Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information for Ligand-Controlled Chemoselectivity in Gold Catalyzed Cascade Cyclization of 1,4-Diene-Tethered 2-Alkynylbenzaldehydes

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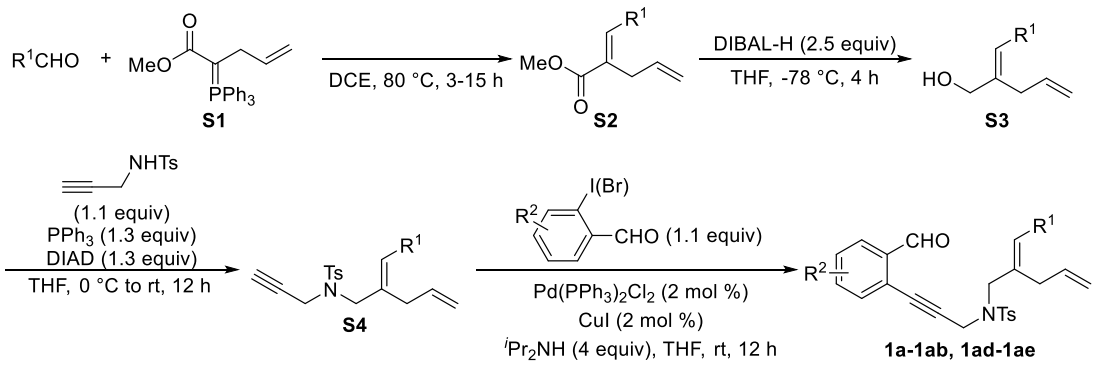
1. General information

All commercial chemicals were used without additional purification, unless otherwise stated. All (phosphine)AuNTf$_2$ and (NHC)AuNTf$_2$ catalysts were prepared following literature procedures.[S1] THF and toluene were dried over Na/benzophenone and 1,2-dichloroethanne was dried over CaH_2. Analytical thin layer chromatography (TLC) was performed using pre-coated silica gel plate. Visualization was achieved by UV-vis light (254 nm). Flash column chromatography was performed using silica gel and gradient solvent system (petroleum ether: EtOAc as eluent). ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a 400 or 600 MHz spectrometer in $CDCl_3$. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), td (triplet of doublets), dt (doublet of triplet) or m (multiplet). The number of protons (*n*) for a given resonance is indicated by *n*H and coupling constants are reported as a *J* value in Hz. High resolution mass spectra (HRMS) were obtained on a LC/HRMS TOF mass spectrometer using simultaneous electrospray (ESI). Melting points were determined using a digital melting point apparatus.

2. Preparation and characterization of starting materials

2.1. General procedure A



Step 1: To a 100 mL round-bottom flask equipped with a reflux condenser and stirring bar were added methyl 2-(triphenyl-phosphanylidene)pent-4-enoate **S1** (9.735 g, 26 mmol, 1.3 equiv), aldehyde derivative (20 mmol, 1.0 equiv) and $(CH_2Cl)_2$ (60 mL). The reaction mixture was allowed to stir at 80 ^{o}C for 3–15 h until full consumption of the aldehyde, as indicated by TLC analysis.[S2] The resulting mixture was cooled to room temperature and concentrated under reduced pressure. The

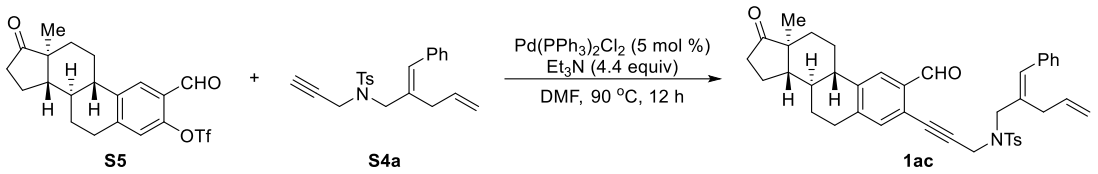
residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford **S2**.

Step 2: To a solution of the resulting 1,4-diene ester **S2** (1 equiv) in anhydrous THF (0.25 M) at –78 ℃ was added DIBAL-H (1.0 M in hexanes, 2.5 equiv) dropwise and the reaction mixture was stirred –78 ℃ for 4 h. The reaction mixture was quenched carefully with hydrochloric acid (1 N) and ethyl acetate and vigorously stirred for 1 h, extracted with EtOAc and the combined organic layers were washed with brine and dried over $MgSO_4$. After filtration and concentration, the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc) to give the 1,4-dienol **S3**.

Step 3: To a solution of triphenylphosphine (1.3 equiv), 1,4-dienol **S3** (1.0 equiv) and 4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1.1 equiv) in anhydrous THF (0.4 M) at 0 ℃ was added diisopropyl azodicarboxylate (DIAD, 1.3 equiv) dropwise. The mixture was warmed to room temperature and stirred for 12 h.[S3] The mixture was concentrated and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford the 1,4-diene-ynes **S4**.

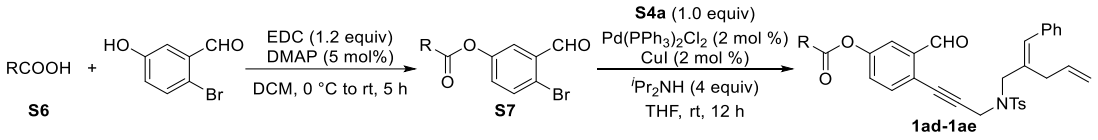
Step 4: To an oven-dried round-bottom flask equipped with a stirring bar were added 2-iodo(bromo)-benzaldehyde derivatives (1.1 equiv), 1,4-diene-ynes **S4** (1.0 equiv, if solid, added at this time), $Pd(PPh_3)_2Cl_2$ (2 mol %) and CuI (2 mol %) in anhydrous THF (0.2 M) was added diisopropylamine ($^iPr_2NH$, 4.0 equiv) under an argon atmosphere at 0 ^oC. 1,4-diene-ynes **S4** (if liquid, dissolved in THF and added at this time by a syringe). The reaction mixture was stirred at room temperature for 12 h until full consumption of the starting material (monitored by TLC). Upon completion, the reaction mixture was quenched with saturated NH_4Cl solution and extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$. After filtration and concentration, the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford **1a-1ab** and **1ad-1ae.**

2.2. General procedure B



Following a slightly modified reported procedure, to a solution of **S5** (860 mg, 2 mmol) and the above **S4a** (877 mg, 2.4 mmol) in DMF (5 mL) were added $Pd(PPh_3)_2Cl_2$ (70.2 mg, 0.1 mmol) and Et_3N (8.8 mmol, 4.4 equiv) under argon atmosphere at room temperature.[S4,S5] The resulting mixture was then heated at 90 ℃ for 12 h overnight. The reaction was cooled to room temperature and quenched with saturated NH_4Cl solution (15 mL), extracted with EtOAc (2 × 15 mL). The combined organic extracts were washed with saturated brine (10 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 9:1 to 4:1) to afford **1ac** (297 mg, 23%) as a pale-yellow oil.

2.3. General procedure C

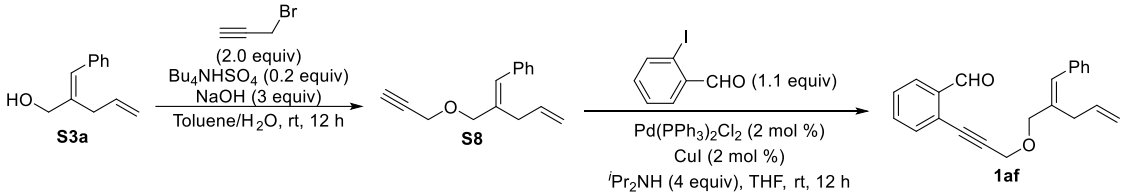


Step 1: Following a slightly modified reported procedure,[S6] to a solution of 2-bromo-5-hydroxybenzaldehyde (402 mg, 2.0 mmol), acid derivatives (2.0 mmol) and DMAP (12.2 mg, 0.1 mmol) in CH_2Cl_2 (8 mL) was added dropwise a solution of EDC (*N*-(3-Dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrochloride) (2.4 mmol) in CH_2Cl_2 (5 mL) at 0 ℃ under an argon atmosphere. The reaction mixture was stirred at room temperature for 5 h. Upon completion, based on monitoring by TLC analysis, the reaction mixture was quenched with H_2O and extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc) to provide **S7**.

Step 2: To an oven-dried round-bottom flask equipped with a stirring bar were added

S7 (1.1 equiv), 1,4-diene-ynes **S4a** (1.0 equiv), $Pd(PPh_3)_2Cl_2$ (2 mol %) and CuI (2 mol %) in anhydrous THF (0.2 M) was added diisopropylamine ($^iPr_2NH$, 4.0 equiv) under an argon atmosphere at 0 ^oC. The reaction mixture was stirred at room temperature for 12 h. The reaction mixture was quenched with saturated NH_4Cl solution and extracted with EtOAc (2 × 15 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. After filtration and concentration, the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford **1ad-1ae.**

2.4. General procedure D

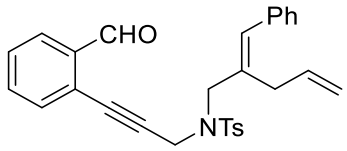


Step 1: To a solution of **S3a** (348 mg, 2.0 mmol), Bu_4NHSO_4 (136 mg, 0.4 mmol) and NaOH (240 mg, 6 mmol) in Toluene-H_2O (9 mL, 2:1, v:v) was added dropwise propargylic bromide (0.4 mL, 2 equiv) at room temperature. The reaction mixture was stirred at room temperature for 12 h until full consumption of the starting material (monitored by TLC). Upon completion, the reaction mixture was quenched with saturated NH_4Cl solution and extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford **S8**.

Step 2: To an oven-dried round-bottom flask equipped with a stirring bar were added 2-iodo-benzaldehyde derivatives (1.1 equiv), **S8** (1.0 equiv), $Pd(PPh_3)_2Cl_2$ (2 mol %) and CuI (2 mol %) in anhydrous THF (0.2 M) was added diisopropylamine ($^iPr_2NH$, 4.0 equiv) under an argon atmosphere at 0 ^oC. The reaction mixture was stirred at room temperature for 12 h until full consumption of the starting material (monitored by TLC). Upon completion, the reaction mixture was quenched with saturated NH_4Cl solution and extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$. After filtration and concentration, the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc) to

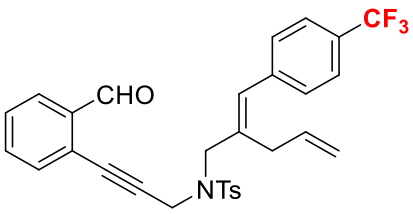
afford **1af**.

(*E*)-*N*-(2-benzylidenepent-4-en-1-yl)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1a)



The title compound was prepared according to general procedure A in 56% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a colorless solid, mp 80–82 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.91 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.82–7.75 (m, 2H), 7.51–7.49 (m, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.34–7.32 (m, 2H), 7.30–7.24 (m, 3H), 7.23–7.21 (m, 3H), 6.63 (s, 1H), 5.98–5.92 (m, 1H), 5.21 (d, *J* = 17.2 Hz, 1H), 5.17 (d, *J* = 10.1 Hz, 1H), 4.40 (s, 2H), 3.98 (s, 2H), 3.10 (d, *J* = 5.8 Hz, 2H), 2.26 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.6, 143.9, 136.4, 135.9, 135.8, 134.7, 133.6, 133.4, 133.3, 131.4, 129.6, 128.8, 128.5, 128.3, 127.7, 127.3, 127.2, 125.6, 116.9, 89.1, 81.7, 52.6, 36.6, 32.8, 21.3; **HRMS (ESI)** calcd for $C_{29}H_{28}NO_3S$ $[M+H]^+$: 470.1784; found: 470.1788.

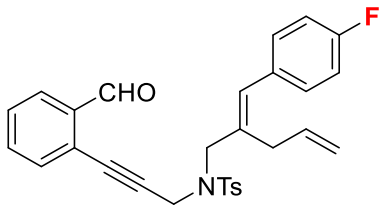
(*E*)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methyl-*N*-(2-(4-(trifluoromethyl)benzylidene)pent-4-en-1-yl)benzenesulfonamide (1b)



The title compound was prepared according to general procedure A in 49% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a yellow solid, mp 104–106 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.90 (s, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H),

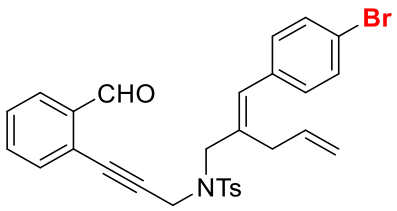
7.38 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 3H), 6.68 (s, 1H), 5.96–5.90 (m, 1H), 5.22–5.18 (m, 2H), 4.41 (s, 2H), 4.01 (s, 2H), 3.07 (d, *J* = 5.9 Hz, 2H), 2.26 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.6, 144.0, 140.0, 135.9, 135.8, 135.7, 134.2, 133.6, 133.4, 129.7, 129.6, 129.2, 128.9, 128.8, 127.7, 127.4, 125.4, 125.3, 125.2, 117.2, 88.8, 81.9, 52.3, 36.8, 32.9, 21.3; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -62.50; **HRMS (ESI)** calcd for $C_{30}H_{27}F_3NO_3S$ $[M+H]^+$: 538.1658; found: 538.1678.

(*E*)-*N*-(2-(4-fluorobenzylidene)pent-4-en-1-yl)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1c)



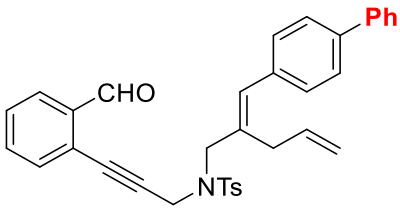
The title compound was prepared according to general procedure A in 43% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a pale-yellow solid, mp 87–90 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.90 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.51 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.26–7.20 (m, 5H), 7.01 (t, *J* = 8.7 Hz, 2H), 6.60 (s, 1H), 5.96–5.90 (m, 1H), 5.25–5.14 (m, 2H), 4.39 (s, 2H), 3.97 (s, 2H), 3.06 (d, *J* = 5.9 Hz, 2H), 2.26 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.6, 162.7, 161.1, 143.9, 135.8 (d, *J* = 1.2 Hz), 134.5, 133.6, 133.4 (d, *J* = 9.2 Hz), 132.4 (d, *J* = 3.1 Hz), 130.2, 130.2, 129.6, 128.9, 127.7, 127.3, 125.5, 116.9, 115.3, 115.2, 88.9, 81.7, 52.5, 36.6, 32.7, 21.3; **HRMS (ESI)** calcd for $C_{29}H_{27}FNO_3S$ $[M+H]^+$: 488.1690; found: 488.1695.

(*E*)-*N*-(2-(4-bromobenzylidene)pent-4-en-1-yl)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1d)



The title compound was prepared according to general procedure A in 35% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a yellow solid, mp 126–127 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.89 (s, 1H), 7.84 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.50 (td, *J* = 7.6, 1.4 Hz, 1H), 7.47–7.40 (m, 3H), 7.21 (d, *J* = 8.0 Hz, 3H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.57 (s, 1H), 5.95–5.88 (m, 1H), 5.22–5.14 (m, 2H), 4.39 (s, 2H), 3.97 (s, 2H), 3.05 (d, *J* = 6.0 Hz, 2H), 2.26 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.6, 143.9, 135.8, 135.3, 134.3, 134.3, 133.6, 133.4, 131.4, 130.1, 129.9, 129.6, 128.9, 127.7, 127.3, 125.5, 121.2, 117.1, 88.9, 81.8, 52.4, 36.7, 32.8, 21.3; **HRMS (ESI)** calcd for $C_{29}H_{27}BrNO_3S$ $[M+H]^+$: 548.0890; found: 548.0909.

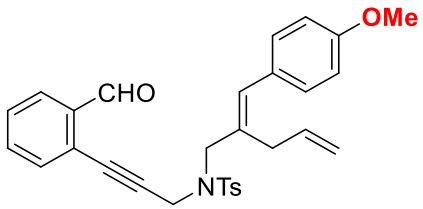
(*E*)-*N*-(2-([1,1'-biphenyl]-4-ylmethylene)pent-4-en-1-yl)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1e)



The title compound was prepared according to general procedure A in 50% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to afford the product as a pale-yellow solid, mp 100–102 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.94 (s, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.45–7.42 (m, 3H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.24 (t, *J* = 7.9 Hz, 3H), 6.68 (s, 1H), 6.03–5.96 (m, 1H), 5.26 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.21 (d, *J* = 10.1 Hz, 1H), 4.43 (s, 2H), 4.02 (s, 2H), 3.16 (d, *J* = 6.0 Hz, 2H), 2.27 (s, 3H); **^{13}C**

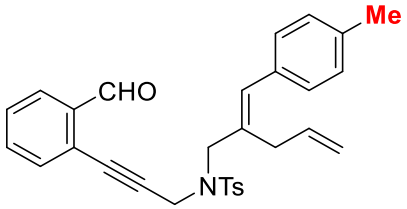
NMR (150 MHz, $CDCl_3$) δ 190.6, 143.9, 140.5, 139.9, 135.8, 135.8, 135.4, 134.6, 133.5, 133.5, 133.4, 130.9, 129.6, 128.9, 128.8, 128.8, 127.7, 127.3, 127.2, 126.9, 126.9, 125.6, 116.9, 89.0, 81.7, 52.7, 36.6, 32.9, 21.3; **HRMS (ESI)** calcd for $C_{35}H_{32}NO_3S$ $[M+H]^+$: 546.2097; found: 546.2120.

(*E*)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-*N*-(2-(4-methoxybenzylidene)pent-4-en-1-yl)-4-methylbenzenesulfonamide (1f)



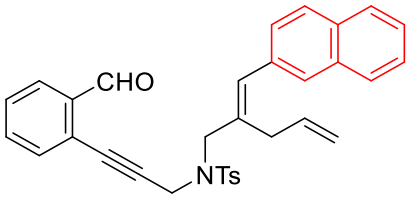
The title compound was prepared according to general procedure A in 38% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 11:1) to afford the product as a yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.91 (s, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.50 (td, *J* = 7.6, 0.9 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.22 (dd, *J* = 13.8, 8.1 Hz, 5H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.56 (s, 1H), 5.99–5.92 (m, 1H), 5.21 (dd, *J* = 17.2, 1.4 Hz, 1H), 5.17 (dd, *J* = 10.1, 1.1 Hz, 1H), 4.39 (s, 2H), 3.96 (s, 2H), 3.80 (s, 3H), 3.10 (d, *J* = 5.9 Hz, 2H), 2.25 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.6, 158.7, 143.8, 135.8, 135.7, 134.7, 133.5, 133.3, 131.4, 130.9, 129.8, 129.6, 128.9, 128.8, 127.6, 127.1, 125.6, 116.7, 113.7, 89.1, 81.6, 55.2, 52.7, 36.4, 32.6, 21.3; **HRMS (ESI)** calcd for $C_{30}H_{29}KNO_4S$ $[M+K]^+$: 538.1449; found: 538.1475.

(*E*)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methyl-*N*-(2-(4-methylbenzylidene)pent-4-en-1-yl)benzenesulfonamide (1g)



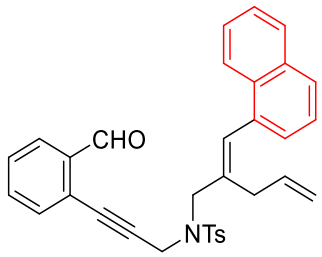
The title compound was prepared according to general procedure A in 36% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.91 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 7.7 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 6.9 Hz, 3H), 7.18 (d, *J* = 7.7 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 2H), 6.59 (s, 1H), 5.98–5.92 (m, 1H), 5.21 (d, *J* = 17.1 Hz, 1H), 5.17 (d, *J* = 10.1 Hz, 1H), 4.39 (s, 2H), 3.97 (s, 2H), 3.10 (d, *J* = 5.8 Hz, 2H), 2.34 (s, 3H), 2.26 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.6, 143.8, 137.1, 135.9, 135.8, 134.7, 133.6, 133.5, 133.4, 132.5, 131.4, 129.6, 129.0, 128.8, 128.5, 127.7, 127.1, 125.7, 116.9, 89.1, 81.6, 52.7, 36.5, 32.8, 21.3, 21.2; **HRMS (ESI)** calcd for $C_{30}H_{30}NO_3S$ $[M+H]^+$: 484.1941; found: 484.1962.

(*E*)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methyl-*N*-(2-(naphthalen-2-ylmethylene)pent-4-en-1-yl)benzenesulfonamide (1h)



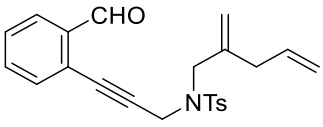
The title compound was prepared according to general procedure A in 33% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a brown solid, mp 128–129 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.95 (s, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.80 (t, *J* = 8.0 Hz, 5H), 7.76 (s, 1H),7.53–7.39 (m, 5H), 7.24 (t, *J* = 8.6 Hz, 3H), 6.79 (s, 1H), 6.05–5.98 (m, 1H), 5.27 (d, *J* = 17.1 Hz, 1H), 5.22 (d, *J* = 10.1 Hz, 1H), 4.45 (s, 2H), 4.05 (s, 2H), 3.18 (d, *J* = 5.7 Hz, 2H), 2.27 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.6, 143.9, 135.9, 135.8, 134.7, 133.9, 133.8, 133.6, 133.4, 133.2, 132.4, 131.3, 129.6, 128.8, 127.9, 127.8, 127.7, 127.6, 127.5, 127.2, 126.7, 126.2, 126.0, 125.6, 117.1, 89.1, 81.7, 52.6, 36.7, 32.9, 21.3; **HRMS (ESI)** calcd for $C_{33}H_{29}KNO_3S$ $[M+K]^+$: 558.1500; found: 558.1505.

(*E*)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methyl-*N*-(2-(naphthalen-1-ylmethylene)pent-4-en-1-yl)benzenesulfonamide (1i)



The title compound was prepared according to general procedure A in 29% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 15:1) to afford the product as a yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.00 (s, 1H), 8.00–7.95 (m, 1H), 7.88–7.85 (m, 4H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.51–7.45 (m, 4H), 7.43–7.40 (m, 2H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.27–7.24 (m, 2H), 7.16 (s, 1H), 5.96–5.89 (m, 1H), 5.21 (dd, *J* = 17.1, 1.6 Hz, 1H), 5.17 (dd, *J* = 10.1, 1.4 Hz, 1H), 4.58 (s, 2H), 4.20 (s, 2H), 3.01 (d, *J* = 6.4 Hz, 2H), 2.29 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.3, 143.8, 135.6, 135.5, 135.1, 134.9, 133.5, 133.4, 133.3, 133.2, 131.6, 129.5, 129.4, 128.7, 128.3, 127.7, 127.5, 127.1, 126.0, 125.9, 125.7, 125.2, 125.1, 124.3, 116.9, 88.8, 81.8, 51.7, 36.7, 32.9, 21.2; **HRMS (ESI)** calcd for $C_{33}H_{30}NO_3S$ $[M+H]^+$: 519.1868; found: 519.1872.

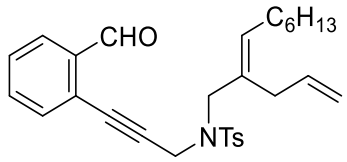
***N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methyl-*N*-(2-methylenepent-4-en-1-yl)benzenesulfonamide (1j)**



The title compound was prepared according to general procedure A in 24% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to afford the product as a yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.86 (s, 1H), 7.82 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.48 (td, *J* = 7.6, 1.3 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 3H), 5.88–5.81 (m, 1H), 5.13 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.11–5.04 (m, 3H), 4.33 (s, 2H), 3.84 (s,

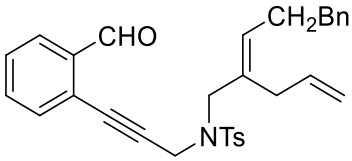
2H), 2.86 (d, *J* = 6.9 Hz, 2H), 2.24 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 190.6, 143.8, 141.5, 135.7, 134.9, 133.5, 133.3, 129.6, 128.8, 127.6, 127.0, 125.6, 117.2, 115.9, 88.9, 81.5, 51.5, 37.4, 36.4, 21.3; **HRMS (ESI)** calcd for $C_{23}H_{23}KNO_3S$ $[M+K]^+$: 432.1030; found: 432.1039.

(*E*)-*N*-(2-allylnon-2-en-1-yl)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1k)



The title compound was prepared according to general procedure A in 23% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a yellow oil; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 9.86 (d, *J* = 0.7 Hz, 1H), 7.84 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.49 (td, *J* = 7.6, 1.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.20–7.12 m, 3H), 5.82–5.76 (m, 1H), 5.49 (t, *J* = 7.3 Hz, 1H), 5.12 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.04 (dd, *J* = 10.0, 1.6 Hz, 1H), 4.30 (s, 2H), 3.78 (s, 2H), 2.87 (d, *J* = 6.5 Hz, 2H), 2.23 (s, 3H), 2.08 (dd, *J* = 14.6, 7.3 Hz, 2H), 1.37–1.20 (m, 8H), 0.86 (dt, *J* = 10.4, 7.0 Hz, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 190.7, 143.7, 135.9, 135.8, 134.9, 133.5, 133.3, 133.1, 130.5, 129.5, 128.7, 127.7, 126.9, 125.8, 116.1, 89.3, 81.3, 52.6, 36.1, 32.2, 31.6, 29.4, 28.9, 27.9, 22.6, 21.3, 14.0; **HRMS (ESI)** calcd for $C_{29}H_{36}NO_3S$ $[M+H]^+$: 478.2410; found: 478.2429.

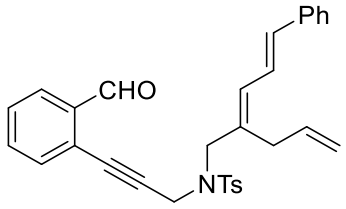
(*E*)-*N*-(2-allyl-5-phenylpent-2-en-1-yl)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1l)



The title compound was prepared according to general procedure A in 21% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum

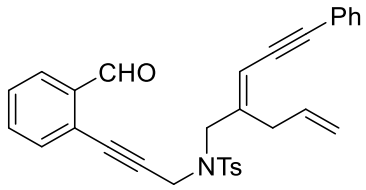
ether/EtOAc = 50:1 to 25:1) to afford the product as a colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.85 (s, 1H), 7.85 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.50 (td, *J* = 7.5, 1.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.25–7.22 (m, 2H), 7.20–7.07 (m, 6H), 5.74–5.64 (m, 1H), 5.50 (t, *J* = 7.2 Hz, 1H), 5.08 (dd, *J* = 17.1, 1.6 Hz, 1H), 5.02 (dd, *J* = 10.0, 1.4 Hz, 1H), 4.15 (s, 2H), 3.74 (s, 2H), 2.80 (d, *J* = 6.4 Hz, 2H), 2.68 (t, *J* = 7.4 Hz, 2H), 2.45 (d, *J* = 7.3 Hz, 1H), 2.41 (d, *J* = 7.3 Hz, 1H), 2.23 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 190.7, 143.7, 141.4, 135.8, 135.7, 134.7, 133.5, 133.3, 131.6, 131.5, 129.5, 128.7, 128.4, 128.3, 127.6, 127.0, 125.9, 125.8, 116.1, 89.2, 81.4, 52.4, 36.0, 35.5, 32.1, 29.6, 213; **HRMS (ESI)** calcd for $C_{31}H_{32}NO_3S$ $[M+H]^+$: 498.2097; found: 498.2099.

***N*-((2*E*,4*E*)-2-allyl-5-phenylpenta-2,4-dien-1-yl)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1m)**



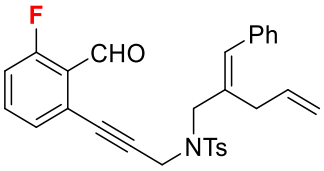
The title compound was prepared according to general procedure A in 13% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to afford the product as a yellow solid, mp 120–121 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.91 (d, *J* = 0.5 Hz, 1H), 7.86 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.51 (td, *J* = 7.6, 1.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.25–7.20 (m, 4H), 7.01 (dd, *J* = 15.5, 11.0 Hz, 1H), 6.58 (d, *J* = 15.5 Hz, 1H), 6.27 (d, *J* = 11.0 Hz, 1H), 5.90–5.83 (m, 1H), 5.19 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.11 (dd, *J* = 10.0, 1.4 Hz, 1H), 4.34 (s, 2H), 3.92 (s, 2H), 3.11 (d, *J* = 6.5 Hz, 2H), 2.26 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.7, 143.8, 137.1, 135.9, 135.8, 134.7, 134.2, 133.6, 133.4, 133.4, 130.8, 129.6, 128.8, 128.6, 127.9, 127.7, 127.1, 126.5, 125.7, 123.8, 116.7, 89.1, 81.6, 52.6, 36.6, 32.9, 21.3; **HRMS (ESI)** calcd for $C_{31}H_{30}NO_3S$ $[M+H]^+$: 496.1941; found: 496.1944.

(*E*)-*N*-(2-allyl-5-phenylpent-2-en-4-yn-1-yl)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1n)



The title compound was prepared according to general procedure A in 9% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to afford the product as a yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.87 (s, 1H), 7.84 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.49 (td, *J* = 7.6, 1.3 Hz, 1H), 7.44–7.41 (m, 3H), 7.33–7.31 (m, 3H), 7.22 (t, *J* = 7.8 Hz, 3H), 5.94–5.88 (m, 1H), 5.83 (s, 1H), 5.25 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.13 (dd, *J* = 10.0, 1.3 Hz, 1H), 4.35 (s, 2H), 3.95 (s, 2H), 3.22 (d, *J* = 6.9 Hz, 2H), 2.26 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.4, 145.8, 143.9, 135.6, 135.5, 133.7, 133.4, 133.3, 131.3, 129.5, 128.8, 128.2, 127.5, 127.1, 125.2, 122.9, 117.3, 110.4, 94.4, 88.5, 85.7, 81.8, 50.9, 36.8, 35.3, 21.2; **HRMS (ESI)** calcd for $C_{31}H_{28}NO_3S$ $[M+H]^+$: 494.1784; found: 494.1802.

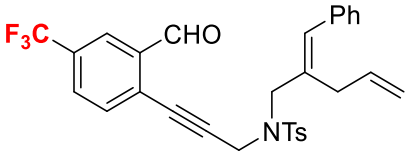
(*E*)-*N*-(2-benzylidenepent-4-en-1-yl)-*N*-(3-(3-fluoro-2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1o)



The title compound was prepared according to general procedure A in 43% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to afford the product as a colorless solid, mp 108–110 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.08 (s, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.46–7.42 (m, 1H), 7.35–7.31 (m, 2H), 7.29 (d, *J* = 7.4 Hz, 2H), 7.26–7.23 (m, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.13–7.09 (m, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 6.70 (s, 1H), 5.98–5.92 (m, 1H), 5.21 (dd, *J* = 17.2, 1.3 Hz, 1H), 5.17 (d, *J* = 10.1 Hz, 1H), 4.39 (s, 2H), 4.02 (s, 2H),

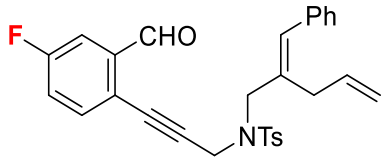
3.09 (d, *J* = 6.0 Hz, 2H), 2.28 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 186.9 (d, *J* = 3.6 Hz), 162.7 (d, *J* = 262.3 Hz), 143.6, 136.5, 135.9, 134.7, 134.6 (d, *J* = 10.5 Hz), 133.3, 131.5, 129.8 (d, *J* = 3.6 Hz), 129.5, 128.5, 128.3, 127.7, 127.2, 125.6 (d, *J* = 3.2 Hz), 124.2 (d, *J* = 8.2 Hz), 117.0, 116.9, 89.7, 81.8, 52.5, 36.5, 32.7, 21.3; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -116.60 (dd, *J* = 10.4, 5.4 Hz); **HRMS (ESI)** calcd for $C_{29}H_{26}FKNO_3S$ $[M+K]^+$: 526.1249; found: 526.1265.

(*E*)-*N*-(2-benzylidenepent-4-en-1-yl)-*N*-(3-(2-formyl-4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1p)



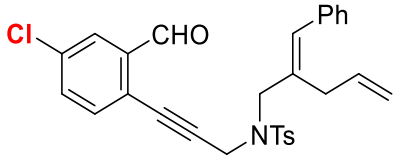
The title compound was prepared according to general procedure A in 49% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 11:1) to afford the product as a colorless solid, mp 130–132 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.90 (s, 1H), 8.11 (s, 1H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.30–7.25 (m, 3H), 7.23 (d, *J* = 8.1 Hz, 2H), 6.62 (s, 1H), 5.97–5.91 (m, 1H), 5.21 (d, *J* = 17.2 Hz, 1H), 5.17 (d, *J* = 10.1 Hz, 1H), 4.43 (s, 2H), 3.99 (s, 2H), 3.09 (d, *J* = 5.9 Hz, 2H), 2.28 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 189.1, 143.9, 136.3, 136.0, 135.8, 134.6, 133.9, 133.2, 131.5, 130.9 (d, *J* = 34.0 Hz), 129.8 (d, *J* = 3.5 Hz), 129.7, 128.7, 128.5, 128.3, 127.7, 127.3, 124.3 (d, *J* = 3.8 Hz), 124.0, 117.0, 92.1, 80.5, 52.7, 36.5, 32.7, 21.3; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -63.22; **HRMS (ESI)** calcd for $C_{30}H_{27}F_3NO_3S$ $[M+H]^+$: 538.1658; found: 538.1664.

(*E*)-*N*-(2-benzylidenepent-4-en-1-yl)-*N*-(3-(4-fluoro-2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1q)



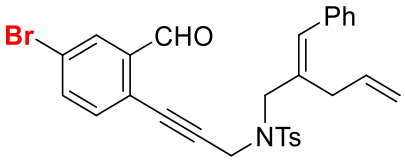
The title compound was prepared according to general procedure A in 51% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to afford the product as a pale-yellow solid, mp 87–89 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.83 (d, *J* = 3.1 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.52 (dd, *J* = 8.5, 2.6 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.28–7.26 (m, 3H), 7.25–7.19 (m, 4H), 6.61 (s, 1H), 5.97–5.90 (m, 1H), 5.20 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.17 (dd, *J* = 10.1, 1.5 Hz, 1H), 4.39 (s, 2H), 3.97 (s, 2H), 3.09 (d, *J* = 6.1 Hz, 2H), 2.30 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 189.4, 162.4 (d, *J* = 253.8 Hz), 143.9, 137.8 (d, *J* = 6.5 Hz), 136.3, 135.9, 135.4 (d, *J* = 7.7 Hz), 134.6, 133.3, 131.4, 129.6, 128.5, 128.3, 127.7, 127.3, 121.7 (d, *J* = 3.2 Hz), 121.2 (d, *J* = 22.6 Hz), 116.9, 113.6 (d, *J* = 22.9 Hz), 88.9, 80.6, 52.6, 36.5, 32.8, 21.4; **HRMS (ESI)** calcd for $C_{29}H_{27}FNO_3S$ $[M+H]^+$: 488.1690; found: 488.1705.

(*E*)-*N*-(2-benzylidenepent-4-en-1-yl)-*N*-(3-(4-chloro-2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1r)



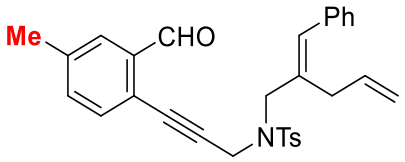
The title compound was prepared according to general procedure A in 54% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to afford the product as a pale-yellow solid, mp 121–123 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.82 (s, 1H), 7.81 (d, *J* = 2.1 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.46 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.26 (dd, *J* = 8.9, 5.1 Hz, 3H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 1H), 6.61 (s, 1H), 5.97–5.90 (m, 1H), 5.20 (dd, *J* = 17.2, 1.3 Hz, 1H), 5.17 (dd, *J* = 10.1 Hz, 1.0 Hz, 1H), 4.39 (s, 2H), 3.97 (s, 2H), 3.09 (d, *J* = 5.9 Hz, 2H), 2.30 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 189.3, 143.9, 136.9, 136.3, 135.9, 135.4, 134.6, 134.5, 133.6, 133.3, 131.4, 129.6, 128.5, 128.3, 127.7, 127.3, 127.1, 123.8, 116.9, 90.2, 80.6, 52.6, 36.5, 32.7, 21.4; **HRMS (ESI)** calcd for $C_{29}H_{27}ClNO_3S$ $[M+H]^+$: 504.1395; found: 504.1418.

(*E*)-*N*-(2-benzylidenepent-4-en-1-yl)-*N*-(3-(4-bromo-2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1s)



The title compound was prepared according to general procedure A in 35% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 30:1) to afford the product as a colorless solid, mp 130–132 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.80 (s, 1H), 7.96 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.28–7.25 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 1H), 6.61 (s, 1H), 5.97–5.90 (m, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 5.16 (d, *J* = 10.1 Hz, 1H), 4.39 (s, 2H), 3.97 (s, 2H), 3.08 (d, *J* = 5.9 Hz, 2H), 2.29 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 189.2, 143.9, 136.9, 136.5, 136.3, 135.8, 134.7, 134.6, 133.3, 131.4, 130.2, 129.6, 128.5, 128.3, 127.7, 127.3, 124.2, 123.4, 116.9, 90.4, 80.7, 52.6, 36.5, 32.7, 21.4; **HRMS (ESI)** calcd for $C_{29}H_{26}BrNNaO_3S$ $[M+Na]^+$: 570.0709; found: 570.0737.

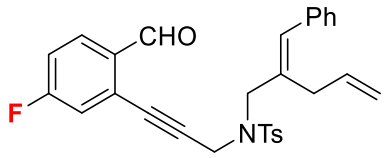
(*E*)-*N*-(2-benzylidenepent-4-en-1-yl)-*N*-(3-(2-formyl-4-methylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1t)



The title compound was prepared according to general procedure A in 48% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to afford the product as a yellow solid, mp 84–86 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.88 (s, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.65 (s, 1H), 7.34–7.30 (m, 3H), 7.30–7.28 (m, 2H), 7.27–7.23 (m, 2H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 1H), 6.64 (s, 1H), 5.98–5.92 (m, 1H), 5.22 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.17 (dd, *J* = 10.1, 1.4 Hz, 1H), 4.40 (s, 2H), 3.99 (s, 2H), 3.10 (d, *J* = 6.0 Hz, 2H), 2.39 (s, 3H), 2.28 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.8, 143.8, 139.3, 136.4, 135.8,

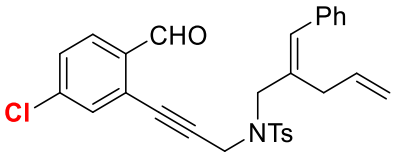
135.6, 134.6, 134.4, 133.3, 133.3, 131.3, 129.6, 128.5, 128.3, 127.6, 127.4, 127.2, 122.8, 116.9, 88.1, 81.7, 52.4, 36.5, 32.7, 21.3, 21.2; **HRMS (ESI)** calcd for $C_{30}H_{30}NO_3S$ $[M+H]^+$: 484.1941; found: 484.1919.

(*E*)-*N*-(2-benzylidenepent-4-en-1-yl)-*N*-(3-(5-fluoro-2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1u)



The title compound was prepared according to general procedure A in 48% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 20:1) to afford the product as a pale-yellow solid, mp 103–104 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.88 (s, 1H), 7.87 (dd, *J* = 8.7, 5.9 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 2H), 7.27–7.24 (m, 3H), 7.11 (td, *J* = 8.3, 2.3 Hz, 1H), 6.80 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.63 (s, 1H), 5.98–5.92 (m, 1H), 5.22 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.17 (dd, *J* = 10.1, 1.4 Hz, 1H), 4.41 (s, 2H), 3.99 (s, 2H), 3.10 (d, *J* = 6.0 Hz, 2H), 2.30 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 188.9, 165.3 (d, *J* = 257.2 Hz), 143.9, 136.2, 135.8, 134.5, 133.2, 132.5 (d, *J* = 2.8 Hz), 131.3, 129.9 (d, *J* = 10.1 Hz), 129.6, 128.4, 128.2, 127.8 (d, *J* = 10.9 Hz), 127.6, 127.2, 119.9 (d, *J* = 23.7 Hz), 116.9, 116.7 (d, *J* = 22.0 Hz), 90.2, 80.4, 52.6, 36.4, 32.7, 21.2; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -103.10 (dd, *J* = 14.4, 8.3 Hz); **HRMS (ESI)** calcd for $C_{29}H_{27}FNO_3S$ $[M+H]^+$: 488.1690; found: 488.1694.

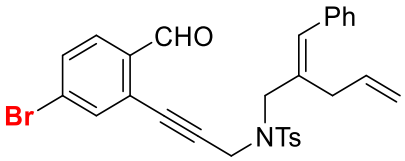
(*E*)-*N*-(2-benzylidenepent-4-en-1-yl)-*N*-(3-(5-chloro-2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1v)



The title compound was prepared according to general procedure A in 64% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum

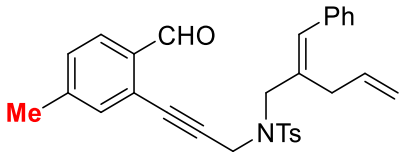
ether/EtOAc = 25:1 to 11:1) to afford the product as a colorless solid, mp 78–80 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.91 (s, 1H), 7.78 (t, *J* = 7.4 Hz, 3H), 7.38 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.30–7.22 (m, 5H), 7.10 (d, *J* = 2.0 Hz, 1H), 6.62 (s, 1H), 5.98–5.91 (m, 1H), 5.21 (dd, *J* = 17.2, 1.5 Hz, 1H), 5.17 (dd, *J* = 10.1, 1.3 Hz, 1H), 4.40 (s, 2H), 3.98 (s, 2H), 3.09 (d, *J* = 6.1 Hz, 2H), 2.32 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 189.3, 143.9, 139.9, 136.2, 135.8, 134.5, 134.1, 133.2, 133.0, 131.4, 129.6, 129.3, 128.5, 128.4, 128.3, 127.7, 127.2, 126.8, 116.9, 90.3, 80.3, 52.6, 36.4, 32.7, 21.3; **HRMS (ESI)** calcd for $C_{29}H_{27}ClNO_3S$ $[M+H]^+$: 504.1395; found: 504.1410.

(*E*)-*N*-(2-benzylidenepent-4-en-1-yl)-*N*-(3-(5-bromo-2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1w)



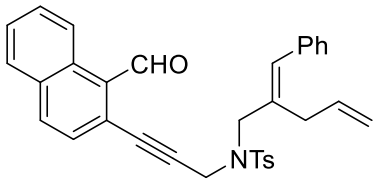
The title compound was prepared according to general procedure A in 63% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a colorless solid, mp 90–92 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.90 (s, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.56 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.30–7.22 (m, 6H), 6.61 (s, 1H), 5.98–5.91 (m, 1H), 5.21 (dd, *J* = 17.2, 1.4 Hz, 1H), 5.18 (dd, *J* = 10.1, 1.2 Hz, 1H), 4.40 (s, 2H), 3.97 (s, 2H), 3.09 (d, *J* = 6.0 Hz, 2H), 2.33 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 189.6, 144.0, 136.3, 136.0, 135.8, 134.6, 134.5, 133.2, 132.3, 131.5, 129.7, 128.6, 128.5, 128.5, 128.4, 127.8, 127.3, 126.9, 117.0, 90.5, 80.3, 52.6, 36.5, 32.8, 21.5; **HRMS (ESI)** calcd for $C_{29}H_{27}BrNO_3S$ $[M+H]^+$: 548.0890; found: 548.0887.

(*E*)-*N*-(2-benzylidenepent-4-en-1-yl)-*N*-(3-(2-formyl-5-methylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1x)



The title compound was prepared according to general procedure A in 20% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 11:1) to afford the product as a yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.85 (s, 1H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.4 Hz, 2H), 7.26 (d, *J* = 5.3 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 3H), 7.02 (s, 1H), 6.64 (s, 1H), 5.98–5.92 (m, 1H), 5.21 (dd, *J* = 17.2, 1.3 Hz, 1H), 5.17 (d, *J* = 10.1 Hz, 1H), 4.40 (s, 2H), 3.98 (s, 2H), 3.10 (d, *J* = 6.0 Hz, 2H), 2.37 (s, 3H), 2.28 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.3, 144.6, 143.8, 136.4, 135.8, 134.7, 133.7, 133.6, 133.3, 131.4, 129.8, 129.6, 128.5, 128.3, 127.7, 127.2, 125.6, 116.9, 88.5, 81.9, 52.5, 36.6, 32.7, 21.5, 21.4; **HRMS (ESI)** calcd for $C_{30}H_{30}NO_3S$ $[M+H]^+$: 484.1941; found: 484.1954.

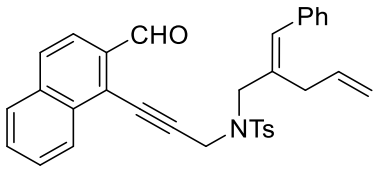
(*E*)-*N*-(2-benzylidenepent-4-en-1-yl)-*N*-(3-(1-formylnaphthalen-2-yl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1y)



The title compound was prepared according to general procedure A in 55% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 15:1) to afford the product as a colorless solid, mp 132–134 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.40 (s, 1H), 9.24 (d, *J* = 8.7 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 7.3 Hz, 2H), 7.26 (d, *J* = 5.3 Hz, 1H), 7.24–7.22 (m, 3H), 6.66 (s, 1H), 6.00–5.93 (m, 1H), 5.23 (d, *J* =

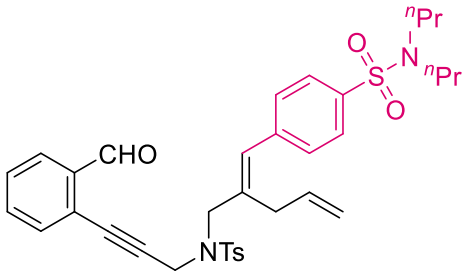
17.2 Hz, 1H), 5.19 (d, *J* = 10.0 Hz, 1H), 4.46 (s, 2H), 4.01 (s, 2H), 3.12 (d, *J* = 6.0 Hz, 2H), 2.21 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 193.2, 143.9, 136.4, 135.8, 134.6, 134.2, 133.3, 133.1, 131.5, 131.4, 129.9, 129.8, 129.7, 129.2, 128.9, 128.5, 128.3, 128.2, 127.7, 127.3, 125.5, 116.9, 91.5, 82.9, 52.7, 36.7, 32.8, 21.3; **HRMS (ESI)** calcd for $C_{33}H_{30}NO_3S$ $[M+H]^+$: 520.1941; found: 520.1964.

(*E*)-*N*-(2-benzylidenepent-4-en-1-yl)-*N*-(3-(2-formylnaphthalen-1-yl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1z)



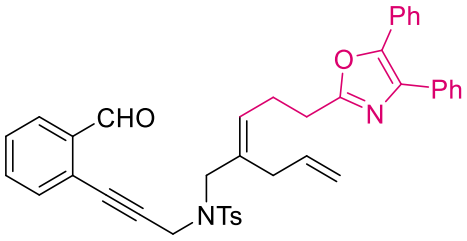
The title compound was prepared according to general procedure A in 44% overall yield over 4 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 15:1) to afford the product as a colorless solid, mp 116–118 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.11 (s, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.91–7.85 (m, 3H), 7.80 (d, *J* = 7.9 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.27–7.24 (m, 1H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.68 (s, 1H), 6.00–5.94 (m, 1H), 5.24 (d, *J* = 17.2 Hz, 1H), 5.18 (d, *J* = 10.1 Hz, 1H), 4.60 (s, 2H), 4.08 (s, 2H), 3.14 (d, *J* = 5.9 Hz, 2H), 2.11 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.0, 143.9, 136.3, 135.7, 135.5, 134.6, 134.3, 133.3, 132.9, 131.4, 129.6, 129.3, 129.1, 128.5, 128.4, 128.3, 127.7, 127.5, 127.2, 126.8, 126.1, 121.7, 116.9, 95.1, 79.5, 52.7, 36.7, 32.7, 21.2; **HRMS (ESI)** calcd for $C_{33}H_{30}NO_3S$ $[M+H]^+$: 520.1941; found: 520.1939.

(*E*)-*N*-(2-(4-(*N*,*N*-dipropylsulfamoyl)benzylidene)pent-4-en-1-yl)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1aa)



The title compound was prepared according to general procedure A in 31% overall yield over 4 steps from probenecid derived aldehyde.[S7] It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 6:1) to afford the product as a pale-yellow solid, mp 113–114 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.89 (s, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.78–7.71 (m, 4H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 3H), 6.66 (s, 1H), 5.94–5.88 (m, 1H), 5.18 (d, *J* = 9.3 Hz, 1H), 5.16 (s, 1H), 4.39 (s, 2H), 3.99 (s, 2H), 3.07–3.05 (m, 6H), 2.24 (s, 3H), 1.60–1.48 (m, 4H), 0.86–0.83 (m, 6H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.5, 143.9, 140.4, 138.5, 136.2, 135.7, 135.6, 134.1, 133.5, 133.3, 129.6, 129.2, 128.9, 128.9, 127.6, 127.3, 126.9, 125.2, 88.7, 81.8, 52.3, 49.9, 36.8, 32.9, 21.9, 21.3, 11.1; **HRMS (ESI)** calcd for $C_{35}H_{41}N_2O_5S_2$ $[M+H]^+$: 633.2451; found: 633.2480.

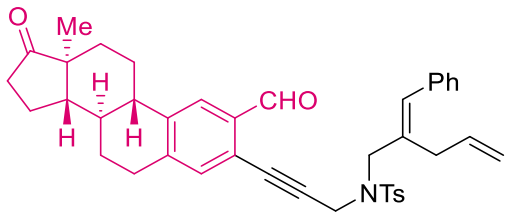
(*E*)-*N*-(2-allyl-5-(4,5-diphenyloxazol-2-yl)pent-2-en-1-yl)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1ab)



The title compound was prepared according to general procedure A in 32% overall yield over 4 steps from oxaprozin derived aldehyde.[S7] It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 9:1) to afford the product as a yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.80 (s, 1H), 7.79 (d, *J* = 7.7

Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.63–7.57 (m, 2H), 7.56–7.51 (m, 2H), 7.40 (td, *J* = 7.5, 1.2 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.33–7.26 (m, 6H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 1H), 5.80–5.74 (m, 1H), 5.61 (t, *J* = 7.3 Hz, 1H), 5.12 (dd, *J* = 17.1, 1.4 Hz, 1H), 5.02 (dd, *J* = 10.0, 0.9 Hz, 1H), 4.21 (s, 2H), 3.79 (s, 2H), 2.94–2.91 (m, 4H), 2.67 (d, *J* = 7.2 Hz, 1H), 2.65 (d, *J* = 7.2 Hz, 1H), 2.18 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.4, 162.3, 145.1, 143.6, 135.6, 135.5, 134.9, 134.4, 133.3, 133.2, 132.6, 132.2, 129.9, 129.3, 128.7, 128.5, 128.4, 128.3, 128.3, 127.8, 127.6, 127.4, 126.8, 126.2, 125.5, 116.1, 88.8, 81.2, 52.1, 35.9, 31.9, 27.8, 25.3, 21.1; **HRMS (ESI)** calcd for $C_{40}H_{37}N_2O_4S$ $[M+H]^+$: 641.2469; found: 641.2500.

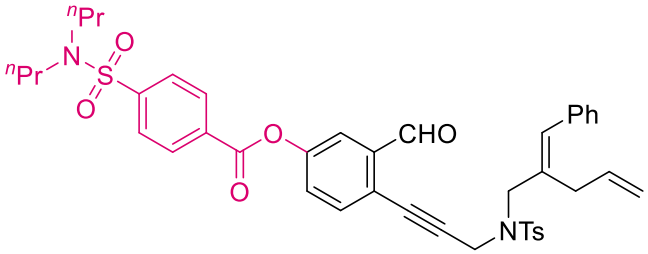
***N*-(2-((*E*)-benzylidene)pent-4-en-1-yl)-*N*-(3-((8*R*,9*S*,13*S*,14*S*)-2-formyl-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl) prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1ac)**



The title compound was prepared according to general procedure B in 23% yield. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 9:1 to 4:1) to afford the product as a pale-yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.80 (s, 1H), 7.79 (s, 1H), 7.78 (d, *J* = 2.2 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.3 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 3H), 6.97 (s, 1H), 6.62 (s, 1H), 5.97–5.91 (m, 1H), 5.20 (dd, *J* = 17.2, 1.5 Hz, 1H), 5.16 (dd, *J* = 10.1, 1.3 Hz, 1H), 4.39 (s, 2H), 3.97 (s, 2H), 3.09 (d, *J* = 6.0 Hz, 2H), 2.98–2.83 (m, 2H), 2.55–2.48 (m, 2H), 2.30 (s, 4H), 2.20–2.11 (m, 1H), 2.11– 2.03 (m, 2H), 2.03–1.97 (m, 1H), 1.70–1.42 (m, 7H), 0.91 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 220.1, 190.5, 143.7, 143.5, 141.3, 136.4, 135.9, 134.7, 133.7, 133.6, 133.3, 131.3, 129.6, 128.5, 128.3, 127.7, 127.2, 124.2, 122.9, 116.9, 87.9, 81.8, 52.5, 50.3, 47.8, 44.2, 37.6, 36.6, 35.7, 32.7, 31.3, 29.4, 25.9, 25.4, 21.5,

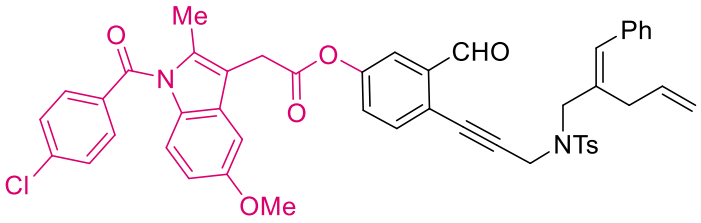
21.4, 13.7; **HRMS (ESI)** calcd for $C_{41}H_{43}NNaO_4S$ $[M+Na]^+$: 668.2805; found: 668.2827.

(*E*)-4-(3-((*N*-(2-benzylidenepent-4-en-1-yl)-4-methylphenyl)sulfonamido)prop-1-yn-1-yl)-3-formylphenyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (1ad)



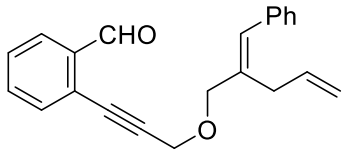
The title compound was prepared according to general procedure C in 20% overall yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 9:1 to 5:1) to afford the product as a yellow solid, mp 56–58 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.89 (s, 1H), 8.30 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 2.4 Hz, 1H), 7.40 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.34–7.30 (m, 3H), 7.28 (d, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 3H), 6.63 (s, 1H), 5.98–5.91 (m, 1H), 5.21 (dd, *J* = 17.2, 1.4 Hz, 1H), 5.17 (dd, *J* = 10.1, 1.2 Hz, 1H), 4.41 (s, 2H), 3.99 (s, 2H), 3.15–3.12 (m, 4H), 3.09 (d, *J* = 6.0 Hz, 2H), 2.30 (s, 3H), 1.59–1.53 (m, 4H), 0.88 (t, *J* = 7.4 Hz, 7H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 189.4, 163.2, 150.7, 145.3, 143.9, 137.1, 136.3, 135.8, 134.7, 134.6, 133.2, 131.8, 131.3, 130.8, 129.6, 128.4, 128.3, 127.6, 127.2, 127.2, 127.0, 123.3, 120.0, 116.9, 89.5, 80.7, 52.6, 49.8, 36.5, 32.7, 21.8, 21.3, 11.1; **HRMS (ESI)** calcd for $C_{42}H_{44}N_2NaO_7S_2$ $[M+Na]^+$: 775.2482; found: 775.2496.

(*E*)-4-(3-((*N*-(2-benzylidenepent-4-en-1-yl)-4-methylphenyl)sulfonamido)prop-1-yn-1-yl)-3-formylphenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl) acetate (1ae)



The title compound was prepared according to general procedure C in 25% overall yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 9:1 to 5:1) to afford the product as a yellow solid, mp 64–66 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.83 (s, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.54 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.28 (s, 1H), 7.27 (s, 1H), 7.23 (d, *J* = 1.3 Hz, 3H), 7.22 (s, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 6.89 (d, *J* = 9.0 Hz, 1H), 6.71 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.61 (s, 1H), 5.97–5.91 (m, 1H), 5.20 (dd, *J* = 17.2, 1.5 Hz, 1H), 5.17 (dd, *J* = 10.1, 1.3 Hz, 1H), 4.39 (s, 2H), 3.97 (s, 2H), 3.92 (s, 2H), 3.85 (s, 3H), 3.09 (d, *J* = 6.0 Hz, 2H), 2.46 (s, 3H), 2.28 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 189.5, 168.7, 168.3, 156.1, 150.8, 143.9, 139.4, 137.0, 136.4, 136.3, 135.8, 134.6, 134.6, 133.7, 133.3, 131.3, 131.2, 130.8, 130.3, 129.6, 129.2, 128.5, 128.3, 127.7, 127.3, 127.0, 123.1, 119.9, 116.9, 115.0, 111.7, 111.3, 101.2, 89.3, 80.8, 55.7, 52.6, 36.5, 32.7, 30.4, 21.4, 13.4; **HRMS (ESI)** calcd for $C_{48}H_{41}ClN_2NaO_7S$ $[M+Na]^+$: 847.2215; found: 847.2217.

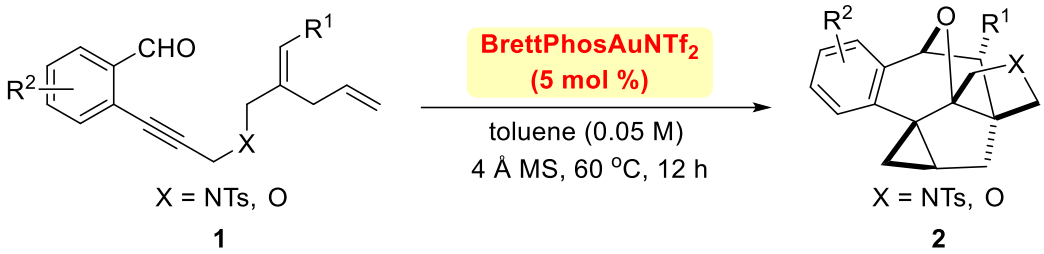
(*E*)-2-(3-((2-benzylidenepent-4-en-1-yl)oxy)prop-1-yn-1-yl)benzaldehyde (1af)



The title compound was prepared according to general procedure D in 49% overall yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1 to 25:1) to afford the product as a yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.55 (s, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.59–7.57 (m, 1H), 7.56 (td, *J* = 7.4, 1.2 Hz, 1H), 7.47–7.44 (m, 1H), 7.35–7.31 (m, 4H), 7.26–7.24 (m, 1H), 6.72 (s, 1H), 5.97–5.90 (m, 1H), 5.18–5.13 (m, 2H), 4.49 (s, 2H), 4.23 (s, 2H), 3.09 (d, *J* = 6.1 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.4, 136.8, 136.1, 135.6, 135.3, 133.7,

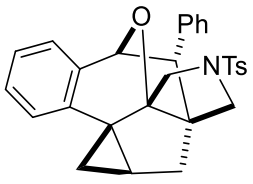
133.5, 129.5, 128.8, 128.6, 128.2, 127.2, 126.9, 126.1, 116.4, 92.5, 81.9, 73.6, 57.8, 33.0; **HRMS (ESI)** calcd for $C_{22}H_{21}O_2$ $[M+H]^+$: 317.1536; found: 317.1542.

3. General procedure for BrettPhosAuNTf$_2$-catalyzed *6-endo-dig* oxycyclization/[3 + 2] cycloaddition/cyclopropanation



To a solution of **1** (0.15 mmol) and 4 Å MS (150 mg) in anhydrous toluene (3 mL) was added BrettPhosAuNTf$_2$ (5 mol %) under an argon atmosphere. The reaction mixture was stirred at 60 °C for 12 h. Upon completion, the reaction mixture was cooled down to room temperature and filtered through celite, washed with CH_2Cl_2 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether: EtOAc) to give the product **2**.

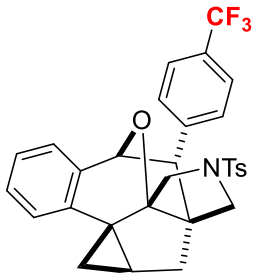
(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-12-phenyl-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrole (2a)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 11:1) to give the product **2a** in 87% yield (61 mg); colorless solid, mp 153–155 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.31–7.26 (m, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.12–7.10 (m, 3H), 7.06 (d, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 7.4 Hz, 2H), 5.42 (d, *J* = 7.3 Hz, 1H), 3.89 (d, *J* = 7.3 Hz, 1H), 3.74

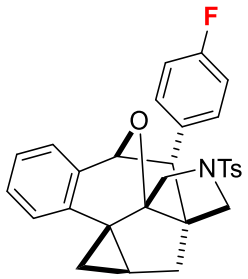
(dd, *J* = 10.4, 7.1 Hz, 2H), 3.30 (d, *J* = 11.6 Hz, 1H), 2.88 (d, *J* = 9.2 Hz, 1H), 2.45 (s, 3H), 2.15 (dd, *J* = 8.8, 6.8 Hz, 1H), 1.44 (t, *J* = 6.0 Hz, 1H), 1.40 (dd, *J* = 14.2, 7.2 Hz, 1H), 1.32 (dd, *J* = 14.2, 4.0 Hz, 1H), 0.84–0.71 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.6, 142.0, 137.5, 136.6, 133.1, 129.7, 129.1, 128.4, 128.2, 127.6, 127.0, 126.5, 124.6, 120.3, 99.0, 84.3, 76.7, 57.7, 57.6, 52.2, 36.7, 34.0, 29.9, 21.5, 21.3; **HRMS (ESI)** calcd for $C_{29}H_{28}NO_3S$ $[M+H]^+$: 470.1784; found: 470.1795.

(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-3-tosyl-12-(4-(trifluoromethyl)phenyl)-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrole (2b)**



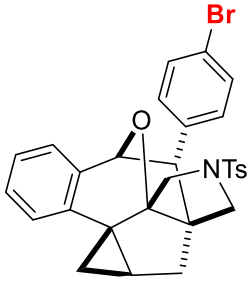
Column chromatography (petroleum ether/EtOAc = 20:1 to 9:1) to give the product **2b** in 60% yield (48 mg); colorless solid, mp 200–201 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.36 (t, *J* = 8.2 Hz, 4H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 2H), 5.43 (d, *J* = 7.3 Hz, 1H), 3.92 (d, *J* = 7.3 Hz, 1H), 3.75 (d, *J* = 3.5 Hz, 1H), 3.73 (s, 1H), 3.30 (d, *J* = 11.7 Hz, 1H), 2.88 (d, *J* = 9.2 Hz, 1H), 2.45 (s, 3H), 2.18–2.15 (m, 1H), 1.46 (t, *J* = 6.0 Hz, 1H), 1.35 (d, *J* = 5.4 Hz, 2H), 0.77–0.73 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.78, 141.4, 140.9, 137.4, 133.1, 129.8, 129.5, 129.2, 128.8, 127.6, 126.5, 125.2, 125.1, 124.8, 123.0, 120.5, 99.2, 84.1, 57.5, 57.4, 52.1, 36.7, 33.9, 29.8, 21.6, 21.4; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -62.70; **HRMS (ESI)** calcd for $C_{30}H_{27}F_3NO_3S$ $[M+H]^+$: 538.1658; found: 538.1649.

(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-12-(4-fluorophenyl)-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrole (2c)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 11:1) to give the product **2c** in 91% yield (66 mg); colorless solid, mp 188–190 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.31–7.26 (m, 1H), 7.10 (t, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 7.3 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.79 (t, *J* = 8.3 Hz, 2H), 6.60–6.51 (m, 2H), 5.39 (d, *J* = 7.2 Hz, 1H), 3.86 (d, *J* = 7.2 Hz, 1H), 3.74–3.70 (m, 2H), 3.29 (d, *J* = 11.6 Hz, 1H), 2.84 (d, *J* = 9.1 Hz, 1H), 2.44 (s, 3H), 2.15 (t, *J* = 7.8 Hz, 1H), 1.44 (t, *J* = 5.8 Hz, 1H), 1.38 (dd, *J* = 14.1, 7.1 Hz, 1H), 1.33 (dd, *J* = 14.3, 3.5 Hz, 1H), 0.78–0.73 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 161.7 (d, *J* = 246.7 Hz), 143.7, 141.6, 137.5, 133.1, 132.2 (d, *J* = 3.4 Hz), 130.7 (d, *J* = 7.7 Hz), 129.8, 128.6, 127.6, 126.5, 124.7, 120.4, 115.1 (d, *J* = 21.0 Hz), 99.1, 84.3, 76.6, 57.5, 56.9, 52.2, 36.7, 33.9, 29.8, 21.6, 21.3; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -115.16; **HRMS (ESI)** calcd for $C_{29}H_{26}FKNO_3S$ $[M+K]^+$: 526.1249; found: 526.1263.

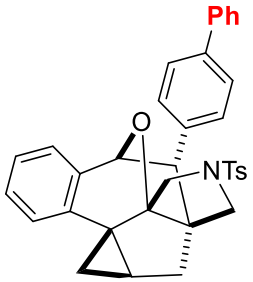
(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-12-(4-bromophenyl)-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrole (2d)**



Column chromatography (petroleum ether/EtOAc = 50:1 to 20:1) to give the product **2d** in 77% yield (63 mg); colorless solid, mp 209–210 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.92 (d, *J* =

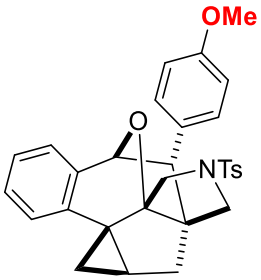
7.6 Hz, 1H), 6.46 (d, *J* = 8.4 Hz, 2H), 5.39 (d, *J* = 7.3 Hz, 1H), 3.81 (d, *J* = 7.3 Hz, 1H), 3.71 (dd, *J* = 12.2, 10.7 Hz, 2H), 3.28 (d, *J* = 11.7 Hz, 1H), 2.83 (d, *J* = 9.2 Hz, 1H), 2.44 (s, 3H), 2.15 (dd, *J* = 8.6, 7.2 Hz, 1H), 1.44 (t, *J* = 6.0 Hz, 1H), 1.39 (dd, *J* = 14.3, 7.1 Hz, 1H), 1.34 (dd, *J* = 14.3, 4.1 Hz, 1H) 0.76–0.72 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.7, 141.5, 137.5, 135.6, 133.1, 131.4, 130.9, 129.8, 128.7, 127.6, 126.5, 124.7, 121.1, 120.4, 99.1, 84.2, 76.7, 57.5, 57.1, 52.2, 36.7, 34.0, 29.8, 21.6, 21.4; **HRMS (ESI)** calcd for $C_{29}H_{27}BrNO_3S$ $[M+H]^+$: 548.0890; found: 548.0905.

(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-12-([1,1'-biphenyl]-4-yl)-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrole (2e)**



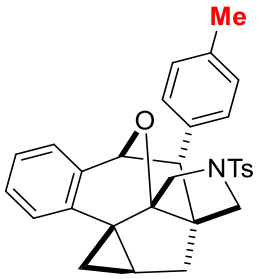
Column chromatography (petroleum ether/EtOAc = 20:1 to 11:1) to give the product **2e** in 62% yield (51 mg); colorless solid, mp 143–145 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 4H), 7.32–7.29 (m, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 6.8 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 8.3 Hz, 2H), 5.45 (d, *J* = 7.3 Hz, 1H), 3.93 (d, *J* = 7.3 Hz, 1H), 3.77 (s, 1H), 3.75 (d, *J* = 1.8 Hz, 1H), 3.32 (d, *J* = 11.6 Hz, 1H), 2.90 (d, *J* = 9.2 Hz, 1H), 2.46 (s, 3H), 2.17 (dd, *J* = 8.8, 6.9 Hz, 1H), 1.51–1.45 (m, 2H), 1.37–1.34 (m, 1H), 0.86–0.82 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.6, 141.9, 140.3, 139.8, 137.5, 135.6, 133.1, 129.8, 129.6, 128.7, 128.5, 127.6, 127.3, 126.8, 126.8, 126.5, 124.6, 120.3, 99.1, 84.3, 57.6, 57.5, 52.2, 36.7, 34.1, 29.9, 21.6, 21.4; **HRMS (ESI)** calcd for $C_{35}H_{32}NO_3S$ $[M+H]^+$: 546.2097; found: 546.2109.

(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-12-(4-methoxyphenyl)-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrole (2f)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 7:1) to give the product **2f** in 56% yield (42 mg); colorless solid, mp 122–125 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.28–7.25 (m, 1H), 7.10 (td, *J* = 7.4, 0.8 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 8.8 Hz, 2H), 6.50 (d, *J* = 8.7 Hz, 2H), 5.38 (d, *J* = 7.4 Hz, 1H), 3.83 (d, *J* = 7.4 Hz, 1H), 3.73–3.69 (m, 5H), 3.28 (d, *J* = 11.6 Hz, 1H), 2.83 (d, *J* = 9.2 Hz, 1H), 2.44 (s, 3H), 2.14 (dd, *J* = 8.9, 6.8 Hz, 1H), 1.44–1.40 (m, 2H), 1.31 (dd, *J* = 14.2, 4.0 Hz, 1H), 0.80–0.76 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 158.5, 143.6, 142.1, 137.6, 133.2, 130.3, 129.8, 128.4, 128.4, 127.6, 126.5, 124.6, 120.3, 113.6, 99.1, 84.4, 76.6, 57.6, 57.1, 55.1, 52.3, 36.7, 34.1, 29.9, 21.6, 21.3; **HRMS (ESI)** calcd for $C_{30}H_{30}NO_4S$ $[M+H]^+$: 500.1890; found: 500.1876.

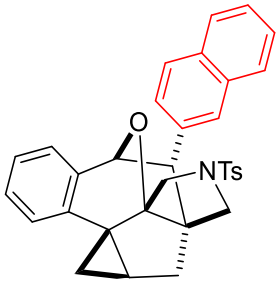
(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-12-(*p*-tolyl)-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrole (2g)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 9:1) to give the product **2g** in 81% yield (58 mg); colorless solid, mp 143–144 ℃; **^{1}H NMR (600 MHz,**

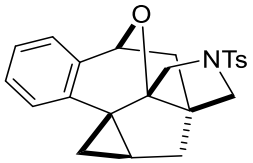
$CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.28–7.26 (m, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.93–6.91 (m, 3H), 6.48 (d, *J* = 8.0 Hz, 2H), 5.39 (d, *J* = 7.3 Hz, 1H), 3.85 (d, *J* = 7.3 Hz, 1H), 3.72 (dd, *J* = 13.9, 10.4 Hz, 2H), 3.29 (d, *J* = 11.6 Hz, 1H), 2.85 (d, *J* = 9.2 Hz, 1H), 2.45 (s, 3H), 2.24 (s, 3H), 2.15 (dd, *J* = 8.7, 7.0 Hz, 1H), 1.44–1.40 (m, 2H), 1.31 (dd, *J* = 14.2, 4.0 Hz, 2H), 0.81–0.77 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.6, 142.1, 137.5, 136.7, 133.4, 133.1, 129.7, 129.1, 128.9, 128.4, 127.6, 126.5, 124.5, 120.3, 99.1, 84.4, 76.6, 57.6, 57.5, 52.3, 36.7, 34.1, 29.9, 21.5, 21.3, 20.8; **HRMS (ESI)** calcd for $C_{30}H_{29}KNO_3S$ $[M+K]^+$: 522.1500; found: 522.1522.

(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-12-(naphthalen-2-yl)-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrole (2h)**



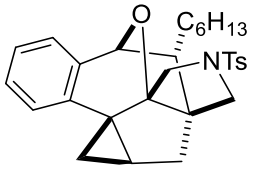
Column chromatography (petroleum ether/EtOAc = 20:1 to 11:1) to give the product **2h** in 79% yield (62 mg); colorless solid, mp 181–184 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.42–7.33 (m, 6H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 7.3 Hz, 1H), 7.01 (s, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 5.50 (d, *J* = 7.3 Hz, 1H), 4.06 (d, *J* = 7.3 Hz, 1H), 3.80 (d, *J* = 9.1 Hz, 1H), 3.76 (d, *J* = 11.5 Hz, 1H), 3.34 (d, *J* = 11.6 Hz, 1H), 2.95 (d, *J* = 9.1 Hz, 1H), 2.46 (s, 3H), 2.17 (dd, *J* = 8.6, 7.1 Hz, 1H), 1.45 (t, *J* = 6.1 Hz, 1H), 1.40 (dd, *J* = 14.2, 7.2 Hz, 1H), 1.32 (dd, *J* = 14.3, 4.1 Hz, 1H), 0.82–0.78 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.7, 142.2, 137.7, 134.1, 133.2, 132.9, 132.3, 129.8, 128.7, 127.8, 127.7, 127.7, 127.4, 126.6, 126.1, 125.9, 124.7, 120.4, 99.3, 84.34, 57.7, 52.3, 36.8, 34.3, 30.0, 21.6, 21.5; **HRMS (ESI)** calcd for $C_{33}H_{29}NNaO_3S$ $[M+Na]^+$: 542.1760; found: 542.1784.

(1a*S,4a*S**,6*S**,10b*R**,11a*R**)-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrole (2j)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 7:1) to give the product **2j** in 93% yield (56 mg); colorless solid, mp 167–168 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.18–7.15 (m, 1H), 7.08–7.05 (m, 2H), 6.87 (d, *J* = 7.5 Hz, 1H), 5.15 (dd, *J* = 7.9, 1.4 Hz, 1H), 3.63 (d, *J* = 9.5 Hz, 1H), 3.59 (d, *J* = 11.8 Hz, 1H), 3.35 (d, *J* = 11.8 Hz, 1H), 2.76 (d, *J* = 9.5 Hz, 1H), 2.54 (dd, *J* = 13.4, 7.9 Hz, 1H), 2.43 (s, 3H), 2.21 (dd, *J* = 8.8, 6.9 Hz, 1H), 2.03 (dd, *J* = 13.7, 7.1 Hz, 1H), 1.74 (dd, *J* = 13.4, 1.6 Hz, 1H), 1.42 (dd, *J* = 6.6, 5.3 Hz, 1H), 1.39 (dd, *J* = 13.7, 4.4 Hz, 1H), 1.08–1.04 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.5, 143.4, 137.8, 133.6, 129.6, 127.7, 127.4, 124.4, 123.9, 120.3, 97.4, 79.7, 72.1, 54.7, 50.7, 41.1, 34.2, 34.1, 32.1, 22.5, 21.5; **HRMS (ESI)** calcd for $C_{23}H_{23}KNO_3S$ $[M+K]^+$: 432.1030; found: 432.1049.

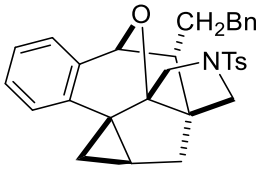
(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-12-hexyl-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrole (2k)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 11:1) to give the product **2k** in 77% yield (56 mg); colorless solid, mp 114–115 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 6.8 Hz, 1H), 7.09–7.04 (m, 2H), 6.83 (d, *J* = 7.5 Hz, 1H), 5.21 (d, *J* = 7.3 Hz, 1H), 3.64 (t, *J* = 10.6 Hz, 2H), 3.27 (d, *J* = 11.7 Hz, 1H), 2.67 (d, *J* = 9.4 Hz, 1H), 2.46–2.43 (m, 4H), 2.15–2.13 (m, 1H), 2.01 (dd, *J* = 14.2, 7.2 Hz, 1H), 1.43–1.40 (m, 2H), 1.29–1.10 (m, 10H),

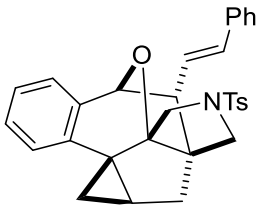
0.84 (t, *J* = 7.1 Hz, 4H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.4, 140.4, 137.9, 133.4, 129.6, 127.9, 127.5, 126.2, 124.1, 119.9, 98.5, 84.6, 74.2, 56.9, 51.6, 49.5, 35.4, 34.8, 31.5, 29.2, 29.0, 28.9, 28.2, 22.4, 22.2, 21.5, 13.9; **HRMS (ESI)** calcd for $C_{29}H_{35}KNO_3S$ $[M+K]^+$: 516.1969; found: 516.1993.

(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-12-phenethyl-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrole (2l)**



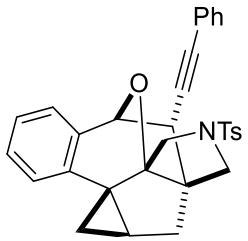
Column chromatography (petroleum ether/EtOAc = 20:1 to 9:1) to give the product **2l** in 67% yield (50 mg); colorless solid, mp 199–201 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.23–7.13 (m, 5H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 2H), 6.83 (d, *J* = 7.5 Hz, 1H), 5.28 (d, *J* = 7.2 Hz, 1H), 3.63 (dd, *J* = 10.4, 3.6 Hz, 2H), 3.28 (d, *J* = 11.7 Hz, 1H), 2.67 (d, *J* = 9.4 Hz, 1H), 2.64–2.59 (m, 1H), 2.54–2.49 (m, 1H), 2.41 (s, 3H), 2.12 (t, *J* = 7.7 Hz, 1H), 2.00 (dd, *J* = 14.3, 7.2 Hz, 1H), 1.59–1.53 (m, 1H), 1.41–1.38 (m, 2H), 1.15–1.08 (m, 1H), 0.82–0.78 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.4, 141.3, 139.9, 137.9, 133.4, 129.6, 128.4, 128.1, 128.1, 127.4, 126.2, 125.9, 124.1, 120.1, 98.5, 84.4, 74.2, 56.7, 51.5, 48.7, 35.3, 35.2, 34.7, 30.6, 28.9, 22.3, 21.5; **HRMS (ESI)** calcd for $C_{31}H_{31}NNaO_3S$ $[M+Na]^+$: 520.1917; found: 520.1934.

(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-12-((*E*)-styryl)-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrole (2m)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 11:1) to give the product **2m** in 53% yield (39 mg); colorless solid, mp 236–238 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.26–7.19 (m, 4H), 7.09 (d, *J* = 6.5 Hz, 1H), 7.06 (d, *J* = 7.3 Hz, 1H), 7.02 (d, *J* = 6.7 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.45 (d, *J* = 15.6 Hz, 1H), 5.35 (dd, *J* = 15.6, 10.2 Hz, 1H), 5.26 (d, *J* = 7.5 Hz, 1H), 3.68 (dd, *J* = 10.5, 8.2 Hz, 2H), 3.41–3.34 (m, 2H), 2.82 (d, *J* = 9.4 Hz, 1H), 2.44 (s, 3H), 2.22–2.18 (m, 1H), 2.07–2.02 (m, 1H), 1.47 (t, *J* = 6.3 Hz, 1H), 1.39 (dd, *J* = 14.2, 4.3 Hz, 1H), 0.91–0.84 m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.6, 140.4, 137.5, 136.6, 134.6, 133.4, 129.7, 128.5, 128.2, 127.6, 127.5, 126.5, 126.2, 125.9, 124.5, 120.1, 98.3, 84.4, 56.1, 53.8, 51.5, 35.4, 34.3, 29.3, 21.9, 21.6; **HRMS (ESI)** calcd for $C_{31}H_{30}NO_3S$ $[M+H]^+$: 496.1941; found: 496.1939.

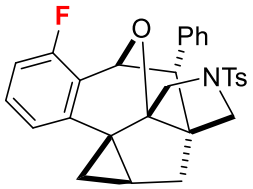
(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-12-(phenylethynyl)-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrole (2n)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 11:1) to give the product **2n** in 83% yield (62 mg); colorless solid, mp 225–228 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.23–7.08 (m, 6H), 6.90 (d, *J* = 7.8 Hz, 2H), 6.85 (d, *J* = 7.5 Hz, 1H), 5.41 (d, *J* = 7.5 Hz, 1H), 3.72 (d, *J* = 9.5 Hz, 1H), 3.67–3.65 (m, 2H), 3.38 (d, *J* = 11.8 Hz, 1H), 2.78 (d, *J* = 9.5 Hz, 1H), 2.44 (s, 3H), 2.41 (t, *J* = 7.1 Hz, 1H), 2.17 (t, *J* = 7.8 Hz, 1H), 1.44–1.37 (m, 2H), 1.26 (s,

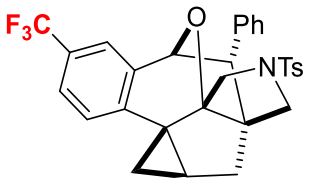
1H), 1.03–0.97 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.6, 140.4, 137.6, 133.5, 131.3, 129.7, 128.2, 128.1, 127.9, 127.5, 125.9, 124.2, 122.7, 119.9, 98.5, 86.1, 85.9, 83.9, 75.7, 55.3, 51.1, 43.5, 35.6, 34.5, 30.2, 22.2, 21.6; **HRMS (ESI)** calcd for $C_{31}H_{27}NNaO_3S$ $[M+Na]^+$: 516.1604; found: 516.1625.

(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-7-fluoro-12-phenyl-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrole (2o)**



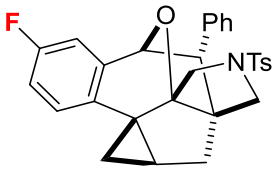
Column chromatography (petroleum ether/EtOAc = 20:1 to 11:1) to give the product **2o** in 62% yield (45 mg); colorless solid, mp 210–211 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.25–7.22 (m, 1H), 7.18–7.16 (m, 1H), 7.13 (t, *J* = 7.3 Hz, 2H), 6.83 (t, *J* = 8.6 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 7.3 Hz, 2H), 5.83 (d, *J* = 7.3 Hz, 1H), 3.90 (d, *J* = 7.4 Hz, 1H), 3.74 (d, *J* = 7.4 Hz, 1H), 3.72 (d, *J* = 4.9 Hz, 1H), 3.27 (d, *J* = 11.6 Hz, 1H), 2.83 (d, *J* = 9.2 Hz, 1H), 2.45 (s, 3H), 2.14 (dd, *J* = 8.9, 6.9 Hz, 1H), 1.48 (t, *J* = 6.1 Hz, 1H), 1.46 (t, *J* = 7.3 Hz, 1H), 1.36 (dd, *J* = 14.3, 4.0 Hz, 1H), 0.85–0.81 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 158.7 (d, *J* = 246.8 Hz), 143.8, 140.3, 136.3, 132.9, 129.8, 129.6 (d, *J* = 8.3 Hz), 128.9 (d, *J* = 16.0 Hz), 128.5, 128.5, 127.6, 127.3, 116.0, 111.8 (d, *J* = 21.6 Hz), 99.2, 57.7, 57.3, 52.3, 36.9, 34.3, 29.9, 21.7, 21.6; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -123.22 (dd, *J* = 9.0, 5.7 Hz); **HRMS (ESI)** calcd for $C_{29}H_{27}FNO_3S$ $[M+H]^+$: 488.1690; found: 488.1699.

(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-12-phenyl-3-tosyl-8-(trifluoromethyl)-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrole (2p)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 9:1) to give the product **2p** in 64% yield (51 mg); colorless solid, mp 151–152 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.30 (s, 1H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.55 (d, *J* = 7.4 Hz, 2H), 5.45 (d, *J* = 7.3 Hz, 1H), 3.91 (d, *J* = 7.4 Hz, 1H), 3.75 (d, *J* = 11.7 Hz, 1H), 3.73 (d, *J* = 9.2 Hz, 1H), 3.28 (d, *J* = 11.7 Hz, 1H), 2.84 (d, *J* = 9.2 Hz, 1H), 2.45 (s, 3H), 2.20 (dd, *J* = 8.9, 7.0 Hz, 1H), 1.54 (d, *J* = 6.4 Hz, 1H), 1.44 (dd, *J* = 14.3, 7.2 Hz, 1H), 1.38 (dd, *J* = 14.3, 4.1 Hz, 1H), 0.90–0.86 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.8, 142.7, 142.1, 136.0, 135.9, 133.0, 130.5, 129.8, 128.9, 128.5, 127.6, 127.4, 125.6 (d, *J* = 3.5 Hz), 123.1 (d, *J* = 3.5 Hz), 120.7, 99.3, 84.0, 76.9, 57.9, 57.6, 52.2, 37.2, 34.9, 29.8, 21.8, 21.6; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -62.03; **HRMS (ESI)** calcd for $C_{30}H_{26}F_3KNO_3S$ $[M+K]^+$: 576.1217; found: 576.1244.

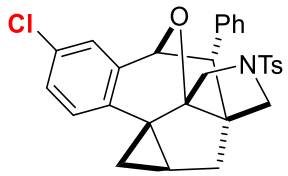
(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-8-fluoro-12-phenyl-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrole (2q)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 9:1) to give the product **2q** in 83% yield (60 mg); colorless solid, mp 195–198 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.19–7.16 (m, 1H), 7.14–7.11 (m, 2H), 6.97 (td, *J* = 8.7, 2.6 Hz, 1H), 6.87 (dd, *J* = 8.4, 5.2 Hz, 1H), 6.81 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.61–6.60 (m, 2H), 5.36 (d, *J* = 7.4 Hz, 1H), 3.87 (d, *J* = 7.4 Hz, 1H), 3.73 (d, *J* = 5.0 Hz, 1H), 3.71 (d, *J* = 2.5 Hz, 1H), 3.27 (d, *J* = 11.7 Hz, 1H), 2.84

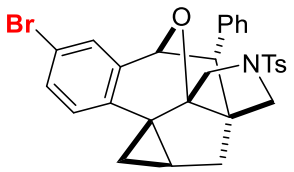
(d, *J* = 9.2 Hz, 1H), 2.45 (s, 3H), 2.11 (dd, *J* = 8.9, 6.9 Hz, 1H), 1.43 (dd, *J* = 6.4, 5.4 Hz, 1H), 1.40 (dd, *J* = 14.3, 7.2 Hz, 1H), 1.31 (dd, *J* = 14.3, 4.1 Hz, 1H), 0.80–0.76 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 160.2 (d, *J* = 244.4 Hz), 144.1 (d, *J* = 6.6 Hz), 143.7, 136.2, 133.3 (d, *J* = 2.6 Hz), 133.1, 129.8, 129.1, 128.4, 127.6, 127.3, 121.8 (d, *J* = 8.1 Hz), 114. (d, *J* = 21.5 Hz), 113.9 (d, *J* = 22.3 Hz), 99.1, 83.9, 76.7, 57.8, 57.6, 52.1, 36.2, 33.8, 29.8, 21.6, 21.4; **HRMS (ESI)** calcd for $C_{29}H_{26}FKNO_3S$ $[M+K]^+$: 526.1249; found: 526.1255.

(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-8-chloro-12-phenyl-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrole (2r)**



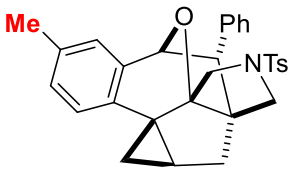
Column chromatography (petroleum ether/EtOAc = 20:1 to 11:1) to give the product **2r** in 81% yield (62 mg); colorless solid, mp 211–212 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.26–7.24 (m, 1H), 7.19–7.13 (m, 3H), 7.06 (s, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 6.60 (d, *J* = 7.4 Hz, 2H), 5.35 (d, *J* = 7.3 Hz, 1H), 3.87 (d, *J* = 7.3 Hz, 1H), 3.72 (dd, *J* = 10.4, 5.3 Hz, 2H), 3.27 (d, *J* = 11.7 Hz, 1H), 2.84 (d, *J* = 9.2 Hz, 1H), 2.45 (s, 3H), 2.11 (t, *J* = 8.3 Hz, 1H), 1.46 (t, *J* = 6.0 Hz, 1H), 1.40 (dd, *J* = 14.2, 7.2 Hz, 1H), 1.32 (dd, *J* = 14.3, 3.9 Hz, 1H), 0.84–0.79 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.8, 143.7, 136.3, 136.1, 133.0, 130.3, 129.8, 129.0, 128.4, 128.4, 127.6, 127.3, 126.6, 121.7, 99.2, 83.8, 76.7, 57.8, 57.5, 52.1, 36.5, 34.2, 29.8, 21.6, 21.5; **HRMS (ESI)** calcd for $C_{29}H_{26}ClKNO_3S$ $[M+K]^+$: 542.0954; found: 542.0959.

(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-8-bromo-12-phenyl-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrole (2s)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 11:1) to give the product **2s** in 86% yield (71 mg); colorless solid, mp 199–202 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 7.9 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.20 (s, 1H), 7.18 (d, *J* = 6.9 Hz, 1H), 7.14 (t, *J* = 7.3 Hz, 2H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.60 (d, *J* = 7.5 Hz, 2H), 5.34 (d, *J* = 7.3 Hz, 1H), 3.87 (d, *J* = 7.3 Hz, 1H), 3.72 (d, *J* = 7.2 Hz, 1H), 3.70 (d, *J* = 4.6 Hz, 1H), 3.27 (d, *J* = 11.7 Hz, 1H), 2.83 (d, *J* = 9.2 Hz, 1H), 2.45 (s, 3H), 2.11 (t, *J* = 7.9 Hz, 1H), 1.46 (t, *J* = 6.0 Hz, 1H), 1.40 (dd, *J* = 14.4, 7.3 Hz, 1H), 1.34–1.26 (m, 3H), 0.84–0.80 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 144.2, 143.7, 136.8, 136.1, 133.0, 131.4, 129.8, 129.4， 129.1, 128.5, 127.6, 127.3, 122.1, 118.2, 99.2, 83.7, 57.9, 57.5, 52.2, 36.6, 34.3, 29.8, 21.6, 21.5; **HRMS (ESI)** calcd for $C_{29}H_{26}BrNNaO_3S$ $[M+Na]^+$: 570.0709; found: 570.0717.

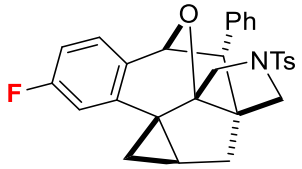
(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-8-methyl-12-phenyl-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrole (2t)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 9:1) to give the product **2t** in 77% yield (56 mg); colorless oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.17–7.15 (m, 1H), 7.12 (t, *J* = 7.3 Hz, 2H), 7.08 (dd, *J* = 7.6, 0.7 Hz, 1H), 6.89 (s, 1H), 6.81 (d, *J* = 7.7 Hz, 1H), 6.62 (d, *J* = 7.3 Hz, 2H), 5.37 (d, *J* = 7.3 Hz, 1H), 3.87 (d, *J* = 7.3 Hz, 1H), 3.72 (d, *J* = 5.2 Hz, 1H), 3.71 (d, *J* = 2.7 Hz, 1H), 3.29 (d, *J* = 11.6 Hz, 1H), 2.87 (d, *J* = 9.2 Hz, 1H), 2.45 (s, 3H), 2.29 (s, 3H), 2.10 (dd, *J* = 8.9, 6.8 Hz, 1H), 1.40–1.35 (m, 2H), 1.29 (dd, *J* = 14.3, 4.1 Hz, 1H), 0.77–0.72 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.6, 142.0, 136.7,

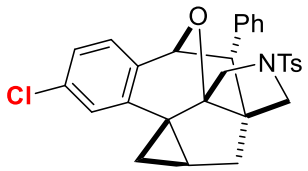
134.4, 134.2, 133.2, 129.7, 129.2, 128.9, 128.2, 127.6, 127.4, 127.0, 120.2, 99.1, 84.3, 76.7, 57.7, 57.6, 52.2, 36.3, 33.7, 29.9, 21.6, 21.3, 21.0; **HRMS (ESI)** calcd for $C_{30}H_{30}NO_3S$ $[M+H]^+$: 484.1941; found: 484.1940.

(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-9-fluoro-12-phenyl-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrole (2u)**



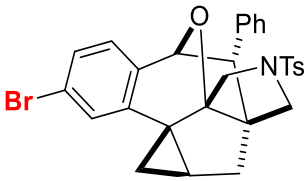
Column chromatography (petroleum ether/EtOAc = 20:1 to 9:1) to give the product **2u** in 66% yield (48 mg); colorless solid, mp 160–162 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 2H), 7.00 (dd, *J* = 8.2, 5.5 Hz, 1H), 6.79 (td, *J* = 8.6, 2.5 Hz, 1H), 6.63 (dd, *J* = 9.2, 2.5 Hz, 1H), 6.59 (d, *J* = 7.4 Hz, 2H), 5.40 (d, *J* = 7.3 Hz, 1H), 3.86 (d, *J* = 7.3 Hz, 1H), 3.73 (d, *J* = 7.3 Hz, 1H), 3.71 (d, *J* = 4.8 Hz, 1H), 3.28 (d, *J* = 11.7 Hz, 1H), 2.84 (d, *J* = 9.2 Hz, 1H), 2.45 (s, 3H), 2.09 (dd, *J* = 8.9, 7.0 Hz, 1H), 1.48 (t, *J* = 6.5 Hz, 1H), 1.41 (dd, *J* = 14.3, 7.2 Hz, 1H), 1.33 (dd, *J* = 14.3, 4.1 Hz, 1H), 0.88–0.83 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 163.1 (d, *J* = 246.0 Hz), 143.7, 140.3 (d, *J* = 8.2 Hz), 137.8 (d, *J* = 3.0 Hz), 136.4, 133.1, 129.8, 129.1, 128.4, 127.8 (d, *J* = 8.7 Hz), 127.7, 127.6, 127.2, 111.0 (d, *J* = 21.6 Hz), 108.1 (d, *J* = 23.1 Hz), 98.8, 83.8, 57.8, 57.6, 52.2, 37.0, 34.5, 29.9, 21.8, 21.6; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -112.83 (td, *J* = 9.0, 5.7 Hz); **HRMS (ESI)** calcd for $C_{29}H_{27}FNO_3S$ $[M+H]^+$: 488.1690; found: 488.1684.

(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-9-chloro-12-phenyl-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrole (2v)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 9:1) to give the product **2v** in 61% yield (46 mg); colorless solid, mp 190–193 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 2H), 7.08 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 1H), 6.90 (d, *J* = 1.7 Hz, 1H), 6.60 (d, *J* = 7.4 Hz, 2H), 5.38 (d, *J* = 7.3 Hz, 1H), 3.87 (d, *J* = 7.3 Hz, 1H), 3.72 (d, *J* = 5.8 Hz, 2H), 3.71 (d, *J* = 3.4 Hz, 1H), 3.27 (d, *J* = 11.7 Hz, 1H), 2.83 (d, *J* = 9.2 Hz, 1H), 2.45 (s, 3H), 2.12 (dd, *J* = 8.8, 7.0 Hz, 1H), 1.47 (t, *J* = 6.2 Hz, 1H), 1.41 (dd, *J* = 14.3, 7.2 Hz, 1H), 1.33 (dd, *J* = 14.3, 4.1 Hz, 1H), 0.88–0.84 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.7, 140.5, 139.8, 136.2, 134.1, 133.1, 129.8, 129.1, 128.4, 127.6, 127.6, 127.3, 124.6, 120.9, 98.9, 83.8, 57.8, 57.6, 52.2, 36.8, 34.5, 29.8, 21.6, 21.5; **HRMS (ESI)** calcd for $C_{29}H_{27}ClNO_3S$ $[M+H]^+$: 504.1395; found: 504.1418.

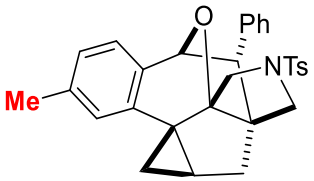
(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-9-bromo-12-phenyl-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrole (2w)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 11:1) to give the product **2w** in 75% yield (62 mg); colorless solid, mp 195–198 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.24 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.13 (t, *J* = 7.4 Hz, 2H), 7.05 (d, *J* = 1.7 Hz, 1H), 6.92

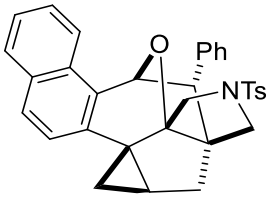
(d, *J* = 7.9 Hz, 1H), 6.60 (d, *J* = 7.3 Hz, 2H), 5.37 (d, *J* = 7.3 Hz, 1H), 3.86 (d, *J* = 7.3 Hz, 1H), 3.72 (d, *J* = 4.6 Hz, 1H), 3.70 (d, *J* = 2.0 Hz, 1H), 3.26 (d, *J* = 11.7 Hz, 1H), 2.83 (d, *J* = 9.2 Hz, 1H), 2.45 (s, 3H), 2.12 (dd, *J* = 8.9, 7.0 Hz, 1H), 1.47 (t, *J* = 6.4 Hz, 1H), 1.41 (dd, *J* = 14.3, 7.2 Hz, 1H), 1.33 (dd, *J* = 14.3, 4.1 Hz, 1H), 0.88–0.84 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.7, 141.0, 140.0, 136.2, 133.0, 129.8, 129.1, 128.4, 127.9, 127.6, 127.5, 127.3, 123.8, 122.3, 99.1, 83.8, 57.8, 57.6, 52.2, 36.8, 34.5, 29.8, 21.6; **HRMS (ESI)** calcd for $C_{29}H_{26}BrNNaO_3S$ $[M+Na]^+$: 570.0709; found: 570.0734.

