, $J = 7.1$ Hz, 2H), 2.35 (s, 3H), 0.85 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.7, 147.1, 143.6, 141.0, 140.5, 137.0, 136.3, 133.5, 129.3(9)(2C), 129.3(5), 128.8, 128.5(4)(2C), 128.4(6) (2C), 128.2(2C), 128.1, 127.5(2C), 126.5(2C), 65.0, 64.6, 61.2, 49.0, 21.6, 13.6; HRMS (ESI-TOF, m/z): calcd for $\text{C}_{29}\text{H}_{29}\text{NNaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 526.1664, found: 526.1655.

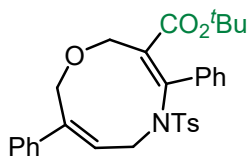


3b: Following the general procedure **A**, compound **3b** was obtained as a white solid in 95% yield (93.1 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 128-130 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.56 – 7.51 (m, 2H), 7.37 – 7.22 (m, 6H), 7.22 – 7.14 (m, 2H), 7.11 – 7.01 (m, 4H), 6.63 (t, $J = 8.2$ Hz, 1H), 4.63 (d, $J = 12.7$ Hz, 1H), 4.54 – 4.47 (m, 2H), 4.39 (d, $J = 12.4$ Hz, 1H), 4.24 (d, $J = 12.7$ Hz, 1H), 4.19 (dd, $J = 14.6, 8.8$ Hz, 1H), 3.49 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 169.2, 147.6, 143.6, 140.9, 140.5, 136.8, 136.3, 133.2, 129.5, 129.4 (2C), 128.9, 128.6 (2C), 128.3(3) (2C), 128.3(1) (2C), 128.2, 127.5(2C), 126.5 (2C), 65.0, 64.5, 52.2, 49.0, 21.6; HRMS (ESI-TOF, m/z): calcd for $\text{C}_{28}\text{H}_{27}\text{NNaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 512.1508, found: 512.1502.



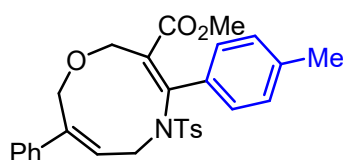
3c: Following the general procedure **A**, compound **3c** was obtained as a white solid in 92% yield (98.2 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 142-144 °C; ¹H NMR (400 MHz, CDCl₃)

δ 7.56 – 7.50 (m, 2H), 7.39 – 7.27 (m, 5H), 7.12 – 7.05 (m, 2H), 7.05 – 6.98 (m, 2H), 6.71 – 6.64 (m, 2H), 6.59 (t, *J* = 8.2 Hz, 1H), 4.61 (d, *J* = 12.6 Hz, 1H), 4.54 – 4.45 (m, 2H), 4.40 (d, *J* = 12.4 Hz, 1H), 4.25 – 4.14 (m, 2H), 4.00 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 2.37 (s, 3H), 0.94 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 169.0, 160.7, 143.5, 140.5, 136.6, 131.9, 130.0(2C), 129.4(0) (2C), 129.3(8), 128.8, 128.5(2C), 128.1, 127.6(2C), 126.5(2C), 113.7(2C), 65.1, 64.4, 61.2, 55.5, 49.0, 21.6, 13.9. **HRMS** (ESI-TOF, *m/z*): calcd for C₃₀H₃₁NNaO₆S [M+Na]⁺: 556.1170, found: 556.1761.



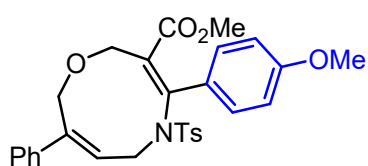
3d: Following the general procedure **A**, compound **3d** was obtained as a white solid in 80% yield (85.1 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 123-125 °C;

¹H NMR (400 MHz, CDCl₃) δ 7.59 – 7.52 (m, 2H), 7.38 – 7.25 (m, 5H), 7.25 – 7.20 (m, 1H), 7.21 – 7.12 (m, 2H), 7.14 – 7.07 (m, 2H), 7.08 – 7.01 (m, 2H), 6.57 (t, *J* = 8.3 Hz, 1H), 4.62 (d, *J* = 12.6 Hz, 1H), 4.54 – 4.37 (m, 3H), 4.26 – 4.14 (m, 2H), 2.35 (s, 3H), 1.16 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ 167.5, 145.7, 143.5, 141.2, 140.5, 137.3, 136.3, 134.9, 129.4(2), 129.1, 128.7(2C), 128.5(2C), 128.3, 128.1(5)(2C), 128.0(8), 127.5(2C), 126.5(2C), 81.8, 65.3, 64.7, 48.9(3C), 27.6, 21.6. **HRMS** (ESI-TOF, *m/z*): calcd for C₃₁H₃₃NNaO₅S [M+Na]⁺: 554.1977, found: 554.1970.



3e: Following the general procedure **A**, compound **3e** was obtained as a white solid in 92% yield (92.7 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 129-131 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.55 –

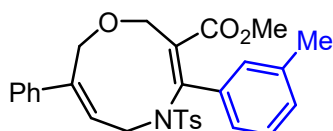
7.51 (m, 2H), 7.37 – 7.25 (m, 5H), 7.08 – 7.03 (m, 2H), 7.00 – 6.90 (m, 4H), 6.61 (t, *J* = 8.2 Hz, 1H), 4.60 (d, *J* = 12.7 Hz, 1H), 4.55 – 4.46 (m, 2H), 4.38 (d, *J* = 12.4 Hz, 1H), 4.23 – 4.15 (m, 2H), 3.52 (s, 3H), 2.36 (s, 3H), 2.32 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 169.3, 147.7, 143.5, 140.8, 140.5, 139.7, 136.5, 133.9, 132.3, 129.3(2C), 129.0(2C), 128.9, 128.5(2C), 128.2(2C), 128.1, 127.5(2C), 126.5(2C), 65.0, 64.4, 52.2, 49.1, 21.6, 21.5; **HRMS** (ESI-TOF, *m/z*): calcd for C₂₉H₂₉NNaO₅S [M+Na]⁺: 526.1664, found: 526.1656.



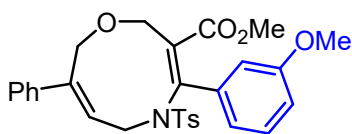
3f: Following the general procedure **A**, compound **3f** was obtained as a white solid in 93% yield (96.7 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 141-142 °C; ¹H NMR (400 MHz, CDCl₃)

δ 7.56 – 7.50 (m, 2H), 7.39 – 7.27 (m, 5H), 7.12 – 7.05 (m, 2H), 7.04 – 6.97 (m, 2H), 6.74 – 6.65

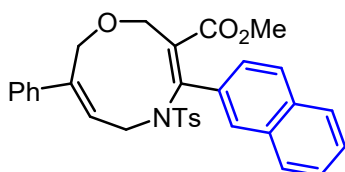
(m, 2H), 6.61 (t, $J = 8.2$ Hz, 1H), 4.60 (d, $J = 12.7$ Hz, 1H), 4.56 – 4.44 (m, 2H), 4.38 (d, $J = 12.3$ Hz, 1H), 4.24 – 4.12 (m, 2H), 3.79 (s, 3H), 3.53 (s, 3H), 2.36 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 169.5, 160.7, 147.5, 143.5, 140.8, 140.5, 136.6, 131.4, 129.8(2C), 129.4(2C), 129.1, 129.0, 128.5(2C), 128.1, 127.5(2C), 126.5(2C), 113.7(2C), 65.0, 64.3, 55.4, 52.2, 49.0, 21.6; **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{29}\text{H}_{29}\text{NNaO}_6\text{S}$ $[\text{M}+\text{Na}]^+$: 542.1613, found: 542.1604.



3g: Following the general procedure **A**, compound **3g** was obtained as a white solid in 94% yield (94.6 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 137-139 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.58 – 7.54 (m, 2H), 7.37 – 7.28 (m, 3H), 7.24 – 7.19 (m, 2H), 7.10 – 7.03 (m, 4H), 6.96 – 6.92 (m, 1H), 6.72 (s, 1H), 6.67 (t, $J = 8.2$ Hz, 1H), 4.65 (d, $J = 12.7$ Hz, 1H), 4.55 – 4.48 (m, 2H), 4.38 (d, $J = 12.4$ Hz, 1H), 4.30 (d, $J = 12.7$ Hz, 1H), 4.17 (dd, $J = 14.7, 8.9$ Hz, 1H), 3.51 (s, 3H), 2.35 (s, 3H), 2.12 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 169.3, 147.9, 143.5, 140.6, 140.4, 137.8, 136.4, 136.2, 132.9, 130.3, 129.3(2C), 129.2, 128.6, 128.5(2C), 128.3, 128.1, 127.5(2C), 126.5(2C), 126.0, 64.9, 64.3, 52.2, 49.2, 21.5, 21.2; **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{29}\text{H}_{29}\text{NNaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 526.6028, found: 526.1654.

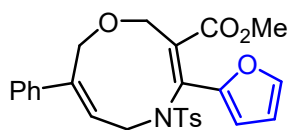


3h: Following the general procedure **A**, compound **3h** was obtained as a white solid in 92% yield (95.6 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 144-145 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.59 – 7.52 (m, 2H), 7.39 – 7.23 (m, 5H), 7.14 – 7.03 (m, 3H), 6.85 – 6.78 (m, 1H), 6.74 – 6.68 (m, 1H), 6.65 (t, 1H), 6.51 – 6.46 (m, 1H), 4.64 (d, $J = 12.7$ Hz, 1H), 4.55 – 4.45 (m, 2H), 4.38 (d, $J = 12.4$ Hz, 1H), 4.29 (d, $J = 12.7$ Hz, 1H), 4.16 (dd, $J = 14.7, 8.9$ Hz, 1H), 3.63 (s, 3H), 3.52 (s, 3H), 2.36 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 169.2, 159.4, 147.3, 143.6, 140.8, 140.4, 137.7, 136.4, 133.3, 129.4, 129.3(2C), 129.1, 128.6(2C), 128.2, 127.5(2C), 126.5(2C), 121.1, 115.6, 113.2, 64.9, 64.4, 55.1, 52.3, 49.1, 21.6; **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{29}\text{H}_{29}\text{NNaO}_6\text{S}$ $[\text{M}+\text{Na}]^+$: 542.1613, found: 542.1604.

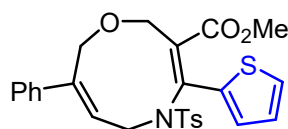


3i: Following the general procedure **A**, compound **3i** was obtained as a white solid in 90% yield (97.1 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 177-178 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 – 7.74 (m, 1H), 7.67 – 7.41 (m, 7H), 7.39 – 7.27 (m, 3H), 7.19 – 7.12 (m, 3H), 6.84 – 6.75 (m, 2H), 6.70 (t, $J = 8.2$ Hz, 1H), 4.72 (d, $J = 12.7$ Hz, 1H), 4.64 (dd, $J = 14.6, 7.6$ Hz, 1H), 4.54 (d, $J = 12.4$ Hz, 1H), 4.44 (d, $J = 12.4$ Hz, 1H), 4.39 – 4.22 (m, 2H), 3.46 (s, 3H), 2.15 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 169.2, 147.8, 143.6, 140.8, 140.5, 136.5, 133.6, 133.3, 132.8, 129.2(2C), 129.2, 128.6(2C), 128.5, 128.3, 128.2, 128.0, 127.7, 127.2(2C), 127.1,

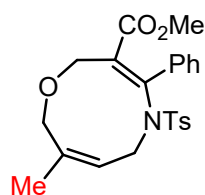
126.5(2C), 126.4, 125.6, 65.0, 64.5, 52.3, 49.5, 21.4; **HRMS** (ESI-TOF, m/z): calcd for C₃₂H₂₉NNaO₅S [M+Na]⁺: 562.1664, found: 562.1657.



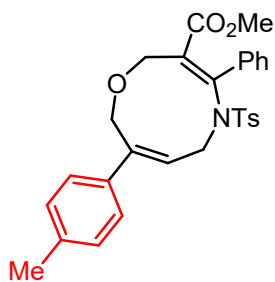
3j: Following the general procedure **A**, compound **3j** was obtained as a white solid in 80% yield (76.7 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 127-129 °C; **¹H NMR** (600 MHz, CDCl₃) δ 7.6 – 7.5 (m, 2H), 7.5 – 7.4 (m, 2H), 7.4 – 7.3 (m, 3H), 7.3 – 7.2 (m, 3H), 6.5 (t, *J* = 8.1 Hz, 1H), 6.3 – 6.3 (m, 2H), 4.5 (dd, *J* = 14.9, 7.5 Hz, 1H), 4.4 (d, *J* = 12.5 Hz, 1H), 4.3 (d, *J* = 12.6 Hz, 1H), 4.3 (d, *J* = 12.5 Hz, 1H), 4.0 (d, *J* = 12.6 Hz, 1H), 4.0 (dd, *J* = 14.9, 8.6 Hz, 1H), 3.7 (s, 3H), 2.4 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 168.7, 149.2, 144.2, 143.9, 141.0, 140.4, 136.5, 134.8, 130.8, 129.7(2C), 128.9, 128.5(2C), 128.1, 127.7(2C), 126.5(2C), 113.3, 111.8, 64.2, 63.9, 52.4, 47.8, 21.7; **HRMS** (ESI-TOF, m/z): calcd for C₂₆H₂₅NNaO₆S [M+Na]⁺: 502.1300, found: 502.1294.



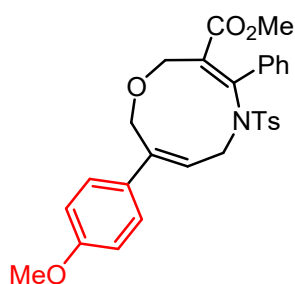
3k: Following the general procedure **A**, compound **3k** was obtained as a white solid in 82% yield (81.3 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 132-134 °C; **¹H NMR** (600 MHz, CDCl₃) δ 7.58 – 7.40 (m, 4H), 7.37 – 7.24 (m, 4H), 7.16 – 7.12 (m, 2H), 6.98 – 6.83 (m, 2H), 6.59 (t, *J* = 8.1 Hz, 1H), 4.50 – 4.42 (m, 3H), 4.34 (d, *J* = 12.5 Hz, 1H), 4.14 (d, *J* = 12.7 Hz, 1H), 4.07 (dd, *J* = 14.7, 8.6 Hz, 1H), 3.62 (s, 3H), 2.38 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 168.9, 143.8, 141.0, 140.4, 139.3, 139.2, 136.4, 133.0, 129.5(2C), 129.2, 128.7, 128.5(2C), 128.4, 128.1, 127.4(2C), 127.1, 126.5(2C), 64.8, 64.3, 52.5, 48.0, 21.7; **HRMS** (ESI-TOF, m/z): calcd for C₂₆H₂₅NNaO₅S₂ [M+Na]⁺: 518.1072, found: 518.1064.



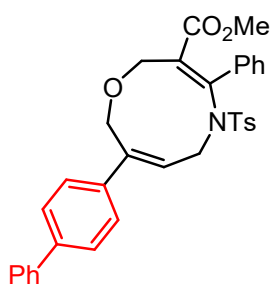
3l: Following the general procedure **A**, compound **3l** was obtained as a white solid in 85% yield (72.7 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 85-86 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.3 – 7.1 (m, 5H), 7.1 – 7.0 (m, 4H), 6.1 (t, *J* = 8.1 Hz, 1H), 4.5 (d, *J* = 12.4 Hz, 1H), 4.3 (dd, *J* = 14.5, 7.8 Hz, 1H), 4.2 – 4.0 (m, 3H), 3.9 (d, *J* = 11.7 Hz, 1H), 3.5 (s, 3H), 2.4 (s, 3H), 1.9 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 169.3, 147.2, 143.5, 139.4, 137.0, 136.4, 133.3, 129.4, 129.3(2C), 128.3(1) (2C), 128.2(6) (2C), 127.5(2C), 126.9, 66.0, 65.2, 52.2, 48.8, 22.5, 21.6; **HRMS** (ESI-TOF, m/z): calcd for C₂₃H₂₅NNaO₅S [M+Na]⁺: 450.1351, found: 450.1345.



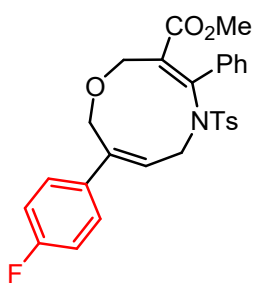
3m: Following the general procedure **A**, compound **3m** was obtained as a white solid in 93% yield (93.7 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 138-139 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.46 – 7.40 (m, 2H), 7.31 – 7.26 (m, 1H), 7.25 – 7.23 (m, 2H), 7.20 – 7.13 (m, 4H), 7.11 – 7.03 (m, 4H), 6.59 (t, $J = 8.2$ Hz, 1H), 4.61 (d, $J = 12.7$ Hz, 1H), 4.54 – 4.46 (m, 2H), 4.37 (d, $J = 12.4$ Hz, 1H), 4.25 – 4.15 (m, 2H), 3.49 (s, 3H), 2.35 (s, 6H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 169.2, 147.5, 143.6, 140.7, 138.0, 137.5, 136.8, 136.4, 133.2, 129.5, 129.4(2C), 129.3(2C), 128.3(2) (2C), 128.2(9) (2C), 128.0, 127.5(2C), 126.4(2C), 64.9, 64.4, 52.2, 49.1, 21.6, 21.2; **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{29}\text{H}_{29}\text{NNaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 526.1664, found: 526.1657.



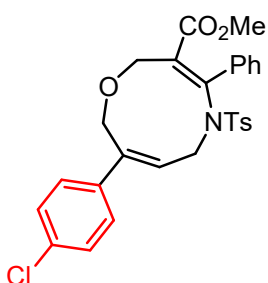
3n: Following the general procedure **A**, compound **3n** was obtained as a white solid in 93% yield (96.6 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 147-148 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.51 – 7.46 (m, 2H), 7.31 – 7.25 (m, 1H), 7.26 – 7.21 (m, 2H), 7.19 – 7.13 (m, 2H), 7.10 – 7.02 (m, 4H), 6.90 – 6.84 (m, 2H), 6.56 (t, $J = 8.2$ Hz, 1H), 4.61 (d, $J = 12.7$ Hz, 1H), 4.53 – 4.45 (m, 2H), 4.37 (d, $J = 12.4$ Hz, 1H), 4.23 (d, $J = 12.7$ Hz, 1H), 4.17 (dd, $J = 14.7, 8.9$ Hz, 1H), 3.82 (s, 3H), 3.49 (s, 3H), 2.35 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 169.2, 159.7, 147.6, 143.6, 140.2, 136.8, 136.4, 133.2, 132.8, 129.4(4), 129.39(2C), 128.3(2) (2C), 128.2(9) (2C), 127.7(2C), 127.5(2C), 127.2, 113.9(2C), 64.9, 64.4, 55.4, 52.2, 49.2, 21.6; **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{29}\text{H}_{29}\text{NNaO}_6\text{S}$ $[\text{M}+\text{Na}]^+$: 542.1613, found: 542.1607.



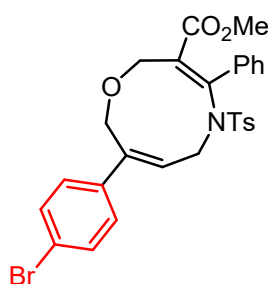
3o: Following the general procedure **A**, compound **3o** was obtained as a white solid in 86% yield (97.3 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 179-181 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.65 – 7.56 (m, 6H), 7.48 – 7.42 (m, 2H), 7.38 – 7.34 (m, 1H), 7.32 – 7.27 (m, 1H), 7.27 – 7.22 (m, 2H), 7.20 – 7.14 (m, 2H), 7.11 – 7.04 (m, 4H), 6.70 (t, $J = 8.2$ Hz, 1H), 4.66 (d, $J = 12.7$ Hz, 1H), 4.57 – 4.50 (m, 2H), 4.42 (d, $J = 12.5$ Hz, 1H), 4.27 (d, $J = 12.7$ Hz, 1H), 4.21 (dd, $J = 14.6, 8.8$ Hz, 1H), 3.51 (s, 3H), 2.36 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 169.2, 143.6, 141.0, 140.7, 140.4, 139.3, 136.8, 136.3, 133.2, 129.5, 129.4(2C), 128.9(2C), 128.8, 128.3(2C), 128.3(2C) 127.6, 127.5(2C), 127.3(2C), 127.2(2C), 126.9(2C), 65.0, 64.3, 52.2, 49.1, 21.6; **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{34}\text{H}_{31}\text{NNaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 588.1821, found: 588.1815.



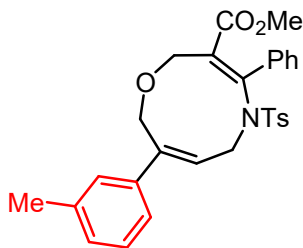
3p: Following the general procedure **A**, compound **3p** was obtained as a white solid in 94% yield (95.4 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 154-155 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.5 – 7.5 (m, 2H), 7.3 – 7.3 (m, 1H), 7.2 – 7.2 (m, 2H), 7.2 – 7.1 (m, 2H), 7.1 – 7.0 (m, 6H), 6.6 (t, $J = 8.2$ Hz, 1H), 4.6 (d, $J = 12.7$ Hz, 1H), 4.5 (dd, $J = 14.7, 7.6$ Hz, 1H), 4.4 (d, $J = 12.5$ Hz, 1H), 4.4 (d, $J = 12.5$ Hz, 1H), 4.2 (d, $J = 12.7$ Hz, 1H), 4.2 (dd, $J = 14.6, 8.8$ Hz, 1H), 3.5 (s, 3H), 2.3 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 169.1, 162.8 (d, $J = 247.5$ Hz), 147.7, 143.7, 139.9, 136.6, 136.6 (d, $J = 3.2$ Hz), 136.3, 133.1, 129.5, 129.4(2C), 128.9, 128.3(2)(2C), 128.3(2)(2C)128.2(5) (d, $J = 8.2$ Hz)(2C), 127.5(2C), 115.4 (d, $J = 21.4$ Hz)(2C), 64.9, 64.5, 52.2, 48.9, 21.6; $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -114.12 – -114.23 (m, 1F); **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{28}\text{H}_{26}\text{FNNaO}_5\text{S}$ [$\text{M}+\text{Na}$] $^+$: 530.1413, found: 530.1407.



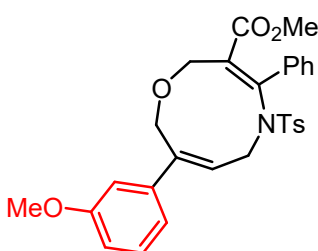
3q: Following the general procedure **A**, compound **3q** was obtained as a white solid in 94% yield (98.3 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 160-161 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.51 – 7.45 (m, 2H), 7.35 – 7.27 (m, 3H), 7.24 – 7.20 (m, 2H), 7.19 – 7.13 (m, 2H), 7.10 – 7.02 (m, 4H), 6.62 (t, $J = 8.2$ Hz, 1H), 4.64 (d, $J = 12.7$ Hz, 1H), 4.49 (dd, $J = 14.6, 7.6$ Hz, 1H), 4.44 (d, $J = 12.5$ Hz, 1H), 4.37 (d, $J = 12.5$ Hz, 1H), 4.23 (d, $J = 12.7$ Hz, 1H), 4.17 (dd, $J = 14.6, 8.8$ Hz, 1H), 3.50 (s, 3H), 2.35 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 169.1, 147.7, 143.7, 139.8, 138.9, 136.6, 136.2, 134.1, 133.1, 129.5, 129.4, 129.4(2C), 128.7(2C), 128.3(2C), 128.3(2C), 127.9(2C), 127.5(2C), 65.0, 64.3, 52.2, 48.9, 21.6; **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{28}\text{H}_{26}\text{ClNNaO}_5\text{S}$ [$\text{M}+\text{Na}$] $^+$: 546.1118, found: 546.1112.



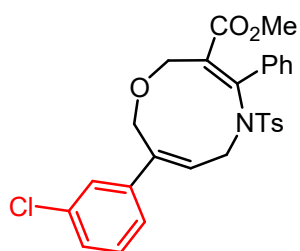
3r: Following the general procedure **A**, compound **3r** was obtained as a white solid in 90% yield (102.3 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 172-174 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.49 – 7.44 (m, 2H), 7.44 – 7.39 (m, 2H), 7.32 – 7.26 (m, 1H), 7.25 – 7.20 (m, 2H), 7.19 – 7.13 (m, 2H), 7.09 – 7.03 (m, 4H), 6.63 (t, $J = 8.2$ Hz, 1H), 4.64 (d, $J = 12.7$ Hz, 1H), 4.49 (dd, $J = 14.6, 7.6$ Hz, 1H), 4.44 (d, $J = 12.5$ Hz, 1H), 4.36 (d, $J = 12.5$ Hz, 1H), 4.22 (d, $J = 12.7$ Hz, 1H), 4.17 (dd, $J = 14.6, 8.8$ Hz, 1H), 3.50 (s, 3H), 2.35 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 169.1, 147.7, 143.7, 139.9, 139.4, 136.6, 136.2, 133.1, 131.7(2C), 129.6, 129.5, 129.4(2C), 128.3(2C), 128.3(2C), 128.2(2C), 127.5(2C), 122.4, 65.0, 64.3, 52.2, 48.9, 21.6; **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{28}\text{H}_{26}\text{BrNNaO}_5\text{S}$ [$\text{M}+\text{Na}$] $^+$: 590.0613, found: 590.0608.



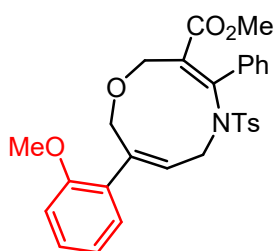
3s: Following the general procedure **A**, compound **3s** was obtained as a white solid in 93% yield (93.7 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 142-144 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.43 – 7.00 (m, 13H), 6.62 (t, J = 8.2 Hz, 1H), 4.63 (d, J = 12.6 Hz, 1H), 4.55 – 4.46 (m, 2H), 4.37 (d, J = 12.3 Hz, 1H), 4.28 – 4.13 (m, 2H), 3.49 (s, 3H), 2.36 (s, 3H), 2.35 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 169.2, 147.6, 143.6, 140.9, 140.4, 138.1, 136.8, 136.4, 133.2, 129.5, 129.4(2C), 128.9, 128.7, 128.5, 128.3(2) (2C), 128.3(0) (2C), 127.5(2C), 127.2, 123.6, 64.9, 64.5, 52.2, 49.1, 21.6, 21.6; **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{29}\text{H}_{29}\text{NNaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 526.1664, found: 526.1654.



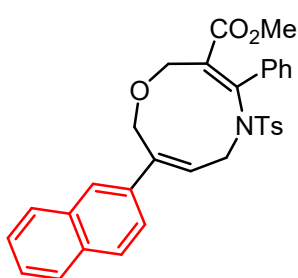
3t: Following the general procedure **A**, compound **3t** was obtained as a white solid in 94% yield (97.6 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 147-149 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.31 – 7.23 (m, 4H), 7.20 – 7.14 (m, 2H), 7.14 – 7.10 (m, 1H), 7.09 – 7.03 (m, 5H), 6.88 – 6.83 (m, 1H), 6.62 (t, J = 8.2 Hz, 1H), 4.63 (d, J = 12.7 Hz, 1H), 4.54 – 4.45 (m, 2H), 4.37 (d, J = 12.4 Hz, 1H), 4.23 (d, J = 12.7 Hz, 1H), 4.18 (dd, J = 14.6, 8.8 Hz, 1H), 3.82 (s, 3H), 3.49 (s, 3H), 2.35 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 169.2, 159.8, 147.5, 143.7, 142.0, 140.9, 136.8, 136.3, 133.2, 129.5(2), 129.4(8), 129.4(2C), 129.1, 128.3(2)(2C), 128.3(0)(2C), 127.5(2C), 119.0, 113.7, 112.2, 64.9, 64.6, 55.4, 52.2, 49.0, 21.6; **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{29}\text{H}_{29}\text{NNaO}_6\text{S}$ $[\text{M}+\text{Na}]^+$: 542.1613, found: 542.1607.



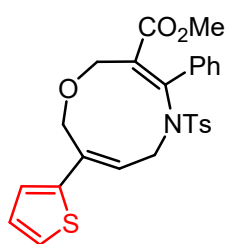
3u: Following the general procedure **A**, compound **3u** was obtained as a white solid in 94% yield (98.5 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 155-156 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.53 – 7.49 (m, 1H), 7.45 – 7.39 (m, 1H), 7.32 – 7.22 (m, 5H), 7.20 – 7.14 (m, 2H), 7.10 – 7.04 (m, 4H), 6.62 (t, J = 8.2 Hz, 1H), 4.64 (d, J = 12.7 Hz, 1H), 4.50 (dd, J = 14.6, 7.7 Hz, 1H), 4.44 (d, J = 12.5 Hz, 1H), 4.36 (d, J = 12.5 Hz, 1H), 4.23 – 4.14 (m, 2H), 3.50 (s, 3H), 2.36 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 169.1, 147.6, 143.8, 142.3, 139.9, 136.7, 136.2, 134.5, 133.1, 130.0, 129.8, 129.6, 129.5(2C), 128.3(4)(2C), 128.3(2)(2C), 128.2, 127.5(2C), 126.7, 124.7, 65.0, 64.3, 52.2, 48.8, 21.6; **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{28}\text{H}_{26}\text{ClNNaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 546.1118, found: 546.1113.



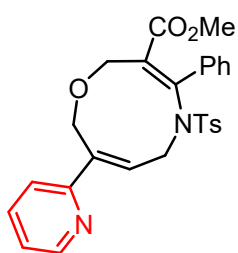
3v: Following the general procedure **A**, compound **3v** was obtained as a white solid in 89% yield (92.5 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 136-138 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.35 – 7.18 (m, 6H), 7.16 – 7.08 (m, 5H), 6.95 – 6.82 (m, 2H), 6.29 (t, *J* = 8.3 Hz, 1H), 4.55 (d, *J* = 12.4 Hz, 2H), 4.46 (dd, *J* = 14.5, 7.8 Hz, 1H), 4.39 – 4.23 (m, 2H), 4.18 (d, *J* = 12.5 Hz, 1H), 3.79 (s, 3H), 3.49 (s, 3H), 2.39 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 169.2, 156.4, 147.3, 143.7, 141.7, 137.3, 136.4, 132.9, 130.8, 130.5, 130.1, 129.5(2C), 129.4(3), 129.3(7), 128.3(0) (2C), 128.2(9) (2C), 127.6(2C), 120.9, 110.7, 65.2, 64.7, 55.4, 52.1, 48.5, 21.6; **HRMS** (ESI-TOF, *m/z*): calcd for C₂₉H₂₉NNaO₆S [M+Na]⁺: 542.1613, found:542.1606.



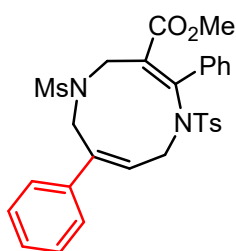
3w: Following the general procedure **A**, compound **3w** was obtained as a white solid in 85% yield (91.7 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 177-178 °C; **¹H NMR** (600 MHz, CDCl₃) δ 8.05 – 8.02 (m, 1H), 7.86 – 7.79 (m, 3H), 7.69 – 7.64 (m, 1H), 7.51 – 7.44 (m, 2H), 7.33 – 7.24 (m, 3H), 7.21 – 7.15 (m, 2H), 7.14 – 7.02 (m, 4H), 6.78 (t, *J* = 8.2 Hz, 1H), 4.67 (d, *J* = 12.8 Hz, 1H), 4.64 (d, *J* = 12.5 Hz, 1H), 4.57 (dd, *J* = 14.6, 7.6 Hz, 1H), 4.48 (d, *J* = 12.5 Hz, 1H), 4.31 – 4.19 (m, 2H), 3.50 (s, 3H), 2.35 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 169.2, 147.6, 143.7, 140.8, 137.6, 136.8, 136.3, 133.5, 133.2, 133.1, 129.5, 129.4(5)(2C), 129.2, 128.5, 128.3(2C), 128.3(2C), 128.1, 127.7, 127.5(2C), 126.4, 126.3, 125.8, 124.3, 65.1, 64.5, 52.2, 49.1, 21.6; **HRMS** (ESI-TOF, *m/z*): calcd for C₃₂H₂₉NNaO₅S [M+Na]⁺: 562.1664, found: 562.1650.



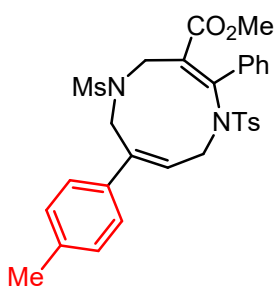
3x: Following the general procedure **A**, compound **3x** was obtained as a white solid in 95% yield (94.2 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 136-138 °C; **¹H NMR** (600 MHz, CDCl₃) δ 7.3 – 7.3 (m, 2H), 7.3 – 7.2 (m, 3H), 7.2 – 7.2 (m, 2H), 7.1 – 7.0 (m, 4H), 7.0 – 7.0 (m, 1H), 6.7 (t, *J* = 8.1 Hz, 1H), 4.6 (d, *J* = 12.6 Hz, 1H), 4.6 – 4.5 (m, 2H), 4.4 (d, *J* = 12.5 Hz, 1H), 4.2 – 4.1 (m, 2H), 3.5 (s, 3H), 2.3 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ 169.1, 148.0, 143.7, 143.6, 136.7, 136.4, 135.1, 133.3, 129.6, 129.5(2C), 128.3(4) (2C), 128.2(8) (2C), 127.8, 127.5(2C), 126.8, 125.4(3), 125.4(2), 65.1, 63.9, 52.2, 49.0, 21.6; **HRMS** (ESI-TOF, *m/z*): calcd for C₂₆H₂₅NNaO₅S₂ [M+Na]⁺: 518.1072, found: 518.1066.



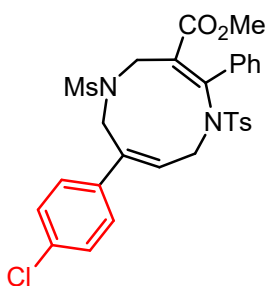
3y: Following the general procedure **A**, compound **3y** was obtained as a white solid in 90% yield (88.4 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 132-133 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.63 – 8.57 (m, 1H), 7.72 – 7.60 (m, 2H), 7.44 – 6.88 (m, 11H), 4.76 (d, $J = 12.4$ Hz, 1H), 4.63 (d, $J = 12.6$ Hz, 1H), 4.53 (dd, $J = 14.7, 7.7$ Hz, 1H), 4.43 (d, $J = 12.4$ Hz, 1H), 4.29 – 4.18 (m, 2H), 3.49 (s, 3H), 2.34 (s, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 169.0, 156.8, 149.3, 147.7, 143.6, 139.9, 136.8, 136.6, 136.0, 133.3, 131.7, 129.5, 129.4(2C), 128.2(9)(2C), 128.2(7)(2C), 127.5(2C), 122.8, 121.3, 65.0, 62.8, 52.2, 48.6, 21.6. **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{27}\text{H}_{26}\text{N}_2\text{NaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 513.1460, found: 513.1451.



