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for

Direct Construction of Biaryl-Bridged 8–11 Membered *N*-Heterocycles via Gold(I)-Catalyzed Intramolecular [4 + 2] Benzannulation of *N*-Tethered Diynyl Benzaldehydes

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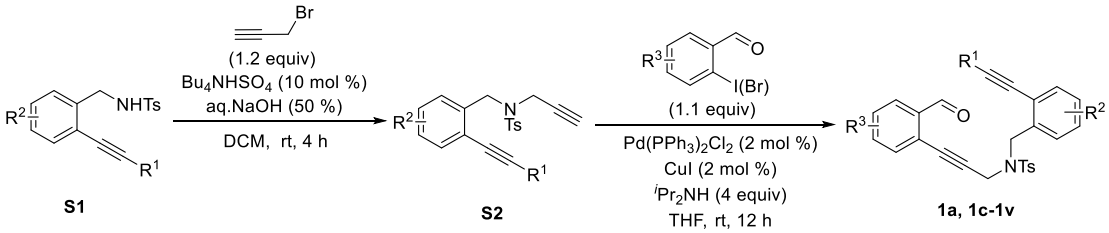
1. General information

THF and toluene were dried using Na/benzophenone, DCE was dried using CaH_2. Analytical thin layer chromatography (TLC) was performed using pre-coated silica gel plate. Visualization was achieved by UV light (254 nm). Flash 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 with either a Bruker AVQ-600 or 400 spectrometer instrument 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 Finnigan MAT95XP LC/HRMS TOF spectrometer using simultaneous electrospray (ESI). Melting points were determined using a digital melting point apparatus (MPA-100).

2. Preparation and characterization of starting materials

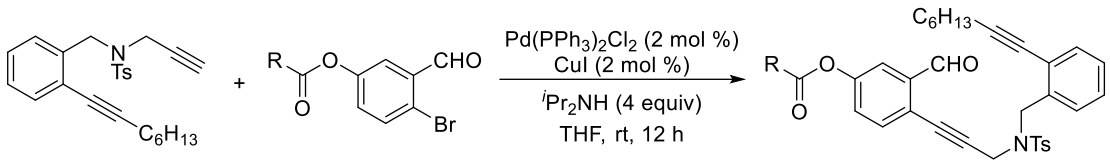
2.1. General Procedure A



Step 1: To a 50 mL round-bottom flask equipped with a stirring bar were added **S1** (2 mmol, 1 equiv),[S1] tetrabutylammonium hydrogen sulfate (0.2 mmol, 0.1 equiv), propargyl bromide (2.4 mmol, 1.2 equiv), 50% aqueous NaOH (2 mL) and DCM (6 mL), and the reaction mixture was allowed to stir at room temperature for 4 h until full consumption of **S1** (as indicated by TLC). The resulting mixture was quenched with water (3 mL) and extracted with DCM, 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 **S2**.

Step 2: To an oven-dried round-bottom flask equipped with a stirring bar were added 2-iodo(bromo)-benzaldehyde derivatives (1.1 equiv), **S2** (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. **S2** (if liquid, dissolved in THF and added at last 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** and **1c-1v.**

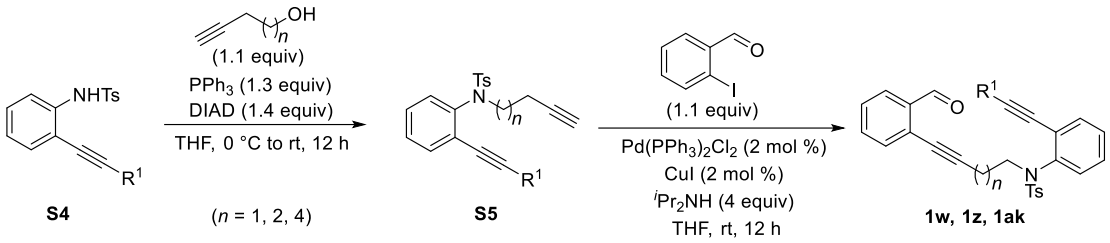
2.2. General Procedure B



S2f **S3** **1x-1y**

The 2-bromo-benzaldehyde derivatives **(S3)** was prepared according to the literature procedure.[S2] To an oven-dried round-bottom flask equipped with a stirring bar were added **S3** (1.1 equiv), **S2f** (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). 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 **1x-1y.**

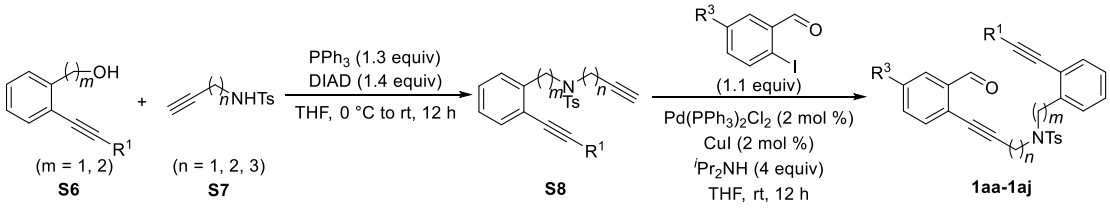
2.3. General Procedure C



Step 1: The Ts-protected 2-(phenylethynyl)aniline **(S4)** was prepared according to the literature procedure.[S3] To a solution of **S4** (1.0 equiv), triphenylphosphine (1.3 equiv) and alkynol (1.1 equiv) in anhydrous THF (0.4 M) at 0 ℃ was added diisopropyl azodicarboxylate (DIAD, 1.4 equiv) dropwise. The mixture was warmed to room temperature and stirred for 12 h until full consumption of the starting material (monitored by TLC). The mixture was concentrated and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford **S5**.

Step 2: To an oven-dried round-bottom flask equipped with a stirring bar were added 2-iodo-benzaldehyde (1.1 equiv), **S5** (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 **1w, 1z and 1ak.**

2.4. General Procedure D

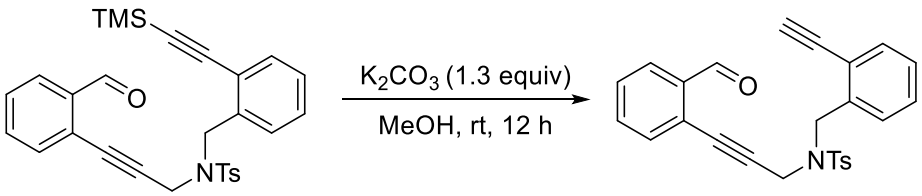


Step 1: S6 and **S7** were prepared according to the literature procedure.[S4-S7] To a solution of triphenylphosphine (1.3 equiv), **S6** (1.0 equiv) and alkyneamine **S7** (1.2 equiv) in anhydrous THF (0.4 M) at 0 ℃ was added diisopropyl azodicarboxylate (DIAD, 1.4 equiv) dropwise. The mixture was warmed to room temperature and stirred

for 12 h until full consumption of the starting material (monitored by TLC). The mixture was concentrated and the residue was purified by 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 °C. 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 **1aa-1aj.**

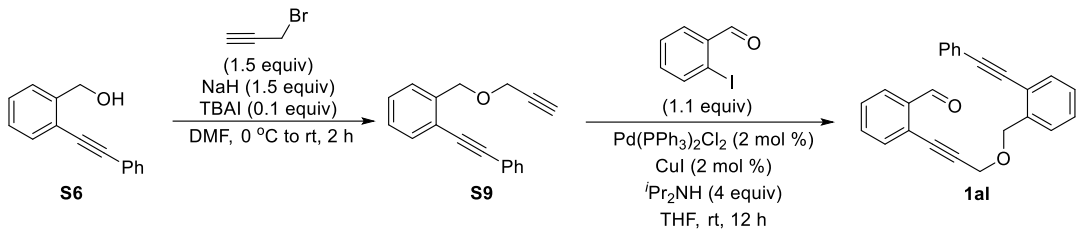
2.5. General Procedure E



1c **1b**

To a stirred solution of **1c** (1 mmol, 1 equiv) in MeOH (4 mL) was added K_2CO_3 (1.3 mmol, 1.3 equiv) at room temperature. The reaction mixture was stirred for 12 h and then concentrated in vacuo. The crude residue was washed with water 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 purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford the desired terminal alkyne **1b**.

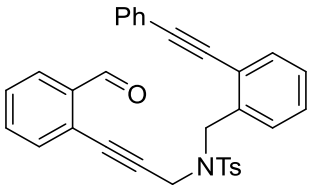
2.6. General Procedure F



Step 1: To a 25 mL oven-dried round-bottom flask equipped with a stirring bar were added **S6** (2 mmol, 1 equiv), and tetrabutylammonium iodide (0.2 mmol, 0.1 equiv) in dry DMF (0.2 M) was added NaH (60% w/w, 3 mmol, 1.5 equiv) under an argon atmosphere at 0 °C. When most of the evolution of H_2 gas had passed, propargyl bromide (3 mmol, 1.5 equiv) was added and the resulting reaction mixture was brought to room temperature and stirred for 2 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 water and 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 **S9**.

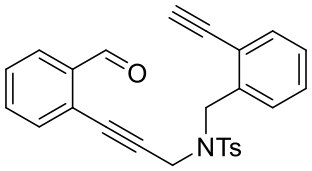
Step 2: To an oven-dried round-bottom flask equipped with a stirring bar were added 2-iodo-benzaldehyde (1.1 equiv), **S9** (1.0 equiv), $Pd(PPh_3)_2Cl_2$ (2 mol %) and CuI (2 mol %) in anhydrous THF (0.2 M) was added diisopropylamine ($^iPr_2NH$, 4.0 equiv) under an argon atmosphere at 0 °C. The reaction 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 the desired diyne **1al**.

***N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methyl-*N*-(2-(phenylethynyl)benzyl) benzenesulfonamide (1a)**



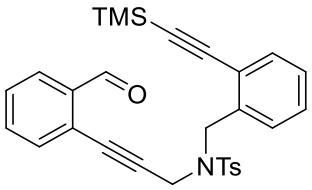
The title compound was prepared according to general procedure **A** in 59% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 10:1) to afford **1a** as a pale-yellow solid, mp 118–120 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.78 (s, 1H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.73–7.68 (m, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.56–7.52 (m, 1H), 7.39 (td, *J* = 7.6, 1.1 Hz, 1H), 7.33–7.28 (m, 5H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.20–7.16 (m, 1H), 7.10 (t, *J* = 7.6 Hz, 2H), 7.06–7.03 (m, 1H), 4.78 (s, 2H), 4.31 (s, 2H), 2.28 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.5, 143.9, 136.5, 135.9, 135.7, 133.3, 133.2, 132.5, 131.4, 129.7, 129.1, 129.0, 128.6, 128.3, 128.1, 128.0, 127.8, 126.7, 125.6, 123.1, 122.6, 94.4, 89.2, 86.7, 81.6, 48.6, 37.1, 21.4; **HRMS (ESI)** calcd for $C_{32}H_{26}NO_3S$ $[M+H]^+$: 504.1628; found: 504.1635.

***N*-(2-ethynylbenzyl)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methyl-benzenesulfonamide (1b)**



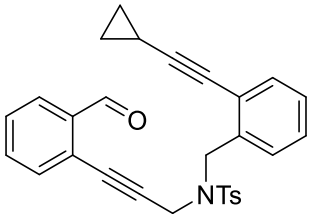
The title compound was prepared according to general procedure **A** and **E** in 47% yield over 3 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 10:1) to afford **1b** as a pale-yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.91 (s, 1H), 7.87–7.80 (m, 3H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.52–7.46 (m, 2H), 7.44–7.38 (m, 2H), 7.31–7.27 (m, 1H), 7.25-7.24 (m, 3H), 4.71 (s, 2H), 4.27 (s, 2H), 3.20 (s, 1H), 2.25 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.9, 144.0, 137.3, 135.8, 135.8, 133.5, 133.3, 133.0, 129.7, 129.5, 128.8, 128.6, 127.9, 127.7, 126.8, 125.9, 121.7, 89.2, 82.5, 81.6, 81.0, 48.4, 37.2, 21.3; **HRMS (ESI)** calcd for $C_{26}H_{22}NO_3S$ $[M+H]^+$: 428.1315; found: 428.1316.

***N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methyl-*N*-(2-((trimethylsilyl)ethynyl) benzyl)benzenesulfonamide (1c)**



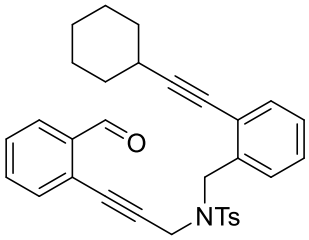
The title compound was prepared according to general procedure **A** in 67% yield over 2 steps.. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 12:1) to afford **1c** as a yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.92–9.77 (m, 1H), 7.84–7.79 (m, 3H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.47–7.42 (m, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.33 (td, *J* = 7.7, 1.1 Hz, 1H), 7.24–7.20 (m, 3H), 7.15 (d, *J* = 7.4 Hz, 1H), 4.68 (s, 2H), 4.31 (s, 2H), 2.26 (s, 3H), 0.07 (s, 9H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.5, 143.8, 136.9, 135.7, 135.7, 133.3, 133.2, 132.7, 129.6, 128.9, 128.7, 127.9, 127.6, 127.5, 126.7, 125.6, 122.5, 101.9, 100.1, 89.0, 81.3, 48.7, 37.3, 21.2, -0.4; **HRMS (ESI)** calcd for $C_{29}H_{30}NO_3SSi$ $[M+H]^+$: 500.1710; found: 500.1719.

***N*-(2-(cyclopropylethynyl)benzyl)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1d)**



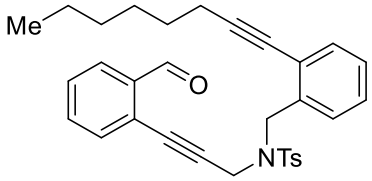
The title compound was prepared according to general procedure **A** in 66% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 10:1) to afford **1d** as a yellow solid, mp 94–96 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.87 (s, 1H), 7.85-7.82 (m, 3H), 7.53-7.50 (m, 2H), 7.41-7.38 (dd, 2H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.25–7.18 (m, 4H), 4.64 (s, 2H), 4.26 (s, 2H), 2.28 (s, 3H), 1.31–1.18 (m, 1H), 0.84–0.50 (m, 4H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.6, 143.8, 136.1, 135.7, 135.6, 133.4, 133.3, 132.3, 129.5, 128.6, 128.5, 127.8, 127.6, 127.6, 126.6, 125.7, 123. 7, 98.8, 89.2, 81.4, 73.0, 48.5, 36.9, 21.2, 8.5, 0.1; **HRMS (ESI)** calcd for $C_{29}H_{26}NO_3S$ $[M+H]^+$:468.1628; found: 468.1631.

***N*-(2-(cyclohexylethynyl)benzyl)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1e)**



The title compound was prepared according to general procedure **A** in 59% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 12:1) to afford **1e** as a colorless solid, mp 112–114 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.84 (s, 1H), 7.85-7.83 (m, 3H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.30–7.17 (m, 4H), 4.70 (s, 2H), 4.33 (s, 2H), 2.41–2.34 (m, 1H), 2.32 (s, 3H), 1.77–1.63 (m, 2H), 1.63–1.50 (m, 2H), 1.49–1.39 (m, 1H), 1.38–1.23 (m, 2H), 1.23–1.05 (m, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 190.7, 143.9, 136.3, 136.0, 135.8, 133.4, 133.3, 132.3, 129.6, 128.7, 128.2, 128.0, 127.7, 127.6, 126.8, 125.9, 123.7, 100.0, 89.5, 81.3, 77.7, 48.6, 37.1, 32.4, 29.7, 25.6, 24.8, 21.4; **HRMS (ESI)** calcd for $C_{32}H_{32}NO_3S$ $[M+H]^+$: 510.2097; found: 510.2097.

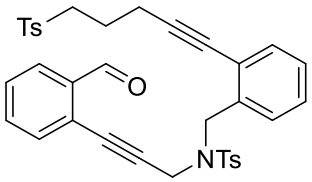
***N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-*N*-(2-(hept-1-yn-1-yl)benzyl)-4-methyl-benzenesulfonamide (1f)**



The title compound was prepared according to general procedure **A** in 53% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 10:1) to afford **1f** as a pale-yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.84 (d, *J* = 0.6 Hz, 1H), 7.88–7.80 (m, 3H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.48 (td, *J* = 7.6, 1.4 Hz, 1H), 7.43–7.37 (m, 2H), 7.31 (td, *J* = 7.6, 1.2 Hz, 1H), 7.25-7.22 (m, 3H), 7.21 (d, *J* = 7.7 Hz, 1H), 4.67 (s, 2H), 4.28 (s, 2H), 2.28 (s, 3H), 2.19 (t, *J* = 7.3 Hz, 2H), 1.45–1.34 (m, 2H), 1.29–1.18 (m, 4H), 1.16-1.14 (m, 2H), 0.84 (t, *J* = 7.3

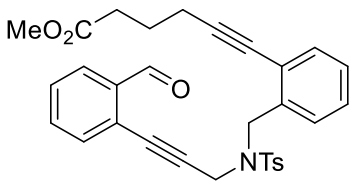
Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.6, 143.8, 136.3, 136.0, 135.8, 133.4, 133.3, 132.4, 129.6, 128.7, 128.5, 128.0, 127.7, 127.7, 126.8, 125.9, 123.8, 96.0, 89.5, 81.4, 77.8, 48.6, 37.0, 31.2, 28.6, 28.5, 22.4, 21.3, 19.4, 14.0; **HRMS (ESI)** calcd for $C_{32}H_{34}NO_3S$ $[M+H]^+$: 512.2254; found: 512.2255.

***N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methyl-*N*-(2-(5-tosylpent-1-yn-1-yl)benzyl)benzenesulfonamide (1g)**



The title compound was prepared according to general procedure **A** in 55% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15:1 to 4:1) to afford **1g** as a pale-yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.82 (s, 1H), 7.85–7.78 (m, 3H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.52–7.46 (m, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.26–7.21 (m, 3H), 7.19 (d, *J* = 7.7 Hz, 1H), 4.59 (s, 2H), 4.20 (s, 2H), 3.22–3.12 (m, 2H), 2.42 (s, 3H), 2.39 (t, *J* = 6.9 Hz, 2H), 2.25 (s, 3H), 1.94–1.85 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.6, 144.6, 143.9, 136.2, 136.0, 135.7, 135.6, 133.6, 133.3, 132.7, 129.9, 129.7, 128.9, 128.8, 128.4, 128.0, 127.9, 127.7, 126.9, 125.7, 123.3, 93.3, 89.2, 81.6, 79.3, 55.2, 48.8, 36.9, 21.9, 21.6, 21.3, 18.3; **HRMS (ESI)** calcd for $C_{36}H_{33}NNaO_5S_2$ $[M+Na]^+$: 646.1692; found: 646.1682.

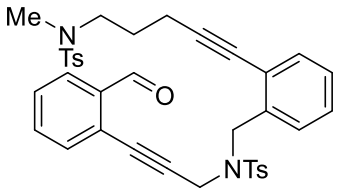
Methyl 6-(2-(((*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methylphenyl) sulfonamido)methyl)phenyl)hex-5-ynoate (1h)



The title compound was prepared according to general procedure **A** in 63% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 10:1) to afford **1h** as a pale-yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.83 (s, 1H), 7.84–7.81 (m, 3H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.5 Hz,

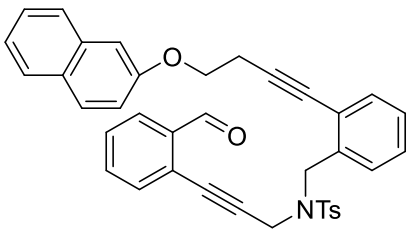
1H), 7.42–7.36 (m, 2H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.25–7.20 (m, 3H), 7.19 (d, *J* = 7.7 Hz, 1H), 4.64 (s, 2H), 4.25 (s, 2H), 3.61 (s, 3H), 2.34 (t, *J* = 7.4 Hz, 2H), 2.30 (t, *J* = 7.0 Hz, 2H), 2.25 (s, 3H), 1.81–1.72 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190. 6, 173.3, 143.8, 136.2, 135.8, 135.7, 133.5, 133.2, 132.5, 129.6, 128.7, 128.6, 128.2, 127.8, 127.7, 126.8, 125.7, 123.5, 94.5, 89.3, 81.4, 78.6, 51.4, 48.7, 37.0, 32.8, 23.7, 21.3, 18.8; **HRMS (ESI)** calcd for $C_{31}H_{30}NO_5S$ $[M+H]^+$: 528.1839; found: 528.1843.

***N*-(2-(5-((*N*,4-dimethylphenyl)sulfonamido)pent-1-yn-1-yl)benzyl)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1i)**



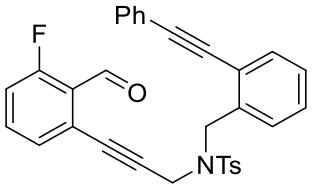
The title compound was prepared according to general procedure **A** in 64% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15:1 to 6:1) to afford **1i** as a pale-yellow solid, mp 92–94 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.85 (s, 1H), 7.83–7.82 (m, 3H), 7.65–7.59 (m, 2H), 7.54–7.46 (m, 2H), 7.39 (t, *J* = 7.1 Hz, 2H), 7.33–7.26 (m, 3H), 7.25–7.15 (m, 4H), 4.65 (s, 2H), 4.23 (s, 2H), 2.99 (t, *J* = 6.9 Hz, 2H), 2.64 (s, 3H), 2.38 (s, 3H), 2.31 (t, *J* = 7.1 Hz, 2H), 2.24 (s, 3H), 1.78–1.64 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.6, 143.8, 143.2, 136.2, 135.7, 135.6, 134.2, 133.6, 133.3, 132.5, 129.6, 129.5, 128.7, 128.6, 128.1, 127.7, 127.6, 127.2, 126.8, 125.6, 123.5, 94.5, 89.2, 81.4, 78.4, 49.1, 48.7, 36.9, 34.8, 26.7, 21.3, 21.2, 16.6; **HRMS (ESI)** calcd for $C_{37}H_{37}N_2O_5S_2$ $[M+H]^+$: 653.2138; found: 653.2139.

***N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methyl-*N*-(2-(4-(naphthalen-2-yloxy)but-1-yn-1-yl)benzyl)benzenesulfonamide (1j)**



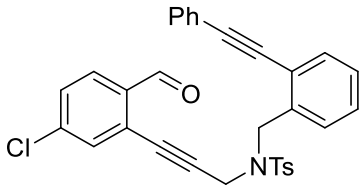
The title compound was prepared according to general procedure **A** in 57% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 12:1 to 10:1) to afford **1j** as a pale-yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.87 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.77–7.75 (m, 2H), 7.70 (dd, *J* = 8.2, 5.1 Hz, 2H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.36–7.26 (m, 4H), 7.17 (d, *J* = 7.8 Hz, 3H), 7.11–7.05 (m, 2H), 4.70 (s, 2H), 4.28 (s, 2H), 4.15 (t, *J* = 7.1 Hz, 2H), 2.84 (t, *J* = 7.1 Hz, 2H), 2.21 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.6, 156.3, 143.8, 136.4, 135.8, 135.7, 134.4, 133.4, 133.2, 132.7, 129.6, 129.3, 129.0, 128.9, 128.7, 128.4, 127.9, 127.7, 127.6, 126.9, 126.7, 126.3, 125.6, 123.6, 123.4, 118.7, 106.9, 91.6, 89.4, 81.5, 79.3, 65.9, 48.8, 37.0, 21.2, 20.5; **HRMS (ESI)** calcd for $C_{38}H_{32}NO_4S$ $[M+H]^+$: 598.2047; found: 598.2045.

***N*-(3-(3-fluoro-2-formylphenyl)prop-2-yn-1-yl)-4-methyl-*N*-(2-(phenylethynyl) benzyl)benzenesulfonamide (1k)**



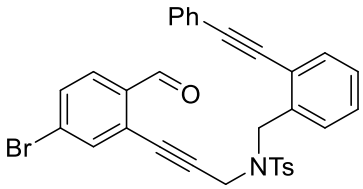
The title compound was prepared according to general procedure **A** in 46% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 12:1 to 10:1) to afford **1k** as a colorless solid, mp 119–120 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.87 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.34–7.28 (m, 3H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.22–7.16 (m, 2H), 7.13 (t, *J* = 7.5 Hz, 2H), 6.96 (t, *J* = 9.4 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 4.79 (s, 2H), 4.28 (s, 2H), 2.30 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 187.1, 162.0 (d, *J* = 263.0 Hz), 143.70, 136.40, 135.8, 134.2 (d, *J* = 10.5 Hz), 132.4, 131.3, 129.6, 129.1, 128.8, 128.2, 128.0, 127.9, 127.8, 126.0 (d, *J* = 3.4 Hz), 123.9 (d, *J* = 8.1 Hz), 123.1, 122.6, 116.8, 116.7, 94.2, 89.9, 86.7, 81.6 (d, *J* = 4.2 Hz), 48.5, 37.0, 21.3; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -115.96 (dd, *J* = 10.4, 5.4 Hz); **HRMS (ESI)** calcd for $C_{32}H_{24}FNNaO_3S$ $[M+Na]^+$: 544.1353; found: 544.1355.

***N*-(3-(5-chloro-2-formylphenyl)prop-2-yn-1-yl)-4-methyl-*N*-(2-(phenylethynyl) benzyl)benzenesulfonamide (1l)**



The title compound was prepared according to general procedure **A** in 44% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 10:1) to afford **1l** as a colorless solid, mp 134–136 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.74 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.34–7.31 (m, 3H), 7.25–7.22 (m, 3H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 2H), 6.90 (s, 1H), 4.77 (s, 2H), 4.30 (s, 2H), 2.38 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 189.3, 144.1, 139.6, 136.3, 135.9, 134.1, 132.9, 132.4, 131.3, 129.7, 129.2, 129.1, 129.0, 128.3, 128.1, 128.1, 128.1, 127.9, 126.9, 123.2, 122.5, 94.3, 90.5, 86.7, 80.4, 48.5, 36.9, 21.5; **HRMS (ESI)** calcd for $C_{32}H_{25}ClNO_3S$ $[M+H]^+$: 538.1238; found: 538.1218.

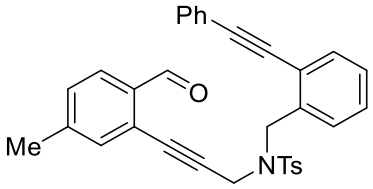
***N*-(3-(5-bromo-2-formylphenyl)prop-2-yn-1-yl)-4-methyl-*N*-(2-(phenylethynyl) benzyl)benzenesulfonamide (1m)**



The title compound was prepared according to general procedure **A** in 56% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 14:1) to afford **1m** as a colorless solid, mp 141–143 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.73 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.43–7.37 (m, 2H), 7.34–7.30 (m, 3H), 7.22 (d, *J* = 7.1 Hz, 2H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.14–7.05 (m, 3H), 4.77 (s, 2H), 4.30 (s, 2H), 2.39 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 189.5, 144.1, 136.3, 135.8, 135.7, 134.4, 132.4, 132.0, 131.2, 129.7, 129.2, 129.0, 128.3, 128.2, 128.1, 128.1, 128.0,

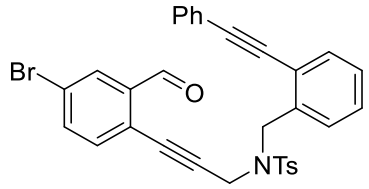
127.9, 127.0, 123.2, 122.5, 94.3, 90.6, 86.7, 80.2, 48.5, 36.9, 21.6; **HRMS (ESI)** calcd for $C_{32}H_{24}BrNNaO_3S$ $[M+Na]^+$: 604.0552; found: 604.0557.

***N*-(3-(2-formyl-5-methylphenyl)prop-2-yn-1-yl)-4-methyl-*N*-(2-(phenylethynyl) benzyl)benzenesulfonamide (1n)**



The title compound was prepared according to general procedure **A** in 41% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 14:1) to afford **1n** as a colorless solid, mp 141–143 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.73 (s, 1H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.68–7.58 (m, 2H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.34–7.27 (m, 3H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.7 Hz, 3H), 6.85 (s, 1H), 4.78 (s, 2H), 4.31 (s, 2H), 2.30 (s, 3H), 2.22 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.2, 144.3, 143.8, 136.5, 135.9, 133.6, 133.5, 132.4, 131.4, 129.6, 129.6, 129.0, 128.9, 128.2, 128.0, 127.9, 127.8, 126.8, 125.6, 123.1, 122.6, 94.4, 88.6, 86.6, 81.8, 48.5, 37.1, 21.4; **HRMS (ESI)** calcd for $C_{33}H_{27}NNaO_3S$ $[M+Na]^+$: 540.1604; found: 540.1596.

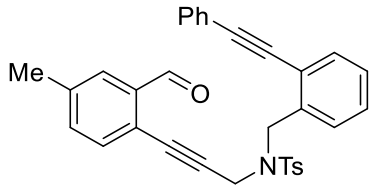
***N*-(3-(4-bromo-2-formylphenyl)prop-2-yn-1-yl)-4-methyl-*N*-(2-(phenylethynyl) benzyl)benzenesulfonamide (1o)**



The title compound was prepared according to general procedure **A** in 61% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 14:1) to afford **1o** as a colorless solid, mp 141–143 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.64 (s, 1H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 2.1 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.53 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.39 (td, *J* = 7.6, 1.2 Hz, 1H), 7.35 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.31 (td, *J* = 7.6, 1.0 Hz, 1H), 7.29–7.26 (m, 2H), 7.24–7.17 (m, 3H), 7.14–7.07 (m, 2H), 6.85 (d, *J* = 8.2 Hz, 1H), 4.76 (s, 2H), 4.28 (s, 2H),

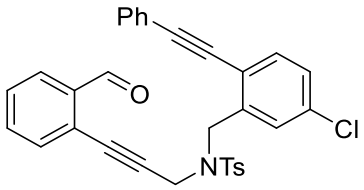
2.33 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 189.1, 143.9, 136.8, 136.3, 136.0, 135.8, 134.5, 132.4, 131.2, 129.7, 129.6, 129.0, 129.0, 128.3, 128.1, 128.0, 127.8, 124.2, 123.1, 123.1, 122.5, 94.2, 90.4, 86.7, 80.8, 48.4, 36.9, 21.4; **HRMS (ESI)** calcd for $C_{32}H_{24}BrNNaO_3S$ $[M+Na]^+$: 604.0552; found: 604.0560.

***N*-(3-(2-formyl-4-methylphenyl)prop-2-yn-1-yl)-4-methyl-*N*-(2-(phenylethynyl) benzyl)benzenesulfonamide (1p)**



The title compound was prepared according to general procedure **A** in 43% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 14:1) to afford **1p** as a colorless solid, mp 120–122 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.74 (s, 1H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.54 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.49 (s, 1H), 7.38 (td, *J* = 7.6, 1.2 Hz, 1H), 7.32 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.26–7.24 (m, 4H), 7.23–7.16 (m, 1H), 7.16–7.05 (m, 3H), 6.94 (d, *J* = 7.9 Hz, 1H), 4.77 (s, 2H), 4.30 (s, 2H), 2.32 (s, 3H), 2.31 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 190.8, 143.9, 139.0, 136.5, 135.9, 135.6, 134.2, 133.2, 132.5, 131.4, 129.7, 129.0, 128.9, 128.2, 128.0, 127.9, 127.8, 127.0, 123.1, 122.9, 122.7, 94.4, 88.3, 86.7, 81.8, 48.6, 37.1, 21.4, 21.2; **HRMS (ESI)** calcd for $C_{33}H_{28}NO_3S$ $[M+H]^+$: 518.1784; found: 518.1786.

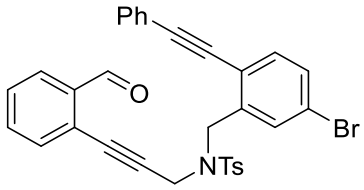
***N*-(5-chloro-2-(phenylethynyl)benzyl)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1q)**



The title compound was prepared according to general procedure **A** in 52% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 14:1 to 12:1) to afford **1q** as a pale-yellow solid, mp 125–127 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.77 (s, 1H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.74–7.69 (m, 1H),

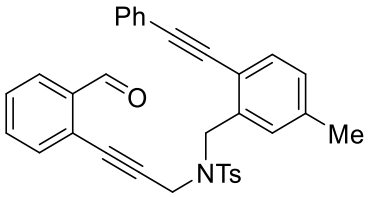
7.62 (d, *J* = 2.0 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.34–7.24 (m, 7H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.7 Hz, 2H), 7.08–7.03 (m, 1H), 4.74 (s, 2H), 4.34 (s, 2H), 2.30 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.3, 144.1, 138.5, 135.6, 134.9, 133.5, 133.3, 133.2, 131.3, 129.7, 128.9, 128.6, 128.5, 128.3, 128.1, 127.7, 126.8, 125.3, 122.2, 121.4, 95.3, 88.8, 85.6, 81.8, 48.3, 37.4, 21.3; **HRMS (ESI)** calcd for $C_{32}H_{25}ClNO_3S$ $[M+H]^+$: 538.1238; found: 538.1240.

***N*-(5-bromo-2-(phenylethynyl)benzyl)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1r)**



The title compound was prepared according to general procedure **A** in 57% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 12:1) to afford **1r** as a colorless solid, mp 144–146 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.78 (s, 1H), 7.84 (d, *J* = 7.2 Hz, 2H), 7.76 (s, 1H), 7.73–7.67 (m, 1H), 7.45–7.40 (m, 1H), 7.37 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.34–7.29 (m, 2H), 7.29–7.26 (m, 2H), 7.24 (d, *J* = 7.0 Hz, 2H), 7.22–7.17 (m, 1H), 7.10 (t, *J* = 7.5 Hz, 2H), 7.07–7.02 (m, 1H), 4.73 (s, 2H), 4.33 (s, 2H), 2.29 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.3, 144.1, 138.6, 135.6, 135.6, 133.6, 133.3, 133.2, 131.8, 131.3, 131.2, 129.7, 128.6, 128.5, 128.1, 127.7, 126.7, 125.3, 123.0, 122.2, 121.8, 95.5, 88.8, 85.6, 81.8, 48.2, 37.3, 21.3; **HRMS (ESI)** calcd for $C_{32}H_{24}BrNNaO_3S$ $[M+ Na]^+$: 604.0552; found: 604.0554.

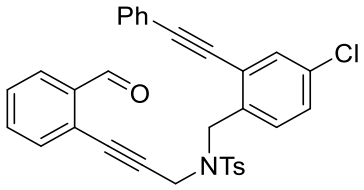
***N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methyl-*N*-(5-methyl-2-(phenylethynyl) benzyl)benzenesulfonamide (1s)**



The title compound was prepared according to general procedure **A** in 43% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 14:1) to afford **1s** as a colorless solid, mp 126–128 ℃; **^{1}H NMR**

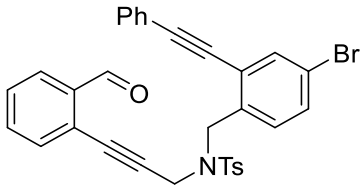
(400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.86 (d, *J* = 7.7 Hz, 2H), 7.73–7.65 (m, 1H), 7.47–7.39 (m, 2H), 7.33–7.27 (m, 2H), 7.26–7.19 (m, 4H), 7.19–7.00 (m, 5H), 4.74 (s, 2H), 4.31 (s, 2H), 2.39 (s, 3H), 2.29 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 190.5, 143.9, 139.3, 136.3, 135.9, 135.7, 133.3, 133.2, 132.3, 131.3, 129.6, 129.6, 128.9, 128.5, 128.1, 128.0, 127.8, 126.6, 125.7, 122.8, 120.1, 93.6, 89.2, 86.9, 81.6, 48.5, 37.1, 21.5, 21.4; **HRMS (ESI)** calcd for $C_{33}H_{28}NO_3S$ $[M+H]^+$: 518.1784; found: 518.1783.

***N*-(4-chloro-2-(phenylethynyl)benzyl)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1t)**



The title compound was prepared according to general procedure **A** in 58% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 12:1) to afford **1t** as a pale-yellow solid, mp 133–134 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.77 (s, 1H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.72–7.68 (m, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 1.8 Hz, 1H), 7.34 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.33–7.27 (m, 4H), 7.25–7.23 (m, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.7 Hz, 2H), 7.06–7.01 (m, 1H), 4.72 (s, 2H), 4.30 (s, 2H), 2.28 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.3, 144.0, 135.7, 135.6, 135.1, 133.7, 133.3, 133.2, 131.9, 131.4, 130.4, 129.7, 129.1, 128.6, 128.1, 127.7, 126.8, 125.4, 124.7, 122.1, 95.4, 88.9, 85.3, 81.8, 48.1, 37.2, 21.3; **HRMS (ESI)** calcd for $C_{32}H_{25}ClNO_3S$ $[M+H]^+$: 538.1238; found: 538.1238.

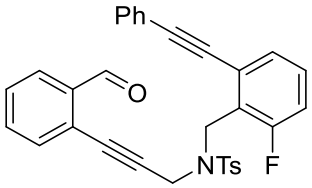
***N*-(4-bromo-2-(phenylethynyl)benzyl)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1u)**



The title compound was prepared according to general procedure **A** in 53% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 10:1) to afford **1u** as a pale-yellow solid, mp 122–124 ℃; **^{1}H**

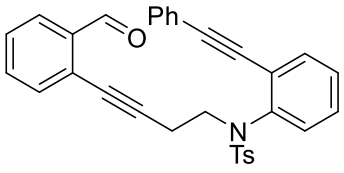
NMR (600 MHz, CDCl3) δ 9.76 (s, 1H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.72–7.69 (m, 1H), 7.68 (d, *J* = 1.7 Hz, 1H), 7.53–7.47 (m, 2H), 7.34–7.27 (m, 4H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.22–7.18 (m, 1H), 7.10 (t, *J* = 7.7 Hz, 2H), 7.06–7.02 (m, 1H), 4.71 (s, 2H), 4.30 (s, 2H), 2.28 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.4, 144.1, 135.7, 135.6, 135.6, 134.8, 133.3, 133.2, 132.0, 131.5, 130.6, 129.7, 128.7, 128.2, 127.7, 126.8, 125.4, 125.0, 122.1, 121.6, 95.6, 88.9, 85.2, 81.8, 48.2, 37.2, 21.4; **HRMS (ESI)** calcd for $C_{32}H_{24}BrNNaO_3S$ $[M+Na]^+$: 604.0552; found: 604.0562.

***N*-(2-fluoro-6-(phenylethynyl)benzyl)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1v)**



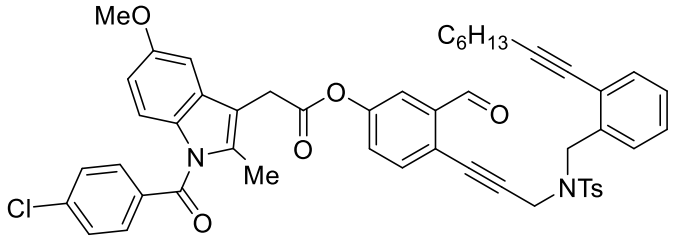
The title compound was prepared according to general procedure **A** in 50% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 10:1) to afford **1v** as a pale-yellow solid, mp 131–133 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.82 (s, 1H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.42–7.36 (m, 2H), 7.35–7.27 (m, 2H), 7.25–7.14 (m, 5H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 8.9 Hz, 1H), 4.81 (s, 2H), 4.28 (s, 2H), 2.22 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.8, 161.9 (d, *J* = 249.7 Hz), 143.8, 135.6 (d, *J* = 9.7 Hz), 133.2 (d, *J* = 7.8 Hz), 131.7, 129.9 (d, *J* = 9.5 Hz), 129.5, 128.8 (d, *J* = 3.1 Hz), 128.6, 128.5, 128.1, 127.9, 126.54, 126.5 (d, *J* = 4.8 Hz), 126.0, 123.3, 123.2, 122.3, 116.0, 115.8, 95.4, 89.5, 85.8, 81.2, 43.3, 37.1, 21.3; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -113.14 (dd, *J* = 8.8, 5.9 Hz); **HRMS (ESI)** calcd for $C_{32}H_{25}FNO_3S$ $[M+H]^+$: 522.1534; found: 522.1536.

***N*-(4-(2-formylphenyl)but-3-yn-1-yl)-4-methyl-*N*-(2-(phenylethynyl)phenyl) benzenesulfonamide (1w)**



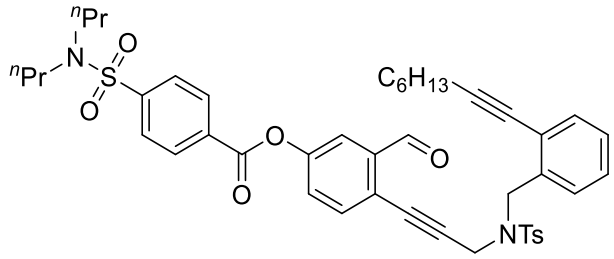
The title compound was prepared according to general procedure **C** in 75% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 10:1) to afford **1w** as a colorless solid, mp 118–120 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.36 (s, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.54–7.49 (m, 1H), 7.47–7.39 (m, 3H), 7.36–7.26 (m, 8H), 7.06 (d, *J* = 6.9 Hz, 2H), 4.05 (t, *J* = 7.1 Hz, 2H), 2.83 (t, *J* = 7.0 Hz, 2H), 2.16 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.4, 143.2, 139.5, 136.7, 135.7, 133.4, 133.3, 133.2, 132.1, 131.2, 129.3, 128.7, 128.4, 128.2, 128.0, 127.3, 126.8, 126.6, 123.5, 122.3, 94.3, 94.0, 85.8, 77.9, 49.1, 21.1, 20.7; **HRMS (ESI)** calcd for $C_{32}H_{26}NO_3S$ $[M+H]^+$: 504.1628; found: 504.1627.

3-Formyl-4-(3-((4-methyl-*N*-(2-(oct-1-yn-1-yl)benzyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (1x)



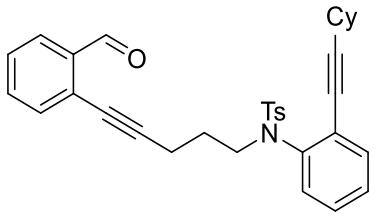
The title compound was prepared according to general procedure **B** in 39% yield. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15:1 to 8:1) to afford **1x** as a pale-yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.80 (s, 1H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.57–7.53 (m, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 7.0 Hz, 1H), 7.34–7.29 (m, 1H), 7.27–7.21 (m, 5H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 1H), 6.73 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.68 (s, 2H), 4.29 (s, 2H), 3.94 (s, 2H), 3.86 (s, 3H), 2.48 (s, 3H), 2.31 (s, 3H), 2.23 (t, *J* = 7.2 Hz, 2H), 1.47–1.41 (m, 2H), 1.33–1.23 (m, 4H), 1.22–1.15 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 189.6, 168.5, 168.2, 156.1, 150.7, 143.9, 139.4, 136.9, 136.3, 136.1, 135.9, 134.4, 133.6, 132.4, 131.1, 130.8, 130.2, 129.6, 129.1, 128.4, 128.0, 127.7, 127.6, 126.9, 123.8, 123.3, 119.5, 115.0, 111.7, 111.3, 101.1, 96.1, 89.7, 80.5, 77.8, 55.6, 48.6, 37.0, 31.1, 30.3, 28.5, 28.5, 22.4, 21.3, 20.5, 19.4, 13.9, 13.3; **HRMS (ESI)** calcd for $C_{51}H_{47}ClN_2NaO_7S$ $[M+Na]^+$: 889.2685; found: 889.2678.

3-formyl-4-(3-((4-methyl-*N*-(2-(oct-1-yn-1-yl)benzyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (1y)



The title compound was prepared according to general procedure **B** in 35% yield. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 15:1 to 7:1) to afford **1y** as a pale-yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.81 (s, 1H), 8.28 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 2.4 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.42–7.35 (m, 2H), 7.31–7.27 (m, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 4.66 (s, 2H), 4.28 (s, 2H), 3.18–3.07 (m, 4H), 2.30 (s, 3H), 2.21 (t, *J* = 7.2 Hz, 2H), 1.62–1.49 (m, 4H), 1.47–1.37 (m, 2H), 1.32–1.12 (m, 6H), 0.87 (t, *J* = 7.4 Hz, 6H), 0.83 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 189.5, 163.1, 150.6, 145.3, 143.9, 137.1, 136.1, 135.9, 134.6, 132.4, 131.9, 130.8, 129.6, 128.4, 128.0, 127.7, 127.6, 127.2, 126.9, 123.7, 123.5, 119.7, 96.1, 89.9, 80.4, 77.8, 49.8, 48.6, 37.0, 31.1, 28.5, 28.5, 22.4, 21.8, 21.3, 19.4, 13.9, 11.0; **HRMS (ESI)** calcd for $C_{45}H_{51}N_2O_7S_2$ $[M+H]^+$: 795.3132; found: 795.3135.

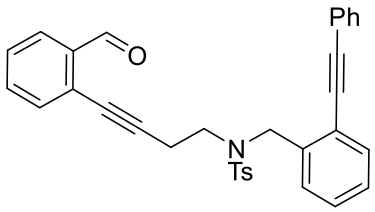
***N*-(2-(cyclohexylethynyl)phenyl)-*N*-(5-(2-formylphenyl)pent-4-yn-1-yl)-4-methylbenzenesulfonamide (1z)**



The title compound was prepared according to general procedure **C** in 64% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 30:1 to 20:1) to afford **1z** as a pale-yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.41 (s, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.38 (dd, *J* = 7.1, 1.9 Hz, 1H), 7.34 (t, *J* = 7.5 Hz,

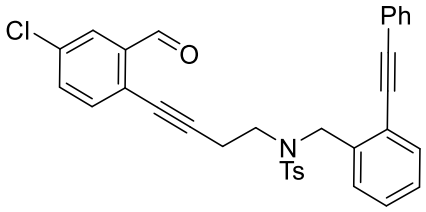
1H), 7.24–7.16 (m, 5H), 3.82 (s, 2H), 2.59 (t, *J* = 7.0 Hz, 2H), 2.36 (s, 3H), 2.32–2.24 (m, 1H), 1.87–1.77 (m, 2H), 1.74–1.61 (m, 4H), 1.54–1.42 (m, 1H), 1.34–1.18 (m, 5H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.7, 142.9, 139.7, 136.7, 135.8, 133.7, 133.5, 133.2, 130.8, 129.2, 127.9, 127.8, 127.8, 127.7, 127.4, 126.6, 124.7, 99.7, 96.6, 76.8, 49.3, 32.1, 29.6, 27.7, 25.6, 24.8, 21.3, 16.9; **HRMS (ESI)** calcd for $C_{33}H_{34}NO_3S$ $[M+H]^+$: 524.2254; found: 524.2254.

***N*-(4-(2-formylphenyl)but-3-yn-1-yl)-4-methyl-*N*-(2-(phenylethynyl)benzyl) benzenesulfonamide (1aa)**



The title compound was prepared according to general procedure **D** in 34% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 10:1) to afford **1aa** as a pale-yellow oil; **^{1}H NMR (600 MHz, CDCl3)** δ 10.29 (s, 1H), 7.85–7.81 (m, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.55–7.50 (m, 2H), 7.47–7.42 (m, 3H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.35–7.32 (m, 1H), 7.32–7.28 (m, 5H), 7.28–7.26 (m, 1H), 4.71 (s, 2H), 3.46 (t, J = 7.6 Hz, 2H), 2.63 (t, *J* = 7.7 Hz, 2H), 2.41 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.6, 143.5, 137.5, 136.6, 135.8, 133.5, 133.3, 132.3, 131.4, 129.8, 128.9, 128.8, 128.5, 128.3, 128.1, 127.7, 127.1, 126.9, 126.7, 122.6, 122.4, 94.4, 93.8, 86.7, 77.9, 50.3, 47.0, 21.4, 20.1; **HRMS (ESI)** calcd for $C_{33}H_{28}NO_3S$ $[M+H]^+$: 518.1784; found: 518.1785.

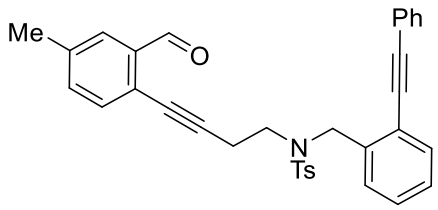
***N*-(4-(4-chloro-2-formylphenyl)but-3-yn-1-yl)-4-methyl-*N*-(2-(phenylethynyl) benzyl)benzenesulfonamide (1ab)**



The title compound was prepared according to general procedure **D** in 38% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum

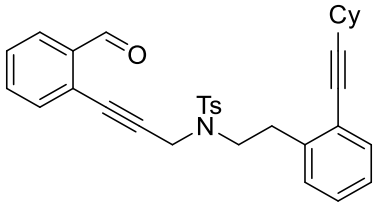
ether/EtOAc = 25:1 to 14:1) to afford **1ab** as a pale-yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.21 (s, 1H), 7.88–7.70 (m, 3H), 7.55–7.48 (m, 2H), 7.42 (d, *J* = 7.1 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.34–7.26 (m, 8H), 4.71 (s, 2H), 3.46 (t, *J* = 7.1 Hz, 2H), 2.63 (t, *J* = 7.1 Hz, 2H), 2.42 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.3, 143.6, 137.5, 136.9, 136.6, 134.6, 133.5, 132.4, 131.4, 129.8, 128.9, 128.6, 128.3, 127.8, 127.2, 126.7, 125.2, 122.6, 122.4, 95.0, 94.4, 86.7, 77.0, 50.4, 46.9, 21.5, 20.2; **HRMS (ESI)** calcd for $C_{33}H_{27}ClNO_3S$ $[M+H]^+$: 552.1395; found: 552.1398.

***N*-(4-(2-formyl-4-methylphenyl)but-3-yn-1-yl)-4-methyl-*N*-(2-(phenylethynyl) benzyl)benzenesulfonamide (1ac)**



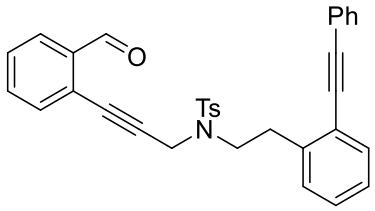
The title compound was prepared according to general procedure **D** in 30% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 14:1) to afford **1ac** as a pale-yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.27 (s, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.63 (s, 1H), 7.56–7.50 (m, 2H), 7.44 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.36–7.27 (m, 7H), 7.27–7.22 (m, 2H), 4.72 (s, 2H), 3.47 (t, *J* = 7.4 Hz, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.41 (s, 3H), 2.35 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.9, 143.6, 138.5, 137.7, 136.7, 135.8, 134.6, 133.3, 132.5, 131.5, 129.9, 129.0, 128.9, 128.6, 128.4, 127.8, 127.3, 127.2, 124.3, 122.8, 122.5, 94.5, 93.0, 86.8, 78.1, 50.4, 47.2, 21.6, 21.3, 20.2; **HRMS (ESI)** calcd for $C_{34}H_{30}NO_3S$ $[M+H]^+$: 532.1941; found: 532.1927.

***N*-(2-(cyclohexylethynyl)phenethyl)-*N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methylbenzenesulfonamide (1ad)**



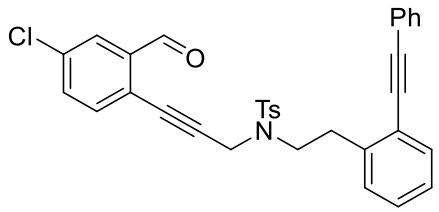
The title compound was prepared according to general procedure **D** in 65% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 16:1) to afford **1ad** as a pale-yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.86 (s, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.44–7.35 (m, 2H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.23–7.18 (m, 2H), 7.18–7.11 (m, 3H), 4.37 (s, 2H), 3.65–3.47 (m, 2H), 3.24–3.08 (m, 2H), 2.67–2.46 (m, 1H), 2.24 (s, 3H), 1.91–1.75 (m, 2H), 1.72–1.60 (m, 2H), 1.55–1.40 (m, 3H), 1.31–1.20 (m, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.5, 143.6, 139.4, 135.8, 135.7, 133.4, 133.2, 132.4, 129.4, 129.3, 128.7, 127.8, 127.5, 126.8, 126.5, 125.6, 123.6, 98.6, 89.5, 81.0, 78.5, 47.0, 37.7, 33.8, 32.6, 29.7, 25.7, 24.8, 21.2; **HRMS (ESI)** calcd for $C_{33}H_{34}NO_3S$ $[M+H]^+$: 524.2254; found: 524.2255.

***N*-(3-(2-formylphenyl)prop-2-yn-1-yl)-4-methyl-*N*-(2-(phenylethynyl)phenethyl) benzenesulfonamide (1ae)**



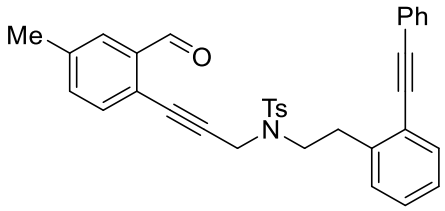
The title compound was prepared according to general procedure **D** in 40% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 14:1) to afford **1ae** as a colorless solid, mp 110–112 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.81 (s, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.51–7.46 (m, 2H), 7.44–7.39 (m, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.35–7.28 (m, 2H), 7.27–7.21 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 1H), 4.42 (s, 2H), 3.63 (t, *J* = 7.3 Hz, 2H), 3.26 (t, *J* = 7.9 Hz, 2H), 2.23 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.6, 143.7, 139.7, 135.8, 135.7, 133.4, 133.3, 132.5, 131.4, 129.6, 129.5, 128.7, 128.7, 128.3, 128.3, 127.5, 126.8, 126.7, 125.6, 122.9, 122.9, 93.3, 89.4, 87.4, 81.2, 47.3, 37.8, 34.0, 21.3; **HRMS (ESI)** calcd for $C_{33}H_{28}NO_3S$ $[M+H]^+$: 518.1784; found: 518.1786.

***N*-(3-(4-chloro-2-formylphenyl)prop-2-yn-1-yl)-4-methyl-*N*-(2-(phenylethynyl) phenethyl)benzenesulfonamide (1af)**



The title compound was prepared according to general procedure **D** in 41% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 16:1) to afford **1af** as a pale-yellow solid, mp 120–122 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.70 (s, 1H), 7.75–7.67 (m, 3H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.48–7.43 (m, 2H), 7.34 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.33–7.28 (m, 2H), 7.26–7.20 (m, 4H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.3 Hz, 1H), 4.40 (s, 2H), 3.6 (t, *J* = 7.4 Hz, 2H), 3.24 (t, *J* = 7.9 Hz, 2H), 2.25 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 189.2, 143.7, 139.6, 136.7, 135.8, 135.2, 134.5, 133.3, 132.5, 131.4, 129.6, 129.5, 128.8, 128.4, 128.3, 127.5, 126.8, 126.8, 123.7, 122.9, 122.8, 93.3, 90.4, 87.4, 80.2, 47.3, 37.8, 34.0, 21.3; **HRMS (ESI)** calcd for $C_{33}H_{27}ClNO_3S$ $[M+H]^+$: 552.1395; found: 552.1398.

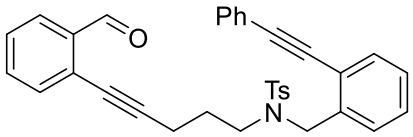
***N*-(3-(2-formyl-4-methylphenyl)prop-2-yn-1-yl)-4-methyl-*N*-(2-(phenylethynyl) phenethyl)benzenesulfonamide (1ag)**



The title compound was prepared according to general procedure **D** in 37% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 14:1) to afford **1ag** as a colorless solid, mp 99–101 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.78 (s, 1H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.59 (s, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.50–7.47 (m, 2H), 7.34–7.20 (m, 7H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 7.9 Hz, 1H), 4.40 (s, 2H), 3.61 (t, *J* = 7.4 Hz, 2H), 3.25 (t, *J* = 8.0 Hz, 2H), 2.36 (s, 3H), 2.25 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 190.8, 143.6, 139.7, 139.1, 135.8, 135.5, 134.3, 133.2, 132.5, 131.4, 129.6, 129.4, 128.7, 128.3, 128.2, 127.5, 127.1, 126.7,

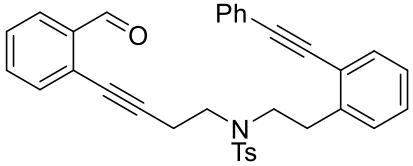
122.9, 122.8, 122.7, 93.3, 88.5, 87.4, 81.3, 47.2, 37.8, 34.0, 21.2, 21.1; **HRMS (ESI)** calcd for $C_{34}H_{30}NO_3S$ $[M+H]^+$: 532.1941; found: 532.1941.

***N*-(5-(2-formylphenyl)pent-4-yn-1-yl)-4-methyl-*N*-(2-(phenylethynyl)benzyl) benzenesulfonamide (1ah)**



The title compound was prepared according to general procedure **D** in 34% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 10:1) to afford **1ah** as a pale-yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.35 (s, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.49–7.44 (m, 2H), 7.44–7.36 (m, 4H), 7.36–7.28 (m, 6H), 7.27–7.25 (m, 1H), 4.64 (s, 2H), 3.29 (t, *J* = 7.4 Hz, 1H), 2.44 (s, 3H), 2.33 (t, *J* = 7.0 Hz, 2H), 1.78–1.68 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.8, 143.4, 137.8, 136.4, 135.9, 133.5, 133.4, 132.3, 131.4, 129.8, 129.1, 128.8, 128.5, 128.3, 127.9, 127.7, 127.4, 127.3, 126.8, 122.8, 122.5, 96.3, 94.2, 86.9, 50.4, 47.8, 27.4, 21.5, 16.9; **HRMS (ESI)** calcd for $C_{34}H_{30}NO_3S$ $[M+H]^+$: 532.1941; found: 532.1942.

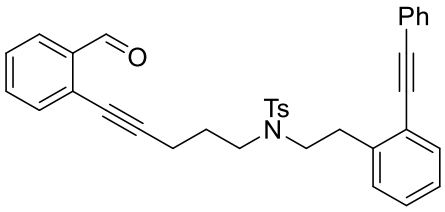
***N*-(4-(2-formylphenyl)but-3-yn-1-yl)-4-methyl-*N*-(2-(phenylethynyl)phenethyl) benzenesulfonamide (1ai)**



The title compound was prepared according to general procedure **D** in 33% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 10:1) to afford **1ai** as a pale-yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.34 (s, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.56–7.50 (m, 3H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.44–7.36 (m, 2H), 7.29–7.20 (m, 8H), 3.55–3.48 (m, 2H), 3.46 (t, *J* = 7.4 Hz, 2H), 3.25–3.14 (m, 2H), 2.74 (t, *J* = 7.4 Hz, 2H), 2.37 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.6, 143.4, 139.9, 136.6, 135.9, 133.6, 133.4, 132.6, 131.4, 129.7, 129.7, 128.8, 128.4, 128.4, 128.2, 127.1, 127.0, 126.9, 126.8, 122.8, 122.7,

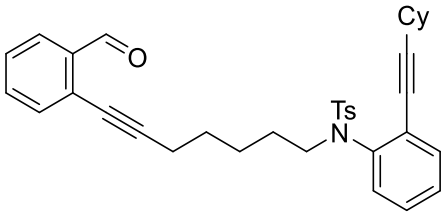
93.8, 93.2, 87.5, 78.1, 49.5, 47.5, 34.8, 21.4, 20.6; **HRMS (ESI)** calcd for $C_{34}H_{30}NO_3S$ $[M+H]^+$: 532.1941; found: 532.1940.

***N*-(5-(2-formylphenyl)pent-4-yn-1-yl)-4-methyl-*N*-(2-(phenylethynyl)phenethyl) benzenesulfonamide (1aj)**



The title compound was prepared according to general procedure **D** in 32% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 12:1) to afford **1aj** as a pale-yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.45 (s, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.54–7.45 (m, 5H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.34–7.30 (m, 3H), 7.29–7.19 (m, 5H), 3.50–3.40 (m, 2H), 3.30 (t, *J* = 7.2 Hz, 2H), 3.23–3.13 (m, 2H), 2.37 (s, 3H), 2.35 (t, *J* = 7.0 Hz, 2H), 1.88–1.79 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.8, 143.2, 140.1, 136.4, 135.9, 133.6, 133.3, 132.4, 131.4, 129.7, 129.6, 128.7, 128.4, 128.4, 127.9, 127.3, 127.1, 126.9, 126.6, 122.9, 122.6, 96.4, 92.9, 87.6, 76.94, 49.25, 48.00, 34.80, 27.57, 21.37, 16.75; **HRMS (ESI)** calcd for $C_{35}H_{31}NNaO_3S$ $[M+Na]^+$: 568.1917; found: 568.1920.

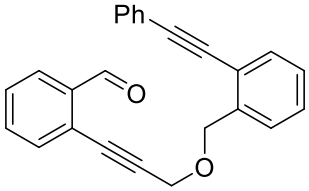
***N*-(2-(cyclohexylethynyl)phenyl)-*N*-(7-(2-formylphenyl)hept-6-yn-1-yl)-4-methylbenzenesulfonamide (1ak)**



The title compound was prepared according to general procedure **C** in 36% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 10:1) to afford **1ak** as a pale-yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.49 (s, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.52–7.47 (m, 2H), 7.39–7.35 (m, 2H), 7.24–7.18 (m, 5H), 3.69 (s, 2H), 2.43 (t, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 2.32–2.25 (m, 1H), 1.72–1.66 (m, 4H), 1.62–1.57 (m, 2H), 1.53–1.48 (m,

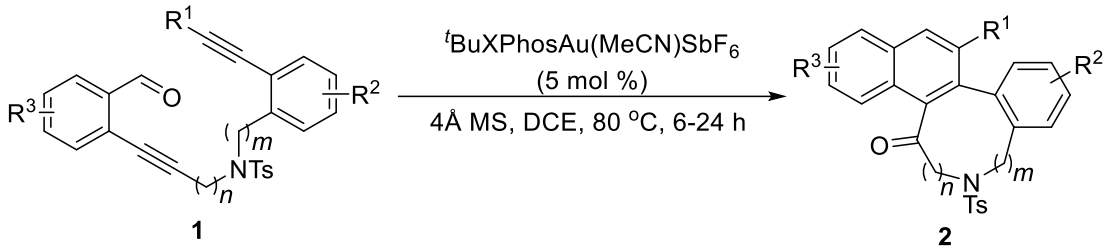
4H), 1.34–1.22 (m, 6H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 192.0, 142.8, 139.6, 137.3, 135.9, 133.7, 133.6, 133.3, 131.4, 129.2, 127.9, 127.8, 127.8, 127.7, 127.7, 126.8, 124.6, 99.6, 97.7, 77.3, 76.4, 49.9, 32.2, 29.7, 28.3, 28.1, 25.9, 25.7, 24.9, 21.4, 19.4; **HRMS (ESI)** calcd for $C_{35}H_{38}NO_3S$ $[M+H]^+$: 552.2567; found: 552.2567.

2-(3-((2-(phenylethynyl)benzyl)oxy)prop-1-yn-1-yl)benzaldehyde (1al)



The title compound was prepared according to general procedure **F** in 54% yield over 2 steps. It was purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1 to 16:1) to afford **1al** as a pale-yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 10.52 (s, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 2H), 7.54–7.46 (m, 4H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.40–7.36 (m, 1H), 7.34–7.25 (m, 4H), 4.97 (s, 2H), 4.57 (s, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 191.3, 138.9, 136.0, 133.6, 133.5, 132.1, 131.4, 128.7, 128.5, 128.3, 128.3, 128.1, 127.7, 127.1, 126.0, 123.0, 122.2, 93.9, 92.4, 86.9, 82.1, 70.1, 58.3; **HRMS (ESI)** calcd for $C_{26}H_{21}O_2$ $[M+H]^+$: 351.1380; found: 351.1388.

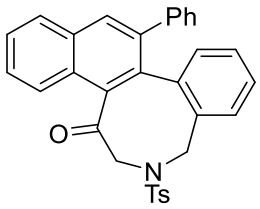
3. General procedure for ^{t}BuXPhosAu(MeCN)SbF$_6$-catalyzed intramolecular [4 + 2] benzannulation



To a solution of **1** (0.1 mmol) and 4 Å MS (50 mg) in anhydrous DCE (2 mL) was added ^{t}BuXPhosAu(MeCN)SbF$_6$ (5 mol %) under an argon atmosphere. The reaction mixture was stirred at 80 °C for 6-24 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

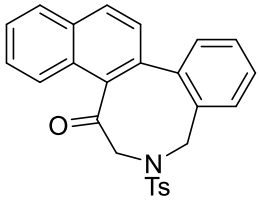
column chromatography on silica gel (eluent: petroleum ether: EtOAc) to give the product **2**.

9-phenyl-3-tosyl-3,4-dihydrobenzo[*c*]naphtho[2,1-*e*]azocin-1(2*H*)-one (2a)



Column chromatography (petroleum ether/EtOAc = 20:1 to 10:1) to afford **2a** in 97% yield (48.8 mg); colorless solid, mp 174–176 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.93 (s, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.23–7.14 (m, 5H), 7.08–7.01 (m, 3H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.68 (d, *J* = 7.6 Hz, 1H), 4.88 (d, *J* = 12.2 Hz, 1H), 4.72 (d, *J* = 19.6 Hz, 1H), 4.43 (d, *J* = 12.2 Hz, 1H), 3.56 (d, *J* = 19.5 Hz, 1H), 2.27 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 207.2, 143.3, 140.0, 139.2, 138.1, 137.9, 135.6, 133.6, 133.2, 133.0, 131.3, 131.0, 130.5, 129.4, 129.4, 128.8, 128.5, 128.3, 128.2, 127.9, 127.5, 126.9, 126.9, 126.7, 125.0, 56.7, 52.1, 21.5; **HRMS (ESI)** calcd for $C_{32}H_{25}NNaO_3S$ $[M+Na]^+$: 526.1447; found: 526.1448.

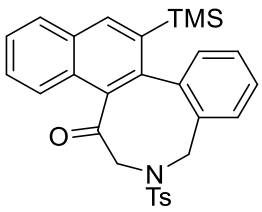
3-tosyl-3,4-dihydrobenzo[*c*]naphtho[2,1-*e*]azocin-1(2*H*)-one (2b)



Column chromatography (petroleum ether/EtOAc = 20:1 to 10:1) to afford **2b** in 94% yield (40.2 mg); colorless solid, mp 223–225 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 8.3 Hz, 1H), 7.86 (d, *J* = 7.4 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.58–7.50 (m, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.39–7.33 (m, 3H), 7.28–7.20 (m, 3H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.67–4.58 (m, 2H), 4.35 (d, *J* = 12.2 Hz, 1H), 3.53 (d, *J* = 19.5 Hz, 1H), 2.30 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 206.6, 143.3, 141.0, 136.7, 135.7, 135.1, 132.9, 131.8, 131.1, 130.7, 130.4, 129.5, 129.4, 129.2, 128.7, 128.1, 127.7, 126.7, 126.5, 126.0,

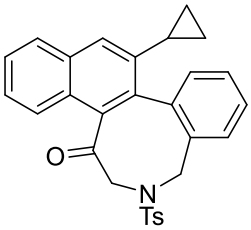
125.5, 56.4, 51.5, 21.5; **HRMS (ESI)** calcd for $C_{26}H_{22}NO_3S$ $[M+H]^+$: 428.1315; found: 428.1316.

3-tosyl-9-(trimethylsilyl)-3,4-dihydrobenzo[*c*]naphtho[2,1-*e*]azocin-1(2*H*)-one (2c)



Column chromatography (petroleum ether/EtOAc = 25:1 to 12:1) to afford **2c** in 92% yield (46.0 mg); colorless solid, mp 158–160 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.07 (s, 1H), 7.90–7.83 (m, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.58–7.49 (m, 2H), 7.39–7.33 (m, 2H), 7.25–7.21 (m, 1H), 7.17 (d, *J* = 8.2 Hz, 2H), 7.12–7.07 (m, 1H), 6.87 (d, *J* = 8.0 Hz, 2H), 4.66 (d, *J* = 19.6 Hz, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.32 (d, *J* = 12.1 Hz, 1H), 3.45 (d, *J* = 19.6 Hz, 1H), 2.29 (s, 3H), -0.02 (s, 9H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 207.8, 143.1, 141.0, 139.2, 137.7, 136.3, 135.6, 135.4, 133.1, 132.1, 131.2, 130.5, 129.2, 129.0, 128.9, 128.7, 128.3, 128.0, 126.6, 126.4, 124.6, 56.5, 51.6, 21.4, 0.1; **HRMS (ESI)** calcd for $C_{29}H_{30}NO_3SSi$ $[M+H]^+$: 500.1710; found: 500.1719.

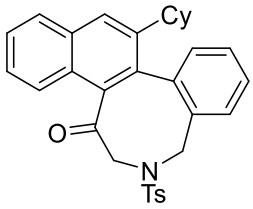
9-cyclopropyl-3-tosyl-3,4-dihydrobenzo[*c*]naphtho[2,1-*e*]azocin-1(2*H*)-one (2d)



Column chromatography (petroleum ether/EtOAc = 20:1 to 10:1) to afford **2d** in 99% yield (46.3 mg); colorless solid, mp 179–181 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.52–7.46 (m, 1H), 7.46–7.34 (m, 4H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.21 (dd, *J* = 7.4, 1.3 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 2H), 4.64 (d, *J* = 19.6 Hz, 1H), 4.58 (d, *J* = 11.9 Hz, 1H), 4.34 (d, *J* = 11.9 Hz, 1H), 3.46 (d, *J* = 19.6 Hz, 1H), 2.28 (s, 3H), 1.59–1.52 (m, 1H), 0.86–0.79 (m, 1H), 0.77–0.70 (m, 1H), 0.70–0.64 (m, 1H), 0.63–0.57 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 207.1, 143.1, 139.1, 137.9, 136.7, 135.9, 135.5, 133.3, 132.5, 131.1, 130.7,

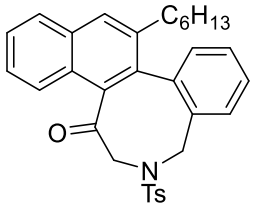
129.3, 128.9, 128.6, 127.6, 127.4, 126.6, 126.5, 126.4, 125.1, 124.7, 56.3, 51.4, 21.4, 13.8, 9.4, 7.7; **HRMS (ESI)** calcd for $C_{29}H_{26}NO_3S$ $[M+H]^+$: 468.1628; found: 468.1634.

