Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

The Access to Azonanes via Pd-Catalyzed Decarboxylative [5 + 4] Cycloaddition with Exclusive Regioselectivity

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Contents

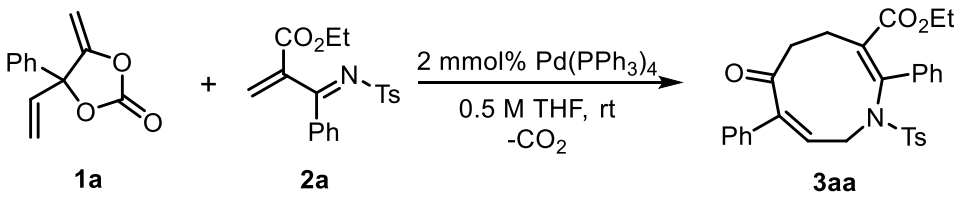
General comments

Commercially available reagents were purchased from Energy, J&K, Strem, Alfa Aesar or TCI, and used without further purification unless otherwise stated. The catalyst were purchased from Strem and were stored in fridge (<–20 °C). Solvents were purchased from Energy and used directly without further purification.

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra were measured on Bruker Avance 400MHz instrument and chemical shifts (δ) are reported in parts per million (ppm). Chemical shifts were reported in ppm on the δ scale relative to $CHCl_3$ (δ = 7.26 for ^{1}H NMR, δ = 77.16 for ^{13}C NMR). Coupling constants were reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Infrared spectra was collected on a bruker ALPHA II spectrometer. Absorption maxima (ν max) was reported in wavenumbers (cm^{-1}). High-resolution ESI mass spectra (HRMS) were determined on WATERS I-Class VION IMS Q Tof LC/MS. Single crystal X-ray diffraction analyses were collected at 100 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation.

All reactions were monitored by thin layer chromatography (TLC) and visualized by UV irradiation or stained with potassium permanganate or 20-30% ethanolic phosphomolybdicacid (PMA) followed by brief heating with a heating gun. Column chromatography was performed on silica gel (200-300 mesh) using a mixture of petroleum ether/ethyl acetate or petroleum ether/dichloromethane as the eluent. The substituted carbonates **1** and 1-azadiene **2** were prepared according to reported procedures.[1-2]

Typical reaction procedure for the formation of 3aa

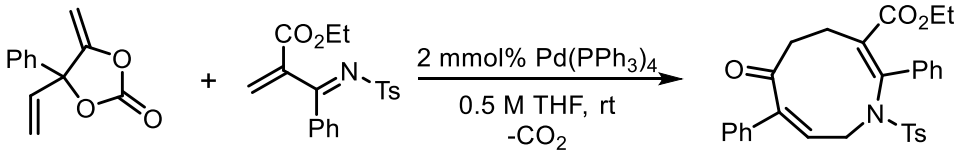


1a **2a** **3aa**

A screw-capped vial was charged with carbonate **1a** (20.2 mg, 0.1 mmol, 1.0 equiv), 1-azadiene **2a** (39.3 mg, 0.11 mmol, 1.1 equiv), and $Pd(PPh_3)_4$ (2.3 mg, 0.002 mmol, 2 mol%) in THF (0.2 mL). The reaction mixture was stirred at room temperature for 3 h. Upon the reaction was finished, the mixture was purified directly by flash chromatography on silica gel to afford the pure product **3aa** (PE:EA = 5:1, R_f = 0.31).

Gram-scale reaction and selective reduction of 3aa

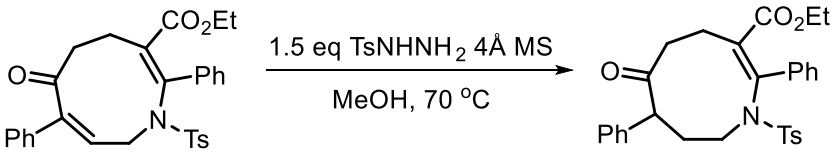
Gram-scale synthesis of 3aa:



3 mmol **1a** 3.3 mmol **2a** 1.26 g, 82% yield **3aa**

A 25 mL of round-bottom flask was charged with carbonate **1a** (606 mg, 3 mmol, 1.0 equiv), azadiene (1.17 mg, 3.3 mmol, 1.1 equiv), and $Pd(PPh_3)_4$ (70 mg, 0.06 mmol, 2 mol%) in THF (6 mL). The reaction mixture was stirred at room temperature. After full conversion was noted, the mixture was purified directly by flash chromatography (PE/EA = 5:1, R_f = 0.34) on silica gel to afford the product **3aa** (1.26 g, 82%) as a white solid.

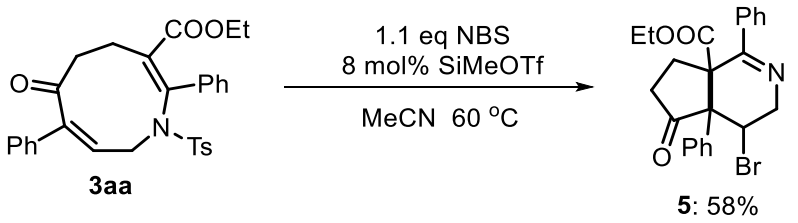
Selective reduction of 3aa:



3aa **4**: 43%

A screw-capped vial was charged with nine-membered *N*-heterocycle **3aa** (51.5 mg, 0.1 mmol, 1.0 equiv), $TsNHNH_2$ (27.9 mg, 0.15 mmol, 1.5 equiv) and 4 Å Molecular sieves (100 mg) in MeOH (2.0 mL). The reaction mixture was stirred at 70 ℃ for 10 h. Upon full conversion was noted, the mixture was purified directly by flash

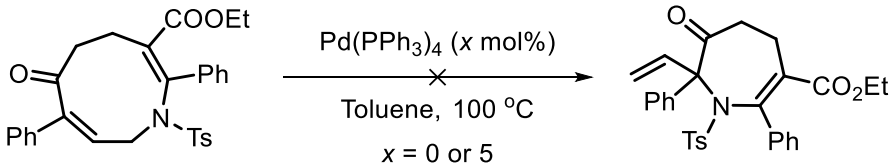
chromatography (PE/EA = 5:1, R_f = 0.43) on silica gel to afford the product **4** as a yellow oil.



3aa **5**: 58%

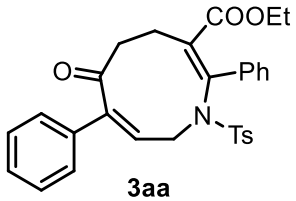
A 1 mL screw-capped vial was charged with nine-membered azonane **3aa** (51.5 mg, 0.1 mmol, 1.0 equiv), SiMeOTf (1.8 mg, 8 mol%) and NBS (19.6 mg, 0.11 mmol, 1.1 equiv) in MeCN (2.0 mL). The reaction mixture was stirred at 60 ℃ for 28 h. After full conversion was noted, the mixture was purified by flash chromatography (PE/EA) on silica gel to afford the product **5** (PE : EA = 5 : 1, R_f = 0.47) as a white solid.

Control experiment:



3aa **3aa'**: y%
x = 0, y = 0
x = 5, y = 0

Characterization data of all the new products

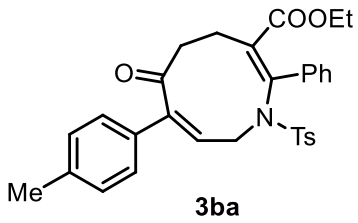


3aa

Ethyl(2*E*,7*Z*)-6-oxo-2,7-diphenyl-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3aa)

The title compound was prepared according to the standard procedure and isolated as a white solid (48.0 mg, 92%), m.p. = 161.9-163.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.6 Hz, 2H), 7.31-7.09 (m, 12H), 6.01 (t, *J* = 8.0 Hz, 1H), 4.25 (dd, *J* = 13.7, 7.2 Hz, 1H), 3.96 (dd, *J* = 13.3, 9.5 Hz, 1H), 3.77-3.58 (m, 2H), 2.76-2.64 (m, 1H), 2.56 (t, *J* = 13.7 Hz, 1H), 2.51-2.42 (m, 1H), 2.35 (s, 3H), 2.33-2.24 (m, 1H), 0.59 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, one carbon signal was overlapped) δ 208.4, 169.1, 149.7, 144.1, 138.4, 135.8, 134.0, 133.0, 129.7, 129.2, 129.1, 129.0 , 128.7 , 128.2 , 127.6 , 126.5 , 120.6, 61.1, 48.8, 41.0, 27.6, 21.7, 13.4. HRMS (ESI) m/z:

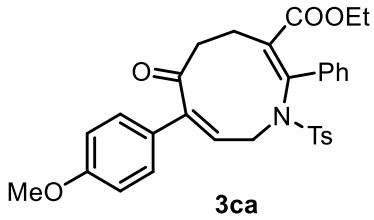
$(M+H)^+$ calcd. for $C_{30}H_{30}NO_5S$ 516.1845, found: 516.1847. IR ν_{max}/cm^{-1} 3058, 3029, 2980, 2931, 1701, 1597, 1350, 1297, 1161, 1091, 799, 766.



3ba

Ethyl(2*E*,7*Z*)-6-oxo-2-phenyl-7-(*p*-tolyl)-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3ba)

The title compound was prepared according to the standard procedure and isolated as a white solid (39.7 mg, 75%), m.p. = 166.9-168.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.28 – 7.23 (m, 2H), 7.22 – 7.16 (m, 4H), 7.16 – 7.07 (m, 4H), 6.04 (t, *J* = 8.2 Hz, 1H), 4.31 (dd, *J* = 13.8, 7.4 Hz, 1H), 4.03 (dd, *J* = 13.8, 9.2 Hz, 1H), 3.82 – 3.67 (m, 2H), 2.82 – 2.71 (m, 1H), 2.68 – 2.48 (m, 2H), 2.41 (s, 3H), 2.39 – 2.33 (m, 1H), 2.33 (d, *J* = 7.1 Hz, 3H), 0.66 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.6, 169.1, 149.6, 144.2, 144.1, 139.3, 138.4, 135.8, 133.0, 131.1, 129.7 , 129.7 , 129.1, 128.7 , 128.2 , 127.6 , 126.4 , 119.7, 61.0, 48.9, 41.0, 27.6, 21.7, 21.4, 13.4. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{31}H_{32}NO_5S$ 530.2001, found: 530.2001. IR ν_{max}/cm^{-1} 3055, 3028, 2980, 2924, 1701, 1598, 1350, 1239, 1161, 1091, 1040, 815, 767.

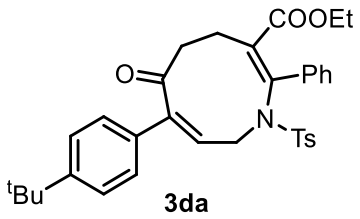


3ca

Ethyl(2*E*,7*Z*)-7-(4-methoxyphenyl)-6-oxo-2-phenyl-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3ca)

The title compound was prepared according to the standard procedure and isolated as a white solid (42.0 mg, 77%), m.p. = 135.8-137.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.31 (m, 1H), 7.29 – 7.24 (m, 2H), 7.24 – 7.13 (m, 6H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.98 (t, *J* = 8.3 Hz, 1H), 4.32 (dd, *J* = 13.7, 7.3 Hz, 1H), 4.01 (dd, *J* = 13.7, 9.4 Hz, 1H), 3.78 (s, 3H), 3.77 – 3.69 (m, 2H), 2.83 – 2.71 (m, 1H), 2.64 – 2.50 (m, 2H), 2.41 (s, 3H), 2.40 – 2.30 (m, 1H), 0.66 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.6, 169.0, 160.5, 149.3, 144.0, 138.5, 135.9, 132.9, 129.7 , 129.0, 128.7 , 128.2 , 127.9 , 127.6 , 126.8, 126.4, 118.6, 114.3 , 61.0, 55.4, 48.9, 41.0, 27.6, 21.7, 13.4. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{31}H_{32}NO_6S$ 546.1950, found:

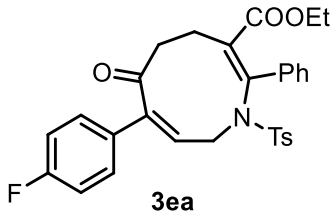
546.1948. IR ν_{max}/cm^{-1} 3059, 3030, 2979, 2959, 2934, 2839, 1699, 1603, 1494, 1349, 1251, 1160, 1090, 1033, 852, 766.



3da

Ethyl(2*E*,7*Z*)-7-(4-(tert-butyl)phenyl)-6-oxo-2-phenyl-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3da)

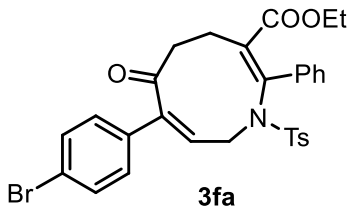
The title compound was prepared according to the standard procedure and isolated as a white solid (46.3 mg, 81%), m.p. = 173.5-176.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.2 Hz, 2H), 7.36-7.29 (m, 3H), 7.28-7.15 (m, 8H), 6.05 (t, 1H), 4.31 (dd, *J* = 13.8, 7.3 Hz, 1H), 4.03 (dd, *J* = 13.8, 9.2 Hz, 1H), 3.84-3.59 (m, 2H), 2.80-2.71 (m, 1H), 2.67-2.51 (m, 2H), 2.47-2.32 (m, 4H), 1.28 (s, 9H), 0.65 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, one carbon signal was overlapped) δ 208.5, 169.1, 152.4, 149.6, 144.1, 138.4, 135.9, 133.1, 131.0, 129.7 , 129.1, 128.7 , 128.2 , 127.6 , 126.2 , 125.9 , 119.5, 61.0, 48.9, 41.0, 34.8, 31.3, 27.6, 21.7, 13.3. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{34}H_{38}NO_5S$ 572.2471, found: 572.2474. IR ν_{max}/cm^{-1} 3059, 3031, 2962, 2905, 2869, 1698, 1598, 1350, 1298, 1160, 1090, 1040, 853, 765.



3ea

Ethyl(2*E*,7*Z*)-7-(4-fluorophenyl)-6-oxo-2-phenyl-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3ea)

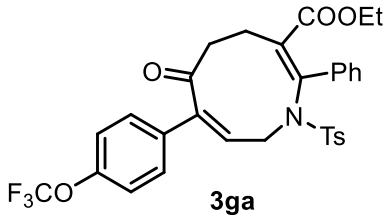
The title compound was prepared according to the standard procedure and isolated as a white solid (45.4 mg, 85%), m.p. = 145.2-148.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.9 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.29-7.16 (m, 8H), 7.00 (t, *J* = 8.5 Hz, 2H), 6.02 (t, *J* = 8.2 Hz, 1H), 4.32 (dd, *J* = 13.8, 7.3 Hz, 1H), 4.01 (dd, *J* = 13.7, 9.3 Hz, 1H), 3.86-3.65 (m, 2H), 2.84-2.72 (m, 1H), 2.66-2.50 (m, 2H), 2.41 (s, 3H), 2.40-2.32 (m, 1H), 0.68 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.0, 169.0, 163.4 (d, *J* = 249.5 Hz), 148.7, 144.1, 144.0, 138.3, 135.8, 132.8, 130.1 (d, *J* = 3.3 Hz), 129.7, 129.2, 128.7, 128.4 (d, *J* = 8.3 Hz), 128.2, 127.6, 120.6, 116.0 (d, *J* = 21.8 Hz), 61.1, 48.7, 40.9, 27.5, 21.7, 13.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.91. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{30}H_{29}FNO_5S$ 534.1750, found: 534.1751. IR ν_{max}/cm^{-1} 3060, 3029, 2981, 2928, 1699, 1599, 1509, 1349, 1298, 1160, 1041, 961, 834, 766, 681.



3fa

Ethyl(2*E*,7*Z*)-7-(4-bromophenyl)-6-oxo-2-phenyl-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3fa)

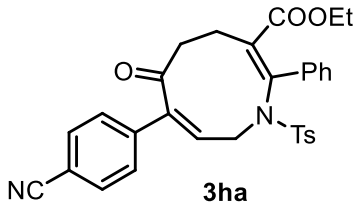
The title compound was prepared according to the standard procedure and isolated as a white solid (54.7 mg, 92%), m.p. = 168.1-170.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.39 (m, 4H), 7.34-7.29 (m, 1H), 7.28-7.24 (m, 2H), 7.21-7.15 (m, 4H), 7.14-7.09 (m, 2H), 6.08 (dd, *J* = 9.0, 7.5 Hz, 1H), 4.30 (dd, *J* = 13.9, 7.3 Hz, 1H), 4.01 (dd, *J* = 13.8, 9.2 Hz, 1H), 3.83-3.68 (m, 2H), 2.84-2.73 (m, 1H), 2.69-2.58 (m, 1H), 2.58-2.49 (m, 1H), 2.41 (s, 3H), 2.39-2.32 (m, 1H), 0.68 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.8, 168.9, 148.5, 144.1, 144.1, 138.1, 135.6, 132.9, 132.8, 132.1, 129.7, 129.1, 128.6, 128.2, 128.1, 127.5, 123.5, 121.4, 61.1, 48.6, 40.9, 27.4, 21.7, 13.4. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{30}H_{29}BrNO_5S$ 594.0950, found: 594.0939. IR ν_{max}/cm^{-1} 3062, 3025, 2981, 2928, 2871, 1719, 1595, 1490, 1446, 1351, 1160, 1091, 1009, 814, 753.



3ga

Ethyl(2*E*,7*Z*)-6-oxo-2-phenyl-1-tosyl-7-(4-(trifluoromethoxy)phenyl)-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3ga)

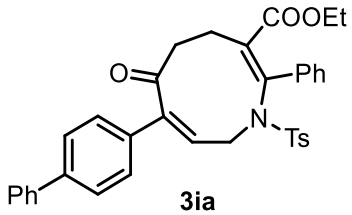
The title compound was prepared according to the standard procedure and isolated as a white solid (56.4 mg, 94%), m.p. = 163.4-166.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.9 Hz, 2H), 7.40 – 7.27 (m, 5H), 7.25 – 7.14 (m, 6H), 6.09 (t, *J* = 8.2 Hz, 1H), 4.35 (dd, *J* = 13.8, 7.2 Hz, 1H), 4.03 (dd, *J* = 13.8, 9.3 Hz, 1H), 3.87 – 3.69 (m, 2H), 2.86 – 2.74 (m, 1H), 2.70 – 2.53 (m, 2H), 2.44 (s, 3H), 2.42 – 2.34 (m, 1H), 0.70 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 207.8, 169.0, 149.9, 148.4, 144.2, 144.0, 138.2, 135.7, 132.8, 132.7, 129.8, 129.2, 128.7, 128.3, 128.1, 127.6, 121.8 (q, *J* = 257 Hz), 121.6, 121.4, 61.1, 48.6, 40.9, 27.5, 21.7, 13.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.87. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{31}H_{29}F_3NO_6S$ 600.1668, found: 600.1663. IR ν_{max}/cm^{-1} 3065, 3030, 2982, 2929, 1703, 1598, 1352, 1255, 1211, 1160, 1091, 920, 852, 755.



3ha

Ethyl(2*E*,7*Z*)-7-(4-cyanophenyl)-6-oxo-2-phenyl-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3ha)

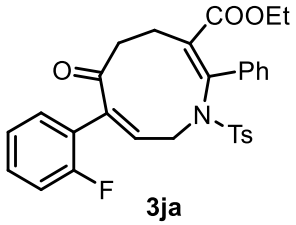
The title compound was prepared according to the standard procedure and isolated as a white solid (36.8 mg, 68%), m.p. = 170.3-173.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.43-7.32 (m, 5H), 7.29-7.25 (m, 2H), 7.18 (dd, *J* = 13.8, 7.8 Hz, 4H), 6.19 (t, 1H), 4.31 (dd, *J* = 14.0, 7.3 Hz, 1H), 4.04 (dd, *J* = 14.0, 9.0 Hz, 1H), 3.85-3.66 (m, 2H), 2.89-2.76 (m, 1H), 2.69 (t, *J* = 13.0 Hz, 1H), 2.61-2.52 (m, 1H), 2.42 (s, 3H), 2.40-2.32 (m, 1H), 0.70 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.2, 168.8, 147.8, 144.3, 144.2, 138.5, 137.9, 135.5, 132.8, 132.8, 129.8, 129.3, 128.7, 128.3, 127.6, 127.2, 124.2, 118.4, 112.9, 61.2, 48.4, 41.2, 27.5, 21.7, 13.5. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{31}H_{29}N_2O_5S$ 541.1797, found: 547.1790. IR ν_{max}/cm^{-1} 3063, 3025, 2981, 2927, 2856, 2229, 1724, 1599, 1447, 1339, 1160, 1090, 1017, 912, 834.



3ia

Ethyl(2*E*,7*Z*)-7-([1,1'-biphenyl]-4-yl)-6-oxo-2-phenyl-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3ia)

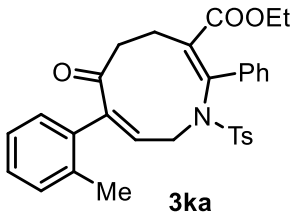
The title compound was prepared according to the standard procedure and isolated as a white solid (53.8 mg, 91%), m.p. = 164.9-166.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.49 (m, 4H), 7.48-7.38 (m, 4H), 7.38-7.29 (m, 4H), 7.27-7.24 (m, 2H), 7.24-7.15 (m, 4H), 6.14 (dd, *J* = 8.9, 7.6 Hz, 1H), 4.34 (dd, *J* = 13.8, 7.4 Hz, 1H), 4.06 (dd, *J* = 13.8, 9.2 Hz, 1H), 3.87-3.65 (m, 2H), 2.88-2.74 (m, 1H), 2.73-2.53 (m, 2H), 2.42 (s, 4H), 0.67 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, one carbon signal was overlapped) δ 208.4, 169.0, 149.3, 144.2, 144.1, 142.0, 140.2, 138.3, 135.8, 133.0, 132.8, 129.7, 129.1, 129.0, 128.7, 128.2, 127.9, 127.6, 127.1, 126.9, 120.5, 61.1, 48.8, 41.1, 27.6, 21.7, 13.4. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{36}H_{34}NO_5S$ 592.2158, found: 592.2160. IR ν_{max}/cm^{-1} 3059, 3030, 2980, 2927, 1699, 1598, 1488, 1446, 1349, 1158, 1089, 1038, 909, 835.



3ja

Ethyl(2*E*,7*Z*)-7-(2-fluorophenyl)-6-oxo-2-phenyl-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3ja)

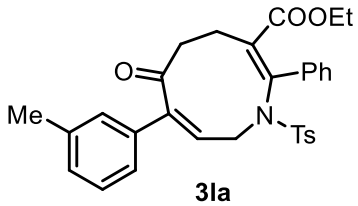
The title compound was prepared according to the standard procedure and isolated as a white solid (48.0 mg, 90%), m.p. = 148.3-152.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.1 Hz, 3H), 7.24-7.11 (m, 7H), 7.07-7.01 (m, 1H), 6.28 (t, *J* = 8.0 Hz, 1H), 4.27 (dd, *J* = 14.1, 7.6 Hz, 1H), 4.07 (dd, *J* = 14.1, 8.5 Hz, 1H), 3.83-3.69 (m, 2H), 2.86-2.70 (m, 2H), 2.64-2.56 (m, 1H), 2.55-2.46 (m, 1H), 2.41 (s, 3H), 0.68 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.1, 169.1, 160.1 (d, *J* = 250.7 Hz), 144.6, 144.1, 143.9, 137.8, 135.7, 133.5, 130.9 (d, *J* = 8.5 Hz), 129.7, 129.5 (d, *J* = 3.1 Hz), 129.1, 128.8, 128.1, 127.7, 125.3 (d, *J* = 4.0 Hz), 124.8 (d, *J* = 3.5 Hz), 122.8 (d, *J* = 13.0 Hz), 116.4 (d, *J* = 22.2 Hz), 61.0, 48.4, 40.7, 27.9, 21.7, 13.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.49. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{30}H_{29}NO_5FS$ 534.1750, found: 534.1746. IR ν_{max}/cm^{-1} 3062, 3032, 2980, 2927, 1704, 1598, 1489, 1448, 1349, 1293, 1159, 1091, 1034, 1019, 913, 913, 764.



3ka

Ethyl(2*E*,7*Z*)-7-(2-fluorophenyl)-6-oxo-2-phenyl-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3ka)

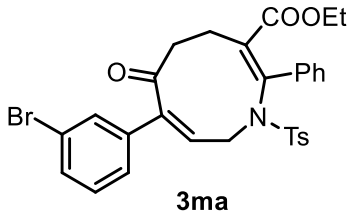
The title compound was prepared according to the standard procedure and isolated as a white solid (33.3 mg, 63%), m.p. = 142.3-145.1 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.5 Hz, 4H), 7.25-7.15 (m, 5H), 7.12 (t, *J* = 8.1 Hz, 4H), 6.00 (t, *J* = 8.0 Hz, 1H), 4.25 (dd, *J* = 14.3, 8.0 Hz, 1H), 4.10 (dd, *J* = 14.3, 8.1 Hz, 1H), 3.97-3.78 (m, 2H), 3.03 (t, *J* = 13.1 Hz, 1H), 2.94-2.80 (m, 1H), 2.57-2.47 (m, 1H), 2.39 (s, 3H), 2.38-2.35 (m, 1H), 2.33 (s, 3H), 0.79 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.7, 169.0, 150.2, 145.5, 143.8, 137.8, 136.9, 135.9, 135.0, 134.0, 131.0, 129.6, 129.4, 129.0, 128.9, 128.8, 128.1, 127.7, 126.3, 125.7, 61.2, 48.7, 40.8, 28.2, 21.7, 20.6, 13.5. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{31}H_{32}NO_5S$ 530.2001, found: 530.1998. IR ν_{max}/cm^{-1} 3060, 2980, 2926, 2871, 1698, 1597, 1445, 1348, 1291, 1202, 1090, 1033, 889, 763.



3la

Ethyl(2*E*,7*Z*)-6-oxo-2-phenyl-7-(m-tolyl)-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3la)

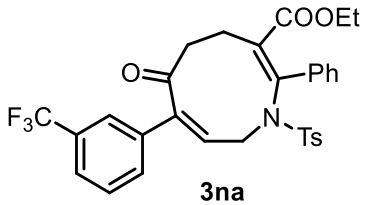
The title compound was prepared according to the standard procedure and isolated as a white solid (50.8 mg, 96%), m.p. = 144.9-149.1 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 6.8 Hz, 1H), 7.28-7.23 (m, 2H), 7.23-7.15 (m, 5H), 7.15-7.03 (m, 3H), 6.09 (t, *J* = 8.1 Hz, 1H), 4.30 (dd, *J* = 13.8, 7.4 Hz, 1H), 4.05 (dd, *J* = 13.7, 9.1 Hz, 1H), 3.85-3.65 (m, 2H), 2.84-2.73 (m, 1H), 2.67 (t, *J* = 13.7 Hz, 1H), 2.59-2.52 (m, 1H), 2.41 (s, 3H), 2.40-2.34 (m, 1H), 2.30 (s, 3H), 0.66 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.5, 169.0, 149.7, 144.3, 144.0, 138.6, 138.3, 135.8, 133.9, 133.1, 130.0, 129.7, 129.1, 128.9, 128.7, 128.1, 127.6, 127.0, 123.7, 120.5, 61.0, 48.9, 41.1, 27.7, 21.7, 21.5, 13.3. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{31}H_{32}NO_5S$ 530.2001, found: 530.2000. IR ν_{max}/cm^{-1} 3057, 3027, 2980, 2925, 2871, 1699, 1599, 1491, 1445, 1350, 1298, 1160, 1091, 1041, 917, 754, 682.



3ma

Ethyl(2*E*,7*Z*)-7-(3-bromophenyl)-6-oxo-2-phenyl-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3ma)

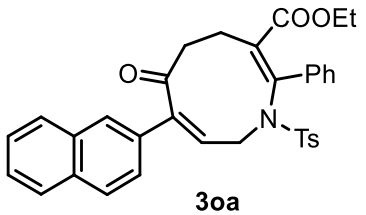
The title compound was prepared according to the standard procedure and isolated as a white solid (53.5 mg, 90%), m.p. = 175.1-178.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.31 (m, 5H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.23-7.14 (m, 6H), 6.07 (t, 1H), 4.31 (dd, *J* = 13.9, 7.3 Hz, 1H), 4.02 (dd, *J* = 13.9, 9.2 Hz, 1H), 3.77 (q, *J* = 7.1 Hz, 2H), 2.85-2.74 (m, 1H), 2.67-2.51 (m, 2H), 2.41 (s, 3H), 2.41-2.33 (m, 1H), 0.68 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.6, 169.0, 148.3, 144.2, 144.1, 138.2, 136.0, 135.7, 132.8, 132.2, 130.5, 129.8, 129.4, 129.2, 128.7, 128.2, 127.6, 125.2, 123.1, 122.1, 61.2, 48.6, 41.0, 27.5, 21.7, 13.4. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{30}H_{29}BrNO_5S$ 594.0950, found: 594.0942. IR ν_{max}/cm^{-1} 3061, 3030, 2981, 2957, 2927, 1701, 1595, 1492, 1445, 1351, 1298, 1161, 1091, 1042, 915, 767.



3na

Ethyl(2*E*,7*Z*)-6-oxo-2-phenyl-1-tosyl-7-(3-(trifluoromethyl)phenyl)-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3na)

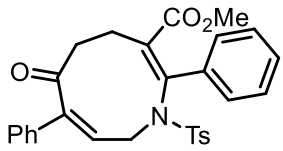
The title compound was prepared according to the standard procedure and isolated as a white solid (43.2 mg, 74%), m.p. = 165.6-169.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 6.2 Hz, 1H), 7.53-7.40 (m, 5H), 7.35 (t, *J* = 14.5 Hz, 1H), 7.30-7.18 (m, 6H), 6.13 (t, *J* = 8.2 Hz, 1H), 4.33 (dd, *J* = 13.9, 7.3 Hz, 1H), 4.05 (dd, *J* = 13.9, 9.2 Hz, 1H), 3.85-3.71 (m, 2H), 2.86-2.74 (m, 1H), 2.64 (t, *J* = 13.7 Hz, 1H), 2.60-2.53 (m, 1H), 2.42 (s, 3H), 2.42-2.33 (m, 1H), 0.65 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.5, 169.0, 148.3, 144.3, 144.0, 138.1, 135.6, 134.8, 132.7, 131.5 (q, *J* = 32.5 Hz), 129.8, 129.8, 129.6, 129.3, 128.6, 128.3, 127.6, 125.9 (q, *J* = 3.6 Hz), 123.8 (q, *J* = 270.9 Hz), 123.1 (q, *J* = 3.8 Hz), 122.6, 61.1, 48.5, 41.0, 27.4, 21.7, 13.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.80. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{31}H_{29}NO_5F_3S$ 584.1719, found: 584.1717. IR ν_{max}/cm^{-1} 3063, 3030, 2982, 2929, 1699, 1598, 1491, 1445, 1329, 1298, 1159, 1125, 1076, 1042, 914, 803, 698.



3oa

Ethyl(2*E*,7*Z*)-7-(naphthalen-2-yl)-6-oxo-2-phenyl-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3oa)

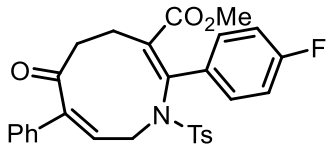
The title compound was prepared according to the standard procedure and isolated as a white solid (47.0 mg, 83%), m.p. = 166.2-169.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.73 (m, 3H), 7.63 (s, 1H), 7.52-7.41 (m, 5H), 7.37-7.32 (m, 1H), 7.27 (t, *J* = 14.5 Hz, 2H), 7.21 (t, *J* = 15.0 Hz, 4H), 6.24 (t, *J* = 8.1 Hz, 1H), 4.38 (dd, *J* = 13.7, 7.3 Hz, 1H), 4.10 (dd, *J* = 13.6, 9.3 Hz, 1H), 3.71 (q, *J* = 7.1 Hz, 2H), 2.86-2.76 (m, 1H), 2.75-2.57 (m, 2H), 2.48-2.43 (m, 1H), 2.42 (s, 3H), 0.63 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.4, 169.0, 149.5, 144.2, 144.1, 138.3, 135.8, 133.4, 133.2, 133.0, 131.1, 129.7 , 129.1, 128.9, 128.7, 128.4, 128.2, 127.8, 127.6, 127.0, 126.8, 126.0, 123.9, 121.0, 61.0, 48.9, 41.2, 27.7, 21.7, 13.4. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{34}H_{32}NO_5S$ 566.2001, found: 566.1996. IR ν_{max}/cm^{-1} 3058, 3028, 2980, 2928, 1700, 1597, 1445, 1349, 1297, 1160, 1090, 1041, 913, 816, 766.



3ab

Methyl(2*E*,7*Z*)-6-oxo-2,7-diphenyl-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3ab)

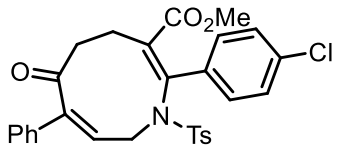
The title compound was prepared according to the standard procedure and isolated as a white solid (42.6 mg, 85%), m.p. = 142.4-145.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.3 Hz, 2H), 7.35-7.29 (m, 4H), 7.28-7.22 (m, 4H), 7.18 (t, *J* = 8.6 Hz, 4H), 6.10 (t, *J* = 8.1 Hz, 1H), 4.26 (dd, *J* = 14.0, 7.5 Hz, 1H), 4.07 (dd, *J* = 14.0, 8.7 Hz, 1H), 3.29 (s, 3H), 2.85-2.71 (m, 2H), 2.60-2.52 (m, 1H), 2.41 (s, 3H), 2.41-2.32 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, one carbon signal was overlapped) δ 208.4, 169.5, 149.5, 144.6, 144.1, 137.8, 135.8, 134.0, 133.0, 129.7, 129.2, 129.0, 128.5, 128.3, 127.6, 126.5, 121.0, 51.9, 48.8, 41.1, 27.8, 21.7. HRMS (ESI) m/z: $(M + H)^+$ calcd. for $C_{29}H_{28}NO_5S$ 502.1688, found: 502.1679. IR ν_{max}/cm^{-1} 3060, 3027, 2951, 2926, 2854, 1715, 1597, 1494, 1446, 1302, 1158, 1090, 1041, 915, 832, 752.



3ac

Methyl(2*E*,7*Z*)-2-(4-fluorophenyl)-6-oxo-7-phenyl-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3ac)

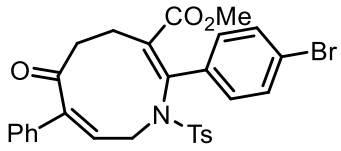
The title compound was prepared according to the standard procedure and isolated as a white solid (47.3 mg, 91%), m.p. = 139.2-140.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.29 (m, 3H), 7.26 – 7.19 (m, 4H), 7.19 – 7.11 (m, 2H), 6.95 (t, *J* = 8.5 Hz, 2H), 6.07 (t, *J* = 8.1 Hz, 1H), 4.27 (dd, *J* = 13.9, 7.4 Hz, 1H), 4.04 (dd, *J* = 13.9, 8.9 Hz, 1H), 3.32 (s, 3H), 2.78 – 2.62 (m, 2H), 2.58 – 2.51 (m, 1H), 2.42 (s, 3H), 2.40 – 2.32 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.2, 169.3, 163.2 (d, *J* = 249.7 Hz), 149.6, 144.3, 143.5, 135.7, 134.1 (d, *J* = 3.3 Hz), 133.8, 132.8, 130.4 (d, *J* = 8.4 Hz), 129.8, 129.3, 129.0, 127.5, 126.4, 120.6, 115.3 (d, *J* = 21.8 Hz), 52.0, 48.7, 41.0, 27.7, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.38. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{29}H_{27}FNO_5S$ 520.1594, found: 520.1591. IR ν_{max}/cm^{-1} 3062, 3032, 2951, 2926, 2855, 1700, 1599, 1506, 1434, 1348, 1230, 1158, 1040, 910, 813, 729.



3ad

Methyl(2*E*,7*Z*)-2-(4-chlorophenyl)-6-oxo-7-phenyl-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3ad)

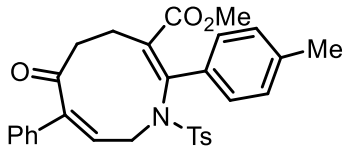
The title compound was prepared according to the standard procedure and isolated as a white solid (38.1 mg, 71%), m.p. = 128.0-135.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.2 Hz, 2H), 7.36-7.29 (m, 3H), 7.28-7.18 (m, 6H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.06 (t, *J* = 8.1 Hz, 1H), 4.28 (dd, *J* = 13.9, 7.4 Hz, 1H), 4.04 (dd, *J* = 13.8, 9.0 Hz, 1H), 3.33 (s, 3H), 2.80-2.70 (m, 1H), 2.64 (t, *J* = 13.2 Hz, 1H), 2.59-2.51 (m, 1H), 2.44 (s, 3H), 2.36 (t, *J* = 14.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.1, 169.2, 149.7, 144.4, 143.3, 136.6, 135.7, 135.3, 133.8, 133.3, 129.8, 129.8, 129.3, 129.0, 128.5, 127.5, 126.5, 120.5, 52.1, 48.9, 41.0, 27.7, 21.7. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{29}H_{27}NO_5SCl$ 536.1298, found: 536.1293. IR ν_{max}/cm^{-1} 3062, 2952, 2924, 2853, 1725, 1595, 1490, 1436, 1300, 1161, 1088, 1040, 838, 813, 720.



3ae

Methyl(2*E*,7*Z*)-2-(4-bromophenyl)-6-oxo-7-phenyl-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3ae)

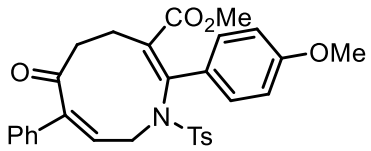
The title compound was prepared according to the standard procedure and isolated as a white solid (53.4 mg, 92%), m.p. = 145.5-147.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.35-7.29 (m, 3H), 7.25-7.18 (m, 4H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.07 (t, *J* = 8.2 Hz, 1H), 4.28 (dd, *J* = 13.9, 7.4 Hz, 1H), 4.04 (dd, *J* = 13.9, 9.0 Hz, 1H), 3.34 (s, 3H), 2.79-2.60 (m, 2H), 2.59-2.50 (m, 1H), 2.44 (s, 3H), 2.36 (td, *J* = 13.1, 3.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.1, 169.1, 149.7, 144.4, 143.4, 137.0, 135.7, 133.8, 133.3, 131.5, 130.0, 129.8, 129.3, 129.0, 127.5, 126.5, 123.6, 120.5, 52.1, 48.9, 41.0, 27.8, 21.8. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{29}H_{27}BrNO_5S$ 580.0793, found: 580.0802. IR ν_{max}/cm^{-1} 3059, 3029, 2950, 2925, 1713, 1596, 1487, 1434, 1351, 1296, 1160, 1090, 910, 936, 762.



3af

Methyl(2*E*,7*Z*)-6-oxo-7-phenyl-2-(p-tolyl)-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3af)

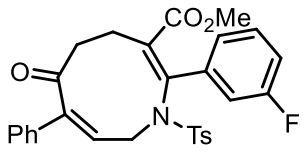
The title compound was prepared according to the standard procedure and isolated as a white solid (40.2 mg, 78%), m.p. = 121.4-127.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.29 (m, 3H), 7.26 – 7.18 (m, 4H), 7.06 (s, 4H), 6.07 (t, *J* = 8.1 Hz, 1H), 4.26 (dd, *J* = 13.9, 7.4 Hz, 1H), 4.05 (dd, *J* = 13.9, 8.8 Hz, 1H), 3.32 (s, 3H), 2.79 – 2.62 (m, 2H), 2.57 – 2.50 (m, 1H), 2.42 (s, 3H), 2.41 – 2.37 (m, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, one carbon stacked at aromatic chemical shift) δ 208.4, 169.7, 149.5, 144.6, 144.0, 139.3, 135.9, 135.0, 134.0, 132.1, 129.7, 129.1, 129.0, 128.4, 127.6, 126.5, 120.9, 51.9, 48.7, 41.1, 27.8, 21.7, 21.5. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{30}H_{30}NO_5S$ 516.1845, found: 516.1840. IR ν_{max}/cm^{-1} 3027, 2951, 2924, 1701, 1599, 1494, 1446, 1348, 1158, 1090, 1040, 909, 815, 729.



3ag

Methyl(2*E*,7*Z*)-2-(4-methoxyphenyl)-6-oxo-7-phenyl-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3ag)

The title compound was prepared according to the standard procedure and isolated as a yellow oil (41.4 mg, 78%), m.p. = 130.6-132.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.2 Hz, 2H), 7.34-7.29 (m, 3H), 7.25-7.19 (m, 4H), 7.09 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.06 (t, *J* = 8.1 Hz, 1H), 4.25 (dd, *J* = 13.9, 7.5 Hz, 1H), 4.05 (dd, *J* = 13.9, 8.8 Hz, 1H), 3.81 (s, 3H), 3.33 (s, 3H), 2.77-2.63 (m, 2H), 2.56-2.49 (m, 1H), 2.42 (s, 3H), 2.40-2.29 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.5, 169.8, 160.4, 149.4, 144.4, 144.0, 135.9, 134.0, 131.3, 130.3, 130.0, 129.7, 129.1, 129.0, 127.6, 126.4, 120.9, 113.6, 55.4, 51.9, 48.6, 41.1, 27.8, 21.7. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{30}H_{30}NO_6S$ 532.1794, found: 532.1793. IR ν_{max}/cm^{-1} 3059, 3030, 3003, 2951, 2839, 1701, 1604, 1510, 1444, 1348, 1300, 1251, 1159, 1090, 1034, 912, 838.

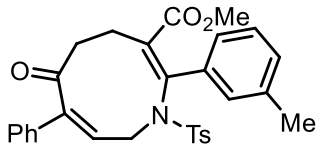


3ah

Methyl(2*E*,7*Z*)-2-(3-fluorophenyl)-6-oxo-7-phenyl-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3ah)

The title compound was prepared according to the standard procedure and isolated as a white solid (35.3 mg, 68%), m.p. = 135.7-137.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.1 Hz, 2H), 7.37-7.30 (m, 3H), 7.30-7.18 (m, 5H), 7.08-6.98 (m, 2H), 6.83 (d,

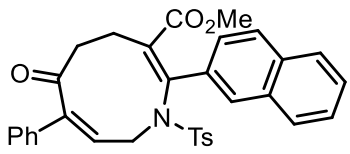
J = 9.4 Hz, 1H), 6.08 (t, *J* = 8.1 Hz, 1H), 4.29 (dd, *J* = 13.9, 7.4 Hz, 1H), 4.05 (dd, *J* = 13.8, 9.0 Hz, 1H), 3.33 (s, 3H), 2.80-2.72 (m, 1H), 2.71-2.62 (m, 1H), 2.59-2.52 (m, 1H), 2.41 (s, 3H), 2.40-2.28 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, one carbon signal was overlapped) δ 208.0, 169.1, 162.5 (d, *J* = 246.8 Hz), 149.7, 144.4, 142.9 (d, *J* = 2.2 Hz), 140.2 (d, *J* = 7.5 Hz), 135.6, 133.8 (d, *J* = 1.5 Hz), 129.8, 129.7, 129.3, 129.0, 127.5, 126.5, 124.5 (d, *J* = 2.8 Hz), 120.5, 116.2 (d, *J* = 21.2 Hz), 115.3 (d, *J* = 22.4 Hz), 52.1, 48.8, 40.9, 27.7, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.96. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{29}H_{27}FNO_5S$ 520.1594, found: 520.1594. IR ν_{max}/cm^{-1} 3063, 3030, 2951, 2926, 2891, 1702, 1584, 1486, 1435, 1349, 1201, 1160, 1090, 1040, 909, 789, 678.



3ai

Methyl(2*E*,7*Z*)-6-oxo-7-phenyl-2-(m-tolyl)-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3ai)

The title compound was prepared according to the standard procedure and isolated as a white solid (48.0 mg, 93%), m.p. = 124.3-129.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.2 Hz, 2H), 7.35-7.29 (m, 3H), 7.29-7.24 (m, 2H), 7.20-7.08 (m, 4H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.81 (s, 1H), 6.14 (t, *J* = 8.1 Hz, 1H), 4.23 (d, *J* = 21.8 Hz, 1H), 4.12 (d, *J* = 22.5 Hz, 1H), 3.32 (s, 3H), 2.93-2.75 (m, 2H), 2.63-2.56 (m, 1H), 2.46-2.41 (m, 1H), 2.40 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.4, 169.6, 149.1, 145.0, 143.9, 137.7, 137.3, 135.9, 134.1, 132.9, 130.0, 129.5, 129.1, 129.0, 128.9, 128.1, 127.6, 126.4, 126.0, 121.4, 51.9, 48.9, 41.3, 28.0, 21.6, 21.3. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{30}H_{30}NO_5S$ 516.1845, found: 516.1840. IR ν_{max}/cm^{-1} 3063, 3030, 2951,2926, 1702, 1584, 1486, 1435, 1350, 1301, 1160, 1090, 1040, 982, 833.

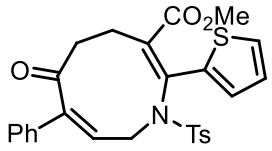


3aj

Methyl(2*E*,7*Z*)-2-(naphthalen-2-yl)-6-oxo-7-phenyl-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3aj)

The title compound was prepared according to the standard procedure and isolated as a white solid (49.7 mg, 90%), m.p. = 146.9-149.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.8 Hz, 1H), 7.63-7.56 (m, 2H), 7.46-7.39 (m, 3H), 7.30-7.16 (m, 9H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.10 (t, *J* = 8.1 Hz, 1H), 4.26 (dd, *J* = 14.0, 7.6 Hz, 1H), 4.11 (dd, *J* =

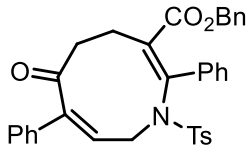
13.9, 8.7 Hz, 1H), 3.16 (s, 3H), 2.87-2.74 (m, 2H), 2.58-2.49 (m, 1H), 2.36-2.32 (m, 1H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.4, 169.5, 149.4, 144.9, 144.0, 135.9, 134.8, 134.0, 133.4, 133.2, 132.9, 129.5, 129.2, 129.0, 128.5, 128.3, 127.8, 127.7, 127.4, 126.9, 126.4, 126.4, 126.0, 121.2, 51.9, 49.1, 41.2, 28.1, 21.5. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{33}H_{30}NO_5S$ 552.1845, found: 552.1844. IR ν_{max}/cm^{-1} 3059, 2951, 2925, 1718, 1678, 1597, 1495, 1434, 1348, 1324, 1155, 1088, 731.