(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-9-methyl-12-phenyl-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrole (2x)**



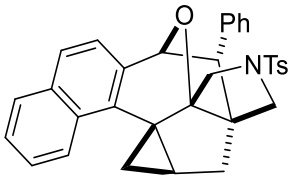
Column chromatography (petroleum ether/EtOAc = 15:1 to 9:1) to give the product **2x** in 67% yield (48 mg); colorless solid, mp 128–130 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.17–7.14 (m, 1H), 7.11 (t, *J* = 7.3 Hz, 2H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.91 (dd, *J* = 7.5, 0.6 Hz, 1H), 6.73 (s, 1H), 6.63 (d, *J* = 7.2 Hz, 2H), 5.38 (d, *J* = 7.3 Hz, 1H), 3.85 (d, *J* = 7.3 Hz, 1H), 3.73 (d, *J* = 8.1 Hz, 1H), 3.71 (d, *J* = 5.7 Hz, 1H), 3.29 (t, *J* = 11.8 Hz, 1H), 2.86 (d, *J* = 9.2 Hz, 1H), 2.45 (s, 3H), 2.34 (s, 3H), 2.13 (dd, *J* = 8.9, 6.7 Hz, 1H), 1.42–1.38 (m, 2H), 1.31 (dd, *J* = 14.3, 4.1 Hz, 1H), 0.80–0.75 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.6, 139.1, 138.2, 137.2, 136.8, 133.2, 129.7, 129.2, 128.2, 127.6, 127.0, 126.4, 125.2, 121.2, 98.9, 84.1, 57.7, 57.6, 52.3, 36.7, 33.9, 29.9, 21.6, 21.5, 21.2; **HRMS (ESI)** calcd for $C_{30}H_{29}KNO_3S$ $[M+K]^+$: 522.1500; found: 522.1518.

(3a*S,4a*R**,5a*R**,12*S**,13a*S**,14*R**)-14-phenyl-2-tosyl-2,3,4a,5-tetrahydro-1*H*,4*H*,12*H*-3a,12-methanobenzo[7',8']isochromeno[3',4':1,5]cyclopropa[4,5]cyclopenta[1,2-*c*]pyrrole (2y)**



Column chromatography (petroleum ether/EtOAc = 15:1 to 7:1) to give the product **2y** in 65% yield (51 mg); colorless solid, mp 184–185 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.82 (t, *J* = 6.8 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.38–7.33 (m, 4H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.96 (t, *J* = 7.7 Hz, 2H), 6.54 (d, *J* = 7.6 Hz, 2H), 6.28 (d, *J* = 7.3 Hz, 1H), 4.09 (d, *J* = 7.3 Hz, 1H), 3.80 (d, *J* = 3.8 Hz, 1H), 3.78 (s, 1H), 3.33 (d, *J* = 11.6 Hz, 1H), 2.94 (d, *J* = 9.1 Hz, 1H), 2.45 (s, 3H), 2.26 (dd, *J* = 8.8, 7.0 Hz, 1H), 1.53 (t, *J* = 6.3 Hz, 1H), 1.44–1.37 (m, 2H), 0.84–0.80 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.7, 137.8, 136.5, 134.9, 133.1, 131.0, 130.3, 129.8, 128.8, 128.1, 128.7, 128.3, 127.6, 126.9, 126.6, 124.7, 121.5, 119.4, 98.6, 79.3, 58.1, 57.7, 52.2, 37.4, 33.4, 29.9, 21.9, 21.6; **HRMS (ESI)** calcd for $C_{33}H_{30}NO_3S$ $[M+H]^+$: 520.1941; found: 520.1959.

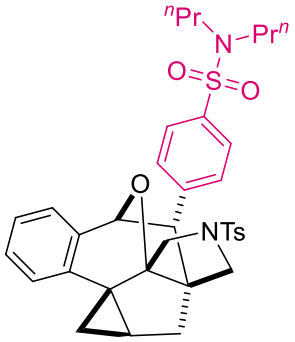
(3a*S,5*S**,11c*R**,12a*R**,13a*S**,14*R**)-14-phenyl-2-tosyl-2,3,12a,13-tetrahydro-1*H*,5*H*,12*H*-5,13a-methanobenzo[5',6']isochromeno[3',4':1,5]cyclopropa[4,5]cyclopenta[1,2-*c*]pyrrole (2z)**



Column chromatography (petroleum ether/EtOAc = 15:1 to 9:1) to give the product **2z** in 61% yield (48 mg); colorless solid, mp 188–191 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.21 (d, *J* = 7.7 Hz, 1H), 7.86–7.84 (m, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.46–7.44 (m, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.17 (dd, *J* = 7.7, 5.4 Hz, 2H), 7.11 (t, *J* = 7.6 Hz, 2H), 6.71 (d, *J* = 7.5 Hz, 2H), 5.50 (d, *J* = 7.2 Hz, 1H),

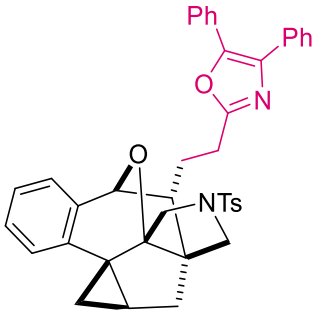
3.94 (d, *J* = 11.4 Hz, 1H), 3.90 (d, *J* = 7.3 Hz, 1H), 3.75 (d, *J* = 9.0 Hz, 1H), 3.30 (d, *J* = 11.4 Hz, 1H), 2.85 (d, *J* = 9.0 Hz, 1H), 2.74 (dd, *J* = 9.3, 7.0 Hz, 1H), 2.46 (s, 3H), 1.84 (t, *J* = 6.2 Hz, 1H), 1.44–1.37 (m, 2H), 0.94–0.88 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.7, 142.2, 136.5, 134.3, 132.9, 132.4, 129.8, 129.3, 129.1, 128.9, 128.3, 127.7, 127.2, 125.5, 125.3, 125.2, 125.1, 123.8, 100.5, 85.4, 76.0, 57.9, 57.6, 52.9, 37.6, 32.8, 30.2, 26.9, 21.6; **HRMS (ESI)** calcd for $C_{33}H_{30}NO_3S$ $[M+H]^+$: 520.1941; found: 520.1950.

***N*,*N*-dipropyl-4-((1a*S**,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-c]pyrrol-12-yl)benzenesulfonamide (2aa)**



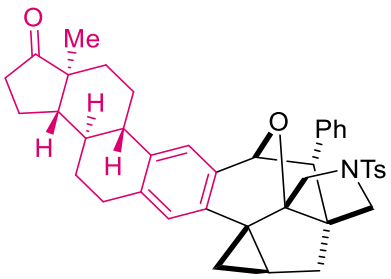
Column chromatography (petroleum ether/EtOAc = 9:1 to 4:1) to give the product **2aa** in 60% yield (53 mg); colorless solid, mp 102–104 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.29 (td, *J* = 7.6, 1.1 Hz, 1H), 7.12 (td, *J* = 7.5, 1.0 Hz, 1H), 7.04 (d, *J* = 7.3 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 2H), 5.42 (d, *J* = 7.3 Hz, 1H), 3.91 (d, *J* = 7.3 Hz, 1H), 3.73 (s, 1H), 3.72 (d, *J* = 2.7 Hz, 1H), 3.29 (d, *J* = 11.7 Hz, 1H), 3.03–3.00 (m, 4H), 2.86 (d, *J* = 9.3 Hz, 1H), 2.44 (s, 3H), 2.16 (dd, *J* = 8.9, 6.9 Hz, 1H), 1.52–1.46 (m, 4H), 1.46–1.44 (m, 1H), 1.37–1.33 (m, 1H), 1.30–1.28 (m, 1H), 0.82 (t, *J* = 7.4 Hz, 6H), 0.73–0.69 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.8, 141.5, 141.3, 139.0, 137.3, 133.0, 129.8, 129.7, 128.8, 127.6, 126.9, 126.5, 124.8, 120.5, 99.1, 84.0, 57.4, 57.2, 52.1, 49.8, 36.7, 33.9, 29.8, 21.9, 21.5, 21.4, 11.1; **HRMS (ESI)** calcd for $C_{35}H_{40}N_2NaO_5S_2$ $[M+Na]^+$: 655.2271; found: 655.2303.

(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-12-(2-(4,5-diphenyloxazol-2-yl)ethyl)-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrole (2ab)**



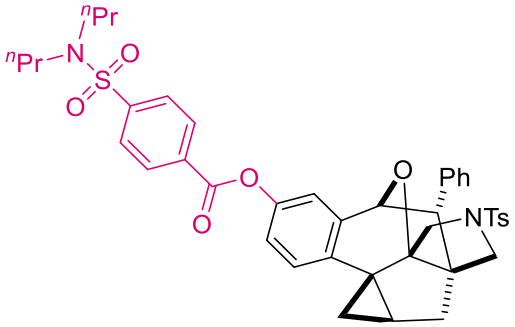
Column chromatography (petroleum ether/EtOAc = 20:1 to 6:1) to give the product **2ab** in 71% yield (68 mg); colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.37–7.30 (m, 8H), 7.22–7.18 (m, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 5.34 (d, *J* = 7.3 Hz, 1H), 3.68 (s, 1H), 3.66 (d, *J* = 3.3 Hz, 1H), 3.30 (d, *J* = 11.8 Hz, 1H), 2.90–2.77 (m, 2H), 2.69 (d, *J* = 9.4 Hz, 1H), 2.64–2.59 (m, 1H), 2.42 (s, 3H), 2.17 (t, *J* = 7.8 Hz, 1H), 2.10 (dd, *J* = 14.5, 7.2 Hz, 1H), 1.90–1.82 (m, 1H), 1.50–1.39 (m, 3H), 0.92–0.86 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 162.2, 145.3, 143.5, 139.8, 137.9, 135.1, 133.3, 132.3, 129.7, 128.8, 128.6, 128.6, 128.5, 128.3, 128.1, 127.8, 127.5, 126.5, 126.2, 124.4, 120.2, 98.7, 84.2, 74.3, 56.7, 51.5, 48.6, 35.4, 34.7, 28.9, 27.3, 25.7, 22.4, 21.5; **HRMS (ESI)** calcd for $C_{40}H_{37}N_2O_4S$ $[M+H]^+$: 641.2469; found: 641.2501.

(1a*S,4a**S*,6*S**,7b*S*,9a*S*,12a*S*,12b*R*,15b*R**,16a*R**,17*R**)-9a-methyl-17-phenyl-3-tosyl-3,4,7b,8,9,9a,11,12,12a,12b,13,14,16,16a-tetradecahydro-1*H*,2*H*-1a,6-methanocyclopenta[5'',6'']naphtho[2'',1'':6',7']isochromeno[3',4':1,5]cyclopropa[4,5]cyclopenta[1,2-*c*]pyrrol-10(6*H*)-one (2ac)**



Column chromatography (petroleum ether/EtOAc = 9:1 to 4:1) to give the product **2ac** in 57% yield (56 mg) as an inseparable mixture of diastereomers in a ratio of 3:1, colorless solid, mp 206–209 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.17–7.12 (m, 3H), 6.99 (s, 1H), 6.67–6.63 (m, 3H), 5.36 (dd, *J* = 14.1, 7.3 Hz, 1H), 3.85 (d, *J* = 7.2 Hz, 1H), 3.72– 3.70 (m, 2H), 3.27 (t, *J* = 9.9 Hz, 1H), 2.91–2.89 (m, 2H), 2.85 (d, *J* = 9.2 Hz, 1H), 2.49 (dd, *J* = 19.1, 8.8 Hz, 1H), 2.44 (s, 3H), 2.29–2.26 (m, 2H), 2.15–2.01 (m, 4H), 1.92–1.86 (m, 1H), 1.66–1.26 (m, 10H), 0.89 (d, *J* = 17.6 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 220.8, 143.6, 139.6, 136.9, 136.6, 136.1, 134.7, 133.3, 129.7, 129.2, 128.3, 128.2, 127.6, 127.0, 124.0, 123.5, 121.0, 99.1, 84.4, 76.7, 57.6, 57.6, 52.3, 50.4, 47.9, 44.3, 38.3, 36.4, 35.8, 33.6, 31.5, 30.1, 29.6, 26.3, 26.2, 21.6, 21.2, 13.9; **HRMS (ESI)** calcd for $C_{41}H_{44}NO_4S$ $[M+H]^+$: 646.2986; found: 646.3018.

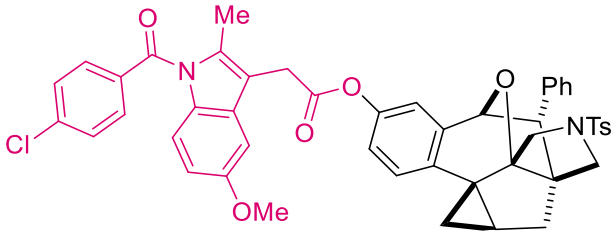
(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-12-phenyl-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrol-8-yl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (2ad)**



Column chromatography (petroleum ether/EtOAc = 9:1 to 4:1) to give the product **2ad** in 73% yield (83 mg); colorless solid, mp 179–181 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.27 (d, *J* = 8.5 Hz, 2H), 7.91 (d, *J* = 8.5 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H),

7.36 (d, *J* = 8.1 Hz, 2H), 7.17–7.14 (m, 4H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.96 (d, *J* = 2.3 Hz, 1H), 6.65 (s, 1H), 6.64 (d, *J* = 1.4 Hz, 1H), 5.41 (d, *J* = 7.3 Hz, 1H), 3.90 (d, *J* = 7.3 Hz, 1H), 3.73 (t, *J* = 10.5 Hz, 2H), 3.30 (d, *J* = 11.6 Hz, 1H), 3.12–3.10 (m, 4H), 2.86 (d, *J* = 9.3 Hz, 1H), 2.45 (s, 3H), 2.16 (dd, *J* = 8.8, 7.0 Hz, 1H), 1.58–1.51 (m, 4H), 1.49–1.47 (m, 1H), 1.43 (dd, *J* = 14.2, 7.3 Hz, 1H), 1.33 (dd, *J* = 14.3, 4.0 Hz, 1H), 0.87 (t, *J* = 7.4 Hz, 7H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 163.9, 147.6, 144.9, 143.8, 143.6, 136.2, 135.8, 133.1, 132.8, 130.7, 129.8, 129.2, 128.5, 127.7, 127.3, 127.2, 121.4, 121.3, 119.9, 99.3, 76.8, 57.9, 57.7, 52.2, 49.9, 36.6, 34.2, 29.9, 21.9, 21.6, 11.2; **HRMS (ESI)** calcd for $C_{42}H_{44}N_2NaO_7S_2$ $[M+Na]^+$: 775.2482; found: 775.2485.

(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-12-phenyl-3-tosyl-3,4,11,11a-tetrahydro-1*H*,2*H*,6*H*-1a,6-methanocyclopropa[3,4]isochromeno[3',4':2,3]cyclopenta[1,2-*c*]pyrrol-8-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (2ae)**



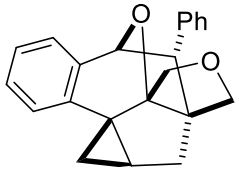
Column chromatography (petroleum ether/EtOAc = 9:1 to 4:1) to give the product **2ae** in 63% yield (78 mg); yellow solid, mp 117–119 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.16–7.11 (m, 3H), 7.01 (d, *J* = 2.4 Hz, 1H), 6.99 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.90–6.87 (m, 2H), 6.81 (d, *J* = 2.2 Hz, 1H), 6.67 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.61 (d, *J* = 7.2 Hz, 2H), 5.35 (d, *J* = 7.4 Hz, 1H), 3.87–3.85 (m, 3H), 3.78 (s, 3H), 3.72 (d, *J* = 5.6 Hz, 1H), 3.71 (d, *J* = 3.0 Hz, 1H), 3.28 (d, *J* = 11.7 Hz, 1H), 2.84 (d, *J* = 9.2 Hz, 1H), 2.44 (s, 3H), 2.42 (s, 3H), 2.12 (dd, *J* = 8.6, 7.0 Hz, 1H), 1.45–1.43 (m, 1H), 1.39 (dd, *J* = 14.2, 7.2 Hz, 1H), 1.31 (dd, *J* = 14.3, 4.0 Hz, 1H), 0.82–0.77 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.2, 168.2, 156.0, 147.7, 143.7, 143.3, 139.3, 136.2, 136.1, 135.3, 133.8, 133.1, 131.1, 130.8, 130.4, 129.7, 129.1, 129.1, 128.4, 127.6,

127.2, 121.2, 121.1, 119.8, 114.9, 111.9, 111.7, 101.1, 99.1, 83.8, 76.7, 57.8, 57.5, 55.6, 52.1, 36.4, 34.1, 30.4, 29.8, 21.5, 21.5, 13.4; **HRMS (ESI)** calcd for $C_{48}H_{41}ClN_2NaO_7S$ $[M+Na]^+$: 848.2215; found: 848.2219.

Column chromatography (petroleum ether/EtOAc = 50:1 to 20:1) to give an inseparable mixture of **2af** and **3af** in a ratio of 1:1.3 in overall yields of 88% yield; colorless oil;

Minor isomer (**2af**):

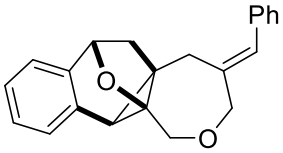
(1a*S,4a*S**,6*S**,10b*R**,11a*R**,12*R**)-12-phenyl-11,11a-dihydro-1*H*,2*H*,4*H*,6*H*-1a,6-methanocyclopropa[2,3]furo[3',4':1,5]cyclopenta[1,2-*c*]isochromene**



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33–7.29 (m, 2H), 7.29–7.23 (m, 1H), 7.17–7.10 (m, 4H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.70 (s, 1H), 5.64 (d, *J* = 7.1 Hz, 1H), 4.11–4.07 (m, 1H), 4.03 (d, *J* = 7.2 Hz, 1H), 4.01 (d, *J* = 10.7 Hz, 1H), 3.94 (d, *J* = 8.4 Hz, 1H), 3.64 (d, *J* = 8.4 Hz, 1H), 2.17 (dd, *J* = 9.0, 6.7 Hz, 1H), 1.51 (dd, *J* = 6.4, 5.6 Hz, 1H), 1.46 (dd, *J* = 14.2, 7.3 Hz, 1H), 1.34 (dd, *J* = 14.2, 4.1 Hz, 1H), 1.28–1.27 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 142.5, 138.1, 137.0, 129.4, 128.3, 128.2, 126.9, 126.7, 124.4, 120.2, 102.1, 86.0, 80.6, 77.0, 71.7, 56.2, 36.3, 34.7, 29.9, 21.3.

Major isomer (**3af**):

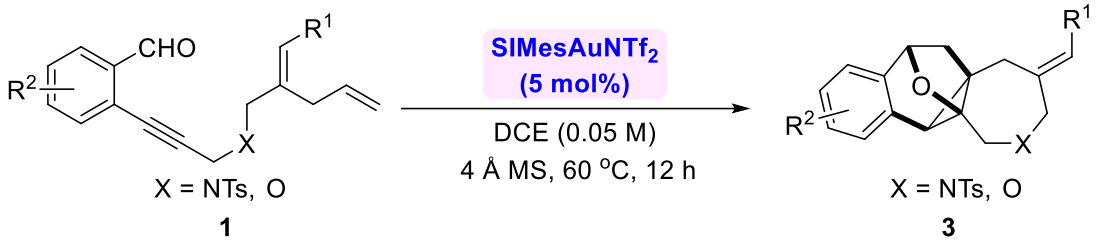
(5a*R,7*S**,11b*S**,11c*S**)-4-((*E*)-benzylidene)-4,5,7,11b-tetrahydro-1*H*,3*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]oxepine**



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34–7.31 (m, 3H), 7.29 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.28–7.24 (m, 3H), 7.19 (td, *J* = 7.3, 1.5 Hz, 1H), 7.14 (d, *J* = 7.3 Hz, 1H), 6.69 (s, 1H), 5.09 (d, *J* = 6.0 Hz, 1H), 4.37 (d, *J* = 12.5 Hz, 1H), 4.33 (d, *J* = 12.9 Hz, 1H),

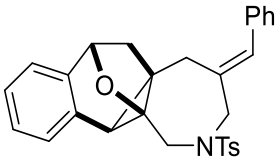
4.18 (d, *J* = 12.9 Hz, 1H), 4.10 (d, *J* = 12.4 Hz, 1H), 3.01 (d, *J* = 13.9 Hz, 1H), 2.93 (d, *J* = 13.9 Hz, 1H), 2.65 (s, 1H), 2.14 (dd, *J* = 11.5, 6.0 Hz, 1H), 1.28 (d, *J* = 11.6 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 136.8, 136.7, 135.6, 132.7, 132.2, 128.6, 128.4, 127.8, 127.1, 126.7, 124.8, 122.2, 81.0, 75.9, 69.7, 66.3, 33.6, 30.7, 26.3, 25.6.

4. General procedure for $SIMesAuNTf_2$-catalyzed 6-*endo-dig* oxycyclization/[3 + 2] cycloaddition/C(sp^3)–H bond insertion



To a solution of **1** (0.15 mmol, 1 equiv) and 4 Å MS (150 mg) in anhydrous $(CH_2Cl)_2$ (3 mL) was added $SIMesAuNTf_2$ (5 mol %) under an argon atmosphere. The reaction mixture was stirred at 60 °C for 12 h. Upon completion, the reaction mixture was cooled down to room temperature and filtered through celite, washed with CH_2Cl_2 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether: EtOAc) to give the product **3**.

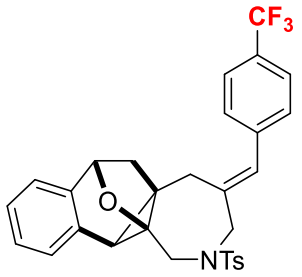
(5a*R,7*S**,11b*S**,11c*S**)-4-((*E*)-benzylidene)-2-tosyl-2,3,4,5,7,11b-hexahydro-1*H*, 6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]azepine (3a)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 11:1) to give the product **3a** in 81% yield (57 mg); colorless solid, mp 180–181 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.33–7.29 (m, 4H), 7.26–7.22 (m, 2H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 6.5 Hz, 1H), 7.16 (dd, *J* = 7.4, 1.0 Hz, 1H), 7.08 (d, *J* = 7.3 Hz, 1H), 6.69 (s, 1H), 4.96 (d, *J* = 5.9 Hz, 1H), 4.33 (d, *J* = 14.1 Hz, 1H), 3.98 (d, *J* =

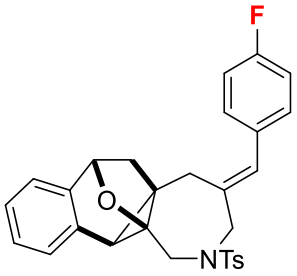
14.4 Hz, 1H), 3.86 (d, *J* = 14.4 Hz, 1H), 3.67 (d, *J* = 14.1 Hz, 1H), 2.86 (s, 2H), 2.45 (s, 1H), 2.44 (s, 1H), 1.88 (dd, *J* = 11.6, 6.0 Hz, 1H), 1.15 (d, *J* = 11.6 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.4, 136.6, 135.3, 134.5, 132.4, 131.6, 129.7, 128.5, 128.4, 127.8, 127.3, 127.2, 126.8, 124.9, 122.1, 75.6, 64.8, 58.5, 48.4, 33.5, 30.2, 26.1, 26.0, 21.5; **HRMS (ESI)** calcd for $C_{29}H_{28}NO_3S$ $[M+H]^+$: 470.1784; found: 470.1789.

(5a*R,7*S**,11b*S**,11c*S**)-2-tosyl-4-((*E*)-4-(trifluoromethyl)benzylidene)-2,3,4,5,7,11b-hexahydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]azepine (3b)**



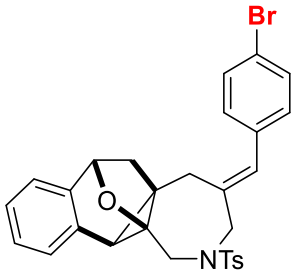
Column chromatography (petroleum ether/EtOAc = 20:1 to 9:1) to give the product **3b** in 63% yield (51 mg); colorless solid, mp 182–184 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 7.7 Hz, 2H), 7.56 (d, *J* = 7.9 Hz, 2H), 7.32 (t, *J* = 8.7 Hz, 4H), 7.28–7.25 (m, 1H), 7.20–7.16 (m, 2H), 7.09 (d, *J* = 7.3 Hz, 1H), 6.72 (s, 1H), 4.97 (d, *J* = 5.8 Hz, 1H), 4.38 (d, *J* = 14.3 Hz, 1H), 4.04 (d, *J* = 14.3 Hz, 1H), 3.81 (d, *J* = 14.3 Hz, 1H), 3.63 (d, *J* = 14.3 Hz, 1H), 2.86 (d, *J* = 14.2 Hz, 1H), 2.83 (d, *J* = 14.2 Hz, 1H), 2.45 (s, 4H), 1.88 (dd, *J* = 11.5, 5.9 Hz, 1H), 1.15 (d, *J* = 11.6 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.5, 140.2, 136.8, 136.5, 135.2, 132.2, 130.1, 129.7, 128.8, 127.9, 127.3, 126.7, 125.4, 125.3, 125.1, 124.9, 122.1, 75.5, 64.6, 58.1, 48.5, 33.5, 30.3, 26.1, 25.9, 21.5; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -62.54; **HRMS (ESI)** calcd for $C_{30}H_{27}F_3NO_3S$ $[M+H]^+$: 538.1658; found: 538.1662.

(5a*R,7*S**,11b*S**,11c*S**)-4-((*E*)-4-fluorobenzylidene)-2-tosyl-2,3,4,5,7,11b-hexahydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]azepine (3c)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 9:1) to give the product **3c** in 82% yield (60 mg); colorless solid, mp 150–152 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.27–7.25 (m, 1H), 7.19–7.16 (m, 4H), 7.09 (d, *J* = 7.3 Hz, 1H), 6.99 (t, *J* = 8.6 Hz, 2H), 6.65 (s, 1H), 4.96 (d, *J* = 5.9 Hz, 1H), 4.33 (d, *J* = 14.1 Hz, 1H), 3.99 (d, *J* = 14.3 Hz, 1H), 3.83 (d, *J* = 14.3 Hz, 1H), 3.63 (d, *J* = 14.1 Hz, 1H), 2.83 (s, 2H), 2.45 (s, 3H), 2.43 (s, 1H), 1.88 (dd, *J* = 11.6, 6.0 Hz, 1H), 1.15 (d, *J* = 11.6 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 161.8 (d, *J* = 247.0 Hz), 143.4, 136.6, 135.3, 134.6, 132.6 (d, *J* = 3.4 Hz), 132.3, 130.5, 130.2 (d, *J* = 7.9 Hz), 129.7, 127.8, 127.3, 126.7, 125.0, 122.1, 115.4 (d, *J* = 21.5 Hz), 75.6, 64.7, 58.3, 48.4, 33.5, 30.2, 26.1, 25.9, 21.5; **HRMS (ESI)** calcd for $C_{29}H_{27}FNO_3S$ $[M+H]^+$: 488.1690; found: 488.1676.

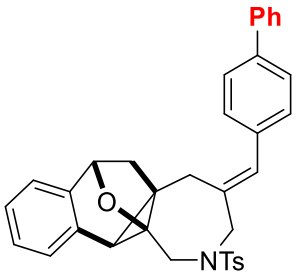
(5a*R,7*S**,11b*S**,11c*S**)-4-((*E*)-4-bromobenzylidene)-2-tosyl-2,3,4,5,7,11b-hexahydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]azepine (3d)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 11:1) to give the product **3d** in 68% yield (56 mg); colorless solid, mp 142–145 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.27–7.25 (m, 1H), 7.19–7.16 (m, 2H), 7.08 (t, *J* = 7.9 Hz, 3H), 6.61 (s, 1H), 4.96 (d, *J* = 5.9 Hz, 1H), 4.33 (d, *J* = 14.2 Hz, 1H), 4.00 (d, *J* = 14.3 Hz, 1H), 3.83 (d, *J* = 14.3 Hz, 1H), 3.63 (d, *J* = 14.2 Hz, 1H), 2.84 (d, *J* = 14.1 Hz, 1H), 2.81 (d, *J* = 14.1 Hz,

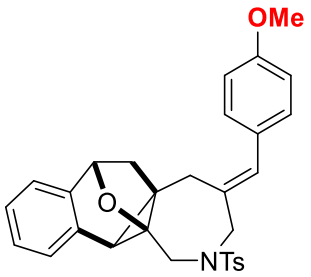
1H), 2.45 (s, 3H), 2.42 (s, 1H), 1.87 (dd, *J* = 11.6, 6.0 Hz, 1H), 1.15 (d, *J* = 11.6 Hz, 1H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 143.4, 136.5, 135.5, 135.4, 135.2, 132.2, 131.5, 130.3, 130.1, 129.7, 127.8, 127.2, 126.7, 125.0, 122.1, 121.1, 75.5, 64.7, 58.3, 48.4, 33.5, 30.2, 26.0, 25.9, 21.5; **HRMS (ESI)** calcd for $C_{29}H_{26}BrNNaO_3S$ $[M+Na]^+$: 570.0709; found: 570.0729.

(5a*R,7*S**,11b*S**,11c*S**,*E*)-4-([1,1'-biphenyl]-4-ylmethylene)-2-tosyl-2,3,4,5,7,11b-hexahydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]azepine (3e)**



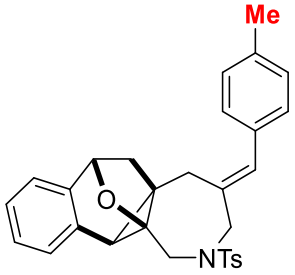
Column chromatography (petroleum ether/EtOAc = 20:1 to 9:1) to give the product **3e** in 66% yield (54 mg); colorless solid, mp 217–218 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 1.1 Hz, 1H), 7.57 (s, 1H), 7.55 (s, 1H), 7.54 (s, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 3H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.27–7.24 (m, 1H), 7.20–7.16 (m, 2H), 7.09 (d, *J* = 7.3 Hz, 1H), 6.72 (s, 1H), 4.98 (d, *J* = 6.0 Hz, 1H), 4.35 (d, *J* = 14.1 Hz, 1H), 3.99 (d, *J* = 14.4 Hz, 1H), 3.88 (d, *J* = 14.4 Hz, 1H), 3.70 (d, *J* = 14.1 Hz, 1H), 2.93 (d, *J* = 14.1 Hz, 1H), 2.90 (d, *J* = 14.1 Hz, 1H), 2.46 (s, 1H), 2.46 (s, 3H), 1.92 (dd, *J* = 11.6, 6.0 Hz, 1H), 1.19 (d, *J* = 11.7 Hz, 1H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 143.4, 140.4, 139.9, 136.6, 135.6, 135.3, 134.6, 132.4, 131.3, 129.7, 129.0, 128.8, 127.8, 127.4, 127.3, 127.1, 126.9, 126.8, 124.9, 122.1, 75.6, 64.8, 58.6, 48.4, 33.6, 30.4, 26.2, 26.1, 21.5; **HRMS (ESI)** calcd for $C_{35}H_{32}NO_3S$ $[M+H]^+$: 546.2097; found: 546.2095.

(5a*R,7*S**,11b*S**,11c*S**)-4-((*E*)-4-methoxybenzylidene)-2-tosyl-2,3,4,5,7,11b-hexahydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]azepine (3f)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 7:1) to give the product **3f** in 48% yield (36 mg); pale-yellow solid, mp 162–164 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.27–7.24 (m, 1H), 7.18–7.14 (m, 4H), 7.09 (d, *J* = 7.0 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.62 (s, 1H), 4.96 (d, *J* = 5.9 Hz, 1H), 4.29 (d, *J* = 14.0 Hz, 1H), 3.95 (d, *J* = 14.4 Hz, 1H), 3.87 (d, *J* = 14.4 Hz, 1H), 3.79 (s, 3H), 3.67 (d, *J* = 14.0 Hz, 1H), 2.88 (d, *J* = 14.1 Hz, 1H), 2.83 (d, *J* = 14.1 Hz, 1H), 2.45 (s, 3H), 2.43 (s, 1H), 1.89 (dd, *J* = 11.6, 6.0 Hz, 1H), 1.17 (d, *J* = 11.6 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 158.7, 143.3, 136.6, 135.4, 132.8, 132.5, 131.3, 129.8, 129.7, 129.1, 127.8, 127.3, 126.8, 124.9, 122.1, 113.8, 75.6, 64.9, 58.7, 55.2, 48.3, 33.6, 30.2, 26.2, 25.9, 21.5; **HRMS (ESI)** calcd for $C_{30}H_{30}NO_4S$ $[M+H]^+$: 500.1890; found: 500.1891.

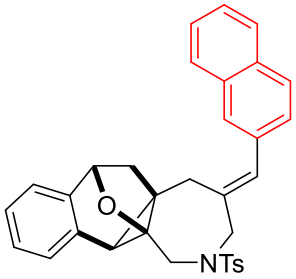
(5a*R,7*S**,11b*S**,11c*S**)-4-((*E*)-4-methylbenzylidene)-2-tosyl-2,3,4,5,7,11b-hexahydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]azepine (3g)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 9:1) to give the product **3g** in 78% yield (57 mg); colorless solid, mp 185–187 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.26–7.24 (m, 1H), 7.18–7.15 (m, 2H), 7.11–7.08 (m, 5H), 6.65 (s, 1 H), 4.95 (d, *J* = 6.0 Hz, 1H), 4.30 (d, *J* =

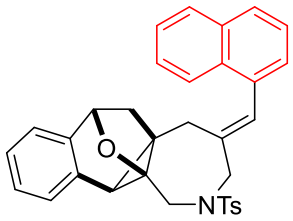
14.1 Hz, 1H), 3.95 (d, *J* = 14.4 Hz, 1H), 3.87 (d, *J* = 14.4 Hz, 1H), 3.68 (d, *J* = 14.0 Hz, 1H), 2.87 (d, *J* = 14.2 Hz, 1H), 2.84 (d, *J* = 14.2 Hz, 1H), 2.45 (s, 3H), 2.42 (s, 1H), 2.32 (s, 3H), 1.88 (dd, *J* = 11.6, 6.0 Hz, 1H), 1.15 (d, *J* = 11.6 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.3, 136.9, 136.6, 135.3, 133.7, 132.5, 131.7, 129.7, 129.1, 128.5, 127.8, 127.3, 126.8, 124.9, 122.1, 75.6, 64.8, 58.6, 48.4, 33.5, 30.2, 26.2, 26.1, 21.5, 21.1; **HRMS (ESI)** calcd for $C_{30}H_{30}NO_3S$ $[M+H]^+$: 484.1941; found: 484.1960.

(5a*R,7*S**,11b*S**,11c*S**,*E*)-4-(naphthalen-2-ylmethylene)-2-tosyl-2,3,4,5,7,11b-hexahydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]azepine (3h)**



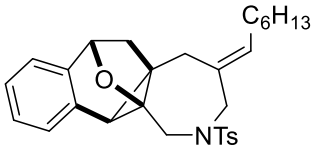
Column chromatography (petroleum ether/EtOAc = 20:1 to 9:1) to give the product **3h** in 81% yield (63 mg); colorless solid, mp 153–155 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.81–7.78 (m, 4H), 7.72–7.70 (m, 1H), 7.68 (s, 1H), 7.47–7.44 (m, 2H), 7.36–7.33 (m, 3H), 7.27–7.25 (m, 1H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.18 (td, *J* = 7.4, 1.1 Hz, 1H), 7.09 (d, *J* = 7.3 Hz, 1H), 6.84 (s, 1 H), 4.97 (d, *J* = 6.0 Hz, 1H), 4.40 (d, *J* = 14.1 Hz, 1H), 4.02 (d, *J* = 14.4 Hz, 1H), 3.91 (d, *J* = 14.4 Hz, 1H), 3.75 (d, *J* = 14.1 Hz, 1H), 2.96 (d, *J* = 14.1 Hz, 1H), 2.91 (d, *J* = 14.1 Hz, 1H), 2.51 (s, 1H), 2.46 (s, 3H), 1.90 (dd, *J* = 11.6, 6.0 Hz, 1H), 1.13 (d, *J* = 11.7 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.4, 136.6, 135.3, 134.9, 134.1, 133.2, 132.3, 131.5, 129.7, 127.9, 127.9, 127.8, 127.6, 127.5, 127.3, 126.7, 126.6, 126.2, 126.0, 124.9, 122.1, 75.5, 64.8, 58.4, 48.5, 33.5, 30.3, 26.3, 26.2, 21.5; **HRMS (ESI)** calcd for $C_{33}H_{29}NNaO_3S$ $[M+Na]^+$: 542.1760; found: 542.1770.

(5a*R,7*S**,11b*S**,11c*S**,*E*)-4-(naphthalen-1-ylmethylene)-2-tosyl-2,3,4,5,7,11b-hexahydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]azepine (3i)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 9:1) to give the product **3i** in 68% yield (53 mg); colorless solid, mp 200–201 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 7.9 Hz, 1H), 7.86–7.85 (m, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.56–7.51 (m, 2H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 7.1 Hz, 1H), 7.21 (td, *J* = 7.5, 1.0 Hz, 1H), 7.13–7.09 (m, 3H), 7.02 (d, *J* = 7.2 Hz, 1H), 4.88 (d, *J* = 6.0 Hz, 1H), 4.54 (d, *J* = 14.2 Hz, 1H), 4.11 (d, *J* = 14.2 Hz, 1H), 3.87 (d, *J* = 14.2 Hz, 1H), 3.75 (d, *J* = 14.1 Hz, 1H), 2.79 (d, *J* = 14.2 Hz, 1H), 2.70 (d, *J* = 14.2 Hz, 1H), 2.48 (s, 3H), 2.46 (s, 1H), 1.76 (dd, *J* = 11.6, 6.0 Hz, 1H), 0.92 (d, *J* = 11.7 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.4, 136.7, 136.5, 135.2, 133.8, 133.5, 132.4, 131.9, 129.9, 129.8, 128.4, 127.8, 127.7, 127.3, 126.7, 126.2, 126.1, 125.9, 125.2, 124.8, 121.9, 75.5, 64.8, 57.7, 48.6, 33.4, 30.5, 25.9, 21.5; **HRMS (ESI)** calcd for $C_{33}H_{30}NO_3S$ $[M+H]^+$: 519.1868; found: 519.1862.

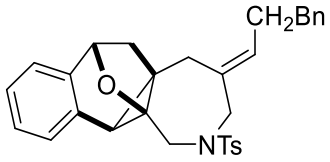
(5a*R,7*S**,11b*S**,11c*S**,*E*)-4-heptylidene-2-tosyl-2,3,4,5,7,11b-hexahydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]azepine (3k)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 11:1) to give the product **3k** in 58% yield (42 mg); colorless solid, mp 127–129 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.27–7.24 (m, 1H), 7.21 (d, *J* = 7.1 Hz, 1H), 7.16 (td, *J* = 7.4, 1.2 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 5.53 (t, *J* = 7.3 Hz, 1H), 4.93 (d, *J* = 6.0 Hz, 1H), 3.97 (d, *J* = 13.7 Hz, 1H), 3.91 (s, 1H), 3.74 (d, *J* = 14.6 Hz, 1H), 3.67 (d, *J* = 13.7 Hz, 1H), 2.72 (d, *J* = 14.1 Hz, 1H), 2.48 (d, *J* =

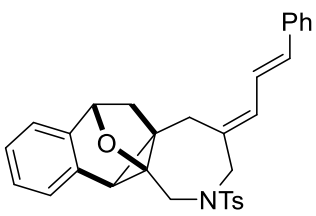
14.1 Hz, 1H), 2.44 (s, 3H), 2.34 (s, 1H), 2.07–1.97 (m, 2H), 1.88 (dd, *J* = 11.4, 6.0 Hz, 1H), 1.36–1.26 (m, 8H), 1.17 (d, *J* = 11.5 Hz, 1H), 0.89 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.2, 136.6, 135.3, 132.6, 132.3, 131.3, 129.5, 127.6, 127.4, 126.6, 124.8, 122.1, 75.4, 65.0, 58.3, 48.3, 33.1, 31.7, 29.5, 29.4, 29.0, 28.1, 27.1, 25.9, 22.6, 21.5, 14.1; **HRMS (ESI)** calcd for $C_{29}H_{36}NO_3S$ $[M+H]^+$: 478.2410; found: 478.2430.

(5a*R,7*S**,11b*S**,11c*S**,*E*)-4-(3-phenylpropylidene)-2-tosyl-2,3,4,5,7,11b-hexahydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]azepine (3l)**



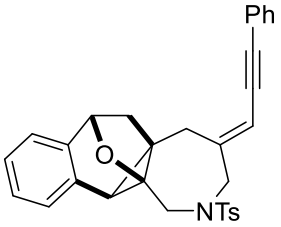
Column chromatography (petroleum ether/EtOAc = 20:1 to 9:1) to give the product **3l** in 70% yield (53 mg); colorless solid, mp 135–138 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.32–7.30 (m, 4H), 7.27–7.24 (m, 1H), 7.22–7.20 (m, 2H), 7.18–7.15 (m, 3H), 7.08 (d, *J* = 7.3 Hz, 1H), 5.59 (t, *J* = 7.2 Hz, 1H), 4.92 (d, *J* = 6.0 Hz, 1H), 3.98 (d, *J* = 13.8 Hz, 1H), 3.90 (d, *J* = 14.5 Hz, 1H), 3.73 (d, *J* = 14.5 Hz, 1H), 3.67 (d, *J* = 13.8 Hz, 1H), 2.71–2.67 (m, 3H), 2.45 (s, 3H), 2.41 (d, *J* = 14.2 Hz, 1H), 2.40–2.35 (m, 2H), 2.33 (s, 1H), 1.83 (dd, *J* = 11.4, 6.0 Hz, 1H), 1.15 (d, *J* = 11.5 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.2, 141.3, 136.5, 135.2, 132.5, 132.4, 130.8, 129.5, 128.4, 128.4, 127.7, 127.3, 126.6, 126.0, 124.9, 122.0, 75.4, 64.9, 58.0, 48.3, 35.7, 33.0, 30.1, 29.5, 27.3, 25.8, 21.5; **HRMS (ESI)** calcd for $C_{31}H_{32}NO_3S$ $[M+H]^+$: 498.2097; found: 498.2077.

(5a*R,7*S**,11b*S**,11c*S**,*E*)-4-((*E*)-3-phenylallylidene)-2-tosyl-2,3,4,5,7,11b-hexahydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]azepine (3m)**



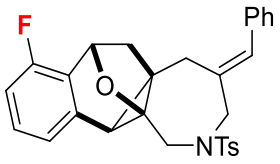
Column chromatography (petroleum ether/EtOAc = 20:1 to 6:1) to give the product **3m** in 91% yield (68 mg); colorless solid, mp 205–207 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 7.9 Hz, 2H), 7.40 (d, *J* = 7.3 Hz, 2H), 7.34–7.31 (m, 4H), 7.26–7.25 (m, 3H), 7.18–7.15 (m, 1H), 7.09 (d, *J* = 7.1 Hz, 1H), 6.95–6.88 (m, 1H), 6.62 (d, *J* = 15.4 Hz, 1H), 6.27 (d, *J* = 10.8 Hz, 1H), 4.94 (d, *J* = 5.7 Hz, 1H), 4.13 (d, *J* = 13.8 Hz, 1H), 3.90–3.79 (m, 2H), 3.76 (d, *J* = 14.2 Hz, 1H), 3.01 (d, *J* = 14.1 Hz, 1H), 2.66 (d, *J* = 14.1 Hz, 1H), 2.45 (s, 4H), 1.97 (dd, *J* = 10.9, 5.9 Hz, 1H), 1.26 (d, *J* = 11.2 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.4, 137.0, 136.3, 135.2, 134.3, 133.9, 132.4, 130.4, 129.6, 128.7, 127.9, 127.7, 127.3, 126.7, 126.4, 124.9, 123.6, 122.1, 75.5, 64.8, 58.2, 48.3, 32.8, 29.9, 27.4, 26.2, 21.5; **HRMS (ESI)** calcd for $C_{31}H_{30}NO_3S$ $[M+H]^+$: 496.1941; found: 496.1939.

(5a*R,7*S**,11b*S**,11c*S**,*E*)-4-(3-phenylprop-2-yn-1-ylidene)-2-tosyl-2,3,4,5,7,11b-hexahydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]azepine (3n)**



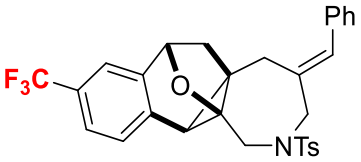
Column chromatography (petroleum ether/EtOAc = 20:1 to 11:1) to give the product **3n** in 80% yield (59 mg); colorless solid, mp 171–174 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.73 (d, *J* = 7.9 Hz, 2H), 7.37 (s, 2H), 7.33 (d, *J* = 7.7 Hz, 2H), 7.28–7.25 (m, 5H), 7.16 (t, *J* = 6.7 Hz, 1H), 7.08 (d, *J* = 6.7 Hz, 1H), 5.75 (s, 1H), 4.94 (d, *J* = 5.5 Hz, 1H), 4.17 (d, *J* = 14.4 Hz, 1H), 3.88 (d, *J* = 14.4 Hz, 1H), 3.79 (d, *J* = 14.4 Hz, 1H), 3.74 (d, *J* = 14.4 Hz, 1H), 3.28 (d, *J* = 13.7 Hz, 1H), 2.62 (d, *J* = 13.7 Hz, 1H), 2.53 (s, 1H), 2.44 (s, 3H), 2.17 (dd, *J* = 11.2, 5.7 Hz, 1H), 1.26 (s, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 146.2, 143.6, 135.9, 135.2, 132.4, 131.3, 129.7, 128.3, 127.8, 127.3, 126.8, 124.9, 122.9, 122.1, 109.9, 93.9, 85.9, 75.6, 64.4, 56.6, 48.4, 32.8, 32.1, 28.0, 25.8, 21.5; **HRMS (ESI)** calcd for $C_{31}H_{28}NO_3S$ $[M+H]^+$: 494.1784; found: 494.1796.

(5a*R,7*S**,11b*S**,11c*S**)-4-((*E*)-benzylidene)-8-fluoro-2-tosyl-2,3,4,5,7,11b-hexahydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]azepine (3o)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 11:1) to give the product **3o** in 65% yield (48 mg); colorless solid, mp 168–169 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.34–7.30 (m, 4H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 7.4 Hz, 2H), 7.19–7.16 (m, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.87 (t, *J* = 8.7 Hz, 1H), 6.70 (s, 1H), 5.38 (d, *J* = 6.0 Hz, 1H), 4.35 (d, *J* = 14.1 Hz, 1H), 4.00 (d, *J* = 14.4 Hz, 1H), 3.83 (d, *J* = 14.4 Hz, 1H), 3.65 (d, *J* = 14.1 Hz, 1H), 2.88 (d, *J* = 14.1 Hz, 1H), 2.85 (d, *J* = 14.1 Hz, 1H), 2.49 (s, 1H), 2.45 (s, 3H), 1.88 (dd, *J* = 11.7, 6.1 Hz, 1H), 1.15 (d, *J* = 11.8 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 156.1 (d, *J* = 245.8 Hz), 143.5, 136.5, 135.5 (d, *J* = 5.7 Hz), 134.2, 131.7, 129.7, 128.7 (d, *J* = 8.0 Hz), 128.5, 128.4, 127.3, 127.2, 122.4 (d, *J* = 3.0 Hz), 121.9 (d, *J* = 18.3 Hz), 111.8 (d, *J* = 21.0 Hz), 68.6, 65.0, 58.4, 48.2, 32.9, 30.0, 26.4, 25.8, 21.5; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -126.59 – -126.67 (m); **HRMS (ESI)** calcd for $C_{29}H_{27}FNO_3S$ $[M+H]^+$: 488.1690; found: 488.1701.

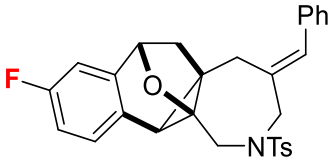
(5a*R,7*S**,11b*S**,11c*S**)-4-((*E*)-benzylidene)-2-tosyl-9-(trifluoromethyl)-2,3,4,5,7,11b-hexahydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]azepine (3p)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 9:1) to give the product **3p** in 92% yield (74 mg); colorless solid, mp 188–190 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.51 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.34–7.29 (m, 6H), 7.25–7.23 (m, 1H), 7.20 (d, *J* = 7.4 Hz, 2H), 6.72 (s, 1H), 5.01 (d, *J* = 6.0 Hz, 1H), 4.37 (d, *J* = 14.1 Hz, 1H), 4.02 (d, *J* = 14.4 Hz, 1H), 3.81 (d, *J* = 14.4 Hz, 1H), 3.64 (d,

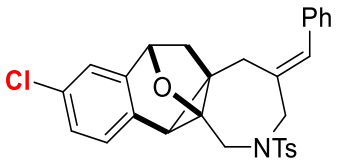
J = 14.1 Hz, 1H), 2.89 (s, 2H), 2.56 (s, 1H), 2.46 (s, 3H), 1.93 (dd, *J* = 11.8, 6.0 Hz, 1H), 1.14 (d, *J* = 11.8 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.5, 136.7, 136.5 (d, *J* = 2.1 Hz), 135.5, 134.1, 131.9, 129.8, 128.5, 128.4, 127.3, 127.2, 127.2, 127.1, 127.0, 125.3, 124.75 (d, *J* = 3.8 Hz), 119.1 (d, *J* = 3.8 Hz), 75.1, 65.4, 58.5, 48.1, 33.1, 29.9, 26.8, 26.0, 21.5; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -61.84; **HRMS (ESI)** calcd for $C_{30}H_{27}F_3NO_3S$ $[M+H]^+$: 538.1658; found: 538.1661.

(5a*R,7*S**,11b*S**,11c*S**)-4-((*E*)-benzylidene)-9-fluoro-2-tosyl-2,3,4,5,7,11b-hexahydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]azepine (3q)**



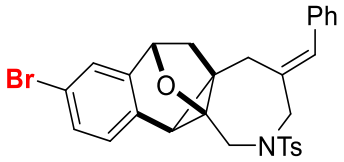
Column chromatography (petroleum ether/EtOAc = 20:1 to 9:1) to give the product **3q** in 93% yield (68 mg); colorless solid, mp 198–199 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 7.9 Hz, 2H), 7.33–7.29 (m, 4H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 7.7 Hz, 2H), 7.12 (dd, *J* = 8.2, 5.1 Hz, 1H), 6.95 (td, *J* = 9.0, 2.5 Hz, 1H), 6.82 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.69 (s, 1H), 4.91 (d, *J* = 6.0 Hz, 1H), 4.32 (d, *J* = 14.1 Hz, 1H), 3.97 (d, *J* = 14.4 Hz, 1H), 3.84 (dd, *J* = 14.4, 2.6 Hz, 1H), 3.67 (d, *J* = 14.1 Hz, 1H), 2.88 (d, *J* = 14.1 Hz, 1H), 2.82 (d, *J* = 14.1 Hz, 1H), 2.45 (s, 4H), 1.87 (dd, *J* = 11.7, 6.0 Hz, 1H), 1.12 (d, *J* = 11.7 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 160.8 (d, *J* = 243.7 Hz), 143.4, 136.7 (d, *J* = 6.9 Hz), 136.6, 136.5, 134.3, 131.6, 129.7, 128.5, 128.4, 128.0 (d, *J* = 1.8 Hz), 127.9 (d, *J* = 7.8 Hz), 127.3, 127.2, 114.3 (d, *J* = 21.6 Hz), 109.6 (d, *J* = 22.4 Hz), 99.9, 75.0, 64.7, 58.5, 48.3, 33.2, 29.9, 25.9, 25.5, 21.5; **HRMS (ESI)** calcd for $C_{29}H_{27}FNO_3S$ $[M+H]^+$: 488.1690; found: 488.1693.

(5a*R,7*S**,11b*S**,11c*S**)-4-((*E*)-benzylidene)-9-chloro-2-tosyl-2,3,4,5,7,11b-hexahydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]azepine (3r)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 9:1) to give the product **3r** in 77% yield (59 mg); colorless solid, mp 198–200 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.33–7.29 (m, 4H), 7.25–7.21 (m, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 1.2 Hz, 1H), 6.69 (s, 1H), 4.90 (d, *J* = 6.0 Hz, 1H), 4.33 (d, *J* = 14.1 Hz, 1H), 3.98 (d, *J* = 14.3 Hz, 1H), 3.81 (d, *J* = 14.3 Hz, 1H), 3.63 (d, *J* = 14.1 Hz, 1H), 2.87 (d, *J* = 14.1 Hz, 1H), 2.84 (d, *J* = 14.1 Hz, 1H), 2.45 (s, 4H), 1.88 (dd, *J* = 11.7, 6.0 Hz, 1H), 1.12 (d, *J* = 11.8 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.5, 136.6, 136.5, 134.2, 131.7, 130.9, 130.7, 129.7, 128.5, 128.4, 128.0, 127.7, 127.3, 127.2, 122.5, 75.0, 64.9, 58.5, 48.2, 33.3, 29.9, 26.3, 25.5, 21.5; **HRMS (ESI)** calcd for $C_{29}H_{26}ClNNaO_3S$ $[M+Na]^+$: 526.1214; found: 526.1238.

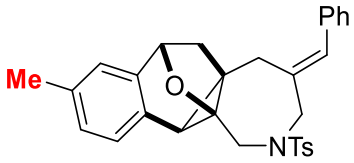
(5a*R,7*S**,12a*S**)-4-((*E*)-benzylidene)-9-bromo-2-tosyl-2,3,4,5,5a,6,7,12-octahydro-1*H*-7,12a-epoxybenzo[5,6]cyclohepta[1,2-*c*]azepine (3s)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 11:1) to give the product **3s** in 74% yield (62 mg); colorless solid, mp 193–194 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.37 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.33–7.29 (m, 4H), 7.26–7.22 (m, 2H), 7.19 (d, *J* = 7.4 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.69 (s, 1H), 4.90 (d, *J* = 6.0 Hz, 1H), 4.34 (d, *J* = 14.1 Hz, 1H), 3.98 (d, *J* = 14.3 Hz, 1H), 3.81 (d, *J* = 14.3 Hz, 1H), 3.63 (d, *J* = 14.1 Hz, 1H), 2.87 (d, *J* = 14.2 Hz, 1H), 2.84 (d, *J* = 14.2 Hz, 1H), 2.45 (s, 3H), 2.44 (s, 1H), 1.88 (dd, *J* = 11.7, 6.0 Hz, 1H), 1.12 (d, *J* = 11.8 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.5, 136.9, 136.5, 134.2, 131.7, 131.5, 130.6, 129.7, 128.5, 128.4, 128.4, 127.3, 127.2, 125.3, 118.6, 74.9, 64.9, 58.4, 48.2, 33.2, 29.9, 26.2, 25.6, 21.5; **HRMS (ESI)** calcd for $C_{29}H_{26}BrNNaO_3S$ $[M+Na]^+$:

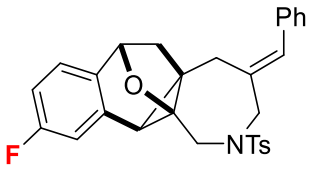
570.0709; found: 570.0725.

(5a*R,7*S**,11b*S**,11c*S**)-4-((*E*)-benzylidene)-9-methyl-2-tosyl-2,3,4,5,7,11b-hexa hydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]azepine (3t)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 9:1) to give the product **3t** in 56% yield (41 mg); colorless solid, mp 190–192 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.32–7.28 (m, 4H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 7.4 Hz, 2H), 7.08–7.05 (m, 2H), 6.91 (s, 1H), 6.69 (s, 1H), 4.91 (d, *J* = 6.0 Hz, 1H), 4.33 (d, *J* = 14.1 Hz, 1H), 3.97 (d, *J* = 14.3 Hz, 1H), 3.85 (d, *J* = 14.3 Hz, 1H), 3.66 (d, *J* = 14.1 Hz, 1H), 2.86 (d, *J* = 14.1 Hz, 1H), 2.82 (d, *J* = 14.1 Hz, 1H), 2.45 (s, 3H), 2.39 (s, 1H), 2.33 (s, 3H), 1.87 (dd, *J* = 11.6, 6.0 Hz, 1H), 1.15 (d, *J* = 11.6 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.3, 136.6, 136.6, 135.3, 134.6, 134.5, 131.6, 129.7, 129.3, 128.5, 128.4, 127.3, 127.1, 126.6, 122.9, 75.6, 64.8, 58.4, 48.5), 33.7, 30.3, 26.1, 25.7, 21.5, 21.1; **HRMS (ESI)** calcd for $C_{30}H_{30}NO_3S$ $[M+H]^+$: 484.1941; found: 484.1941.

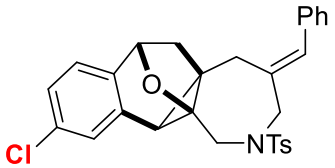
(5a*R,7*S**,11b*S**,11c*S**)-4-((*E*)-benzylidene)-10-fluoro-2-tosyl-2,3,4,5,7,11b-hexa hydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]azepine (3u)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 9:1) to give the product **3u** in 71% yield (53 mg); colorless solid, mp 192–194 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.33–7.30 (m, 4H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.03 (dd, *J* = 7.9, 5.5 Hz, 1H), 6.86–6.82 (m, 2H), 6.70 (s, 1H), 4.95 (d, *J* = 5.9 Hz, 1H), 4.37 (d, *J* = 14.2 Hz, 1H), 4.00 (d, *J* = 14.4 Hz, 1H), 3.84 (d,

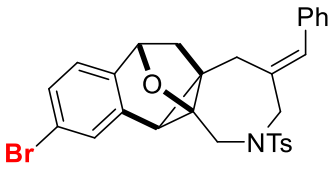
J = 14.4 Hz, 1H), 3.65 (d, *J* = 14.1 Hz, 1H), 2.88–2.83 (m, 2H), 2.46 (s, 3H), 2.37 (s, 1H), 1.89 (dd, *J* = 11.6, 6.0 Hz, 1H), 1.12 (d, *J* = 11.7 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 162.5 (d, *J* = 244.3 Hz), 143.5 (s), 136.7, 136.5, 134.7 (d, *J* = 8.6 Hz), 134.2, 131.8, 131.2 (d, *J* = 2.7 Hz), 129.7, 128.5, 128.4, 127.3, 127.2, 123.6 (d, *J* = 8.8 Hz), 113.8 (d, *J* = 22.4 Hz), 111.5 (d, *J* = 21.9 Hz), 74.9, 64.8, 58.4, 48.2, 33.7, 30.1, 26.5, 26.1, 21.5; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -114.34 (td, *J* = 9.1, 5.5 Hz); **HRMS (ESI)** calcd for $C_{29}H_{27}FNO_3S$ $[M+H]^+$: 488.1690; found: 488.1700.

(5a*R,7*S**,11b*S**,11c*S**)-4-((*E*)-benzylidene)-10-chloro-2-tosyl-2,3,4,5,7,11b-hexahydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]azepine (3v)**



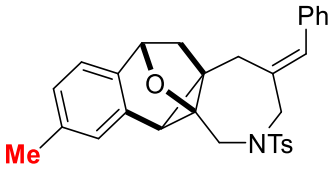
Column chromatography (petroleum ether/EtOAc = 20:1 to 7:1) to give the product **3v** in 77% yield (58 mg); colorless solid, mp 218–219 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.33–7.31 (m, 4H), 7.24 (d, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 1H), 7.08 (s, 1H), 7.01 (d, *J* = 7.9 Hz, 1H), 6.72 (s, 1H), 4.94 (d, *J* = 5.9 Hz, 1H), 4.40 (d, *J* = 14.2 Hz, 1H), 4.01 (d, *J* = 14.5 Hz, 1H), 3.84 (d, *J* = 14.5 Hz, 1H), 3.64 (d, *J* = 14.2 Hz, 1H), 2.88 (d, *J* = 14.1 Hz, 1H), 2.83 (d, *J* = 14.1 Hz, 1H), 2.47 (s, 3H), 2.30 (s, 1H), 1.90 (dd, *J* = 11.6, 6.0 Hz, 1H), 1.12 (d, *J* = 11.7 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.5, 136.8, 136.5, 134.4, 134.2, 133.7, 133.3, 131.9, 129.8, 128.5, 128.5, 127.3, 126.8, 124.9, 123.4, 74.9, 65.0, 58.4, 48.1, 33.5, 30.1, 26.5, 25.6, 21.5; **HRMS (ESI)** calcd for $C_{29}H_{27}ClNO_3S$ $[M+H]^+$: 504.1395; found: 504.1405.

(5a*R,7*S**,11b*S**,11c*S**)-4-((*E*)-benzylidene)-10-bromo-2-tosyl-2,3,4,5,7,11b-hexahydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]azepine (3w)**



Column chromatography (petroleum ether/EtOAc = 20:1 to 11:1) to give the product **3w** in 73% yield (60 mg); colorless solid, mp 219–221 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.33–7.31 (m, 4H), 7.29 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.25–7.23 (m, 2H), 7.19 (d, *J* = 7.3 Hz, 2H), 6.95 (d, *J* = 7.9 Hz, 1H), 6.72 (s, 1H), 4.94 (d, *J* = 6.0 Hz, 1H), 4.41 (d, *J* = 14.2 Hz, 1H), 4.02 (d, *J* = 14.5 Hz, 1H), 3.84 (d, *J* = 14.5 Hz, 1H), 3.63 (d, *J* = 14.2 Hz, 1H), 2.88 (d, *J* = 14.1 Hz, 1H), 2.83 (d, *J* = 14.1 Hz, 1H), 2.48 (s, 3H), 2.29 (s, 1H), 1.90 (dd, *J* = 11.7, 6.0 Hz, 1H), 1.12 (d, *J* = 11.7 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.5, 136.8, 136.5, 134.8, 134.1, 132.0, 129.7, 129.6, 128.5, 128.4, 127.9, 127.3, 123.7, 121.3, 74.9, 65.1, 58.4, 48.0, 33.3, 30.0, 26.5, 25.4, 21.6; **HRMS (ESI)** calcd for $C_{29}H_{26}BrNNaO_3S$ $[M+Na]^+$: 570.0709; found: 570.0741.

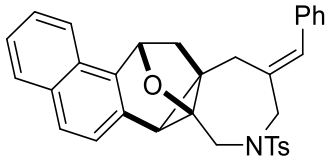
(5a*R,7*S**,11b*S**,11c*S**)-4-((*E*)-benzylidene)-10-methyl-2-tosyl-2,3,4,5,7,11b-hexahydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]azepine (3x)**



Column chromatography (petroleum ether/EtOAc = 15:1 to 9:1) to give the product **3x** in 69% yield (50 mg); colorless solid, mp 197–199 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.33–7.30 (m, 4H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.4 Hz, 2H), 6.99–6.97 (m, 3H), 6.70 (s, 1H), 4.93 (d, *J* = 5.9 Hz, 1H), 4.36 (d, *J* = 14.1 Hz, 1H), 4.00 (d, *J* = 14.3 Hz, 1H), 3.84 (d, *J* = 14.3 Hz, 1H), 3.64 (d, *J* = 14.1 Hz, 1H), 2.88 (d, *J* = 14.1 Hz, 1H), 2.82 (d, *J* = 14.1 Hz, 1H), 2.46 (s, 3H), 2.38 (s, 1H), 2.34 (s, 3H), 1.87 (dd, *J* = 11.5, 6.0 Hz, 1H), 1.15 (d, *J* = 11.6 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.3, 137.5, 136.7, 136.6, 134.5, 132.6, 132.4, 131.7, 129.7, 128.5, 128.4, 127.4, 127.3, 127.1, 125.5, 121.9, 77.2, 77.0, 76.8, 75.3, 64.7,

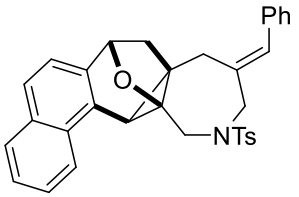
58.5, 48.4, 33.9, 30.3, 26.2, 25.8, 21.5, 21.4; **HRMS (ESI)** calcd for $C_{30}H_{30}NO_3S$ $[M+H]^+$: 484.1941; found: 484.1961.

(5a*S,5b*S**,12*S**,13a*R**)-2-((*E*)-benzylidene)-4-tosyl-2,3,4,5,5b,12-hexahydro-1*H*, 13*H*-5a,12-epoxyphenanthro[2',1':2,3]cyclopropa[1,2-*c*]azepine (3y)**



Column chromatography (petroleum ether/EtOAc = 15:1 to 7:1) to give the product **3y** in 18% yield (14 mg); colorless solid, mp 156–159 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.98 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.77 (dd, *J* = 11.3, 8.3 Hz, 3H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.9 Hz, 3H), 7.31–7.28 (m, 2H), 7.24–7.21 (m, 3H), 6.72 (s, 1H), 5.84 (d, *J* = 6.1 Hz, 1H), 4.38 (d, *J* = 14.2 Hz, 1H), 4.03 (d, *J* = 14.3 Hz, 1H), 3.91 (d, *J* = 14.4 Hz, 1H), 3.70 (d, *J* = 14.1 Hz, 1H), 2.94 (d, *J* = 14.1 Hz, 1H), 2.90 (d, *J* = 14.1 Hz, 1H), 2.59 (s, 1H), 2.47 (s, 3H), 2.00 (dd, *J* = 11.6, 6.1 Hz, 1H), 1.12 (d, *J* = 11.6 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 144.9, 143.4, 136.6, 134.6, 131.7, 130.1, 130.0, 129.7, 128.7, 128.6, 128.4, 127.5, 127.3, 127.2, 126.2, 125.7, 124.5, 121.3, 81.9, 70.8, 64.8, 58.5, 48.3, 33.0, 30.1, 26.6, 21.5; **HRMS (ESI)** calcd for $C_{33}H_{30}NO_3S$ $[M+H]^+$: 520.1941; found: 520.1960.

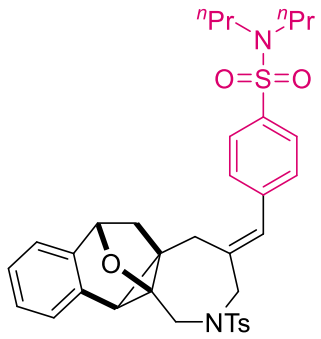
(5a*R,7*S**,13c*S**,13d*S**)-4-((*E*)-benzylidene)-2-tosyl-2,3,4,5,7,13c-hexahydro-1*H*, 6*H*-7,13d-epoxyphenanthro[3',4':2,3]cyclopropa[1,2-*c*]azepine (3z)**



Column chromatography (petroleum ether/EtOAc = 15:1 to 9:1) to give the product **3z** in 30% yield (24 mg); colorless solid, mp 169–170 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.04 (d, *J* = 7.7 Hz, 1H), 7.85–7.84 (m, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.48–7.44 (m, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.29–7.25 (m, 6H),

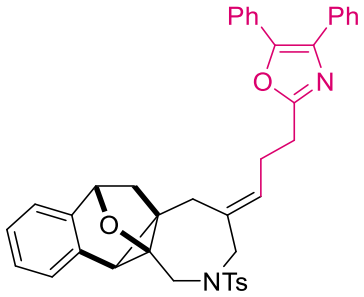
7.20 (t, *J* = 6.9 Hz, 1H), 6.76 (s, 1H), 5.12 (d, *J* = 5.9 Hz, 1H), 4.35 (d, *J* = 14.0 Hz, 1H), 3.98 (d, *J* = 14.5 Hz, 1H), 3.93 (d, *J* = 14.4 Hz, 1H), 3.79 (d, *J* = 14.0 Hz, 1H), 3.30 (s, 1H), 3.01 (d, *J* = 14.0 Hz, 1H), 2.94 (d, *J* = 14.0 Hz, 1H), 2.44 (s, 3H), 1.92 (dd, *J* = 11.6, 5.9 Hz, 1H), 1.16 (d, *J* = 11.6 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.4, 136.6, 136.5, 134.5, 133.3, 131.9, 131.8, 130.9, 129.7, 128.7, 128.6, 128.5, 128.3, 127.3, 127.2, 126.1, 125.4, 124.9, 122.5, 121.3, 75.8, 65.1, 58.7, 48.4, 33.4, 30.1, 26.0, 22.4, 21.5; **HRMS (ESI)** calcd for $C_{33}H_{29}KNO_3S$ $[M+K]^+$: 558.1500; found: 558.1508.

***N*,*N*-dipropyl-4-((*E*)-((5a*R**,7*S**,11b*S**,11c*S**)-2-tosyl-2,3,7,11b-tetrahydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-c]azepin-4(5H)-ylidene)methyl)benzenesulfonamide (3aa)**



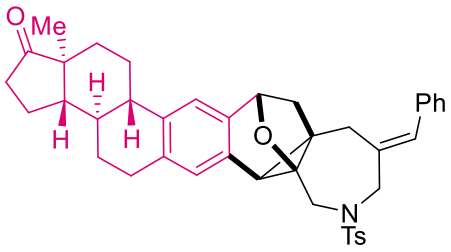
Column chromatography (petroleum ether/EtOAc = 6:1 to 4:1) to give the product **3aa** in 77% yield (68 mg); colorless solid, mp 166–168 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.74–7.72 (m, 4H), 7.32 (d, *J* = 8.0 Hz, 4H), 7.27–7.25 (m, 1H), 7.20–7.16 (m, 2H), 7.09 (d, *J* = 7.3 Hz, 1H), 6.70 (s, 1H), 4.97 (d, *J* = 5.9 Hz, 1H), 4.37 (d, *J* = 14.3 Hz, 1H), 4.03 (d, *J* = 14.3 Hz, 1H), 3.79 (d, *J* = 14.3 Hz, 1H), 3.62 (d, *J* = 14.3 Hz, 1H), 3.07 (dd, *J* = 8.7, 6.3 Hz, 4H), 2.86 (d, *J* = 14.2 Hz, 1H), 2.83 (d, *J* = 14.2 Hz, 1H), 2.45 (s, 1H), 2.44 (s, 3H), 1.87 (dd, *J* = 11.6, 6.0 Hz, 1H), 1.57–1.50 (m, 4H), 1.14 (d, *J* = 11.6 Hz, 1H), 0.85 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.5, 140.6, 138.7, 137.2, 136.4, 135.2, 132.1, 129.9, 129.7, 128.9, 127.8, 127.2, 127.1, 126.7, 125.1, 75.5, 64.6, 58.1, 49.9, 48.4, 33.5, 30.3, 26.0, 25.9, 21.9, 21.5, 11.1; **HRMS (ESI)** calcd for $C_{35}H_{40}N_2NaO_5S_2$ $[M+Na]^+$: 655.2271 ; found:655.2288.

(5a*R,7*S**,11b*S**,11c*S**,*E*)-4-(3-(4,5-diphenyloxazol-2-yl)propylidene)-2-tosyl-2,3,4,5,7,11b-hexahydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]azepine (3ab)**



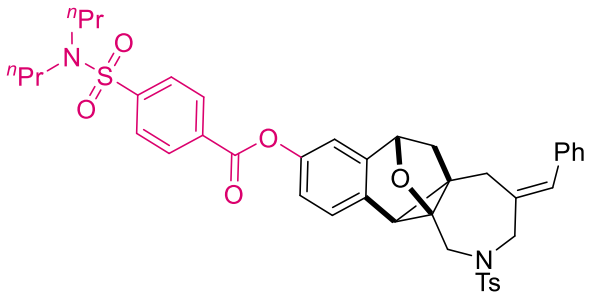
Column chromatography (petroleum ether/EtOAc = 20:1 to 6:1) to give the product **3ab** in 64% yield (62 mg); colorless solid, mp 131–133 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 7.9 Hz, 2H), 7.64 (d, *J* = 7.7 Hz, 2H), 7.58 (d, *J* = 7.7 Hz, 2H), 7.39–7.29 (m, 8H), 7.24–7.21 (m, 2H), 7.17–7.13 (m, 1H), 7.07 (d, *J* = 7.3 Hz, 1H), 5.65 (t, *J* = 7.1 Hz, 1H), 4.90 (d, *J* = 5.9 Hz, 1H), 4.03 (d, *J* = 13.8 Hz, 1H), 3.87 (d, *J* = 14.5 Hz, 1H), 3.78 (d, *J* = 14.5 Hz, 1H), 3.66 (d, *J* = 13.8 Hz, 1H), 2.92 (t, *J* = 7.5 Hz, 2H), 2.80 (d, *J* = 14.2 Hz, 1H), 2.66–2.61 (m, 2H), 2.52 (d, *J* = 14.2 Hz, 1H), 2.43 (s, 3H), 2.38 (s, 1H), 1.89 (dd, *J* = 11.4, 6.0 Hz, 1H), 1.19 (d, *J* = 11.5 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 162.3, 145.3, 143.3, 136.3, 135.2, 135.1, 133.6, 132.4, 129.6, 129.3, 128.9, 128.6, 128.5, 128.4, 128.0, 127.8, 127.7, 127.3, 126.7, 126.4, 124.9, 122.0, 75.4, 64.8, 57.9, 48.3, 33.1, 29.5, 27.9, 27.2, 25.8, 25.6, 21.5; **HRMS (ESI)** calcd for $C_{40}H_{37}N_2O_4S$ $[M+H]^+$: 641.2469; found: 641.2498.

(5a*R,7*S**,8b*S*,10a*S*,13a*S*,13b*R*,16b*S**,16c*S**)-4-((*E*)-benzylidene)-10a-methyl-2-tosyl-2,3,4,5,7,8b,9,10,10a,12,13,13a,13b,14,15,16b-hexadecahydro-1*H*-7,16c-epoxycyclopenta[3',4']tetrapheno[9',8':2,3]cyclopropa[1,2-*c*]azepin-11(6*H*)-one (3ac)**



Column chromatography (petroleum ether/EtOAc = 9:1 to 4:1) to give the product **3ac** in 50% yield (48 mg) as an inseparable mixture of diastereomers in a ratio of 1:1; colorless solid, mp 209–211 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.74 (d, *J* = 7.0 Hz, 2H), 7.32–7.29 (m, 4H), 7.24–7.20 (m, 3H), 7.05 (s, 1H), 6.93 (d, *J* = 9.2 Hz, 1H), 6.71 (s, 1H), 4.92 (d, *J* = 5.3 Hz, 1H), 4.39 (dd, *J* = 19.8, 14.5 Hz, 1H), 4.02 (t, *J* = 14.0 Hz, 1H), 3.79 (d, *J* = 12.9 Hz, 1H), 3.58 (dd, *J* = 13.4, 10.2 Hz, 1H), 2.94–2.92 (m, 3H), 2.77 (dd, *J* = 13.8, 4.5 Hz, 1H), 2.53–2.29 (m, 7H), 2.16–1.88 (m, 5H), 1.64–1.43 (m, 6H), 1.20 (dd, *J* = 22.3, 11.6 Hz, 1H), 0.90 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 220.8, 220.8, 143.3, 136.8, 136.7, 136.6, 136.5, 136.4, 136.1, 134.5, 134.4, 133.1, 133.0, 131.9, 131.9, 129.9, 129.8, 129.7, 128.5, 128.4, 127.3, 127.3, 127.1, 119.3, 119.1, 75.7, 75.6, 64.9, 64.8, 58.6, 58.5, 50.5, 50.4, 48.3, 48.2, 47.9, 44.4, 44.3, 38.3, 38.1, 35.8, 34.2, 34.1, 31.6, 31.5, 30.4, 30.4, 29.5, 29.4, 26.5, 26.4, 26.4, 26.3, 26.0, 25.8, 24.9, 24.8, 21.6, 21.5, 13.8, 13.7; **HRMS (ESI)** calcd for $C_{41}H_{43}NNaO_4S$ $[M+Na]^+$: 668.2805; found: 668.2834.

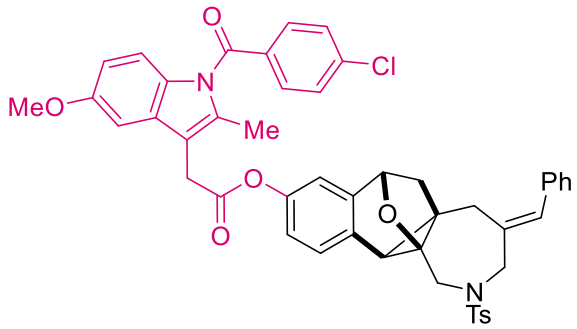
(5a*R,7*S**,11b*S**,11c*S**)-4-((*E*)-benzylidene)-2-tosyl-2,3,4,5,7,11b-hexahydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-c]azepin-9-yl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (3ad)**



Column chromatography (petroleum ether/EtOAc = 9:1 to 4:1) to give the product **3ad** in 66% yield (75 mg); colorless solid, mp 135–137 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.31 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.32 (t, *J* = 8.4 Hz, 4H), 7.25–7.23 (m, 2H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.10 (dd, *J* = 8.1, 2.3 Hz, 1H), 7.00 (d, *J* = 2.2 Hz, 1H), 6.71 (s, 1H), 4.96 (d, *J* = 5.9 Hz, 1H), 4.34 (d, *J* = 14.0 Hz, 1H), 4.00 (d, *J* = 14.3 Hz, 1H), 3.84 (d, *J* = 14.3 Hz, 1H), 3.65 (d, *J* = 14.0

Hz, 1H), 3.15–3.11 (m, 4H), 2.90 (d, *J* = 14.1 Hz, 1H), 2.86 (d, *J* = 14.1 Hz, 1H), 2.51 (s, 1H), 2.45 (s, 3H), 1.91 (dd, *J* = 11.7, 6.0 Hz, 1H), 1.60–1.54 (m, 4H), 1.21 (d, *J* = 11.8 Hz, 1H), 0.89 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 164.1, 148.1, 144.9, 143.5, 136.6, 136.6, 136.4, 134.3, 132.9, 131.9, 130.8, 130.7, 129.8, 128.6, 128.5, 127.8, 127.3, 127.3, 127.2, 120.6, 115.7, 75.2, 65.0, 58.6, 49.9, 48.3, 33.3, 30.1, 26.3, 25.5, 21.9, 21.6, 11.2; **HRMS (ESI)** calcd for $C_{42}H_{44}N_2NaO_7S_2$ $[M+Na]^+$: 775.2482; found: 775.2485.

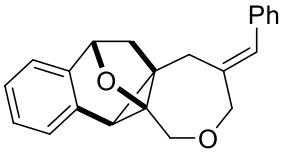
(5a*R,7*S**,11b*S**,11c*S**)-4-((*E*)-benzylidene)-2-tosyl-2,3,4,5,7,11b-hexahydro-1*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-c]azepin-9-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (3ae)**



Column chromatography (petroleum ether/EtOAc = 9:1 to 4:1) to give the product **3ae** in 47% yield (57 mg); yellow solid, mp 175–177 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.32–7.29 (m, 4H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 1H), 7.06 (d, *J* = 2.3 Hz, 1H), 6.94 (dd, *J* = 8.1, 2.2 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 1H), 6.83 (d, *J* = 2.0 Hz, 1H), 6.71–6.69 (m, 2H), 4.90 (d, *J* = 6.0 Hz, 1H), 4.33 (d, *J* = 14.1 Hz, 1H), 3.97 (d, *J* = 14.4 Hz, 1H), 3.89 (s, 2H), 3.84 (s, 3H), 3.82 (d, *J* = 14.4 Hz, 1H), 3.63 (d, *J* = 14.1 Hz, 1H), 2.87 (d, *J* = 14.1 Hz, 1H), 2.82 (d, *J* = 14.1 Hz, 1H), 2.45 (s, 1H), 2.44 (s, 6H), 1.86 (dd, *J* = 11.7, 6.0 Hz, 1H), 1.15 (d, *J* = 11.7 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 169.4, 168.3, 156.1, 148.1, 143.4, 139.3, 136.5, 136.5, 136.1, 136.1, 134.2, 133.8, 131.8, 131.2, 130.8, 130.5, 130.2, 129.7, 129.1, 128.5, 128.4, 127.5, 127.3, 127.2, 120.5, 115.6, 114.9, 112.0, 111.8, 101.2, 75.1, 64.9,

58.5, 55.7, 48.2, 33.3, 30.5, 30.1, 26.2, 25.4, 21.5, 13.4; **HRMS (ESI)** calcd for $C_{48}H_{41}ClN_2NaO_7S$ $[M+Na]^+$: 847.2215; found: 847.2219.

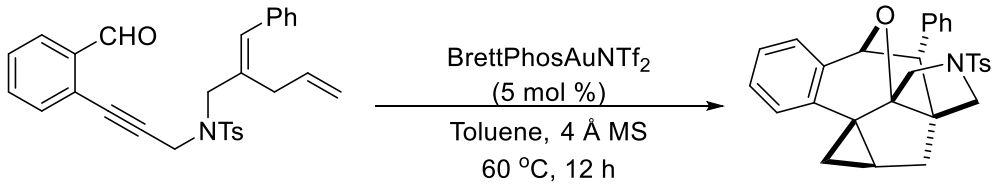
(5a*R,7*S**,11b*S**,11c*S**)-4-((*E*)-benzylidene)-4,5,7,11b-tetrahydro-1*H*,3*H*,6*H*-7,11c-epoxynaphtho[2',1':2,3]cyclopropa[1,2-*c*]oxepine (3af)**



Column chromatography (petroleum ether/EtOAc = 25:1 to 20:1) to give the product **3af** in 72% yield (34 mg); colorless oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.34–7.31 (m, 3H), 7.29 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.28–7.24 (m, 3H), 7.19 (td, *J* = 7.3, 1.5 Hz, 1H), 7.14 (d, *J* = 7.3 Hz, 1H), 6.69 (s, 1H), 5.09 (d, *J* = 6.0 Hz, 1H), 4.37 (d, *J* = 12.5 Hz, 1H), 4.33 (d, *J* = 12.9 Hz, 1H), 4.18 (d, *J* = 12.9 Hz, 1H), 4.10 (d, *J* = 12.4 Hz, 1H), 3.01 (d, *J* = 13.9 Hz, 1H), 2.93 (d, *J* = 13.9 Hz, 1H), 2.65 (s, 1H), 2.14 (dd, *J* = 11.5, 6.0 Hz, 1H), 1.28 (d, *J* = 11.6 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 136.8, 136.7, 135.6, 132.7, 132.2, 128.6, 128.4, 127.8, 127.1, 126.7, 124.8, 122.2, 81.0, 75.9, 69.7, 66.3, 33.6, 30.7, 26.3, 25.6; **HRMS (ESI)** calcd for $C_{22}H_{21}O_2$ $[M+H]^+$: 317.1536; found: 317.1539.

5. Gram-scale synthesis of 2a and 3a and selective transformations

5.1. Gram-scale synthesis of 2a

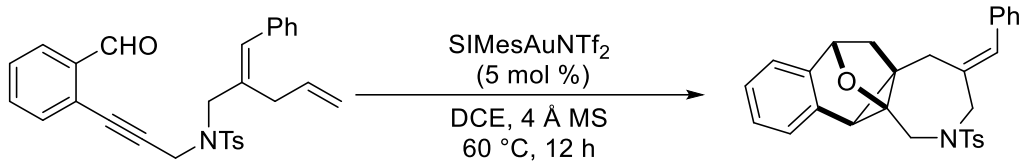


1a (1.08 g, 2.3 mmol) **2a** (950 mg, 88% yield, 16:1)

To a solution of **1a** (1.08 g, 2.3 mmol) and 4 Å MS (2.3 g) in anhydrous toluene (46 mL) was added $BrettPhosAuNTf_2$ (5 mol %) under an argon atmosphere. The reaction mixture was stirred at 60 °C for 12 h. Upon completion, the reaction mixture was cooled down to room temperature and filtered through celite, washed with CH_2Cl_2

and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether: EtOAc = 20:1 to 11:1) to give the product **2a** (950 mg, 88%).

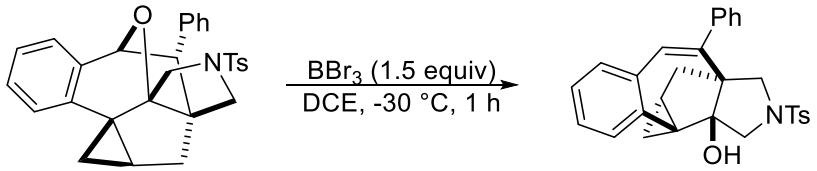
5.2. Gram-scale synthesis of 3a



1a (1.08 g, 2.3 mmol) **3a** (756 mg, 70% yield)

To a solution of **1a** (1.08 g, 2.3 mmol) and 4 Å MS (2.3 g) in anhydrous $(CH_2Cl)_2$ (46 mL) was added $SIMesAuNTf_2$ (5 mol %) under an argon atmosphere. The reaction mixture was stirred at 60 °C for 12 h. Upon completion, the reaction mixture was cooled down to room temperature and filtered through Celite, washed with CH_2Cl_2 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether: EtOAc = 20:1 to 9:1) to give the product **3a** (756 mg, 70%).

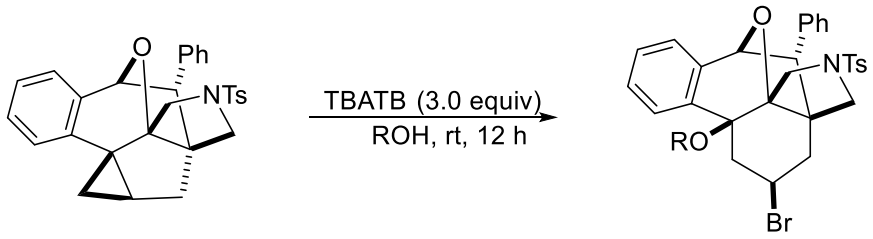
5.3. Synthetic applications of 2a



2a **4** (54%)

In a 25 mL Schlenk flask, **2a** (46.9 mg, 0.1 mmol, 1.0 equiv) was dissolved in anhydrous $(CH_2Cl)_2$ (2 mL) under argon atmosphere. The solution was cooled to –30 °C and then BBr_3 (1.0 M in CH_2Cl_2, 0.15 mL, 1.5 equiv) was added dropwise to the mixture. After stirring at –30 °C for 1 h, the reaction was warmed to room temperature and stirred for another 1 h. The reaction was quenched with saturated $NaHCO_3$, extracted with CH_2Cl_2 twice, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc = 9:1 to 4:1) to afford **4** in 54% yield (25.2 mg) as

a colorless solid, mp 167–169 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.36–7.30 (m, 5H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.21–7.15 (m, 3H), 7.03 (d, *J* = 6.8 Hz, 1H), 6.57 (s, 1H), 3.79 (dd, *J* = 11.3, 2.0 Hz, 1H), 3.48 (d, *J* = 11.3 Hz, 1H), 3.38 (d, *J* = 10.0 Hz, 1H), 2.91 (dd, *J* = 14.0, 7.7 Hz, 1H), 2.77 (d, *J* = 9.9 Hz, 1H), 2.53 (d, *J* = 1.7 Hz, 1H), 2.37 (s, 3H), 1.80 (dd, *J* = 14.0, 5.3 Hz, 1H), 1.76–1.72 (m, 2H), 1.66–1.62 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.6, 143.2, 142.2, 137.8, 137.4, 134.2, 132.7, 131.5, 129.5, 129.2, 128.4, 127.7, 127.6, 127.3, 127.3, 126.9, 83.3, 74.4, 54.9, 51.8, 40.3, 37.1, 28.1, 25.9, 21.5; **HRMS (ESI)** calcd for $C_{29}H_{28}NO_3S$ $[M+H]^+$: 470.1784; found: 470.1786.



2a

R = Me, **5** (95%)
R = Et, **6** (67%)

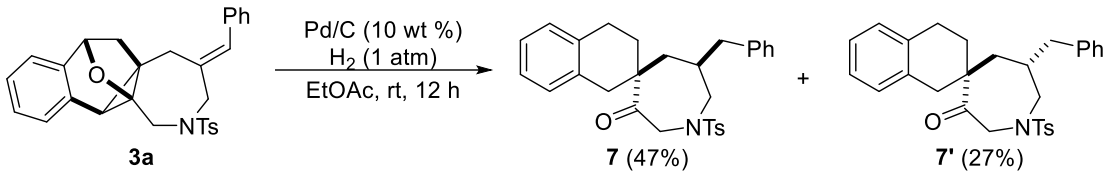
In a 10 mL round-bottomed flask, **2a** (46.9 mg, 0.1 mmol, 1.0 equiv) and TBATB (144.7 mg, 3 equiv) were dissolved in MeOH or EtOH (4 mL) and stirred at room temperature for 12 h. After the reaction was complete (monitored by TLC), the crude reaction mixture was quenched with saturated $NaHCO_3$, extracted with EtOAc, washed with water, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc = 11:1 to 6:1) to give **5** (55.2 mg) and **6** (39.8 mg) in 95% and 67% yields, respectively.

Product **5**: colorless solid, mp 229–230 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 7.3 Hz, 1H), 7.51–7.49 (m, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.29 (td, *J* = 7.4, 1.2 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 2H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.37 (d, *J* = 7.5 Hz, 2H), 5.21 (d, *J* = 6.8 Hz, 1H), 4.29 (d, *J* = 12.0 Hz, 1H), 3.65 (d, *J* = 4.3 Hz, 1H), 3.64 (d, *J* = 1.9 Hz, 1H), 3.35–3.29 (m, 2H), 3.16 (d, *J* = 9.0 Hz, 1H), 2.97 (s, 3H), 2.74–2.71 (m, 1H), 2.46 (s, 3H), 2.17 (t, *J* = 13.0 Hz, 1H), 1.75–1.71 (m, 1H), 1.66–1.62 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.9,

139.1, 134.9, 132.9, 132.9, 129.9, 129.8, 129.6, 128.4, 127.8, 127.7, 127.7, 127.2, 126.9, 94.6, 83.0, 75.9, 65.3, 60.0, 58.4, 53.5, 53.0, 46.0, 42.3, 39.9, 21.6; **HRMS (ESI)** calcd for $C_{30}H_{31}BrNO_4S$ $[M+H]^+$: 580.1152; found: 580.1152.

Product **6:** colorless solid, mp 206–207 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.50–7.48 (m, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.29–7.26 (m, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 2H), 6.88 (d, *J* = 7.4 Hz, 1H), 6.37 (d, *J* = 7.5 Hz, 2H), 5.19 (d, *J* = 6.8 Hz, 1H), 4.31 (d, *J* = 11.9 Hz, 1H), 3.64 (d, *J* = 2.4 Hz, 1H), 3.63 (s, 1H), 3.36–3.26 (m, 3H), 3.15 (d, *J* = 9.0 Hz, 1H), 2.94–2.86 (m, 1H), 2.77–2.74 (m, 1H), 2.46 (s, 3H), 2.19 (t, *J* = 13.0 Hz, 1H), 1.73 (t, *J* = 13.3 Hz, 1H), 1.65–1.62 (m, 1H), 1.01 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.9, 138.7, 135.0, 133.7, 132.9, 129.9, 129.8, 129.5, 128.4, 127.7, 127.7, 127.0, 126.9, 94.7, 83.1, 75. 8, 65.3, 60.9, 60.1, 58.3, 53.1, 46.3, 42.3, 39.9, 21.6, 15.8; **HRMS (ESI)** calcd for $C_{31}H_{33}BrNO_4S$ $[M+H]^+$: 594.1308; found: 594.1309.

5.4. Synthetic application of 3a



In a 10 mL round-bottom flask, Pd/C (4.7 mg, 10 wt%) was added to a solution of **3a** (46.9 mg, 0.1 mmol) in EtOAc (2.0 mL) under argon atmosphere. Then the reaction system was filled with H_2 and stirred at room temperature. After the reaction was complete (monitored by TLC), the crude reaction mixture was filtered through a pad of Celite. After the solvent was concentrated under reduced pressure, the crude product was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 20:1 to 11:1) to afford the desired product **7** (22.3 mg) and its isomer **7'** (12.7 mg) in 47% and 27% yield, respectively.

Product **7**: colorless solid, mp 149–150 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 (d, *J* = 8.3 Hz, 2H), 7.28 (dd, *J* = 7.4, 5.9 Hz, 4H), 7.34–7.20 (m, 1H), 7.13–7.11 (m, 2H), 7.10–7.07 (m, 3H), 7.02–7.00 (m, 1H), 4.45 (dd, *J* = 17.3, 1.7 Hz, 1H), 3.70 (d, *J* = 14.0 Hz, 1H), 3.51 (d, *J* = 17.3 Hz, 1H), 3.24 (d, *J* = 16.4 Hz, 1H), 2.80–2.76 (m, 2H), 2.55 (s, 1H), 2.51 (s, 3H), 2.43 (s, 3H), 2.40–2.35 (m, 1H), 2.33–2.25 (m, 2H), 1.82 (d, *J* = 14.7 Hz, 1H), 1.30–1.23 (m, 2H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 209.9, 143.8, 138.6, 134.9, 134.7, 129.9, 129.3, 128.9, 128.5, 128.4, 126.9, 126.5, 125.8, 125.8, 58.7, 54.4, 50.7, 40.4, 39.1, 38.3, 27.0, 25.9, 21.5; **HRMS (ESI)** calcd for $C_{29}H_{32}NO_3S$ $[M+H]^+$: 474.2097; found: 474.2100.

Product **7'**: colorless solid, mp 153–155 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52 (d, *J* = 8.3 Hz, 2H), 7.30–7.27 (m, 4H), 7.24–7.20 (m, 1H), 7.16–7.13 (m, 1H), 7.12–7.09 (m, 4H), 7.02–7.00 (m, 1H), 4.08 (dd, *J* = 16.2, 1.5 Hz, 1H), 3.75 (d, *J* = 16.0 Hz, 1H), 3.57 (d, *J* = 11.4 Hz, 1H), 3.49 (d, *J* = 16.2 Hz, 1H), 2.91–2.84 (m, 1H), 2.80–2.72 (m, 2H), 2.60–2.54 (m, 1H), 2.47–2.37 (m, 6H), 2.26–2.19 (m, 1H), 1.70–1.64 (m, 2H), 1.40–1.34 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 209.7, 143.8, 138.6, 135.3, 134.7, 134.0, 129.9, 129.6, 128.9, 128.6, 128.5, 127.0, 126.4, 126.2, 125.8, 58.2, 53.6, 50.8,

42.6, 40.5, 38.3, 35.2, 32.4, 25.7, 21.5; **HRMS (ESI)** calcd for $C_{29}H_{31}NNaO_3S$ $[M+Na]^+$: 496.1917; found: 496.1917.