9-cyclohexyl-3-tosyl-3,4-dihydrobenzo[*c*]naphtho[2,1-*e*]azocin-1(2*H*)-one (2e)



Column chromatography (petroleum ether/EtOAc = 20:1 to 12:1) to afford **2e** in 99% yield (50.5 mg); colorless solid, mp 188–190 ℃; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.79 (d, *J* = 8.1 Hz, 1H), 7.76 (s, 1H), 7.61 (d, *J* = 8.3 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.40–7.33 (m, 2H), 7.29 (d, *J* = 3.1 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 2H), 7.10–7.02 (m, 1H), 6.82 (d, *J* = 7.7 Hz, 2H), 4.66 (d, *J* = 19.7 Hz, 1H), 4.51 (d, *J* = 11.8 Hz, 1H), 4.36 (d, *J* = 11.8 Hz, 1H), 3.46 (d, *J* = 19.6 Hz, 1H), 2.31 (d, *J* = 11.4 Hz, 1H), 2.27 (s, 3H), 1.82 (dd, *J* = 27.4, 12.9 Hz, 2H), 1.73–1.62 (m, 2H), 1.62–1.39 (m, 2H), 1.35–1.21 (m, 2H), 1.19–0.96 (m, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 207.3, 143.0, 142.3, 139.1, 136.9, 135.4, 134.5, 133.4, 132.0, 131.2, 131.0, 129.2, 129.0, 128.7, 127.8, 127.3, 126.7, 126.5, 126.3, 124.6, 56.4, 51.5, 40.0, 35.2, 34.2, 26.8, 26.6, 25.9, 21.4; **HRMS (ESI)** calcd for $C_{29}H_{27}BrNO_3S$ $[M+H]^+$: 510.2097; found: 510.2103.

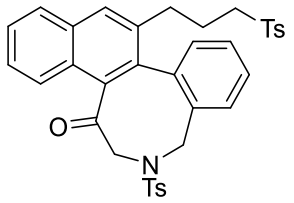
9-hexyl-3-tosyl-3,4-dihydrobenzo[*c*]naphtho[2,1-*e*]azocin-1(2*H*)-one (2f)



Column chromatography (petroleum ether/EtOAc = 20:1 to 10:1) to afford **2f** in 86% yield (44.0 mg); pale-yellow oil; **^{1}H NMR (600 MHz, CDCl3)** δ 7.78 (d, *J* = 8.2 Hz, 1H), 7.72 (s, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.41–7.35 (m, 2H), 7.31–7.27 (m, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.14–7.09 (m, 1H), 6.86 (d, *J* = 8.0 Hz, 2H), 4.65 (d, *J* = 19.7 Hz, 1H), 4.51 (d, *J* = 11.8 Hz, 1H), 4.34 (d, *J* = 11.9 Hz, 1H), 3.44 (d, *J* = 19.7 Hz, 1H), 2.56–2.47 (m, 1H), 2.46–2.38 (m, 1H), 2.28 (s, 3H), 1.45–1.24 (m, 3H), 1.22–1.12 (m, 5H), 0.83 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR**

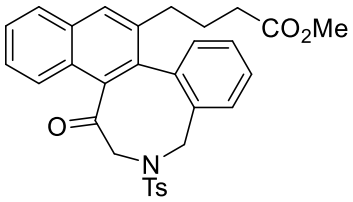
(150 MHz, $CDCl_3$) δ 207.3, 143.1, 139.0, 137.2, 137.2, 137.0, 135.5, 134.8, 133.3, 132.1, 131.3, 130.9, 129.7, 129.3, 129.1, 128.7, 127.6, 127.6, 126.8, 126.6, 126.5, 124.8, 56.4, 51.4, 33.2, 31.4, 30.4, 28.9, 22.4, 21.5, 14.0; **HRMS (ESI)** calcd for $C_{32}H_{34}NO_3S$ $[M+H]^+$: 512.2254; found: 512.2256.

3-tosyl-9-(3-tosylpropyl)-3,4-dihydrobenzo[*c*]naphtho[2,1-*e*]azocin-1(2*H*)-one (2g)



Column chromatography (petroleum ether/EtOAc = 10:1 to 3:1) to afford **2g** in 99% yield (61.8 mg); pale-yellow solid, mp 148–150 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.65 (s, 1H), 7.55–7.45 (m, 2H), 7.36–7.32 (m, 2H), 7.30 (t, *J* = 8.0 Hz, 4H), 7.23–7.17 (m, 1H), 7.05–6.99 (m, 1H), 6.96 (d, *J* = 8.0 Hz, 2H), 4.62 (d, *J* = 19.6 Hz, 1H), 4.53 (d, *J* = 12.4 Hz, 1H), 4.13 (d, *J* = 12.4 Hz, 1H), 3.39 (d, *J* = 19.6 Hz, 1H), 3.03–2.92 (m, 1H), 2.92–2.83 (m, 1H), 2.78–2.68 (m, 1H), 2.59–2.49 (m, 1H), 2.43 (s, 3H), 2.30 (s, 3H), 1.82–1.68 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 207.2, 144.6, 143.2, 138.1, 137.4, 136.0, 135.5, 134.3, 134.0, 133.0, 131.9, 131.2, 130.9, 130.2, 129.8, 129.4, 129.1, 128.9, 127.9, 127.6, 127.1, 126.7, 126.5, 124.8, 56.5, 55.2, 51.4, 31.7, 22.7, 21.5, 21.4; **HRMS (ESI)** calcd for $C_{36}H_{34}NO_5S_2$ $[M+H]^+$: 624.1873; found: 624.1884.

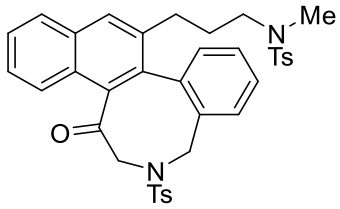
Methyl 4-(1-oxo-3-tosyl-1,2,3,4-tetrahydrobenzo[*c*]naphtho[2,1-*e*]azocin-9-yl)butanoate (2h)



Column chromatography (petroleum ether/EtOAc = 20:1 to 7:1) to afford **2h** in 92% yield (48.5 mg); pale-yellow solid, mp 134–136 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.79 (d, *J* = 8.1 Hz, 1H), 7.73 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.55–7.50 (m, 1H), 7.49–7.44 (m, 1H), 7.40–7.34 (m, 2H), 7.30–7.26 (m, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.12–7.06 (m, 1H), 6.86 (d, *J* = 8.0 Hz, 2H), 4.66 (d, *J* = 19.7 Hz, 1H), 4.52 (d, *J* = 12.0

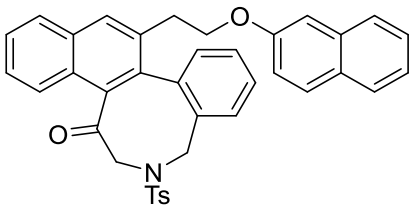
Hz, 1H), 4.32 (d, *J* = 12.0 Hz, 1H), 3.61 (s, 3H), 3.43 (d, *J* = 19.6 Hz, 1H), 2.61–2.53 (m, 1H), 2.52–2.43 (m, 1H), 2.27 (s, 3H), 2.19–2.12 (m, 2H), 1.74–1.65 (m, 2H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 207.2, 173.4, 143.1, 138.6, 137.4, 135.4, 135.4, 134.6, 133.2, 132.0, 131.2, 131.0, 130.0, 129.2, 129.1, 128.8, 127.7, 127.6, 127.0, 126.6, 126.5, 124.8, 56.3, 51.5, 51.3, 33.2, 32.3, 25.3, 21.4; **HRMS (ESI)** calcd for $C_{31}H_{30}NO_5S$ $[M+H]^+$: 528.1839; found: 528.1839.

***N*,4-dimethyl-*N*-(3-(1-oxo-3-tosyl-1,2,3,4-tetrahydrobenzo[*c*]naphtho[2,1-*e*] azocin-9-yl)propyl)benzenesulfonamide (2i)**



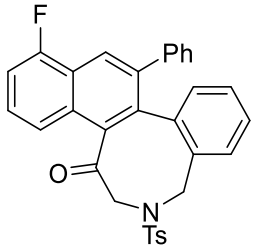
Column chromatography (petroleum ether/EtOAc = 13:1 to 6:1) to afford **2i** in 99% yield (64.6 mg); colorless solid, mp 186–188 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.83 (d, *J* = 8.2 Hz, 1H), 7.80 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.57–7.52 (m, 1H), 7.50–7.45 (m, 1H), 7.45–7.37 (m, 2H), 7.33–7.25 (m, 5H), 7.17–7.11 (m, 1H), 6.93 (d, *J* = 8.0 Hz, 2H), 4.63 (d, *J* = 19.6 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 4.32 (d, *J* = 12.0 Hz, 1H), 3.43 (d, *J* = 19.6 Hz, 1H), 3.01–2.92 (m, 1H), 2.87–2.80 (m, 1H), 2.69–2.61 (m, 1H), 2.57–2.53 (m, 1H), 2.52 (s, 3H), 2.43 (s, 3H), 2.31 (s, 3H), 1.68–1.54 (m, 2H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 207.1, 143.3, 143.2, 138.7, 137.4, 135.6, 135.5, 134.5, 134.3, 133.3, 132.1, 131.2, 131.0, 130.1, 129.6, 129.4, 129.3, 128.9, 127.8, 127.6, 127.3, 127.0, 126.6, 126.6, 124.8, 56.4, 51.5, 49.6, 34.3, 304, 28.4, 21.5; **HRMS (ESI)** calcd for $C_{37}H_{37}N_2O_5S_2$ $[M+H]^+$: 653.2138; found: 653.2147.

9-(2-(naphthalen-2-yloxy)ethyl)-3-tosyl-3,4-dihydrobenzo[*c*]naphtho[2,1-*e*] azocin-1(2*H*)-one (2j)



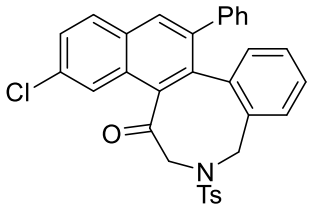
Column chromatography (petroleum ether/EtOAc = 20:1 to 10:1) to afford **2j** in 94% yield (56.2 mg); pale-yellow solid, mp 94–96 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.91 (s, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 9.0 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.52–7.47 (m, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.44–7.37 (m, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.32–7.28 (m, 1H), 7.18 (d, *J* = 7.9 Hz, 3H), 7.03 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.98 (d, *J* = 2.1 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 2H), 4.70 (d, *J* = 19.7 Hz, 1H), 4.65 (d, *J* = 11.9 Hz, 1H), 4.34 (d, *J* = 11.9 Hz, 1H), 4.12 (t, *J* = 6.9 Hz, 2H), 3.48 (d, *J* = 19.6 Hz, 1H), 3.17–2.99 (m, 2H), 2.23 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 207.1, 156.3, 143.0, 138.7, 137.4, 135.4, 134.9, 134.4, 133.2, 132.6, 132.1, 131.5, 131.1, 130.6, 129.5, 129.3, 129.2, 129.0, 129.0, 127.9, 127.7, 127.6, 127.2, 126.7, 126.6, 126.5, 126.4, 124.8, 123.7, 118.6, 106.5, 67.8, 56.4, 51.4, 32.6, 21.4; **HRMS (ESI)** calcd for $C_{38}H_{31}NNaO_4S$ $[M+Na]^+$: 620.1866; found: 620.1869.

11-fluoro-9-phenyl-3-tosyl-3,4-dihydrobenzo[*c*]naphtho[2,1-*e*]azocin-1(2*H*)-one (2k)



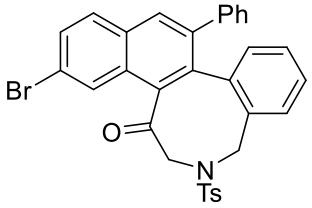
Column chromatography (petroleum ether/EtOAc = 20:1 to 10:1) to afford **2k** in 61% yield (31.8 mg); colorless solid, mp 228–230 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.19 (s, 1H), 7.51–7.43 (m, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.25–7.15 (m, 6H), 7.10–7.02 (m, 3H), 6.96 (d, *J* = 8.1 Hz, 2H), 6.67 (d, *J* = 7.6 Hz, 1H), 4.91 (d, *J* = 12.3 Hz, 1H), 4.74 (d, *J* = 19.6 Hz, 1H), 4.43 (d, *J* = 12.3 Hz, 1H), 3.57 (d, *J* = 19.6 Hz, 1H), 2.29 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 206.8, 158.7 (d, *J* = 253.0 Hz), 143.4, 139.7, 138.8, 138.6 (d, *J* = 1.6 Hz), 137.6 (d, *J* = 2.7 Hz), 135.6, 134.6, 132.9, 131.2, 130.5, 129.7 (d, *J* = 3.9 Hz), 129.4, 129.3, 128. 9, 128.5, 128.0, 127.3 (d, *J* = 8.3 Hz), 127.2, 126.5, 123.5 (d, *J* = 5.2 Hz), 121.0 (d, *J* = 4.2 Hz), 110.4 (d, *J* = 19.7 Hz), 56.7, 52.2, 21.3; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -122.15 (dd, *J* = 10.3, 5.1 Hz); **HRMS (ESI)** calcd for $C_{32}H_{25}FNO_3S$ $[M+H]^+$: 522.1534; found: 522.1536.

13-chloro-9-phenyl-3-tosyl-3,4-dihydrobenzo[*c*]naphtho[2,1-*e*]azocin-1(2*H*)-one (2l)



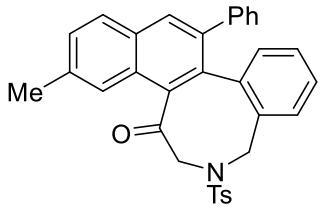
Column chromatography (petroleum ether/EtOAc = 20:1 to 10:1) to afford **2l** in 83% yield (44.7 mg); colorless solid, mp 238–240 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.92 (s, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.53 (s, 1H), 7.48 (d, *J* = 8.7 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.25–7.17 (m, 5H), 7.09–7.01 (m, 3H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.66 (d, *J* = 7.6 Hz, 1H), 4.94 (d, *J* = 12.1 Hz, 1H), 4.64 (d, *J* = 19.8 Hz, 1H), 4.52 (d, *J* = 12.2 Hz, 1H), 3.57 (d, *J* = 19.8 Hz, 1H), 2.28 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 206.4, 143.4, 139.6, 138.9, 138.5, 137.0, 135.9, 134.9, 133.4, 132.9, 131.3, 131.2, 131.0, 130.5, 129.6, 129.4, 129.3, 129.0, 128.9, 128.6, 128.0, 127.8, 127.2, 126.6, 124.1, 56.6, 52.2, 21.5; **HRMS (ESI)** calcd for $C_{32}H_{24}ClNNaO_3S$ $[M+Na]^+$: 560.1058; found: 560.1061.

13-bromo-9-phenyl-3-tosyl-3,4-dihydrobenzo[*c*]naphtho[2,1-*e*]azocin-1(2*H*)-one (2m)



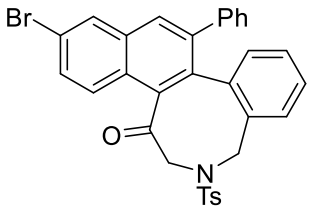
Column chromatography (petroleum ether/EtOAc = 25:1 to 12:1) to afford **2m** in 74% yield (43.1 mg); colorless solid, mp 236–238 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.91 (s, 1H), 7.76–7.68 (m, 2H), 7.60 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.25–7.16 (m, 5H), 7.10–7.01 (m, 3H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.65 (d, *J* = 7.6 Hz, 1H), 4.95 (d, *J* = 12.1 Hz, 1H), 4.65 (d, *J* = 19.8 Hz, 1H), 4.53 (d, *J* = 12.2 Hz, 1H), 3.58 (d, *J* = 19.8 Hz, 1H), 2.27 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 206.4, 143.4, 139.6, 138.8, 138.6, 136.9, 135.9, 134.9, 132.8, 131.5, 131.2, 131.0, 130.5, 130.3, 129.6, 129.4, 129.3, 129.2, 128.9, 128.6, 128.0, 127.3, 127.2, 126.5, 121.8, 56.6, 52.2, 21.5; **HRMS (ESI)** calcd for $C_{32}H_{24}BrNNaO_3S$ $[M+Na]^+$: 604.0552; found: 604.0555.

13-methyl-9-phenyl-3-tosyl-3,4-dihydrobenzo[*c*]naphtho[2,1-*e*]azocin-1(2*H*)-one (2n)



Column chromatography (petroleum ether/EtOAc = 25:1 to 14:1) to afford **2n** in 86% yield (44.5 mg); colorless solid, mp 234–236 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.88 (s, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.42–7.36 (m, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.22–7.14 (m, 5H), 7.06–6.99 (m, 3H), 6.89 (d, *J* = 8.1 Hz, 2H), 6.67 (d, *J* = 7.5 Hz, 1H), 4.86 (d, *J* = 12.1 Hz, 1H), 4.73 (d, *J* = 19.6 Hz, 1H), 4.48 (d, *J* = 12.2 Hz, 1H), 3.58 (d, *J* = 19.6 Hz, 1H), 2.51 (s, 3H), 2.25 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 207.4, 143.2, 140.1, 139.4, 137.3, 137.2, 137.1, 135.6, 133.6, 133.0, 131.5, 131.3, 130.7, 130.5, 129.3, 129.3, 129.2, 128.8, 128.7, 128.2, 128.0, 127.9, 126.8, 126.7, 123.8, 56.7, 52.1, 22.1, 21.4; **HRMS (ESI)** calcd for $C_{33}H_{27}NNaO_3S$ $[M+Na]^+$: 540.1604; found: 540.1606.

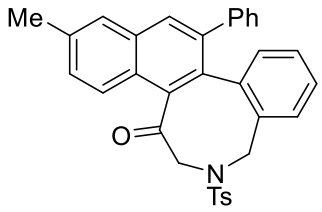
12-bromo-9-phenyl-3-tosyl-3,4-dihydrobenzo[*c*]naphtho[2,1-*e*]azocin-1(2*H*)-one (2o)



Column chromatography (petroleum ether/EtOAc = 25:1 to 14:1) to afford **2o** in 81% yield (47.2 mg); pale-yellow solid, mp 220–222 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.03 (s, 1H), 7.84 (s, 1H), 7.60–7.51 (m, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.23–7.15 (m, 5H), 7.10–7.01 (m, 3H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 7.7 Hz, 1H), 4.95 (d, *J* = 12.2 Hz, 1H), 4.66 (d, *J* = 19.7 Hz, 1H), 4.44 (d, *J* = 12.2 Hz, 1H), 3.56 (d, *J* = 19.6 Hz, 1H), 2.32 (s, 3H); **^{13}C NMR (150 MHz, CDCl3)** δ 206.7, 143.5, 139.5, 139.3, 138.8, 137.9, 135.8, 134.2, 134.1, 132.9, 131.2, 130.7, 130.4, 130.1, 129.9, 129.4, 129.2, 128.8,

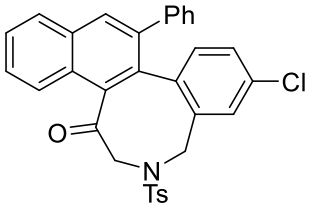
128.5, 128.0, 127.2, 126.9, 126.8, 126.5, 121.1, 56.6, 52.2, 21.5; **HRMS (ESI)** calcd for $C_{32}H_{24}BrNNaO_3S$ $[M+Na]^+$: 604.0552; found: 604.0553.

12-methyl-9-phenyl-3-tosyl-3,4-dihydrobenzo[*c*]naphtho[2,1-*e*]azocin-1(2*H*)-one (2p)



Column chromatography (petroleum ether/EtOAc = 25:1 to 15:1) to afford **2p** in 99% yield (51.2 mg); pale-yellow solid, mp 232–234 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84 (s, 1H), 7.65 (s, 1H), 7.59 (d, *J* = 8.6 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 3H), 7.22–7.08 (m, 5H), 7.08–6.99 (m, 3H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.68 (d, *J* = 7.5 Hz, 1H), 4.89 (d, *J* = 12.1 Hz, 1H), 4.70 (d, *J* = 19.5 Hz, 1H), 4.43 (d, *J* = 12.1 Hz, 1H), 3.55 (d, *J* = 19.5 Hz, 1H), 2.57 (s, 3H), 2.28 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 207.3, 143.2, 140.2, 139.3, 138.0, 137.7, 136.7, 135.6, 133.4, 133.1, 132.6, 131.3, 130.4, 129.8, 129.4, 129.3, 128.7, 128.2, 127.8, 127.1, 126.8, 126.8, 126.6, 124.8, 56.6, 52.1, 21.7, 21.4; **HRMS (ESI)** calcd for $C_{33}H_{27}NNaO_3S$ $[M+Na]^+$: 540.1604; found: 540.1606.

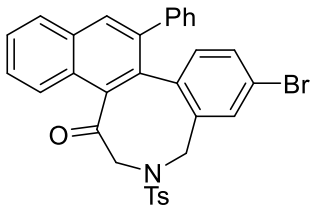
6-chloro-9-phenyl-3-tosyl-3,4-dihydrobenzo[*c*]naphtho[2,1-*e*]azocin-1(2*H*)-one (2q)



Column chromatography (petroleum ether/EtOAc = 25:1 to 12:1) to afford **2q** in 72% yield (38.7 mg); colorless solid, mp 232–234 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.93 (s, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.61–7.56 (m, 1H), 7.56–7.51 (m, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.25–7.20 (m, 3H), 7.19 (d, *J* = 2.1 Hz, 1H), 7.06–7.00 (m, 3H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 8.2 Hz, 1H), 4.87 (d, *J* = 12.5 Hz, 1H), 4.72 (d, *J* = 19.5 Hz, 1H), 4.33 (d, *J* = 12.5 Hz, 1H), 3.57 (d, *J* = 19.4 Hz, 1H), 2.29 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 206.9, 143.6, 139.8, 138.0, 137.9, 137.7,

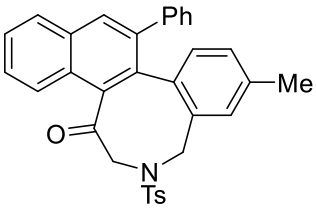
135.4, 134.4, 134.0, 133.3, 133.1, 132.3, 131.2, 130.3, 129.6, 129.3, 129.0, 128.5, 128.2, 128.1, 127.7, 127.2, 127.1, 126.7, 125.0, 56.8, 51.8, 21.5; **HRMS (ESI)** calcd for $C_{32}H_{24}ClNNaO_3S$ $[M+Na]^+$: 560.1058; found: 560.1064.

6-bromo-9-phenyl-3-tosyl-3,4-dihydrobenzo[*c*]naphtho[2,1-*e*]azocin-1(2*H*)-one (2r)



Column chromatography (petroleum ether/EtOAc = 25:1 to 12:1) to afford **2r** in 64% yield (37.3 mg); pale-yellow solid, mp 218–220 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.93 (s, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.58 (t, *J* = 7.1 Hz, 1H), 7.54 (t, *J* = 7.1 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 1.9 Hz, 1H), 7.25–7.19 (m, 3H), 7.16 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.03 (dd, *J* = 6.5, 2.9 Hz, 2H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.55 (d, *J* = 8.2 Hz, 1H), 4.87 (d, *J* = 12.5 Hz, 1H), 4.72 (d, *J* = 19.5 Hz, 1H), 4.32 (d, *J* = 12.5 Hz, 1H), 3.57 (d, *J* = 19.4 Hz, 1H), 2.29 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 206.9, 143.6, 139.7, 138.2, 137.8, 137.8, 135.3, 134.6 133.3, 133.2, 133.2, 132.3, 131.9, 131.1, 129.5, 129.3, 128.4, 128.2, 128.1, 127.7, 127.1, 127.1, 126.7, 125.0, 122.1, 56.8, 51.7, 21.5; **HRMS (ESI)** calcd for $C_{32}H_{24}BrNNaO_3S$ $[M+Na]^+$: 604.0552; found: 604.0555.

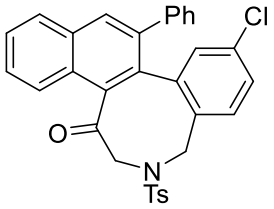
6-methyl-9-phenyl-3-tosyl-3,4-dihydrobenzo[*c*]naphtho[2,1-*e*]azocin-1(2*H*)-one (2s)



Column chromatography (petroleum ether/EtOAc = 30:1 to 14:1) to afford **2s** in 98% yield (50.7 mg); colorless solid, mp 184–185 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.61–7.44 (m, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.24–7.14 (m, 3H), 7.09–7.02 (m, 2H), 6.98 (s, 1H), 6.92 (d, *J* = 7.8

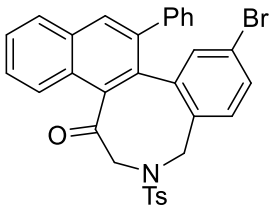
Hz, 2H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.55 (d, *J* = 7.8 Hz, 1H), 4.84 (d, *J* = 12.1 Hz, 1H), 4.70 (d, *J* = 19.5 Hz, 1H), 4.37 (d, *J* = 12.1 Hz, 1H), 3.58 (d, *J* = 19.5 Hz, 1H), 2.27 (s, 3H), 2.25 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 207.4, 143.2, 140.1, 138.2, 138.1, 138.0, 136.1, 135.6, 133.6, 133.1, 132.8, 131.1, 130.9, 130.9, 129.6, 129.4, 129.3, 128.5, 128.1, 127.9, 127.4, 126.8, 126.7, 126.6, 124.9, 56.6, 52.1, 21.4, 20.9; **HRMS (ESI)** calcd for $C_{33}H_{28}NO_3S$ $[M+H]^+$: 518.1784; found: 518.1787.

7-chloro-9-phenyl-3-tosyl-3,4-dihydrobenzo[*c*]naphtho[2,1-*e*]azocin-1(2*H*)-one (2t)



Column chromatography (petroleum ether/EtOAc = 25:1 to 12:1) to afford **2t** in 65% yield (35.0 mg); colorless solid, mp 217–219 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.93 (s, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.62–7.56 (m, 1H), 7.56–7.51 (m, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.25–7.20 (m, 3H), 7.17–7.10 (m, 2H), 7.04 (dd, *J* = 6.5, 2.9 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.68 (d, *J* = 1.9 Hz, 1H), 4.84 (d, *J* = 12.4 Hz, 1H), 4.73 (d, *J* = 19.5 Hz, 1H), 4.40 (d, *J* = 12.5 Hz, 1H), 3.57 (d, *J* = 19.5 Hz, 1H), 2.27 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 206.8, 143.5, 140.9, 139.6, 137.8, 137.8, 135.4, 134.6, 133.3, 132.9, 132.1, 131.7, 131.1, 129.8, 129.5, 129.2, 128.4, 128.4, 128.2, 128.1, 127.7, 127.3, 127.2, 126.6, 125.0, 56.7, 51.5, 21.4; **HRMS (ESI)** calcd for $C_{32}H_{25}ClNO_3S$ $[M+H]^+$: 538.1238; found: 538.1242.

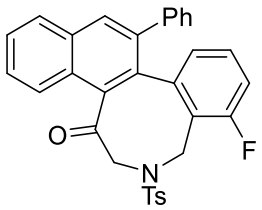
7-bromo-9-phenyl-3-tosyl-3,4-dihydrobenzo[*c*]naphtho[2,1-*e*]azocin-1(2*H*)-one (2u)



Column chromatography (petroleum ether/EtOAc = 25:1 to 10:1) to afford **2u** in 47% yield (27.4 mg); colorless solid, mp 225–227 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.93

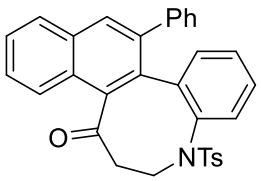
(s, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.29 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.24–7.18 (m, 3H), 7.05 (d, *J* = 8.3 Hz, 1H), 7.04–6.99 (m, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 1.9 Hz, 1H), 4.82 (d, *J* = 12.4 Hz, 1H), 4.72 (d, *J* = 19.5 Hz, 1H), 4.38 (d, *J* = 12.5 Hz, 1H), 3.56 (d, *J* = 19.5 Hz, 1H), 2.27 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 206.7, 143.5, 141.1, 139.6, 137.9, 137.7, 135.8, 135.4, 133.3, 132.1, 131.8, 131.4, 131.1, 130.3, 129.5, 129.2, 128.4, 128.2, 128.1, 127.7, 127.3, 127.2, 126.7, 125.0, 122.7, 56.7, 51.6, 21.5; **HRMS (ESI)** calcd for $C_{32}H_{24}BrNNaO_3S$ $[M+Na]^+$: 604.0552; found: 604.0552.

5-fluoro-9-phenyl-3-tosyl-3,4-dihydrobenzo[*c*]naphtho[2,1-*e*]azocin-1(2*H*)-one (2v)



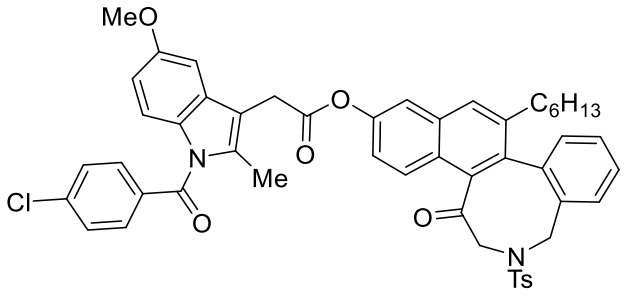
Column chromatography (petroleum ether/EtOAc = 12:1 to 10:1) to afford **2v** in 30% yield (15.6 mg); colorless solid, mp 219–221 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.95 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.62–7.52 (m, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.24–7.16 (m, 3H), 7.10–6.97 (m, 5H), 6.93 (t, *J* = 8.8 Hz, 1H), 6.50 (d, *J* = 7.5 Hz, 1H), 4.92 (d, *J* = 12.5 Hz, 1H), 4.72 (d, *J* = 19.6 Hz, 1H), 4.56 (dd, *J* = 12.5, 2.4 Hz, 1H), 3.52 (d, *J* = 19.6 Hz, 1H), 2.31 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 206.8, 160.7 (d, *J* = 249.1 Hz), 143.5, 141.6, 139.8, 138.3, 137.8, 135.5, 133.2, 132.3, 131.7 (d, *J* = 8.7 Hz), 131.1, 130.0 (d, *J* = 9.1 Hz), 129.5, 129.3, 128.6, 128.5 (d, *J* = 3.3 Hz), 128.2, 128.0, 127.7, 127.1 (d, *J* = 10.7 Hz), 126.7, 125.1, 119.1 (d, *J* = 13.7 Hz), 115.0 (d, *J* = 22.5 Hz), 56.9, 43.0 (d, *J* = 6.2 Hz), 21.5; **^{19}F NMR (565 MHz, $CDCl_3$)** δ -116.82 – -116.93 (m); **HRMS (ESI)** calcd for $C_{32}H_{24}FNNaO_3S$ $[M+Na]^+$: 544.1353; found: 544.1358.

9-phenyl-4-tosyl-3,4-dihydrobenzo[*b*]naphtho[2,1-*d*]azocin-1(2*H*)-one (2w)



Column chromatography (petroleum ether/EtOAc = 20:1 to 10:1) to afford **2w** in 85% yield (40.8 mg); colorless solid, mp 205–207 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.03 (s, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.62–7.56 (m, 1H), 7.54–7.42 (m, 4H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.31–7.26 (m, 3H), 7.25–7.21 (m, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.94–6.82 (m, 3H), 4.39 (ddd, *J* = 13.9, 6.3, 2.8 Hz, 1H), 3.56–3.43 (m, 1H), 3.19 (td, *J* = 11.5, 6.5 Hz, 1H), 2.59 (dt, *J* = 11.1, 3.2 Hz, 1H), 2.22 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 211.1, 143.4, 141.5, 140.5, 139.9, 139.2, 139.0, 136.7, 133.2, 132.8, 130.8, 130.4, 130.1, 129.7, 129.4, 129.3, 128.5, 128.0, 127.8, 127.3, 127.0, 126.9, 123.6, 50.5, 43.8, 21.3; **HRMS (ESI)** calcd for $C_{32}H_{26}NO_3S$ $[M+H]^+$: 504.1628; found: 504.1628.

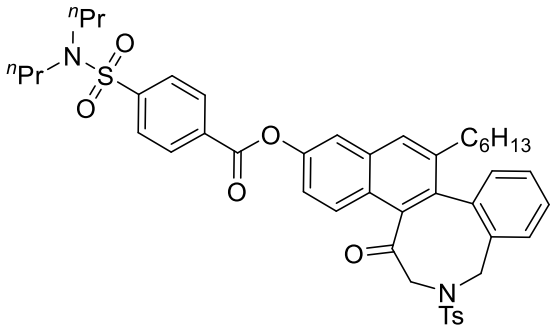
9-hexyl-1-oxo-3-tosyl-1,2,3,4-tetrahydrobenzo[*c*]naphtho[2,1-*e*]azocin-12-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (2x)



Column chromatography (petroleum ether/EtOAc = 20:1 to 8:1) to afford **2x** in 92% yield (79.8 mg); yellow solid, mp 78–80 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.73–7.68 (m, 2H), 7.67–7.61 (m, 2H), 7.53 (d, *J* = 2.3 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.41–7.34 (m, 2H), 7.30–7.27 (m, 1H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.17 (dd, *J* = 9.2, 2.3 Hz, 1H), 7.13 (d, *J* = 2.4 Hz, 1H), 7.11–7.06 (m, 1H), 6.92 (t, *J* = 8.8 Hz, 3H), 6.73 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.62 (d, *J* = 19.7 Hz, 1H), 4.52 (d, *J* = 11.8 Hz, 1H), 4.33 (d, *J* = 11.8 Hz, 1H), 3.99 (s, 2H), 3.87 (s, 3H), 3.42 (d, *J* = 19.7 Hz, 1H), 2.51 (s, 3H), 2.50–2.45 (m, 1H), 2.43–2.37 (m, 1H), 2.22 (s, 3H), 1.38–1.28 (m, 2H), 1.24–1.11 (m, 6H), 0.83 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 206.9, 169.1, 168.3, 156.1,

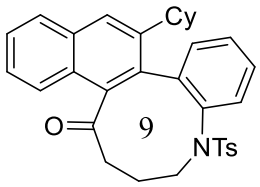
148.9, 143.2, 139.3, 138.7, 138.1, 137.2, 136.2, 135.4, 134.8, 133.8, 133.7, 132.1, 131.3, 131.2, 130.9, 130.8, 130.5, 129.4, 129.3, 129.1, 129.1, 128.8, 126.5, 126.5, 125.6, 121.6, 118.0, 115.0, 111.9, 111.8, 101.2, 56.3, 55.7, 51.3, 33.1, 31.3, 30.6, 30.2, 28.8, 22.3, 21.2, 14.0, 13.4; **HRMS (ESI)** calcd for $C_{51}H_{47}ClN_2NaO_7S$ $[M+Na]^+$: 889.2685; found: 889.2678.

9-hexyl-1-oxo-3-tosyl-1,2,3,4-tetrahydrobenzo[*c*]naphtho[2,1-*e*]azocin-12-yl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (2y)



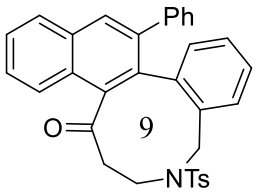
Column chromatography (petroleum ether/EtOAc = 18:1 to 7:1) to afford **2y** in 96% yield (76.3 mg); pale-yellow solid, mp 84–86 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.38 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 9.1 Hz, 1H), 7.71–7.66 (m, 2H), 7.42–7.35 (m, 2H), 7.33 (dd, *J* = 9.1, 2.3 Hz, 1H), 7.30–7.27 (m, 1H), 7.27–7.23 (m, 2H), 7.12–7.08 (m, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.65 (d, *J* = 19.7 Hz, 1H), 4.54 (d, *J* = 11.9 Hz, 1H), 4.34 (d, *J* = 11.9 Hz, 1H), 3.44 (d, *J* = 19.7 Hz, 1H), 3.20–3.10 (m, 4H), 2.55–2.47 (m, 1H), 2.46–2.37 (m, 1H), 2.31 (s, 3H), 1.62–1.53 (m, 4H), 1.41–1.28 (m, 2H), 1.23–1.09 (m, 6H), 0.90 (t, *J* = 7.4 Hz, 6H), 0.83 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 206.9, 163.7, 148.8, 145.0, 143.3, 138.6, 138.3, 137.3, 135.4, 135.0, 133.8, 132.7, 132.1, 131.3, 130.9, 130.8, 129.4, 129.3, 129.1, 128.9, 127.2, 126.8, 126.5, 125.8, 121.6, 118.2, 56.3, 51.3, 50.0, 33.1, 31.3, 30.2, 28.8, 22.3, 21.9, 21.3, 14.0, 11.1; **HRMS (ESI)** calcd for $C_{45}H_{51}N_2O_7S_2$ $[M+H]^+$: 795.3132; found: 795.3135.

10-cyclohexyl-5-tosyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]naphtho[2,1-*d*]azonin-1-one (2z)



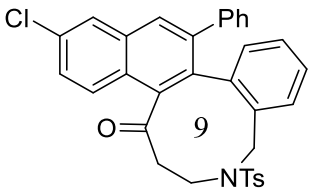
Column chromatography (petroleum ether/EtOAc = 30:1 to 15:1) to afford **2z** in 74% yield (38.8 mg); colorless solid, mp 238–240 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.99 (s, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.57–7.49 (m, 2H), 7.46–7.41 (m, 3H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 7.8 Hz, 2H), 3.47–3.30 (m, 2H), 2.73 (t, *J* = 11.3 Hz, 1H), 2.68–2.56 (m, 2H), 2.27 (s, 3H), 2.15 (d, *J* = 12.0 Hz, 1H), 2.09 (d, *J* = 12.9 Hz, 1H), 2.00–1.89 (m, 1H), 1.85–1.69 (m, 5H), 1.50–1.42 (m, 1H), 1.35–1.25 (m, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 213.1, 146.1, 143.6, 141.7, 141.3, 135.7, 134.3, 132.8, 132.8, 132.3, 129.0, 128.7, 128.3, 128.1, 127.6, 127.1, 126.5, 126.5, 126.0, 125.9, 123.9, 49.9, 42.3, 40.8, 37.9, 33.5, 27.0, 26.9, 26.4, 25.9, 21.4; **HRMS (ESI)** calcd for $C_{33}H_{34}NO_3S$ $[M+H]^+$: 524.2254; found: 524.2255.

10-phenyl-4-tosyl-2,3,4,5-tetrahydro-1*H*-benzo[*c*]naphtho[2,1-*e*]azonin-1-one (2aa)



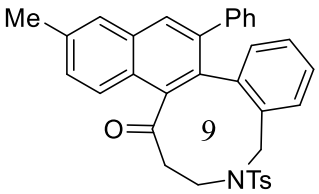
Column chromatography (petroleum ether/EtOAc = 20:1 to 10:1) to afford **2aa** in 71% yield (36.8 mg); colorless solid, mp 186–188 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.90 (s, 1H), 7.61–7.55 (m, 3H), 7.53 (dd, *J* = 6.6, 3.9 Hz, 2H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.19–7.17 (m, 3H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.07 (dd, *J* = 6.3, 2.9 Hz, 2H), 7.02 (d, *J* = 7.6 Hz, 1H), 4.49 (d, *J* = 13.7 Hz, 1H), 3.90 (d, *J* = 13.6 Hz, 1H), 3.45 (dd, *J* = 14.3, 6.9 Hz, 1H), 3.35 (dd, *J* = 14.9, 9.3 Hz, 1H), 3.20 (ddd, *J* = 15.2, 9.3, 2.1 Hz, 1H), 2.66 (dd, *J* = 15.2, 7.6 Hz, 1H), 2.37 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 209.3, 143.5, 140.1, 140.0, 139.2, 138.4, 136.0, 133.4, 133.2, 132.7, 132.2, 130.3, 129.8, 129.7, 129.4, 128.6, 128.5, 127.7, 127.7, 127.5, 127.4, 127.0, 126.9, 126.9, 124.0, 50.8, 46.4, 44.7, 21.5; **HRMS (ESI)** calcd for $C_{33}H_{27}NNaO_3S$ $[M+Na]^+$: 540.1604; found: 540.1603.

13-chloro-10-phenyl-4-tosyl-2,3,4,5-tetrahydro-1*H*-benzo[*c*]naphtho[2,1-*e*]azonin-1-one (2ab)



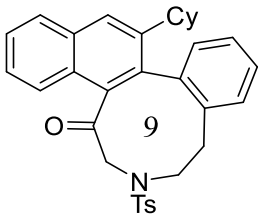
Column chromatography (petroleum ether/EtOAc = 25:1 to 14:1) to afford **2ab** in 81% yield (44.7 mg); colorless solid, mp 215–217 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.92 (s, 1H), 7.81 (s, 1H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 0.9 Hz, 2H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.25–7.15 (m, 7H), 7.10–7.07 (m, 2H), 7.05 (d, *J* = 7.0 Hz, 1H), 4.32 (d, *J* = 13.5 Hz, 1H), 3.96 (d, *J* = 13.5 Hz, 1H), 3.48–3.37 (m, 1H), 3.29–3.15 (m, 2H), 2.60 (dd, *J* = 13.3, 7.1 Hz, 1H), 2.39 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 208.6, 143.6, 140.3, 140.2, 139.6, 138.0, 135.6, 133.5, 133.4, 133.1, 132.7, 132.4, 130.3, 129.7, 129.4, 128.9, 128.7, 128.2, 127.8, 127.8, 127.3, 127.1, 127.0, 125.8, 125.6, 51.2, 46.4, 44.4, 21.5; **HRMS (ESI)** calcd for $C_{33}H_{26}ClNNaO_3S$ $[M+Na]^+$: 574.1214; found: 574.1220.

13-methyl-10-phenyl-4-tosyl-2,3,4,5-tetrahydro-1*H*-benzo[*c*]naphtho[2,1-*e*]azonin-1-one (2ac)



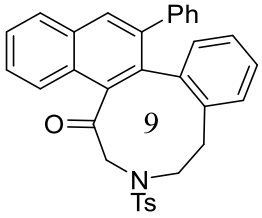
Column chromatography (petroleum ether/EtOAc = 25:1 to 14:1) to afford **2ac** in 73% yield (38.8 mg); colorless solid, mp 229–231 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.81 (s, 1H), 7.71 (s, 1H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.40–7.34 (m, 2H), 7.25–7.12 (m, 7H), 7.09–7.04 (m, 2H), 7.02 (d, *J* = 7.3 Hz, 1H), 4.49 (d, *J* = 13.6 Hz, 1H), 3.90 (d, *J* = 13.6 Hz, 1H), 3.48–3.32 (m, 2H), 3.19 (ddd, *J* = 15.3, 9.1, 2.5 Hz, 1H), 2.64 (ddd, *J* = 15.4, 7.6, 1.5 Hz, 1H), 2.55 (s, 3H), 2.38 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 209.4, 143.4, 140.2, 139.9, 139.1, 138.5, 136.7, 136.0, 133.5, 133.0, 132.2, 130.3, 129.7, 129.6, 129.4, 129.2, 128.4, 127.7, 127.7, 127.5, 127.0, 126.8, 125.8, 123.8, 50.8, 46.4, 44.8, 21.7, 21.4; **HRMS (ESI)** calcd for $C_{34}H_{29}NNaO_3S$ $[M+Na]^+$: 554.1760; found: 554.1764.

10-cyclohexyl-3-tosyl-2,3,4,5-tetrahydro-1*H*-benzo[*d*]naphtho[2,1-*f*]azonin-1-one (2ad)



Column chromatography (petroleum ether/EtOAc = 30:1 to 16:1) to afford **2ad** in 99% yield (51.8 mg); colorless solid, mp 216–218 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.06 – 8.00 (m, 1H), 7.90 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.40 – 7.32 (m, 3H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 7.5 Hz, 1H), 4.15 (d, *J* = 18.9 Hz, 1H), 4.00 – 3.87 (m, 1H), 2.90 – 2.79 (m, 2H), 2.76 – 2.67 (m, 2H), 2.19 (t, *J* = 11.8 Hz, 1H), 1.80 (d, *J* = 11.5 Hz, 2H), 1.73 – 1.61 (m, 4H), 1.40 – 1.33 (m, 1H), 1.30 – 1.21 (m, 1H), 1.19 – 1.06 (m, 1H), 1.03 – 0.93 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 205.8, 143.6, 142.5, 138.6, 138.3, 137.3, 135.2, 134.7, 133.5, 131.4, 129.5, 129.0, 128.5, 128.4, 127.3, 127.2, 126.9, 126.8, 126.4, 126.2, 126.1, 59.9, 53.5, 40.3, 35.3, 34.8, 33.6, 26.8, 26.7, 25.9, 21.3; **HRMS (ESI)** calcd for $C_{33}H_{34}NO_3S$ $[M+H]^+$: 524.2254; found: 524.2255.

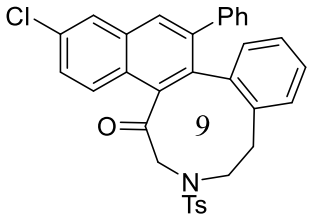
10-phenyl-3-tosyl-2,3,4,5-tetrahydro-1*H*-benzo[*d*]naphtho[2,1-*f*]azonin-1-one (2ae)



Column chromatography (petroleum ether/EtOAc = 25:1 to 14:1) to afford **2ae** in 81% yield (41.9 mg); colorless solid, mp 181–183 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.95 (s, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.66–7.53 (m, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.23–7.10 (m, 9H), 7.08 (d, *J* = 6.7 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 4.13 (d, *J* = 18.9 Hz, 1H), 3.92 (dt, *J* = 13.4, 3.3 Hz, 1H), 2.91–2.84 (m, 1H), 2.82 (d, *J* = 19.0 Hz, 1H), 2.63 (t, *J* = 12.6 Hz, 1H), 2.54 (dd, *J* = 13.5, 3.8 Hz, 1H), 2.38 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 205.4, 143.7, 140.3, 138.5, 138.4, 138.1, 137.8, 134.8,

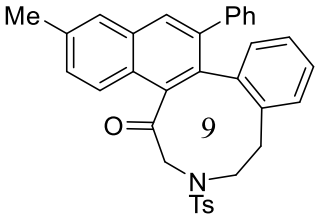
134.8, 133.2, 132.4, 130.5, 129.7, 129.4, 129.3, 129.0, 128.3, 127.8, 127.5, 127.3, 127.0, 126.9, 126.7, 126.6, 126.5, 60.2, 53.6, 35.1, 21.4; **HRMS (ESI)** calcd for $C_{33}H_{28}NO_3S$ $[M+H]^+$: 518.1784; found: 518.1789.

13-chloro-10-phenyl-3-tosyl-2,3,4,5-tetrahydro-1*H*-benzo[*d*]naphtho[2,1-*f*]azonin-1-one (2af)



Column chromatography (petroleum ether/EtOAc = 30:1 to 15:1) to afford **2af** in 85% yield (46.9 mg); colorless solid, mp 203–204 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.05 (d, *J* = 9.1 Hz, 1H), 7.89 (d, *J* = 2.0 Hz, 1H), 7.85 (s, 1H), 7.54 (dd, *J* = 9.1, 2.1 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.25–7.09 (m, 9H), 7.09–7.05 (m, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 4.06 (d, *J* = 19.0 Hz, 1H), 3.93 (dt, *J* = 13.4, 3.3 Hz, 1H), 2.93–2.84 (m, 1H), 2.80 (d, *J* = 19.0 Hz, 1H), 2.62 (t, *J* = 12.6 Hz, 1H), 2.55 (dd, *J* = 13.4, 3.6 Hz, 1H), 2.39 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 204.9, 143.9, 139.9, 139.3, 138.4, 138.0, 137.8, 135.1, 134.7, 133.9, 132.7, 132.3, 129.7, 129.5, 129.3, 129.2, 128.5, 128.4, 127.8, 127.7, 127.6, 127.2, 126.9, 126.6, 126.4, 60.2, 53.6, 35.2, 21.4; **HRMS (ESI)** calcd for $C_{33}H_{26}ClNNaO_3S$ $[M+Na]^+$: 574.1214; found: 574.1216.

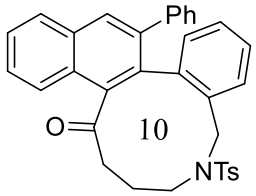
13-methyl-10-phenyl-3-tosyl-2,3,4,5-tetrahydro-1*H*-benzo[*d*]naphtho[2,1-*f*]azonin-1-one (2ag)



Column chromatography (petroleum ether/EtOAc = 25:1 to 14:1) to afford **2ag** in 82% yield (43.6 mg); colorless solid, mp 223–225 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 8.7 Hz, 1H), 7.86 (s, 1H), 7.69 (s, 1H), 7.45 (d, *J* = 8.7 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.24–7.17 (m, 3H), 7.17–7.04 (m, 7H), 6.95 (d, *J* = 7.6 Hz, 1H), 4.11 (d, *J* = 18.9 Hz, 1H), 3.96–3.87 (m, 1H), 2.93–2.84 (m, 1H), 2.81 (d, *J* = 18.9 Hz, 1H), 2.63 (t,

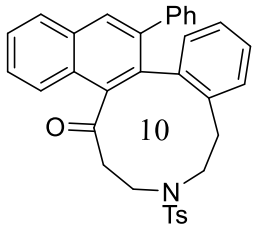
J = 12.7 Hz, 1H), 2.55 (s, 3H), 2.54–2.50 (m, 1H), 2.38 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 205.6, 143.7, 140.5, 138.6, 138.5, 138.0, 137.5, 136.6, 134.9, 133.8, 133.5, 132.5, 129.9, 129.7, 129.4, 129.4, 128.9, 128.3, 127.6, 127.5, 127.3, 126.7, 126.6, 126.5, 126.3, 60.2, 53.6, 35.2, 21.7, 21.4; **HRMS (ESI)** calcd for $C_{34}H_{30}NO_3S$ $[M+H]^+$: 532.1941; found: 532.1945.

11-phenyl-5-tosyl-3,4,5,6-tetrahydrobenzo[*c*]naphtho[2,1-*e*]azecin-1(2*H*)-one (2ah)



Column chromatography (petroleum ether/EtOAc = 25:1 to 10:1) to afford **2ah** in 43% yield (22.9 mg); colorless solid, mp 253–255 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.94–7.88 (m, 2H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.60–7.52 (m, 4H), 7.38–7.31 (m, 2H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.20–7.15 (m, 4H), 7.14–7.10 (m, 2H), 4.09 (d, *J* = 13.9 Hz, 1H), 3.58 (d, *J* = 13.9 Hz, 1H), 2.80–2.64 (m, 2H), 2.39 (s, 3H), 2.38–2.30 (m, 1H), 2.28–2.18 (m, 1H), 1.67–1.58 (m, 1H), 1.55–1.46 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 209.4, 143.3, 140.4, 140.0, 138.9, 138.4, 136.0, 134.6, 133.6, 133.1, 132.9, 130.4, 130.1, 129.7, 129.7, 129.1, 128.5, 128.2, 127.8, 127.8, 127.5, 127.1, 127.0, 126.9, 124.8, 52.8, 48.2, 40.8, 24.3, 21.5; **HRMS (ESI)** calcd for $C_{34}H_{29}NNaO_3S$ $[M+Na]^+$: 554.1760; found: 554.1766.

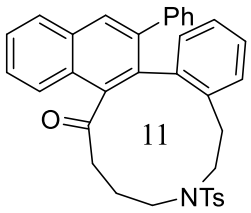
11-phenyl-4-tosyl-3,4,5,6-tetrahydrobenzo[*d*]naphtho[2,1-*f*]azecin-1(2*H*)-one (2ai)



Column chromatography (petroleum ether/EtOAc = 25:1 to 8:1) to afford **2ai** in 24% yield (12.8 mg); colorless solid, mp 208–210 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.97 (s, 1H), 7.95 (d, *J* = 4.2 Hz, 1H), 7.87–7.81 (m, 1H), 7.60–7.54 (m, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.29–7.13 (m, 10H), 6.88 (d, *J* = 7.5 Hz, 1H),

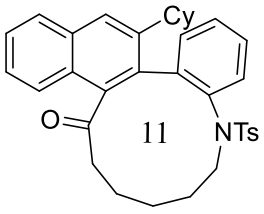
3.33–3.26 (m, 1H), 3.05–2.97 (m, 1H), 2.78–2.62 (m, 4H), 2.35 (s, 3H), 2.32–2.24 (m, 1H), 2.10–1.98 (m, 1H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 207.4, 143.2, 140.5, 139.1, 138.5, 138.4, 138.1, 135.7, 134.5, 133.3, 133.0, 130.6, 129.9, 129.5, 129.4, 129.0, 128.9, 128.5, 127.6, 127.3, 126.7, 126.6, 126.4, 124.9, 51.2, 44.7, 44.5, 34.2, 21.4; **HRMS (ESI)** calcd for $C_{34}H_{30}NO_3S$ $[M+H]^+$: 532.1941; found: 532.1945.

12-phenyl-5-tosyl-2,3,4,5,6,7-hexahydro-1*H*-benzo[*d*]naphtho[2,1-*f*][1] azacycloundecin-1-one (2aj)



Column chromatography (petroleum ether/EtOAc = 20:1 to 10:1) to afford **2aj** in 10% yield (5.5 mg); colorless solid, mp 258–260 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.91 (d, *J* = 7.4 Hz, 1H), 7.89 (s, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.58–7.51 (m, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.37–7.31 (m, 2H), 7.30–7.26 (m, 1H), 7.25–7.12 (m, 6H), 7.08 (d, *J* = 6.7 Hz, 2H), 3.87–3.76 (m, 1H), 2.90–2.79 (m, 1H), 2.62 (dt, *J* = 13.7, 4.3 Hz, 1H), 2.56–2.46 (m, 1H), 2.38 (s, 3H), 2.34 (t, *J* = 8.0 Hz, 1H), 2.31–2.25 (m, 2H), 2.20 (dt, *J* = 15.5, 4.3 Hz, 1H), 1.74–1.65 (m, 1H), 1.62–1.56 (m, 1H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 209.8, 143.5, 140.3, 139.7, 138.9, 138.1, 135.7, 134.3, 134.2, 133.1, 132.3, 129.8, 129.6, 129.5, 128.9, 128.6, 128.4, 127.6, 127.5, 127.5, 126.8, 126.3, 125.0, 48.7, 47.6, 40.1, 31.1, 23.4, 21.4; **HRMS (ESI)** calcd for $C_{35}H_{32}NO_3S$ $[M+H]^+$: 546.2097; found: 546.2104.

12-cyclohexyl-7-tosyl-2,3,4,5,6,7-hexahydro-1*H*-benzo[*b*]naphtho[2,1-*d*][1] azacycloundecin-1-one (2ak)

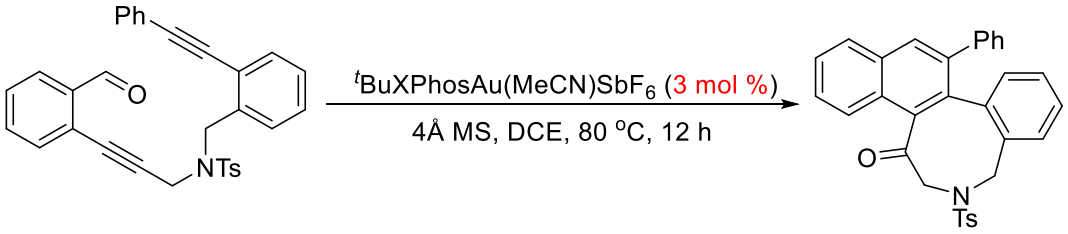


Column chromatography (petroleum ether/EtOAc = 25:1 to 12:1) to afford **2ak** in 37% yield (20.4 mg); pale-yellow solid, mp 180–182 ℃; **^{1}H NMR (600 MHz, CDCl$_3$)** δ

7.94 (s, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.47–7.42 (m, 1H), 7.41–7.36 (m, 1H), 7.33 (dd, *J* = 16.6, 8.1 Hz, 5H), 3.41 (dt, *J* = 16.2, 8.3 Hz, 1H), 3.10–3.00 (m, 1H), 2.84 (dd, *J* = 15.8, 7.2 Hz, 1H), 2.72–2.61 (m, 1H), 2.44 (s, 3H), 2.29 (d, *J* = 11.7 Hz, 1H), 2.20 (dt, *J* = 16.2, 5.2 Hz, 1H), 1.83 (dd, *J* = 16.9, 7.2 Hz, 2H), 1.76–1.67 (m, 1H), 1.64 (d, *J* = 13.0 Hz, 1H), 1.57–1.50 (m, 3H), 1.49–1.44 (m, 1H), 1.31–1.09 (m, 3H), 1.07–0.87 (m, 4H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 209.4, 145.4, 143.4, 138.9, 138.1, 137.8, 136.0, 134.9, 134.3, 133.4, 129.8, 128.5, 128.4, 128.4, 127.6, 126.5, 126.5, 126.3, 126.2, 124.8, 45.7, 41.9, 39.6, 37.3, 31.5, 26.9, 26.3, 25.9, 23.1, 22.7, 21.5, 21.1; **HRMS (ESI)** calcd for $C_{35}H_{37}NNaO_3S$ $[M+Na]^+$: 574.2386; found: 574.2396.

4. Gram-scale synthesis of 2a and 2c and further transformations

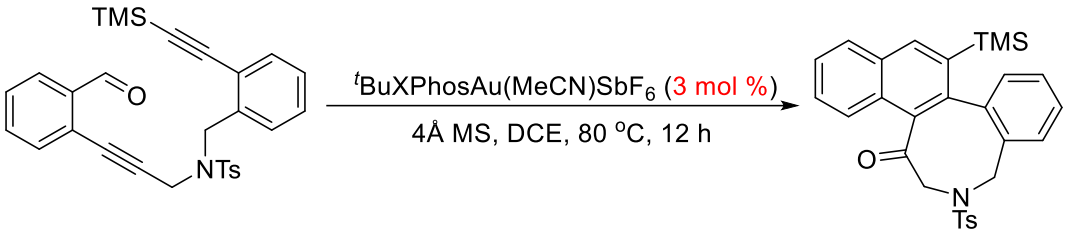
4.1. Gram-scale synthesis of 2a



1a (1.007 g, 2 mmol) **2a** (856 mg, 85% yield)

To a solution of **1a** (1.007 g, 2 mmol) and 4 Å MS (1.000 g) in anhydrous DCE (40 mL) was added ^{t}BuXPhosAu(MeCN)SbF$_6$ (3 mol %) under an argon atmosphere. The reaction mixture was stirred at 80 ^{o}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 = 25:1 to 10:1) to give the product **2a** (856 mg, 85%).

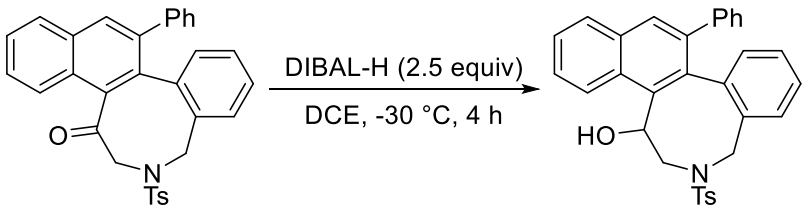
4.2. Gram-scale synthesis of 2c



1a (0.999 g, 2 mmol) **2a** (819 mg, 82% yield)

To a solution of **1c** (0.999 g, 2.0 mmol) and 4 Å MS (1.000 g) in anhydrous DCE (40 mL) was added ^{t}BuXPhosAu(MeCN)SbF_6 (3 mol %) under an argon atmosphere. The reaction mixture was stirred at 80 °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 = 25:1 to 12:1) to give the product **2c** (819 mg, 82%).

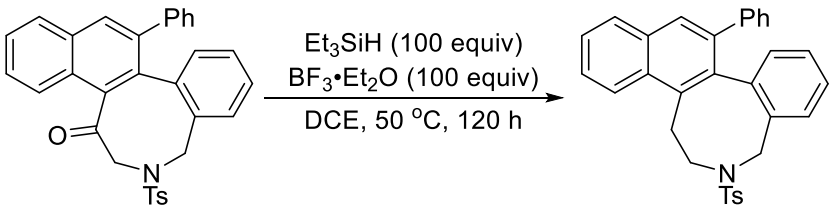
4.3. Synthetic transformation of 2a



2a **3**, 90% yield

To a solution of **2a** (100.7 mg, 0.2 mmol) in 2 mL anhydrous DCE at -30 °C was added DIBAL-H (1.0 M in hexane, 0.5 mL) dropwise and the reaction mixture was stirred -30 °C for 4 h. The reaction was quenched with MeOH (2 mL) at -30 °C and warmed to room temperature and stirred until the mixture became clear. The mixture was extract with EtOAc, washed with brine and dried over $MgSO_4$, then filtrated and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether: EtOAc = 20:1 to 13:1) to afford the product **3** in 90% yield (91.0 mg) as a colorless solid, mp 218–220 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.77–8.69 (m, 1H), 7.93–7.86 (m, 1H), 7.84 (s, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.57–7.49 (m, 2H), 7.33–7.28 (m, 1H), 7.26 (t, *J* = 4.1 Hz, 2H), 7.20–7.13 (m, 3H), 6.97 (td, *J* = 7.6, 0.8 Hz, 1H), 6.95–6.88 (m, 2H), 6.79 (d, *J* = 7.4 Hz,

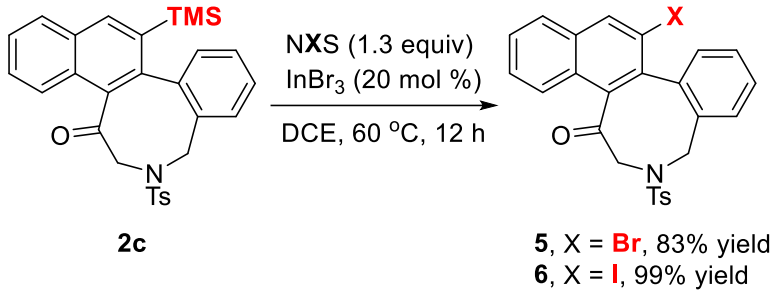
1H), 5.13 (d, *J* = 8.6 Hz, 1H), 4.90 (d, *J* = 14.1 Hz, 1H), 4.34 (d, *J* = 11.5 Hz, 1H), 3.49 (dd, *J* = 11.5, 9.1 Hz, 1H), 3.26 (d, *J* = 14.1 Hz, 1H), 2.37 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 143.4, 141.4, 139.1, 137.7, 137.6, 136.6, 135.8, 134.8, 134.0, 130.9, 130.3, 130.2, 129.8, 129.5, 128.9, 128.8, 128.4, 127.7, 127.1, 127.1, 126.4, 126.4, 126.3, 126.1, 72.1, 53.9, 48.8, 21.4; **HRMS (ESI)** calcd for $C_{32}H_{28}NO_3S$ $[M+H]^+$: 506.1784; found: 506.1785.



2a **4**, 98% yield

To a solution of **2a** (100.7 mg, 0.2 mmol) in DCE (4 mL) was added Et_3SiH (3.18 mL, 20 mmol) and BF_3 Łt_2O (2.47 mL, 20 mmol). The reaction mixture was stirred at 50 °C for 120 h until completion (monitored by TLC). The reaction mixture was cooled down to room temperature and quenched with H_2O and extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether: EtOAc = 50:1 to 25:1) to give the product **4** in 98% yield (96.0 mg) as a colorless solid, mp 168–170 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.25 (d, *J* = 8.3 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 7.4 Hz, 1H), 7.77 – 7.68 (m, 3H), 7.66 – 7.61 (m, 1H), 7.58 – 7.45 (m, 6H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.27 – 7.24 (m, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 4.83 (dd, *J* = 10.1, 4.1 Hz, 1H), 4.09 (dd, *J* = 14.2, 4.2 Hz, 1H), 2.77 (s, 3H), 2.73 (dd, *J* = 14.1, 10.1 Hz, 1H), 2.41 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 146.8, 143.5, 141.2, 140.9, 140.8, 136.6, 136.4, 134.1, 132.6, 129.7, 129.6, 129.2, 128.9, 127.7, 127.6, 127.1, 126.6, 126.3, 125.8, 125.5, 124.2, 123.0, 55.8, 47.2, 37.9, 21.5; **HRMS (ESI)** calcd for $C_{32}H_{28}NO_2S$ $[M+H]^+$:490.1841; found: 490.1851.

4.4. Synthetic transformation of 2c



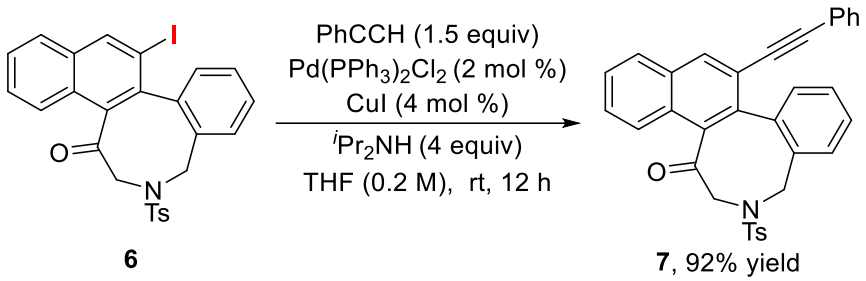
2c

5, X = **Br**, 83% yield
6, X = **I**, 99% yield

To a solution of **2c** (249.9 mg, 0.5 mmol), NBS (115.7 mg, 0.65 mmol) or NIS (146.2 mg, 0.65 mmol) in anhydrous DCE (10 mL) was added $InBr_3$ (35.5 mg, 0.1 mmol) under an argon atmosphere. The mixture was stirred at 60 °C for 12 h until full consumption of the starting material. The mixture was concentrated and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 25:1 to 10:1) to give **5** (210.2 mg) and **6** (273.9 mg) in 83% and 99% yields, respectively.

Compound **5**: pale-yellow solid, mp 163–165 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.21 (s, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.60 – 7.51 (m, 2H), 7.45 – 7.38 (m, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 1.6 Hz, 1H), 7.18 (dd, *J* = 7.3, 1.6 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.61 (d, *J* = 19.7 Hz, 1H), 4.24 (d, *J* = 12.1 Hz, 1H), 3.45 (d, *J* = 19.6 Hz, 1H), 2.32 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 205.7, 143.4, 138.9, 138.5, 135.6, 134.5, 134.1, 133.3, 132.9, 130.9, 130.6, 129.5, 129.3, 129.1, 128.1, 127.9, 127.5, 127.2, 126.6, 125.3, 119.7, 56.3, 51.4, 21.5; **HRMS (ESI)** calcd for $C_{26}H_{21}BrNO_3S$ $[M+H]^+$: 506.0420; found: 506.0422.

Compound **6**: pale-yellow solid, mp 189–191 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.48 (s, 1H), 7.78 – 7.73 (m, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.59 – 7.51 (m, 2H), 7.45 – 7.39 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 2.3 Hz, 1H), 7.15 – 7.08 (m, 1H), 6.97 (d, *J* = 8.1 Hz, 2H), 4.63 (d, *J* = 3.9 Hz, 1H), 4.61 (d, *J* = 11.5 Hz, 1H), 4.25 (d, *J* = 12.2 Hz, 1H), 3.46 (d, *J* = 19.6 Hz, 1H), 2.32 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 205.8, 143.3, 142.0, 140.3, 137.6, 137.2, 135.6, 134.4, 132.9, 130.7, 130.5, 129.4, 129.4, 129.2, 128.5, 128.1, 127.3, 127.0, 126.5, 125.1, 95.4, 56.1, 51.4, 21.5; **HRMS (ESI)** calcd for $C_{26}H_{20}INNaO_3S$ $[M+Na]^+$: 576.0101; found: 576.0111.



6 **7**, 92% yield

To an oven-dried round-bottom flask equipped with a stirring bar were added **6** (110.7 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (28.0 mg, 0.004 mmol) and CuI (15.0 mg, 0.008 mmol) in anhydrous THF (2 mL) was added phenylacetylene (0.033 mL, 0.3 mmol) and diisopropylamine ($^iPr_2NH$, 4.0 equiv) under an argon atmosphere 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 $MgSO_4$. After filtration and concentration, the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc = 25:1 to 10:1) to afford **7** (97.1 mg) in 92% yield as pale-yellow solid, mp 84–86 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.17 (s, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.48 – 7.40 (m, 2H), 7.37 (d, *J* = 8.1 Hz, 3H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.27 – 7.22 (m, 3H), 7.15 – 7.03 (m, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.68 (d, *J* = 12.1 Hz, 1H), 4.65 (d, *J* = 19.7 Hz, 1H), 4.32 (d, *J* = 12.1 Hz, 1H), 3.53 (d, *J* = 19.6 Hz, 1H), 2.30 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 206.2, 143.2, 139.0, 137.2, 135.8, 135.7, 133.8, 133.0, 132.7, 131.3, 131.1, 130.5, 129.4, 129.0, 128.7, 128.6, 128.4, 128.2, 128.2, 128.0, 127.1, 126.6, 125.3, 122.7, 119.6, 94.1, 87.8, 56.4, 51.4, 21.5; **HRMS (ESI)** calcd for $C_{34}H_{26}NO_3S$ $[M+H]^+$: 528.1628; found: 528.1637.