3ak

Methyl(2*E*,7*Z*)-6-oxo-7-phenyl-2-(thiophen-2-yl)-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3ak)

The title compound was prepared according to the standard procedure and isolated as a white solid (36.0 mg, 71%), m.p. = 151.1-153.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.35-7.30 (m, 4H), 7.29-7.22 (m, 4H), 7.01-6.96 (m, 1H), 6.96-6.90 (m, 1H), 6.04 (dd, *J* = 8.2, 7.4 Hz, 1H), 4.17 (dd, *J* = 13.8, 7.1 Hz, 1H), 4.01 (dd, *J* = 13.8, 8.5 Hz, 1H), 3.42 (s, 3H), 2.77-2.66 (m, 1H), 2.64-2.51 (m, 2H), 2.50-2.44 (m, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.2, 169.4, 149.9, 144.3, 140.4, 135.9, 135.6, 134.1, 134.1, 129.8, 129.2, 129.0, 128.9, 128.2, 127.7, 127.1, 126.5, 120.8, 52.2, 47.7, 40.8, 27.7, 21.8. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{27}H_{26}NO_5S_2$ 508.1252, found: 508.1247. IR ν_{max}/cm^{-1} 3062, 3028, 2950, 2926, 1716, 1700, 1597, 1494, 1433, 1352, 1293, 1161, 1091, 1039, 911, 939.

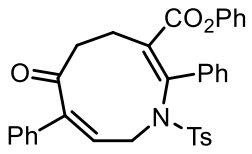


3al

Benzyl(2*E*,7*Z*)-6-oxo-2,7-diphenyl-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3al)

The title compound was prepared according to the standard procedure and isolated as a white solid (48.5 mg, 84%), m.p. = 160.4-162.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.1 Hz, 2H), 7.33-7.30 (m, 1H), 7.27-7.10 (m, 12H), 7.09-7.00 (m, 2H), 6.63 (d, *J* = 7.3 Hz, 2H), 5.97 (dd, *J* = 9.4, 7.2 Hz, 1H), 4.71 (q, *J* = 12.3 Hz, 2H), 4.36 (dd, *J* = 13.6, 7.0 Hz, 1H), 3.98 (dd, *J* = 13.5, 9.7 Hz, 1H), 2.85-2.72 (m, 1H), 2.57-2.47 (m, 2H), 2.41 (s, 3H), 2.38-2.28 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.0, 168.9, 150.1, 144.1, 143.9, 138.4, 135.7, 134.8, 133.6, 132.2, 129.7, 129.2, 129.0, 128.8, 128.7, 128.3, 128.3, 128.2, 128.1, 127.5, 126.5, 120.0, 67.2, 48.6, 40.6, 27.5, 21.7. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{35}H_{32}NO_5S$ 578.2001, found: 578.1997. IR ν_{max}/cm^{-1}

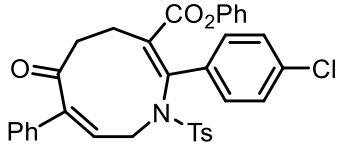
3061, 3031, 2954, 2925, 2887, 1698, 1597, 1494, 1446, 1348, 1294, 1237, 1157, 1089, 1041, 912, 813.



3am

Phenyl(2*E*,7*Z*)-6-oxo-2,7-diphenyl-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3am)

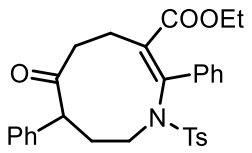
The title compound was prepared according to the standard procedure and isolated as a white solid (50.7 mg, 90%), m.p. = 173.4-177.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.40-7.37 (m, 1H), 7.35-7.32 (m, 3H), 7.32-7.24 (m, 6H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.14 (t, *J* = 8.0 Hz, 2H), 7.12-7.04 (m, 1H), 6.34 (d, *J* = 7.8 Hz, 2H), 6.13 (t, 1H), 4.40 (dd, *J* = 13.8, 7.1 Hz, 1H), 4.09 (dd, *J* = 13.7, 9.4 Hz, 1H), 2.95-2.85 (m, 1H), 2.81-2.68 (m, 1H), 2.66-2.60 (m, 1H), 2.57-2.49 (m, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.2, 167.7, 150.2, 149.9, 145.4, 144.3, 138.2, 135.7, 133.6, 131.8, 129.8, 129.7, 129.3, 129.2, 129.1, 129.1, 128.6, 127.6, 126.5, 126.0, 121.0, 120.1, 48.9, 40.9, 28.0, 21.8. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{34}H_{30}NO_5S$ 564.1845, found: 564.1852. IR ν_{max}/cm^{-1} 3060, 3030, 2957, 2922, 1727, 1698, 1595, 1492, 1446, 1351, 1161, 1091, 1040, 913.



3an

Phenyl(2*E*,7*Z*)-7-(4-chlorophenyl)-6-oxo-2-phenyl-1-tosyl-4,5,6,9-tetrahydro-1*H*-azonine-3-carboxylate (3an)

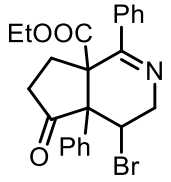
The title compound was prepared according to the standard procedure and isolated as a white solid (34.7 mg, 58%), m.p. = 170.9-173.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.1 Hz, 2H), 7.31-7.23 (m, 11H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 6.38 (d, *J* = 8.0 Hz, 2H), 6.10 (dd, *J* = 9.2, 7.4 Hz, 1H), 4.42 (dd, *J* = 13.7, 7.1 Hz, 1H), 4.06 (dd, *J* = 13.7, 9.6 Hz, 1H), 2.93-2.81 (m, 1H), 2.70-2.57 (m, 2H), 2.57-2.48 (m, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, one carbon signal was overlapped) δ 207.9, 167.3, 150.1, 144.6, 144.2, 136.9, 135.8, 135.7, 133.5, 132.1, 130.3, 129.9, 129.4, 129.4, 129.2, 128.8, 127.5, 126.4, 126.1, 120.8, 119.7, 49.0, 40.8, 27.9, 21.8. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{34}H_{29}NO_5SCl$ 598.1455, found: 598.1452. IR ν_{max}/cm^{-1} 3062, 3031, 2956, 2925, 2855, 1726, 1698, 1593, 1490, 1446, 1351, 1294, 1160, 1090, 1040, 910, 815.



4

Ethyl(*E*)-6-oxo-2,7-diphenyl-1-tosyl-4,5,6,7,8,9-hexahydro-1*H*-azonine-3-carboxylate (4)

The title compound was isolated as a white solid (22.3 mg, 43%), m.p. = 155.1-159.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.37-7.28 (m, 5H), 7.24-7.20 (m, 1H), 7.18-7.10 (m, 4H), 7.00 (d, *J* = 7.6 Hz, 2H), 4.76 (dd, *J* = 11.0, 4.6 Hz, 1H), 3.99-3.82 (m, 3H), 3.53-3.41 (m, 1H), 3.35-3.22 (m, 1H), 2.92 (dt, *J* = 14.0, 4.2 Hz, 1H), 2.77 (dt, 1H), 2.51-2.40 (m, 2H), 2.39 (s, 3H), 2.35-2.28 (m, 1H), 0.76 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.1, 169.0, 147.3, 144.0, 138.1, 136.7, 136.4, 135.3, 129.5, 129.1, 129.0, 128.9, 128.5, 128.2, 128.1, 127.6, 61.0, 51.2, 49.3, 42.1, 34.8, 28.3, 21.7, 13.4. HRMS (ESI) m/z: $(M+H)^+$ calcd. for $C_{30}H_{32}NO_5S$ 518.2001, found: 518.2003. IR ν_{max}/cm^{-1} 3060, 3028, 2979, 2923, 2853, 1705, 1597, 1493, 1446, 1345, 1286, 1159, 1088, 1022, 904, 698, 682.



5

The title compound was isolated as a brown oil (25.5 mg, 0.1 mmol, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 7.41 – 7.32 (m, 6H), 7.06 (s, 2H), 5.28 (dd, *J* = 10.8, 5.4 Hz, 1H), 4.71 (dd, *J* = 19.1, 5.4 Hz, 1H), 4.24 – 4.04 (m, 3H), 2.63 – 2.46 (m, 2H), 2.35 – 2.25 (m, 1H), 2.22 – 2.15 (m, 1H), 1.17 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.8, 169.6, 164.8, 137.8, 136.1, 130.0, 128.76, 128.65, 128.60, 127.5, 127.1, 65.1, 62.6, 61.0, 55.8, 45.6, 37.2, 26.3, 13.9. HRMS (ESI+, MeOH) m/z: $(M + H)^+$ calcd. for $C_{23}H_{23}NO_3Br$ 440.0861, found: 440.0865. IR ν_{max}/cm^{-1} 3060, 2979, 2929, 2856, 1747, 1737, 1715, 1636, 1496, 1444, 1260, 1001, 744, 697.

X-ray molecular structure of 3aa

X-ray molecular structure of **3aa**

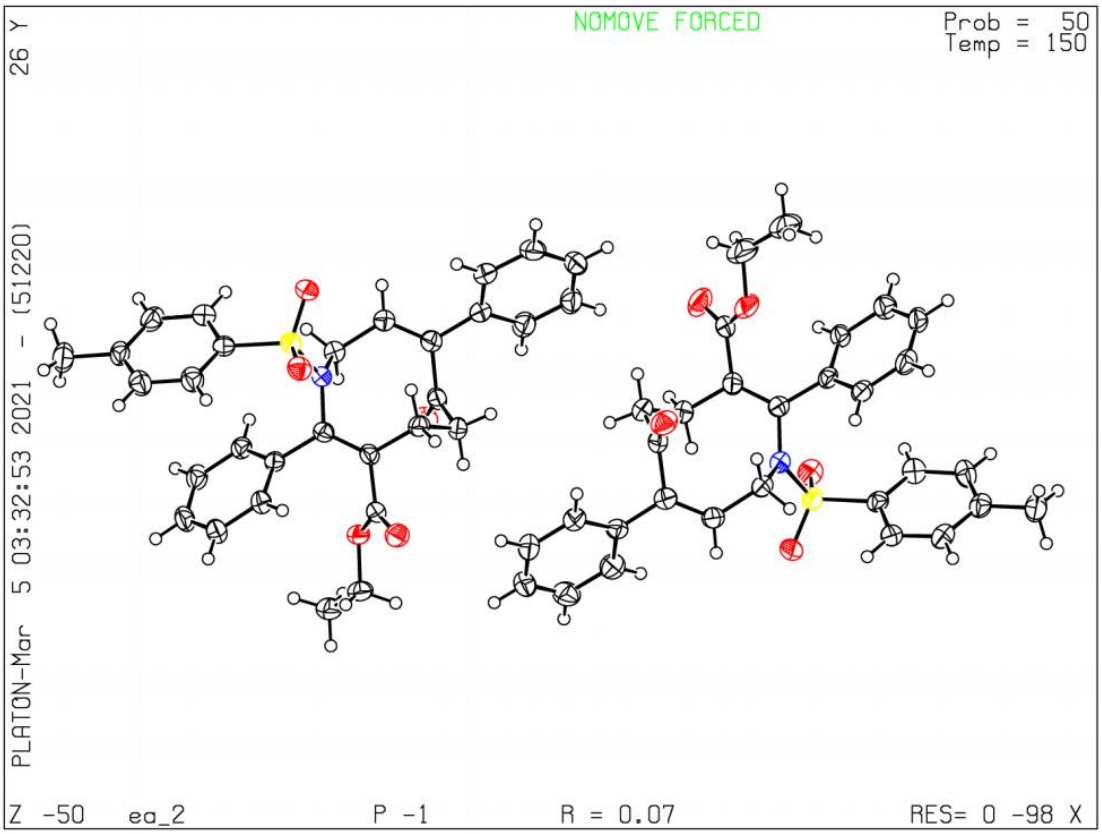


Table 1 Crystal data and structure refinement for 3aa

Identification code	3aa
Empirical formula	$C_{30}H_{29}NO_5S$
Formula weight	515.60
Temperature/K	149.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.2628(8)
b/Å	14.1029(13)
c/Å	21.1489(16)

α/°	99.246(7)
β/°	100.027(7)
γ/°	102.719(8)
Volume/Å^3	2596.2(4)
Z	4
ρ_{calc}g/cm^3	1.319
μ/mm^{-1}	1.445
F(000)	1088.0
Crystal size/mm^3	0.14 × 0.13 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/	4.336 to 149.022
Index ranges	-11 ≤ h ≤ 7, -17 ≤ k ≤ 17, -25 ≤ l ≤ 26
Reflections collected	17164
Independent reflections	10161 [R_{int} = 0.0435, R_{sigma} = 0.0669]
Data/restraints/parameters	10161/16/671
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0703, wR_2 = 0.1625
Final R indexes [all data]	R_1 = 0.1098, wR_2 = 0.1842
Largest diff. peak/hole / e Å^{-3}	0.69/-0.62

Crystal structure determination of 3aa

Crystal Data for $C_{30}H_{29}NO_5S$ (*M* =515.60 g/mol): triclinic, space group P-1 (no. 2), *a* = 9.2628(8) Å, *b* = 14.1029(13) Å, *c* = 21.1489(16) Å, *α* = 99.246(7) , *β* = 100.027(7), *γ* = 102.719(8), *V* = 2596.2(4) Å^3, *Z* = 4, *T* = 149.99(10) K, μ(Cu Kα) = 1.445 mm^{-1}, *Dcalc* = 1.319 g/cm^3, 17164 reflections measured (4.336° ≤ 2θ ≤ 149.022°),

10161 unique (R_{int} = 0.0435, R_{sigma} = 0.0669) which were used in all calculations. The final R_1 was 0.0703 (I > 2σ(I)) and wR_2 was 0.1842 (all data).

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3aa. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	2258.7(10)	7575.7(7)	-576.8(4)	30.7(2)
O1	3124(3)	6910(2)	-794.9(13)	36.6(6)
O2	2925(3)	8620(2)	-367.3(14)	37.5(6)
O3	-37(3)	8349(2)	1662.1(13)	34.8(6)
O4	2056(3)	9617(2)	1938.4(14)	40.5(7)
O5	1458(3)	5925(2)	1580.6(15)	44.4(7)
N1	1704(3)	7200(2)	59.6(14)	29.1(6)
C31	4915(4)	5742(3)	1248.9(18)	33.0(8)
C32	5128(5)	5383(3)	1828(2)	41.2(9)
C33	6535(5)	5277(3)	2109(2)	46.5(11)
C34	7748(5)	5515(3)	1815(2)	48.2(11)
C35	7548(5)	5854(4)	1238(2)	46.7(11)
C36	6137(5)	5963(3)	953(2)	39.2(9)
C37	3419(4)	5919(3)	983.8(19)	32.7(8)
C38	2854(4)	5835(3)	342.9(19)	33.4(8)
C39	1425(4)	6134(3)	80.0(19)	31.8(8)
C40	2653(4)	6360(3)	1488.9(18)	33.4(8)
C41	3469(4)	7404(3)	1849.9(18)	35.1(9)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3aa. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C42	3501(4)	8129(3)	1371.9(18)	33.2(8)
C43	1930(4)	8225(3)	1105.4(18)	28.5(7)
C44	1113(4)	7836(3)	491.0(18)	28.8(7)
C45	1335(4)	8815(3)	1606.1(18)	30.0(8)
C46	-723(5)	8919(3)	2105(2)	41.4(10)
C47	-2354(5)	8361(3)	1994(2)	45.5(10)
C48	-387(4)	8015(3)	231.1(17)	28.6(7)
C49	-1577(4)	7217(3)	-143.2(18)	32.1(8)
C50	-2997(4)	7377(3)	-358.8(19)	38.2(9)
C51	-3244(4)	8307(3)	-214(2)	39.8(9)
C52	-2052(4)	9107(3)	135(2)	39.1(9)
C53	-632(4)	8949(3)	352.5(19)	34.0(8)
C54	639(4)	7403(3)	-1203.0(18)	30.8(8)
C55	-32(4)	6454(3)	-1574.9(19)	36.8(9)
C56	-1339(5)	6303(3)	-2049(2)	41.5(10)
C57	-1980(4)	7084(3)	-2157.8(18)	36.4(9)
C58	-1276(4)	8023(3)	-1791(2)	40.5(9)
C59	30(4)	8179(3)	-1310(2)	39.6(9)
C60	-3425(5)	6896(4)	-2675(2)	52.7(12)
S2	9016.1(10)	7379.5(7)	6020.7(5)	33.1(2)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3aa. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O6	9240(4)	5397(2)	3408.1(15)	60.6(10)
O7	11375(4)	6613(3)	3798.2(15)	62.9(10)
O8	9456(3)	8984(2)	3733.1(14)	45.2(7)
O9	8480(3)	6323(2)	5877.2(14)	42.0(7)
O10	8048(3)	8002(2)	6182.2(14)	39.1(6)
N2	9525(3)	7683(2)	5357.9(15)	31.8(7)
C1	6122(4)	9089(3)	4149.5(18)	32.5(8)
C2	5926(5)	9509(3)	3600(2)	38.7(9)
C3	4549(5)	9703(3)	3357(2)	47.0(11)
C4	3347(5)	9458(4)	3654(2)	49.3(11)
C5	3522(5)	9034(4)	4196(2)	51.2(12)
C6	4908(5)	8852(3)	4444(2)	45.1(10)
C7	8224(4)	8978(3)	5031.6(19)	35.2(8)
C8	7618(4)	8895(3)	4397.0(19)	32.4(8)
C9	8367(4)	8486(3)	3875.8(18)	34.1(8)
C10	7669(5)	7410(3)	3551.1(19)	37.4(9)
C11	7734(4)	6729(3)	4047.7(19)	35.5(9)
C12	9701(4)	8730(3)	5283.7(18)	33.6(8)
C13	9333(4)	6663(3)	4309.6(19)	32.8(8)
C14	10118(4)	7030(3)	4932.1(18)	30.2(8)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3aa. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C15	11599(4)	6841(3)	5202.2(17)	30.5(8)
C16	11844(4)	5904(3)	5061.7(18)	33.2(8)
C17	13251(4)	5734(3)	5283(2)	39.7(9)
C18	14441(4)	6522(3)	5648.5(19)	39.8(9)
C19	14197(4)	7458(3)	5798.2(19)	38.5(9)
C20	12793(4)	7626(3)	5586.7(18)	34.1(8)
C21	10626(4)	7713(3)	6672.1(18)	31.1(8)
C22	11337(4)	7004(3)	6847(2)	39.1(9)
C23	12610(4)	7283(3)	7360(2)	41.6(10)
C24	13191(4)	8258(3)	7688.9(19)	37.2(9)
C25	12431(5)	8949(3)	7505.6(19)	41.0(9)
C26	11150(4)	8699(3)	7004.8(19)	35.7(9)
C27	14584(5)	8565(4)	8236(2)	47.6(11)
C28	9970(5)	6143(3)	3801(2)	40.7(10)
C29	12042(7)	6102(8)	3334(3)	128(3)
C30	13568(7)	6168(7)	3551(3)	128(3)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3aa. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	24.6(4)	36.5(5)	31.0(5)	6.6(4)	7.2(3)	7.4(4)
O1	30.9(13)	43.2(16)	38.1(15)	5.9(12)	10.5(11)	14.1(12)
O2	29.8(13)	39.0(15)	42.2(16)	7.1(12)	8.6(12)	6.1(11)
O3	30.9(13)	41.3(15)	31.9(14)	1.4(11)	9.3(11)	11.2(11)
O4	35.9(14)	37.6(16)	40.8(16)	-3.4(12)	3.0(12)	7.2(12)
O5	39.2(15)	52.8(19)	45.3(17)	14.2(14)	16.8(13)	11.4(13)
N1	27.5(15)	32.5(17)	27.9(15)	5.1(12)	5.1(12)	10.7(12)
C31	36.4(19)	35(2)	28.4(19)	3.4(15)	7.0(15)	12.4(16)
C32	45(2)	44(2)	35(2)	9.3(18)	6.5(18)	11.7(19)
C33	58(3)	45(3)	36(2)	6.4(19)	-2(2)	22(2)
C34	45(2)	51(3)	46(3)	-4(2)	-2(2)	25(2)
C35	38(2)	58(3)	44(2)	-2(2)	12.2(19)	18(2)
C36	40(2)	48(2)	31(2)	3.0(17)	9.4(17)	15.7(18)
C37	32.4(19)	36(2)	32.1(19)	7.9(16)	8.0(15)	11.0(16)
C38	36.1(19)	34(2)	31.0(19)	5.3(15)	6.6(15)	12.6(16)
C39	31.6(18)	34(2)	30.9(19)	6.3(15)	5.8(15)	10.2(15)
C40	29.7(18)	45(2)	30.4(19)	13.7(17)	6.7(15)	16.0(17)
C41	30.4(18)	48(2)	26.7(18)	6.4(16)	3.2(15)	13.3(17)
C42	27.1(18)	37(2)	30.7(19)	-0.8(16)	3.8(15)	5.8(15)
C43	23.3(16)	30.2(19)	31.3(18)	5.3(15)	4.0(14)	7.6(14)
C44	27.6(17)	29.5(19)	30.6(19)	7.2(15)	8.1(14)	8.3(14)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3aa. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C45	28.0(17)	34(2)	29.9(18)	7.6(15)	5.2(14)	11.8(15)
C46	39(2)	50(3)	36(2)	0.2(18)	13.9(17)	14.9(19)
C47	40(2)	55(3)	42(2)	4(2)	14.8(19)	16(2)
C48	25.8(17)	35(2)	25.9(18)	6.5(15)	7.2(14)	8.0(15)
C49	31.0(18)	38(2)	28.0(18)	7.6(15)	7.0(15)	8.5(16)
C50	28.4(18)	51(3)	32(2)	10.8(18)	4.9(16)	5.3(17)
C51	26.0(18)	57(3)	39(2)	15.4(19)	4.4(16)	13.8(18)
C52	36(2)	47(2)	38(2)	12.7(18)	5.0(17)	17.4(18)
C53	28.6(18)	38(2)	34(2)	6.7(16)	2.9(15)	8.5(16)
C54	28.7(18)	37(2)	29.8(19)	7.9(15)	11.0(15)	9.2(15)
C55	38(2)	39(2)	35(2)	4.9(17)	9.3(17)	14.5(17)
C56	38(2)	47(2)	32(2)	-0.4(18)	3.9(17)	4.2(18)
C57	31.0(19)	56(3)	26.2(19)	15.9(18)	7.3(15)	12.5(18)
C58	36(2)	50(3)	41(2)	18.6(19)	10.1(17)	14.8(19)
C59	35(2)	47(2)	39(2)	13.1(18)	8.3(17)	10.6(18)
C60	41(2)	77(4)	37(2)	15(2)	-0.1(19)	14(2)
S2	27.8(4)	40.4(5)	30.0(5)	6.6(4)	6.7(4)	6.3(4)
O6	94(3)	47.3(19)	33.7(17)	-6.0(14)	-9.3(17)	32.3(18)
O7	52.9(19)	114(3)	26.3(15)	3.7(17)	12.1(14)	35(2)
O8	43.6(16)	54.6(19)	36.5(16)	6.4(13)	15.0(13)	7.9(14)
O9	37.7(15)	43.4(17)	40.8(16)	7.7(13)	8.9(12)	2.1(12)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3aa. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O10	31.3(13)	53.7(18)	37.4(15)	9.7(13)	11.5(11)	17.5(12)
N2	33.2(16)	34.0(17)	27.1(16)	3.6(13)	4.0(13)	10.0(13)
C1	38(2)	31(2)	30.9(19)	4.6(15)	8.3(16)	14.3(16)
C2	40(2)	45(2)	32(2)	7.6(17)	8.6(17)	12.6(18)
C3	51(3)	55(3)	35(2)	7.8(19)	-0.3(19)	22(2)
C4	39(2)	59(3)	46(3)	0(2)	-2.0(19)	22(2)
C5	38(2)	64(3)	53(3)	6(2)	16(2)	15(2)
C6	49(2)	51(3)	40(2)	13.6(19)	13.5(19)	15(2)
C7	41(2)	37(2)	32(2)	8.0(16)	10.8(16)	15.6(17)
C8	36.1(19)	28.7(19)	33(2)	7.5(15)	9.9(16)	7.7(15)
C9	34.2(19)	42(2)	27.5(19)	9.5(16)	4.7(15)	13.4(17)
C10	39(2)	44(2)	26.8(19)	1.1(16)	2.4(16)	12.9(18)
C11	33.0(19)	39(2)	31(2)	2.7(16)	0.8(15)	11.0(16)
C12	37(2)	35(2)	27.5(18)	3.6(15)	5.3(15)	9.6(16)
C13	32.2(19)	34(2)	30.0(19)	5.4(15)	2.6(15)	9.3(16)
C14	31.0(18)	30.4(19)	28.6(18)	4.6(15)	6.8(14)	7.4(15)
C15	27.3(17)	40(2)	23.1(17)	6.6(15)	5.9(14)	6.1(15)
C16	26.2(17)	41(2)	30.9(19)	7.0(16)	3.9(15)	8.3(16)
C17	36(2)	45(2)	38(2)	8.9(18)	7.1(17)	10.2(18)
C18	28.2(19)	57(3)	32(2)	9.3(18)	1.1(16)	10.8(18)
C19	31.4(19)	49(2)	28.7(19)	4.8(17)	3.7(15)	0.2(17)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3aa. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C20	32.3(19)	40(2)	26.5(18)	3.1(16)	6.5(15)	5.6(16)
C21	32.4(18)	37(2)	25.1(18)	8.0(15)	10.4(15)	7.8(16)
C22	38(2)	37(2)	41(2)	10.0(17)	7.2(17)	6.7(17)
C23	36(2)	49(3)	43(2)	21(2)	4.7(18)	12.9(19)
C24	32.3(19)	51(2)	29.3(19)	13.0(17)	10.8(16)	6.2(17)
C25	44(2)	44(2)	30(2)	3.3(17)	5.0(17)	7.3(19)
C26	40(2)	39(2)	31(2)	6.9(16)	8.0(16)	16.1(17)
C27	37(2)	69(3)	35(2)	15(2)	4.4(18)	10(2)
C28	46(2)	50(3)	31(2)	5.9(18)	1.4(17)	29(2)
C29	78(3)	256(7)	47(3)	-31(4)	9(2)	87(4)
C30	76(3)	249(7)	53(3)	-39(4)	7(3)	83(4)

Table 4 Bond Lengths for 3aa.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O1	1.434(3)	S2	O9	1.427(3)
S1	O2	1.428(3)	S2	O10	1.431(3)
S1	N1	1.645(3)	S2	N2	1.644(3)
S1	C54	1.763(4)	S2	C21	1.764(4)
O3	C45	1.331(4)	O6	C28	1.210(5)
O3	C46	1.454(4)	O7	C28	1.326(6)

Table 4 Bond Lengths for 3aa.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O4	C45	1.211(5)	O7	C29	1.429(6)
O5	C40	1.206(5)	O8	C9	1.209(5)
N1	C39	1.476(5)	N2	C12	1.487(5)
N1	C44	1.437(5)	N2	C14	1.445(5)
C31	C32	1.397(5)	C1	C2	1.389(5)
C31	C36	1.387(5)	C1	C6	1.381(6)
C31	C37	1.491(5)	C1	C8	1.494(5)
C32	C33	1.386(6)	C2	C3	1.391(6)
C33	C34	1.380(7)	C3	C4	1.378(7)
C34	C35	1.376(7)	C4	C5	1.376(7)
C35	C36	1.394(6)	C5	C6	1.394(6)
C37	C38	1.341(5)	C7	C8	1.337(5)
C37	C40	1.509(5)	C7	C12	1.515(5)
C38	C39	1.518(5)	C8	C9	1.506(5)
C40	C41	1.506(6)	C9	C10	1.507(5)
C41	C42	1.548(5)	C10	C11	1.536(5)
C42	C43	1.510(5)	C11	C13	1.517(5)
C43	C44	1.345(5)	C13	C14	1.346(5)
C43	C45	1.497(5)	C13	C28	1.483(5)
C44	C48	1.494(5)	C14	C15	1.488(5)
C46	C47	1.500(6)	C15	C16	1.385(5)

Table 4 Bond Lengths for 3aa.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C48	C49	1.404(5)	C15	C20	1.403(5)
C48	C53	1.376(5)	C16	C17	1.391(5)
C49	C50	1.395(5)	C17	C18	1.391(6)
C50	C51	1.376(6)	C18	C19	1.384(6)
C51	C52	1.392(6)	C19	C20	1.384(5)
C52	C53	1.394(5)	C21	C22	1.376(5)
C54	C55	1.386(5)	C21	C26	1.391(5)
C54	C59	1.369(6)	C22	C23	1.392(6)
C55	C56	1.384(5)	C23	C24	1.379(6)
C56	C57	1.392(6)	C24	C25	1.386(6)
C57	C58	1.376(6)	C24	C27	1.505(5)
C57	C60	1.516(5)	C25	C26	1.383(5)
C58	C59	1.389(6)	C29	C30	1.386(6)

Table 5 Bond Angles for 3aa

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	S1	N1	105.05(16)	O9	S2	O10	121.21(18)
O1	S1	C54	108.05(17)	O9	S2	N2	106.23(17)
O2	S1	O1	121.16(16)	O9	S2	C21	107.78(18)
O2	S1	N1	106.03(16)	O10	S2	N2	104.89(17)
O2	S1	C54	107.65(17)	O10	S2	C21	107.11(18)

Table 5 Bond Angles for 3aa

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	S1	C54	108.33(16)	N2	S2	C21	109.21(17)
C45	O3	C46	115.2(3)	C28	O7	C29	114.2(5)
C39	N1	S1	119.1(2)	C12	N2	S2	118.2(2)
C44	N1	S1	119.5(2)	C14	N2	S2	121.3(3)
C44	N1	C39	119.3(3)	C14	N2	C12	119.0(3)
C32	C31	C37	119.7(4)	C2	C1	C8	119.4(4)
C36	C31	C32	118.4(4)	C6	C1	C2	118.4(4)
C36	C31	C37	121.9(4)	C6	C1	C8	122.2(4)
C33	C32	C31	120.8(4)	C1	C2	C3	120.9(4)
C34	C33	C32	120.2(4)	C4	C3	C2	119.9(4)
C35	C34	C33	119.6(4)	C5	C4	C3	119.7(4)
C34	C35	C36	120.5(4)	C4	C5	C6	120.3(4)
C31	C36	C35	120.5(4)	C1	C6	C5	120.7(4)
C31	C37	C40	115.6(3)	C8	C7	C12	124.4(4)
C38	C37	C31	123.8(4)	C1	C8	C9	115.4(3)
C38	C37	C40	120.0(3)	C7	C8	C1	124.1(4)
C37	C38	C39	123.7(4)	C7	C8	C9	120.2(3)
N1	C39	C38	113.2(3)	O8	C9	C8	122.4(4)
O5	C40	C37	122.7(4)	O8	C9	C10	122.6(4)
O5	C40	C41	122.7(4)	C8	C9	C10	115.0(3)
C41	C40	C37	114.6(3)	C9	C10	C11	111.7(3)

Table 5 Bond Angles for 3aa

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C40	C41	C42	110.5(3)	C13	C11	C10	112.7(3)
C43	C42	C41	111.4(3)	N2	C12	C7	114.2(3)
C44	C43	C42	125.6(3)	C14	C13	C11	124.9(4)
C44	C43	C45	121.8(3)	C14	C13	C28	122.4(3)
C45	C43	C42	112.6(3)	C28	C13	C11	112.7(3)
N1	C44	C48	117.8(3)	N2	C14	C15	117.7(3)
C43	C44	N1	118.3(3)	C13	C14	N2	118.2(3)
C43	C44	C48	123.9(3)	C13	C14	C15	124.0(3)
O3	C45	C43	112.8(3)	C16	C15	C14	121.1(3)
O4	C45	O3	124.0(3)	C16	C15	C20	118.8(3)
O4	C45	C43	123.1(3)	C20	C15	C14	120.1(4)
O3	C46	C47	106.9(3)	C15	C16	C17	121.3(4)
C49	C48	C44	119.6(3)	C18	C17	C16	119.5(4)
C53	C48	C44	121.3(3)	C19	C18	C17	119.4(4)
C53	C48	C49	119.1(3)	C18	C19	C20	121.2(4)
C50	C49	C48	119.5(4)	C19	C20	C15	119.7(4)
C51	C50	C49	120.9(4)	C22	C21	S2	120.2(3)
C50	C51	C52	119.7(4)	C22	C21	C26	121.1(4)
C51	C52	C53	119.5(4)	C26	C21	S2	118.8(3)
C48	C53	C52	121.2(4)	C21	C22	C23	119.3(4)
C55	C54	S1	118.3(3)	C24	C23	C22	121.3(4)

Table 5 Bond Angles for 3aa

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C59	C54	S1	121.1(3)	C23	C24	C25	117.7(4)
C59	C54	C55	120.5(4)	C23	C24	C27	121.5(4)
C56	C55	C54	118.8(4)	C25	C24	C27	120.9(4)
C55	C56	C57	121.2(4)	C26	C25	C24	122.7(4)
C56	C57	C60	120.1(4)	C25	C26	C21	117.8(4)
C58	C57	C56	118.9(4)	O6	C28	O7	124.0(4)
C58	C57	C60	121.0(4)	O6	C28	C13	122.8(4)
C57	C58	C59	120.2(4)	O7	C28	C13	113.1(4)
C54	C59	C58	120.3(4)	C30	C29	O7	114.7(5)

Table 6 Torsion Angles for 3aa.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	N1	C39	C38	84.2(3)	S2	N2	C12	C7	-81.0(4)
S1	N1	C44	C43	-112.0(3)	S2	N2	C14	C13	117.3(4)
S1	N1	C44	C48	68.8(4)	S2	N2	C14	C15	-65.4(4)
S1	C54	C55	C56	177.4(3)	S2	C21	C22	C23	179.8(3)
S1	C54	C59	C58	-177.8(3)	S2	C21	C26	C25	-178.8(3)
O1	S1	N1	C39	-31.0(3)	O8	C9	C10	C11	118.9(4)
O1	S1	N1	C44	165.5(3)	O9	S2	N2	C12	162.3(3)
O1	S1	C54	C55	35.0(3)	O9	S2	N2	C14	-31.6(3)
O1	S1	C54	C59	-146.8(3)	O9	S2	C21	C22	14.4(4)

Table 6 Torsion Angles for 3aa.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O2	S1	N1	C39	-160.5(3)	O9	S2	C21	C26	-165.2(3)
O2	S1	N1	C44	36.1(3)	O10	S2	N2	C12	32.8(3)
O2	S1	C54	C55	167.4(3)	O10	S2	N2	C14	-161.1(3)
O2	S1	C54	C59	-14.3(4)	O10	S2	C21	C22	146.3(3)
O5	C40	C41	C42	-113.1(4)	O10	S2	C21	C26	-33.3(3)
N1	S1	C54	C55	-78.3(3)	N2	S2	C21	C22	-100.6(3)
N1	S1	C54	C59	99.9(3)	N2	S2	C21	C26	79.8(3)
N1	C44	C48	C49	43.1(5)	N2	C14	C15	C16	140.1(4)
N1	C44	C48	C53	-137.1(4)	N2	C14	C15	C20	-42.2(5)
C31	C32	C33	C34	-0.7(7)	C1	C2	C3	C4	-1.4(7)
C31	C37	C38	C39	-172.4(4)	C1	C8	C9	O8	106.4(4)
C31	C37	C40	O5	-116.2(4)	C1	C8	C9	C10	-74.2(4)
C31	C37	C40	C41	66.2(4)	C2	C1	C6	C5	-0.2(7)
C32	C31	C36	C35	-1.6(6)	C2	C1	C8	C7	145.1(4)
C32	C31	C37	C38	-149.7(4)	C2	C1	C8	C9	-41.0(5)
C32	C31	C37	C40	39.5(5)	C2	C3	C4	C5	0.8(7)
C32	C33	C34	C35	-0.4(7)	C3	C4	C5	C6	0.1(7)
C33	C34	C35	C36	0.5(7)	C4	C5	C6	C1	-0.4(7)
C34	C35	C36	C31	0.6(7)	C6	C1	C2	C3	1.1(6)
C36	C31	C32	C33	1.7(6)	C6	C1	C8	C7	-35.8(6)
C36	C31	C37	C38	33.1(6)	C6	C1	C8	C9	138.1(4)

Table 6 Torsion Angles for 3aa.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C36	C31	C37	C40	-137.7(4)	C7	C8	C9	O8	-79.5(5)
C37	C31	C32	C33	-175.5(4)	C7	C8	C9	C10	99.9(4)
C37	C31	C36	C35	175.5(4)	C8	C1	C2	C3	-179.8(4)
C37	C38	C39	N1	85.3(5)	C8	C1	C6	C5	-179.3(4)
C37	C40	C41	C42	64.5(4)	C8	C7	C12	N2	-90.4(5)
C38	C37	C40	O5	72.7(5)	C8	C9	C10	C11	-60.5(4)
C38	C37	C40	C41	-105.0(4)	C9	C10	C11	C13	-69.7(4)
C39	N1	C44	C43	84.7(4)	C10	C11	C13	C14	112.1(4)
C39	N1	C44	C48	-94.6(4)	C10	C11	C13	C28	-67.9(4)
C40	C37	C38	C39	-2.0(6)	C11	C13	C14	N2	-11.4(6)
C40	C41	C42	C43	66.6(4)	C11	C13	C14	C15	171.4(4)
C41	C42	C43	C44	-107.0(4)	C11	C13	C28	O6	-41.9(6)
C41	C42	C43	C45	73.0(4)	C11	C13	C28	O7	134.0(4)
C42	C43	C44	N1	5.9(6)	C12	N2	C14	C13	-76.7(4)
C42	C43	C44	C48	-175.0(3)	C12	N2	C14	C15	100.7(4)
C42	C43	C45	O3	-128.5(3)	C12	C7	C8	C1	176.6(4)
C42	C43	C45	O4	49.1(5)	C12	C7	C8	C9	3.0(6)
C43	C44	C48	C49	-136.1(4)	C13	C14	C15	C16	-42.8(6)
C43	C44	C48	C53	43.7(5)	C13	C14	C15	C20	134.9(4)
C44	N1	C39	C38	-112.3(4)	C14	N2	C12	C7	112.5(4)
C44	C43	C45	O3	51.5(5)	C14	C13	C28	O6	138.1(4)

Table 6 Torsion Angles for 3aa.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C44	C43	C45	O4	-130.9(4)	C14	C13	C28	O7	-46.0(6)
C44	C48	C49	C50	176.9(3)	C14	C15	C16	C17	176.4(4)
C44	C48	C53	C52	-177.0(4)	C14	C15	C20	C19	-175.6(3)
C45	O3	C46	C47	168.5(3)	C15	C16	C17	C18	-0.4(6)
C45	C43	C44	N1	-174.1(3)	C16	C15	C20	C19	2.2(6)
C45	C43	C44	C48	5.1(6)	C16	C17	C18	C19	1.3(6)
C46	O3	C45	O4	7.0(5)	C17	C18	C19	C20	-0.4(6)
C46	O3	C45	C43	-175.4(3)	C18	C19	C20	C15	-1.4(6)
C48	C49	C50	C51	0.5(6)	C20	C15	C16	C17	-1.3(6)
C49	C48	C53	C52	2.8(6)	C21	S2	N2	C12	-81.7(3)
C49	C50	C51	C52	1.9(6)	C21	S2	N2	C14	84.4(3)
C50	C51	C52	C53	-2.0(6)	C21	C22	C23	C24	-1.4(6)
C51	C52	C53	C48	-0.4(6)	C22	C21	C26	C25	1.6(6)
C53	C48	C49	C50	-2.9(5)	C22	C23	C24	C25	2.3(6)
C54	S1	N1	C39	84.2(3)	C22	C23	C24	C27	-178.9(4)
C54	S1	N1	C44	-79.2(3)	C23	C24	C25	C26	-1.3(6)
C54	C55	C56	C57	0.2(6)	C24	C25	C26	C21	-0.6(6)
C55	C54	C59	C58	0.4(6)	C26	C21	C22	C23	-0.6(6)
C55	C56	C57	C58	1.1(6)	C27	C24	C25	C26	179.9(4)
C55	C56	C57	C60	-179.2(4)	C28	O7	C29	C30	-142.0(8)
C56	C57	C58	C59	-1.5(6)	C28	C13	C14	N2	168.6(4)

Table 6 Torsion Angles for 3aa.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C57	C58	C59	C54	0.8(6)	C28	C13	C14	C15	-8.6(6)
C59	C54	C55	C56	-0.9(6)	C29	O7	C28	O6	-7.0(7)
C60	C57	C58	C59	178.7(4)	C29	O7	C28	C13	177.1(5)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3aa.

Atom	*x*	*y*	*z*	U(eq)
H32	4314.93	5213.69	2027.22	49
H33	6663.69	5043.8	2496.52	56
H34	8693.7	5447.74	2004.65	58
H35	8362.09	6010.2	1037.63	56
H36	6012.73	6186.36	561.54	47
H38	3366.77	5579.49	42.89	40
H39A	972.64	5744.6	-359.65	38
H39B	704.22	5979.33	353.97	38
H41A	4498.1	7422.9	2056.34	42
H41B	2959.48	7610.1	2191.72	42
H42A	4143.13	8776.88	1599.38	40
H42B	3932.61	7889.38	1010.47	40
H46A	-648.46	9577.51	2011.85	50
H46B	-211.02	8986.36	2556.59	50

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3aa.

Atom	*x*	*y*	*z*	U(eq)
H47A	-2859.03	8330.78	1551.44	68
H47B	-2834.91	8696.79	2294.35	68
H47C	-2410.81	7699.82	2064.49	68
H49	-1418.85	6587.34	-246.7	39
H50	-3788.64	6848.33	-603.71	46
H51	-4203.95	8400.93	-349.12	48
H52	-2201.76	9741.16	223.52	47
H53	165.58	9484.08	583.7	41
H55	389.33	5928.09	-1506.61	44
H56	-1799.09	5668.48	-2300.63	50
H58	-1677.38	8554.29	-1864.82	49
H59	493.01	8813.64	-1059.82	47
H60A	-3424.23	6393.42	-3039.78	79
H60B	-3480.73	7498.58	-2822.14	79
H60C	-4284.93	6675.49	-2490.38	79
H2	6726.52	9662.38	3391.54	46
H3	4440.86	9998.04	2994.76	56
H4	2421.3	9579	3489.83	59
H5	2712.07	8867.13	4396.72	61
H6	5017.38	8568.81	4811.18	54
H7	7704.7	9203.78	5338.75	42

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3aa.

Atom	*x*	*y*	*z*	U(eq)
H10A	8202.93	7217.19	3215.94	45
H10B	6620.04	7328.03	3338.42	45
H11A	7317.16	6976.37	4411.99	43
H11B	7107.06	6067.81	3838.94	43
H12A	10366.45	8864.23	4983.93	40
H12B	10188.19	9165.78	5706.21	40
H16	11052.36	5376.82	4814.69	40
H17	13394.76	5099.08	5186.71	48
H18	15391.82	6420.25	5791.38	48
H19	14991.28	7983.35	6045.19	46
H20	12641.11	8256.44	5699.06	41
H22	10970.85	6345.61	6623.5	47
H23	13077.37	6801.34	7484.74	50
H25	12798.69	9606.97	7728.82	49
H26	10655.33	9175.47	6894.03	43
H27A	15421.38	8927.09	8088.94	71
H27B	14819	7983.67	8364.74	71
H27C	14399.29	8978.47	8605.05	71
H29A	11493.21	5406.31	3218.88	153
H29B	11915.18	6367.84	2938.38	153
H30A	13892.85	5734.9	3237.55	193

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3aa.

