Supporting Information

Unprecedented Synthesis of aza-Benzodioxepine Derivatives using a Rh-Catalyzed Tandem 1,3-Rearrangement and [3+2] Cycloaddition of Carbonyltriazoles

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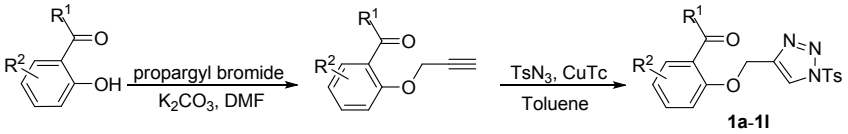
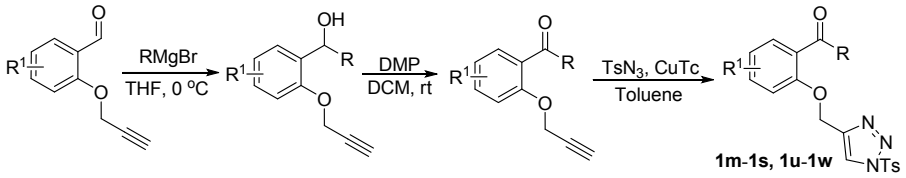
1. General Remarks. MP was obtained with a Yanagimoto micro melting point apparatus and is uncorrected. ^{1}H NMR spectra were recorded for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard or DMSO-d_6. *J*-values are in Hz. HRMS was measured by a Finnigan MA+ mass spectrometer. Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure. All reactions were performed under argon using standard Schlenk techniques.

2. General procedure for the synthesis of triazoles 1, 3, 4, 6.



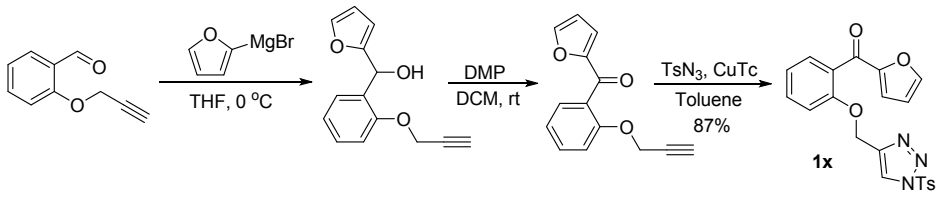
Salicylaldehyde (10.0 mmol, 1.0 equiv) was suspended in DMF (20 mL), followed by addition of K_2CO_3 (20.0 mmol, 2 equiv). The suspension was stirred for 10 min, and then propargyl bromide (15.0 mmol, 1.5 equiv) was added via a syringe at room temperature. The reaction mixture was stirred for 2 h at room temperature, whereupon a deep-yellow mixture was obtained. The reaction mixture was added into a large amount of water in a flask, producing the corresponding products as precipitates. After filtration, the crude product was washed with water (3 x 20 mL) and was used to the next step without further purification.

CuTc (0.4 mmol, 0.04 equiv) was added into a solution of the obtained alkyne product (10.0 mmol, 1.0 equiv) in toluene (10 mL). The reaction mixture was stirred for 3 min at room temperature, followed by addition of TsN_3 (12 mmol, 1.2 equiv) via a syringe. The reaction mixture was stirred for 5 h at room temperature and the resulting mixture was directly subjected to a flash column chromatography to get the pure product.



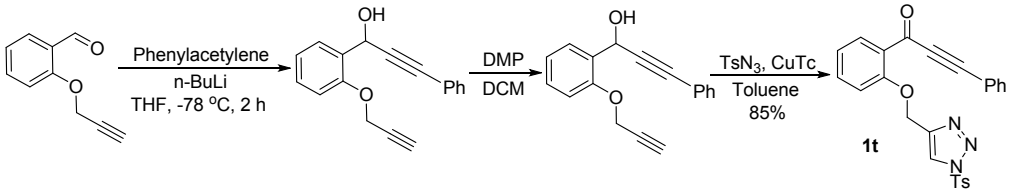
To a 100 mL flame dried flask were added 2-(prop-2-ynyloxy)benzaldehyde (10 mmol, 1.60 g) and THF (50 mL), the mixture was cooled to 0 °C and then bromomagnesium (1.0 M, 13 mL) solution in THF was added dropwise. After 2 h, cold water was added to quench the reaction. The reaction mixture was diluted with DCM. After extraction, the organic layers were dried over Mg_2SO_4, filtered and concentrated in vacuo, and the crude product was purified by silica gel chromatography to give a yellow oily product. The obtained intermediate was dissolved in DCM, then DMP was added into this mixture and the resulting mixture was stirred at room temperature for 2 h. The reaction mixture was concentrated and the residue was purified by silica gel chromatography to give the desired ketone as colorless oil. The triazoles were then synthesized

according to the same procedure depicted above.



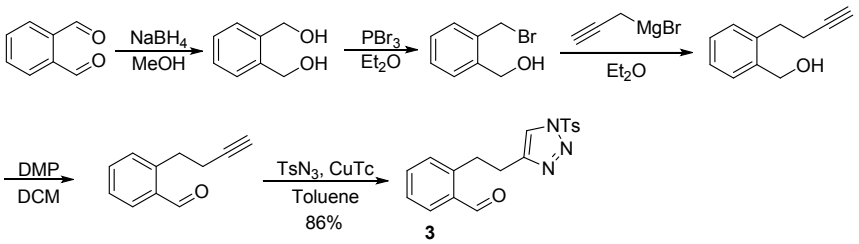
To a 100 mL flame dried flask were added Mg (16 mmol, 384 mg) and THF (15 mL) via a syringe and iodine under Ar, then a part of 2-bromofuran solution (15 mmol, 2.2 g) in THF (10 mL) was added dropwise to the reaction mixture, and the resulting mixture was heated until the brown color disappeared, and then the other part of 2-bromofuran in THF solution was added dropwise to this mixture slowly. The reaction mixture was stirred for 1 h at room temperature.

The mixture obtained as mentioned above was added dropwise to the solution of aldehyde in THF (10 mL) at 0 °C, and the resulting mixture was stirred for 2 h. Then, cold water was added to quench the reaction. The reaction mixture was diluted with EA (ethyl acetate). After extraction, the organic layers were washed by water, brine, and dried over anhydrous Mg_2SO_4, filtered and concentrated in vacuo. The crude product was purified by silica gel chromatography to give a yellow oily product. The obtained intermediate was used to the next steps following the same procedure depicted above to give product **1x** in 87% yield.

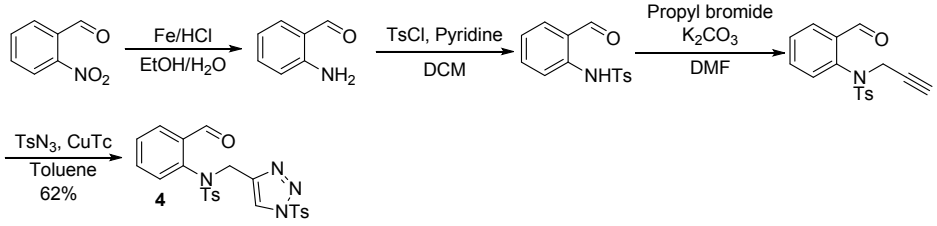


To a 100 mL flame dried flask were added *n*-BuLi (2.5 M, 4.8 mL) and THF (15 mL) under Ar, the solution was cooled to -78 °C, and then phenylacetylene (12 mmol, 1.23 g) was added dropwise, and the resulting mixture was stirred for 2 h at this temperature. Aldehyde (10 mmol, 1.6 g) in THF (15 mL) was added dropwise to the reaction mixture. The solution was warmed naturally to the room temperature and was stirred overnight. Cold water was added to quench the reaction. The reaction mixture was diluted with EA (ethyl acetate). After extraction, the organic layers were washed by water, brine, and dried over anhydrous Mg_2SO_4, filtered and concentrated in vacuo, and the crude product was purified by silica gel chromatography to give a yellow oily

product. The obtained intermediate was used to the next steps following the same procedure depicted above. The corresponding product **1t** was obtained in 85% yield.

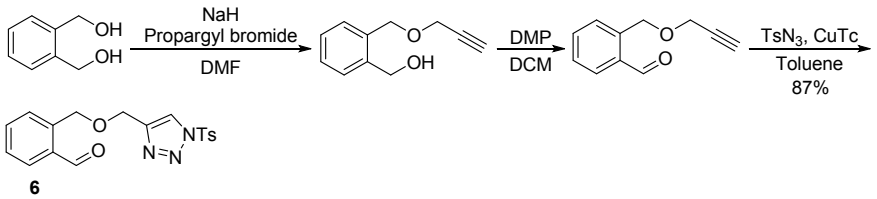


(2-(Bromomethyl)phenyl)methanol[1] and prop-2-yn-1-ylmagnesium bromide[2] were synthesized according to the previously reported procedure. The synthesis of (2-(but-3-yn-1-yl)phenyl)methanol: (2-(Bromomethyl)phenyl)methanol in ether was added to a flame-dried flask, the mixture was cooled to 0 ^{o}C, then prop-2-yn-1-ylmagnesium bromide in ether was added dropwise to this mixture. The solution was warmed naturally to the room temperature and was stirred overnight. Cold water was added to quench the reaction. The reaction mixture was diluted with ether. After extraction, the organic layers were washed by water, brine, and dried over anhydrous Mg_2SO_4, filtered and concentrated in vacuo. The crude obtained intermediate was used to the next steps following the same procedure depicted above. The corresponding product **3** was obtained in 86% yield.



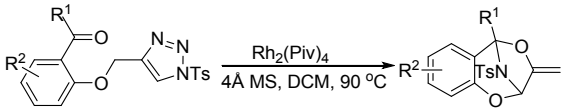
N-(2-formylphenyl)-4-methylbenzenesulfonamide[3] and N-(2-formylphenyl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide[4] were synthesized according to the previously reported procedure. Preparation for 2-Aminobenzaldehyde: 2-Nitrobenzaldehyde (10 mmol, 1.51 g) was added to a three-neck flask under Ar, followed by addition of EtOH:H_2O/4:1 (25 ml) via a syringe, the solution was heated to reflux. Fe (60 mmol, 3.36 g) was added to this reaction mixture, then two drops of concentrated hydrochloric acid was added via syringe. After 5 hours, the mixture was cooled to room temperature and the solid was filtered off, the solution was concentrated and dissolved with DCM, washed by water, brine, and dried over anhydrous

Mg_2SO_4, filtered and concentrated to give the product as a yellow oil, which was used to the next steps without further purification. The N-(2-formylphenyl)-4-methyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide **4** was synthesized in 62% yield according to the same procedure depicted above.



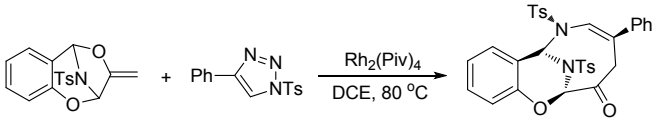
To a solution of 1,2-phenylenedimethanol (10 mmol, 1.38 g) in DMF (20 ml), NaH (60%) (10 mmol, 400 mg) was added portionwise at 0 °C. The mixture was stirred for 20 min at room temperature, then propargyl bromide (10 mmol, 1.19 g) was added dropwise to the reaction mixture at 0 °C, the mixture was stirred overnight at rt. Water was added to quench the reaction. After extraction by EA, the organic layers were washed by water, brine, and dried over anhydrous Mg_2SO_4, filtered and concentrated in vacuo. The crude obtained intermediate was used to the next steps following the same procedure depicted above. The corresponding product **6** was obtained in 87% yield.

3. General procedure for the synthesis of 2.



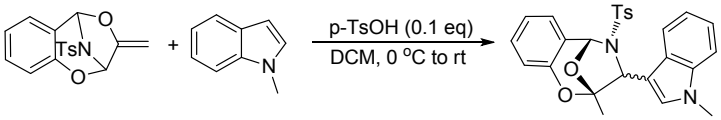
To a flame-dried flask were added the triazole (0.2 mmol, 1.0 equiv), 4Å MS (30 mg) and the $Rh_2(Piv)_4$ (0.004 mmol, 0.02 equiv), the flask was evacuated and backfilled with Ar for 3 times. DCM (2.0 mL) was added to this flask via a syringe under Ar. The reaction mixture was stirred for 4 hours at 90 °C. Appropriate amount of silica gel was added to the reaction mixture and the solvent was removed under vacuum, the crude product was purified by silica gel chromatography (PE:EA = 10:1) to give the desired product **2**.

4. General procedure for the synthesis of 9a and 9b.



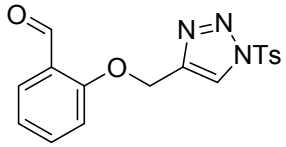
To a flame-dried flask were added **2a** or **2g** (0.2 mmol, 1.0 equiv) and 4-phenyl-1-tosyl-1H-1,2,3-triazole (0.2 mmol, 1.0 equiv), the flask was evacuated and backfilled with Ar for 3 times. DCE (2.0 mL) was added to this flask via a syringe under Ar. The reaction mixture was stirred for 3 hours at 80 °C. Appropriate amount of silica gel was added to the reaction mixture and the solvent was removed under vacuum, the crude product was purified by silica gel chromatography (PE:EA = 8:1) to give the desired product **9a** or **9b**.

5. General procedure for the synthesis of 10.



To a 10 mL flame-dried flask were added **2a** (0.2 mmol, 66 mg), indole (0.5 mmol, 65 mg) and DCM (2 mL), the mixture was cooled to 0 °C and then p-TsOH (0.02 mmol, 4 mg) was added under Ar. The reaction was slowly warmed to room temperature and stirred until **2a** was consumed completely. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography to give the product (68 mg, 74%).

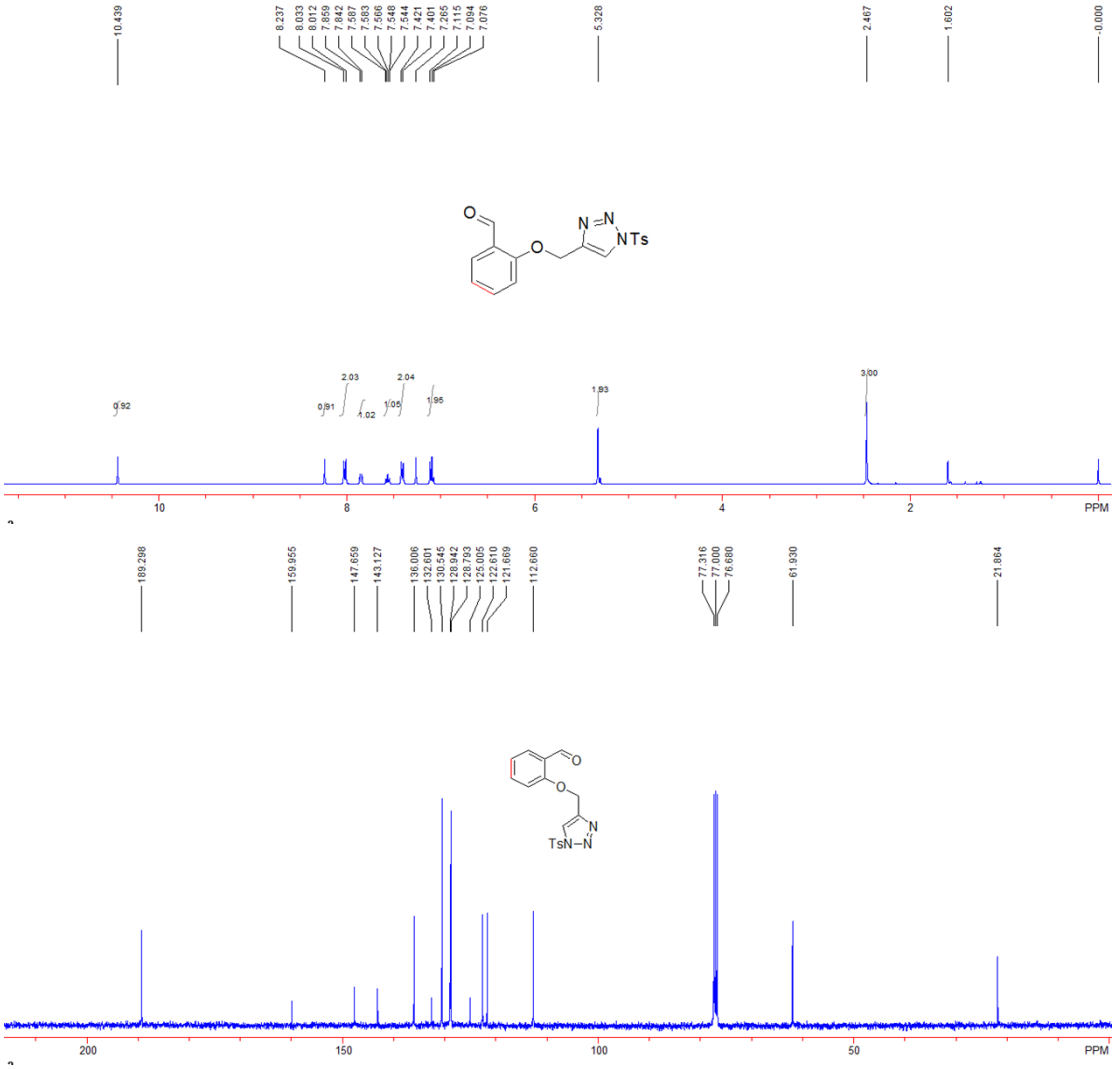
6. Characterization and spectra charts.

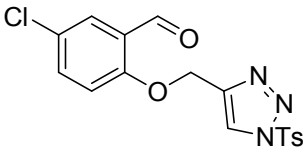


2-[1-(Toluene-4-sulfonyl)-1H-[1,2,3]triazol-4-ylmethoxy]-benzaldehyde 1a.

10.0 mmol scale, 3.18 g, a white solid, 89% yield. m.p.: 150-154 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.47 (s, 3H, CH_3), 5.33 (s, 2H, CH_2), 7.07-7.12 (m, 2H, Ar), 7.41 (d, J = 8.4 Hz, 2H, Ar), 7.57 (ddd, J = 7.6 Hz, J = 7.6 Hz, J = 1.6 Hz, 1H, Ar), 7.85 (d, J = 6.8 Hz, 1H, Ar), 8.02 (d, J = 8.4 Hz, 2H, Ar), 8.24 (s, 1H, CH=), 10.44 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.9, 61.9, 112.7, 121.7, 122.6, 125.0, 128.8, 128.9, 130.5, 132.6, 136.0, 143.1, 147.6, 160.0, 189.3. IR (CH_2Cl_2) ν 3148, 1683, 1601, 1391, 1305, 1179, 1169, 1123, 970, 796, 754, 668 cm^{-1}.

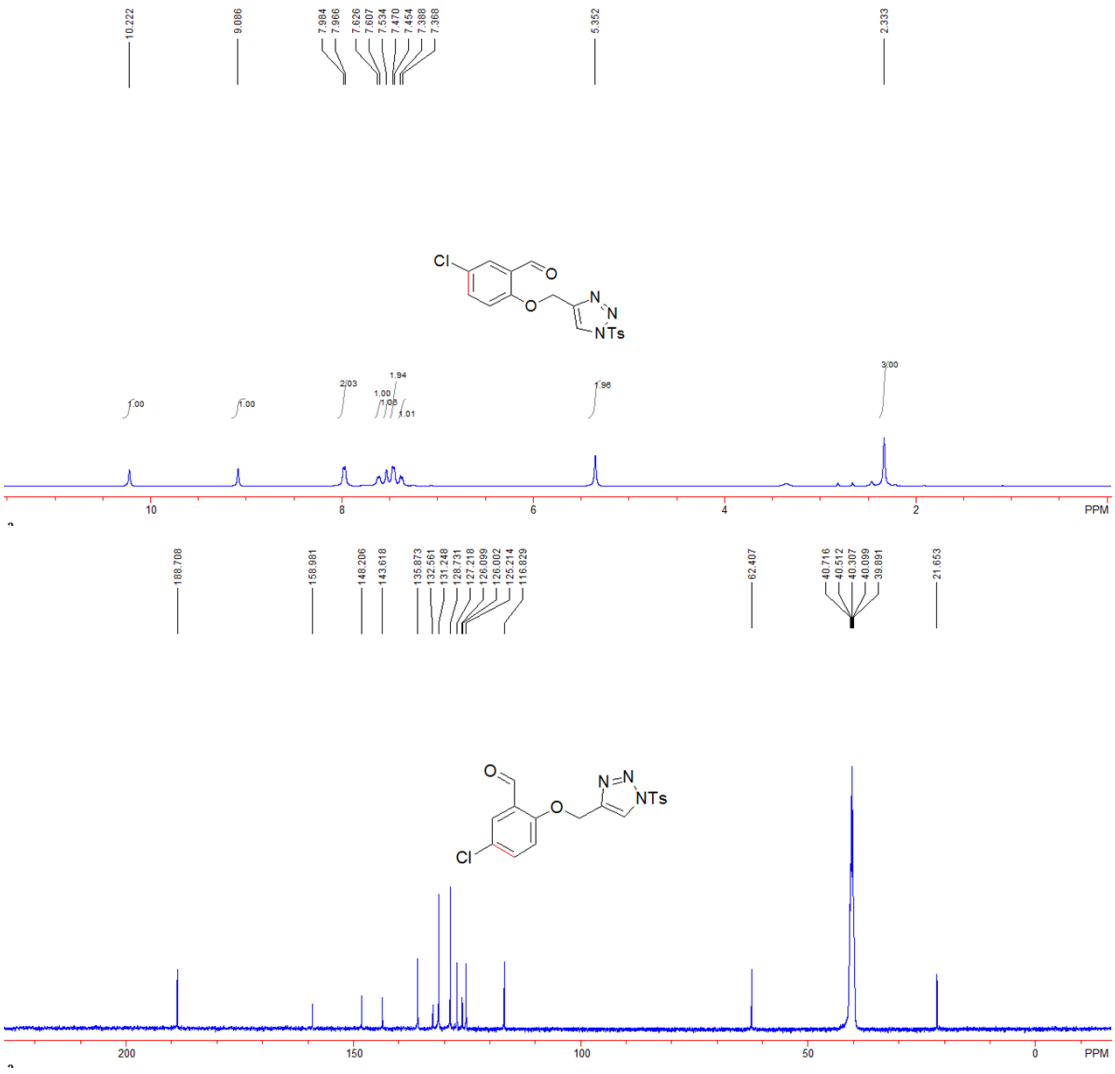
HRMS (ESI) Calcd. for $C_{17}H_{16}N_3O_4S^+$ (M^++H) requires 358.0856, found: 358.0854.

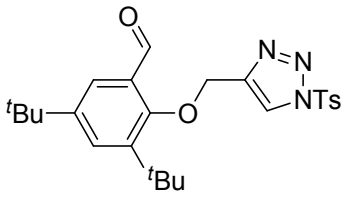




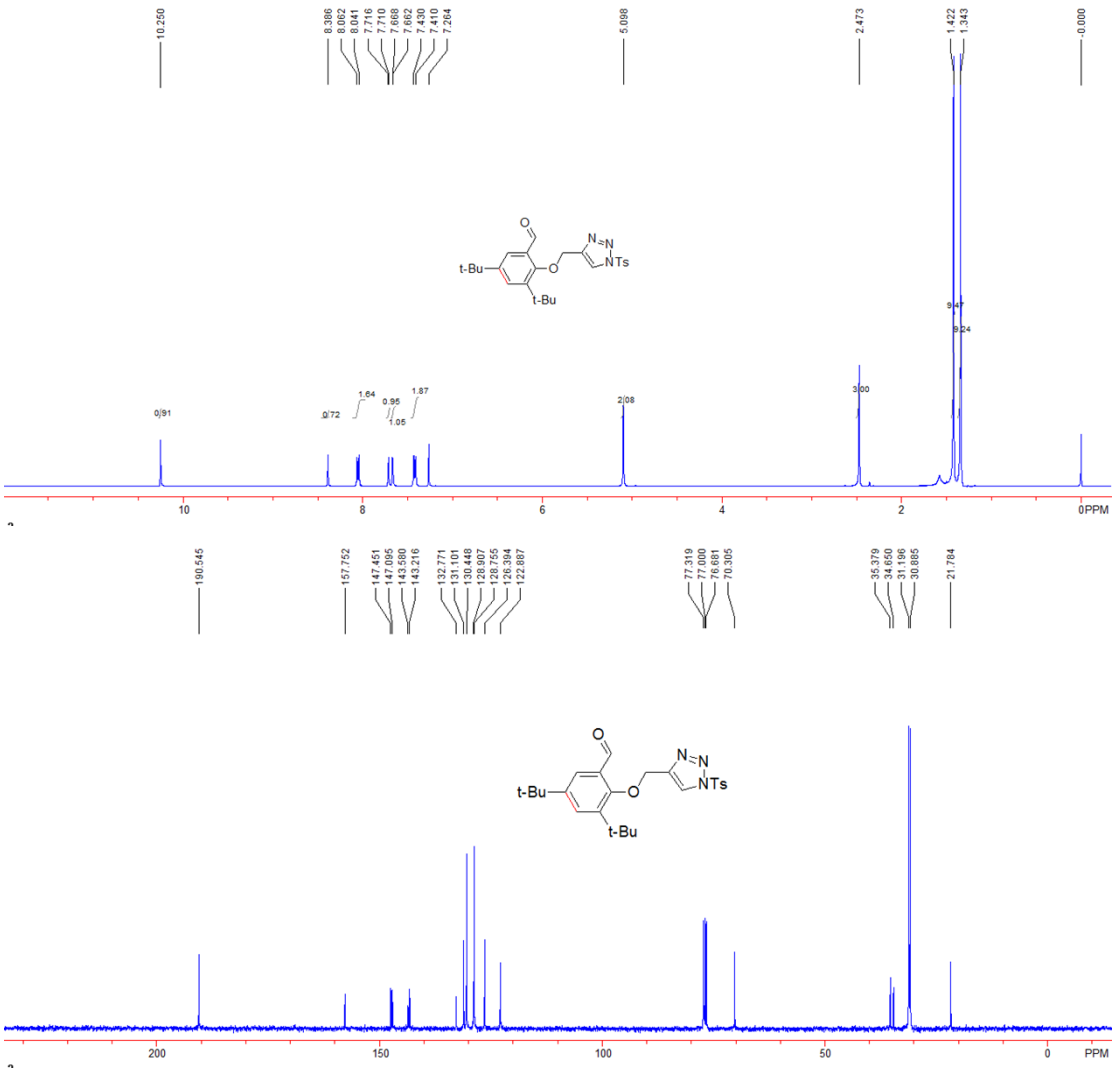
5-Chloro-2-[1-(toluene-4-sulfonyl)-1H-[1,2,3]triazol-4-ylmethoxy]-benzaldehyde 1b.

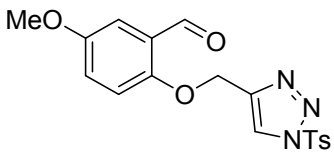
10.0 mmol scale, 3.84 g, a yellow solid, 98% yield. m.p.: 141-143 °C. ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 2.33 (s, 3H, CH_3), 5.35 (s, 2H, CH_2), 7.37 (d, J = 8.0 Hz, 1H, Ar), 7.46 (d, J = 6.8 Hz, 2H, Ar), 7.53 (s, 1H, Ar), 7.62 (d, J = 8.0 Hz, 1H, Ar), 7.97 (d, J = 6.8 Hz, 2H, Ar), 9.09 (s, 1H, CH=), 10.22 (s, 1H, CHO). ^{13}C NMR (DMSO-d_6, 100 MHz, TMS) δ 21.6, 62.4, 116.8, 125.2, 126.0, 126.1, 127.2, 128.7, 131.2, 132.6, 135.9, 143.6, 148.2, 159.0, 188.7. IR (CH_2Cl_2) ν 3142, 1688, 1593, 1395, 1267, 1191, 1179, 1127, 1013, 978, 811, 671 cm^{-1}. HRMS (ESI) Calcd. for $C_{17}H_{15}ClN_3O_4S^+$ (M^++H) requires 392.0466, found: 392.0454.





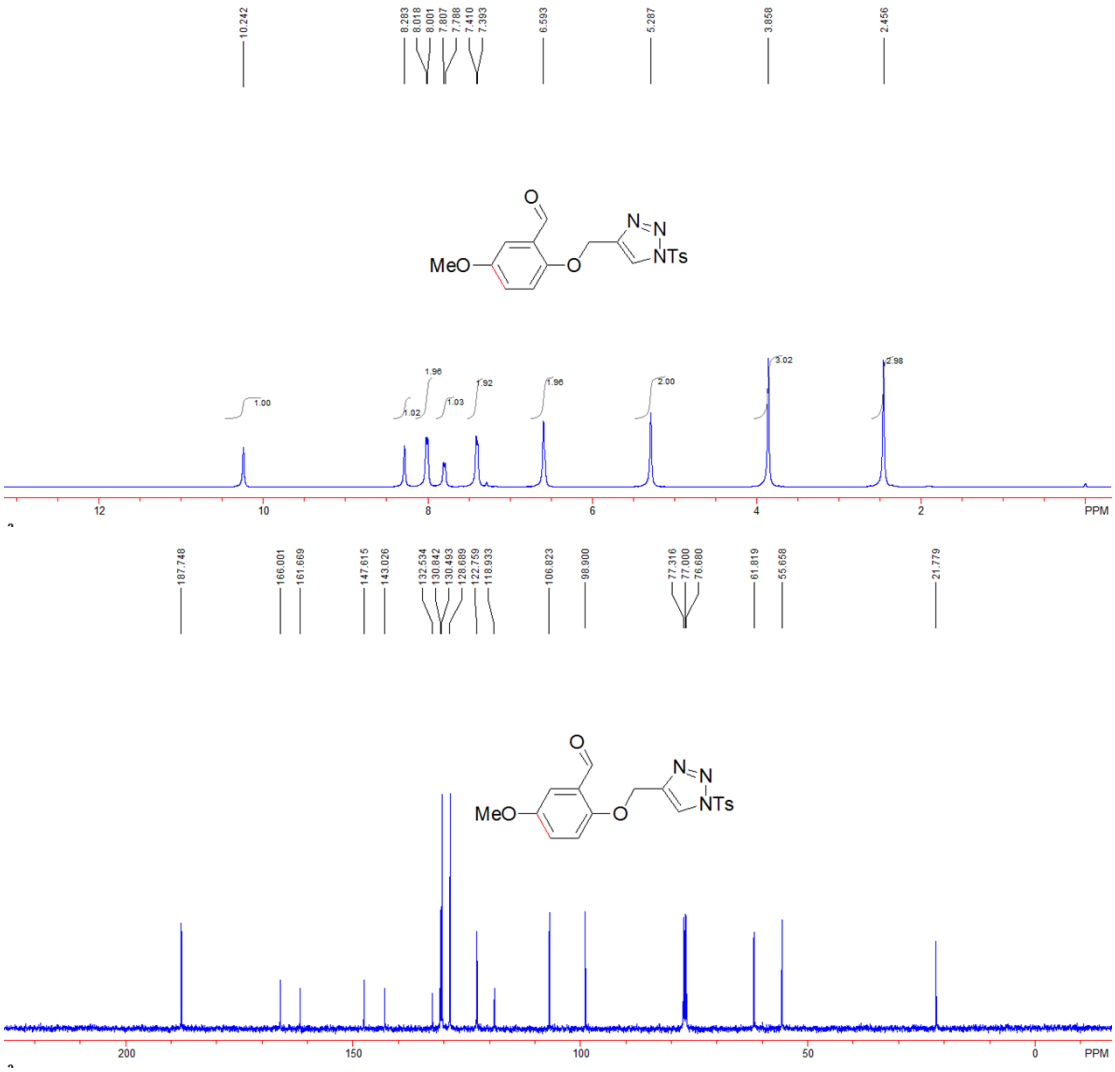
3,5-Di-tert-butyl-2-[1-(toluene-4-sulfonyl)-1H-[1,2,3]triazol-4-ylmethoxy]-benzaldehyde 1c. 10.0 mmol scale, 3.14 g, a white solid, 67% yield. m.p.: 154-156 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.34 (s, 9H, CH_3), 1.42 (s, 9H, CH_3), 2.47 (s, 3H, CH_3), 5.10 (s, 2H, CH_2), 7.42 (d, J = 8.0 Hz, 2H, Ar), 7.67 (d, J = 2.4 Hz, 1H, Ar), 7.71 (d, J = 2.4 Hz, 1H, Ar), 8.05 (d, J = 8.0 Hz, 2H, Ar), 8.39 (s, 1H, CH=), 10.25 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 30.9, 31.2, 34.6, 35.4, 70.3, 122.9, 126.4, 128.8, 128.9, 130.4, 131.1, 132.8, 143.2, 143.6, 147.1, 147.4, 157.8, 190.5. IR (CH_2Cl_2) ν 2964, 1680, 1389, 1364, 1196, 1174, 1093, 1014, 971, 813, 704, 684 cm^{-1}. HRMS (ESI) Calcd. for $C_{25}H_{32}N_3O_4S^+$ (M^++H) requires 470.2108, found: 470.2091.

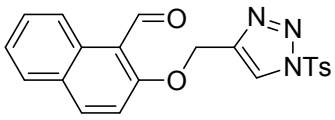




5-Methoxy-2-[1-(toluene-4-sulfonyl)-1H-[1,2,3]triazol-4-ylmethoxy]-benzaldehyde 1d.

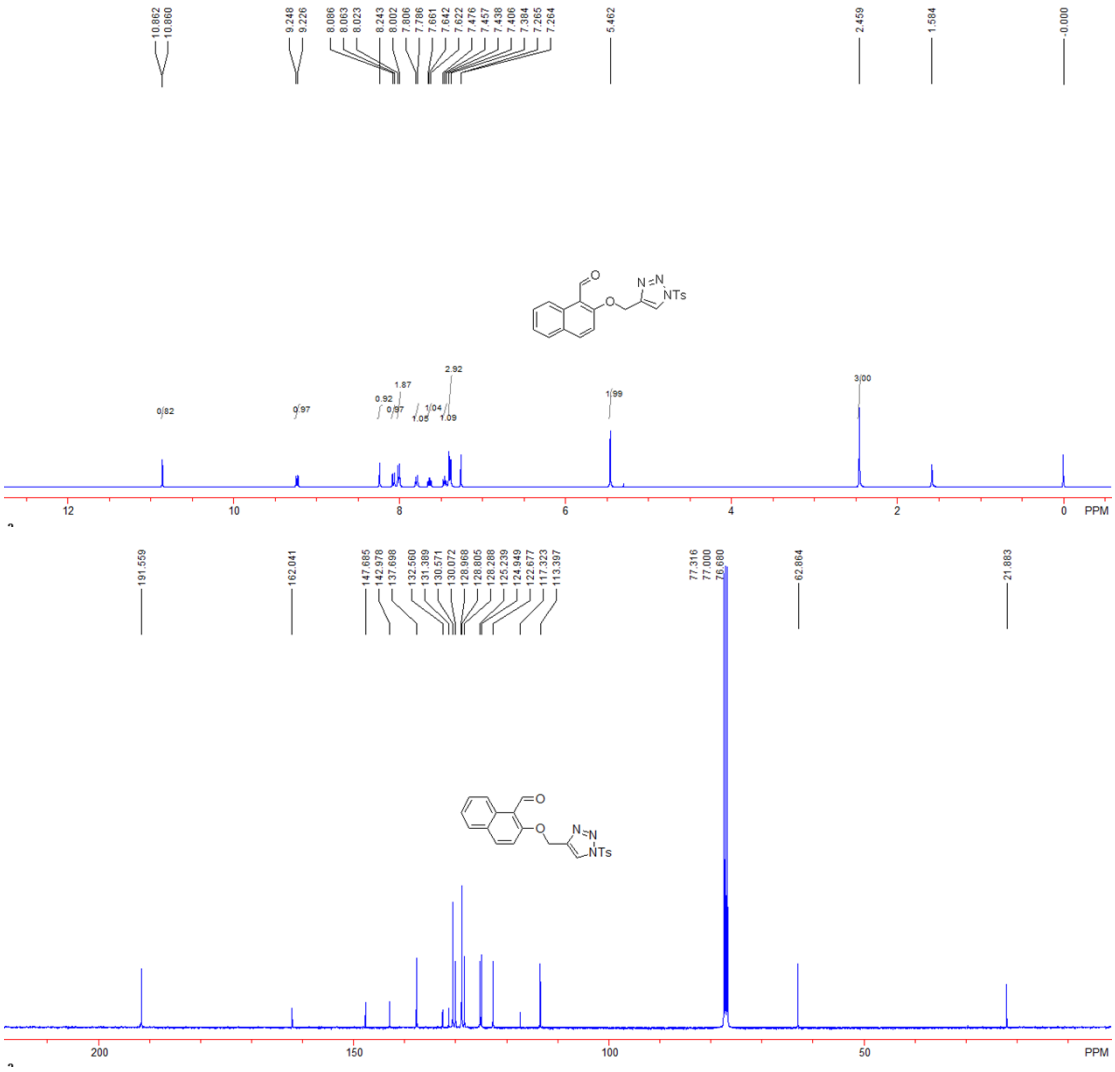
10.0 mmol scale, 3.40 g, a yellow solid, 88% yield. m.p.: 110-112 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.46 (s, 3H, CH_3), 3.86 (s, 3H, CH_3), 5.29 (s, 2H, CH_2), 6.59 (s, 2H, Ar), 7.40 (d, J = 6.8 Hz, 2H, Ar), 7.79 (d, J = 7.6 Hz, 1H, Ar), 8.00 (d, J = 6.8 Hz, 2H, Ar), 8.28 (s, 1H, CH=), 10.24 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 55.7, 61.8, 98.9, 106.8, 118.9, 122.8, 128.7, 130.5, 130.8, 132.5, 143.0, 147.6, 161.7, 166.0, 187.8. IR (CH_2Cl_2) ν 3141, 1680, 1593, 1390, 1262, 1212, 1191, 1167, 1120, 1010, 971, 810, 669 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{18}N_3O_5S^+$ (M^++H) requires 388.0962, found: 388.0958.

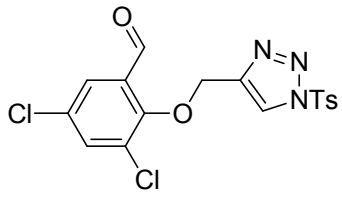




2-[1-(Toluene-4-sulfonyl)-1H-[1,2,3]triazol-4-ylmethoxy]-naphthalene-1-carbaldehyde 1e.