5. ^{1}H, ^{13}C and ^{19}F NMR Spectra

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

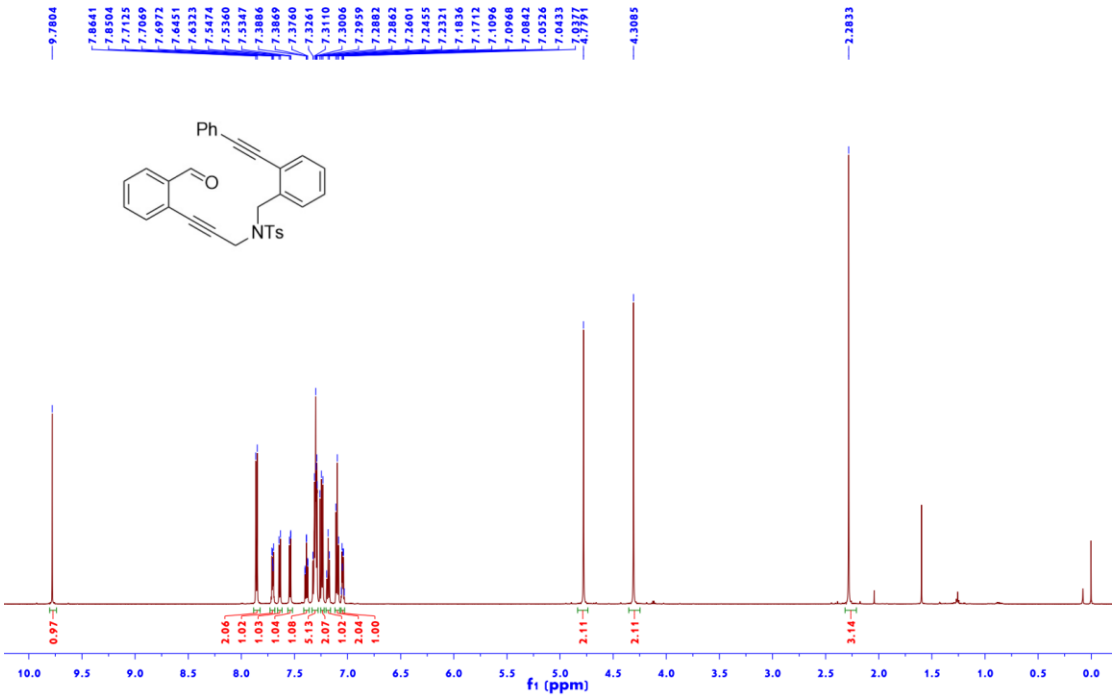


Figure S2 ^{13}C NMR (150 MHz, $CDCl_3$) of 1a

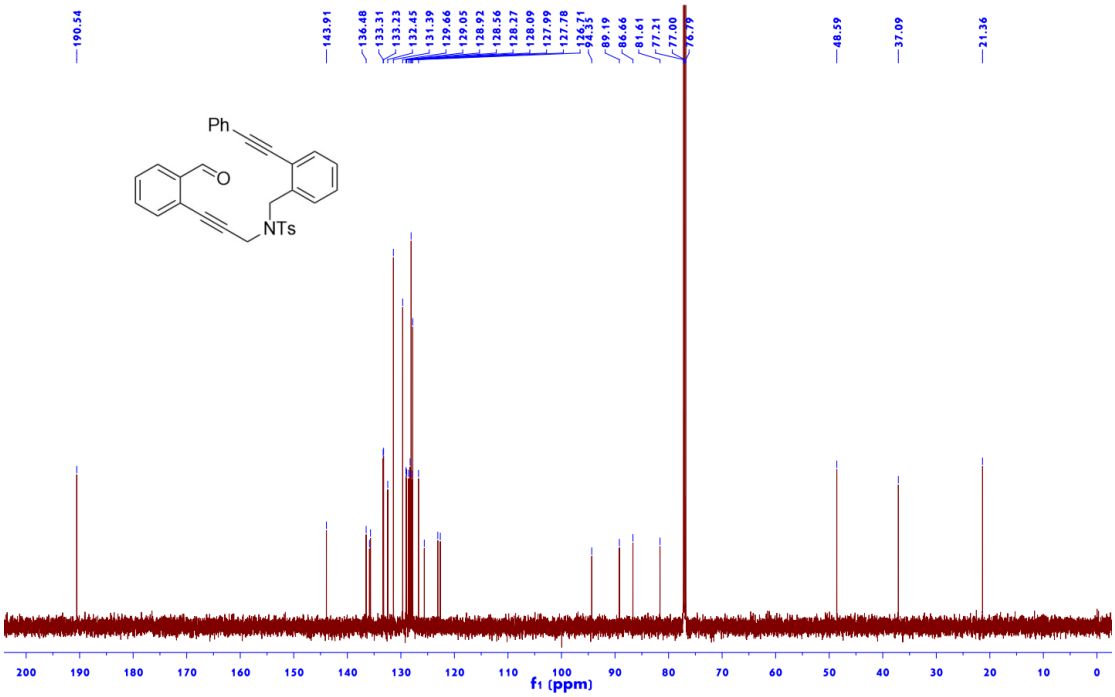


Figure S3 ^{1}H NMR (600 MHz, $CDCl_3$) of 1b

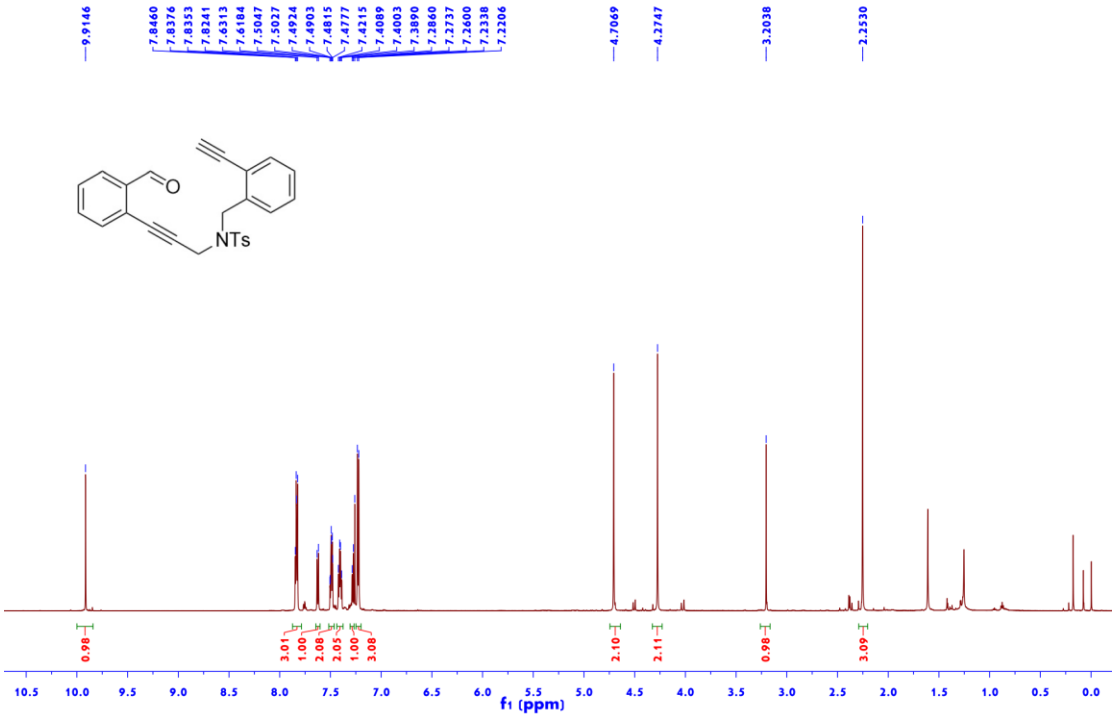


Figure S4 ^{13}C NMR (150 MHz, $CDCl_3$) of 1b

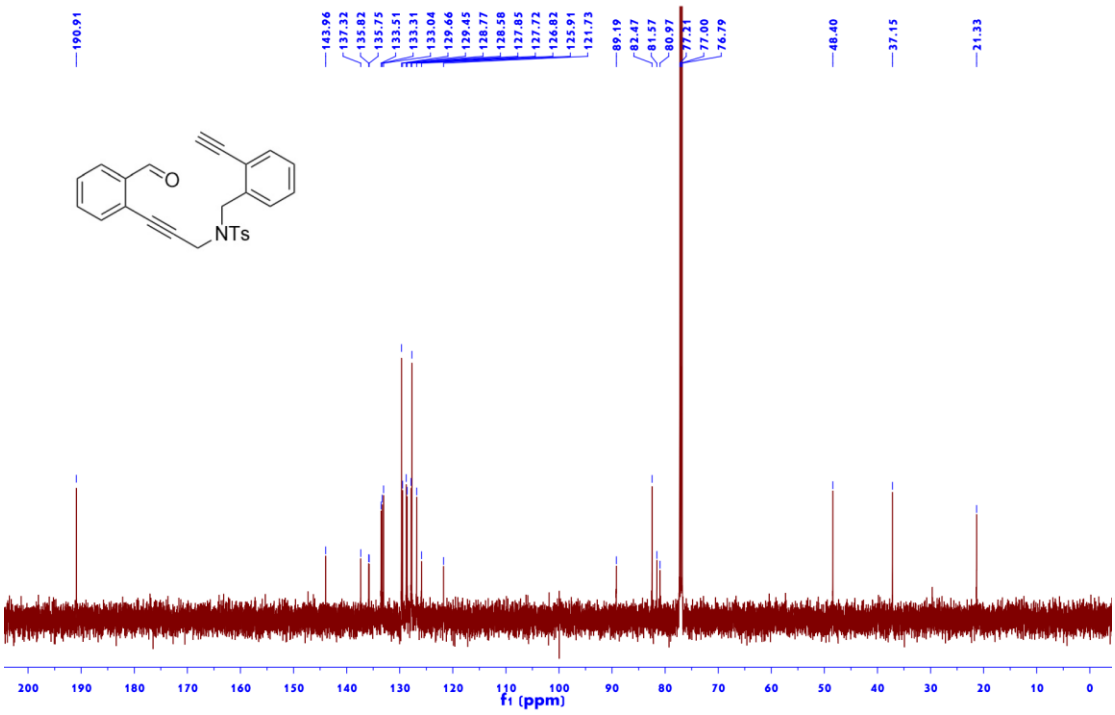


Figure S5 ^{1}H NMR (600 MHz, $CDCl_3$) of 1c

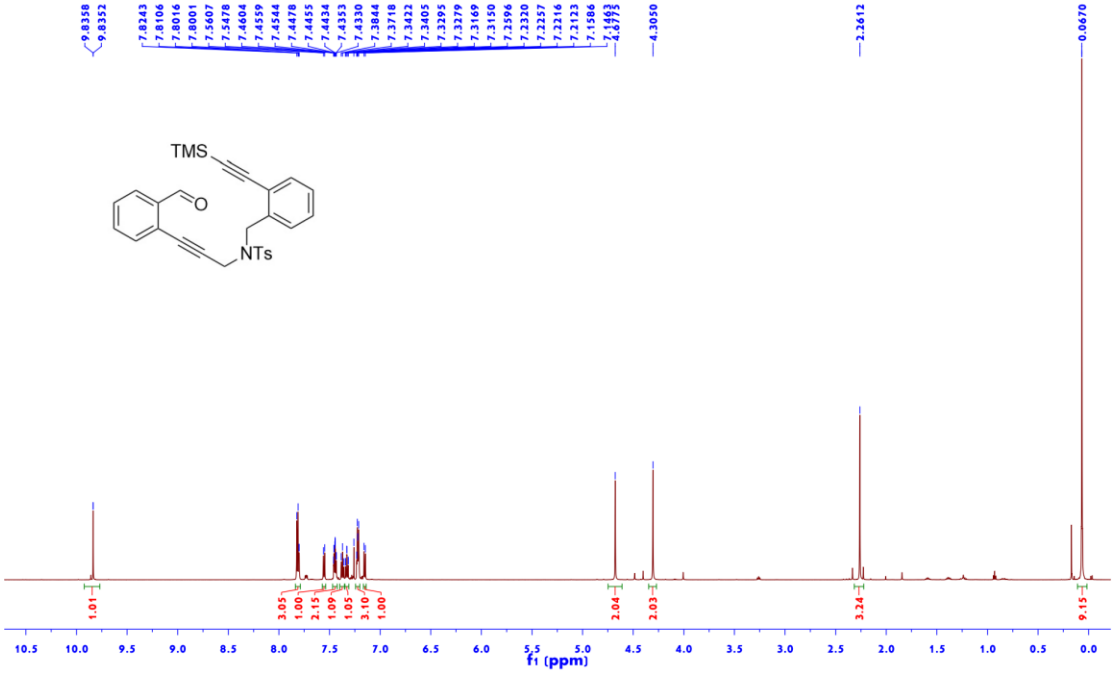


Figure S6 ^{13}C NMR (150 MHz, $CDCl_3$) of 1c

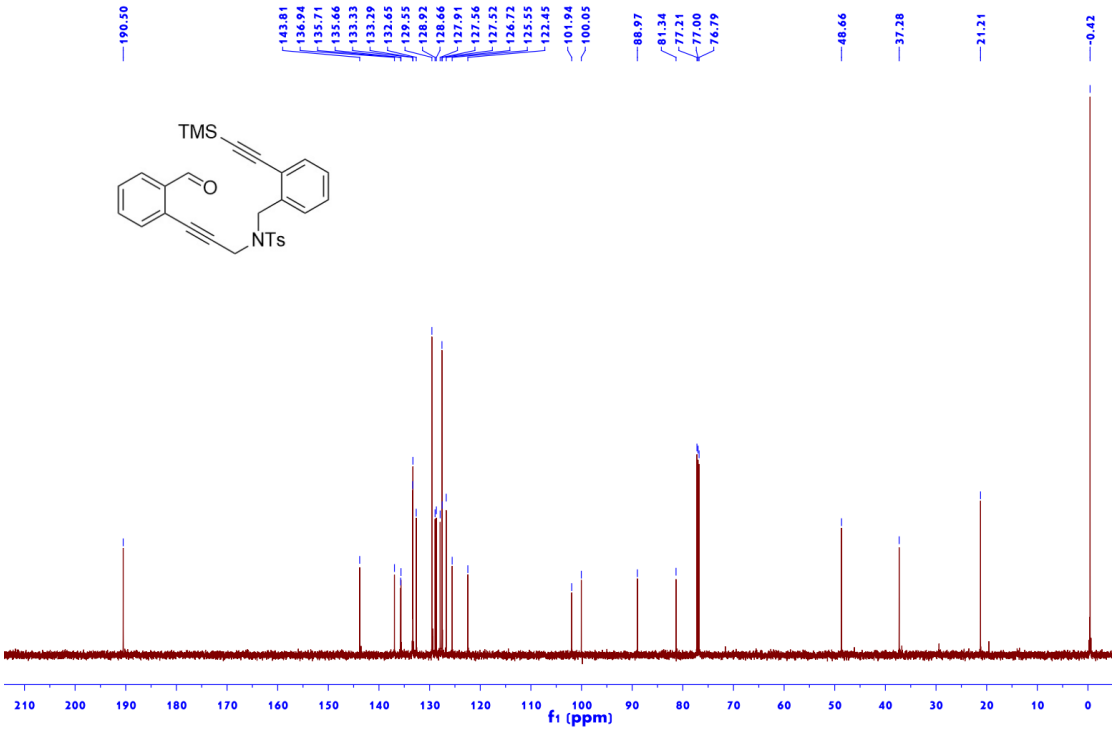


Figure S7 ^{1}H NMR (400 MHz, $CDCl_3$) of 1d

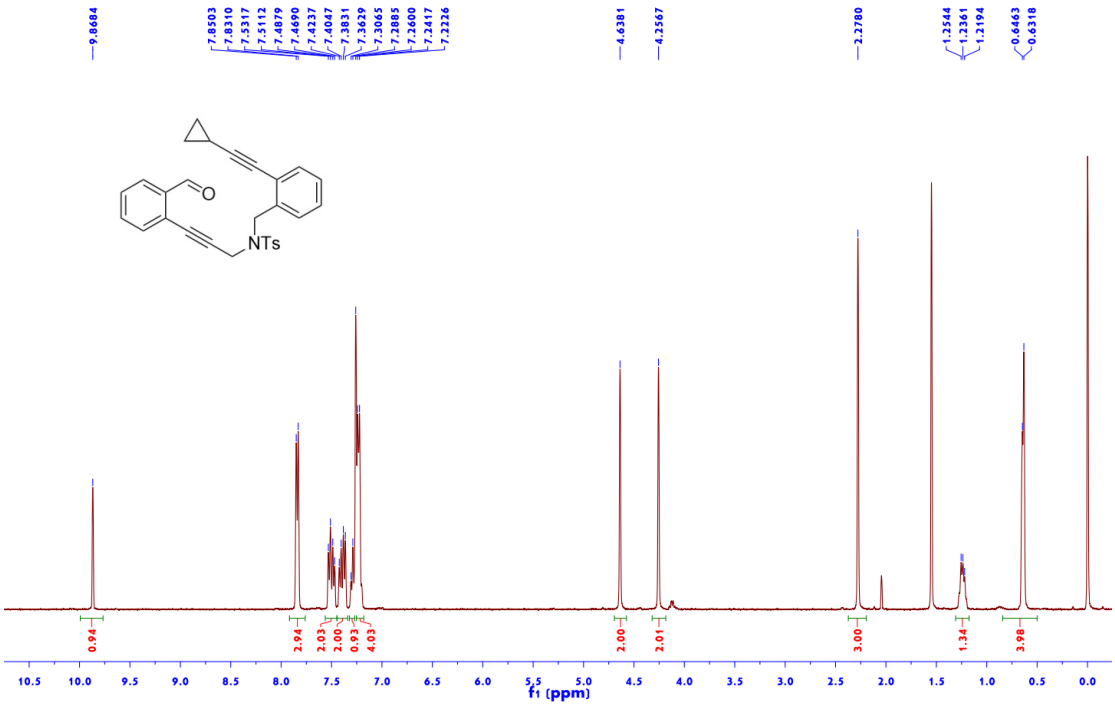


Figure S8 ^{13}C NMR (150 MHz, $CDCl_3$) of 1d

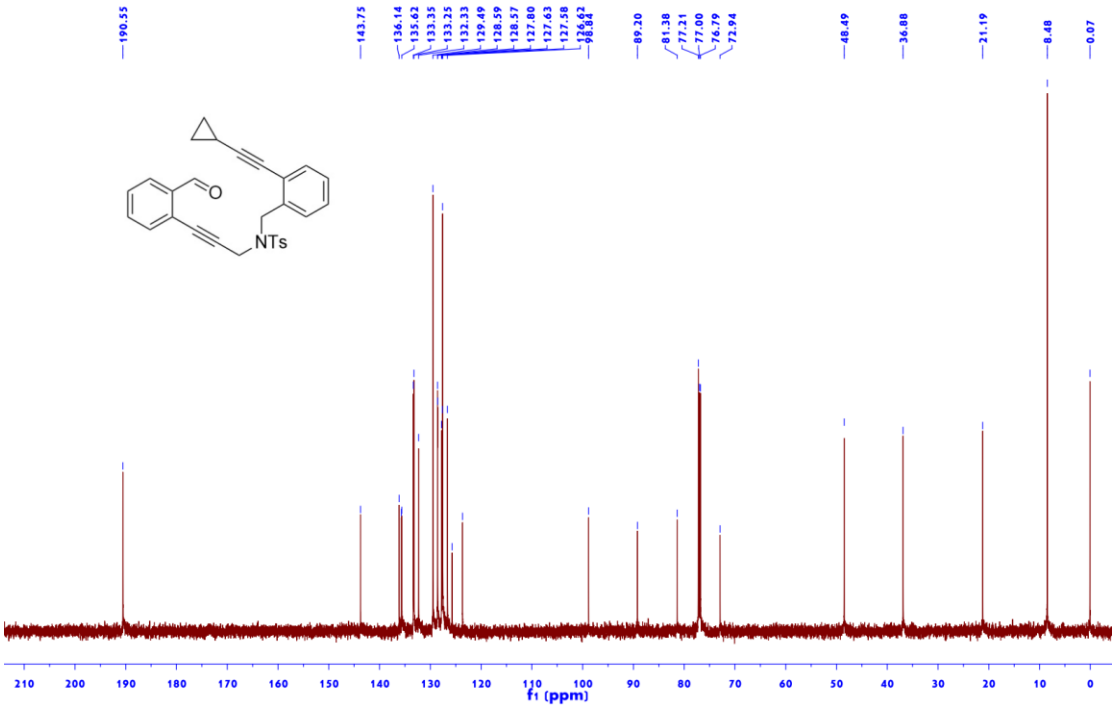


Figure S9 ^{1}H NMR (400 MHz, $CDCl_3$) of 1e

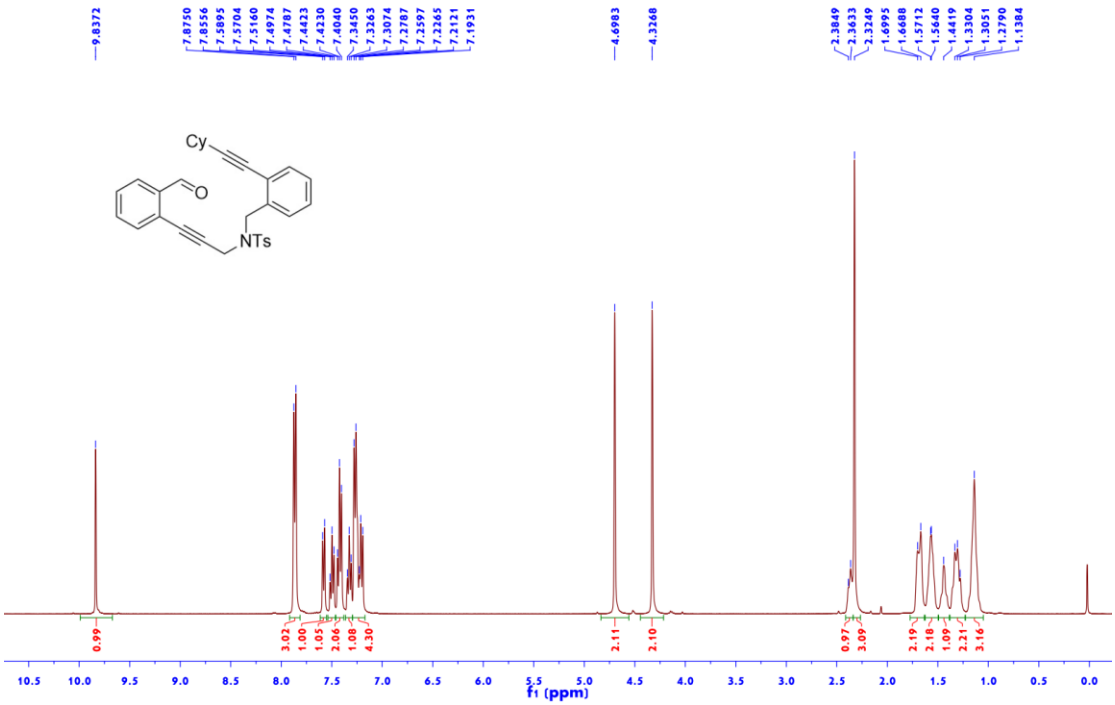


Figure S10 ^{13}C NMR (100 MHz, $CDCl_3$) of 1e

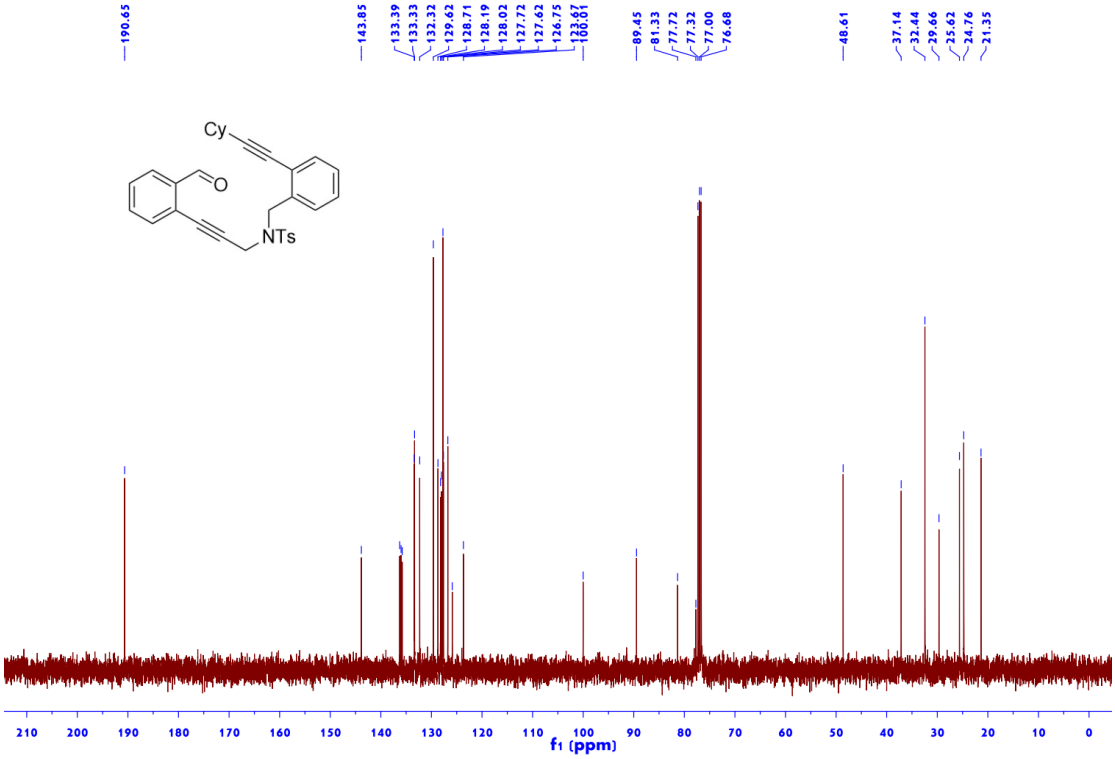


Figure S11 ^{1}H NMR (600 MHz, $CDCl_3$) of 1f

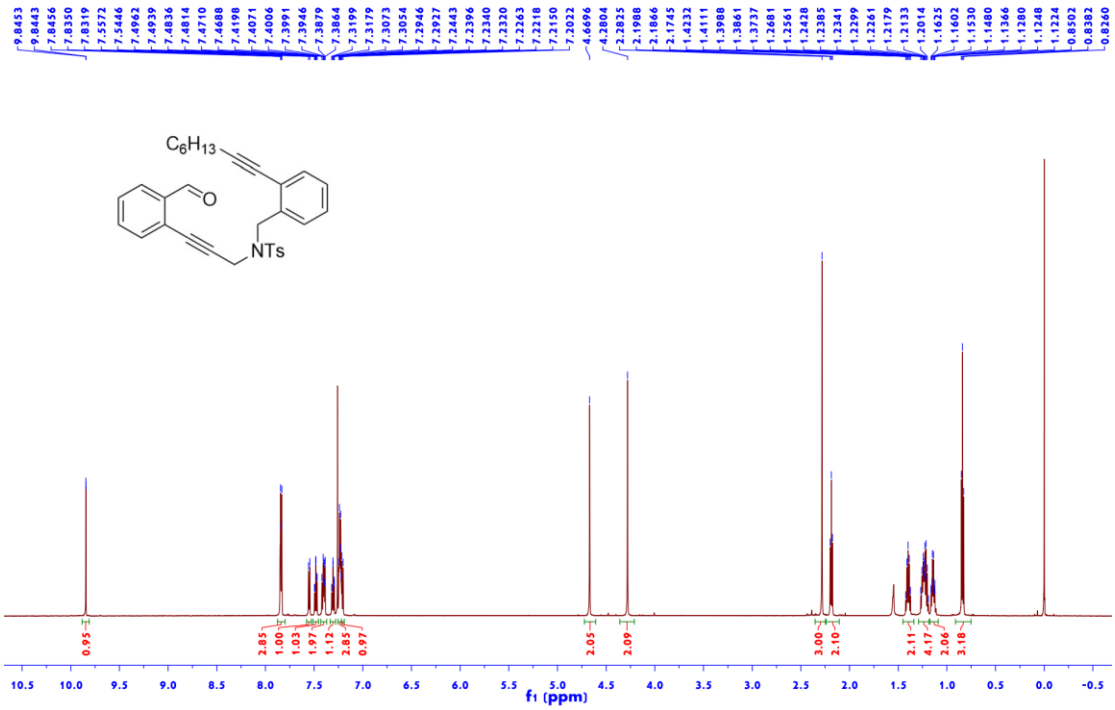


Figure S12 ^{13}C NMR (150 MHz, $CDCl_3$) of 1f

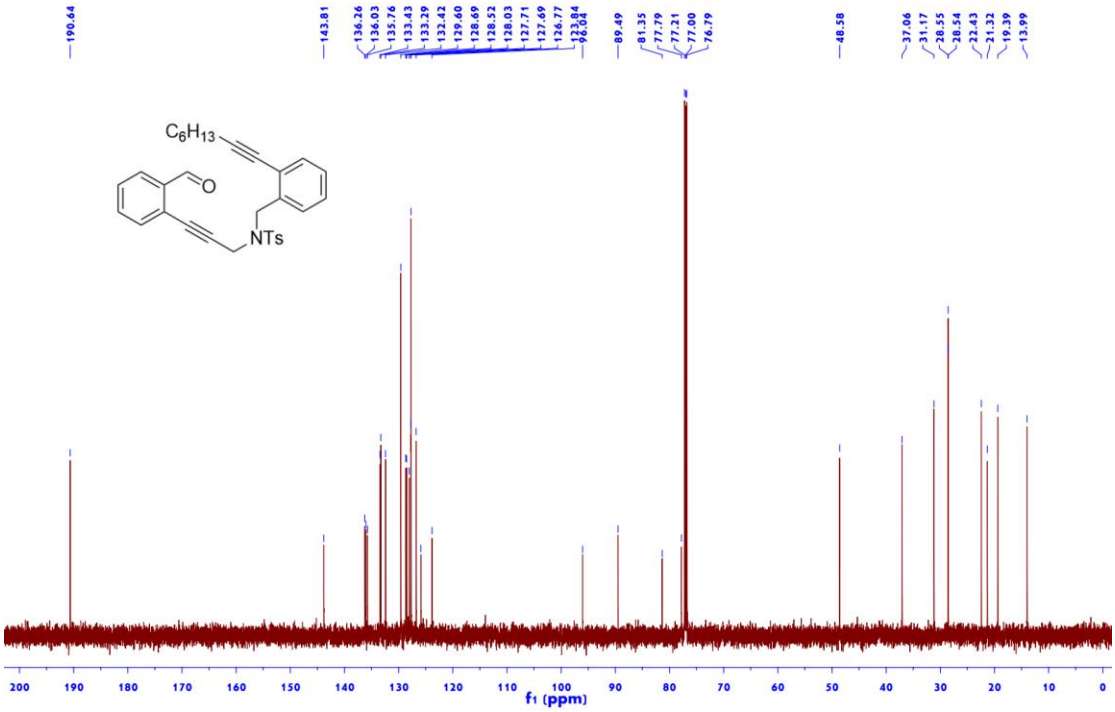


Figure S13 ^{1}H NMR (600 MHz, $CDCl_3$) of 1g

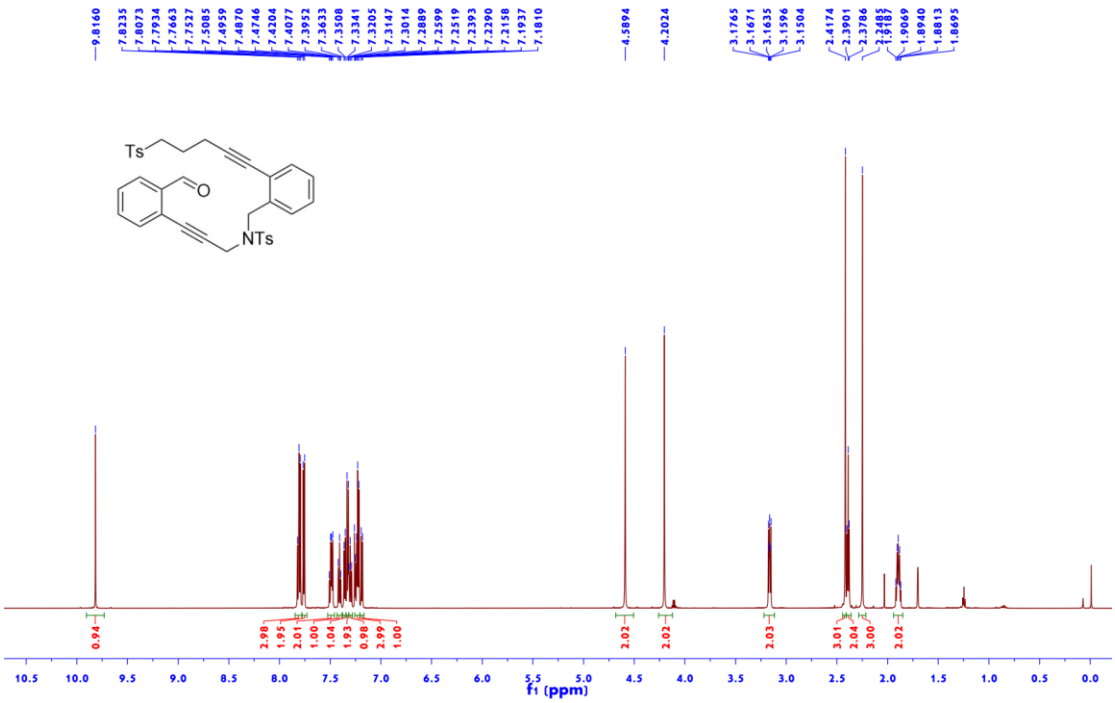


Figure S14 ^{13}C NMR (150 MHz, $CDCl_3$) of 1g

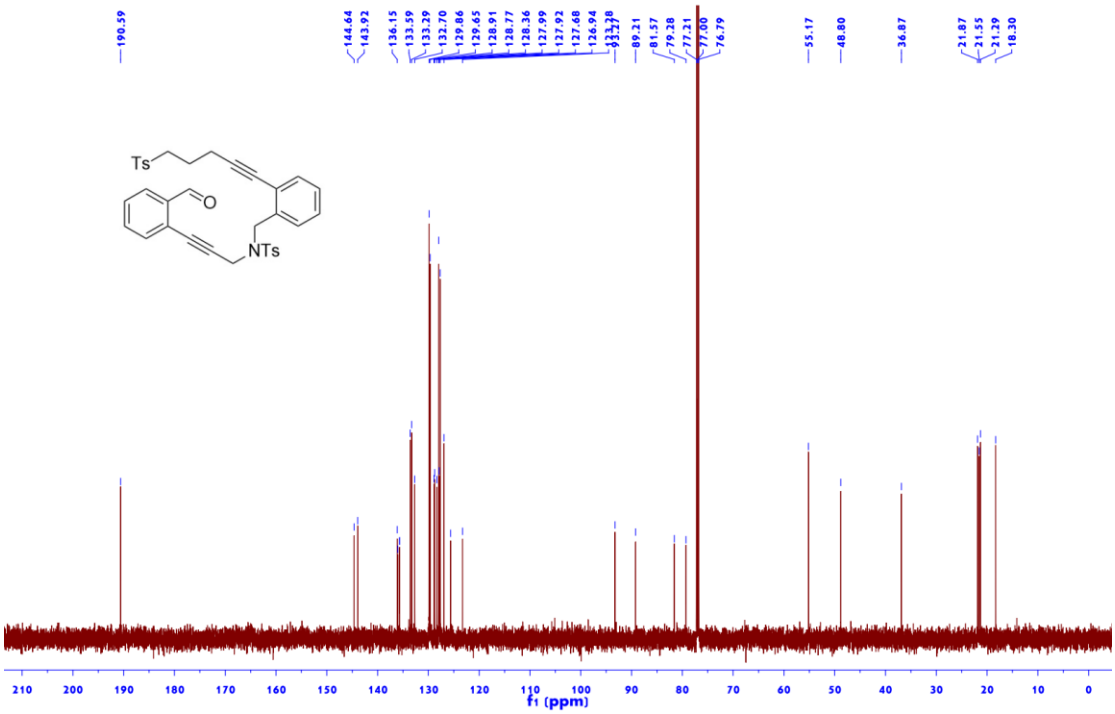


Figure S15 ^{1}H NMR (600 MHz, $CDCl_3$) of 1h

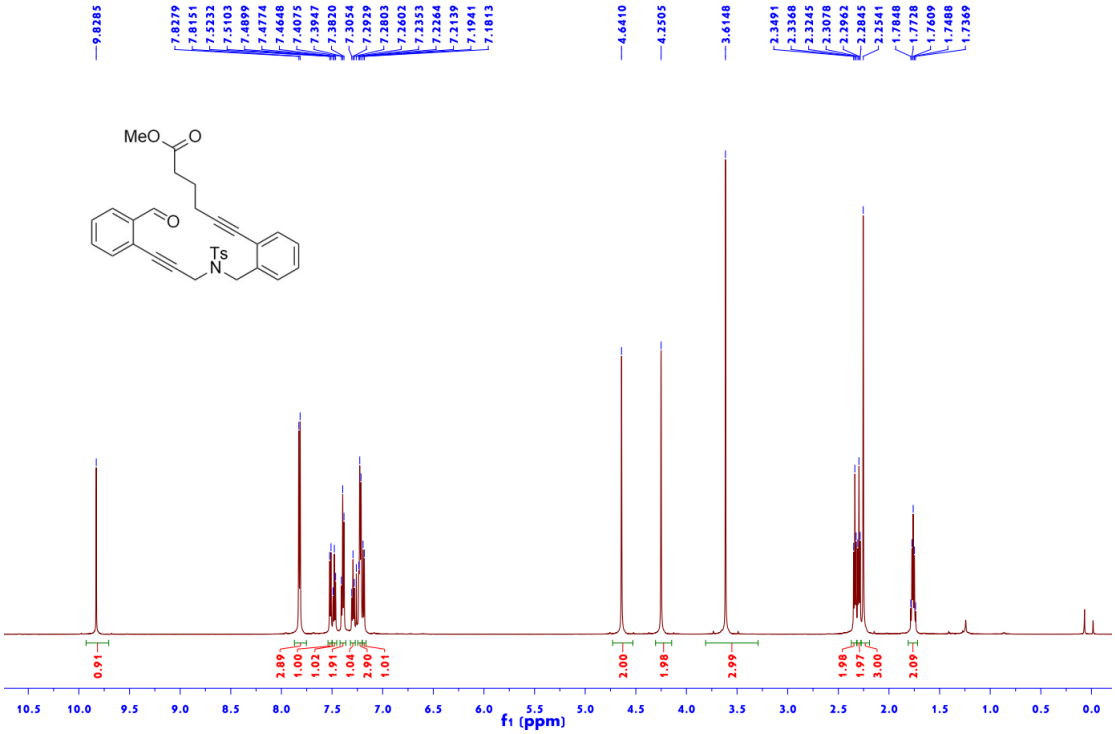


Figure S16 ^{13}C NMR (150 MHz, $CDCl_3$)of 1h

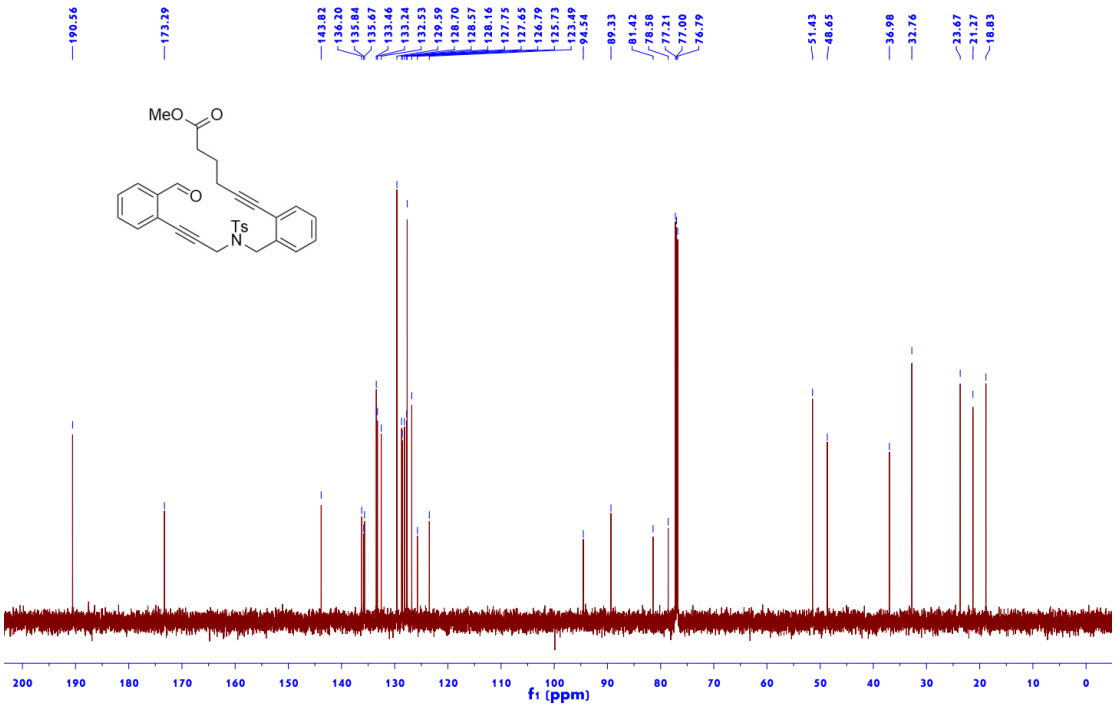


Figure S17 ^{1}H NMR (600 MHz, $CDCl_3$) of 1i

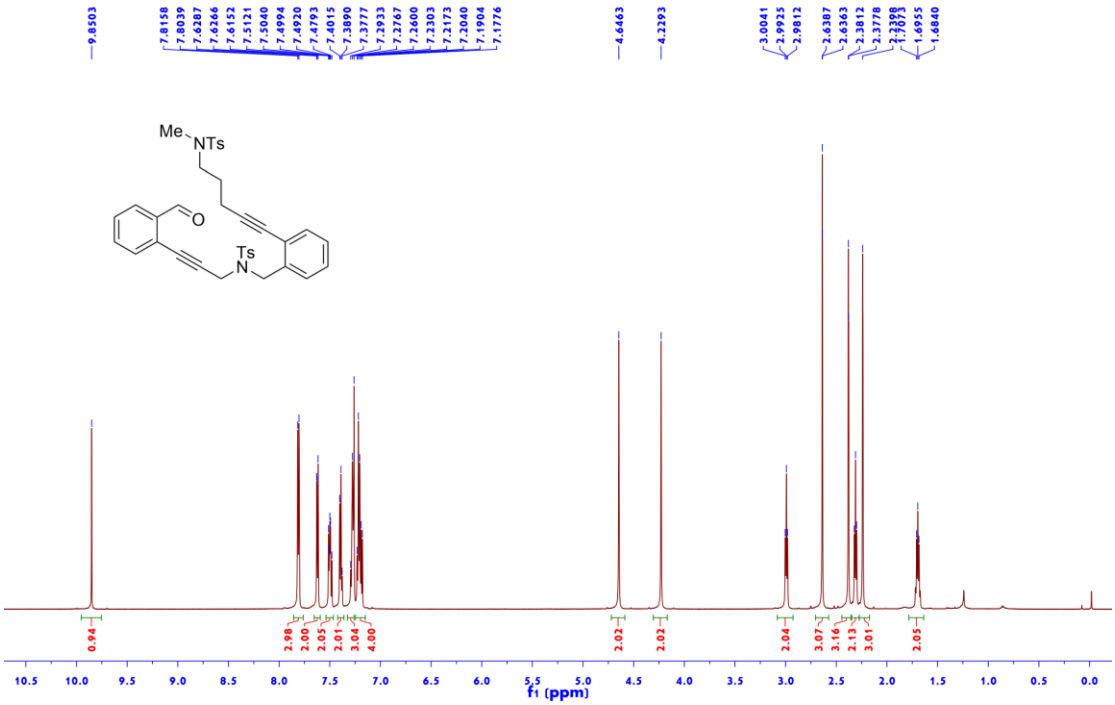


Figure S18 ^{13}C NMR (150 MHz, $CDCl_3$) of 1i

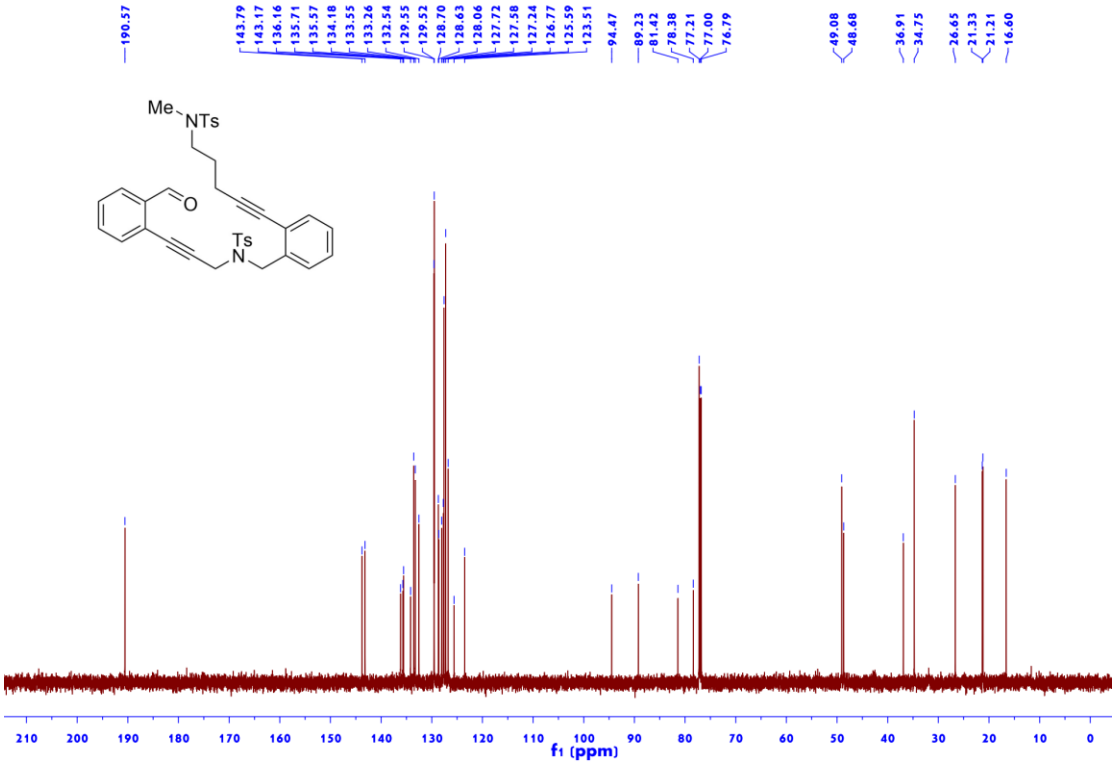


Figure S19 ^{1}H NMR (600 MHz, $CDCl_3$) of 1j

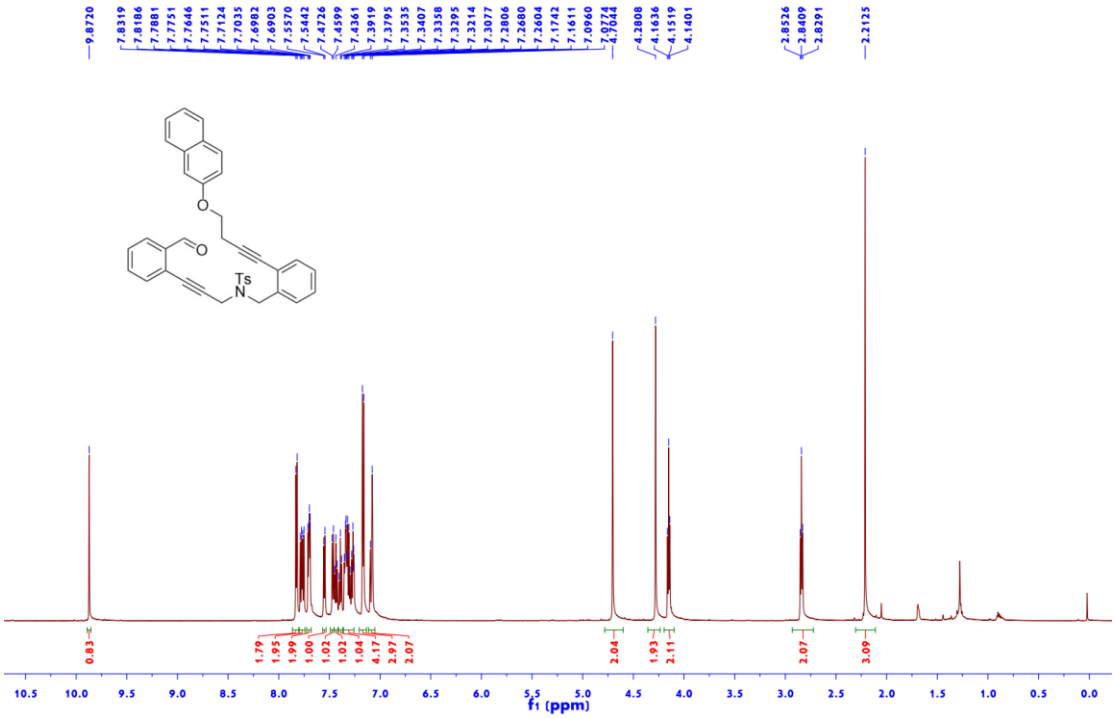


Figure S20 ^{13}C NMR (150 MHz, $CDCl_3$) of 1j

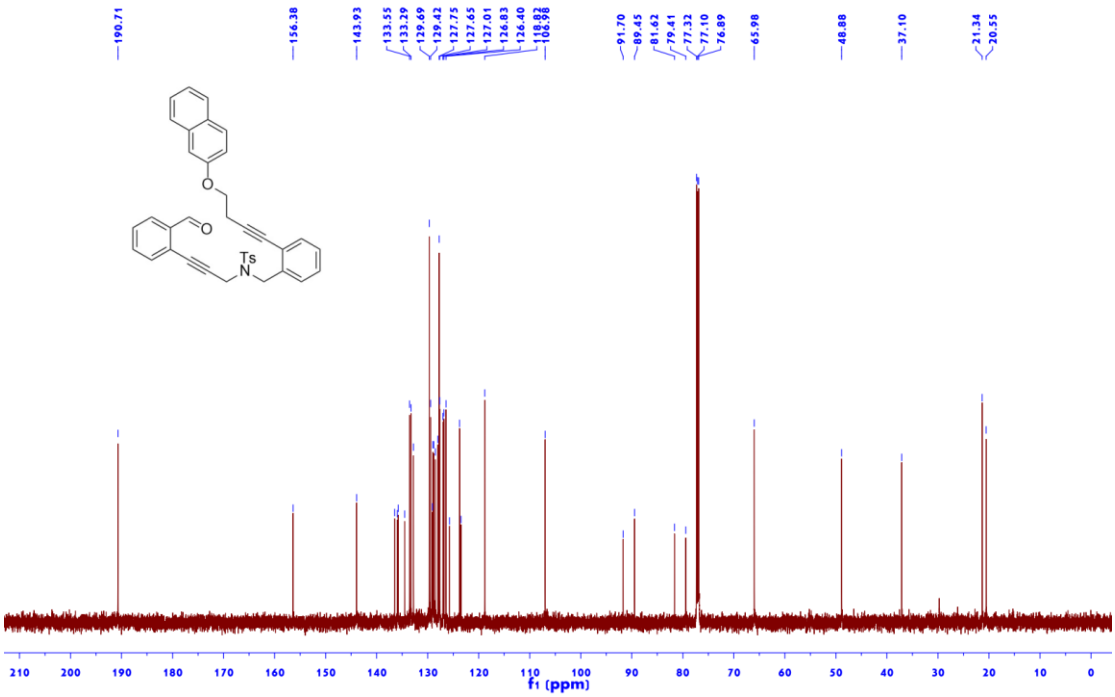


Figure S21 ^{1}H NMR (600 MHz, $CDCl_3$) of 1k

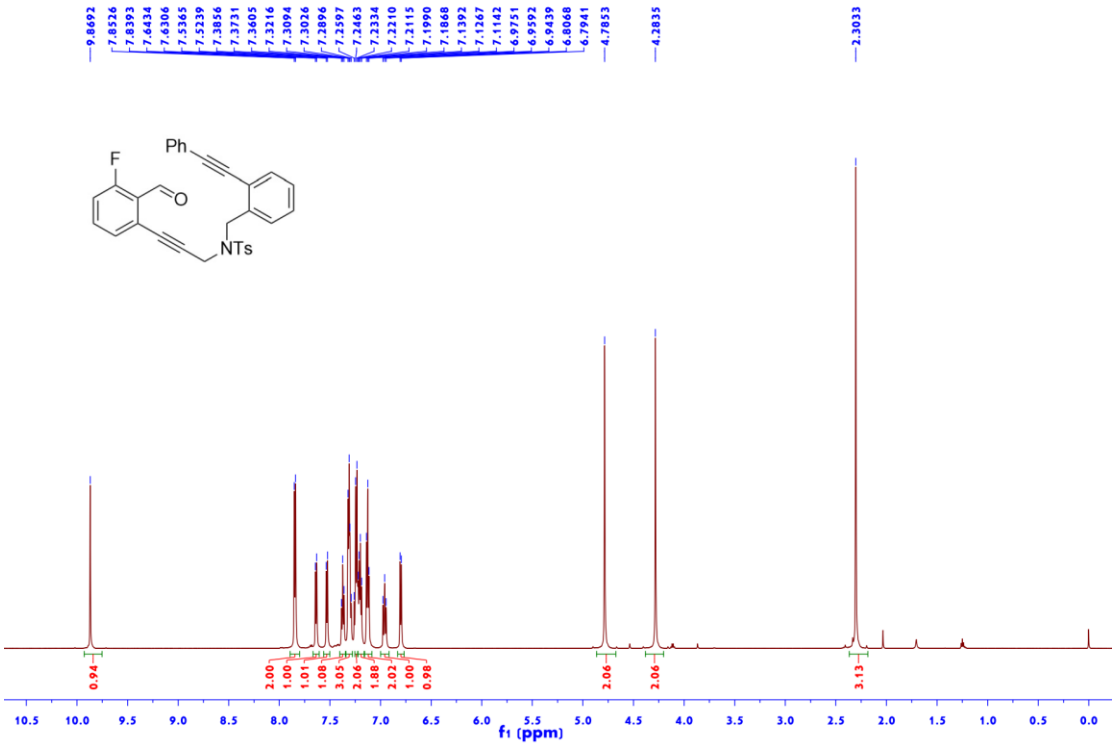


Figure S22 ^{13}C NMR (150 MHz, $CDCl_3$) of 1k

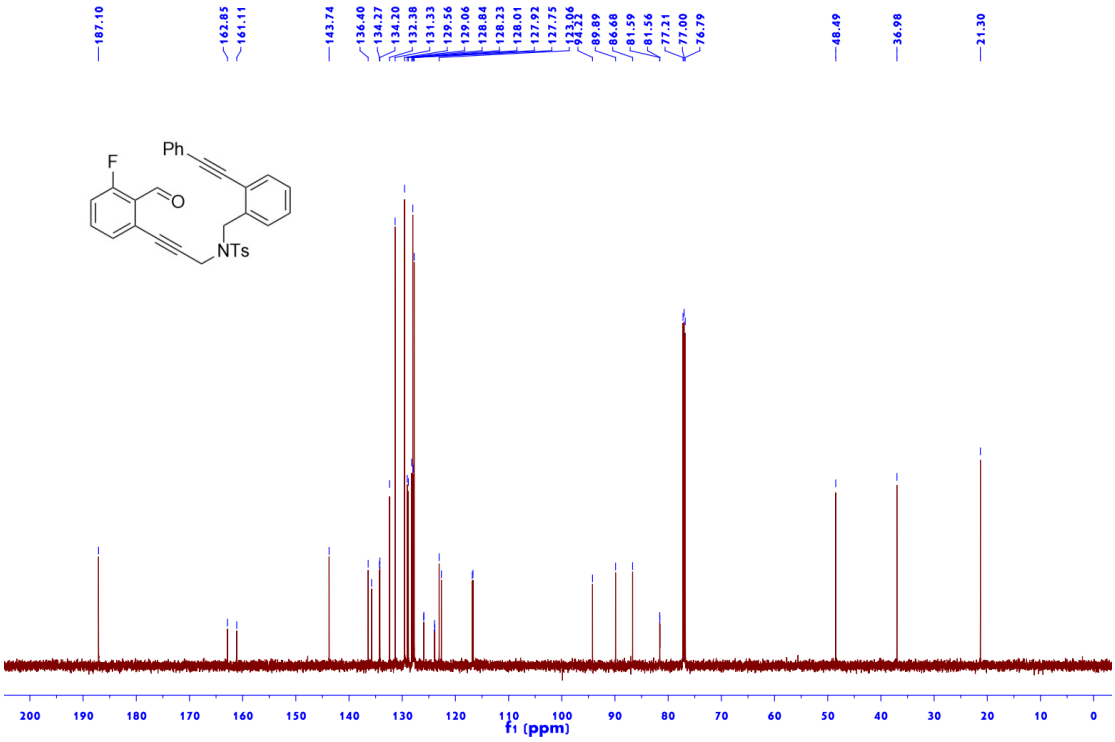


Figure S23 ^{19}F NMR (565 MHz, $CDCl_3$) of 1k

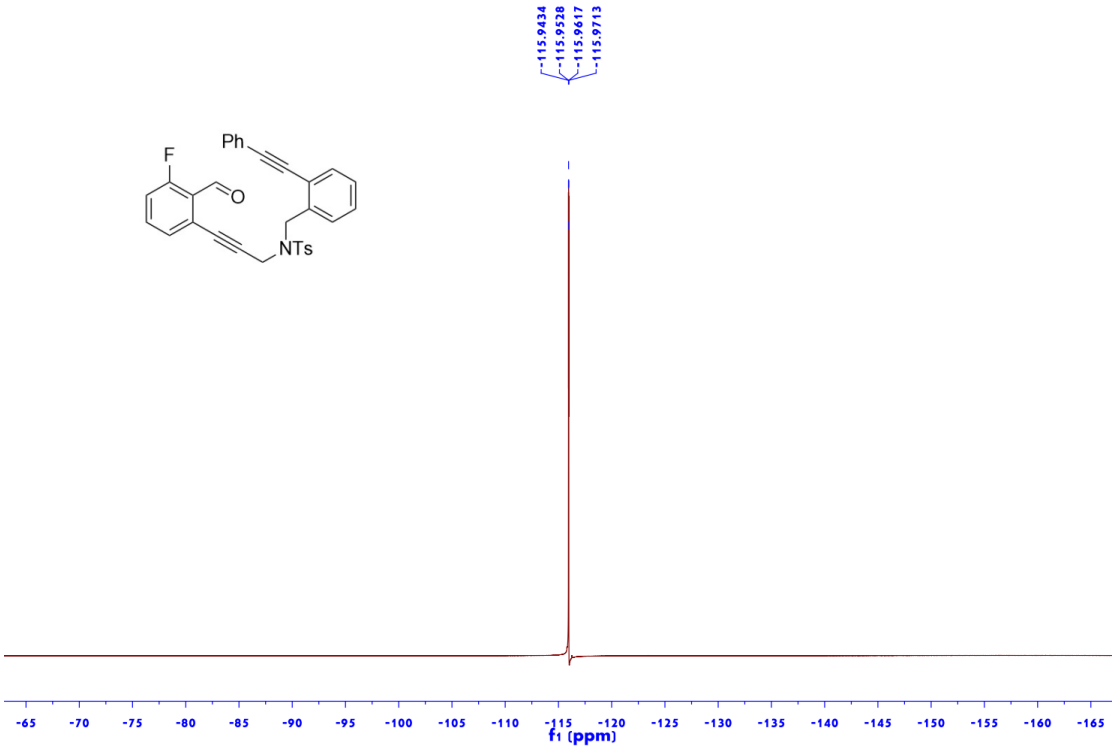


Figure S24 ^{1}H NMR (600 MHz, $CDCl_3$) of 1l

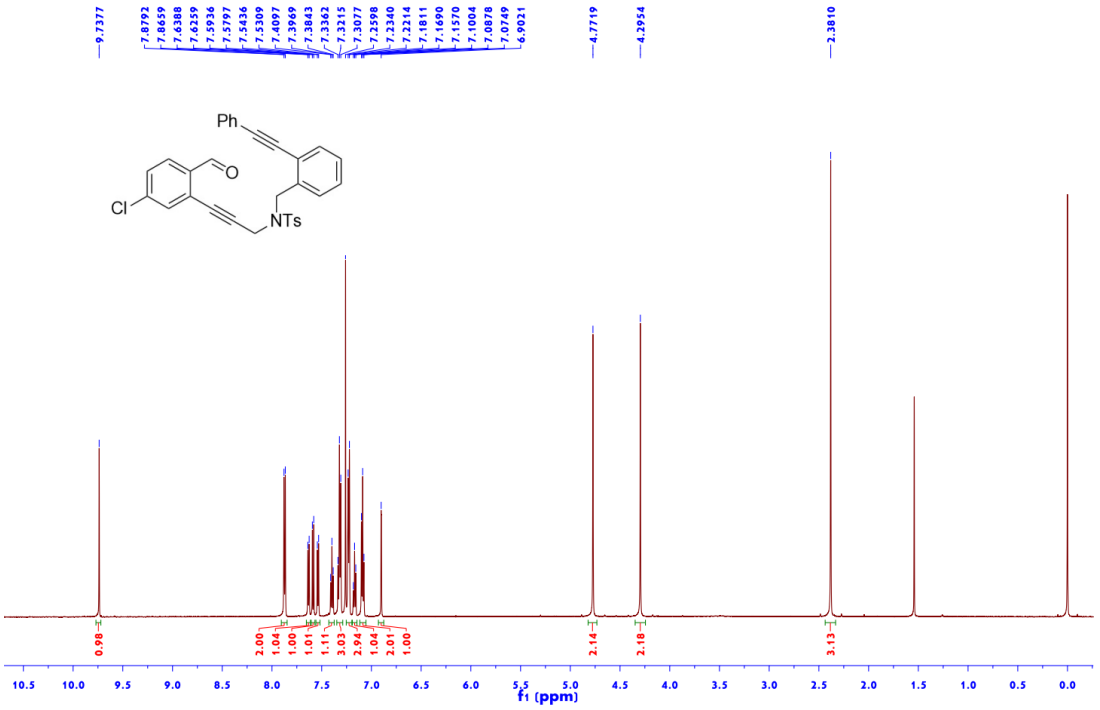


Figure S25 ^{13}C NMR (150 MHz, $CDCl_3$) of 1l

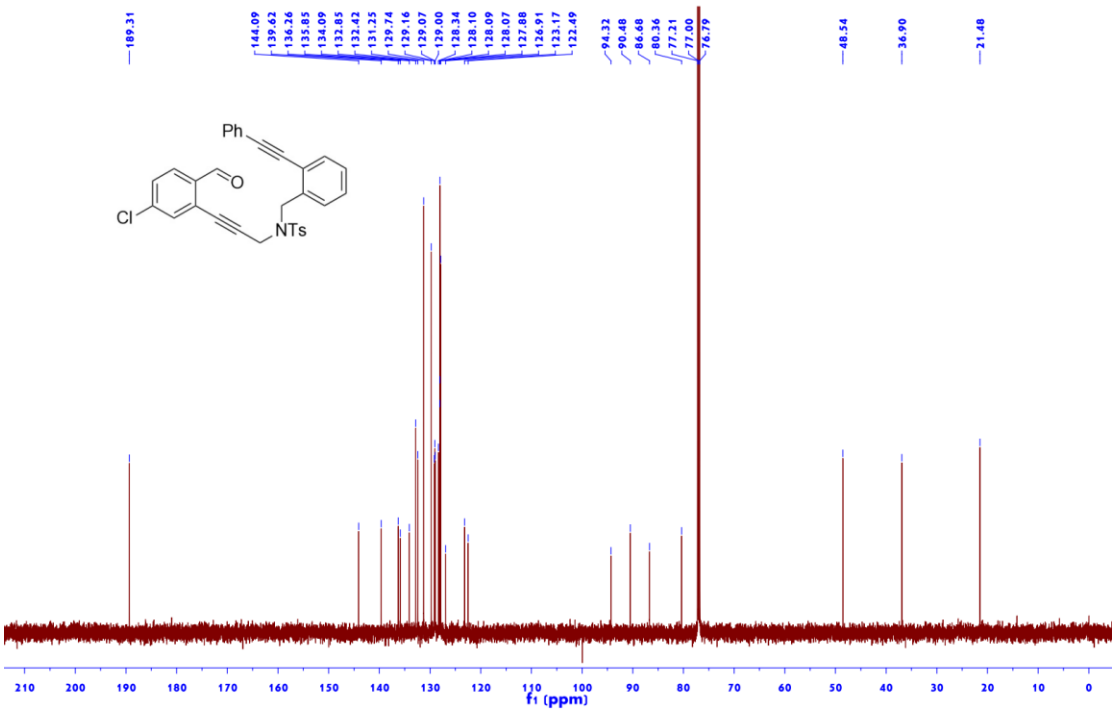


Figure S26 ^{1}H NMR (600 MHz, $CDCl_3$) of 1m

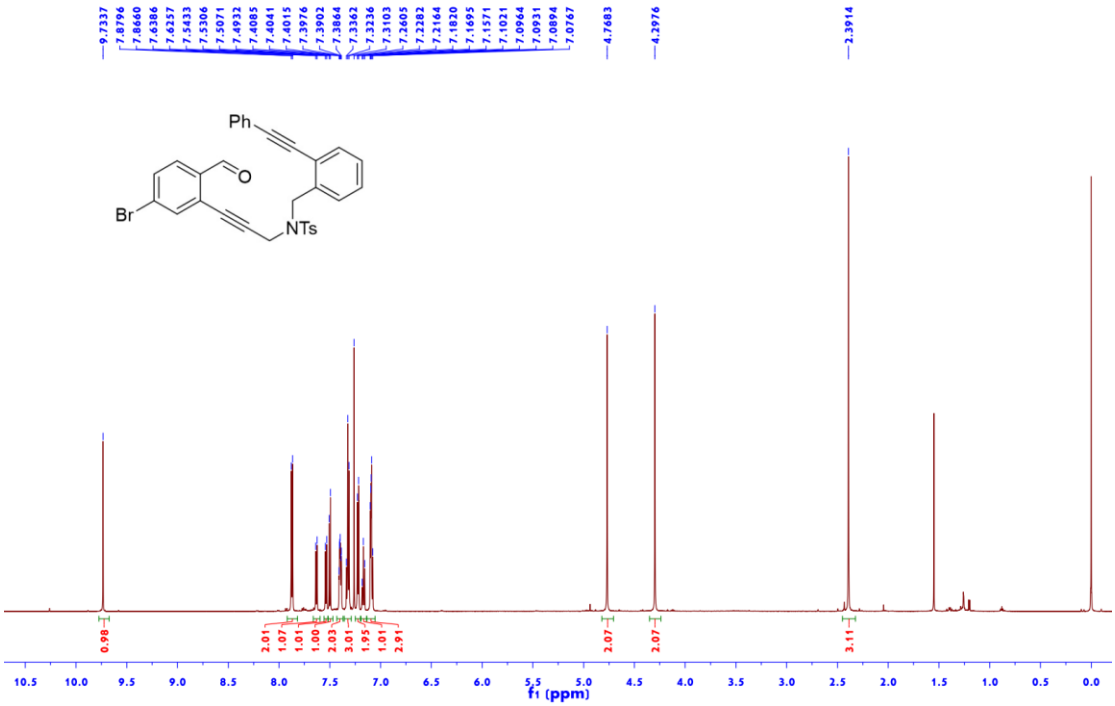


Figure S27 ^{13}C NMR (150 MHz, $CDCl_3$) of 1m

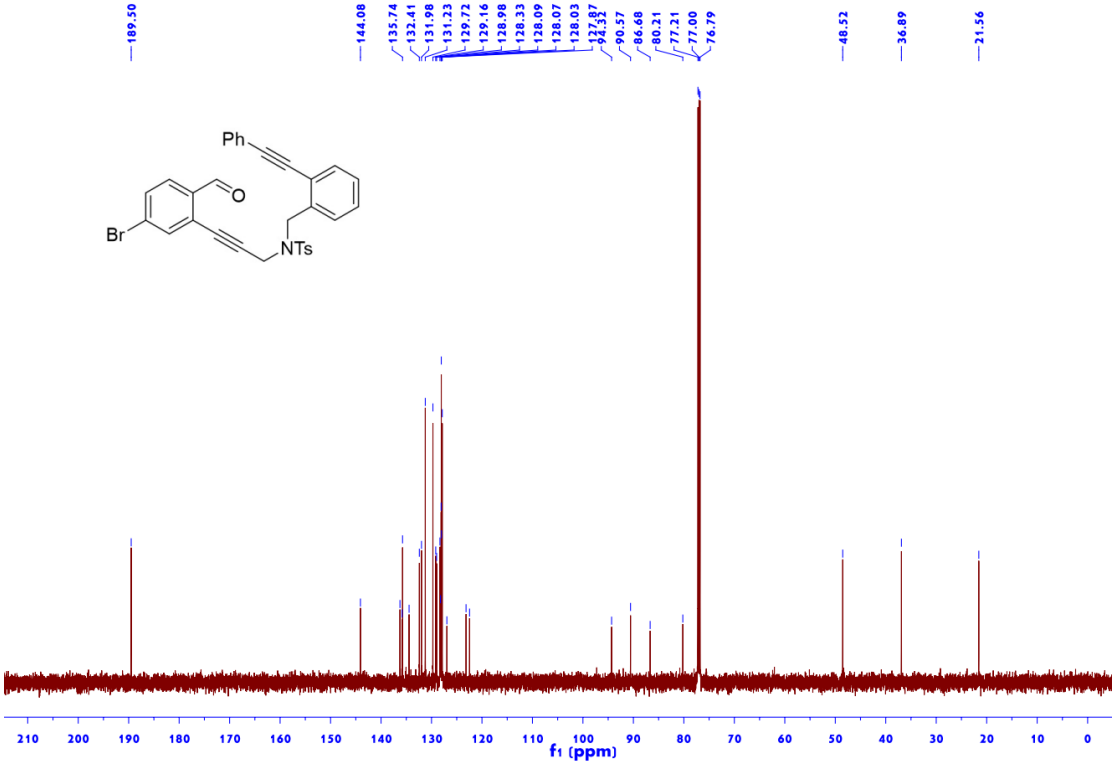


Figure S28 ^{1}H NMR (600 MHz, $CDCl_3$) of 1n

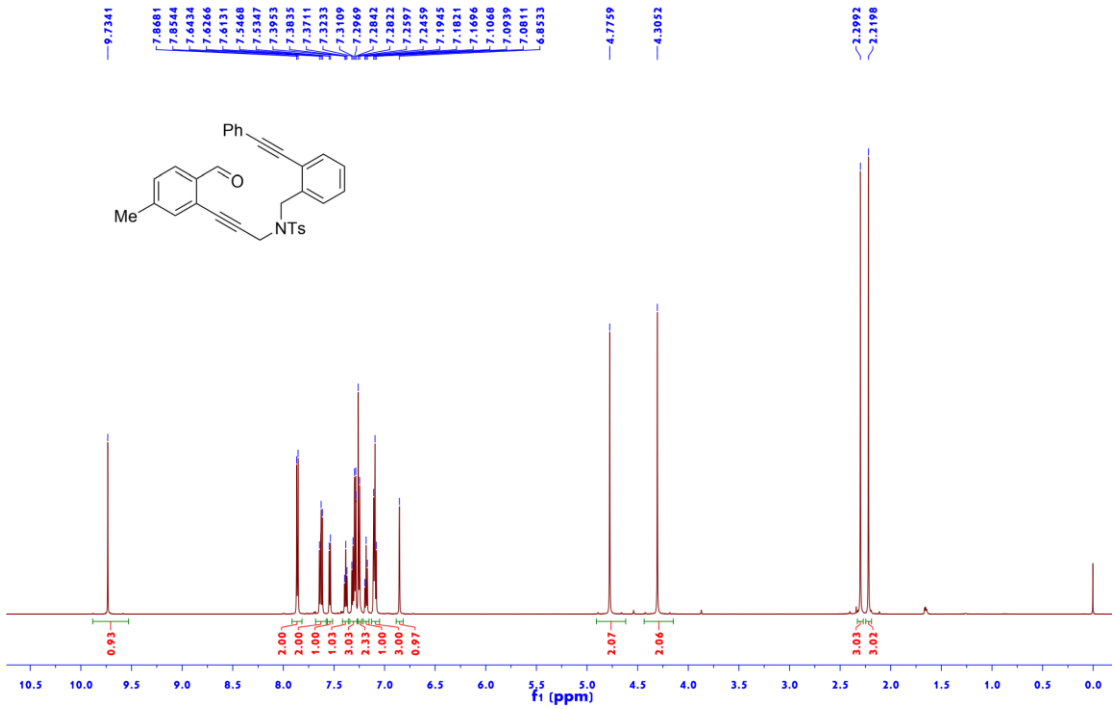


Figure S29 ^{13}C NMR (150 MHz, $CDCl_3$) of 1n

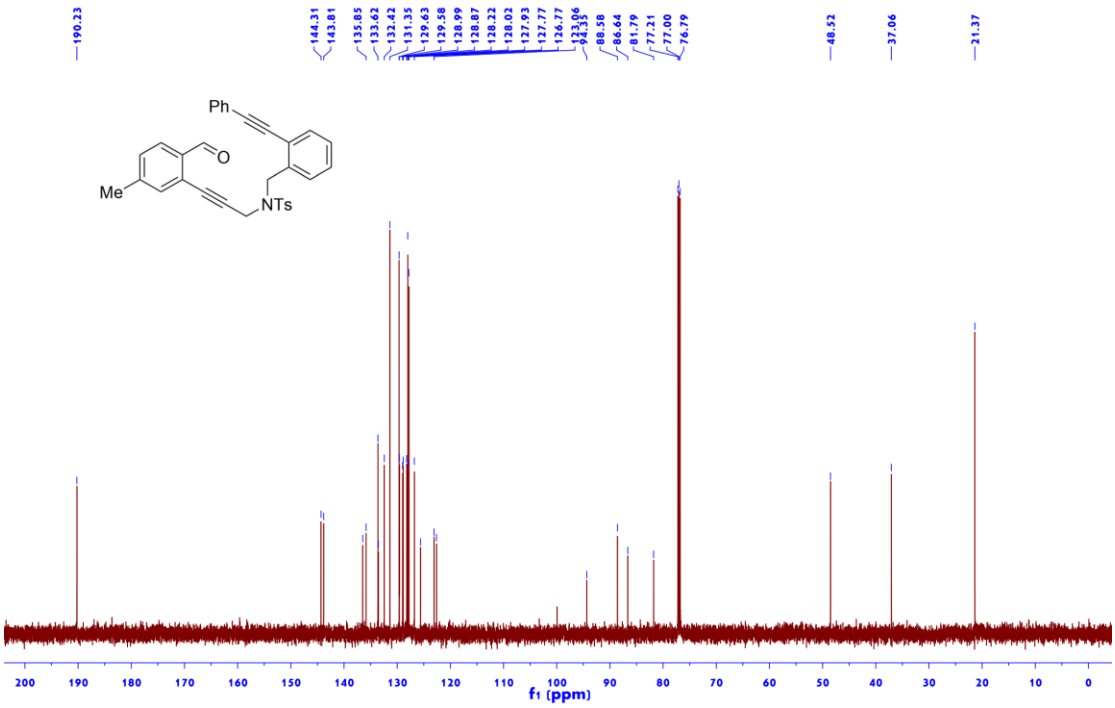


Figure S30 ^{1}H NMR (600 MHz, $CDCl_3$) of 1o

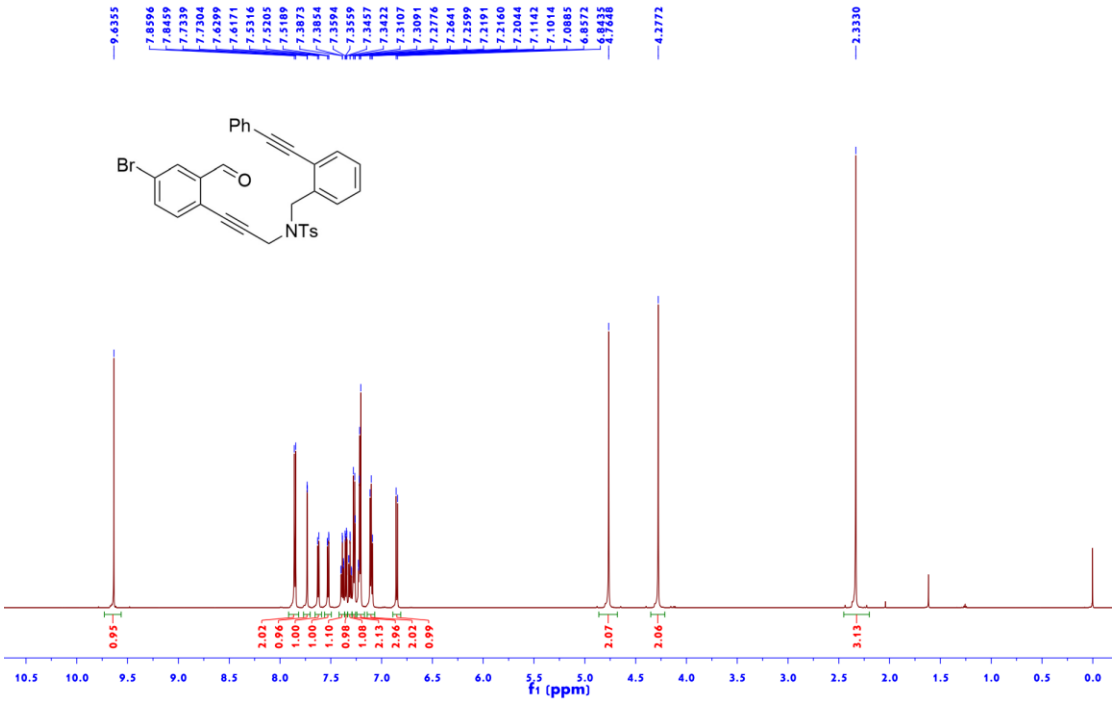