6. ^{1}H, ^{13}C and ^{19}F NMR Spectra

Figure S1 ^{1}H NMR (600 MHz, $CDCl_3$) of 1a

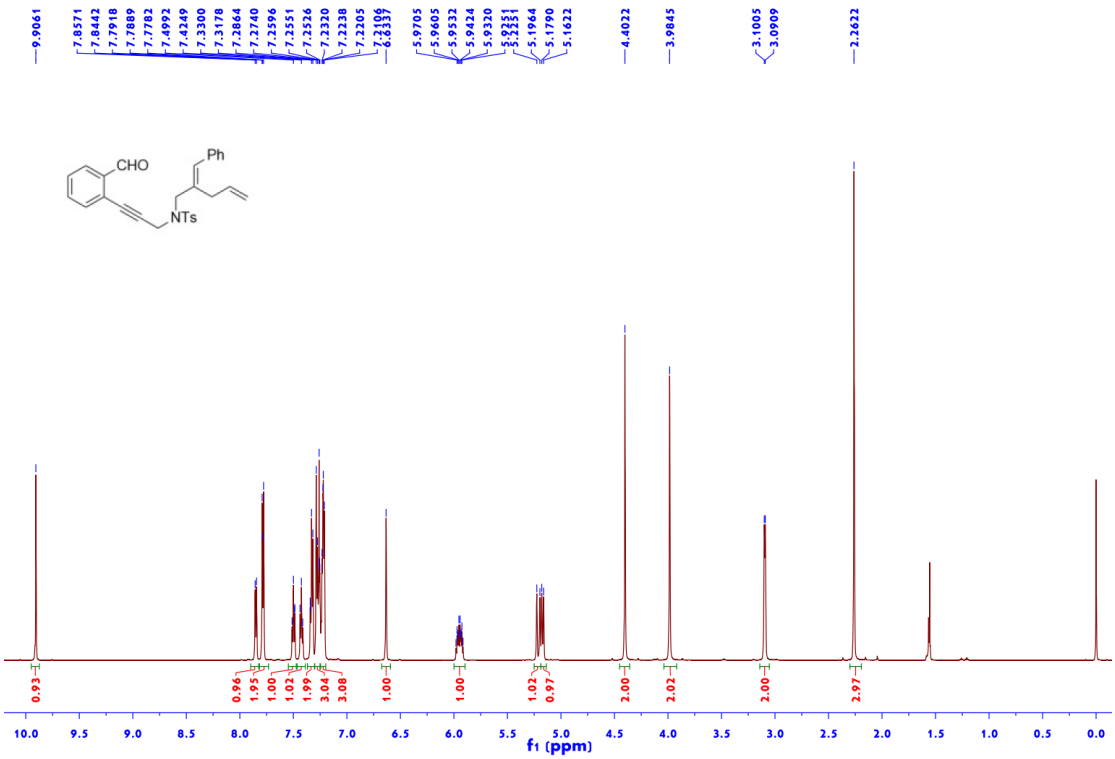


Figure S2 ^{13}C NMR (150 MHz, $CDCl_3$) of 1a

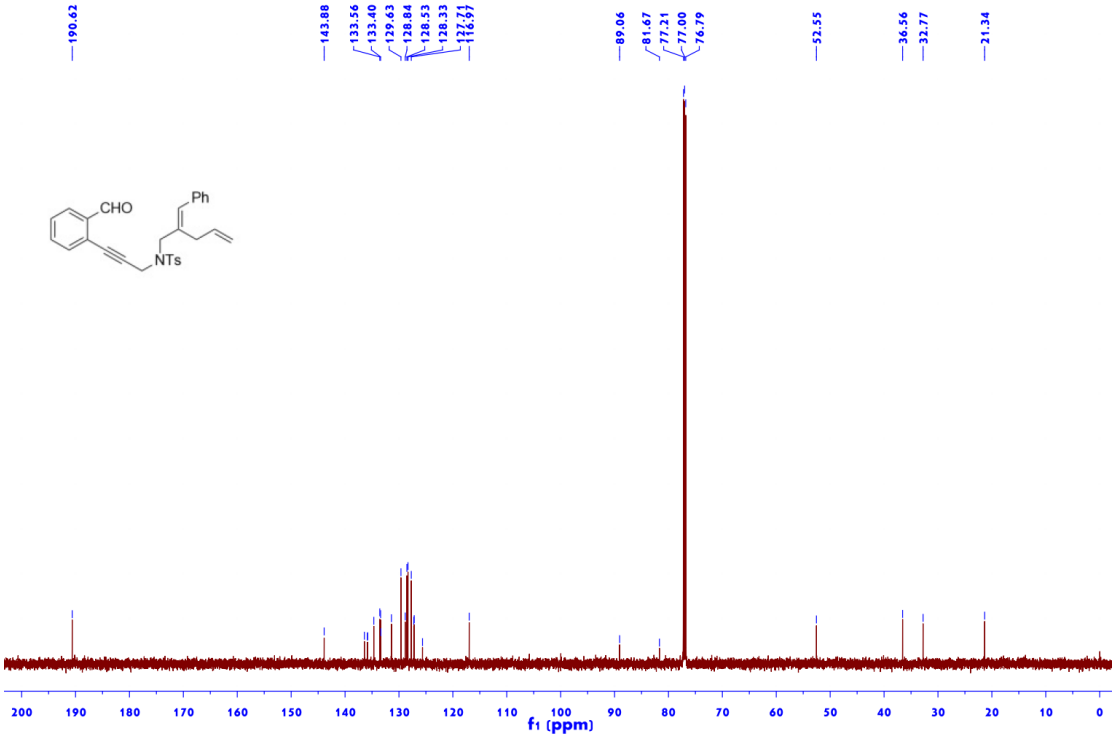


Figure S3 ^{1}H NMR (600 MHz, $CDCl_3$) of 1b

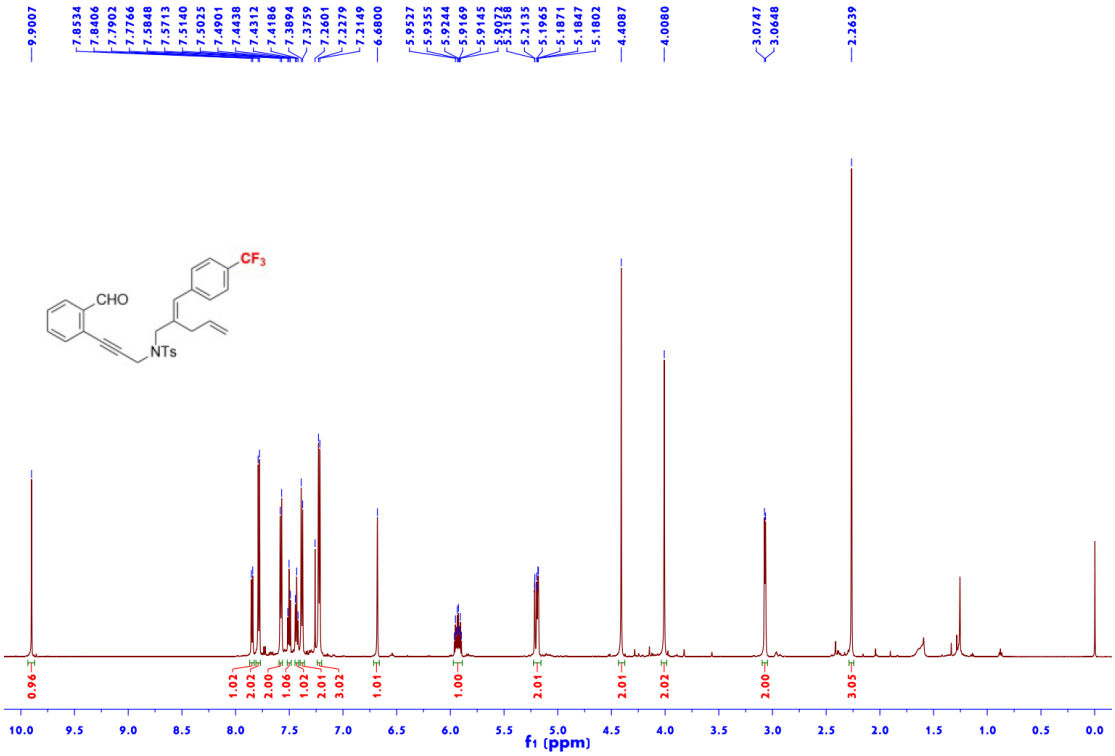


Figure S4 ^{13}C NMR (150 MHz, $CDCl_3$) of 1b

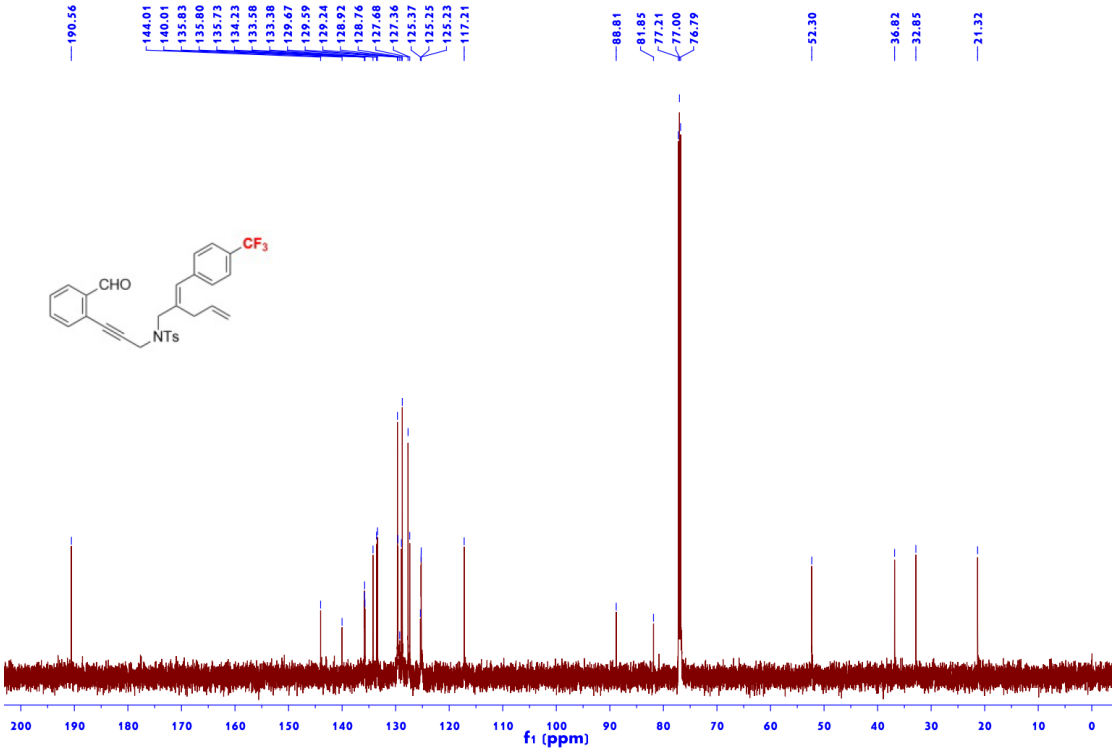


Figure S5 ^{19}F NMR (565 MHz, $CDCl_3$) of 1b

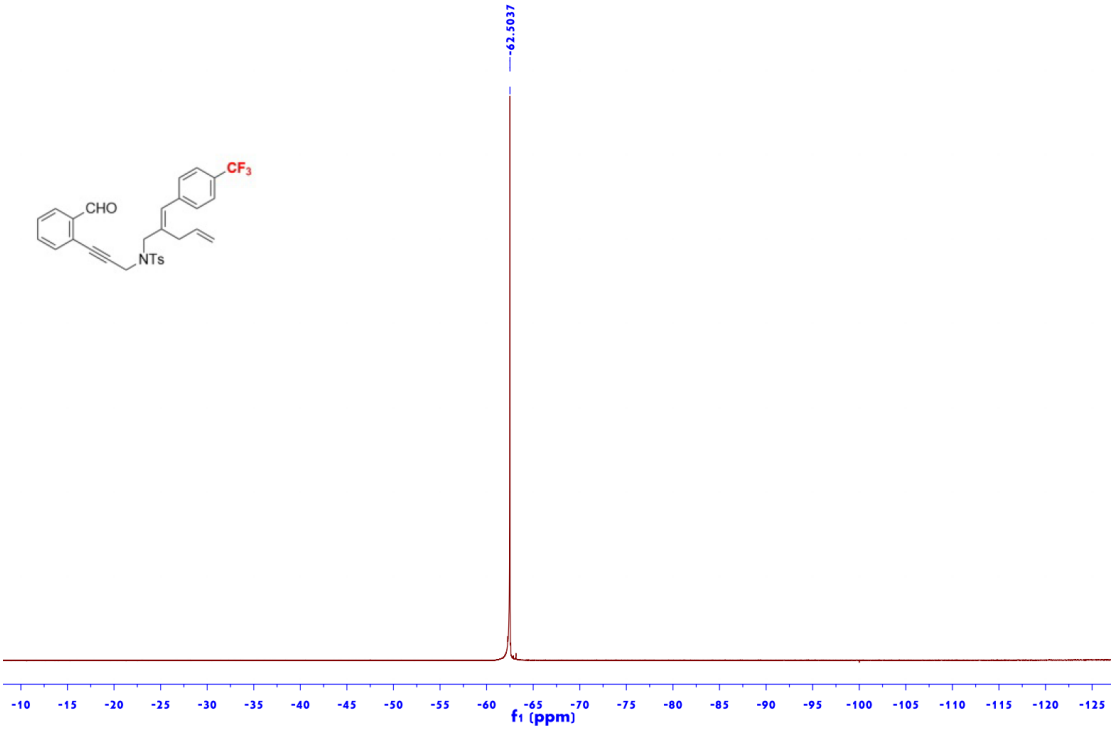


Figure S6 ^{1}H NMR (600 MHz, $CDCl_3$) of 1c

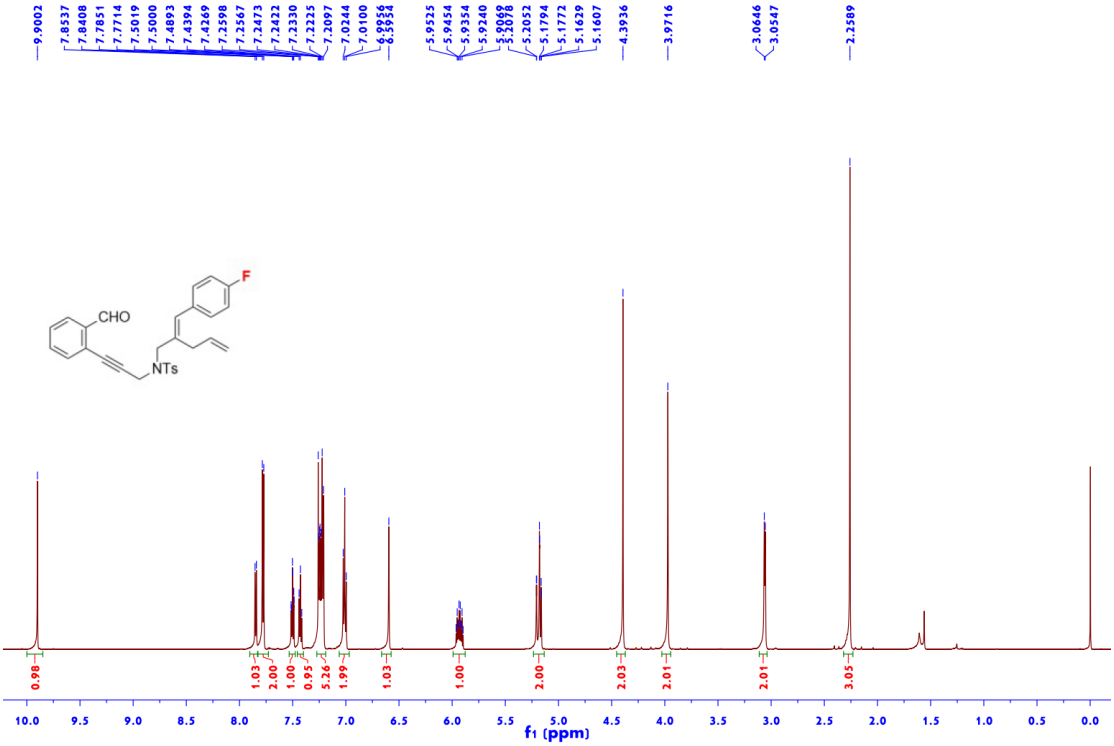


Figure S7 ^{13}C NMR (150 MHz, $CDCl_3$) of 1c

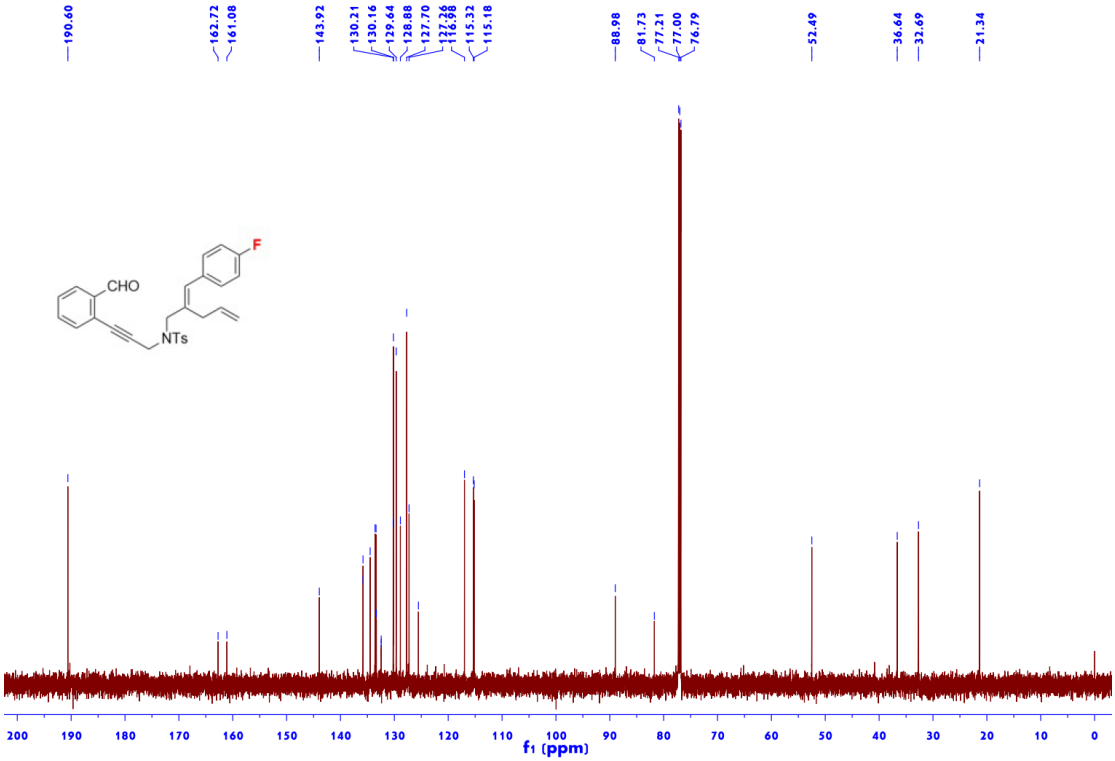


Figure S8 ^{1}H NMR (600 MHz, $CDCl_3$) of 1d

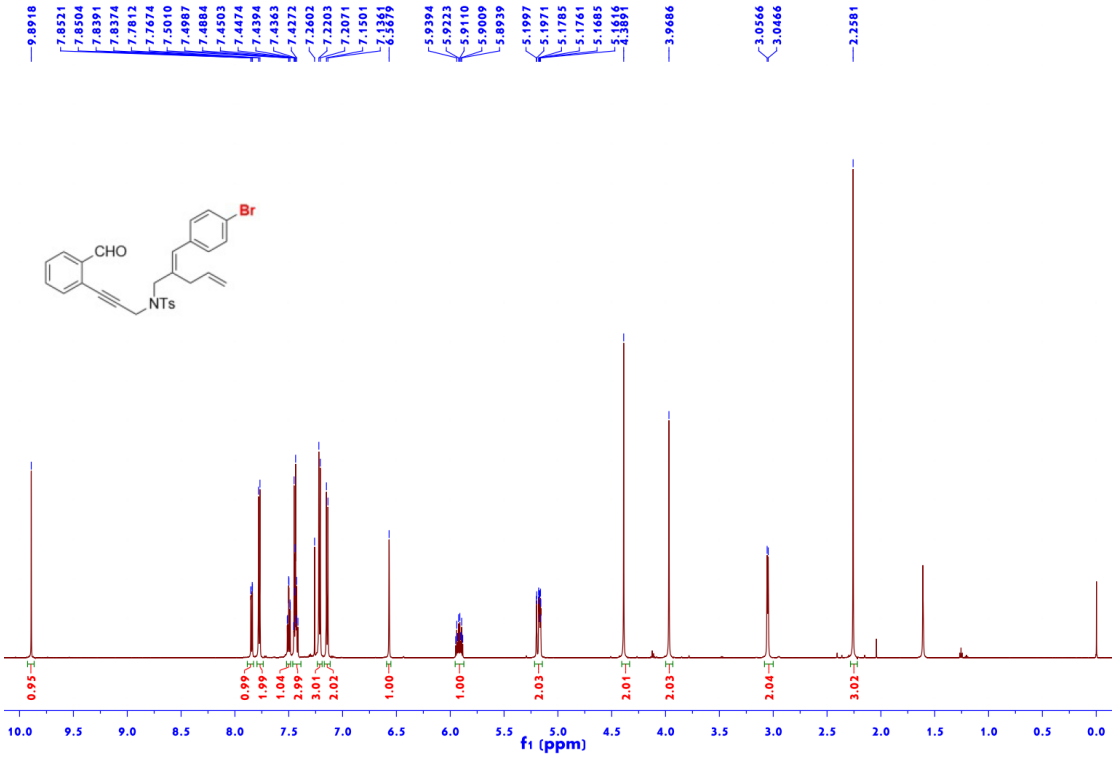


Figure S9 ^{13}C NMR (150 MHz, $CDCl_3$) of 1d

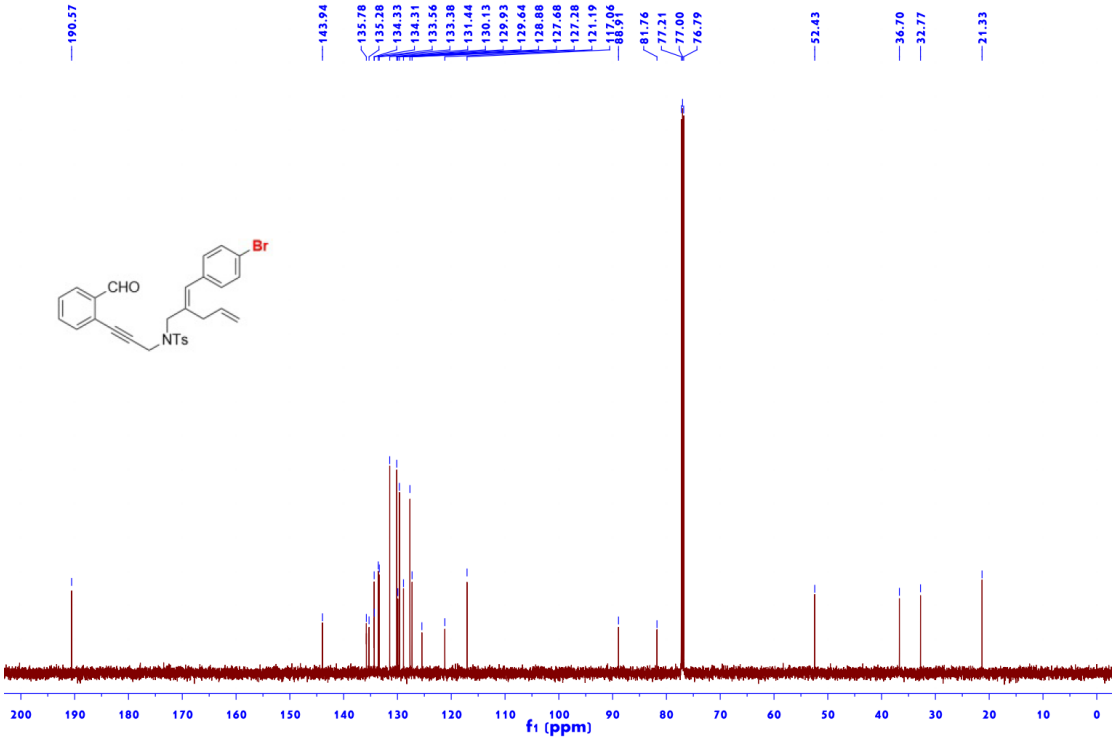


Figure S10 ^{1}H NMR (600 MHz, $CDCl_3$) of 1e

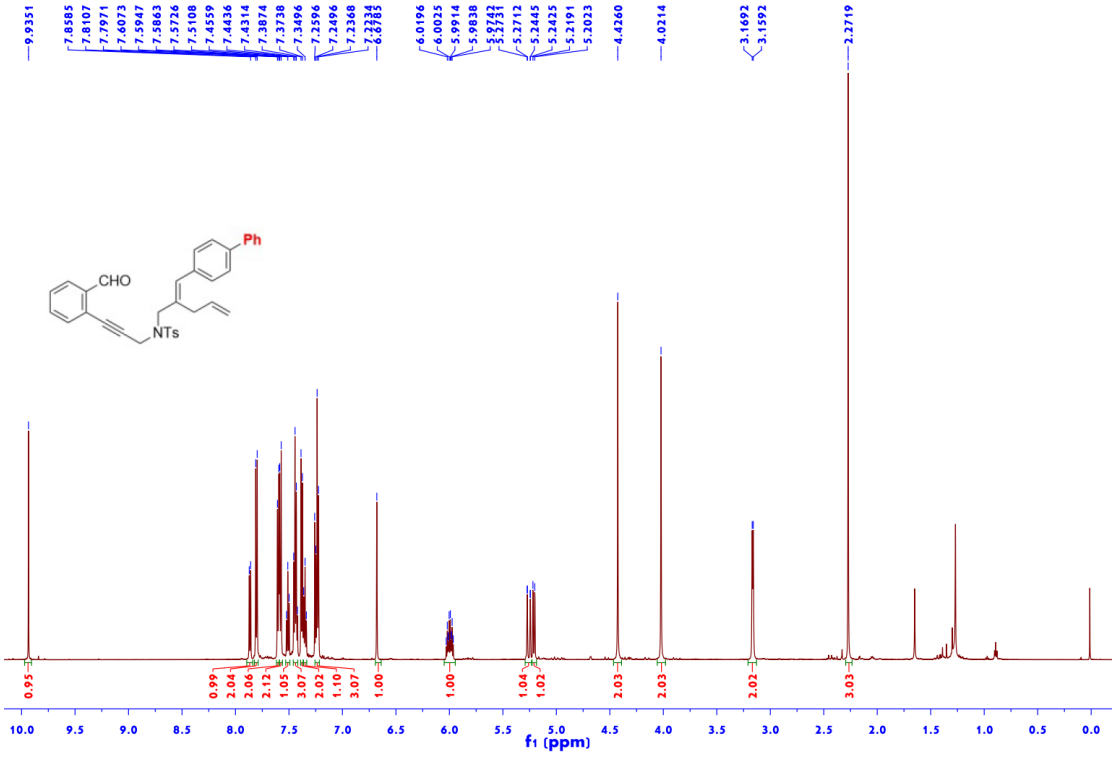


Figure S11 ^{13}C NMR (150 MHz, $CDCl_3$) of 1e

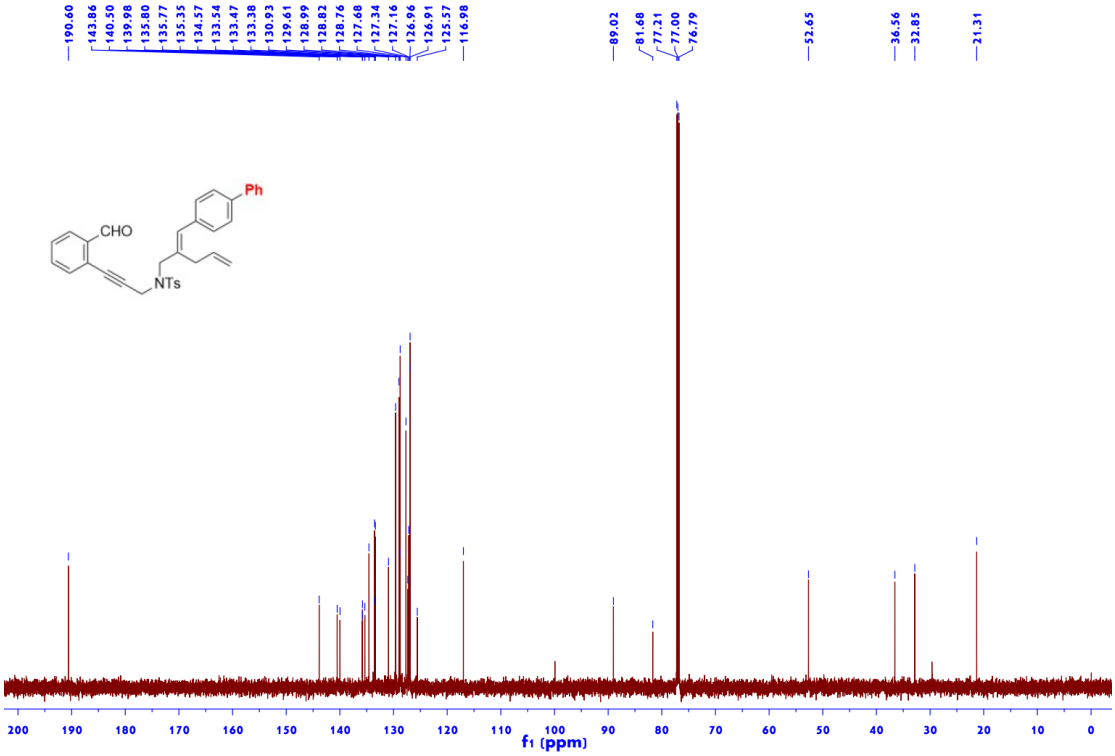


Figure S12 ^{1}H NMR (600 MHz, $CDCl_3$) of 1f

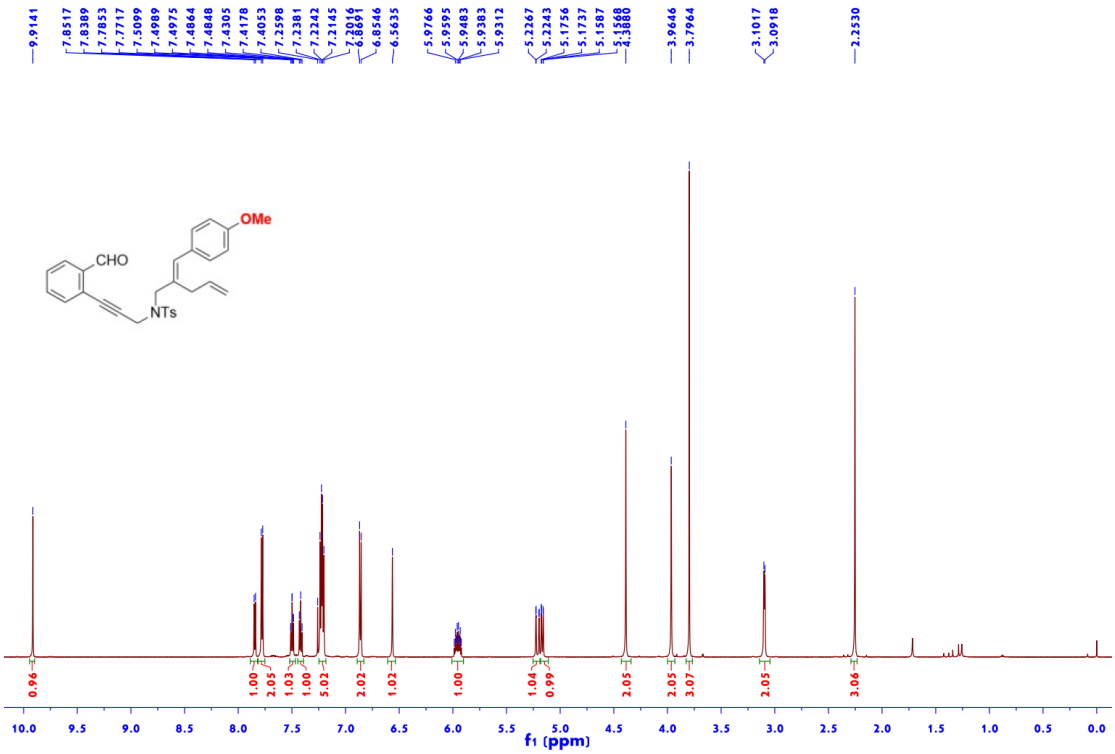


Figure S13 ^{13}C NMR (150 MHz, $CDCl_3$) of 1f

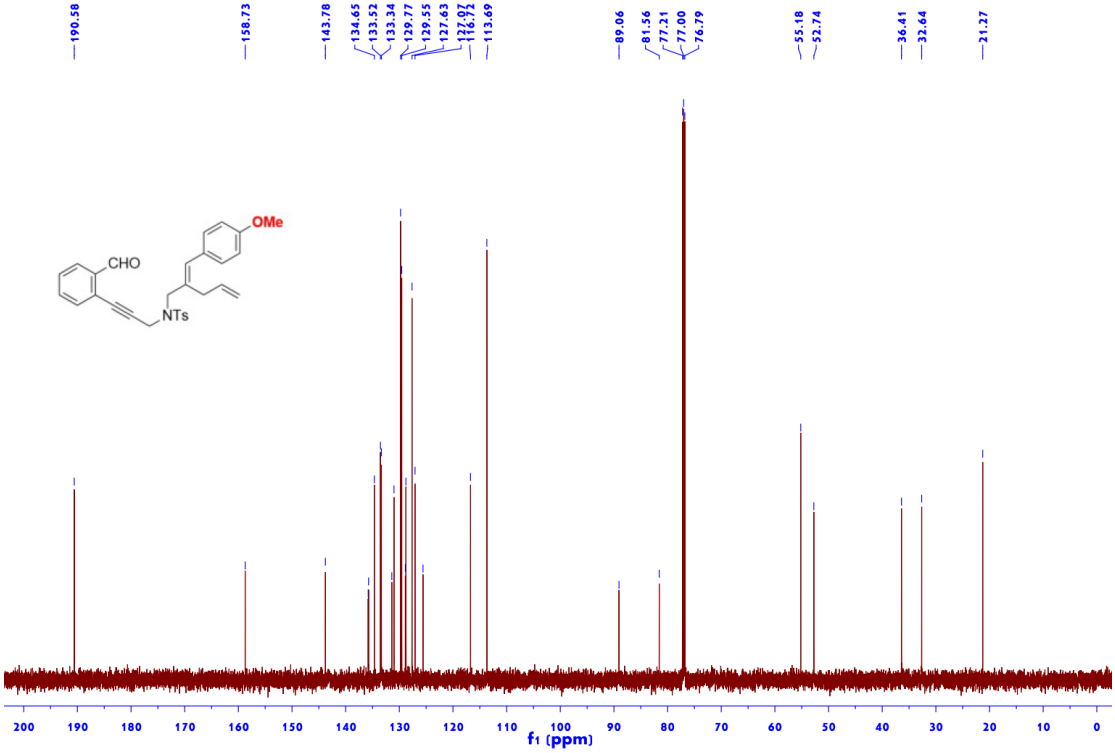


Figure S14 ^{1}H NMR (600 MHz, $CDCl_3$) of 1g

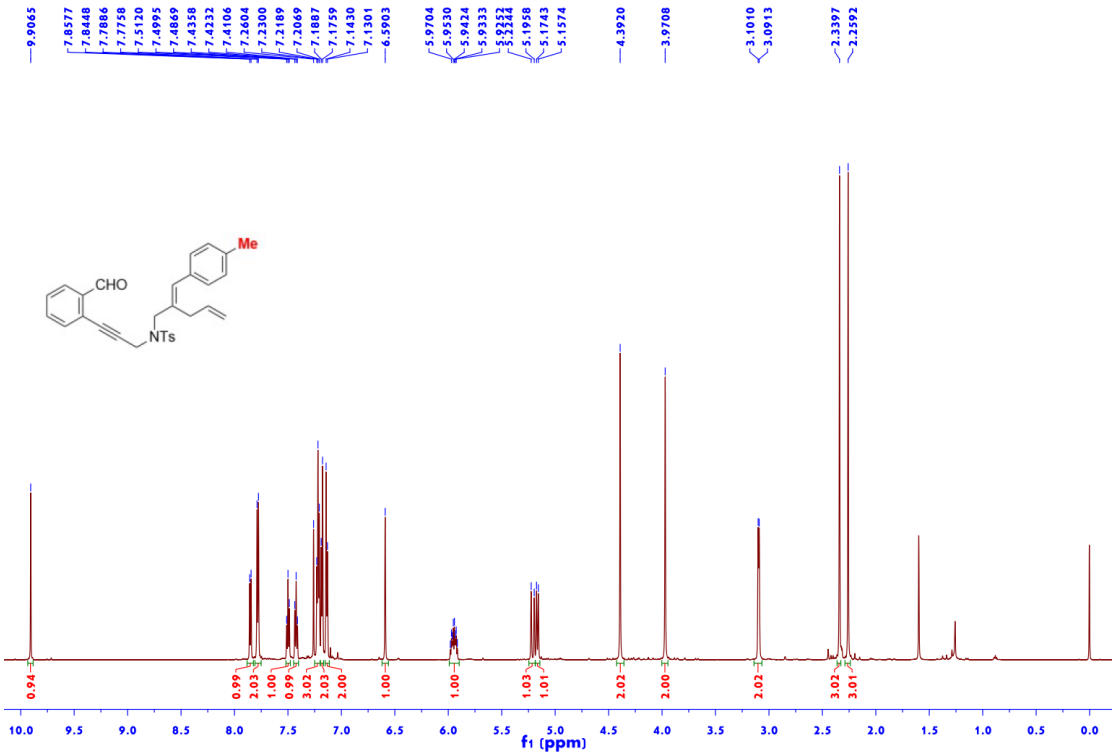


Figure S15 ^{13}C NMR (150 MHz, $CDCl_3$) of 1g

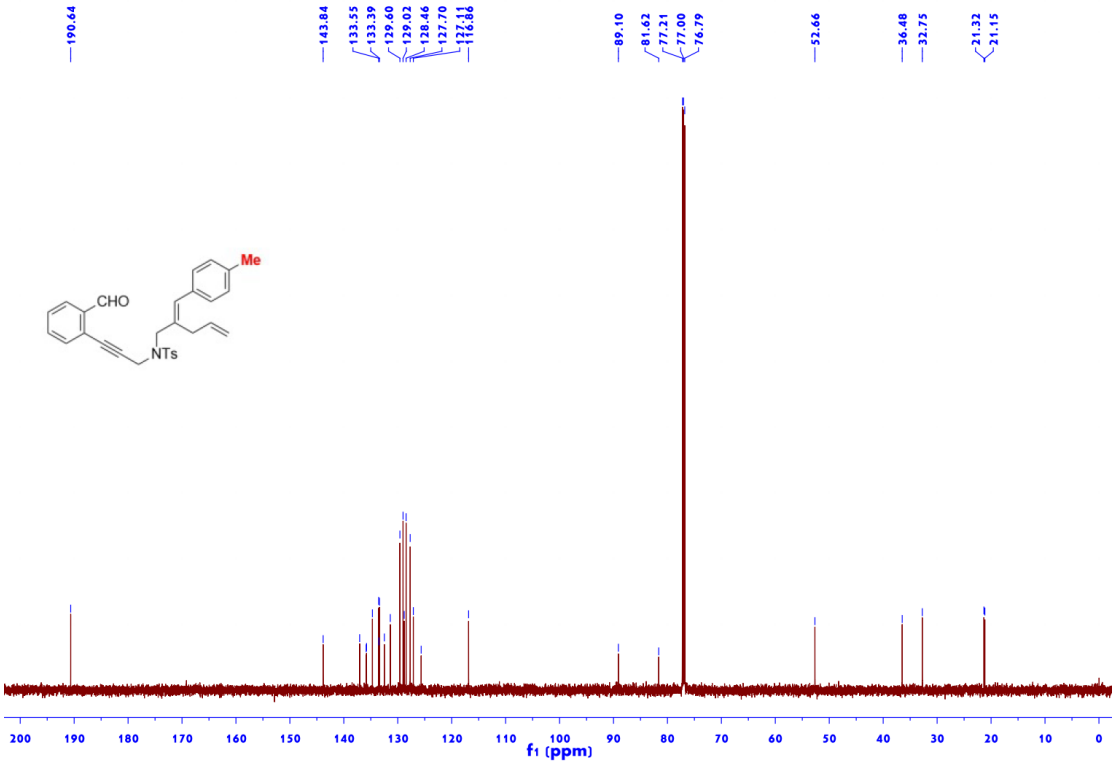


Figure S16 ^{1}H NMR (600 MHz, $CDCl_3$) of 1h

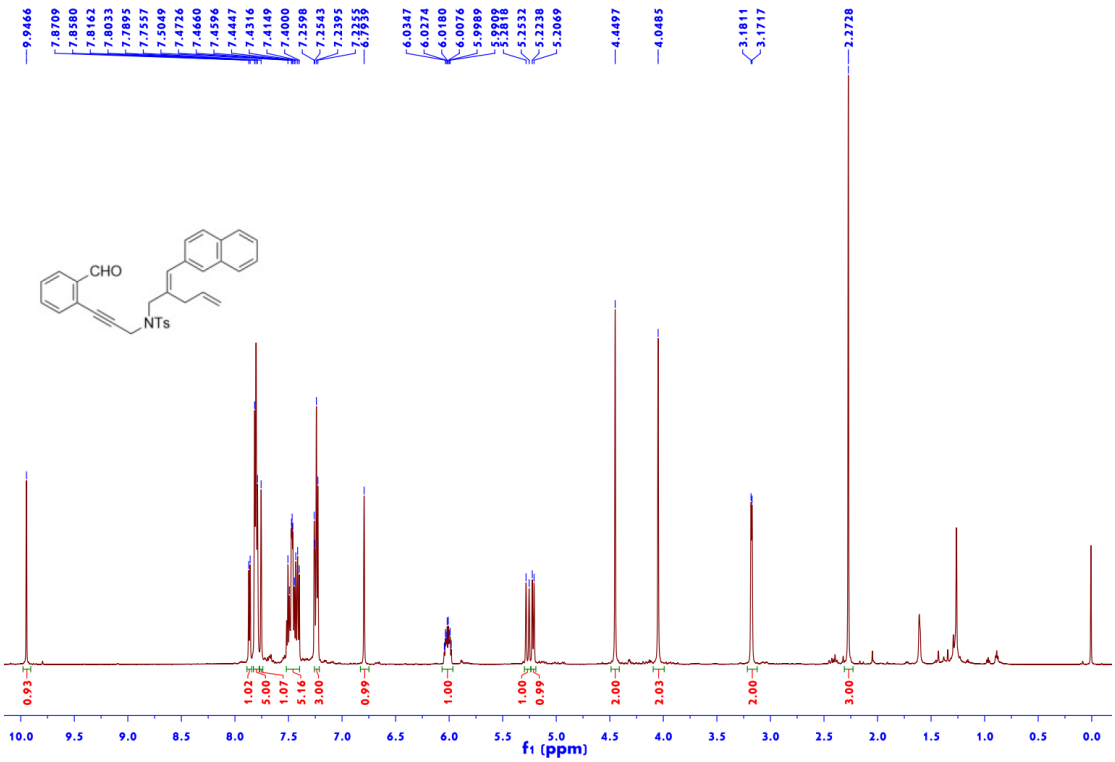


Figure S17 ^{13}C NMR (150 MHz, $CDCl_3$) of 1h

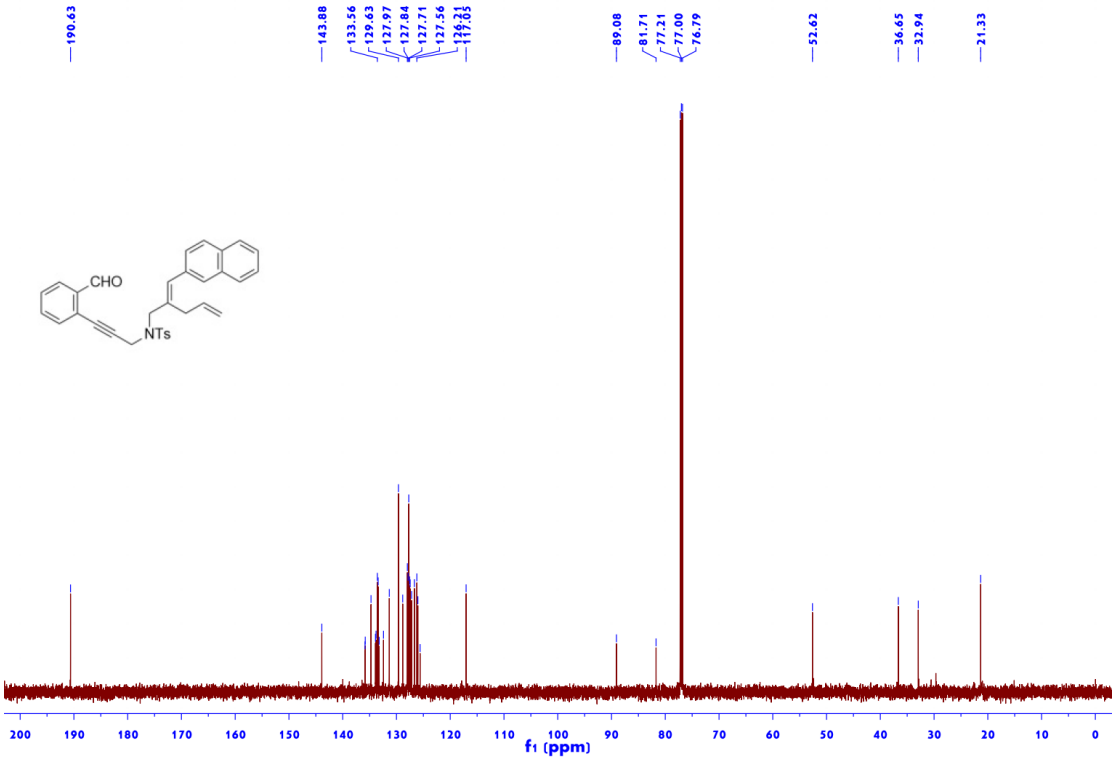


Figure S18 ^{1}H NMR (600 MHz, $CDCl_3$) of 1i

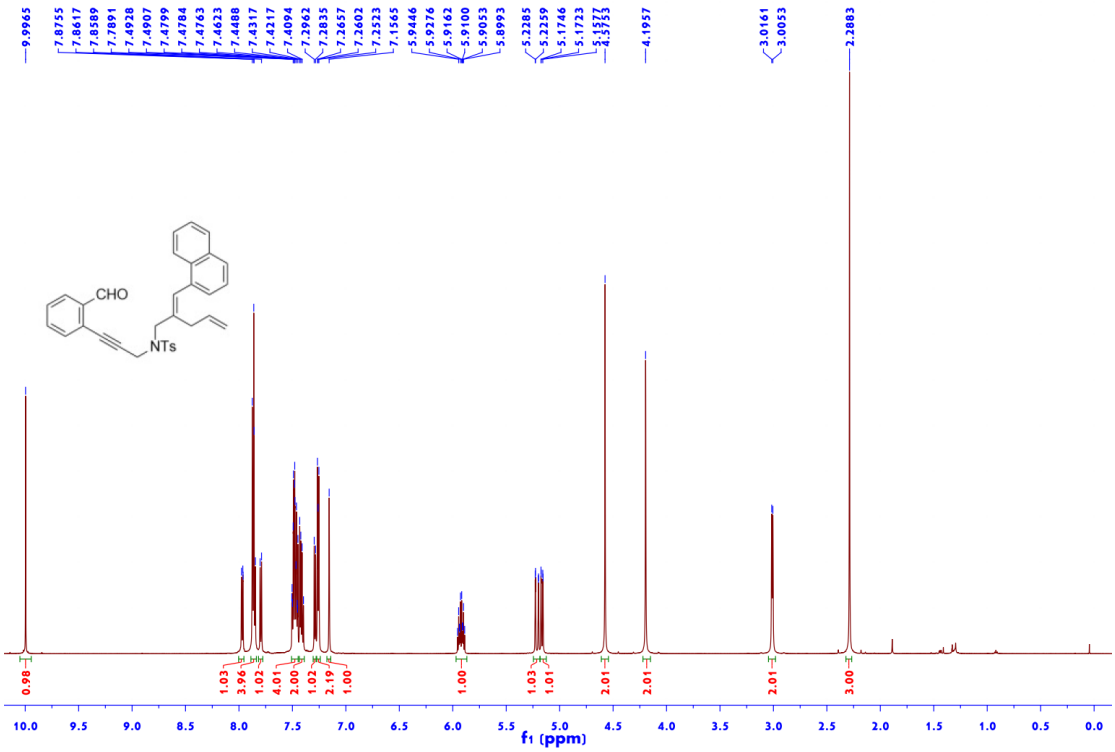


Figure S19 ^{13}C NMR (150 MHz, $CDCl_3$) of 1i

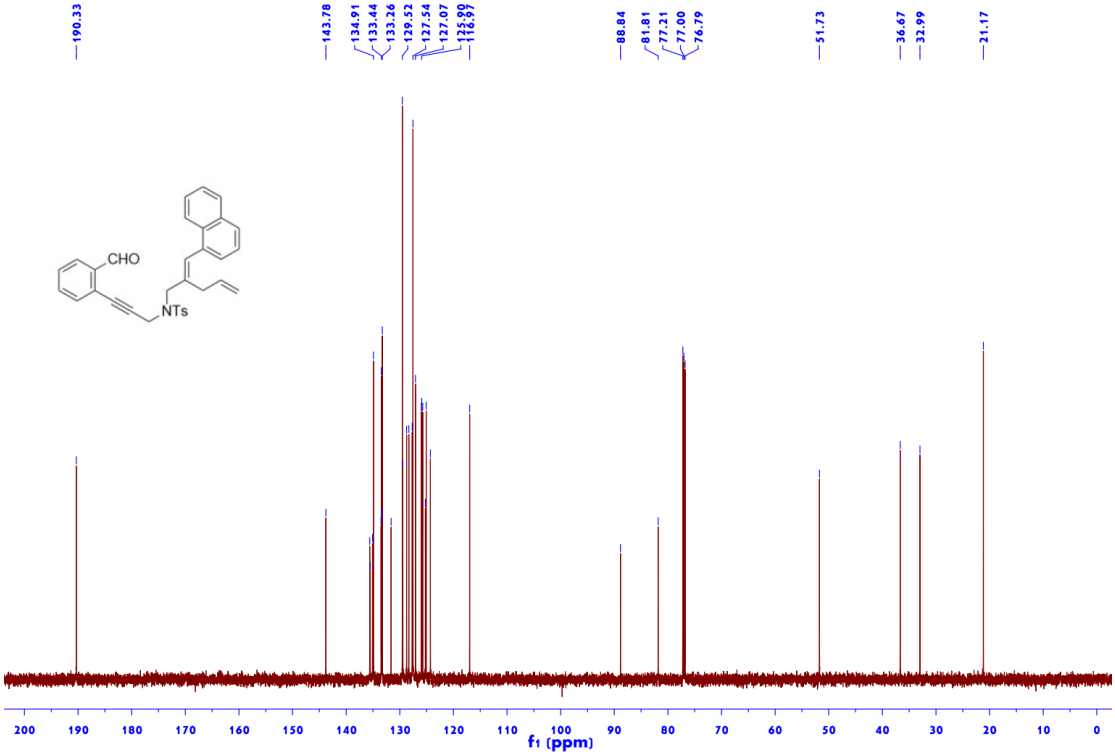


Figure S20 ^{1}H NMR (600 MHz, $CDCl_3$) of 1j

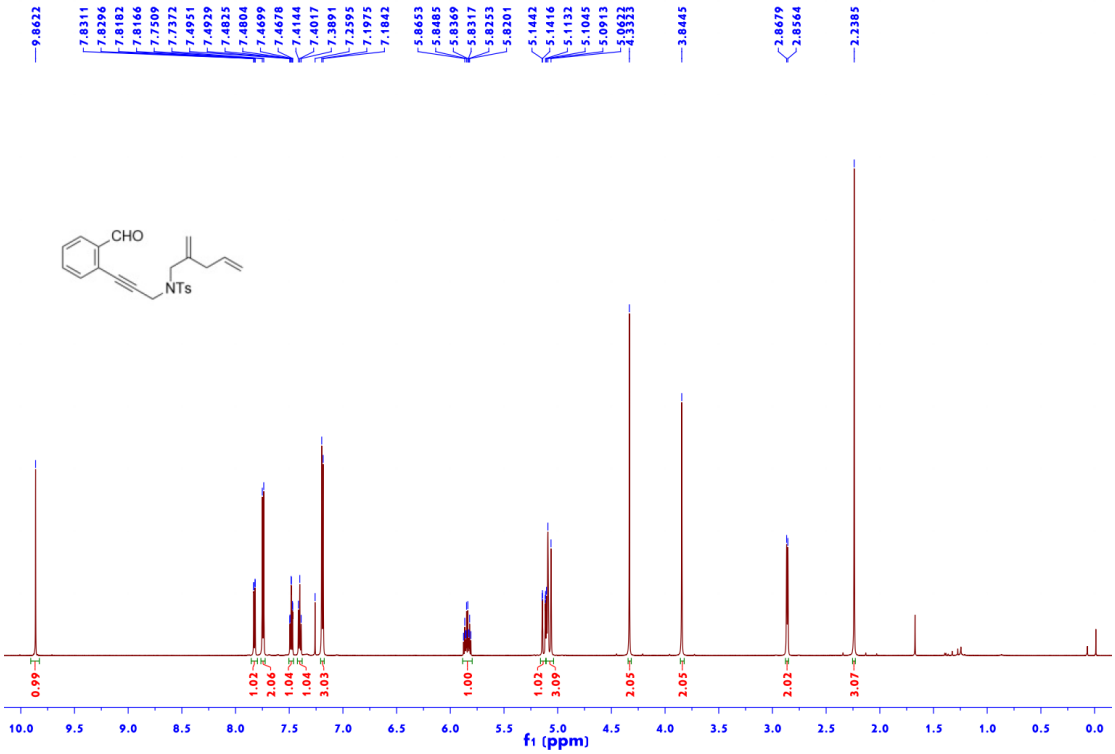


Figure S21 ^{13}C NMR (150 MHz, $CDCl_3$) of 1j

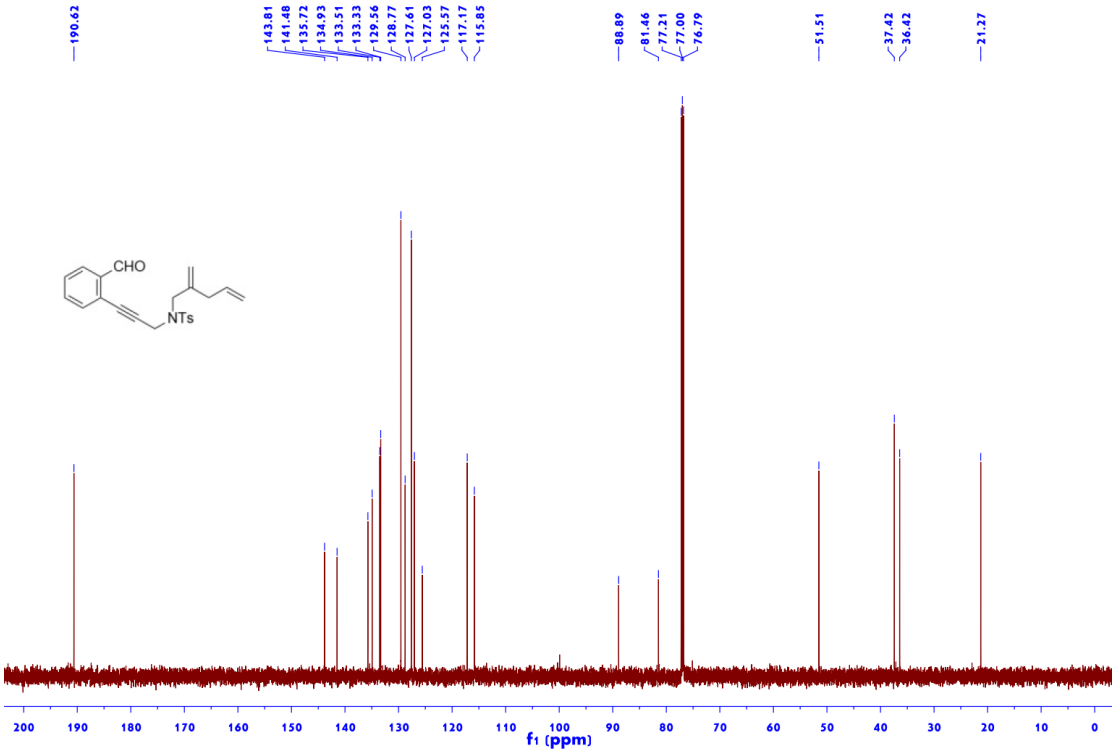


Figure S22 ^{1}H NMR (600 MHz, $CDCl_3$) of 1k

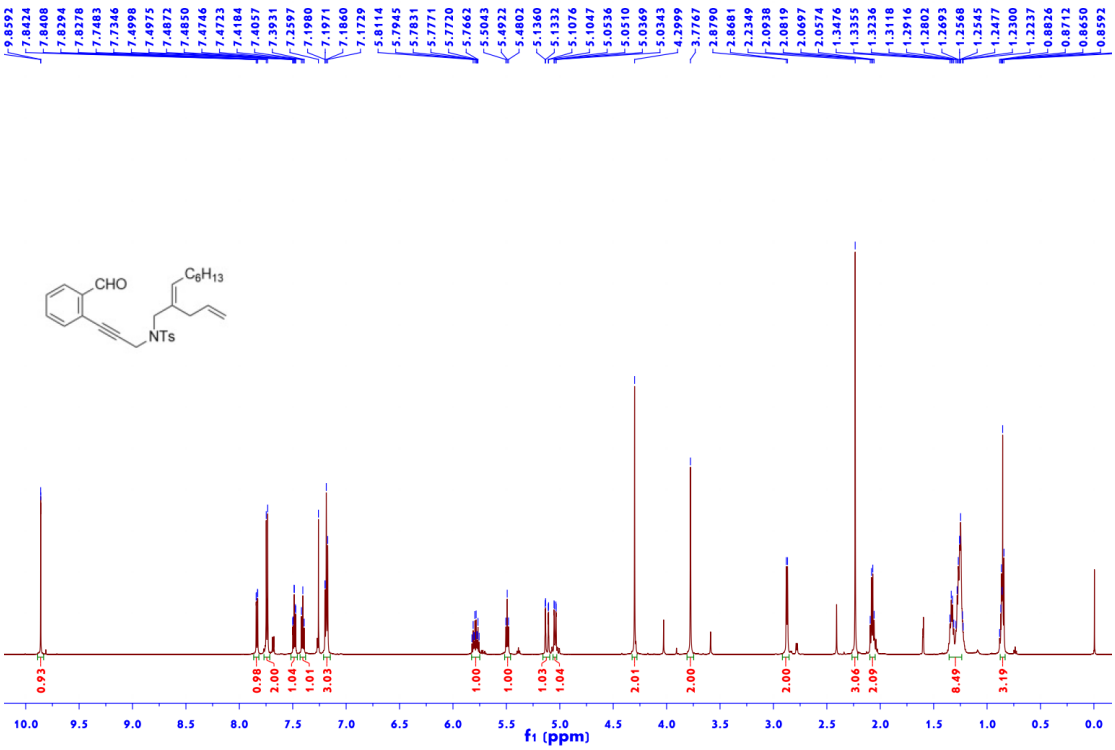


Figure S23 ^{13}C NMR (150 MHz, $CDCl_3$) of 1k

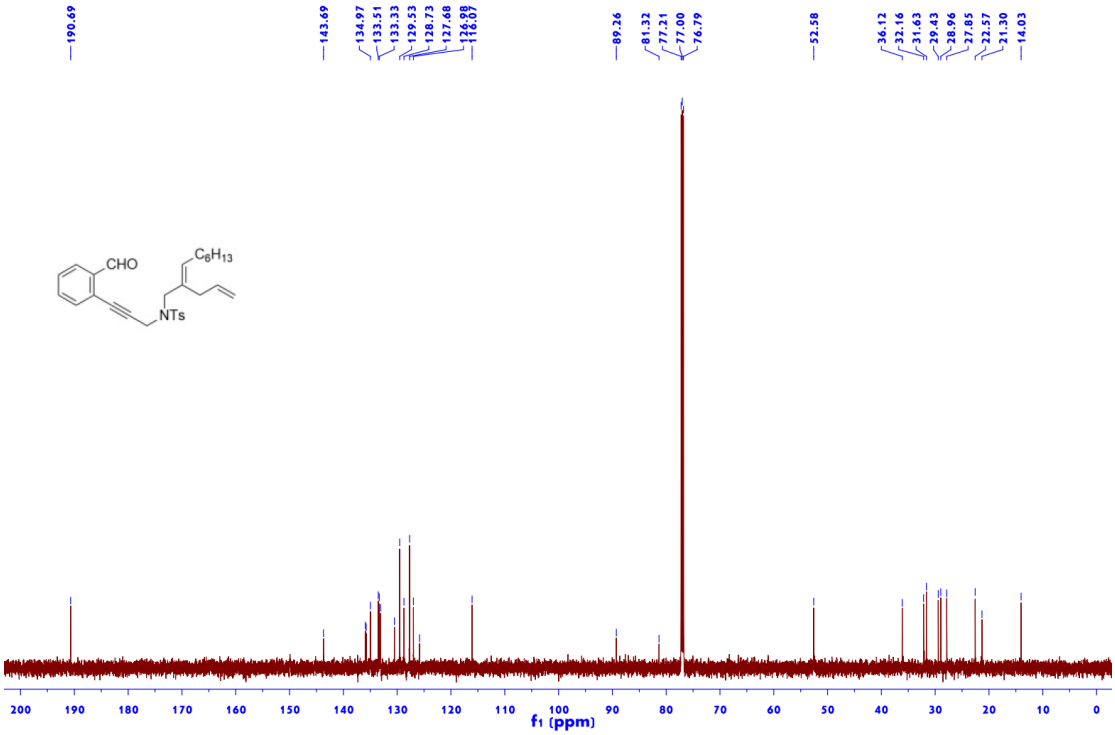


Figure S24 ^{1}H NMR (600 MHz, $CDCl_3$) of 1l

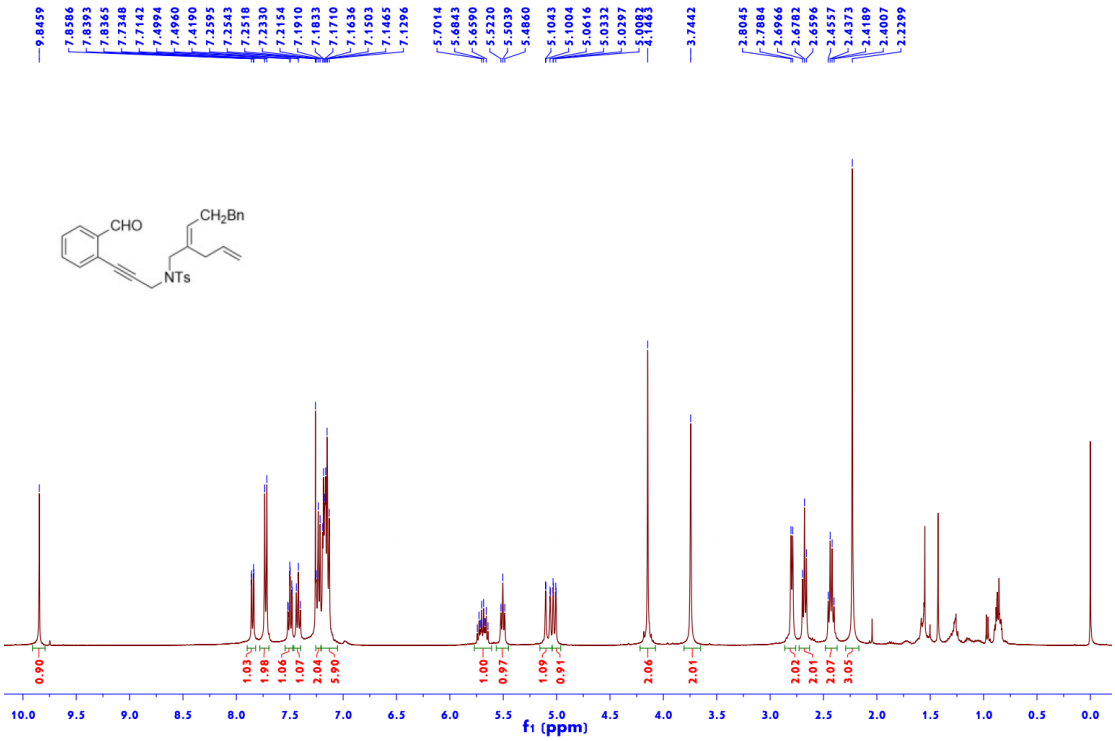


Figure S25 ^{13}C NMR (100 MHz, $CDCl_3$) of 1l

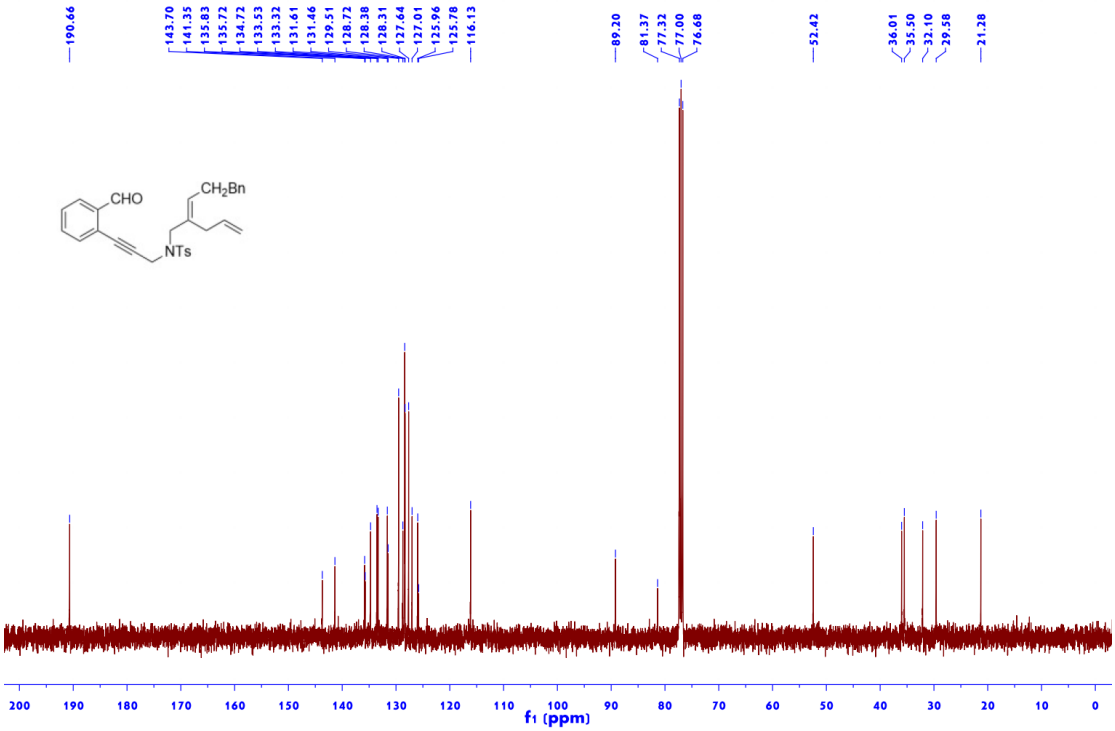


Figure S26 ^{1}H NMR (400 MHz, $CDCl_3$) of 1m

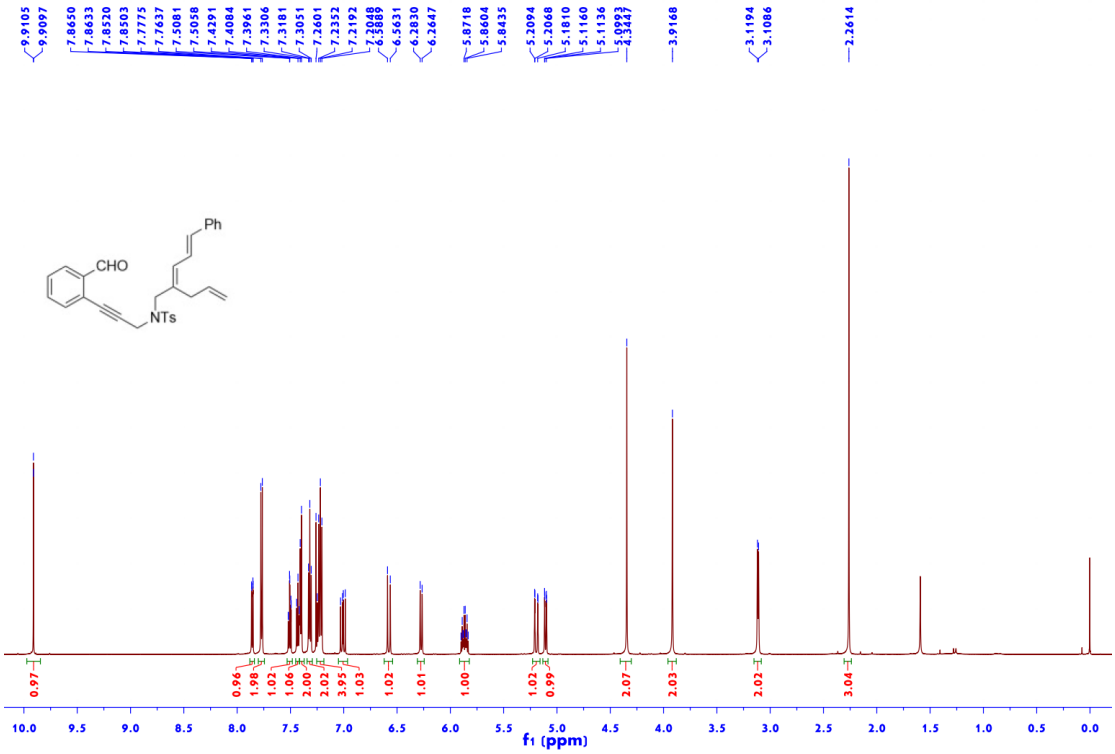


Figure S27 ^{13}C NMR (100 MHz, $CDCl_3$) of 1m

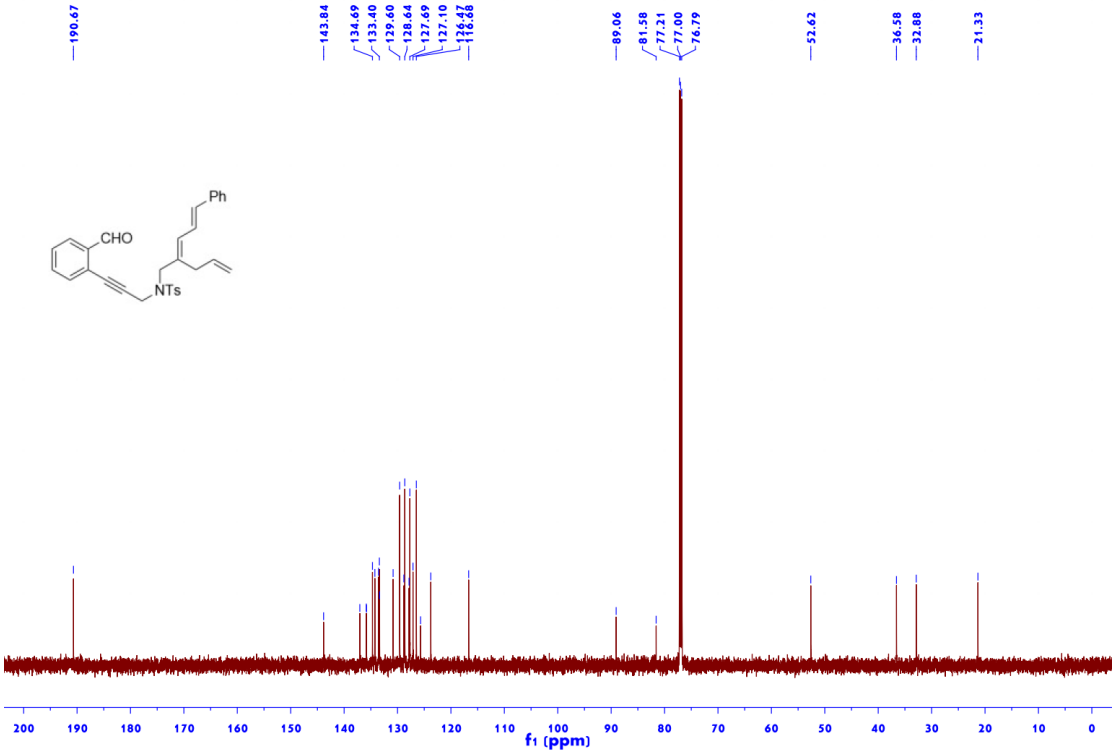


Figure S28 ^{1}H NMR (600 MHz, $CDCl_3$) of 1n

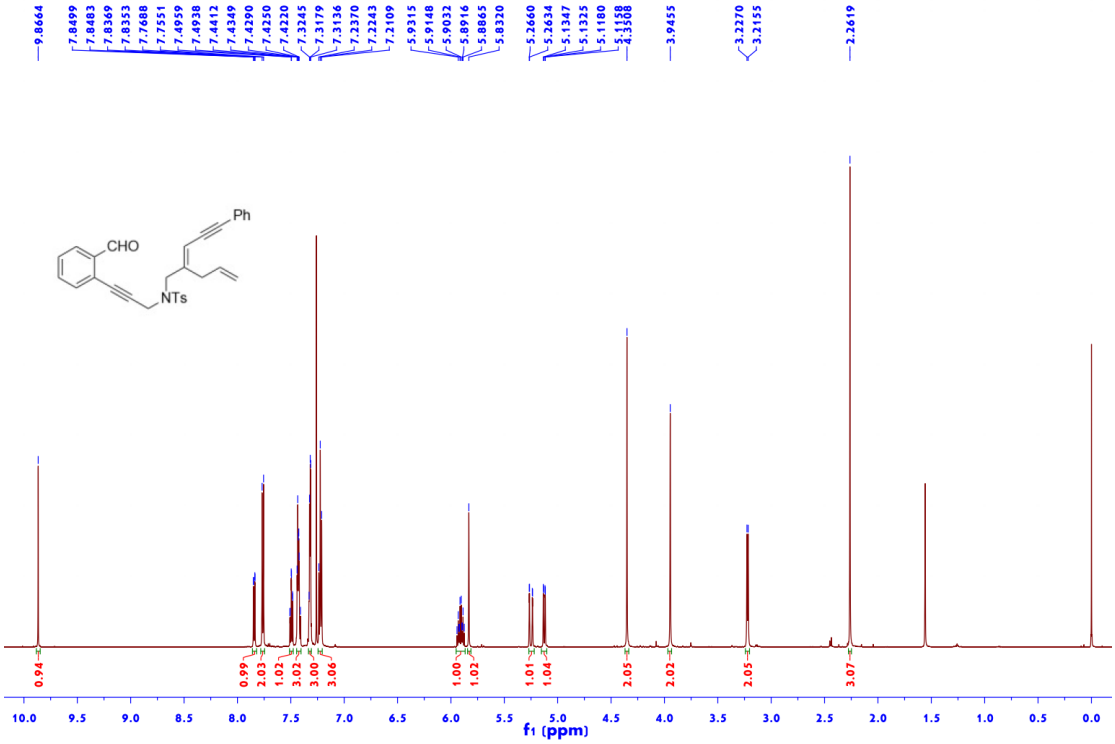


Figure S29 ^{13}C NMR (150 MHz, $CDCl_3$) of 1n

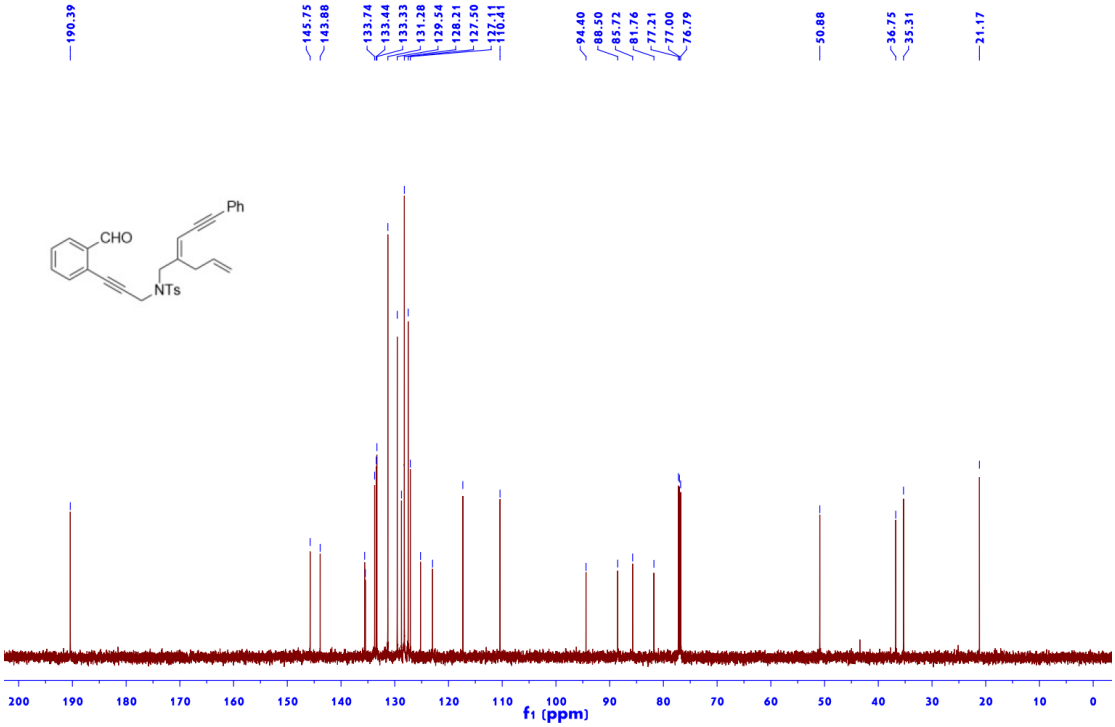


Figure S30 ^{1}H NMR (600 MHz, $CDCl_3$) of 1o

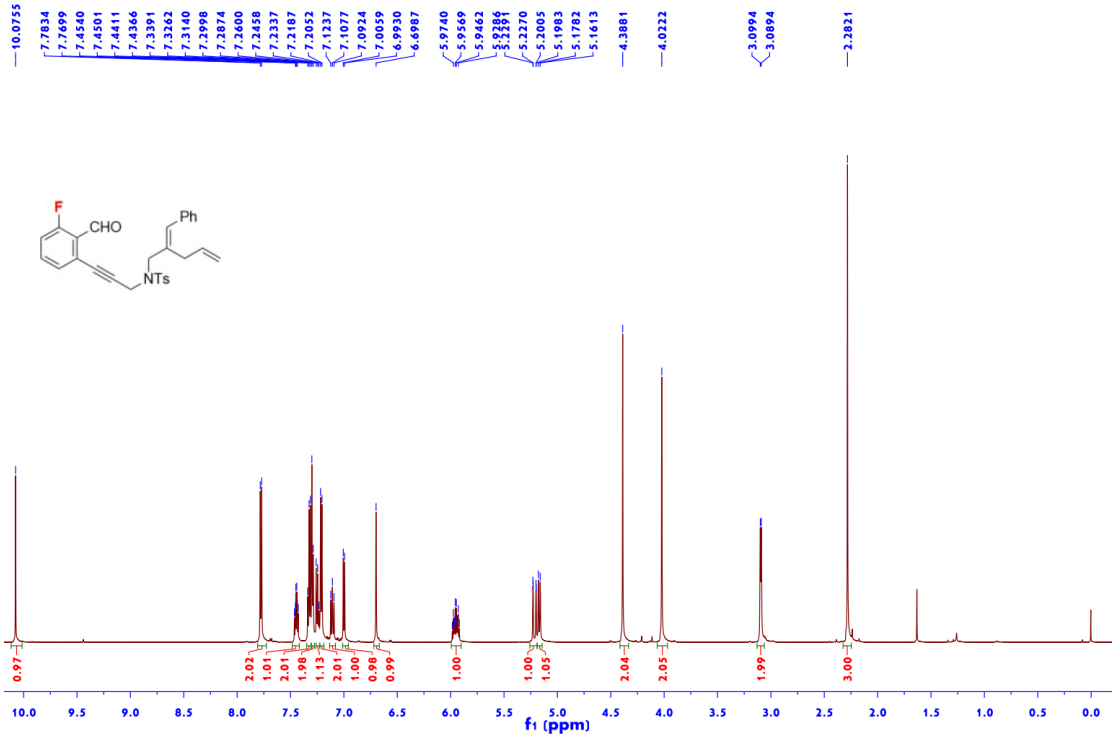


Figure S31 ^{13}C NMR (150 MHz, $CDCl_3$) of 1o

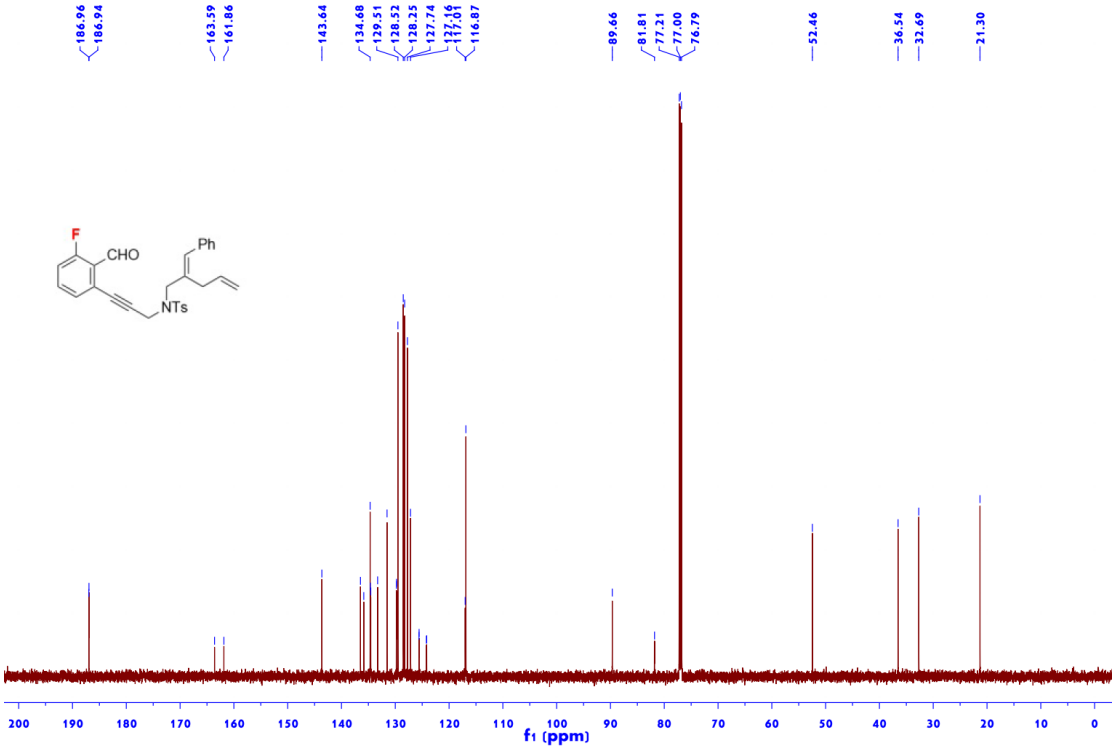


Figure S32 ^{19}F NMR (565 MHz, $CDCl_3$) of 1o

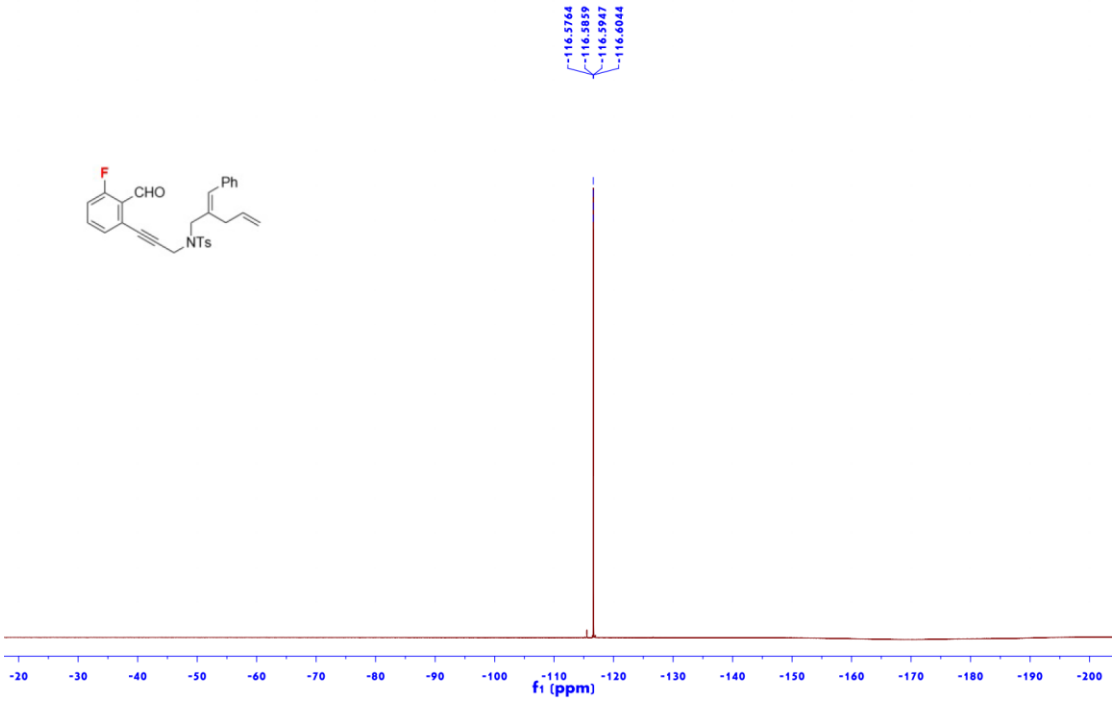


Figure S33 ^{1}H NMR (600 MHz, $CDCl_3$) of 1p

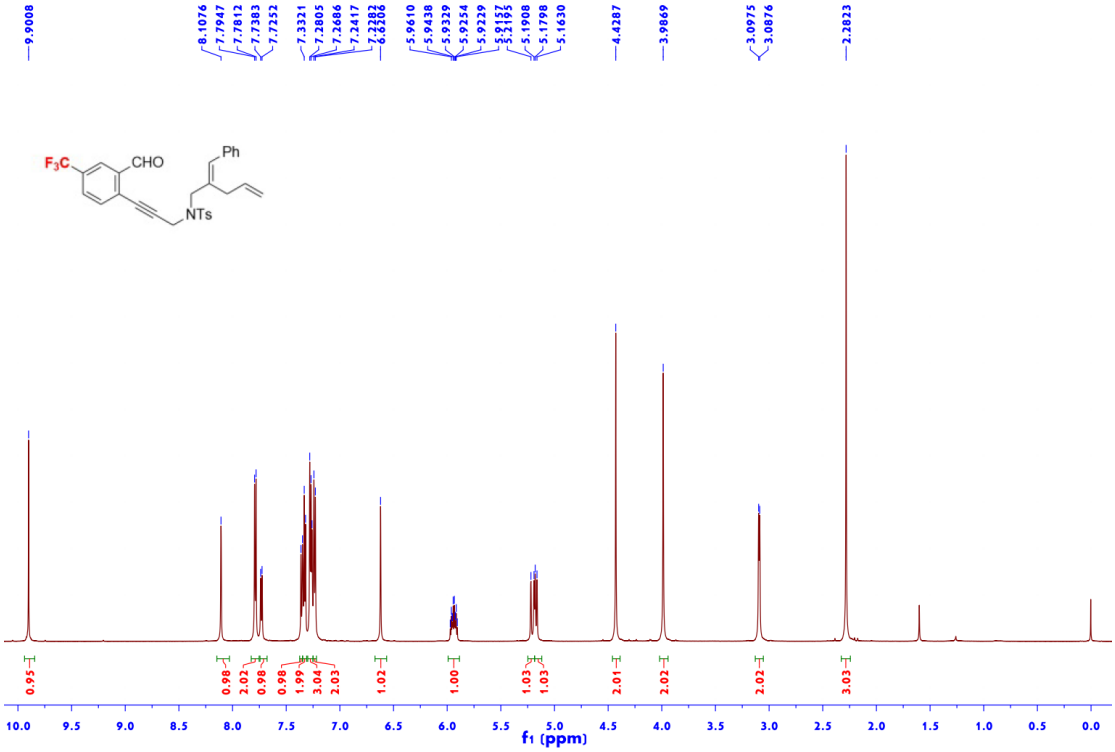


Figure S34 ^{13}C NMR (150 MHz, $CDCl_3$) of 1p

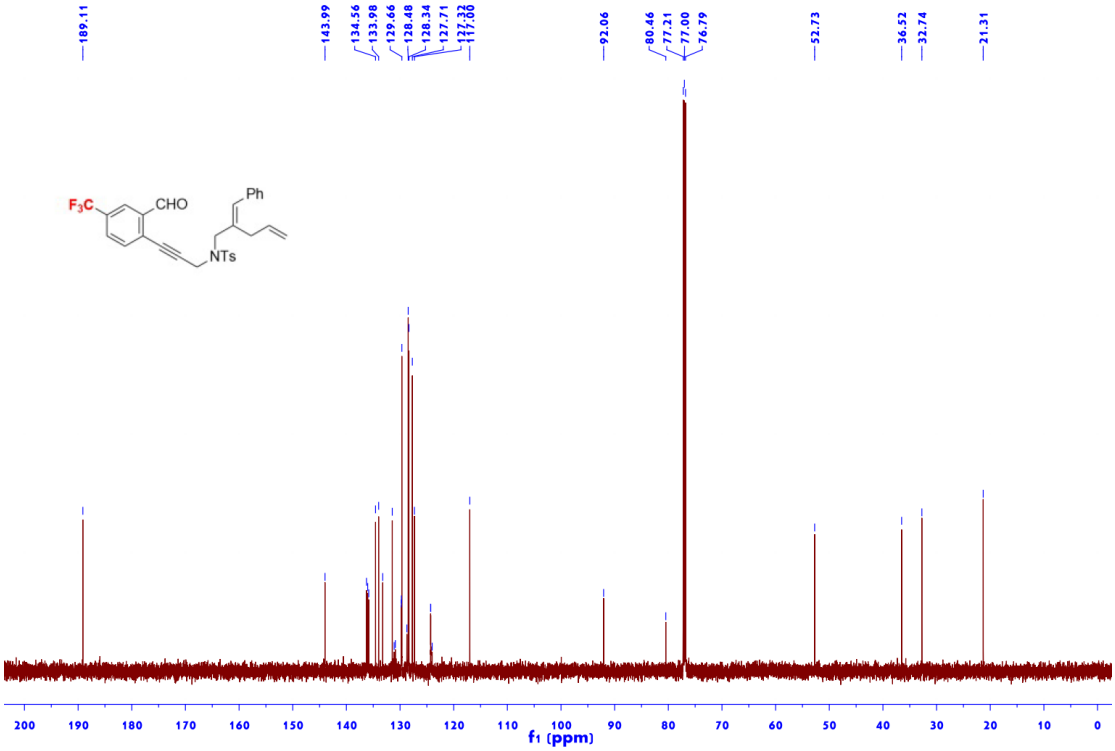


Figure S35 ^{19}F NMR (565 MHz, $CDCl_3$) of 1p

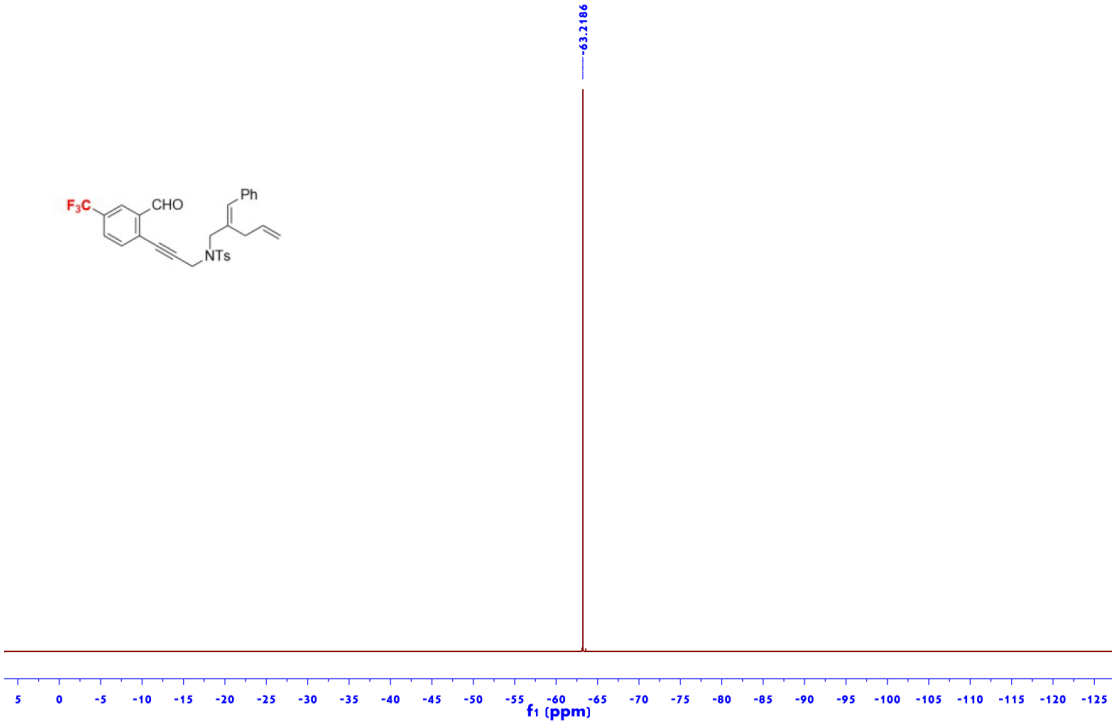


Figure S36 ^{1}H NMR (600 MHz, $CDCl_3$) of 1q

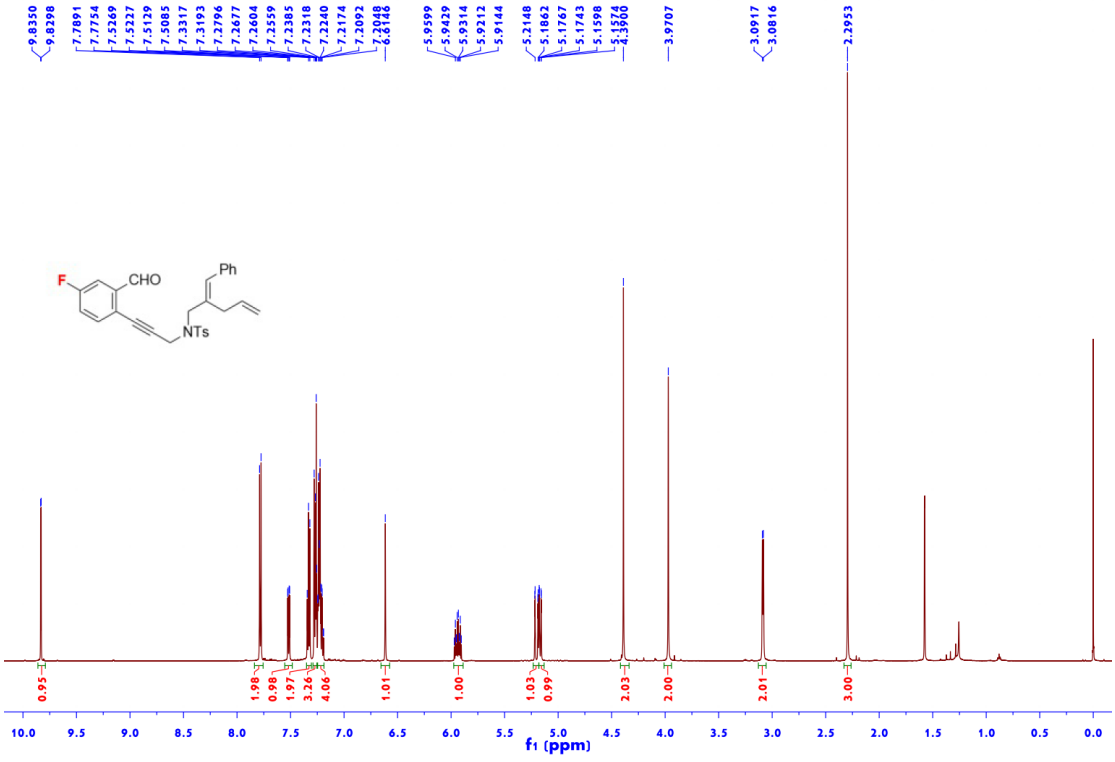


Figure S37 ^{13}C NMR (150 MHz, $CDCl_3$) of 1q

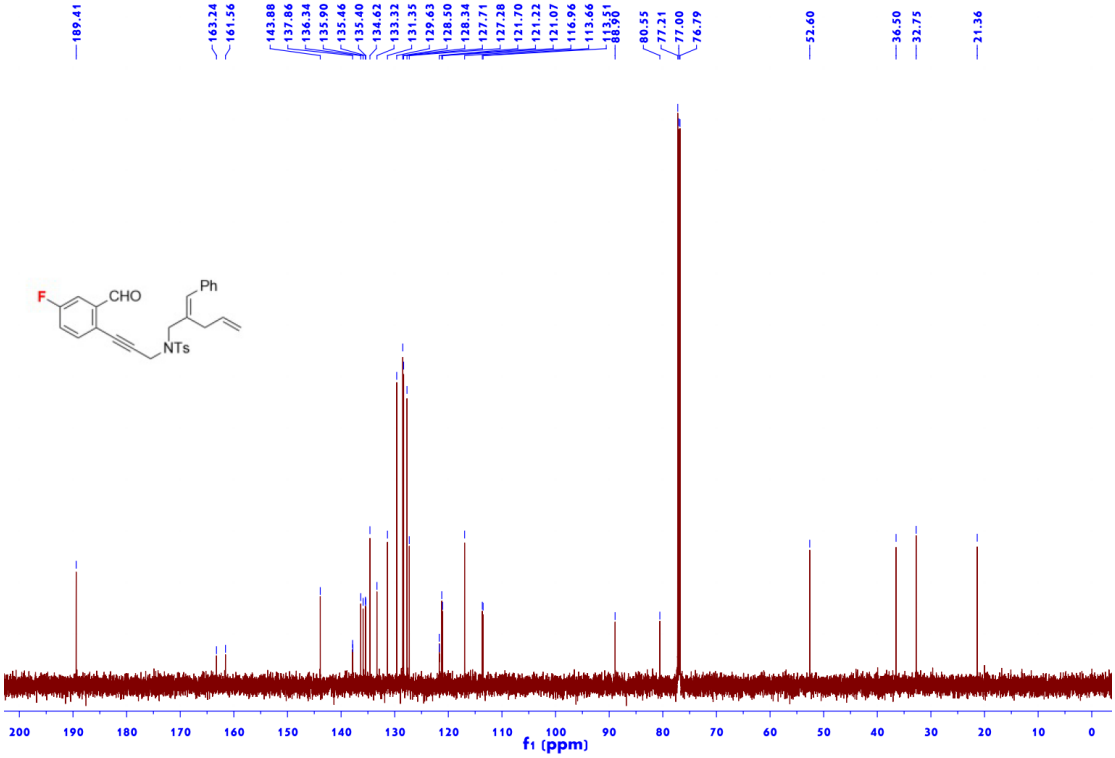


Figure S38 ^{1}H NMR (600 MHz, $CDCl_3$) of 1r

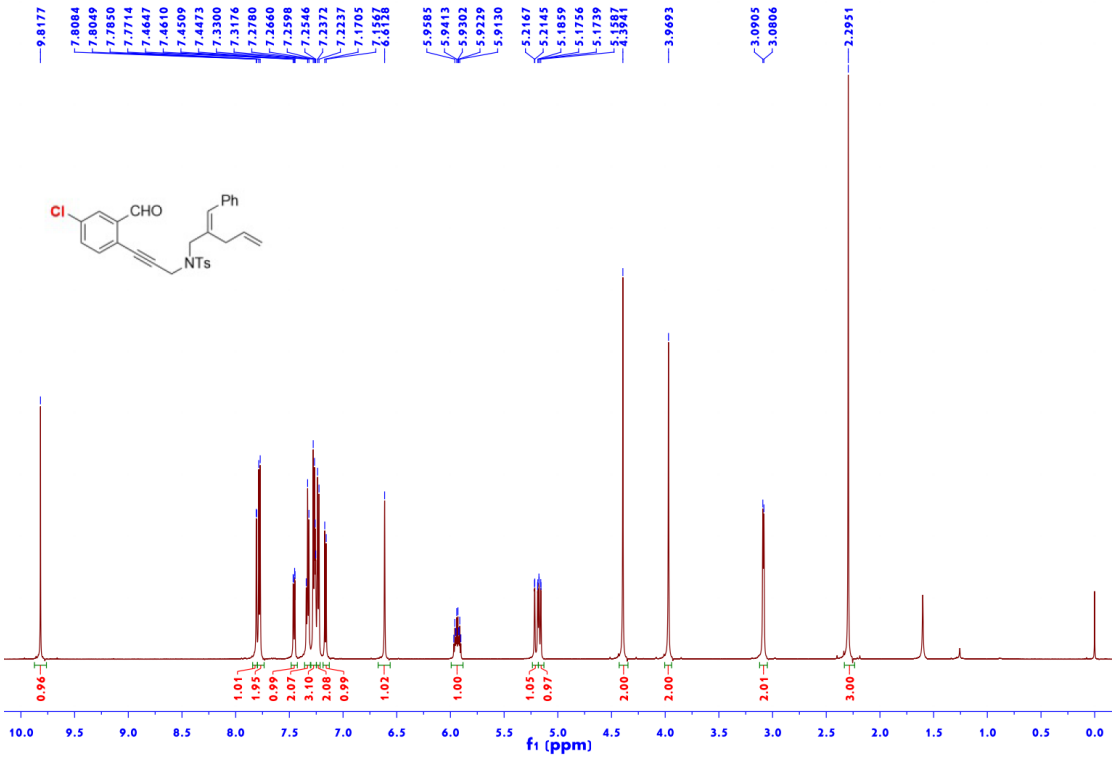


Figure S39 ^{13}C NMR (150 MHz, $CDCl_3$) of 1r

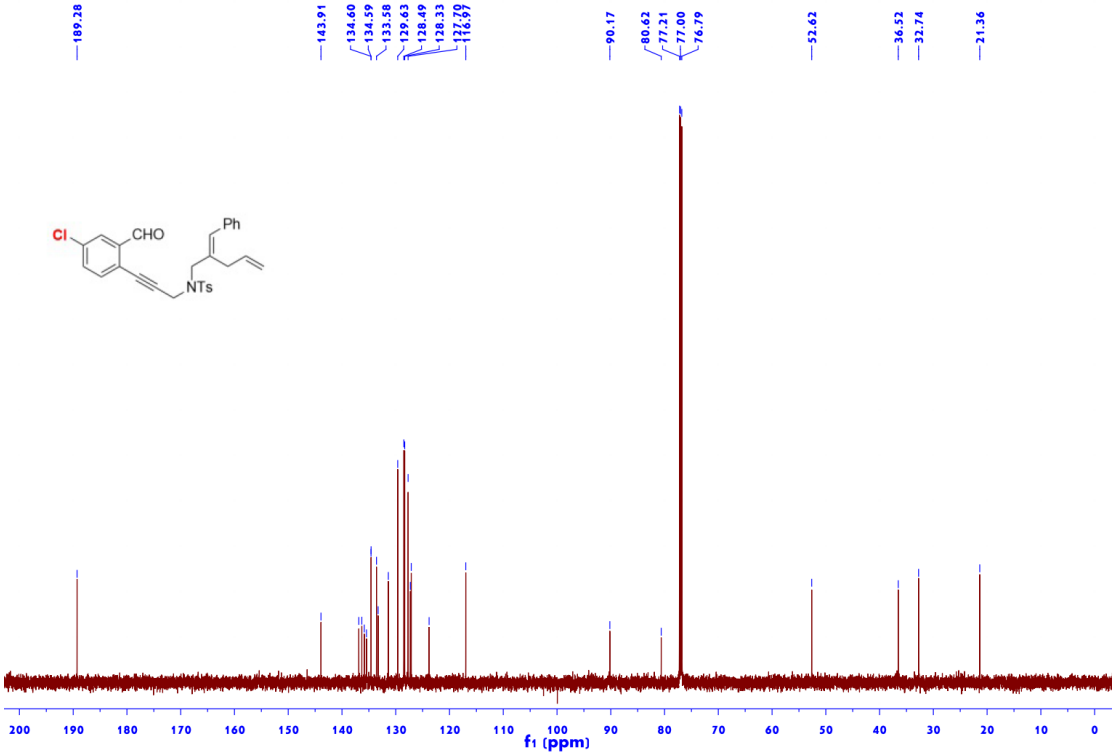


Figure S40 ^{1}H NMR (600 MHz, $CDCl_3$) of 1s

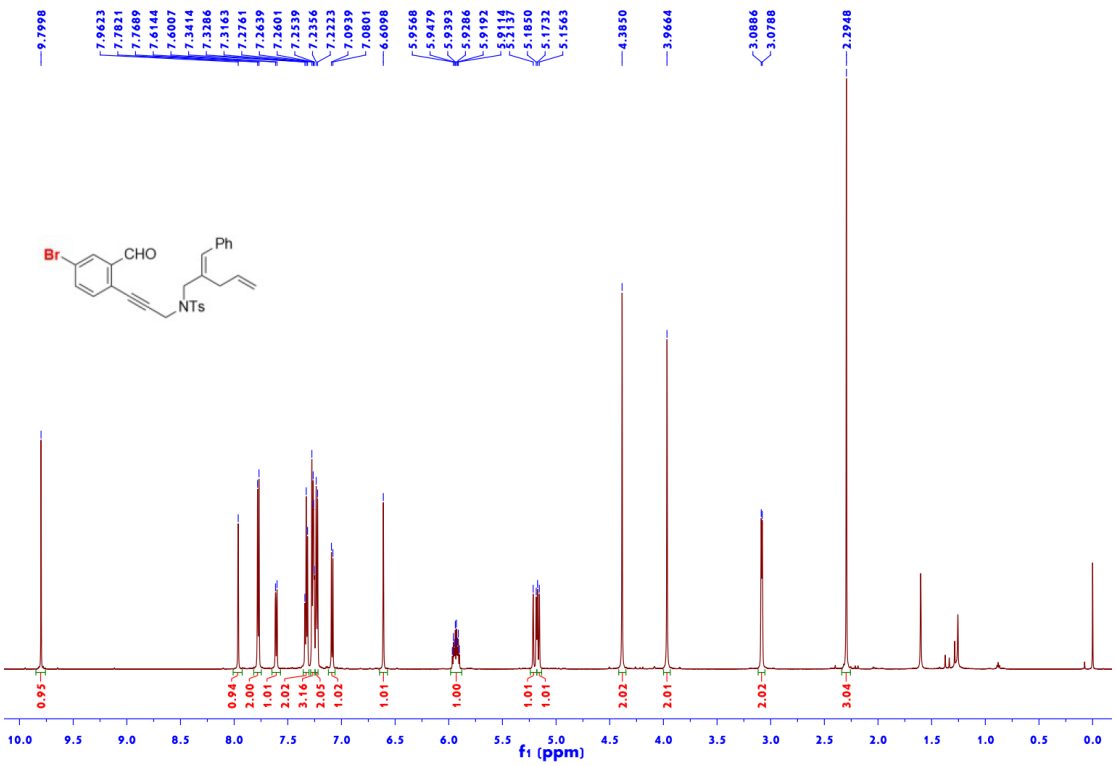


Figure S41 ^{13}C NMR (150 MHz, $CDCl_3$) of 1s

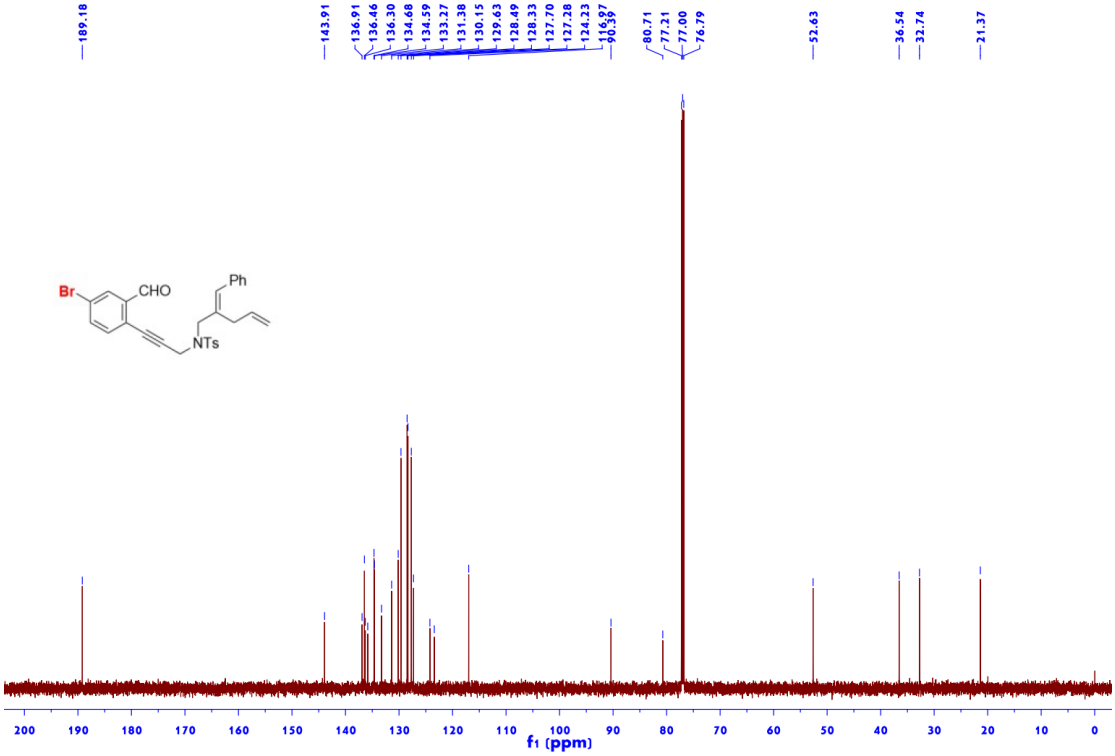


Figure S42 ^{1}H NMR (600 MHz, $CDCl_3$) of 1t

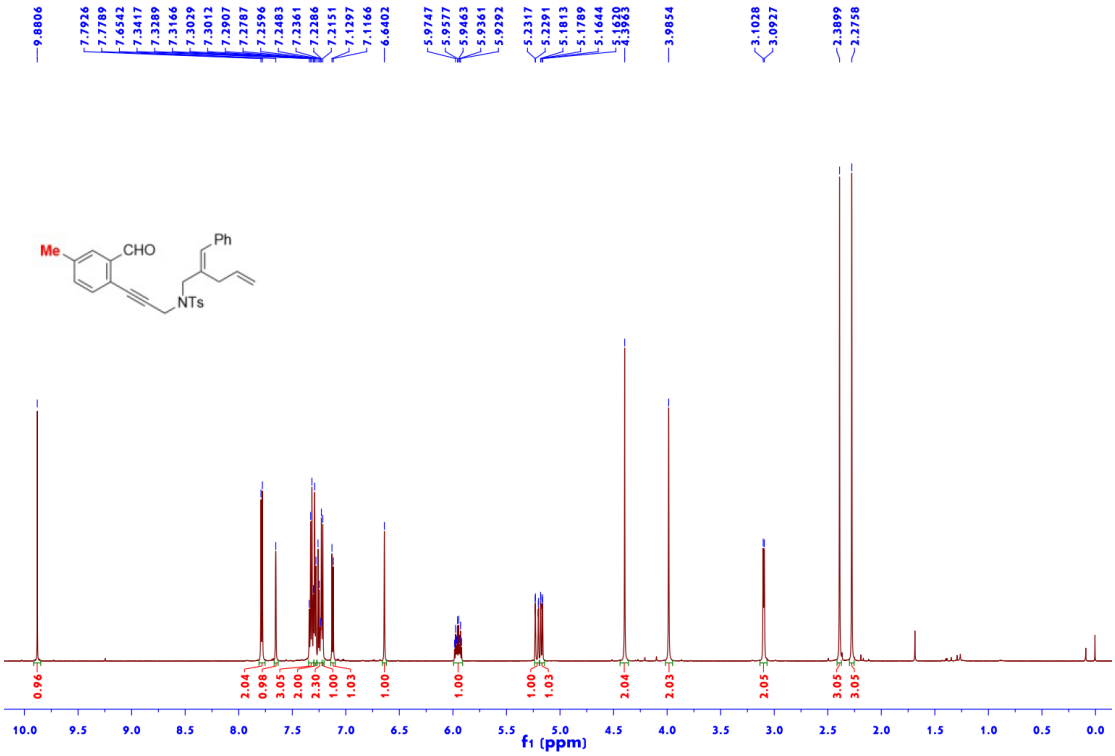


Figure S43 ^{13}C NMR (150 MHz, $CDCl_3$) of 1t

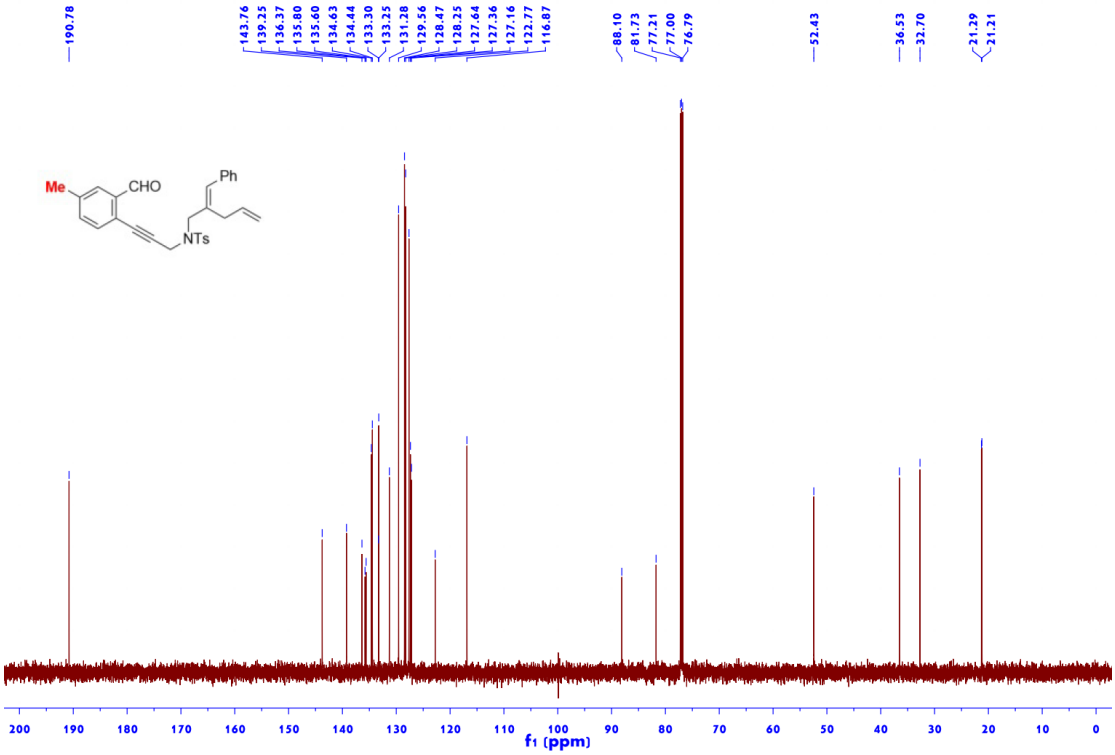


Figure S44 ^{1}H NMR (600 MHz, $CDCl_3$) of 1u

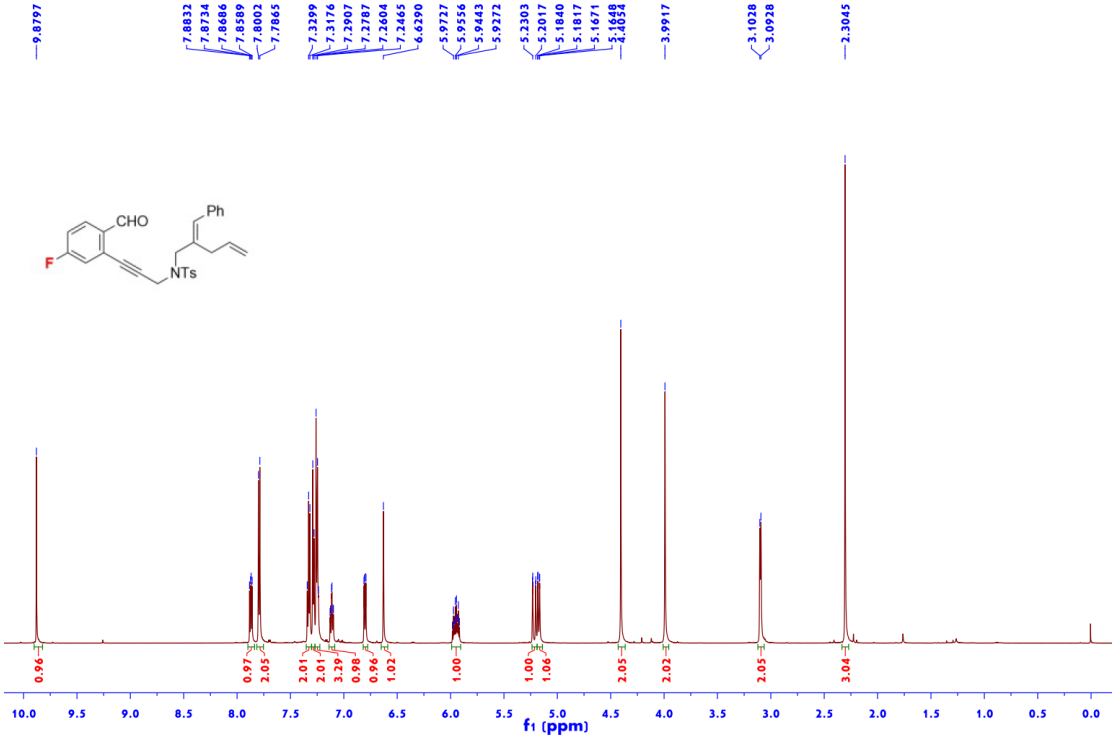


Figure S45 ^{13}C NMR (150 MHz, $CDCl_3$) of 1u

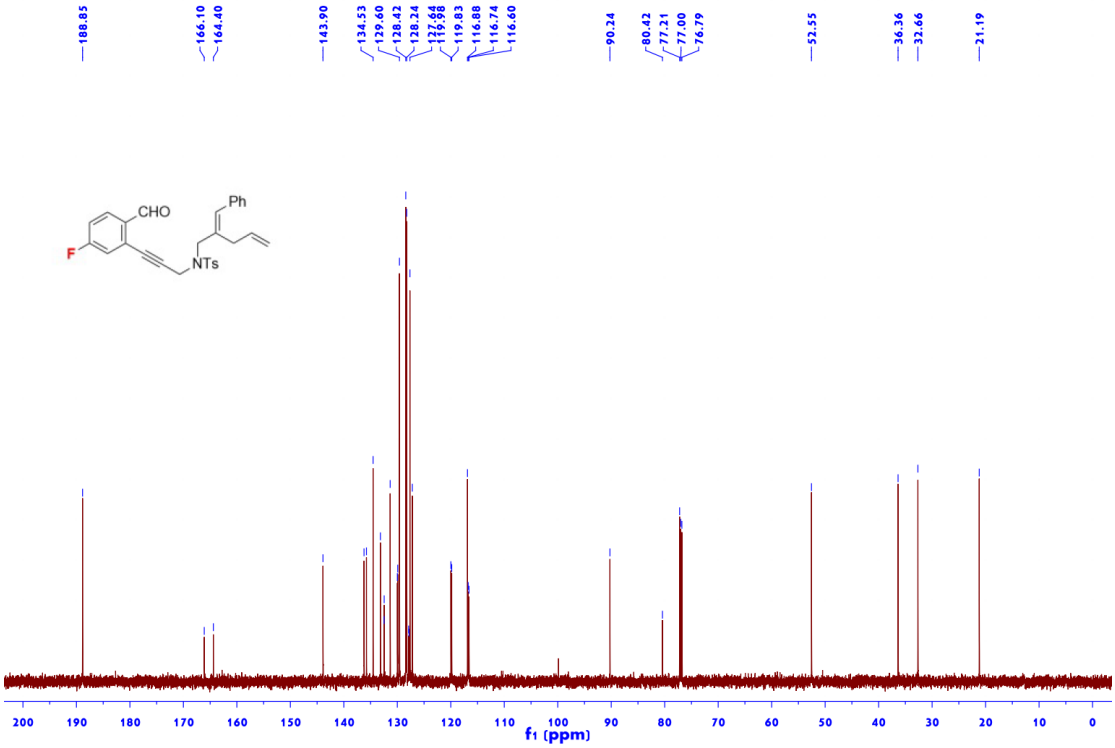


Figure S46 ^{19}F NMR (565 MHz, $CDCl_3$) of 1u