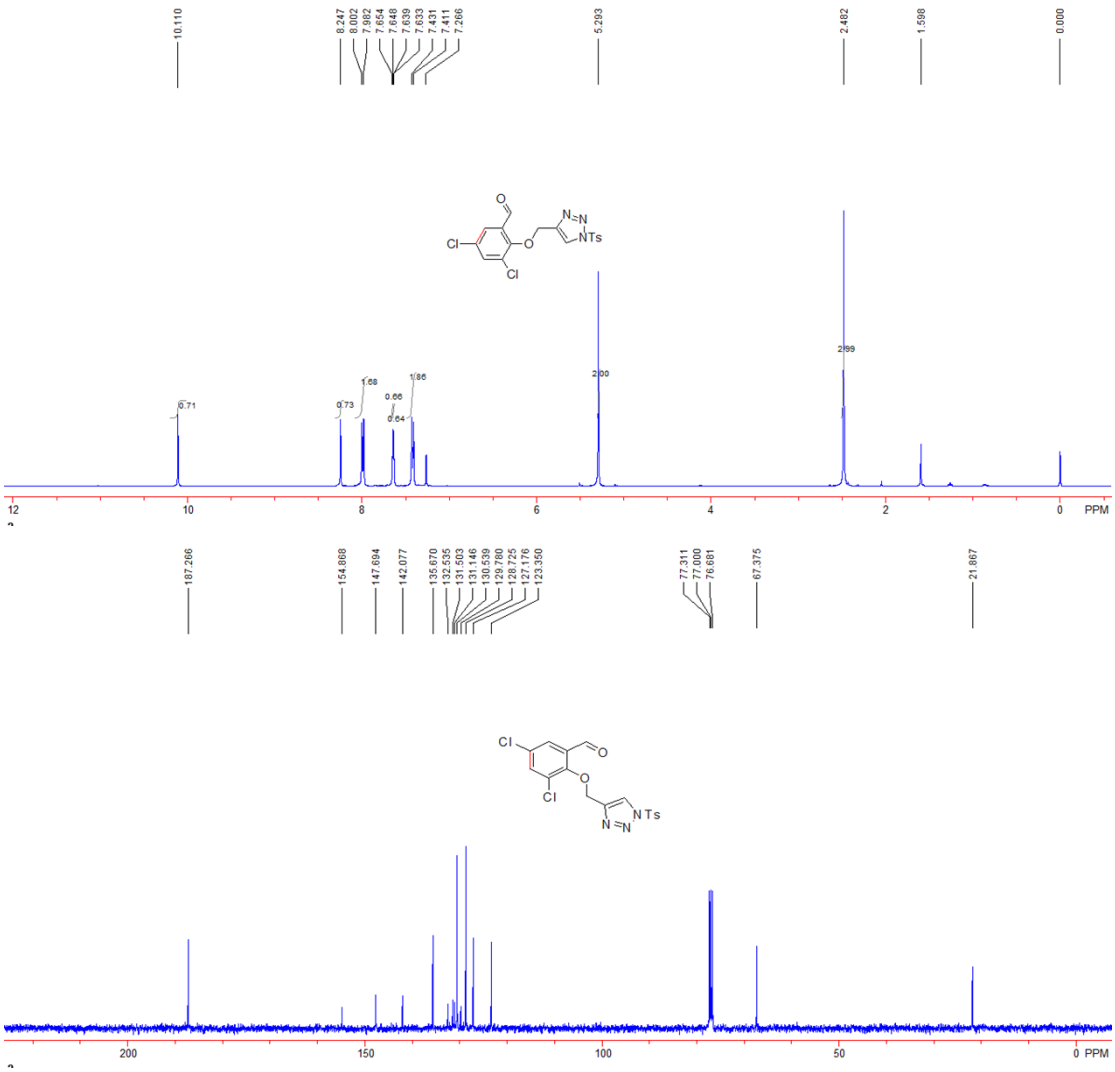
10.0 mmol scale, 3.3g, a yellow solid, 83% yield. m.p.: 140-142 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.46 (s, 3H, CH_3), 5.46 (s, 2H, CH_2), 7.39 (d, J = 8.8 Hz, 3H, Ar), 7.46 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H, Ar), 7.63 (d, J = 8.0 Hz, 1H, Ar), 7.80 (d, J = 8.0 Hz, 1H, Ar), 8.01 (d, J = 8.8 Hz, 2H, Ar), 8.07 (d, J = 8.8 Hz, 1H, Ar), 8.24 (s, 1H, CH=), 9.24 (d, J = 8.8 Hz, 1H, Ar), 10.86 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.9, 62.9, 113.4, 117.3, 122.7, 124.9, 125.2, 128.3, 128.8, 128.9, 130.1, 130.6, 131.4, 132.6, 137.7, 143.0, 147.7, 162.0, 191.6. IR (CH_2Cl_2) ν 3129, 2825, 1663, 1590, 1510, 1390, 1241, 1188, 1174, 1158, 1078, 1060, 975, 810, 670 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{18}N_3O_4S^+$ (M^++H) requires 408.1013, found: 408.1000.

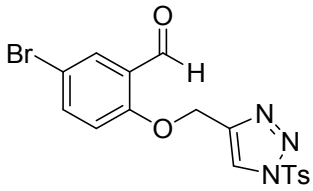




3,5-Dichloro-2-[1-(toluene-4-sulfonyl)-1H-[1,2,3]triazol-4-ylmethoxy]-benzaldehyde 1f.

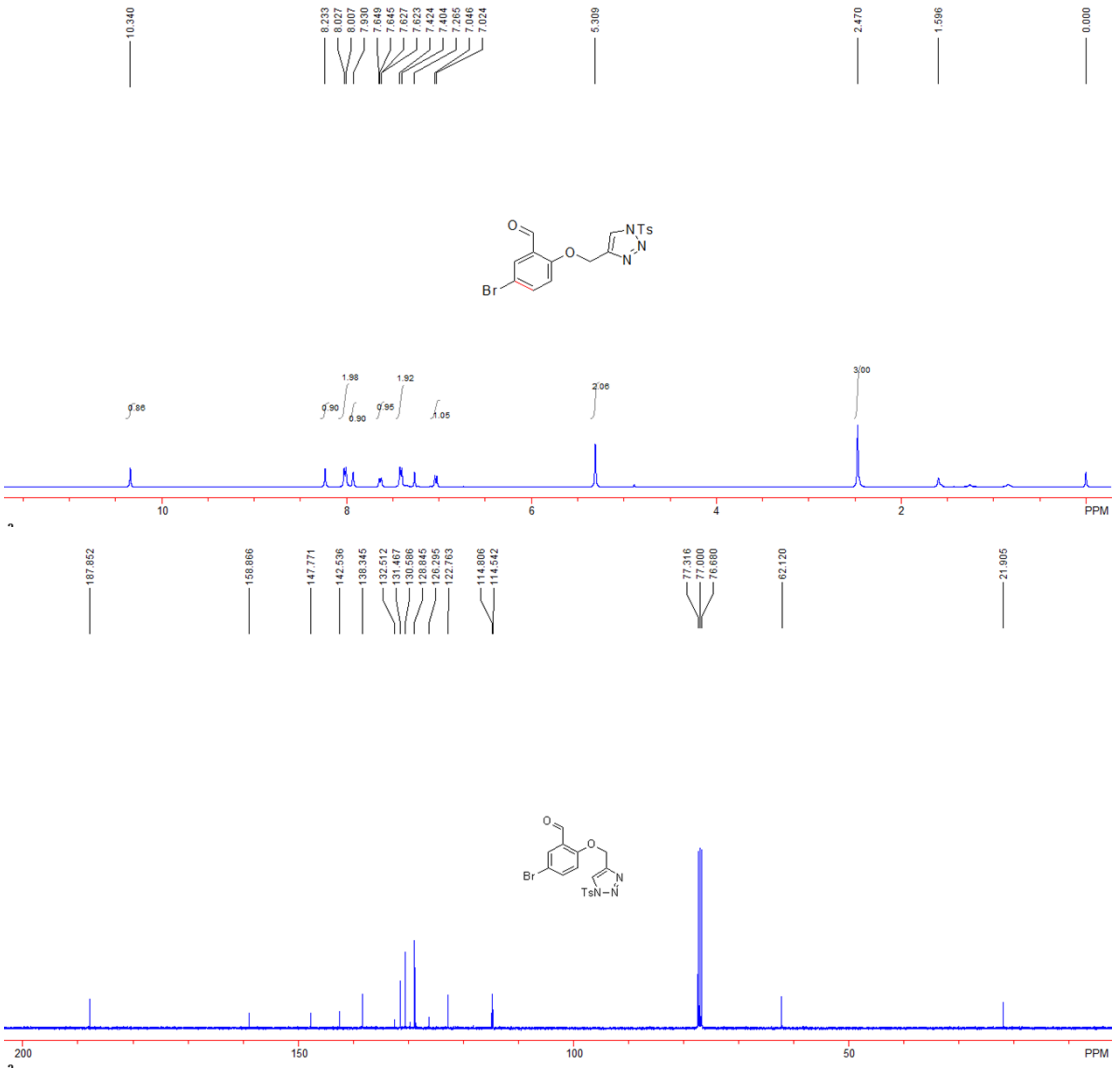
10.0 mmol scale, 3.07g, a yellow solid, 72% yield. m.p.: 138-140 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.48 (s, 3H, CH_3), 5.29 (s, 2H, CH_2), 7.42 (d, J = 8.0 Hz, 2H, Ar), 7.64 (d, J = 2.4 Hz, 1H, Ar), 7.65 (d, J = 2.4 Hz, 1H, Ar), 7.99 (d, J = 8.0 Hz, 2H, Ar), 8.25 (s, 1H, CH=), 10.11 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.9, 67.4, 123.4, 127.2, 128.7, 129.8, 130.5, 131.1, 131.5, 132.5, 135.7, 142.1, 147.7, 154.9, 187.3. IR (CH_2Cl_2) ν 3158, 2125, 1688, 1588, 1435, 1212, 1193, 1162, 1089, 983, 816, 672 cm^{-1}. HRMS (ESI) Calcd. for $C_{17}H_{14}Cl_2N_3O_4S^+$ (M^++H) requires 426.0077, found: 426.0070.

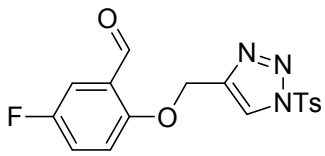




5-Bromo-2-[1-(toluene-4-sulfonyl)-1H-[1,2,3]triazol-4-ylmethoxy]-benzaldehyde 1g.

10.0 mmol scale, 3.35 g, a white solid, 77% yield. m.p.: 172-174 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.47 (s, 3H, CH_3), 5.31 (s, 2H, CH_2), 7.03 (d, J = 8.8 Hz, 1H, Ar), 7.41 (d, J = 8.0 Hz, 2H, Ar), 7.63 (dd, J = 8.8 Hz, J = 1.6 Hz, 1H, Ar), 7.93 (s, 1H, Ar), 8.02 (d, J = 8.0 Hz, 2H, Ar), 8.23 (s, 1H, CH=), 10.34 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.9, 62.1, 114.5, 114.8, 122.8, 126.3, 128.8, 130.6, 131.5, 132.5, 138.3, 142.5, 147.8, 158.9, 187.8. IR (CH_2Cl_2) ν 3000, 2984, 1686, 1589, 1392, 1275, 1259, 1193, 1171, 975, 760, 752, 667 cm^{-1}. HRMS (ESI) Calcd. for $C_{17}H_{15}BrN_3O_4S^+$ (M^++H) requires 435.9961, found: 435.9965.

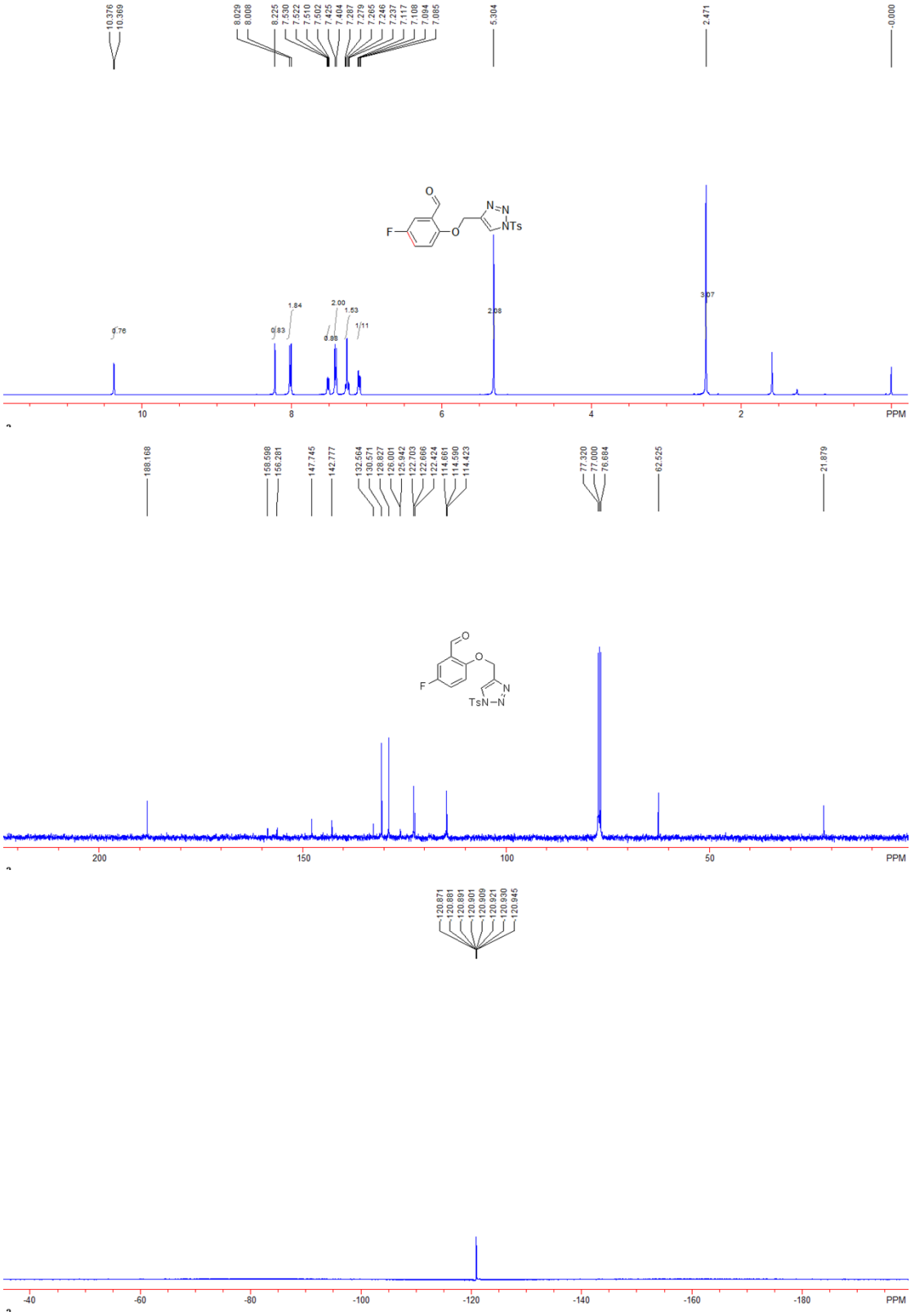


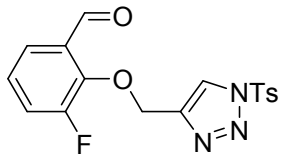


5-Fluoro-2-[1-(toluene-4-sulfonyl)-1H-[1,2,3]triazol-4-ylmethoxy]-benzaldehyde 1h.

10.0 mmol scale, 3.41 g, a white solid, 91% yield. m.p.: 144-146 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.47 (s, 3H, CH_3), 5.30 (s, 2H, CH_2), 7.10 (dd, J = 9.2 Hz, J = 3.6 Hz, 1H, Ar), 7.23-7.29 (m, 1H, Ar), 7.41 (d, J = 8.4 Hz, 2H, Ar), 7.52 (dd, J = 8.0 Hz, J = 3.6 Hz, 1H, Ar), 8.02 (d, J = 8.4 Hz, 2H, Ar), 8.22 (s, 1H, CH=), 10.37 (d, J = 2.8 Hz, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.9, 82.5, 114.5 (d, J = 16.7 Hz), 114.7, 122.4, 122.7 (d, J = 3.7 Hz), 126.0 (d, J = 5.9 Hz), 128.8, 130.6, 132.6, 142.8, 147.7, 157.4 (d, J = 231.7 Hz), 188.2. ^{19}F NMR ($CDCl_3$, 376 MHz, CF_3COOH) δ -120.945 ~ -120.871 (m). IR (CH_2Cl_2) ν 3154, 3117, 1683, 1593, 1488, 1404, 1390, 1263, 1247, 1151, 1088, 1017, 973, 805, 768, 700, 668 cm^{-1}. HRMS (ESI) Calcd. for

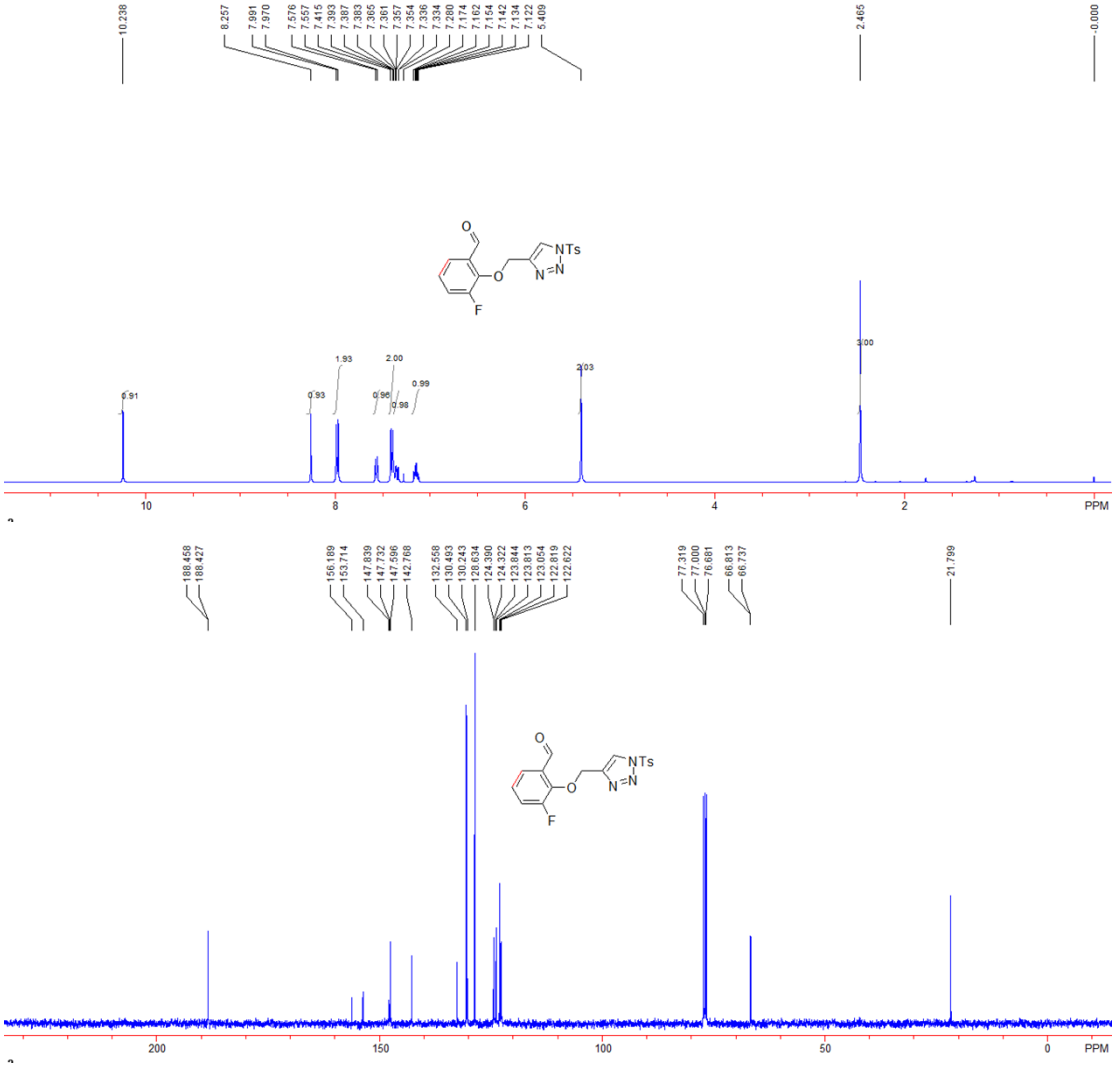
$C_{17}H_{15}FN_3O_4S^+$ (M^++H) requires 376.0762, found: 376.0764.

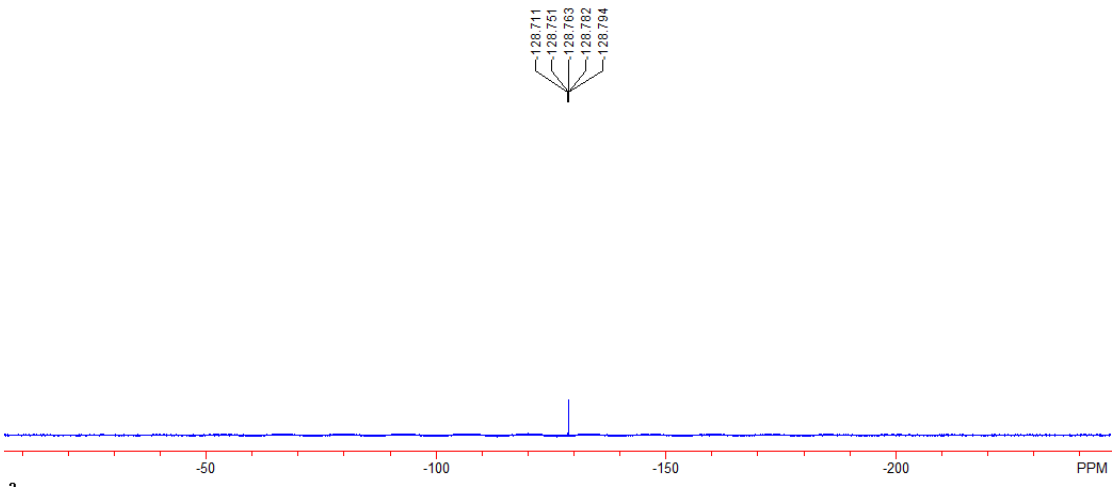


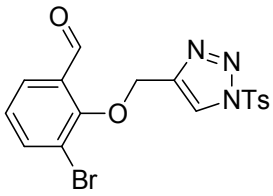


3-Fluoro-2-[1-(toluene-4-sulfonyl)-1H-[1,2,3]triazol-4-ylmethoxy]-benzaldehyde 1i.

10.0 mmol scale, 2.96 g, a white solid, 79% yield. m.p.: 140-142 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.47 (s, 3H, CH_3), 5.41 (s, 2H, CH_2), 7.12-7.18 (m, 1H, Ar), 7.33-7.39 (m, 1H, Ar), 7.40 (d, *J* = 8.8 Hz, 2H, Ar), 7.56 (d, *J* = 8.0 Hz, 1H, Ar), 7.98 (d, *J* = 8.8 Hz, 2H, Ar), 8.26 (s, 1H, CH=), 10.24 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 66.7 (d, *J* = 7.6 Hz), 122.7 (d, *J* = 19.7 Hz), 123.0, 123.8 (d, *J* = 3.1 Hz), 124.3 (d, *J* = 6.8 Hz), 128.6, 130.2, 130.5, 132.6, 142.8, 147.6, 147.7 (d, *J* = 10.7 Hz), 154.9 (d, *J* = 247.5 Hz), 188.4 (d, *J* = 3.1 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz, CF_3COOH) δ -128.794 ~ -128.711 (m). IR (CH_2Cl_2) ν 3153, 3113, 2886, 1684, 1590, 1483, 1389, 1270, 1249, 1191, 1178, 1026, 973, 811, 780, 756, 668 cm^{-1}. HRMS (ESI) Calcd. for $C_{17}H_{15}FN_3O_4S^+$ (M^++H) requires 376.0762, found: 376.0750.

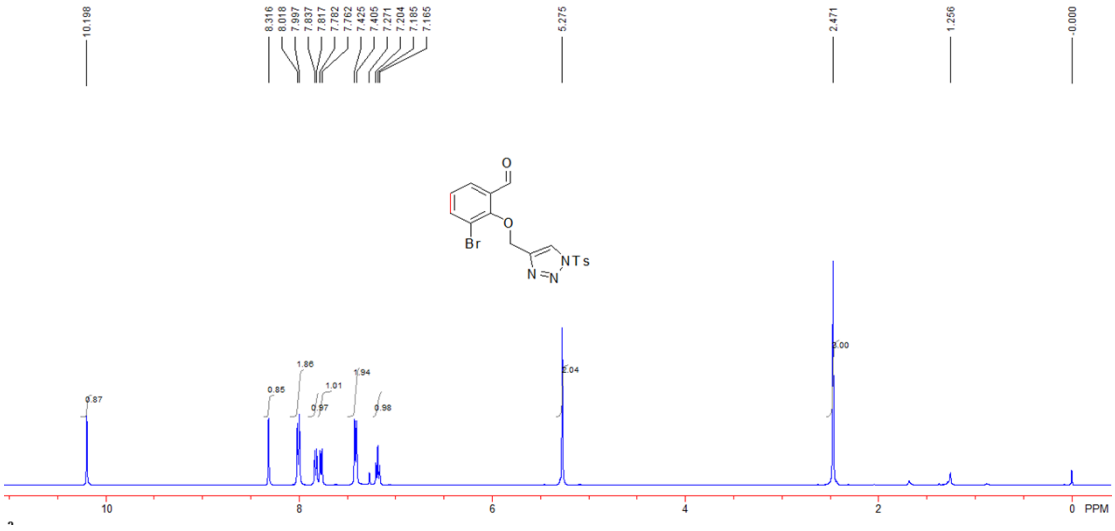


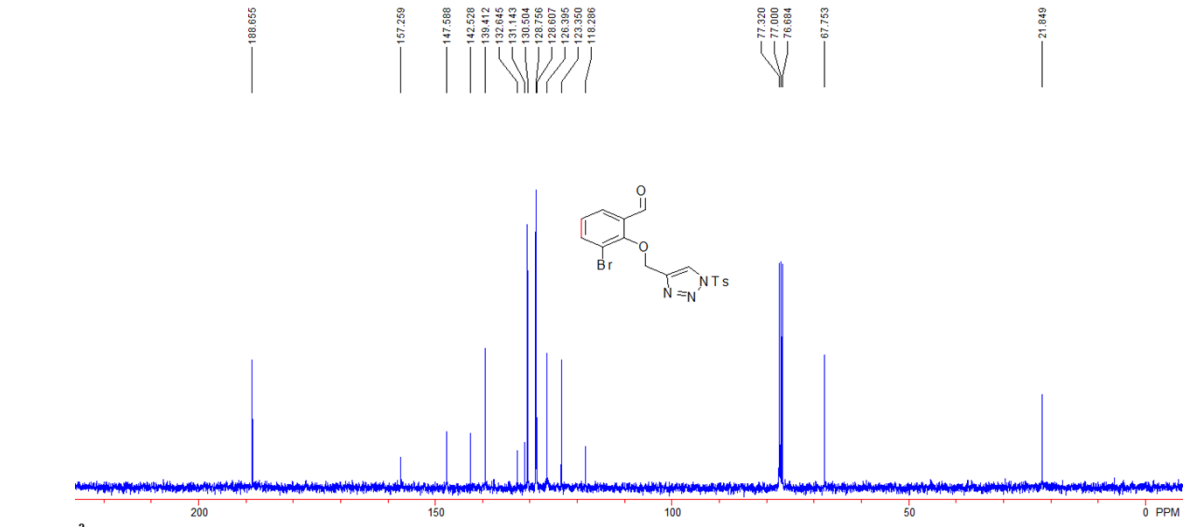


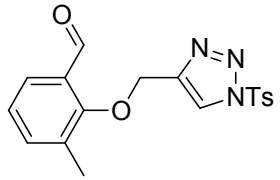


3-Bromo-2-[1-(toluene-4-sulfonyl)-1H-[1,2,3]triazol-4-ylmethoxy]-benzaldehyde 1j.

10.0 mmol scale, 3.48 g, a white solid, 80% yield. m.p.: 131-133 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.47 (s, 3H, CH_3), 5.28 (s, 2H, CH_2), 7.18 (dd, J = 8.0 Hz, J = 8.0 Hz, 1H, Ar), 7.41 (d, J = 8.0 Hz, 2H, Ar), 7.77 (d, J = 8.0 Hz, 1H, Ar), 7.83 (d, J = 8.0 Hz, 1H, Ar), 8.00 (d, J = 8.0 Hz, 2H, Ar), 8.32 (s, 1H, CH=), 10.20 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 67.8, 118.3, 123.4, 126.4, 128.6, 128.8, 130.5, 131.1, 132.6, 139.4, 142.5, 147.6, 157.3, 188.6. IR (CH_2Cl_2) ν 3251, 1697, 1590, 1437, 1350, 1216, 1157, 1088, 988, 826, 810, 763, 717, 663 cm^{-1}. HRMS (ESI) Calcd. for $C_{17}H_{15}BrN_3O_4S^+$ (M^++H) requires 435.9961, found: 435.9953.

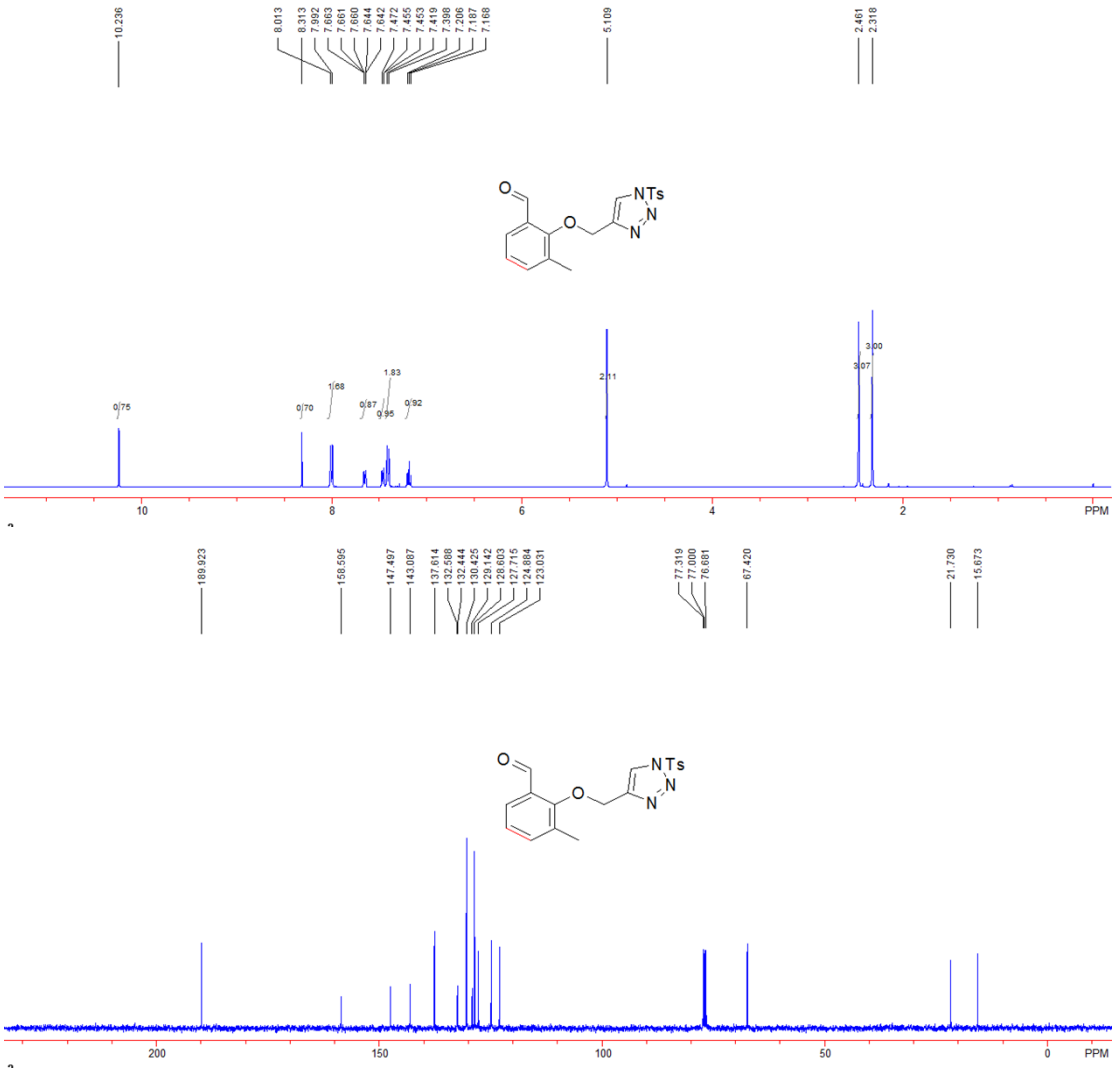


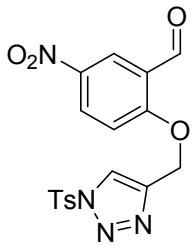




3-Methyl-2-[1-(toluene-4-sulfonyl)-1H-[1,2,3]triazol-4-ylmethoxy]-benzaldehyde 1k.

10.0 mmol scale, 2.78 g, a white solid, 75% yield. m.p.: 115-117 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.32 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 5.11 (s, 2H, CH_2), 7.19 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H, Ar), 7.41 (d, J = 8.4 Hz, 2H, Ar), 7.45-7.48 (m, 1H, Ar), 7.64-7.67 (m, 1H, Ar), 8.00 (d, J = 8.4 Hz, 2H, Ar), 8.31 (s, 1H, CH=), 10.24 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 15.7, 21.7, 67.4, 123.0, 124.9, 127.7, 128.6, 129.1, 130.4, 132.4, 132.6, 137.6, 143.1, 147.5, 158.6, 189.9. IR (CH_2Cl_2) ν 3077, 2858, 1688, 1666, 1587, 1396, 1379, 1250, 1193, 1176, 1162, 1085, 991, 975, 953, 812, 782, 757, 702, 668 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{18}N_3O_4S^+$ (M^++H) requires 372.1013, found: 372.1007.

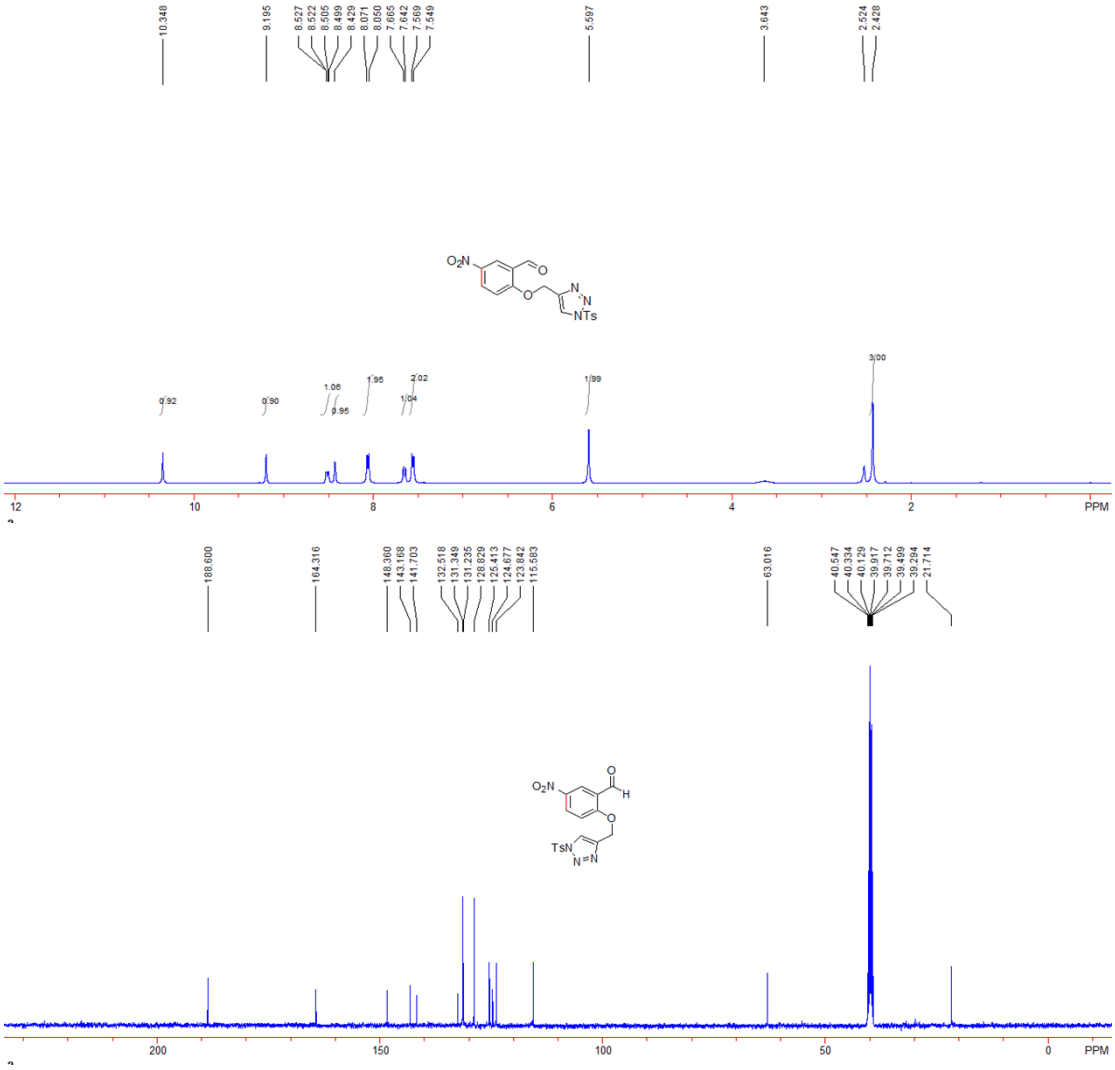


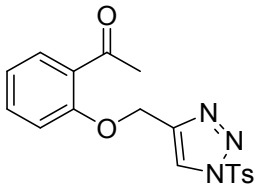


5-Nitro-2-[1-(toluene-4-sulfonyl)-1H-[1,2,3]triazol-4-ylmethoxy]-benzaldehyde 1l.

10.0 mmol scale, 3.01 g, a white solid, 75% yield. m.p.: 165-167 ^{o}C. ^{1}H NMR (DMSO-d_6, 400 MHz, TMS) δ 2.43 (s, 3H, CH_3), 5.60 (s, 2H, CH_2), 7.56 (d, J = 8.0 Hz, 2H, Ar), 7.65 (d, J = 9.2 Hz, 1H, Ar), 8.06 (d, J = 8.4 Hz, 2H, Ar), 8.43 (s, 1H, Ar), 8.51 (dd, J = 9.2 Hz, J = 2.4 Hz, 1H, Ar), 9.19 (s, 1H, CH=), 10.35 (s, 1H, CHO). ^{13}C NMR (DMSO-d_6, 100 MHz, TMS) δ 21.7, 63.0, 115.6, 123.8, 124.7, 125.4, 128.8, 131.2, 131.3, 132.5, 141.7, 143.2, 148.4, 164.3, 188.6. IR (CH_2Cl_2) ν 3150, 3110, 2919, 1694, 1611, 1589, 1522, 1400, 1337, 1273, 1223, 1192, 1177, 1034, 1014, 983, 834, 766, 748, 672 cm^{-1}. HRMS (ESI) Calcd. for $C_{17}H_{15}N_4O_6S^+$ (M^++H) requires

403.0707, found: 403.0707.