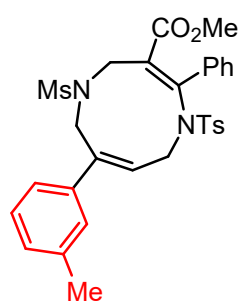
5a: Following the general procedure **A**, compound **5a** was obtained as a white solid in 83% yield (94.1 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1); m.p.: 138-140 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.54 – 7.47 (m, 2H), 7.42 – 7.32 (m, 3H), 7.32 – 7.26 (m, 1H), 7.25 – 7.21 (m, 2H), 7.18 – 7.13 (m, 2H), 7.10 – 7.04 (m, 4H), 6.49 (t, $J = 8.2$ Hz, 1H), 4.81 (d, $J = 15.0$ Hz, 1H), 4.59 (d, $J = 14.0$ Hz, 1H), 4.44 (dd, $J = 14.7, 7.5$ Hz, 1H), 4.23 (dd, $J = 14.7, 8.9$ Hz, 1H), 4.14 (d, $J = 14.9$ Hz, 1H), 3.96 (d, $J = 13.9$ Hz, 1H), 3.54 (s, 3H), 2.36 (s, 3H), 2.08 (s, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 168.1, 145.8, 143.8, 140.8, 139.9, 136.1, 135.9, 132.7, 129.6, 129.5, 129.4(2C), 128.9(2)(2C), 128.9(1), 128.4(2C), 128.2(2C), 127.6(2C), 127.5(2C), 52.5, 48.6, 45.8, 44.7, 39.4, 21.6. **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{29}\text{H}_{30}\text{N}_2\text{NaO}_6\text{S}_2$ $[\text{M}+\text{Na}]^+$: 589.1443, found: 589.1439.



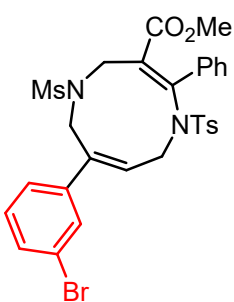
5b: Following the general procedure **A**, compound **5b** was obtained as a white solid in 75% yield (87.1 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1); m.p.: 155-157 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.40 – 7.36 (m, 2H), 7.31 – 7.25 (m, 1H), 7.25 – 7.09 (m, 6H), 7.09 – 7.03 (m, 4H), 6.45 (t, $J = 8.2$ Hz, 1H), 4.79 (d, $J = 14.9$ Hz, 1H), 4.58 (d, $J = 14.0$ Hz, 1H), 4.44 (dd, $J = 14.7, 7.5$ Hz, 1H), 4.22 (dd, $J = 14.7, 8.9$ Hz, 1H), 4.12 (d, $J = 14.9$ Hz, 1H), 3.94 (d, $J = 14.0$ Hz, 1H), 3.54 (s, 3H), 2.36 (d, $J = 6.1$ Hz, 6H), 2.10 (s, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 168.1, 145.8, 143.7, 140.7, 138.9, 136.9, 136.2, 135.9, 132.7, 129.6(2C), 129.5, 129.4(2C), 128.8, 128.4(2C), 128.2(2C), 127.5(2C), 127.4(2C), 52.4, 48.7, 45.8, 44.6, 39.5, 21.6, 21.3. **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{30}\text{H}_{32}\text{N}_2\text{NaO}_6\text{S}_2$ $[\text{M}+\text{Na}]^+$: 603.1599, found: 603.1597.



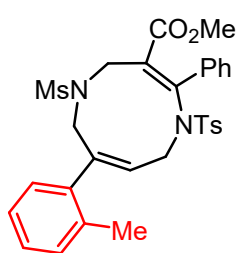
5c: Following the general procedure **A**, compound **5c** was obtained as a white solid in 78% yield (93.6 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1); m.p.: 169-171 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.46 – 7.41 (m, 2H), 7.37 – 7.32 (m, 2H), 7.32 – 7.25 (m, 1H), 7.23 – 7.19 (m, 2H), 7.18 – 7.13 (m, 2H), 7.08 – 7.03 (m, 4H), 6.45 (t, $J = 8.2$ Hz, 1H), 4.72 (d, $J = 14.8$ Hz, 1H), 4.61 (d, $J = 14.2$ Hz, 1H), 4.44 (dd, $J = 14.6, 7.7$ Hz, 1H), 4.22 (dd, $J = 14.6, 8.7$ Hz, 1H), 4.14 (d, $J = 14.9$ Hz, 1H), 3.93 (d, $J = 14.1$ Hz, 1H), 3.52 (s, 3H), 2.36 (s, 3H), 2.26 (s, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 168.1, 145.8, 143.9, 139.9, 138.2, 136.1, 135.7, 134.8(2), 134.8(0), 132.4, 129.8, 129.6, 129.4(2C), 129.0(2C), 128.8(2C), 128.4(2C), 128.2(2C), 127.5, 52.4, 48.4, 46.0, 44.6, 39.6, 21.6. **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{29}\text{H}_{29}\text{ClN}_2\text{NaO}_6\text{S}_2$ $[\text{M}+\text{Na}]^+$: 623.1053, found: 603.1033.



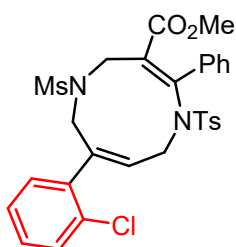
5d: Following the general procedure **A**, compound **5d** was obtained as a white solid in 62% yield (72.0 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1); m.p.: 162-163 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.33 – 7.21 (m, 6H), 7.18 – 7.13 (m, 3H), 7.10 – 7.04 (m, 4H), 6.48 (t, $J = 8.1$ Hz, 1H), 4.80 (d, $J = 15.0$ Hz, 1H), 4.59 (d, $J = 14.0$ Hz, 1H), 4.44 (dd, $J = 14.7, 7.4$ Hz, 1H), 4.22 (dd, $J = 14.7, 8.9$ Hz, 1H), 4.11 (d, $J = 15.0$ Hz, 1H), 3.95 (d, $J = 14.0$ Hz, 1H), 3.55 (s, 3H), 2.38 (s, 3H), 2.36 (s, 3H), 2.08 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 168.1, 145.8, 143.7, 140.9, 139.9, 138.7, 136.2, 136.0, 132.8, 129.6, 129.5, 129.4, 129.4(2C), 128.8, 128.4(2C), 128.2, 128.2(2C), 127.6(2C), 124.6, 52.5, 48.7, 45.7, 44.7, 39.5, 21.6, 21.6. **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{30}\text{H}_{32}\text{N}_2\text{NaO}_6\text{S}_2$ $[\text{M}+\text{Na}]^+$: 603.1599, found: 603.1590.



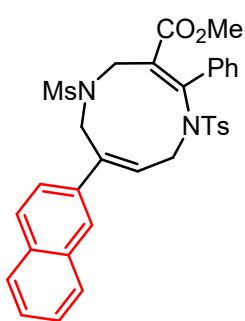
5e: Following the general procedure **A**, compound **5e** was obtained as a white solid in 76% yield (97.9 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1); m.p.: 182-184 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.59 – 7.56 (m, 1H), 7.49 – 7.45 (m, 1H), 7.45 – 7.40 (m, 1H), 7.33 – 7.21 (m, 4H), 7.20 – 7.15 (m, 2H), 7.11 – 7.04 (m, 4H), 6.42 (t, $J = 8.1$ Hz, 1H), 4.67 (d, $J = 14.8$ Hz, 1H), 4.61 (d, $J = 14.2$ Hz, 1H), 4.47 (dd, $J = 14.5, 7.7$ Hz, 1H), 4.23 (dd, $J = 14.5, 8.7$ Hz, 1H), 4.15 (d, $J = 14.8$ Hz, 1H), 3.87 (d, $J = 14.2$ Hz, 1H), 3.52 (s, 3H), 2.38 (s, 3H), 2.29 (s, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 168.2, 145.7, 144.0, 142.0, 139.9, 136.3, 135.8, 132.3, 131.8, 130.5, 130.3, 130.1, 129.6, 129.5(2C), 128.5(2C), 128.2(2C), 127.5(2C), 126.0, 122.9, 52.5, 48.3, 46.1, 44.7, 39.6, 21.6. **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{29}\text{H}_{29}\text{BrN}_2\text{NaO}_6\text{S}_2$ $[\text{M}+\text{Na}]^+$: 667.0548, found: 667.0557.



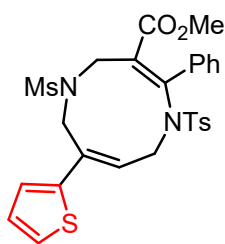
5f: Following the general procedure **A**, compound **5f** was obtained as a white solid in 48% yield (55.8 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1); m.p.: 171-172 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.31 – 7.20 (m, 5H), 7.19 – 7.11 (m, 4H), 7.11 – 7.08 (m, 2H), 7.07 – 7.03 (m, 2H), 6.32 (dd, $J = 8.9, 7.2$ Hz, 1H), 4.68 (d, $J = 14.1$ Hz, 1H), 4.59 (d, $J = 14.9$ Hz, 1H), 4.42 (dd, $J = 14.9, 7.2$ Hz, 1H), 4.22 (dd, $J = 14.8, 9.0$ Hz, 1H), 4.13 – 4.05 (m, 2H), 3.57 (s, 3H), 2.38 (s, 3H), 2.36 (s, 3H), 2.08 (s, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 168.2, 146.0, 143.7, 141.5, 140.1, 136.1, 136.0, 135.4, 132.9, 131.7, 130.9, 129.9, 129.6, 129.4(2C), 128.6, 128.4(2C), 128.2(2C), 127.6(2C), 126.1, 52.5, 48.4, 45.7, 45.4, 40.0, 21.6, 20.1. **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{30}\text{H}_{32}\text{N}_2\text{NaO}_6\text{S}_2$ $[\text{M}+\text{Na}]^+$: 603.1599, found: 603.1581.



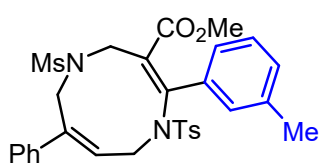
5g: Following the general procedure **A**, compound **5g** was obtained as a white solid in 52% yield (62.5 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1); m.p.: 181-183 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.44 – 7.37 (m, 1H), 7.35 – 7.20 (m, 6H), 7.20 – 7.14 (m, 2H), 7.11 – 7.04 (m, 4H), 6.37 – 6.31 (m, 1H), 4.76 (d, $J = 14.9$ Hz, 1H), 4.72 (dd, $J = 14.4, 1.1$ Hz, 1H), 4.44 (dd, $J = 14.8, 7.3$ Hz, 1H), 4.22 (dd, $J = 14.7, 9.0$ Hz, 1H), 4.14 – 4.04 (m, 2H), 3.54 (s, 3H), 2.36 (s, 3H), 2.31 (s, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 168.4, 146.3, 143.8, 140.0, 139.0, 136.2, 135.9, 132.5(6), 132.5(3), 132.4(7), 131.6, 129.9, 129.8, 129.6, 129.4(2C), 128.4(2C), 128.2(2C), 127.5(2C), 127.1, 52.5, 48.2, 45.8, 44.8, 40.2, 21.6. **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{29}\text{H}_{29}\text{ClN}_2\text{NaO}_6\text{S}_2$ $[\text{M}+\text{Na}]^+$: 623.1053, found: 623.1030.



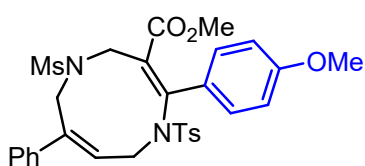
5h: Following the general procedure **A**, compound **5h** was obtained as a white solid in 79% yield (97.5 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1); m.p.: 184-185 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.02 – 7.94 (m, 1H), 7.93 – 7.79 (m, 3H), 7.65 – 7.57 (m, 1H), 7.56 – 7.45 (m, 2H), 7.33 – 7.23 (m, 3H), 7.20 – 7.14 (m, 2H), 7.13 – 7.04 (m, 4H), 6.62 (t, $J = 8.1$ Hz, 1H), 4.91 (d, $J = 14.9$ Hz, 1H), 4.62 (d, $J = 14.1$ Hz, 1H), 4.50 (dd, $J = 14.7, 7.6$ Hz, 1H), 4.34 – 4.21 (m, 2H), 4.02 (d, $J = 14.1$ Hz, 1H), 3.53 (s, 3H), 2.37 (s, 3H), 2.06 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 168.1, 145.7, 143.8, 140.9, 137.1, 136.2, 135.9, 133.3(1), 133.2(9), 132.7, 129.6, 129.5(2C), 128.6, 128.4(6), 128.4(6)(2C), 128.3(2C), 127.8, 127.6(2C), 126.8(3), 126.8(0), 126.7(6), 125.0, 52.5, 48.7, 45.9, 44.6, 39.6, 21.6. **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{33}\text{H}_{32}\text{N}_2\text{NaO}_6\text{S}_2$ $[\text{M}+\text{Na}]^+$: 639.1599, found: 639.1594.



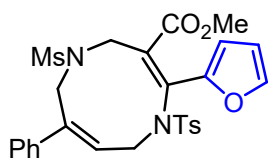
5i: Following the general procedure **A**, compound **5i** was obtained as a white solid in 82% yield (94.0 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1); m.p.: 147-148 °C; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.37 – 7.34 (m, 1H), 7.31 – 7.23 (m, 4H), 7.19 – 7.14 (m, 2H), 7.13 – 7.06 (m, 4H), 7.05 – 7.00 (m, 1H), 6.57 (t, J = 8.2 Hz, 1H), 4.72 (d, J = 14.9 Hz, 1H), 4.57 – 4.47 (m, 2H), 4.24 – 4.13 (m, 2H), 3.87 (d, J = 14.2 Hz, 1H), 3.50 (s, 3H), 2.45 (s, 3H), 2.36 (s, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 168.2, 145.8, 143.8, 143.0, 136.2, 135.9, 134.5, 132.2, 129.6, 129.5(2C), 128.4(2C), 128.2(2C), 128.0, 127.5(2C), 127.2, 126.3, 126.2, 52.4, 48.7, 46.0, 44.6, 39.2, 21.6. **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{27}\text{H}_{28}\text{N}_2\text{NaO}_6\text{S}_3$ $[\text{M}+\text{Na}]^+$: 595.1007, found: 595.0983.



5j: Following the general procedure **A**, compound **5j** was obtained as a white solid in 78% yield (90.6 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1); m.p.: 158-159 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.55 – 7.48 (m, 2H), 7.43 – 7.31 (m, 3H), 7.25 – 7.19 (m, 2H), 7.12 – 7.02 (m, 4H), 6.98 – 6.92 (m, 1H), 6.72 – 6.67 (m, 1H), 6.52 (t, J = 8.2 Hz, 1H), 4.83 (d, J = 14.9 Hz, 1H), 4.59 (d, J = 14.0 Hz, 1H), 4.45 (dd, J = 14.8, 7.4 Hz, 1H), 4.21 (dd, J = 14.8, 8.9 Hz, 1H), 4.12 (d, J = 14.9 Hz, 1H), 4.00 (d, J = 14.0 Hz, 1H), 3.56 (s, 3H), 2.37 (s, 3H), 2.11 (s, 3H), 2.07 (s, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 168.1, 146.1, 143.6, 140.7, 140.0, 138.0, 136.0, 135.7, 132.4, 130.4, 129.8, 129.3(2C), 128.9(2)(2C), 128.9(0), 128.5, 128.4, 127.6(2C), 127.5(2C), 125.9, 52.4, 48.8, 45.8, 44.6, 39.5, 21.5, 21.2. **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{30}\text{H}_{32}\text{N}_2\text{NaO}_6\text{S}_2$ $[\text{M}+\text{Na}]^+$: 603.1599, found: 603,1589.

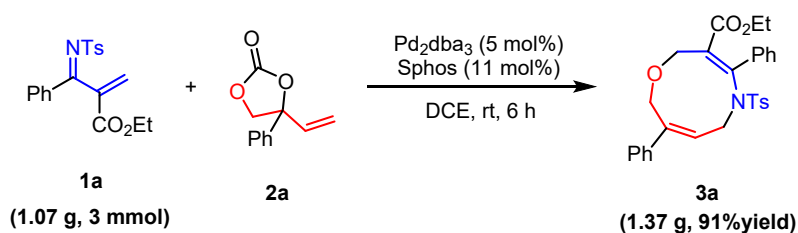


5k: Following the general procedure **A**, compound **5k** was obtained as a white solid in 82% yield (97.9 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1); m.p.: 160-161 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.51 – 7.45 (m, 2H), 7.42 – 7.32 (m, 3H), 7.31 – 7.27 (m, 2H), 7.13 – 7.06 (m, 2H), 7.04 – 6.95 (m, 2H), 6.70 – 6.60 (m, 2H), 6.52 – 6.42 (m, 1H), 4.78 (d, J = 14.9 Hz, 1H), 4.61 – 4.53 (m, 1H), 4.45 (dd, J = 14.7, 7.5 Hz, 1H), 4.26 – 4.10 (m, 2H), 3.92 (d, J = 14.1 Hz, 1H), 3.79 (s, 3H), 3.57 (s, 3H), 2.38 (s, 3H), 2.08 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 168.4, 160.7, 145.7, 143.7, 140.8, 140.0, 136.2, 131.0, 129.7(2C), 129.6, 129.4(2C), 128.9(1)(2C), 128.8(8), 128.5, 127.6(1)(2C), 127.5(9)(2C), 113.8(2C), 55.4, 52.4, 48.6, 45.9, 44.7, 39.5, 21.6. **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{30}\text{H}_{32}\text{N}_2\text{NaO}_7\text{S}_2$ $[\text{M}+\text{Na}]^+$: 619.1549, found: 619.1540.



5I: Following the general procedure **A**, compound **5I** was obtained as a white solid in 72% yield (80.2 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1); m.p.: 142-143 °C; **¹H NMR** (600 MHz, CDCl₃) δ 7.61 – 7.56 (m, 2H), 7.44 – 7.31 (m, 5H), 7.28 – 7.24 (m, 2H), 7.20 – 7.17 (m, 1H), 6.39 – 6.34 (m, 1H), 6.30 – 6.27 (m, 1H), 6.22 – 6.19 (m, 1H), 4.75 (d, *J* = 15.0 Hz, 1H), 4.45 – 4.37 (m, 2H), 4.04 (d, *J* = 15.1 Hz, 1H), 3.99 (dd, *J* = 15.1, 8.7 Hz, 1H), 3.91 (d, *J* = 14.1 Hz, 1H), 3.77 (s, 3H), 2.44 (s, 3H), 2.04 (s, 3H). **¹³C NMR** (150 MHz, CDCl₃) δ 167.6, 148.5, 144.1, 144.0, 141.2, 140.2, 136.3, 133.5, 130.2, 129.8(2C), 129.6, 128.9(2C), 128.8, 127.7(2C), 127.6(2C), 113.0, 111.7, 52.7, 47.5, 45.1, 44.7, 40.0, 21.7. **HRMS** (ESI-TOF, *m/z*): calcd for C₂₇H₂₈N₂NaO₇S₂ [M+Na]⁺: 579.1236, found: 579.1226.

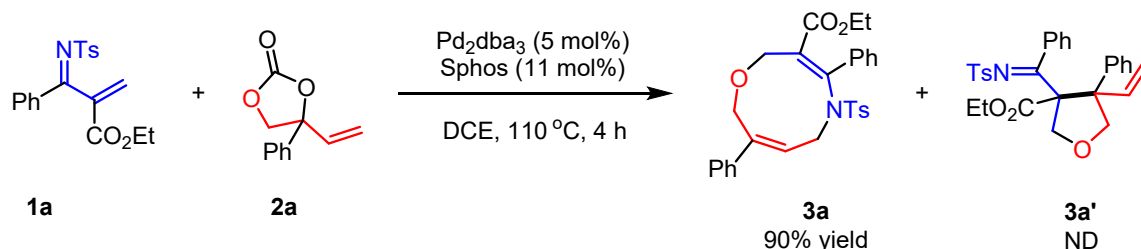
Scale-up experiment



Under a nitrogen atmosphere, Pd₂(dba)₃ (137.1 mg, 0.15 mmol) and Sphos (137.6 mg, 0.33 mmol) were dissolved in 1, 2-dichloroethane (30.0 mL), and stirred at room temperature for approximately 30 min. Then, 1-azadienes **1a** (1.07 g, 3 mmol) and vinyl ethylene carbonates **2a** (855.1 mg, 4.5 mmol) was added sequentially. The reaction mixture was allowed to stir at 25 °C for 6 h. After concentrated, the residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, v/v) to provide the desired product **3a** (1.37 g, 91% yield).

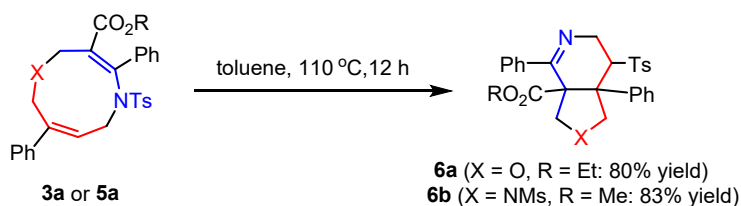
Control experiment and synthetic transformation of **3a** and **5a**

1.

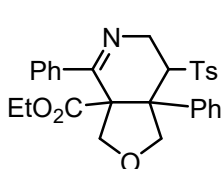


Under a nitrogen atmosphere, Pd₂(dba)₃ (9.2 mg, 0.01 mmol) and Sphos (9.1 mg, 0.022 mmol) were dissolved in 1, 2-dichloroethane (2.0 mL), and stirred at room temperature for approximately 30 min. Then, 1-azadienes **1** (71.5 mg, 0.2 mmol) and vinyl ethylene carbonates **2** (57.1 mg, 0.3 mmol) were added sequentially. The reaction mixture was allowed to stir at 110 °C for 4 h and then directly purified by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, v/v) to provide the only product **3a** obtained with high yield (90%), without any [3+2] product **3a'**.

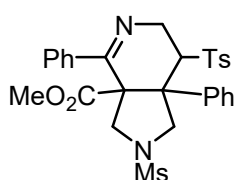
2.



Under nitrogen atmosphere, compound **3a** or **5a** (0.1 mmol) was added into a flame-dried Schlenk tube equipped with a magnetic stirring bar. Anhydrous toluene (1.0 mL) was added *via* syringe to the reaction tube. The reaction mixture was stirred at 110 °C for 12 hours and then directly purified by silica gel chromatography (petroleum ether/ethyl acetate = 4:1, v/v) to provide the [4.3.0] bicyclic product **6a** or **6b**.



6a: Following the control experiment procedure 2, compound **6a** was obtained as a white solid in 80% yield (40.3 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1); m.p.: 101-103 °C ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.48 – 7.28 (m, 7H), 7.25 – 6.95 (m, 7H), 4.90 (d, $J = 10.5$ Hz, 1H), 4.83 – 4.72 (m, 2H), 4.50 (dd, $J = 20.7, 12.2$ Hz, 1H), 4.34 – 4.27 (m, 2H), 3.98 (d, $J = 9.5$ Hz, 1H), 3.91 – 3.80 (m, 1H), 3.79 – 3.68 (m, 1H), 2.37 (s, 3H), 0.92 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 168.7, 163.9, 144.6, 137.9, 137.3, 136.1, 129.8, 129.7(2C), 128.5(2C), 128.4(2C), 128.0(2C), 127.6, 127.5(6) (2C), 127.0(2C), 72.0, 70.6, 63.8, 62.1, 60.0, 52.4, 46.5, 21.7, 13.5. **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{29}\text{H}_{29}\text{NNaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 526.1664, found: 526.1658.



6b: Following the control experiment procedure 2, compound **6b** was obtained as a white solid in 83% yield (46.5 mg); purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1); m.p.: 146-147 °C ; $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.52 – 7.31 (m, 7H), 7.28 – 6.68 (m, 7H), 4.92 (dd, $J = 20.0, 6.5$ Hz, 1H), 4.82 (dd, $J = 10.0, 6.5$ Hz, 1H), 4.68 (dd, $J = 20.0, 10.1$ Hz, 1H), 4.58 (d, $J = 11.6$ Hz, 1H), 3.77 (d, $J = 11.6$ Hz, 1H), 3.71 (s, 2H), 3.55 (s, 3H), 2.67 (s, 3H), 2.38 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 168.49, 162.49, 144.52, 137.17, 137.02, 134.65, 130.31, 129.60(2C), 128.83(2C), 128.30(2C), 128.03, 126.95(2C), 126.81(2C), 61.77, 59.46, 53.09, 51.17, 50.59, 49.67, 46.72, 37.17, 21.55. **HRMS** (ESI-TOF, m/z): calcd for $\text{C}_{29}\text{H}_{30}\text{N}_2\text{NaO}_6\text{S}_2$ $[\text{M}+\text{Na}]^+$: 589.1437, found: 589.1439.

3. The absolute configuration determination of 3c

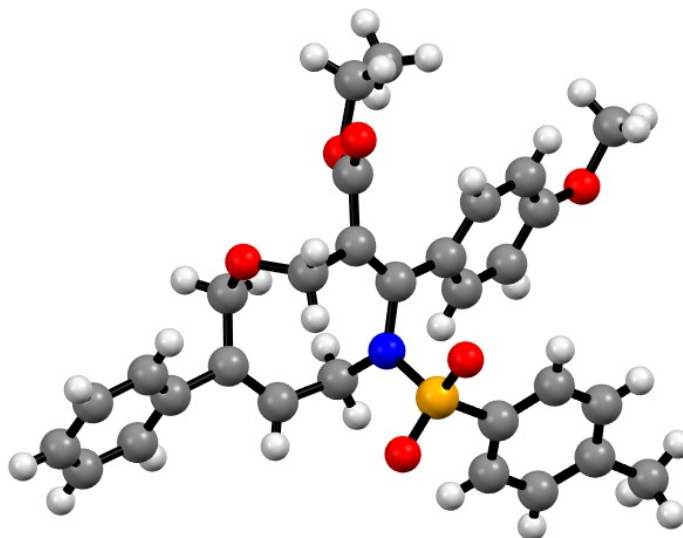


Fig S1. X-ray structure of 3c.

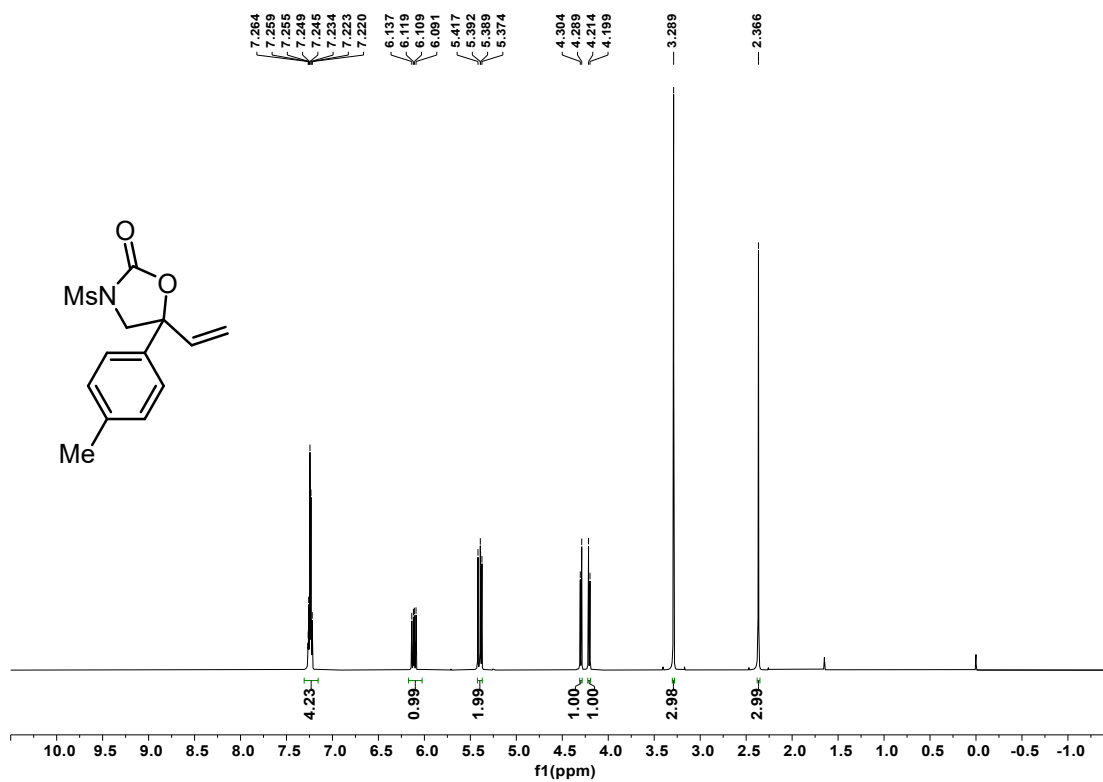
Crystal data and structure refinement for CCDC 2235404

Identification code	20220906zm01_0m	
Empirical formula	C ₃₀ H ₃₁ N O ₆ S	
Formula weight	533.62	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 1 21/n	
Unit cell dimensions	a = 14.656(5) Å	□ $\alpha = 90^\circ$.
	b = 9.799(4) Å	□ $\beta = 99.933(14)$.
	c = 19.177(7) Å	□ $\gamma = 90^\circ$.
Volume	2713.1(18) Å ³	
Z	4	
Density (calculated)	1.306 Mg/m ³	
Absorption coefficient	0.164 mm ⁻¹	
F(000)	1128.0	
Crystal size	0.540 x 0.480 x 0.360 mm ³	
Theta range for data collection	2.341 to 27.679°.	
Index ranges	-19 ≤ h ≤ 18, -12 ≤ k ≤ 12, -24 ≤ l ≤ 24	
Reflections collected	37759	
Independent reflections	6247 [R(int) = 0.0905]	
Completeness to theta = 27.679°	98.6 %	

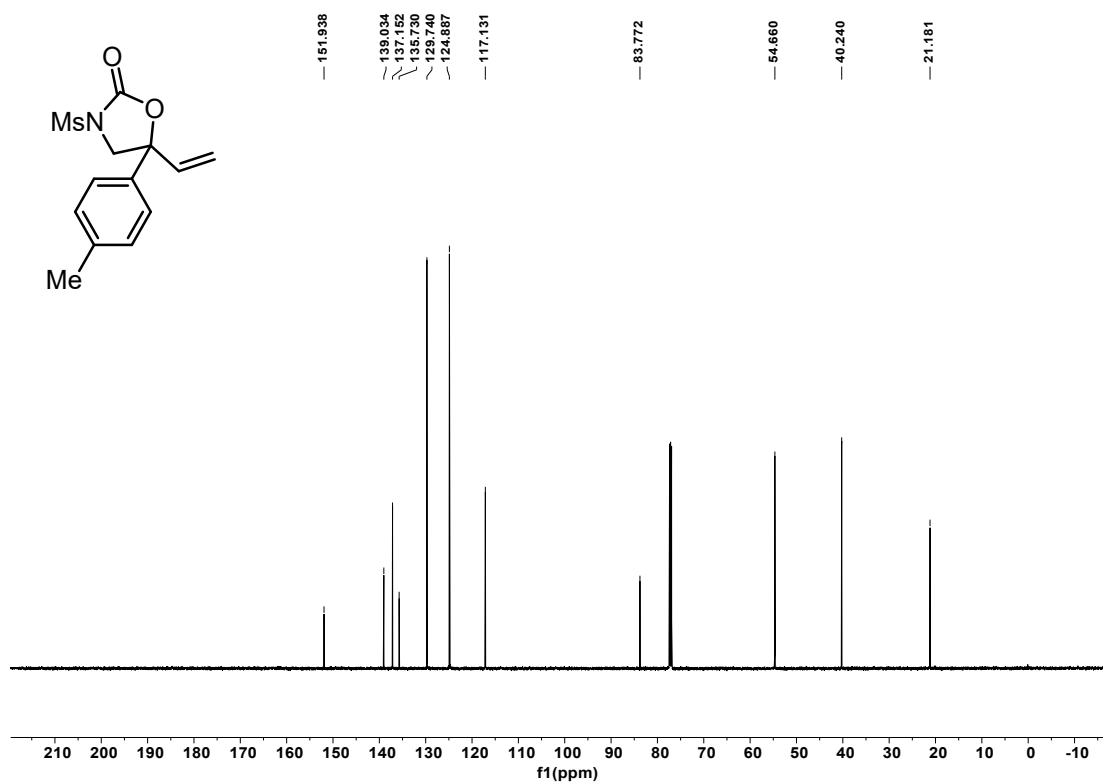
Absorption correction	multi-scan
Max. and min. transmission	0.7456 and 0.6093
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6247 / 56 / 366
Goodness-of-fit on F^2	0.968
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0500, wR2 = 0.1362
R indices (all data)	R1 = 0.0943, wR2 = 0.1665
Extinction coefficient	0.020(3)
Largest diff. peak and hole	0.222 and -0.294 e.Å ⁻³

4. ^1H and ^{13}C NMR spectra

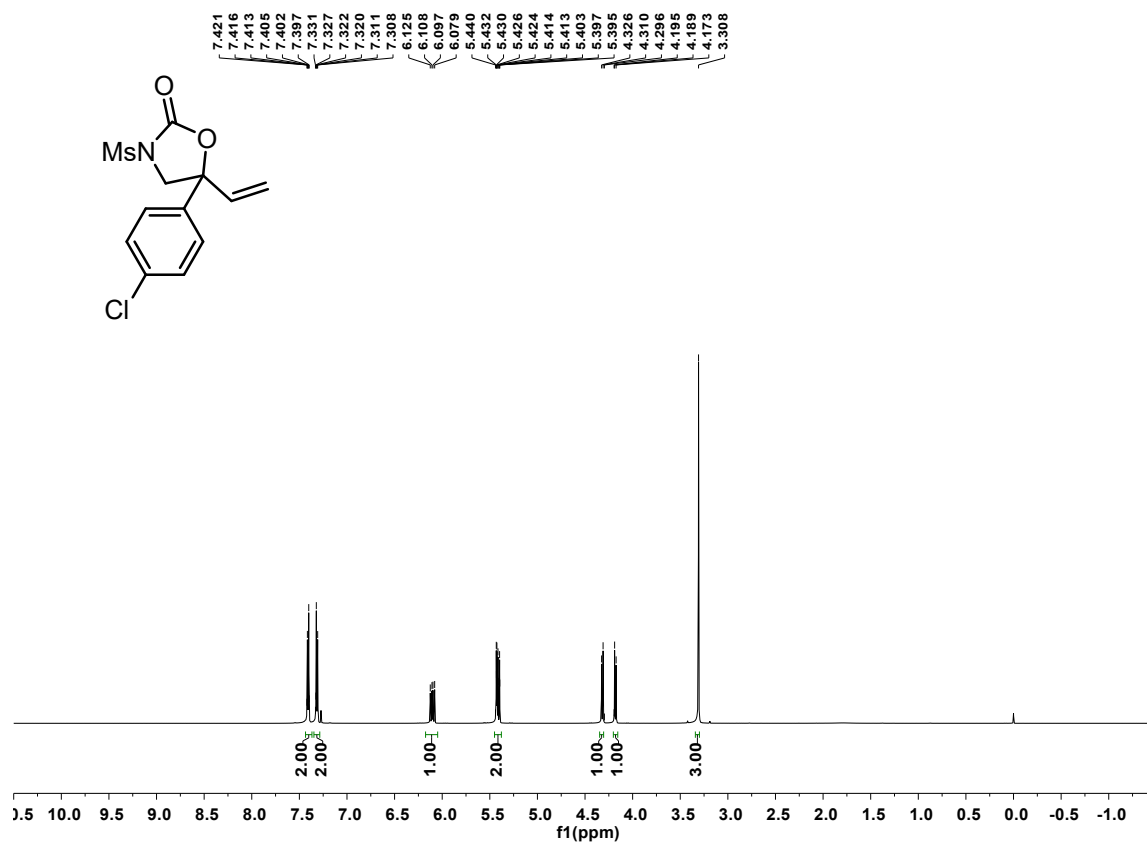
^1H NMR of **4b** in CDCl_3 (600 MHz)