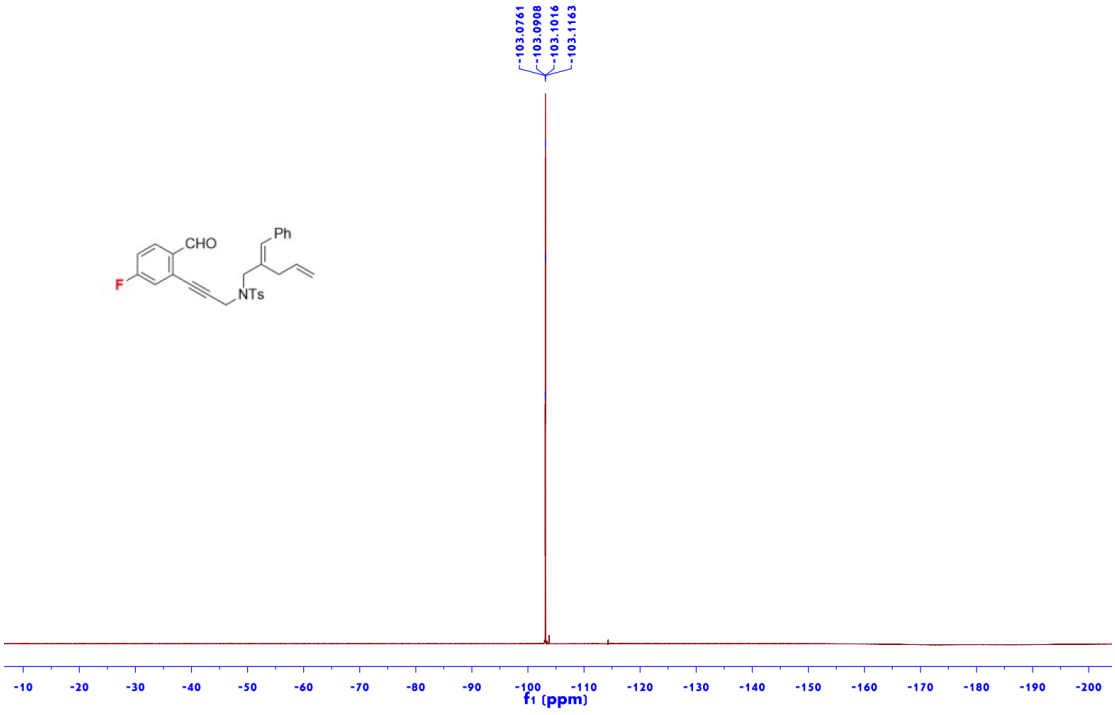


Figure S47 ^{1}H NMR (600 MHz, $CDCl_3$) of 1v

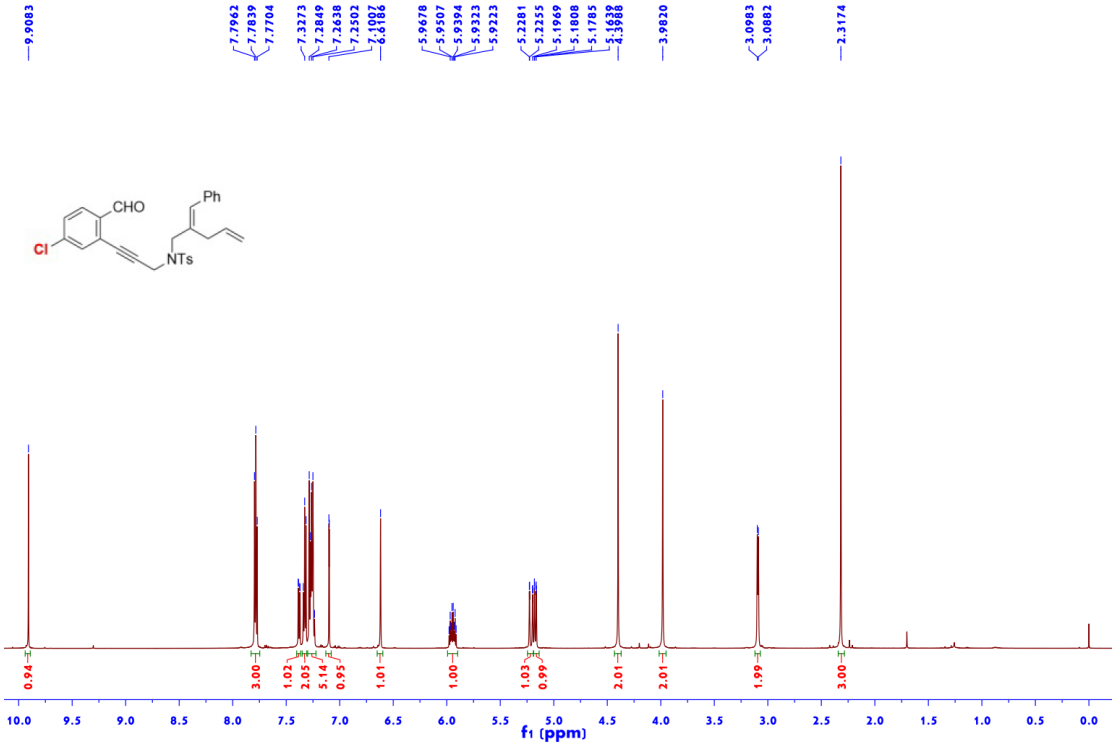


Figure S48 ^{13}C NMR (150 MHz, $CDCl_3$) of 1v

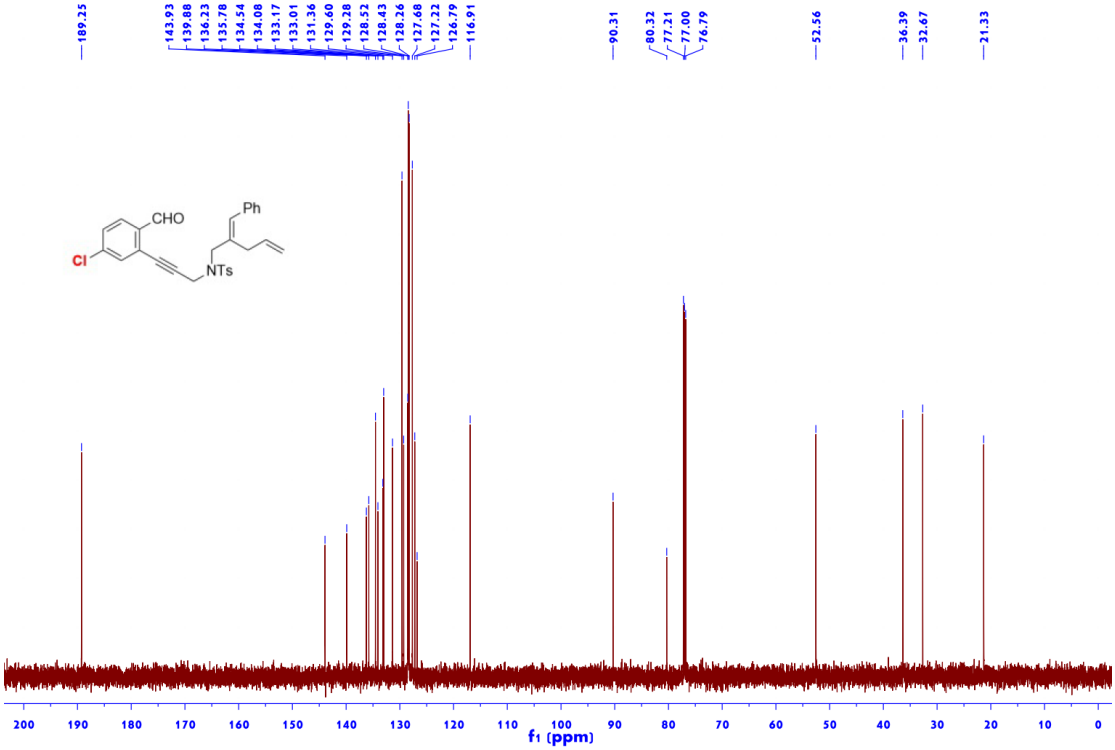


Figure S49 ^{1}H NMR (600 MHz, $CDCl_3$) of 1w

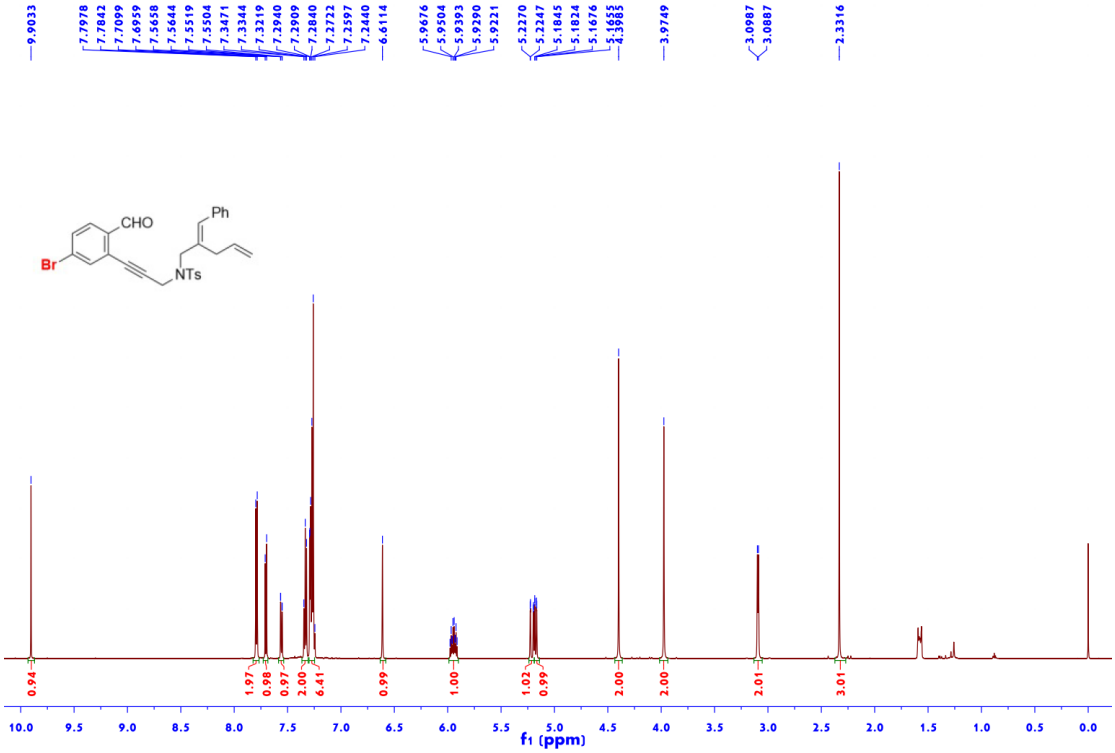


Figure S50 ^{13}C NMR (150 MHz, $CDCl_3$) of 1w

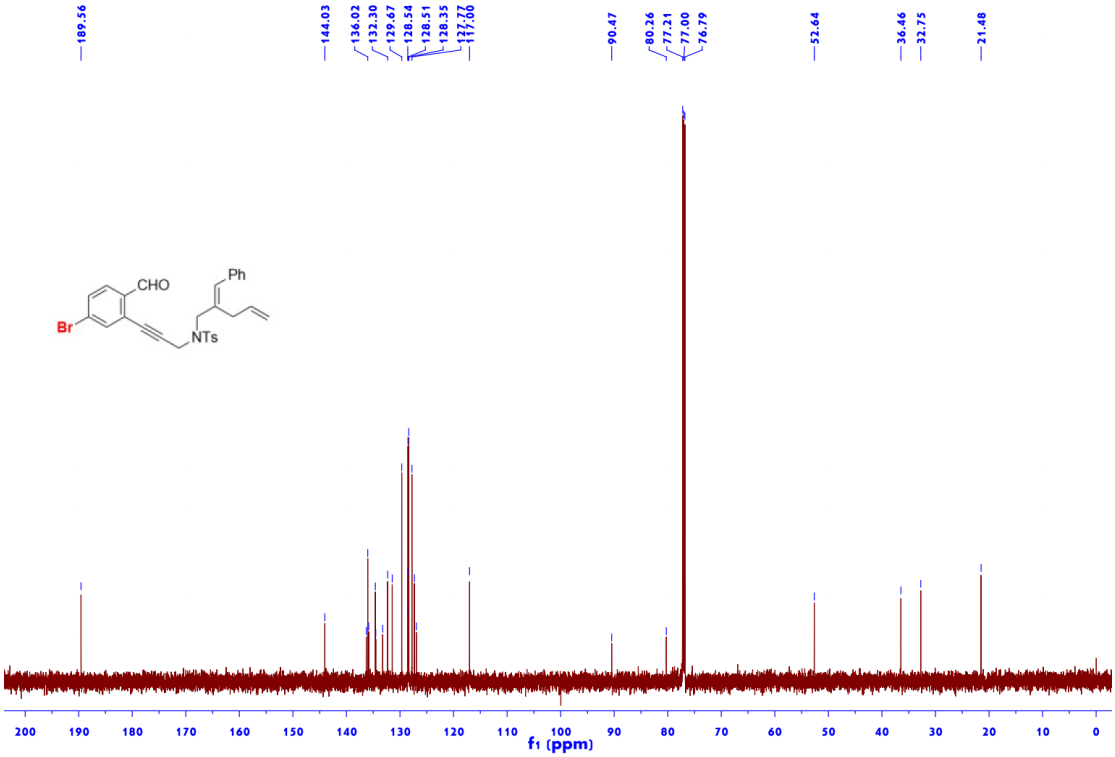


Figure S51 ^{1}H NMR (600 MHz, $CDCl_3$) of 1x

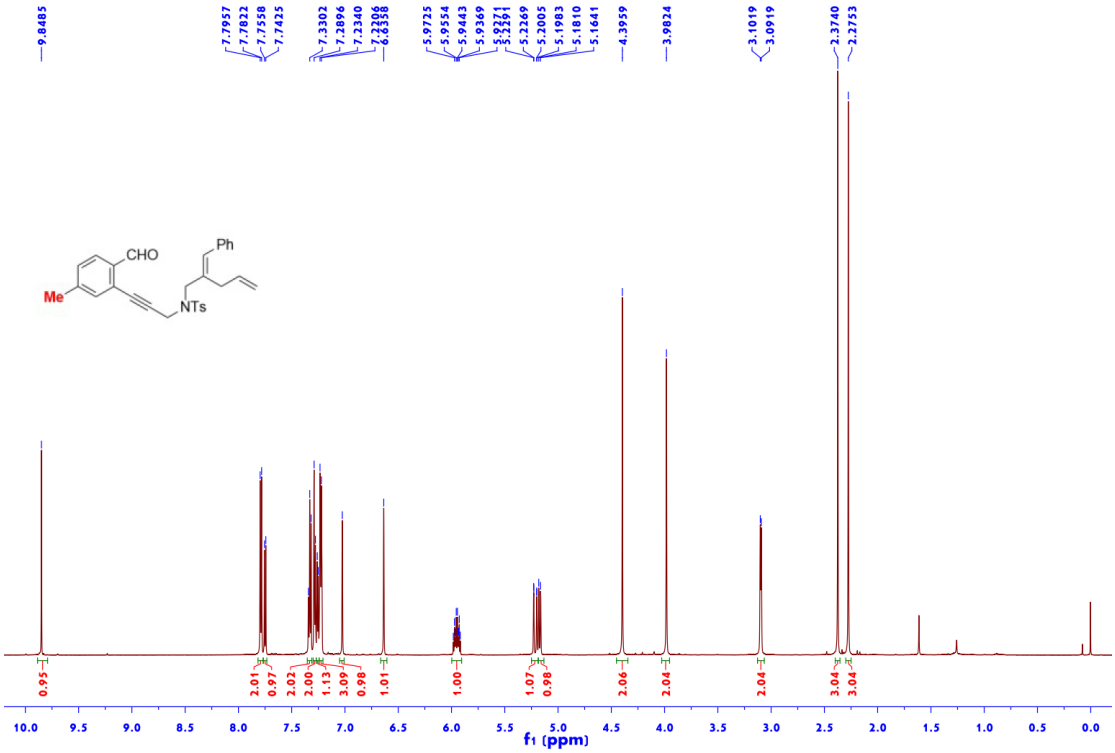


Figure S52 ^{13}C NMR (150 MHz, $CDCl_3$) of 1x

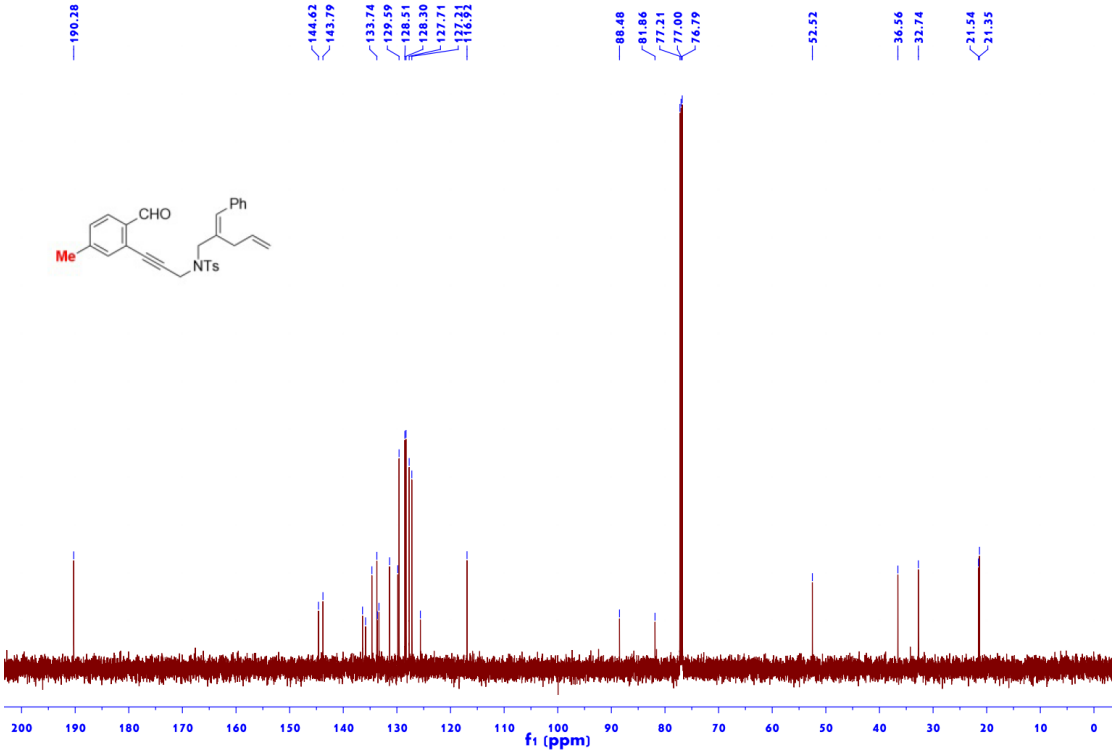


Figure S53 ^{1}H NMR (600 MHz, $CDCl_3$) of 1y

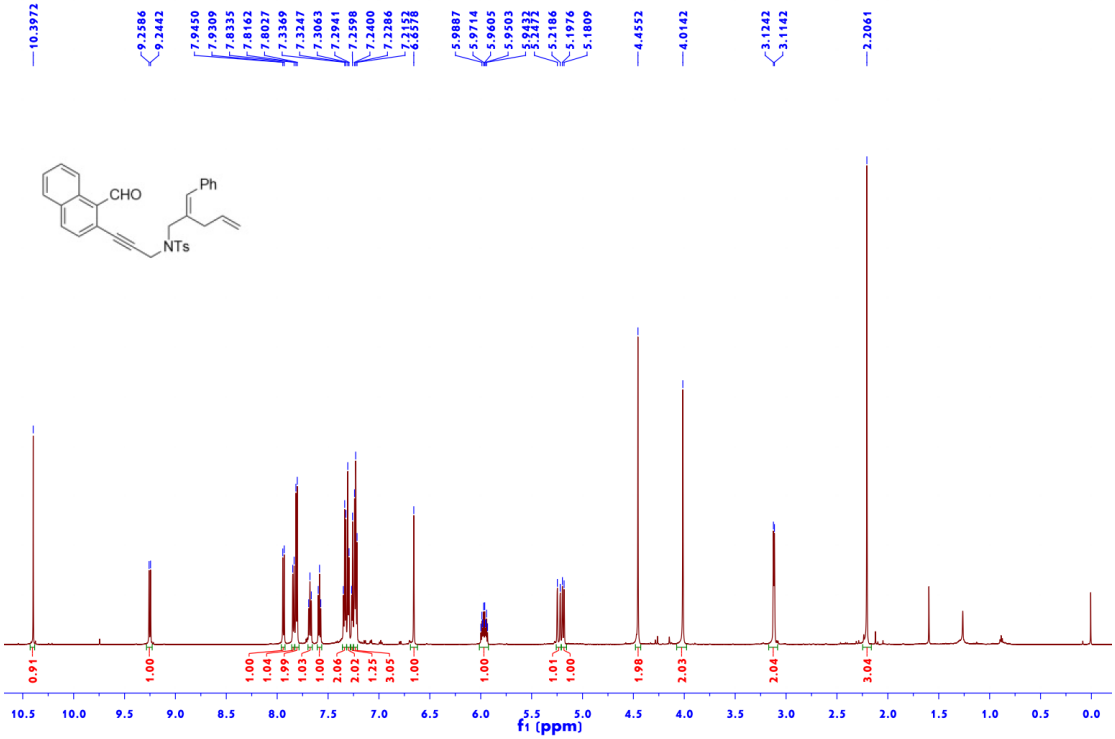


Figure S54 ^{13}C NMR (150 MHz, $CDCl_3$) of 1y

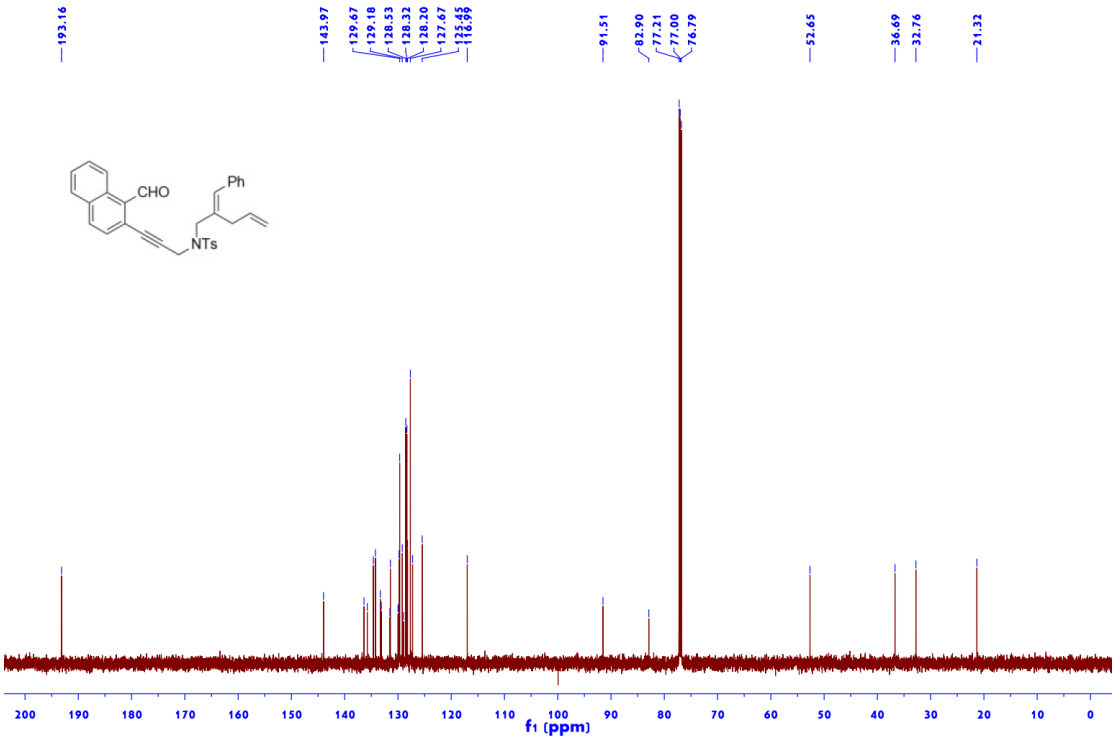


Figure S55 ^{1}H NMR (600 MHz, $CDCl_3$) of 1z

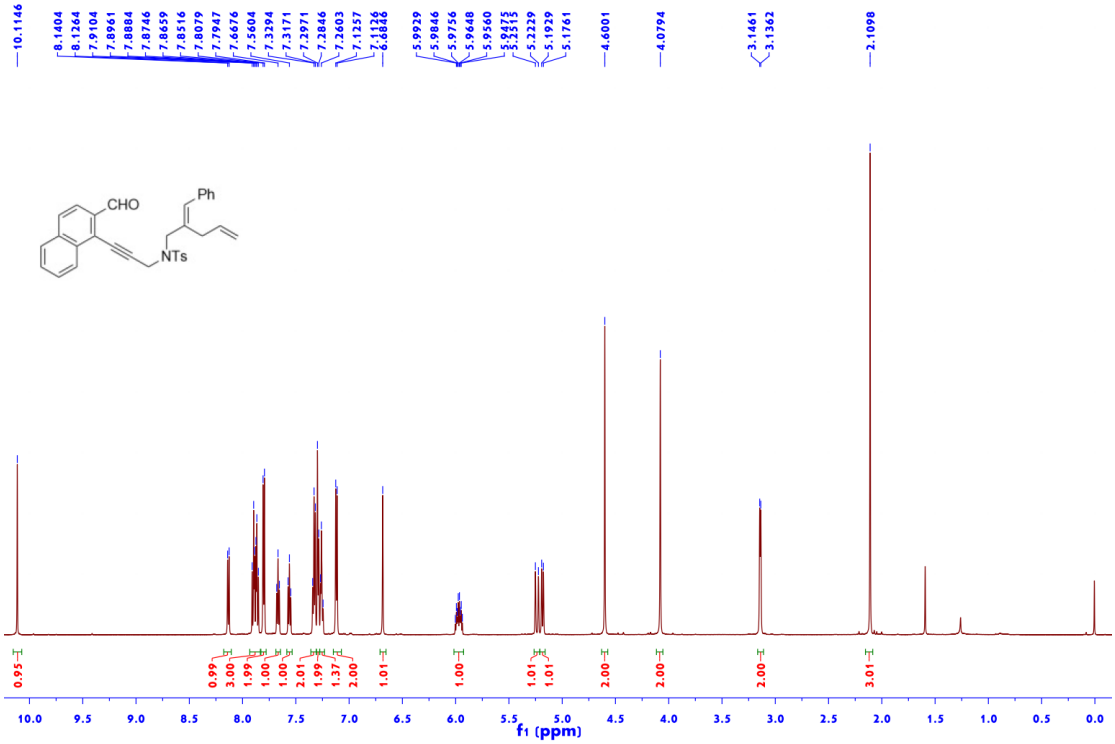


Figure S56 ^{13}C NMR (150 MHz, $CDCl_3$) of 1z

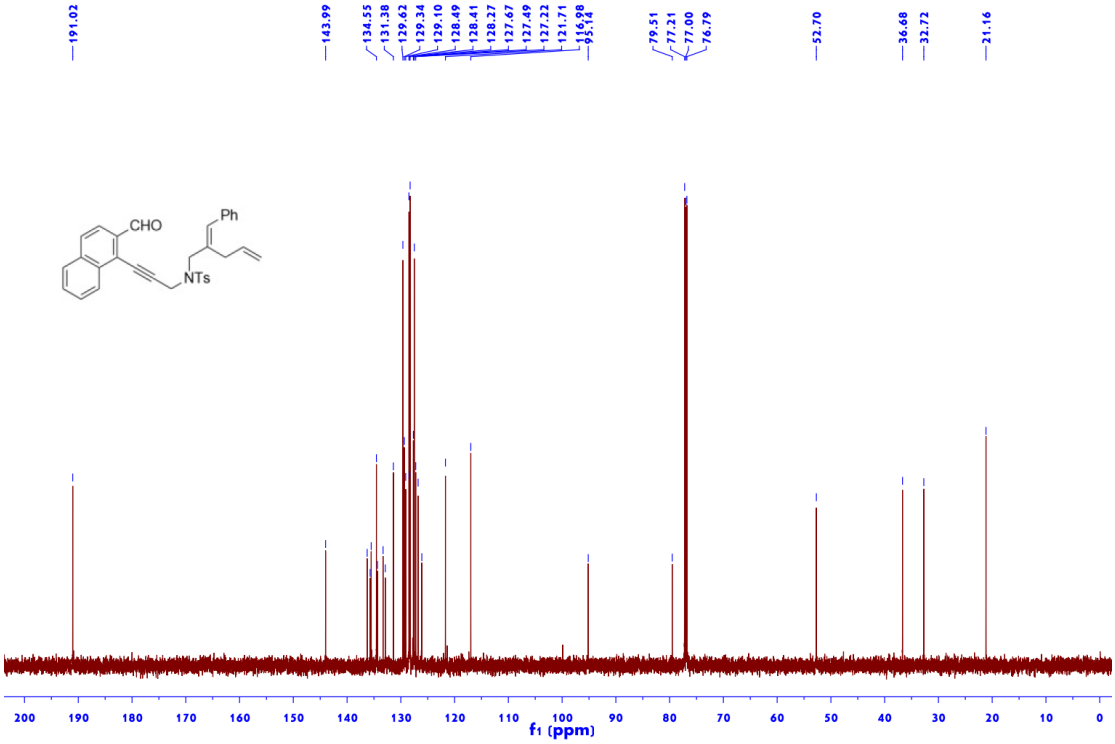


Figure S57 ^{1}H NMR (600 MHz, $CDCl_3$) of 1aa

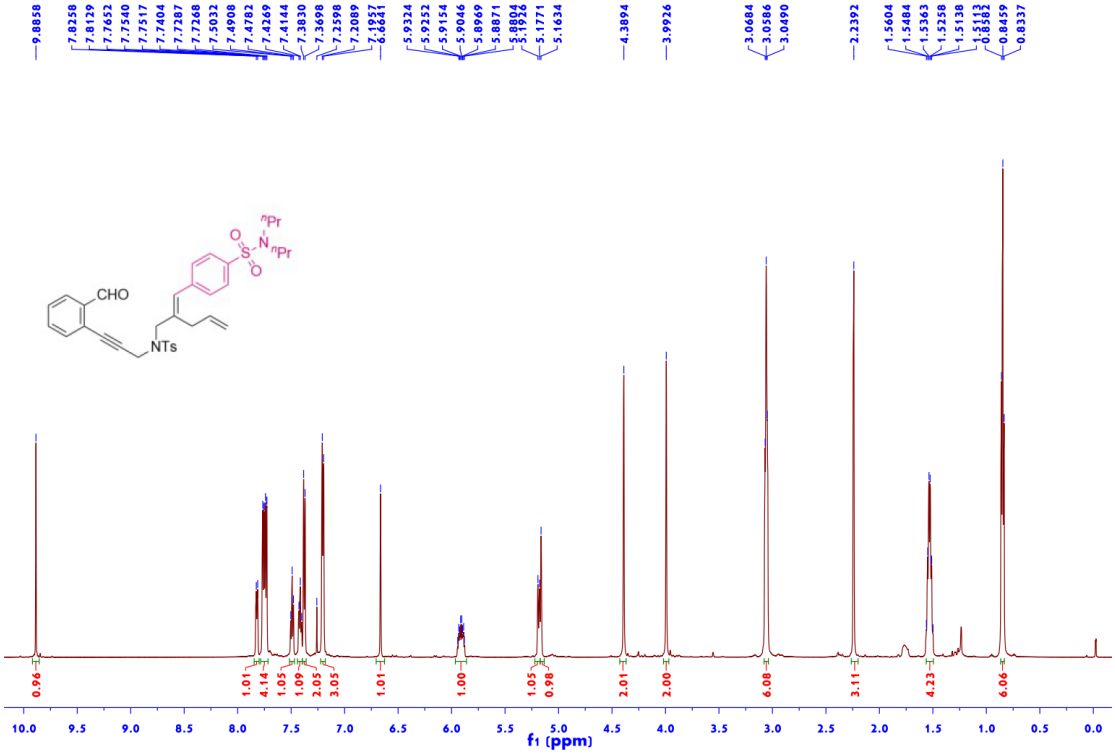


Figure S58 ^{13}C NMR (150 MHz, $CDCl_3$) of 1aa

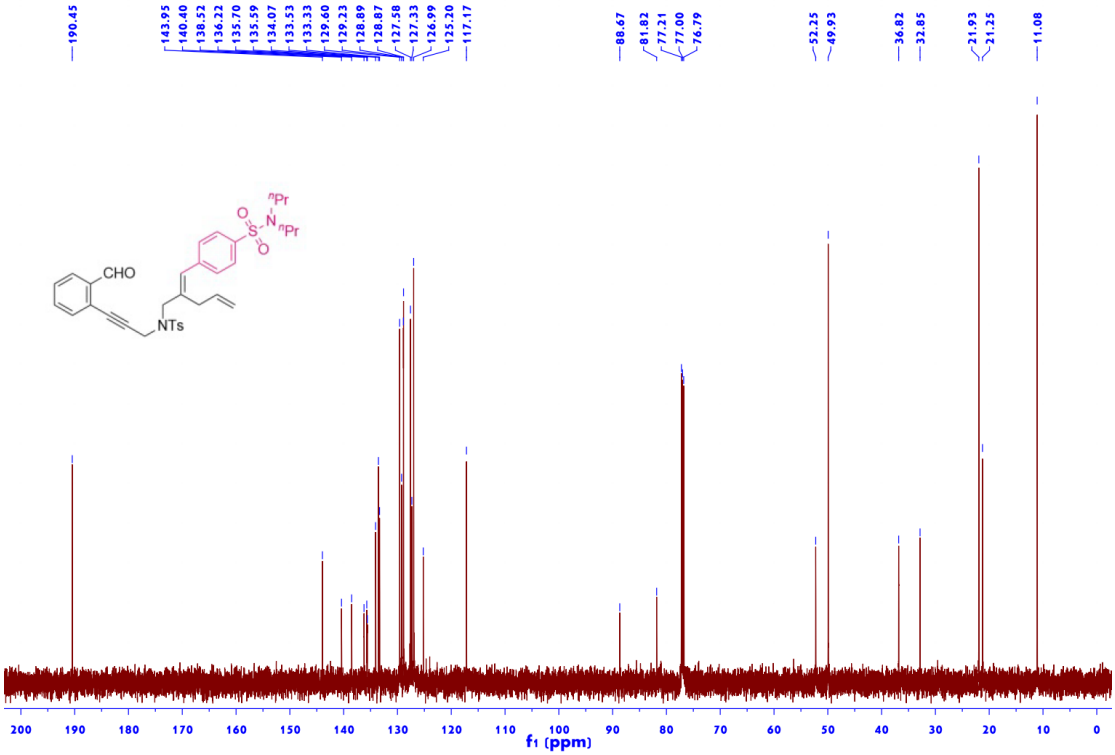


Figure S59 ^{1}H NMR (600 MHz, $CDCl_3$) of 1ab

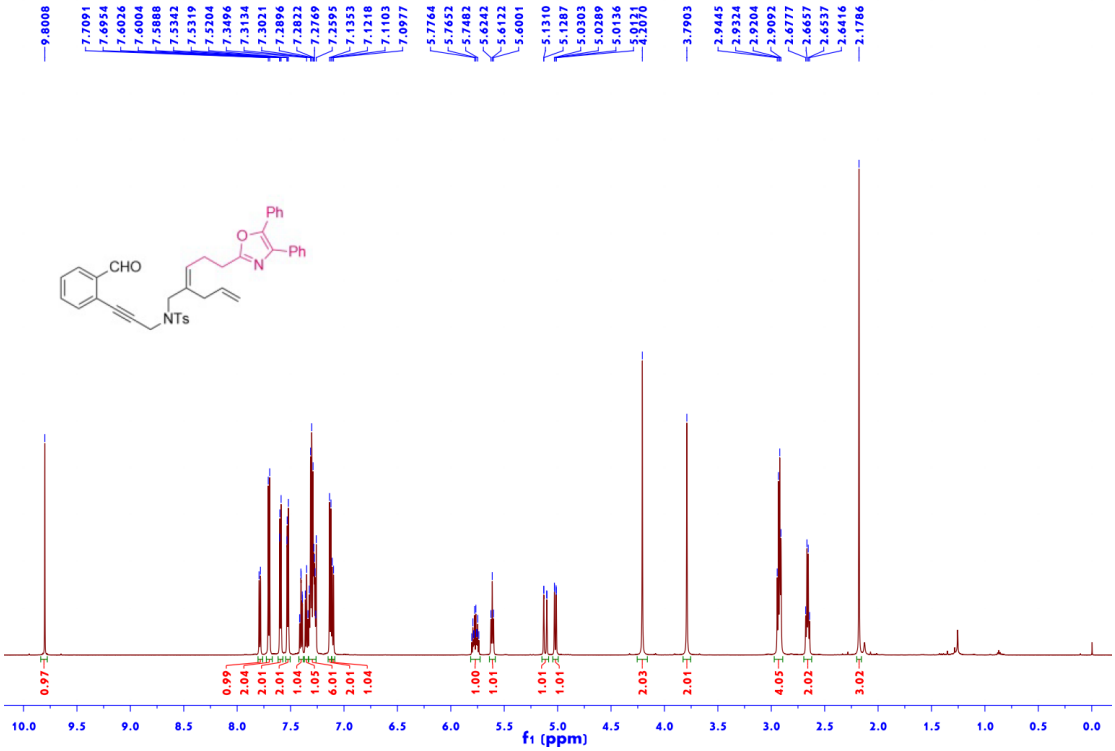


Figure S60 ^{13}C NMR (150 MHz, $CDCl_3$) of 1ab

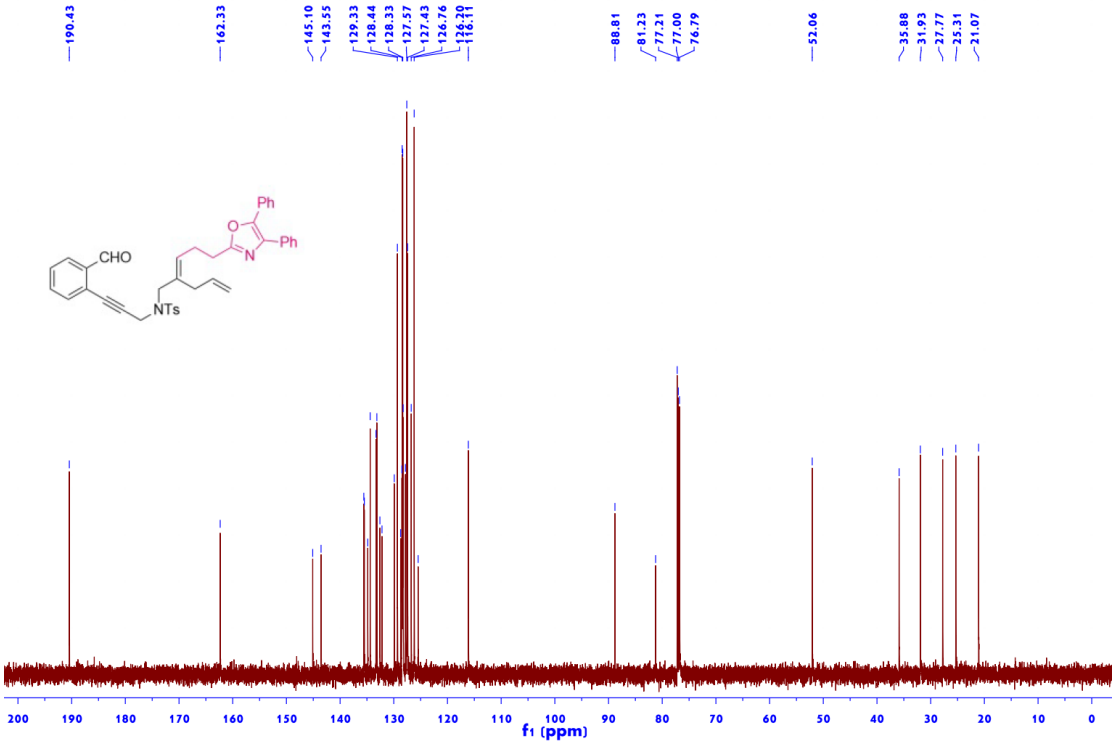


Figure S61 ^{1}H NMR (600 MHz, $CDCl_3$) of 1ac

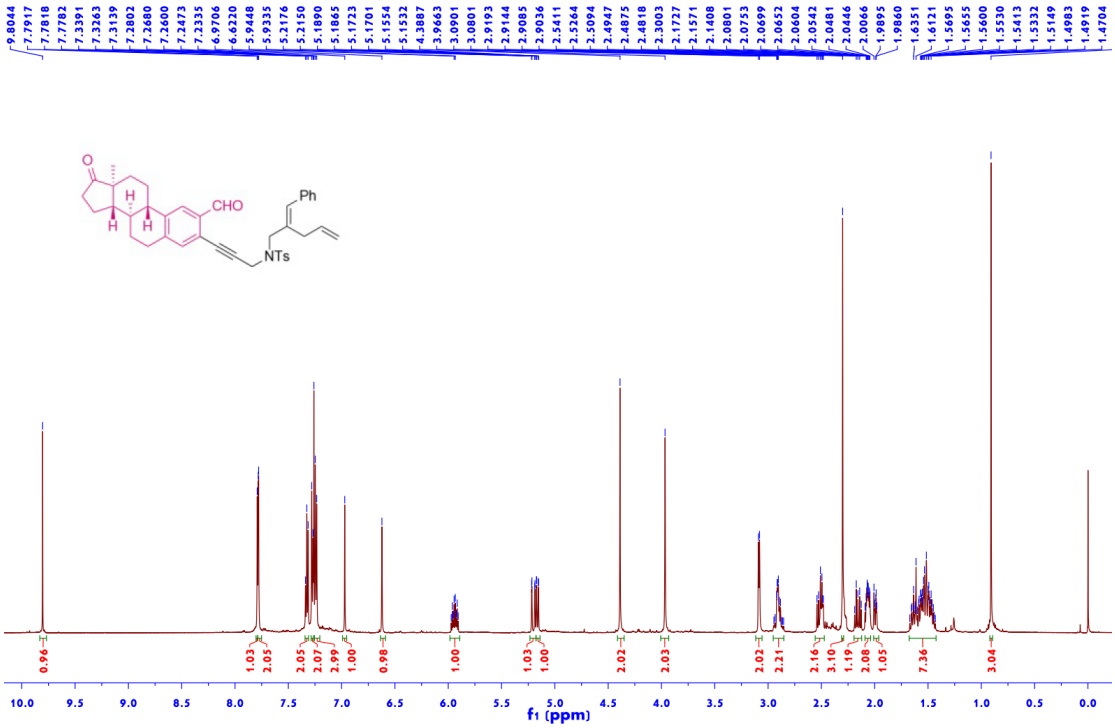


Figure S62 ^{13}C NMR (150 MHz, $CDCl_3$) of 1ac

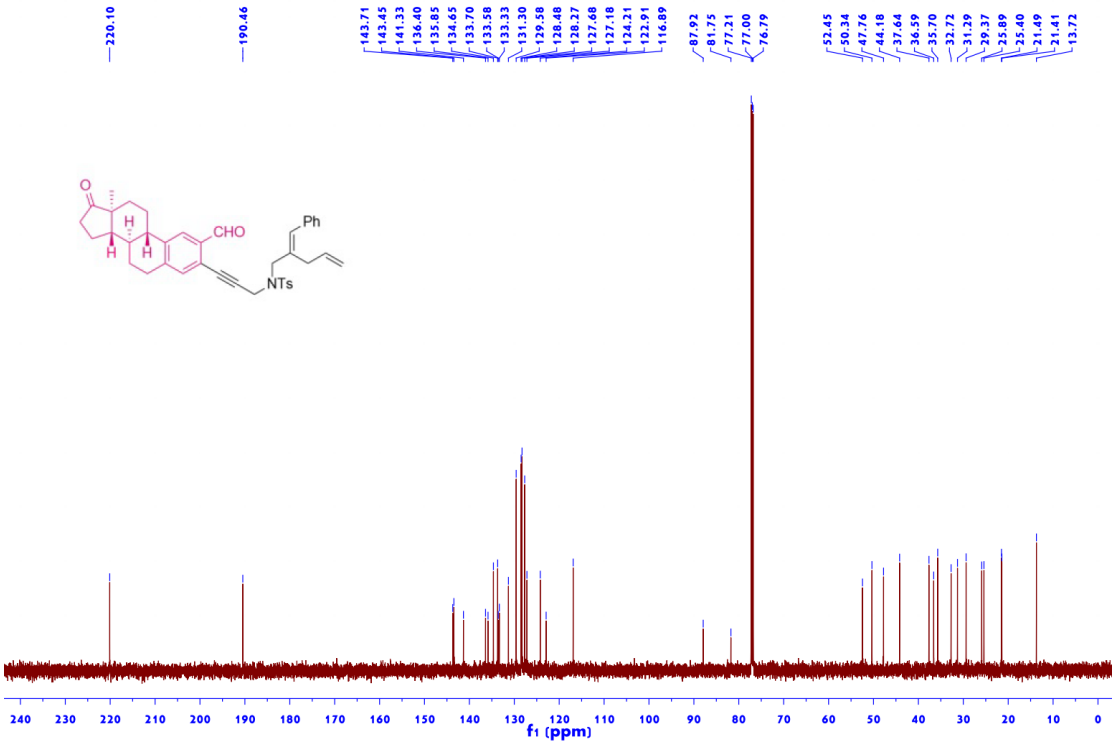


Figure S63 ^{1}H NMR (600 MHz, $CDCl_3$) of 1ad

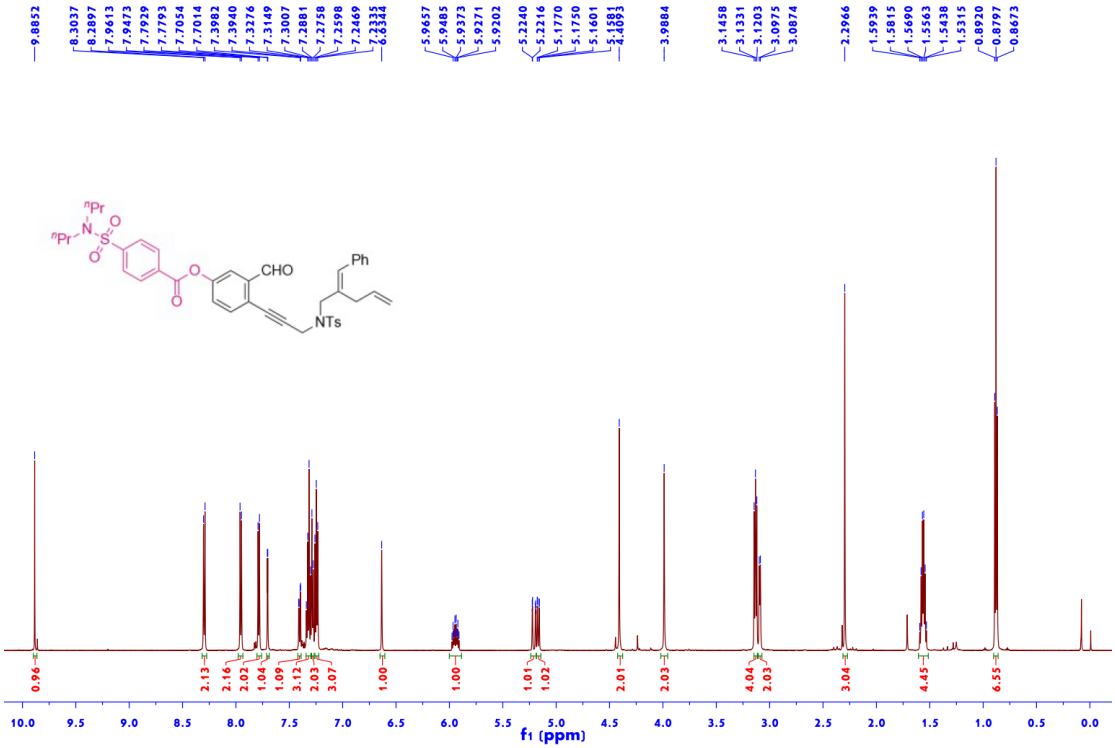


Figure S64 ^{13}C NMR (150 MHz, $CDCl_3$) of 1ad

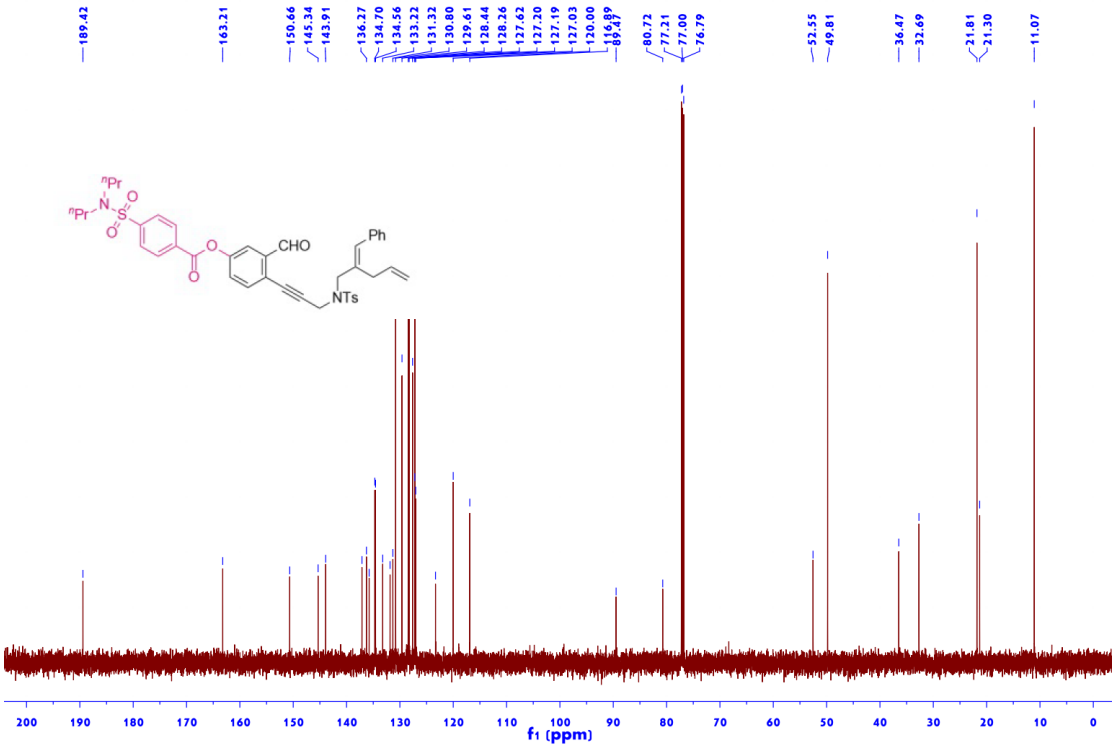


Figure S65 ^{1}H NMR (600 MHz, $CDCl_3$) of 1ae

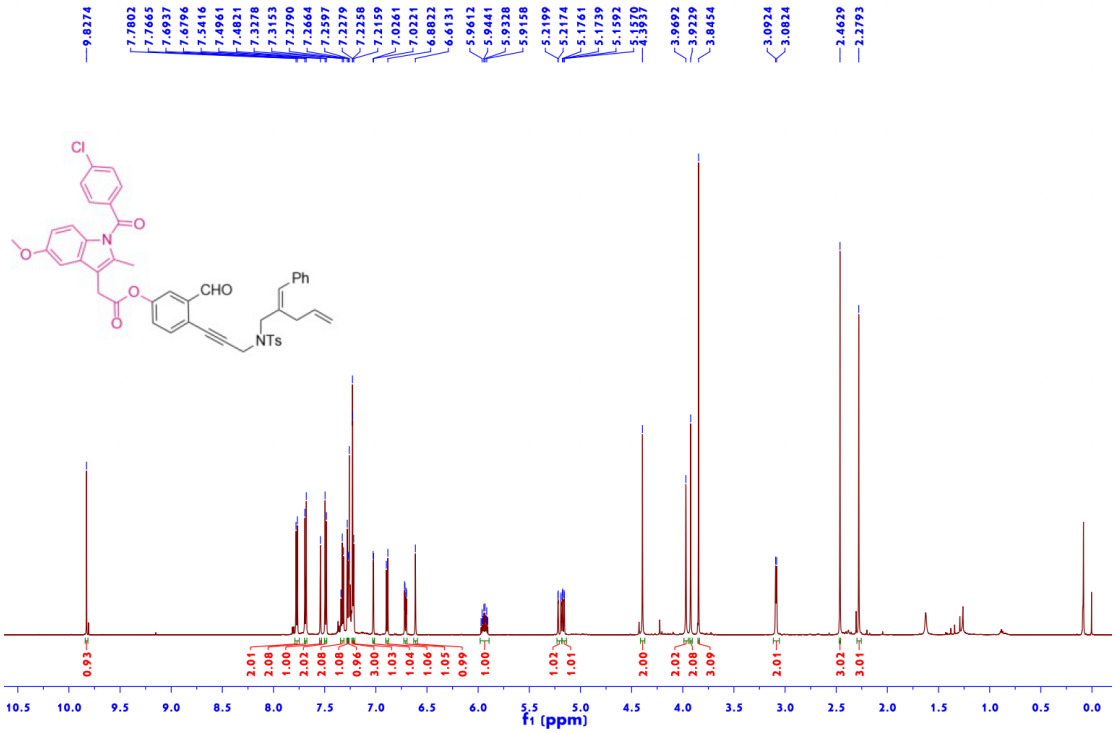


Figure S66 ^{13}C NMR (150 MHz, $CDCl_3$) of 1ae

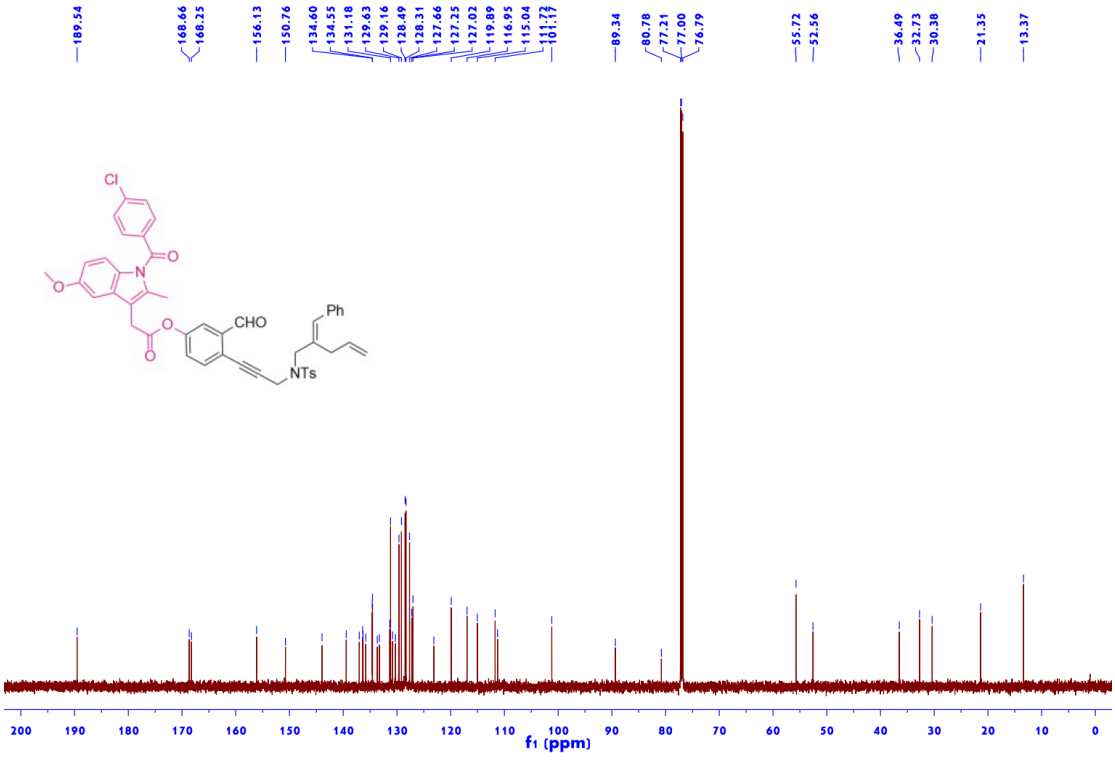


Figure S67 ^{1}H NMR (600 MHz, $CDCl_3$) of 1af

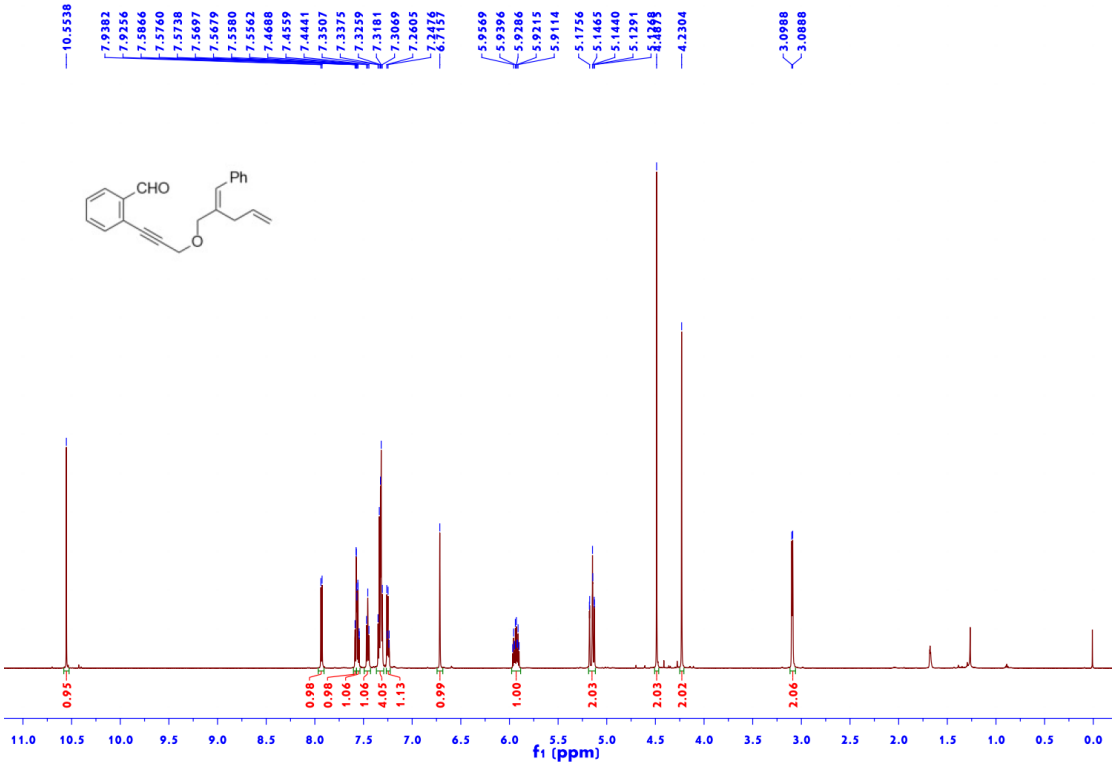


Figure S68 ^{13}C NMR (150 MHz, $CDCl_3$) of 1af

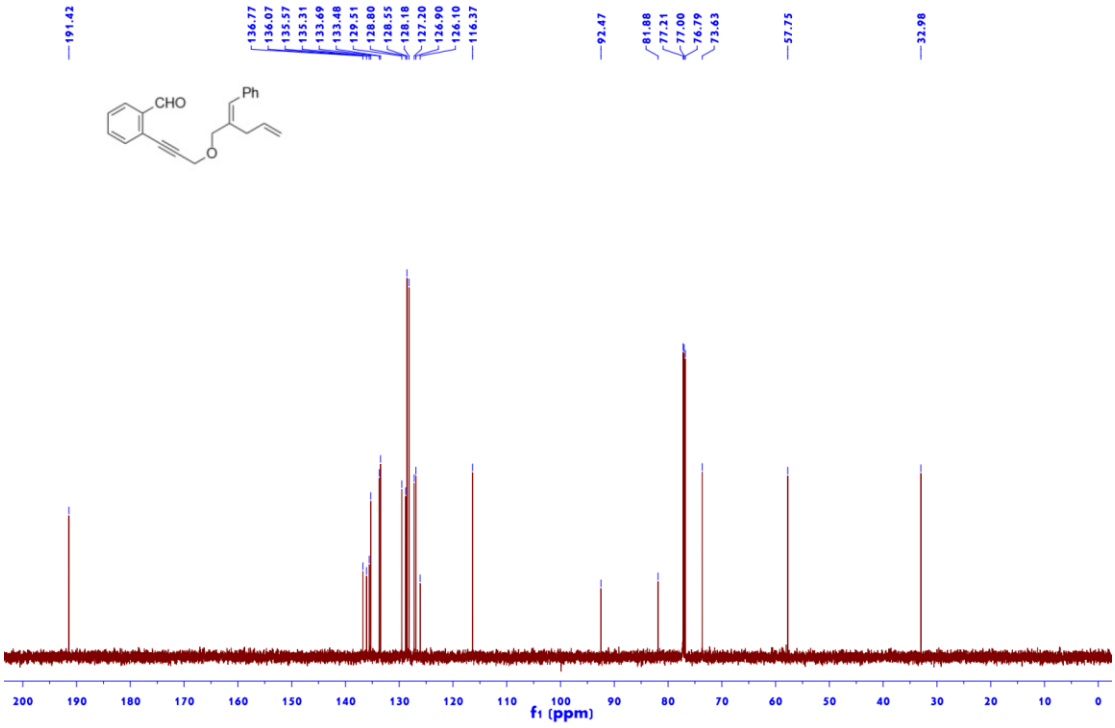


Figure S69 ^{1}H NMR (600 MHz, $CDCl_3$) of 2a

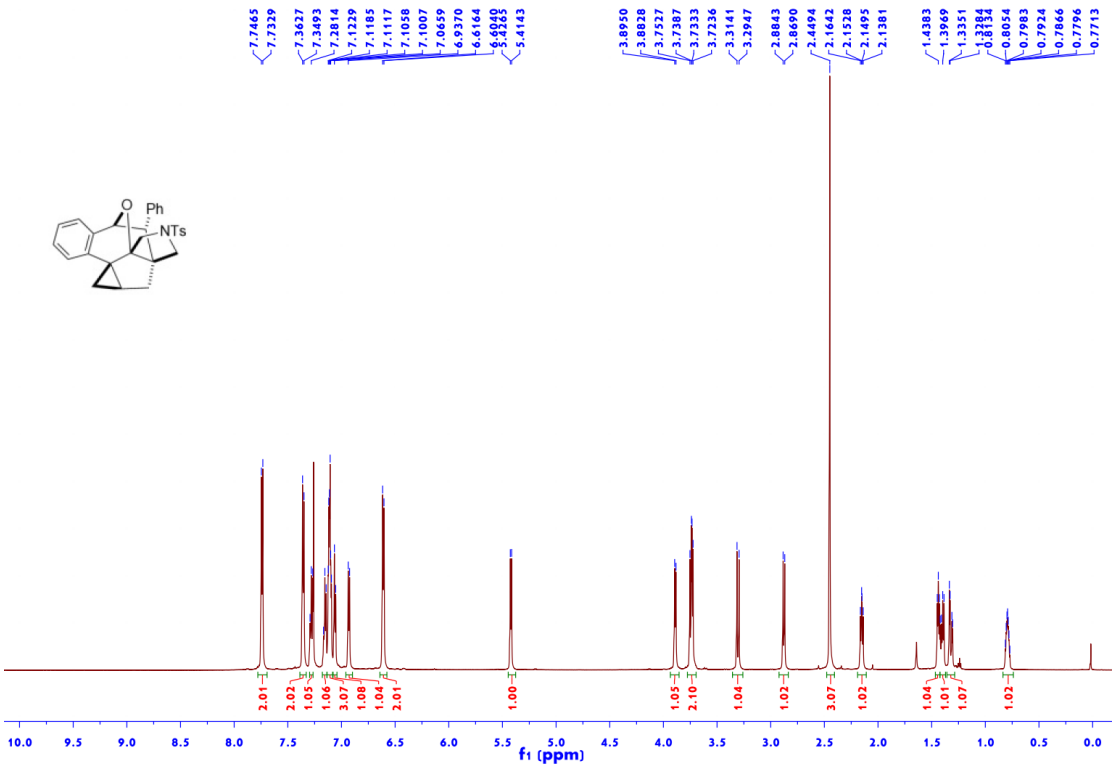


Figure S70 ^{13}C NMR (150 MHz, $CDCl_3$) of 2a

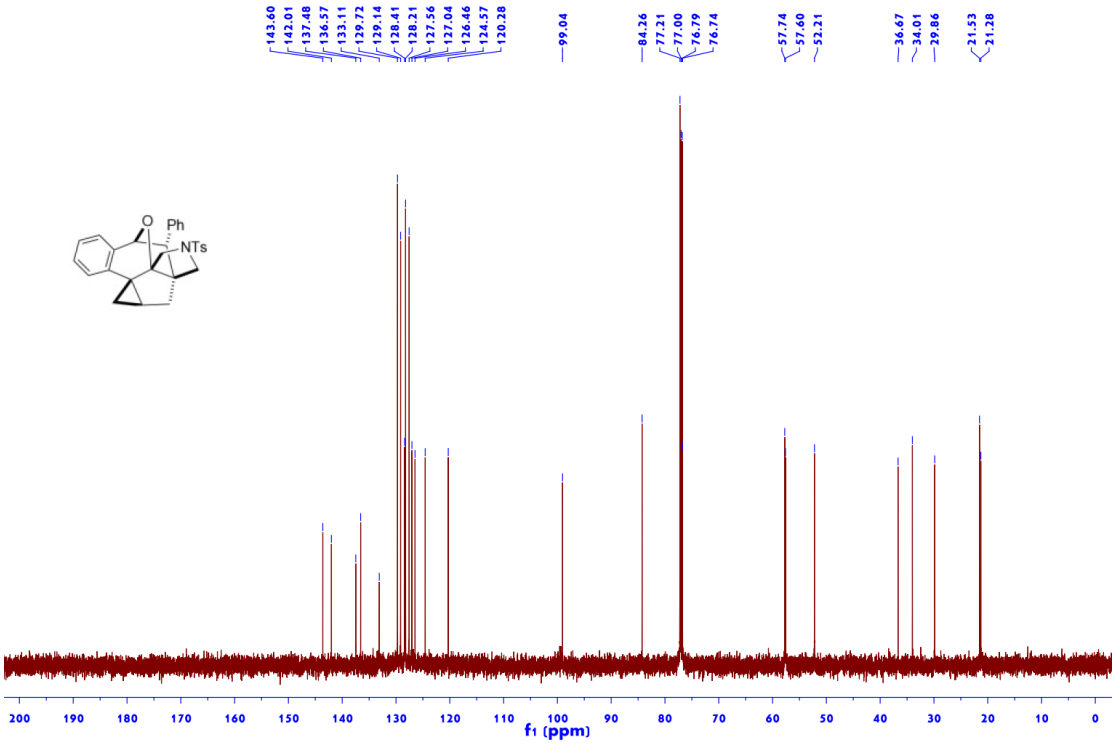


Figure S71 ^{1}H NMR (600 MHz, $CDCl_3$) of 2b

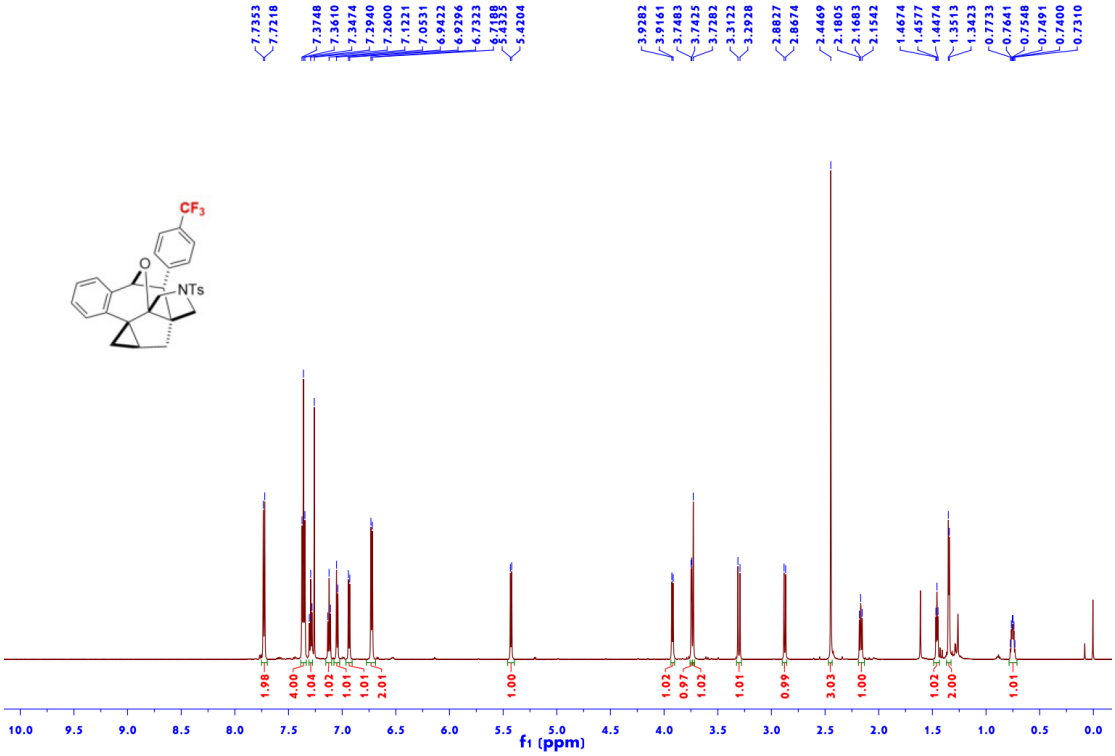


Figure S72 ^{13}C NMR (150 MHz, $CDCl_3$) of 2b

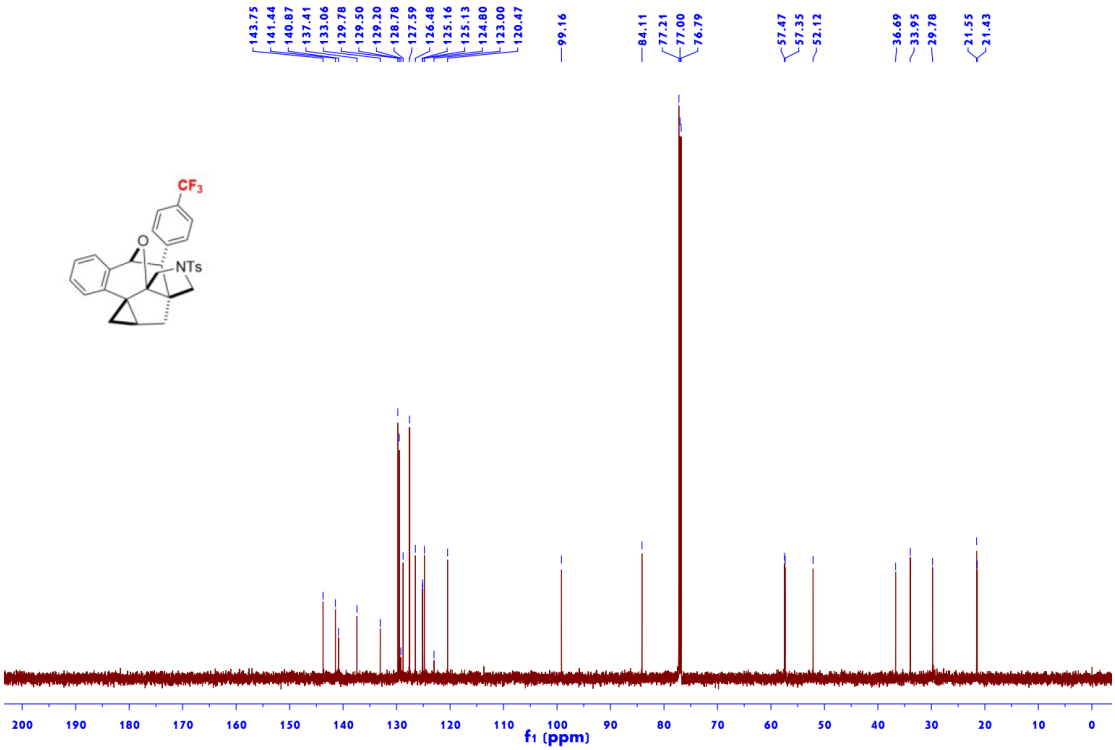


Figure S73 ^{19}F NMR (565 MHz, $CDCl_3$) of 2b

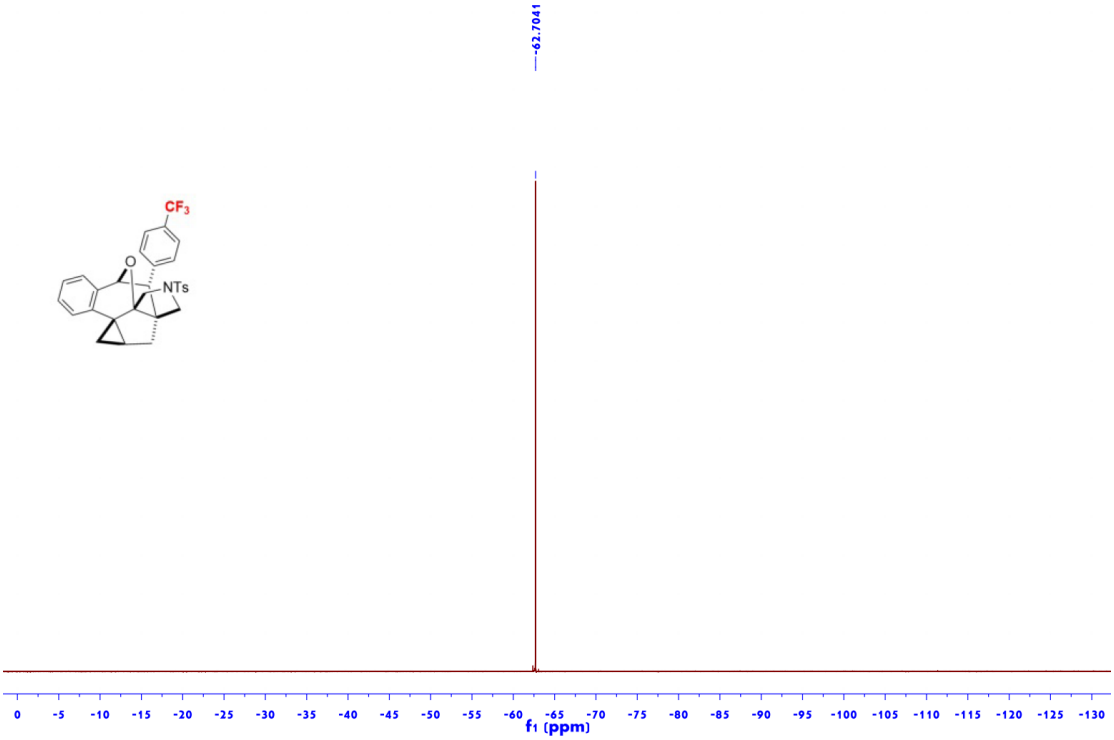


Figure S74 ^{1}H NMR (600 MHz, $CDCl_3$) of 2c

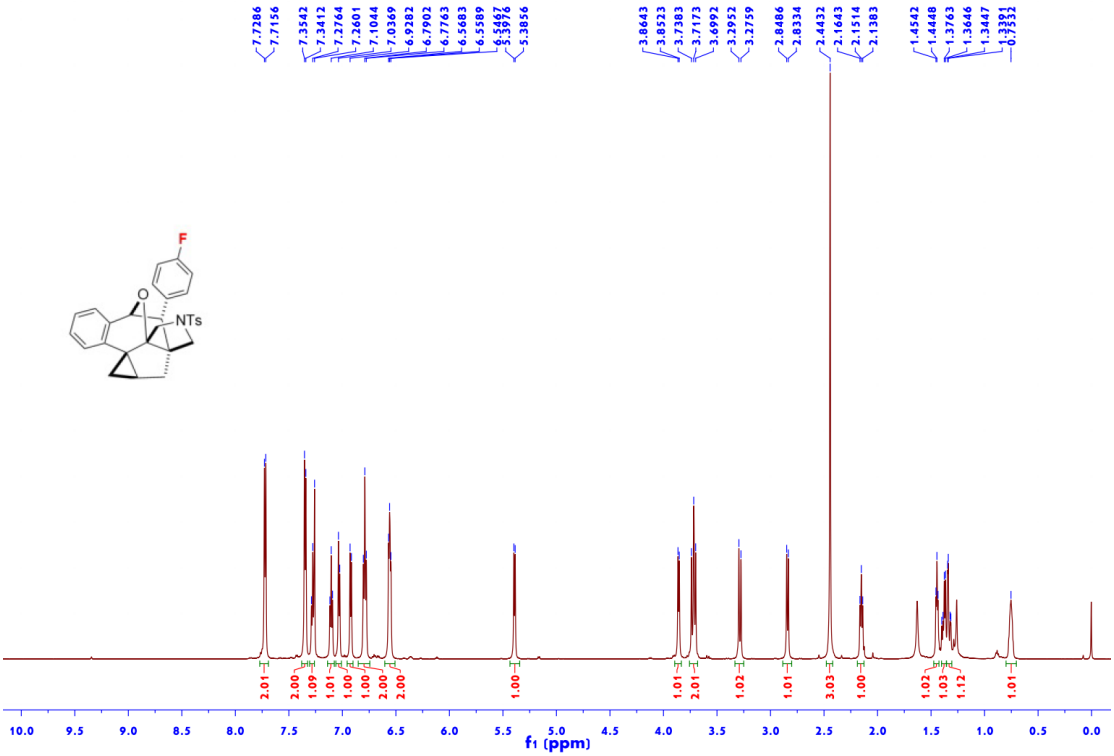


Figure S75 ^{13}C NMR (150 MHz, $CDCl_3$) of 2c

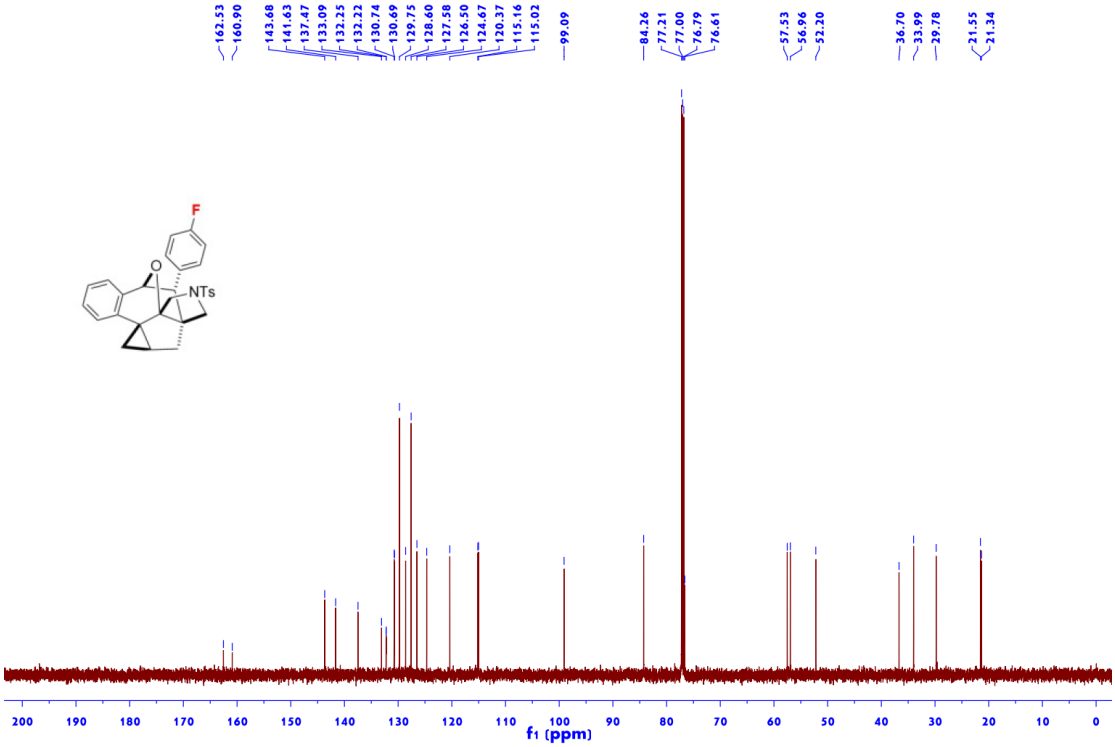


Figure S76 ^{19}F NMR (565 MHz, $CDCl_3$) of 2c

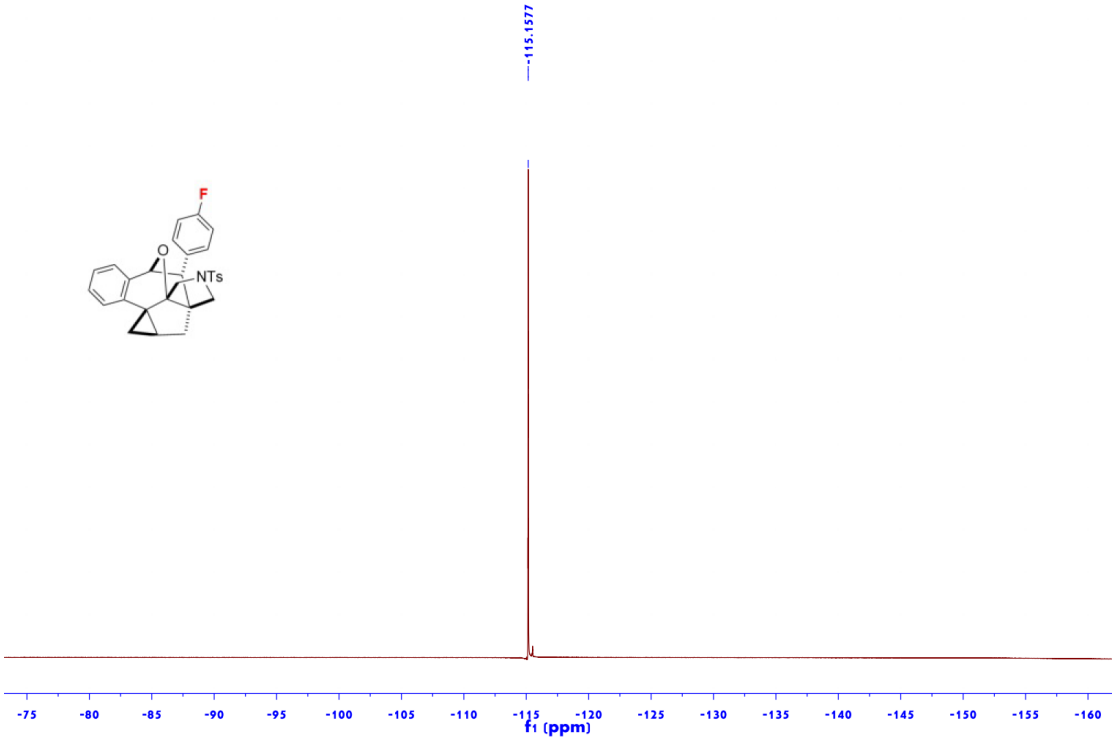


Figure S77 ^{1}H NMR (600 MHz, $CDCl_3$) of 2d

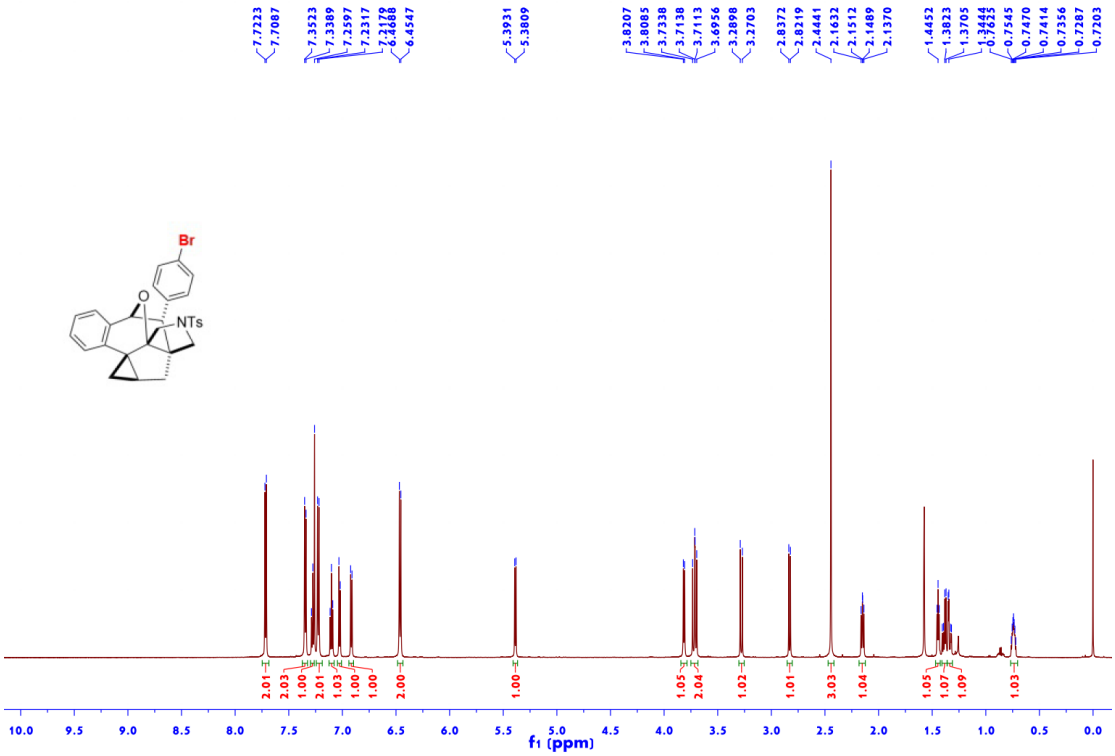


Figure S78 ^{13}C NMR (150 MHz, $CDCl_3$) of 2d

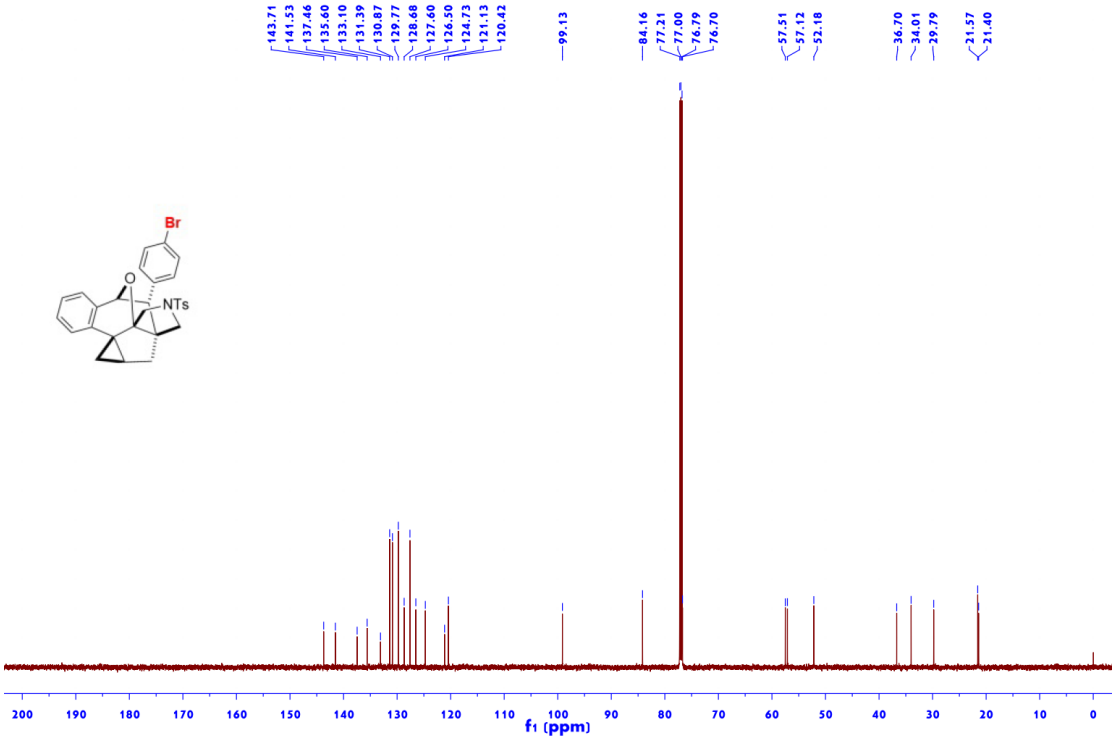


Figure S79 ^{1}H NMR (600 MHz, $CDCl_3$) of 2e

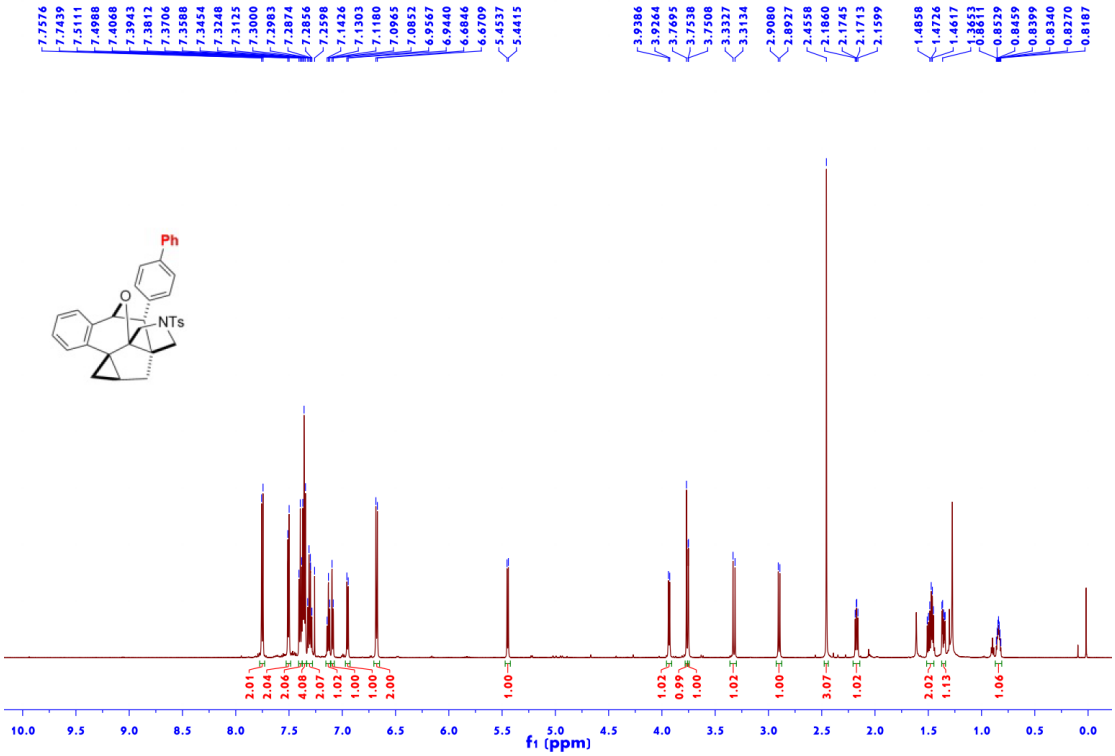


Figure S80 ^{13}C NMR (150 MHz, $CDCl_3$) of 2e

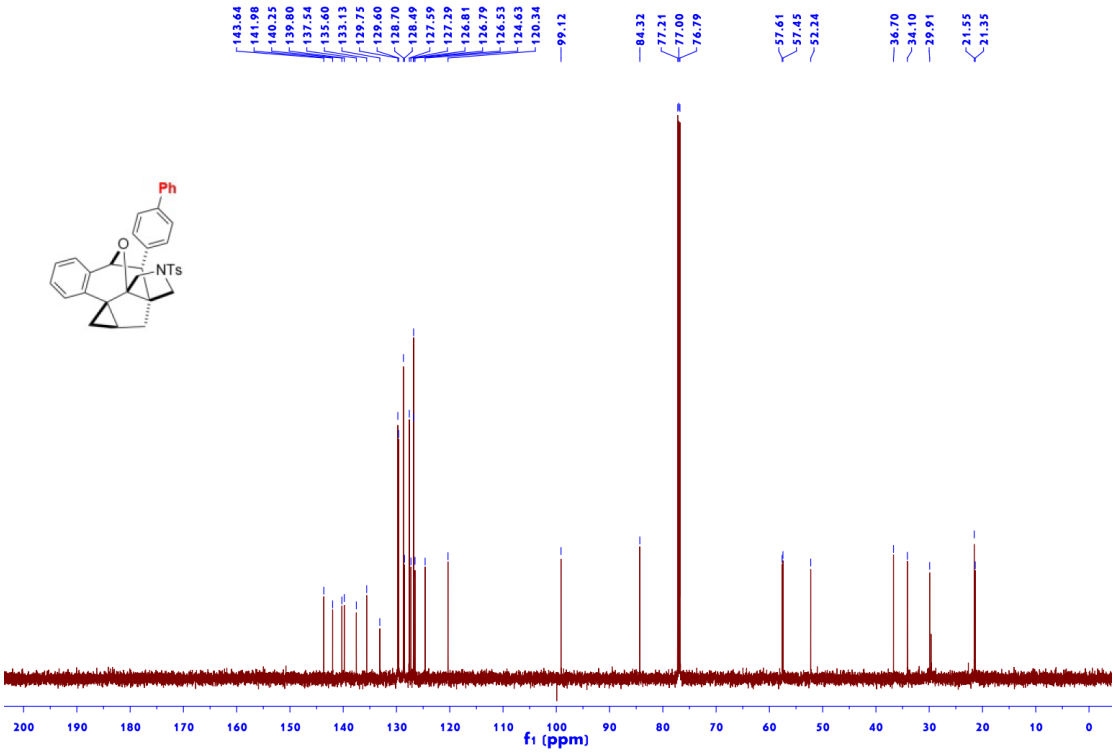


Figure S81 ^{1}H NMR (600 MHz, $CDCl_3$) of 2f

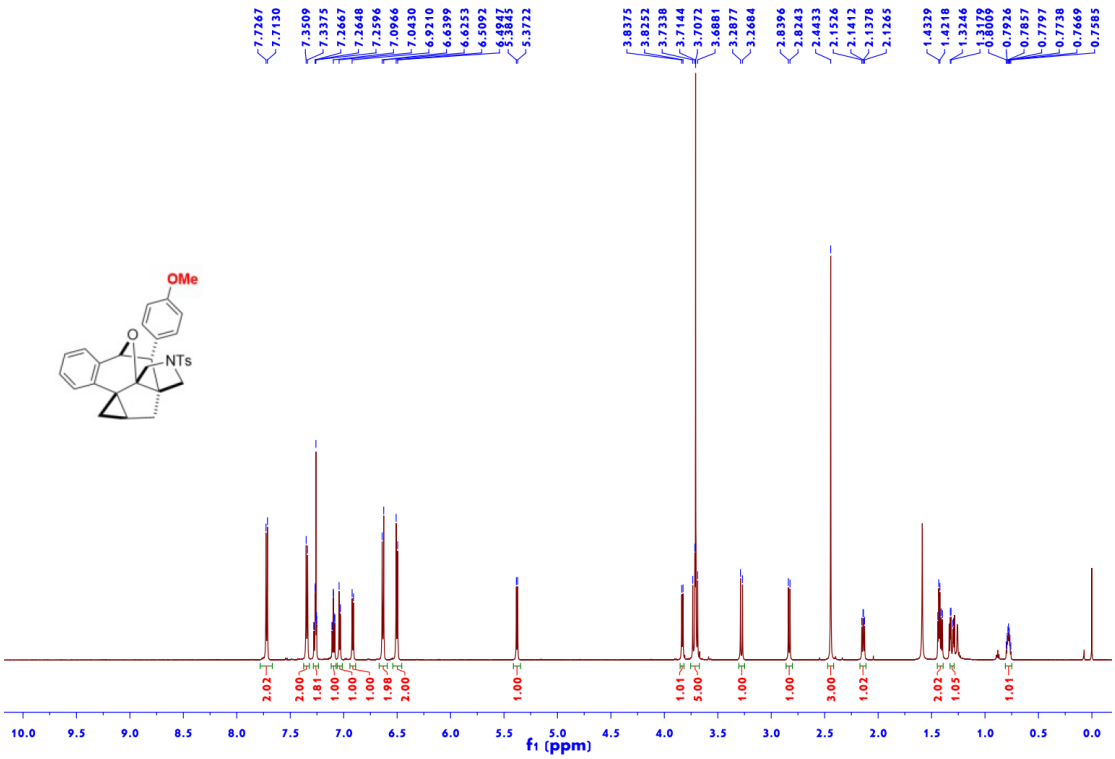


Figure S82 ^{13}C NMR (150 MHz, $CDCl_3$) of 2f

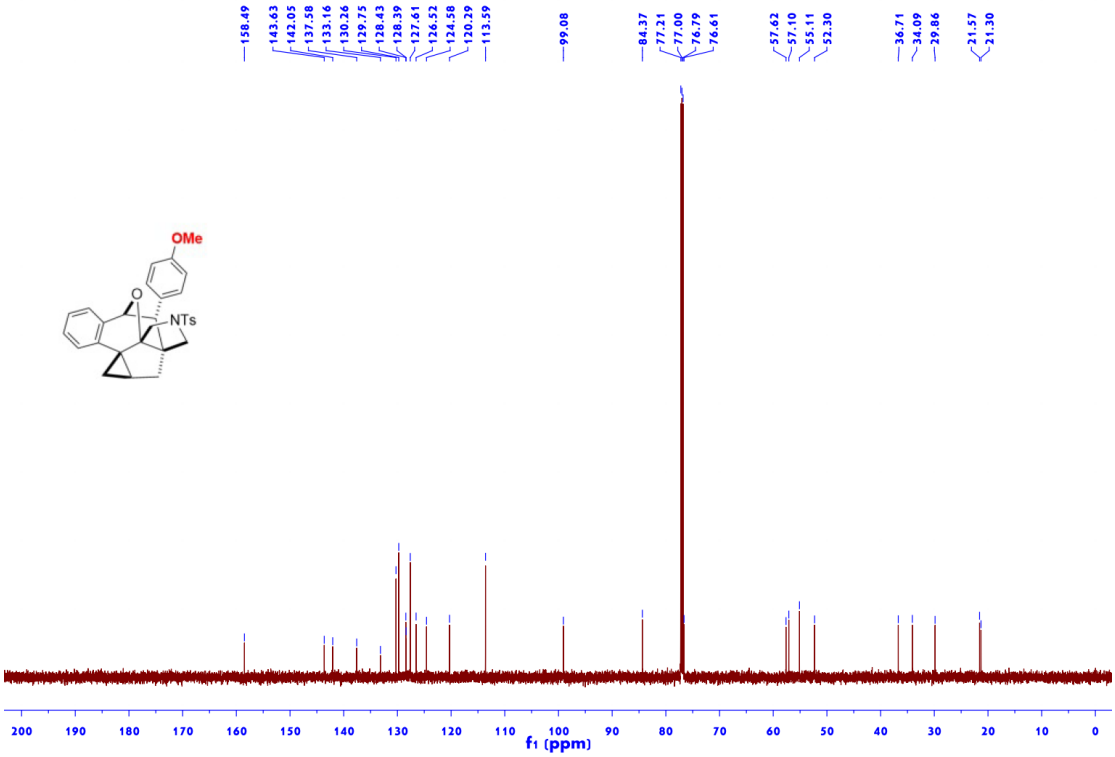


Figure S83 ^{1}H NMR (600 MHz, $CDCl_3$) of 2g

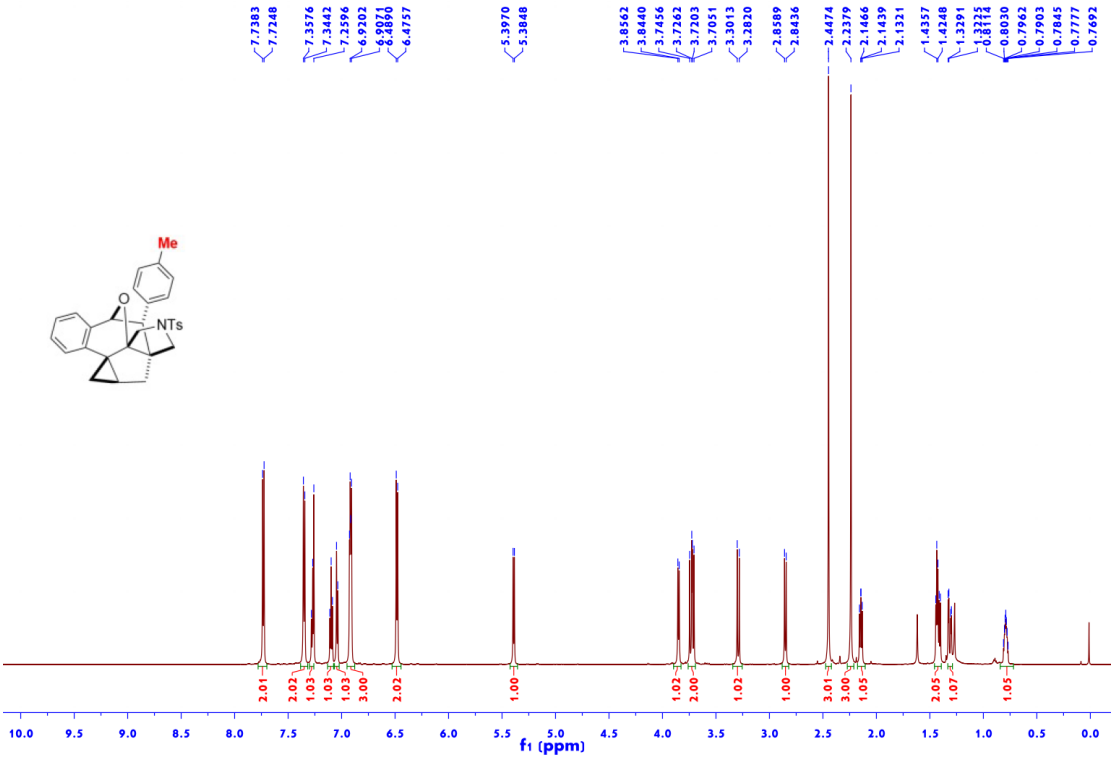


Figure S84 ^{13}C NMR (150 MHz, $CDCl_3$) of 2g

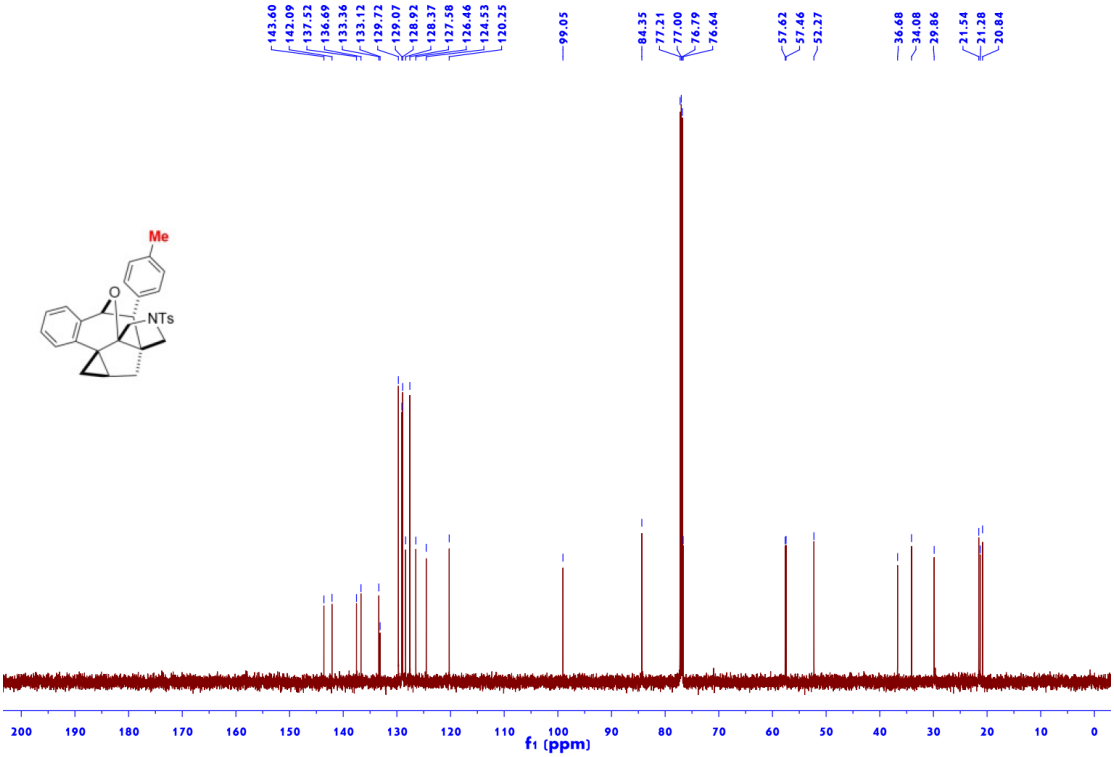


Figure S85 ^{1}H NMR (600 MHz, $CDCl_3$) of 2h

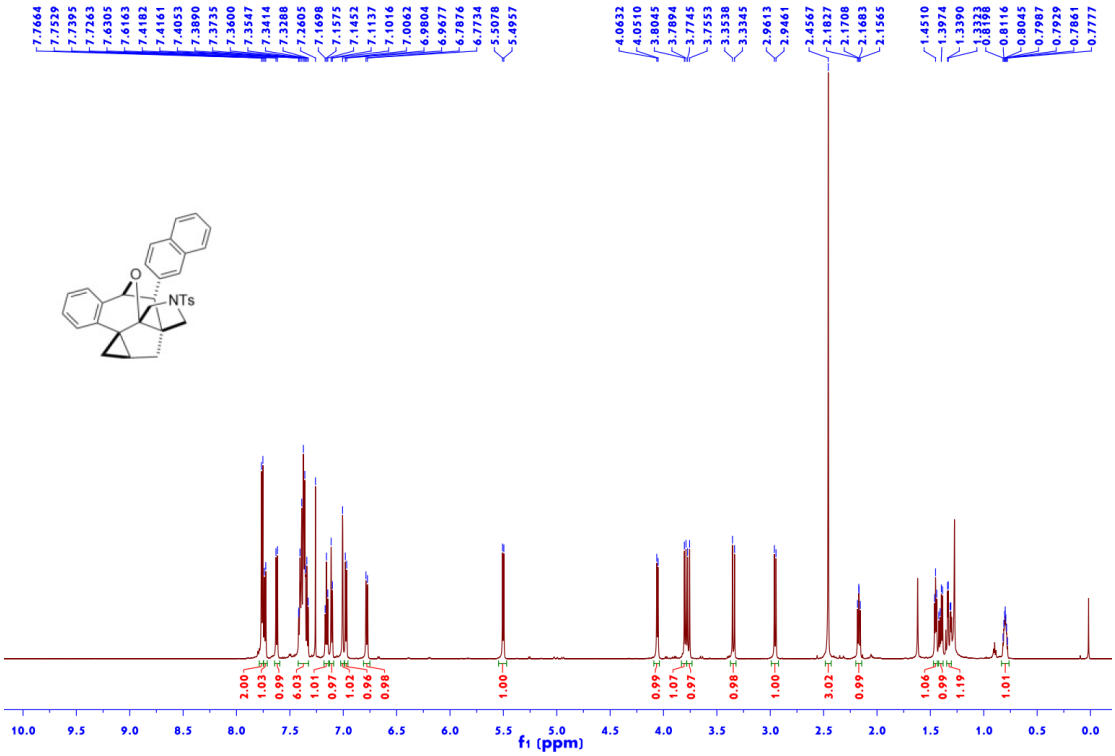


Figure S86 ^{13}C NMR (150 MHz, $CDCl_3$) of 2h

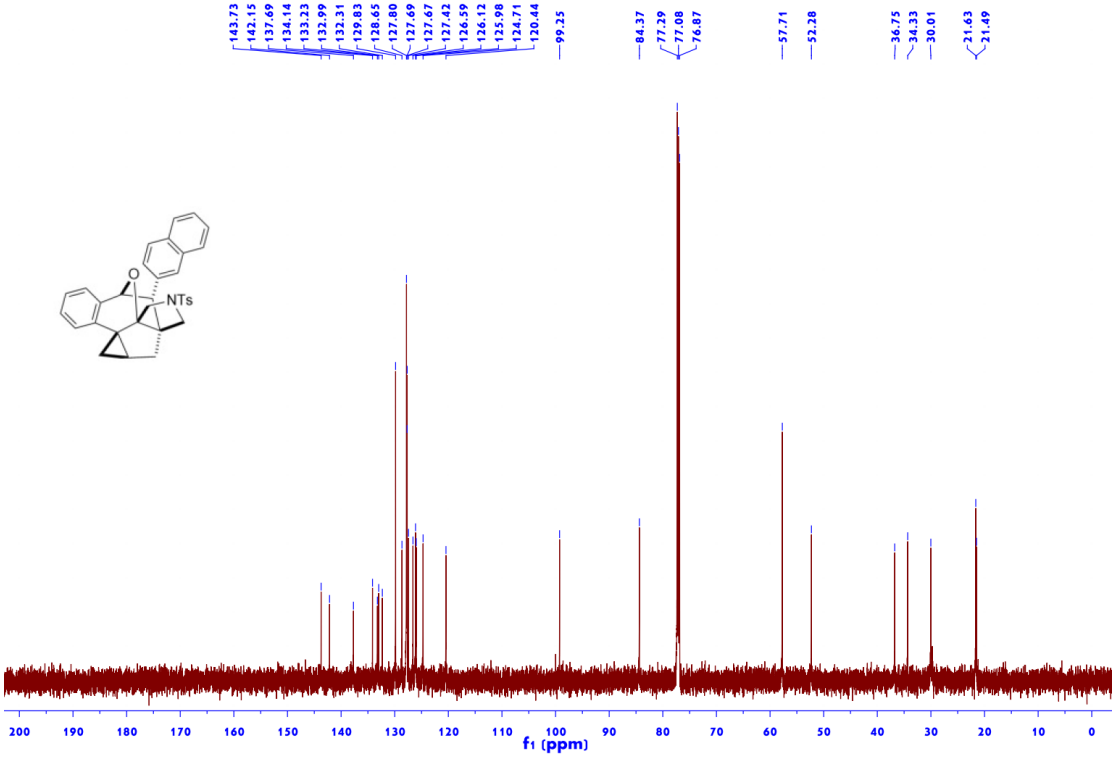


Figure S87 ^{1}H NMR (600 MHz, $CDCl_3$) of 2j

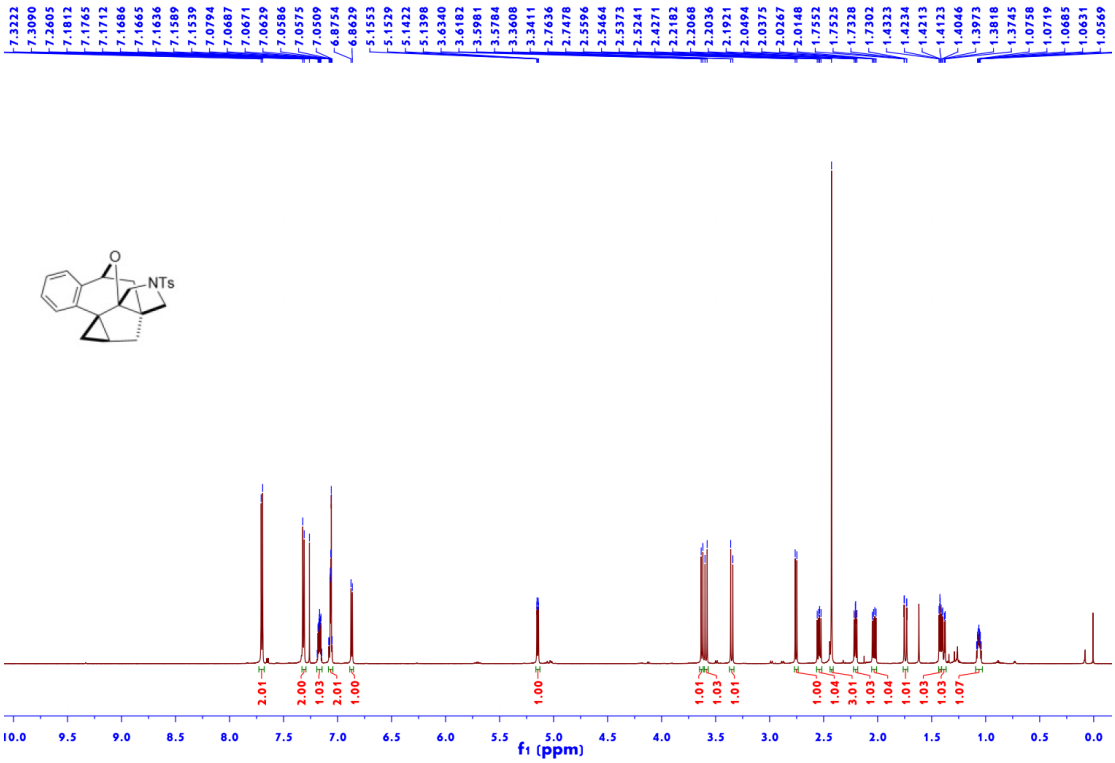


Figure S88 ^{13}C NMR (150 MHz, $CDCl_3$) of 2j

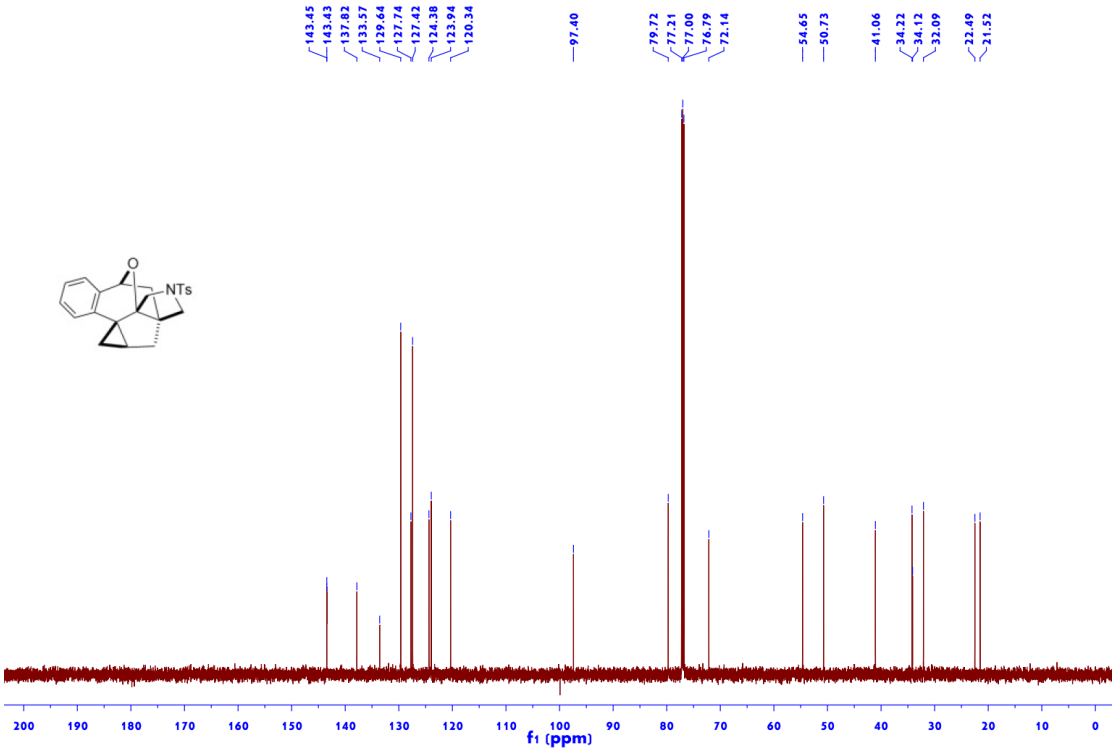


Figure S89 ^{1}H NMR (600 MHz, $CDCl_3$) of 2k

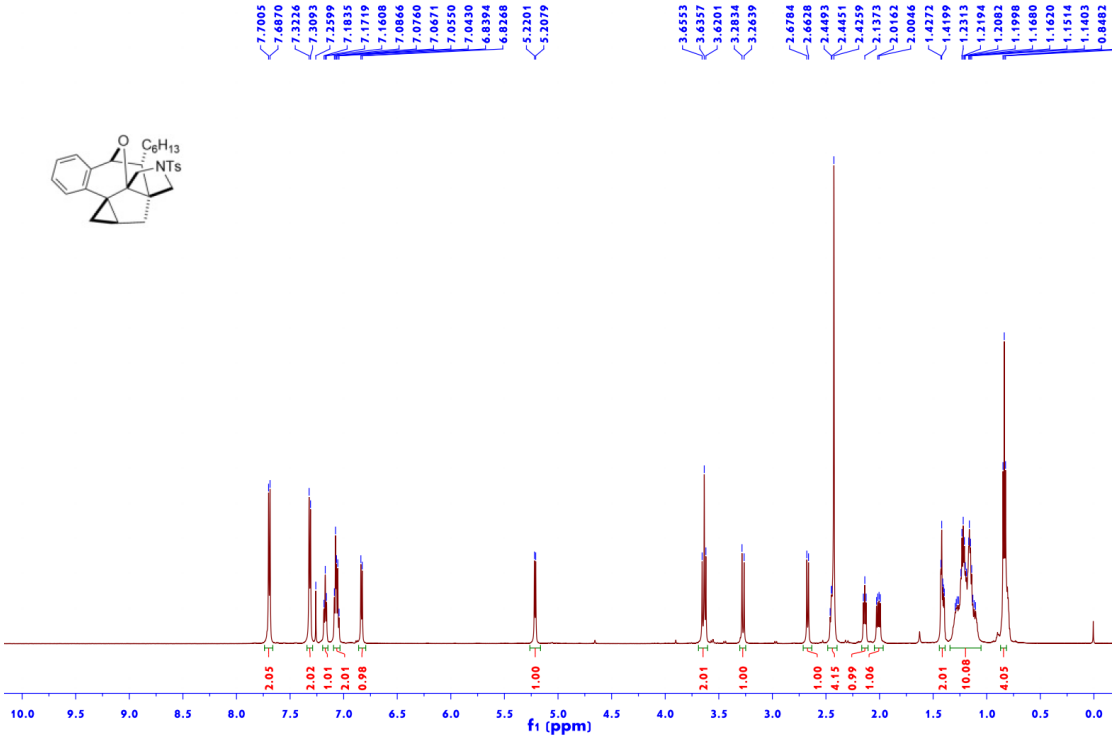


Figure S90 ^{13}C NMR (150 MHz, $CDCl_3$) of 2k

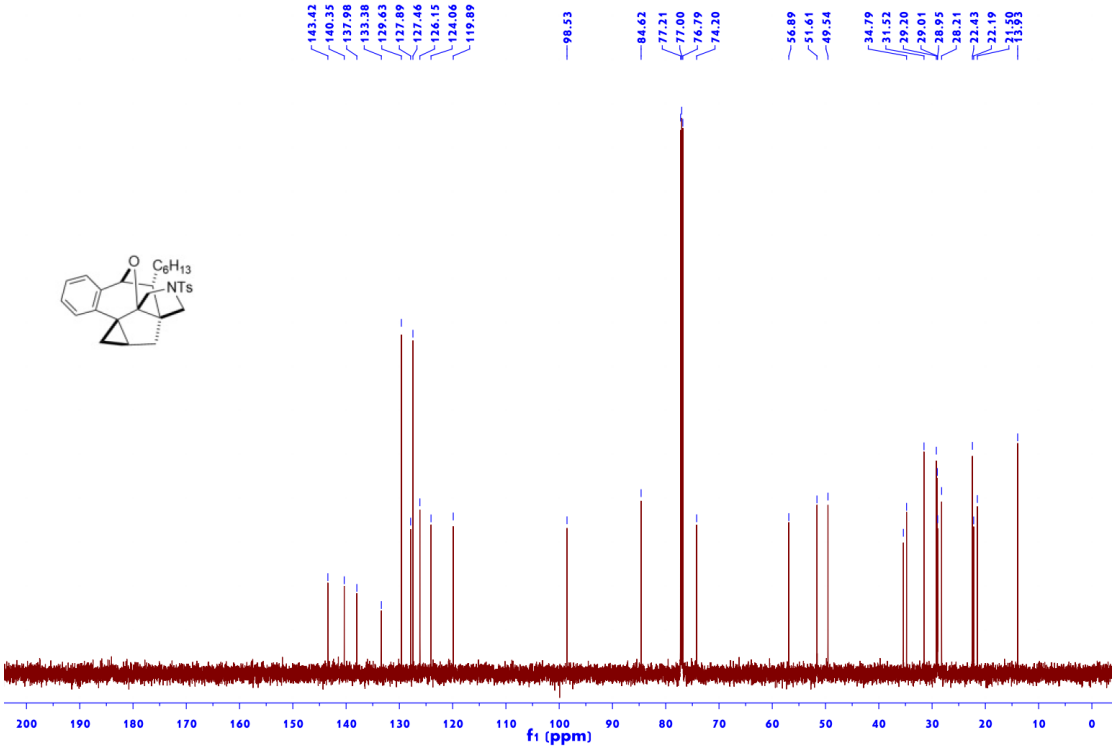


Figure S91 ^{1}H NMR (600 MHz, $CDCl_3$) of 2l

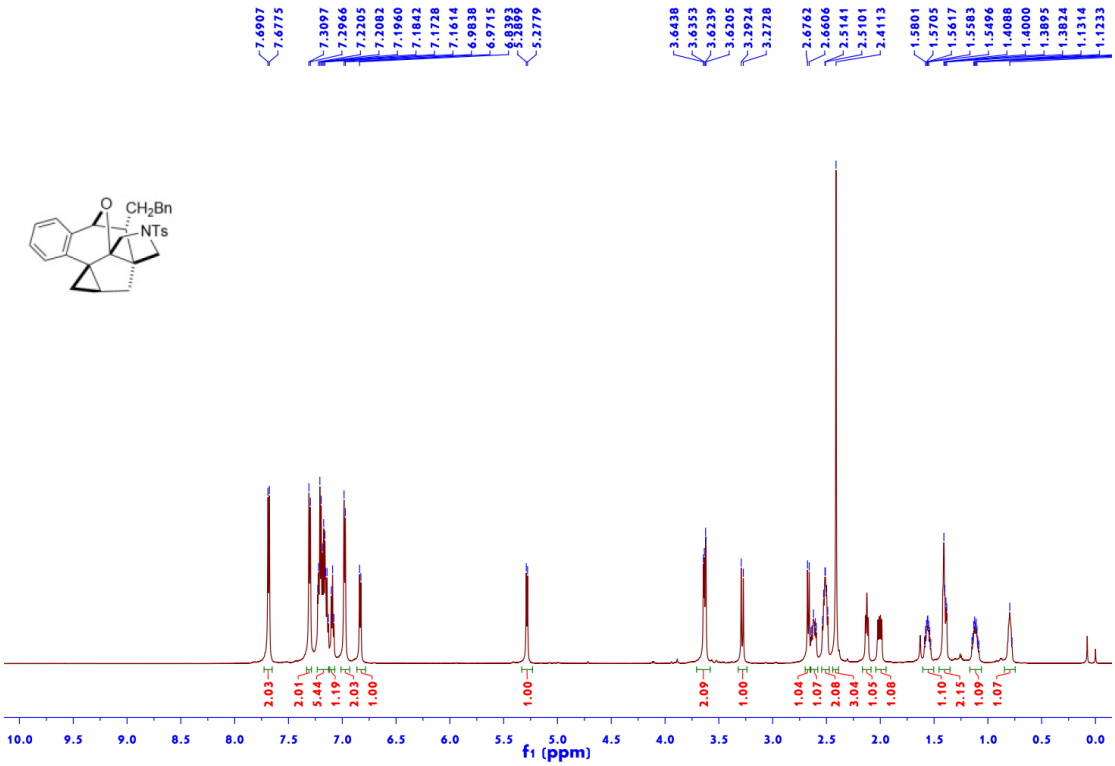