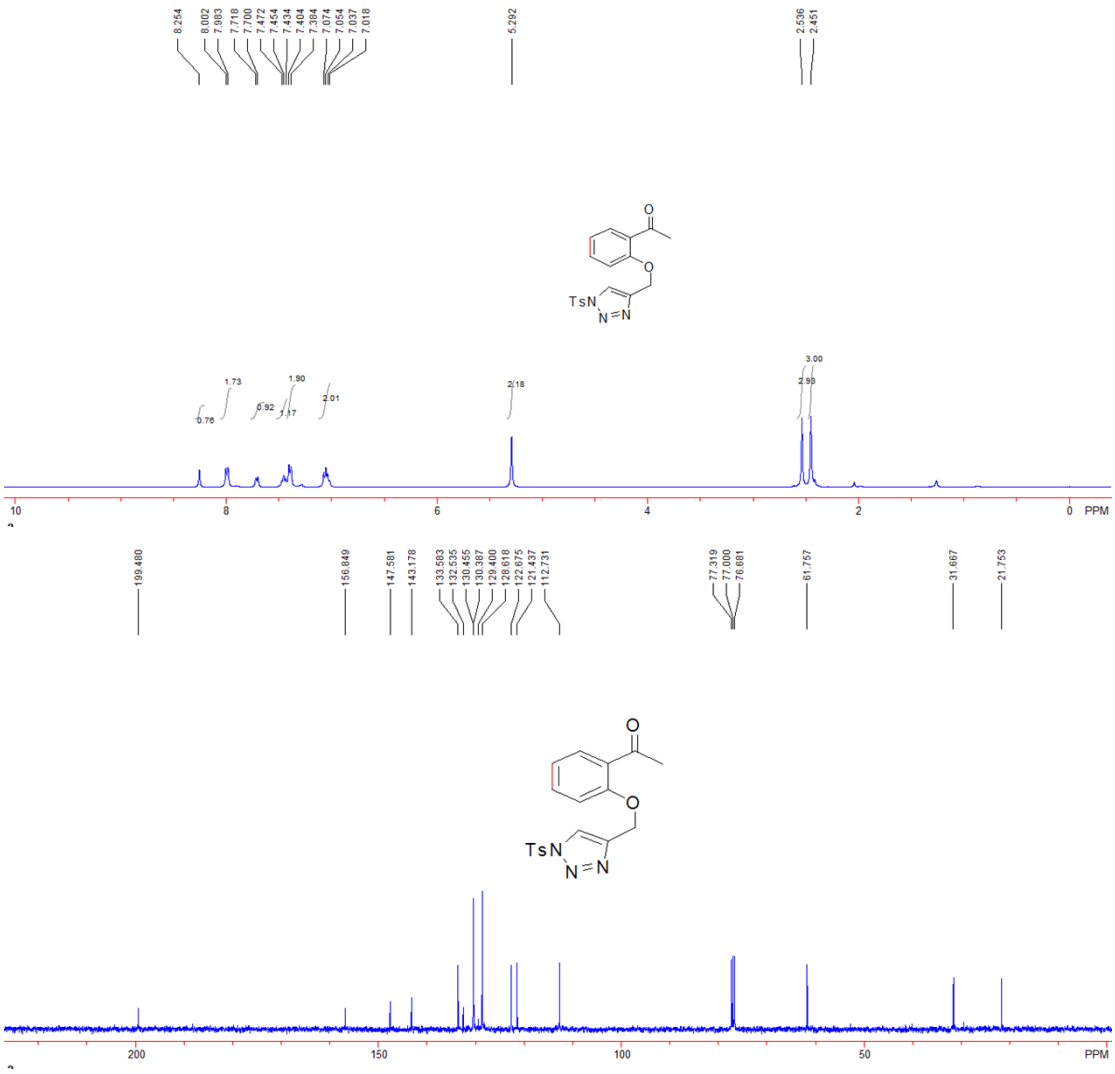


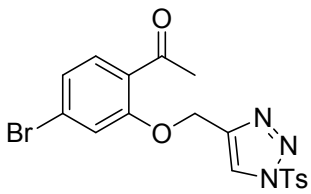


1-{2-[1-(Toluene-4-sulfonyl)-1H-[1,2,3]triazol-4-ylmethoxy]-phenyl}-ethanone 1m.

10.0 mmol scale, 3.01 g, a white solid, 60% yield. m.p.: 135-137 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.45 (s, 3H, CH_3), 2.54 (s, 3H, CH_3), 5.29 (s, 2H, CH_2), 7.01-7.08 (m, 2H, Ar), 7.39 (d, J = 8.0 Hz, 2H, Ar), 7.45 (dd, J = 8.0 Hz, J = 8.0 Hz, 1H, Ar), 7.71 (d, J = 8.0 Hz, 1H, Ar), 7.99 (d, J = 8.0 Hz, 2H, Ar), 8.25 (s, 1H, CH=). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 31.7, 61.8, 112.7, 121.4, 122.7, 128.6, 129.4, 130.4, 130.5, 132.5, 133.6, 143.2, 147.6, 156.8, 199.5. IR (CH_2Cl_2) ν 3097, 1659, 1586, 1390, 1379, 1236, 1193, 1175, 1160, 1079, 991, 965, 950, 812, 767,

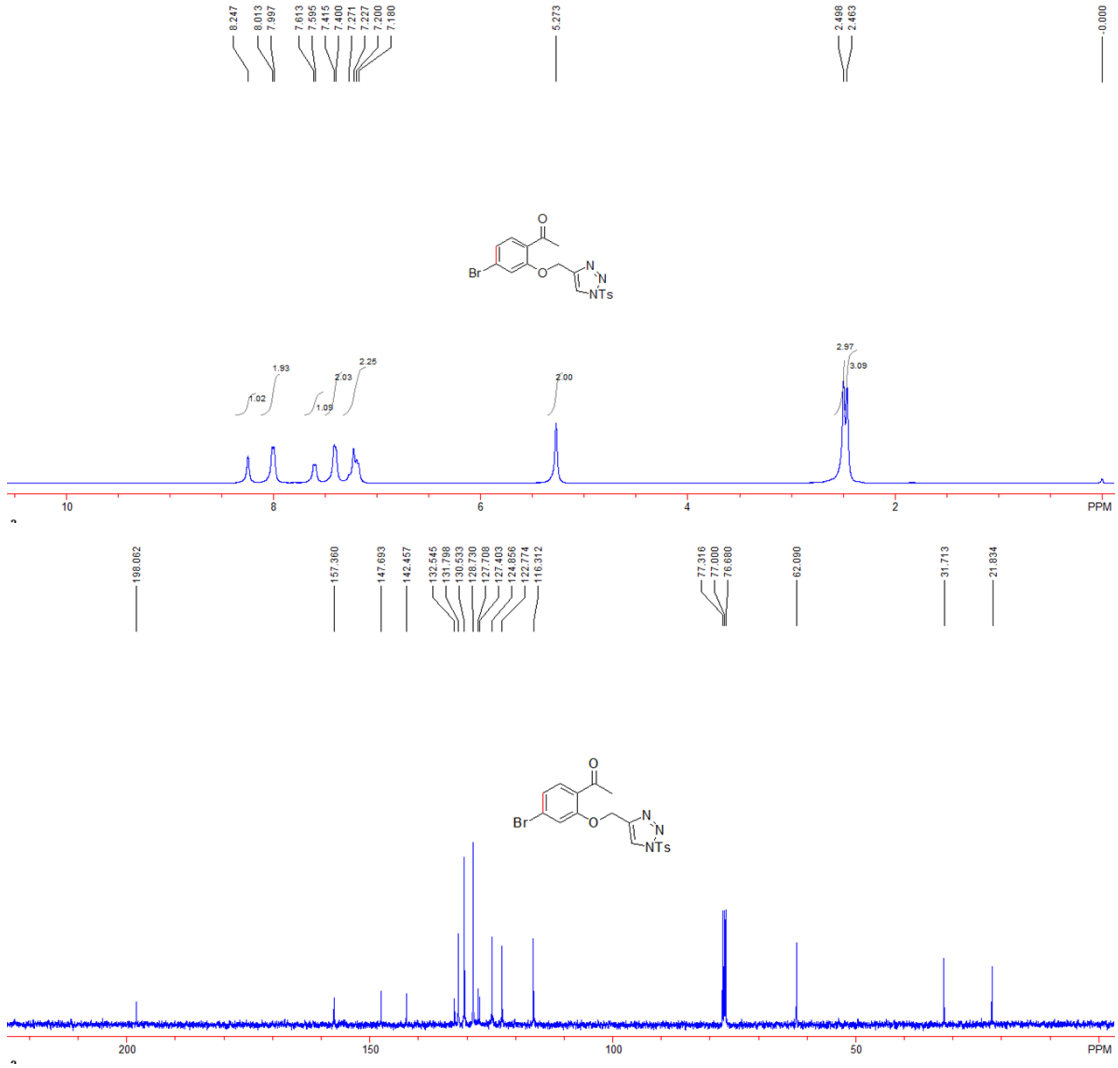
757, 670 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{18}N_3O_4S^+$ (M^++H) requires 372.1013, found: 372.1005.

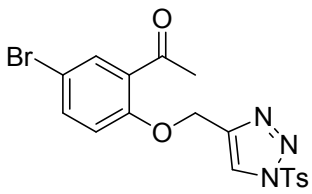




1-{4-Bromo-2-[1-(toluene-4-sulfonyl)-1H-[1,2,3]triazol-4-ylmethoxy]-phenyl}-ethanone 1n. 10.0 mmol scale, 3.91 g, a white solid, 87% yield. m.p.: 164-166 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.46 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 5.27 (s, 2H, CH_2), 7.18-7.23 (m, 2H, Ar), 7.40 (d, *J* = 6.4 Hz, 2H, Ar), 7.60 (d, *J* = 7.2 Hz, 1H, Ar), 8.00 (d, *J* = 6.4 Hz, 2H, Ar), 8.25 (s, 1H, CH=). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 31.7, 62.1, 116.3, 122.8, 124.8, 127.4, 127.7, 128.7, 130.5, 131.8, 132.5, 142.4, 147.7, 157.4, 198.1. IR (CH_2Cl_2) ν 3158, 3052, 1667, 1582, 1478,

1392, 1274, 1231, 1216, 1195, 1174, 1127, 1091, 1003, 963, 893, 837, 825, 812, 710, 702, 668 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{17}BrN_3O_4S^+$ (M^++H) requires 450.0118, found: 450.0133.

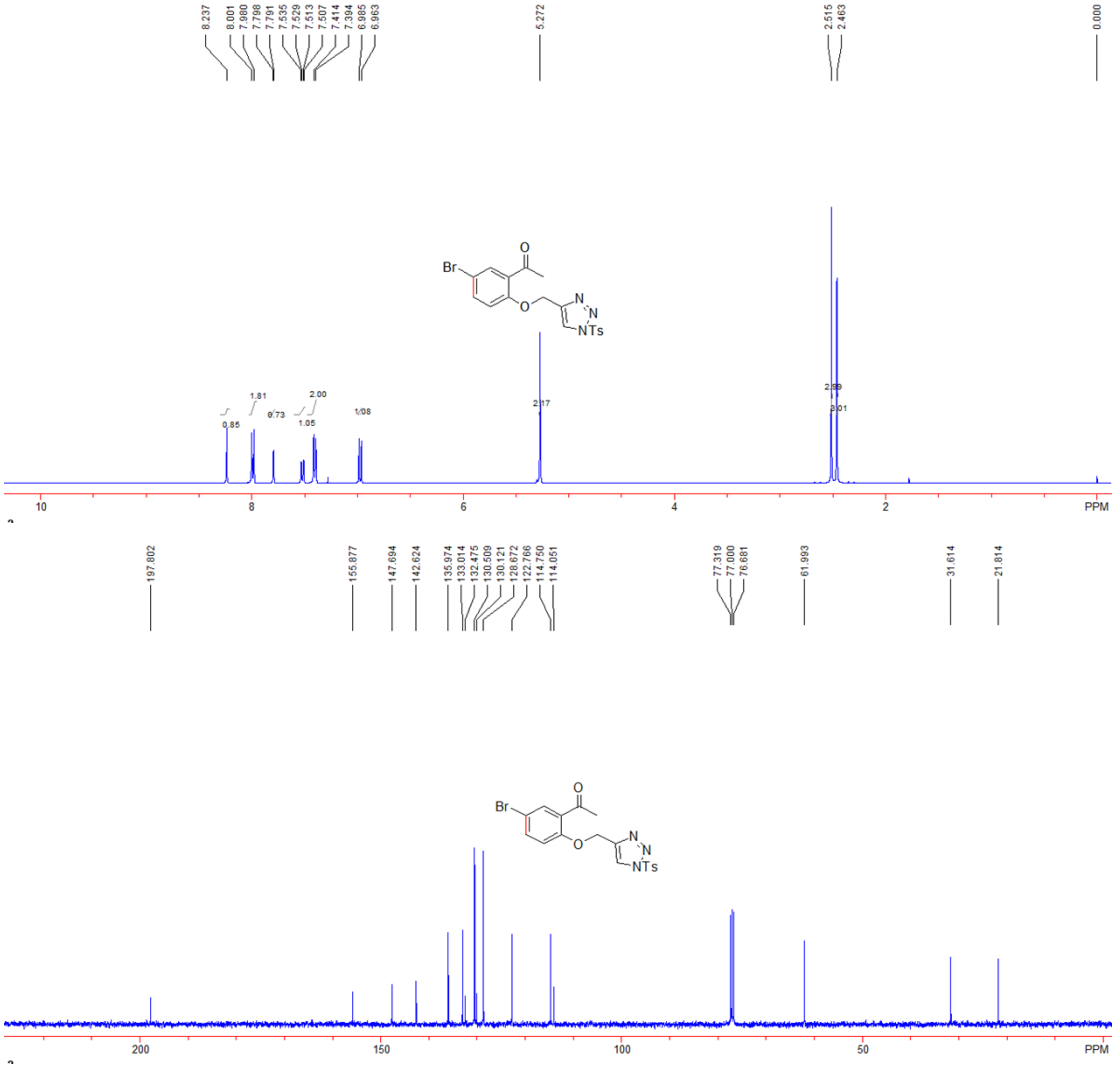


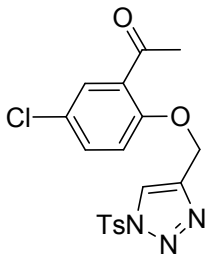


1-(5-bromo-2-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy)phenyl)ethanone 1o.

10.0 mmol scale, 3.86 g, a white solid, 68% yield. m.p.: 127-129 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.46 (s, 3H, CH_3), 2.52 (s, 3H, CH_3), 5.27 (s, 2H, CH_2), 6.97 (d, J = 8.8 Hz, 1H, Ar), 7.40 (d, J = 8.0 Hz, 2H, Ar), 7.52 (dd, J = 8.8 Hz, J = 2.4 Hz, 1H, Ar), 7.79 (d, J = 2.4 Hz, 1H, Ar), 7.99 (d, J = 8.0 Hz, 2H, Ar), 8.24 (s, 1H, CH=). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 31.6, 62.0, 114.0, 114.8, 122.8, 128.7, 130.1, 130.5, 132.5, 133.0, 136.0, 142.6, 147.7, 155.9, 197.8. IR

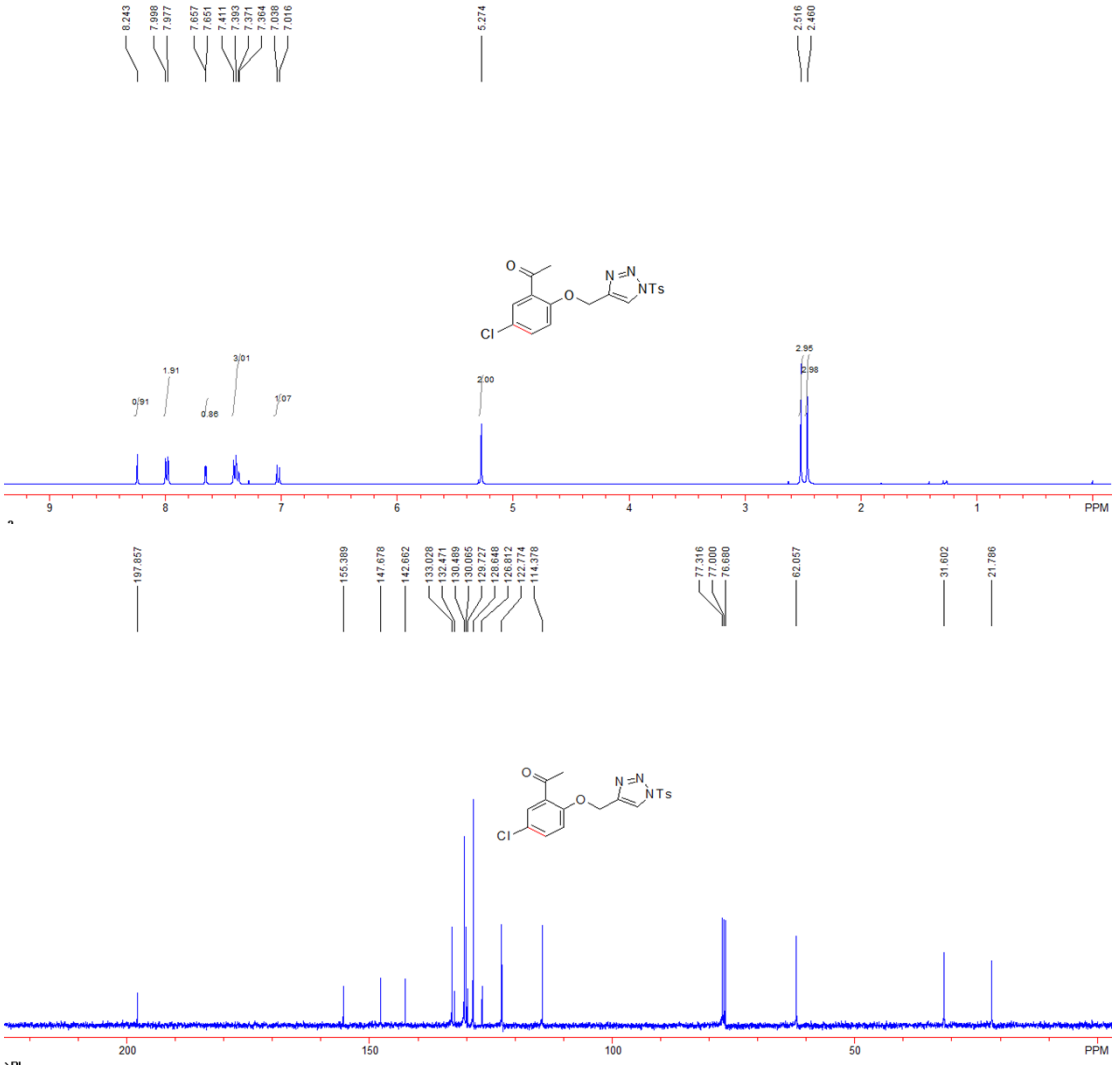
(CH_2Cl_2) ν 3150, 3097, 2927, 1660, 1589, 1486, 1386, 1374, 1277, 1236, 1192, 1176, 1158, 1087, 1007, 981, 963, 822, 811, 796, 697, 667 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{17}BrN_3O_4S^+$ (M^++H) requires 450.0118, found: 450.0101.

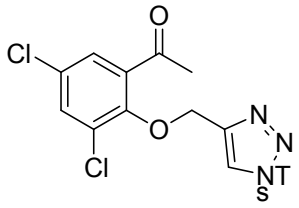




1-{5-Chloro-2-[1-(toluene-4-sulfonyl)-1H-[1,2,3]triazol-4-ylmethoxy]-phenyl}-ethanone 1p. 10.0 mmol scale, 3.20 g, a white solid, 76% yield. m.p.: 140-142 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.46 (s, 3H, CH_3), 2.52 (s, 3H, CH_3), 5.27 (s, 2H, CH_2), 7.03 (d, *J* = 8.8 Hz, 1H, Ar), 7.36-7.42 (m, 3H, Ar), 7.65 (d, *J* = 2.4 Hz, 1H, Ar), 7.99 (d, *J* = 8.4 Hz, 2H, Ar), 8.24 (s, 1H,

CH=). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 31.6, 62.0, 114.4, 122.8, 126.8, 128.6, 129.7, 130.1, 130.5, 132.5, 133.0, 142.7, 147.7, 155.4, 197.8. IR (CH_2Cl_2) ν 3150, 3101, 2927, 1660, 1592, 1486, 1400, 1386, 1375, 1277, 1216, 1192, 1176, 1157, 1087, 1007, 982, 841, 824, 810, 667 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{17}ClN_3O_4S^+$ (M^++H) requires 406.0623, found: 406.0616.

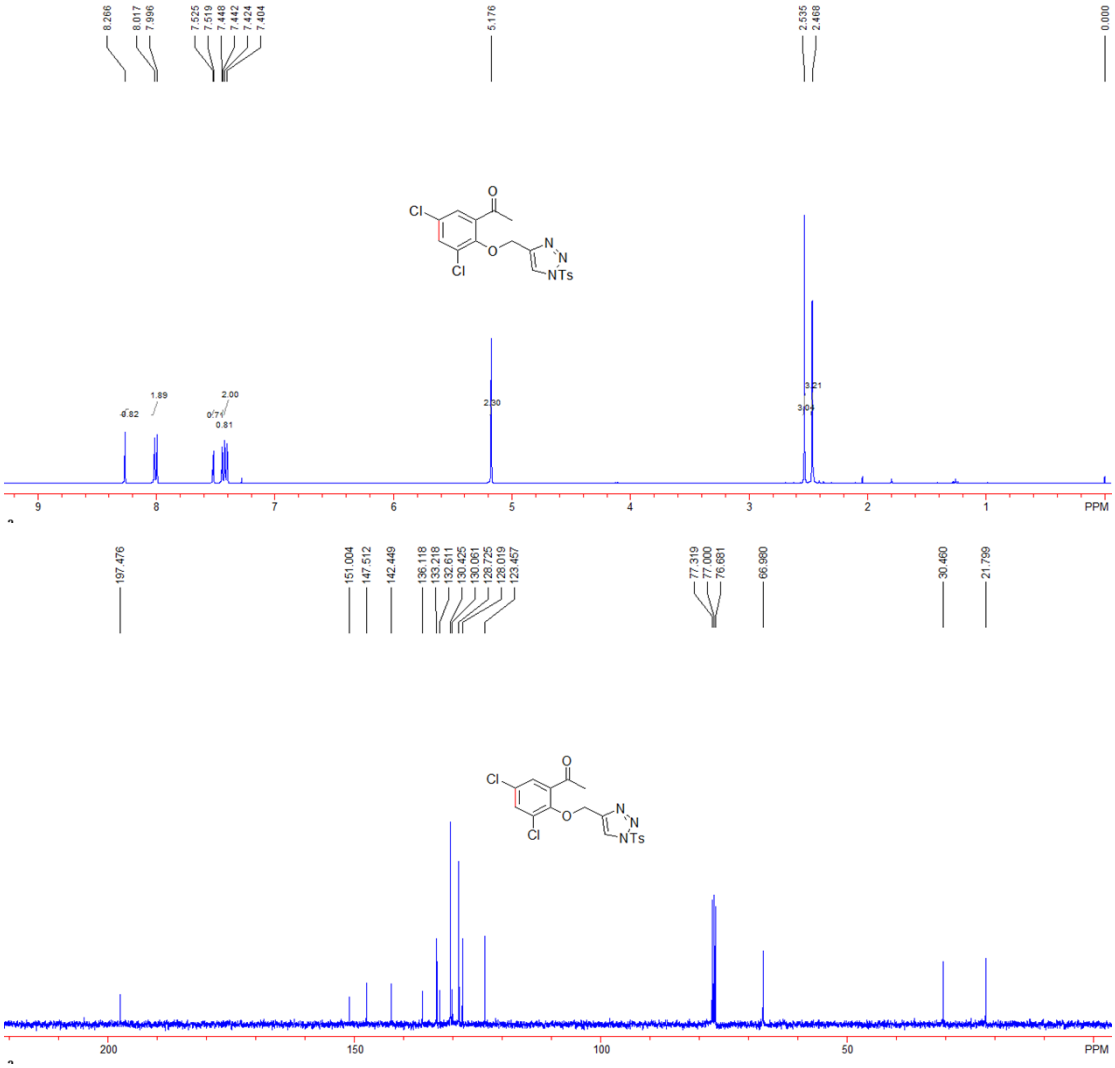


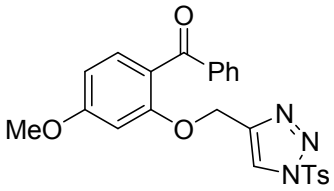


1-{3,5-Dichloro-2-[1-(toluene-4-sulfonyl)-1H-[1,2,3]triazol-4-ylmethoxy]-phenyl}-ethanone 1q.

10.0 mmol scale, 3.56 g, a white solid, 81% yield. m.p.: 120-122 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.47 (s, 3H, CH_3), 2.54 (s, 3H, CH_3), 5.18 (s, 2H, CH_2), 7.41 (d, J = 8.0 Hz, 2H, Ar), 7.45

(d, J = 2.4 Hz, 1H, Ar), 7.52 (d, J = 2.4 Hz, 1H, Ar), 8.00 (d, J = 8.0 Hz, 2H, Ar), 8.27 (s, 1H, CH=). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 30.5, 67.0, 123.4, 128.0, 128.7, 130.0, 130.4, 132.6, 133.2, 136.1, 142.4, 147.5, 151.0, 197.5. IR (CH_2Cl_2) ν 3150, 3069, 1682, 1592, 1437, 1393, 1379, 1358, 1233, 1215, 1190, 1178, 1088, 1016, 984, 896, 812, 790, 699, 675 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{16}Cl_2N_3O_4S^+$ (M^++H) requires 440.0233, found: 440.0212.

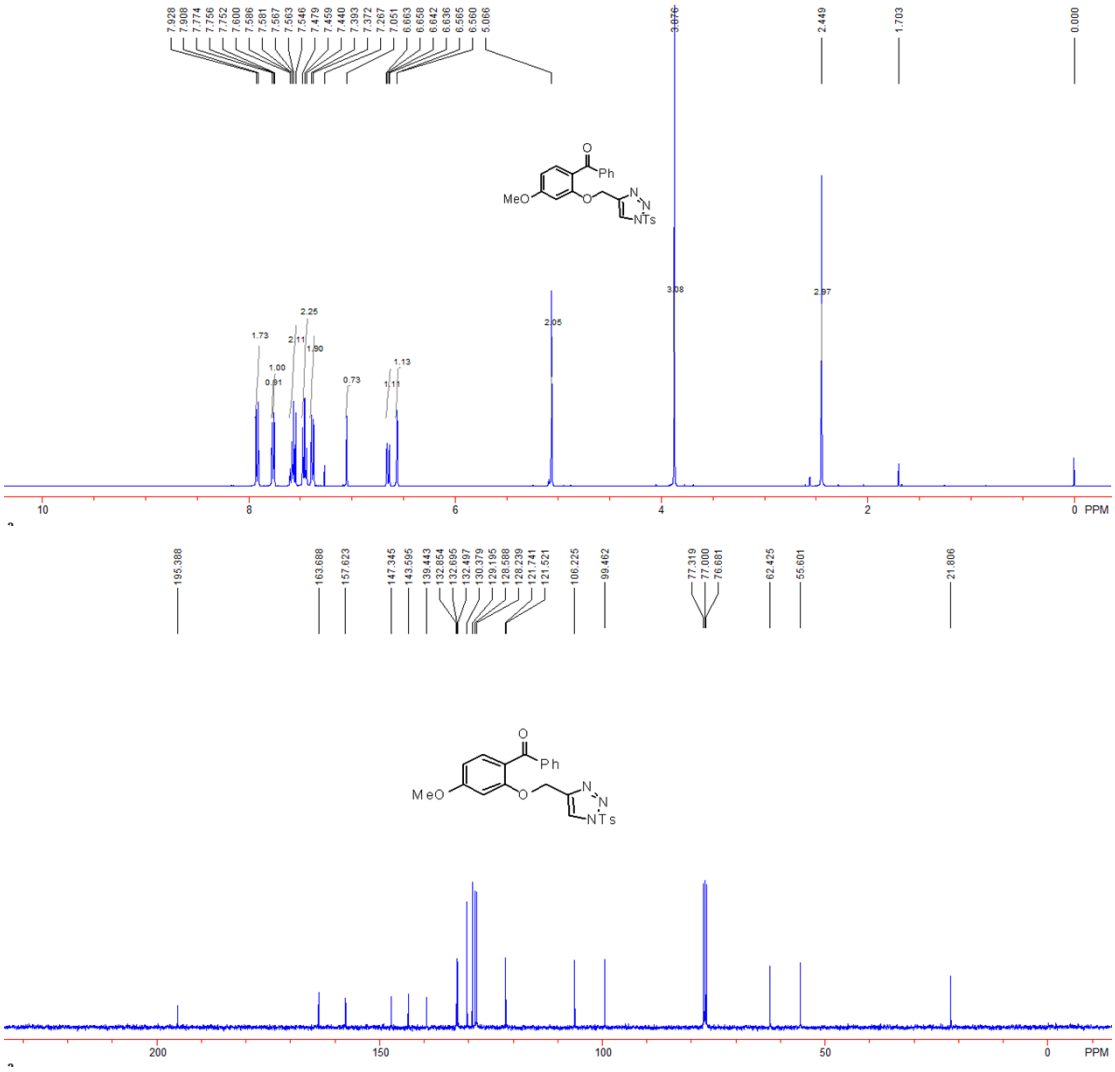


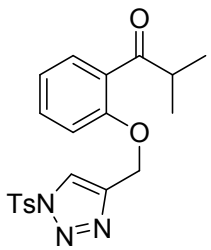


(4-methoxy-2-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy)phenyl)(phenyl)methanone 1r.

10.0 mmol scale, 3.75 g, a white solid, 81% yield. m.p.: 155-162 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.45 (s, 3H, CH_3), 3.88 (s, 3H, CH_3), 5.07 (s, 2H, CH_2), 6.56 (d, J = 2.0 Hz, 1H, Ar),

6.64 (dd, J = 8.4 Hz, J = 2.0 Hz, 1H, Ar), 7.05 (s, 1H, Ar), 7.38 (d, J = 8.4 Hz, 2H, Ar), 7.44-7.48 (m, 2H, Ar), 7.54-7.60 (m, 2H, Ar), 7.75 (d, J = 2.0 Hz, 1H, Ar), 7.77 (s, 1H, CH=), 7.92 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 55.6, 62.4, 99.5, 106.2, 121.5, 121.7, 128.2, 128.6, 129.2, 130.4, 132.5, 132.7, 132.8, 139.4, 143.6, 147.3, 157.6, 163.7, 195.4. IR (CH_2Cl_2) ν 3154, 1595, 1388, 1287, 1194, 1165, 1123, 1037, 978, 827, 816, 702, 671 cm^{-1}. HRMS (ESI) Calcd. for $C_{24}H_{22}N_3O_5S^+$ (M^++H) requires 464.1275, found: 464.1269.

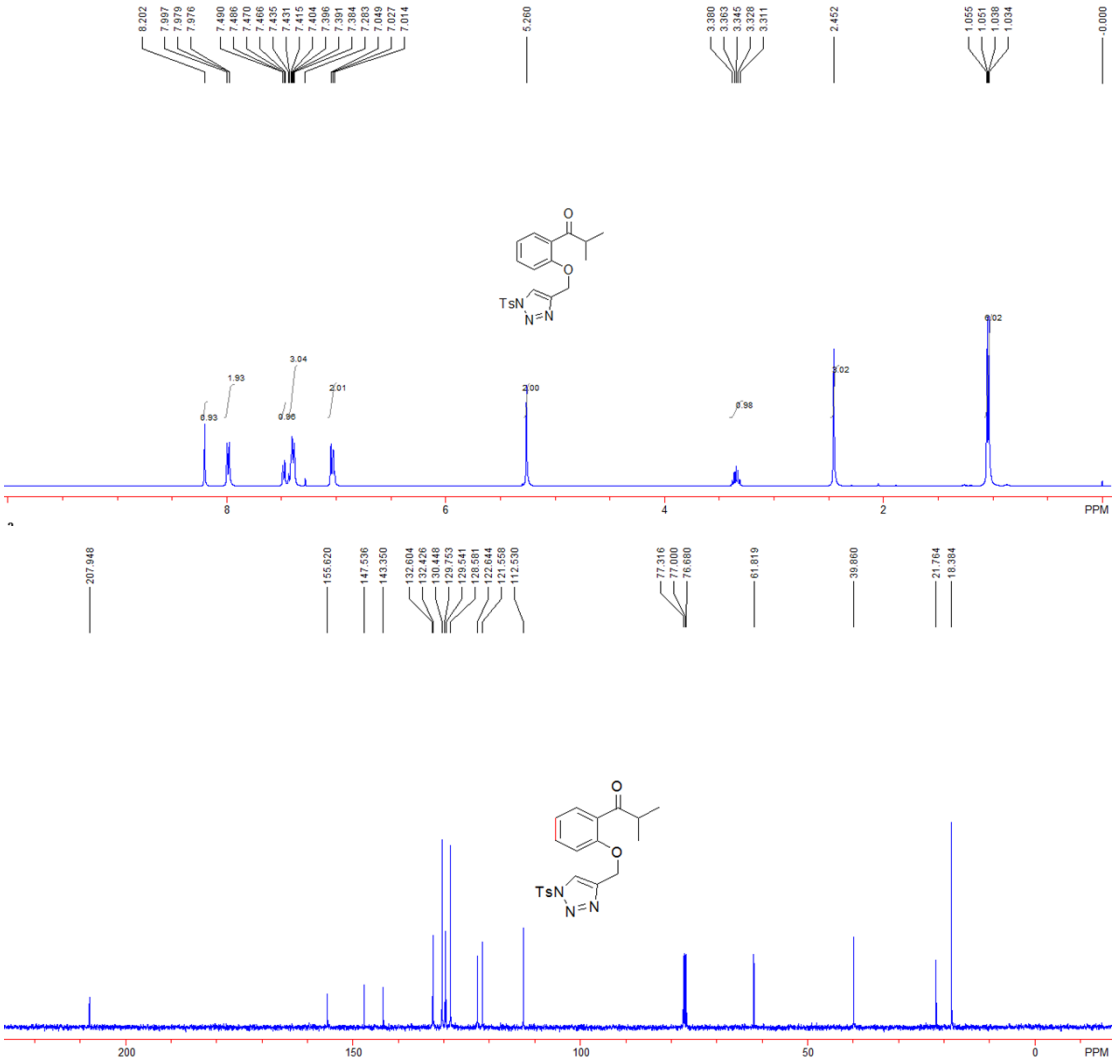


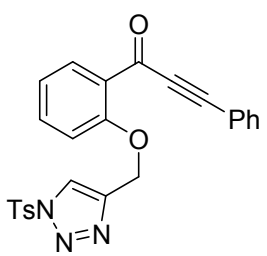


2-methyl-1-(2-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy)phenyl)propan-1-one 1s.

10 mmol scale, 3.51 g, a white solid, 88% yield. m.p.: 154-156 °C. ^{1}H NMR ($CDCl_3$, 400 MHz,

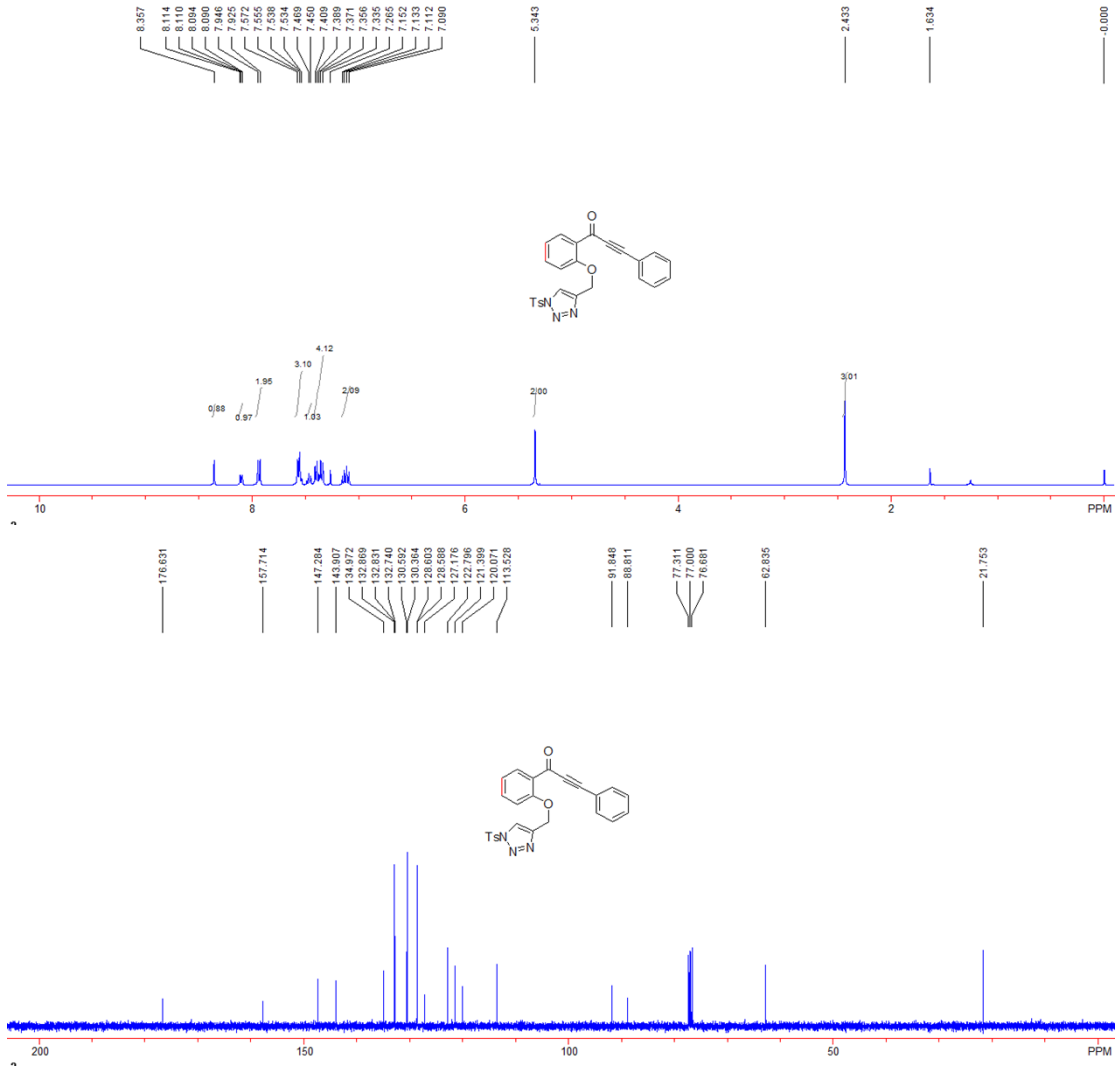
TMS) δ 1.04 (d, J = 6.8 Hz, 3H, CH_3), 1.05 (d, J = 6.8 Hz, 3H, CH_3), 2.45 (s, 3H, CH_3), 3.31-3.38 (m, 1H, CH), 5.26 (s, 2H, CH_2), 7.01-7.05 (m, 2H, Ar), 7.38-7.44 (m, 3H, Ar), 7.48 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H, Ar), 7.98 (d, J = 8.4 Hz, 2H, Ar), 8.20 (s, 1H, CH=). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.4, 21.8, 39.9, 61.8, 112.5, 121.6, 122.6, 128.6, 129.5, 129.8, 130.4, 132.4, 132.6, 143.4, 147.5, 155.6, 207.9. IR (CH_2Cl_2) ν 3129, 3093, 2959, 2923, 1671, 1594, 1447, 1387, 1281, 1255, 1212, 1193, 1160, 1088, 1010, 964, 867, 836, 814, 746, 702, 671 cm^{-1}. HRMS (ESI) Calcd. for $C_{20}H_{22}N_3O_4S^+$ (M^++H) requires 400.1326, found: 400.1334.

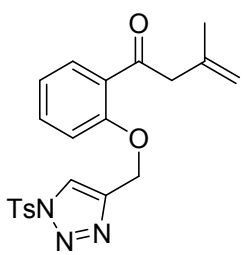




3-phenyl-1-(2-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy)phenyl)prop-2-yn-1-one 1t.