Atom	*x*	*y*	*z*	U(eq)
H30B	13724.27	5973.45	3966.98	193
H30C	14144.33	6839.48	3597.37	193

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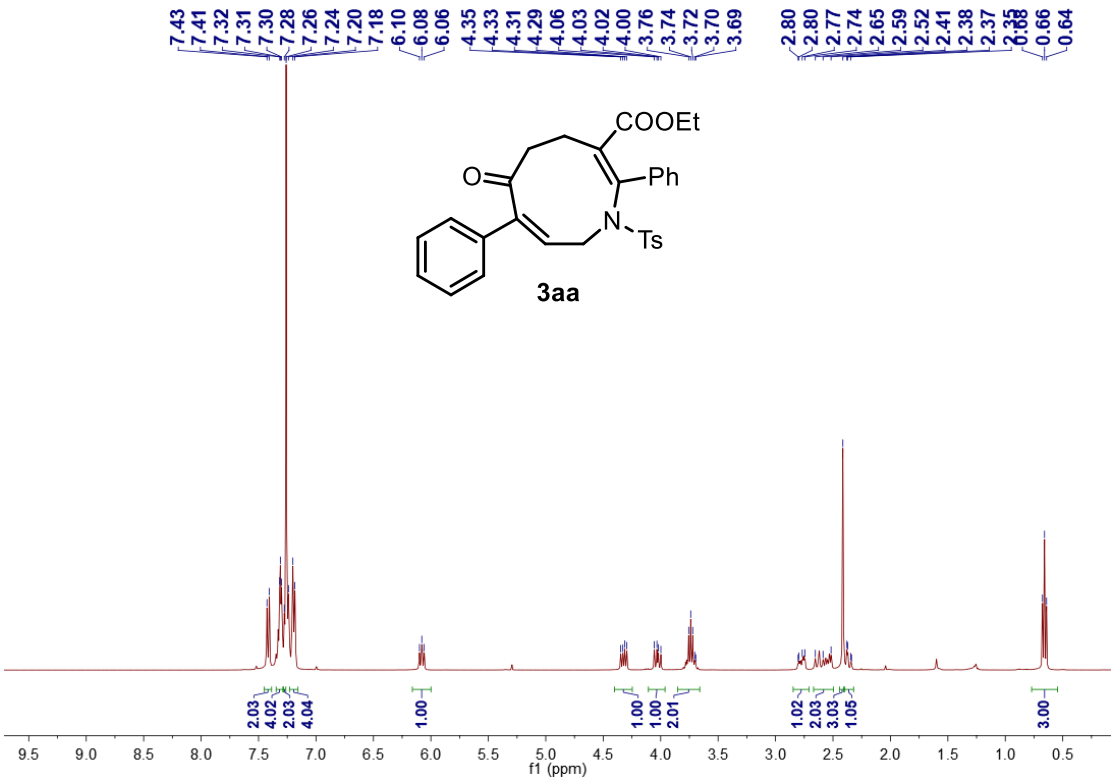
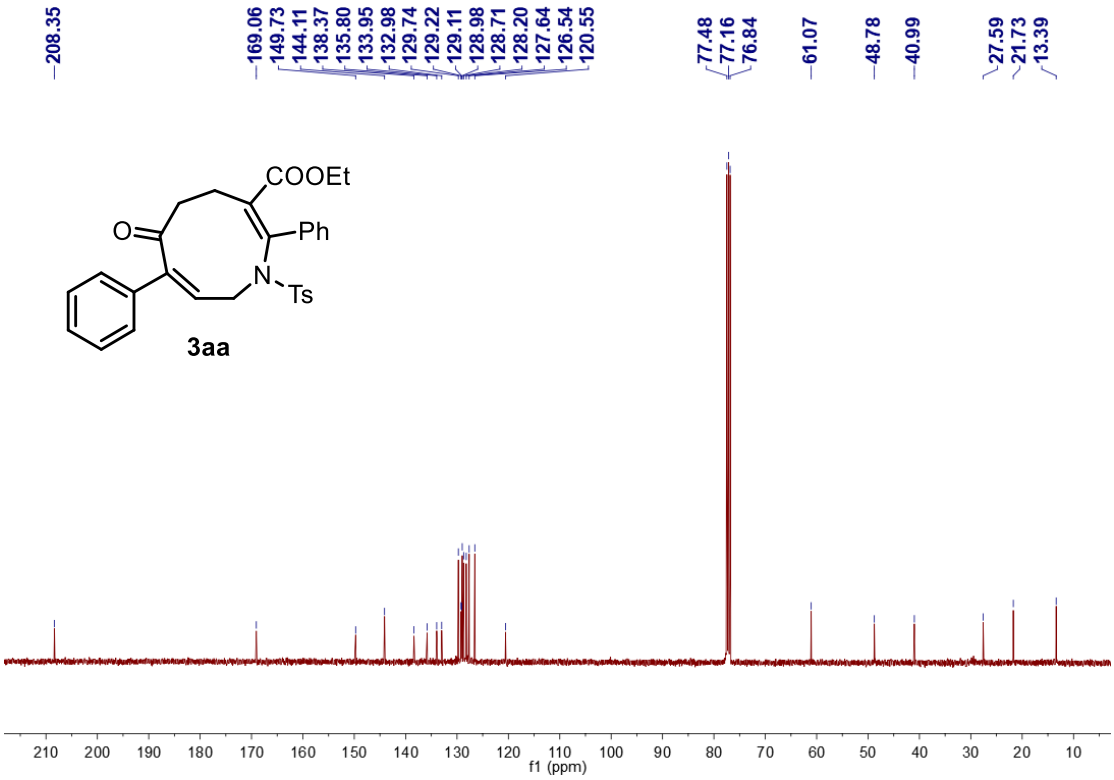
Characterization spectra of all the new products

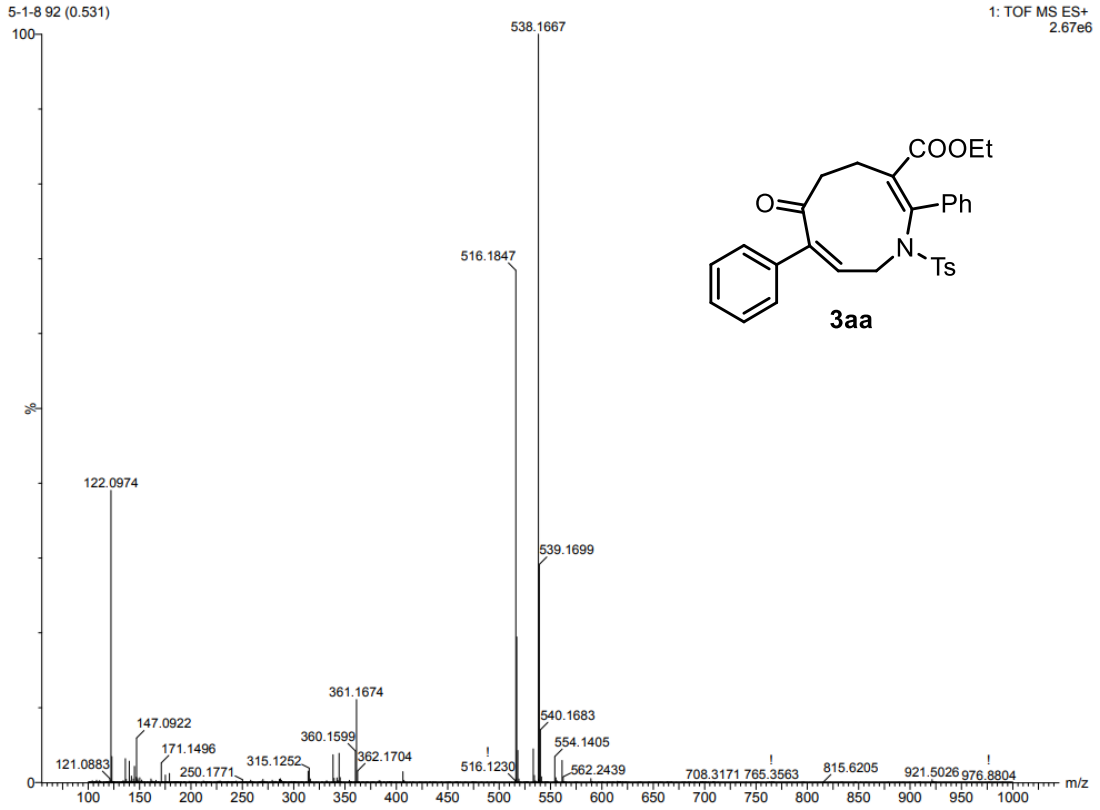
^{1}H NMR (400 MHz, $CDCl_3$) of **3aa**



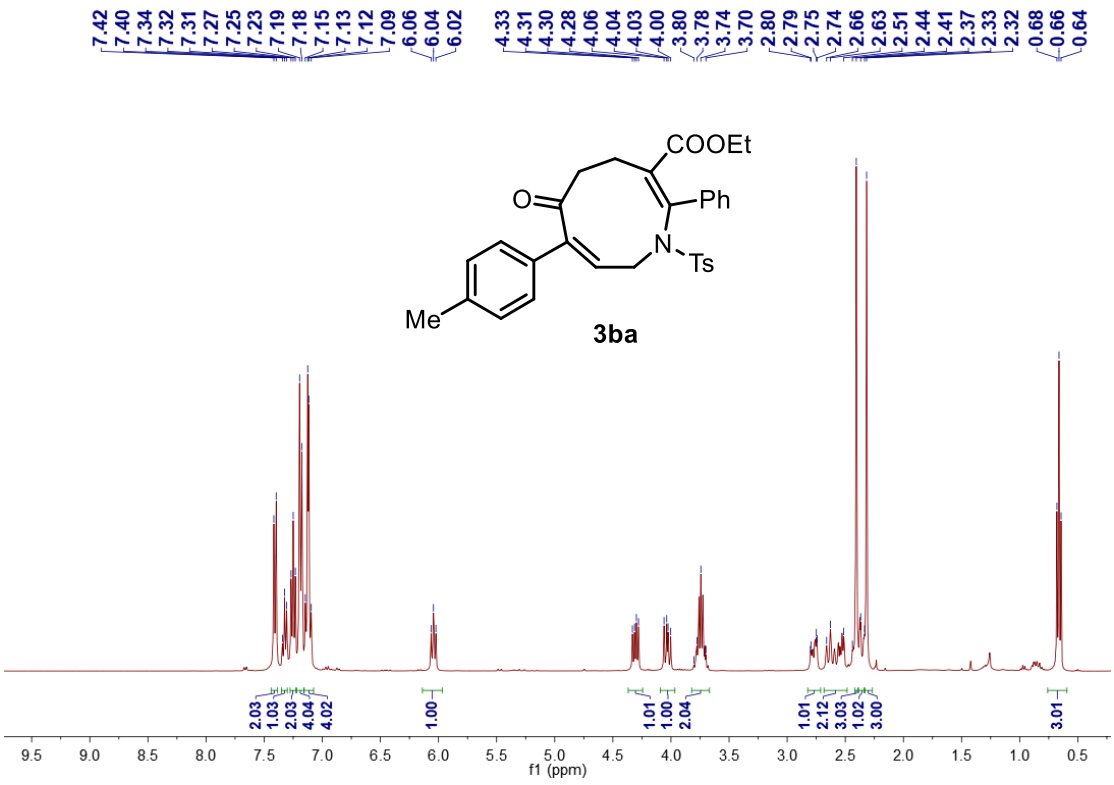
^{13}C NMR (100 MHz, $CDCl_3$) of **3aa**



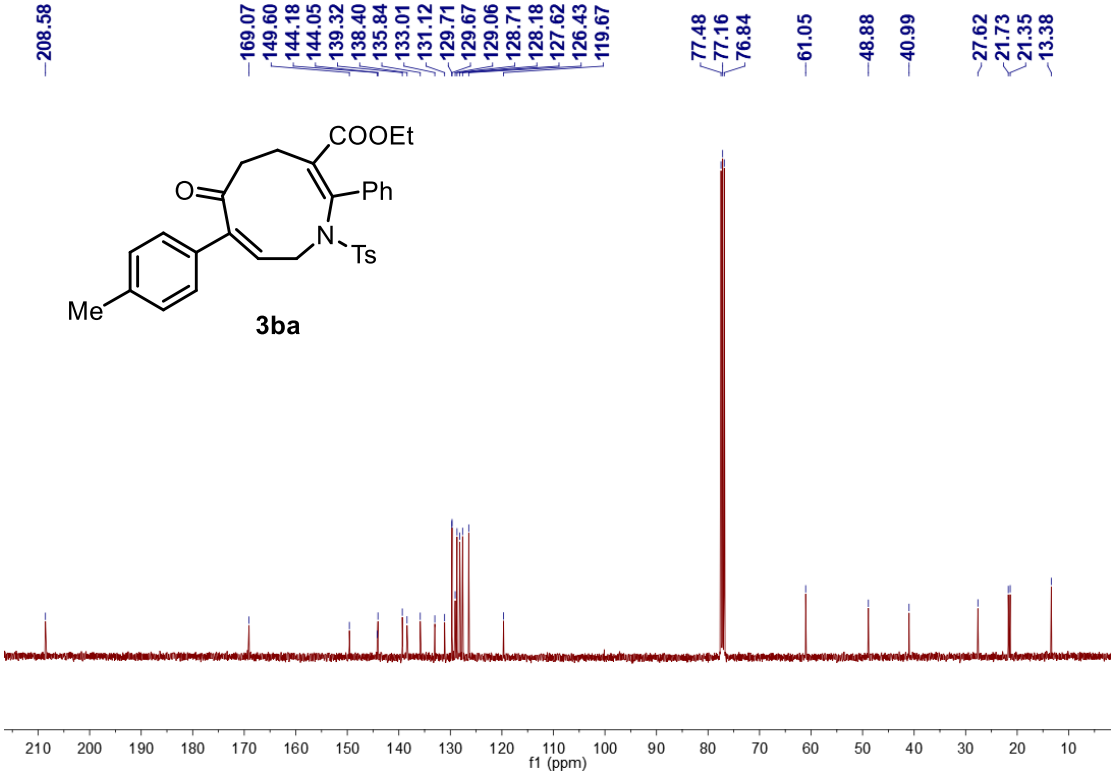
HRMS of **3aa**



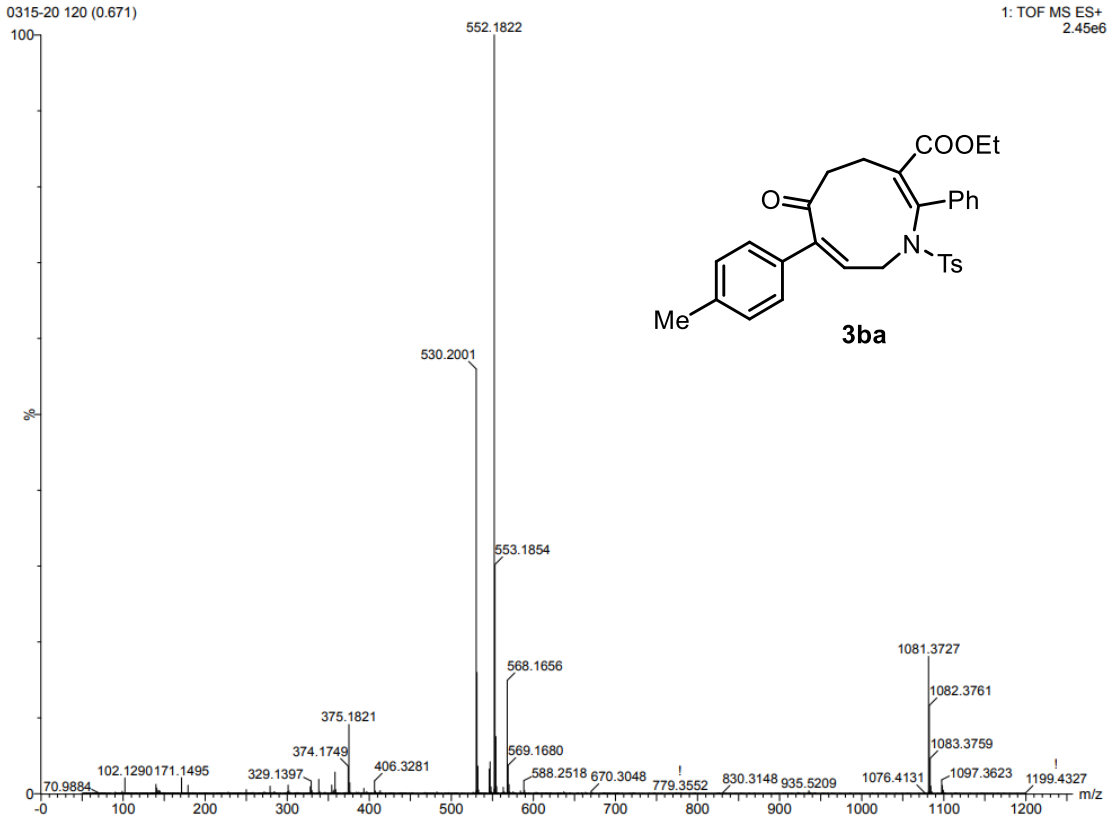
^{1}H NMR (400 MHz, $CDCl_3$) of **3ba**



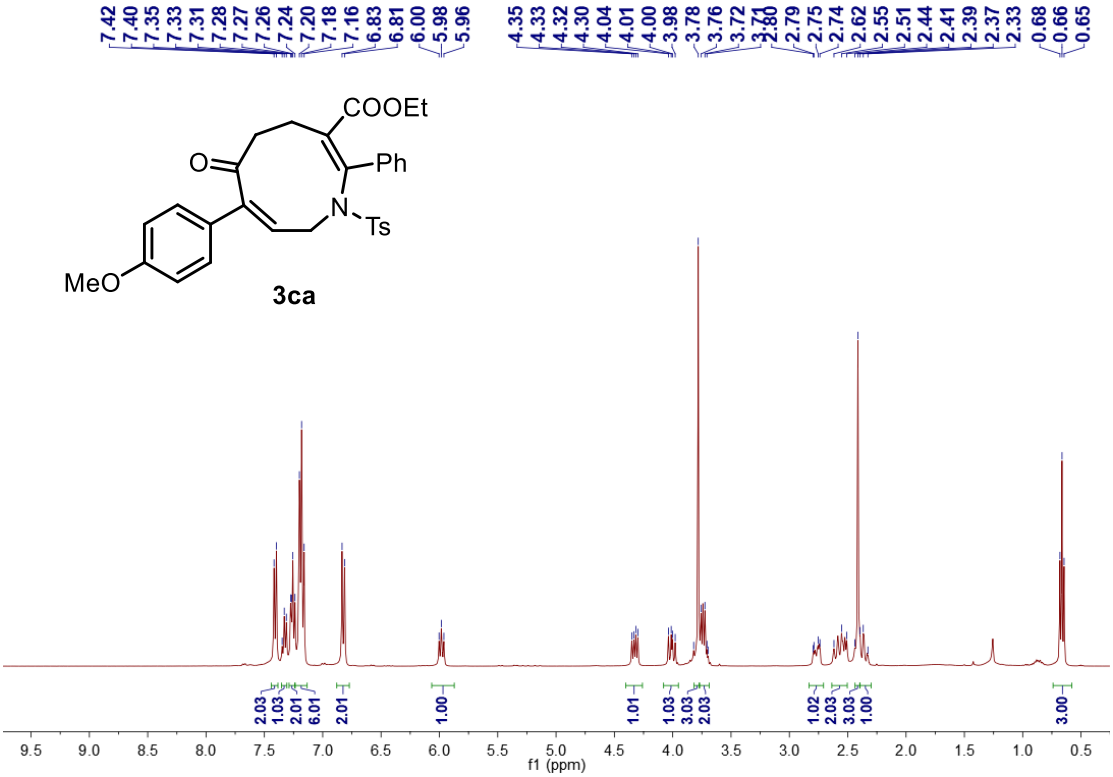
^{13}C NMR (100 MHz, $CDCl_3$) of **3ba**



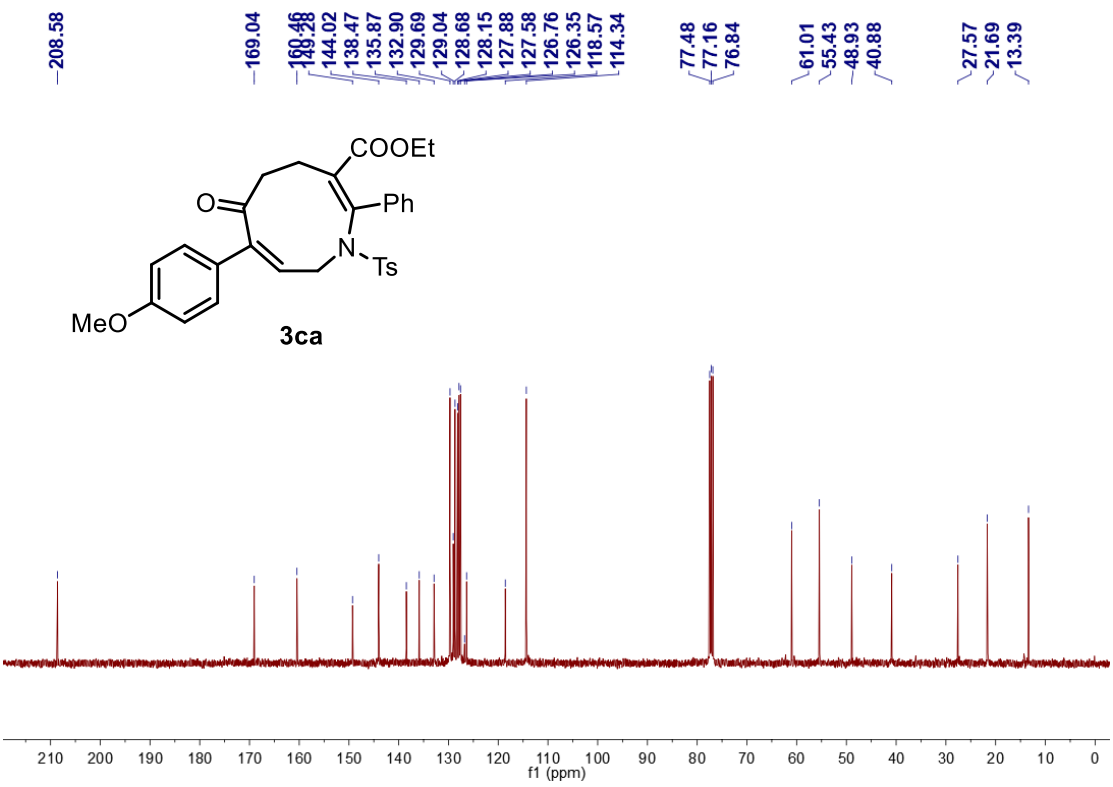
HRMS of **3ba**



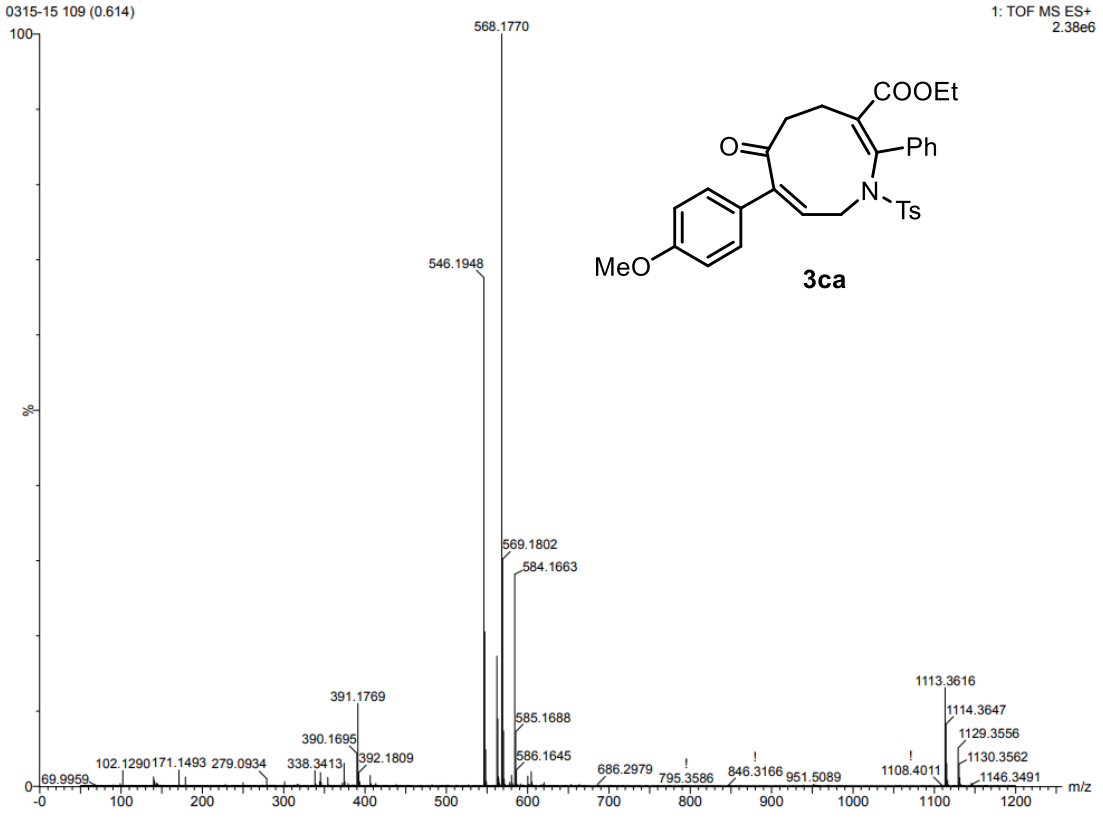
^{1}H NMR (400 MHz, $CDCl_3$) of **3ca**



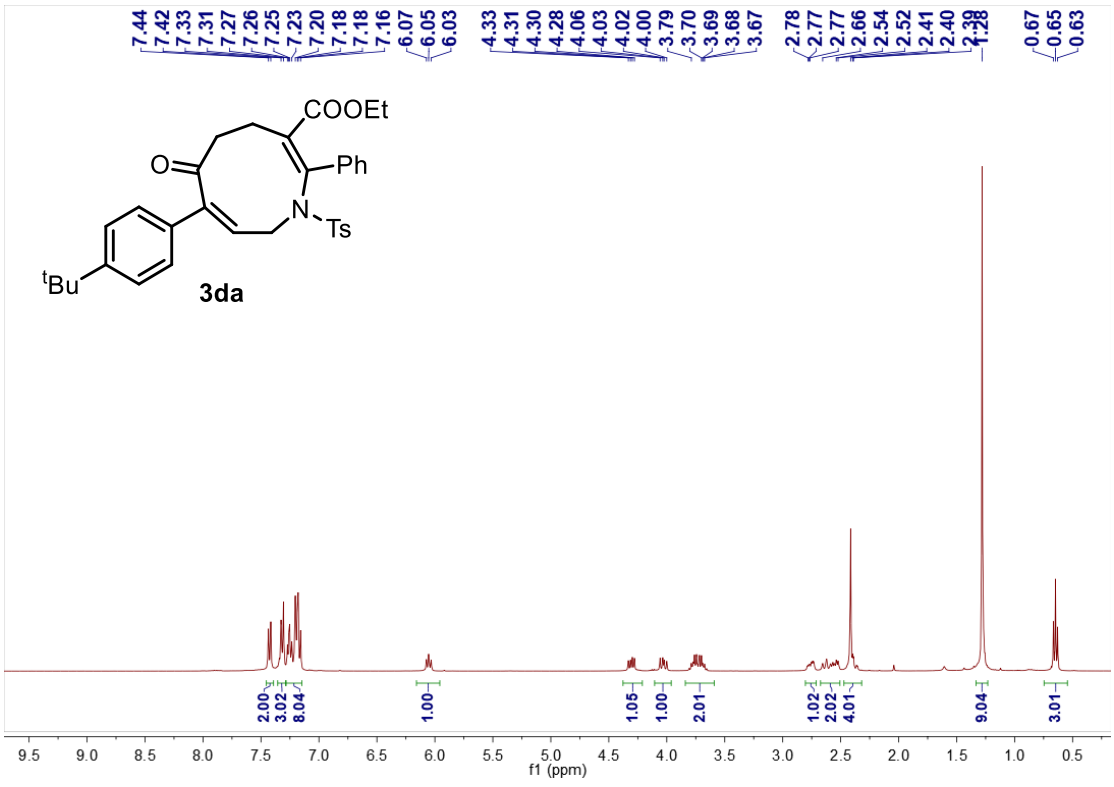
^{13}C NMR (100 MHz, $CDCl_3$) of **3ca**



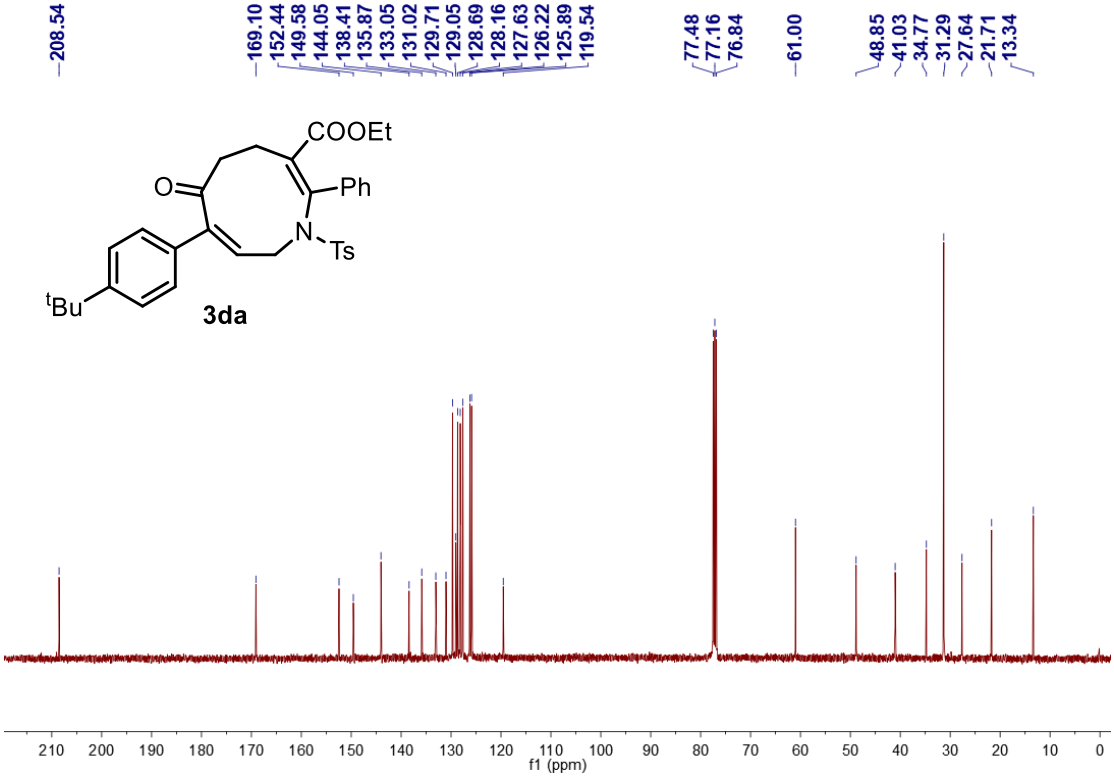
HRMS of **3ca**



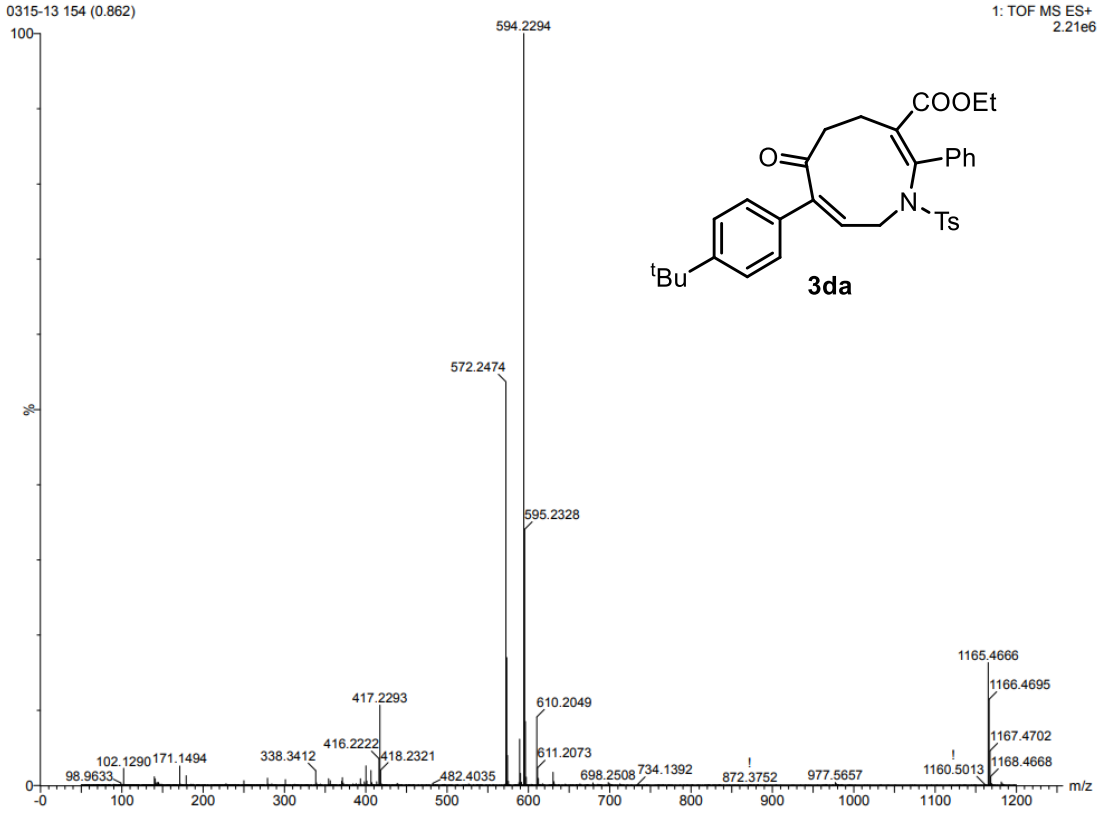
^{1}H NMR (400 MHz, $CDCl_3$) of **3da**



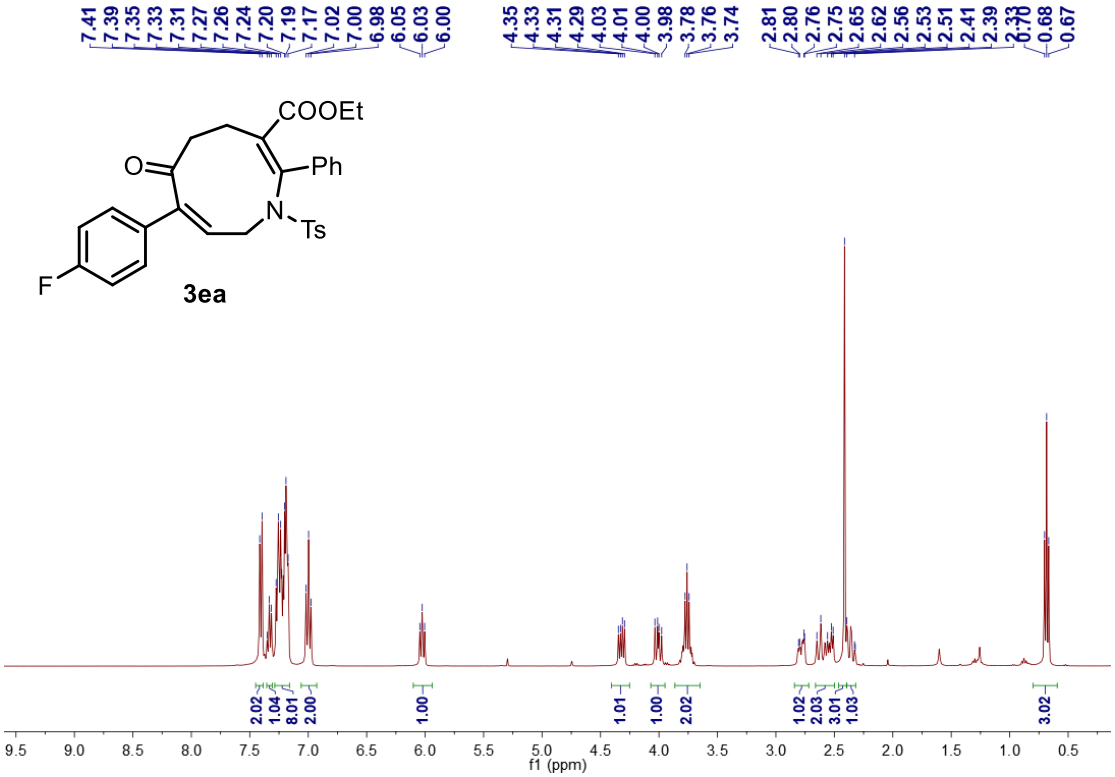
^{13}C NMR (100 MHz, $CDCl_3$) of **3da**



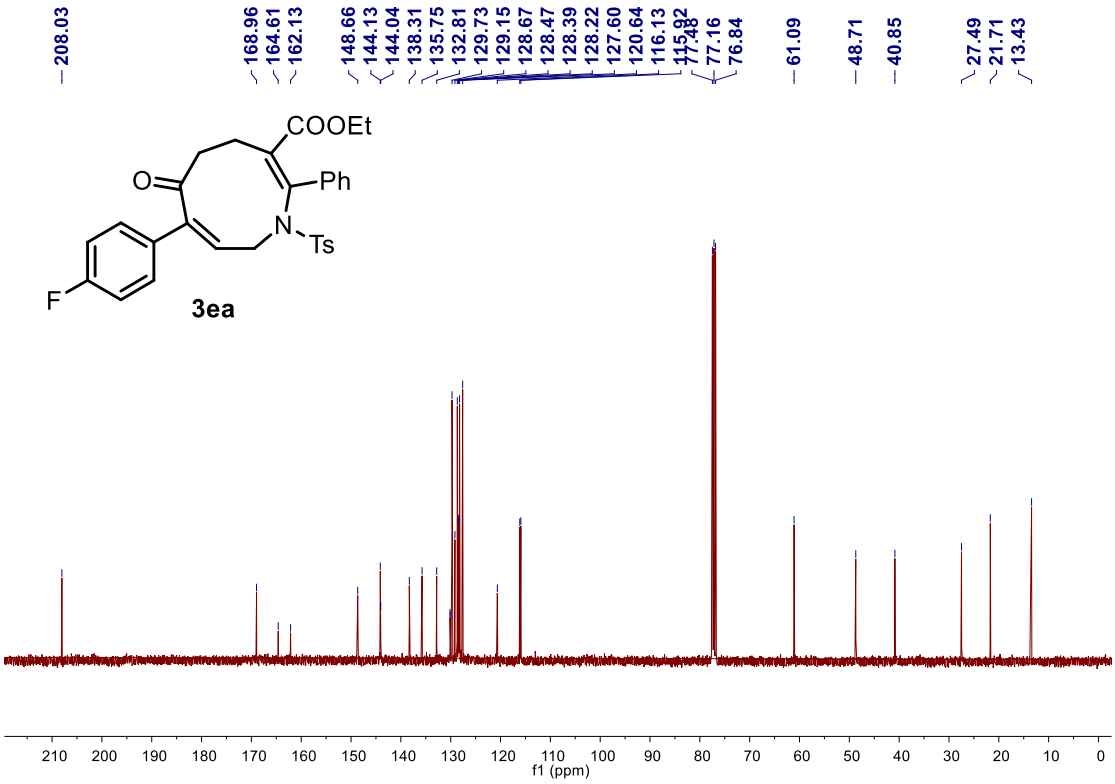
HRMS of **3da**



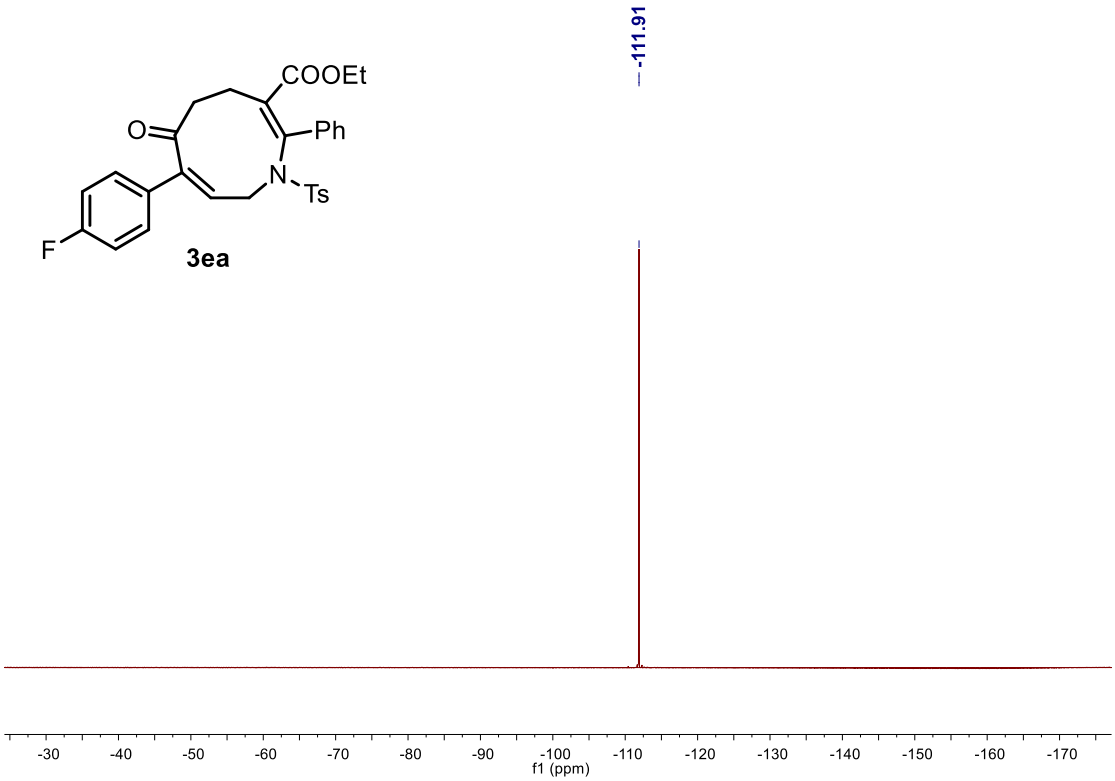
^{1}H NMR (400 MHz, $CDCl_3$) of **3ea**



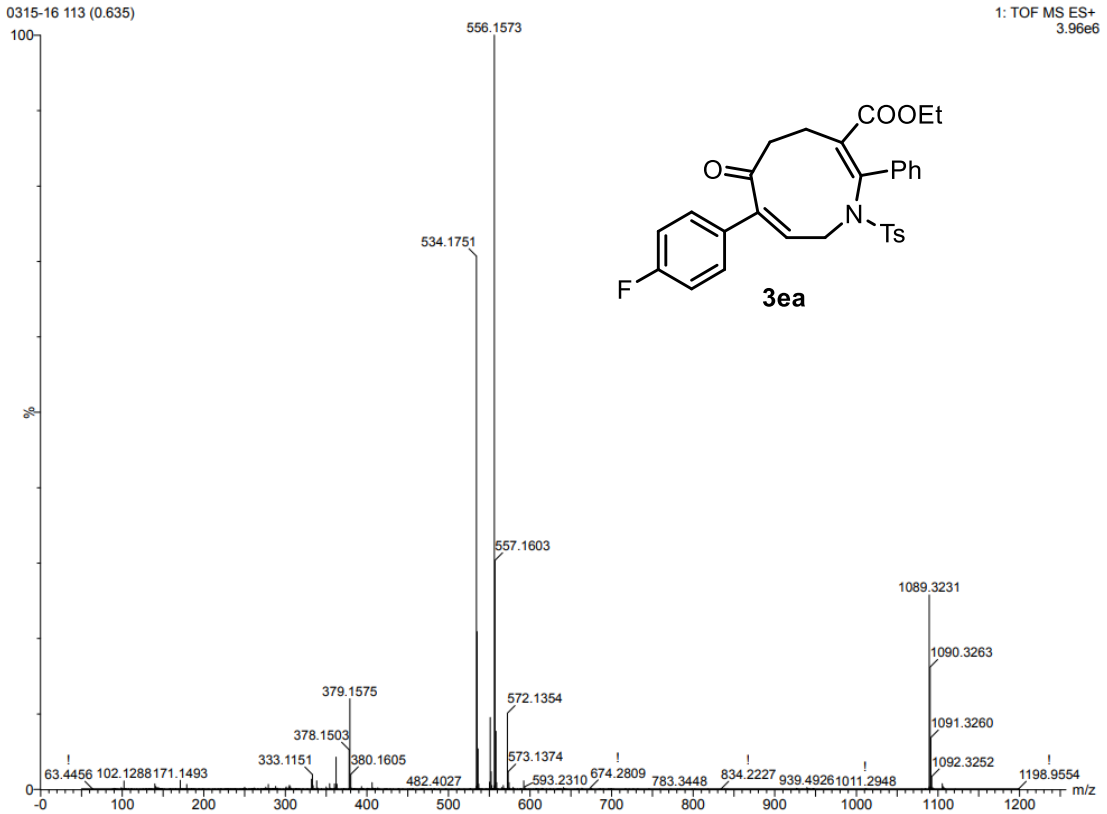
^{13}C NMR (100 MHz, $CDCl_3$) of **3ea**



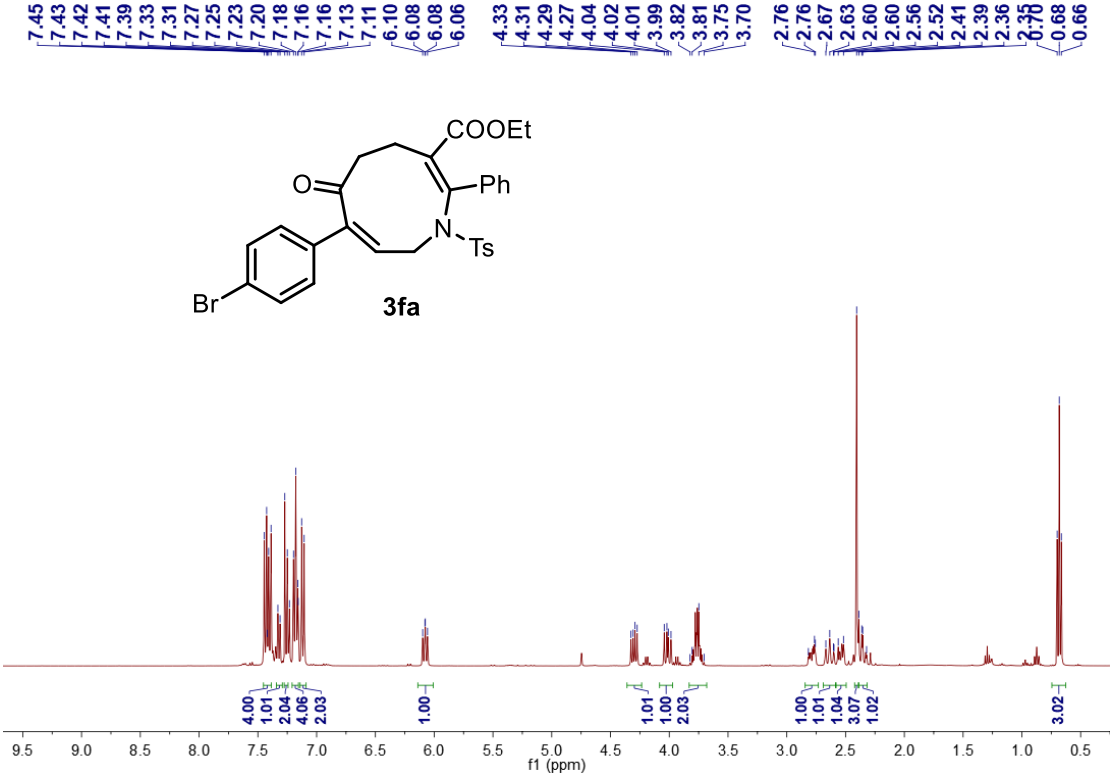
^{19}F NMR (376 MHz, $CDCl_3$) of **3ea**