Figure S92 ^{13}C NMR (150 MHz, $CDCl_3$) of 2l

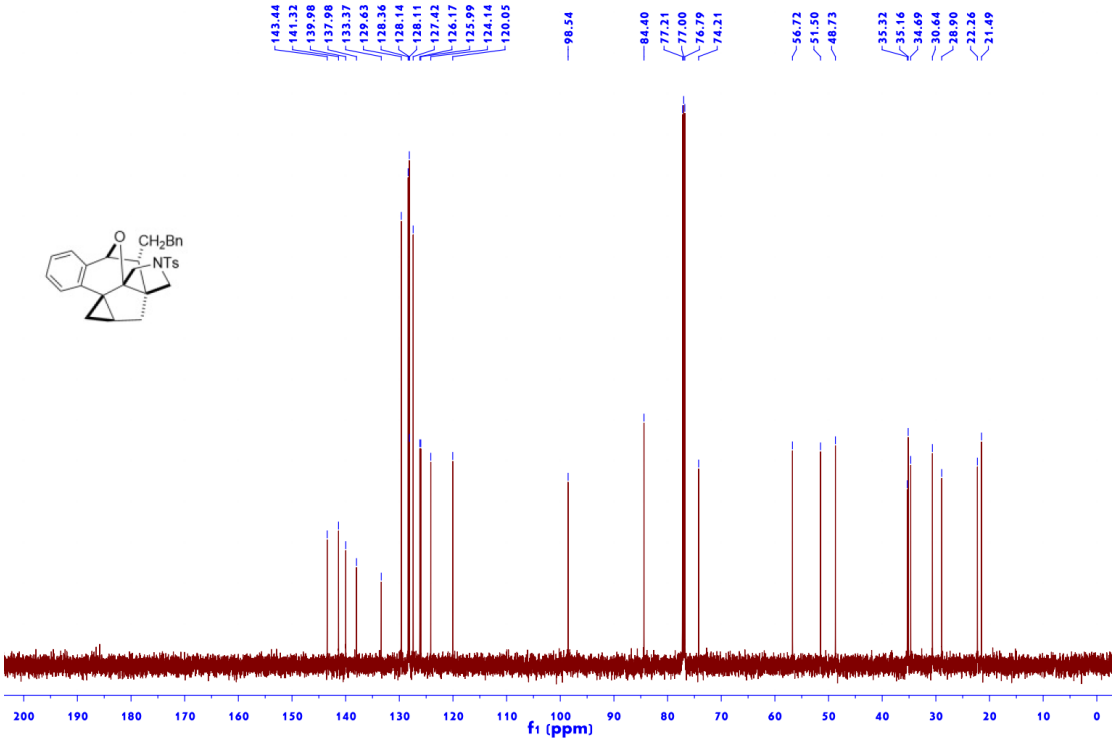


Figure S93 ^{1}H NMR (400 MHz, $CDCl_3$) of 2m

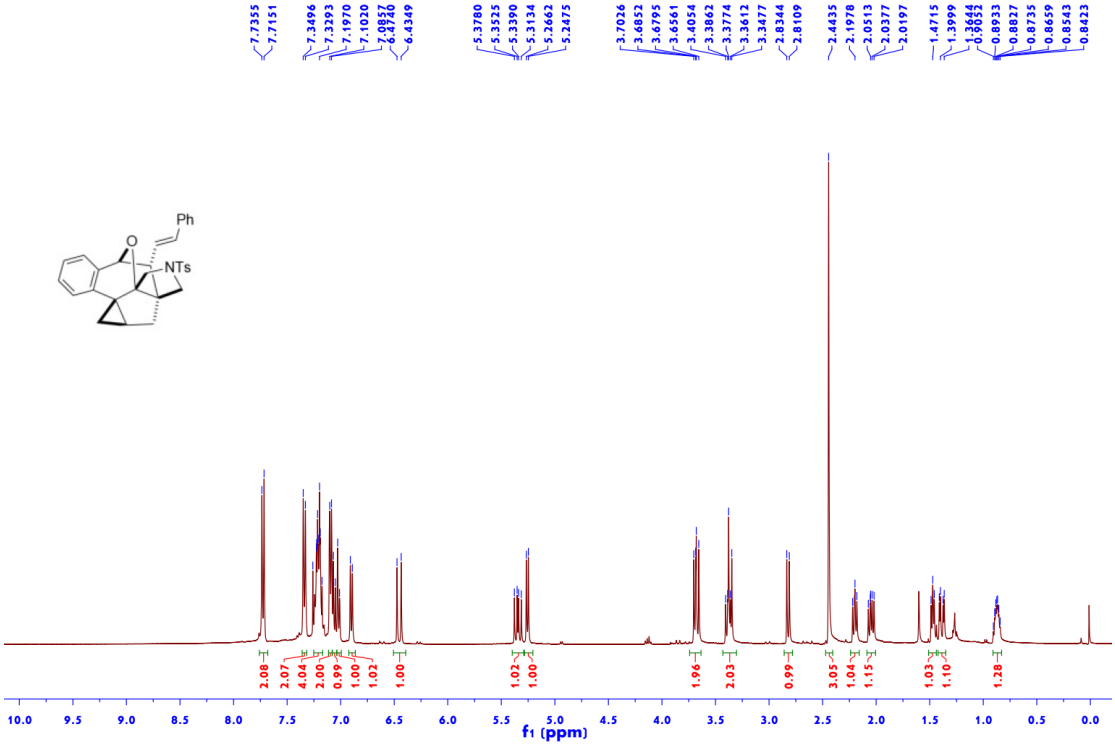


Figure S94 ^{13}C NMR (100 MHz, $CDCl_3$) of 2m

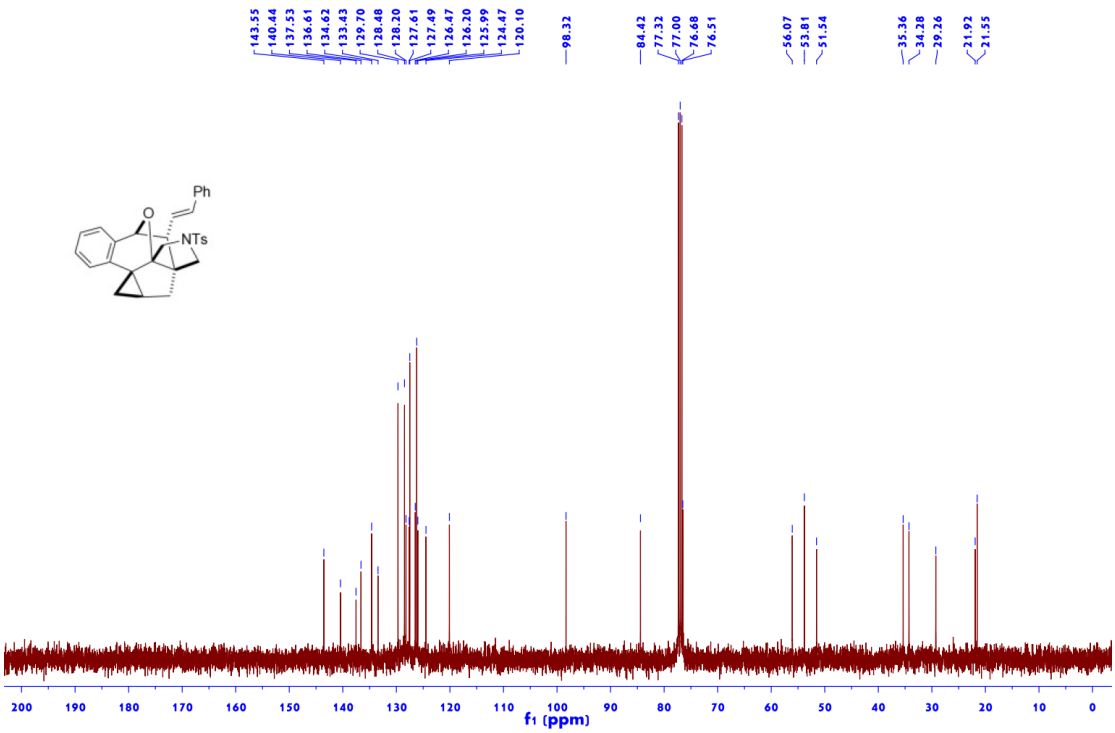


Figure S95 ^{1}H NMR (400 MHz, $CDCl_3$) of 2n

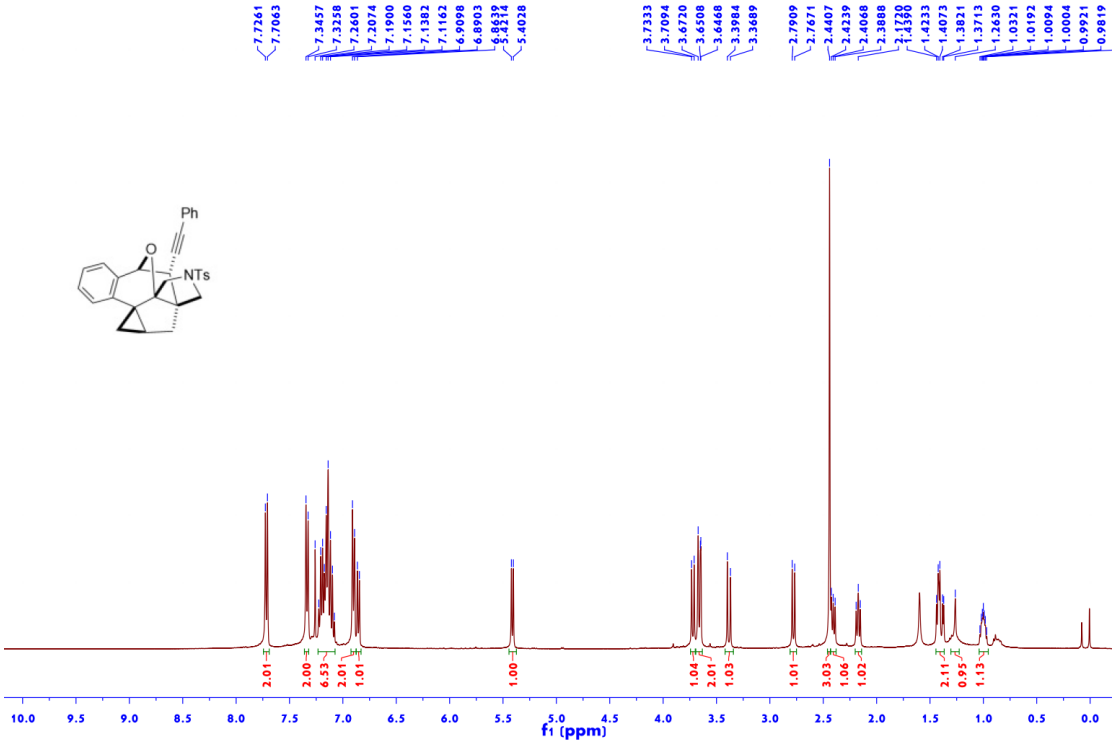


Figure S96 ^{13}C NMR (100 MHz, $CDCl_3$) of 2n

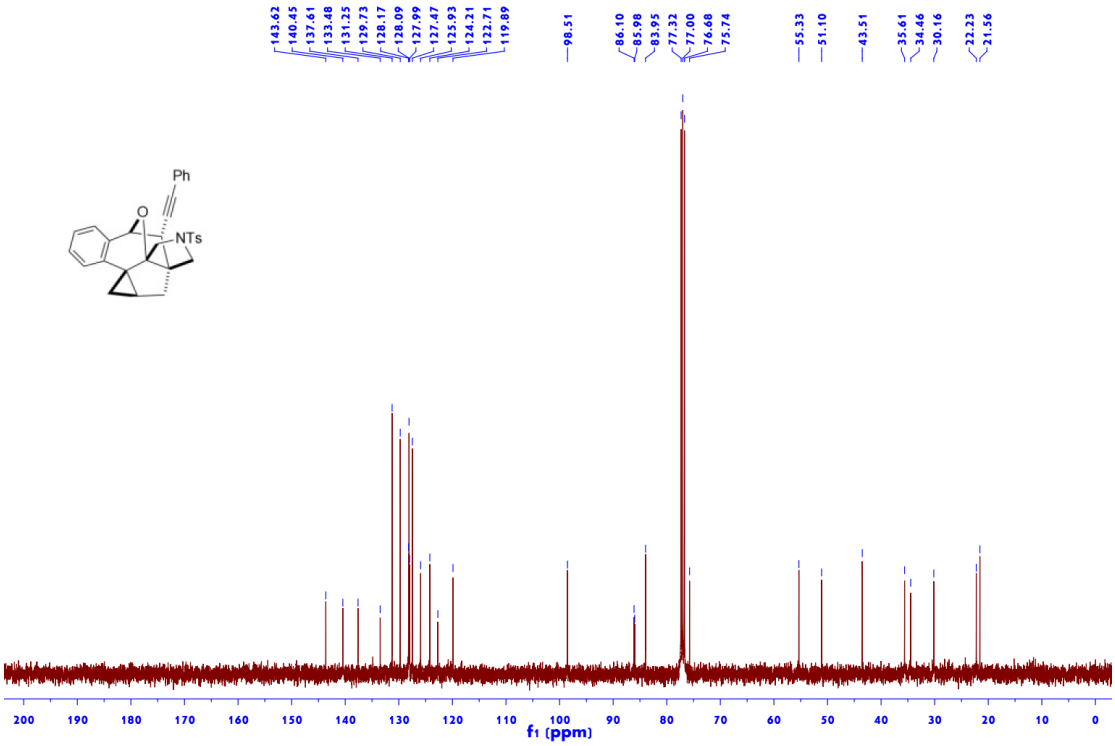


Figure S97 ^{1}H NMR (600 MHz, $CDCl_3$) of 2o

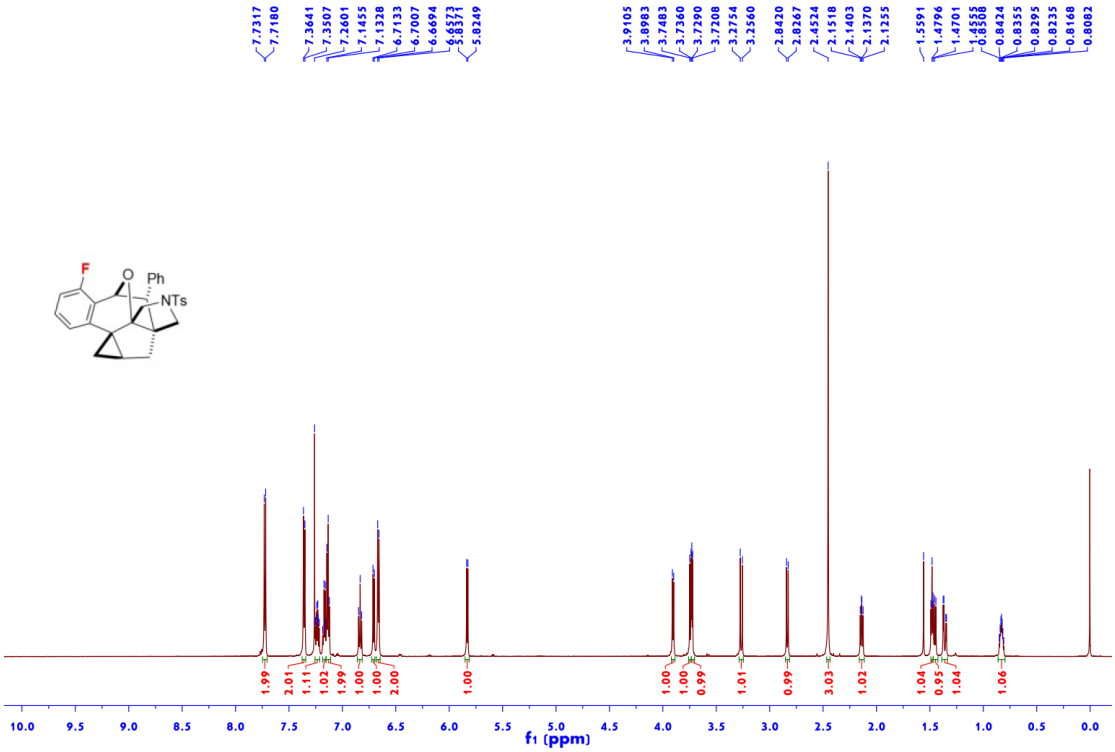


Figure S98 ^{13}C NMR (150 MHz, $CDCl_3$) of 2o

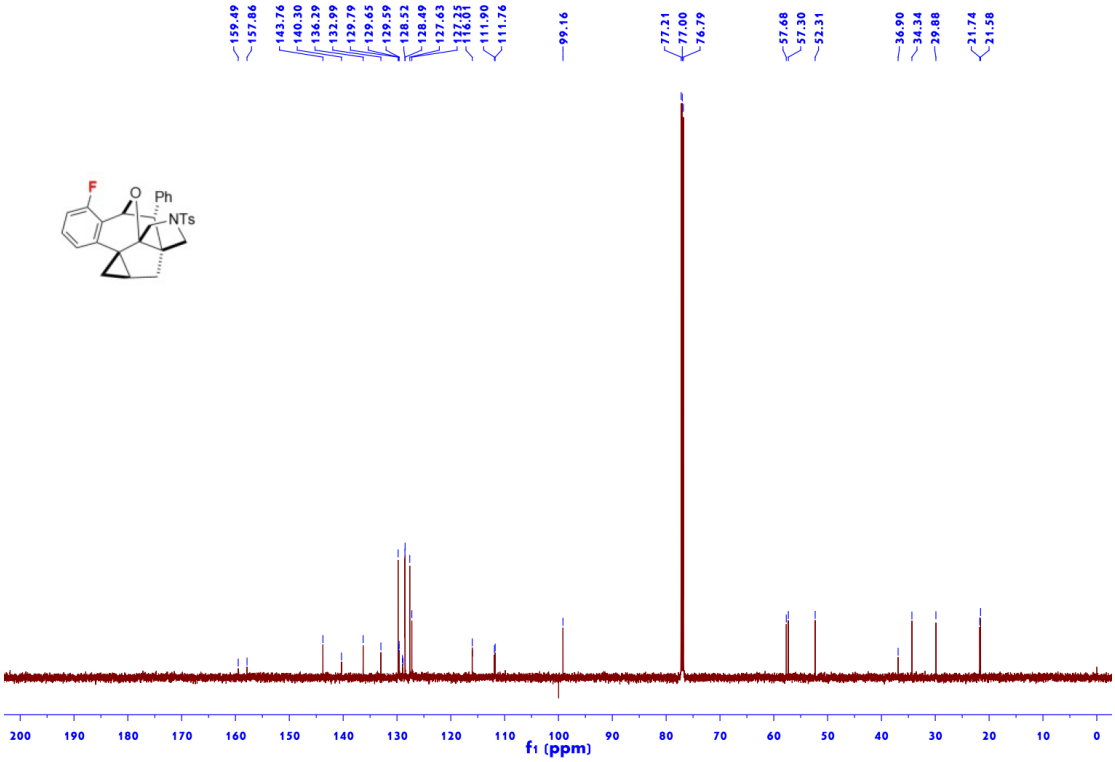


Figure S99 ^{19}F NMR (565 MHz, $CDCl_3$) of 2o

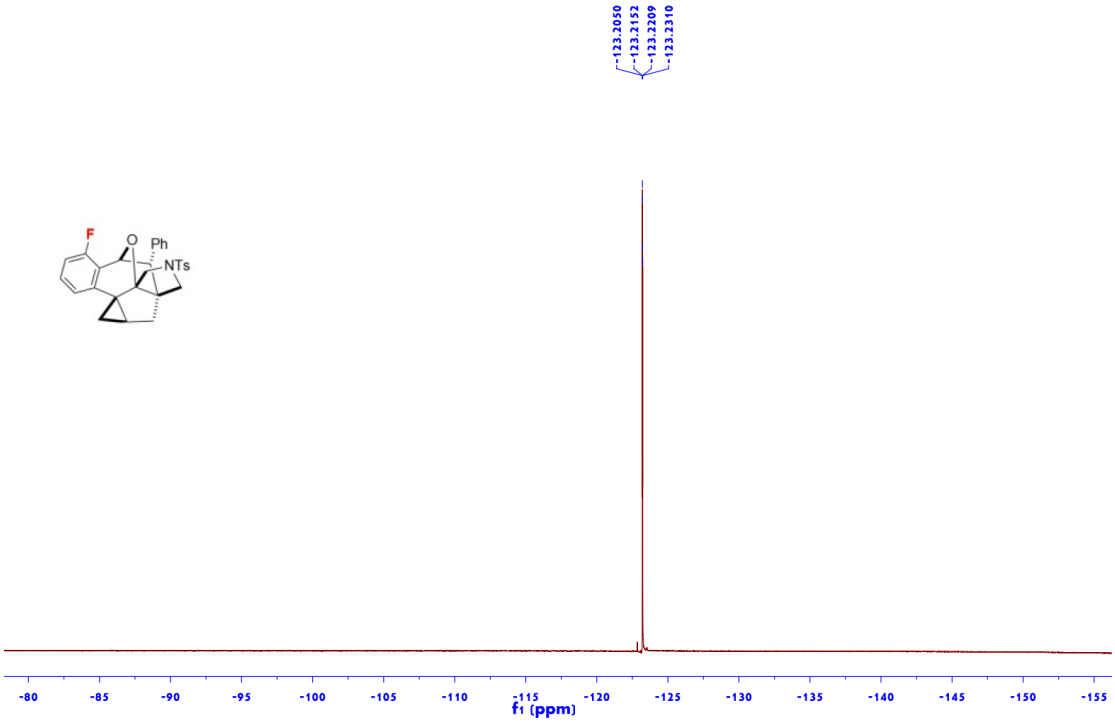


Figure S100 ^{1}H NMR (600 MHz, $CDCl_3$) of 2p

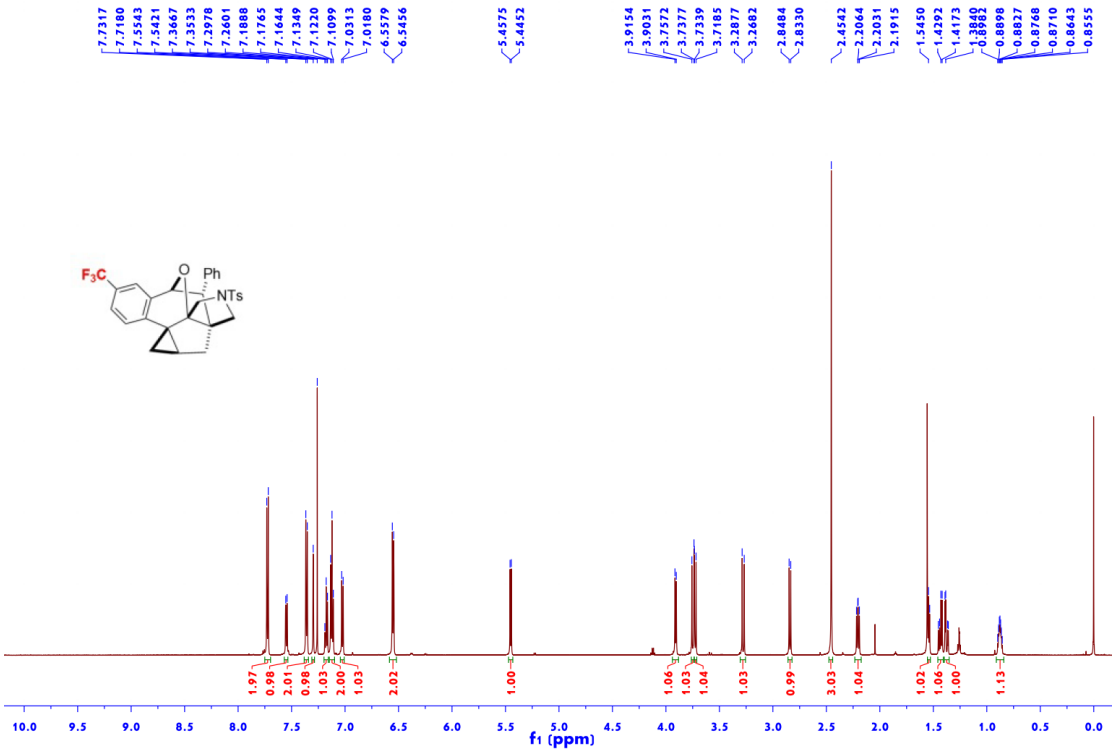


Figure S101 ^{13}C NMR (150 MHz, $CDCl_3$) of 2p

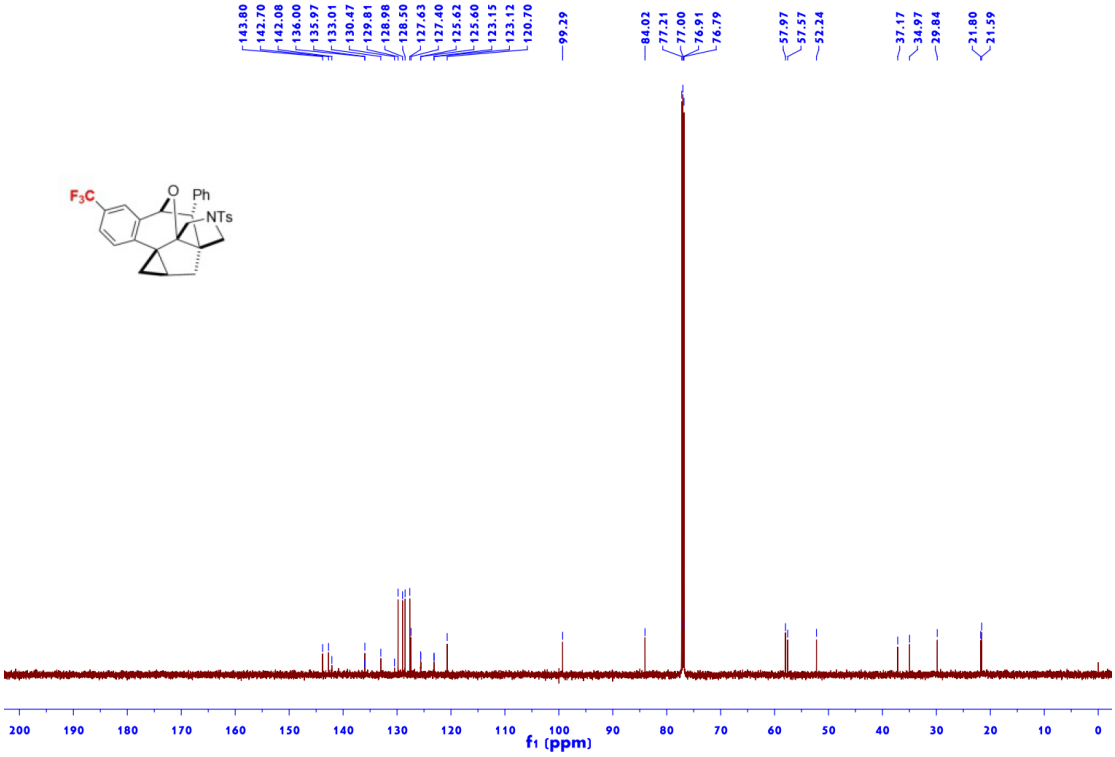


Figure S102 ^{19}F NMR (565 MHz, $CDCl_3$) of 2p

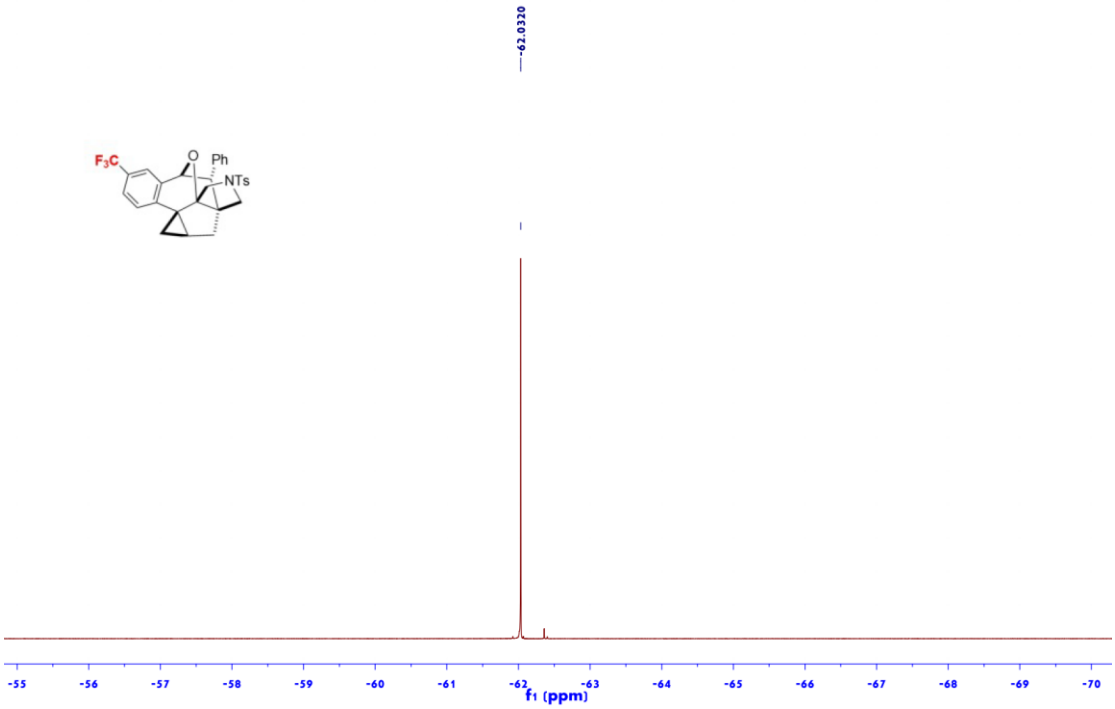


Figure S103 ^{1}H NMR (600 MHz, $CDCl_3$) of 2q

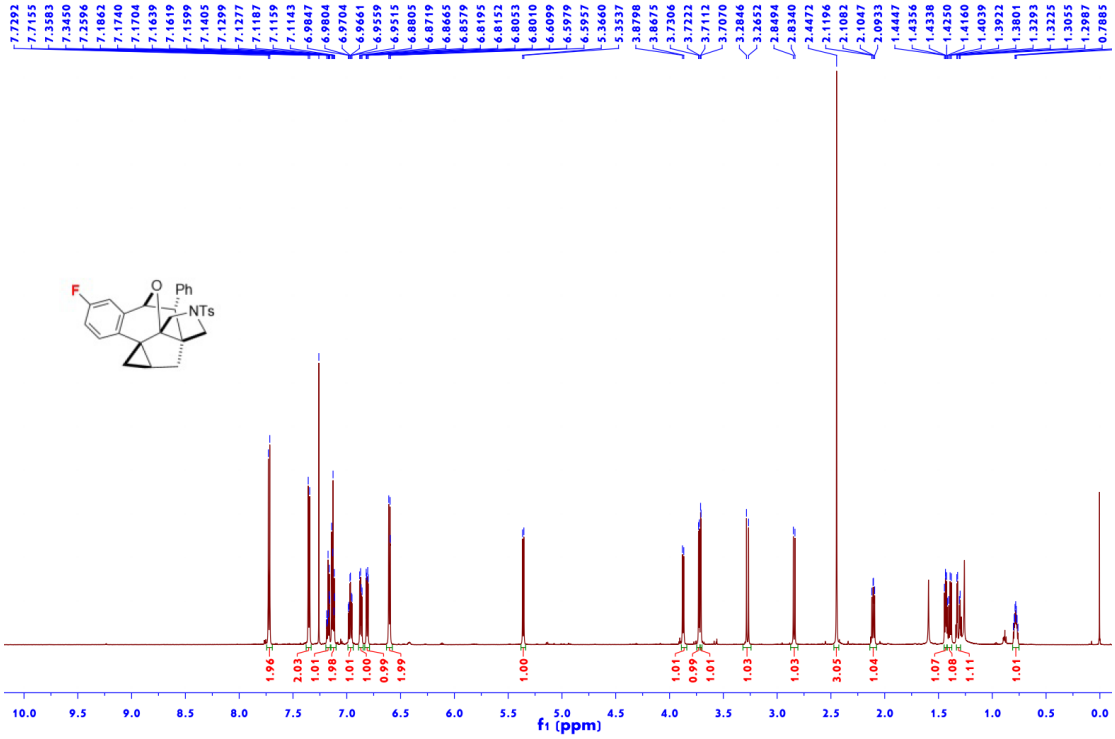


Figure S104 ^{13}C NMR (150 MHz, $CDCl_3$) of 2q

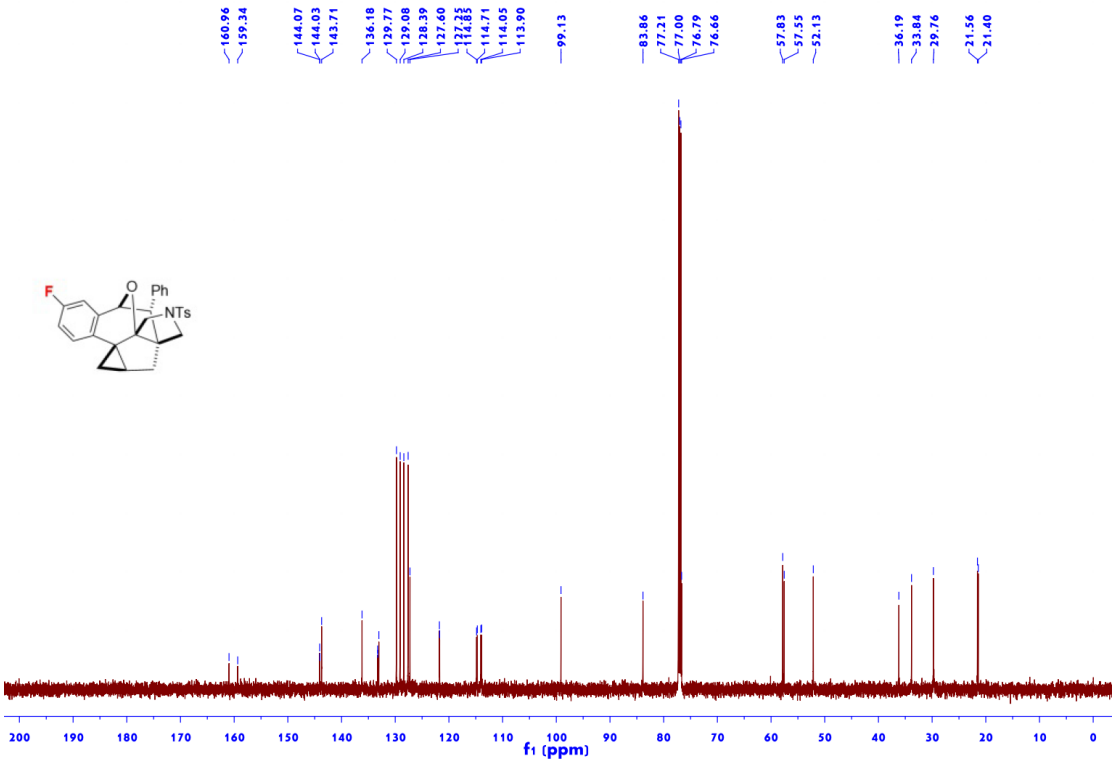


Figure S105 ^{1}H NMR (600 MHz, $CDCl_3$) of 2r

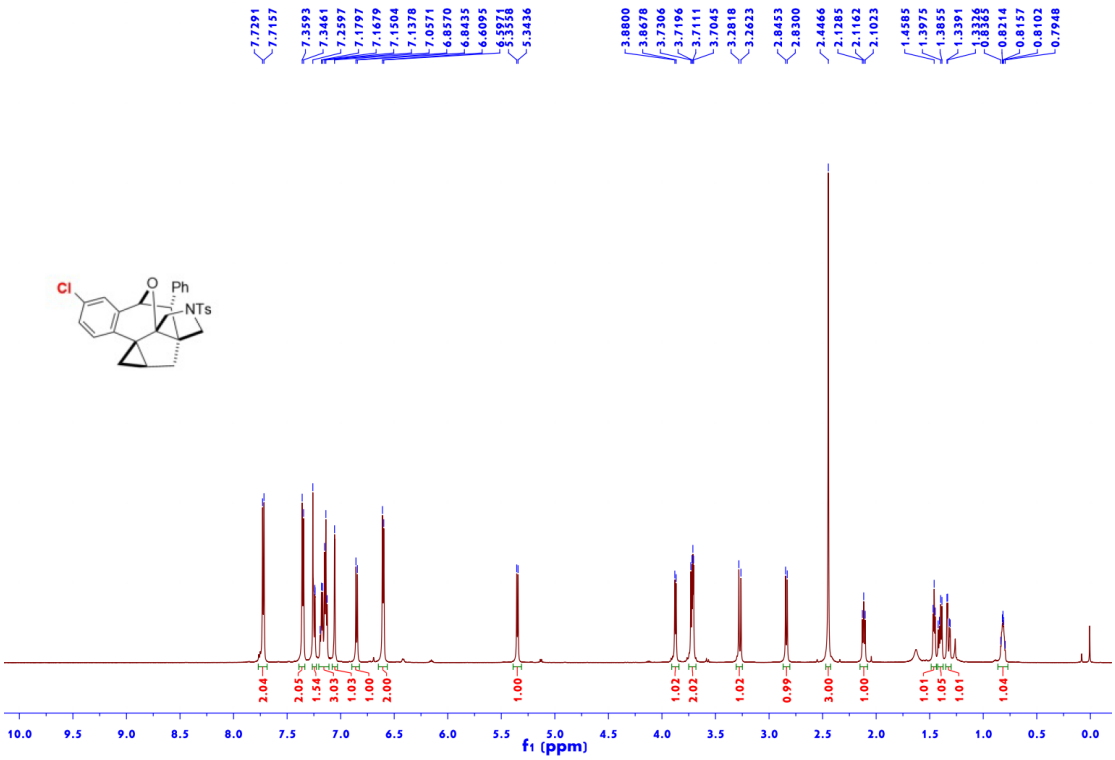


Figure S106 ^{13}C NMR (150 MHz, $CDCl_3$) of 2r

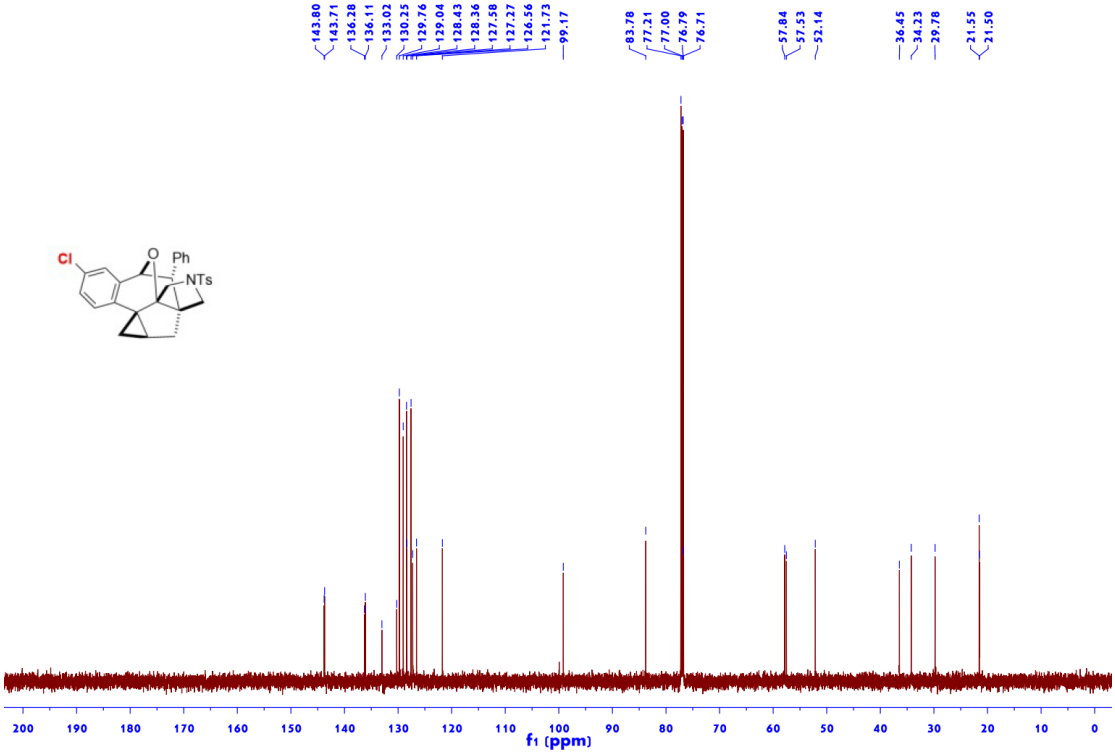


Figure S107 ^{1}H NMR (600 MHz, $CDCl_3$) of 2s

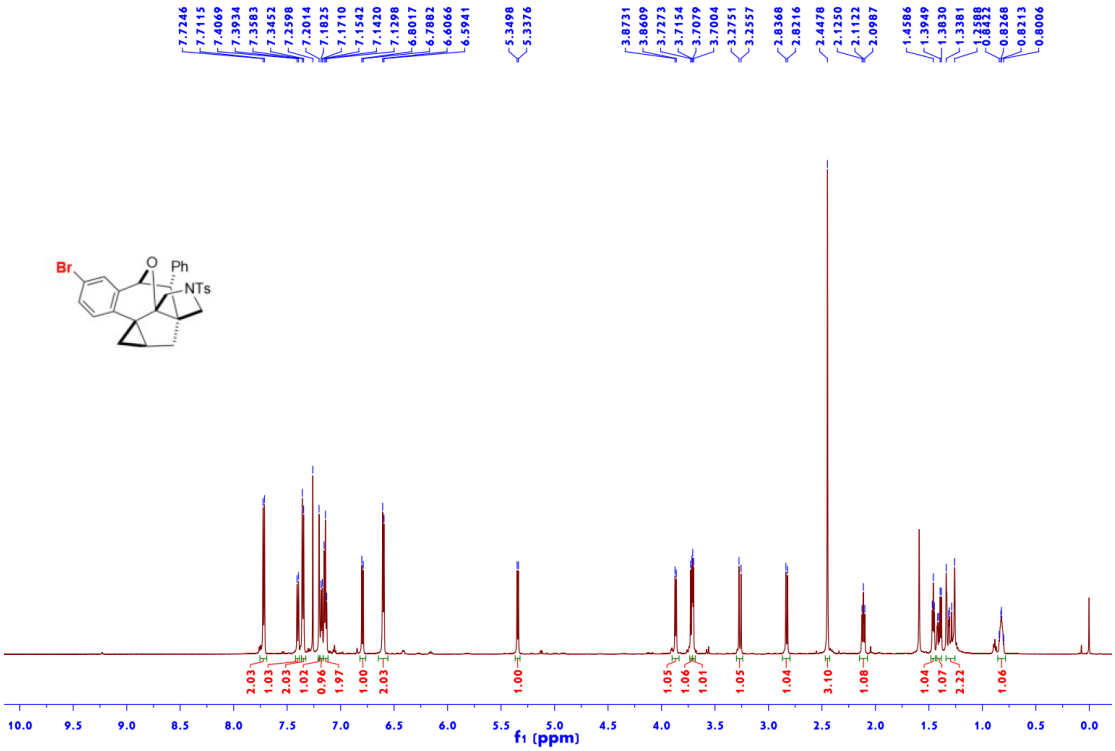


Figure S108 ^{13}C NMR (150 MHz, $CDCl_3$) of 2s

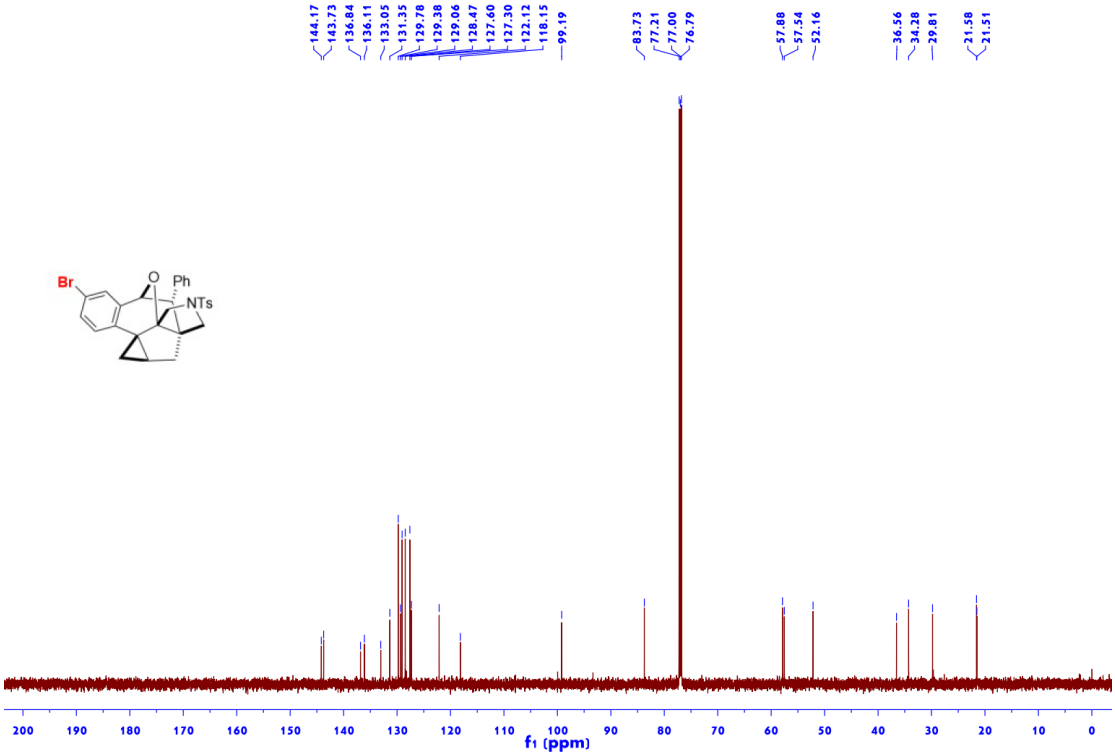


Figure S109 ^{1}H NMR (600 MHz, $CDCl_3$) of 2t

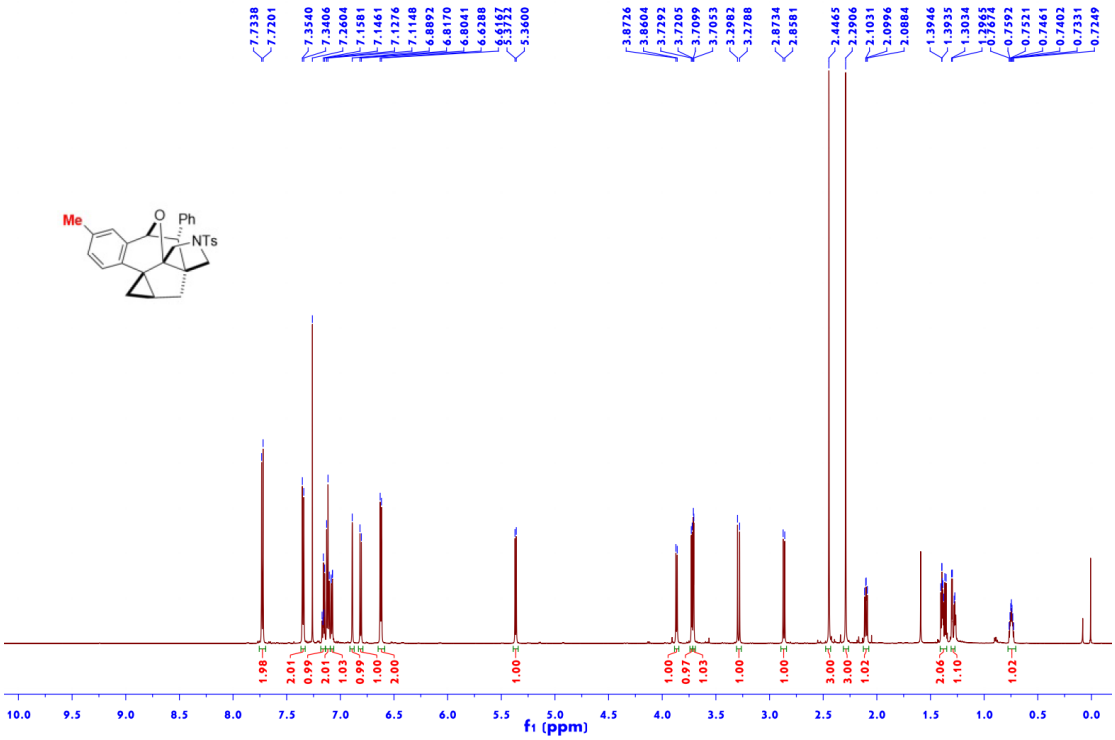


Figure S110 ^{13}C NMR (150 MHz, $CDCl_3$) of 2t

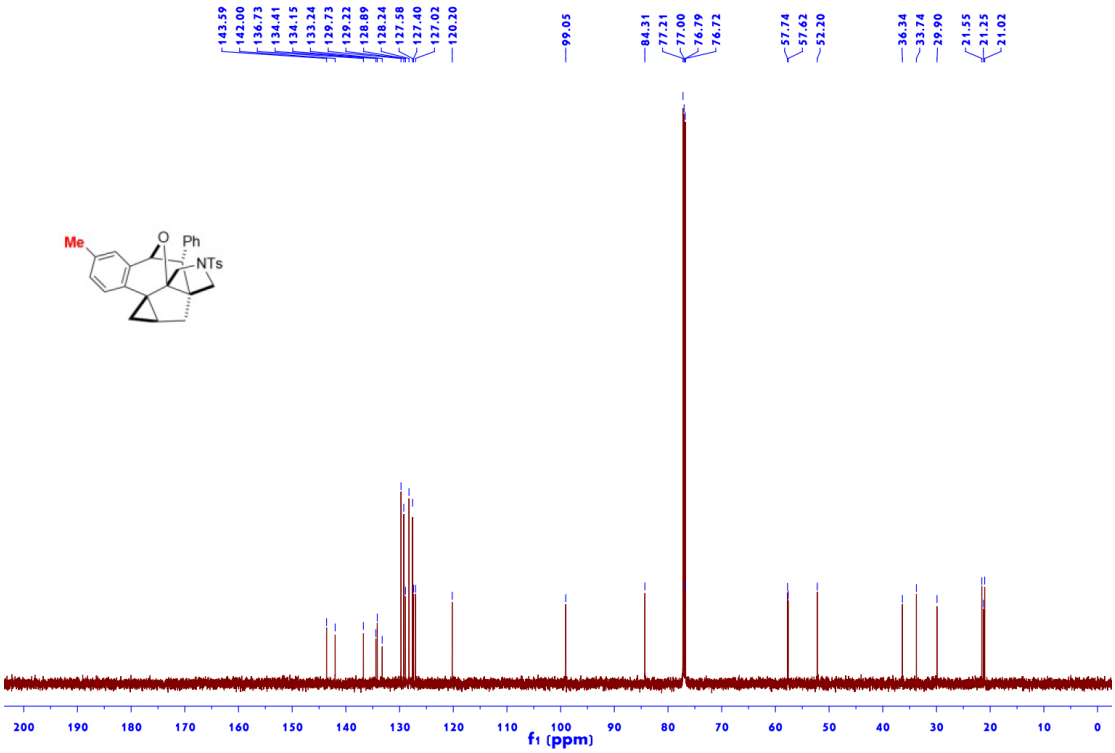


Figure S111 ^{1}H NMR (600 MHz, $CDCl_3$) of 2u

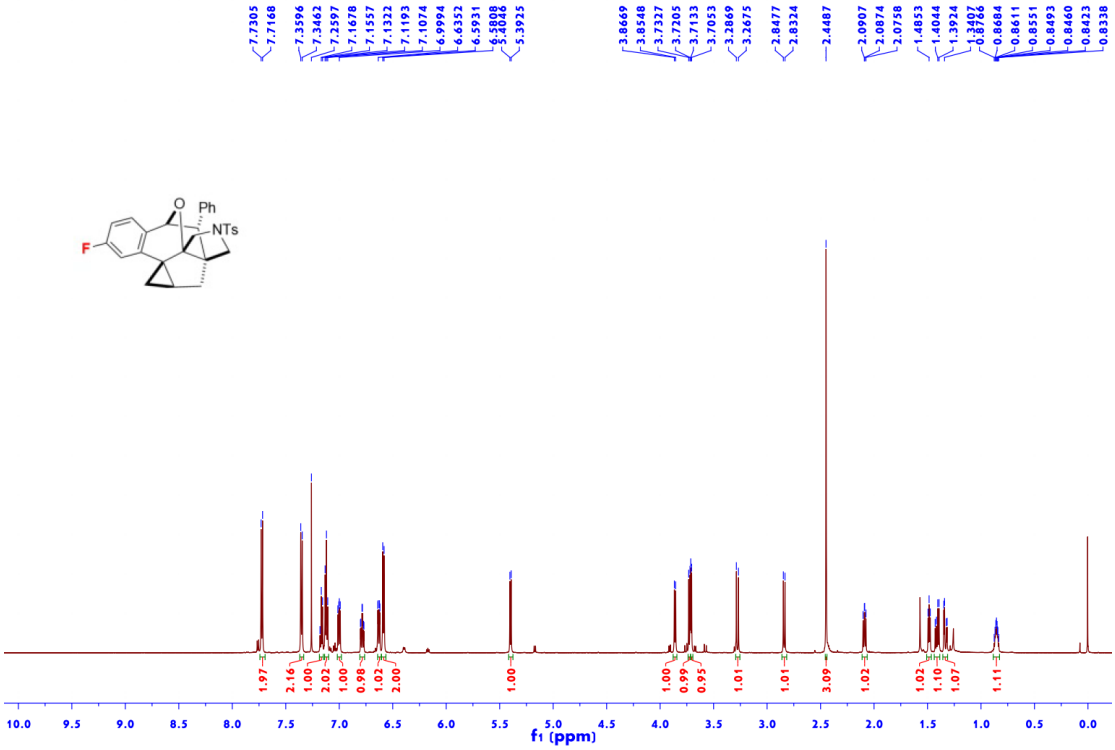


Figure S112 ^{13}C NMR (150 MHz, $CDCl_3$) of 2u

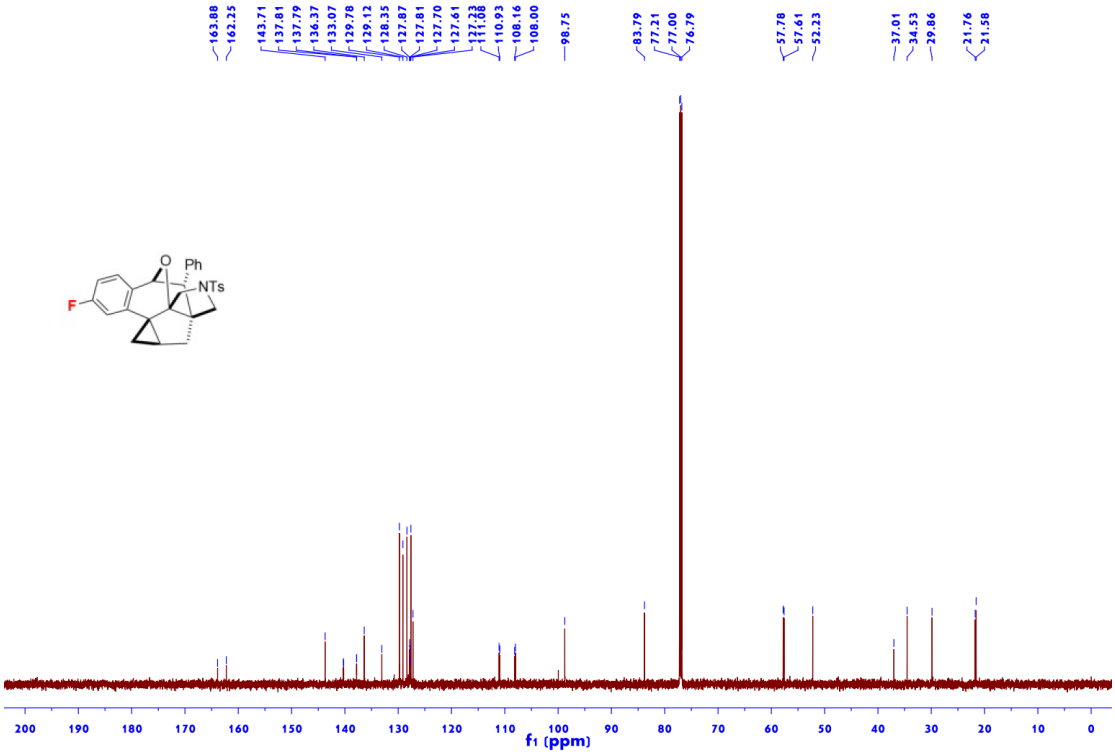


Figure S113 ^{19}F NMR (565 MHz, $CDCl_3$) of 2u

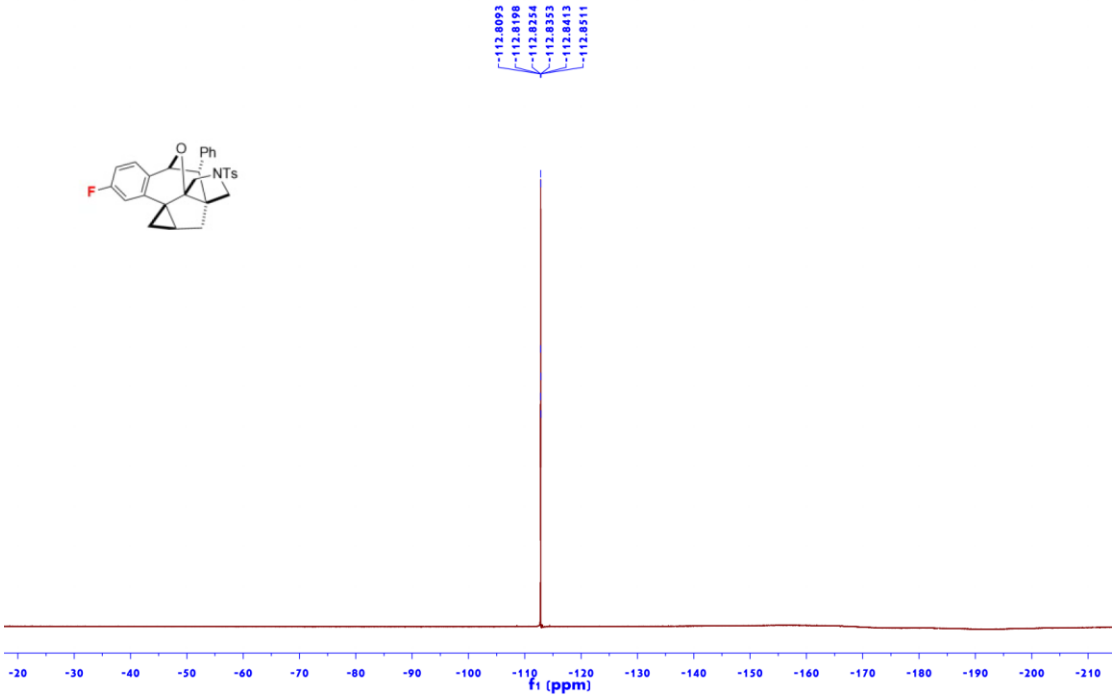


Figure S114 ^{1}H NMR (600 MHz, $CDCl_3$) of 2v

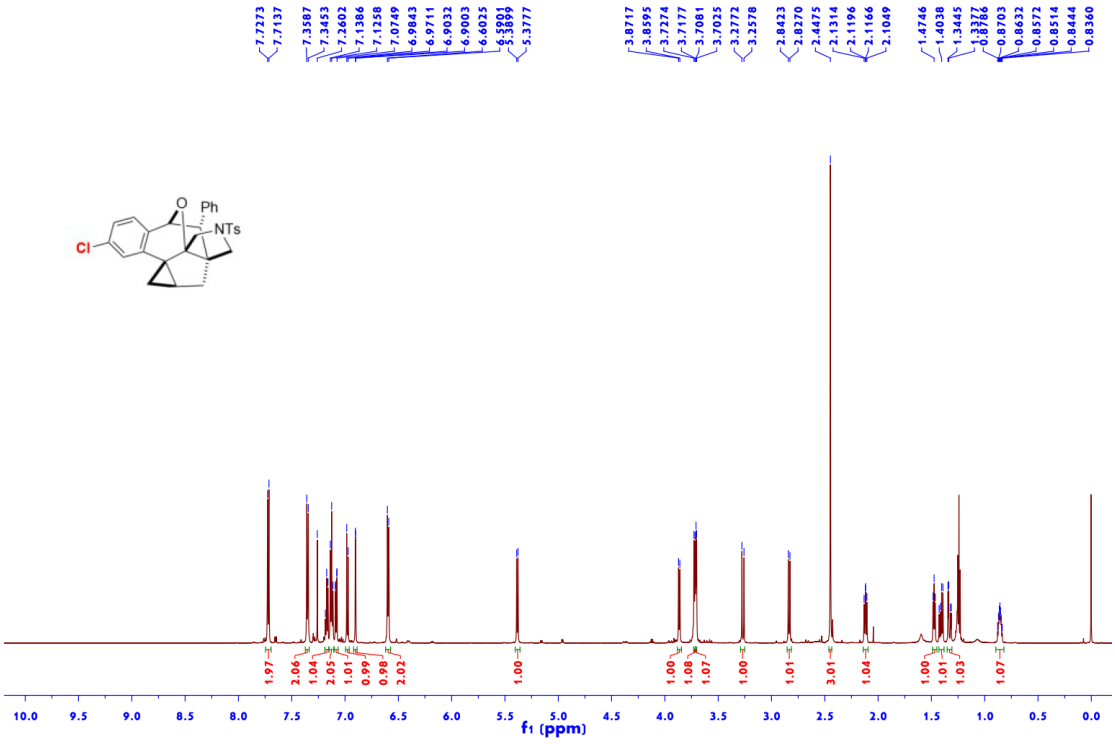


Figure S115 ^{13}C NMR (150 MHz, $CDCl_3$) of 2v

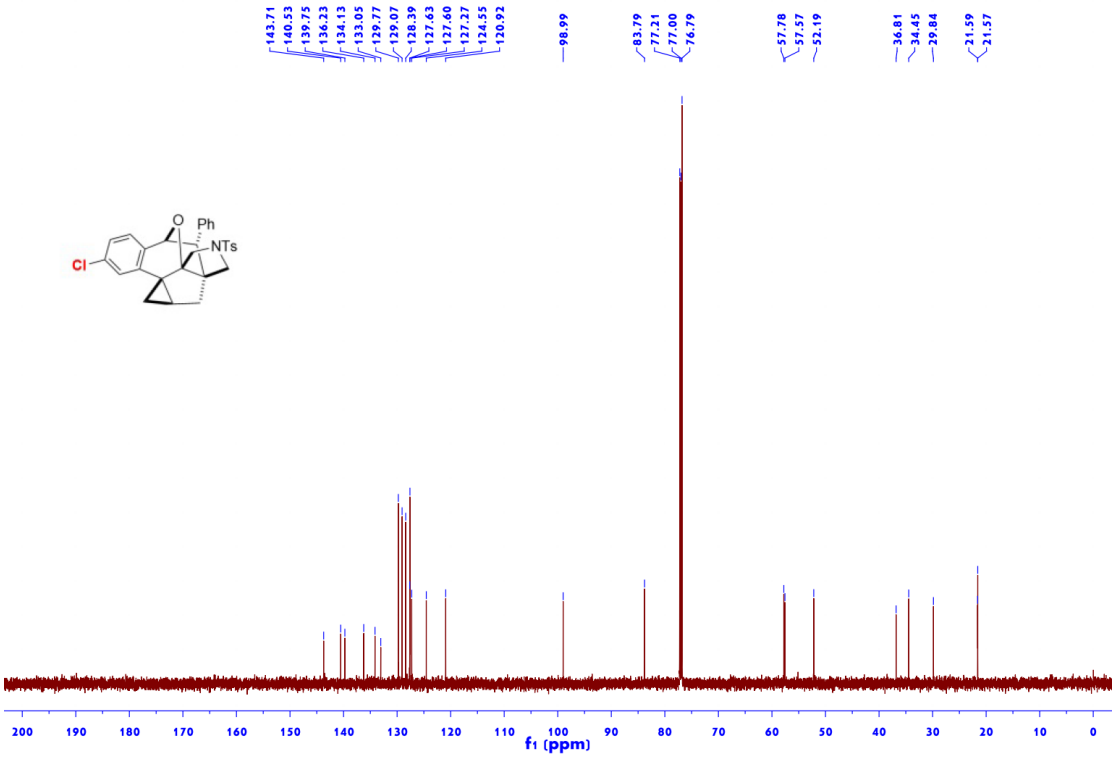


Figure S116 ^{1}H NMR (600 MHz, $CDCl_3$) of 2w

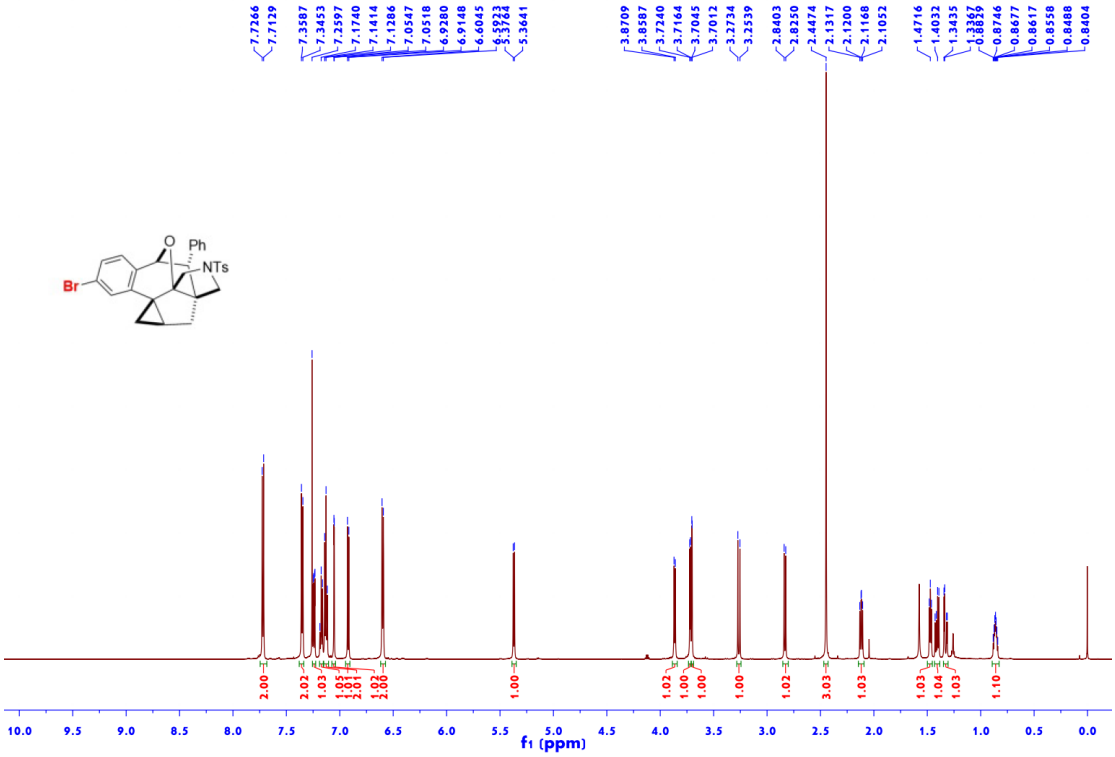


Figure S117 ^{13}C NMR (150 MHz, $CDCl_3$) of 2w

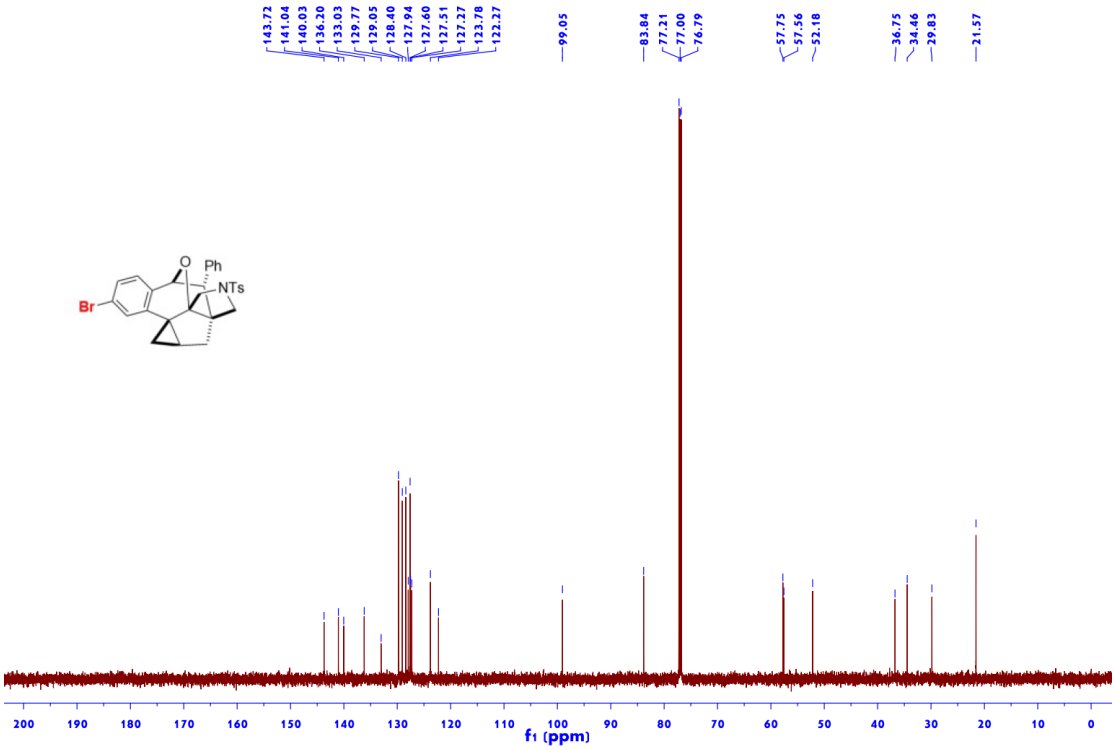


Figure S118 ^{1}H NMR (600 MHz, $CDCl_3$) of 2x

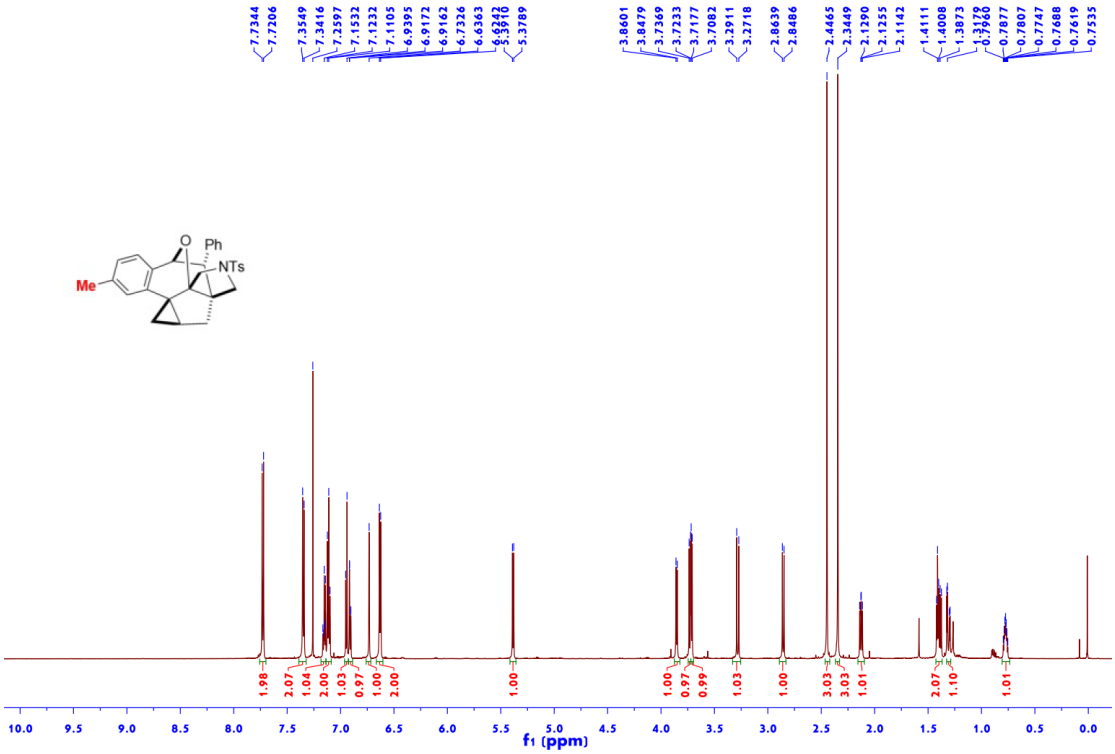


Figure S119 ^{13}C NMR (150 MHz, $CDCl_3$) of 2x

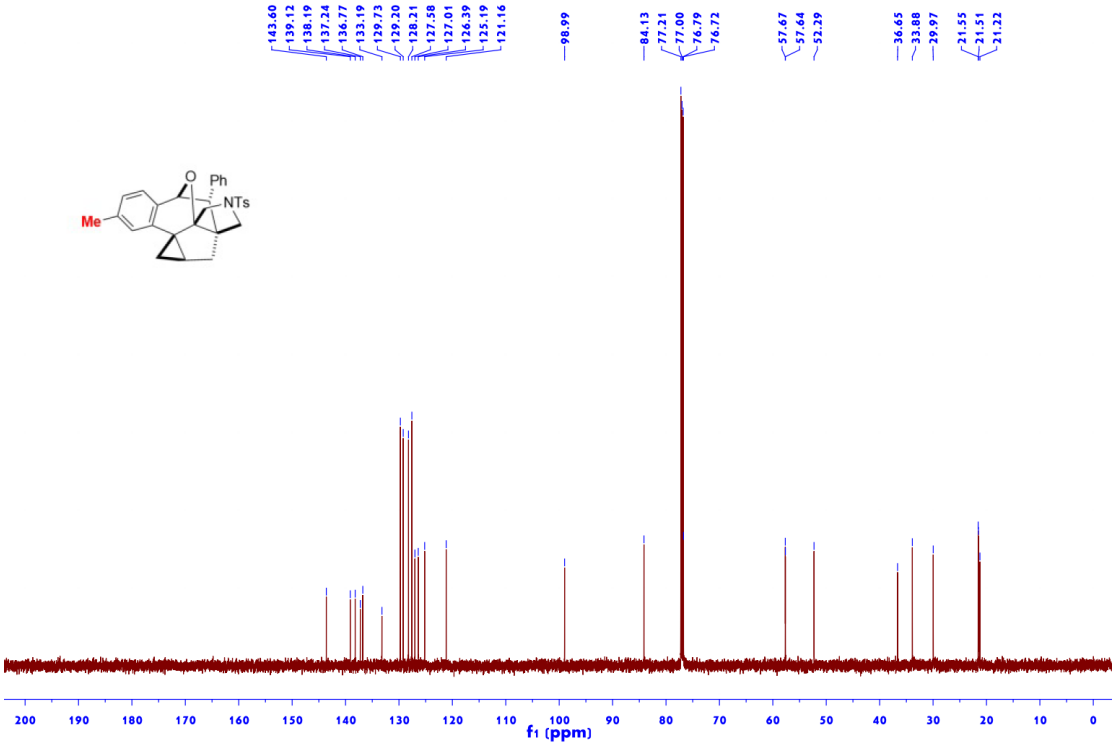


Figure S120 ^{1}H NMR (600 MHz, $CDCl_3$) of 2y

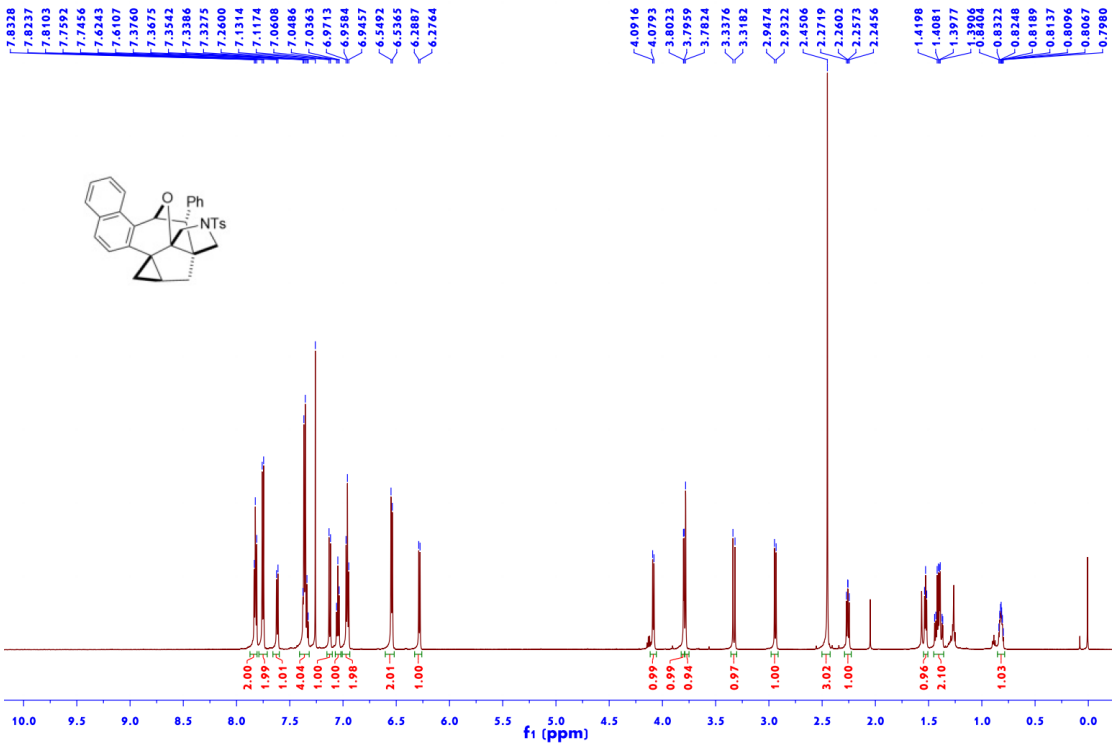


Figure S121 ^{13}C NMR (150 MHz, $CDCl_3$) of 2y

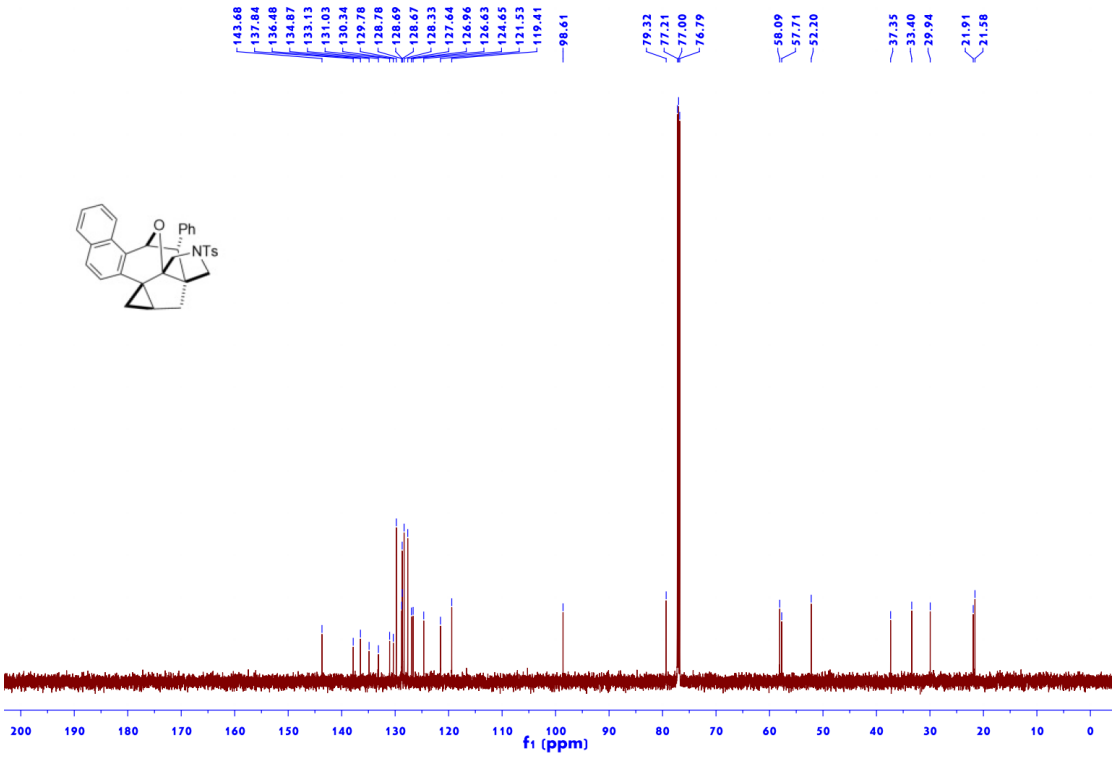


Figure S122 ^{1}H NMR (600 MHz, $CDCl_3$) of 2z

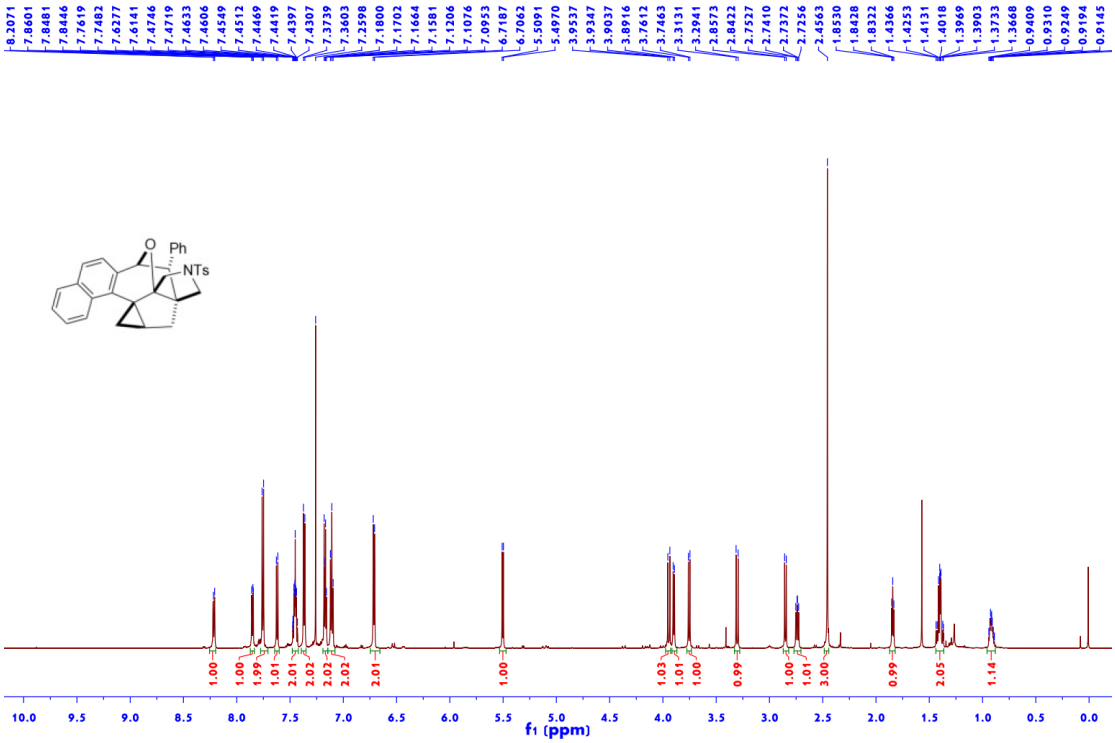


Figure S123 ^{13}C NMR (150 MHz, $CDCl_3$) of 2z

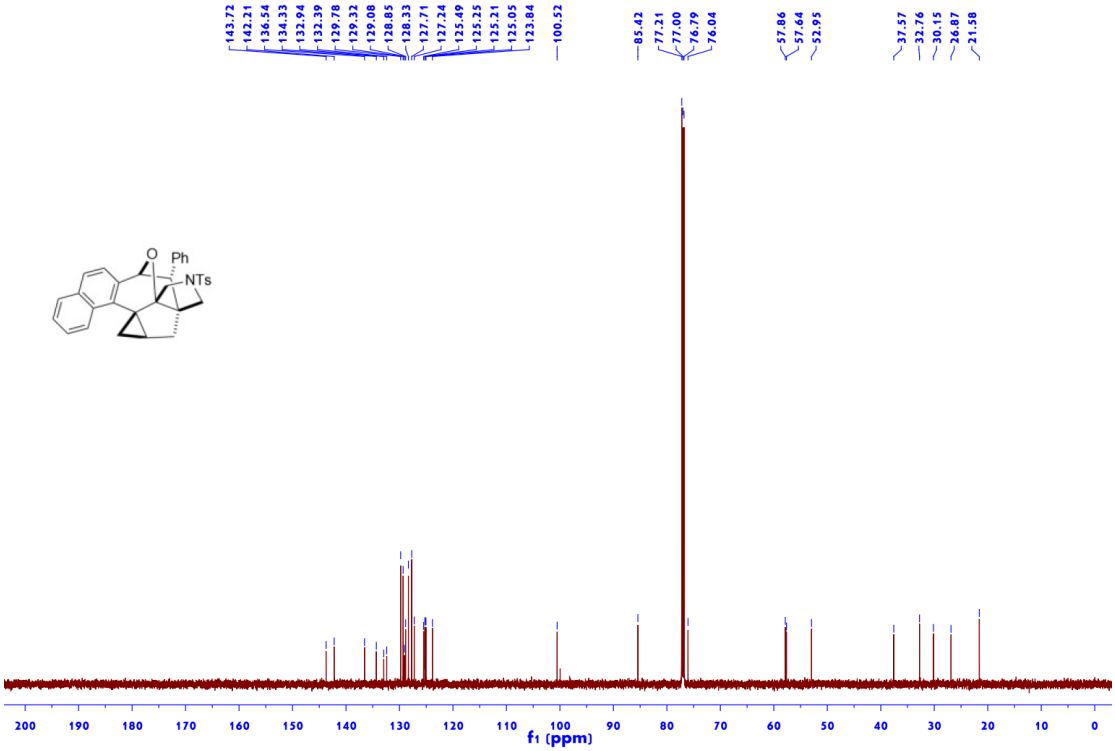


Figure S124 ^{1}H NMR (600 MHz, $CDCl_3$) of 2aa

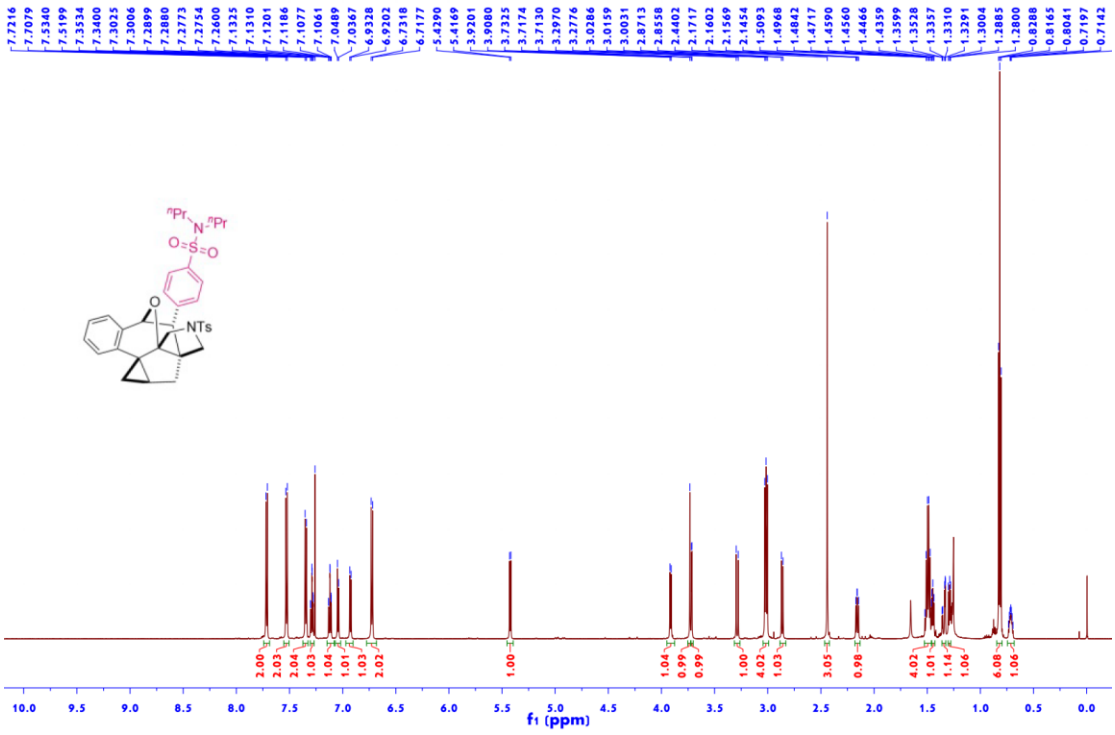


Figure S125 ^{13}C NMR (150 MHz, $CDCl_3$) of 2aa

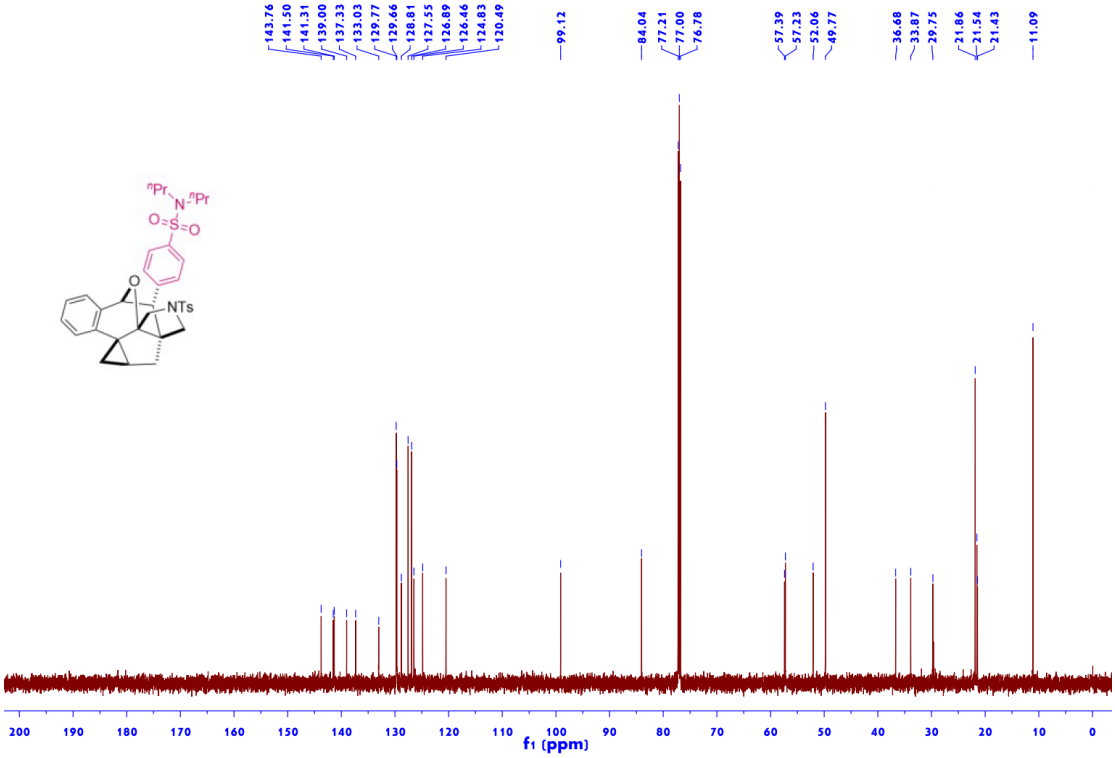


Figure S126 ^{1}H NMR (400 MHz, $CDCl_3$) of 2ab

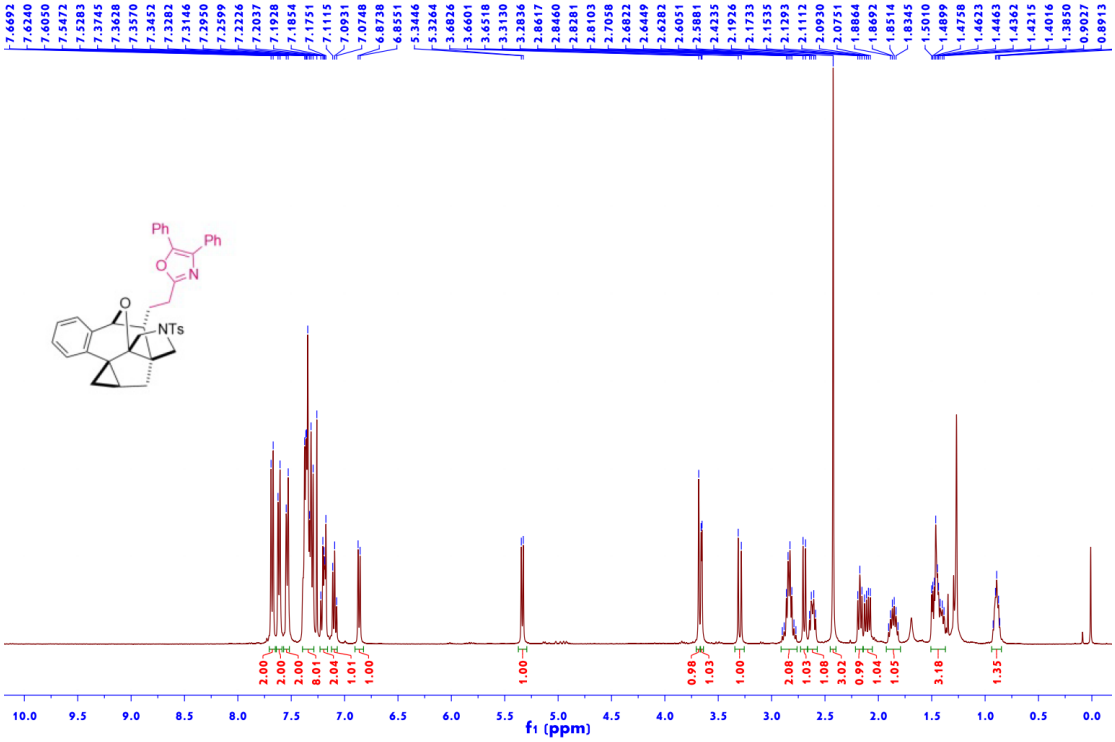


Figure S127 ^{13}C NMR (100 MHz, $CDCl_3$) of 2ab

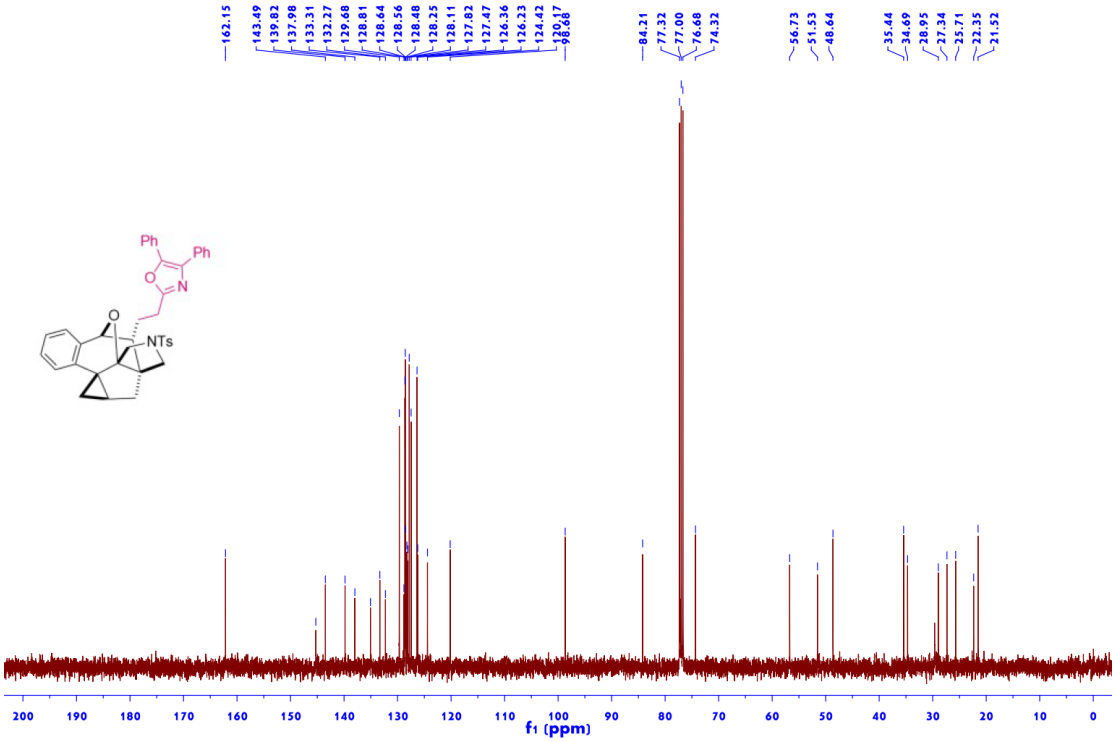


Figure S128 ^{1}H NMR (600 MHz, $CDCl_3$) of 2ac

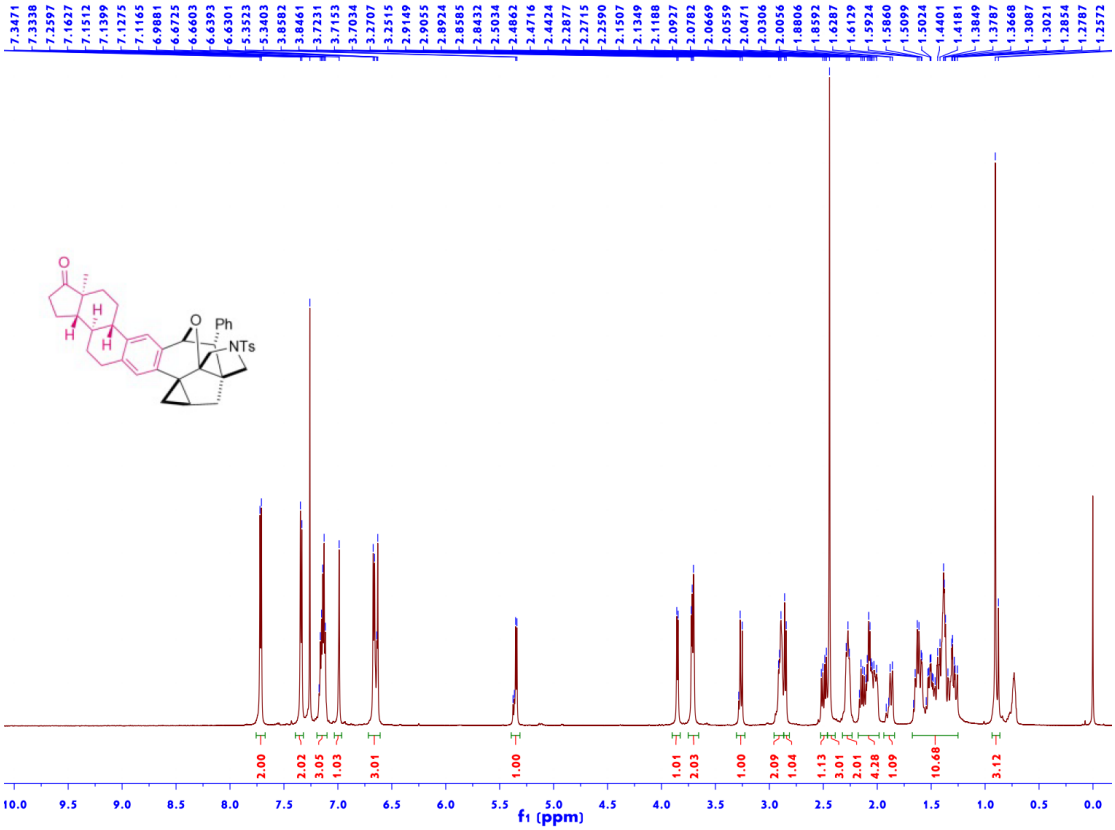


Figure S129 ^{13}C NMR (150 MHz, $CDCl_3$) of 2ac

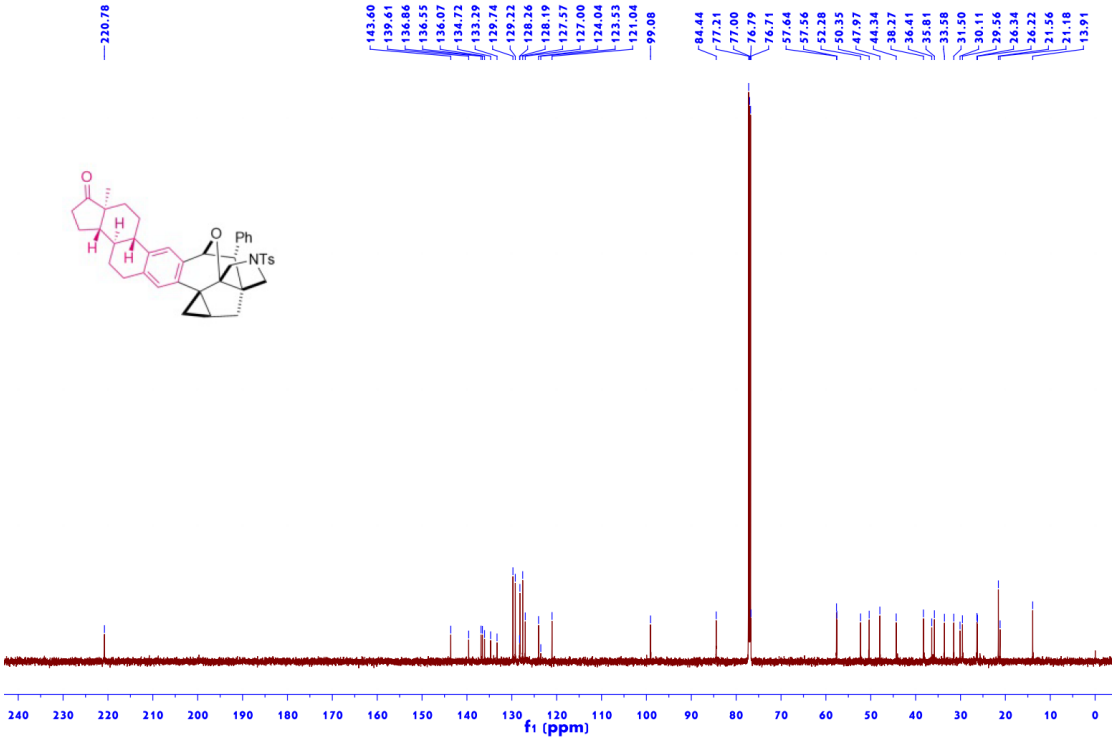


Figure S130 ^{1}H NMR (600 MHz, $CDCl_3$) of 2ad

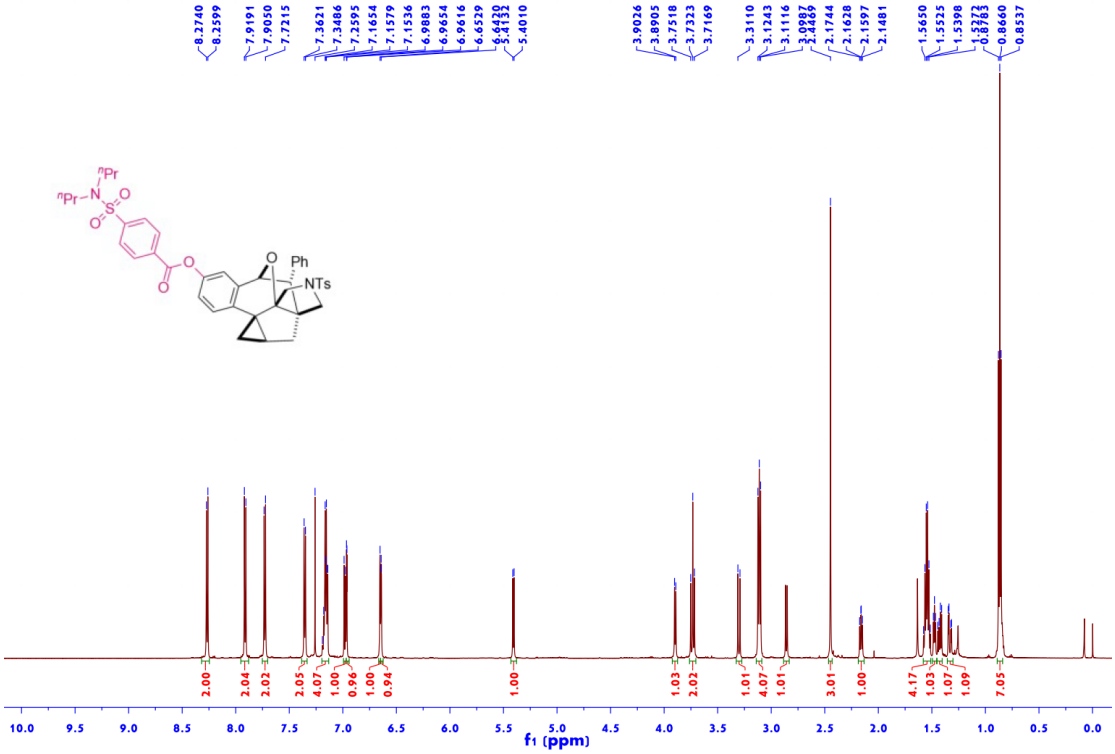


Figure S131 ^{13}C NMR (150 MHz, $CDCl_3$) of 2ad

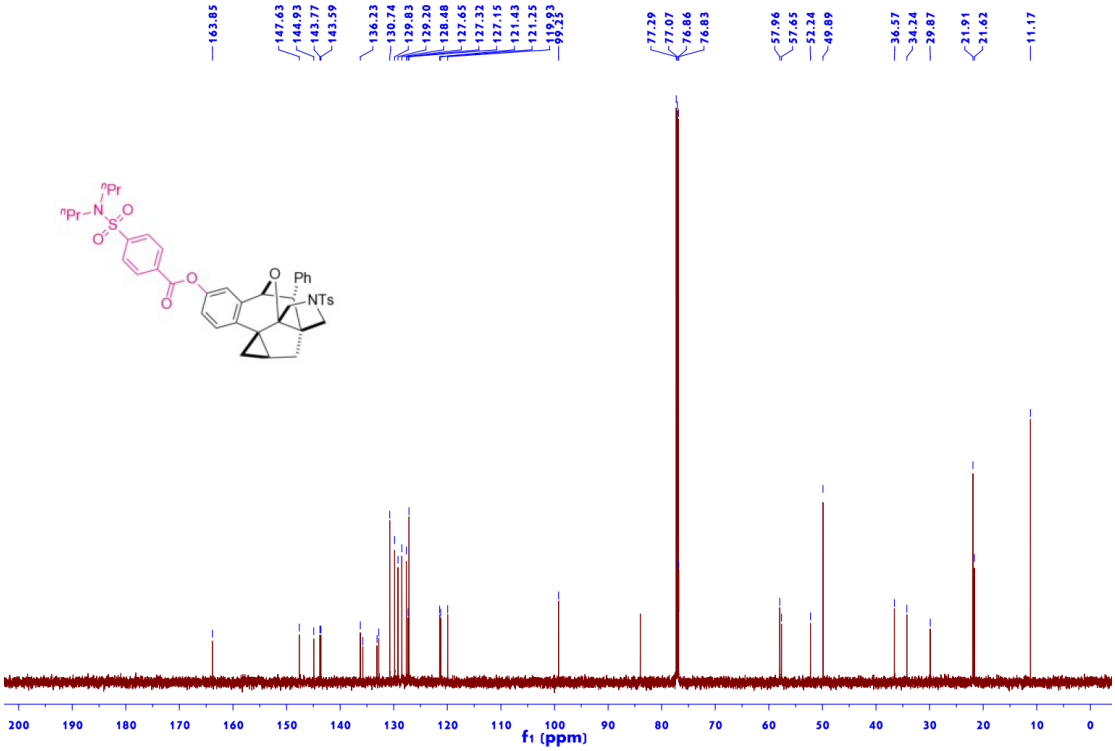


Figure S132 ^{1}H NMR (600 MHz, $CDCl_3$) of 2ae

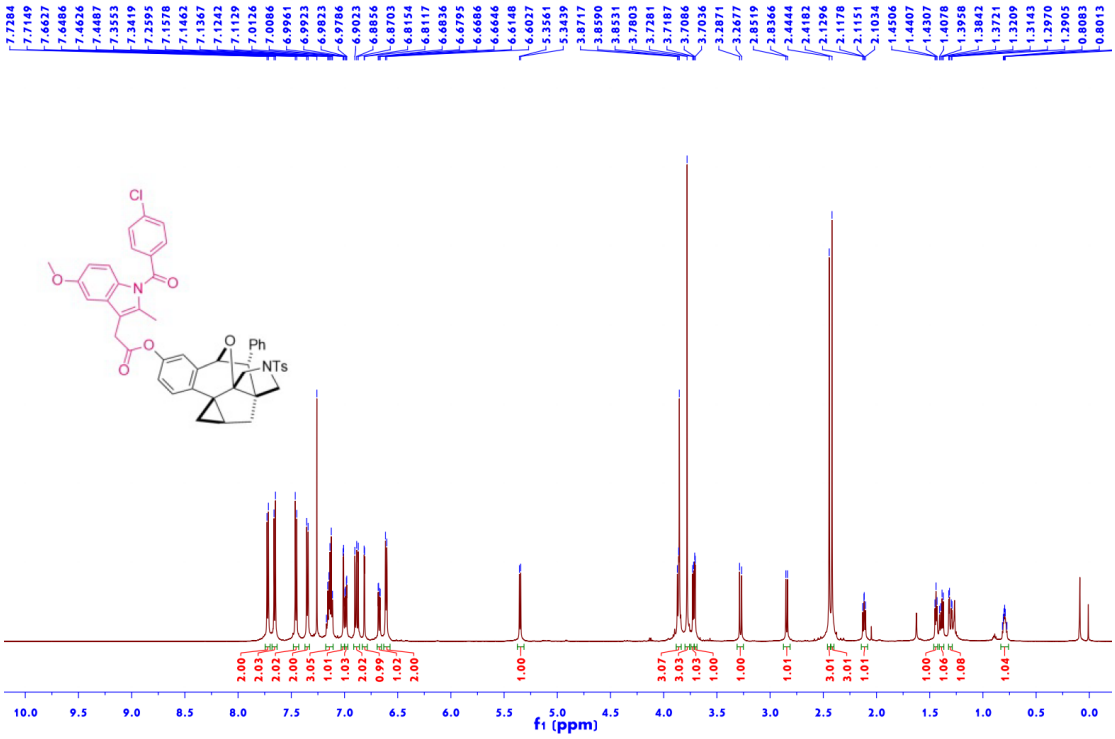


Figure S133 ^{13}C NMR (150 MHz, $CDCl_3$) of 2ae

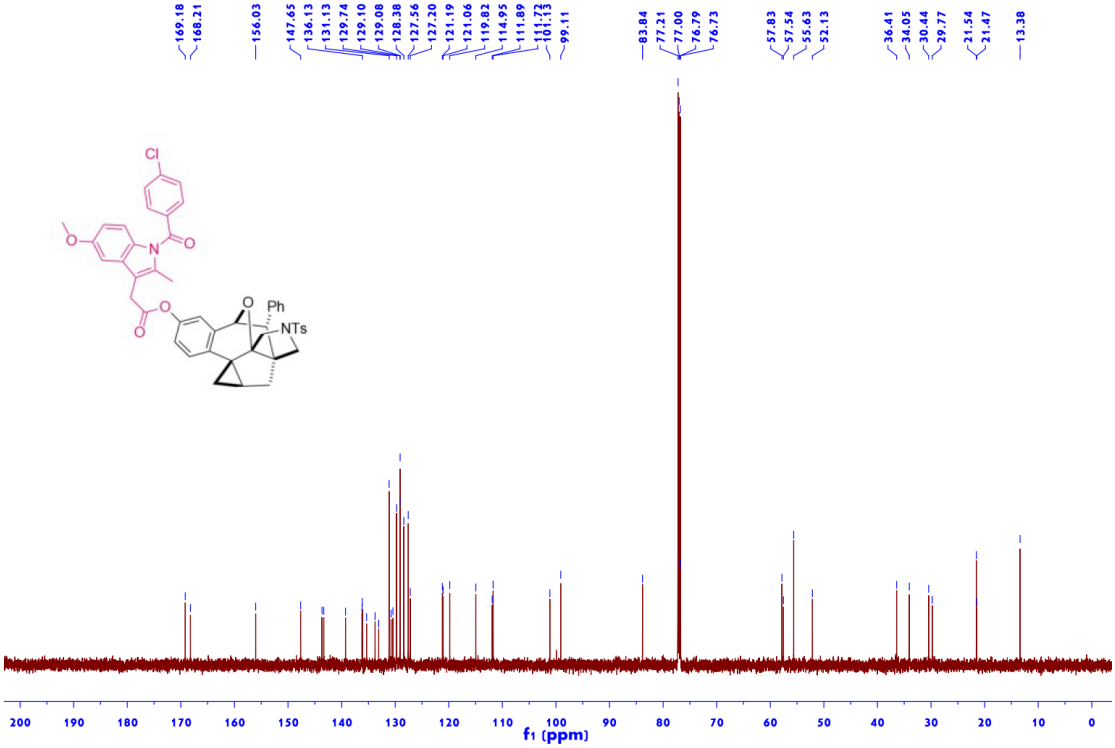


Figure S134 ^{1}H NMR (600 MHz, $CDCl_3$) of 2af and 3af

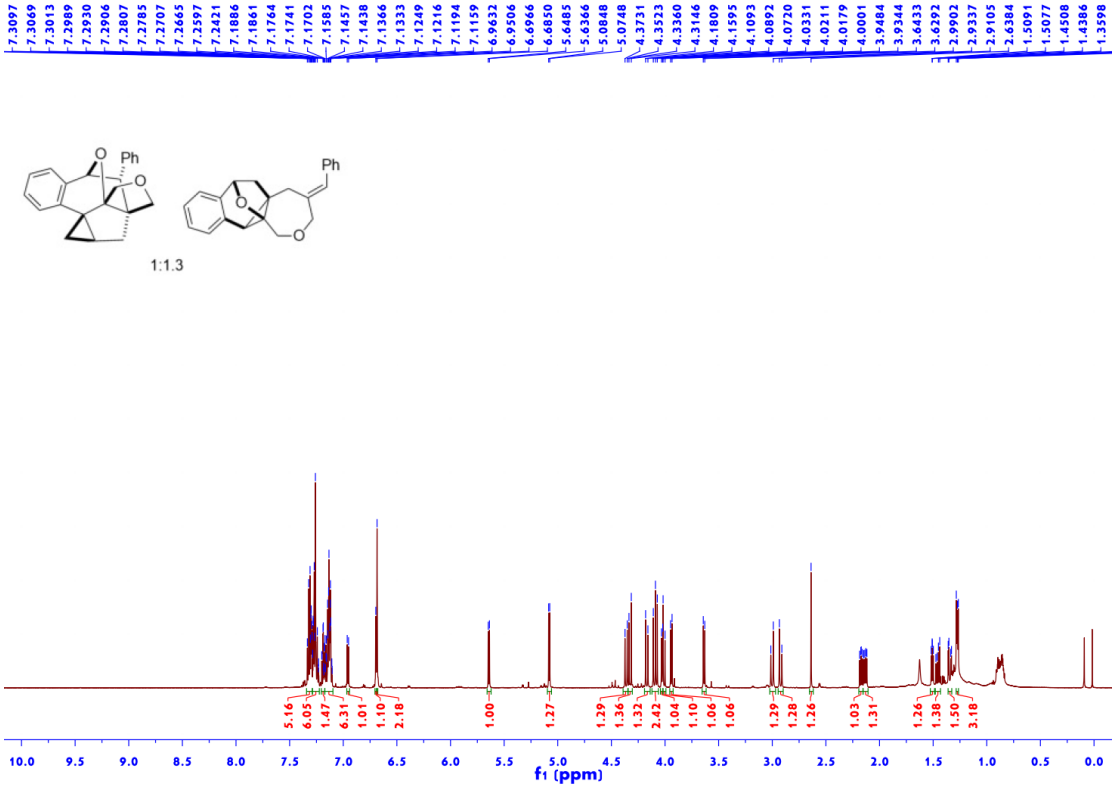


Figure S135 ^{13}C NMR (150 MHz, $CDCl_3$) of 2af and 3af

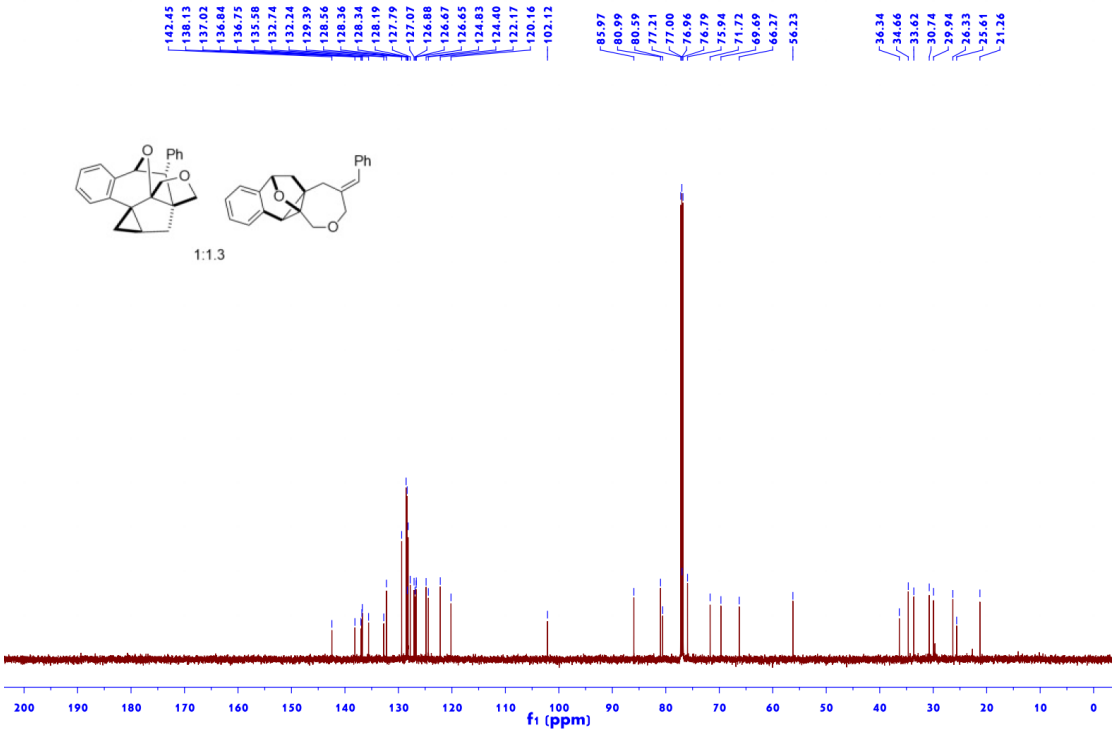


Figure S136 ^{1}H NMR (600 MHz, $CDCl_3$) of 3a

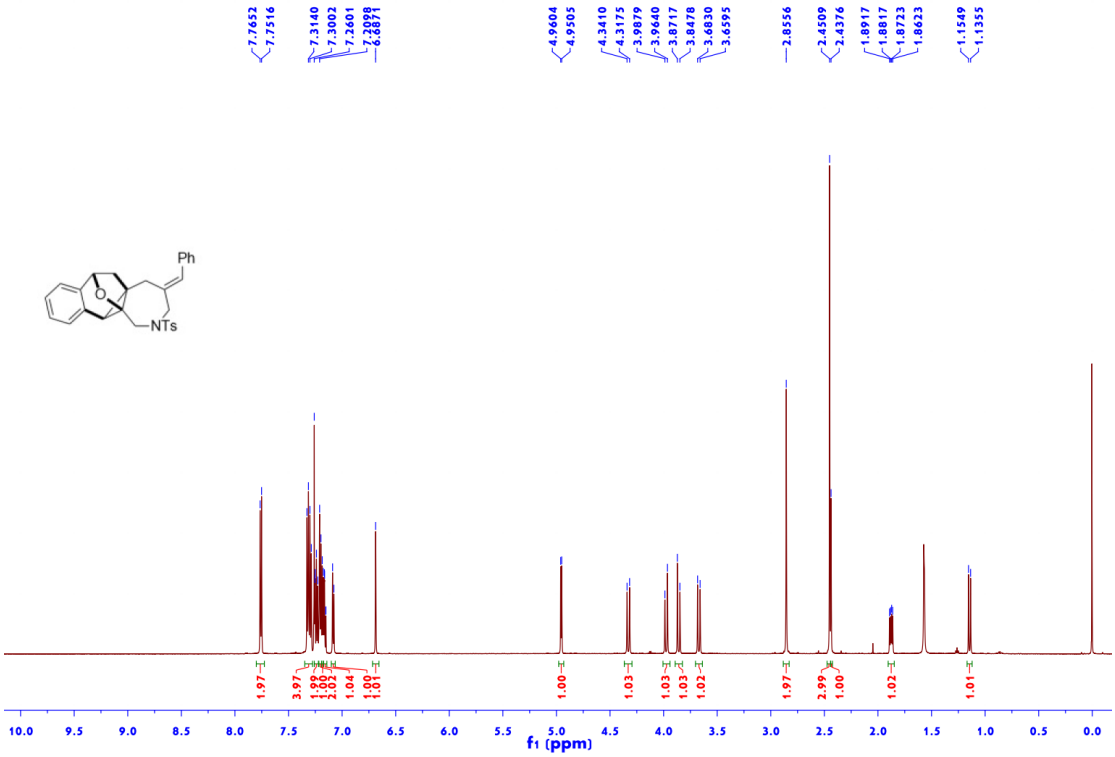