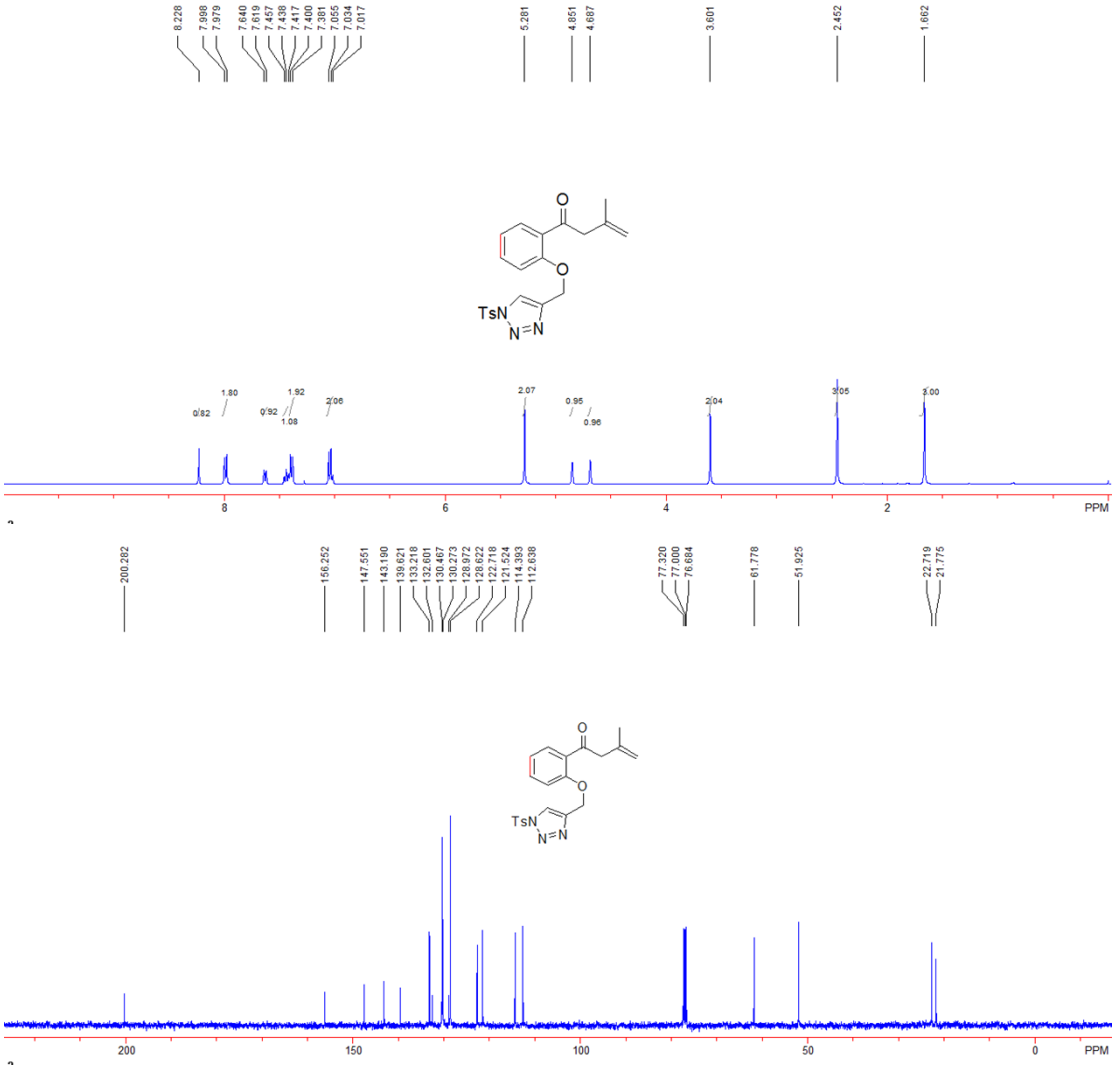
10.0 mmol scale, 3.88 g, a white solid, 85% yield. m.p.: 115-117 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.43 (s, 3H, CH_3), 5.34 (s, 2H, CH_2), 7.09-7.16 (m, 2H, Ar), 7.33-7.41 (m, 4H, Ar), 7.46 (d, J = 7.6 Hz, 1H, Ar), 7.53-7.58 (m, 3H, Ar), 7.93 (d, J = 8.4 Hz, 2H, Ar), 8.10 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H, Ar), 8.36 (s, 1H, CH=). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 62.8, 88.8, 91.8, 113.5, 120.1, 121.4, 122.8, 127.2, 128.6, 128.7, 130.4, 130.6, 132.7, 132.8, 132.9. 135.0, 143.9, 147.3, 157.7, 176.6. IR (CH_2Cl_2) ν 3142, 3109, 2915, 2850, 2198, 1624, 1612, 1589, 1483, 1447, 1391, 1305, 1236, 1194, 1180, 1159, 1120, 1016, 1005, 995, 967, 826, 817, 751, 700, 672 cm^{-1}. HRMS (ESI) Calcd. for $C_{25}H_{20}N_3O_4S^+$ (M^++H) requires 458.1169, found: 458.1179.

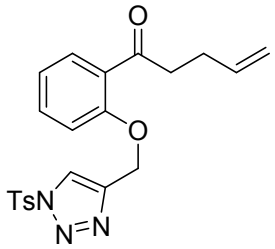




3-methyl-1-(2-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy)phenyl)but-3-en-1-one 1u.

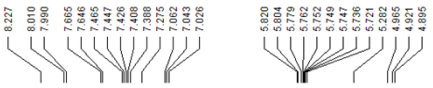
10 mmol scale, 3.58 g, a white solid, 87% yield. m.p.: 102-103 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.66 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 3.60 (s, 2H, CH_2), 4.69 (s, 1H, CH_2=), 4.85 (s, 1H, CH_2=), 5.28 (s, 2H, CH_2), 7.01-7.06 (m, 2H, Ar), 7.39 (d, *J* = 7.6 Hz, 2H, Ar), 7.44 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H, Ar), 7.63 (d, *J* = 8.0 Hz, 1H, Ar), 7.99 (d, *J* = 7.6 Hz, 2H, Ar), 8.23 (s, 1H, CH=). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 22.7, 51.9, 61.8, 112.6, 114.4, 121.5, 122.7, 128.6, 129.0, 130.3, 130.5, 132.6, 133.2, 139.6, 143.2, 147.6, 156.2, 200.3. IR (CH_2Cl_2) ν 3133, 3121, 2906, 1659, 1594, 1485, 1448, 1403, 1389, 1287, 1277, 1240, 1214, 1191, 11175, 1034, 1017, 983, 912, 837, 756, 702, 669 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{22}N_3O_4S^+$ (M^++H) requires 412.1326, found: 412.1342.

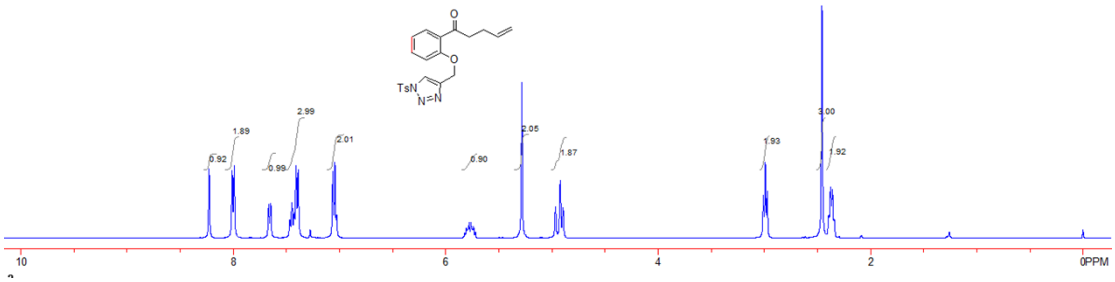


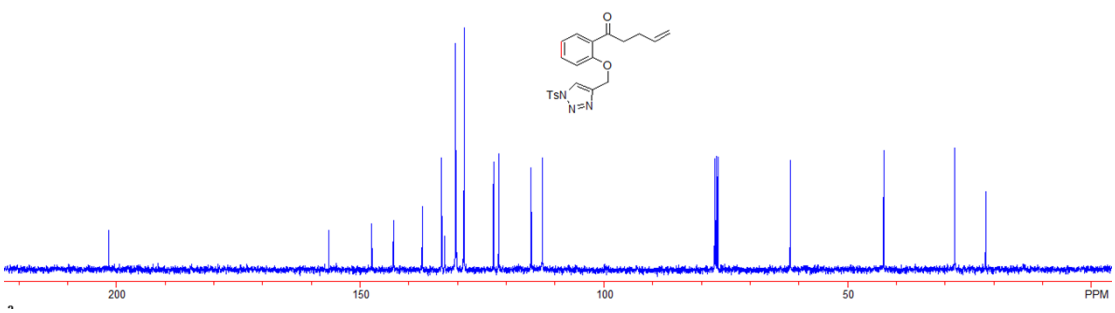


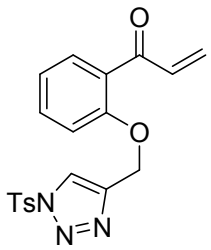
1-(2-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy)phenyl)pent-4-en-1-one 1v.

10 mmol scale, 3.58 g, a white solid, 87% yield. m.p.: 100-102 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.34-2.40 (m, 2H, CH_2), 2.46 (s, 3H, CH_3), 2.99 (t, *J* = 7.6 Hz, 2H, CH_2), 4.89-4.97 (m, 2H, CH_2=), 5.28 (s, 2H, CH_2), 5.72-5.82 (m, 1H, CH=), 7.02-7.07 (m, 2H, Ar), 7.38-7.47 (m, 3H, Ar), 7.65 (d, *J* = 7.6 Hz, 1H, Ar), 8.00 (d, *J* = 8.0 Hz, 2H, Ar), 8.23 (s, 1H, CH=). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 28.1, 42.7, 61.8, 112.6, 114.9, 121.6, 122.6, 128.7, 128.8, 130.2, 130.5, 132.6, 133.2, 137.2, 143.2, 147.6, 156.4, 201.5. IR (CH_2Cl_2) ν 3153, 2927, 2356, 1957, 1654, 1594, 1487, 1447, 1311, 1220, 1116, 1089, 1030, 1006, 951, 920, 820, 770, 683 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{22}N_3O_4S^+$ (M^++H) requires 412.1326, found: 412.1323.



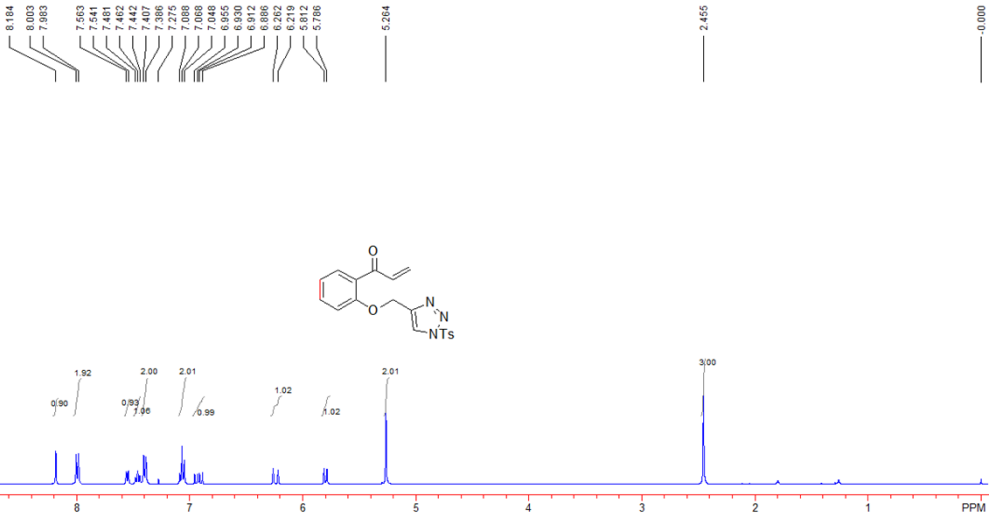


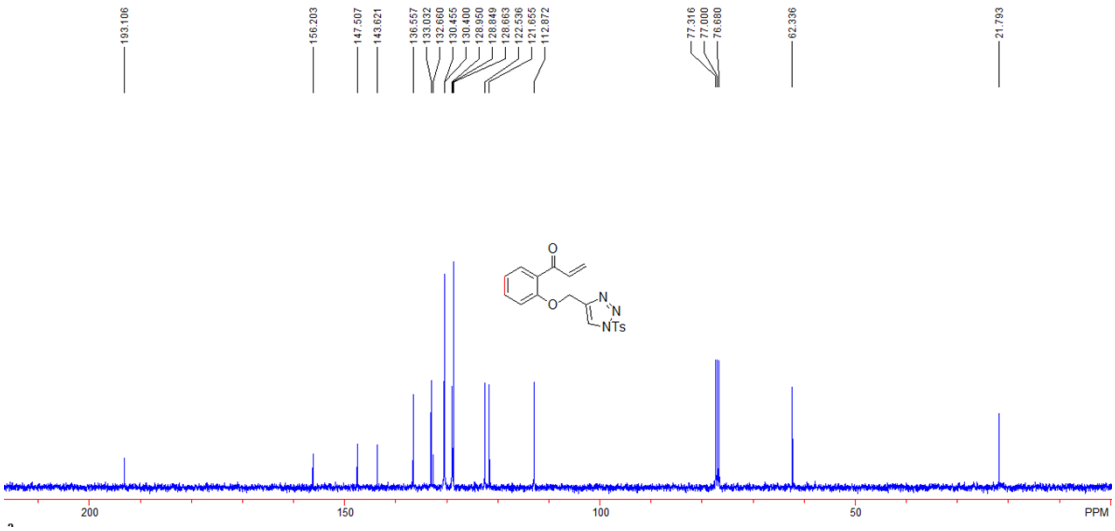


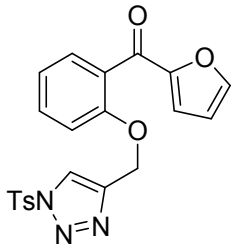


1-(2-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy)phenyl)prop-2-en-1-one 1w.

10 mmol scale, 1.99 g, a white solid, 52% yield. m.p.: 120-122 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.46 (s, 3H, CH_3), 5.26 (s, 2H, CH_2), 5.79 (d, J = 10.4 Hz, 1H, CH_2=), 6.24 (d, J = 17.2 Hz, 1H, CH_2=), 6.92 (dd, J = 17.2 Hz, J = 10.4 Hz, 1H, CH=), 7.04-7.09 (m, 2H, Ar), 7.39 (d, J = 8.4 Hz, 2H, Ar), 7.46 (dd, J = 8.0 Hz, J = 8.0 Hz, 1H, Ar), 7.55 (d, J = 8.4 Hz, 1H, Ar), 7.99 (d, J = 8.4 Hz, 2H, Ar), 8.18 (s, 1H, CH=). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 62.3, 112.9, 121.6, 122.5, 128.7, 128.8, 128.9, 130.4, 130.5, 132.6, 133.0, 136.6, 143.6, 147.5, 156.2, 193.1. IR (CH_2Cl_2) ν 3125, 3093, 2846, 1651, 1604, 1591, 1482, 1391, 1297, 1280, 1208, 1194, 1174, 1165, 1116, 1115, 1017, 1000, 970, 817, 761, 723, 699, 670 cm^{-1}. HRMS (ESI) Calcd. for $C_{19}H_{18}N_3O_4S^+$ (M^++H) requires 384.1013, found: 384.1023.

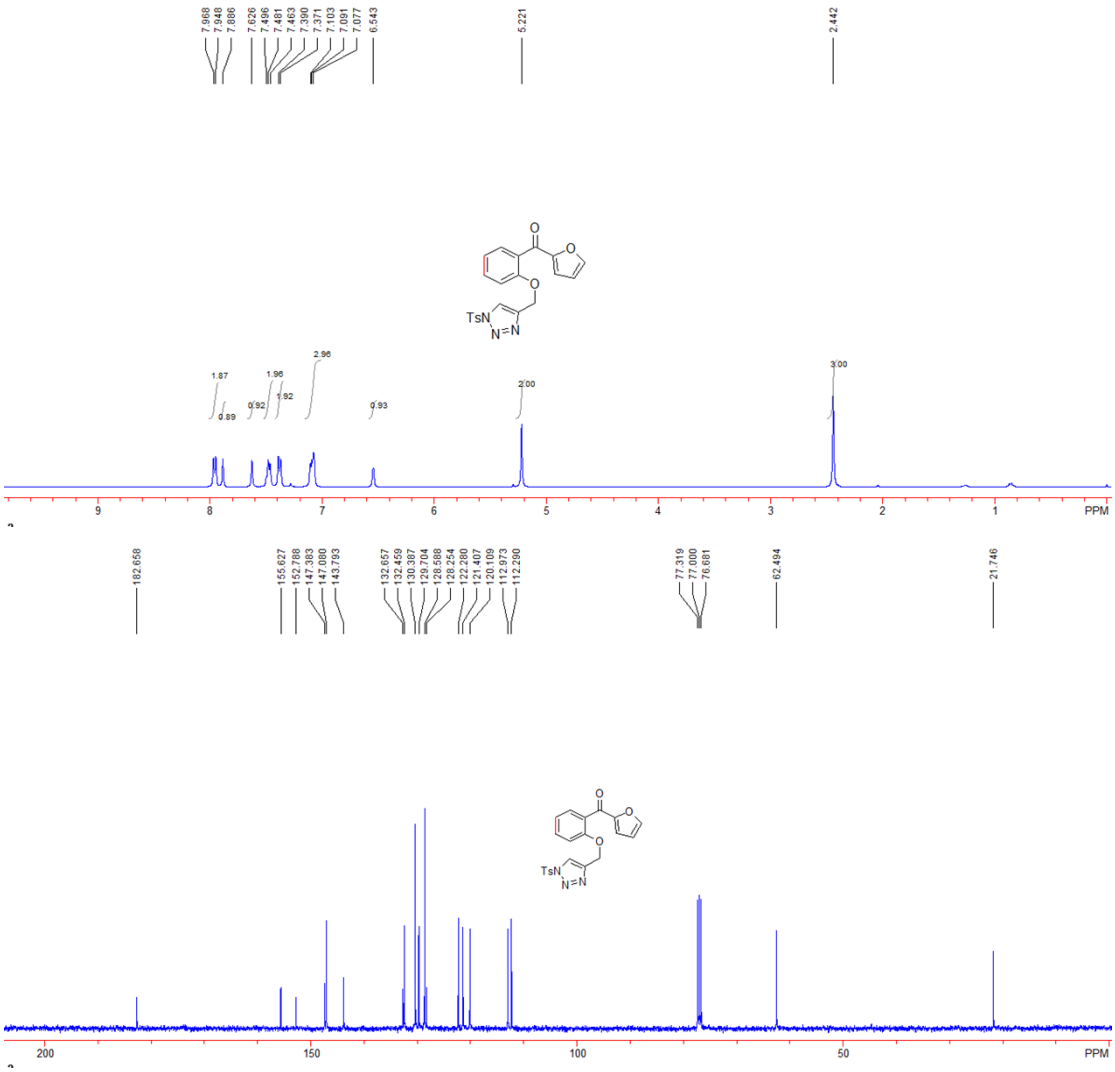


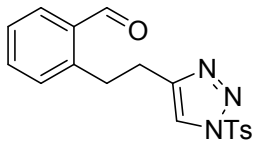




furan-2-yl(2-((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy)phenyl)methanone 1x.

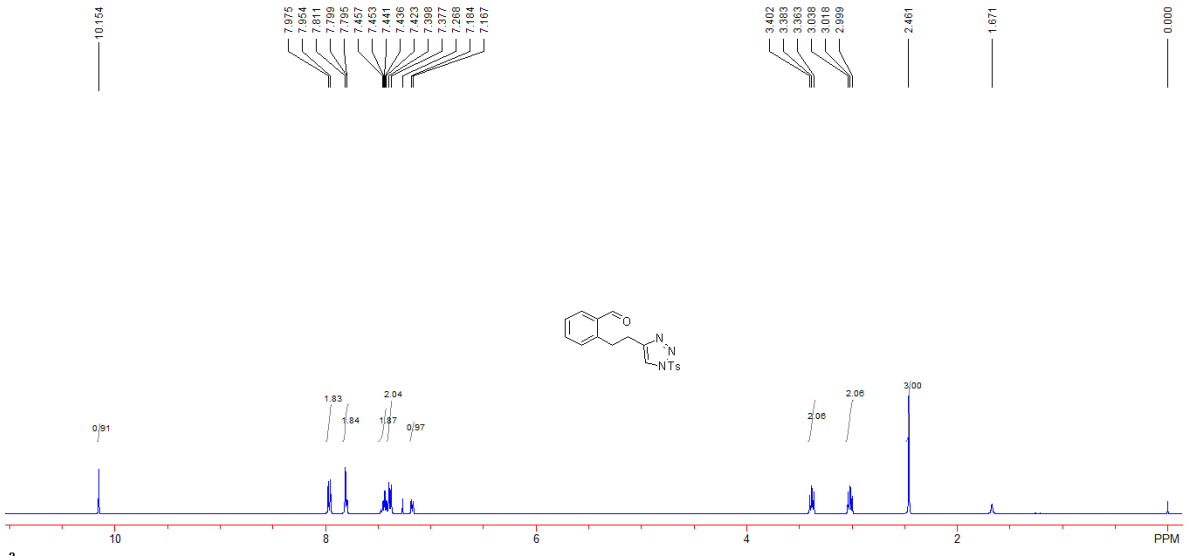
10 mmol scale, 3.68 g, a white solid, 87% yield. m.p.: 135-137 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.44 (s, 3H, CH_3), 5.22 (s, 2H, CH_2), 6.54 (s, 1H, Ar), 7.07-7.11 (m, 3H, Ar), 7.38 (d, J = 8.0 Hz, 2H, Ar), 7.46-7.50 (m, 2H, Ar), 7.63 (s, 1H, Ar), 7.89 (s, 1H, CH=), 7.95 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 62.5, 112.3, 113.0, 120.1, 121.4, 122.3, 128.2, 128.6, 129.7, 130.4, 132.4, 132.6, 143.8, 147.1, 147.4, 152.8, 155.6, 182.6. IR (CH_2Cl_2) ν 3149, 3064, 1652, 1562, 1487, 1461, 1389, 1310, 1300, 1275, 1245, 1195, 1177, 1019, 955, 888, 874, 814, 771, 754, 673, 665 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{18}N_3O_5S^+$ (M^++H) requires 424.0962, found: 424.0976.

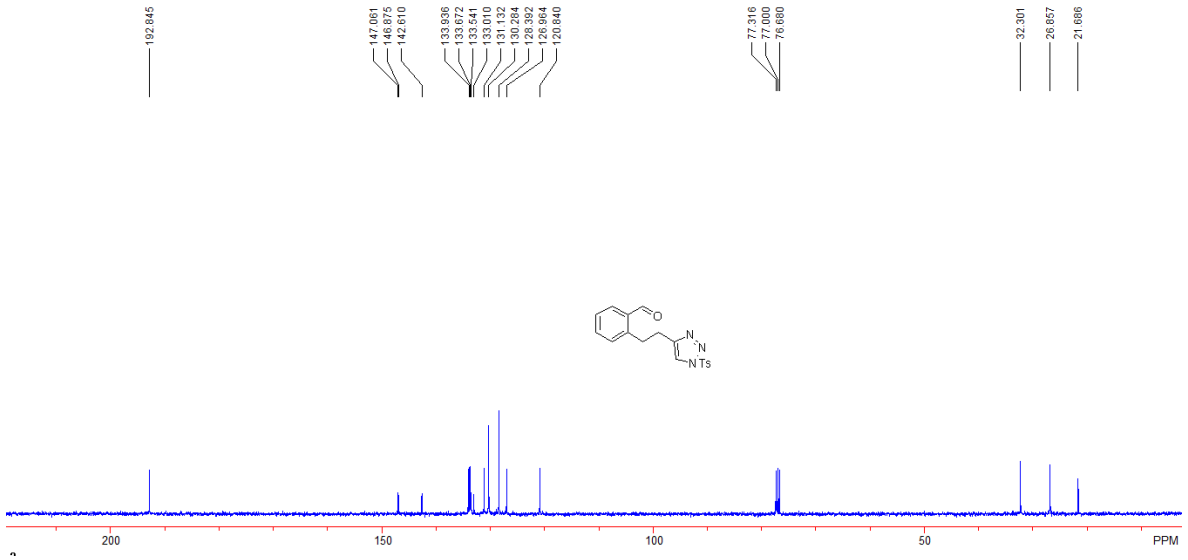


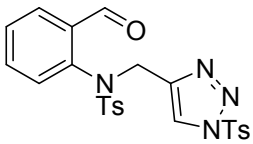


2-(2-(1-tosyl-1H-1,2,3-triazol-4-yl)ethyl)benzaldehyde 3.

10.0 mmol scale, 3.05 g, a white solid, 86% yield. m.p.: 84-86 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.46 (s, 3H, CH_3), 3.02 (t, J = 8.0 Hz, 2H, CH_2), 3.38 (t, J = 8.0 Hz, 2H, CH_2), 7.17 (d, J = 6.8 Hz, 1H, Ar), 7.39 (d, J = 8.4 Hz, 2H, Ar), 7.42-7.48 (m, 2H, Ar), 7.79-7.82 (m, 2H, Ar, CH=), 7.98 (d, J = 8.4 Hz, 2H, Ar), 10.15 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.7, 26.8, 32.3, 120.8, 127.0, 128.4, 130.3, 131.1, 133.0, 133.5, 133.7, 133.9, 142.6, 146.9, 147.1, 192.8. IR (CH_2Cl_2) ν 3125, 3089, 2919, 2753, 1694, 1597, 1574, 1388, 1372, 1193, 1181, 1091, 1019, 964, 814, 757, 700, 684, 665 cm^{-1}. MS (MALDI) m/z: 356.1 ($M+H^+$, 100); HRMS (MALDI) Calcd. for $C_{18}H_{18}N_3O_3S^+$ (M^++H) requires 356.1063, found: 356.1060.



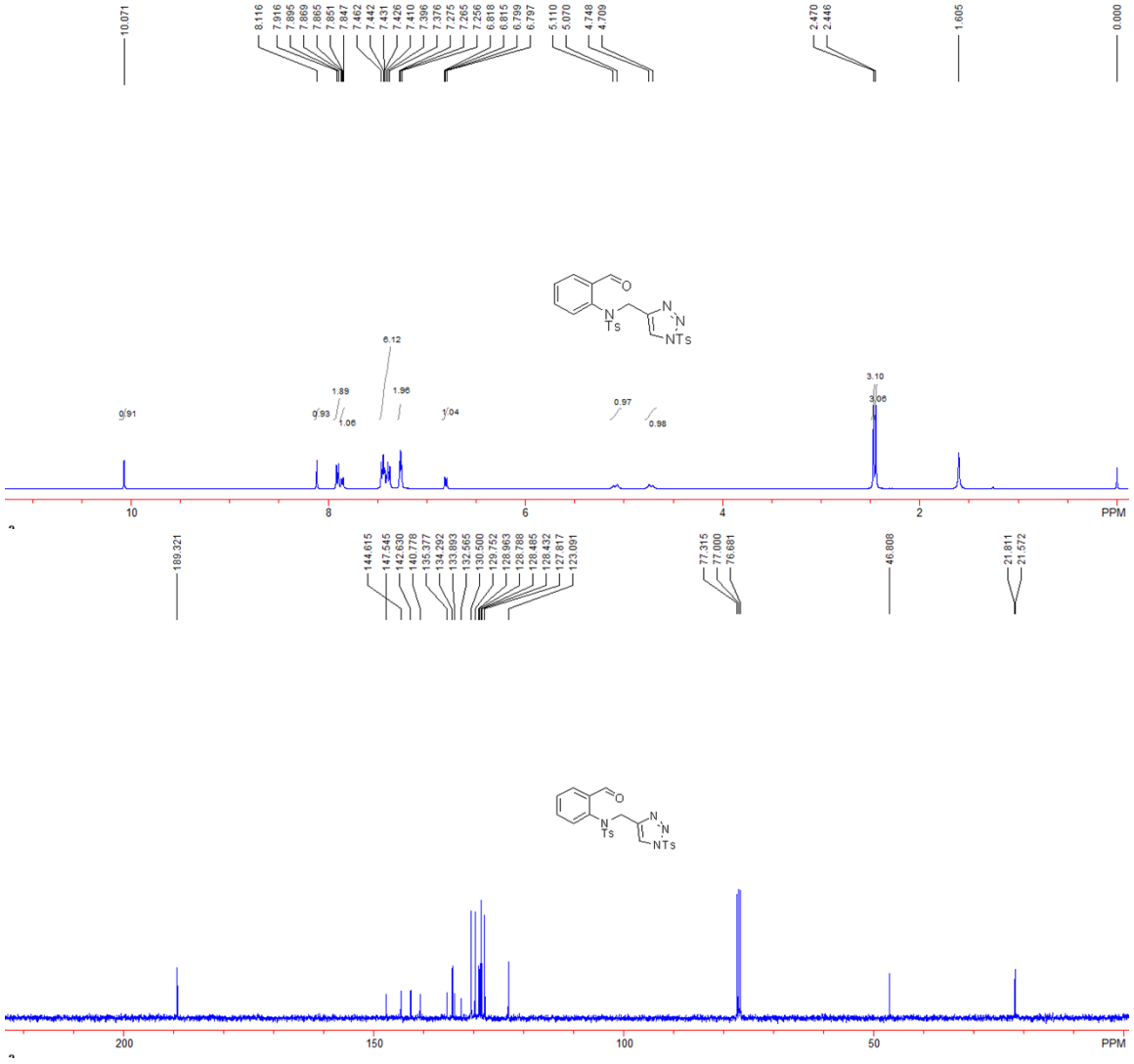


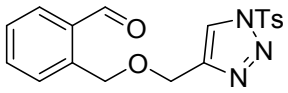


N-(2-formylphenyl)-4-methyl-N-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)benzenesulfonamide 4.

10.0 mmol scale, 3.17 g, a white solid, 62% yield. m.p.: 92-94 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.45 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 4.73 (d, J = 16.4 Hz, 1H, CH), 5.09 (d, J = 16.4 Hz, 1H, CH), 6.81 (dd, J = 7.6 Hz, J = 1.2 Hz, 1H, Ar), 7.27 (d, J = 8.0 Hz, 2H, Ar), 7.37-7.47 (m, 6H, Ar), 7.86 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H, Ar), 7.91 (d, J = 8.4 Hz, 2H, Ar), 8.12 (s, 1H, CH=), 10.07 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 21.8, 46.8, 123.1, 127.8, 128.4, 128.5, 128.8, 129.0, 129.8, 130.5, 132.6, 133.9, 134.3, 135.4, 140.8, 142.6, 144.6, 147.5,

189.3. IR (CH_2Cl_2) ν 3153, 2886, 1692, 1594, 1455, 1392, 1346, 1195, 1179, 1160, 109, 1067, 1011, 966, 864, 813, 724, 660 cm^{-1}. HRMS (ESI) Calcd. for $C_{24}H_{23}N_4O_5S_2^+$ (M^++H) requires 511.1104, found: 511.1113.

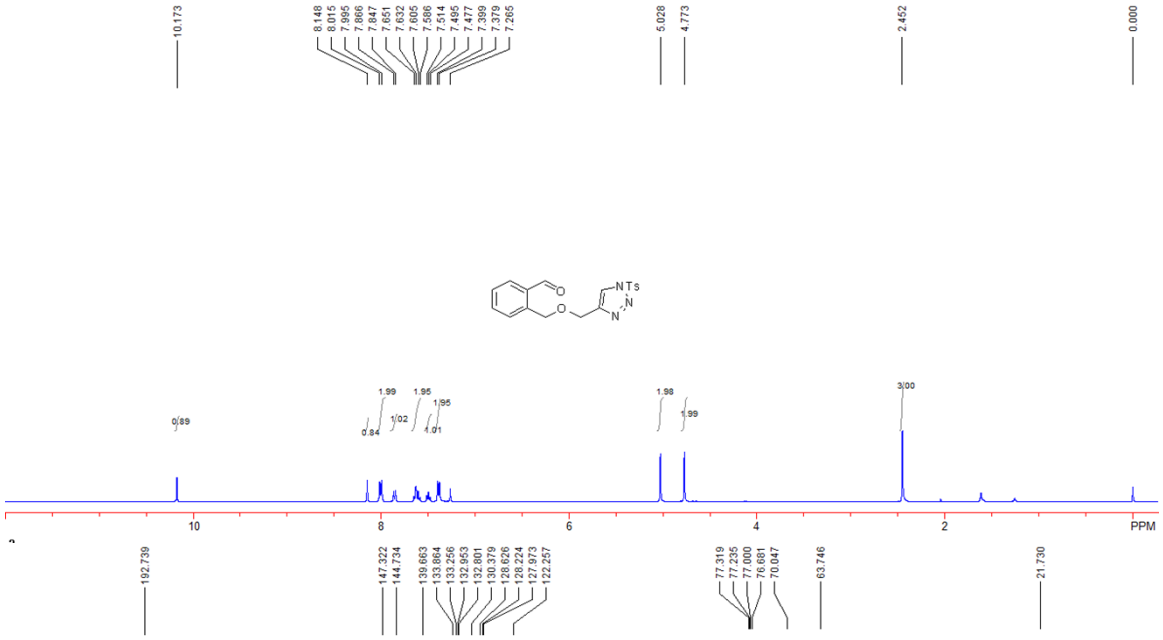


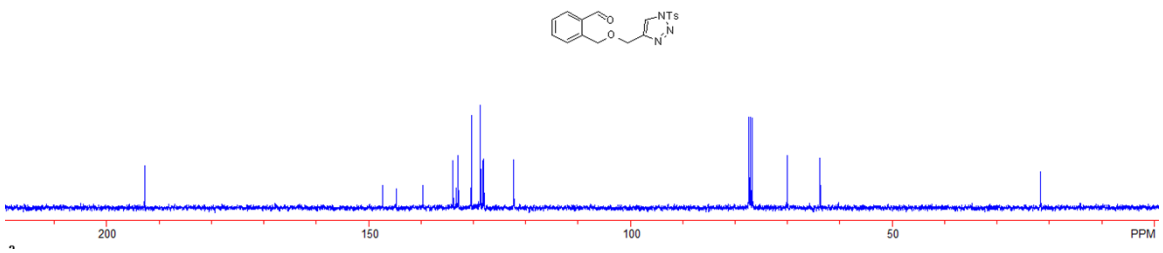


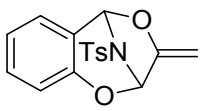
2-(((1-tosyl-1H-1,2,3-triazol-4-yl)methoxy)methyl)benzaldehyde 6.

10.0 mmol scale, 3.27 g, a white solid, 87% yield. m.p.: 97-99 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.45 (s, 3H, CH_3), 4.77 (s, 2H, CH_2), 5.03 (s, 2H, CH_2), 7.39 (d, J = 8.0 Hz, 2H, Ar), 7.49 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H, Ar), 7.58-7.66 (m, 2H, Ar), 7.85 (d, J = 7.6 Hz, 1H, Ar), 8.00 (d, J = 8.0 Hz, 2H, Ar), 8.15 (s, 1H, CH=), 10.17 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.7, 63.7, 70.0, 122.2, 128.0, 128.2, 128.6, 130.4, 132.8, 132.9, 133.2, 133.9, 139.7, 144.7, 147.3, 192.7. IR (CH_2Cl_2) ν 3145, 2862, 2769, 1690, 1588, 1674, 1385, 1370, 1296, 1195, 1173,

1109, 1081, 1017, 1011, 991, 973, 959, 758, 703, 678, 659 cm^{-1}. MS (MALDI) m/z: 372.1 ($M+H^+$, 100); HRMS (MALDI) Calcd. for $C_{18}H_{18}N_3O_4S^+$ (M^++H) requires 372.1013, found: 372.1007.



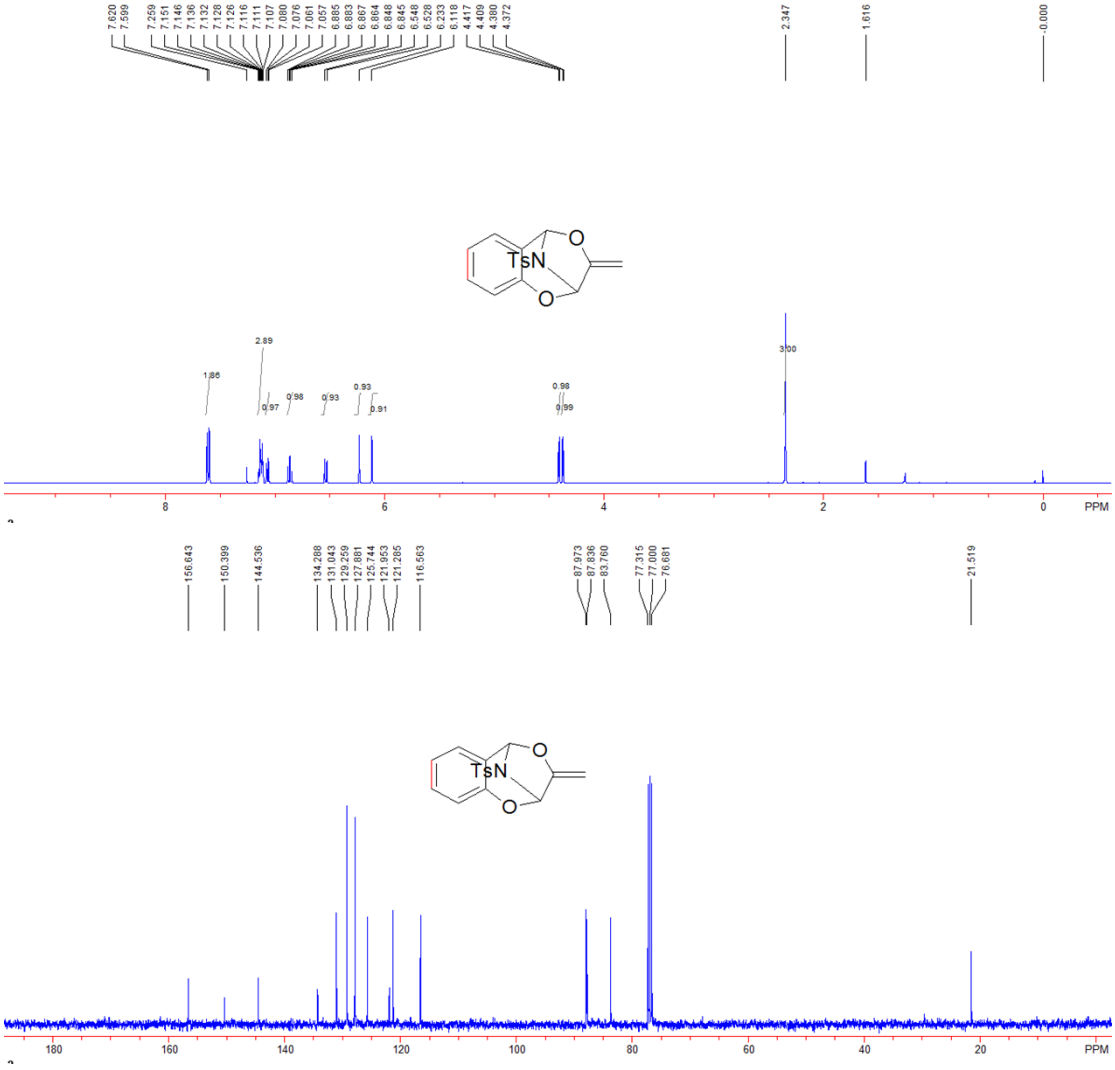


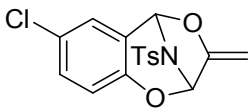


10-Methylene-12-(toluene-4-sulfonyl)-8,11-dioxa-12-aza-tricyclo[7.2.1.02,7]dodeca-2,4,6-triene 2a.