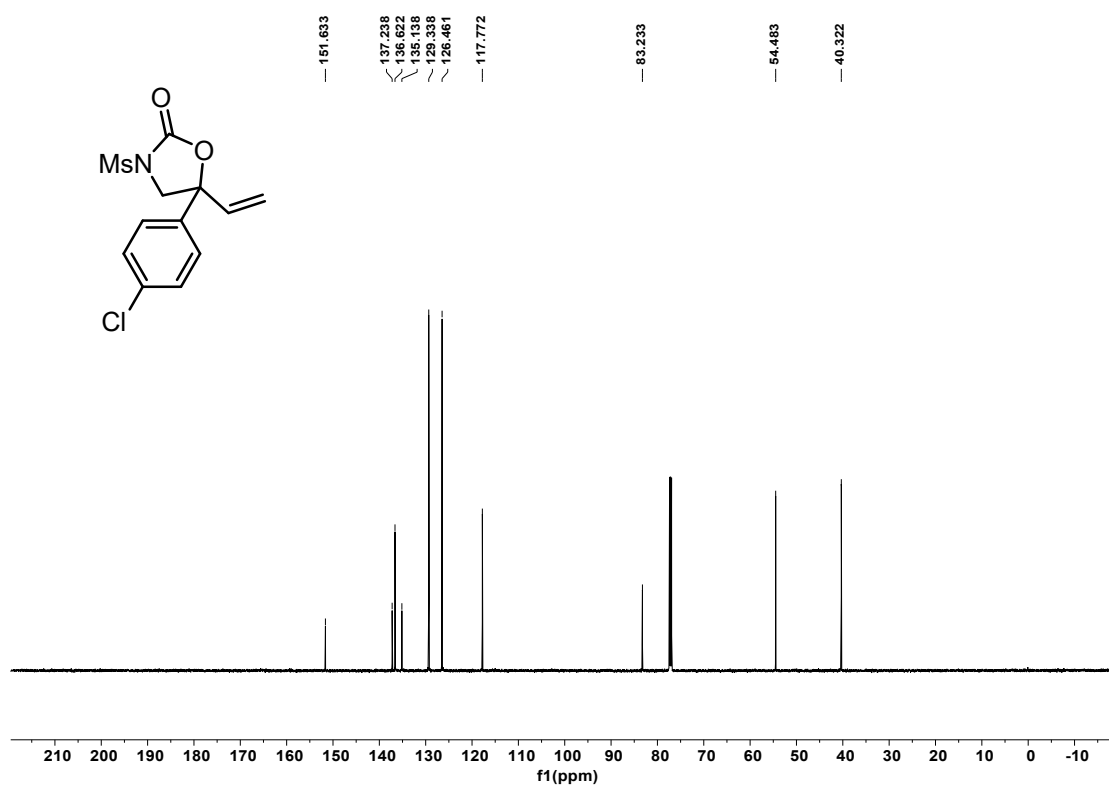
^{13}C NMR of **4b** in CDCl_3 (150 MHz)



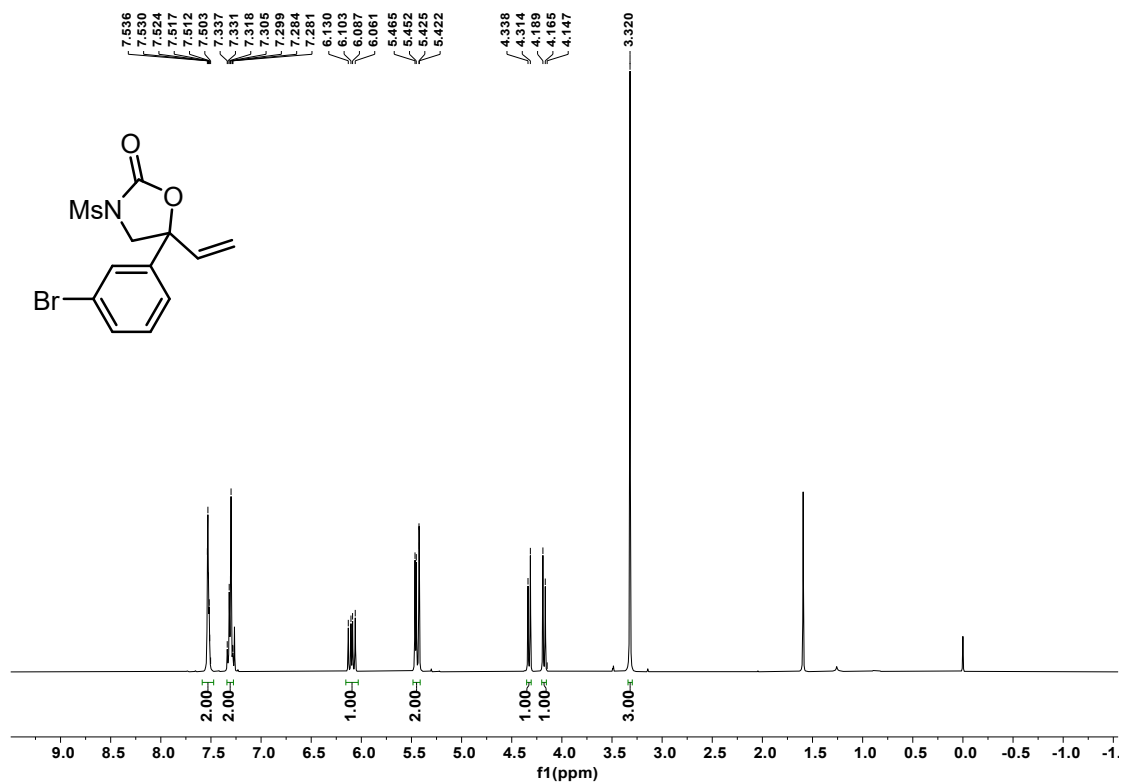
^1H NMR of **4c** in CDCl_3 (600 MHz)



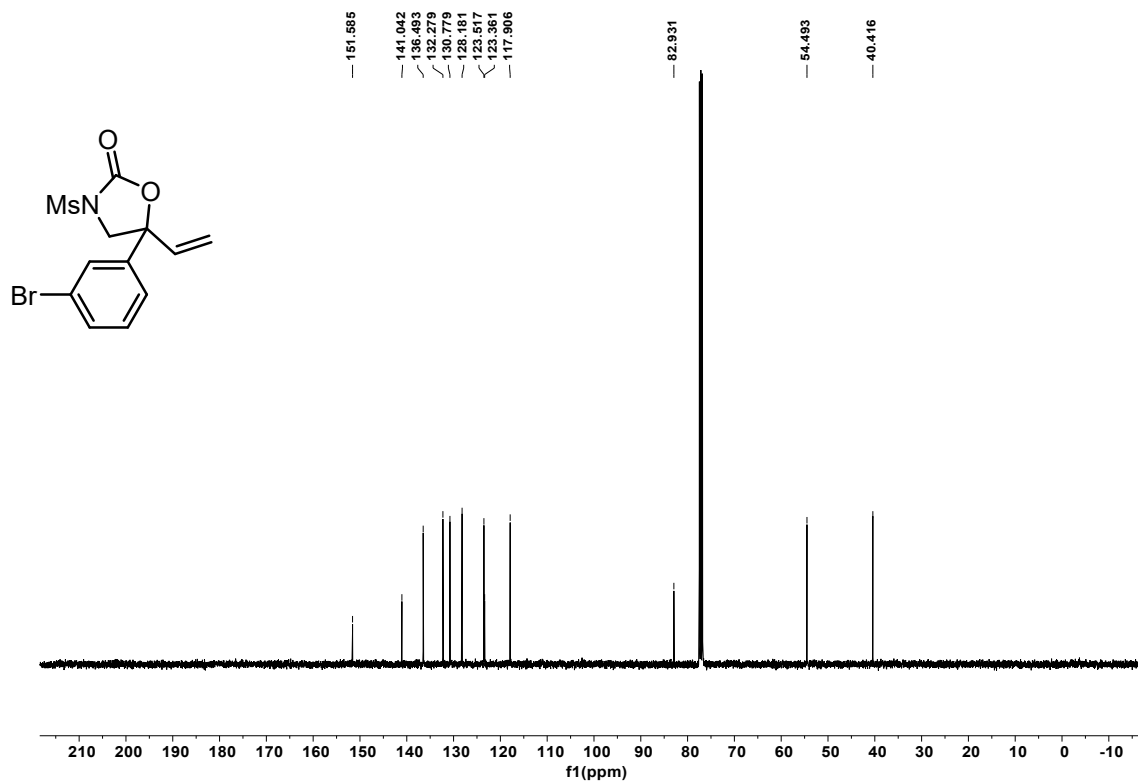
^{13}C NMR of **4c** in CDCl_3 (150 MHz)



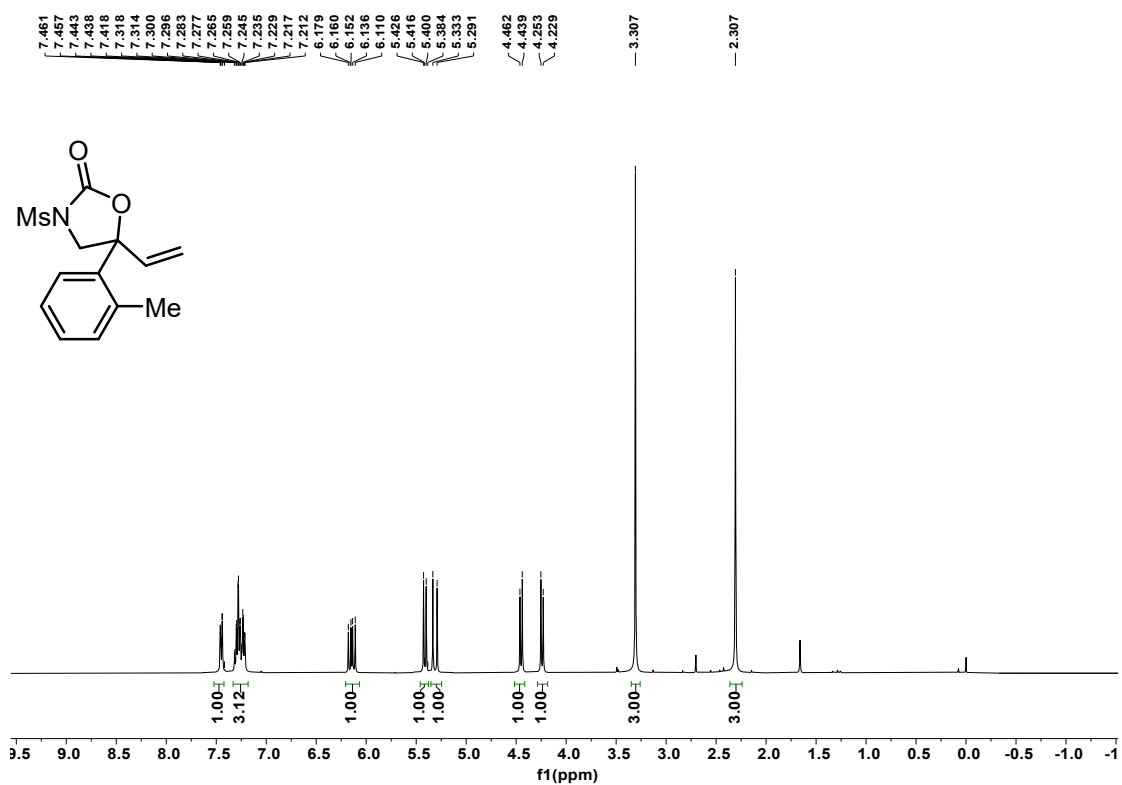
^1H NMR of **4e** in CDCl_3 (400 MHz)



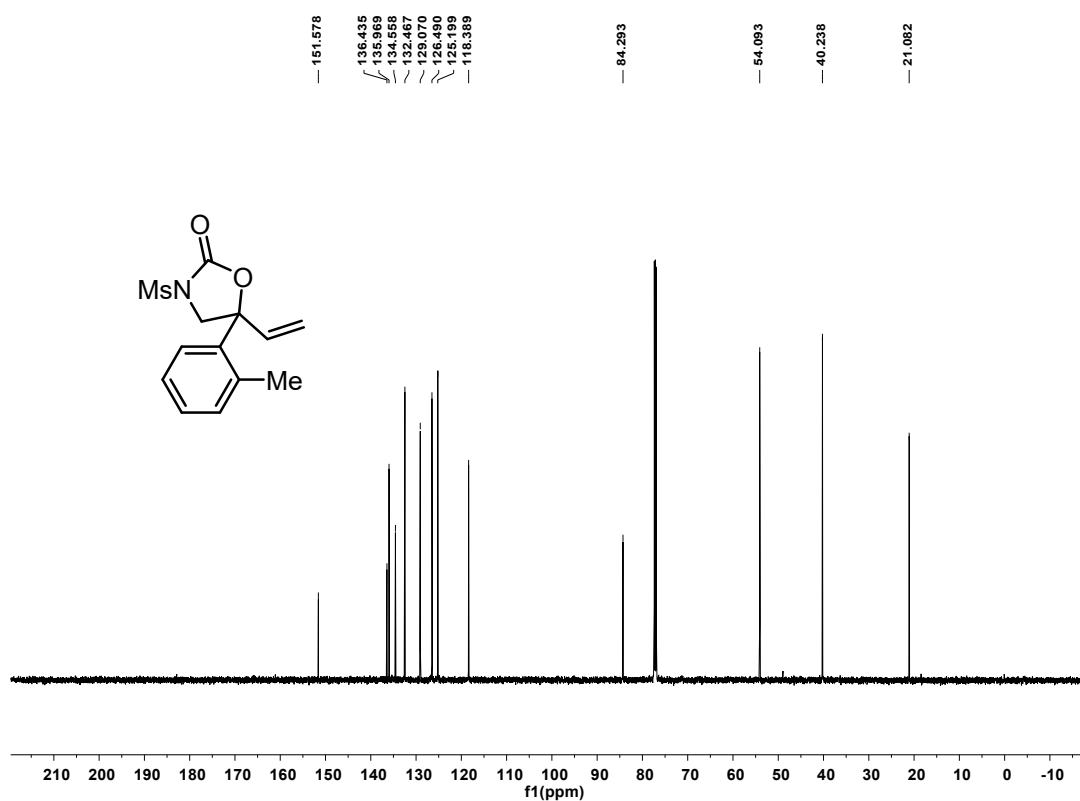
^{13}C NMR of **4e** in CDCl_3 (100 MHz)



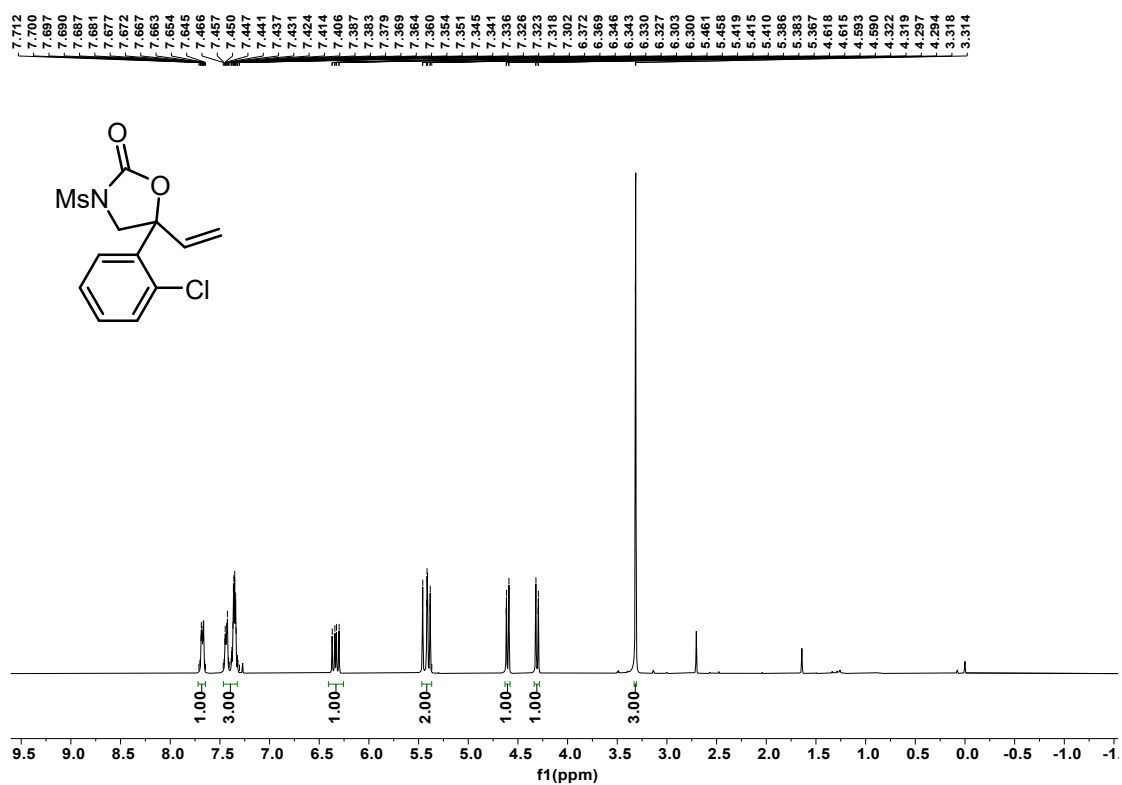
^1H NMR of **4f** in CDCl_3 (400 MHz)



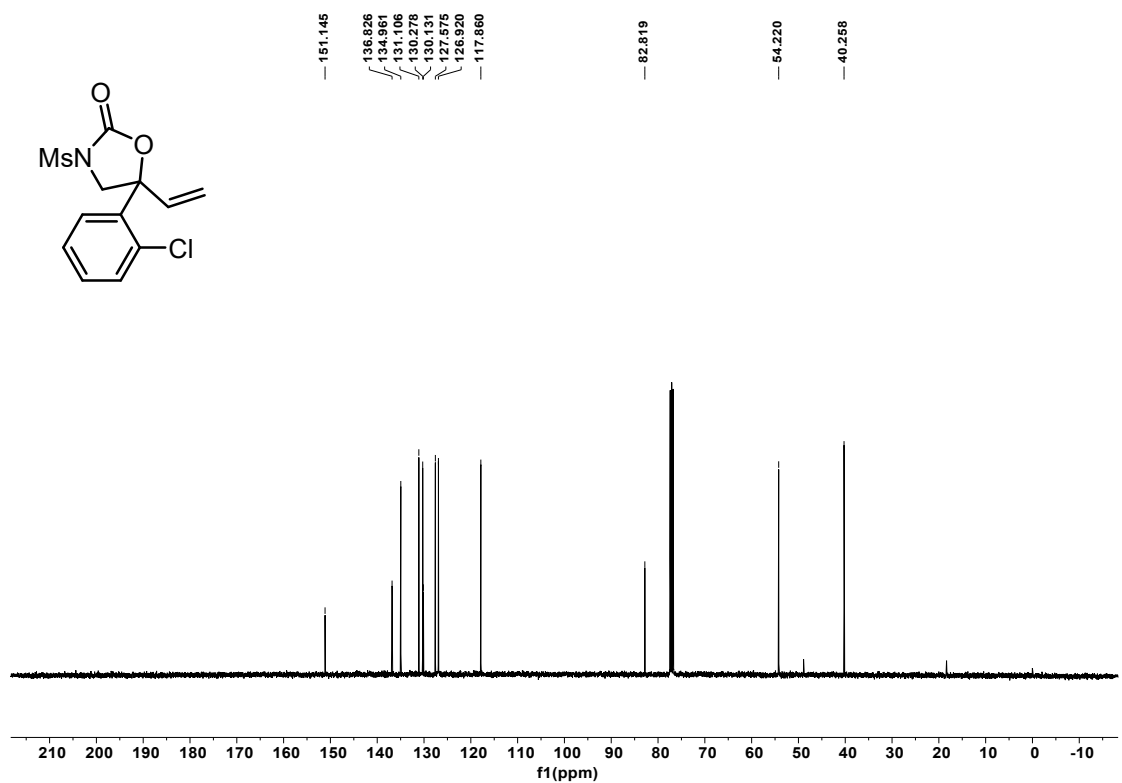
^{13}C NMR of **4f** in CDCl_3 (150 MHz)



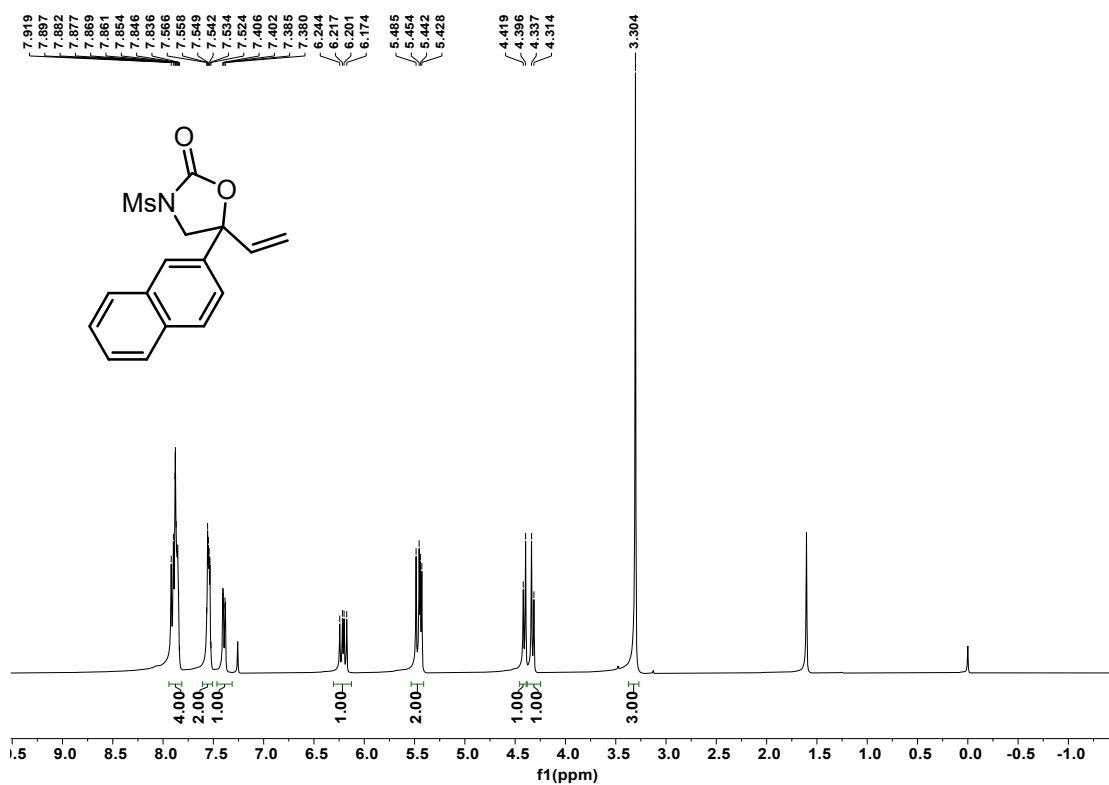
¹H NMR of 4g in CDCl₃ (400 MHz)



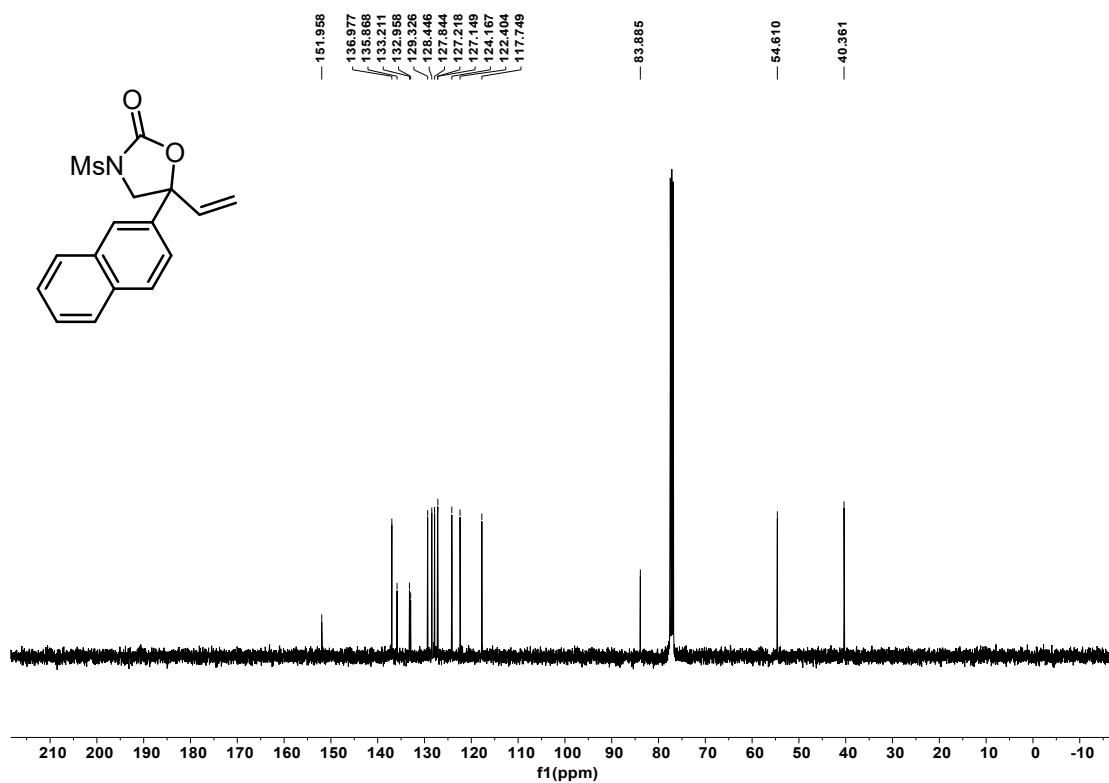
¹³C NMR of 4g in CDCl₃ (100 MHz)



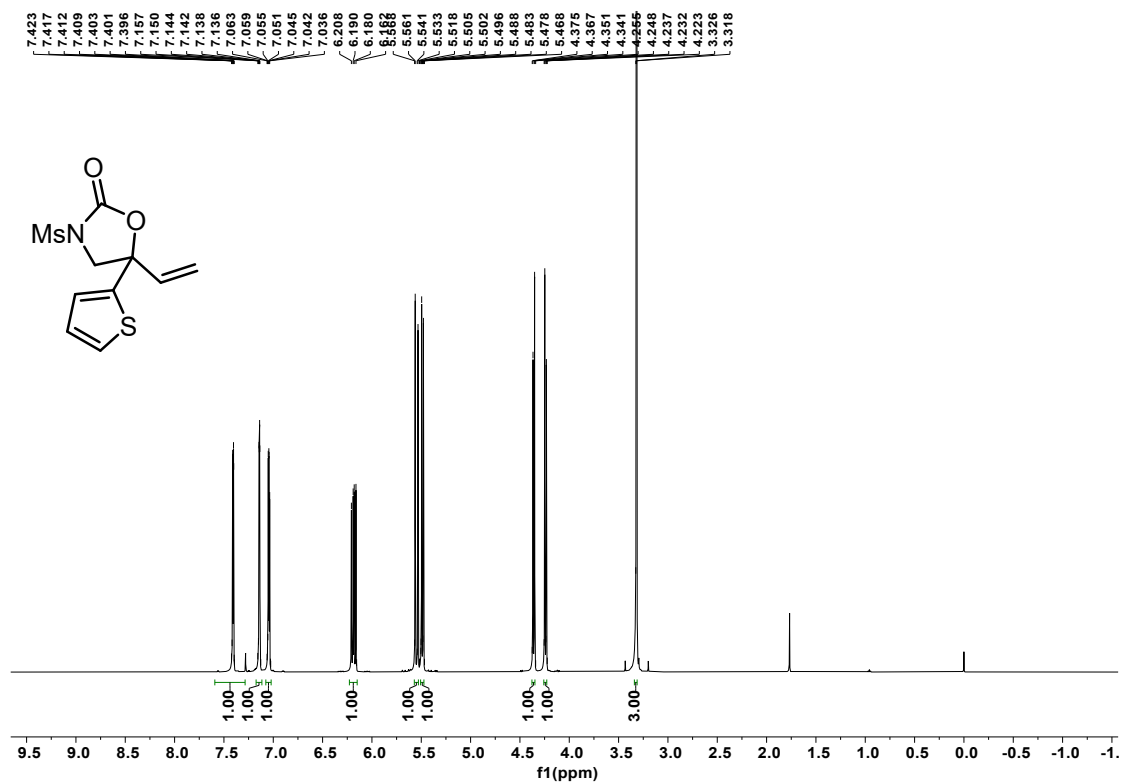
^1H NMR of **4h** in CDCl_3 (400 MHz)



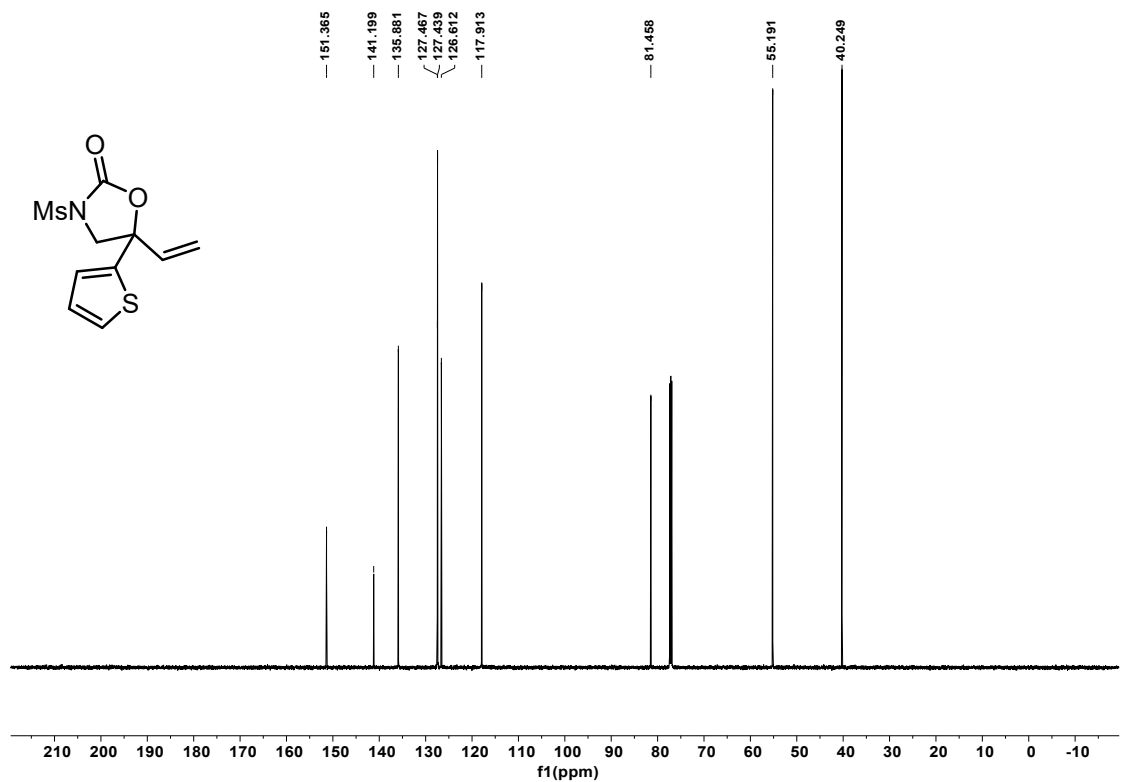
^{13}C NMR of **4h** in CDCl_3 (100 MHz)



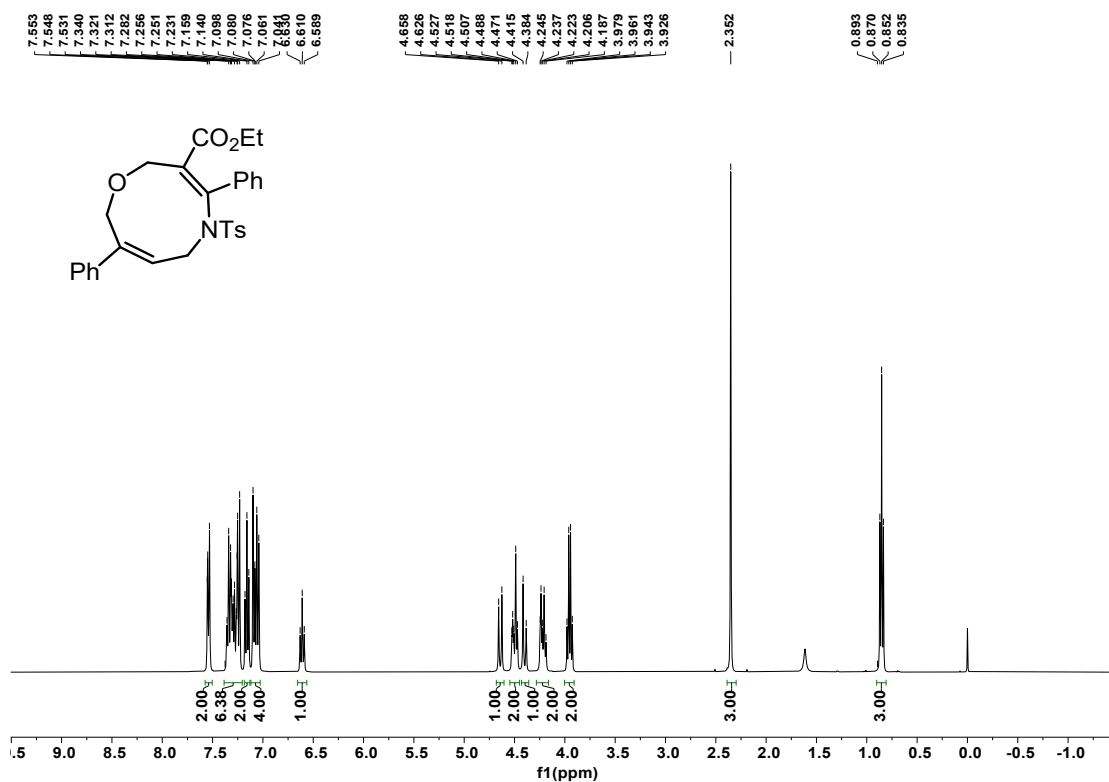
^1H NMR of **4i** in CDCl_3 (600 MHz)