Figure S31 ^{13}C NMR (150 MHz, $CDCl_3$) of 1o

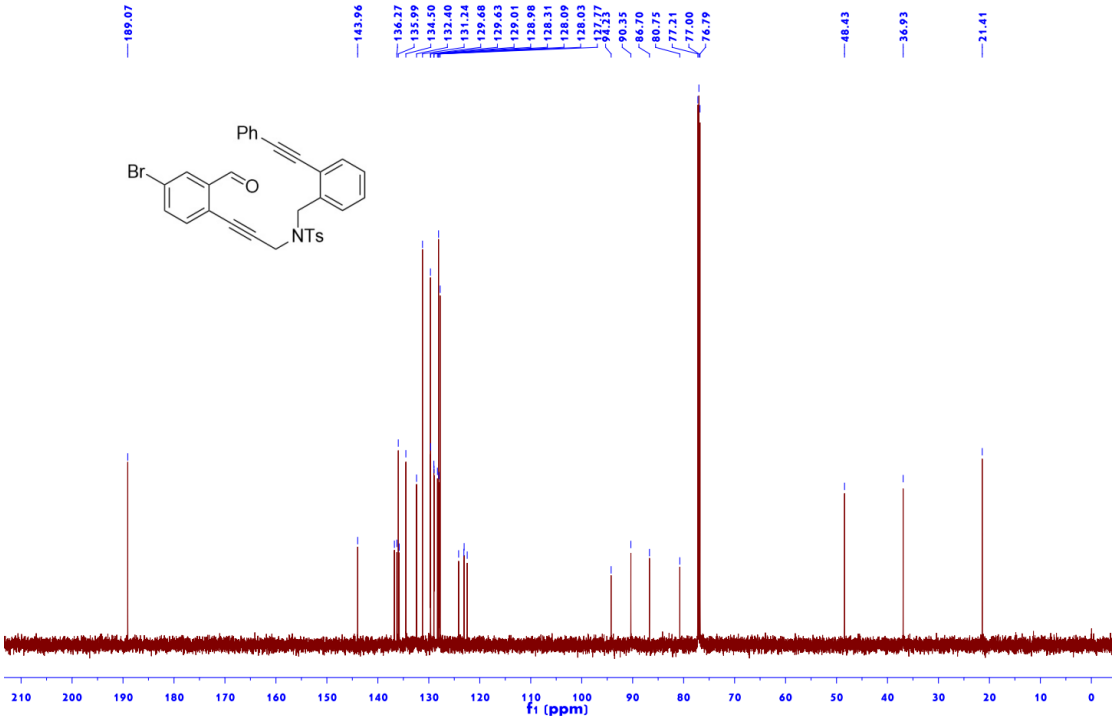


Figure S32 ^{1}H NMR (400 MHz, $CDCl_3$) of 1p

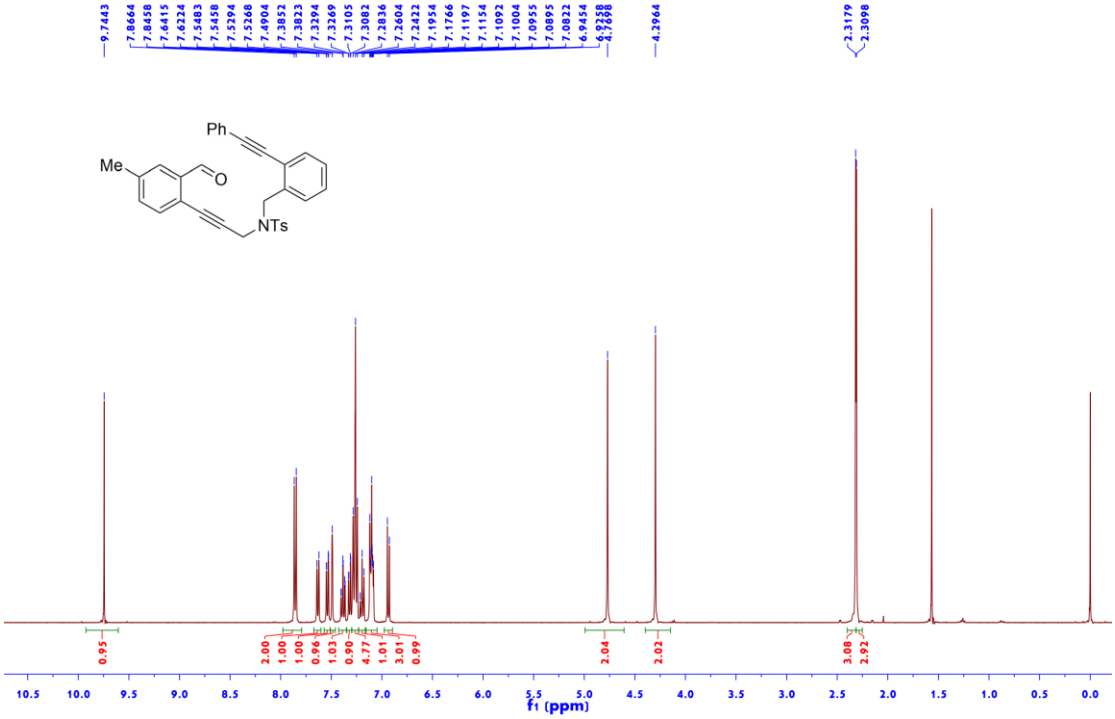


Figure S33 ^{13}C NMR (100 MHz, $CDCl_3$) of 1p

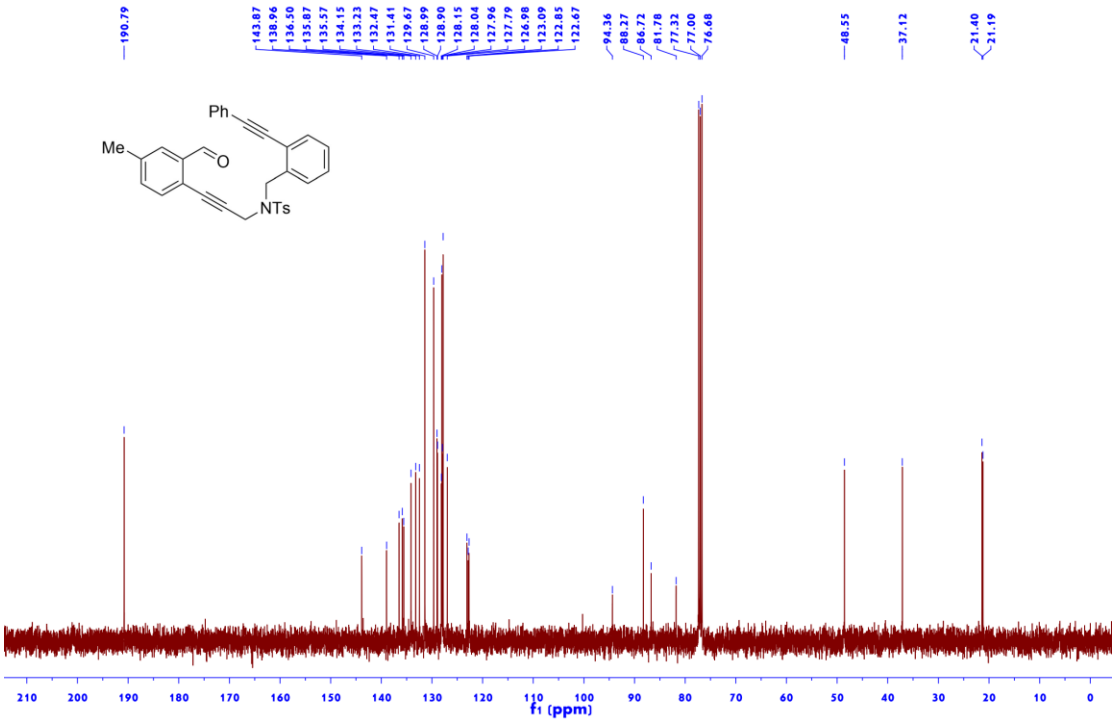


Figure S34 ^{1}H NMR (600 MHz, $CDCl_3$) of 1q

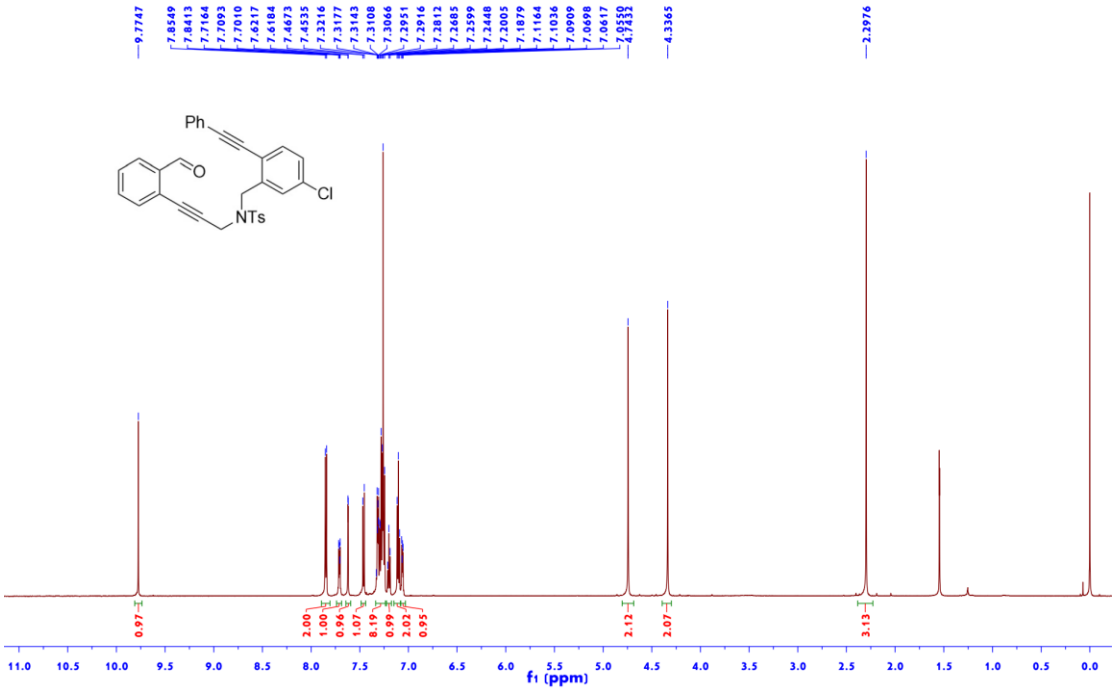


Figure S35 ^{13}C NMR (150 MHz, $CDCl_3$) of 1q

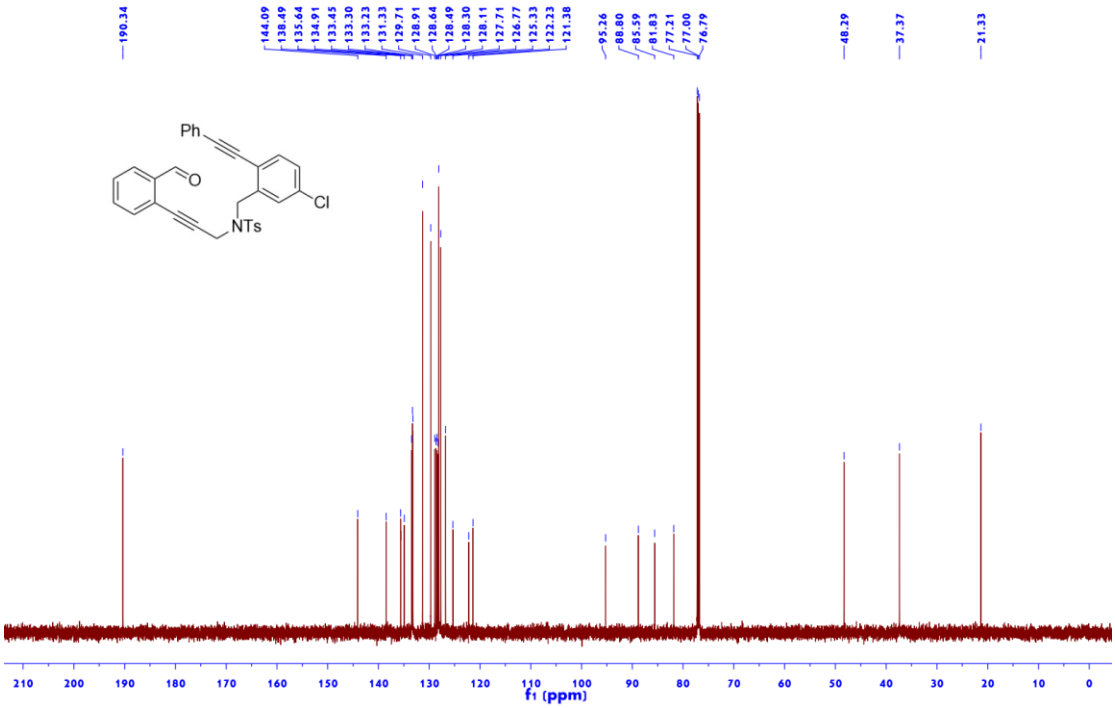


Figure S36 ^{1}H NMR (600 MHz, $CDCl_3$) of 1r

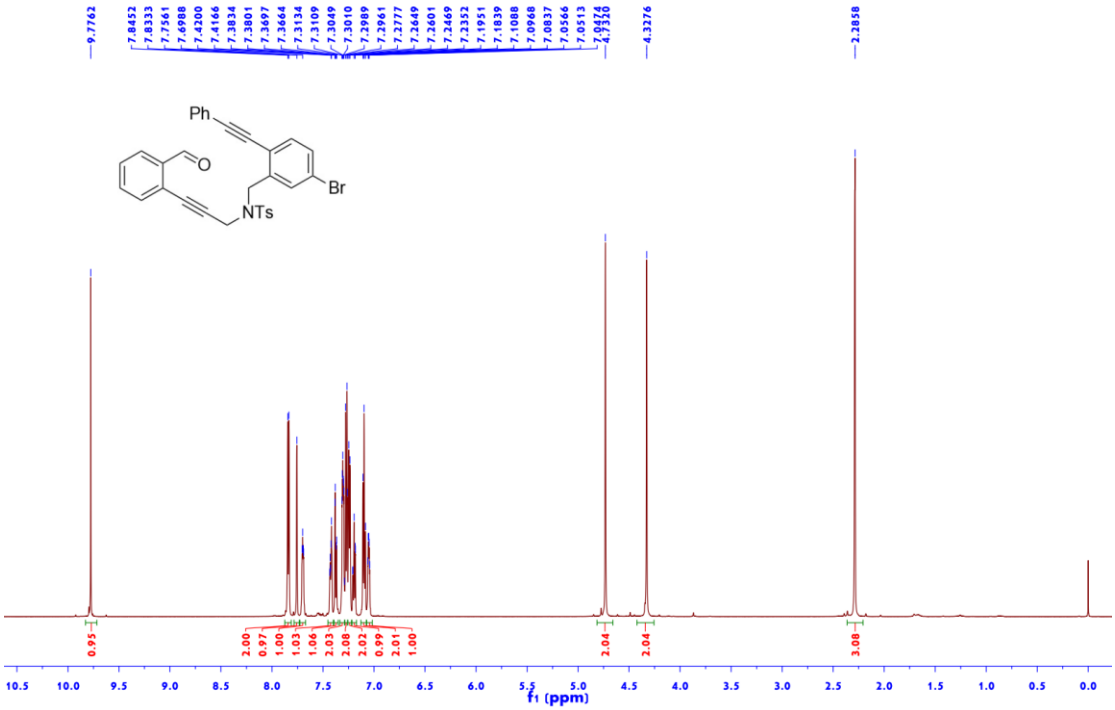


Figure S37 ^{13}C NMR (150 MHz, $CDCl_3$) of 1r

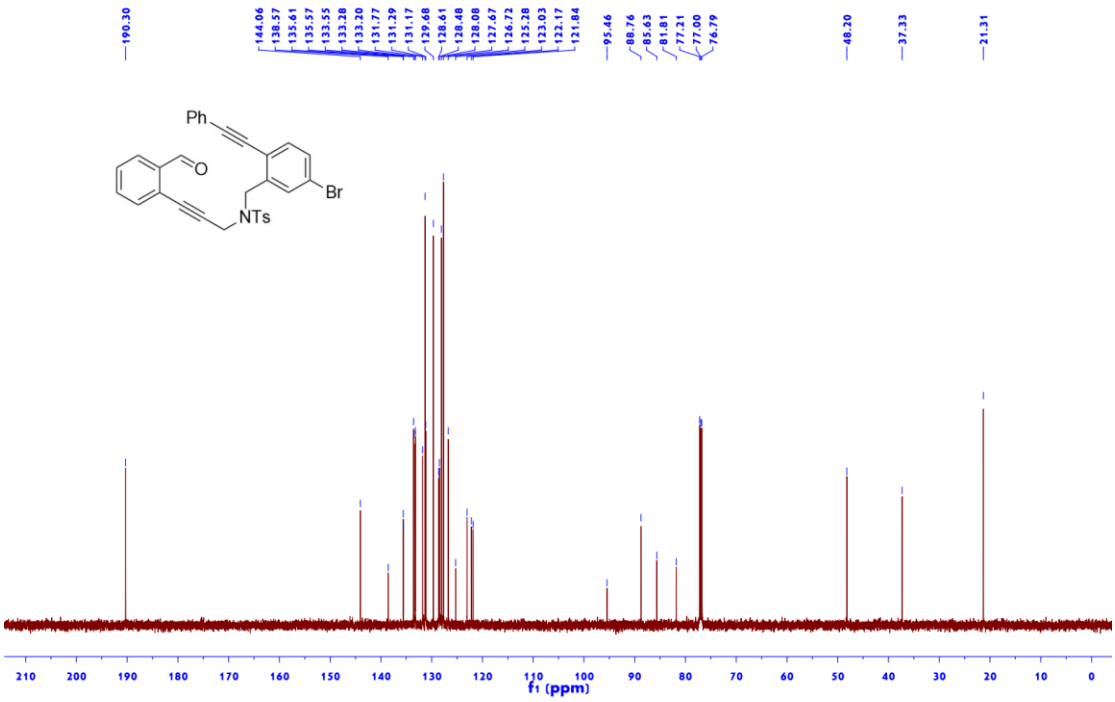


Figure S38 ^{1}H NMR (400 MHz, $CDCl_3$) of 1s

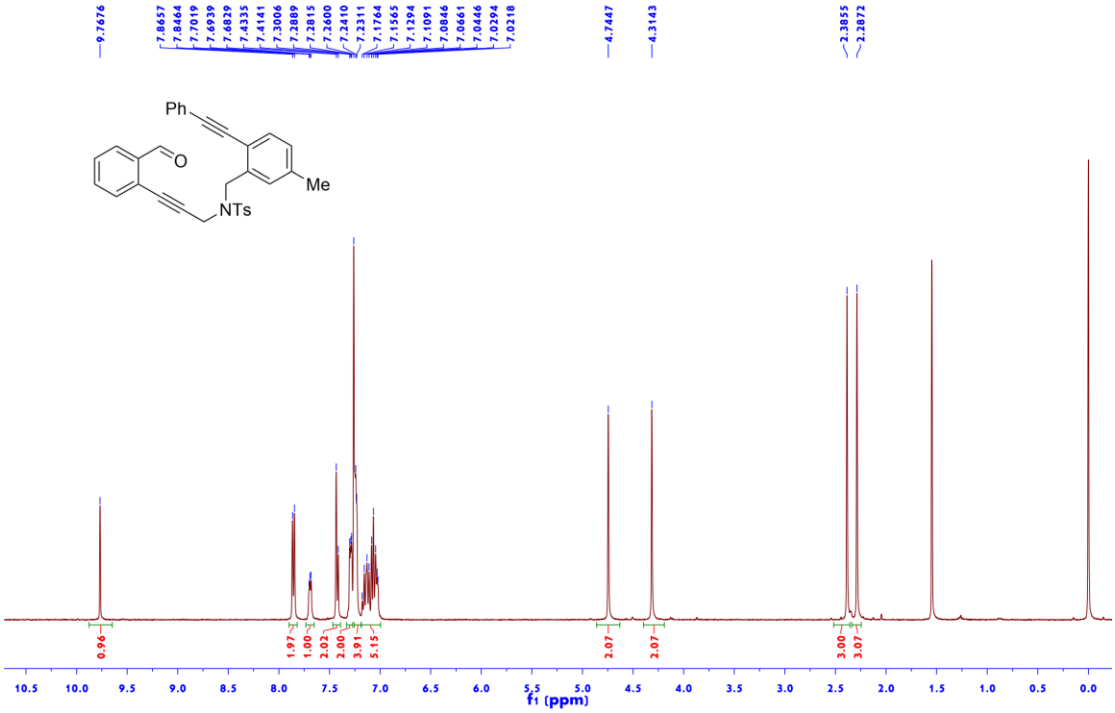


Figure S39 ^{13}C NMR (100 MHz, $CDCl_3$) of 1s

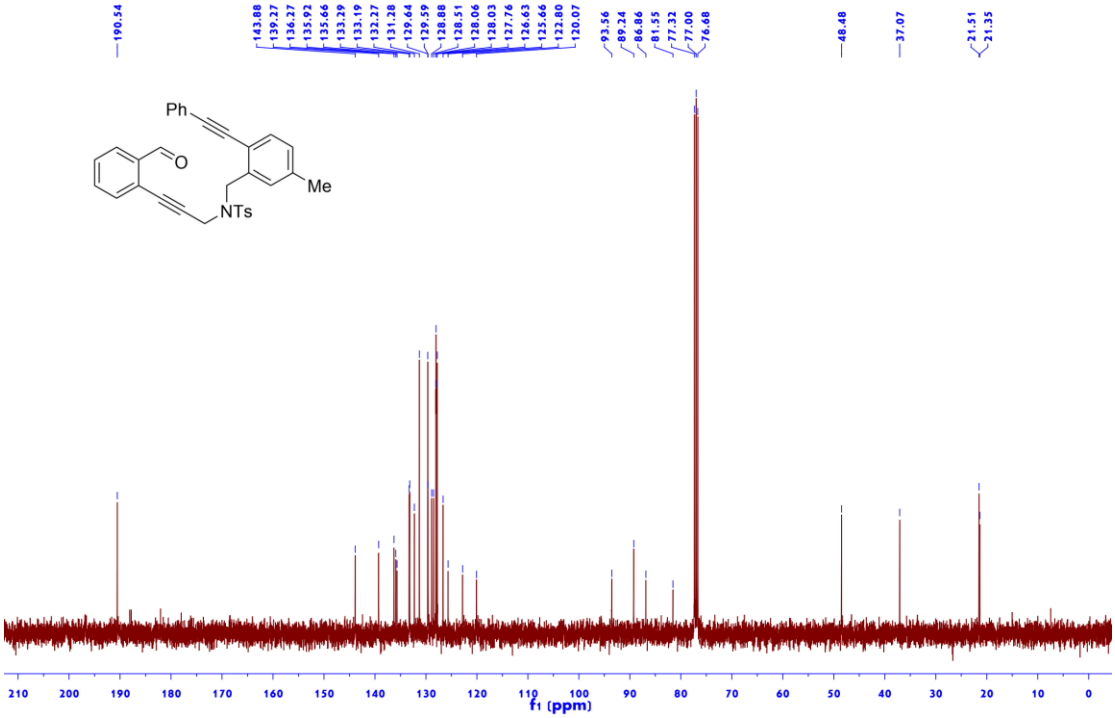


Figure S40 ^{1}H NMR (600 MHz, $CDCl_3$) of 1t

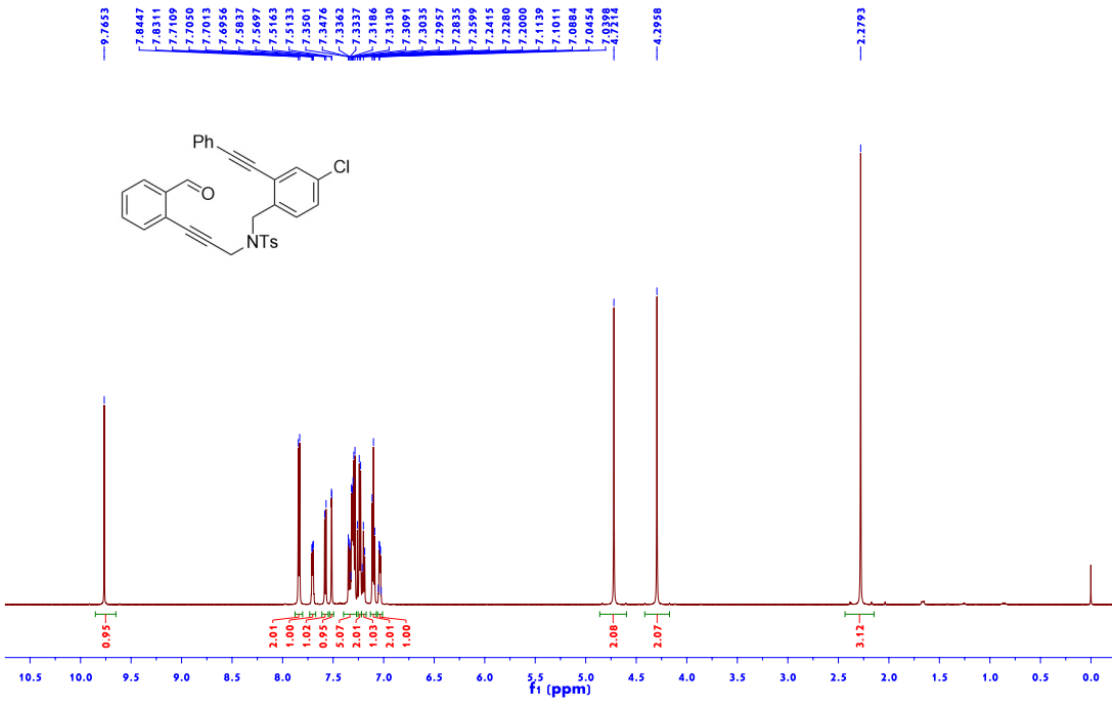


Figure S41 ^{13}C NMR (150 MHz, $CDCl_3$) of 1t

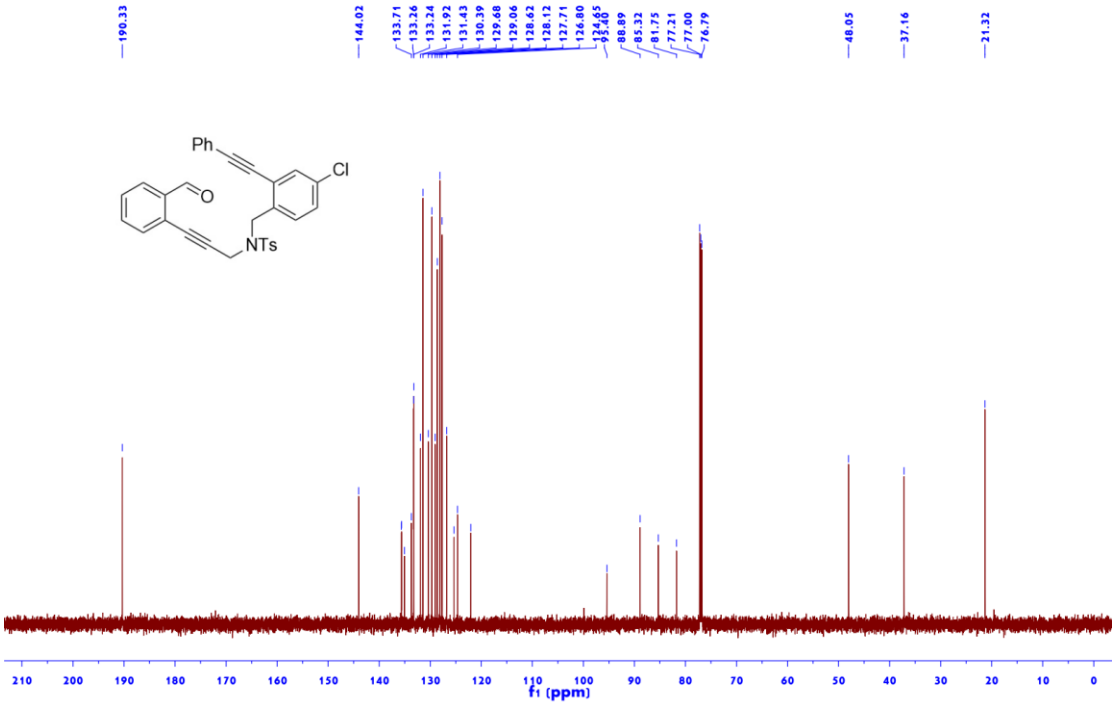


Figure S42 ^{1}H NMR (600 MHz, $CDCl_3$) of 1u

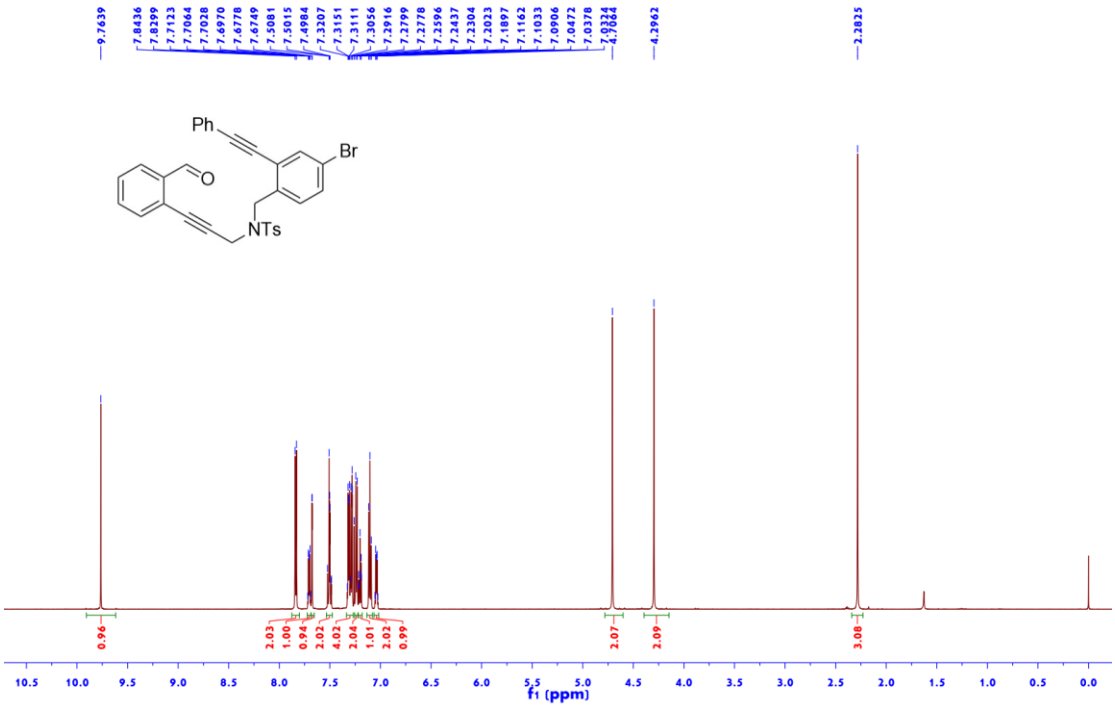


Figure S43 ^{13}C NMR (150 MHz, $CDCl_3$) of 1u

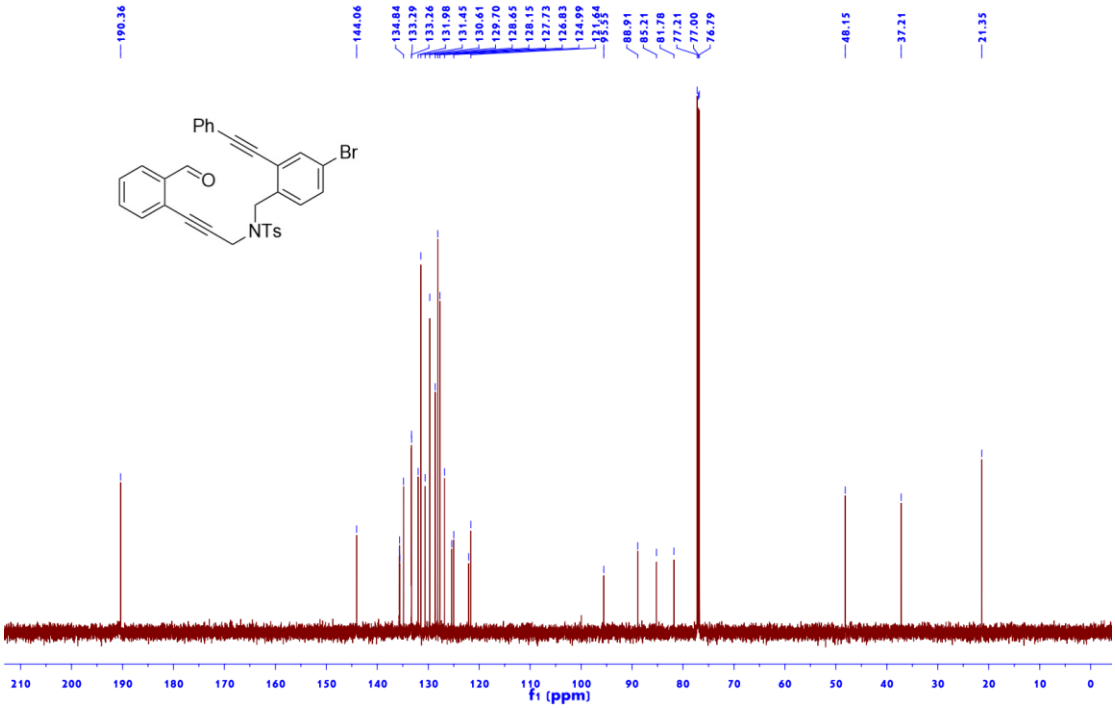


Figure S44 ^{1}H NMR (600 MHz, $CDCl_3$) of 1v

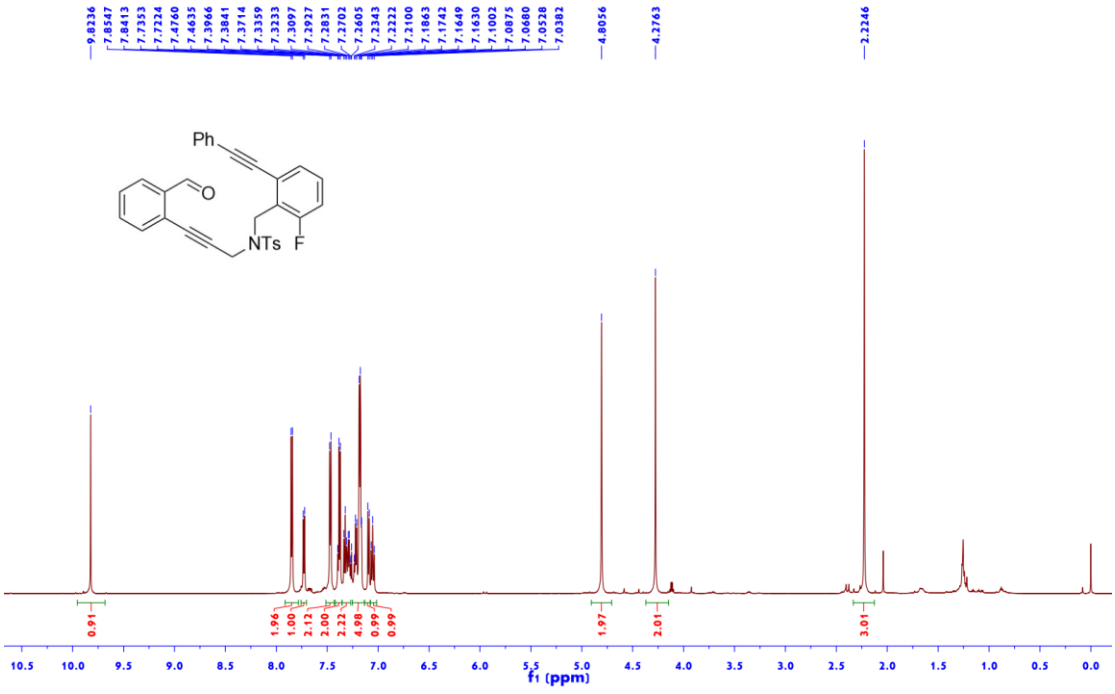


Figure S45 ^{13}C NMR (150 MHz, $CDCl_3$) of 1v

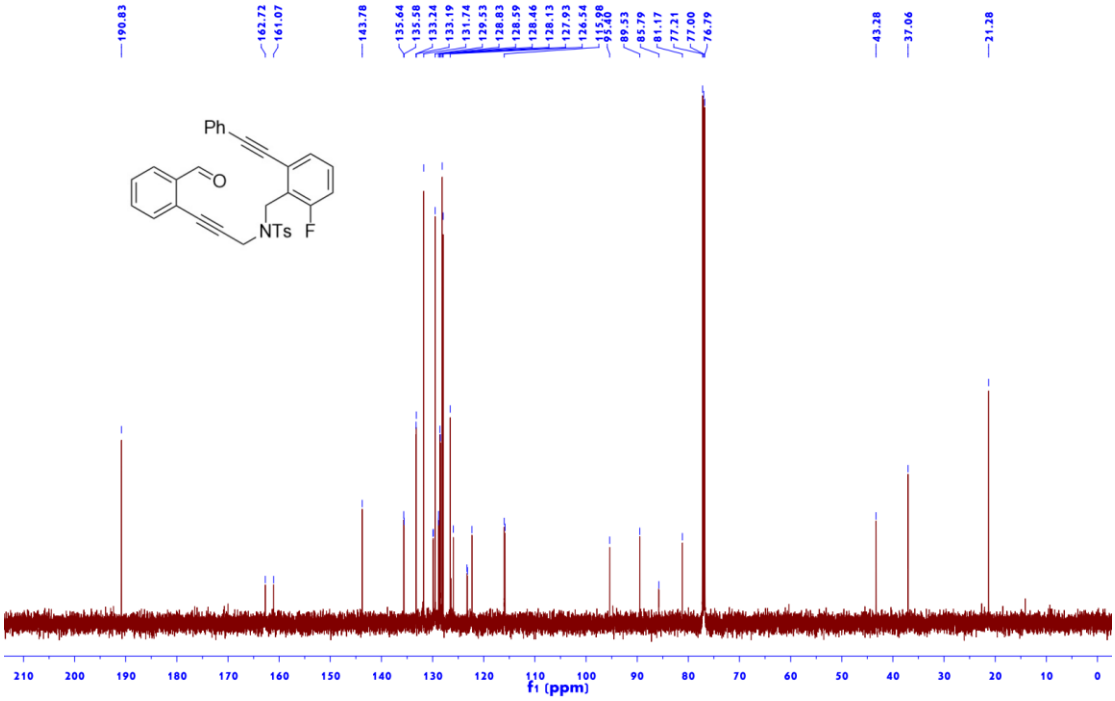


Figure S46 ^{19}F NMR (565 MHz, $CDCl_3$) of 1v

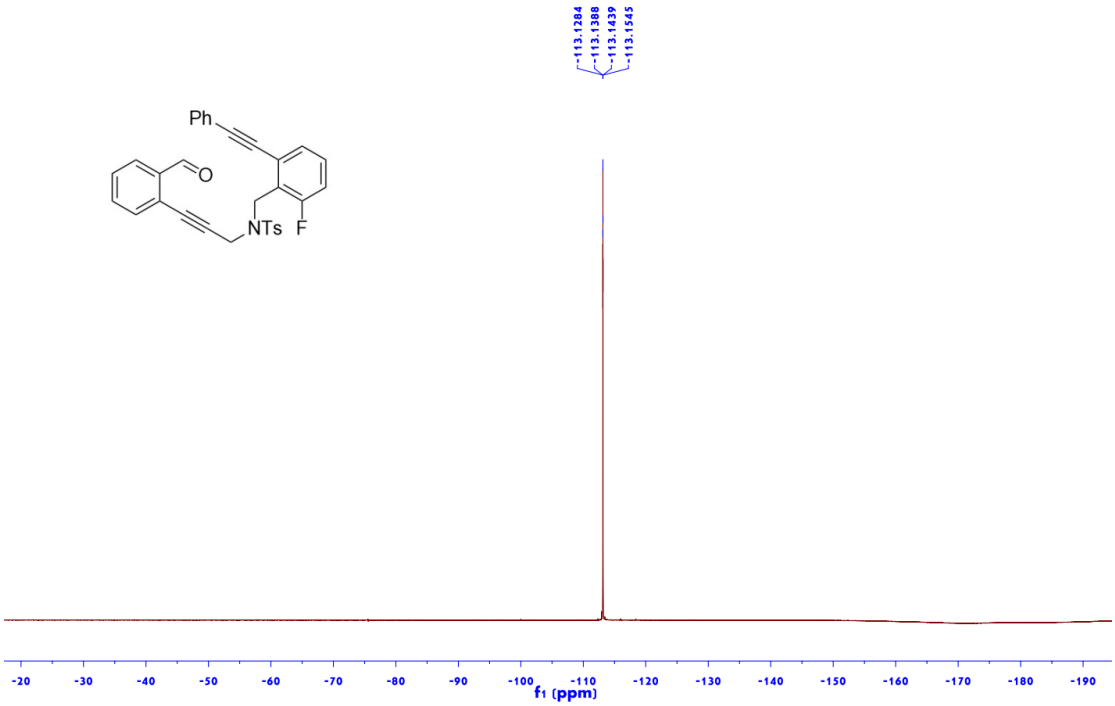


Figure S47 ^{1}H NMR (600 MHz, $CDCl_3$) of 1w

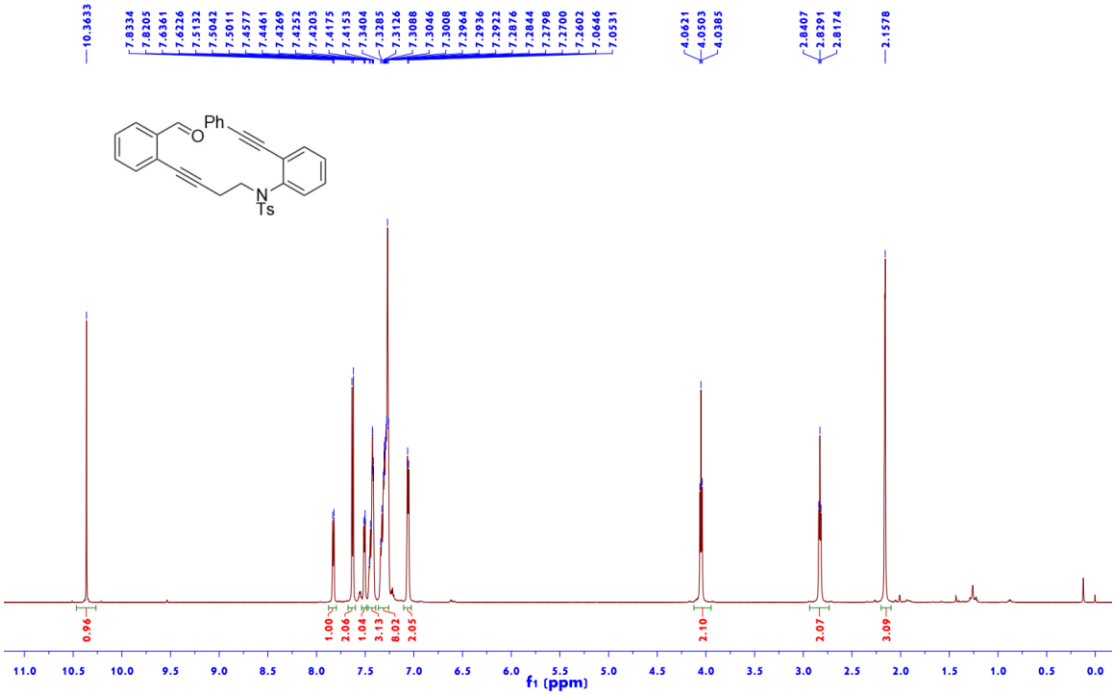


Figure S48 ^{13}C NMR (150 MHz, $CDCl_3$) of 1w

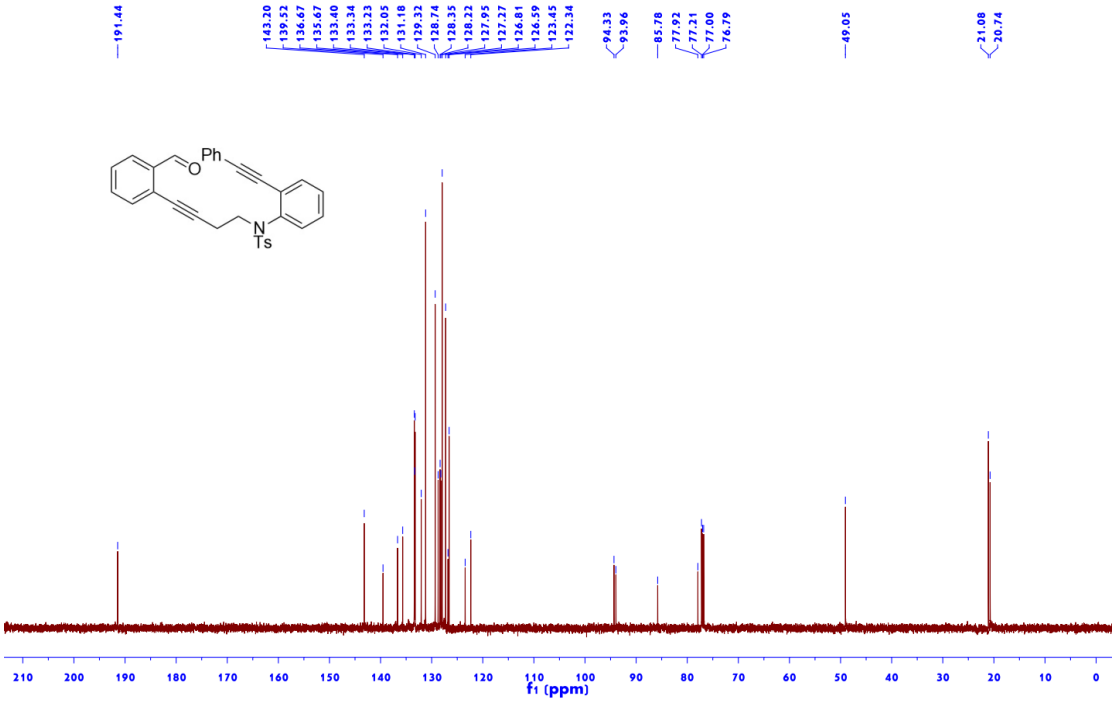


Figure S49 ^{1}H NMR (600 MHz, $CDCl_3$) of 1x

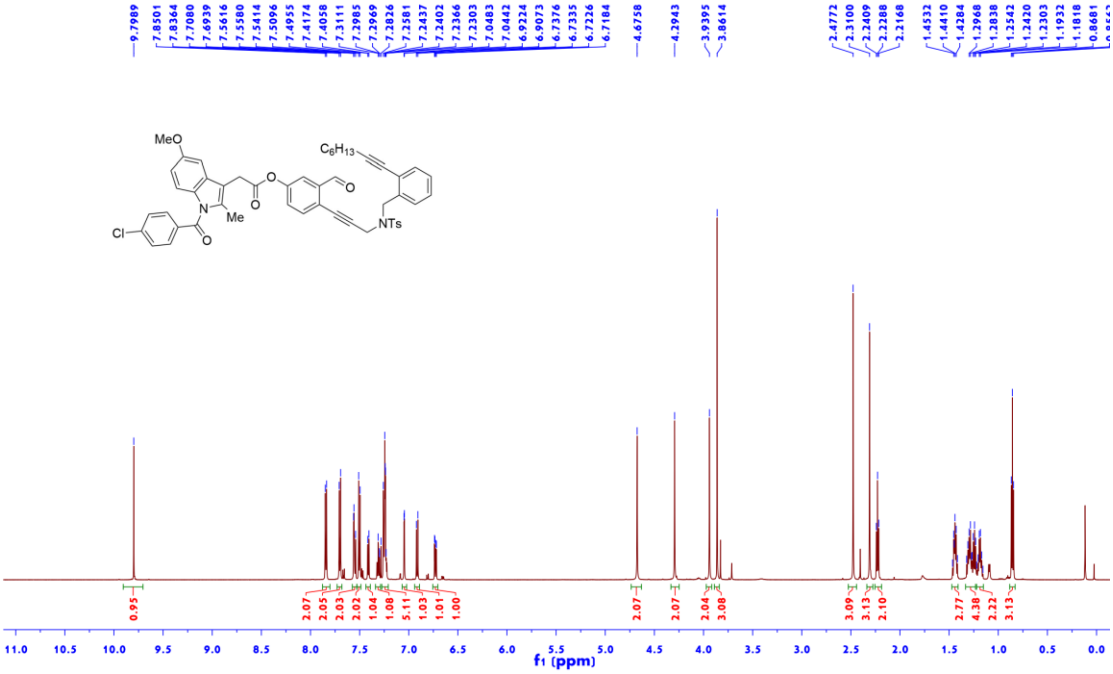


Figure S50 ^{13}C NMR (150 MHz, $CDCl_3$) of 1x

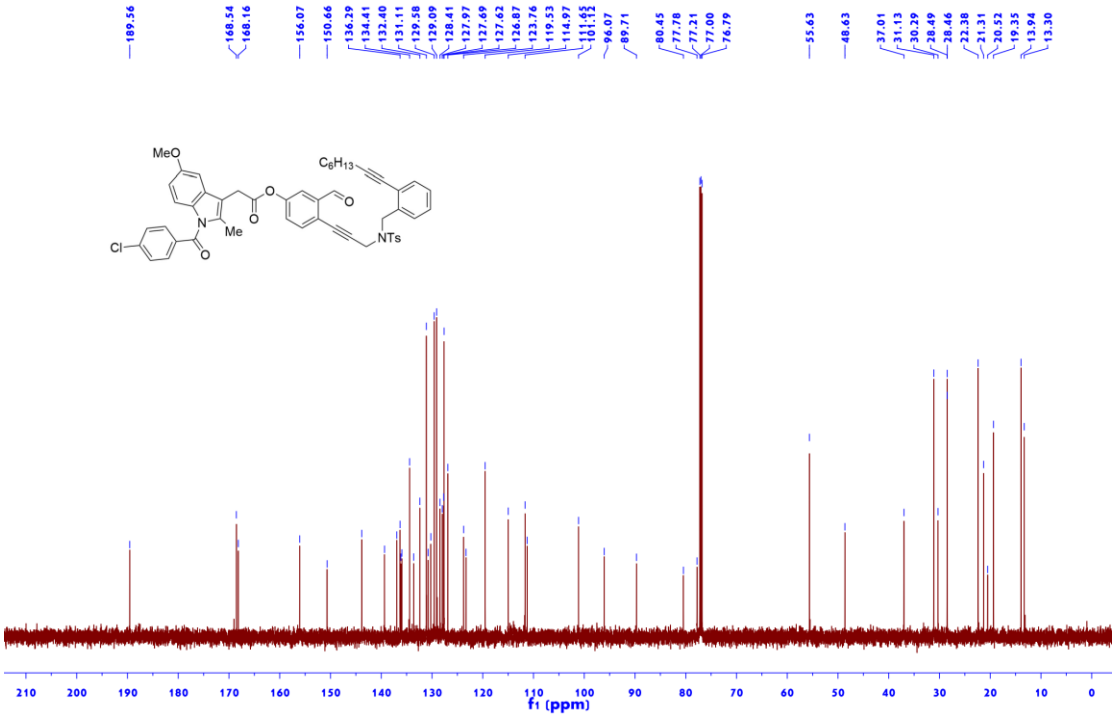


Figure S51 ^{1}H NMR (600 MHz, $CDCl_3$) of 1y

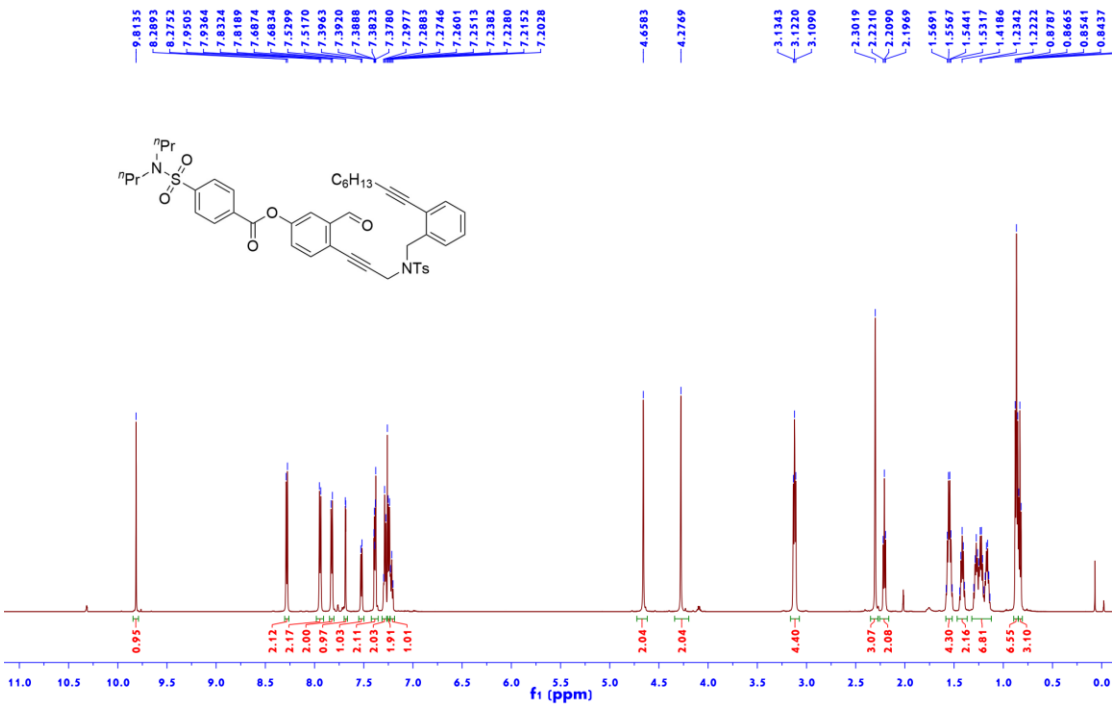


Figure S52 ^{13}C NMR (150 MHz, $CDCl_3$) of 1y

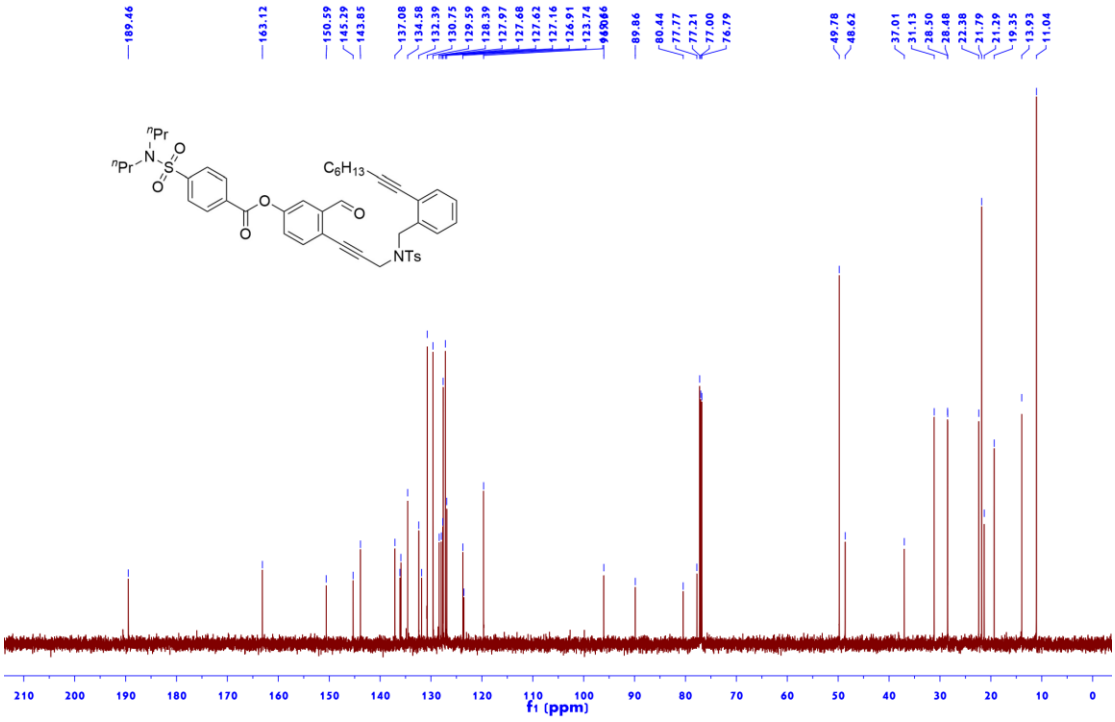


Figure S53 ^{1}H NMR (600 MHz, $CDCl_3$) of 1z

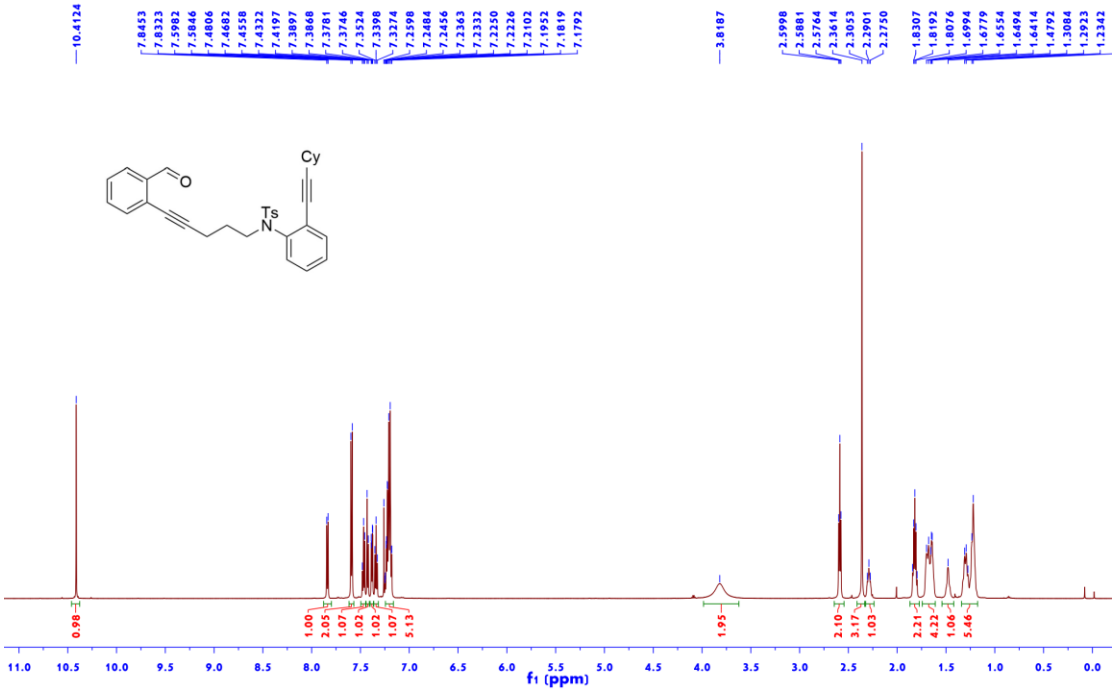


Figure S54 ^{13}C NMR (150 MHz, $CDCl_3$) of 1z

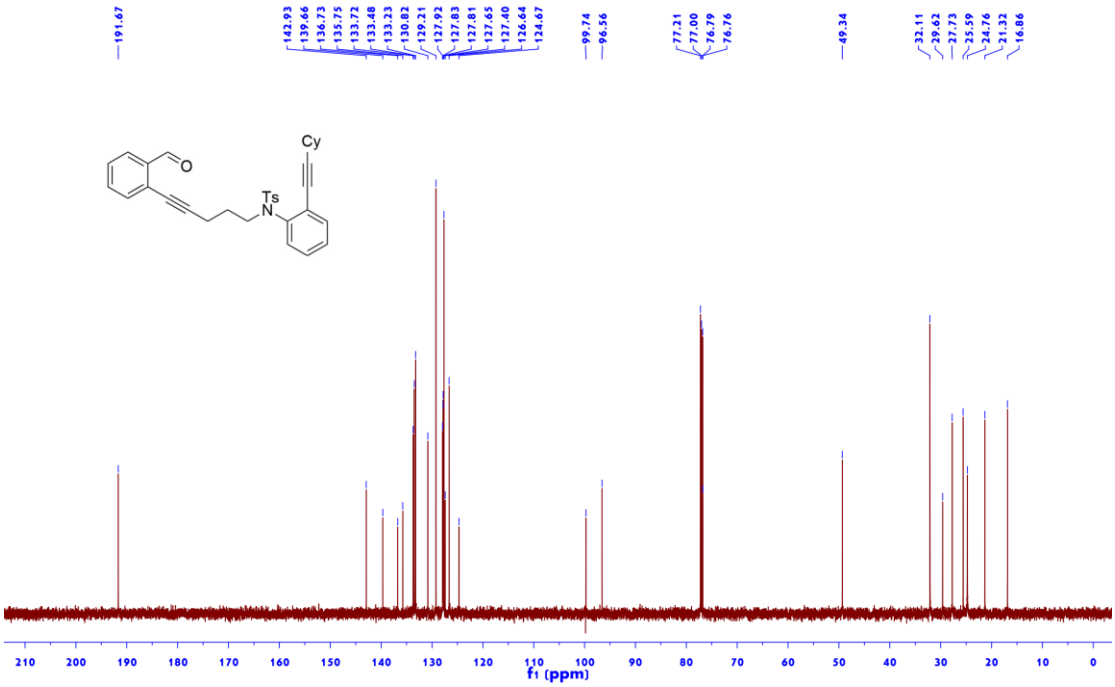


Figure S55 ^{1}H NMR (600 MHz, $CDCl_3$) of 1aa

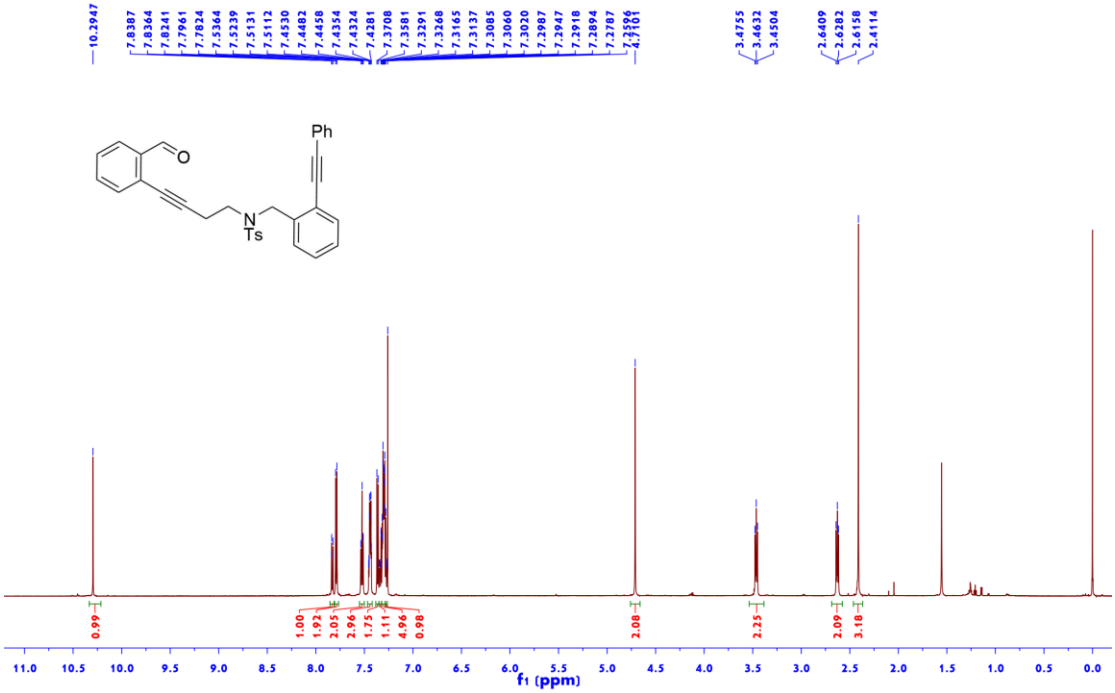


Figure S56 ^{13}C NMR (150 MHz, $CDCl_3$) of 1aa

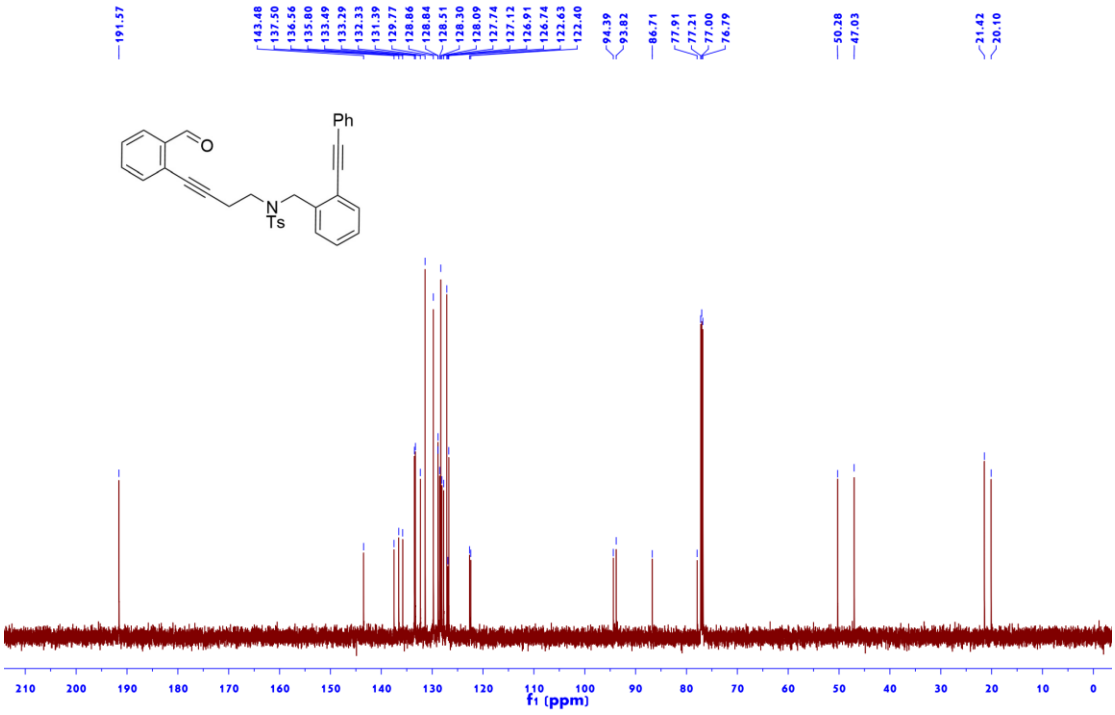


Figure S57 ^{1}H NMR (600 MHz, $CDCl_3$) of 1ab

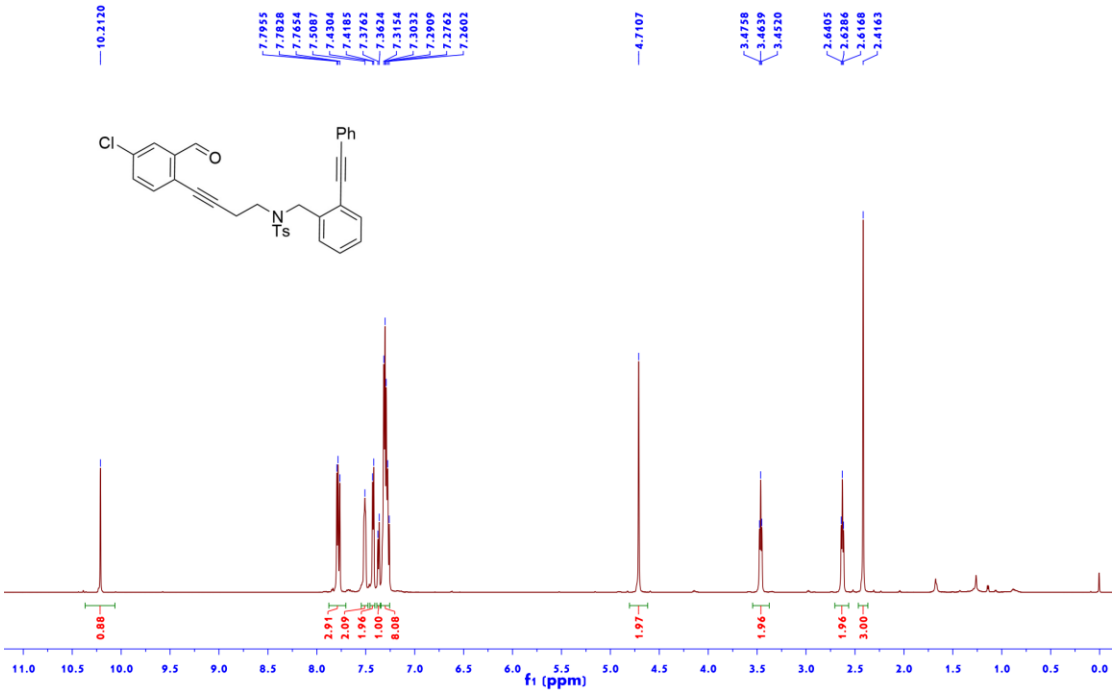


Figure S58 ^{13}C NMR (150 MHz, $CDCl_3$) of 1ab

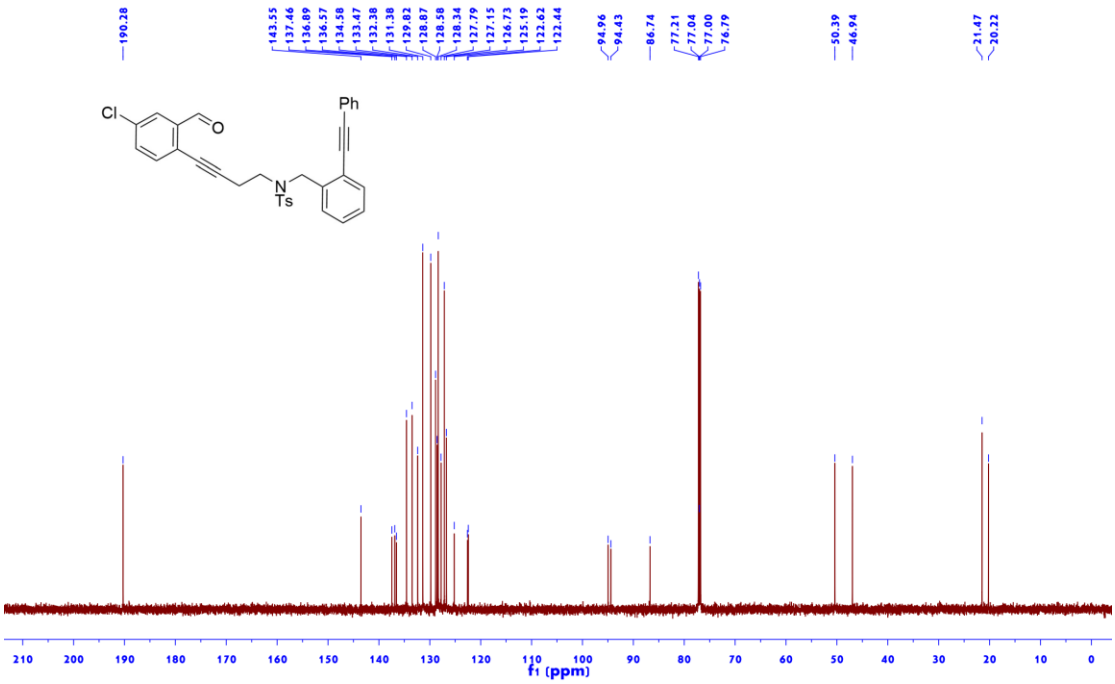


Figure S59 ^{1}H NMR (600 MHz, $CDCl_3$) of 1ac

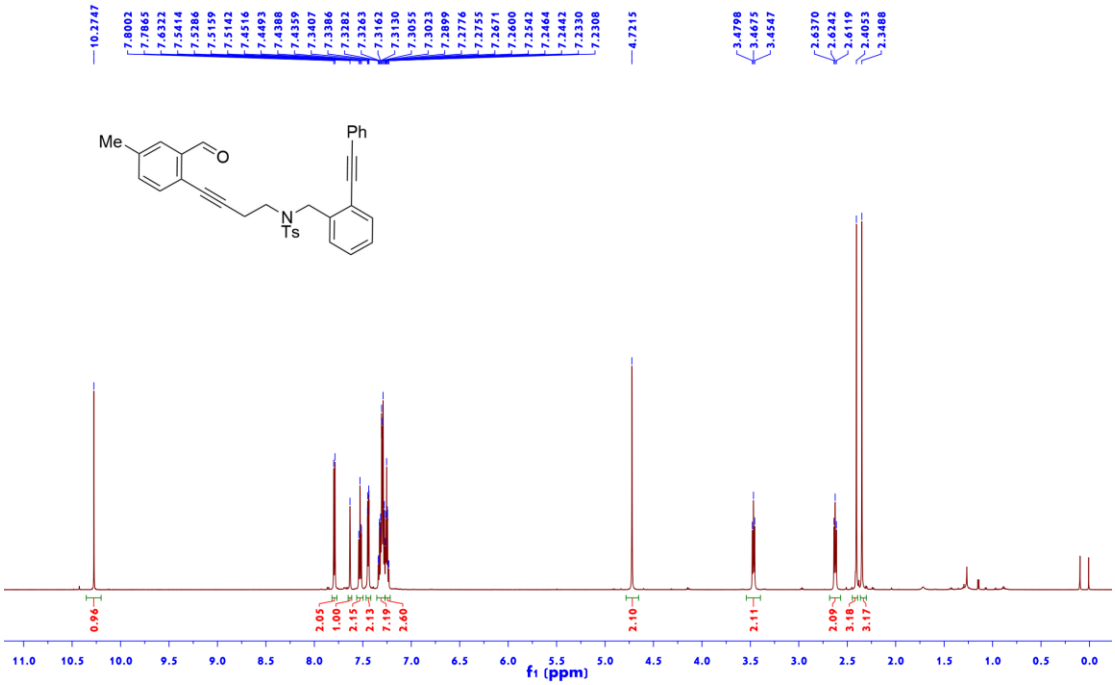


Figure S60 ^{13}C NMR (150 MHz, $CDCl_3$) of 1ac

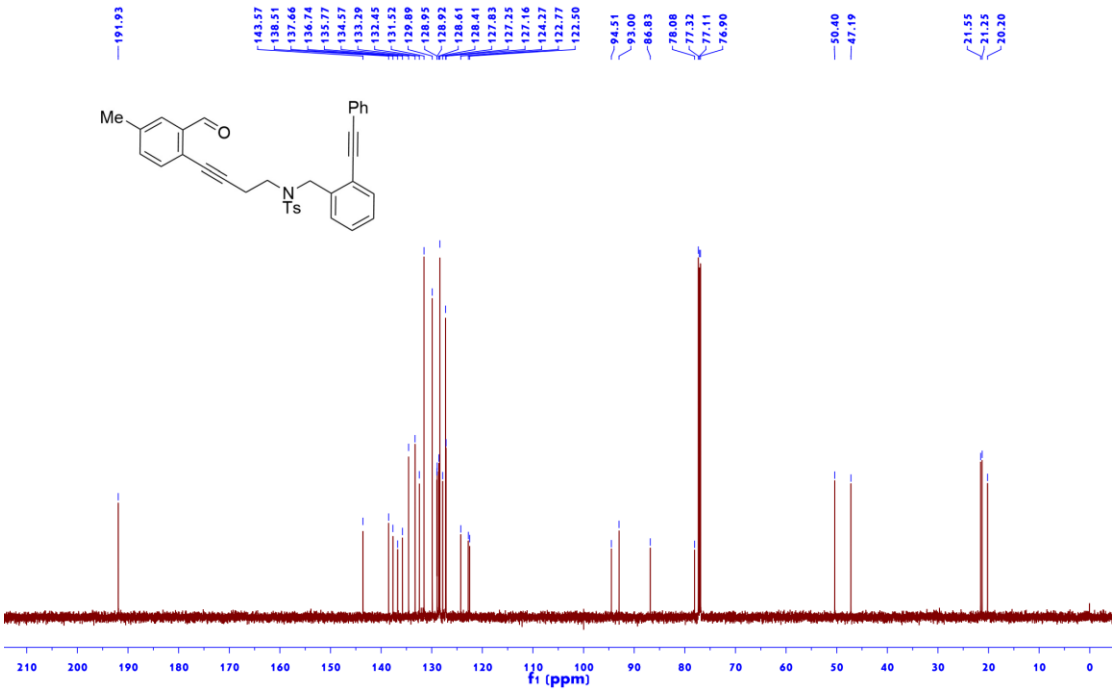


Figure S61 ^{1}H NMR (600 MHz, $CDCl_3$) of 1ad

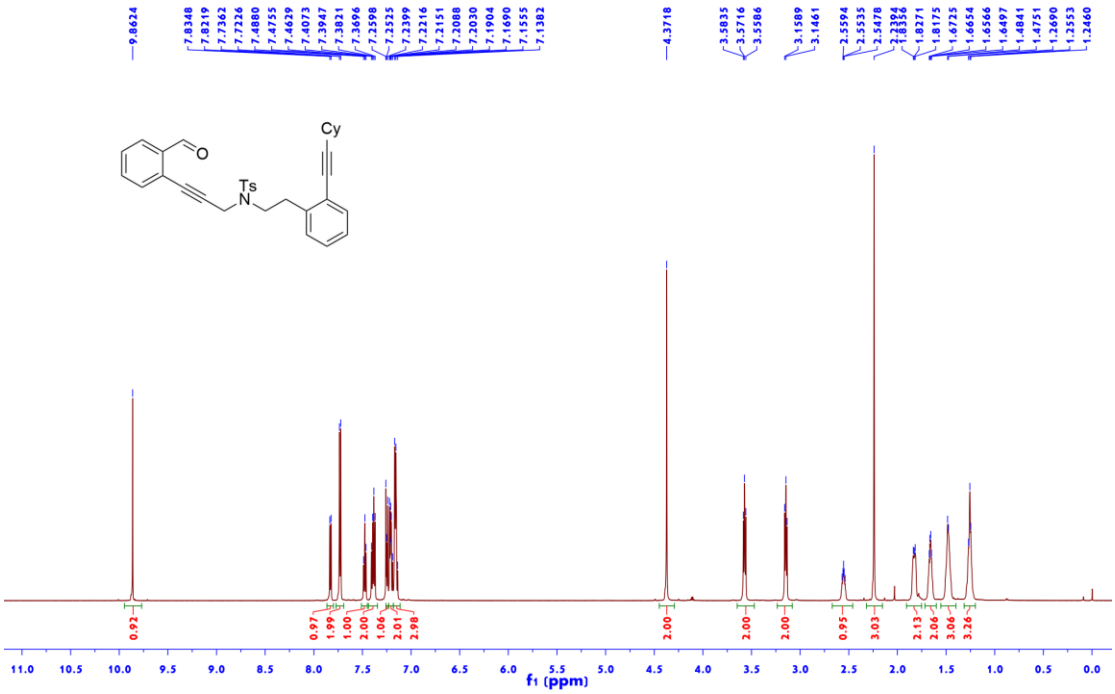