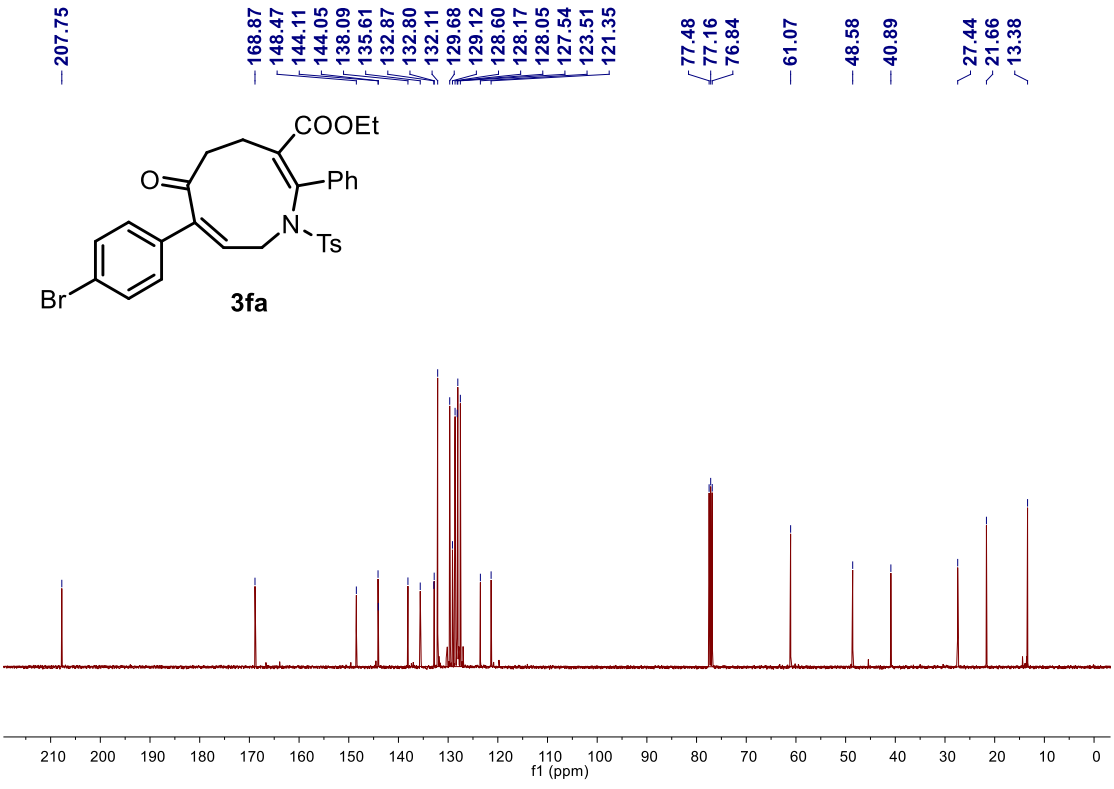
HRMS of **3ea**



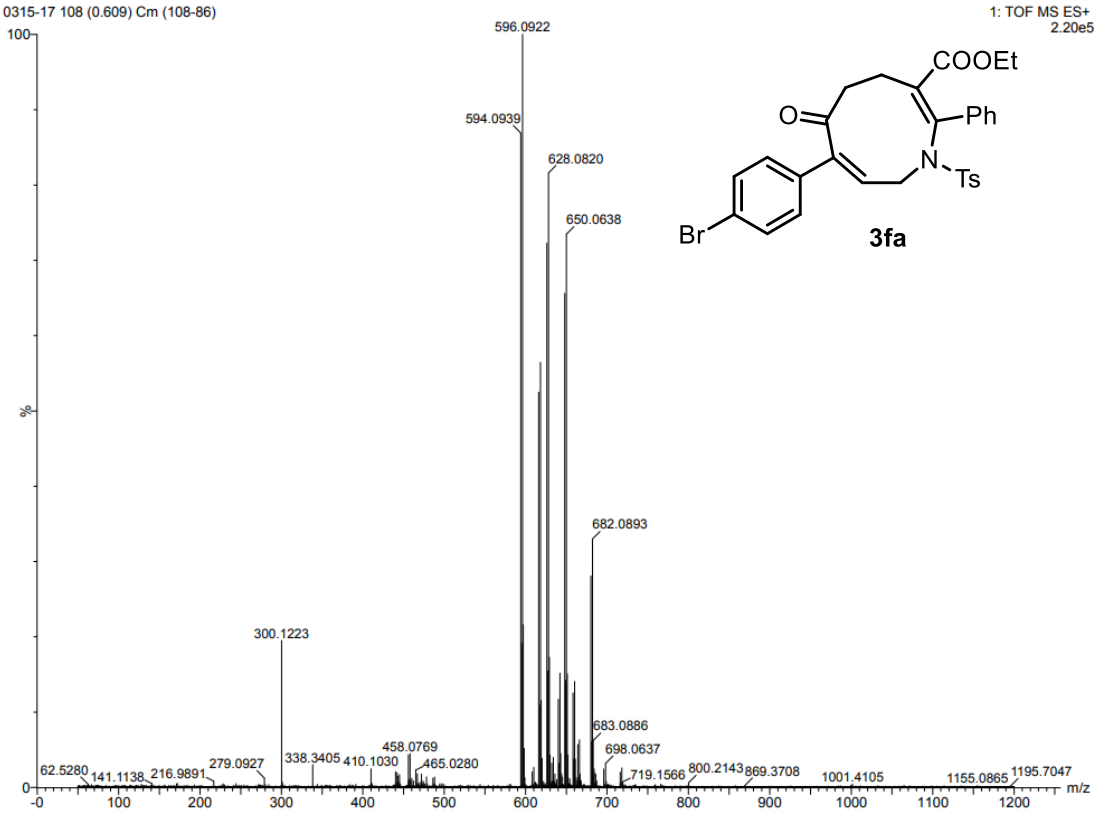
^{1}H NMR (400 MHz, $CDCl_3$) of **3fa**



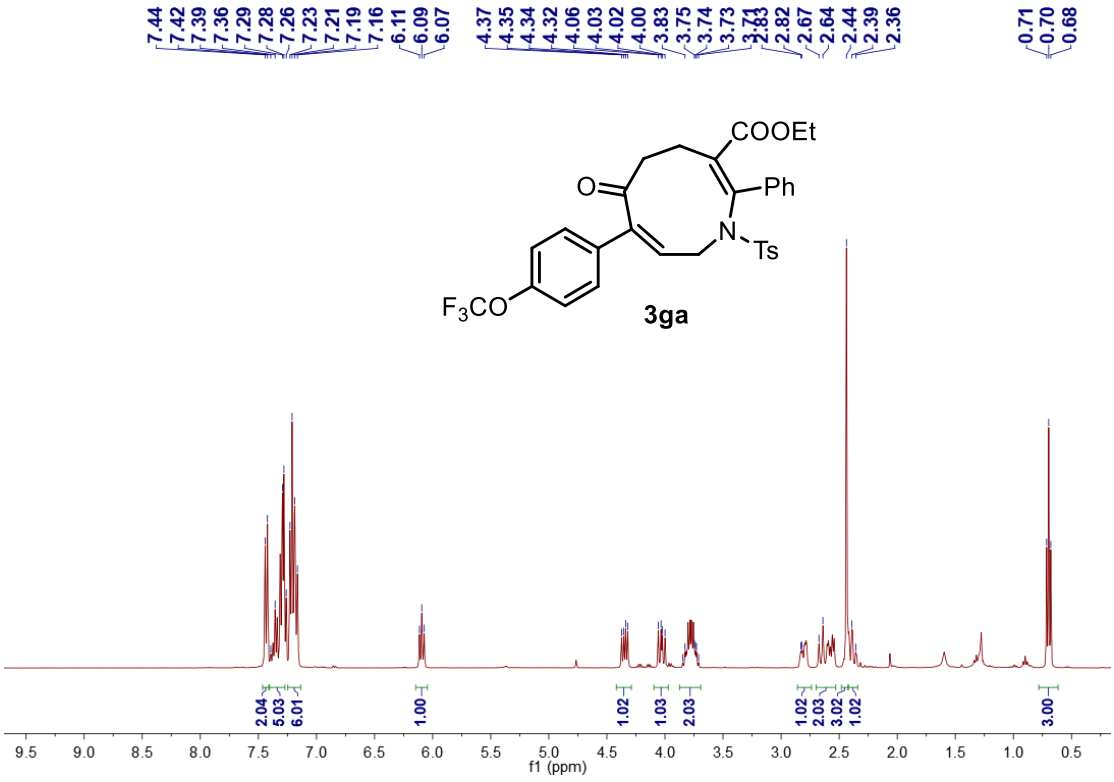
^{13}C NMR (100 MHz, $CDCl_3$) of **3fa**



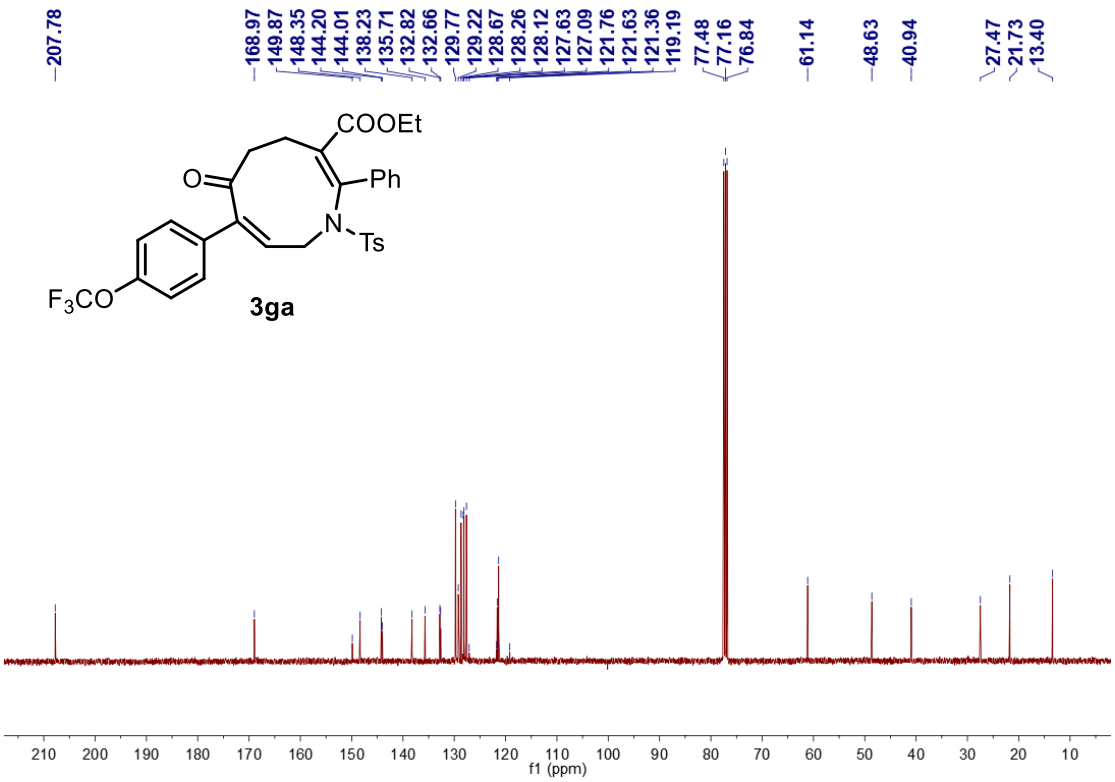
HRMS of **3fa**



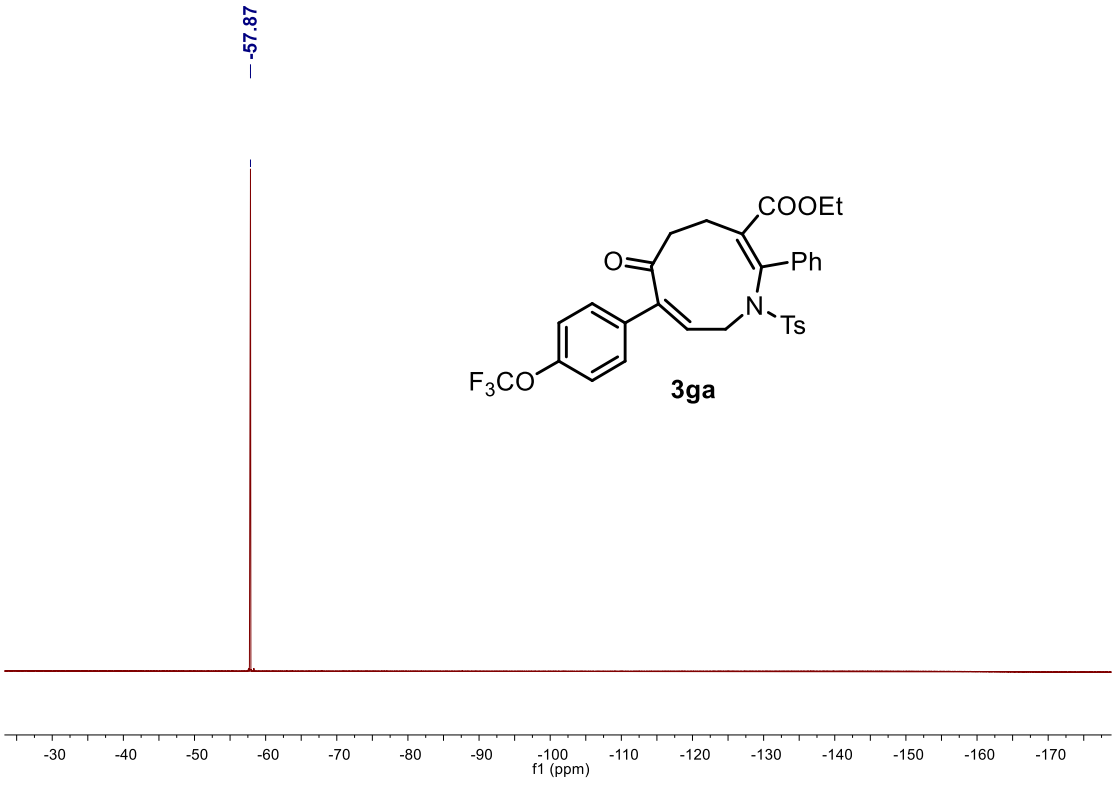
^{1}H NMR (400 MHz, $CDCl_3$) of **3ga**



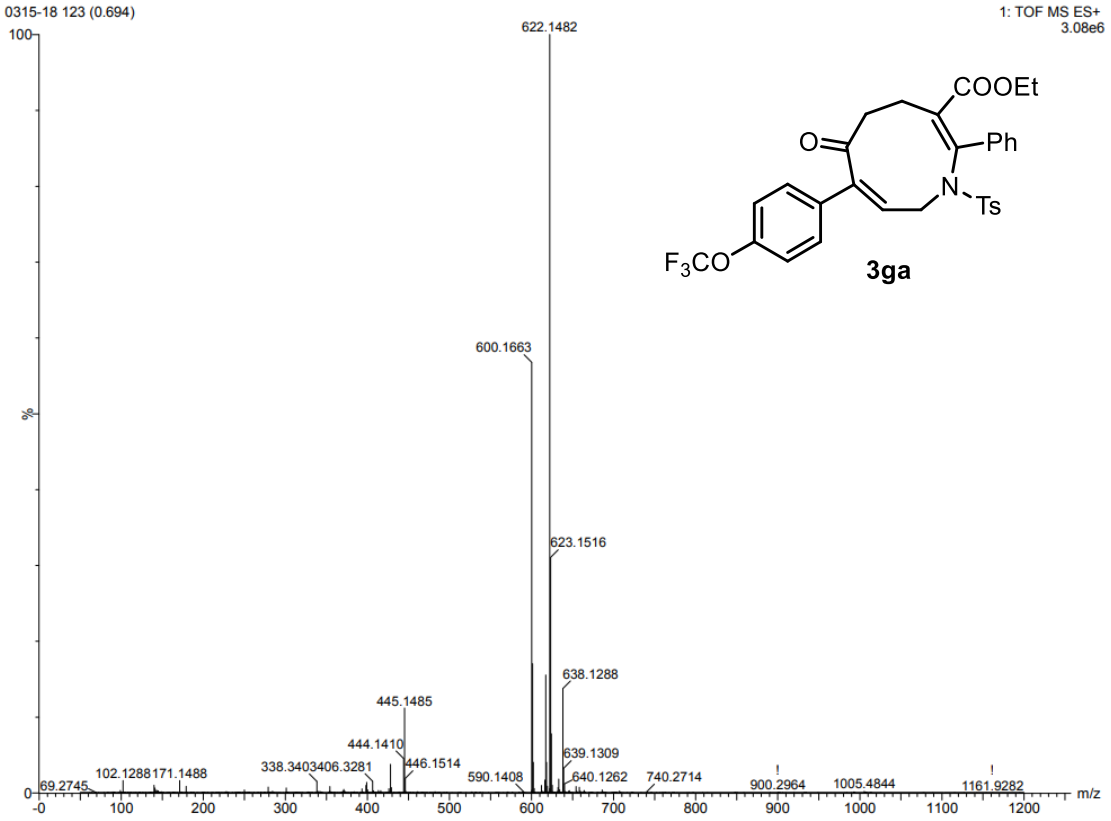
^{13}C NMR (100 MHz, $CDCl_3$) of **3ga**



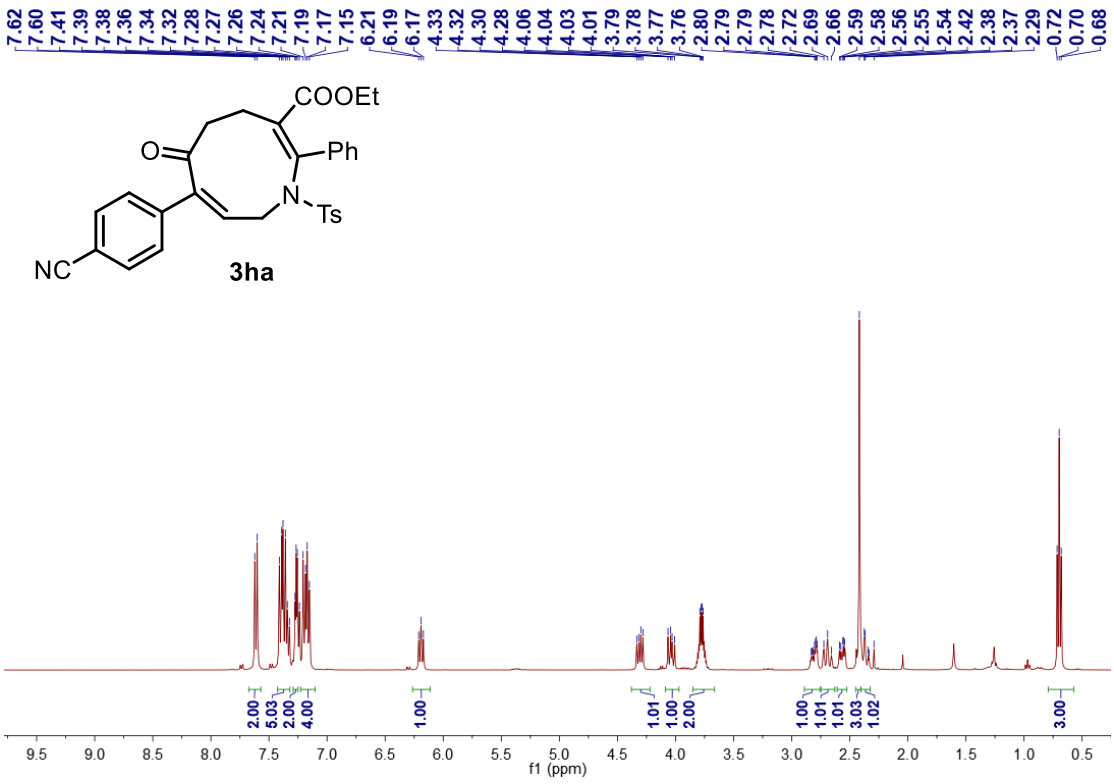
^{19}F NMR (376 MHz, $CDCl_3$) of **3ga**



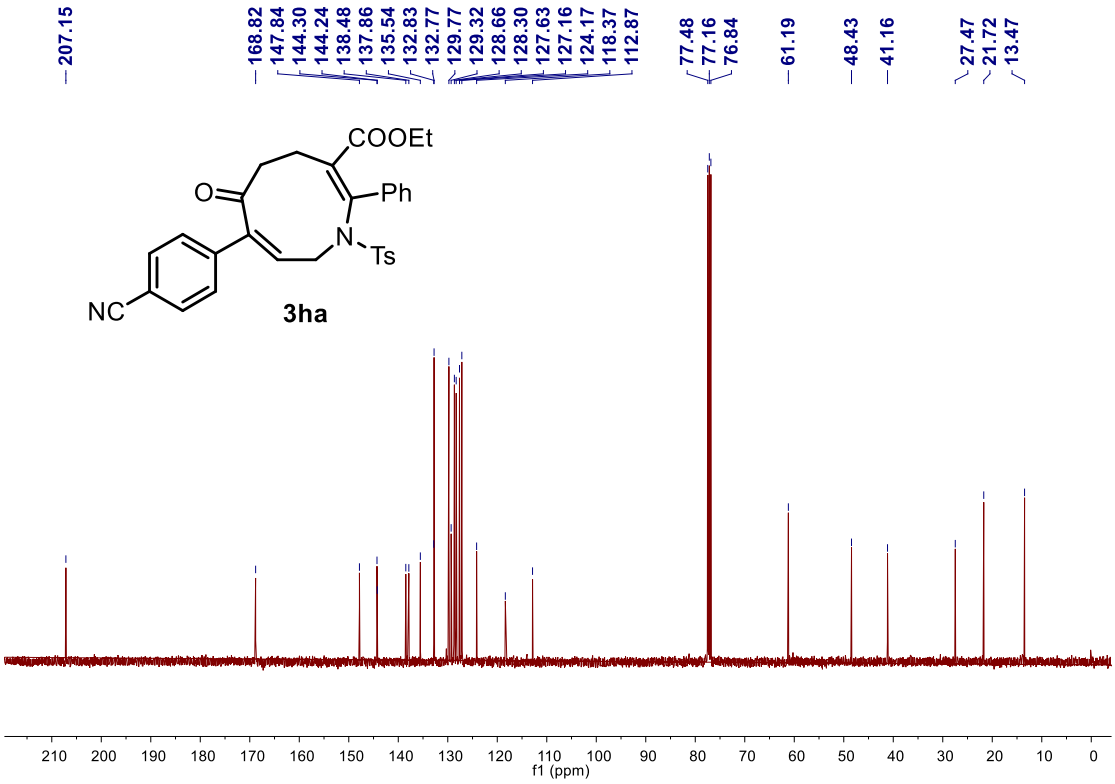
HRMS of **3ga**



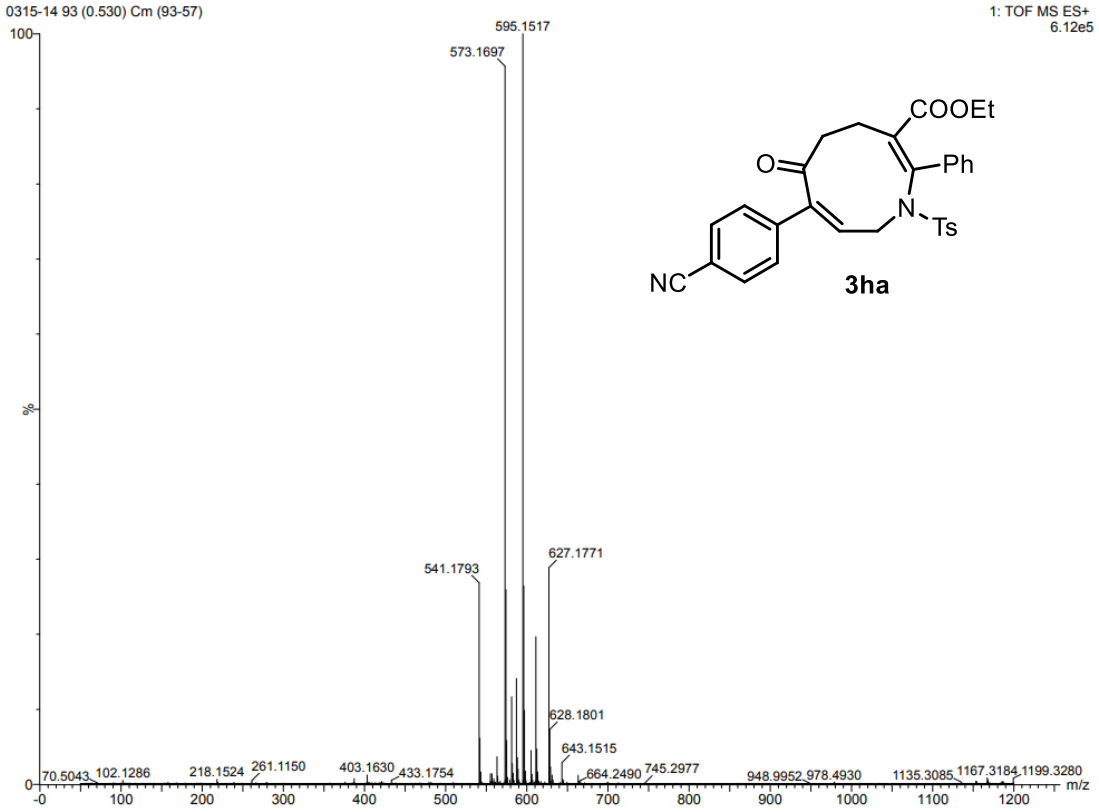
^{1}H NMR (400 MHz, $CDCl_3$) of **3ha**



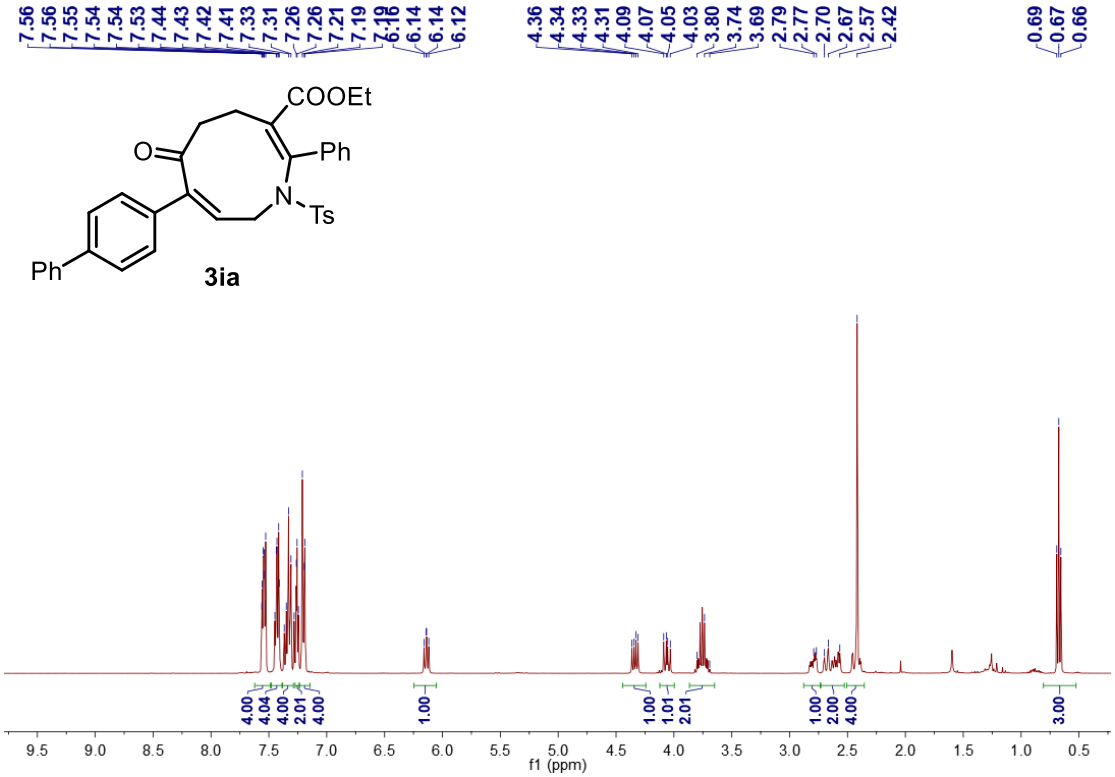
^{13}C NMR (100 MHz, $CDCl_3$) of **3ha**



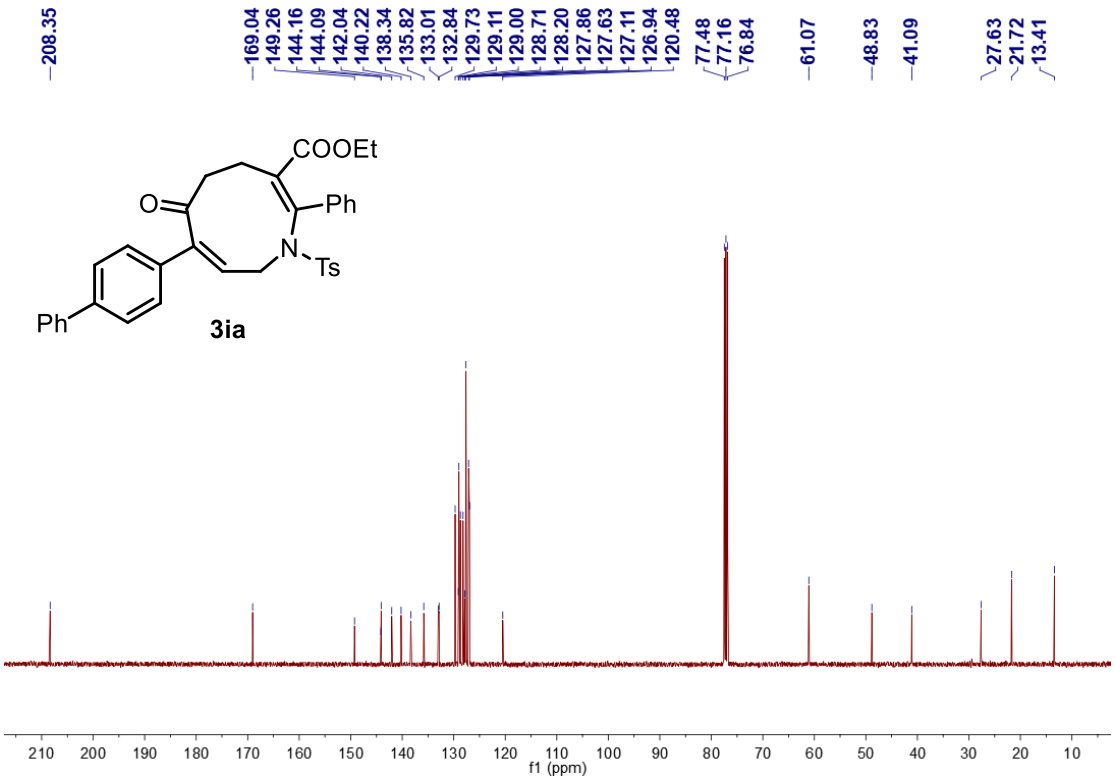
HRMS of **3ha**



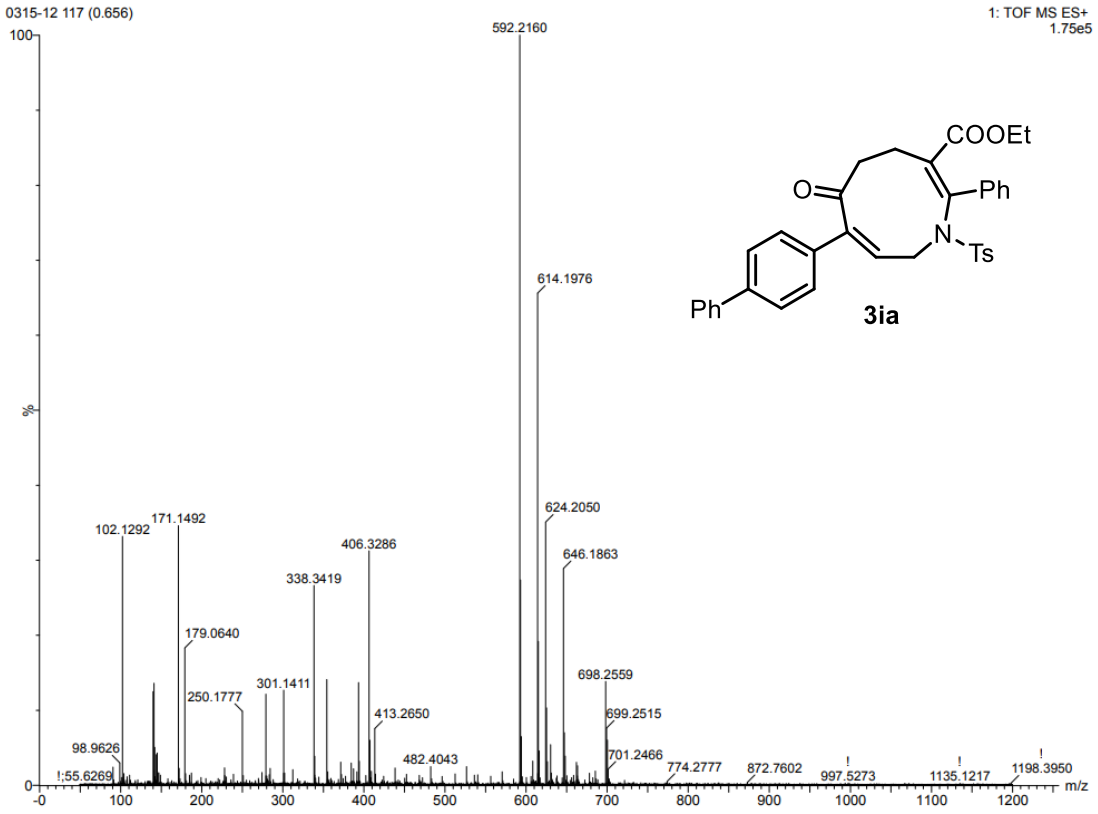
^{1}H NMR (400 MHz, $CDCl_3$) of **3ia**



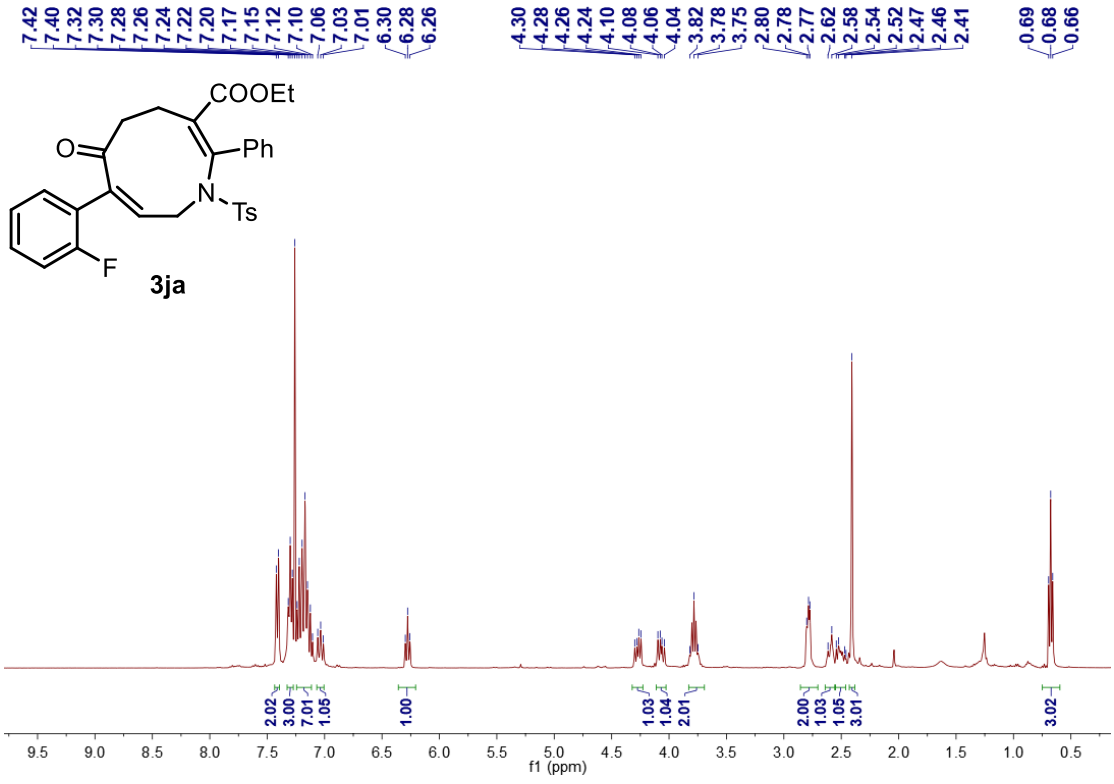
^{13}C NMR (100 MHz, $CDCl_3$) of **3ia**



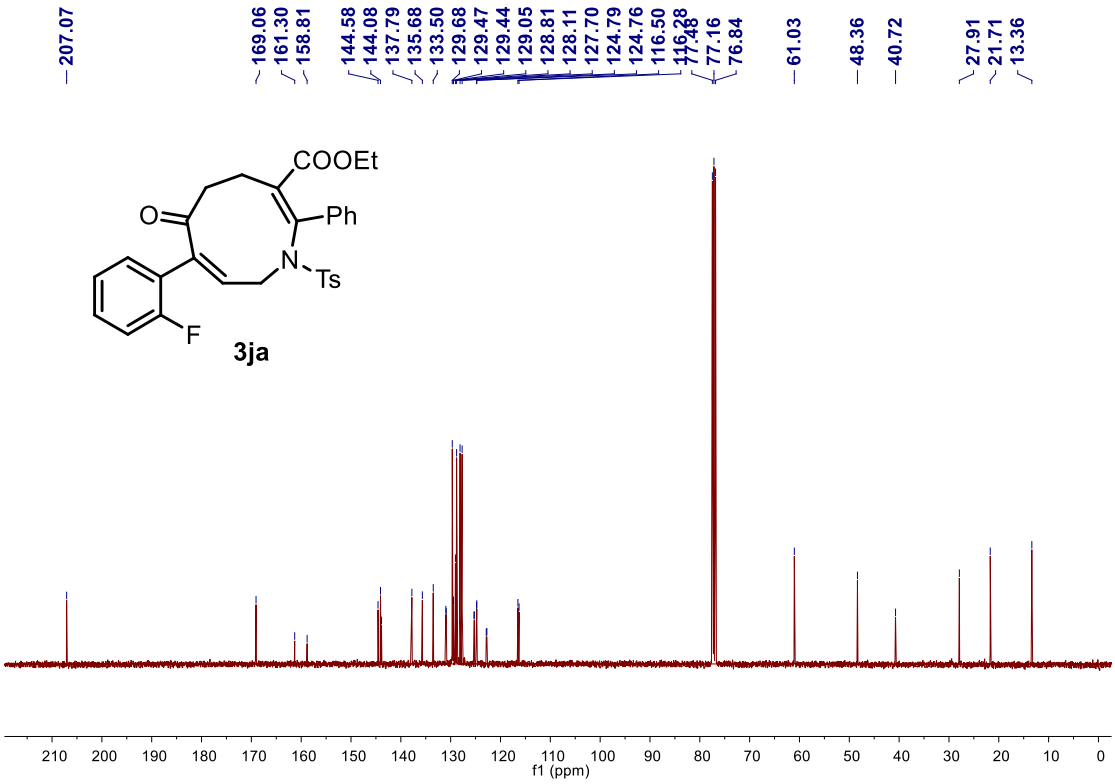
HRMS of **3ia**



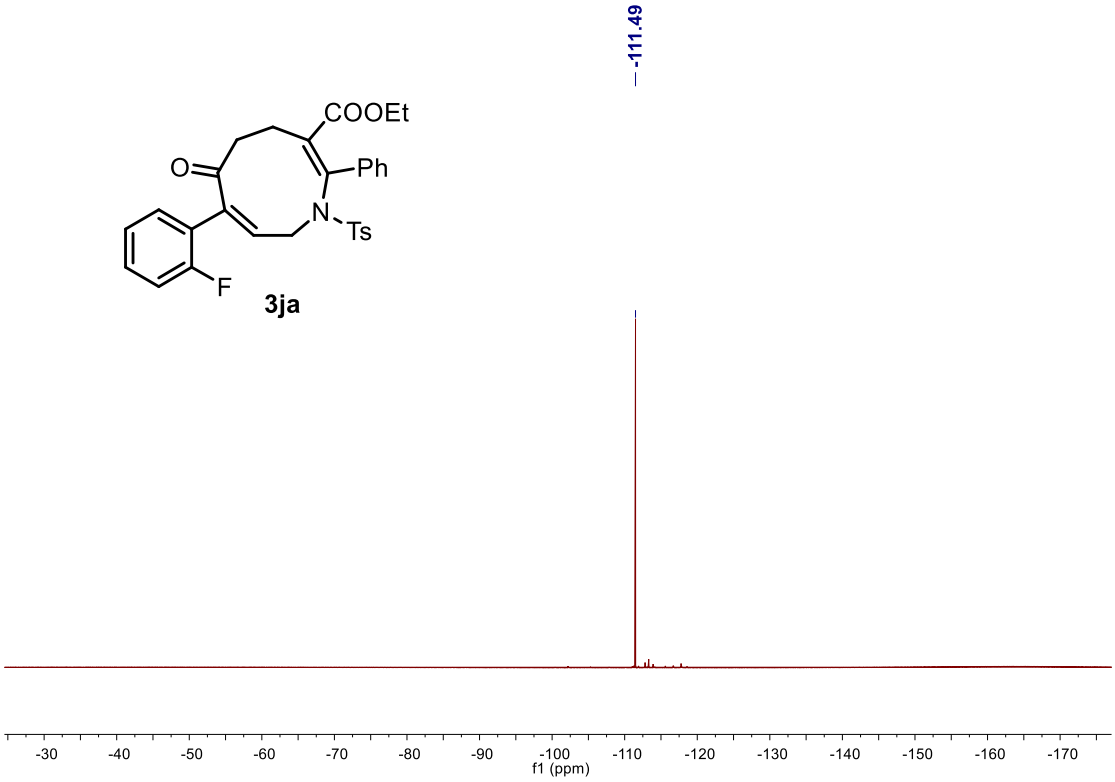
^{1}H NMR (400 MHz, $CDCl_3$) of **3ja**



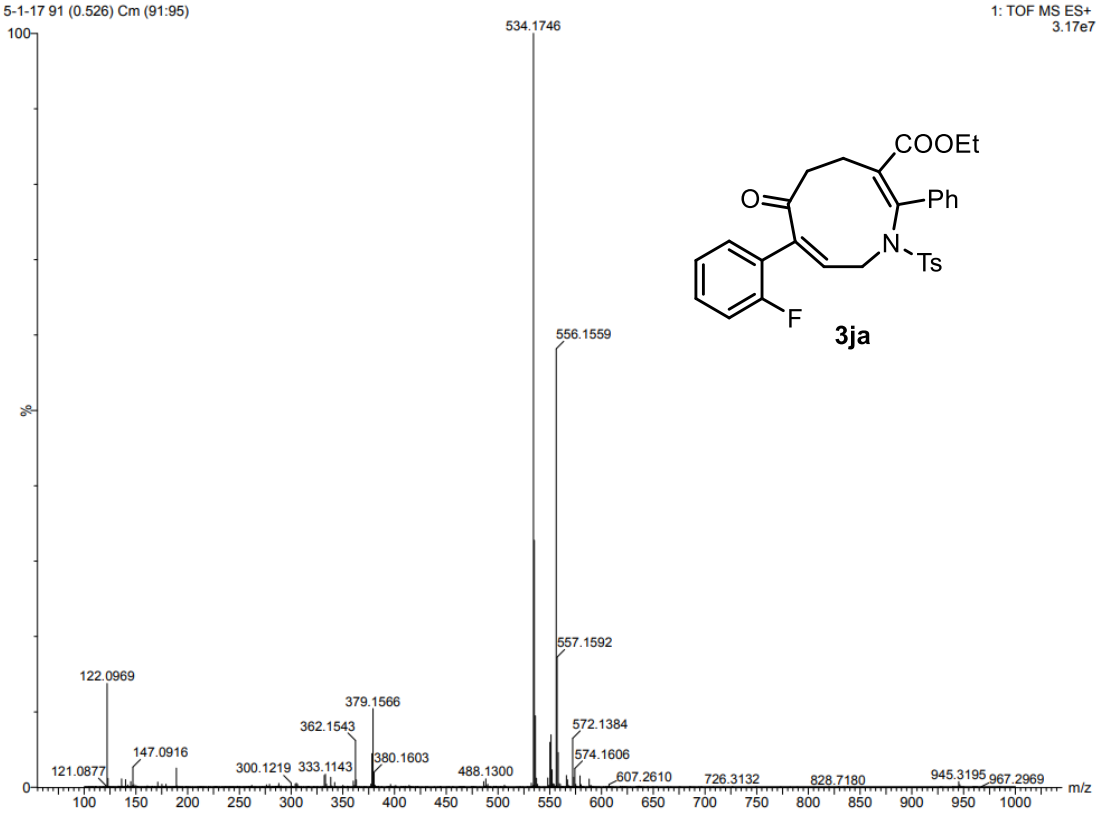
^{13}C NMR (100 MHz, $CDCl_3$) of **3ja**