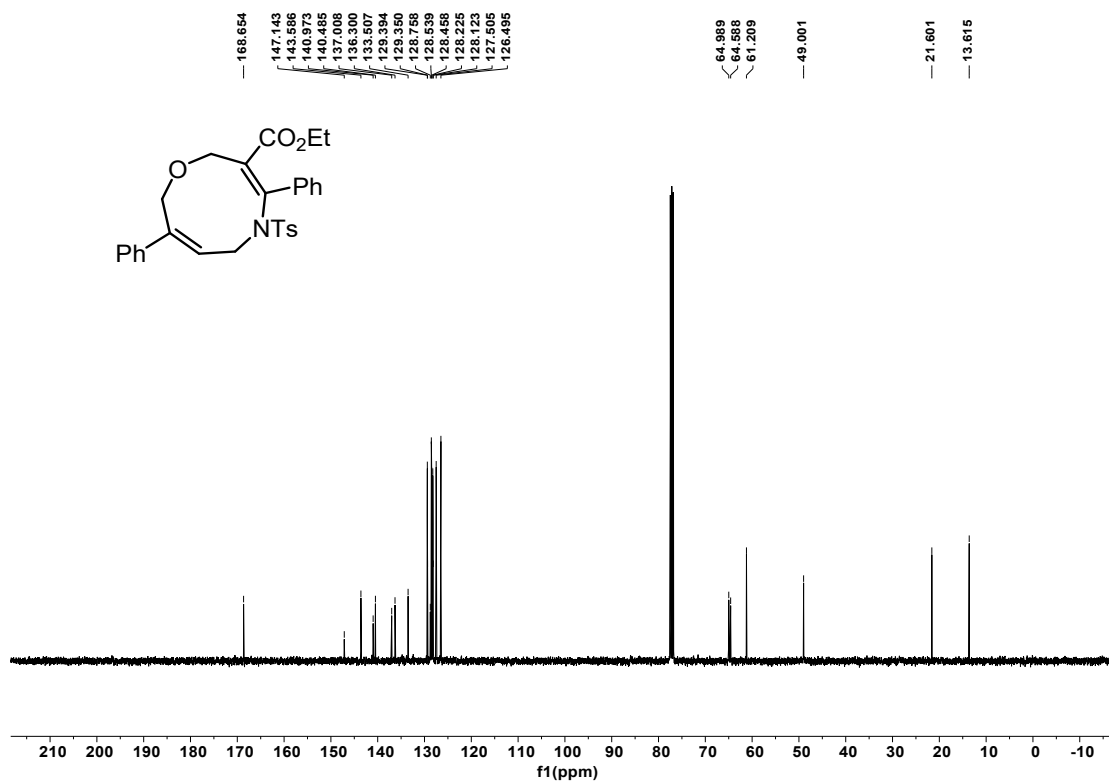
^{13}C NMR of **4i** in CDCl_3 (150 MHz)



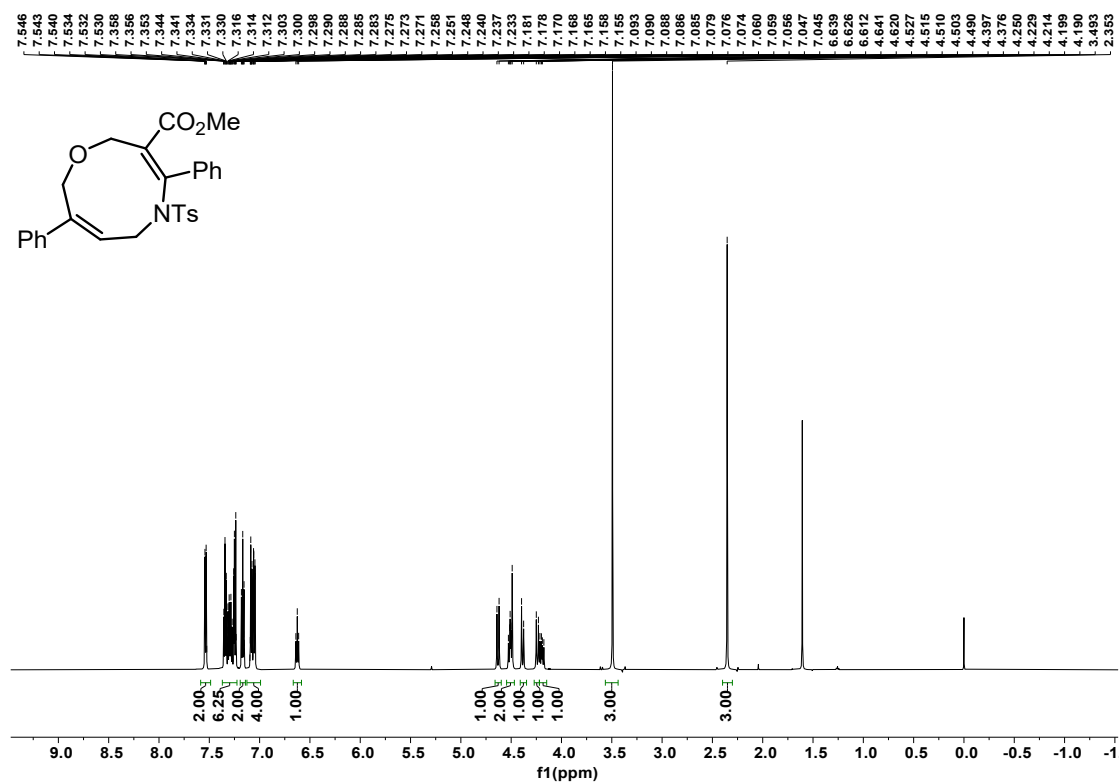
^1H NMR of **3a** in CDCl_3 (400 MHz)



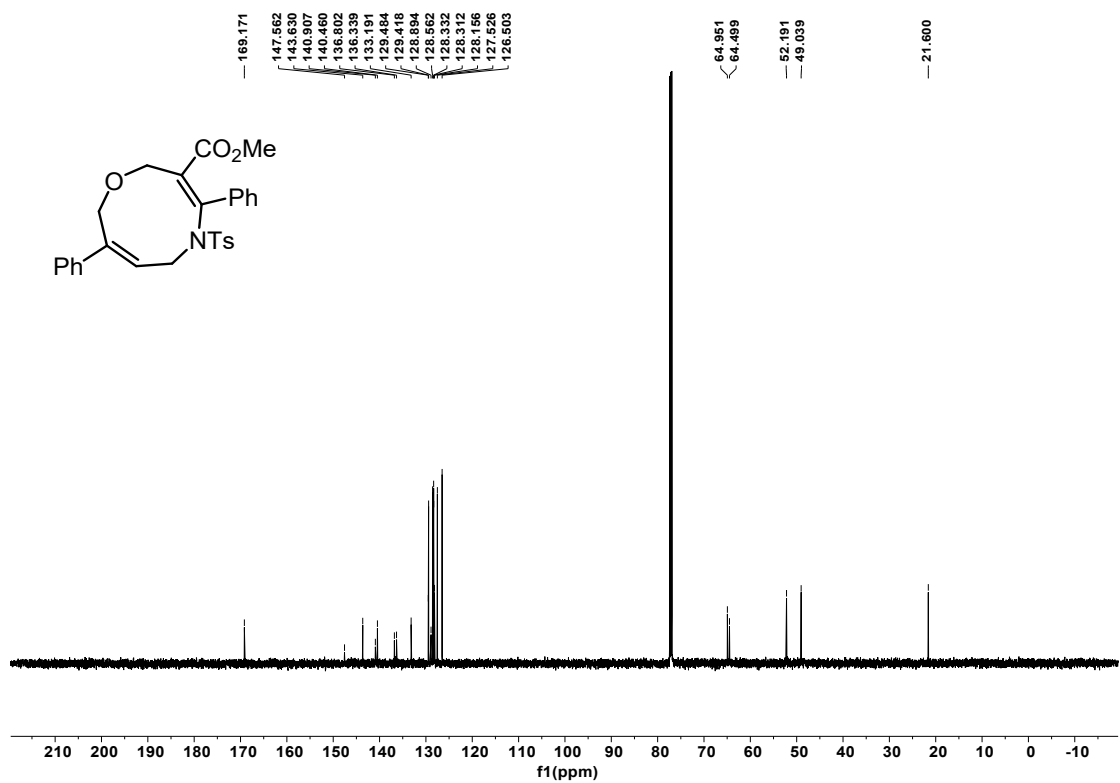
^{13}C NMR of **3a** in CDCl_3 (100 MHz)



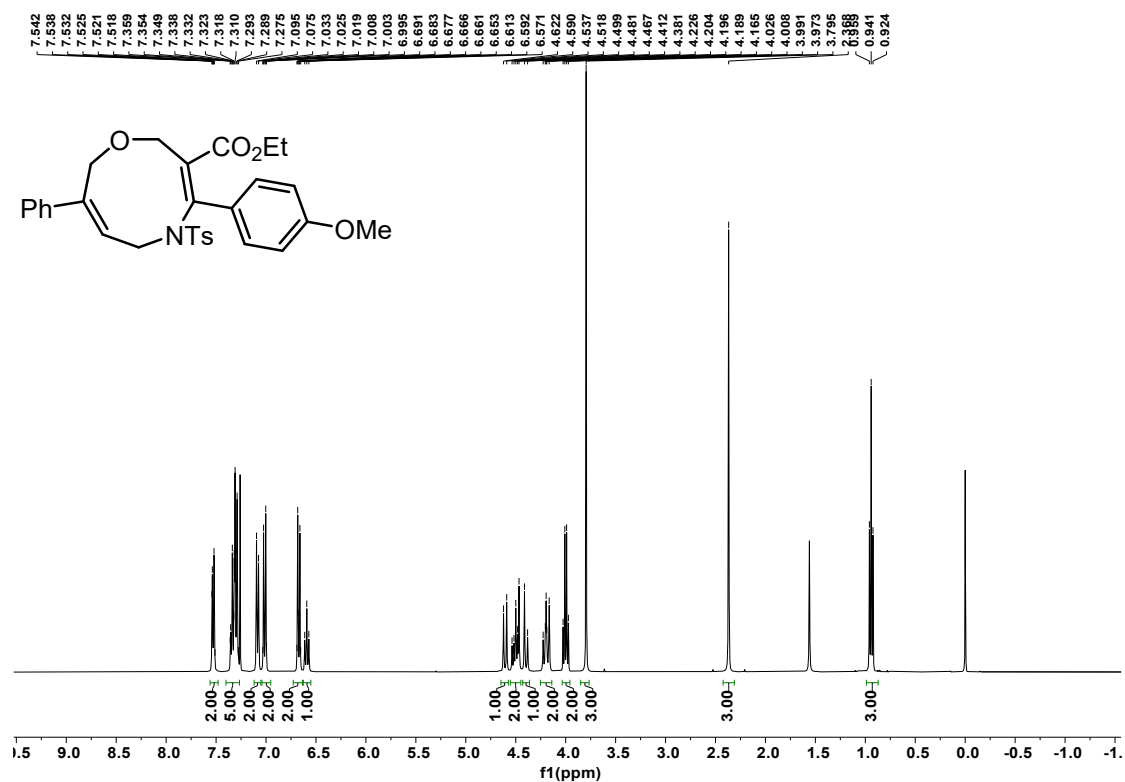
^1H NMR of **3b** in CDCl_3 (600 MHz)



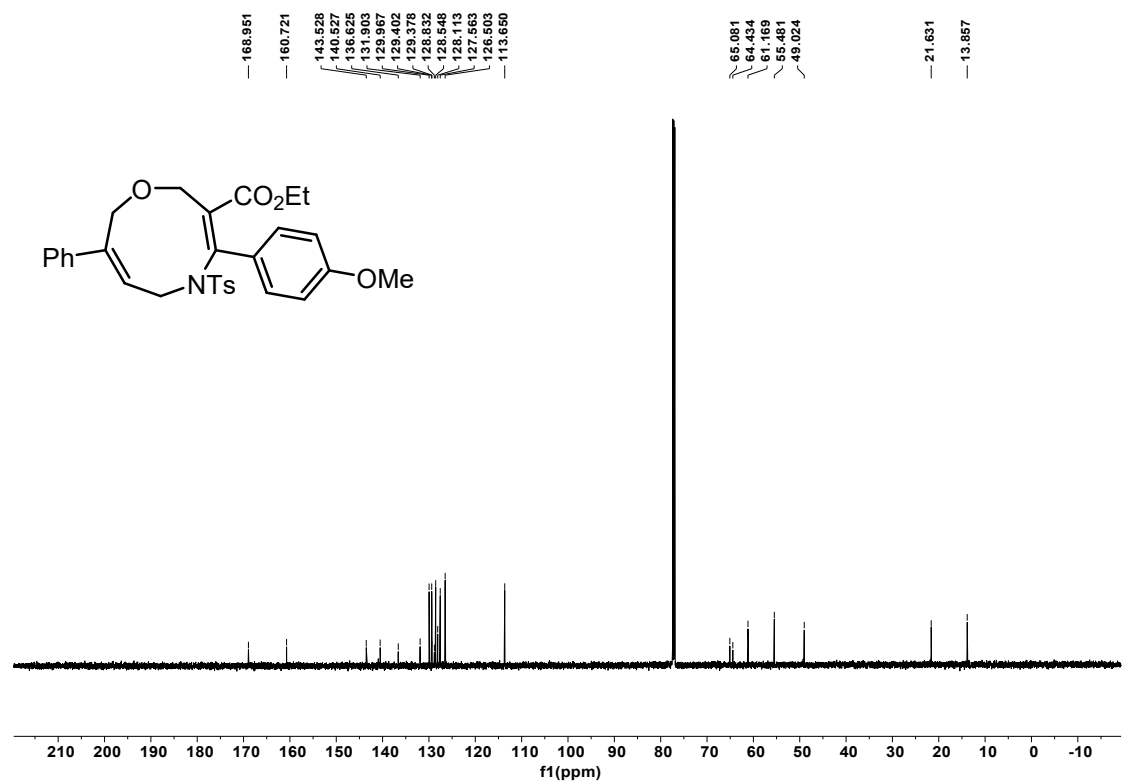
^{13}C NMR of **3b** in CDCl_3 (150 MHz)



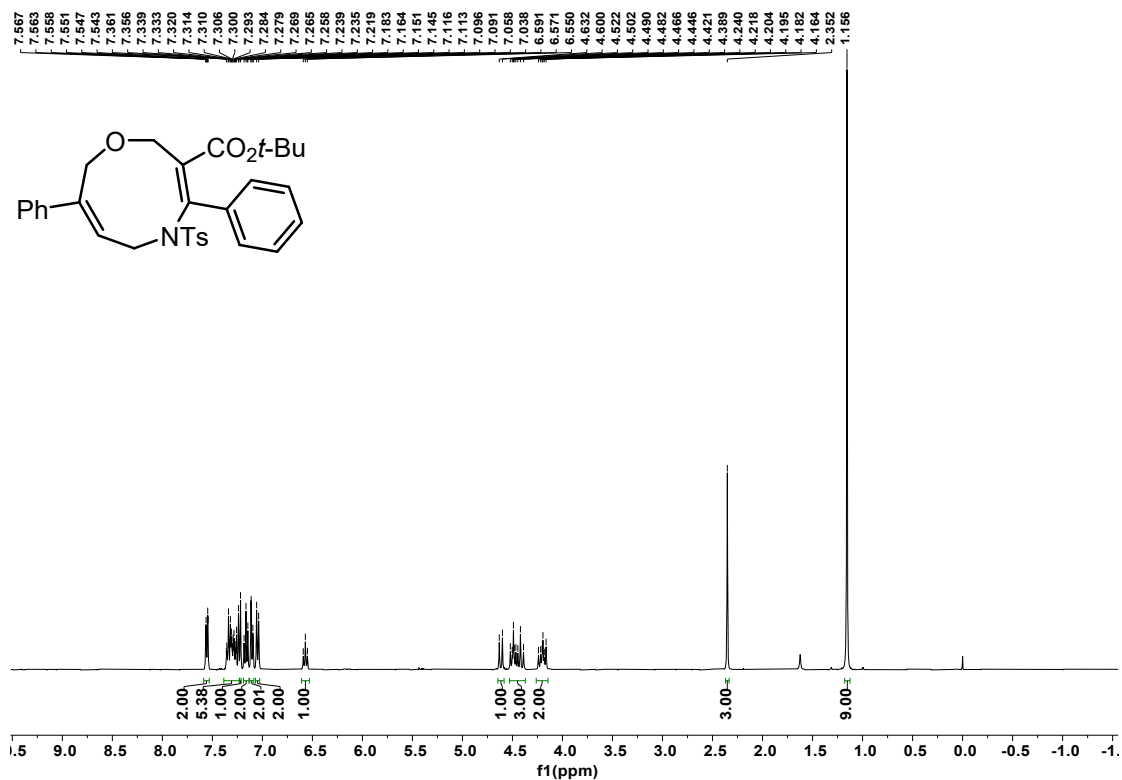
^1H NMR of **3c** in CDCl_3 (400 MHz)



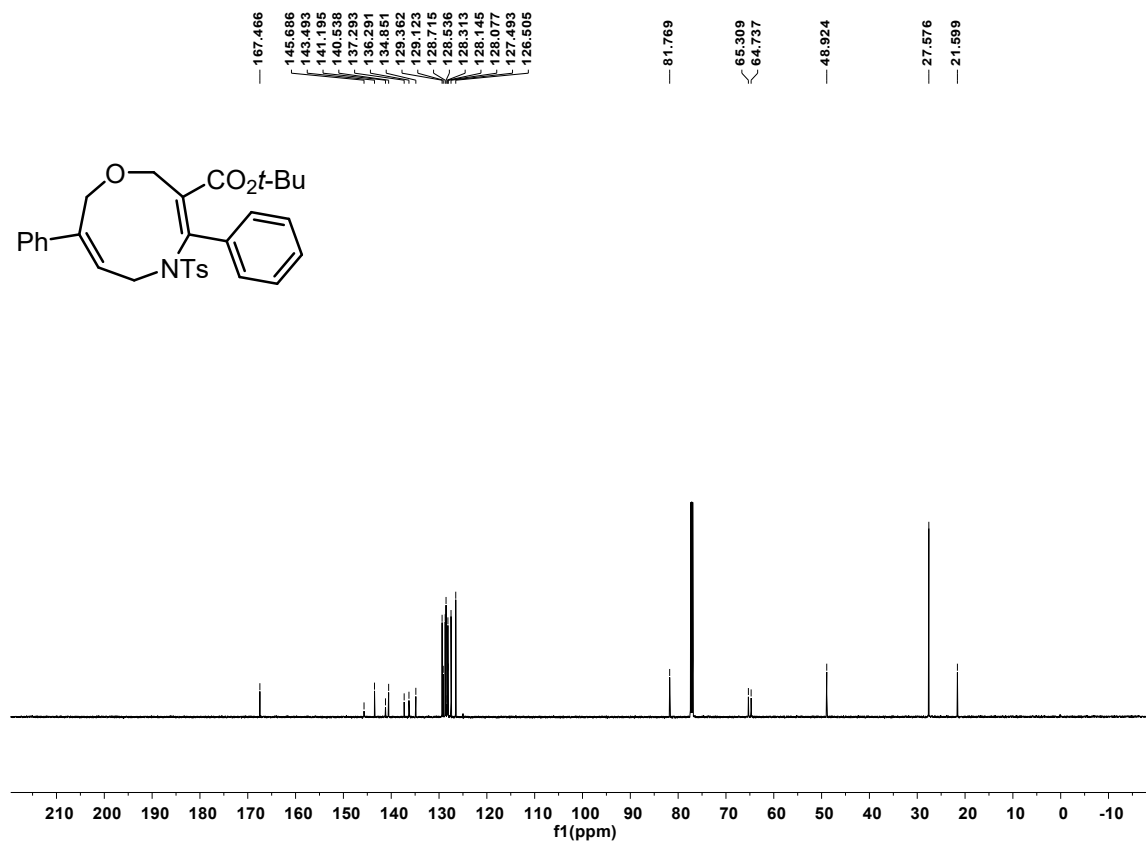
^{13}C NMR of **3c** in CDCl_3 (150 MHz)



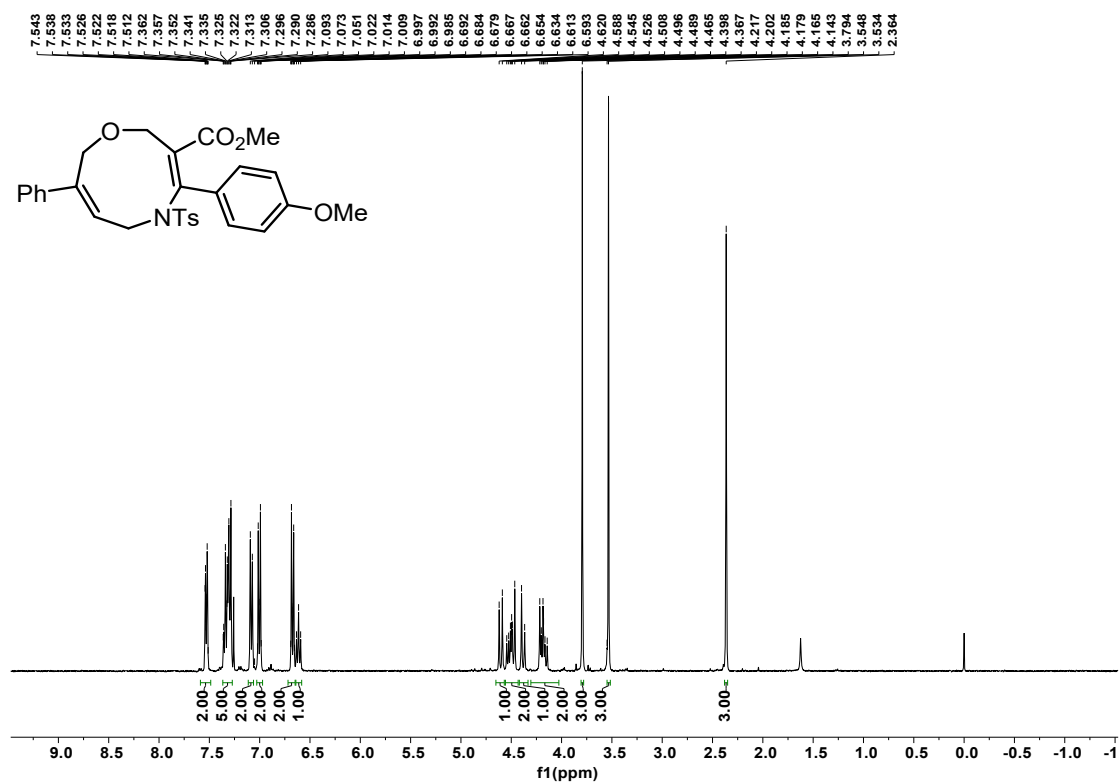
¹H NMR of **3d** in CDCl₃ (400 MHz)



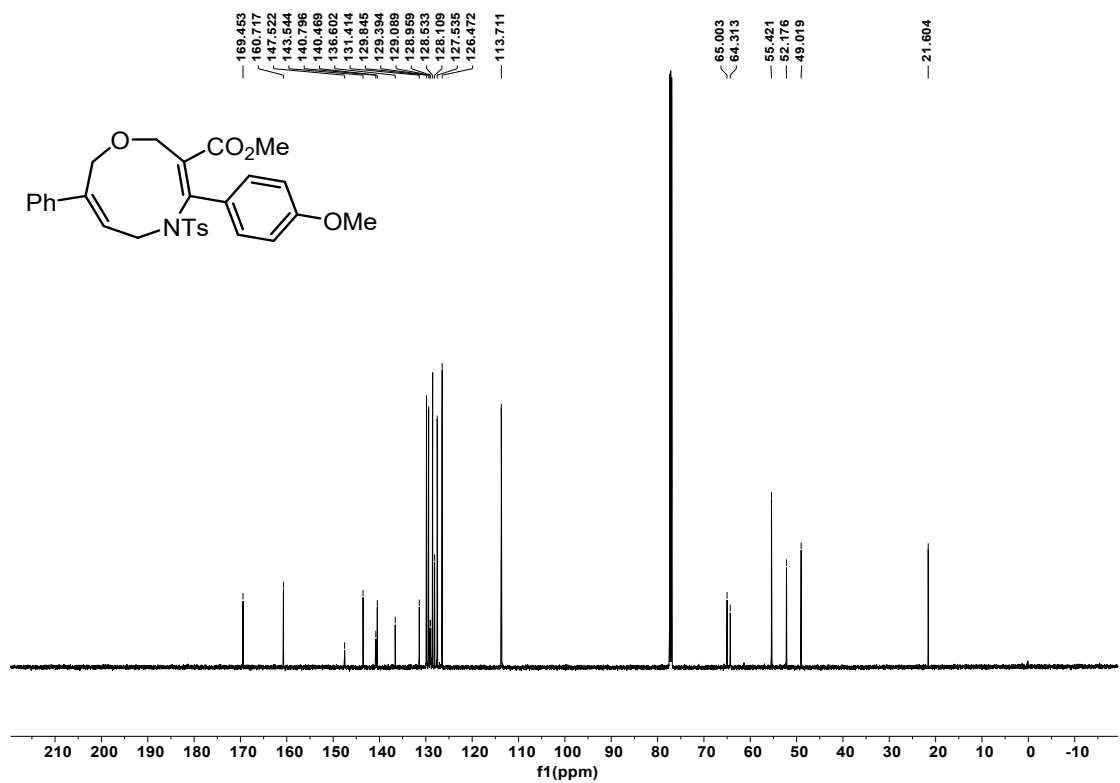
¹³C NMR of **3d** in CDCl₃ (150 MHz)



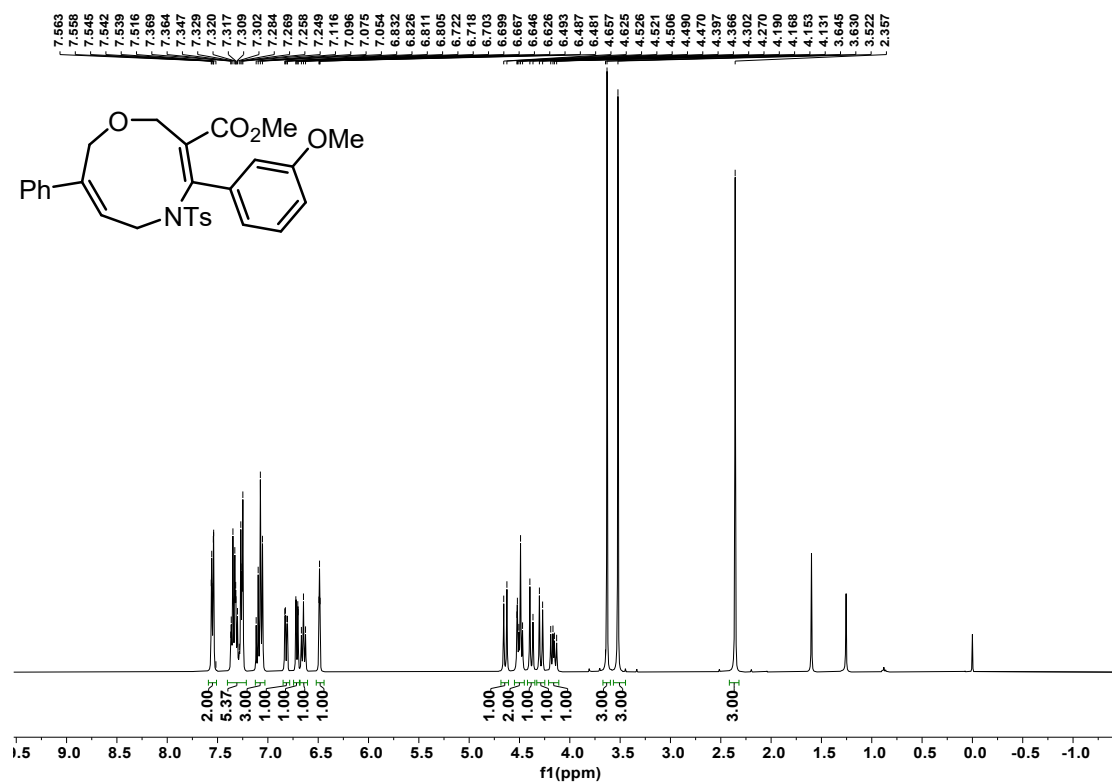
^1H NMR of **3f** in CDCl_3 (600 MHz)



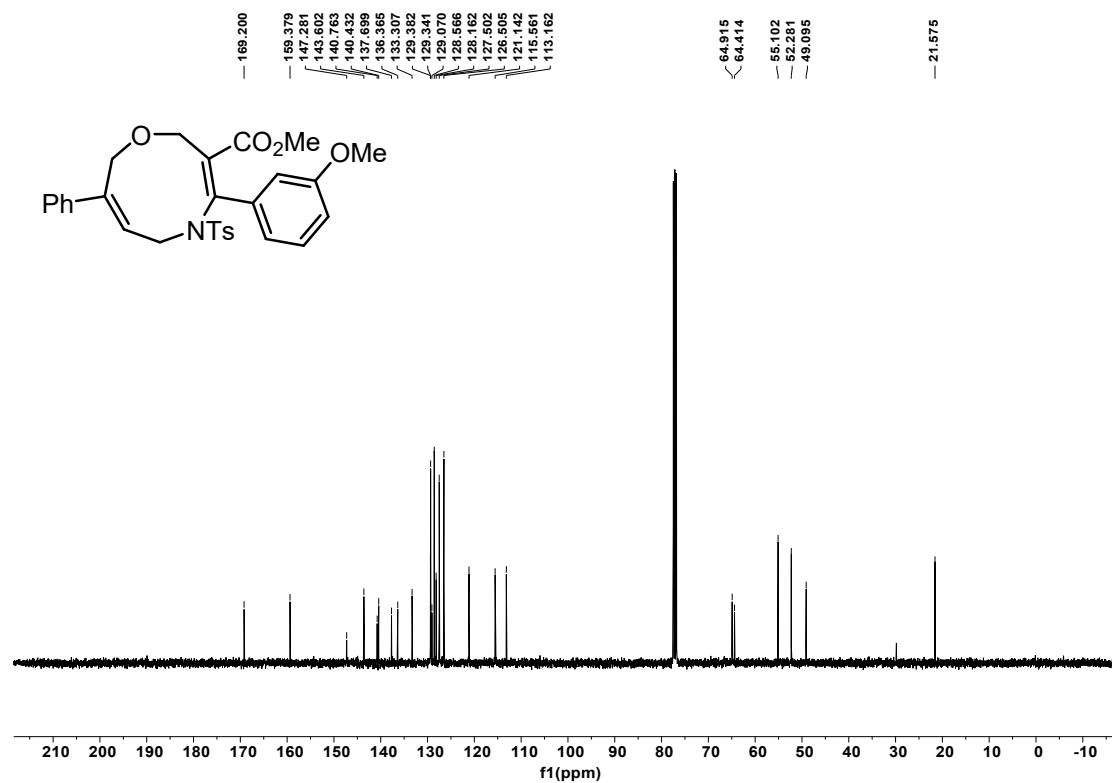
^{13}C NMR of **3f** in CDCl_3 (150 MHz)



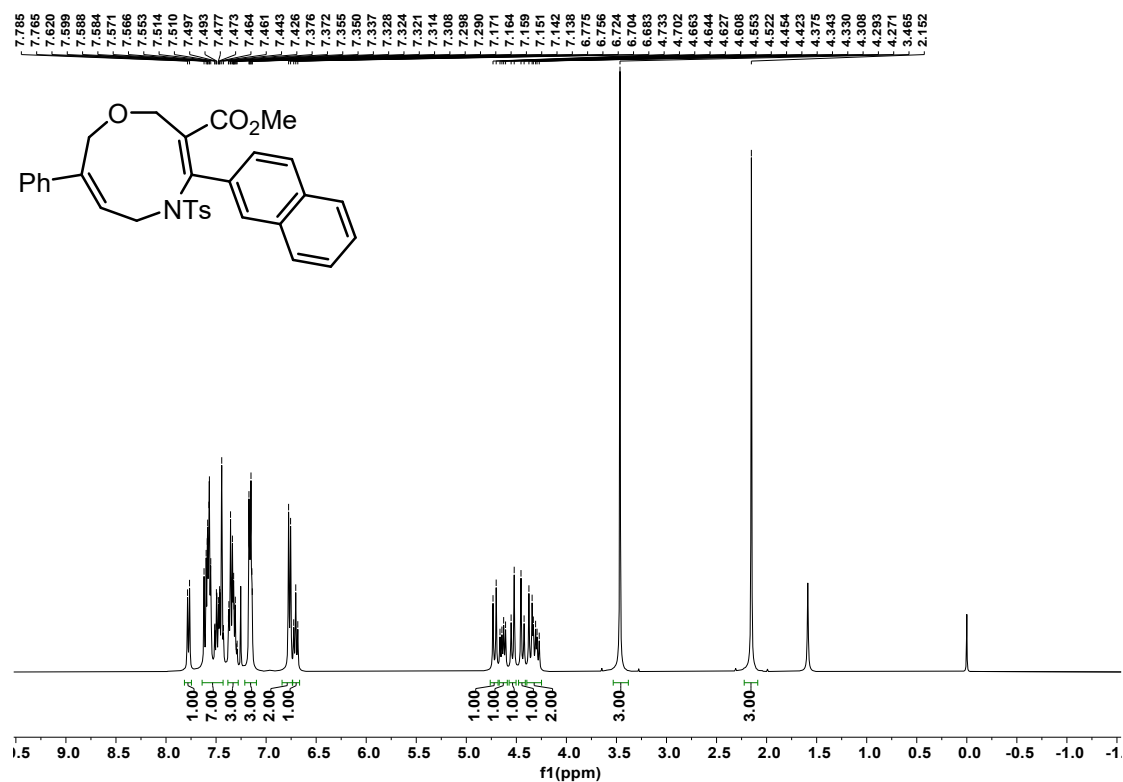
^1H NMR of **3h** in CDCl_3 (400 MHz)