0.2 mmol scale, 53 mg, a white solid, 80% yield. m.p.: 136-138 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.35 (s, 3H, CH_3), 4.38 (d, J = 3.2 Hz, 1H, CH_2=), 4.41 (d, J = 3.2 Hz, 1H, CH_2=), 6.11 (s, 1H, CH), 6.23 (s, 1H, CH), 6.53 (d, J = 8.0 Hz, 1H, Ar), 6.87 (ddd, J = 8.0 Hz, J = 8.0 Hz, J = 1.2 Hz, 1H, Ar), 7.07 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H, Ar), 7.10-7.16 (m, 3H, Ar), 7.61 (d, J = 8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 83.8, 87.8, 88.0, 116.6, 121.3, 122.0,

125.7, 127.9, 129.2, 131.0, 134.3, 144.5, 150.4, 156.6. IR (CH_2Cl_2) ν 3043, 2923, 1482, 1354, 1187, 1113, 1022, 1012, 934, 838, 751, 673 cm^{-1}. HRMS (ESI) Calcd. for $C_{17}H_{16}NO_4S^+$ (M^++H) requires 330.0795, found: 330.0792.

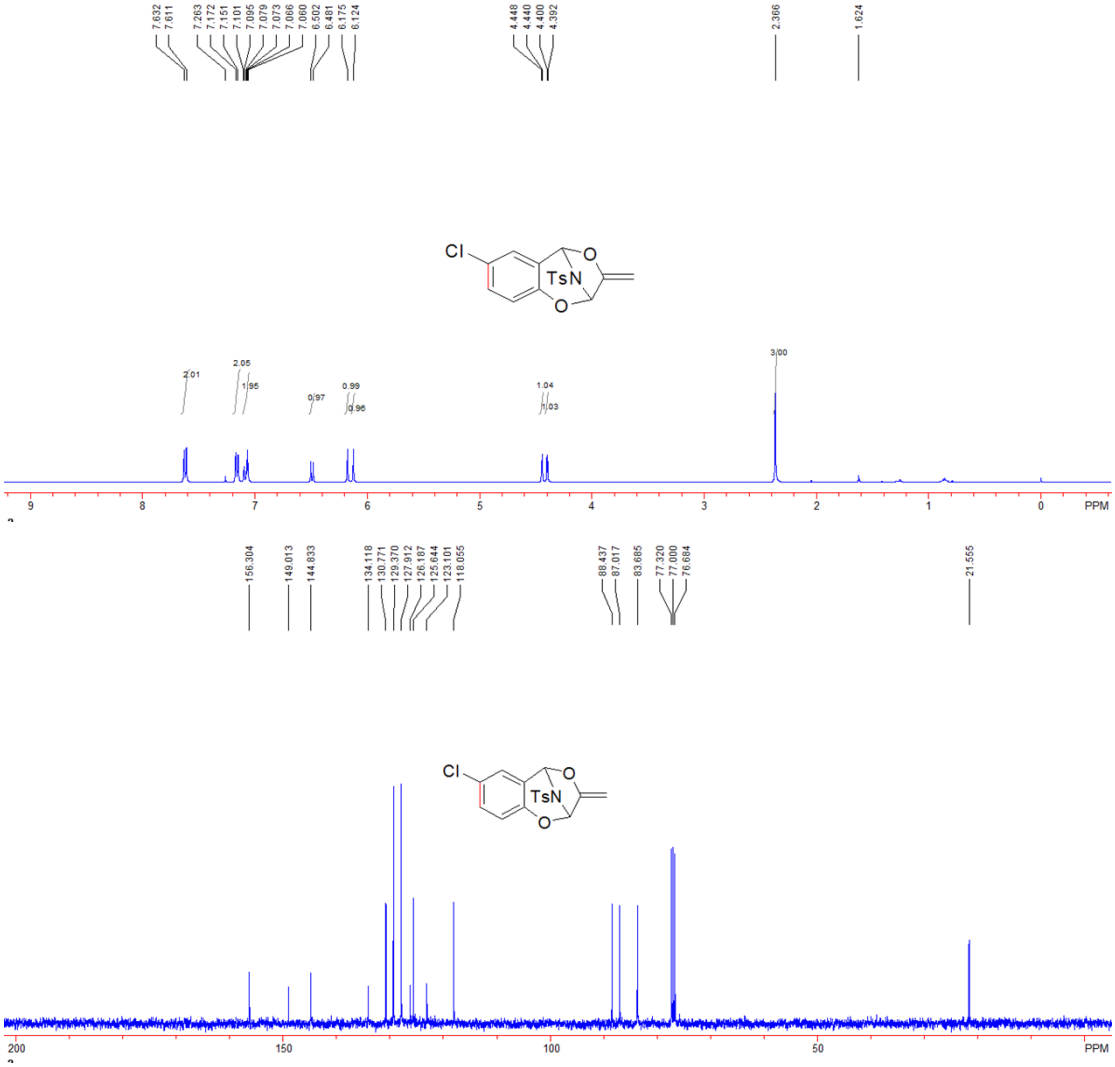


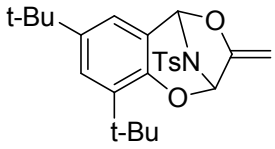


4-Chloro-10-methylene-12-(toluene-4-sulfonyl)-8,11-dioxa-12-aza-tricyclo[7.2.1.02,7]dodeca-2,4,6-triene 2b.

0.2 mmol scale, 58 mg, a white solid, 80% yield. m.p.: 102-104 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.37 (s, 3H, CH_3), 4.40 (d, J = 3.2 Hz, 1H, CH_2=), 4.44 (d, J = 3.2 Hz, 1H, CH_2=), 6.12 (s, 1H, CH), 6.18 (s, 1H, CH), 6.49 (d, J = 8.4 Hz, 1H, Ar), 7.06-7.11 (m, 2H, Ar), 7.16 (d, J = 8.4 Hz, 2H, Ar), 7.62 (d, J = 8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 83.7, 87.0, 88.4, 118.0, 123.1, 125.6, 126.2, 127.9, 129.4, 130.8, 134.1, 144.8, 149.0, 156.3. IR

(CH_2Cl_2) ν 3117, 3054, 3010, 2919, 1673, 1596, 1479, 1355, 1315, 1271, 1179, 1160, 1124, 1000, 937, 889, 847, 817, 779, 761, 677, 663 cm^{-1}. HRMS (ESI) Calcd. for $C_{17}H_{15}ClNO_4S^+$ (M^++H) requires 364.0405, found: 364.0398.

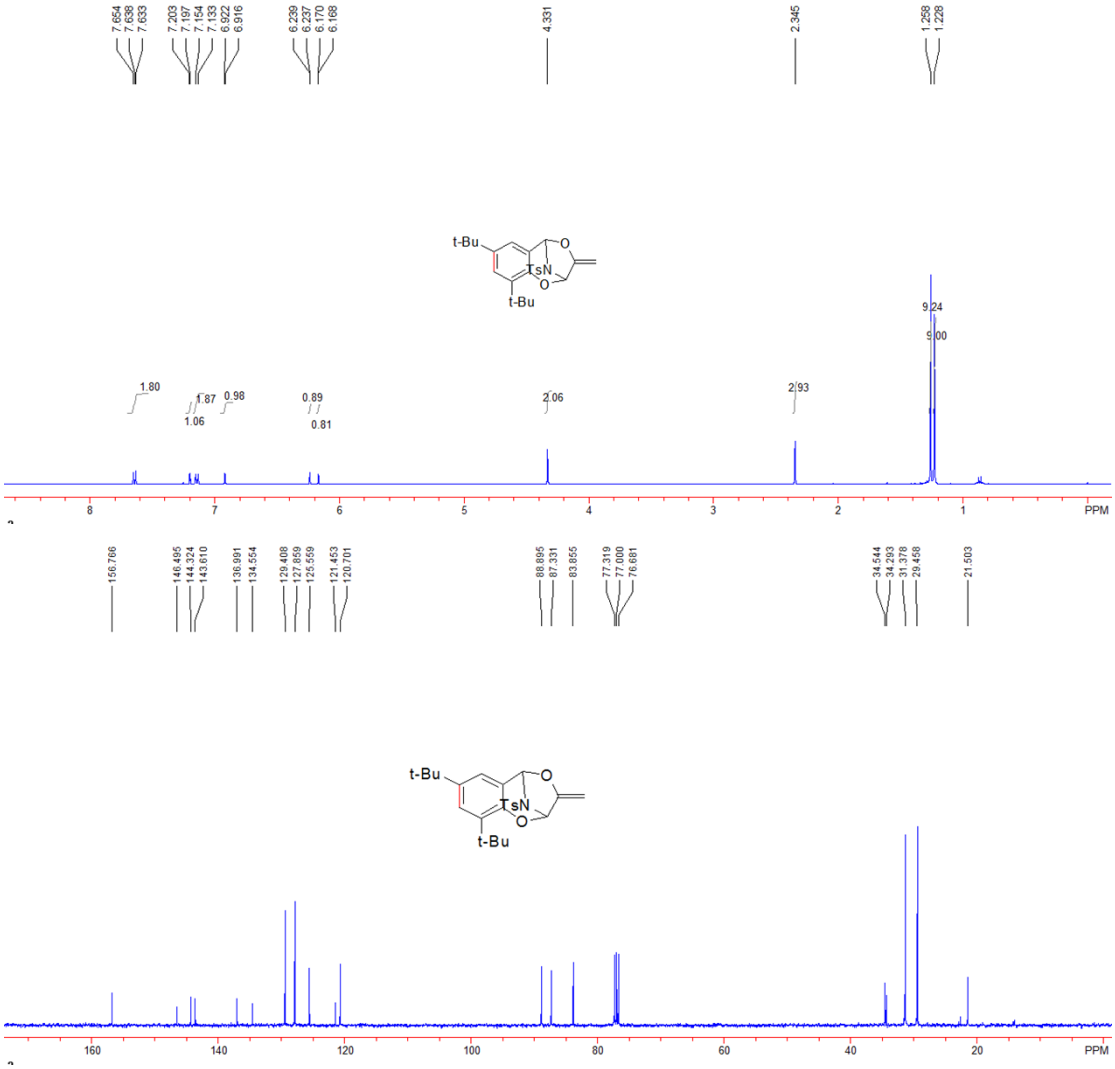


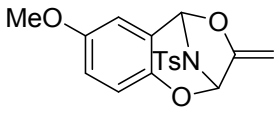


4,6-Di-tert-butyl-10-methylene-12-(toluene-4-sulfonyl)-8,11-dioxa-12-aza-tricyclo[7.2.1.02,7]dodeca-2,4,6-triene 2c.

0.2 mmol scale, 65 mg, a white solid, 74% yield. m.p.: 115-117 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.23 (s, 9H, CH_3), 1.26 (s, 9H, CH_3), 2.34 (s, 3H, CH_3), 4.33 (s, 2H, CH_2=), 6.17 (d, 1H, *J* = 0.8 Hz, CH), 6.24 (d, *J* = 0.8 Hz, 1H, CH), 6.92 (d, *J* = 2.4 Hz, 1H, Ar), 7.14 (d, *J* = 8.4 Hz, 2H, Ar), 7.20 (d, *J* = 2.4 Hz, 1H, Ar), 7.63-7.66 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS)

δ 21.5, 29.4, 31.4, 34.3, 34.5, 83.8, 87.3, 88.9, 120.7, 121.4, 125.6, 127.8, 129.4, 134.6, 137.0, 143.6, 144.3, 146.5, 156.8. IR (CH_2Cl_2) ν 2955, 1678, 1475, 1355, 1165, 1125, 1093, 972, 934, 853, 709, 678 cm^{-1}. HRMS (ESI) Calcd. for $C_{25}H_{32}NO_4S^+$ (M^++H) requires 442.2047, found: 442.2040.

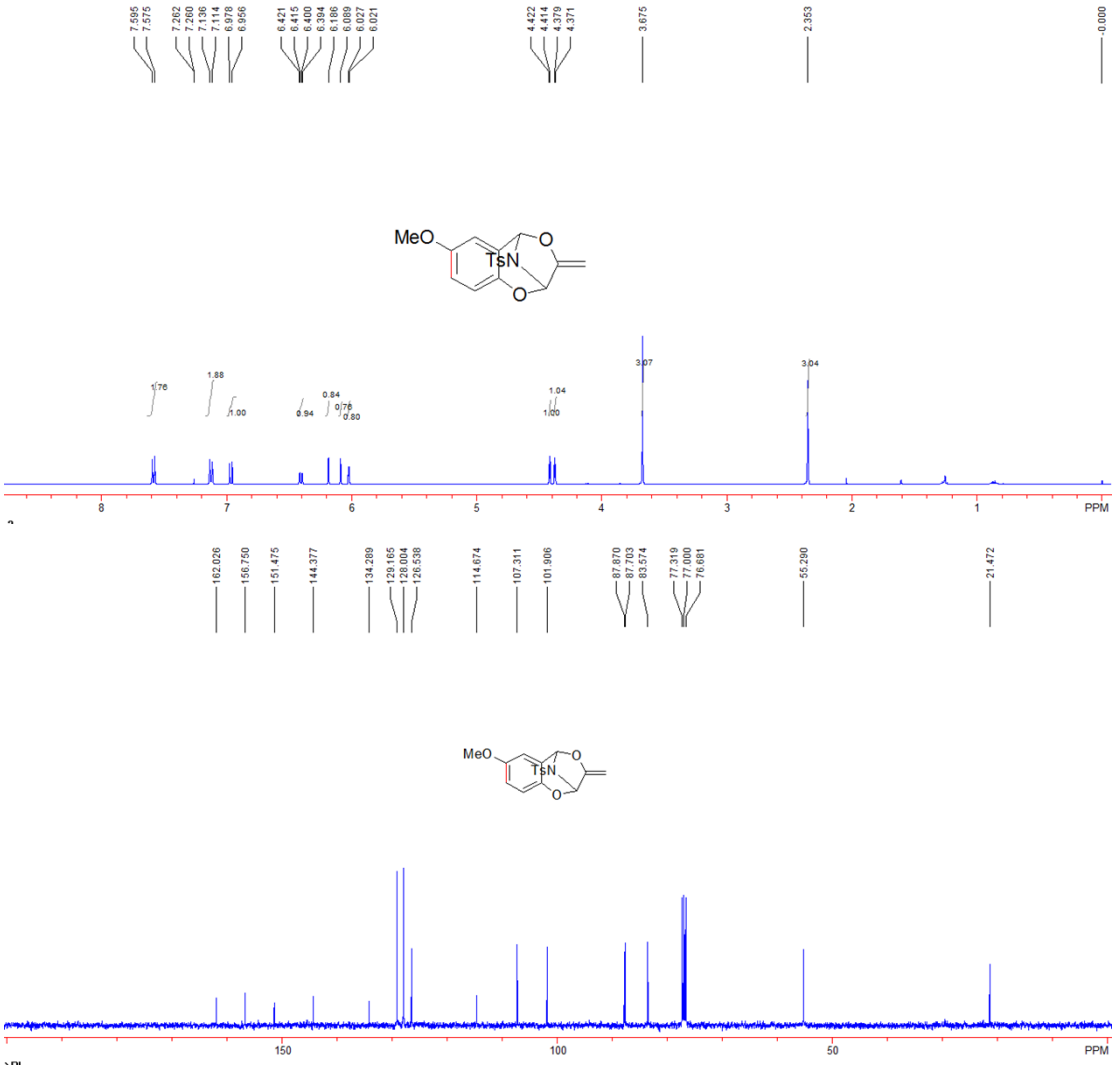


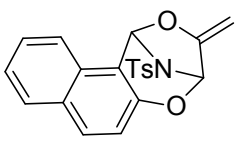


4-Methoxy-10-methylene-12-(toluene-4-sulfonyl)-8,11-dioxa-12-aza-tricyclo[7.2.1.02,7]dodeca-2,4,6-triene 2d.

0.2 mmol scale, 52mg, a white solid, 72% yield. m.p.: 114-116 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.35 (s, 3H, CH_3), 3.67 (s, 3H, CH_3), 4.37 (d, J = 3.2 Hz, 1H, CH_2=), 4.41 (d, J = 3.2 Hz, 1H, CH_2=), 6.02 (d, J = 2.4 Hz, 1H, Ar), 6.09 (s, 1H, CH), 6.19 (s, 1H, CH), 6.40 (dd, J = 8.4 Hz, J = 2.4 Hz, 1H, Ar), 6.96 (d, J = 8.4 Hz, 1H, Ar), 7.12 (d, J = 8.8 Hz, 2H, Ar), 7.58 (d, J = 8.8 Hz,

2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 55.3, 83.6, 87.7, 87.9, 101.9, 107.3, 114.7, 126.5, 128.0, 129.2, 134.3, 144.4, 151.5, 156.8, 162.0. IR (CH_2Cl_2) ν 2927, 2834, 1680, 1615, 1502, 1441, 1357, 1265, 1169, 1157, 1099, 1042, 1016, 979, 944, 860, 826, 810, 674, 666 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{18}NO_5S^+$ (M^++H) requires 360.0900, found: 360.0902.

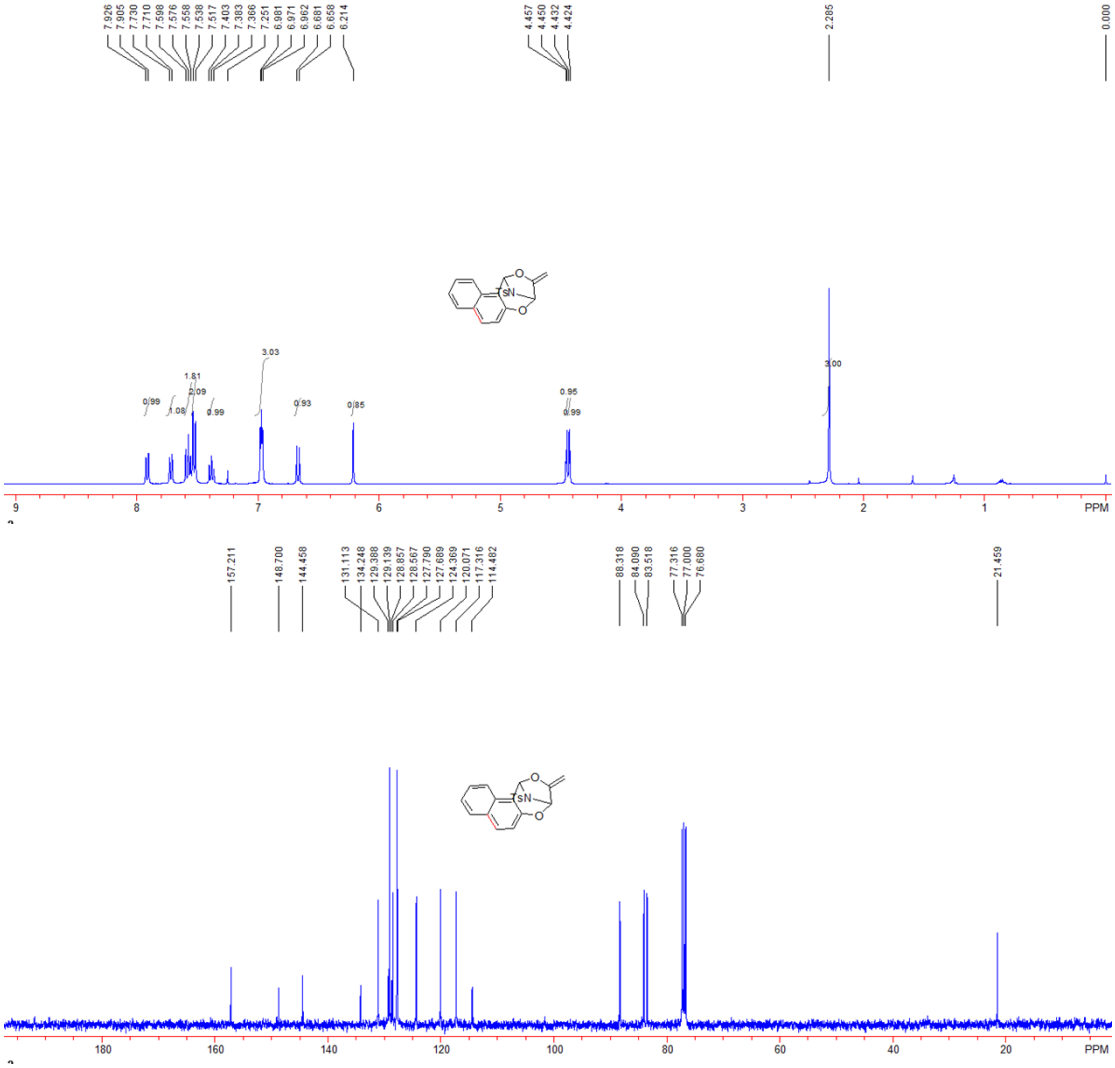


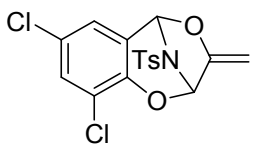


3-methylene-12-tosyl-3,4-dihydro-1H-1,4-epiminonaphtho[2,1-e][1,4]dioxepine 2e.

0.2 mmol scale, 54 mg, a white solid, 71% yield. m.p.: 142-144 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.28 (s, 3H, CH_3), 4.43 (d, J = 3.2 Hz, 1H, CH_2=), 4.45 (d, J = 3.2 Hz, 1H, CH_2=), 6.21 (s, 1H, CH), 6.67 (d, J = 9.2 Hz, 1H, Ar), 6.96-6.98 (m, 3H), 7.38 (dd, J = 8.0 Hz, J = 8.0 Hz, 1H, Ar), 7.52 (d, J = 8.4 Hz, 2H, Ar), 7.58 (dd, J = 8.0 Hz, J = 8.0 Hz, 2H, Ar), 7.72 (d, J = 8.0 Hz,

1H, Ar), 7.91 (d, J = 8.4 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 83.5, 84.1, 88.3, 114.4, 117.3, 120.1, 124.4, 127.7, 127.8, 128.6, 128.8, 129.1, 129.4, 131.1, 134.2, 144.4, 148.7, 157.2. IR (CH_2Cl_2) ν 3036, 2919, 2862, 1674, 1596, 1516, 1463, 1441, 1357, 1264, 1227, 1164, 1092, 1069, 981, 944, 853, 813, 734, 702, 683, 670 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{18}NO_4S^+$ (M^++H) requires 380.0951, found: 380.0945.

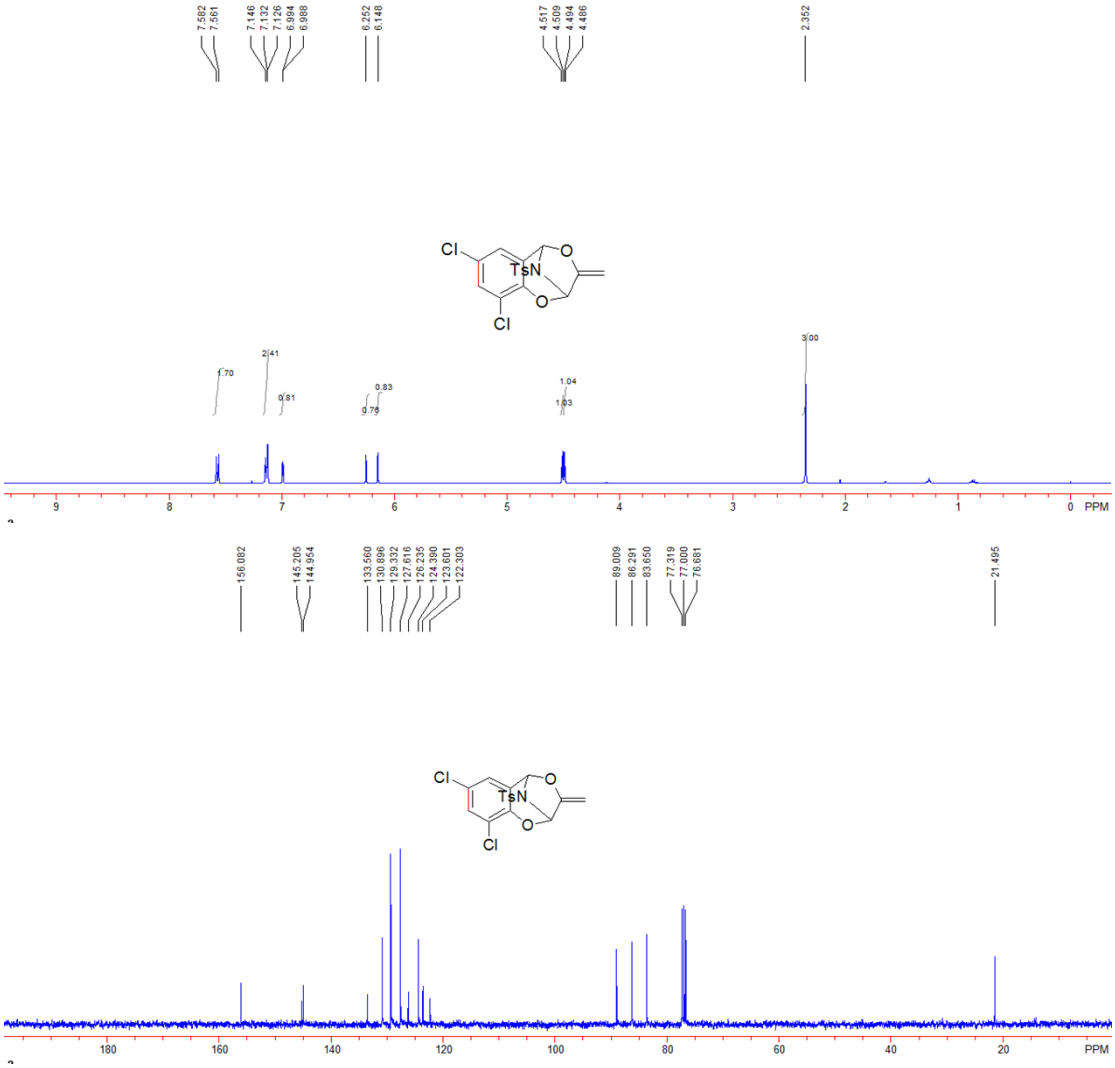


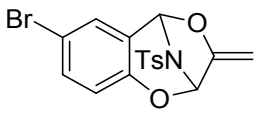


4,6-Dichloro-10-methylene-12-(toluene-4-sulfonyl)-8,11-dioxa-12-aza-tricyclo[7.2.1.02,7]dodeca-2,4,6-triene 2f.

0.2 mmol scale, 72mg, a white solid, 90% yield. m.p.: 126-128 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.35 (s, 3H, CH_3), 4.49 (d, J = 3.2 Hz, 1H, CH_2=), 4.51 (d, J = 3.2 Hz, 1H, CH_2=), 6.15

(s, 1H, CH), 6.25 (s, 1H, CH), 6.99 (d, J = 2.4 Hz, 1H, Ar), 7.12-7.15 (m, 3H, Ar), 7.57 (d, J = 8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 83.6, 86.3, 89.0, 122.3, 123.6, 124.4, 126.2, 127.6, 129.3, 130.9, 133.6, 144.9, 145.2, 156.1. IR (CH_2Cl_2) ν 3089, 2919, 1682, 1591, 1460, 1357, 1303, 1177, 1159, 1101, 1024, 997, 955, 919, 860, 848, 814, 735, 704, 676 cm^{-1}. HRMS (ESI) Calcd. for $C_{17}H_{14}Cl_2NO_4S^+$ (M^++H) requires 398.0015, found: 398.0001.

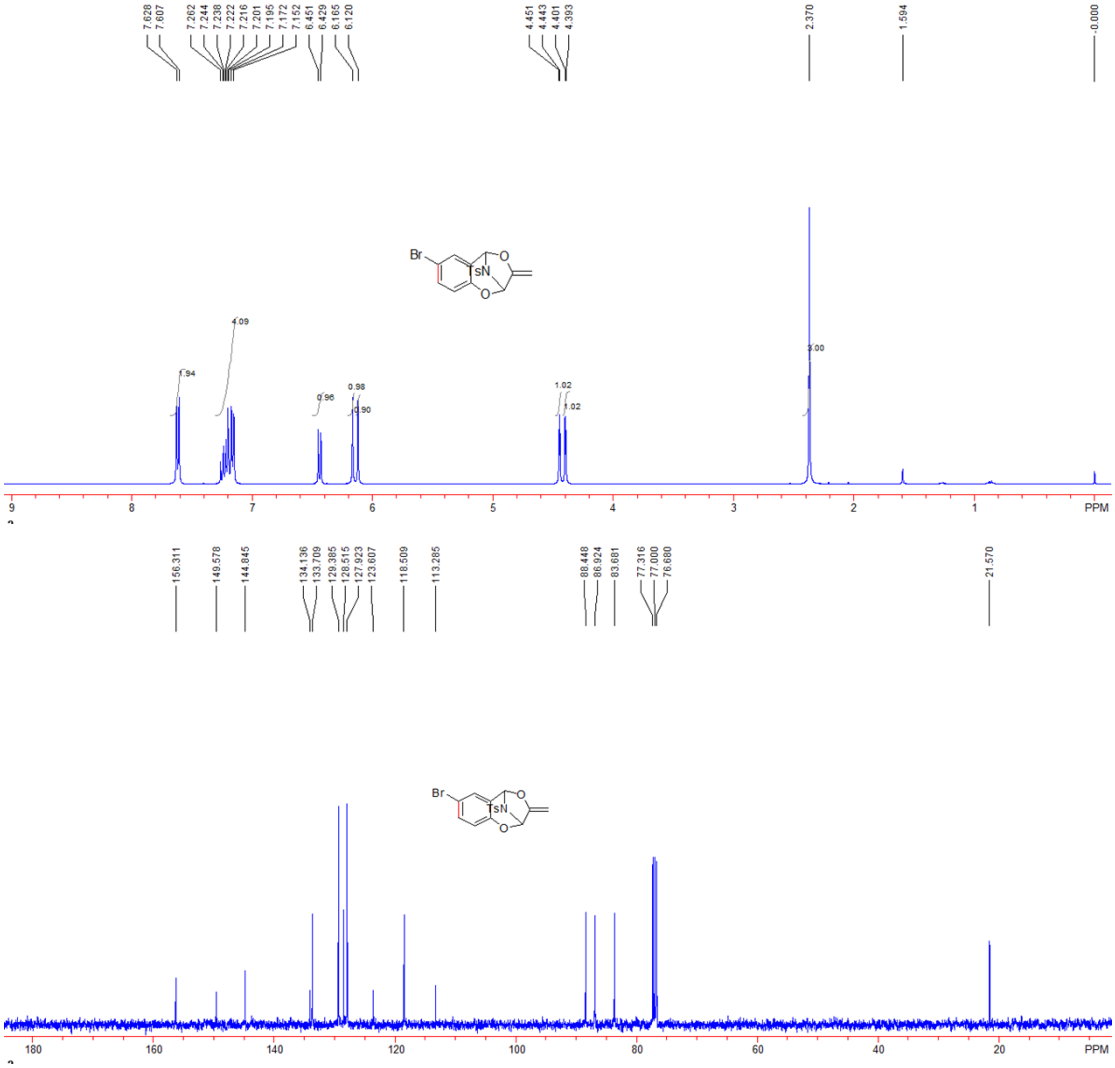


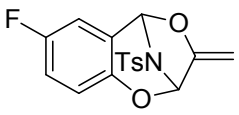


4-Bromo-10-methylene-12-(toluene-4-sulfonyl)-8,11-dioxa-12-aza-tricyclo[7.2.1.02,7]dodeca-2,4,6-triene 2g.

0.2 mmol scale, 72 mg, a white solid, 89% yield. m.p.: 112-114 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.37 (s, 3H, CH_3), 4.40 (d, J = 3.2 Hz, 1H, CH_2=), 4.44 (d, J = 3.2 Hz, 1H, CH_2=), 6.12 (s, 1H, CH), 6.16 (s, 1H, CH), 6.44 (d, J = 8.8 Hz, 1H, Ar), 7.16 (d, J = 8.0 Hz, 2H, Ar), 7.19-

7.27 (m, 2H, Ar), 7.62 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 83.7, 86.9, 88.4, 113.3, 118.5, 123.6, 127.9, 128.5, 129.4, 133.7, 134.1, 144.8, 149.6, 156.3. IR (CH_2Cl_2) ν 3066, 3014, 2916, 1681, 1594, 1466, 1382, 1376, 1337, 1272, 1185, 1163, 1130, 1040 ,1024, 958, 936, 871, 853, 816, 798, 716, 699, 600 cm^{-1}. HRMS (ESI) Calcd. for $C_{17}H_{15}BrNO_4S^+$ (M^++H) requires 407.9900, found: 407.9888.

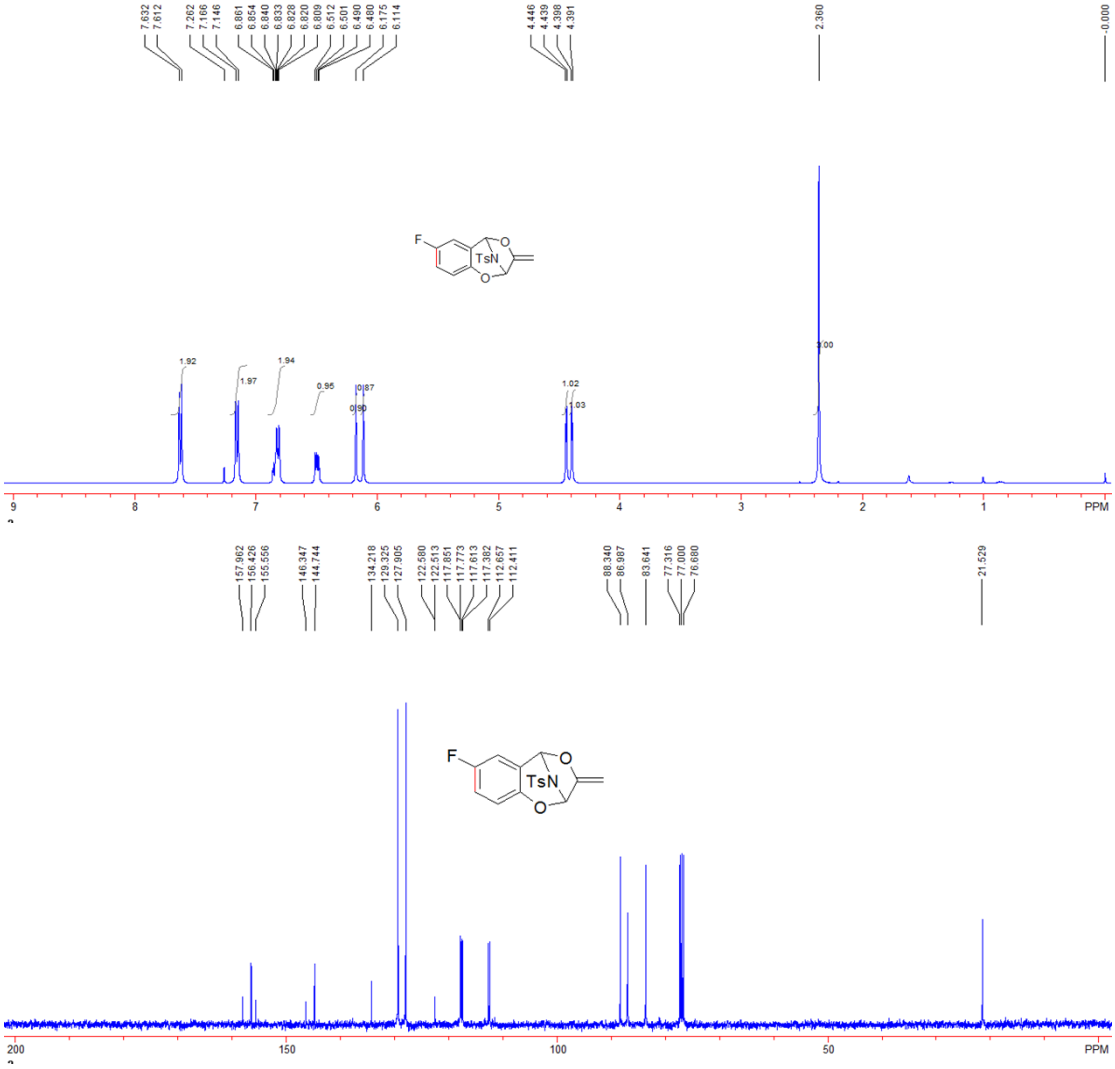


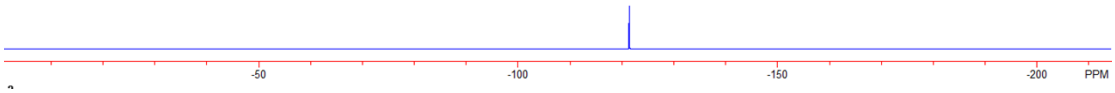


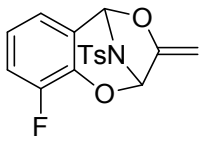
4-Fluoro-10-methylene-12-(toluene-4-sulfonyl)-8,11-dioxa-12-aza-tricyclo[7.2.1.02,7]dodeca-2,4,6-triene.

0.2 mmol scale, 63 mg, a white solid, 91% yield. m.p.: 104-106 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.36 (s, 3H, CH_3), 4.40 (d, J = 2.8 Hz, 1H, CH_2=), 4.44 (d, J = 2.8 Hz, 1H, CH_2=), 6.11 (s, 1H, CH), 6.18 (s, 1H, CH), 6.50 (dd, J = 8.0 Hz, J = 4.0 Hz, 1H, Ar), 6.80-6.87 (m, 2H, Ar),

7.15 (d, J = 8.0 Hz, 2H, Ar), 7.62 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 83.6, 87.0, 88.3, 112.5 (d, J = 24.6 Hz), 117.5 (d, J = 23.1 Hz), 117.8 (d, J = 7.8 Hz), 122.5 (d, J = 6.7 Hz), 127.9, 129.3, 134.2, 144.7, 146.3, 156.4, 156.7 (J = 240.6 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz, CF_3COOH) δ -121.418 ~ -121.366 (m). IR (CH_2Cl_2) ν 3052, 2919, 1680, 1596, 1483, 1355, 1348, 1305, 1184, 1160, 1088, 1023, 996, 949, 863, 850, 814, 706, 676 cm^{-1}. HRMS (ESI) Calcd. for $C_{17}H_{15}FNO_4S^+$ (M^++H) requires 348.0700, found: 348.0699.