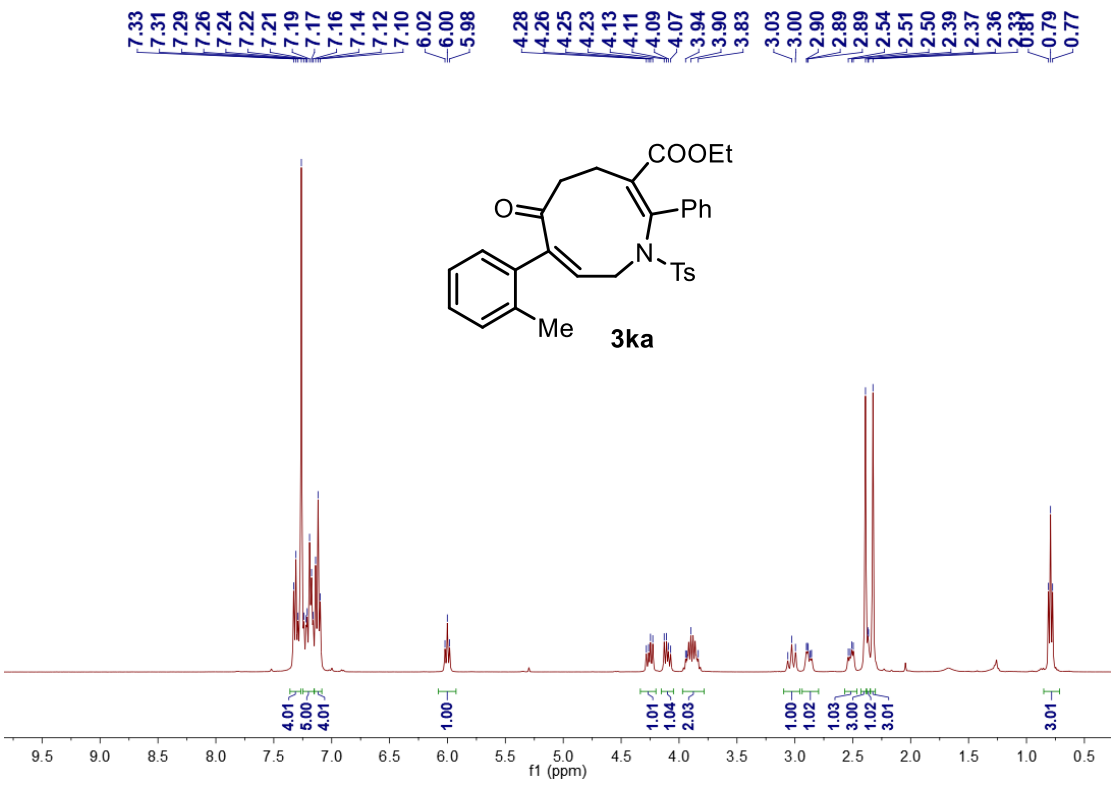
^{19}F NMR (376 MHz, $CDCl_3$) of **3ja**



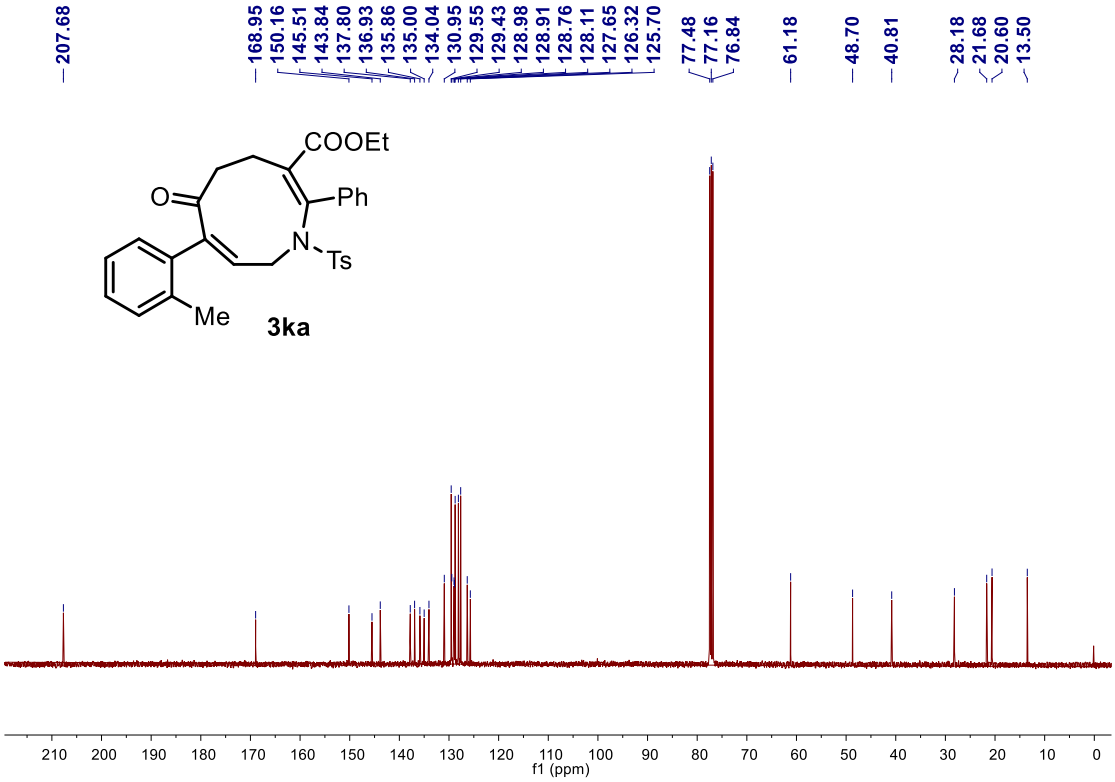
HRMS of **3ja**



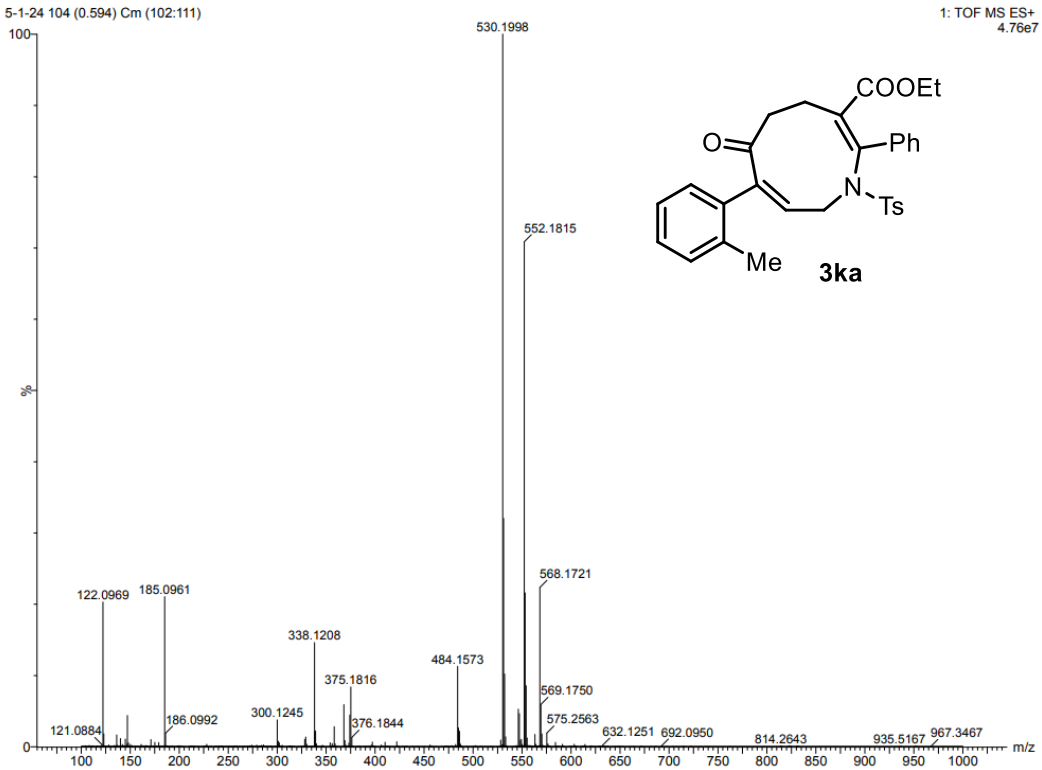
^{1}H NMR (400 MHz, $CDCl_3$) of **3ka**



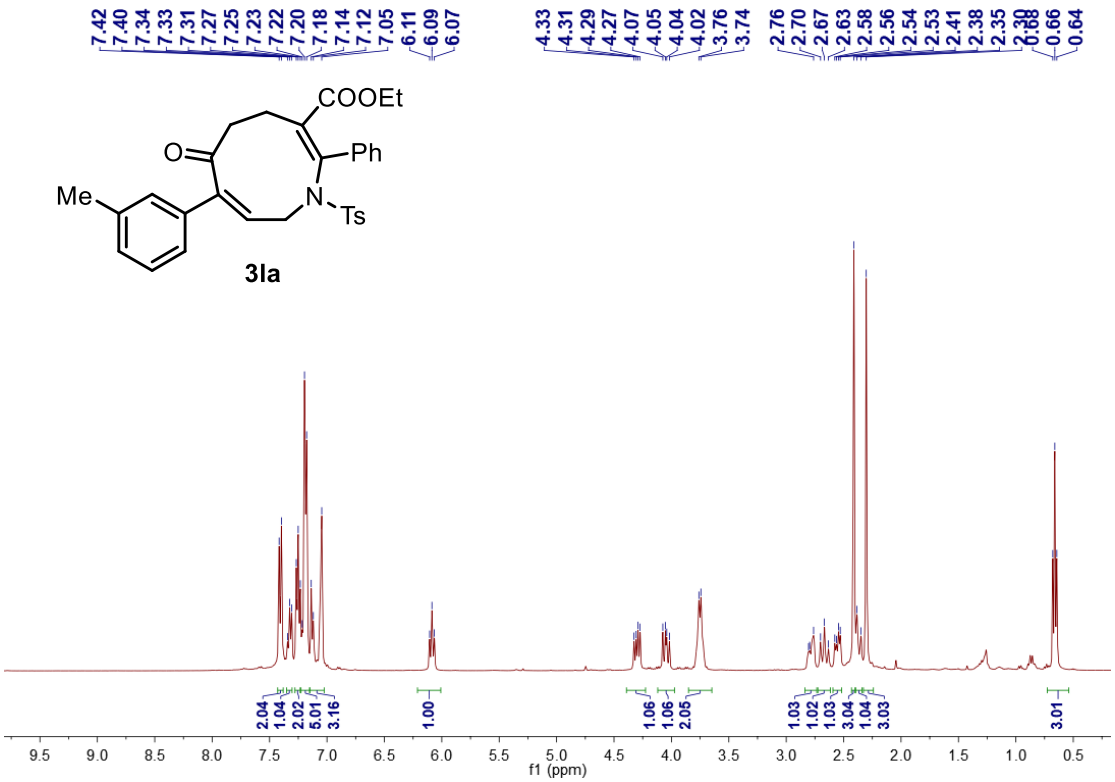
^{13}C NMR (100 MHz, $CDCl_3$) of **3ka**



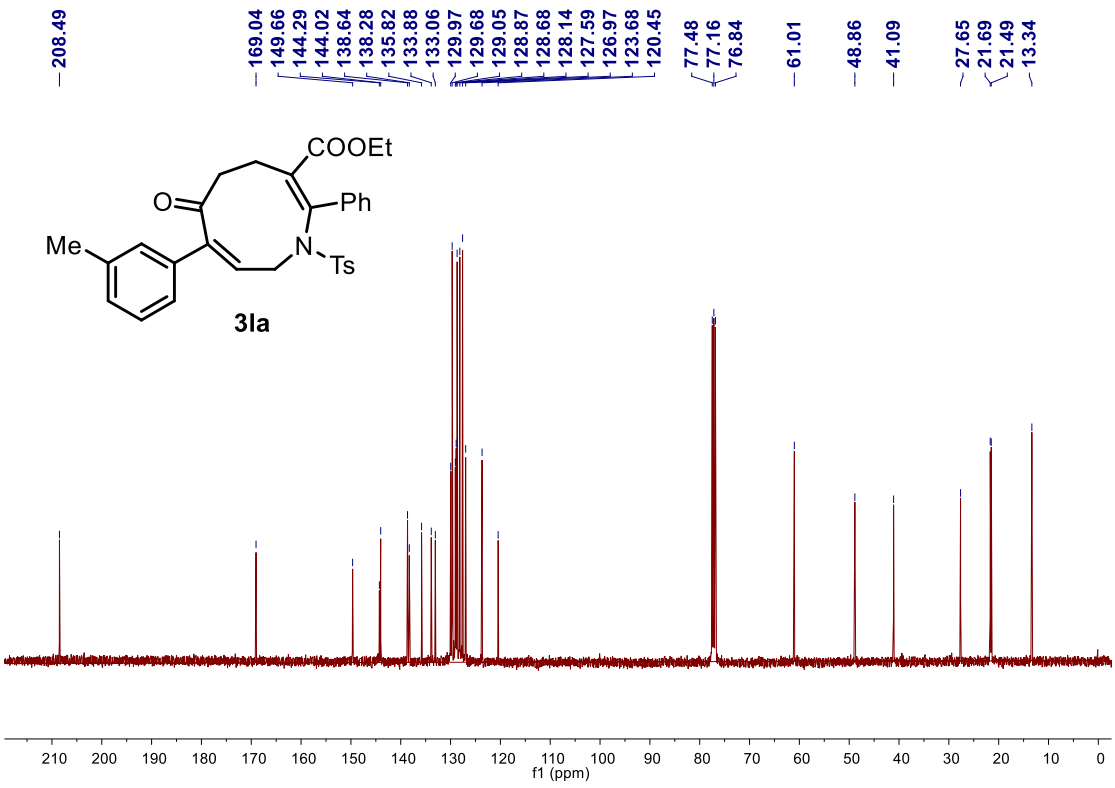
HRMS of **3ka**



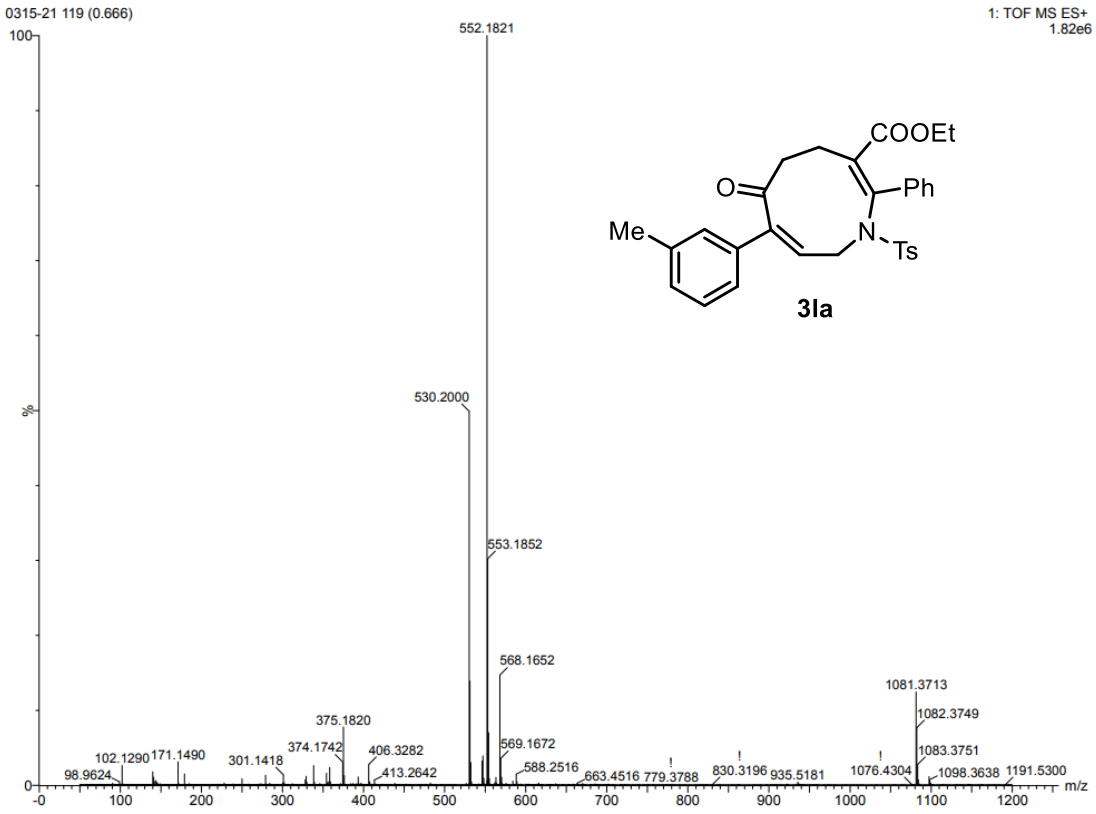
^{1}H NMR (400 MHz, $CDCl_3$) of **3la**



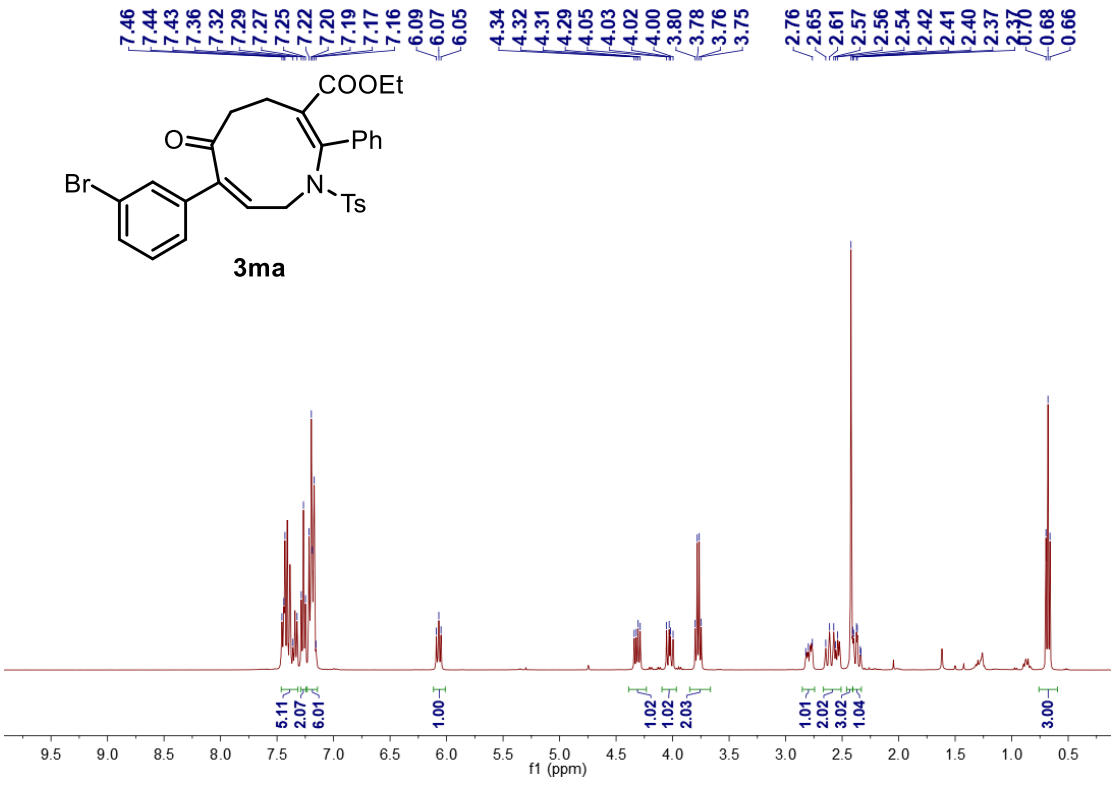
^{13}C NMR (100 MHz, $CDCl_3$) of **3la**



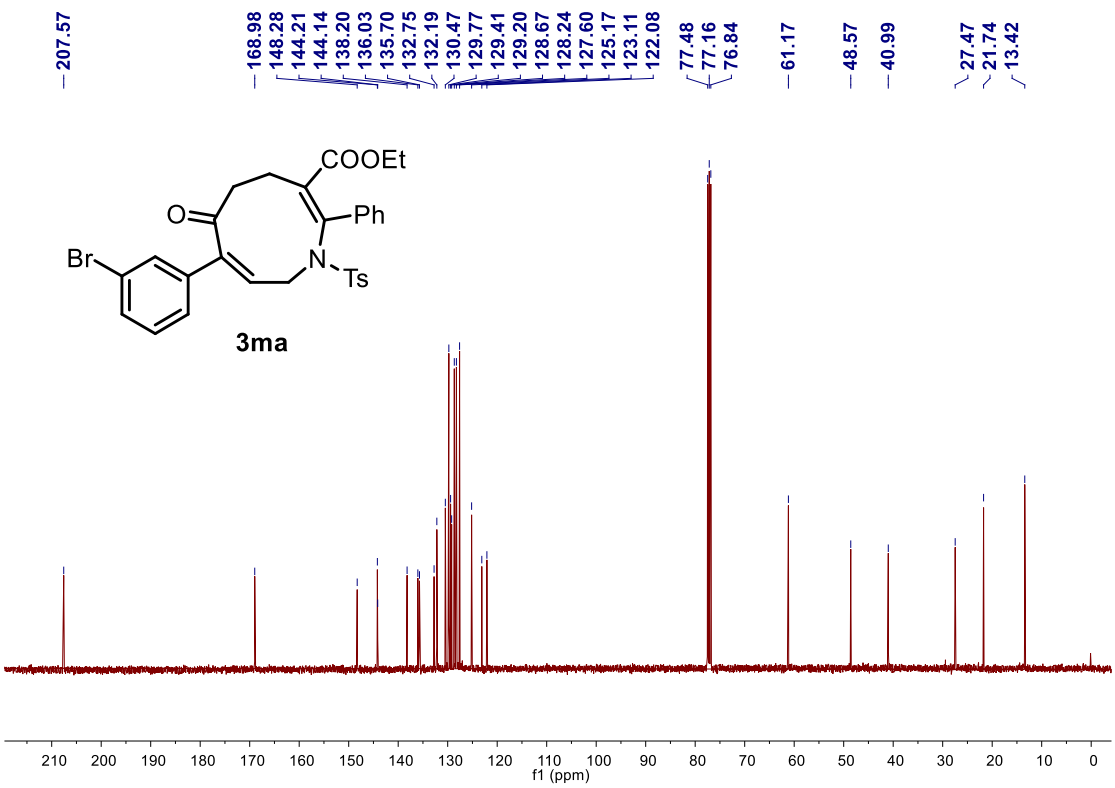
HRMS of **3la**



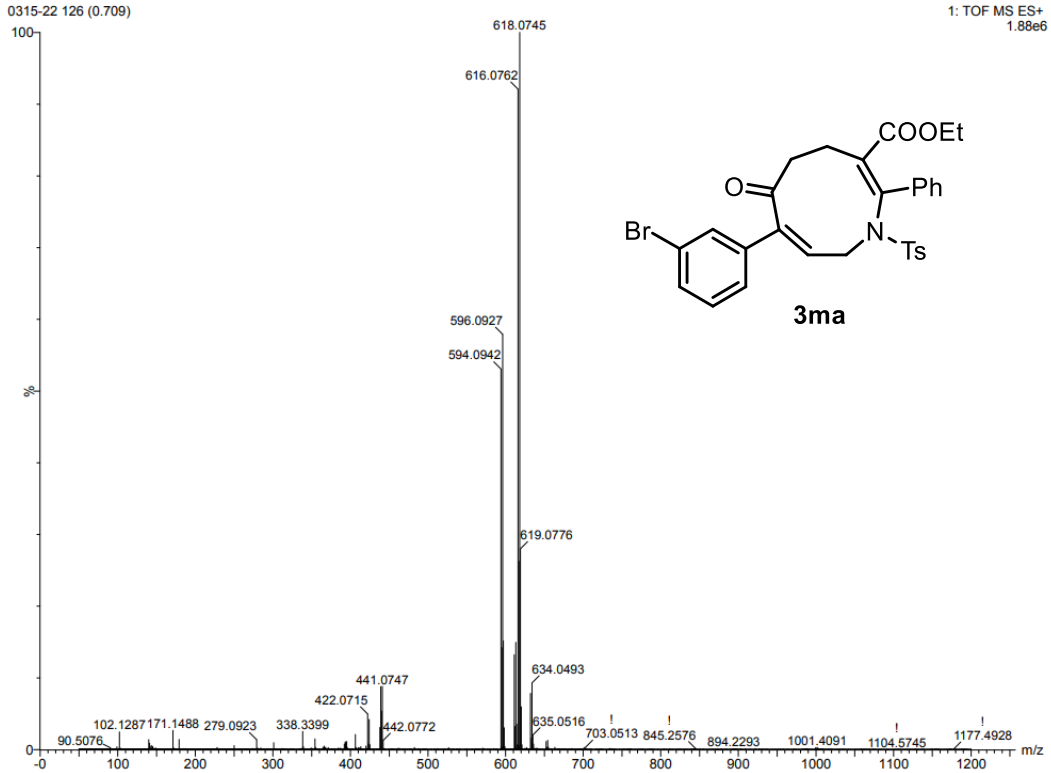
^{1}H NMR (400 MHz, $CDCl_3$) of **3ma**



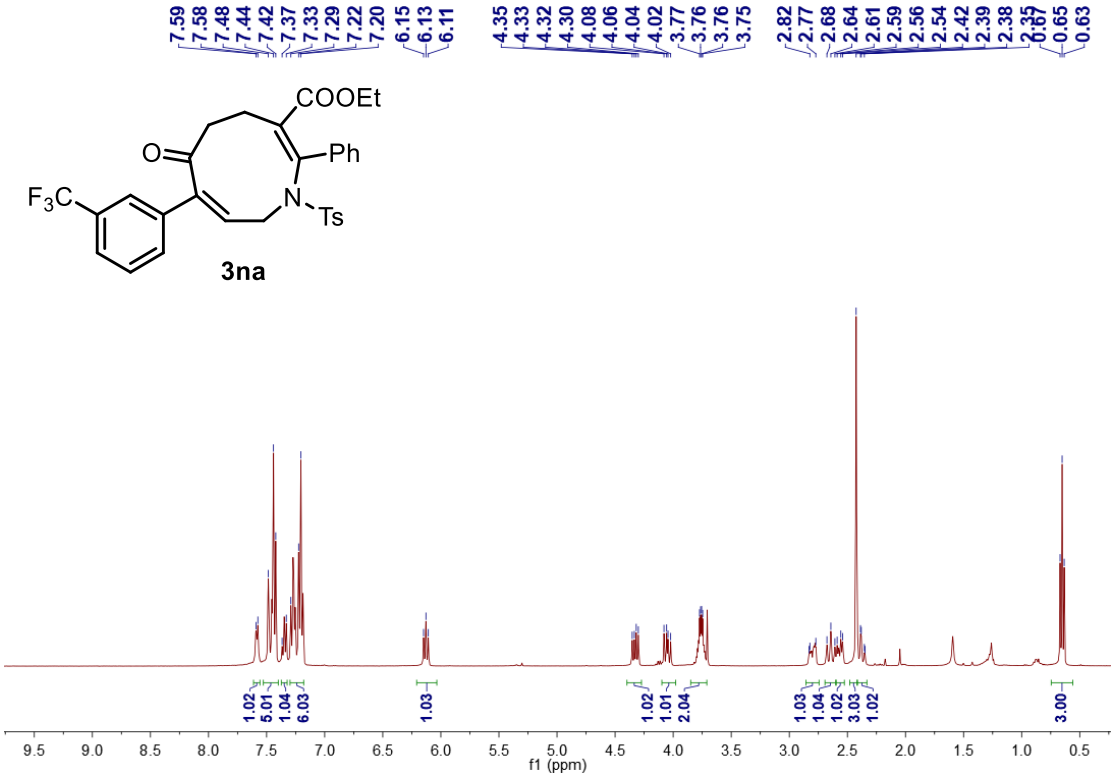
^{13}C NMR (100 MHz, $CDCl_3$) of **3ma**



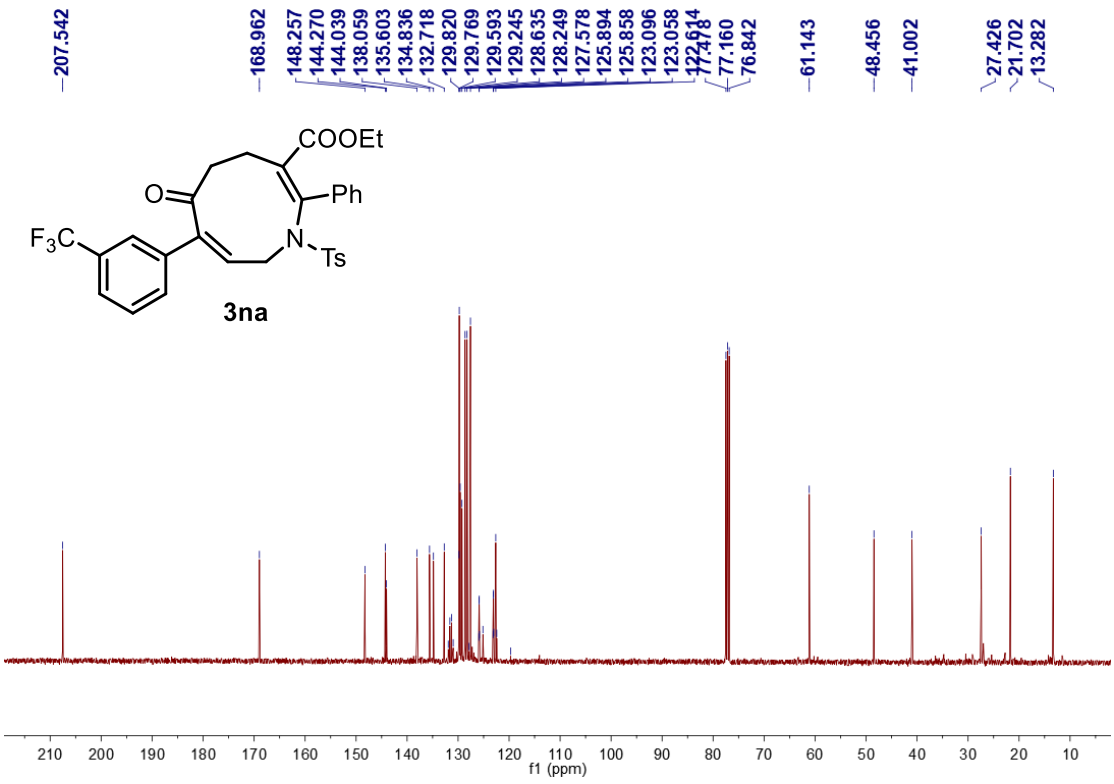
HRMS of **3ma**



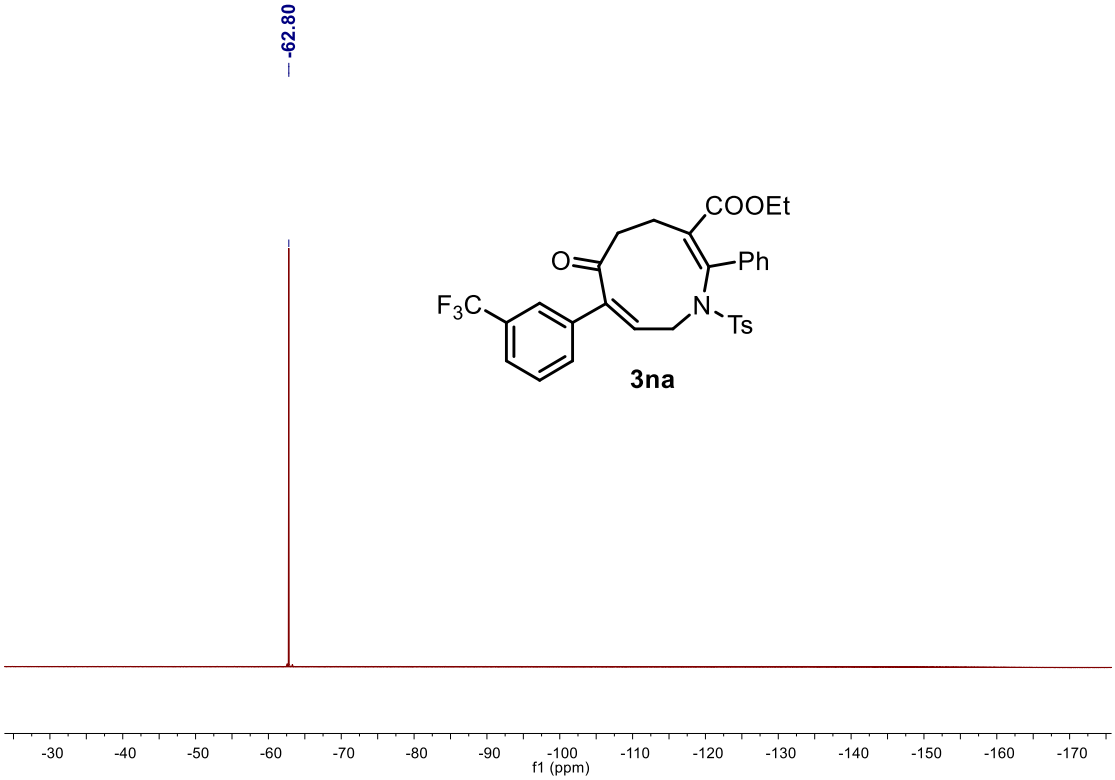
^{1}H NMR (400 MHz, $CDCl_3$) of **3na**



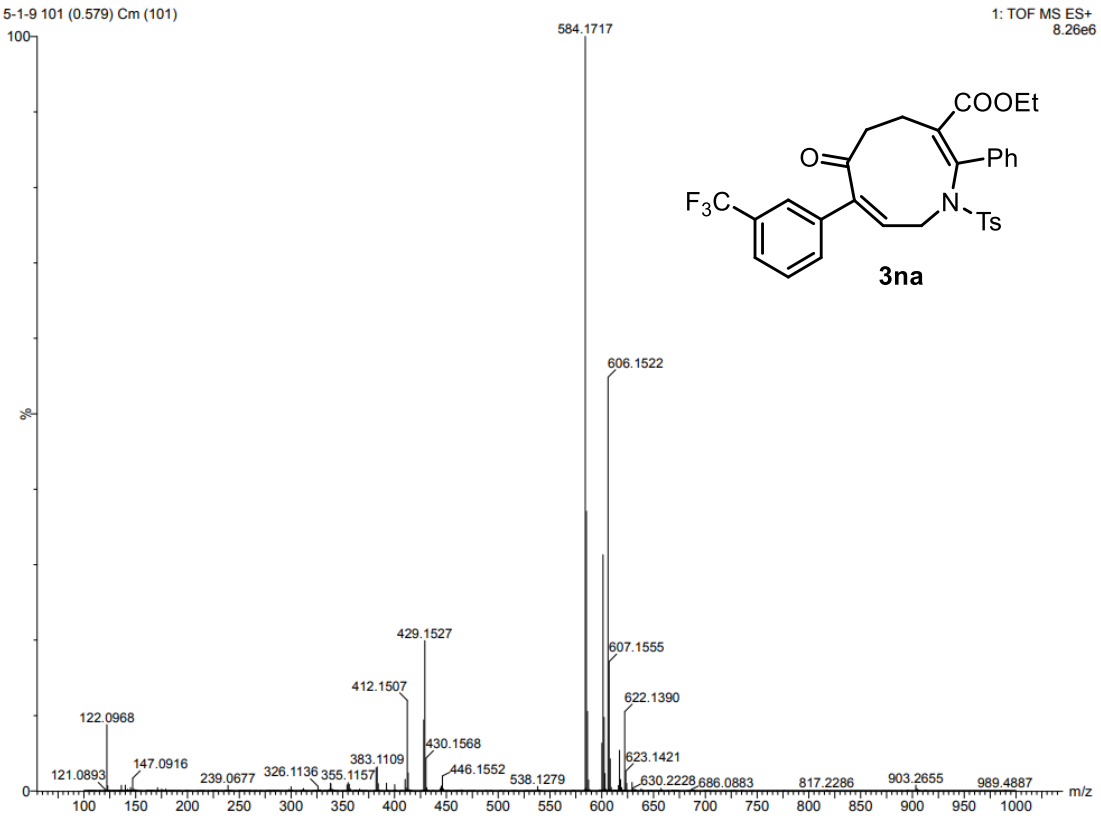
^{13}C NMR (100 MHz, $CDCl_3$) of **3na**



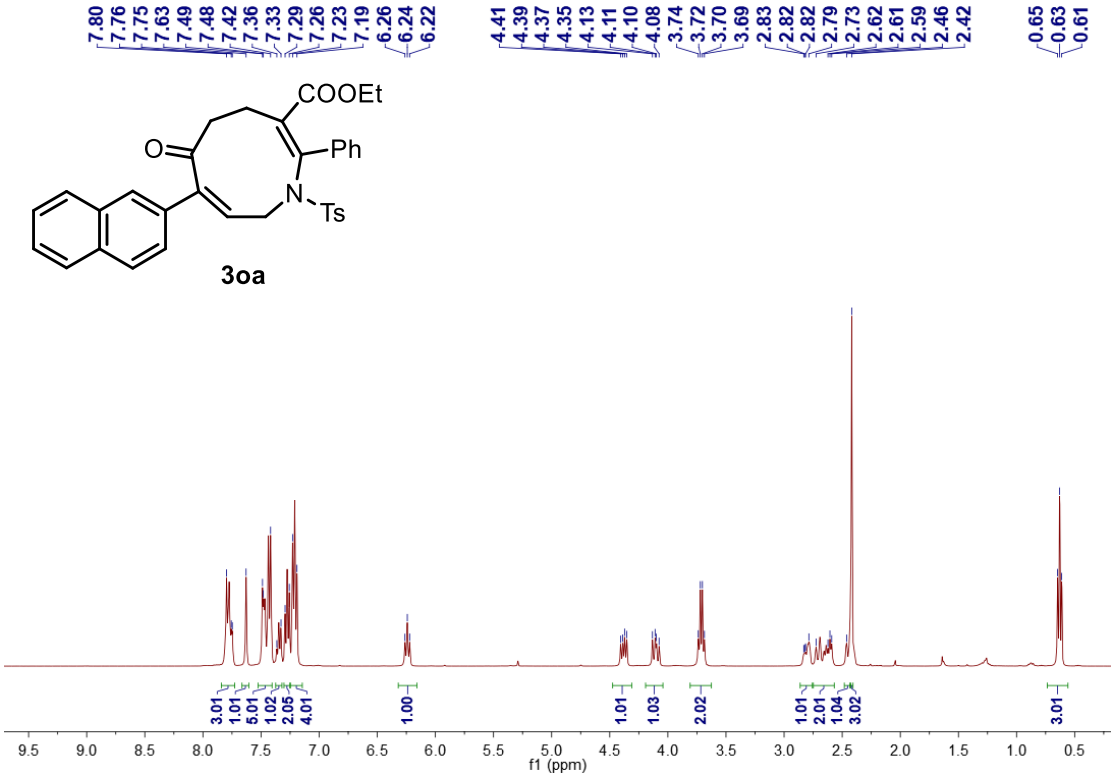
^{19}F NMR (376 MHz, $CDCl_3$) of **3na**



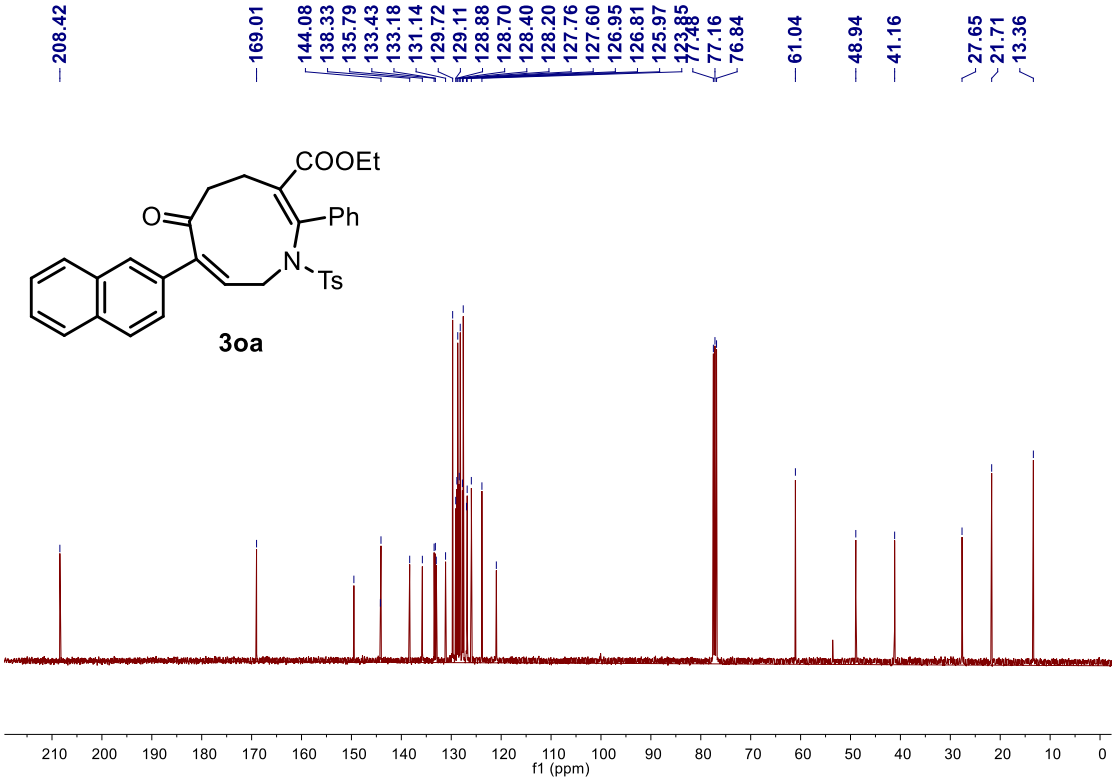
HRMS of **3na**



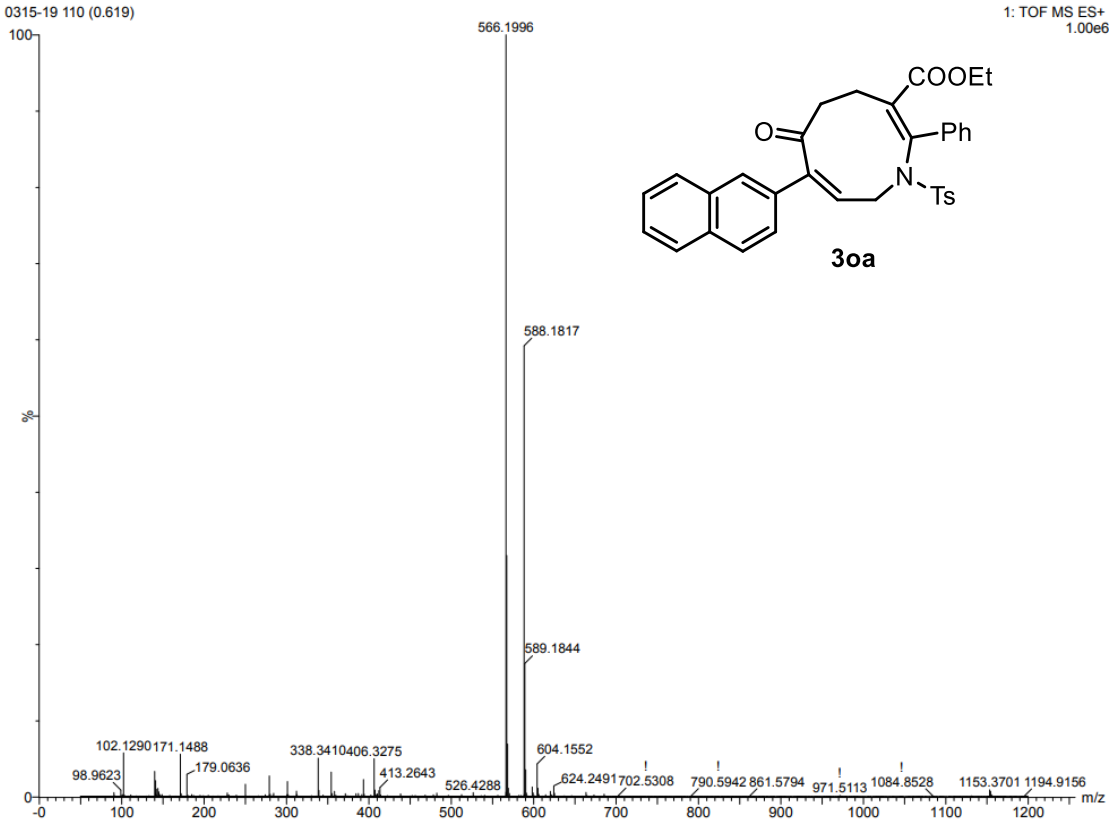
^{1}H NMR (400 MHz, $CDCl_3$) of **3oa**



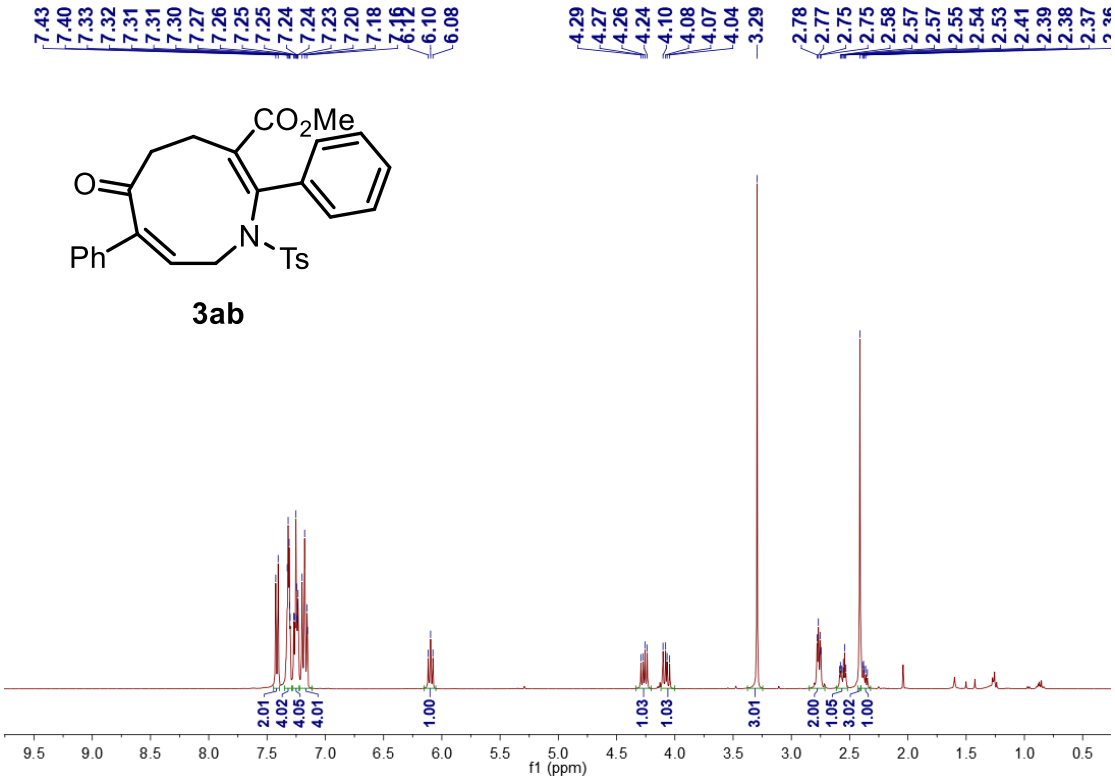
^{13}C NMR (100 MHz, $CDCl_3$) of **3oa**