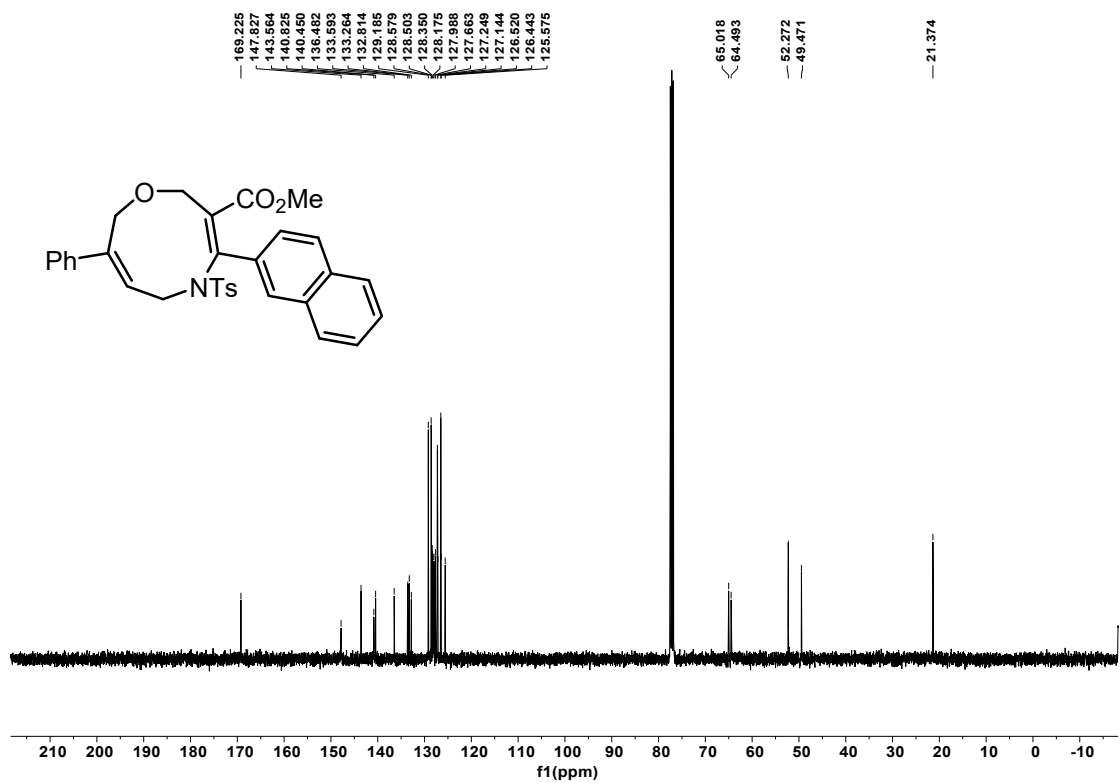
^{13}C NMR of **3h** in CDCl_3 (100 MHz)



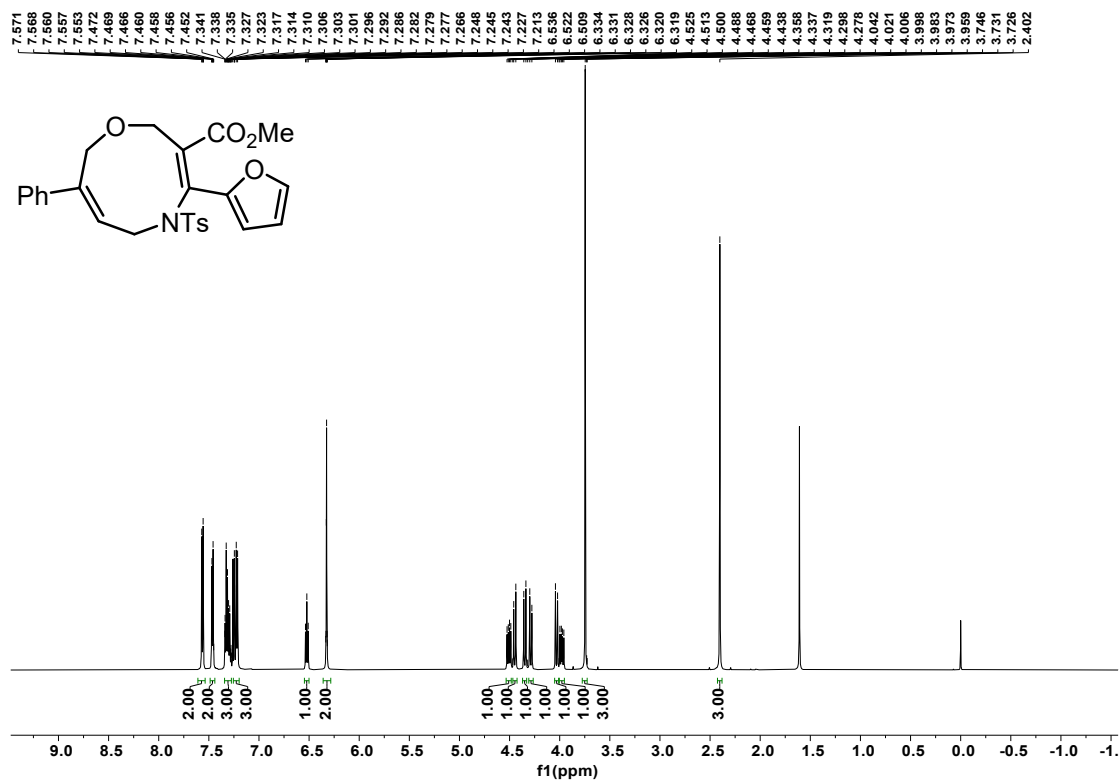
^1H NMR of **3i** in CDCl_3 (400 MHz)



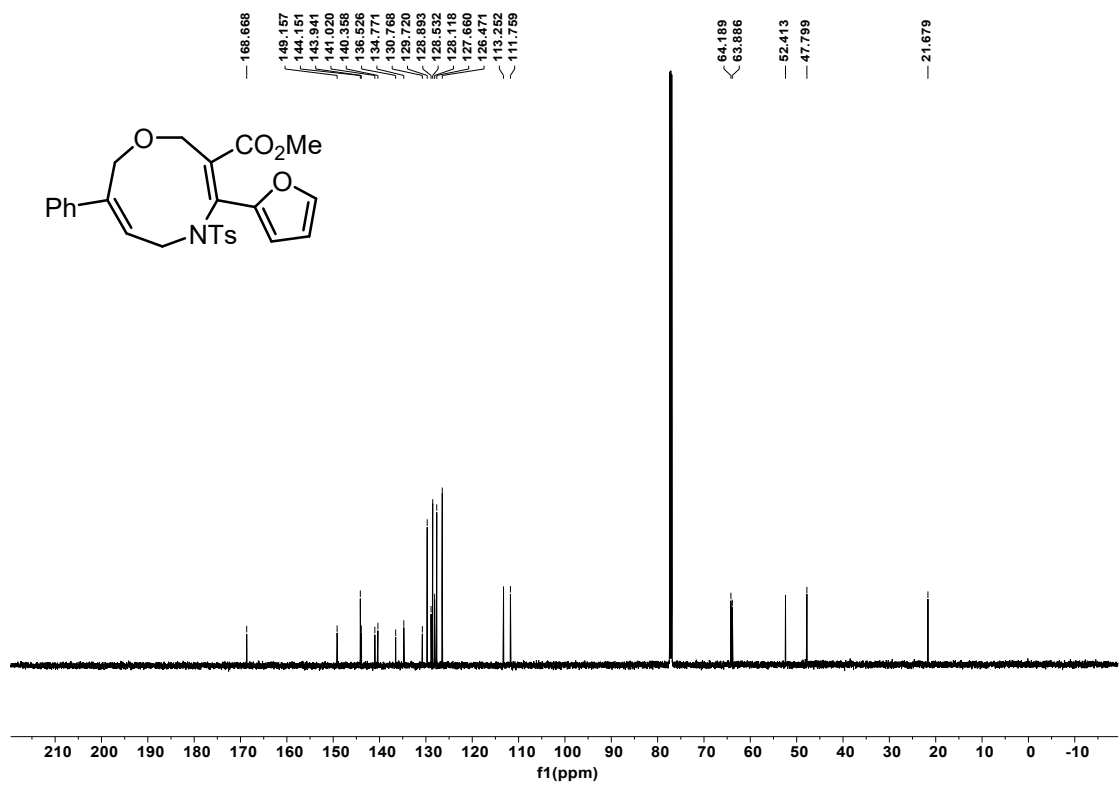
^{13}C NMR of **3i** in CDCl_3 (100 MHz)



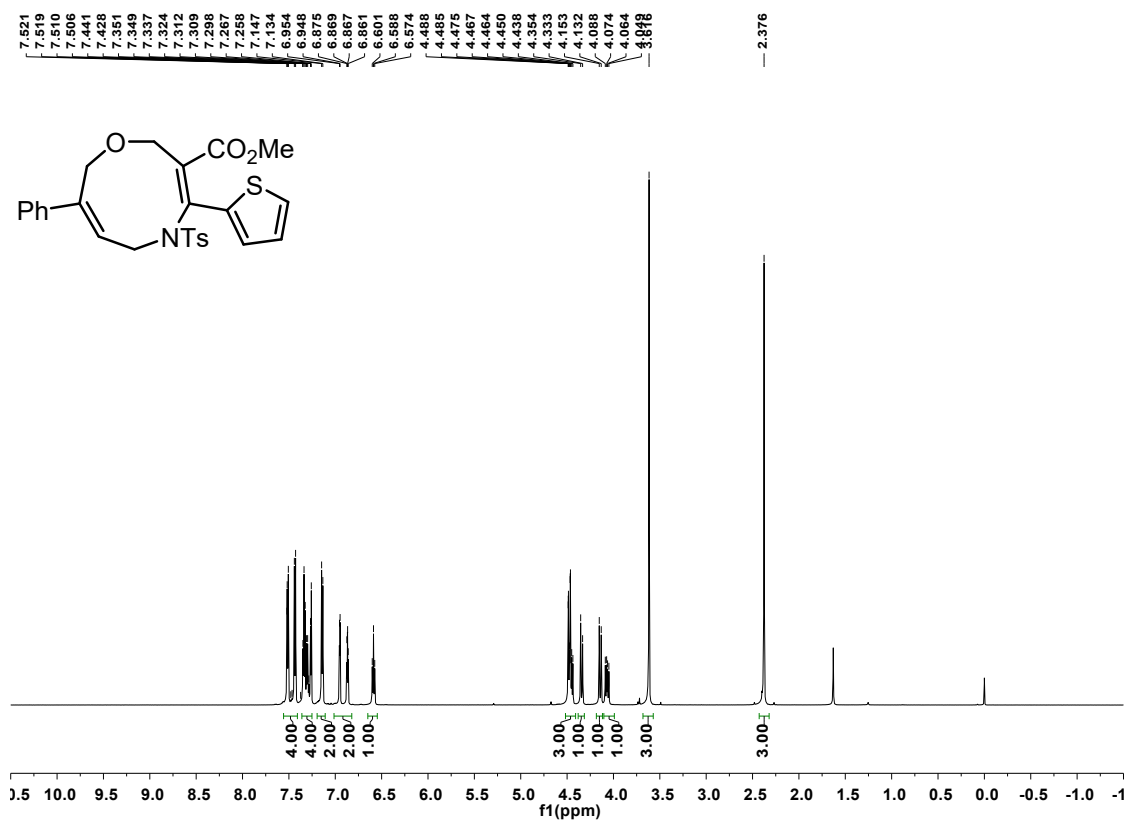
^1H NMR of **3j** in CDCl_3 (600 MHz)



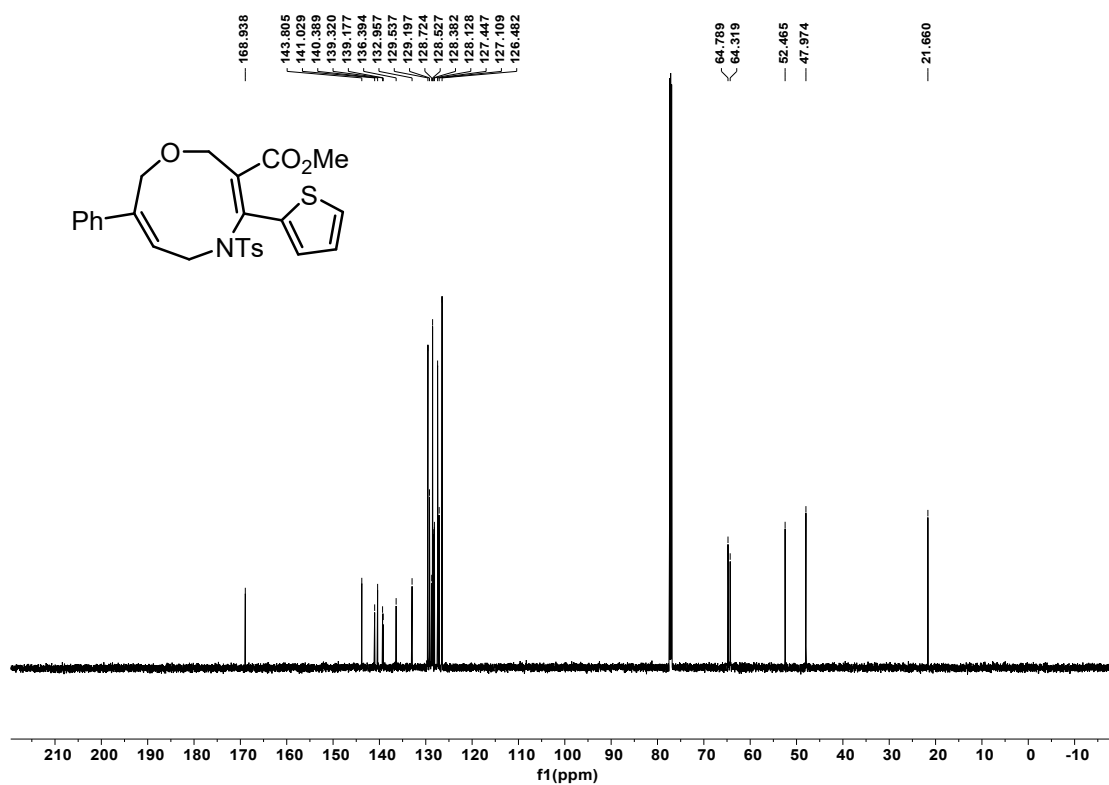
^{13}C NMR of **3j** in CDCl_3 (150 MHz)



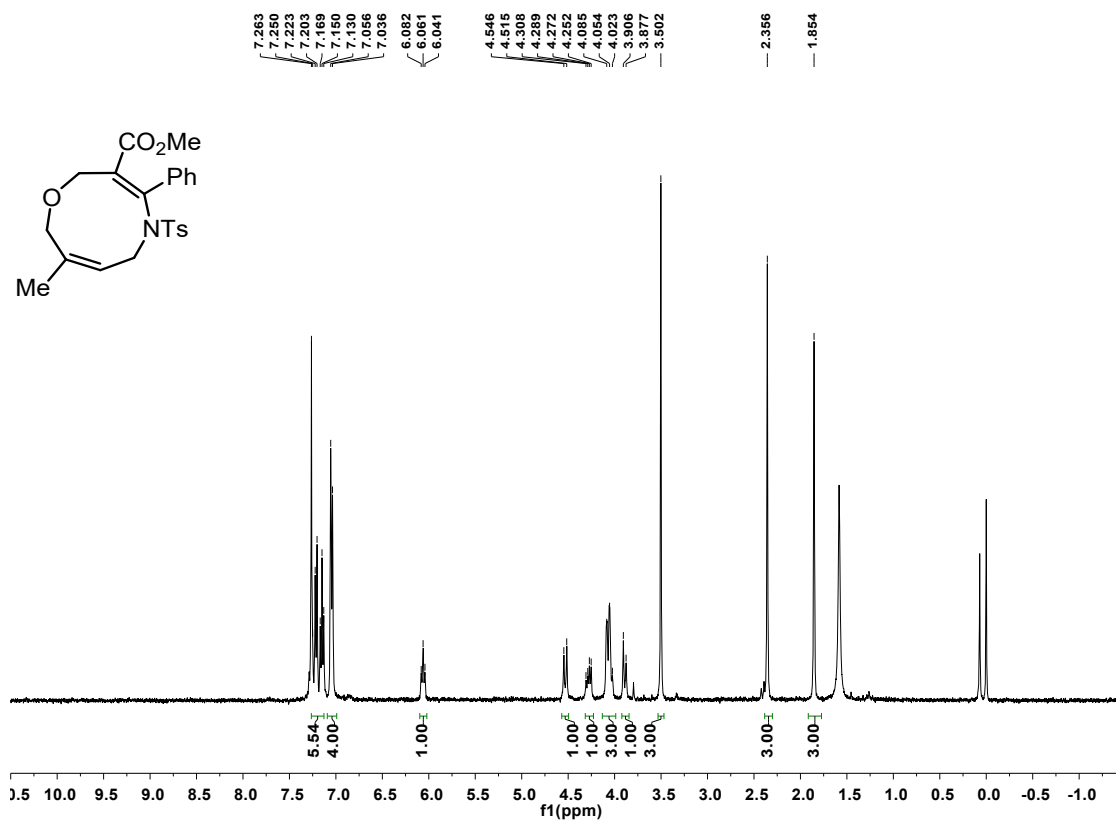
^1H NMR of **3k** in CDCl_3 (600 MHz)



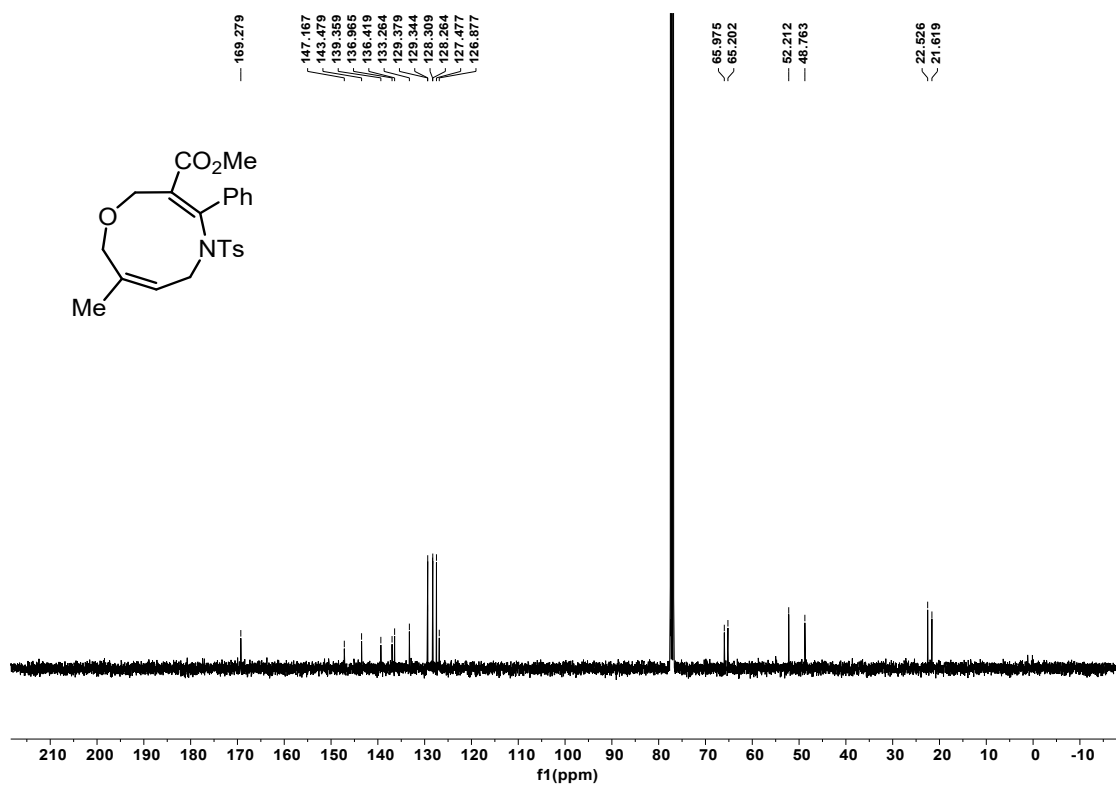
^{13}C NMR of **3k** in CDCl_3 (150 MHz)



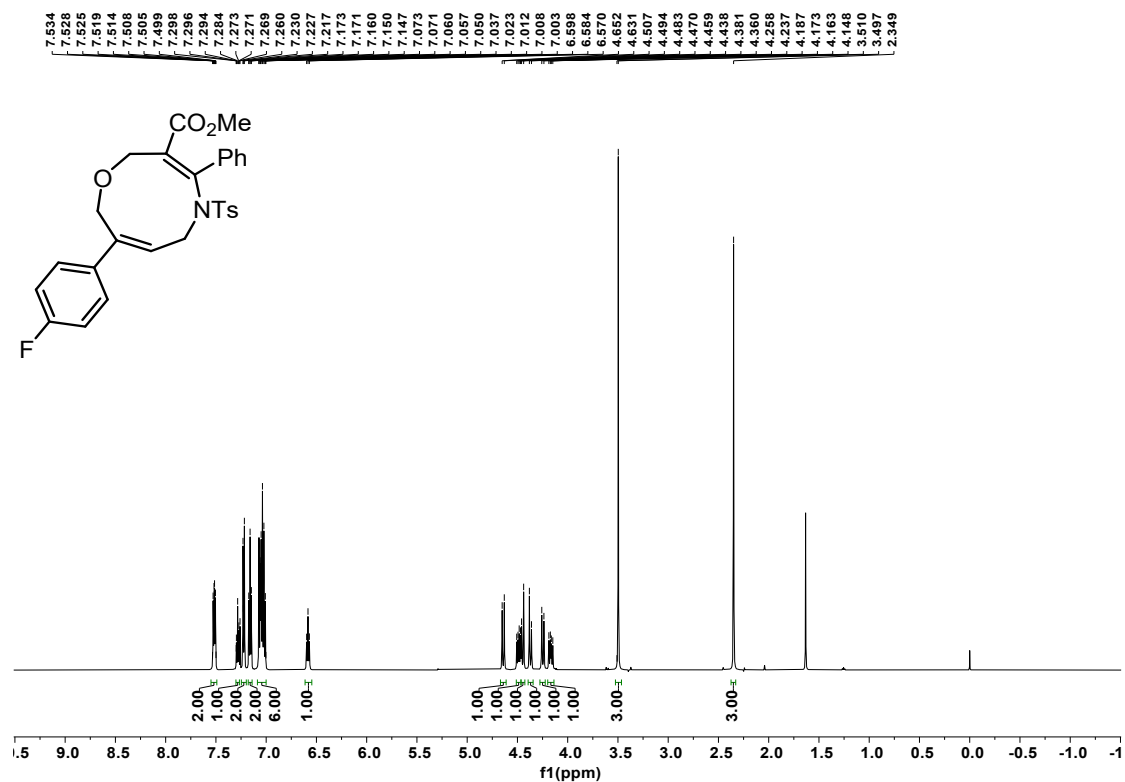
^1H NMR of **31** in CDCl_3 (400 MHz)



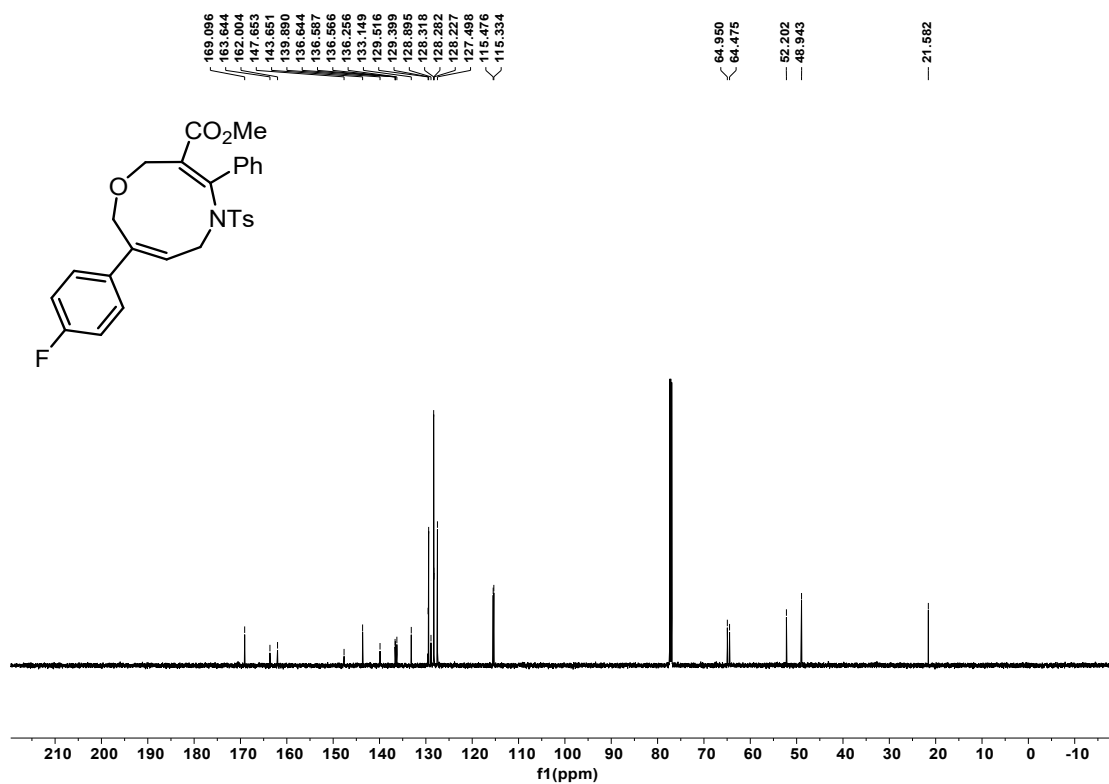
^{13}C NMR of **31** in CDCl_3 (100 MHz)



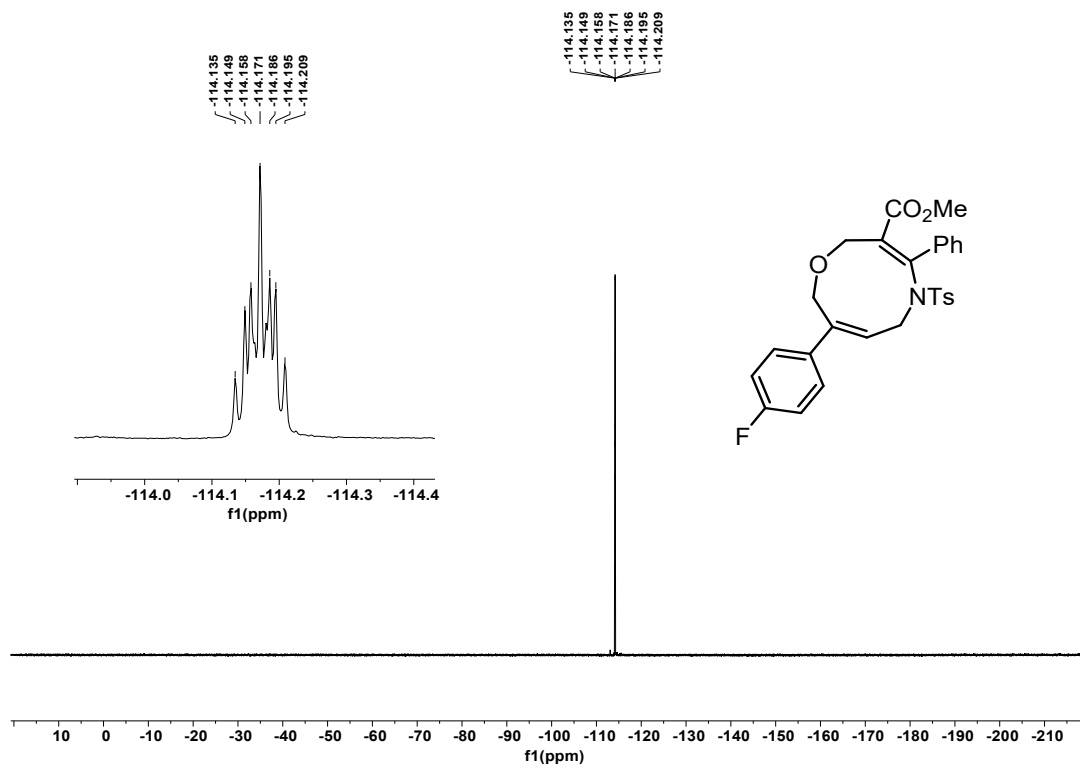
¹H NMR of **3p** in CDCl₃ (600 MHz)



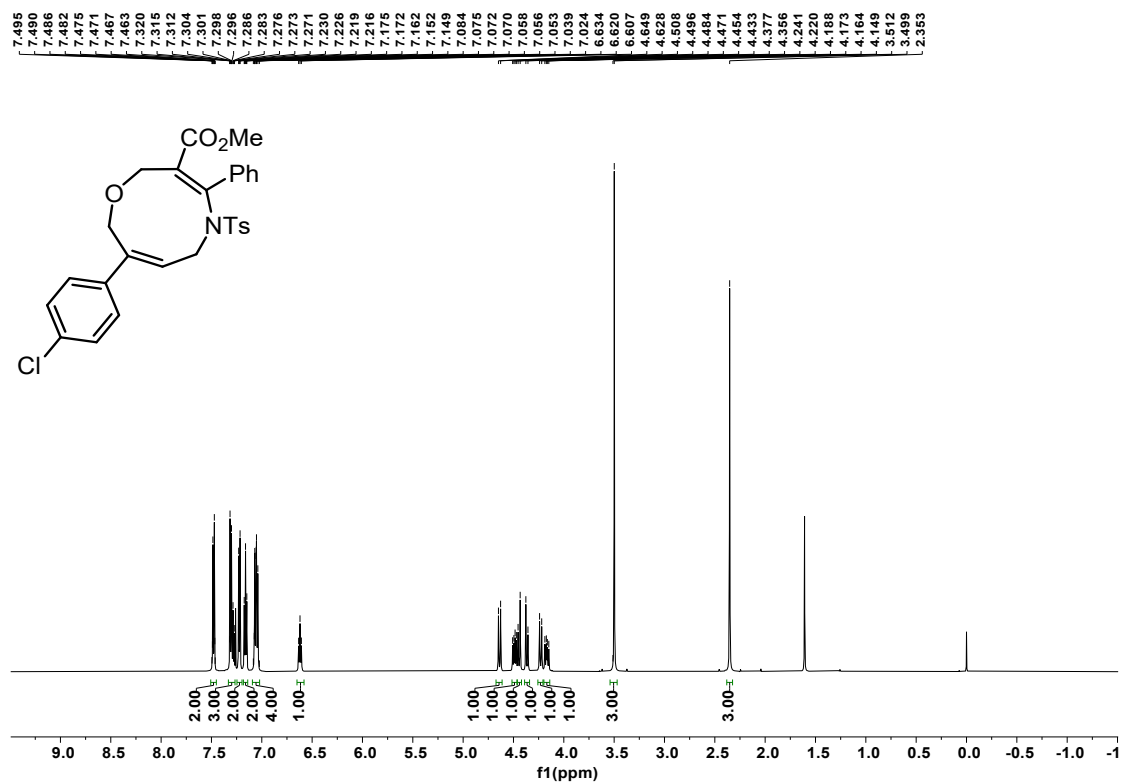
¹³C NMR of **3p** in CDCl₃ (150 MHz)



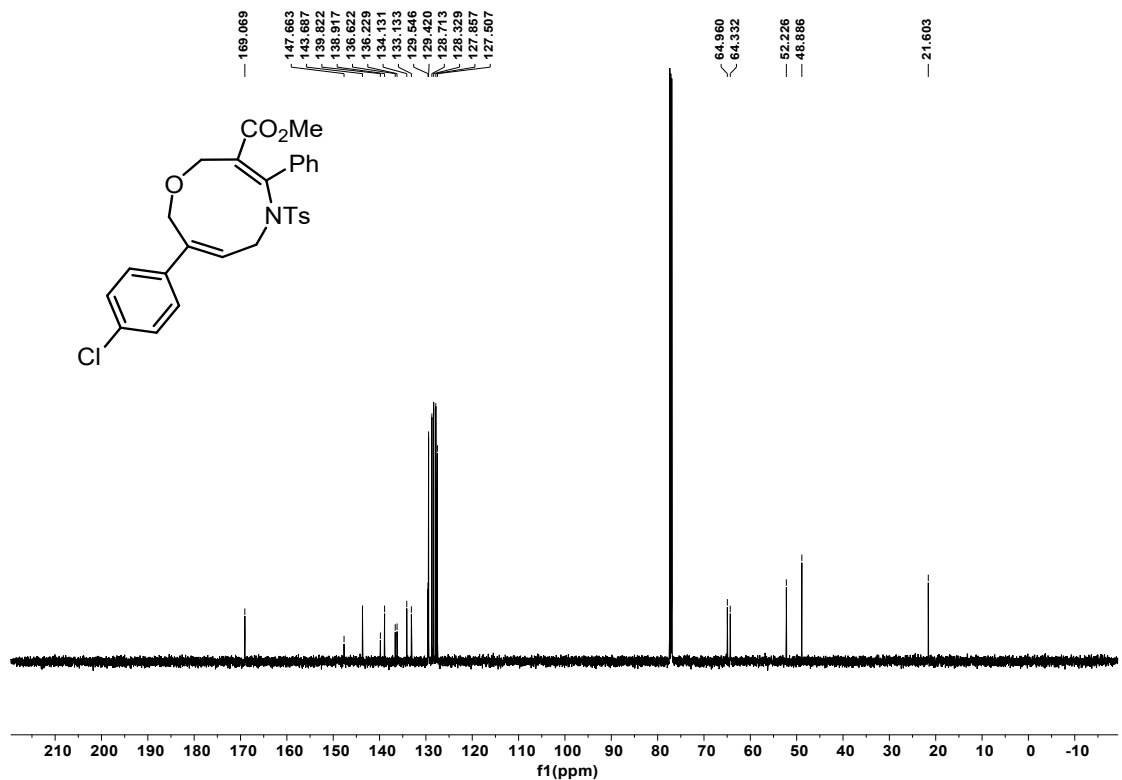
^{19}F NMR of **3p** in CDCl_3 (376 MHz)