Figure S137 ^{13}C NMR (150 MHz, $CDCl_3$) of 3a

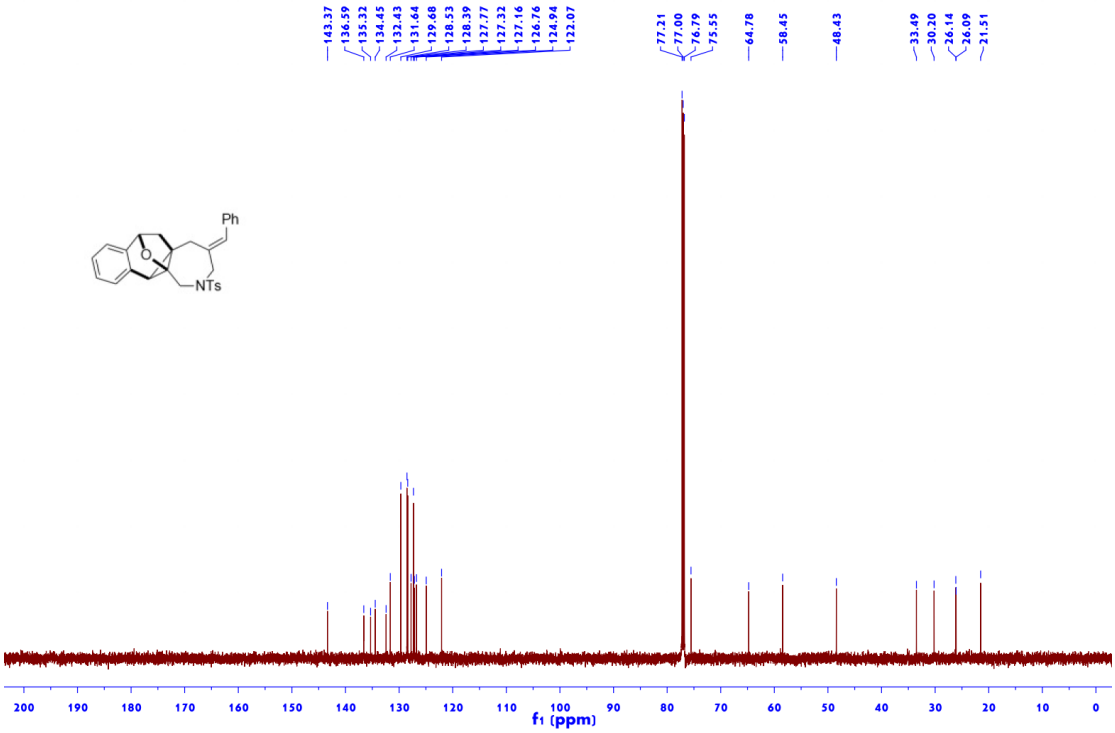


Figure S138 ^{1}H NMR (600 MHz, $CDCl_3$) of 3b

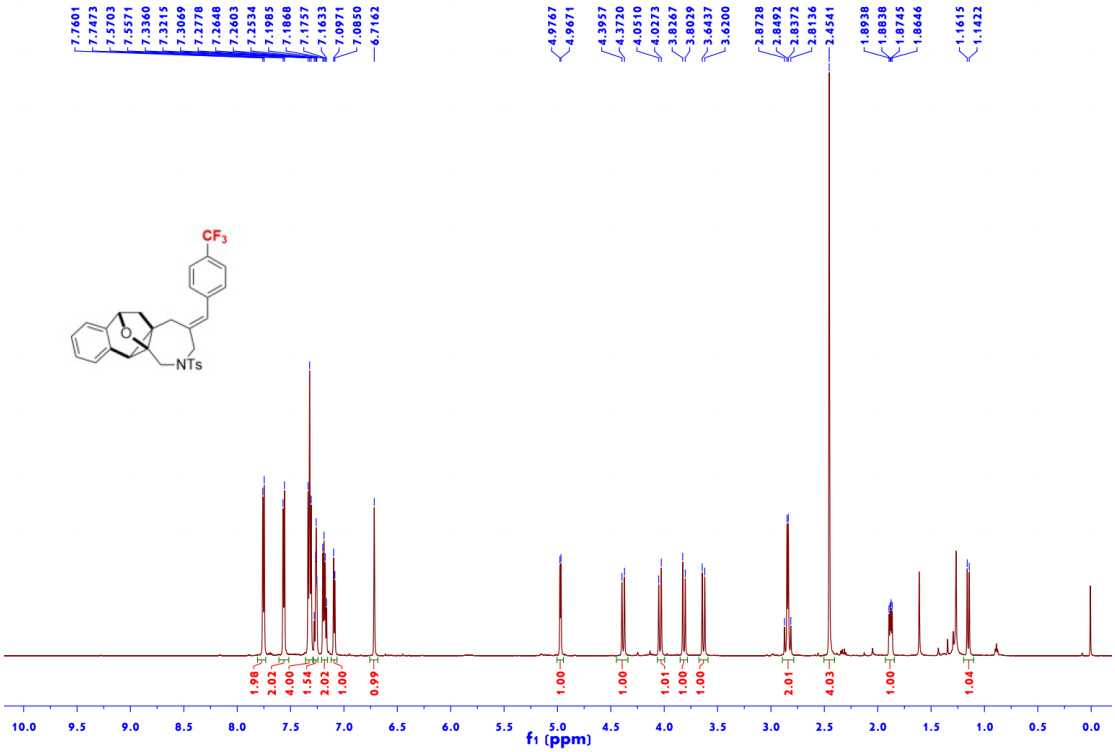


Figure S139 ^{13}C NMR (150 MHz, $CDCl_3$) of 3b

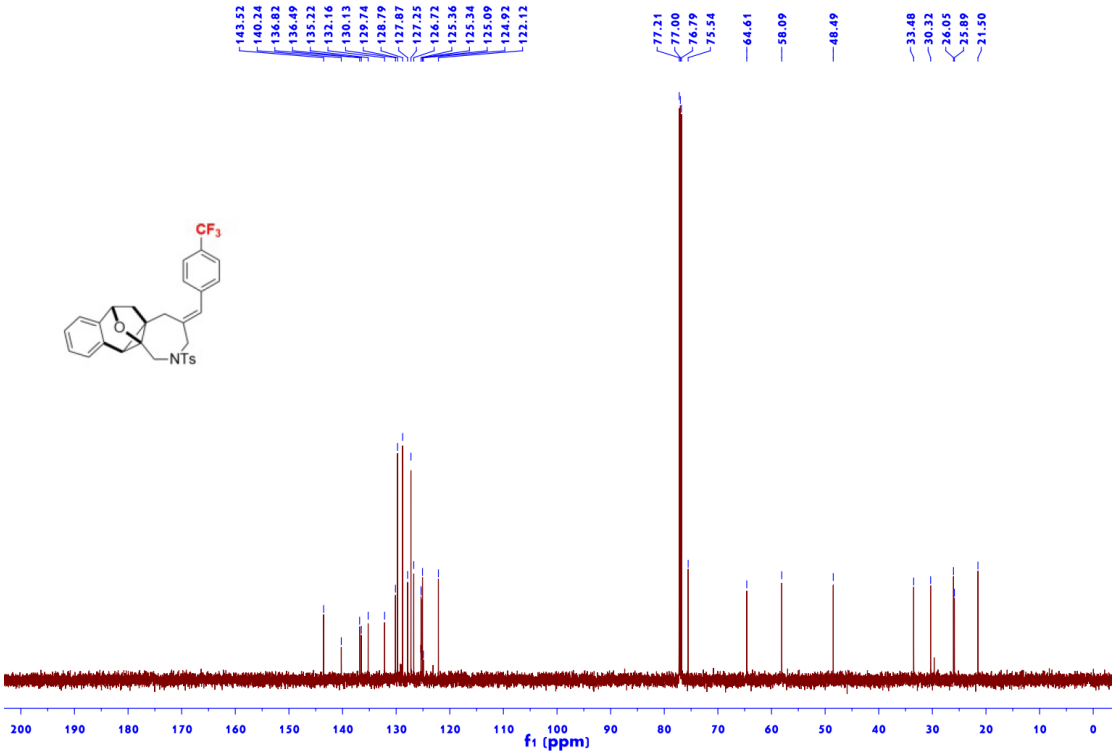


Figure S140 ^{19}F NMR (565 MHz, $CDCl_3$) of 3b

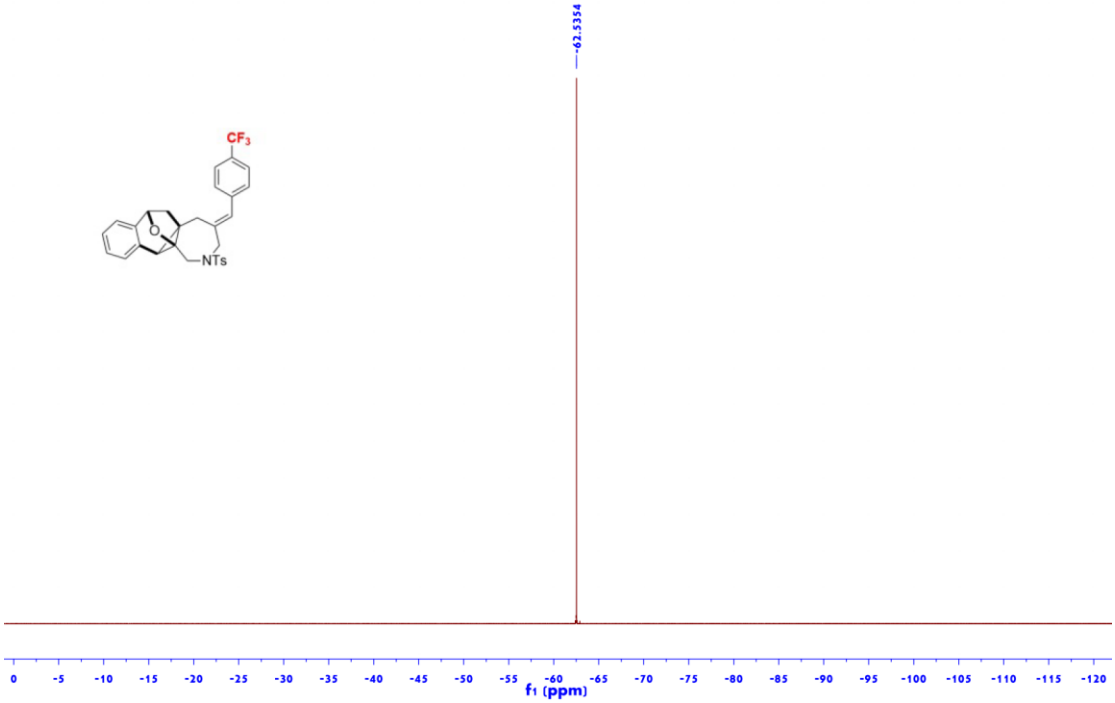


Figure S141 ^{1}H NMR (600 MHz, $CDCl_3$) of 3c

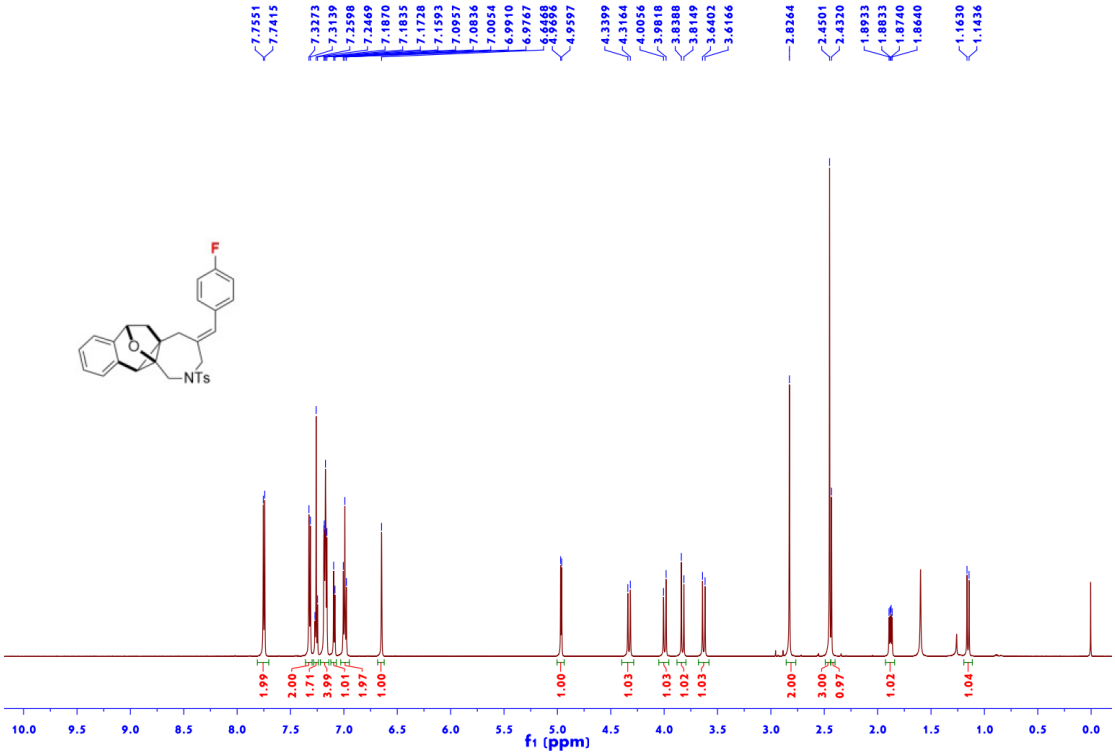


Figure S142 ^{13}C NMR (150 MHz, $CDCl_3$) of 3c

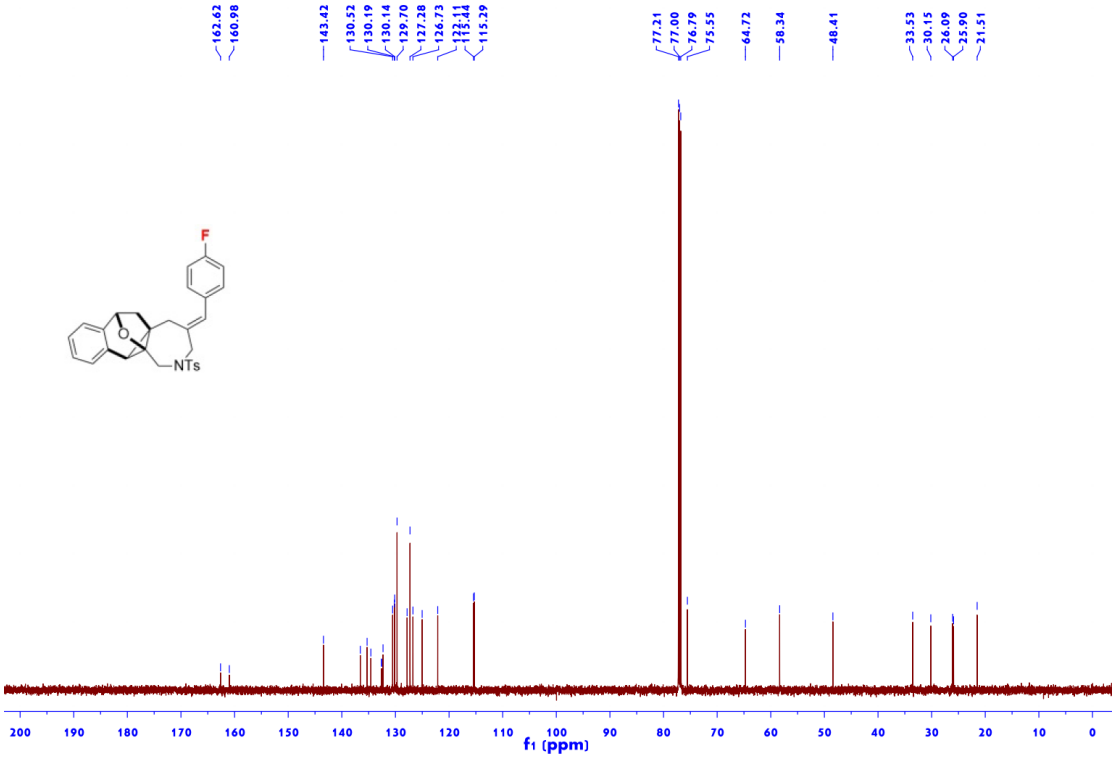


Figure S143 ^{1}H NMR (600 MHz, $CDCl_3$) of 3d

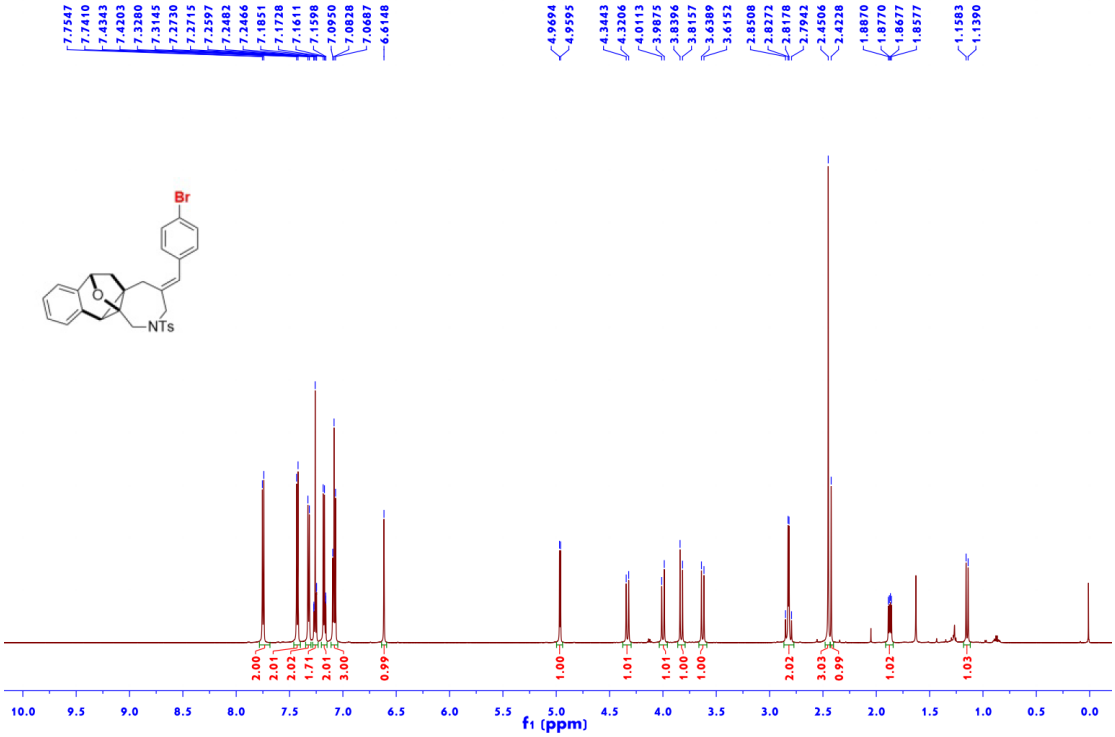


Figure S144 ^{13}C NMR (150 MHz, $CDCl_3$) of 3d

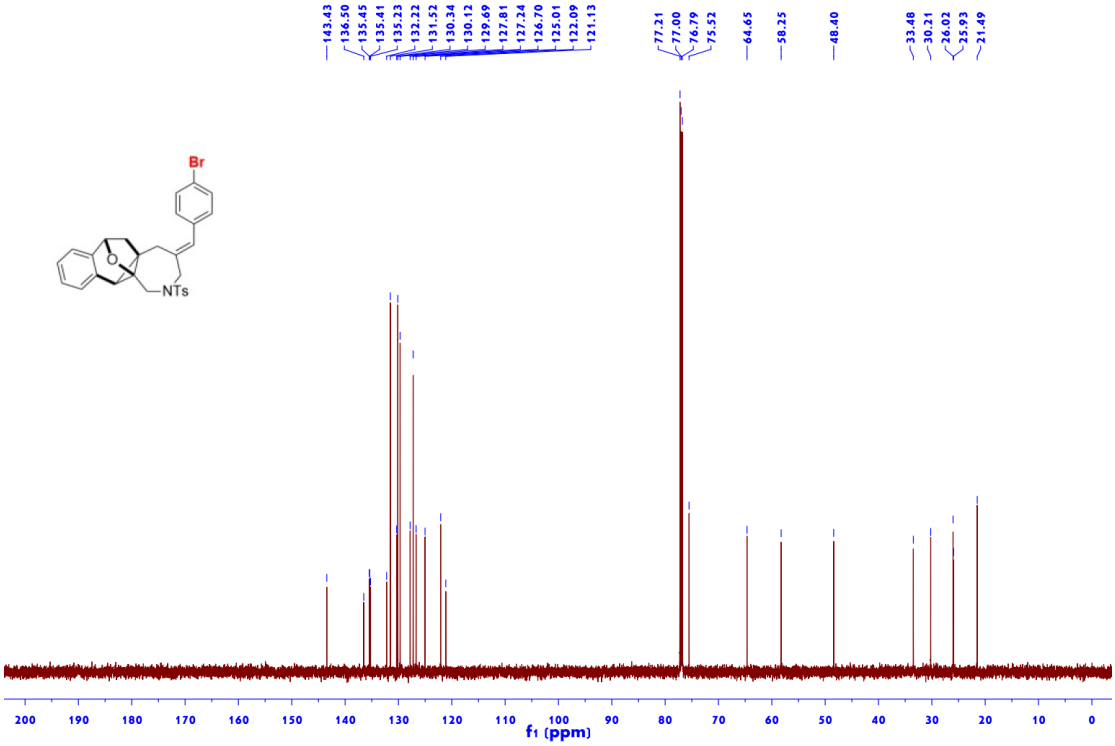


Figure S145 ^{1}H NMR (600 MHz, $CDCl_3$) of 3e

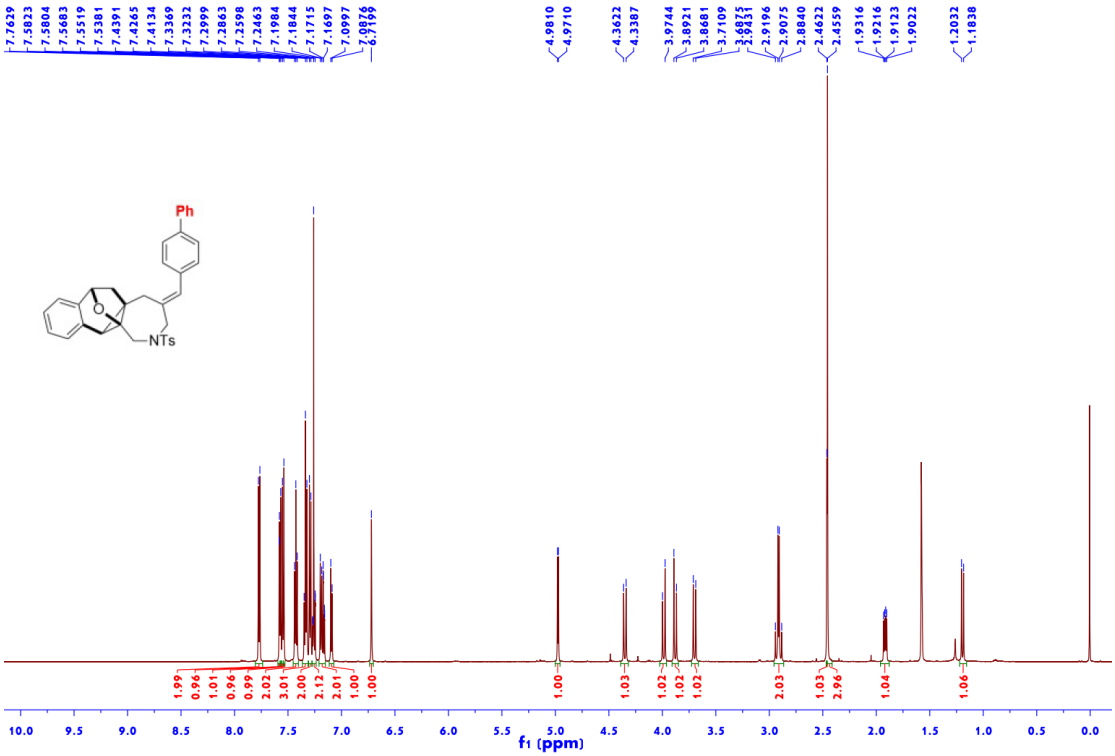


Figure S146 ^{13}C NMR (150 MHz, $CDCl_3$) of 3e

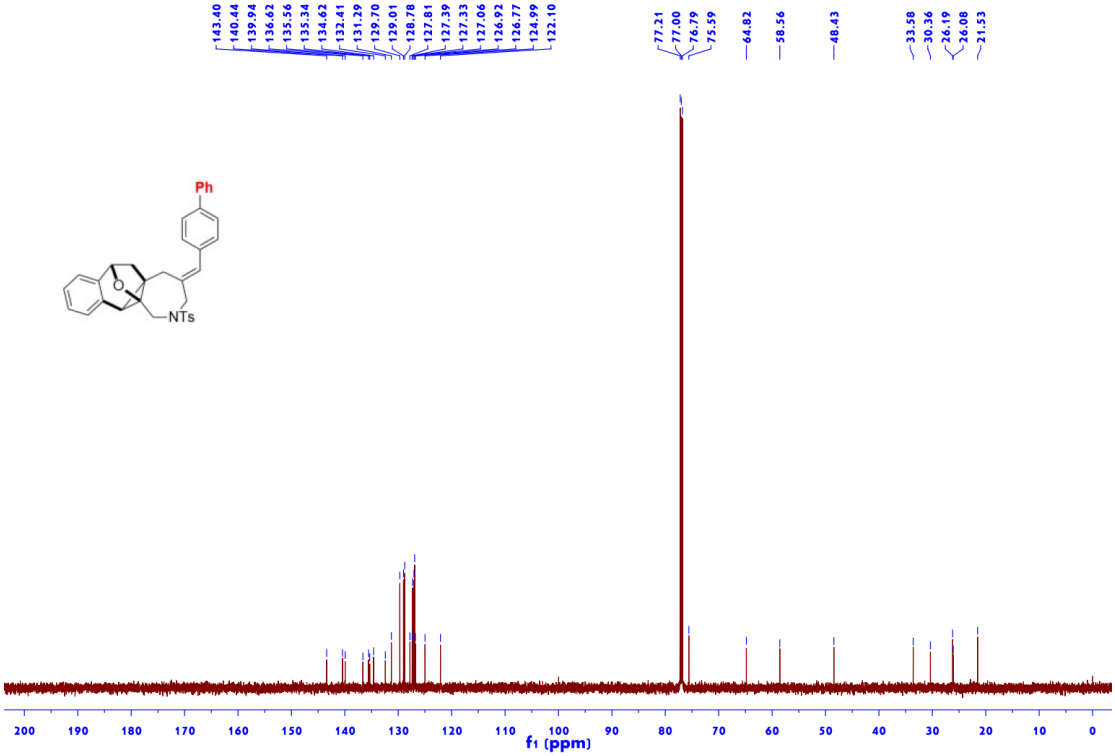


Figure S147 ^{1}H NMR (600 MHz, $CDCl_3$) of 3f

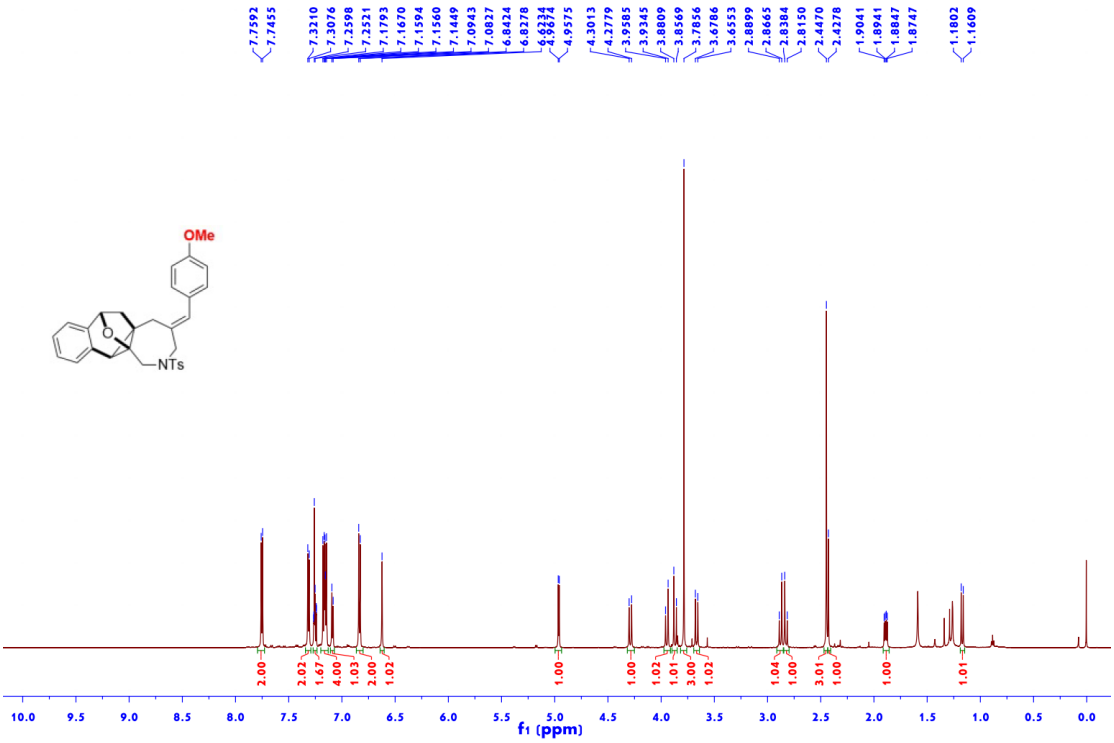


Figure S148 ^{13}C NMR (150 MHz, $CDCl_3$) of 3f

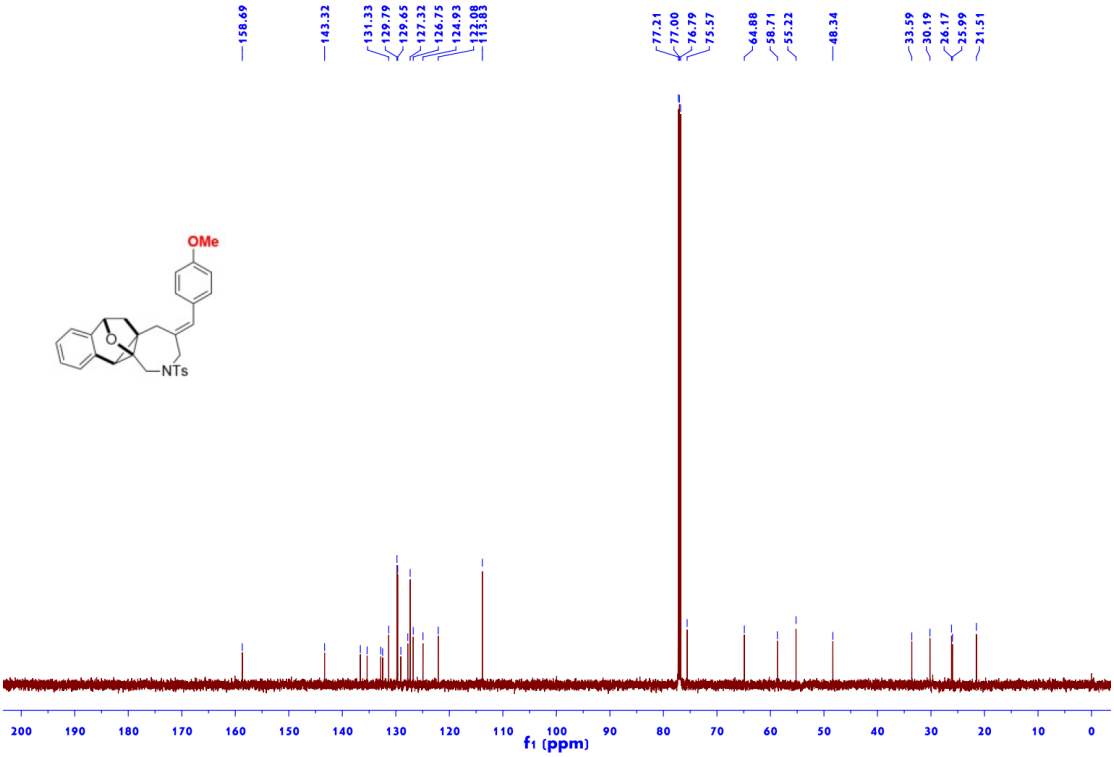


Figure S149 ^{1}H NMR (600 MHz, $CDCl_3$) of 3g

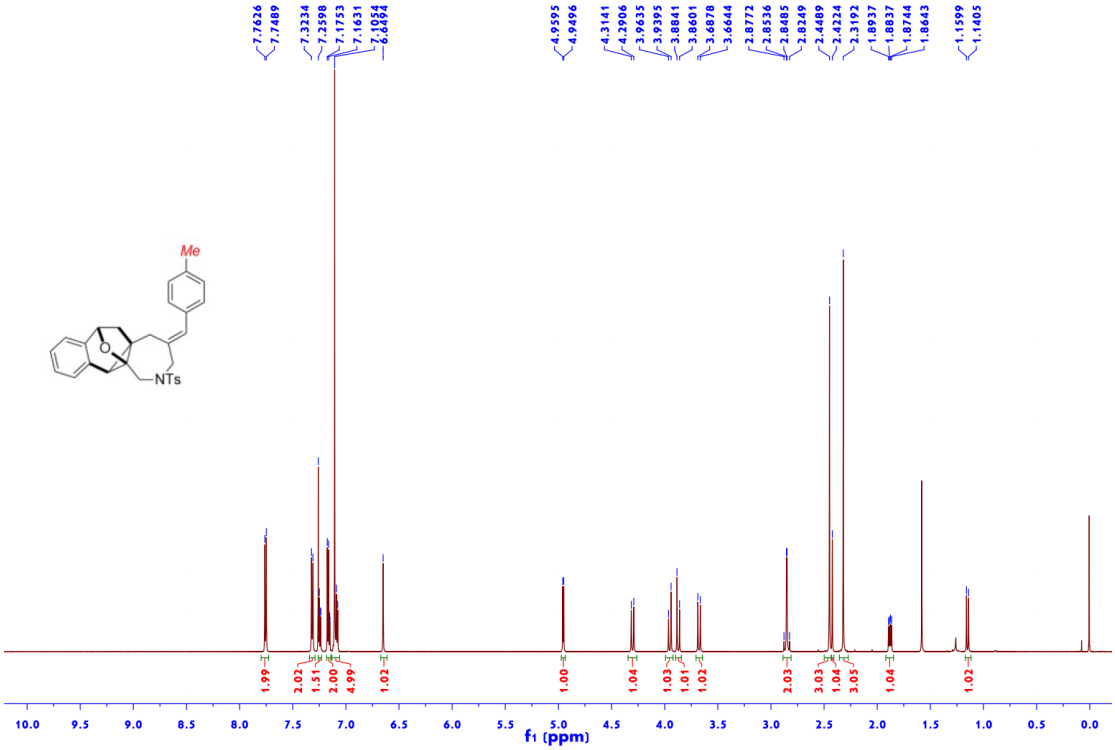


Figure S150 ^{13}C NMR (150 MHz, $CDCl_3$) of 3g

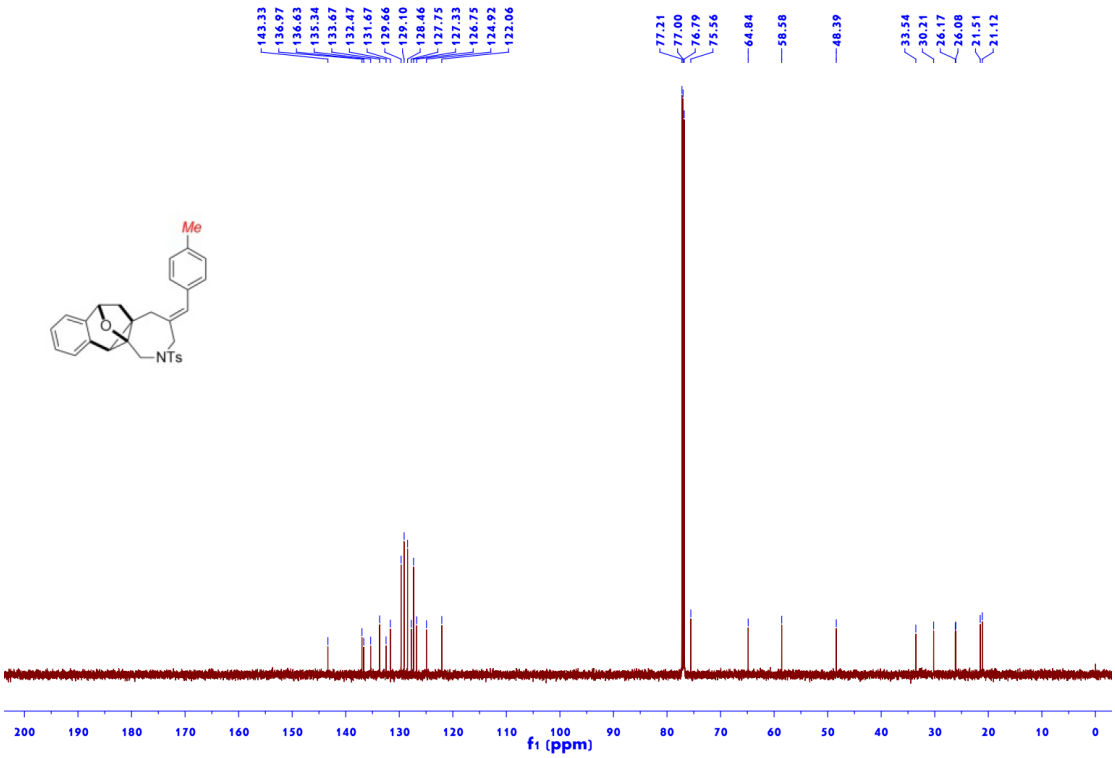


Figure S151 ^{1}H NMR (600 MHz, $CDCl_3$) of 3h

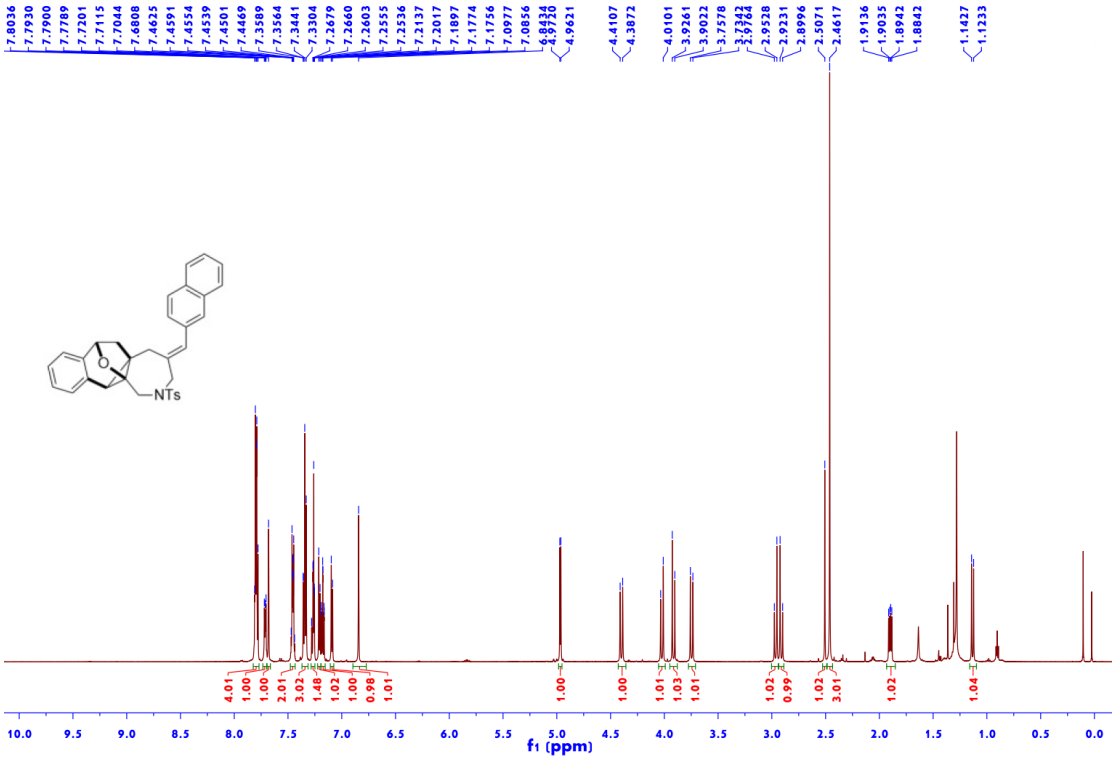


Figure S152 ^{13}C NMR (150 MHz, $CDCl_3$) of 3h

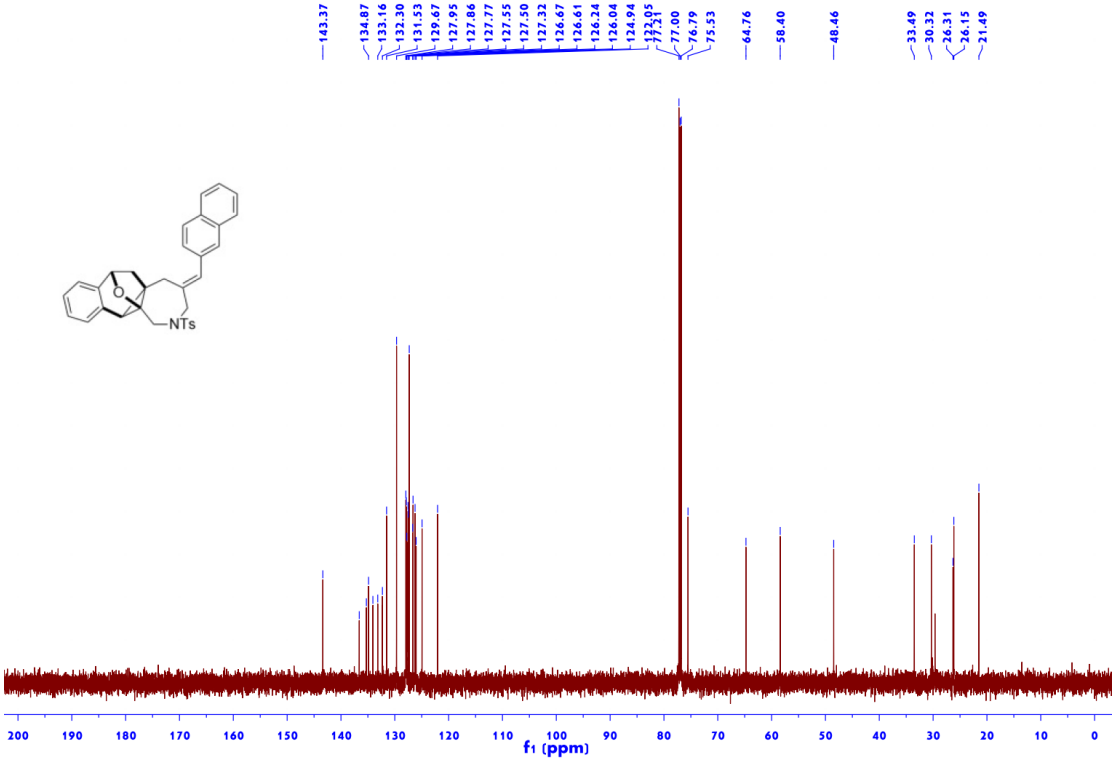


Figure S153 ^{1}H NMR (600 MHz, $CDCl_3$) of 3i

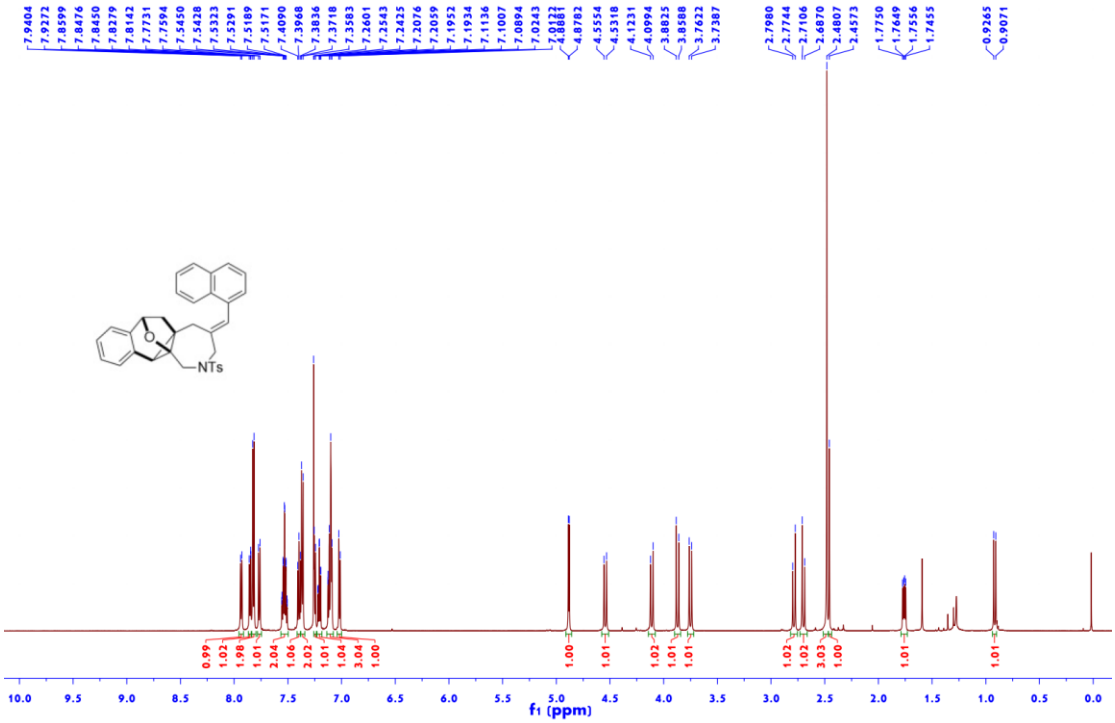


Figure S154 ^{13}C NMR (150 MHz, $CDCl_3$) of 3i

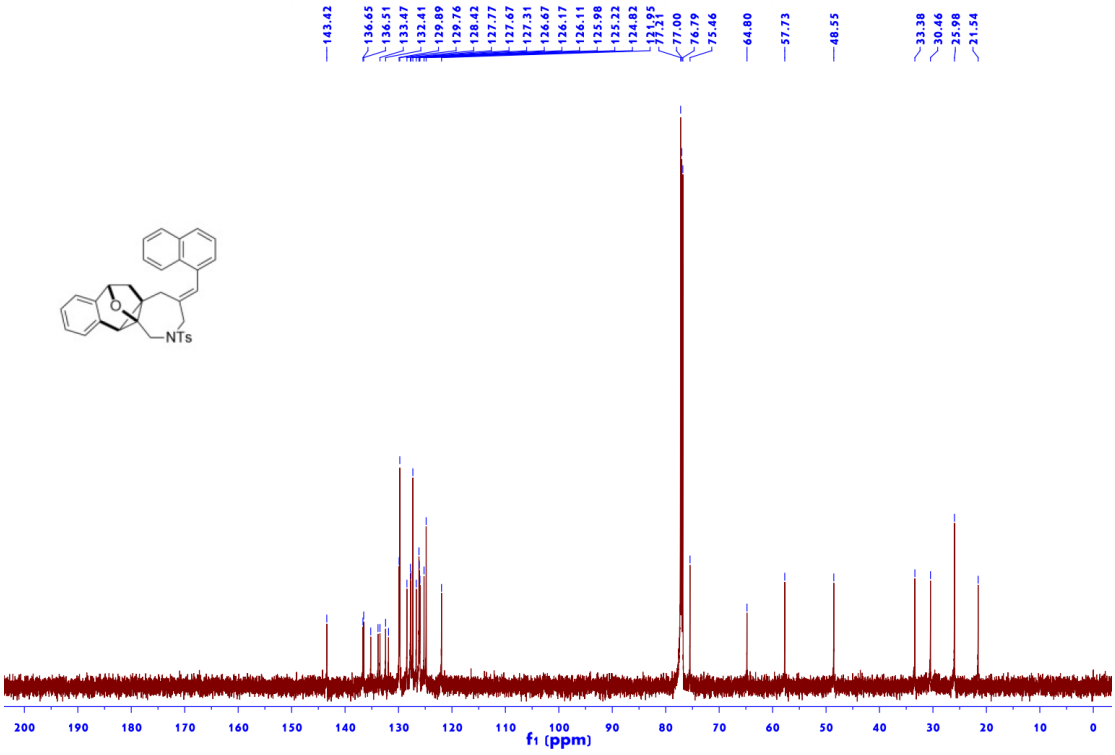


Figure S155 ^{1}H NMR (600 MHz, $CDCl_3$) of 3k

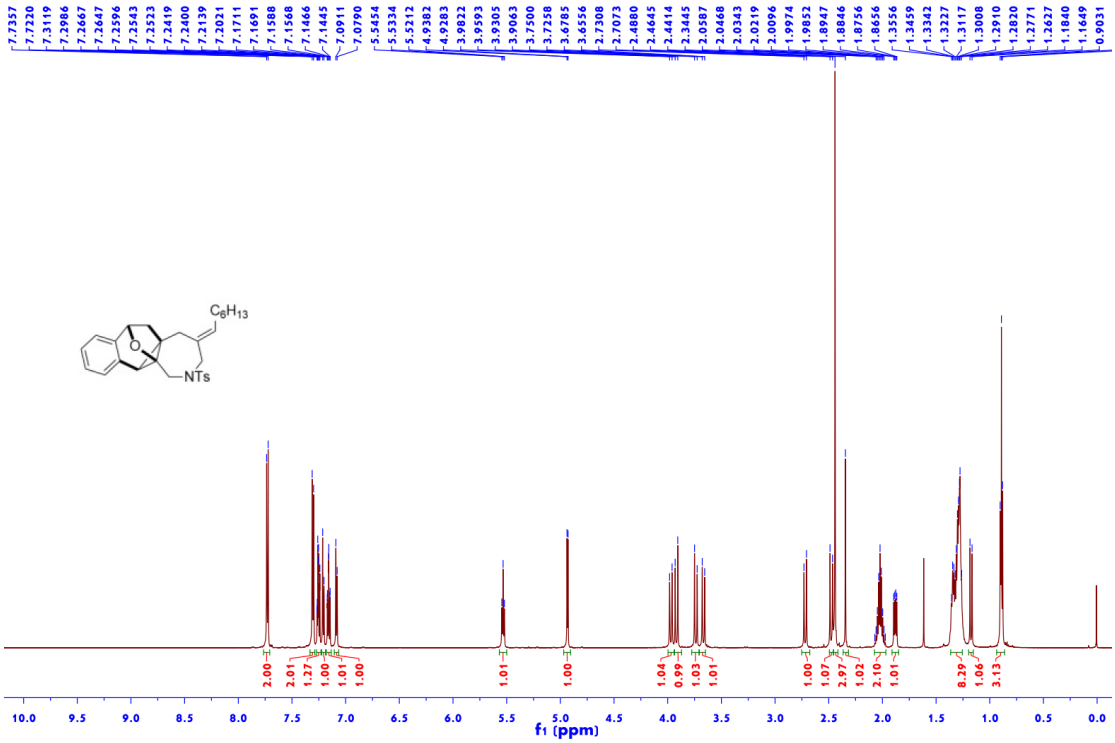


Figure S156 ^{13}C NMR (150 MHz, $CDCl_3$) of 3k

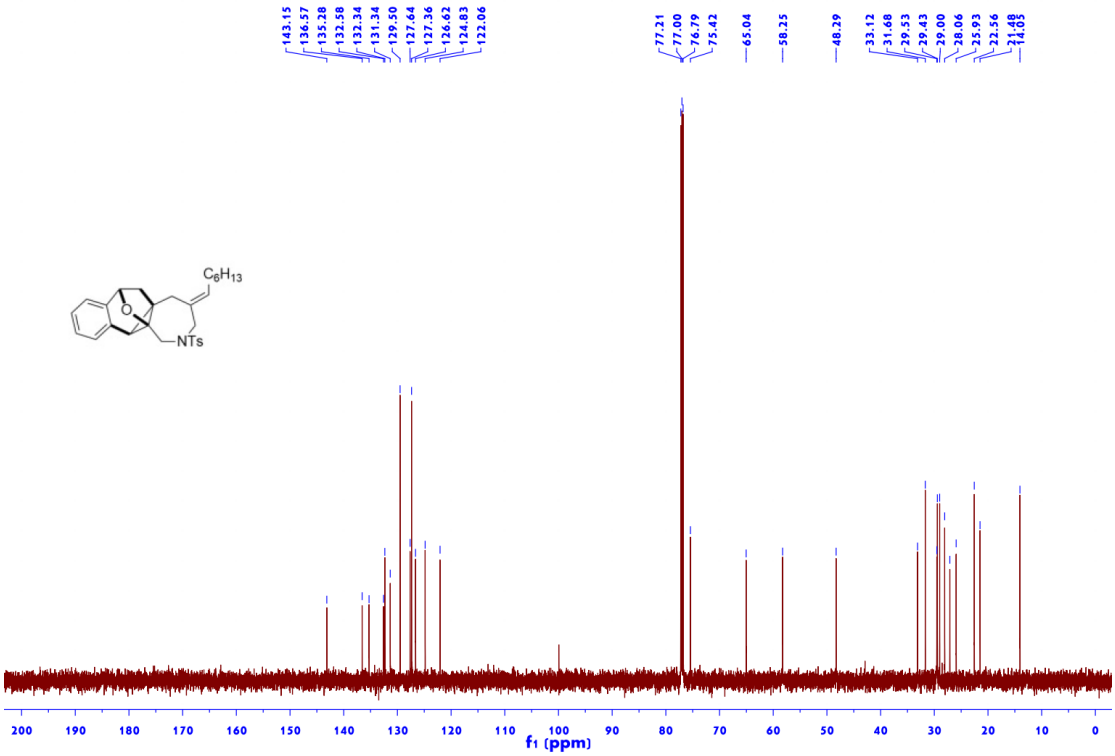


Figure S157 ^{1}H NMR (600 MHz, $CDCl_3$) of 3l

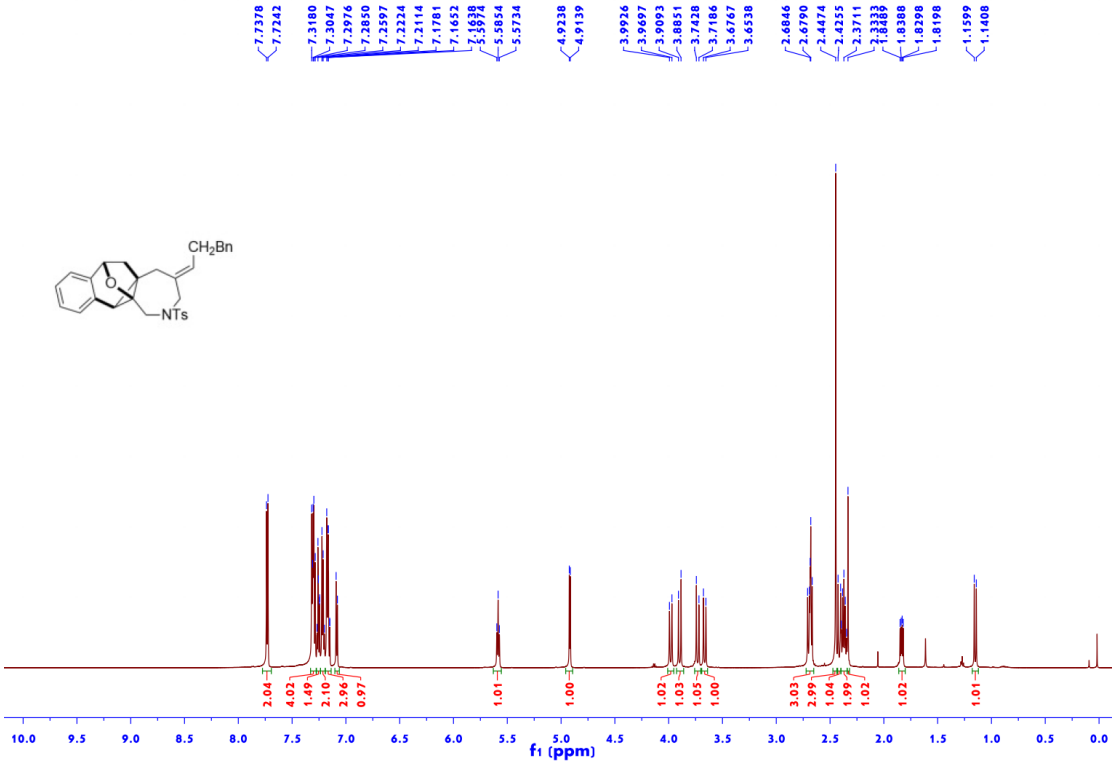


Figure S158 ^{13}C NMR (150 MHz, $CDCl_3$) of 3l

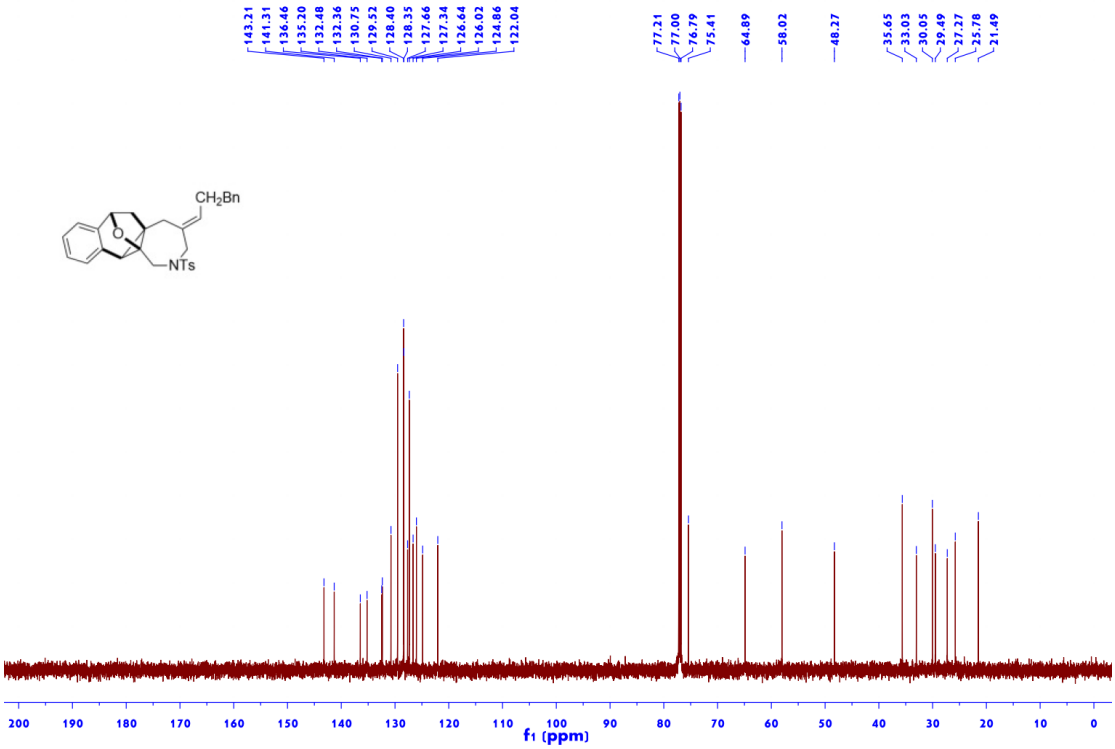


Figure S159 ^{1}H NMR (400 MHz, $CDCl_3$) of 3m

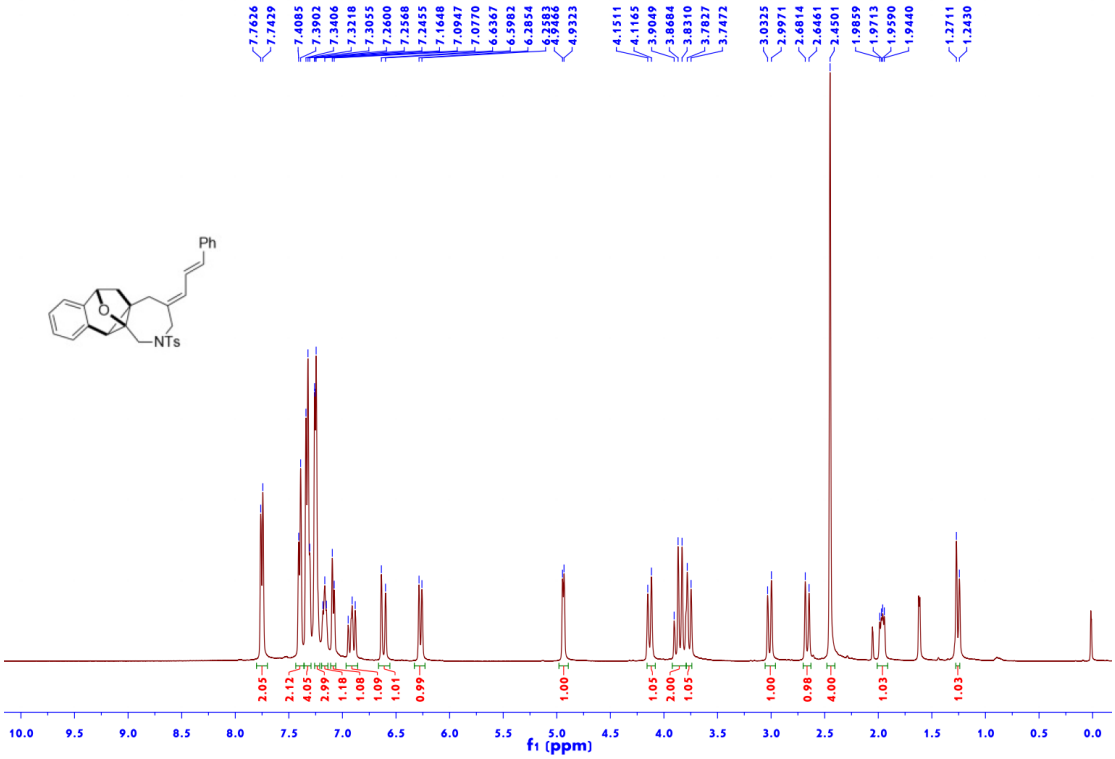


Figure S160 ^{13}C NMR (100 MHz, $CDCl_3$) of 3m

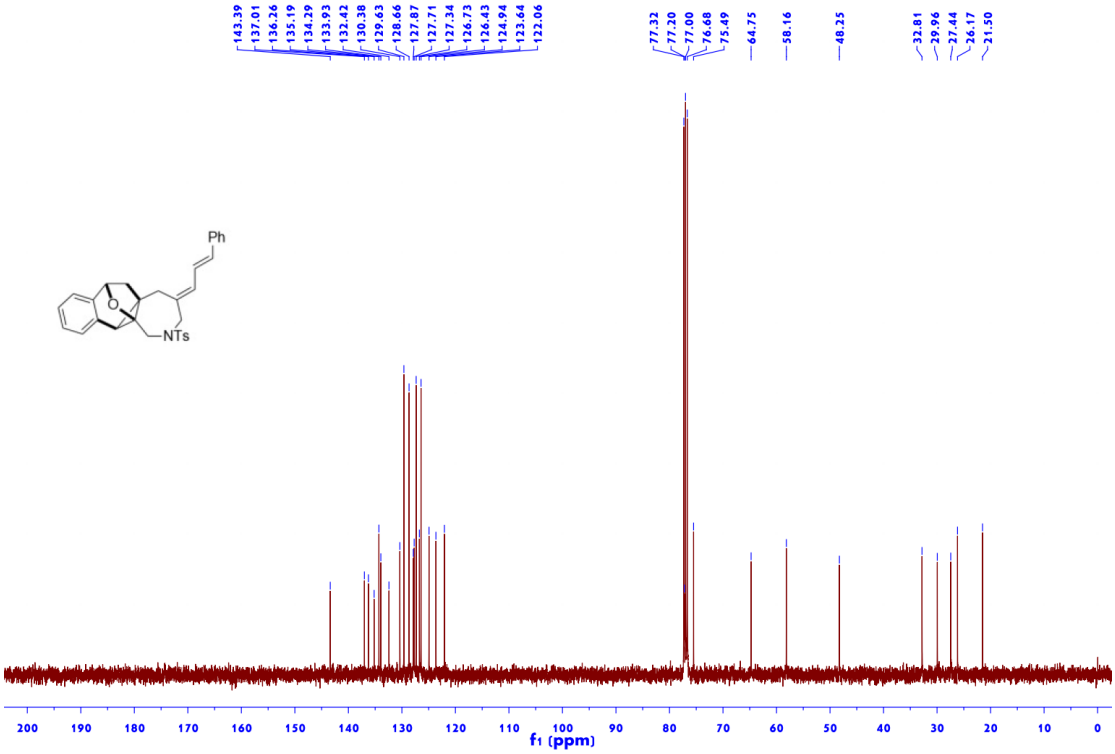


Figure S161 ^{1}H NMR (600 MHz, $CDCl_3$) of 3n

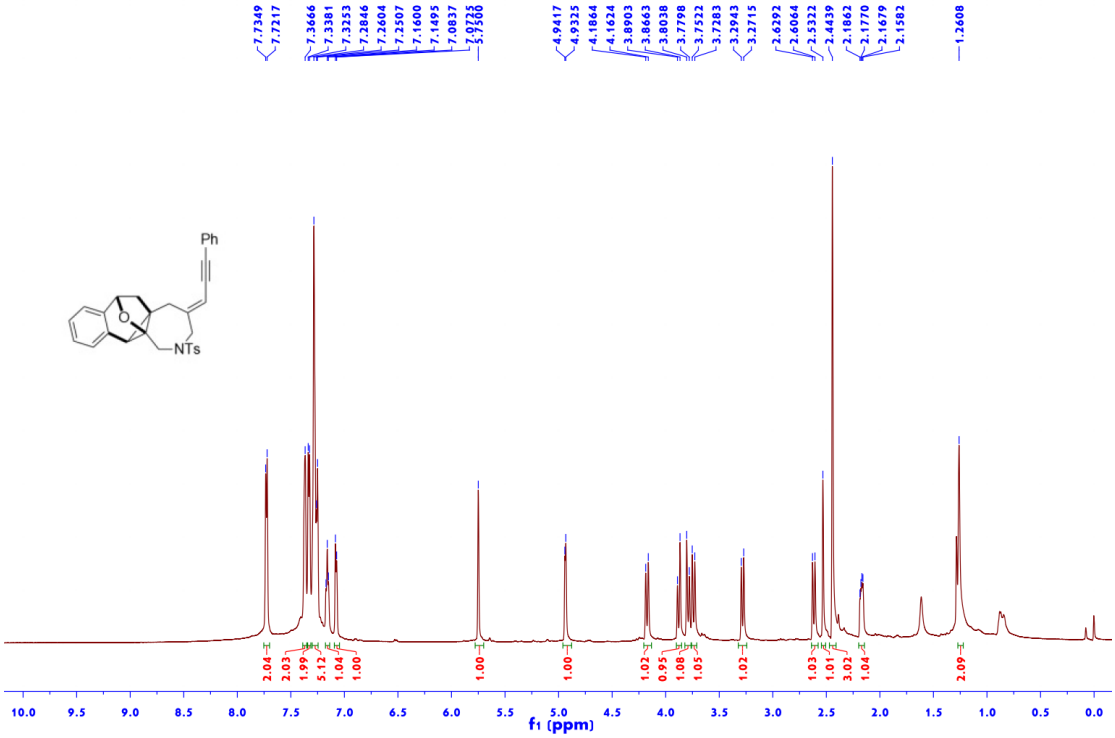


Figure S162 ^{13}C NMR (150 MHz, $CDCl_3$) of 3n

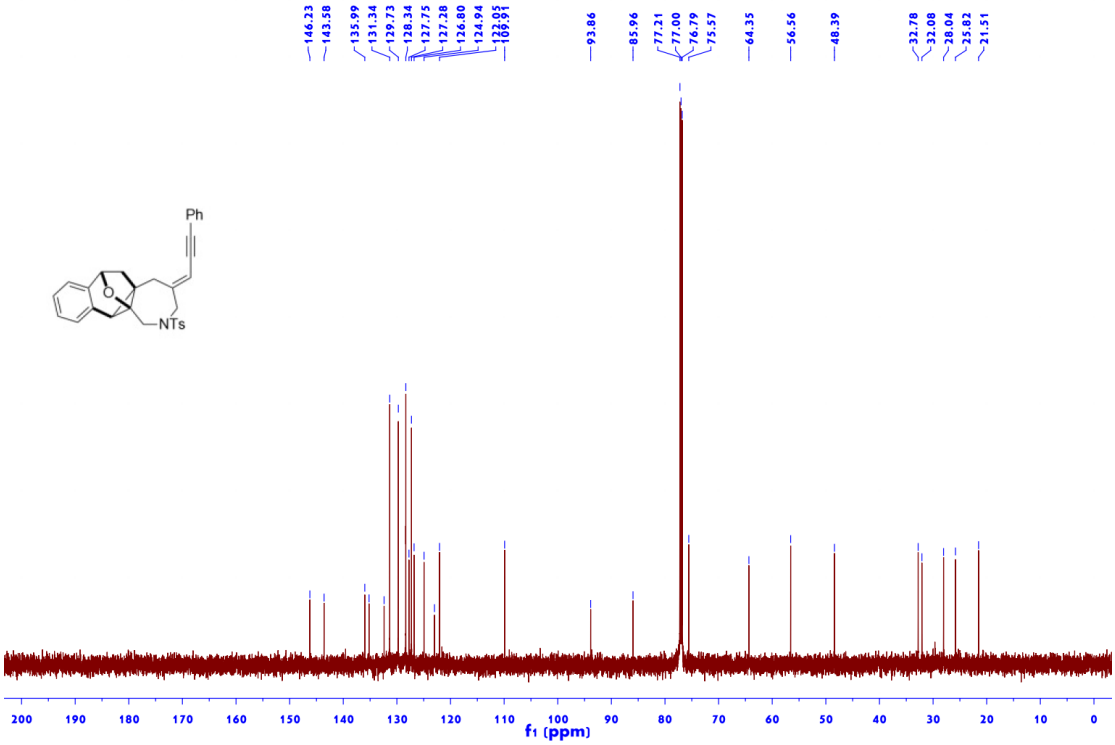


Figure S163 ^{1}H NMR (600 MHz, $CDCl_3$) of 3o

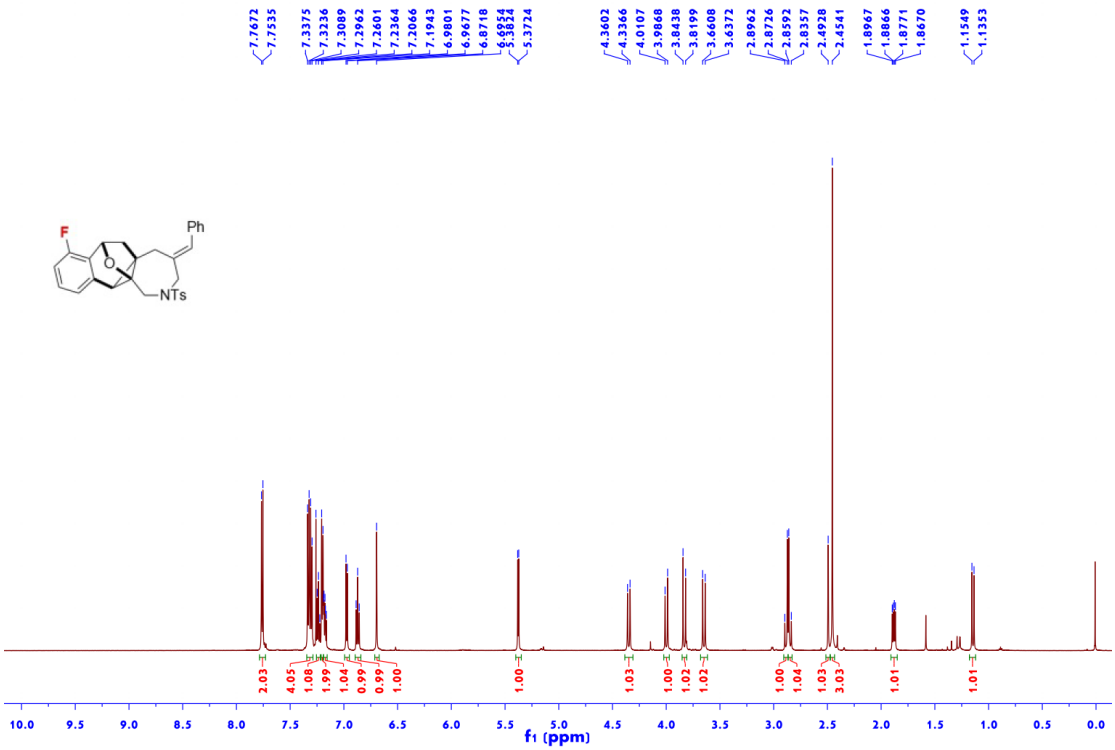


Figure S164 ^{13}C NMR (150 MHz, $CDCl_3$) of 3o

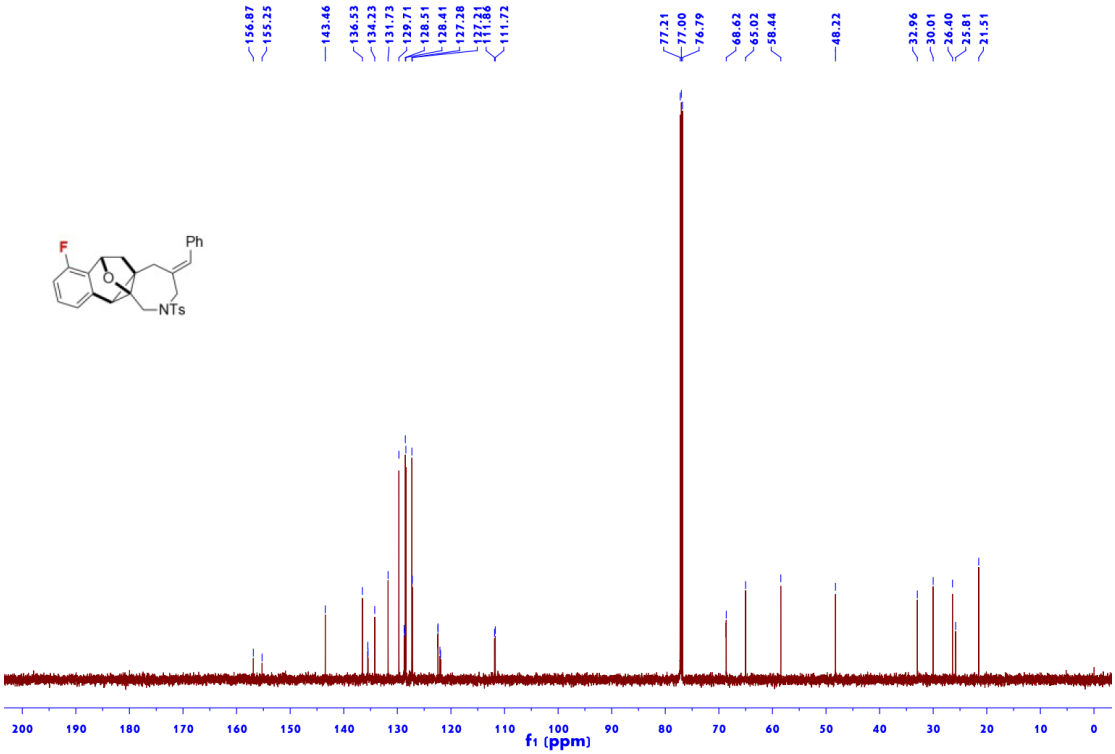


Figure S165 ^{19}F NMR (565 MHz, $CDCl_3$) of 3o

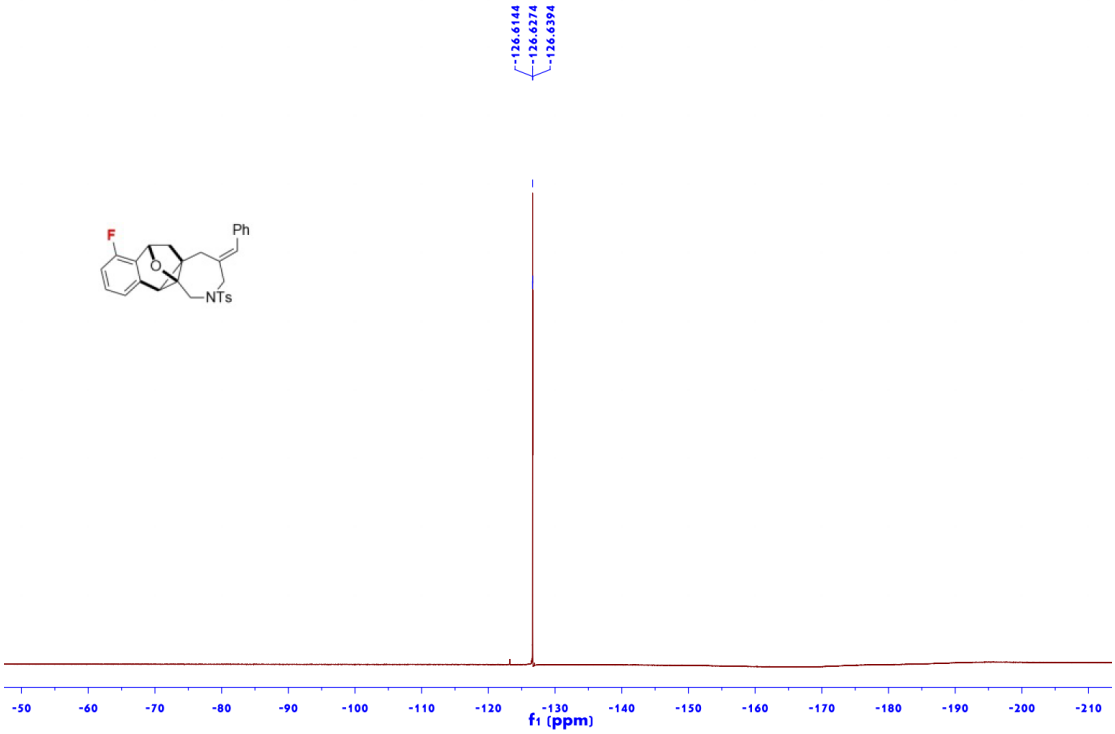


Figure S166 ^{1}H NMR (600 MHz, $CDCl_3$) of 3p

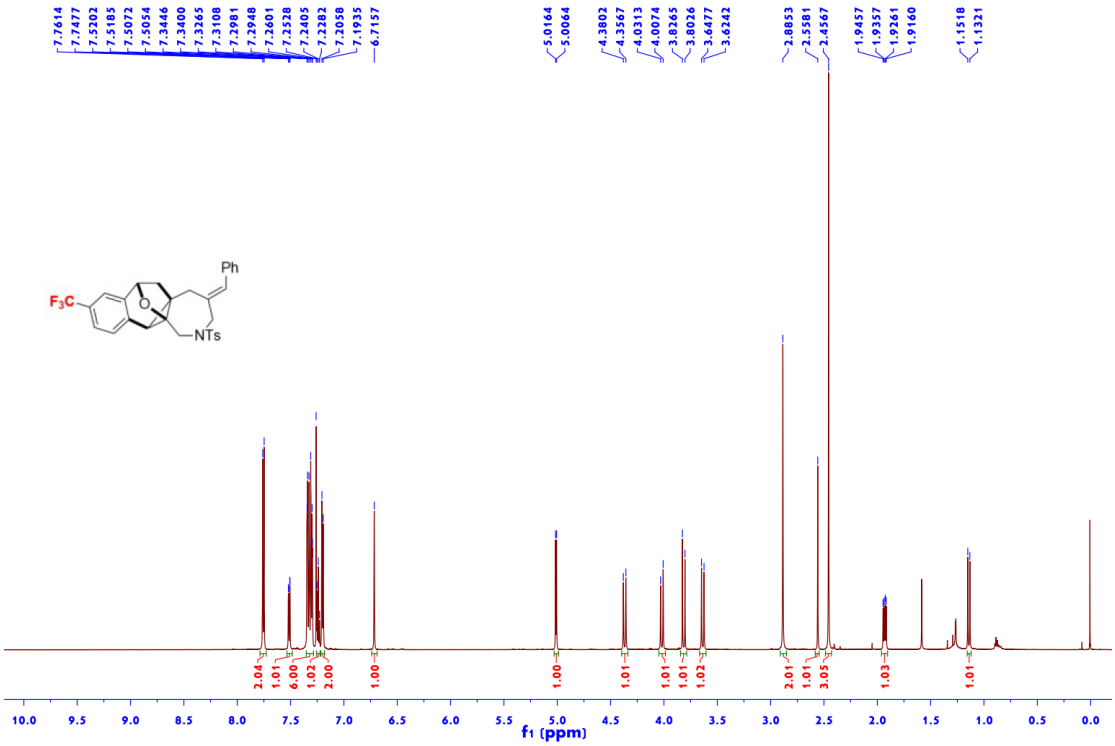


Figure S167 ^{13}C NMR (150 MHz, $CDCl_3$) of 3p

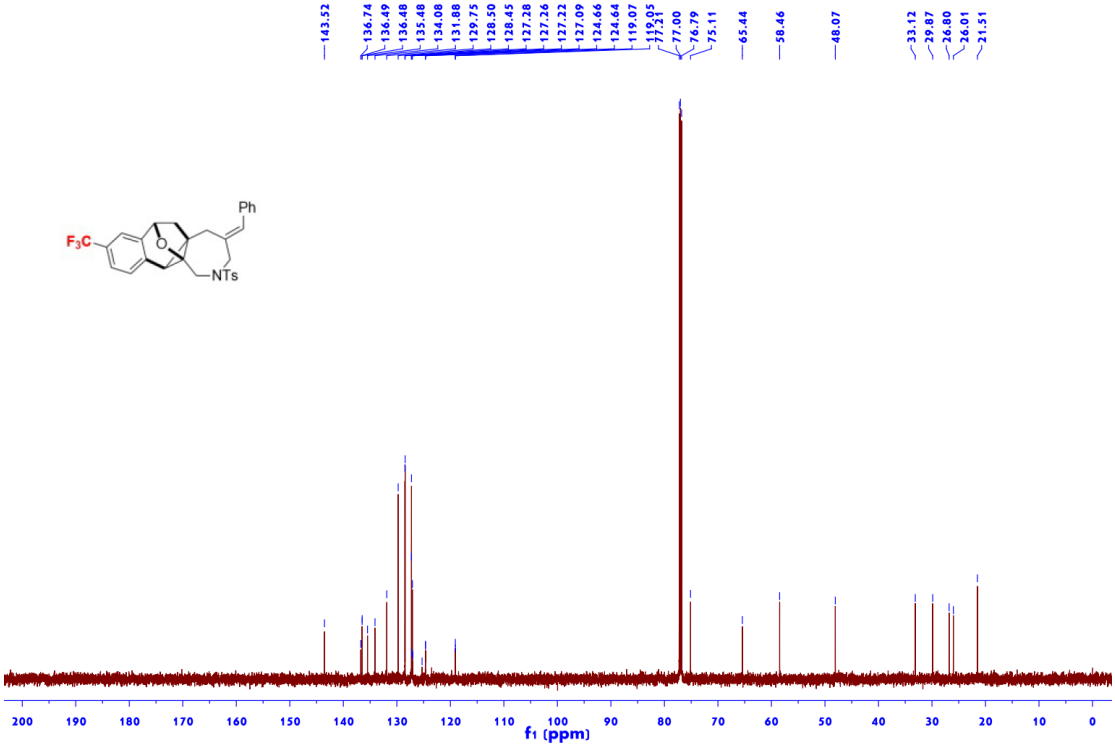


Figure S168 ^{19}F NMR (565 MHz, $CDCl_3$) of 3p

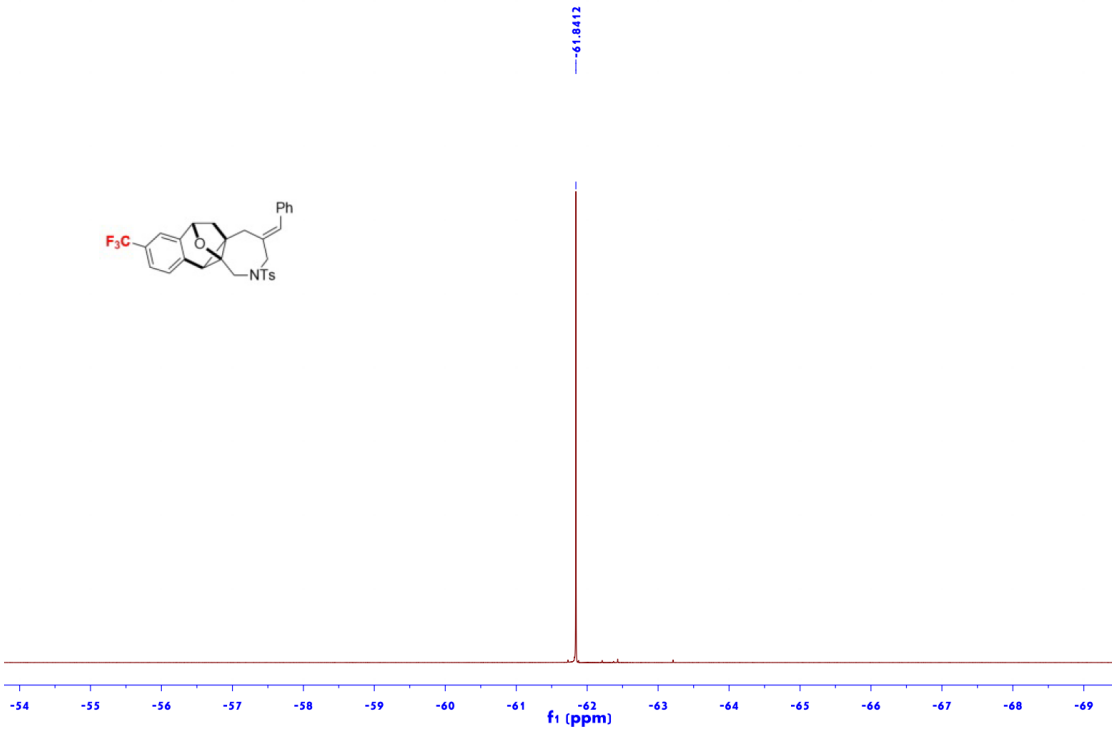


Figure S169 ^{1}H NMR (600 MHz, $CDCl_3$) of 3q

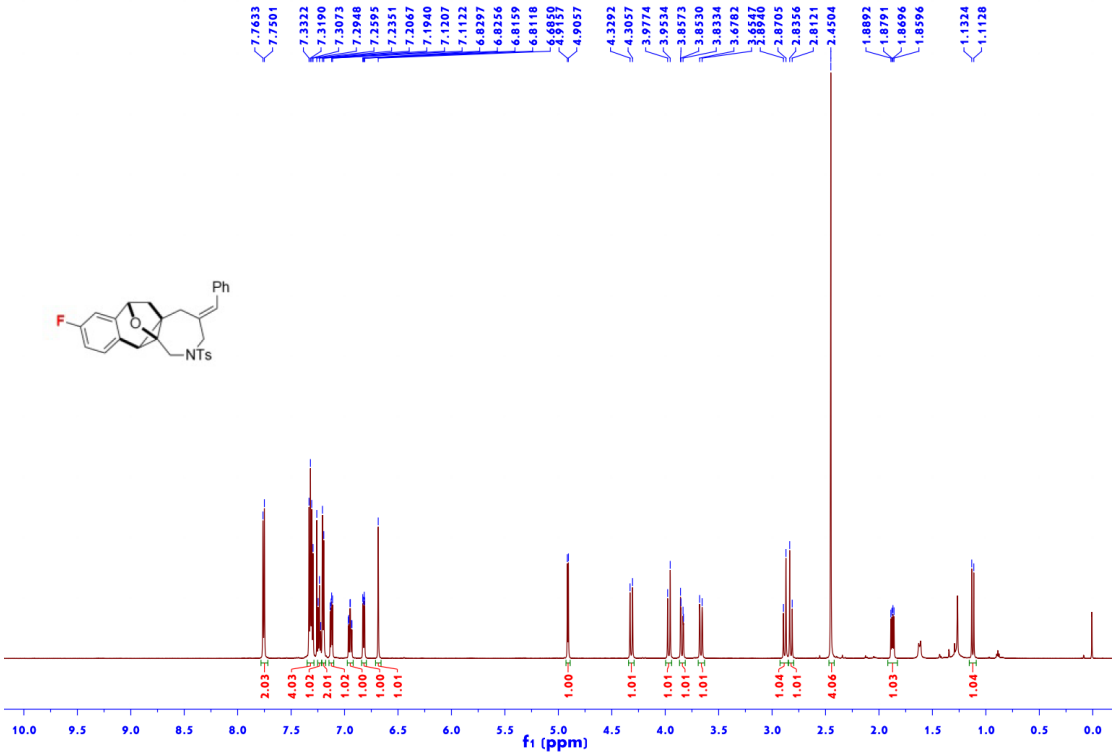


Figure S170 ^{13}C NMR (150 MHz, $CDCl_3$) of 3q

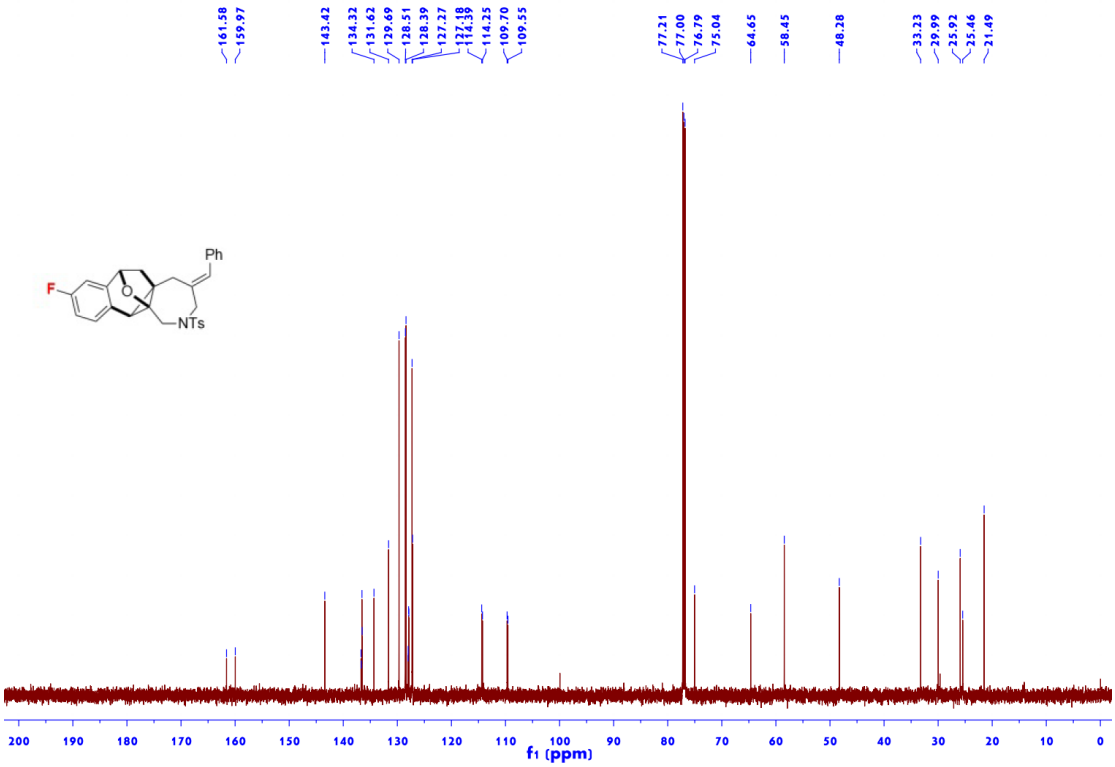


Figure S171 ^{1}H NMR (600 MHz, $CDCl_3$) of 3r

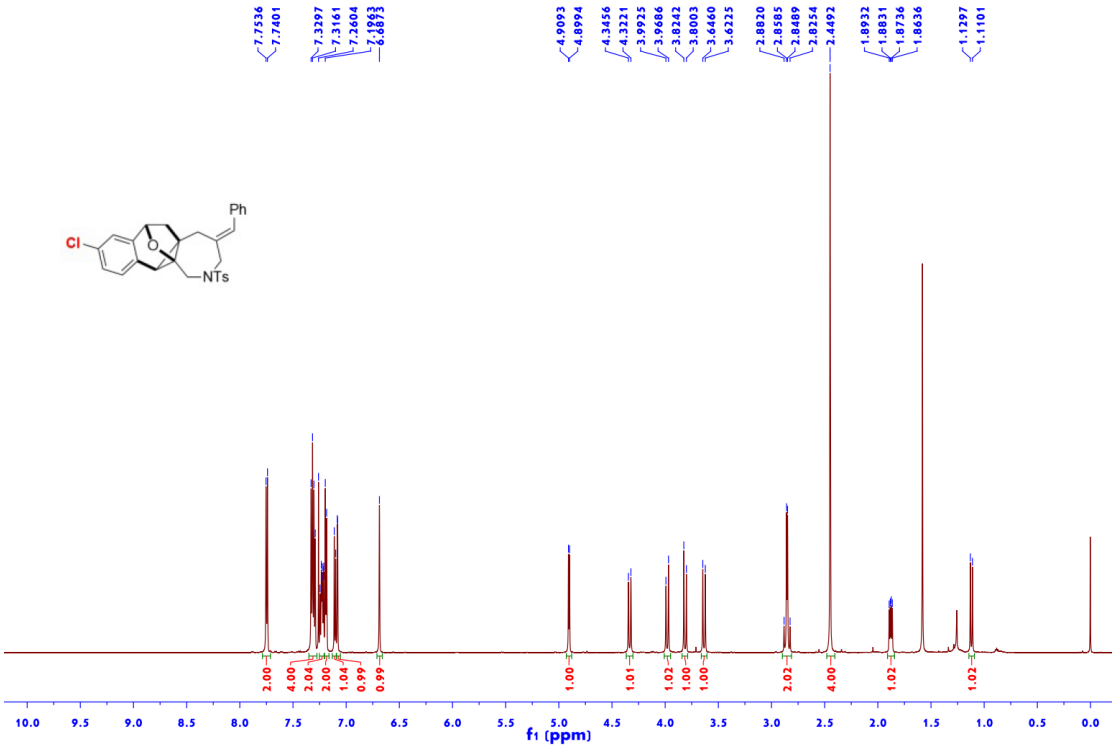


Figure S172 ^{13}C NMR (150 MHz, $CDCl_3$) of 3r

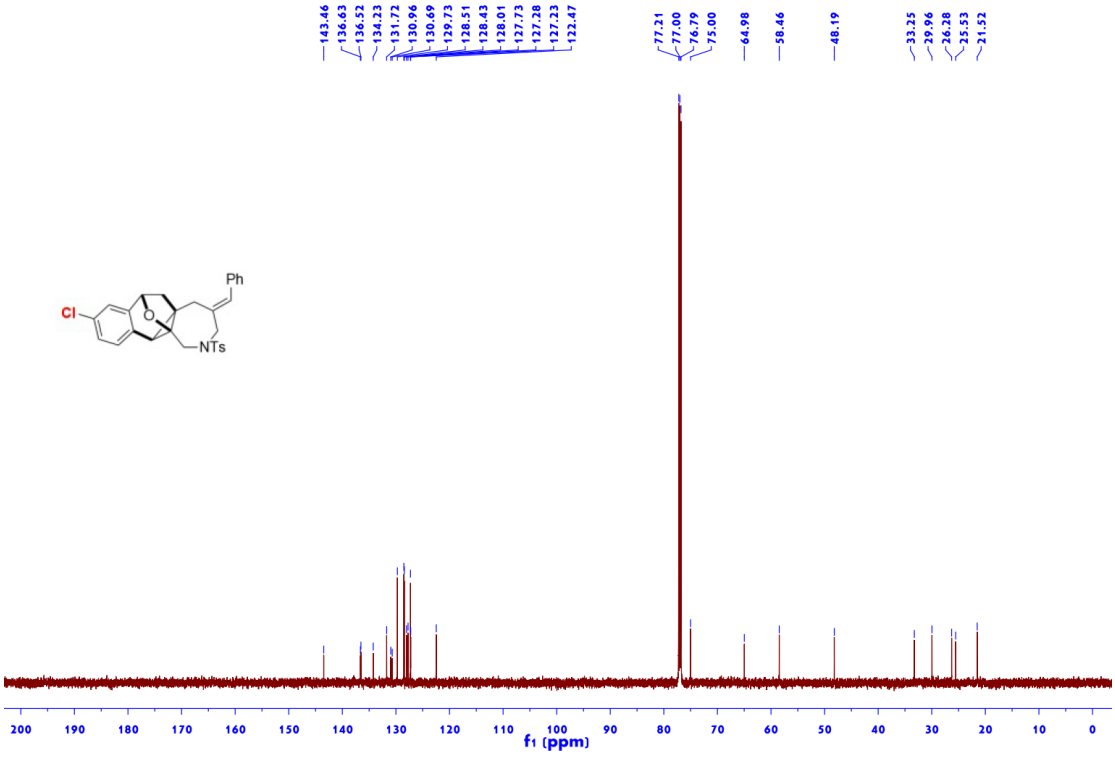


Figure S173 ^{1}H NMR (600 MHz, $CDCl_3$) of 3s

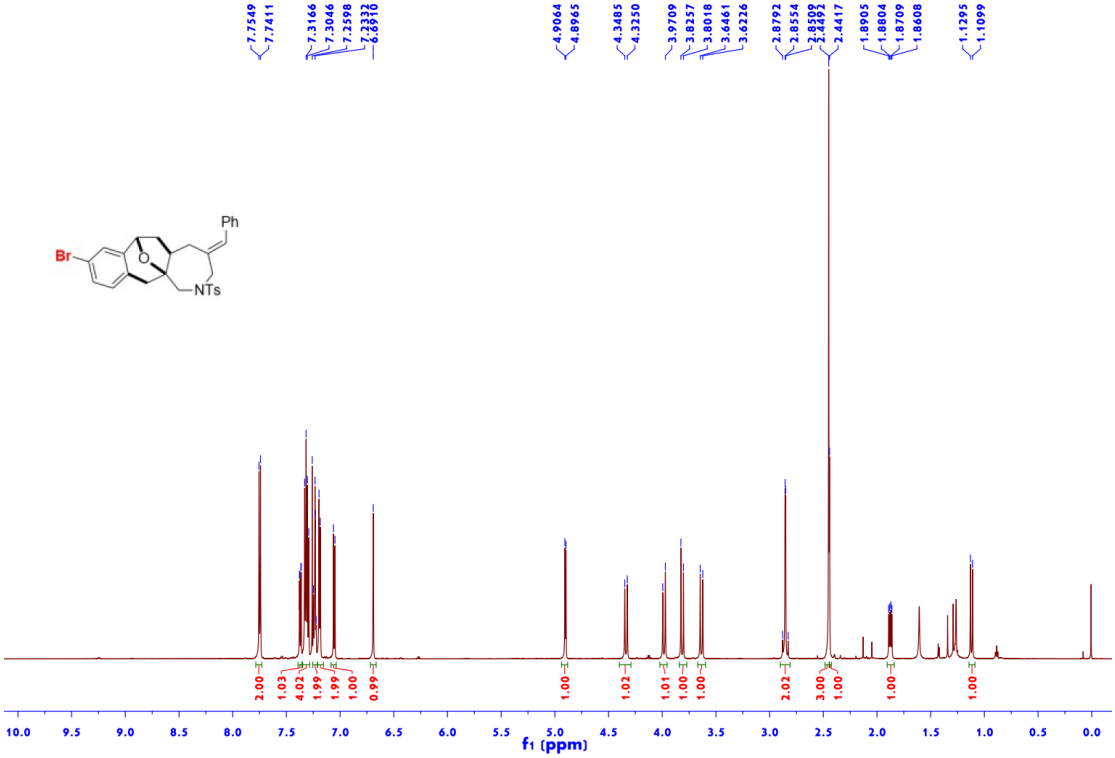


Figure S174 ^{13}C NMR (150 MHz, $CDCl_3$) of 3s

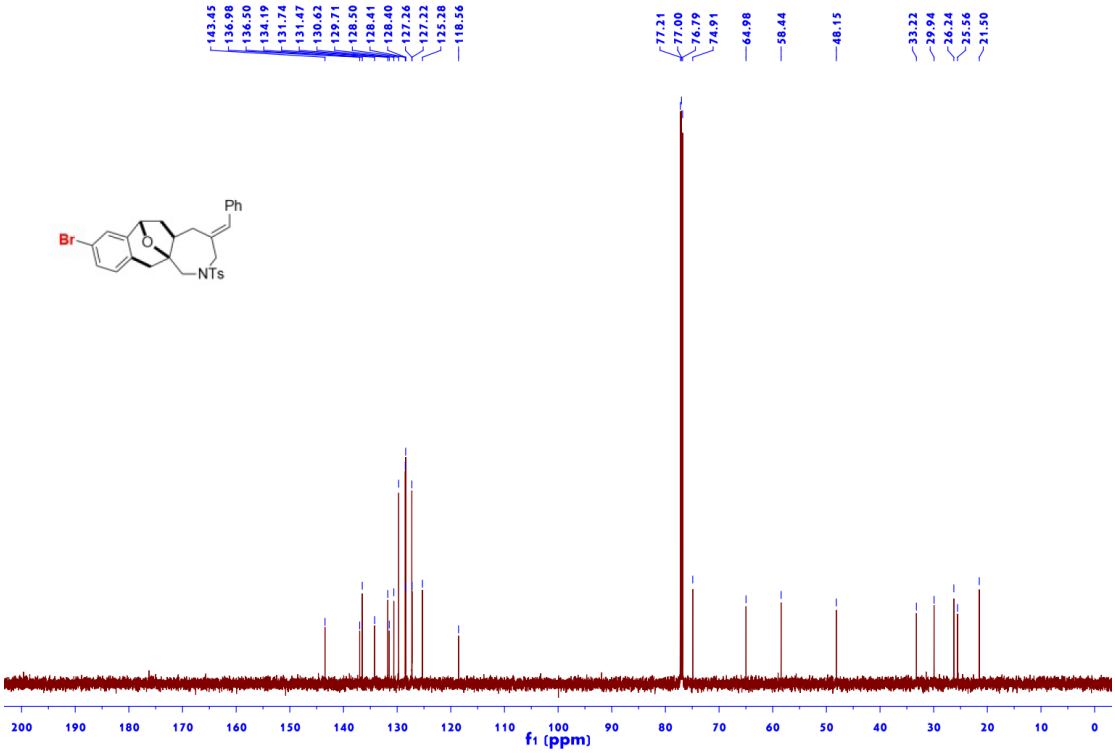


Figure S175 ^{1}H NMR (600 MHz, $CDCl_3$) of 3t

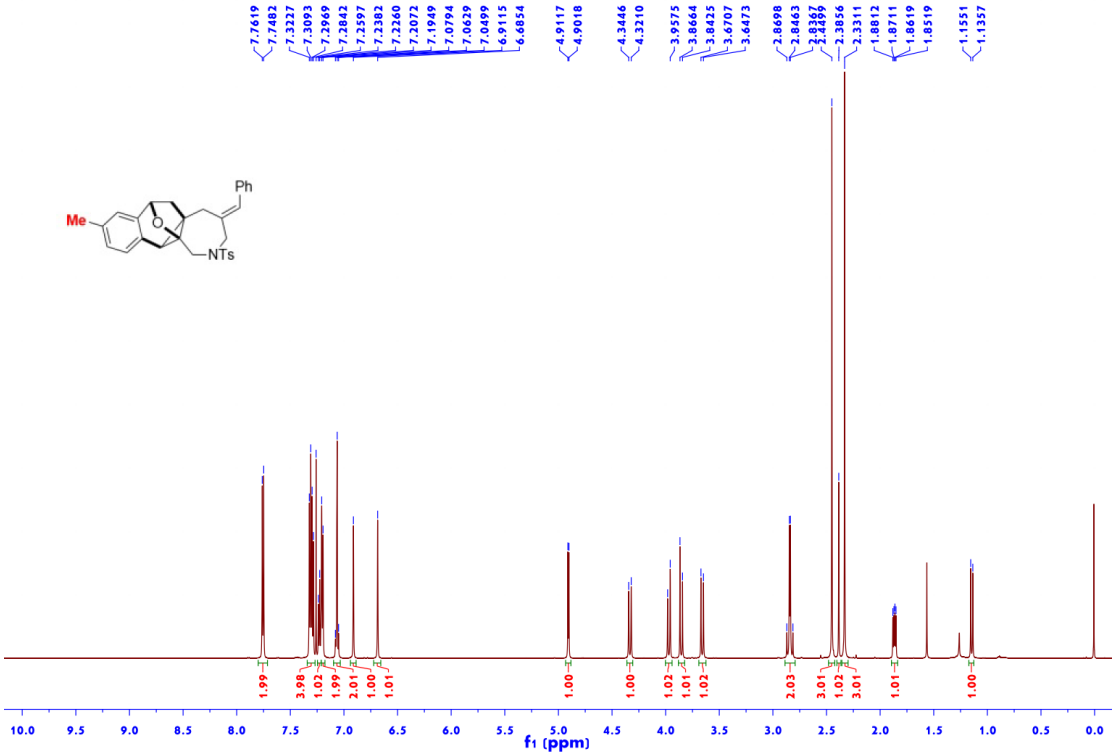


Figure S176 ^{13}C NMR (150 MHz, $CDCl_3$) of 3t

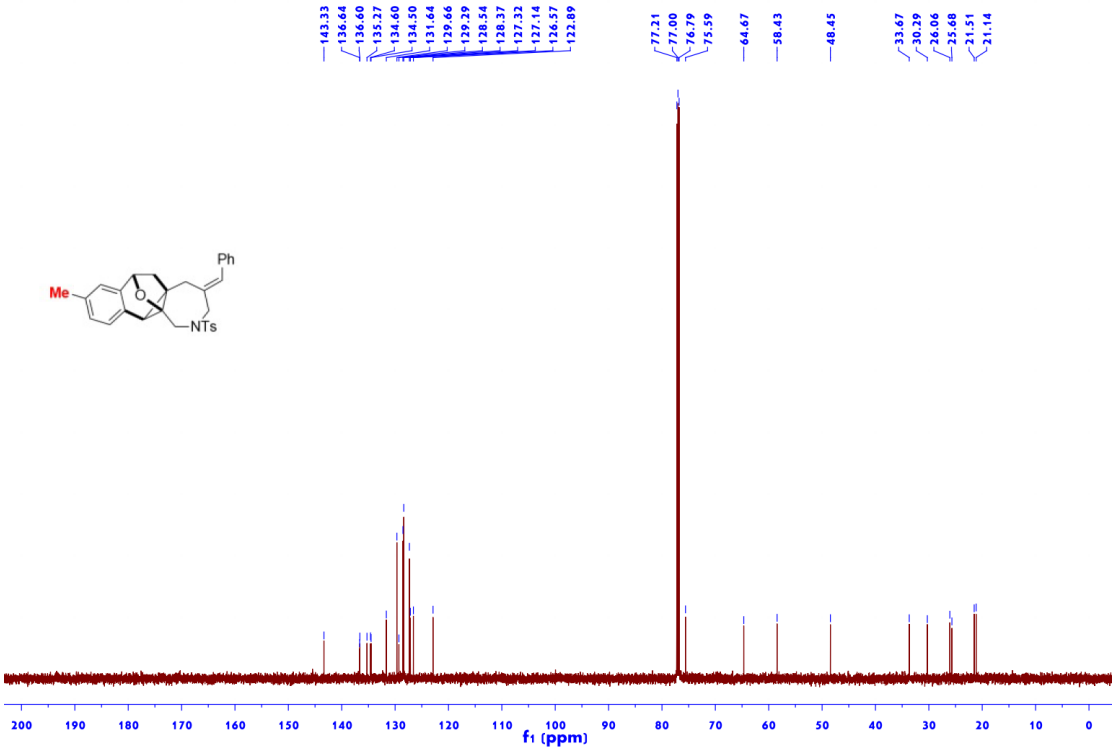


Figure S177 ^{1}H NMR (600 MHz, $CDCl_3$) of 3u

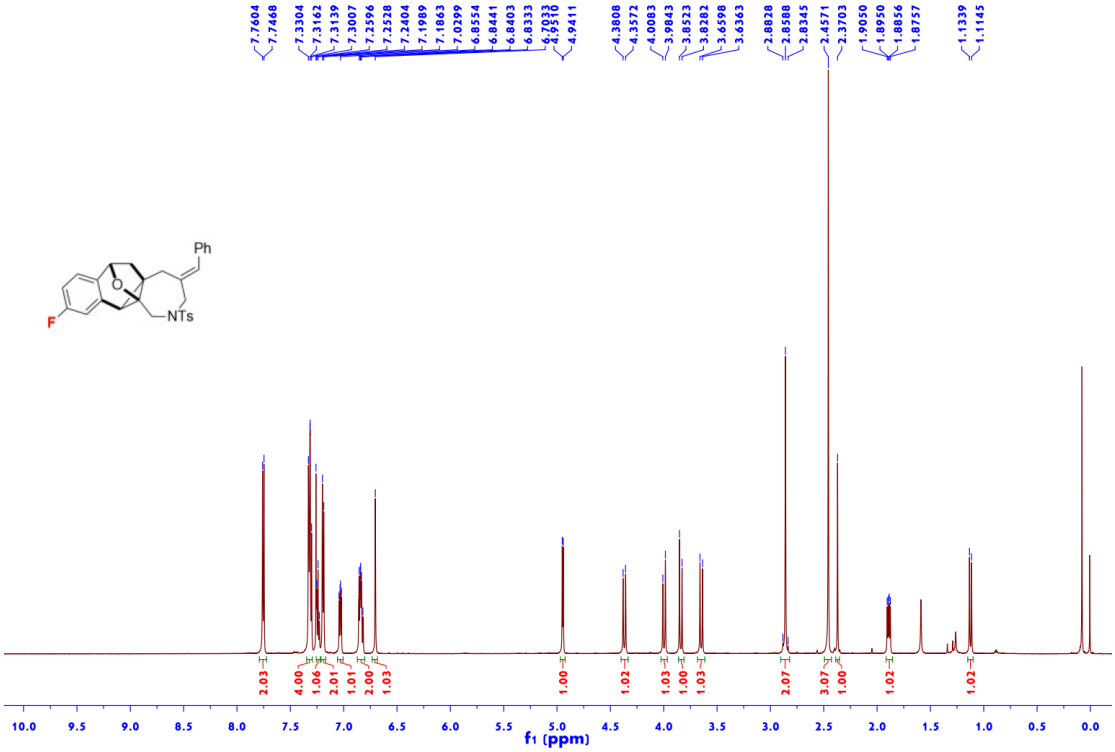


Figure S178 ^{13}C NMR (150 MHz, $CDCl_3$) of 3u

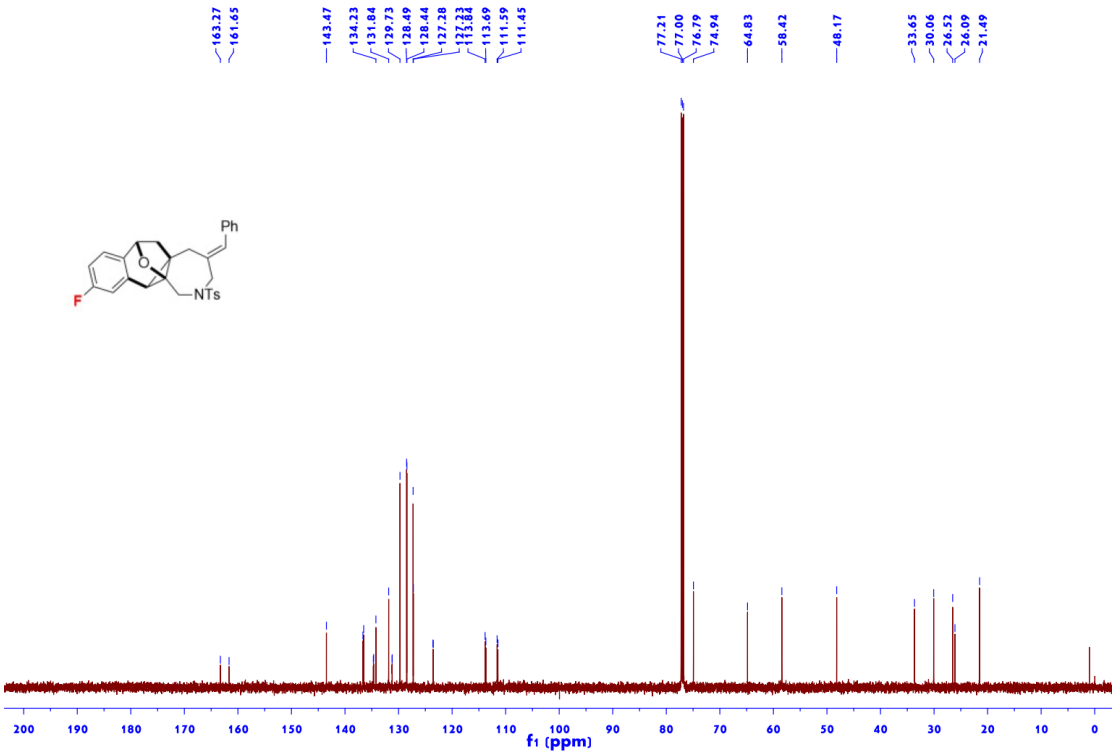


Figure S179 ^{19}F NMR (565 MHz, $CDCl_3$) of 3u

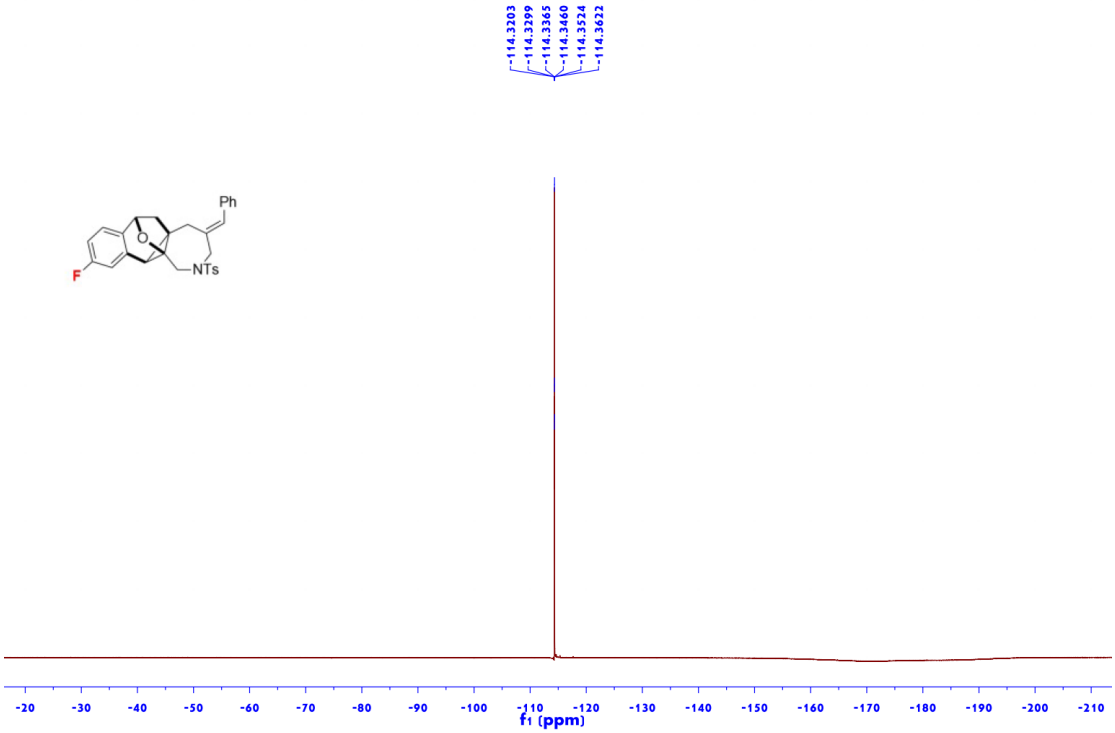


Figure S180 ^{1}H NMR (600 MHz, $CDCl_3$) of 3v

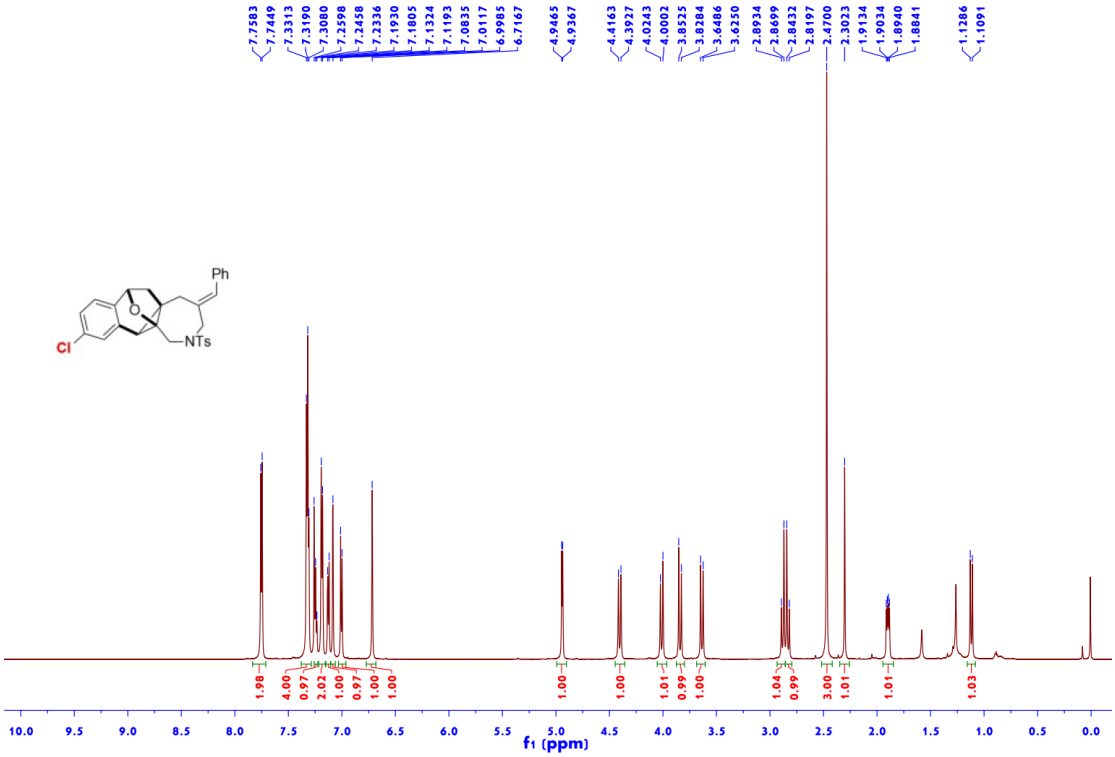


Figure S181 ^{13}C NMR (150 MHz, $CDCl_3$) of 3v

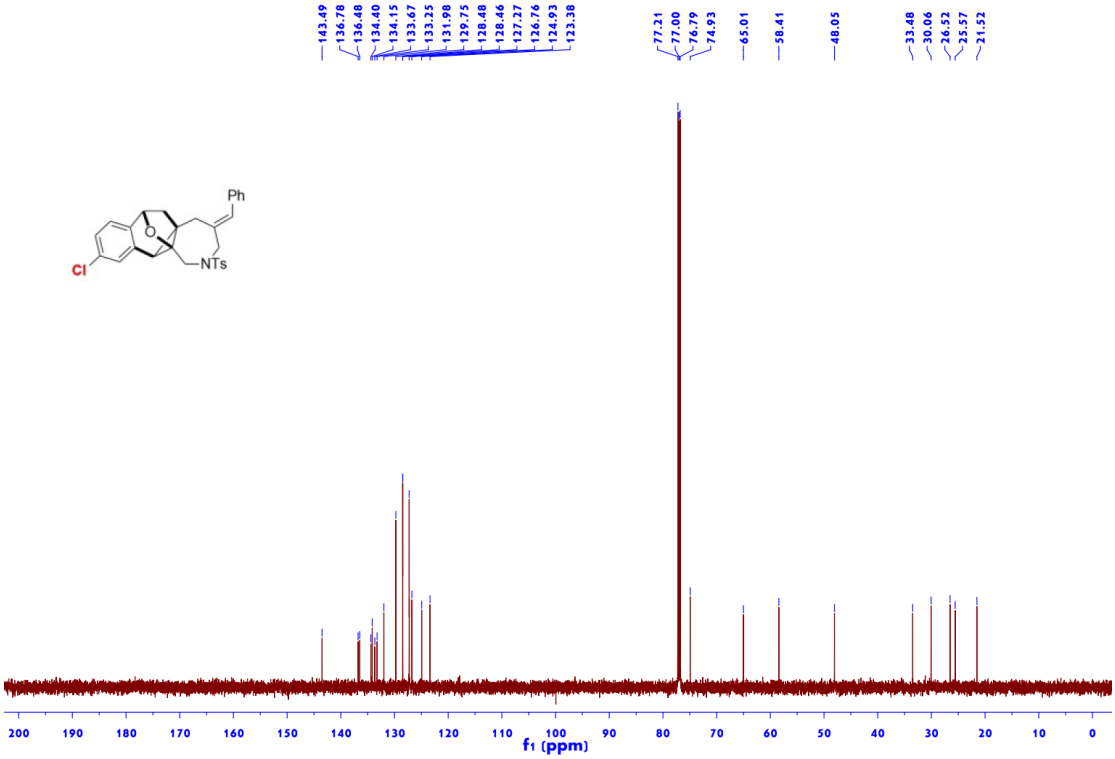