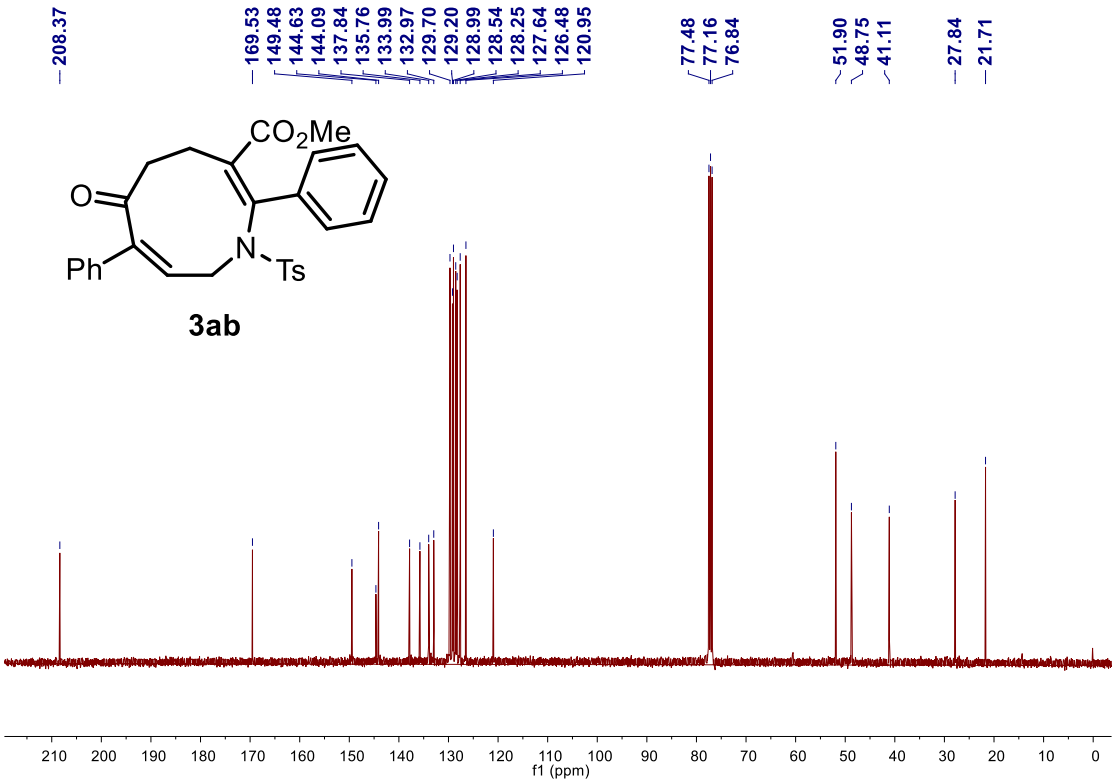
HRMS of **3oa**



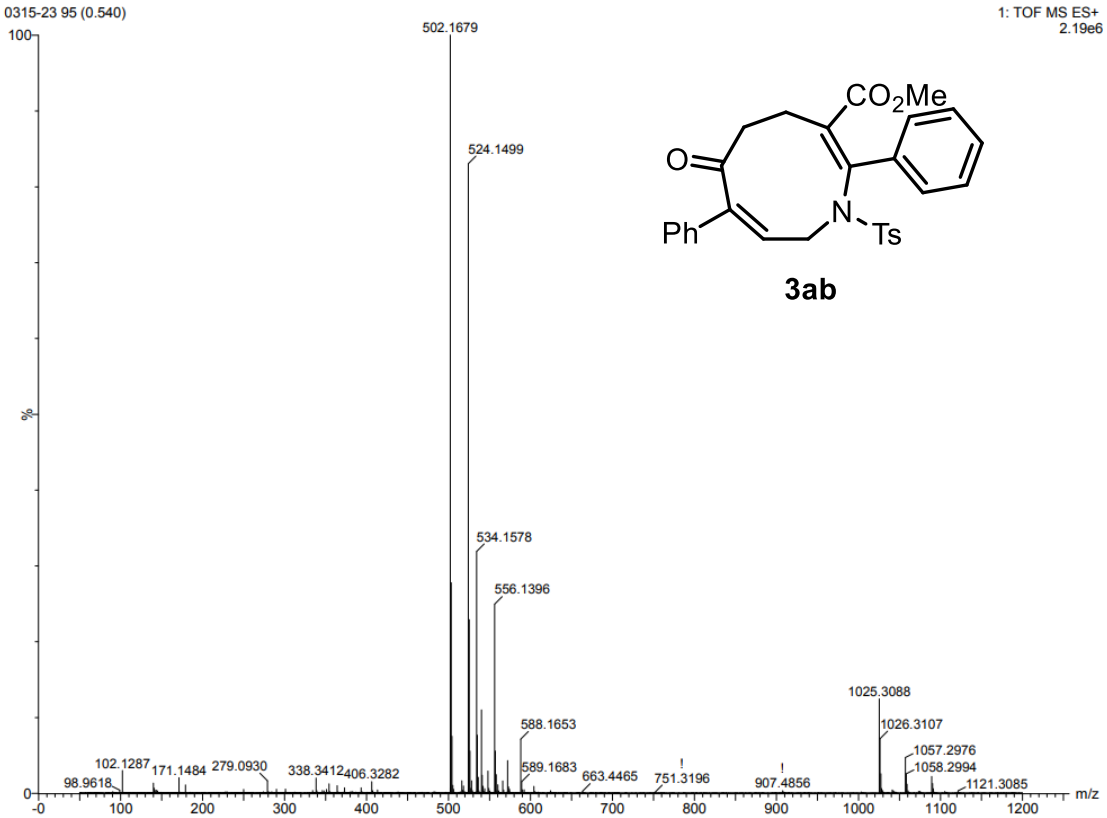
^{1}H NMR (400 MHz, $CDCl_3$) of **3ab**



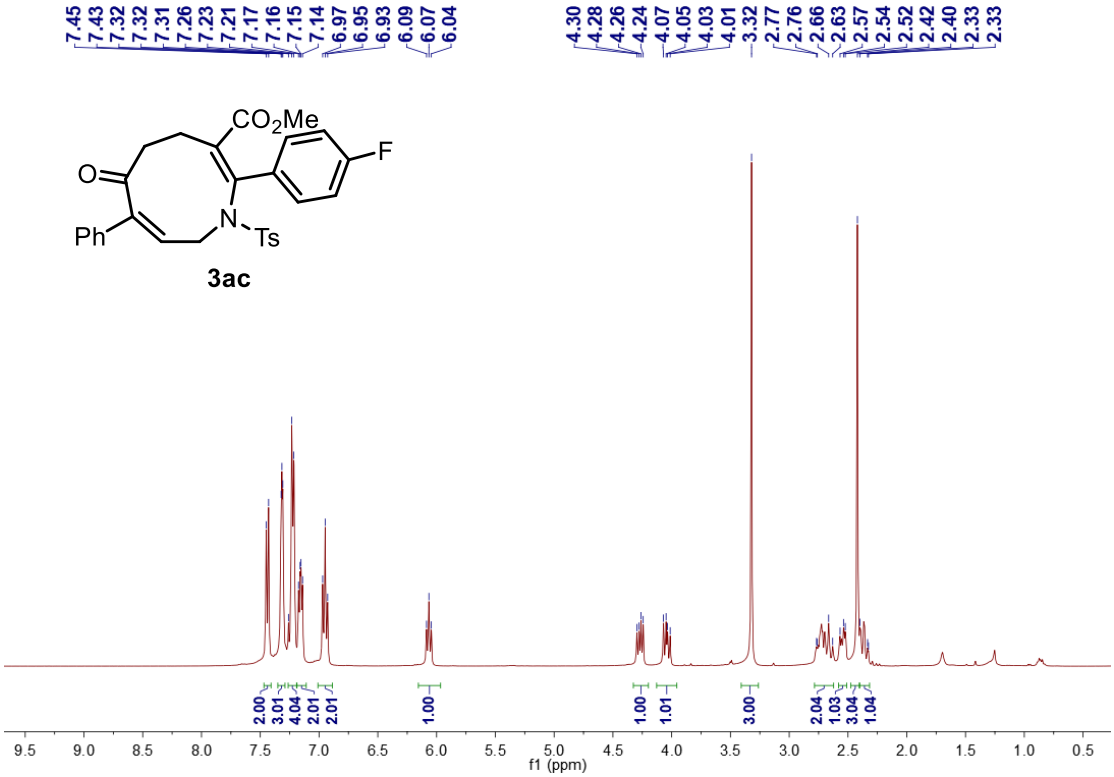
^{13}C NMR (100 MHz, $CDCl_3$) of **3ab**



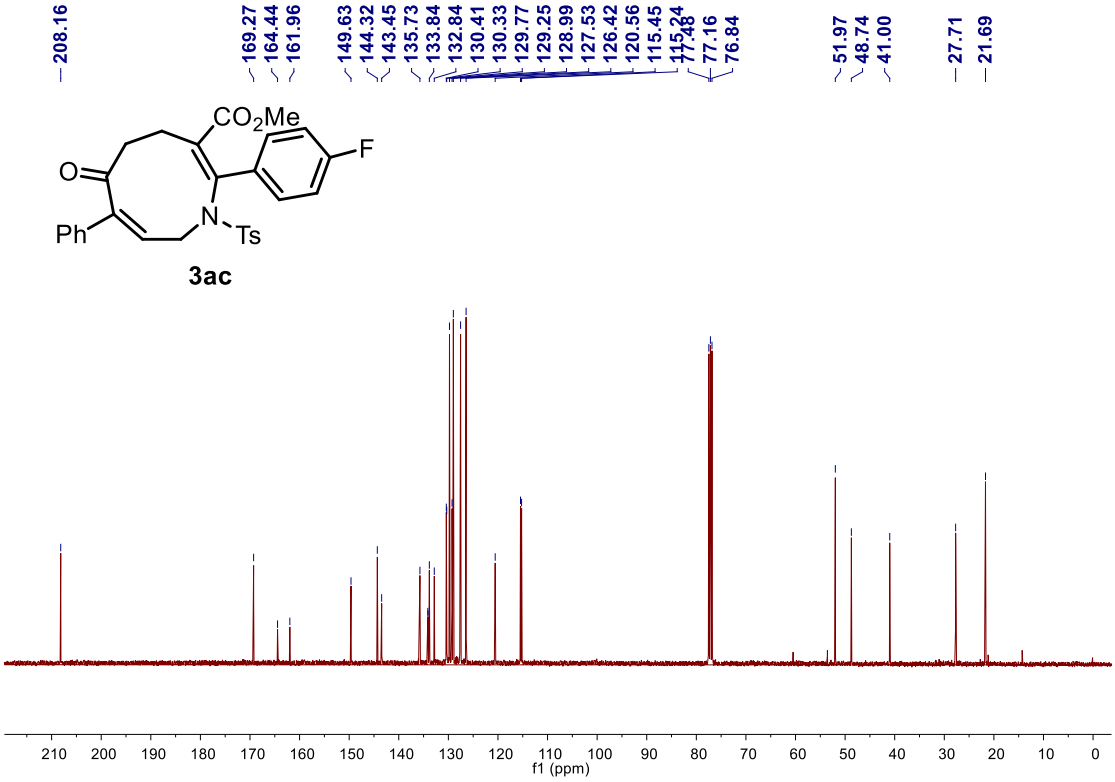
HRMS of **3ab**



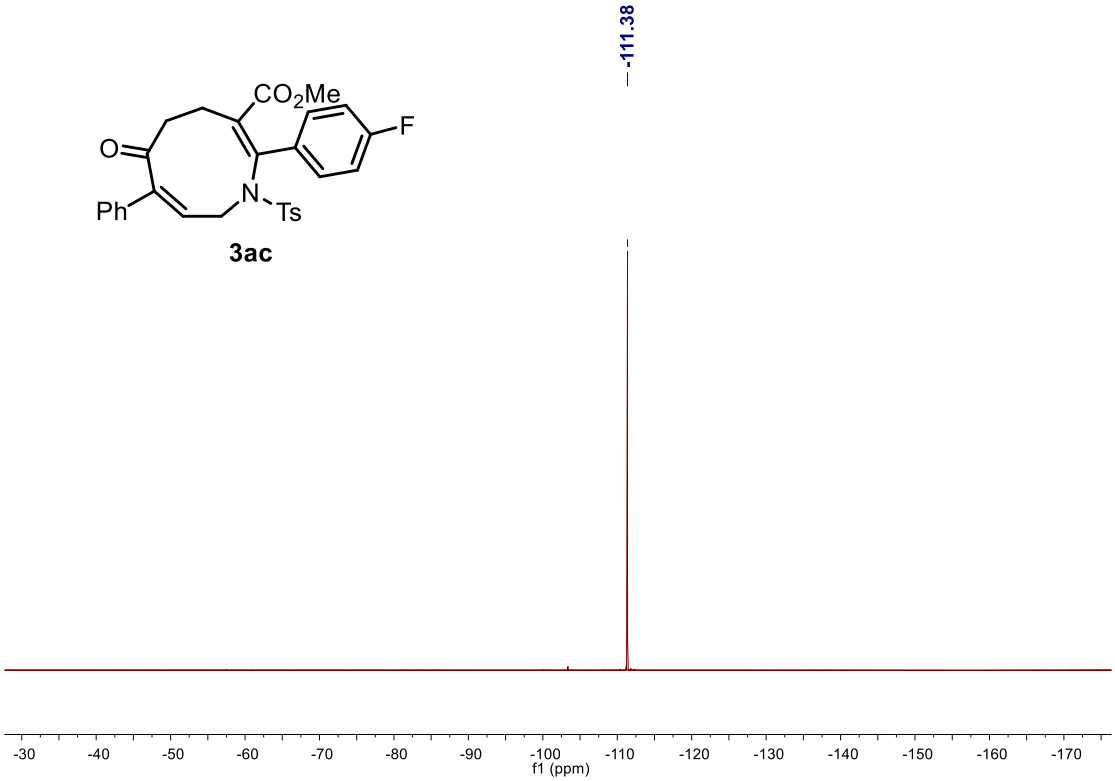
^{1}H NMR (400 MHz, $CDCl_3$) of **3ac**



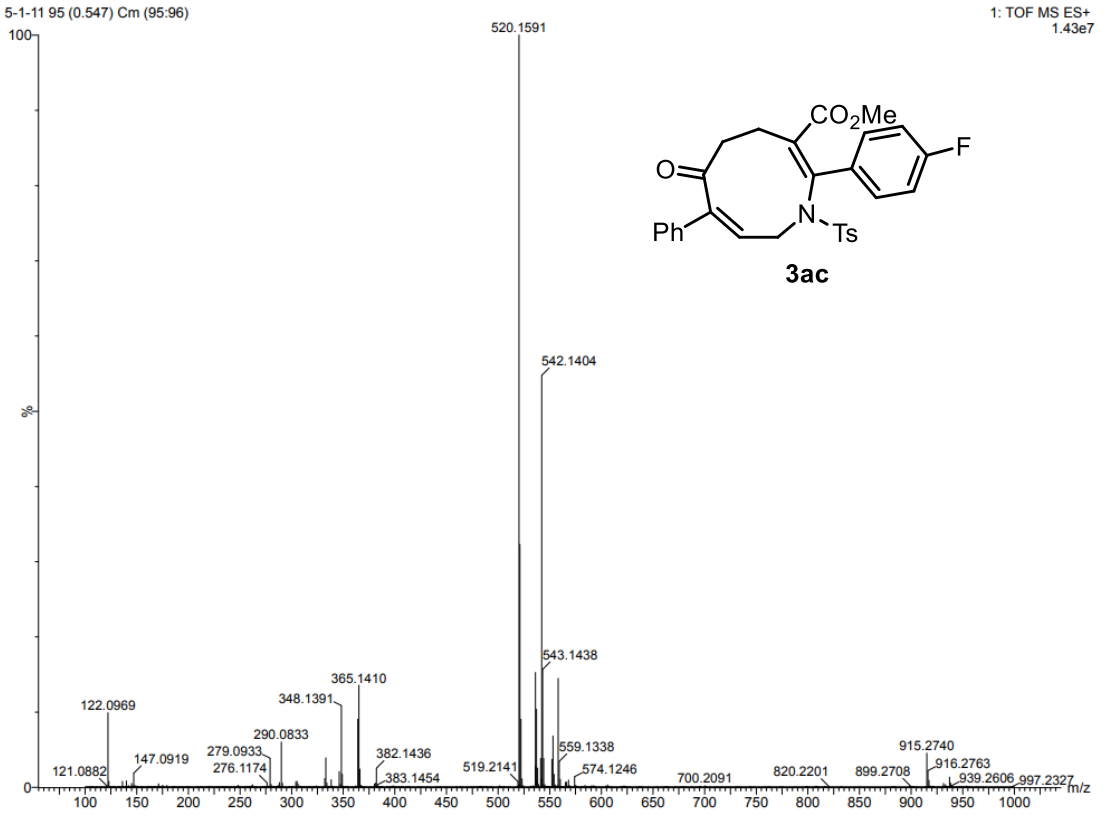
^{13}C NMR (100 MHz, $CDCl_3$) of **3ac**



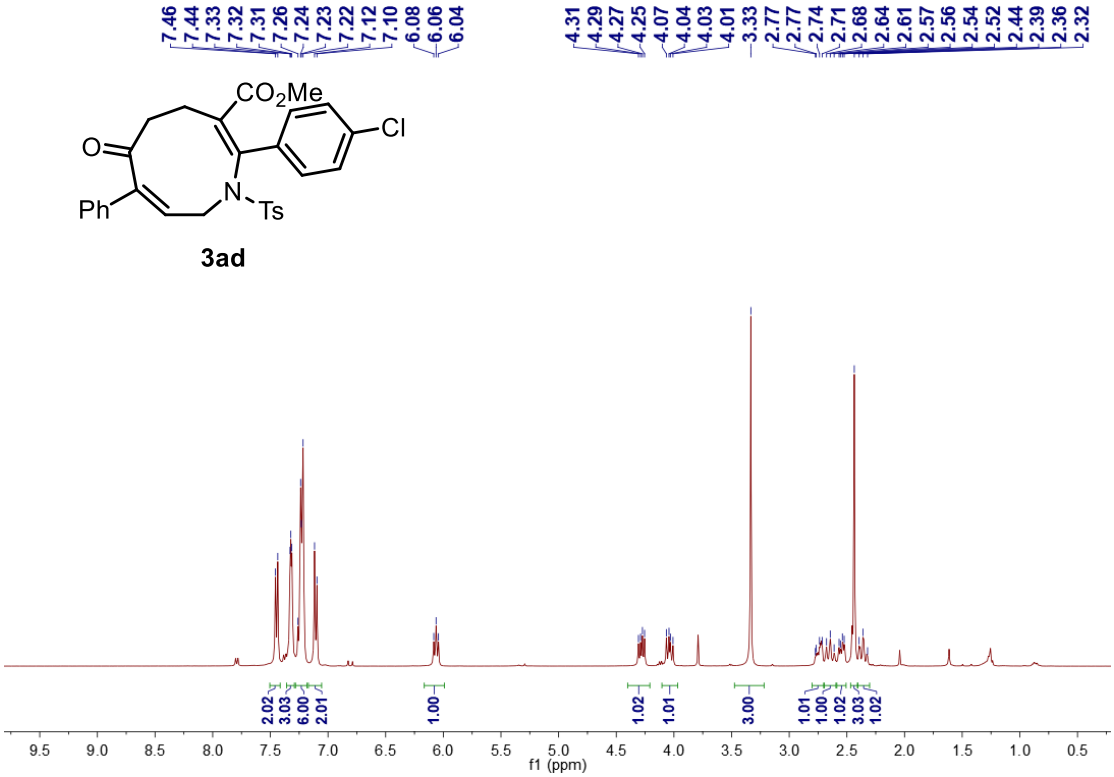
^{19}F NMR (376 MHz, $CDCl_3$) of **3ac**



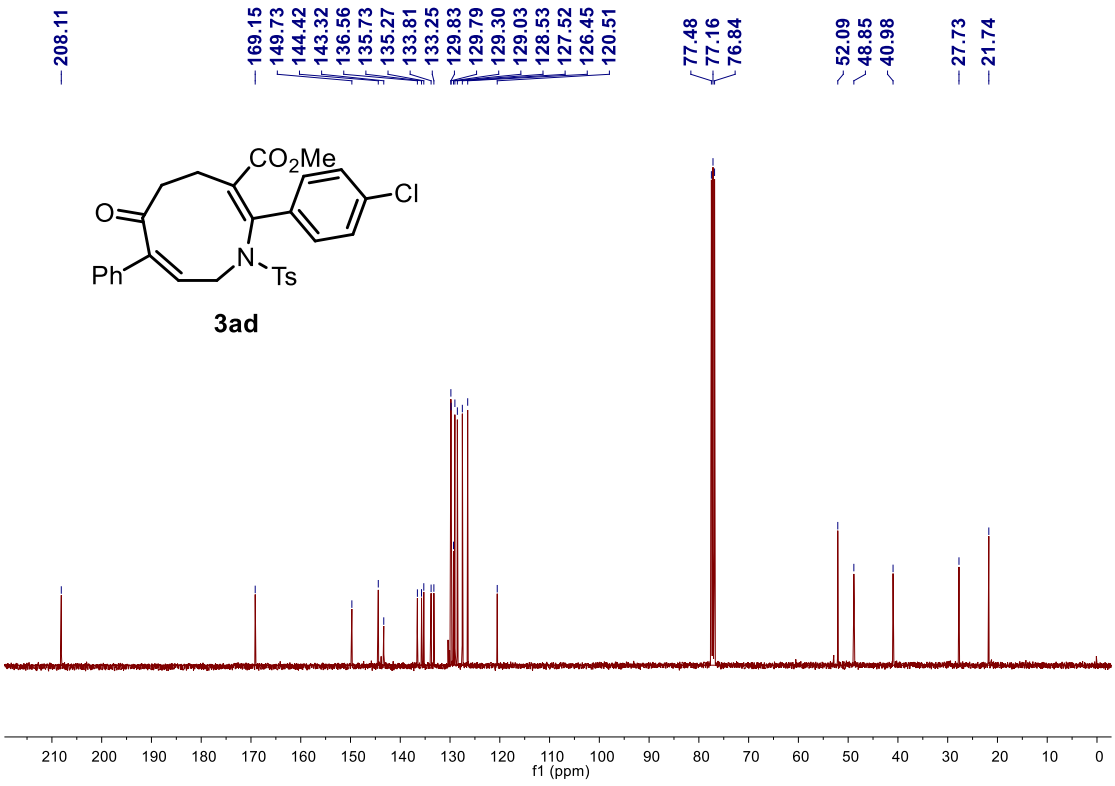
HRMS of **3ac**



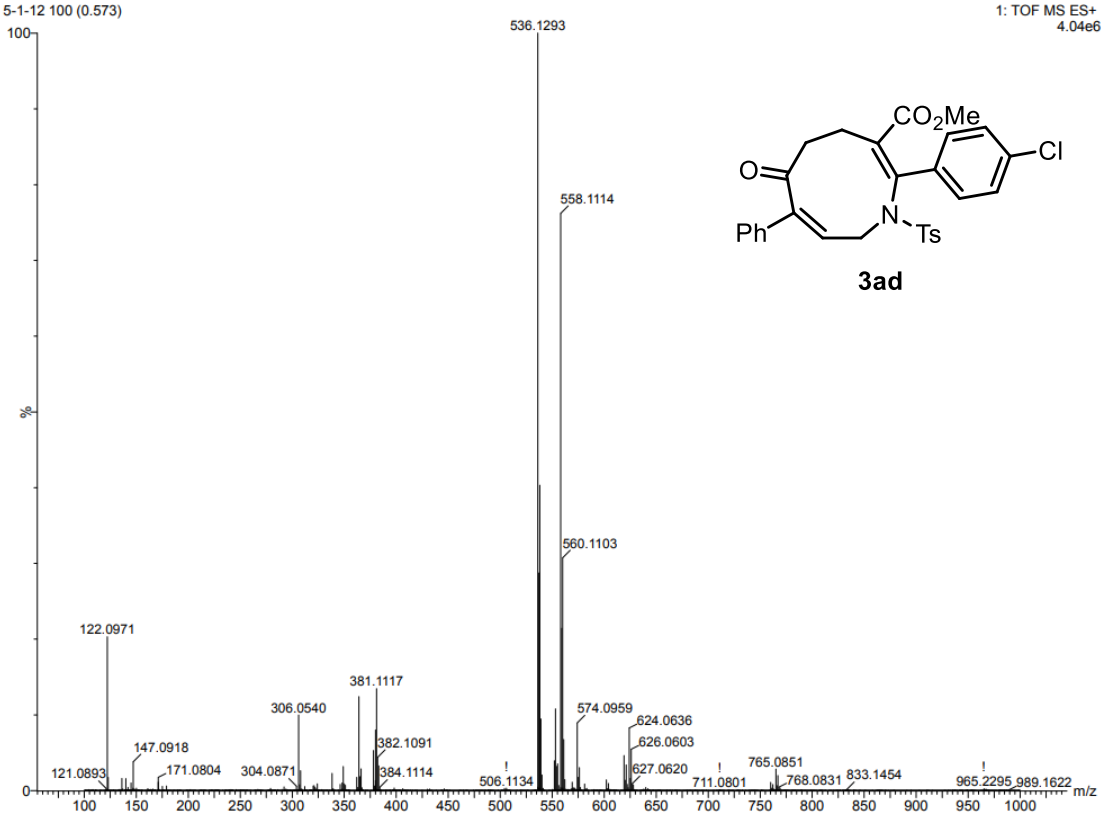
^{1}H NMR (400 MHz, $CDCl_3$) of **3ad**



^{13}C NMR (100 MHz, $CDCl_3$) of **3ad**

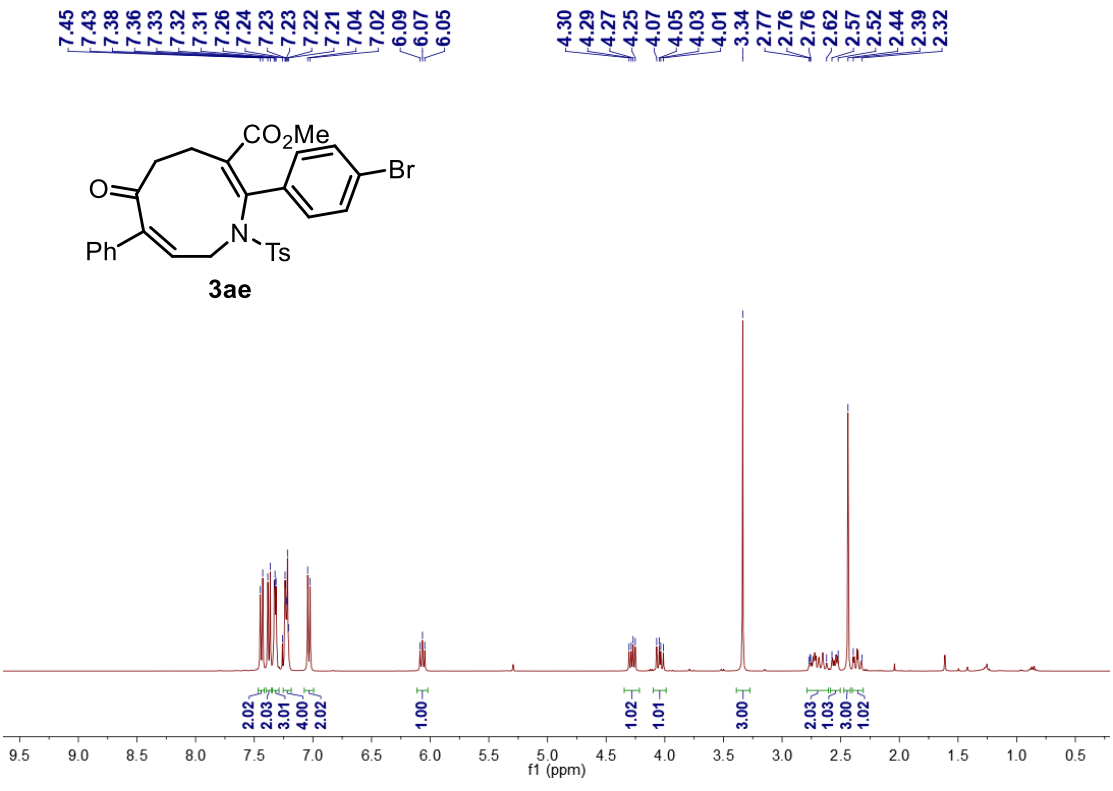


HRMS of **3ad**



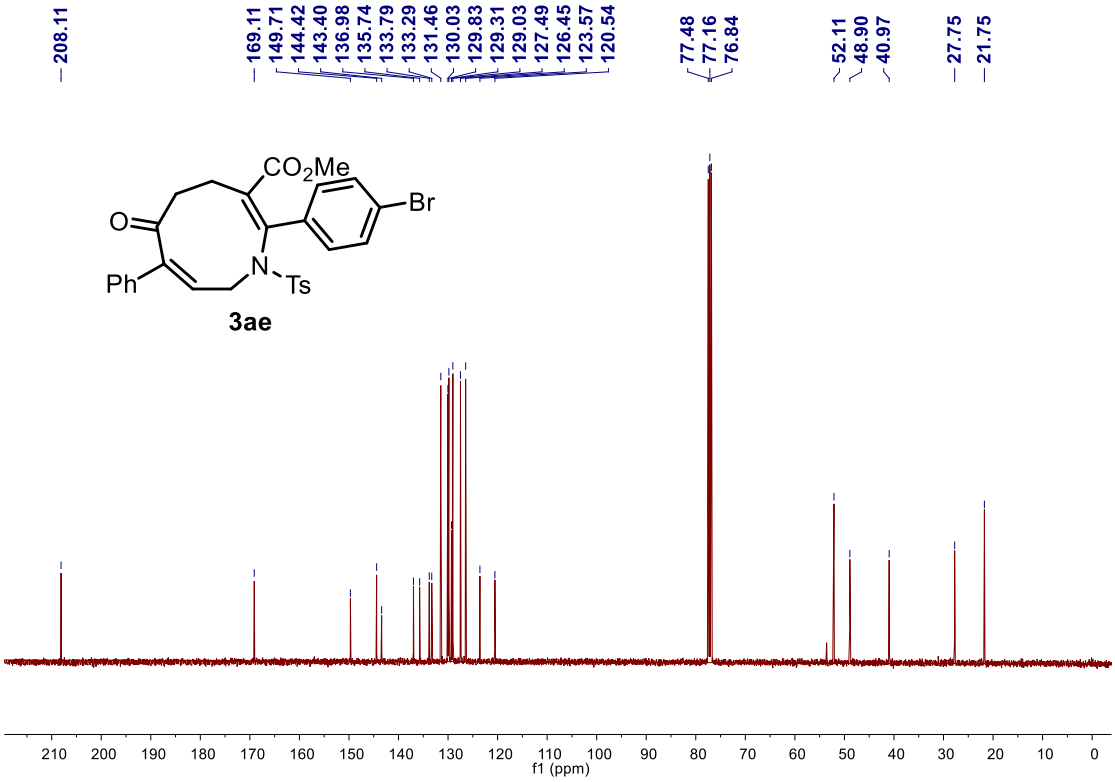
3ad

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

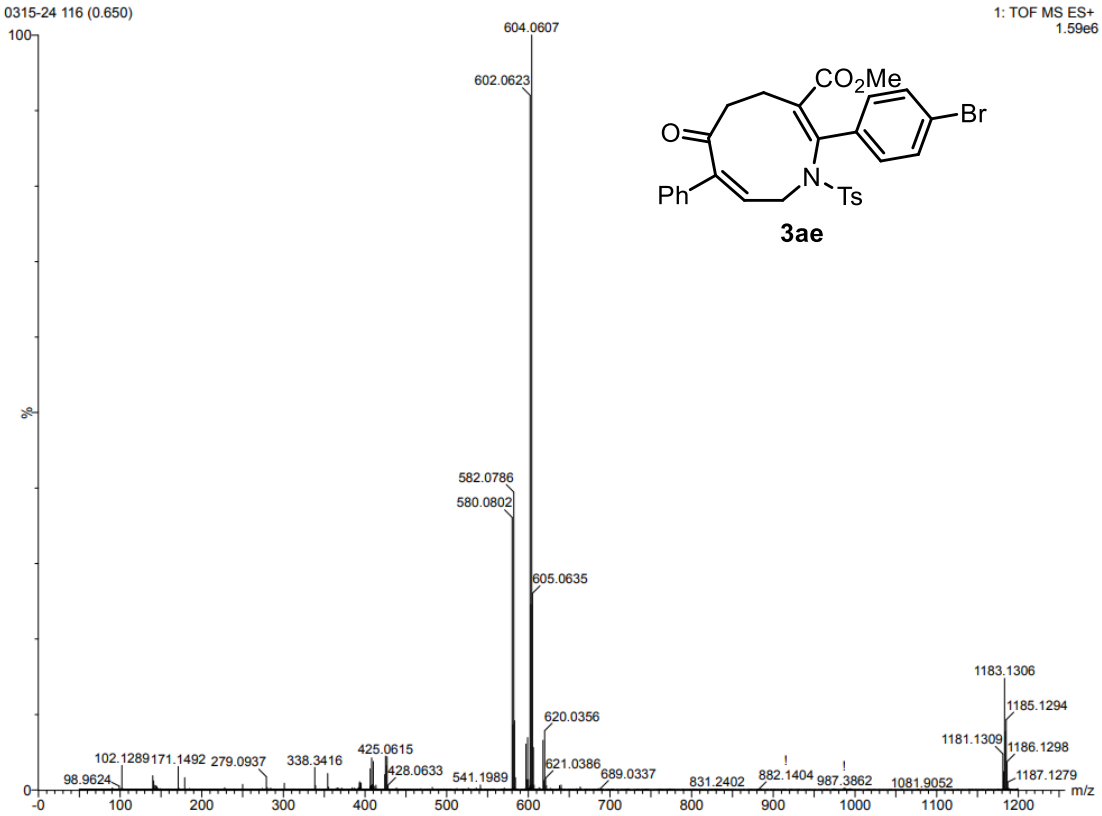


3ae

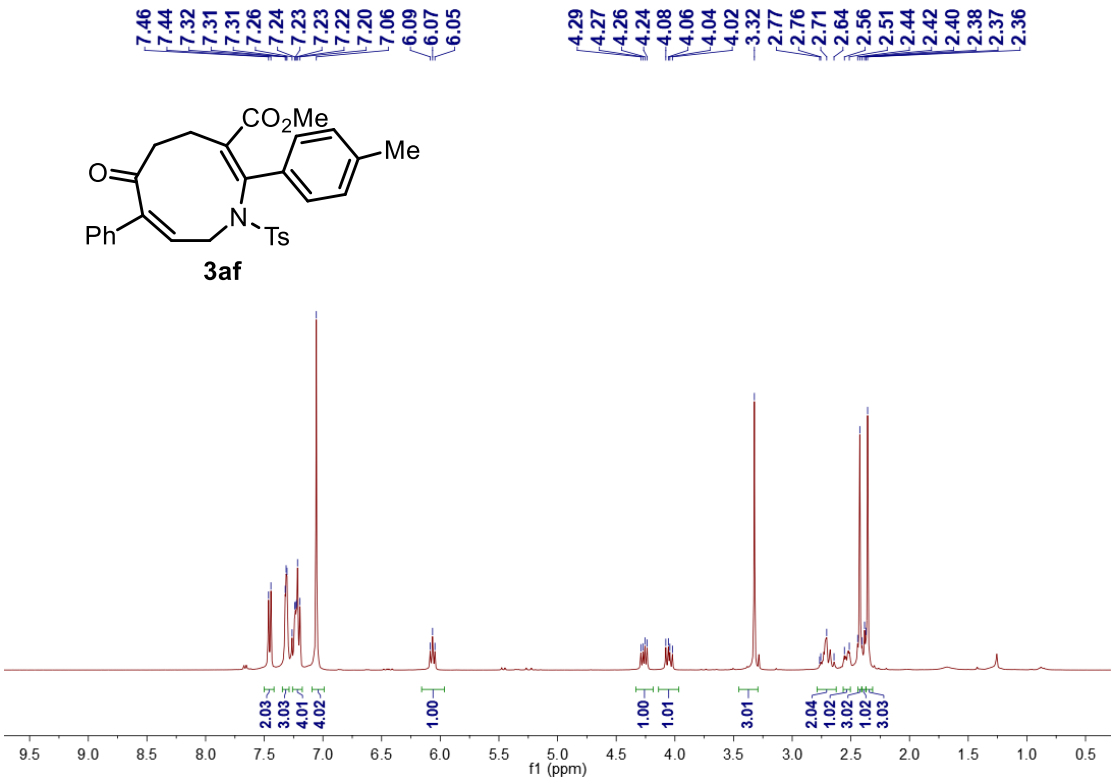
^{13}C NMR (100 MHz, $CDCl_3$) of **3ae**



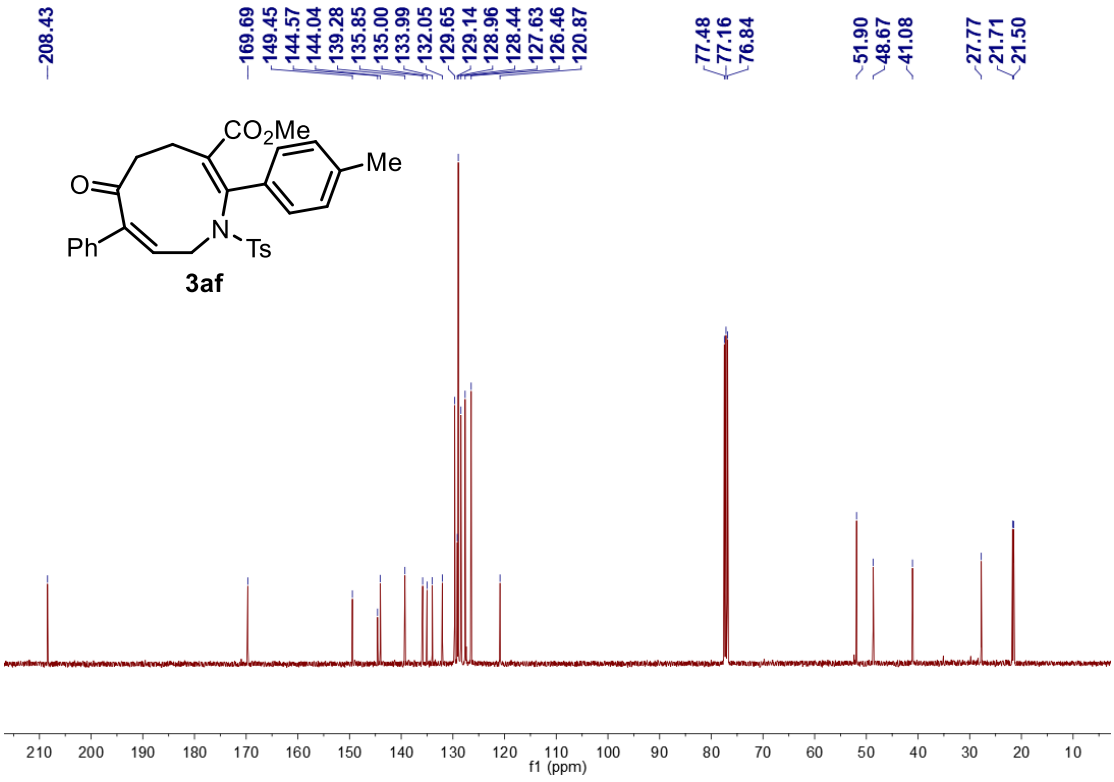
HRMS of **3ae**



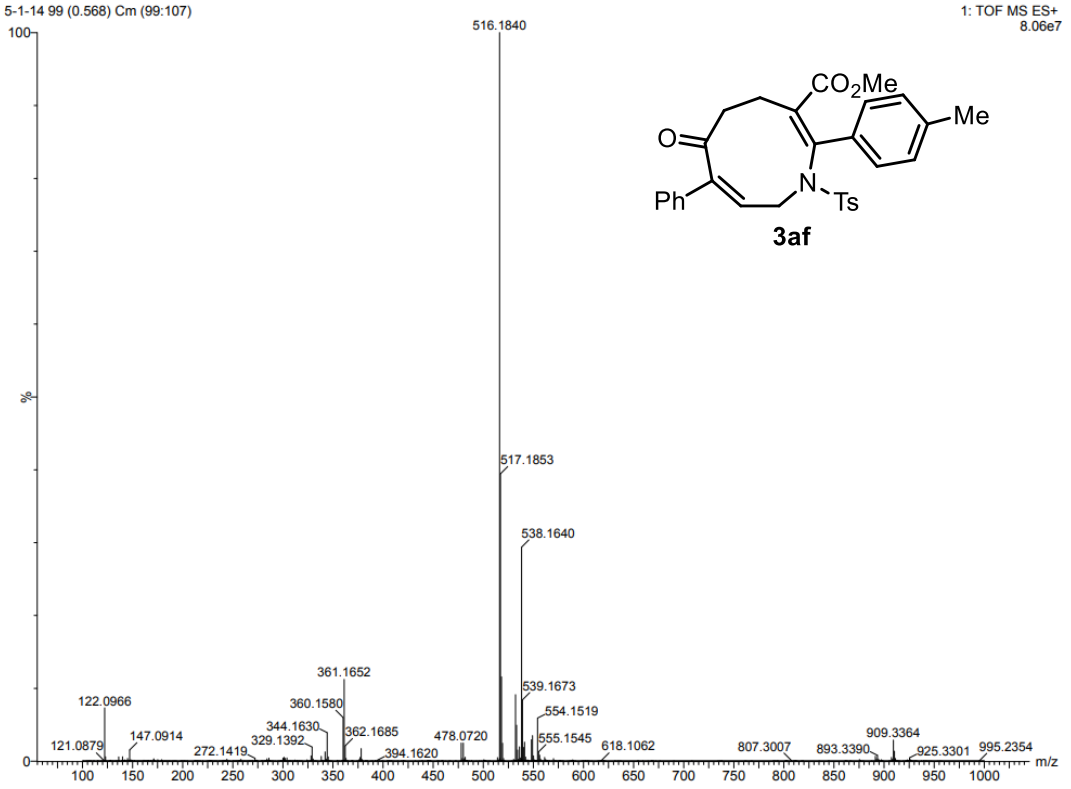
^{1}H NMR (400 MHz, $CDCl_3$) of **3af**



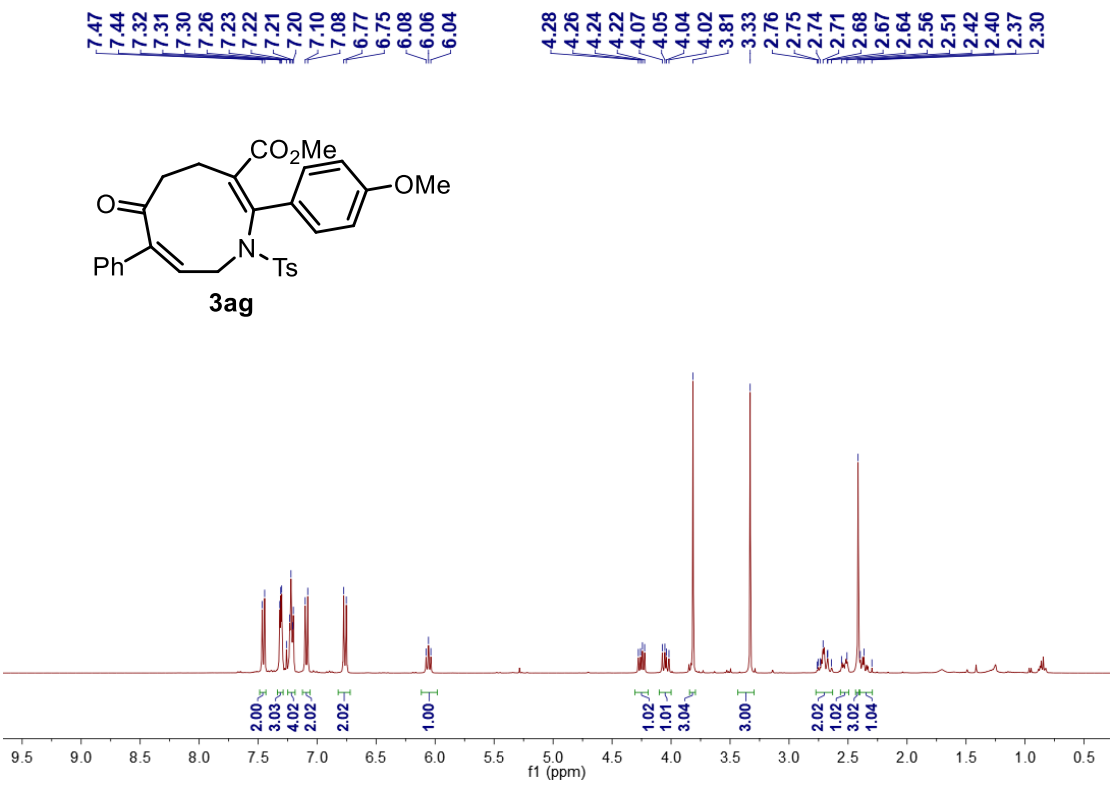
^{13}C NMR (100 MHz, $CDCl_3$) of **3af**