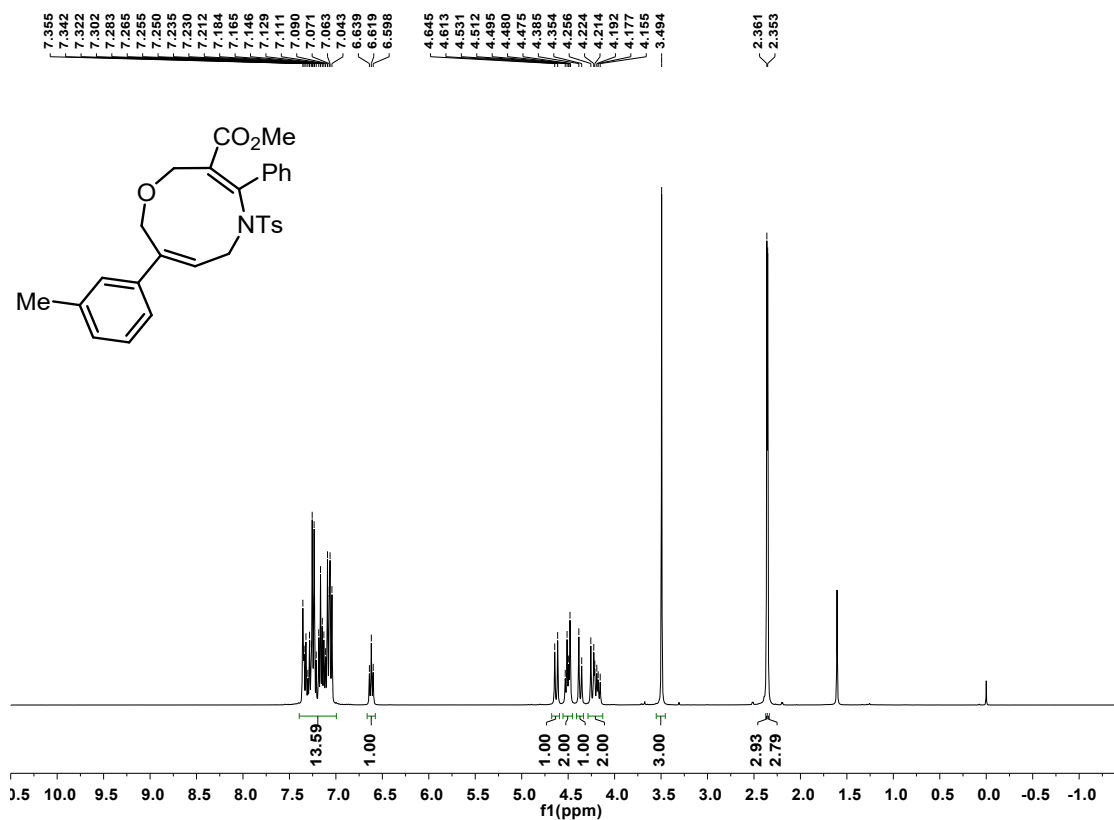
¹H NMR of **3q** in CDCl₃ (600 MHz)



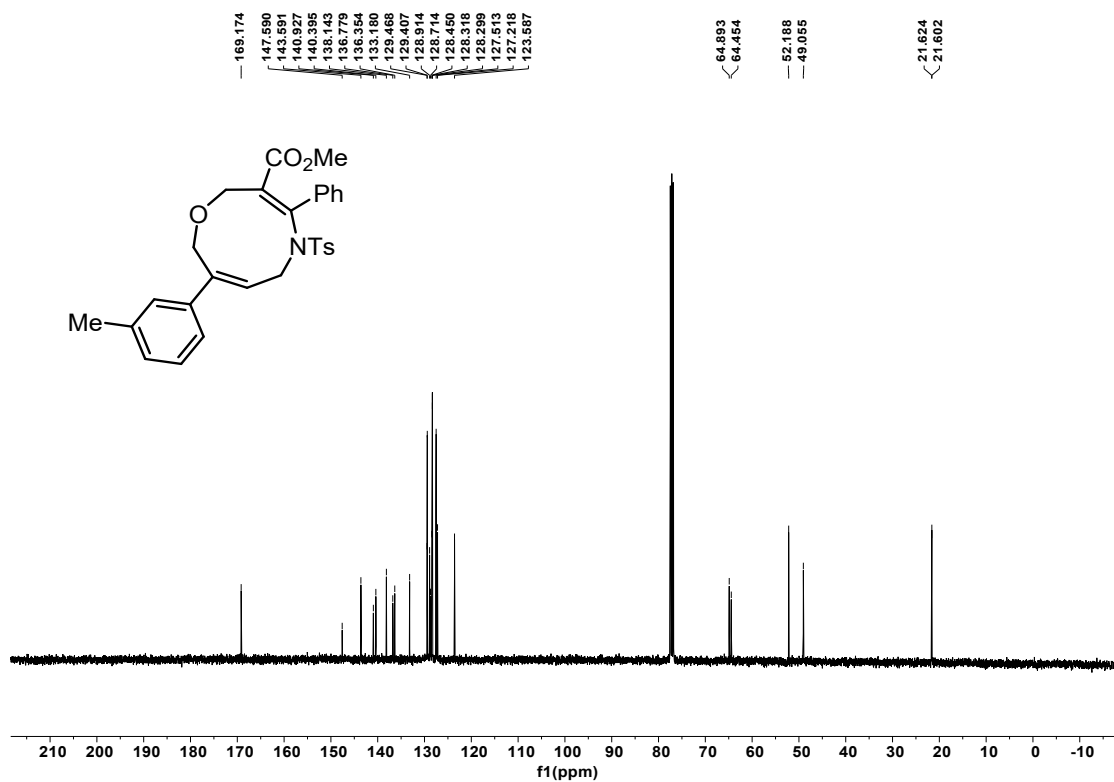
¹³C NMR of **3q** in CDCl₃ (150 MHz)



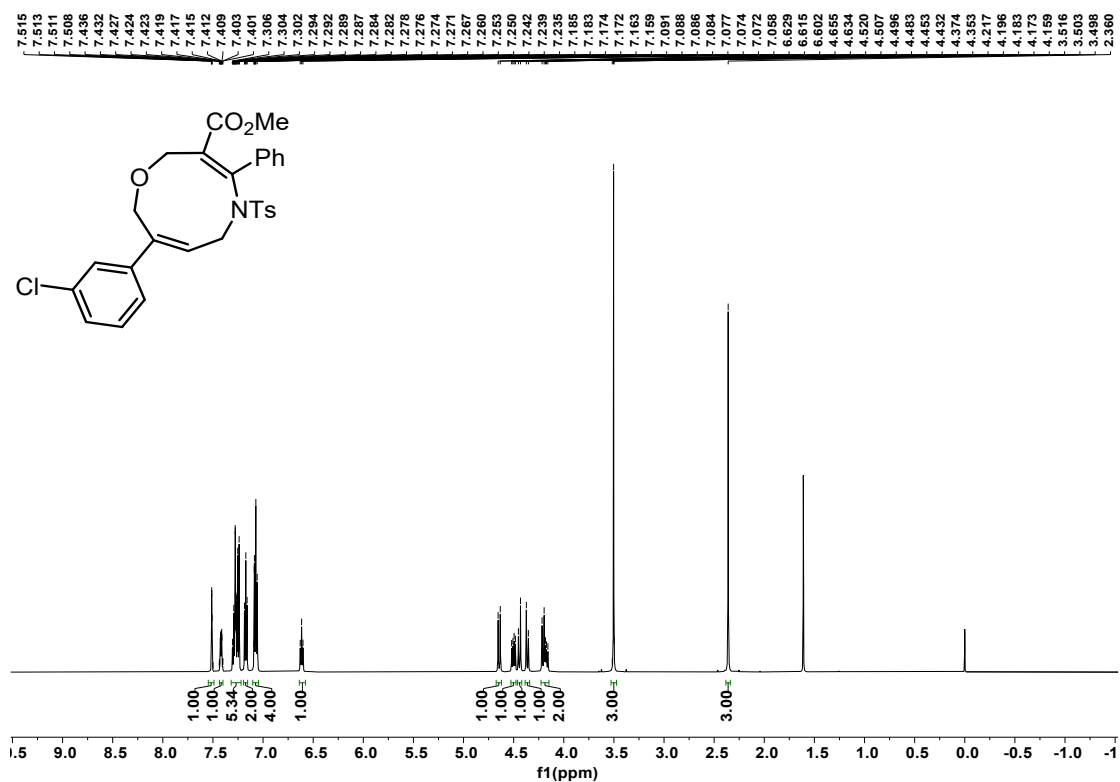
^1H NMR of **3s** in CDCl_3 (400 MHz)



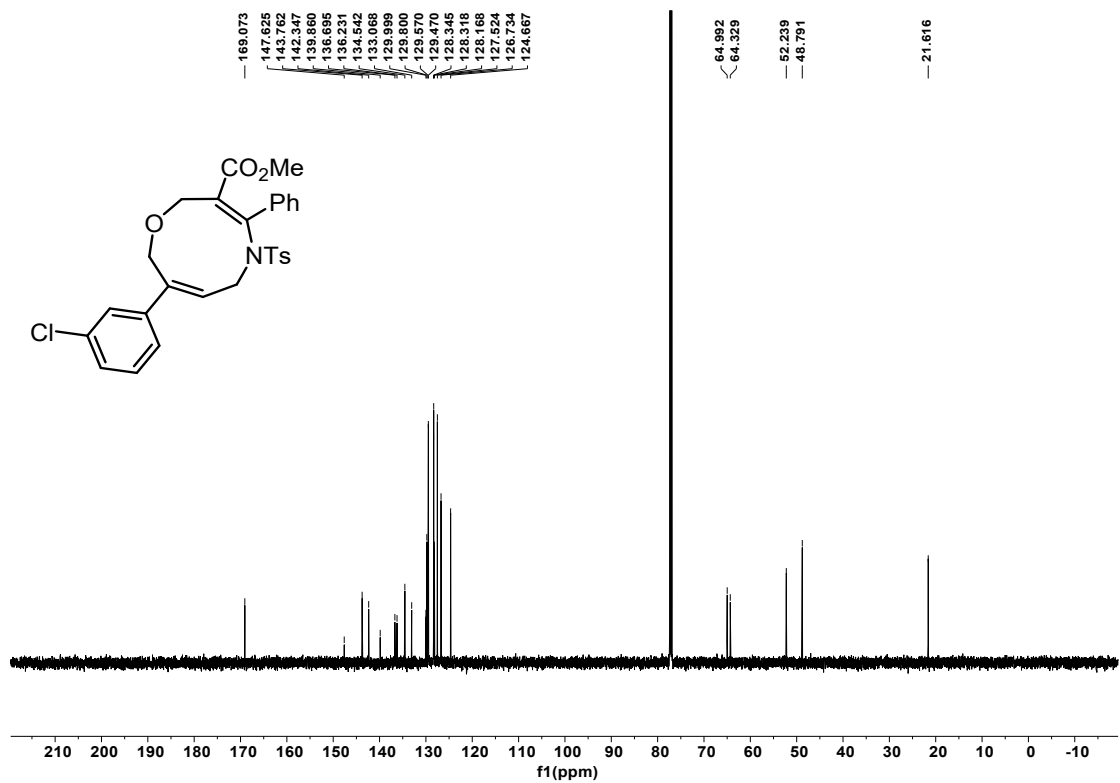
^{13}C NMR of **3s** in CDCl_3 (100 MHz)



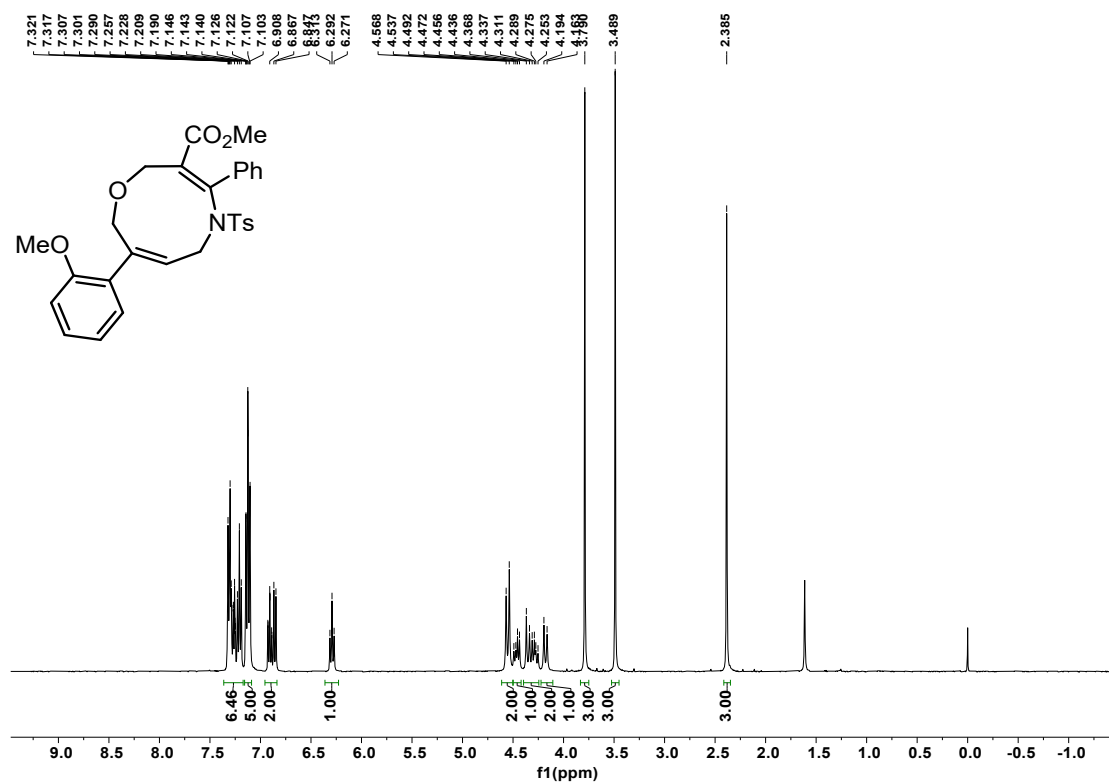
^1H NMR of **3u** in CDCl_3 (600 MHz)



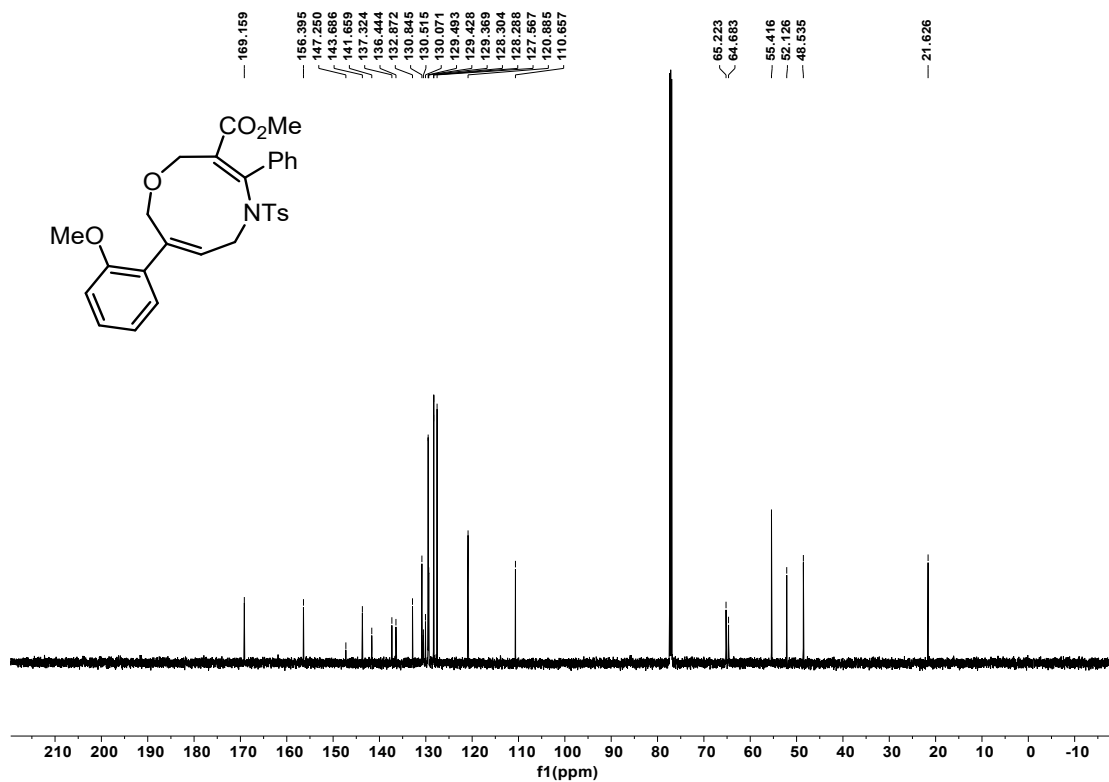
^{13}C NMR of **3u** in CDCl_3 (150 MHz)



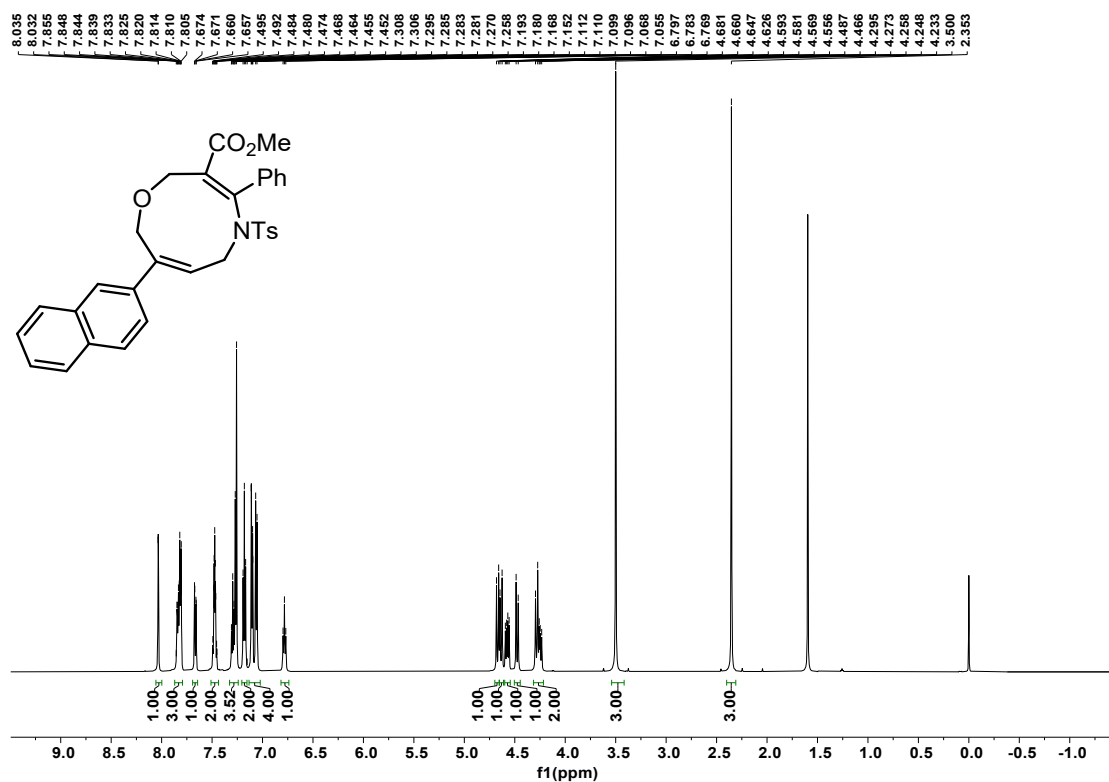
^1H NMR of **3v** in CDCl_3 (400 MHz)



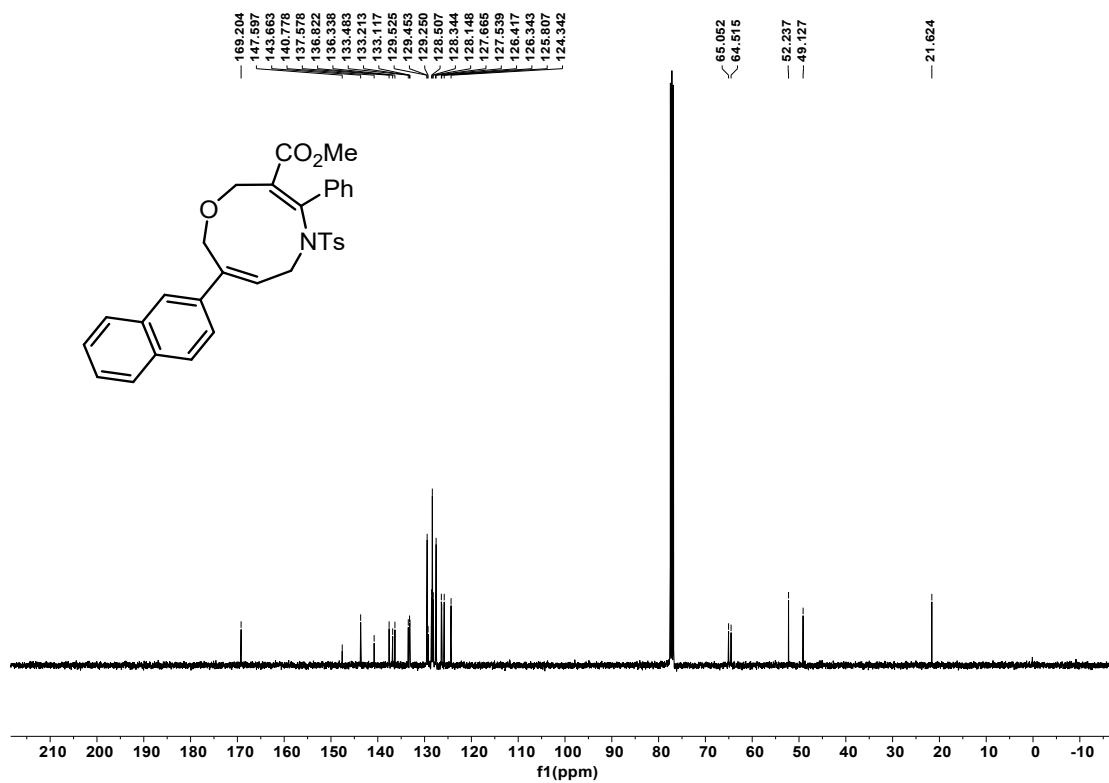
^{13}C NMR of **3v** in CDCl_3 (150 MHz)



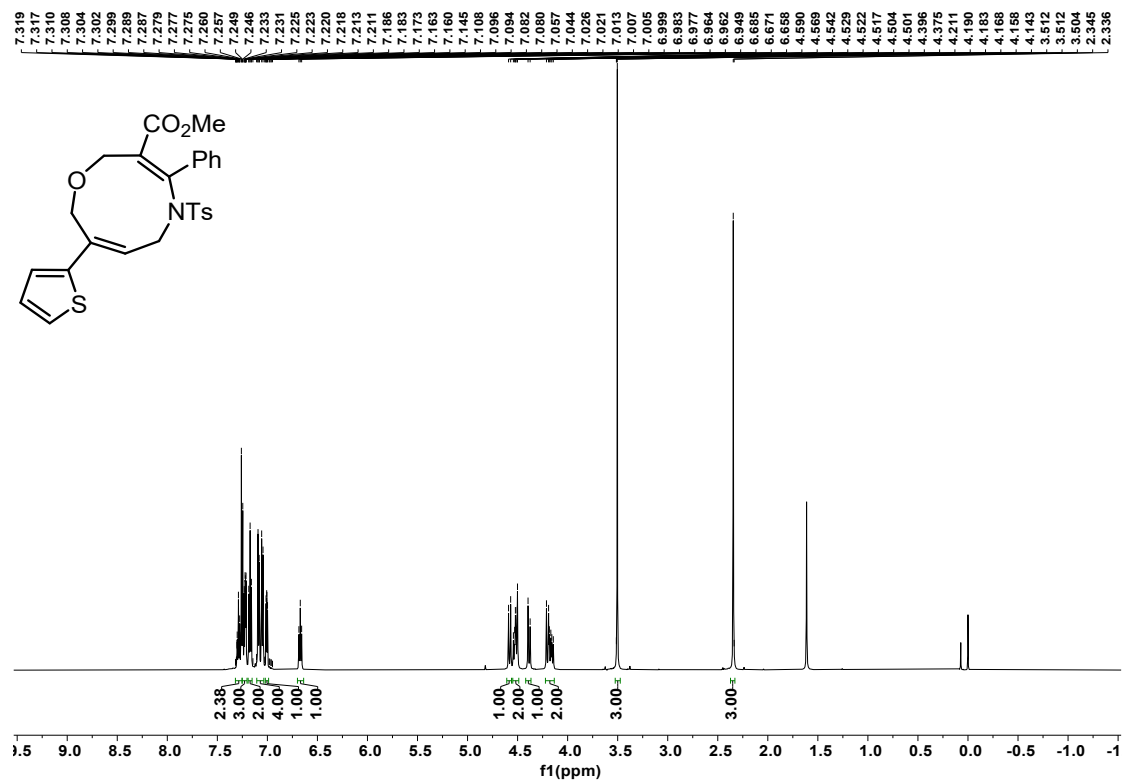
^1H NMR of **3w** in CDCl_3 (600 MHz)



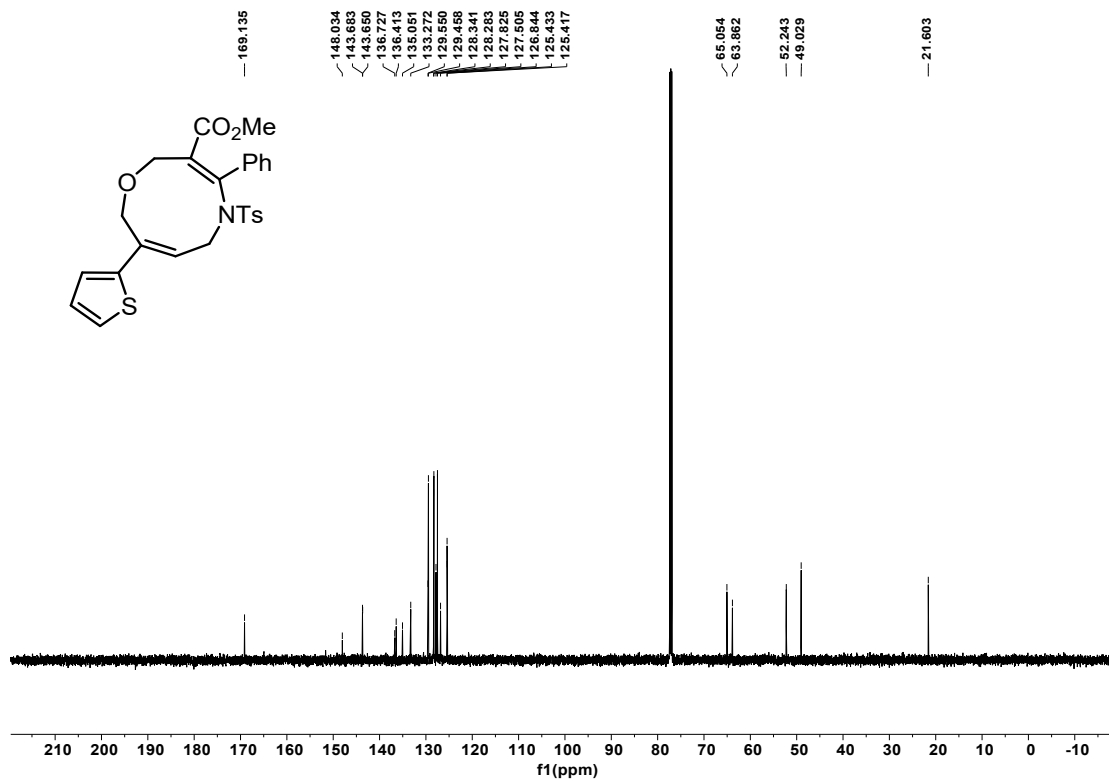
^{13}C NMR of **3w** in CDCl_3 (100 MHz)



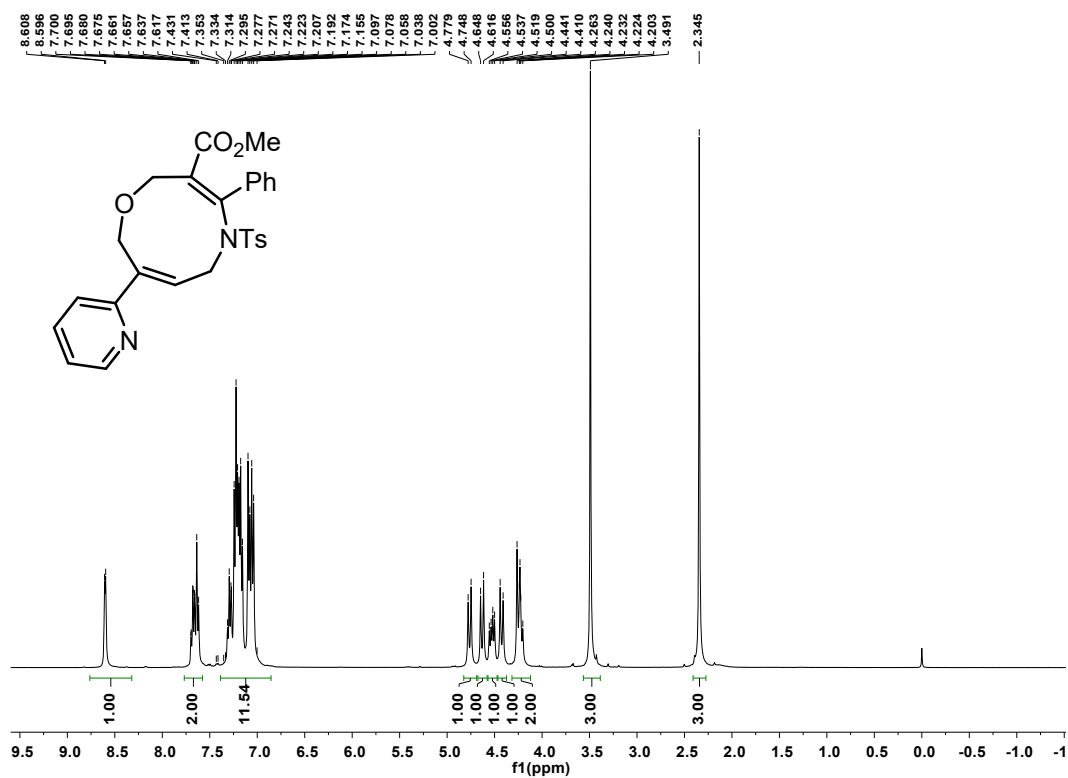
^1H NMR of **3x** in CDCl_3 (600 MHz)



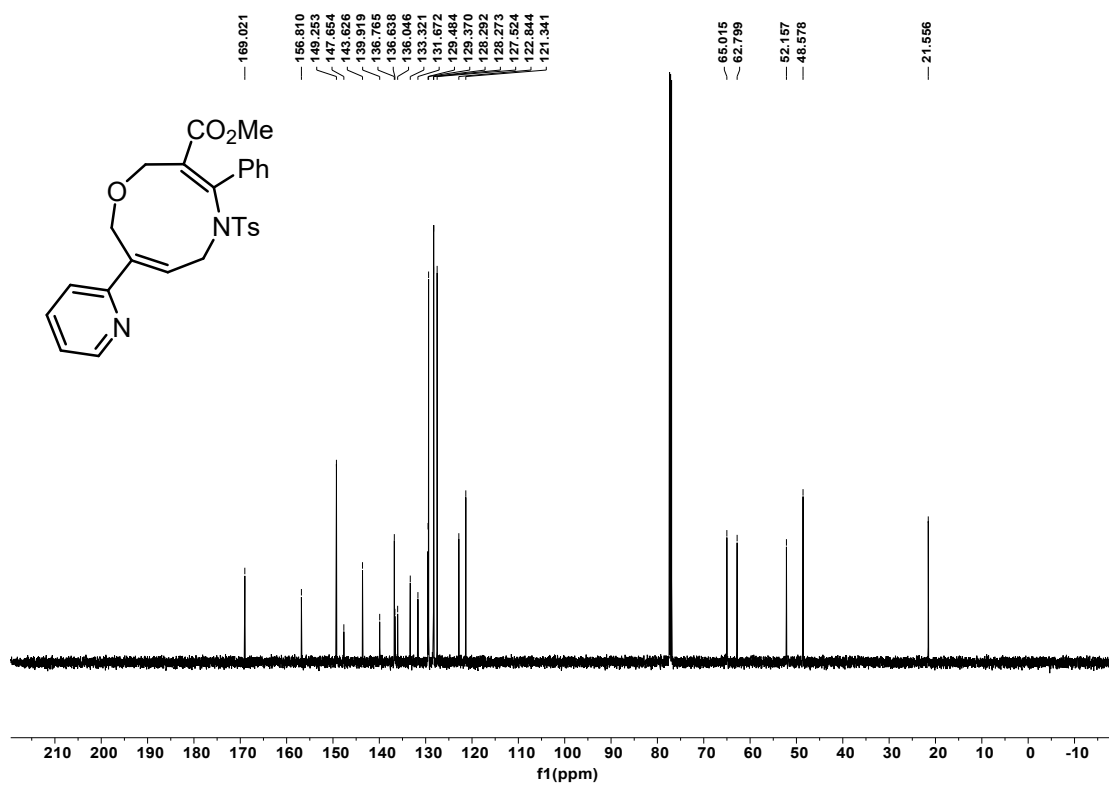
^{13}C NMR of **3x** in CDCl_3 (150 MHz)



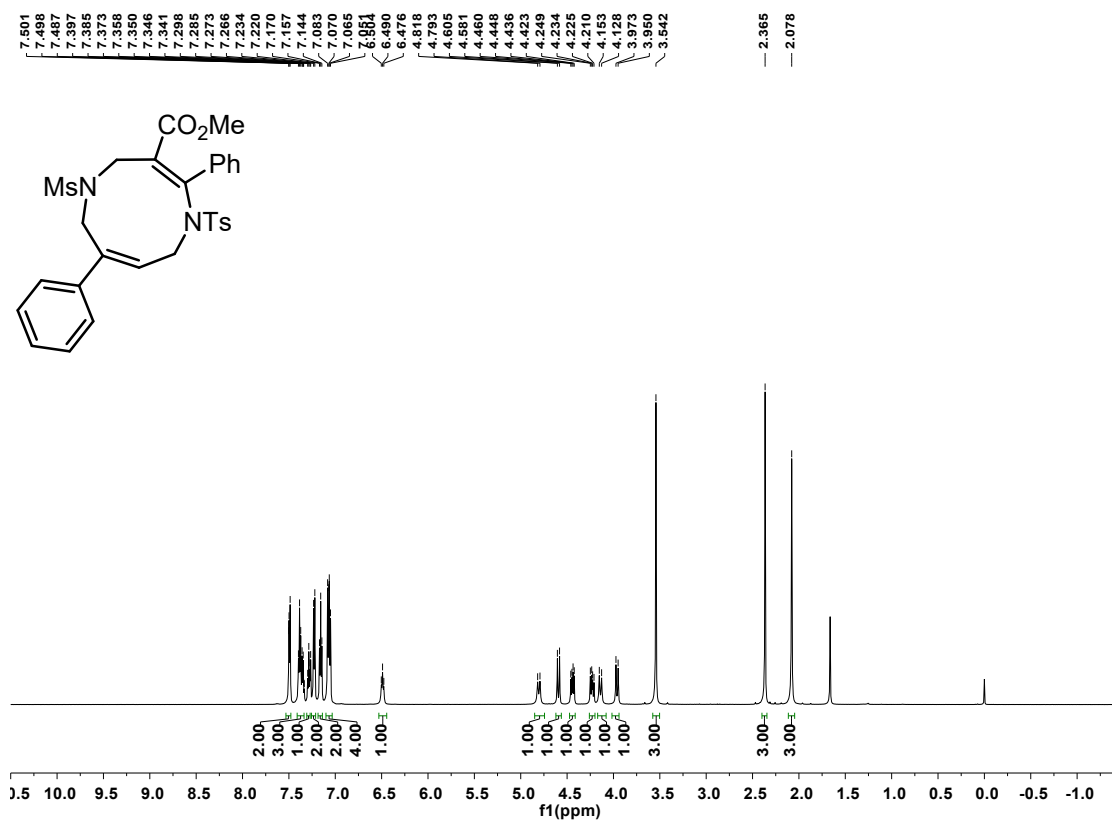
^1H NMR of **3y** in CDCl_3 (600 MHz)