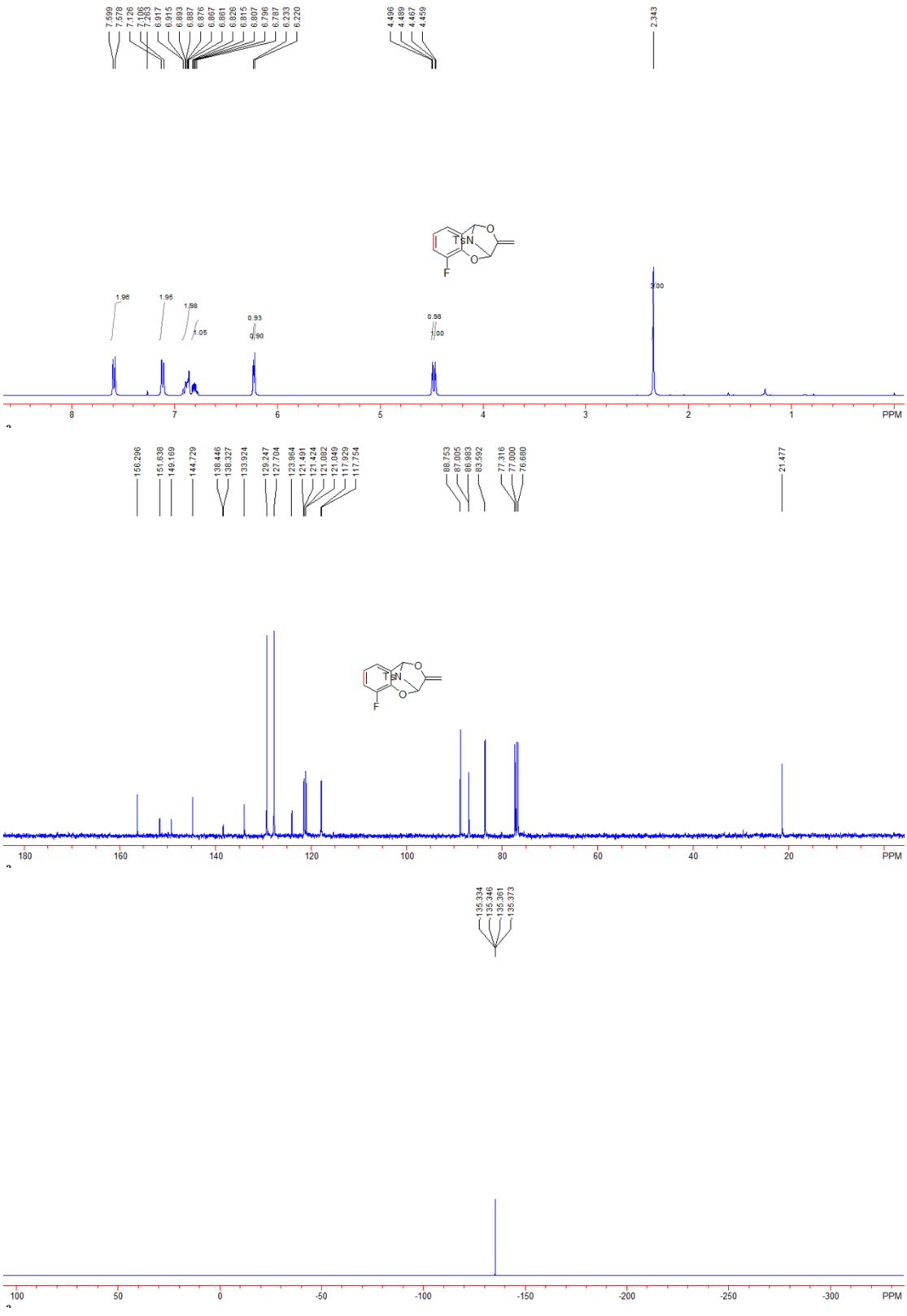






6-Fluoro-10-methylene-12-(toluene-4-sulfonyl)-8,11-dioxa-12-aza-tricyclo[7.2.1.02,7]dodeca-2,4,6-triene 2i.

0.2 mmol scale, 61 mg, a white solid, 88% yield. m.p.: 151-153 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.34 (s, 3H, CH_3), 4.46 (d, J = 3.2 Hz, 1H, CH_2=), 4.49 (d, J = 3.2 Hz, 1H, CH_2=), 6.22 (s, 1H, CH), 6.23 (s, 1H, CH), 6.78-6.83 (m, 1H, Ar), 6.86-6.92 (m, 2H, Ar), 7.12 (d, J = 8.0 Hz, 2H, Ar), 7.59 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 83.6, 87.0 (d, J = 2.2 Hz), 88.8, 117.8 (d, J = 17.5 Hz), 121.0 (d, J = 3.3 Hz), 121.4 (d, J = 6.7 Hz), 124.0, 127.7, 129.2, 133.9, 138.4 (d, J = 11.9 Hz), 144.7, 150.4 (J = 246.9 Hz), 156.3. ^{19}F NMR ($CDCl_3$, 376 MHz, CF_3COOH) δ -135.373 ~ -135.334 (m). IR (CH_2Cl_2) ν 3053, 2953, 2854, 1678, 1592, 1487, 1467, 1353, 1329, 1262, 1209, 1172, 1097, 1074, 1006, 994, 976, 920, 868, 851, 810, 755, 702, 671 cm^{-1}. HRMS (ESI) Calcd. for $C_{17}H_{15}FNO_4S^+$ (M^++H) requires 348.0700, found: 348.0701.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O
F
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1.95
1.98
1.05
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7
6
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PPM
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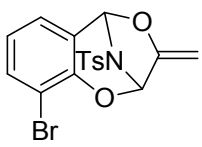
TsN
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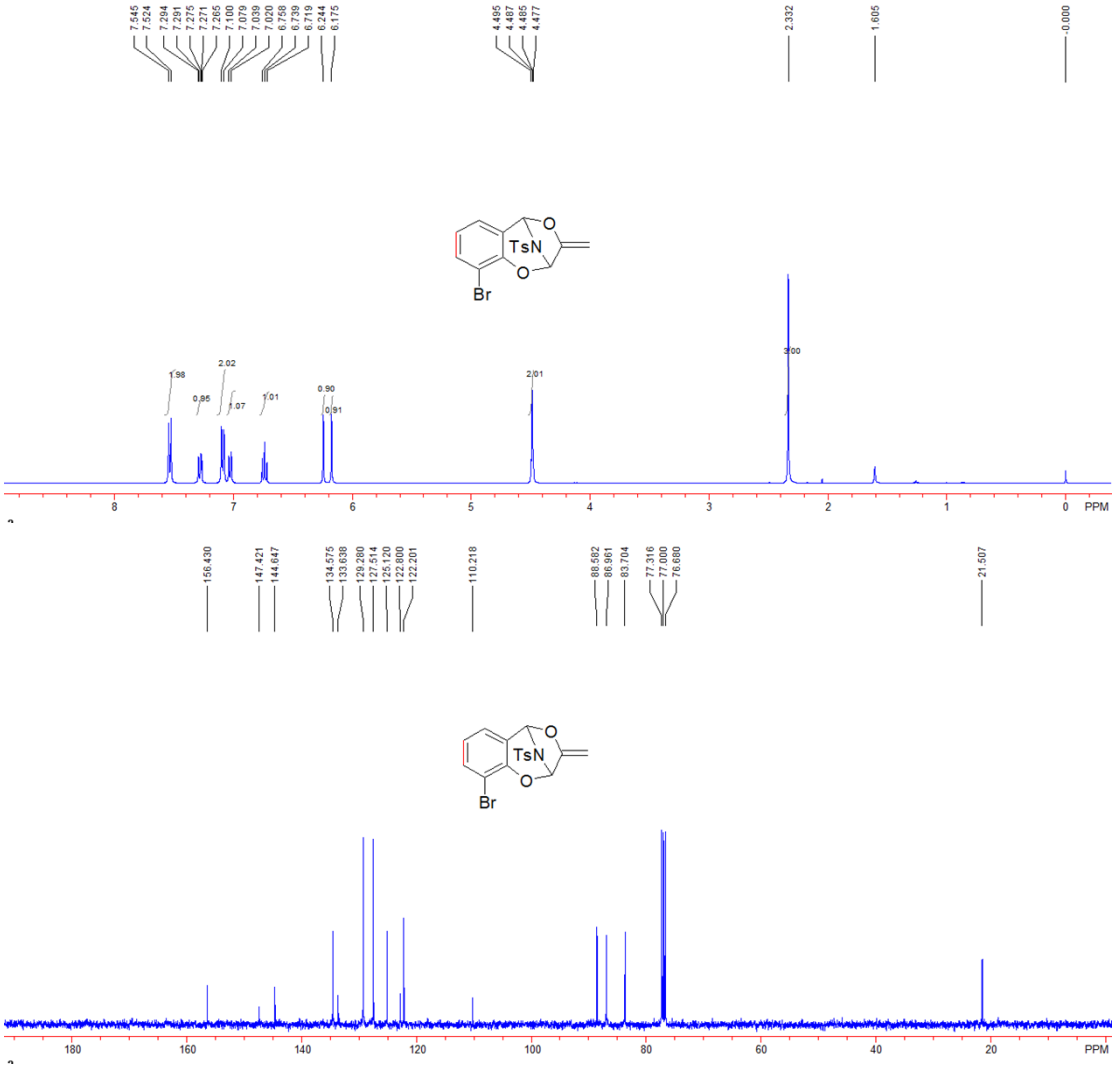
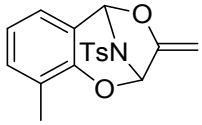
O
Br

6-Bromo-10-methylene-12-(toluene-4-sulfonyl)-8,11-dioxa-12-aza-tricyclo[7.2.1.02,7]dodeca-2,4,6-triene 2j.

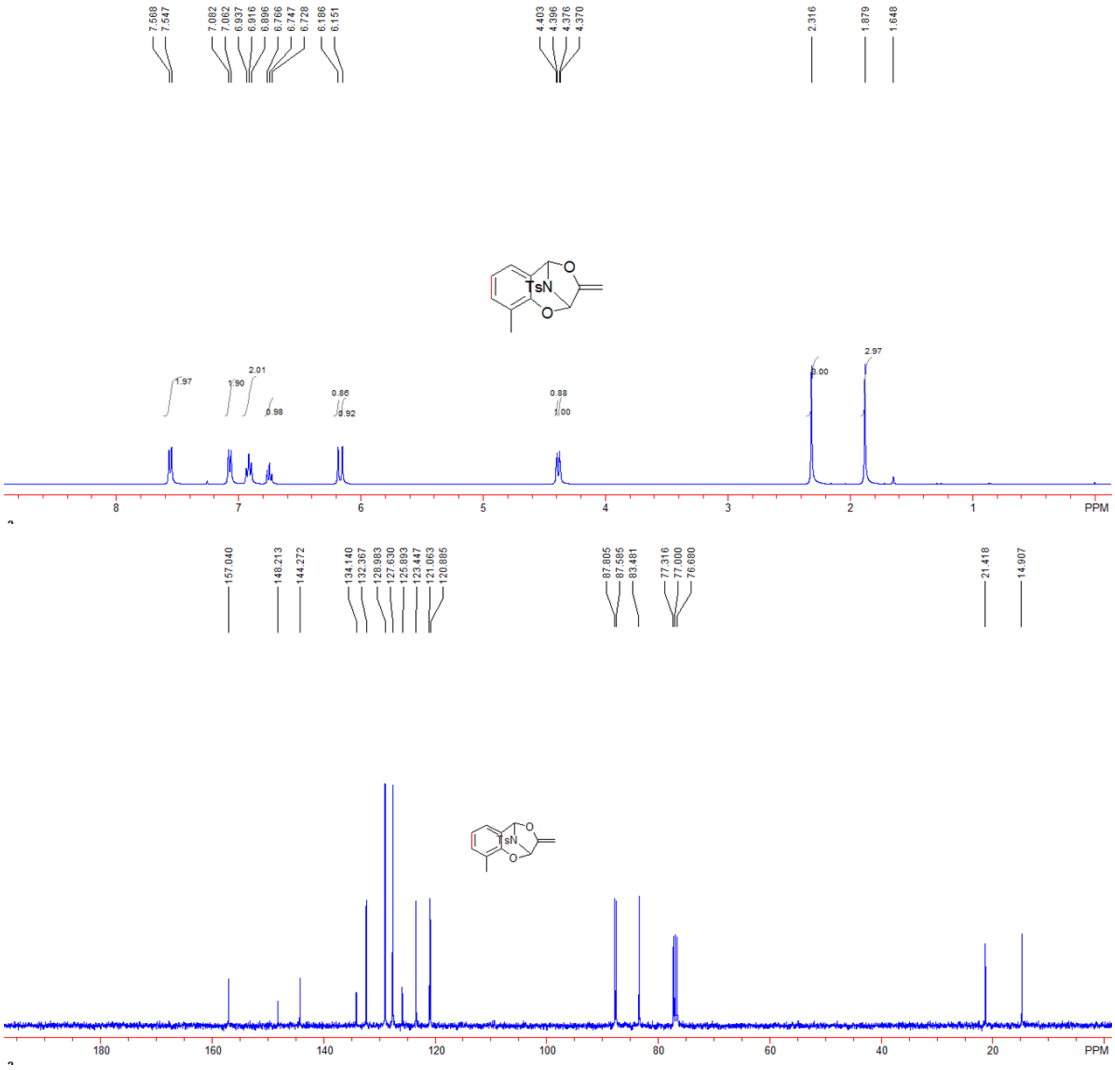
0.2 mmol scale, 54 mg, a white solid, 66% yield. m.p.: 171-173 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.33 (s, 3H, CH_3), 4.48 (d, *J* = 3.2 Hz, 1H, CH_2=), 4.49 (d, *J* = 3.2 Hz, 1H, CH_2=), 6.18 (s, 1H, CH), 6.24 (s, 1H, CH), 6.74 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H, Ar), 7.03 (d, *J* = 7.6 Hz, 1H, Ar), 7.09 (d, *J* = 8.4 Hz, 2H, Ar), 7.26-7.30 (m, 1H, Ar), 7.53 (d, *J* = 8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 83.7, 87.0, 88.6, 110.2, 122.2, 122.8, 125.1, 127.5, 129.3, 133.6, 134.6, 144.6, 147.4, 156.4. IR (CH_2Cl_2) ν 3036, 1680, 1597, 1453, 1353, 1301, 1216, 1166, 1092, 995, 941, 848, 814, 793, 755, 682 cm^{-1}. HRMS (ESI) Calcd. for $C_{17}H_{15}BrNO_4S^+$ (M^++H) requires 407.9900, found: 407.9899.

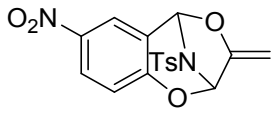




6-Methyl-10-methylene-12-(toluene-4-sulfonyl)-8,11-dioxa-12-aza-tricyclo[7.2.1.02,7]dodeca-2,4,6-triene 2k.

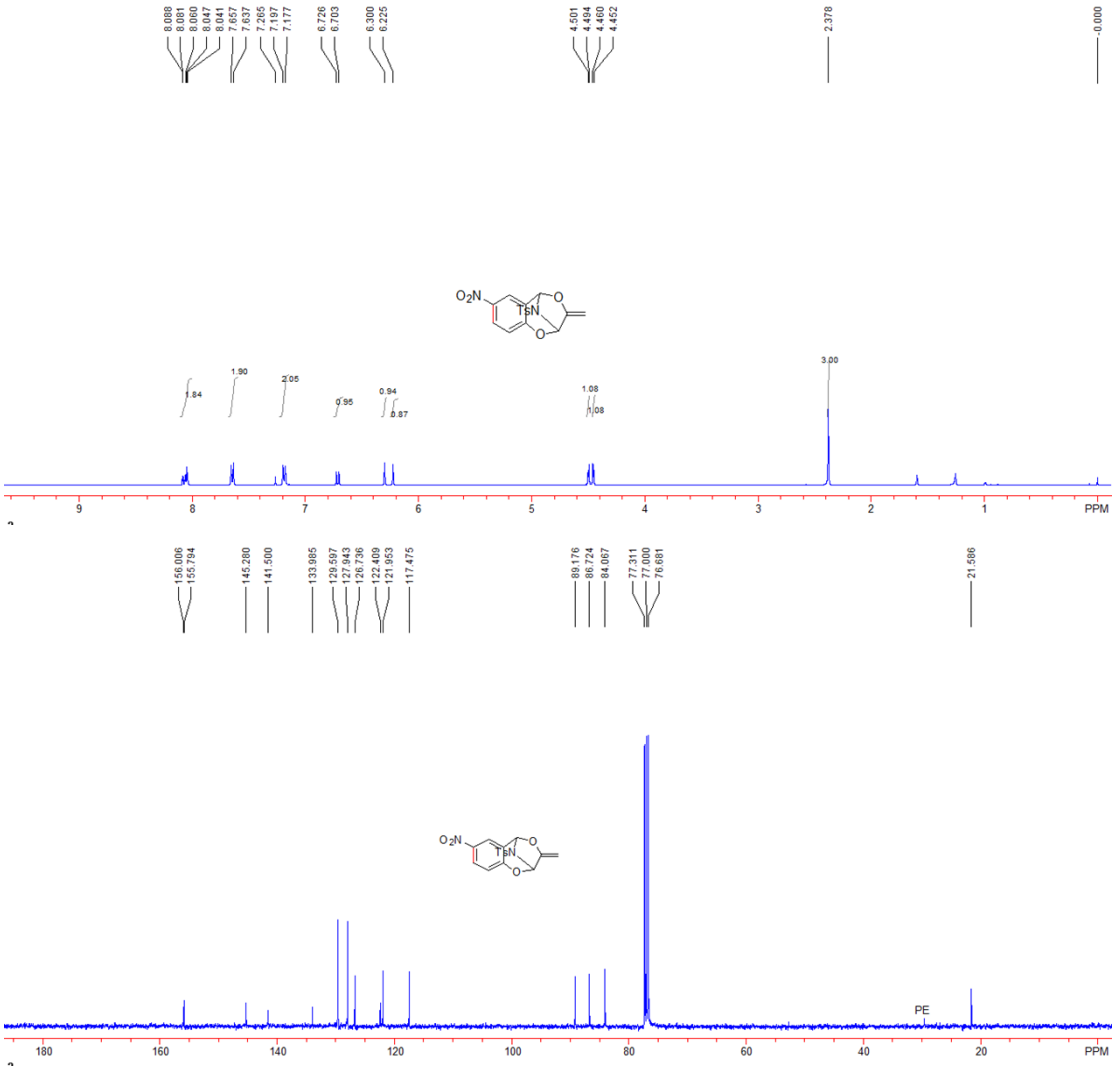
0.2 mmol scale, 58 mg, a white solid, 84% yield. m.p.: 140-142 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.88 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 4.37 (d, *J* = 2.8 Hz, 1H, CH_2=), 4.40 (d, *J* = 2.8 Hz, 1H, CH_2=), 6.15 (s, 1H, CH), 6.19 (s, 1H, CH), 6.75 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H, Ar), 6.92 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 2H, Ar), 7.07 (d, *J* = 8.0 Hz, 2H, Ar), 7.55 (d, *J* = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.9, 21.4, 83.5, 87.6, 87.8, 120.9, 121.1, 123.4, 125.9, 127.6, 129.0, 132.4, 134.1, 144.3, 148.2, 157.0. IR (CH_2Cl_2) ν 3044, 2919, 1670, 1599, 1477, 1451, 1351, 1333, 1183, 1206, 1165, 1093, 992, 959, 839, 813, 798, 765, 696, 683, 667 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{18}NO_4S^+$ (M^++H) requires 344.0951, found: 344.0950.

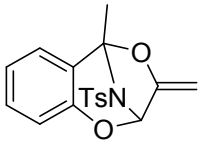




10-Methylene-4-nitro-12-(toluene-4-sulfonyl)-8,11-dioxa-12-aza-tricyclo[7.2.1.02,7]dodeca-2,4,6-triene 2l.

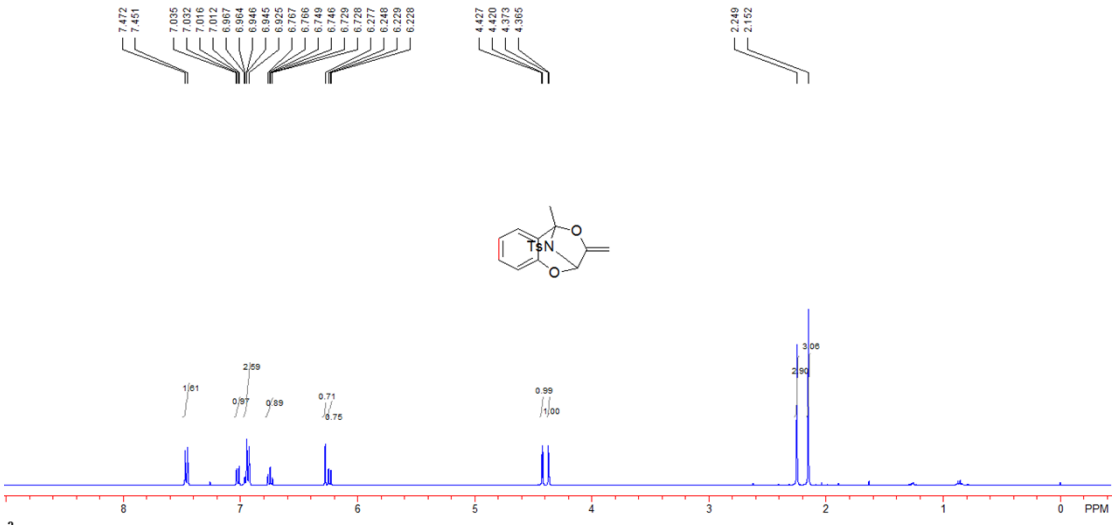
0.2 mmol scale, 65 mg, a white solid, 87% yield. m.p.: 175-177 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.38 (s, 3H, CH_3), 4.46 (d, *J* = 3.2 Hz, 1H, CH_2=), 4.50 (d, *J* = 3.2 Hz, 1H, CH_2=), 6.22 (s, 1H, CH), 6.30 (s, 1H, CH), 6.71 (d, *J* = 9.2 Hz, 1H, Ar), 7.19 (d, *J* = 8.0 Hz, 2H, Ar), 7.64 (d, *J* = 8.0 Hz, 2H, Ar), 8.04-8.09 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 84.1, 86.7, 89.2, 117.5, 122.0, 122.4, 126.7, 127.9, 129.6, 134.0, 141.5, 145.3, 155.8, 156.0. IR (CH_2Cl_2) ν 3048, 2915, 2854, 1684, 1619, 1588, 1519, 1475, 1363, 1340, 1305, 1221, 1186, 1164, 1096, 1087, 996, 934, 855, 842, 706, 678 cm^{-1}. HRMS (ESI) Calcd. for $C_{17}H_{15}N_2O_6S^+$ (M^++H) requires 375.0645, found: 375.0646.

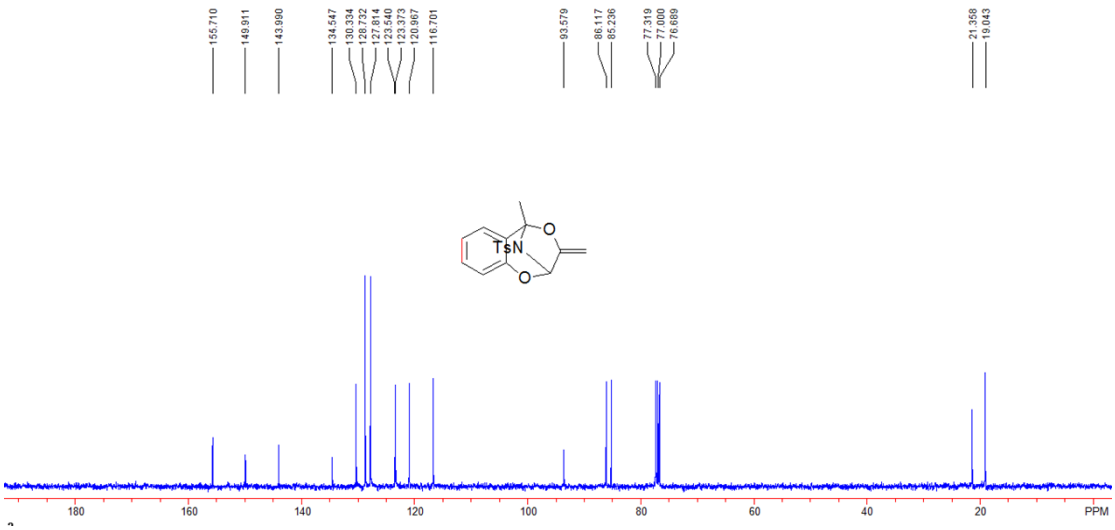


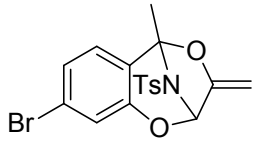


1-Methyl-10-methylene-12-(toluene-4-sulfonyl)-8,11-dioxa-12-aza-tricyclo[7.2.1.02,7]dodeca-2,4,6-triene 2m.

0.2 mmol scale, 63mg, a white solid, 92% yield. m.p.: 99-101 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.15 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 4.37 (d, J = 3.2 Hz, 1H, CH_2=), 4.42 (d, J = 3.2 Hz, 1H, CH_2=), 6.23 (d, J = 8.0 Hz, 1H, Ar), 6.28 (s, 1H, CH), 6.75 (ddd, J = 8.0 Hz, J = 8.0 Hz, J = 0.4 Hz, 1H, Ar), 6.92-6.97 (m, 3H, Ar), 7.02 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H, Ar), 7.46 (d, J = 8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.0, 21.4, 85.2, 86.1, 93.6, 116.7, 121.0, 123.4, 123.5, 127.8, 128.7, 130.3, 134.5, 144.0, 149.9, 155.7. IR (CH_2Cl_2) ν 3024, 2919, 1688, 1599, 1494, 1457, 1358, 1290, 1253, 1166, 1114, 1091, 969, 954, 859, 763, 702, 689, 664 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{18}NO_4S^+$ (M^++H) requires 344.0951, found: 344.0942.

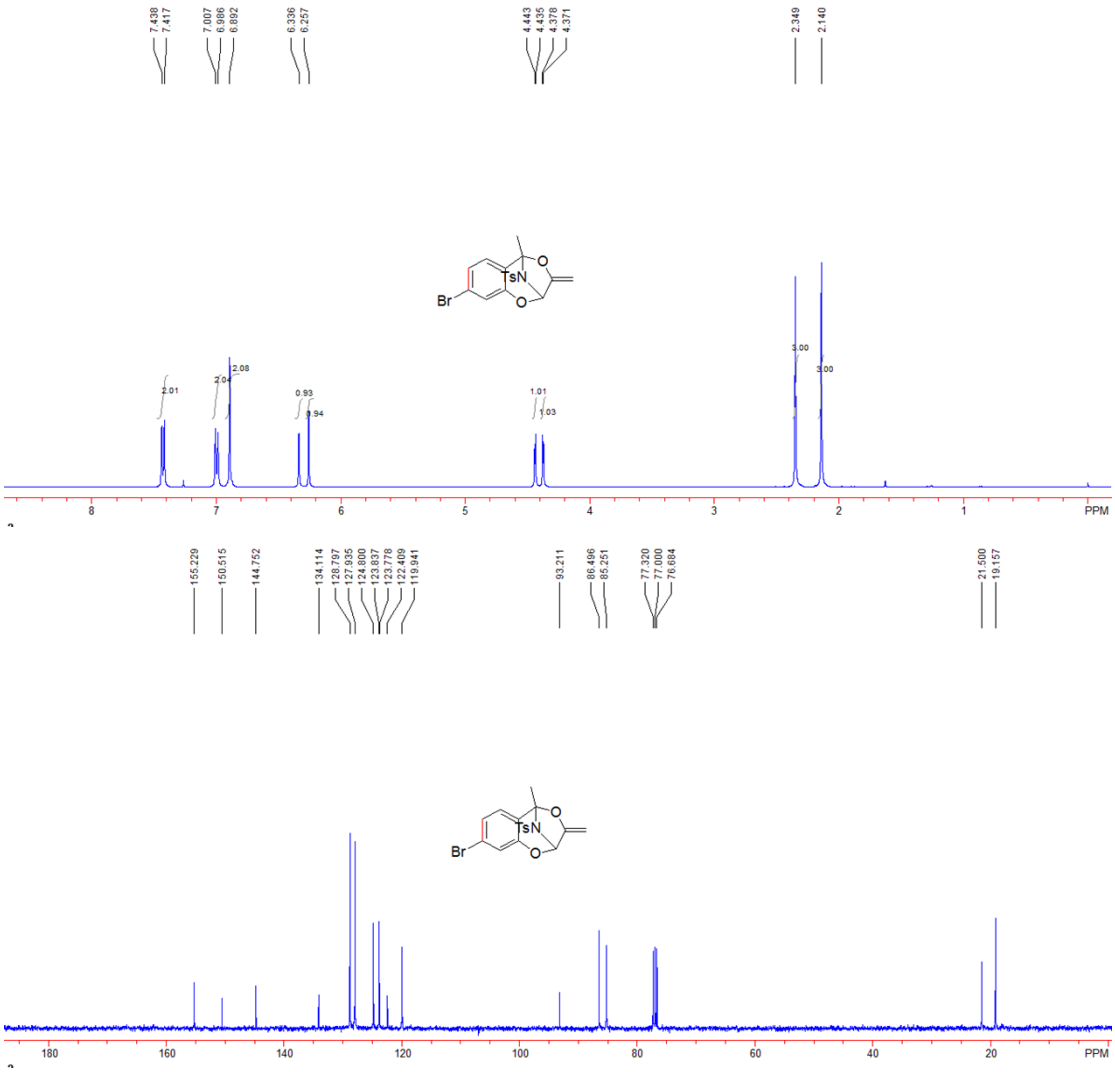


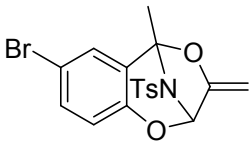




8-bromo-5-methyl-3-methylene-10-tosyl-3,5-dihydro-2H-2,5-epiminobenzo[e][1,4]dioxepine 2n.

0.2 mmol scale, 76 mg, a white solid, 91% yield. m.p.: 156-158 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.14 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 4.37 (d, J = 3.2 Hz, 1H, CH_2=), 4.43 (d, J = 3.2 Hz, 1H, CH_2=), 6.26 (s, 1H), 6.34 (s, 1H), 6.89 (s, 2H, Ar), 6.99 (d, J = 8.4 Hz, 2H, Ar), 7.42 (d, J = 8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.2, 21.5, 85.2, 86.5, 93.2, 119.9, 122.4, 123.7, 123.8, 124.8, 127.9, 128.8, 134.1, 144.8, 150.5, 155.2. IR (CH_2Cl_2) ν 3117, 3080, 2919, 1682, 1600, 1572, 1481, 1414, 1357, 1288, 1251, 1165, 1130, 1110, 1086, 961, 892, 870, 855, 841, 813, 803, 783, 705, 698, 660 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{17}BrNO_4S^+$ (M^++H) requires 422.0056, found: 422.0047.

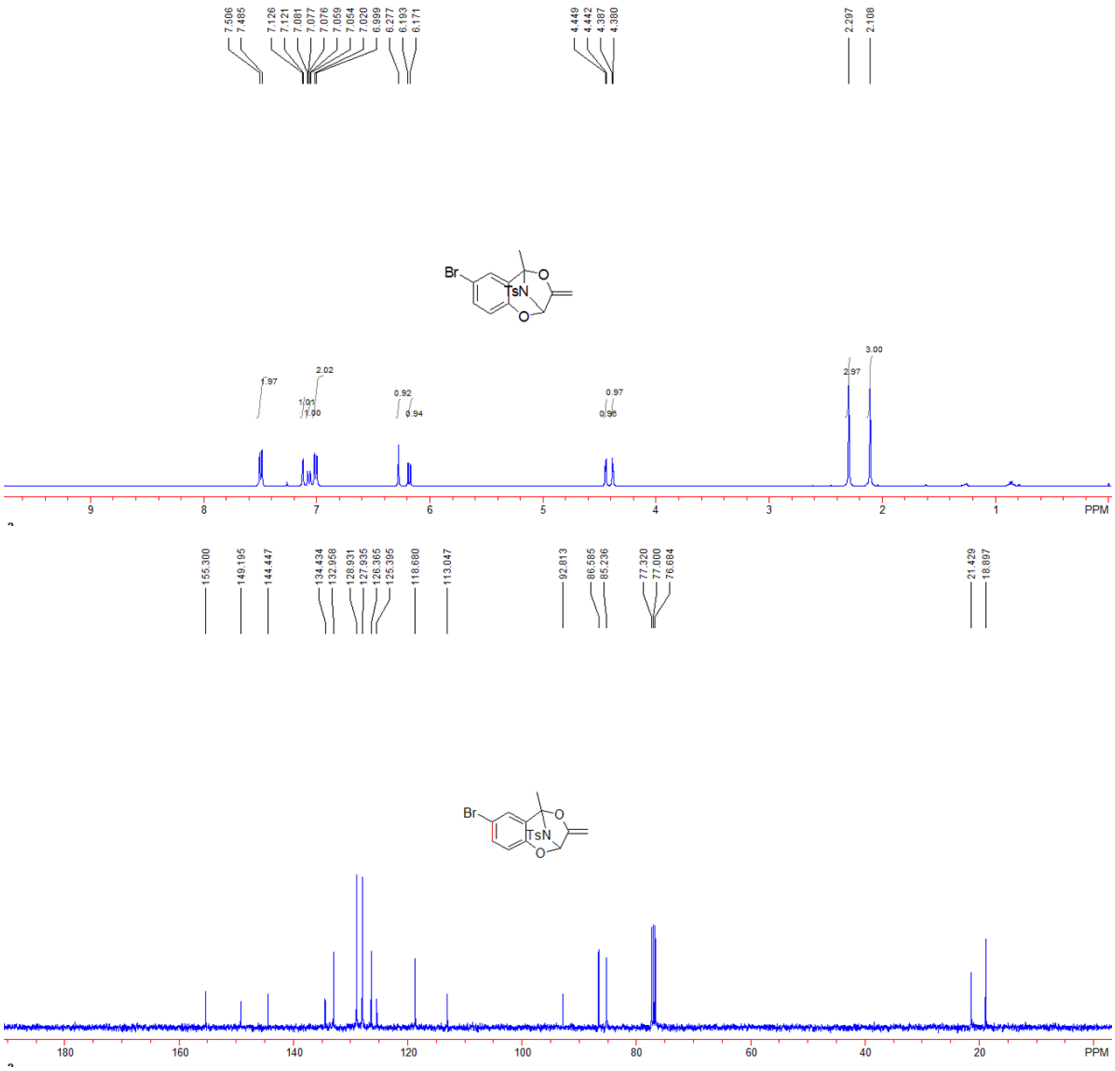


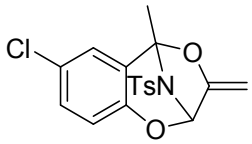


7-bromo-5-methyl-3-methylene-10-tosyl-3,5-dihydro-2H-2,5-epiminobenzo[e][1,4]dioxepine 2o.

0.2 mmol scale, 79 mg, a white solid, 94% yield. m.p.: 106-108 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.11 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 4.38 (d, J = 2.8 Hz, 1H, CH_2=), 4.45 (d, J = 2.8 Hz, 1H, CH_2=), 6.18 (d, J = 8.8 Hz, 1H, Ar), 6.28 (s, 1H, CH), 7.01 (d, J = 8.4 Hz, 2H, Ar), 7.07 (dd, J = 8.8 Hz, J = 2.0 Hz, 1H, Ar), 7.12 (d, J = 2.0 Hz, 1H, Ar), 7.49 (d, J = 8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.9, 21.4, 85.2, 86.6, 92.8, 113.0, 118.7, 125.4, 126.4, 127.9, 128.9, 132.9, 134.4, 144.4, 149.2, 155.3. IR (CH_2Cl_2) ν 3053, 3032, 2914, 1685, 1596, 1473, 1365, 1276, 1252, 1207, 1186, 1164, 1130, 1112, 1089, 966, 879, 864, 839, 816, 765, 705, 663

cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{17}BrNO_4S^+$ (M^++H) requires 422.0056, found: 422.0049.

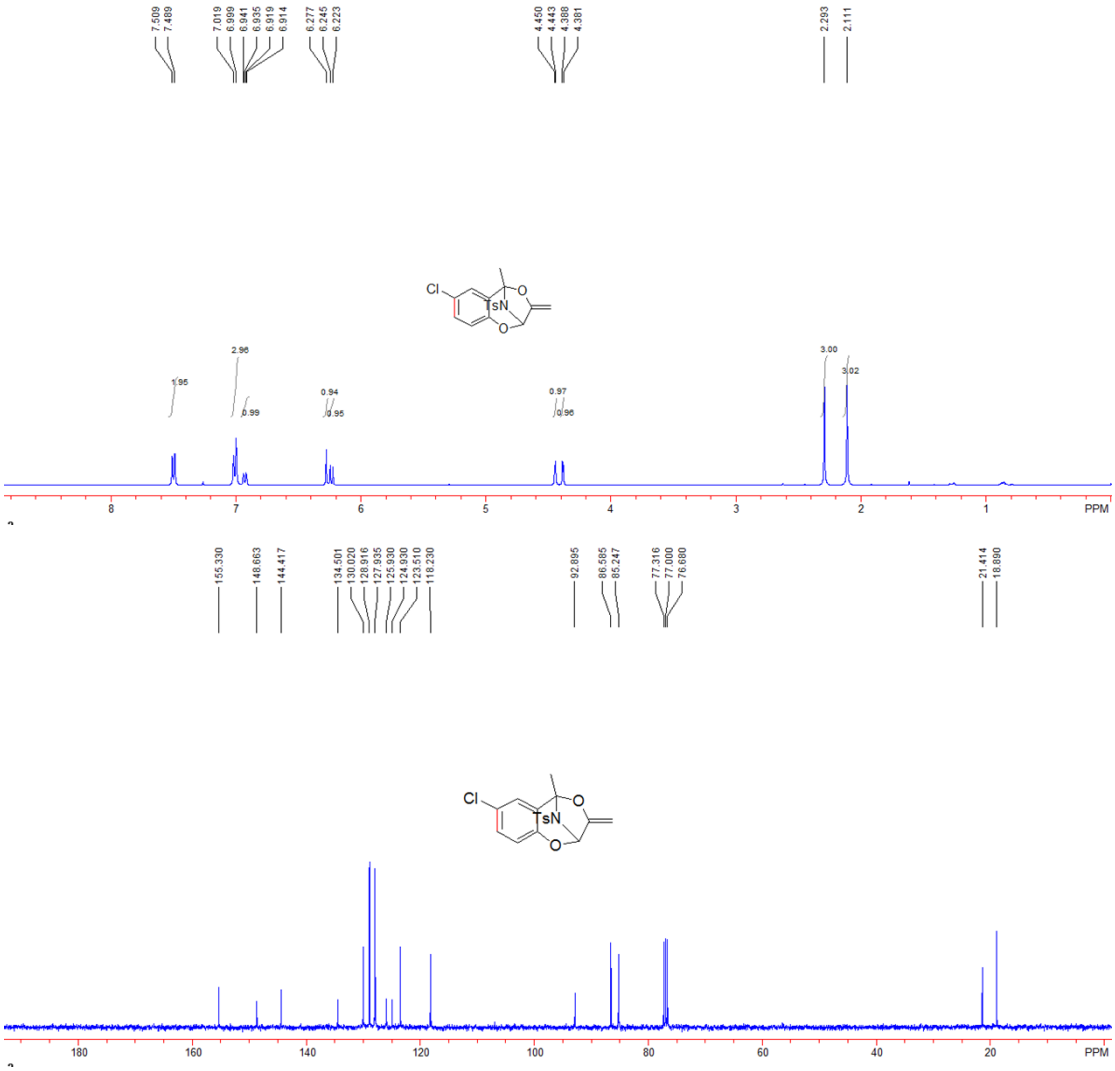


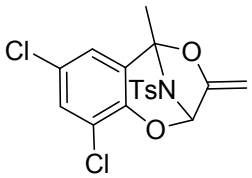


7-chloro-5-methyl-3-methylene-10-tosyl-3,5-dihydro-2H-2,5-epiminobenzo[e][1,4]dioxepine 2p.