Figure S62 ^{13}C NMR (150 MHz, $CDCl_3$) of 1ad

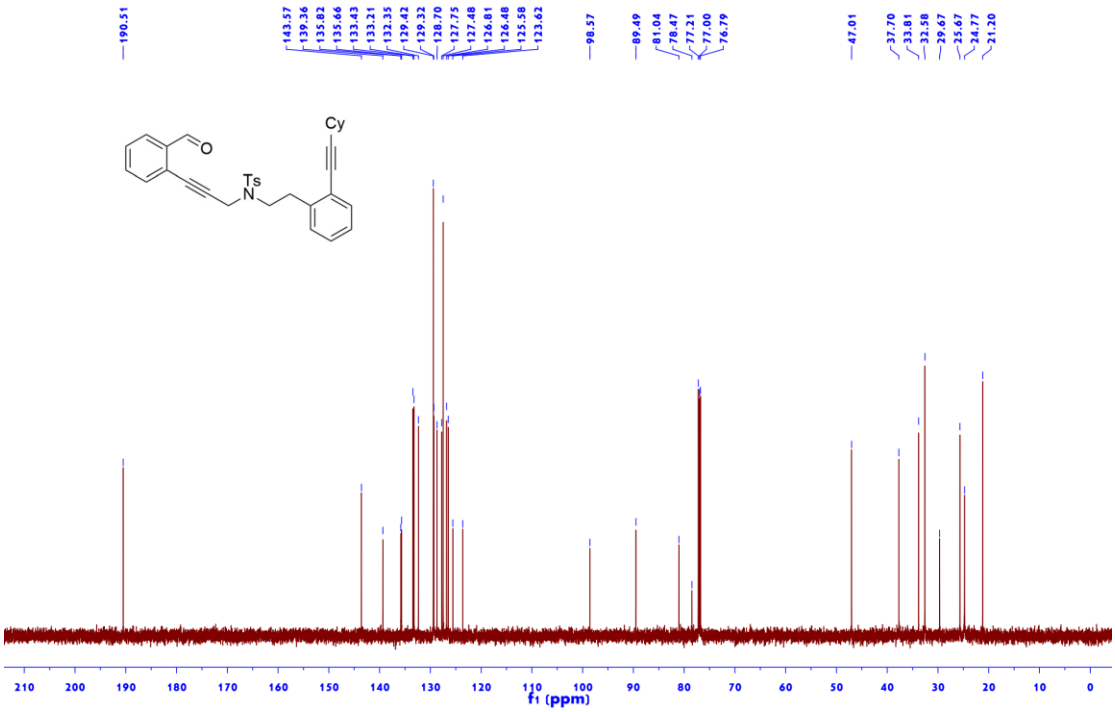


Figure S63 ^{1}H NMR (600 MHz, $CDCl_3$) of 1ae

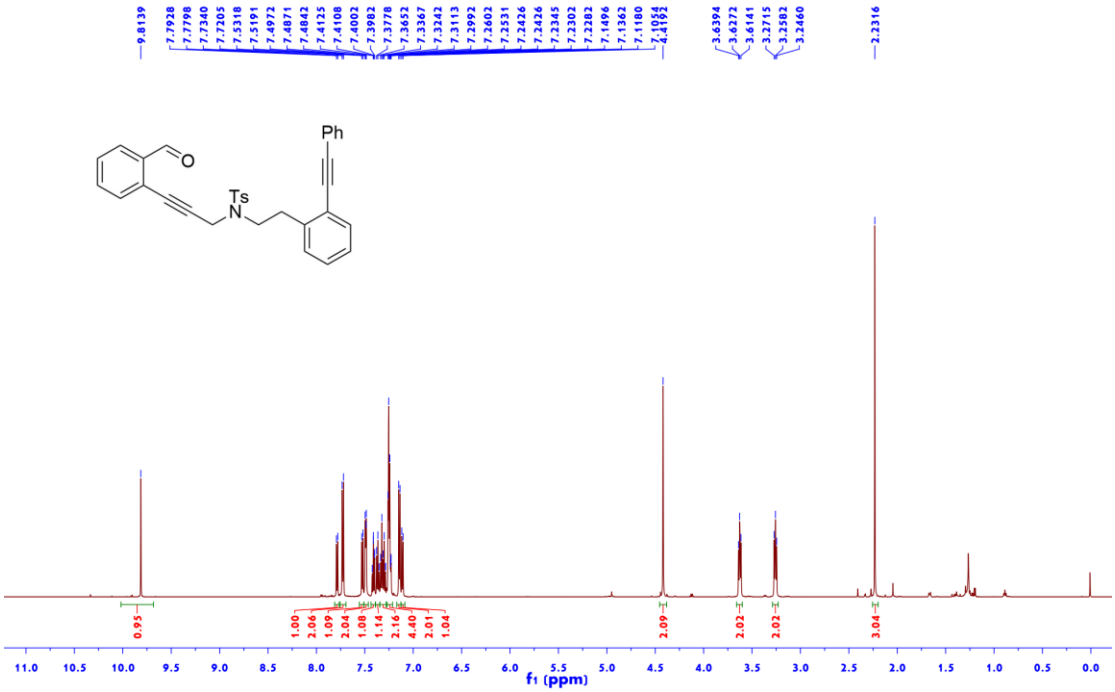


Figure S64 ^{13}C NMR (150 MHz, $CDCl_3$) of 1ae

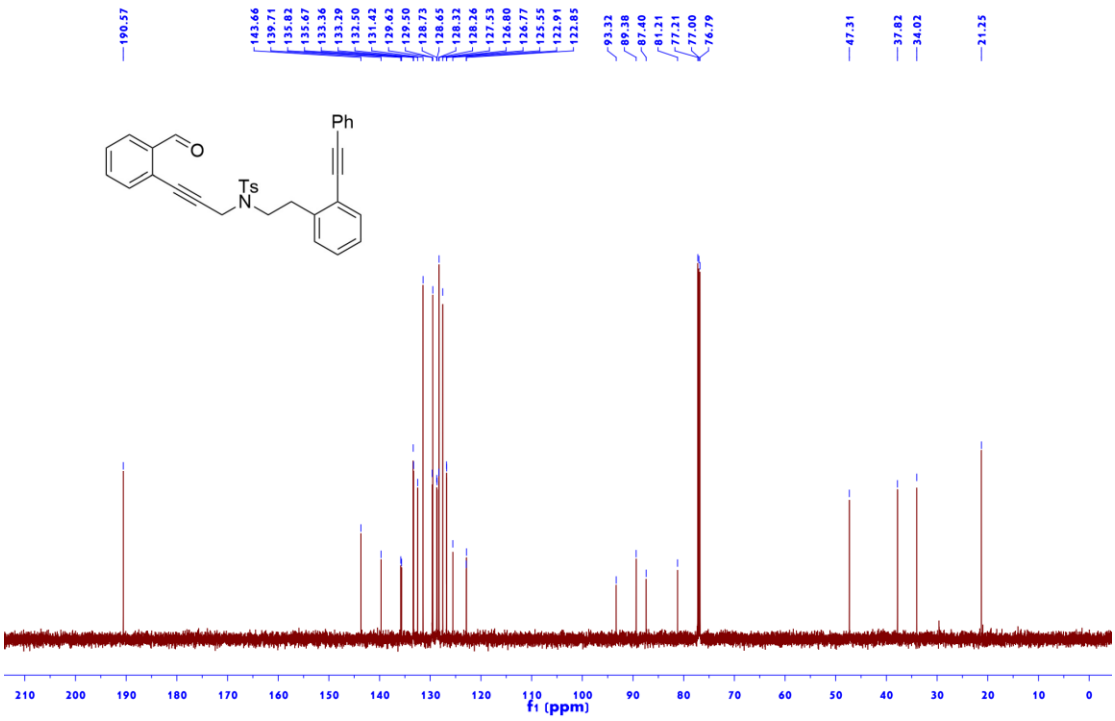


Figure S65 ^{1}H NMR (600 MHz, $CDCl_3$) of 1af

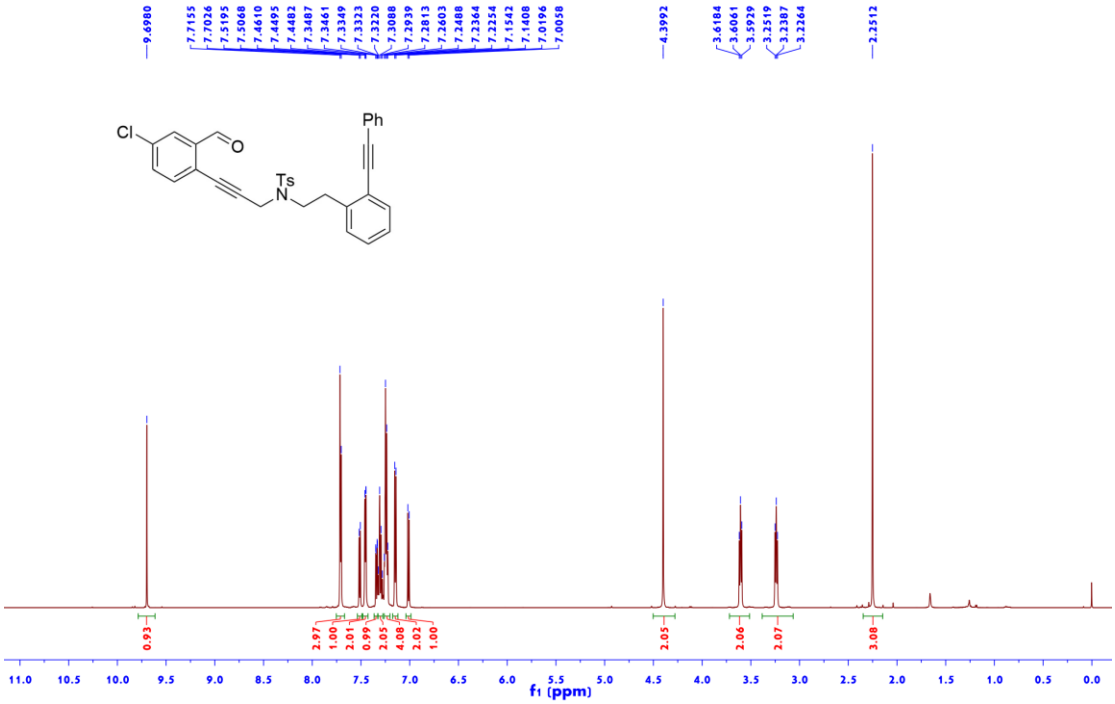


Figure S66 ^{13}C NMR (150 MHz, $CDCl_3$) of 1af

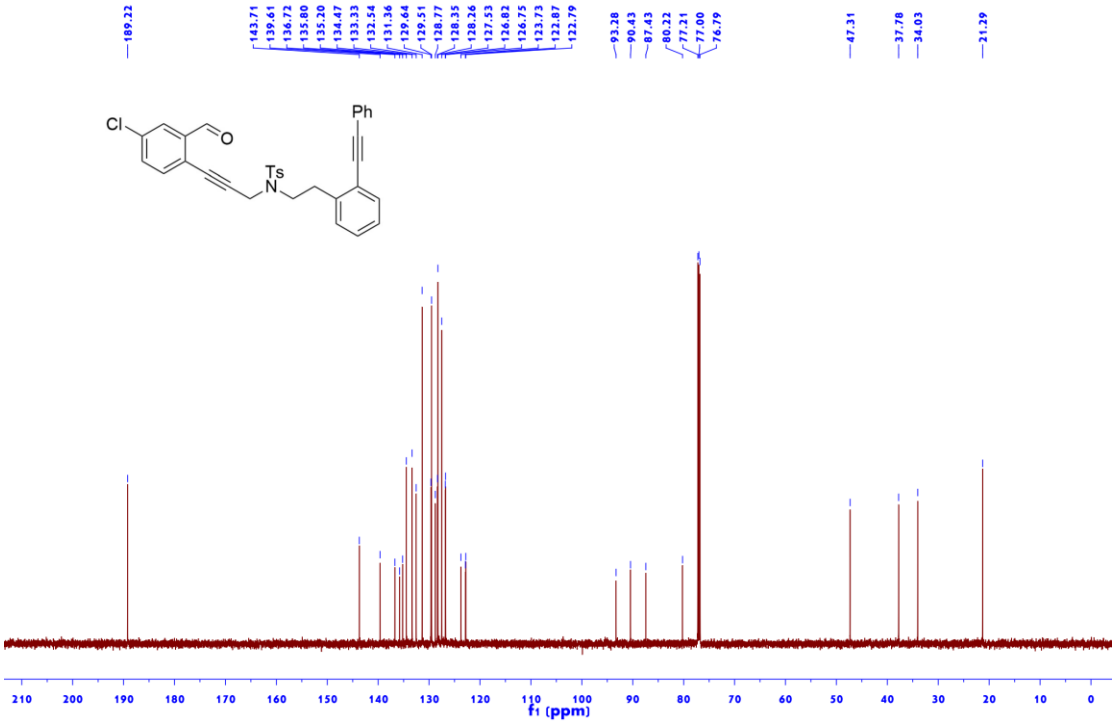


Figure S67 ^{1}H NMR (600 MHz, $CDCl_3$) of 1ag

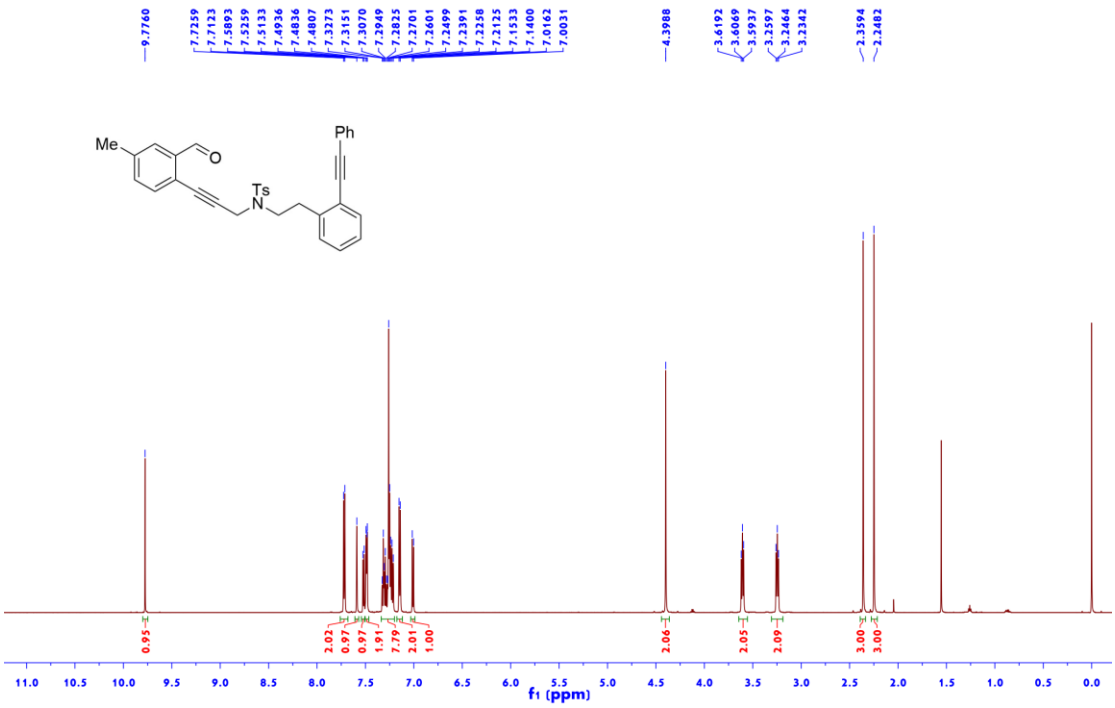


Figure S68 ^{13}C NMR (150 MHz, $CDCl_3$) of 1ag

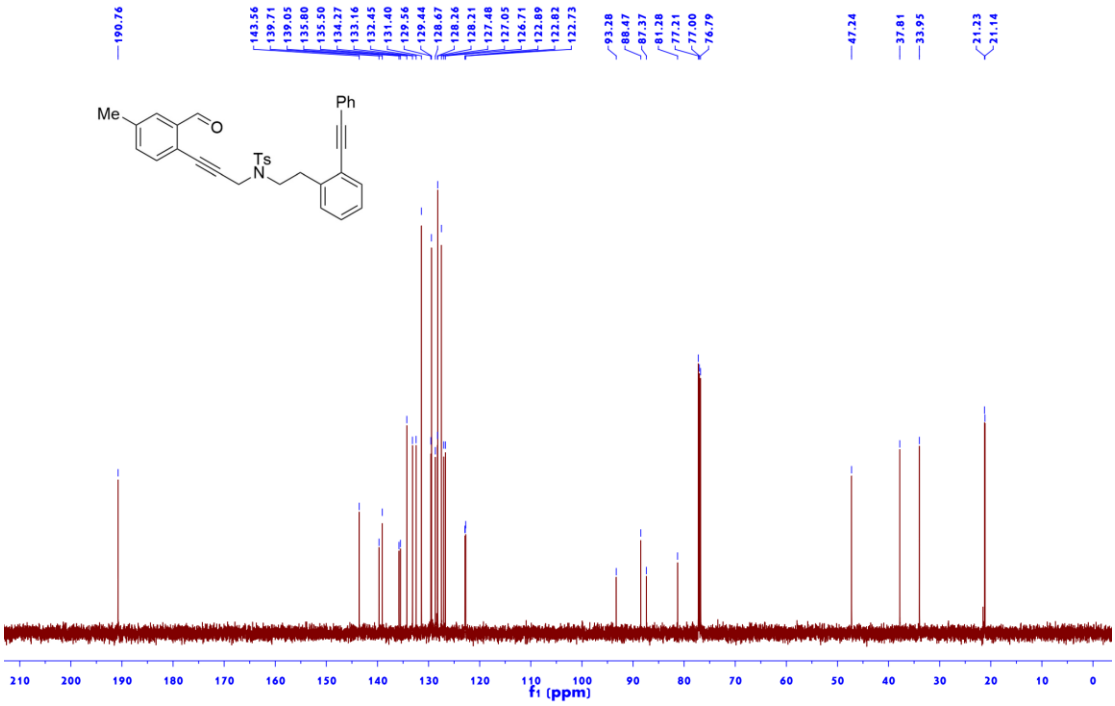


Figure S69 ^{1}H NMR (600 MHz, $CDCl_3$) of 1ah

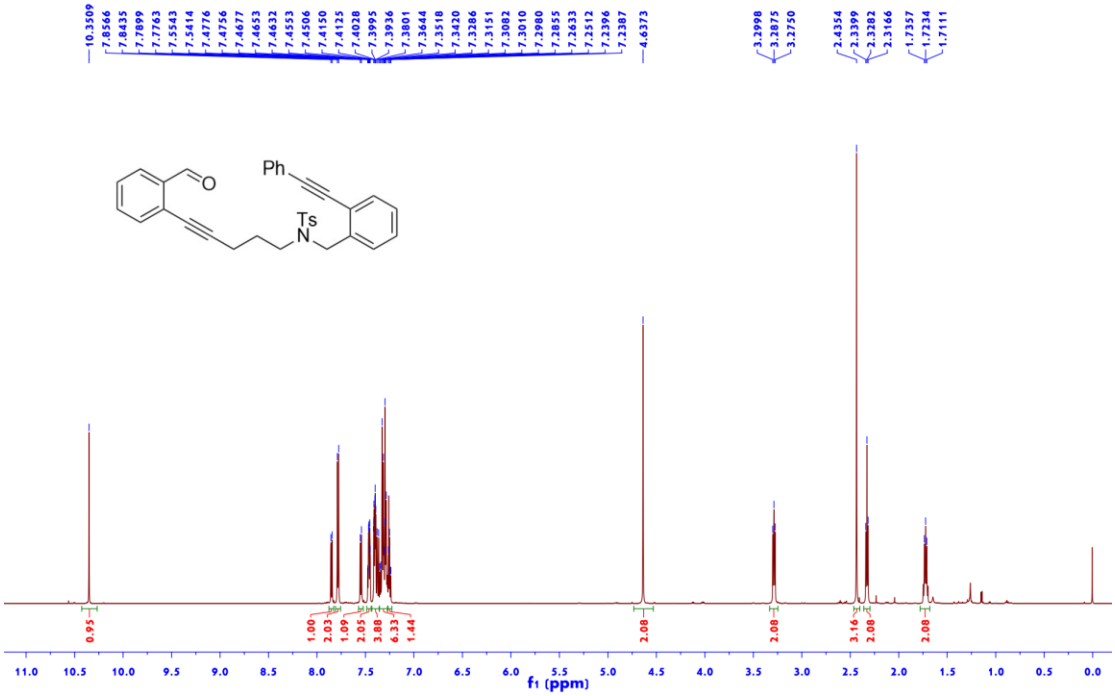


Figure S70 ^{13}C NMR (150 MHz, $CDCl_3$) of 1ah

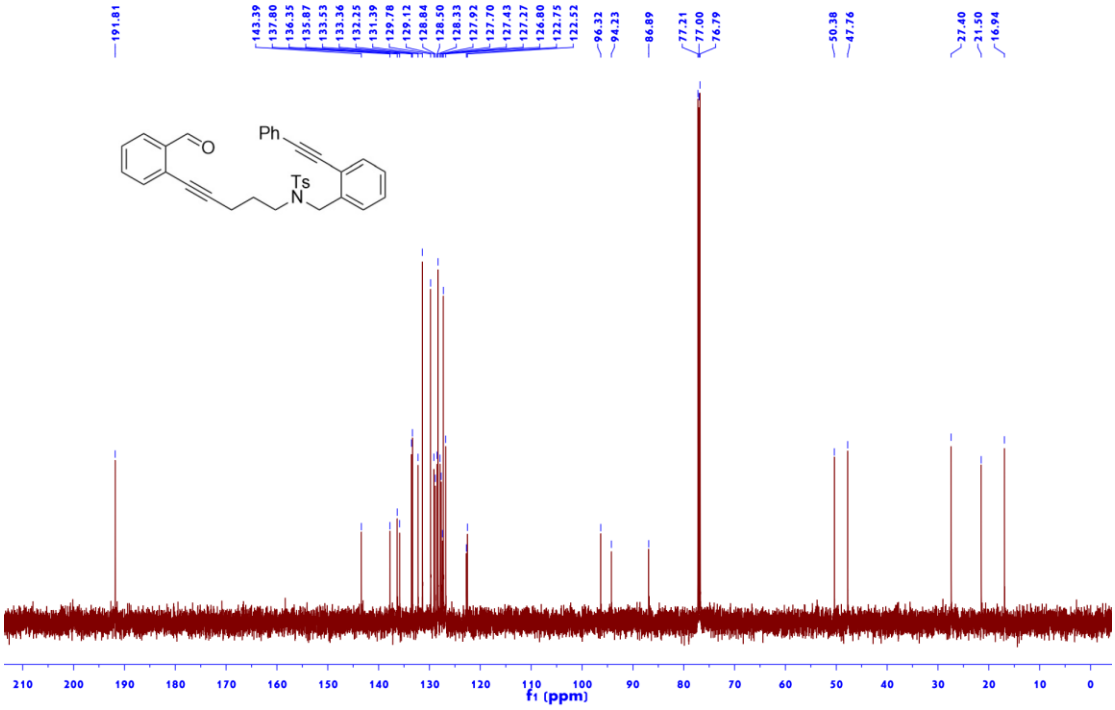


Figure S71 ^{1}H NMR (600 MHz, $CDCl_3$) of 1ai

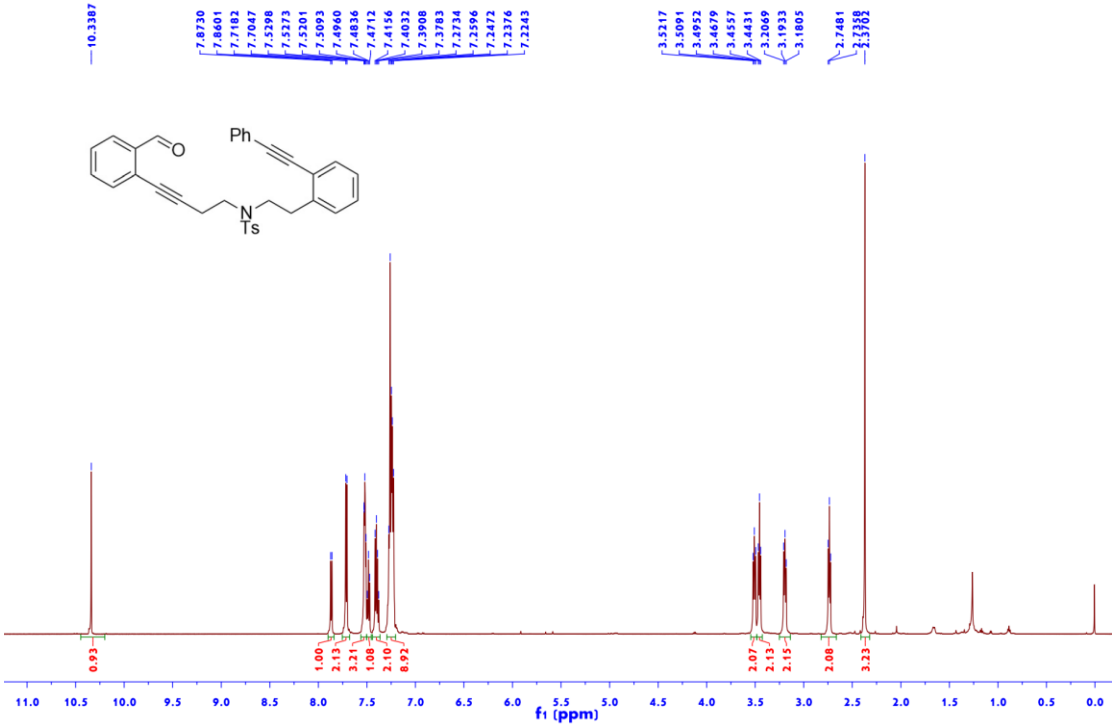


Figure S72 ^{13}C NMR (150 MHz, $CDCl_3$) of 1ai

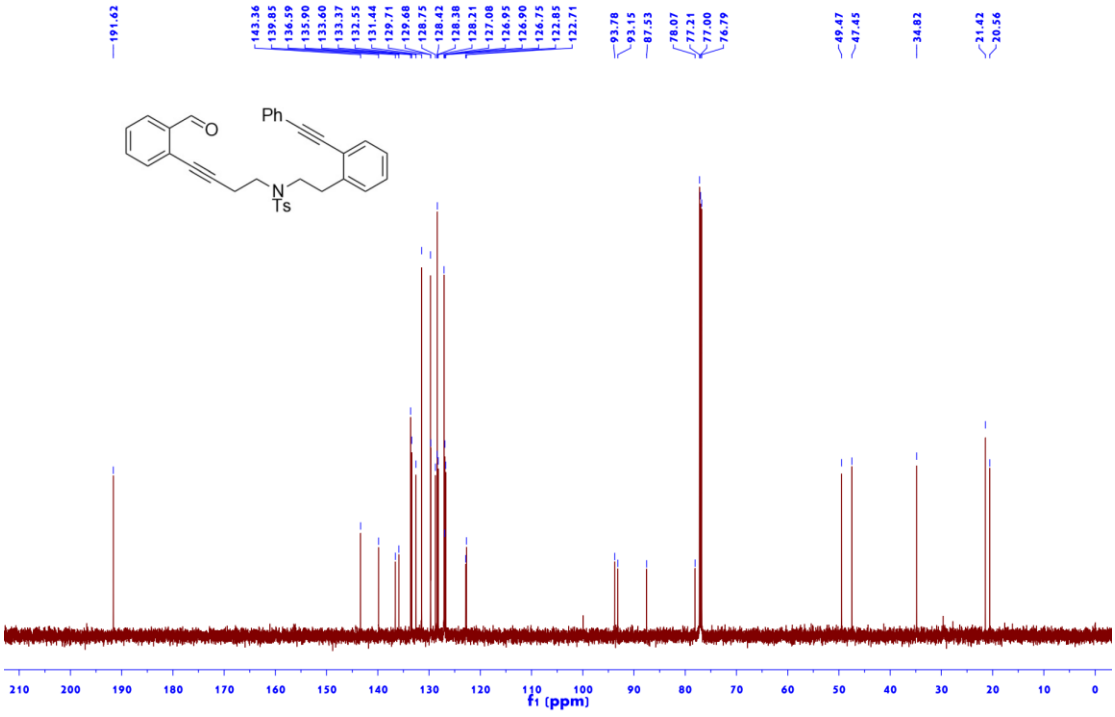


Figure S73 ^{1}H NMR (600 MHz, $CDCl_3$) of 1aj

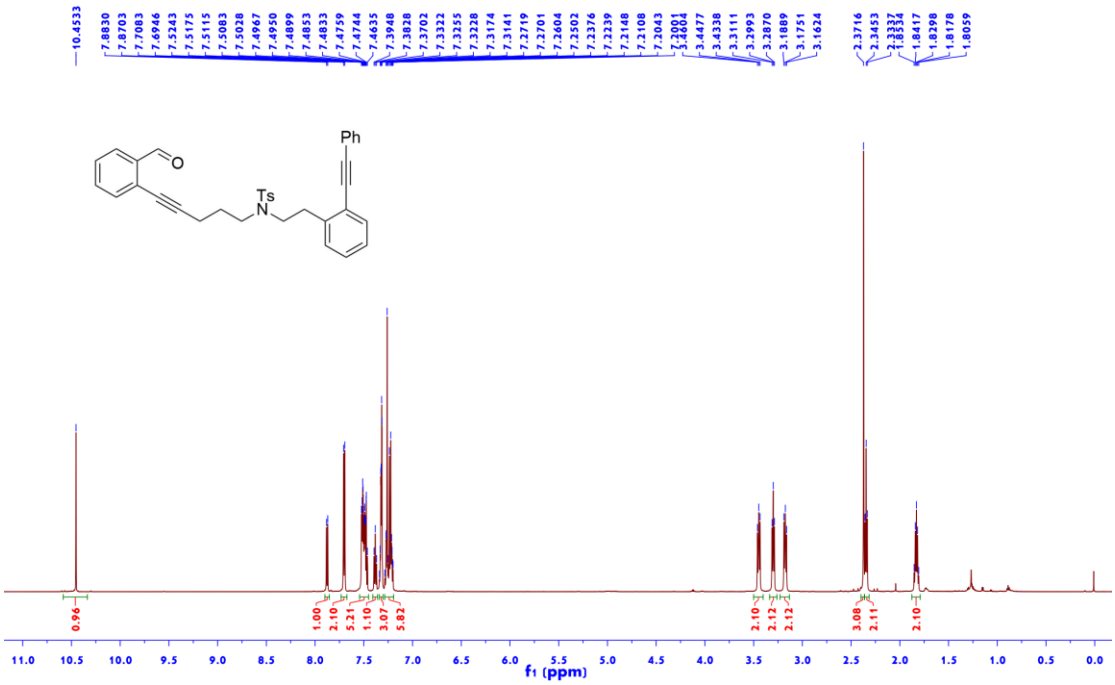


Figure S74 ^{13}C NMR (150 MHz, $CDCl_3$) of 1aj

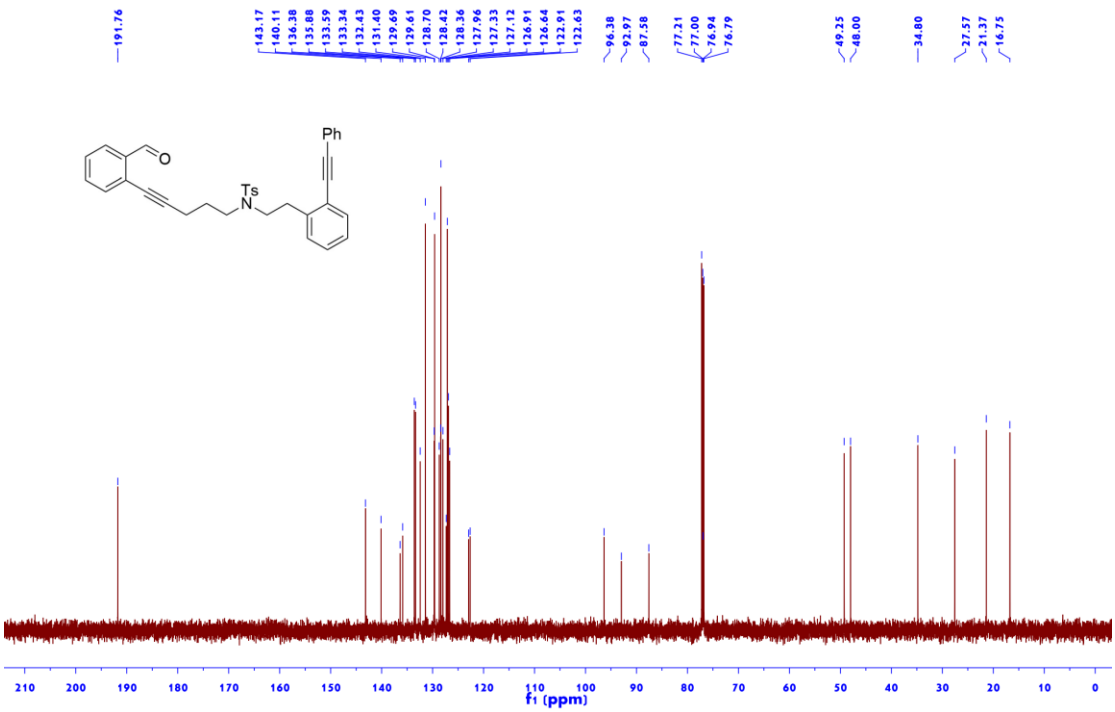


Figure S75 ^{1}H NMR (600 MHz, $CDCl_3$) of 1ak

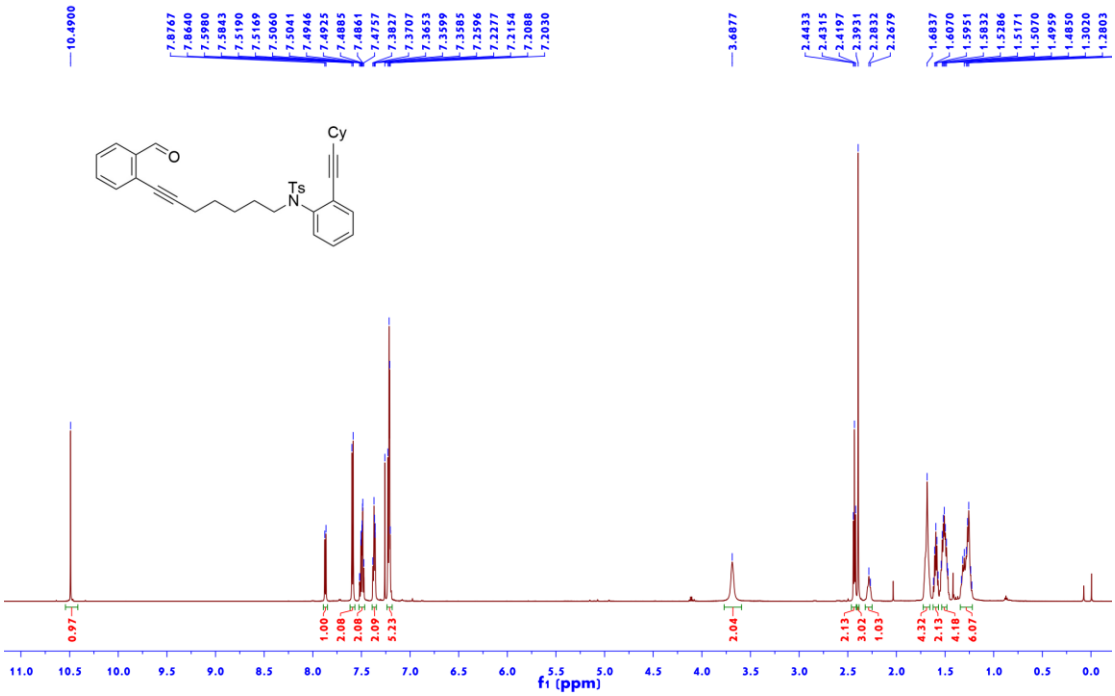


Figure S76 ^{13}C NMR (150 MHz, $CDCl_3$) of 1ak

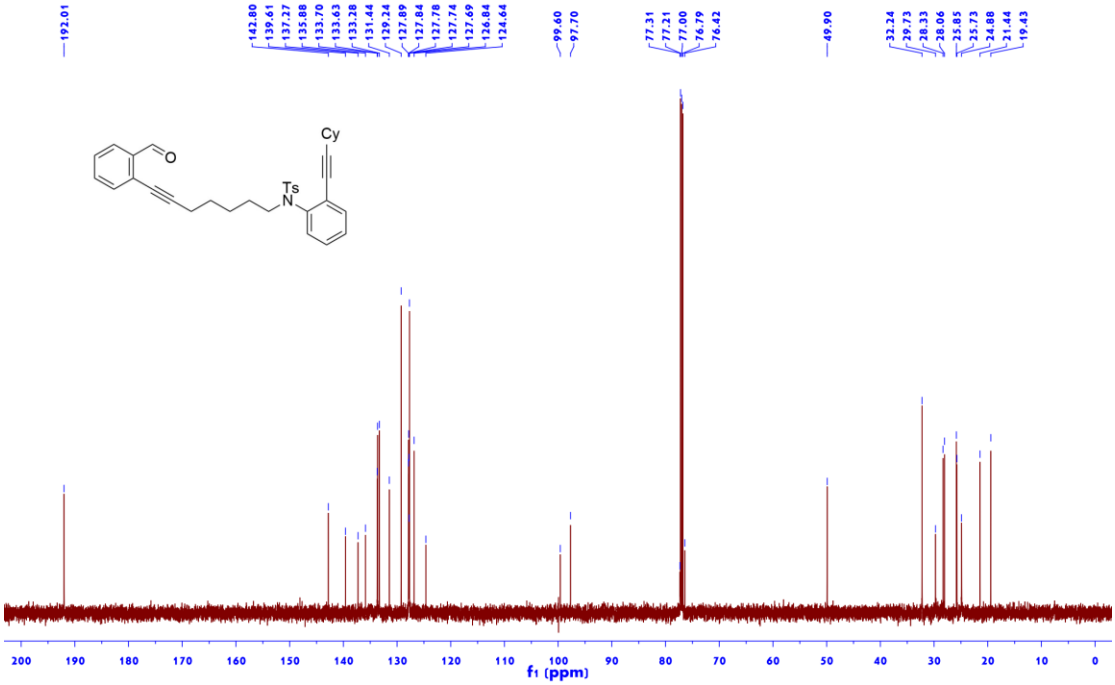


Figure S77 ^{1}H NMR (600 MHz, $CDCl_3$) of 1al

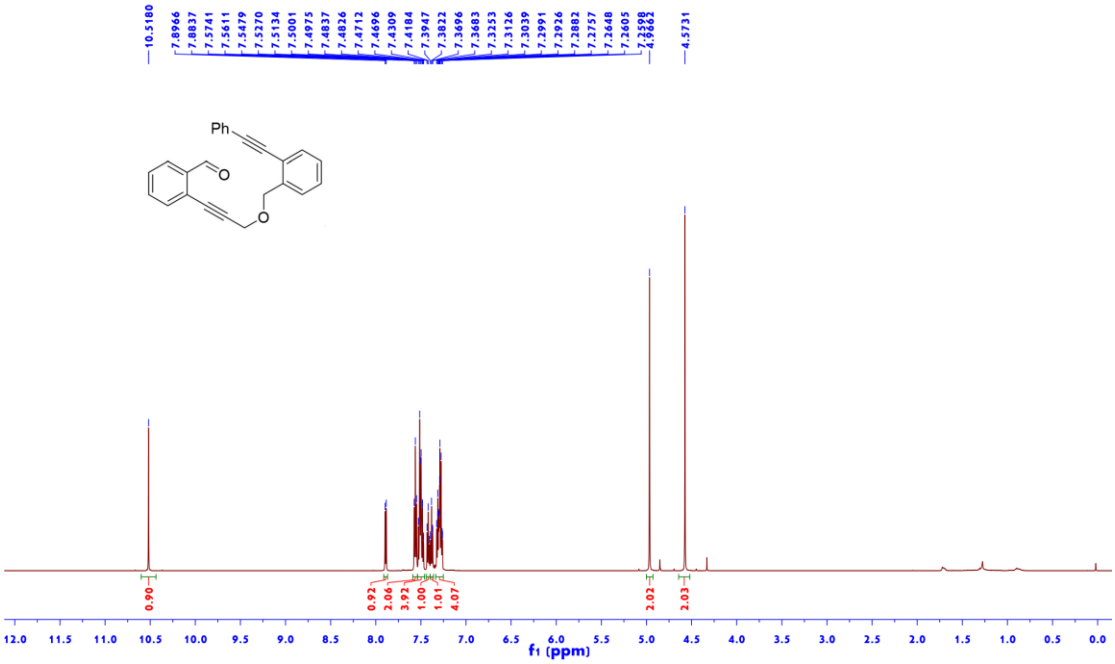


Figure S78 ^{13}C NMR (150 MHz, $CDCl_3$) of 1al

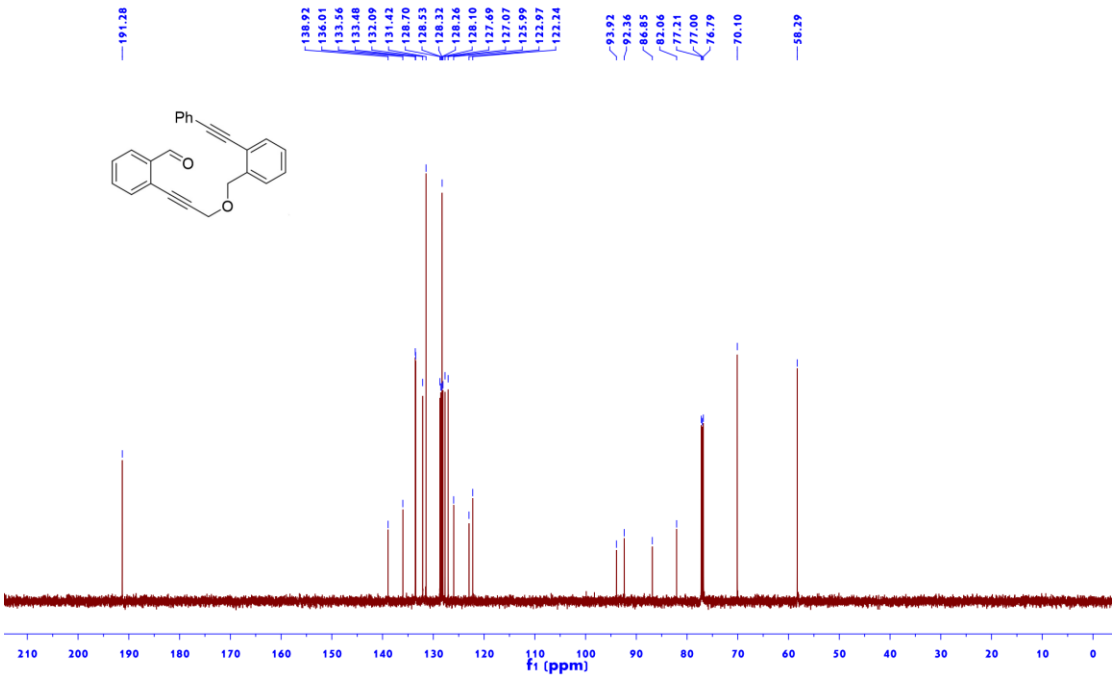


Figure S79 ^{1}H NMR (600 MHz, $CDCl_3$) of 2a

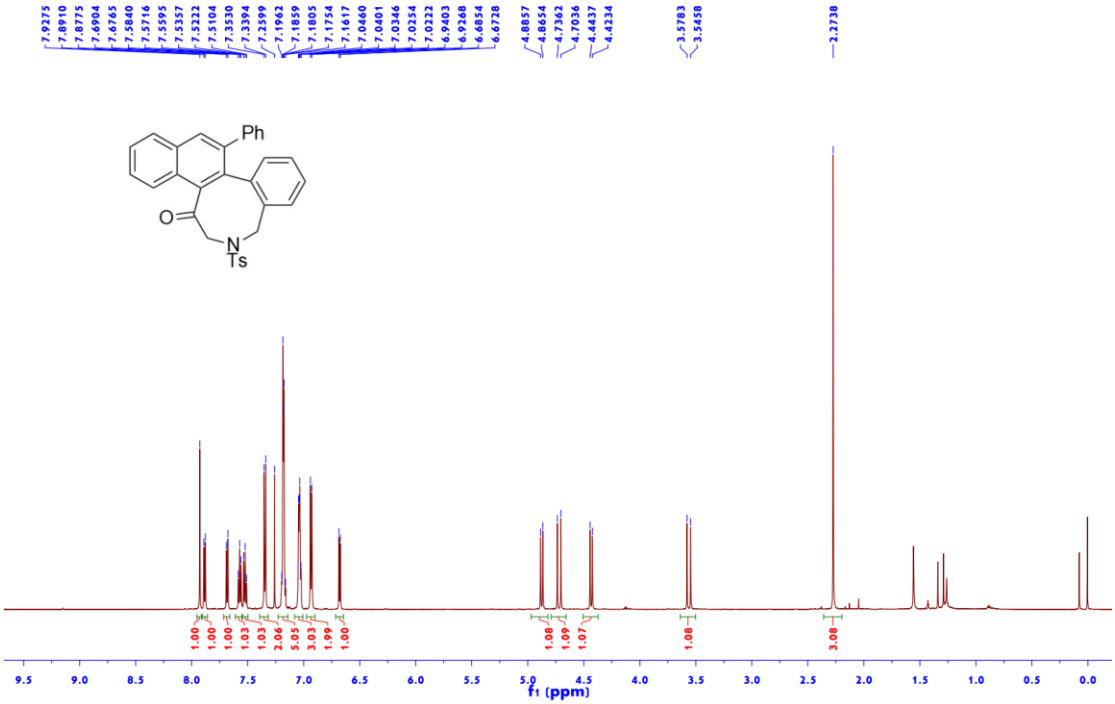


Figure S80 ^{13}C NMR (150 MHz, $CDCl_3$) of 2a

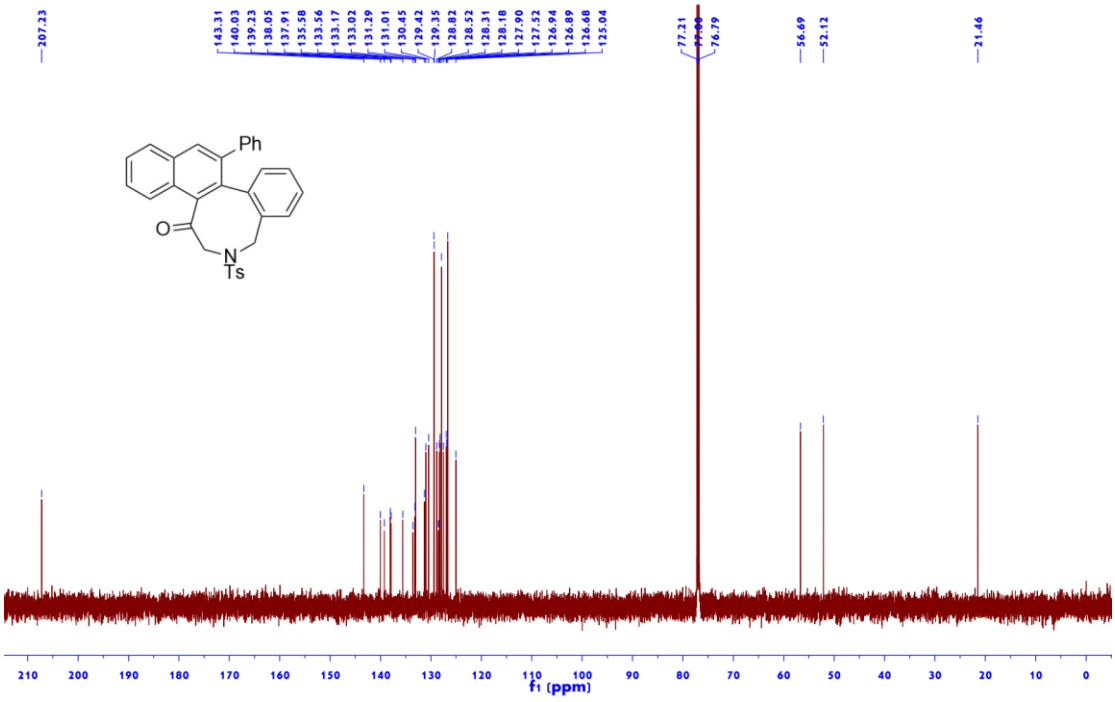


Figure S81 ^{1}H NMR (600 MHz, $CDCl_3$) of 2b

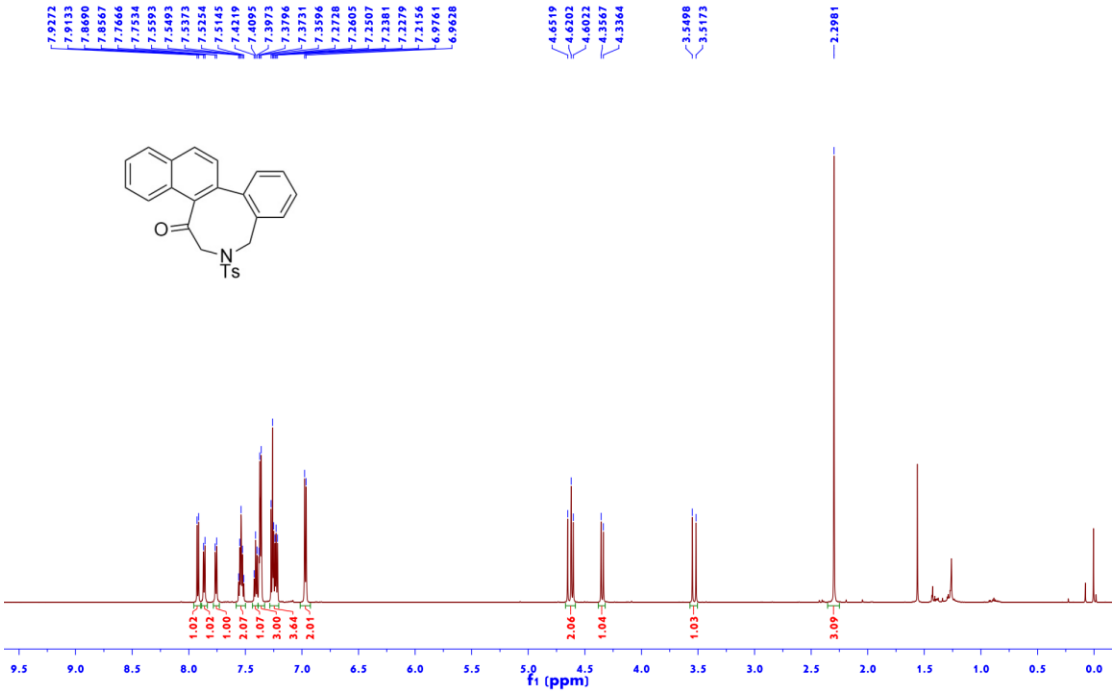


Figure S82 ^{13}C NMR (150 MHz, $CDCl_3$) of 2b

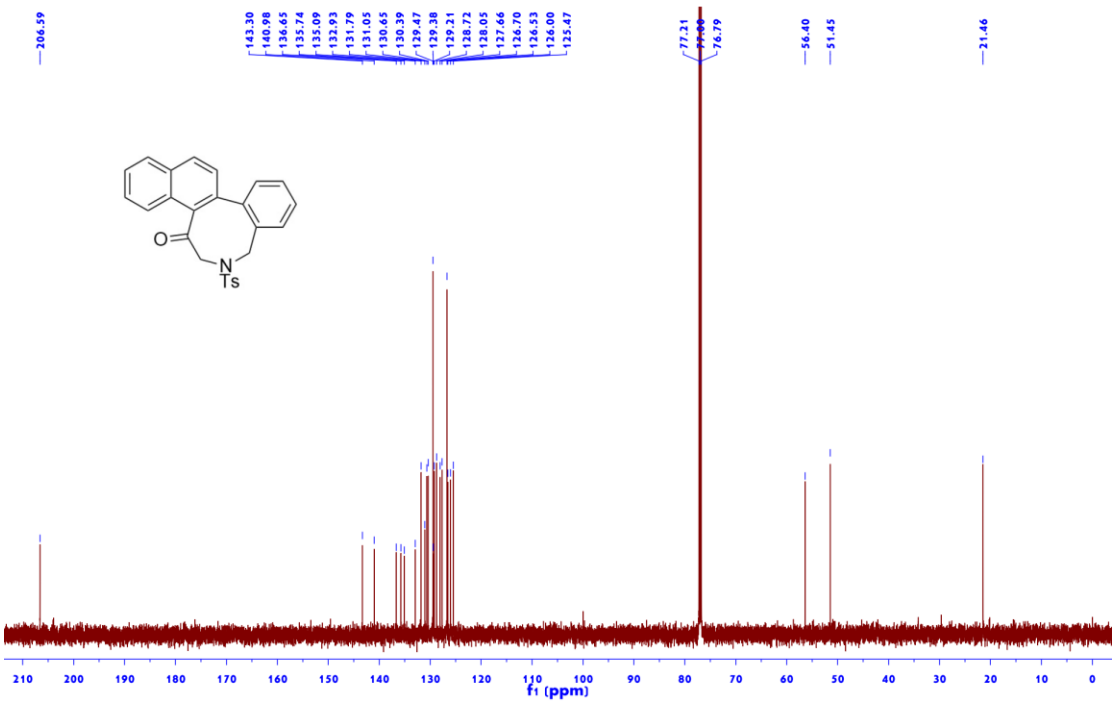


Figure S83 ^{1}H NMR (600 MHz, $CDCl_3$) of 2c

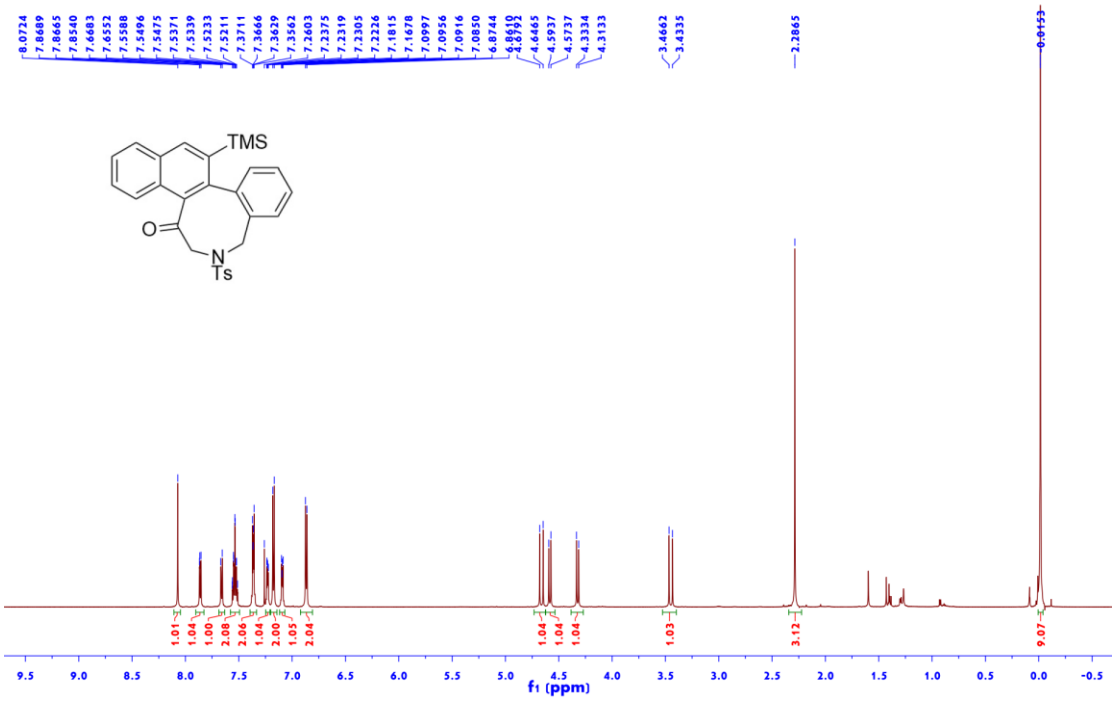


Figure S84 ^{13}C NMR (150 MHz, $CDCl_3$) of 2c

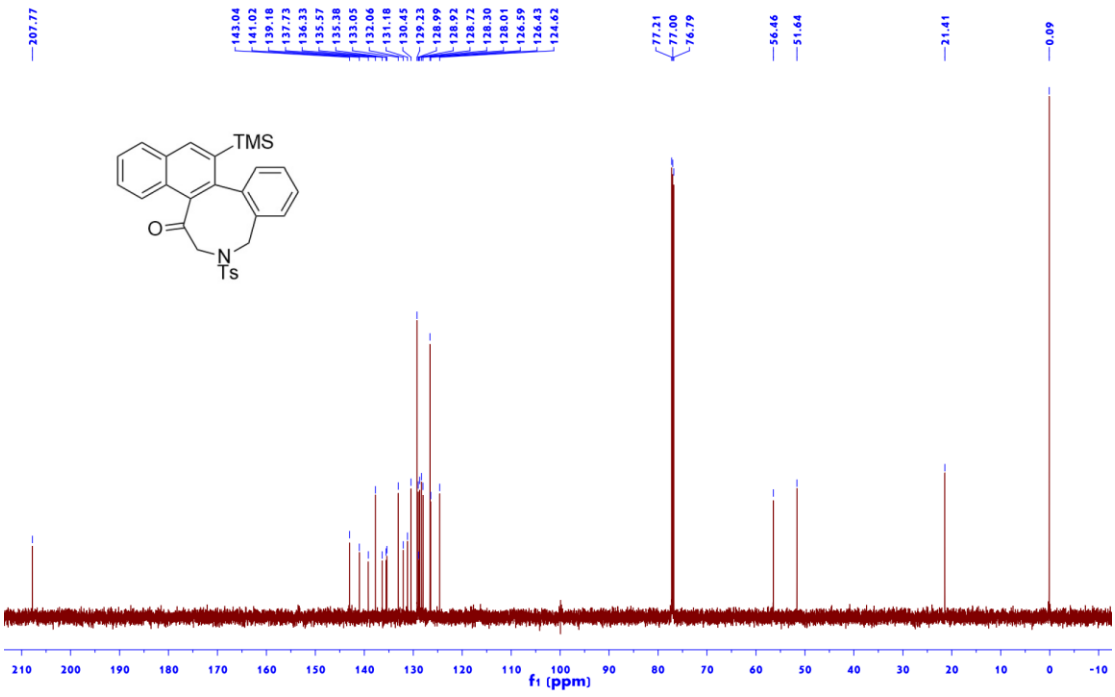


Figure S85 ^{1}H NMR (600 MHz, $CDCl_3$) of 2d

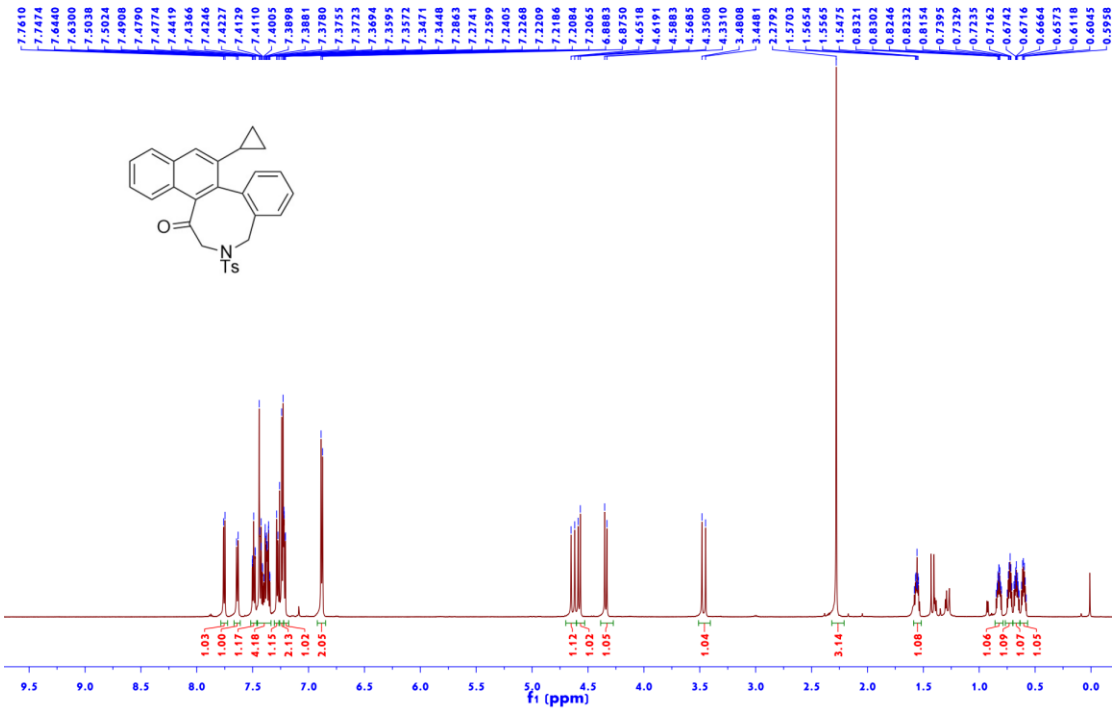


Figure S86 ^{13}C NMR (150 MHz, $CDCl_3$) of 2d

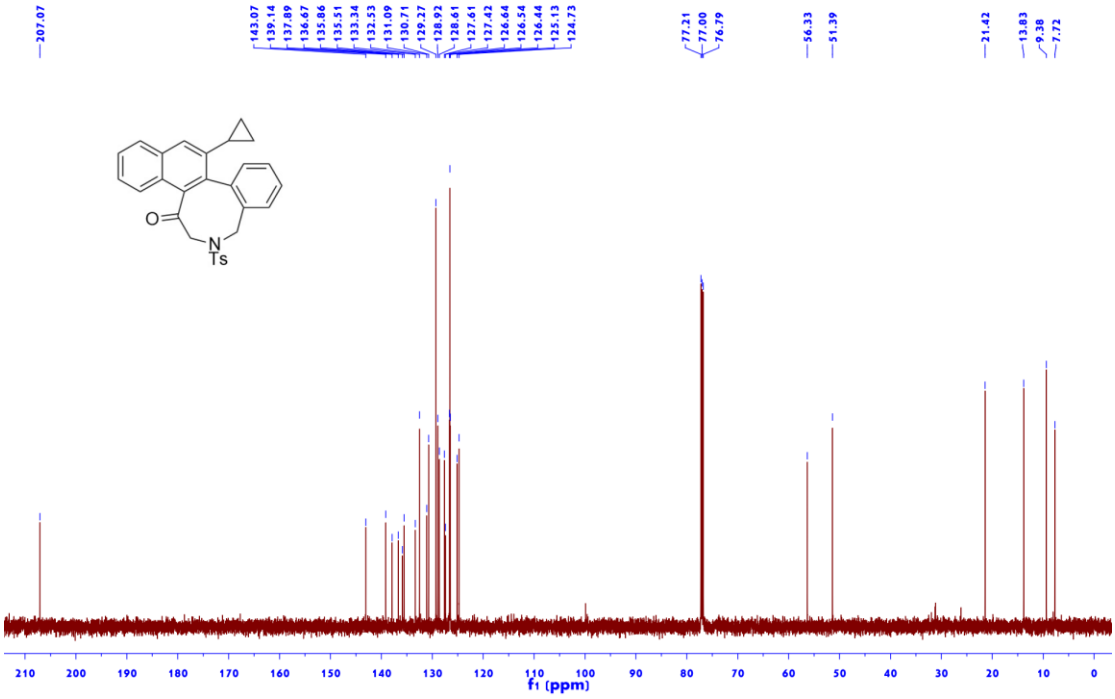


Figure S87 ^{1}H NMR (400 MHz, $CDCl_3$) of 2e

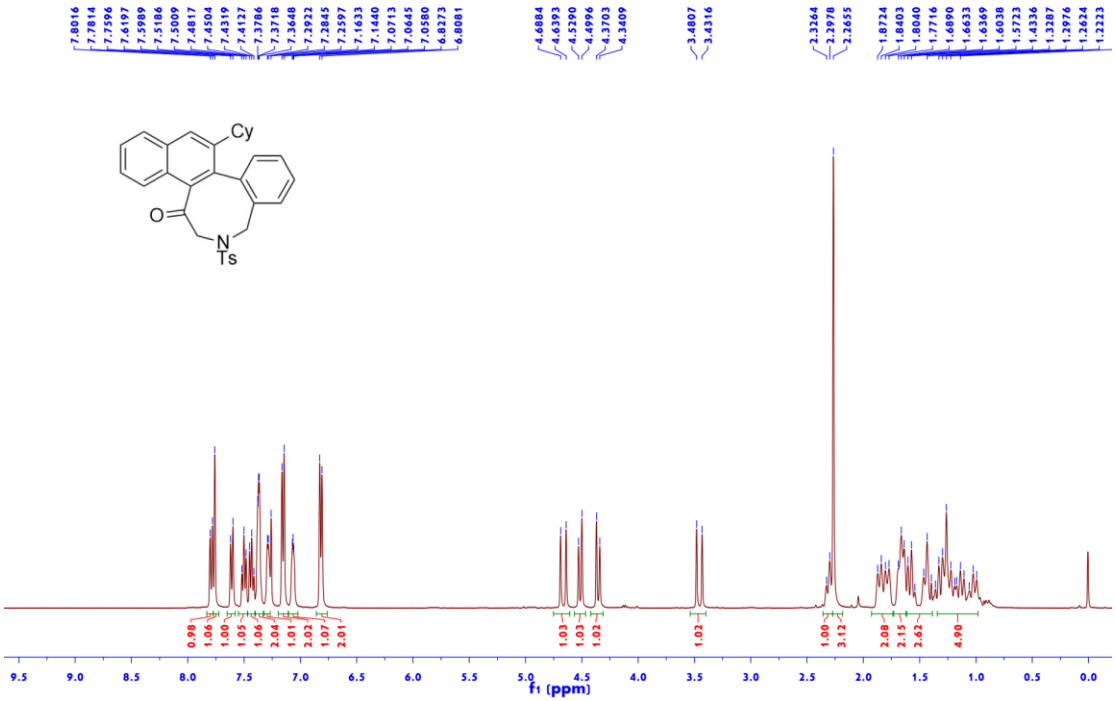


Figure S88 ^{13}C NMR (100 MHz, $CDCl_3$) of 2e

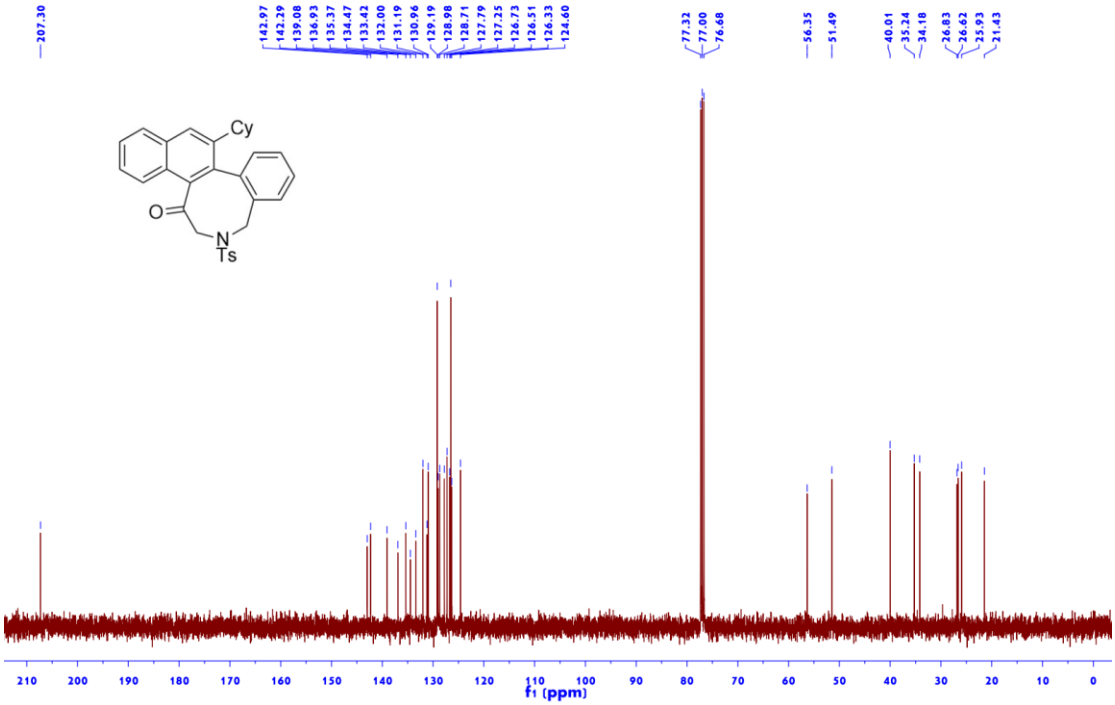


Figure S89 ^{1}H NMR (600 MHz, $CDCl_3$) of 2f

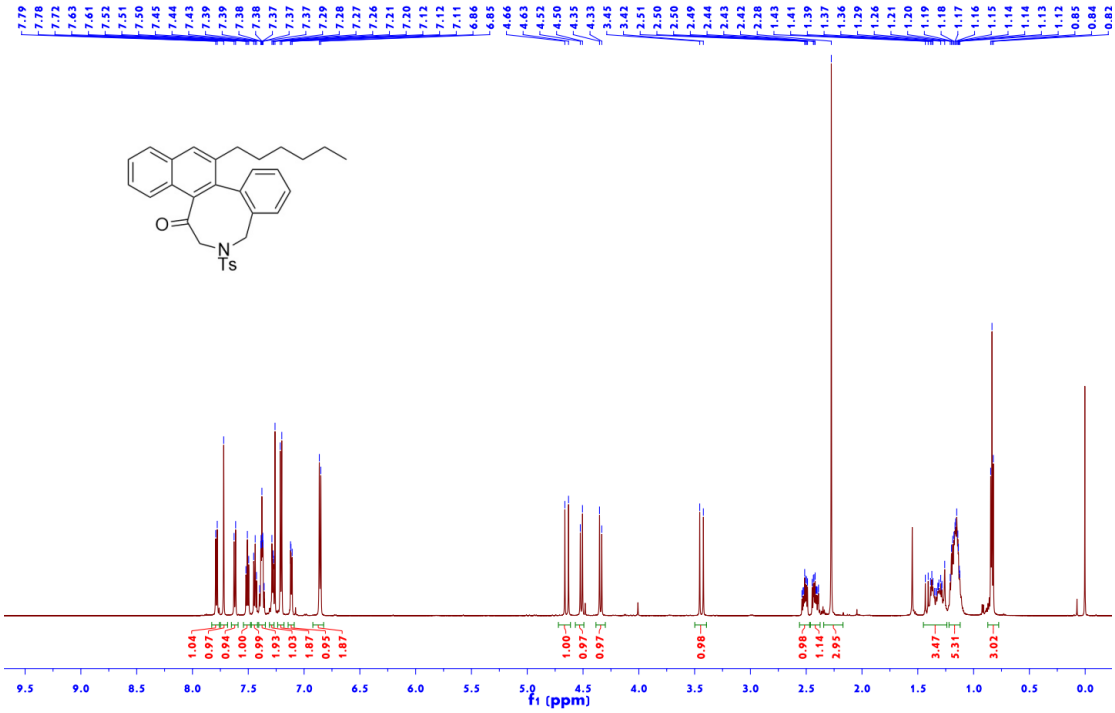


Figure S90 ^{13}C NMR (150 MHz, $CDCl_3$) of 2f

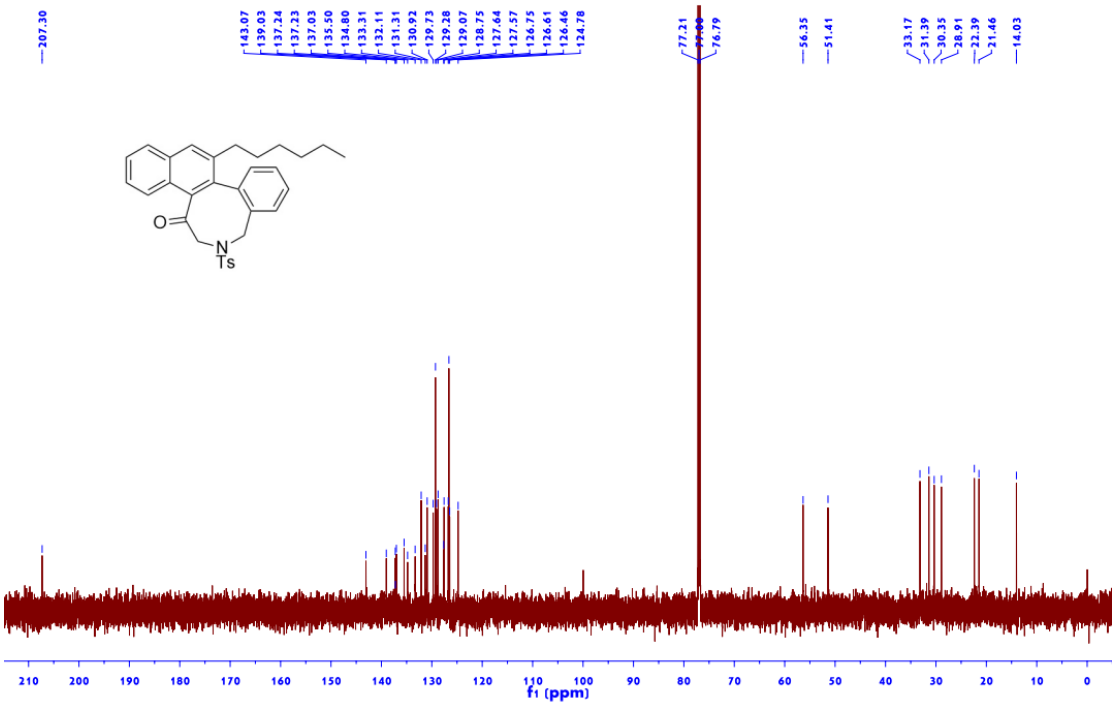


Figure S91 ^{1}H NMR (600 MHz, $CDCl_3$) of 2g

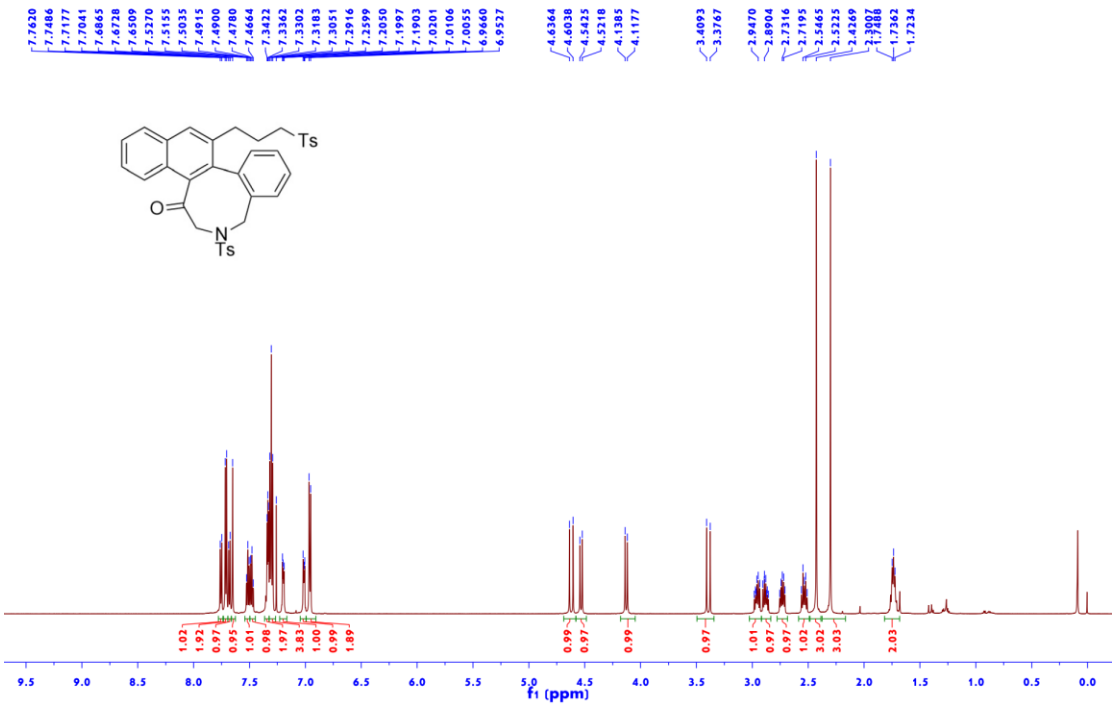


Figure S92 ^{13}C NMR (150 MHz, $CDCl_3$) of 2g