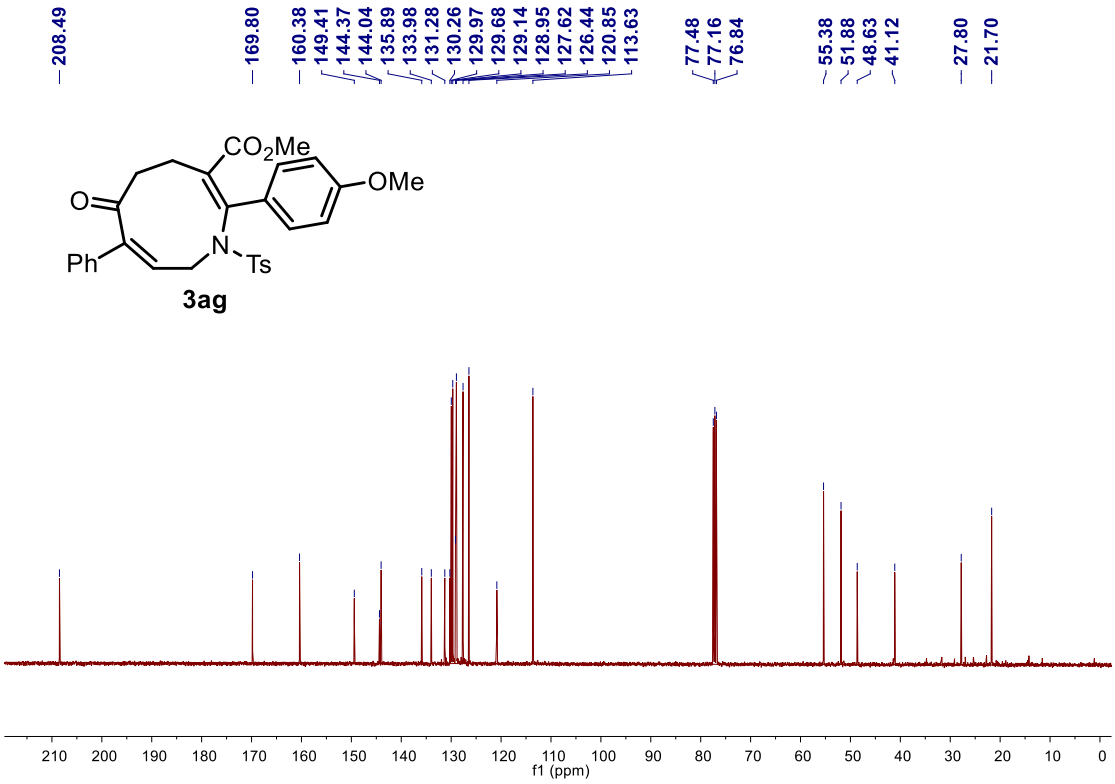
HRMS of **3af**



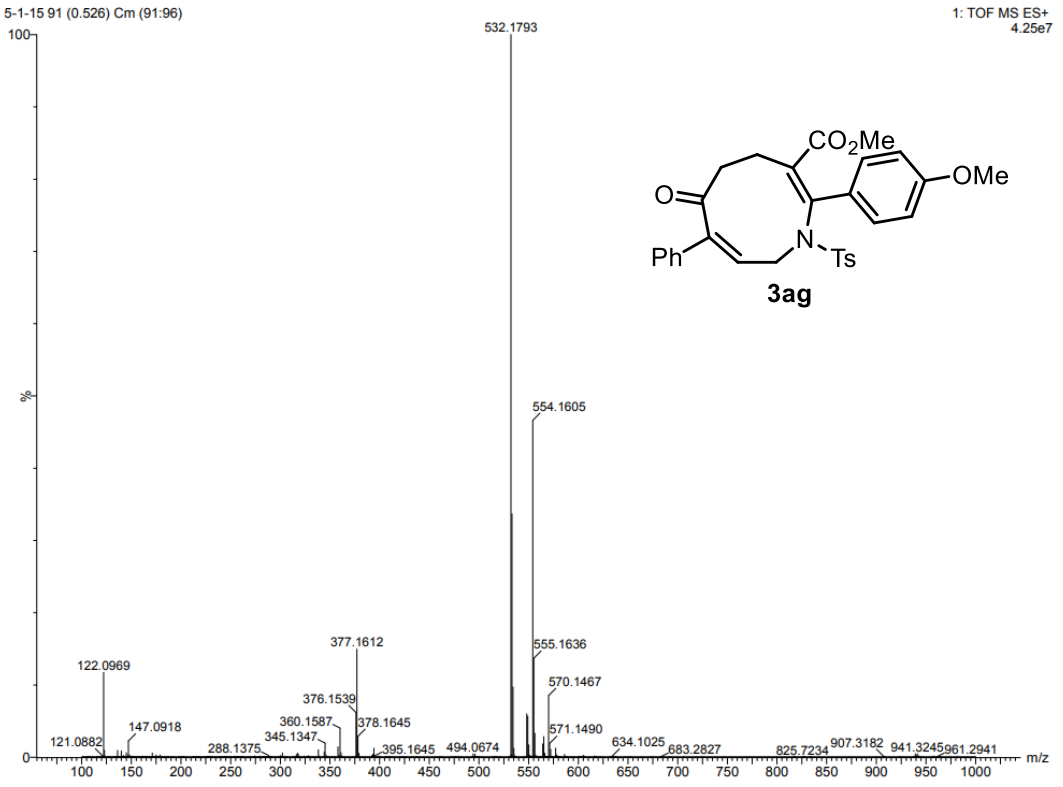
^{1}H NMR (400 MHz, $CDCl_3$) of **3ag**



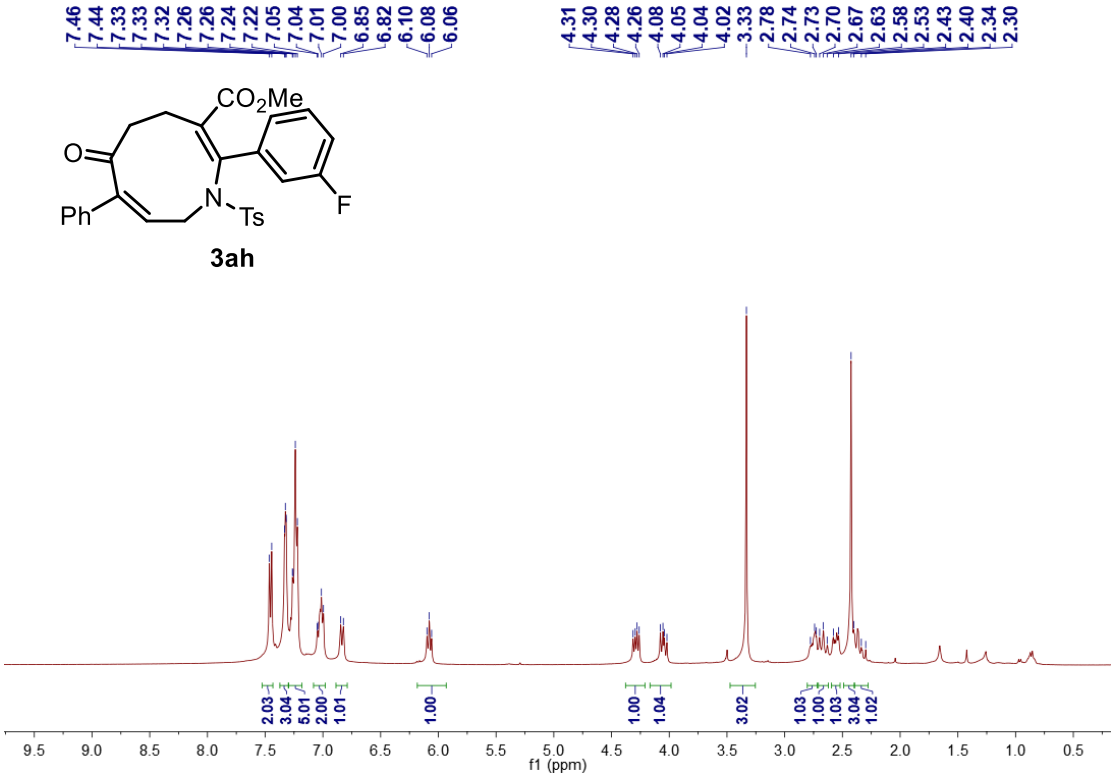
^{13}C NMR (100 MHz, $CDCl_3$) of **3ag**



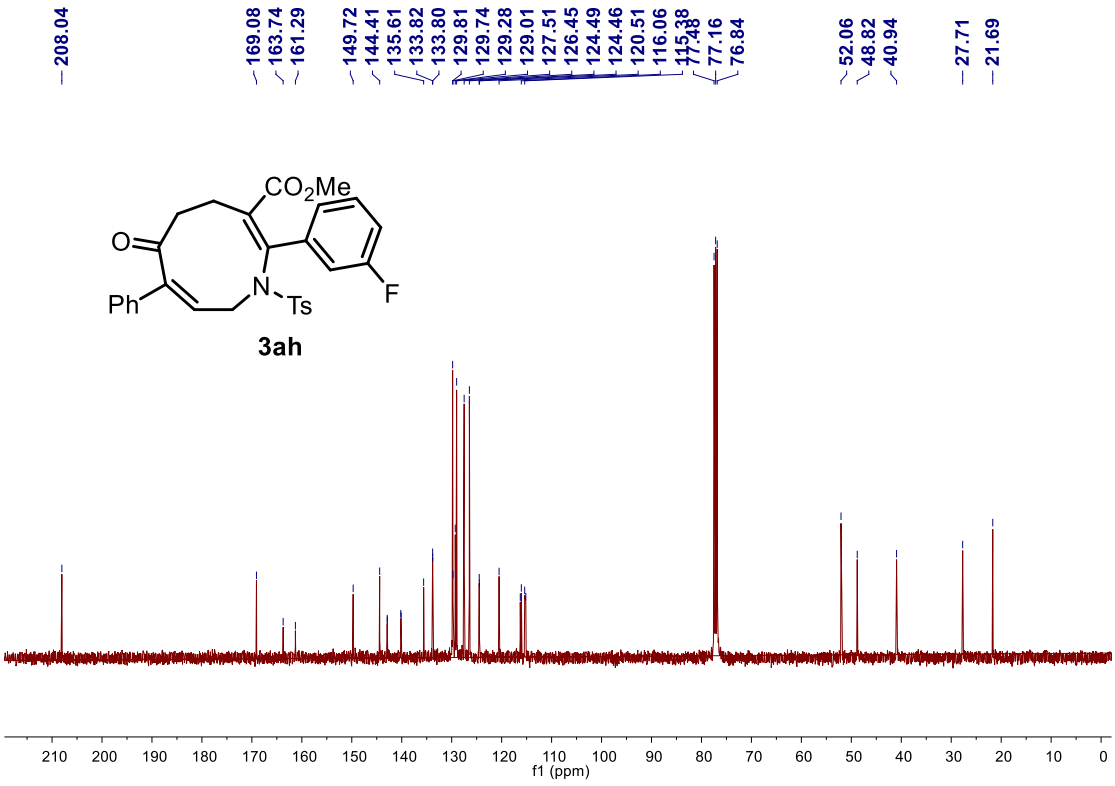
HRMS of **3ag**



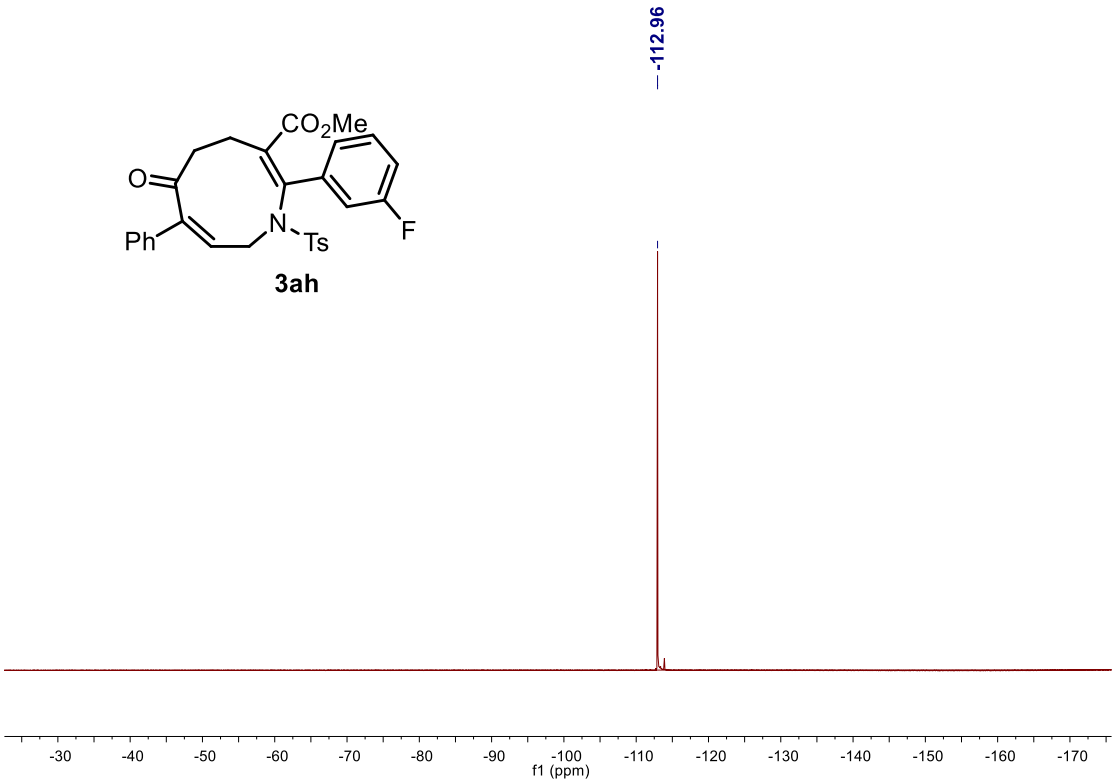
^{1}H NMR (400 MHz, $CDCl_3$) of **3ah**



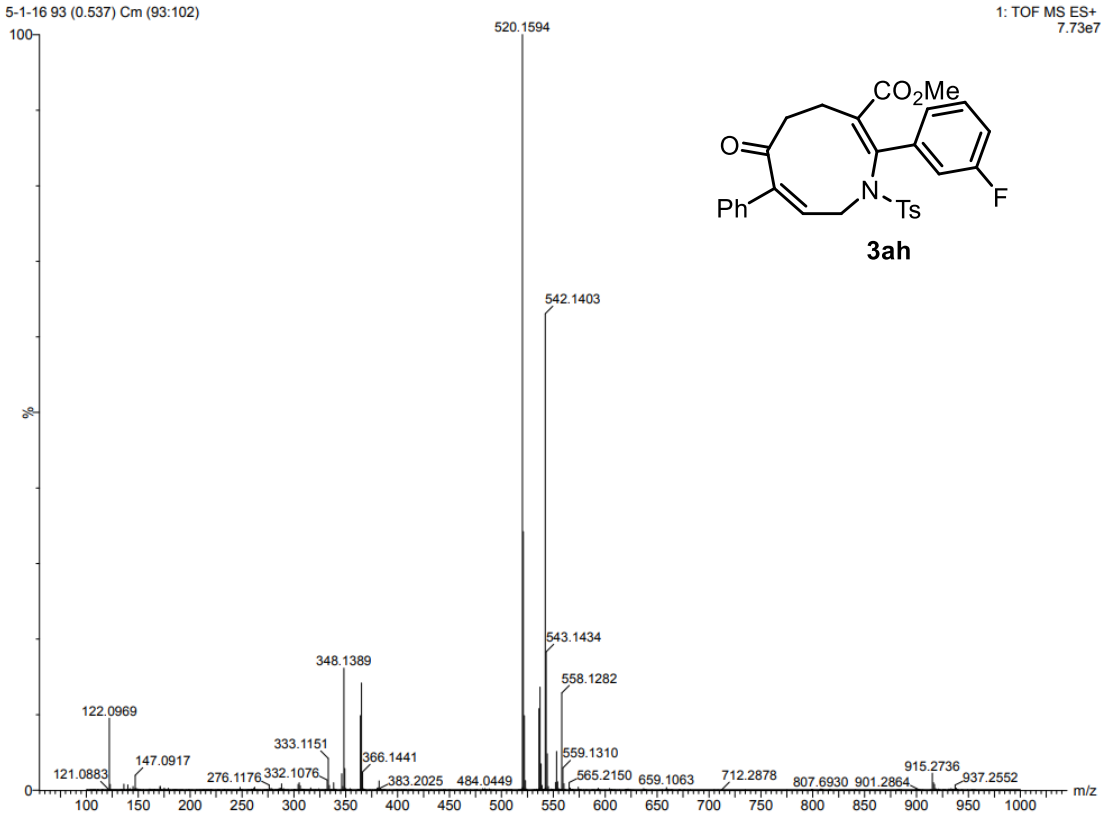
^{13}C NMR (100 MHz, $CDCl_3$) of **3ah**



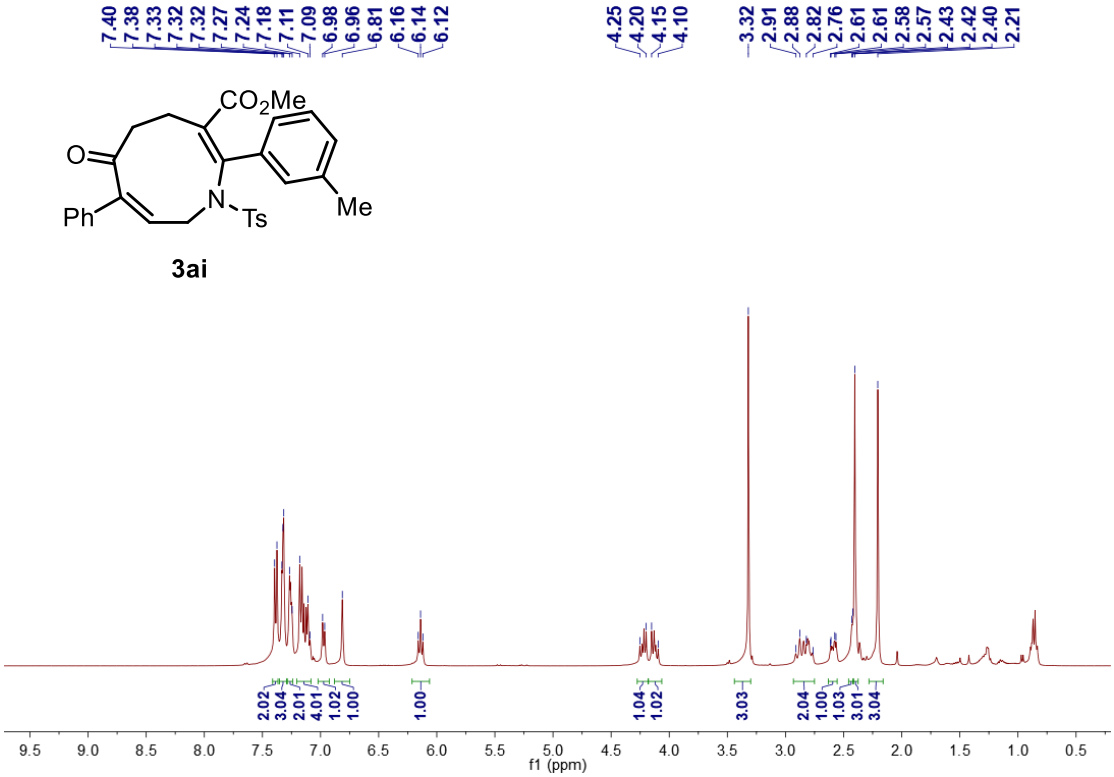
^{19}F NMR (376 MHz, $CDCl_3$) of **3ah**



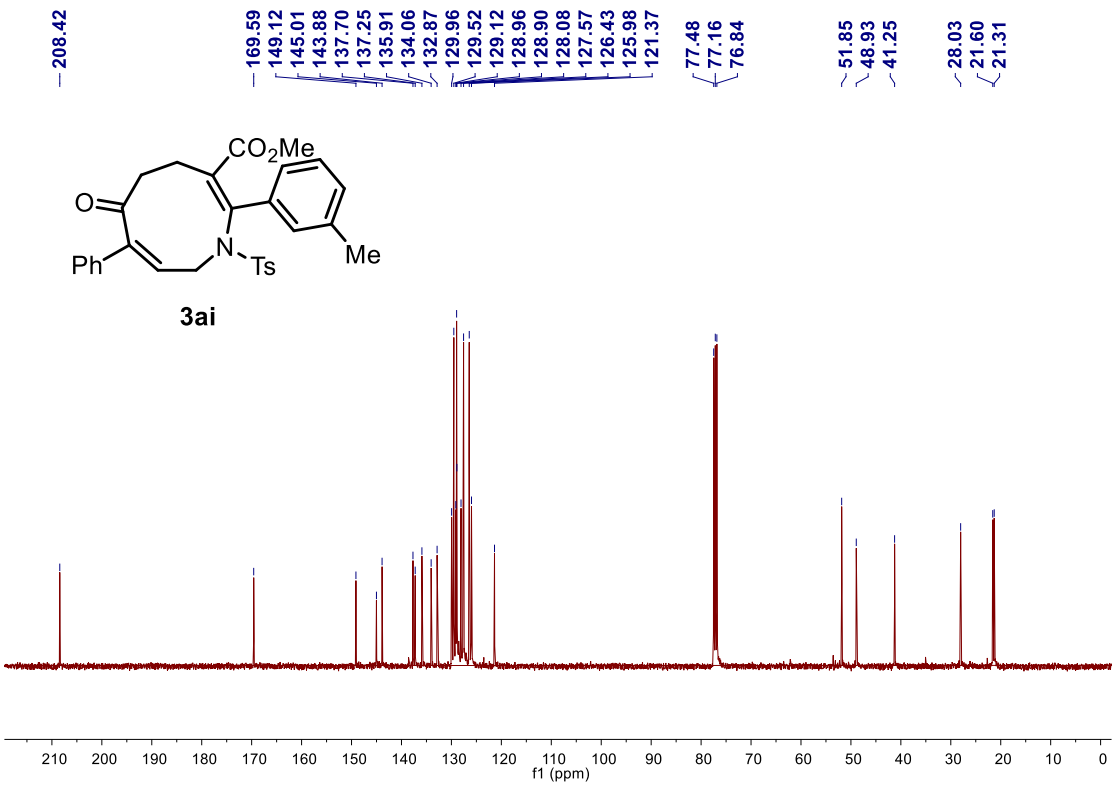
HRMS of **3ah**



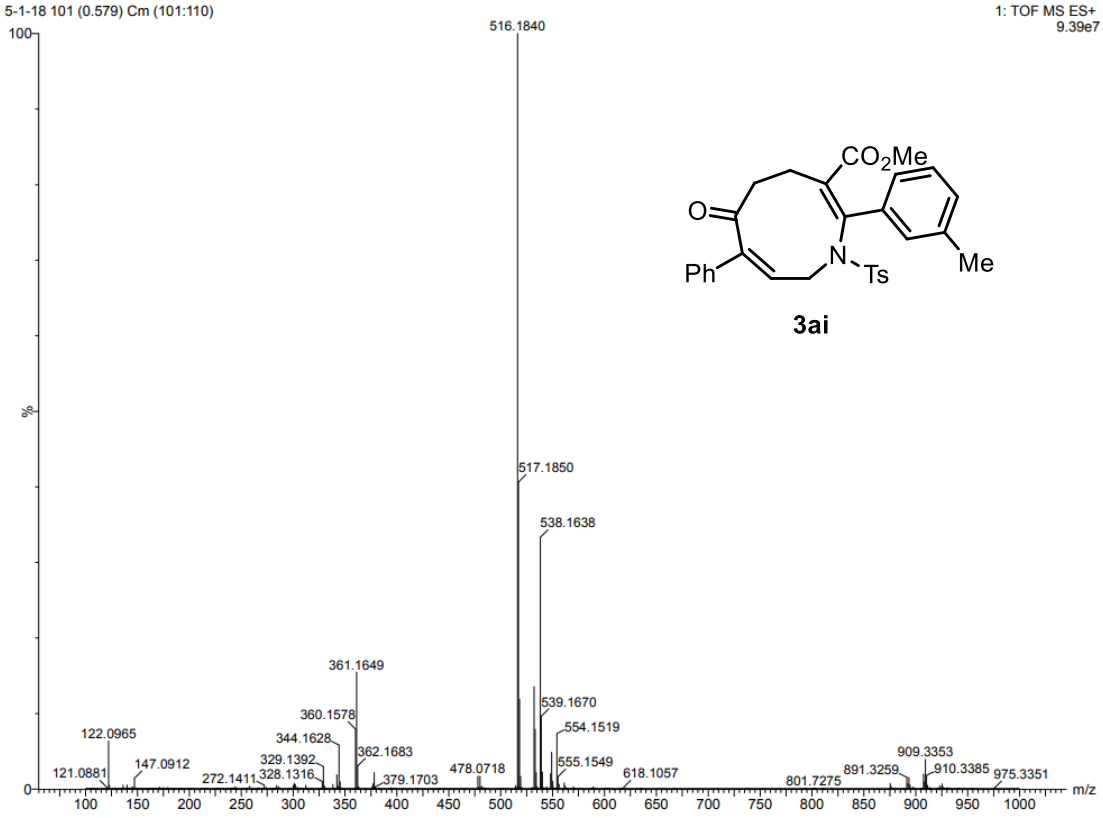
^{1}H NMR (400 MHz, $CDCl_3$) of **3ai**



^{13}C NMR (100 MHz, $CDCl_3$) of **3ai**

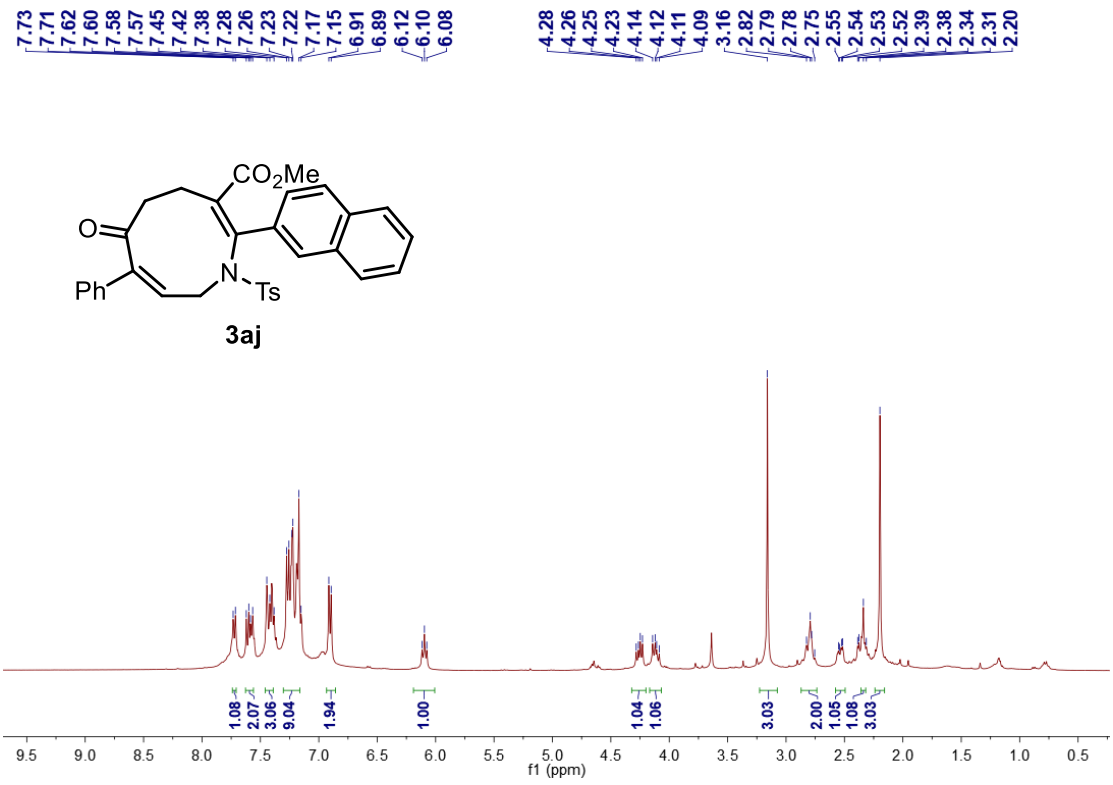


HRMS of **3ai**



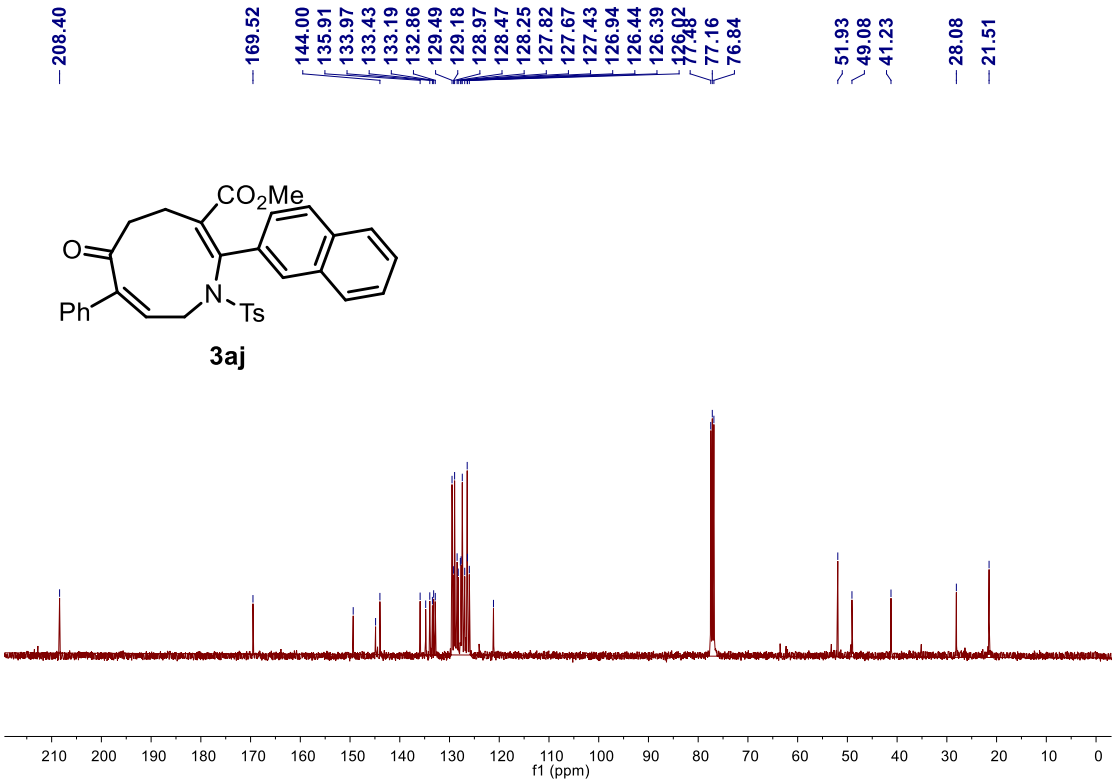
3ai

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

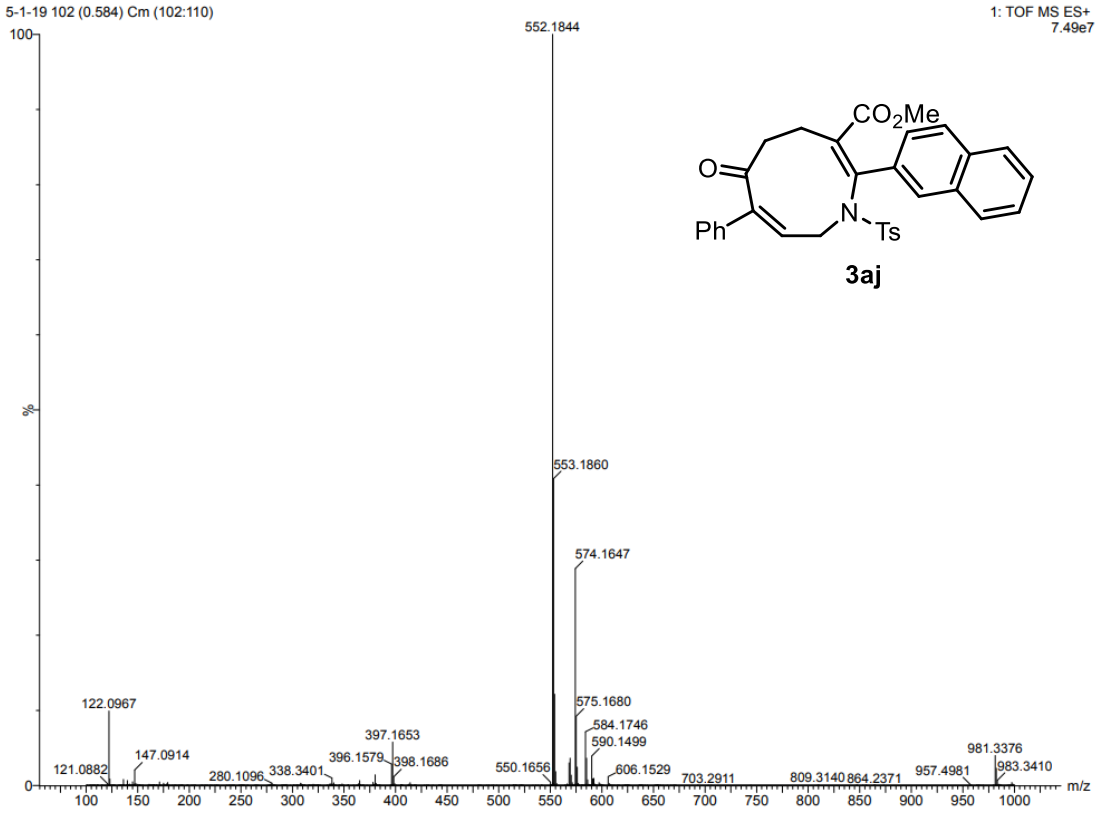


3aj

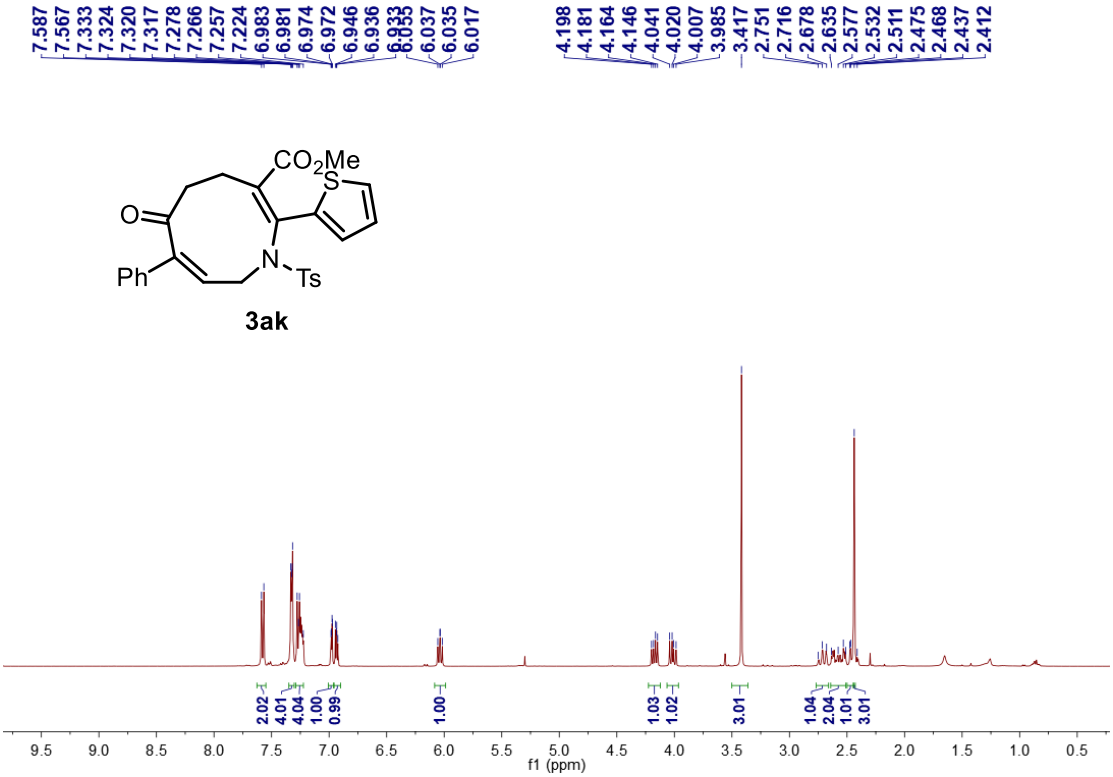
^{13}C NMR (100 MHz, $CDCl_3$) of **3aj**



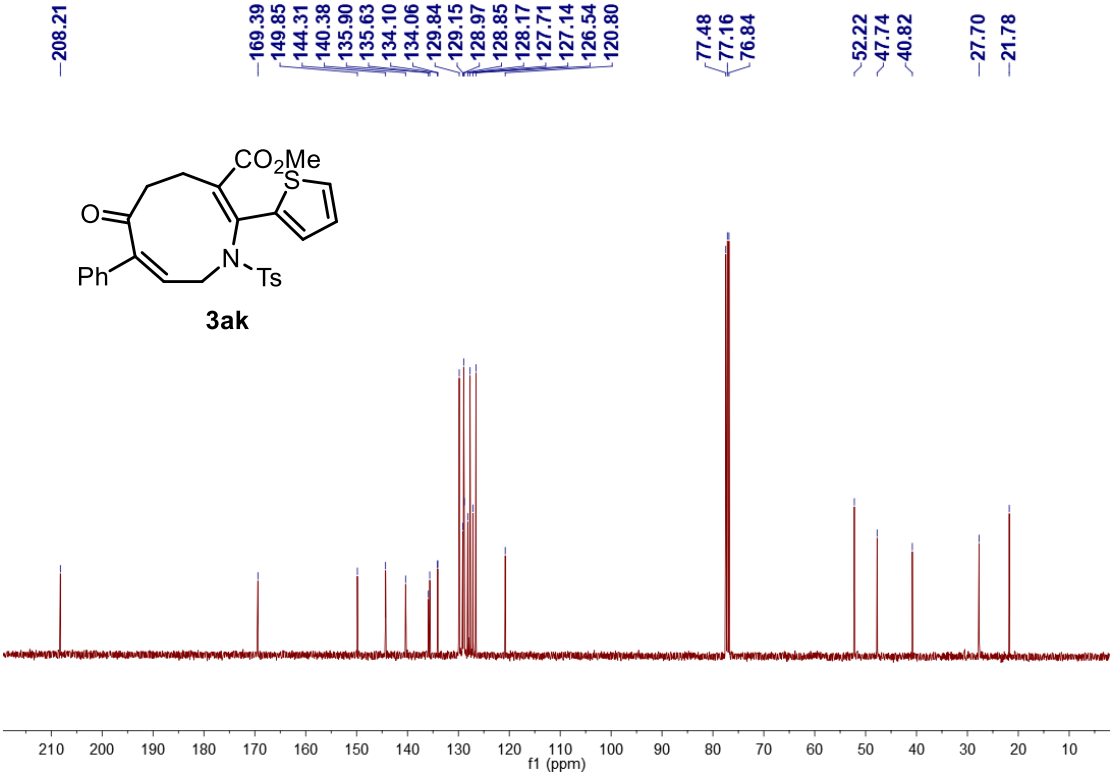
HRMS of **3aj**



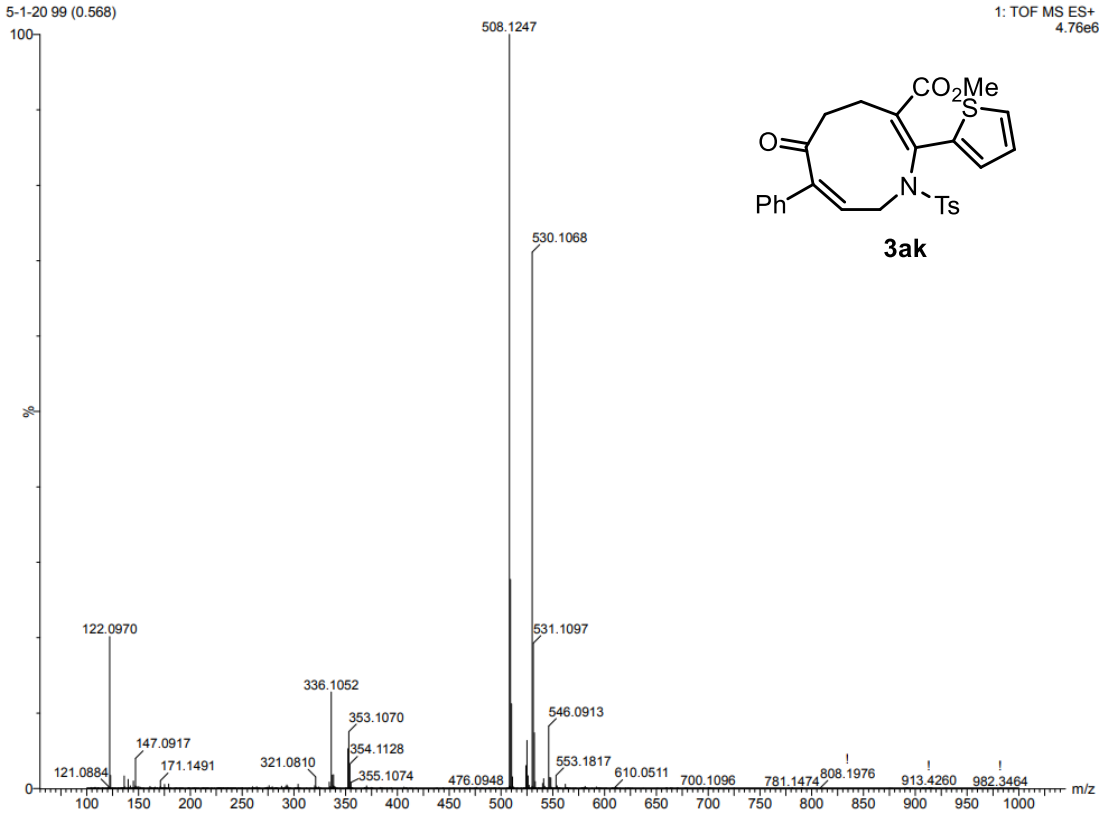
^{1}H NMR (400 MHz, $CDCl_3$) of **3ak**