0.2 mmol scale, 62 mg, a white solid, 83% yield. m.p.: 97-99 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.12 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 4.38 (d, J = 3.2 Hz, 1H, CH_2=), 4.45 (d, J = 3.2 Hz, 1H, CH_2=), 6.23 (d, J = 8.4 Hz, 1H, Ar), 6.28 (s, 1H, CH), 6.93 (dd, J = 8.4 Hz, J = 2.4 Hz, 1H, Ar), 7.00-7.02 (m, 3H, Ar), 7.50 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 18.9, 21.4, 85.2, 86.6, 92.9, 118.2, 123.5, 124.9, 125.9, 127.9, 128.9, 130.0, 134.5, 144.4, 148.7, 155.3. IR (CH_2Cl_2) ν 3048, 2927, 2854, 1685, 1592, 1476, 1365, 1285, 1275, 1185, 1166, 1129,

1113, 1091, 1008, 966, 945, 882, 845, 819, 766, 709, 665, 658 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{17}ClNO_4S^+$ (M^++H) requires 378.0561, found: 378.0557.

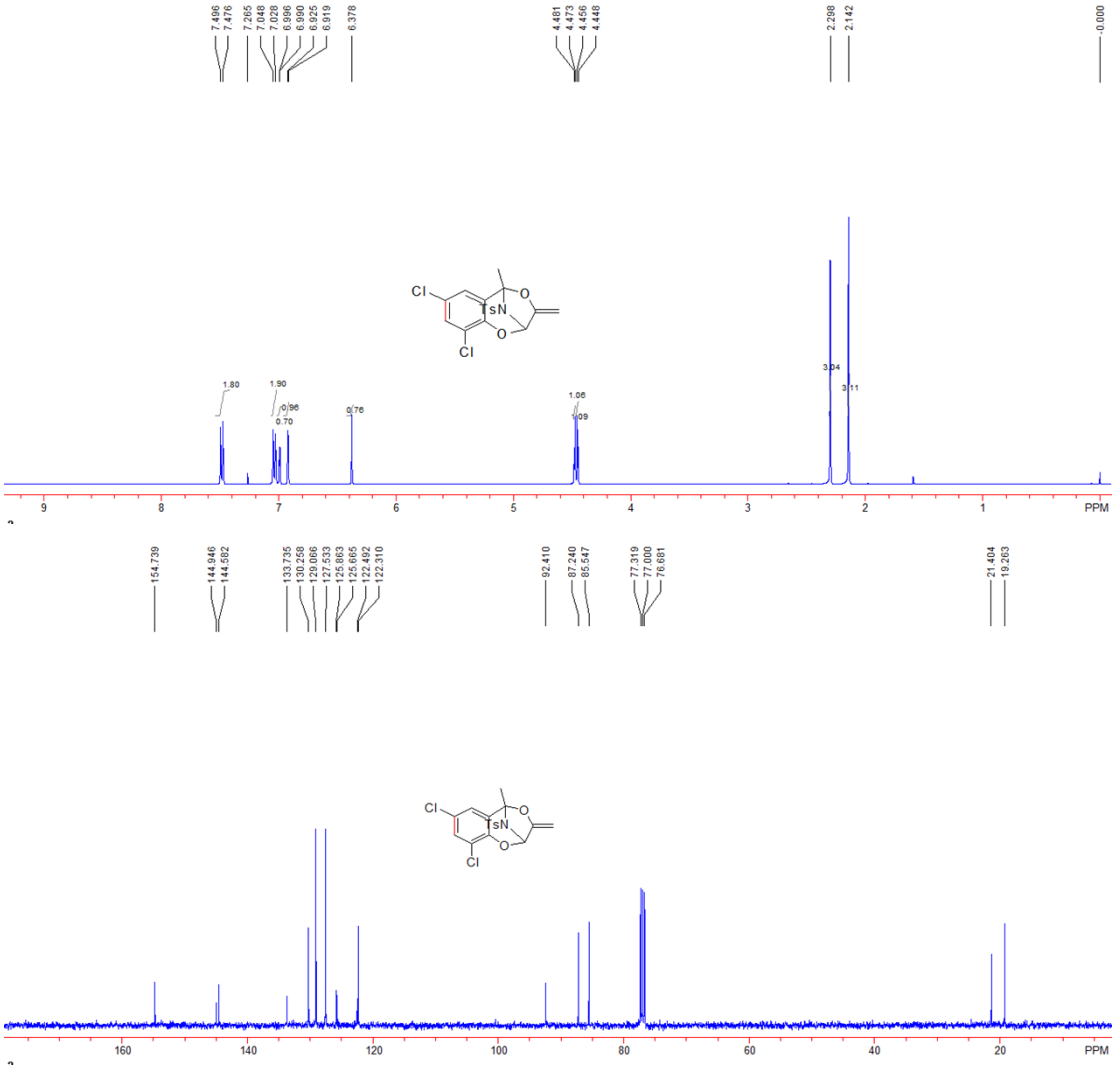


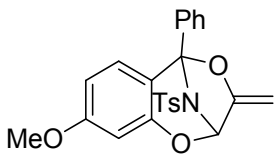


7,9-dichloro-5-methyl-3-methylene-10-tosyl-3,5-dihydro-2H-2,5-epiminobenzo[e][1,4]dioxepine 2q.

0.2 mmol scale, 72 mg, a white solid, 87% yield. m.p.: 156-158 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.14 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 4.45 (d, J = 3.2 Hz, 1H, CH_2=), 4.48 (d, J = 3.2 Hz, 1H, CH_2=), 6.38 (s, 1H, CH), 6.92 (d, J = 2.4 Hz, 1H, Ar), 6.99 (d, J = 2.4 Hz, 1H, Ar), 7.03 (d, J = 8.0 Hz, 2H, Ar), 7.48 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.3, 21.4,

85.5, 87.2, 92.4, 122.3, 122.5, 125.7, 125.9, 127.5, 129.1, 130.2, 133.7, 144.6, 144.9, 154.7. IR (CH_2Cl_2) ν 3069, 3032, 2991, 1686, 1594, 1456, 1360, 1259, 1255, 1208, 1179, 1164, 1115, 1075, 1010, 979, 924, 890, 868, 849, 816, 714, 703, 659 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{16}Cl_2NO_4S^+$ (M^++H) requires 412.0172, found: 412.0158.

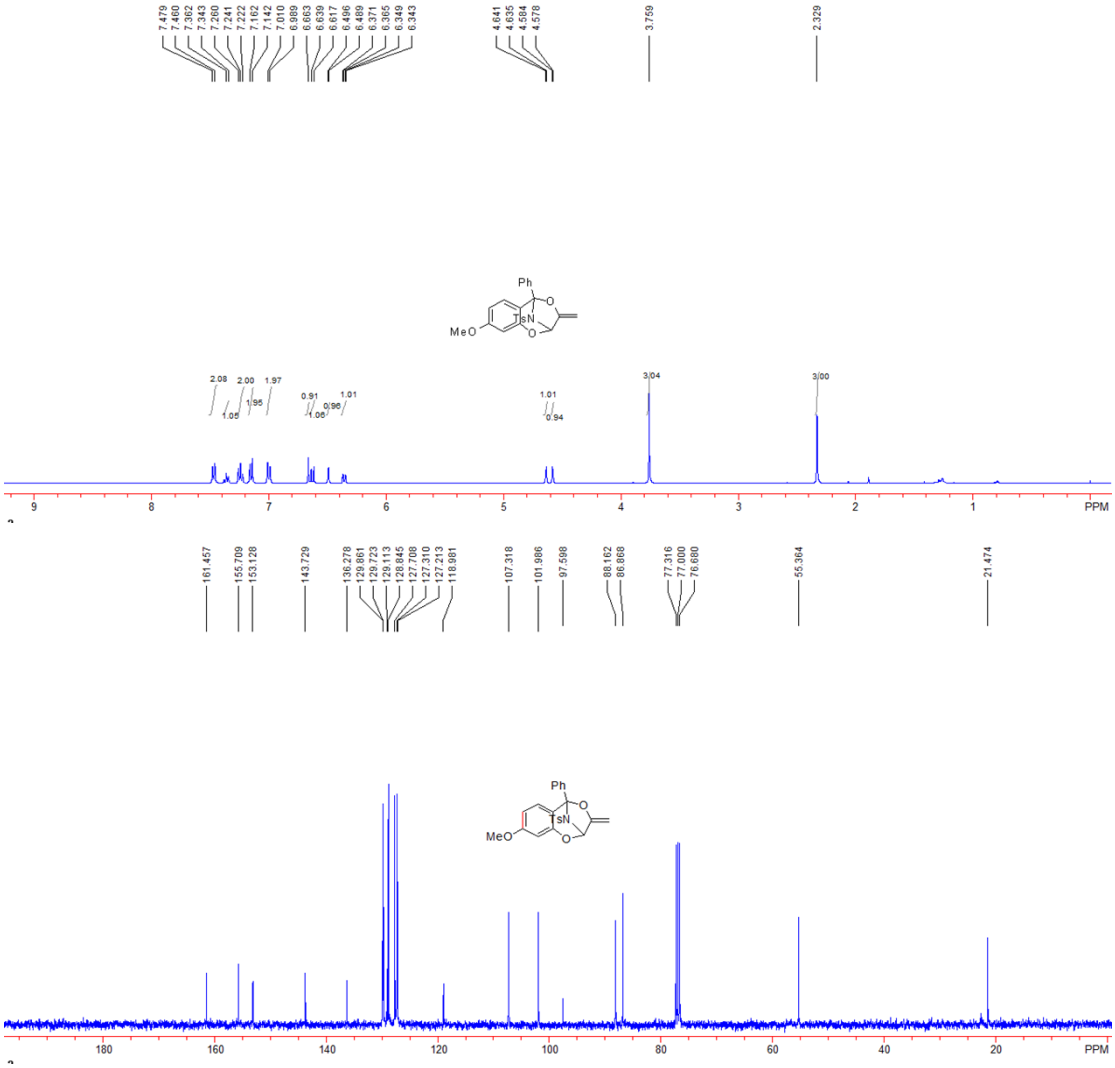


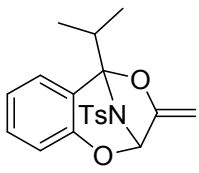


5-Methoxy-10-methylene-1-phenyl-12-(toluene-4-sulfonyl)-8,11-dioxa-12-aza-tricyclo[7.2.1.02,7]dodeca-2,4,6-triene 2r.

0.2 mmol scale, 65 mg, a white solid, 75% yield. m.p.: 105-107 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.33 (s, 3H, CH_3), 3.76 (s, 3H, CH_3), 4.58 (d, J = 2.0 Hz, 1H, CH_2=), 4.64 (d, J = 2.0 Hz, 1H, CH_2=), 6.35 (dd, J = 8.8 Hz, J = 2.0 Hz, 1H, Ar), 6.48 (d, J = 2.0 Hz, 1H, Ar), 6.62 (d, J =

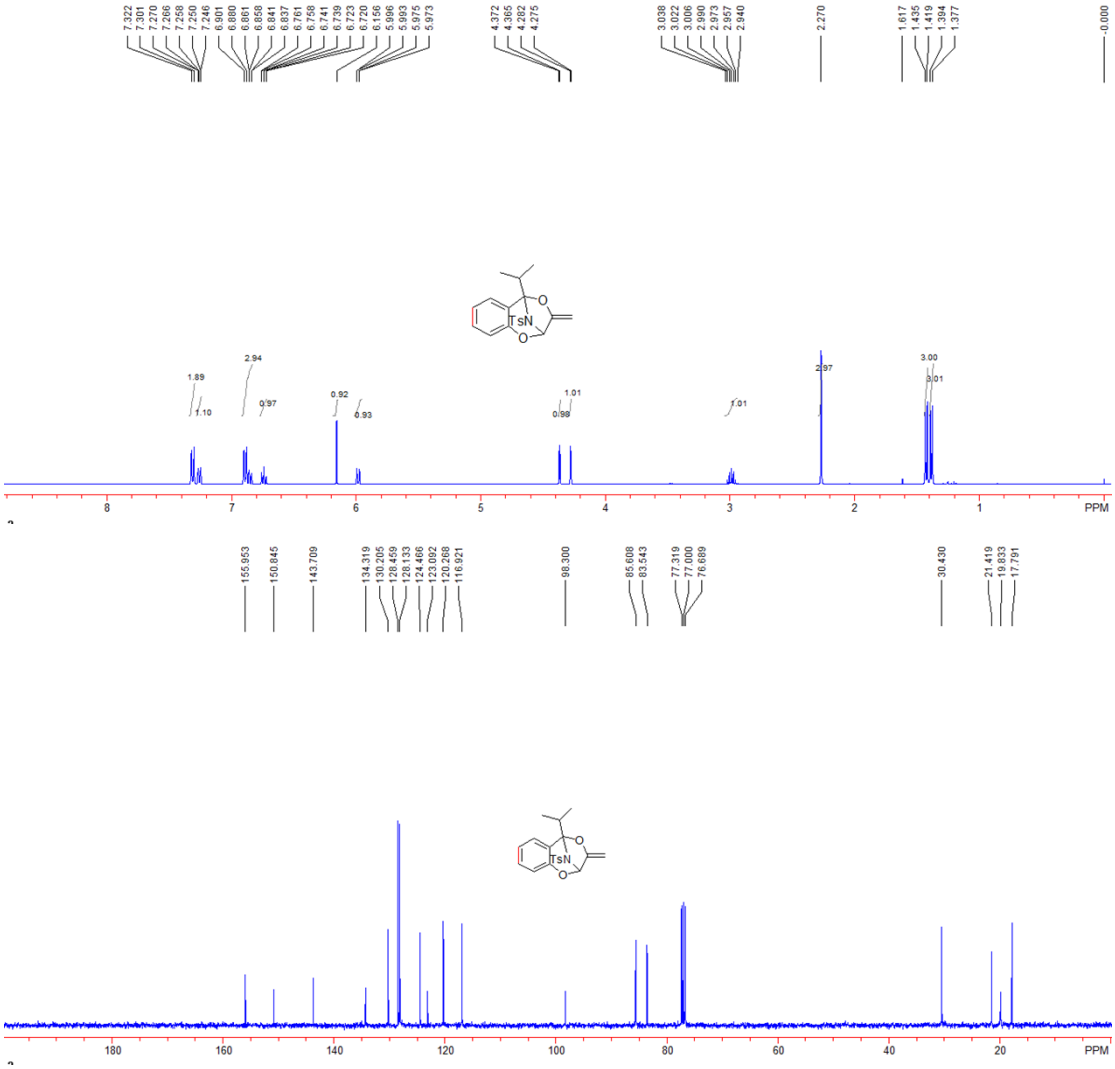
8.8 Hz, 1H, Ar), 6.66 (s, 1H, CH), 6.99 (d, J = 8.0 Hz, 2H, Ar), 7.15 (d, J = 8.0 Hz, J = 8.0 Hz, 2H, Ar), 7.24 (d, J = 7.6 Hz, 1H, Ar), 7.36 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H, Ar), 7.46 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 55.4, 86.9, 88.2, 97.6, 102.0, 107.3, 119.0, 127.2, 127.3, 127.7, 128.8, 129.1, 129.7, 129.9, 136.3, 143.7, 153.1, 155.7, 161.4. IR (CH_2Cl_2) ν 3271, 3061, 2924, 1733, 1617, 1597, 1501, 1443, 1341, 1281, 1255, 1158, 1110, 1091 ,1027, 837, 812, 756, 699, 673 cm^{-1}. HRMS (ESI) Calcd. for $C_{24}H_{22}NO_5S^+$ (M^++H) requires 436.1213, found: 436.1203.

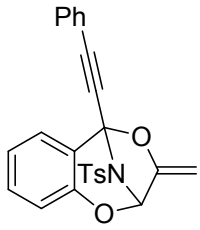




5-isopropyl-3-methylene-10-tosyl-3,5-dihydro-2H-2,5-epiminobenzo[e][1,4]dioxepine 2s.

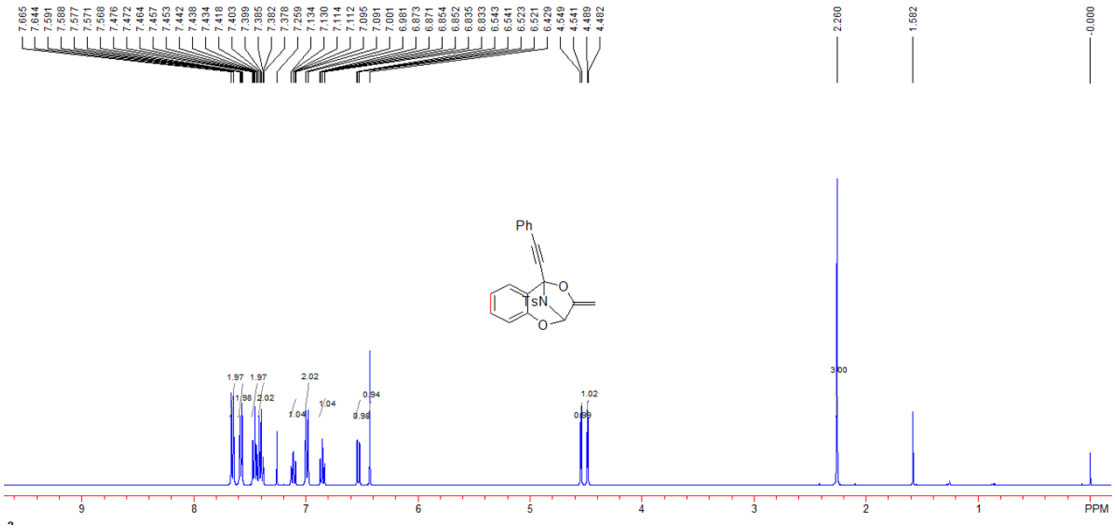
0.2 mmol scale, 68 mg, a white solid, 92% yield. m.p.: 154-156 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.38 (d, J = 6.8 Hz, 3H, CH_3), 1.42 (d, J = 6.8 Hz, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.94-3.04 (m, 1H, CH), 4.28 (d, J = 2.8 Hz, 1H, CH_2=), 4.37 (d, J = 2.8 Hz, 1H, CH_2=), 5.97 (dd, J = 8.0 Hz, J = 0.8 Hz, 1H, Ar), 6.16 (s, 1H, CH), 6.74 (ddd, J = 7.6 Hz, J = 7.6 Hz, J = 0.8 Hz, 1H, Ar), 6.83-6.91 (m, 3H, Ar), 7.26 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H, Ar), 7.31 (d, J = 8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 17.8, 19.8, 21.4, 30.4, 83.5, 85.6, 98.3, 116.9, 120.3, 123.1, 124.5, 128.1, 128.4, 130.2, 134.3, 143.7, 150.8, 155.9. IR (CH_2Cl_2) ν 3048, 2991, 2939, 2874, 1686, 1607, 1599, 1574, 1478, 1455, 1358, 1288, 1251, 1202, 1183, 1161, 1090, 1022, 1012, 980, 958, 917, 898, 861, 781, 754, 694, 662 cm^{-1}. HRMS (ESI) Calcd. for $C_{20}H_{22}NO_4S^+$ (M^++H) requires 372.1264, found: 372.1274.

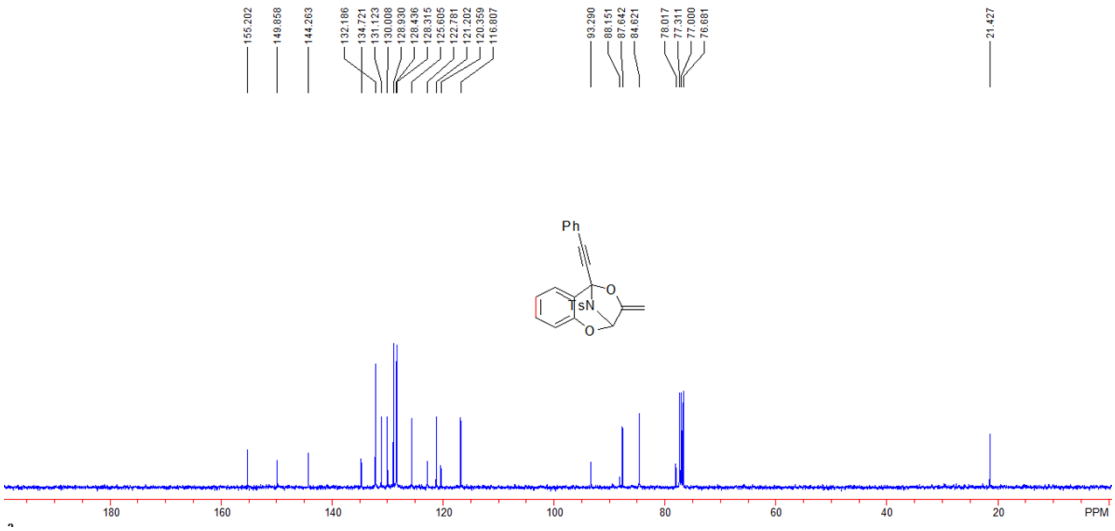


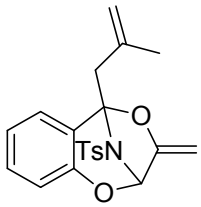


3-methylene-5-(phenylethynyl)-10-tosyl-3,5-dihydro-2H-2,5-epiminobenzo[e][1,4]dioxepine 2t.

0.2 mmol scale, 45 mg, a white solid, 53% yield. m.p.: 125-127 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.26 (s, 3H, CH_3), 4.48 (d, *J* = 2.8 Hz, 1H, CH_2=), 4.54 (d, *J* = 2.8 Hz, 1H, CH_2=), 6.43 (s, 1H, CH), 6.53 (dd, *J* = 8.0 Hz, *J* = 0.8 Hz, 1H, Ar), 6.85 (ddd, *J* = 8.0 Hz, *J* = 8.0 Hz, *J* = 0.8 Hz, 1H, Ar), 6.99 (d, *J* = 8.0 Hz, 2H, Ar), 7.11 (ddd, *J* = 8.0 Hz, *J* = 8.0 Hz, *J* = 0.8 Hz, 1H, Ar), 7.37-7.42 (m, *J* = 8.0 Hz, 2H, Ar), 7.43-7.48 (m, 2H, Ar), 7.56-7.60 (m, 2H, Ar), 7.65 (d, *J* = 8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 78.0, 84.6, 87.6, 88.2, 93.3, 116.8, 120.4, 121.2, 122.8, 125.6, 128.3, 128.4, 128.9, 130.0, 131.1, 132.2, 134.7, 144.3, 149.8, 155.2. IR (CH_2Cl_2) ν 3138, 3044, 2910, 2248, 1686, 1585, 1491, 1477, 1458, 1355, 1328, 1247, 1187, 1164, 1141, 1116, 1089, 1071, 1032, 983, 956, 926, 890, 860, 811, 754, 702, 686, 659 cm^{-1}. HRMS (ESI) Calcd. for $C_{25}H_{20}NO_4S^+$ (M^++H) requires 430.1108, found: 430.1116.

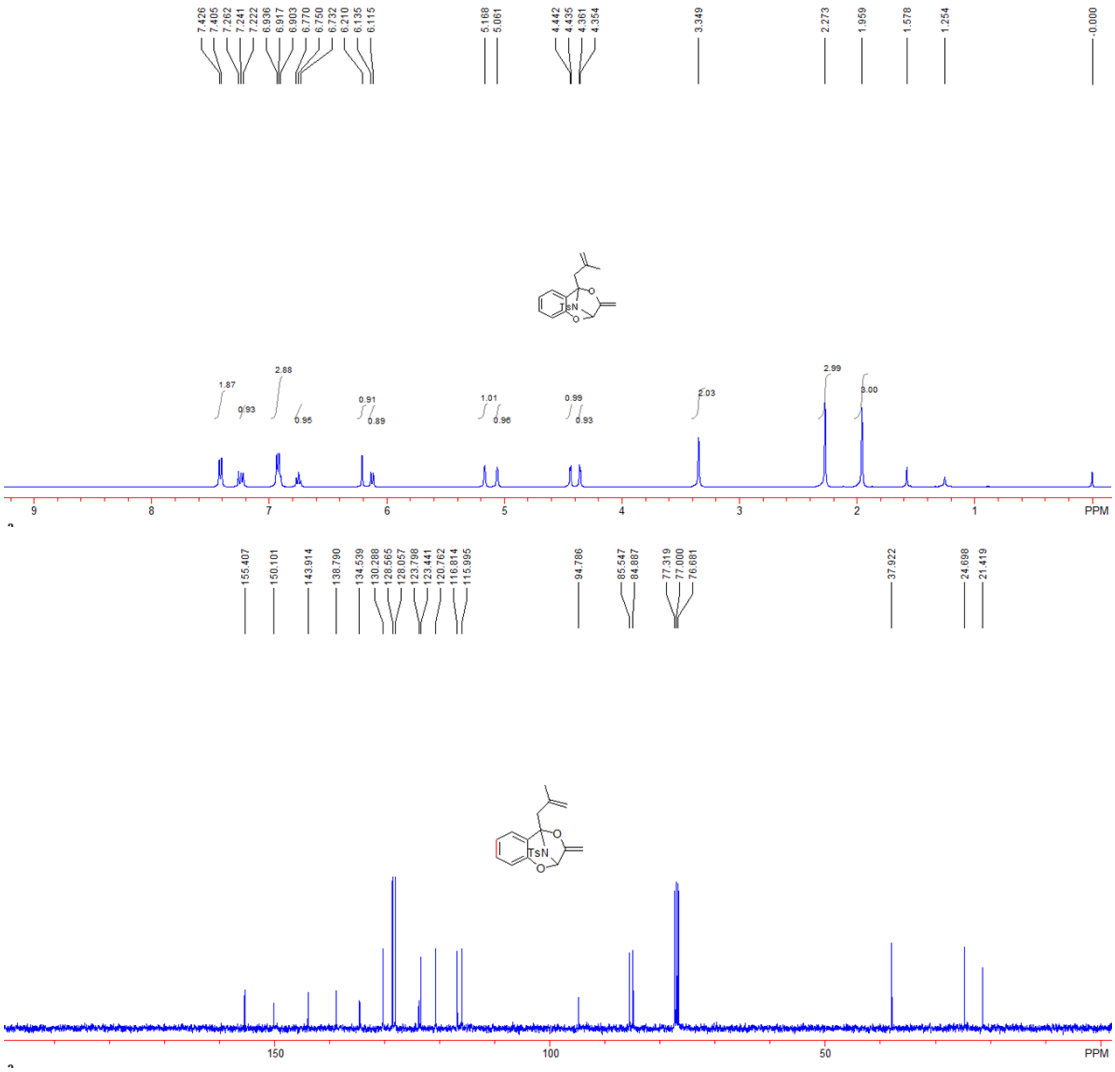


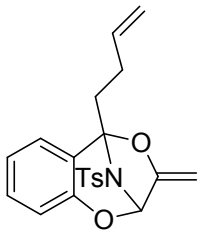




5-(2-methylallyl)-3-methylene-10-tosyl-3,5-dihydro-2H-2,5-epiminobenzo[e][1,4]dioxepine 2u.

0.2 mmol scale, 48 mg, a white solid, 63% yield. m.p.: 92-94 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.96 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 3.35 (s, 2H, CH_2), 4.36 (d, J = 2.8 Hz, 1H, CH=), 4.44 (d, J = 2.8 Hz, 1H, CH_2=), 5.06 (s, 1H, CH_2=), 5.17 (s, 1H, CH=), 6.12 (d, J = 8.0 Hz, 1H, Ar), 6.21 (s, 1H, CH), 6.75 (dd, J = 8.0 Hz, J = 8.0 Hz, 1H, Ar), 6.90-6.94 (m, 3H, Ar), 7.23 (d, J = 8.0 Hz, 1H, Ar), 7.41 (d, J = 8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 24.6, 37.9, 84.9, 85.5, 94.8, 116.0, 116.8, 120.8, 123.4, 123.8, 128.0, 128.6, 130.3, 134.5, 138.8, 143.9, 150.1, 155.4. IR (CH_2Cl_2) ν 2919, 2850, 1675, 1611, 1582, 1483, 1457, 1354, 1275, 1194, 1161, 1117, 1077, 1067, 978, 968, 915, 845, 760, 703, 660 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{22}NO_4S^+$ (M^++H) requires 384.1264, found: 384.1276.

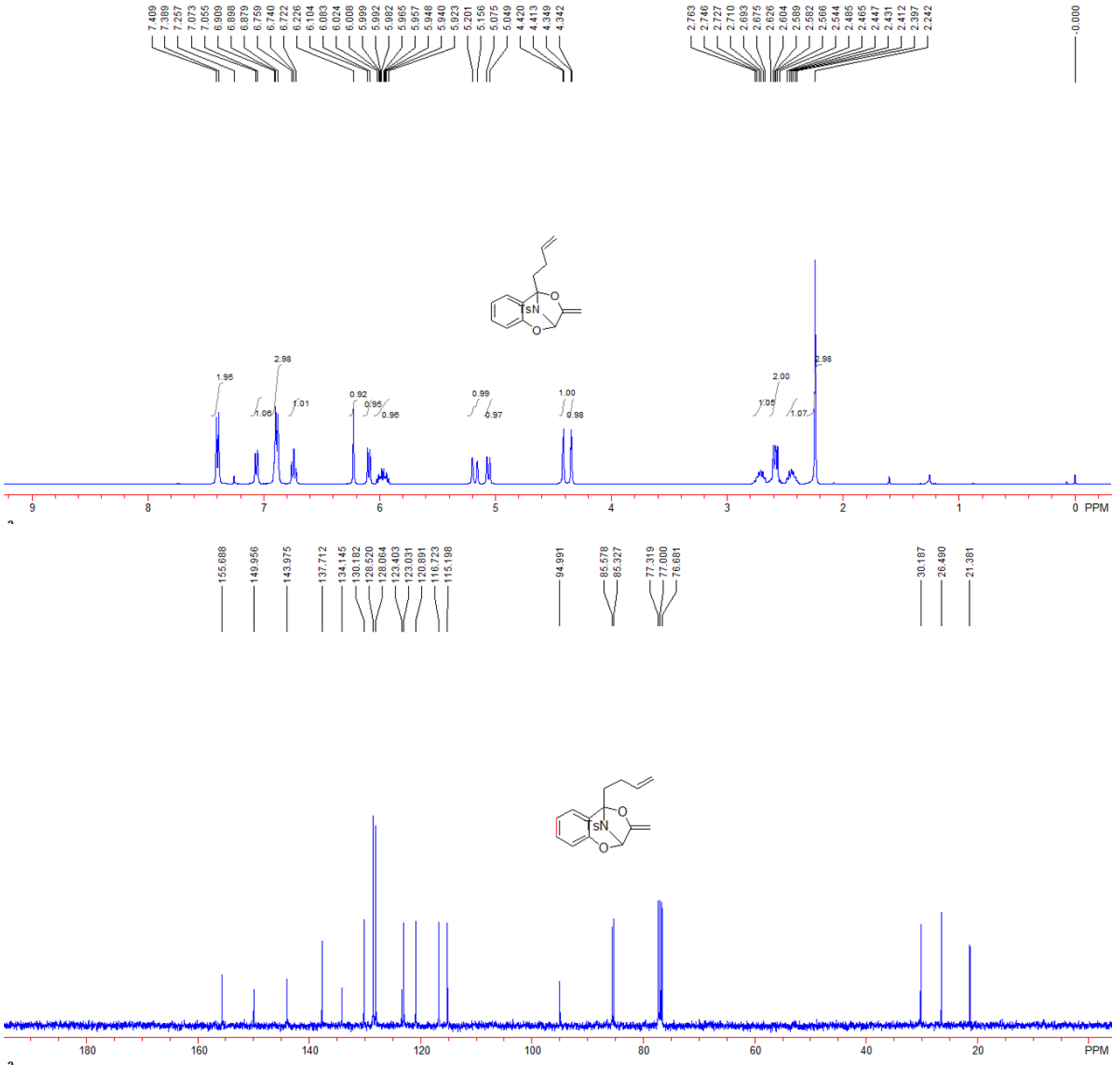


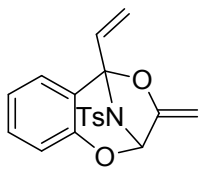


5-(but-3-en-1-yl)-3-methylene-10-tosyl-3,5-dihydro-2H-2,5-epiminobenzo[e][1,4]dioxepine 2v.

0.2 mmol scale, 61 mg, a white solid, 79% yield. m.p.: 134-136°C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.24 (s, 3H, CH_3), 2.39-2.49 (m, 1H, CH_2), 2.54-2.63 (m, 2H, CH_2), 2.67-2.77 (m, 1H, CH), 4.34 (d, *J* = 2.8 Hz, 1H, CH=), 4.42 (d, *J* = 2.8 Hz, 1H, CH_2=), 5.06 (d, *J* = 10.4 Hz, 1H, CH_2=), 5.18 (d, *J* = 18.0 Hz, 1H, CH_2=), 5.92-6.03 (m, 1H, CH=), 6.09 (d, *J* = 7.6 Hz, 1H, Ar), 6.23 (s, 1H, CH), 6.74 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H, Ar), 6.87-6.91 (m, 3H, Ar), 7.06 (d, *J* = 7.6 Hz, 1H, Ar), 7.40 (d, *J* = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 26.5,

30.2, 85.3, 85.6, 95.0, 115.2, 116.7, 120.9, 123.0, 123.4, 128.1, 128.5, 130.2, 134.1, 137.7, 144.0, 149.9, 155.7. IR (CH_2Cl_2) ν 3076, 2931, 2858, 1693, 1661, 1479, 1346, 1290, 1200, 1163, 1112, 1075, 977, 960, 943, 892, 833, 753, 744, 705, 695, 667 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{12}NO_4S^+$ (M^++H) requires 384.1264, found: 384.1263.

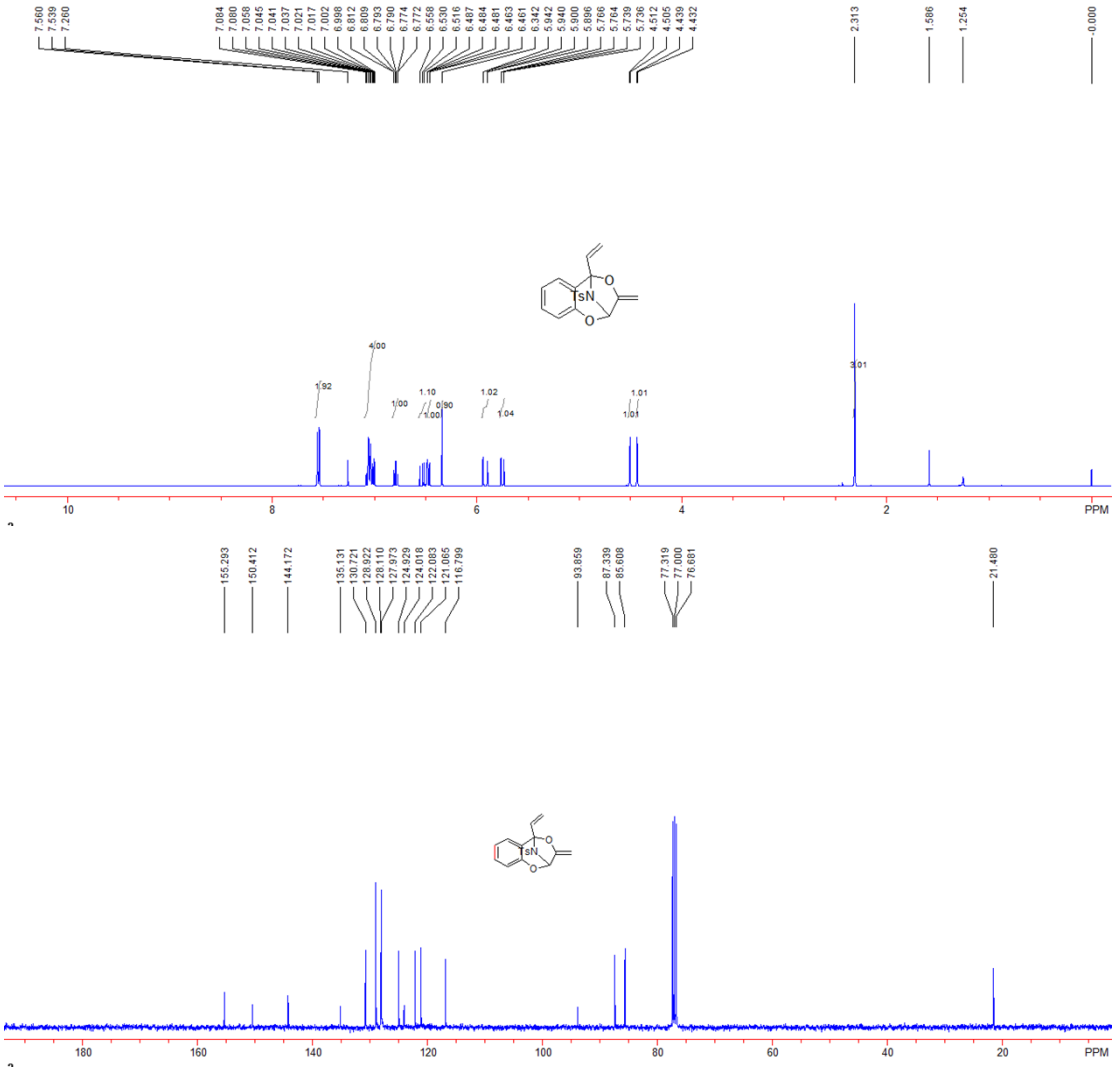


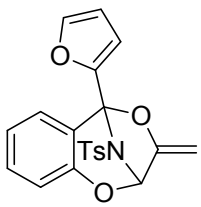


3-methylene-10-tosyl-5-vinyl-3,5-dihydro-2H-2,5-epiminobenzo[e][1,4]dioxepine 2w.