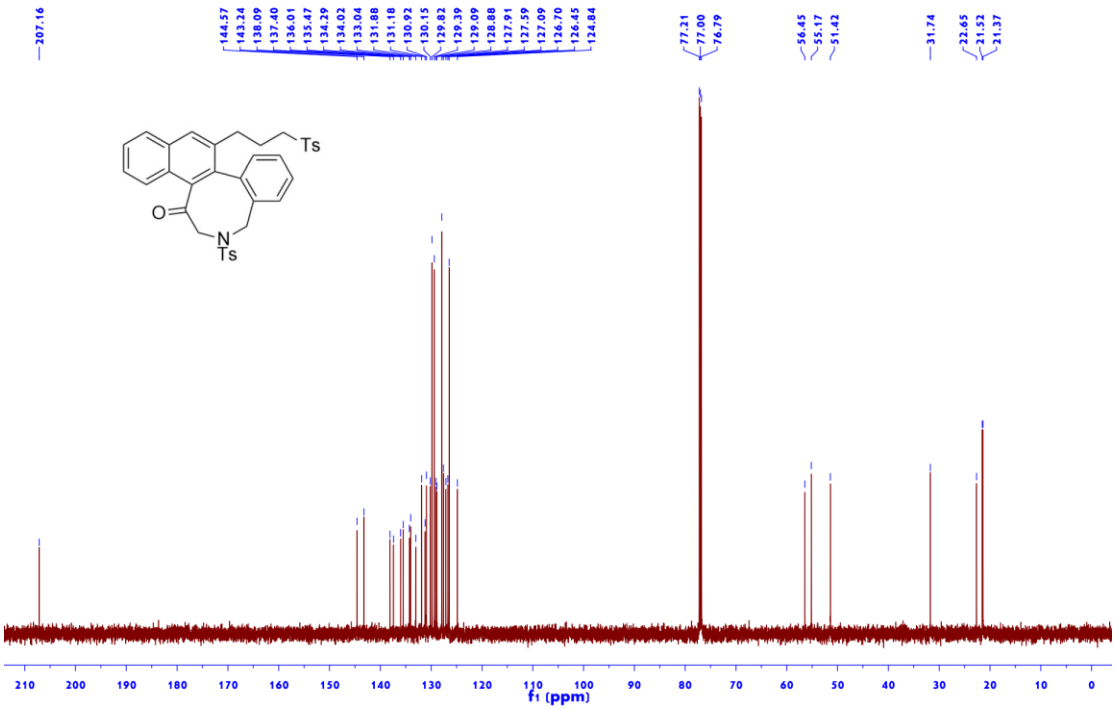


Figure S93 ^{1}H NMR (600 MHz, $CDCl_3$) of 2h

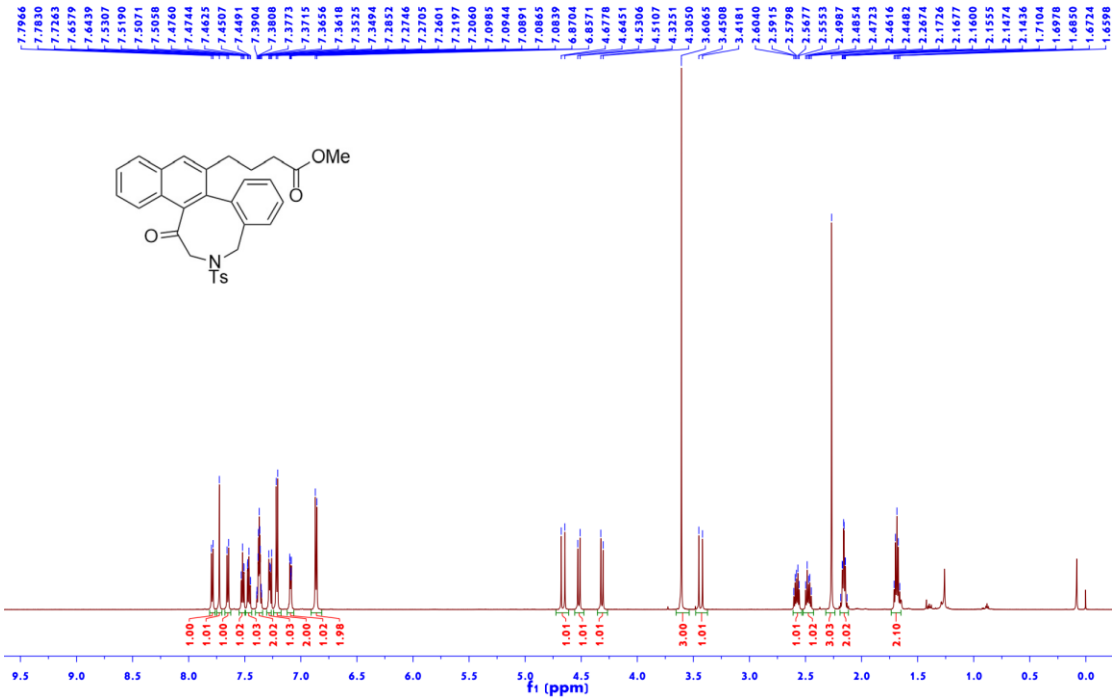


Figure S94 ^{13}C NMR (150 MHz, $CDCl_3$) of 2h

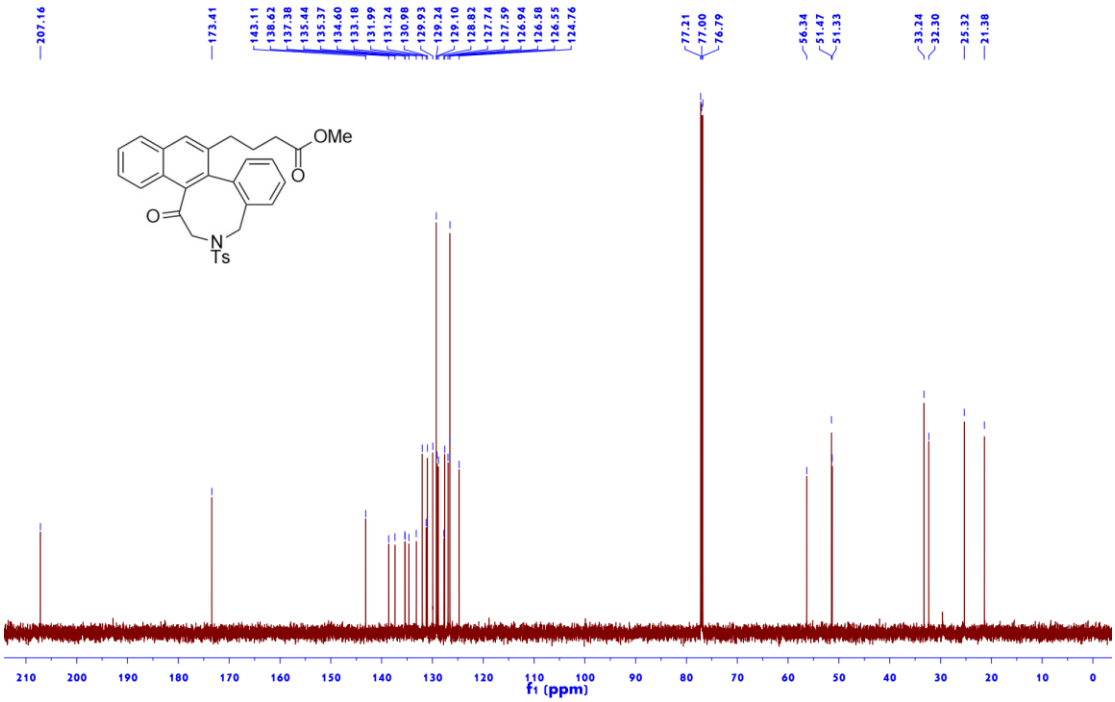


Figure S95 ^{1}H NMR (600 MHz, $CDCl_3$) of 2i

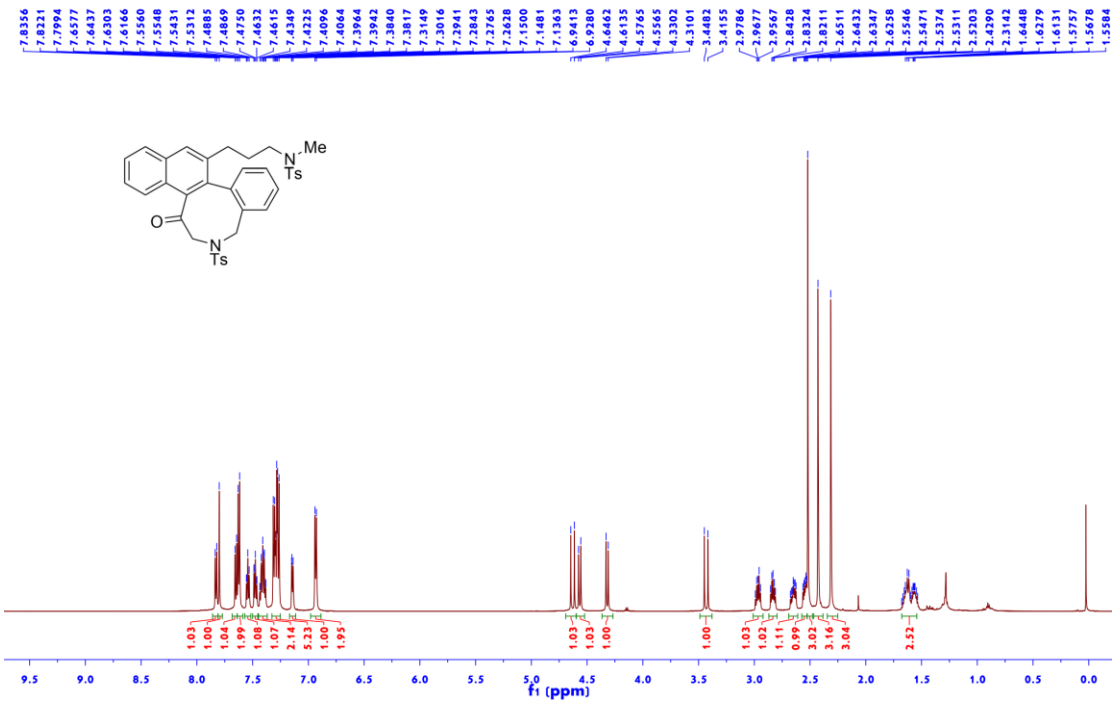


Figure S96 ^{13}C NMR (150 MHz, $CDCl_3$) of 2i

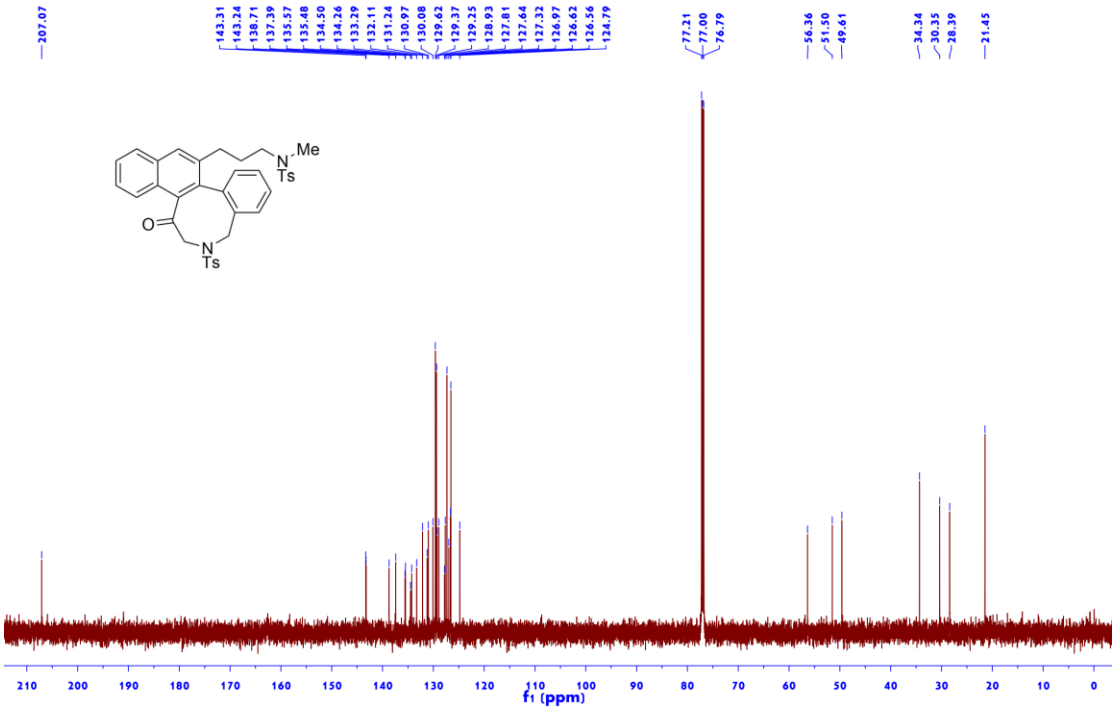


Figure S97 ^{1}H NMR (600 MHz, $CDCl_3$) of 2j

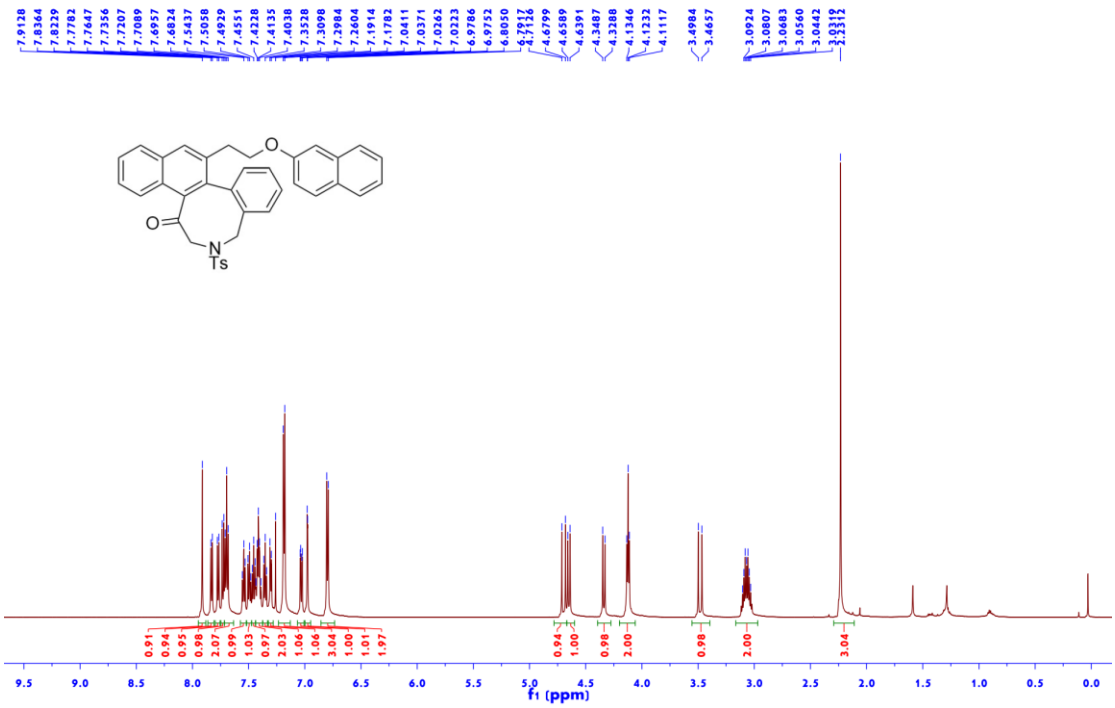


Figure S98 ^{13}C NMR (150 MHz, $CDCl_3$) of 2j

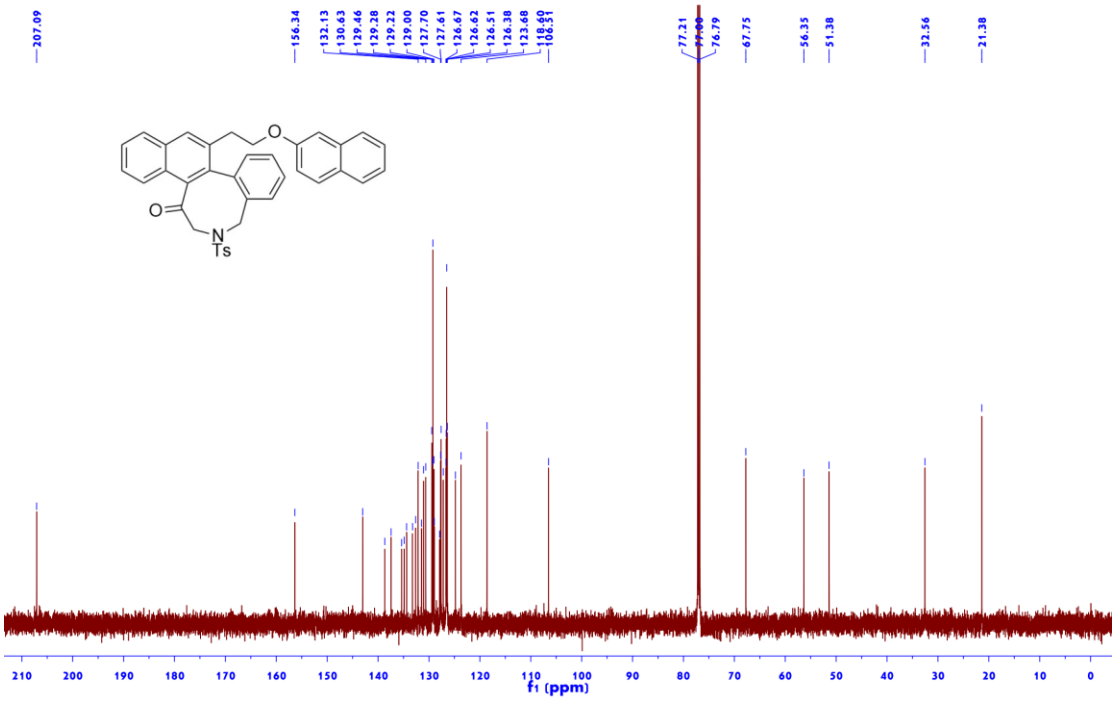


Figure S99 ^{1}H NMR (600 MHz, $CDCl_3$) of 2k

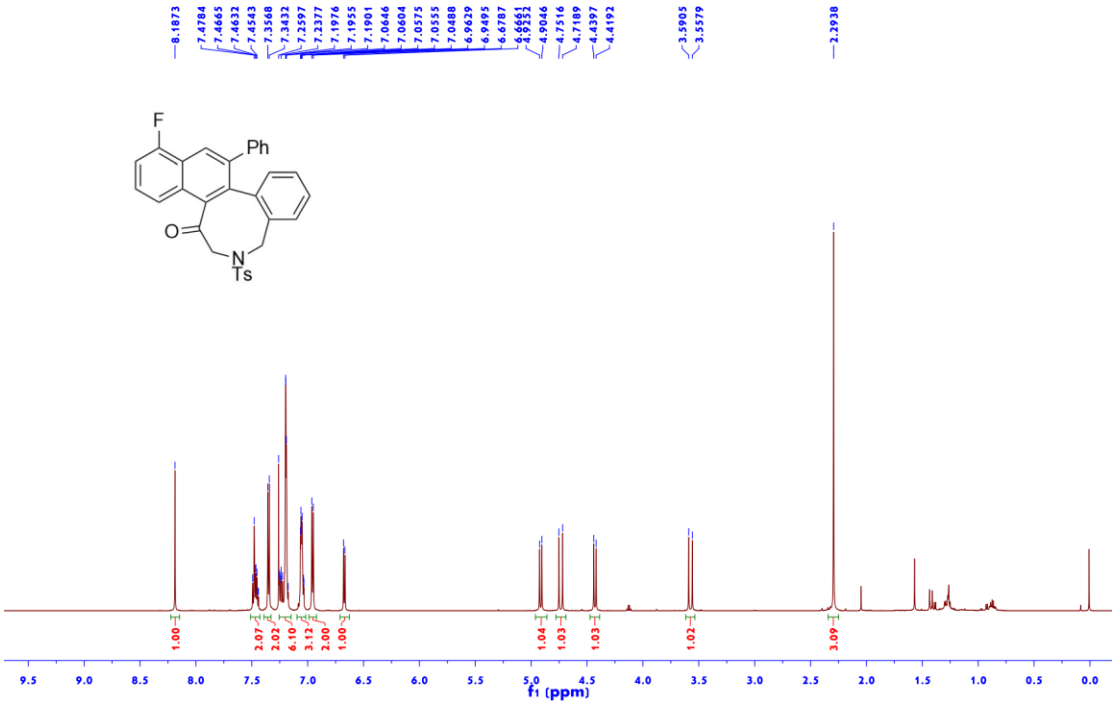


Figure S100 ^{13}C NMR (150 MHz, $CDCl_3$) of 2k

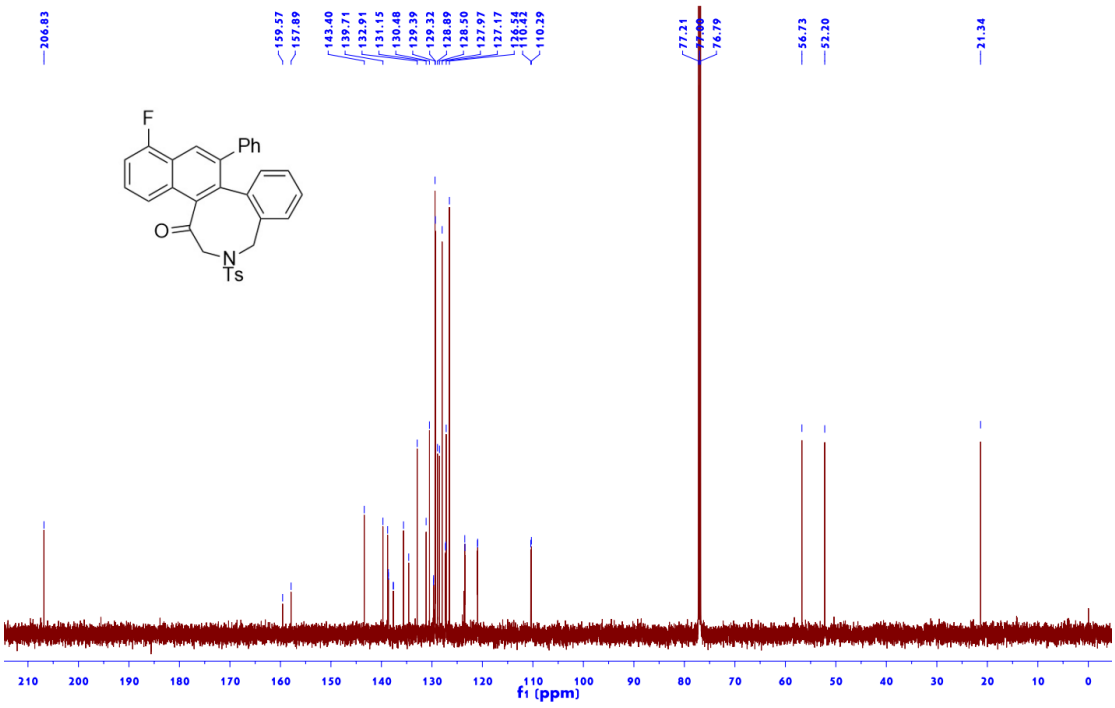


Figure S101 ^{19}F NMR (565 MHz, $CDCl_3$) of 2k

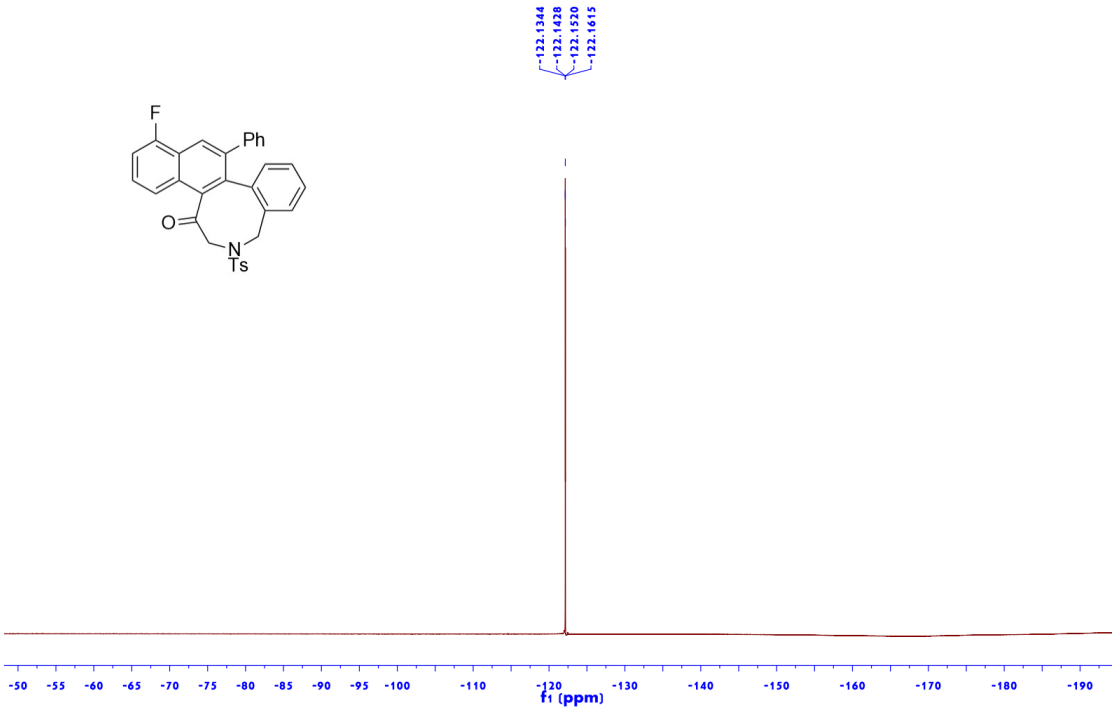


Figure S102 ^{1}H NMR (600 MHz, $CDCl_3$) of 2l

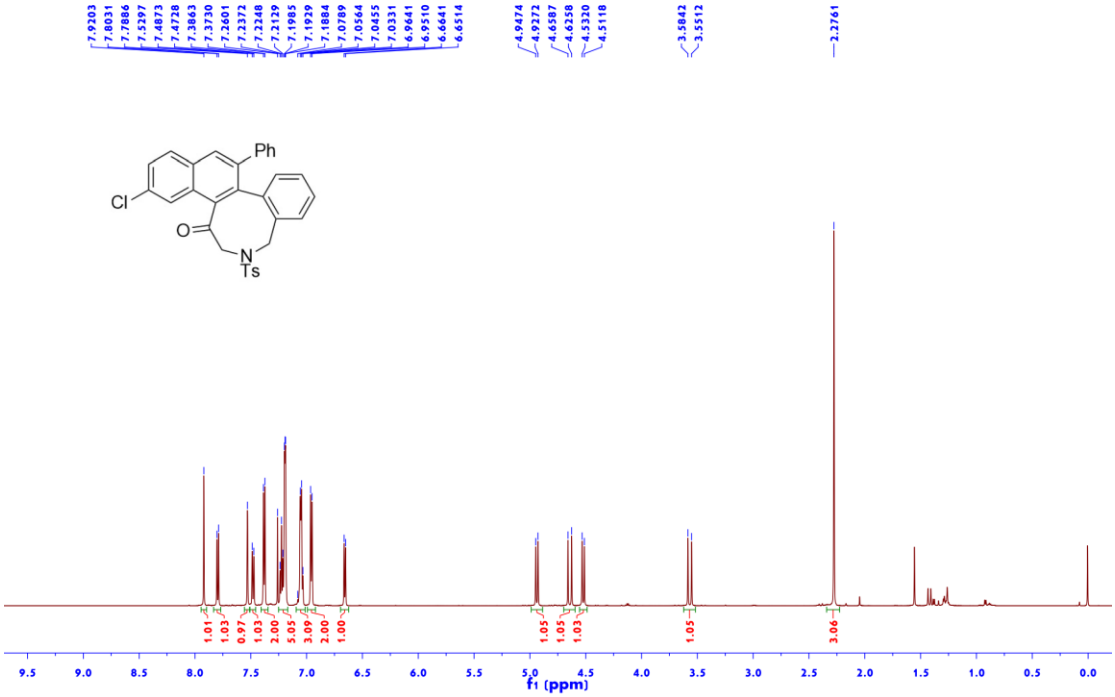


Figure S103 ^{13}C NMR (150 MHz, $CDCl_3$) of 2l

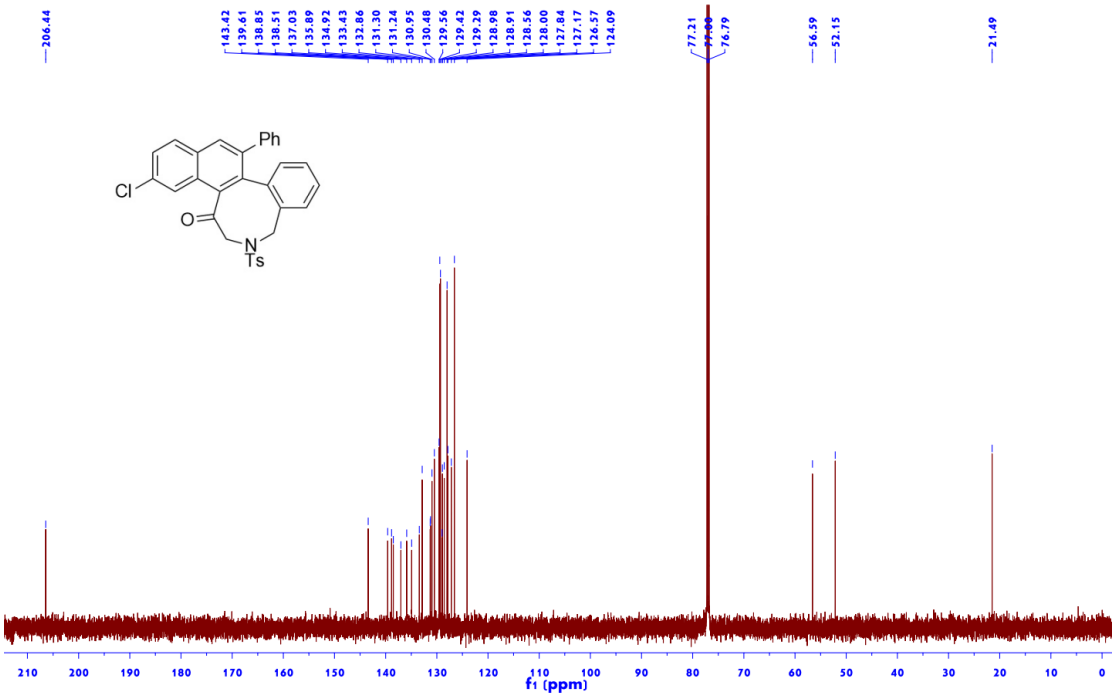


Figure S104 ^{1}H NMR (600 MHz, $CDCl_3$) of 2m

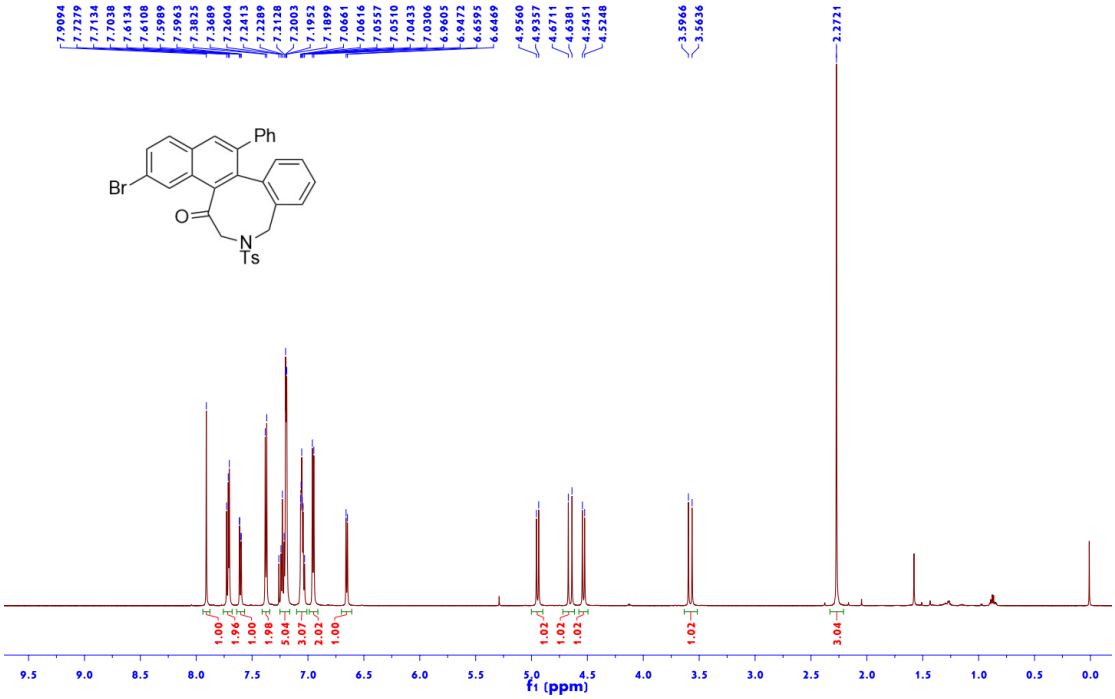


Figure S105 ^{13}C NMR (150 MHz, $CDCl_3$) of 2m

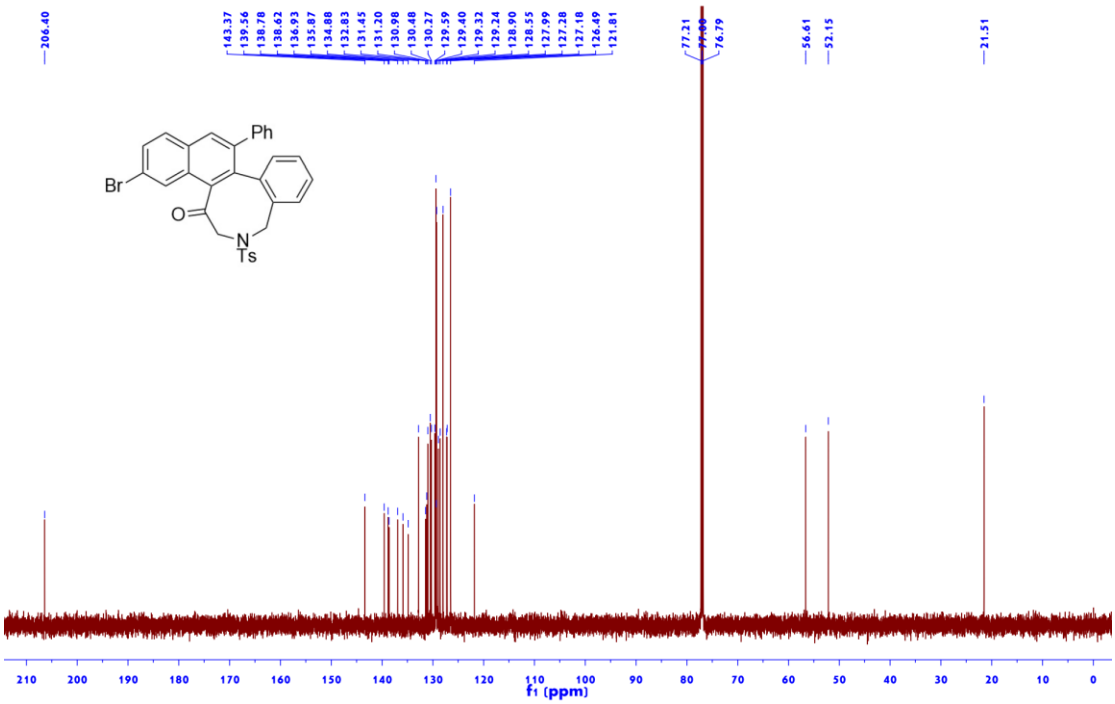


Figure S106 ^{1}H NMR (600 MHz, $CDCl_3$) of 2n

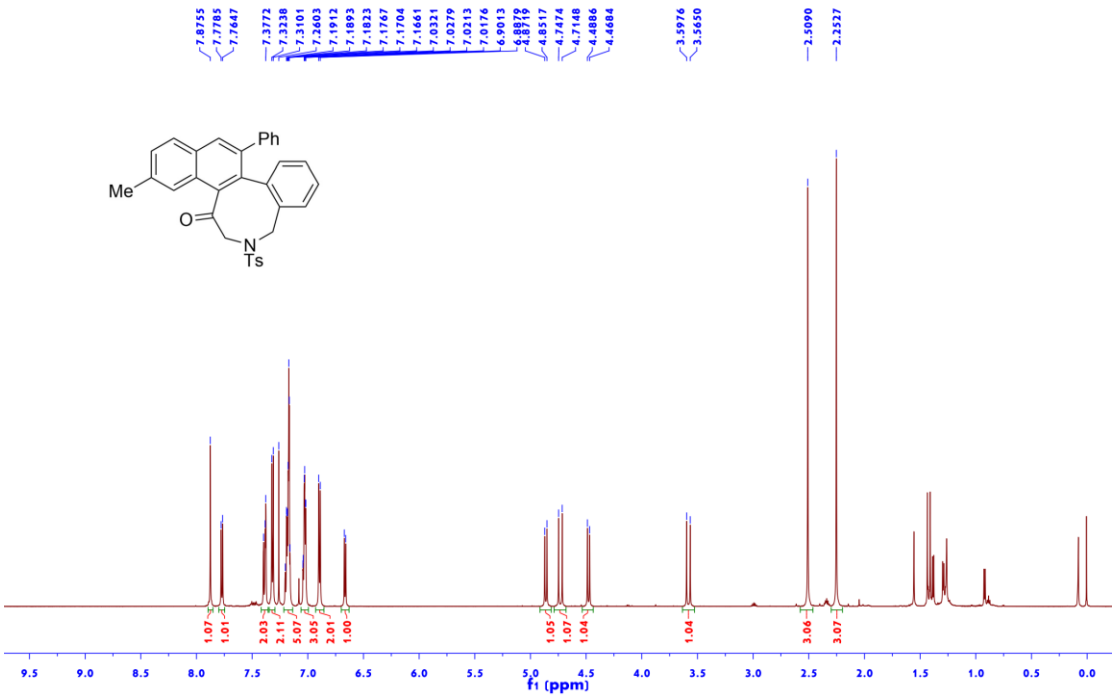


Figure S107 ^{13}C NMR (150 MHz, $CDCl_3$) of 2n

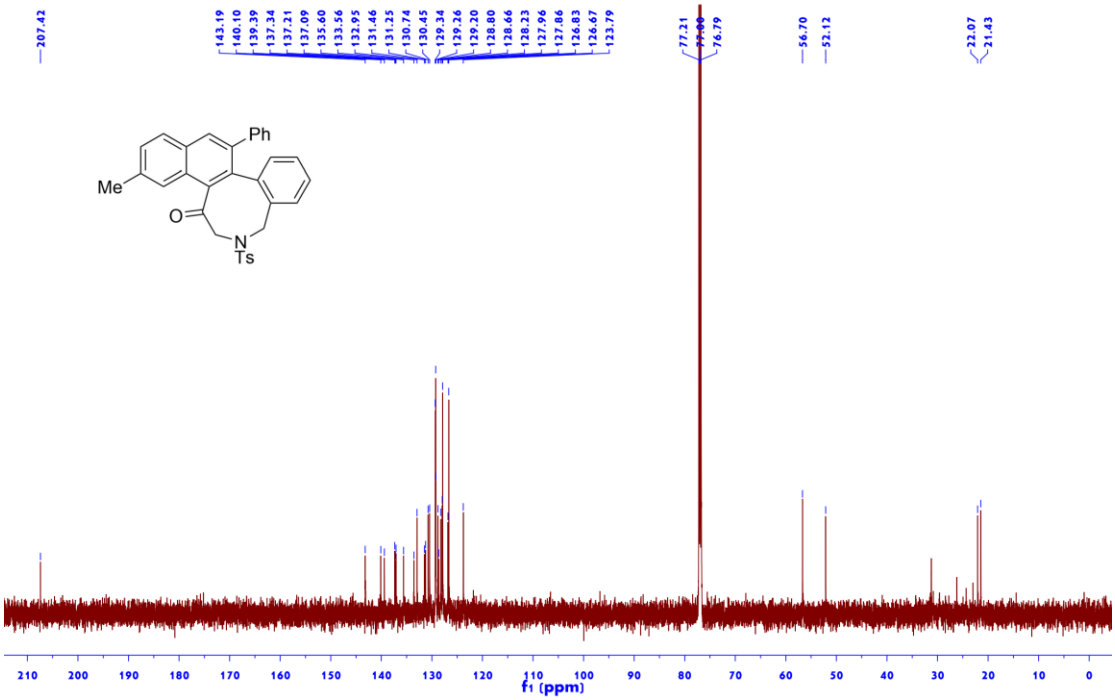


Figure S108 ^{1}H NMR (600 MHz, $CDCl_3$) of 2o

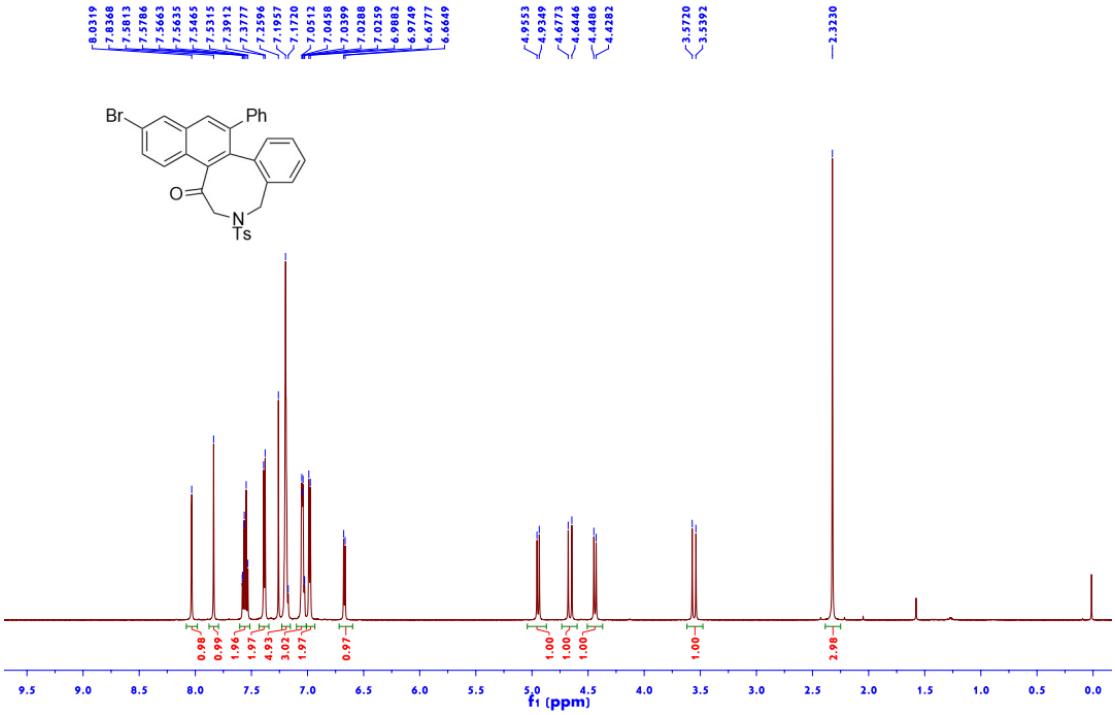


Figure S109 ^{13}C NMR (150 MHz, $CDCl_3$) of 2o

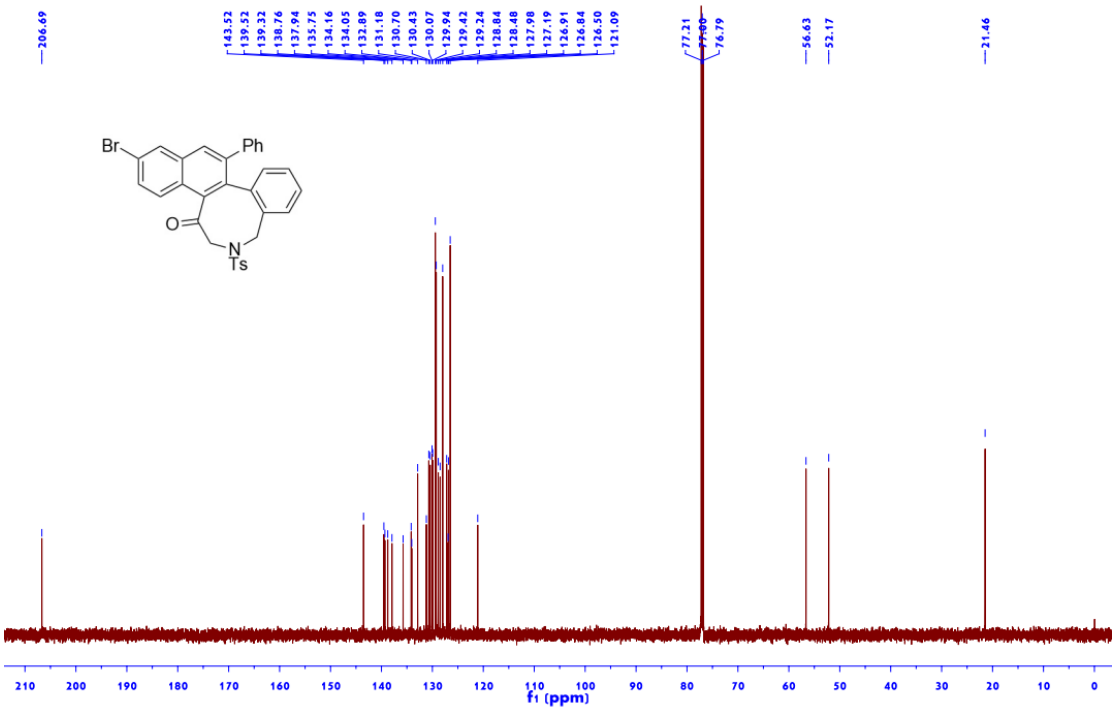


Figure S110 ^{1}H NMR (400 MHz, $CDCl_3$) of 2p

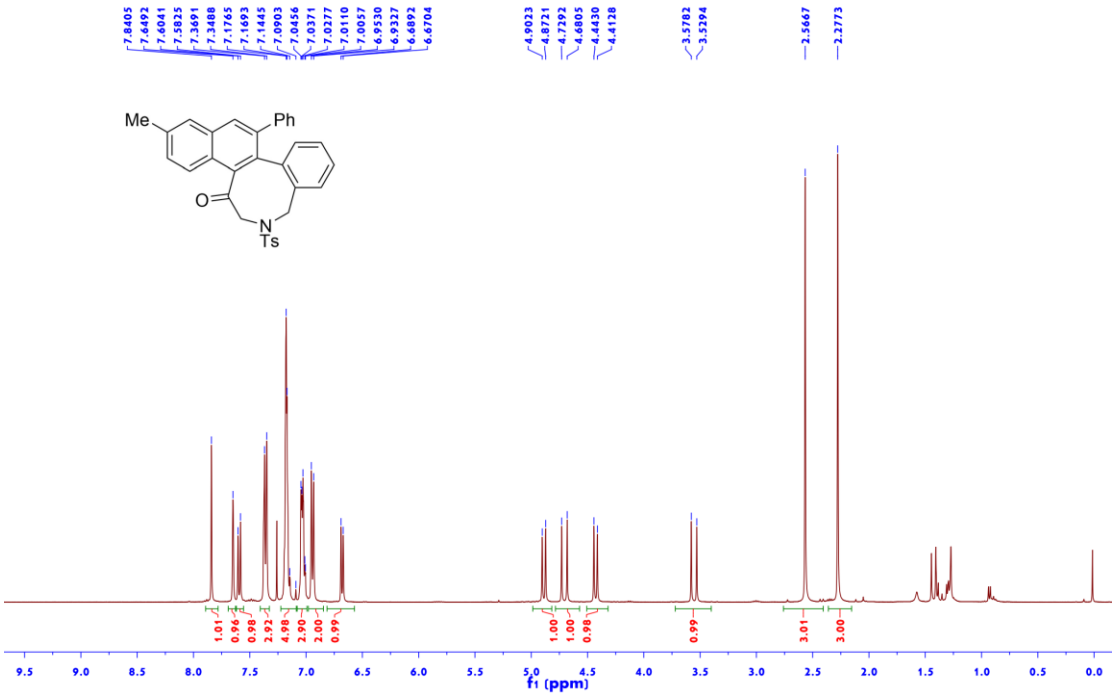


Figure S111 ^{13}C NMR (100 MHz, $CDCl_3$) of 2p

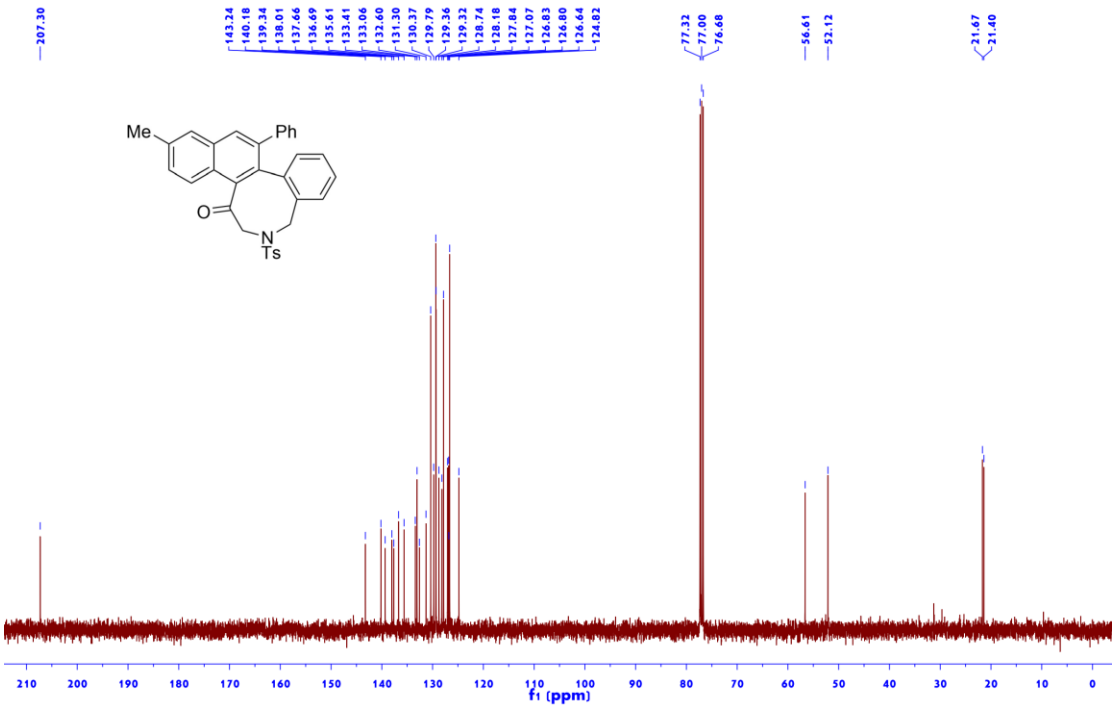


Figure S112 ^{1}H NMR (600 MHz, $CDCl_3$) of 2q

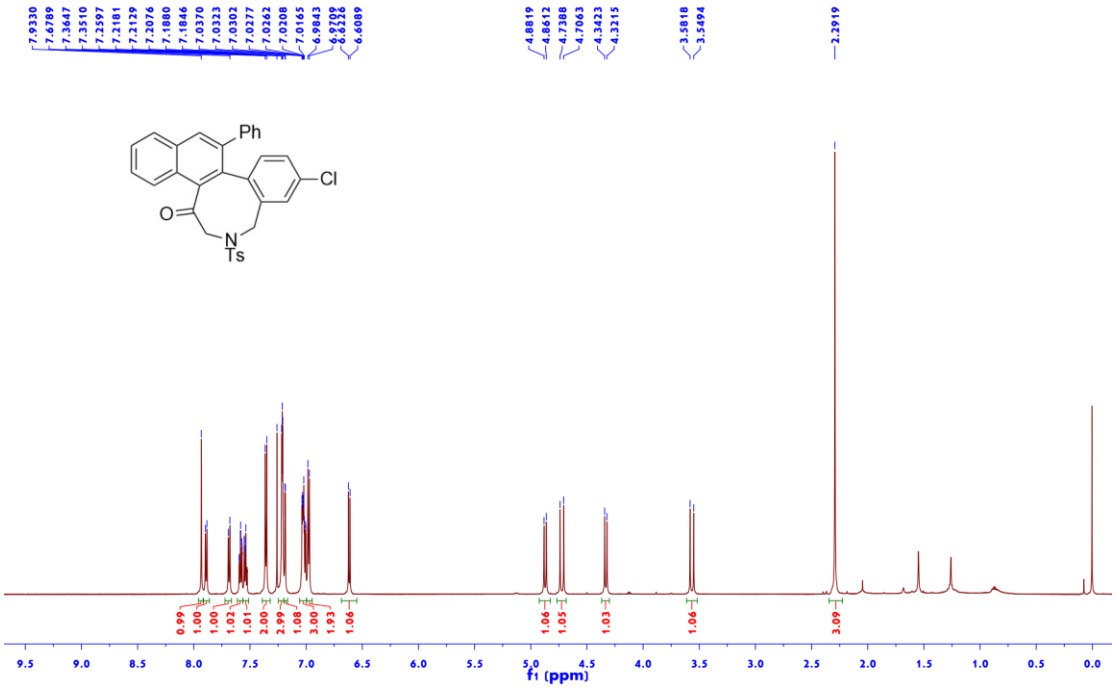


Figure S113 ^{13}C NMR (150 MHz, $CDCl_3$) of 2q

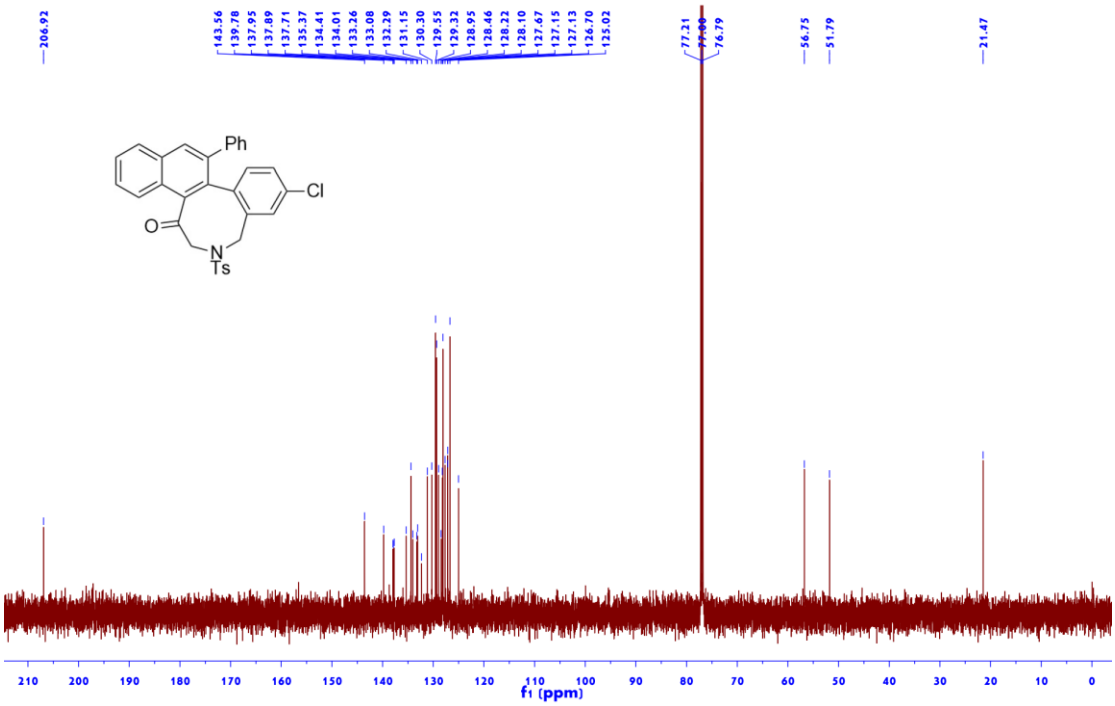


Figure S114 ^{1}H NMR (600 MHz, $CDCl_3$) of 2r

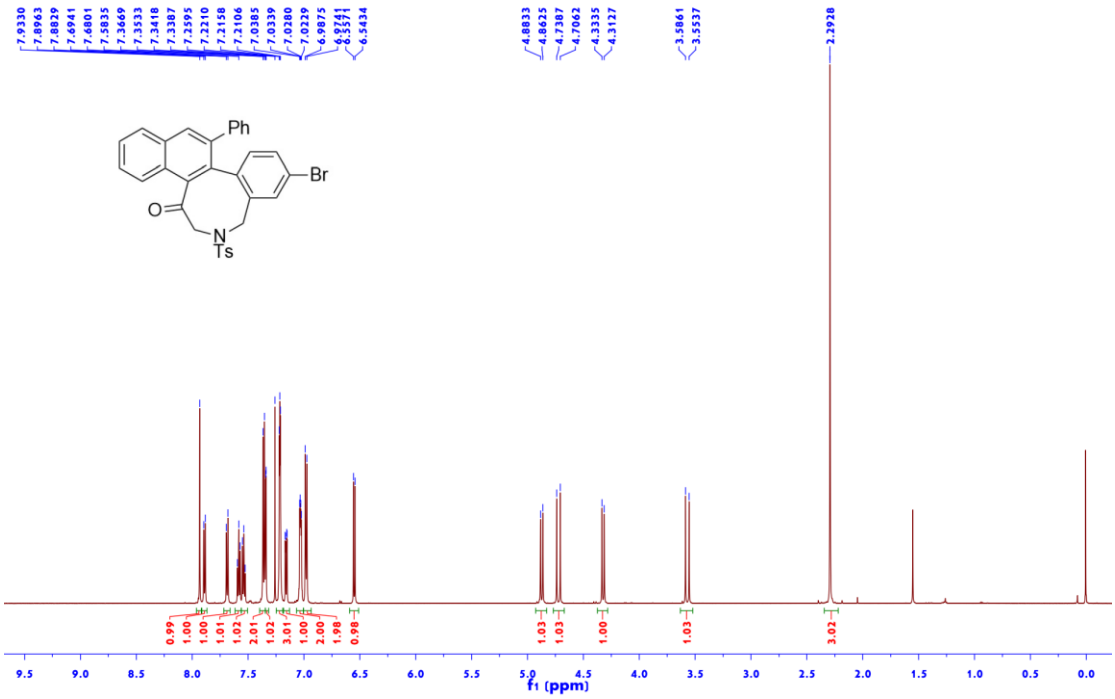


Figure S115 ^{13}C NMR (150 MHz, $CDCl_3$) of 2r

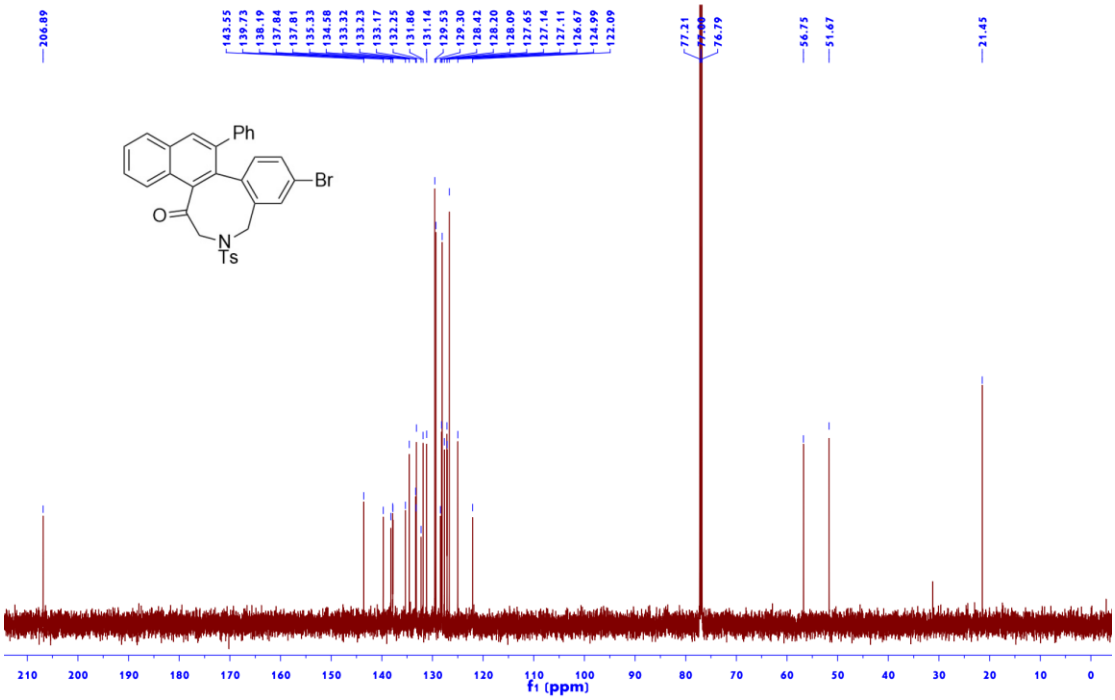


Figure S116 ^{1}H NMR (400 MHz, $CDCl_3$) of 2s

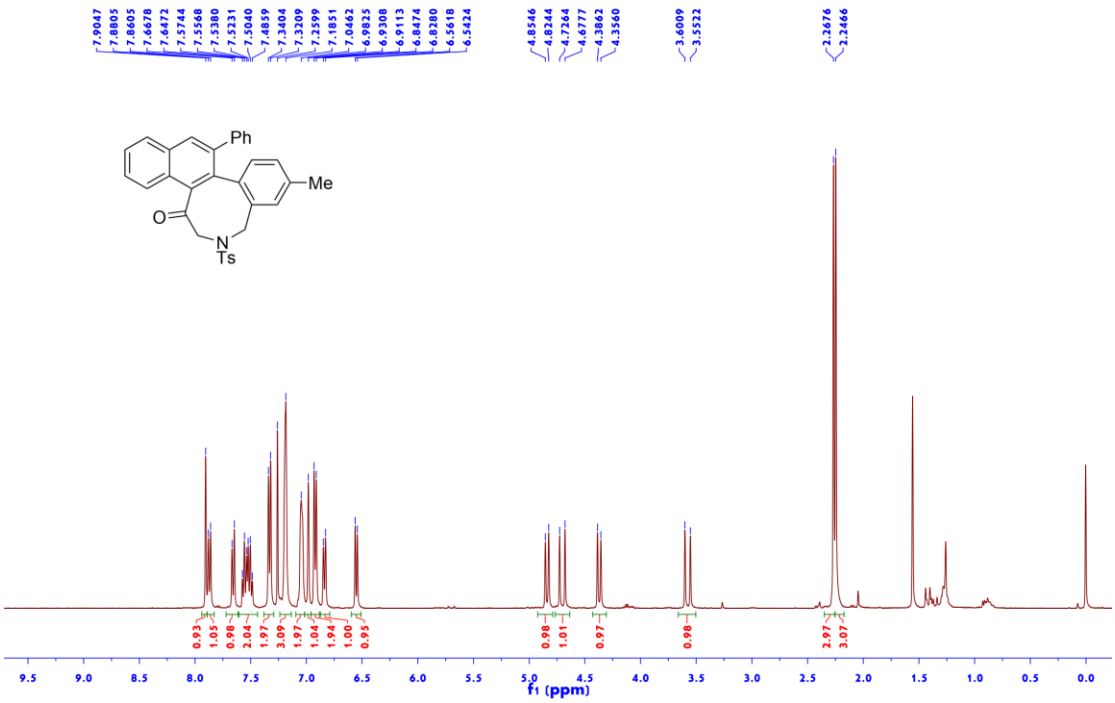


Figure S117 ^{13}C NMR (150 MHz, $CDCl_3$) of 2s

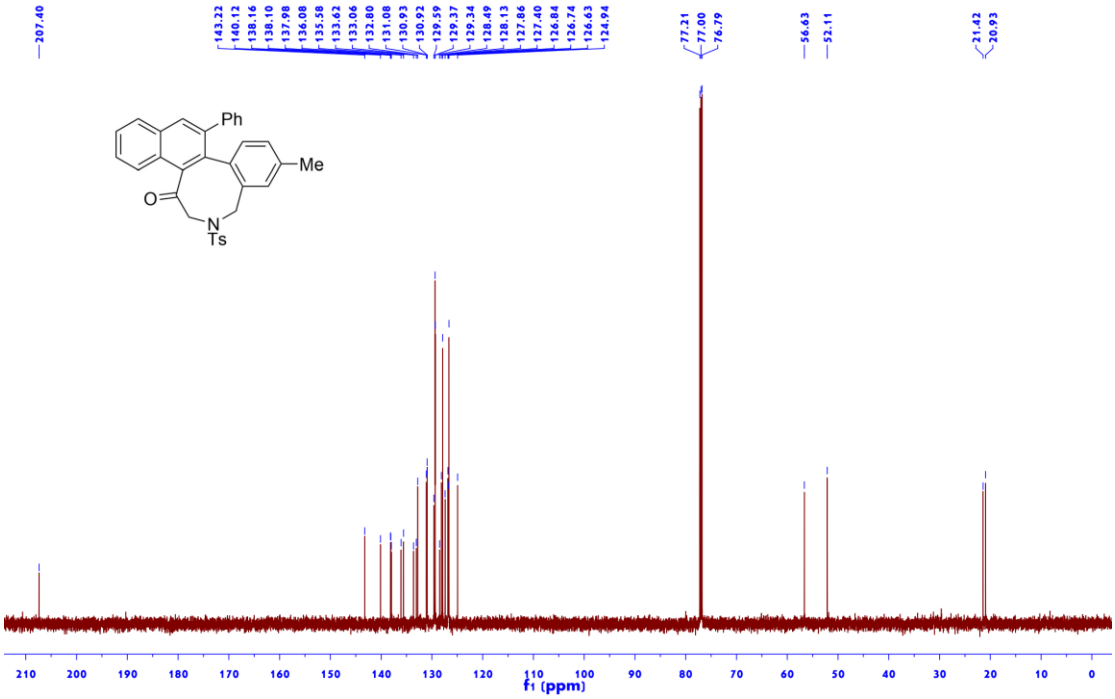


Figure S118 ^{1}H NMR (600 MHz, $CDCl_3$) of 2t

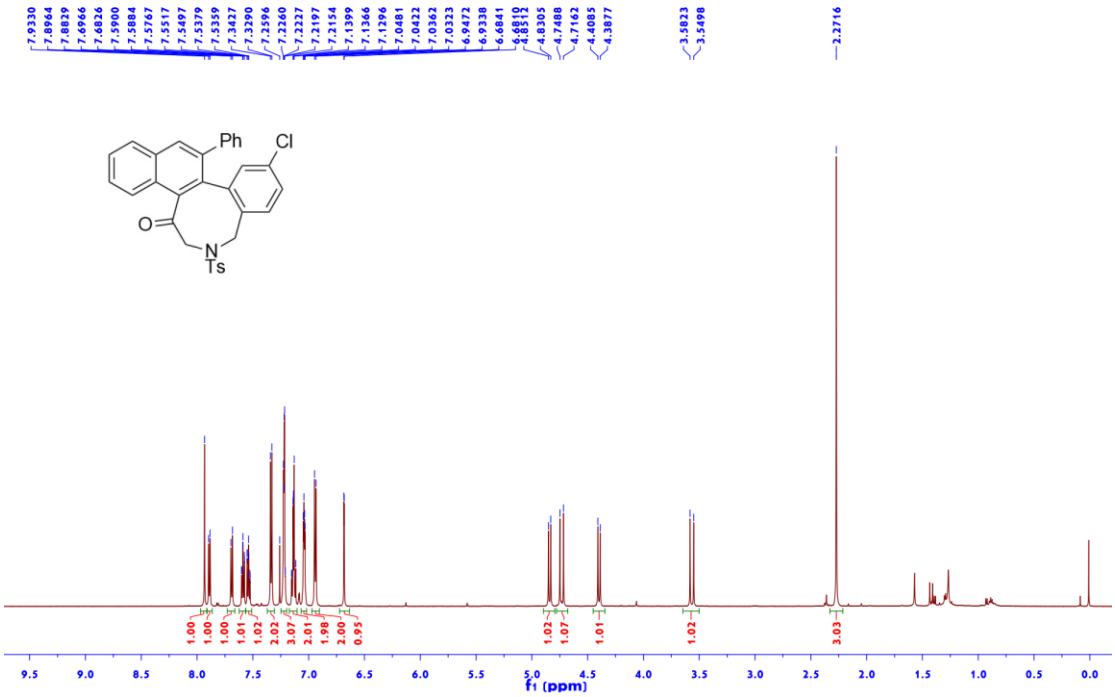


Figure S119 ^{13}C NMR (150 MHz, $CDCl_3$) of 2t

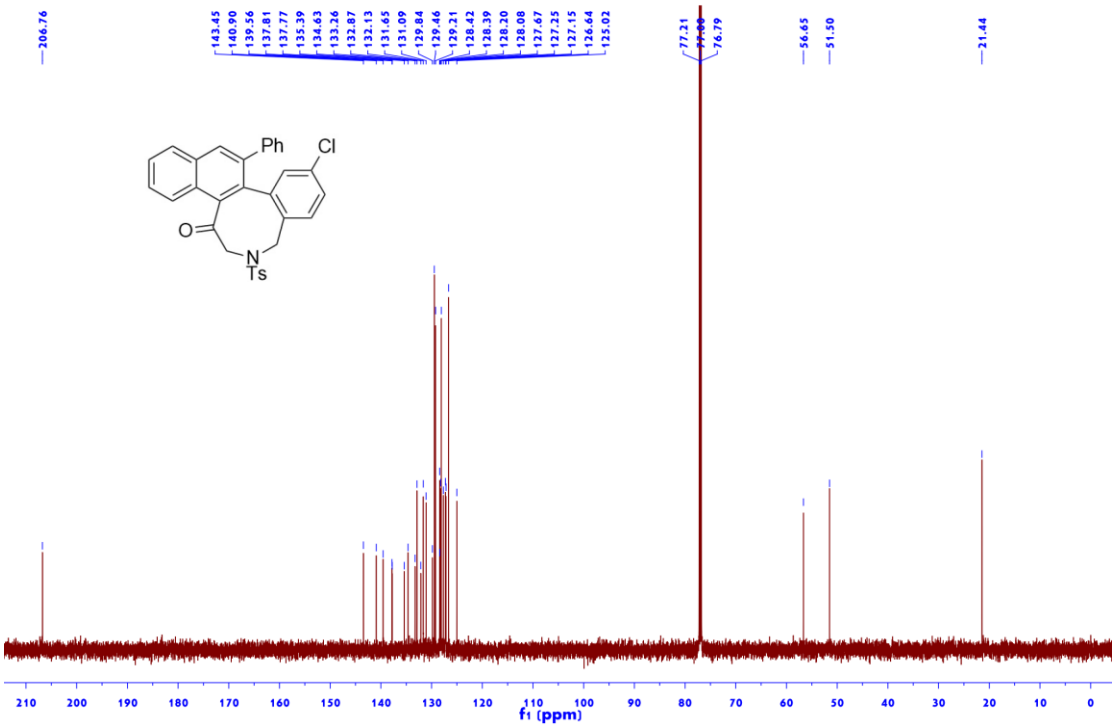


Figure S120 ^{1}H NMR (600 MHz, $CDCl_3$) of 2u

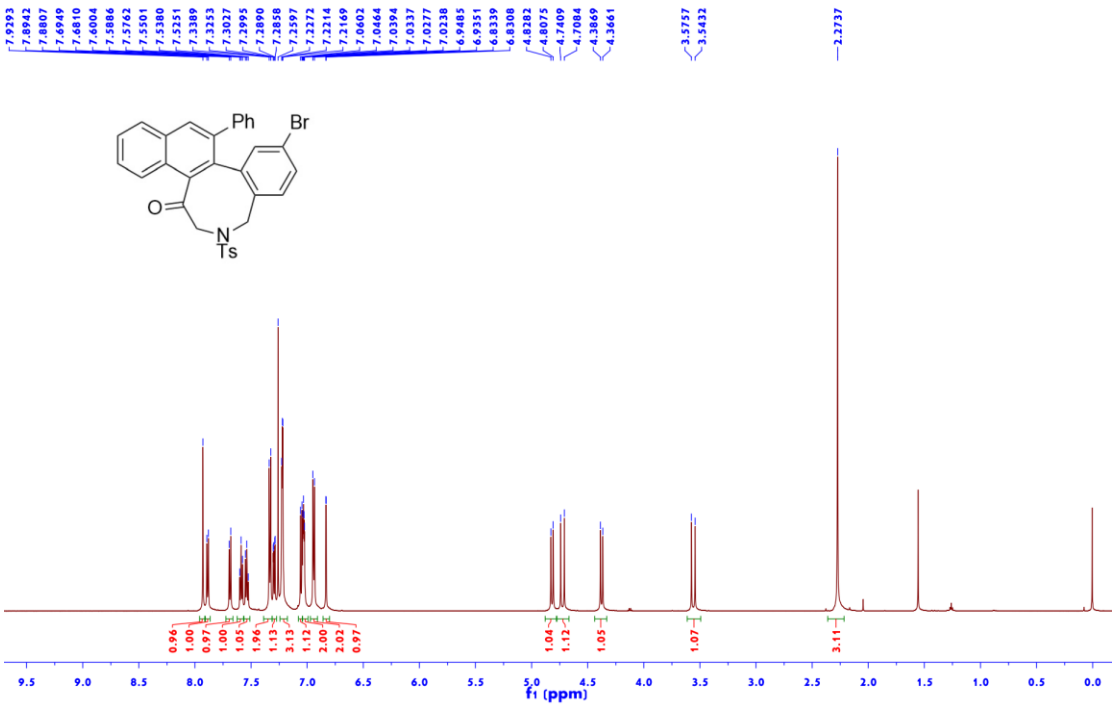


Figure S121 ^{13}C NMR (150 MHz, $CDCl_3$) of 2u

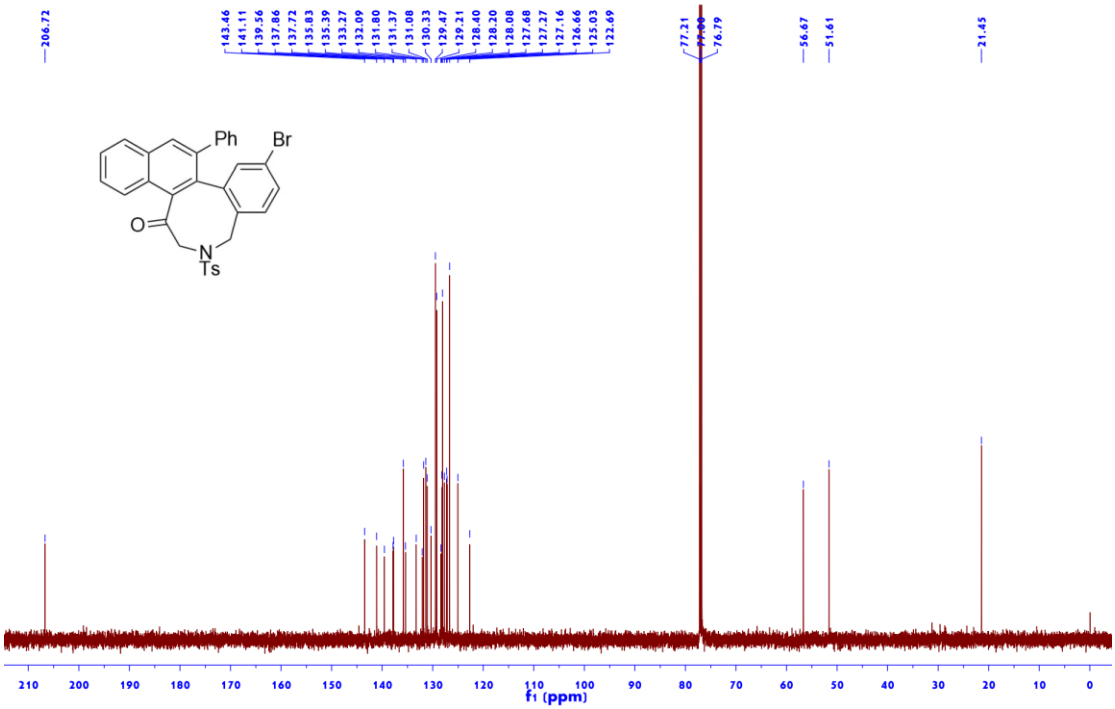


Figure S122 ^{1}H NMR (600 MHz, $CDCl_3$) of 2v

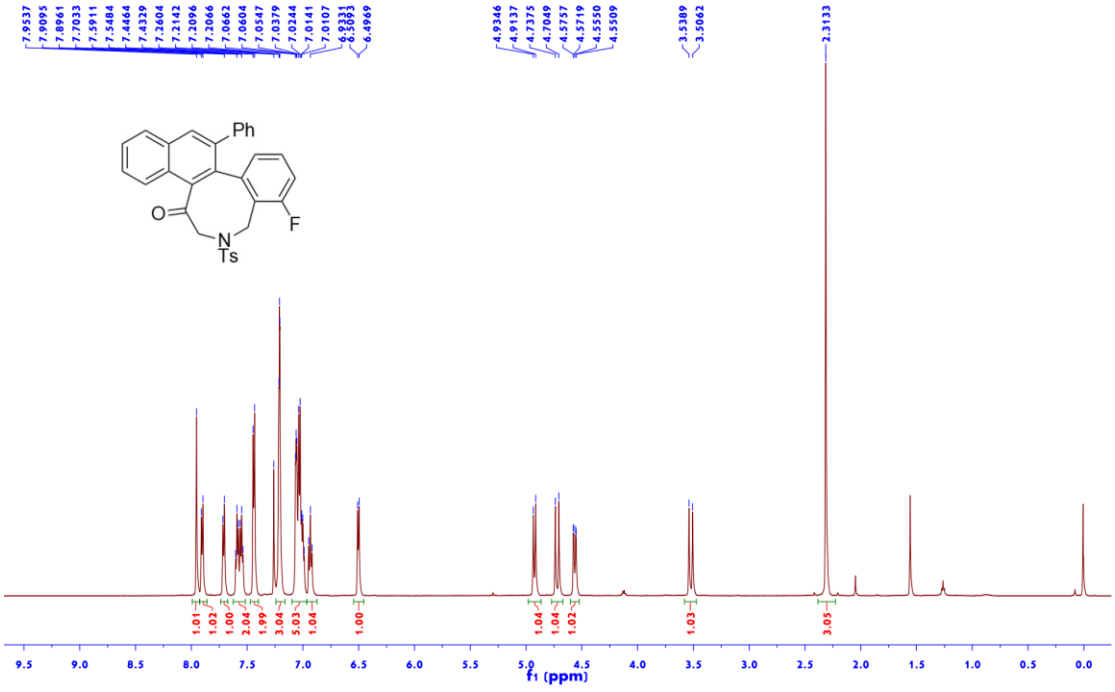