Figure S182 ^{1}H NMR (600 MHz, $CDCl_3$) of 3w

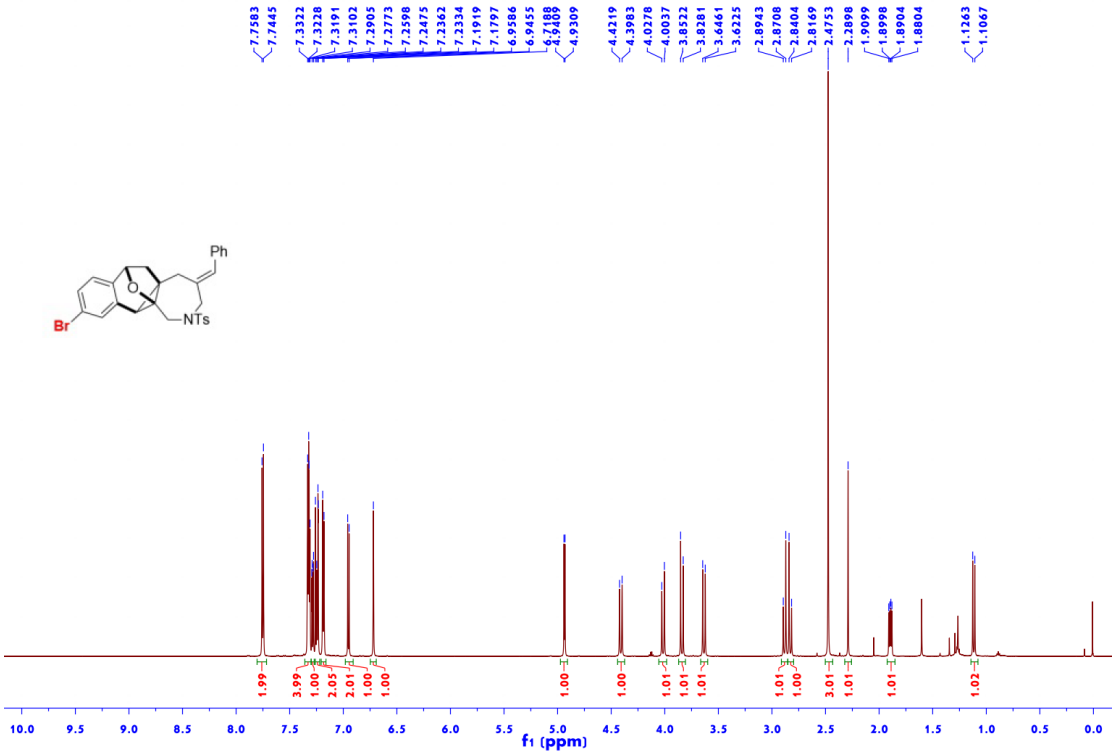


Figure S183 ^{13}C NMR (150 MHz, $CDCl_3$) of 3w

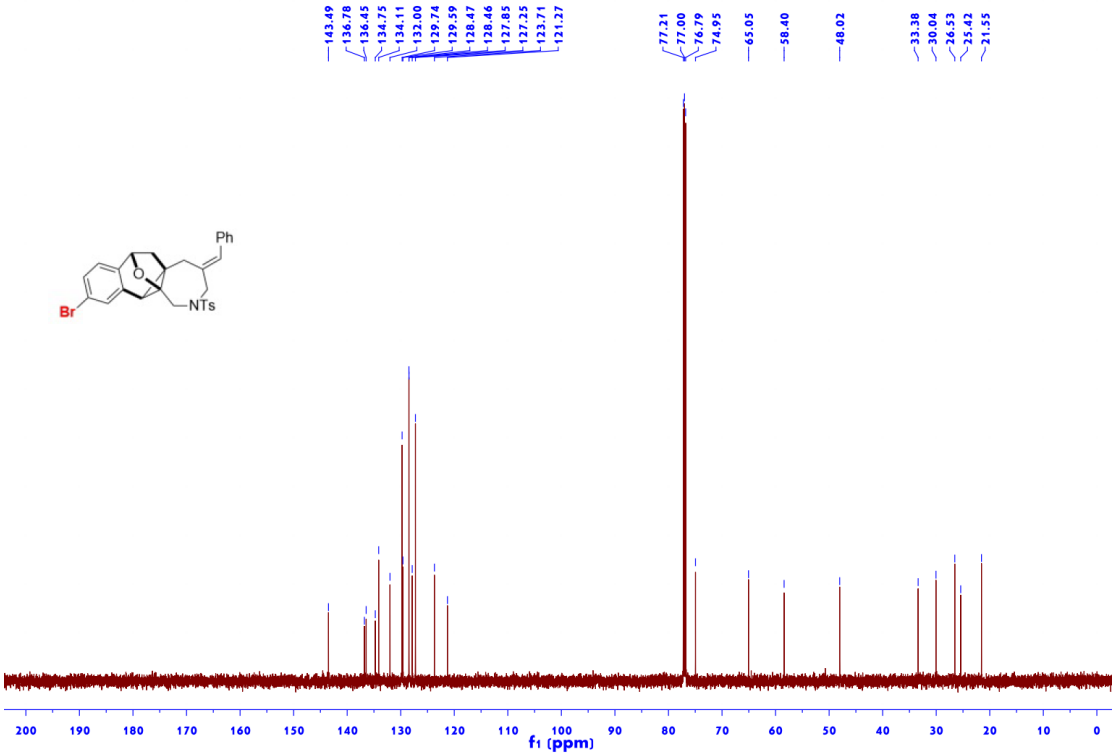


Figure S184 ^{1}H NMR (600 MHz, $CDCl_3$) of 3x

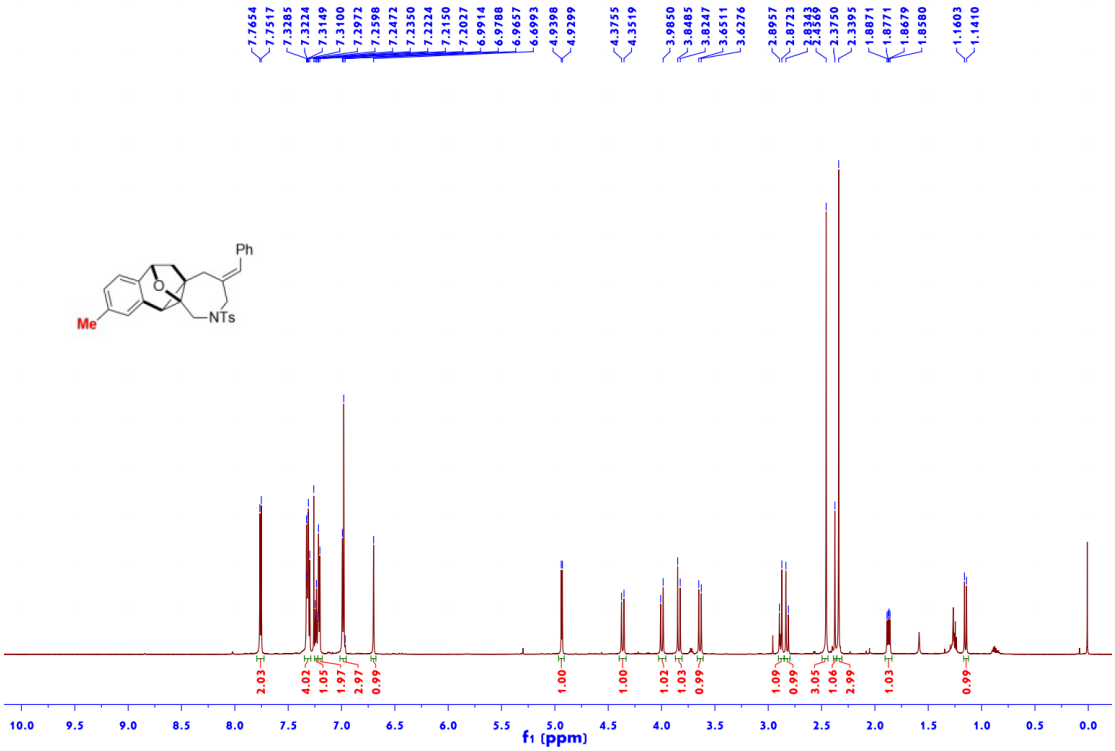


Figure S185 ^{13}C NMR (150 MHz, $CDCl_3$) of 3x

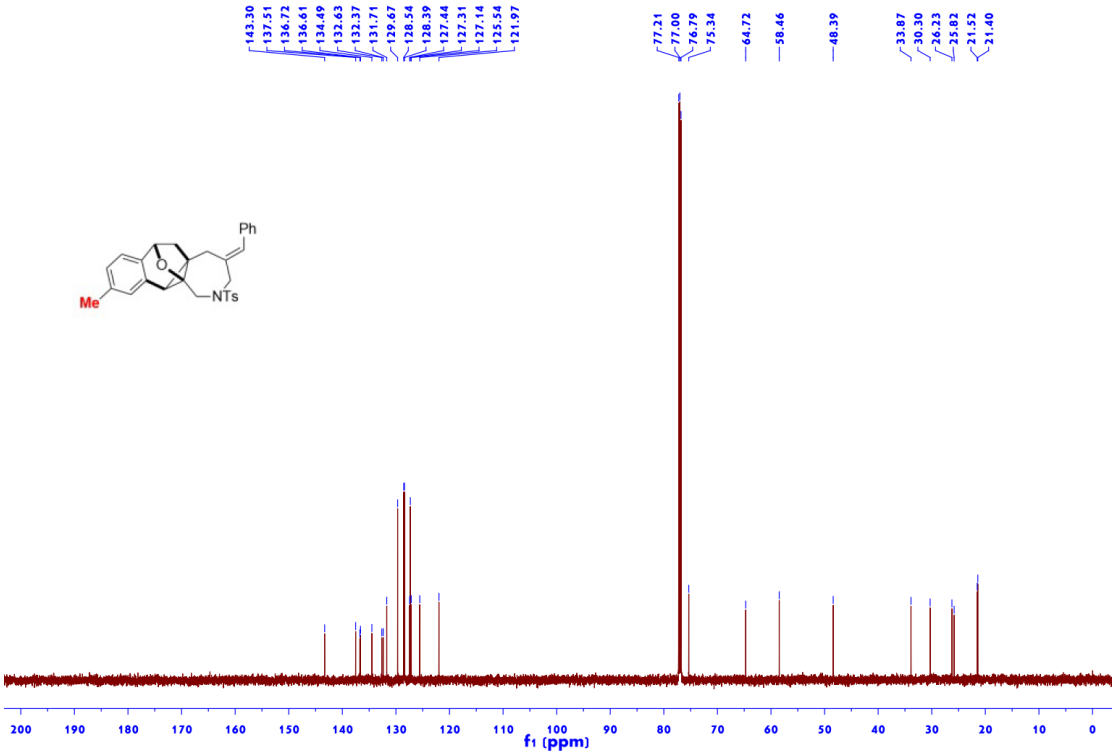


Figure S186 ^{1}H NMR (600 MHz, $CDCl_3$) of 3y

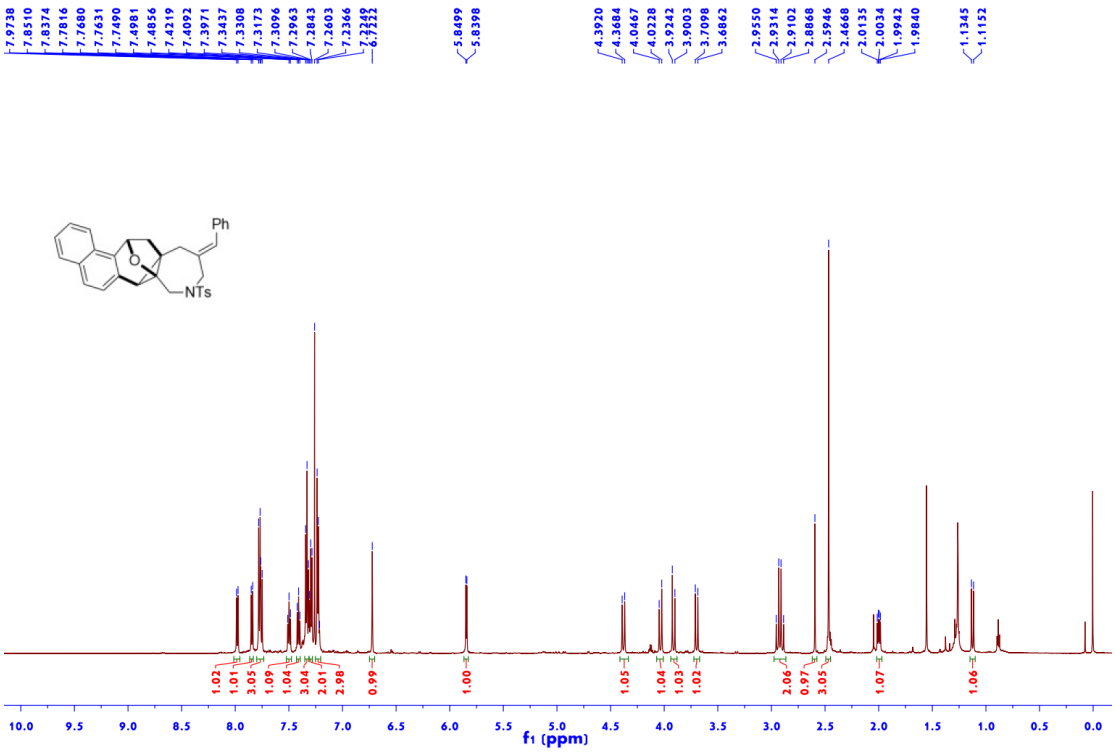


Figure S187 ^{13}C NMR (150 MHz, $CDCl_3$) of 3y

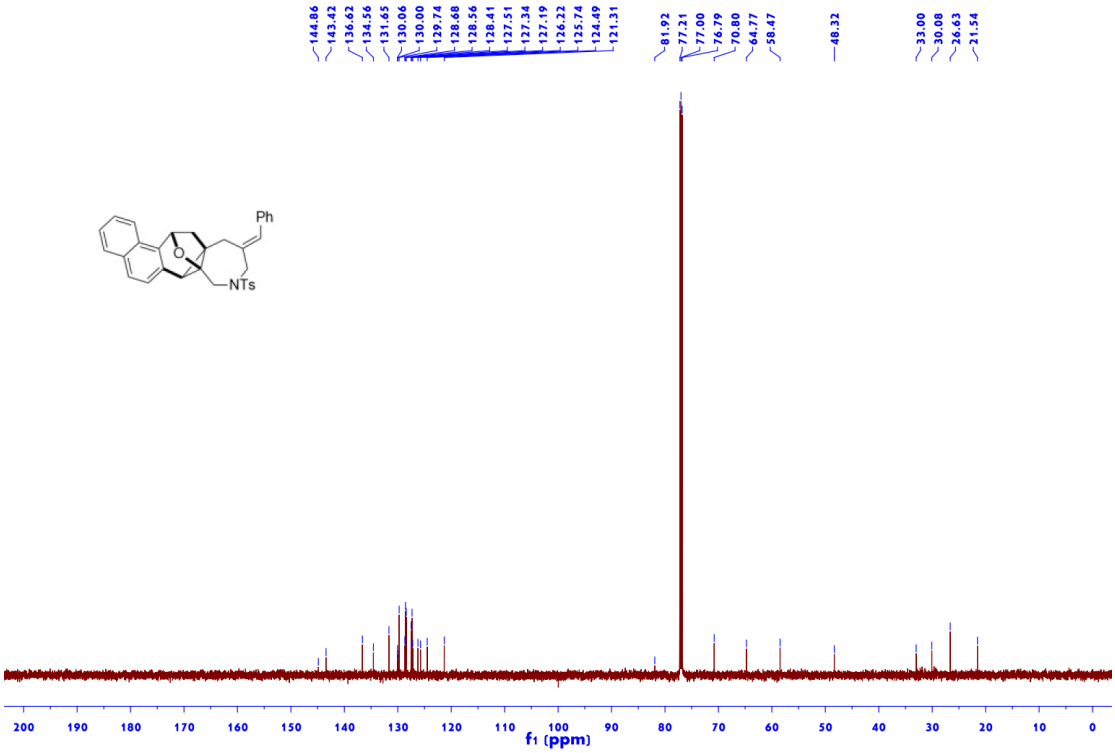


Figure S188 ^{1}H NMR (600 MHz, $CDCl_3$) of 3z

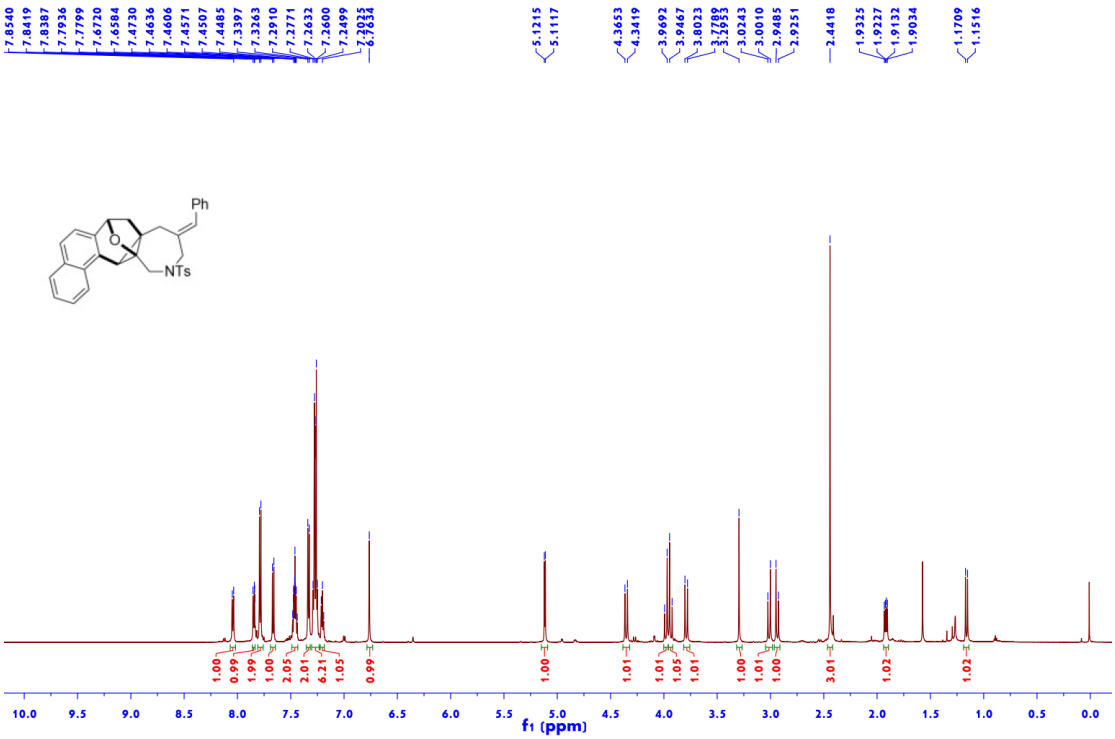


Figure S189 ^{13}C NMR (150 MHz, $CDCl_3$) of 3z

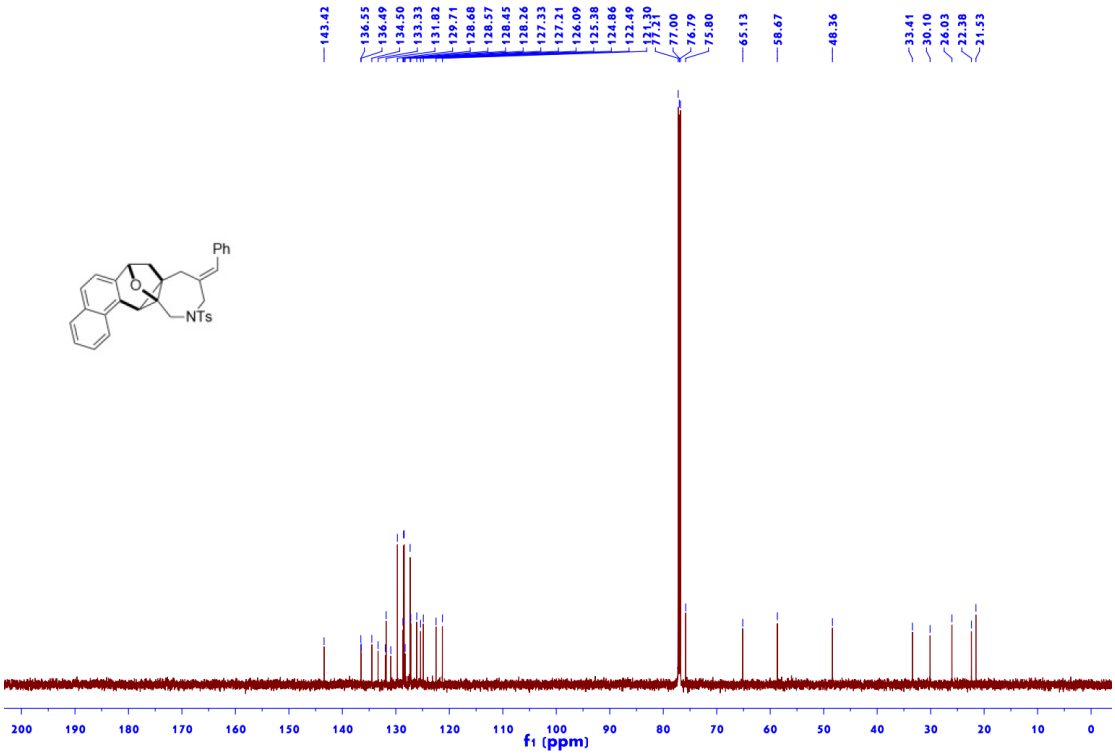


Figure S190 ^{1}H NMR (600 MHz, $CDCl_3$) of 3aa

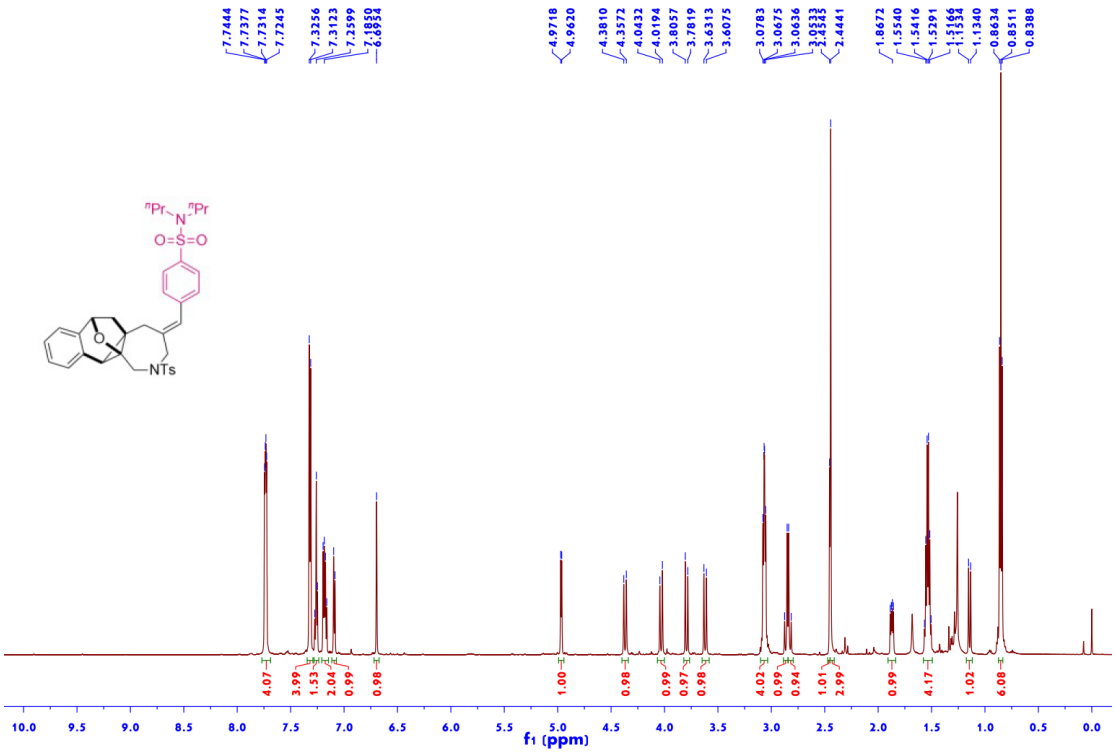


Figure S191 ^{13}C NMR (150 MHz, $CDCl_3$) of 3aa

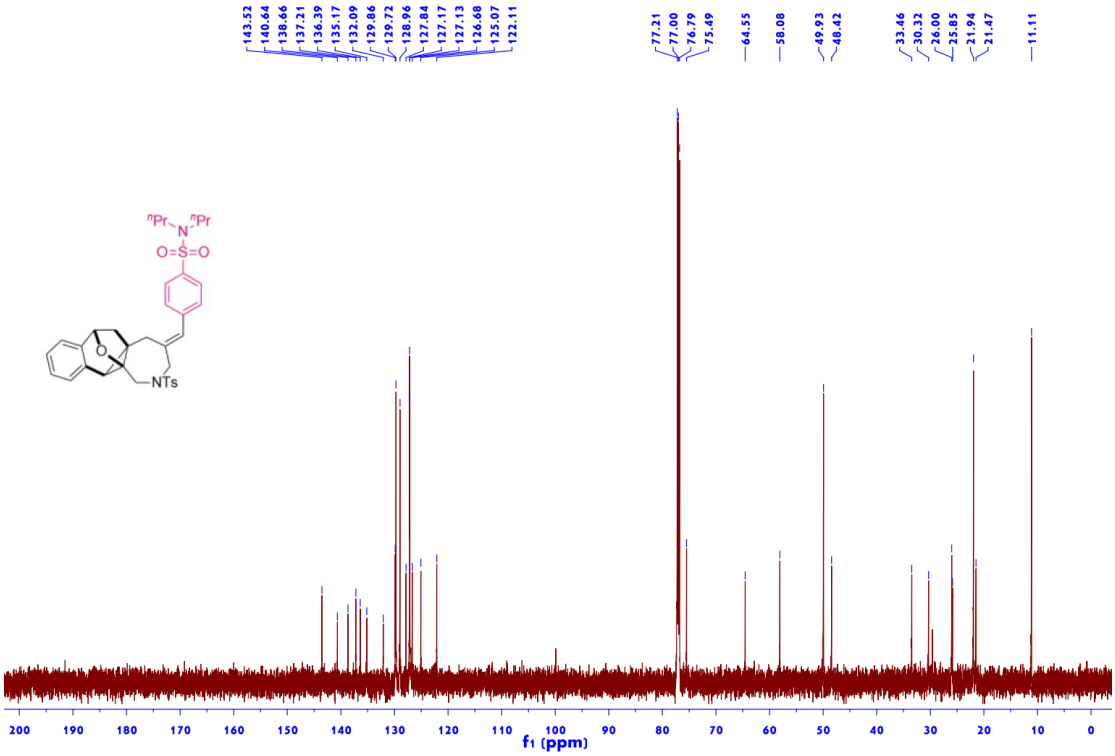


Figure S192 ^{1}H NMR (400 MHz, $CDCl_3$) of 3ab

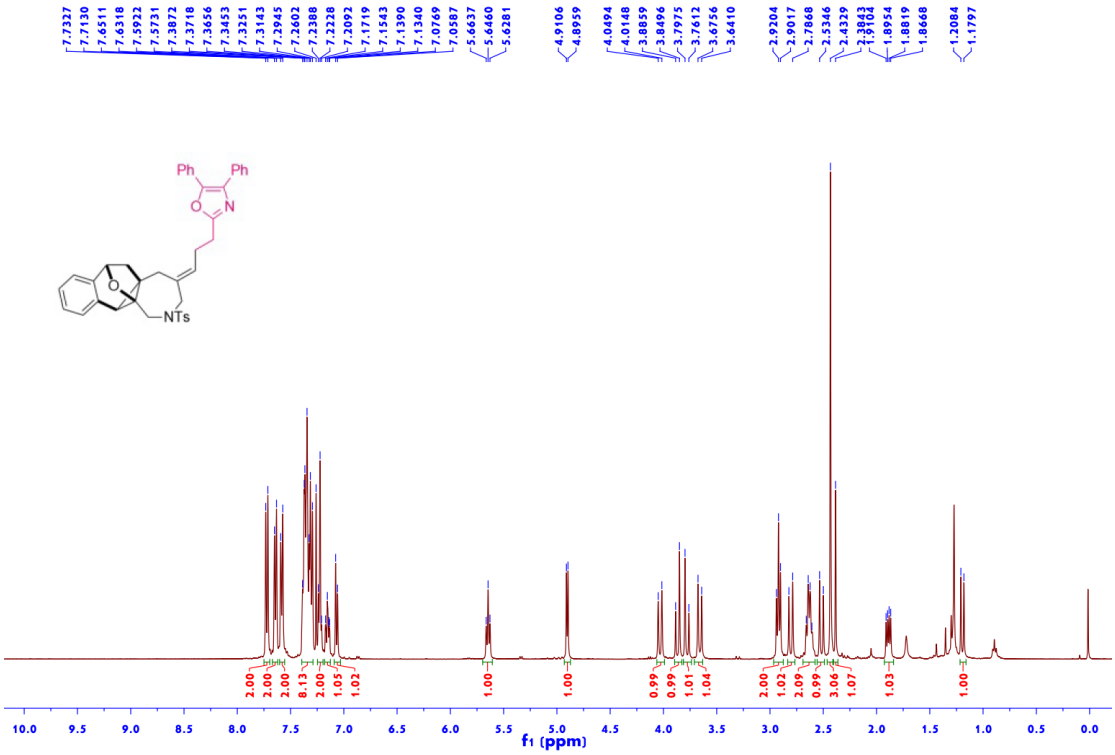


Figure S193 ^{13}C NMR (100 MHz, $CDCl_3$) of 3ab

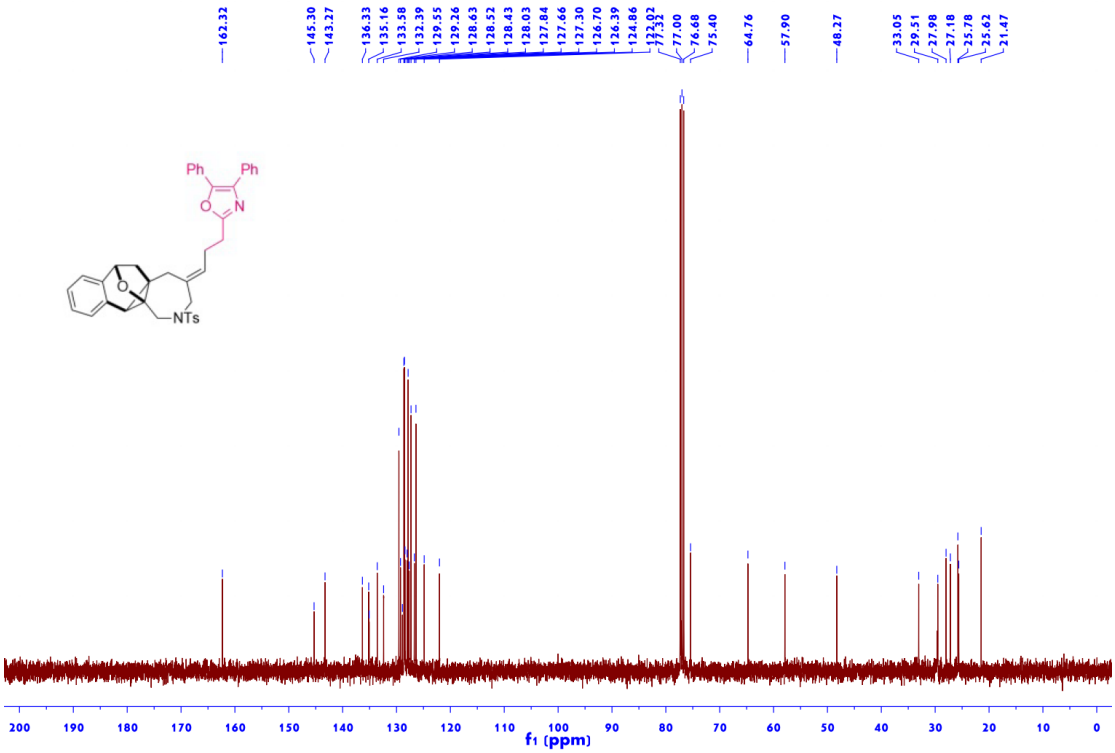


Figure S194 ^{1}H NMR (600 MHz, $CDCl_3$) of 3ac

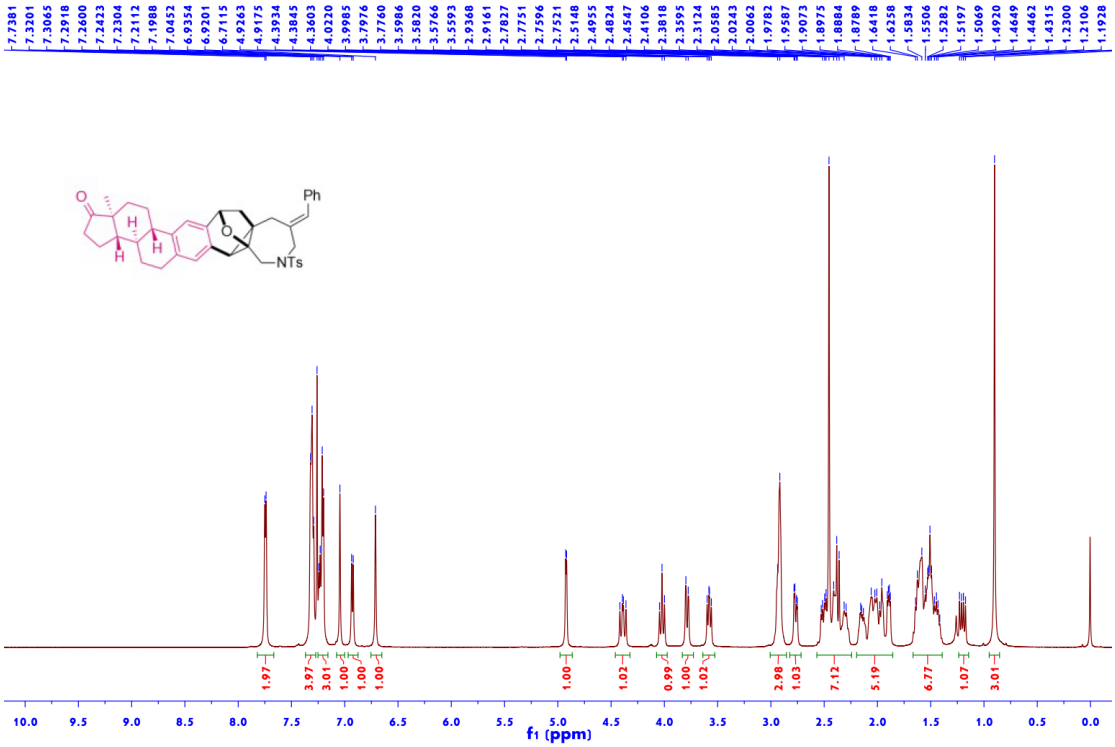


Figure S195 ^{13}C NMR (150 MHz, $CDCl_3$) of 3ac

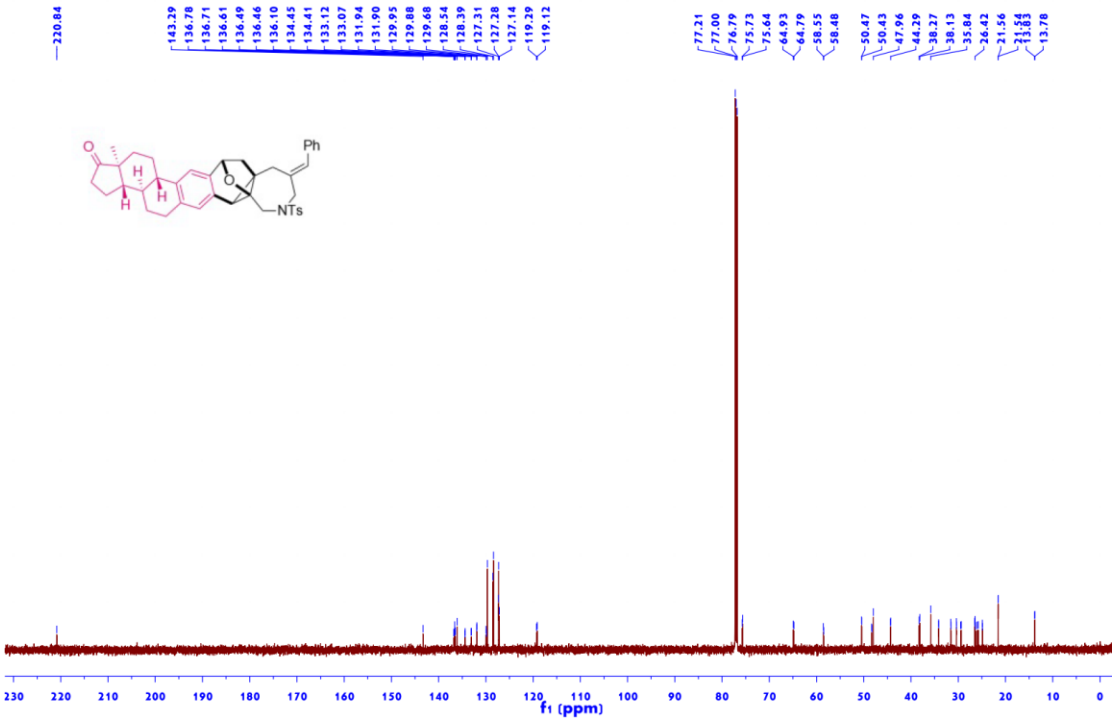


Figure S196 ^{1}H NMR (600 MHz, $CDCl_3$) of 3ad

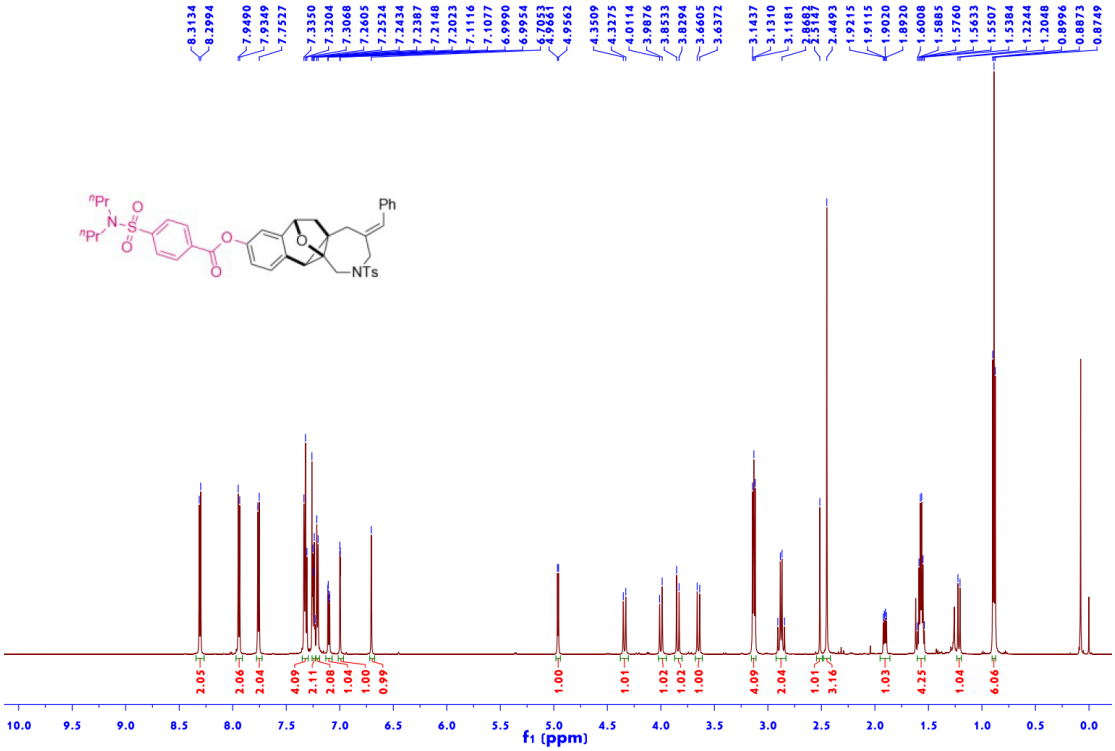


Figure S197 ^{13}C NMR (150 MHz, $CDCl_3$) of 3ad

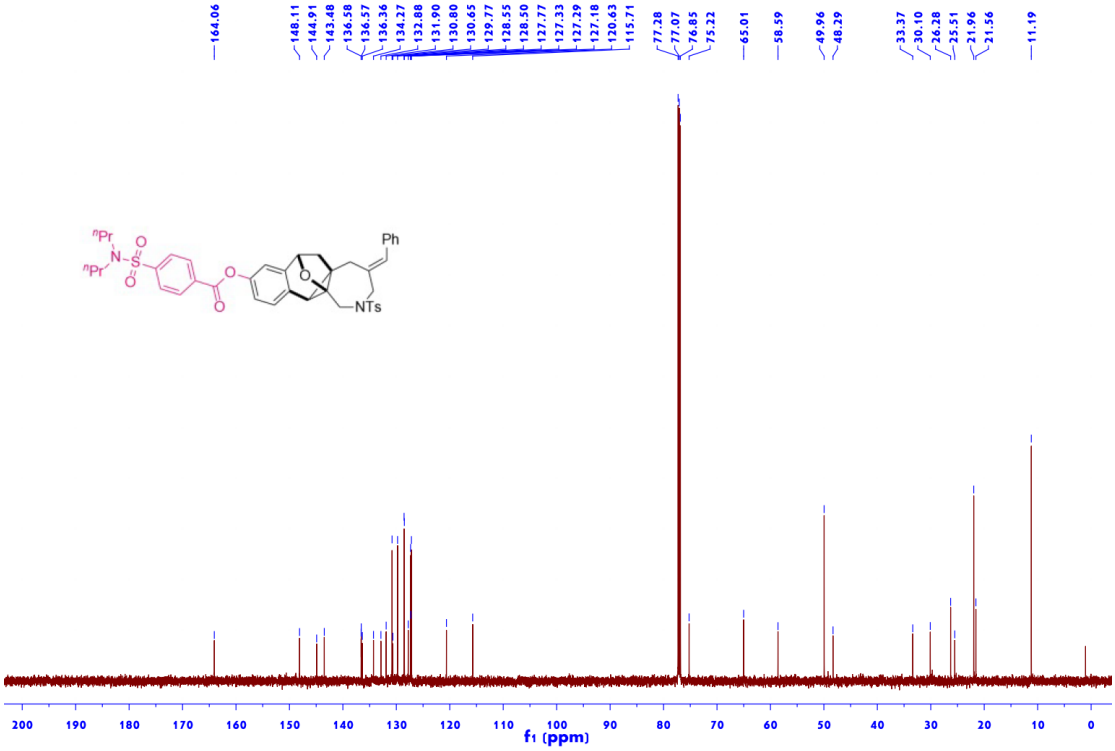


Figure S198 ^{1}H NMR (600 MHz, $CDCl_3$) of 3ae

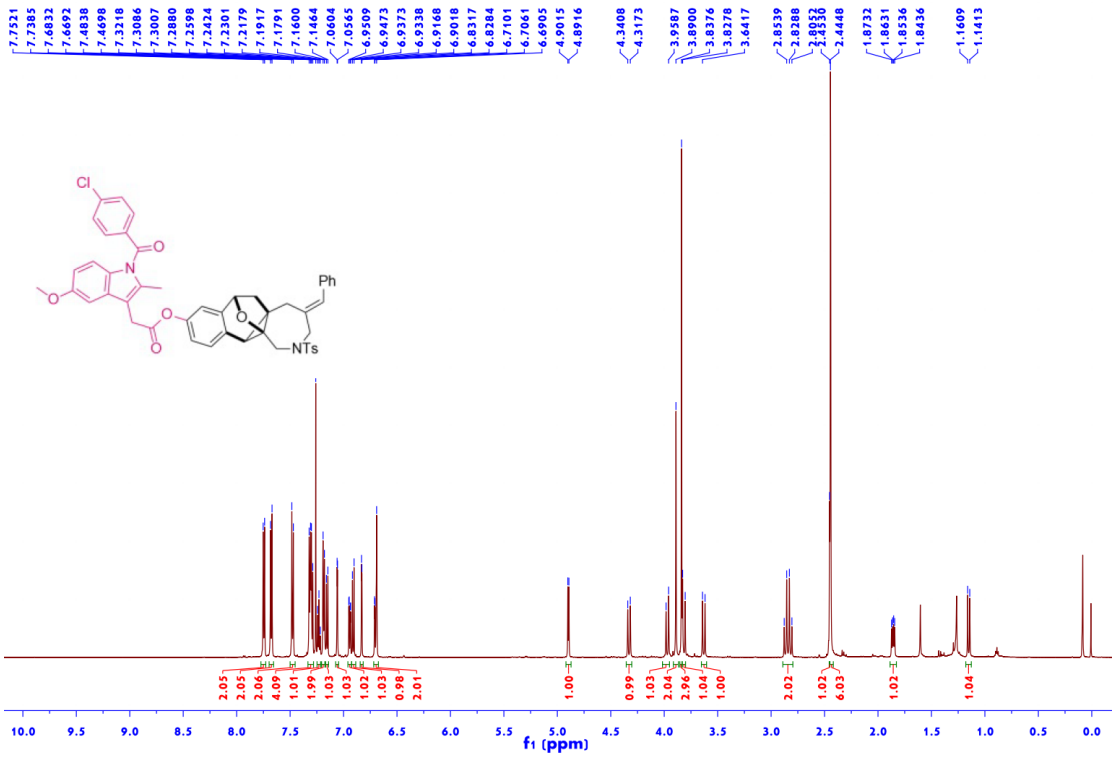


Figure S199 ^{13}C NMR (150 MHz, $CDCl_3$) of 3ae

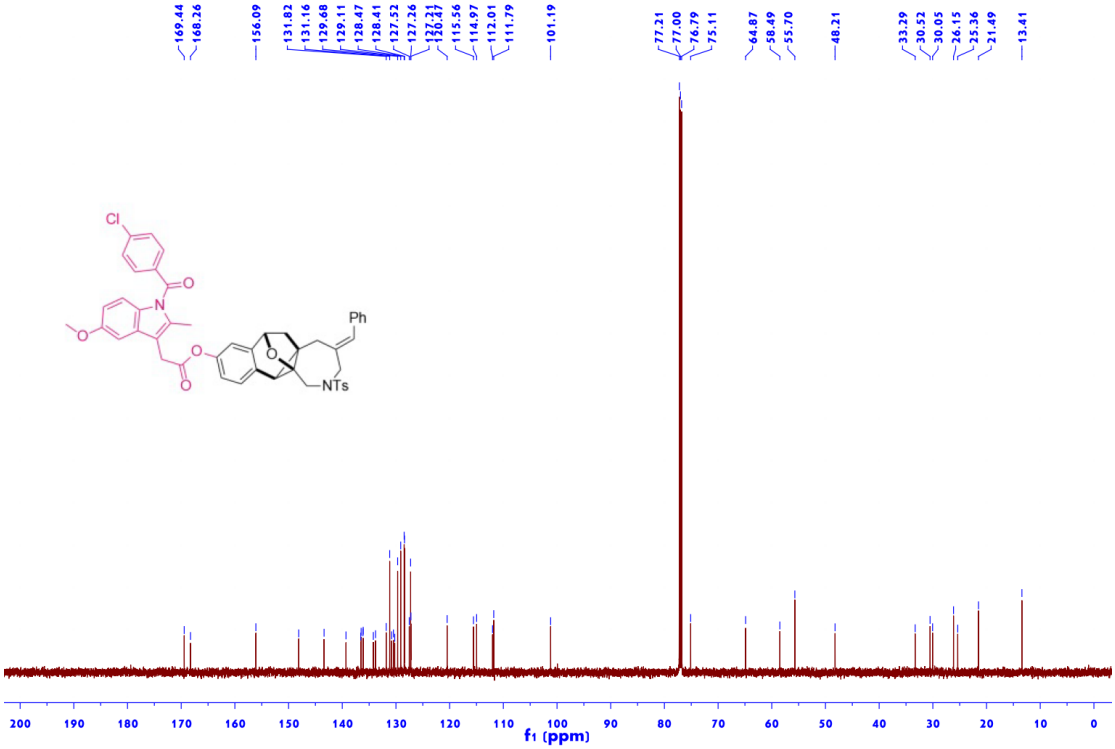


Figure S200 ^{1}H NMR (600 MHz, $CDCl_3$) of 3af

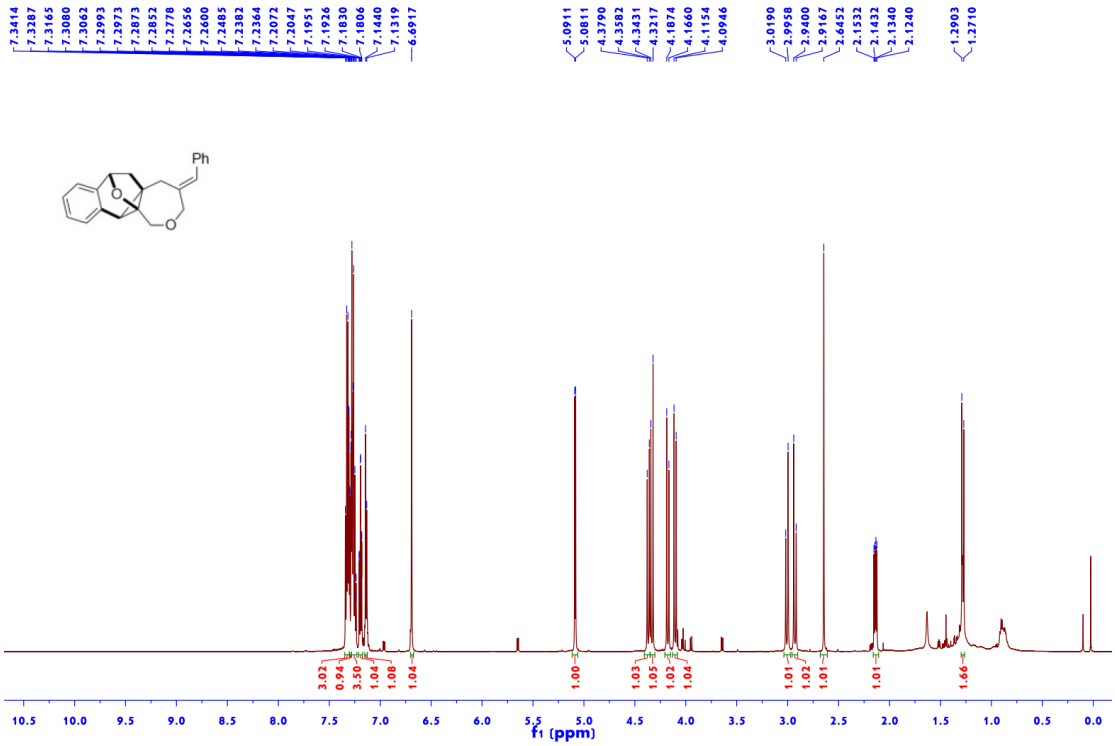


Figure S201 ^{13}C NMR (150 MHz, $CDCl_3$) of 3af

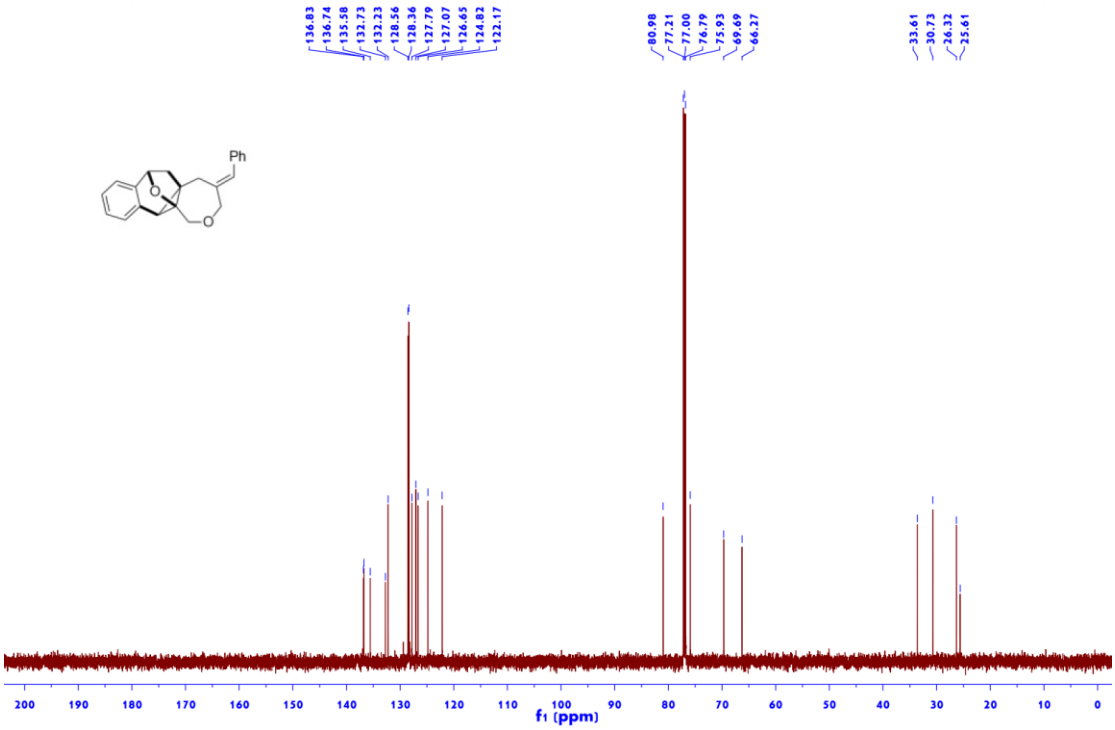


Figure S202 ^{1}H NMR (600 MHz, $CDCl_3$) of 4

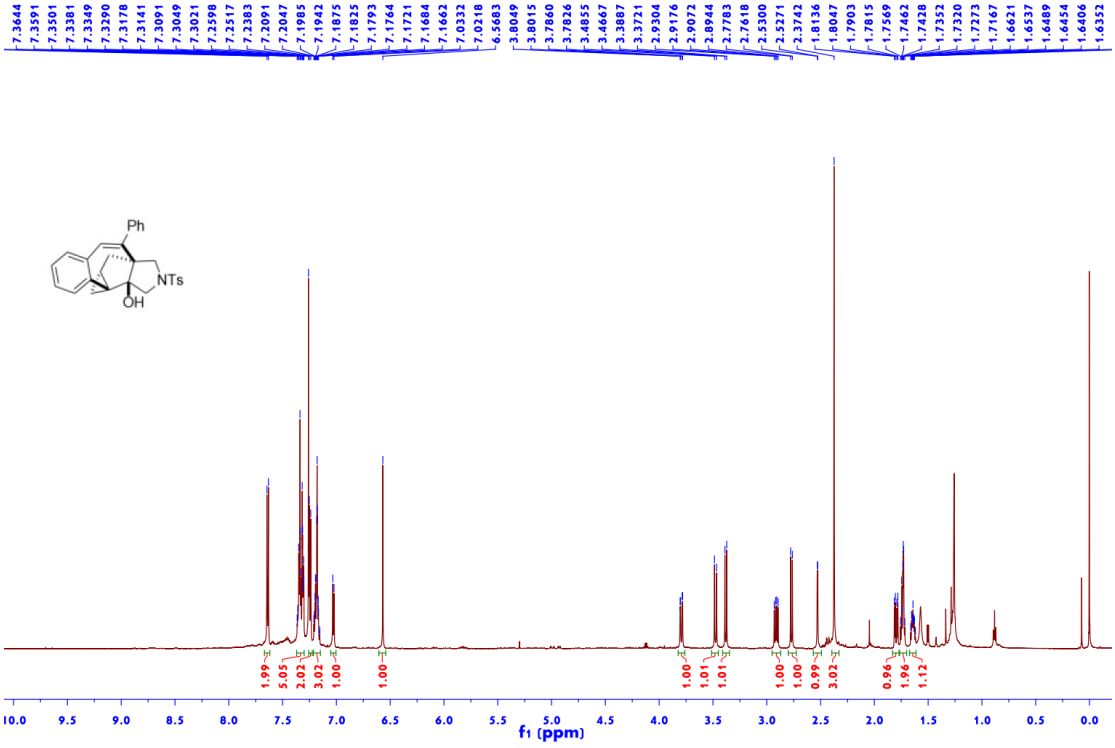


Figure S203 ^{13}C NMR (150 MHz, $CDCl_3$) of 4

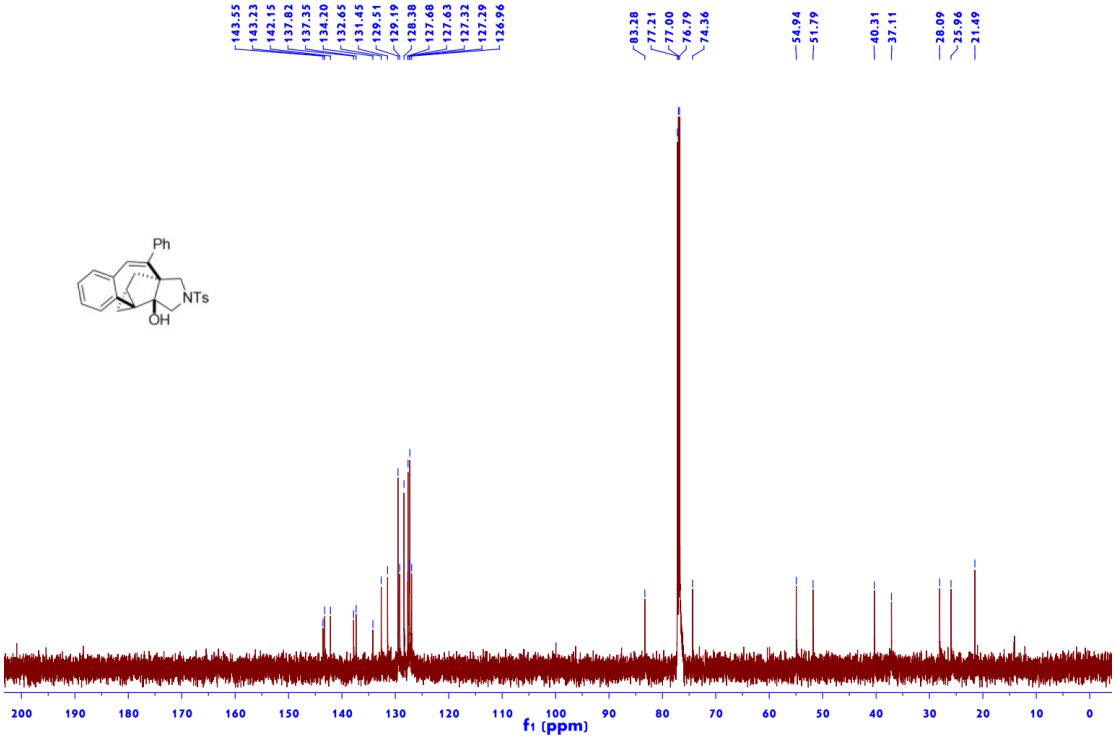


Figure S204 ^{1}H NMR (600 MHz, $CDCl_3$) of 5

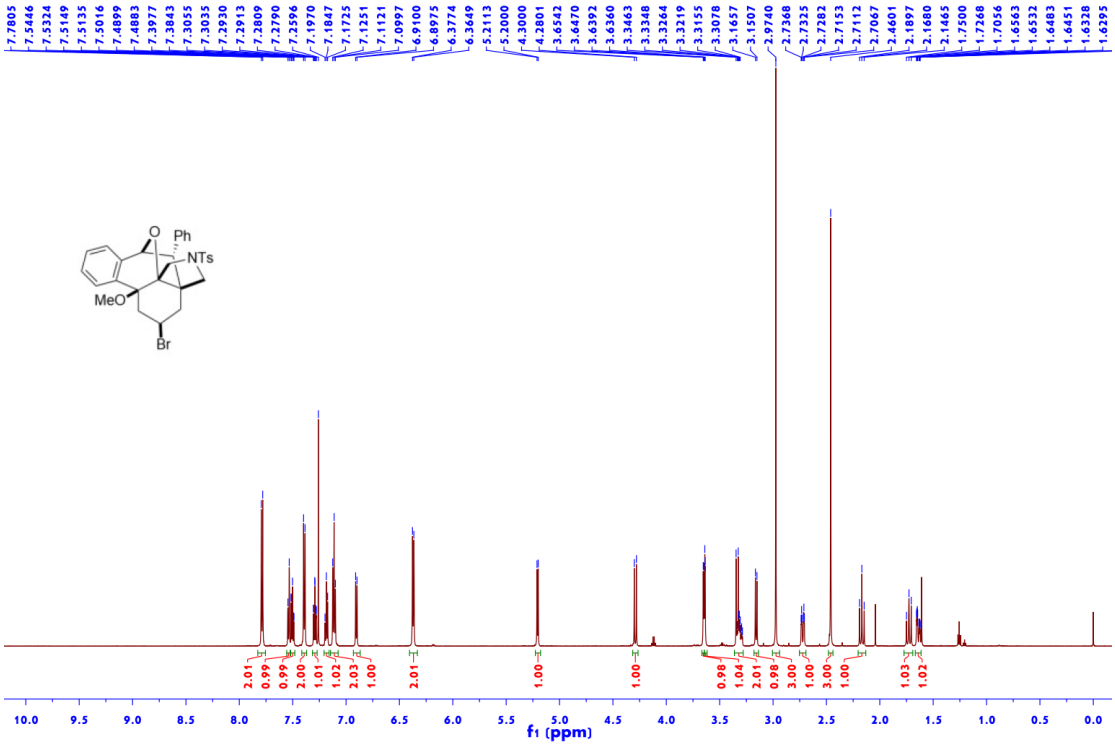


Figure S205 ^{13}C NMR (150 MHz, $CDCl_3$) of 5

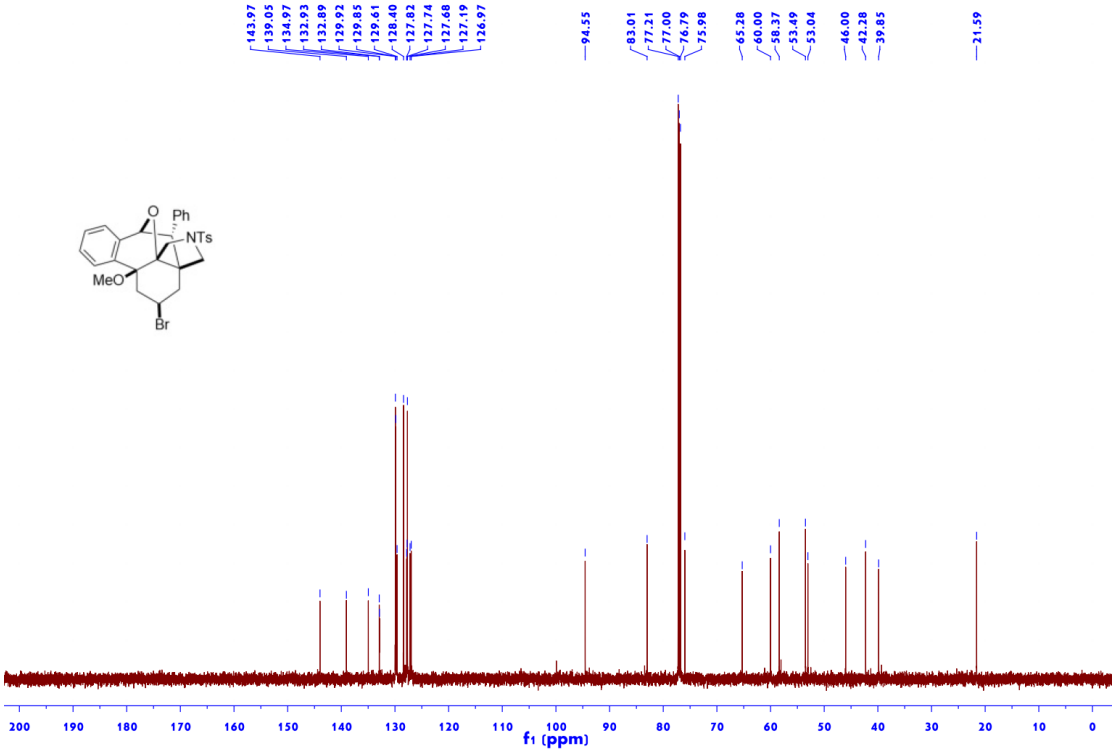


Figure S206 ^{1}H NMR (600 MHz, $CDCl_3$) of 6

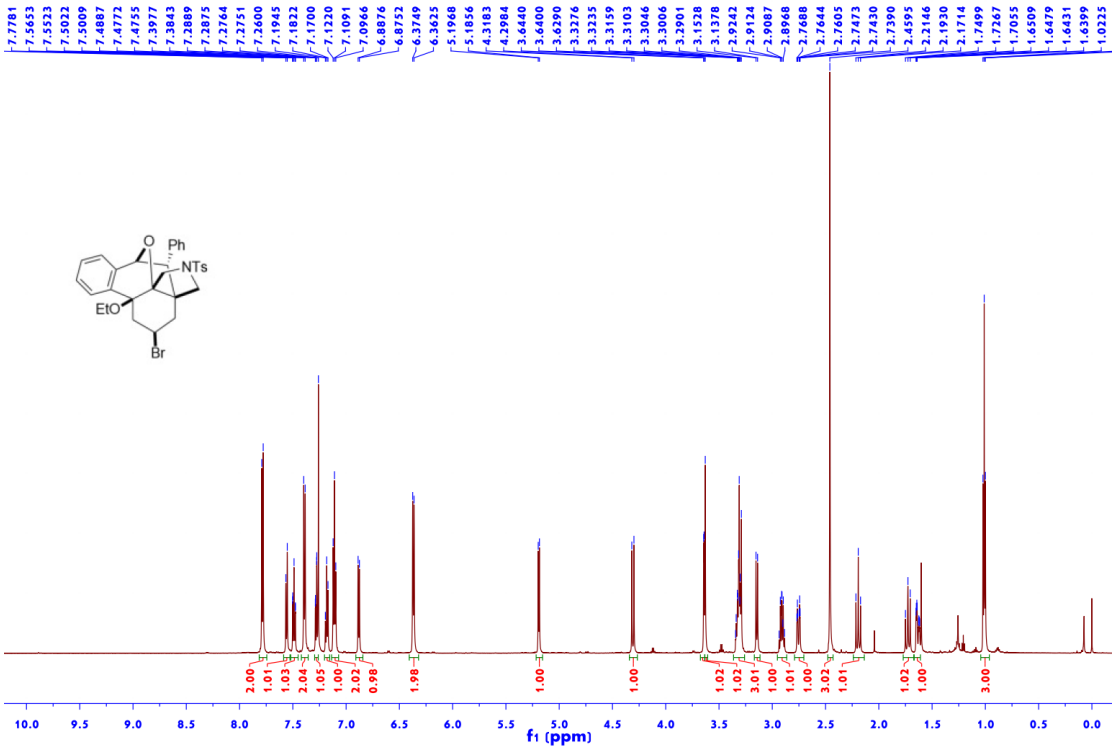


Figure S207 ^{13}C NMR (150 MHz, $CDCl_3$) of 6

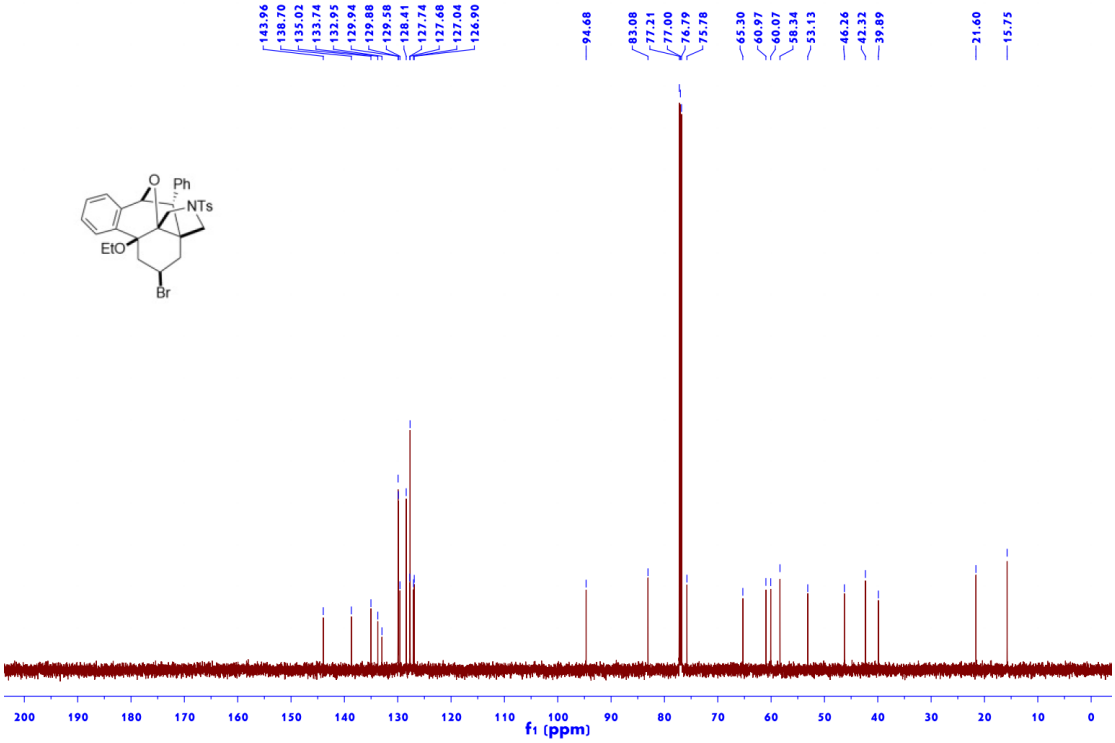


Figure S208 ^{1}H NMR (400 MHz, $CDCl_3$) of 7

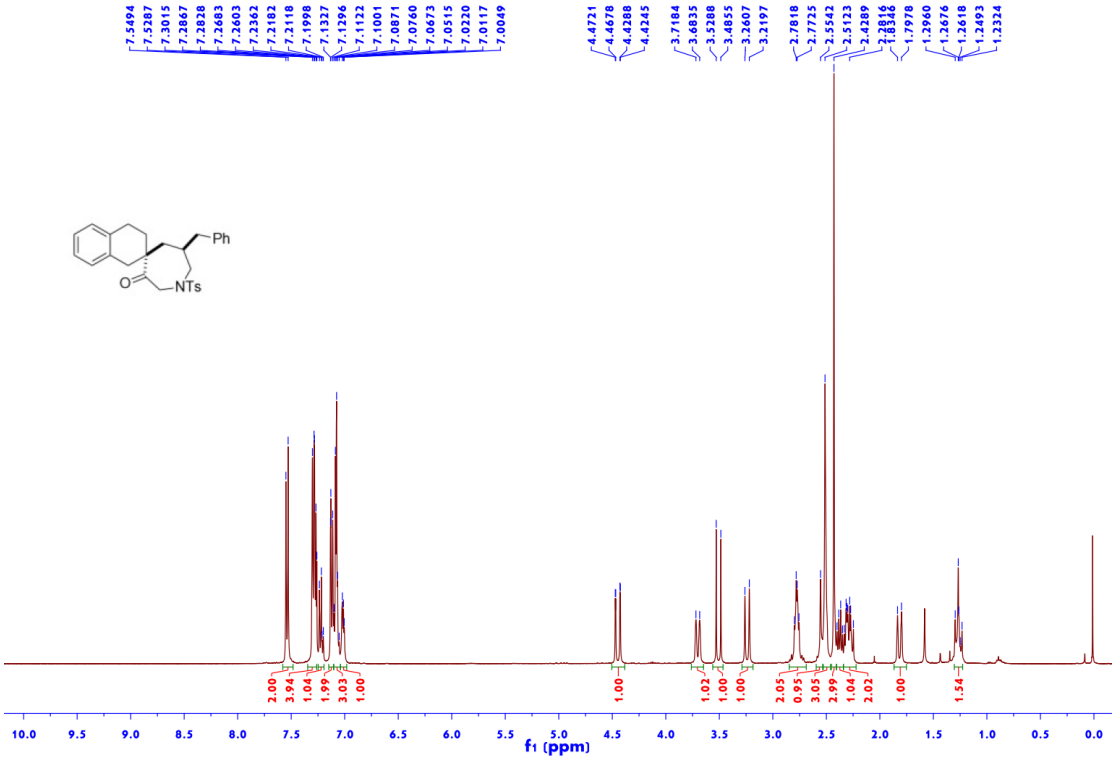


Figure S209 ^{13}C NMR (150 MHz, $CDCl_3$) of 7

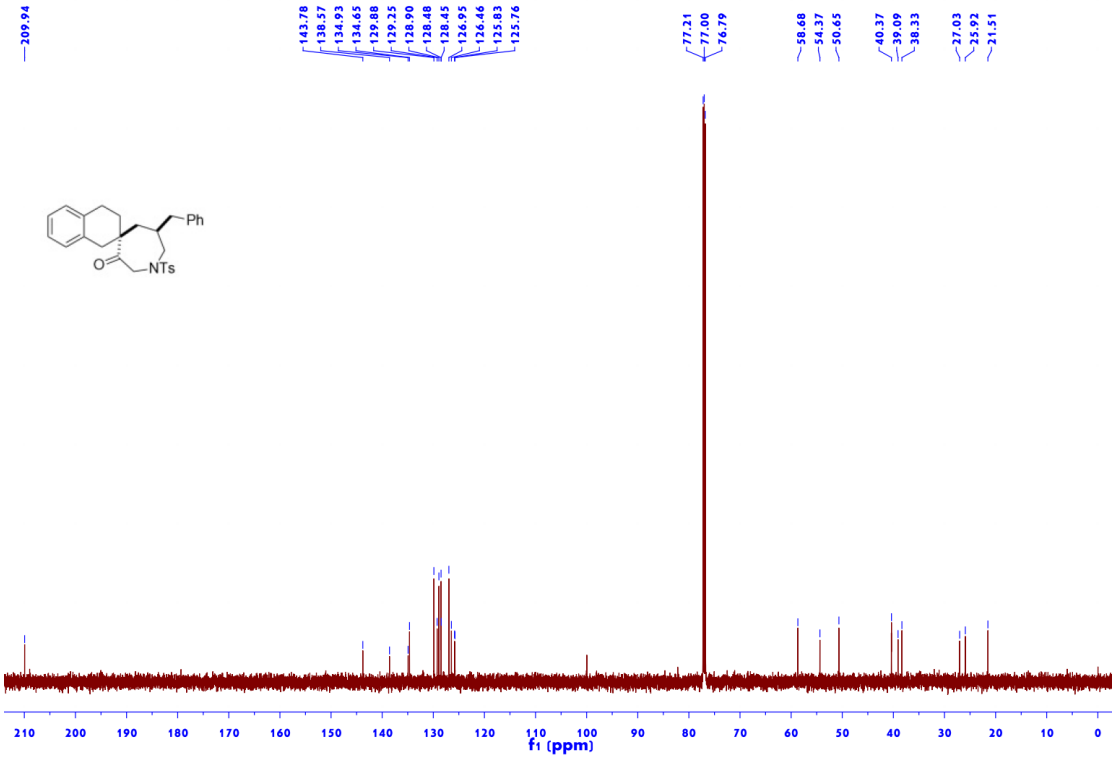


Figure S210 ^{1}H NMR (400 MHz, $CDCl_3$) of 7'

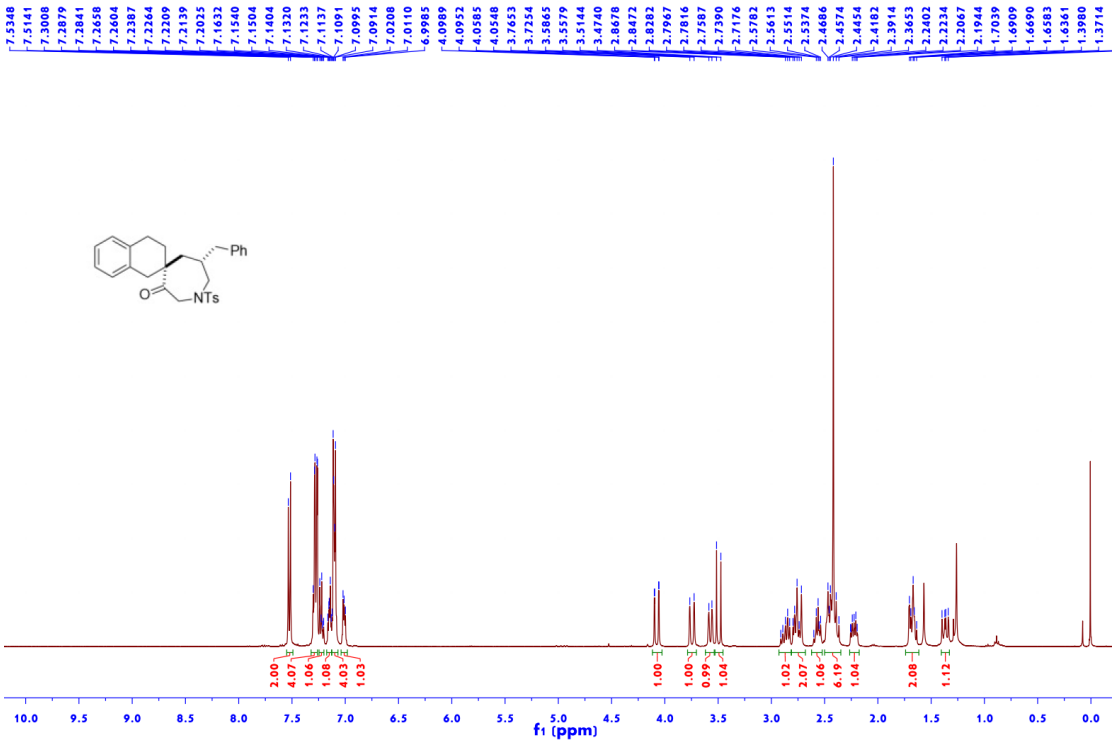
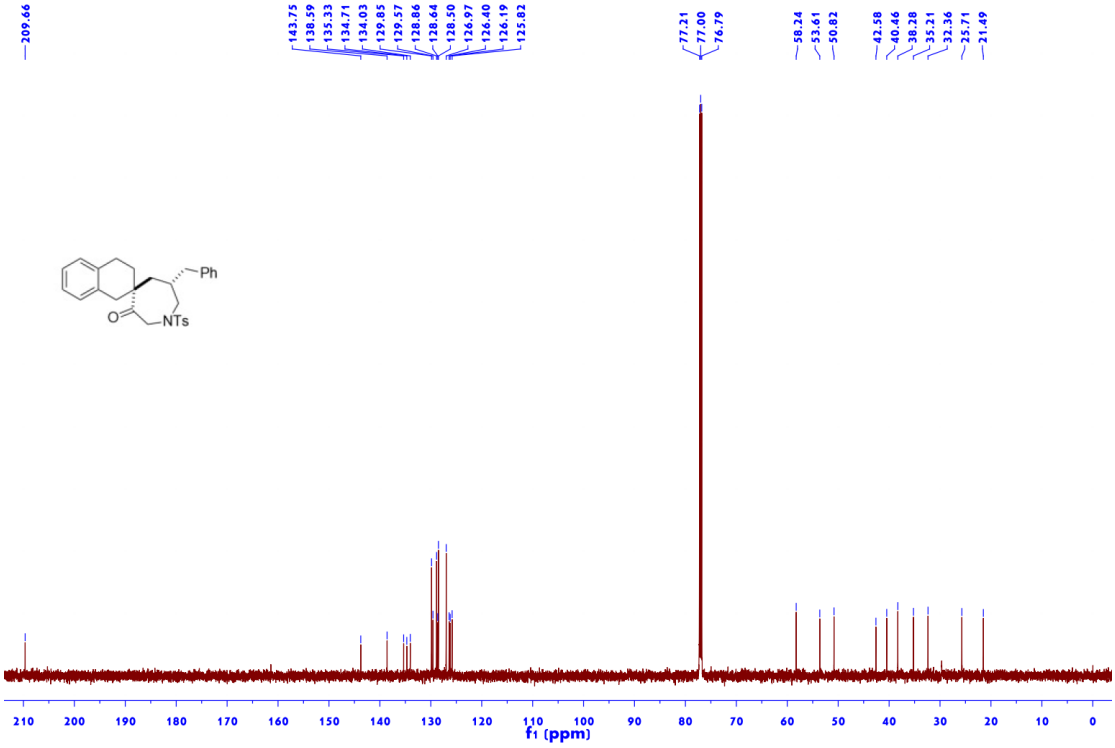


Figure S211 ^{13}C NMR (150 MHz, $CDCl_3$) of 7'



7. X-ray crystal structures of 2a, 3m, 4, 6, and 7'

Crystal preparation: Compound **2a**, **3m**, **4, 6** and **7'** (30 mg) were dissolved in hexane/EA = 9:1 (10 mL) in 25 mL round bottom flask and the resultant solution were allowed to slowly evaporate at room temperature to get pure crystals suitable for X-ray diffraction analysis. The intensity data were collected at 100 K or 150 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation. More information on crystal structures can also be obtained from the Cambridge Crystallographic Data Centre (CCDC) with deposition numbers 2174040 (**2a**), 2174041 (**3m**), 2174042 (**4**), 2174043 (**6**), and 2174044 (**7'**) respectively.

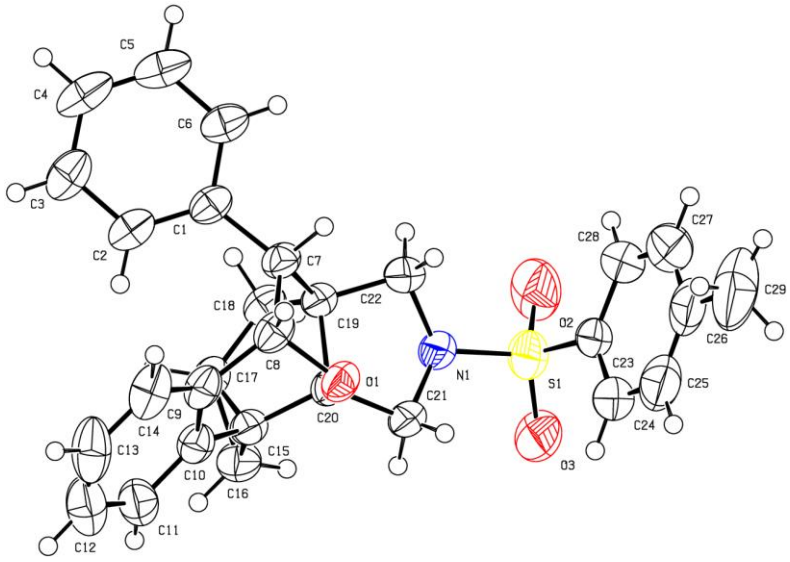


Figure S206. ORTEP Drawing of **2a** with Thermal Ellipsoids at 30% Probability Levels (CCDC 2174040).

Table S1 Crystal data and structure refinement for 2a.

Identification code	**2a**
Empirical formula	$C_{29}H_{27}NO_3S$
Formula weight	469.57
Temperature/K	293(2)
Crystal system	monoclinic
Space group	C2/c

a/Å	40.961(4)
b/Å	7.1221(7)
c/Å	16.3787(13)
α/°	90
β/°	94.020(8)
γ/°	90
Volume/Å^3	4766.4(7)
Z	8
ρ_{calc}g/cm^3	1.309
μ/mm^{-1}	0.168
F(000)	1984.0
Crystal size/mm^3	0.14 × 0.13 × 0.12
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.986 to 49.982
Index ranges	-48 ≤ h ≤ 42, -8 ≤ k ≤ 8, -19 ≤ l ≤ 19
Reflections collected	13061
Independent reflections	4165 [R_{int} = 0.0561, R_{sigma} = 0.0678]