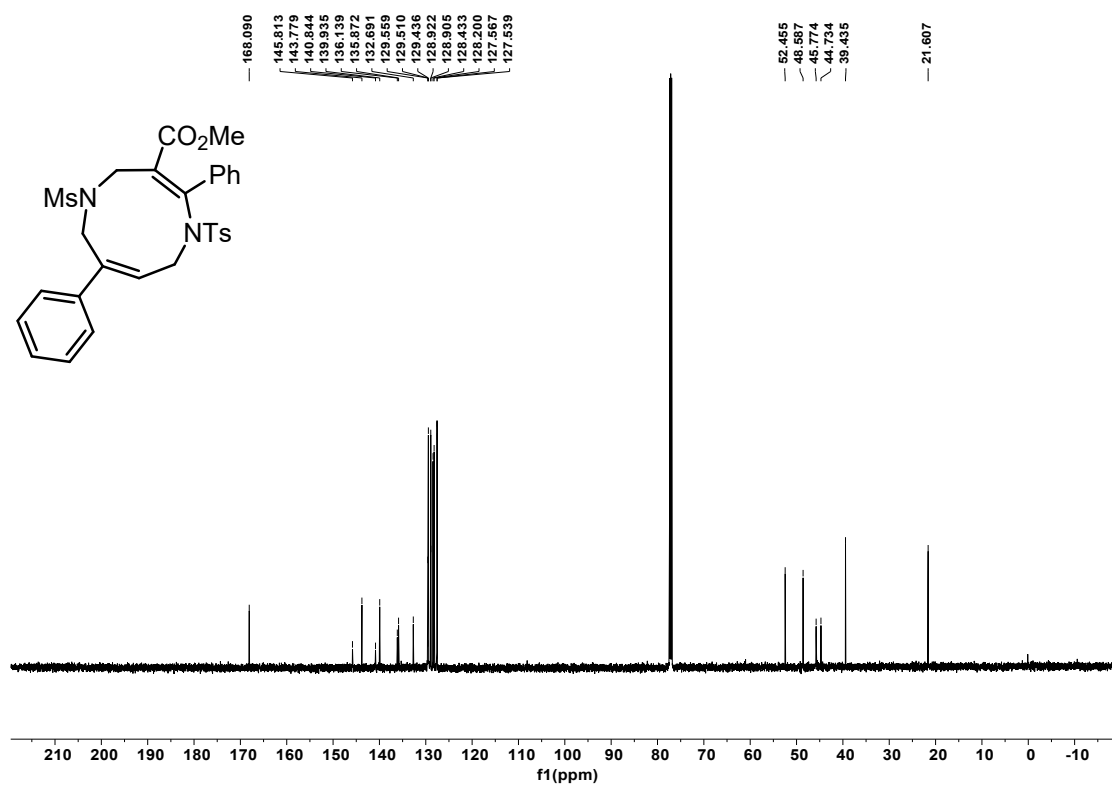
^{13}C NMR of **3y** in CDCl_3 (150 MHz)



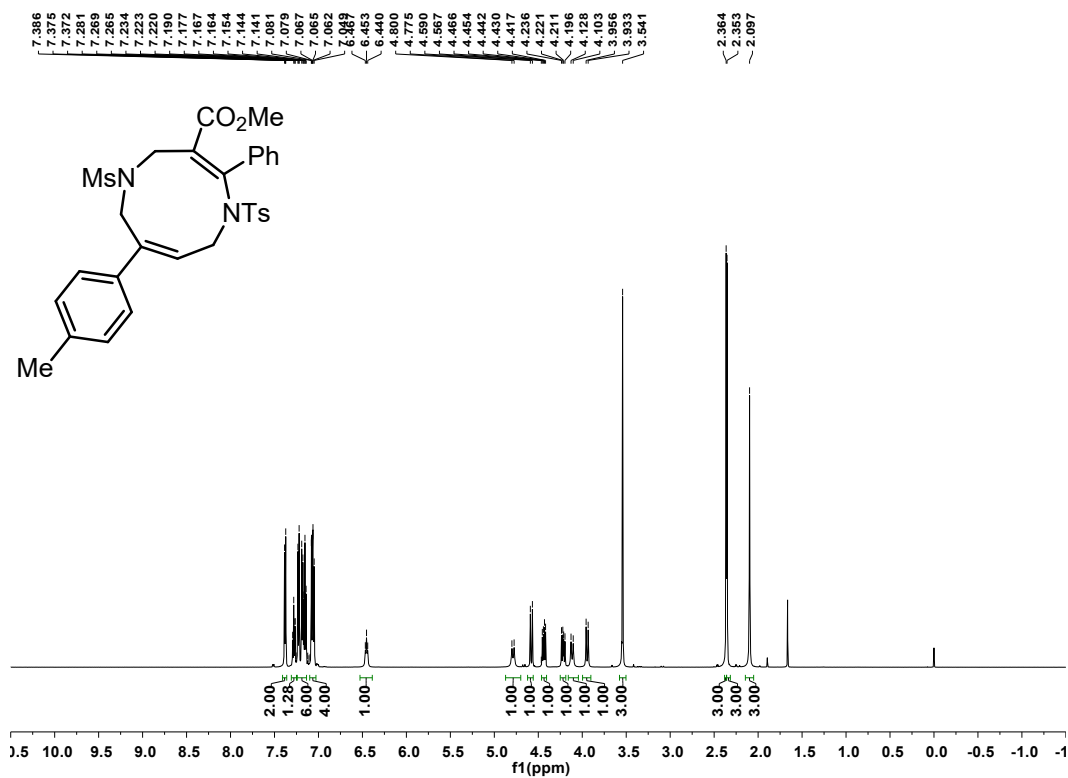
^1H NMR of **5a** in CDCl_3 (600 MHz)



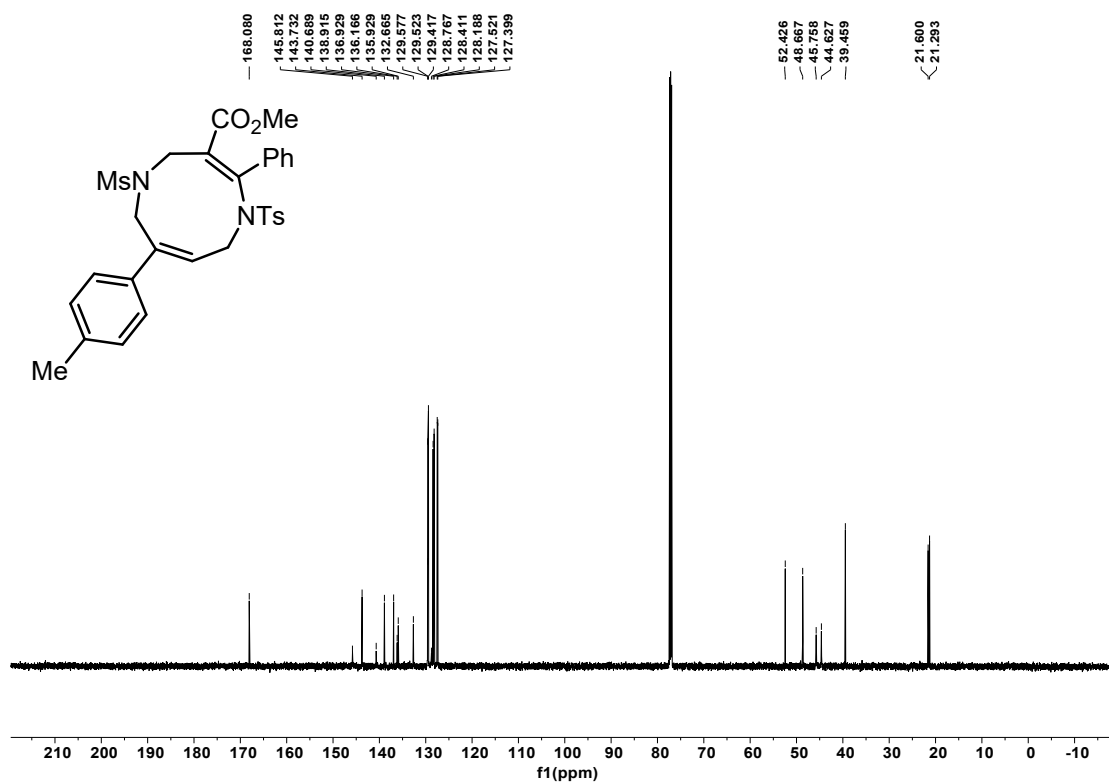
^{13}C NMR of **5a** in CDCl_3 (150 MHz)



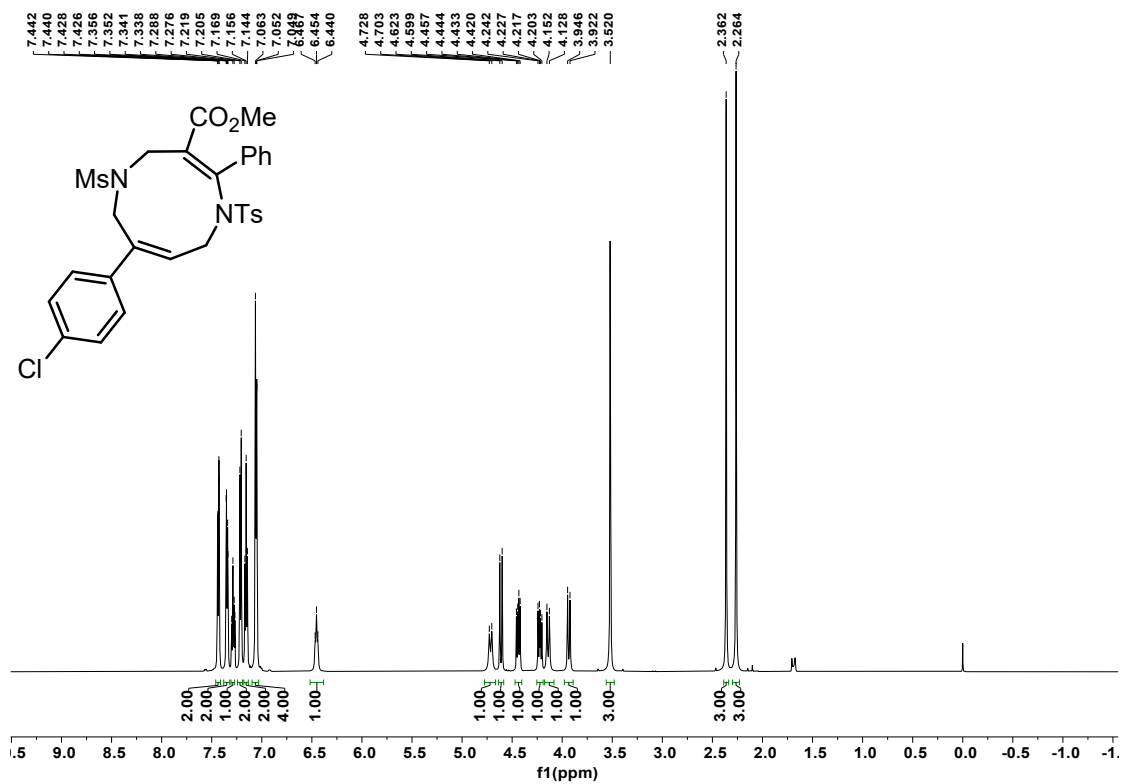
^1H NMR of **5b** in CDCl_3 (600 MHz)



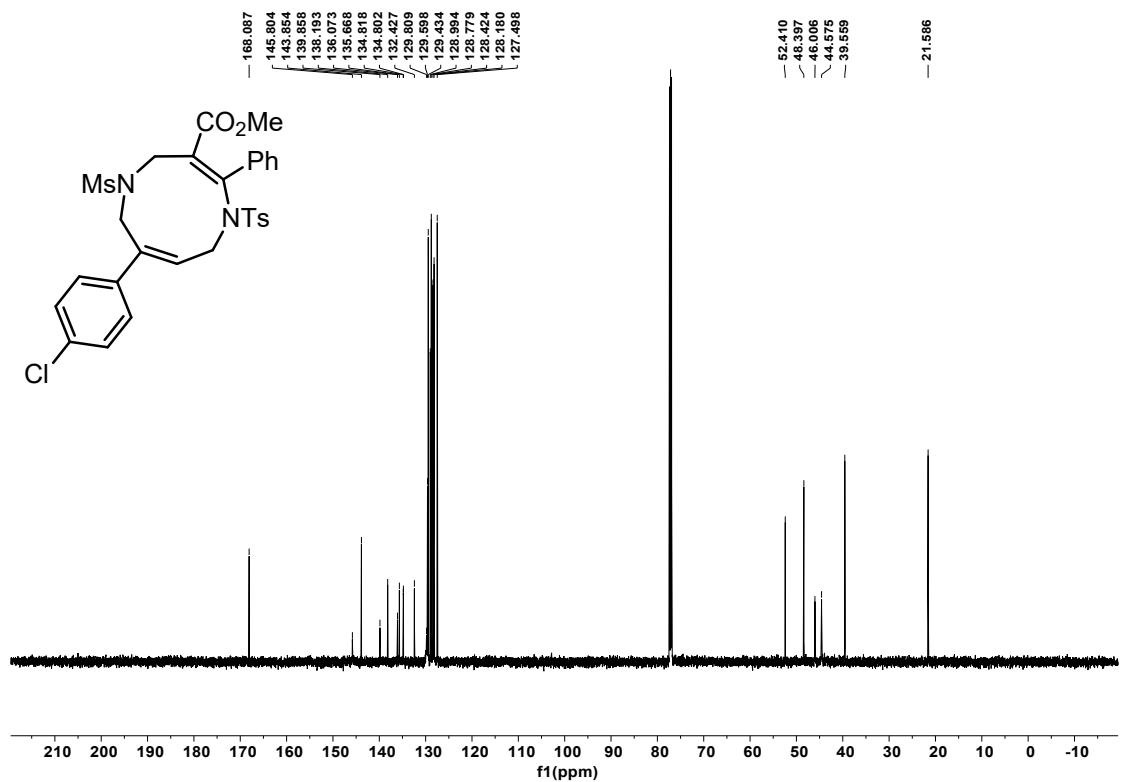
^{13}C NMR of **5b** in CDCl_3 (150 MHz)



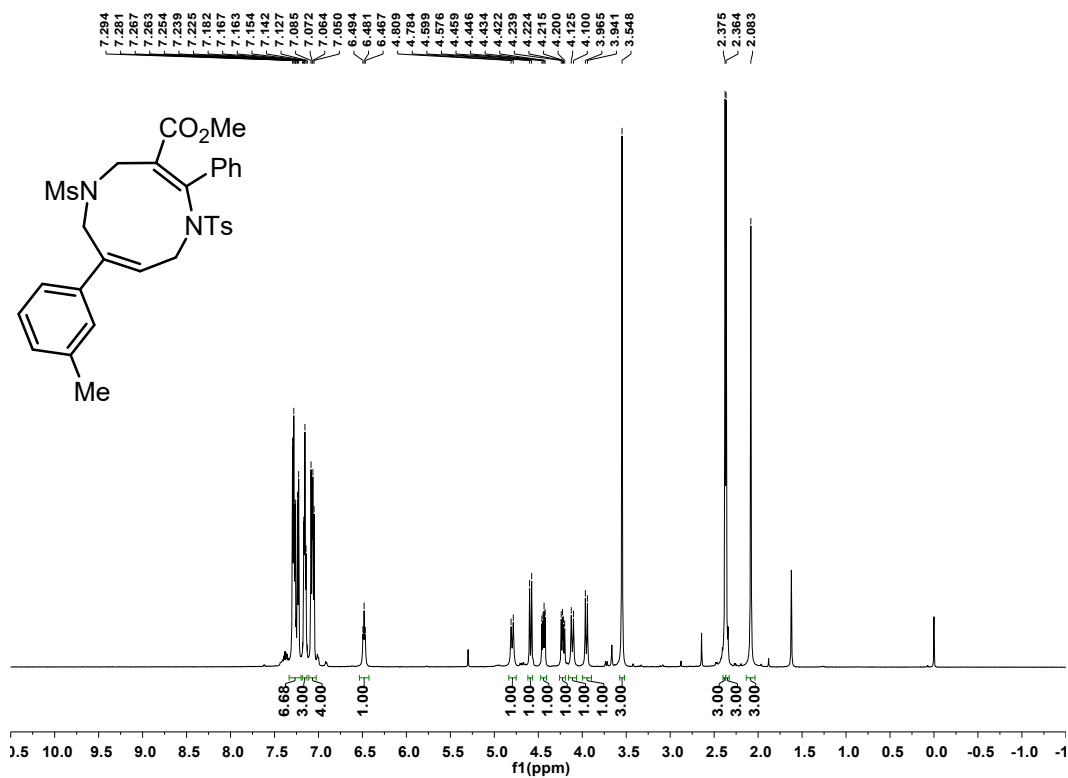
^1H NMR of **5c** in CDCl_3 (600 MHz)



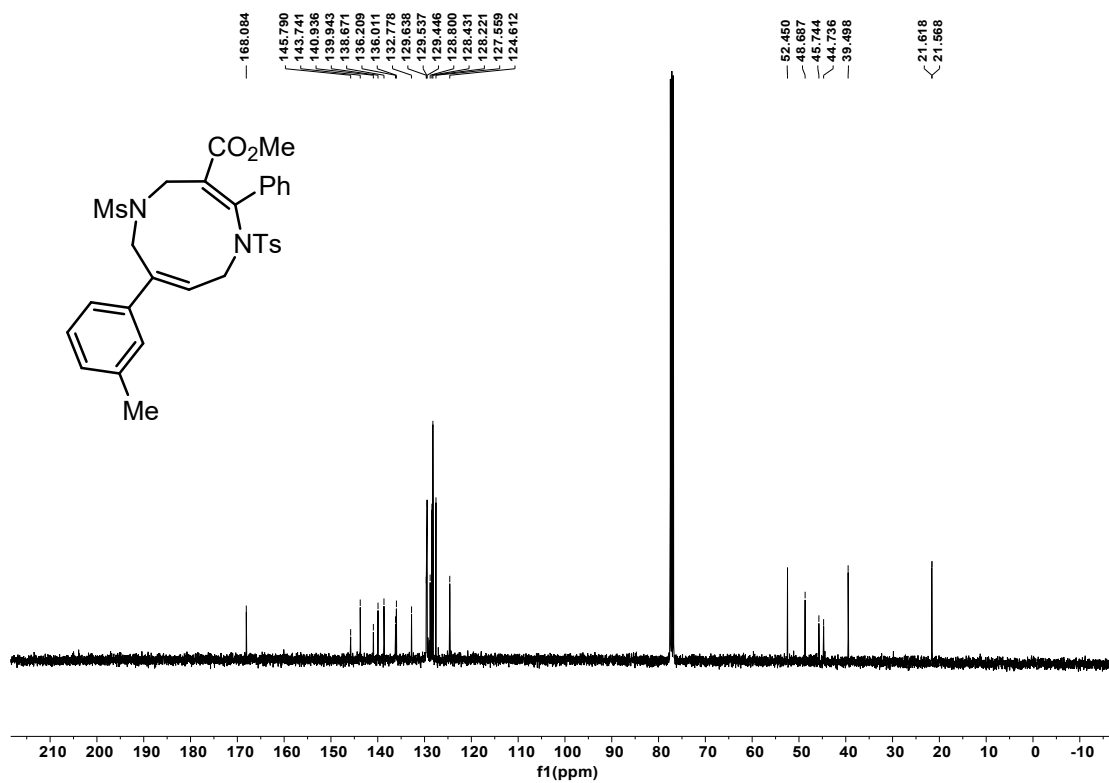
^{13}C NMR of **5c** in CDCl_3 (150 MHz)



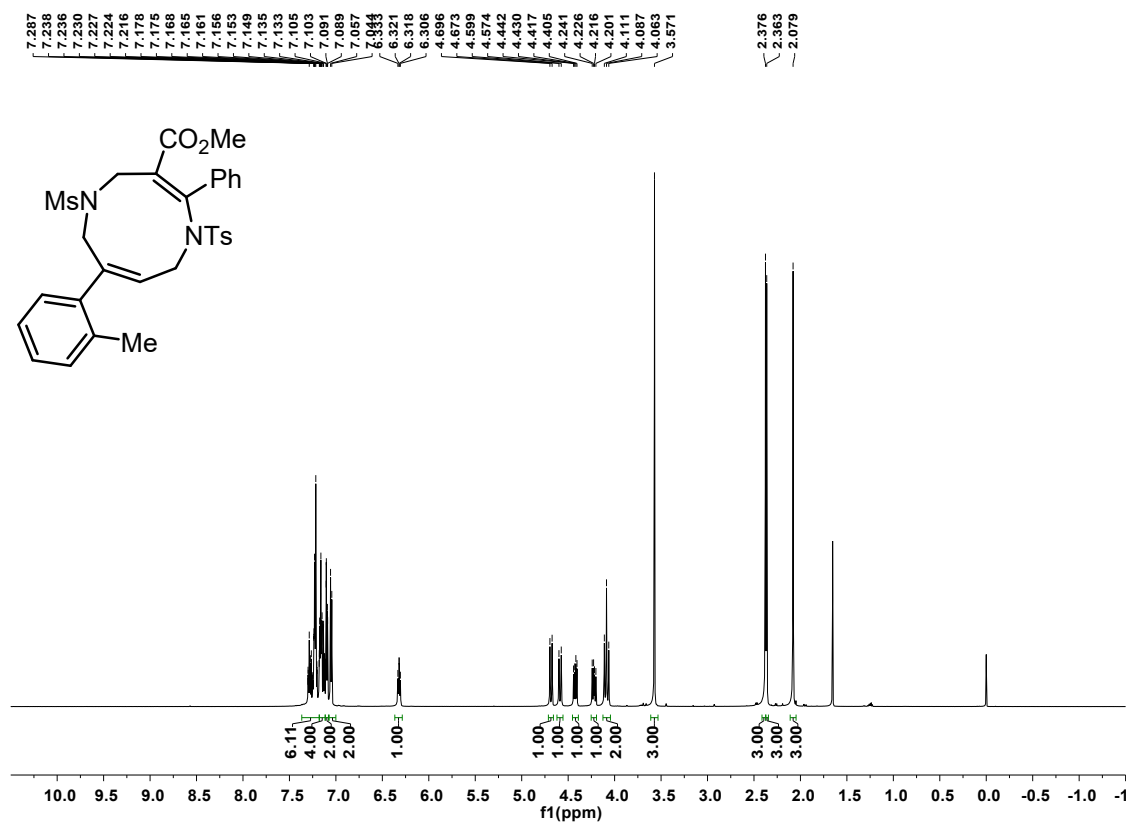
^1H NMR of **5d** in CDCl_3 (600 MHz)



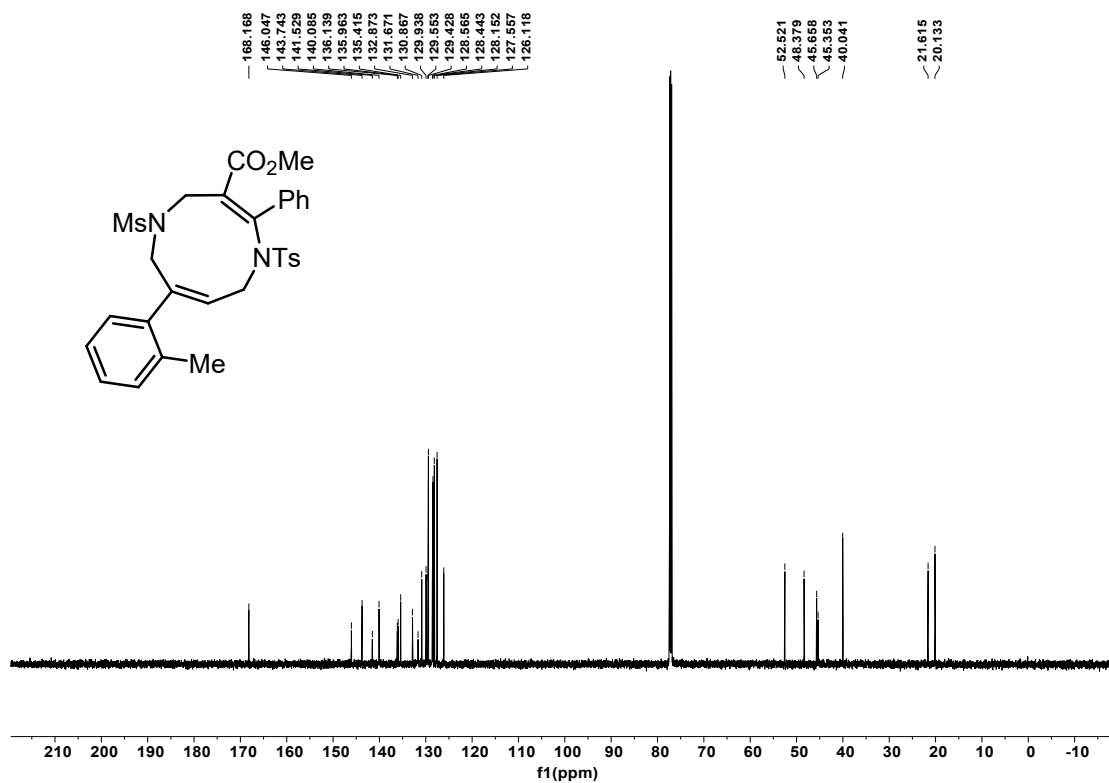
^{13}C NMR of **5d** in CDCl_3 (100 MHz)



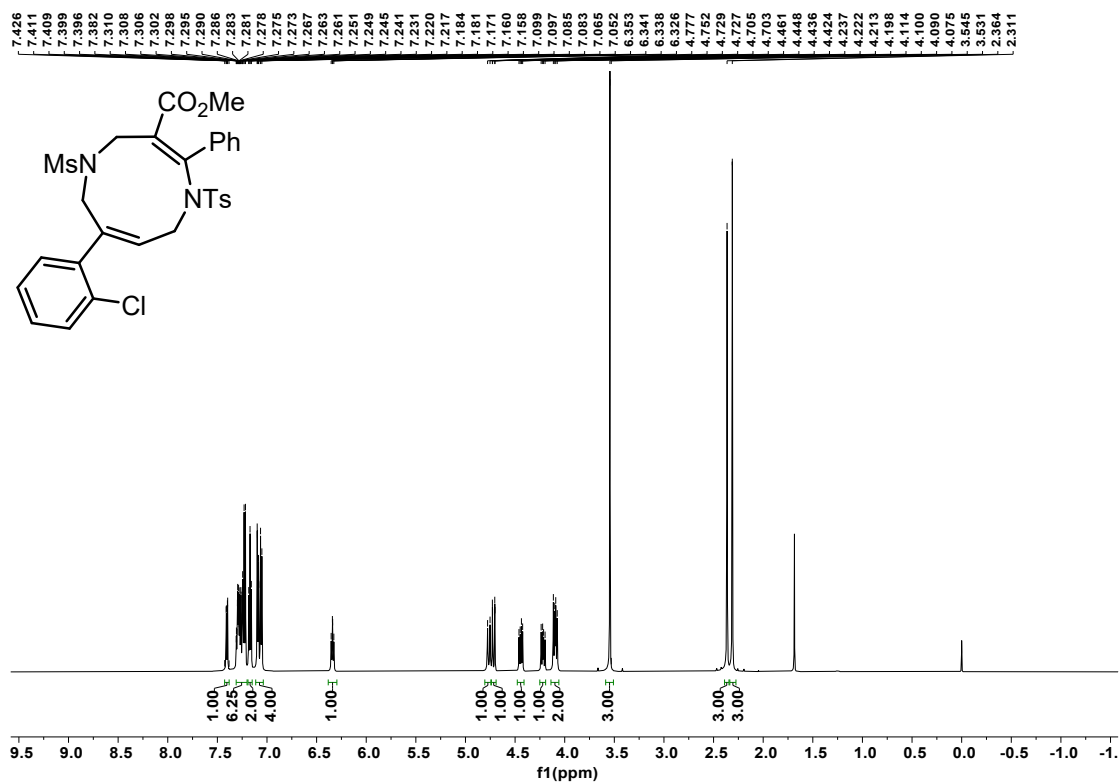
^1H NMR of **5f** in CDCl_3 (600 MHz)



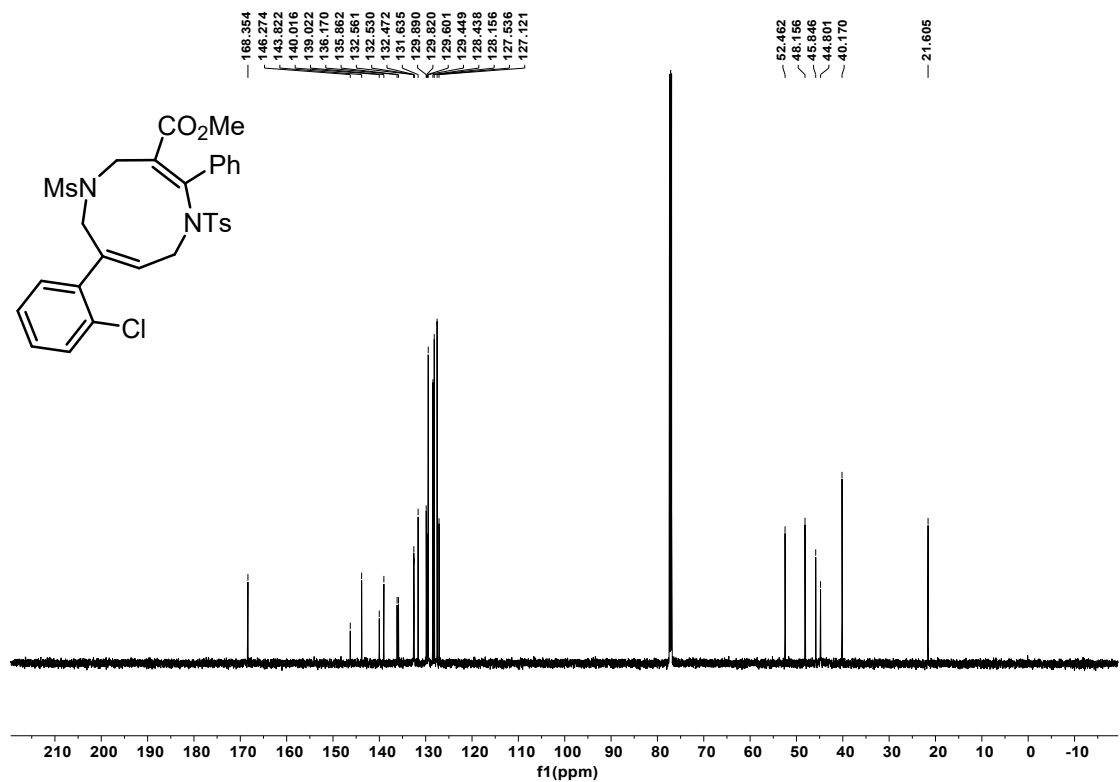
^{13}C NMR of **5f** in CDCl_3 (150 MHz)



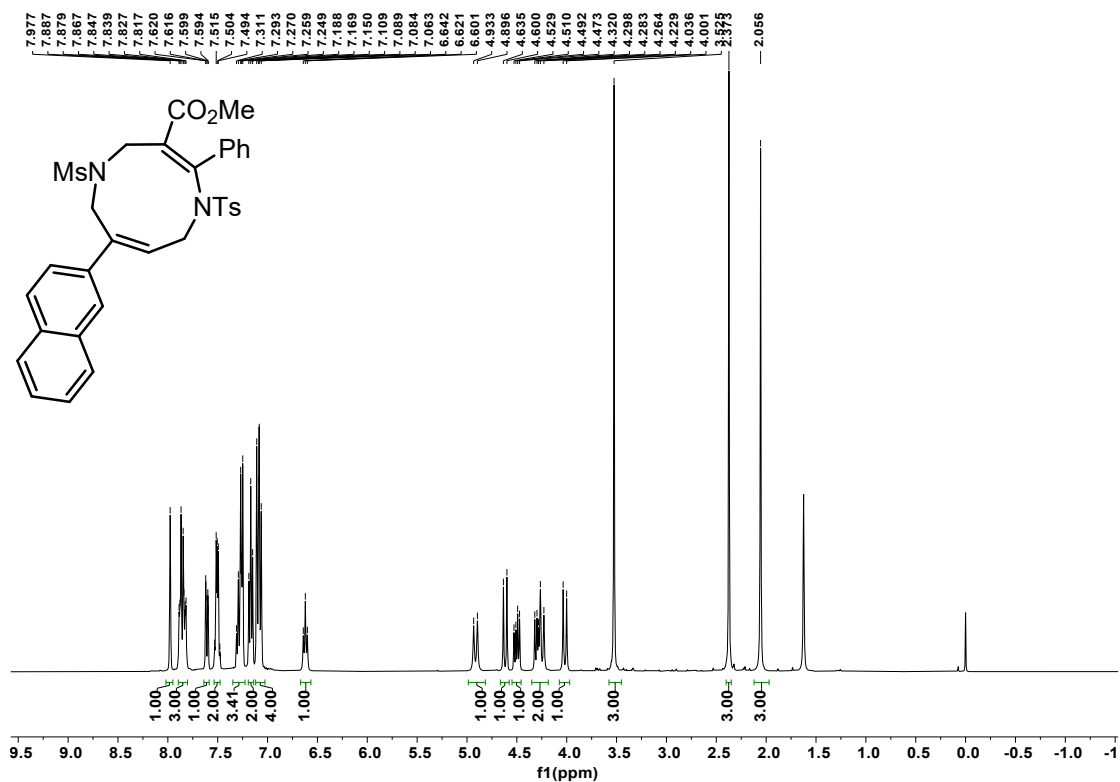
¹H NMR of **5g** in CDCl₃ (600 MHz)