Figure S123 ^{13}C NMR (150 MHz, $CDCl_3$) of 2v

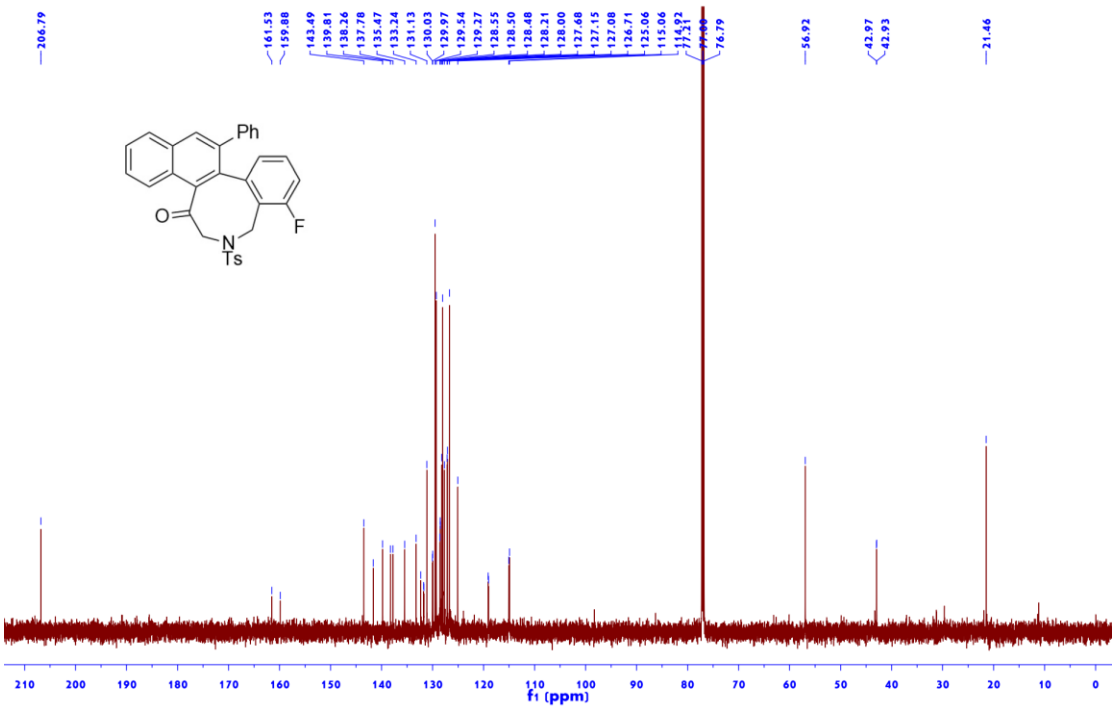


Figure S124 ^{19}F NMR (565 MHz, $CDCl_3$) of 2v

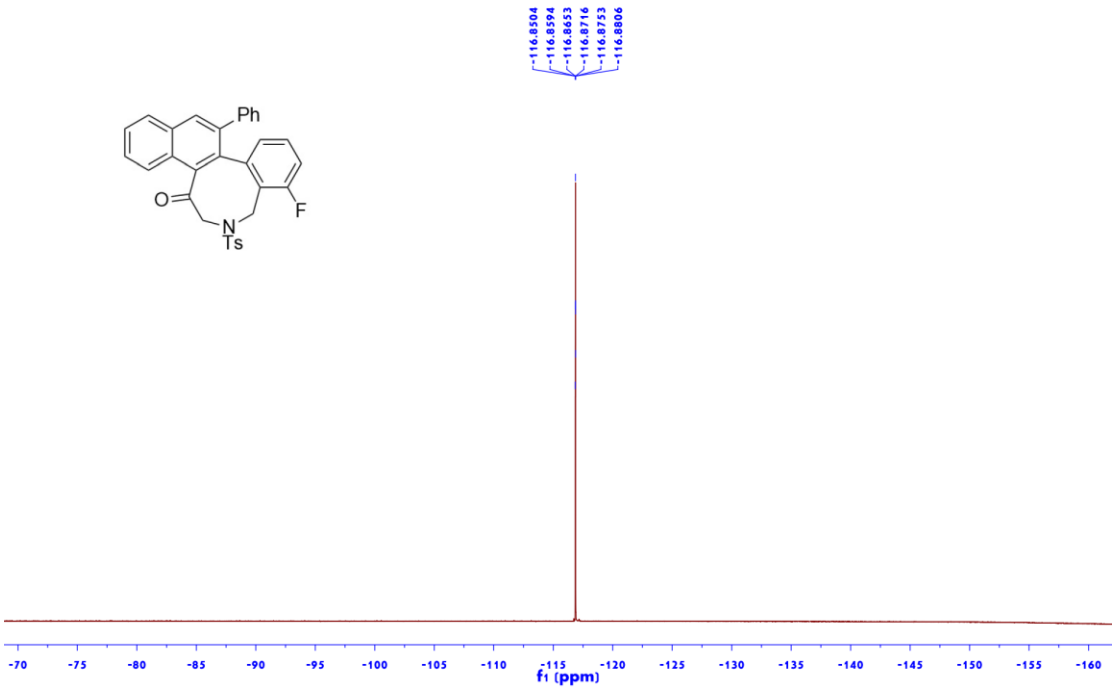


Figure S125 ^{1}H NMR (600 MHz, $CDCl_3$) of 2w

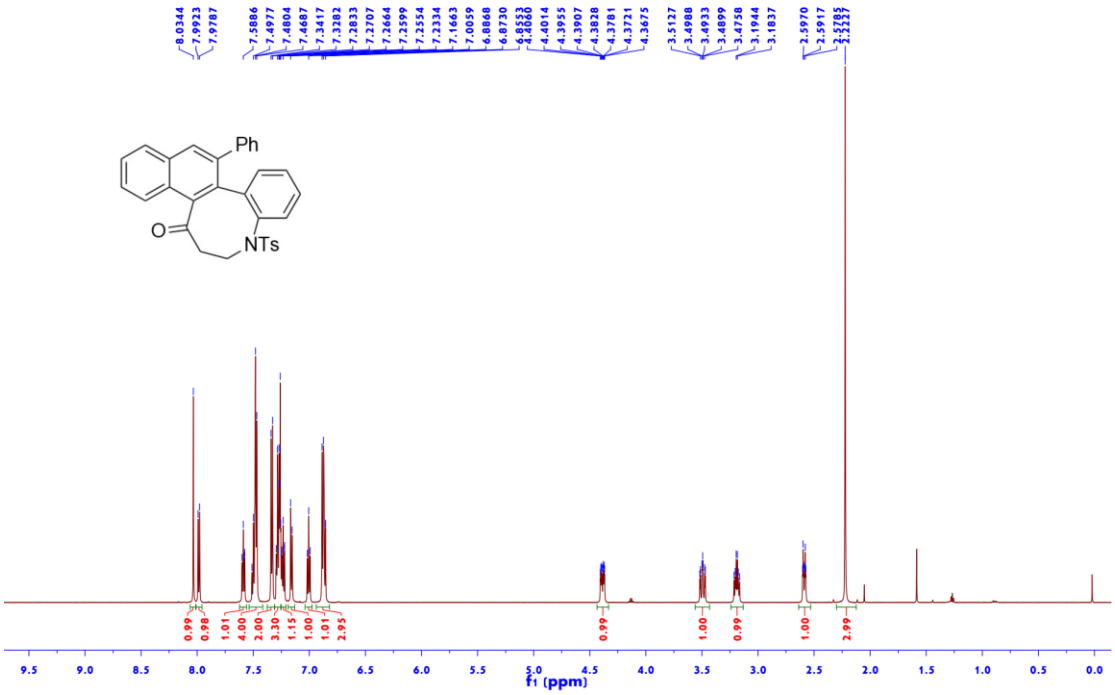


Figure S126 ^{13}C NMR (150 MHz, $CDCl_3$) of 2w

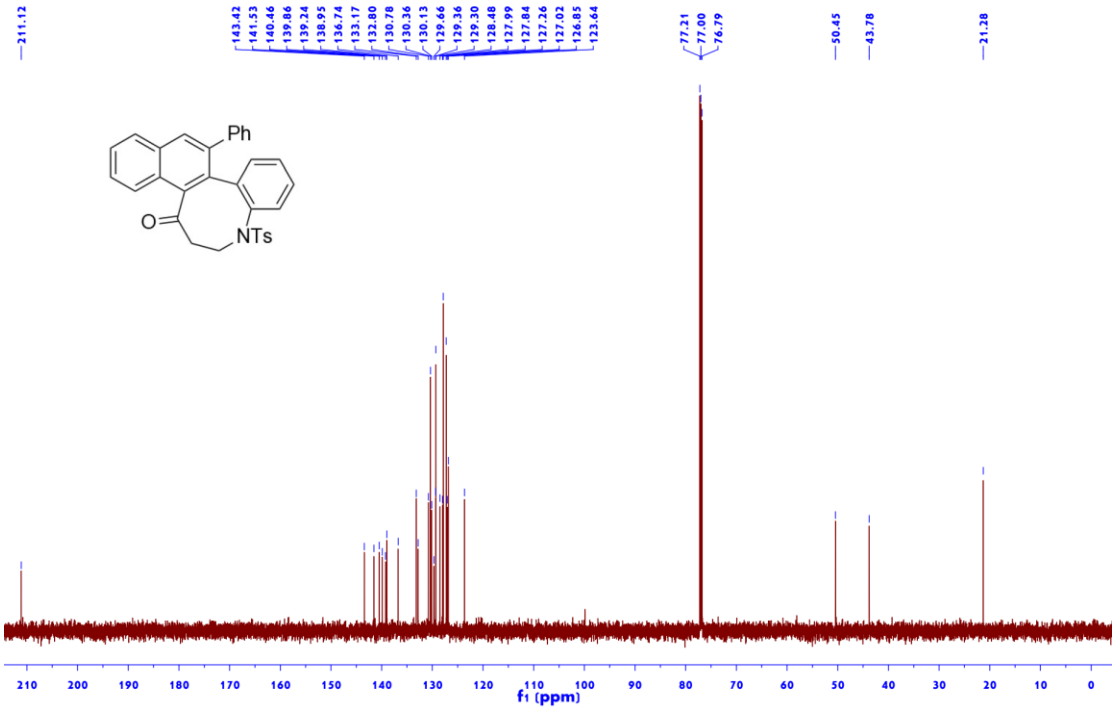


Figure S127 ^{1}H NMR (600 MHz, $CDCl_3$) of 2x

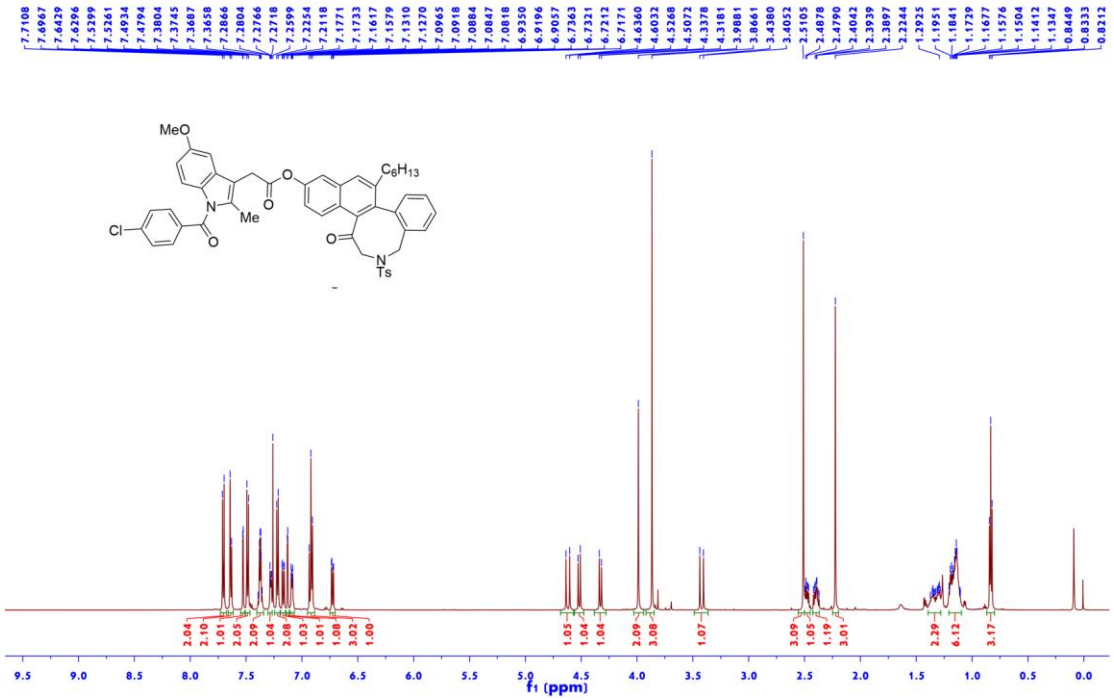


Figure S128 ^{13}C NMR (150 MHz, $CDCl_3$) of 2x

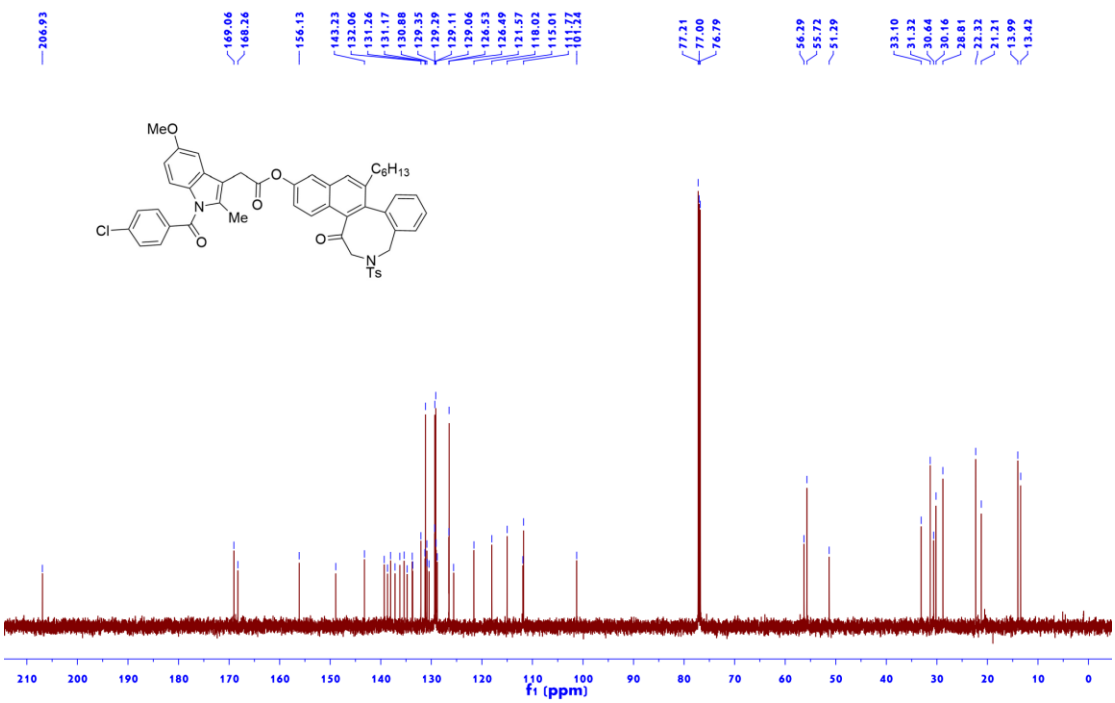


Figure S129 ^{1}H NMR (600 MHz, $CDCl_3$) of 2y

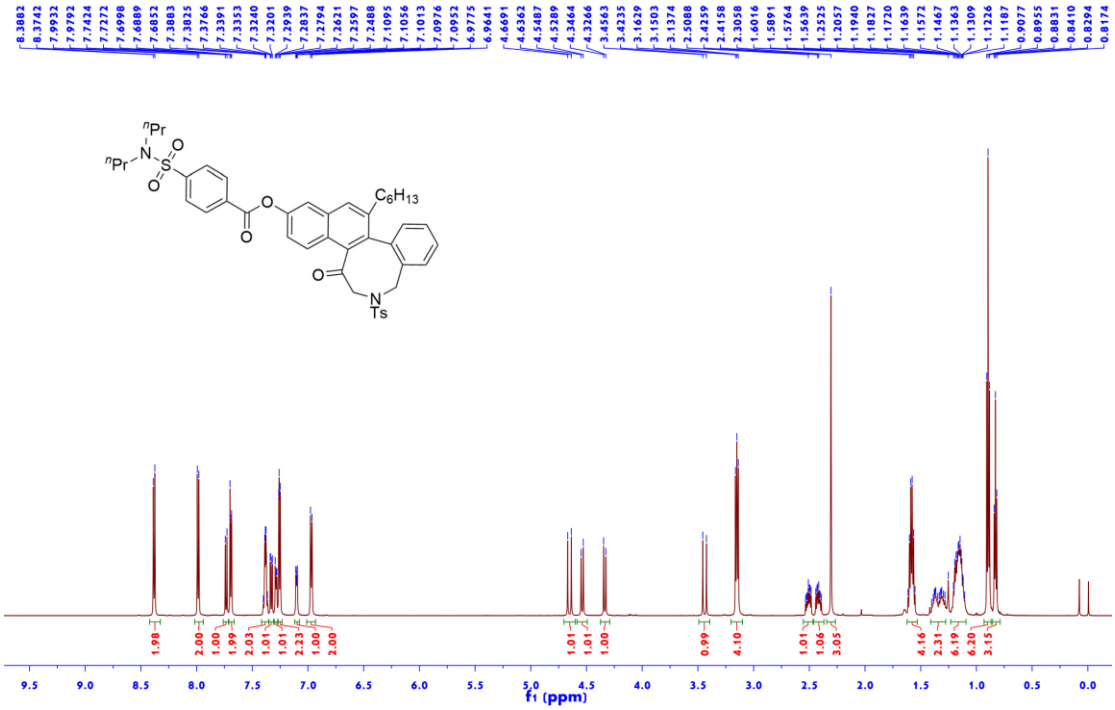


Figure S130 ^{13}C NMR (150 MHz, $CDCl_3$) of 2y

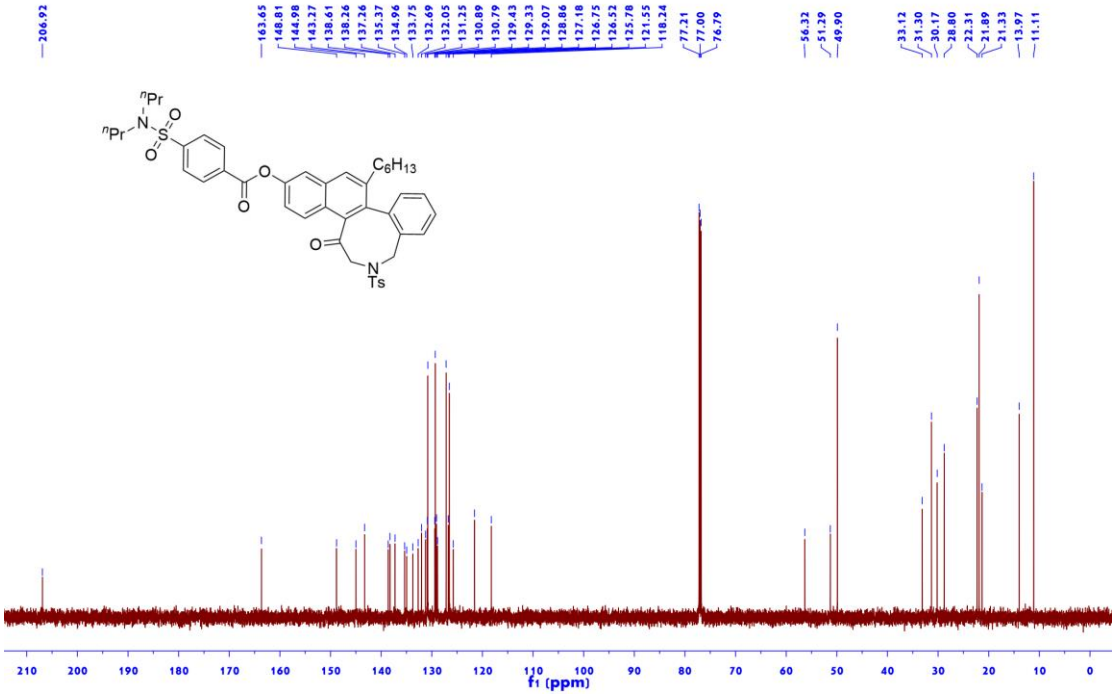


Figure S131 ^{1}H NMR (600 MHz, $CDCl_3$) of 2z

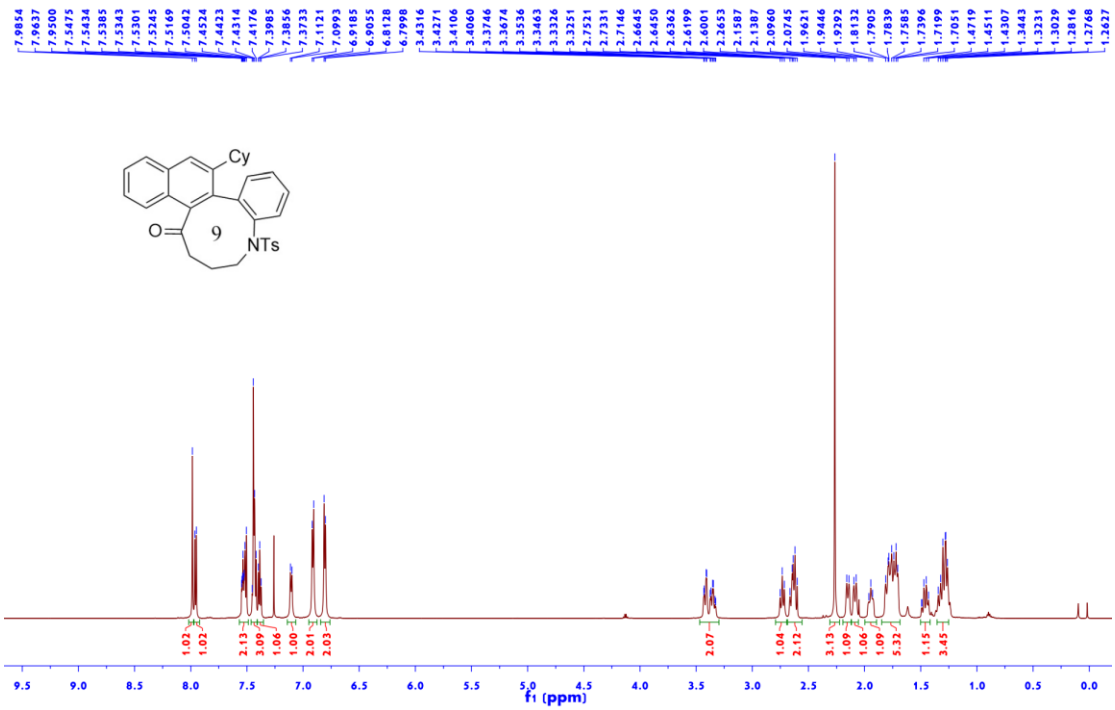


Figure S132 ^{13}C NMR (150 MHz, $CDCl_3$) of 2z

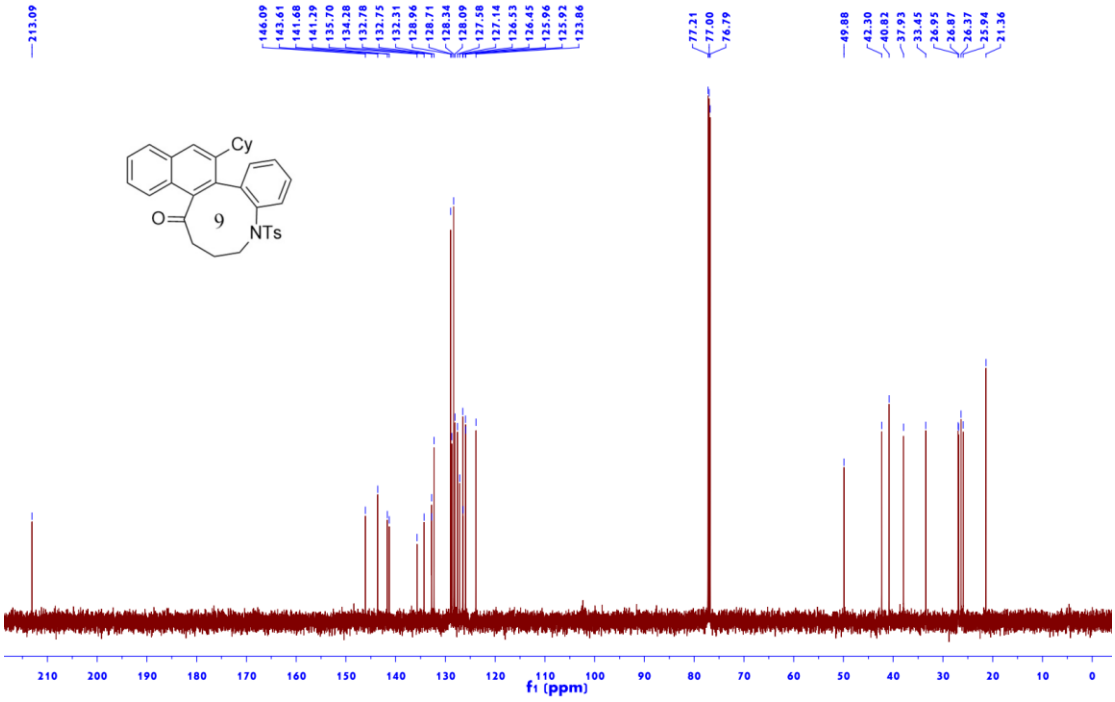


Figure S133 ^{1}H NMR (600 MHz, $CDCl_3$) of 2aa

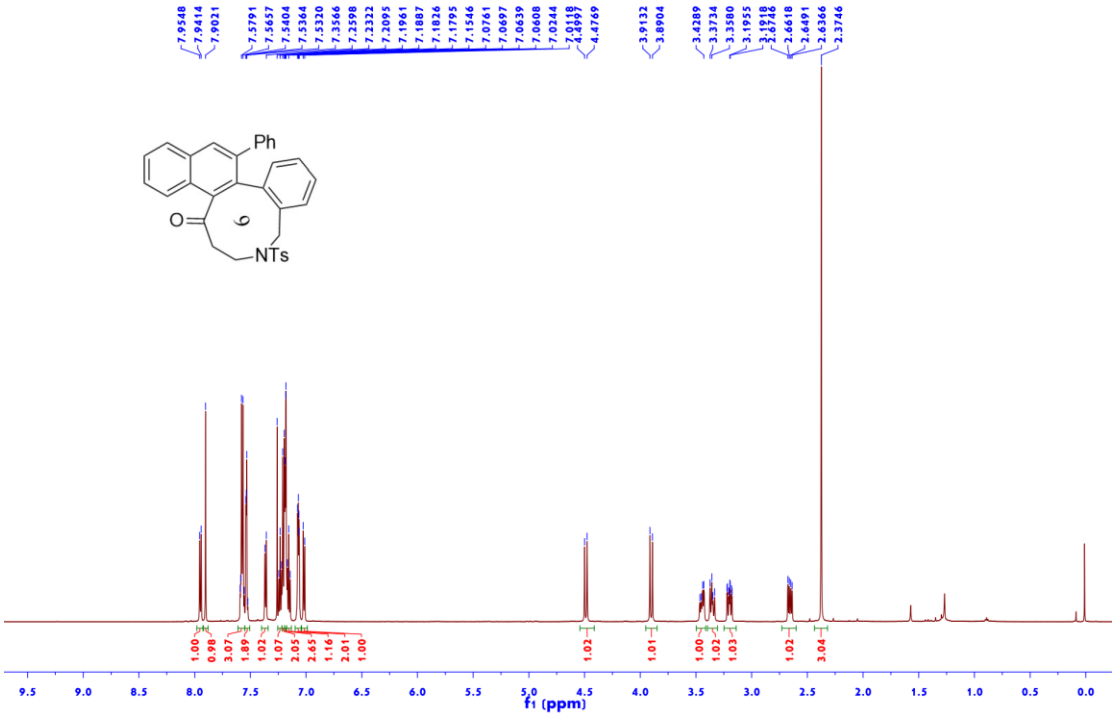


Figure S134 ^{13}C NMR (150 MHz, $CDCl_3$) of 2aa

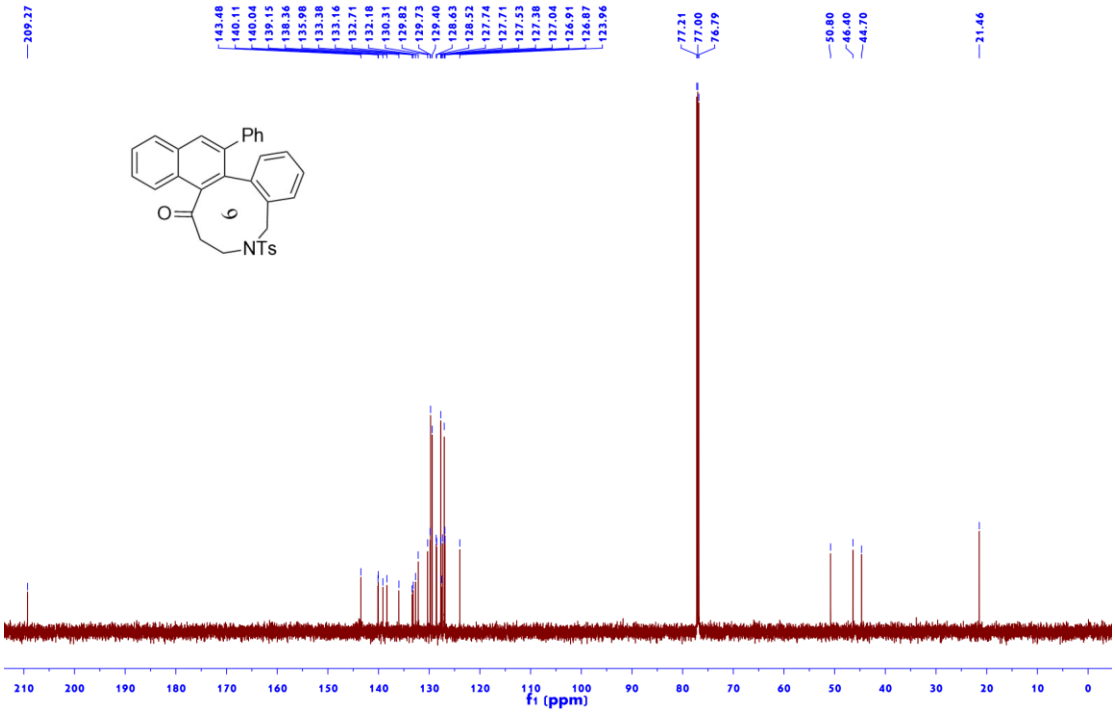


Figure S135 ^{1}H NMR (600 MHz, $CDCl_3$) of 2ab

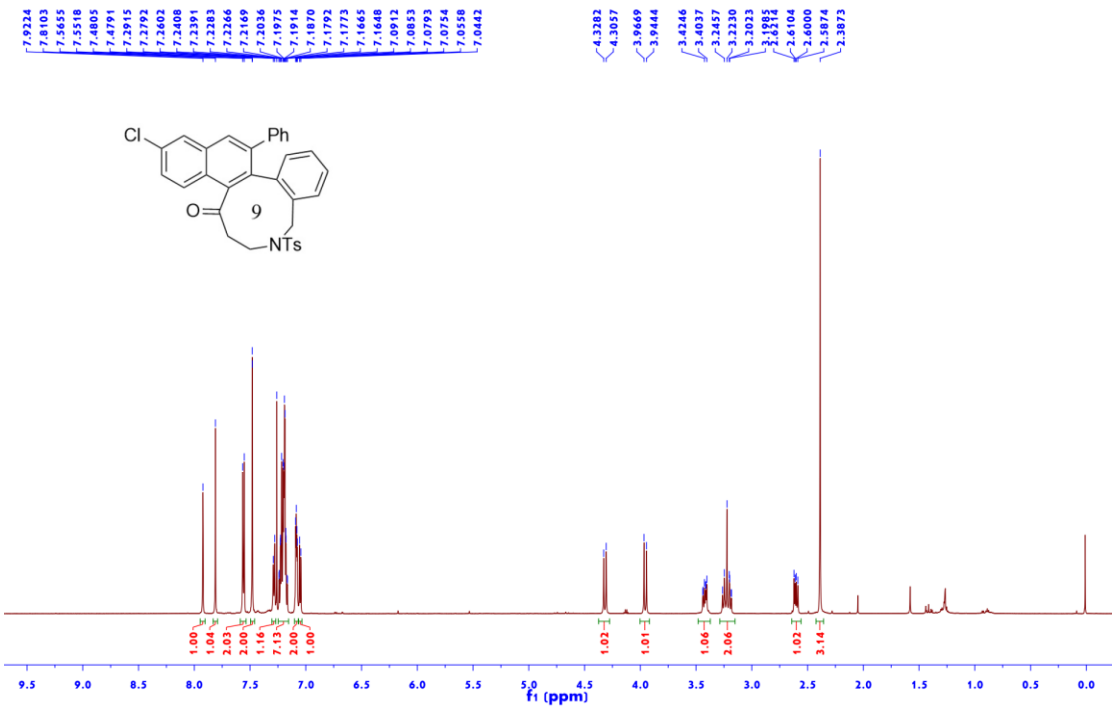


Figure S136 ^{13}C NMR (150 MHz, $CDCl_3$) of 2ab

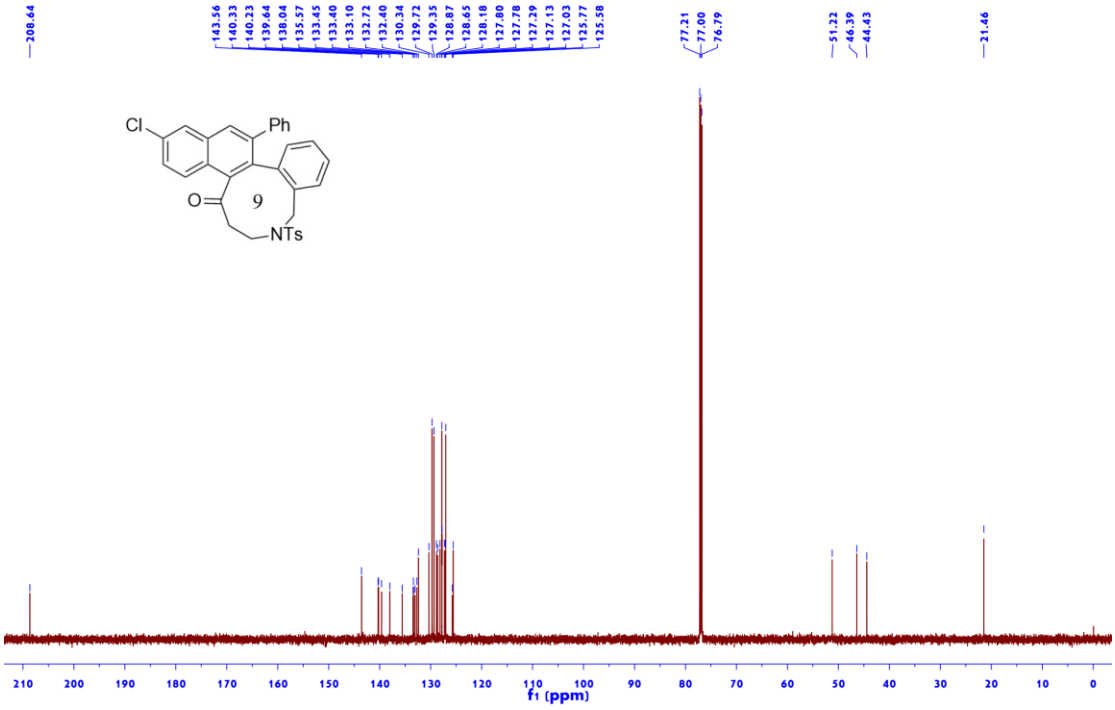


Figure S137 ^{1}H NMR (600 MHz, $CDCl_3$) of 2ac

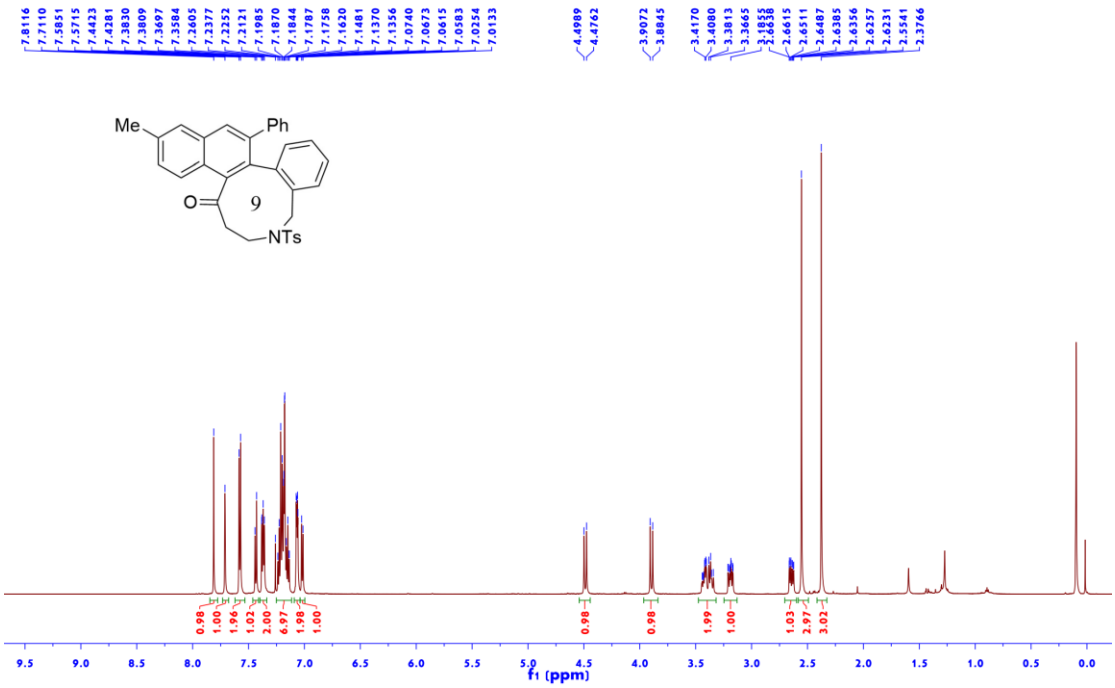


Figure S138 ^{13}C NMR (150 MHz, $CDCl_3$) of 2ac

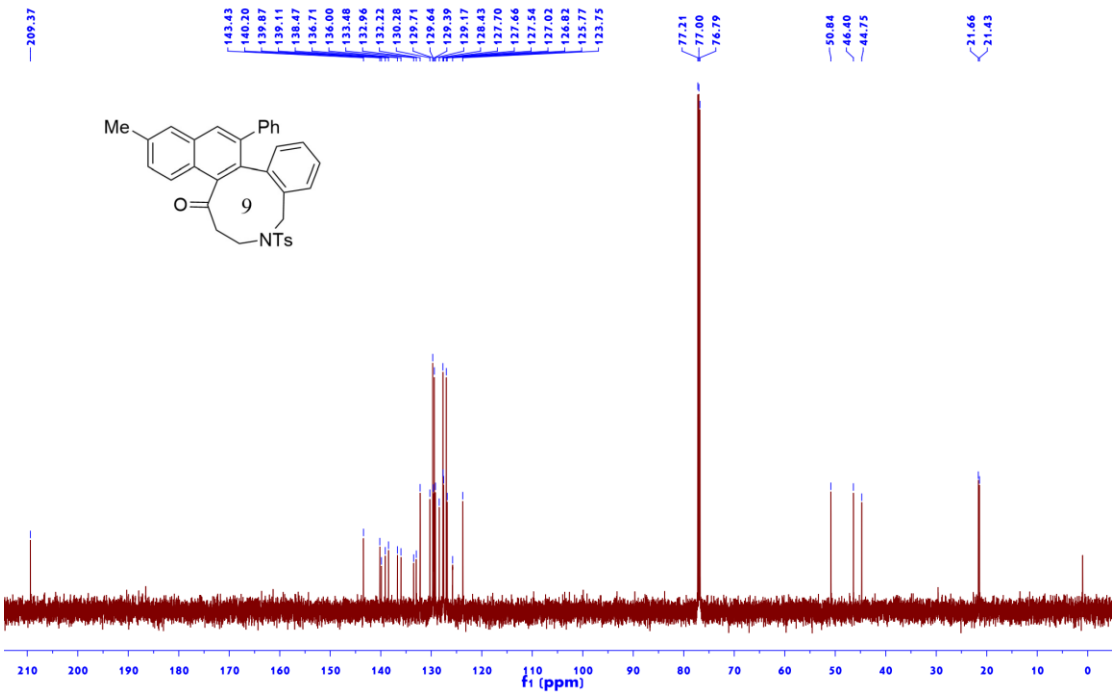


Figure S139 ^{1}H NMR (600 MHz, $CDCl_3$) of 2ad

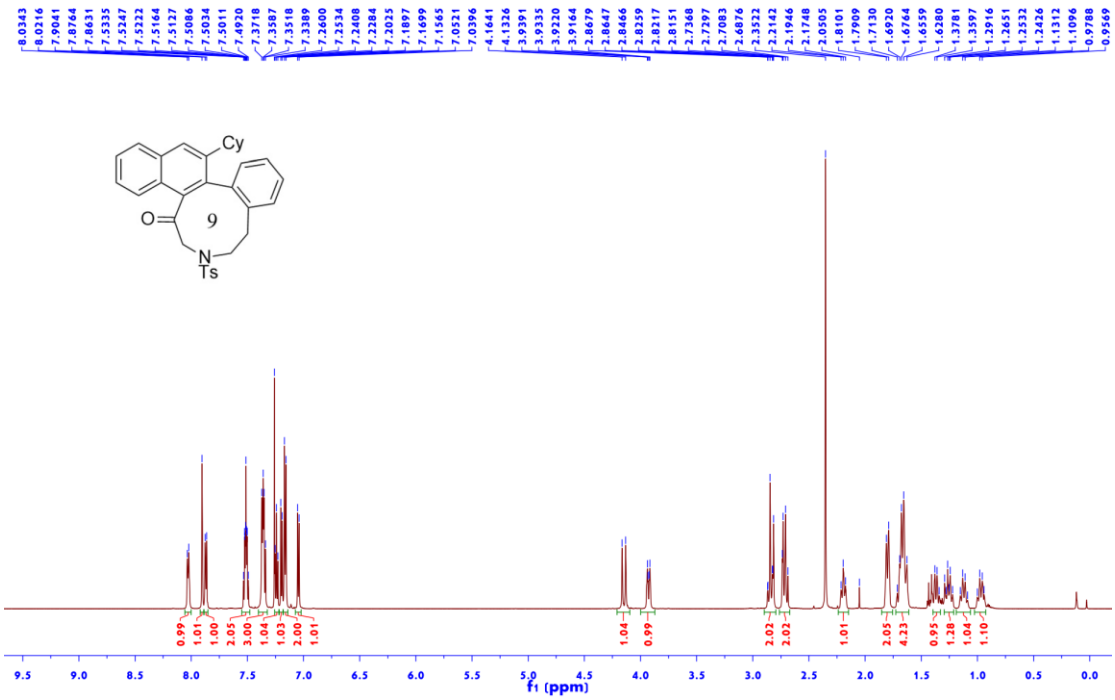


Figure S140 ^{13}C NMR (150 MHz, $CDCl_3$) of 2ad

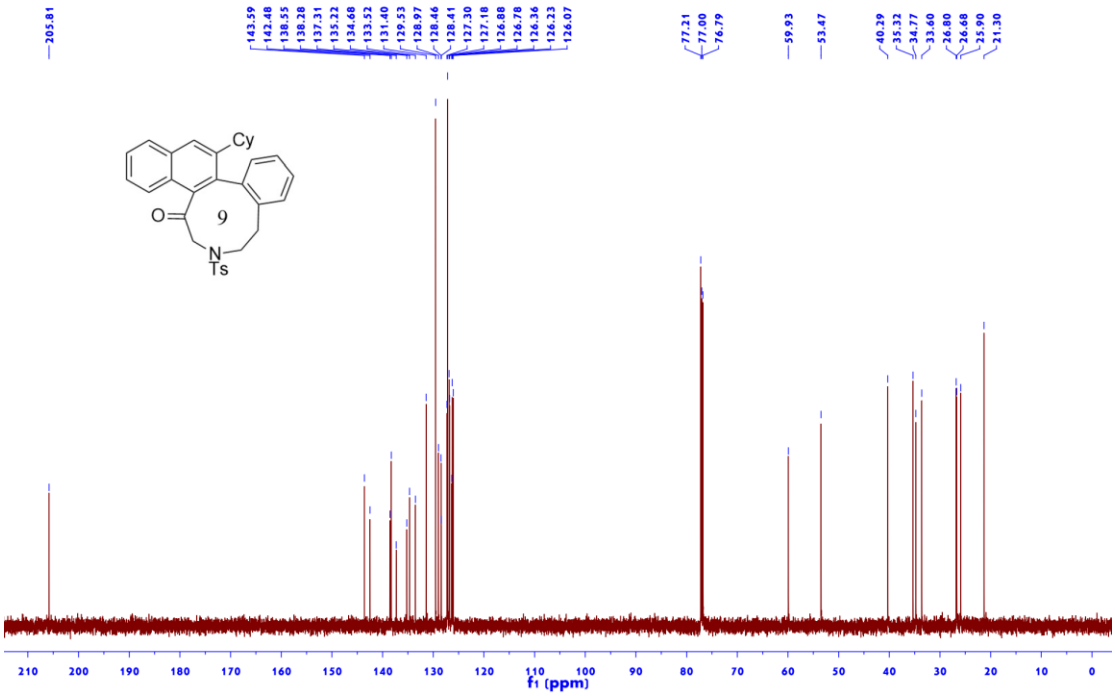


Figure S141 ^{1}H NMR (600 MHz, $CDCl_3$) of 2ae

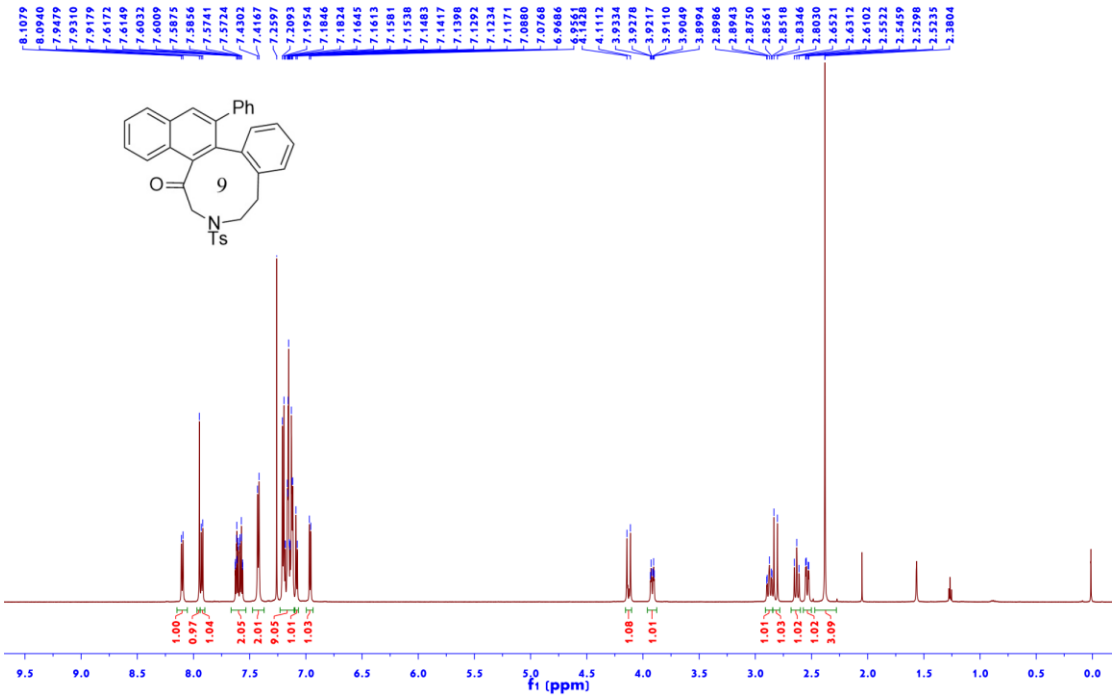


Figure S142 ^{13}C NMR (150 MHz, $CDCl_3$) of 2ae

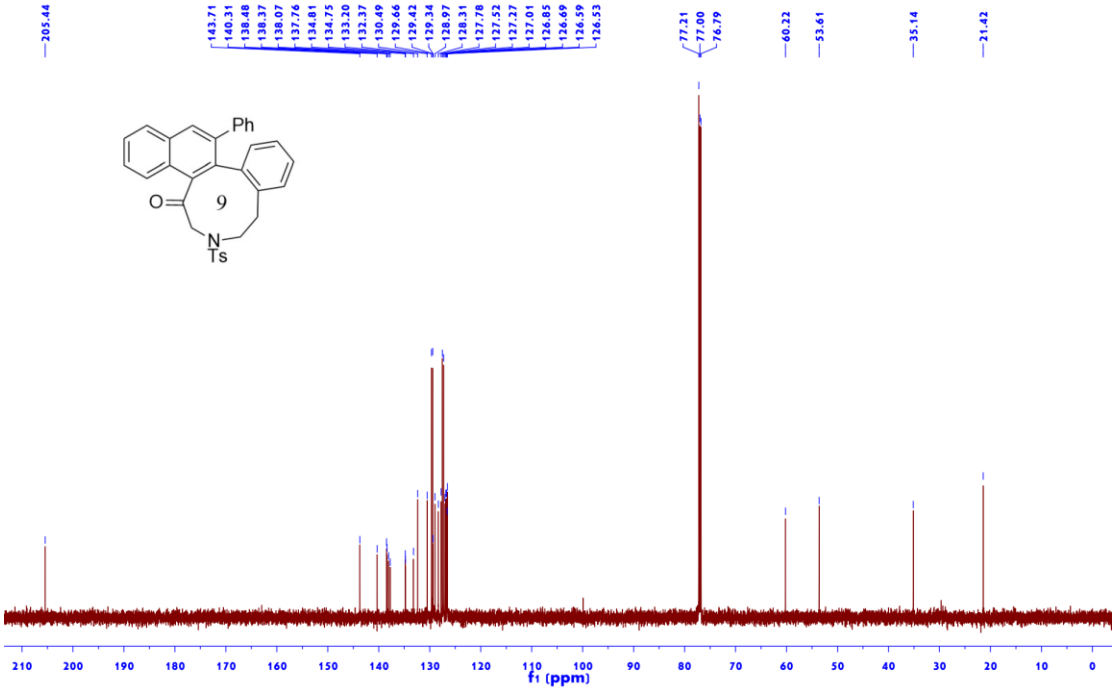


Figure S143 ^{1}H NMR (600 MHz, $CDCl_3$) of 2af

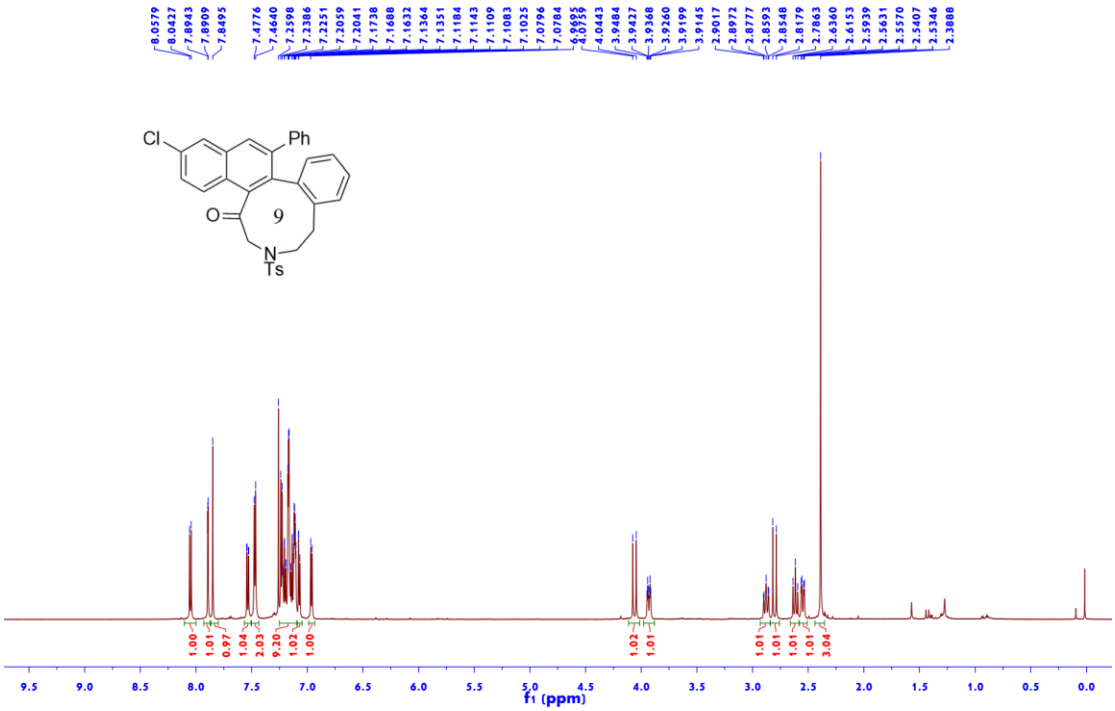


Figure S144 ^{13}C NMR (150 MHz, $CDCl_3$) of 2af

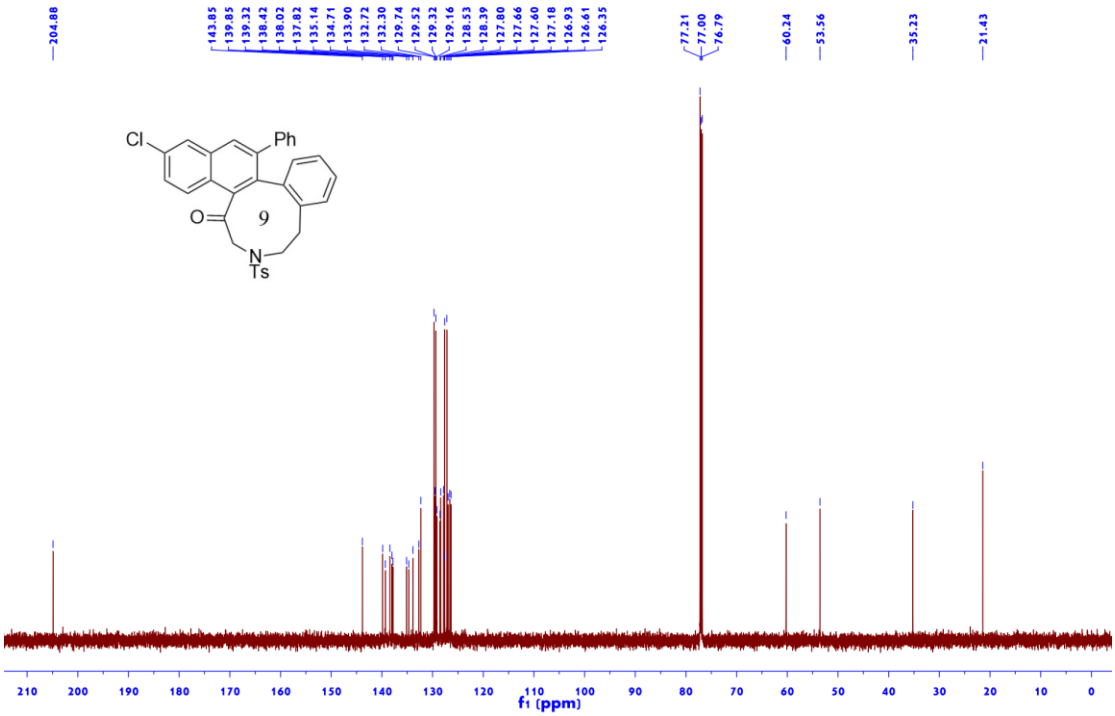


Figure S145 ^{1}H NMR (600 MHz, $CDCl_3$) of 2ag

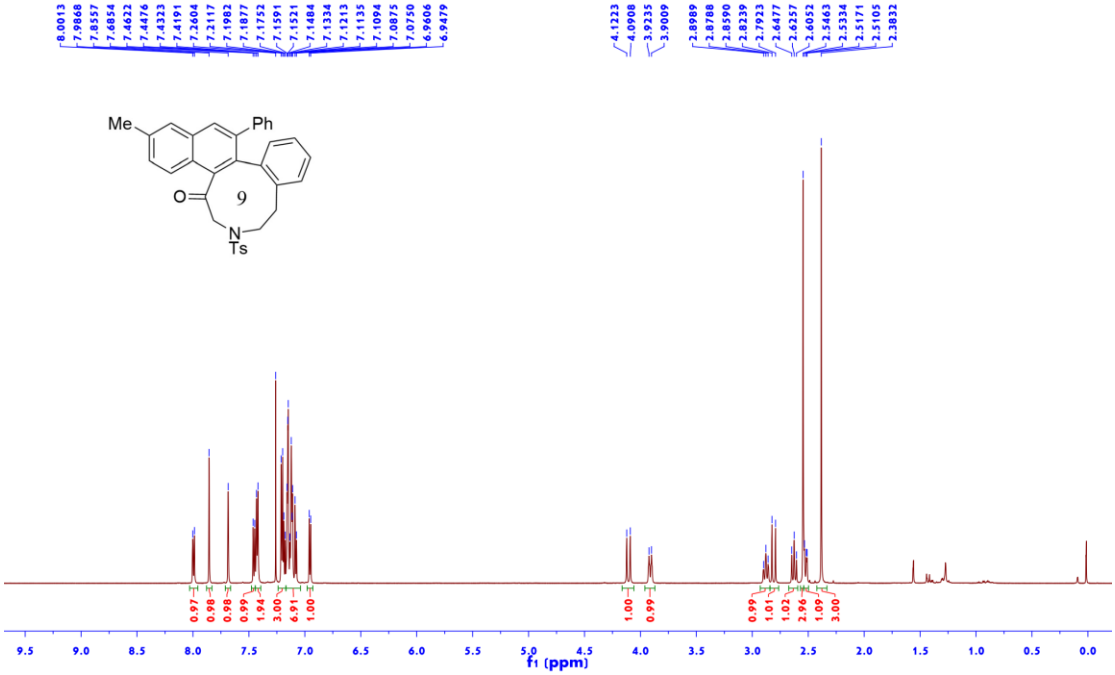


Figure S146 ^{13}C NMR (150 MHz, $CDCl_3$) of 2ag

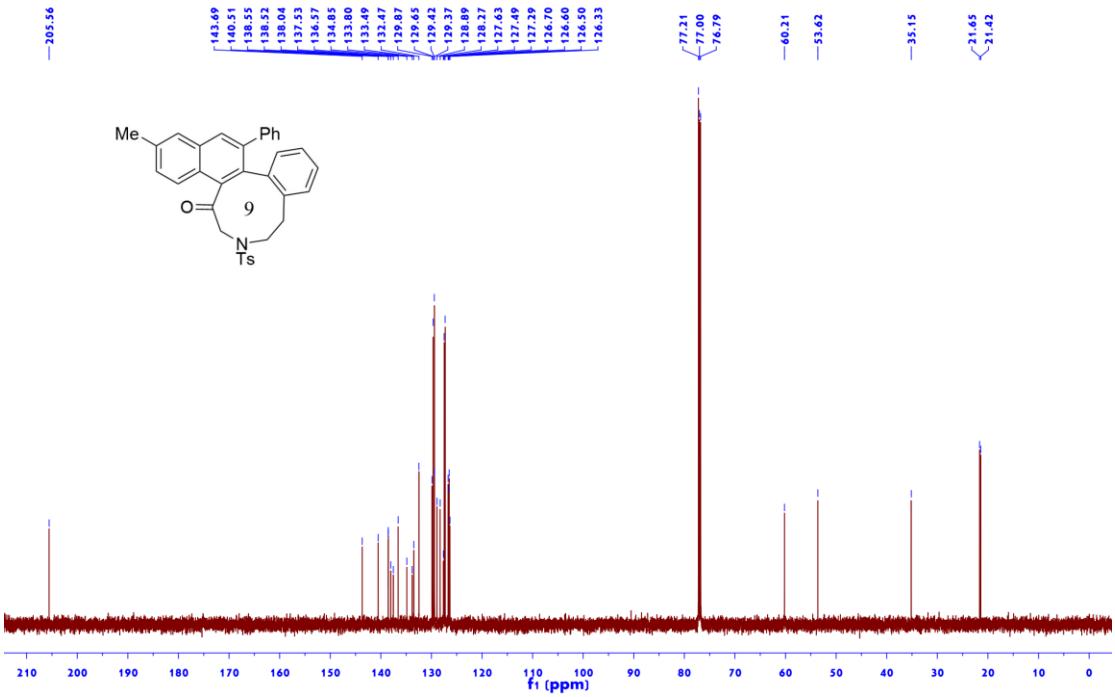


Figure S147 ^{1}H NMR (600 MHz, $CDCl_3$) of 2ah

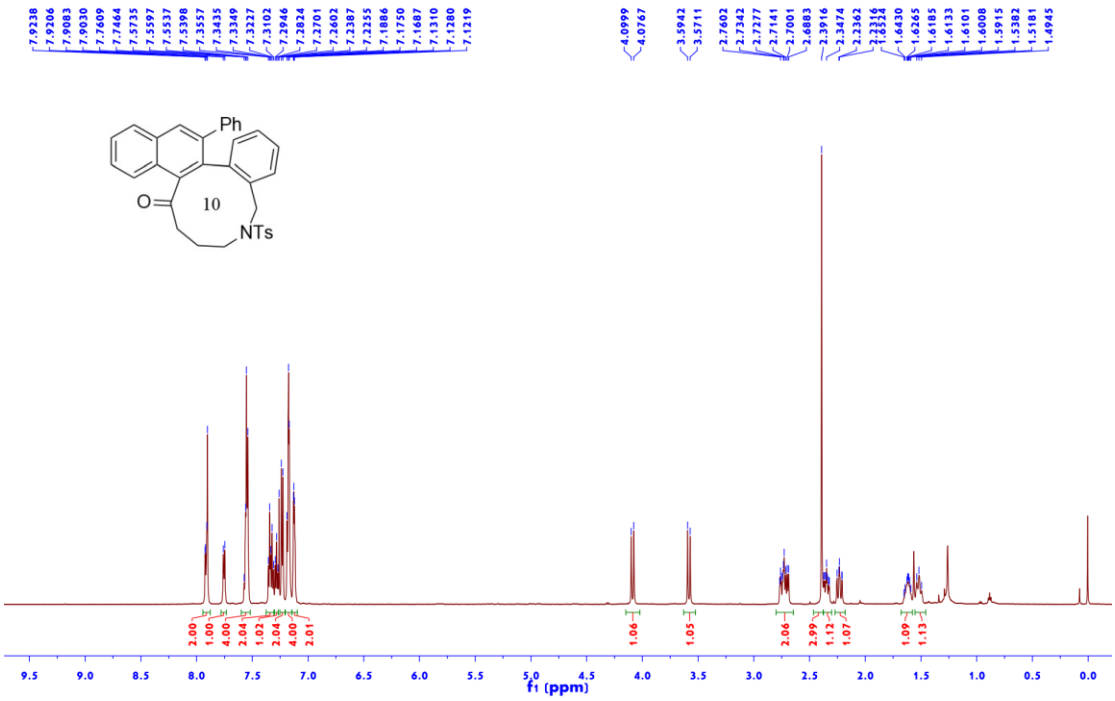


Figure S148 ^{13}C NMR (150 MHz, $CDCl_3$) of 2ah

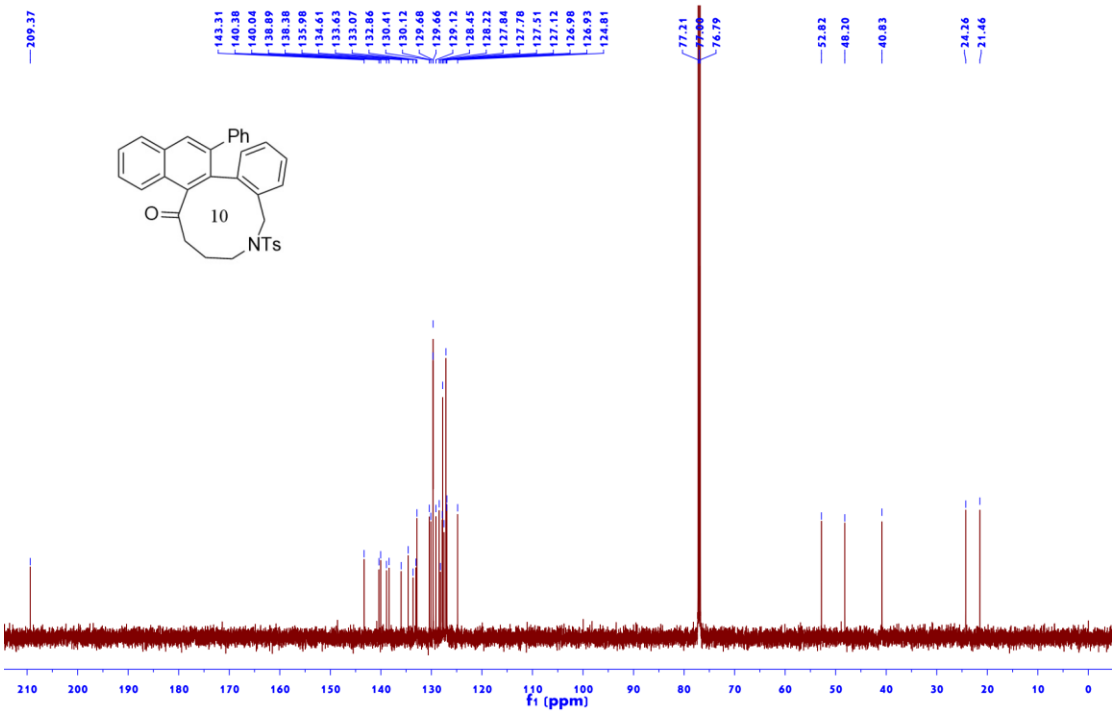


Figure S149 ^{1}H NMR (600 MHz, $CDCl_3$) of 2ai

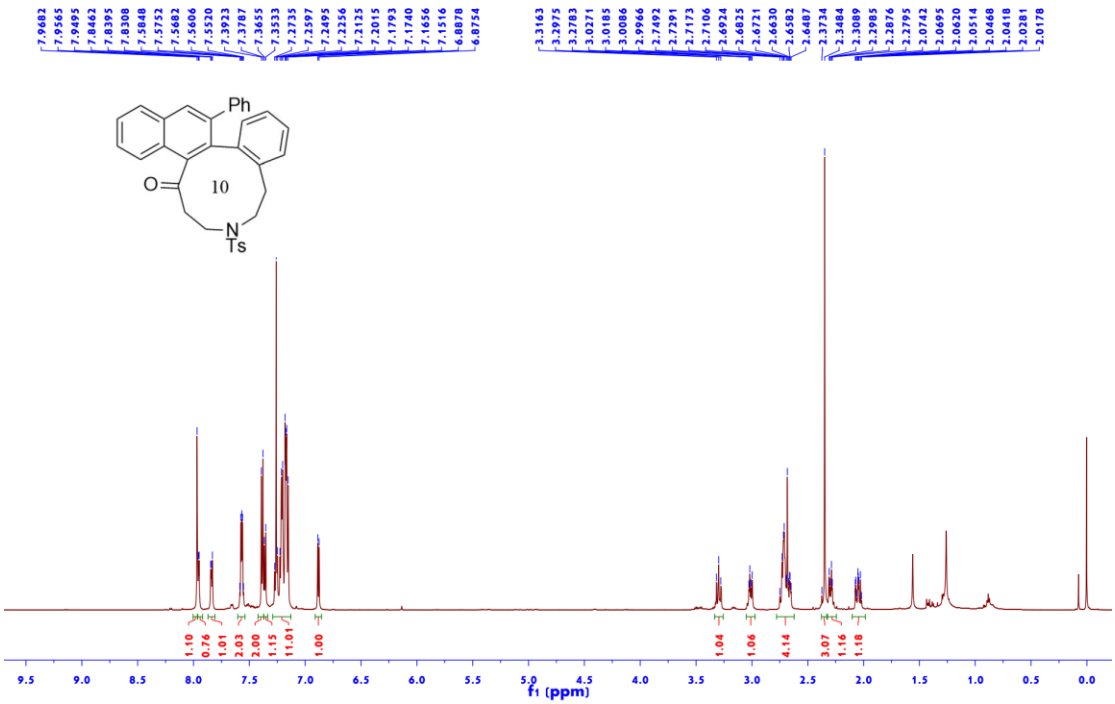


Figure S150 ^{13}C NMR (150 MHz, $CDCl_3$) of 2ai

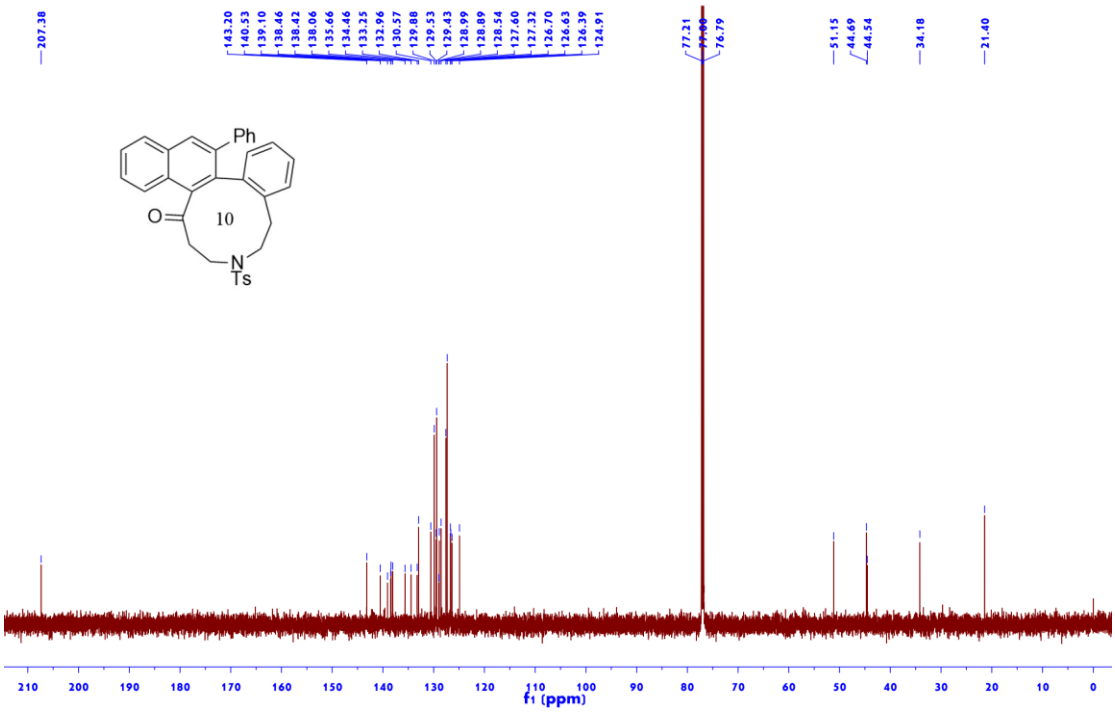


Figure S151 ^{1}H NMR (600 MHz, $CDCl_3$) of 2aj

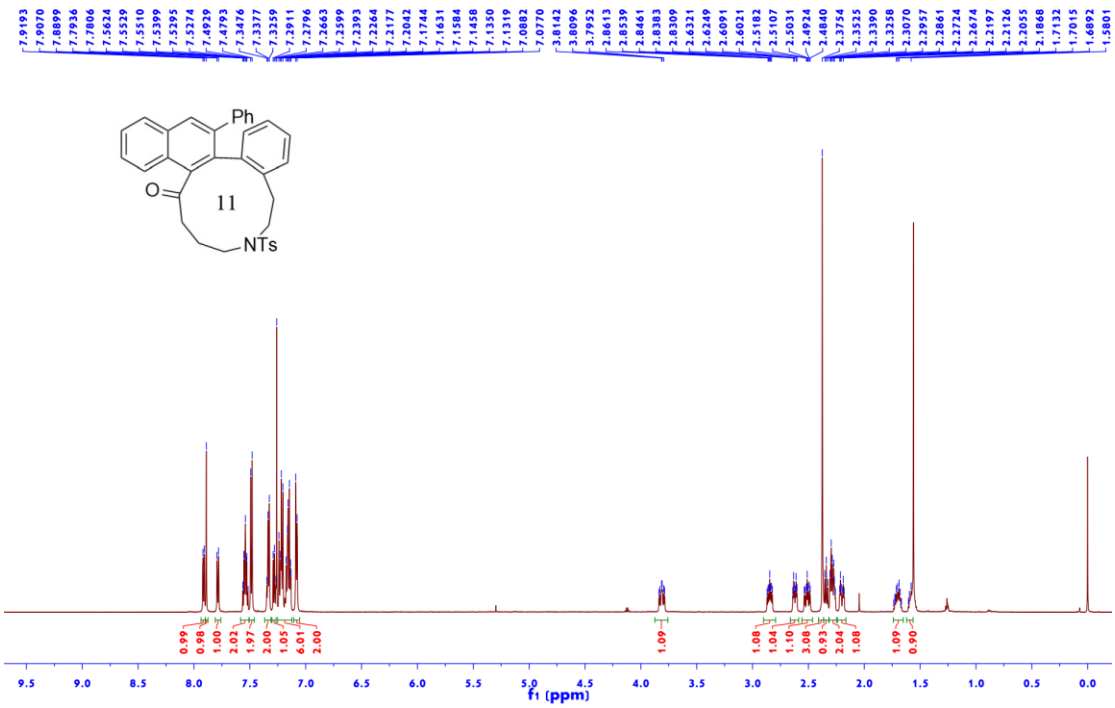


Figure S152 ^{13}C NMR (150 MHz, $CDCl_3$) of 2aj

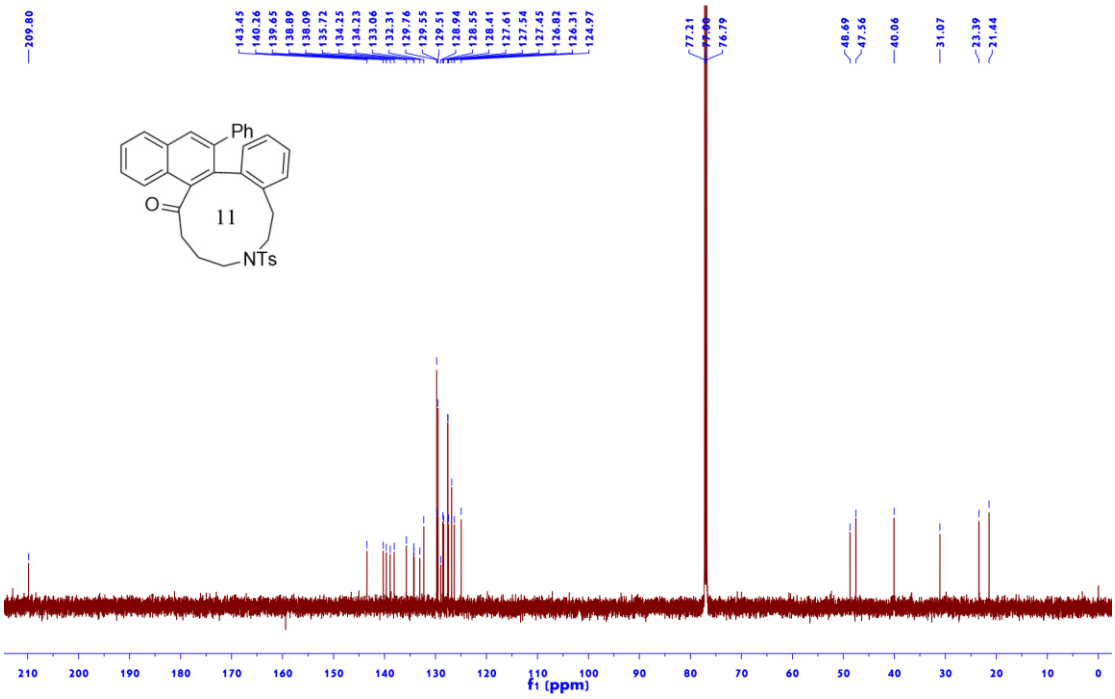