^{13}C NMR (100 MHz, $CDCl_3$) of **3ak**

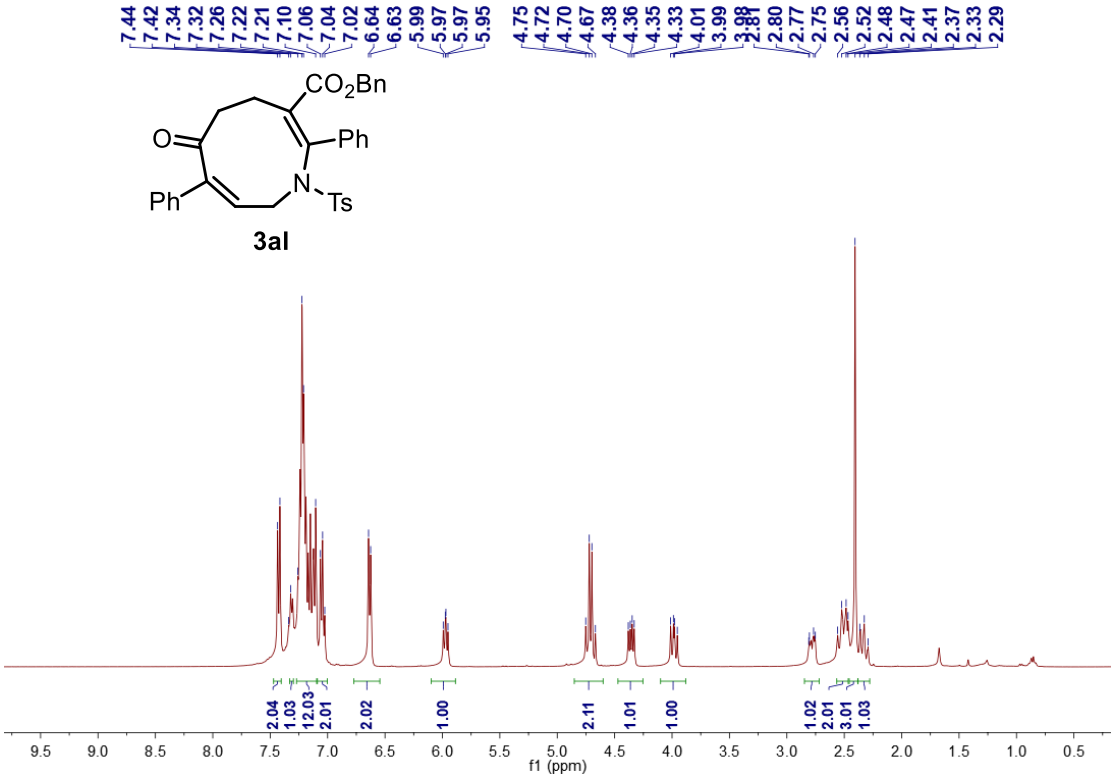


HRMS of **3ak**



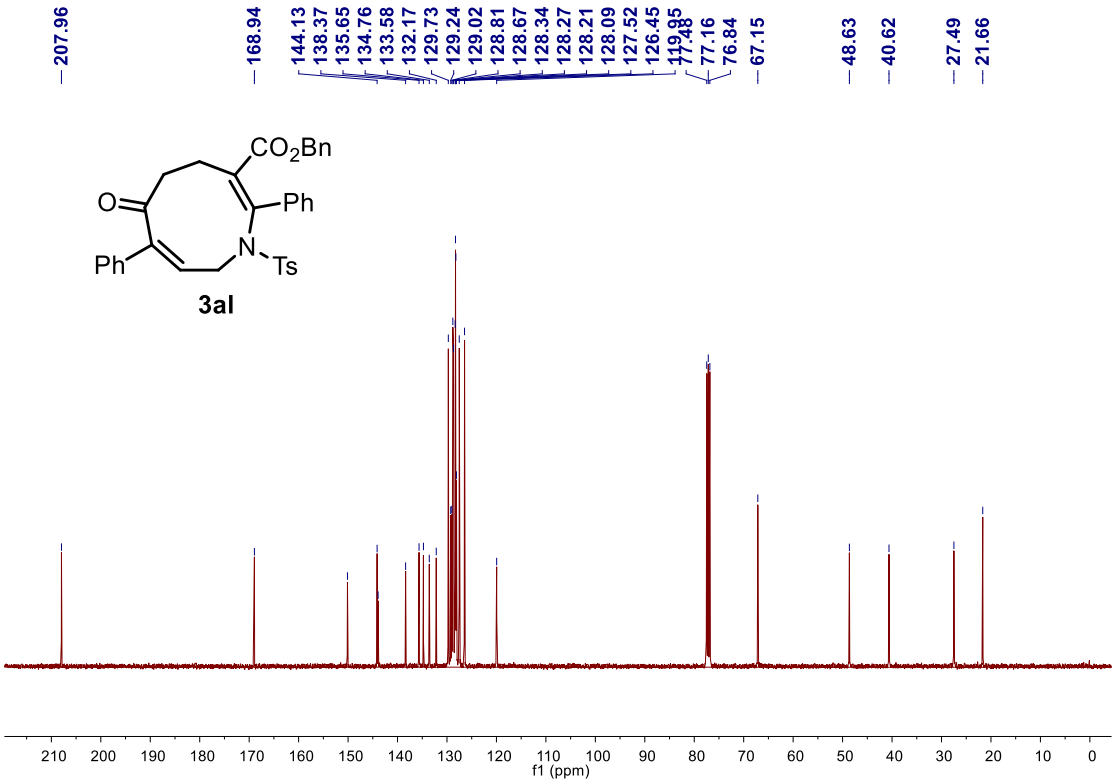
3ak

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

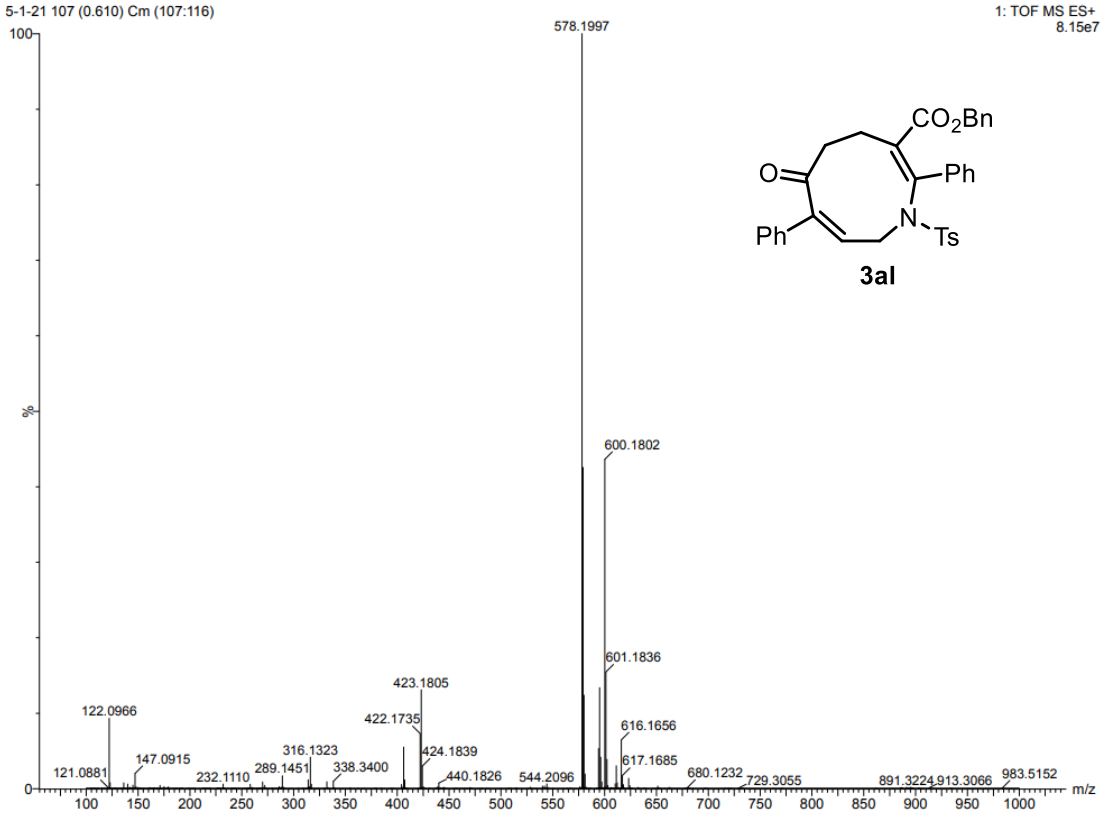


3al

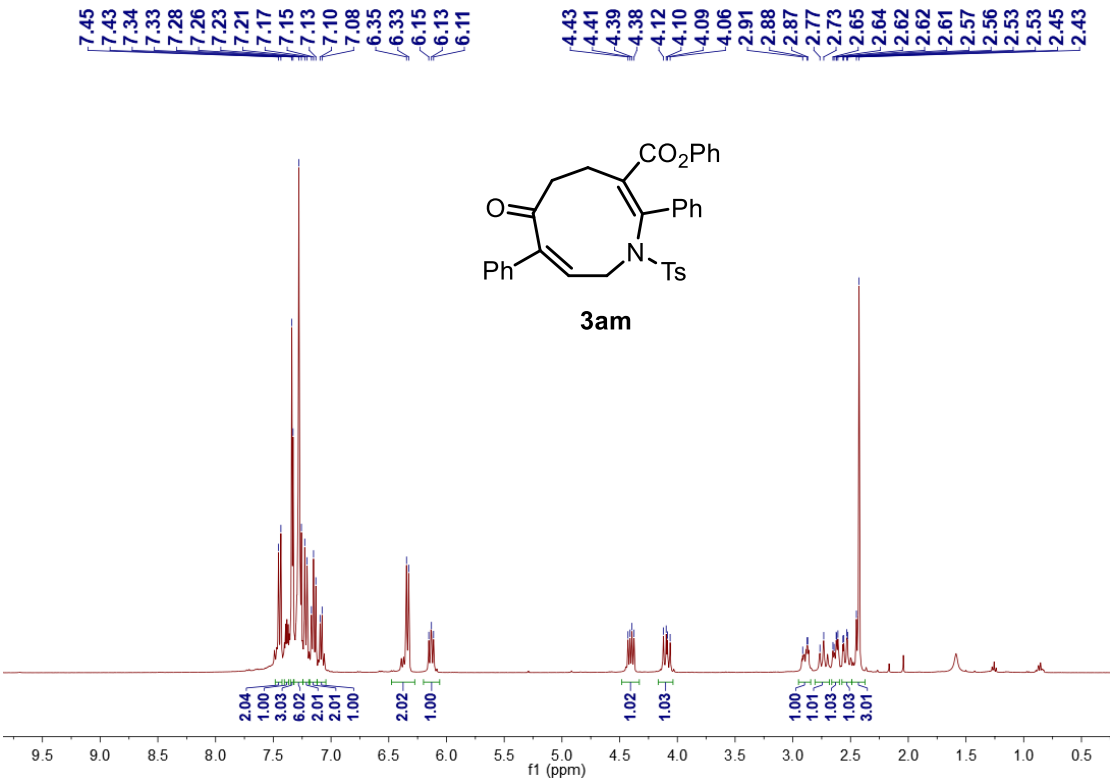
^{13}C NMR (100 MHz, $CDCl_3$) of **3al**



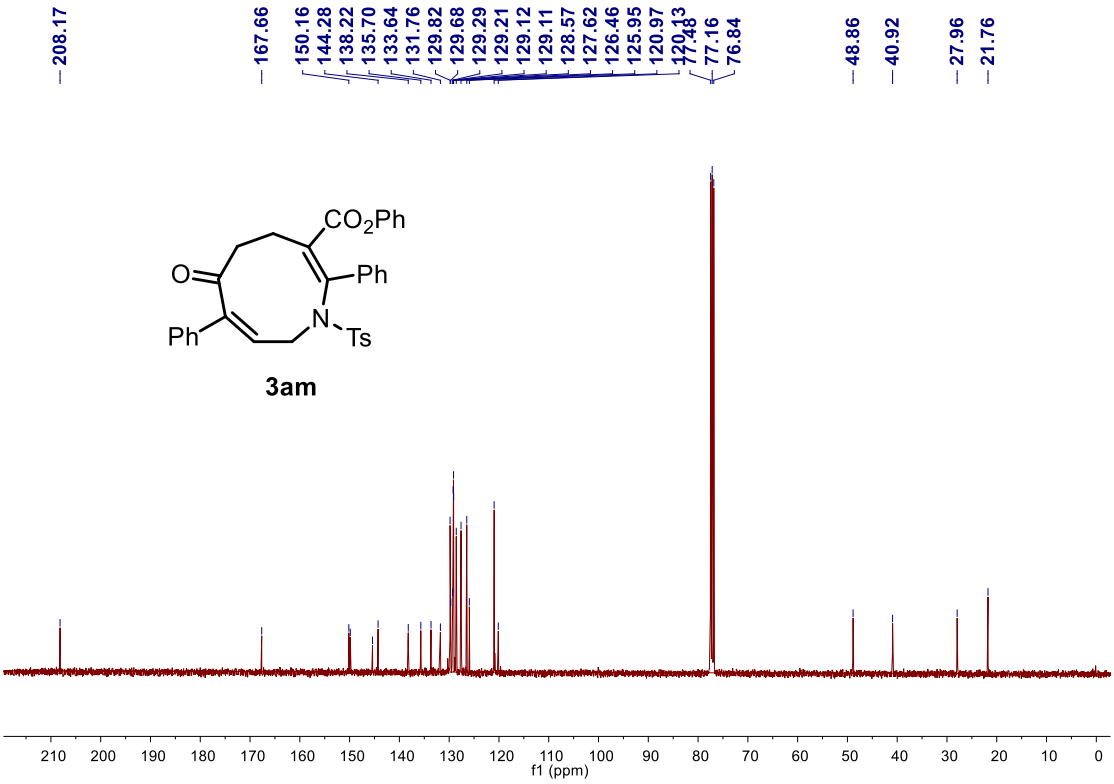
HRMS of **3al**



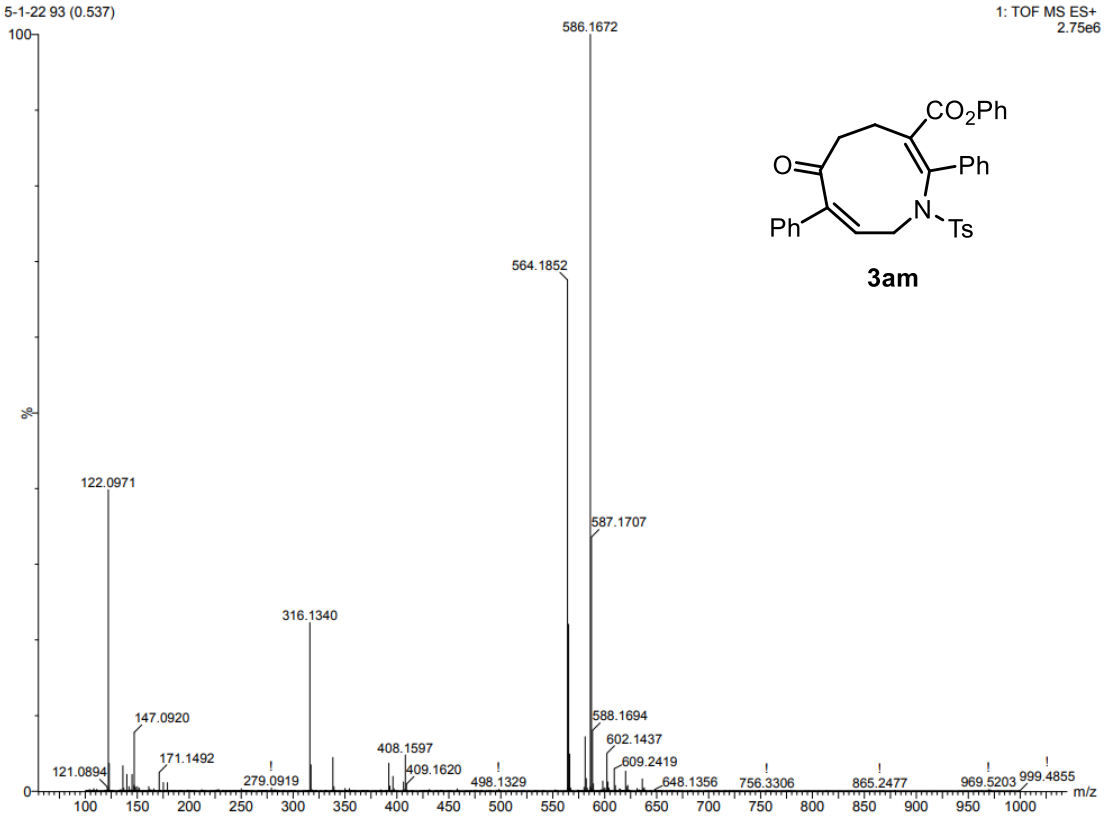
^{1}H NMR (400 MHz, $CDCl_3$) of **3am**



^{13}C NMR (100 MHz, $CDCl_3$) of **3am**

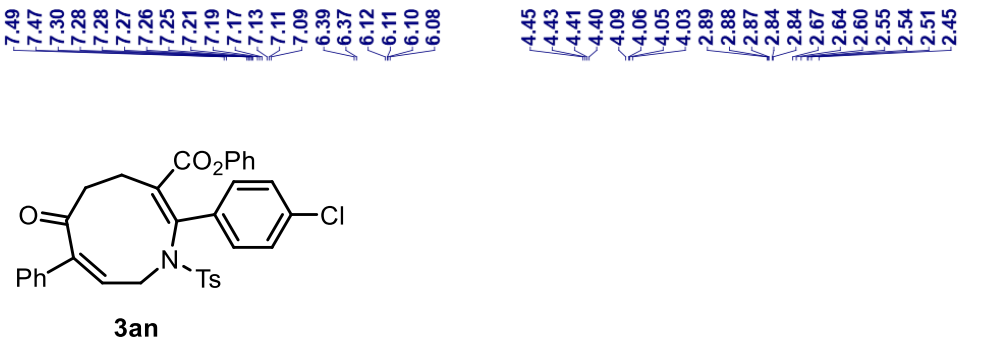


HRMS of **3am**

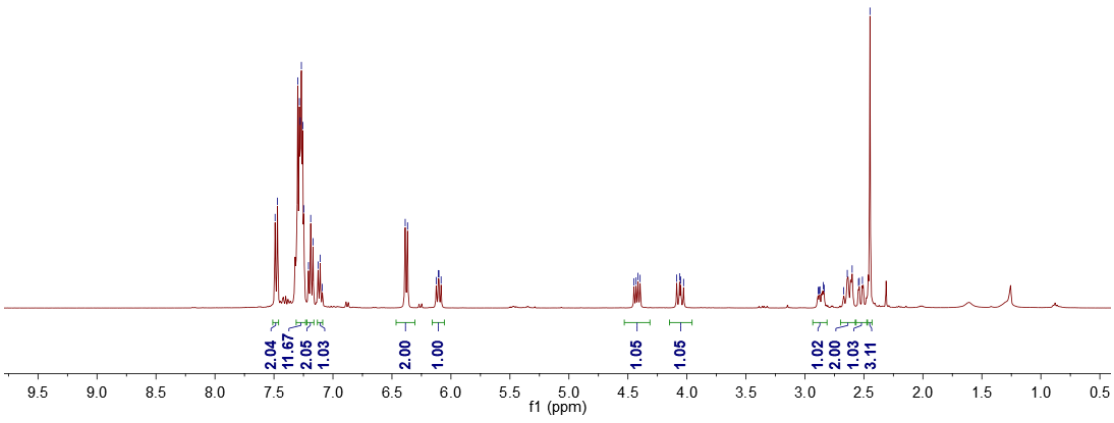


3am

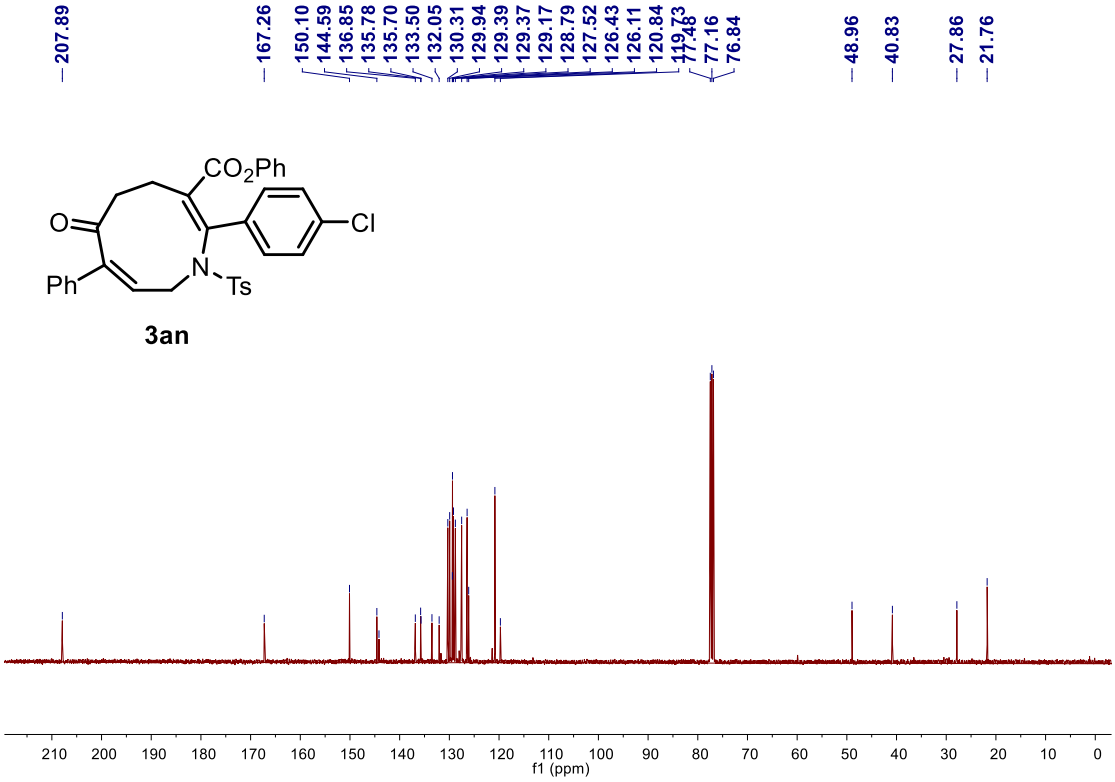
^{1}H NMR (400 MHz, $CDCl_3$) of **3an**



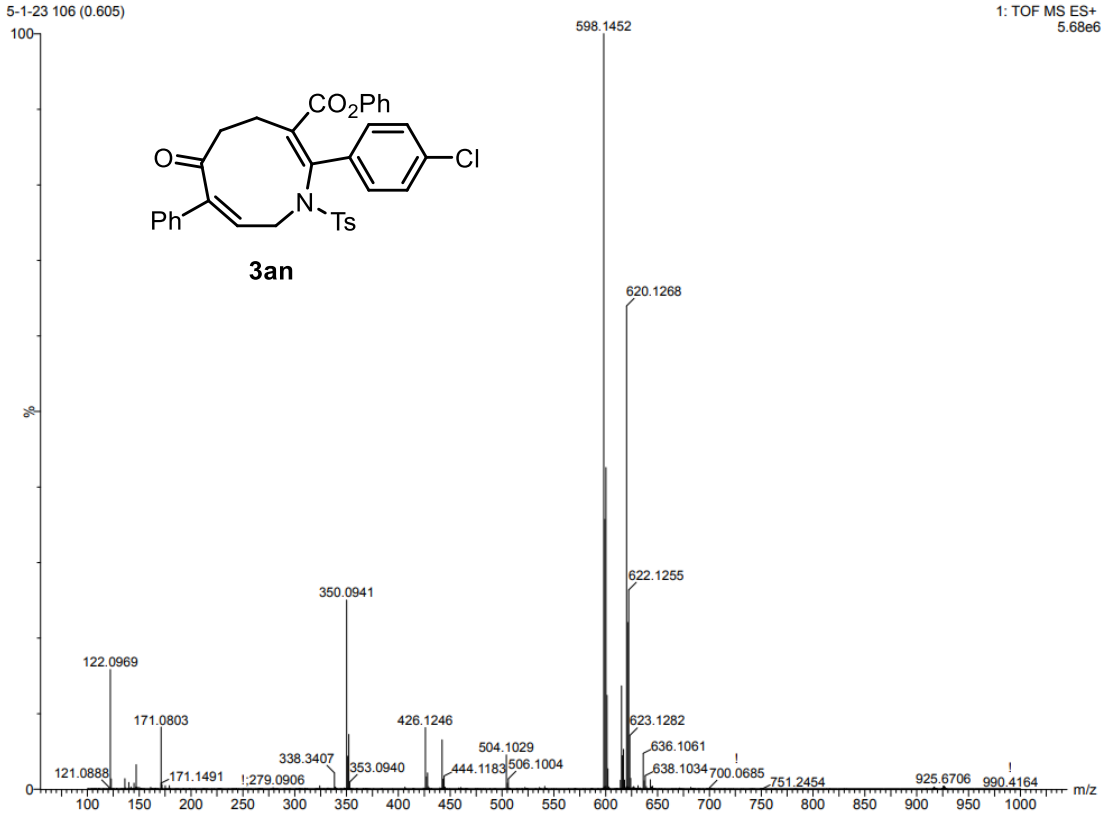
3an



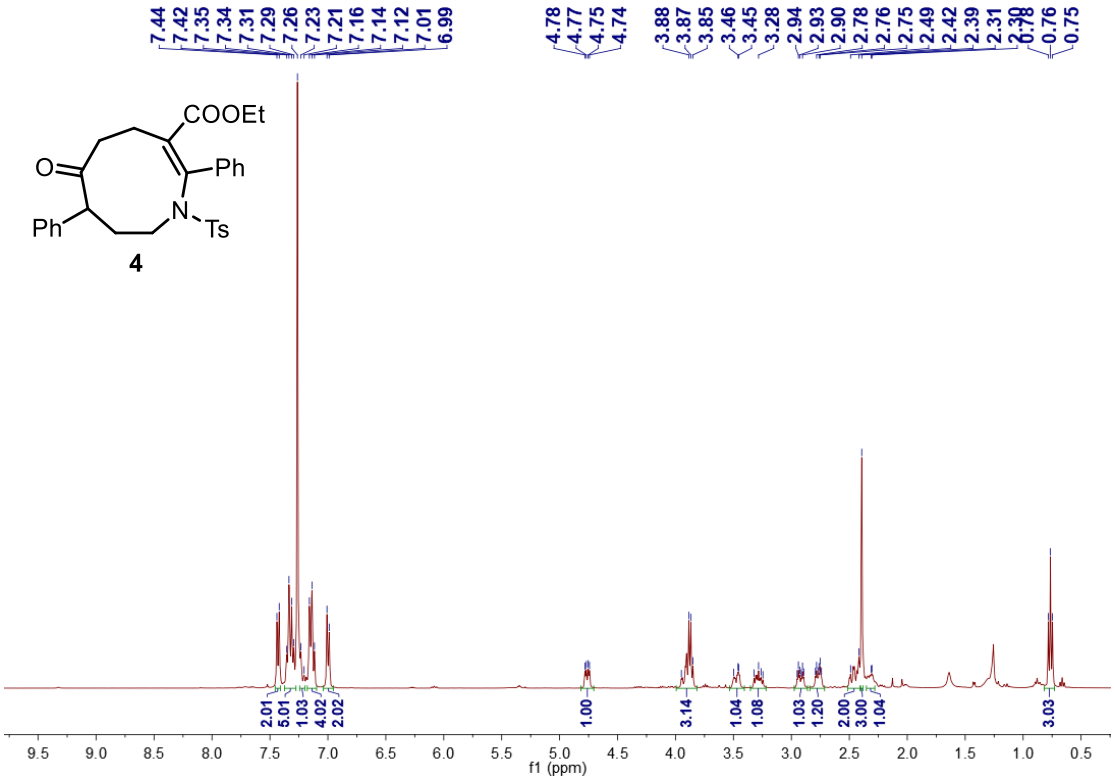
^{13}C NMR (100 MHz, $CDCl_3$) of **3an**



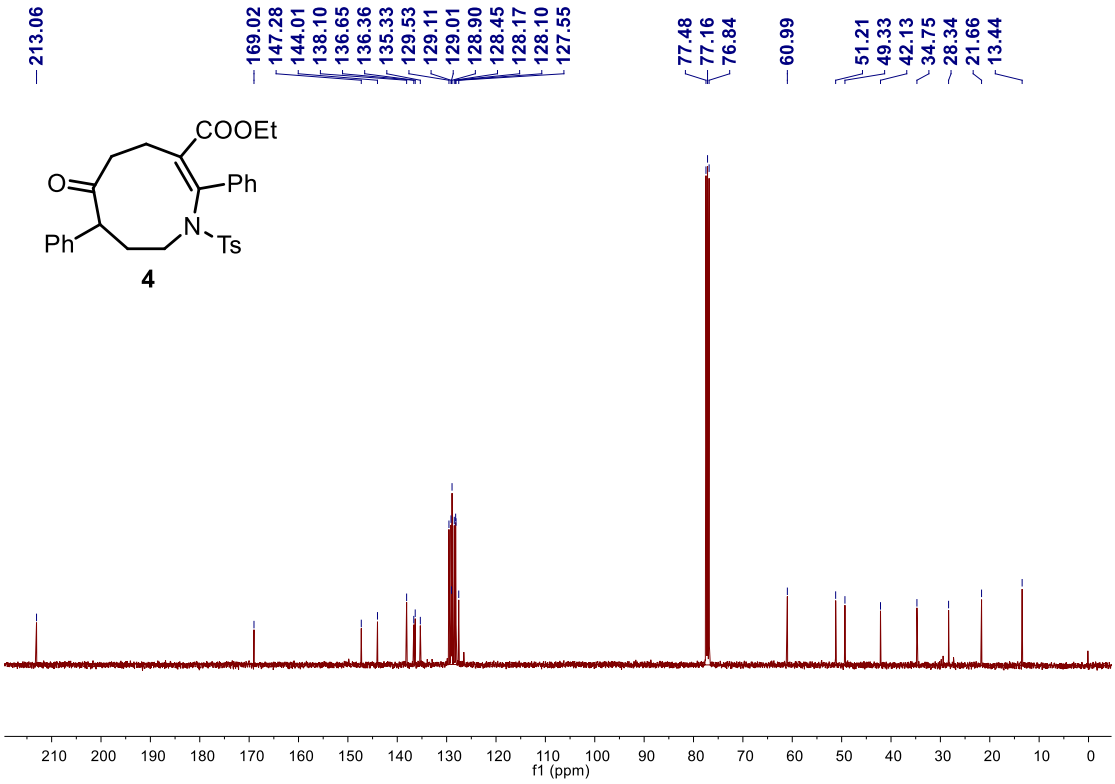
HRMS of **3an**



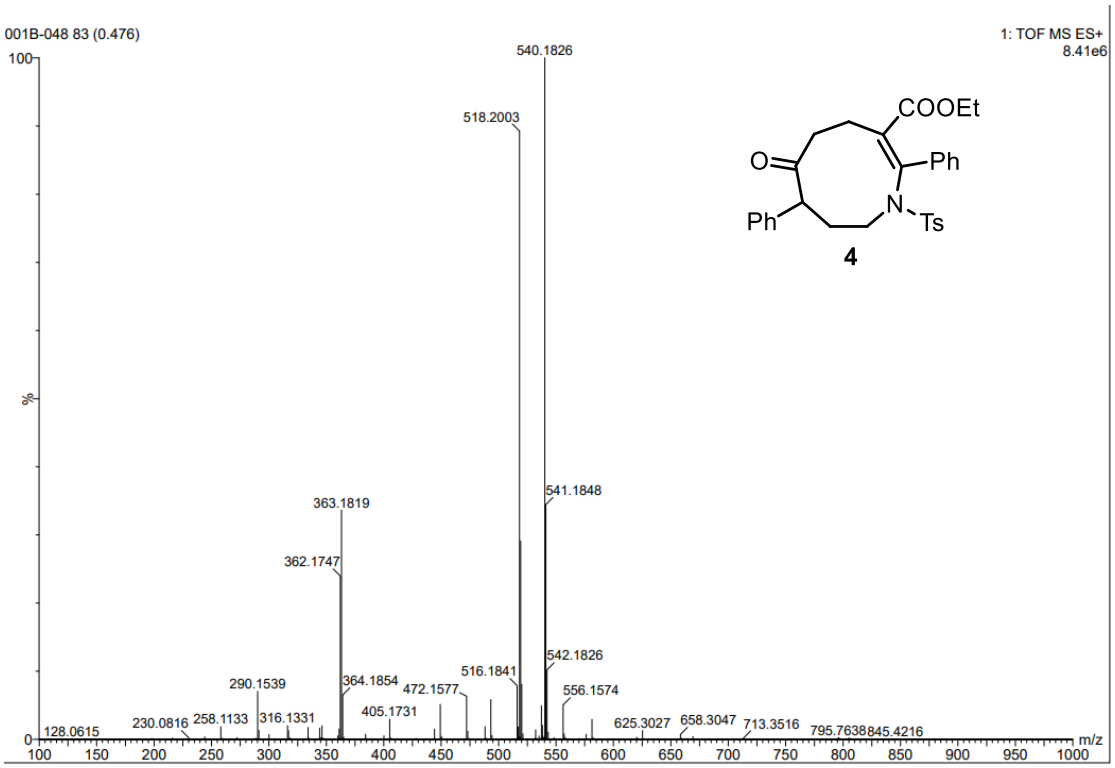
^{1}H NMR (400 MHz, $CDCl_3$) of **4**



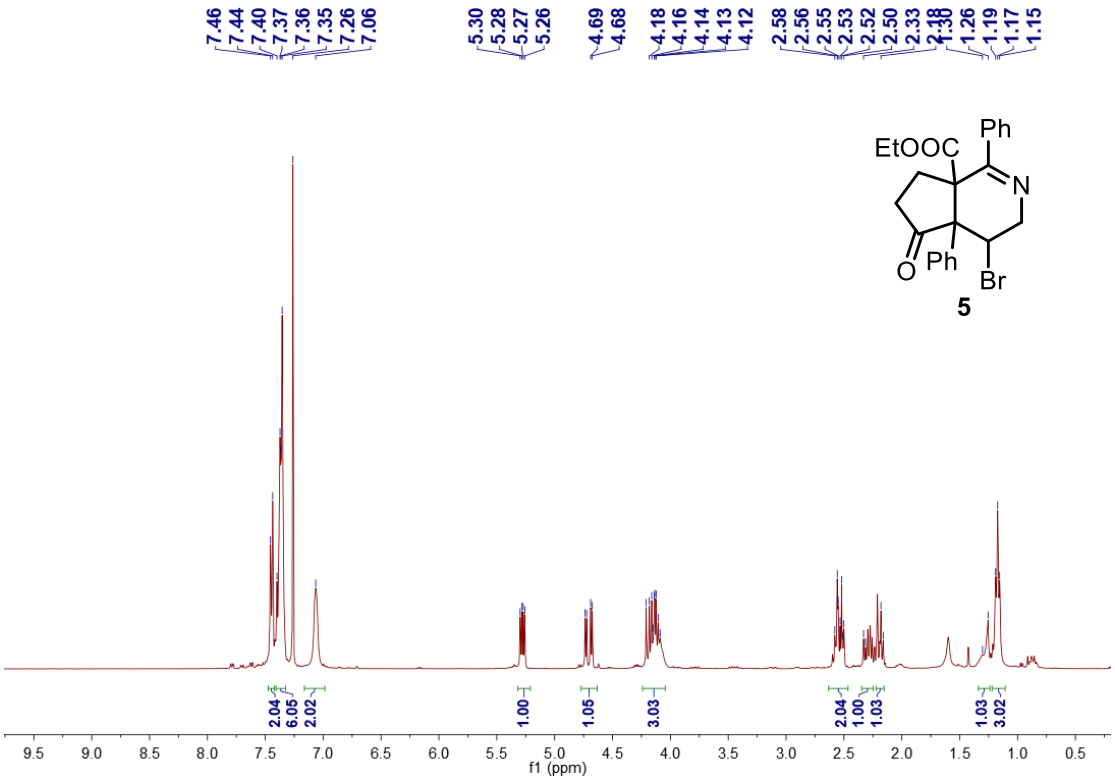
^{13}C NMR (100 MHz, $CDCl_3$) of **4**



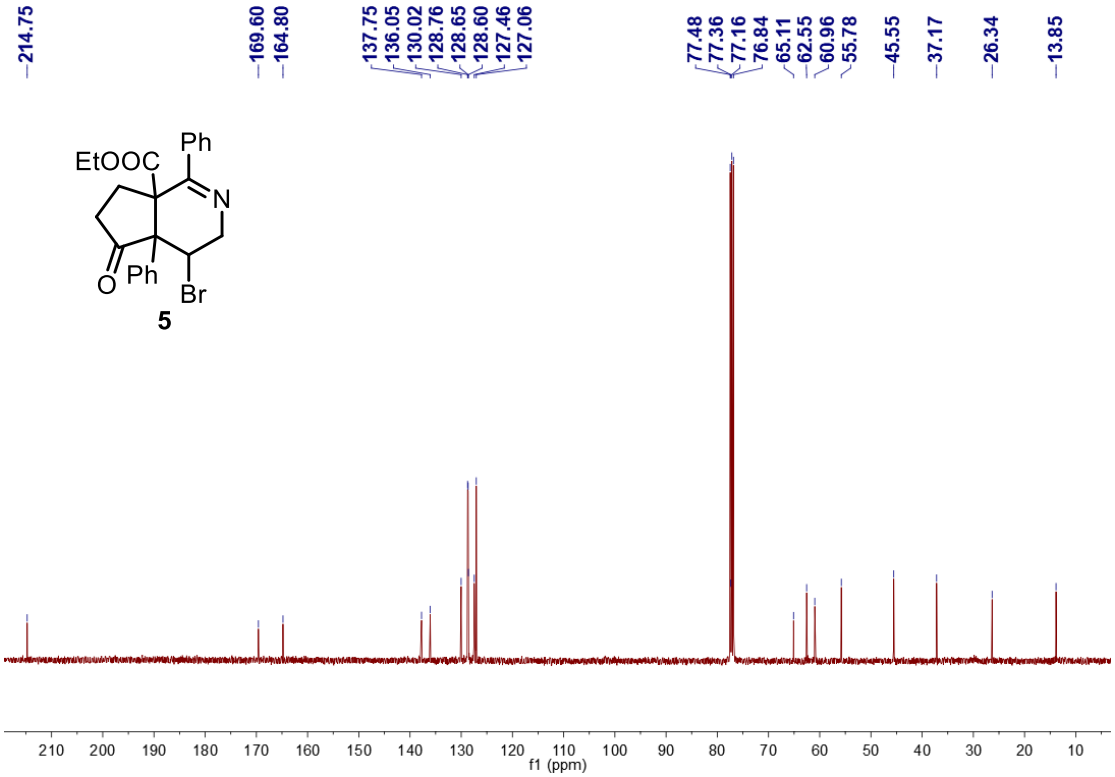
HRMS of **4**



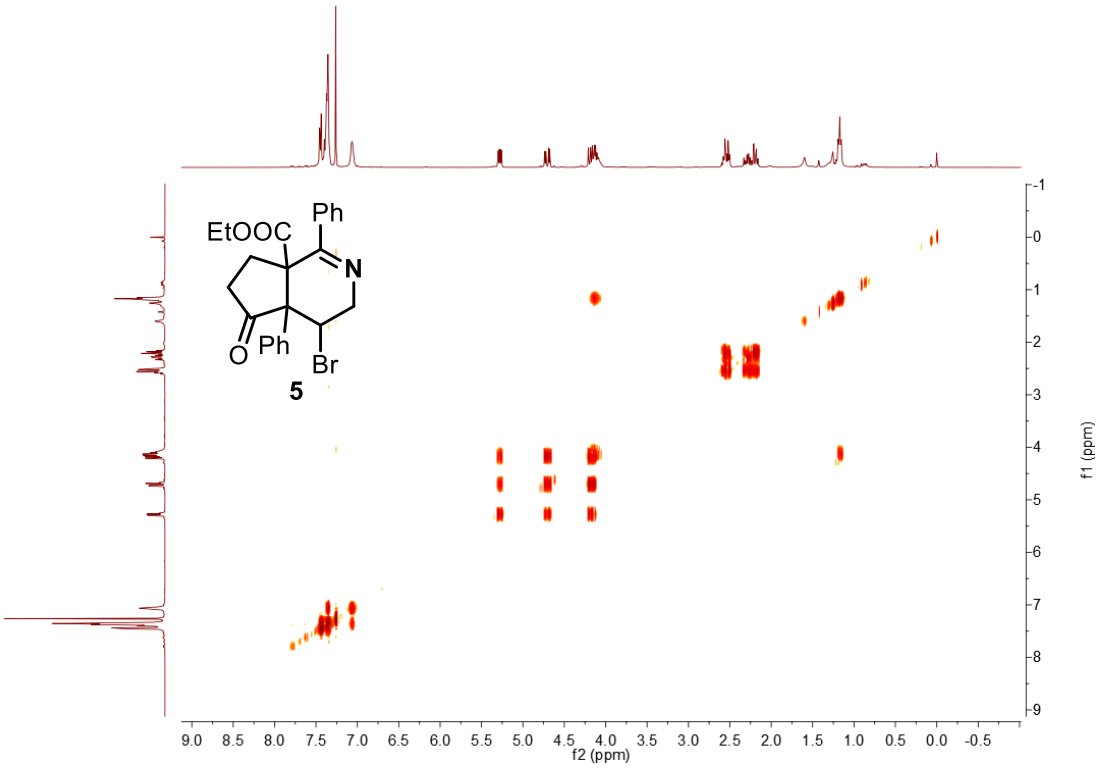
^{1}H NMR (400 MHz, $CDCl_3$) of **5**



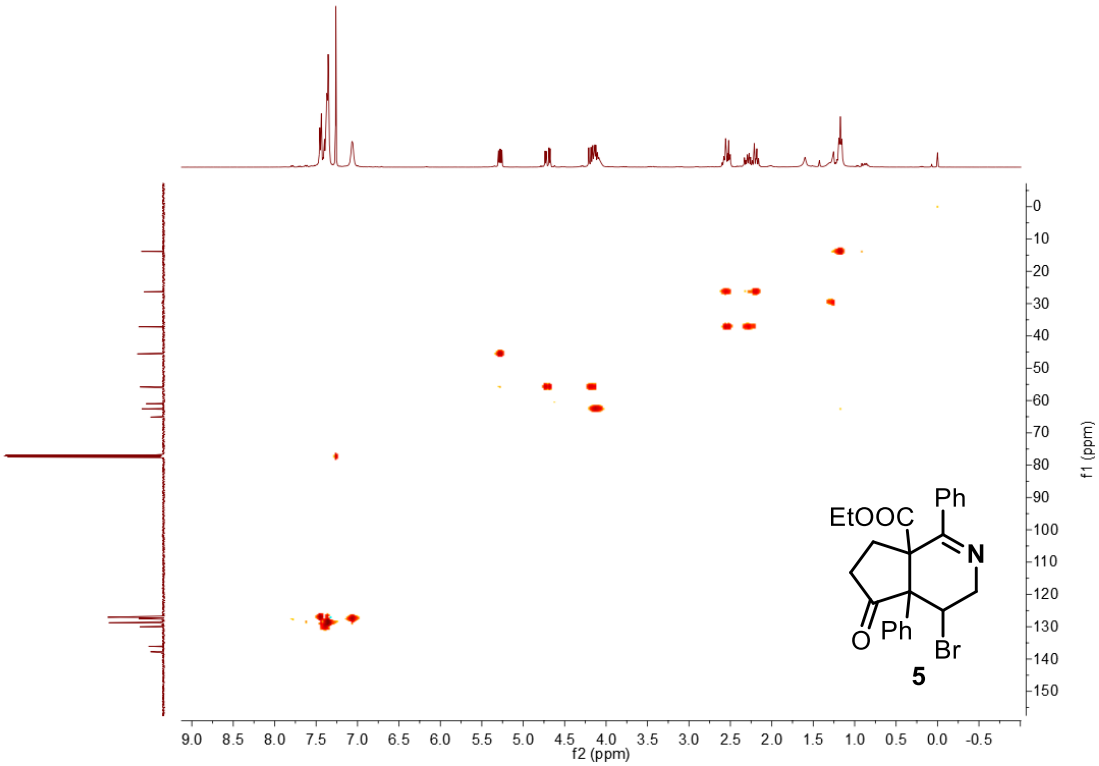
^{13}C NMR (100 MHz, $CDCl_3$) of **5**



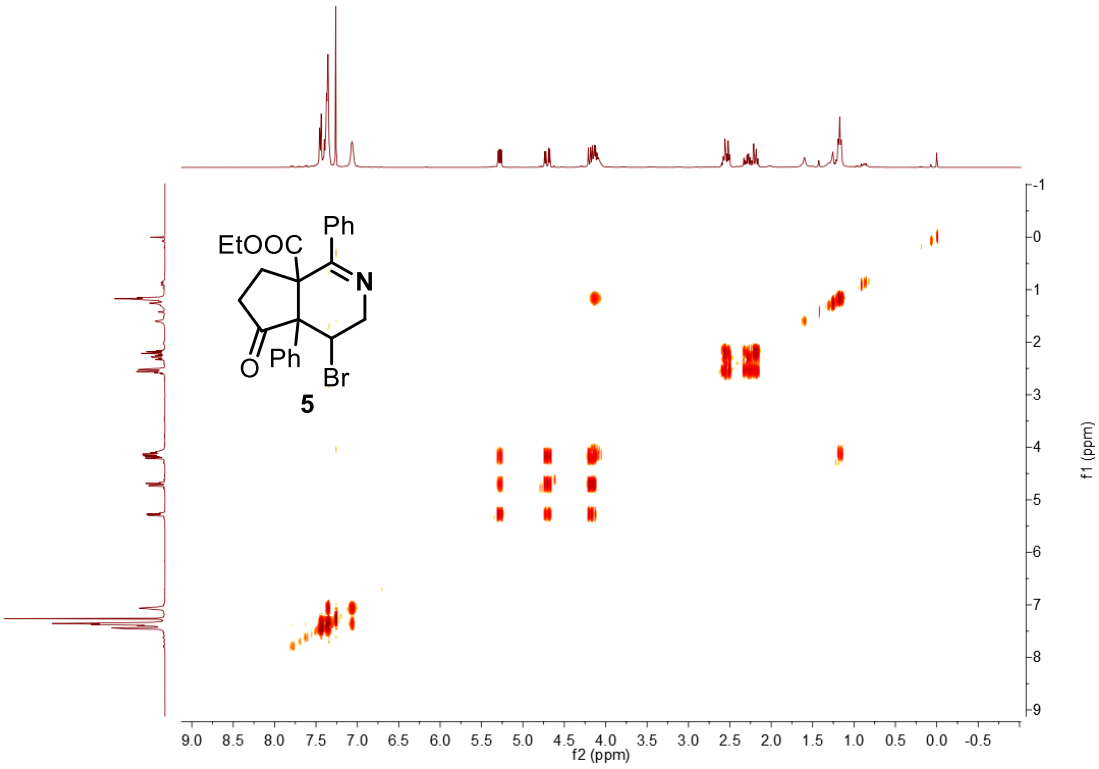
COSY of **5**



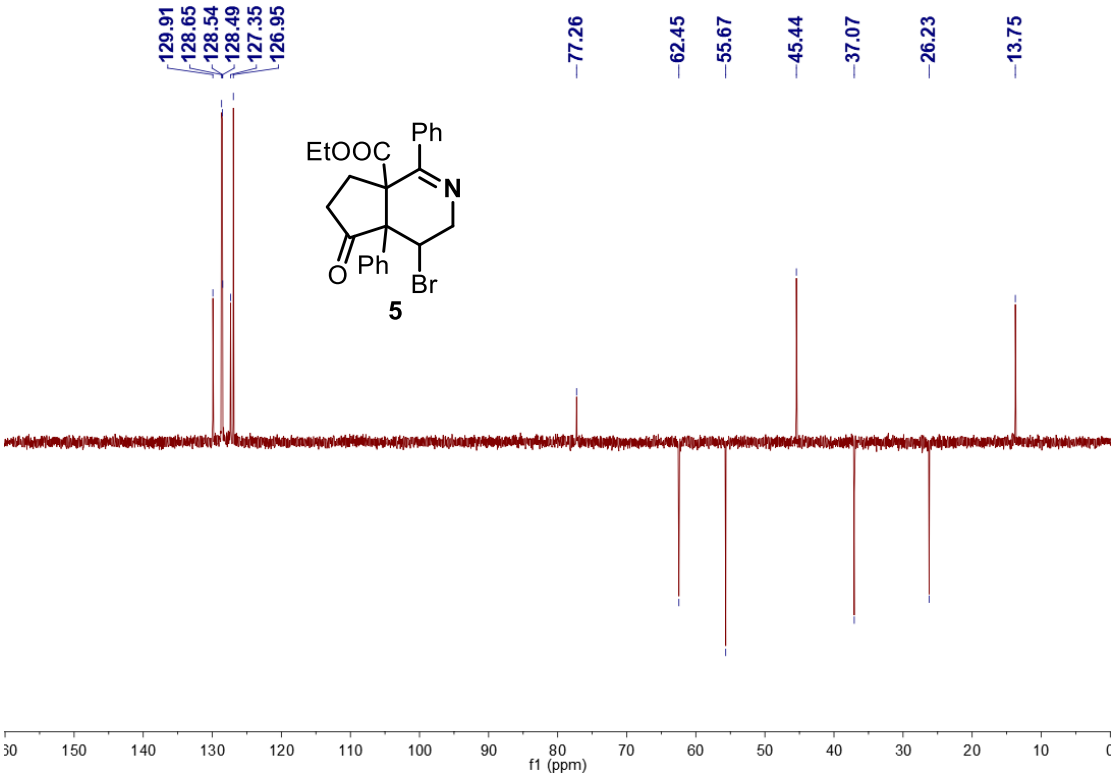
HSQC of **5**



HMBC of **5**



DEPT135 of **5**



HRMS of **5**