Data/restraints/parameters	4165/7/308
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0560, wR_2 = 0.1137
Final R indexes [all data]	R_1 = 0.1028, wR_2 = 0.1395
Largest diff. peak/hole / e Å^{-3}	0.16/-0.27

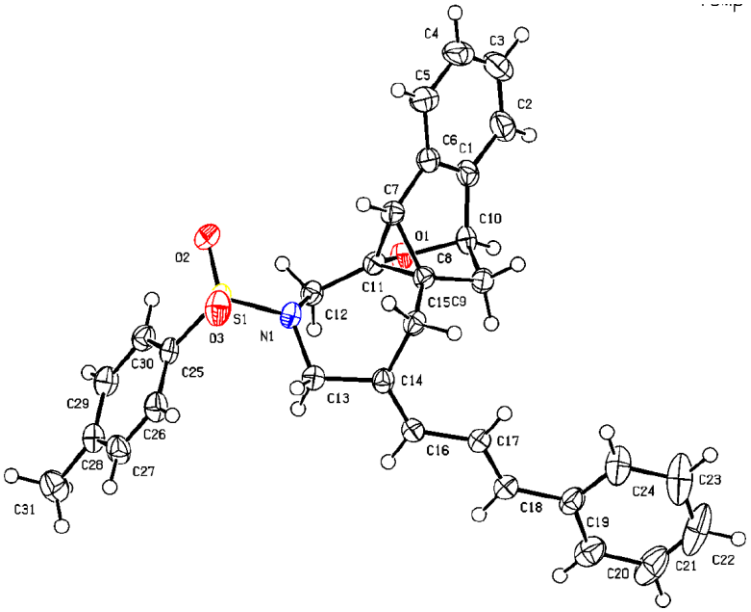


Figure S207. ORTEP Drawing of **3m** with Thermal Ellipsoids at 30% Probability Levels (CCDC 2174041).

Table S2 Crystal data and structure refinement for 3m.

Identification code	**3m**
Empirical formula	$C_{31}H_{29}NO_3S$
Formula weight	495.61
Temperature/K	179.99(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.9025(7)
b/Å	17.1335(8)
c/Å	13.3176(9)
α/°	90
β/°	108.457(7)
γ/°	90
Volume/Å^3	2576.2(3)
Z	4
ρ_{calc}g/cm^3	1.278

μ/mm^{-1}	0.159
F(000)	1048.0
Crystal size/mm^3	0.15 × 0.12 × 0.09
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.32 to 49.998
Index ranges	-14 ≤ h ≤ 14, -19 ≤ k ≤ 20, -15 ≤ l ≤ 12
Reflections collected	12542
Independent reflections	4542 [R_{int} = 0.0324, R_{sigma} = 0.0403]
Data/restraints/parameters	4542/0/326
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0427, wR_2 = 0.0996
Final R indexes [all data]	R_1 = 0.0542, wR_2 = 0.1066
Largest diff. peak/hole / e Å^{-3}	0.27/-0.33

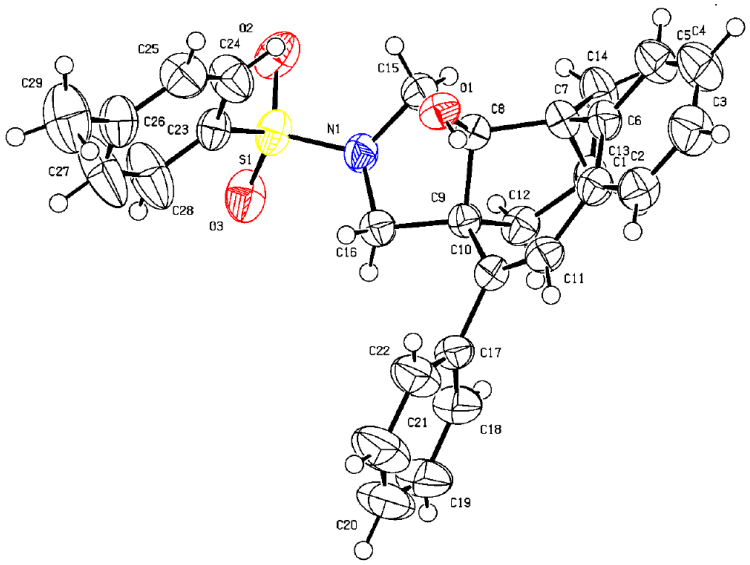


Figure S208. ORTEP Drawing of **4** with Thermal Ellipsoids at 30% Probability Levels (CCDC 2174042).

Table S3 Crystal data and structure refinement for 4.

Identification code	**4**
Empirical formula	$C_{29}H_{27}NO_3S$
Formula weight	469.57

Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	9.866(3)
b/Å	10.368(3)
c/Å	13.134(3)
α/°	67.204(6)
β/°	78.549(7)
γ/°	76.355(7)
Volume/Å^3	1194.8(6)
Z	2
ρ_{calc}g/cm^3	1.305
μ/mm^{-1}	0.167
F(000)	496.0
Crystal size/mm^3	0.14 × 0.11 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.132 to 50.05
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -15 ≤ l ≤ 15
Reflections collected	28658
Independent reflections	4187 [R_{int} = 0.0726, R_{sigma} = 0.0575]
Data/restraints/parameters	4187/0/304
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0521, wR_2 = 0.0956
Final R indexes [all data]	R_1 = 0.0938, wR_2 = 0.1129
Largest diff. peak/hole / e Å^{-3}	0.22/-0.23

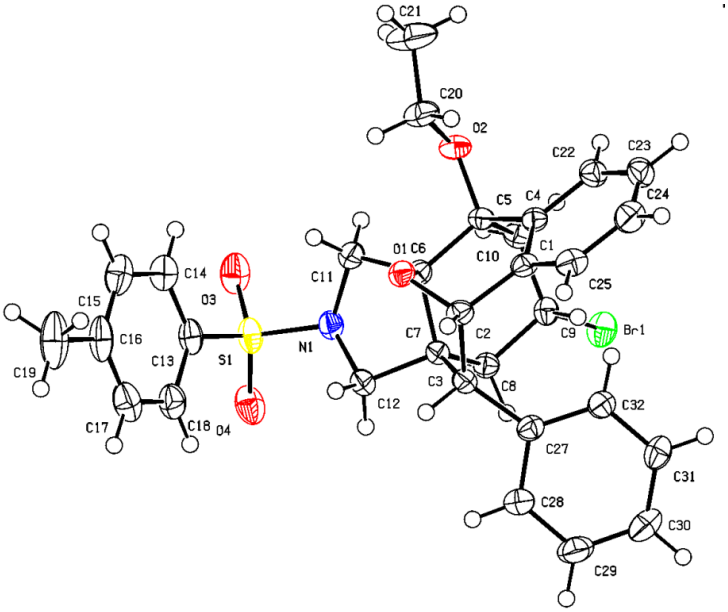


Figure S209. ORTEP Drawing of **6** with Thermal Ellipsoids at 30% Probability Levels (CCDC 2174043).

Table S4 Crystal data and structure refinement for 6.

Identification code	**6**
Empirical formula	$C_{31}H_{32}BrNO_4S$
Formula weight	594.54
Temperature/K	170.01(19)
Crystal system	monoclinic
Space group	I2/a
a/Å	15.7774(2)
b/Å	10.1799(2)
c/Å	41.4812(7)
α/°	90
β/°	97.329(2)
γ/°	90
Volume/Å^3	6607.96(19)
Z	8
ρ_{calc}g/cm^3	1.195

μ/mm^{-1}	2.538
F(000)	2464.0
Crystal size/mm^3	0.15 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.596 to 148.546
Index ranges	-19 ≤ h ≤ 11, -11 ≤ k ≤ 12, -47 ≤ l ≤ 51
Reflections collected	13010
Independent reflections	6548 [R_{int} = 0.0299, R_{sigma} = 0.0373]
Data/restraints/parameters	6548/0/345
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0380, wR_2 = 0.1048
Final R indexes [all data]	R_1 = 0.0418, wR_2 = 0.1085
Largest diff. peak/hole / e Å^{-3}	0.33/-0.58

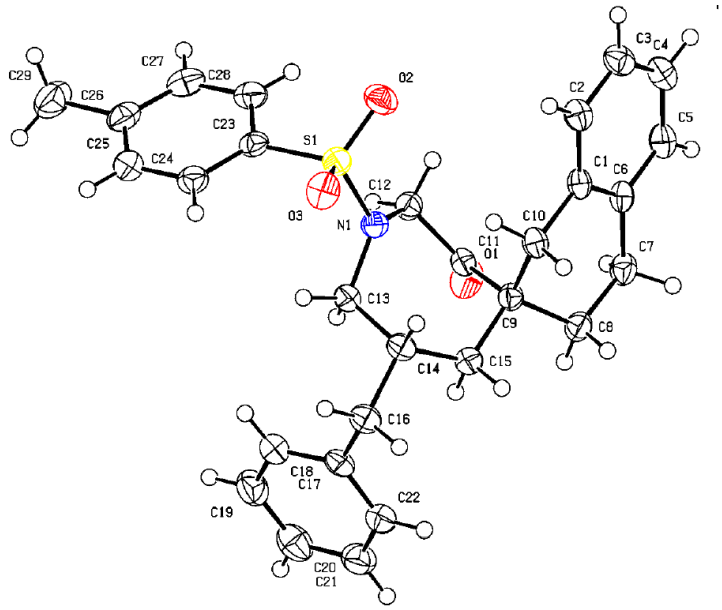


Figure S210. ORTEP Drawing of **7'** with Thermal Ellipsoids at 30% Probability Levels (CCDC 2174044).

Table S5 Crystal data and structure refinement for 7'.

Identification code	**7'**
Empirical formula	$C_{29}H_{31}NO_3S$
Formula weight	473.61
Temperature/K	200.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.5942(2)
b/Å	10.2077(2)
c/Å	13.7721(3)
α/°	85.391(2)
β/°	77.094(2)
γ/°	66.714(2)
Volume/Å^3	1207.56(5)
Z	2
ρ_{calc}g/cm^3	1.303
μ/mm^{-1}	1.438
F(000)	504.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.584 to 143.25
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 12, -12 ≤ l ≤ 16
Reflections collected	11822
Independent reflections	4575 [R_{int} = 0.0117, R_{sigma} = 0.0130]
Data/restraints/parameters	4575/0/308
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0349, wR_2 = 0.0920

Final R indexes [all data]	R_1 = 0.0356, wR_2 = 0.0926
Largest diff. peak/hole / e Å^{-3}	0.23/-0.47

8. References

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