Figure S153 ^{1}H NMR (600 MHz, $CDCl_3$) of 2ak

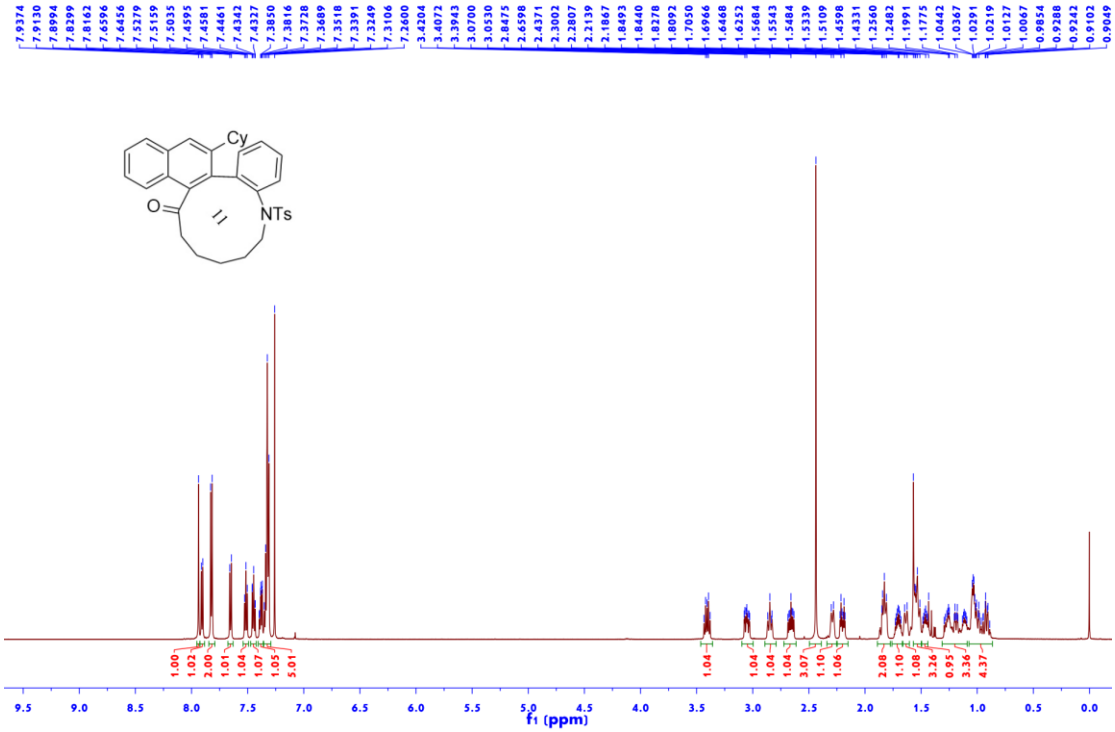


Figure S154 ^{13}C NMR (150 MHz, $CDCl_3$) of 2ak

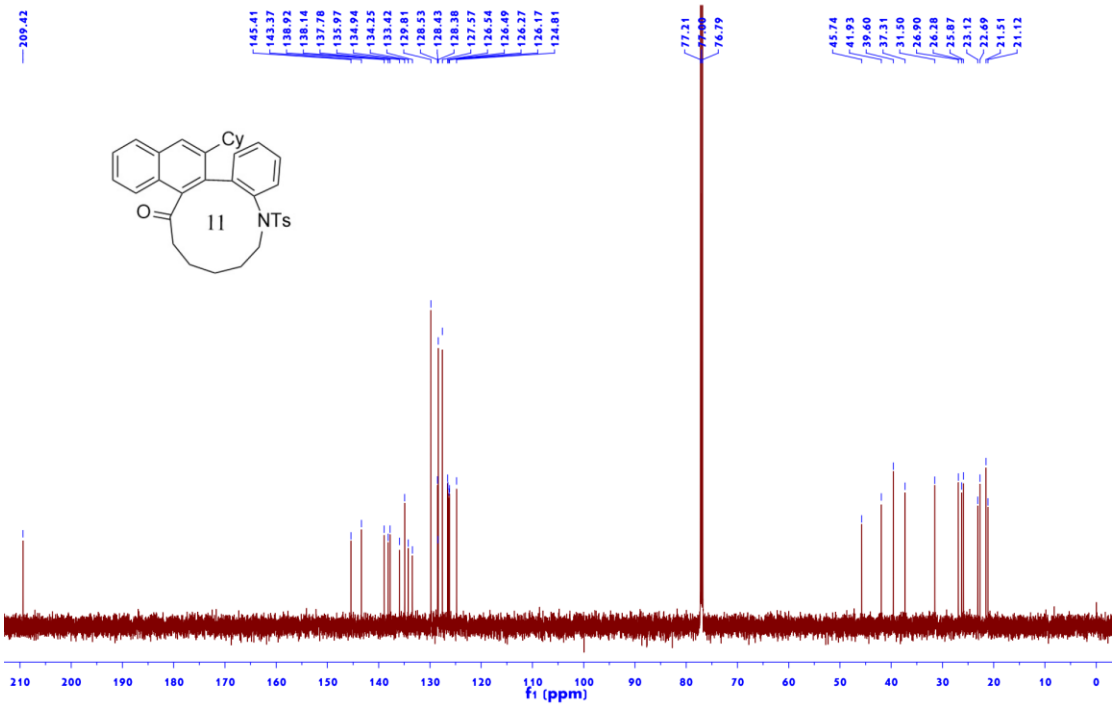


Figure S155 ^{1}H NMR (600 MHz, $CDCl_3$) of 3

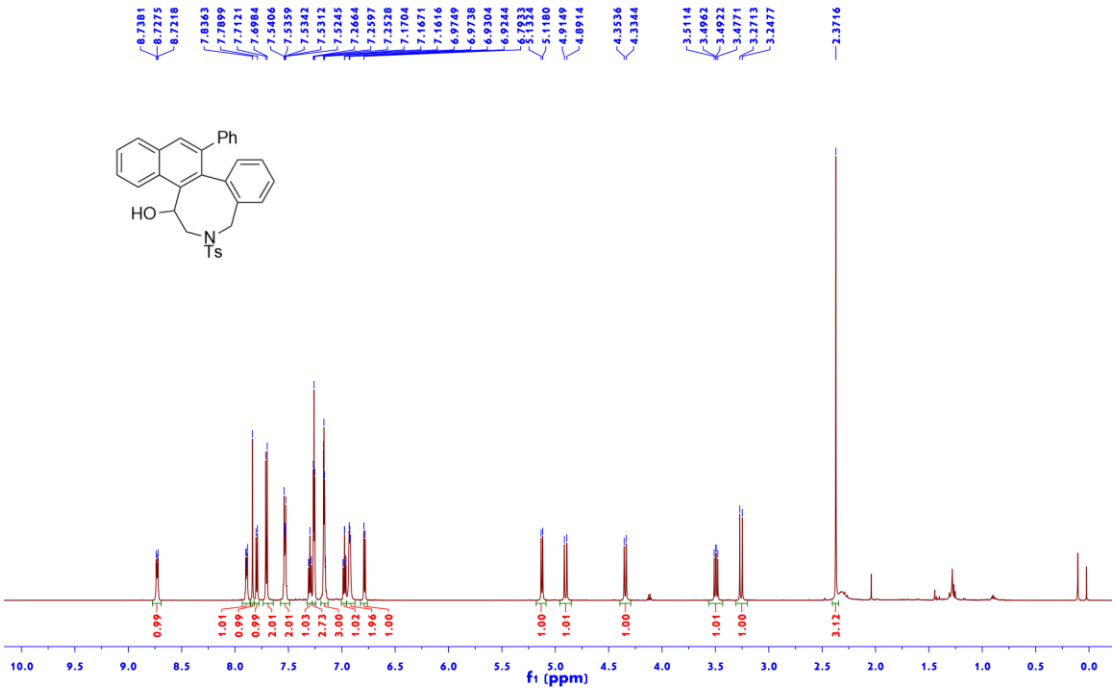


Figure S156 ^{13}C NMR (150 MHz, $CDCl_3$) of 3

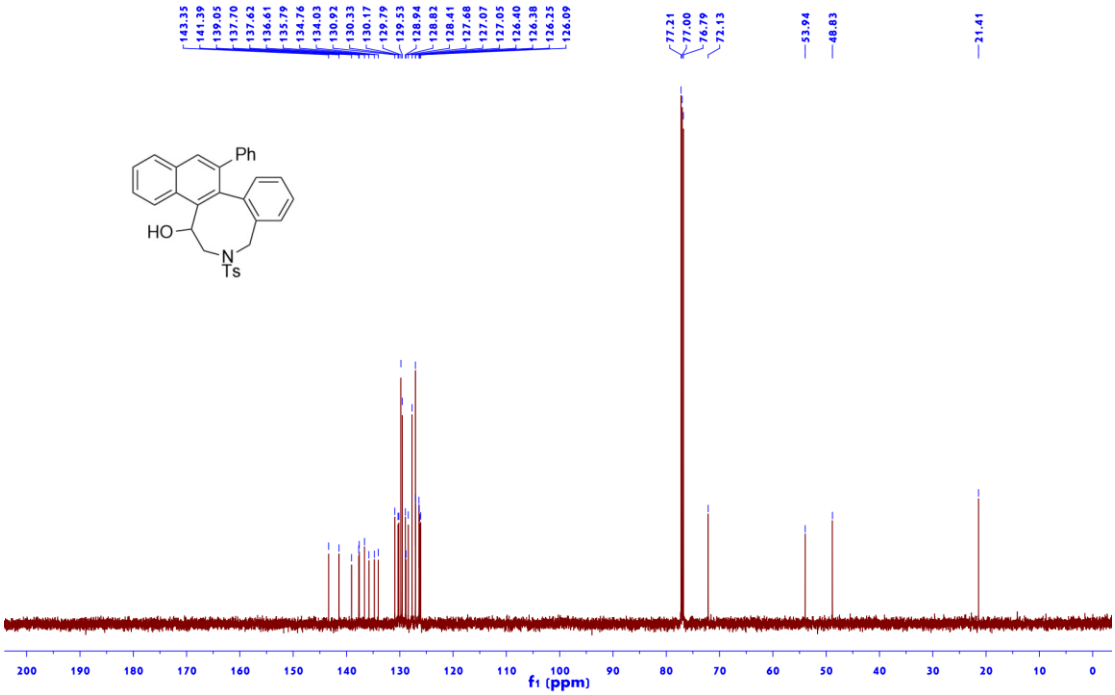


Figure S157 ^{1}H NMR (600 MHz, $CDCl_3$) of 4

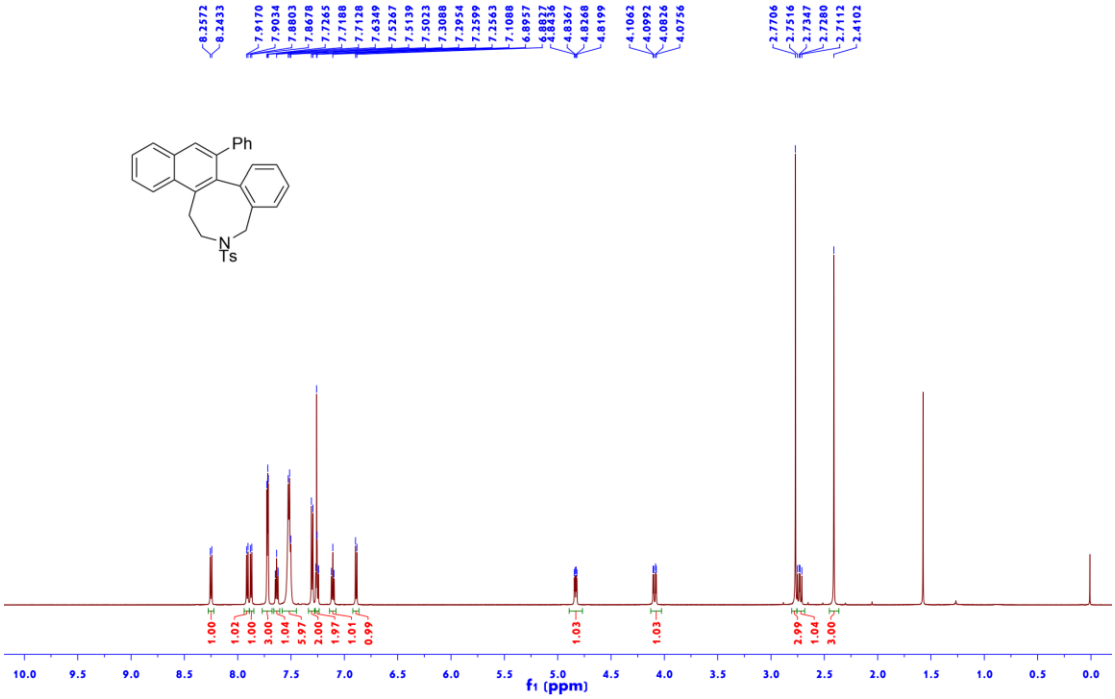


Figure S158 ^{13}C NMR (150 MHz, $CDCl_3$) of 4

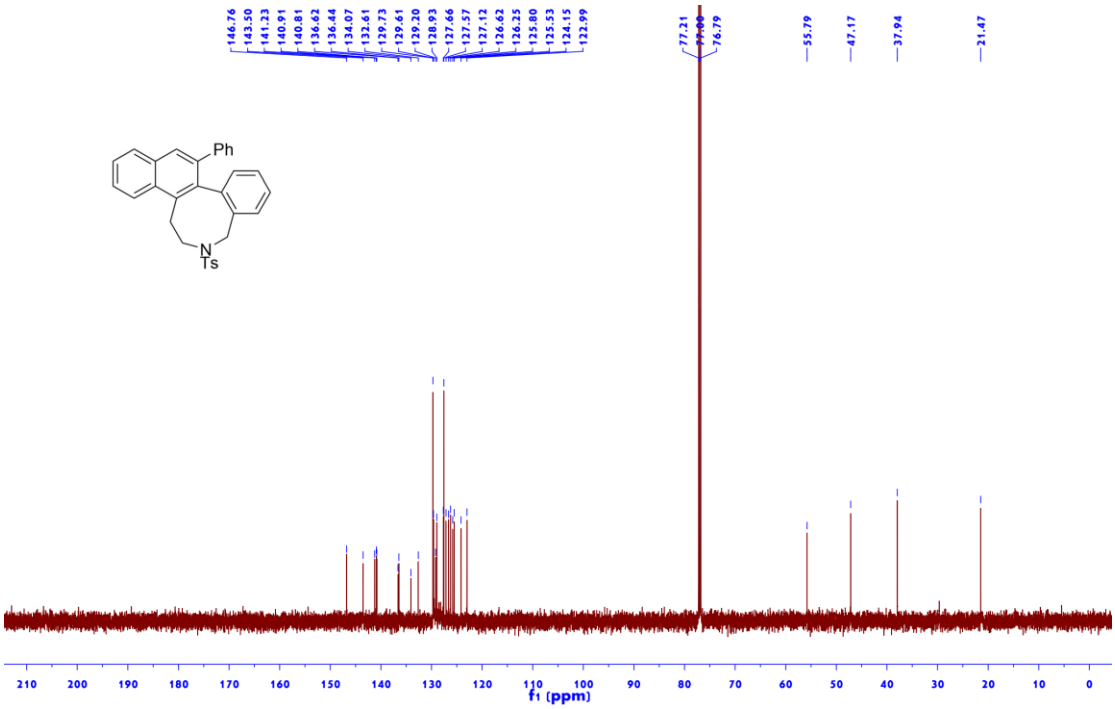


Figure S159 ^{1}H NMR (600 MHz, $CDCl_3$) of 5

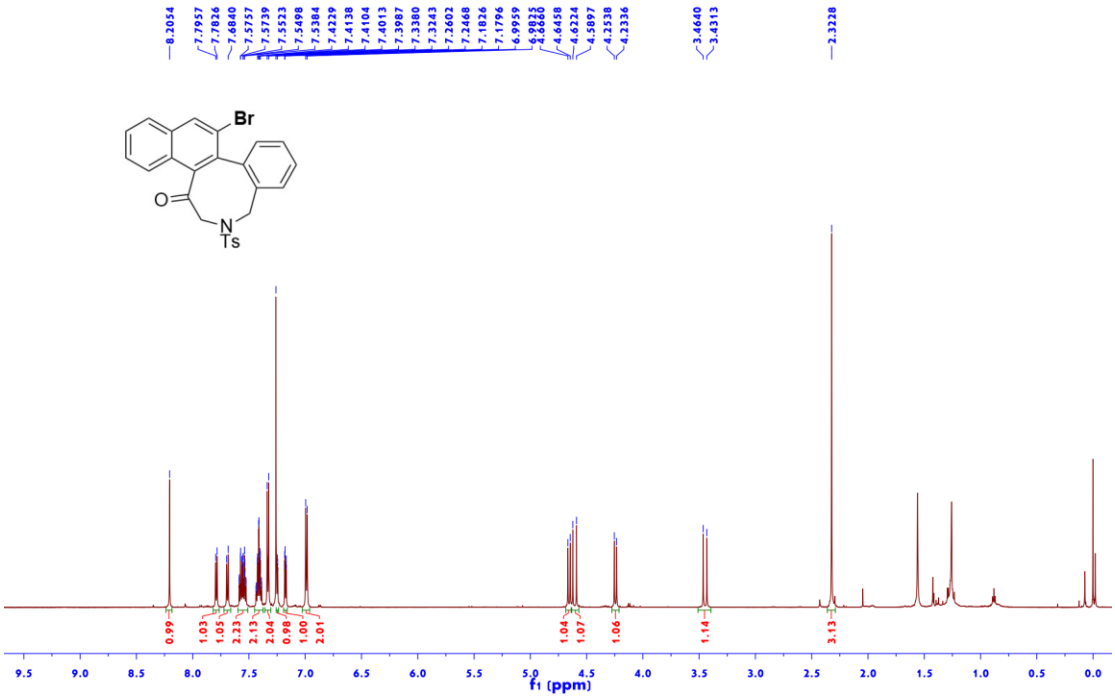


Figure S160 ^{13}C NMR (150 MHz, $CDCl_3$) of 5

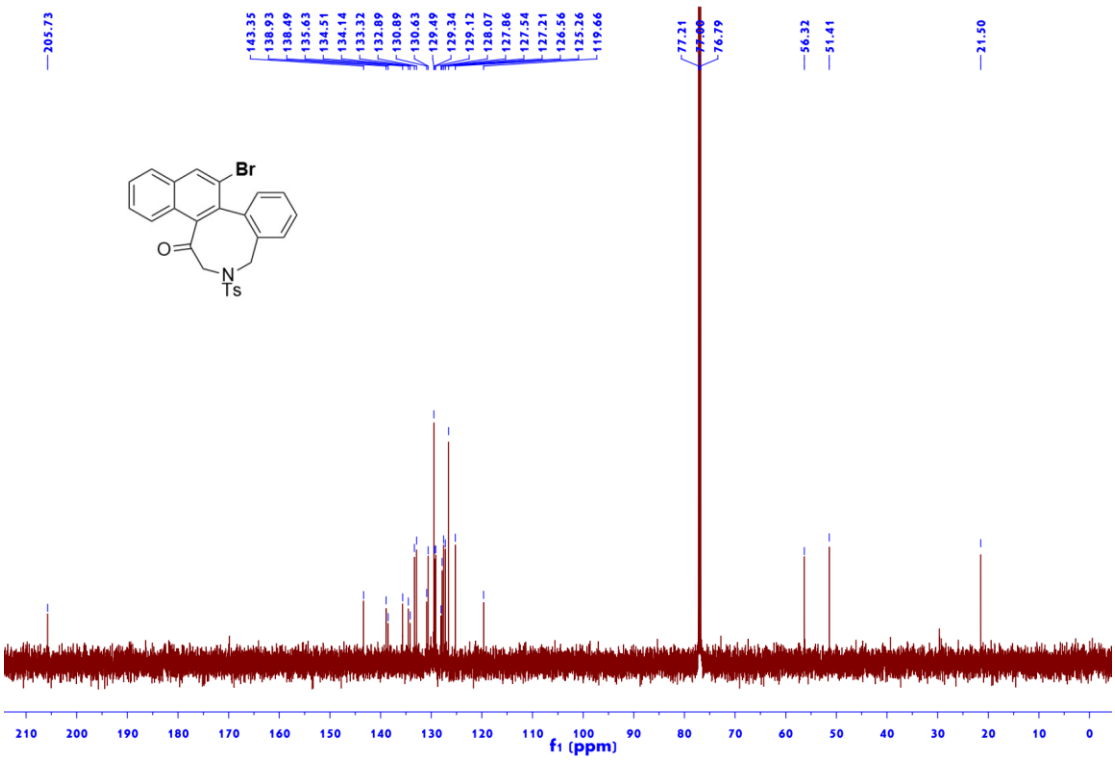


Figure S161 ^{1}H NMR (600 MHz, $CDCl_3$) of 6

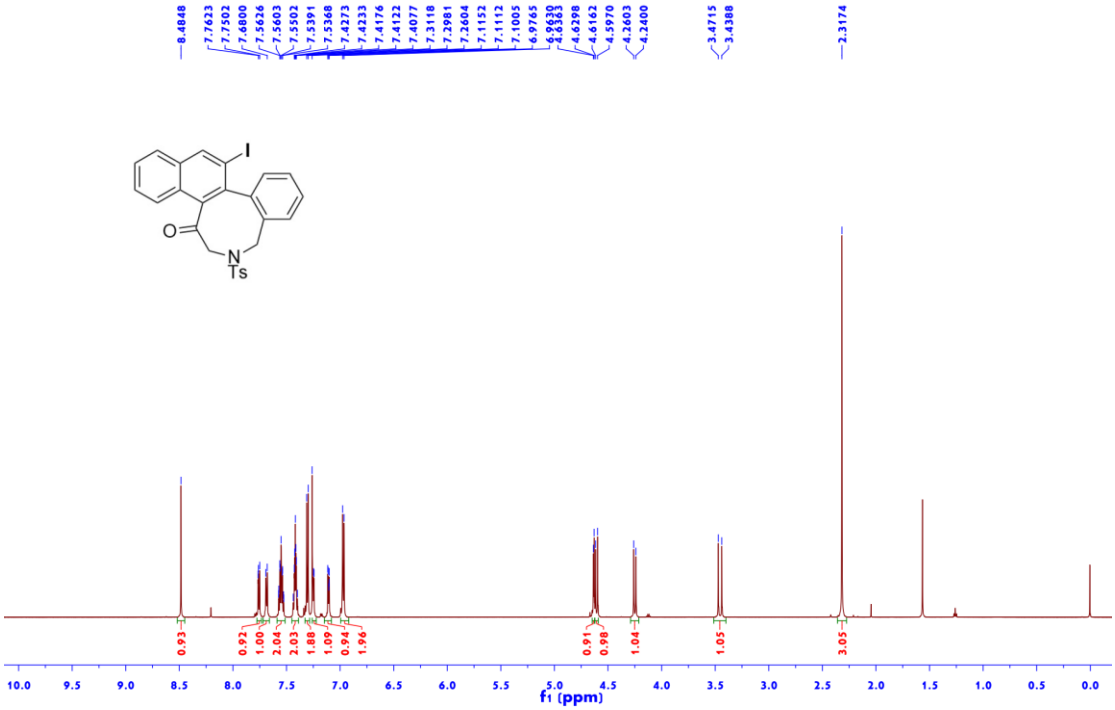


Figure S162 ^{13}C NMR (150 MHz, $CDCl_3$) of 6

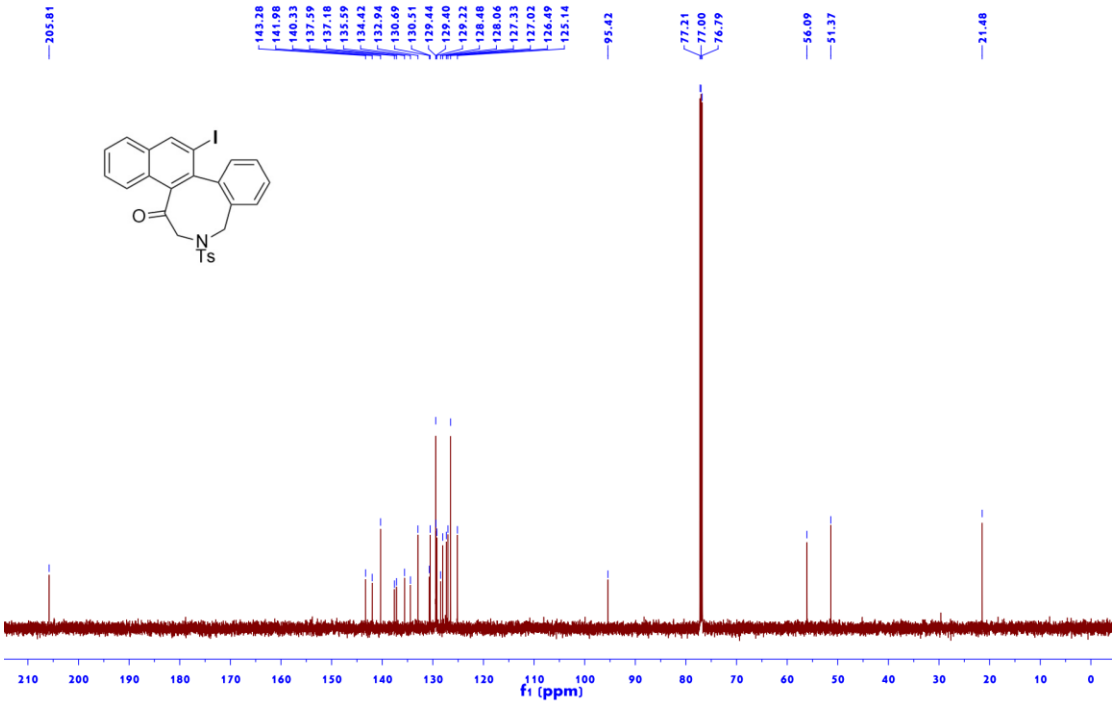


Figure S163 ^{1}H NMR (600 MHz, $CDCl_3$) of 7

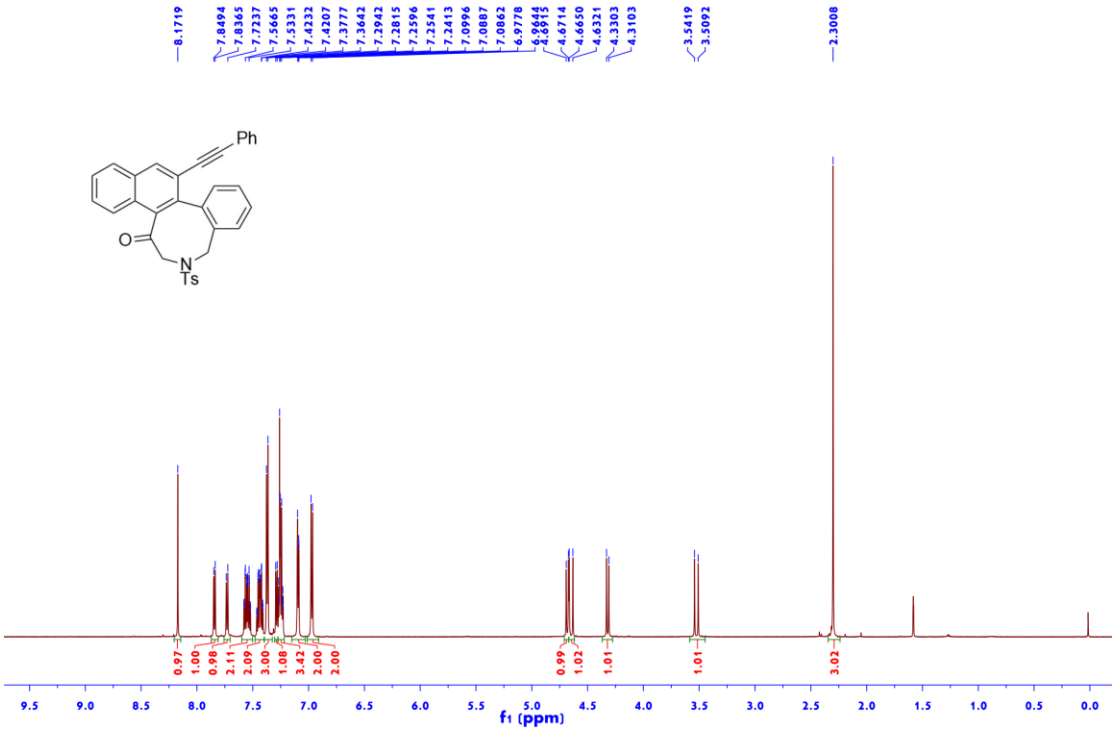
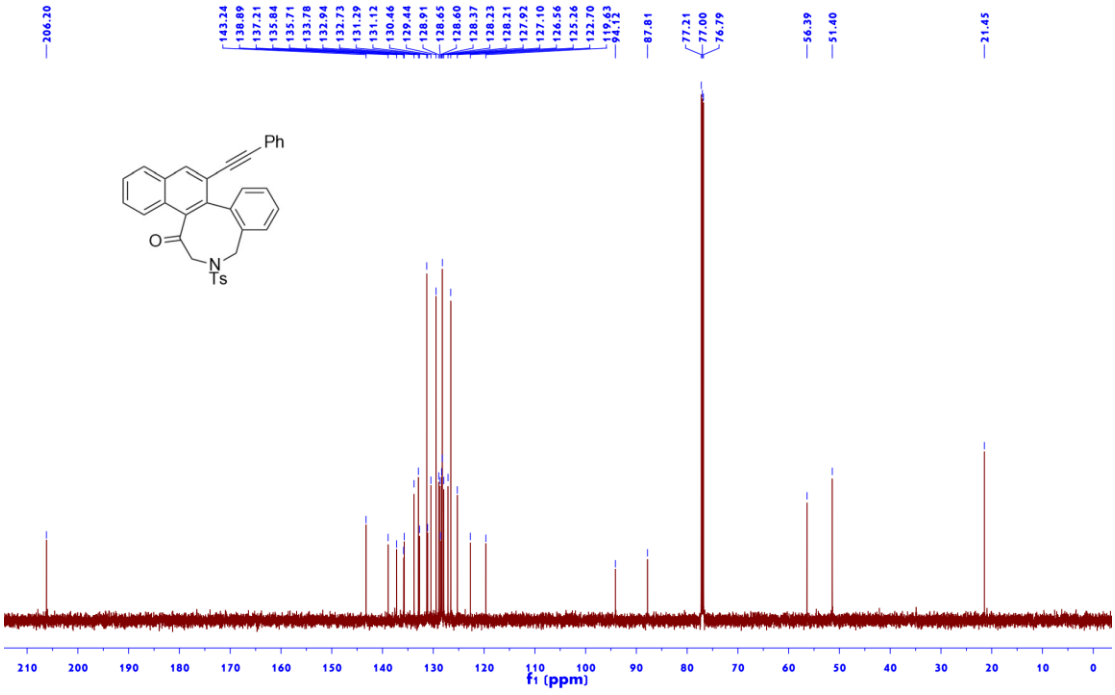


Figure S164 ^{13}C NMR (150 MHz, $CDCl_3$) of 7



6. X-ray crystal structure of 2a

Crystal preparation: Compound **2a** (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 2232496 (**2a**).

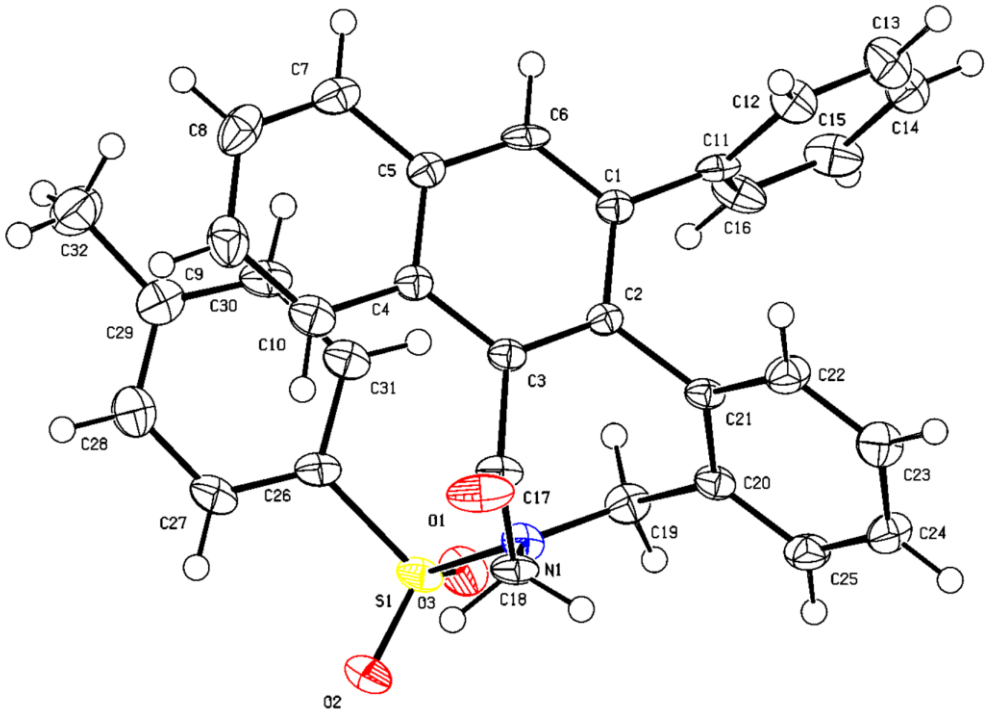


Figure S165. ORTEP Drawing of **2a** with Thermal Ellipsoids at 30% Probability Levels (CCDC 2232496).

Table S1 Crystal data and structure refinement for 2a.

Identification code	**2a**
Empirical formula	$C_{32}H_{25}NO_3S$
Formula weight	503.59
Temperature/K	179.99(10)

Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.7554(8)
b/Å	13.6091(19)
c/Å	20.639(3)
α/°	90
β/°	91.860(9)
γ/°	90
Volume/Å^3	2458.0(5)
Z	4
ρ_{calc}g/cm^3	1.361
μ/mm^{-1}	0.168
F(000)	1056.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.956 to 49.994
Index ranges	$-10 \leq h \leq 9$, $-16 \leq k \leq 15$, $-20 \leq l \leq 24$
Reflections collected	15092
Independent reflections	4340 [R_{int} = 0.0910, R_{sigma} = 0.0754]
Data/restraints/parameters	4340/30/335
Goodness-of-fit on F^2	1.085
Final R indexes [I>=2σ (I)]	R_1 = 0.1131, wR_2 = 0.2842
Final R indexes [all data]	R_1 = 0.1305, wR_2 = 0.2937
Largest diff. peak/hole / e Å^{-3}	0.92/-0.54

7. References

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[S3] (a) K. Hiroya, S. Itoh and T. Sakamoto, Development of an efficient procedure for indole ring synthesis from 2-ethynylaniline derivatives catalyzed by Cu(II) salts and its application to natural product synthesis, *J. Org. Chem.*, **2004**, *69*, 1126–1136; (b) Y. Zhao, Y. Hu, H. Wang, X. Li and B. Wan, Transition-metal controlled diastereodivergent radical cyclization/azidation cascade of 1,7-enynes, *J. Org. Chem.*, 2016, **81**, 4412–4420.

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