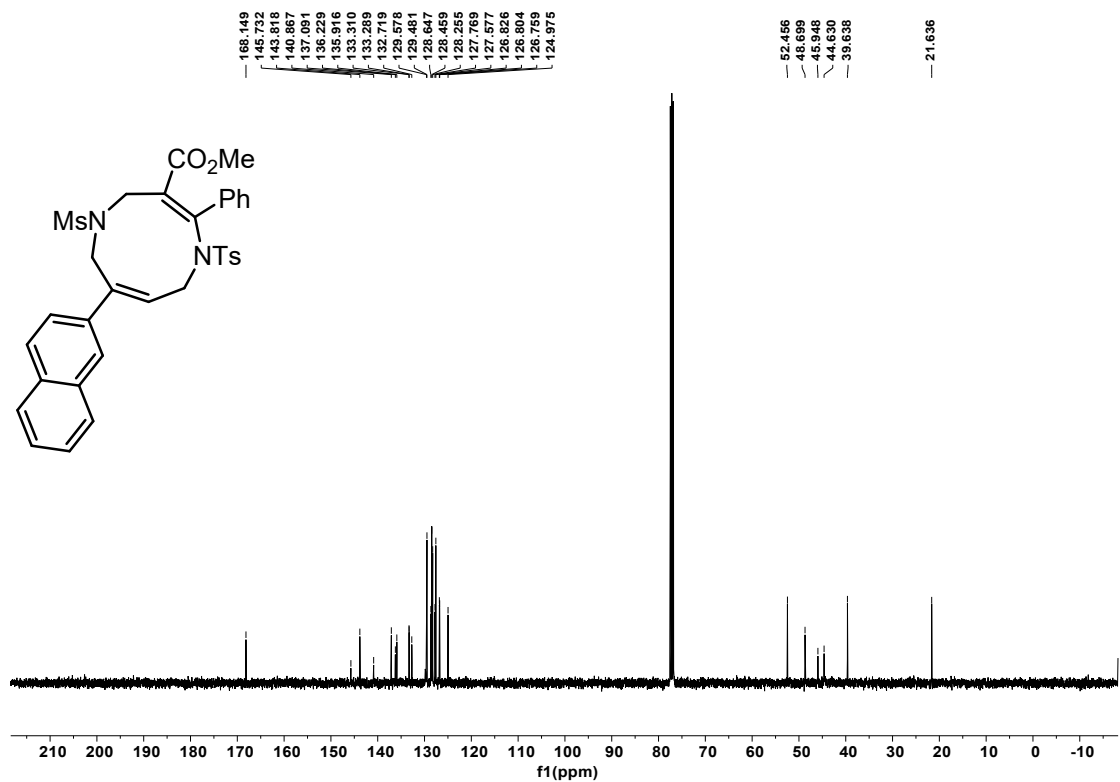
¹³C NMR of **5g** in CDCl₃ (150 MHz)



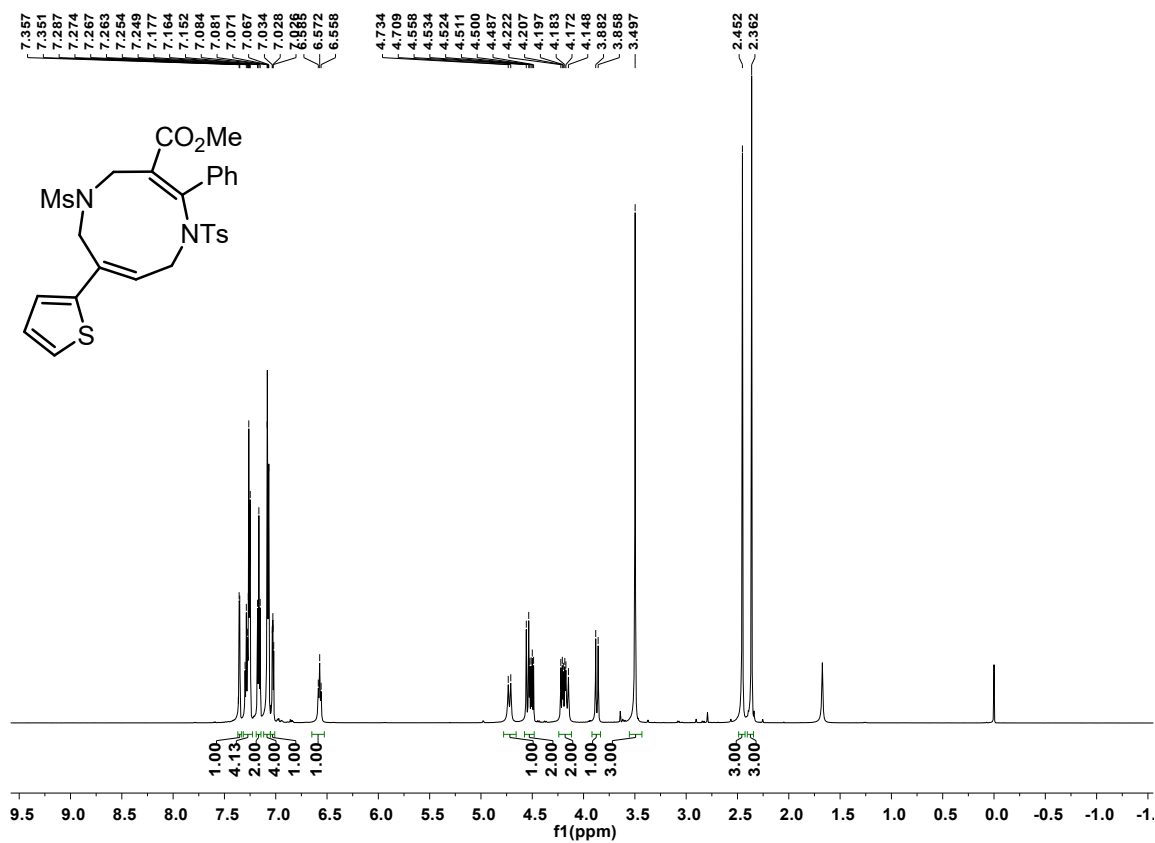
^1H NMR of **5h** in CDCl_3 (400 MHz)



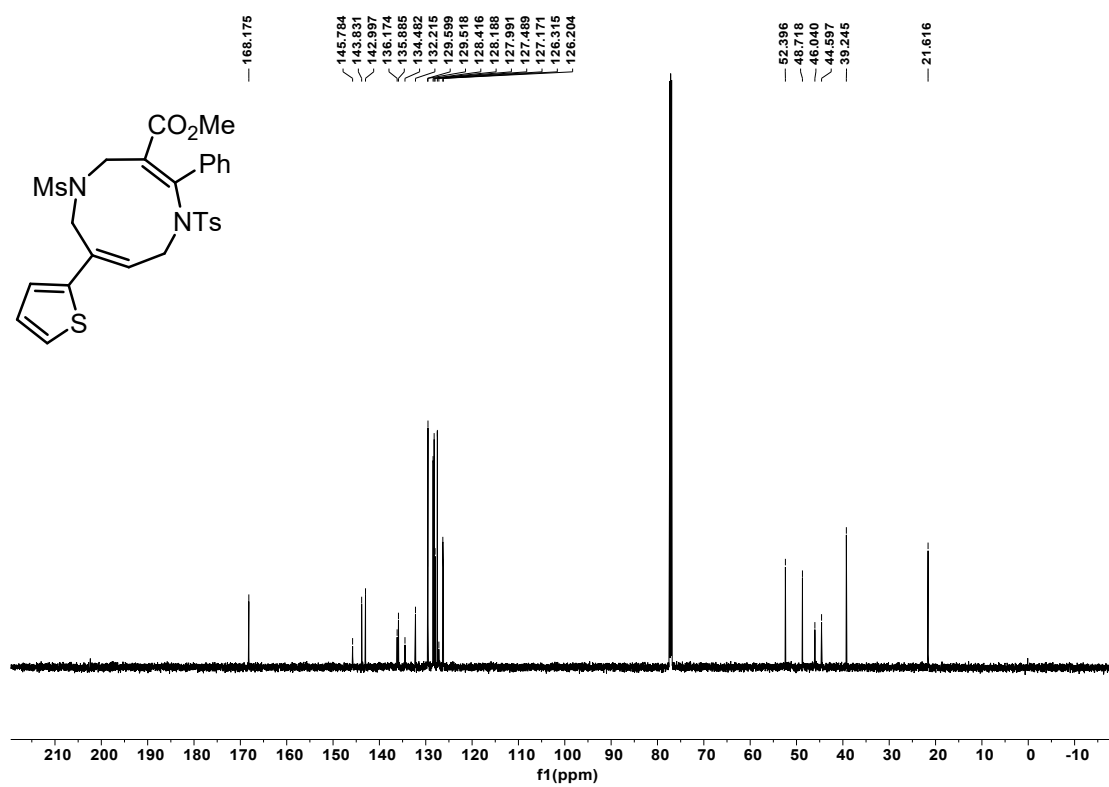
^{13}C NMR of **5h** in CDCl_3 (100 MHz)



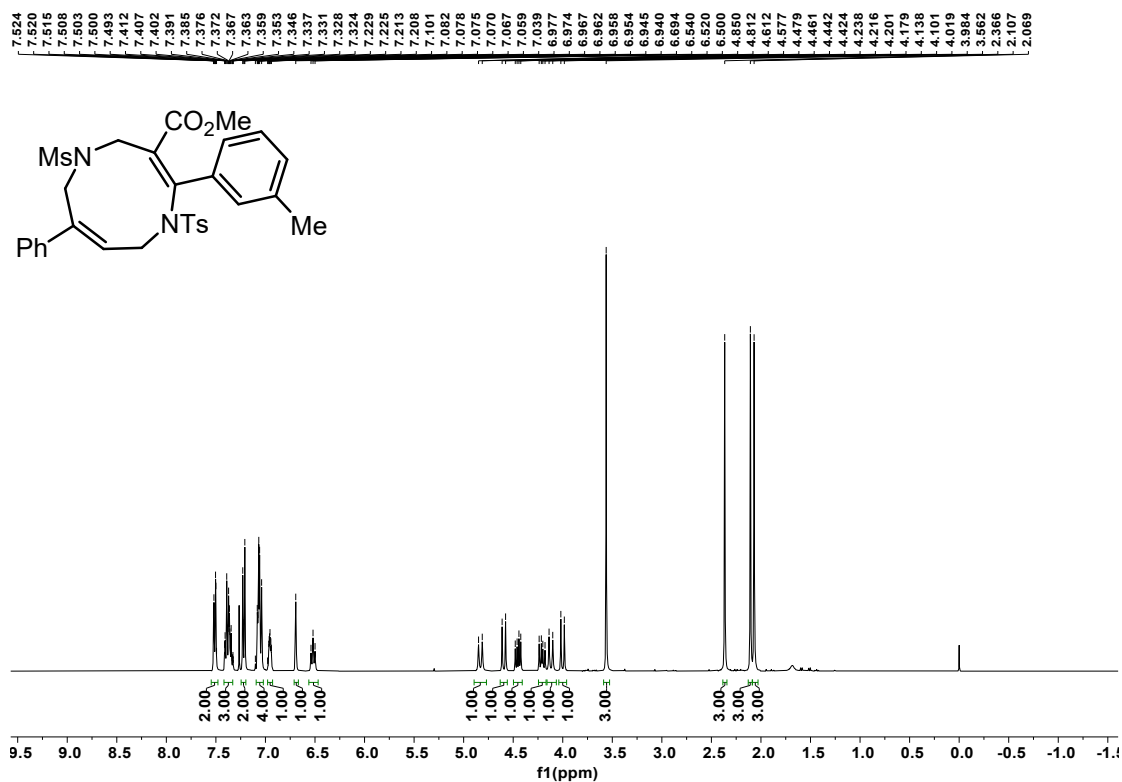
^1H NMR of **5i** in CDCl_3 (600 MHz)



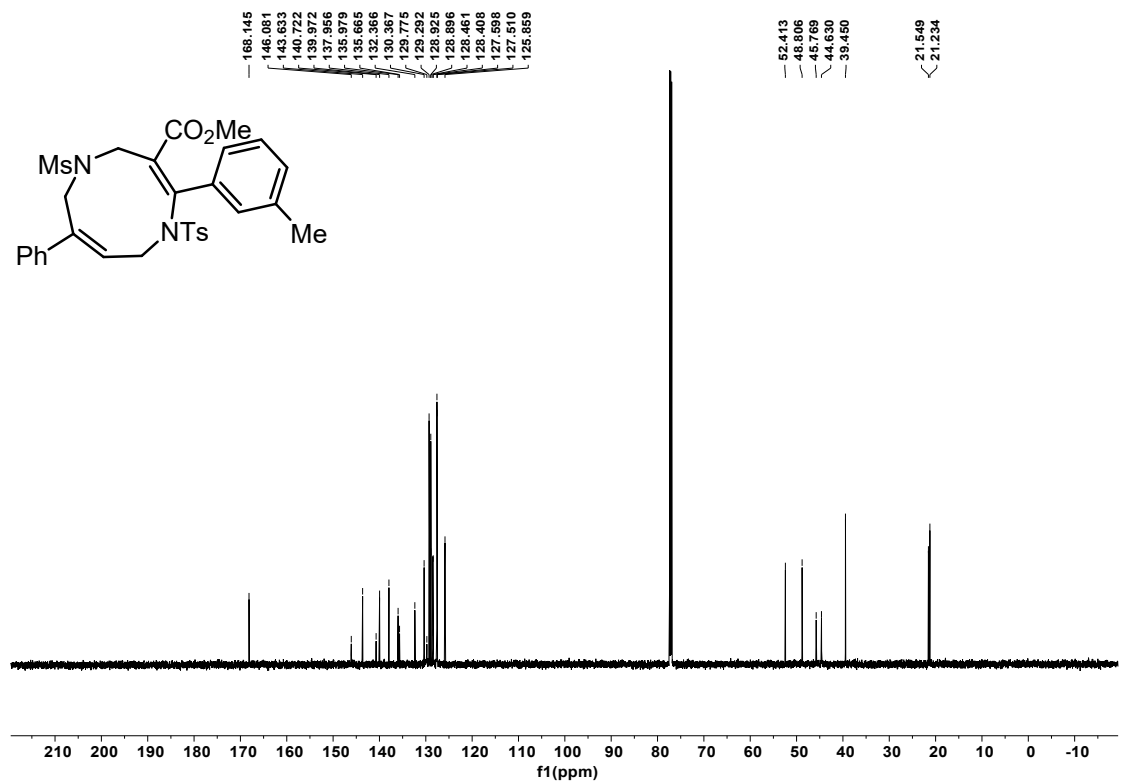
^{13}C NMR of **5i** in CDCl_3 (150 MHz)



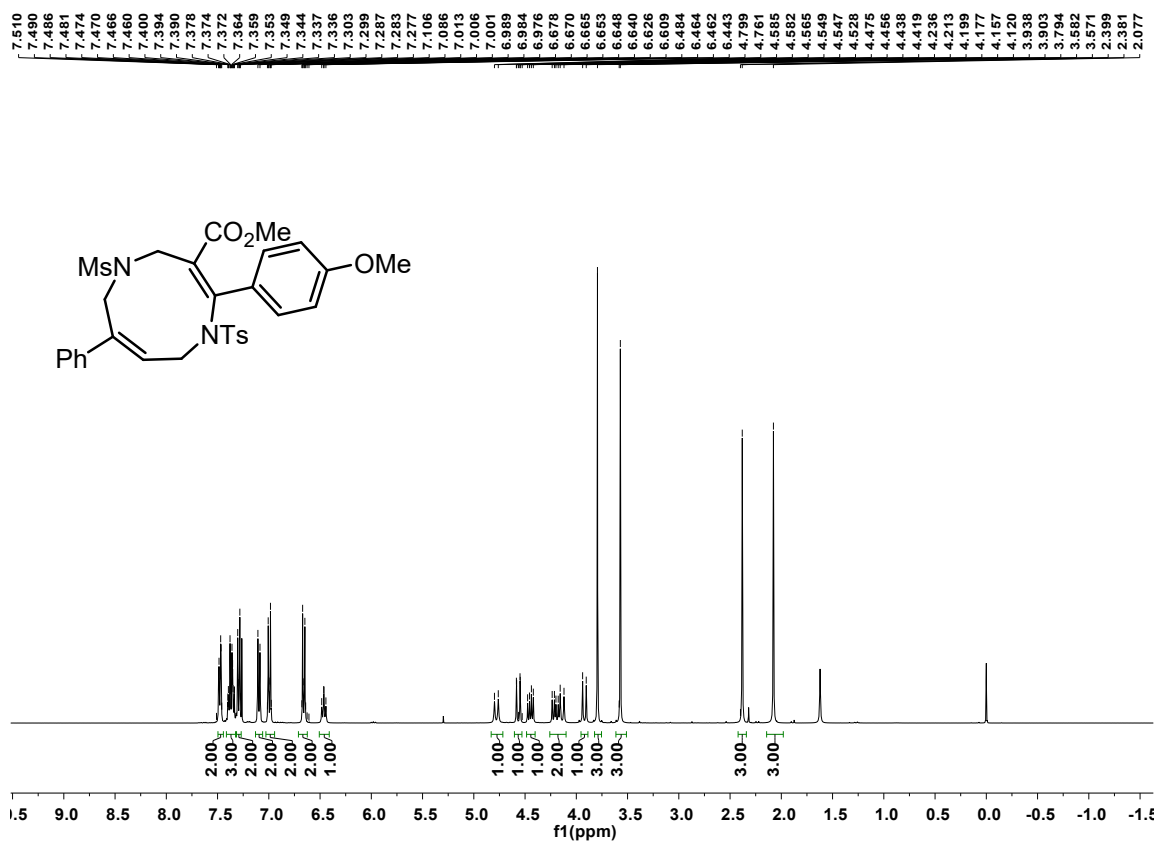
^1H NMR of **5j** in CDCl_3 (400 MHz)



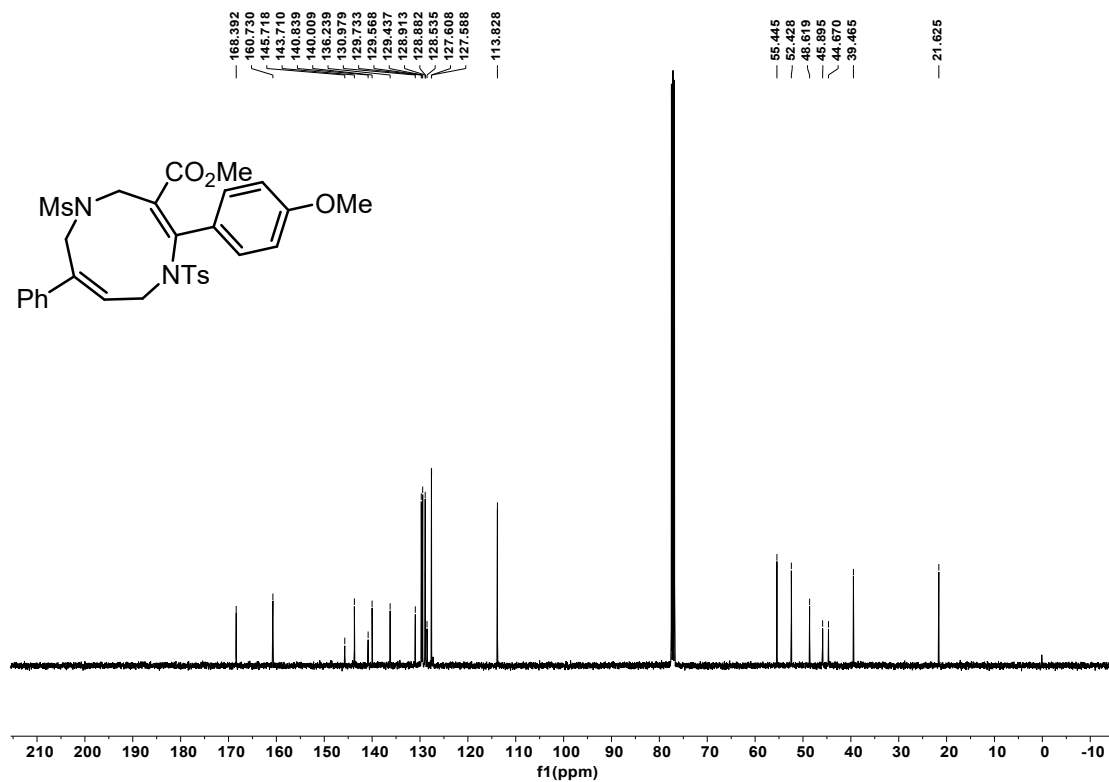
^{13}C NMR of **5j** in CDCl_3 (150 MHz)



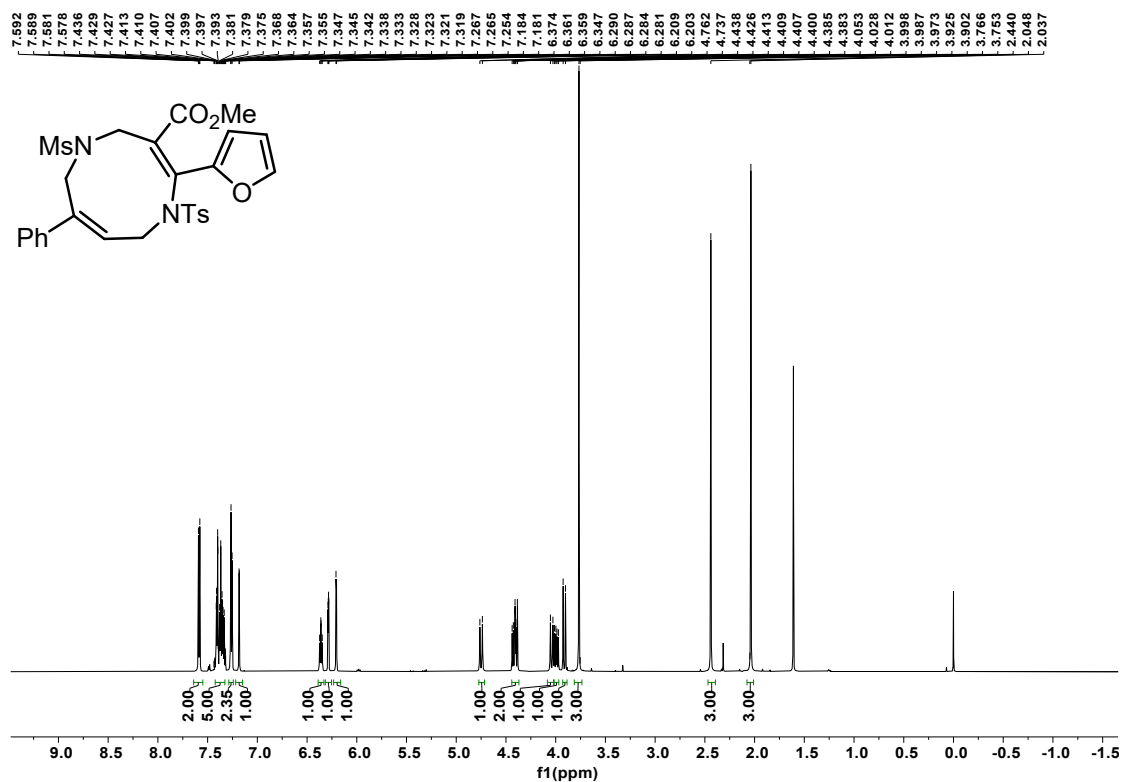
^1H NMR of **5k** in CDCl_3 (400 MHz)



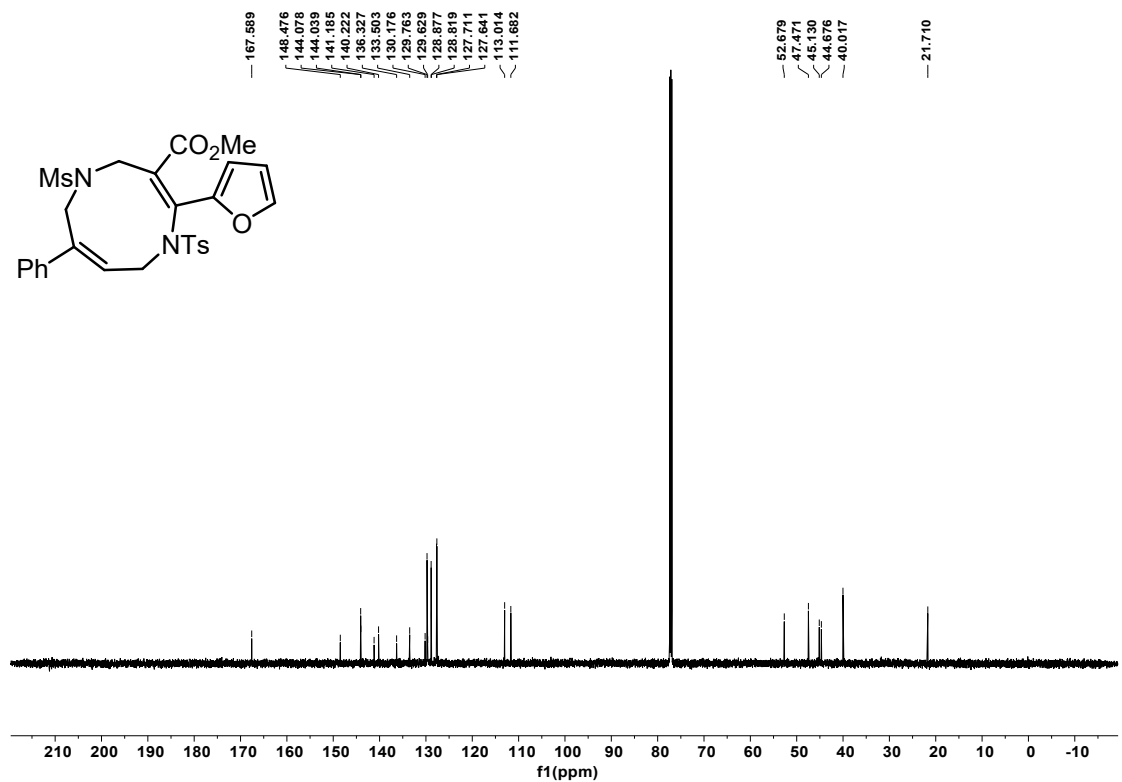
^{13}C NMR of **5k** in CDCl_3 (100 MHz)



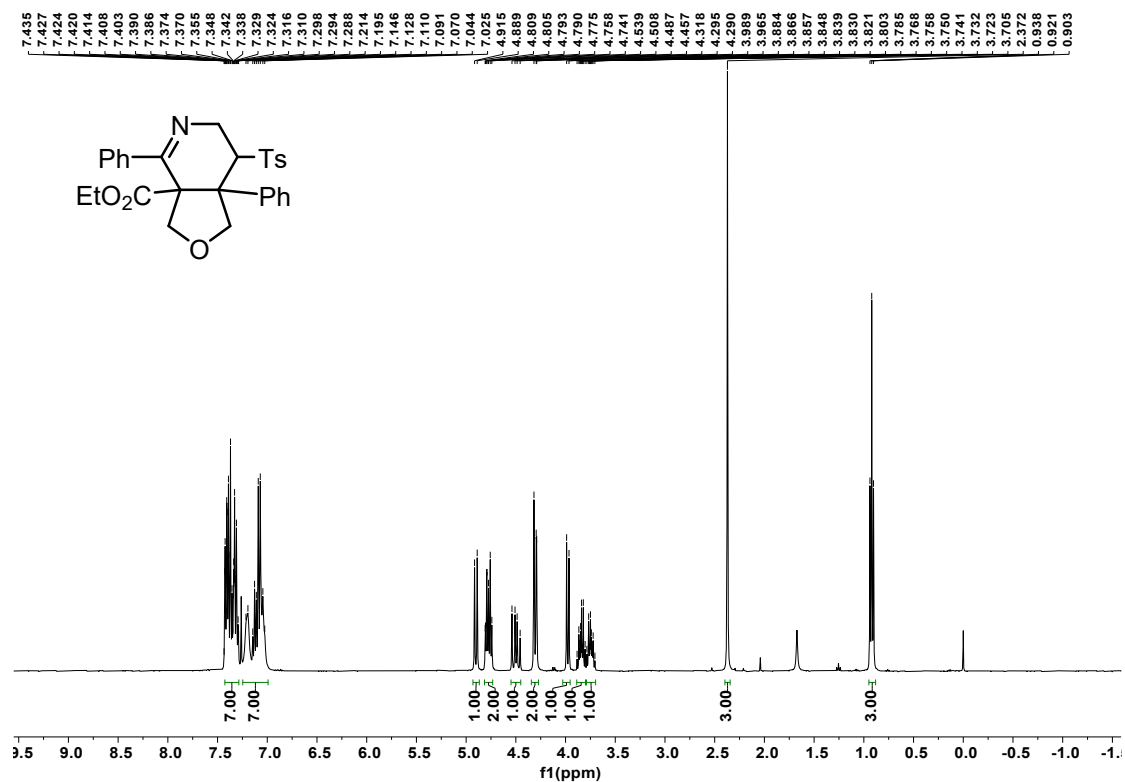
^1H NMR of **5I** in CDCl_3 (600 MHz)



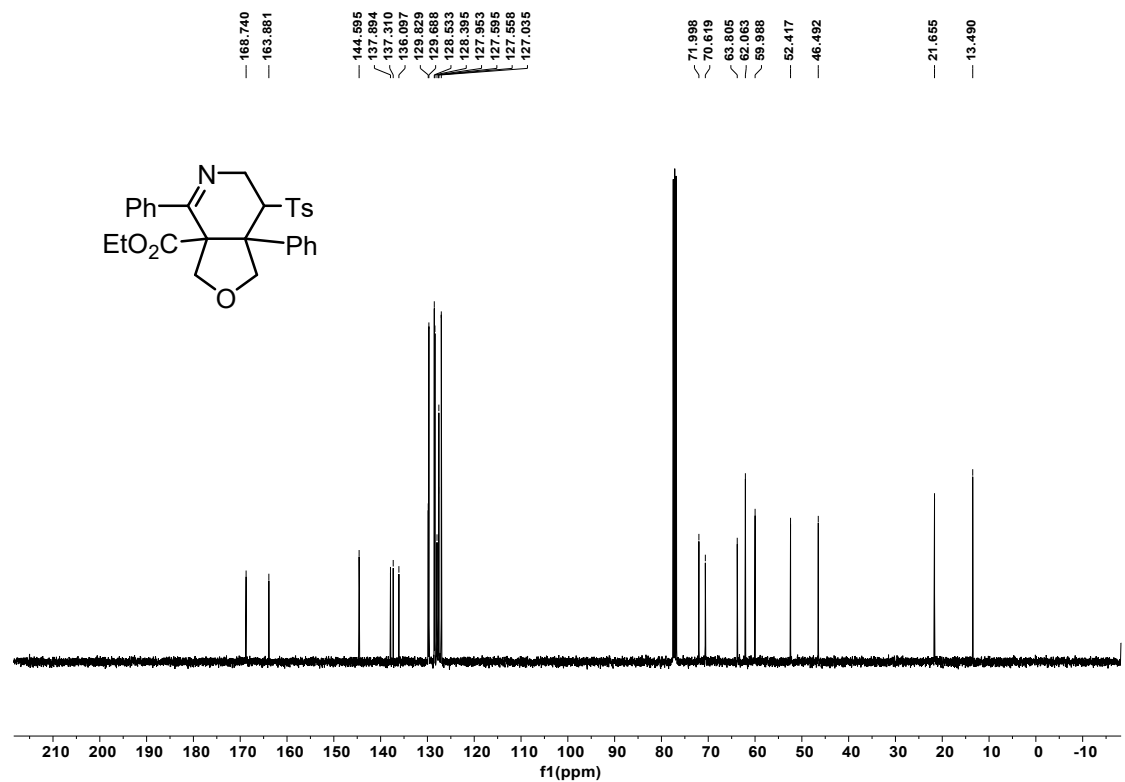
^{13}C NMR of **5I** in CDCl_3 (150 MHz)



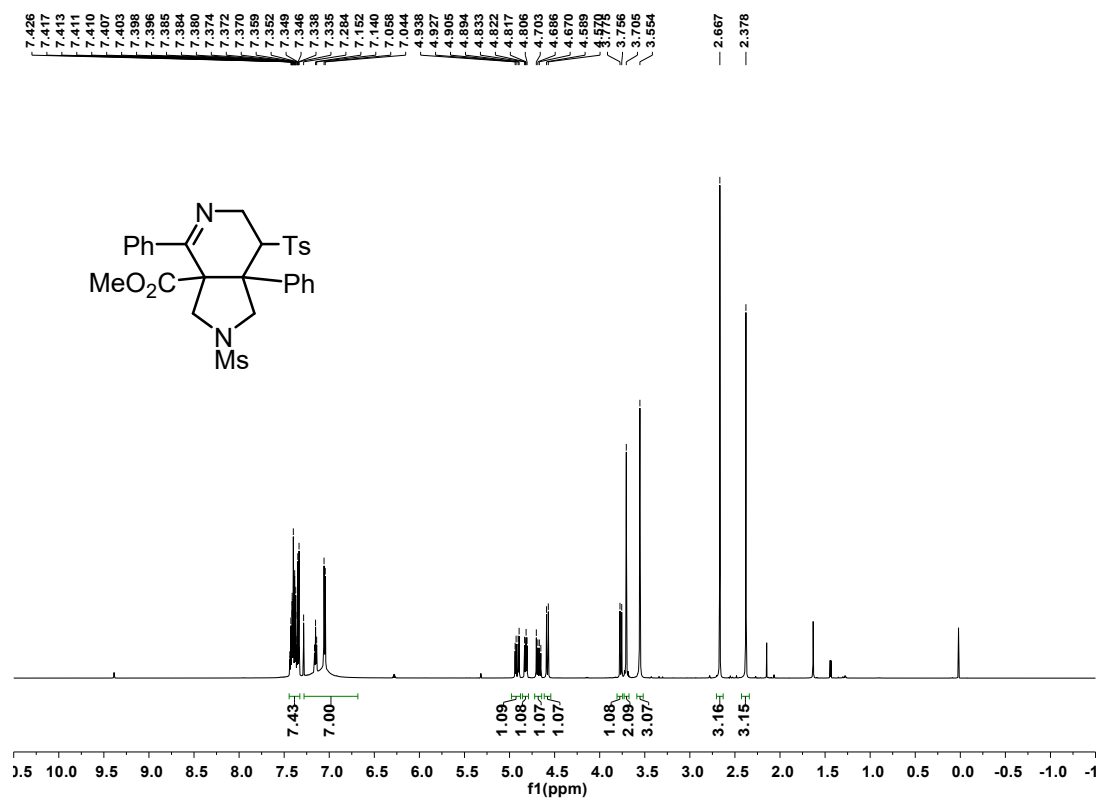
^1H NMR of **6a** in CDCl_3 (400 MHz)



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



^1H NMR of **6b** in CDCl_3 (600 MHz)



^{13}C NMR of **6b** in CDCl_3 (150 MHz)