0.2 mmol scale, 50 mg, a white solid, 70% yield. m.p.: 139-141 °C. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.31 (s, 3H, CH_3), 4.43 (d, J = 2.8 Hz, 1H, CH=), 4.51 (d, J = 2.8 Hz, 1H, CH=), 5.75 (dd, J = 11.2 Hz, J = 1.2 Hz, 1H, CH=), 5.93 (dd, J = 16.8 Hz, J = 1.6 Hz, 1H, CH=), 6.34 (s, 1H, CH),

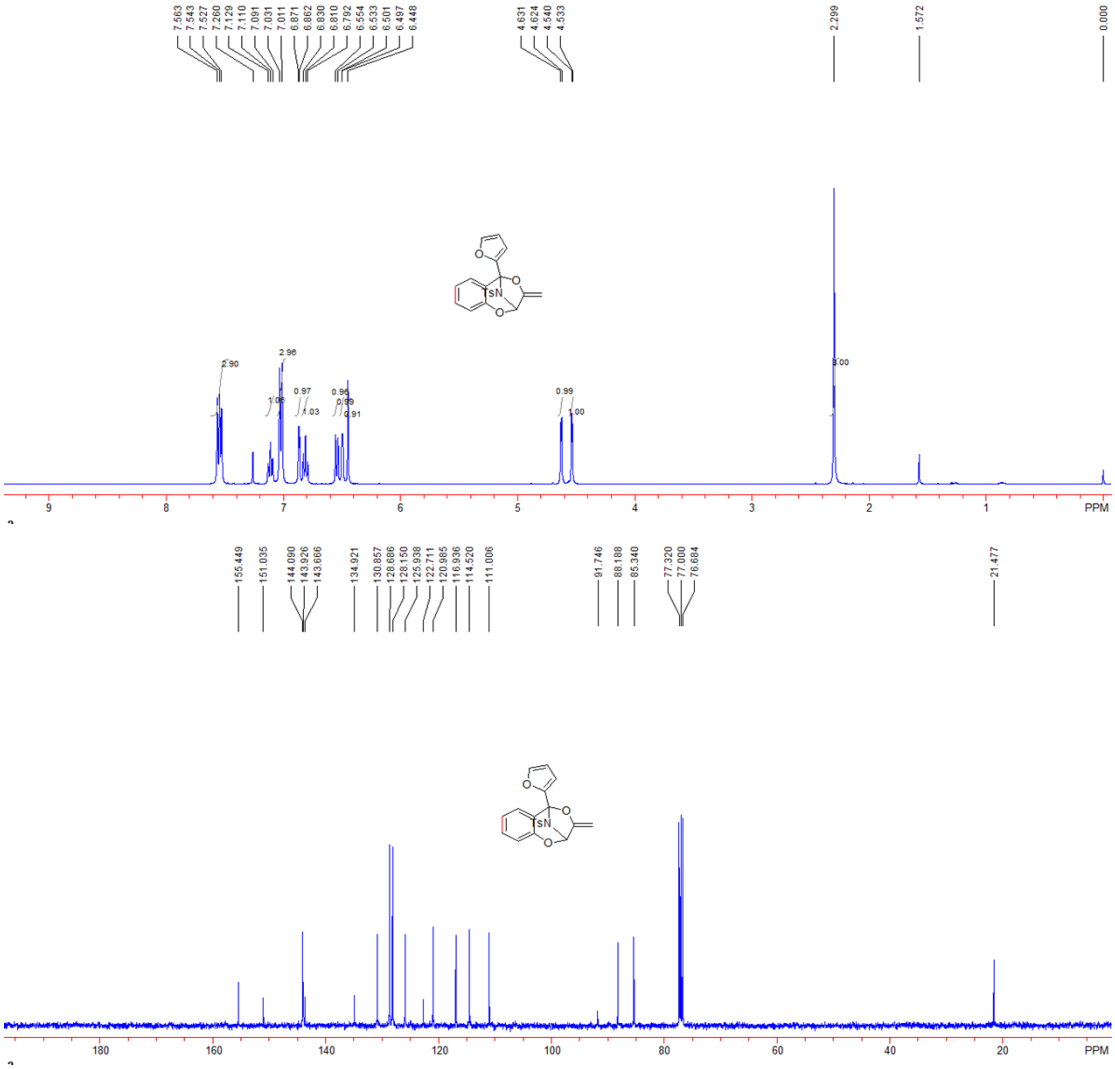
6.47 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H, Ar), 6.52 (dd, *J* = 16.8 Hz, *J* = 11.2 Hz, 1H, CH=), 6.79 (ddd, *J* = 7.6 Hz, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H, Ar), 6.99-7.09 (m, 4H, Ar), 7.55 (d, *J* = 8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 85.6, 87.3, 93.8, 116.8, 121.1, 122.1, 124.0, 124.9, 128.0, 128.1, 128.9, 130.7, 135.1, 144.2, 150.4, 155.3. IR (CH_2Cl_2) ν 3072, 3048, 2842, 1682, 1584, 1481, 1461, 1359, 1343, 1263, 1185, 1162, 1112, 1086, 1052, 1039, 1001, 959, 944, 889, 859, 803, 757, 665 cm^{-1}. HRMS (ESI) Calcd. for $C_{19}H_{18}NO_4S^+$ (M^++H) requires 356.0951, found: 356.0965.

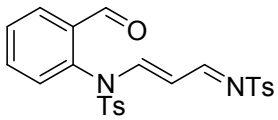




5-(furan-2-yl)-3-methylene-10-tosyl-3,5-dihydro-2H-2,5-epiminobenzo[e][1,4]dioxepine 2x.

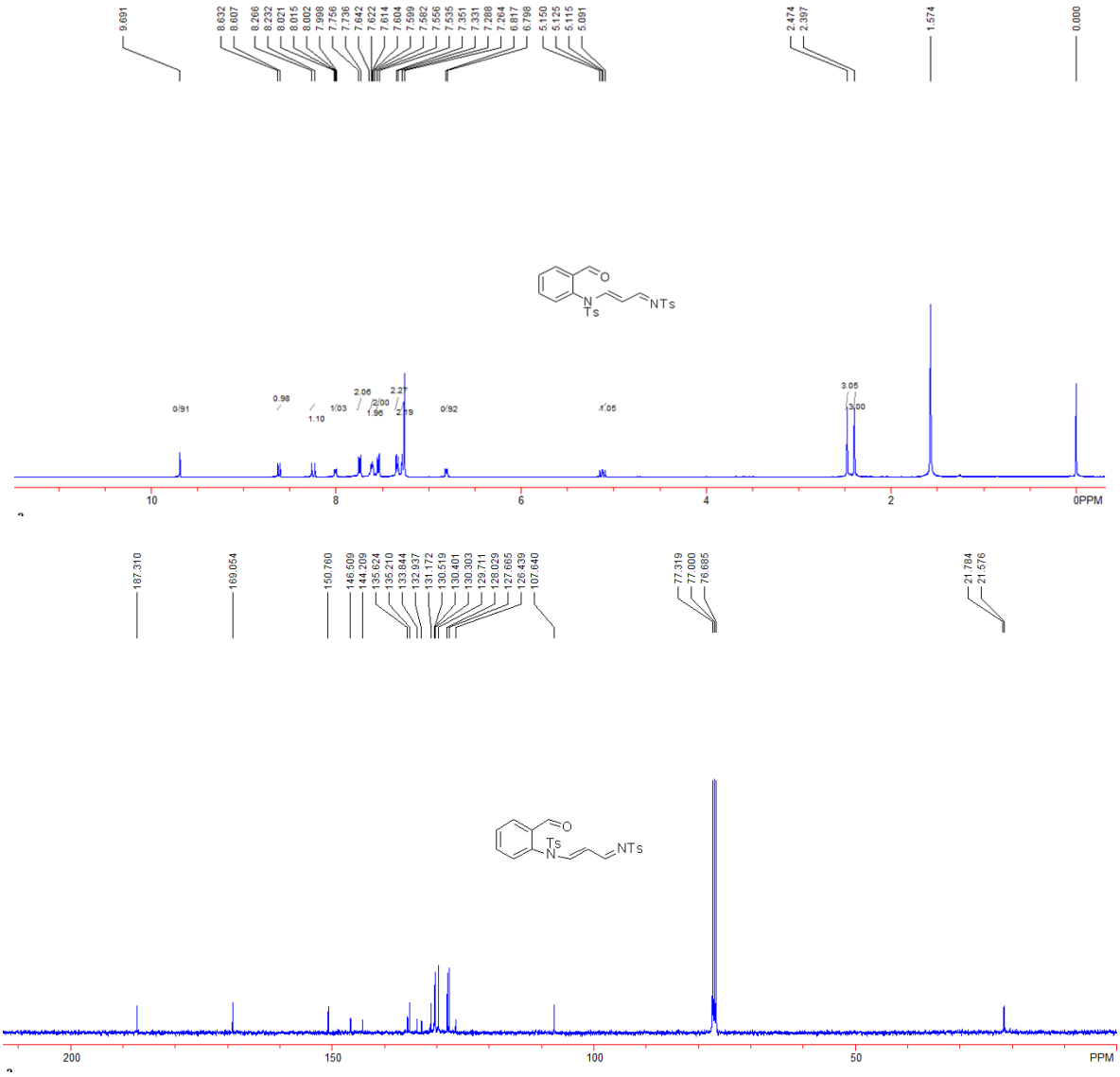
0.2 mmol scale, 42mg, a white solid, 53% yield. m.p.: 144-146 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.30 (s, 3H, CH_3), 4.54 (d, J = 2.8 Hz, 1H, CH=), 4.63 (d, J = 2.8 Hz, 1H, CH=), 6.45 (s, 1H, CH), 6.50 (d, J = 1.6 Hz, 1H, Ar), 6.54 (d, J = 8.4 Hz, 1H, Ar), 6.81 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H, Ar), 6.87 (d, J = 3.6 Hz, 1H, Ar), 7.02 (d, J = 8.0 Hz, 3H, Ar), 7.11 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H, Ar), 7.52-7.57 (m, 3H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 85.3, 88.2, 91.7, 111.0, 114.5, 116.9, 121.0, 122.7, 125.9, 128.2, 128.7, 130.8, 134.9, 143.7, 143.9, 144.1, 151.0, 155.4. IR (CH_2Cl_2) ν 3069, 3052, 1700, 1675, 1592, 1481, 1459, 1352, 1273, 1252, 1162, 1115, 108, 1006, 990, 960, 903, 836, 810, 789, 752, 702, 685, 658 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{18}NO_5S^+$ (M^++H) requires 396.0900, found: 396.0917.

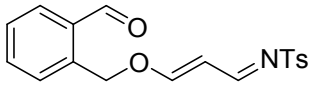




N-(2-formylphenyl)-4-methyl-N-((1E)-3-(tosylimino)prop-1-en-1-yl)benzenesulfonamide 5.

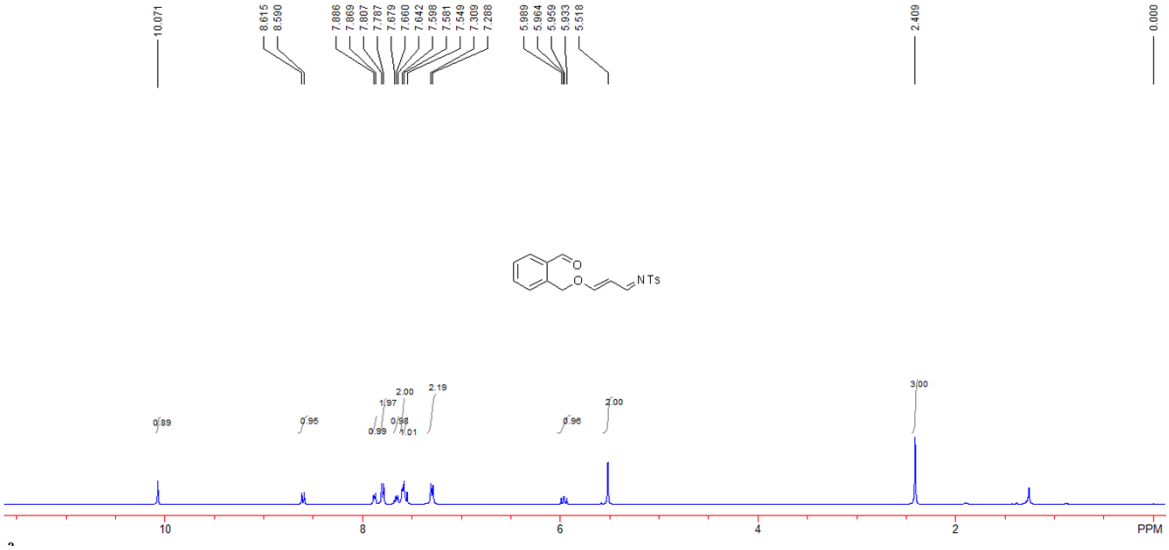
0.2 mmol scale, 56 mg, a white solid, 59% yield. m.p.: 158-160 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.40 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 5.12 (dd, *J* = 13.6 Hz, *J* = 9.6 Hz, 1H, CH=), 6.81 (d, *J* = 7.6 Hz, 1H, Ar), 7.28 (d, *J* = 8.0 Hz, 2H, Ar), 7.34 (d, *J* = 8.0 Hz, 2H, Ar), 7.54 (d, *J* = 8.0 Hz, 2H, Ar), 7.58-7.65 (m, 2H, Ar), 7.75 (d, *J* = 8.0 Hz, 2H, Ar), 8.00 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 1H, Ar), 8.25 (d, *J* = 13.6 Hz, 1H, CH=), 8.62 (d, *J* = 9.6 Hz, 1H, CH=NTs), 9.69 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 21.8, 107.6, 126.4, 127.7, 128.0, 129.7, 130.3, 130.4, 130.5, 131.2, 132.9, 133.8, 135.2, 135.6, 144.2, 146.5, 150.8, 169.0, 187.3. IR (CH_2Cl_2) ν 3038, 2923, 2854, 1698, 1605, 1594, 1574, 1374, 1319, 1289, 1191, 1153, 1081, 924, 811, 775, 719, 665 cm^{-1}. MS (ESI) m/z: 483.0 ($M+H^+$, 100); MS (MALDI) m/z: 483.1 ($M+H^+$, 100); HRMS (MALDI) Calcd. for $C_{24}H_{23}N_2O_5S_2^+$ (M^++H) requires 483.1043, found: 483.1050.

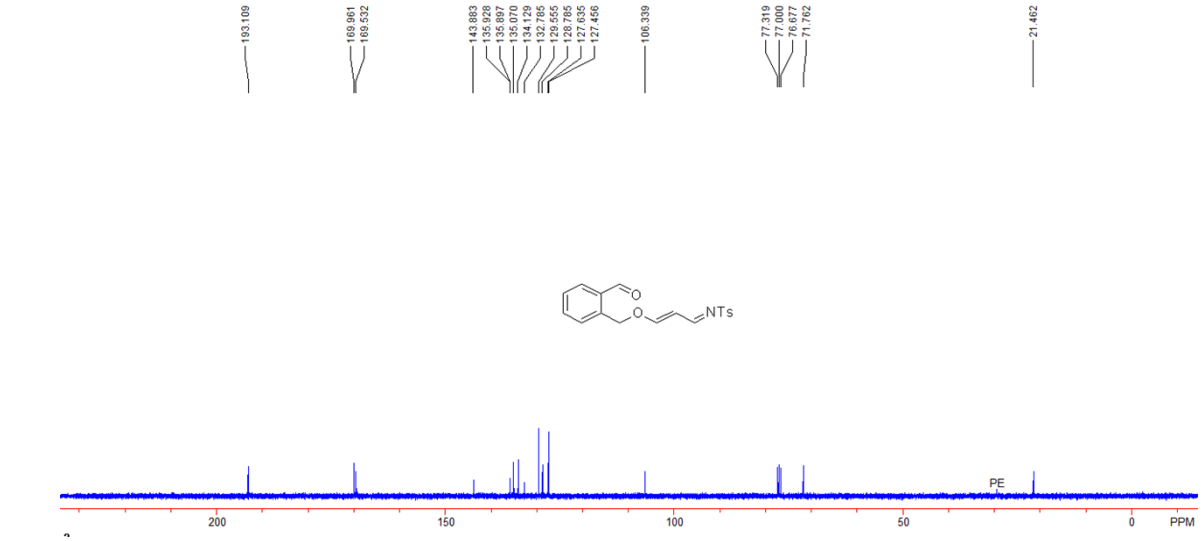


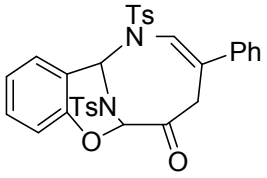


N-((E)-3-((2-formylbenzyl)oxy)allylidene)-4-methylbenzenesulfonamide 7.

0.2 mmol scale, 66 mg, a colorless oil, 97% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.41 (s, 3H, CH_3), 5.52 (s, 2H, CH_2), 5.96 (dd, *J* = 12.4 Hz, *J* = 10.0 Hz, 1H, CH=), 7.30 (d, *J* = 8.4 Hz, 2H, Ar), 7.57 (d, *J* = 12.4 Hz, 1H, CH=), 7.59 (d, *J* = 6.8 Hz, 2H, Ar), 7.66 (dd, *J* = 7.6 Hz, *J* = 7.6 Hz, 1H, Ar), 7.80 (d, *J* = 8.0 Hz, 2H, Ar), 7.88 (d, *J* = 6.8 Hz, 1H, Ar), 8.60 (d, *J* = 10.0 Hz, 1H, CH=NTs), 10.07 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 71.8, 106.3, 127.4, 127.6, 128.8, 129.6, 132.8, 134.1, 135.1, 135.90, 135.93, 143.9, 169.5, 170.0, 193.1. IR (CH_2Cl_2) ν 3077, 2927, 2850, 1692, 1612, 1598, 1576, 1315, 1288, 1175, 1147, 1085, 1017, 946, 803, 783, 756, 677, 657 cm^{-1}. MS (ESI) m/z: 365.9 ($M+Na^+$, 100); MS (MALDI) m/z: 344.1 ($M+H^+$, 100); HRMS (MALDI) Calcd. for $C_{18}H_{18}NO_4S^+$ (M^++H) requires 344.0951, found: 344.0950.

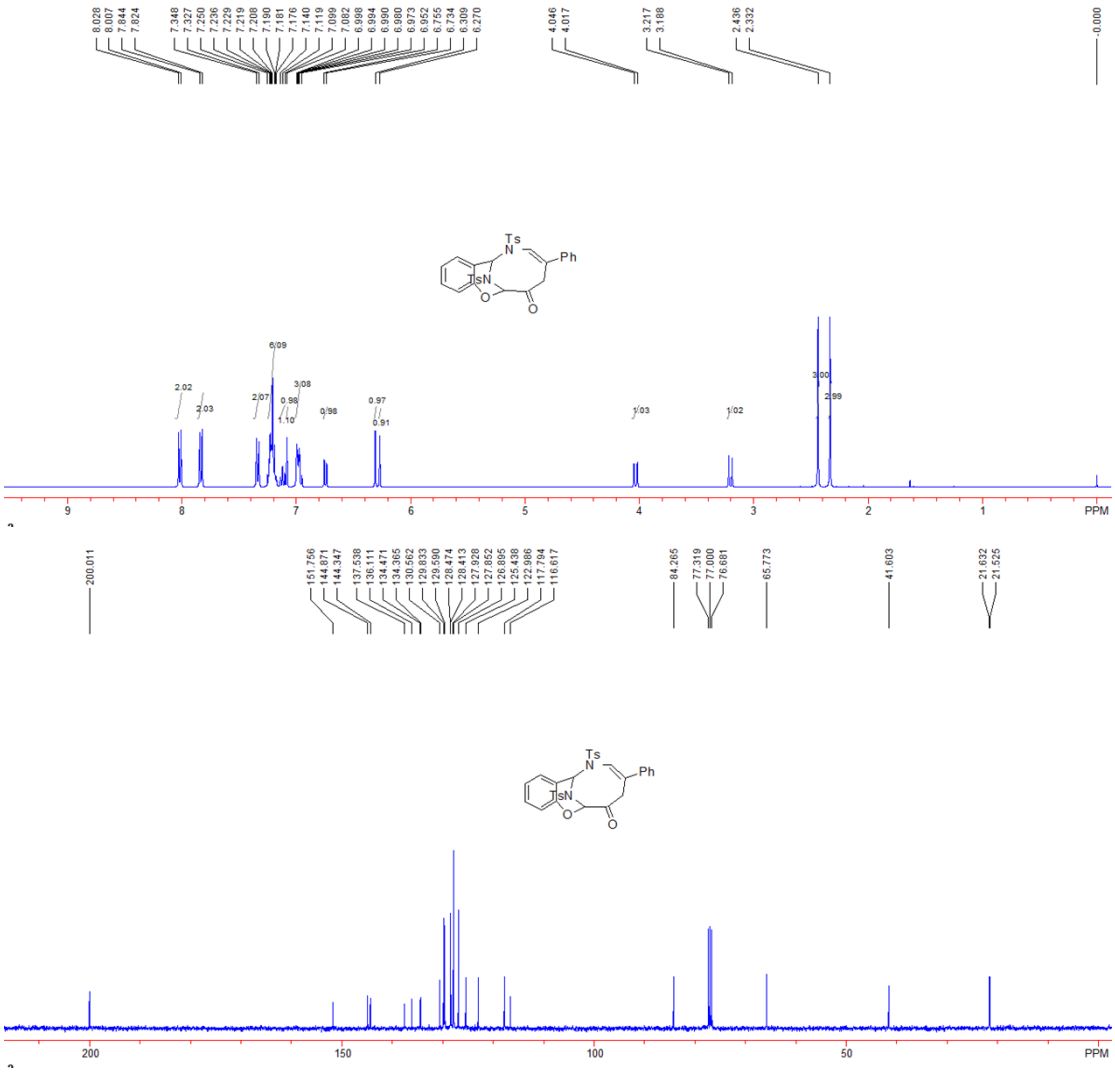


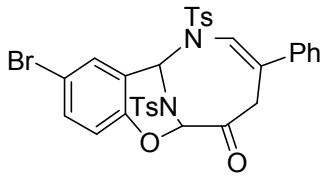




5-Phenyl-7,13-ditosyl-7,8-dihydro-2H-2,8-epiminobenzo[b][1,5]oxazecin-3(4H)-one 9a.

0.2 mmol scale, 92 mg, a white solid, 77% yield. m.p.: 201-203 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.33 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.20 (d, J = 11.6 Hz, 1H, CH), 4.03 (d, J = 11.6 Hz, 1H, CH), 6.27 (s, 1H, CH), 6.31 (s, 1H, CH), 6.74 (d, J = 8.4 Hz, 1H, Ar), 6.95-7.00 (m, 3H, Ar), 7.08 (s, 1H, CH=), 7.12 (dd, J = 8.4 Hz, J = 8.4 Hz, 1H, Ar), 7.17-7.25 (m, 6H, Ar), 7.34 (d, J = 8.4 Hz, 2H, Ar), 7.83 (d, J = 8.4, 2H, Ar), 8.01 (d, J = 8.4, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 21.6, 41.6, 65.8, 84.3, 116.6, 117.8, 123.0, 125.4, 126.9, 127.8, 127.9, 128.0, 128.4, 128.5, 129.6, 129.8, 130.6, 134.4, 134.5, 136.1, 137.5, 144.3, 144.9, 151.8, 200.0. IR (CH_2Cl_2) ν 3048, 2959, 1732, 1594, 1485, 1457, 1360, 1328, 1315, 1171, 1157, 1088, 1041, 995, 970, 919, 809, 776, 764, 703, 695, 676, 659 cm^{-1}. HRMS (ESI) Calcd. for $C_{32}H_{32}N_3O_6S_2^+$ $(M+NH_4)^+$ requires 618.1727, found: 618.1727.

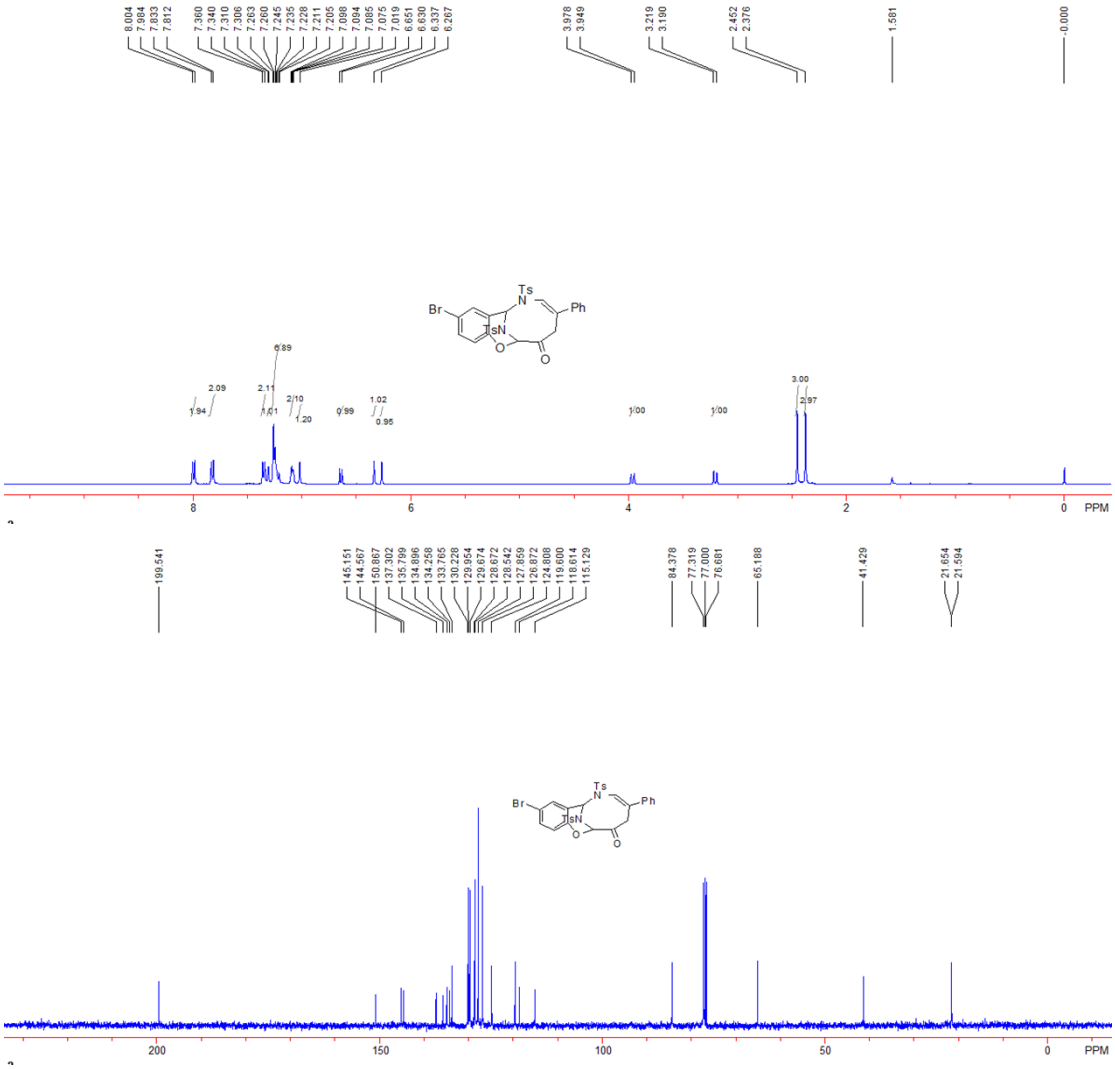


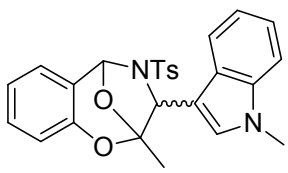


10-Bromo-5-phenyl-7,13-ditosyl-7,8-dihydro-2H-2,8-epiminobenzo[b][1,5]oxazecin-3(4H)-one 9b.

0.2 mmol scale, 96 mg, a white solid, 71% yield. m.p.: 179-181 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.38 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 3.20 (d, J = 11.6 Hz, 1H, CH), 3.96 (d, J = 11.6 Hz, 1H, CH), 6.27 (s, 1H, CH), 6.34 (s, 1H, CH), 6.64 (d, J = 8.4 Hz, 1H, Ar), 7.02 (s, 1H, CH=), 7.07-7.10 (m, 2H, Ar), 7.20-7.27 (m, 6H, Ar), 7.31 (d, J = 2.4 Hz, 1H, Ar), 7.35 (d, J = 8.0 Hz, 2H, Ar), 7.82 (d, J = 8.0 Hz, 2H, Ar), 7.99 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 21.7, 41.4, 65.2, 84.4, 115.1, 118.6, 119.6, 124.8, 126.9, 127.8, 128.5, 128.7, 129.7,

129.9, 130.2, 133.8, 134.2, 134.9, 135.8, 137.3, 144.6, 145.2, 150.9, 199.5. IR (CH_2Cl_2) ν 3056, 2983, 1733, 1592, 1477, 1347, 1332, 1287, 1161, 1090, 1041, 1026, 973, 868, 857, 845, 759, 689, 682, 66, 657 cm^{-1}. HRMS (ESI) Calcd. for $C_{32}H_{31}BrN_3O_6S_2^+$ (M^++NH_4) requires 696.0832, found: 696.0840.

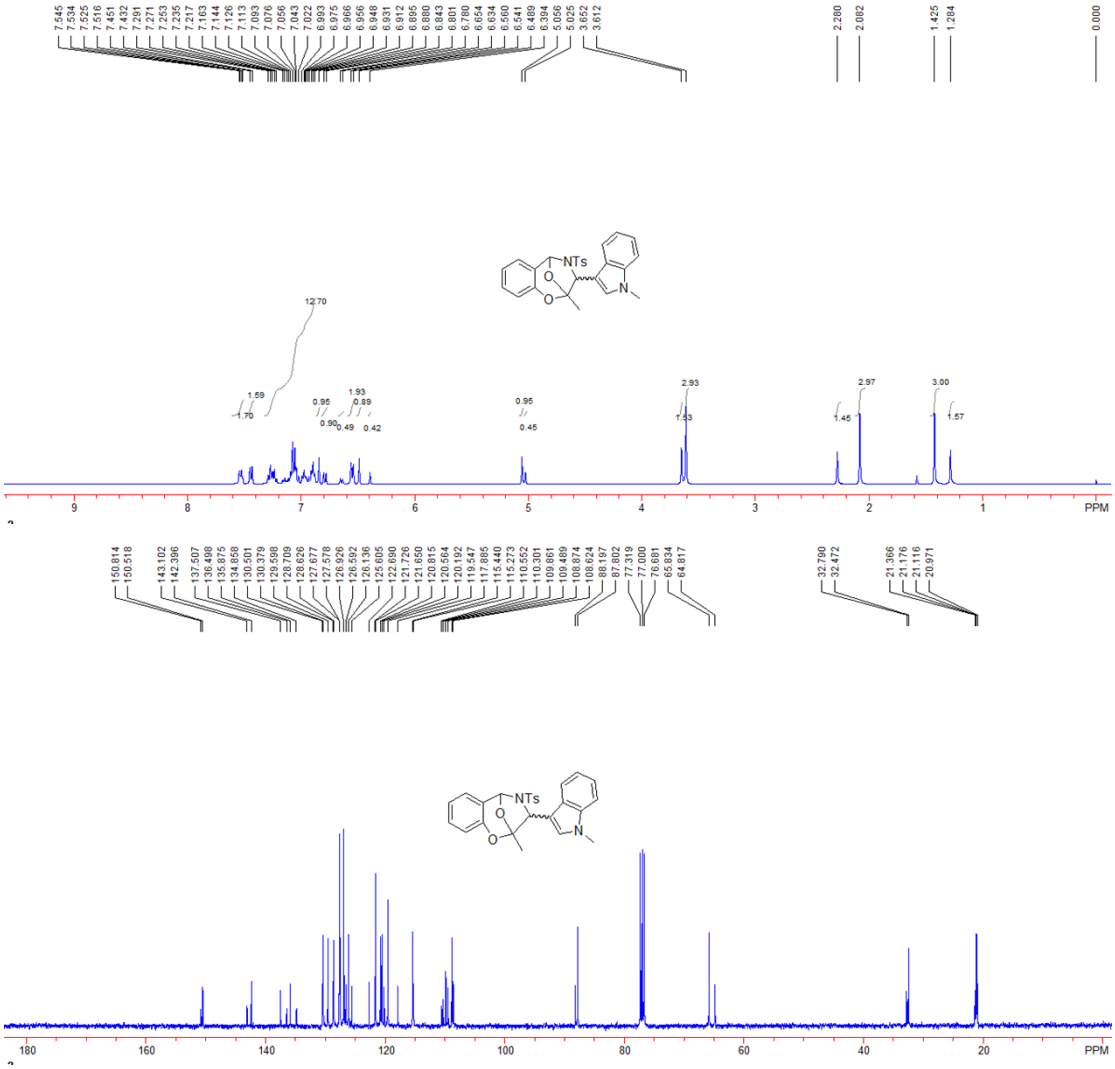




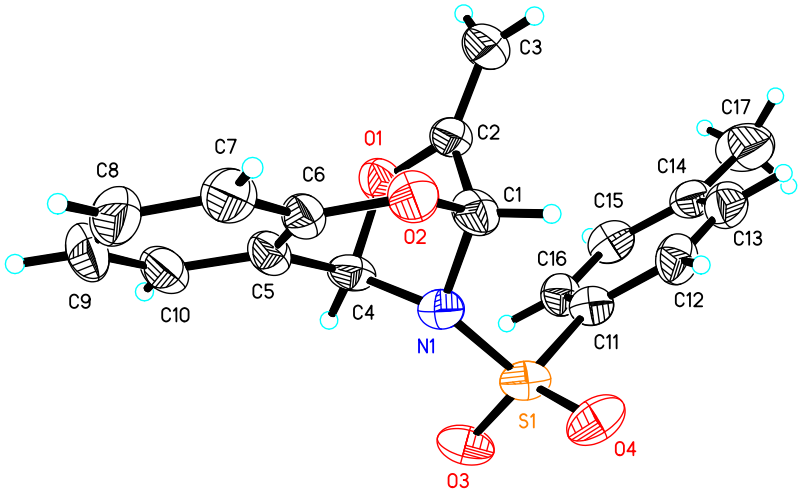
2-Eethyl-3-(1-methyl-1H-indol-3-yl)-4-tosyl-2,3,4,5-tetrahydro-2,5-epoxybenzo[f][1,4]oxazepine 10.

0.2 mmol scale, 74 mg, a white solid, 74% yield. m.p.: 220-225 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.28 (s, 1.5H, CH_3), 1.42 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 2.28 (s, 1.5H, CH_3), 3.61 (s,

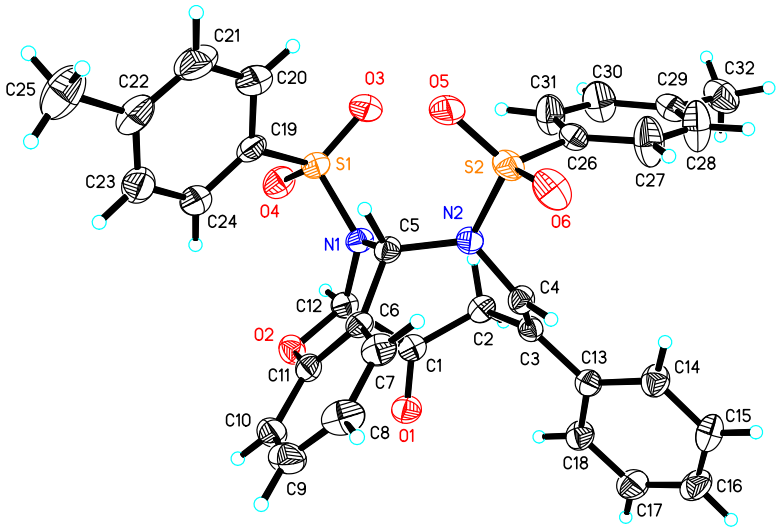
3H, CH_3), 3.65 (s, 1.5H, CH_3), 5.02 (s, 0.5H, CH), 5.06 (s, 1H, CH), 6.39 (s, 0.5H, CH), 6.49 (s, 1H, CH), 6.55 (d, J = 7.6 Hz, 2H, Ar), 6.64 (d, J = 8.0 Hz, 0.5H, CH), 6.79 (d, J = 8.4 Hz, 1H, Ar), 6.84 (s, 1H, Ar), 6.88-7.30 (m, 12H, Ar), 7.44 (d, J = 7.6 Hz, 1.5H, Ar), 7.51-7.55 (m, 1.5H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.0, 21.1, 21.2, 21.4, 32.5, 32.8, 64.8, 65.8, 87.8, 88.2, 108.6, 108.9, 109.5, 109.9, 110.3, 110.6, 115.3, 115.4, 117.9, 119.5, 120.2, 120.6, 120.8, 121.6, 121.7, 122.7, 125.6, 126.1, 126.6, 126.9, 127.6, 127.7, 128.6, 128.7, 129.6, 130.4, 130.5, 134.8, 135.9, 136.5, 137.5, 142.4, 143.1, 150.5, 150.8. IR (CH_2Cl_2) ν 2935, 2846, 1613, 1594, 1483, 1459, 1314, 1264, 1152, 1100, 1088, 1035, 1014, 997, 919, 903, 734, 715, 699, 677 cm^{-1}. HRMS (ESI) Calcd. for $C_{26}H_{25}N_2O_4S^+$ ($M+H^+$) requires 461.1530, found: 461.1525.



7. Crystallographic Information of 2a, 9a, and 10.

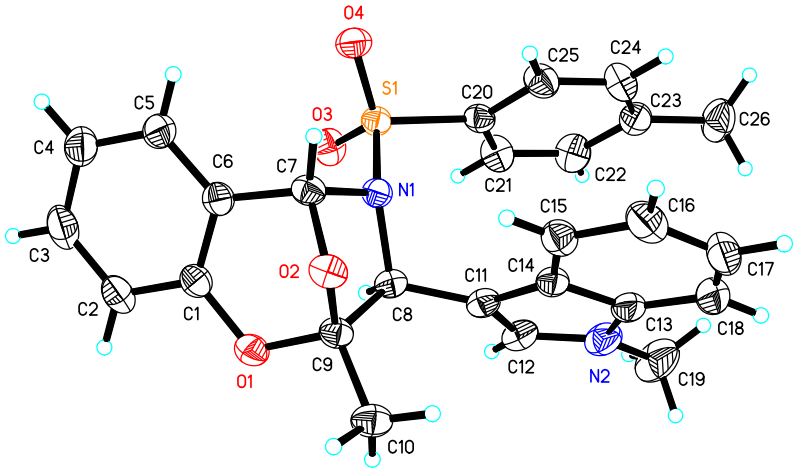


The crystal data of **2a** have been deposited in CCDC with number 962969. Empirical Formula: $C_{17}H_{15}NO_4S$; Formula Weight: 329.36; Crystal Color, Habit: colorless; Crystal System: Orthorhombic; Crystal size: 0.141 x 0.078 x 0.069; Lattice Parameters: a = 17.324(8)Å, b = 15.968(8)Å, c = 5.799(3)Å, α = 90°, β = 90°, γ = 90°, V = 1604.1(13)Å^3; Space group: Pna2(1); Z = 4; D_{calc} = 1.364 g/cm^3; F_{000} = 688; Final R indices [I>2sigma(I)]: R1 = 0.0658; wR2 = 0.1480.



The crystal data of **9a** have been deposited in CCDC with number 1001752. Empirical formula: $C_{32}H_{28}N_2O_6S_2$, Formula weight: 600.68, Temperature: 293(2) K, Crystal system: Monoclinic, Space group: P21/c, Unit cell dimensions: a = 17.4958(18) Å, α = 90°; b = 11.4975(12) Å, β = 115.554(2)°; c = 15.7284(17) Å, γ = 90°. Volume: 2854.4(5) Å^3, Z = 4, Density (calculated): 1.398 Mg/m^3, F(000): 1256, Crystal size: 0.211 x 0.154 x 0.102 mm^3, Final R indices

[I>2sigma(I)]: R1 = 0.0511, wR2 = 0.1211.



The crystal data of **10** have been deposited in CCDC with number 1001749. Empirical formula: $C_{26}H_{24}N_2O_4S$, Formula weight: 460.53, Temperature: 293(2) K, Crystal system: Monoclinic, Space group: P21/c, Unit cell dimensions: a = 8.7752(9) Å, α = 90°; b = 24.925(3) Å, β = 92.290(2)°; c = 10.2418(11) Å, γ = 90°. Volume: 2238.3(4) $Å^3$, Z = 4, Density (calculated): 1.367 Mg/m^3, F(000): 968, Crystal size: 0.211 x 0.175 x 0.123 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0522, wR2 = 0.1324.

8. Reference

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